Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting information:

# Asymmetric transfer hydrogenation of boronic acid pinacol ester (Bpin)-containing acetophenones.

Ye Zheng[a] and Martin Wills[a]*

a Department of Chemistry, The University of Warwick, Coventry, CV4 7AL, UK. M.wills@warwick.ac.uk

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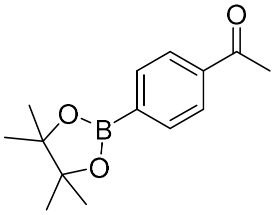
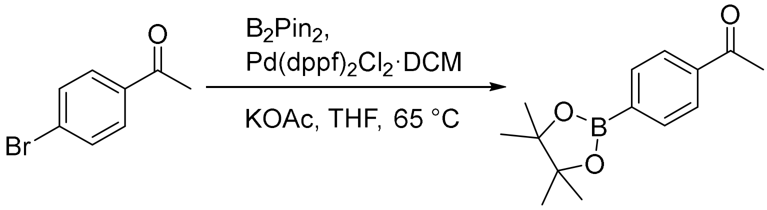
## General experimental details.

Reagents and solvents were used as purchased and without further purification. Reactions were carried out under a nitrogen atmosphere unless otherwise specified. Reactions at elevated temperature were maintained by thermostatically controlled oil-baths or aluminium heating blocks. A temperature of 0 °C refers to an ice slush bath, -78 °C to a dry ice acetone bath. NMR spectra were recorded on a Bruker AV (250 MHz), Bruker DPX (300 or 400MHz) or Bruker DRX (500 MHz). Chemical shifts are rounded to the nearest 0.01 ppm for 1H spectra and the nearest 0.1 ppm for 13C spectra and are referenced to the solvent chemical shift. Coupling constants are rounded to the nearest 0.1 Hz. Mass spectra were recorded on an Esquire 2000 and high-resolution mass spectra were recorded on a Bruker Micro ToF or MaXis. IR spectra were recorded on a PerkinElmer spectrum100 and peaks are reported in wavenumbers. Optical rotations were measured on an Optical Activity Ltd. AA-1000 Polarimeter and are reported in deg dm−1 cm3 g−1. The chiral GC measurements were performed using a Hewlett-Packard 1050 instrument linked to a PC running DataApex Clarity software. HPLC measurements were performed out using a Hewlett Packard 1050 Series with a quaternary pump, autosampler and variable wavelength detector linked to a PC running DataApex Clarity software. Melting points were determined on a Stuart scientific melting point apparatus and are uncorrected. Flash column chromatography was performed using silica gel of 230-400 mesh size. Thin layer chromatography was carried out on aluminium backed silica gel 60(F254) plates, visualised using 254nm UV light, potassium permanganate or cerium ammonium molybdate (CAM). Column chromatography was performed either by gradient elution (reported as a range, e.g. EtOAc/Petroleum ether (2-12%)), or by isocratic elution.

**Data related to Table 1.**

1-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one **6**.

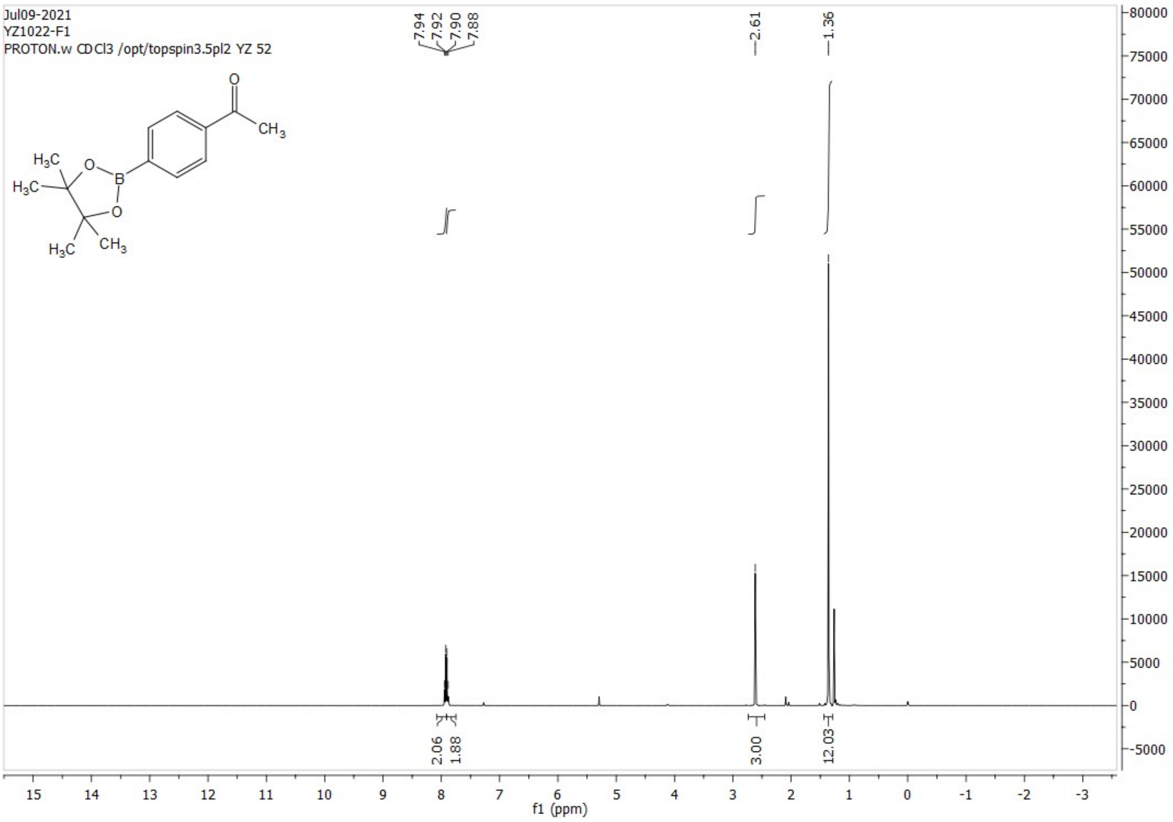




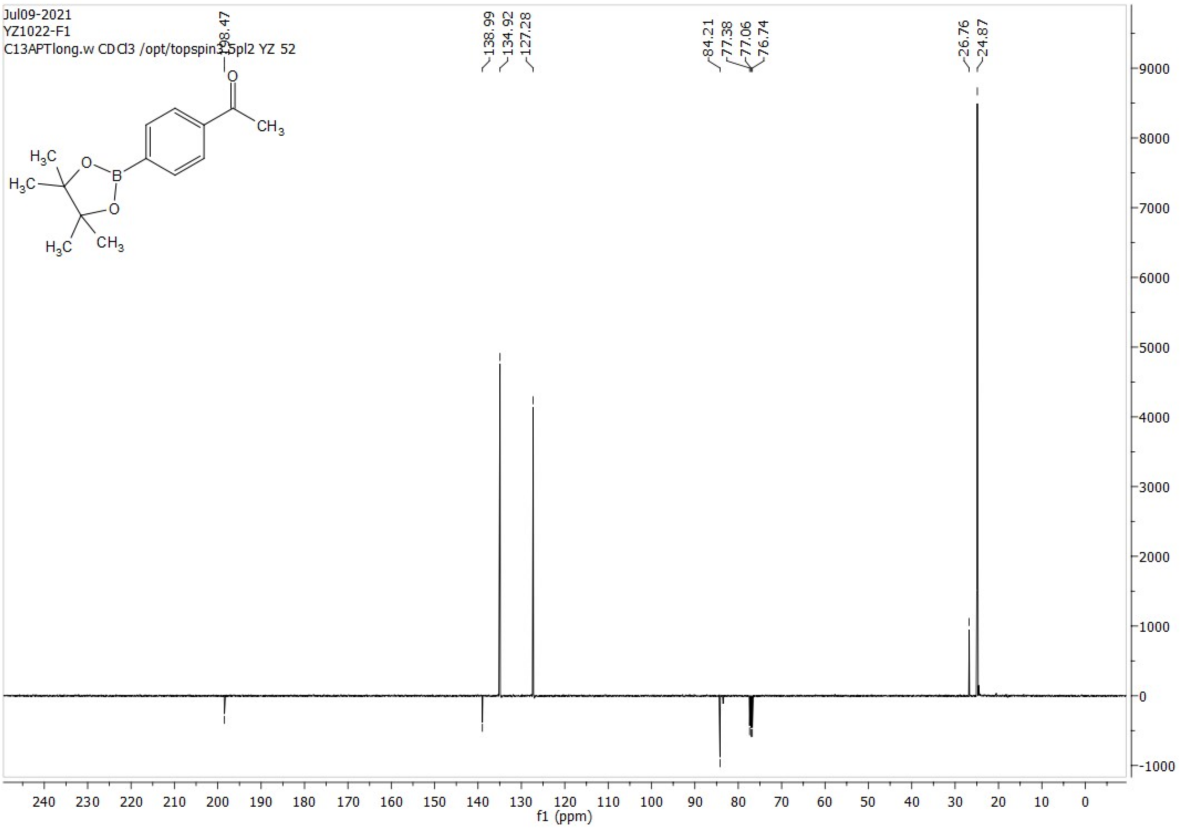
This compound has been reported and fully characterized: J. Ratniyom, N. Dechnarong, S. Yotphan and S. Kiatisevi, *Eur. J. Org. Chem.* 2014, **7**, 1381-1385.

A round-bottom flask was charged with 4’-bromoacetophenone (995 mg, 5.00 mmol), bis(pinacolato)diboron (1.52 g, 6.00 mmol), potassium acetate (1.47 g, 15.0 mmol), THF (30 mL) and Pd(dppf)$_2$Cl$_2$·DCM (204 mg, 0.250 mmol). The reaction mixture was heated to 65 °C and left stirring under the nitrogen atmosphere overnight, followed by TLC (9:1 hexane: EtOAc). The mixture was quenched by distilled water (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried (MgSO$_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-20% ethyl acetate in hexane to give 1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one **6** as a yellow solid (896 mg, 3.64 mmol, 73%). TLC: Rf ca 0.50 (9:1 hexane: EtOAc), strong UV and KMnO$_4$; $\delta_H$ (400 MHz, CDCl$_3$) 7.94 (2H, d, *J* = 7.9, ArH), 7.90 (2H, d, *J* = 7.9, ArH), 2.61 (3H, s, CH$_3$), 1.36 (12H, s, CH$_3$) ppm; $\delta_C$ (100 MHz, CDCl$_3$) 198.47 (C), 138.99 (C), 134.92 (CH), 127.28 (CH), 84.21 (C), 26.76 (CH$_3$), 24.87 (CH$_3$) ppm; m/z (ES-API+) 269.1 (M$^+$ + 23, 100%). Data matched that reported.

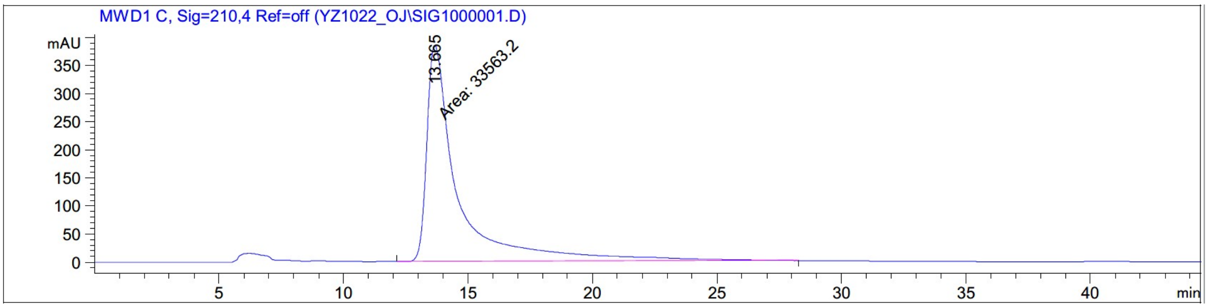
$^{1}H$ NMR (400 MHz, $CDCl_3$)



$^{13}C$ NMR (100 MHz, $CDCl_3$)



HPLC of 1-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one



```
Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width      Area       Height      Area
  #   [min]        [min]    [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  13.665 MM     1.4529 3.35632e4   385.01184 100.0000

Totals :                   3.35632e4   385.01184
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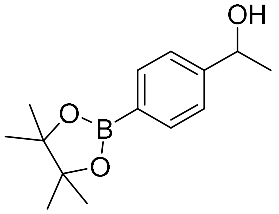
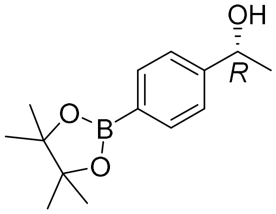
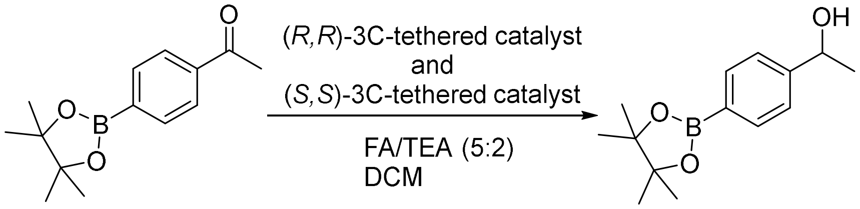
Racemic and (*R*)-1-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol **7**.

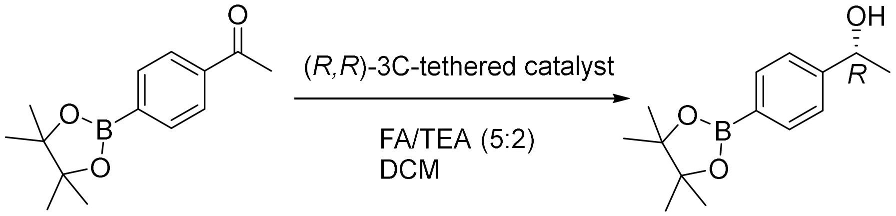




Racemic was formed by use of combined ATH catalysts:



Asymmetric:



This compound has been reported and fully characterized: L. H. Andrade and T. Barcello, *Org. Lett.* 2009, **11**, 3052-3055.

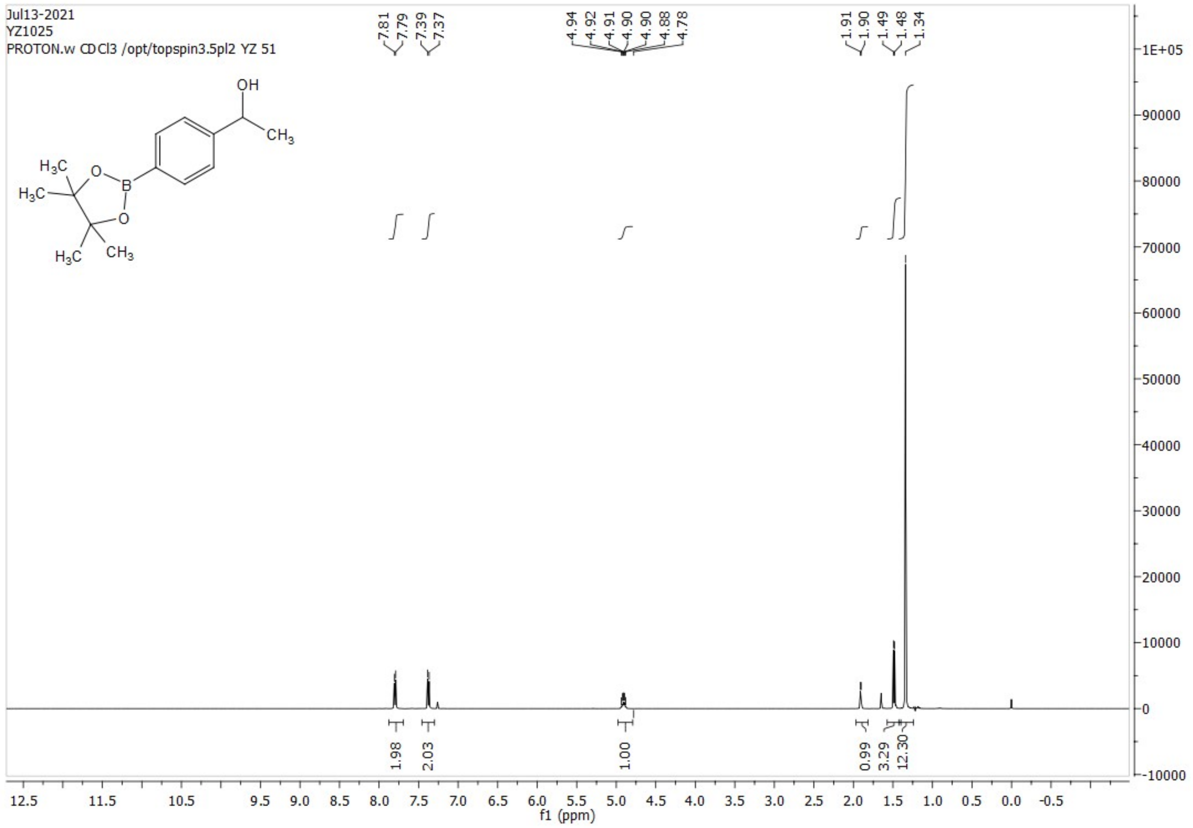
**Synthesis of racemic standard:**

(*R,R*)-3C-Tethered Ru(II)-TsDPEN catalyst **2** (1.4 mg, 2.2 μmol, 0.5 mol%) and (*S,S*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (1.4 mg, 2.2 μmol, 0.5 mol%) were added to FA: TEA (5:2 azeotropic mixture, 0.50 mL) at rt and the mixture was stirred under a nitrogen atmosphere for 15 minutes; after which a solution of 1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one **6** (110 mg, 0.447 mmol) in DCM (0.70 mL) was added. The reaction mixture was stirrer under a nitrogen atmosphere and followed by TLC (4:1 hexane: EtOAc). After 24 hours, the reaction was quenched using saturated $NaHCO_3$ solution (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried ($MgSO_4$) and filtered. The solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-50% EtOAc in hexane to give 1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol **7** as a white solid (95.0 mg, 0.383 mmol, 86%). TLC: Rf ca 0.20 (4:1 hexane: EtOAc), strong UV and $KMnO_4$; $\delta_H$ (400 MHz, $CDCl_3$) 7.81 (2H, d, $J = 7.9$, ArH), 7.39 (2H, d, $J = 7.9$, ArH), 4.94-4.78

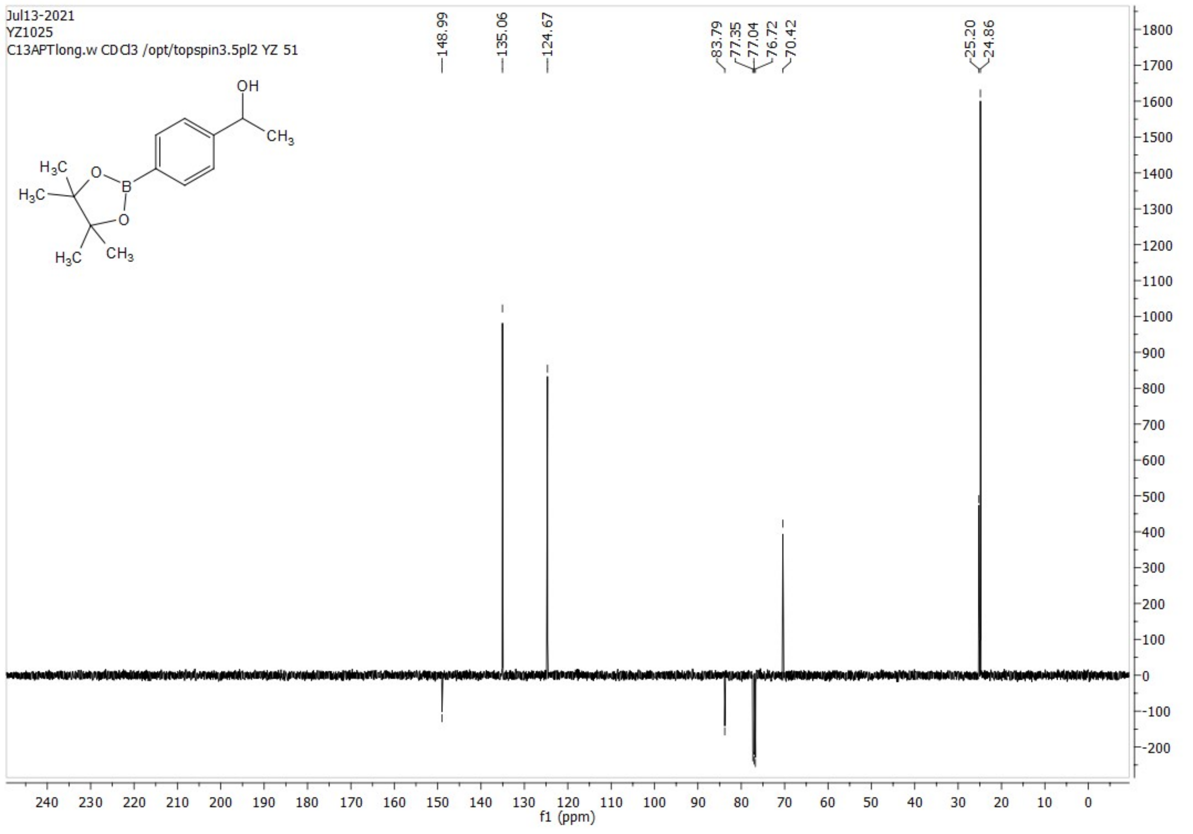
(1H, m, CH), 1.91 (1H, d, *J* = 3.6, OH), 1.49 (3H, d, *J* = 6.5, $CH_3$), 1.34 (12H, s, $CH_3$) ppm; $\delta_C$ (100 MHz, $CDCl_3$) 148.99 (C), 135.06 (CH), 124.67 (CH), 83.79 (C), 70.42 (CH), 25.20 ($CH_3$), 24.86 ($CH_3$) ppm; m/z (ES-API+) 271.1 ($M^+$ + 23, 100%). Data matched that reported. Enantiomeric excess and conversion determined by HPLC analysis (Chiralcel OJ, 30 cm x 6 mm column, hexane:iPrOH 95:5, 0.5 mL/min, T = 25°C) ketone 13.7 min, *R* isomer 17.2 min and *S* isomer 22.3 min.

ATH of 1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one **6**. (*R,R*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (2.8 mg, 4.5 μmol, 1 mol%) was added to FA: TEA (5:2 azeotropic mixture, 0.50 mL) at rt and the mixture was stirred under a nitrogen atmosphere for 15 minutes; after which a solution of 1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one **6** (110 mg, 0.447 mmol) in DCM (0.70 mL) was added. The reaction mixture was stirred under a nitrogen atmosphere and followed by TLC (4:1 hexane: EtOAc). After 24 hours, the reaction was quenched using saturated $NaHCO_3$ solution (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried ($MgSO_4$) and filtered. The solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-50% EtOAc in hexane to give 1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol **7** as a white solid (100 mg, 0.403 mmol, 90%). The reaction was also followed by HPLC (Chiralcel OJ, 30 cm x 6mm column, hexane:iPrOH 95:5, 0.5 mL/min, T = 25°C): 100% conversion; $[\alpha]_D^{26}$ +34.0 (c 0.360 in $CHCl_3$) 98% ee (*R*) (lit. $[\alpha]_D^{24}$ -31.4 (c 1.0 in $CHCl_3$) >99% ee (*S*)) Reference: L. H. Andrade, T. Barcelos; *Org. Lett.* 2009, **11**, 3052-3055. The same column and solvent combination were used in this paper.

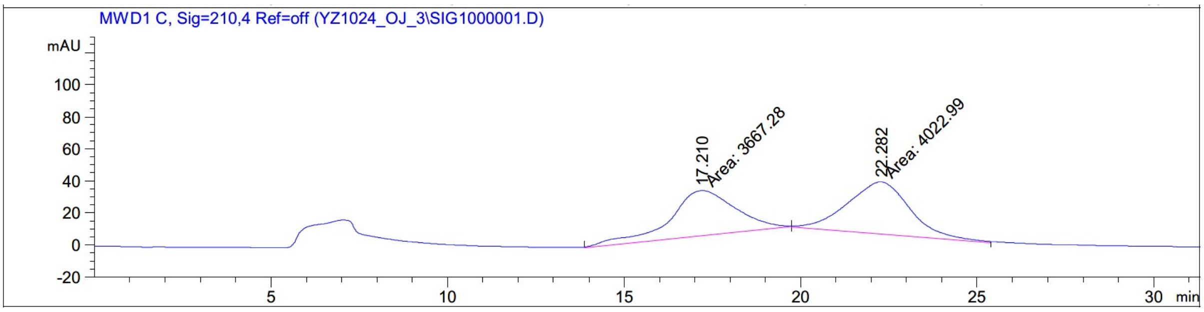
$^{1}$H NMR (400 MHz, CDCl$_3$)



$^{13}$C NMR (100 MHz, CDCl$_3$)



HPLC of racemic 1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol **7**



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Signal 2: MWD1 C, Sig=210,4 Ref=off

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  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  17.210 MM    2.1733 3667.28247   28.12326  47.6873
   2  22.282 MM    2.0609 4022.98975   32.53387  52.3127

Totals :                  7690.27222   60.65713
```
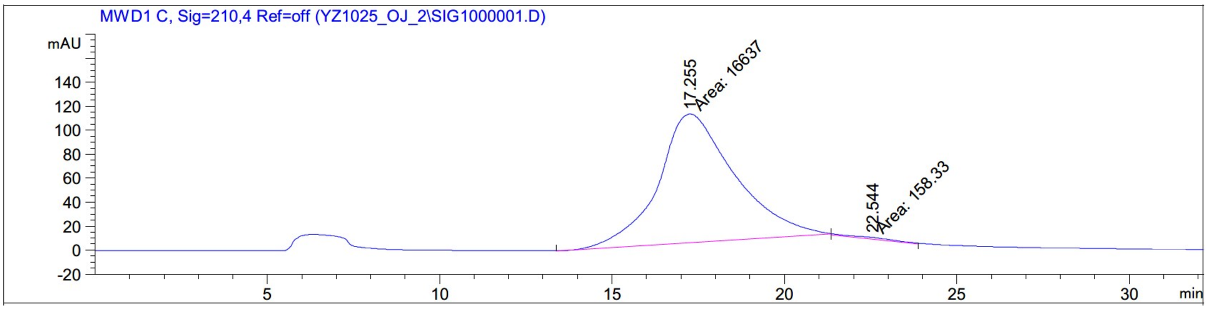

HPLC after ATH of 1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one **6**.

Using (*R,R*)-3C-Tethered Ru(II)-TsDPEN catalyst **2** (DCM as solvent, after 24 hours, white solid, 100 mg, 0.403 mmol, 90% yield, 100% conversion, 98% ee, *R* configuration)



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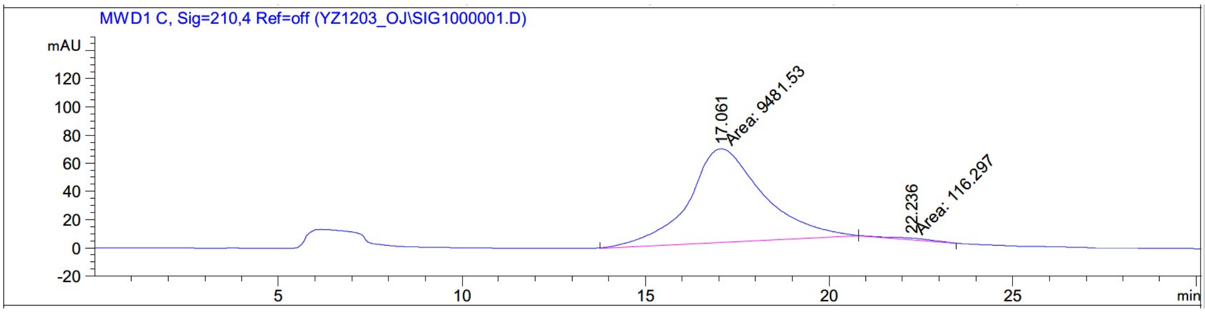
Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  17.255 MM     2.5820 1.66370e4  107.38913 99.0573
   2  22.544 MM     1.5886  158.32979   1.49962  0.9427

Totals :                   1.67953e4  108.88875
```

Using (*R,R*)-3C-Tethered Ru(II)-TsDPEN catalyst **2** (neat, after 24 hours, white solid, 58.0 mg, 0.234 mmol, 72% yield, 100% conversion, 98% ee, *R* configuration)



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----|-------|----|-------|----------|----------|--------|
   1  17.061 MM     2.3736 9481.53418   66.57746 98.7883
   2  22.236 MM     1.4365  116.29687    1.34934  1.2117

Totals :                   9597.83105   67.92680
```
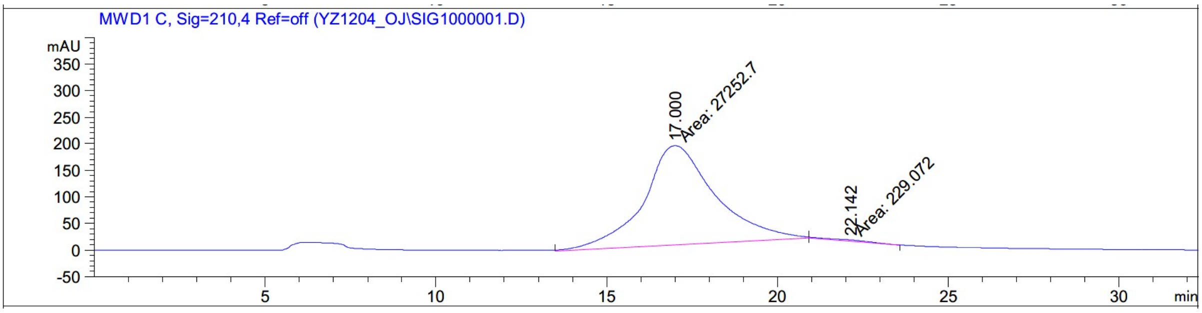

Using (*R,R*)-3C-Tethered Ru(II)-TsDPEN catalyst **2** (MeOH as solvent, after 24 hours, white solid, 40.0 mg, 0.161 mmol, 50% yield, 100% conversion, 98% ee, *R* configuration)



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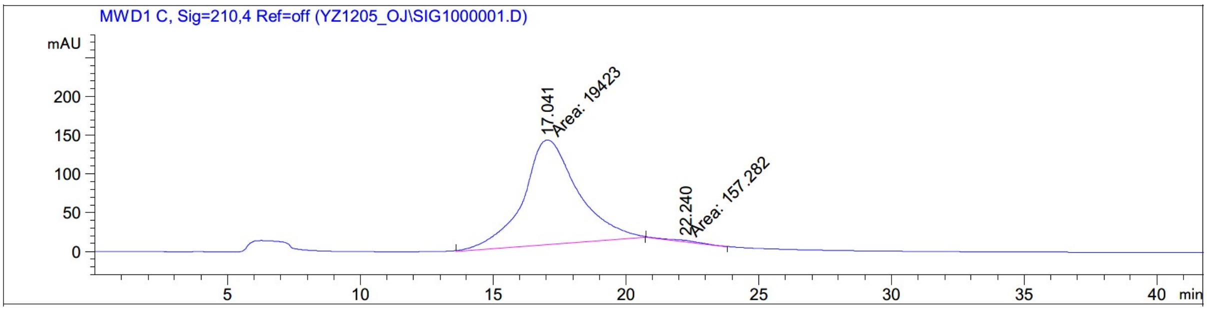
Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  17.000 MM    2.4354 2.72527e4  186.50215  99.1665
   2  22.142 MM    1.4675  229.07237   2.43233   0.8335

Totals :                  2.74817e4  188.93448
```

Using (*R*,*R*)-3C-Tethered Ru(II)-TsDPEN catalyst **2** (MeCN as solvent, after 24 hours, white solid, 47.0 mg, 0.190 mmol, 58% yield, 100% conversion, 98% ee, *R* configuration)



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Peak RetTime Type  Width     Area      Height     Area
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----|-------|----|-------|----------|----------|--------|
   1  17.041 MM    2.3940 1.94230e4  135.21985  99.1967
   2  22.240 MM    1.4674  157.28229   1.81303   0.8033

Totals :                  1.95803e4  137.03287
```
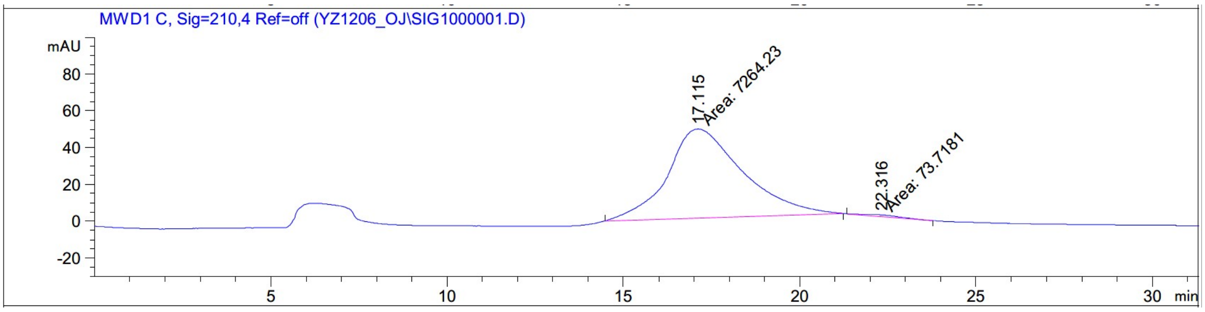

Using pentafluorinated (*R*,*R*)-Noyori Ru(II)-TsDPEN catalyst **3** (DCM as solvent, after 72 hours, white solid, 42.0 mg, 0.169 mmol, 52% yield, 100% conversion, 98% ee, *R* configuration)



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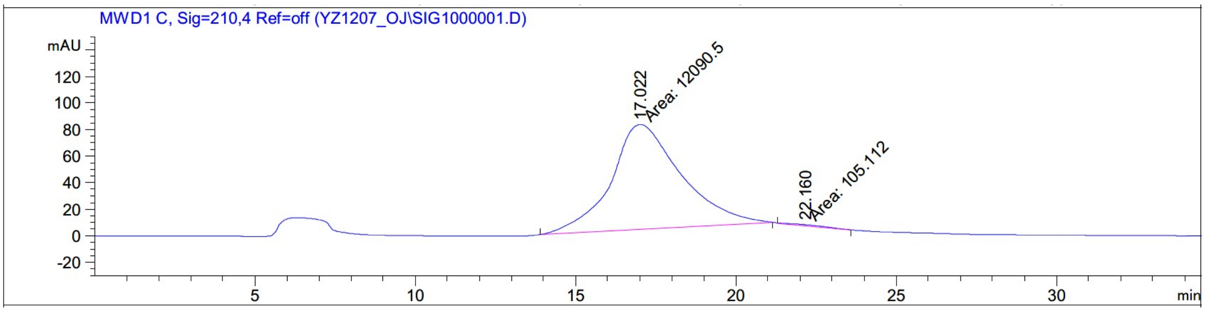
Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  17.115 MM    2.4918 7264.23242   48.58672  98.9954
   2  22.316 MM    1.2543   73.71809 9.79529e-1  1.0046

Totals :                  7337.95051   49.56625
```

Using (*R,R*)-Noyori Ru(II)-TsDPEN catalyst **1** (DCM as solvent, after 72 hours, white solid, 45.0 mg, 0.181 mmol, 56% yield, 100% conversion, 98% ee, *R* configuration)



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----|-------|----|-------|----------|----------|--------|
   1  17.022 MM    2.5472 1.20905e4    79.11017  99.1381
   2  22.160 MM    1.5707  105.11175    1.11534   0.8619

Totals :                  1.21956e4    80.22551
```
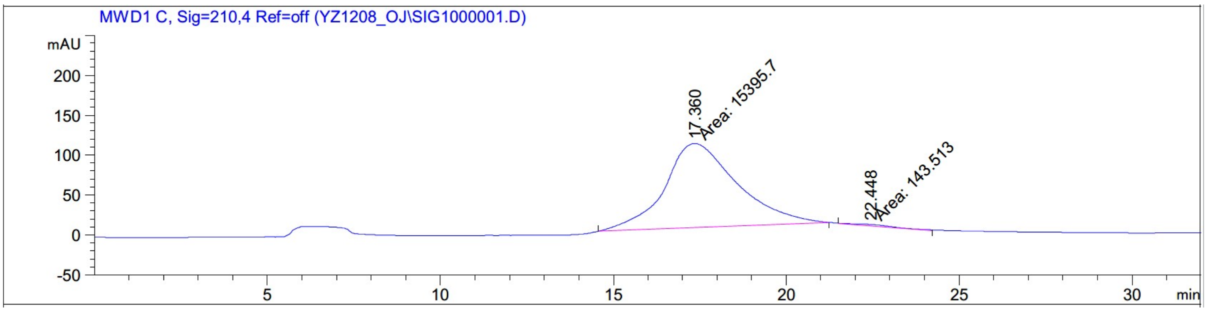

Using (*R,R*)-3C-Tethered, 4-methoxy-Ru(II)-TsDPEN catalyst **4** (use DCM as solvent, after 24 hours, white solid, 43.0 mg, 0.173 mmol, 53% yield, 100% conversion, 98% ee, *R* configuration)



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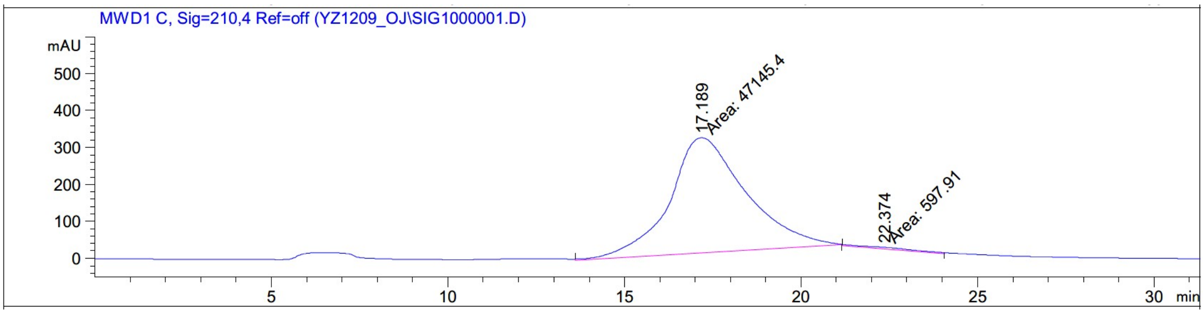
Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area       Height      Area
  #    [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  17.360 MM    2.4403 1.53957e4   105.14993  99.0764
   2  22.448 MM    1.2331  143.51328    1.93978   0.9236

Totals :                  1.55392e4   107.08972
```

Using (*R,R*)-benzyl-tethered Ru(II)-TsDPEN catalyst **5** (DCM as solvent, after 24 hours, white solid, 43.0 mg, 0.173 mmol, 53% yield, 100% conversion, 97% ee, *R* configuration).



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Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area       Height      Area
  #    [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  17.189 MM    2.5194 4.71454e4   311.88705  98.7477
   2  22.374 MM T  2.0992  597.91016    4.74706   1.2523

Totals :                  4.77433e4   316.63411
```
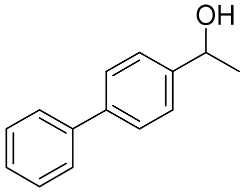
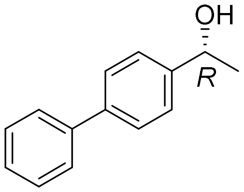
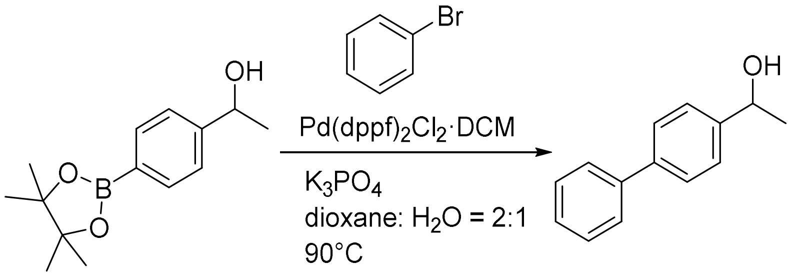
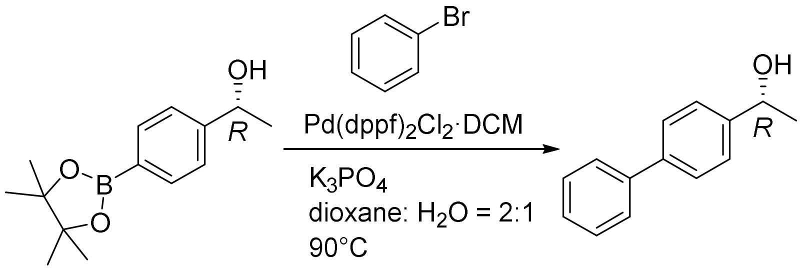

Racemic and (*R*)-1-([1,1'-Biphenyl]-4-yl)ethan-1-ol **8**.









This compound has been reported and fully characterized: L. H. Andrade, T. Barcellos, *Org. Lett.* 2009, **11**, 3052-3055.

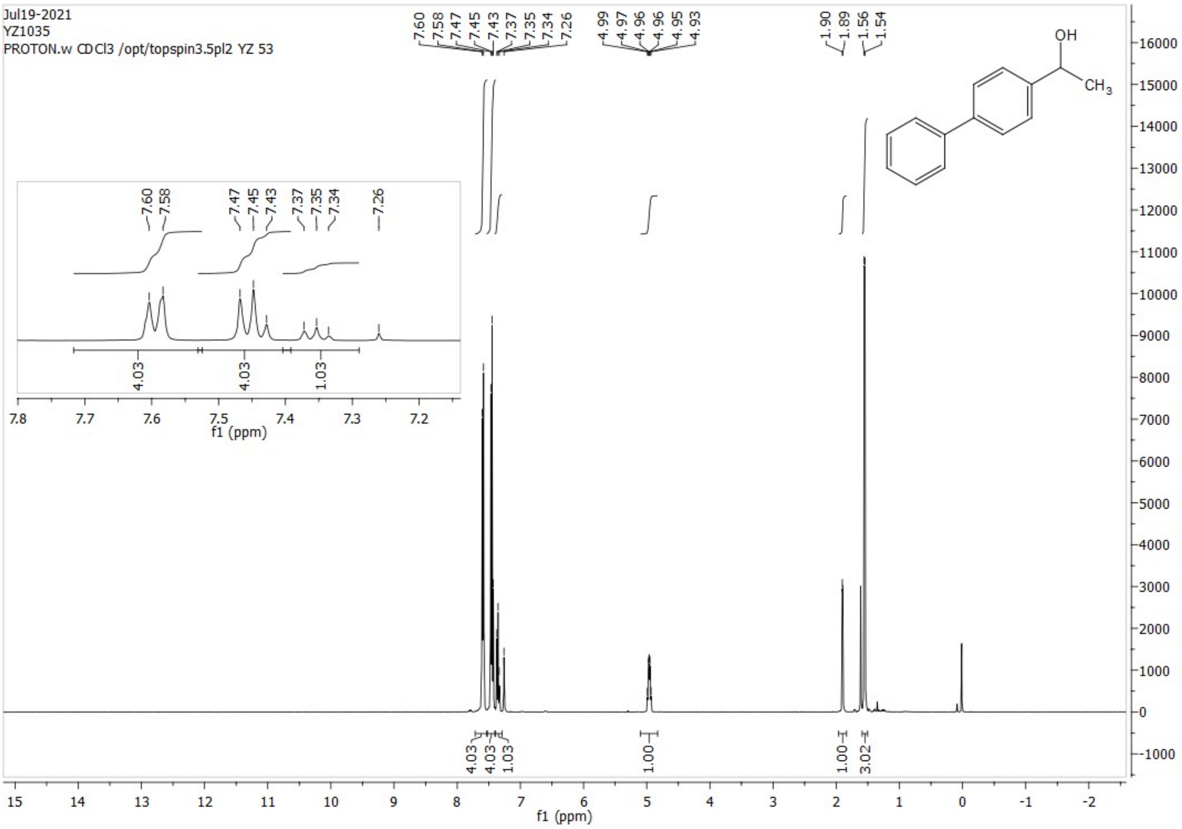
Racemic.

To a solution of racemic 1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol (190 mg, 0.766 mmol), bromobenzene (181 mg, 1.15 mmol) and tripotassium phosphate (488 mg, 2.30 mmol) in dioxane (3.8 mL) and distilled water (1.9 mL) was added Pd(dppf)$_2$Cl$_2$·DCM (31.3 mg, 0.0383 mmol). The reaction mixture was heated to 90 °C and left stirring under the nitrogen atmosphere overnight, followed by TLC (9:1 hexane: EtOAc). The mixture was quenched by distilled water (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried (MgSO$_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-20% ethyl acetate in hexane to give racemic 1-([1,1'-biphenyl]-4-yl)ethan-1-ol **8** as a white solid (72.0 mg, 0.364 mmol, 47%). TLC: Rf ca 0.20 (9:1 hexane: EtOAc), strong UV and KMnO$_4$; $\delta_H$ (400 MHz, CDCl$_3$) 7.60-7.58 (4H, m, ArH), 7.47-7.43 (4H, m, ArH), 7.34 (1H, t, $J$ = 7.3, ArH), 4.98-4.92 (1H, m, ArCH), 1.89 (1H, d, $J$ = 3.4, OH), 1.54 (3H,

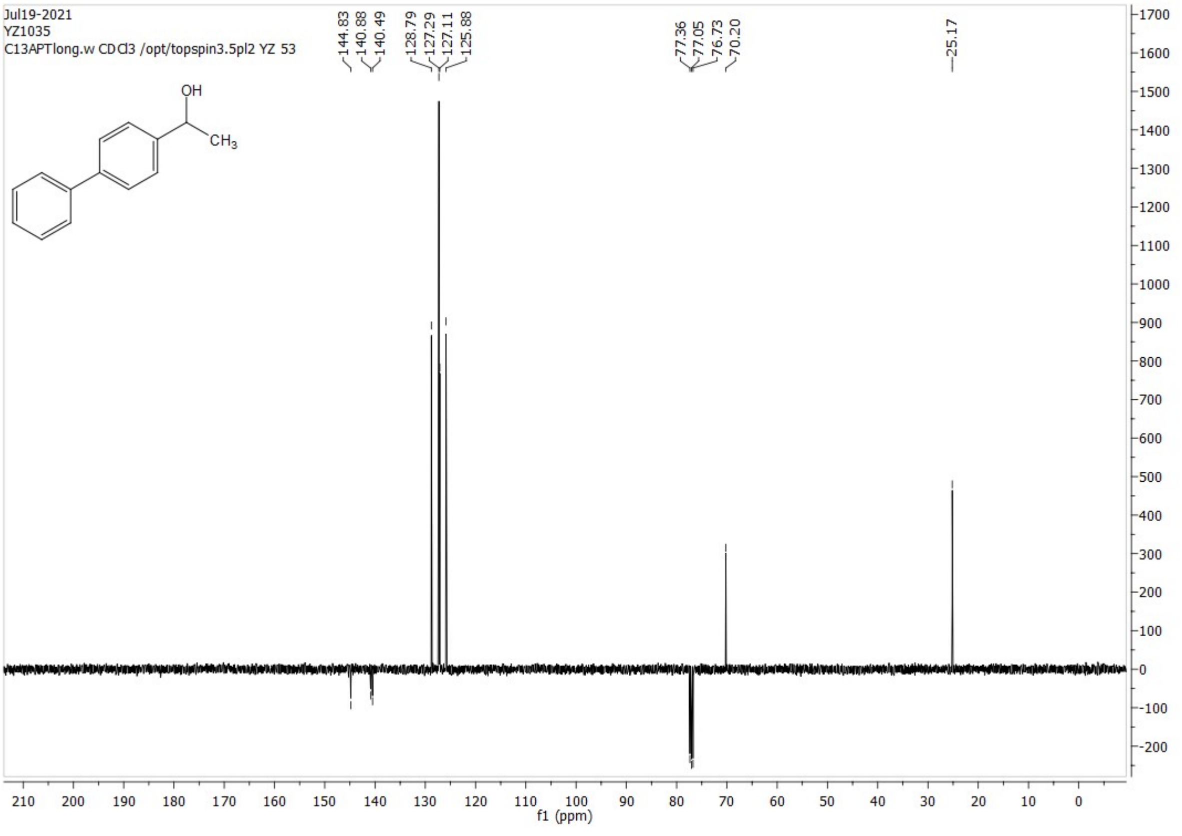
d, *J* = 6.5, $CH_3$) ppm; $\delta_C$ (100 MHz, $CDCl_3$) 144.83 (C), 140.88 (C), 140.49 (C), 128.79 (CH), 127.29 (CH), 127.11 (CH), 125.88 (CH), 70.20 (CH), 25.17 ($CH_3$) ppm; m/z (ES-API+) 221.0 ($M^+$ + 23, 100%). Data matched that reported.
Enantiomeric excess and conversion determined by HPLC analysis (Chiralcel ADH, 30 cm x 6mm column, hexane:iPrOH 95:5, 0.5 mL/min, T = 25°C) *S* isomer 23.0 min and *R* isomer 25.1 min.

Asymmetric.
To a solution of (*R*)-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol (156 mg, 0.629 mmol), bromobenzene (148 mg, 0.944 mmol) and tripotassium phosphate (401 mg, 1.89 mmol) in dioxane (3.1 mL) and distilled water (1.6 mL) was added $Pd(dppf)_2Cl_2 \cdot DCM$ (25.8 mg, 0.0315 mmol). The reaction mixture was heated to 90 °C and left stirring under the nitrogen atmosphere overnight, followed by TLC (9:1 hexane: EtOAc). The mixture was quenched by distilled water (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried ($MgSO_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-20% ethyl acetate in hexane to give (*R*)-1-([1,1'-biphenyl]-4-yl)ethan-1-ol **8** as a white solid (60.0 mg, 0.306 mmol, 49%). The reaction was also followed by HPLC (Chiralpak ADH, 30 cm x 6mm column, hexane:iPrOH 95:5, 0.5 mL/min, T = 25°C): $[\alpha]_D^{31}$ +35.2 (c 0.740 in $CHCl_3$) 96% ee (*R*) (lit. $[\alpha]_D^{24}$ -46.6 (c 1.0 in $CHCl_3$) 96% ee (*S*)) Reference: L. H. Andrade, T. Barcelos; *Org. Lett.* 2009, **11**, 3052-3055.

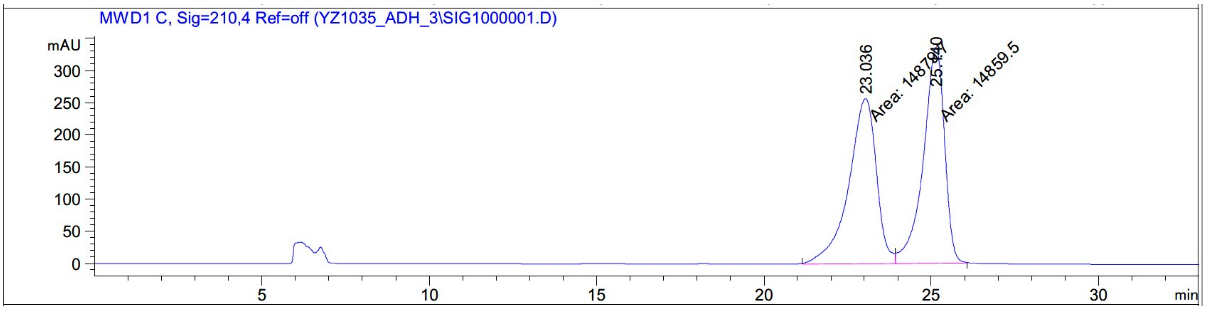
$^1$H NMR (400 MHz, CDCl$_3$)



$^{13}$C NMR (100 MHz, CDCl$_3$)



HPLC of racemic 1-([1,1'-biphenyl]-4-yl)ethan-1-ol **8**.



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   2  25.140 FM    0.7374 1.48595e4  335.83981  49.9661

Totals :                  2.97392e4  592.80423
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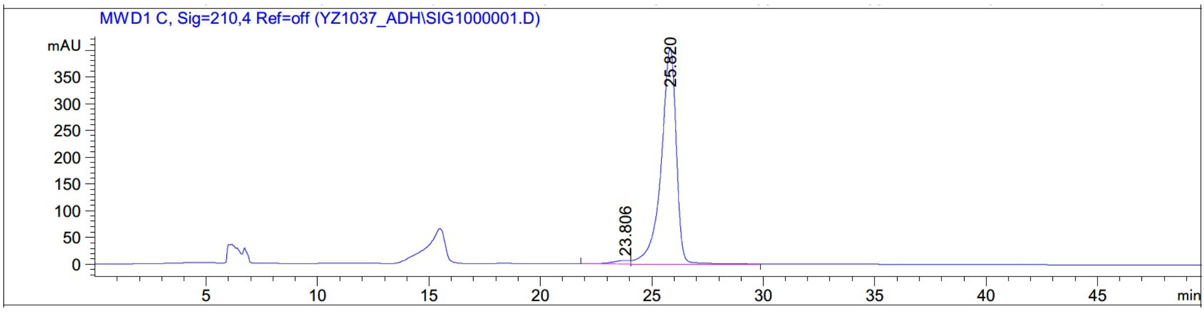
HPLC of 1-([1,1'-biphenyl]-4-yl)ethan-1-ol **8**. (96% ee, *R* configuration)



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Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
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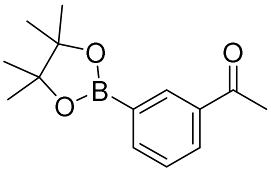
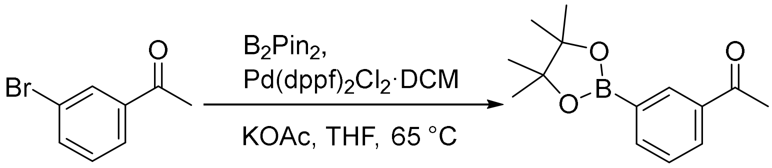
----|-------|----|-------|----------|----------|--------|
   1  23.806 BV    0.6397  343.31085    6.46352   1.7795
   2  25.820 VB    0.7059 1.89497e4  403.49734  98.2205

Totals :                  1.92930e4  409.96086
```

**Data related to Figure 4.**

1-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one.



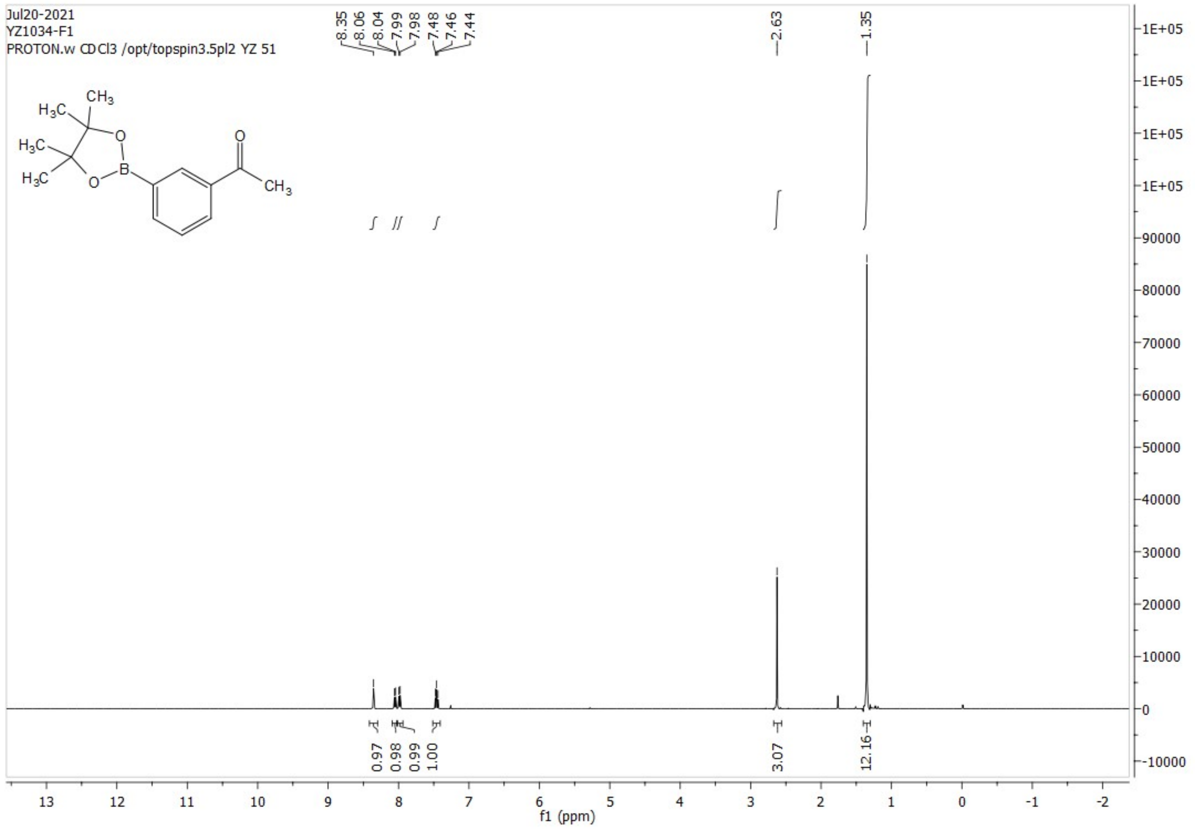


This compound has been reported and fully characterized.

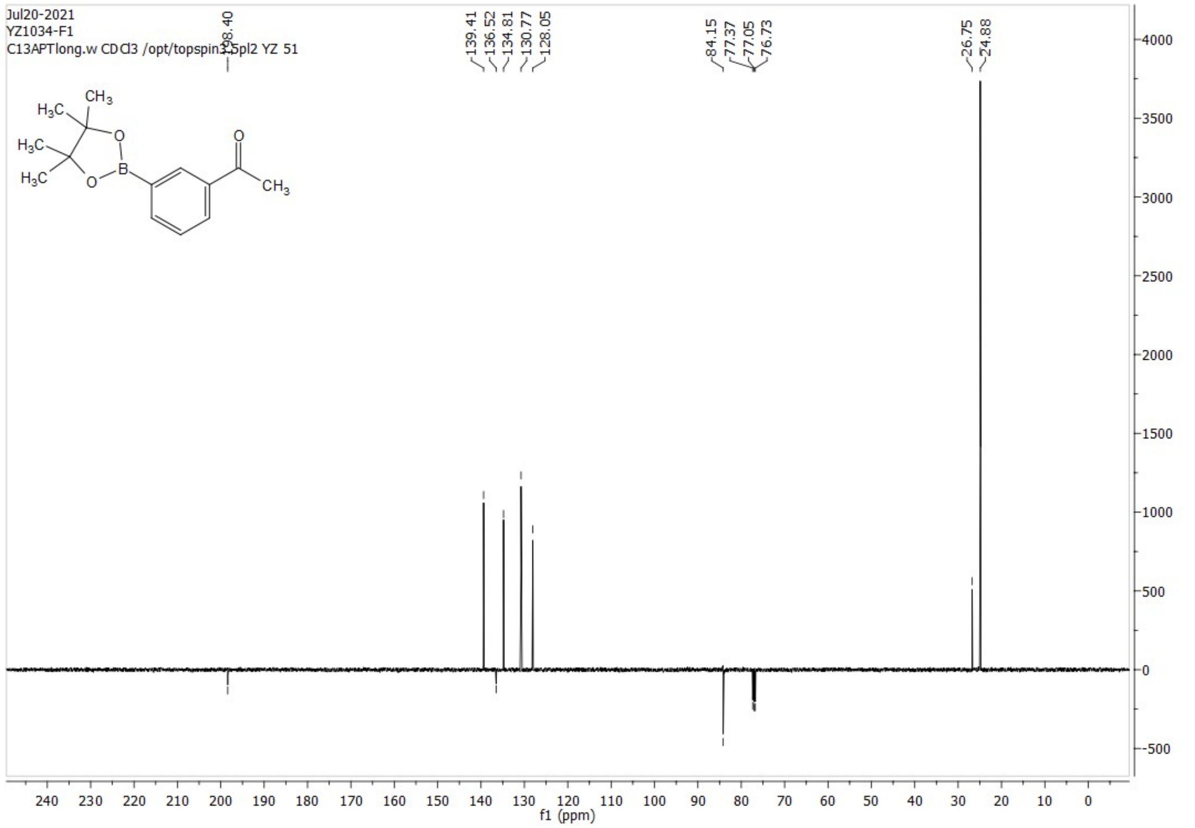
Reference: X. Zhao, M. Wu, Y. Liu and S. Cao, *Org. Lett.* 2018, **20**, 5564-5568.

A round-bottom flask was charged with 3’-bromoacetophenone (398 mg, 2.00 mmol), bis(pinacolato)diboron (610 mg, 2.40 mmol), potassium acetate (588 mg, 6.00 mmol), THF (12 mL) and Pd(dppf)$_2$Cl$_2$·DCM (81.7 mg, 0.100 mmol). The reaction mixture was heated to 65 °C and left stirring under the nitrogen atmosphere overnight, followed by TLC (9:1 hexane: EtOAc). The mixture was quenched by distilled water (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried (MgSO$_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-50% ethyl acetate in hexane to give 1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one as a colorless oil (362 mg, 1.47 mmol, 74%). TLC: Rf ca 0.30 (9:1 hexane: EtOAc), strong UV and KMnO$_4$; $\delta_H$ (400 MHz, CDCl$_3$) 8.35 (1H, s, ArH), 8.06 (1H, d, $J$ = 7.3, ArH), 7.99 (1H, d, $J$ = 7.3, ArH), 7.46 (1H, t, $J$ = 7.6, ArH), 2.63 (3H, s, CH$_3$), 1.35 (12H, s, CH$_3$) ppm; $\delta_C$ (100 MHz, CDCl$_3$) 198.40 (C), 139.41 (CH), 136.52 (C), 134.81 (CH), 130.77 (CH), 128.05 (CH), 84.15 (C), 26.75 (CH$_3$), 24.88 (CH$_3$) ppm; m/z (ES-API+) 269.1 (M$^+$ + 23, 100%). Data matched that reported.

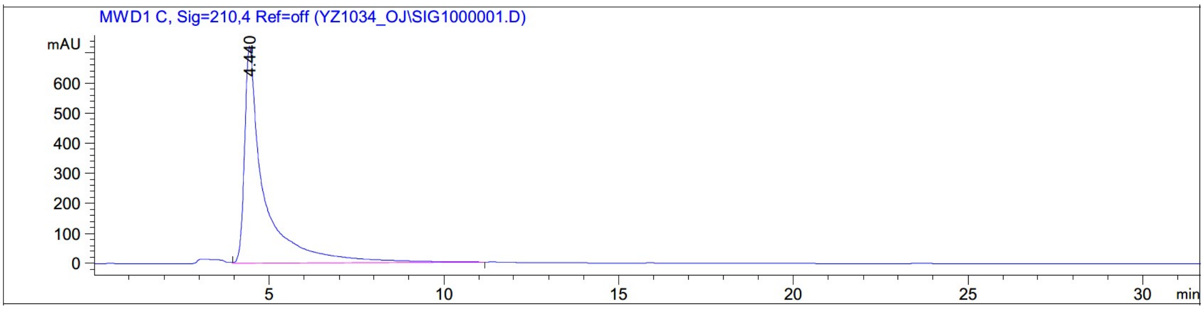
$^{1}$H NMR (400 MHz, CDCl$_3$)



$^{13}$C NMR (100 MHz, CDCl$_3$)



HPLC of 1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one



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Signal 2: MWD1 C, Sig=210,4 Ref=off

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----|-------|----|-------|----------|----------|--------|
   1   4.440 VB    0.5296 2.81960e4  721.96869 100.0000

Totals :                  2.81960e4  721.96869
```
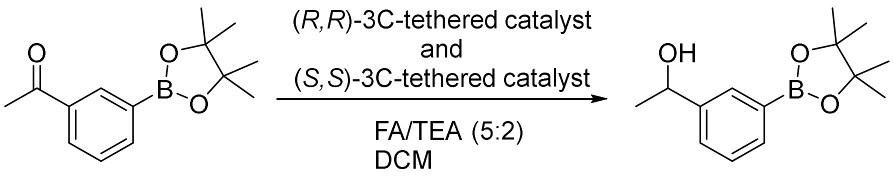
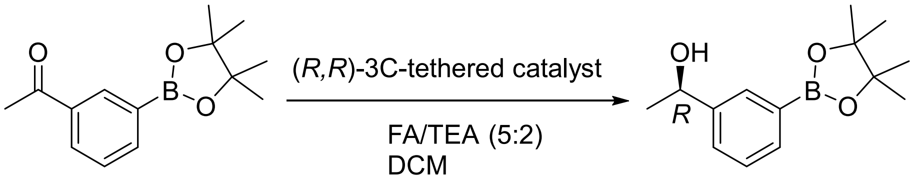

Racemic and (*R*)-1-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol **9**.

racemic:



Asymmetric:



This compound has been reported and fully characterized.

Reference: L. H. Andrade, T. Barcelos; *Org. Lett.* 2009, **11**, 3052-3055.

**Synthesis of a racemic standard:**

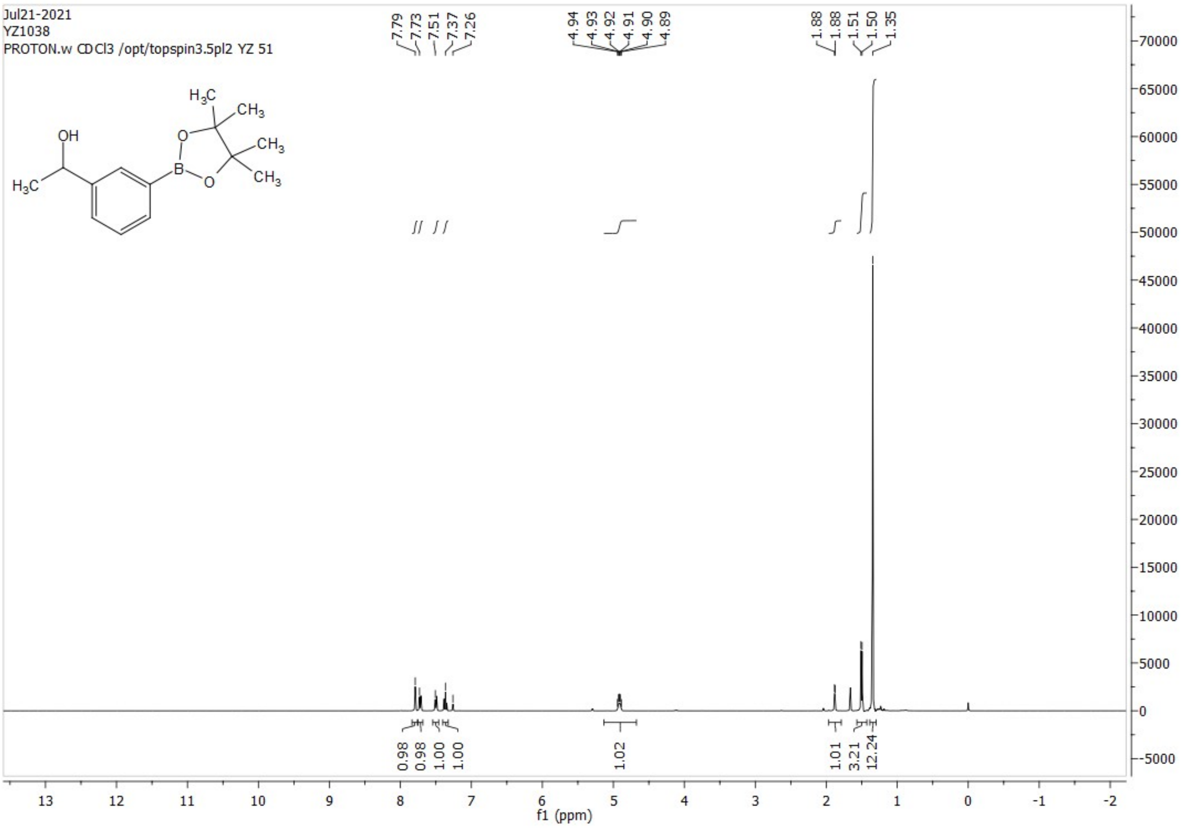
(*R,R*)-3C-Tethered Ru(II)-TsDPEN catalyst **2** (2.3 mg, 3.7 μmol, 0.5 mol%) and (*S,S*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (2.3 mg, 3.7 μmol, 0.5 mol%) were added to FA: TEA (5:2 azeotropic mixture, 0.81 mL) at rt and the mixture was stirred under a nitrogen atmosphere for 15 minutes; after which a solution of 1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one (180 mg, 0.732 mmol) in DCM (1.13 mL) was added. The reaction mixture was stirrer under a nitrogen atmosphere and followed by TLC (4:1 hexane: EtOAc). After 24 hours, the reaction was quenched using saturated $NaHCO_3$ solution (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried ($MgSO_4$) and filtered. The solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-50% EtOAc in hexane to give 1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol **9** as a colorless oil (110 mg, 0.444 mmol, 61%). TLC: Rf ca 0.20 (4:1 hexane: EtOAc), strong UV and $KMnO_4$; $\delta_H$ (400 MHz, $CDCl_3$) 7.79 (1H, s, ArH), 7.73 (1H, d, $J$ = 7.2, ArH), 7.51 (1H, d, $J$ = 7.6, ArH), 7.37 (1H, t, $J$ = 7.5, ArH), 4.94-4.89 (1H, m, CH), 1.88 (1H, d, $J$ = 3.0, OH), 1.51 (3H, d, $J$ = 6.4, $CH_3$), 1.35 (12H, s, $CH_3$) ppm; $\delta_C$ (100 MHz, $CDCl_3$) 145.07 (C), 133.99 (CH), 131.74 (CH), 128.31 (CH), 128.01 (CH), 83.86 (C), 70.48 (CH), 25.14

($CH_3$), 24.88 ($CH_3$) ppm; m/z (ES-API+) 271.1 ($M^+$ + 23, 100%). Data matched that reported.

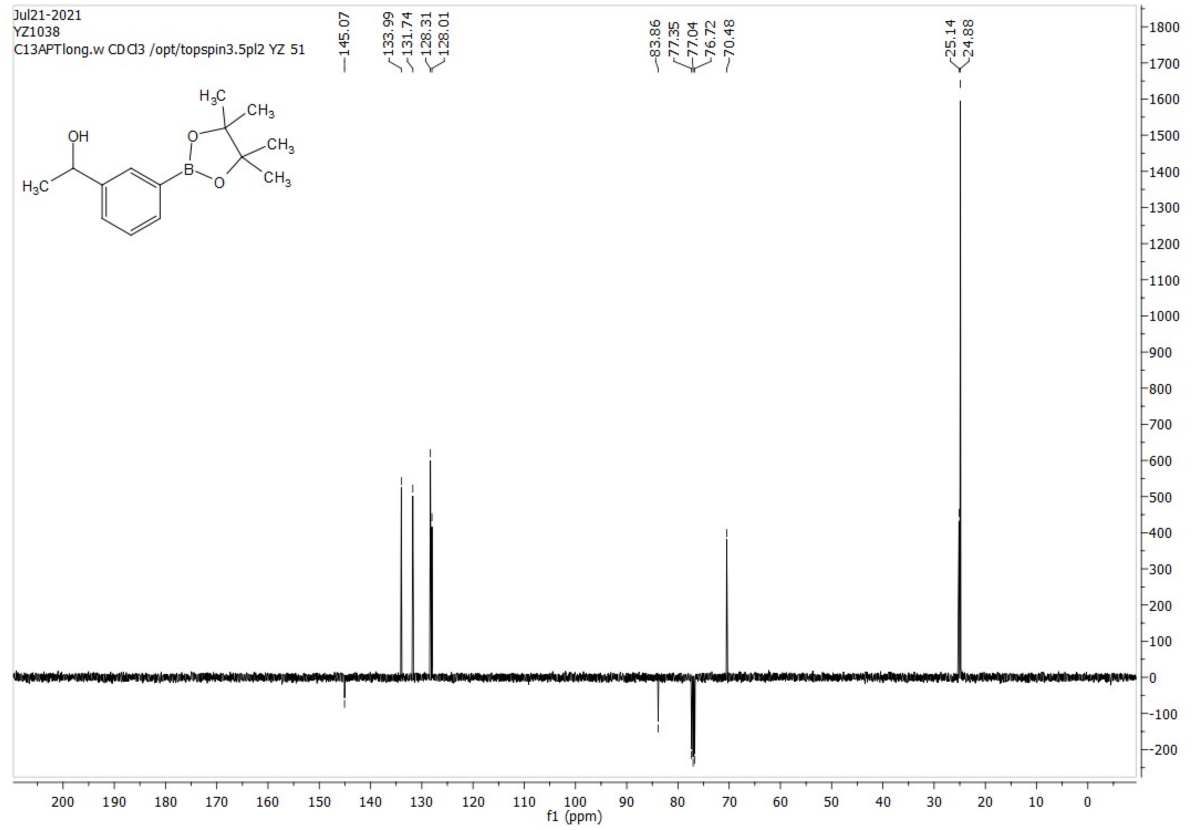
Enantiomeric excess and conversion determined by HPLC analysis (Chiralcel OJ, 30 cm x 6mm column, hexane:iPrOH 95:5, 1.0 mL/min, T = 25°C) ketone 4.4 min, *R* isomer 21.9 min and *S* isomer 7.2 min. The same column and conditions were used as in the paper referenced above.

ATH of 1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one using (*R,R*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (4.5 mg, 7.3 μmol, 1 mol%) was added to FA: TEA (5:2 azeotropic mixture, 0.81 mL) at rt and the mixture was stirred under a nitrogen atmosphere for 15 minutes; after which a solution of 1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one (180 mg, 0.732 mmol) in DCM (1.13 mL) was added. The reaction mixture was stirred under a nitrogen atmosphere and followed by TLC (4:1 hexane: EtOAc). After 24 hours, the reaction was quenched using saturated $NaHCO_3$ solution (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried ($MgSO_4$) and filtered. The solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-50% EtOAc in hexane to give (*R*)-1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol **9** as a colourless oil (111 mg, 0.448 mmol, 61%). The reaction was also followed by HPLC (Chiralcel OJ, 30 cm x 6 mm column, hexane:iPrOH 95:5, 1.0 mL/min, T = 25°C): $[\alpha]_D^{31}$ +31.9 (c 0.808 in $CHCl_3$) 98% ee (*R*) (lit. $[\alpha]_D^{27}$ -27.2 (c 1.14 in $CHCl_3$) >99% ee (*S*)) Reference: L. H. Andrade, T. Barcelos; *Org. Lett.* 2009, **11**, 3052-3055.

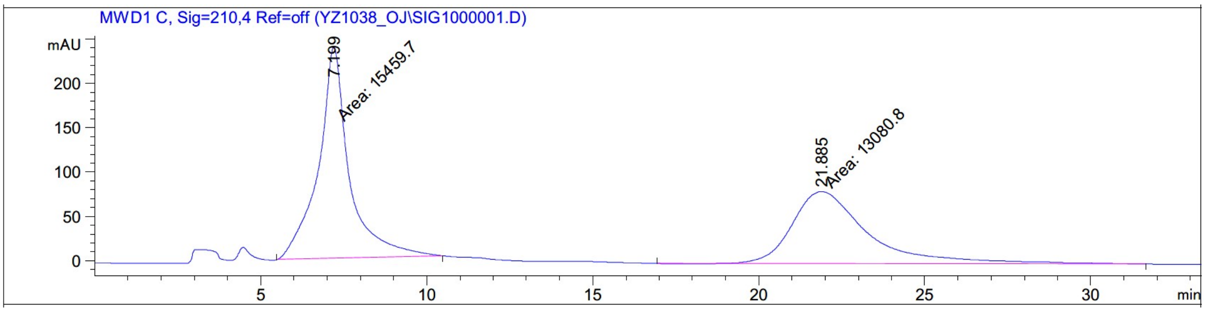
$^{1}H$ NMR (400 MHz, $CDCl_3$)



$^{13}C$ NMR (100 MHz, $CDCl_3$)



HPLC of racemic 1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol **9**



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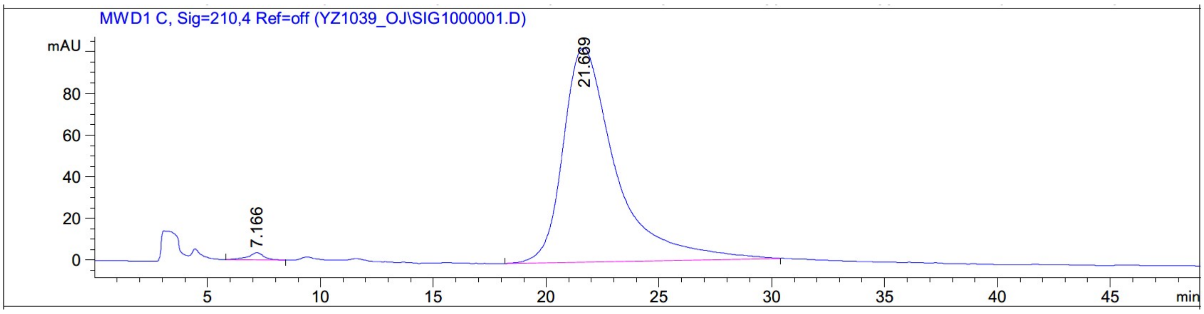
   1   7.199 MM    1.0811 1.54597e4  238.32399  54.1675
   2  21.885 MM    2.6813 1.30808e4   81.31003  45.8325

Totals :                  2.85405e4  319.63402
```

HPLC after ATH of 1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one (*R,R*)-3C-Tethered Ru(II)-TsDPEN catalyst **2** (after 24 hours, 100% conversion, 98% ee, *R* configuration)



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Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   7.166 BB    0.5901  174.96596    3.54352   1.0387
   2  21.669 BB    1.9898 1.66704e4  102.69458  98.9613

Totals :                  1.68453e4  106.23810
```
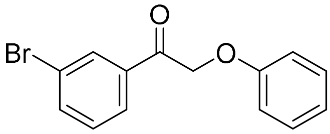
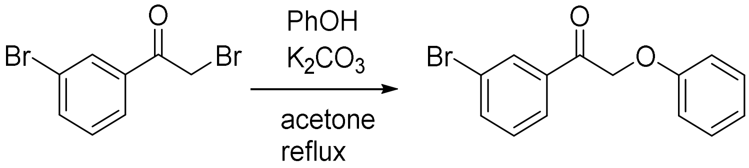

1-(3-Bromophenyl)-2-phenoxyethan-1-one.

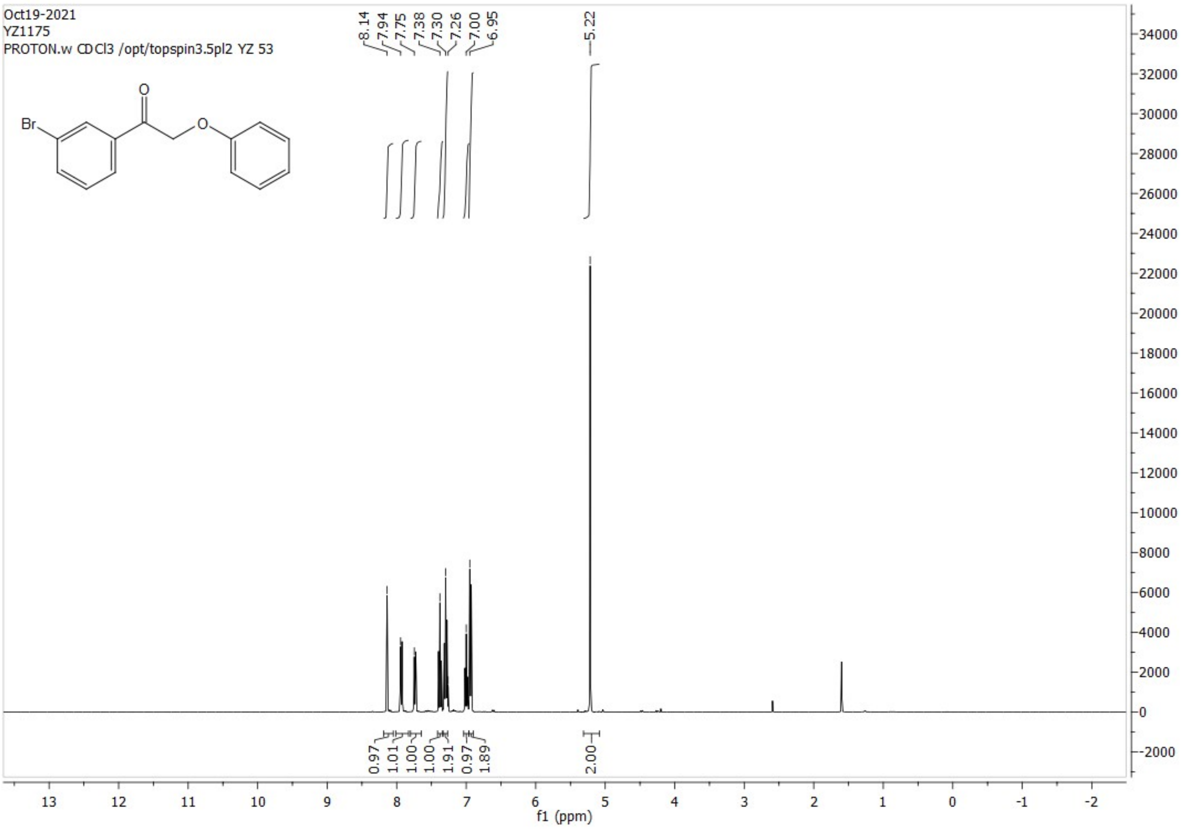




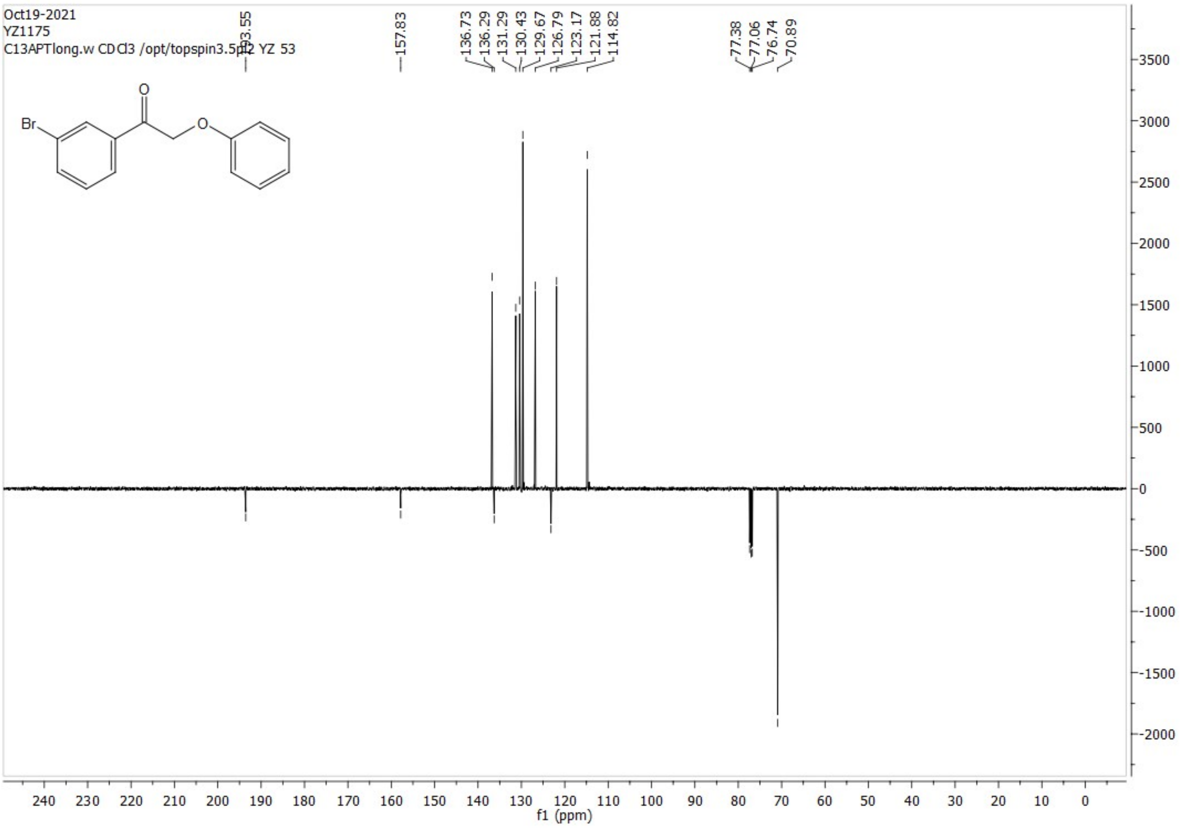
This compound has been reported and fully characterized: K. Huang, M. Ortiz-Marciales, W. Correa, E. Pomales, X. Y. Lopez, *J. Org. Chem.* 2009, **74**, 4195-4202.

A round-bottom flask was charged with 2,3′-dibromoacetophenone (1.39 g, 5.00 mmol), potassium carbonate (690 mg, 5.00 mmol), phenol (470 mg, 5.00 mmol) and acetone (5 mL). The reaction mixture was heated to reflux and left stirring under the nitrogen atmosphere overnight, followed by TLC (9:1 hexane: EtOAc). The mixture was quenched by distilled water (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried ($MgSO_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-10% ethyl acetate in hexane to give 1-(3-bromophenyl)-2-phenoxyethan-1-one as a yellow solid (473 mg, 1.63 mmol, 33%). TLC: Rf ca 0.50 (9:1 hexane: EtOAc), strong UV and $KMnO_4$; $\delta_H$ (400 MHz, $CDCl_3$) 8.14 (1H, s, ArH), 7.94 (1H, d, $J = 7.8$, ArH), 7.75 (1H, d, $J = 8.0$, ArH), 7.38 (1H, t, $J = 7.9$, ArH), 7.30 (2H, t, $J = 7.9$, ArH), 7.00 (1H, t, $J = 7.9$, ArH), 6.95 (2H, d, $J = 8.4$, ArH), 5.22 (2H, s, $CH_2$) ppm; $\delta_C$ (100 MHz, $CDCl_3$) 193.55 (C), 157.83 (C), 136.73 (CH), 136.29 (C), 131.43 (CH), 130.43 (CH), 129.67 (CH), 126.79 (CH), 123.17 (C), 121.88 (CH), 114.82 (CH), 70.89 ($CH_2$) ppm; m/z (ES-API+) 313.0 ($M^+ + 23$, 100%). Data matched that reported.

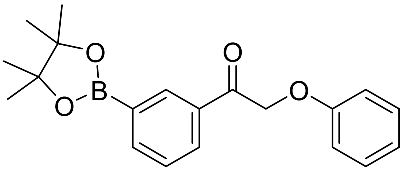
$^{1}$H NMR (400 MHz, CDCl$_3$)

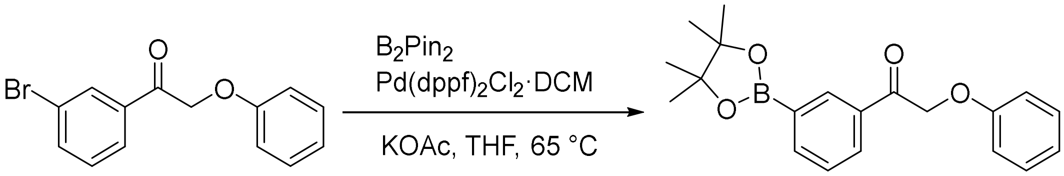


$^{13}$C NMR (100 MHz, CDCl$_3$)



2-Phenoxy-1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one.



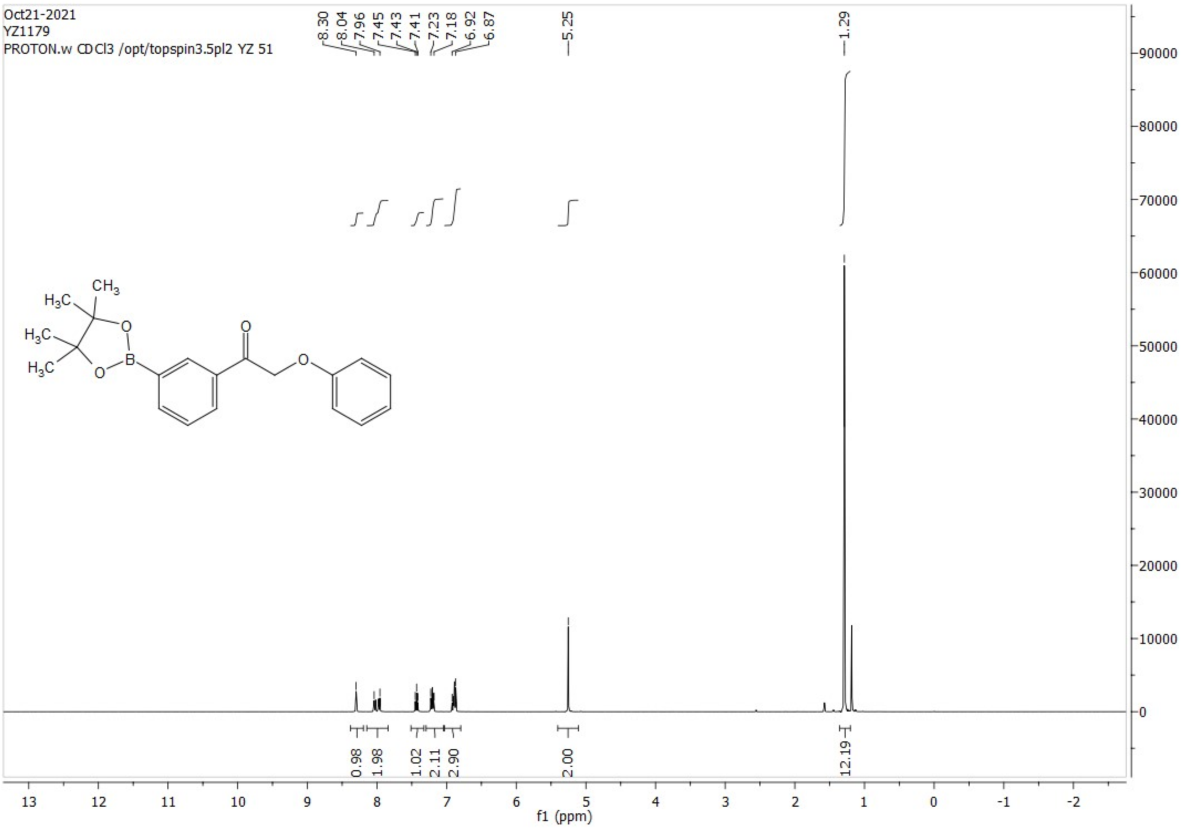


This compound is novel.

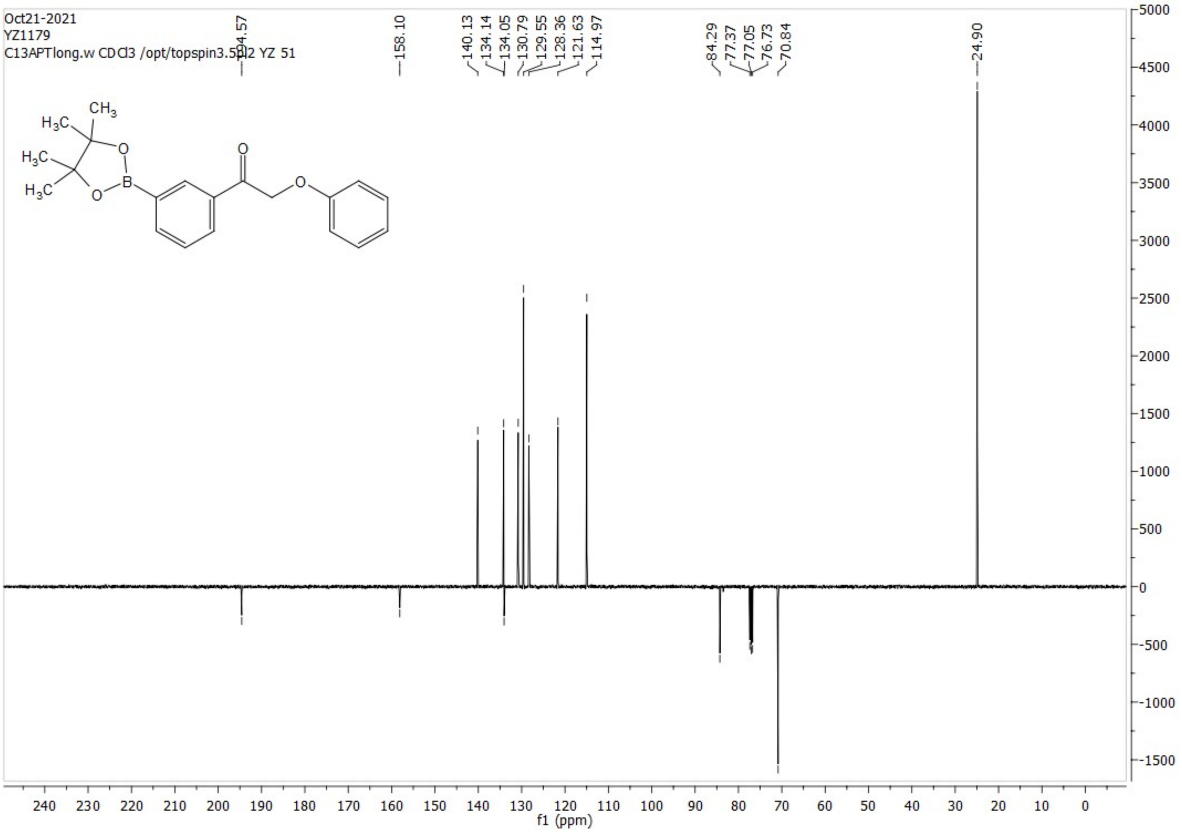
A round-bottom flask was charged with 1-(3-bromophenyl)-2-phenoxyethan-1-one (470 mg, 1.62 mmol), bis(pinacolato)diboron (493 mg, 1.94 mmol), potassium acetate (476 mg, 4.86 mmol), THF (8 mL) and $Pd(dppf)_2Cl_2{\cdot}DCM$ (66.2 mg, 0.0810 mmol). The reaction mixture was heated to 65 °C and left stirring under the nitrogen atmosphere overnight, followed by TLC (9:1 hexane: EtOAc). The mixture was quenched by distilled water (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried ($MgSO_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-10% ethyl acetate in hexane to give 2-phenoxy-1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one as a white solid (321 mg, 0.950 mmol, 59%). TLC: Rf ca 0.50 (9:1 hexane: EtOAc), strong UV and $KMnO_4$; Mp: 87°C; HRMS: (ESI+): [M+H]+, Calcd for $C_{20}H_{23}BNaO_4$ 361.1571; Found 361.1582; 4.0 ppm error; $\nu_{max}$ 3061, 2975, 1702, 1600, 1488, 1389, 1371, 1329, 1209, 1120, 1076 $cm^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 8.30 (1H, s, ArH), 8.04-7.69 (2H, m, ArH), 7.43 (1H, t, *J* = 7.6, ArH), 7.23-7.18 (2H, m, ArH), 6.92-6.87 (3H, m, ArH), 5.25 (2H, s, $CH_2$), 1.29 (12H, s, $CH_3$) ppm; $\delta_C$ (100 MHz, $CDCl_3$) 194.57 (C), 158.10 (C), 140.13 (CH), 134.14 (CH), 134.05 (C), 130.79 (CH), 129.55 (CH), 128.36 (CH), 121.63 (CH), 114.97 (CH), 84.29 (C), 70.84 ($CH_2$), 24.90 ($CH_3$) ppm; m/z (ES-API+) 361.1 ($M^+$ + 23, 100%).

Enantiomeric excess and conversion determined by HPLC analysis (Chiralpak IA, 30 cm x 6mm column, hexane:iPrOH 90:10, 1.0 mL/min, T = 25°C) ketone 5.2 min, *R* and *S* isomers 6.8 min and 8.5 min.

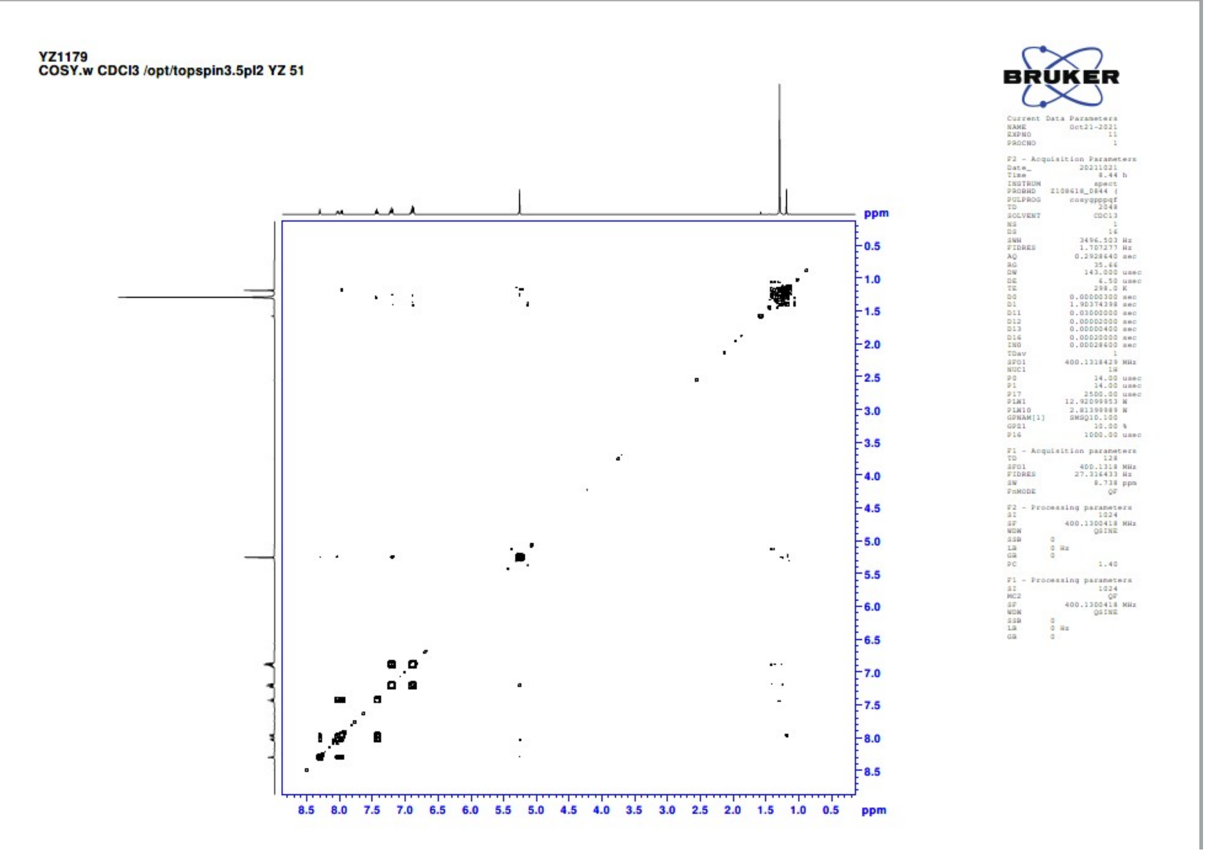
$^1H$ NMR (400 MHz, $CDCl_3$)



$^{13}C$ NMR (100 MHz, $CDCl_3$)



COSY (400 MHz, $CDCl_3$)



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PROCNO                 1

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F1 - Acquisition parameters
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FnMODE                QF

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GB         0
PC                  1.40

F1 - Processing parameters
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MC2                   QF
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WDW                QSINE
SSB        0
LB         0 Hz
GB         0
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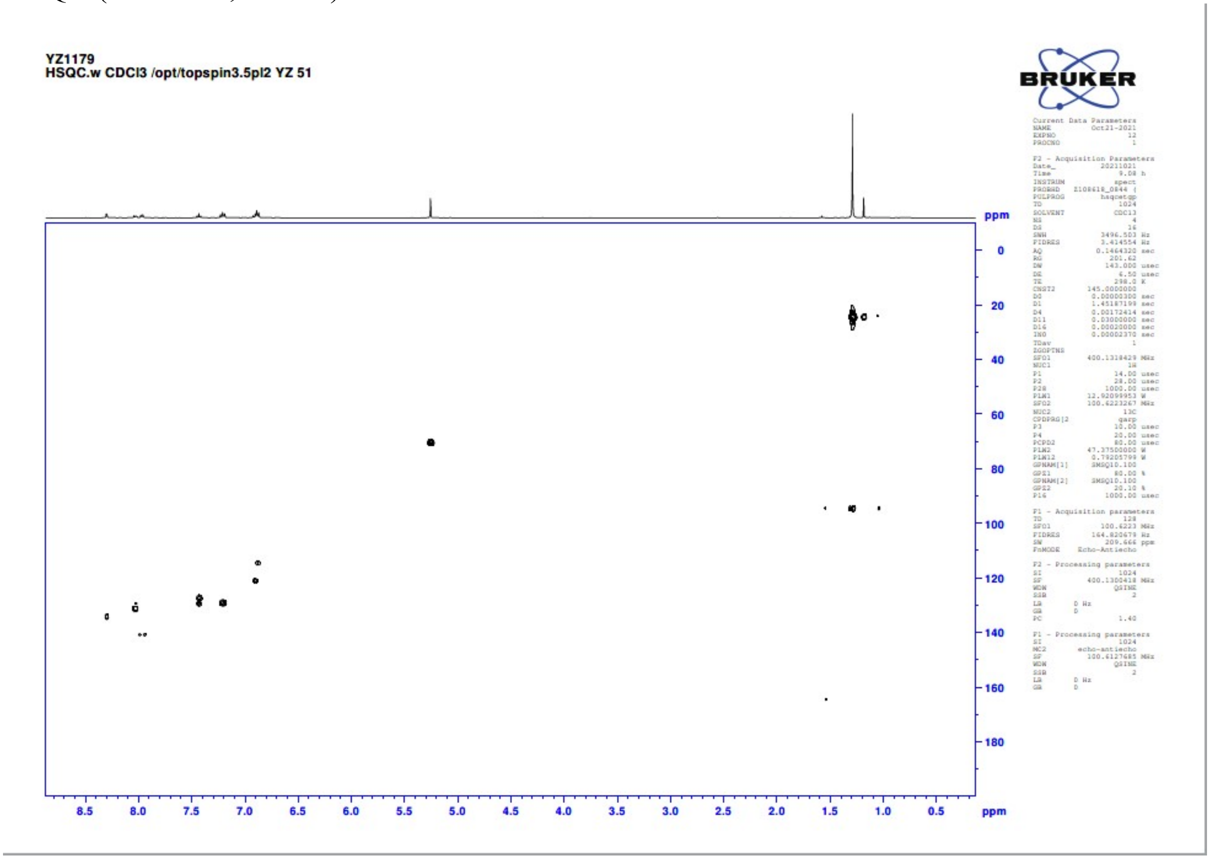
HSQC (400 MHz, $CDCl_3$)



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NAME          Oct21-2021
EXPNO                 12
PROCNO                 1

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PULPROG         hsqcetgp
TD                  1024
SOLVENT            CDCl3
NS                     4
DS                    16
SWH             3496.503 Hz
FIDRES          3.414554 Hz
AQ             0.1464320 sec
RG                201.62
DW               143.000 usec
DE                  6.50 usec
TE                 298.0 K
CNST2        145.0000000
D0            0.00000300 sec
D1            1.45187199 sec
D4            0.00172414 sec
D11           0.03000000 sec
D16           0.00020000 sec
IN0           0.00002370 sec
TDav                   1
ZGOPTNS
SFO1         400.1318429 MHz
NUC1                  1H
P1                 14.00 usec
P2                 28.00 usec
P28              1000.00 usec
PLW1         12.92099953 W
SFO2         100.6223267 MHz
NUC2                 13C
CPDPRG[2            garp
P3                 10.00 usec
P4                 20.00 usec
PCPD2              80.00 usec
PLW2         47.37500000 W
PLW12         0.79205799 W
GPNAM[1]      SMSQ10.100
GPZ1               80.00 %
GPNAM[2]      SMSQ10.100
GPZ2               20.10 %
P16              1000.00 usec

F1 - Acquisition parameters
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SFO1            100.6223 MHz
FIDRES        164.820679 Hz
SW               209.666 ppm
FnMODE      Echo-Antiecho

F2 - Processing parameters
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SF           400.1300418 MHz
WDW                QSINE
SSB                    2
LB         0 Hz
GB         0
PC                  1.40

F1 - Processing parameters
SI                  1024
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SF           100.6127685 MHz
WDW                QSINE
SSB                    2
LB         0 Hz
GB         0
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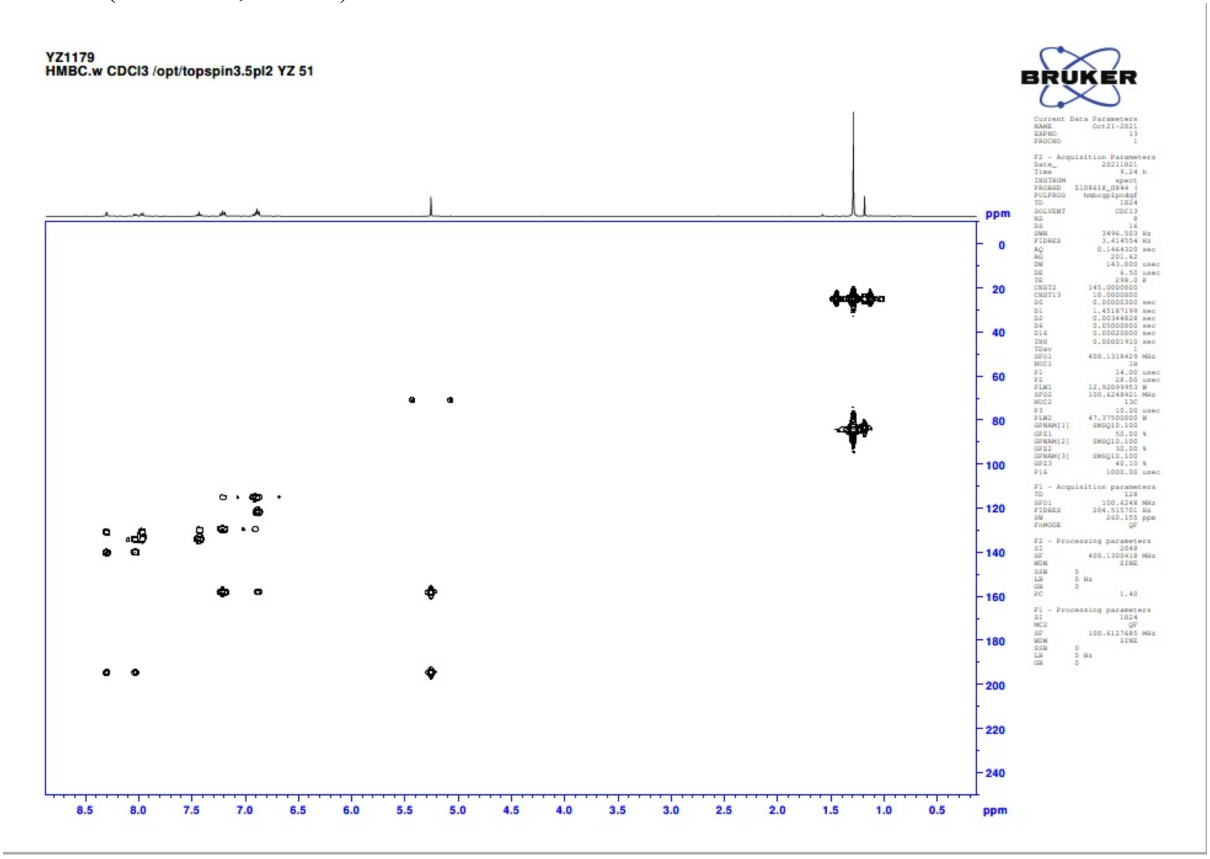
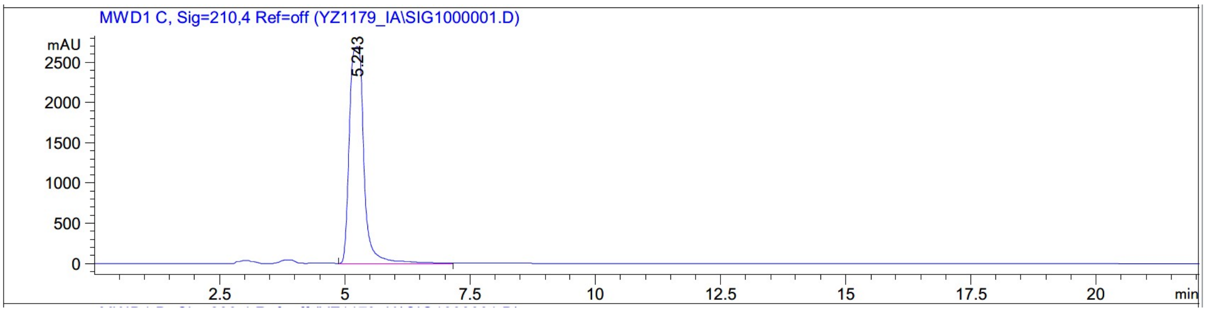
HMBC (400 MHz, CDCl$_3$)



HPLC of 2-phenoxy-1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one



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Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width      Area       Height      Area
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----|-------|----|-------|----------|----------|--------|
   1   5.243 BV     0.3134 5.38266e4  2690.06665 100.0000

Totals :                   5.38266e4  2690.06665
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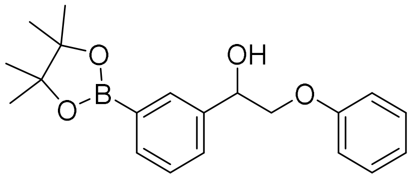
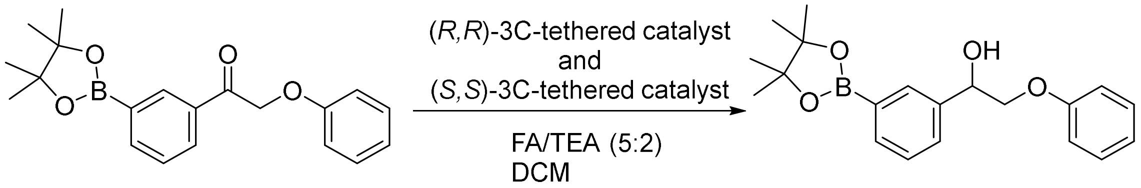
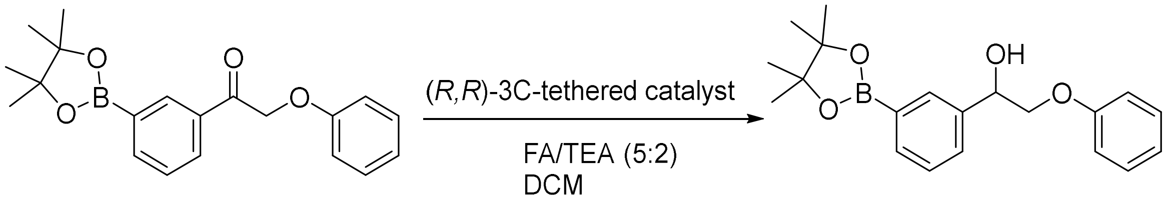
Racemic and (*S*)-phenoxy-1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol **10**.







This compound is novel.

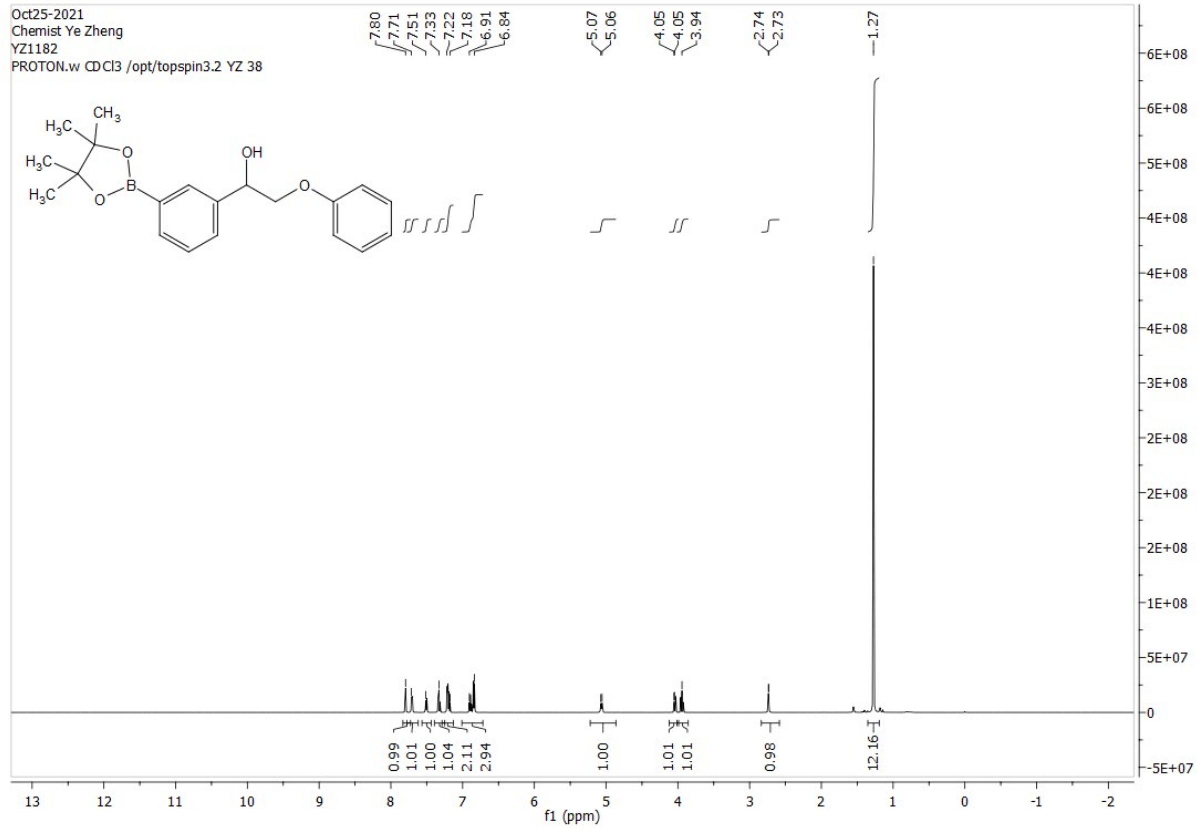
**Synthesis of a racemic standard:**

(*R,R*)-3C-Tethered Ru(II)-TsDPEN catalyst **2** (0.74 mg, 1.2 μmol, 0.5 mol%) and (*S,S*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (0.74 mg, 1.2 μmol, 0.5 mol%) were added to FA: TEA (5:2 azeotropic mixture, 0.36 mL) at rt and the mixture was stirred under a nitrogen atmosphere for 15 minutes; after which a solution of 2-phenoxy-1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one (80.0 mg, 0.237 mmol) in DCM (0.54 mL) was added. The reaction mixture was stirrer under a nitrogen atmosphere and followed by TLC (9:1 hexane: EtOAc). After 72 hours, the reaction was quenched using saturated $NaHCO_3$ solution (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried ($MgSO_4$) and filtered. The solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-20% EtOAc in hexane to give 2-phenoxy-1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol **10** as a yellow oil (45.0 mg, 0.132 mmol, 56%). TLC: Rf ca 0.20 (9:1 hexane: EtOAc), strong UV and $KMnO_4$; HRMS: (found (ESI+): [M+H]+, Calcd for $C_{20}H_{25}BNaO_4$ 363.1738; Found 363.1738; 1.1 ppm error; $\nu_{max}$ 3456 (br), 2977, 2928, 1599, 1495, 1353, 1240, 1107, 1038, 752 cm$^{-1}$; $\delta_H$ (500 MHz, $CDCl_3$) 7.80 (1H, s, ArH), 7.71 (1H, d, *J* = 7.3, ArH), 7.51 (1H, d, *J* = 7.7, ArH), 7.33 (1H, t, *J* = 7.5, ArH), 7.22-7.18 (2H, m, ArH),

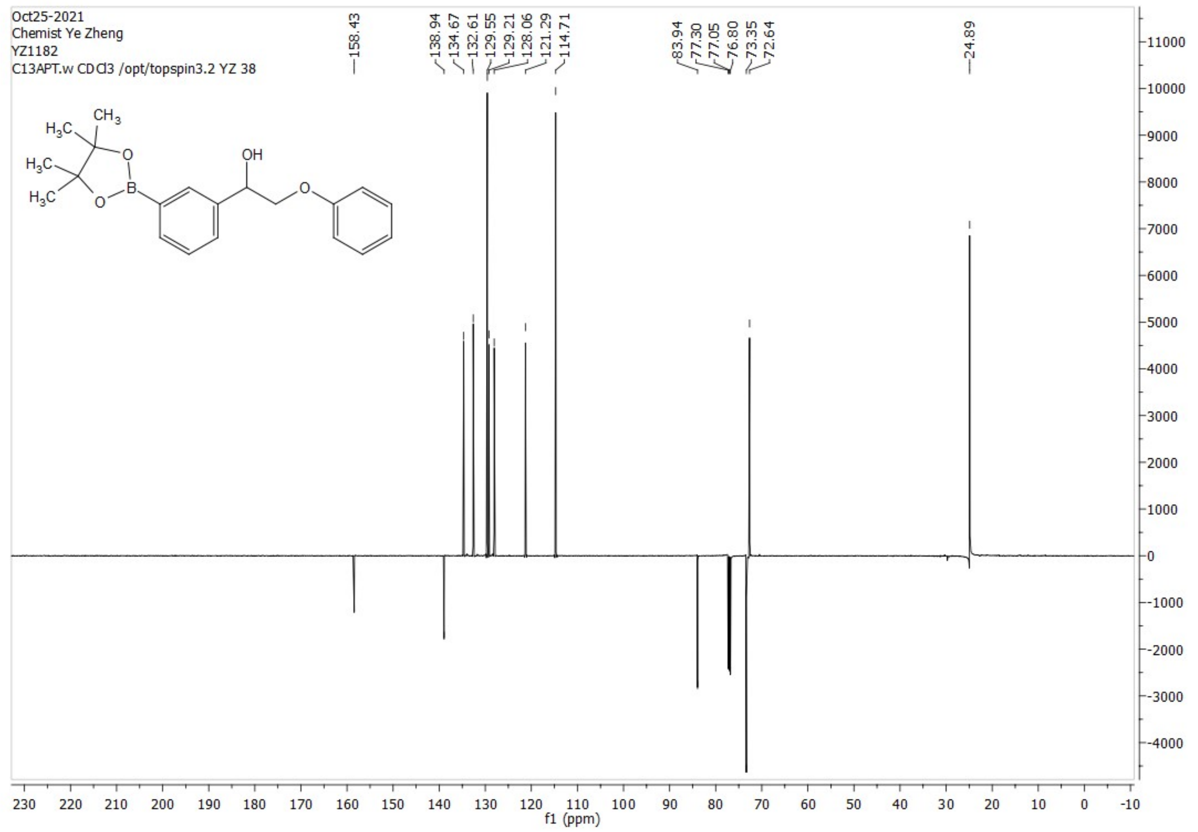
6.91-6.84 (3H, m, ArH), 5.07 (1H, d, *J* = 8.8, ArCH), 4.05 (1H, dd, *J* = 9.6, 3.1, $CH_2$), 3.94 (1H, t, *J* = 9.3, $CH_2$), 2.74 (1H, d, *J* = 2.0, OH), 1.27 (12H, s, $CH_3$) ppm; $\delta_C$ (125 MHz, $CDCl_3$) 158.43 (C), 128.94 (C), 134.67 (CH), 132.61 (CH), 129.55 (CH), 129.21 (CH), 128.06 (CH), 121.29 (CH), 114.71 (CH), 83.94 (C), 73.35 ($CH_2$), 72.64 (CH), 24.89 ($CH_3$) ppm; m/z (ES-API+) 363.2 ($M^+$ + 23, 100%).
Enantiomeric excess and conversion determined by HPLC analysis (Chiralpak IA, 30 cm x 6mm column, hexane:iPrOH 90:10, 1.0 mL/min, T = 25°C) ketone 5.2 min, *R* and *S* isomers 6.8 min and 8.5 min, configuration assigned by analogy with **9**.

ATH of 2-phenoxy-1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one:
(*R,R*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (1.5 mg, 2.4 μmol, 1 mol%) was added to FA: TEA (5:2 azeotropic mixture, 0.36 mL) at rt and the mixture was stirred under a nitrogen atmosphere for 15 minutes; after which a solution of 2-phenoxy-1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one (80.0 mg, 0.237 mmol) in DCM (0.54 mL) was added. The reaction mixture was stirrer under a nitrogen atmosphere and followed by TLC (9:1 hexane: EtOAc). After 72 hours, the reaction was quenched using saturated $NaHCO_3$ solution (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried ($MgSO_4$) and filtered. The solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-20% EtOAc in hexane to give (*S*)-2-phenoxy-1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol **10** as a yellow oil (49.0 mg, 0.144 mmol, 61%). The reaction was also followed by HPLC (Chiralpak IA, 30 cm x 6mm column, hexane:iPrOH 90:10, 1.0 mL/min, T = 25°C): $[\alpha]_D^{23}$ +47.0 (c 0.245 in $CHCl_3$) 97% ee.

