

Supporting information:

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

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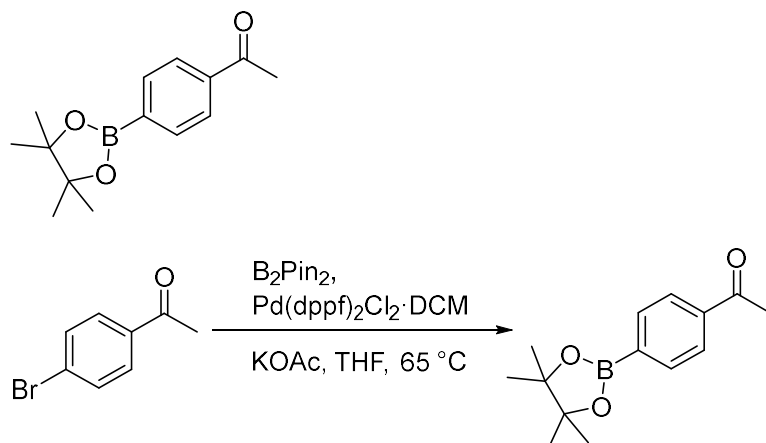
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General experimental details.

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**.

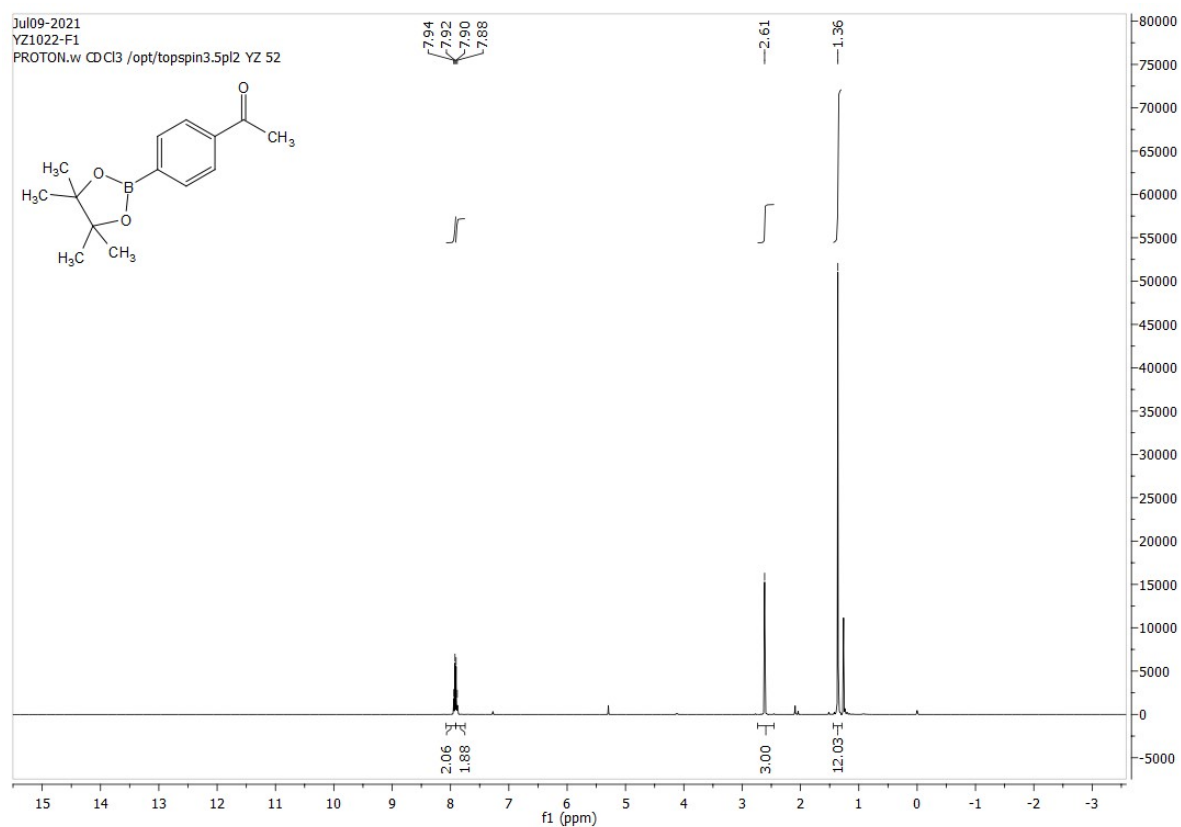


This compound has been reported and fully characterized: J. Ratniyom, N.

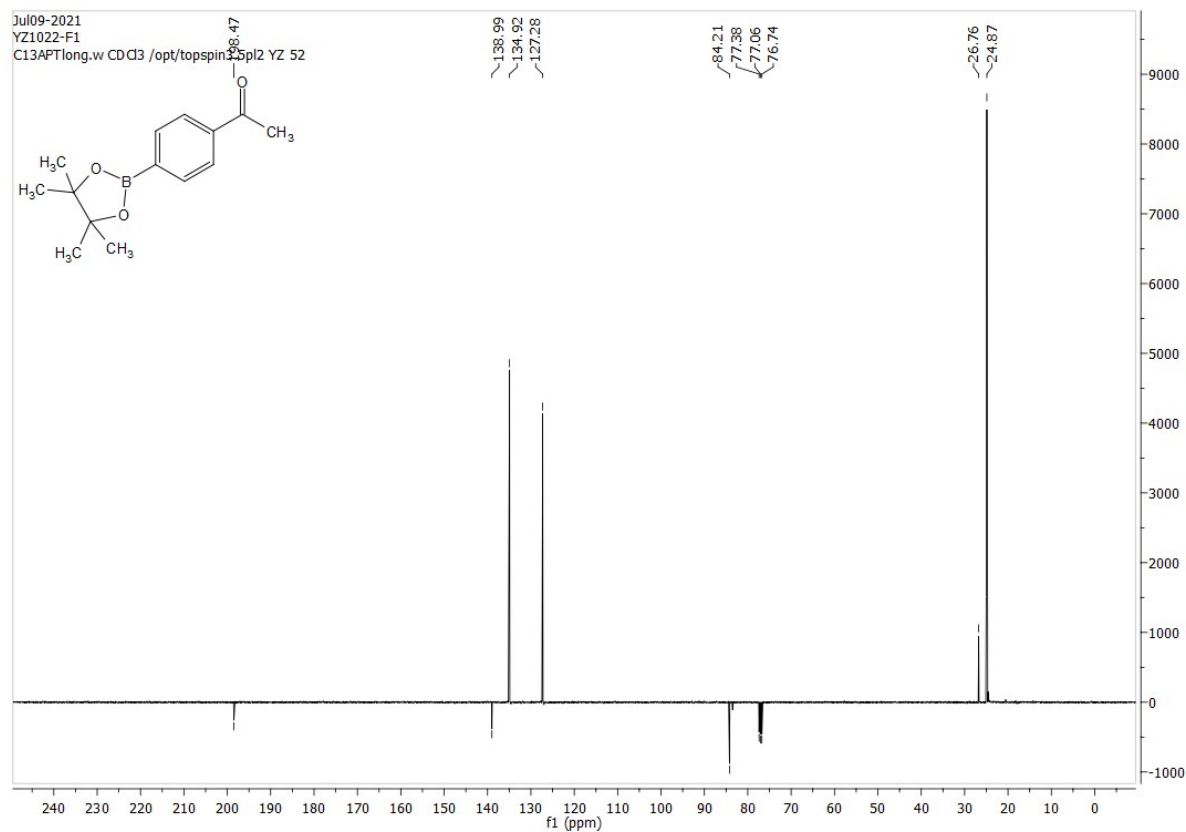
Dechnarong, S. Yotphan and S. Kiatisevi, *Eur. J. Org. Chem.* 2014, 7, 1381-1385.

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 $Pd(dppf)_2Cl_2 \cdot DCM$ (204 mg, 0.250 mmol). The reaction mixture was heated to $65\text{ }^\circ C$ 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 ($3 \times 20\text{ mL}$), 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: R_f ca 0.50 (9:1 hexane: EtOAc), strong UV and $KMnO_4$; δ_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; δ_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.

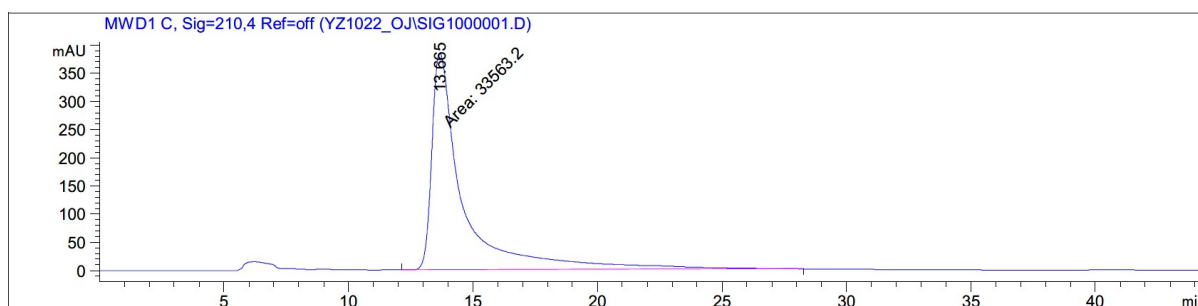
^1H NMR (400 MHz, CDCl_3)



^{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

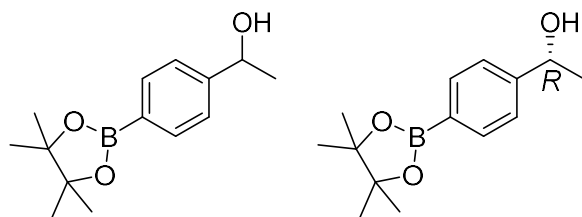


Signal 2: MWD1 C, Sig=210,4 Ref=off

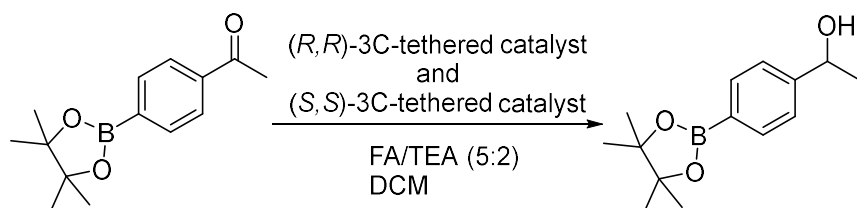
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.665	MM	1.4529	3.35632e4	385.01184	100.0000

Totals : 3.35632e4 385.01184

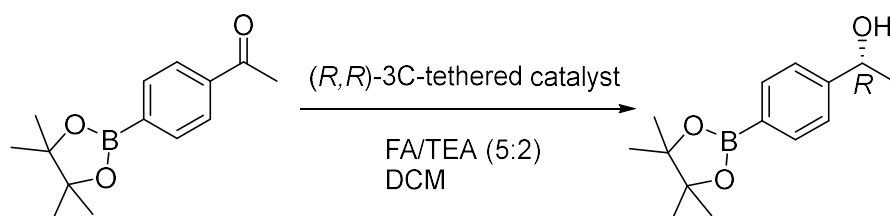
Racemic and (*R*)-1-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol **7**.



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.

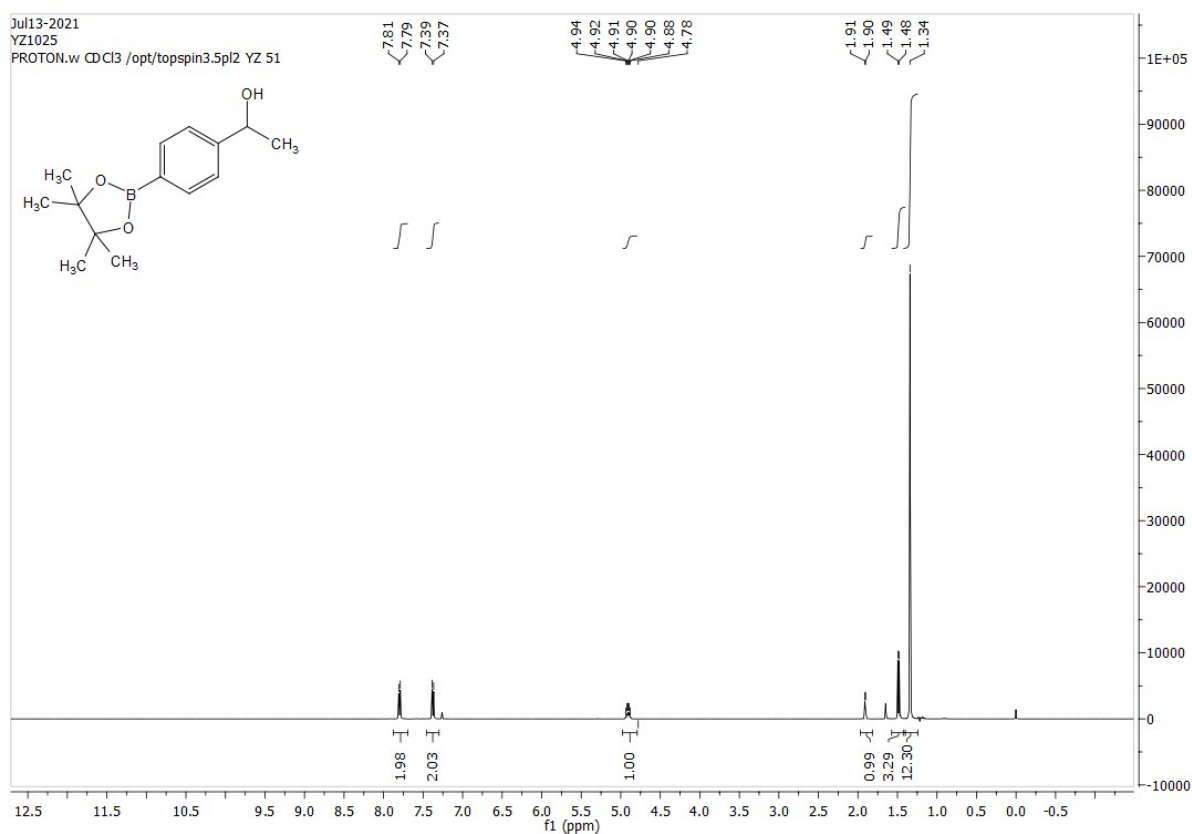
Synthesis of racemic standard:

(*R,R*)-3C-Tethered Ru(II)-TsDPEN catalyst **2** (1.4 mg, 2.2 μ mol, 0.5 mol%) and (*S,S*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (1.4 mg, 2.2 μ mol, 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 stirred under a nitrogen atmosphere and followed by TLC (4:1 hexane: EtOAc). After 24 hours, the reaction was quenched using saturated NaHCO₃ 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 0-50% 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: R_f ca 0.20 (4:1 hexane: EtOAc), strong UV and KMnO₄; δ_{H} (400 MHz, CDCl₃) 7.81 (2H, d, *J* = 7.9, ArH), 7.39 (2H, d, *J* = 7.9, ArH), 4.94-4.78

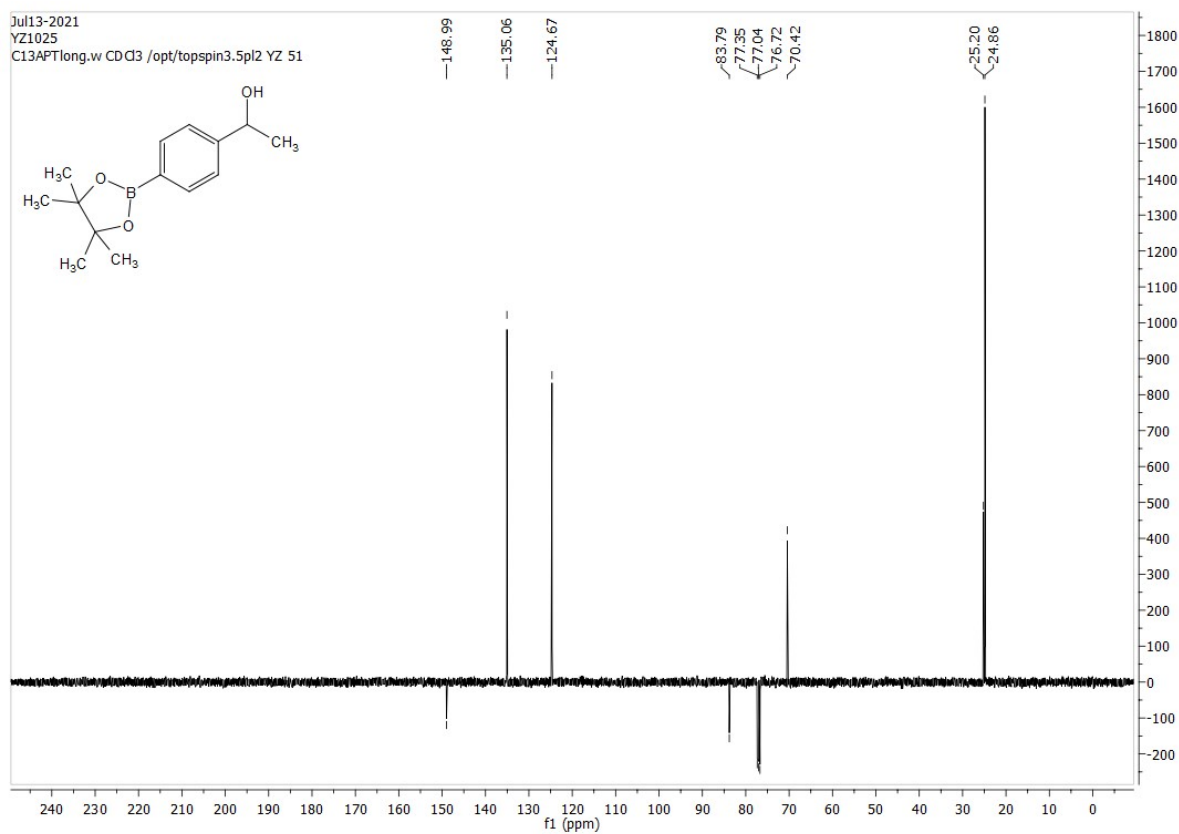
(1H, m, CH), 1.91 (1H, d, $J = 3.6$, OH), 1.49 (3H, d, $J = 6.5$, CH₃), 1.34 (12H, s, CH₃) ppm; δ_C (100 MHz, CDCl₃) 148.99 (C), 135.06 (CH), 124.67 (CH), 83.79 (C), 70.42 (CH), 25.20 (CH₃), 24.86 (CH₃) ppm; m/z (ES-API+) 271.1 ($M^+ + 23$, 100%). Data matched that reported. Enantiomeric excess and conversion determined by HPLC analysis (Chiralcel OJ, 30 cm x 6 mm column, hexane:iPrOH 95:5, 0.5 mL/min, $T = 25^\circ\text{C}$) 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 NaHCO₃ 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 0-50% 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, $T = 25^\circ\text{C}$): 100% conversion; $[\alpha]_D^{26} +34.0$ (c 0.360 in CHCl₃) 98% ee (*R*) (lit. $[\alpha]_D^{24} -31.4$ (c 1.0 in CHCl₃) >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.

^1H NMR (400 MHz, CDCl_3)

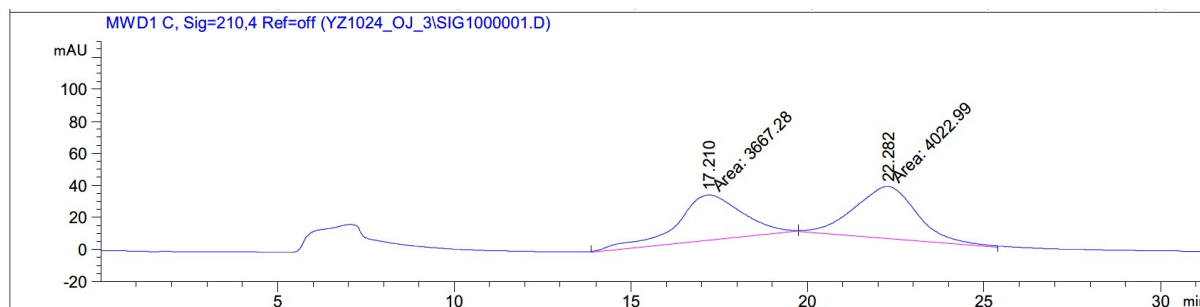


^{13}C NMR (100 MHz, CDCl_3)



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

7



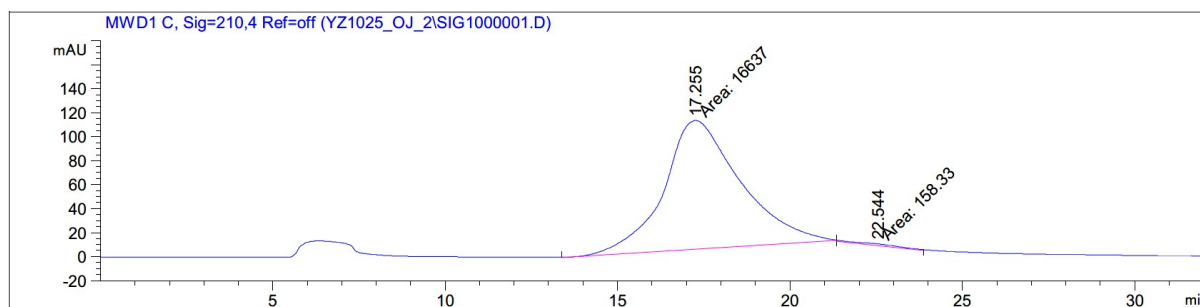
Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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)

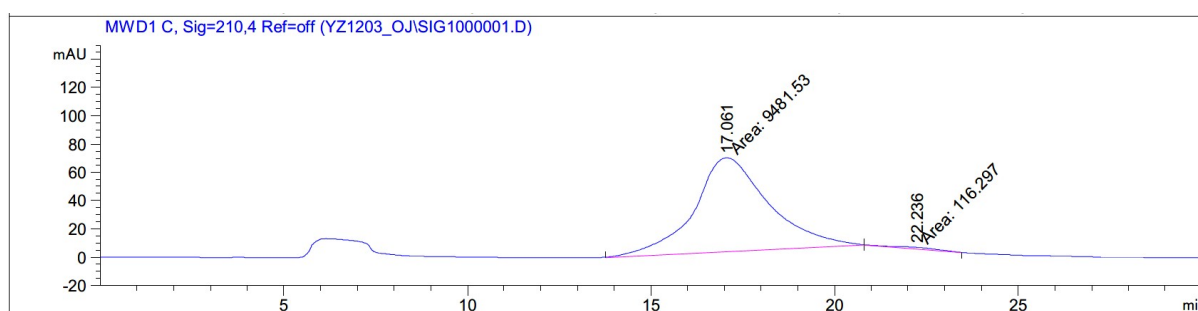


Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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)

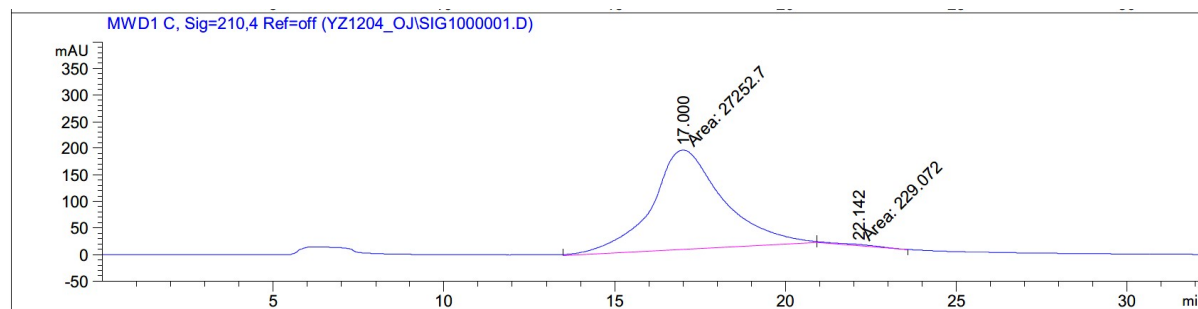


Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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)

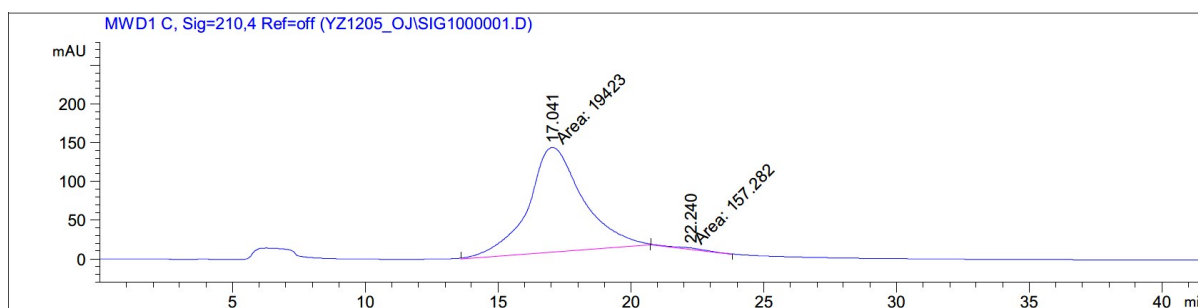


Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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)

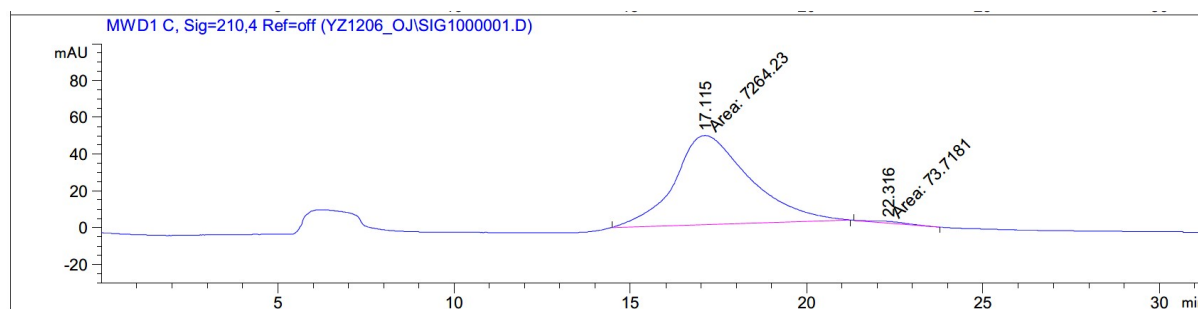


Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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)

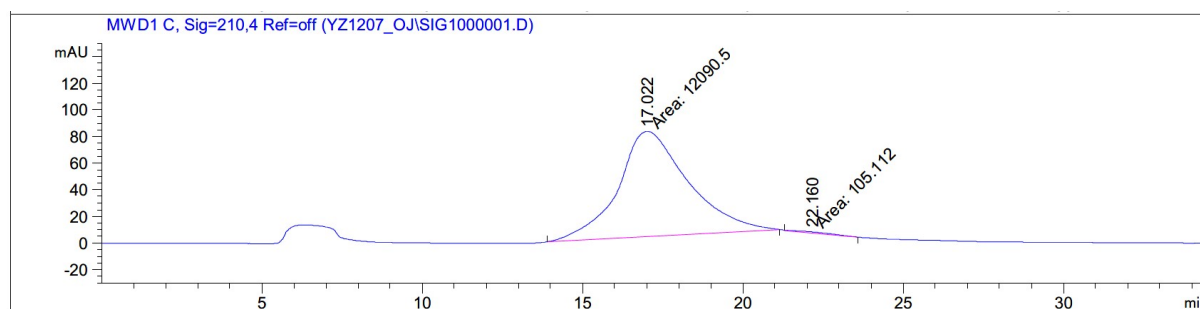


Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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)

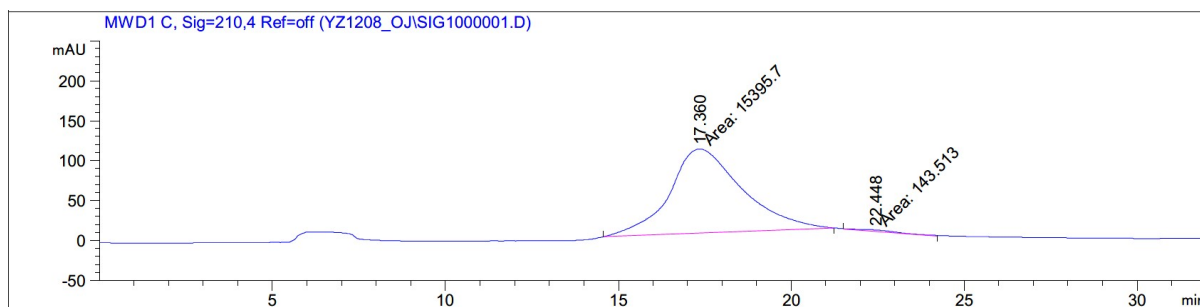


Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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)

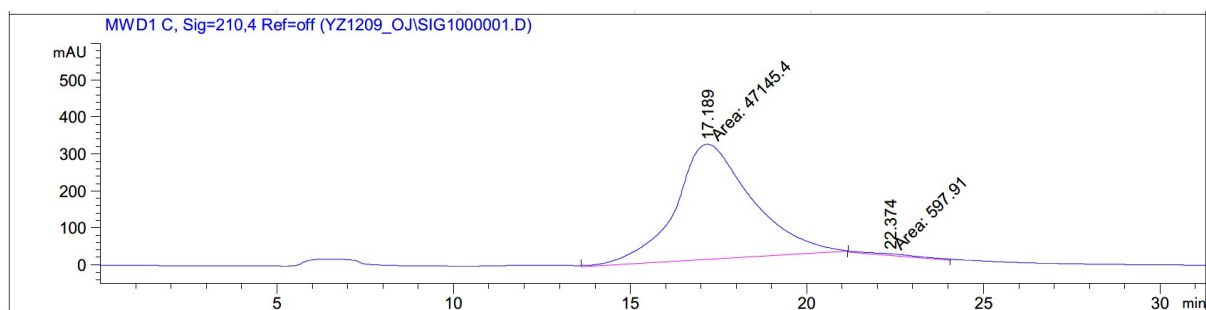


Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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).

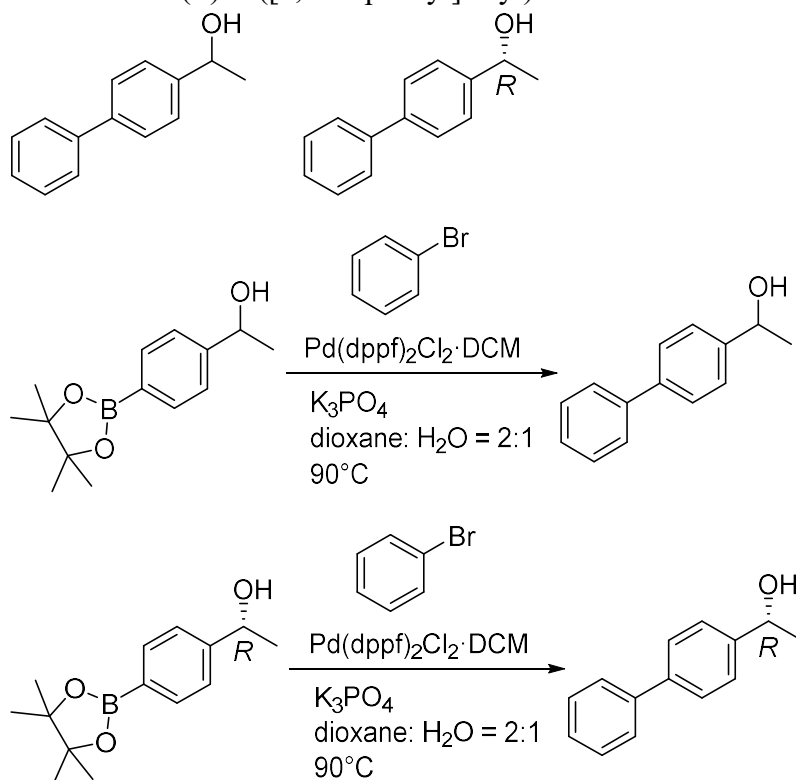


Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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 $\text{Pd(dppf)}_2\text{Cl}_2 \cdot \text{DCM}$ (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: R_f ca 0.20 (9:1 hexane: EtOAc), strong UV and KMnO_4 ; δ_{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,

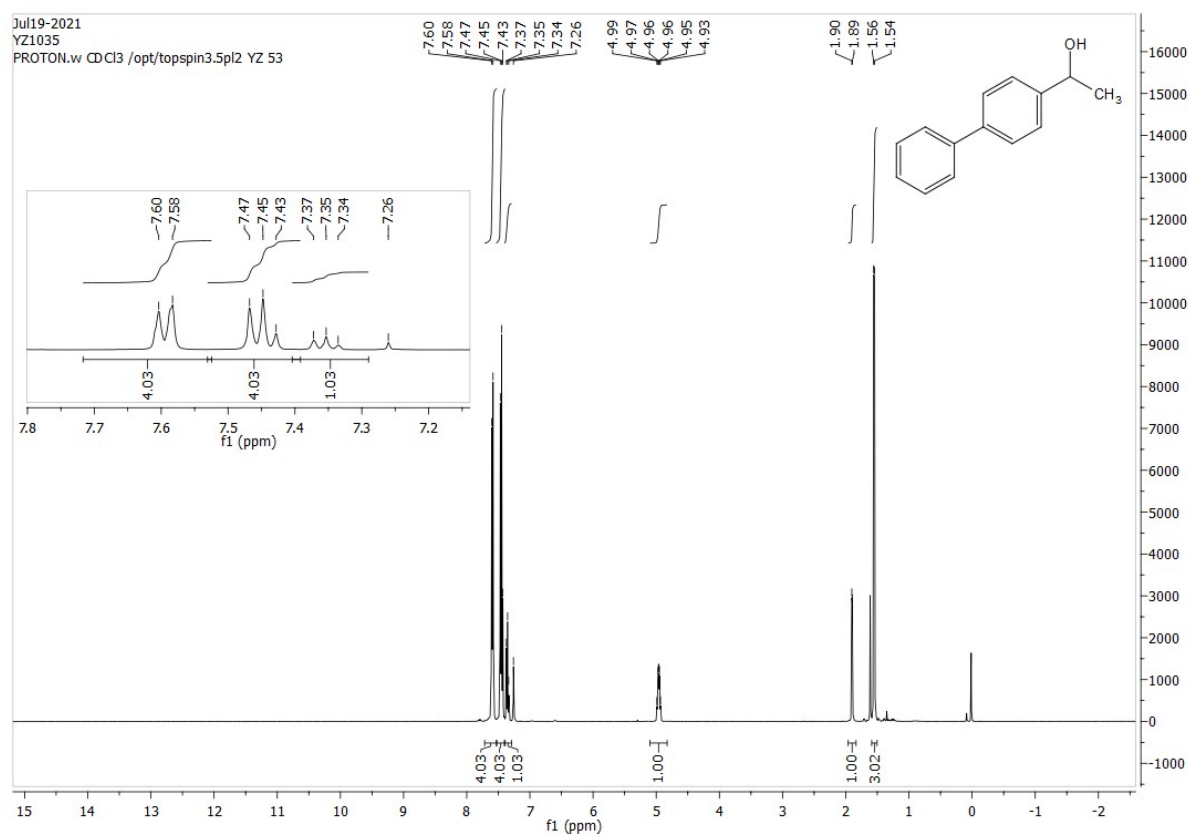
d, $J = 6.5$, CH₃) ppm; δ_C (100 MHz, CDCl₃) 144.83 (C), 140.88 (C), 140.49 (C), 128.79 (CH), 127.29 (CH), 127.11 (CH), 125.88 (CH), 70.20 (CH), 25.17 (CH₃) ppm; m/z (ES-API⁺) 221.0 ($M^+ + 23$, 100%). Data matched that reported.

Enantiomeric excess and conversion determined by HPLC analysis (Chiralcel ADH, 30 cm x 6mm column, hexane:iPrOH 95:5, 0.5 mL/min, $T = 25^\circ\text{C}$) *S* isomer 23.0 min and *R* isomer 25.1 min.