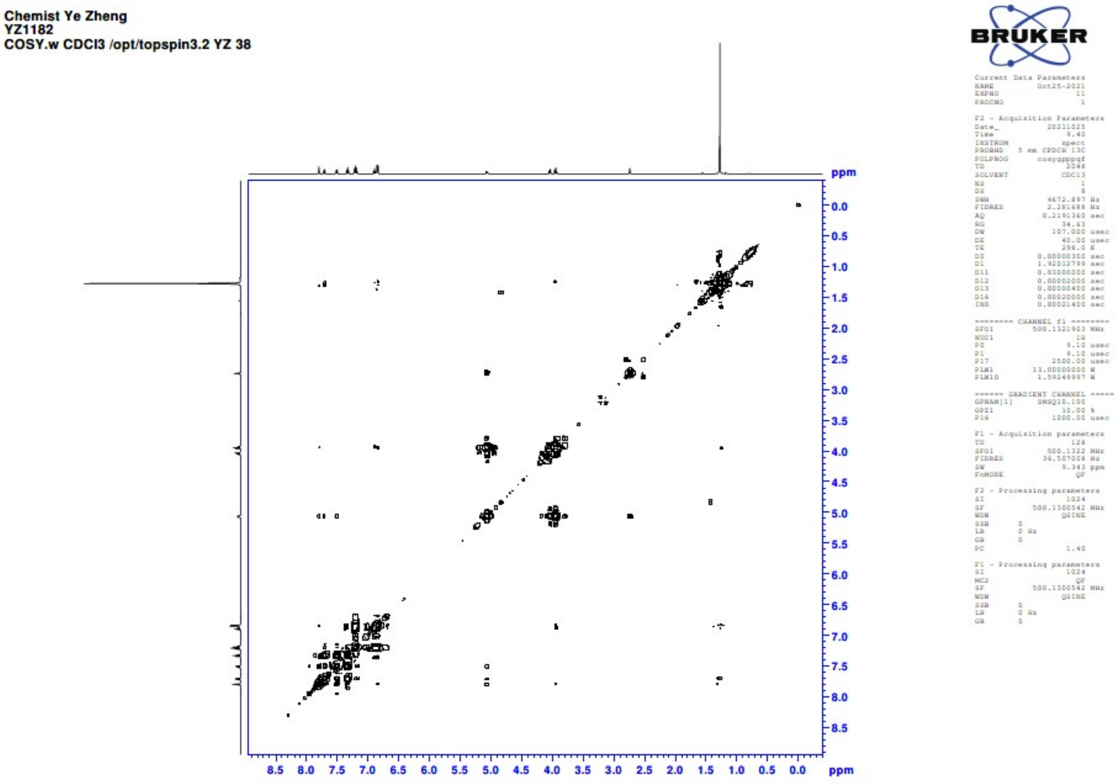
$^{1}$H NMR (500 MHz, $CDCl_3$)



$^{13}$C NMR (125 MHz, $CDCl_3$)



COSY (500 MHz, $CDCl_3$)



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PROCNO                 1

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PULPROG        cosygpppqf
TD                  2048
SOLVENT            CDCl3
NS                     1
DS                     8
SWH             4672.897 Hz
FIDRES          2.281688 Hz
AQ             0.2191360 sec
RG                 34.63
DW               107.000 usec
DE                 40.00 usec
TE                 298.0 K
D0            0.00000300 sec
D1            1.92012799 sec
D11           0.03000000 sec
D12           0.00002000 sec
D13           0.00000400 sec
D16           0.00020000 sec
IN0           0.00021400 sec

======== CHANNEL f1 ========
SFO1         500.1321903 MHz
NUC1                  1H
P0                  9.10 usec
P1                  9.10 usec
P17              2500.00 usec
PLW1         13.00000000 W
PLW10         1.59249997 W

====== GRADIENT CHANNEL =====
GPNAM[1]       SMSQ10.100
GPZ1               10.00 %
P16              1000.00 usec

F1 - Acquisition parameters
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SFO1            500.1322 MHz
FIDRES         36.507008 Hz
SW                 9.343 ppm
FnMODE                QF

F2 - Processing parameters
SI                  1024
SF           500.1300542 MHz
WDW                QSINE
SSB       0
LB        0 Hz
GB        0
PC                  1.40

F1 - Processing parameters
SI                  1024
MC2                   QF
SF           500.1300542 MHz
WDW                QSINE
SSB       0
LB        0 Hz
GB        0
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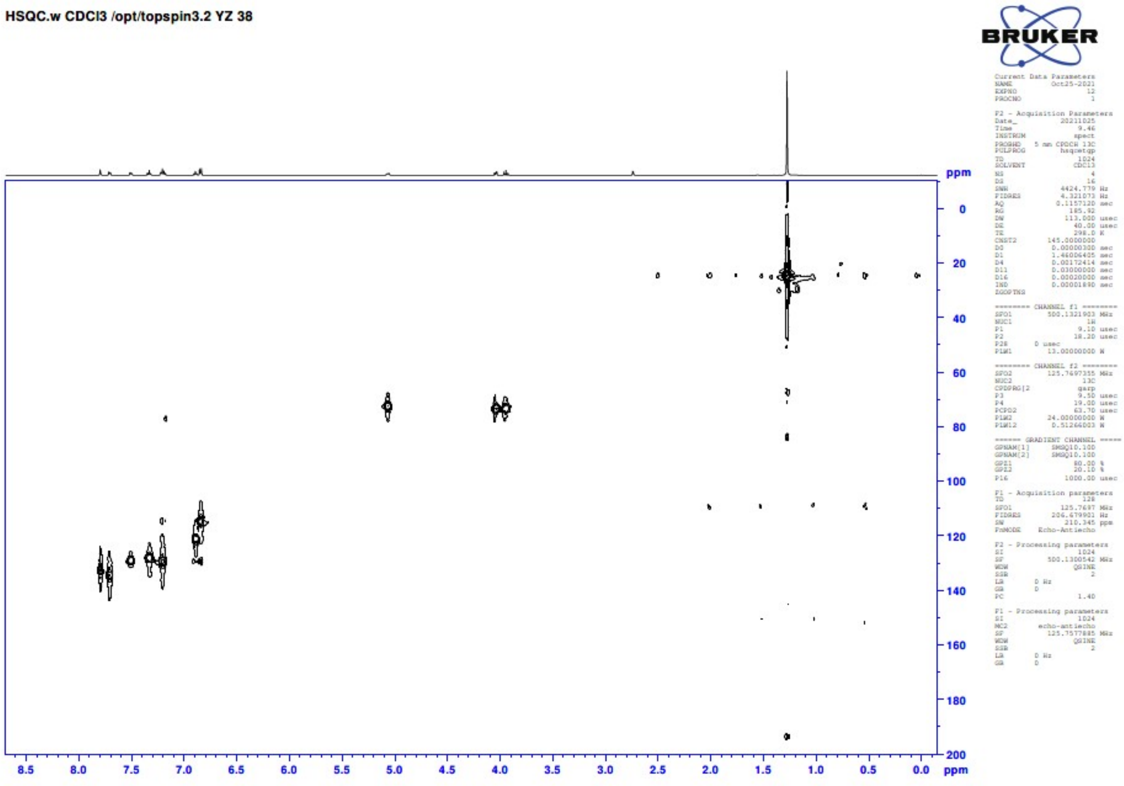
HSQC (500 MHz, $CDCl_3$)



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PROCNO                 1

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TD                  1024
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NS                     4
DS                    16
SWH             4424.779 Hz
FIDRES          4.321073 Hz
AQ             0.1157120 sec
RG                185.92
DW               113.000 usec
DE                 40.00 usec
TE                 298.0 K
CNST2        145.0000000
D0            0.00000300 sec
D1            1.46006405 sec
D4            0.00172414 sec
D11           0.03000000 sec
D16           0.00020000 sec
IN0           0.00001890 sec
ZGOPTNS

======== CHANNEL f1 ========
SFO1         500.1321903 MHz
NUC1                  1H
P1                  9.10 usec
P2                 18.20 usec
P28       0 usec
PLW1         13.00000000 W

======== CHANNEL f2 ========
SFO2         125.7697355 MHz
NUC2                 13C
CPDPRG[2            garp
P3                  9.50 usec
P4                 19.00 usec
PCPD2              63.70 usec
PLW2         24.00000000 W
PLW12         0.51266003 W

====== GRADIENT CHANNEL =====
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GPNAM[2]       SMSQ10.100
GPZ1               80.00 %
GPZ2               20.10 %
P16              1000.00 usec

F1 - Acquisition parameters
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FIDRES        206.679901 Hz
SW               210.345 ppm
FnMODE      Echo-Antiecho

F2 - Processing parameters
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SF           500.1300542 MHz
WDW                QSINE
SSB                    2
LB        0 Hz
GB        0
PC                  1.40

F1 - Processing parameters
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SSB                    2
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GB        0
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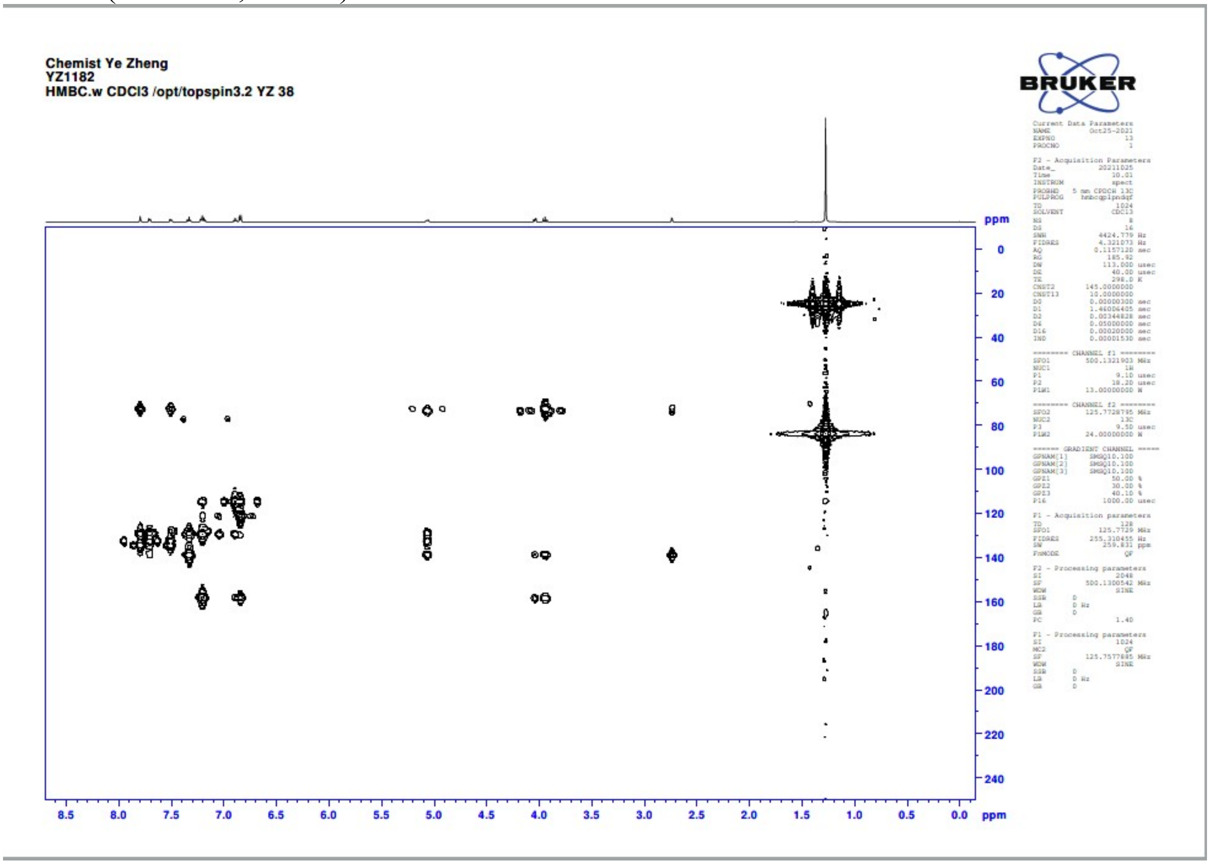
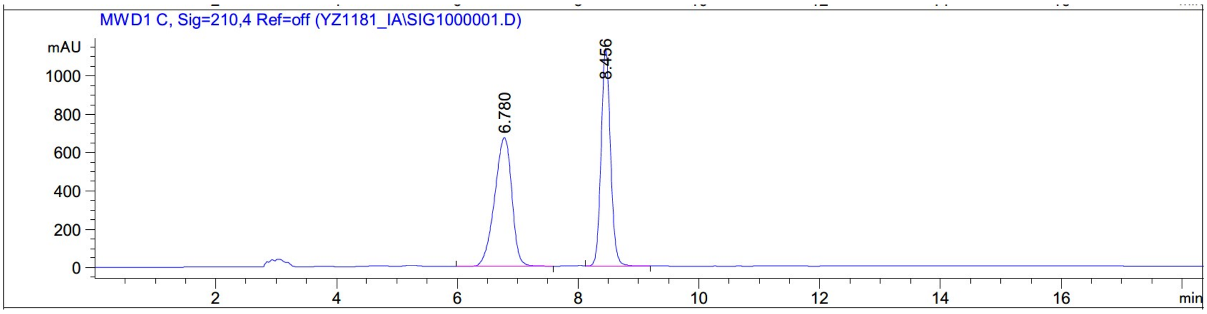
HMBC (500 MHz, $CDCl_3$)



HPLC of racemic 2-phenoxy-1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol **10**.



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Signal 2: MWD1 C, Sig=210,4 Ref=off

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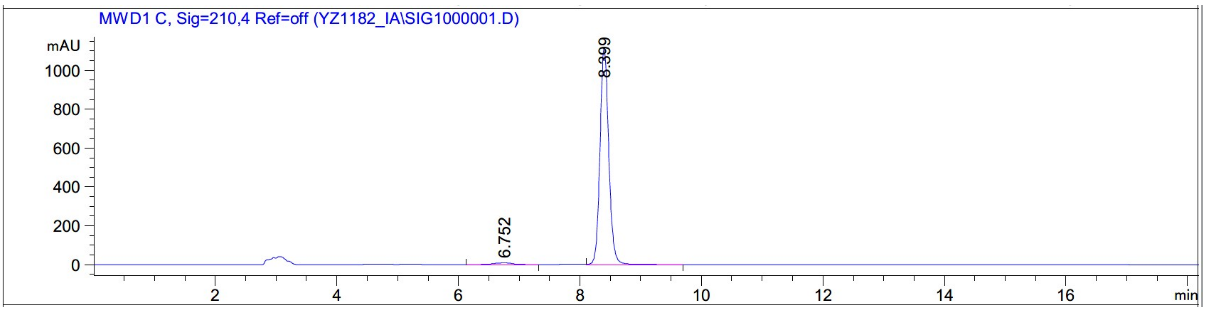
   1   6.780 BB    0.3077 1.33341e4  671.41089  52.0903
   2   8.456 VV    0.1683 1.22639e4 1133.00598  47.9097

Totals :                  2.55980e4 1804.41687
```

HPLC after ATH of 2-phenoxy-1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one using (*R,R*)-3C-Tethered Ru(II)-TsDPEN catalyst **2** (after 72 hours, 100% conversion, 97% ee).



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Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   6.752 BB    0.3197  192.61708    9.07122   1.6897
   2   8.399 VB    0.1552 1.12071e4  1116.03772  98.3103

Totals :                  1.13997e4  1125.10894
```
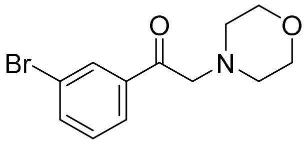
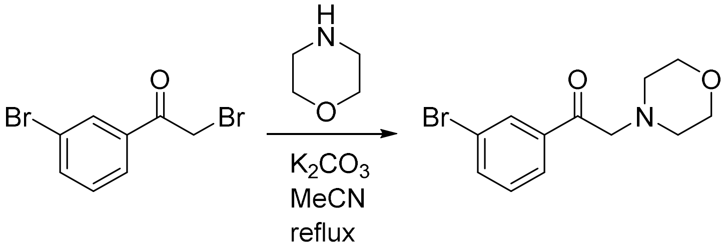

1-(3-Bromophenyl)-2-morpholinoethan-1-one.

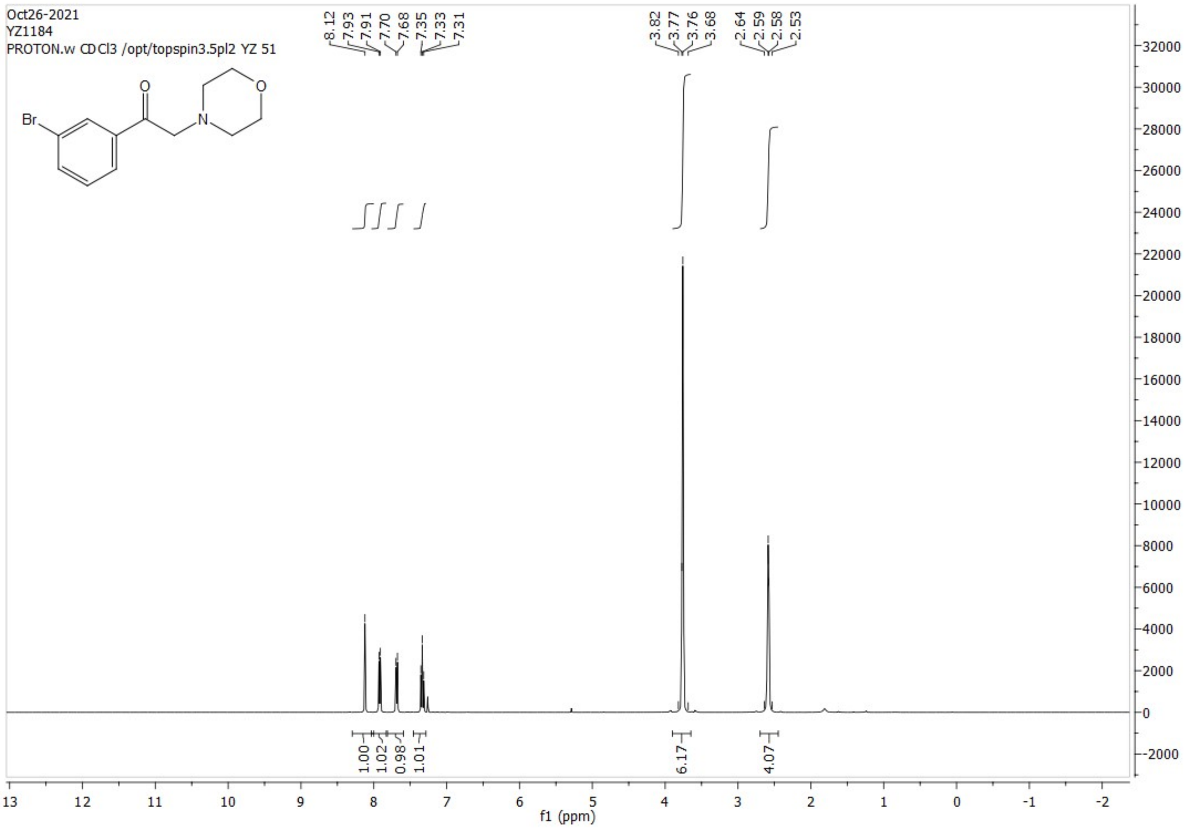




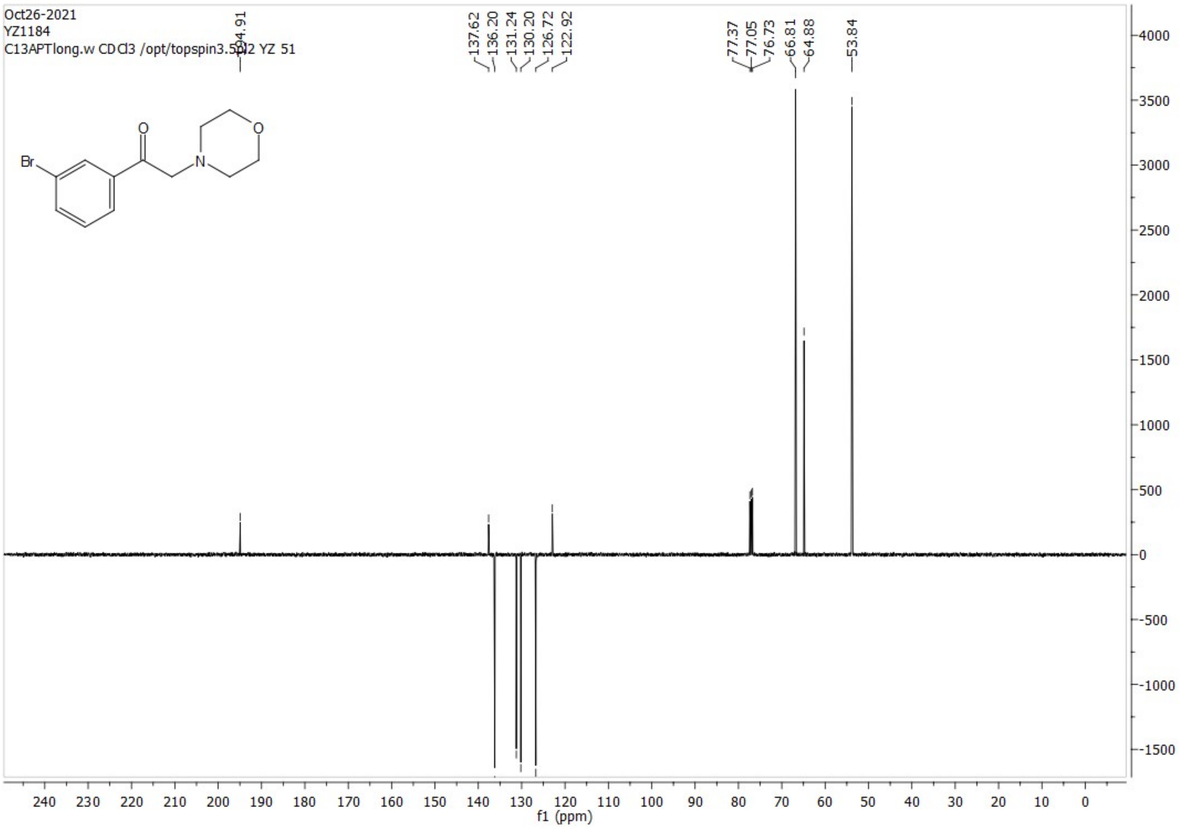
This compound is novel.

To a solution of 2-bromo-1-(3-bromophenyl)ethan-1-one (2.00 g, 7.25 mmol) in MeCN (40 mL) was added morpholine (948 mg, 10.9 mmol) and potassium carbonate (3.00 g, 21.7 mmol). The reaction mixture was heated to 85 °C and left stirring under a nitrogen atmosphere for 1 hour, followed by TLC (1:1 hexane: EtOAc). The mixture was quenched by distilled water (20 mL). $Et_2O$ (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with $Et_2O$ (3 × 20 mL), and the combined organic layers were dried ($MgSO_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 50-100% ethyl acetate in hexane to give 1-(4-bromophenyl)-2-morpholinoethan-1-one as a yellow solid (1.82 g, 6.43 mmol, 89%). TLC: Rf ca 0.40 (1:1 hexane: EtOAc), strong UV and $KMnO_4$; Mp: 75°C; HRMS: (found (ESI+): [M+H]+, Calcd for $C_{12}H_{15}BNO_2$ 284.0278; Found 284.0281; 0.9 ppm error; $\nu_{max}$ 2963, 2863, 1696, 1564, 1449, 1416, 1298, 1213, 1163, 1142, 1107, 10840, 900, 864, 783 $cm^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 8.12 (1H, s, ArH), 7.93 (1H, d, $J$ = 7.9, ArH), 7.70 (1H, d, $J$ = 7.9, ArH), 7.33 (1H, t, $J$ = 7.9, ArH), 3.82-3.68 (6H, m, $CH_2$), 2.64-2.53 (4H, m, $CH_2$) ppm; $\delta_C$ (100 MHz, $CDCl_3$) 194.91 (C), 137.62 (C), 136.20 (CH), 131.24 (CH), 130.20 (CH), 126.72 (CH), 122.92 (C), 66.81 ($CH_2$), 64.88 ($CH_2$), 53.84 ($CH_2$) ppm; m/z (ES-API+) 284.0 ($M^+$ + 23, 100%).

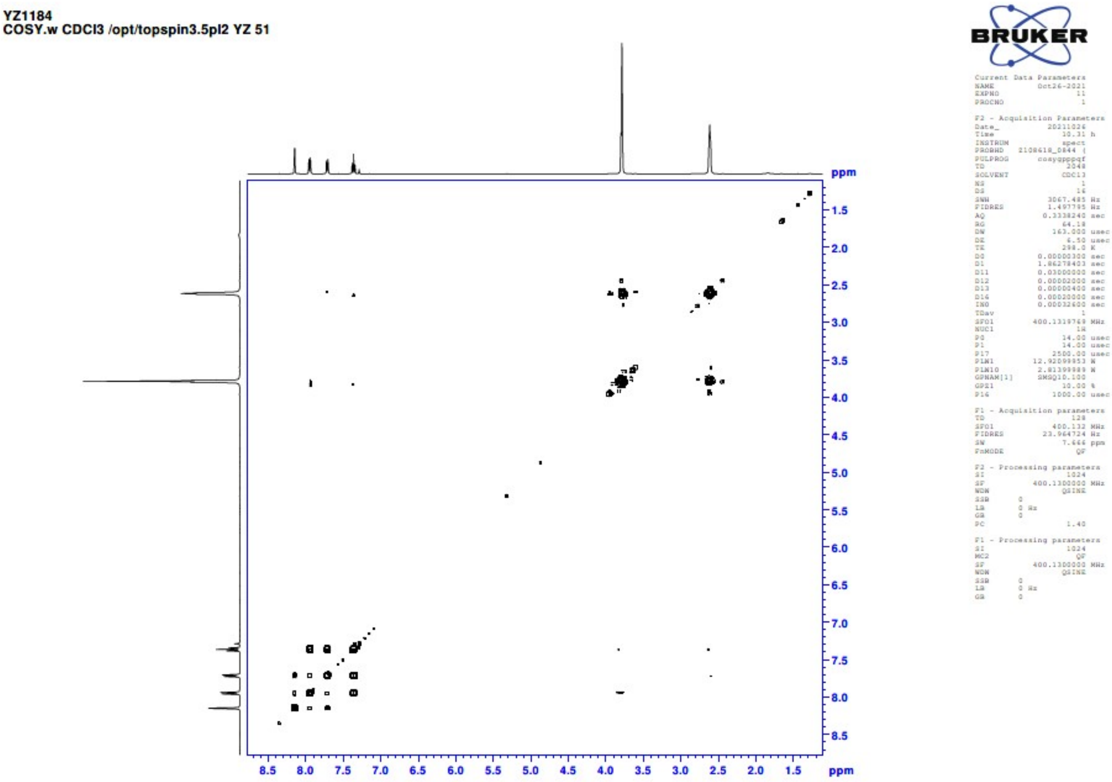
$^1$H NMR (400 MHz, $CDCl_3$)



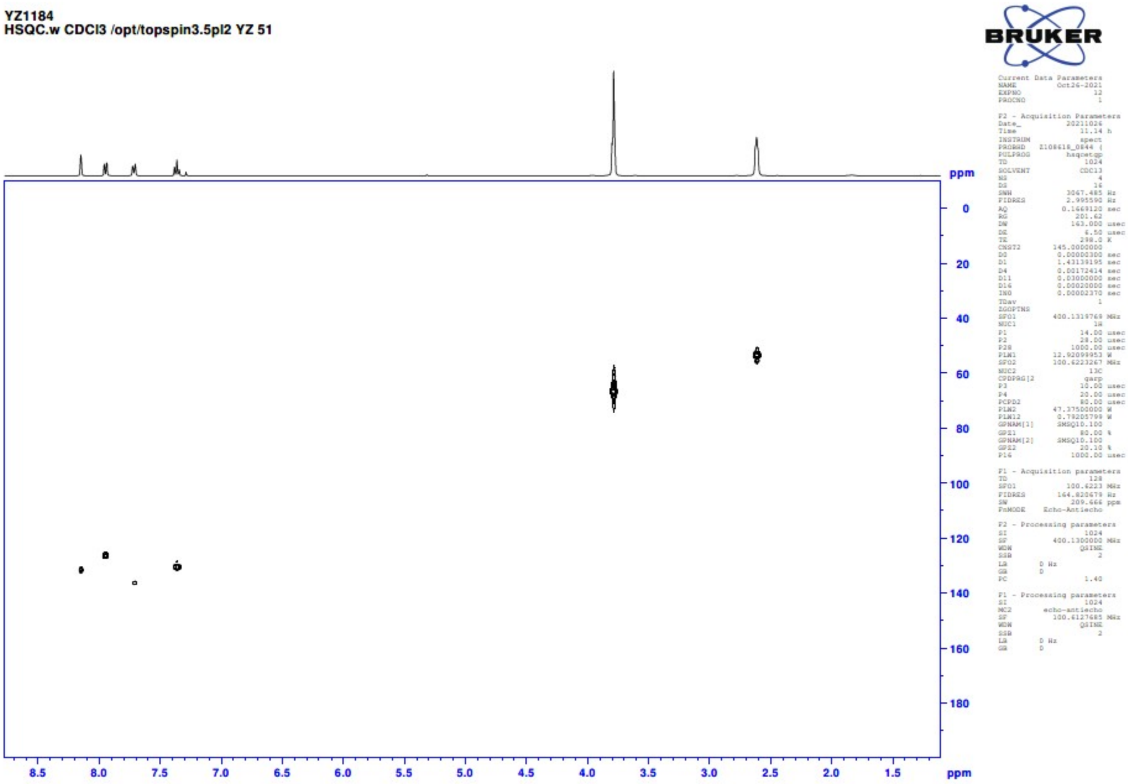
$^{13}$C NMR (100 MHz, $CDCl_3$)



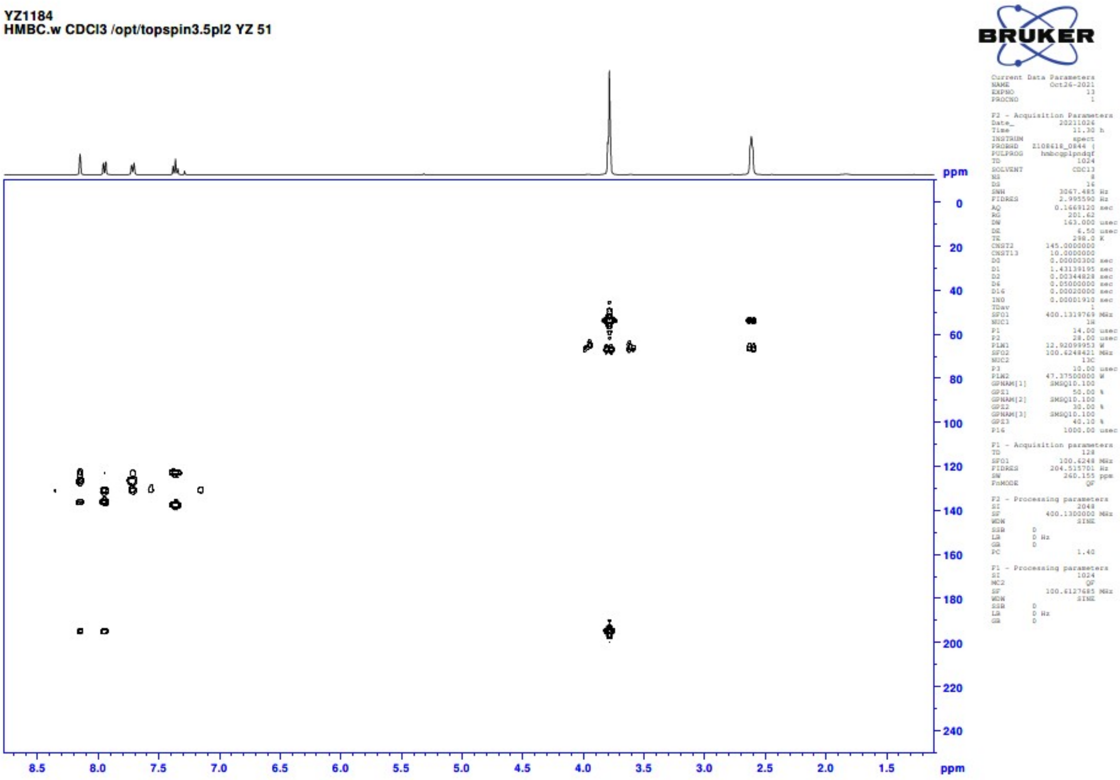
COSY (400 MHz, $CDCl_3$)



HSQC (400 MHz, $CDCl_3$)



HMBC (400 MHz, $CDCl_3$)



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YZ1184
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Current Data Parameters
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EXPNO                 13
PROCNO                 1

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PULPROG     hmbcgplpndqf
TD                  1024
SOLVENT            CDCl3
NS                     8
DS                    16
SWH             3267.485 Hz
FIDRES          2.995590 Hz
AQ             0.1669120 sec
RG                201.62
DW               163.000 usec
DE                  6.50 usec
TE                 298.0 K
CNST2        145.0000000
CNST13        10.0000000
D0            0.00000300 sec
D1            1.43139195 sec
D2            0.00344828 sec
D6            0.05000000 sec
D16           0.00020000 sec
IN0           0.00001910 sec
TDav                   1
SFO1         400.1319769 MHz
NUC1                  1H
P1                 14.00 usec
P2                 28.00 usec
PLW1         12.92099953 W
SFO2         100.6248421 MHz
NUC2                 13C
P3                 10.00 usec
PLW2         47.37500000 W
GPNAM[1]      SMSQ10.100
GPZ1               50.00 %
GPNAM[2]      SMSQ10.100
GPZ2               30.00 %
GPNAM[3]      SMSQ10.100
GPZ3               40.10 %
P16              1000.00 usec

F1 - Acquisition parameters
TD                   128
SFO1            100.6248 MHz
FIDRES        204.515701 Hz
SW               260.155 ppm
FnMODE                QF

F2 - Processing parameters
SI                  2048
SF           400.1300000 MHz
WDW                 SINE
SSB       0
LB        0 Hz
GB        0
PC                  1.40

F1 - Processing parameters
SI                  1024
MC2                   QF
SF           100.6127685 MHz
WDW                 SINE
SSB       0
LB        0 Hz
GB        0
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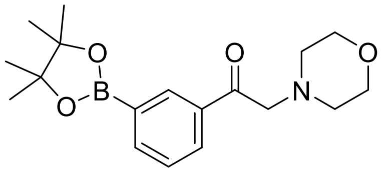
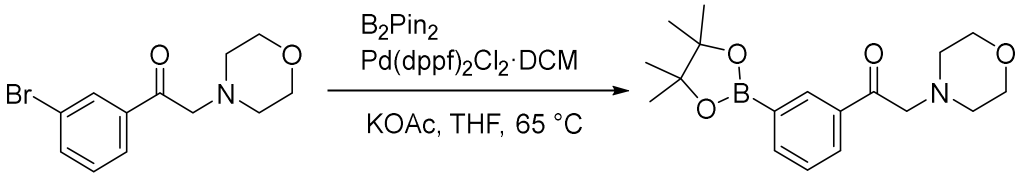
### 2-Morpholino-1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one.

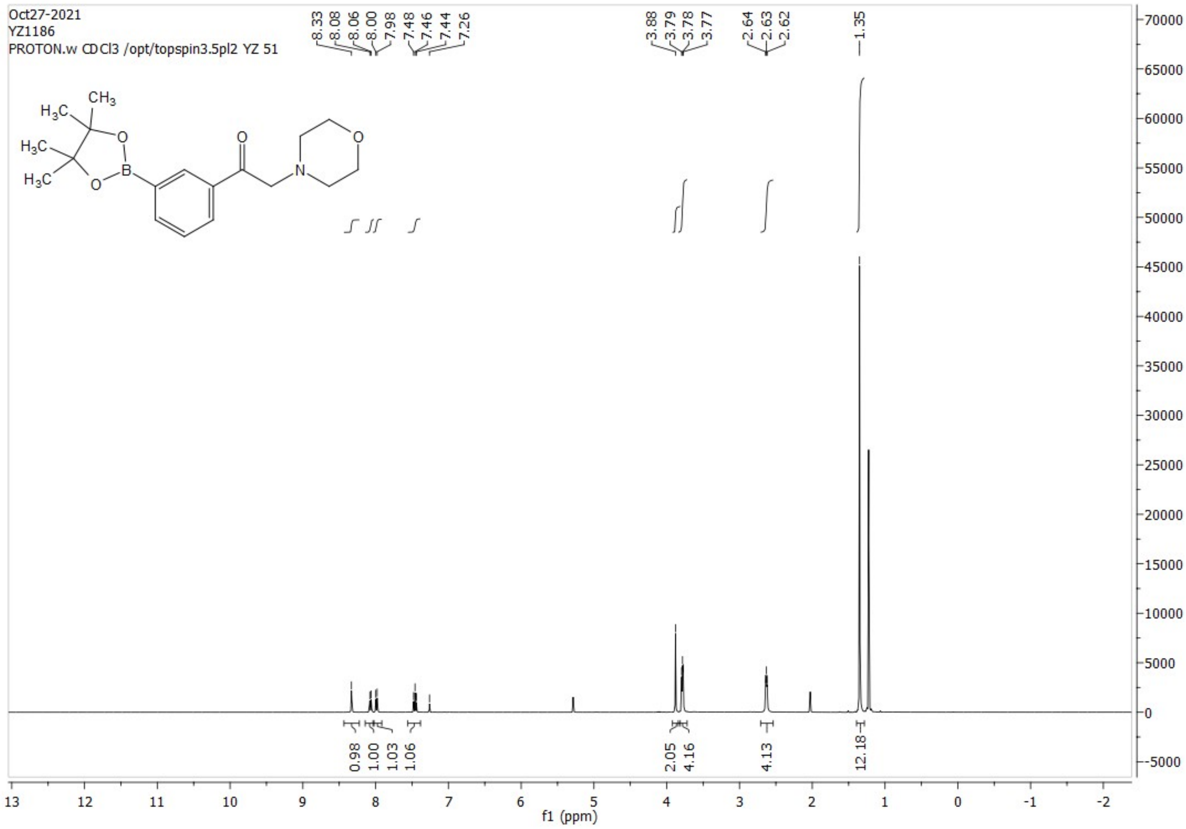




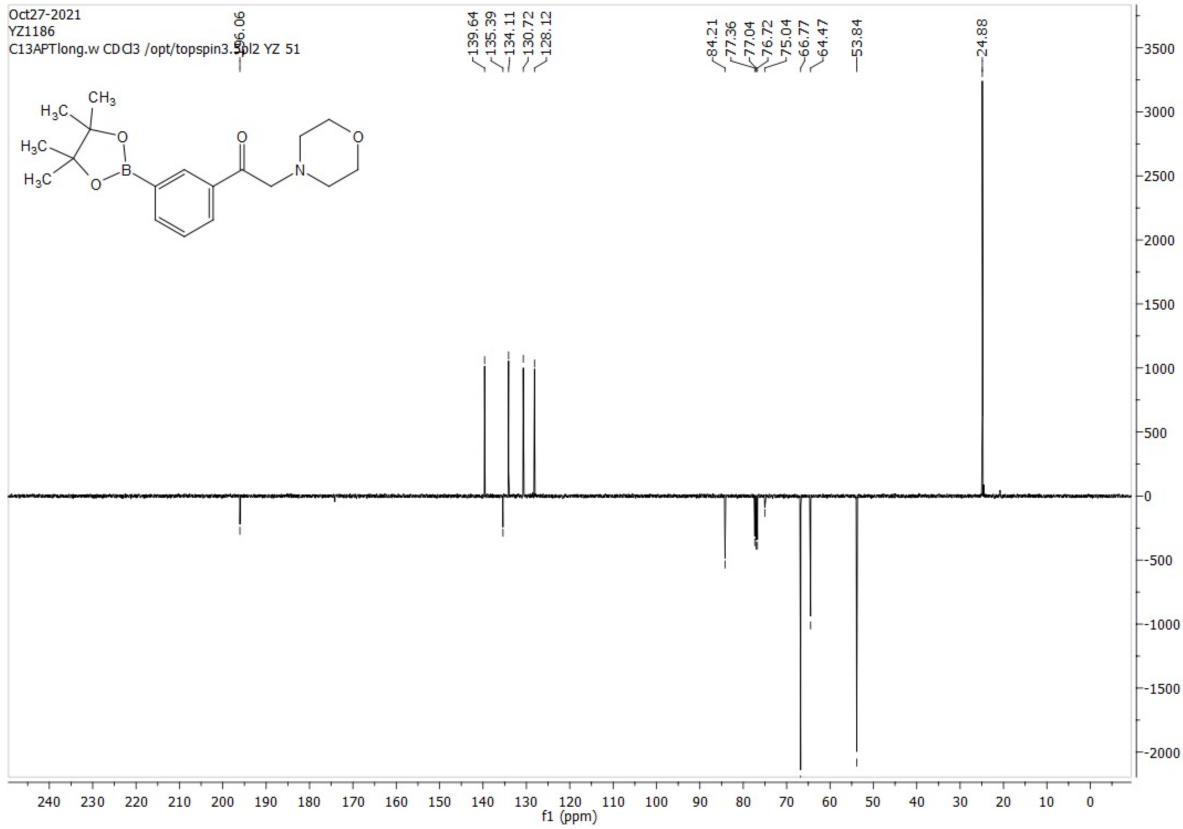
This compound is novel.

A round-bottom flask was charged with 1-(3-bromophenyl)-2-morpholinoethan-1-one (1.80 g, 6.36 mmol), bis(pinacolato)diboron (1.94 g, 7.63 mmol), potassium acetate (1.87 g, 19.1 mmol), THF (31 mL) and $Pd(dppf)_2Cl_2$·DCM (260 mg, 0.318 mmol). The reaction mixture was heated to 65 °C and left stirring under the nitrogen atmosphere overnight, followed by TLC (1:1 hexane: EtOAc). The mixture was quenched by distilled water (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried ($MgSO_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 50-100% ethyl acetate in hexane to give 2-morpholino-1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one as a brown oil (955 mg, 2.89 mmol, 47%). TLC: Rf ca 0.20 (1:1 hexane: EtOAc), strong UV and $KMnO_4$; HRMS: (found (ESI+): [M+H]+, Calcd for $C_{18}H_{27}BNO_4$ 332.2027; Found 332.2028; 1.3 ppm error; $\nu_{max}$ 2976, 1696, 1599, 1357, 1312, 1214, 1140, 1114, 961 $cm^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 8.33 (1H, s, ArH), 8.08 (1H, d, *J* = 7.6, ArH), 8.00 (1H, d, *J* = 7.6, ArH), 7.46 (1H, t, *J* = 7.6, ArH), 3.88 (2H, s, $CH_2$), 3.79-3.77 (4H, m, $CH_2$), 2.64-2.62 (4H, m, $CH_2$), 1.35 (12H, s, $CH_3$) ppm; $\delta_C$ (100 MHz, $CDCl_3$) 196.06 (C), 139.64 (CH), 135.39 (C), 134.11 (CH), 130.72 (CH), 128.12 (CH), 84.21 (C), 66.66 ($CH_2$), 64.47 ($CH_2$), 53.84 ($CH_2$), 24.88 ($CH_3$) ppm; m/z (ES-API+) 332.2 ($M^+$ + 1, 100%). Enantiomeric excess and conversion determined by HPLC analysis (Chiralpak IC, 30 cm x 6mm column, hexane:iPrOH 90:10, 1.0 mL/min, T = 25°C) ketone 15.6 min, *R* and *S* isomers 12.3 min and 21.1 min.

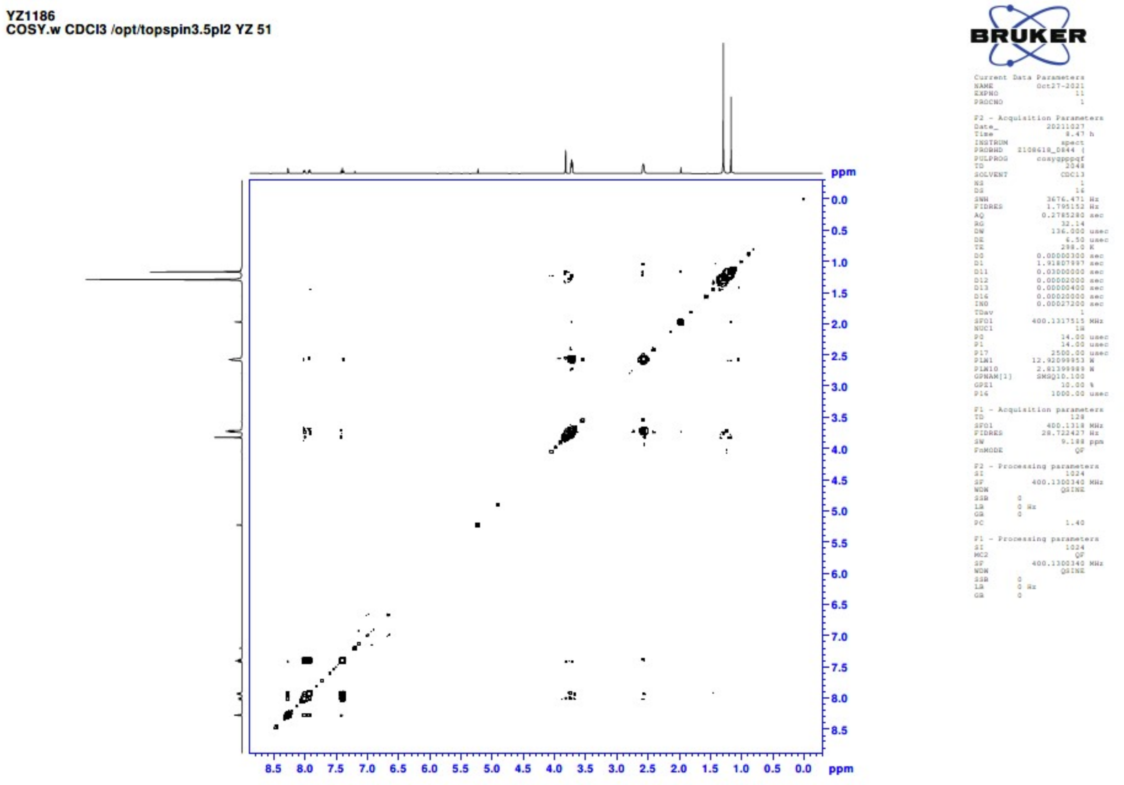
$^1$H NMR (400 MHz, CDCl$_3$)



$^{13}$C NMR (100 MHz, CDCl$_3$)



COSY (400 MHz, $CDCl_3$)



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TD                    2048
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GPZ1                 10.00 %
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F1 - Acquisition parameters
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FnMODE                  QF

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GB       0
PC                    1.40

F1 - Processing parameters
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WDW                  QSINE
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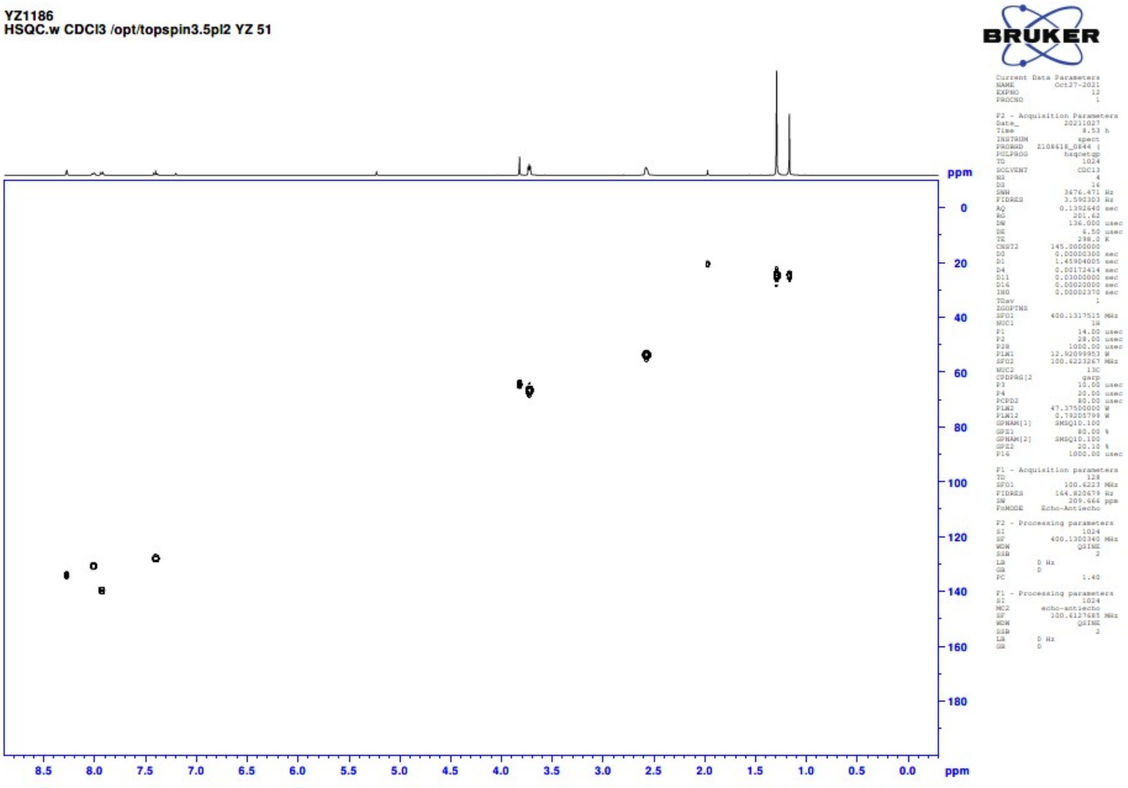
HSQC (400 MHz, $CDCl_3$)



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PROCNO                   1

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PULPROG          hsqcetgp
TD                    1024
SOLVENT              CDCl3
NS                       4
DS                      16
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FIDRES            3.590303 Hz
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NUC1                    1H
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P2                   28.00 usec
P28                1000.00 usec
PLW1           12.92099953 W
SFO2           100.6223267 MHz
NUC2                   13C
CPDPRG[2             garp
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P4                   20.00 usec
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GPZ1                 80.00 %
GPNAM[2]        SMSQ10.100
GPZ2                 20.10 %
P16                1000.00 usec

F1 - Acquisition parameters
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FIDRES          164.820679 Hz
SW                 209.666 ppm
FnMODE     Echo-Antiecho

F2 - Processing parameters
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WDW                  QSINE
SSB                      2
LB       0 Hz
GB       0
PC                    1.40

F1 - Processing parameters
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GB       0
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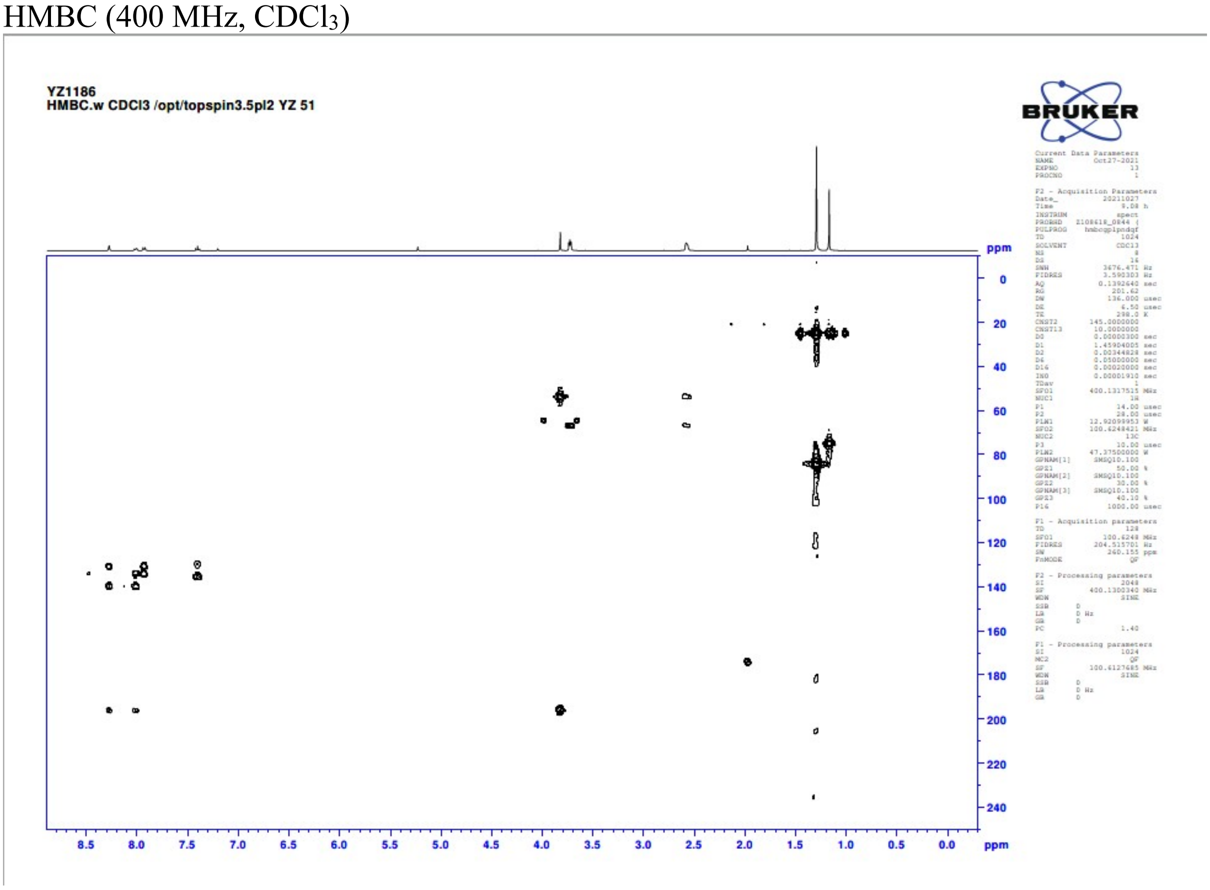
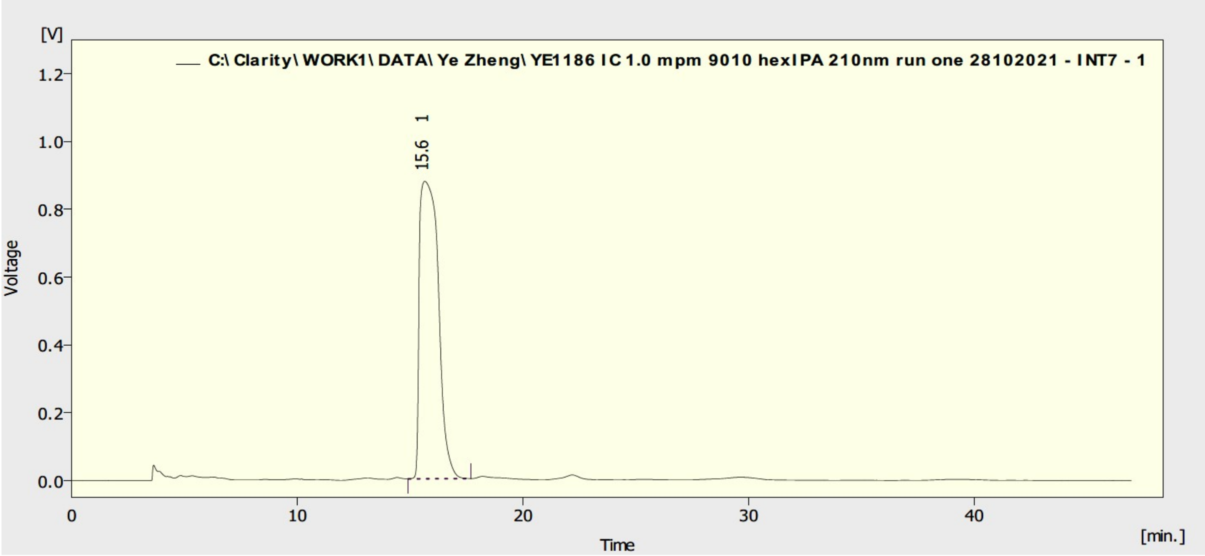
HMBC (400 MHz, $CDCl_3$)



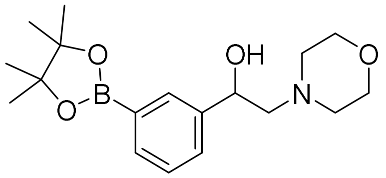
HPLC of 2-morpholino-1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one

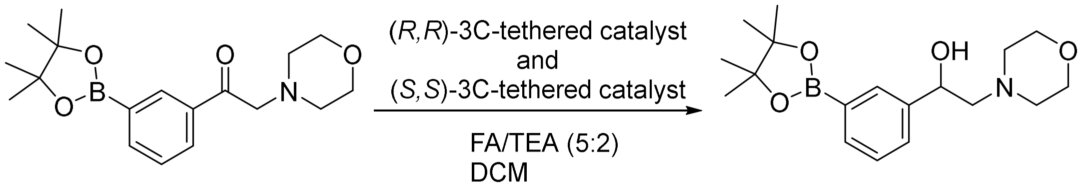


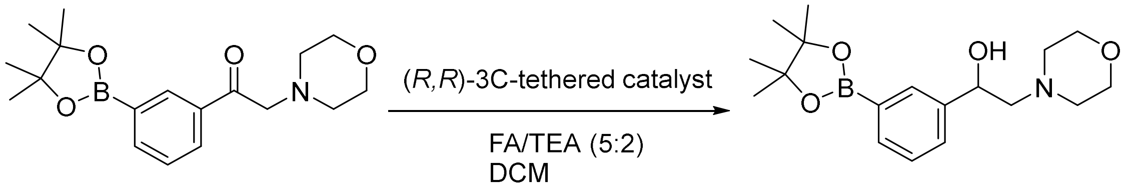
*Result Table (Uncal - C:\Clarity\WORK1\DATA\Ye Zheng\YE1186 IC 1.0 mpm 9010 hexIPA 210nm run one 28102021 - INT7 - 1)*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Compound Name |
|---|---|---|---|---|---|---|---|
| 1 | 15.647 | 50995.875 | 877.576 | 100.0 | 100.0 | 0.94 | |
| | Total | 50995.875 | 877.576 | 100.0 | 100.0 | | |

Racemic and (*S*)-2-Morpholino-1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol **11**.







This compound is novel.

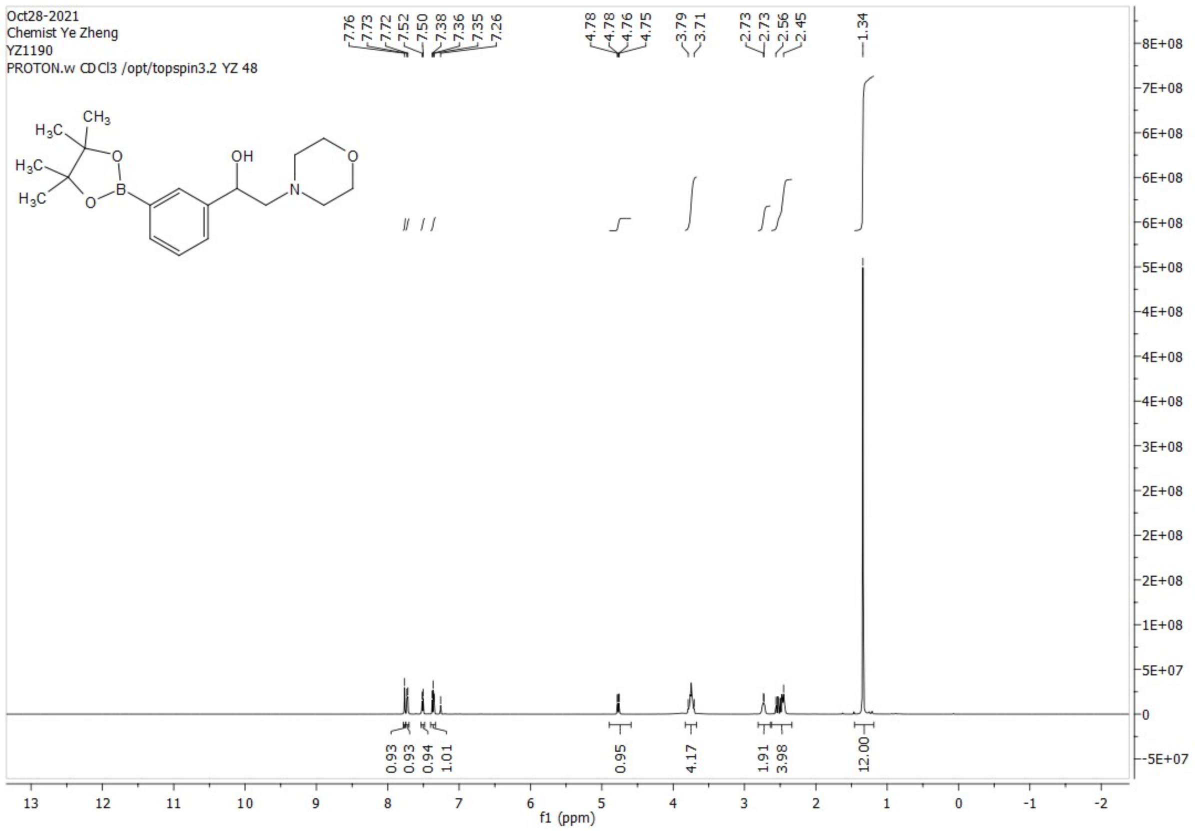
**Synthesis of a racemic standard:**

(*R,R*)-3C-Tethered Ru(II)-TsDPEN catalyst **2** (0.75 mg, 1.2 μmol, 0.5 mol%) and (*S,S*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (0.75 mg, 1.2 μmol, 0.5 mol%) were added to FA: TEA (5:2 azeotropic mixture, 0.36 mL) at rt and the mixture was stirred under a nitrogen atmosphere for 15 minutes; after which a solution of 2-morpholino-1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one (80.0 mg, 0.242 mmol) in DCM (0.50 mL) was added. The reaction mixture was stirrer under a nitrogen atmosphere and followed by TLC (5:95 MeOH: DCM). After 72 hours, the reaction was quenched using saturated $NaHCO_3$ solution (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried ($MgSO_4$) and filtered. The solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-5% MeOH in DCM to give 2-morpholino-1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol **11** as a yellow oil (55.0 mg, 0.165 mmol, 68%). TLC: Rf ca 0.20 (5:95 MeOH: DCM), strong UV and $KMnO_4$; HRMS: (found (ESI+): [M+H]+, Calcd for $C_{18}H_{29}BNO_4$ 334.2180; Found 334.2184; 2.4 ppm error; $\nu_{max}$ 3422 (br), 3162, 2975, 2859, 1431, 1354, 1139, 1112, 1069, 1006 $cm^{-1}$; $\delta_H$ (500 MHz, $CDCl_3$) 7.76 (1H, s, ArH), 7.73 (1H, d, *J* = 7.5, ArH), 7.52 (1H, d, *J* = 7.5, ArH), 7.36 (1H, t, *J* = 7.5, ArH), 4.78 (1H, dd, *J* = 10.5, 3.3, ArCH), 3.79-3.71 (4H, m, $CH_2$), 2.73 (2H, d, *J* = 3.8, $CH_2$), 2.56-2.45 (4H, m, $CH_2$), 1.34 (12H, s, $CH_3$) ppm; $\delta_C$ (125 MHz, $CDCl_3$) 141.13 (C), 134.12 (CH), 132.22 (CH), 128.83 (CH), 127.92 (CH), 83.83 (C), 68.58 (CH), 67.07 ($CH_2$), 66.64 ($CH_2$), 53.44 ($CH_2$), 24.88 ($CH_3$) ppm; m/z (ES-API+) 334.2 ($M^+$ + 1, 100%). Enantiomeric excess and conversion determined by HPLC analysis (Chiralpak IC, 30 cm x 6mm column, hexane:iPrOH 90:10, 1.0 mL/min, T = 25°C) ketone 15.6 min, *R* and *S* isomers 12.3 min and 21.1 min. Configuration assigned by analogy with **9**.

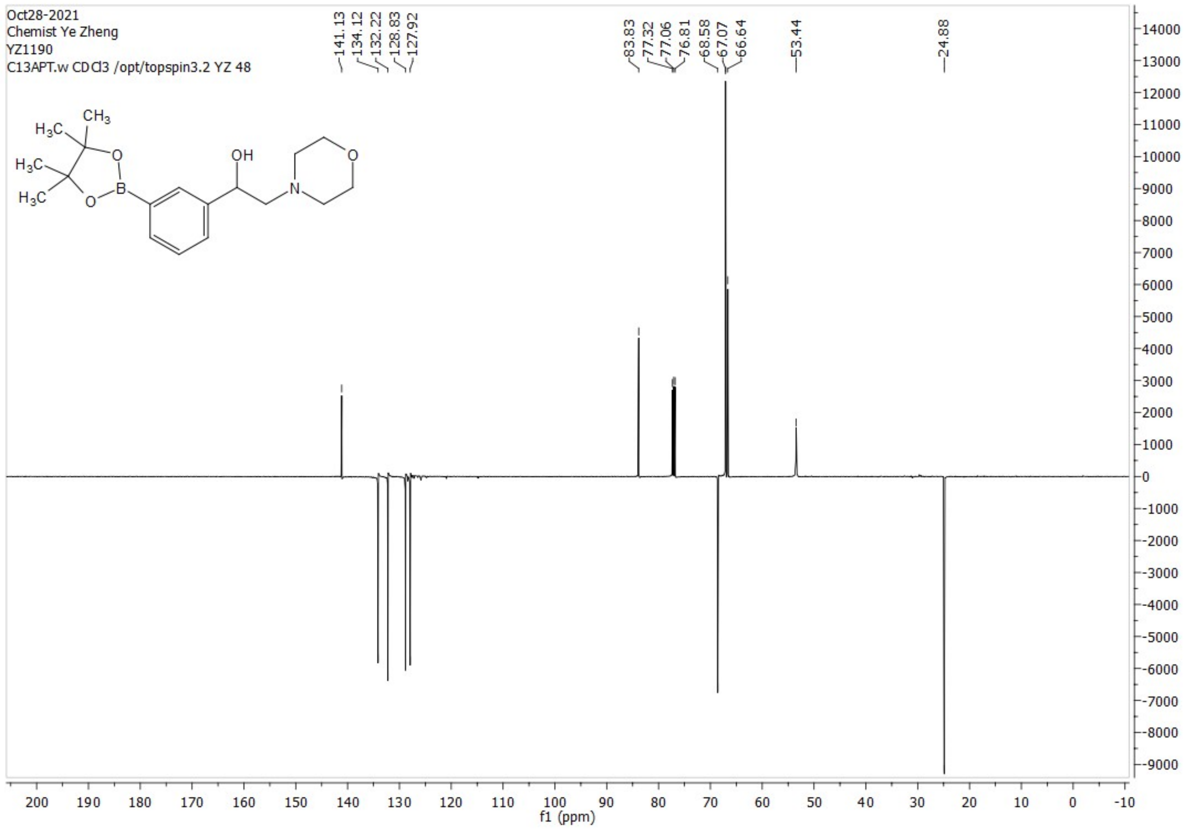
ATH of 2-morpholino-1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one:

(*R,R*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (1.50 mg, 2.42 μmol, 1 mol%) was added to FA: TEA (5:2 azeotropic mixture, 0.36 mL) at rt and the mixture was stirred under a nitrogen atmosphere for 15 minutes; after which a solution of 2-morpholino-1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one (80.0 mg, 0.242 mmol) in DCM (0.50 mL) was added. The reaction mixture was stirrer under a nitrogen atmosphere and followed by TLC (5:95 MeOH: DCM). After 72 hours, the reaction was quenched using saturated $NaHCO_3$ solution (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried (MgSO4) and filtered. The solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-5% MeOH in DCM to give (*S*)-2-morpholino-1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol **11** as a yellow oil (45.0 mg, 0.135 mmol, 56%). The reaction was also followed by HPLC (Chiralpak IC, 30 cm x 6mm column, hexane:iPrOH 90:10, 1.0 mL/min, T = 25°C): $[\alpha]_D^{22}$ +62.0 (c 0.300 in $CHCl_3$) 93% ee.

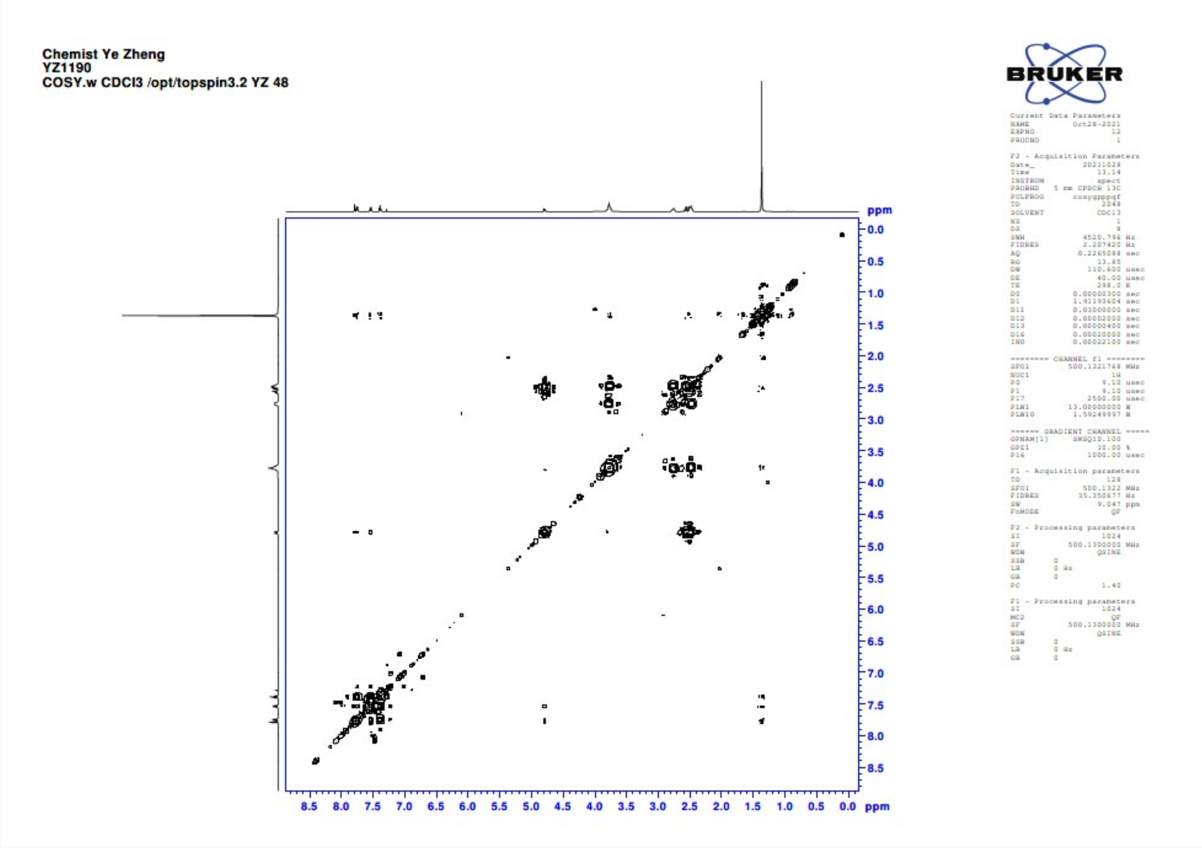
$^1$H NMR (500 MHz, $CDCl_3$)



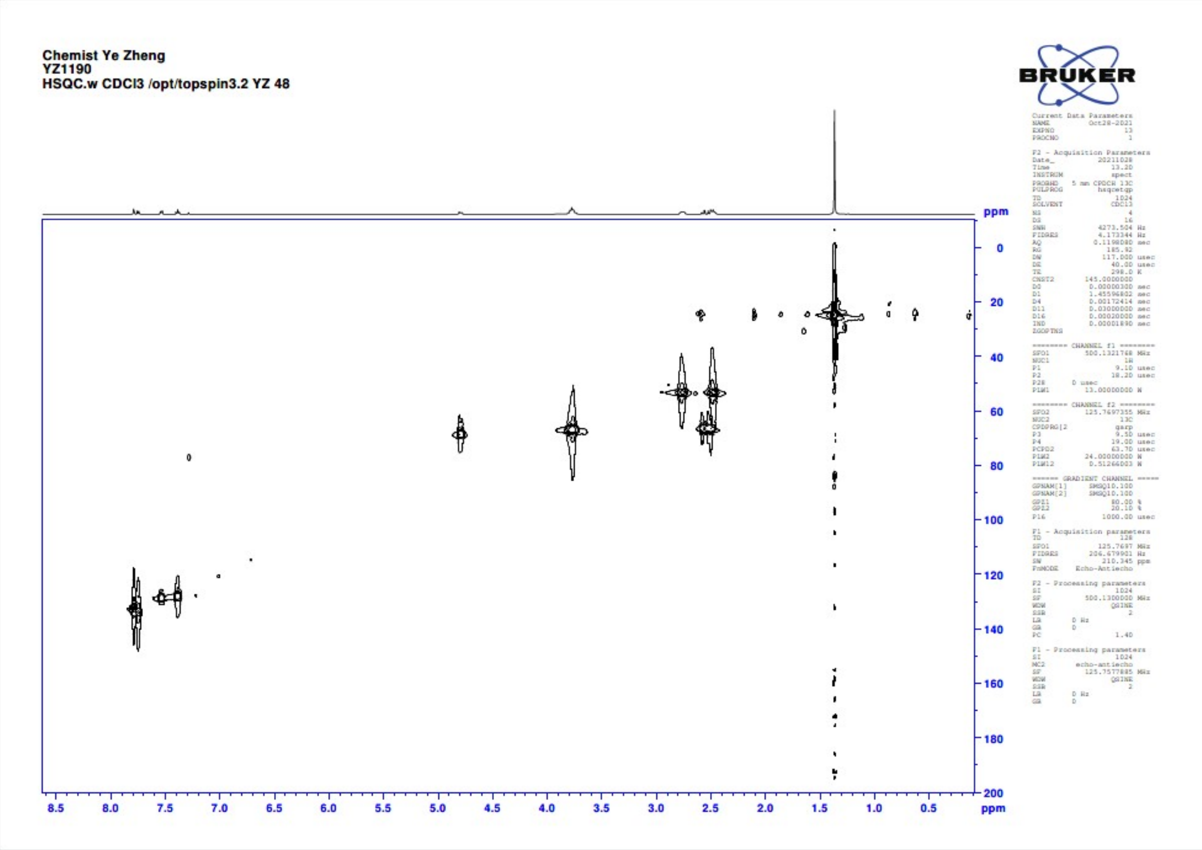
$^{13}$C NMR (125 MHz, $CDCl_3$)



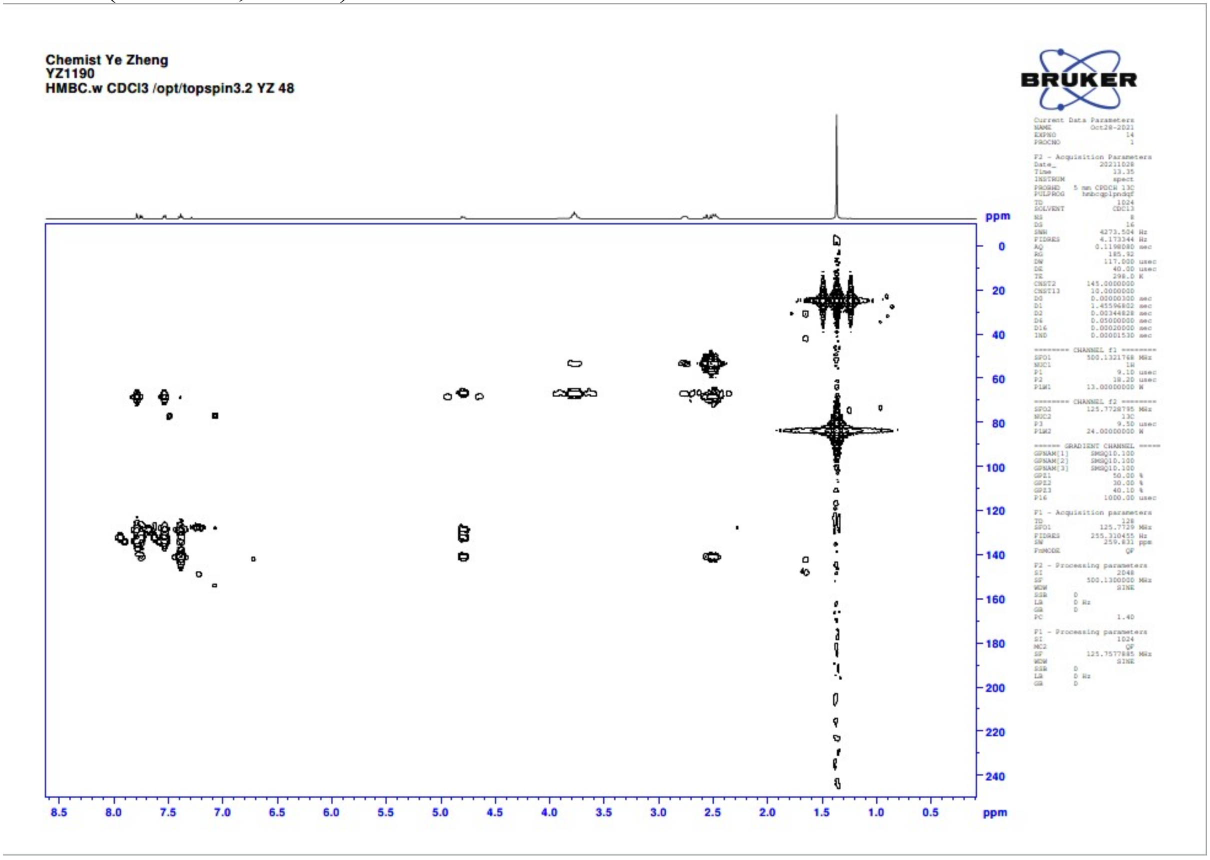
COSY (500 MHz, $CDCl_3$)



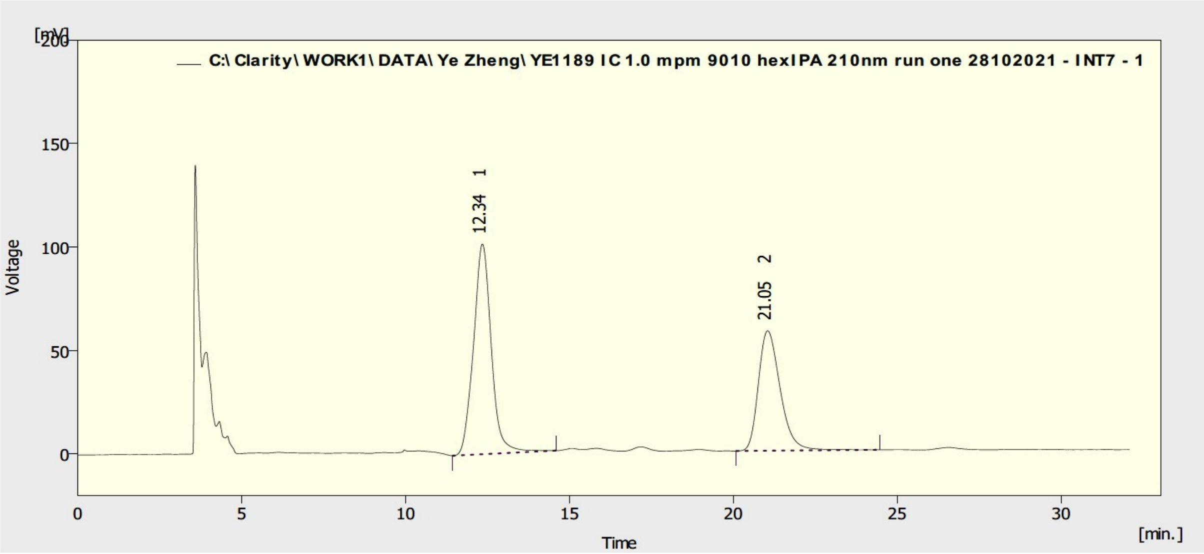
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)



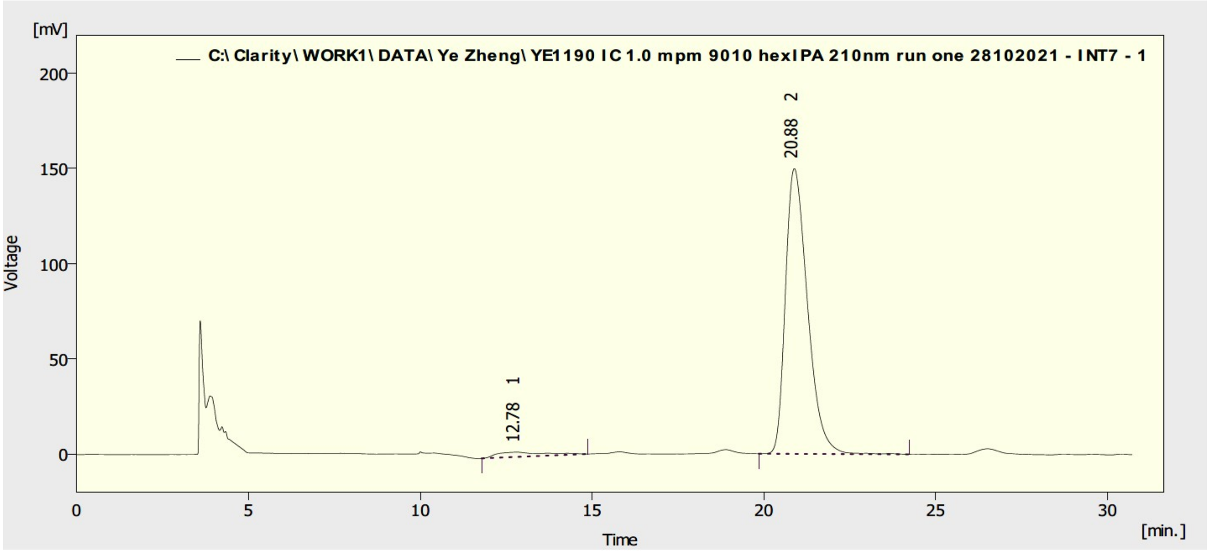
HPLC of racemic 2-morpholino-1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol **11**.



*Result Table (Uncal - C:\Clarity\WORK1\DATA\Ye Zheng\YE1189 IC 1.0 mpm 9010 hexIPA 210nm run one 28102021 - INT7 - 1)*

|  | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Compound Name |
|---|---|---|---|---|---|---|---|
| 1 | 12.343 | 3830.213 | 101.638 | 58.8 | 63.7 | 0.56 |  |
| 2 | 21.047 | 2683.526 | 57.964 | 41.2 | 36.3 | 0.70 |  |
|  | Total | 6513.740 | 159.602 | 100.0 | 100.0 |  |  |

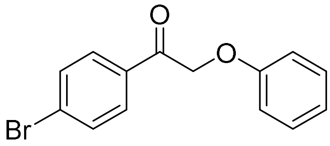
HPLC after ATH of 2-morpholino-1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one using (*R,R*)-3C-Tethered Ru(II)-TsDPEN catalyst **2** (after 72 hours, 100% conversion, 93% ee).

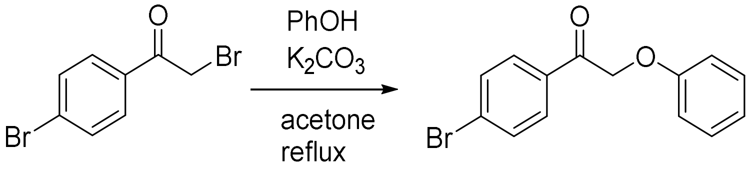


*Result Table (Uncal - C:\Clarity\WORK1\DATA\Ye Zheng\YE1190 IC 1.0 mpm 9010 hexIPA 210nm run one 28102021 - INT7 - 1)*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Compound Name |
|---|---|---|---|---|---|---|---|
| 1 | 12.783 | 242.696 | 2.528 | 3.5 | 1.7 | 2.70 | |
| 2 | 20.883 | 6703.125 | 149.862 | 96.5 | 98.3 | 0.69 | |
| | Total | 6945.821 | 152.390 | 100.0 | 100.0 | | |

1-(4-Bromophenyl)-2-phenoxyethan-1-one.



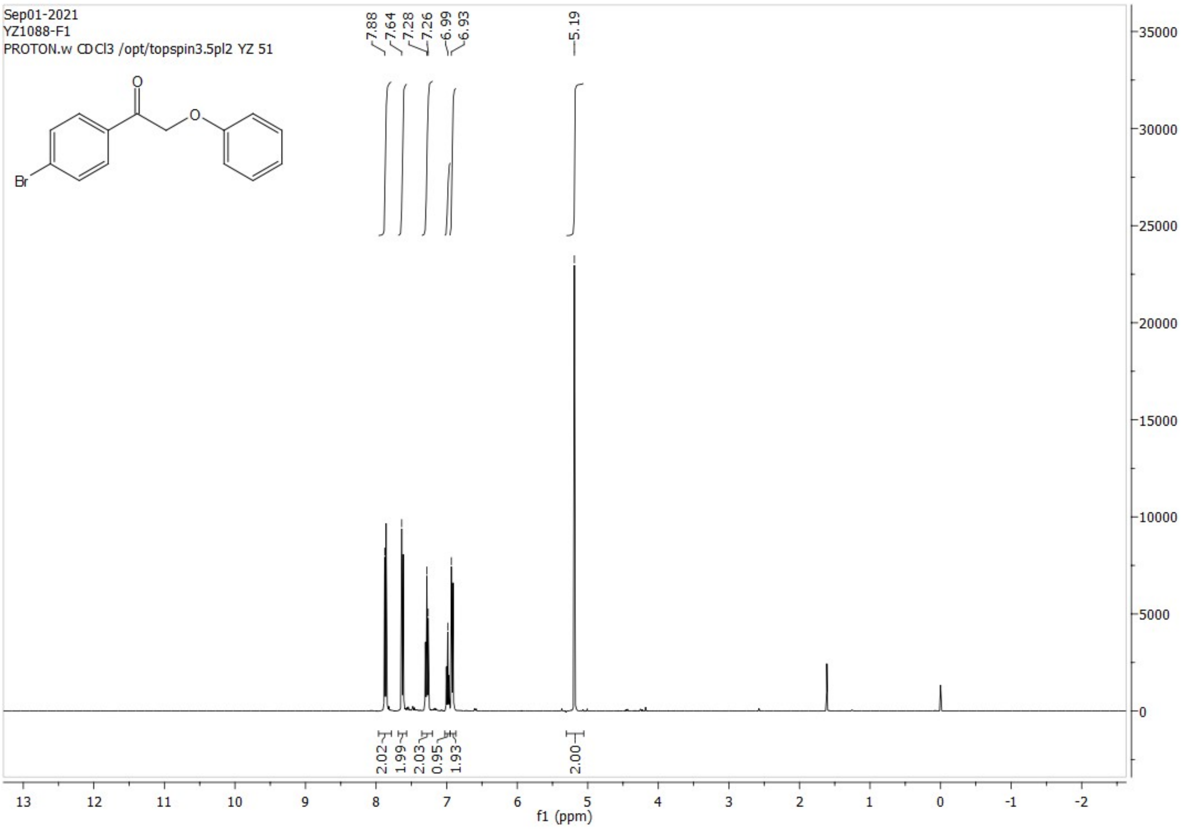


This compound has been reported and fully characterized. Reference: K. Gao, M. Xu, C. Cai, Y. Ding, J. Chen, B. Liu, Y. Xia, *Org. Lett.* 2020, **22**, 6055-6060.

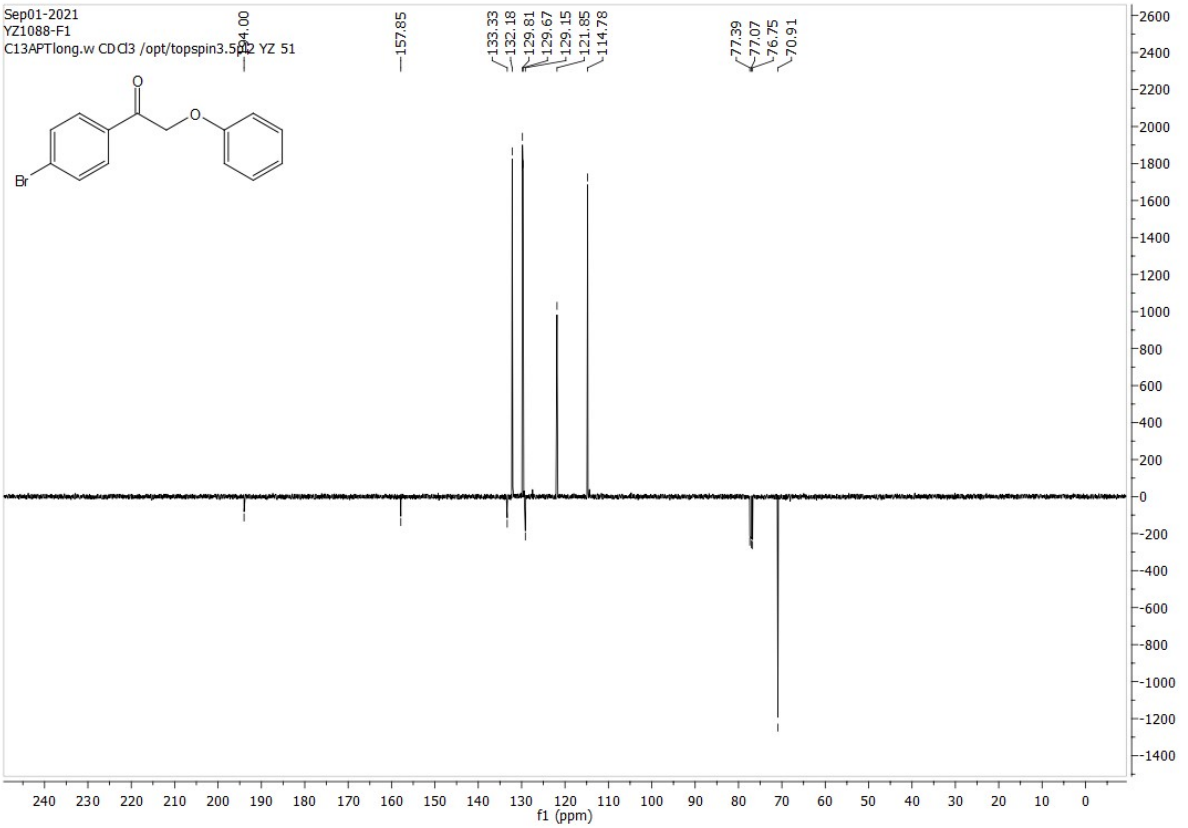
A round-bottom flask was charged with 2,4′-dibromoacetophenone (834 mg, 3.00 mmol), potassium carbonate (414 mg, 3.00 mmol), phenol (282 mg, 3.00 mmol) and acetone (2 mL). The reaction mixture was heated to reflux and left stirring under the nitrogen atmosphere overnight, followed by TLC (9:1 hexane: EtOAc). The mixture was quenched by distilled water (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried ($MgSO_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-10% ethyl acetate in hexane to give 1-(4-bromophenyl)-2-phenoxyethan-1-one as a yellow solid (534 mg, 1.84 mmol, 61%).

TLC: Rf ca 0.50 (9:1 hexane: EtOAc), strong UV and $KMnO_4$; $\delta_H$ (400 MHz, $CDCl_3$) 7.88 (2H, d, $J$ = 8.5, ArH), 7.64 (2H, d, $J$ = 8.5, ArH), 7.28 (2H, dd, $J$ = 13.5, 6.1, ArH), 6.99 (1H, t, $J$ = 7.3, ArH), 6.93 (2H, d, $J$ = 8.5, ArH), 5.19 (2H, s, $CH_2$) ppm; $\delta_C$ (100 MHz, $CDCl_3$) 194.00 (C), 157.85 (C), 133.33 (C), 132.18 (CH), 129.81 (CH), 129.67 (CH), 129.15 (C), 121.85 (CH), 114.78 (CH), 70.91 ($CH_2$) ppm; m/z (ES-API+) 313.0 ($M^+$ + 23, 100%). Data matched that reported.

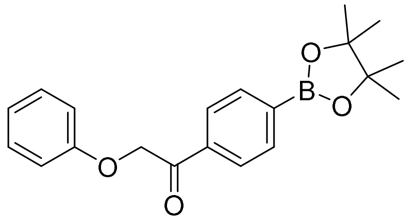
$^{1}H$ NMR (400 MHz, $CDCl_3$)

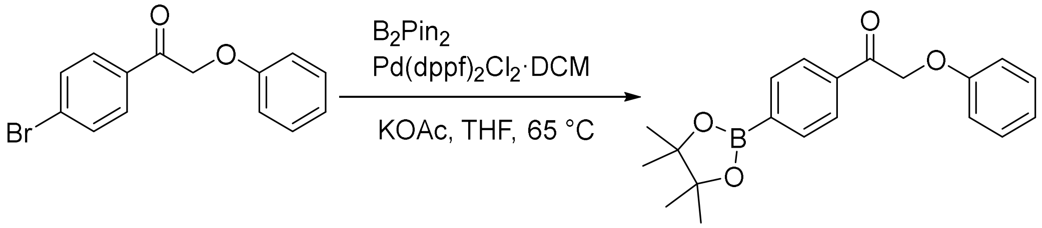


$^{13}C$ NMR (100 MHz, $CDCl_3$)



2-Phenoxy-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one.



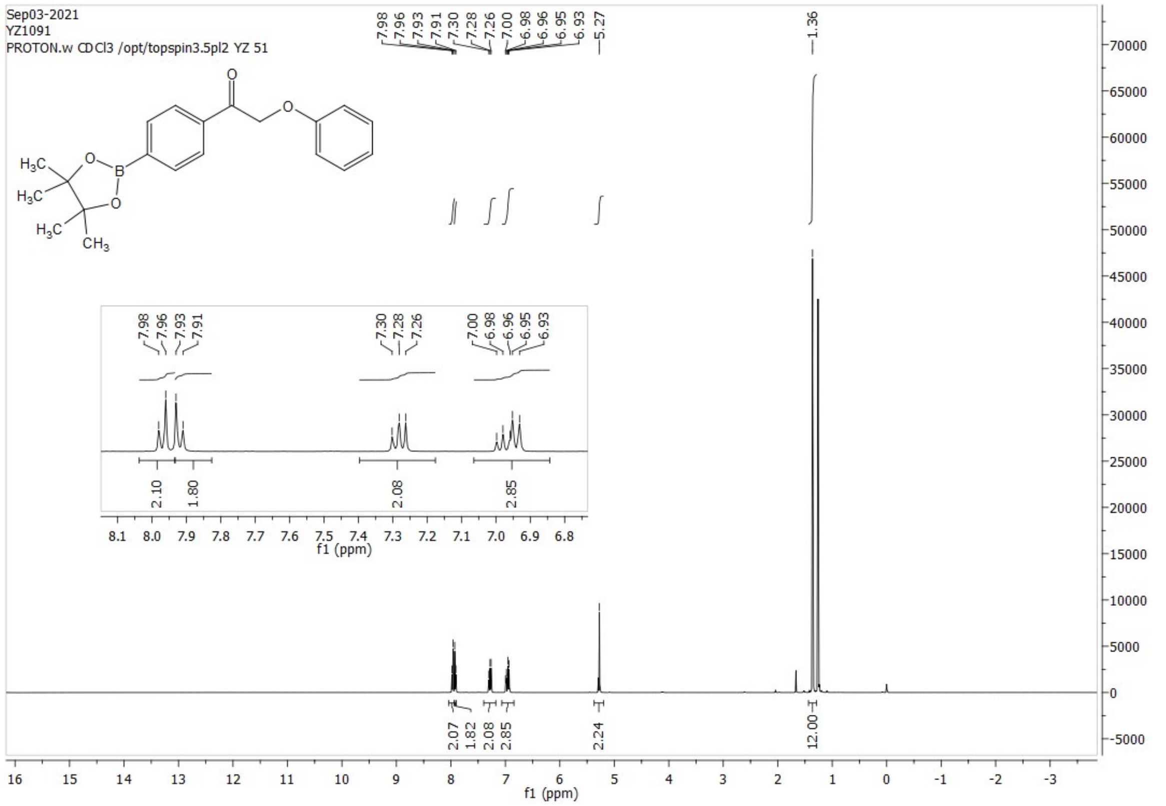


This compound is novel.

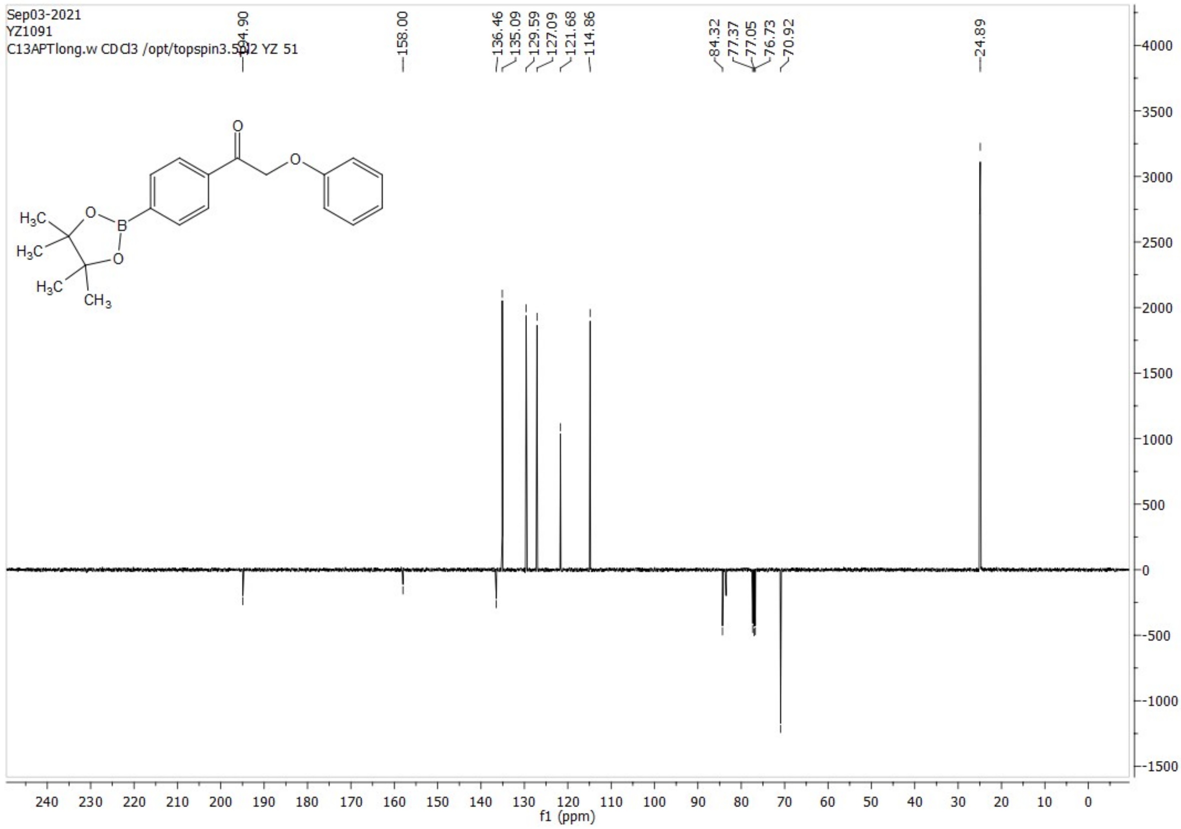
A round-bottom flask was charged with 1-(4-bromophenyl)-2-phenoxyethan-1-one (860 mg, 2.97 mmol), bis(pinacolato)diboron (904 mg, 3.56 mmol), potassium acetate (873 mg, 8.91 mmol), THF (15 mL) and $Pd(dppf)_2Cl_2 \cdot DCM$ (122 mg, 0.149 mmol). The reaction mixture was heated to 65 °C and left stirring under the nitrogen atmosphere overnight, followed by TLC (9:1 hexane: EtOAc). The mixture was quenched by distilled water (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried ($MgSO_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-20% ethyl acetate in hexane to give 2-phenoxy-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one as a yellow oil (830 mg, 2.46 mmol, 83%). TLC: Rf ca 0.40 (9:1 hexane: EtOAc), strong UV and $KMnO_4$; HRMS: (found (ESI+): [M+H]+, Calcd for $C_{20}H_{23}BNaO_4$ 361.1577; Found 361.1582; 2.2 ppm error; $\nu_{max}$ 2978, 2931, 1704, 1599, 1495, 1356, 1303, 1211, 1142, 1122, 1086, 961 cm$^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 7.98 (2H, d, *J* = 7.9, ArH), 7.93 (2H, d, *J* = 7.9, ArH), 7.30-7.26 (2H, m, ArH), 7.00-6.93 (3H, m, ArH), 5.27 (2H, s, $CH_2$), 1.36 (12H, s, $CH_3$) ppm; $\delta_C$ (100 MHz, $CDCl_3$) 194.90 (C), 158.00 (C), 136.46 (C), 135.09 (CH), 129.59 (CH), 127.09 (CH), 121.68 (CH), 114.86 (CH), 84.32 (C), 70.92 ($CH_2$), 24.89 ($CH_3$) ppm; m/z (ES-API+) 361.1 ($M^+$ + 23, 100%).

Enantiomeric excess and conversion determined by HPLC analysis (Chiralcel ODH, 30 cm x 6mm column, hexane:iPrOH 95:5, 1.0 mL/min, T = 25°C) ketone 16.6 min, *R* isomer 18.0 min and *S* isomers 30.7 min.

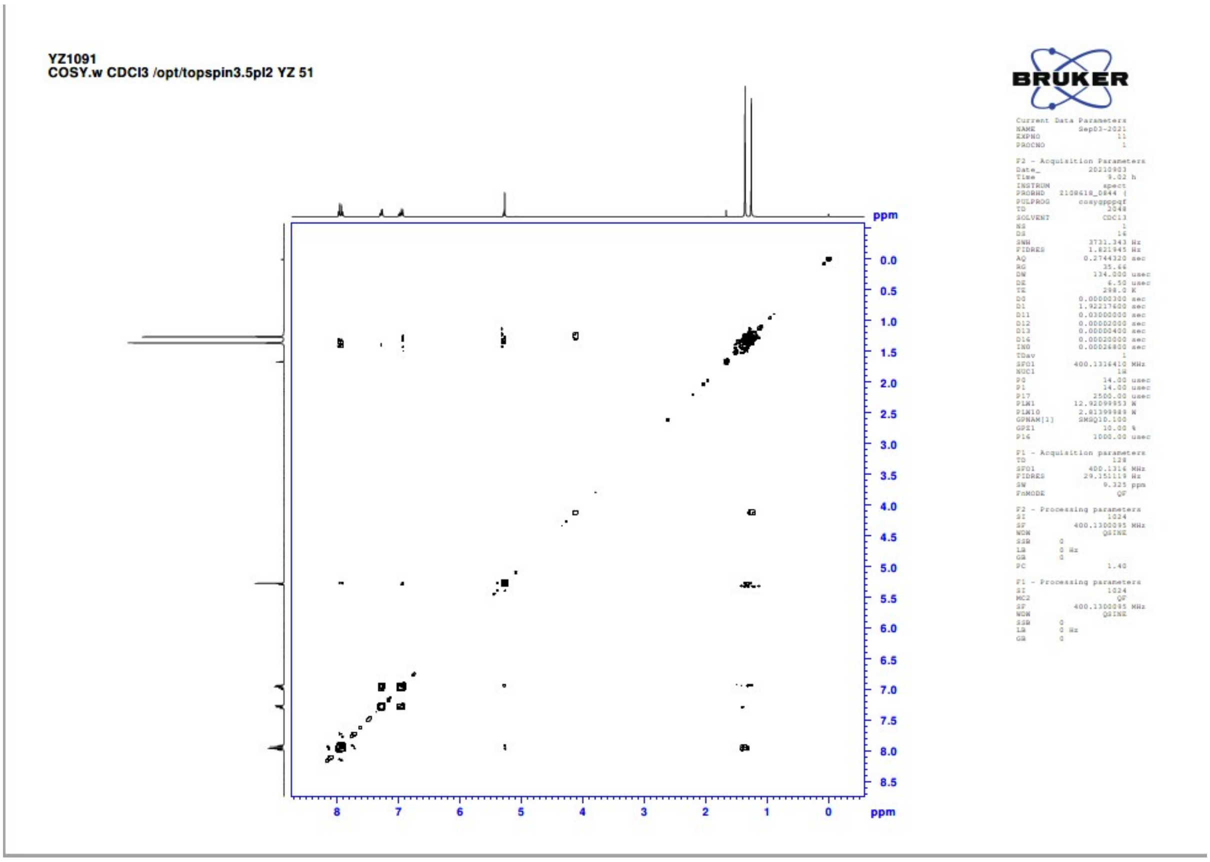
$^1$H NMR (400 MHz, CDCl$_3$)



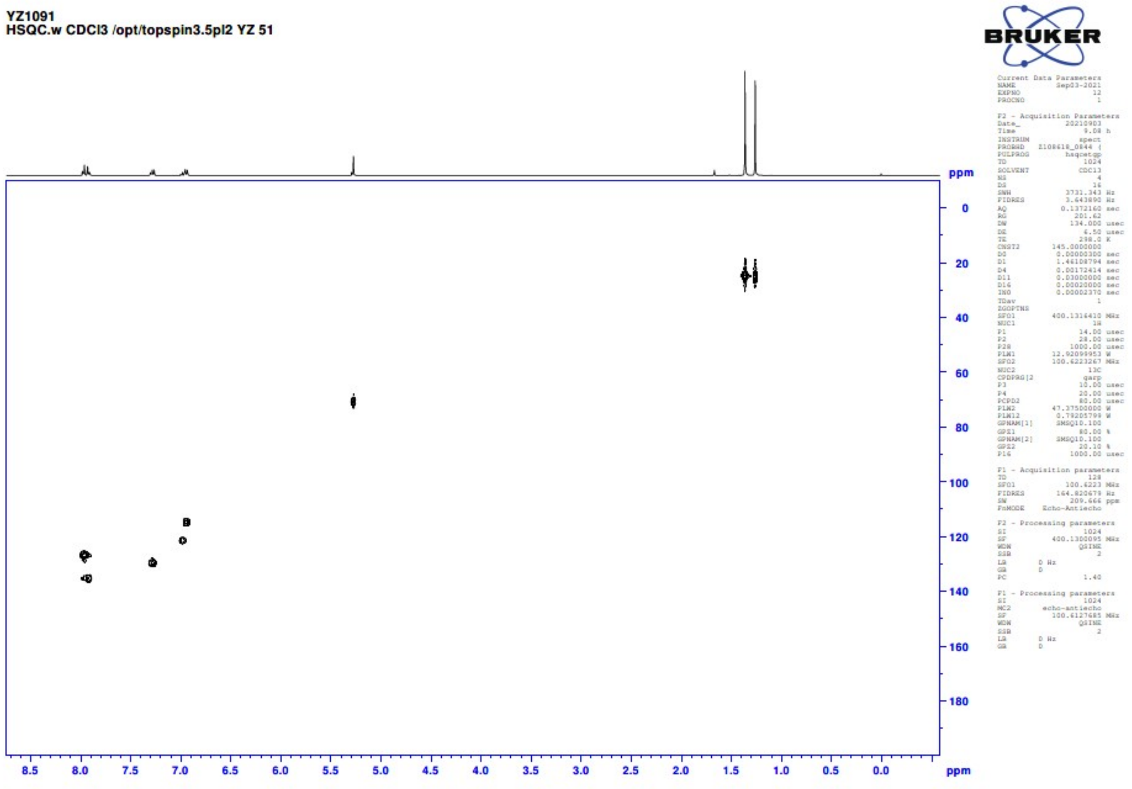
$^{13}$C NMR (100 MHz, CDCl$_3$)



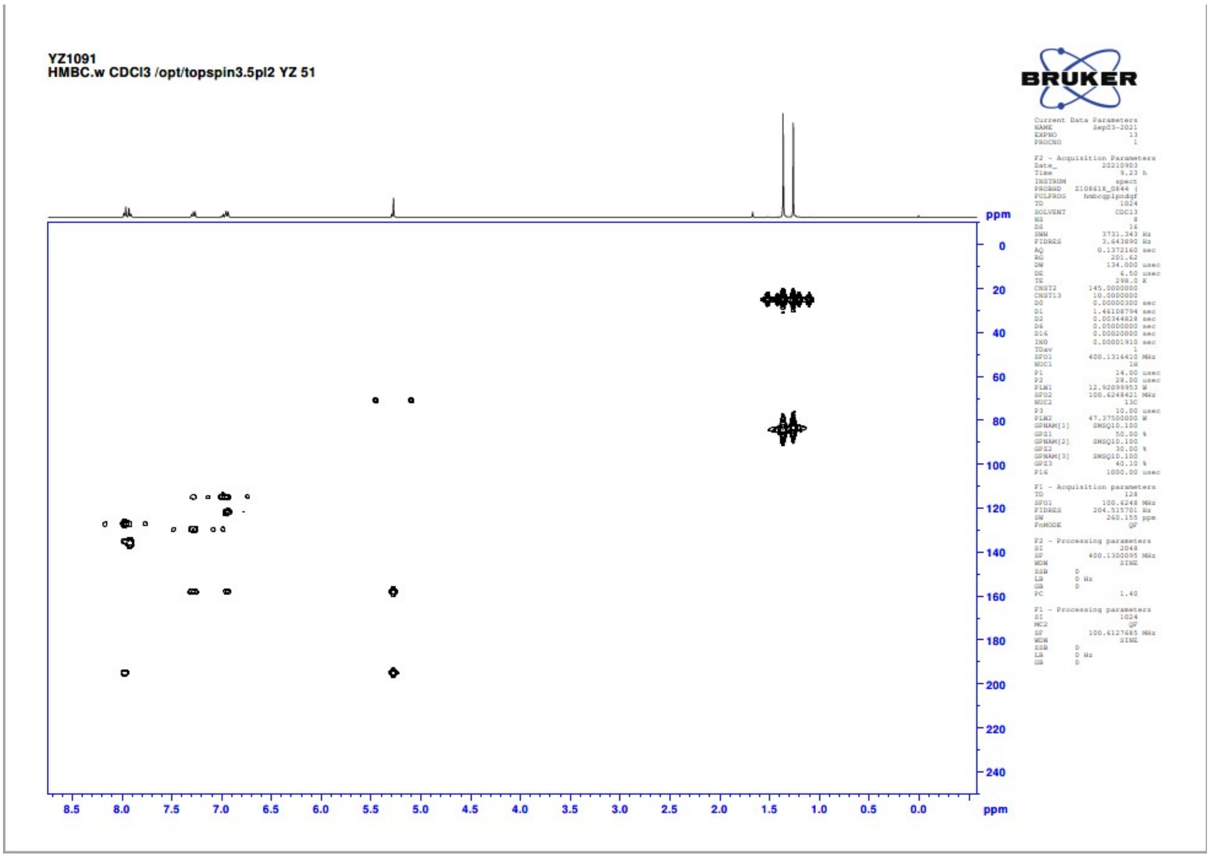
COSY (400 MHz, CDCl$_3$)



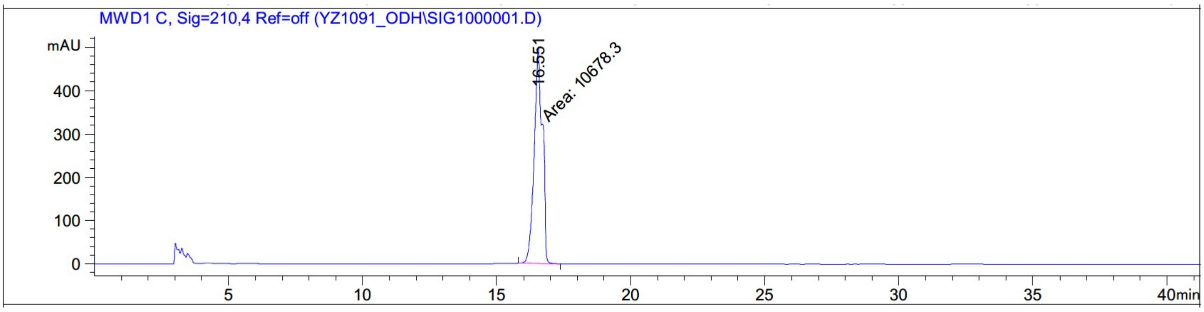
HSQC (400 MHz, CDCl₃)



HMBC (400 MHz, CDCl₃)



HPLC of 2-phenoxy-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one



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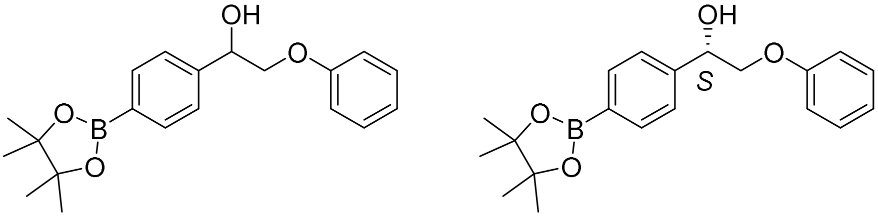
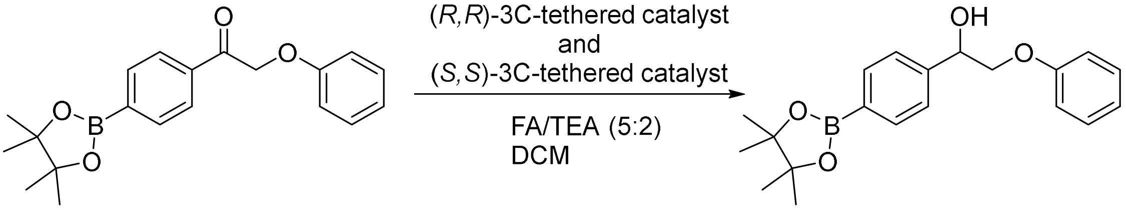
Signal 2: MWD1 C, Sig=210,4 Ref=off

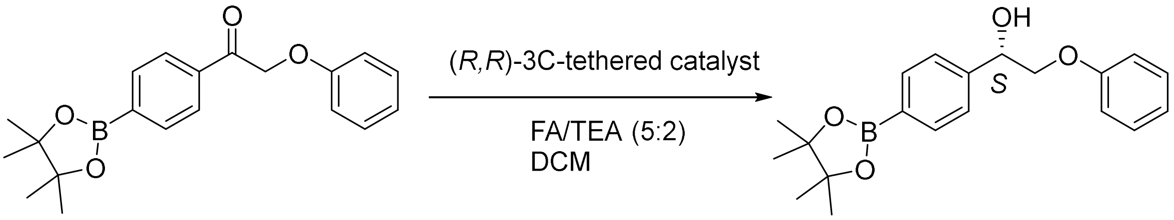
Peak RetTime Type  Width     Area       Height      Area
  #    [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  16.551 MM     0.3566 1.06783e4   499.12787 100.0000

Totals :                   1.06783e4   499.12787
```

Racemic and (*S*)-2-phenoxy-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol **12**.







This compound is novel.

**Synthesis of a racemic standard:**

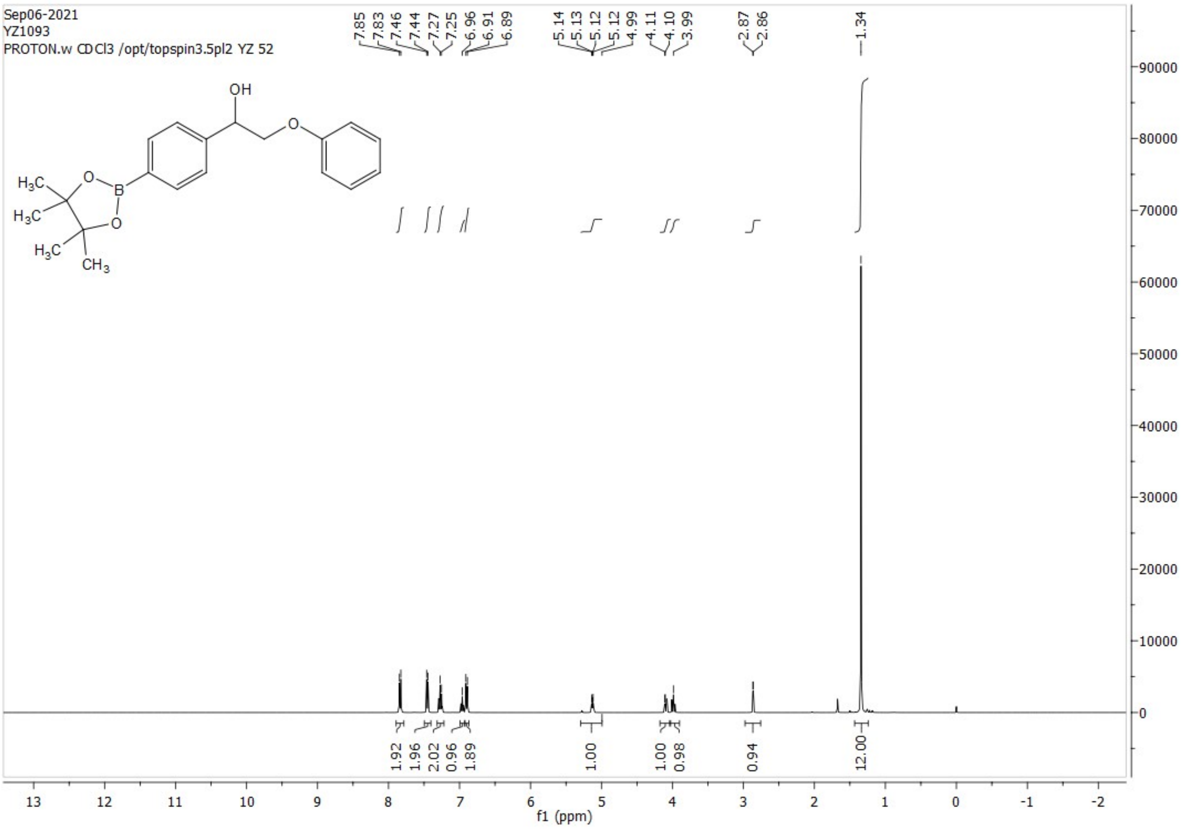
(*R,R*)-3C-Tethered Ru(II)-TsDPEN catalyst **2** (1.1 mg, 1.8 μmol, 0.5 mol%) and (*S,S*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (1.1 mg, 1.8 μmol, 0.5 mol%) were added to FA: TEA (5:2 azeotropic mixture, 0.54 mL) at rt and the mixture was stirred under a nitrogen atmosphere for 15 minutes, after which a solution of 2-phenoxy-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one (120 mg, 0.355 mmol) in DCM (0.75 mL) was added. The reaction mixture was stirrer under a nitrogen atmosphere and followed by TLC (4:1 hexane: EtOAc). After 72 hours, the reaction was quenched using saturated $NaHCO_3$ solution (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried ($MgSO_4$) and filtered. The solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-20% EtOAc in hexane to give 2-phenoxy-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol **12** as a colorless oil (60.0 mg, 0.176 mmol, 50%). TLC: Rf ca 0.20 (4:1 hexane: EtOAc), strong UV and $KMnO_4$; HRMS: (found (ESI+): [M+H]+, Calcd for $C_{20}H_{25}BNaO_4$ 363.1741; Found 363.1738; 0.3 ppm error; $\nu_{max}$ 3461 (br), 2977, 2928, 1599, 1495, 1397, 1357, 1241, 1141, 1086, 1019, 731 cm$^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 7.85 (2H, d, *J* = 7.8, ArH), 7.46 (2H, d, *J* = 7.8, ArH), 7.27 (2H, t, *J* = 7.8, ArH), 6.96 (1H, t, *J* = 7.3, ArH), 6.91 (2H, d, *J* = 8.3, ArH), 5.13 (1H, dd, *J* = 6.1, 2.6, ArCH), 4.10 (1H, dd, *J* = 9.6, 3.1, $CH_2$), 3.99 (1H, t, *J* = 9.2, $CH_2$), 2.87 (1H, d, *J* = 2.6, OH), 1.34 (12H, s, $CH_3$) ppm; $\delta_C$ (100 MHz, $CDCl_3$) 158.39 (C), 142.77 (C), 135.06 (CH), 129.58 (CH), 125.58 (CH), 121.34 (CH), 114.68 (CH), 83.89 (C), 72.24 ($CH_2$), 72.61 (CH), 24.89 ($CH_3$) ppm; m/z (ES-API+) 363.2 ($M^+$ + 23, 100%).

Enantiomeric excess and conversion determined by HPLC analysis (Chiralcel ODH, 30 cm x 6mm column, hexane:iPrOH 95:5, 1.0 mL/min, T = 25°C) ketone 16.6 min, *R* isomer 18.0 min and *S* isomers 30.7 min..

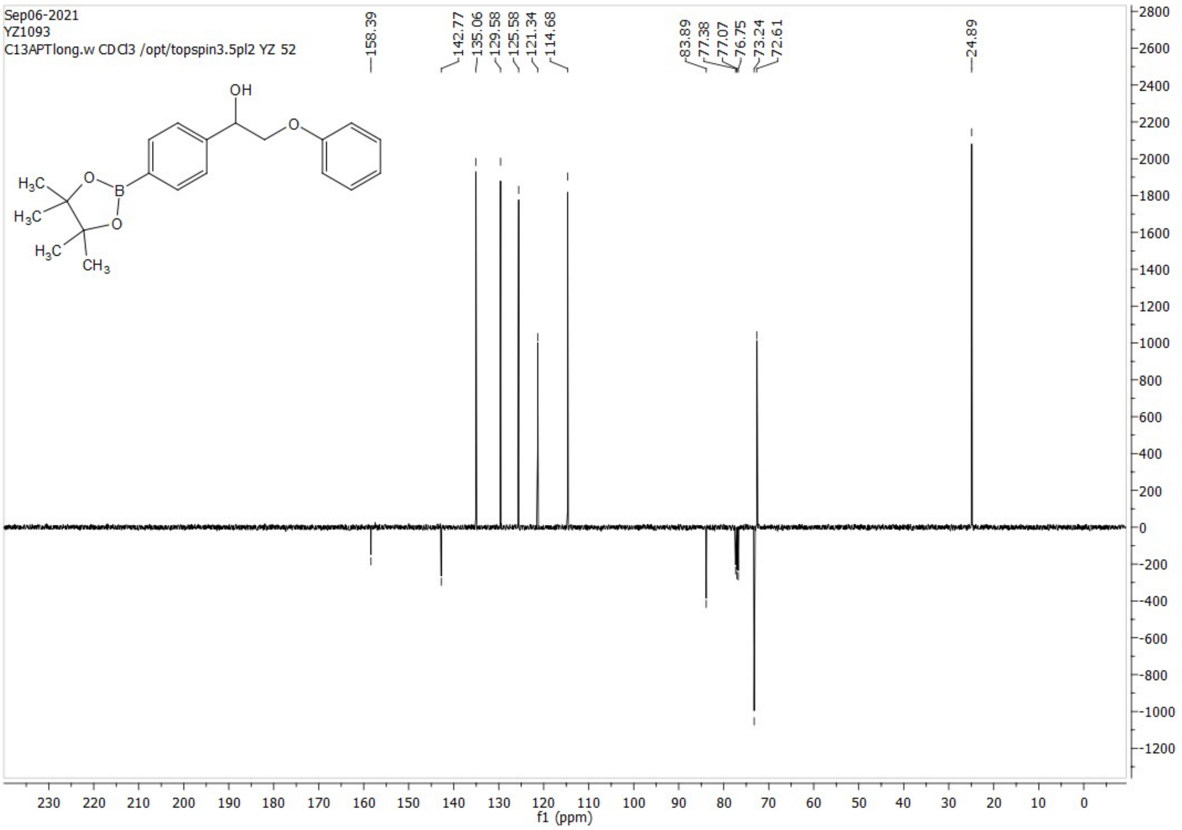
ATH of 2-phenoxy-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one:

(*R,R*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (2.2 mg, 3.6 μmol, 1 mol%) was added to FA: TEA (5:2 azeotropic mixture, 0.54 mL) at rt and the mixture was stirred under a nitrogen atmosphere for 15 minutes; after which a solution of 2-phenoxy-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one (120 mg, 0.355 mmol) in DCM (0.75 mL) was added. The reaction mixture was stirred under a nitrogen atmosphere and followed by TLC (4:1 hexane: EtOAc). After 72 hours, the reaction was quenched using saturated $NaHCO_3$ solution (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried ($MgSO_4$) and filtered. The solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-50% EtOAc in hexane to give (*S*)-2-phenoxy-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol **12** as a colorless oil (61.0 mg, 0.179 mmol, 51%). The reaction was also followed by HPLC (Chiralcel ODH, 30 cm x 6mm column, hexane:iPrOH 95:5, 1.0 mL/min, T = 25°C): $[\alpha]_D^{26}$ +31.3 (c 0.408 in $CHCl_3$) 97% ee (*S* configuration, confirmed by methylation, as described below).

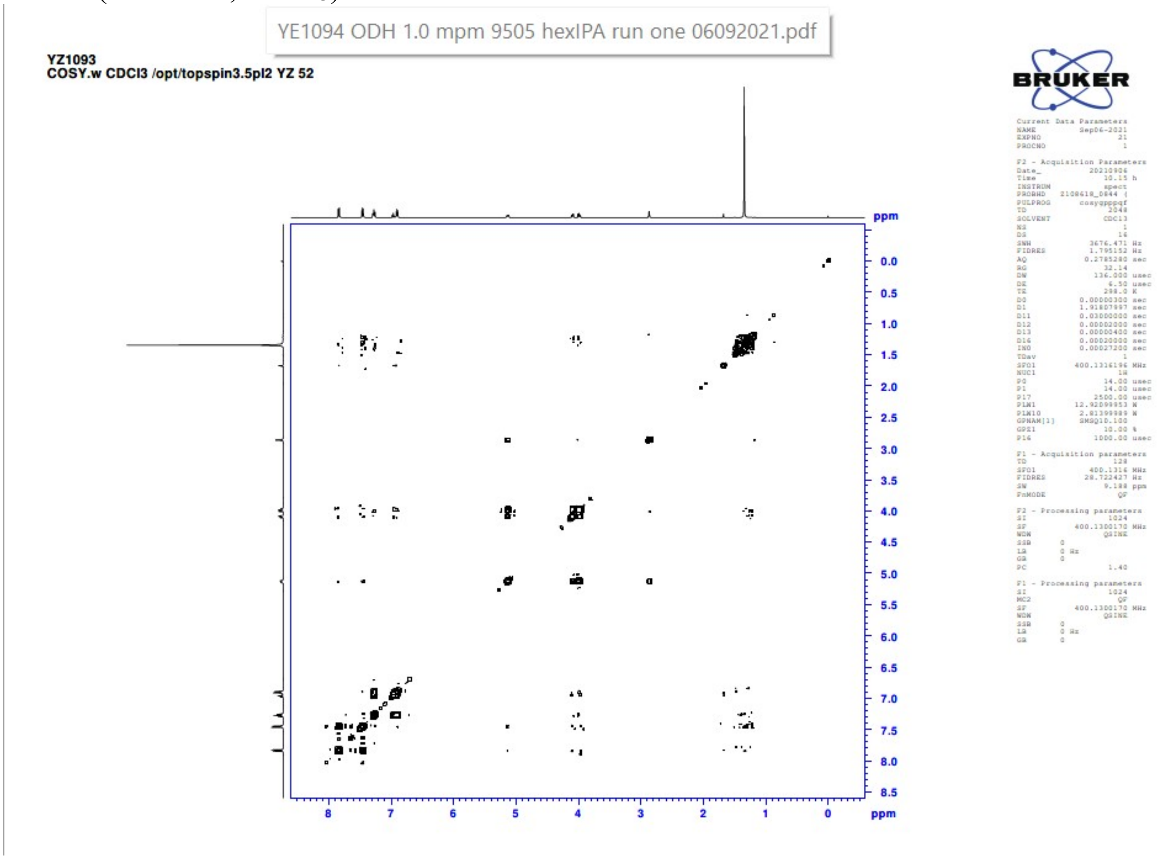
$^{1}$H NMR (400 MHz, CDCl$_3$)



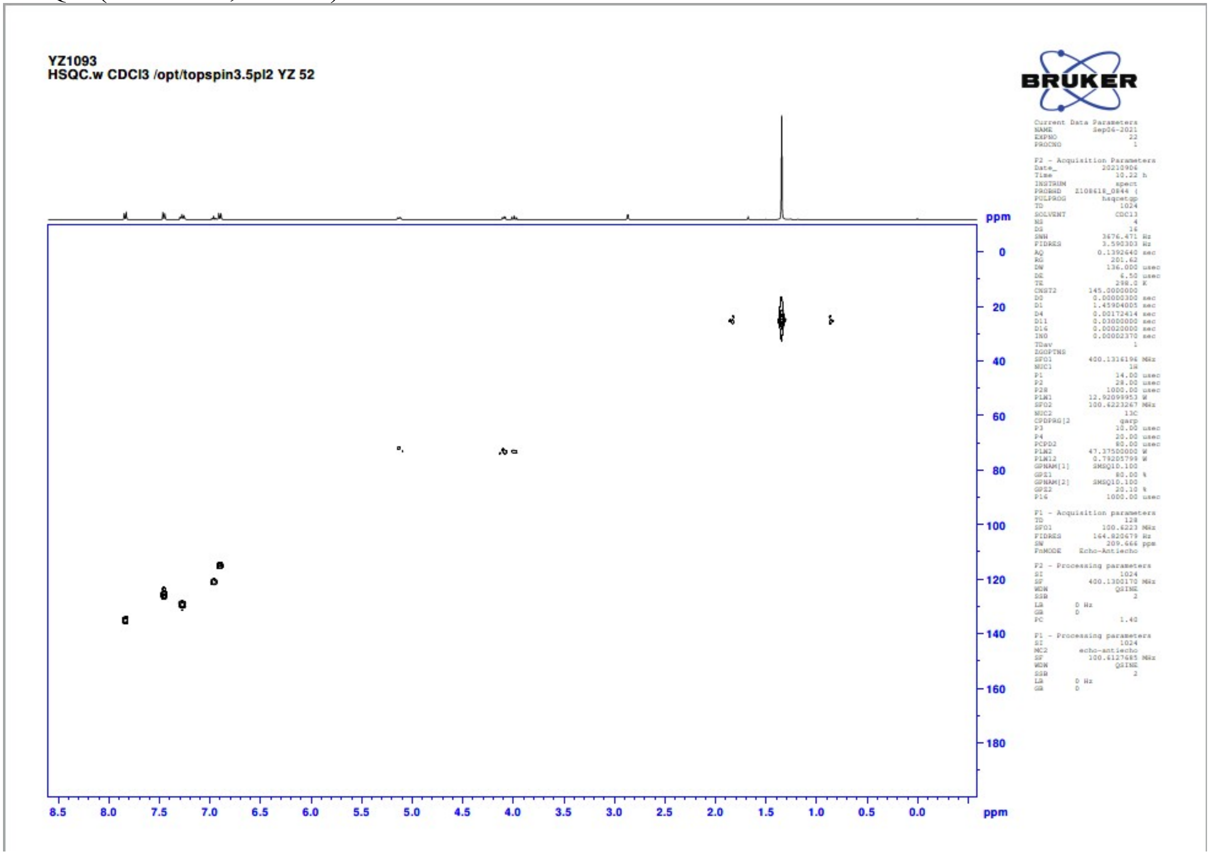
$^{13}$C NMR (100 MHz, CDCl$_3$)



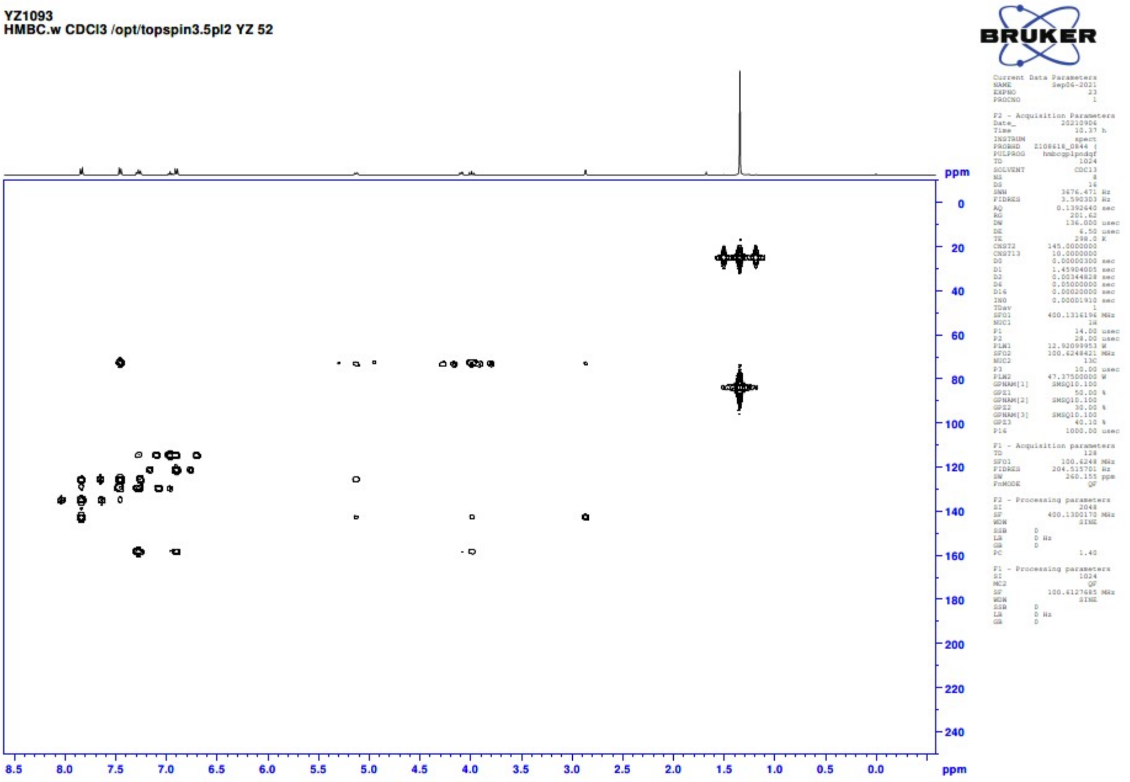
COSY (400 MHz, CDCl$_3$)



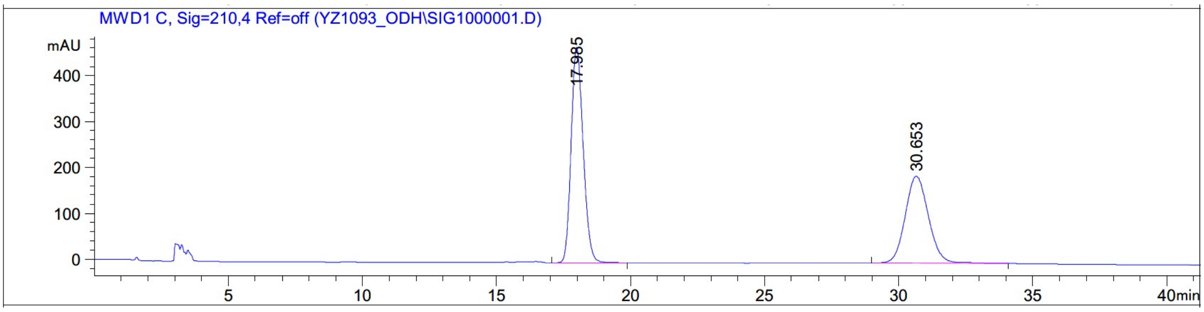
HSQC (400 MHz, CDCl$_3$)



HMBC (400 MHz, $CDCl_3$)



HPLC of racemic 2-phenoxy-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol **12.**



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   2  30.653 BB    0.9316 1.13716e4  189.09644  43.7815

Totals :                  2.59735e4  657.71753
```
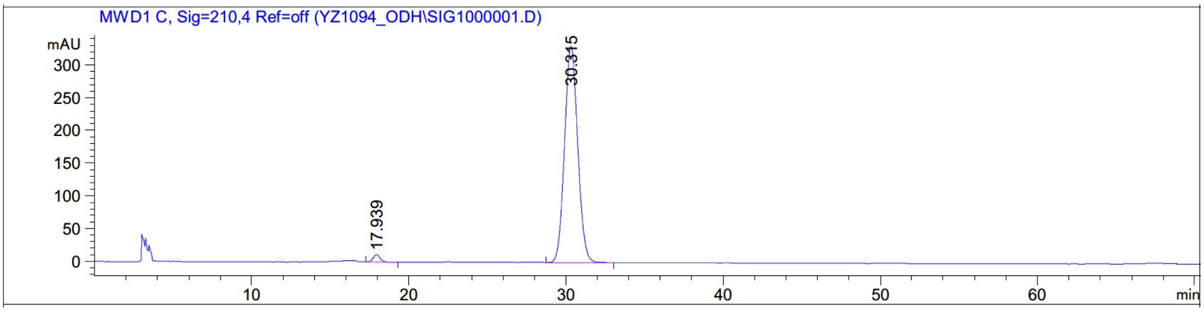

HPLC after ATH of 2-phenoxy-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one using ((*R,R*)-3C-Tethered Ru(II)-TsDPEN catalyst **2** (after 72 hours, 100% conversion, 97% ee, *S* configuration).