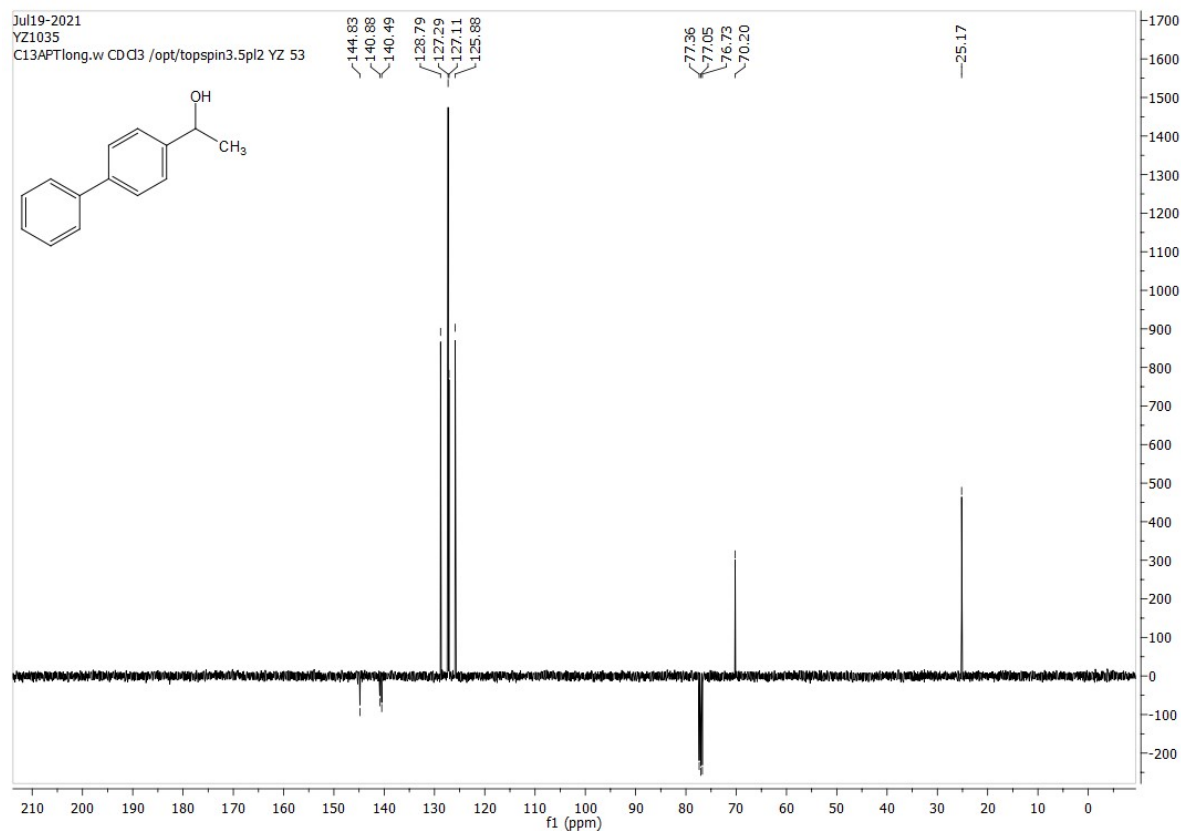
Asymmetric.

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)₂Cl₂·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 (MgSO₄) 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, $T = 25^\circ\text{C}$): $[\alpha]_D^{31} +35.2$ (c 0.740 in CHCl₃) 96% ee (*R*) (lit. $[\alpha]_D^{24} -46.6$ (c 1.0 in CHCl₃) 96% ee (*S*)) Reference: L. H. Andrade, T. Barcelos; *Org. Lett.* 2009, **11**, 3052-3055.

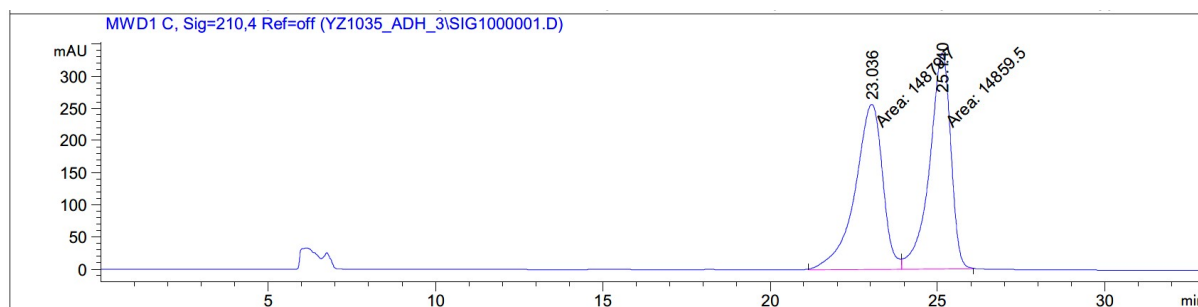
^1H NMR (400 MHz, CDCl_3)



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



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

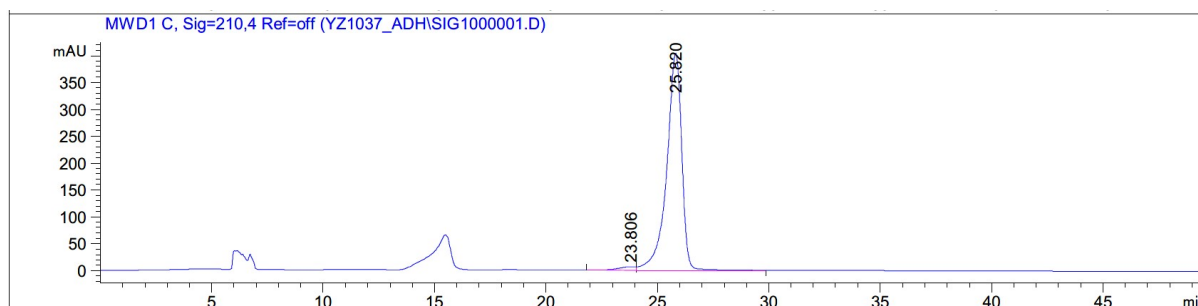


Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.036	MF	0.9651	1.48797e4	256.96442	50.0339
2	25.140	FM	0.7374	1.48595e4	335.83981	49.9661

Totals : 2.97392e4 592.80423

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



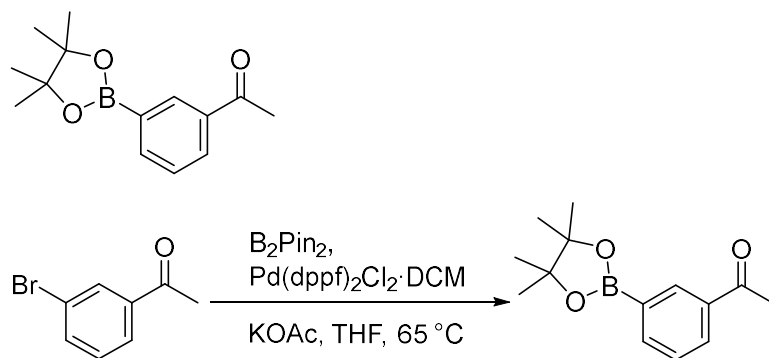
Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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.

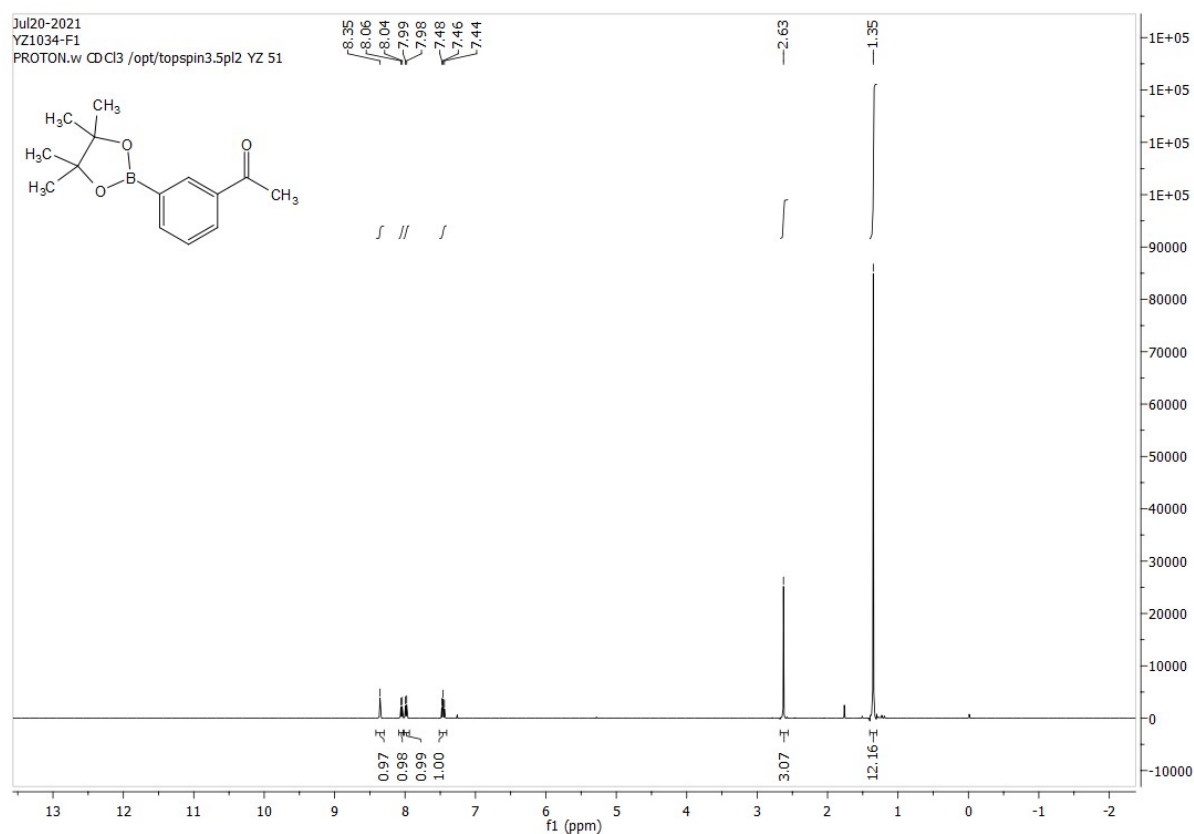


This compound has been reported and fully characterized.

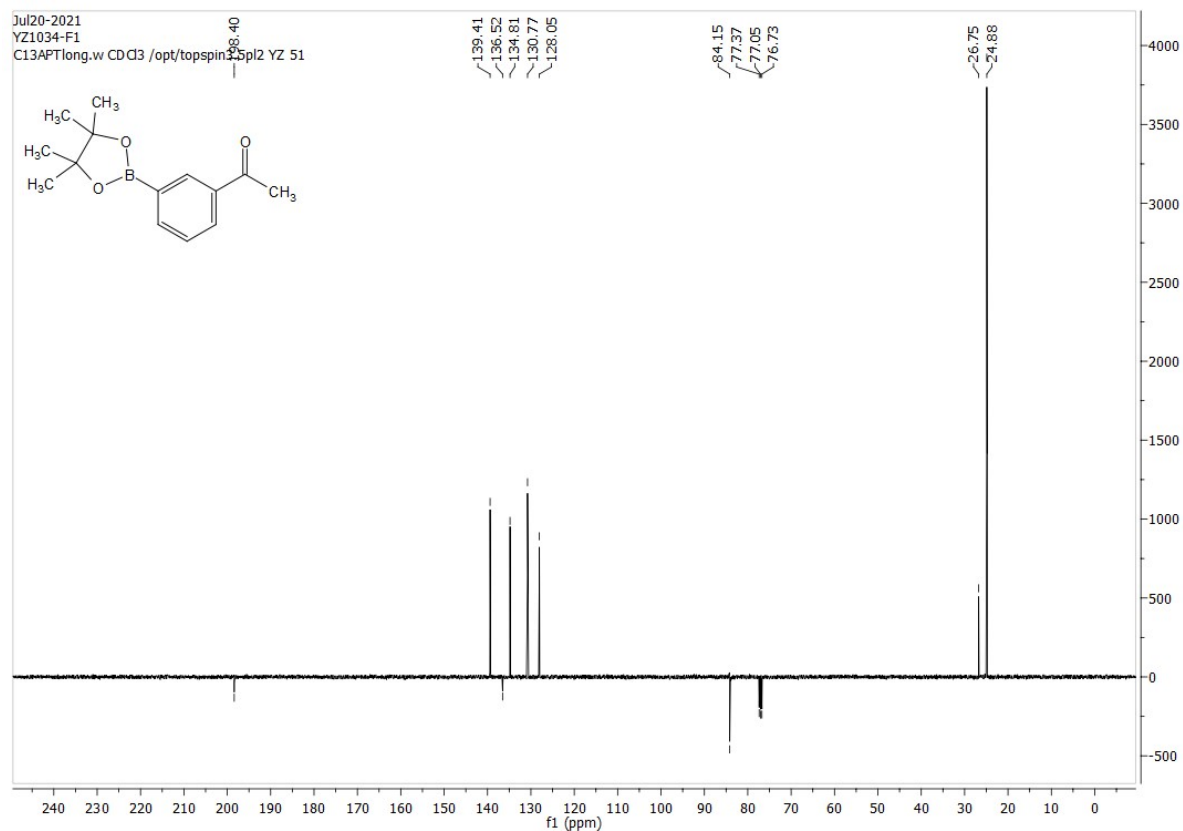
Reference: X. Zhao, M. Wu, Y. Liu and S. Cao, *Org. Lett.* 2018, **20**, 5564-5568.

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 $Pd(dppf)_2Cl_2 \cdot DCM$ (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: R_f ca 0.30 (9:1 hexane: EtOAc), strong UV and $KMnO_4$; δ_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; δ_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.

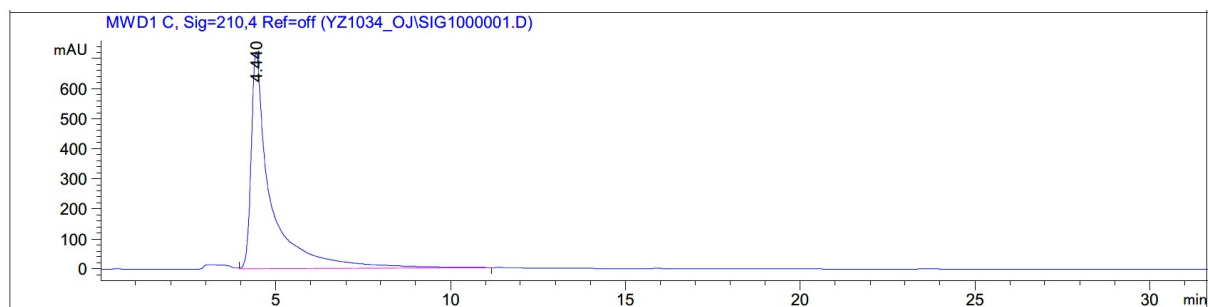
^1H NMR (400 MHz, CDCl_3)



^{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



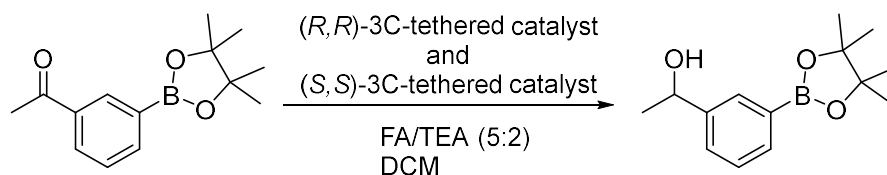
Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.440	VB	0.5296	2.81960e4	721.96869	100.0000

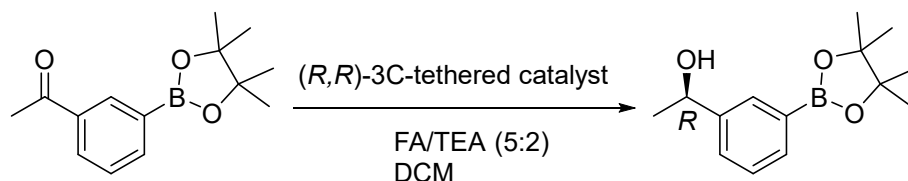
Totals : 2.81960e4 721.96869

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:

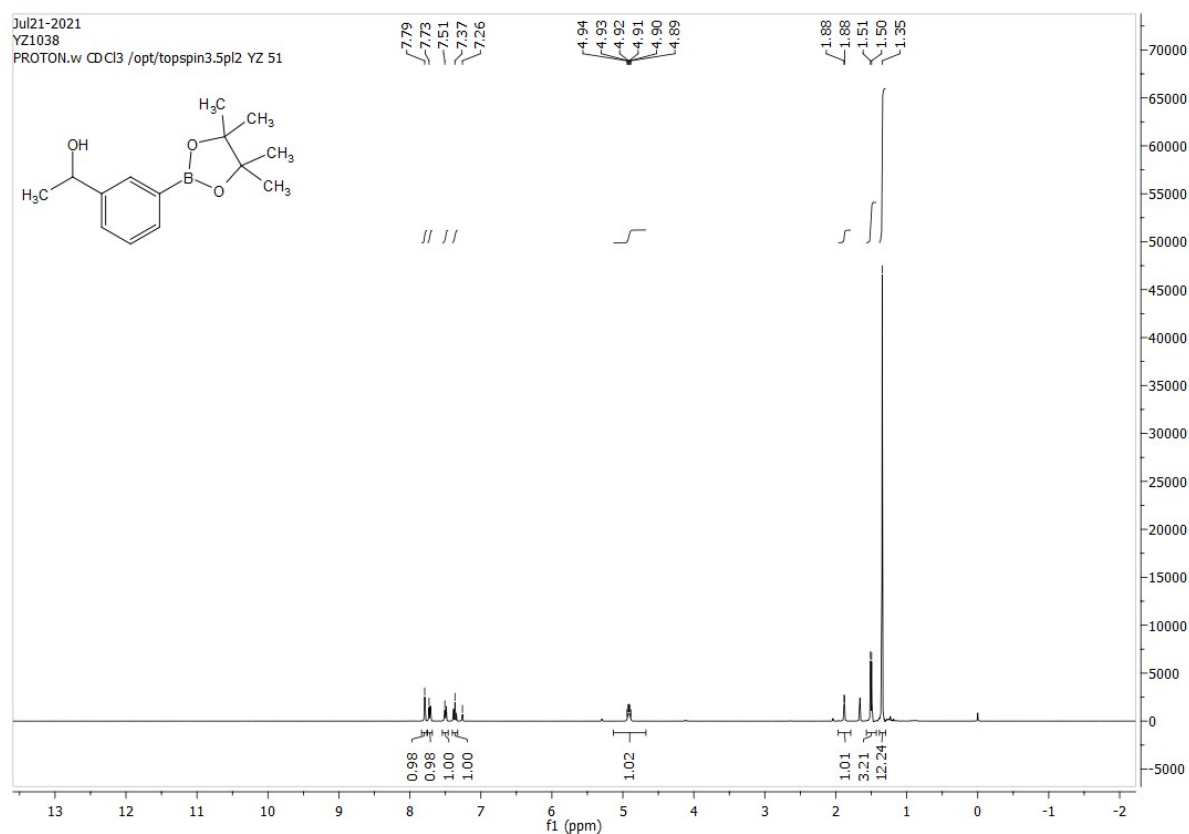
(*R,R*)-3C-Tethered Ru(II)-TsDPEN catalyst **2** (2.3 mg, 3.7 μ mol, 0.5 mol%) and (*S,S*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (2.3 mg, 3.7 μ mol, 0.5 mol%) were added to FA: TEA (5:2 azeotropic mixture, 0.81 mL) at rt and the mixture was stirred under a nitrogen atmosphere for 15 minutes; after 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 stirred under a nitrogen atmosphere and followed by TLC (4:1 hexane: EtOAc). After 24 hours, the reaction was quenched using saturated NaHCO₃ 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 0-50% 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: R_f ca 0.20 (4:1 hexane: EtOAc), strong UV and KMnO₄; δ_{H} (400 MHz, CDCl₃) 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, CH₃), 1.35 (12H, s, CH₃) ppm; δ_{C} (100 MHz, CDCl₃) 145.07 (C), 133.99 (CH), 131.74 (CH), 128.31 (CH), 128.01 (CH), 83.86 (C), 70.48 (CH), 25.14

(CH₃), 24.88 (CH₃) ppm; m/z (ES-API+) 271.1 (M⁺ + 23, 100%). Data matched that reported.