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Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  17.939 BB    0.4509  339.09100   11.27375   1.7322
   2  30.315 BB    0.9045 1.92372e4   330.79166  98.2678

Totals :                  1.95763e4   342.06540
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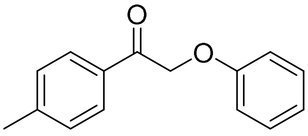
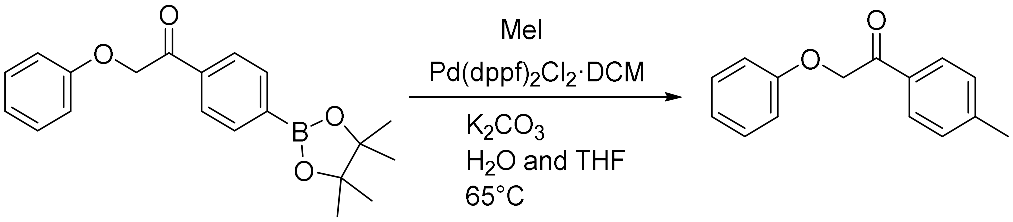
2-Phenoxy-1-(*p*-tolyl)ethan-1-one **20**.

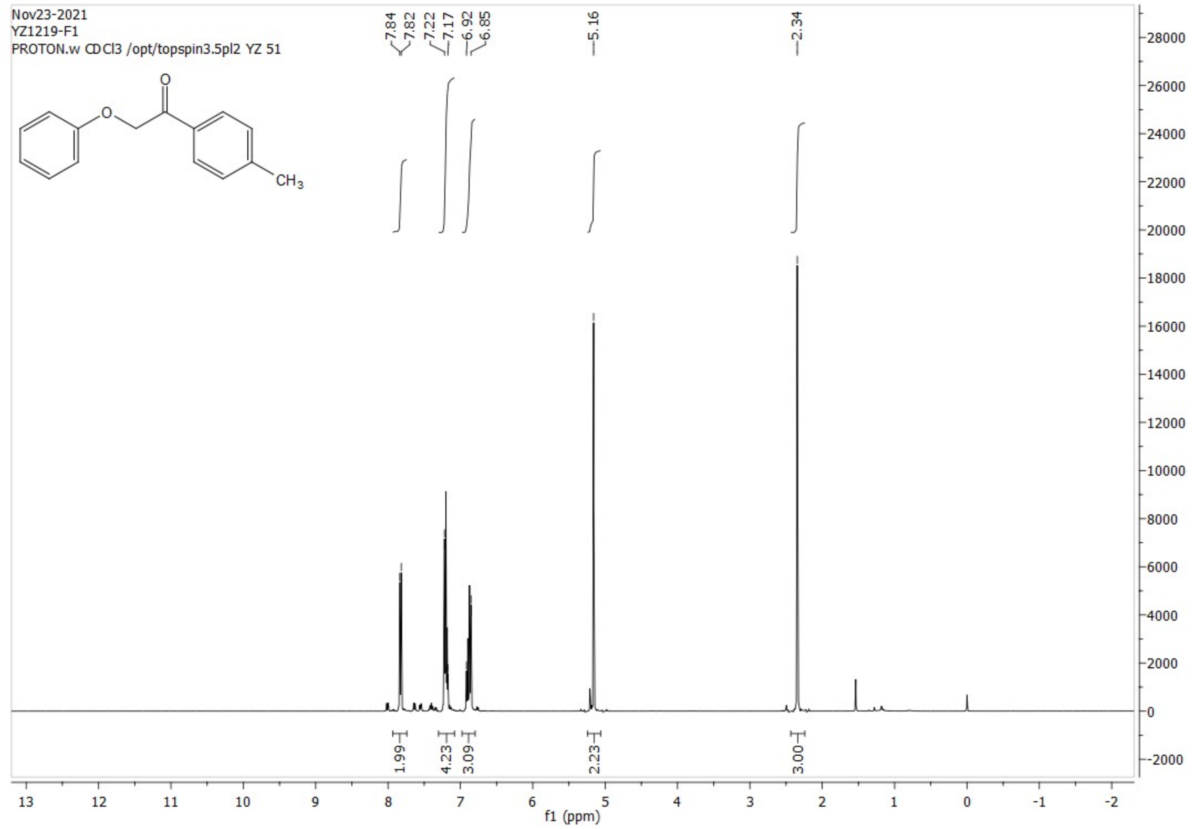




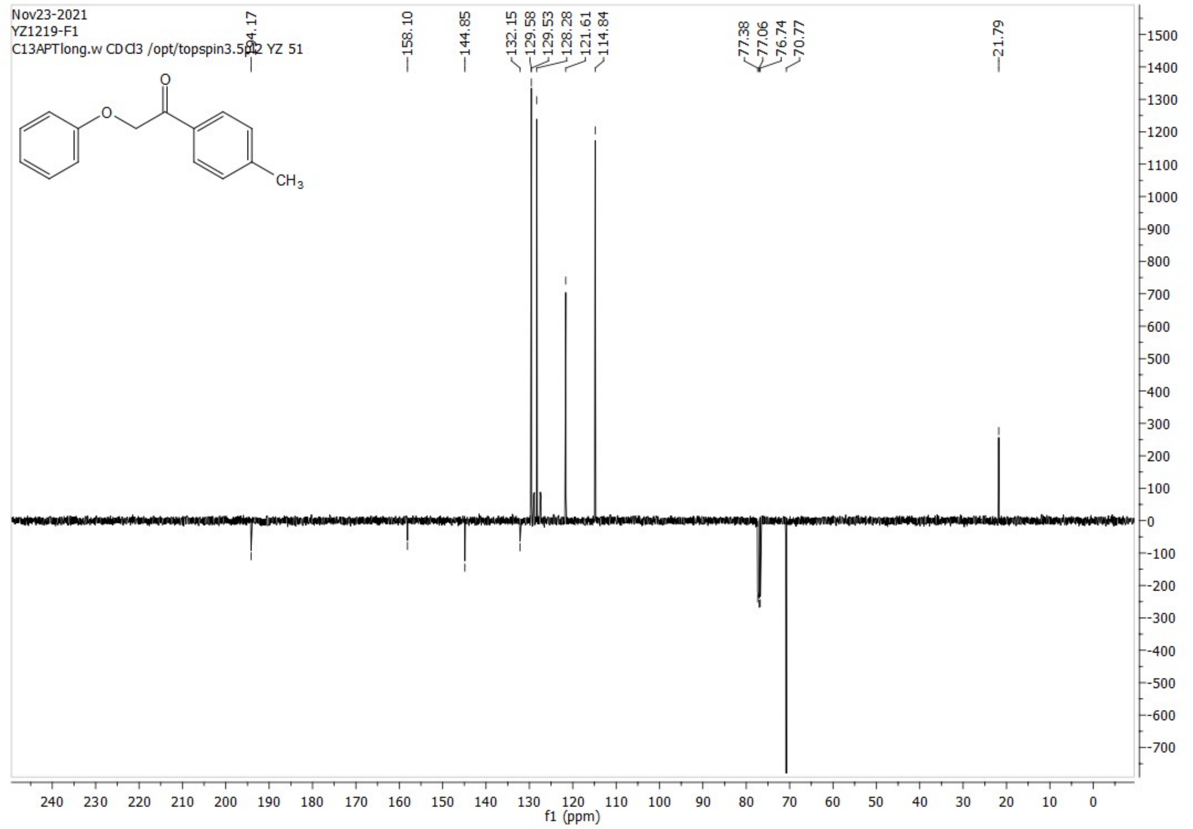
This compound has been reported and fully characterized: Y. Zhou, G. E. Klinger, E. L. Hegg, C. M. Saffron, J. E. Jackson, *J. Am. Chem. Soc.* 2020, **142**, 4037-4050.

To a solution of 2-phenoxy-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one (680 mg, 2.00 mmol), iodomethane (568 mg, 4.00 mmol) and potassium carbonate (552 mg, 4.00 mmol) in THF (38 mL) was added Pd(dppf)$_2$Cl$_2$·DCM (81.7 mg, 0.100 mmol) and distilled water (0.258 mL). The reaction mixture was heated to 65 °C and left stirring under the nitrogen atmosphere overnight, followed by TLC (9:1 hexane: EtOAc). The mixture was quenched by distilled water (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried ($MgSO_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-10% ethyl acetate in hexane to give 2-phenoxy-1-(*p*-tolyl)ethan-1-one **20** as a white solid (118 mg, 0.522 mmol, 26%). TLC: Rf ca 0.50 (9:1 hexane: EtOAc), strong UV and $KMnO_4$; $\delta_H$ (400 MHz, $CDCl_3$) 7.84 (2H, d, $J$ = 8.2, ArH), 7.22-7.17 (4H, m, ArH), 6.02-6.85 (3H, m, ArH), 5.16 (2H, s, $CH_2$), 2.34 (3H, s, $CH_3$) ppm; $\delta_C$ (100 MHz, $CDCl_3$) 194.17 (C), 158.10 (C), 144.85 (C), 132.15 (C), 129.58 (CH), 129.53 (CH), 128.28 (CH), 121.61 (CH), 114.84 (CH), 70.77 ($CH_2$), 21.19 ($CH_3$) ppm; m/z (ES-API+) 249.1 ($M^+$ + 1, 100%). Data matched that reported. Enantiomeric excess and conversion determined by HPLC analysis (Chiralcel ODH, 30 cm x 6mm column, hexane:iPrOH 90:10, 1.0 mL/min, T = 25°C) ketone 15.8 min, *R* isomer 11.3 min and *S* isomer 20.4 min.

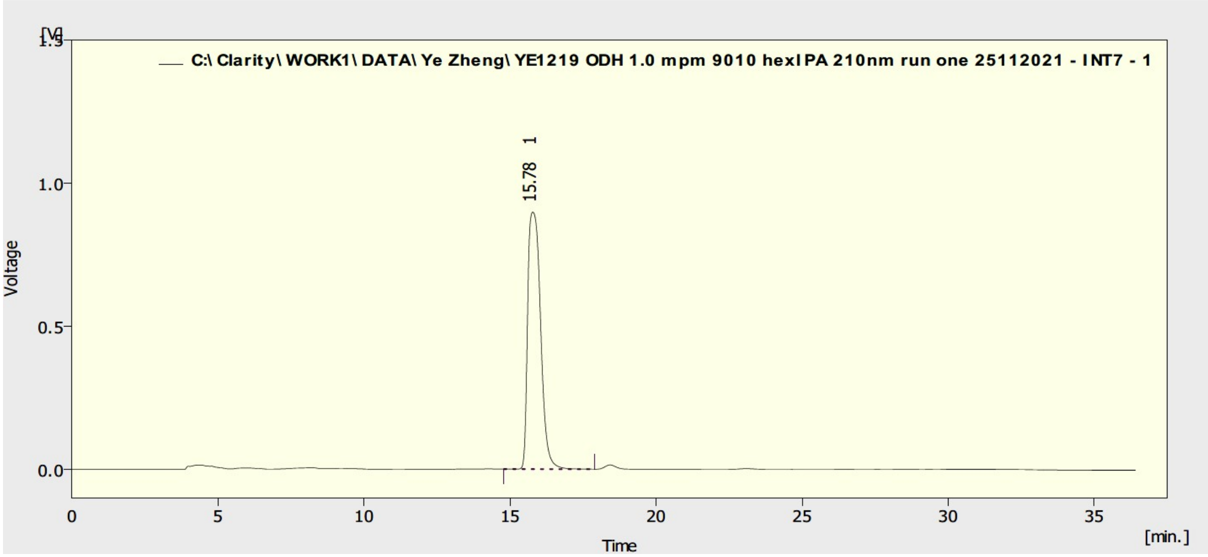
$^1$H NMR (400 MHz, CDCl$_3$)



$^{13}$C NMR (100 MHz, CDCl$_3$)



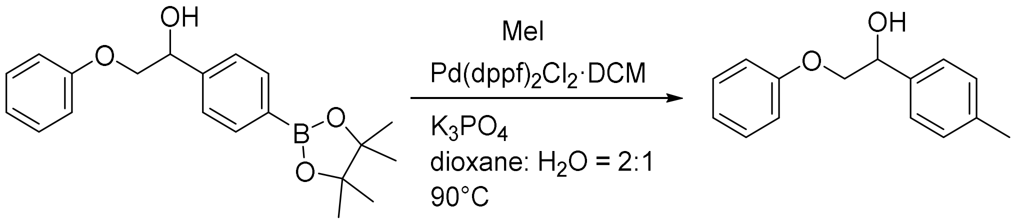
HPLC of 2-phenoxy-1-(*p*-tolyl)ethan-1-one **20**

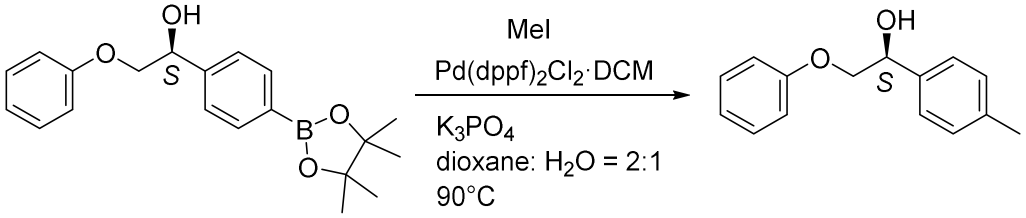


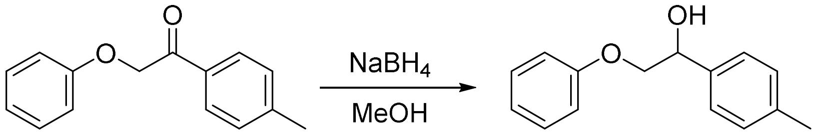
*Result Table (Uncal - C:\Clarity\WORK1\DATA\Ye Zheng\YE1219 ODH 1.0 mpm 9010 hexIPA 210nm run one 25112021 - INT7 - 1)*

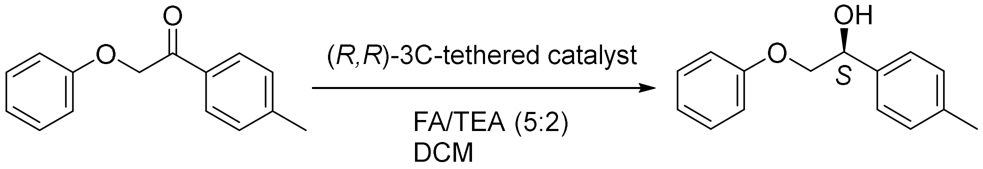
|  | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Compound Name |
|---|---|---|---|---|---|---|---|
| 1 | 15.777 | 27525.701 | 897.697 | 100.0 | 100.0 | 0.48 |  |
|  | Total | 27525.701 | 897.697 | 100.0 | 100.0 |  |  |

Racemic and (*S*)-2-Phenoxy-1-(*p*-tolyl)ethan-1-ol **19** by coupling with (*S*)-**12** and ATH of **20**.









This compound has been reported and fully characterized.

Reference: K. Huang, M. Oritiz-Marciales, W. Correa, E. Pomales, X. Y. Lopez, *J. Org. Chem.* 2009, **74**, 4195-4202.

Racemic 2-phenoxy-1-(*p*-tolyl)ethan-1-ol **19** by coupling reaction.

To a solution of racemic 2-phenoxy-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol **12** (216 mg, 0.635 mmol), iodomethane (135 mg, 0.953 mmol) and tripotassium phosphate (405 mg, 1.91 mmol) in dioxane (3.2 mL) and distilled water (1.6 mL) was added Pd(dppf)$_2$Cl$_2$·DCM (26.0 mg, 0.0318 mmol). The reaction mixture was heated to 90 °C and left stirring under the nitrogen atmosphere overnight, followed by TLC (9:1 hexane: EtOAc). The mixture was quenched by distilled water (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried (MgSO$_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-20% ethyl acetate in hexane to give racemic 2-phenoxy-1-(*p*-tolyl)ethan-1-ol **19** as a colorless oil(92.0 mg, 0.404 mmol, 64%). TLC: Rf ca 0.40 (9:1 hexane: EtOAc), strong UV and $KMnO_4$; $\delta_H$ (400 MHz, $CDCl_3$) 7.35 (2H, d, *J* = 7.9, ArH), 7.30-7.25 (2H, m, ArH), 7.21 (2H, d, *J* = 7.9, ArH), 6.97 (1H, t, *J* = 7.3, ArH), 6.93 (2H, d, *J* = 8.3, ArH), 5.10 (1H, dd, *J* = 8.8, 3.0, ArCH), 4.09 (1H, dd, *J* = 9.6, 3.2, $CH_2$), 4.00 (1H, t, *J* = 9.2, $CH_2$), 2.73 (1H, s, OH), 2.36 (3H, s, $CH_3$) ppm; $\delta_C$ (100 MHz, $CDCl_3$) 158.43 (C), 137.97 (C), 136.68 (C), 129.57 (CH), 129.27 (CH), 126.24 (CH), 121.28 (CH), 114.65 (CH), 73.32 ($CH_2$), 72.46 (CH), 21.19 ($CH_3$) ppm; m/z (ES-API+) 251.1 ($M^+$ + 23, 100%). Data matched that reported.

Enantiomeric excess and conversion determined by HPLC analysis (Chiralcel ODH, 30 cm x 6mm column, hexane:iPrOH 90:10, 1.0 mL/min, T = 25°C) ketone 15.8 min, *R* isomer 11.3 min and *S* isomer 20.4 min. The same column was used as reported in the reference above.

(*S*)-2-phenoxy-1-(*p*-tolyl)ethan-1-ol **19** by a coupling reaction.

To a solution of (*S*)-2-phenoxy-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol **12** (216 mg, 0.635 mmol), iodomethane (135 mg, 0.953 mmol) and tripotassium phosphate (405 mg, 1.91 mmol) in dioxane (3.2 mL) and distilled water (1.6 mL) was added $Pd(dppf)_2Cl_2{\cdot}DCM$ (26.0 mg, 0.0318 mmol). The reaction mixture was heated to 90 °C and left stirring under the nitrogen atmosphere overnight, followed by TLC (9:1 hexane: EtOAc). The mixture was quenched by distilled water (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried ($MgSO_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-20% ethyl acetate in hexane to give (*S*)-2-phenoxy-1-(*p*-tolyl)ethan-1-ol **19** as a colorless oil (95.0 mg, 0.417 mmol, 66%). The reaction was also followed by HPLC (Chiralcel ODH, 30 cm x 6mm column, hexane:iPrOH 90:10, 1.0 mL/min, T = 25°C): $[\alpha]_D^{23}$ +113 (c 0.300 in $CHCl_3$) 96% ee (*S*) (lit. $[\alpha]_D^{20}$ +43 (c 1.2 in $CHCl_3$) 98% ee. (*S*))

Reference: K. Huang, M. Oritiz-Marciales, W. Correa, E. Pomales, X. Y. Lopez, *J. Org. Chem.* 2009, **74**, 4195-4202.

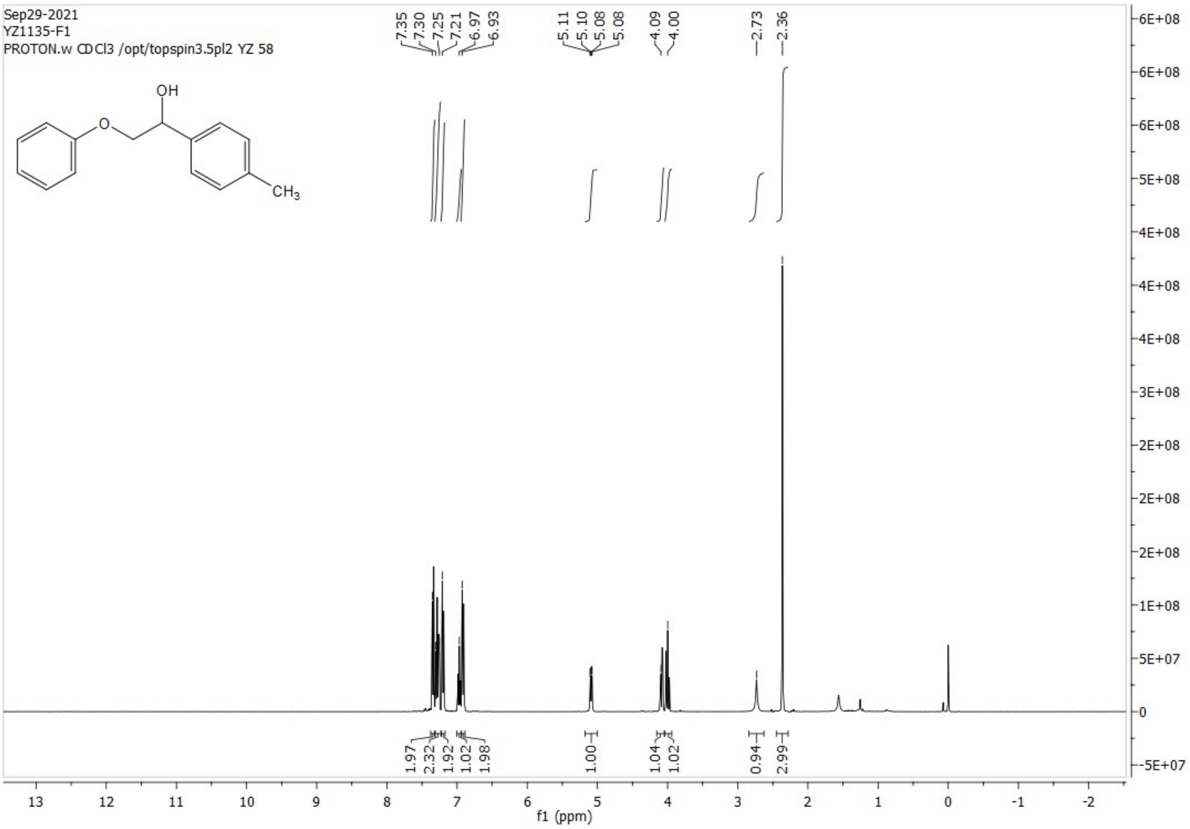
Racemic 2-phenoxy-1-(*p*-tolyl)ethan-1-ol **19** by $NaBH_4$ reduction of ketone)

To a solution of 2-phenoxy-1-(*p*-tolyl)ethan-1-one **20** (50.0 mg, 0.221 mmol) in MeOH (1.1 mL) was added sodium borohydride (16.8 mg, 0.442 mmol). The reaction was stirred for 4 hours. TLC (9:1 hexane: EtOAc) after this time indicated full conversion. Distilled water (20 mL) was added, and the mixture was extracted with EtOAc (3 × 20ml), dried with $MgSO_4$, and the solvent was removed under vacuum to give 2-phenoxy-1-(*p*-tolyl)ethan-1-ol **19** as a colorless oil (48.0 mg, 0.211 mmol, 95%).

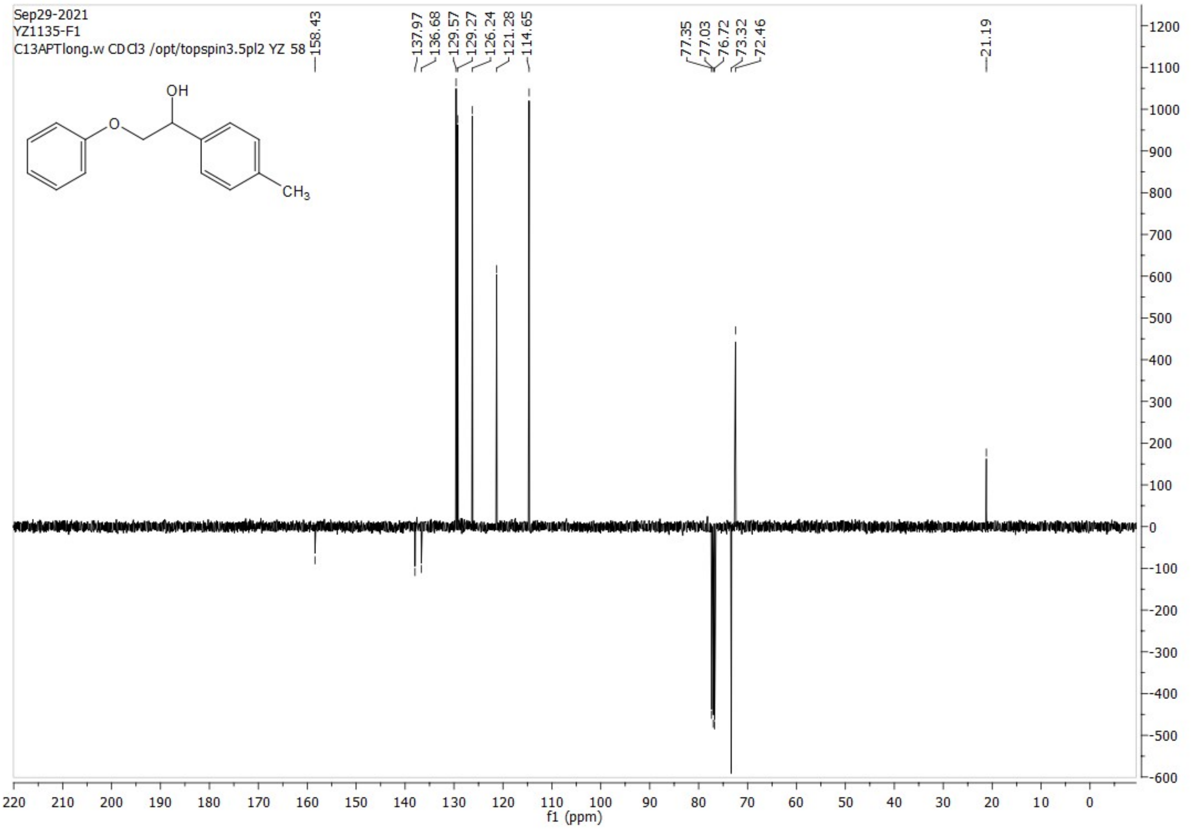
ATH of 2-phenoxy-1-(p-tolyl)ethan-1-one **20**.

(*R,R*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (1.1 mg, 1.2 μmol, 1 mol%) was added to FA: TEA (5:2 azeotropic mixture, 0.18 mL) at rt and the mixture was stirred under a nitrogen atmosphere for 15 minutes; after which a solution of 2-phenoxy-1-(*p*-tolyl)ethan-1-one **20** (40.0 mg, 0.177 mmol) in DCM (0.25 mL) was added. The reaction mixture was stirrer under a nitrogen atmosphere and followed by TLC (4:1 hexane: EtOAc). After 72 hours, the reaction was quenched using saturated $NaHCO_3$ solution (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried ($MgSO_4$) and filtered. The solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-50% ethyl acetate in hexane to give (*S*)-2-phenoxy-1-(*p*-tolyl)ethan-1-ol **19** as a colorless oil (18.0 mg, 0.0789 mmol, 45%). The reaction was also followed by HPLC (Chiralcel ODH, 30 cm x 6mm column, hexane:iPrOH 90:10, 1.0 mL/min, T = 25°C): 96% ee (*S*).

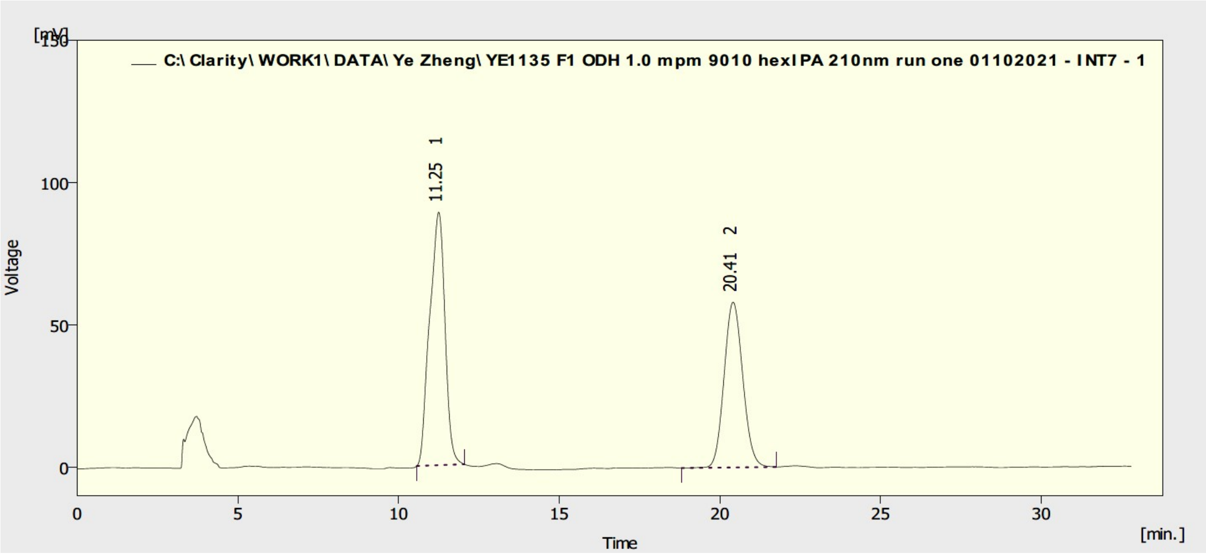
$^1$H NMR (400 MHz, CDCl$_3$)



$^{13}$C NMR (100 MHz, CDCl$_3$)



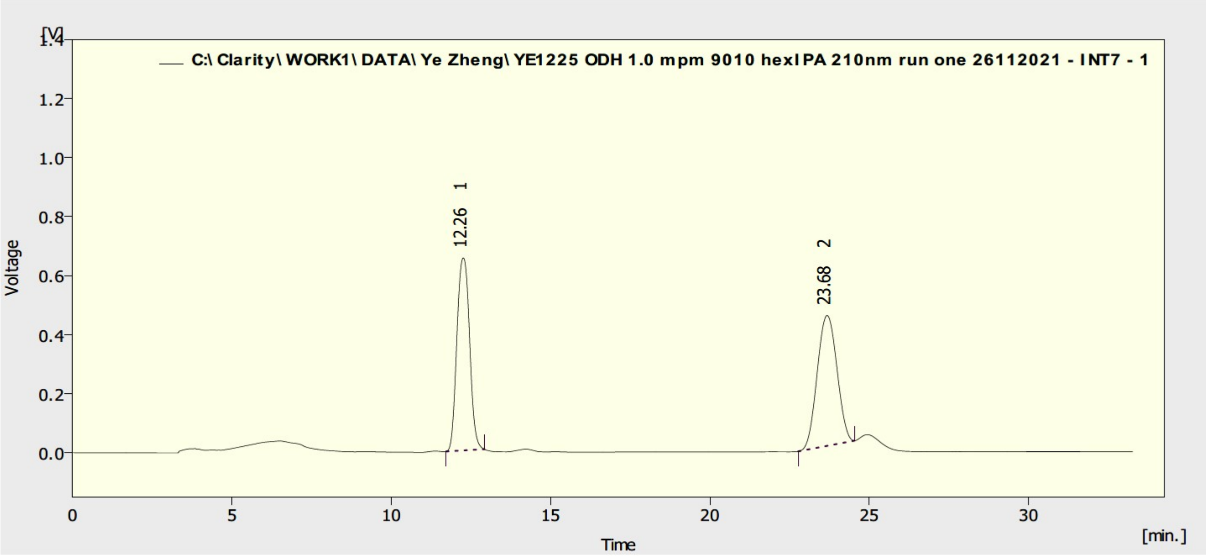
HPLC of racemic 2-phenoxy-1-(p-tolyl)ethan-1-ol **19** from coupling.



*Result Table (Uncal - C:\Clarity\WORK1\DATA\Ye Zheng\YE1135 F1 ODH 1.0 mpm 9010 hexIPA 210nm run one 01102021 - INT7 - 1)*

|  | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Compound Name |
|---|---|---|---|---|---|---|---|
| 1 | 11.247 | 2939.259 | 88.889 | 55.6 | 60.5 | 0.55 |  |
| 2 | 20.410 | 2350.964 | 58.081 | 44.4 | 39.5 | 0.63 |  |
|  | Total | 5290.223 | 146.970 | 100.0 | 100.0 |  |  |

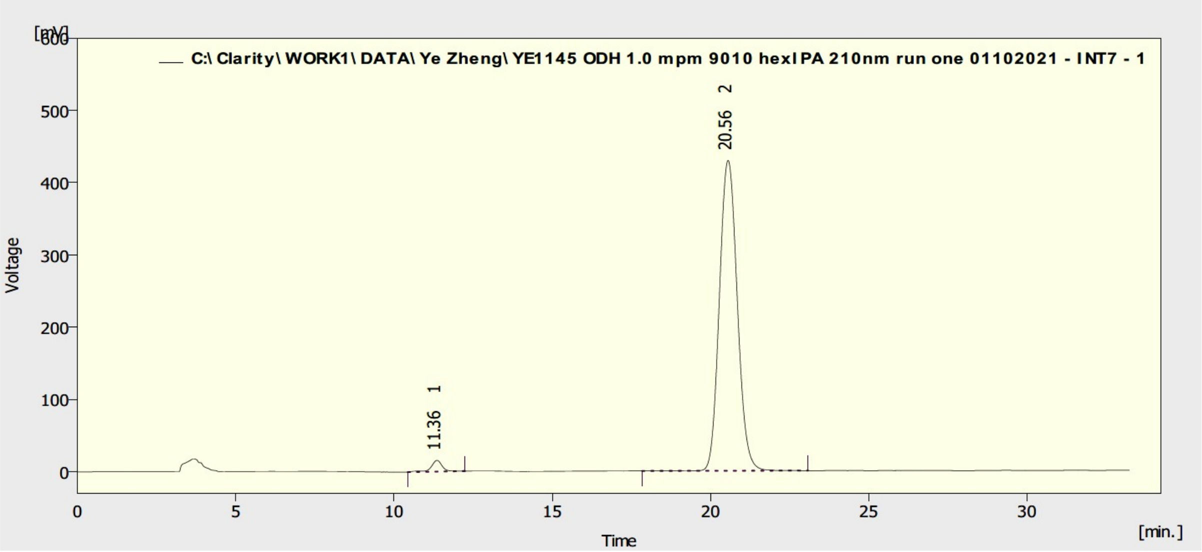
HPLC of racemic 2-phenoxy-1-(p-tolyl)ethan-1-ol **19** via reduction of **20** with $NaBH_4$.



*Result Table (Uncal - C:\Clarity\WORK1\DATA\Ye Zheng\YE1225 ODH 1.0 mpm 9010 hexIPA 210nm run one 26112021 - INT7 - 1)*

|  | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Compound Name |
|---|---|---|---|---|---|---|---|
| 1 | 12.260 | 17988.782 | 652.412 | 48.6 | 59.6 | 0.44 |  |
| 2 | 23.677 | 19014.163 | 442.080 | 51.4 | 40.4 | 0.69 |  |
|  | Total | 37002.945 | 1094.493 | 100.0 | 100.0 |  |  |

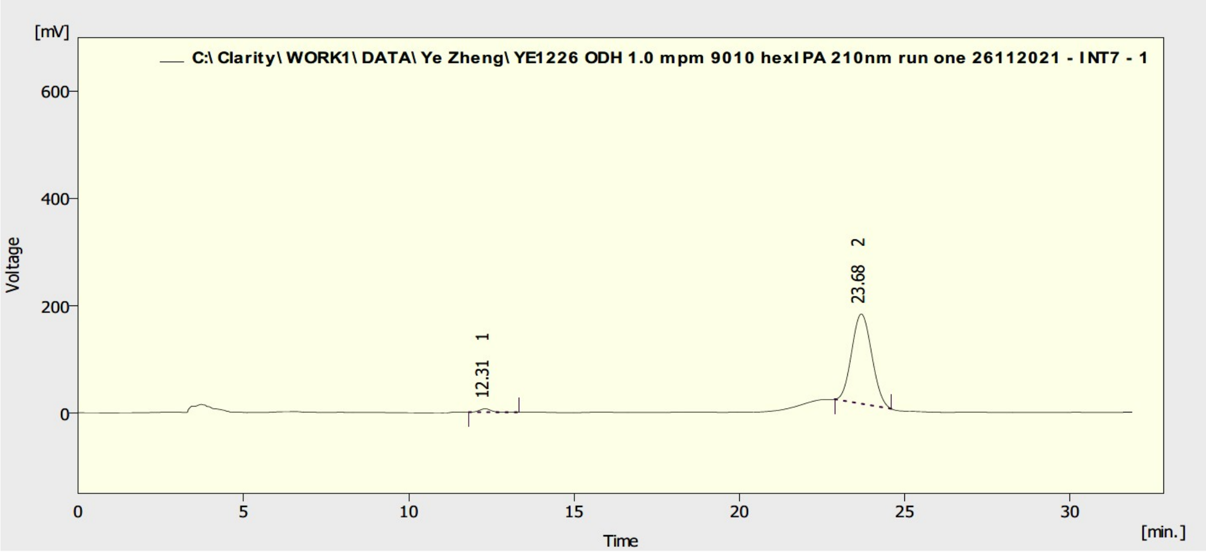
HPLC of (*S*)-2-phenoxy-1-(p-tolyl)ethan-1-ol **19** from coupling with (*S*)-**12** (96% ee, *S* configuration).



*Result Table (Uncal - C:\Clarity\WORK1\DATA\Ye Zheng\YE1145 ODH 1.0 mpm 9010 hexIPA 210nm run one 01102021 - INT7 - 1)*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Compound Name |
|---|---|---|---|---|---|---|---|
| 1 | 11.360 | 374.961 | 15.657 | 2.2 | 3.5 | 0.33 | |
| 2 | 20.557 | 16887.249 | 429.611 | 97.8 | 96.5 | 0.61 | |
| | Total | 17262.210 | 445.268 | 100.0 | 100.0 | | |

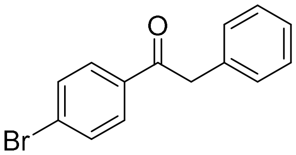
HPLC after ATH of 2-phenoxy-1-(*p*-tolyl)ethan-1-one **20** using (*R*,*R*)-3C-Tethered Ru(II)-TsDPEN catalyst **2** (after 72 hours, 100% conversion, 96% ee).

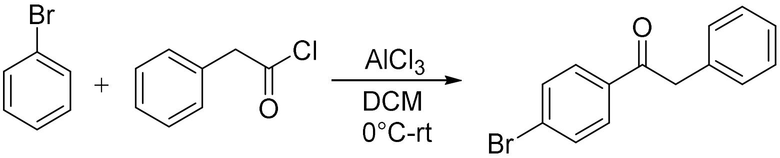


*Result Table (Uncal - C:\Clarity\WORK1\DATA\Ye Zheng\YE1226 ODH 1.0 mpm 9010 hexIPA 210nm run one 26112021 - INT7 - 1)*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Compound Name |
|---|---|---|---|---|---|---|---|
| 1 | 12.310 | 158.090 | 6.489 | 2.2 | 3.7 | 0.37 | |
| 2 | 23.683 | 7068.289 | 167.301 | 97.8 | 96.3 | 0.67 | |
| | Total | 7226.379 | 173.790 | 100.0 | 100.0 | | |

**Compound name:** 1-(4-Bromophenyl)-2-phenylethanone.

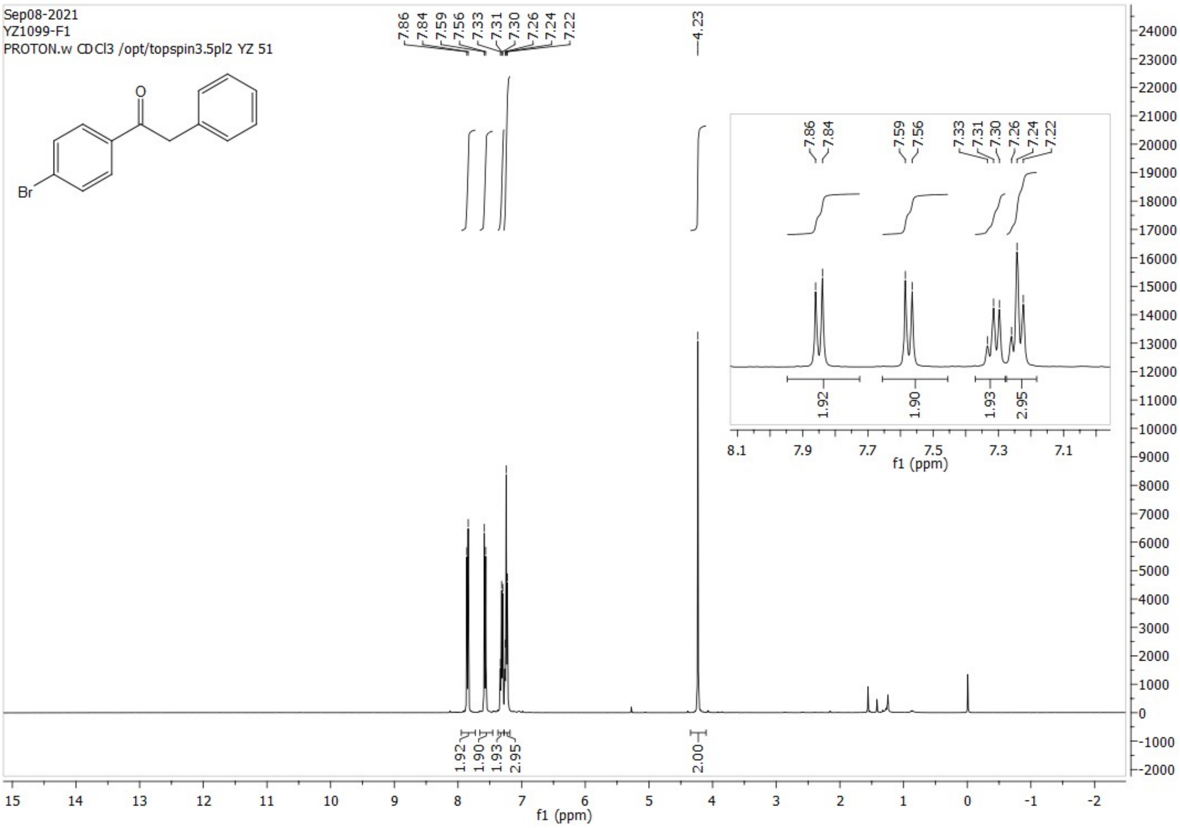




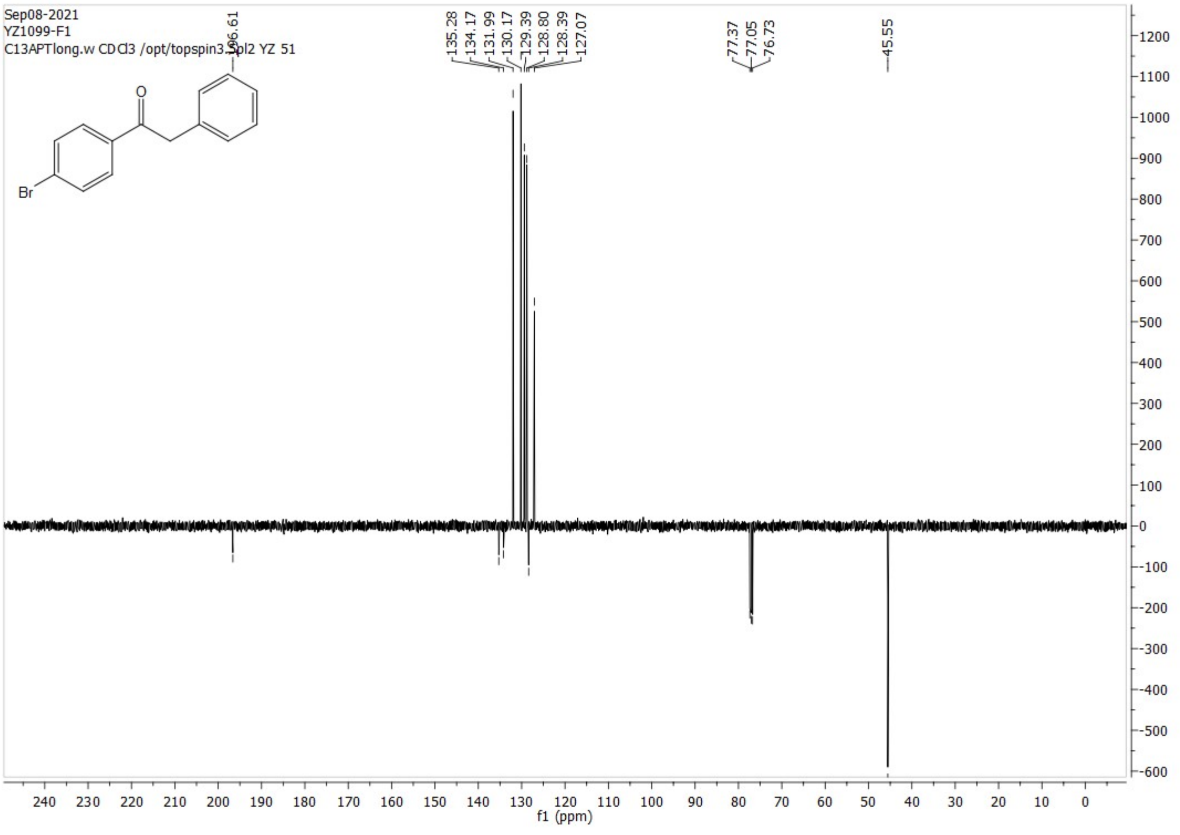
This compound has been reported and fully characterized: A. I. Khalaf, J. K. Huggan, C. J. Suckling, C. L. Gibson, K. Stewart, F. Giordani, M. P. Barrett, P. E. Wong, K. L. Barrack, W. N. Hunter, *J. Med. Chem.* 2014, **57**, 6479-6494.

To a solution of bromobenzene (314 mg, 2.00 mmol) in DCM (1.2 mL) at 0 °C was added $AlCl_3$ (217 mg, 2.04 mmol) and a solution of 2-phenylacetyl chloride (315 mg, 2.04 mmol) in DCM (0.6 mL). The reaction mixture was then stirred under a nitrogen atmosphere at 0 °C for 15 minutes. Then the reaction mixture was heated to 50 °C and left stirring under the nitrogen atmosphere for 5 hours. After which the reaction mixture was cooled down to rt and left stirring under the nitrogen atmosphere overnight. The mixture was poured into ice water and quenched with 2M HCl solution (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried ($MgSO_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-20% ethyl acetate in hexane to give 1-(4-bromophenyl)-2-phenylethan-1-one as a yellow solid (99.0 mg, 0.361 mmol, 18%). TLC: Rf ca 0.70 (9:1 hexane: EtOAc), strong UV and $KMnO_4$; $\delta_H$ (400 MHz, $CDCl_3$) 7.86 (2H, d, *J* = 8.5, ArH), 7.59 (2H, d, *J* = 8.5, ArH), 7.33-7.30 (2H, m, ArH), 7.26-7.22 (3H, m, ArH), 4.24 (2H, s, $CH_2$) ppm; $\delta_C$ (100 MHz, $CDCl_3$) 196.61 (C), 135.28 (C), 134.17 (C), 131.99 (CH), 130.17 (CH), 129.39 (CH), 128.80 (CH), 128.39 (C), 127.07 (CH), 45.55 ($CH_2$) ppm; m/z (ES-API+) 297.0 ($M^+$ + 23, 100%). Data matched that reported.

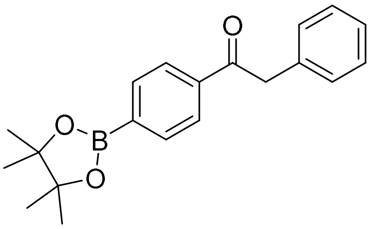
$^1$H NMR (400 MHz, CDCl$_3$)

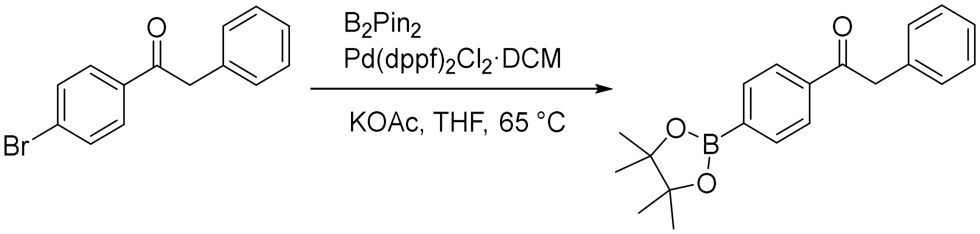


$^{13}$C NMR (100 MHz, CDCl$_3$)



2-Phenyl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one.



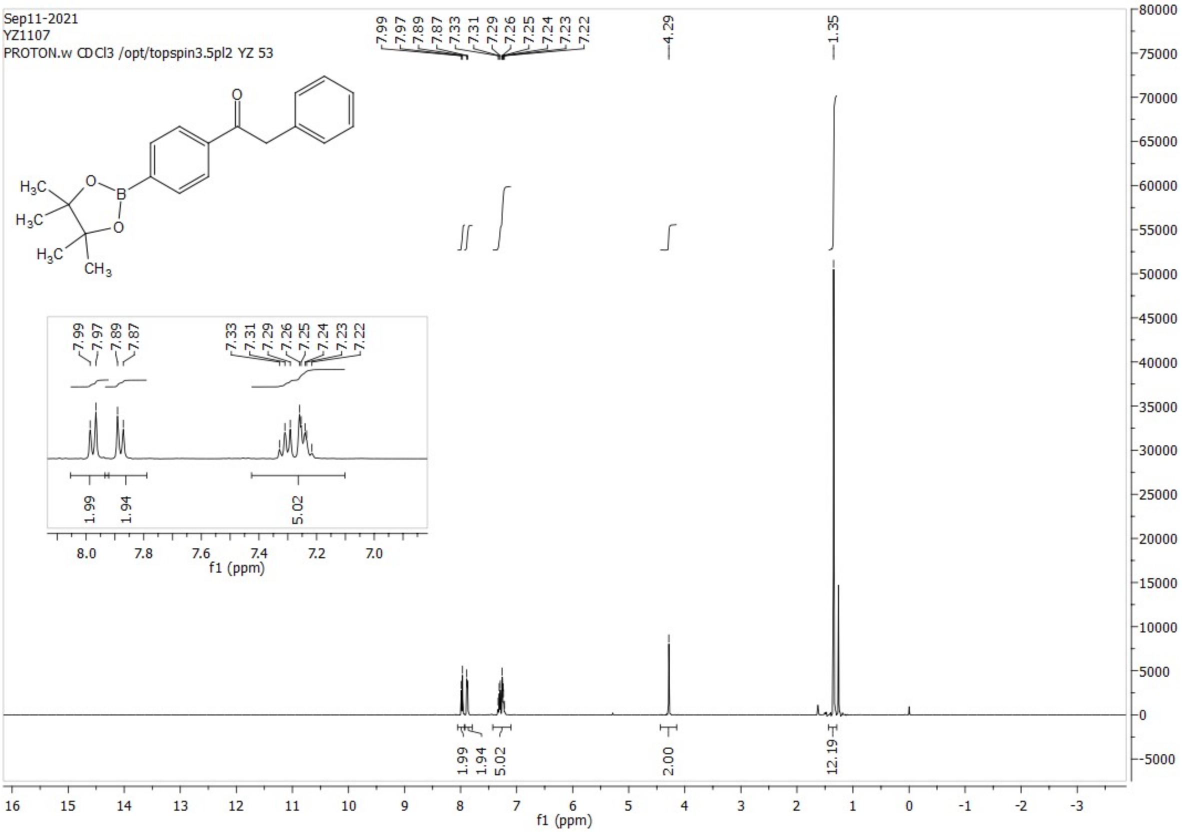


This compound has been reported and fully characterized: B. Lee, P. J. Chirik, *J. Am. Chem. Soc.* 2020, **142**, 2429-2437.

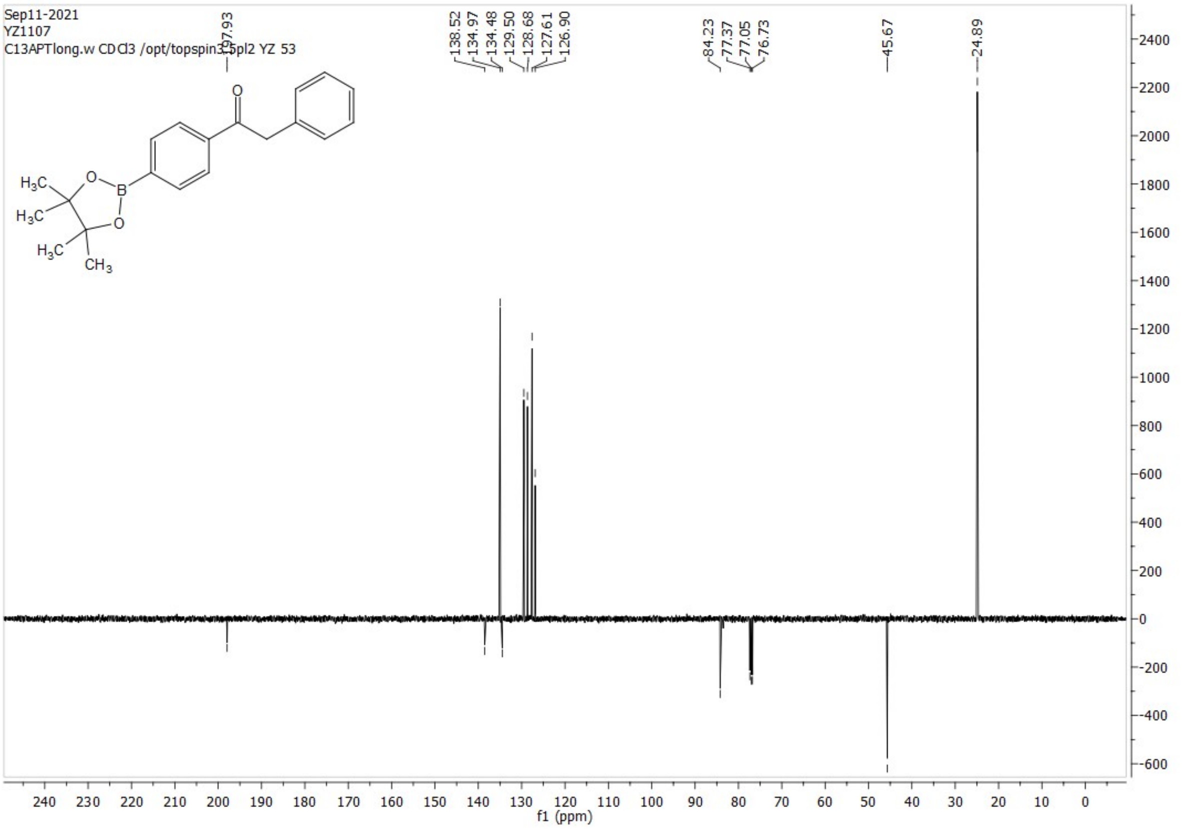
A round-bottom flask was charged with 1-(4-bromophenyl)-2-phenylethan-1-one (236 mg, 0.861 mmol), bis(pinacolato)diboron (262 mg, 1.03 mmol), potassium acetate (253 mg, 2.58 mmol), THF (4.3 mL) and Pd(dppf)$_2$Cl$_2$·DCM (35.2 mg, 0.0431 mmol). The reaction mixture was heated to 65 °C and left stirring under the nitrogen atmosphere overnight, followed by TLC (9:1 hexane: EtOAc). The mixture was quenched by distilled water (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried (MgSO$_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-20% ethyl acetate in hexane to give 2-phenyl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one as a yellow solid (113 mg, 0.351 mmol, 41%). TLC: Rf ca 0.70 (9:1 hexane: EtOAc), strong UV and KMnO$_4$; $\delta_H$ (400 MHz, CDCl$_3$) 7.99 (2H, d, $J$ = 8.0, ArH), 7.89 (2H, d, $J$ = 8.0, ArH), 7.33-7.22 (5H, m, ArH), 4.29 (2H, s, CH$_2$), 1.35 (12H, s, CH$_3$) ppm; $\delta_C$ (100 MHz, CDCl$_3$) 197.93 (C), 138.52 (C), 134.97 (CH), 134.48 (C), 129.50 (CH), 128.68 (CH), 127.61 (CH), 126.90 (CH), 84.23 (C), 45.67 (CH$_2$), 24.89 (CH$_3$) ppm; m/z (ES-API+) 345.1 (M$^+$ + 23, 100%). Data matched that reported.

Enantiomeric excess and conversion determined by HPLC analysis (Chiralcel ODH, 30 cm x 6mm column, hexane:iPrOH 90:10, 1.0 mL/min, T = 25°C) ketone 6.3 min, *R* and *S* isomers 6.2 min and 8.3 min.

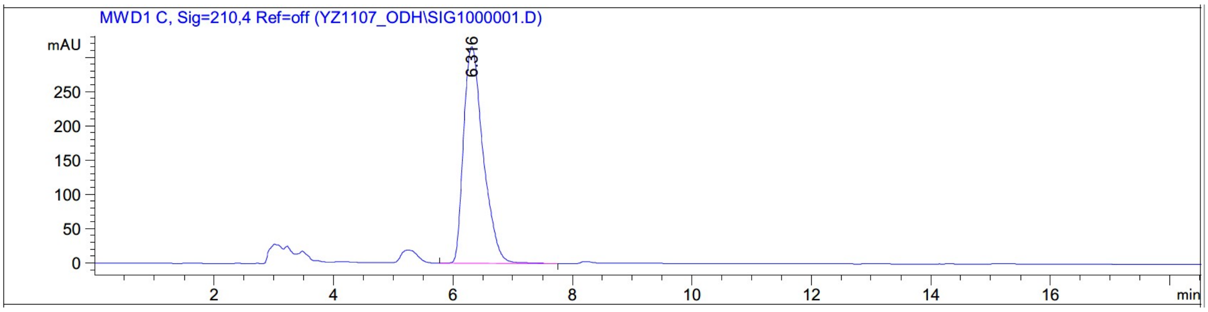
$^{1}$H NMR (400 MHz, CDCl$_3$)



$^{13}$C NMR (100 MHz, CDCl$_3$)

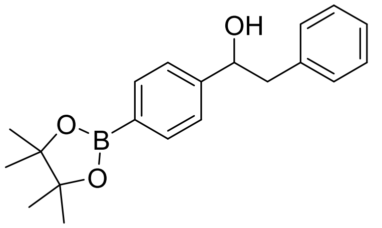


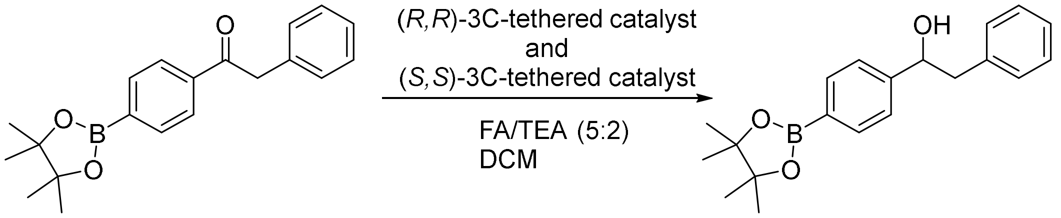
HPLC of 2-phenyl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one

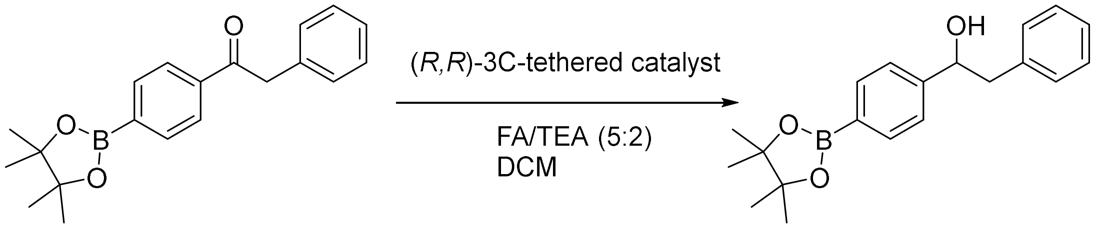


```
Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width      Area       Height      Area
  #   [min]        [min]    [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   6.316 BB     0.3495 7180.31592  315.49176 100.0000

Totals :                   7180.31592  315.49176
```

Racemic and (*R*)-2-phenyl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol **13**.







This compound is novel.

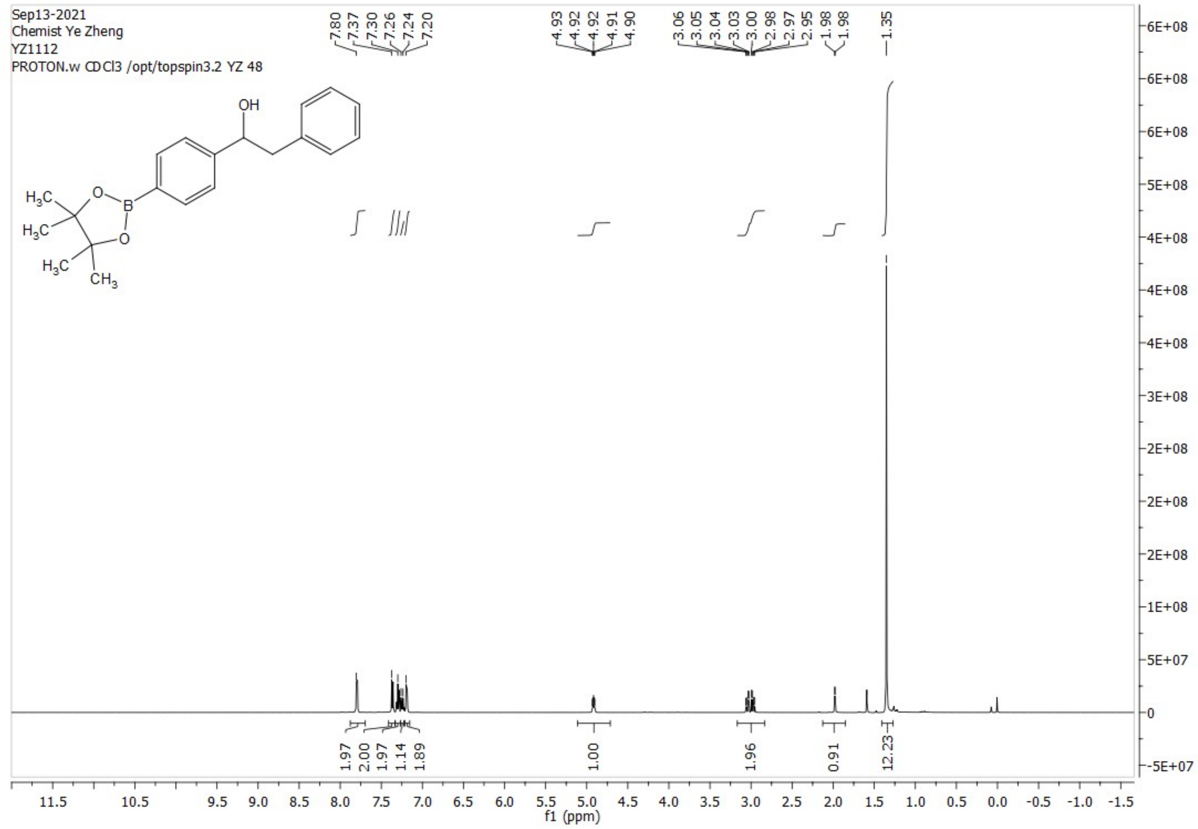
**Synthesis of a racemic standard:**

(*R,R*)-3C-Tethered Ru(II)-TsDPEN catalyst **2** (0.38 mg, 0.62 μmol, 0.5 mol%) and (*S,S*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (0.38 mg, 0.62 μmol, 0.5 mol%) were added to FA: TEA (5:2 azeotropic mixture, 0.18 mL) at rt and the mixture was stirred under a nitrogen atmosphere for 15 minutes; after which a solution of 2-phenyl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one (40.0 mg, 0.124 mmol) in DCM (0.25 mL) was added. The reaction mixture was stirrer under a nitrogen atmosphere and followed by TLC (4:1 hexane: EtOAc). After 72 hours, the reaction was quenched using saturated $NaHCO_3$ solution (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried ($MgSO_4$) and filtered. The solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-20% EtOAc in hexane to give 2-phenyl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol **13** as a colorless oil (21.0 mg, 0.0648 mmol, 52%). TLC: Rf ca 0.20 (4:1 hexane: EtOAc), strong UV and $KMnO_4$; HRMS: (found (ESI+): [M+H]+, Calcd for $C_{20}H_{25}BNaO_3$ 347.1789; Found 347.1789; 1.1 ppm error; $\nu_{max}$ 3434 (br), 3036, 2920, 1467, 1455, 1398, 1319, 1231, 1164, 1088, 1018, 802 $cm^{-1}$; $\delta_H$ (500 MHz, $CDCl_3$) 7.80 (2H, d, *J* = 7.9, ArH), 7.37 (2H, d, *J* = 7.9, ArH), 7.30 (2H, t, *J* = 7.3, ArH), 7.24 (1H, t, *J* = 7.3, ArH), 7.20 (2H, d, *J* = 7.1, ArH), 4.93-4.90 (1H, m, ArCH), 3.06-2.95 (2H, m, $CH_2$), 1.98 (1H, d, *J* = 2.9, OH), 1.35 (12H, s, $CH_3$) ppm; $\delta_C$ (125 MHz, $CDCl_3$) 136.96 (C), 137.89 (C), 134.95 (CH), 129.55 (CH), 128.54 (CH), 126.66 (CH), 125.22 (CH), 83.81 (C), 75.32 (CH), 46.05 ($CH_2$), 24.89 ($CH_3$) ppm; m/z (ES-API+) 347.2 ($M^+$ + 23, 100%). Enantiomeric excess and conversion determined by HPLC analysis (Chiralcel ODH, 30 cm x 6mm column, hexane:iPrOH 90:10, 1.0 mL/min, T = 25°C) ketone 6.3 min, *R* and *S* isomers 6.2 min and 8.3 min, configuration was assigned by analogy with **12**.

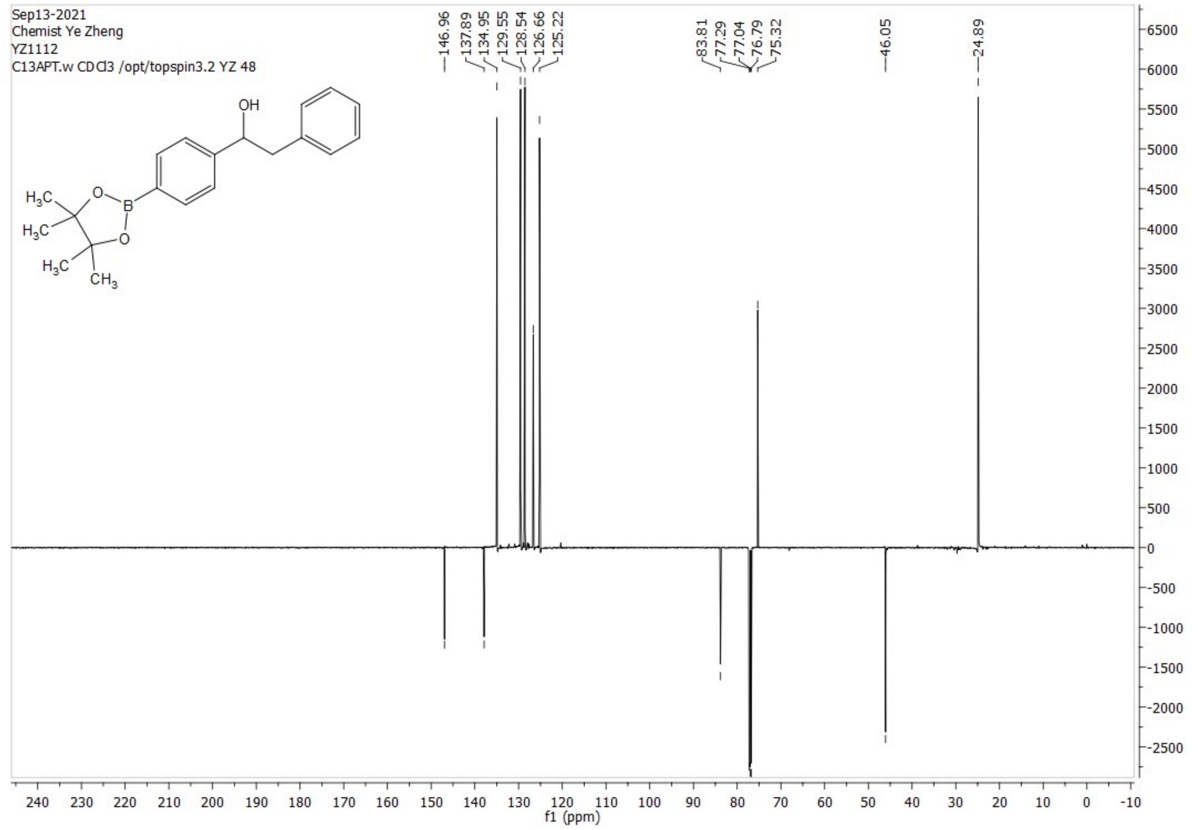
ATH of 2-phenyl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one:

(*R,R*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (0.77 mg, 1.2 μmol, 1 mol%) was added to FA: TEA (5:2 azeotropic mixture, 0.18 mL) at rt and the mixture was stirred under a nitrogen atmosphere for 15 minutes; after which a solution of 2-phenyl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one (40.0 mg, 0.124 mmol) in DCM (0.25 mL) was added. The reaction mixture was stirrer under a nitrogen atmosphere and followed by TLC (4:1 hexane: EtOAc). After 72 hours, the reaction was quenched using saturated $NaHCO_3$ solution (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried ($MgSO_4$) and filtered. The solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-50% EtOAc in hexane to give (*R*)-2-phenyl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol **13** as a colorless oil (20.0 mg, 0.0617 mmol, 50%). The reaction was also followed by HPLC (Chiralcel ODH, 30 cm x 6mm column, hexane:iPrOH 90:10, 1.0 mL/min, T = 25°C): $[\alpha]_D^{25}$ +0.75 (c 0.400 in $CHCl_3$) 96% ee.

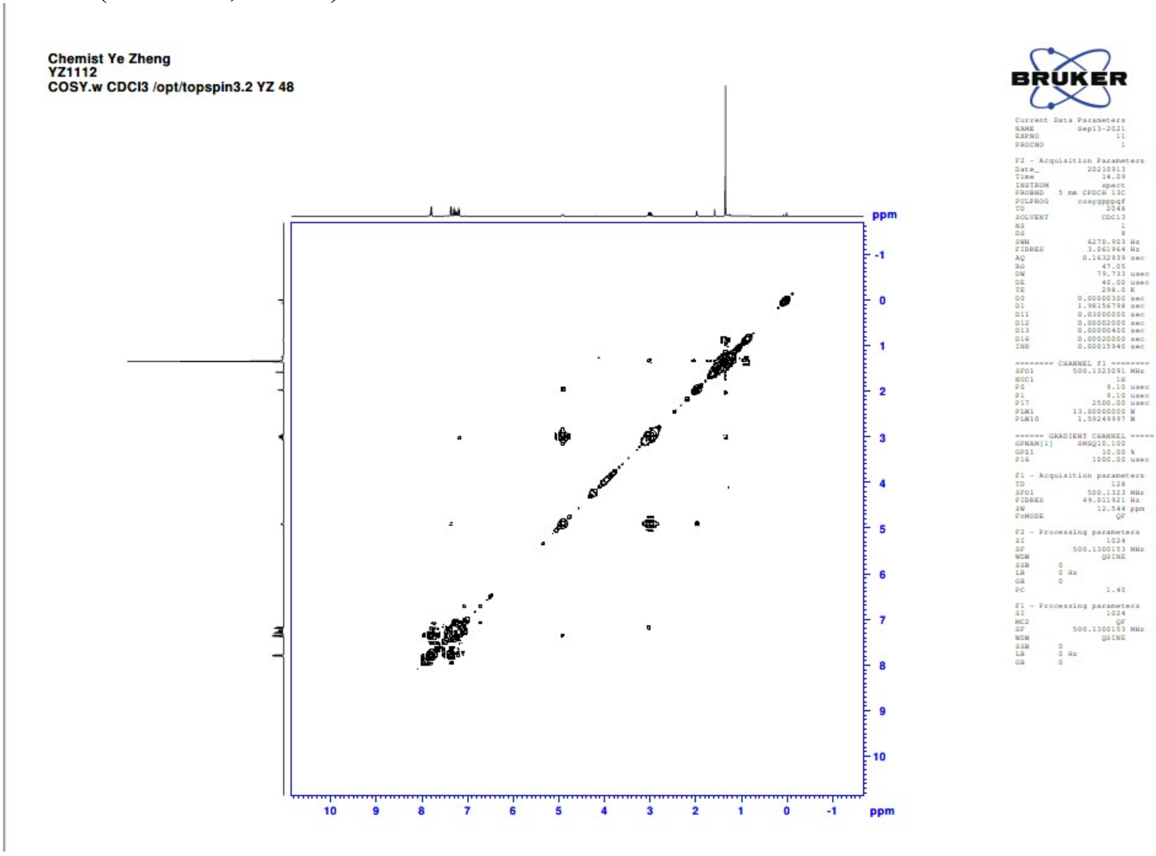
$^{1}H$ NMR (500 MHz, $CDCl_3$)



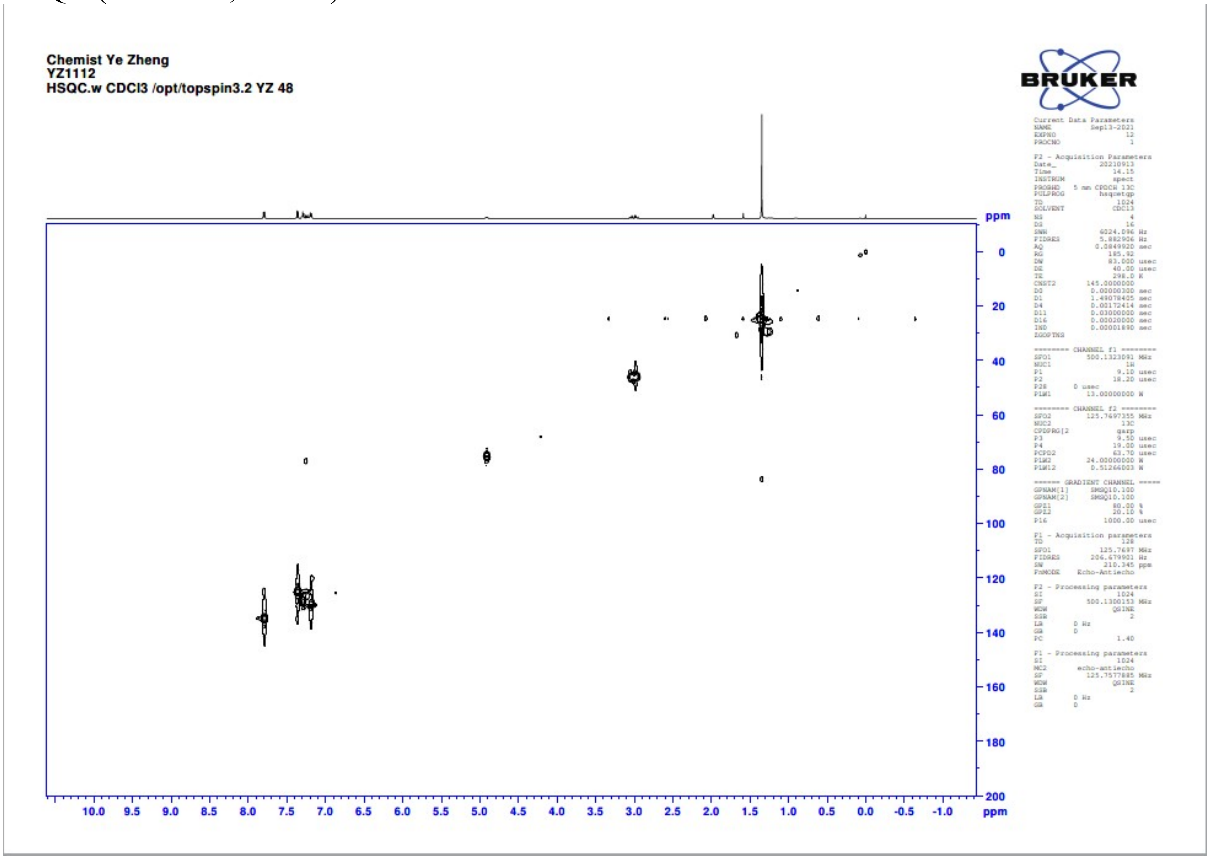
$^{13}C$ NMR (125 MHz, $CDCl_3$)



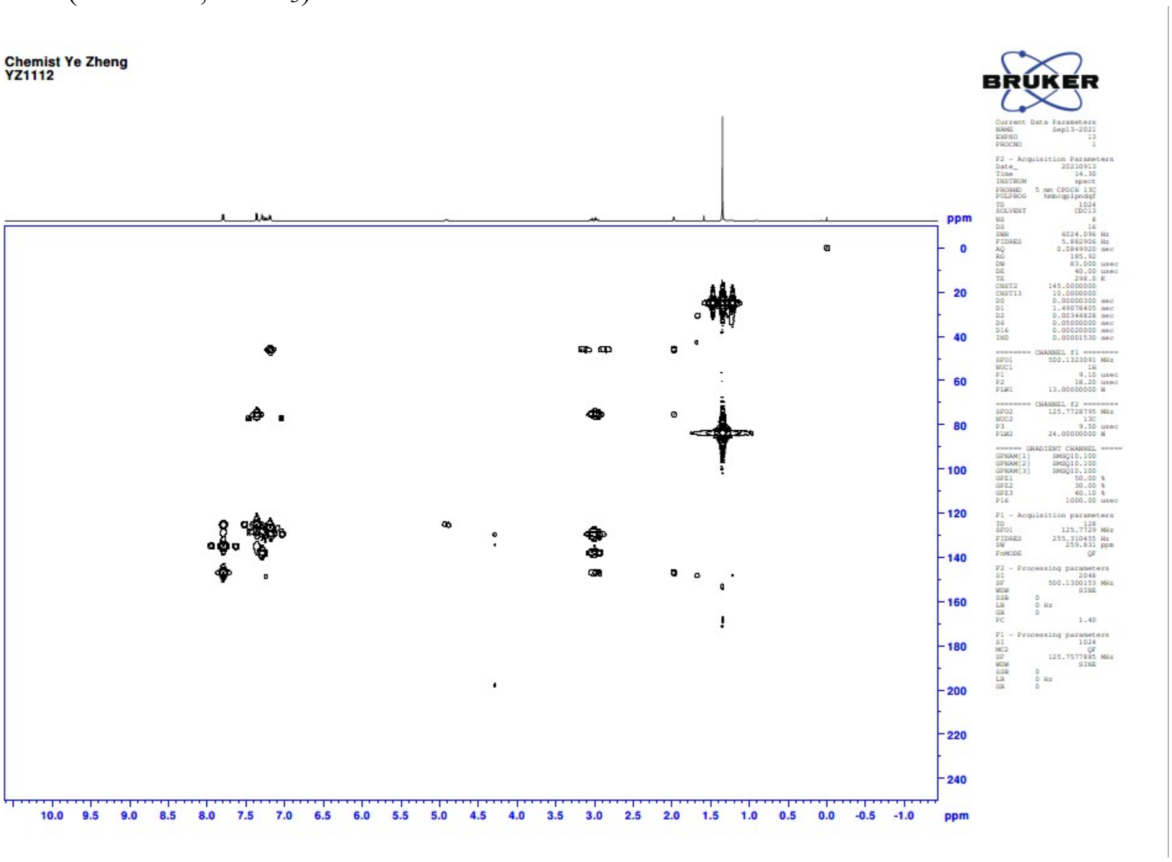
COSY (500 MHz, $CDCl_3$)



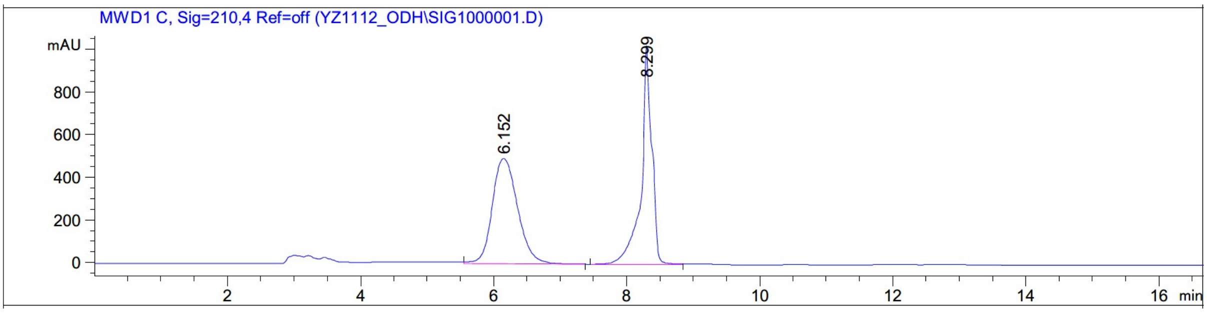
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)



HPLC of racemic 2-phenyl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol **13**.



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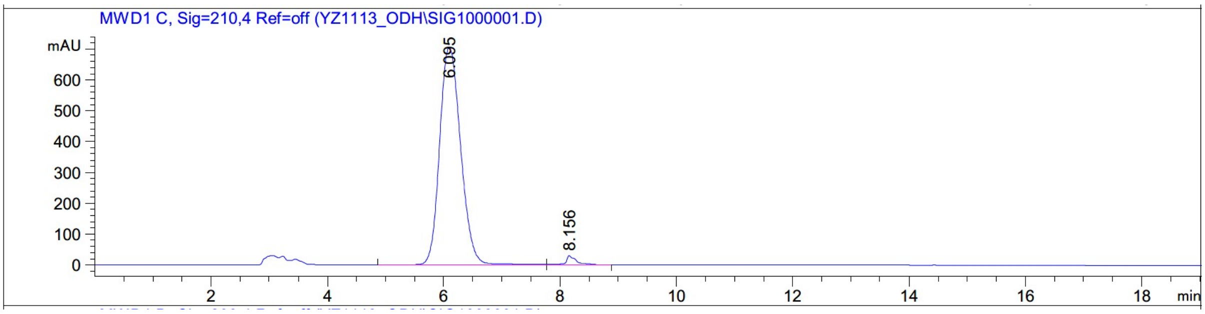
Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.152 VB    0.4106 1.30077e4  491.83240  53.2590
   2   8.299 BV    0.1467 1.14158e4 1019.23132  46.7410

Totals :                  2.44234e4 1511.06372
```

HPLC after ATH of 2-phenyl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one using (*R,R*)-3C-Tethered Ru(II)-TsDPEN catalyst **2** (after 72 hours, 100% conversion, 96% ee).

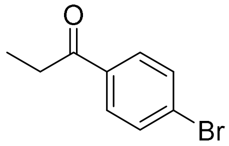


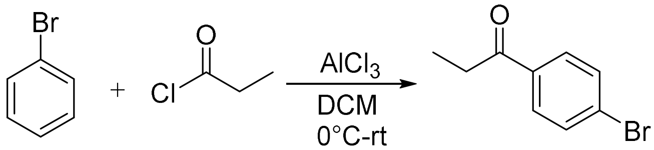
```
Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   6.095 VV    0.3915 1.77342e4  705.02429  97.9442
   2   8.156 VB    0.1581  372.23267  30.55074   2.0558