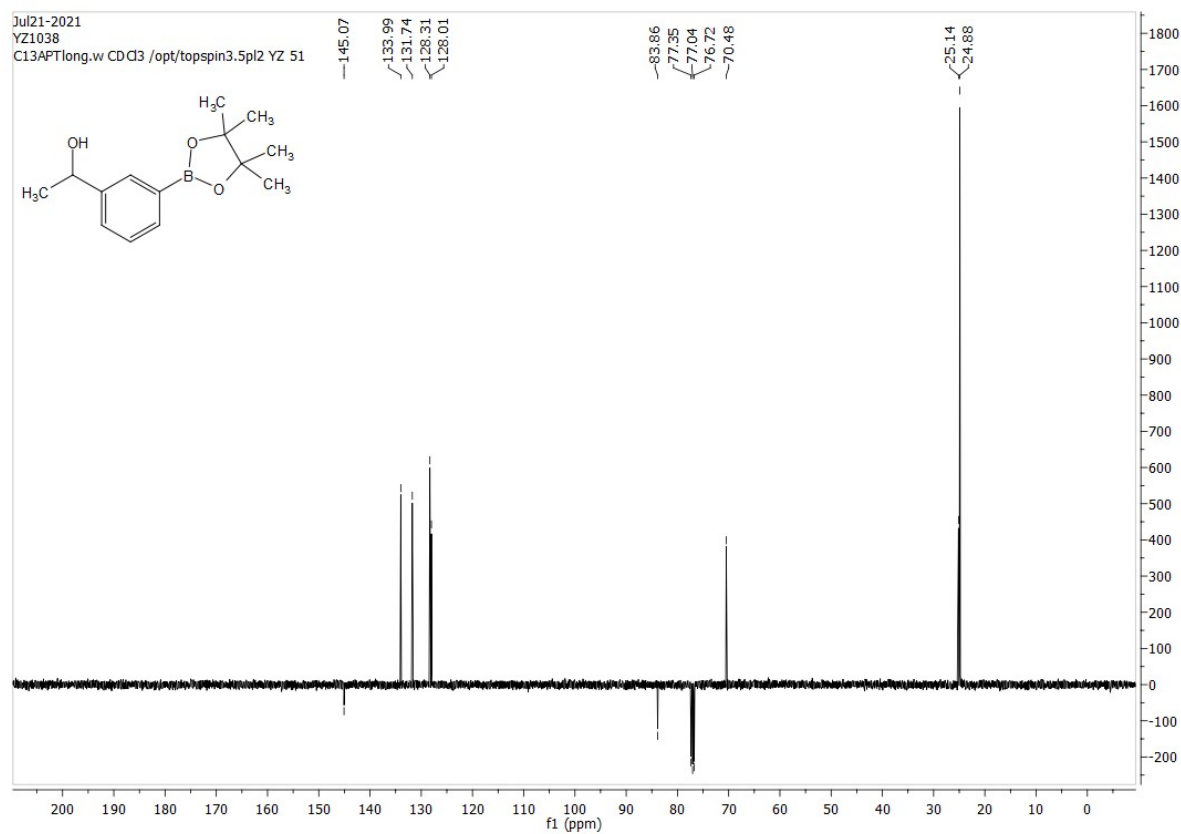
Enantiomeric excess and conversion determined by HPLC analysis (Chiralcel OJ, 30 cm x 6mm column, hexane:iPrOH 95:5, 1.0 mL/min, T = 25°C) ketone 4.4 min, *R* isomer 21.9 min and *S* isomer 7.2 min. The same column and conditions were used as in the paper referenced above.

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 NaHCO₃ 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 0-50% 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): [α]_D³¹ +31.9 (c 0.808 in CHCl₃) 98% ee (*R*) (lit. [α]_D²⁷ -27.2 (c 1.14 in CHCl₃) >99% ee (*S*))
Reference: L. H. Andrade, T. Barcelos; *Org. Lett.* 2009, **11**, 3052-3055.

^1H NMR (400 MHz, CDCl_3)

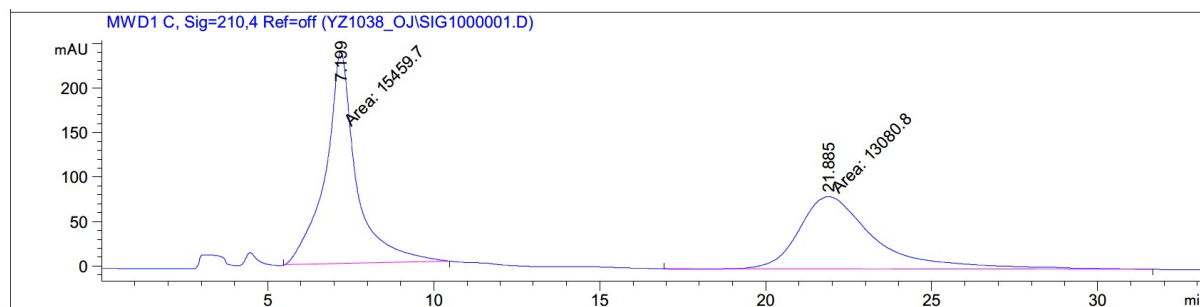


^{13}C NMR (100 MHz, CDCl_3)



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

9

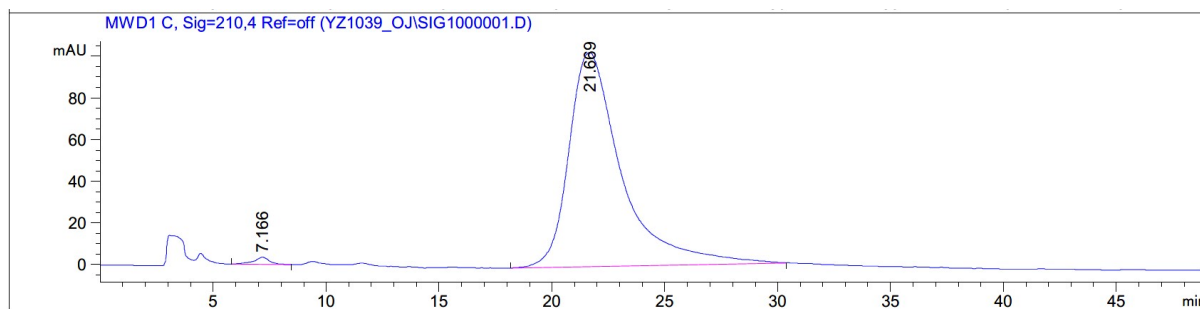


Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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)

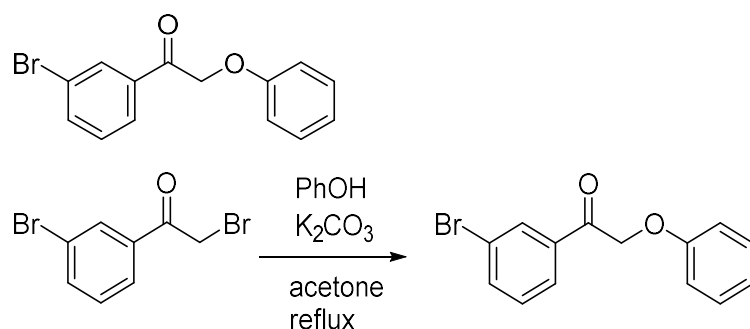


Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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

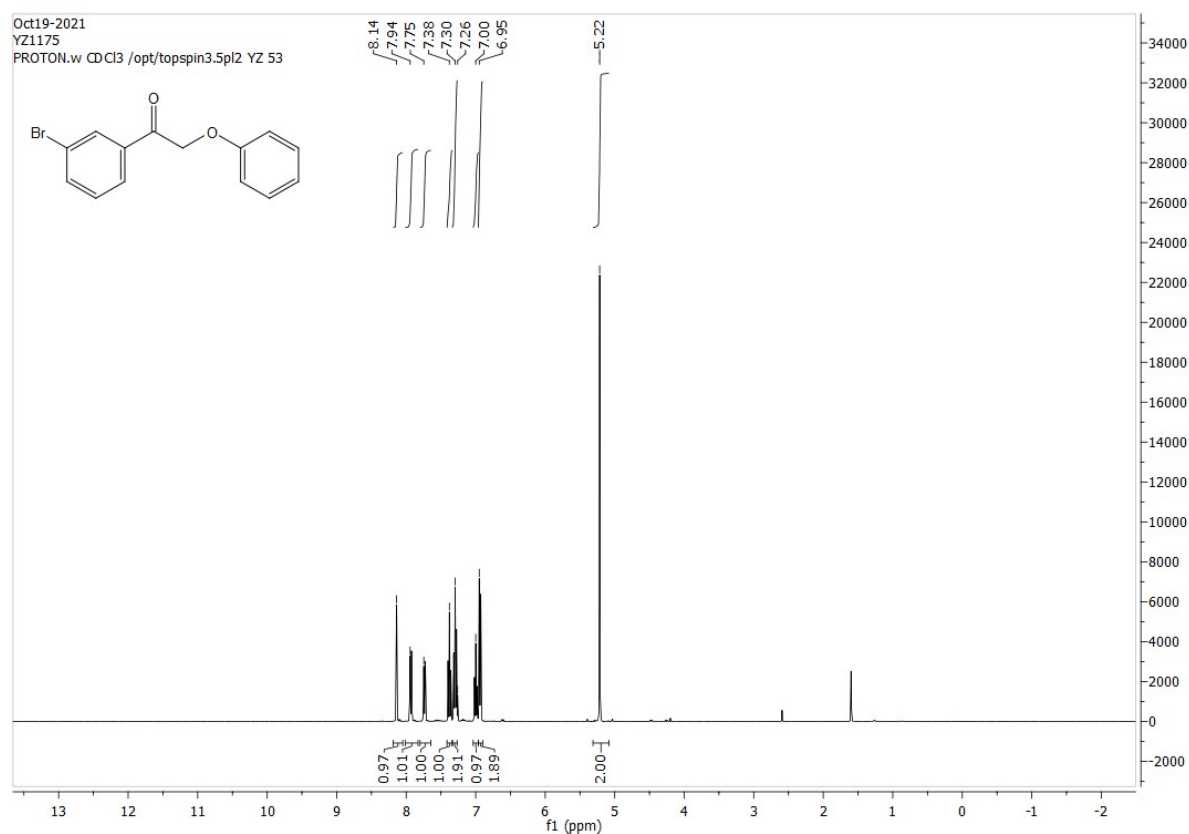
1-(3-Bromophenyl)-2-phenoxyethan-1-one.



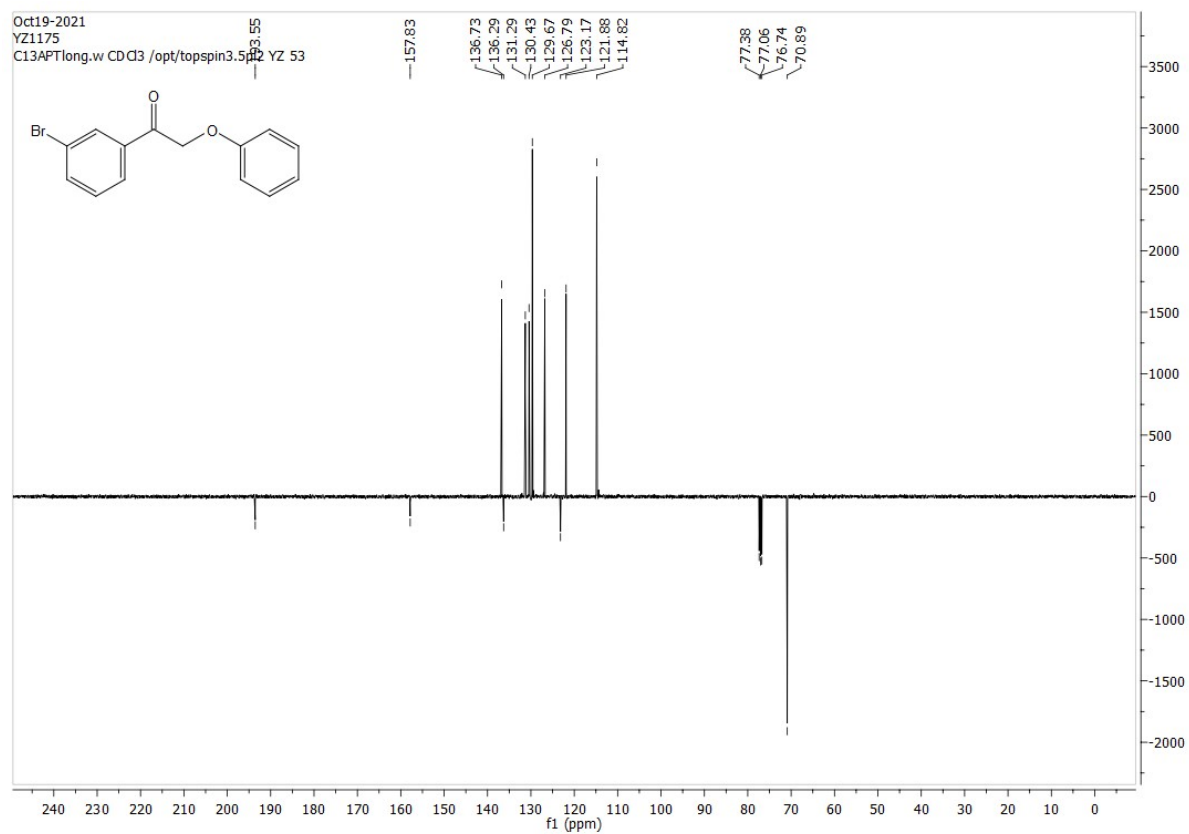
This compound has been reported and fully characterized: K. Huang, M. Ortiz-Marciales, W. Correa, E. Pomales, X. Y. Lopez, *J. Org. Chem.* 2009, **74**, 4195-4202.

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: R_f ca 0.50 (9:1 hexane: EtOAc), strong UV and $KMnO_4$; δ_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; δ_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.

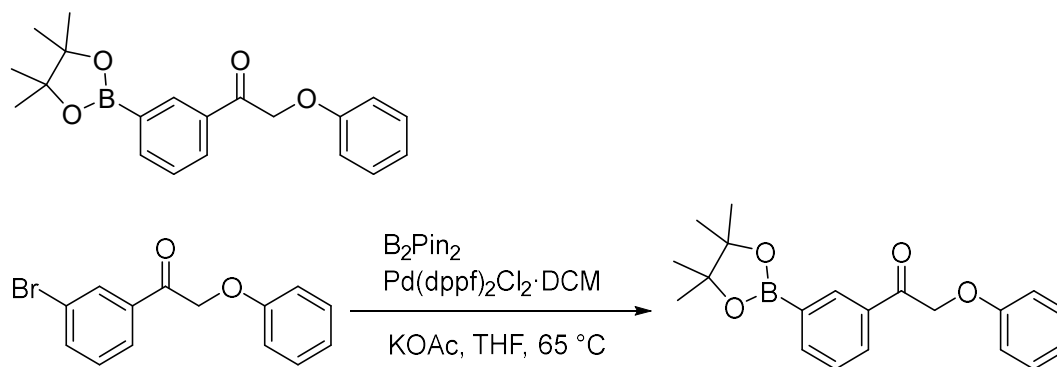
^1H NMR (400 MHz, CDCl_3)



^{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.

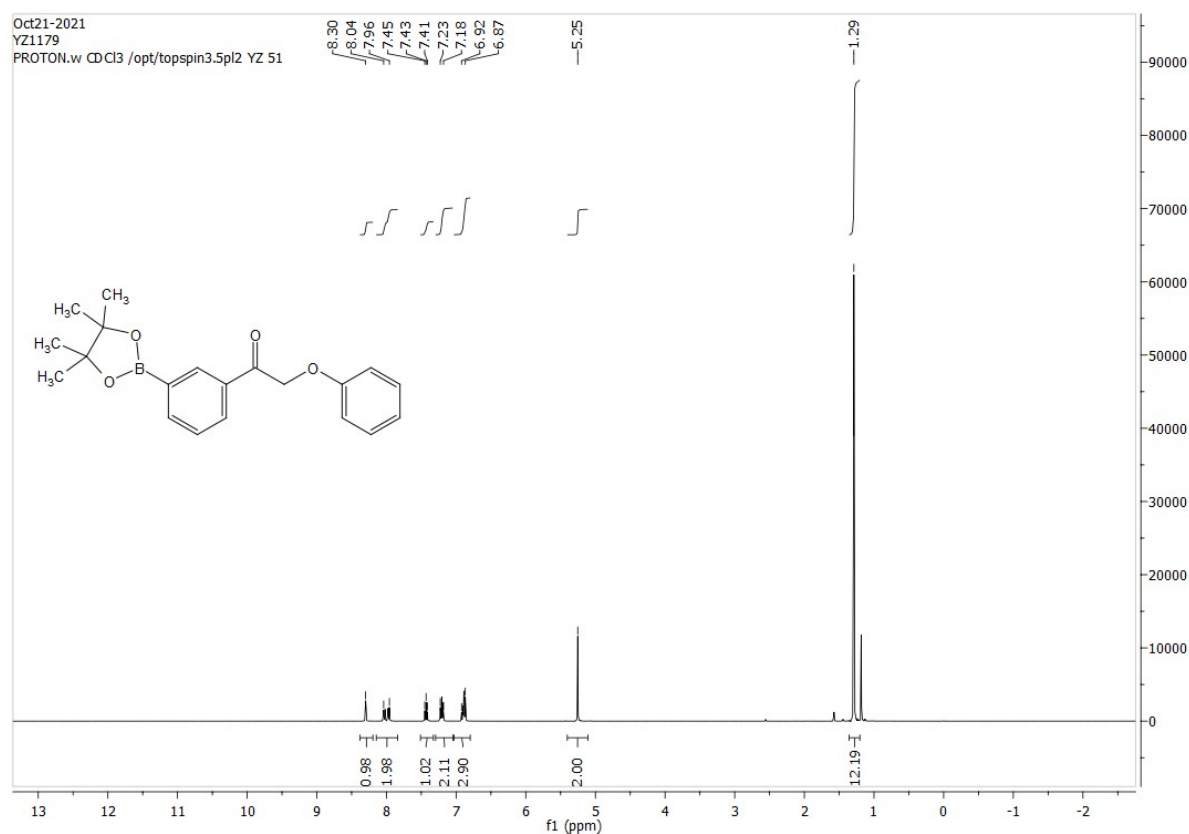


This compound is novel.

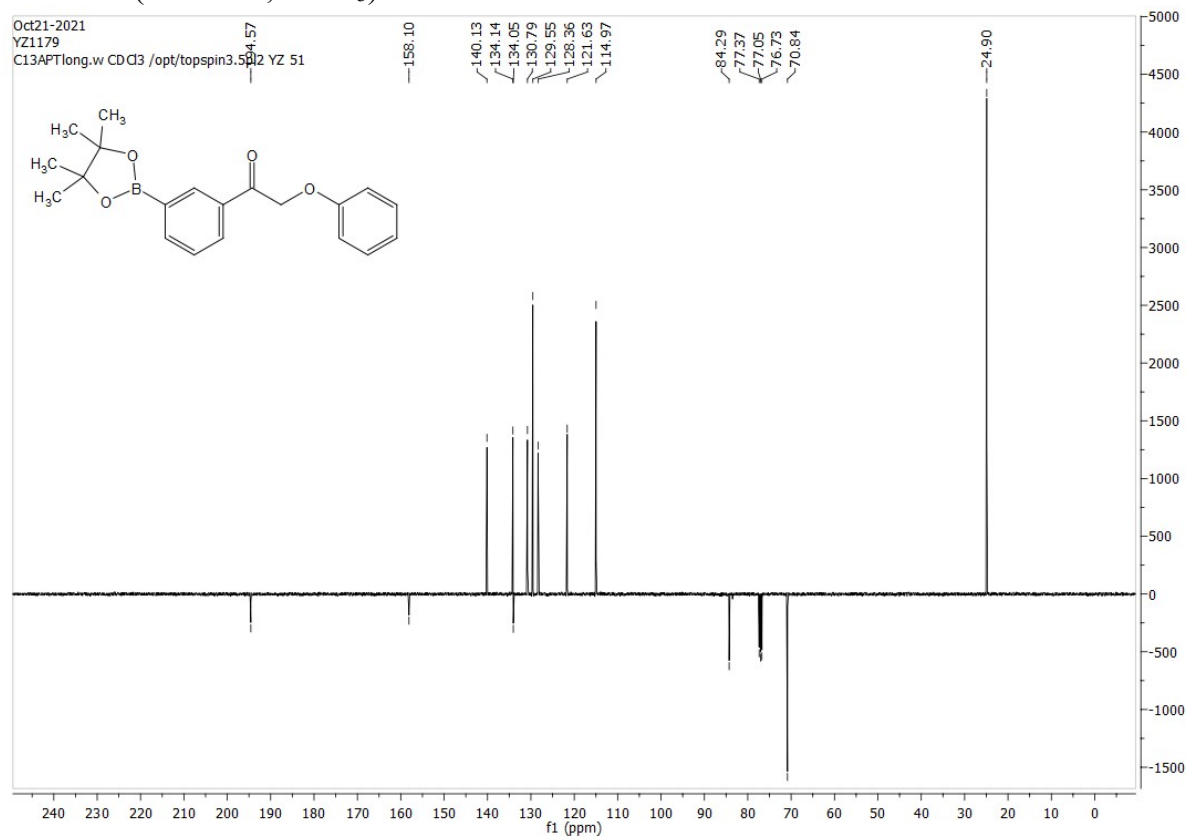
A round-bottom flask was charged with 1-(3-bromophenyl)-2-phenoxyethan-1-one (470 mg, 1.62 mmol), bis(pinacolato)diboron (493 mg, 1.94 mmol), potassium acetate (476 mg, 4.86 mmol), THF (8 mL) and $Pd(dppf)_2Cl_2 \cdot DCM$ (66.2 mg, 0.0810 mmol). The reaction mixture was heated to 65 °C and left stirring 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: R_f 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; ν_{max} 3061, 2975, 1702, 1600, 1488, 1389, 1371, 1329, 1209, 1120, 1076 cm^{-1} ; δ_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; δ_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, $T = 25^\circ C$) ketone 5.2 min, *R* and *S* isomers 6.8 min and 8.5 min.

^1H NMR (400 MHz, CDCl_3)

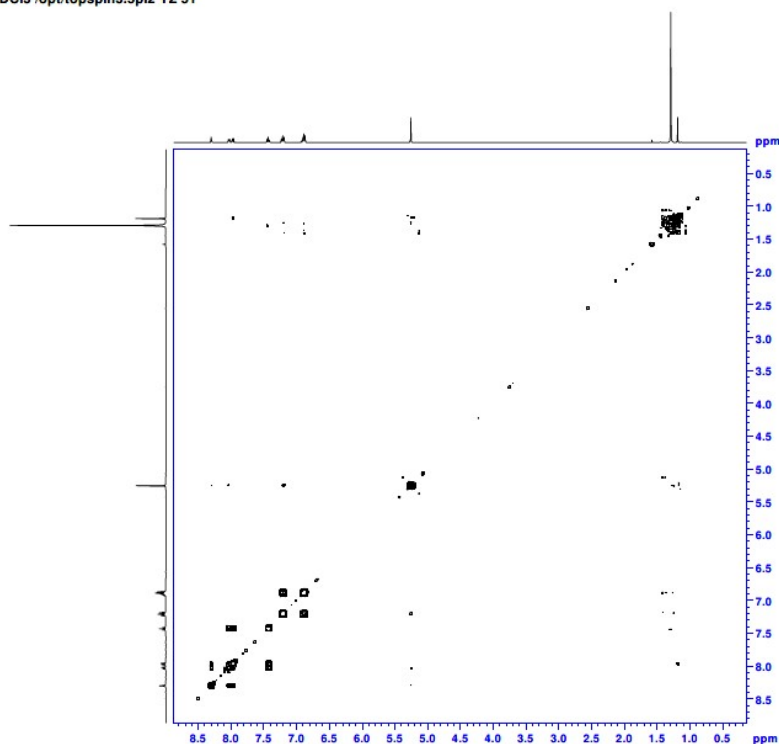


^{13}C NMR (100 MHz, CDCl_3)



COSY (400 MHz, CDCl₃)

YZ1179
COSY.w CDCl₃ /opt/topspin3.5pl2 YZ 51

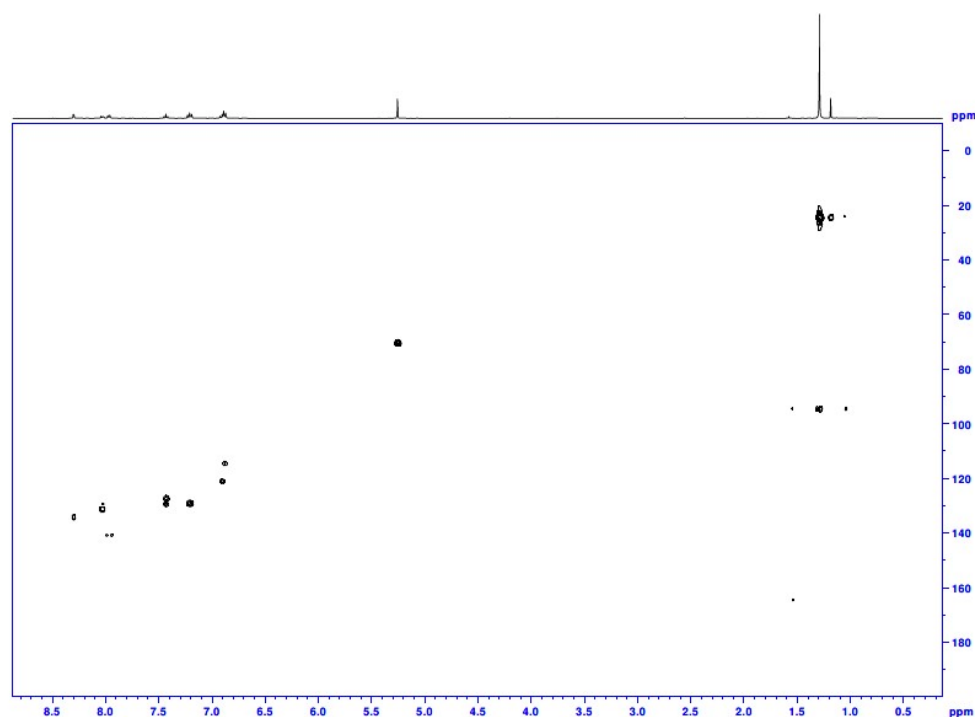


Current Data Parameters
NAME Oct21-2021
EXPNO 11
PROCNO 1

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SOLVENT CDCl₃
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SWH 3496.103 Hz
FIDRES 1.707279 Hz
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RG 32.44
DW 143.000 usec
DE 4.50 usec
TE 299.0 K
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D12 0.00000000 sec
D13 0.00000000 sec
D14 0.00000000 sec
D15 0.00000000 sec
D16 0.00000000 sec
D17 0.00000000 sec
TDav 1
SFO1 400.1318429 MHz
NUC1 13
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HSQC (400 MHz, CDCl₃)

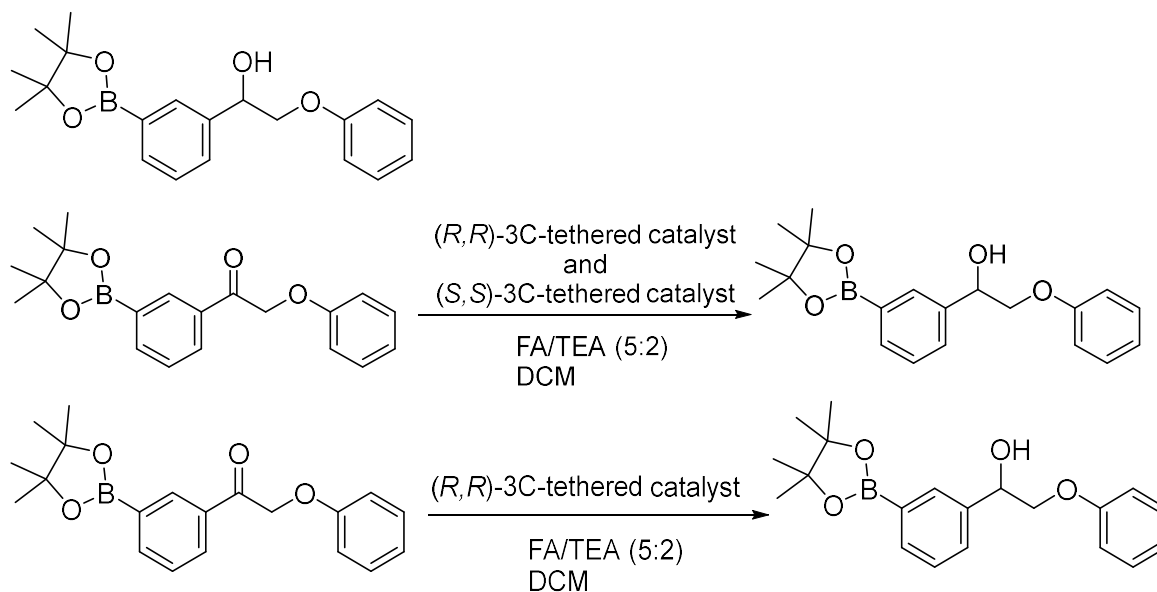
YZ1179
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Current Data Parameters
NAME Oct21-2021
EXPNO 12
PROCNO 1

F2 - Acquisition Parameters
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PULPROG zgpg30
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SOLVENT CDCl₃
NS 1
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SWH 3496.103 Hz
FIDRES 1.707279 Hz
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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:

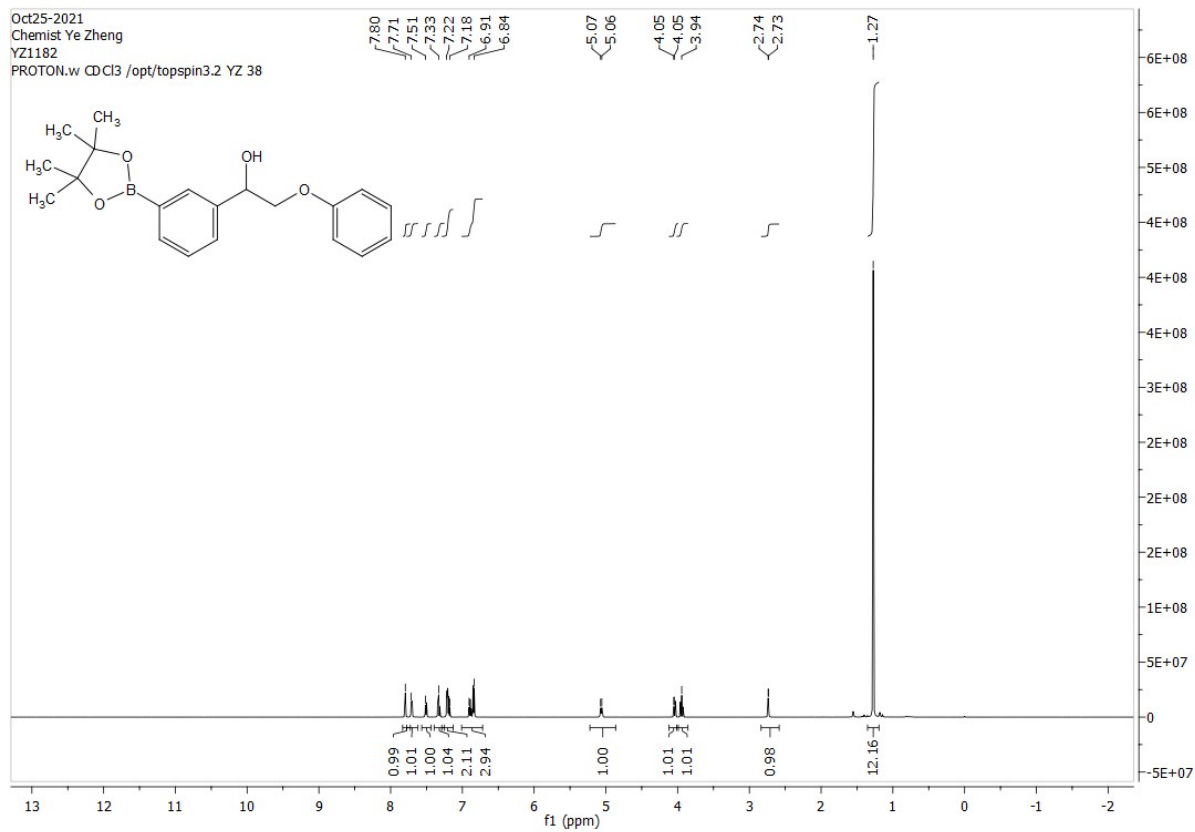
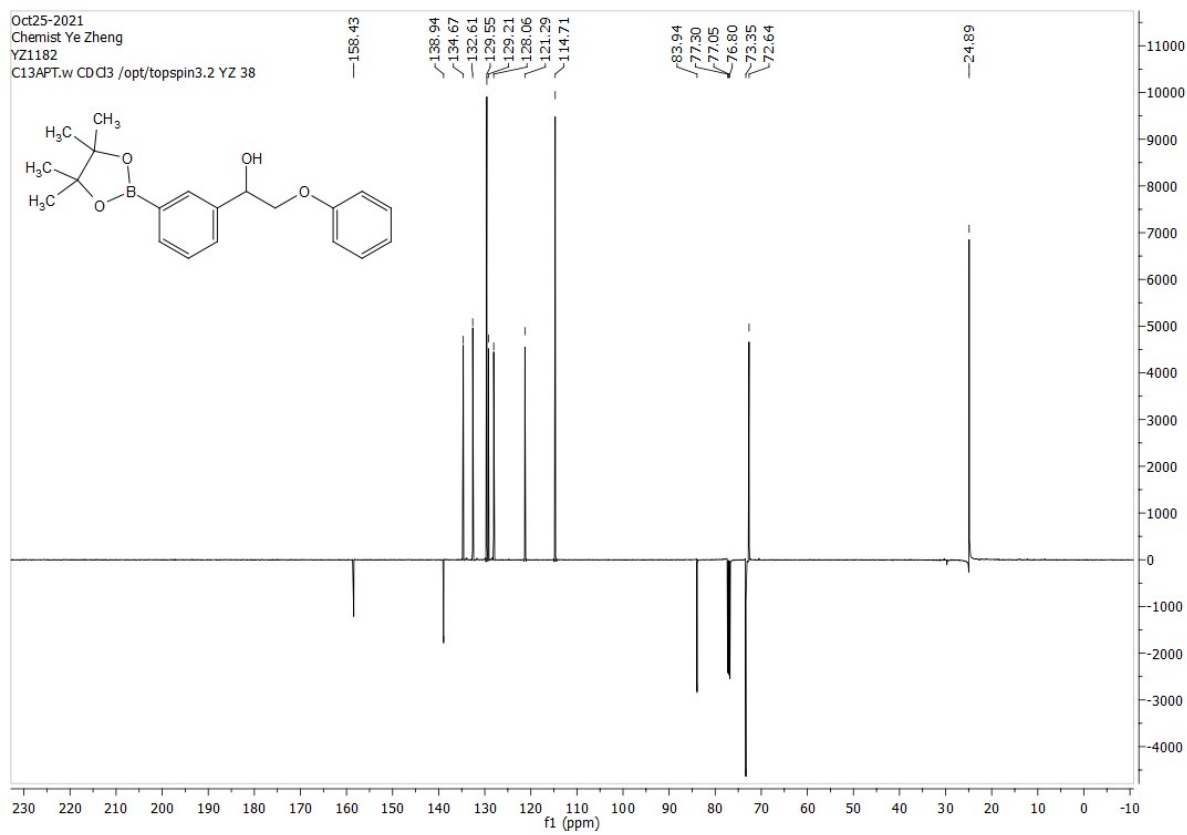
(*R,R*)-3C-Tethered Ru(II)-TsDPEN catalyst **2** (0.74 mg, 1.2 μ mol, 0.5 mol%) and (*S,S*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (0.74 mg, 1.2 μ mol, 0.5 mol%) were added to FA: TEA (5:2 azeotropic mixture, 0.36 mL) at rt and the mixture was stirred under a nitrogen atmosphere for 15 minutes; after 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 stirred under a nitrogen atmosphere and followed by TLC (9:1 hexane: EtOAc). After 72 hours, the reaction was quenched using saturated NaHCO₃ 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 0-20% 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: R_f ca 0.20 (9:1 hexane: EtOAc), strong UV and KMnO₄; HRMS: (found (ESI⁺): [M+H]⁺, Calcd for C₂₀H₂₅BNaO₄ 363.1738; Found 363.1738; 1.1 ppm error; ν_{max} 3456 (br), 2977, 2928, 1599, 1495, 1353, 1240, 1107, 1038, 752 cm⁻¹; δ_{H} (500 MHz, CDCl₃) 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, $J = 9.6, 3.1$, CH₂), 3.94 (1H, t, $J = 9.3$, CH₂), 2.74 (1H, d, $J = 2.0$, OH), 1.27 (12H, s, CH₃) ppm; δ_c (125 MHz, CDCl₃) 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 (CH₂), 72.64 (CH), 24.89 (CH₃) 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, $T = 25^\circ\text{C}$) ketone 5.2 min, *R* and *S* isomers 6.8 min and 8.5 min, configuration assigned by analogy with **9**.