Totals :                  1.81064e4  735.57503
```

1-(4-Bromophenyl)propan-1-one.

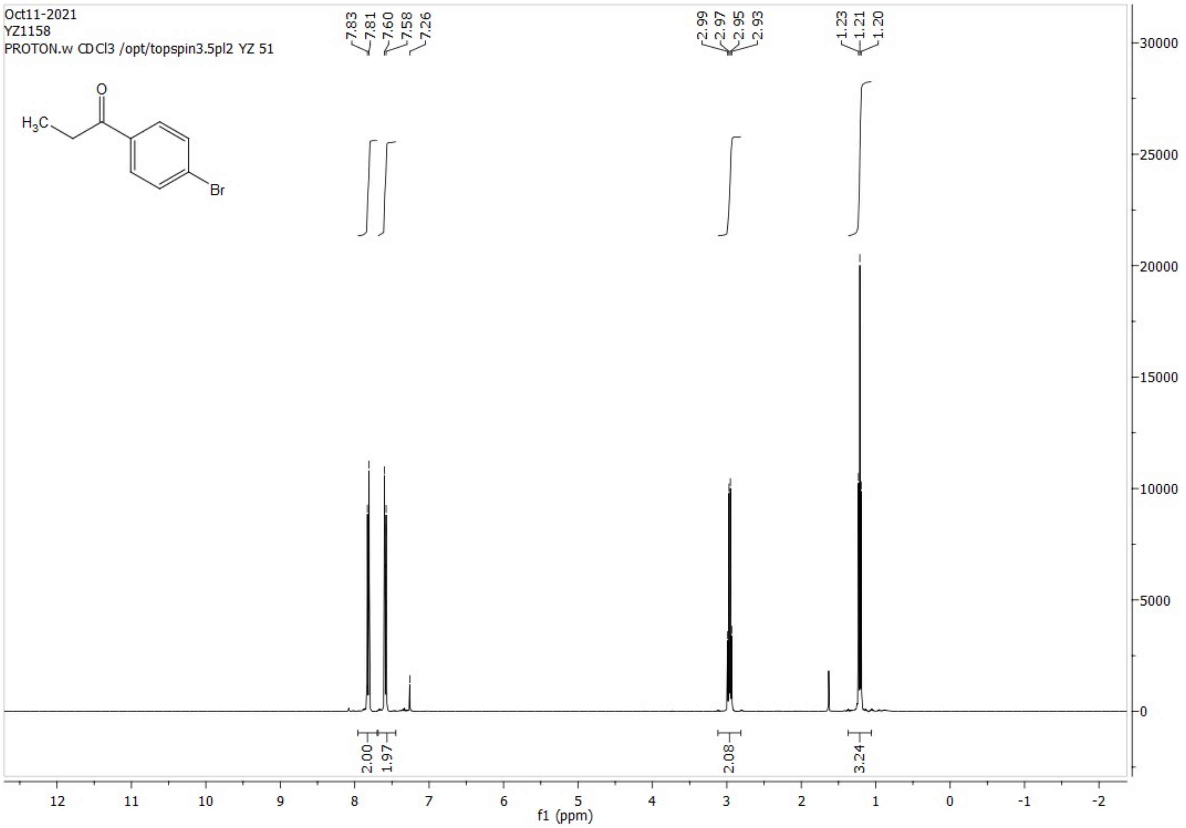




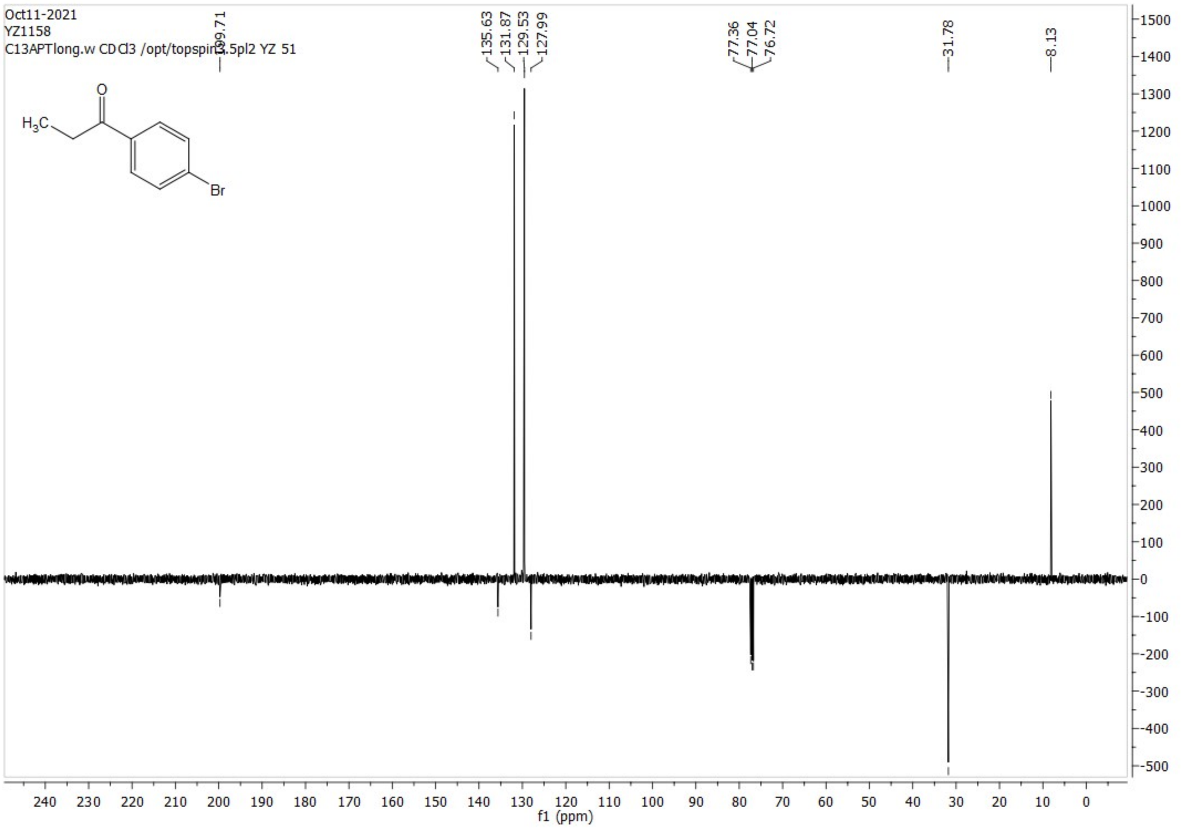
This compound has been reported and fully characterized: N. Rios-Lombardia, C. Vidal, M. Cocina, F. Moris, J. Garcia-Alvarez, J. Gonzalez-Sabin, *Chem. Commun.* 2015, **51**, 10937-10940.

To a solution of bromobenzene (318 mg, 2.00 mmol) was in DCM (1.2 mL) at 0 °C was added $AlCl_3$ (319 mg, 2.40 mmol) and a solution of propionyl chloride (189 mg, 2.04 mmol). The reaction mixture was stirred under a nitrogen atmosphere for 15 minutes. Then the reaction mixture was heated to 50 °C and left stirring under the nitrogen atmosphere for 2 hours, followed by TLC (9:1 hexane: EtOAc). The mixture was poured into ice water and quenched with 2M HCl solution (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried ($MgSO_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-5% ethyl acetate in hexane to give 1-(4-bromophenyl)propan-1-one as a yellow solid (190 mg, 0.896 mmol, 45%). TLC: Rf ca 0.70 (9:1 hexane: EtOAc), strong UV and $KMnO_4$; $\delta_H$ (400 MHz, $CDCl_3$) 7.83 (2H, d, $J$ = 8.5, ArH), 7.60 (1H, d, $J$ = 8.5, ArH), 2.97 (2H, q, $J$ = 7.2, $CH_2$), 1.21 (3H, t, $J$ = 7.2, $CH_3$) ppm; $\delta_C$ (100 MHz, $CDCl_3$) 199.71 (C), 135.63 (C), 131.87 (CH), 129.53 (CH), 127.99 (C), 31.78 ($CH_2$), 8.13 ($CH_3$) ppm. Data matched that reported.

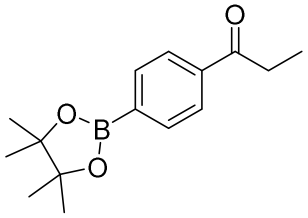
$^{1}$H NMR (400 MHz, CDCl$_3$)

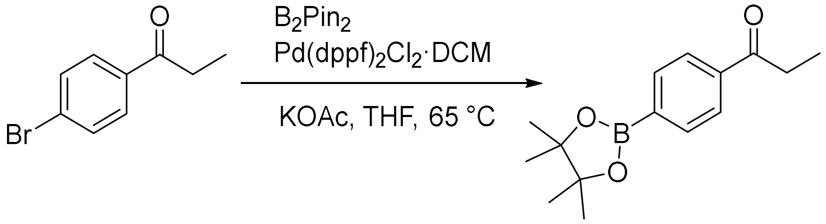


$^{13}$C NMR (100 MHz, CDCl$_3$)



### 1-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propan-1-one.

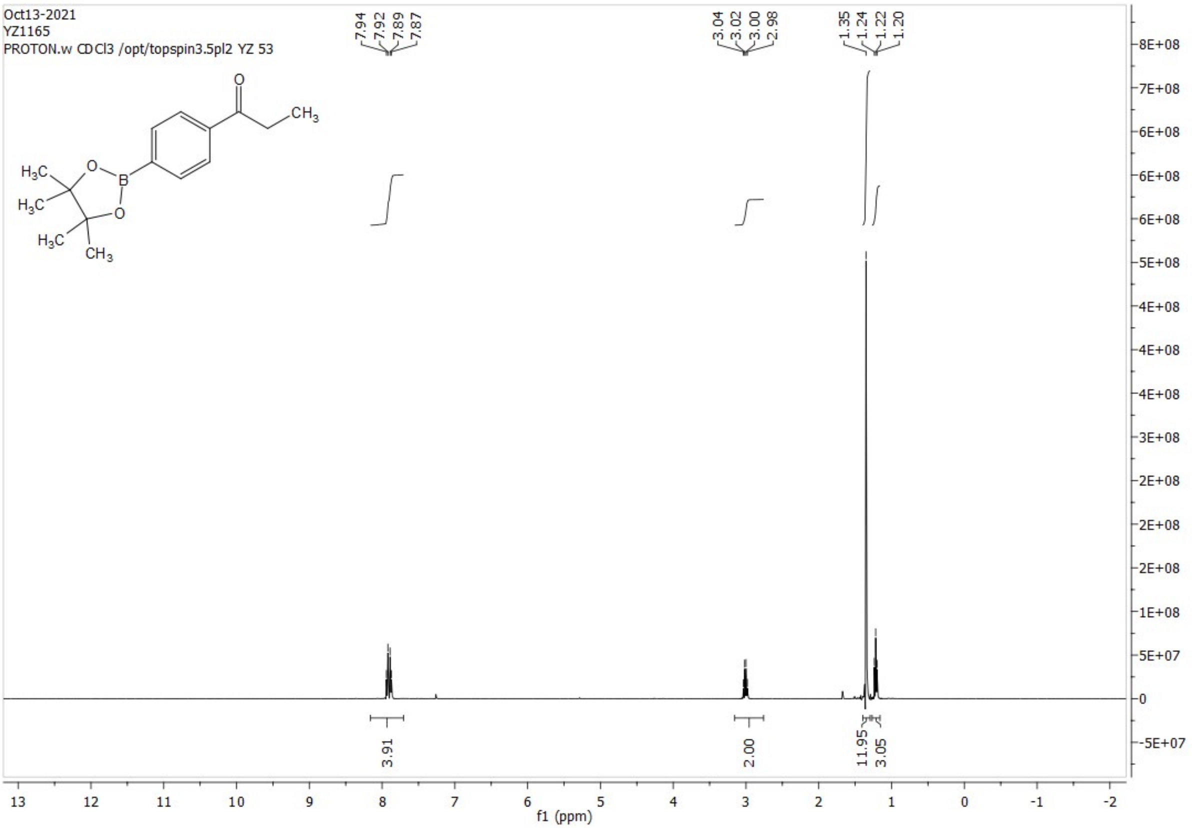




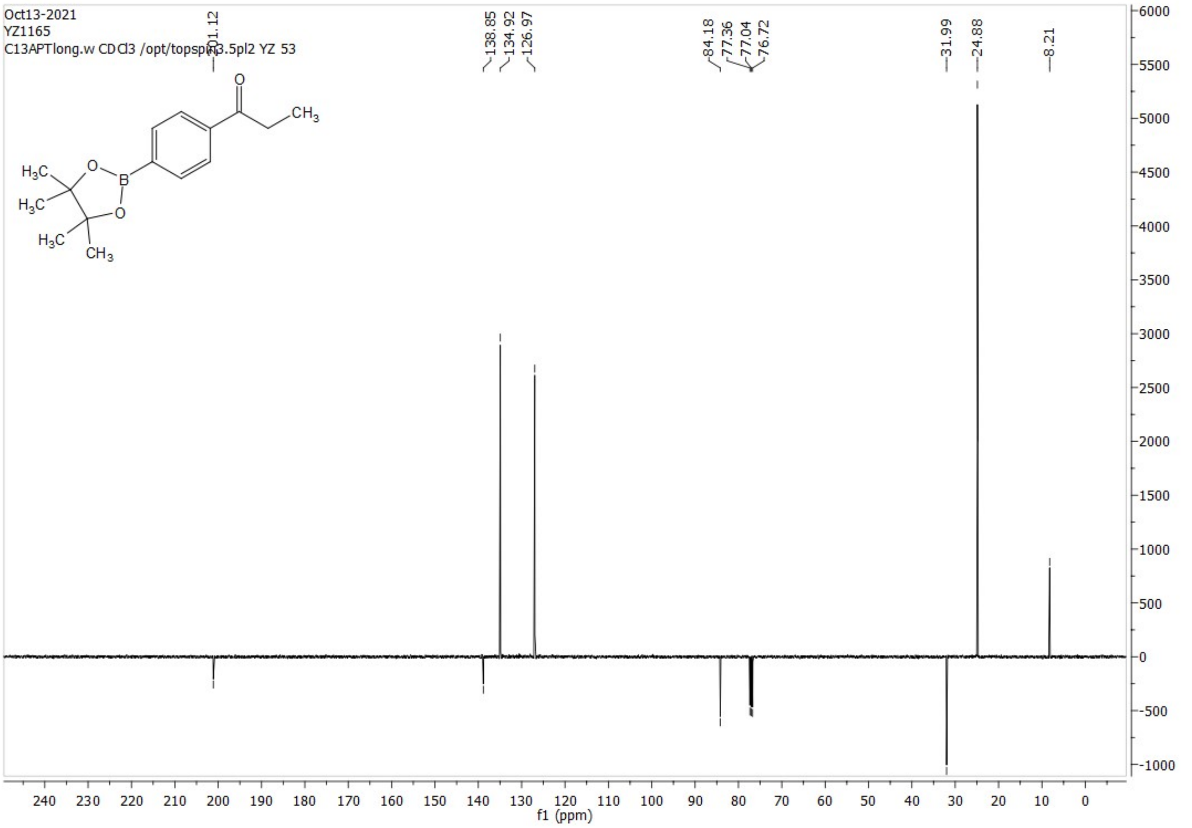
This compound has been reported and fully characterized: T. Kusukawa, Y. Kojima, F. Kannen, *Chem. Lett.* 2019, **48**, 1213-1216.

A round-bottom flask was charged with 1-(4-bromophenyl)propan-1-one (815 mg, 3.83 mmol), bis(pinacolato)diboron (1.17 g, 4.60 mmol), potassium acetate (1.13 g, 11.5 mmol), THF (19 mL) and Pd(dppf)$_2$Cl$_2$·DCM (157 mg, 0.192 mmol). The reaction mixture was heated to 65 °C and left stirring under the nitrogen atmosphere overnight, followed by TLC (9:1 hexane: EtOAc). The mixture was quenched by distilled water (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried (MgSO$_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-10% ethyl acetate in hexane to give 1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propan-1-one as a white solid (527 mg, 2.03 mmol, 53%). TLC: Rf ca 0.50 (9:1 hexane: EtOAc), strong UV and KMnO$_4$; $\delta_H$ (400 MHz, CDCl$_3$) 7.92 (4H, dd, $J$ = 19.7, 7.9, ArH), 3.02 (2H, q, $J$ = 7.2, ArCH), 1.35 (12H, s, CH$_3$), 1.24 (3H, t, $J$ = 7.2, CH$_3$) ppm; $\delta_C$ (100 MHz, CDCl$_3$) 201.12 (C), 138.85 (C), 134.92 (CH), 126.97 (CH), 84.18 (C), 31.99 (CH$_2$), 24.88 (CH$_3$), 8.21 (CH$_3$) ppm; m/z (ES-API+) 283.1 ($M^+ + 23$, 100%). Data matched that reported.

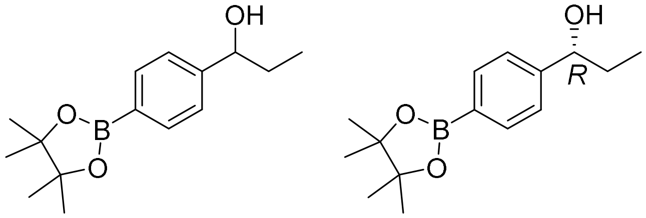
$^{1}$H NMR (400 MHz, CDCl$_3$)

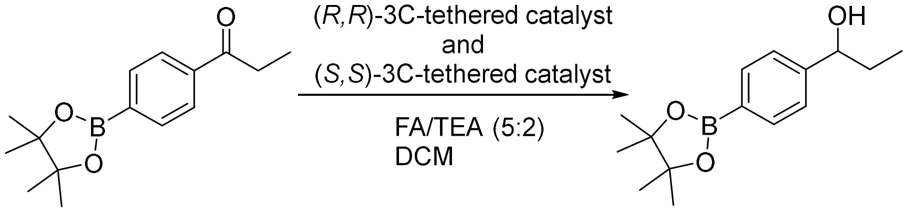


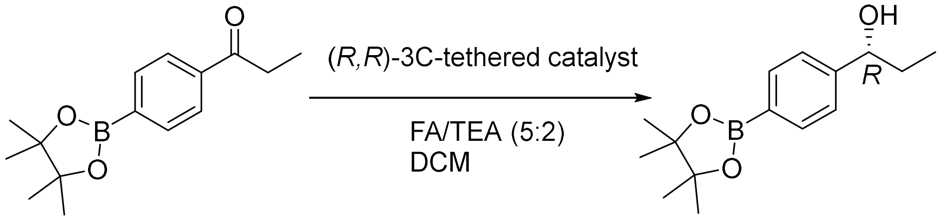
$^{13}$C NMR (100 MHz, CDCl$_3$)



Racemic and (*R*)-1-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propan-1-ol **14**.







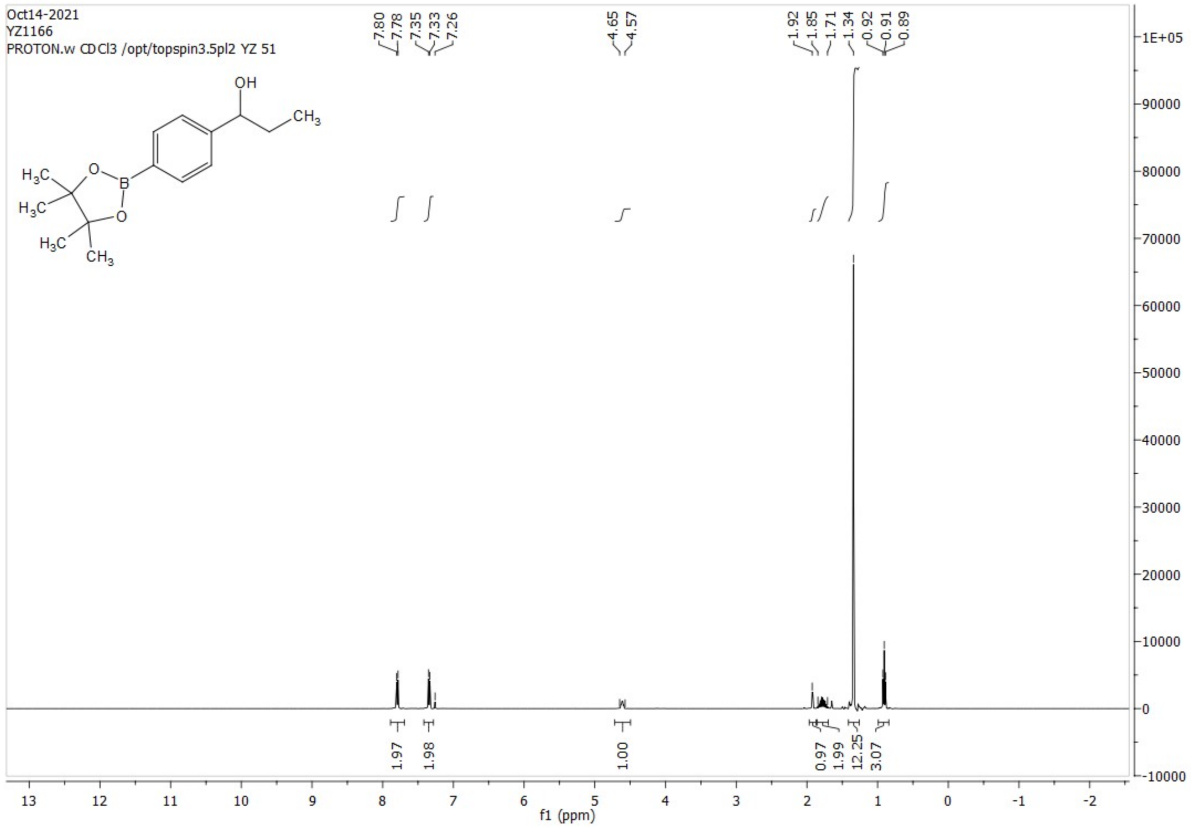
This compound is novel.

**Synthesis of a racemic standard:**

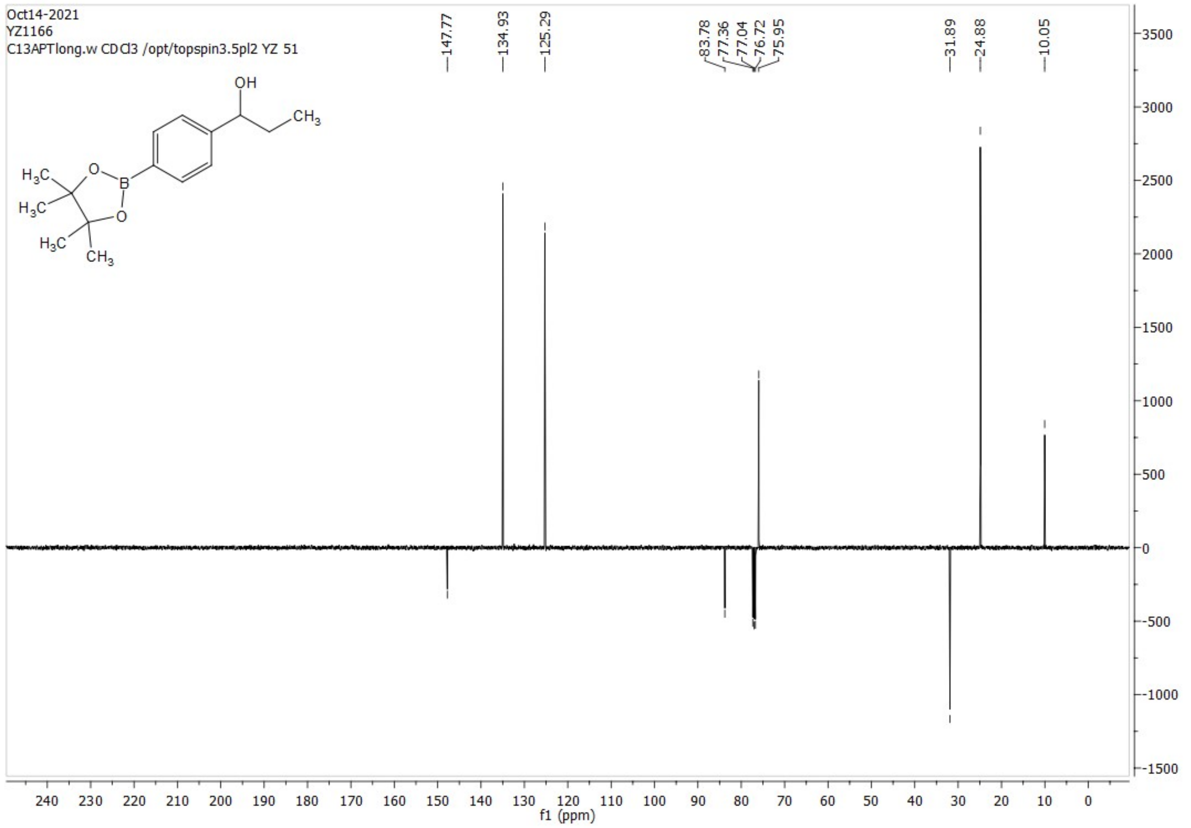
(*R,R*)-3C-Tethered Ru(II)-TsDPEN catalyst **2** (1.1 mg, 1.7 µmol, 0.5 mol%) and (*S,S*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (1.1 mg, 1.7 µmol, 0.5 mol%) were added to FA: TEA (5:2 azeotropic mixture, 0.41 mL) at rt and the mixture was stirred under a nitrogen atmosphere for 15 minutes; after which a solution of 1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propan-1-one (90.0 mg, 0.346 mmol) in DCM (0.56 mL) was added. The reaction mixture was stirrer under a nitrogen atmosphere and followed by TLC (9:1 hexane: EtOAc). After 24 hours, the reaction was quenched using saturated $NaHCO_3$ solution (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried ($MgSO_4$) and filtered. The solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-20% EtOAc in hexane to give 1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propan-1-ol **14** as a white solid (61.0 mg, 0.233 mmol, 67%). TLC: Rf ca 0.20 (9:1 hexane: EtOAc), strong UV and $KMnO_4$; Mp: 82°C; HRMS: (found (ESI+): [M+H]+, Calcd for $C_{15}H_{23}BNaO_3$ 285.1632; Found 285.1632; 1.2 ppm error; $\nu_{max}$ 3258 (br), 2976, 2877, 1397, 1356, 1334, 1320, 1141, 1088, 1085, 1006, 962, 858 $cm^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 7.80 (2H, d, *J* = 7.9, ArH), 7.35 (2H, d, *J* = 7.9, ArH), 4.65-4.57 (1H, m, ArCH), 1.92 (1H, d, *J* = 3.3, OH), 1.85-1.71 (2H, m, $CH_2$), 1.34 (12H, s, $CH_3$), 0.91 (3H, t, *J* = 7.4, $CH_3$) ppm; $\delta_C$ (100 MHz, $CDCl_3$) 147.77 (C), 134.93 (CH), 125.29 (CH), 83.79 (C), 79.95 (CH), 31.89 ($CH_2$), 24.88 ($CH_3$), 10.05 ($CH_3$) ppm; m/z (ES-API+) 285.1 ($M^+$ + 23, 100%).

ATH of 1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propan-1-one): (*R,R*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (2.2 mg, 3.5 μmol, 1 mol%) was added to FA: TEA (5:2 azeotropic mixture, 0.41 mL) at rt and the mixture was stirred under a nitrogen atmosphere for 15 minutes; after which a solution of 1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propan-1-one (90.0 mg, 0.346 mmol) in DCM (0.56 mL) was added. The reaction mixture was stirrer under a nitrogen atmosphere and followed by TLC (9:1 hexane: EtOAc). After 24 hours, the reaction was quenched using saturated $NaHCO_3$ solution (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried ($MgSO_4$) and filtered. The solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-20% EtOAc in hexane to give (*R*)-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propan-1-ol **14** as a a white solid (62.0 mg, 0.237 mmol, 68%). The reaction can't be separated in HPLC: 100% conversion, $[\alpha]_D^{26}$ +25.8 (c 0.485 in $CHCl_3$), 94% ee, *S* configuration (ee and configuration were confirmed by comparison with compound after reaction with bromobenzene)

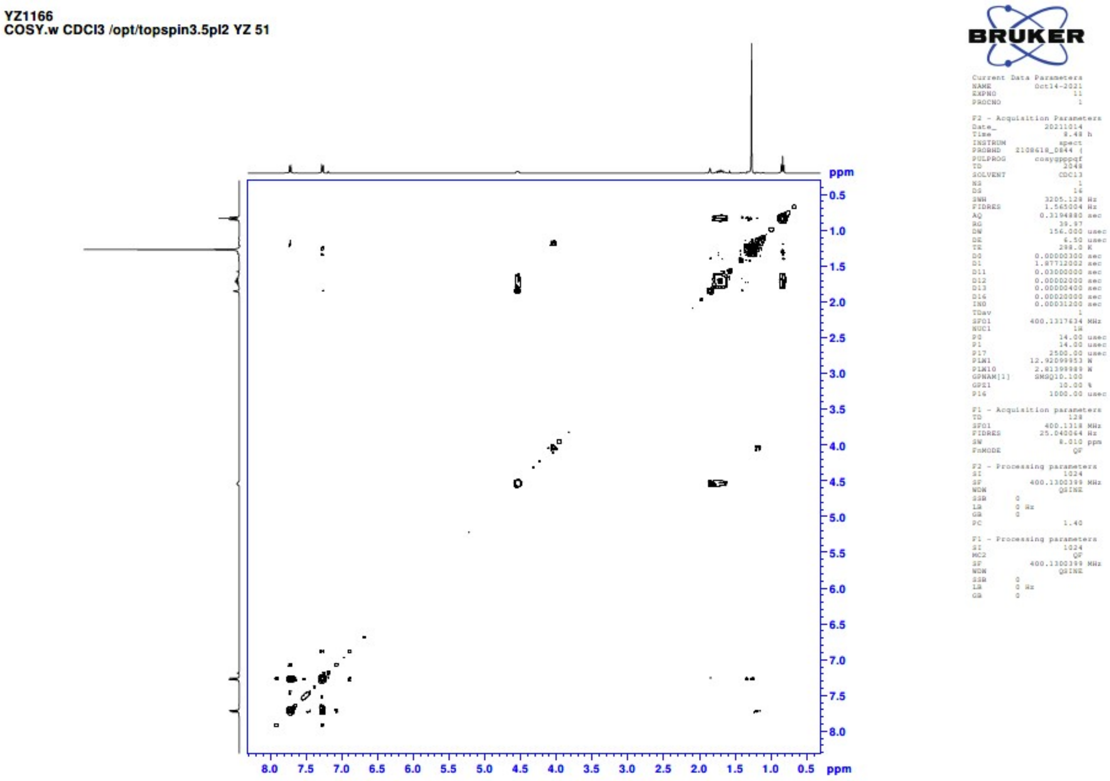
$^{1}$H NMR (400 MHz, CDCl$_3$)



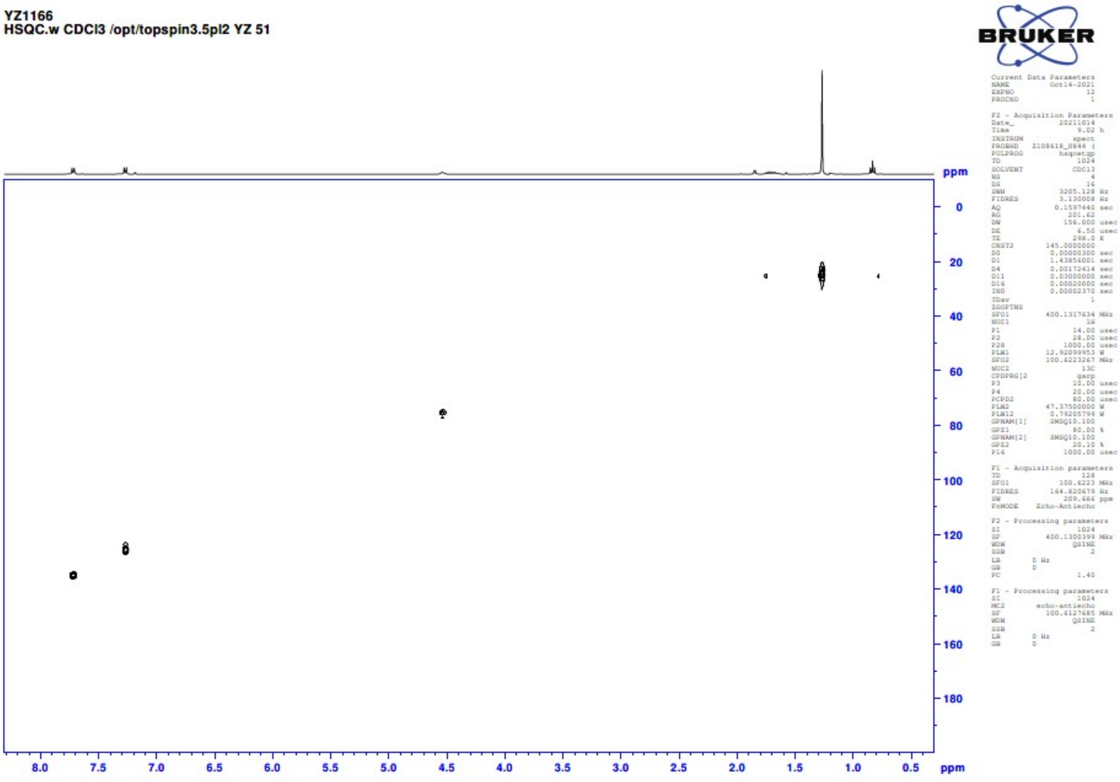
$^{13}$C NMR (100 MHz, CDCl$_3$)



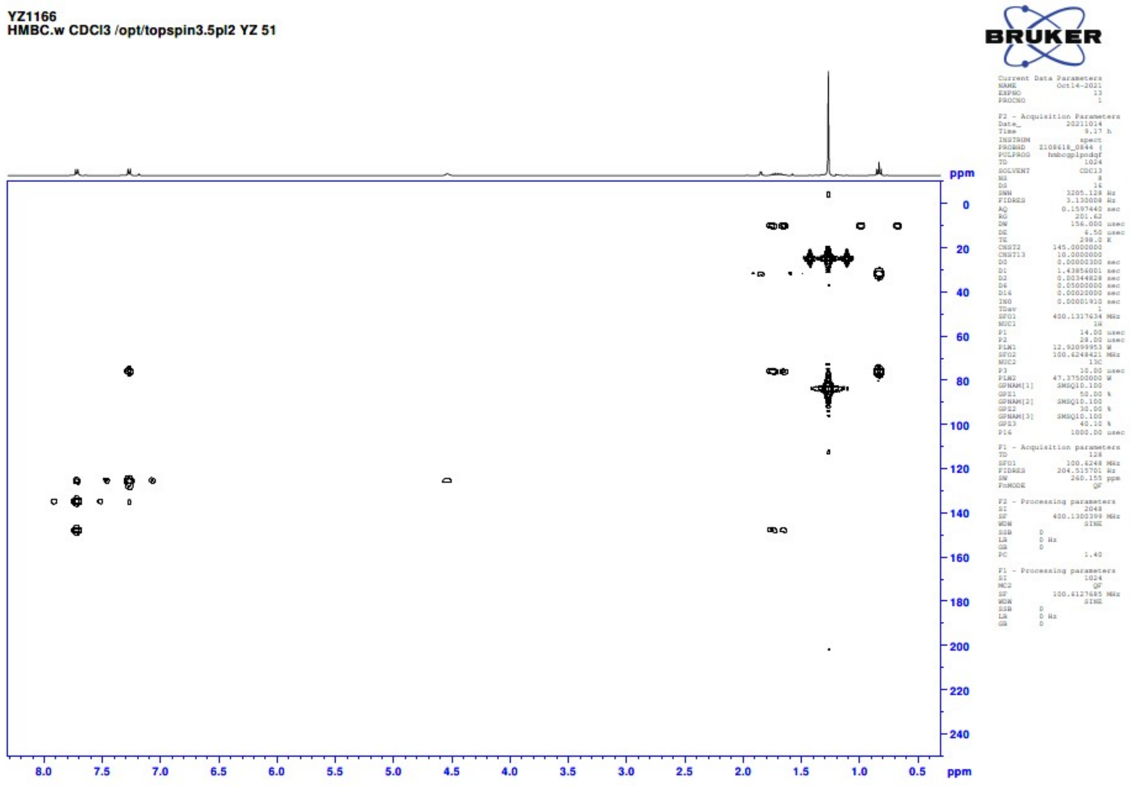
COSY (400 MHz, CDCl$_3$)



HSQC (400 MHz, CDCl$_3$)



HMBC (400 MHz, $CDCl_3$)



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PC                  1.40

F1 - Processing parameters
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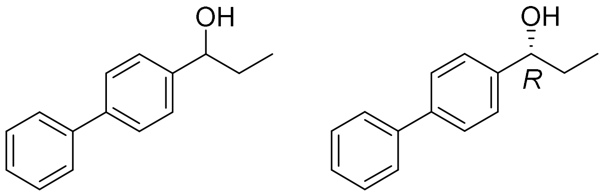
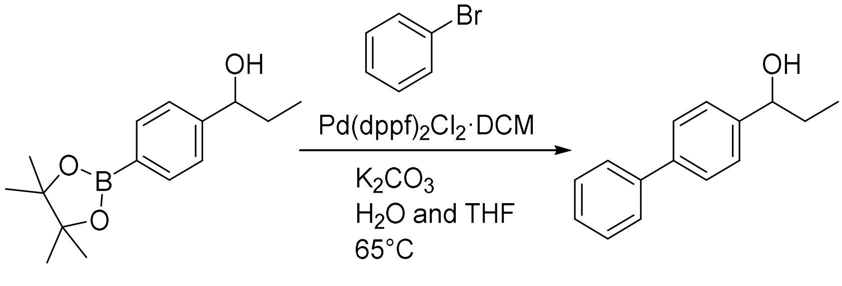
Racemic and (*R*)-1-([1,1'-Biphenyl]-4-yl)propan-1-ol **21**.





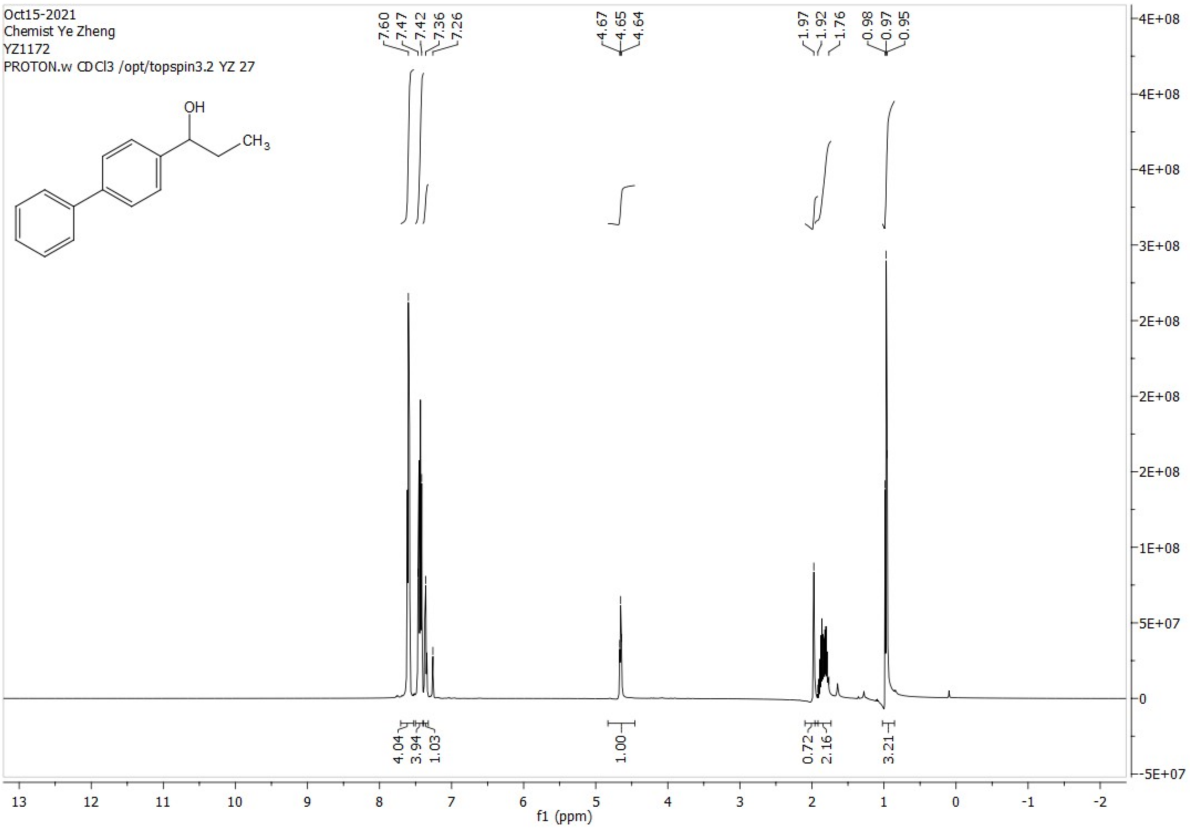
This compound has been reported and fully characterized: Q. Wang, S. Li C.-J. Hou, T.-T. Chu, X.-P. Hu; *Appl. Organomet. Chem.* 2019, **33**, e5108.

Racemic: To a solution of racemic 1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propan-1-ol **14** (90.0 mg, 0.344 mmol), bromobenzene (108 mg, 0.688 mmol) and potassium carbonate (94.9 mg, 0.688 mmol) in THF (6.7 mL) was added $Pd(dppf)_2Cl_2{\cdot}DCM$ (14.1 mg, 0.0172 mmol) and distilled water (0.0433 mL). The reaction mixture was heated to 65 °C and left stirring under the nitrogen atmosphere overnight, followed by TLC (9:1 hexane: EtOAc). The mixture was quenched by distilled water (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried ($MgSO_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-20% ethyl acetate in hexane to give racemic 1-([1,1'-biphenyl]-4-yl)propan-1-ol **21** as a white solid (45.0 mg, 0.212 mmol, 62%). TLC: Rf ca 0.20 (9:1 hexane: EtOAc), strong UV and $KMnO_4$; $\delta_H$ (500 MHz, $CDCl_3$) 7.60 (4H, t, *J* = 7.2, ArH), 7.47-7.42 (4H, m, ArH), 7.36 (1H, t, *J* = 7.2, ArH), 4.65 (1H, t, *J* = 6.4, ArCH), 1.97 (1H, s, OH), 1.92-1.76 (2H, m, $CH_2$), 0.97 (3H, t, *J* = 7.4, $CH_3$) ppm; $\delta_C$ (125 MHz, $CDCl_3$) 143.66 (C), 140.90 (C), 140.45 (C), 128.80 (CH), 127.28 (CH), 127.10 (CH), 126.46 (CH), 75.79 (CH), 31.90 ($CH_2$), 10.22 ($CH_3$) ppm; m/z (ES-API+) 235.1 ($M^+$ + 23, 100%). Data matched that reported.

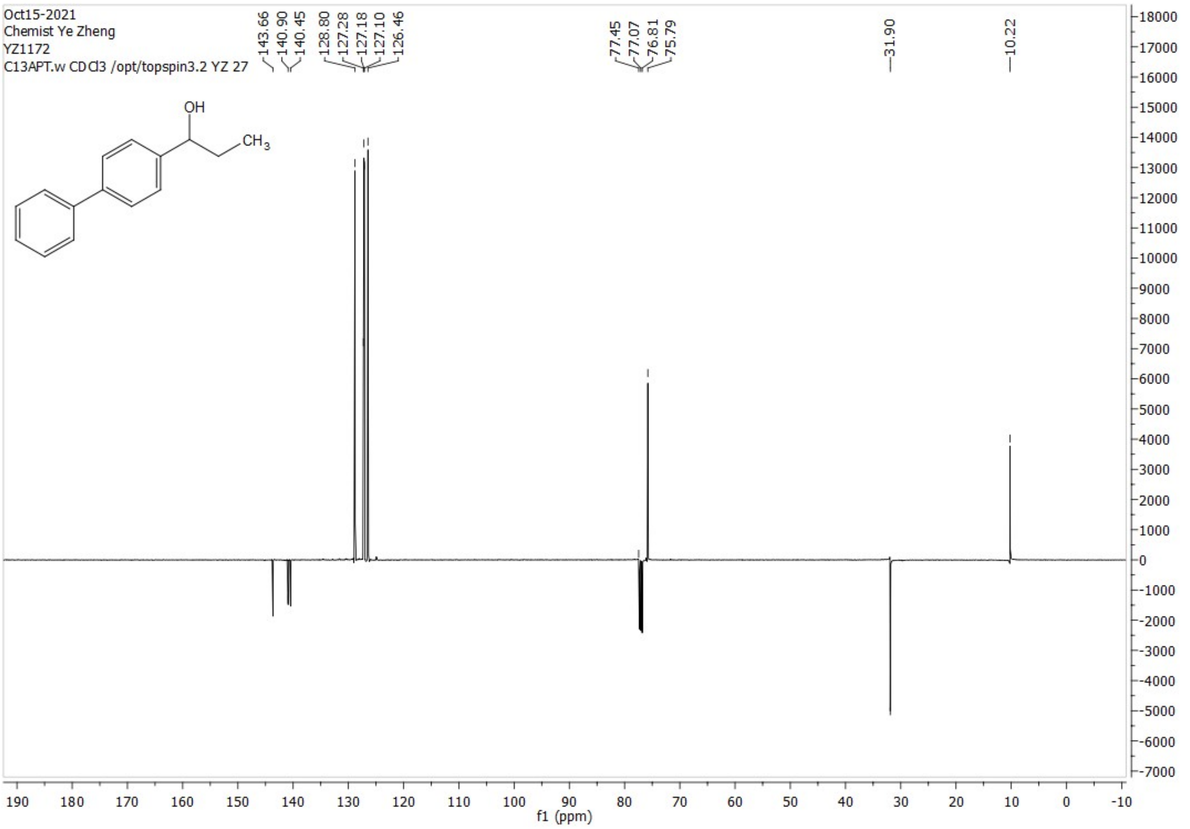
Enantiomeric excess and conversion determined by HPLC analysis (Chiralcel ADH, 30 cm x 6mm column, hexane:iPrOH 95:5, 1.0 mL/min, T = 25°C) *S* isomer 25.9 min and *R* isomer 28.7 min. The same column and solvent combination was used in the reference above, permitting determination of the configuration of **21** and also of its precursor, **14**.

Asymmetric: To a solution of (*R*)-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propan-1-ol **14** (90.0 mg, 0.344 mmol), bromobenzene (108 mg, 0.688 mmol) and potassium carbonate (94.9 mg, 0.688 mmol) in THF (6.7 mL) was added Pd(dppf)$_2$Cl$_2$·DCM (14.1 mg, 0.0172 mmol) and distilled water (0.0433 mL). The reaction mixture was heated to 65 °C and left stirring under the nitrogen atmosphere overnight, followed by TLC (9:1 hexane: EtOAc). The mixture was quenched by distilled water (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried (MgSO$_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-20% ethyl acetate in hexane to give (*R*)-1-([1,1'-biphenyl]-4-yl)propan-1-ol **21** as a white solid (46.0 mg, 0.217 mmol, 63%). The reaction was also followed by HPLC (Chiralcel ADH, 30 cm x 6mm column, hexane:iPrOH 95:5, 1.0 mL/min, T = 25°C): $[\alpha]_D^{23}$ +35.5 (c 0.300 in DCM) 94% ee (*R*) (lit. $[\alpha]_D^{20}$ +24.5 (c 1.06 in DCM) 90% ee (*R*)) Reference: Q. Wang, S. Li C.-J. Hou, T.-T. Chu, X.-P. Hu; *Appl. Organomet. Chem.* 2019, **33**, e5108.

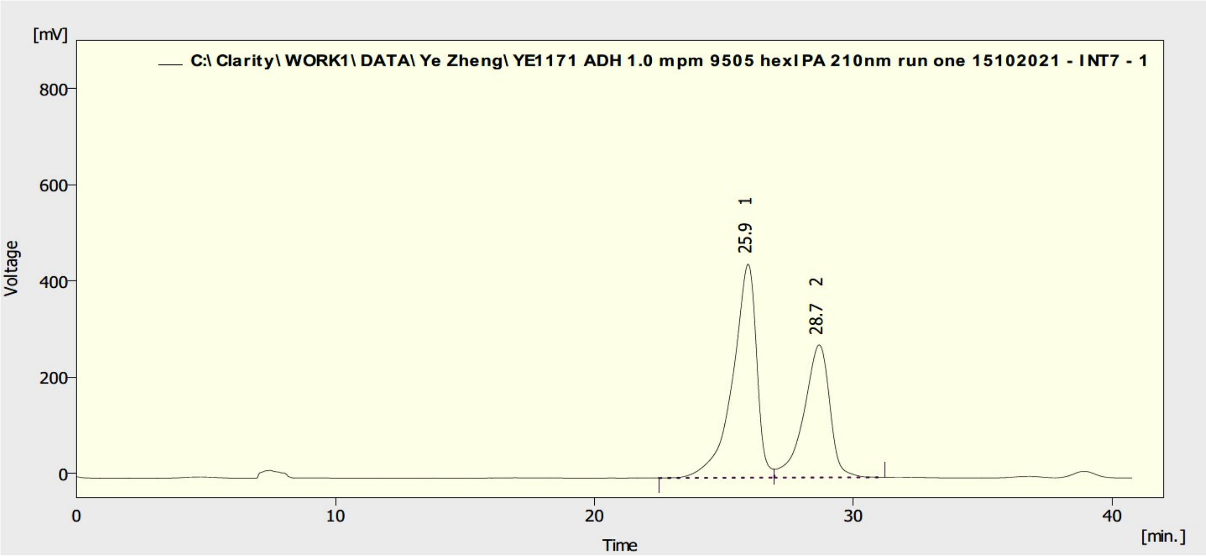
$^{1}H$ NMR (500 MHz, $CDCl_3$)



$^{13}C$ NMR (125 MHz, $CDCl_3$)



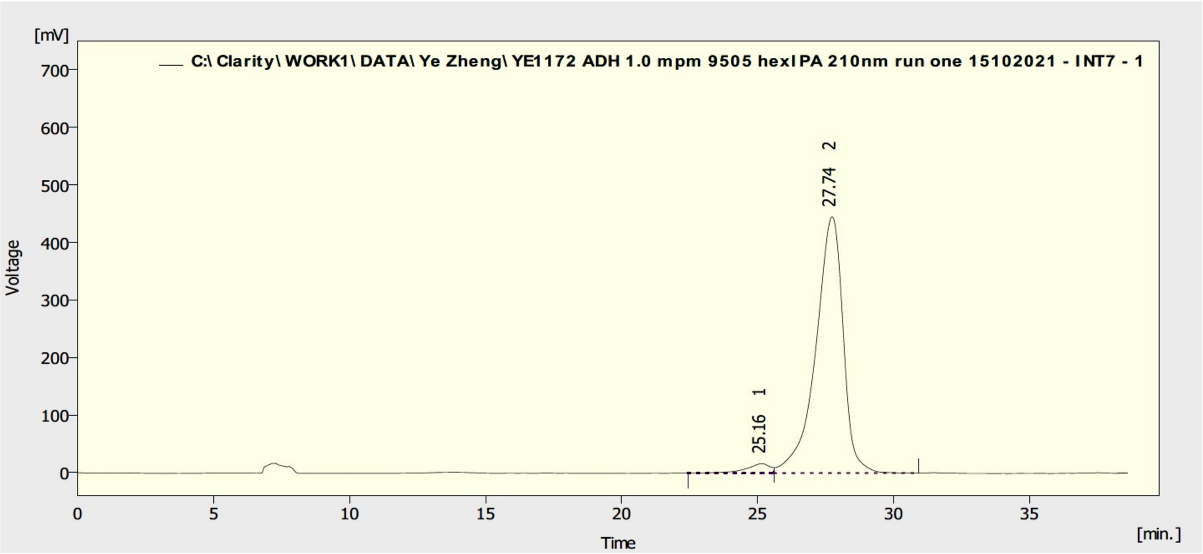
HPLC of racemic 1-([1,1'-biphenyl]-4-yl)propan-1-ol **21**.



*Result Table (Uncal - C:\Clarity\WORK1\DATA\Ye Zheng\YE1171 ADH 1.0 mpm 9505 hexIPA 210nm run one 15102021 - INT7 - 1)*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Compound Name |
|---|---|---|---|---|---|---|---|
| 1 | 25.937 | 28590.630 | 443.760 | 59.9 | 61.7 | 0.92 | |
| 2 | 28.683 | 19152.484 | 275.525 | 40.1 | 38.3 | 1.02 | |
| | Total | 47743.113 | 719.284 | 100.0 | 100.0 | | |

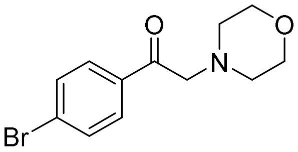
HPLC of (*R*)-1-([1,1'-biphenyl]-4-yl)propan-1-ol **21** (94% ee, *R* configuration)

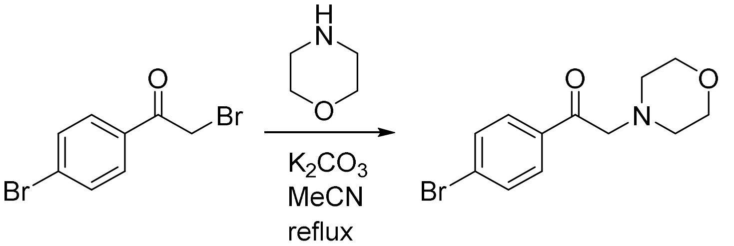


*Result Table (Uncal - C:\Clarity\WORK1\DATA\Ye Zheng\YE1172 ADH 1.0 mpm 9505 hexIPA 210nm run one 15102021 - INT7 - 1)*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Compound Name |
|---|---|---|---|---|---|---|---|
| 1 | 25.160 | 1011.309 | 16.333 | 3.1 | 3.5 | 0.99 | |
| 2 | 27.743 | 31229.442 | 445.299 | 96.9 | 96.5 | 1.03 | |
| | Total | 32240.752 | 461.632 | 100.0 | 100.0 | | |

1-(4-Bromophenyl)-2-morpholinoethan-1-one.

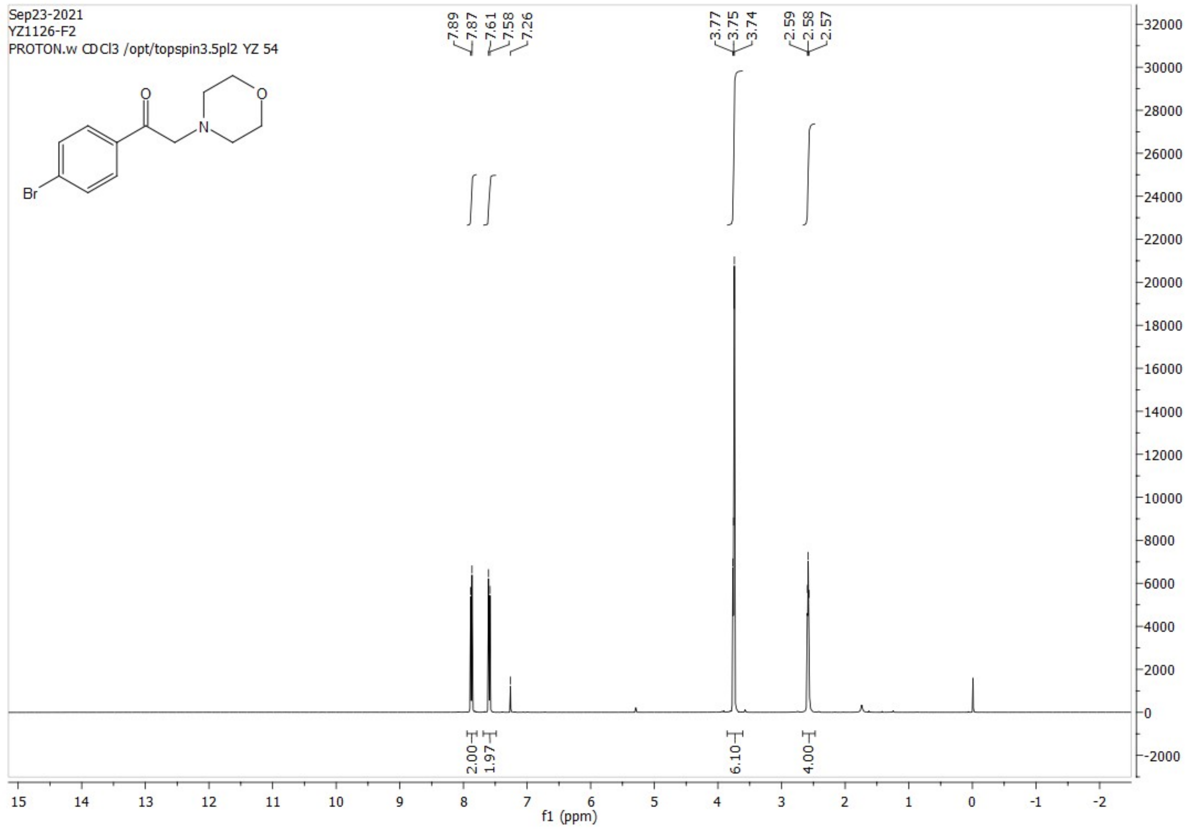




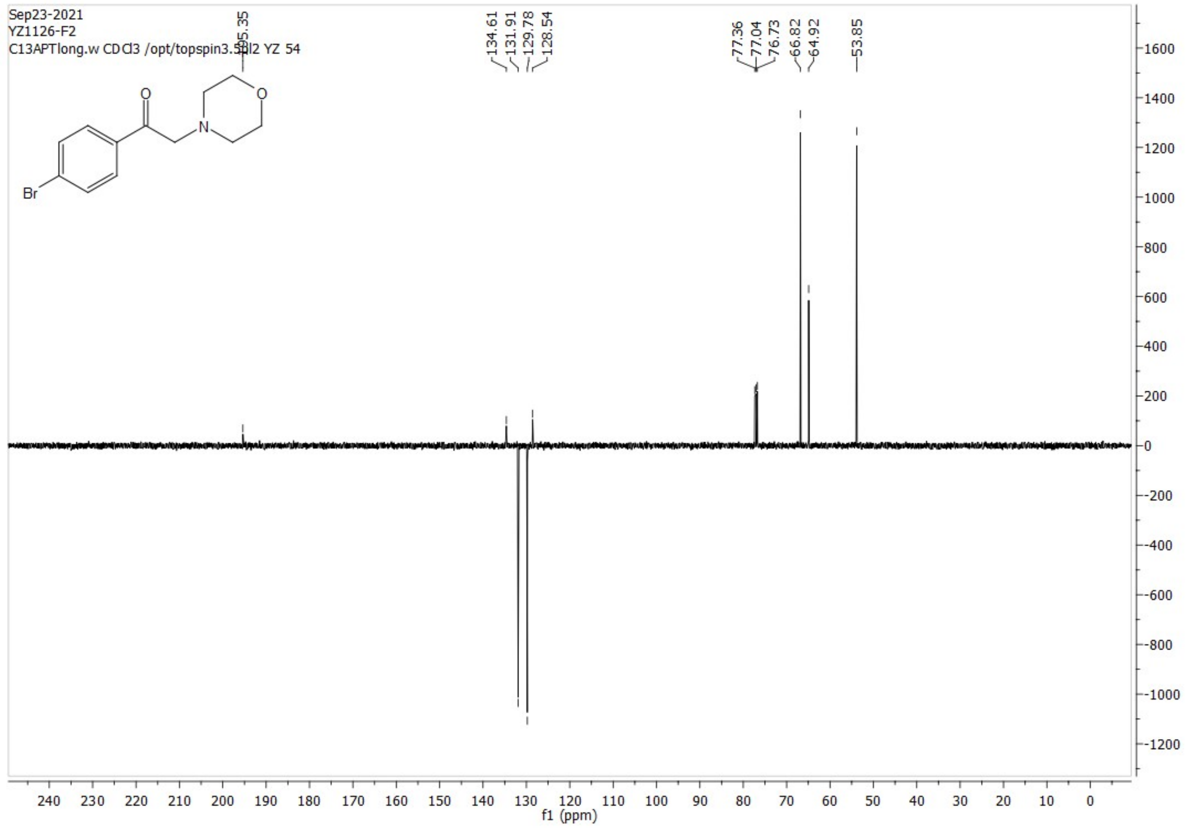
This compound has been reported and fully characterized: C. T. Bahner, E. Kite, F. Pierce, L. M. Rives, M. D. Pickens, C. Myers, *J. Am. Chem. Soc.* 1951, **73**, 4011-4013.

To a solution of 2-bromo-1-(4-bromophenyl)ethan-1-one (2.00 g, 7.25 mmol) in MeCN (40 mL) was added morpholine (948 mg, 10.9 mmol) and potassium carbonate (3.00 g, 21.7 mmol). The reaction mixture was heated to 85 °C and left stirring under a nitrogen atmosphere for 1 hour, followed by TLC (1:1 hexane: EtOAc). The mixture was quenched by distilled water (20 mL). $Et_2O$ (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with $Et_2O$ (3 × 20 mL), and the combined organic layers were dried ($MgSO_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 50-100% ethyl acetate in hexane to give 1-(4-bromophenyl)-2-morpholinoethan-1-one as a yellow solid (1.72 g, 6.08 mmol, 84%). TLC: Rf ca 0.20 (1:1 hexane: EtOAc), strong UV and $KMnO_4$; $\delta_H$ (400 MHz, $CDCl_3$) 7.89 (2H, d, *J* = 8.5, ArH), 7.61 (2H, d, *J* = 8.5, ArH), 3.77-3.74 (6H, m, $CH_2$), 2.59-2.57 (4H, m, $CH_2$) ppm; $\delta_C$ (100 MHz, $CDCl_3$) 195.35 (C), 134.61 (C), 131.91 (CH), 129.78 (CH), 128.54 (C), 66.82 ($CH_2$), 64.92 ($CH_2$), 53.85 ($CH_2$) ppm; m/z (ES-API+) 284.0 ($M^+$ + 1, 100%). Data matched that reported.

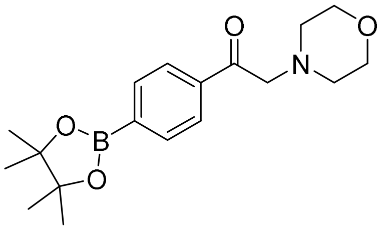
$^{1}$H NMR (400 MHz, CDCl$_3$)

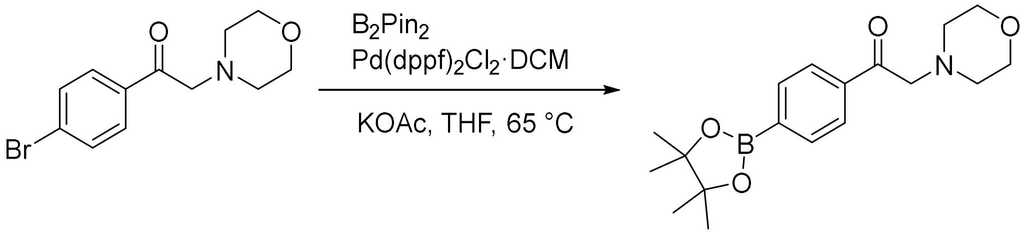


$^{13}$C NMR (100 MHz, CDCl$_3$)



2-Morpholino-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one.



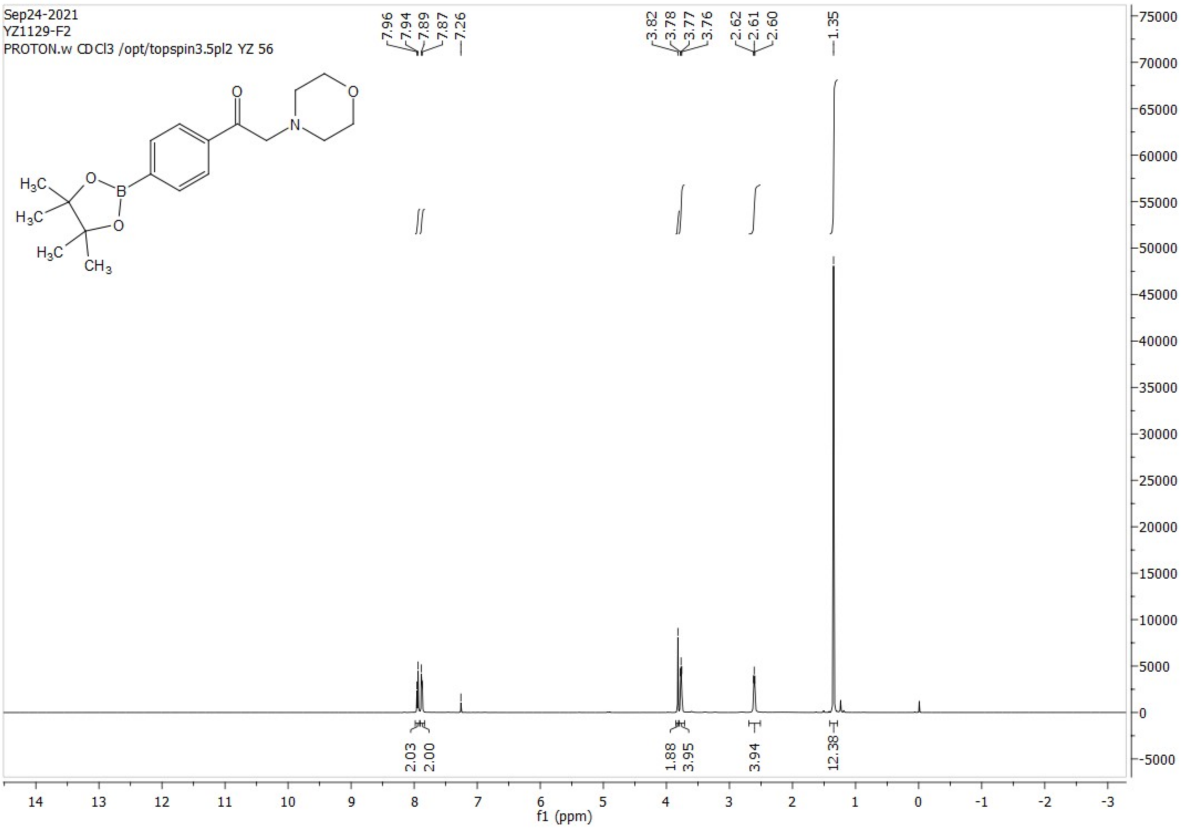


This compound is novel.

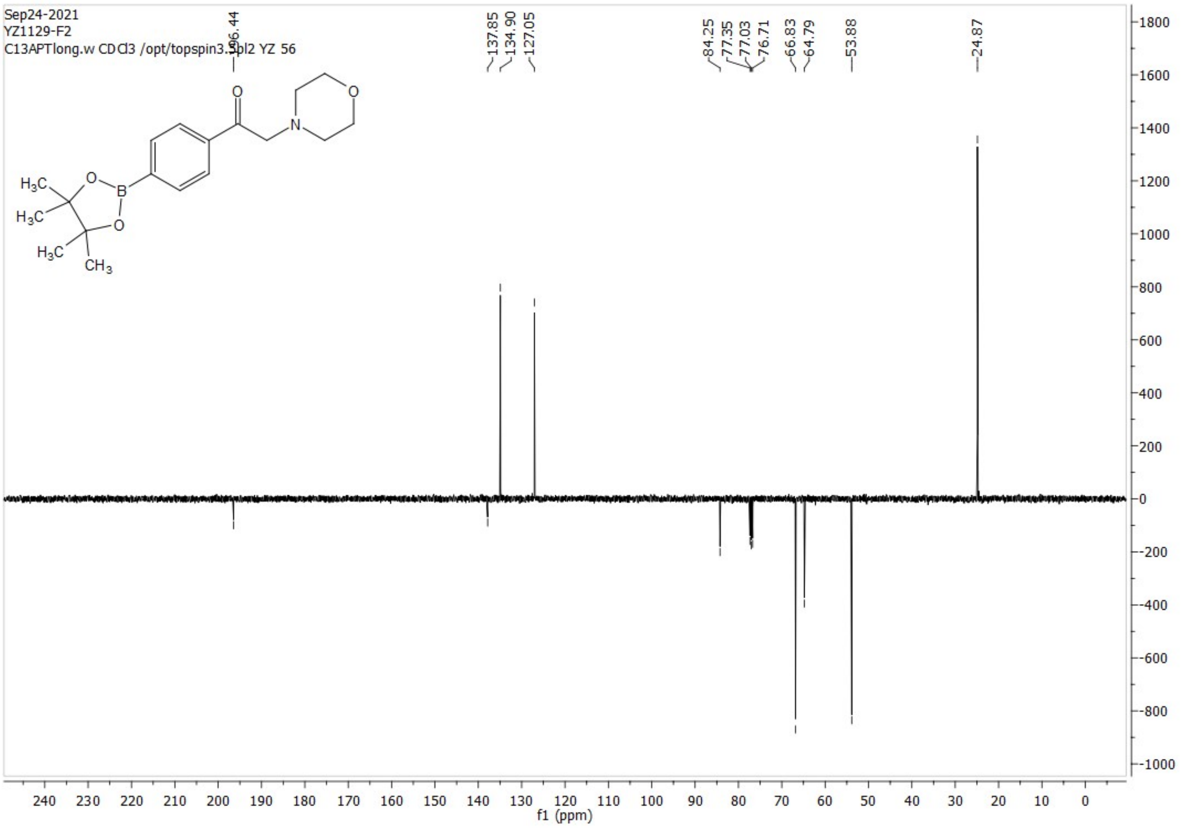
A round-bottom flask was charged with 1-(4-bromophenyl)-2-morpholinoethan-1-one (1.72 g, 6.07 mmol), bis(pinacolato)diboron (1.85 g, 7.28 mmol), potassium acetate (1.78 g, 18.2 mmol), THF (30 mL) and $Pd(dppf)_2Cl_2 \cdot DCM$ (248 mg, 0.304 mmol). The reaction mixture was heated to 65 °C and left stirring under the nitrogen atmosphere overnight, followed by TLC (1:1 hexane: EtOAc). The mixture was quenched by distilled water (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried ($MgSO_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 50-100% ethyl acetate in hexane to give 2-morpholino-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one as an orange solid (1.20 g, 3.63 mmol, 60%). TLC: Rf ca 0.20 (1:1 hexane: EtOAc), strong UV and $KMnO_4$; Mp: 69 °C; HRMS: (found (ESI+): [M+H]+, Calcd for $C_{18}H_{27}BNO_4$ 332.2023; Found 332.2028; 2.0 ppm error; $\nu_{max}$ 2977, 1697, 1508, 1452, 1397, 1357, 1217, 1142, 1115, 1088, 856 $cm^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 7.96 (2H, d, *J* = 8.1, ArH), 7.89 (2H, d, *J* = 8.1, ArH), 3.82 (2H, s, $CH_2$), 3.78-3.76 (4H, m, $CH_2$), 2.62-2.60 (4H, m, $CH_2$), 1.35 (12H, s, $CH_3$) ppm; $\delta_C$ (100 MHz, $CDCl_3$) 196.44 (C), 137.85 (C), 134.90 (CH), 127.05 (CH), 84.25 (C), 66.38 ($CH_2$), 64.79 ($CH_2$), 53.88 ($CH_2$), 24.87 ($CH_3$) ppm; m/z (ES-API+) 332.2 ($M^+$ + 1, 100%).

Enantiomeric excess and conversion determined by HPLC analysis (Chiralpak IC, 30 cm x 6mm column, hexane:iPrOH 90:10, 1.0 mL/min, T = 25°C) ketone 14.8 min, *R* and *S* isomers 15.7 min and 17.3 min.

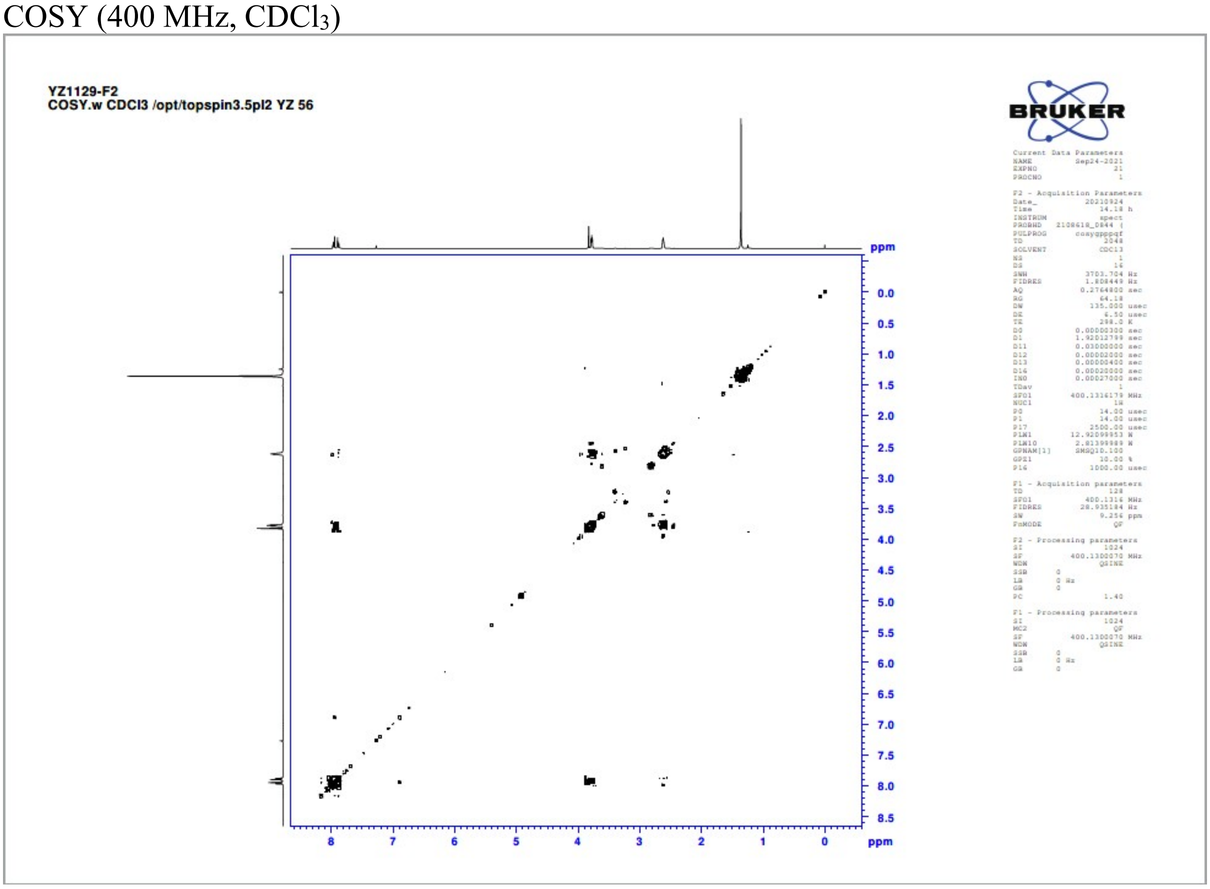
$^1$H NMR (400 MHz, CDCl$_3$)



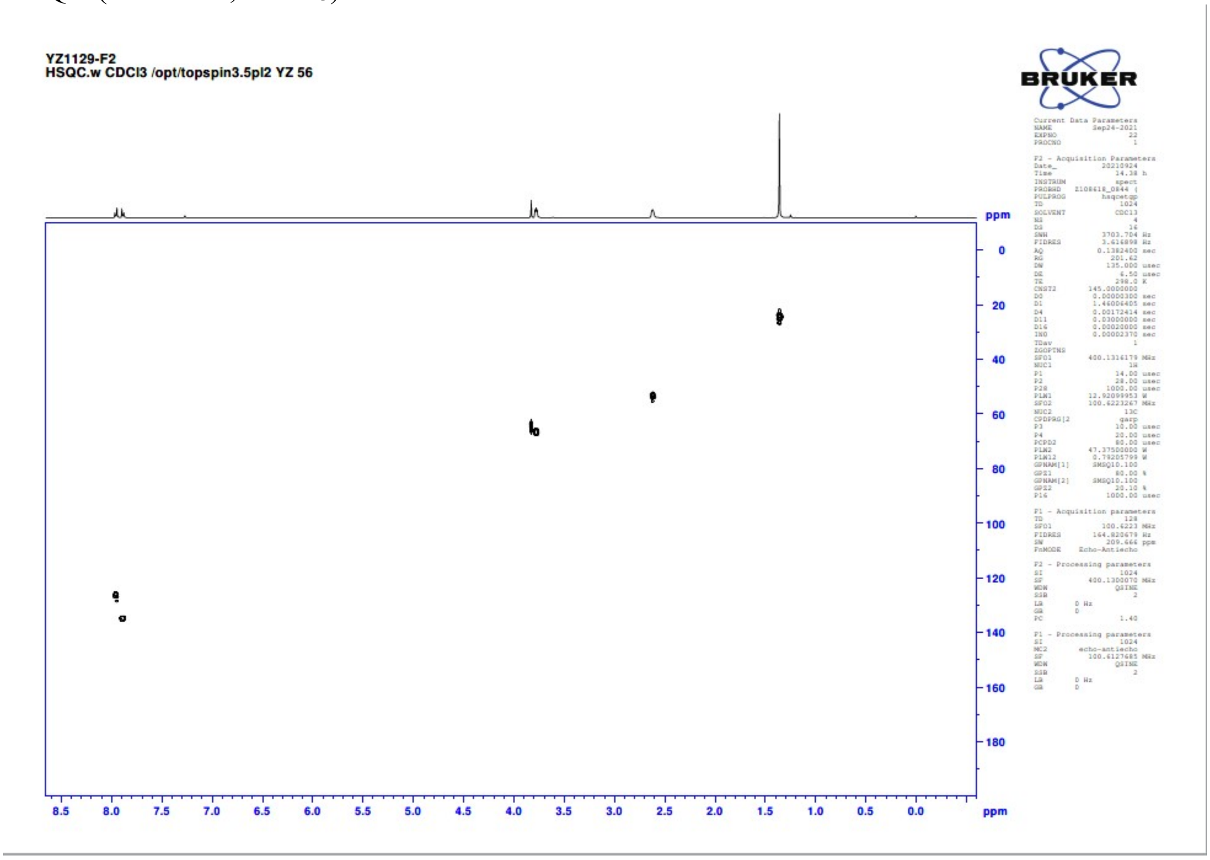
$^{13}$C NMR (100 MHz, CDCl$_3$)



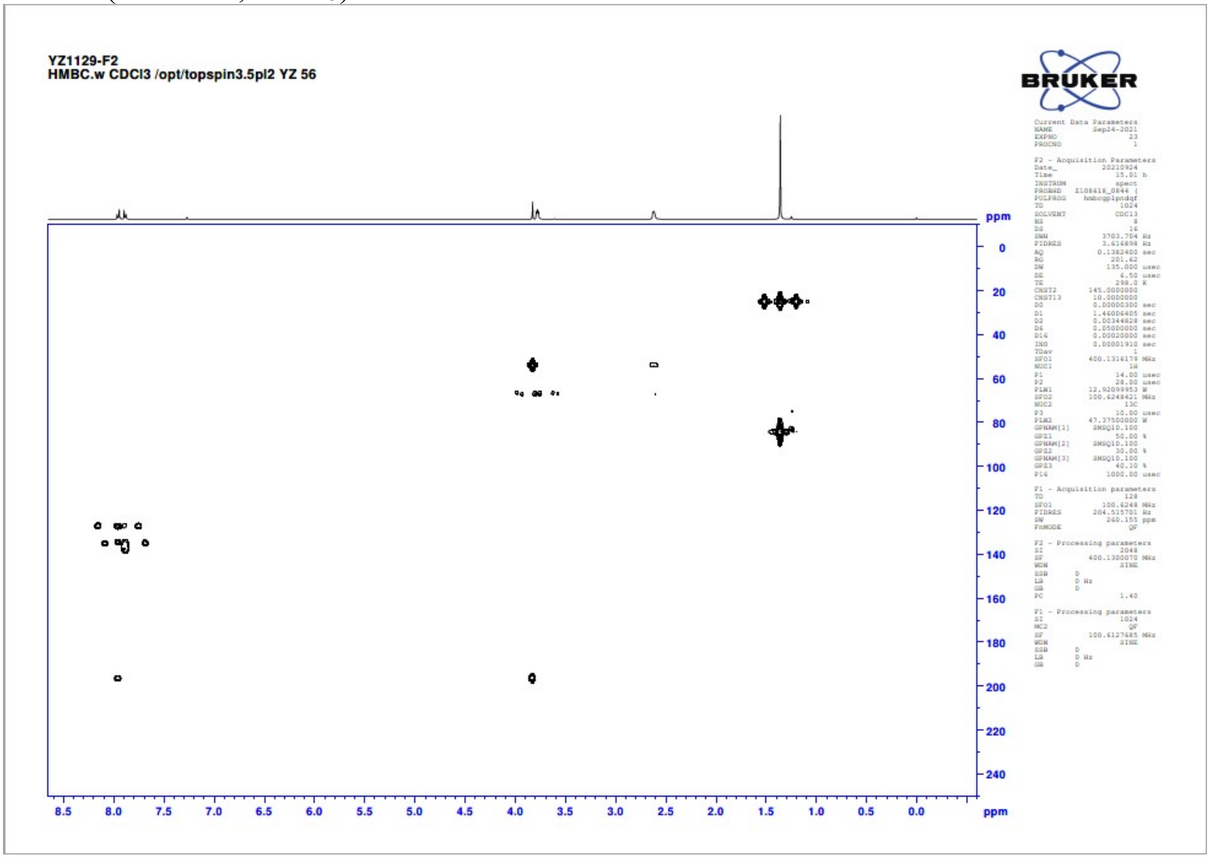
COSY (400 MHz, $CDCl_3$)



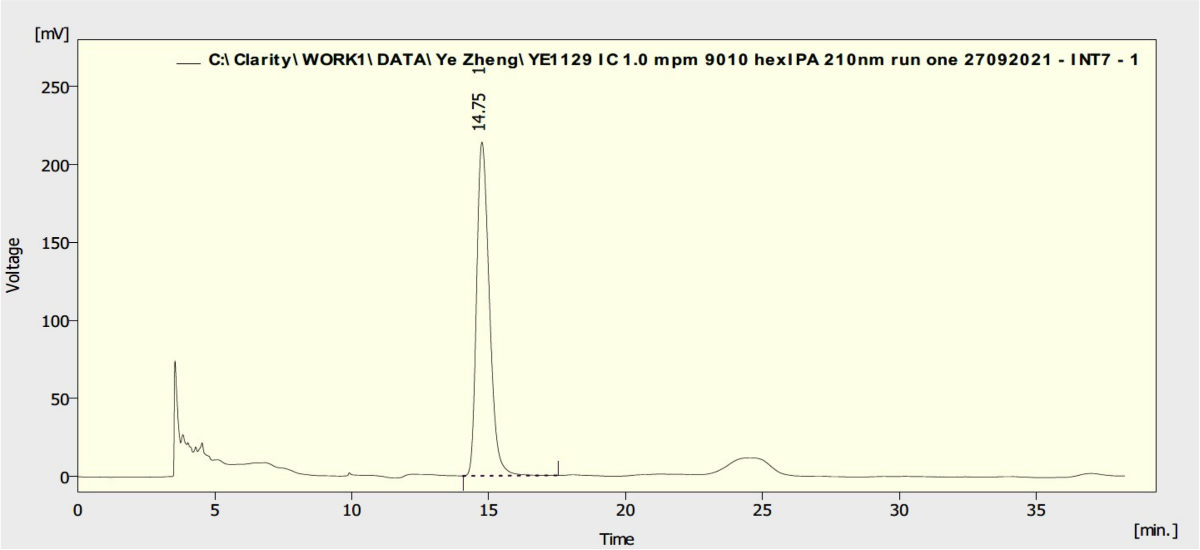
HSQC (400 MHz, $CDCl_3$)

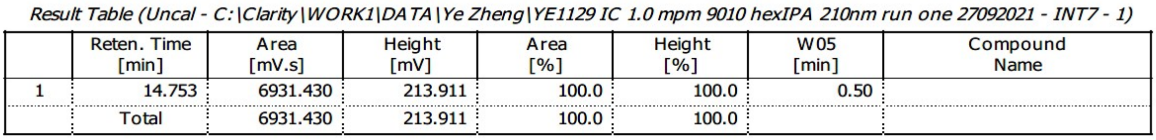


HMBC (400 MHz, $CDCl_3$)



HPLC of 2-morpholino-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one

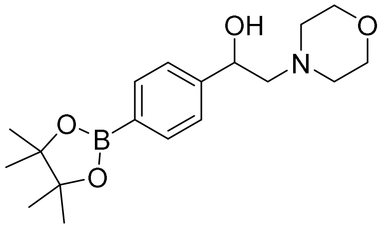


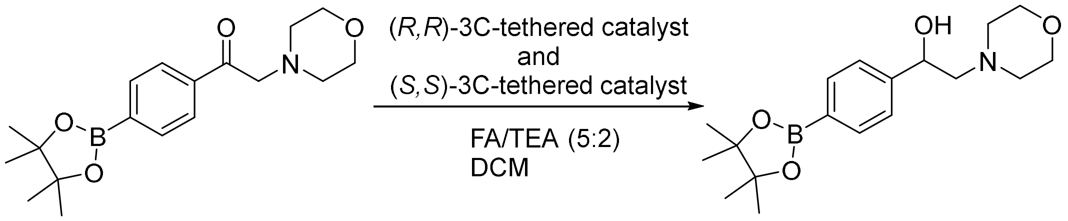


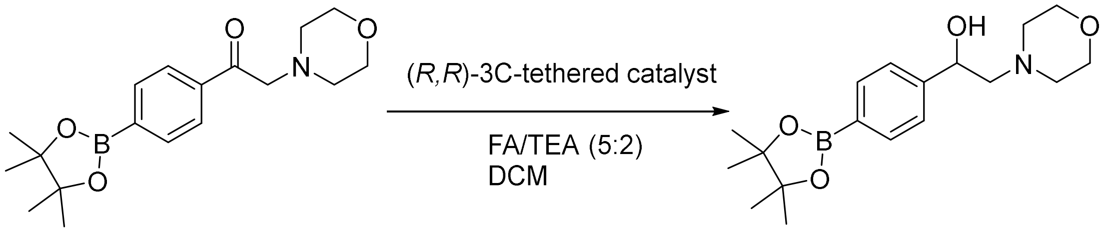
*Result Table (Uncal - C:\Clarity\WORK1\DATA\Ye Zheng\YE1129 IC 1.0 mpm 9010 hexIPA 210nm run one 27092021 - INT7 - 1)*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Compound Name |
|---|---|---|---|---|---|---|---|
| 1 | 14.753 | 6931.430 | 213.911 | 100.0 | 100.0 | 0.50 | |
| | Total | 6931.430 | 213.911 | 100.0 | 100.0 | | |

Racemic and (*S*)-2-Morpholino-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol **15**.







This compound is novel.

**Synthesis of a racemic standard:**

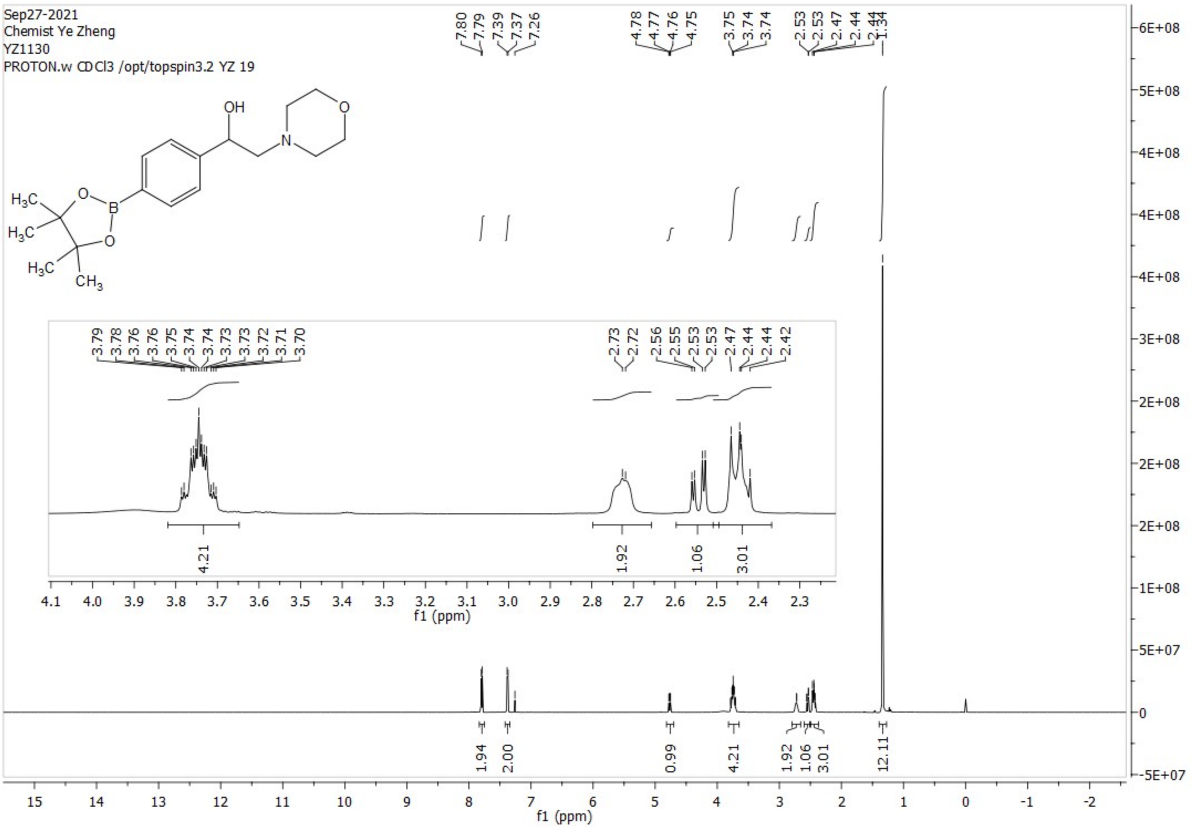
(*R,R*)-3C-Tethered Ru(II)-TsDPEN catalyst **2** (0.75 mg, 1.2 μmol, 0.5 mol%) and (*S,S*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (0.75 mg, 1.2 μmol, 0.5 mol%) were added to FA: TEA (5:2 azeotropic mixture, 0.36 mL) at rt and the mixture was stirred under a nitrogen atmosphere for 15 minutes; after which a solution of 2-morpholino-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one (80.0 mg, 0.242 mmol) in DCM (0.50 mL) was added. The reaction mixture was stirrer under a nitrogen atmosphere and followed by TLC (5:95 MeOH: DCM). After 72 hours, the reaction was quenched using saturated $NaHCO_3$ solution (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried ($MgSO_4$) and filtered. The solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-5% MeOH in DCM to give 2-morpholino-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol **15** as a yellow oil (43.2 mg, 0.130 mmol, 54%). TLC: Rf ca 0.20 (5:95 MeOH: DCM), strong UV and $KMnO_4$; HRMS: (found (ESI+): [M+H]+, Calcd for $C_{18}H_{29}BNO_4$ 334.2179; Found 334.2184; 2.5 ppm error; $\nu_{max}$ 3432 (br), 2973, 2854, 1391, 1356, 1319, 1144, 1113, 1086, 1070, 1016, 871 cm$^{-1}$; $\delta_H$ (500 MHz, $CDCl_3$) 7.80 (2H, d, *J* = 7.9, ArH), 7.39 (2H, d, *J* = 7.9, ArH), 4.77 (1H, dd, *J* = 10.3, 5.3, ArCH), 3.79-3.70 (4H, m, $CH_2$), 2.73 (2H, d, *J* = 3.8, $CH_2$), 2.55 (1H, dd, *J* = 12.5, 3.4, $CH_2$), 2.47-2.42 (3H, m, $CH_2$), 1.34 (12H, s, $CH_3$) ppm; $\delta_C$ (125 MHz, $CDCl_3$) 145.15 (C), 134.91 (CH), 125.08 (CH), 83.78 (C), 68.56 (CH), 67.05 ($CH_2$), 66.54 ($CH_2$), 53.46 ($CH_2$), 24.87 ($CH_3$) ppm; m/z (ES-API+) 334.2 ($M^+$ + 1, 100%).

Enantiomeric excess and conversion determined by HPLC analysis (Chiralpak IC, 30 cm x 6mm column, hexane:iPrOH 90:10, 1.0 mL/min, T = 25°C) ketone 14.8 min, *R* and *S* isomers 15.7 min and 17.3 min. Configuration was assigned by analogy with **12**.

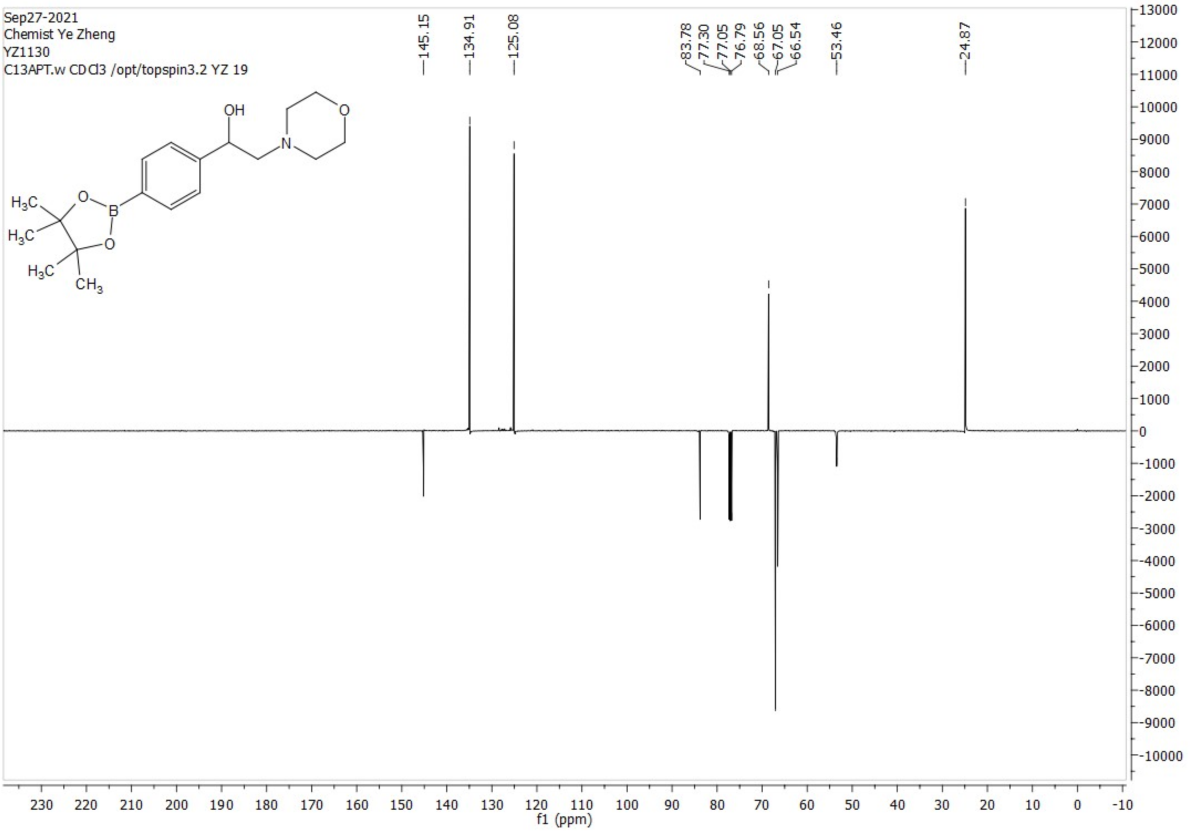
ATH of 2-morpholino-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one):

(*R,R*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (1.5 mg, 2.4 μmol, 1 mol%) was added to FA: TEA (5:2 azeotropic mixture, 0.36 mL) at rt and the mixture was stirred under a nitrogen atmosphere for 15 minutes; after which a solution of 2-morpholino-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one (80.0 mg, 0.242 mmol) in DCM (0.50 mL) was added. The reaction mixture was stirrer under a nitrogen atmosphere and followed by TLC (5:95 MeOH: DCM). After 72 hours, the reaction was quenched using saturated $NaHCO_3$ solution (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried ($MgSO_4$) and filtered. The solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-5% MeOH in DCM to give (*S*)-2-morpholino-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol **15** as a yellow oil (46.8 mg, 0.141 mmol, 58%). The reaction was also followed by HPLC (Chiralpak IC, 30 cm x 6mm column, hexane:iPrOH 90:10, 1.0 mL/min, T = 25°C): $[\alpha]_D^{24}$ +44.3 (c 0.263 in $CHCl_3$) 99% ee.

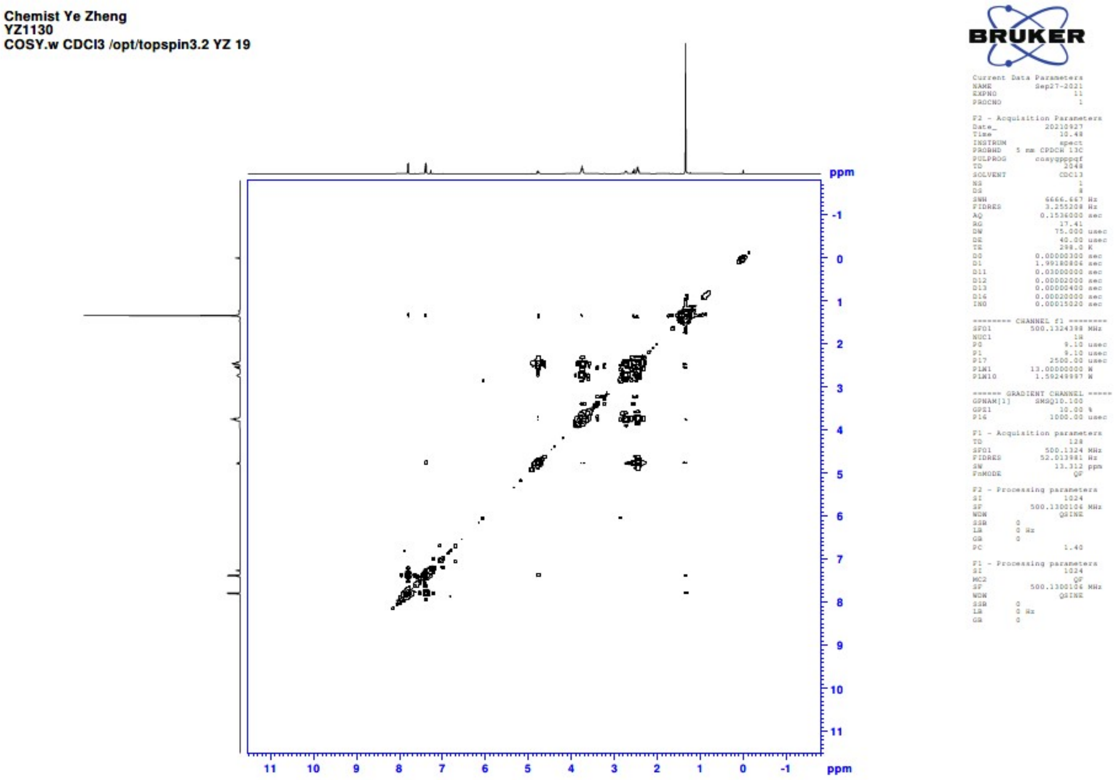
$^1$H NMR (500 MHz, CDCl$_3$)



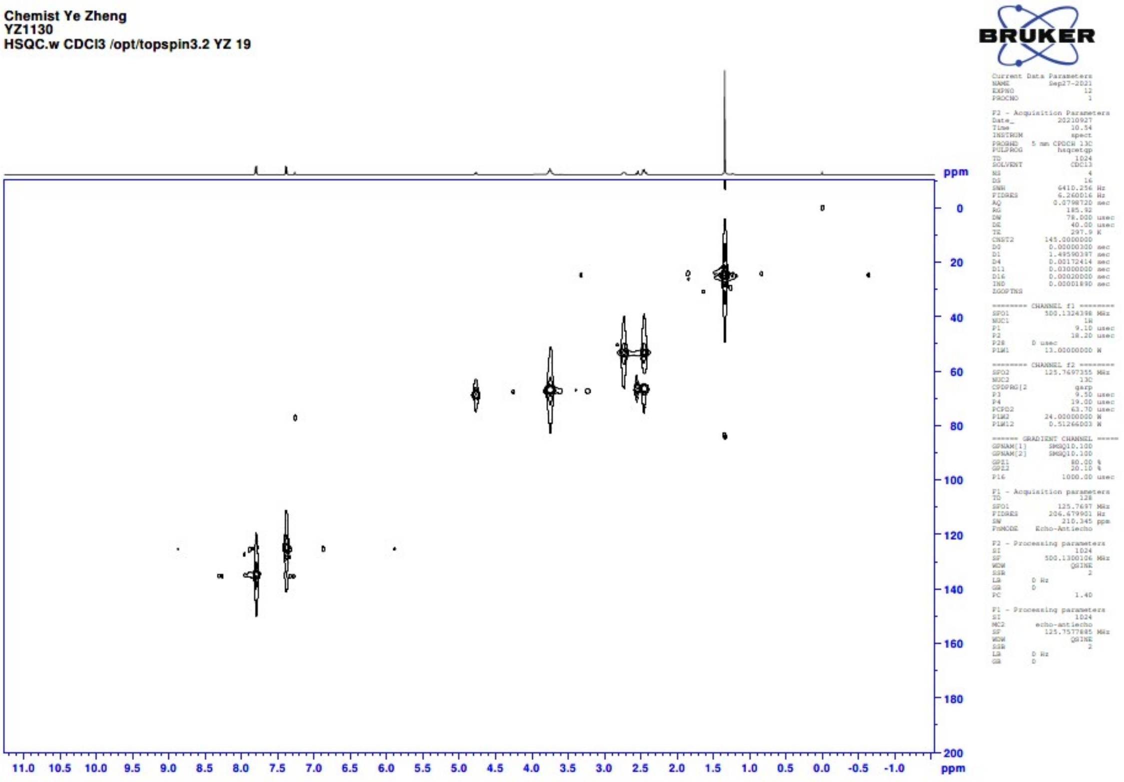
$^{13}$C NMR (125 MHz, CDCl$_3$)



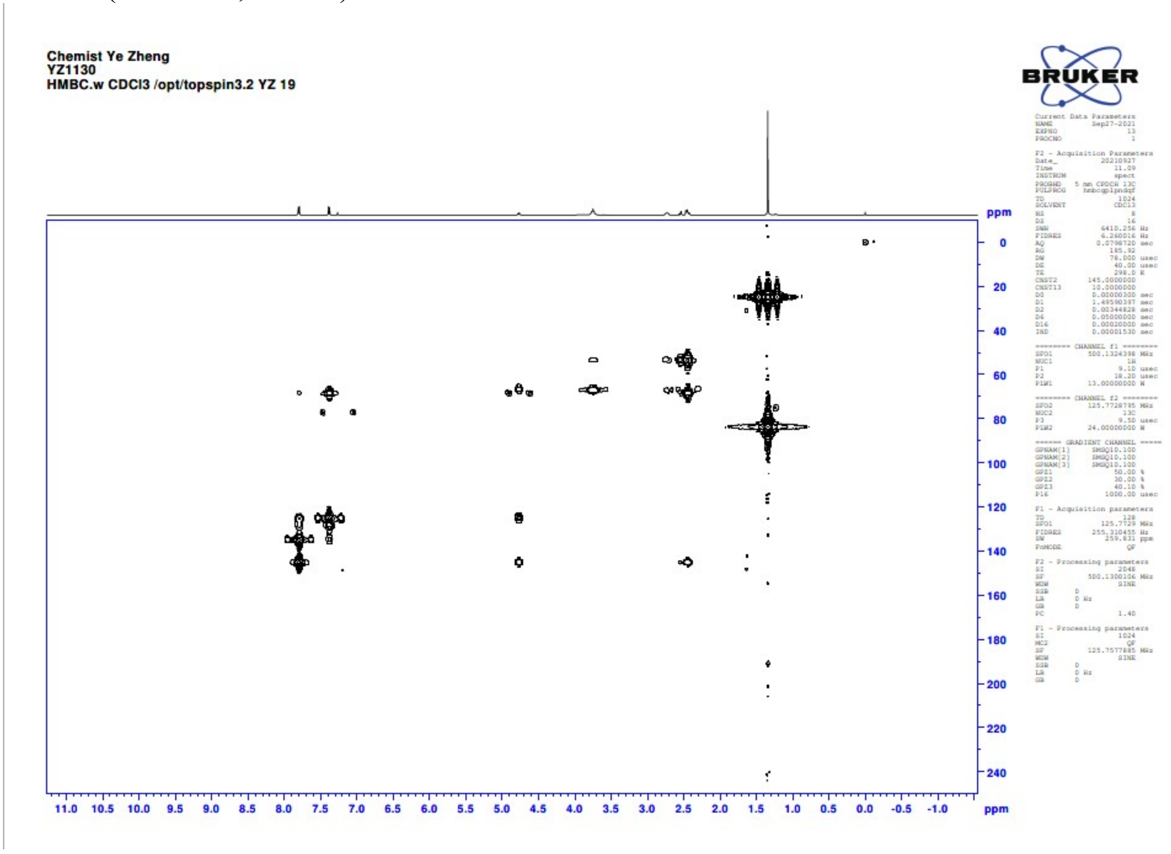
COSY (500 MHz, $CDCl_3$)



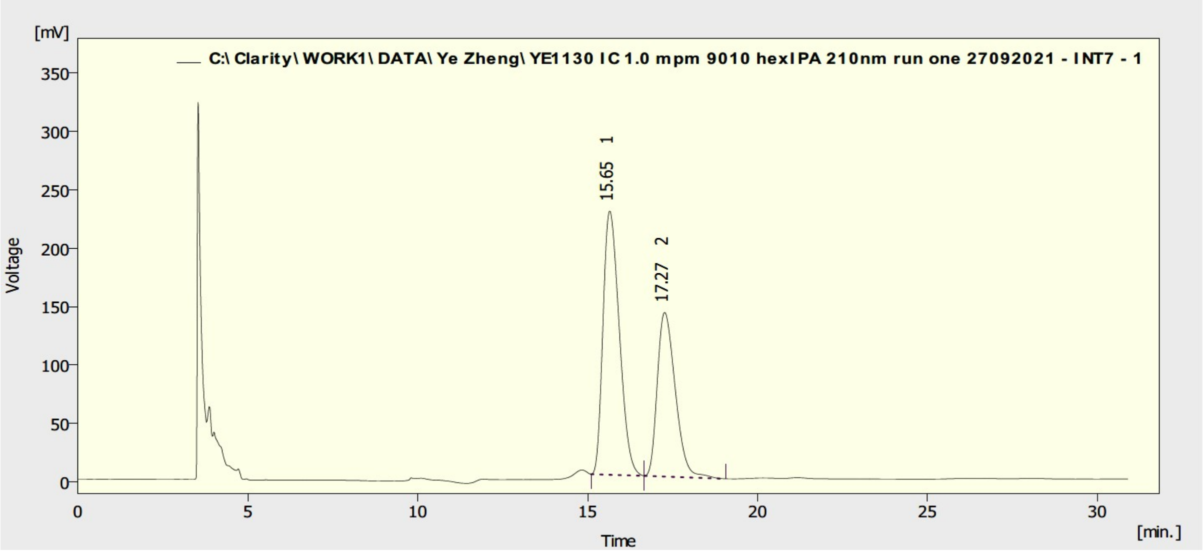
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)



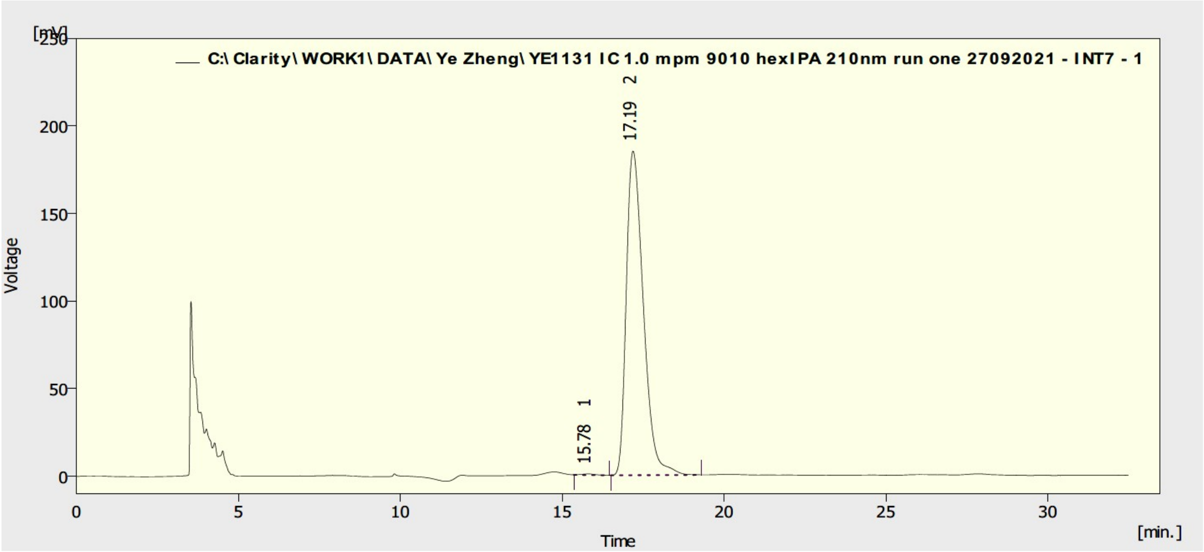
HPLC of racemic 2-morpholino-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol **15**.



*Result Table (Uncal - C:\Clarity\WORK1\DATA\Ye Zheng\YE1130 IC 1.0 mpm 9010 hexIPA 210nm run one 27092021 - INT7 - 1)*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Compound Name |
|---|---|---|---|---|---|---|---|
| 1 | 15.650 | 7523.293 | 225.931 | 59.2 | 61.6 | 0.53 | |
| 2 | 17.267 | 5186.478 | 140.707 | 40.8 | 38.4 | 0.57 | |
| | Total | 12709.771 | 366.638 | 100.0 | 100.0 | | |

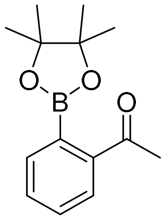
HPLC after ATH of 2-morpholino-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one using (*R,R*)-3C-Tethered Ru(II)-TsDPEN catalyst **2** (after 72 hours, 100% conversion, 99% ee).

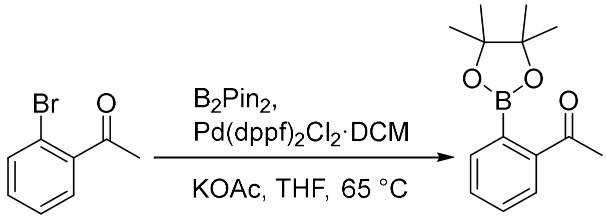


*Result Table (Uncal - C:\Clarity\WORK1\DATA\Ye Zheng\YE1131 IC 1.0 mpm 9010 hexIPA 210nm run one 27092021 - INT7 - 1)*

|  | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Compound Name |
|---|---|---|---|---|---|---|---|
| 1 | 15.777 | 18.359 | 0.647 | 0.3 | 0.3 | 0.45 |  |
| 2 | 17.190 | 6784.357 | 185.156 | 99.7 | 99.7 | 0.56 |  |
|  | Total | 6802.716 | 185.803 | 100.0 | 100.0 |  |  |

1-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one **16**.

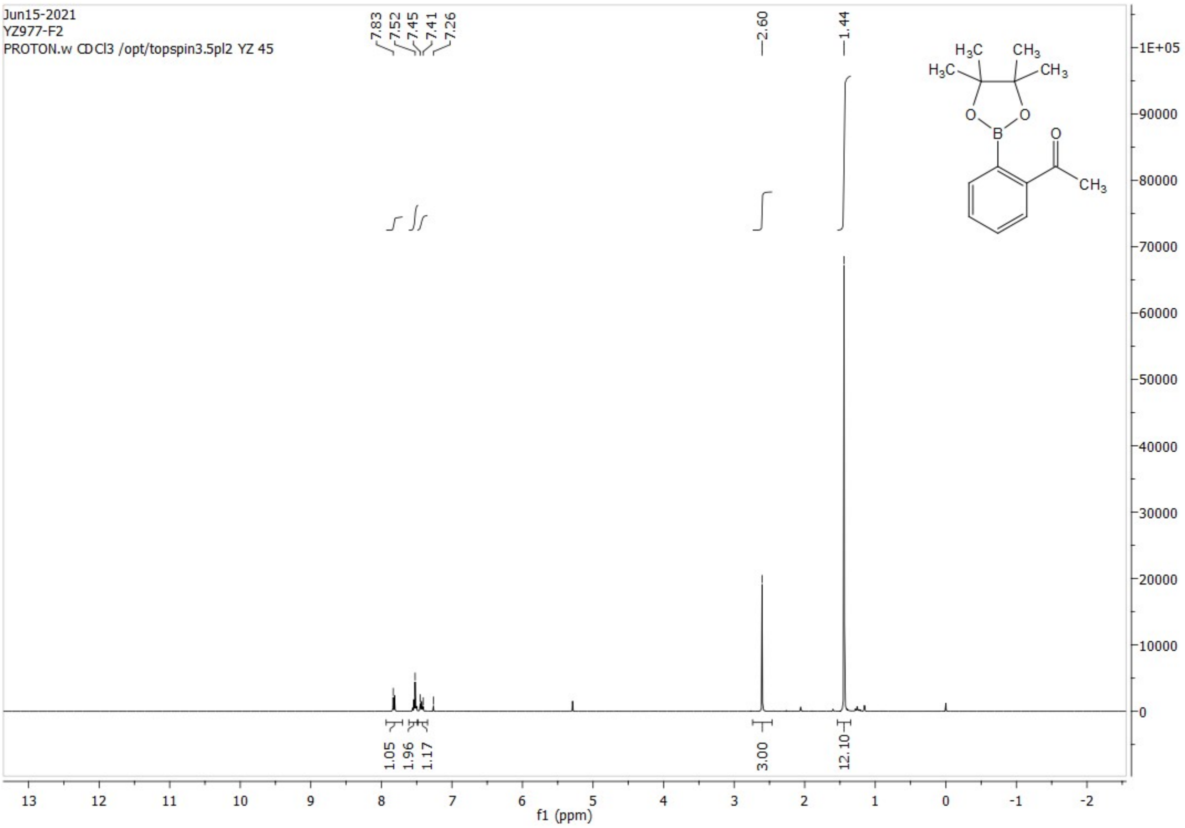




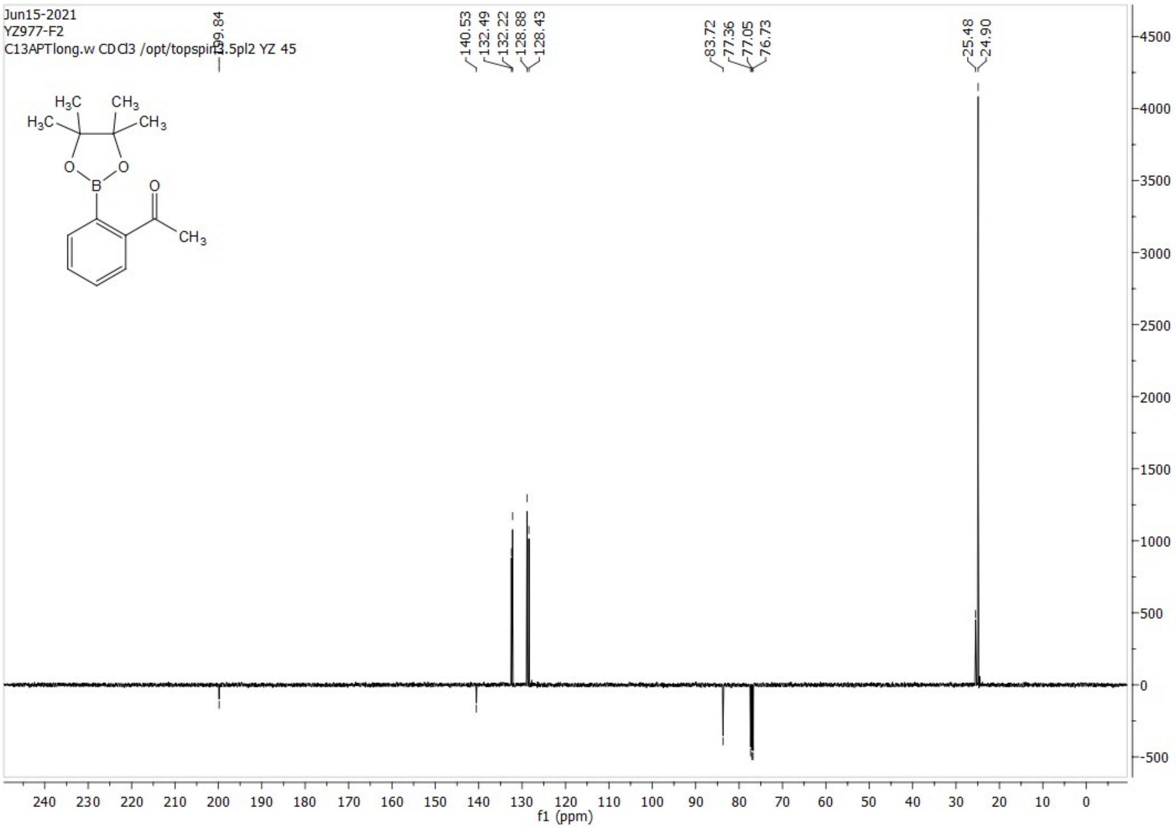
This compound has been reported and fully characterized: N. Su, T. Deng, D. J. Wink and T. G. Driver, *Org. Lett.* 2017, **19**, 3990-3993.

A round-bottom flask was charged with 2'-bromoacetophenone (398 mg, 2.00 mmol), bis(pinacolato)diboron (610 mg, 2.40 mmol), potassium acetate (588 mg, 6.00 mmol), THF (12 mL) and $Pd(dppf)_2Cl_2·DCM$ (81.7 mg, 0.100 mmol). The reaction mixture was heated to 65 °C and left stirring under the nitrogen atmosphere overnight, followed by TLC (9:1 hexane: EtOAc). The mixture was quenched by distilled water (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried ($MgSO_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-20% ethyl acetate in hexane to give 1-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one **16** as a yellow solid (379 mg, 1.54 mmol, 77%). TLC: Rf ca 0.50 (9:1 hexane: EtOAc), strong UV and $KMnO_4$; $\delta_H$ (400 MHz, $CDCl_3$) 7.83 (1H, d, $J = 7.7$, ArH), 7.52 (2H, d, $J = 7.7$, ArH), 7.45-7.41 (1H, m, ArH), 2.60 (3H, s, $CH_3$), 1.44 (12H, s, $CH_3$) ppm; $\delta_C$ (100 MHz, $CDCl_3$) 199.84 (C), 140.53 (C), 132.49 (CH), 132.22 (CH), 128.88 (CH), 128.43 (CH), 83.72 (C), 25.48 ($CH_3$), 24.90 ($CH_3$) ppm. Data matched that reported.

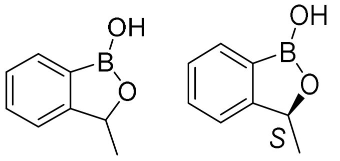
$^1$H NMR (400 MHz, CDCl$_3$)

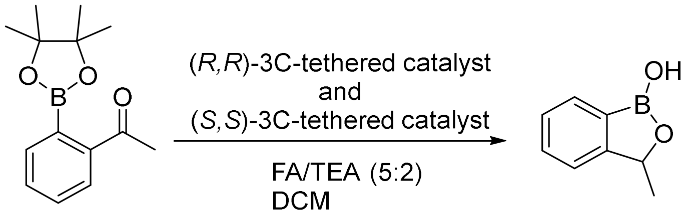


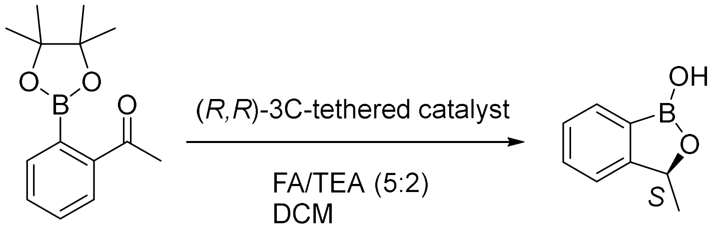
$^{13}$C NMR (100 MHz, CDCl$_3$)



Racemic and (*S*)-3-methylbenzo[c][1,2]oxaborol-1(3*H*)-ol **17**.







This compound has been reported and fully characterized: Supriya Rej and Naoto Chatani, *J. Am. Chem. Soc.* 2021, **43**, 2920-2929.

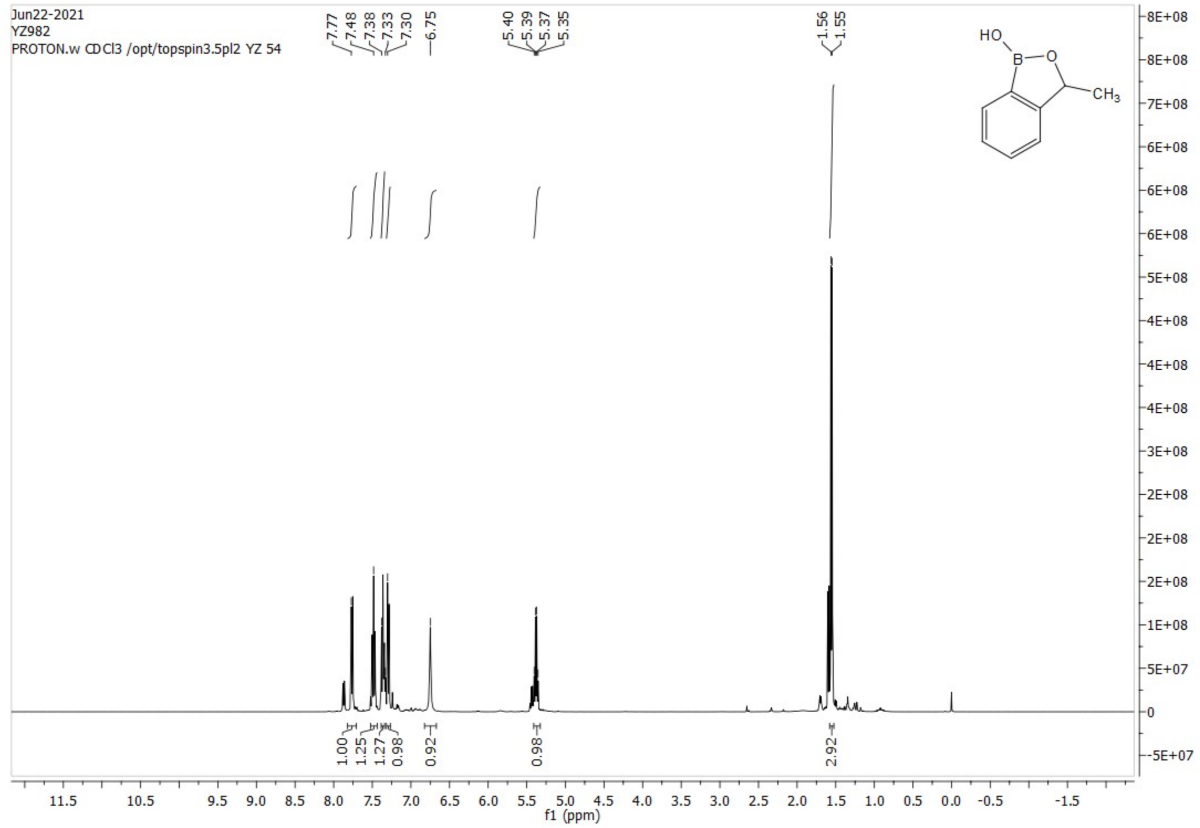
**Synthesis of a racemic standard:**

(*R,R*)-3C-Tethered Ru(II)-TsDPEN catalyst **2** (3.1 mg, 5.0 µmol, 0.5 mol%) and (*S,S*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (3.1 mg, 5.0 µmol, 0.5 mol%) were added to FA: TEA (5:2 azeotropic mixture, 0.90 mL) at rt and the mixture was stirred under a nitrogen atmosphere for 15 minutes; after which a solution of 1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one **16** (199 mg, 1.00 mmol) in DCM (1.24 mL) was added. The reaction mixture was stirrer under a nitrogen atmosphere and followed by TLC (4:1 hexane: EtOAc). After 72 hours, the reaction was quenched using saturated NaHCO$_3$ solution (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried (MgSO$_4$) and filtered. The solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-50% EtOAc in hexane to give methyl 3-methylbenzo[c][1,2]oxaborol-1(3*H*)-ol **17** as a colorless oil (57.8 mg, 0.391 mmol, 39%). TLC: Rf ca 0.20 (4:1 hexane: EtOAc), strong UV and KMnO$_4$; $\delta_H$ (400 MHz, CDCl$_3$) 7.76 (1H, d, *J* = 7.3, ArH), 7.48 (1H, t, *J* = 7.7, ArH), 7.38-7.33 (1H, m, ArH), 7.30 (1H, d, *J* = 7.6, ArH), 6.75 (1H, s, OH), 5.39 (1H, q, *J* = 6.7, ArCH), 1.56 (1H, d, *J* = 6.7, CH$_3$) ppm; $\delta_C$ (100 MHz, CDCl$_3$) 158.01 (C), 131.19 (CH), 130.66

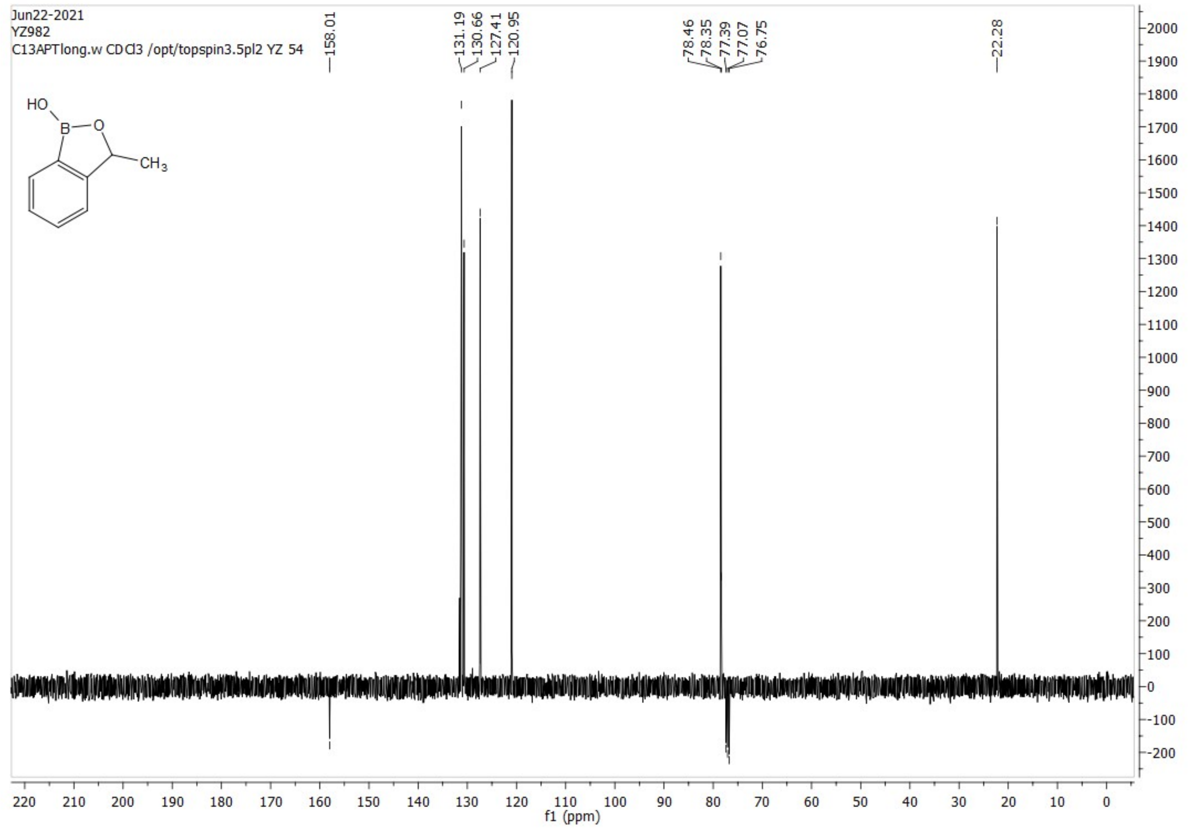
(CH), 127.41 (CH), 120.95 (CH), 78.46 (CH), 22.38 ($CH_3$) ppm. Data matched that reported.

ATH of 1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one) **16**: (*R,R*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (5.6 mg, 9.0 μmol, 1 mol%) was added to FA: TEA (5:2 azeotropic mixture, 0.81 mL) at rt and the mixture was stirred under a nitrogen atmosphere for 15 minutes; after which a solution of 1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one **16** (179 mg, 0.900 mmol) in DCM (1.12 mL) was added. The reaction mixture was stirred under a nitrogen atmosphere and followed by TLC (4:1 hexane: EtOAc). After 72 hours, the reaction was quenched using saturated $NaHCO_3$ solution (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried ($MgSO_4$) and filtered. The solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-50% EtOAc in hexane to give methyl 3-methylbenzo[c][1,2]oxaborol-1(3*H*)-ol **17** as a colorless oil (63.8 mg, 0.431 mmol, 48%). The reaction mixture could not be resolved by chiral HPLC: 100% conversion, 31% ee, *S* configuration; ee and configuration were confirmed by comparison with compound after reaction with bromopyridine.

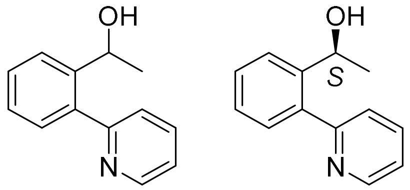
$^1$H NMR (400 MHz, $CDCl_3$)

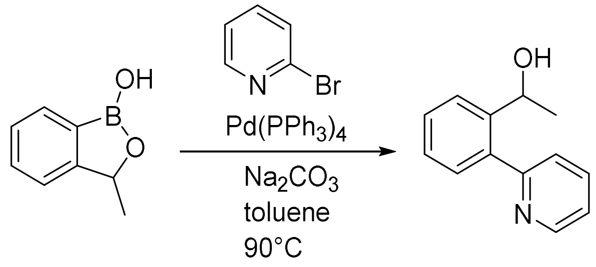


$^{13}$C NMR (100 MHz, $CDCl_3$)



Racemic and (*S*)-1-(2-(Pyridin-2-yl)phenyl)ethan-1-ol **18**.





This compound has been reported and fully characterized: E. Liardo, N. Rios-Lombardia, F. Moris, J. Gonzalez-Sabin and F. Rebolledo, *Eur. J. Org. Chem.* 2018, **23**, 3031-3035.

Racemic.

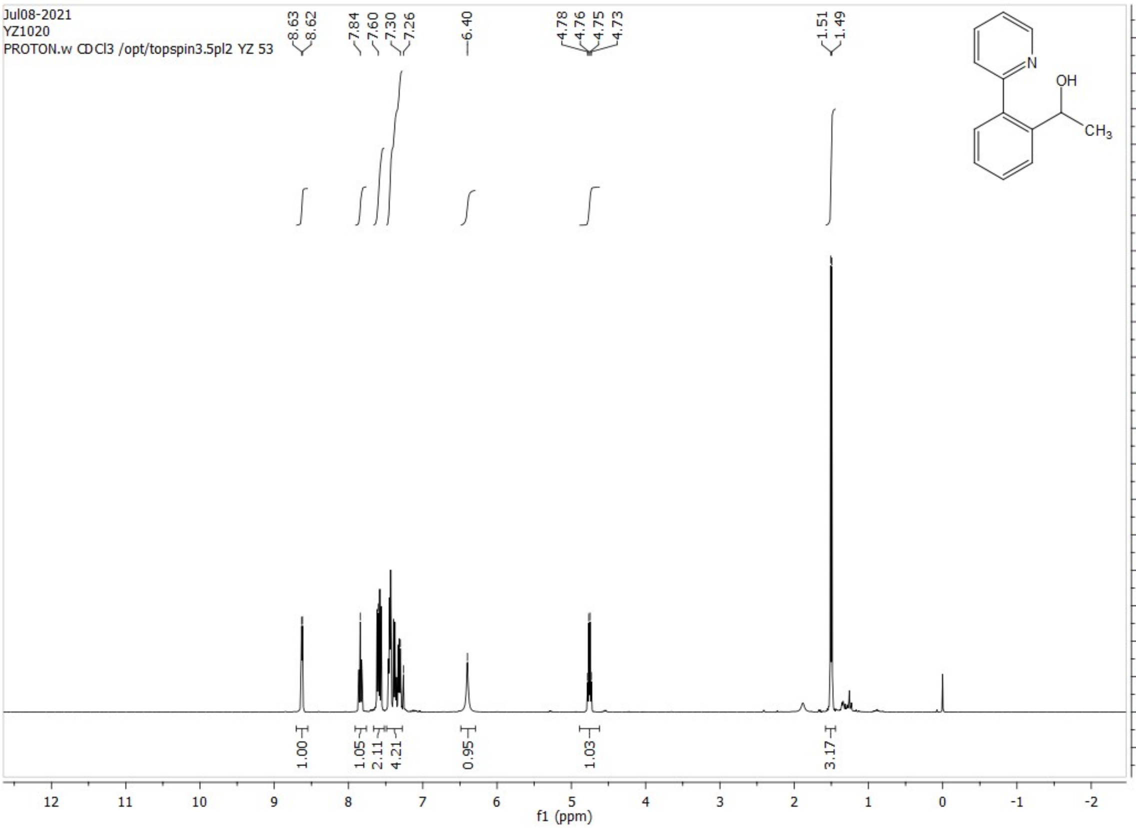
To a solution of $Pd(PPh_3)_4$ (70.5 mg, 0.0610 mmol) in toluene (7.3 mL) was added 2-bromopyridine (386 mg, 2.44 mmol), racemic 3-methylbenzo[c][1,2]oxaborol-1(3*H*)-ol **17** (180 mg, 1.22 mmol) and sodium carbonate (0.732 mL, 20% w/v). The reaction mixture was heated to 90 °C and left stirring under the nitrogen atmosphere overnight, followed by TLC (2:1 hexane: EtOAc). The mixture was quenched by distilled water (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried ($MgSO_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 20-100% ethyl acetate in hexane to give racemic 1-(2-(pyridin-2-yl)phenyl)ethan-1-ol **18** as a colorless oil (51.8 mg, 0.260 mmol, 21%). TLC: Rf ca 0.20 (2:1 hexane: EtOAc), strong UV and $KMnO_4$; $\delta_H$ (400 MHz, $CDCl_3$) 8.63 (1H, d, *J* = 4.6, H in pyridine), 7.84 (1H, td, *J* = 7.8, 1.5, ArH), 7.60 (2H, dd, *J* = 15.3, 7.7, ArH), 7.46-7.30 (4H, m, ArH + H in pyridine), 6.40 (1H, s, OH), 4.76 (1H, q, *J* = 6.6, CH), 1.51 (3H, d, *J* = 6.6, $CH_3$) ppm; $\delta_C$ (100 MHz, $CDCl_3$) 159.88 (C), 147.89 (CH), 143.45 (C), 139.57 (C), 137.55 (CH), 130.64 (CH), 129.18 (CH), 127.58 (CH), 126.49 (CH), 124.27 (CH), 122.18 (CH), 66.77 (CH), 20.42 ($CH_3$) ppm; m/z (ES-API+) 222.1 ($M^+$ + 23, 100%). Data matched that reported.

Enantiomeric excess and conversion determined by HPLC analysis (Chiralcel OD, 30 cm x 6mm column, hexane:iPrOH 90:10, 0.8 mL/min, T = 25°C) *S* isomer 11.8 min and *R* isomer 15.4 min. The same column and solvent combination was used in the literature reference above.

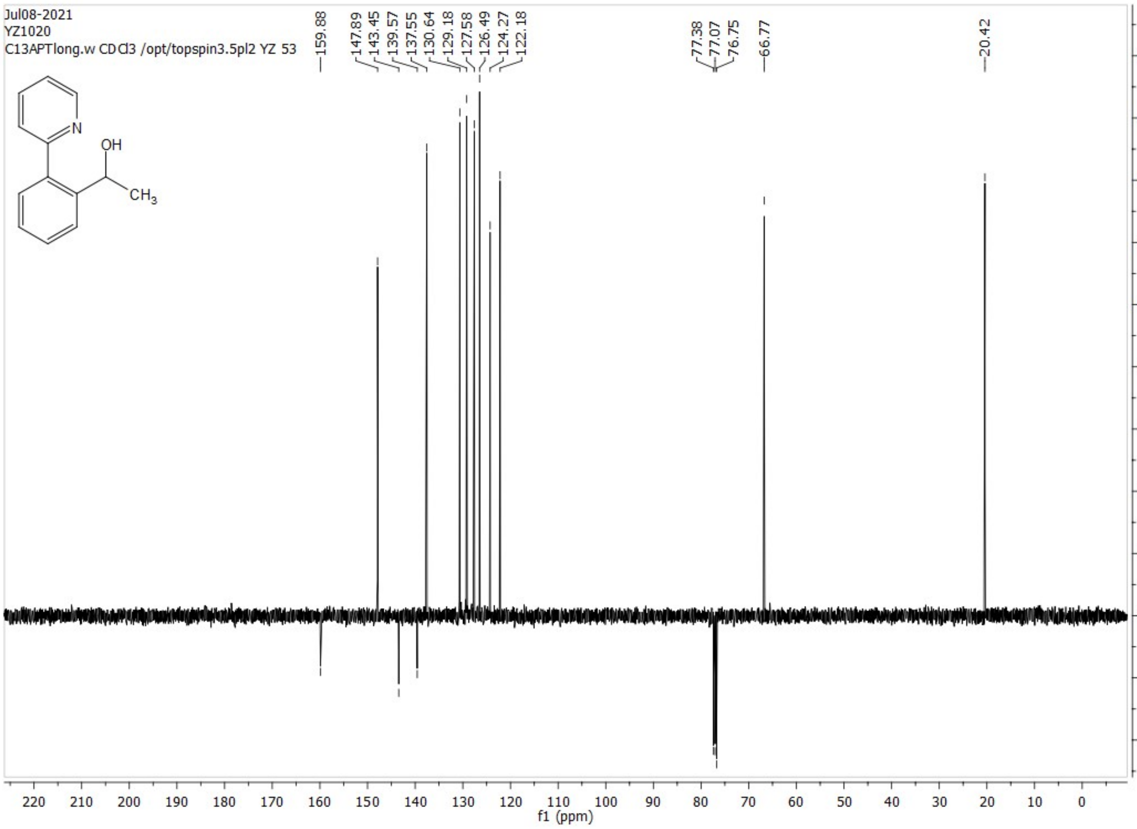
Asymmetric.

To a solution of $Pd(PPh_3)_4$ (24.6 mg, 0.0213 mmol) in toluene (2.6 mL) was added 2-bromopyridine (135 mg, 0.852 mmol), asymmetric 3-methylbenzo[c][1,2]oxaborol-1(3*H*)-ol **17** (63.0 mg, 0.426 mmol) and sodium carbonate (0.256 mL, 20% w/v). The reaction mixture was heated to 90 °C and left stirring under the nitrogen atmosphere overnight, followed by TLC (2:1 hexane: EtOAc). The mixture was quenched by distilled water (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried ($MgSO_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 20-100% ethyl acetate in hexane to give (*S*)-1-(2-(pyridin-2-yl)phenyl)ethan-1-ol **18** as a colorless oil (23.2 mg, 0.117 mmol, 27%). The reaction was also followed by HPLC (Chiralcel OD, 30 cm x 6mm column, hexane:iPrOH 90:10, 0.8 mL/min, T = 25°C); $[\alpha]_D^{26}$ -11.4 (c 0.460 in $CHCl_3$) 31% ee (*S*) (lit. $[\alpha]_D^{26}$ -14.3 (c 0.40 in $CHCl_3$) >99% ee (*S*)) Reference: E. Liardo, N. Rios-Lombardia, F. Moris, J. Gonzalez-Sabin, F. Rebolledo; *Eur. J. Org. Chem.* 2018, **23**, 3031-3035.

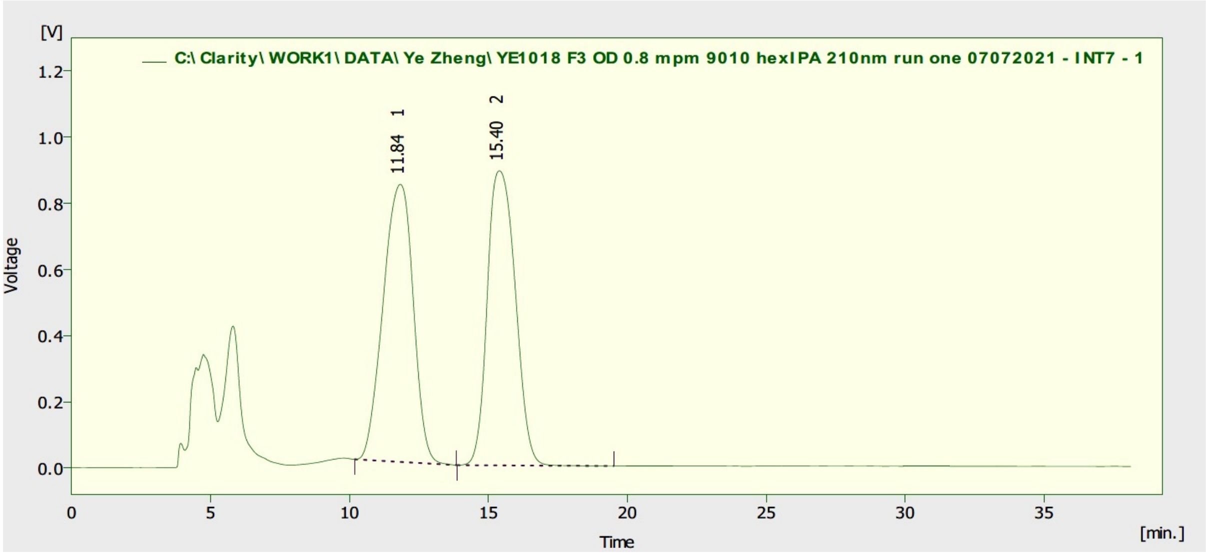
$^1$H NMR (400 MHz, CDCl$_3$)



$^{13}$C NMR (100 MHz, CDCl$_3$)



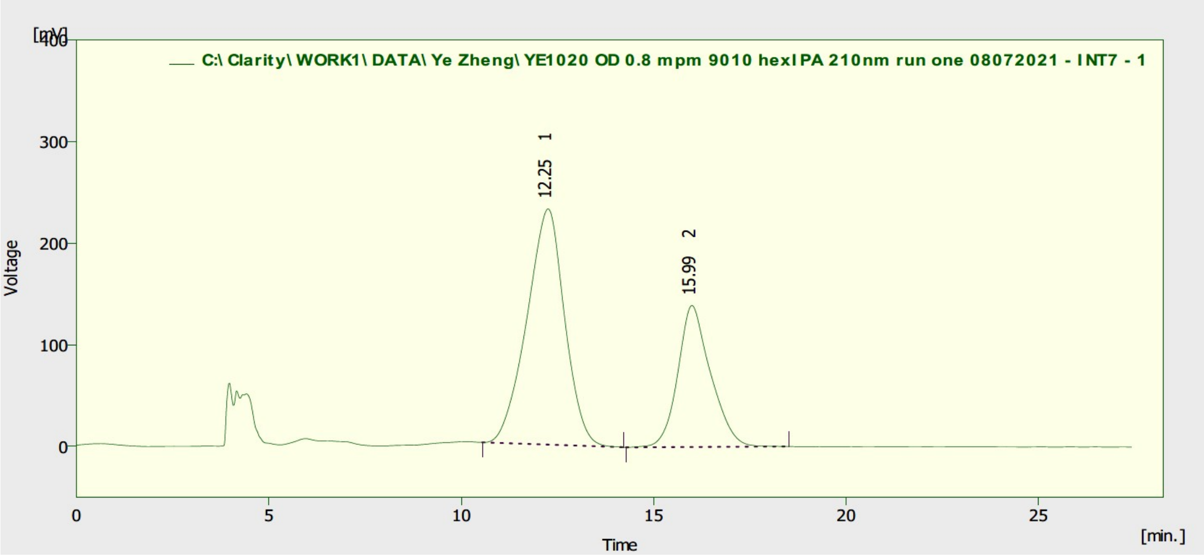
HPLC of racemic 1-(2-(pyridin-2-yl)phenyl)ethan-1-ol **18**.



*Result Table (Uncal - C:\Clarity\WORK1\DATA\Ye Zheng\YE1018 F3 OD 0.8 mpm 9010 hexIPA 210nm run one 07072021 - INT7 - 1)*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Compound Name |
|---|---|---|---|---|---|---|---|
| 1 | 11.837 | 63188.573 | 838.607 | 50.3 | 48.5 | 1.21 | |
| 2 | 15.397 | 62316.573 | 890.003 | 49.7 | 51.5 | 1.12 | |
| | Total | 125505.145 | 1728.610 | 100.0 | 100.0 | | |

HPLC of 1-(2-(pyridin-2-yl)phenyl)ethan-1-ol **18** (31% ee, *S* configuration).

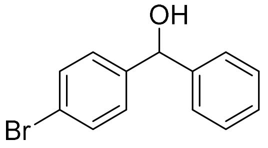


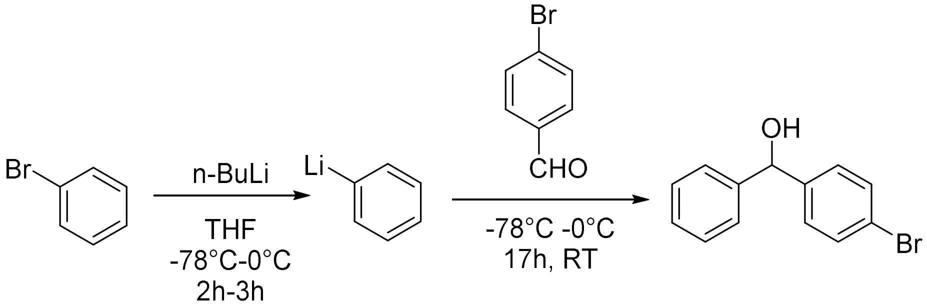
*Result Table (Uncal - C:\Clarity\WORK1\DATA\Ye Zheng\YE1020 OD 0.8 mpm 9010 hexIPA 210nm run one 08072021 - INT7 - 1)*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Compound Name |
|---|---|---|---|---|---|---|---|
| 1 | 12.253 | 15807.306 | 231.898 | 65.7 | 62.5 | 1.05 | |
| 2 | 15.990 | 8245.177 | 139.198 | 34.3 | 37.5 | 0.89 | |
| | Total | 24052.483 | 371.095 | 100.0 | 100.0 | | |

**Data related to Figure 5.**

(4-Bromophenyl)(phenyl)methanol.

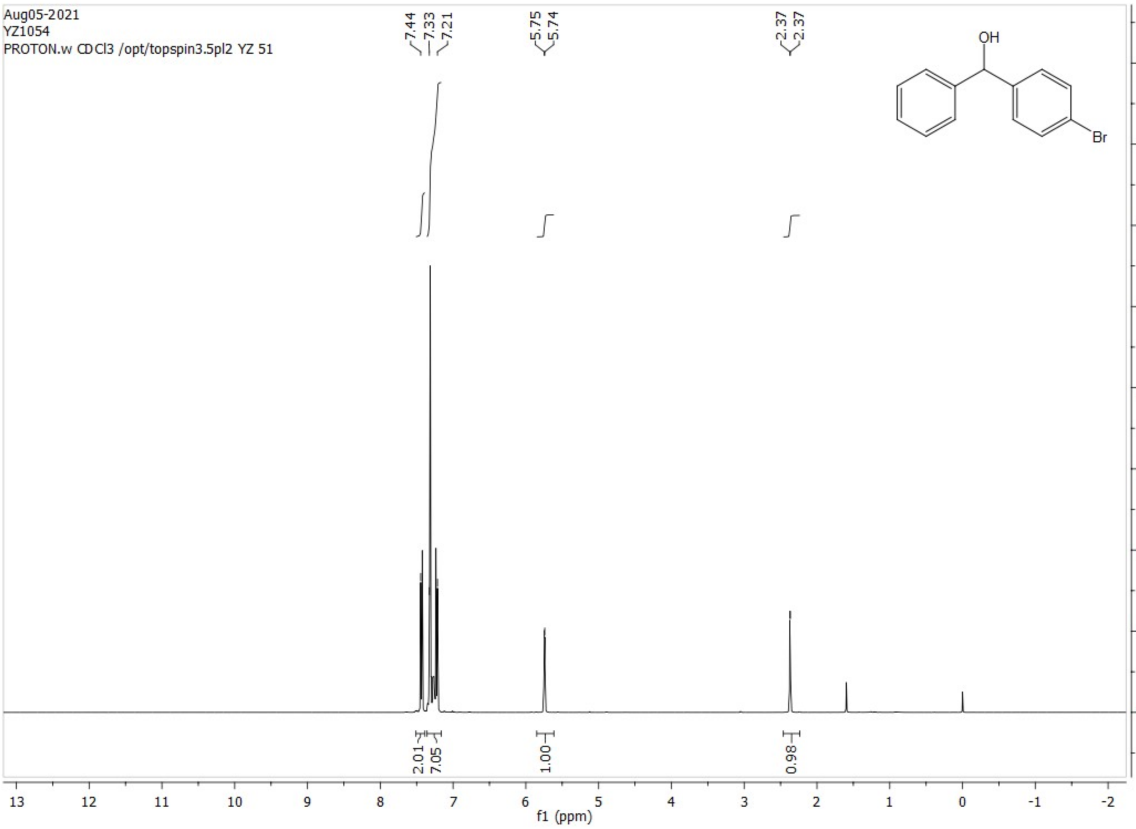




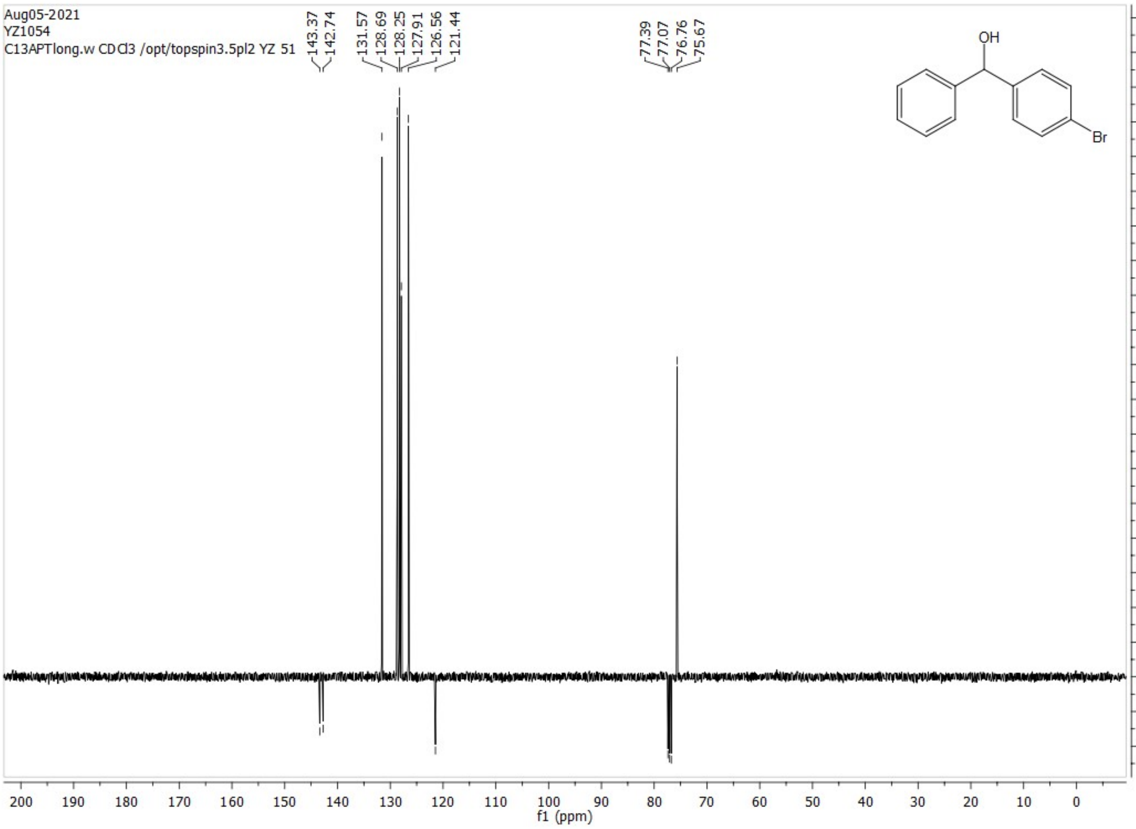
This compound has been reported and fully characterized: M. Das, D. F. O’Shea, *J. Org. Chem.* 2014, **79**, 5595-5607.

To a solution of bromobenzene (432 mg, 2.75 mmol) in THF (3.3 mL) at -78 °C was added dropwise a solution of n-butyllithium (1.00 mL, 2.5M in hexanes, 2.50 mmol). The reaction mixture was then stirred under a nitrogen atmosphere for 2-3 hours, after which 4-bromobenzaldehyde (463 mg, 2.50 mmol) was added dropwise. The reaction mixture was left stirring under the nitrogen atmosphere and allowed to warm to rt. The reaction was followed by TLC (9:1 hexane: EtOAc). The mixture was quenched by saturated $NH_4Cl$ solution (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried ($MgSO_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-20% EtOAc in hexane to give (4-bromophenyl)(phenyl)methanol as a yellow oil (456 mg, 1.74 mmol, 70%). TLC: Rf ca 0.20 (9:1 hexane: EtOAc), strong UV and $KMnO_4$; $\delta_H$ (400 MHz, $CDCl_3$) 7.44 (2H, d, *J* = 8.4, ArH), 7.33-7.21 (7H, m, ArH), 5.75 (1H, d, *J* = 3.4, ArCH), 2.37 (1H, d, *J* = 3.4, OH) ppm; $\delta_C$ (100 MHz, $CDCl_3$) 143.37 (C), 142.74 (C), 131.57 (CH), 128.69 (CH), 128.25 (CH), 127.91 (CH), 126.56 (CH), 121.44 (C), 75.67 (CH) ppm; m/z (ES-API+) 285.0 ($M^+$ + 23, 100%). Data matched that reported.

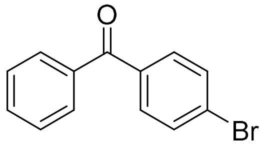
$^1$H NMR (400 MHz, $CDCl_3$)

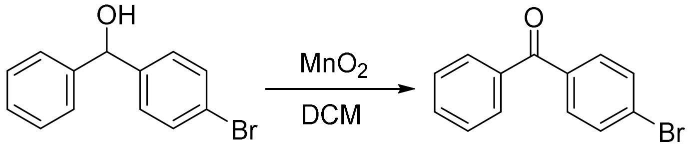


$^{13}$C NMR (100 MHz, $CDCl_3$)



(4-Bromophenyl)(phenyl)methanone.

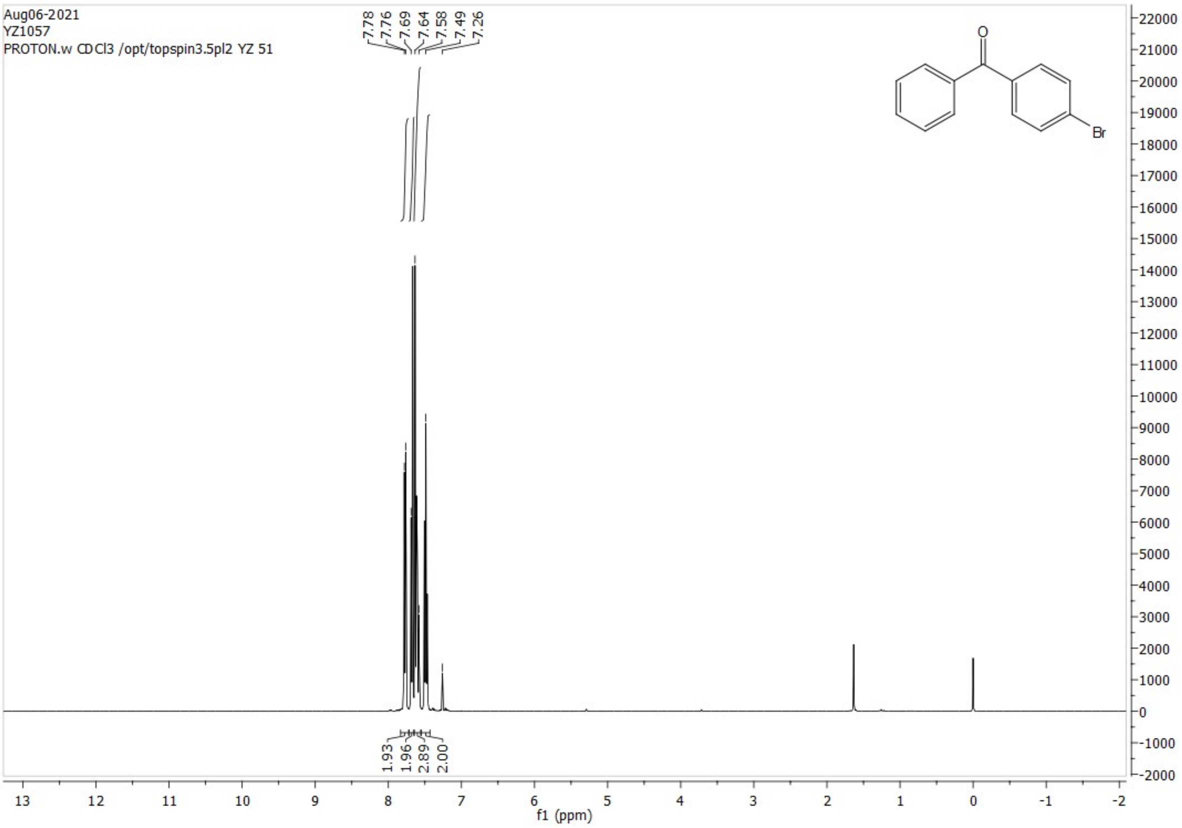




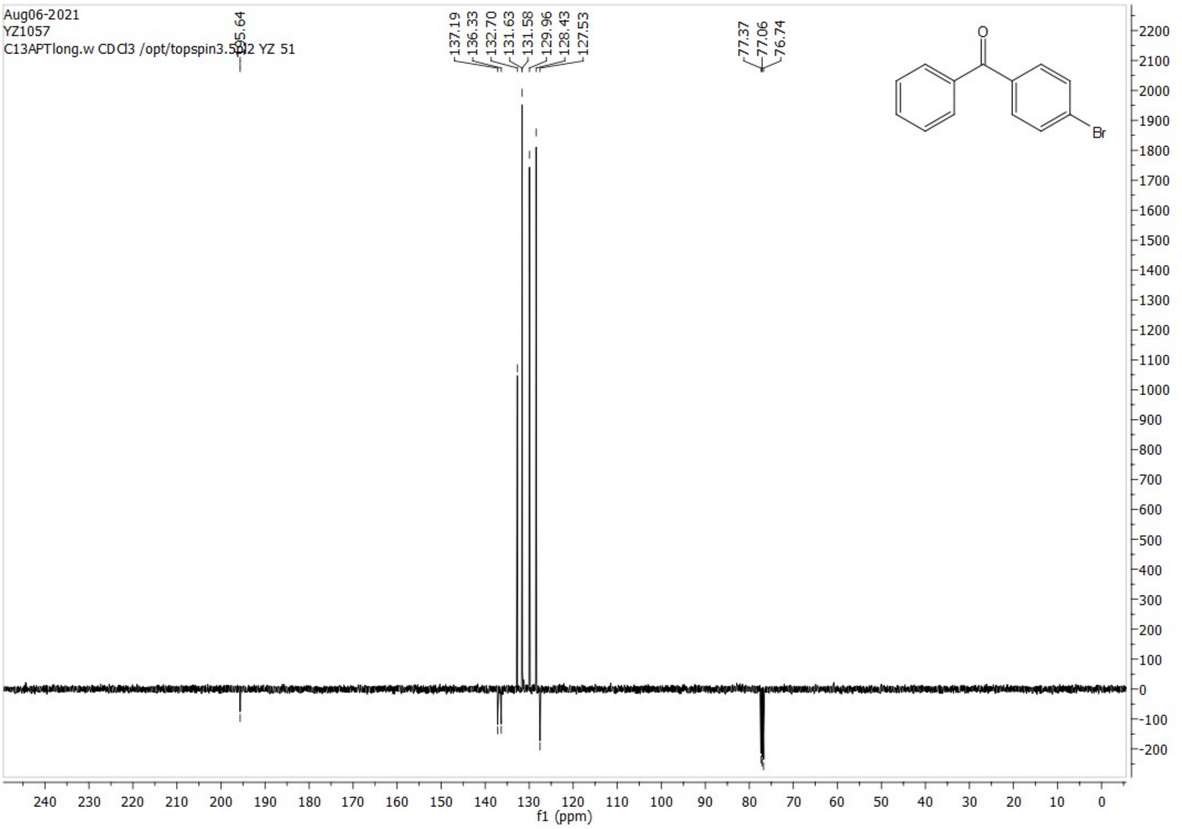
This compound has been reported and fully characterized: B. Skillinghaug, C.Skold, J. Rydfjord, F. Svensson, M. Behrends, J. Savmarker, P. J. R. Sjoberg, M. Larhed, *J. Org. Chem.* 2014, **79**, 12018-12032.

To a solution of (2-bromophenyl)(phenyl)methanol (450 mg, 1.72 mmol) in DCM (10 mL) at rt was added manganese dioxide (2.24 g, 25.8 mmol). The reaction mixture was left to stir under a nitrogen atmosphere overnight. TLC (9:1 hexane: EtOAc) after this time indicated full conversion. The solids were removed by gravity filtration and washed with DCM. The combined solvent was removed to give the product as a white solid (360 mg, 1.38 mmol, 81%). TLC: Rf ca 0.40 (9:1 hexane: EtOAc), strong UV and $KMnO_4$; $\delta_H$ (400 MHz, $CDCl_3$) 7.78-7.76 (2H, m, ArH), 7.69 (2H, d, *J* = 8.5, ArH), 7.64-7.58 (3H, m, ArH), 7.49 (2H, t, *J* = 7.6, ArH) ppm; $\delta_C$ (100 MHz, $CDCl_3$) 195.64 (C), 137.19 (C), 136.33 (C), 132.70 (CH), 131.63 (CH), 131.58 (CH), 129.96 (CH), 128.43 (CH), 127.53 (C) ppm; m/z (ES-API+) 283.0 ($M^+$ + 23, 100%). Data matched that reported.

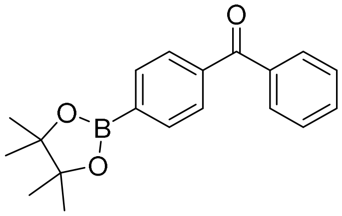
$^1$H NMR (400 MHz, CDCl$_3$)

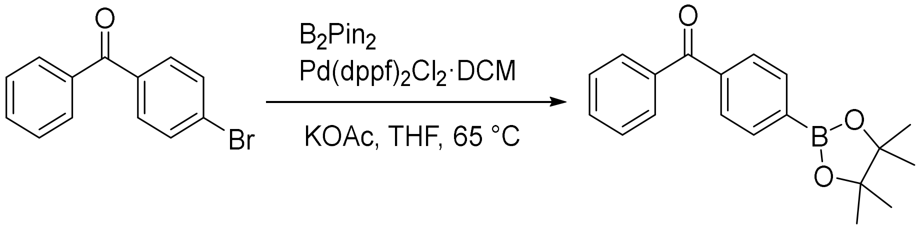


$^{13}$C NMR (100 MHz, CDCl$_3$)



Phenyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone.



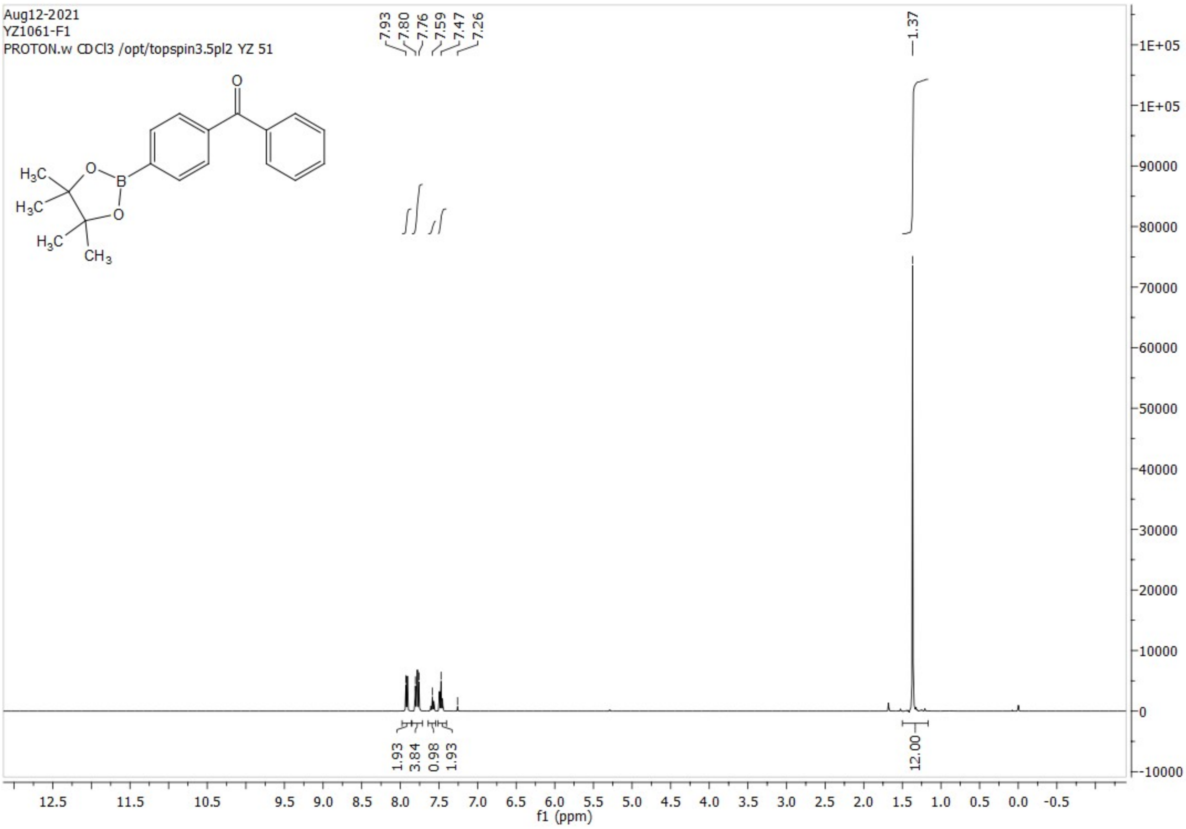


This compound has been reported and fully characterized: S. Barroso, M. Joksch, P. Puylaert, S. Tin, S. J. Bell, L. Donnellan S. Duguid, C. Muir, P. Zhao, B. Farina, D. N. Tran, J. G. de Vries, *J. Org. Chem.* 2021, **86**, 103-109.

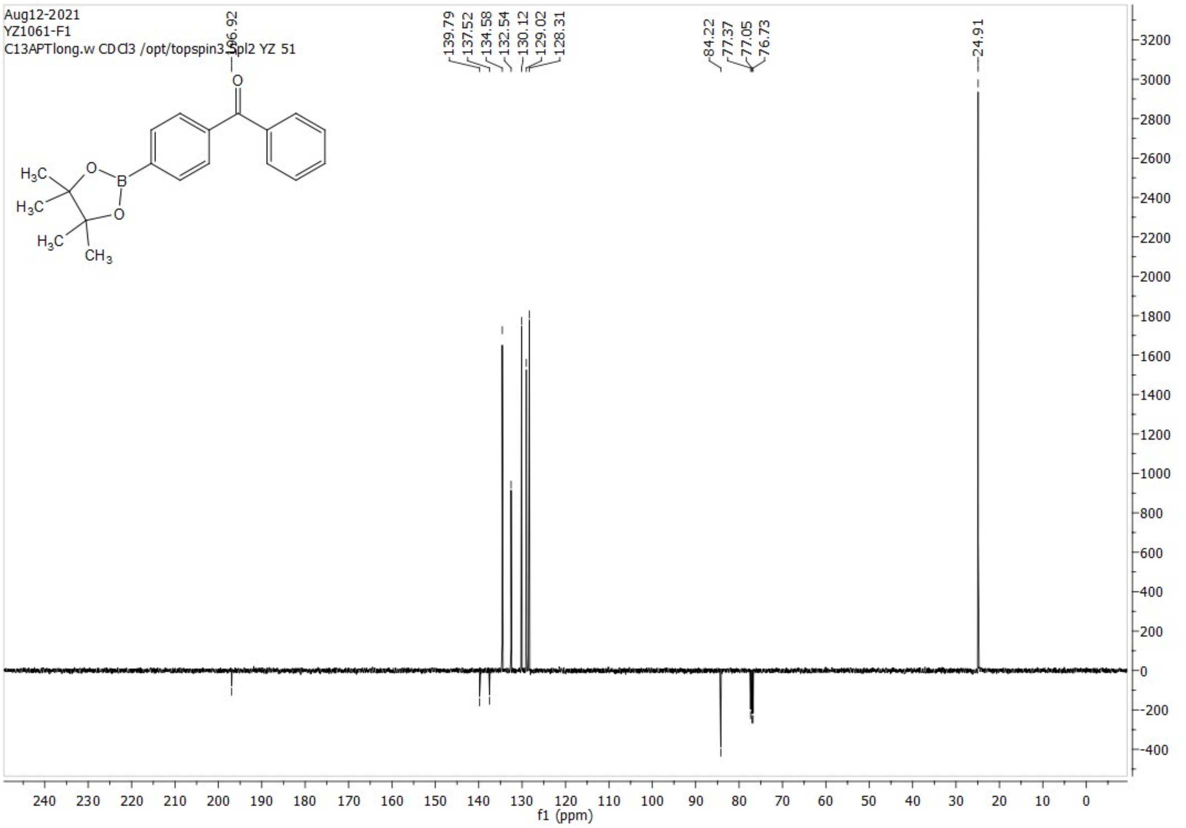
A round-bottom flask was charged with (4-bromophenyl)(phenyl)methanone (260 mg, 1.00 mmol), bis(pinacolato)diboron (305 mg, 1.20 mmol), potassium acetate (294 mg, 3.00 mmol), THF (5 mL) and Pd(dppf)$_2$Cl$_2$·DCM (40.9 mg, 0.0500 mmol). The reaction mixture was heated to 65 °C and left stirring under the nitrogen atmosphere for 2 days, followed by TLC (4:1 hexane: EtOAc). The mixture was quenched by distilled water (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried ($MgSO_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-20% ethyl acetate in hexane to give phenyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone as a white solid (110 mg, 0.357 mmol, 36%). TLC: Rf ca 0.50 (4:1 hexane: EtOAc), strong UV and $KMnO_4$; $\delta_H$ (500 MHz, $CDCl_3$) 7.93 (2H, d, *J* = 8.0, ArH), 7.80-7.76 (4H, m, ArH), 7.59 (1H, t, *J* = 7.5, ArH), 7.47 (2H, t, *J* = 7.5, ArH), 1.37 (12H, s, $CH_3$) ppm; $\delta_C$ (125 MHz, $CDCl_3$) 196.92 (C), 139.79 (C), 137.52 (C), 134.58 (CH), 132.54 (CH), 130.12 (CH), 129.02 (CH), 128.31 (CH), 84.22 (C), 24.91 ($CH_3$) ppm; m/z (ES-API+) 331.1 ($M^+$ + 23, 100%). Data matched that reported.

Enantiomeric excess and conversion determined by HPLC analysis (Chiralcel OJ, 30 cm x 6mm column, hexane:iPrOH 90:10, 1.0 mL/min, T = 25°C) ketone 5.5 min, *R* and *S* isomers 11.8 min and 18.8 min.

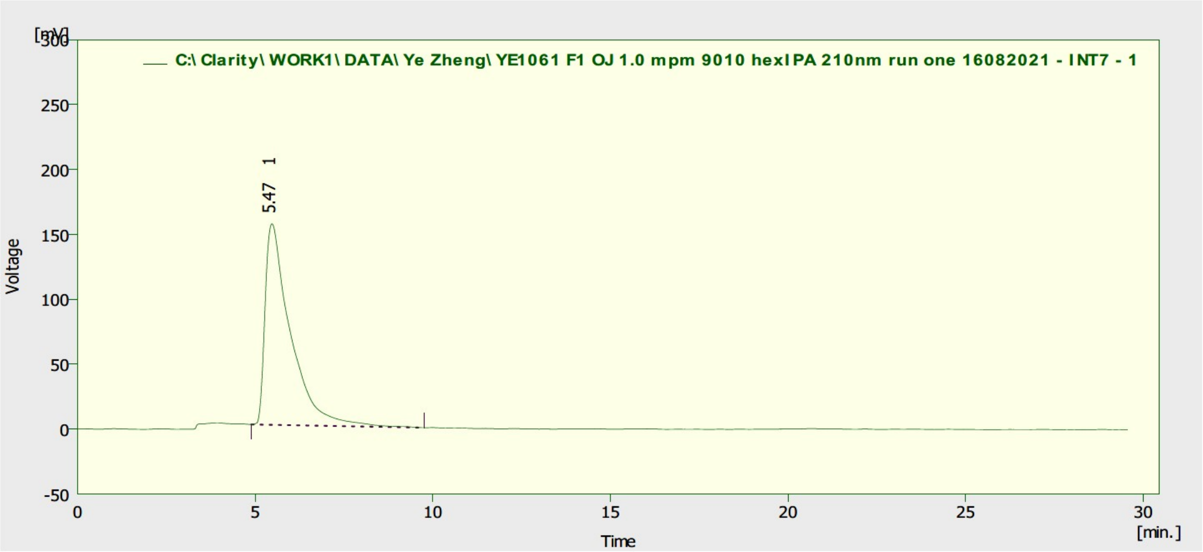
$^{1}$H NMR (400 MHz, CDCl$_3$)



$^{13}$C NMR (100 MHz, CDCl$_3$)



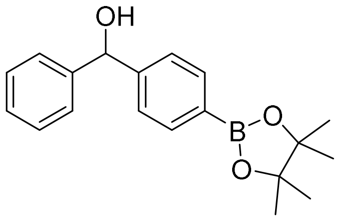
HPLC of phenyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone

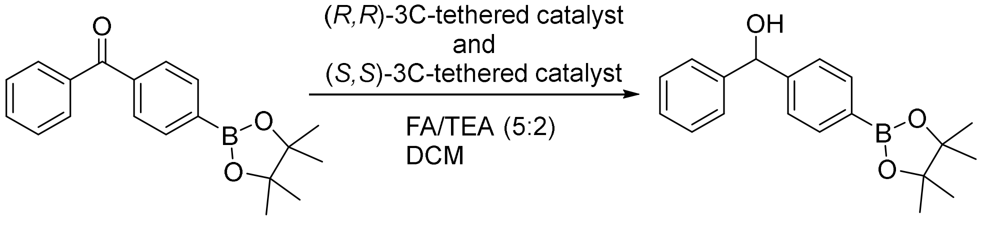


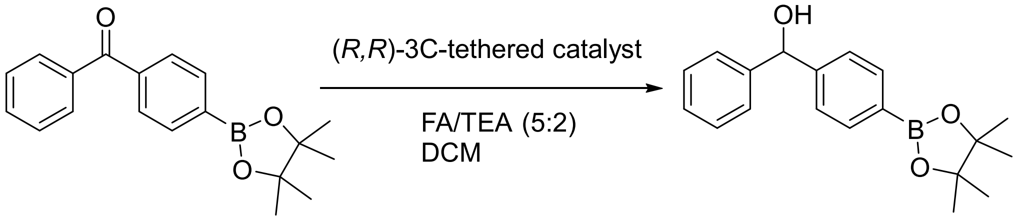
*Result Table (Uncal - C: \Clarity\WORK1\DATA\Ye Zheng\YE1061 F1 OJ 1.0 mpm 9010 hexIPA 210nm run one 16082021 - INT7 - 1)*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Compound Name |
|---|---|---|---|---|---|---|---|
| 1 | 5.470 | 7721.544 | 154.977 | 100.0 | 100.0 | 0.69 | |
| | Total | 7721.544 | 154.977 | 100.0 | 100.0 | | |

Phenyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanol **22**.







This compound has been reported and fully characterized: Y. Ashikari, T. Kawaguchi, K. Mandai, Y. Aizawa, A. Nagaki, *J. Am. Chem. Soc.* 2020, **142**, 17039-17047.

**Synthesis of a racemic standard:**

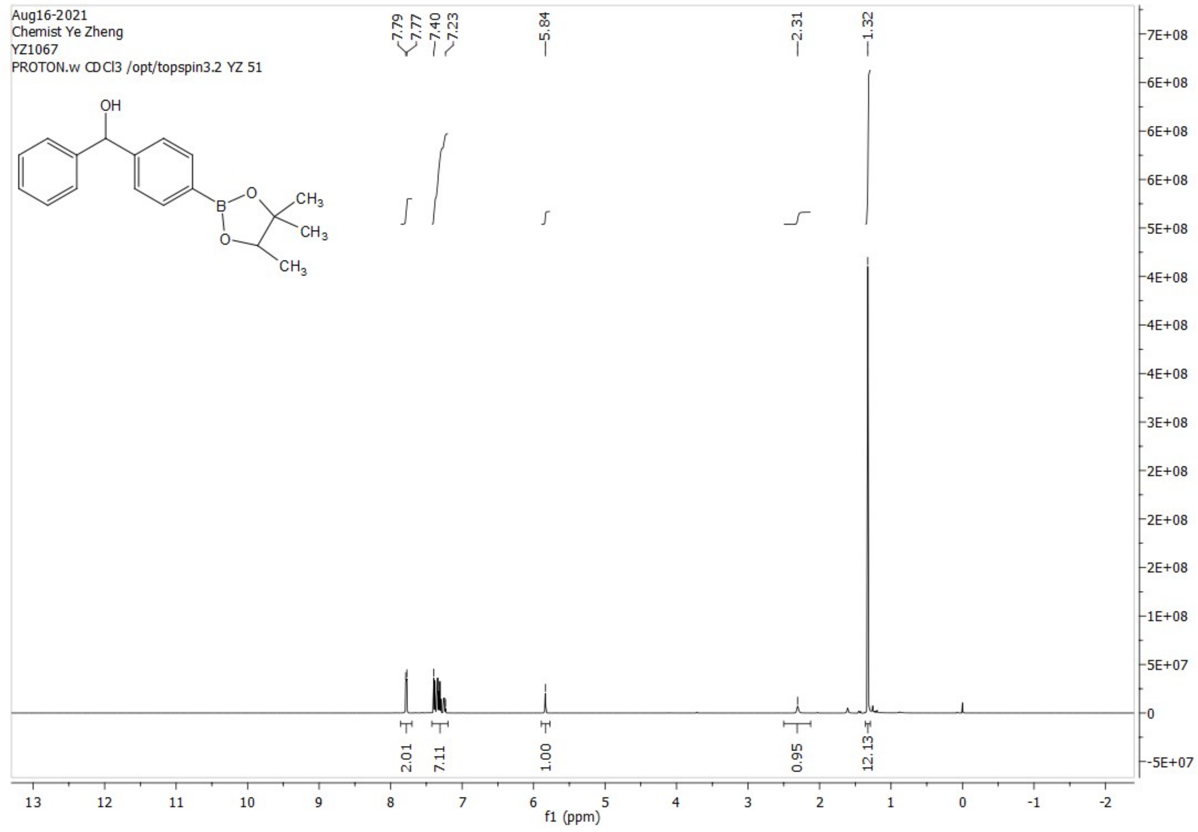
(*R,R*)-3C-Tethered Ru(II)-TsDPEN catalyst **2** (0.40 mg, 0.65 μmol, 0.5 mol%) and (*S,S*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (0.40 mg, 0.65 μmol, 0.5 mol%) were added to FA: TEA (5:2 azeotropic mixture, 0.18 mL) at rt and the mixture was stirred under a nitrogen atmosphere for 15 minutes; after which a solution of phenyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone (40.0 mg, 0.130 mmol) in DCM (0.25 mL) was added. The reaction mixture was stirrer under a nitrogen atmosphere and followed by TLC (9:1 hexane: EtOAc). After 72 hours, the reaction was quenched using saturated $NaHCO_3$ solution (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried ($MgSO_4$) and filtered. The solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-50% EtOAc in hexane to give phenyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanol **22** as a colorless oil (17.7 mg, 0.0571 mmol, 54%). TLC: Rf ca 0.20 (9:1 hexane: EtOAc), strong UV and $KMnO_4$; $\delta_H$ (500 MHz, $CDCl_3$) 7.79 (2H, d, $J$ = 8.0, ArH), 7.40-7.23 (7H, m, ArH), 5.84 (1H, s, ArCH), 2.31 (1H, s, OH), 1.32 (12H, s, $CH_3$) ppm; $\delta_C$ (125 MHz, $CDCl_3$)

146.83 (C), 143.68 (C), 135.02 (CH), 128.54 (CH), 127.66 (CH), 126.64 (CH), 125.78 (CH), 83.81 (C), 76.28 (CH), 24.86 ($CH_3$) ppm; m/z (ES-API+) 333.2 ($M^+$ + 23, 100%). Data matched that reported.

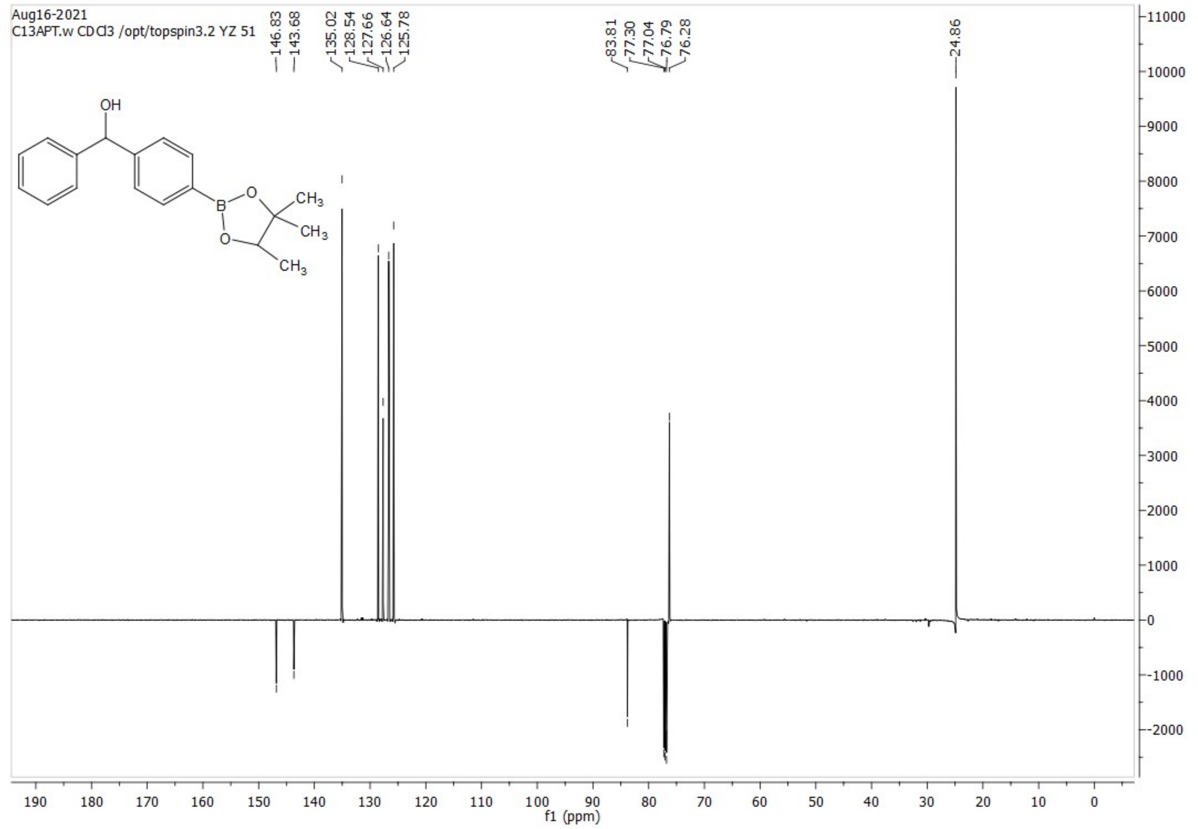
Enantiomeric excess and conversion determined by HPLC analysis (Chiralcel OJ, 30 cm x 6mm column, hexane:iPrOH 90:10, 1.0 mL/min, T = 25°C) ketone 5.5 min, *R* and *S* isomers 11.8 min and 18.8 min, configuration is not confirmed.

ATH of phenyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone): (*R,R*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (0.806 mg, 0.130 μmol, 1 mol%) was added to FA: TEA (5:2 azeotropic mixture, 0.18 mL) at rt and the mixture was stirred under a nitrogen atmosphere for 15 minutes; after which a solution of phenyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone (40.0 mg, 0.130 mmol) in DCM (0.25 mL) was added. The reaction mixture was stirred under a nitrogen atmosphere and followed by TLC (9:1 hexane: EtOAc). After 72 hours, the reaction was quenched using saturated $NaHCO_3$ solution (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried ($MgSO_4$) and filtered. The solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-50% EtOAc in hexane to give phenyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanol **22** as a colorless oil (12.4 mg, 0.0400 mmol, 31%). The reaction was also followed by HPLC (Chiralcel OJ, 30 cm x 6mm column, hexane:iPrOH 90:10, 1.0 mL/min, T = 25°C): 8% ee.

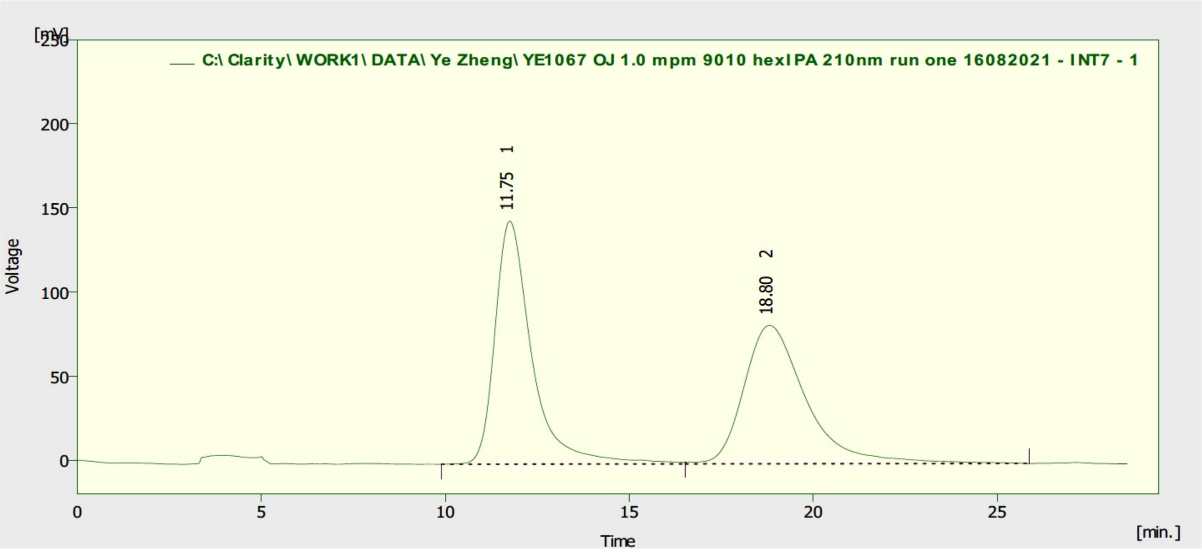
$^1$H NMR (500 MHz, CDCl$_3$)



$^{13}$C NMR (125 MHz, CDCl$_3$)



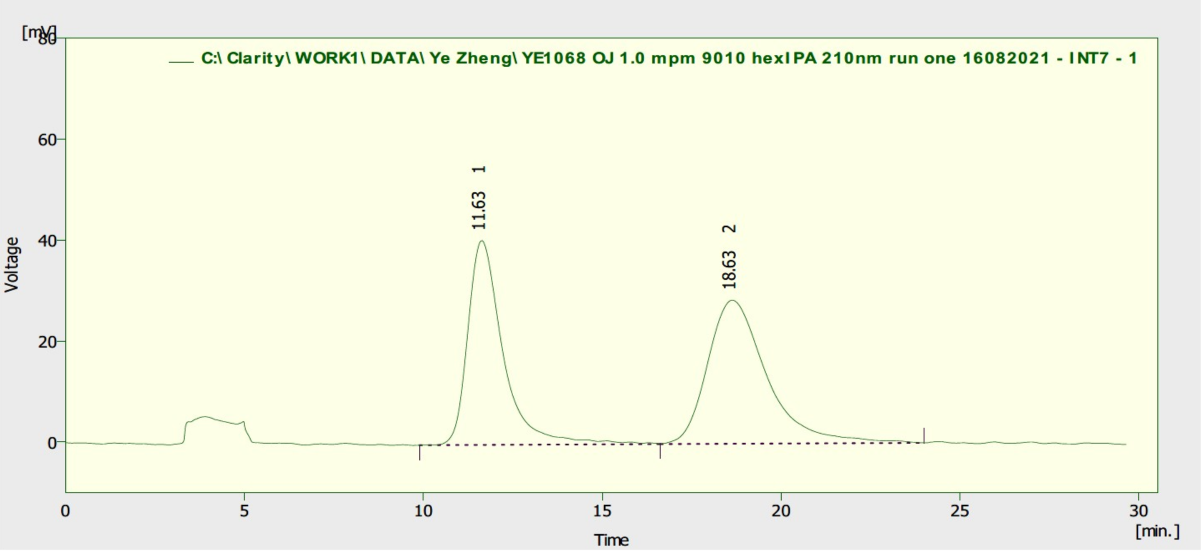
HPLC of racemic phenyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanol **22**



*Result Table (Uncal - C:\Clarity\WORK1\DATA\Ye Zheng\YE1067 OJ 1.0 mpm 9010 hexIPA 210nm run one 16082021 - INT7 - 1)*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Compound Name |
|---|---|---|---|---|---|---|---|
| 1 | 11.753 | 10119.368 | 144.496 | 51.1 | 63.7 | 0.98 | |
| 2 | 18.803 | 9687.162 | 82.356 | 48.9 | 36.3 | 1.70 | |
| | Total | 19806.530 | 226.852 | 100.0 | 100.0 | | |

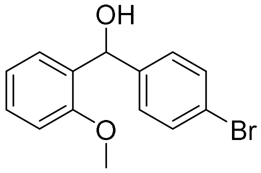
HPLC after ATH of phenyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone using (*R,R*)-3C-Tethered Ru(II)-TsDPEN catalyst **2** (after 72 hours, 100% conversion, 8% ee)

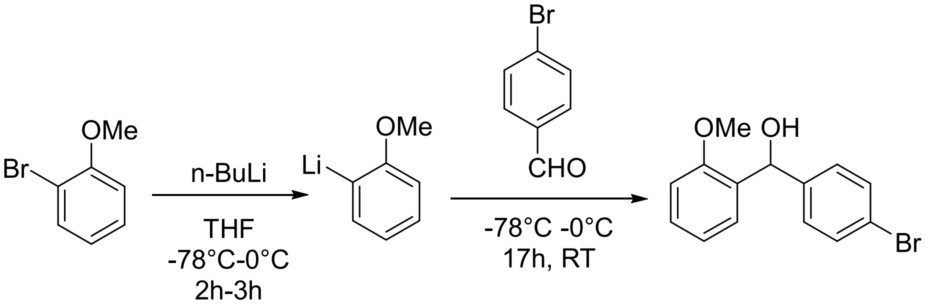


*Result Table (Uncal - C:\Clarity\WORK1\DATA\Ye Zheng\YE1068 OJ 1.0 mpm 9010 hexIPA 210nm run one 16082021 - INT7 - 1)*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Compound Name |
|---|---|---|---|---|---|---|---|
| 1 | 11.630 | 2790.133 | 40.447 | 46.1 | 58.7 | 0.97 | |
| 2 | 18.633 | 3268.610 | 28.428 | 53.9 | 41.3 | 1.67 | |
| | Total | 6058.743 | 68.875 | 100.0 | 100.0 | | |

(4-Bromophenyl)(2-methoxyphenyl)methanol.

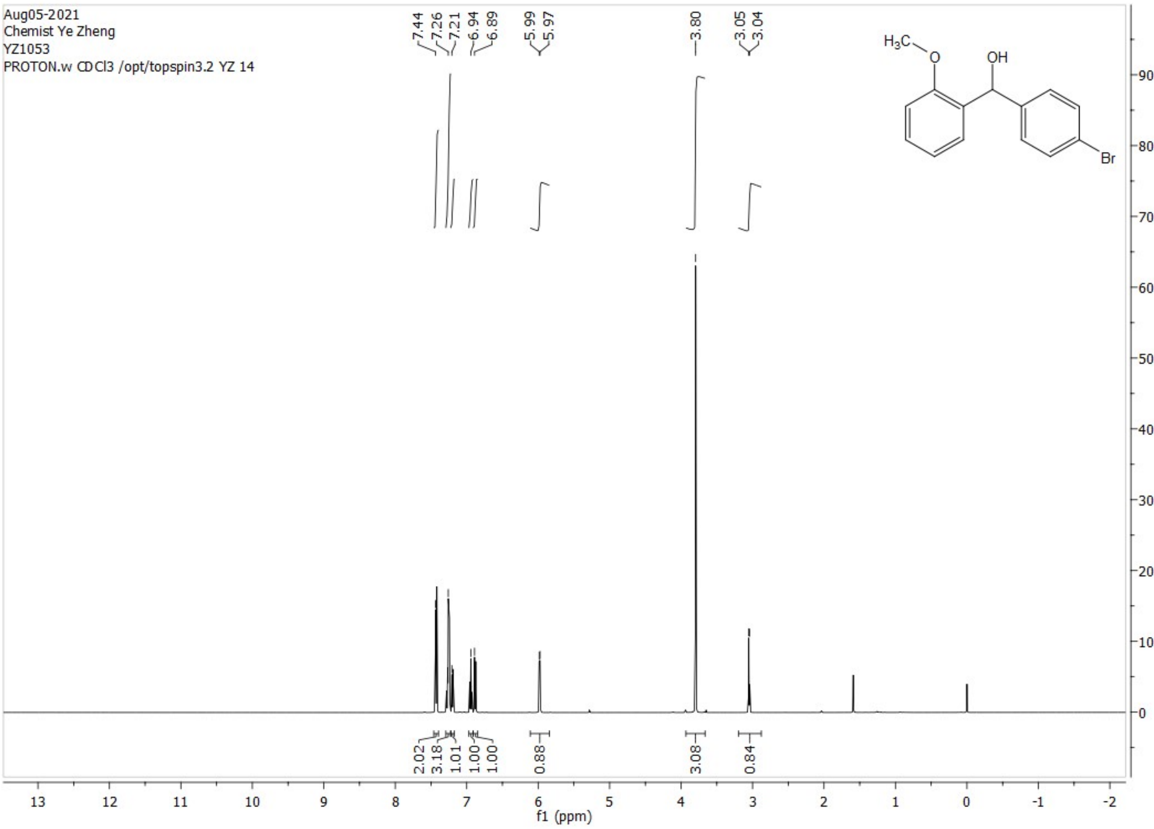




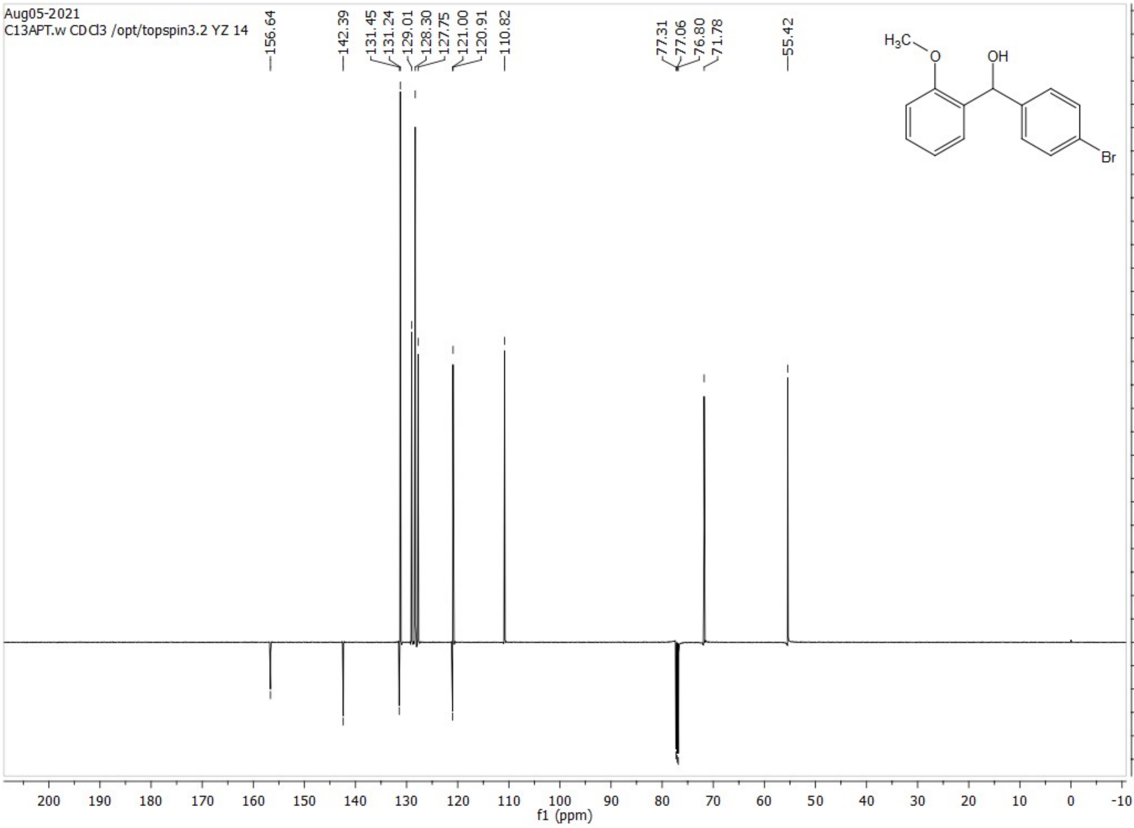
This compound is novel.

To a solution of 2-bromoanisole (514 mg, 2.75 mmol) in THF (3.3 mL) at -78 °C was added dropwise a solution of n-butyllithium (1.00 mL, 2.5M in hexanes, 2.50 mmol). The reaction mixture was then stirred under a nitrogen atmosphere for 2-3 hours, after which 4-bromobenzaldehyde (463 mg, 2.50 mmol) was added dropwise. The reaction mixture was left stirring under the nitrogen atmosphere and allowed to warm to rt. The reaction was followed by TLC (9:1 hexane: EtOAc). The mixture was quenched by saturated $NH_4Cl$ solution (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried ($MgSO_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-20% EtOAc in hexane to give (4-bromophenyl)(2-methoxyphenyl)methanol as a white solid (564 mg, 1.93 mmol, 77%). TLC: Rf ca 0.20 (9:1 hexane: EtOAc), strong UV and $KMnO_4$; Mp: 75°C; HRMS: (found (ESI+): [M+H]+, Calcd for $C_{14}H_{13}{}^{79}BrNaO_2$ 314.9983; Found 314.9991; 2.7 ppm error); $\nu_{max}$ 3212 (br), 2998, 2938, 1587, 1485, 1462, 1437, 1279, 1240, 1184, 1046, 1029, 807, 751 cm$^{-1}$; $\delta_H$ (500 MHz, $CDCl_3$) 7.44 (2H, d, *J* = 8.5, ArH), 7.26 (3H, ddd, *J* = 6.9, 6.3, 2.1, ArH), 7.21 (1H, dd, *J* = 7.5, ArH), 6.94 (1H, t, *J* = 7.5, ArH), 6.89 (1H, d, *J* = 8.2, ArH), 5.99 (1H, d, *J* = 5.6, ArCH), 3.80 (3H, s, $OCH_3$), 3.05 (1H, d, *J* = 5.6, OH) ppm; $\delta_C$ (125 MHz, $CDCl_3$) 156.64 (C), 142.39 (C), 131.45 (C), 131.24 (CH), 129.01 (CH), 128.30 (CH), 127.75 (CH), 121.00 (C), 120.91 (CH), 110.82 (CH), 72.78 (CH), 55.42 ($CH_3$) ppm; m/z (ES-API+) 315.0 ($M^+$ + 23, 100%).

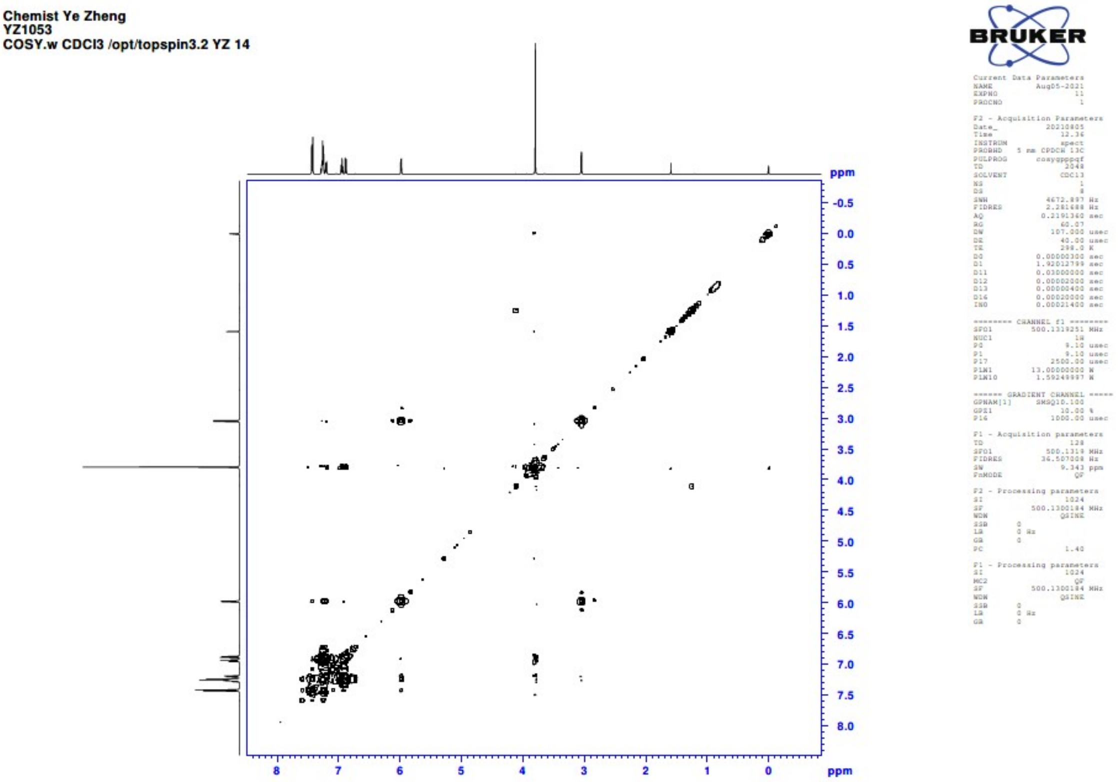
$^{1}$H NMR (500 MHz, CDCl$_3$)



$^{13}$C NMR (125 MHz, CDCl$_3$)



COSY (500 MHz, $CDCl_3$)



**Chemist Ye Zheng**
**YZ1053**
**COSY.w CDCl3 /opt/topspin3.2 YZ 14**

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Current Data Parameters
NAME           Aug05-2021
EXPNO                  11
PROCNO                  1

F2 - Acquisition Parameters
Date_            20210805
Time                12.36
INSTRUM             spect
PROBHD   5 mm CPDCH 13C
PULPROG        cosygpppqf
TD                   2048
SOLVENT             CDCl3
NS                      1
DS                      8
SWH              4672.897 Hz
FIDRES           2.281688 Hz
AQ              0.2191360 sec
RG                  60.07
DW                107.000 usec
DE                  40.00 usec
TE                  298.0 K
D0             0.00000300 sec
D1             1.92012799 sec
D11            0.03000000 sec
D12            0.00002000 sec
D13            0.00000400 sec
D16            0.00020000 sec
IN0            0.00021400 sec

======== CHANNEL f1 ========
SFO1          500.1319251 MHz
NUC1                   1H
P0                   9.10 usec
P1                   9.10 usec
P17               2500.00 usec
PLW1          13.00000000 W
PLW10          1.59249997 W

====== GRADIENT CHANNEL =====
GPNAM[1]       SMSQ10.100
GPZ1                10.00 %
P16               1000.00 usec

F1 - Acquisition parameters
TD                    128
SFO1             500.1319 MHz
FIDRES          36.507008 Hz
SW                  9.343 ppm
FnMODE                 QF

F2 - Processing parameters
SI                   1024
SF            500.1300184 MHz
WDW                 QSINE
SSB       0
LB        0 Hz
GB        0
PC                   1.40

F1 - Processing parameters
SI                   1024
MC2                    QF
SF            500.1300184 MHz
WDW                 QSINE
SSB       0
LB        0 Hz
GB        0
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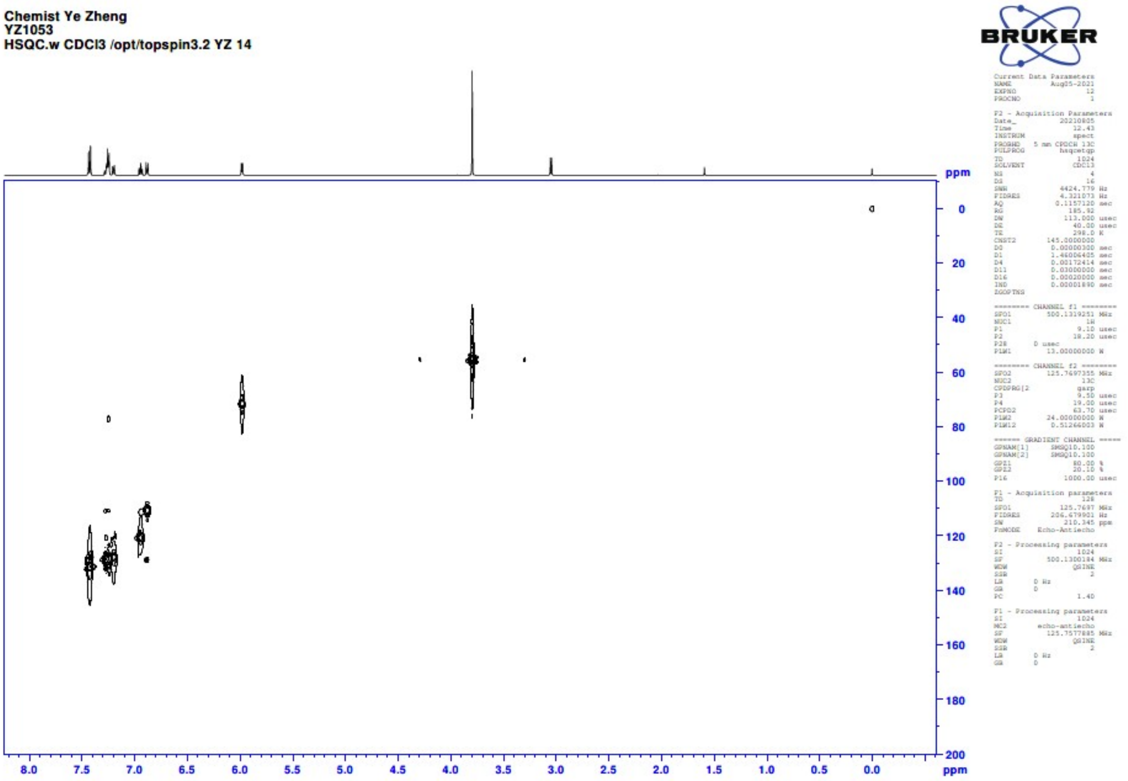
HSQC (500 MHz, $CDCl_3$)



**Chemist Ye Zheng**
**YZ1053**
**HSQC.w CDCl3 /opt/topspin3.2 YZ 14**