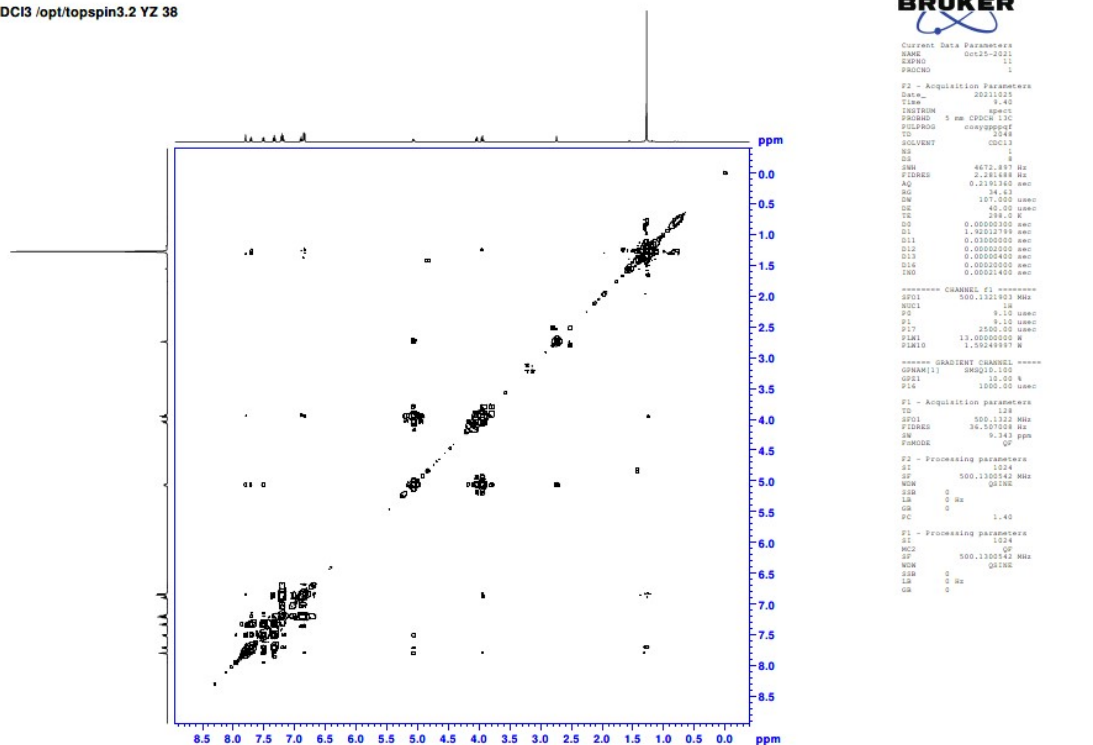
ATH of 2-phenoxy-1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one:

(*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 stirred under a nitrogen atmosphere and followed by TLC (9:1 hexane: EtOAc). After 72 hours, the reaction was quenched using saturated NaHCO₃ 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 0-20% 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, $T = 25^\circ\text{C}$): $[\alpha]_D^{23} +47.0$ (c 0.245 in CHCl₃) 97% ee.

¹H NMR (500 MHz, CDCl₃) ^{13}C NMR (125 MHz, CDCl_3)

COSY (500 MHz, CDCl₃)

Chemist Ye Zheng
YZ1182
COSY.w CDCI3 /opt/topspin3.2 YZ 38



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Current Data Parameters
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EXPNO        11
PROCNO       11

F2 - Acquisition Parameters
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TD           65536
SOLVENT      CDCl3
NS            504
DS            1
SWH           4672.897 Hz
F2FREQ       2.214184 Hz
AQ            0.2191362 sec
RG            34.43
AQ            187.000 usec
DE            40.00 usec
TE            299.0 K
0.00000000 sec
D1            1.92017399 sec
D11           0.03000000 sec
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D13           0.00000400 sec
D14           0.00020000 sec
D15           0.00010000 sec

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PWL1      13.00000000 N
PWL10     1.59249897 N

***** GRADIENT CHANNEL *****
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GSE1      10.00 N
P16       1000.00 uWatt

F1 - Acquisition parameters
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FIDRES    36.507008 Hz
SW        6.343 pps
SOLVENT    CD

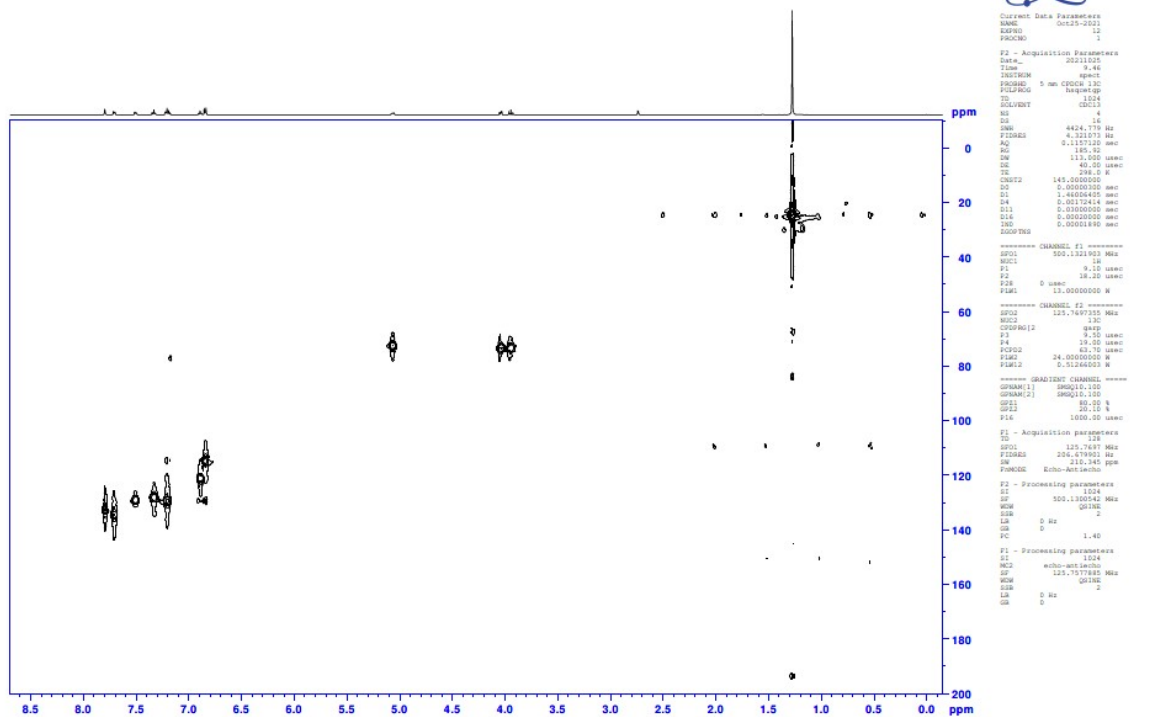
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F1 - Processing parameters	
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F1 - Processing parameters
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WDW         QWINE
SSB         0
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HSQC (500 MHz, CDCl₃)HSQC.w CDCI3 /opt/topspin3.2 YZ 38 

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Current Data Parameters
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EXPNO        12
PROCNO       12

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SOLVENT       CDCl3
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DS            16
SWH           48424.775 Hz
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AQ            0.1157120 sec
RG            189.12
WDW            113.000 used
SSB            40.50 used
GB            298.00
CNETZ2        145.0000000
DZ            0.0000000 sec
DZ1           1.4400000 sec
D4            0.00172414 sec
D51           0.0000000 sec
D6            0.0000000 sec
D62           0.0001890 sec
END
ENDPROCFS
===== /F2/ENDPROC=====

```

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SP01      500.1321093 Mhz
MC01      1W
P1        9.10 used
P2        18.20 used
P2R       0 used
FREQ1     13.02000000 W

***** CHANNEL f2 *****
SP02      125.7697355 Mhz
MC02      3.3C
CP02PRG[2] gap
P3        9.50 used
P4        19.00 used
P4PRG2    63.70 used
FREQ2     24.00000000 W
FREQ2L    0.51266003 W

***** GRADIENT CHANNEL *****
GRPHAW[1]  SRG10.150
GRPHAW[2]  SRG10.150
GP1       80.00 %
GP2       20.10 %

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```

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

F2 - Processing parameters
SI        1024
SF        500.130542 MHz
WDW       GQ1N1
SSB        2
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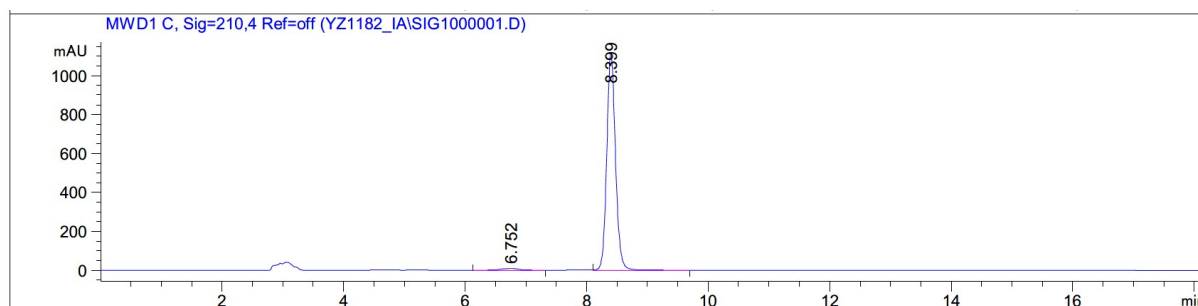
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F1 - Processing parameters
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GCMW             QG1NE
SSB              2
LB              0 Hz
GB              0

```


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).

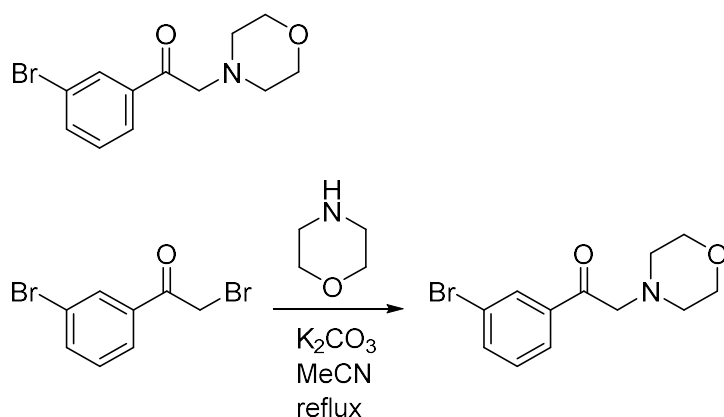


Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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

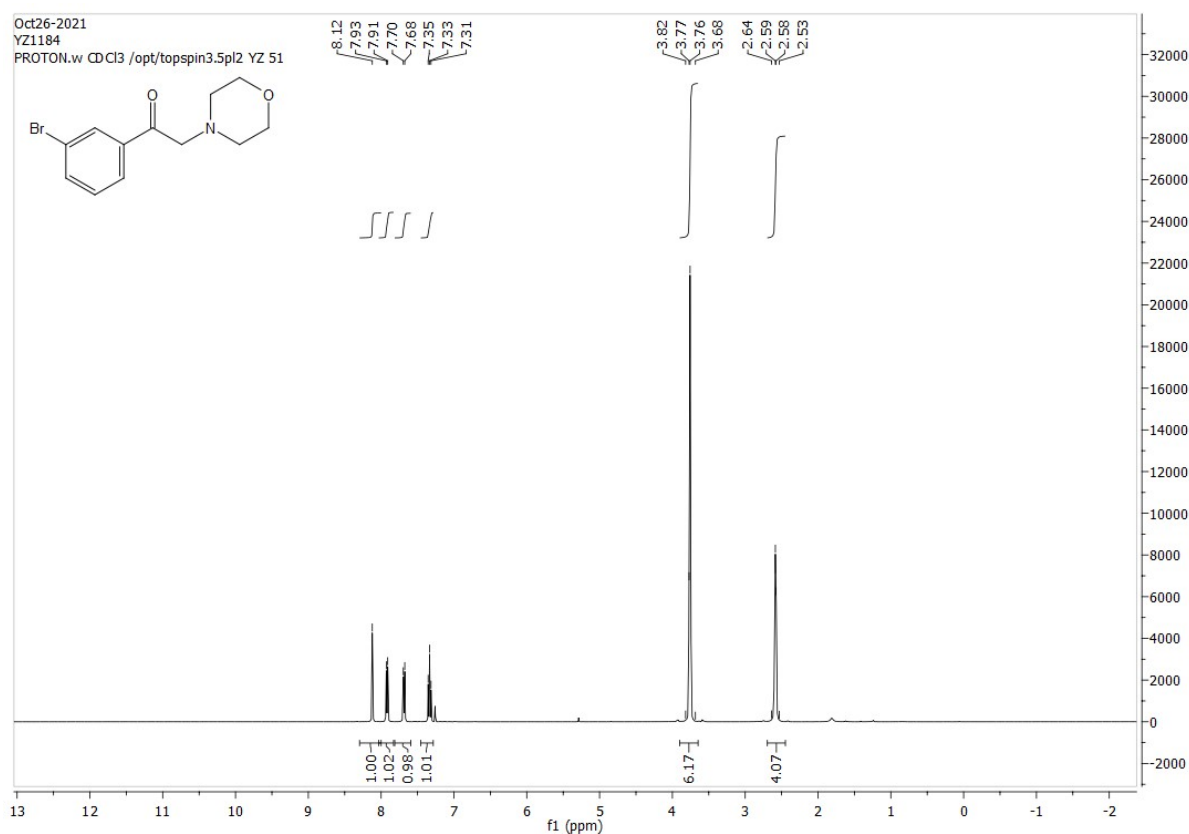
1-(3-Bromophenyl)-2-morpholinoethan-1-one.



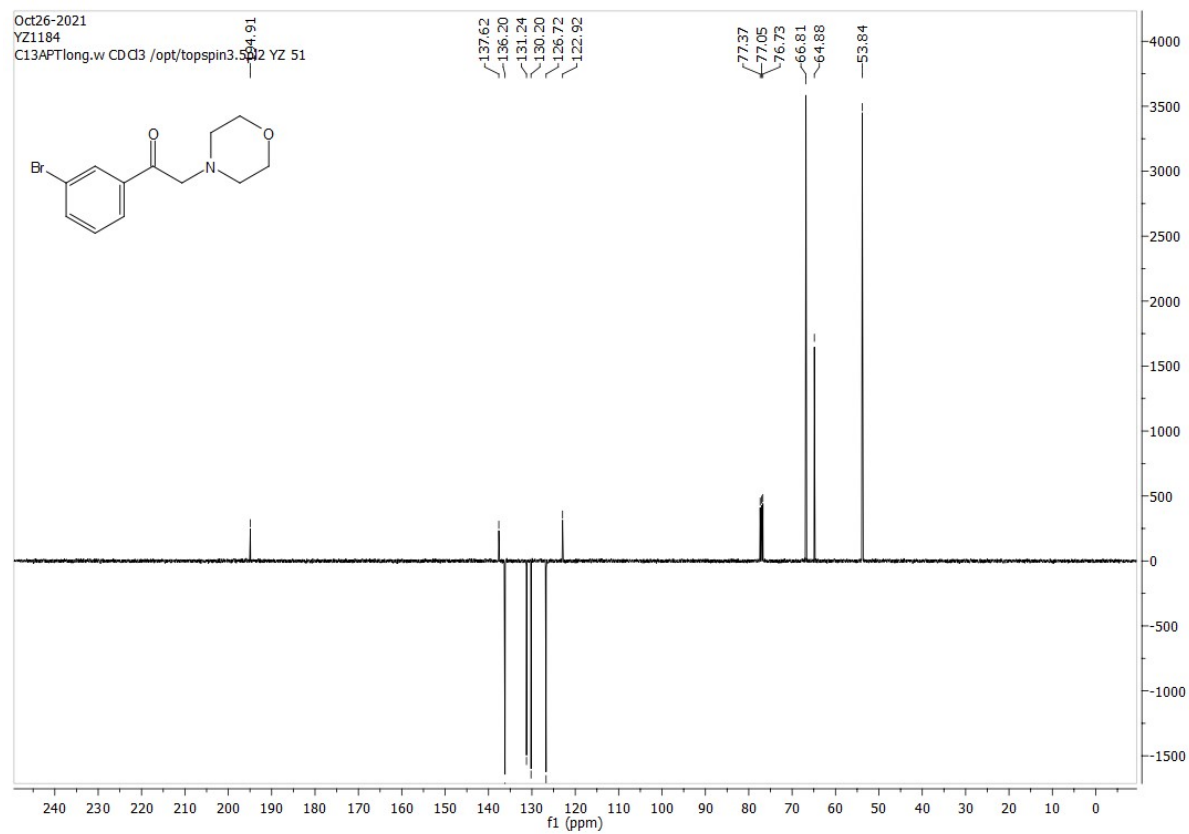
This compound is novel.