```
Current Data Parameters
NAME           Aug05-2021
EXPNO                  12
PROCNO                  1

F2 - Acquisition Parameters
Date_            20210805
Time                12.43
INSTRUM             spect
PROBHD   5 mm CPDCH 13C
PULPROG          hsqcetgp
TD                   1024
SOLVENT             CDCl3
NS                      4
DS                     16
SWH              4424.779 Hz
FIDRES           4.321073 Hz
AQ              0.1157120 sec
RG                 185.92
DW                113.000 usec
DE                  40.00 usec
TE                  298.0 K
CNST2         145.0000000
D0             0.00000300 sec
D1             1.46006405 sec
D4             0.00172414 sec
D11            0.03000000 sec
D16            0.00020000 sec
IN0            0.00001890 sec
ZGOPTNS

======== CHANNEL f1 ========
SFO1          500.1319251 MHz
NUC1                   1H
P1                   9.10 usec
P2                  18.20 usec
P28       0 usec
PLW1          13.00000000 W

======== CHANNEL f2 ========
SFO2          125.7697355 MHz
NUC2                  13C
CPDPRG[2             garp
P3                   9.50 usec
P4                  19.00 usec
PCPD2               63.70 usec
PLW2          24.00000000 W
PLW12          0.51266003 W

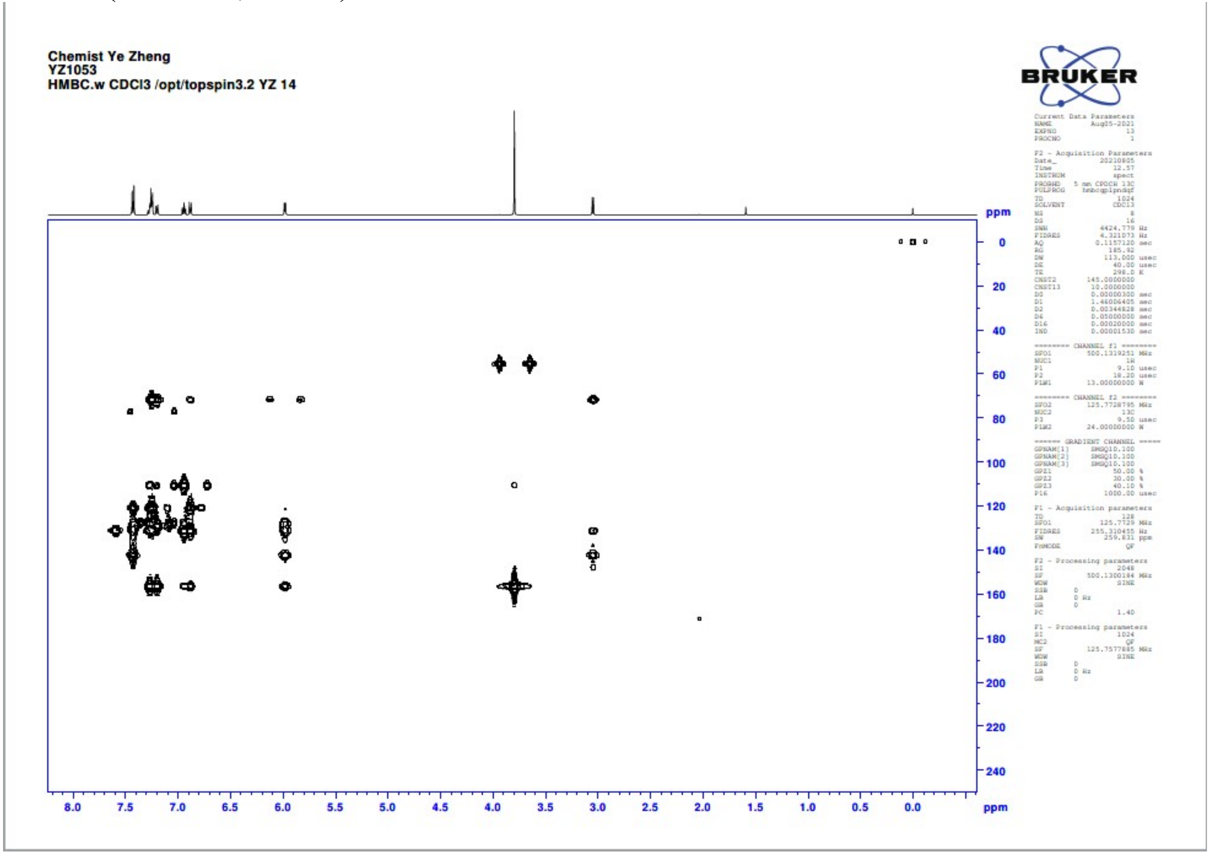
====== GRADIENT CHANNEL =====
GPNAM[1]       SMSQ10.100
GPNAM[2]       SMSQ10.100
GPZ1                80.00 %
GPZ2                20.10 %
P16               1000.00 usec

F1 - Acquisition parameters
TD                    128
SFO1             125.7697 MHz
FIDRES         206.679901 Hz
SW                210.345 ppm
FnMODE       Echo-Antiecho

F2 - Processing parameters
SI                   1024
SF            500.1300184 MHz
WDW                 QSINE
SSB                     2
LB        0 Hz
GB        0
PC                   1.40

F1 - Processing parameters
SI                   1024
MC2          echo-antiecho
SF            125.7577885 MHz
WDW                 QSINE
SSB                     2
LB        0 Hz
GB        0
```

HMBC (500 MHz, $CDCl_3$)



**Chemist Ye Zheng**
**YZ1053**
**HMBC.w CDCl3 /opt/topspin3.2 YZ 14**

```
Current Data Parameters
NAME          Aug05-2021
EXPNO                 13
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210805
Time               12.57
INSTRUM            spect
PROBHD   5 mm CPDCH 13C
PULPROG      hmbcgplpndqf
TD                  1024
SOLVENT            CDCl3
NS                     8
DS                    16
SWH            4424.779 Hz
FIDRES         4.321073 Hz
AQ            0.1157120 sec
RG                185.92
DW               113.000 usec
DE                 40.00 usec
TE                 298.0 K
CNST2        145.0000000
CNST13        10.0000000
D0            0.00000300 sec
D1            1.46006405 sec
D2            0.00344828 sec
D6            0.05000000 sec
D16           0.00020000 sec
IN0           0.00001530 sec

======== CHANNEL f1 ========
SFO1        500.1319251 MHz
NUC1                 1H
P1                 9.10 usec
P2                18.20 usec
PLW1        13.00000000 W

======== CHANNEL f2 ========
SFO2        125.7728795 MHz
NUC2                13C
P3                 9.50 usec
PLW2        24.00000000 W

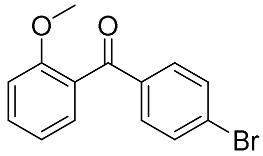
====== GRADIENT CHANNEL =====
GPNAM[1]      SMSQ10.100
GPNAM[2]      SMSQ10.100
GPNAM[3]      SMSQ10.100
GPZ1               50.00 %
GPZ2               30.00 %
GPZ3               40.10 %
P16              1000.00 usec

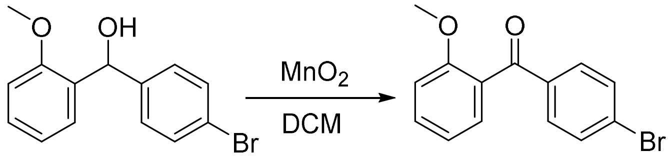
F1 - Acquisition parameters
TD                   128
SFO1         125.7729 MHz
FIDRES       255.310455 Hz
SW             259.831 ppm
FnMODE                QF

F2 - Processing parameters
SI                  2048
SF          500.1300184 MHz
WDW                 SINE
SSB       0
LB        0 Hz
GB        0
PC                  1.40

F1 - Processing parameters
SI                  1024
MC2                   QF
SF          125.7577885 MHz
WDW                 SINE
SSB       0
LB        0 Hz
GB        0
```

(4-Bromophenyl)(2-methoxyphenyl)methanone.

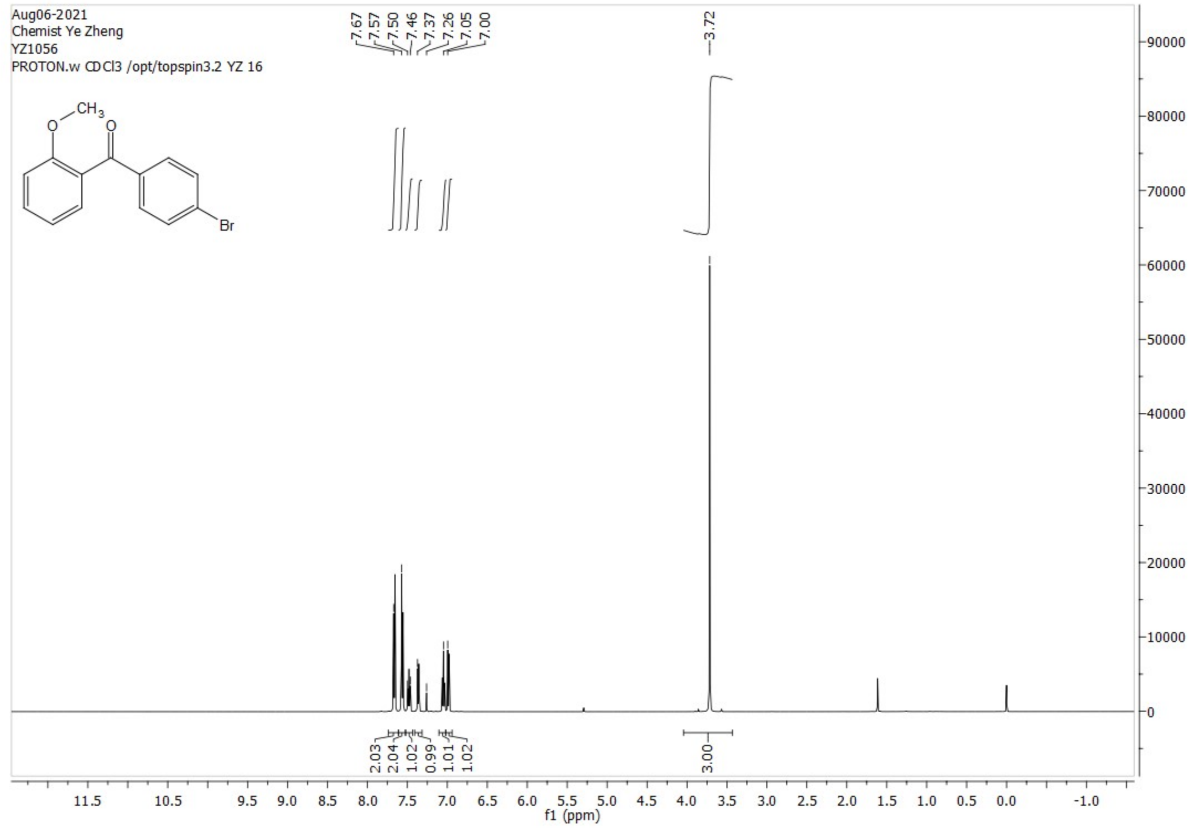




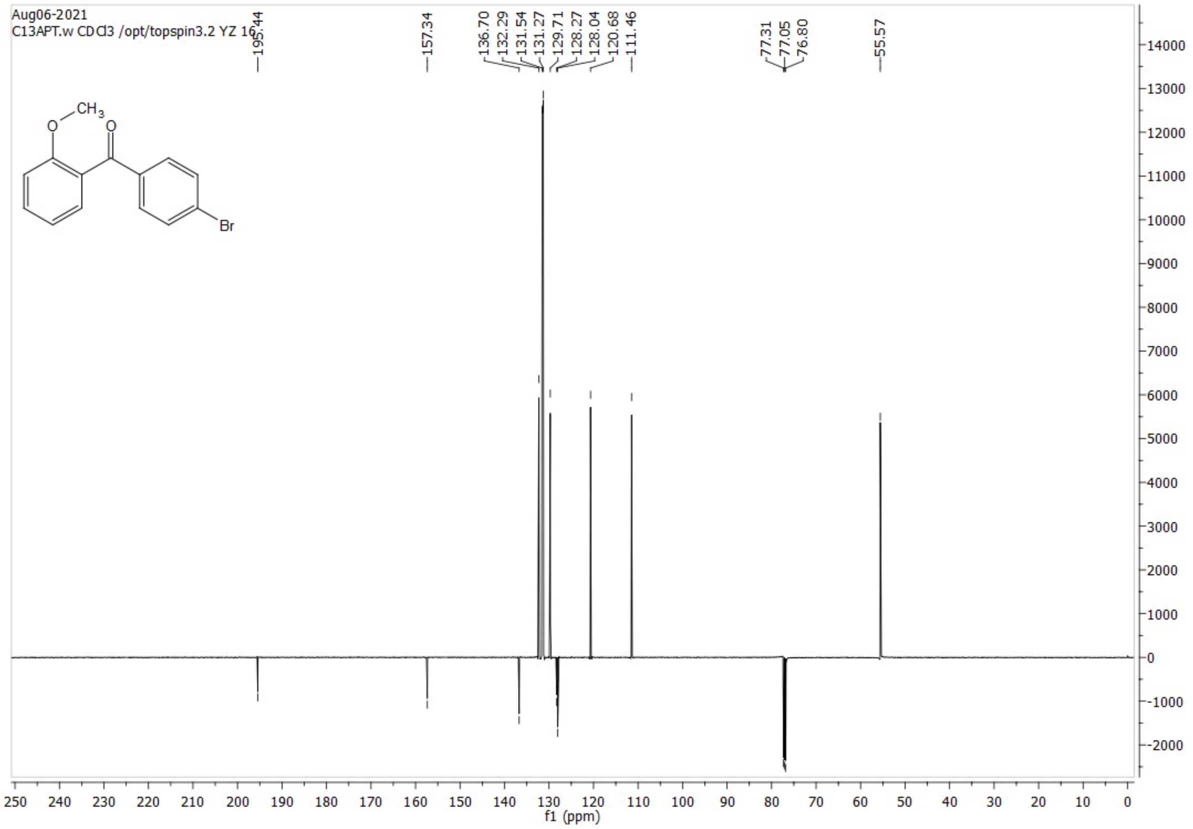
This compound is novel.

To a solution of (4-bromophenyl)(2-methoxyphenyl)methanol (560 mg, 1.92 mmol) in DCM (12 mL) at rt was added manganese dioxide (2.50 g, 28.8 mmol). The reaction mixture was left to stir under a nitrogen atmosphere overnight. TLC (9:1 hexane: EtOAc) after this time indicated full conversion. The solids were removed by gravity filtration and washed with DCM. The combined solvent was removed to give the product a white solid (337 mg, 1.16 mmol, 61%). TLC: Rf ca 0.40 (9:1 hexane: EtOAc), strong UV and $KMnO_4$; Mp: 108°C; HRMS: (found (ESI+): [M+H]+, Calcd for $C_{14}H_{11}{}^{79}BrNaO_2$ 312.9831; Found 312.9835; 1.1 ppm error; $\nu_{max}$ 3091, 2979, 1658, 1599, 1580, 1482, 1451, 1294, 1241, 1065, 1011, 923, 729 $cm^{-1}$; $\delta_H$ (500 MHz, $CDCl_3$) 7.67 (2H, d, *J* = 8.5, ArH), 7.57 (2H, d, *J* = 8.5, ArH), 7.50-7.46 (1H, m, ArH), 7.37 (1H, dd, *J* = 7.5, 1.6, ArH), 7.05 (1H, t, *J* = 7.5, ArH), 7.00 (1H, d, *J* = 8.5, ArH), 3.72 (3H, s, $OCH_3$) ppm; $\delta_C$ (125 MHz, $CDCl_3$) 195.44 (C), 157.34 (C), 136.70 (C), 132.29 (CH), 131.54 (CH), 131.27 (CH), 129.71 (CH), 128.27 (C), 128.04 (C), 120.68 (CH), 111.46 (CH), 55.57 ($CH_3$) ppm; m/z (ES-API+) 313.0 ($M^+$ + 23, 100%).

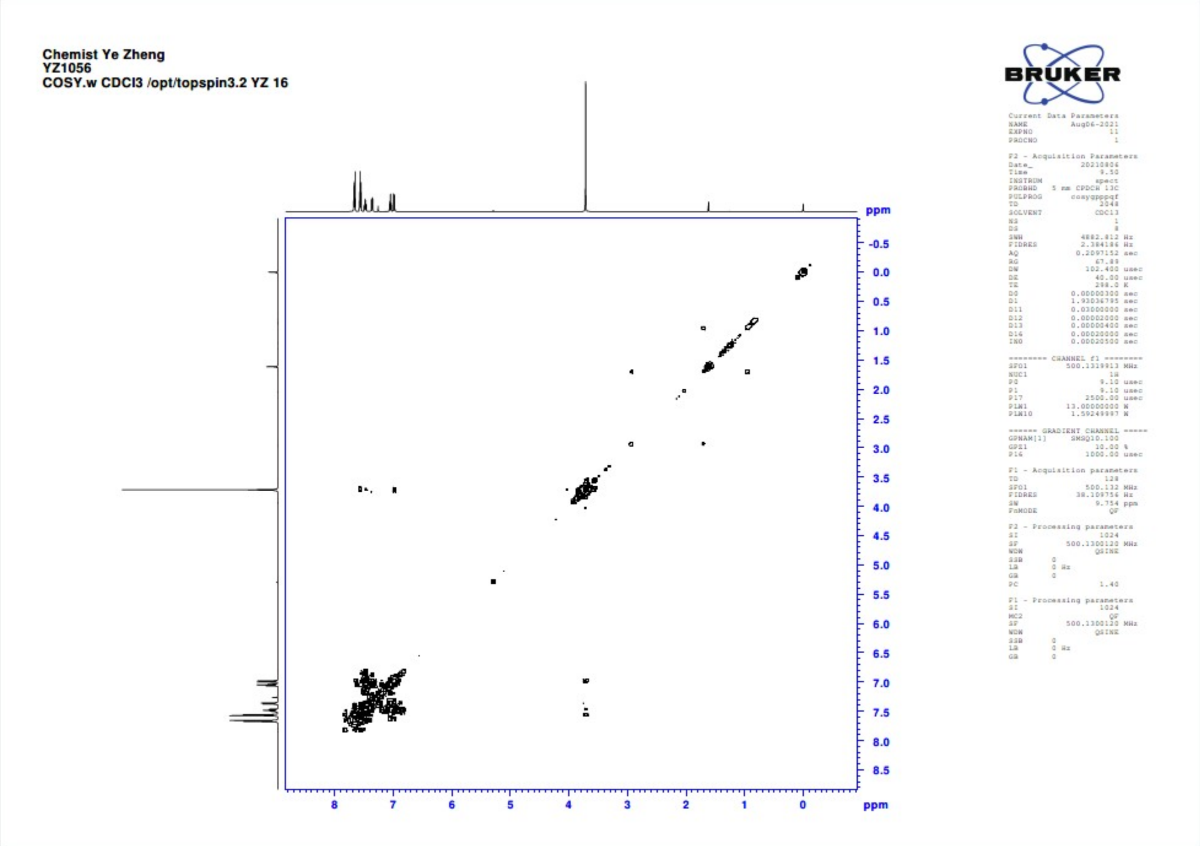
$^{1}$H NMR (500 MHz, CDCl$_3$)



$^{13}$C NMR (125 MHz, CDCl$_3$)



COSY (500 MHz, CDCl$_3$)



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Current Data Parameters
NAME          Aug06-2021
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210806
Time                9.50
INSTRUM            spect
PROBHD   5 mm CPDCH 13C
PULPROG       cosygpppqf
TD                  2048
SOLVENT            CDCl3
NS                     1
DS                     8
SWH             4882.812 Hz
FIDRES          2.384186 Hz
AQ             0.2097152 sec
RG                 67.89
DW               102.400 usec
DE                 40.00 usec
TE                 298.0 K
D0            0.00000300 sec
D1            1.93036795 sec
D11           0.03000000 sec
D12           0.00002000 sec
D13           0.00000400 sec
D16           0.00020000 sec
IN0           0.00020500 sec

======== CHANNEL f1 ========
SFO1         500.1319913 MHz
NUC1                  1H
P0                  9.10 usec
P1                  9.10 usec
P17              2500.00 usec
PLW1         13.00000000 W
PLW10         1.59249997 W

====== GRADIENT CHANNEL =====
GPNAM[1]        SMSQ10.100
GPZ1               10.00 %
P16              1000.00 usec

F1 - Acquisition parameters
TD                   128
SFO1             500.132 MHz
FIDRES         38.109756 Hz
SW                 9.754 ppm
FnMODE                QF

F2 - Processing parameters
SI                  1024
SF           500.1300120 MHz
WDW                QSINE
SSB      0
LB       0 Hz
GB       0
PC                  1.40

F1 - Processing parameters
SI                  1024
MC2                   QF
SF           500.1300120 MHz
WDW                QSINE
SSB      0
LB       0 Hz
GB       0
```
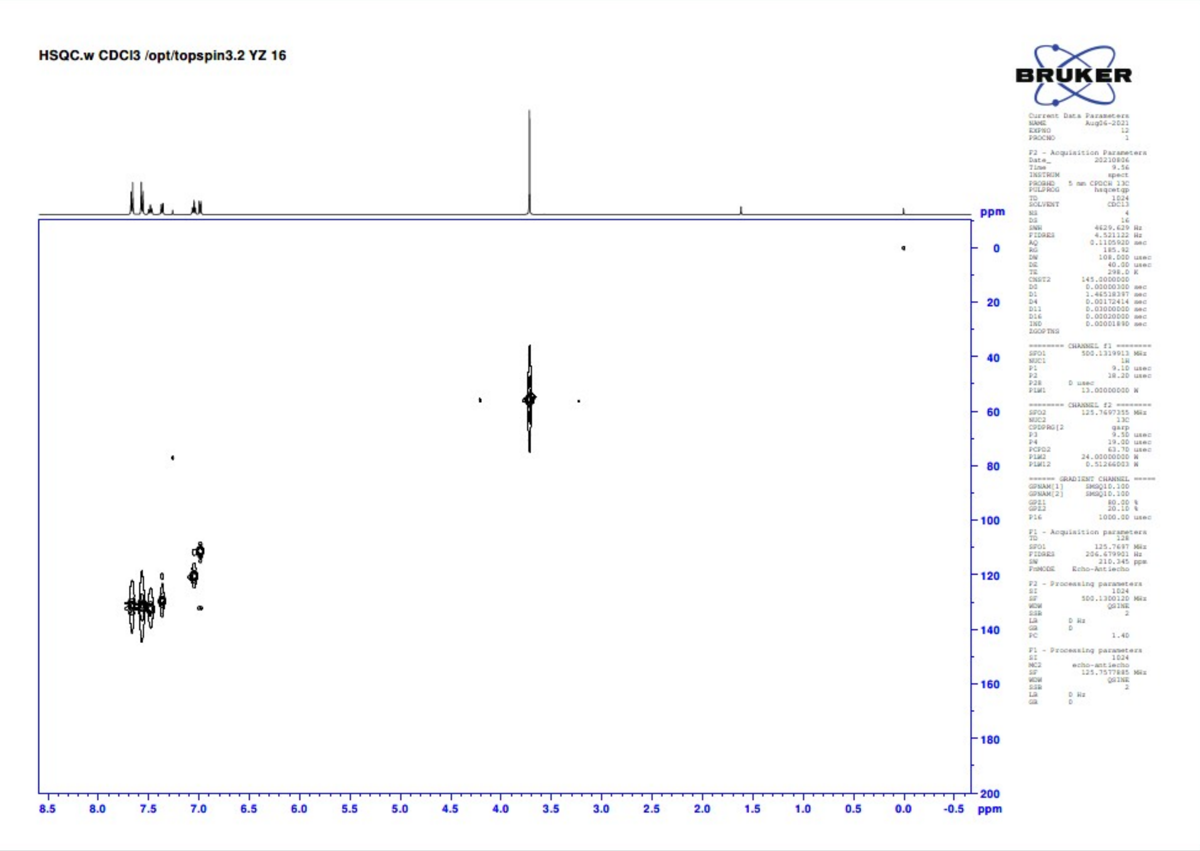

HSQC (500 MHz, CDCl$_3$)



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Current Data Parameters
NAME          Aug06-2021
EXPNO                 12
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210806
Time                9.56
INSTRUM            spect
PROBHD   5 mm CPDCH 13C
PULPROG         hsqcetgp
TD                  1024
SOLVENT            CDCl3
NS                     4
DS                    16
SWH             4629.629 Hz
FIDRES          4.521122 Hz
AQ             0.1105920 sec
RG                185.92
DW               108.000 usec
DE                 40.00 usec
TE                 298.0 K
CNST2        145.0000000
D0            0.00000300 sec
D1            1.46518397 sec
D4            0.00172414 sec
D11           0.03000000 sec
D16           0.00020000 sec
IN0           0.00001890 sec
ZGOPTNS

======== CHANNEL f1 ========
SFO1         500.1319913 MHz
NUC1                  1H
P1                  9.10 usec
P2                 18.20 usec
P28      0 usec
PLW1         13.00000000 W

======== CHANNEL f2 ========
SFO2         125.7697355 MHz
NUC2                 13C
CPDPRG[2            garp
P3                  9.50 usec
P4                 19.00 usec
PCPD2              63.70 usec
PLW2         24.00000000 W
PLW12         0.51266003 W

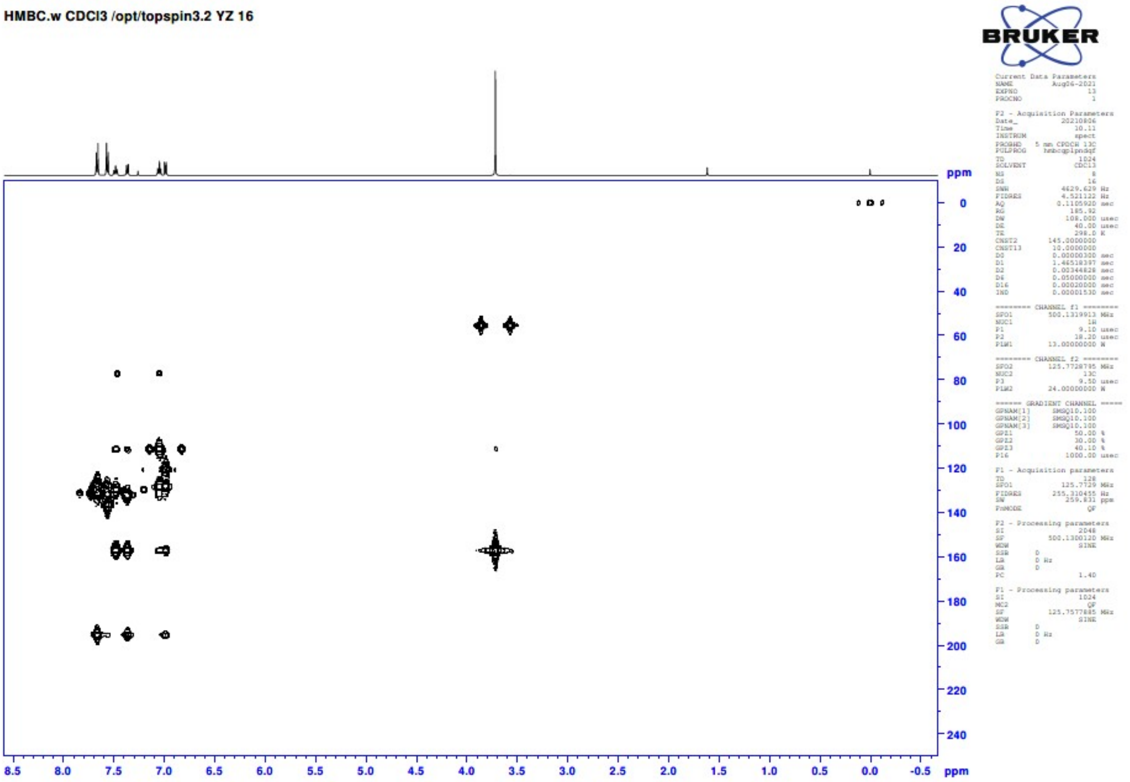
====== GRADIENT CHANNEL =====
GPNAM[1]        SMSQ10.100
GPNAM[2]        SMSQ10.100
GPZ1               80.00 %
GPZ2               20.10 %
P16              1000.00 usec

F1 - Acquisition parameters
TD                   128
SFO1            125.7697 MHz
FIDRES        206.679901 Hz
SW               210.345 ppm
FnMODE      Echo-Antiecho

F2 - Processing parameters
SI                  1024
SF           500.1300120 MHz
WDW                QSINE
SSB                    2
LB       0 Hz
GB       0
PC                  1.40

F1 - Processing parameters
SI                  1024
MC2         echo-antiecho
SF           125.7577885 MHz
WDW                QSINE
SSB                    2
LB       0 Hz
GB       0
```

# HMBC (500 MHz, CDCl$_3$)



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Current Data Parameters
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EXPNO                 13
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210806
Time               10.11
INSTRUM            spect
PROBHD   5 mm CPDCH 13C
PULPROG      hmbcgplpndqf
TD                  1024
SOLVENT            CDCl3
NS                     8
DS                    16
SWH             4629.629 Hz
FIDRES          4.521122 Hz
AQ             0.1105920 sec
RG                185.92
DW               108.000 usec
DE                 40.00 usec
TE                 298.0 K
CNST2        145.0000000
CNST13        10.0000000
D0            0.00000300 sec
D1            1.46518397 sec
D2            0.00344828 sec
D6            0.05000000 sec
D16           0.00020000 sec
IN0           0.00001530 sec

======== CHANNEL f1 ========
SFO1         500.1319913 MHz
NUC1                  1H
P1                  9.10 usec
P2                 18.20 usec
PLW1         13.00000000 W

======== CHANNEL f2 ========
SFO2         125.7728795 MHz
NUC2                 13C
P3                  9.50 usec
PLW2         24.00000000 W

====== GRADIENT CHANNEL =====
GPNAM[1]      SMSQ10.100
GPNAM[2]      SMSQ10.100
GPNAM[3]      SMSQ10.100
GPZ1               50.00 %
GPZ2               30.00 %
GPZ3               40.10 %
P16              1000.00 usec

F1 - Acquisition parameters
TD                   128
SFO1            125.7729 MHz
FIDRES        255.310455 Hz
SW               259.831 ppm
FnMODE                QF

F2 - Processing parameters
SI                  2048
SF           500.1300120 MHz
WDW                 SINE
SSB      0
LB       0 Hz
GB       0
PC                  1.40

F1 - Processing parameters
SI                  1024
MC2                   QF
SF           125.7577885 MHz
WDW                 SINE
SSB      0
LB       0 Hz
GB       0
```
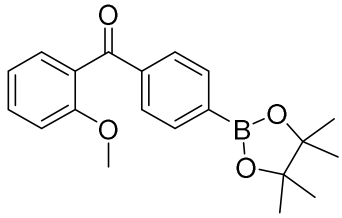
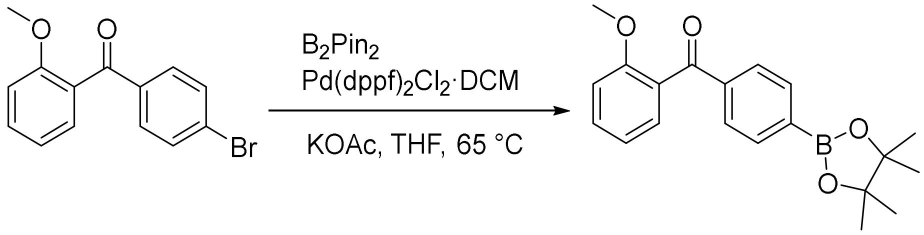

(2-Methoxyphenyl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone.

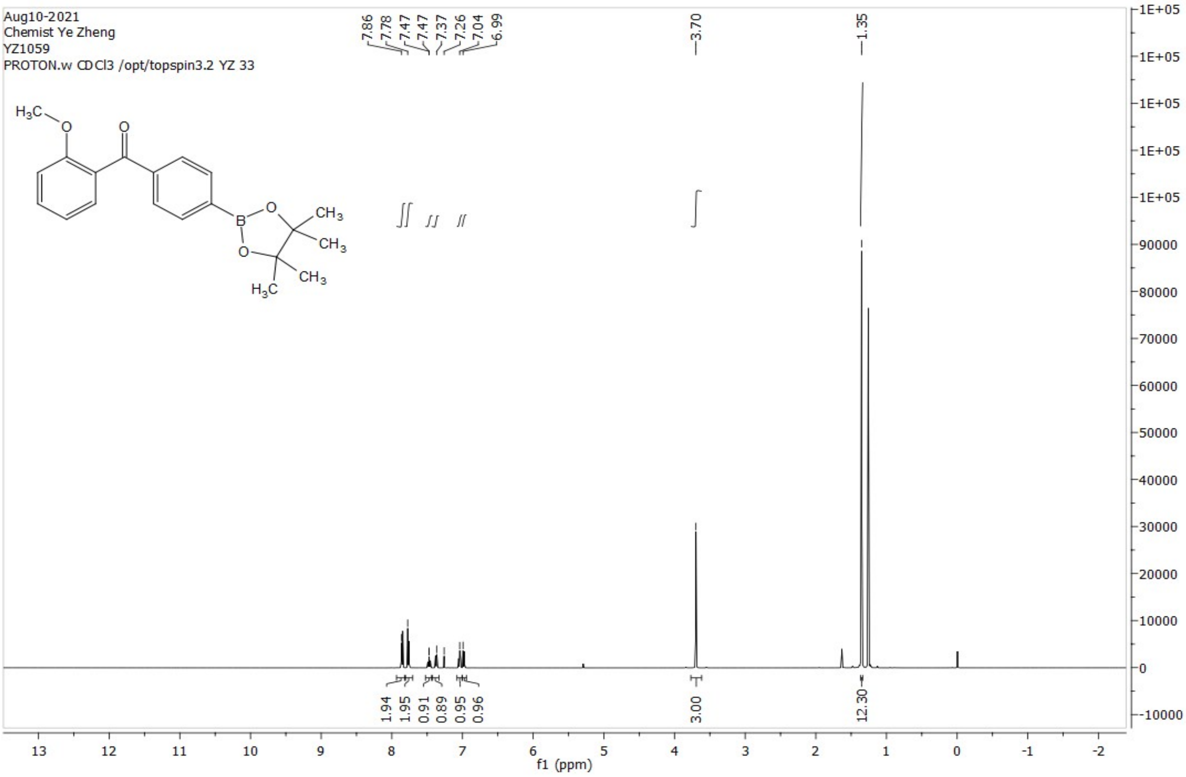




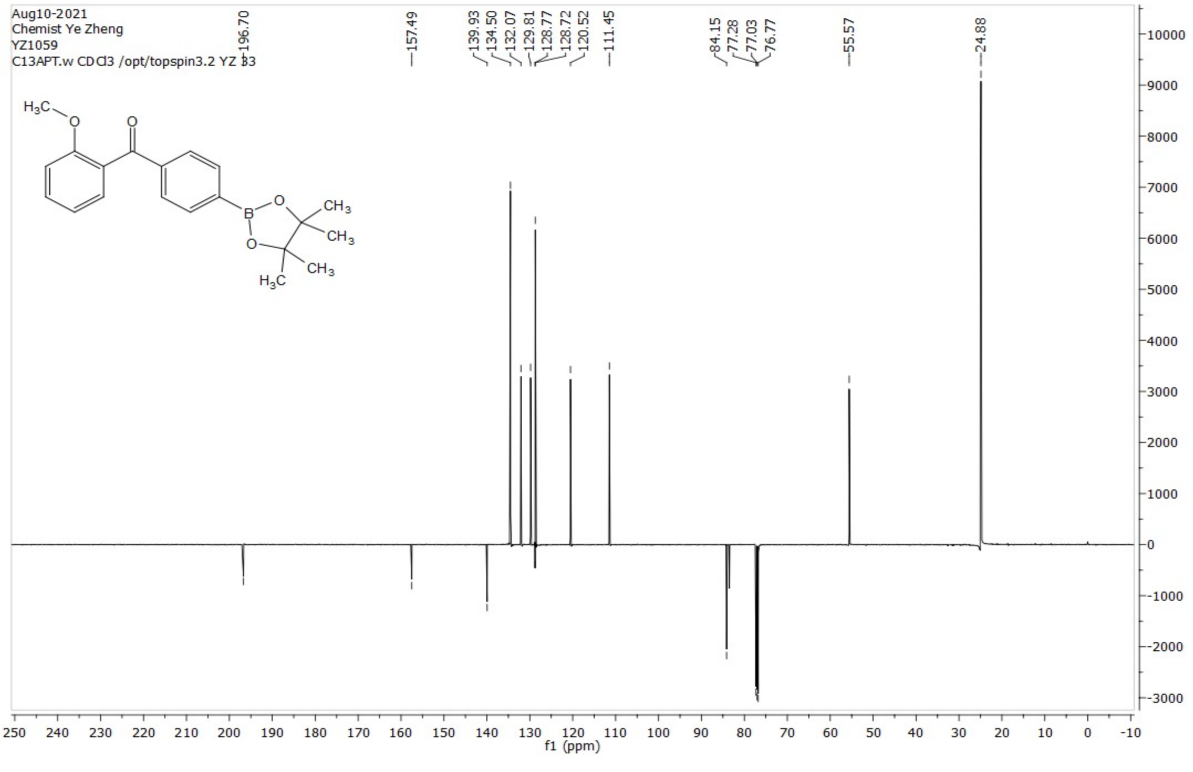
This compound is novel.

A round-bottom flask was charged with (4-bromophenyl)(2-methoxyphenyl)methanone (337 mg, 1.16 mmol), bis(pinacolato)diboron (353 mg, 1.39 mmol), potassium acetate (341 mg, 3.48 mmol), THF (7 mL) and Pd(dppf)$_2$Cl$_2$·DCM (47.4 mg, 0.0580 mmol). The reaction mixture was heated to 65 °C and left stirring under the nitrogen atmosphere overnight, followed by TLC (9:1 hexane: EtOAc). The mixture was quenched by distilled water (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried (MgSO$_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-20% ethyl acetate in hexane to give (2-methoxyphenyl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone as a white solid (195 mg, 0.577 mmol, 50%). TLC: Rf ca 0.20 (9:1 hexane: EtOAc), strong UV and KMnO$_4$; Mp: 146°C; HRMS: (found (ESI+): [M+H]+, Calcd for $C_{20}H_{23}BNaO_4$ 361.1579; Found 361.1582; 1.7 ppm error; $\nu_{max}$ 2973, 2929, 1662, 1596, 1505, 1484, 1359, 1265, 1207, 1136, 1088, 1024, 946, 848, 757 cm$^{-1}$; $\delta_H$ (500 MHz, CDCl$_3$) 7.86 (2H, d, *J* = 8.1, ArH), 7.78 (2H, d, *J* = 8.1, ArH), 7.47 (1H, td, *J* = 8.5, 1.7, ArH), 7.37 (1H, dd, *J* = 7.5, 1.7, ArH), 7.04 (1H, t, *J* = 7.4, ArH), 6.99 (1H, d, *J* = 8.4, ArH), 3.70 (3H, s, OCH$_3$), 1.35 (12H, s, CH$_3$) ppm; $\delta_C$ (125 MHz, CDCl$_3$) 196.70 (C), 157.49 (C), 139.93 (C), 134.50 (CH), 132.07 (CH), 129.81 (CH), 128.77 (C), 128.72 (CH), 120.52 (CH), 111.45 (CH), 83.15 (C), 55.57 (CH$_3$), 24.88 (CH$_3$) ppm; m/z (ES-API+) 361.1 (M$^+$ + 23, 100%). Enantiomeric excess and conversion determined by HPLC analysis (Chiralcel ODH, 30 cm x 6mm column, hexane:iPrOH 90:10, 1.0 mL/min, T = 25°C) ketone 6.3 min, *R* and *S* isomers 9.1 min and 11.6 min.

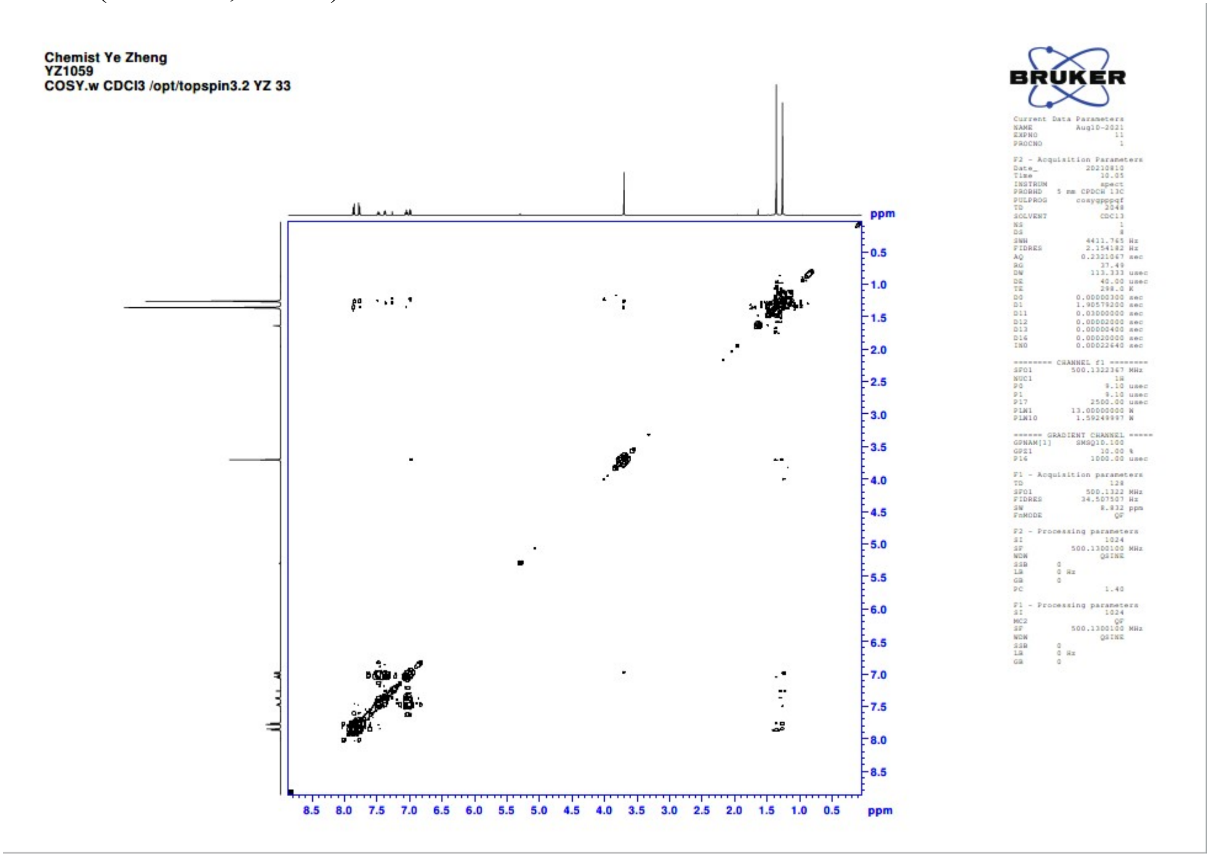
$^1$H NMR (500 MHz, $CDCl_3$)



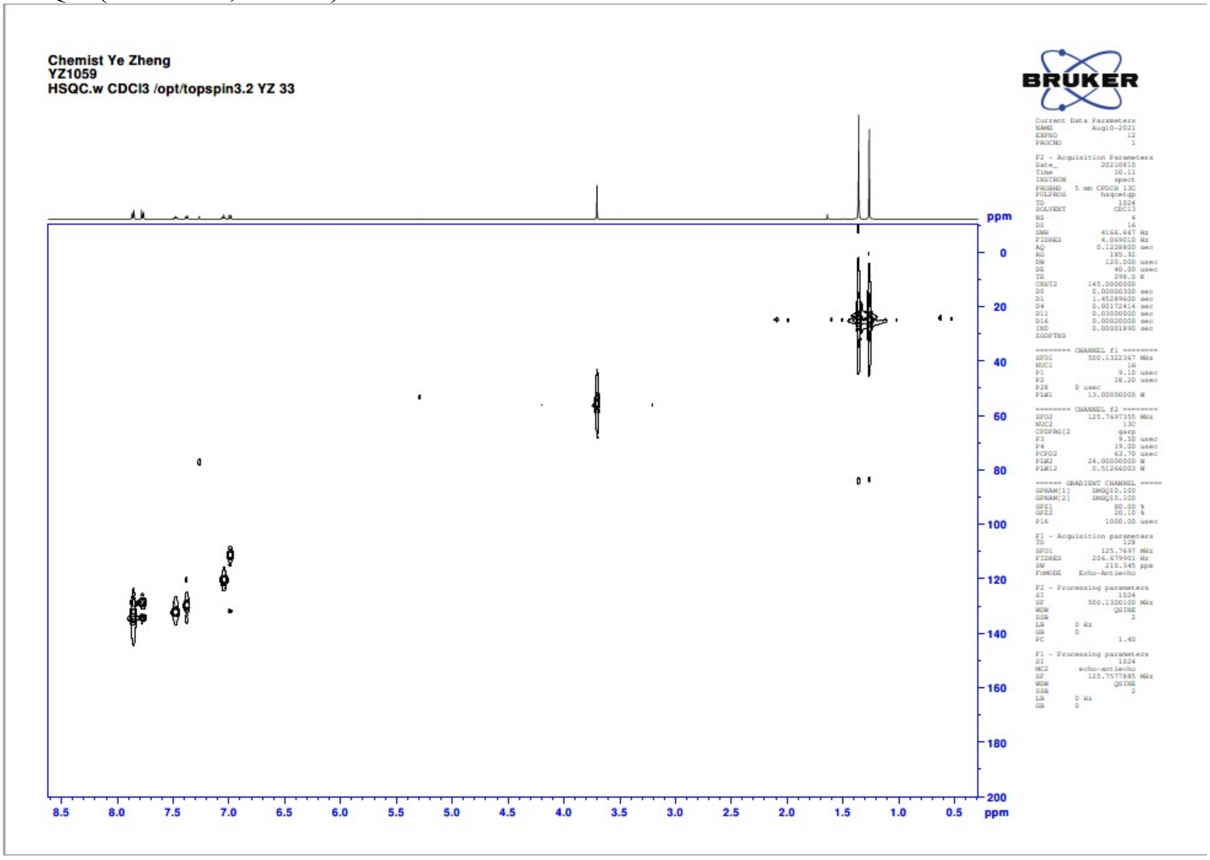
$^{13}$C NMR (125 MHz, $CDCl_3$)



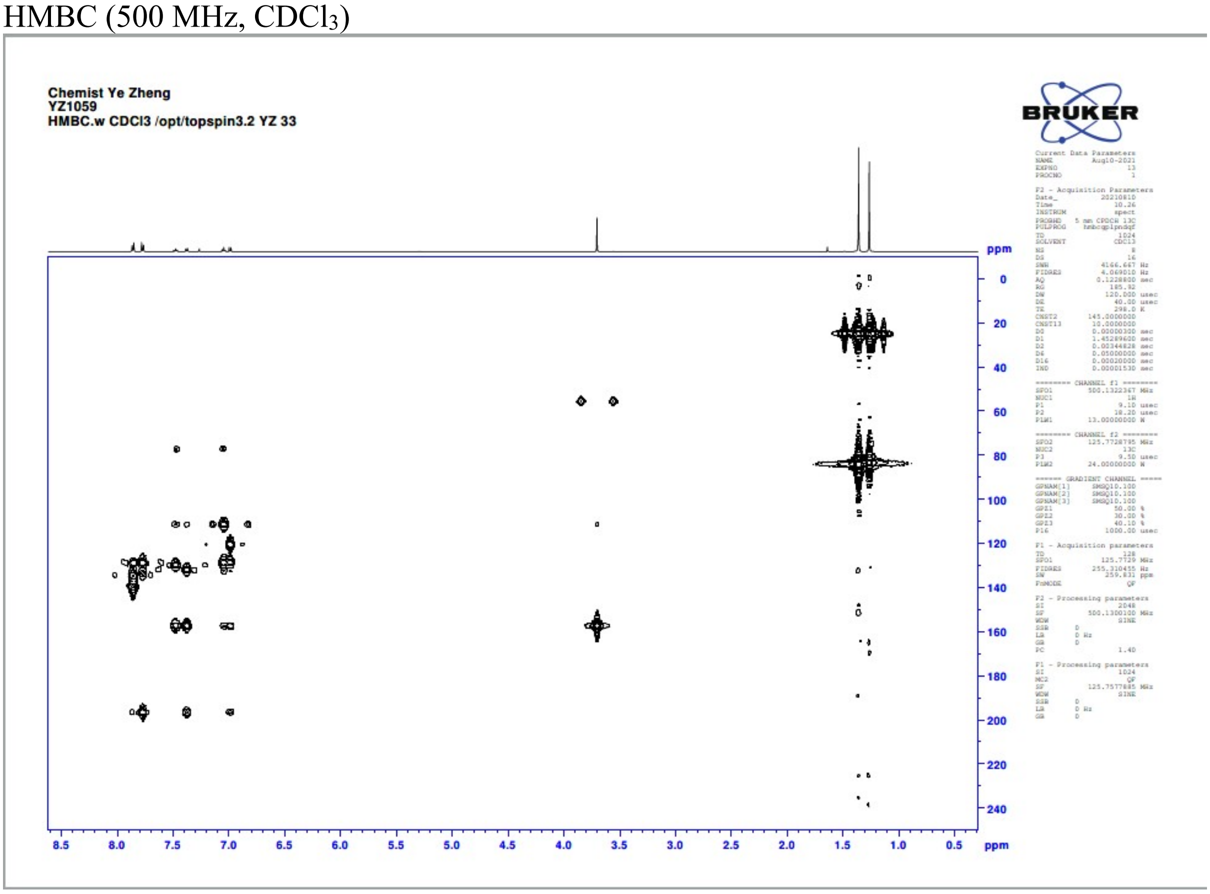
COSY (500 MHz, $CDCl_3$)



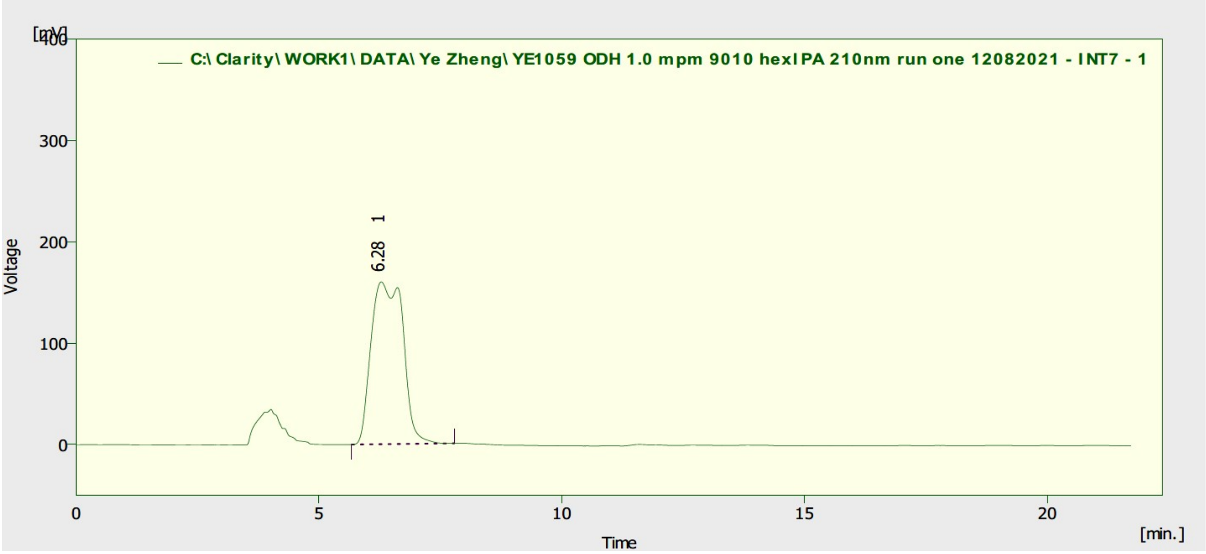
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)



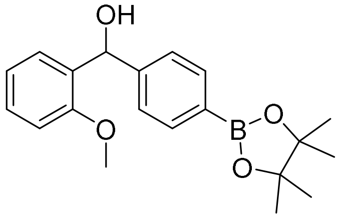
HPLC of (2-methoxyphenyl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone

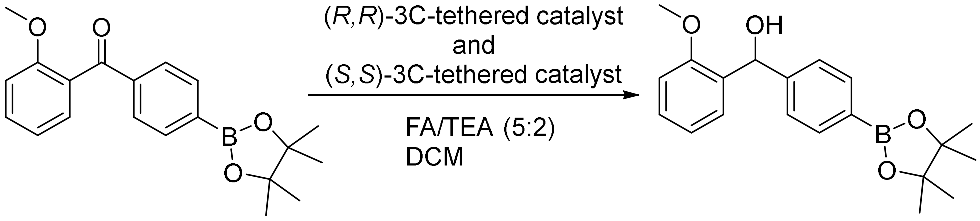


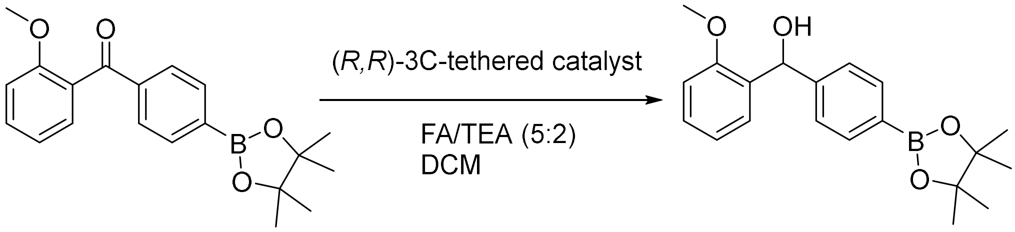
*Result Table (Uncal - C:\Clarity\WORK1\DATA\Ye Zheng\YE1059 ODH 1.0 mpm 9010 hexIPA 210nm run one 12082021 - INT7 - 1)*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Compound Name |
|---|---|---|---|---|---|---|---|
| 1 | 6.280 | 7324.343 | 160.069 | 100.0 | 100.0 | 0.76 | |
| | Total | 7324.343 | 160.069 | 100.0 | 100.0 | | |

(2-Methoxyphenyl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanol **23**.







This compound is novel.

**Synthesis of a racemic standard:**

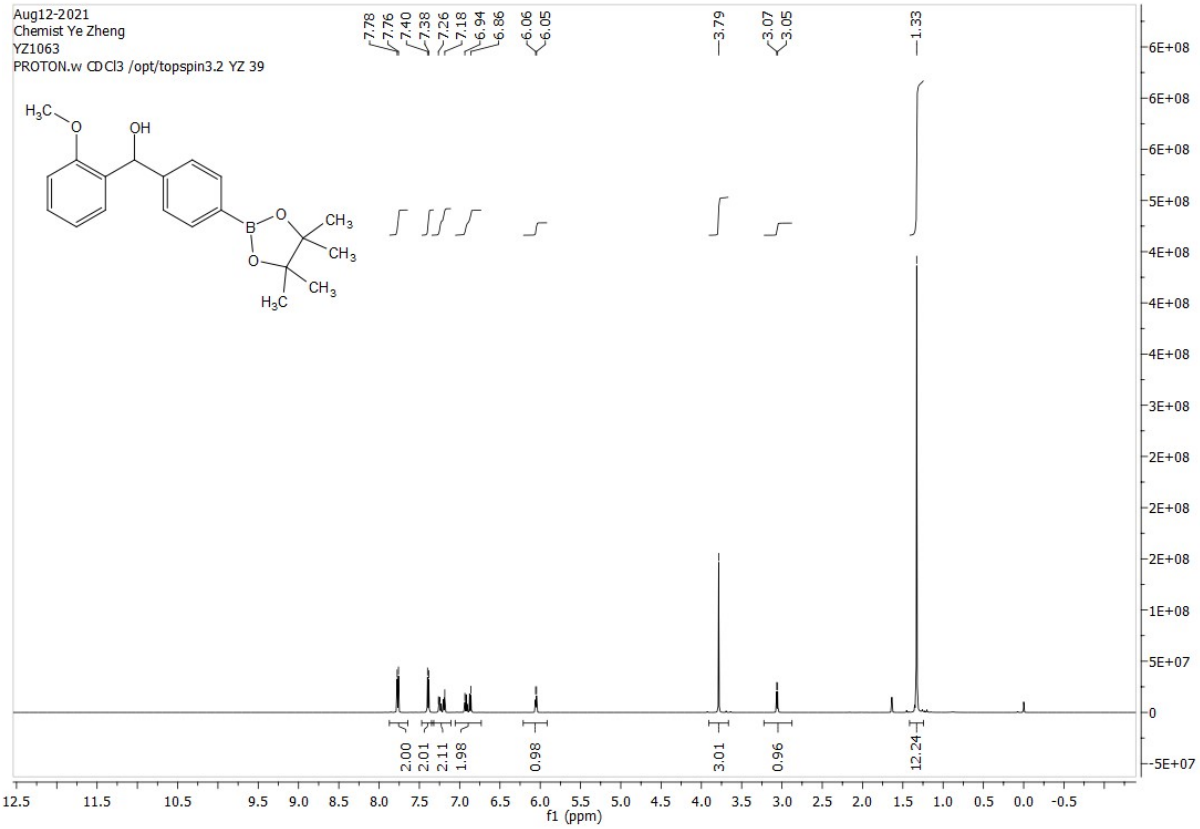
(*R,R*)-3C-Tethered Ru(II)-TsDPEN catalyst **2** (0.738 mg, 1.19 μmol, 0.5 mol%) and (*S,S*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (0.738 mg, 1.19 μmol, 0.5 mol%) were added to FA: TEA (5:2 azeotropic mixture, 0.36 mL) at rt and the mixture was stirred under a nitrogen atmosphere for 15 minutes; after which a solution of (2-methoxyphenyl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone (80.0 mg, 0.237 mmol) in DCM (0.50 mL) was added. The reaction mixture was stirrer under a nitrogen atmosphere and followed by TLC (4:1 hexane: EtOAc). After 72 hours, the reaction was quenched using saturated $NaHCO_3$ solution (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried ($MgSO_4$) and filtered. The solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-50% EtOAc in hexane to give (2-methoxyphenyl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanol **23** as a colorless oil (64.0 mg, 0.188 mmol, 80%). TLC: Rf ca 0.20 (4:1 hexane: EtOAc), strong UV and $KMnO_4$; HRMS: (found (ESI+): [M+H]+, Calcd for $C_{20}H_{25}BNaO_4$ 363.1738; Found 363.1738; 1.0 ppm error; $\nu_{max}$ 3323 (br), 2978, 2936, 2837, 1611, 1489, 1463, 1298, 1240, 1164, 1048, 962 cm$^{-1}$; $\delta_H$ (500 MHz, $CDCl_3$) 7.78 (2H, d, *J* = 8.0, ArH), 7.40 (2H, d, *J* = 8.0, ArH), 7.25-7.18 (2H, m, ArH), 6.94-6.86 (2H, m, ArH), 6.06 (1H, d, *J* = 5.6, ArCH), 3.79 (3H, s, $OCH_3$), 3.07 (1H, d, *J* = 5.6, OH), 1.33 (12H, s, $CH_3$) ppm; $\delta_C$ (125 MHz, $CDCl_3$) 156.77 (C), 146.45 (C), 134.69 (CH), 131.81 (C), 128.82 (CH), 128.00 (CH), 125.83 (CH), 120.83 (CH), 110.77 (CH), 83.73 (C), 72.34 (CH), 55.42 ($CH_3$), 24.88 ($CH_3$) ppm; m/z (ES-API+) 363.2 ($M^+$ + 23, 100%).

Enantiomeric excess and conversion determined by HPLC analysis (Chiralcel ODH, 30 cm x 6mm column, hexane:iPrOH 90:10, 1.0 mL/min, T = 25°C) ketone 6.3 min, *R* and *S* isomers 9.1 min and 11.6 min, configuration is not confirmed.

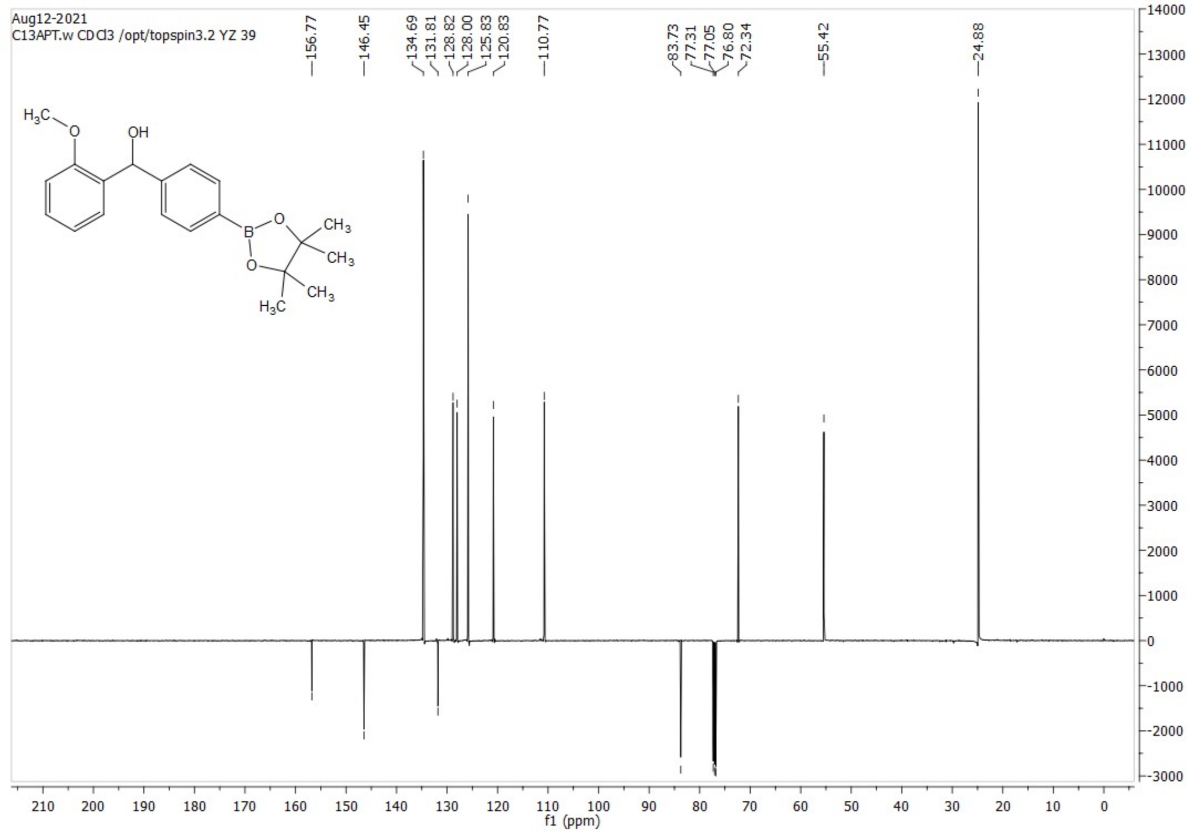
ATH of (2-methoxyphenyl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone.

(*R,R*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (1.47 mg, 2.37 μmol, 1 mol%) was added to FA: TEA (5:2 azeotropic mixture, 0.36 mL) at rt and the mixture was stirred under a nitrogen atmosphere for 15 minutes; after which a solution of (2-methoxyphenyl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone (80.0 mg, 0.237 mmol) in DCM (0.50 mL) was added. The reaction mixture was stirred under a nitrogen atmosphere and followed by TLC (4:1 hexane: EtOAc). After 72 hours, the reaction was quenched using saturated $NaHCO_3$ solution (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried ($MgSO_4$) and filtered. The solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-50% EtOAc in hexane to give (2-methoxyphenyl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanol **23** as a colorless oil (50.8 mg, 0.150 mmol, 63%). The reaction was also followed by HPLC (Chiralcel ODH, 30 cm x 6mm column, hexane:iPrOH 90:10, 1.0 mL/min, T = 25°C): $[\alpha]_D^{26}$ -27.1 (c 0.376 in $CHCl_3$) 55% ee.

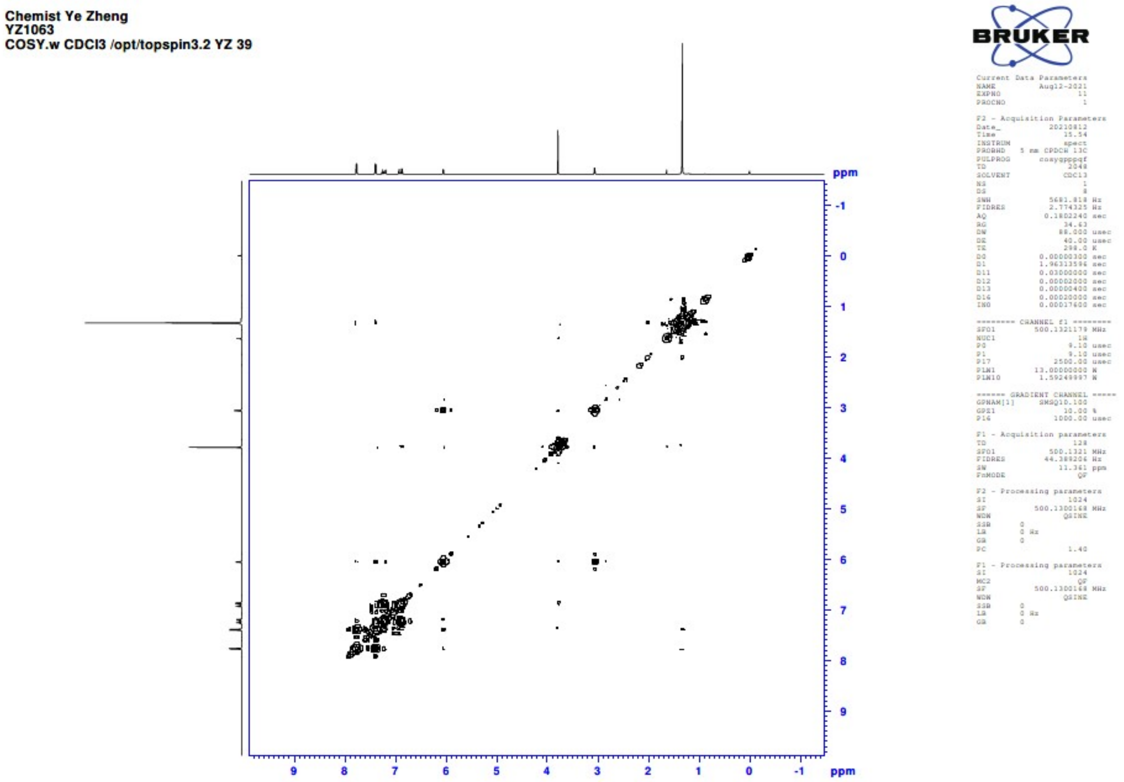
$^1$H NMR (500 MHz, CDCl$_3$)



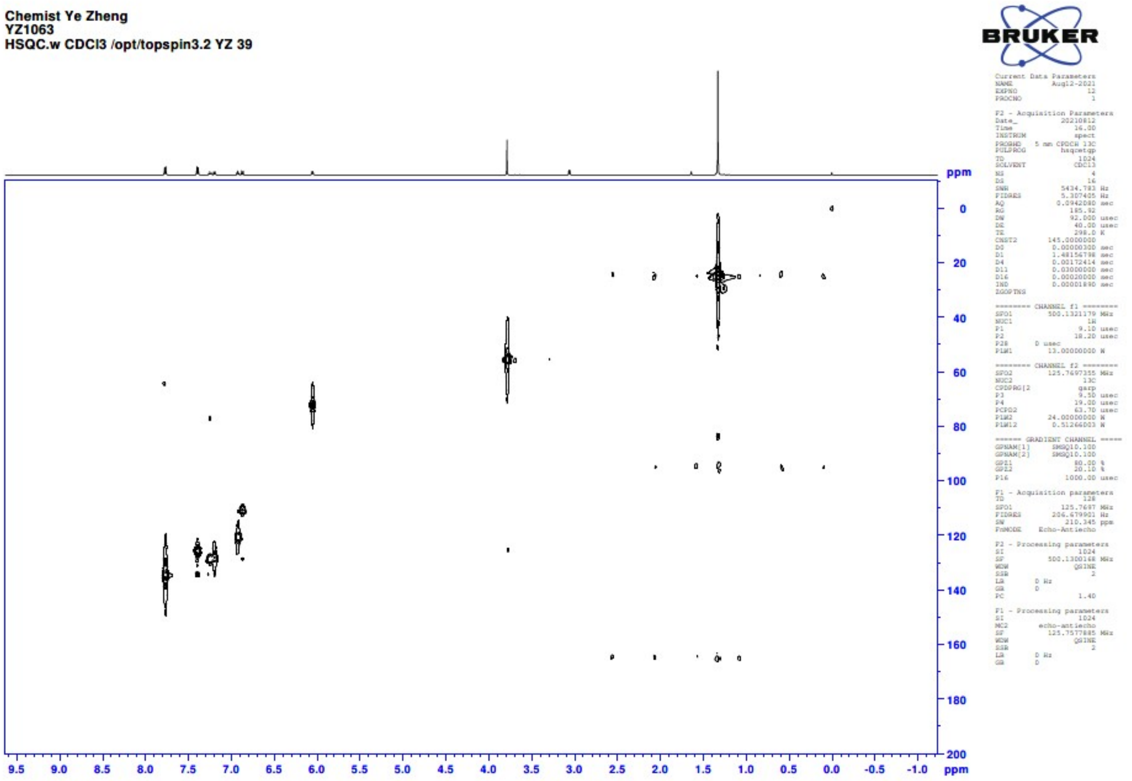
$^{13}$C NMR (125 MHz, CDCl$_3$)



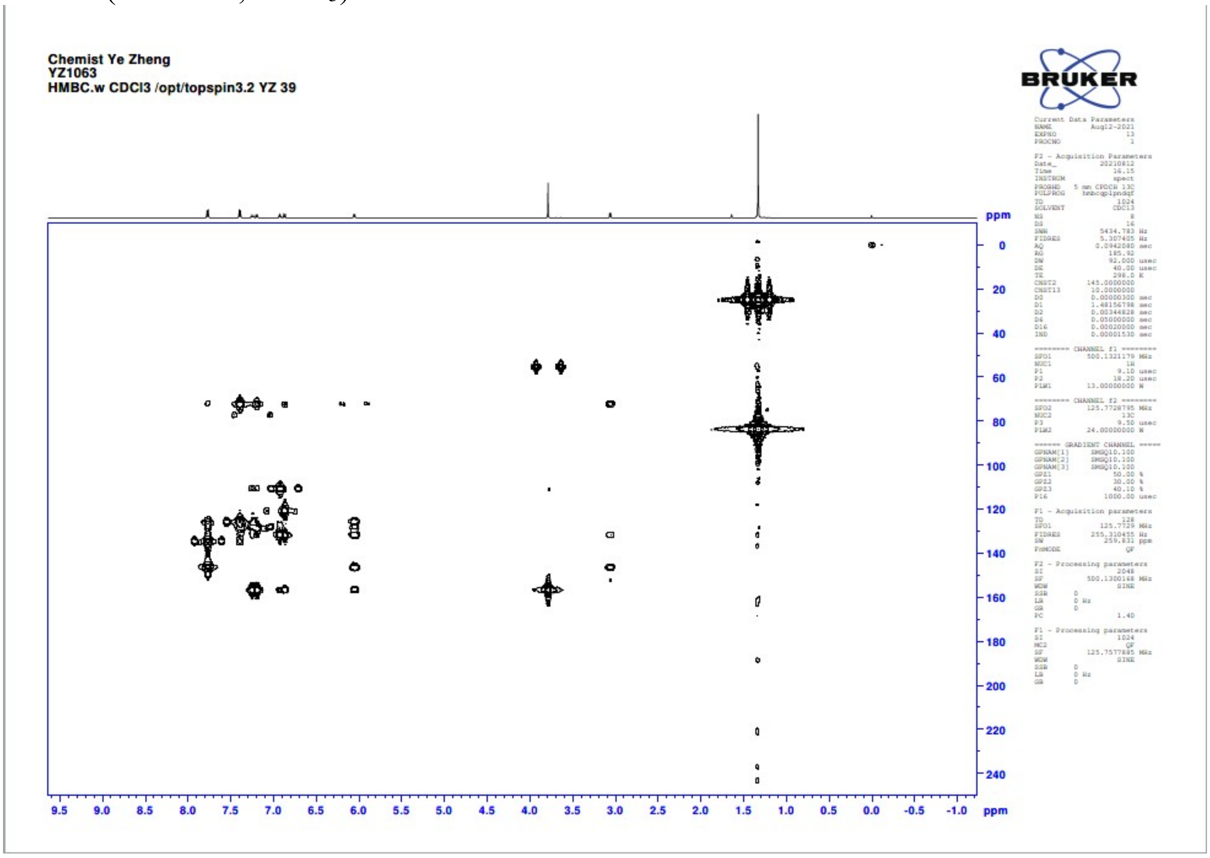
COSY (500 MHz, $CDCl_3$)



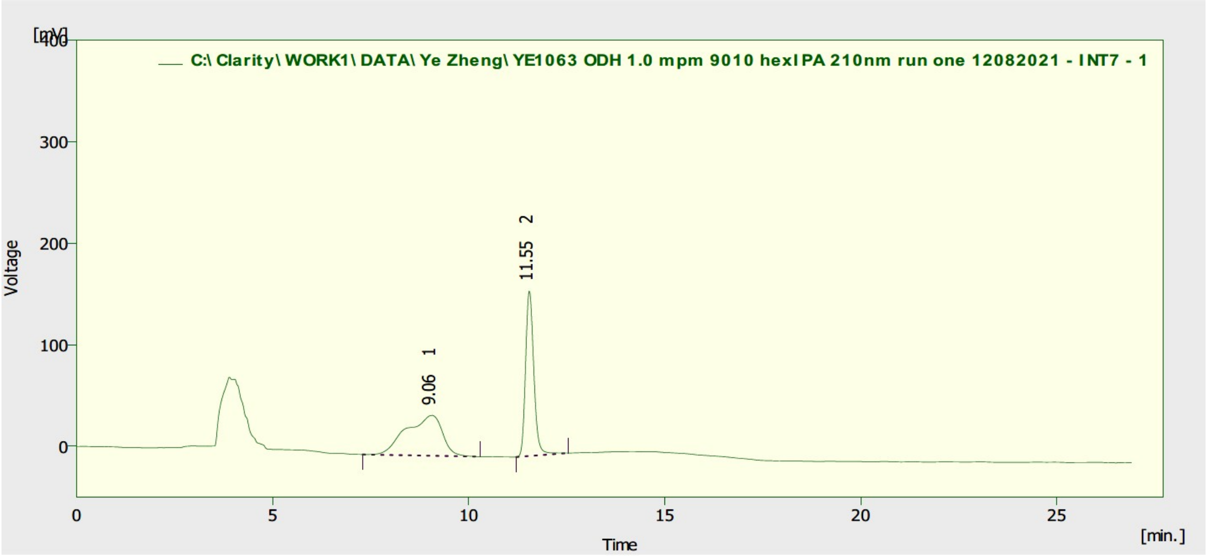
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)



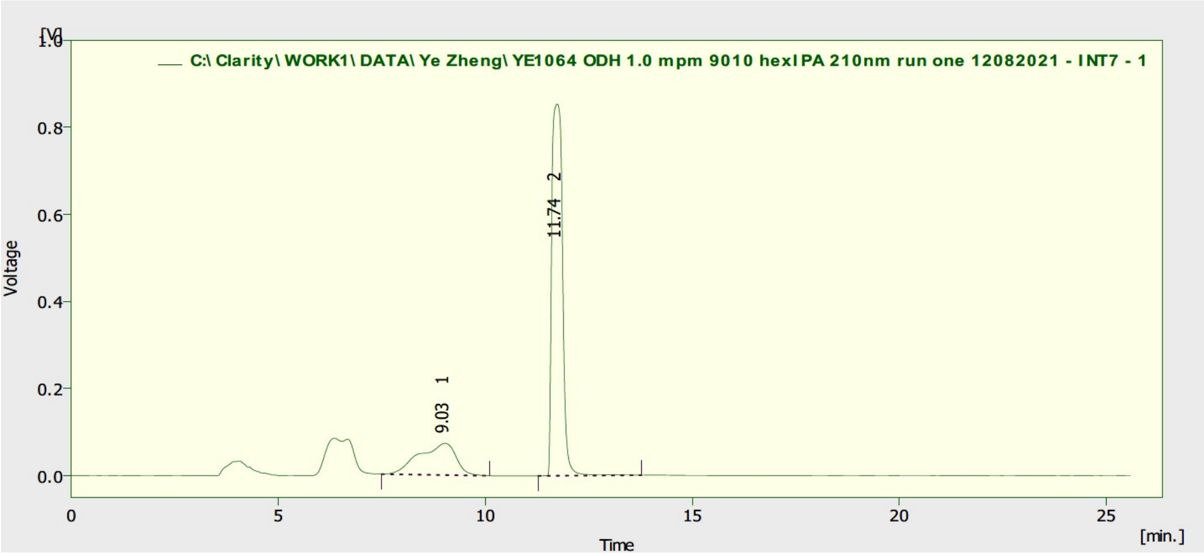
HPLC of racemic (2-methoxyphenyl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanol **23**.