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). Et₂O (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with Et₂O (3 × 20 mL), and the combined organic layers were dried (MgSO₄) 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: R_f ca 0.40 (1:1 hexane: EtOAc), strong UV and KMnO₄; Mp: 75°C; HRMS: (found (ESI⁺): [M+H]⁺, Calcd for C₁₂H₁₅BrNO₂ 284.0278; Found 284.0281; 0.9 ppm error; ν_{\max} 2963, 2863, 1696, 1564, 1449, 1416, 1298, 1213, 1163, 1142, 1107, 10840, 900, 864, 783 cm⁻¹; δ_H (400 MHz, CDCl₃) 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, CH₂), 2.64-2.53 (4H, m, CH₂) ppm; δ_C (100 MHz, CDCl₃) 194.91 (C), 137.62 (C), 136.20 (CH), 131.24 (CH), 130.20 (CH), 126.72 (CH), 122.92 (C), 66.81 (CH₂), 64.88 (CH₂), 53.84 (CH₂) ppm; m/z (ES-API⁺) 284.0 (M⁺ + 23, 100%).

^1H NMR (400 MHz, CDCl_3)

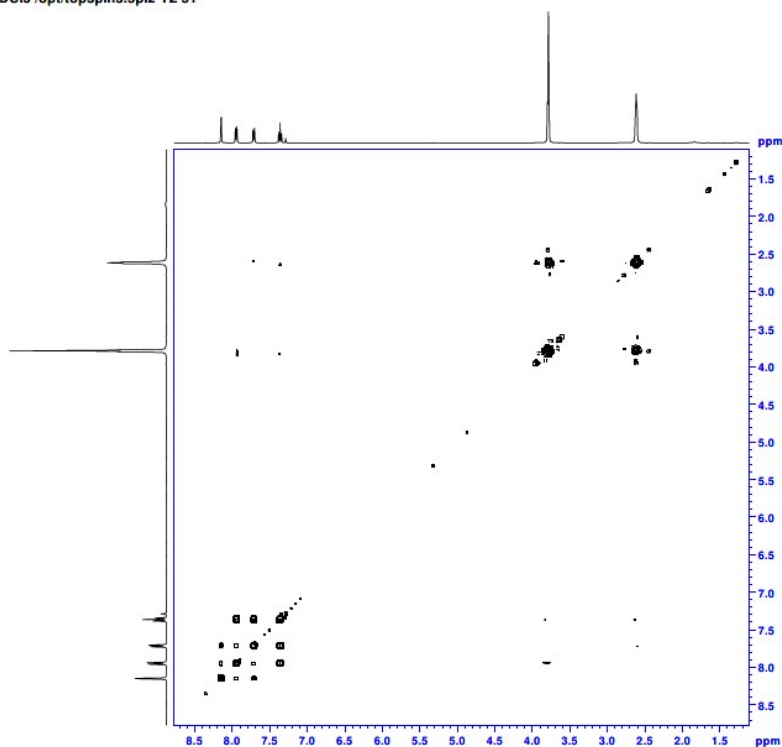
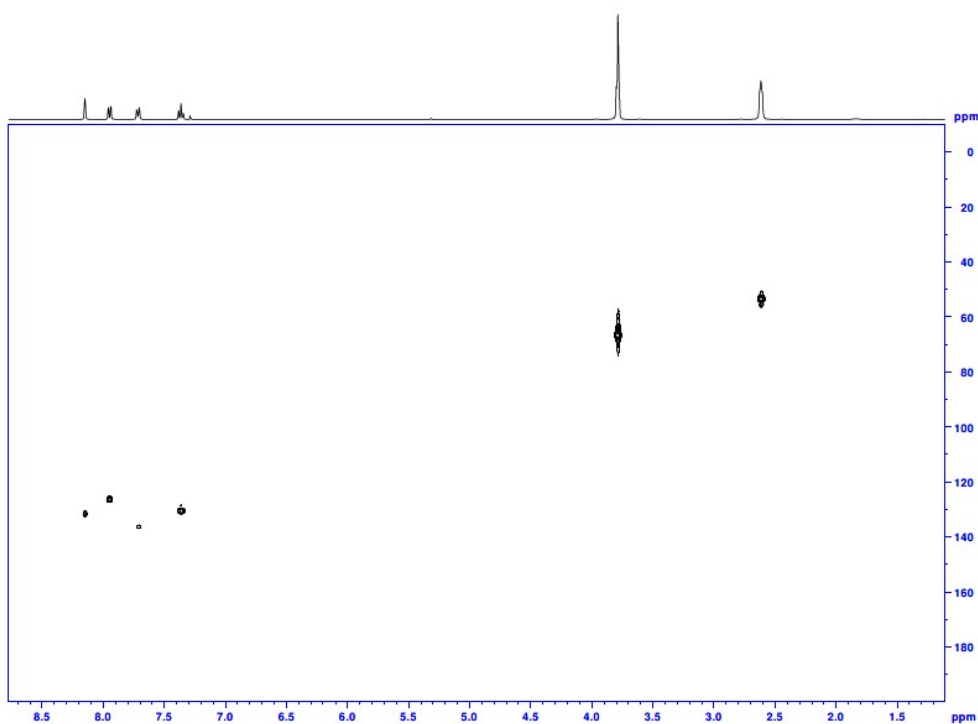


^{13}C NMR (100 MHz, CDCl_3)



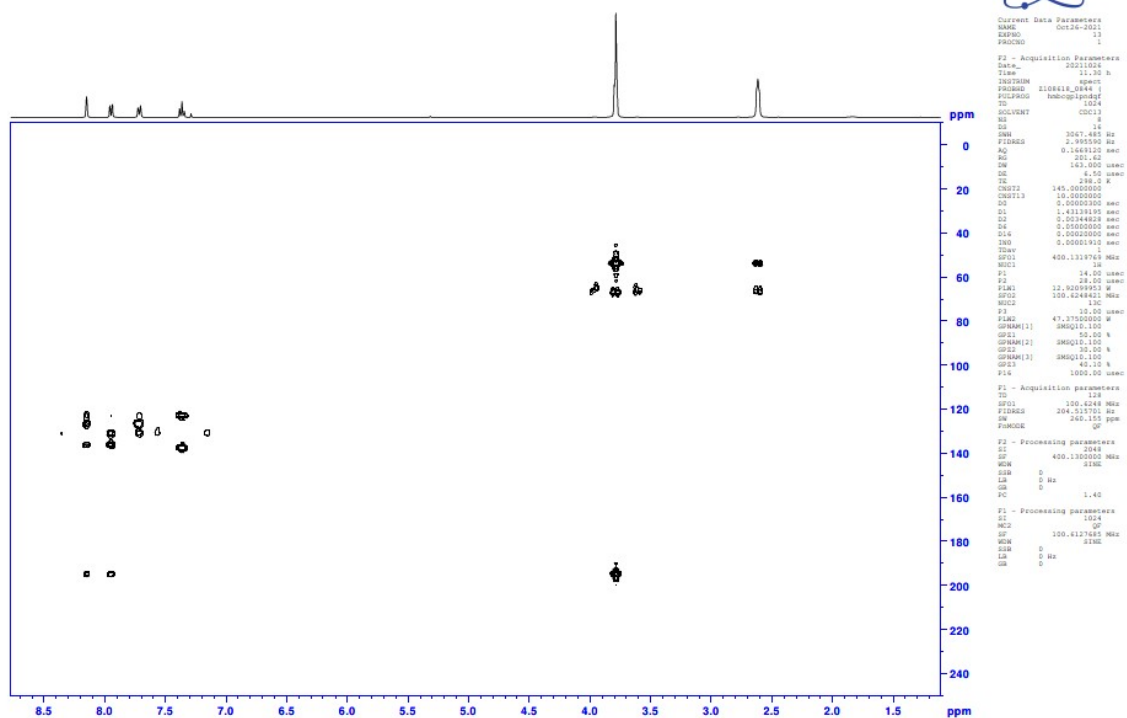
COSY (400 MHz, CDCl₃)

YZ1184
COSY.w CDCI3 /opt/topspin3.5pl2 YZ 51

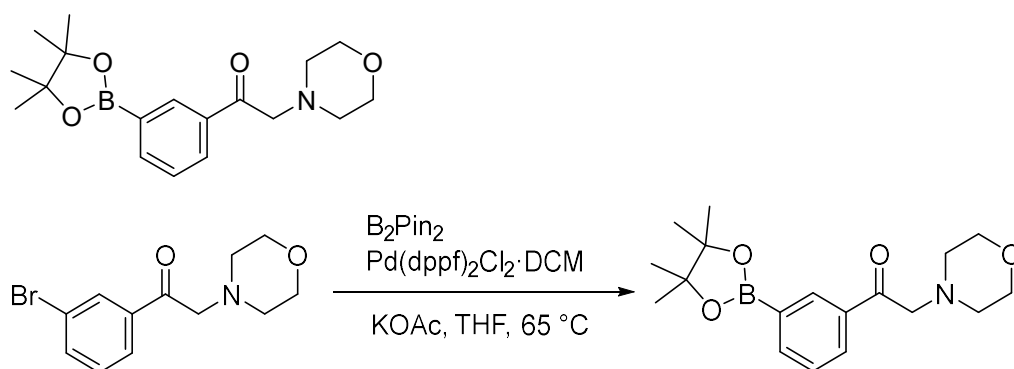
[illegible]HSQC (400 MHz, CDCl₃)YZ1184
HSQC.w CDCI3 /opt/topspin3.5pl2 YZ 51[illegible]

HMBC (400 MHz, CDCl₃)

YZ1184
HMBC.w CDCl₃ /opt/topspin3.5pl2 YZ 51



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



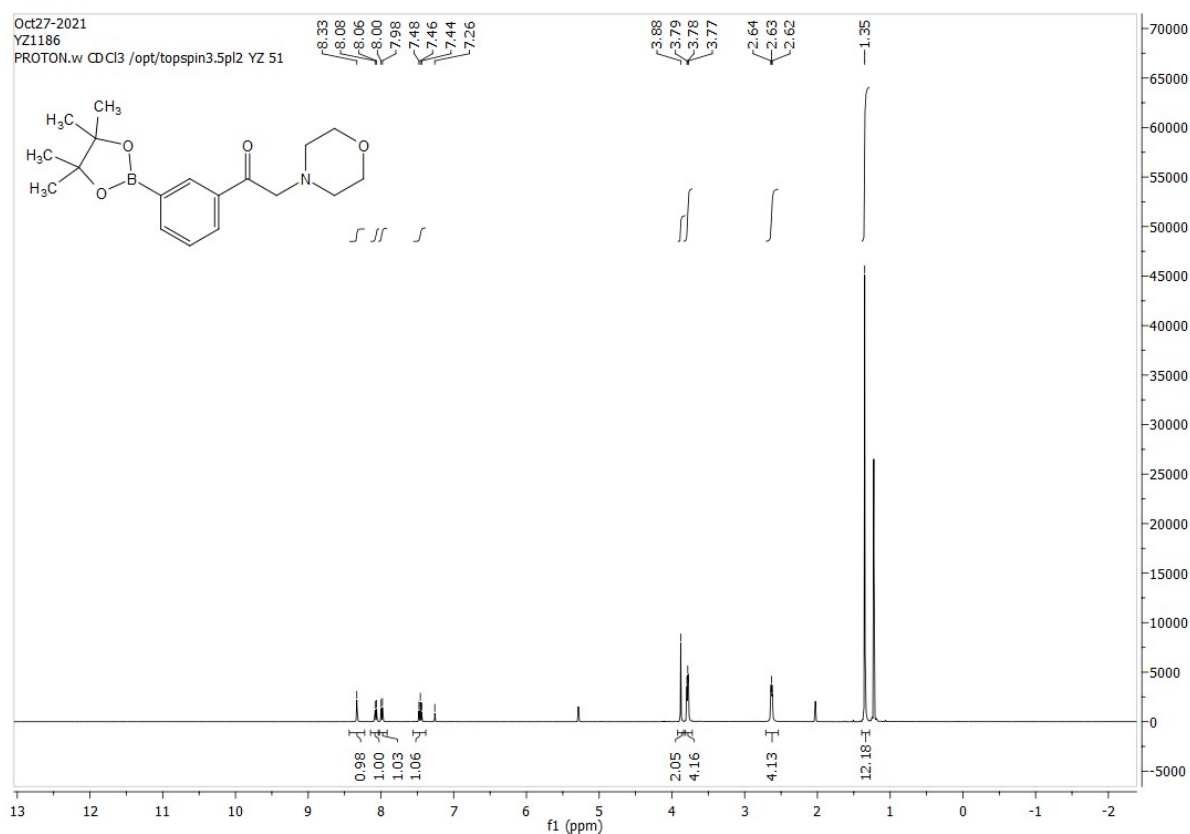
This compound is novel.

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 $Pd(dppf)_2Cl_2 \cdot DCM$ (260 mg, 0.318 mmol).

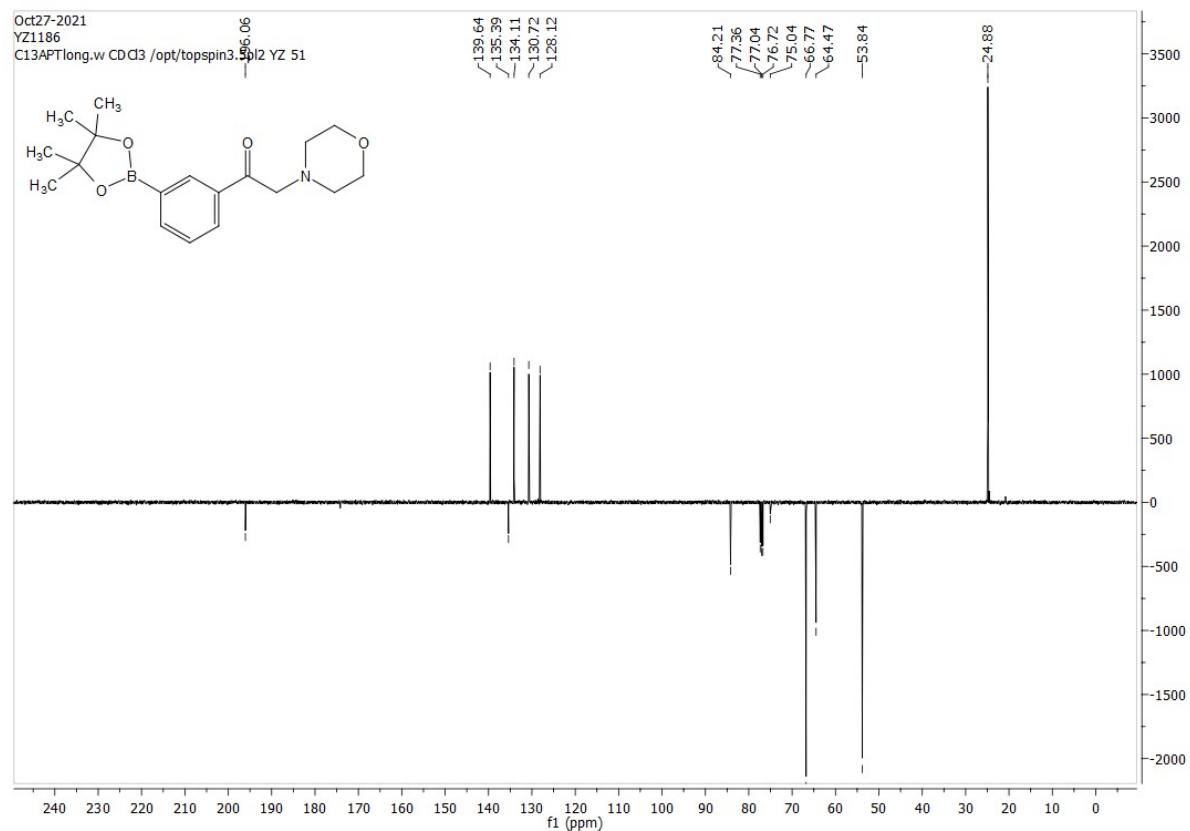
The reaction mixture was heated to 65 °C and left stirring under the nitrogen atmosphere overnight, followed by TLC (1:1 hexane: EtOAc). The mixture was quenched by distilled water (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3×20 mL), 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: R_f 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; ν_{max} 2976, 1696, 1599, 1357, 1312, 1214, 1140, 1114, 961 cm^{-1} ; δ_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; δ_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, $T = 25^\circ C$) ketone 15.6 min, *R* and *S* isomers 12.3 min and 21.1 min.