*Result Table (Uncal - C:\Clarity\WORK1\DATA\Ye Zheng\YE1063 ODH 1.0 mpm 9010 hexIPA 210nm run one 12082021 - INT7 - 1)*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Compound Name |
|---|---|---|---|---|---|---|---|
| 1 | 9.057 | 2555.751 | 39.823 | 51.8 | 19.7 | 1.16 | |
| 2 | 11.547 | 2379.687 | 162.712 | 48.2 | 80.3 | 0.22 | |
| | Total | 4935.438 | 202.535 | 100.0 | 100.0 | | |

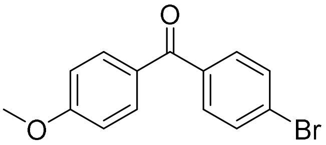
HPLC after ATH of (2-methoxyphenyl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone using (*R,R*)-3C-Tethered Ru(II)-TsDPEN catalyst **2** (after 72 hours, 100% conversion, 55% ee).

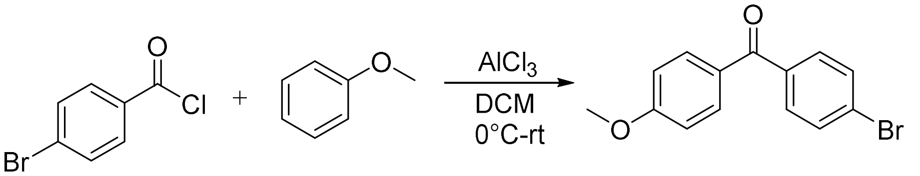


*Result Table (Uncal - C:\Clarity\WORK1\DATA\Ye Zheng\YE1064 ODH 1.0 mpm 9010 hexIPA 210nm run one 12082021 - INT7 - 1)*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Compound Name |
|---|---|---|---|---|---|---|---|
| 1 | 9.030 | 4519.241 | 72.936 | 22.7 | 7.9 | 1.12 | |
| 2 | 11.737 | 15346.803 | 853.846 | 77.3 | 92.1 | 0.29 | |
| | Total | 19866.043 | 926.782 | 100.0 | 100.0 | | |

(4-Bromophenyl)(4-methoxyphenyl)methanone.

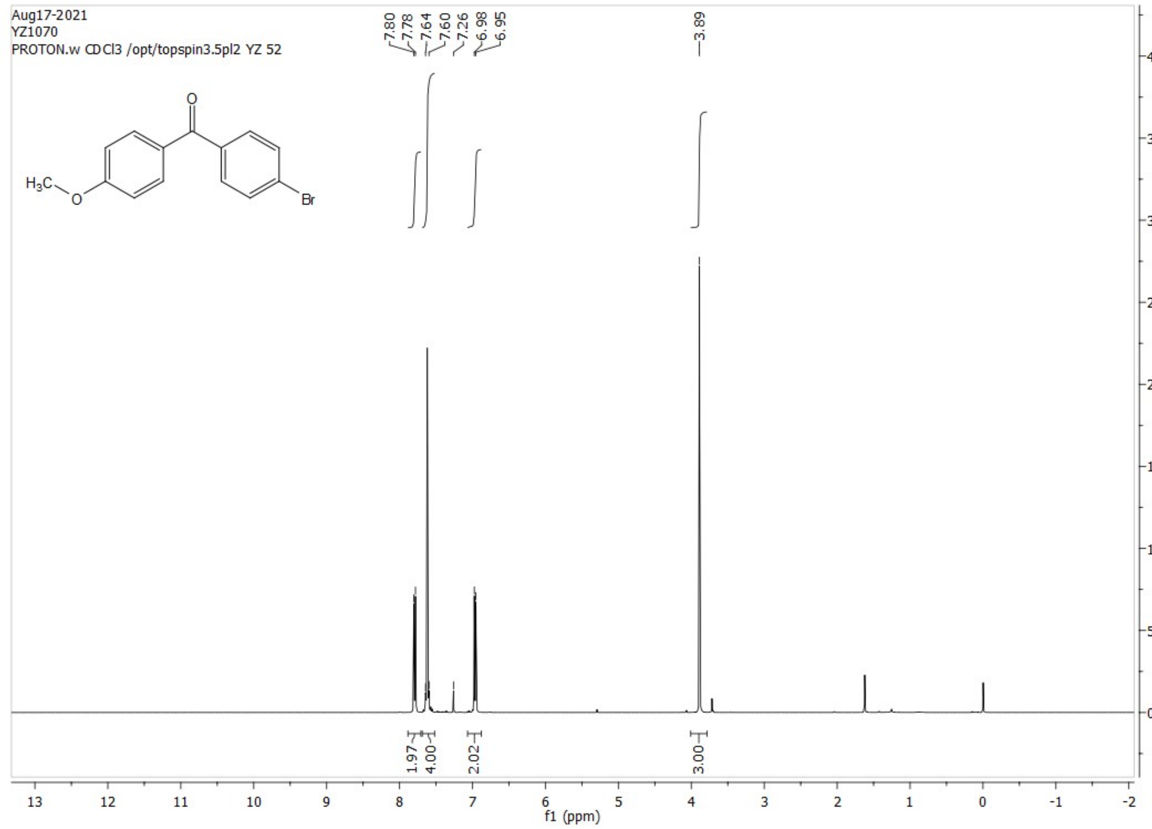




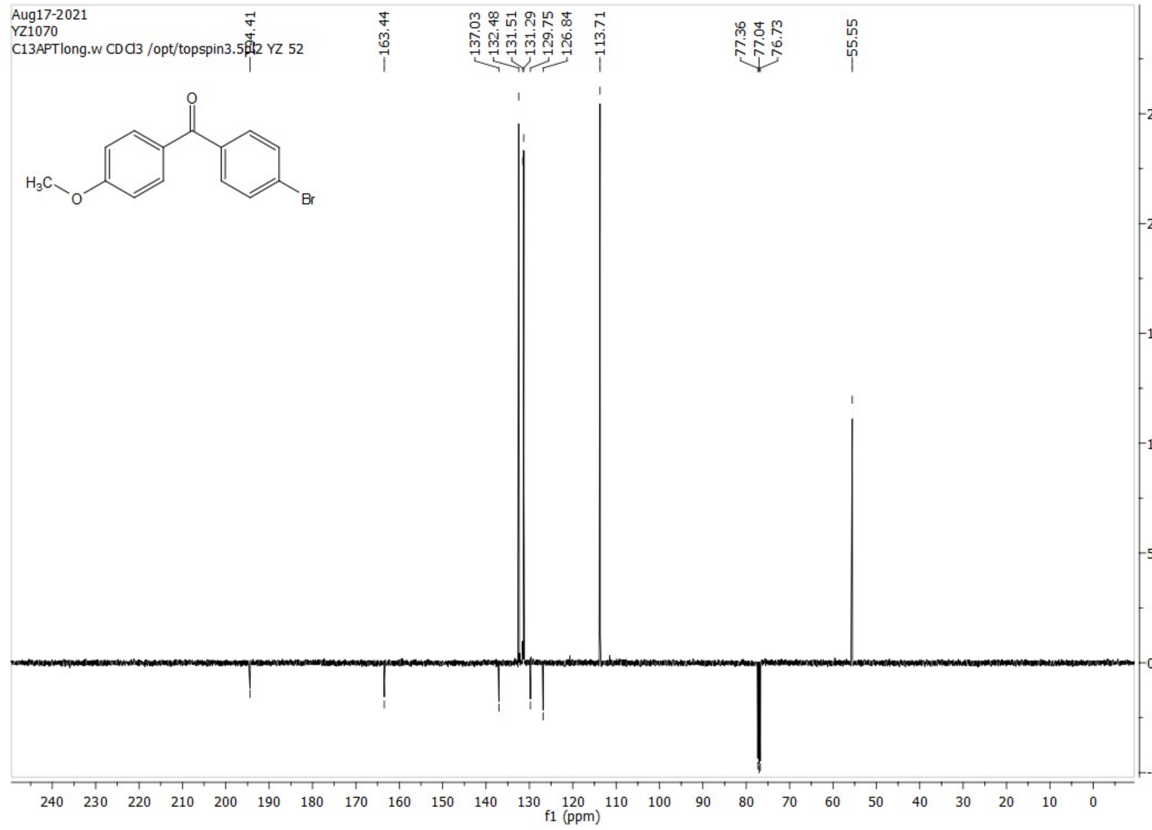
This compound has been reported and fully characterized: L. Dong, G.-R. Chen, X.-P. HeS. Vidal, *Org. Biomol. Chem.* 2019, **17**, 9251-9256.

To a solution of 4-bromobenzoyl chloride (250 mg, 1.14 mmol) was in DCM (5 mL) at 0 °C was added dropwise anisole (155 mg, 1.43 mmol) and $AlCl_3$ (190 mg, 1.43 mmol). The reaction mixture was warmed to rt and left stirring under the nitrogen atmosphere for 2 hours, followed by TLC (9:1 hexane: EtOAc). The mixture was poured into ice water, quenched with 2M HCl solution (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried ($MgSO_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-20% ethyl acetate in hexane to give (4-bromophenyl)(4-methoxyphenyl)methanone as a white solid (226 mg, 0.780 mmol, 68%). TLC: Rf ca 0.20 (9:1 hexane: EtOAc), strong UV and $KMnO_4$; $\delta_H$ (400 MHz, $CDCl_3$) 7.80 (2H, d, *J* = 8.8, ArH), 7.64-7.60 (4H, m, ArH), 6.98 (2H, d, *J* = 8.8, ArH), 3.89 (3H, s, $CH_3$) ppm; $\delta_C$ (100 MHz, $CDCl_3$) 194.41 (C), 163.44 (C), 137.03 (C), 132.48 (CH), 131.51 (CH), 131.29 (CH), 129.75 (C), 126.84 (C), 113.71 (CH), 55.55 ($CH_3$) ppm; m/z (ES-API+) 331.0 ($M^+$ + 23, 100%). Data matched that reported.

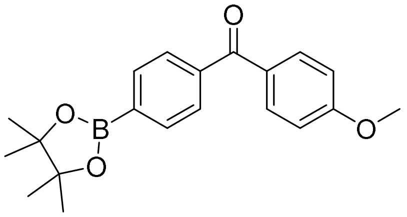
$^{1}$H NMR (400 MHz, CDCl$_3$)

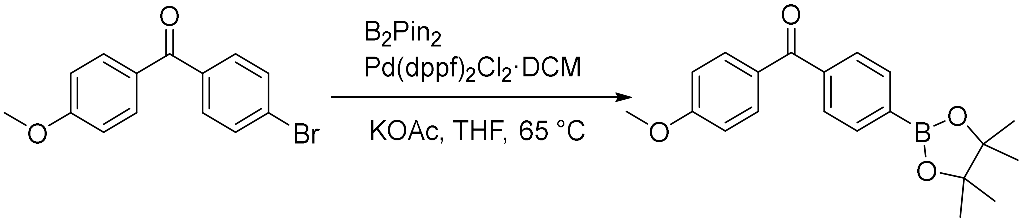


$^{13}$C NMR (100 MHz, CDCl$_3$)



(4-Methoxyphenyl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone.

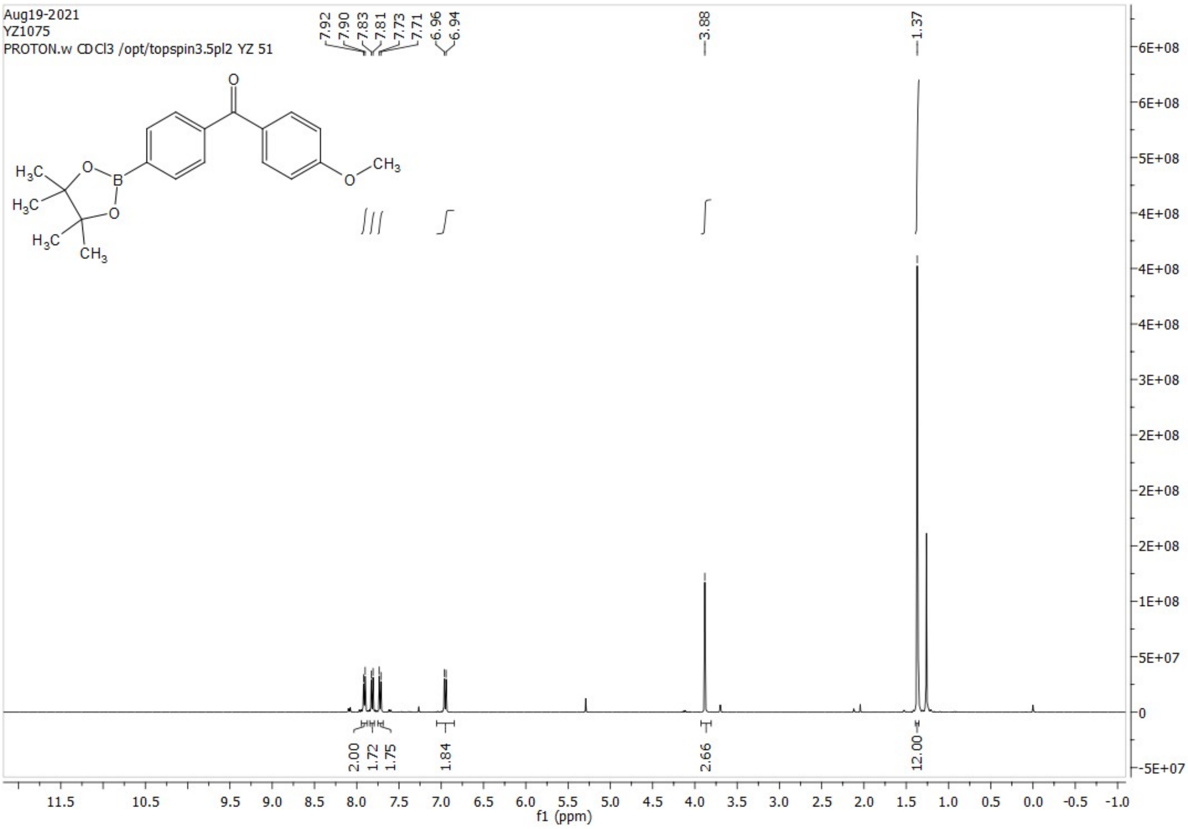




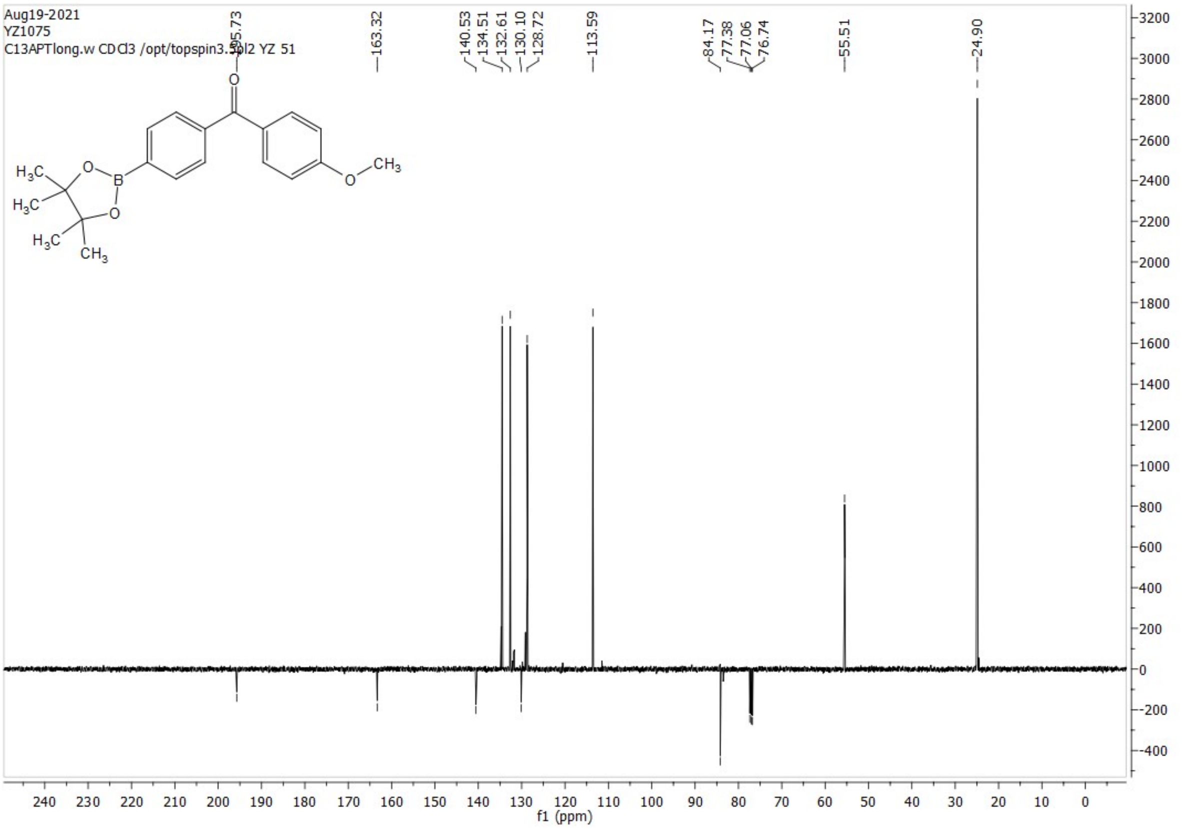
This compound is novel.

A round-bottom flask was charged with (4-bromophenyl)(4-methoxyphenyl)methanone (1.44 g, 4.97 mmol), bis(pinacolato)diboron (1.51 g, 5.96 mmol), potassium acetate (1.46 g, 14.9 mmol), THF (25 mL) and Pd(dppf)$_2$Cl$_2$·DCM (203 mg, 0.249 mmol). The reaction mixture was heated to 65 °C and left stirring under the nitrogen atmosphere overnight, followed by TLC (9:1 hexane: EtOAc). The mixture was quenched by distilled water (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried (MgSO$_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-20% ethyl acetate in hexane to give (4-methoxyphenyl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone as a white solid (1.43 g, 4.23 mmol, 85%). TLC: Rf ca 0.40 (9:1 hexane: EtOAc), strong UV and KMnO$_4$; Mp: 88°C; HRMS: (found (ESI+): [M+H]+, Calcd for $C_{20}H_{23}BNaO_4$ 361.1584; Found 361.1582; 0.4 ppm error; $\nu_{max}$ 2976, 2931, 1649, 1597, 1504, 1396, 1255, 1123, 1085, 927, 821 cm$^{-1}$; $\delta_H$ (500 MHz, CDCl$_3$) 7.92 (2H, d, *J* = 7.9, ArH), 7.83 (2H, d, *J* = 8.8, ArH), 7.73 (2H, d, *J* = 7.9, ArH), 6.96 (2H, d, *J* = 8.8, ArH), 3.88 (3H, s, OCH$_3$), 1.37 (12H, s, CH$_3$) ppm; $\delta_C$ (125 MHz, CDCl$_3$) 195.73 (C), 163.32 (C), 140.53 (C), 134.51 (CH), 132.61 (CH), 130.10 (C), 128.72 (CH), 113.59 (CH), 84.17 (C), 55.51 (CH$_3$), 24.90 (CH$_3$) ppm; m/z (ES-API+) 361.1 (M$^+$ + 23, 100%). Enantiomeric excess and conversion determined by HPLC analysis (Chiralpak IG, 30 cm x 6mm column, hexane:iPrOH 95:5, 0.5 mL/min, T = 25°C) ketone 35.0 min, *R* and *S* isomers 48.3 min and 52.5 min.

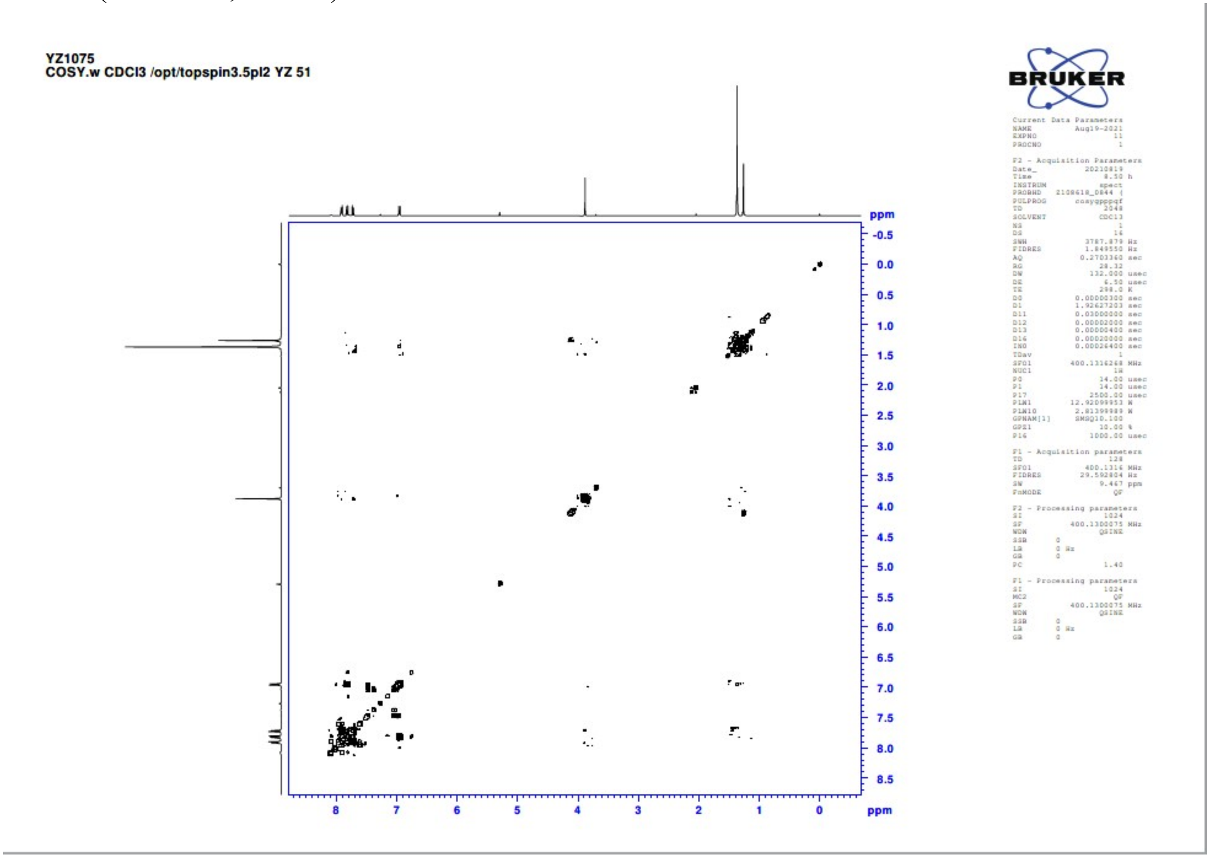
$^{1}H$ NMR (500 MHz, $CDCl_3$)



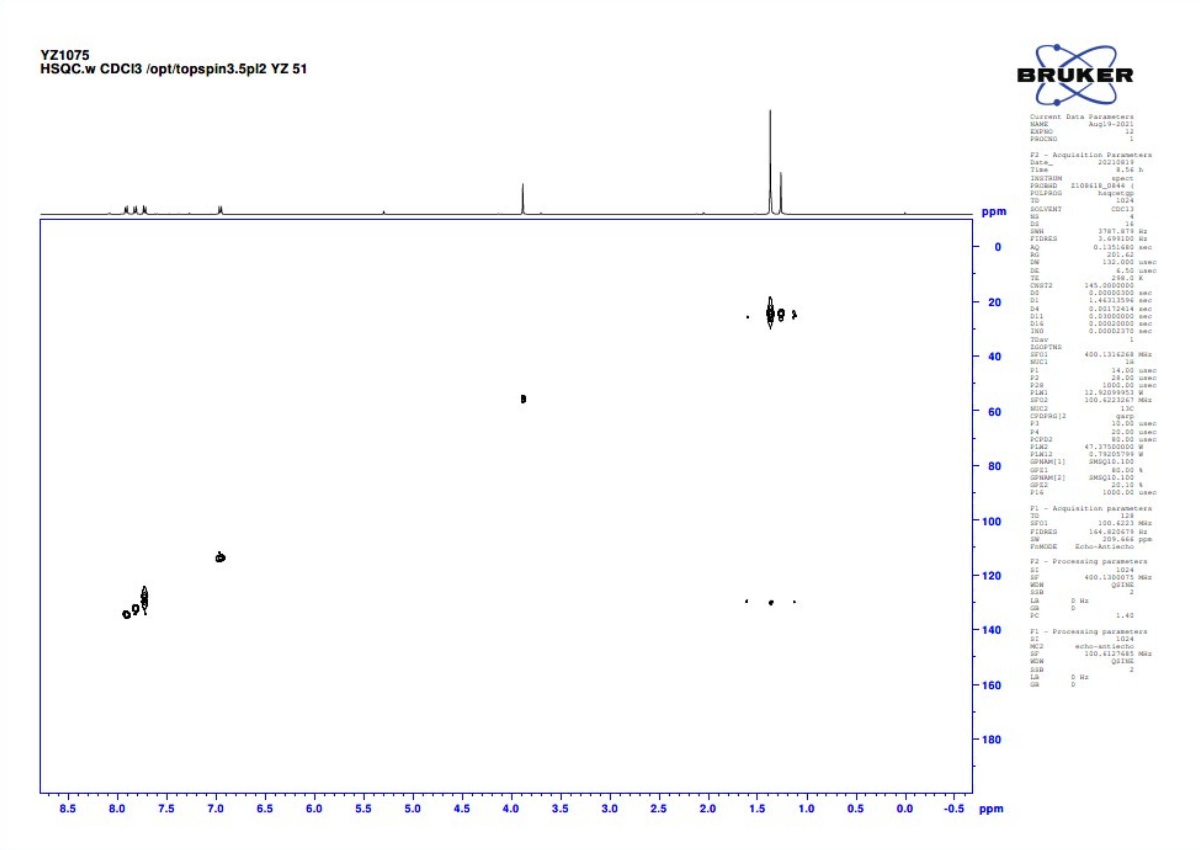
$^{13}C$ NMR (125 MHz, $CDCl_3$)



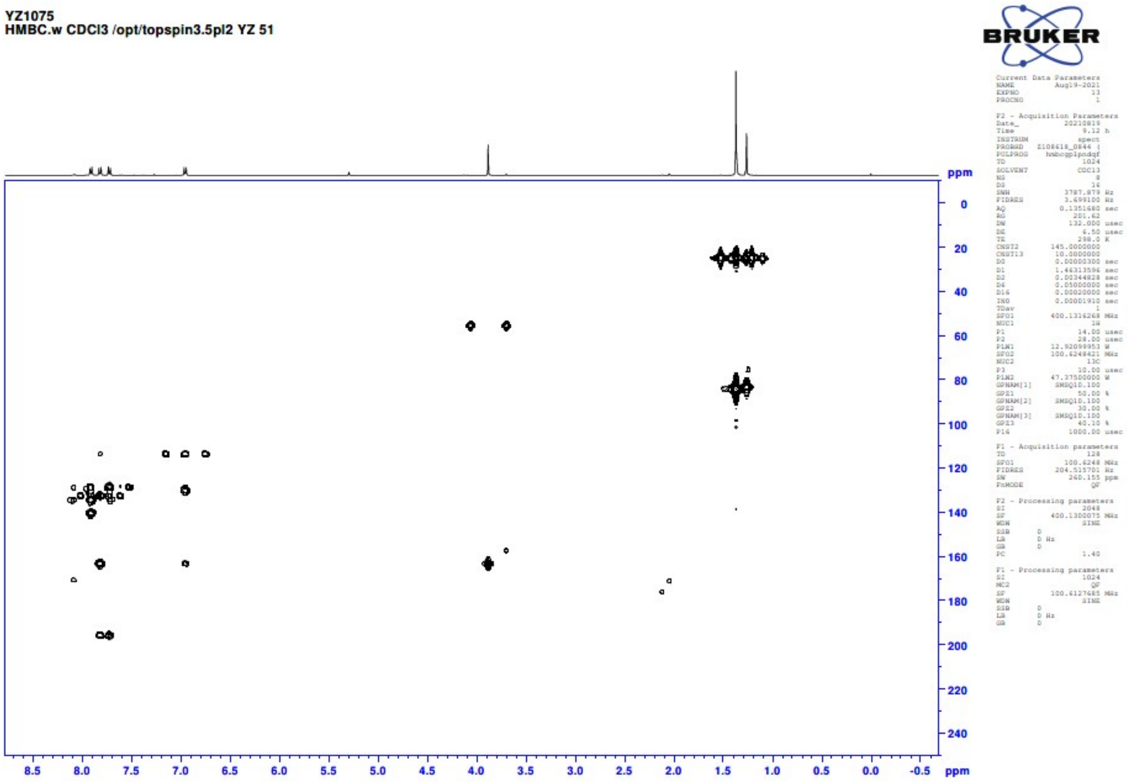
COSY (500 MHz, $CDCl_3$)



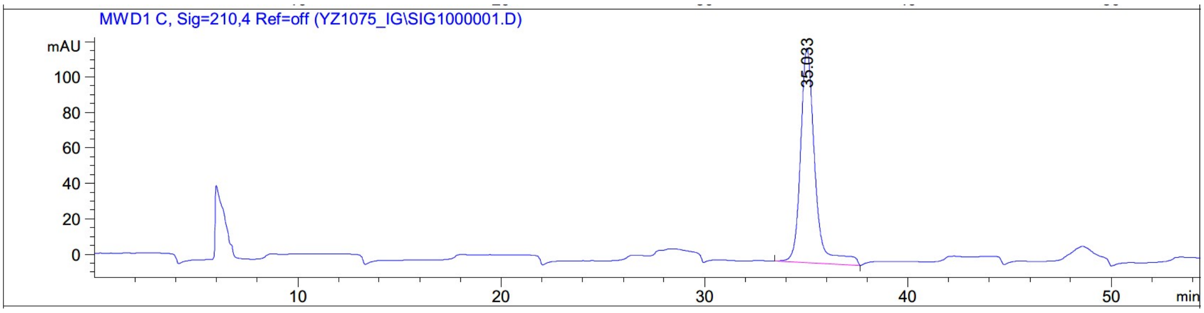
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)



HPLC of (4-methoxyphenyl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone



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Signal 2: MWD1 C, Sig=210,4 Ref=off

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  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  35.033 BB    0.7380 5954.32764  121.02700 100.0000

Totals :                  5954.32764  121.02700
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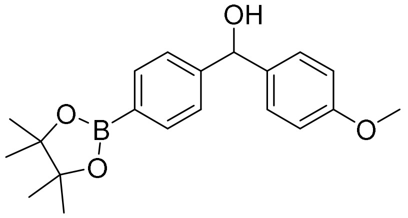
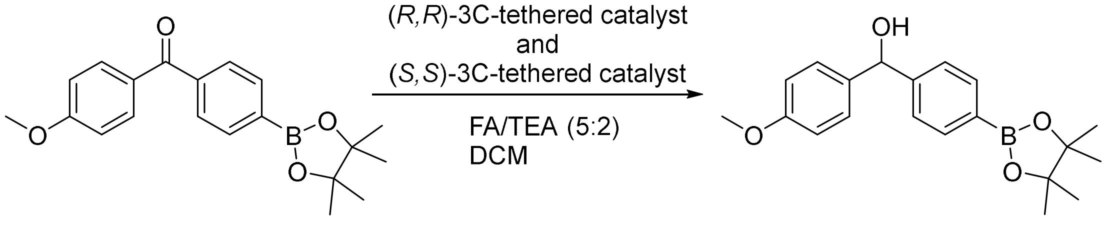
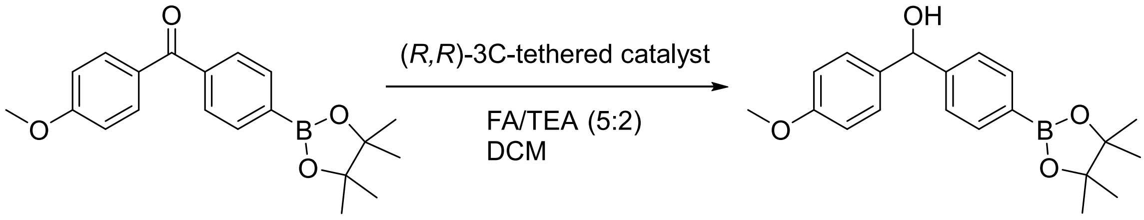
(4-Methoxyphenyl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanol **24**.







This compound is novel.

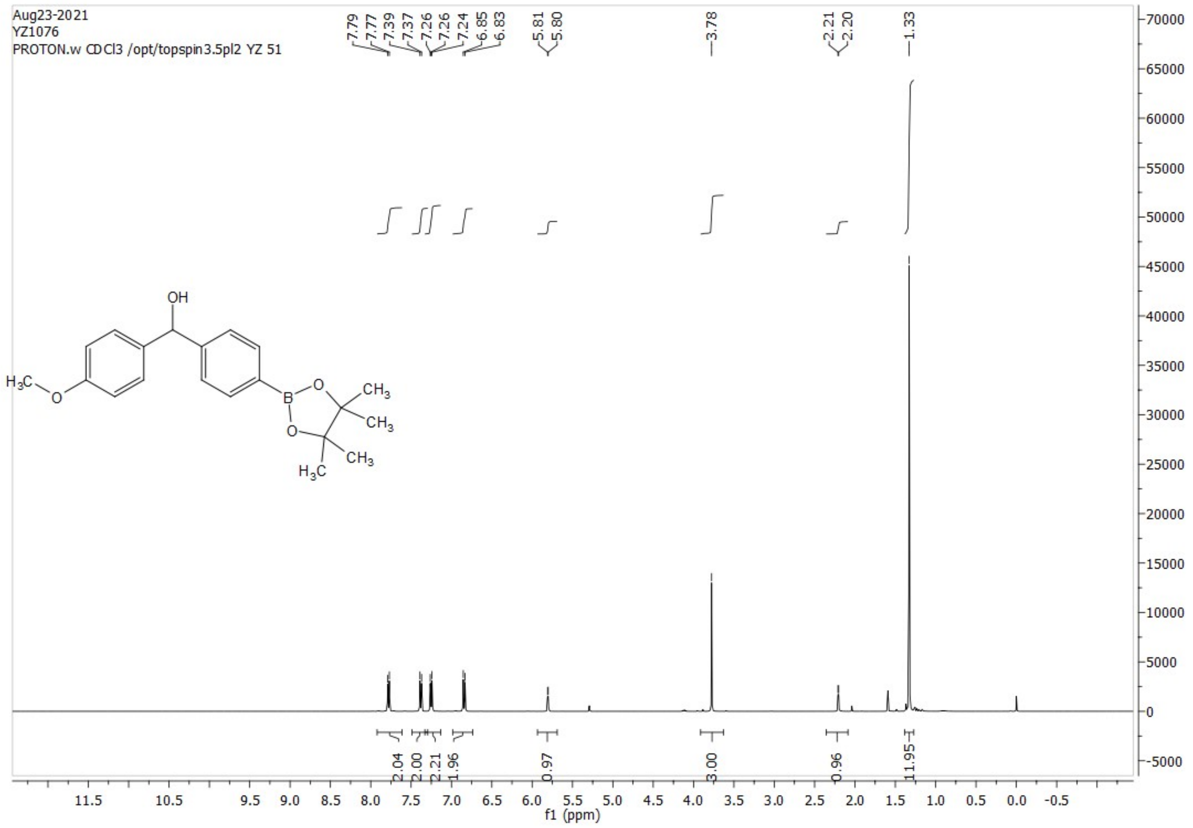
**Synthesis of a racemic standard:**

(*R,R*)-3C-Tethered Ru(II)-TsDPEN catalyst (0.74 mg, 1.2 µmol, 0.5 mol%) and (*S,S*)-3C-tethered Ru(II)-TsDPEN catalyst (0.74 mg, 1.2 µmol, 0.5 mol%) were added to FA: TEA (5:2 azeotropic mixture, 0.36 mL) at rt and the mixture was stirred under a nitrogen atmosphere for 15 minutes; after which a solution of (4-methoxyphenyl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone (80.0 mg, 0.237 mmol) in DCM (0.50 mL) was added. The reaction mixture was stirrer under a nitrogen atmosphere and followed by TLC (4:1 hexane: EtOAc). After 72 hours, the reaction was quenched using saturated $NaHCO_3$ solution (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried ($MgSO_4$) and filtered. The solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-50% EtOAc in hexane to give (4-methoxyphenyl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanol **24** as a colorless oil (41.5 mg, 0.122 mmol, 52%). TLC: Rf ca 0.40 (4:1 hexane: EtOAc), strong UV and $KMnO_4$; HRMS: (found (ESI+): [M+H]+, Calcd for $C_{20}H_{25}BNaO_4$ 363.1738; Found 363.1738; 1.0 ppm error; $\nu_{max}$ 3451 (br), 2977, 2933, 2836, 1611,

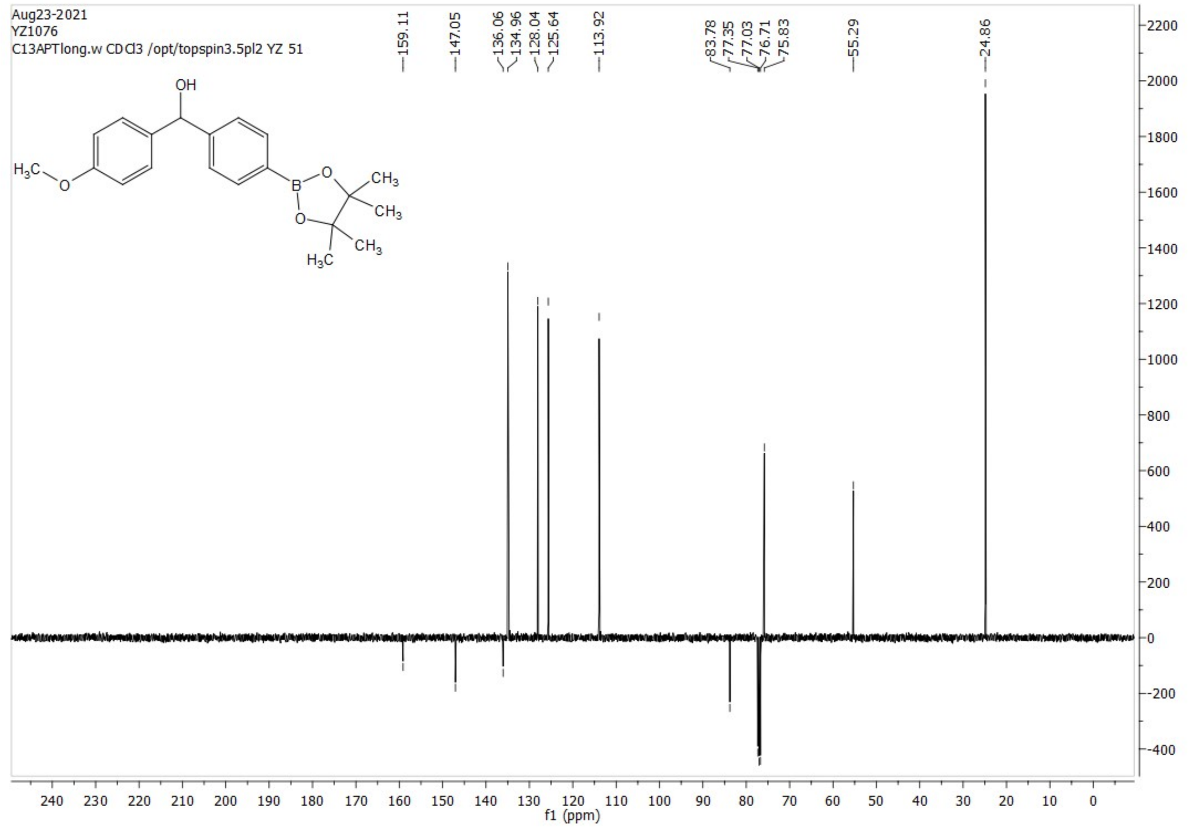
1510, 1397, 1318, 1245, 1169, 1141, 1085, 961 cm$^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 7.79 (2H, d, *J* = 7.9, ArH), 7.39 (2H, d, *J* = 7.9, ArH), 7.26-7.24 (2H, m, ArH), 6.85 (2H, d, *J* = 8.6, ArH), 5.81 (1H, d, *J* = 3.5, ArCH), 3.78 (3H, s, $OCH_3$), 2.21 (1H, d, *J* = 3.5, OH), 1.33 (12H, s, $CH_3$) ppm; $\delta_C$ (100 MHz, $CDCl_3$) 159.11 (C), 147.05 (C), 136.06 (C), 134.96 (CH), 128.04 (CH), 125.64 (CH), 113.92 (CH), 83.78 (C), 75.83 (CH), 55.29 ($CH_3$), 24.86 ($CH_3$) ppm; m/z (ES-API+) 363.2 ($M^+$ + 23, 100%).
Enantiomeric excess and conversion determined by HPLC analysis (Chiralpak IG, 30 cm x 6mm column, hexane:iPrOH 95:5, 0.5 mL/min, T = 25°C) ketone 35.0 min, *R* and *S* isomers 48.3 min and 52.5 min, configuration is not confirmed.

ATH of (4-methoxyphenyl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone using (*R,R*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (1.5 mg, 2.4 μmol, 1 mol%) was added to FA: TEA (5:2 azeotropic mixture, 0.36 mL) at rt and the mixture was stirred under a nitrogen atmosphere for 15 minutes; after which a solution of (4-methoxyphenyl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone (80.0 mg, 0.237 mmol) in DCM (0.50 mL) was added. The reaction mixture was stirred under a nitrogen atmosphere and followed by TLC (4:1 hexane: EtOAc). After 72 hours, the reaction was quenched using saturated $NaHCO_3$ solution (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried ($MgSO_4$) and filtered. The solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-50% EtOAc in hexane to give (4-methoxyphenyl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanol **24** as a colorless oil (42.5 mg, 0.125 mmol, 53%). The reaction was also followed by HPLC (Chiralpak IG, 30 cm x 6mm column, hexane:iPrOH 95:5, 0.5 mL/min, T = 25°C): $[\alpha]_D^{26}$ -2.35 (c 0.680 in $CHCl_3$) 20% ee.

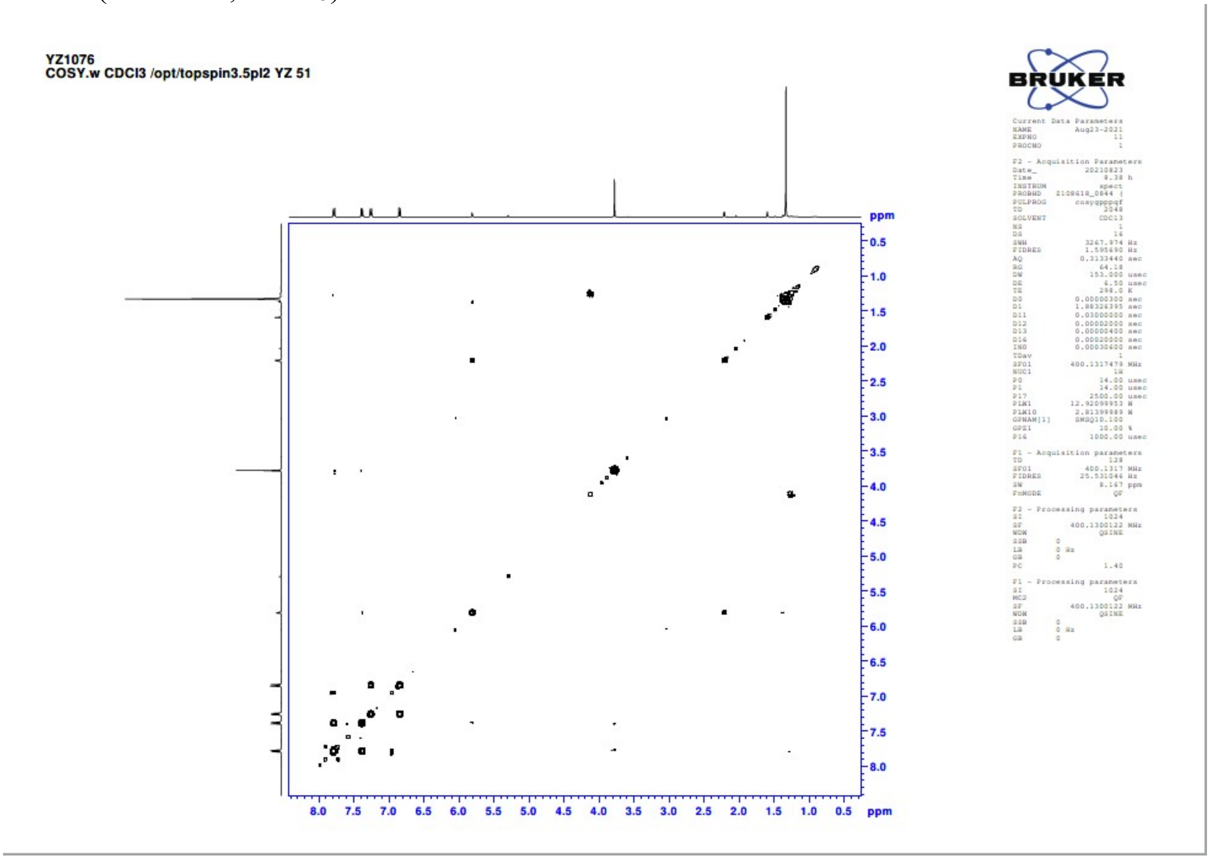
$^1H$ NMR (400 MHz, $CDCl_3$)



$^{13}C$ NMR (100 MHz, $CDCl_3$)



COSY (400 MHz, $CDCl_3$)


**YZ1076**
**COSY.w CDCl3 /opt/topspin3.5pl2 YZ 51**

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Current Data Parameters
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EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
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PULPROG       cosygpppqf
TD                  2048
SOLVENT            CDCl3
NS                     1
DS                    16
SWH             3267.974 Hz
FIDRES          1.595690 Hz
AQ             0.3133440 sec
RG                 64.18
DW               153.000 usec
DE                  6.50 usec
TE                 298.0 K
D0            0.00000300 sec
D1            1.88326395 sec
D11           0.03000000 sec
D12           0.00002000 sec
D13           0.00000400 sec
D16           0.00020000 sec
IN0           0.00030600 sec
TDav                   1
SFO1         400.1317479 MHz
NUC1                  1H
P0                 14.00 usec
P1                 14.00 usec
P17              2500.00 usec
PLW1         12.92099953 W
PLW10         2.81399989 W
GPNAM[1]       SMSQ10.100
GPZ1               10.00 %
P16              1000.00 usec

F1 - Acquisition parameters
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SFO1            400.1317 MHz
FIDRES         25.531046 Hz
SW                 8.167 ppm
FnMODE                QF

F2 - Processing parameters
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SF           400.1300122 MHz
WDW                QSINE
SSB       0
LB        0 Hz
GB        0
PC                  1.40

F1 - Processing parameters
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MC2                   QF
SF           400.1300122 MHz
WDW                QSINE
SSB       0
LB        0 Hz
GB        0
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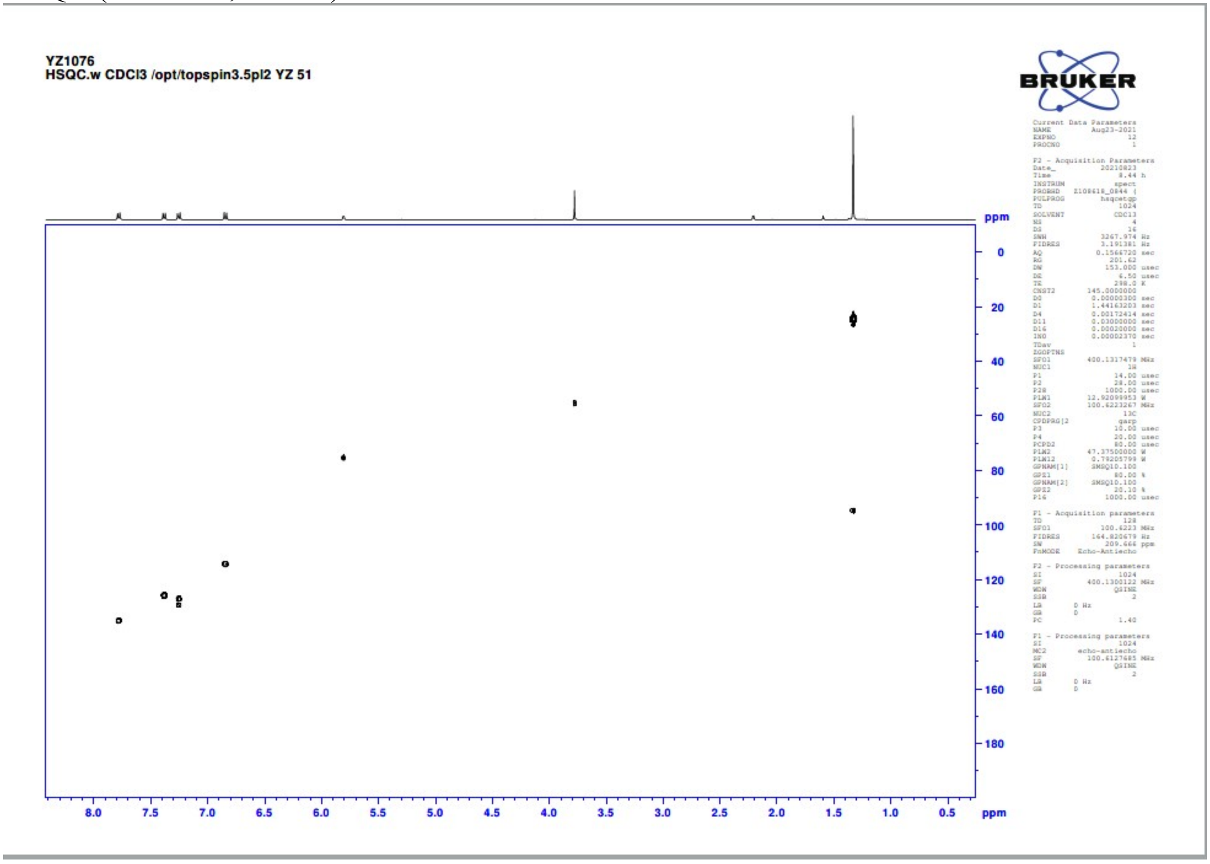
HSQC (400 MHz, $CDCl_3$)


**YZ1076**
**HSQC.w CDCl3 /opt/topspin3.5pl2 YZ 51**

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PROCNO                 1

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TD                  1024
SOLVENT            CDCl3
NS                     4
DS                    16
SWH             3267.974 Hz
FIDRES          3.191381 Hz
AQ             0.1566720 sec
RG                201.62
DW               153.000 usec
DE                  6.50 usec
TE                 298.0 K
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D1            1.44163203 sec
D4            0.00172414 sec
D11           0.03000000 sec
D16           0.00020000 sec
IN0           0.00002370 sec
TDav                   1
ZGOPTNS
SFO1         400.1317479 MHz
NUC1                  1H
P1                 14.00 usec
P2                 28.00 usec
P28              1000.00 usec
PLW1         12.92099953 W
SFO2         100.6223267 MHz
NUC2                 13C
CPDPRG[2            garp
P3                 10.00 usec
P4                 20.00 usec
PCPD2              80.00 usec
PLW2         47.37500000 W
PLW12         0.79205799 W
GPNAM[1]      SMSQ10.100
GPZ1               80.00 %
GPNAM[2]      SMSQ10.100
GPZ2               20.10 %
P16              1000.00 usec

F1 - Acquisition parameters
TD                   128
SFO1            100.6223 MHz
FIDRES        164.820679 Hz
SW               209.666 ppm
FnMODE    Echo-Antiecho

F2 - Processing parameters
SI                  1024
SF           400.1300122 MHz
WDW                QSINE
SSB                    2
LB        0 Hz
GB        0
PC                  1.40

F1 - Processing parameters
SI                  1024
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SF           100.6127685 MHz
WDW                QSINE
SSB                    2
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GB        0
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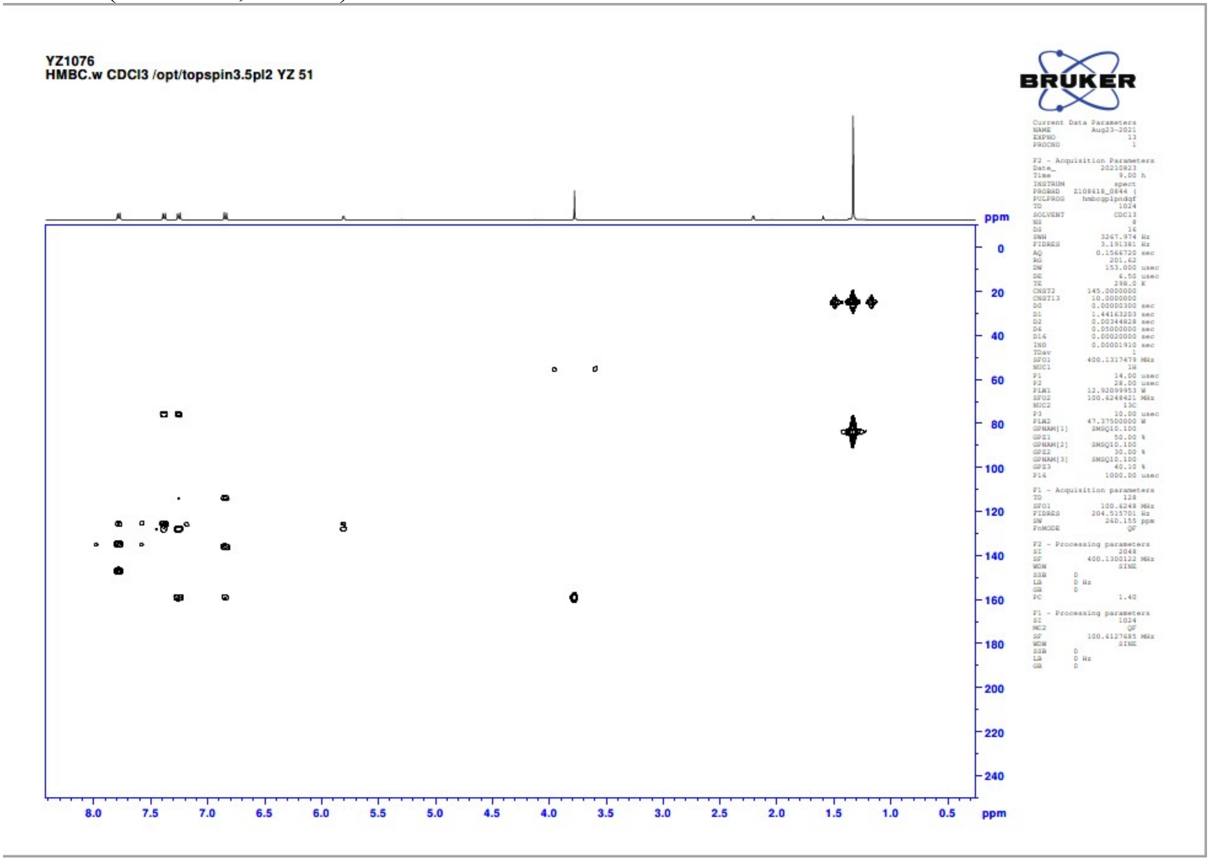
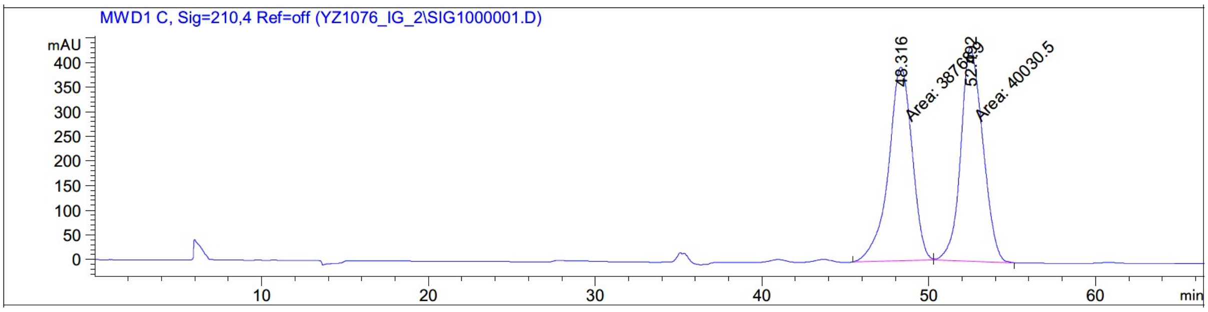
HMBC (400 MHz, $CDCl_3$)



HPLC of racemic (4-methoxyphenyl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanol **24**.



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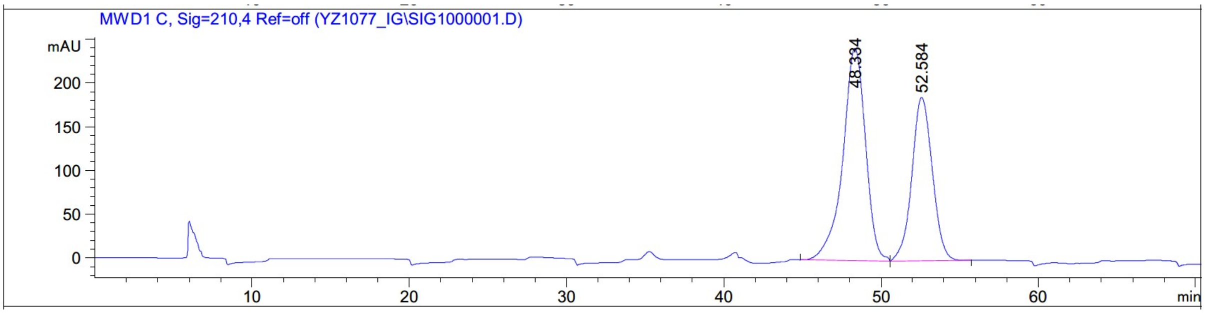
Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  48.316 MM     1.6431 3.87689e4  393.24020  49.1995
   2  52.492 MM     1.5328 4.00305e4  435.27069  50.8005
```

HPLC after ATH of (4-methoxyphenyl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone using (*R,R*)-3C-Tethered Ru(II)-TsDPEN catalyst **2** (after 72 hours, 100% conversion, 20% ee).

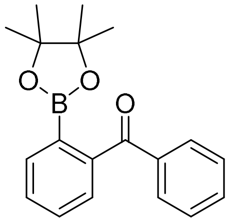


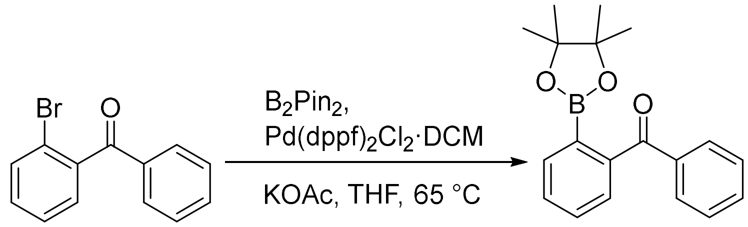
```
Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  48.334 BB     1.5246 2.45206e4  242.71507  59.1423
   2  52.584 BB     1.3859 1.69397e4  186.80972  40.8577

Totals :                   4.14603e4  429.52480
```

Phenyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone.



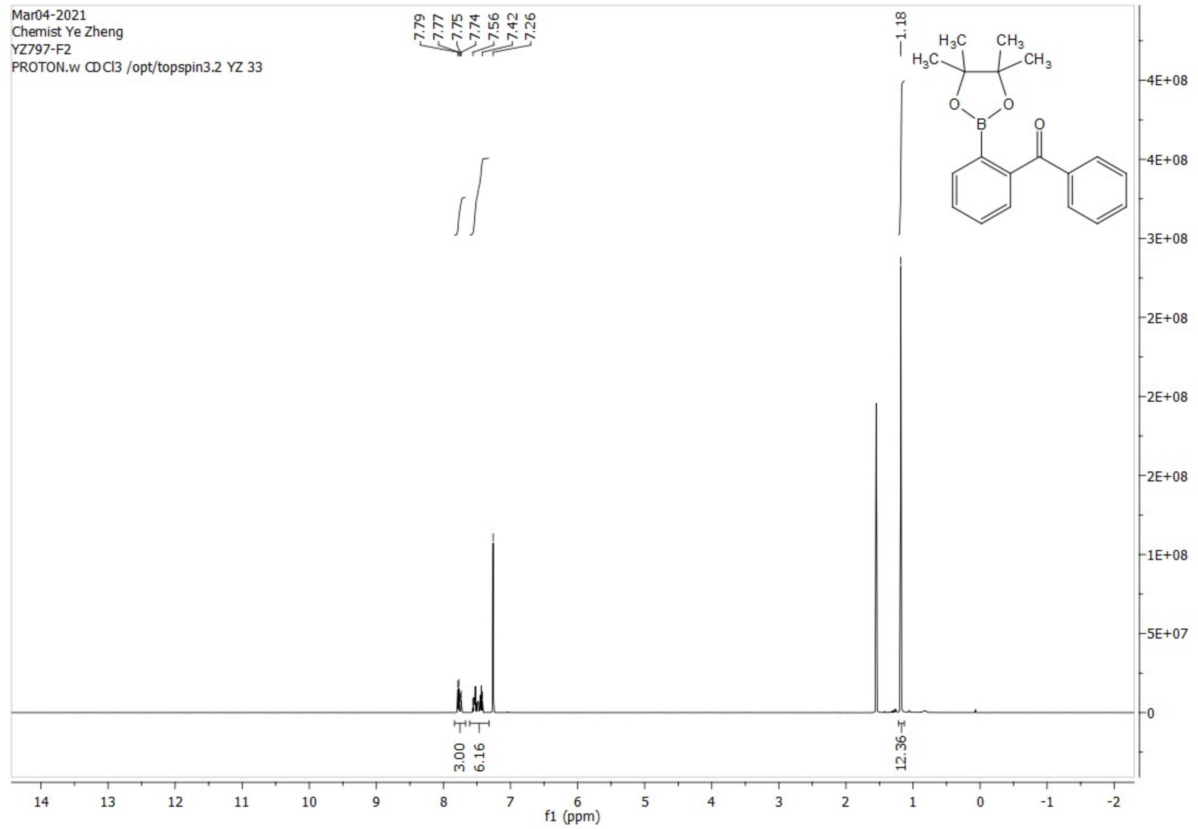


This compound has been reported and fully characterized: K. L. Billingsley, T. E. Barder and S. L. Buchwald, *Angew. Chem., Int. Ed.*, 2007, **46**, 55359-5363.

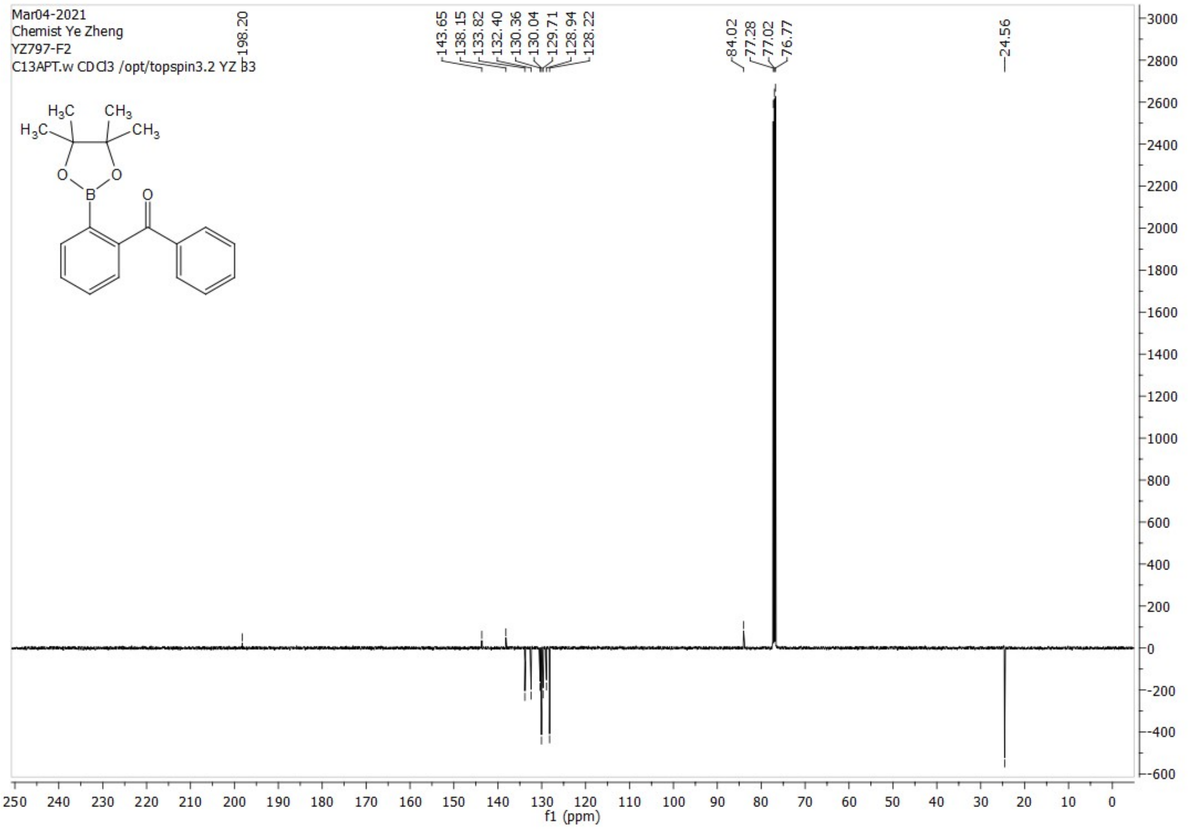
A round-bottom flask was charged with 2-bromobenzophenone (130 mg, 0.500 mmol), bis(pinacolato)diboron (152 mg, 0.600 mmol), potassium acetate (147 mg, 1.50 mmol), THF (3.2 mL) and $Pd(dppf)_2Cl_2 \cdot DCM$ (20.4 mg, 0.0250 mmol). The reaction mixture was heated to 65 °C and left stirring under the nitrogen atmosphere overnight, followed by TLC (9:1 hexane: EtOAc). The mixture was quenched by distilled water (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried ($MgSO_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-50% ethyl acetate in hexane to give phenyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone as a white solid (50.5 mg, 0.164 mmol, 33%). TLC: Rf ca 0.50 (9:1 hexane: EtOAc), strong UV and $KMnO_4$; $\delta_H$ (500 MHz, $CDCl_3$) 7.79 (3H, dd, *J* = 17.3, 7.2, ArH), 7.56-7.42 (6H, m, ArH), 1.18 (12H, s, $CH_3$) ppm; $\delta_C$ (125 MHz, $CDCl_3$) 198.20 (C), 143.65 (C), 138.15 (C), 133.82 (CH), 132.40 (CH), 130.36 (CH), 130.04 (CH), 129.71 (CH), 128.94 (CH), 128.22 (CH), 84.02 (C), 24.56 ($CH_3$) ppm. Data matched that reported.

Enantiomeric excess and conversion determined by HPLC analysis (Chiralpak ODH, 30 cm x 6mm column, hexane:iPrOH 95:5, 1.0 mL/min, T = 25°C) ketone 5.4 min, *R* and *S* isomers 4.2 min and 5.5 min.

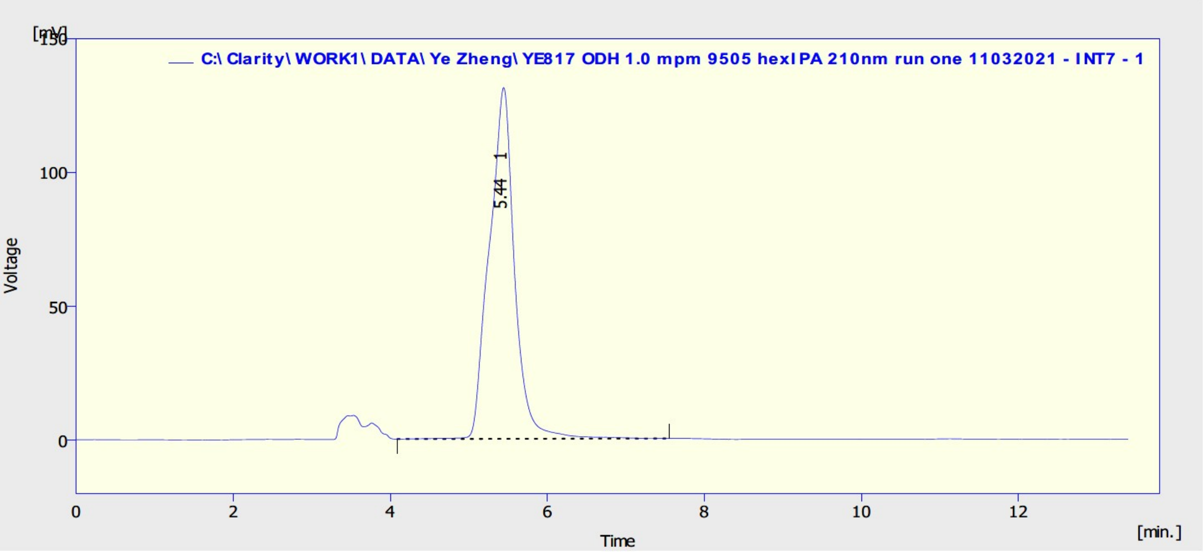
$^{1}H$ NMR (500 MHz, $CDCl_3$)



$^{13}C$ NMR (125 MHz, $CDCl_3$)



HPLC of phenyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone

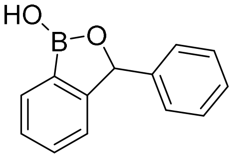


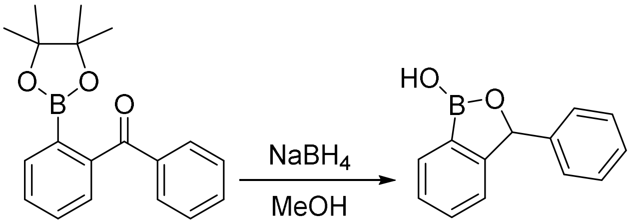
*Result Table (Uncal - C:\Clarity\WORK1\DATA\Ye Zheng\YE817 ODH 1.0 mpm 9505 hexIPA 210nm run one 11032021 - INT7 - 1)*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Compound Name |
|---|---|---|---|---|---|---|---|
| 1 | 5.443 | 2940.350 | 131.262 | 100.0 | 100.0 | 0.34 | |
| | Total | 2940.350 | 131.262 | 100.0 | 100.0 | | |

3-Phenylbenzo[c][1,2]oxaborol-1(3H)-ol **25**.

**Compound picture：**





This compound has been reported (racemic) but not fully characterized: D. S. Gunasekera, D. J. Gerold, N. S. Aalderks, J. S. Chandra, C. A. Maanu, P. Kiprof, V. V. Zhdankin and M. V. R. Reddy, *Tetrahedron*, 2007, **63**, 9401-9405.

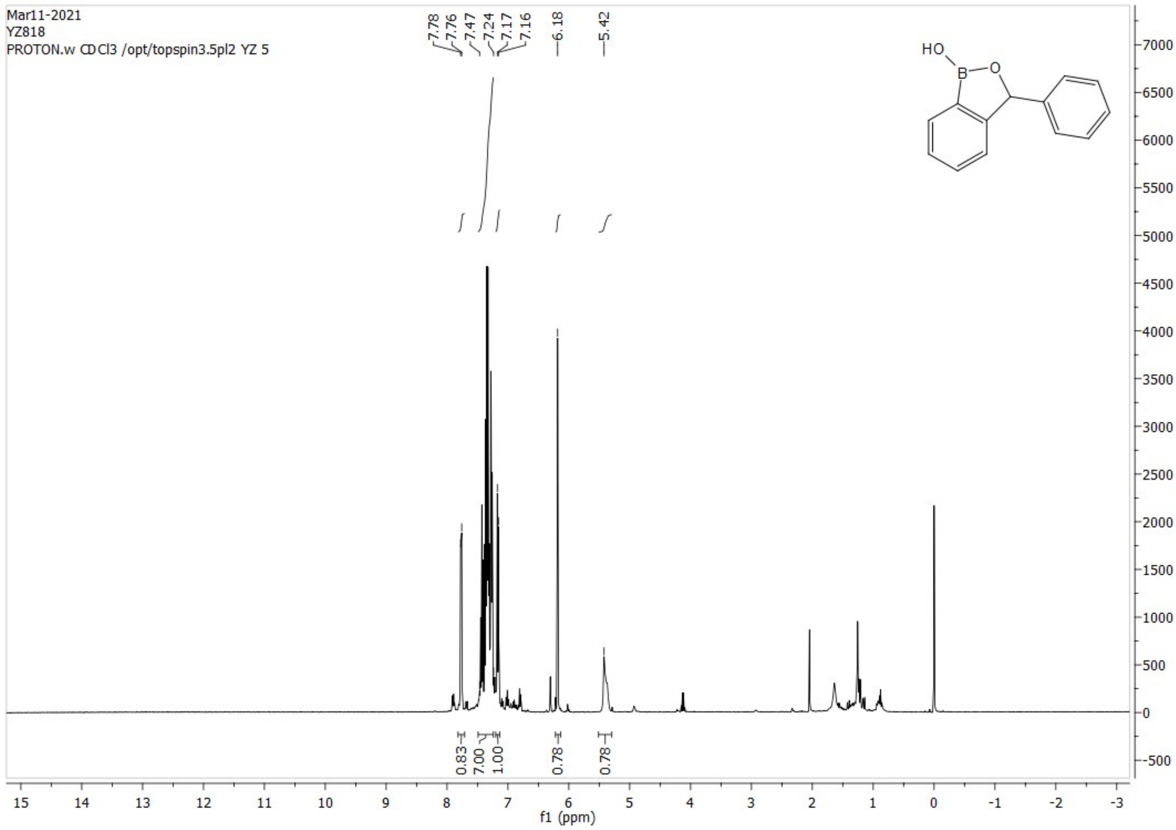
To a solution of phenyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone (153 mg, 0.497 mmol) in MeOH (2.5 mL) was added sodium borohydride (37.8 mg, 0.994 mmol). The reaction was stirred for 4 hours. TLC (9:1 hexane: EtOAc) after this time indicated full conversion. Distilled water (20 mL) was added, and the mixture was extracted with EtOAc (3 × 20ml), dried with $MgSO_4$. Solvent was removed to give the crude product. The reaction was followed by TLC (9:1 hexane: EtOAc). The product was isolated via flash chromatography on silica eluted with 0-50% ethyl acetate in hexane to give 3-phenylbenzo[c][1,2]oxaborol-1(3H)-ol **25** as a white solid (41.5 mg, 0.198 mmol, 40%). TLC: Rf ca 0.20 (9:1 hexane: EtOAc), strong UV and $KMnO_4$; $\delta_H$ (400 MHz, $CDCl_3$) 7.78 (1H, d, *J* = 7.2, ArH), 7.47-7.24 (7H, m, ArH), 7.17 (1H, d, *J* = 7.6, ArH), 6.18 (1H, s, ArCH), 5.42 (1H, s, OH) ppm; $\delta_C$ (100 MHz, $CDCl_3$) 156.76 (C), 140.11 (C), 131.50 (CH), 131.41 (CH), 130.42 (CH), 128.71 (CH), 128.41 (CH), 127.61 (CH), 126.88 (CH), 122.37 (CH), 83.79 (CH) ppm. Data matched that reported.

Enantiomeric excess and conversion determined by HPLC analysis (Chiralcel ODH, 30 cm x 6mm column, hexane:iPrOH 95:5, 1.0 mL/min, T = 25°C) ketone 5.4 min, *R* and *S* isomers 4.2 min and 5.5 min, configuration is not confirmed.

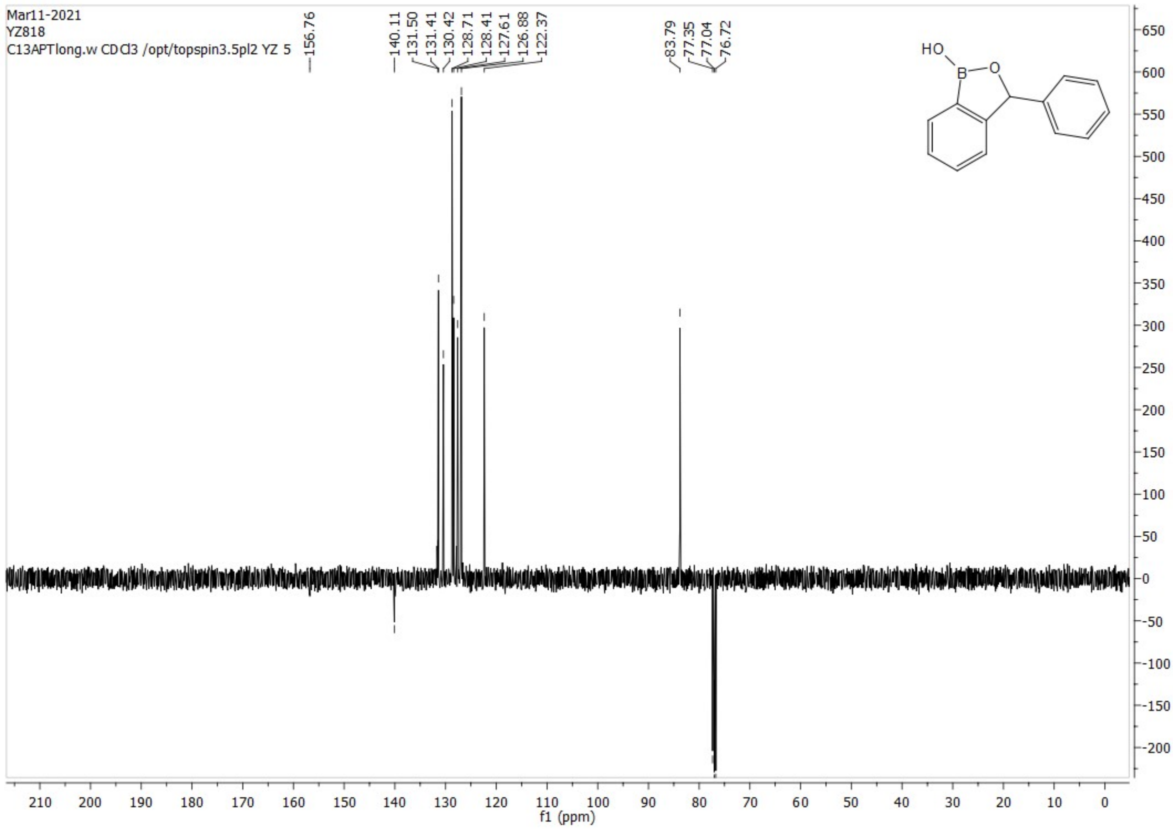
ATH of phenyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone).

(*R,R*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (2.0 mg, 0.0033 mmol, 1 mol%) was added to FA: TEA (5:2 azeotropic mixture, 0.45 mL) at rt and the mixture was stirred under a nitrogen inert atmosphere for 10-15 minutes; after which a solution of phenyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone (100 mg, 0.325 mmol) in DCM (0.63 mL) was added. The reaction mixture was stirrer under a nitrogen atmosphere, followed by TLC (9:1 hexane: EtOAc). After 72 hours, the reaction was quenched using saturated $NaHCO_3$ solution (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried ($MgSO_4$) and filtered. The solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-50% ethyl acetate in hexane to give 3-phenylbenzo[c][1,2]oxaborol-1(3H)-ol **25** (47.0 mg, 0.224 mmol, 69%). The reaction was also followed by HPLC analysis (Chiralcel ODH, 30 cm x 6mm column, hexane:iPrOH 95:5, 1.0 mL/min, T = 25°C): 100% conversion; $[\alpha]_D^{17}$ +2.29 (c 0.940 in $CHCl_3$) 23% ee.

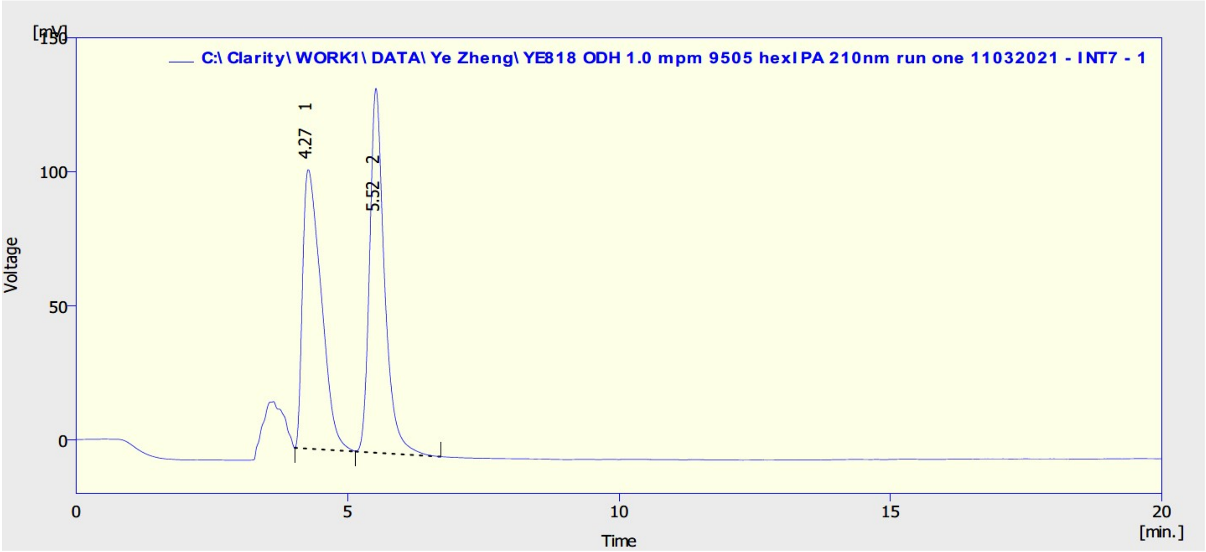
$^1$H NMR (400 MHz, CDCl$_3$)



$^{13}$C NMR (100 MHz, CDCl$_3$)



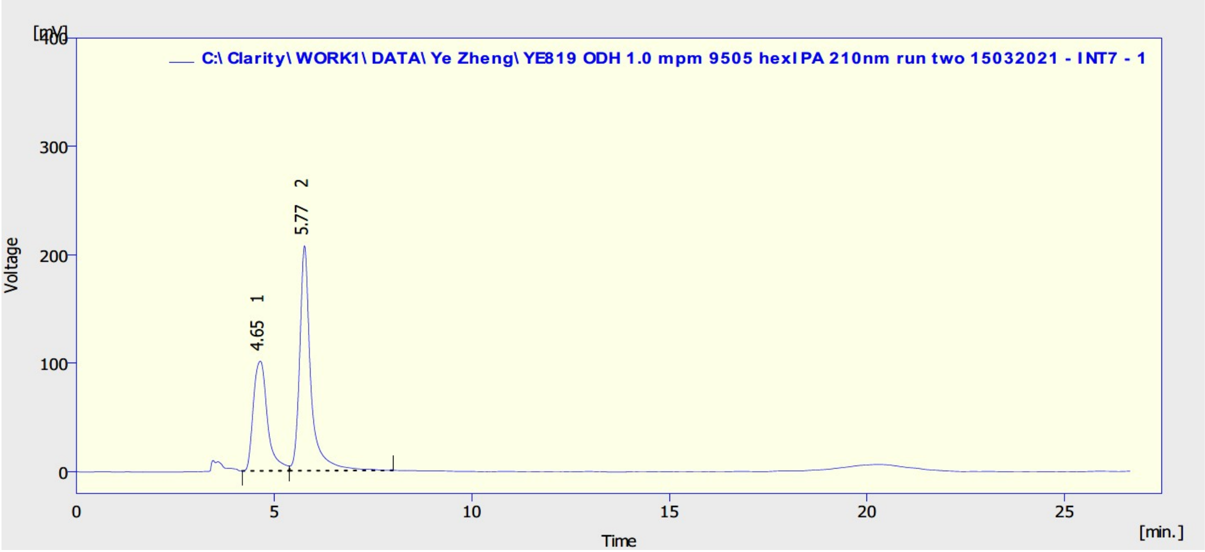
HPLC of racemic phenylbenzo[c][1,2]oxaborol-1(3H)-ol **25**.



*Result Table (Uncal - C:\Clarity\WORK1\DATA\Ye Zheng\YE818 ODH 1.0 mpm 9505 hexIPA 210nm run one 11032021 - INT7 - 1)*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Compound Name |
|---|---|---|---|---|---|---|---|
| 1 | 4.273 | 2472.933 | 104.144 | 48.8 | 43.4 | 0.38 | |
| 2 | 5.520 | 2592.828 | 135.885 | 51.2 | 56.6 | 0.28 | |
| | Total | 5065.761 | 240.029 | 100.0 | 100.0 | | |

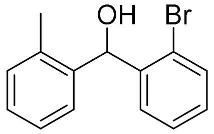
HPLC after ATH of phenyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone using (*R,R*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (after 72 hours, 100% conversion, 23% ee)

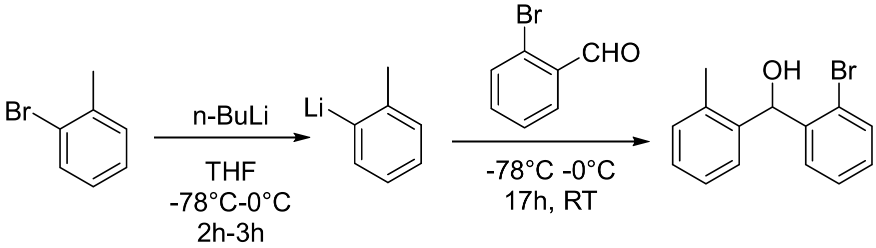


*Result Table (Uncal - C:\Clarity\WORK1\DATA\Ye Zheng\YE819 ODH 1.0 mpm 9505 hexIPA 210nm run two 15032021 - INT7 - 1)*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Compound Name |
|---|---|---|---|---|---|---|---|
| 1 | 4.647 | 2529.556 | 101.207 | 38.3 | 32.8 | 0.37 | |
| 2 | 5.767 | 4078.658 | 207.434 | 61.7 | 67.2 | 0.26 | |
| | Total | 6608.214 | 308.641 | 100.0 | 100.0 | | |

(2-Bromophenyl)(o-tolyl)methanol.

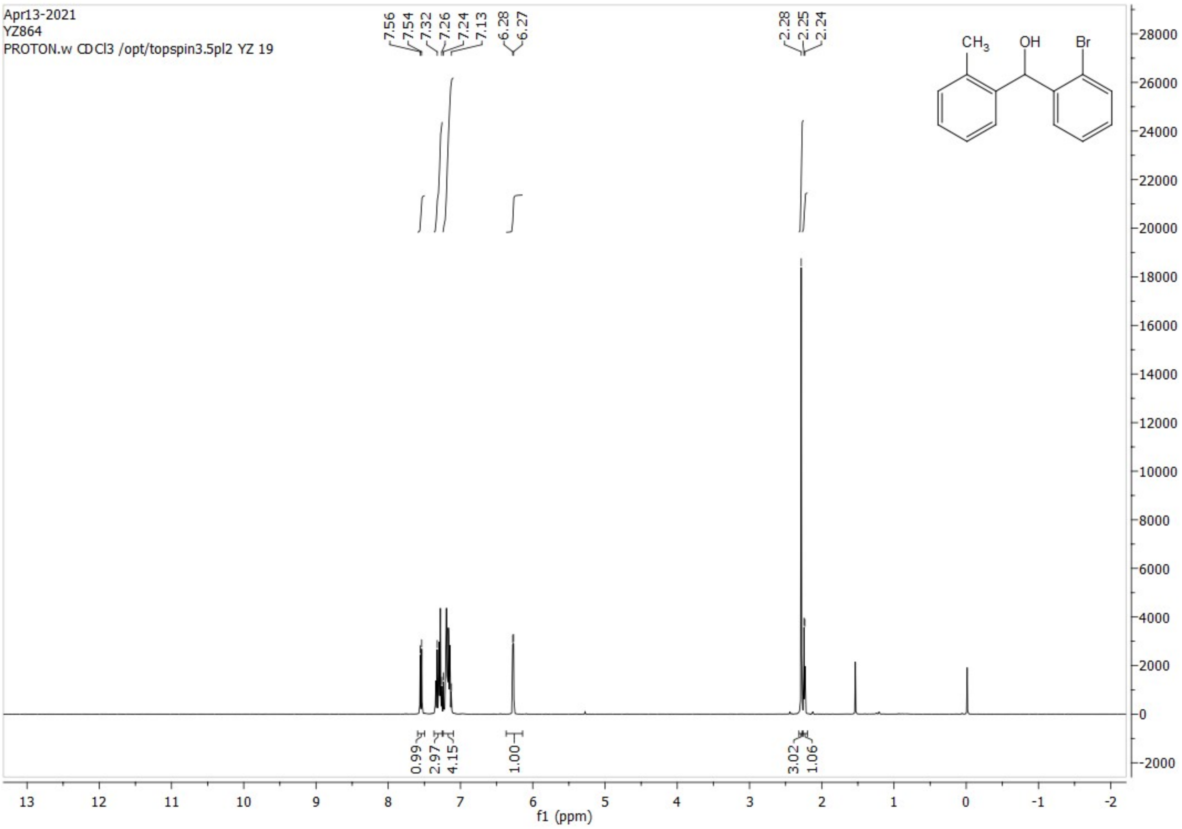




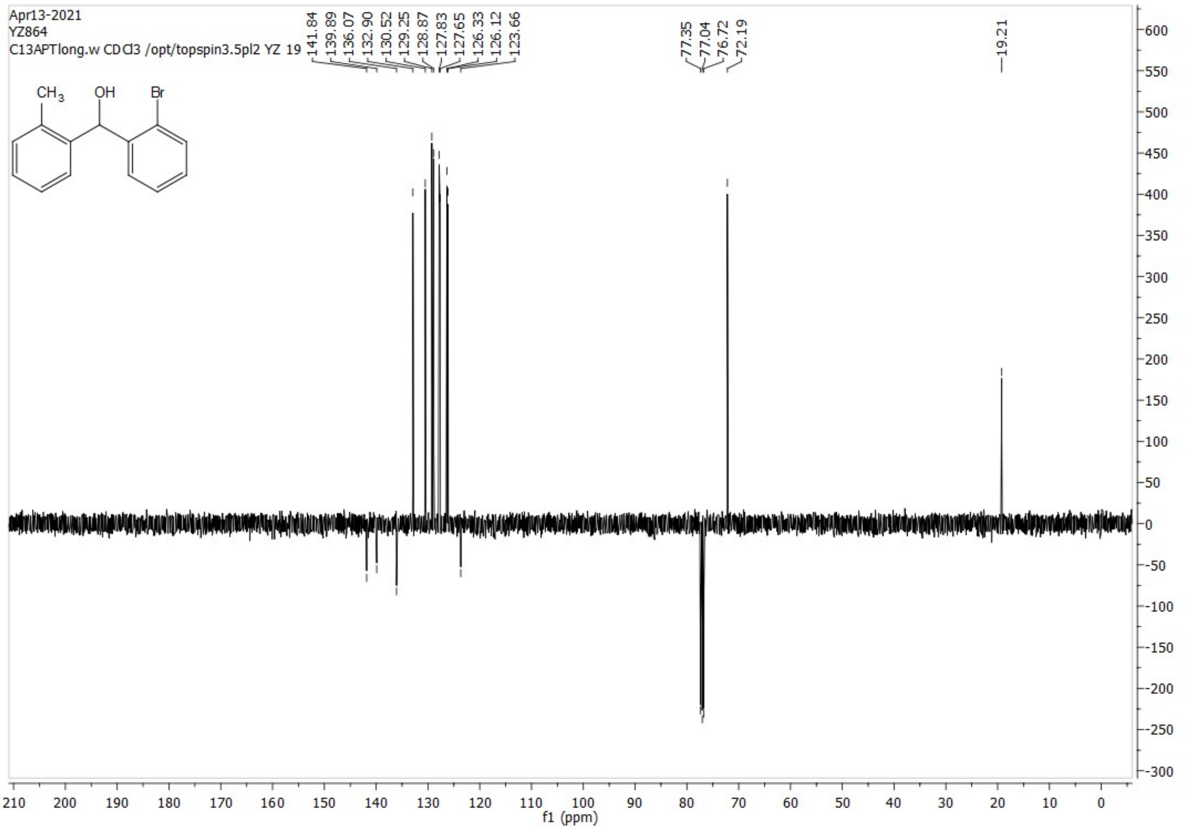
This compound has been reported and fully characterized: Yuan-Xi Liao, Chun-Hui Xing, Matthew Israel, Qiao-Sheng Hu, *Tetrahedron Letters*, 2011, **52**, 3324-3328

To a solution of 2-bromotoluene (188 mg, 1.10 mmol) in THF (2.4 mL) at -78 °C was added dropwise a solution of n-butyllithium (0.400 mL, 2.5M in hexanes, 1.00 mmol). The reaction mixture was then stirred under a nitrogen atmosphere for 2-3 hours, after which 2-bromobenzaldehyde (185 mg, 1.00 mmol) was added dropwise. The reaction mixture was left stirring under the nitrogen atmosphere and allowed to warm to rt. The reaction was followed by TLC (9:1 hexane: EtOAc). The mixture was quenched by saturated $NH_4Cl$ solution (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried ($MgSO_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-20% EtOAc in hexane to give (2-bromophenyl)(o-tolyl)methanol as a white solid (256 mg, 0.928 mmol, 93%). TLC: Rf ca 0.30 TLC (9:1 hexane: EtOAc)., strong UV and $KMnO_4$; $\delta_H$ (400 MHz, $CDCl_3$) 7.56 (1H, d, *J* = 7.9, ArH), 7.32 (3H, dt, *J* = 14.9, 6.8, ArH), 7.24-7.13 (4H, m, ArH), 6.28 (1H, d, *J* = 4.5, Ar*CH*OH), 2.28 (3H, s, $CH_3$), 2.25 (1H, d, *J* = 4.5, ArCH*OH*) ppm; $\delta_C$ (100 MHz, $CDCl_3$) 141.84 (C), 139.89 (C), 136.07 (C), 132.90 (CH), 130.52 (CH), 129.25 (CH), 128.87 (CH), 127.83 (CH), 127.65 (CH), 126.33 (CH), 126.12 (CH), 123.66 (C), 72.19 (CH), 19.21 ($CH_3$) ppm.

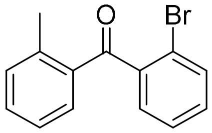
$^{1}H$ NMR (400 MHz, $CDCl_3$)

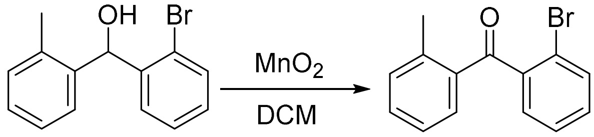


$^{13}C$ NMR (100 MHz, $CDCl_3$)



### (2-Bromophenyl)(*o*-tolyl)methanone.

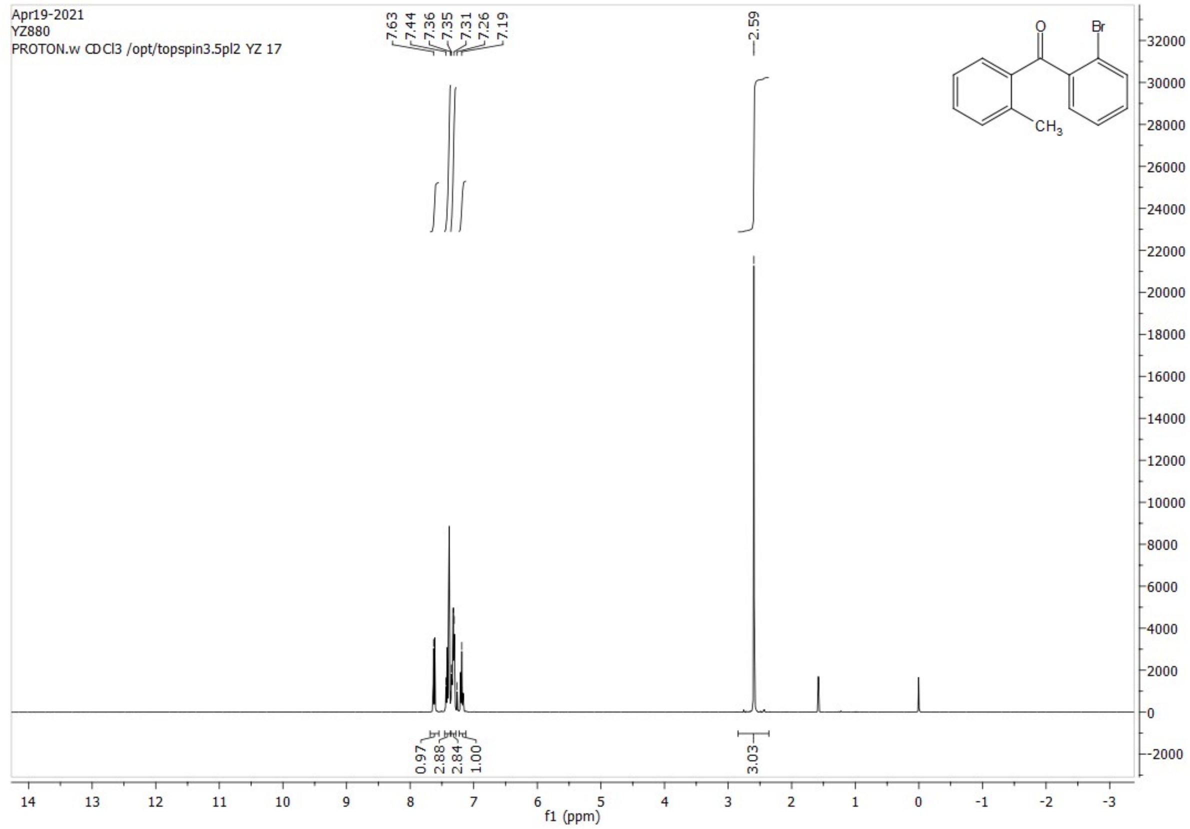




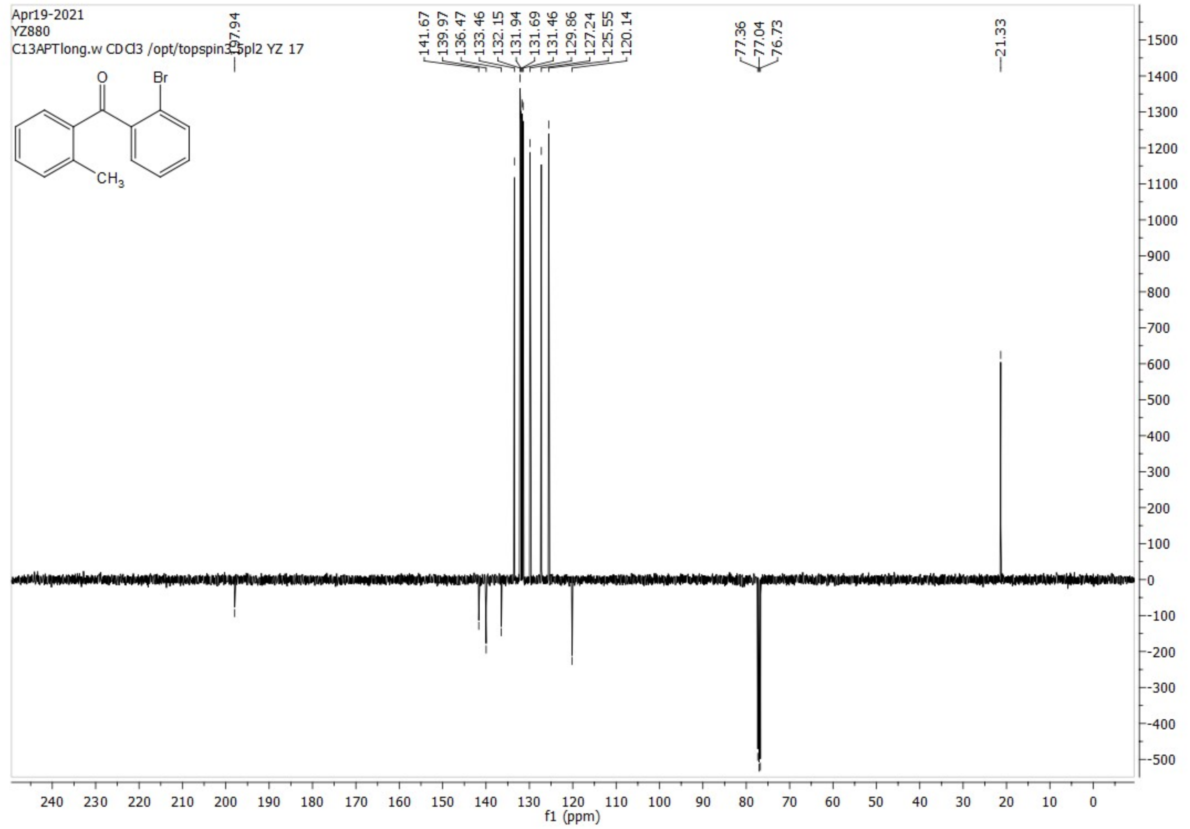
This compound has been reported and fully characterized: P. Sharma, S. Rohilla and N. Jain, *J. Org. Chem.*, 2017, **82**, 1105-1113.

To a solution of (2-bromophenyl)(*o*-tolyl)methanol (1.00 g, 3.62 mmol) in DCM (25 mL) at rt was added manganese dioxide (9.47 g, 109 mmol). The reaction mixture was left to stir under a nitrogen atmosphere overnight. TLC (9:1 hexane: EtOAc) after this time indicated full conversion. The solids were removed by gravity filtration and washed with DCM. The combined solvent was removed to give the product as a colorless oil (854 mg, 3.12 mmol, 86%). TLC: Rf ca 0.50 (9:1 hexane: EtOAc), strong UV and $KMnO_4$; $\delta_H$ (400 MHz, $CDCl_3$) 7.63 (1H, d, *J* = 7.8, ArH), 7.44-7.36 (3H, m, ArH), 7.35-7.31 (3H, m, ArH), 7.19 (1H, t, *J* = 7.5, ArH), 2.59 (3H, s, $CH_3$) ppm; $\delta_C$ (100 MHz, $CDCl_3$) 197.94 (C), 141.67 (C), 139.97 (C), 136.47 (C), 133.46 (CH), 132.15 (CH), 131.94 (CH), 131.69 (CH), 131.46 (CH), 129.86 (CH), 127.24 (CH), 125.55 (CH), 120.14 (C), 21.33 ($CH_3$) ppm. Data matched that reported.

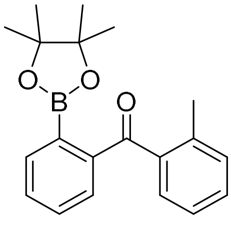
$^1$H NMR (400 MHz, CDCl$_3$)

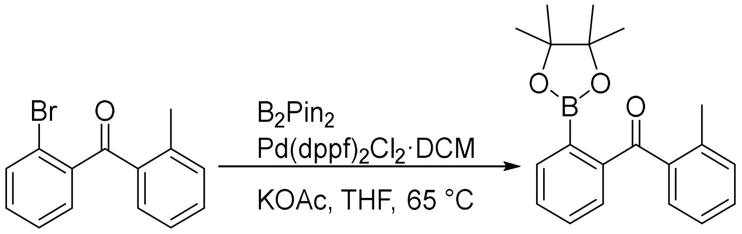


$^{13}$C NMR (100 MHz, CDCl$_3$)



(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)(*o*-tolyl)methanone.



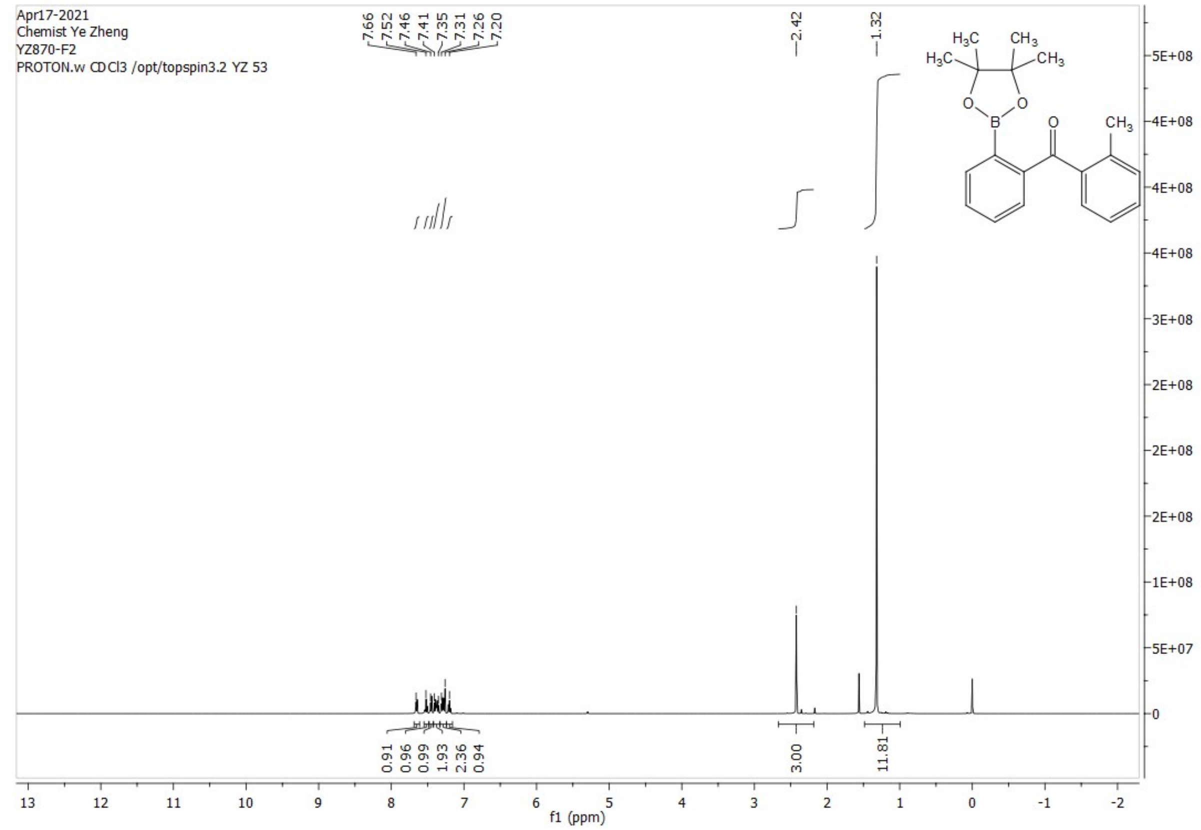


This compound is novel.

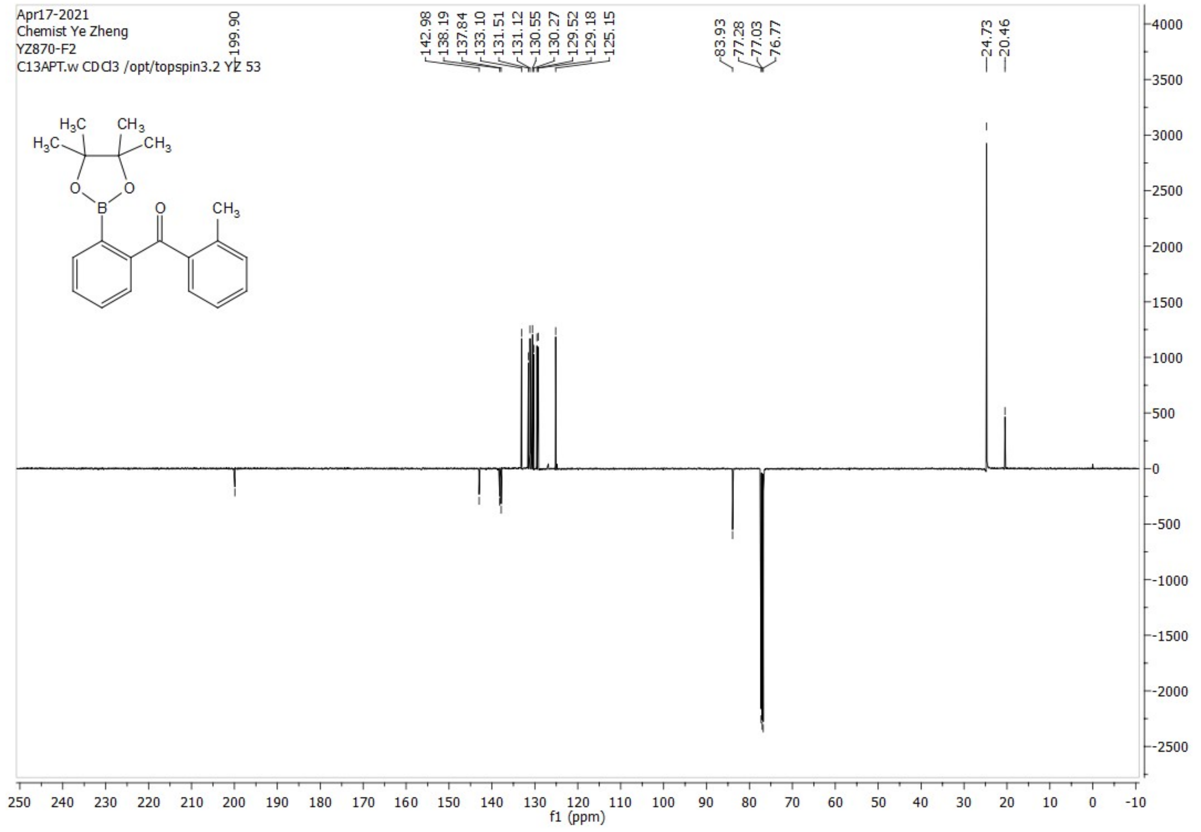
A round-bottom flask was charged with (2-bromophenyl)(*o*-tolyl)methanone (706 mg, 2.58 mmol), bis(pinacolato)diboron (787 mg, 3.10 mmol), potassium acetate (759 mg, 7.74 mmol), THF (16 mL) and $Pd(dppf)_2Cl_2{\cdot}DCM$ (105 mg, 0.129 mmol). The reaction mixture was heated to 65 °C and left stirring under the nitrogen atmosphere overnight, followed by TLC (9:1 hexane: EtOAc). The mixture was quenched by distilled water (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried ($MgSO_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-10% ethyl acetate in hexane to give (2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)(*o*-tolyl)methanone as a white solid (462 mg, 1.43 mmol, 56%). TLC: Rf ca 0.70 (9:1 hexane: EtOAc), strong UV and $KMnO_4$; Mp: 124 °C; HRMS: (found (ESI+): [M+H]+, Calcd for $C_{20}H_{23}BNaO_3$ 345.1632; Found 345.1635; 0.3 ppm error); $\nu_{max}$ 2972, 2926, 1649, 1561, 1370, 1340, 1301, 1267, 1254, 1144, 1108, 1069, 1033, 932, 855, 751 $cm^{-1}$; $\delta_H$ (500 MHz, $CDCl_3$) 7.66 (1H, d, *J* = 7.2, ArH), 7.52 (1H, td, *J* = 7.3, 1.0, ArH), 7.46 (1H, d, *J* = 7.4, ArH), 7.41-7.35 (2H, m, ArH), 7.31-7.26 (2H, m, ArH), 7.20 (1H, t, *J* = 7.4, ArH), 2.42 (3H, s, $CH_3$), 1.32 (12H, s, $CH_3$) ppm; $\delta_C$ (125 MHz, $CDCl_3$) 199.90 (C), 142.98 (C), 138.19 (C), 137.84 (C), 133.10 (CH), 131.51 (CH), 131.12 (CH), 130.55 (CH), 130.27 (CH), 129.52 (CH), 129.18 (CH), 125.15 (CH), 83.93 (C), 24.73 ($CH_3$), 20.46 ($CH_3$) ppm; m/z (ES-API+) 345.2 ($M^+$ + 23, 100%).

Enantiomeric excess and conversion determined by HPLC analysis (Chiralcel OJ, 30 cm x 6mm column, hexane:iPrOH 97:3, 0.5 mL/min, T = 25°C) ketone 13.6 min, *R* and *S* isomers 14.9 min and 19.0 min.

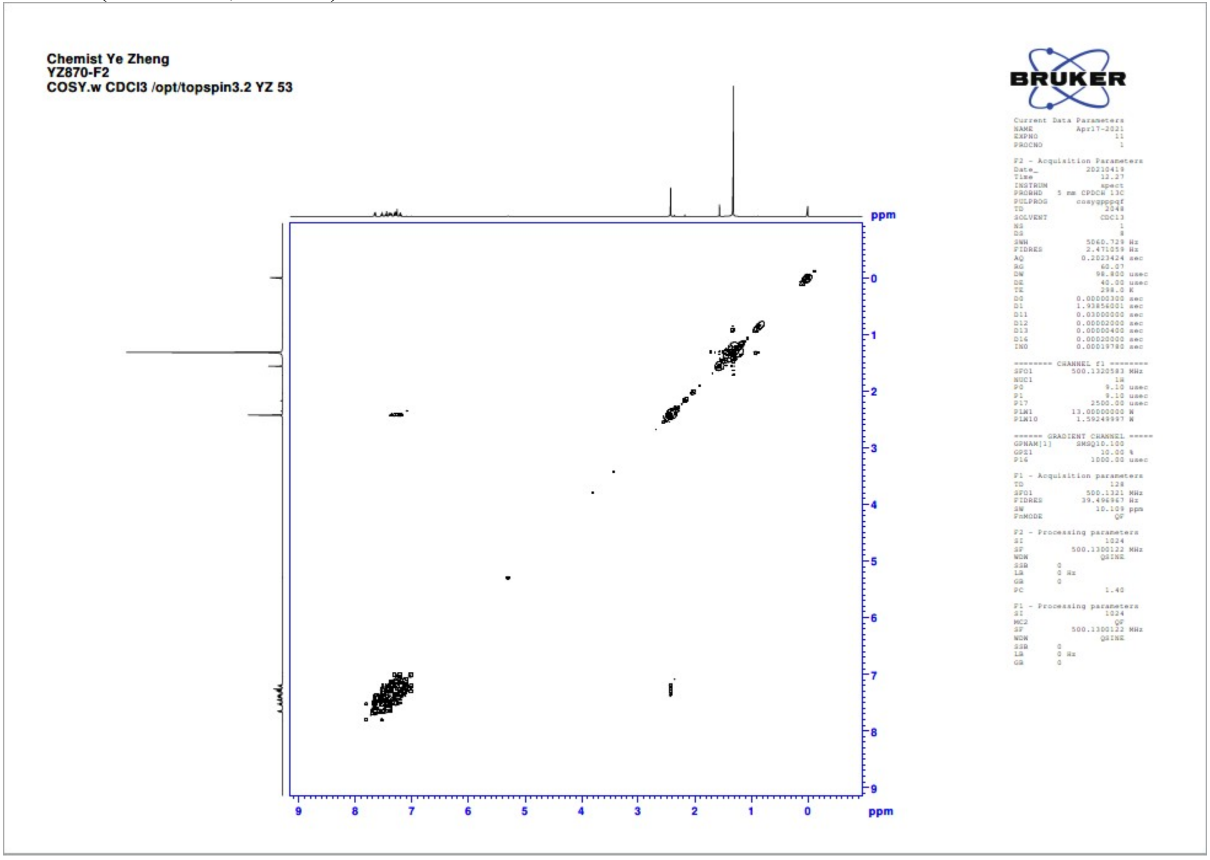
$^1H$ NMR (500 MHz, $CDCl_3$)



$^{13}C$ NMR (125 MHz, $CDCl_3$)



COSY (500 MHz, $CDCl_3$)



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Current Data Parameters
NAME          Apr17-2021
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210419
Time               12.27
INSTRUM            spect
PROBHD   5 mm CPDCH 13C
PULPROG        cosygpppqf
TD                  2048
SOLVENT            CDCl3
NS                     1
DS                     8
SWH             5060.729 Hz
FIDRES          2.471059 Hz
AQ             0.2023424 sec
RG                 60.07
DW                98.800 usec
DE                 40.00 usec
TE                 298.0 K
D0            0.00000300 sec
D1            1.93856001 sec
D11           0.03000000 sec
D12           0.00002000 sec
D13           0.00000400 sec
D16           0.00020000 sec
IN0           0.00019780 sec

======== CHANNEL f1 ========
SFO1         500.1320583 MHz
NUC1                  1H
P0                  9.10 usec
P1                  9.10 usec
P17              2500.00 usec
PLW1         13.00000000 W
PLW10         1.59249997 W

====== GRADIENT CHANNEL =====
GPNAM[1]      SMSQ10.100
GPZ1               10.00 %
P16              1000.00 usec

F1 - Acquisition parameters
TD                   128
SFO1            500.1321 MHz
FIDRES         39.496967 Hz
SW                10.109 ppm
FnMODE                QF

F2 - Processing parameters
SI                  1024
SF           500.1300122 MHz
WDW                QSINE
SSB        0
LB         0 Hz
GB         0
PC                  1.40

F1 - Processing parameters
SI                  1024
MC2                   QF
SF           500.1300122 MHz
WDW                QSINE
SSB        0
LB         0 Hz
GB         0
```
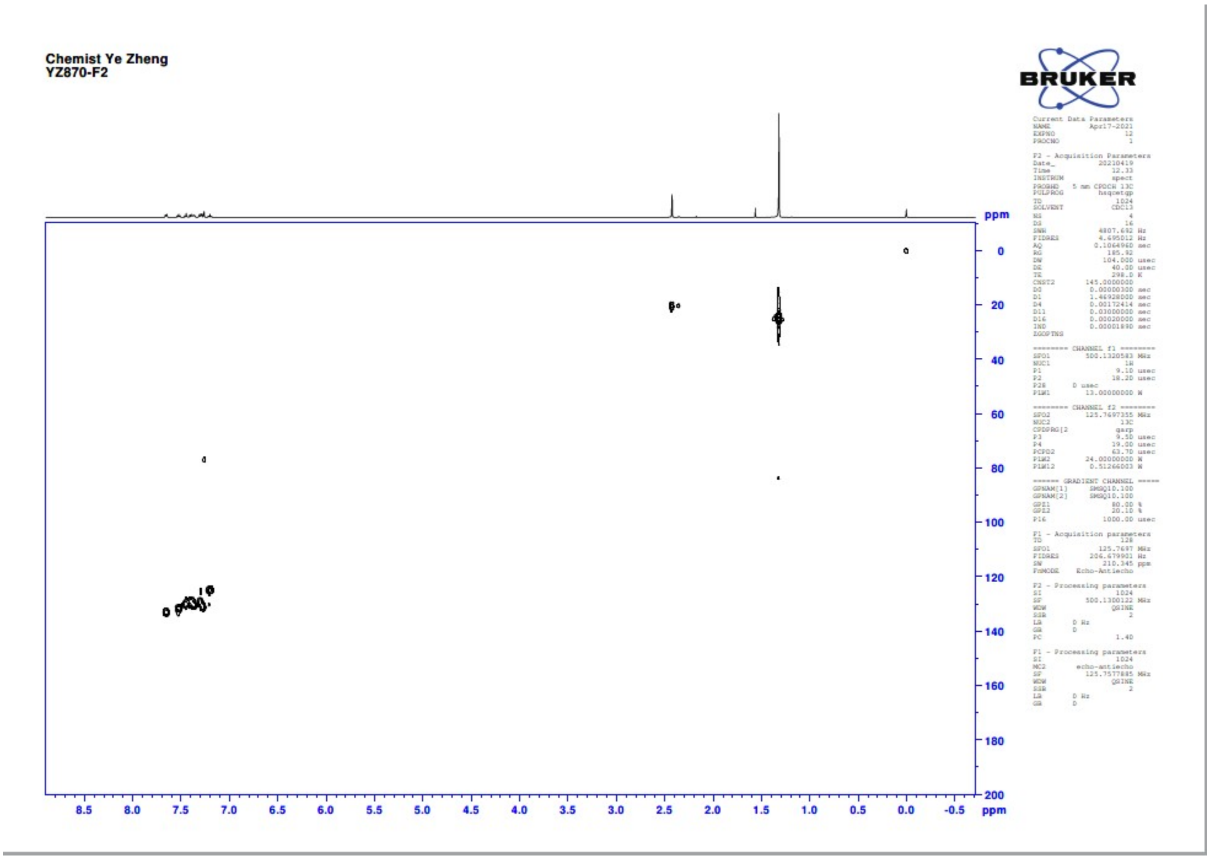

HSQC (500 MHz, $CDCl_3$)



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Current Data Parameters
NAME          Apr17-2021
EXPNO                 12
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210419
Time               12.33
INSTRUM            spect
PROBHD   5 mm CPDCH 13C
PULPROG          hsqcetgp
TD                  1024
SOLVENT            CDCl3
NS                     4
DS                    16
SWH             4807.692 Hz
FIDRES          4.695012 Hz
AQ             0.1064960 sec
RG                185.92
DW               104.000 usec
DE                 40.00 usec
TE                 298.0 K
CNST2        145.0000000
D0            0.00000300 sec
D1            1.46928000 sec
D4            0.00172414 sec
D11           0.03000000 sec
D16           0.00020000 sec
IN0           0.00001890 sec
ZGOPTNS

======== CHANNEL f1 ========
SFO1         500.1320583 MHz
NUC1                  1H
P1                  9.10 usec
P2                 18.20 usec
P28        0 usec
PLW1         13.00000000 W

======== CHANNEL f2 ========
SFO2         125.7697355 MHz
NUC2                 13C
CPDPRG[2            garp
P3                  9.50 usec
P4                 19.00 usec
PCPD2              63.70 usec
PLW2         24.00000000 W
PLW12         0.51266003 W

====== GRADIENT CHANNEL =====
GPNAM[1]      SMSQ10.100
GPNAM[2]      SMSQ10.100
GPZ1               80.00 %
GPZ2               20.10 %
P16              1000.00 usec

F1 - Acquisition parameters
TD                   128
SFO1            125.7697 MHz
FIDRES        206.679901 Hz
SW               210.345 ppm
FnMODE     Echo-Antiecho

F2 - Processing parameters
SI                  1024
SF           500.1300122 MHz
WDW                QSINE
SSB                    2
LB         0 Hz
GB         0
PC                  1.40

F1 - Processing parameters
SI                  1024
MC2         echo-antiecho
SF           125.7577885 MHz
WDW                QSINE
SSB                    2
LB         0 Hz
GB         0
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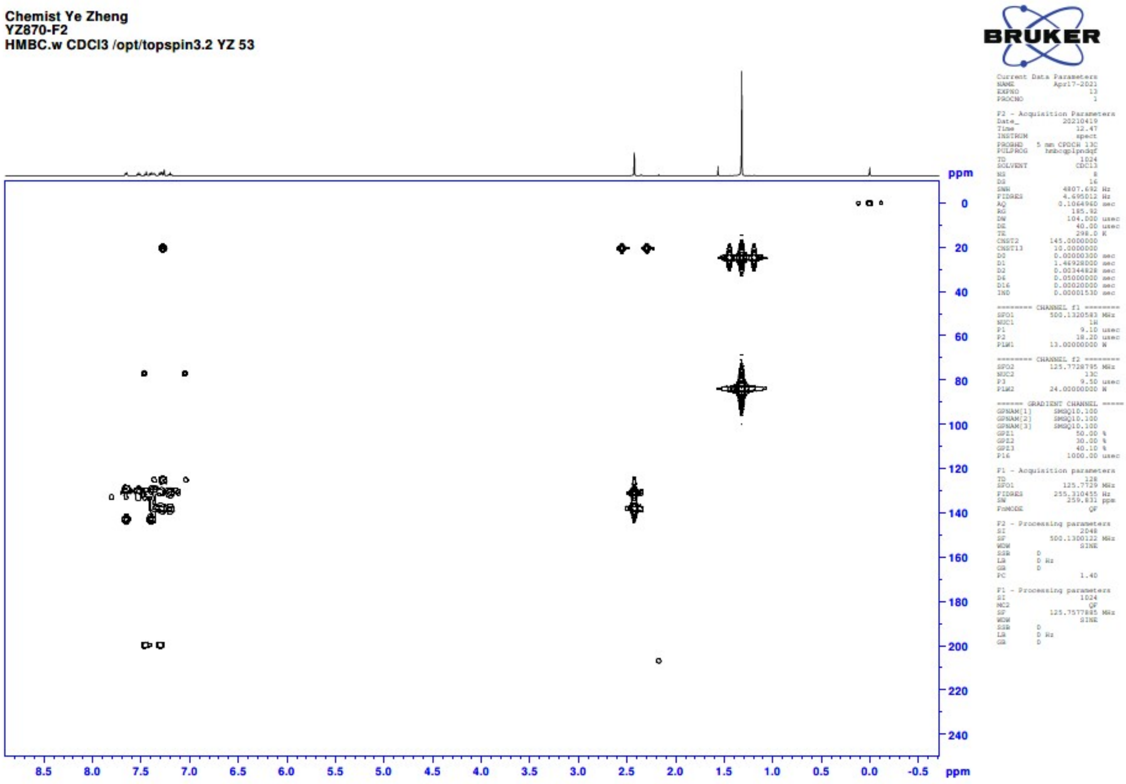
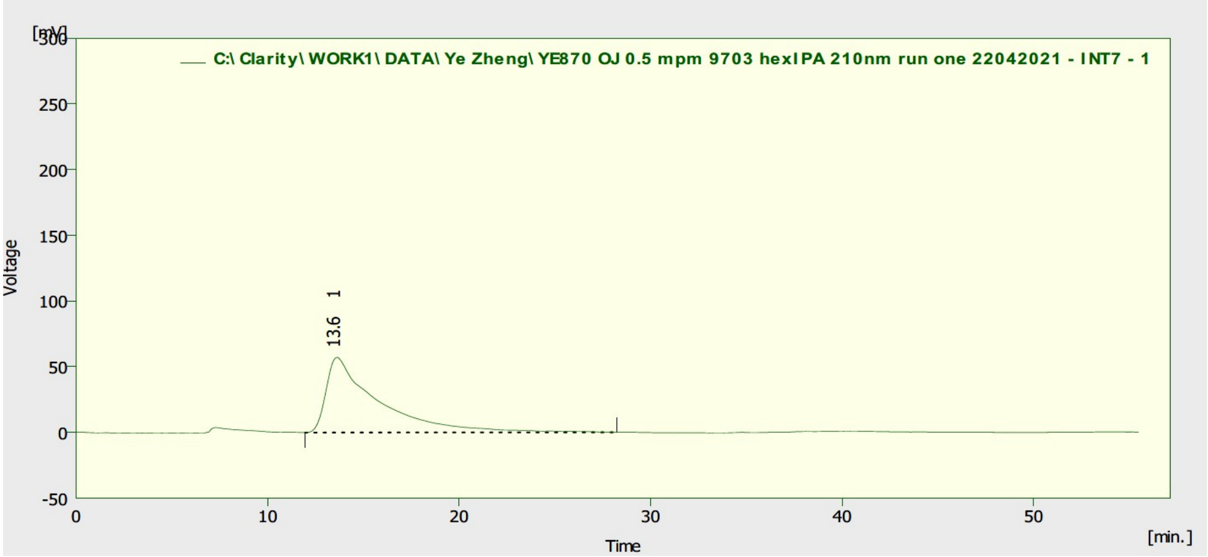
HMBC (500 MHz, $CDCl_3$)



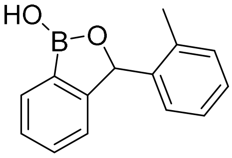
HPLC of (2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)(*o*-tolyl)methanone

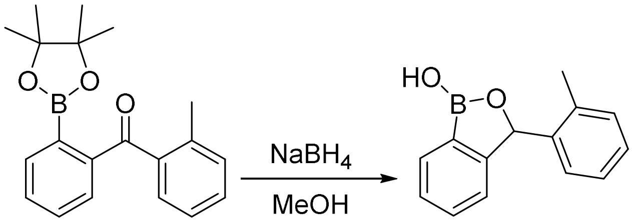


*Result Table (Uncal - C:\Clarity\WORK1\DATA\Ye Zheng\YE870 OJ 0.5 mpm 9703 hexIPA 210nm run one 22042021 - INT7 - 1)*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Compound Name |
|---|---|---|---|---|---|---|---|
| 1 | 13.600 | 10779.113 | 57.243 | 100.0 | 100.0 | 2.35 | |
| | Total | 10779.113 | 57.243 | 100.0 | 100.0 | | |

3-(*o*-Tolyl)benzo[*c*][1,2]oxaborol-1(*3H*)-ol **26**.





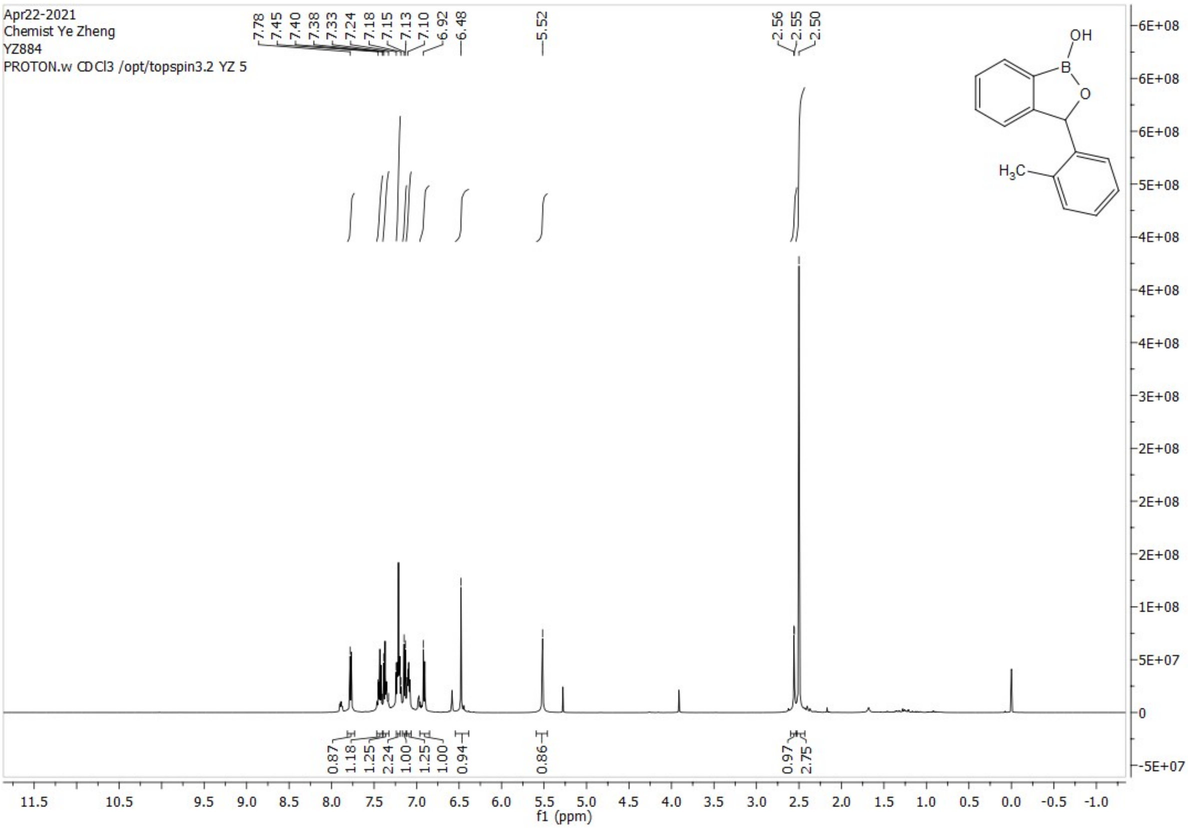
This compound is novel.

To a solution of (2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)(*o*-tolyl)methanone (245 mg, 0.761 mmol) in MeOH (4.5 mL) was added sodium borohydride (57.8 mg, 1.52 mmol). The reaction was stirred for 4 hours. TLC (4:1 hexane: EtOAc) after this time indicated full conversion. Distilled water (20 mL) was added, and the mixture was extracted with EtOAc (3 × 20ml), dried with $MgSO_4$. Solvent was removed to give the crude product. The reaction was followed by TLC (4:1 hexane: EtOAc). The product was isolated via flash chromatography on silica eluted with 0-50% ethyl acetate in hexane to give 3-(*o*-tolyl)benzo[*c*][1,2]oxaborol-1(*3H*)-ol **26** as a white solid (103 mg, 0.460 mmol, 60%). TLC: Rf ca 0.20 (4:1 hexane: EtOAc), strong UV and $KMnO_4$; Mp: 121 °C; HRMS: (found (ESI+): [M+H]+, Calcd for $C_{14}H_{13}BNaO_2$ 247.0913; Found 247.0901; -3.9 ppm error); $\nu_{max}$ 3381 (br), 3020, 2975, 1604, 1489, 1382, 1344, 1287, 1143, 1108, 1080, 974, 757, 732 $cm^{-1}$; $\delta_H$ (500 MHz, $CDCl_3$) 7.78 (1H, d, *J* = 7.3, ArH), 7.43-7.40 (1H, m, ArH), 7.38-7.33 (1H, m, ArH), 7.23-7.18 (2H, m, ArH), 7.15 (1H, d, *J* = 7.3, ArH), 7.10 (1H, dt, *J* = 8.4, 3.3, ArH), 6.92 (1H, d, *J* = 7.7, ArH), 6.48 (1H, s, ArCH), 5.52 (1H, s, OH), 2.56 (1H, d, *J* = 2.2, OH), 2.50 (3H, s, $CH_3$) ppm; $\delta_C$ (125 MHz, $CDCl_3$) 156.53 (C), 137.84 (C), 136.61 (C), 131.31 (CH), 130.87 (CH), 130.51 (CH), 128.38 (CH), 127.53 (CH), 127.18 (CH), 126.27 (CH), 122.38 (CH), 81.19 (C), 81.03 (CH), 19.47 ($CH_3$) ppm. m/z (ES-API+) 247.1 ($M^+$ + 23, 100%).

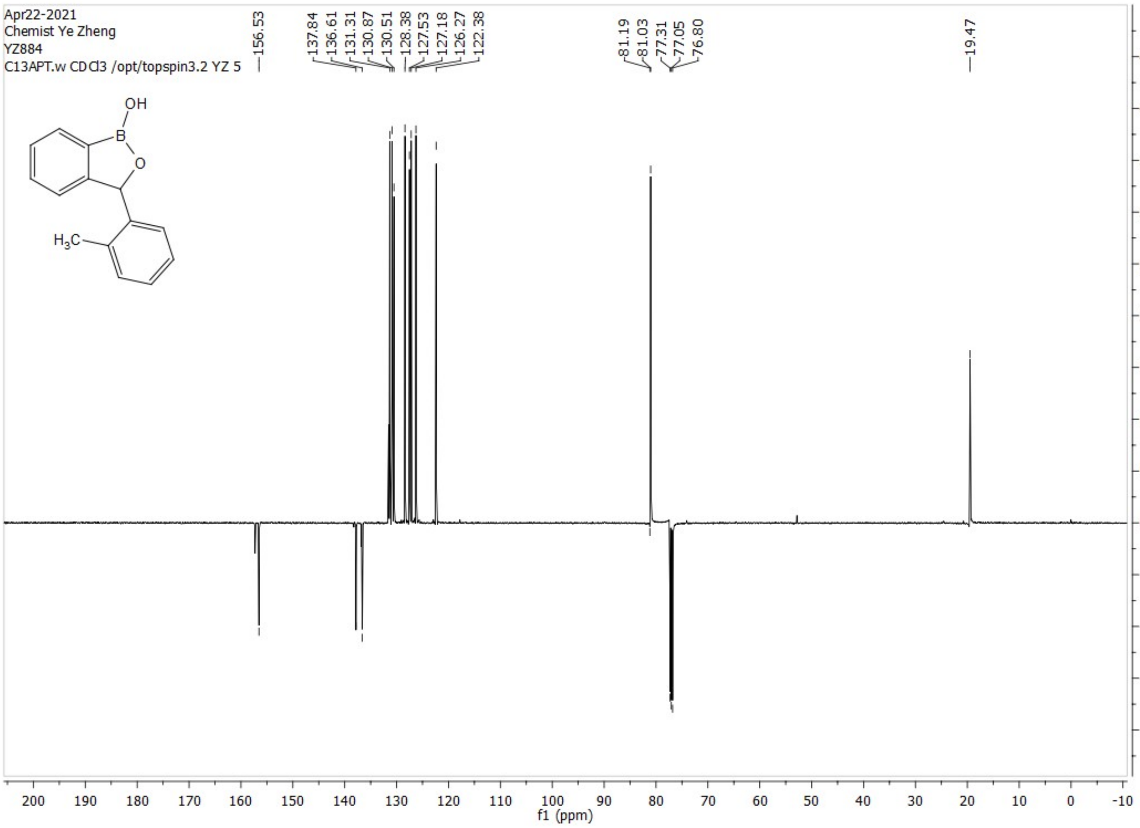
Enantiomeric excess and conversion determined by HPLC analysis (Chiralcel OJ, 30 cm x 6mm column, hexane:iPrOH 97:3, 0.5 mL/min, T = 25°C) ketone 13.6 min, *R* and *S* isomers 14.9 min and 19.0 min, configuration is not confirmed.

ATH of (2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)(*o*-tolyl)methanone. (*R,R*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (4.00 mg, 0.00640 mmol, 1mol%) was added to FA: TEA (5:2 azeotropic mixture, 0.93 mL) at rt and the mixture was stirred under a nitrogen inert atmosphere for 10-15 minutes; after which a solution of (2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)(*o*-tolyl)methanone (206 mg, 0.640 mmol) in DCM (1.30 mL) was added. The reaction mixture was stirrer under a nitrogen atmosphere, followed by TLC (4:1 hexane: EtOAc). After 72 hours, the reaction was quenched using saturated $NaHCO_3$ solution (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried ($MgSO_4$) and filtered. The solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-50% ethyl acetate in hexane to give 3-(*o*-Tolyl)benzo[c][1,2]oxaborol-1(3H)-ol **26** (38.0 mg, 0.170 mmol, 27%). The reaction was also followed by HPLC analysis (Chiralcel OJ, 30 cm x 6mm column, hexane:iPrOH 97:3, 0.5 mL/min, T = 25°C): 100% conversion, 6% ee

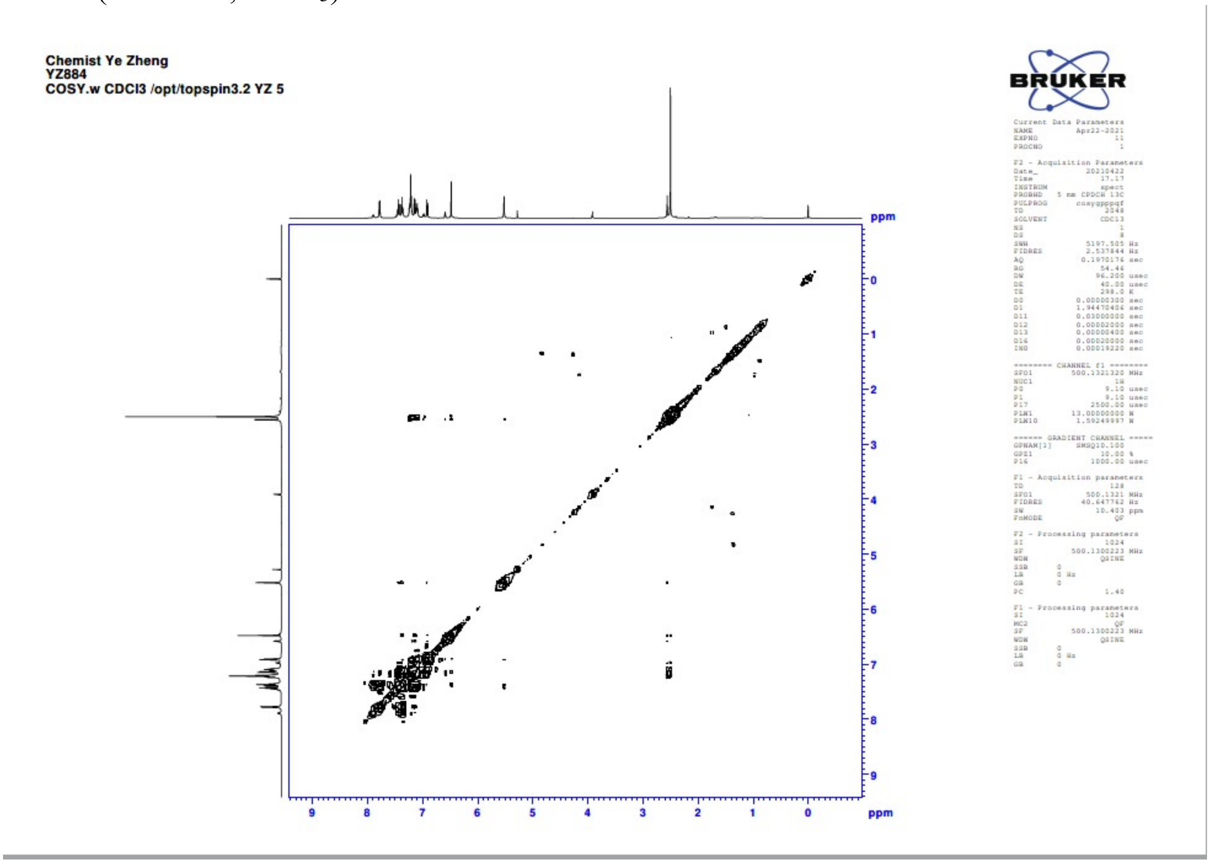
$^1$H NMR (500 MHz, CDCl$_3$)



$^{13}$C NMR (125 MHz, CDCl$_3$)



COSY (500 MHz, $CDCl_3$)



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Current Data Parameters
NAME           Apr22-2021
EXPNO                  11
PROCNO                  1

F2 - Acquisition Parameters
Date_            20210422
Time                17.17
INSTRUM             spect
PROBHD   5 mm CPDCH 13C
PULPROG         cosygpppqf
TD                   2048
SOLVENT             CDCl3
NS                      1
DS                      8
SWH              5197.505 Hz
FIDRES           2.537844 Hz
AQ              0.1970176 sec
RG                  54.46
DW                 96.200 usec
DE                  40.00 usec
TE                  298.0 K
D0             0.00000300 sec
D1             1.94470406 sec
D11            0.03000000 sec
D12            0.00002000 sec
D13            0.00000400 sec
D16            0.00020000 sec
IN0            0.00019220 sec

======== CHANNEL f1 ========
SFO1          500.1321320 MHz
NUC1                   1H
P0                   9.10 usec
P1                   9.10 usec
P17               2500.00 usec
PLW1          13.00000000 W
PLW10          1.59249997 W

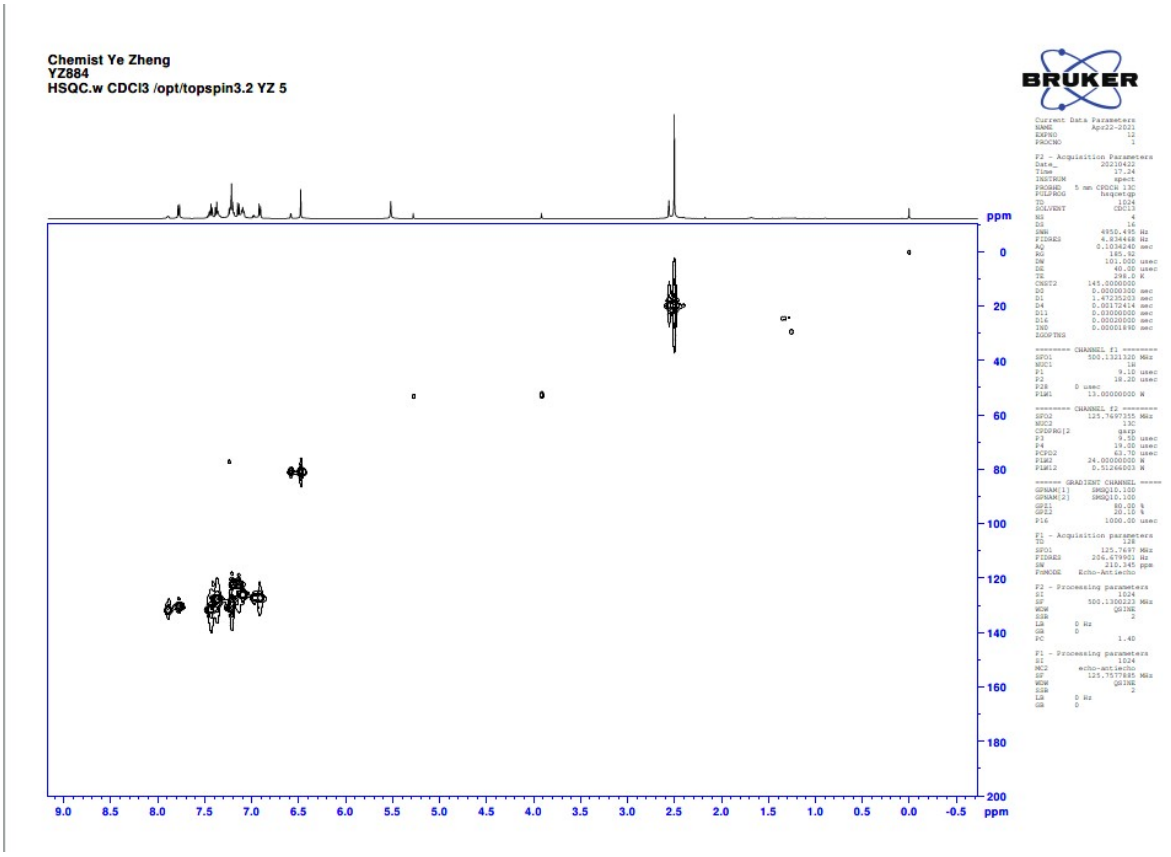
====== GRADIENT CHANNEL =====
GPNAM[1]       SMSQ10.100
GPZ1                10.00 %
P16               1000.00 usec

F1 - Acquisition parameters
TD                    128
SFO1             500.1321 MHz
FIDRES          40.647762 Hz
SW                 10.403 ppm
FnMODE                 QF

F2 - Processing parameters
SI                   1024
SF            500.1300223 MHz
WDW                 QSINE
SSB       0
LB        0 Hz
GB        0
PC                   1.40

F1 - Processing parameters
SI                   1024
MC2                    QF
SF            500.1300223 MHz
WDW                 QSINE
SSB       0
LB        0 Hz
GB        0
```

HSQC (500 MHz, $CDCl_3$)



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Current Data Parameters
NAME          Apr22-2021
EXPNO                 12
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210422
Time               17.24
INSTRUM            spect
PROBHD   5 mm CPDCH 13C
PULPROG          hsqcetgp
TD                  1024
SOLVENT            CDCl3
NS                     4
DS                    16
SWH             4950.495 Hz
FIDRES          4.834468 Hz
AQ             0.1034240 sec
RG                185.92
DW               101.000 usec
DE                 40.00 usec
TE                 298.0 K
CNST2        145.0000000
D0            0.00000300 sec
D1            1.47235203 sec
D4            0.00172414 sec
D11           0.03000000 sec
D16           0.00020000 sec
IN0           0.00001890 sec
ZGOPTNS

======== CHANNEL f1 ========
SFO1         500.1321320 MHz
NUC1                  1H
P1                  9.10 usec
P2                 18.20 usec
P28       0 usec
PLW1         13.00000000 W

======== CHANNEL f2 ========
SFO2         125.7697355 MHz
NUC2                 13C
CPDPRG[2            garp
P3                  9.50 usec
P4                 19.00 usec
PCPD2              63.70 usec
PLW2         24.00000000 W
PLW12         0.51266003 W

====== GRADIENT CHANNEL =====
GPNAM[1]      SMSQ10.100
GPNAM[2]      SMSQ10.100
GPZ1               80.00 %
GPZ2               20.10 %
P16              1000.00 usec

F1 - Acquisition parameters
TD                   128
SFO1            125.7697 MHz
FIDRES        206.679901 Hz
SW               210.345 ppm
FnMODE    Echo-Antiecho

F2 - Processing parameters
SI                  1024
SF           500.1300223 MHz
WDW                QSINE
SSB                    2
LB        0 Hz
GB        0
PC                  1.40

F1 - Processing parameters
SI                  1024
MC2        echo-antiecho
SF           125.7577885 MHz
WDW                QSINE
SSB                    2
LB        0 Hz
GB        0
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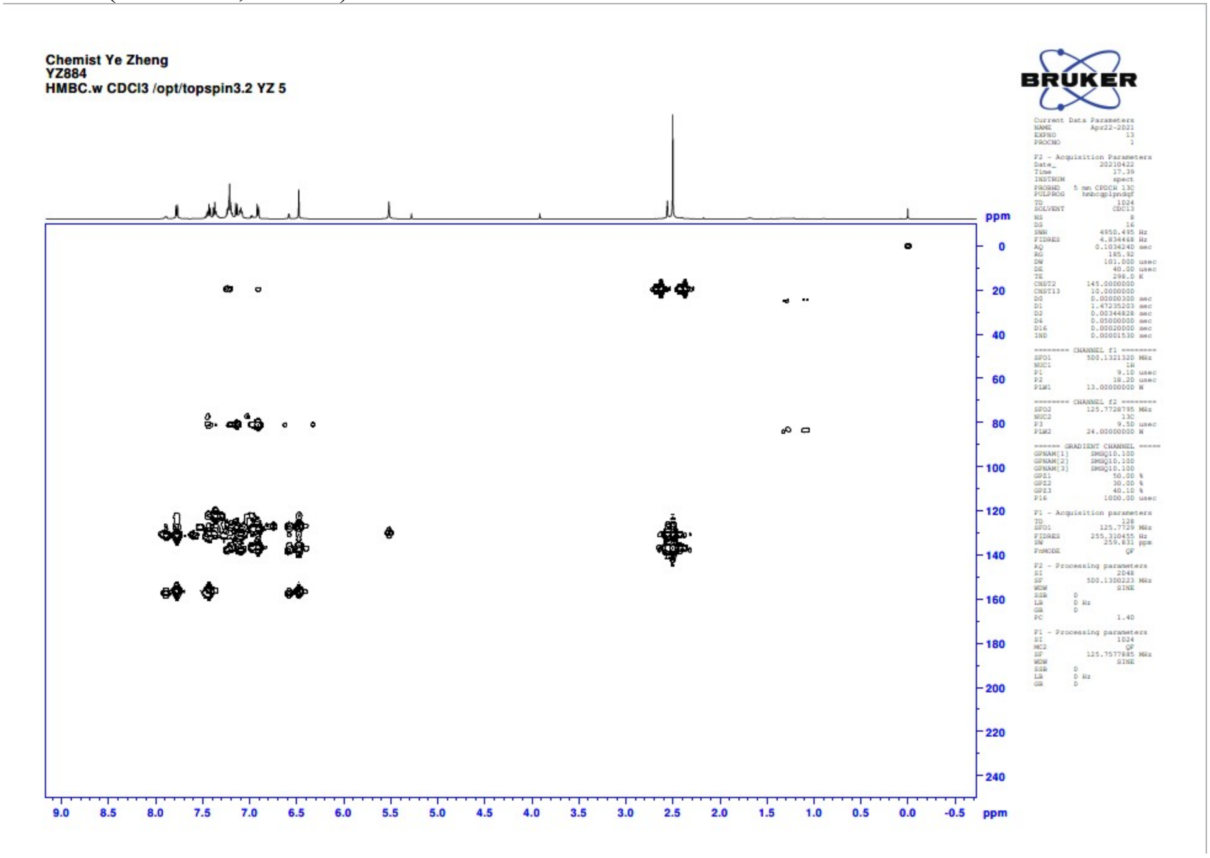
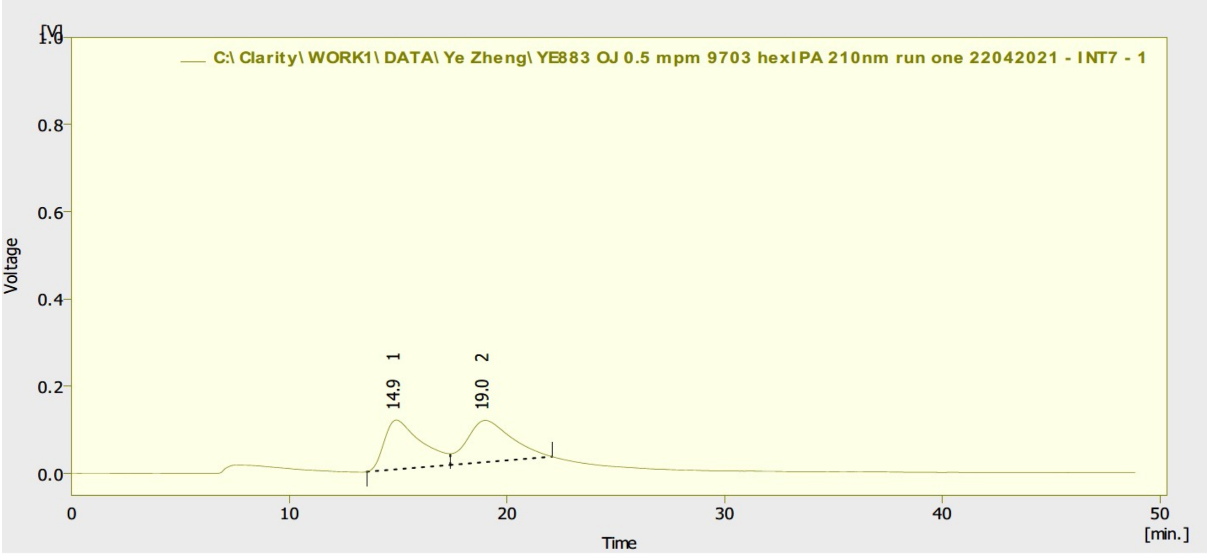
HMBC (500 MHz, $CDCl_3$)



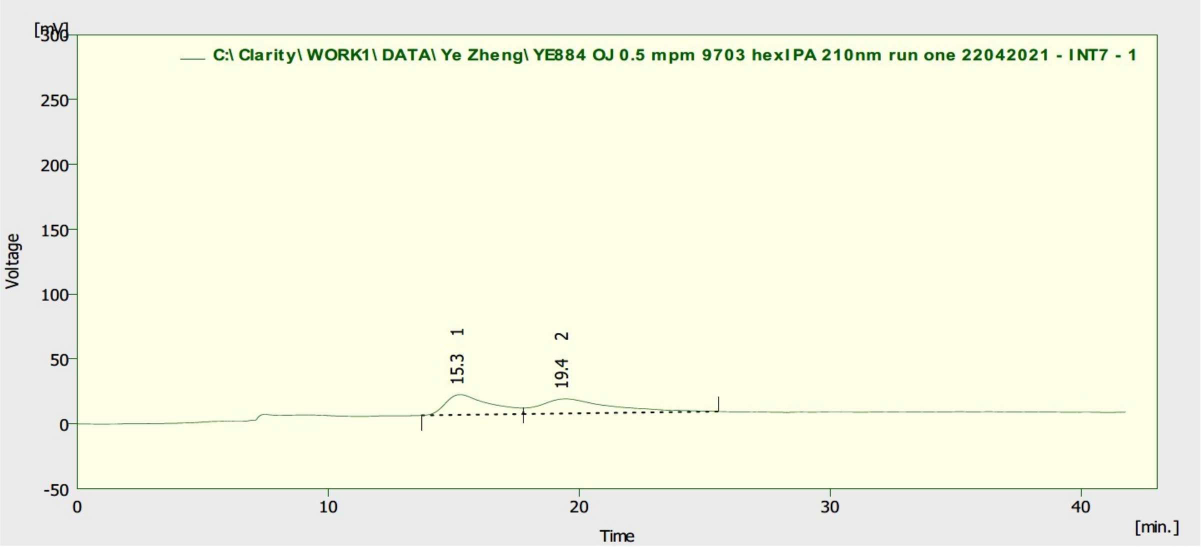
HPLC of racemic 3-(*o*-Tolyl)benzo[*c*][1,2]oxaborol-1(*3H*)-ol **26**



*Result Table (Uncal - C:\Clarity\WORK1\DATA\Ye Zheng\YE883 OJ 0.5 mpm 9703 hexIPA 210nm run one 22042021 - INT7 - 1)*

|  | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Compound Name |
|---|---|---|---|---|---|---|---|
| 1 | 14.917 | 13397.934 | 113.066 | 49.4 | 54.2 | 1.97 |  |
| 2 | 18.993 | 13704.596 | 95.691 | 50.6 | 45.8 | 2.34 |  |
|  | Total | 27102.530 | 208.756 | 100.0 | 100.0 |  |  |

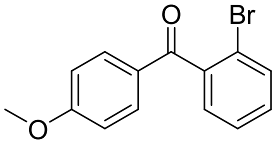
HPLC after ATH of (2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)(*o*-tolyl)methanone using (*R,R*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (after 72 hours, 100% conversion, 6% ee).

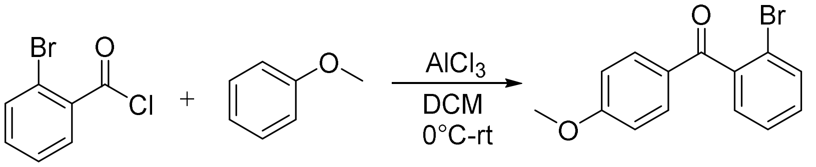


*Result Table (Uncal - C:\Clarity\WORK1\DATA\Ye Zheng\YE884 OJ 0.5 mpm 9703 hexIPA 210nm run one 22042021 - INT7 - 1)*

|  | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Compound Name |
|---|---|---|---|---|---|---|---|
| 1 | 15.260 | 1962.019 | 15.618 | 47.0 | 58.1 | 2.03 |  |
| 2 | 19.420 | 2213.636 | 11.259 | 53.0 | 41.9 | 2.99 |  |
|  | Total | 4175.654 | 26.877 | 100.0 | 100.0 |  |  |

(2-Bromophenyl)(4-methoxyphenyl)methanone.



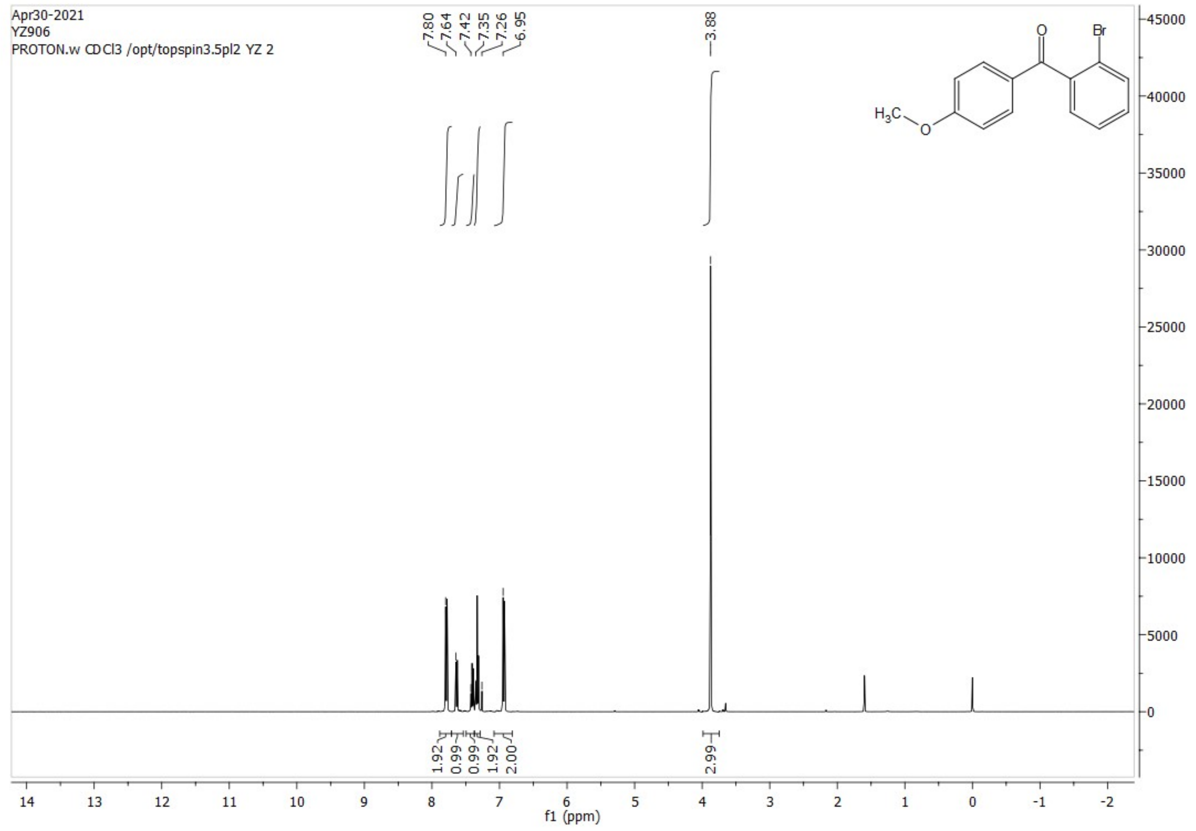


This compound has been reported and fully characterized: F. Ling, H. Hou, J. Chen, S. Nian, X. Yi, Z. Wang, D. Song and W. Zhong, *Org. Lett.* 2019, **21**, 3937-3941.

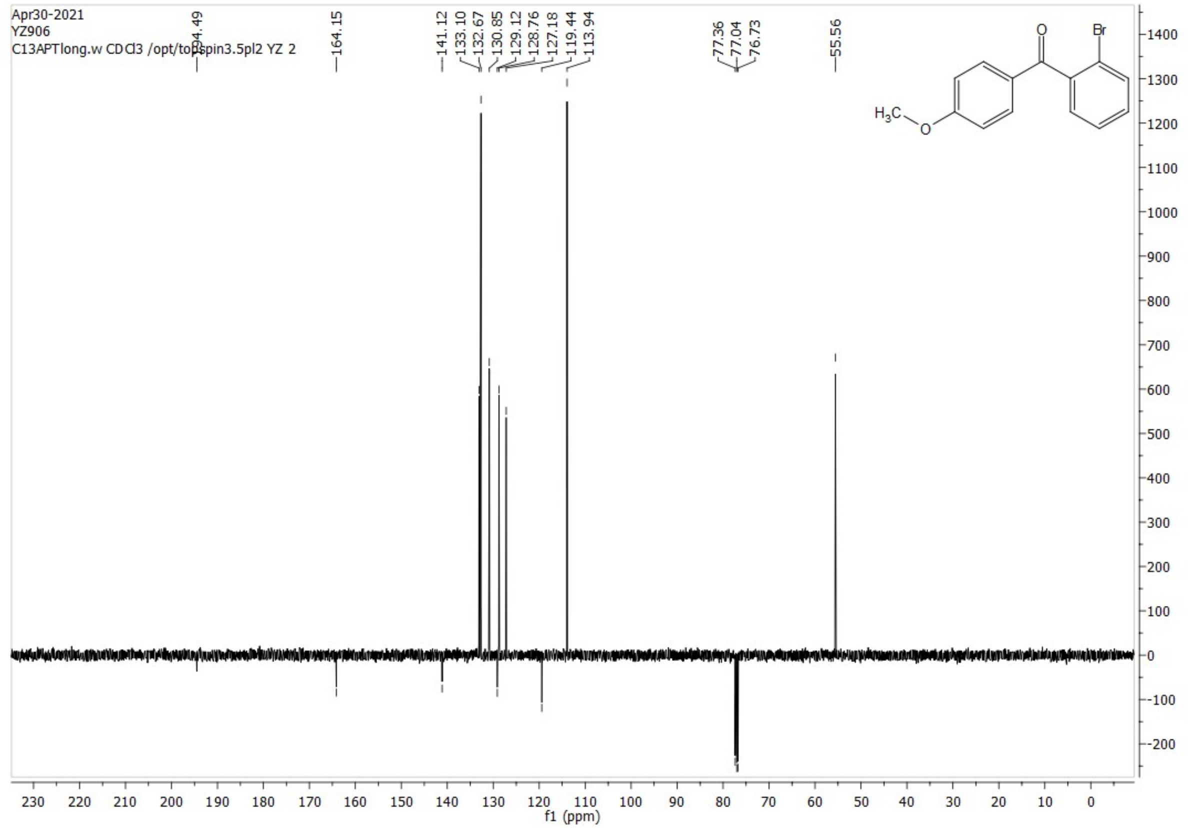
To a solution of 2-bromobenzoyl chloride (438 mg, 2.00 mmol) was in DCM (10 mL) at 0 °C was added dropwise anisole (281 mg, 2.60 mmol). The reaction mixture was then stirred under a nitrogen atmosphere for 30 minutes, after which $AlCl_3$ (319 mg, 2.40 mmol) was added. The reaction mixture was left stirring under the nitrogen atmosphere for 2 hours and followed by TLC (9:1 hexane: EtOAc). The mixture was poured into ice water. DCM (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with DCM (3 × 20 mL), and the combined organic layers were dried ($MgSO_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-20% ethyl acetate in hexane to give (2-bromophenyl)(4-methoxyphenyl)methanone as a white solid (540 mg, 1.86 mmol, 93%).

TLC: Rf ca 0.50 (9:1 hexane: EtOAc), strong UV and $KMnO_4$; $\delta_H$ (400 MHz, $CDCl_3$) 7.80 (2H, d, *J* = 8.8, ArH), 7.64 (1H, d, *J* = 8.0, ArH), 7.41 (1H, t, *J* = 7.4, ArH), 7.35 (2H, dd, *J* = 12.2, 4.6, ArH), 6.95 (2H, d, *J* = 8.8, ArH), 3.88 (3H, s, $CH_3$) ppm; $\delta_C$ (100 MHz, $CDCl_3$) 194.49 (C), 164.15 (C), 141.12 (C), 133.10 (CH), 132.67 (CH), 130.85 (CH), 129.12 (C), 128.76 (CH), 127.18 (CH), 119.44 (C), 113.94 (CH), 55.56 ($CH_3$) ppm; m/z (ES-API+) 313.0 ($M^+$ + 23, 100%). Data matched that reported.

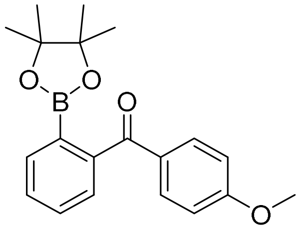
$^{1}$H NMR (400 MHz, $CDCl_3$)

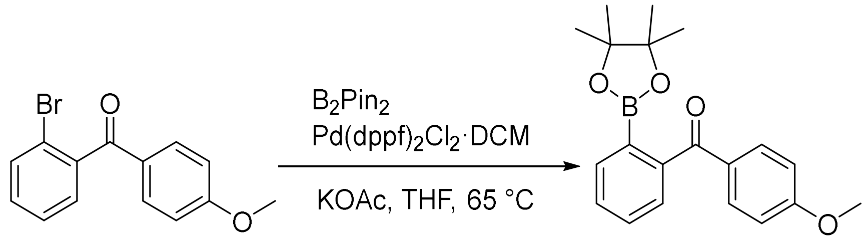


$^{13}$C NMR (100 MHz, $CDCl_3$)



(4-Methoxyphenyl)(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone.

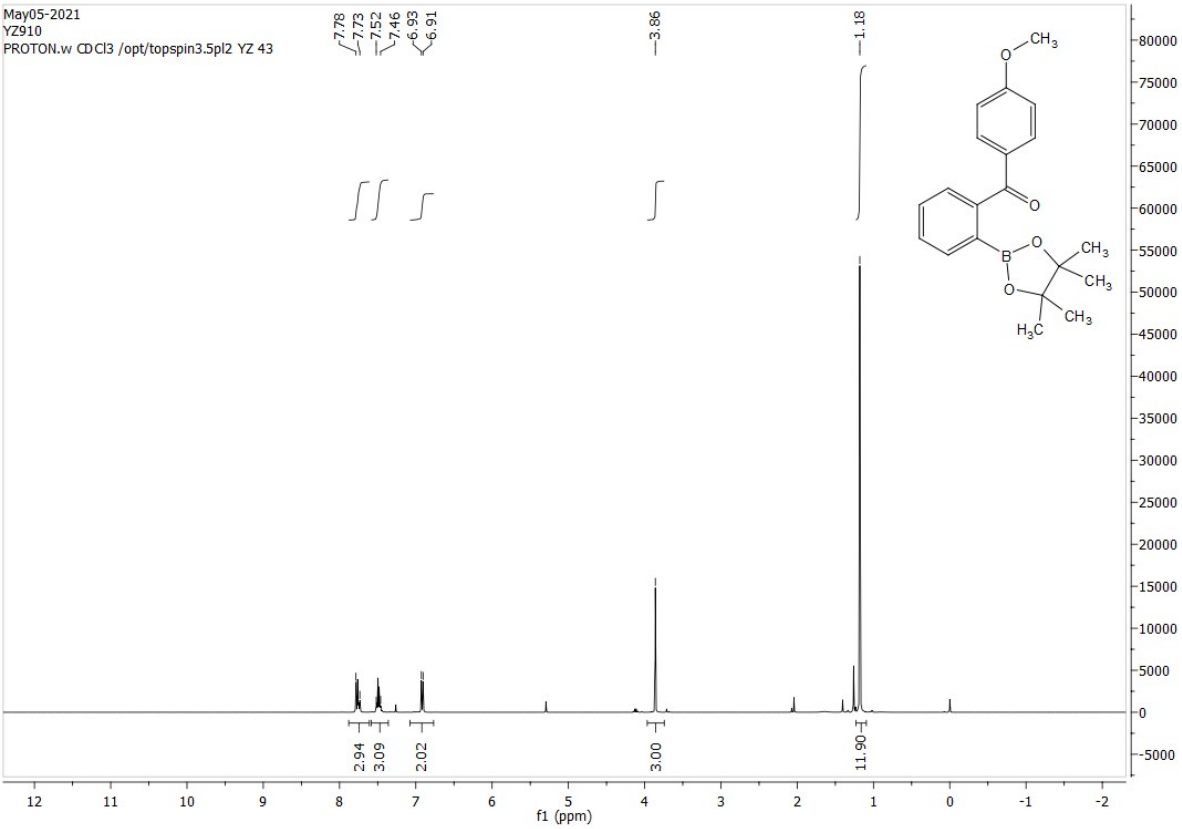




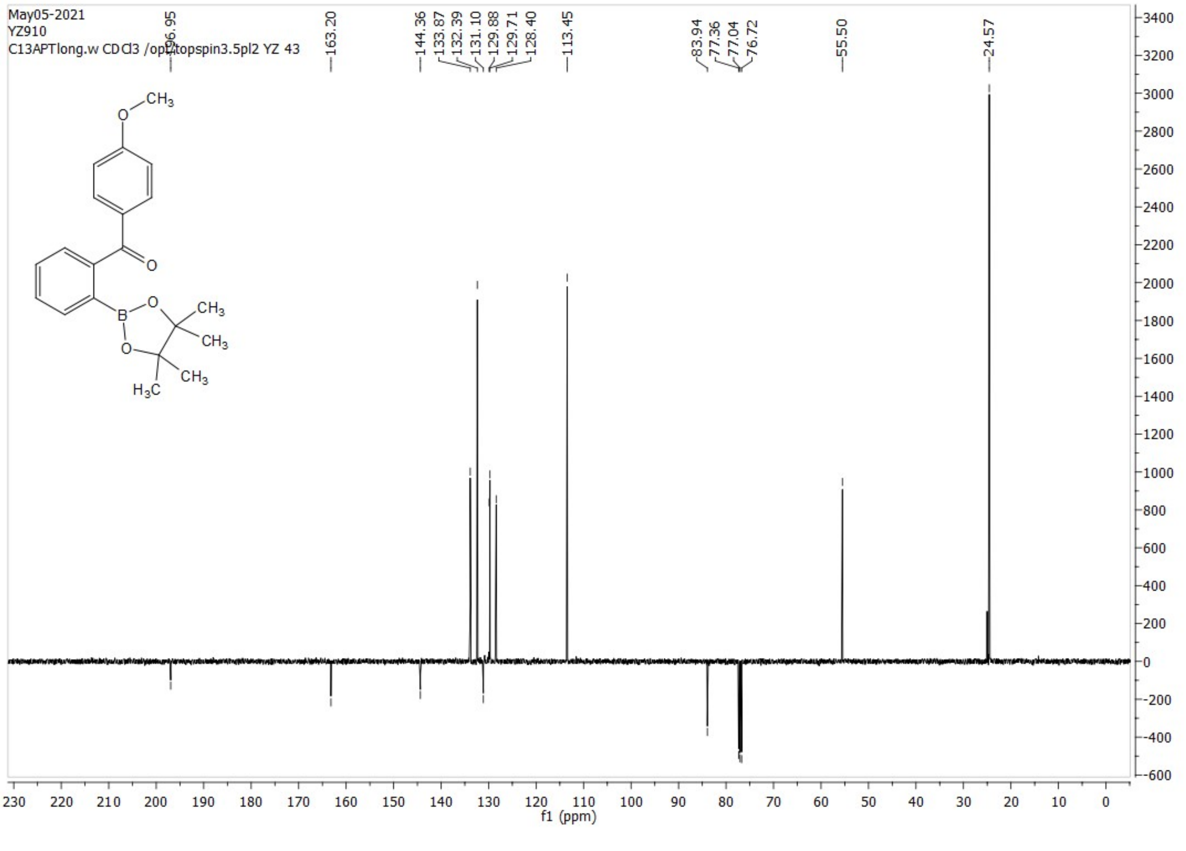
This compound is novel.

A round-bottom flask was charged with (2-bromophenyl)(4-methoxyphenyl)methanone (645 mg, 2.20 mmol), bis(pinacolato)diboron (676 mg, 2.66 mmol), potassium acetate (653 mg, 6.66 mmol), THF (14 mL) and $Pd(dppf)_2Cl_2$·DCM (90.7 mg, 0.111 mmol). The reaction mixture was heated to 65 °C and left stirring under the nitrogen atmosphere overnight, followed by TLC (9:1 hexane: EtOAc). The mixture was quenched by distilled water (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried ($MgSO_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-10% ethyl acetate in hexane to give (4-methoxyphenyl)(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone as a yellow oil (367 mg, 1.09 mmol, 49%). TLC: Rf ca 0.40 (9:1 hexane: EtOAc), strong UV and $KMnO_4$; HRMS: (found (ESI+): [M+H]+, Calcd for $C_{20}H_{23}BNaO_4$ 361.1579; Found 361.1582; 1.7 ppm error); $\nu_{max}$ 2977, 2933, 1656, 1596, 1563, 1348, 1213, 1114, 1096, 1028, 932, 855, 753 $cm^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 7.78-7.73 (3H, m, ArH), 7.52-7.46 (3H, m, ArH), 6.93 (2H, d, *J* = 8.8, ArH), 3.86 (3H, s, $OCH_3$), 1.18 (12H, s, $CH_3$) ppm; $\delta_C$ (100 MHz, $CDCl_3$) 196.95 (C), 163.20 (C), 144.36 (C), 133.87 (CH), 132.39 (CH), 131.10 (C), 129.88 (CH), 129.71 (CH), 128.40 (CH), 113.45 (CH), 83.94 (C), 55.50 ($CH_3$), 24.57 ($CH_3$) ppm; m/z (ES-API+) 361.2 ($M^+$ + 23, 100%). Enantiomeric excess and conversion determined by HPLC analysis (Chiralcel IC, 30 cm x 6mm column, hexane:iPrOH 95:5, 1.0 mL/min, T = 25°C) ketone 17.1 min, *R* and *S* isomers 4.4 min and 5.9 min, configuration is not confirmed.

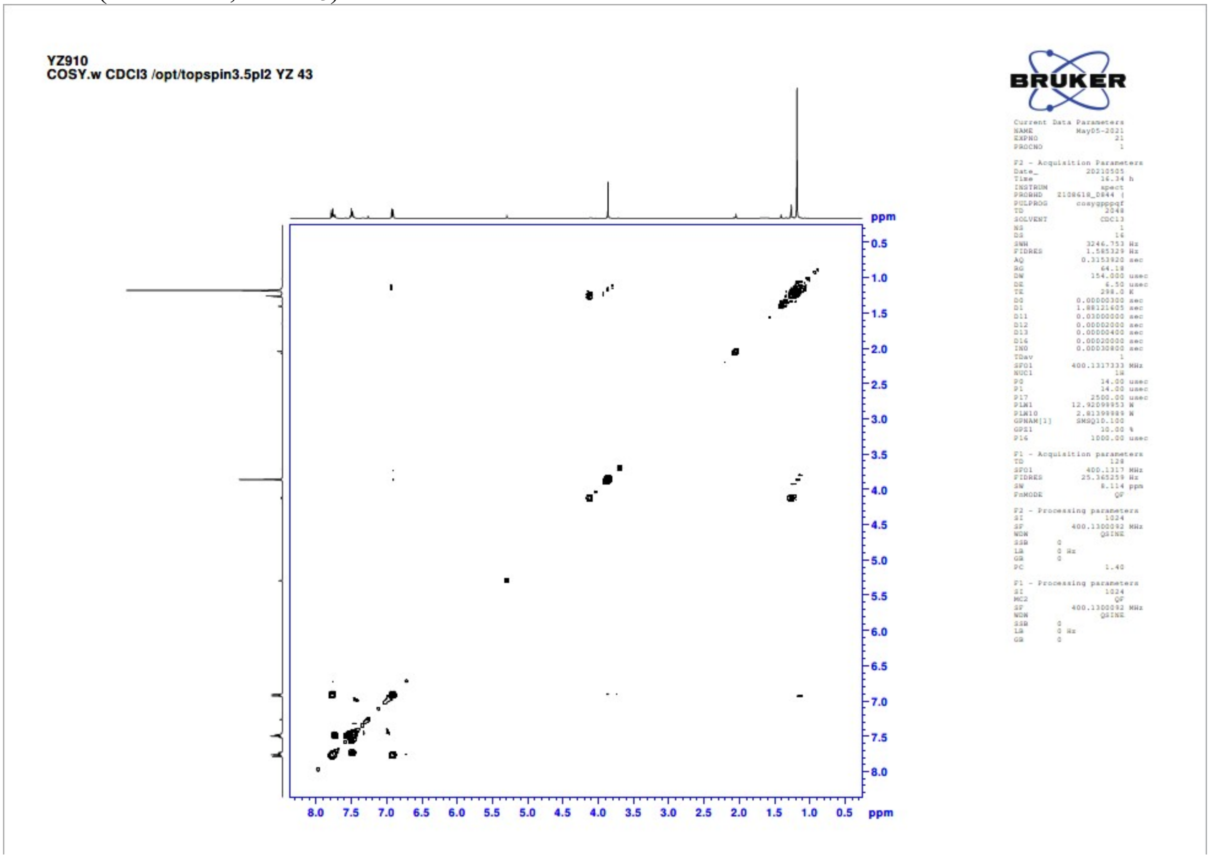
$^1$H NMR (400 MHz, $CDCl_3$)



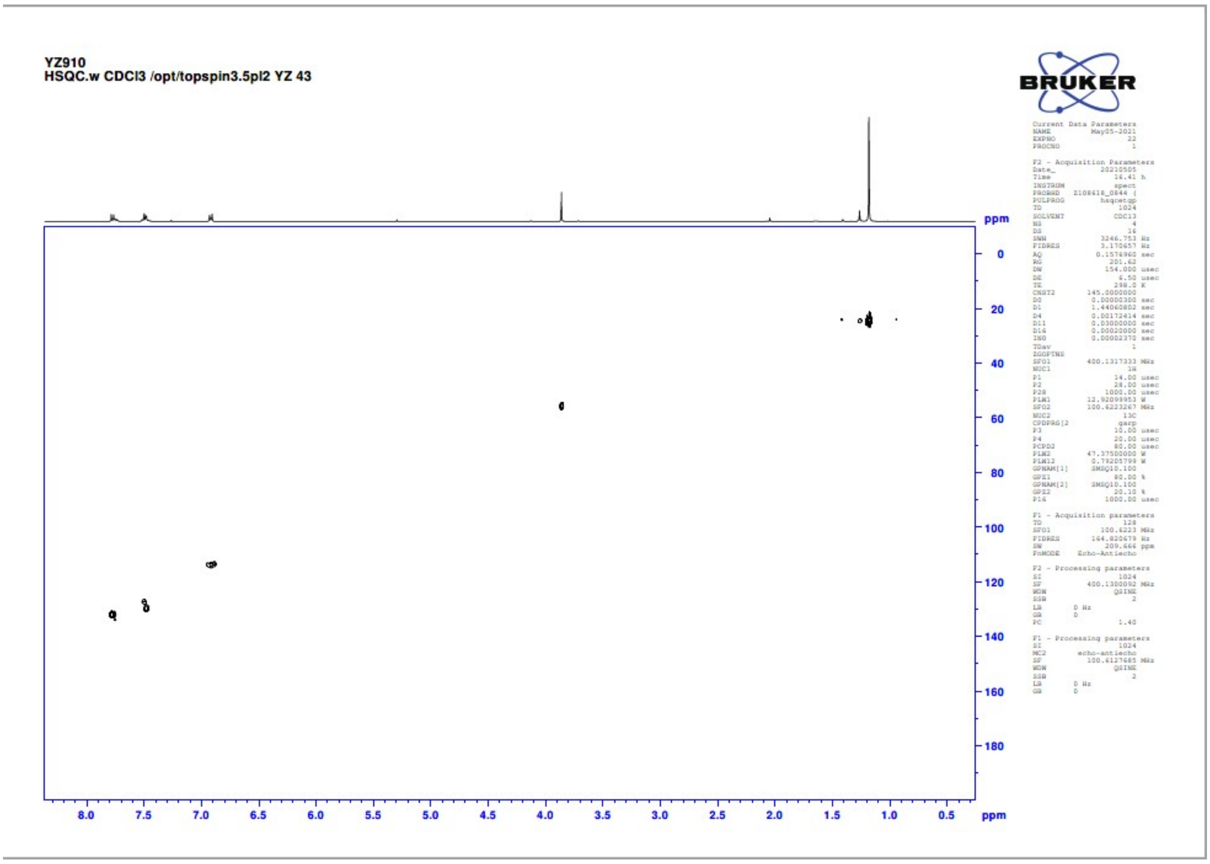
$^{13}$C NMR (100 MHz, $CDCl_3$)



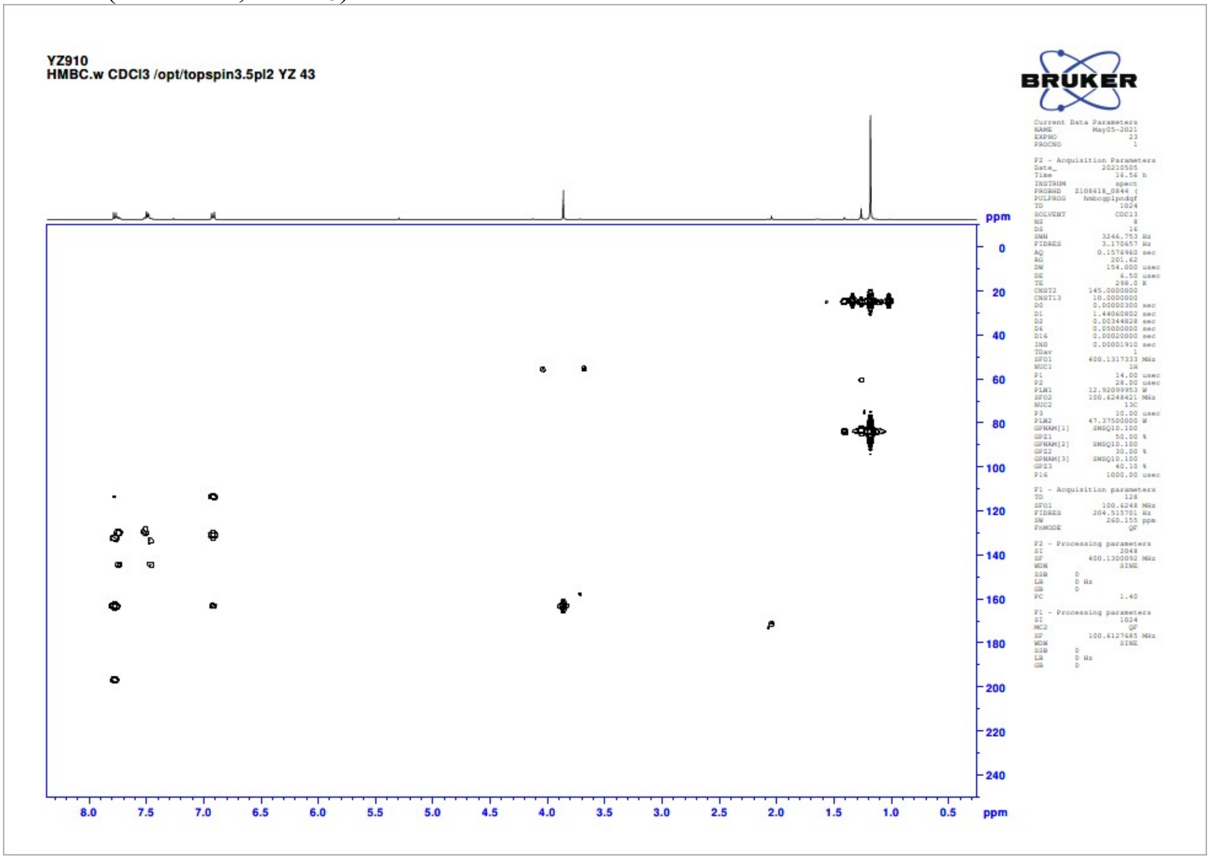
COSY (400 MHz, $CDCl_3$)



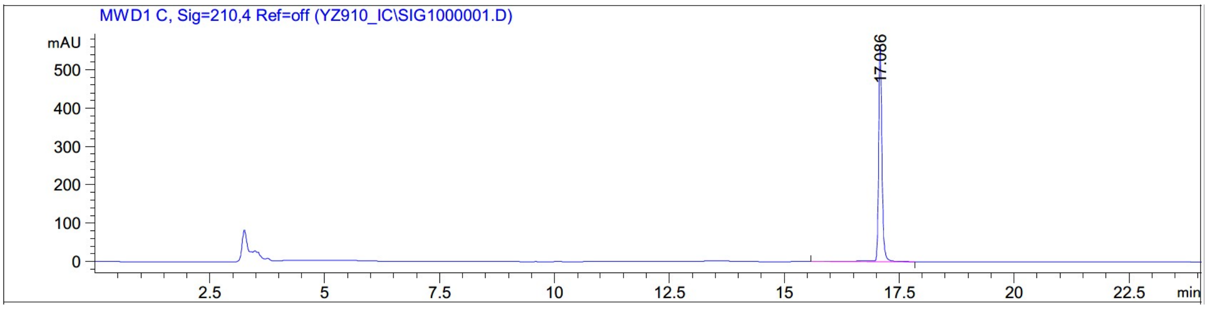
HSQC (400 MHz, $CDCl_3$)



HMBC (400 MHz, $CDCl_3$)



HPLC of (4-methoxyphenyl)(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone



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Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  17.086 BB    0.0782 2923.16113  566.39697 100.0000

Totals :                  2923.16113  566.39697
```
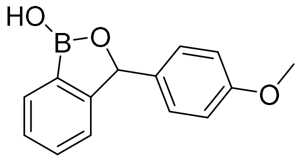
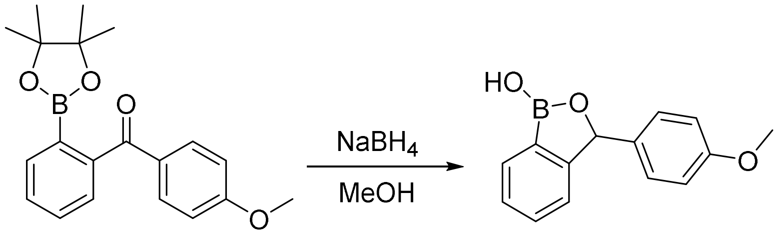

3-(4-Methoxyphenyl)benzo[*c*][1,2]oxaborol-1(*3H*)-ol **27**.





This compound is novel.

To a solution of (4-methoxyphenyl)(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone (245 mg, 0.725 mmol) in MeOH (4.3 mL) was added sodium borohydride (55.1 mg, 1.45 mmol). The reaction was stirred for 4 hours. TLC (4:1 hexane: EtOAc) after this time indicated full conversion. Distilled water (20 mL) was added, and the mixture was extracted with EtOAc (3 × 20ml), dried with $MgSO_4$. Solvent was removed to give the crude product. The reaction was followed by TLC (4:1 hexane: EtOAc). The product was isolated via flash chromatography on silica eluted with 0-50% ethyl acetate in hexane to give 3-(4-methoxyphenyl)-benzo[*c*][1,2]oxaborol-1(*3H*)-ol **27** as a white solid (61.6 mg, 0.256 mmol, 35%). TLC: Rf ca 0.20 (4:1 hexane: EtOAc), strong UV and $KMnO_4$; Mp: 99 °C; HRMS: (found (ESI+): [M+H]+, Calcd for $C_{14}H_{13}BNaO_3$ 263.0857; Found 263.0850; -1.5 ppm error); $\nu_{max}$ 3358 (br), 1607, 1509, 1476, 1420, 1276, 1254, 1172, 1025, 951, 819, 739 $cm^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 7.78 (1H, d, *J* = 7.2, ArH), 7.39 (2H, tt, *J* = 16.1, 8.0, ArH), 7.23-7.14 (3H, m, ArH), 6.89 (2H, d, *J* = 8.6, ArH), 6.16 (1H, s, ArCH), 5.66 (1H, s, OH), 3.80 (3H, s, $CH_3$) ppm; $\delta_C$ (100 MHz, $CDCl_3$) 159.73 (C), 156.81 (C), 132.23 (C), 131.35 (CH), 130.38 (CH), 128.49 (CH), 127.55 (CH), 122.41 (CH), 114.10 (CH), 83.56 (CH), 55.31 ($CH_3$) ppm. m/z (ES-API+) 263.1 ($M^+$ + 23, 100%).

Enantiomeric excess and conversion determined by HPLC analysis (Chiralcel IC, 30 cm x 6mm column, hexane:iPrOH 95:5, 1.0 mL/min, T = 25°C) ketone 17.1 min, *R* and *S* isomers 4.4 min and 5.9 min, configuration is not confirmed.

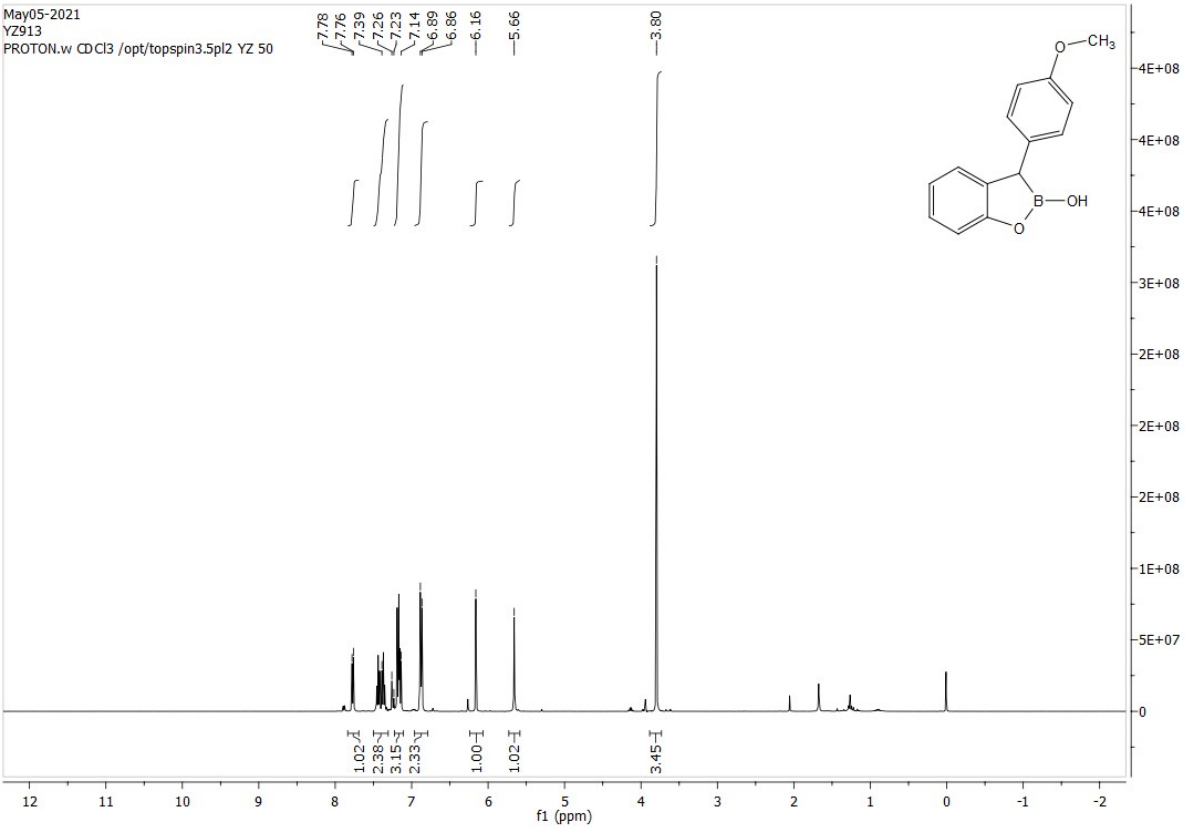
ATH of (4-methoxyphenyl)(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone.

(*R,R*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (1.66 mg, 0.00267 mmol, 1 mol%) was added to FA: TEA (5:2 azeotropic mixture, 0.41 mL) at rt and the mixture was stirred under a nitrogen inert atmosphere for 10-15 minutes; after which a solution of (4-methoxyphenyl)(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone (90.0 mg, 0.267 mmol) in DCM (0.56 mL) was added. The reaction mixture was stirred under a nitrogen atmosphere, followed by TLC (4:1 hexane: EtOAc). After 72 hours, the reaction was quenched using saturated $NaHCO_3$ solution (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried ($MgSO_4$) and filtered. The solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-50% ethyl acetate in hexane to give 3-(4-methoxyphenyl)benzo[*c*][1,2]oxaborol-1(*3H*)-ol **27** (25.0 mg, 0.104 mmol, 88%). The reaction was also followed by HPLC analysis (Chiralcel IC, 30 cm x 6mm column, hexane:iPrOH 95:5, 1.0 mL/min, T = 25°C): 100% conversion; $[\alpha]_D^{25}$ +2.79 (c 0.179 in $CHCl_3$) 23% ee

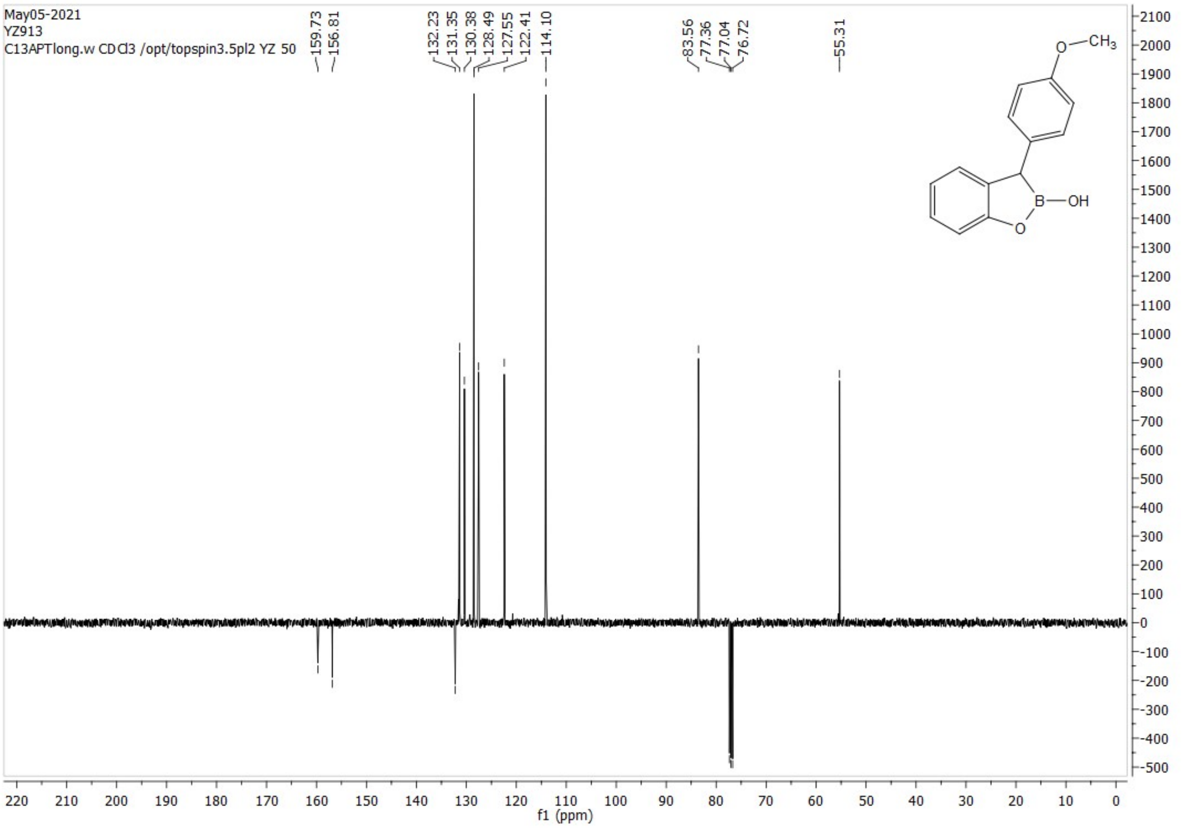
A control reaction in the absence of catalyst was carried out:

A solution of (4-methoxyphenyl)(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone (90.0 mg, 0.267 mmol) in DCM (0.56 mL) was added to FA: TEA (5:2 azeotropic mixture, 0.41 mL) at rt. The reaction mixture was stirred under a nitrogen atmosphere, followed by TLC (4:1 hexane: EtOAc). After 24 hours, the reaction was quenched using saturated $NaHCO_3$ solution (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried ($MgSO_4$) and filtered. The solvent was removed to give the crude product. NMR indicated that no product was formed.

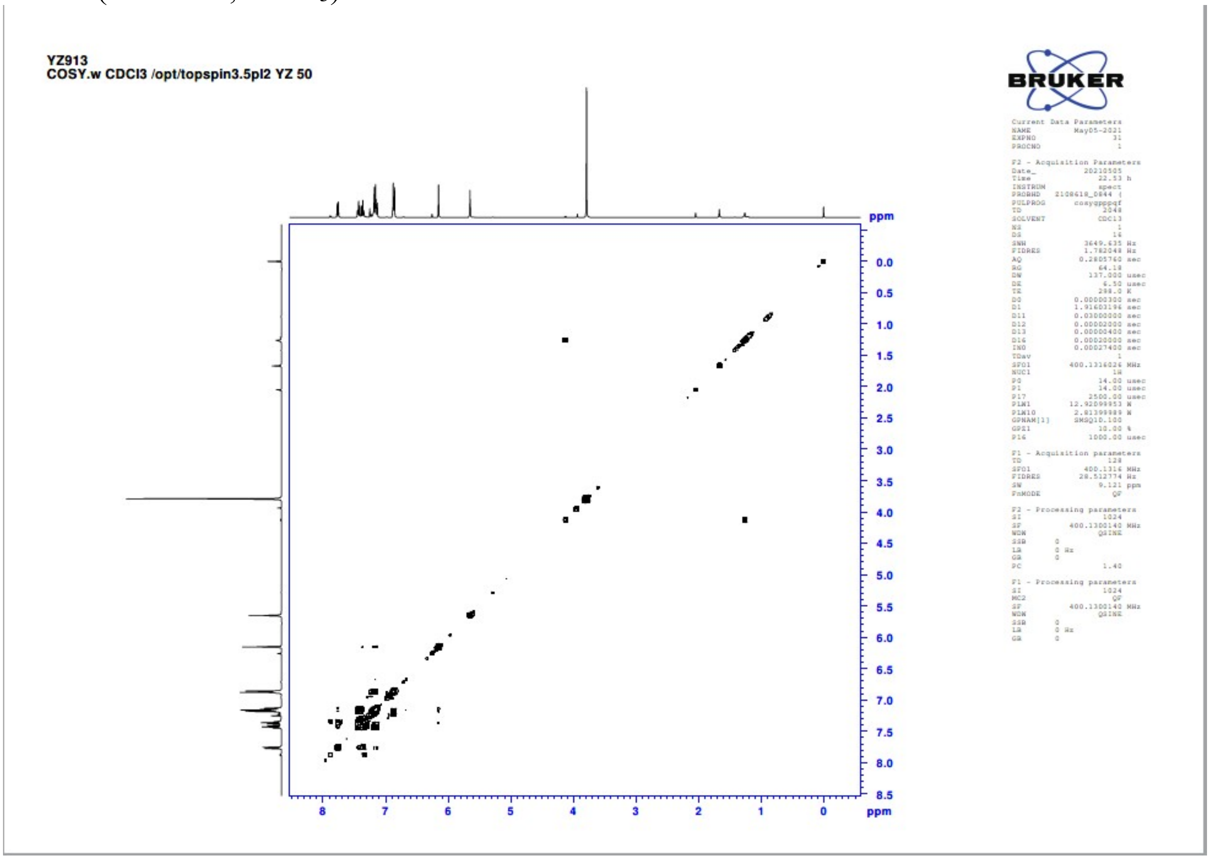
$^1$H NMR (400 MHz, CDCl$_3$)



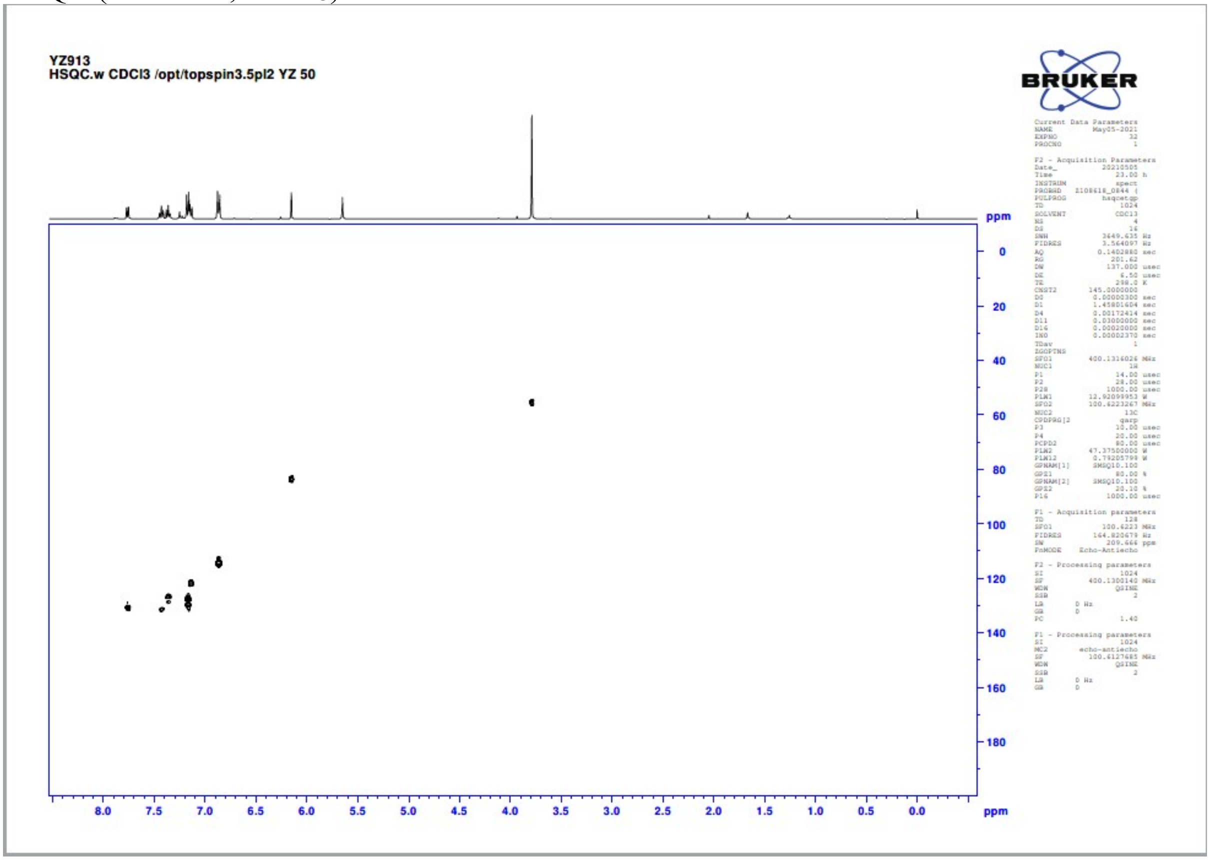
$^{13}$C NMR (100 MHz, CDCl$_3$)



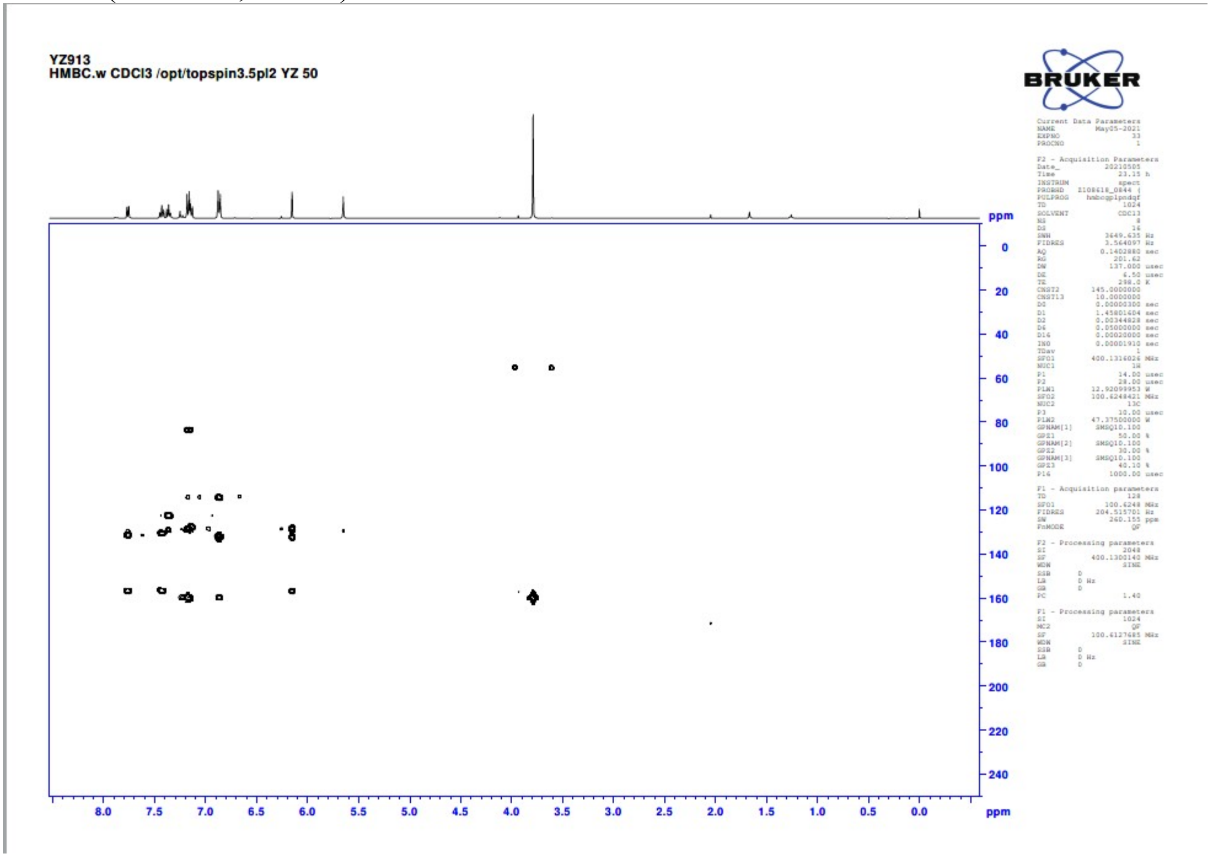
COSY (400 MHz, $CDCl_3$)



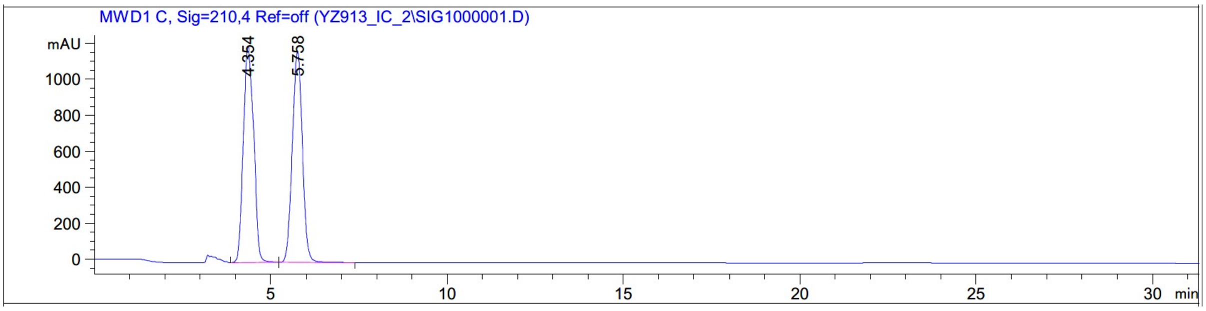
HSQC (400 MHz, $CDCl_3$)



HMBC (400 MHz, $CDCl_3$)



HPLC of racemic 3-(4-methoxyphenyl)benzo[*c*][1,2]oxaborol-1(*3H*)-ol **27**.



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----|-------|----|-------|----------|----------|--------|
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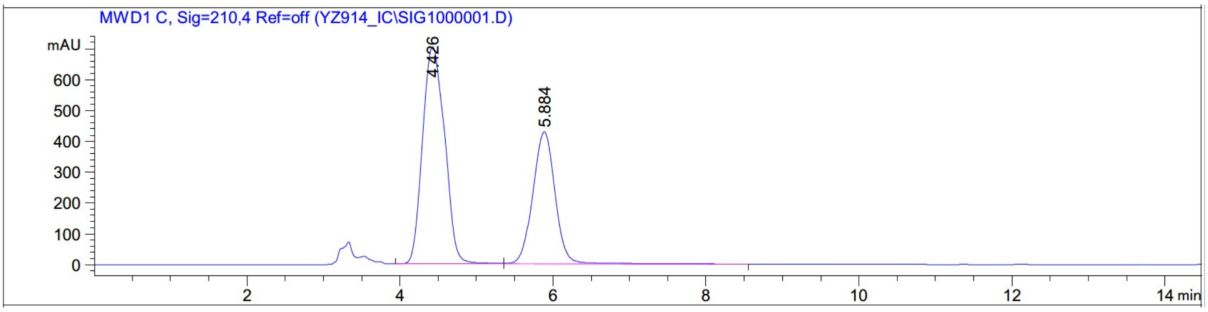
   2   5.758 BB    0.3099 2.32276e4 1168.52063  48.6837

Totals :                  4.77112e4 2371.86975
```

HPLC after ATH of (4-methoxyphenyl)(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone using (*R,R*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (after 72 hours, 100% conversion, 23% ee).



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Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area       Height     Area
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----|-------|----|-------|----------|----------|--------|
   1   4.426 BV    0.2986 1.40280e4   703.47296  61.4937
   2   5.884 VB    0.3174 8784.09668  427.98706  38.5063

Totals :                  2.28121e4  1131.46002
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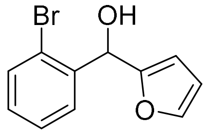
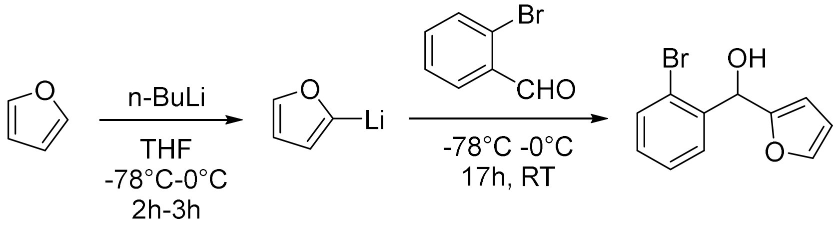
### (2-Bromophenyl)(furan-2-yl)methanol.

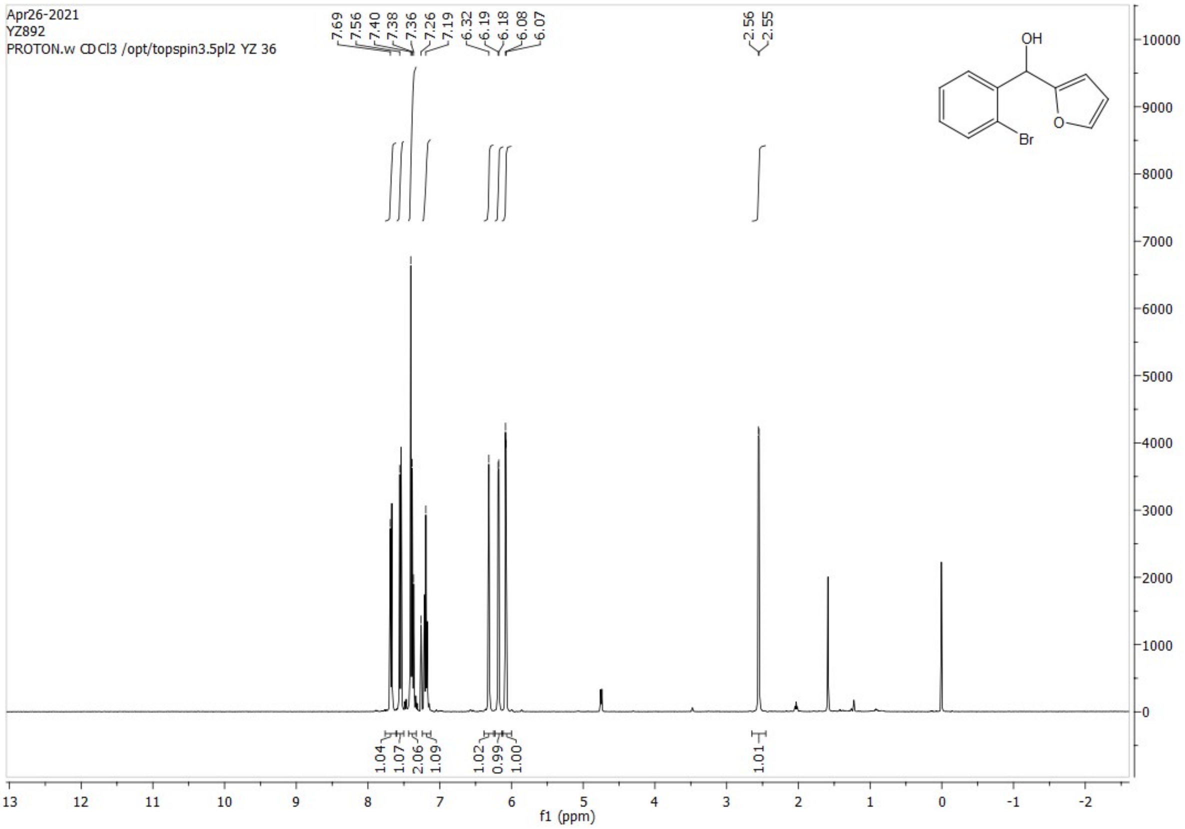




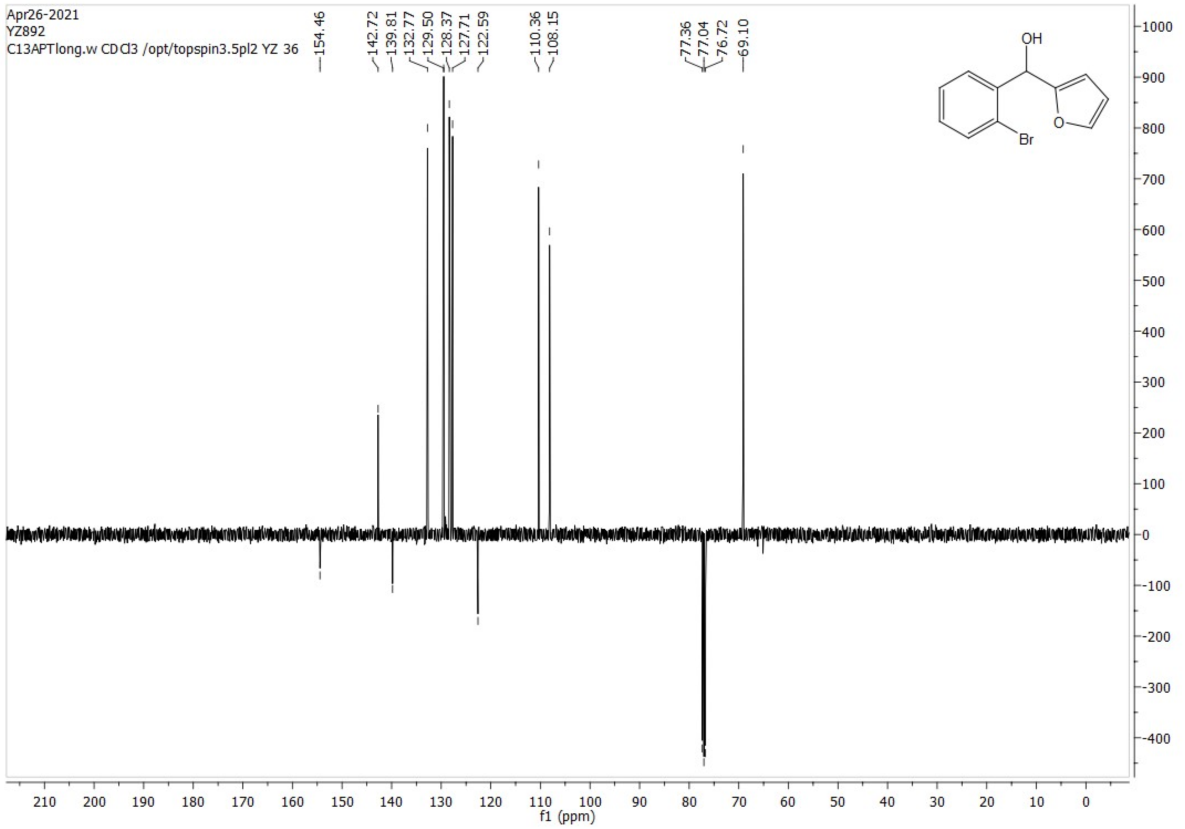
This compound has been reported and fully characterized: M. Tang, Y. Kong, B. Chu and D. Feng, *Adv, Synth. Catal.* 2016, **358**, 926-939.

To a solution of furan (374 mg, 5.50 mmol) in THF (10 mL) at -78 °C was added dropwise a solution of n-butyllithium (1.70 mL, 2.5M in hexanes, 4.25 mmol). The reaction mixture was then stirred under a nitrogen atmosphere for 2 hours, after which 2-bromobenzaldehyde (638 mg, 3.45 mmol) was added dropwise. The reaction mixture was left stirring under the nitrogen atmosphere and allowed to warm to rt. The reaction was followed by TLC (9:1 hexane: ethyl acetate). The mixture was quenched by saturated $NH_4Cl$ solution (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried ($MgSO_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-50% ethyl acetate in hexane to give (2-bromophenyl)(furan-2-yl)methanol as a yellow oil (860 mg, 3.43 mmol, 99%). TLC: Rf ca 0.30 (9:1 hexane: EtOAc), strong UV and $KMnO_4$; $\delta_H$ (400 MHz, $CDCl_3$) 7.69 (1H, d, *J* = 7.7, ArH), 7.56 (1H, d, *J* = 8.0, ArH), 7.40-7.36 (2H, m, ArH), 7.19 (1H, t, *J* = 7.6, H in furan), 6.32 (1H, s, H in furan), 6.19 (1H, d, *J* = 4.1, H in furan), 6.08 (1H, d, *J* = 4.0, Ar*CH*OH), 2.56 (1H, d, *J* = 4.0, ArCH*OH*) ppm; $\delta_C$ (100 MHz, $CDCl_3$) 154.45 (C), 142.72 (CH), 139.81 (C), 132.77 (CH), 129.50 (CH), 128.37 (CH), 127.71 (CH), 122.59 (C), 110.38 (CH), 108.15 (CH), 69.10 (CH) ppm; m/z (ES-API+) 274.9 ($M^+$ + 23, 100%). Data matched that reported.

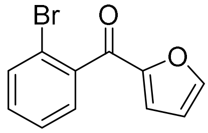
$^1H$ NMR (400 MHz, $CDCl_3$)



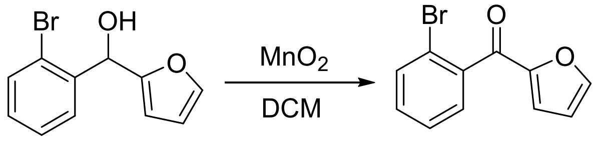
$^{13}C$ NMR (100 MHz, $CDCl_3$)



**(2-Bromophenyl)(furan-2-yl)methanone.**



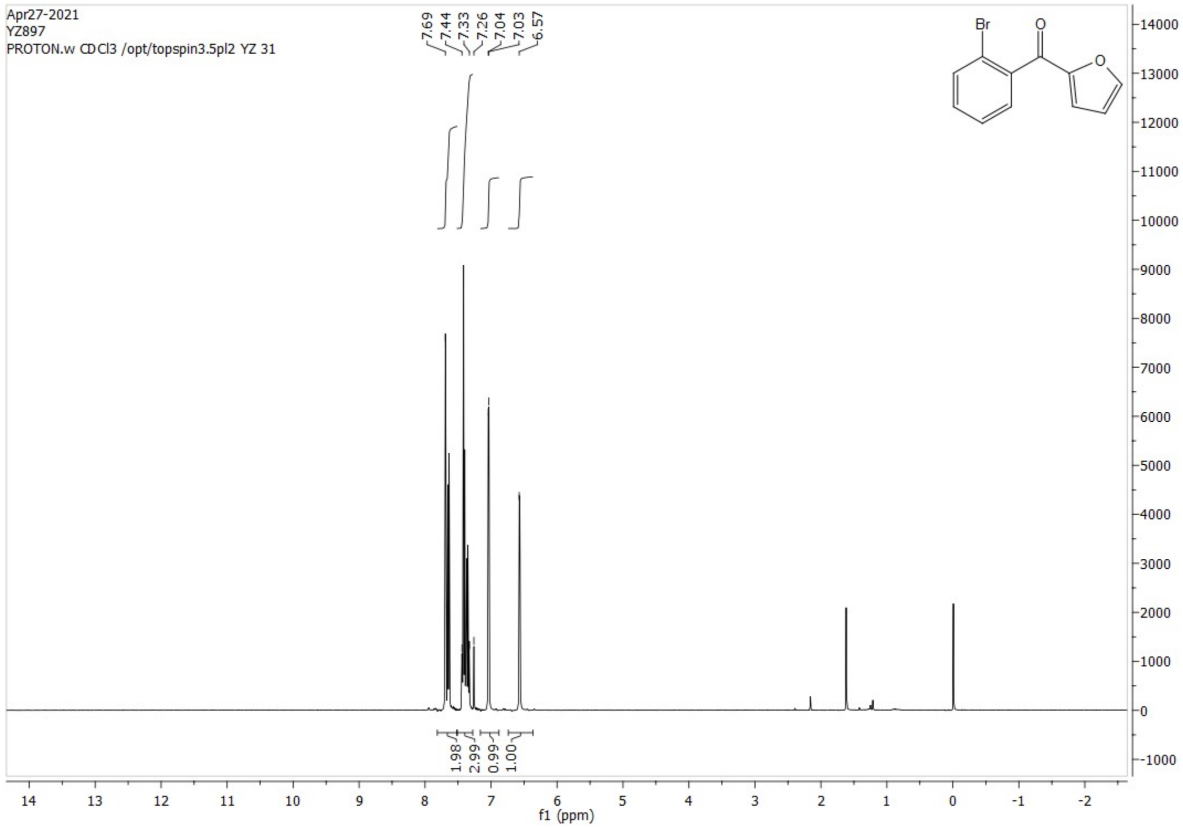
YZ897



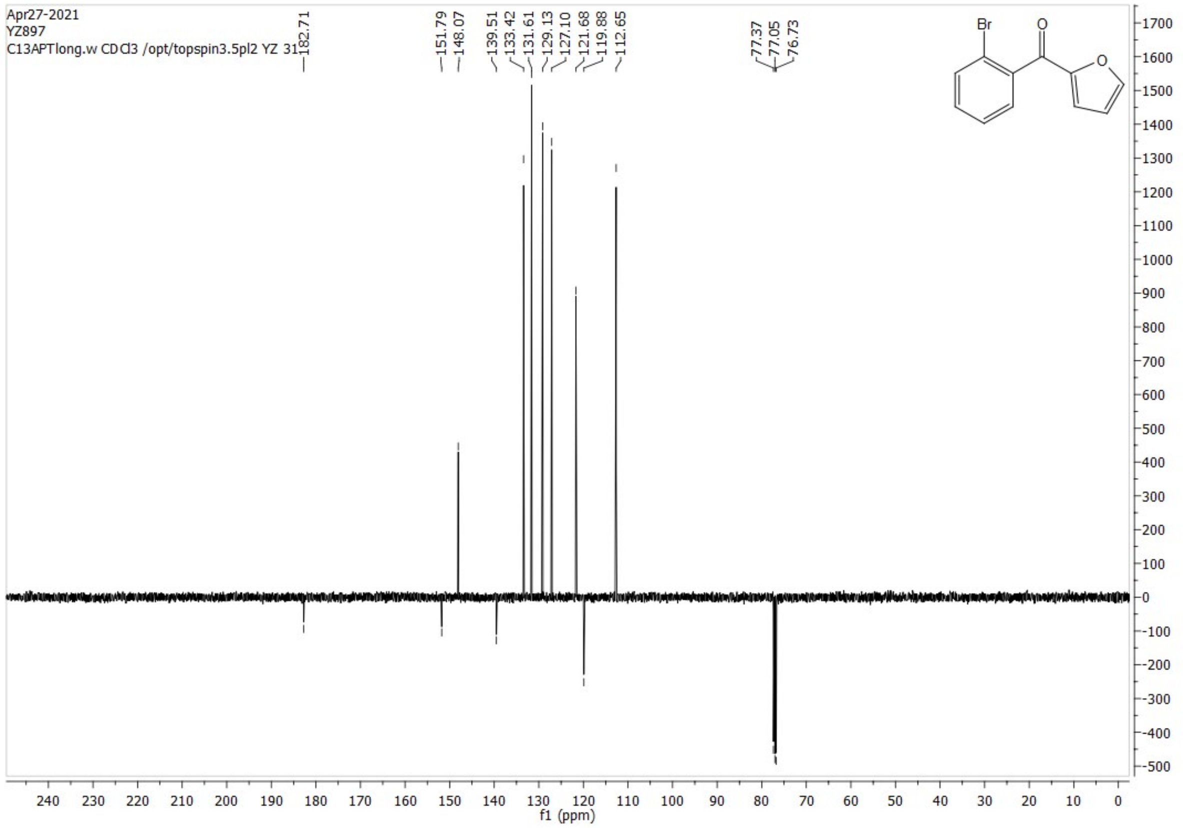
This compound has been reported but not fully characterized: M. Tang, Y. Kong, B. Chu and D. Feng, *Adv, Synth. Catal.* 2016, **358**, 926-939.

To a solution of (2-bromophenyl)(furan-2-yl)methanol (860 mg, 3.43 mmol) in DCM (23 mL) at rt was added manganese dioxide (4.48 g, 51.5 mmol). The reaction mixture was left to stir under a nitrogen atmosphere overnight. TLC (9:1 hexane: EtOAc) after this time indicated full conversion. The solids were removed by gravity filtration and washed with DCM. The combined solvent was removed to give the product as a colorless oil (363 mg, 1.46 mmol, 43%). TLC: Rf ca 0.50 (9:1 hexane: EtOAc), strong UV and $KMnO_4$; HRMS: (found (ESI+): [M+Na]+, Calcd for $C_{11}H_7{}^{79}BrNaO_2$ 272.9501; Found 272.9495; -2.4 ppm error); $\nu_{max}$ 3130, 1652, 1561, 1457, 1390, 1298, 1150, 1018, 956, 743, 68 $cm^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 7.69 (2H, dd, *J* = 18.3, 4.2, ArH), 7.44-7.33 (3H, m, H in furan + ArH), 7.04 (1H, d, *J* = 3.6, H in furan), 6.57 (1H, dd, *J* = 3.5, 1.2, H in furan) ppm; $\delta_C$ (100 MHz, $CDCl_3$) 182.71 (C), 151.79 (C), 148.07 (CH), 139.51 (C), 133.42 (CH), 131.61 (CH), 129.13 (CH), 127.10 (CH), 121.69 (CH), 119.88 (C), 112.65 (CH) ppm; m/z (ES-API+) 272.9 ($M^+$ + 23, 100%).

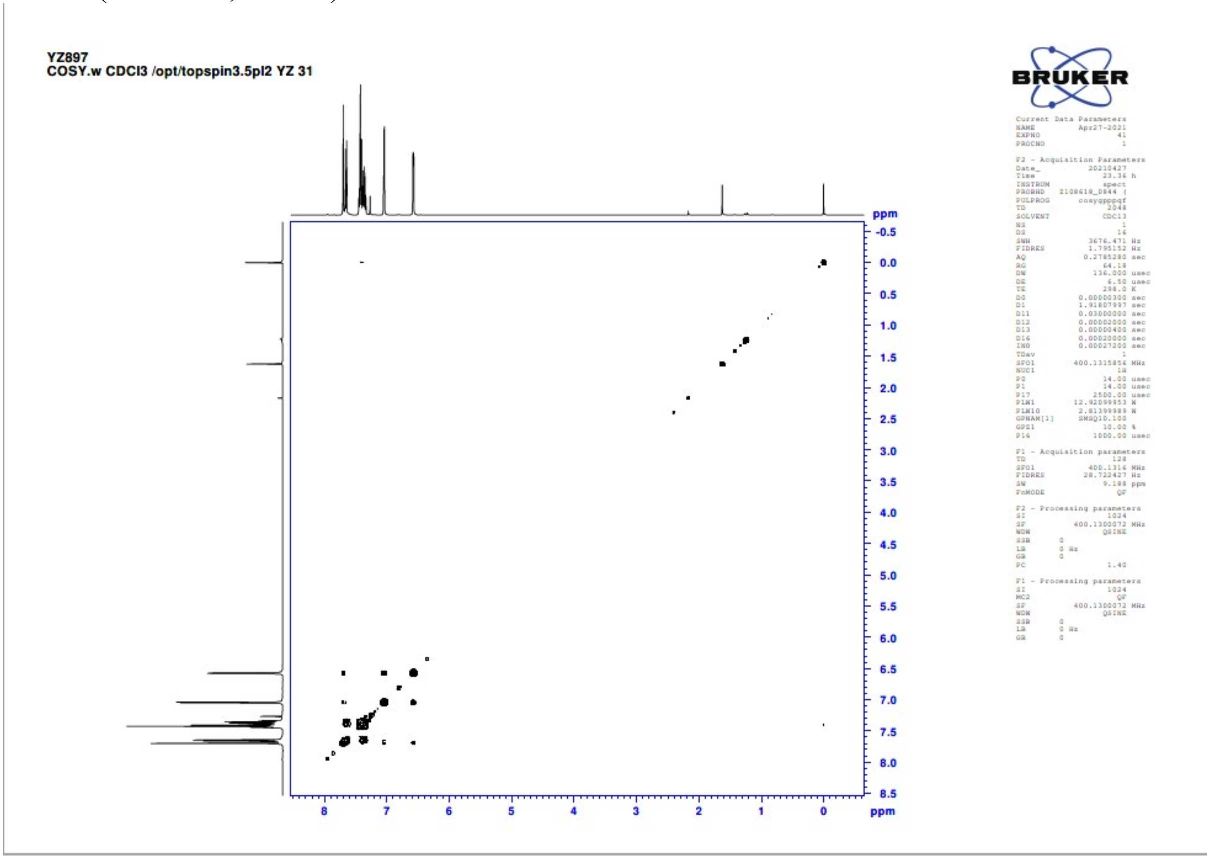
$^1$H NMR (400 MHz, CDCl$_3$)



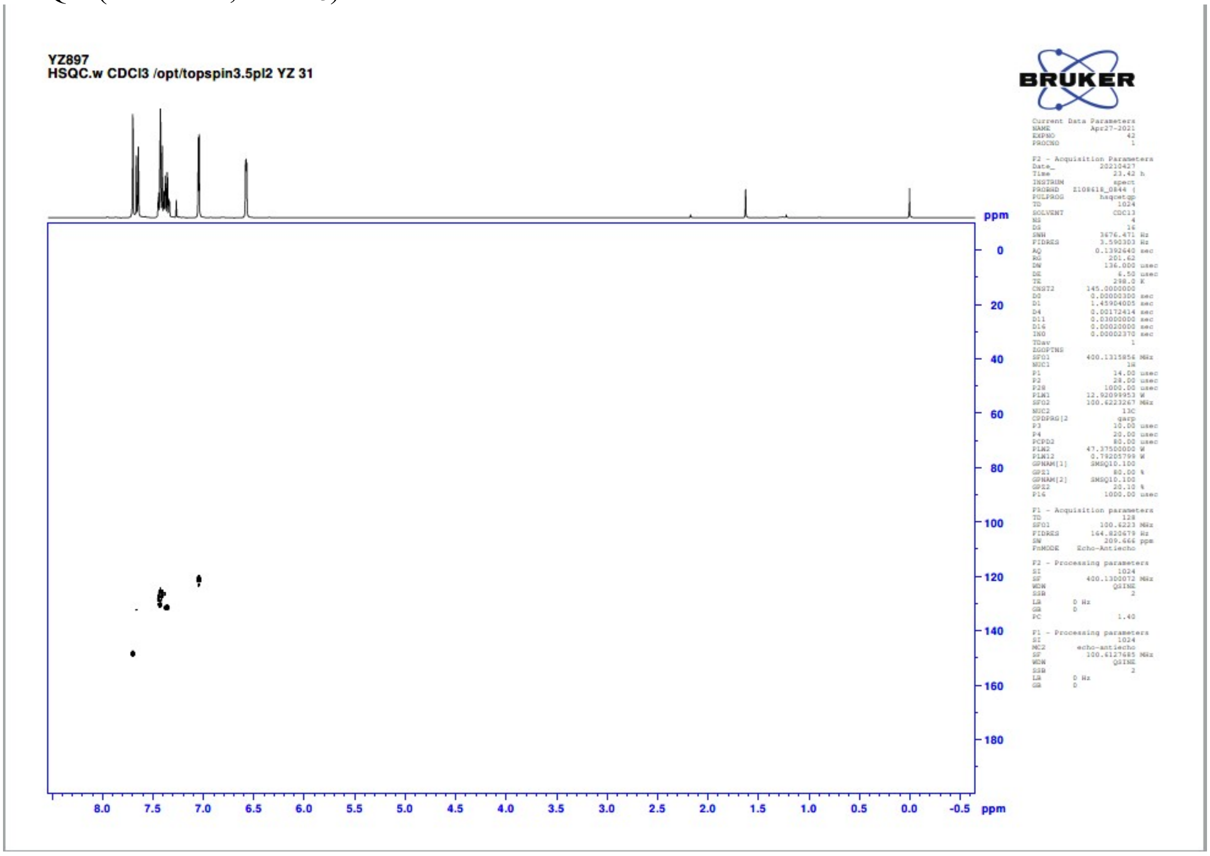
$^{13}$C NMR (100 MHz, CDCl$_3$)



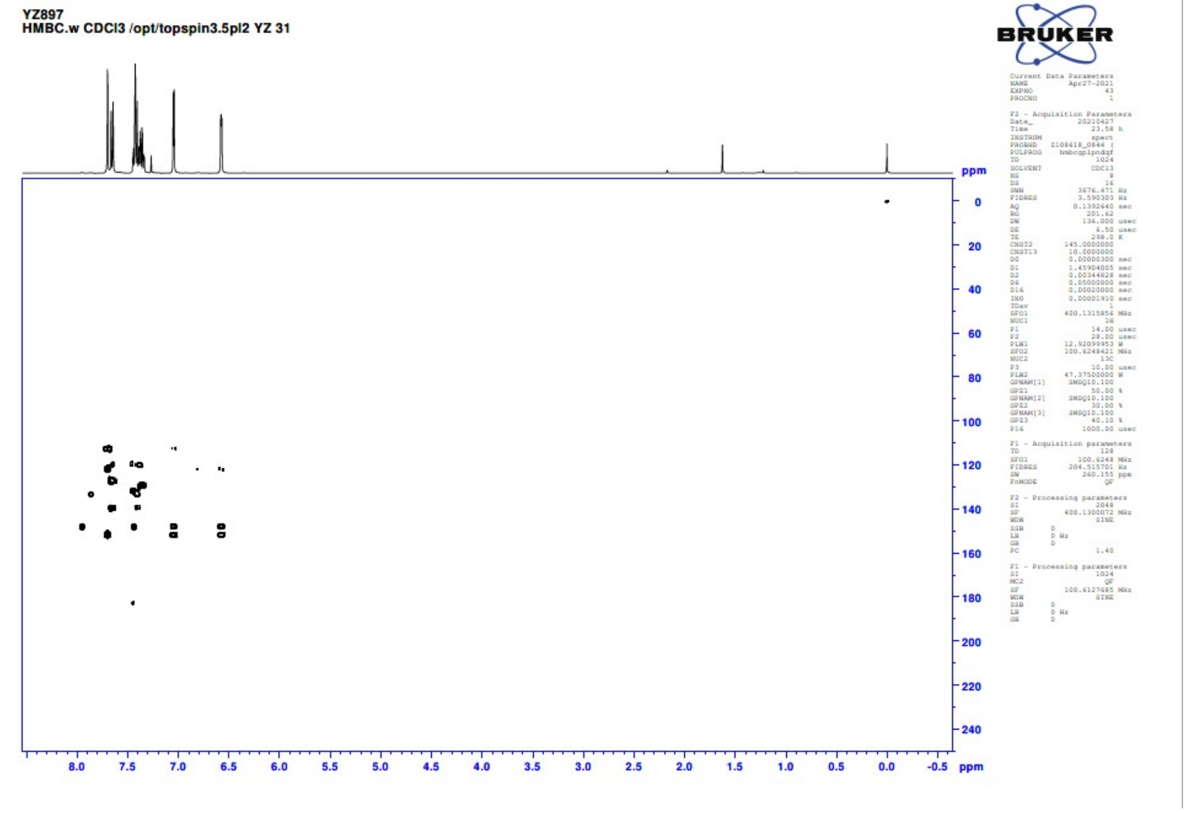
COSY (400 MHz, $CDCl_3$)



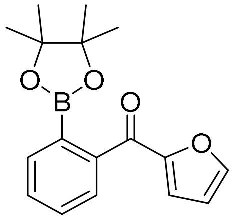
HSQC (400 MHz, $CDCl_3$)

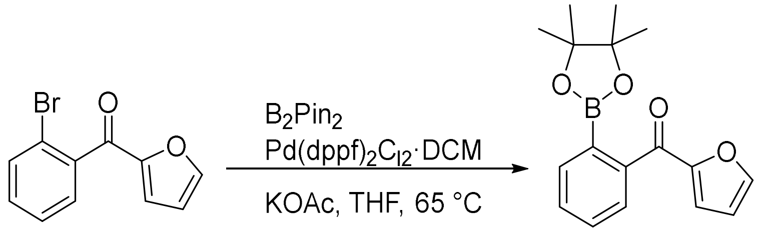


HMBC (400 MHz, $CDCl_3$)



Furan-2-yl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone.



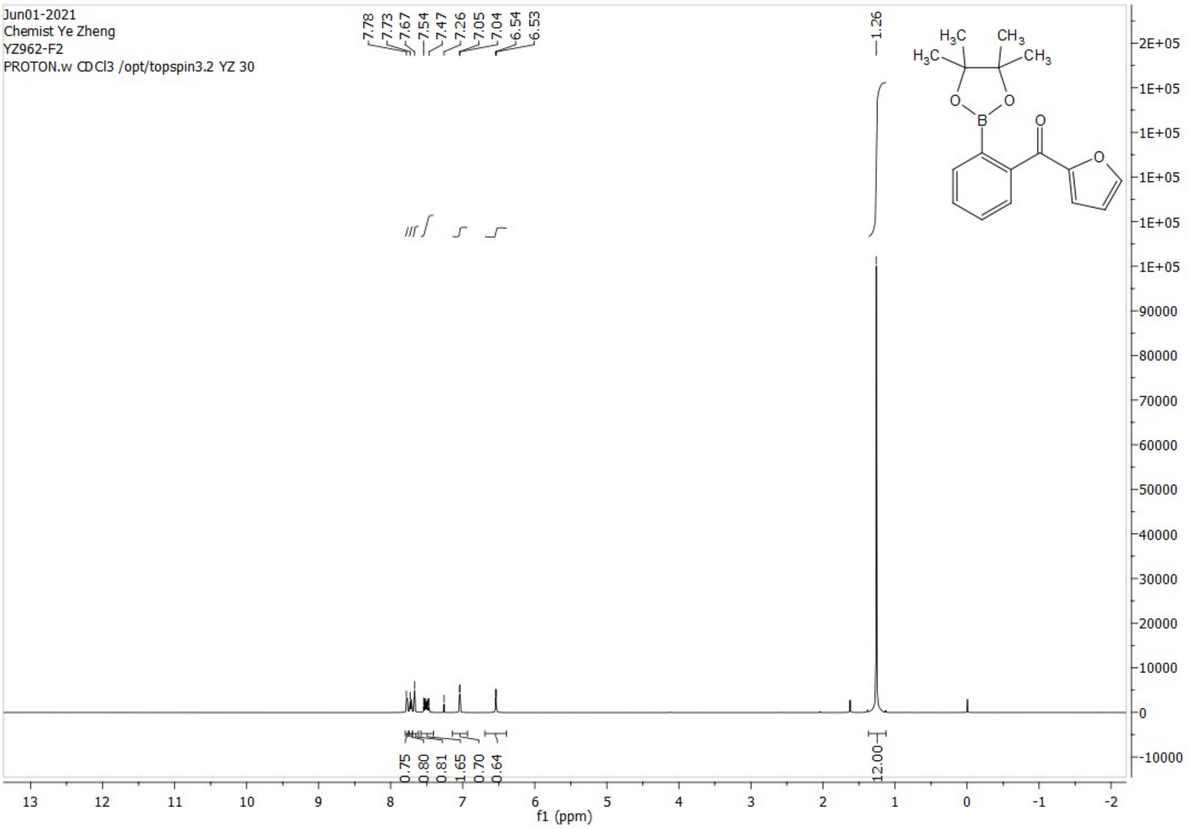


This compound is novel.

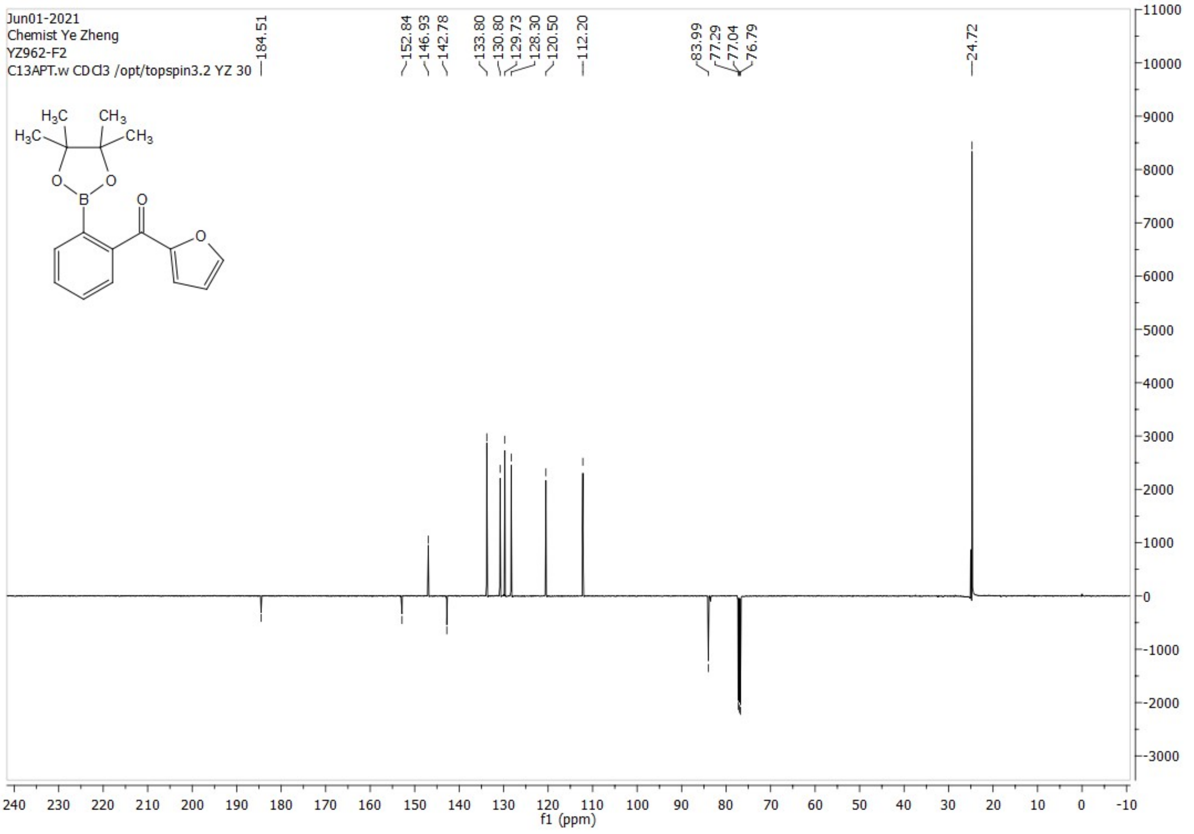
A round-bottom flask was charged with (2-bromophenyl)(furan-2-yl)methanone (560 mg, 2.25 mmol), bis(pinacolato)diboron (686 mg, 2.70 mmol), potassium acetate (662 mg, 6.75 mmol), THF (14 mL) and Pd(dppf)$_2$Cl$_2$·DCM (92.3 mg, 0.113 mmol). The reaction mixture was heated to 65 °C and left stirring under the nitrogen atmosphere overnight, followed by TLC (4:1 hexane: EtOAc). The mixture was quenched by distilled water (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried (MgSO$_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-10% ethyl acetate in hexane to give furan-2-yl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone as a yellow oil (228 mg, 0.765 mmol, 34%). TLC: Rf ca 0.20 (4:1 hexane: EtOAc), strong UV and KMnO$_4$; HRMS: (found (ESI+): [M+H]+, Calcd for $C_{17}H_{19}BNaO_4$ 321.1267; Found 321.1269; 1.5 ppm error); $\nu_{max}$ 2978, 1653, 1564, 1462, 1346, 1304, 1143, 1037 cm$^{-1}$; $\delta_H$ (500 MHz, CDCl$_3$) 7.78 (1H, d, *J* = 7.3, ArH), 7.73 (1H, d, *J* = 8.0, ArH), 7.67 (1H, d, *J* = 0.9, ArH), 7.54-7.47 (2H, m, ArH + H in furan), 7.05 (1H, d, *J* = 3.5, H in furan), 6.54 (1H, dd, *J* = 3.5, 1.7, H in furan), 1.26 (12H, s, CH$_3$) ppm; $\delta_C$ (125 MHz, CDCl$_3$) 184.51 (C), 152.84 (C), 146.93 (CH), 142.77 (C), 133.80 (CH), 130.80 (CH), 129.73 (CH), 128.30 (CH), 120.50 (CH), 112.20 (CH), 83.99 (C), 24.72 (CH$_3$) ppm; m/z (ES-API+) 321.1 (M$^+$ + 23, 100%).

Enantiomeric excess and conversion determined by HPLC analysis (Chiralcel OJ, 30 cm x 6mm column, hexane:iPrOH 95:5, 1.0 mL/min, T = 25°C) ketone 19.6 min, *R* and *S* isomers 6.7 min and 13.3 min.

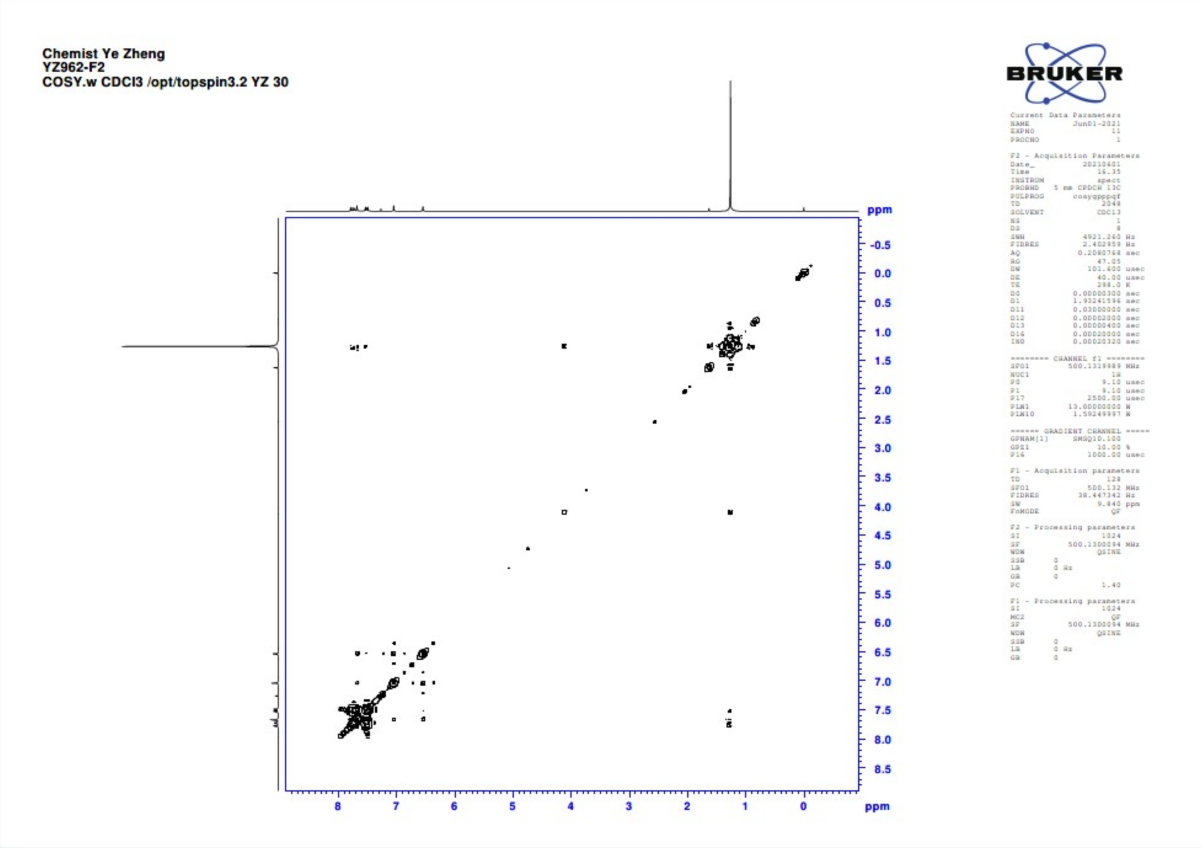
$^1$H NMR (500 MHz, $CDCl_3$)



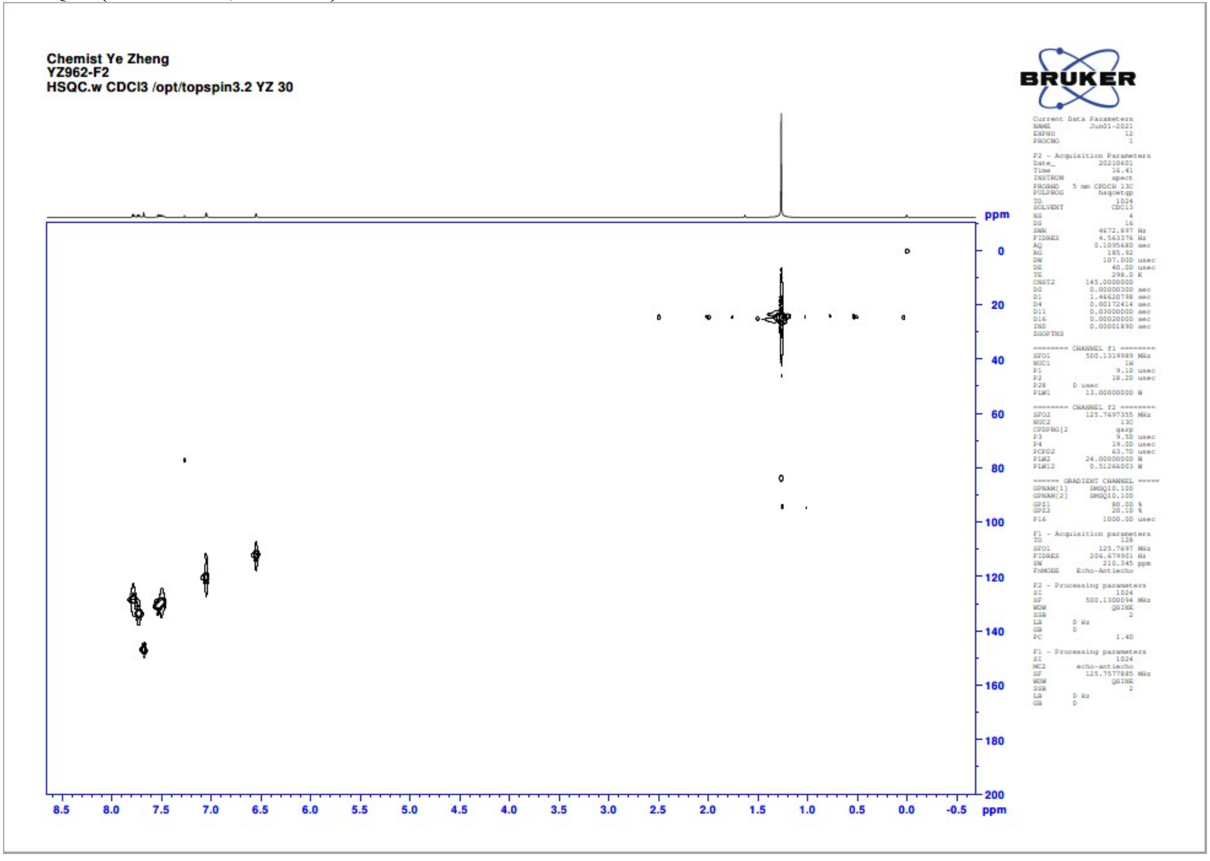
$^{13}$C NMR (125 MHz, $CDCl_3$)



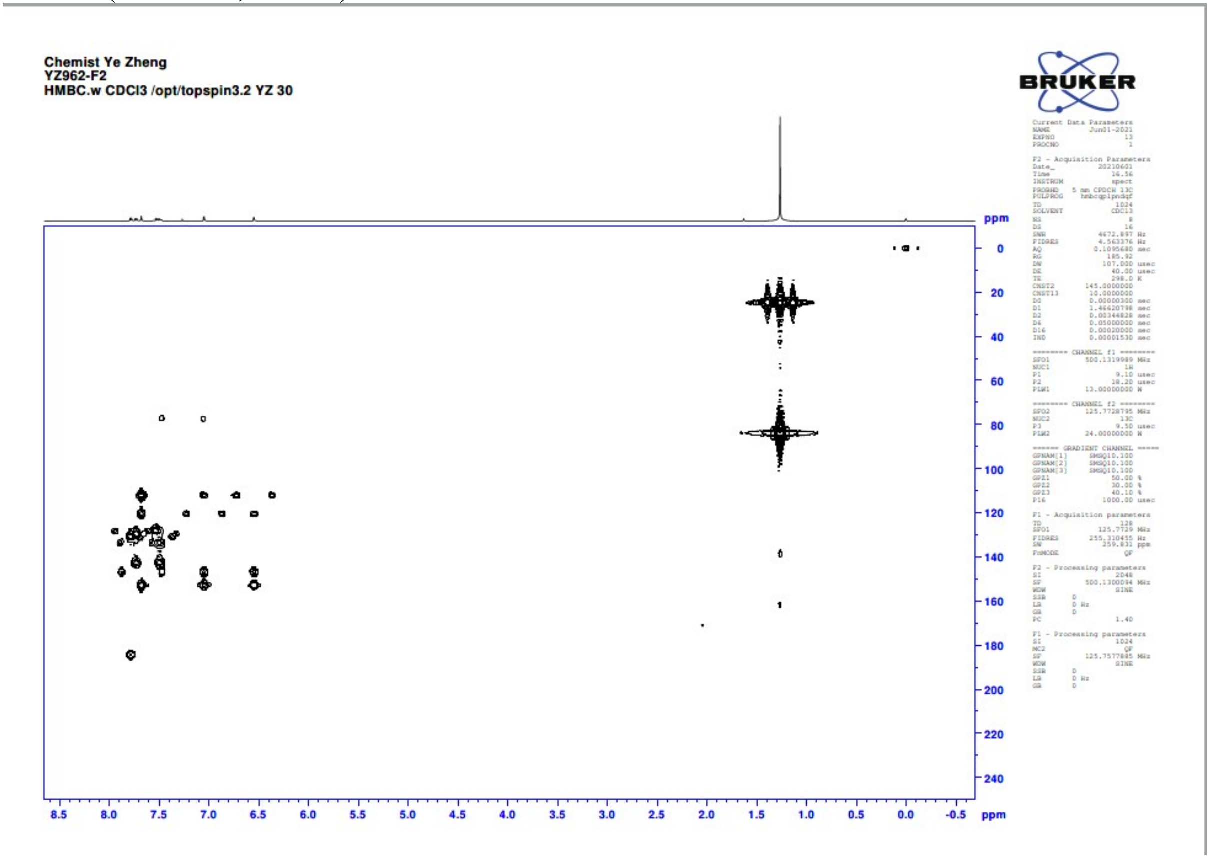
COSY (500 MHz, $CDCl_3$)



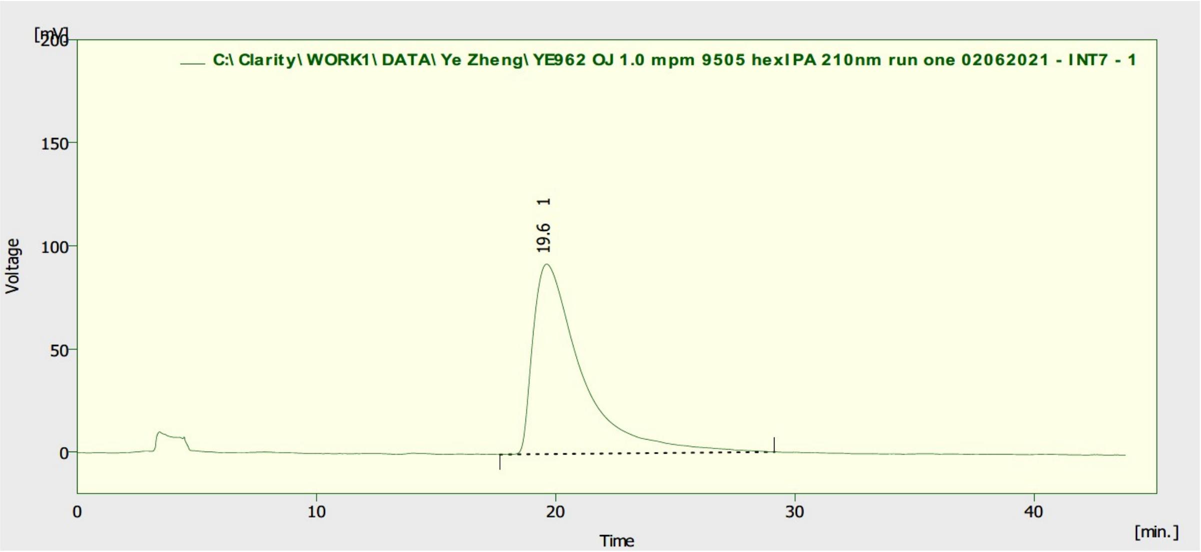
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)



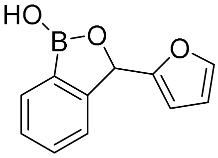
HPLC of furan-2-yl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone

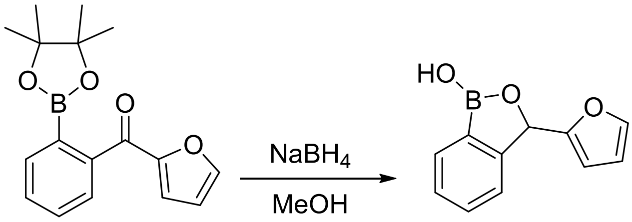


*Result Table (Uncal - C:\Clarity\WORK1\DATA\Ye Zheng\YE962 OJ 1.0 mpm 9505 hexIPA 210nm run one 02062021 - INT7 - 1)*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Compound Name |
|---|---|---|---|---|---|---|---|
| 1 | 19.620 | 13060.040 | 92.090 | 100.0 | 100.0 | 1.93 | |
| | Total | 13060.040 | 92.090 | 100.0 | 100.0 | | |

3-(Furan-2-yl)benzo[c][1,2]oxaborol-1(3*H*)-ol **28**.





This compound has been reported in racemic form and fully characterization: J. Zhu, Y. Wei, D. Lin, C. Ou, L. Xie, Y. Zhao, W. Huang, *Org. Biomol. Chem.* 2015, **13**, 11362-11368.

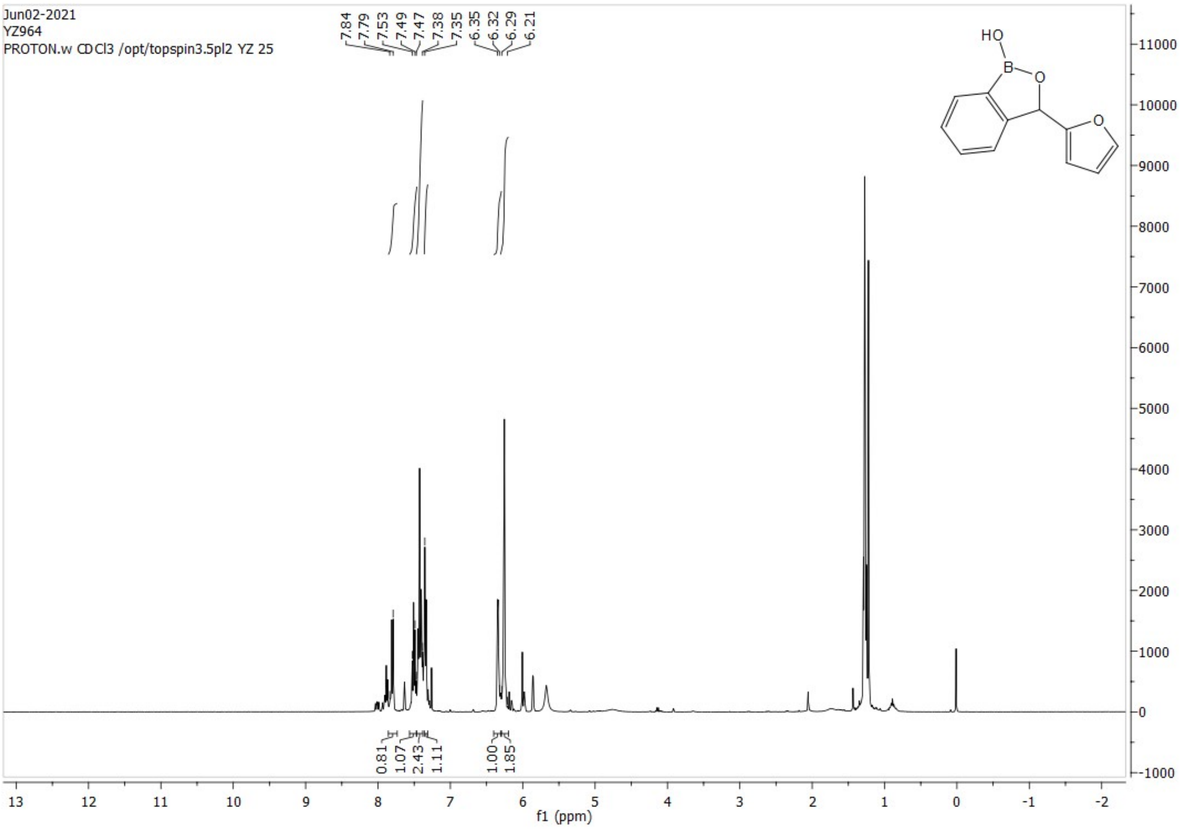
To a solution of furan-2-yl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone (120 mg, 0.403 mmol) in MeOH (2.5 mL) was added sodium borohydride (30.6 mg, 0.806 mmol). The reaction was stirred for 4 hours. TLC (1:1 hexane: EtOAc) after this time indicated full conversion. Distilled water (20 mL) was added, and the mixture was extracted with EtOAc (3 × 20ml), dried with $MgSO_4$. Solvent was removed to give the crude product. The reaction was followed by TLC (1:1 hexane: EtOAc). The product was isolated via flash chromatography on silica eluted with 0-50% ethyl acetate in hexane to give 3-(furan-2-yl)benzo[c][1,2]oxaborol-1(3*H*)-ol **28** as a white solid (42.0 mg, 0.210 mmol, 52%). TLC: Rf ca 0.20 (1:1 hexane: EtOAc), strong UV and $KMnO_4$; $\delta_H$ (400 MHz, $CDCl_3$) 7.84-7.79 (1H, m, ArH), 7.53-7.49 (1H, m, ArH), 7.47-7.38 (2H, m, ArH), 7.35 (1H, d, *J* = 7.5, H in furan), 6.35-6.32 (1H, m, H in furan), 6.29-6.21 (2H, m, H in furan + ArCH) ppm; $\delta_C$ (100 MHz, $CDCl_3$) 153.40 (C), 152.85 (C), 143.35 (CH), 131.31 (CH), 130.62 (CH), 128.08 (CH), 122.34 (CH), 110.29 (CH), 108.54 (CH), 76.67 (CH) ppm. m/z (ES-API+) 247.1 ($M^+$ + 23, 100%). Data matched that reported.

Enantiomeric excess and conversion determined by HPLC analysis (Chiralcel OJ, 30 cm x 6mm column, hexane:iPrOH 95:5, 1.0 mL/min, T = 25°C) ketone 19.6 min, *R* and *S* isomers 6.7 min and 13.3 min, configuration is not confirmed.

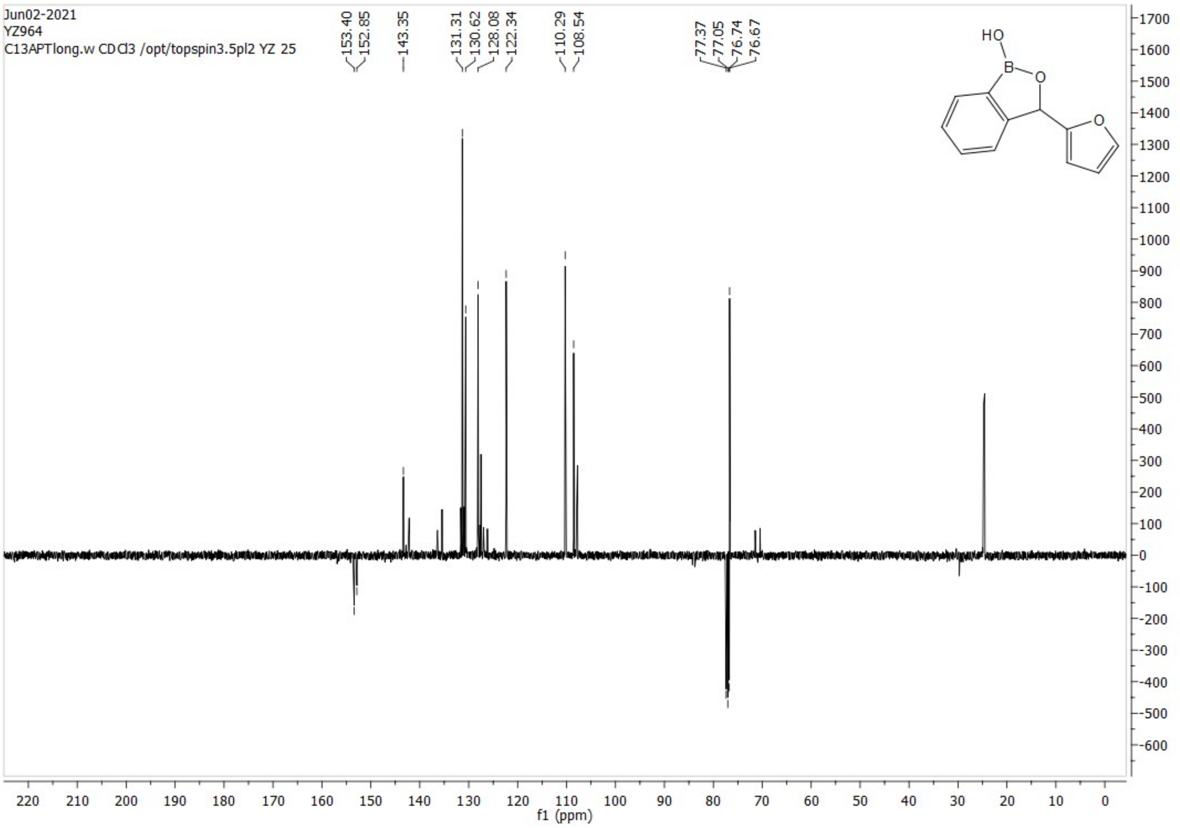
ATH of furan-2-yl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone.

(*R,R*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (2.50 mg, 0.00403 mmol, 1mol%) was added to FA: TEA (5:2 azeotropic mixture, 0.54 mL) at rt and the mixture was stirred under a nitrogen inert atmosphere for 10-15 minutes; after which a solution furan-2-yl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone (120 mg, 0.403 mmol) in DCM (0.75 mL) was added. The reaction mixture was stirrer under a nitrogen atmosphere, followed by TLC (1:1 hexane: EtOAc). After 72 hours, the reaction was quenched using saturated $NaHCO_3$ solution (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried ($MgSO_4$) and filtered. The solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-50% ethyl acetate in hexane to give 3-(furan-2-yl)benzo[c][1,2]oxaborol-1(3*H*)-ol **28** (16.0 mg, 0.0800 mmol, 20%). The reaction was also followed by HPLC analysis (Chiralcel OJ, 30 cm x 6mm column, hexane:iPrOH 95:5, 1.0 mL/min, T = 25°C): 100% conversion, 5% ee

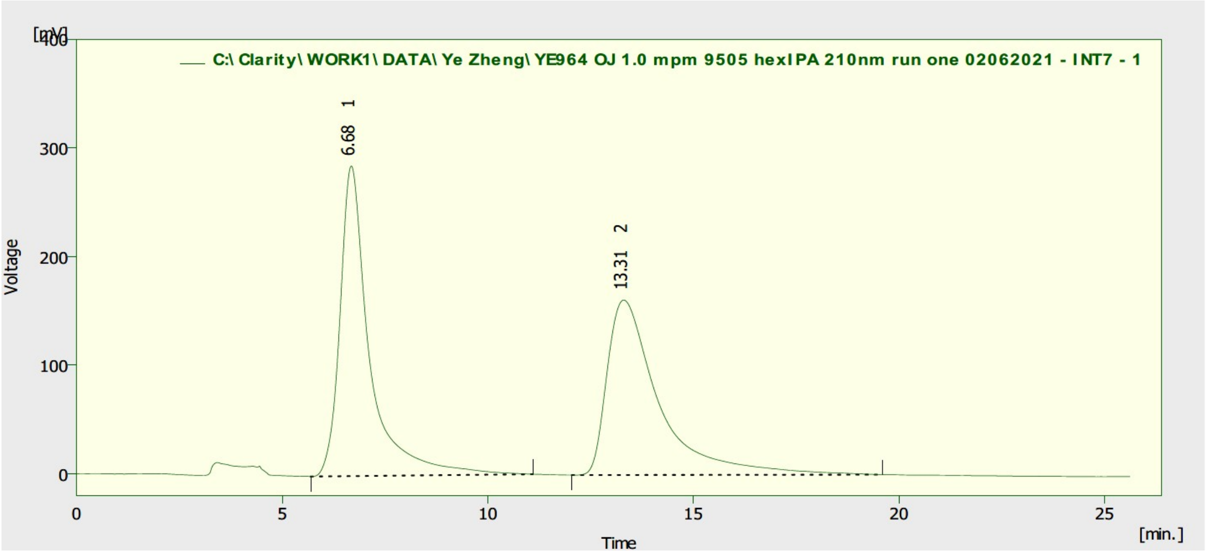
$^1$H NMR (400 MHz, $CDCl_3$)



$^{13}$C NMR (100 MHz, $CDCl_3$)



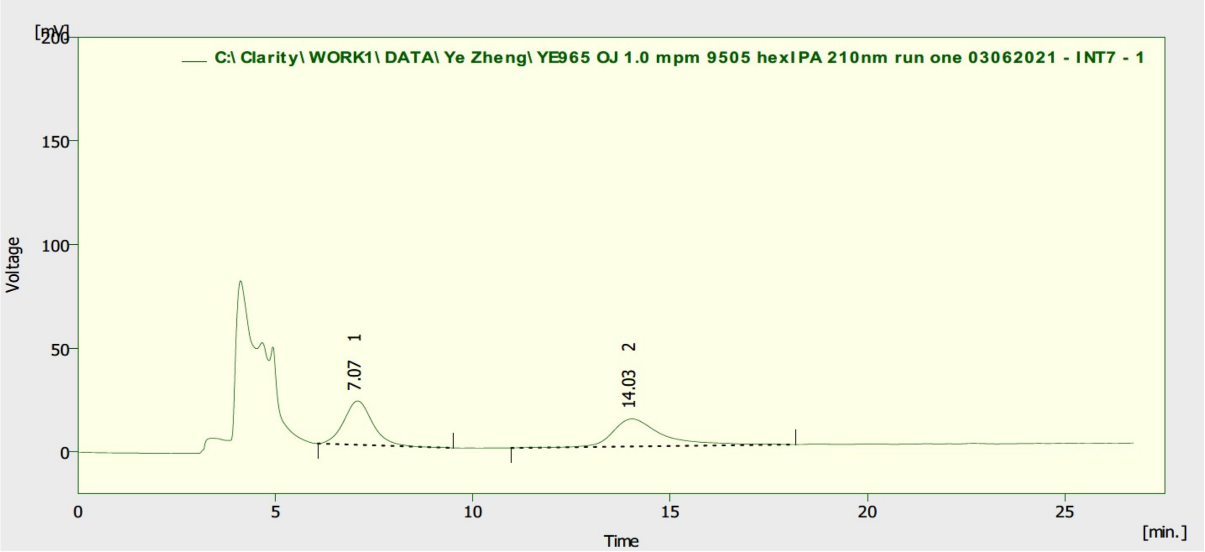
HPLC of racemic 3-(furan-2-yl)benzo[c][1,2]oxaborol-1(3*H*)-ol **28**.



*Result Table (Uncal - C:\Clarity\WORK1\DATA\Ye Zheng\YE964 OJ 1.0 mpm 9505 hexIPA 210nm run one 02062021 - INT7 - 1)*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Compound Name |
|---|---|---|---|---|---|---|---|
| 1 | 6.680 | 14338.745 | 285.453 | 50.3 | 63.9 | 0.63 | |
| 2 | 13.307 | 14157.038 | 161.086 | 49.7 | 36.1 | 1.18 | |
| | Total | 28495.782 | 446.540 | 100.0 | 100.0 | | |

HPLC after ATH of furan-2-yl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone using (*R,R*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (after 72 hours, 100% conversion, 4.8% ee)

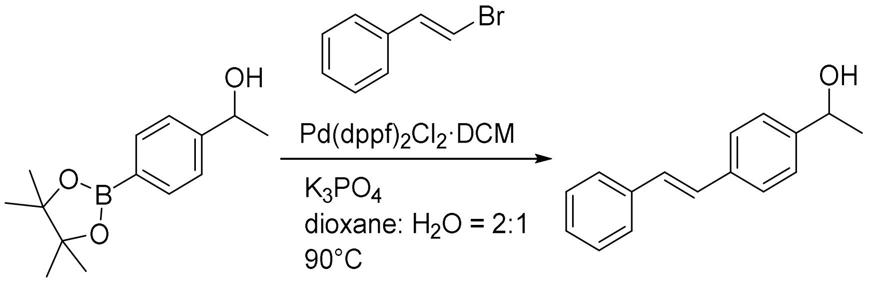


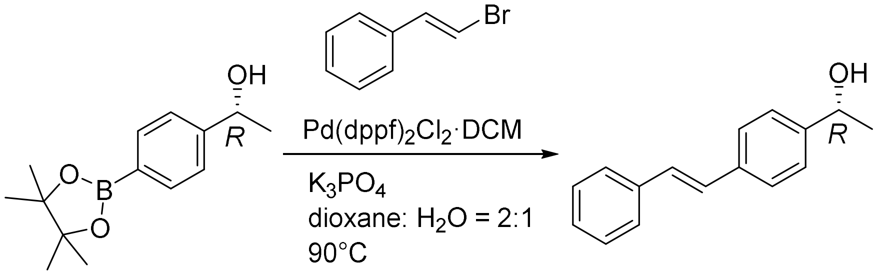
*Result Table (Uncal - C:\Clarity\WORK1\DATA\Ye Zheng\YE965 OJ 1.0 mpm 9505 hexIPA 210nm run one 03062021 - INT7 - 1)*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Compound Name |
|---|---|---|---|---|---|---|---|
| 1 | 7.073 | 1072.229 | 21.170 | 47.6 | 61.5 | 0.76 | |
| 2 | 14.027 | 1182.198 | 13.265 | 52.4 | 38.5 | 1.19 | |
| | Total | 2254.427 | 34.435 | 100.0 | 100.0 | | |

**Data related to Figure 6.**

1-(4-Styrylphenyl)ethan-1-ol **29**.





This compound has been reported and fully characterized: X. Shu, R. Jin, Z. Zhao, T. Cheng and G. Liu, *Chem. Commun.* 2018, **54**, 13244-13247.

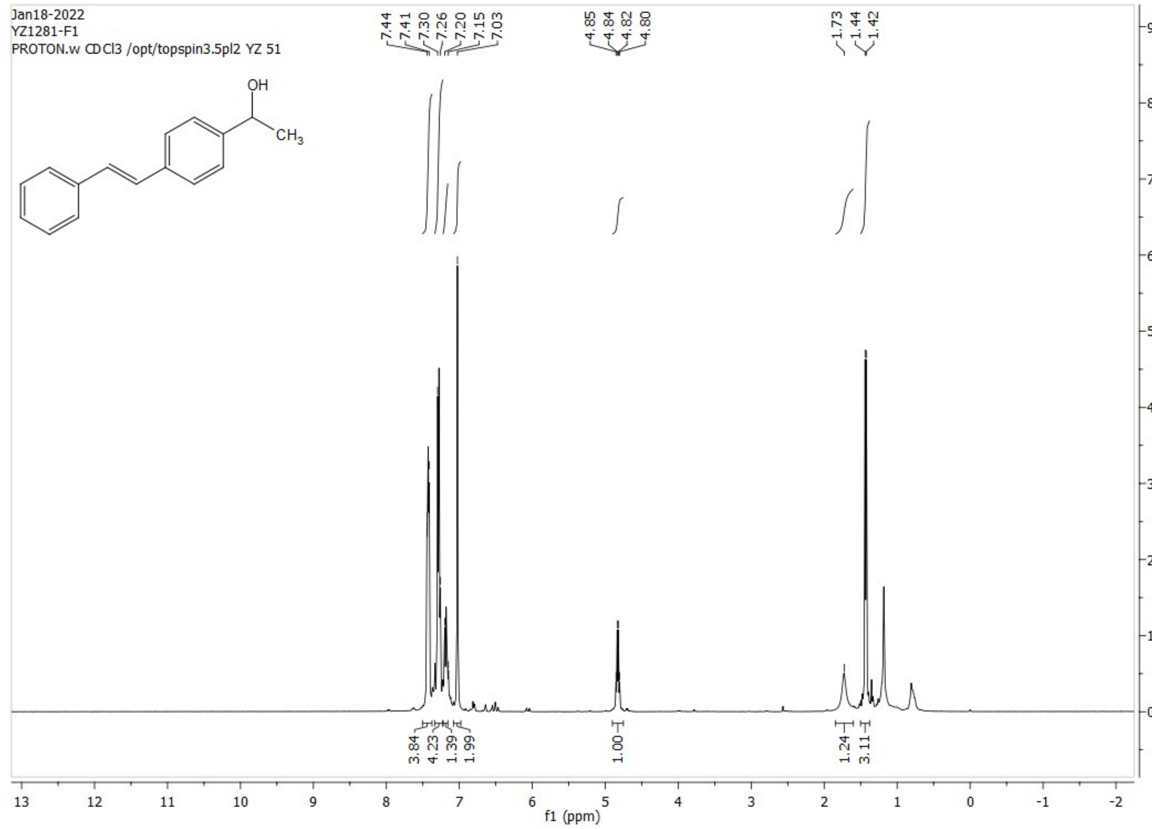
Racemic: To a solution of racemic 1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol **7** (52.0 mg, 0.210 mmol), β-bromostyrene (57.6 mg, 0.315 mmol) and tripotassium phosphate (134 mg, 0.630 mmol) in dioxane (1 mL) and distilled water (0.5 mL) was added Pd(dppf)$_2$Cl$_2$·DCM (8.58 mg, 0.0105 mmol). The reaction mixture was heated to 90 °C and left stirring under the nitrogen atmosphere overnight, followed by TLC (4:1 hexane: EtOAc). The mixture was quenched by distilled water (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried ($MgSO_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-20% ethyl acetate in hexane to give racemic 1-(4-styrylphenyl)ethan-1-ol **29** as a white solid (32.0 mg, 0.143 mmol, 68%). TLC: Rf ca 0.30 (4:1 hexane: EtOAc), strong UV and $KMnO_4$; $\delta_H$ (400 MHz, $CDCl_3$) 7.44-7.41 (4H, m, ArH), 7.30-7.26 (4H, m, ArH), 7.20-7.15 (1H, m, ArH), 7.03 (2H, s, CH=CH), 4.84 (1H, q, *J* = 6.4, ArCH), 1.73 (1H, s, OH), 1.44 (3H, d, *J* = 6.4, $CH_3$) ppm; $\delta_C$ (100 MHz, $CDCl_3$) 145.24 (C), 137.32 (C), 136.67 (C), 128.71 (CH), 128.68 (CH), 128.30 (CH), 127.66 (CH), 126.52 (CH), 125.79 (CH), 70.22 (CH), 25.12 ($CH_3$) ppm; m/z (ES-API+) 247.1 ($M^+$ + 23, 100%). Data matched that reported.

Enantiomeric excess and conversion determined by HPLC analysis (Chiralcel IG, 30 cm x 6mm column, hexane:iPrOH 95:5, 0.5 mL/min, T = 25°C) *R* isomer 38.0 min and *S* isomer 41.3 min.

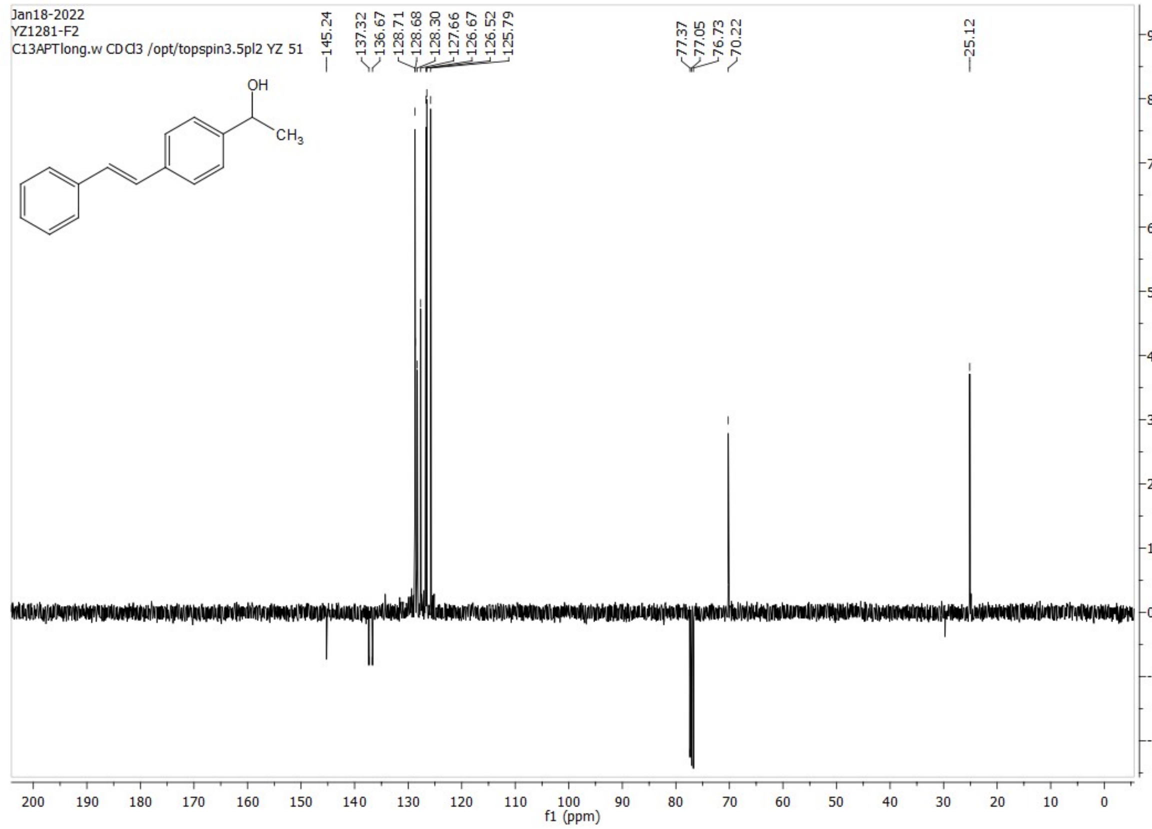
Asymmetric:

To a solution of (*R*)-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol **7** (100 mg, 0.403 mmol), β-bromostyrene (111 mg, 0.605 mmol) and tripotassium phosphate (257 mg, 1.21 mmol) in dioxane (2 mL) and distilled water (1 mL) was added $Pd(dppf)_2Cl_2 \cdot DCM$ (16.5 mg, 0.0202 mmol). The reaction mixture was heated to 90 °C and left stirring under the nitrogen atmosphere overnight, followed by TLC (4:1 hexane: EtOAc). The mixture was quenched by distilled water (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried ($MgSO_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-20% ethyl acetate in hexane to give (*R*)-1-(4-styrylphenyl)ethan-1-ol **29** as a white solid (67.0 mg, 0.299 mmol, 74%). The reaction was also followed by HPLC (Chiralcel IG, 30 cm x 6mm column, hexane:iPrOH 95:5, 0.5 mL/min, T = 25°C): $[\alpha]_D^{30}$ +35 (c 0.180 in $CHCl_3$) 98% ee (*R*).

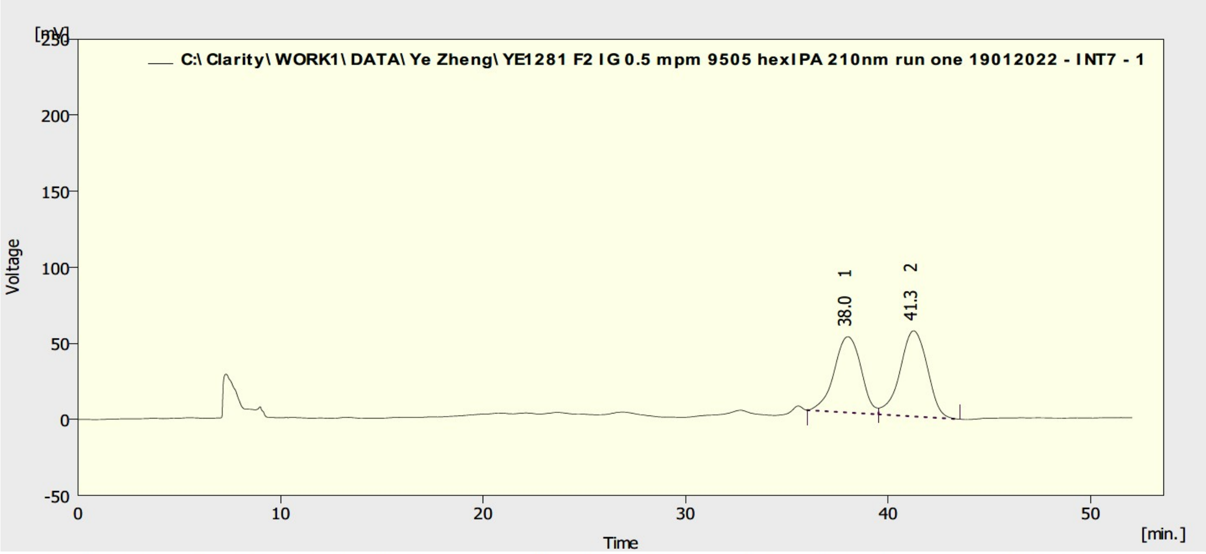
$^1$H NMR (400 MHz, CDCl$_3$)



$^{13}$C NMR (100 MHz, CDCl$_3$)



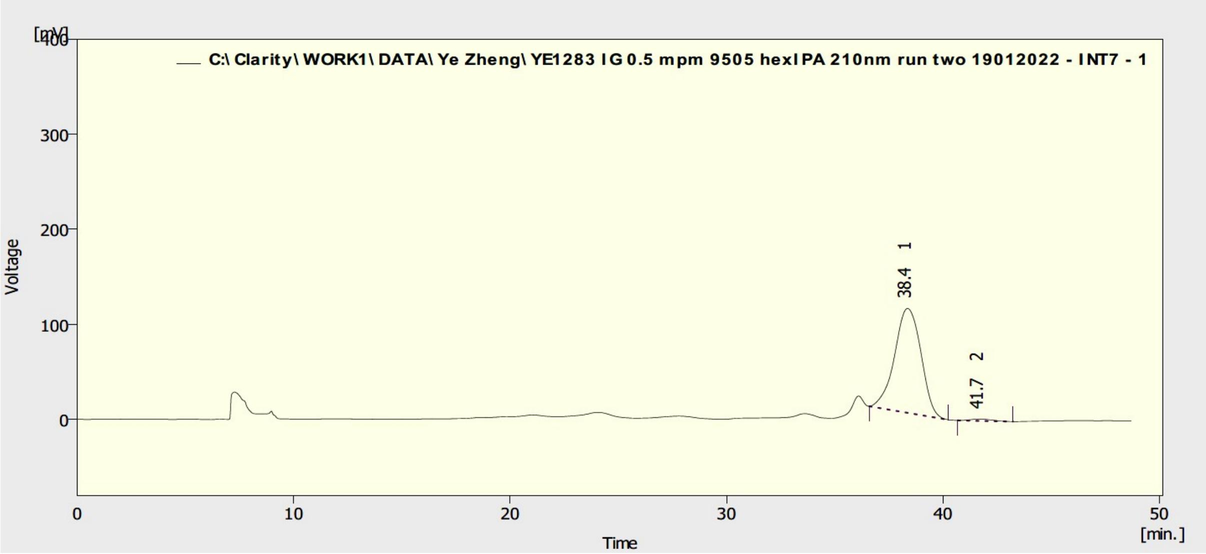
HPLC of racemic 1-(4-styrylphenyl)ethan-1-ol **29**.



*Result Table (Uncal - C:\Clarity\WORK1\DATA\Ye Zheng\YE1281 F2 IG 0.5 mpm 9505 hexIPA 210nm run one 19012022 - INT7 - 1)*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Compound Name |
|---|---|---|---|---|---|---|---|
| 1 | 38.007 | 4630.356 | 49.923 | 46.6 | 46.9 | 1.45 | |
| 2 | 41.257 | 5301.890 | 56.409 | 53.4 | 53.1 | 1.46 | |
| | Total | 9932.246 | 106.332 | 100.0 | 100.0 | | |

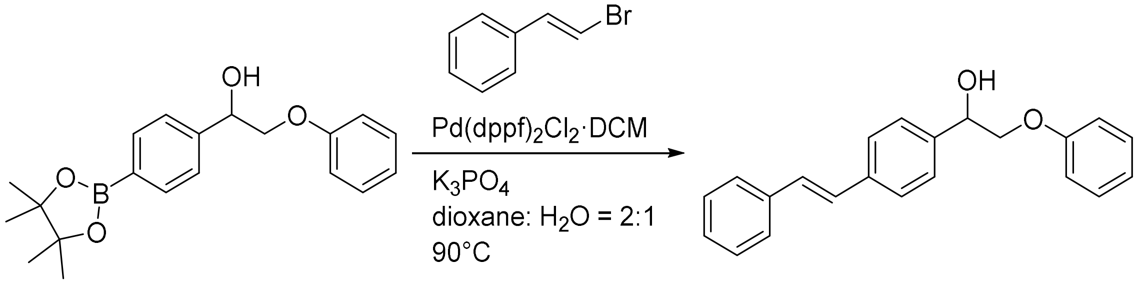
HPLC of 1-(4-styrylphenyl)ethan-1-ol **29** (97% ee, *R* configuration).

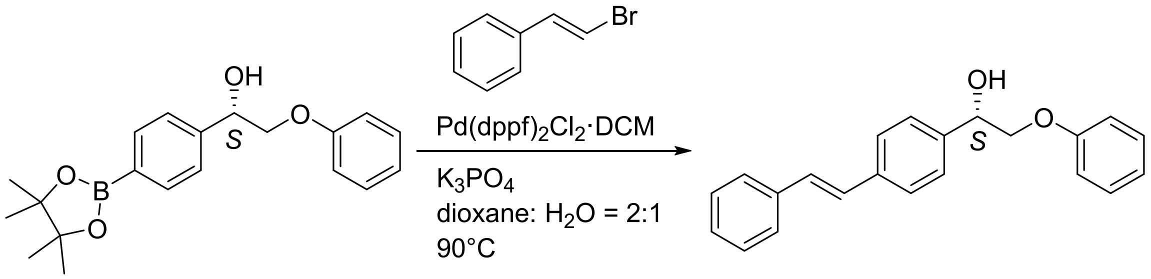


*Result Table (Uncal - C:\Clarity\WORK1\DATA\Ye Zheng\YE1283 IG 0.5 mpm 9505 hexIPA 210nm run two 19012022 - INT7 - 1)*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Compound Name |
|---|---|---|---|---|---|---|---|
| 1 | 38.367 | 9324.242 | 109.836 | 98.6 | 98.3 | 1.33 | |
| 2 | 41.703 | 130.272 | 1.902 | 1.4 | 1.7 | 1.10 | |
| | Total | 9454.514 | 111.738 | 100.0 | 100.0 | | |

2-Phenoxy-1-(4-styrylphenyl)ethan-1-ol **30**.





This compound is novel.

Racemic:

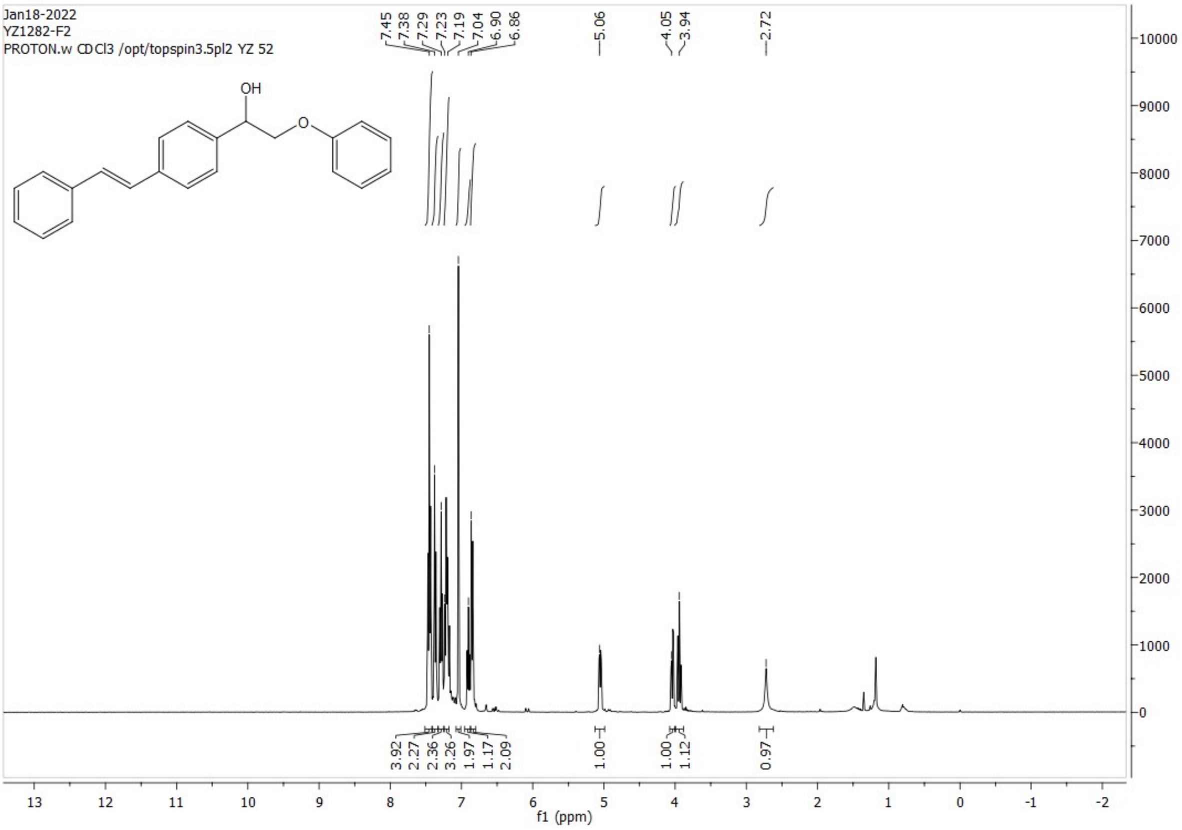
To a solution of racemic 2-phenoxy-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol **12** (88.0 mg, 0.259 mmol), β-bromostyrene (71.2 mg, 0.389 mmol) and tripotassium phosphate (165 mg, 0.777 mmol) in dioxane (1.3 mL) and distilled water (0.7 mL) was added Pd(dppf)$_2$Cl$_2$·DCM (10.6 mg, 0.0130 mmol). The reaction mixture was heated to 90 °C and left stirring under the nitrogen atmosphere overnight, followed by TLC (4:1 hexane: EtOAc). The mixture was quenched by distilled water (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried ($MgSO_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-20% ethyl acetate in hexane to give racemic 2-phenoxy-1-(4-styrylphenyl)ethan-1-ol **30** as a yellow solid (40.0 mg, 0.127 mmol, 49%). TLC: Rf ca 0.40 (4:1 hexane: EtOAc), strong UV and $KMnO_4$; Mp: 128 °C; HRMS: (found (ESI+): [M+H]+, Calcd for $C_{22}H_{20}NaO_2$ 339.1353; Found 339.1356; 0.8 ppm error; $\nu_{max}$ 3393 (br), 3055, 3024, 2922, 2868, 1598, 1586, 1493, 1449, 1239, 1172, 1076, 1037, 1017 cm$^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 7.45 (4H, t, *J* = 7.6, ArH), 7.38 (2H, d, *J* = 8.0, ArH), 7.29 (2H, t, *J* = 7.5, ArH), 7.23-7.19 (3H, m, ArH), 7.04 (2H, s, CH=CH), 6.90 (1H, t, *J* = 7.3, ArH), 6.86 (2H, d, *J* = 8.2, ArH), 5.06 (1H, dd, *J* = 8.7, 2.7, ArCH), 4.05 (1H, dd, *J* = 9.6, 3.0, $CH_2$), 3.94 (1H, t, *J* = 9.2, $CH_2$), 2.72 (1H, s, OH) ppm; $\delta_C$ (100 MHz, $CDCl_3$) 158.39 (C), 138.99 (C), 137.36 (C), 137.23 (C), 129.61 (CH), 129.05 (CH), 128.74 (CH), 128.18 (CH), 127.76 (CH), 126.70 (CH), 126.68 (CH), 126.57 (CH), 121.37 (CH), 114.68 (CH), 73.20 ($CH_2$), 72.43 (CH) ppm; m/z (ES-API+) 339.1 ($M^+$ + 23, 100%).

Enantiomeric excess and conversion determined by HPLC analysis (Chiralcel ODH, 30 cm x 6mm column, hexane:iPrOH 80:20, 1.0 mL/min, T = 25°C) *R* isomer 14.9 min and *S* isomer 21.2 min.

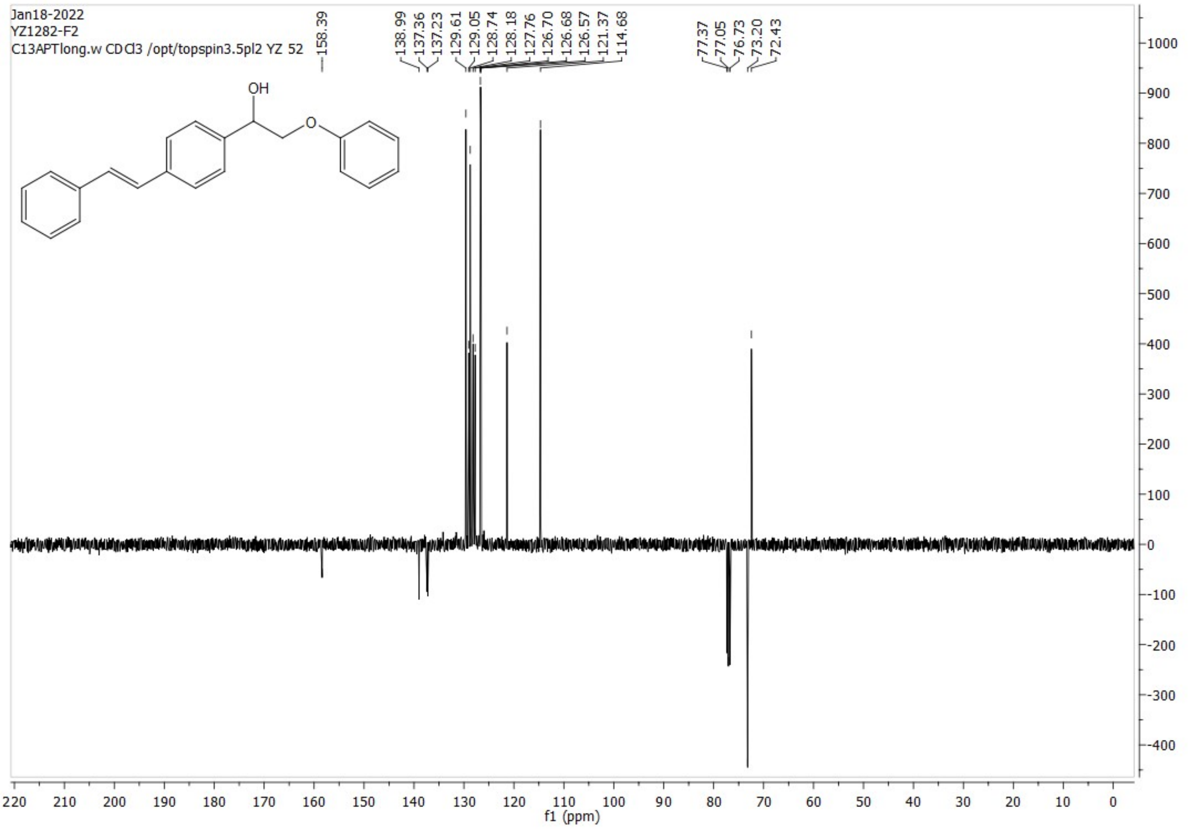
Asymmteric:

To a solution of (*S*)-2-phenoxy-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol **12** (145 mg, 0.426 mmol), β-bromostyrene (117 mg, 0.639 mmol) and tripotassium phosphate (271 mg, 1.28 mmol) in dioxane (2.1 mL) and distilled water (1.1 mL) was added $Pd(dppf)_2Cl_2 \cdot DCM$ (17.4 mg, 0.0213 mmol). The reaction mixture was heated to 90 °C and left stirring under the nitrogen atmosphere overnight, followed by TLC (4:1 hexane: EtOAc). The mixture was quenched by distilled water (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried ($MgSO_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-20% ethyl acetate in hexane to give (*S*)-2-phenoxy-1-(4-styrylphenyl)ethan-1-ol **30** as a yellow solid (68.0 mg, 0.215 mmol, 50%). The reaction was also followed by HPLC (Chiralcel ODH, 30 cm x 6mm column, hexane:iPrOH 80:20, 1.0 mL/min, T = 25°C): $[\alpha]_D^{30}$ +43.3 (c 0.187 in $CHCl_3$) 96% ee (*S*)

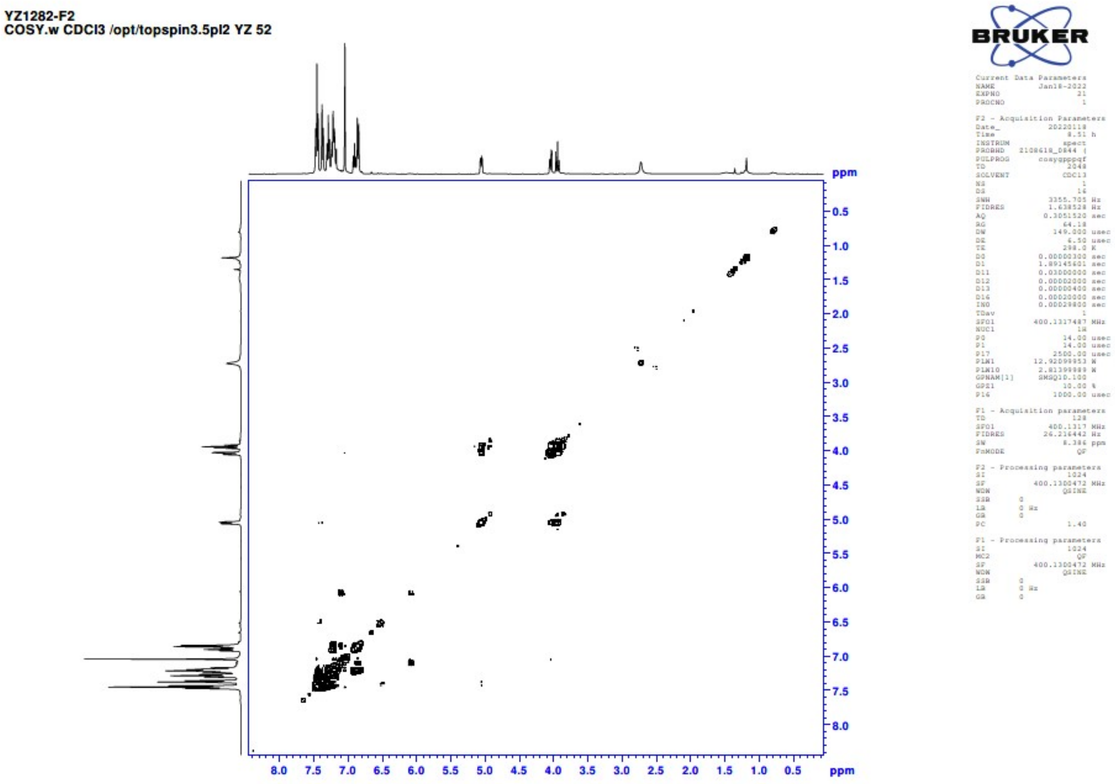
$^1$H NMR (400 MHz, $CDCl_3$)



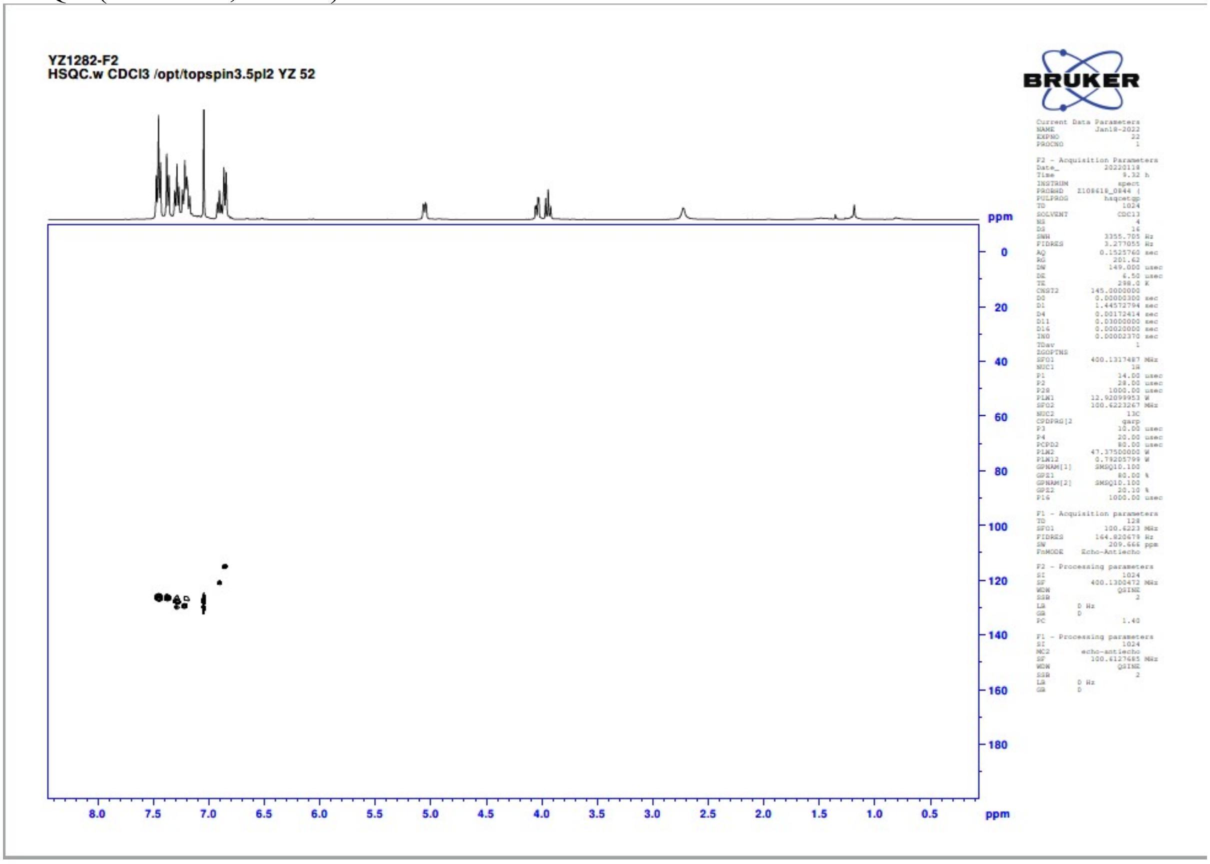
$^{13}$C NMR (100 MHz, $CDCl_3$)



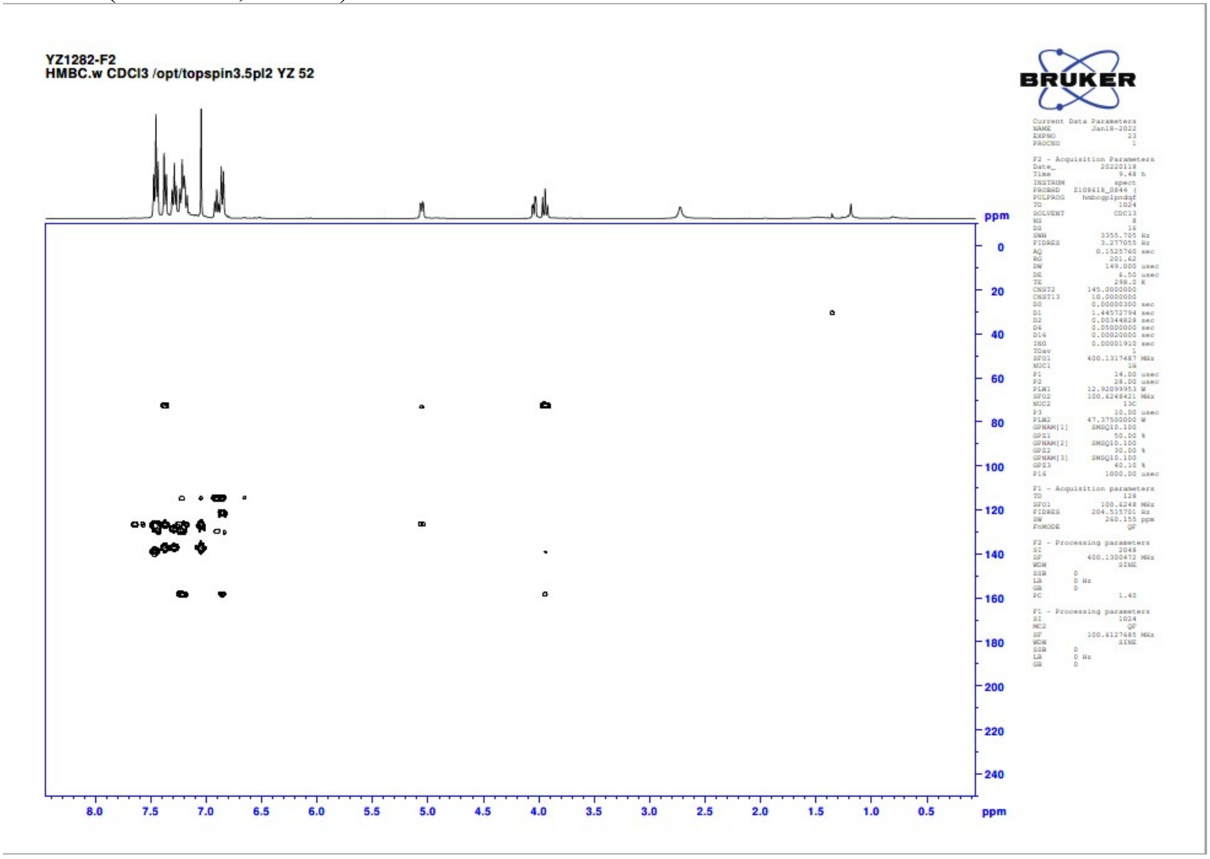
COSY (400 MHz, $CDCl_3$)



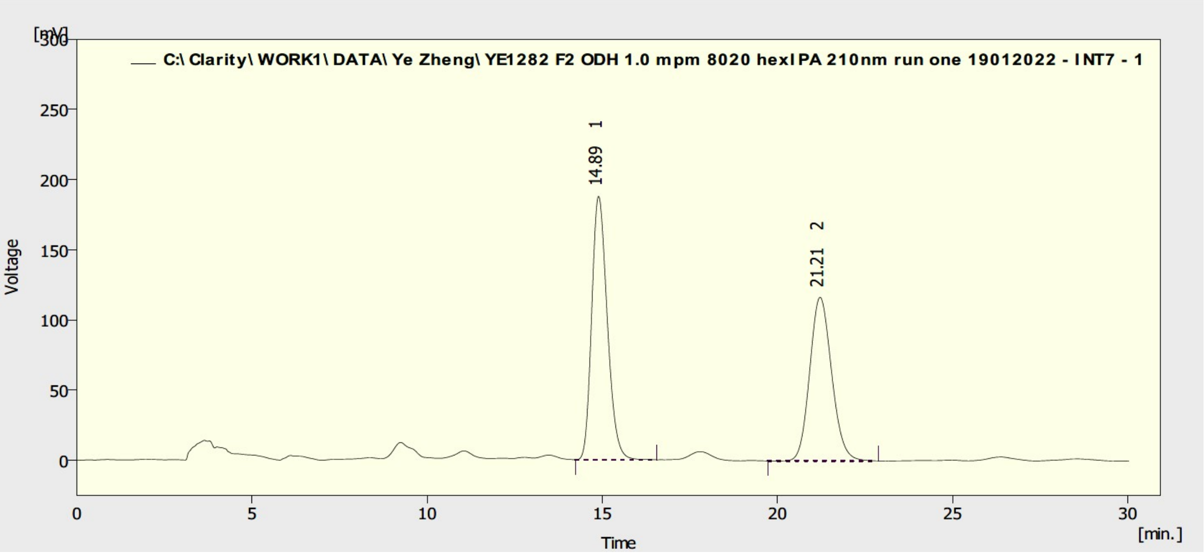
HSQC (400 MHz, $CDCl_3$)



HMBC (400 MHz, $CDCl_3$)



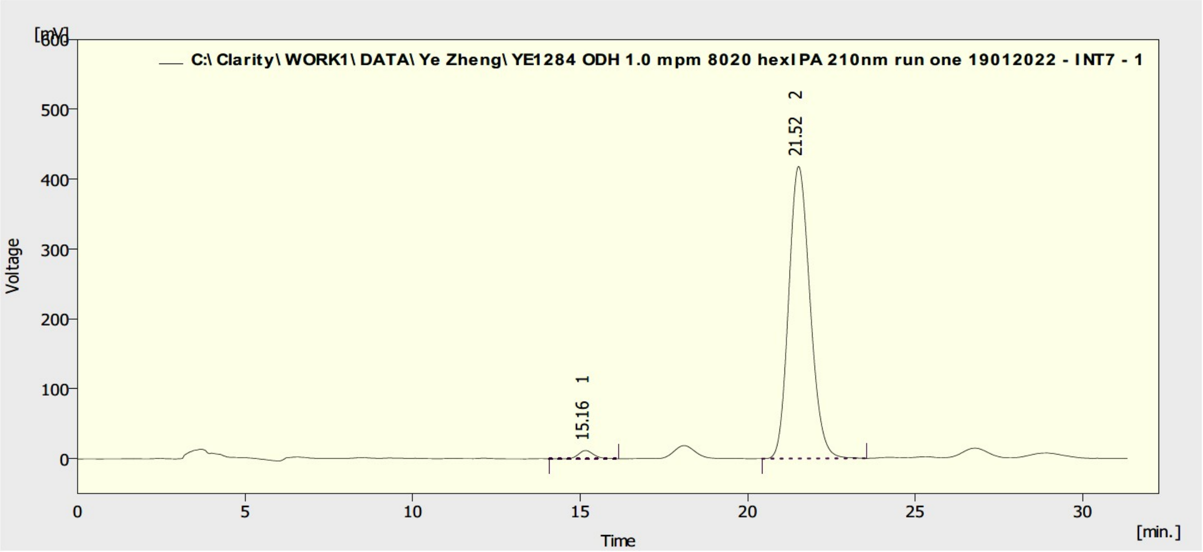
HPLC of racemic 2-phenoxy-1-(4-styrylphenyl)ethan-1-ol **30**.



*Result Table (Uncal - C:\Clarity\WORK1\DATA\Ye Zheng\YE1282 F2 ODH 1.0 mpm 8020 hexIPA 210nm run one 19012022 - INT7 - 1)*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Compound Name |
|---|---|---|---|---|---|---|---|
| 1 | 14.890 | 5810.358 | 187.900 | 53.4 | 61.7 | 0.48 | |
| 2 | 21.213 | 5078.512 | 116.595 | 46.6 | 38.3 | 0.67 | |
| | Total | 10888.870 | 304.495 | 100.0 | 100.0 | | |

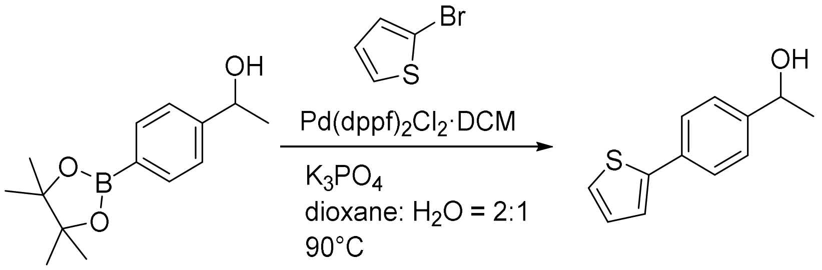
HPLC of 2-phenoxy-1-(4-styrylphenyl)ethan-1-ol (96% ee, *S* configuration) **30**.

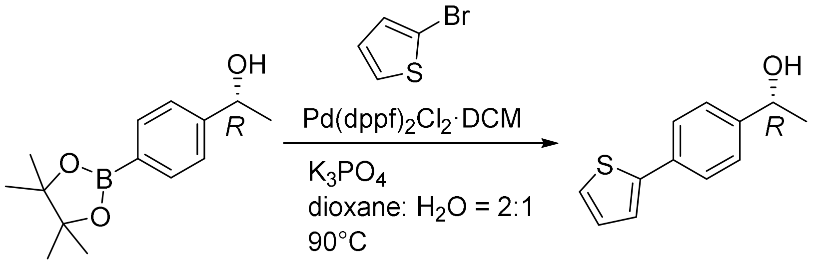


*Result Table (Uncal - C:\Clarity\WORK1\DATA\Ye Zheng\YE1284 ODH 1.0 mpm 8020 hexIPA 210nm run one 19012022 - INT7 - 1)*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Compound Name |
|---|---|---|---|---|---|---|---|
| 1 | 15.157 | 376.237 | 11.899 | 2.0 | 2.8 | 0.48 | |
| 2 | 21.523 | 18540.023 | 418.263 | 98.0 | 97.2 | 0.69 | |
| | Total | 18916.260 | 430.162 | 100.0 | 100.0 | | |

1-(4-(Thiophen-2-yl)phenyl)ethan-1-ol **31**.





This compound is novel.

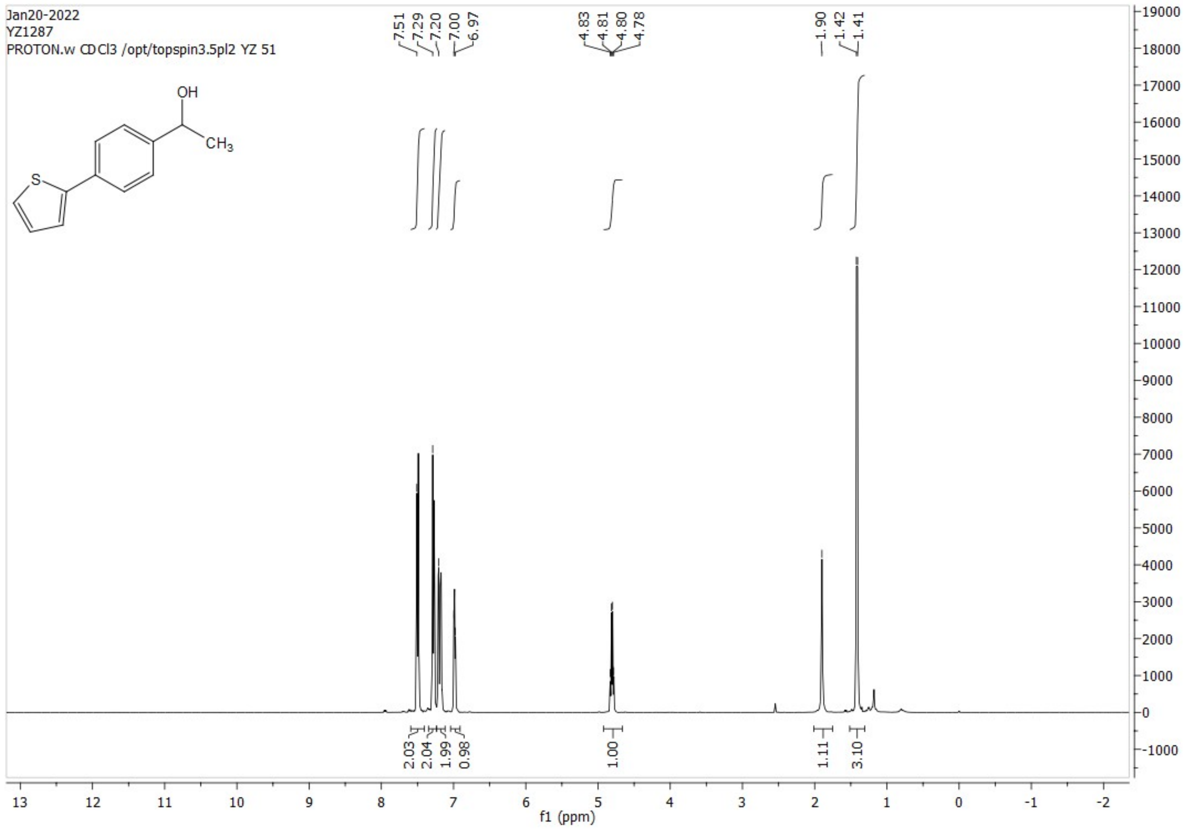
Racemic:

To a solution of racemic 1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol **7** (89.0 mg, 0.359 mmol), 2-bromothiophene (87.9 mg, 0.539 mmol) and tripotassium phosphate (229 mg, 1.08 mmol) in dioxane (1.8 mL) and distilled water (0.9 mL) was added Pd(dppf)$_2$Cl$_2$·DCM (14.7 mg, 0.0180 mmol). The reaction mixture was heated to 90 °C and left stirring under the nitrogen atmosphere overnight, followed by TLC (4:1 hexane: EtOAc). The mixture was quenched by distilled water (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried (MgSO$_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-20% ethyl acetate in hexane to give racemic 1-(4-(thiophen-2-yl)phenyl)ethan-1-ol **31** as a yellow solid (37.0 mg, 0.181 mmol, 51%). TLC: Rf ca 0.40 (4:1 hexane: EtOAc), strong UV and KMnO$_4$; Mp: 80 °C; HRMS: (found (ESI+): [M+H]+, Calcd for $C_{12}H_{12}NaO_2S$ 227.0508; Found 227.0501; -3.2 ppm error; $\nu_{max}$ 3269 (br), 3100, 3067, 2969, 1426, 1406, 1256, 1208, 1070, 1004, 815, 685 cm$^{-1}$; $\delta_H$ (400 MHz, CDCl$_3$) 7.51 (2H, d, *J* = 8.1, ArH), 7.29 (2H, d, *J* = 8.1, ArH), 7.20 (2H, dd, *J* = 11.5, 4.0, ArH), 7.00-6.97 (1H, m, ArH), 4.81 (1H, q, *J* = 6.5, ArCH), 1.90 (1H, s, OH), 1.42 (3H, d, *J* = 6.5, CH$_3$) ppm; $\delta_C$ (100 MHz, CDCl$_3$) 145.09 (C), 144.15 (C), 133.65 (C), 128.05 (CH), 126.08 (CH), 125.99 (CH), 124.78 (CH), 123.08 (CH), 70.10 (CH), 25.14 ($CH_3$) ppm; m/z (ES-API+) 227.0 ($M^+$ + 23, 100%). Enantiomeric excess and conversion determined by HPLC analysis (Chiralcel IB, 30 cm x 6mm column, hexane:iPrOH 90:10, 1.0 mL/min, T = 25°C) *S* isomer 7.2 min and *R* isomer 8.5 min.

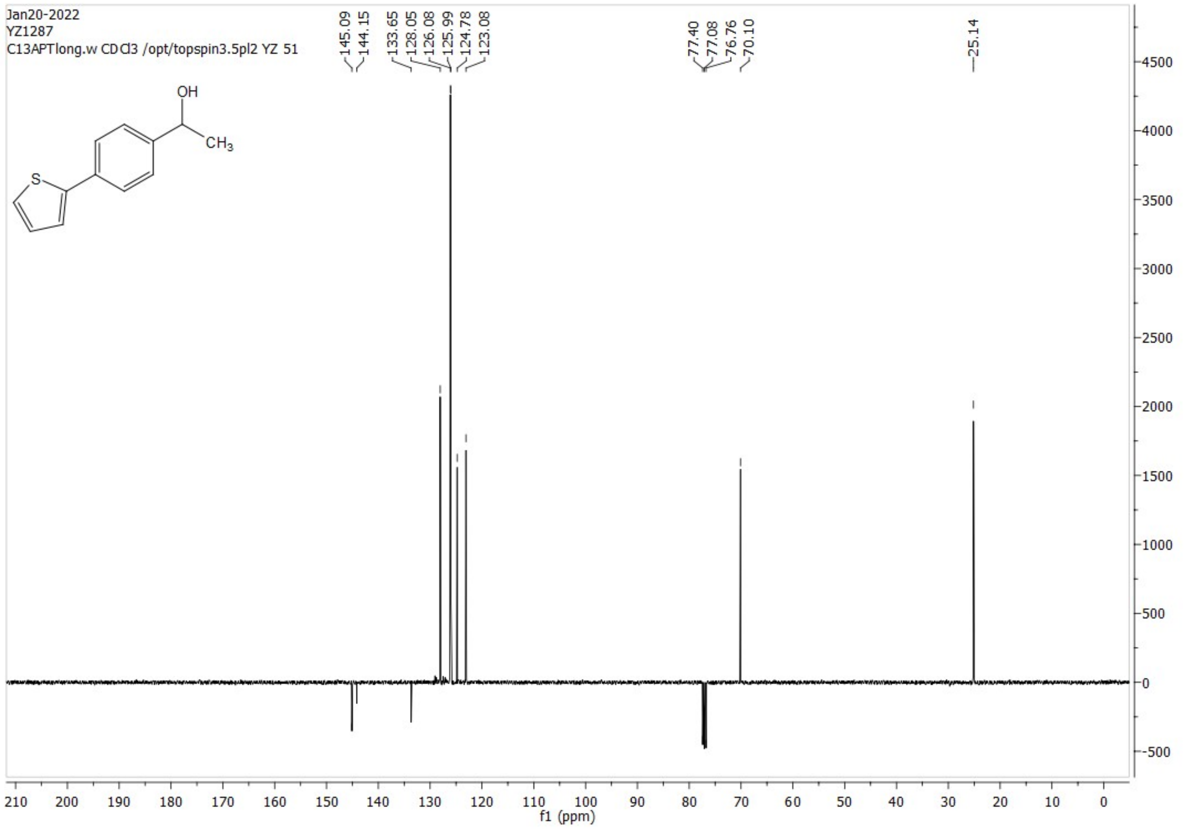
Asymmetric.

To a solution of (*R*)-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol **7** (80.0 mg, 0.323 mmol), 2-bromothiophene (79.1 mg, 0.485 mmol) and tripotassium phosphate (205 mg, 0.969 mmol) in dioxane (1.6 mL) and distilled water (0.8 mL) was added $Pd(dppf)_2Cl_2 \cdot DCM$ (13.3 mg, 0.0162 mmol). The reaction mixture was heated to 90 °C and left stirring under the nitrogen atmosphere overnight, followed by TLC (4:1 hexane: EtOAc). The mixture was quenched by distilled water (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried ($MgSO_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-20% ethyl acetate in hexane to give (*R*)-1-(4-(thiophen-2-yl)phenyl)ethan-1-ol **31** as a yellow solid (44.0 mg, 0.216 mmol, 67%). The reaction was also followed by HPLC (Chiralcel IB, 30 cm x 6mm column, hexane:iPrOH 90:10, 1.0 mL/min, T = 25°C): $[\alpha]_D^{26}$ +30.7 (c 0.176 in $CHCl_3$) 94% ee (*R*).

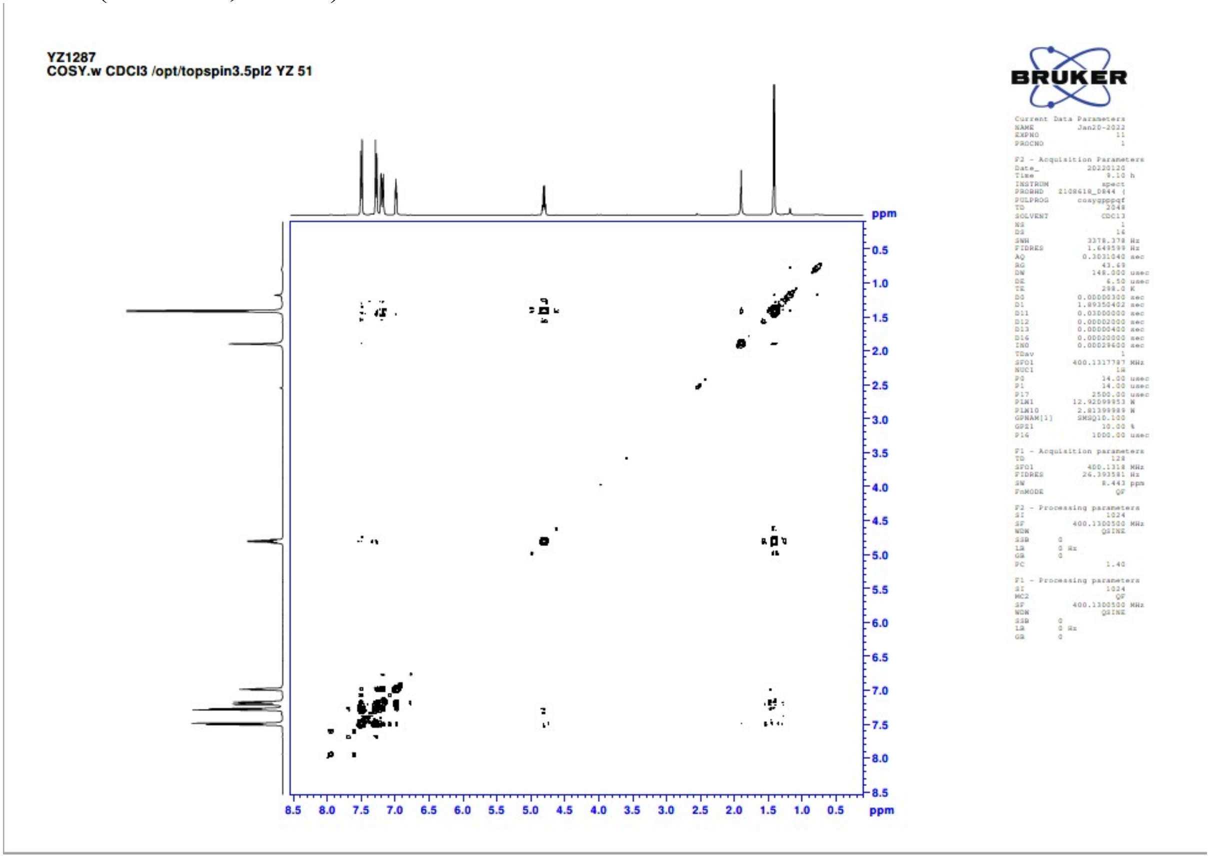
$^1$H NMR (400 MHz, CDCl$_3$)



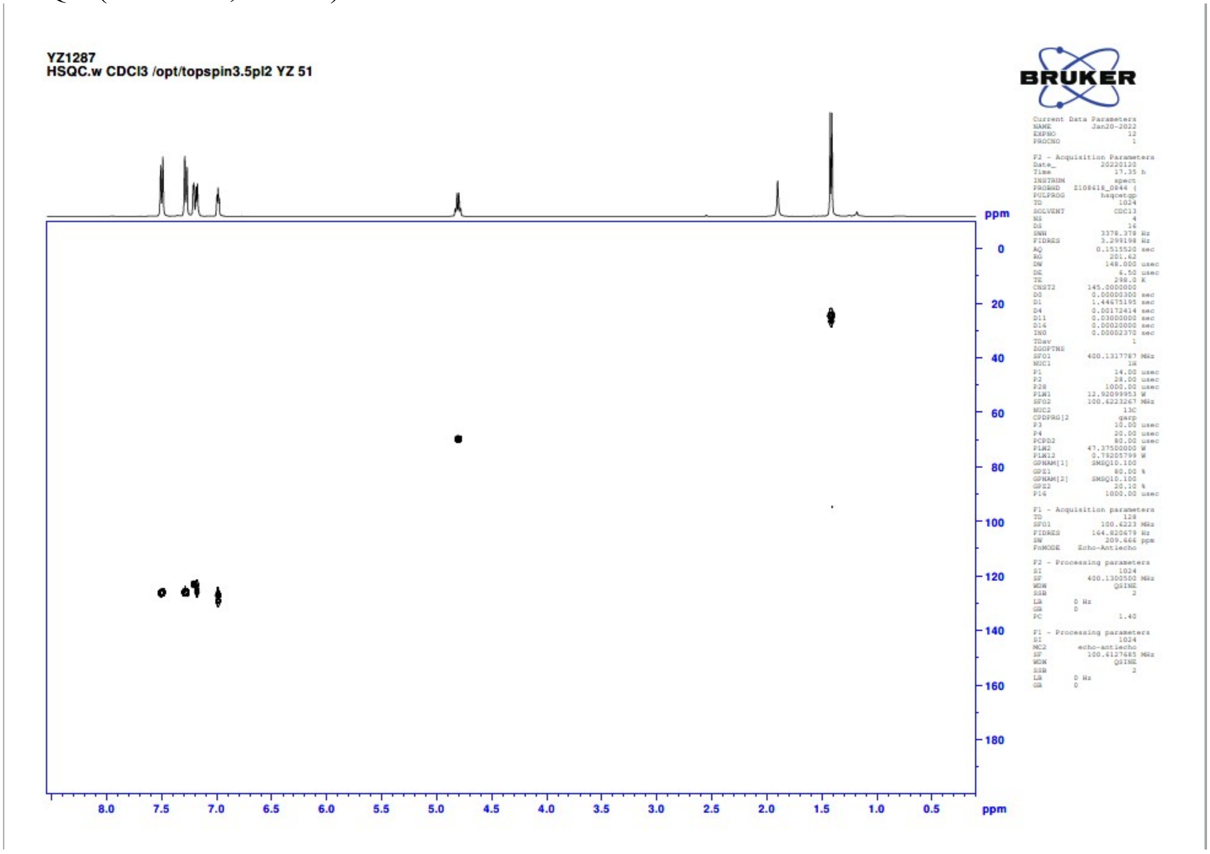
$^{13}$C NMR (100 MHz, CDCl$_3$)



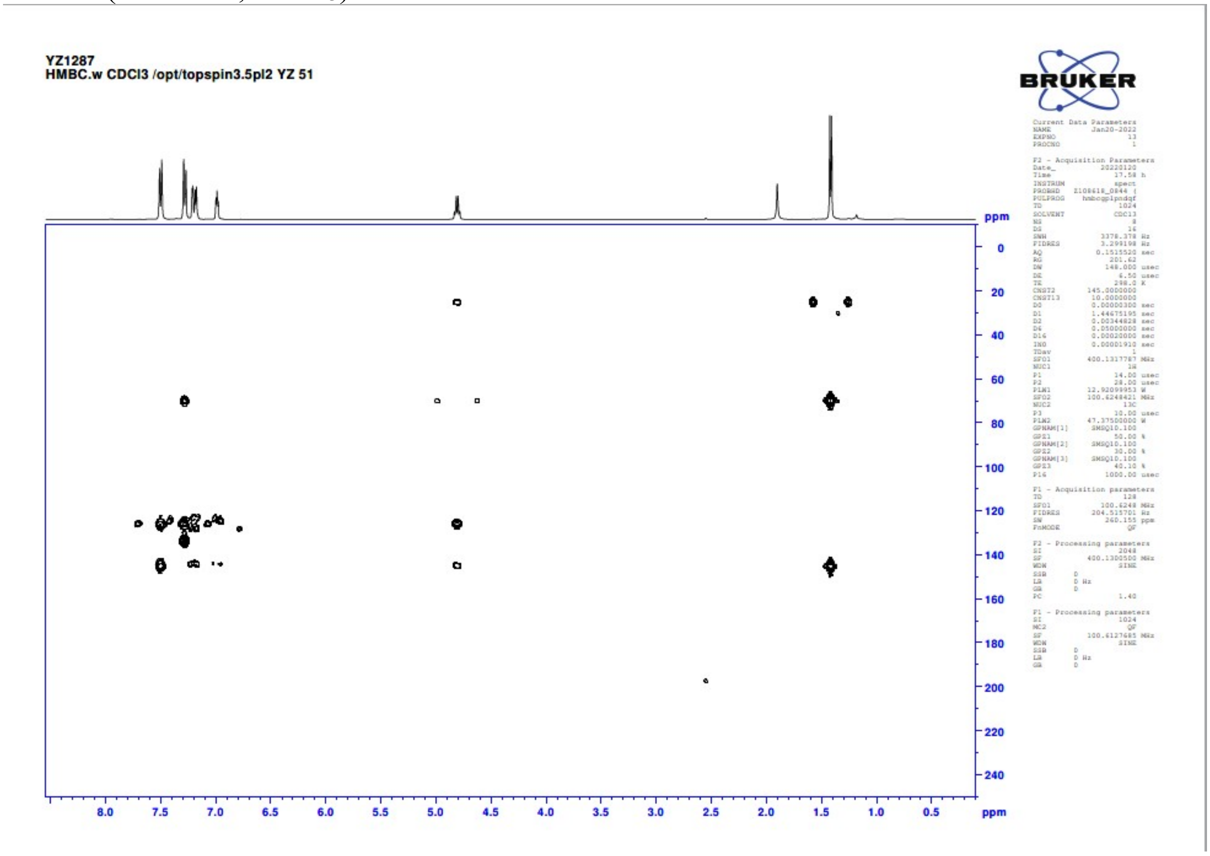
COSY (400 MHz, $CDCl_3$)



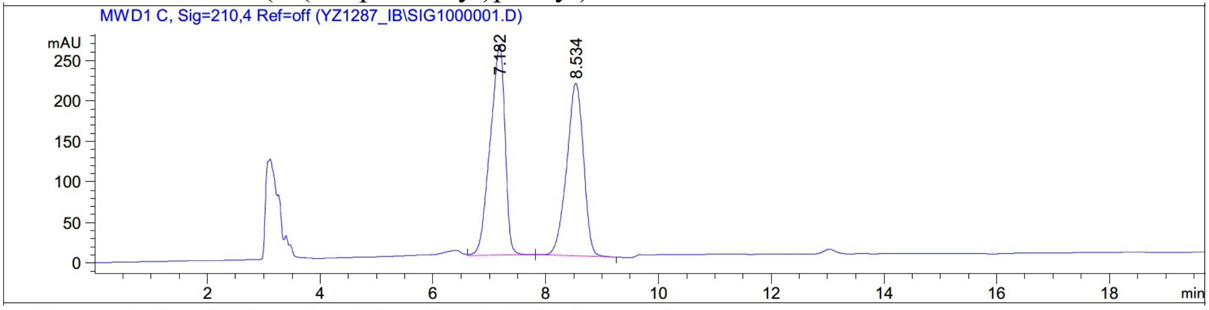
HSQC (400 MHz, $CDCl_3$)



HMBC (400 MHz, CDCl$_3$)



HPLC of racemic 1-(4-(thiophen-2-yl)phenyl)ethan-1-ol **31**.



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Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
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----|-------|----|-------|----------|----------|--------|
   1   7.182 VB    0.2672 4741.12158  259.43713  51.7521
   2   8.534 BB    0.3162 4420.10303  212.92924  48.2479

Totals :                  9161.22461  472.36638
```
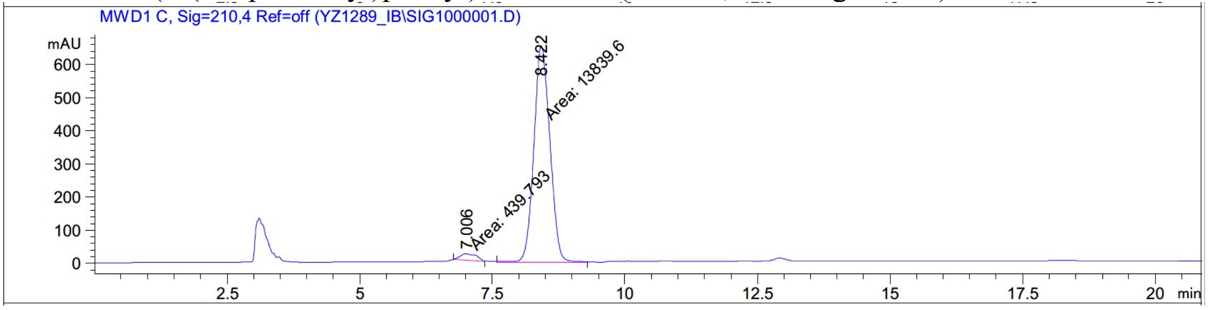

HPLC of 1-(4-(thiophen-2-yl)phenyl)ethan-1-ol (94% ee, *R* configuration) **31**.



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Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   7.006 MM    0.3669  439.79285   19.97597   3.0799
   2   8.422 MM    0.3524 1.38396e4   654.60272  96.9201

Totals :                  1.42794e4   674.57869
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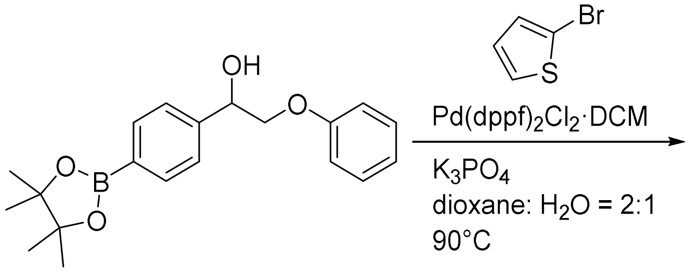
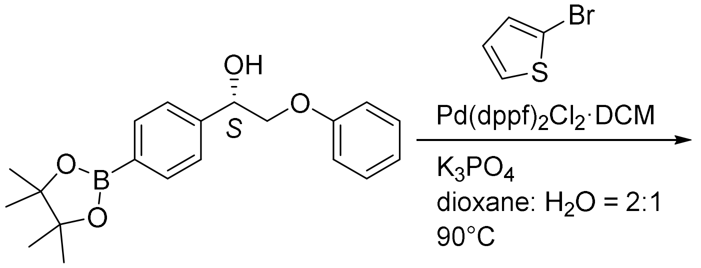
2-Phenoxy-1-(4-(thiophen-2-yl)phenyl)ethan-1-ol **32**.





This compound is novel.

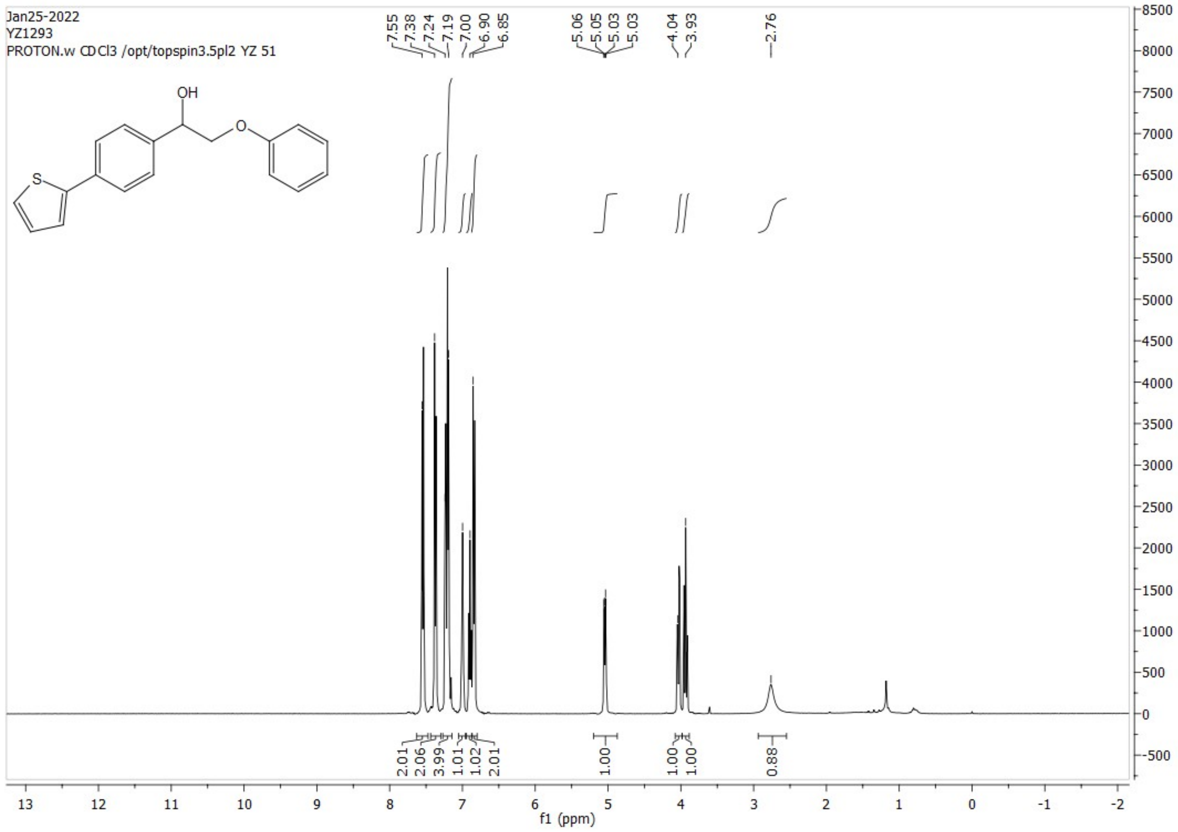
Racemic.

To a solution of racemic 2-phenoxy-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol **12** (82.0 mg, 0.241 mmol), 2-bromothiophene (59.0 mg, 0.362 mmol) and tripotassium phosphate (153 mg, 0.723 mmol) in dioxane (1.2 mL) and distilled water (0.6 mL) was added $Pd(dppf)_2Cl_2$·DCM (9.89 mg, 0.0121 mmol). The reaction mixture was heated to 90 °C and left stirring under the nitrogen atmosphere overnight, followed by TLC (4:1 hexane: EtOAc). The mixture was quenched by distilled water (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried ($MgSO_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-20% ethyl acetate in hexane to give racemic 2-phenoxy-1-(4-(thiophen-2-yl)phenyl)ethan-1-ol **32** as a yellow solid (45.0 mg, 0.152 mmol, 63%). TLC: Rf ca 0.40 (4:1 hexane: EtOAc), strong UV and $KMnO_4$; Mp: 104 °C; HRMS: (found (ESI+): [M+H]+, Calcd for $C_{18}H_{16}NaO_2S$ 319.0759; Found 319.0763; 1.3 ppm error; $\nu_{max}$ 3382 (br), 3104, 3066, 3027, 2922, 2868, 1597, 1586, 1493, 1453, 1300, 1290, 1239, 1078, 1037, 1017 816, 751,688 cm$^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 7.55 (2H, d, *J* = 8.0, ArH), 7.38 (2H, d, *J* = 8.0, ArH), 7.24-7.19 (4H, m, ArH + H of thiophene), 7.00 (1H, t, *J* = 4.2, H of thiophene), 6.90 (1H, t, *J* = 7.3, ArH), 6.85 (2H, d, *J* = 8.2, ArH), 5.05 (1H, dd, *J* = 8.6, 2.6, ArCH), 4.04 (1H, dd, *J* = 9.5, 2.9, $CH_2$), 3.93 (1H, t, *J* =

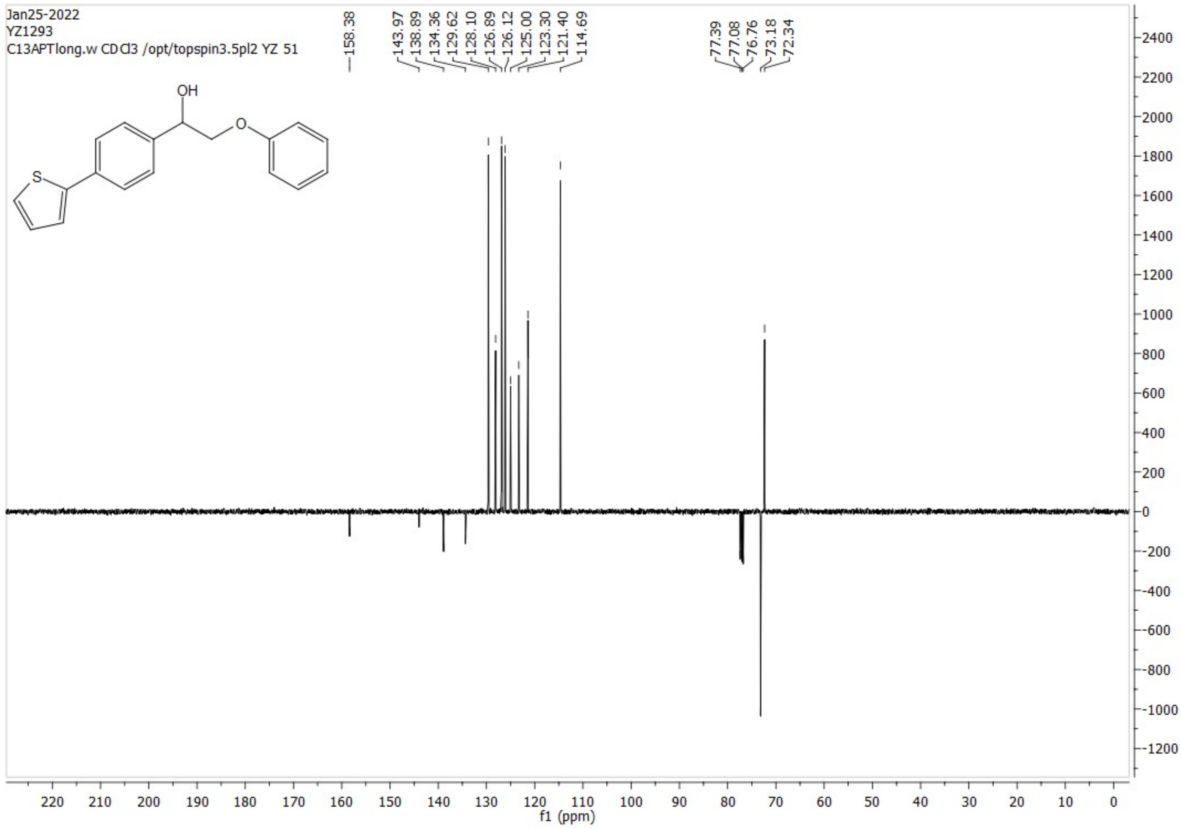
9.1, $CH_2$), 2.76 (1H, s, OH) ppm; $\delta_C$ (100 MHz, $CDCl_3$) 158.38 (C), 143.97 (C), 138.89 (C), 134.36 (C), 129.62 (CH), 128.10 (CH), 126.89 (CH), 126.12 (CH), 125.00 (CH), 123.30 (CH), 121.40 (CH), 114.69 (CH), 73.18 ($CH_2$), 72.34 (CH) ppm; m/z (ES-API+) 319.1 ($M^+$ + 23, 100%).
Enantiomeric excess and conversion determined by HPLC analysis (Chiralcel IB, 30 cm x 6mm column, hexane:iPrOH 90:10, 1.0 mL/min, T = 25°C) *R* isomer 12.0 min and *S* isomer 19.9 min.

Asymmetric.
To a solution of (*S*)-2-phenoxy-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol **12** (86.0 mg, 0.253 mmol), 2-bromothiophene (61.9 mg, 0.380 mmol) and tripotassium phosphate (161 mg, 0.759 mmol) in dioxane (1.3 mL) and distilled water (0.7 mL) was added $Pd(dppf)_2Cl_2{\cdot}DCM$ (10.4 mg, 0.0127 mmol). The reaction mixture was heated to 90 °C and left stirring under the nitrogen atmosphere overnight, followed by TLC (4:1 hexane: EtOAc). The mixture was quenched by distilled water (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried ($MgSO_4$) and filtered. Solvent was removed to give the crude product. The product was isolated via flash chromatography on silica eluted with 0-20% ethyl acetate in hexane to give (*S*)-2-phenoxy-1-(4-(thiophen-2-yl)phenyl)ethan-1-ol **32** as a yellow solid (47.0 mg, 0.159 mmol, 63%). The reaction was also followed by HPLC (Chiralcel IB, 30 cm x 6mm column, hexane:iPrOH 90:10, 1.0 mL/min, T = 25°C): $[\alpha]_D^{26}$ +33.6 (c 0.180 in $CHCl_3$) 96% ee (*S*)

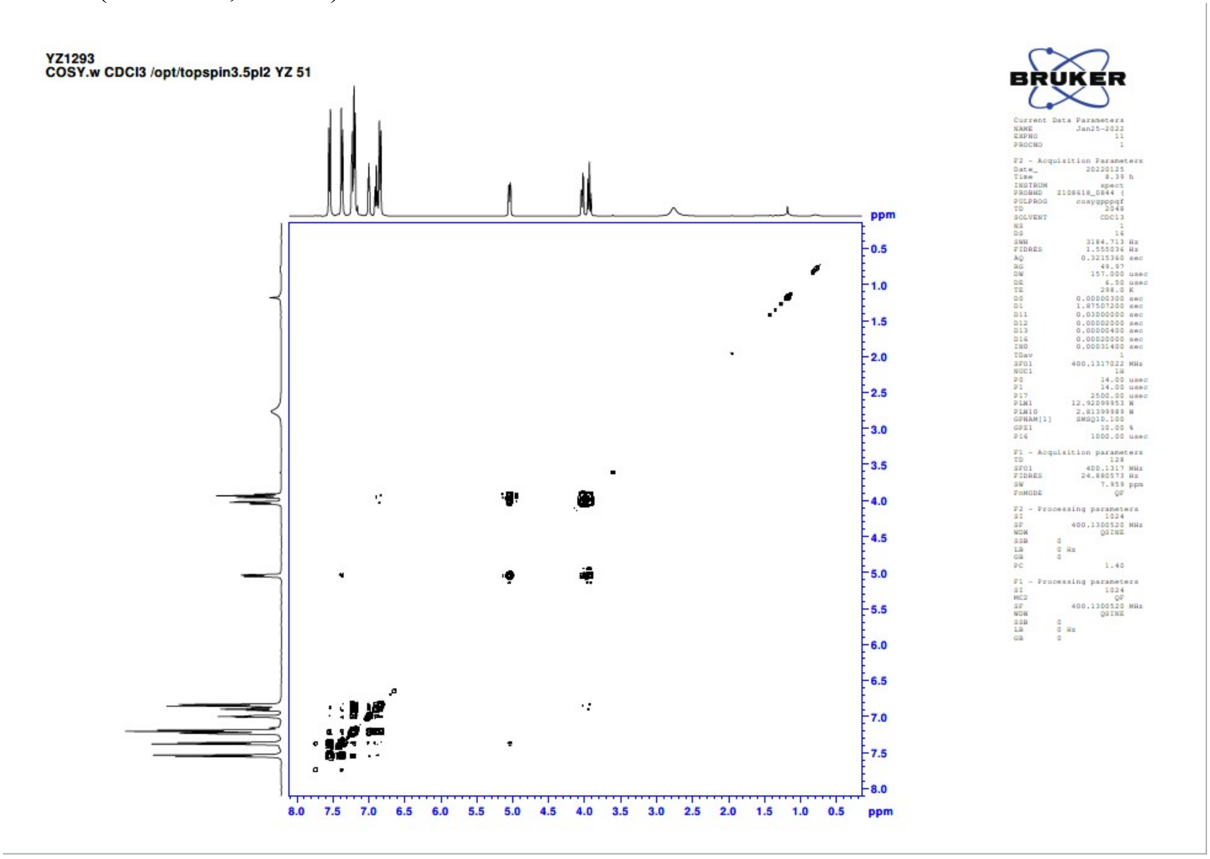
$^1$H NMR (400 MHz, CDCl$_3$)



$^{13}$C NMR (100 MHz, CDCl$_3$)



COSY (400 MHz, $CDCl_3$)



**YZ1293**
**COSY.w CDCl3 /opt/topspin3.5pl2 YZ 51**

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Current Data Parameters
NAME          Jan25-2022
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220125
Time              8.39 h
INSTRUM            spect
PROBHD   Z108618_0844 (
PULPROG        cosygpppqf
TD                  2048
SOLVENT            CDCl3
NS                     1
DS                    16
SWH             3184.713 Hz
FIDRES          1.555036 Hz
AQ             0.3215360 sec
RG                 49.97
DW               157.000 usec
DE                  6.50 usec
TE                 298.0 K
D0            0.00000300 sec
D1            1.87507200 sec
D11           0.03000000 sec
D12           0.00002000 sec
D13           0.00000400 sec
D16           0.00020000 sec
IN0           0.00031400 sec
TDav                   1
SFO1         400.1317022 MHz
NUC1                  1H
P0                 14.00 usec
P1                 14.00 usec
P17              2500.00 usec
PLW1         12.92099953 W
PLW10         2.81399989 W
GPNAM[1]      SMSQ10.100
GPZ1               10.00 %
P16              1000.00 usec

F1 - Acquisition parameters
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SFO1            400.1317 MHz
FIDRES         24.880573 Hz
SW                 7.959 ppm
FnMODE                QF

F2 - Processing parameters
SI                  1024
SF           400.1300520 MHz
WDW                QSINE
SSB       0
LB        0 Hz
GB        0
PC                  1.40

F1 - Processing parameters
SI                  1024
MC2                   QF
SF           400.1300520 MHz
WDW                QSINE
SSB       0
LB        0 Hz
GB        0
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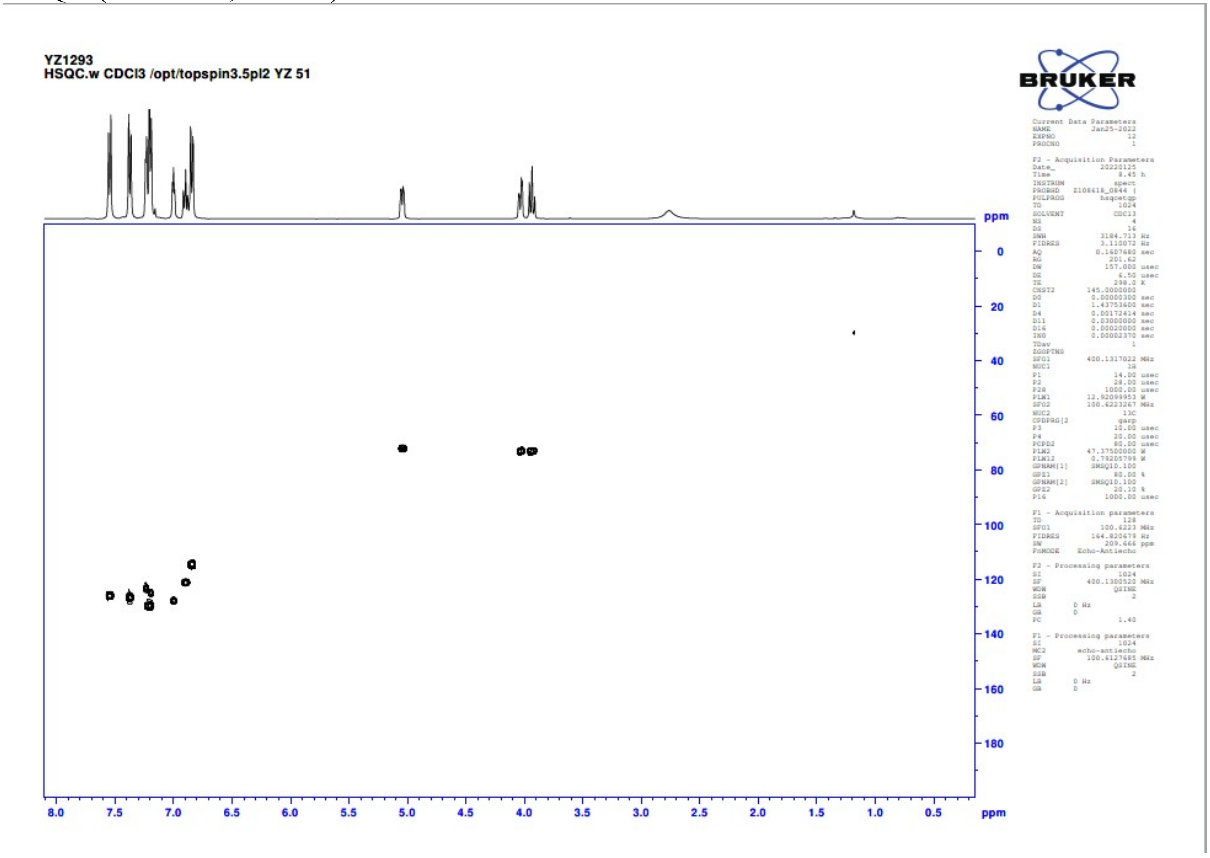
HSQC (400 MHz, $CDCl_3$)



**YZ1293**
**HSQC.w CDCl3 /opt/topspin3.5pl2 YZ 51**

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EXPNO                 12
PROCNO                 1

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PULPROG         hsqcetgp
TD                  1024
SOLVENT            CDCl3
NS                     4
DS                    16
SWH             3184.713 Hz
FIDRES          3.110072 Hz
AQ             0.1607680 sec
RG                201.62
DW               157.000 usec
DE                  6.50 usec
TE                 298.0 K
CNST2        145.0000000
D0            0.00000300 sec
D1            1.43753600 sec
D4            0.00172414 sec
D11           0.03000000 sec
D16           0.00020000 sec
IN0           0.00002370 sec
TDav                   1
ZGOPTNS
SFO1         400.1317022 MHz
NUC1                  1H
P1                 14.00 usec
P2                 28.00 usec
P28              1000.00 usec
PLW1         12.92099953 W
SFO2         100.6223267 MHz
NUC2                 13C
CPDPRG[2            garp
P3                 10.00 usec
P4                 20.00 usec
PCPD2              80.00 usec
PLW2         47.37500000 W
PLW12         0.79205799 W
GPNAM[1]      SMSQ10.100
GPZ1               80.00 %
GPNAM[2]      SMSQ10.100
GPZ2               20.10 %
P16              1000.00 usec

F1 - Acquisition parameters
TD                   128
SFO1            100.6223 MHz
FIDRES        164.820679 Hz
SW               209.666 ppm
FnMODE     Echo-Antiecho

F2 - Processing parameters
SI                  1024
SF           400.1300520 MHz
WDW                QSINE
SSB                    2
LB        0 Hz
GB        0
PC                  1.40

F1 - Processing parameters
SI                  1024
MC2        echo-antiecho
SF           100.6127685 MHz
WDW                QSINE
SSB                    2
LB        0 Hz
GB        0
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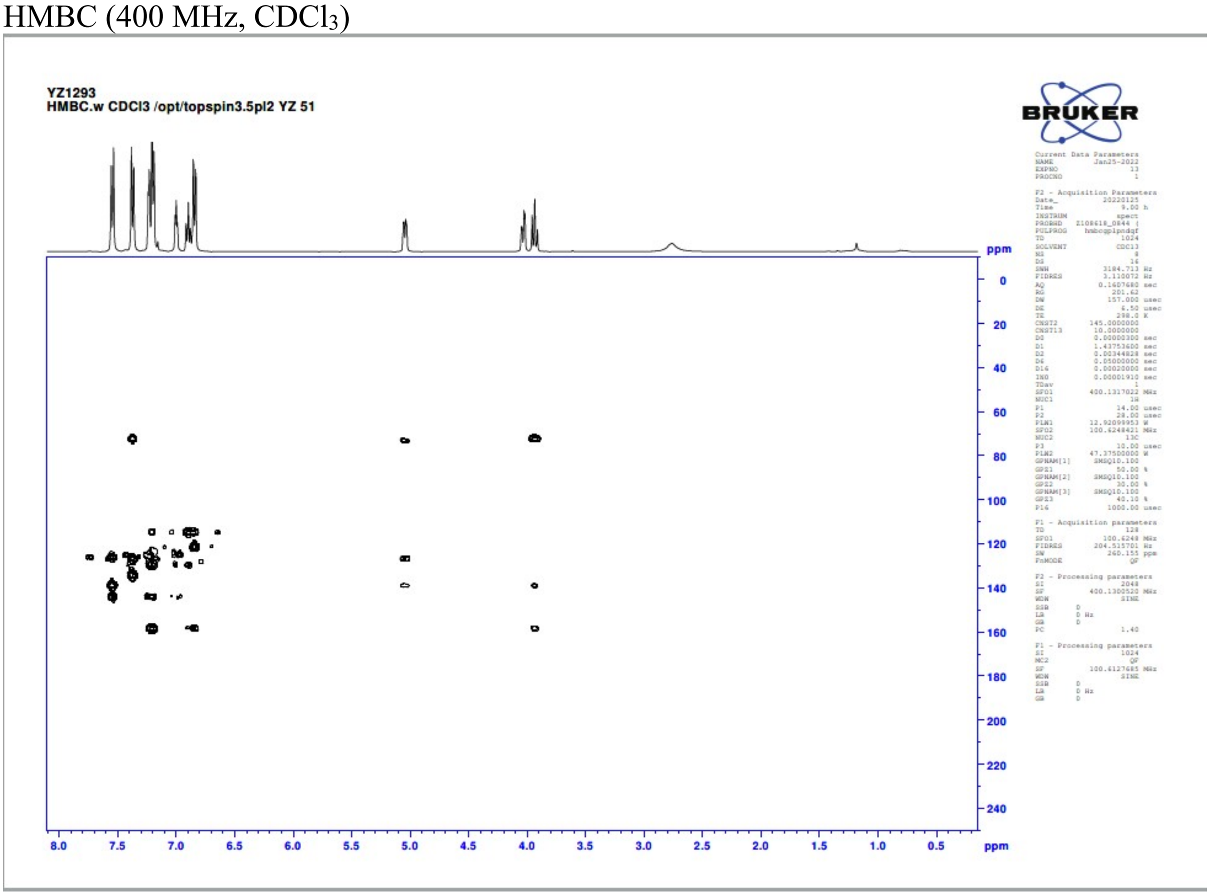
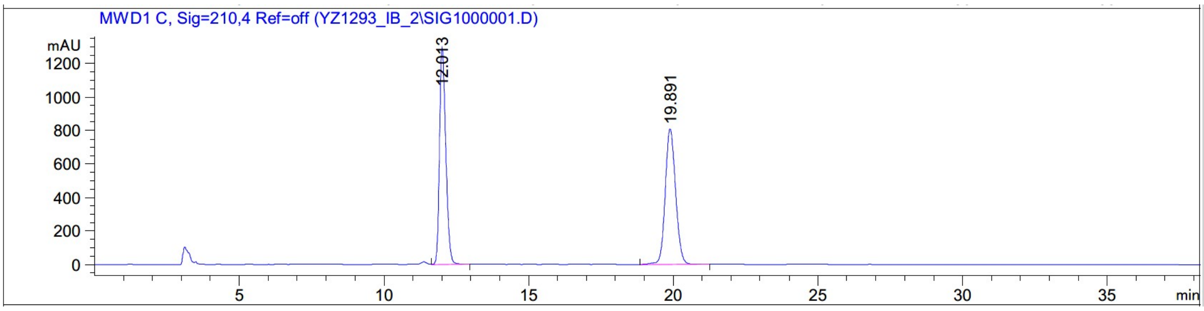
HMBC (400 MHz, $CDCl_3$)



HPLC of racemic 2-phenoxy-1-(4-styrylphenyl)ethan-1-ol



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Signal 2: MWD1 C, Sig=210,4 Ref=off

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   1  12.013 VV    0.2309 1.94369e4 1296.40540  49.1425
   2  19.891 BB    0.3835 2.01152e4  810.63892  50.8575

Totals :                  3.95522e4 2107.04431
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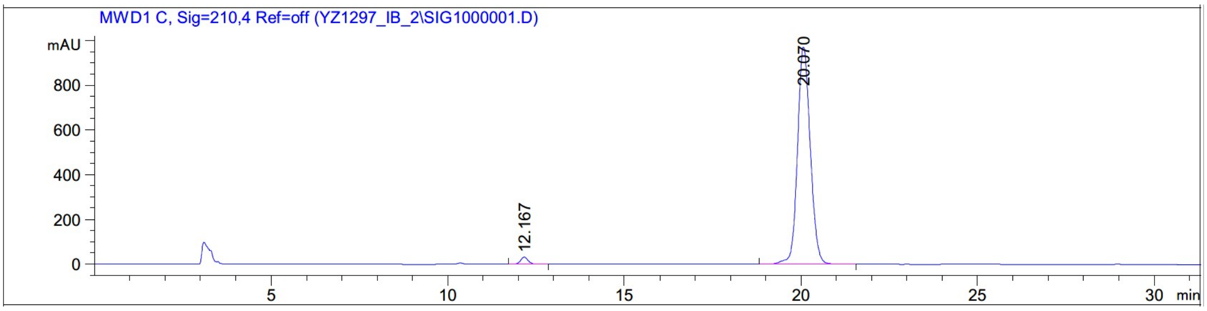
HPLC of 2-phenoxy-1-(4-styrylphenyl)ethan-1-ol (96% ee, *S* configuration)



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Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
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----|-------|----|-------|----------|----------|--------|
   1  12.167 BB    0.2254  455.74054   31.39051   1.8301
   2  20.070 BB    0.3892 2.44474e4  972.84558  98.1699

Totals :                  2.49032e4  1004.23609
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