^1H NMR (400 MHz, CDCl_3)

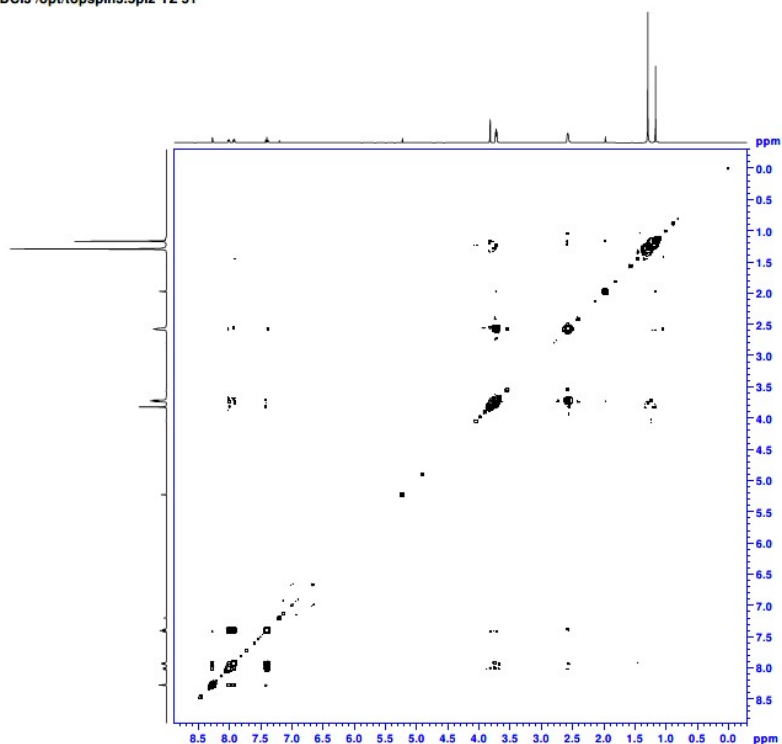


^{13}C NMR (100 MHz, CDCl_3)



COSY (400 MHz, CDCl₃)

YZ1186
COSY.w CDCl₃ /opt/topspin3.5pl2 YZ 51



Current Data Parameters
NAME Oct27-2021
EXPNO 12
PROCNO 1

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PROBHD 1HBOA18_0044
PULPROG zgpg30
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SOLVENT CDCl₃
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DS 4
SWH 3676.471 Hz
FIDRES 1.795132 Hz
AQ 0.2785280 sec
RG 32.14
SW 136.000 usec
TE 298.2 K
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D12 0.03000000 sec
D13 0.00000000 sec
D16 0.00000000 sec
DRO 0.00007100 sec
TDav 1
SFO1 400.1317515 MHz
NUC1 1H
P1 14.00 usec
P2 14.00 usec
P3 250.00 usec
P4 12.92099953 Hz
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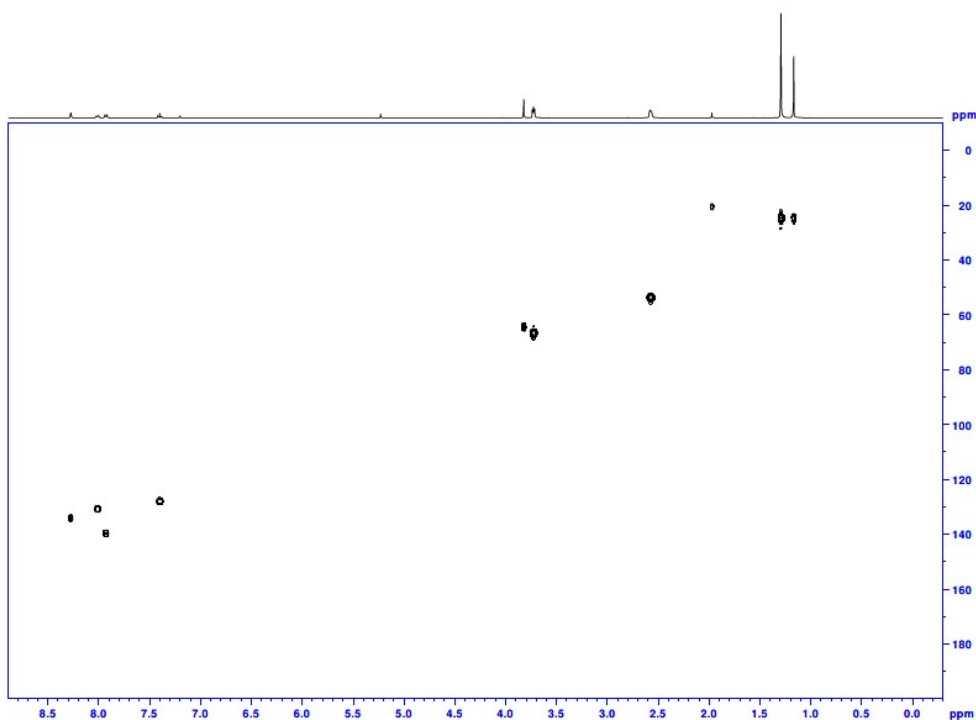
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RG 32.14
SW 136.000 usec
TE 298.2 K
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D12 0.03000000 sec
D13 0.00000000 sec
D16 0.00000000 sec
DRO 0.00007100 sec
TDav 1
SFO1 400.1317515 MHz
NUC1 1H
P1 14.00 usec
P2 14.00 usec
P3 250.00 usec
P4 12.92099953 Hz
P4B2 2.81399988 Hz
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GPRM12 0.00010.100
GPRM13 0.00010.100
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F2 - Processing parameters
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WDW 0
SSB 0
LA 0 Hz
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F1 - Processing parameters
SI 32768
SF 400.1300440 MHz
WDW 0
SSB 0
LA 0 Hz
GB 0
PC 1.40

HSQC (400 MHz, CDCl₃)

YZ1186
HSQC.w CDCl₃ /opt/topspin3.5pl2 YZ 51



Current Data Parameters
NAME Oct27-2021
EXPNO 12
PROCNO 1

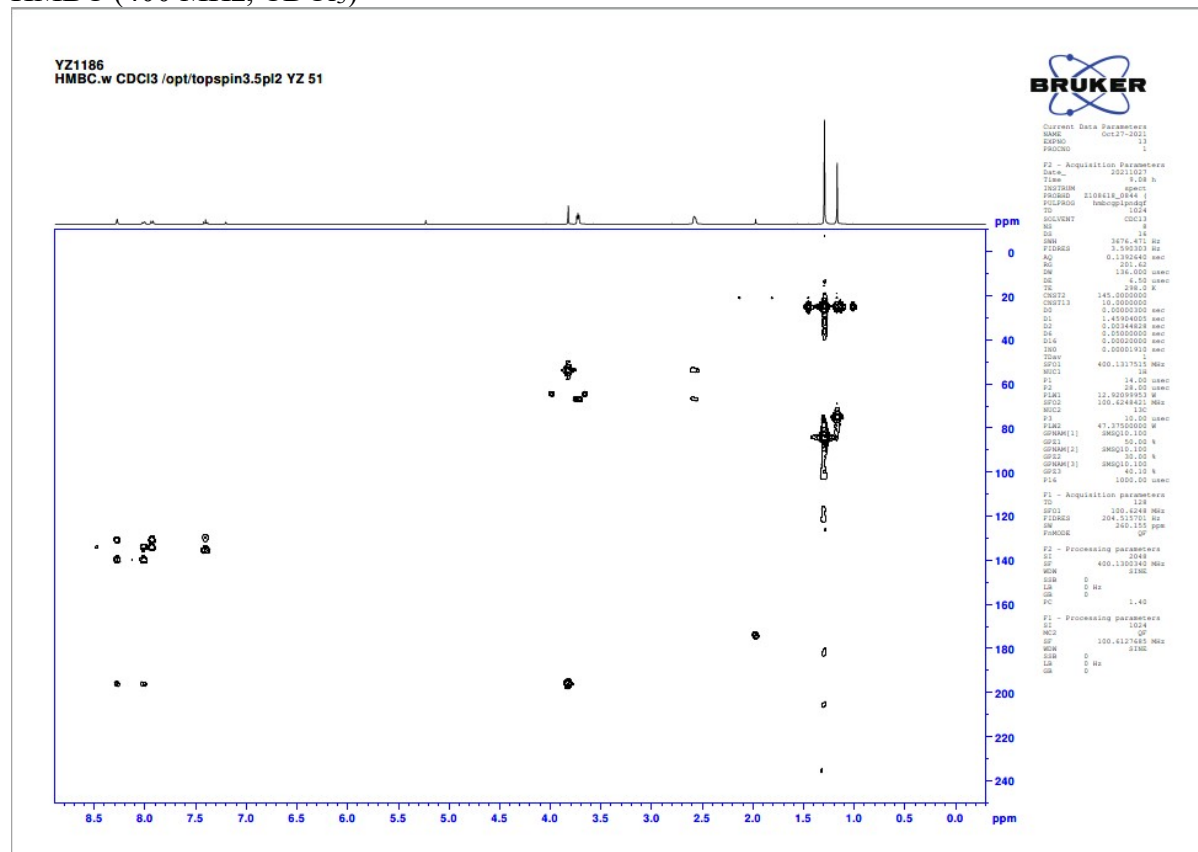
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SOLVENT CDCl₃
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FIDRES 1.795132 Hz
AQ 0.2785280 sec
RG 32.14
SW 136.000 usec
TE 298.2 K
D1 0.00000000 sec
D11 1.91607987 sec
D12 0.03000000 sec
D13 0.00000000 sec
D16 0.00000000 sec
DRO 0.00007100 sec
TDav 1
SFO1 400.1317515 MHz
NUC1 1H
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P2 14.00 usec
P3 250.00 usec
P4 12.92099953 Hz
P4B2 2.81399988 Hz
GPRM11 0.00010.100
GPRM12 0.00010.100
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D12 0.03000000 sec
D13 0.00000000 sec
D16 0.00000000 sec
DRO 0.00007100 sec
TDav 1
SFO1 400.1317515 MHz
NUC1 1H
P1 14.00 usec
P2 14.00 usec
P3 250.00 usec
P4 12.92099953 Hz
P4B2 2.81399988 Hz
GPRM11 0.00010.100
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GPRM13 0.00010.100
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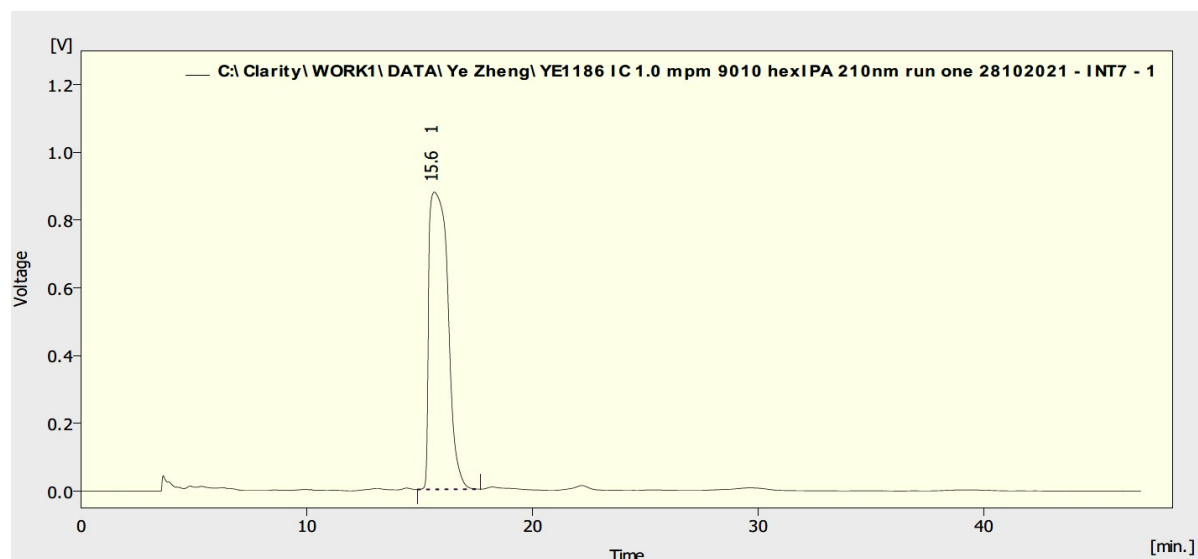
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F1 - Processing parameters
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SSB 0
LA 0 Hz
GB 0
PC 1.40

HMBC (400 MHz, CDCl₃)



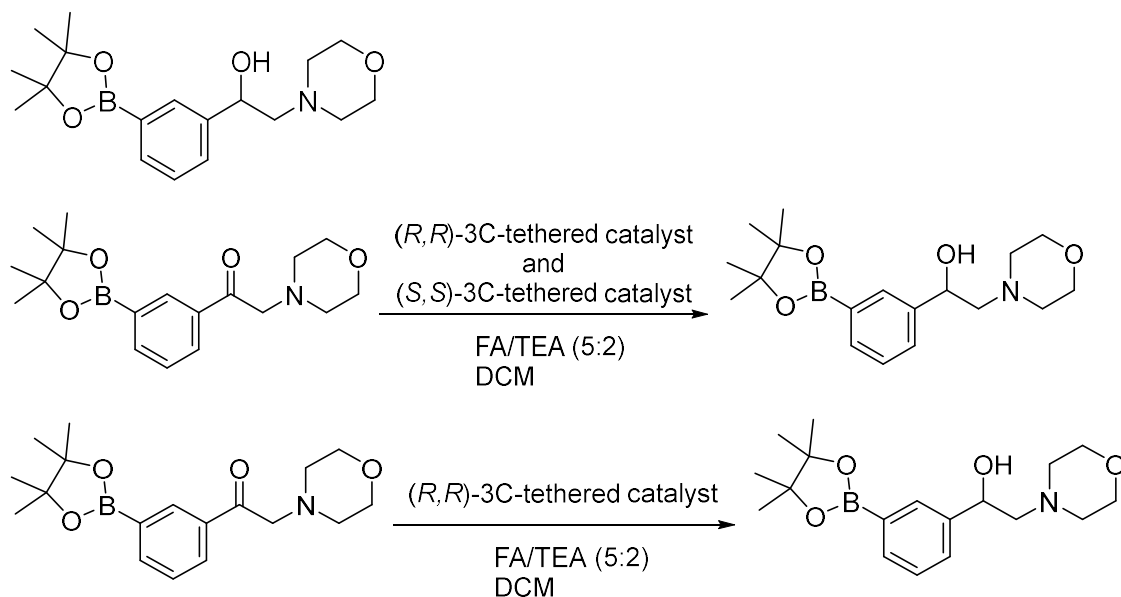
HPLC of 2-morpholino-1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one



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:

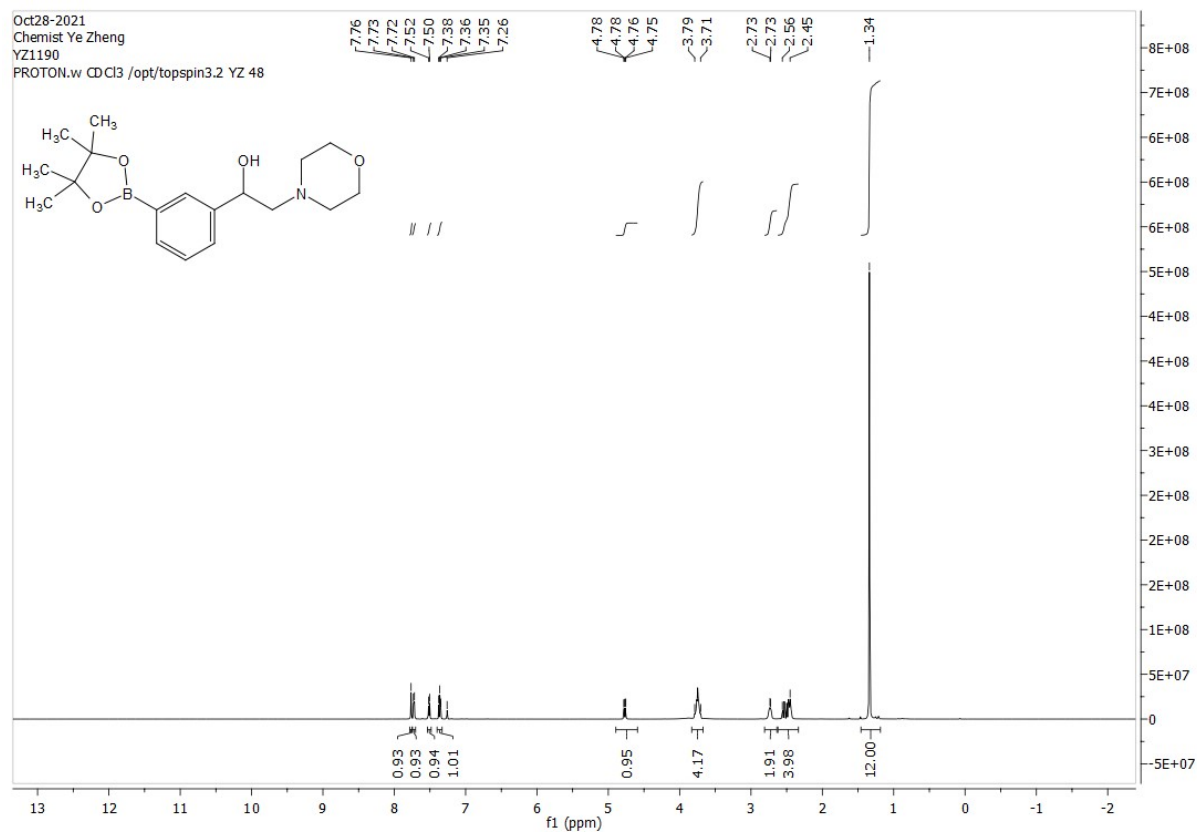
(*R,R*)-3C-Tethered Ru(II)-TsDPEN catalyst **2** (0.75 mg, 1.2 μ mol, 0.5 mol%) and (*S,S*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (0.75 mg, 1.2 μ mol, 0.5 mol%) were added to FA: TEA (5:2 azeotropic mixture, 0.36 mL) at rt and the mixture was stirred under a nitrogen atmosphere for 15 minutes; after 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 stirred under a nitrogen atmosphere and followed by TLC (5:95 MeOH: DCM). After 72 hours, the reaction was quenched using saturated NaHCO₃ 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 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: R_f ca 0.20 (5:95 MeOH: DCM), strong UV and KMnO₄; HRMS: (found (ESI⁺): [M+H]⁺, Calcd for C₁₈H₂₉BNO₄ 334.2180; Found 334.2184; 2.4 ppm error; ν_{max} 3422 (br), 3162, 2975, 2859, 1431, 1354, 1139, 1112, 1069, 1006 cm⁻¹; δ_{H} (500 MHz, CDCl₃) 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, CH₂), 2.73 (2H, d, $J = 3.8$, CH₂), 2.56-2.45 (4H, m, CH₂), 1.34 (12H, s, CH₃) ppm; δ_c (125 MHz, CDCl₃) 141.13 (C), 134.12 (CH), 132.22 (CH), 128.83 (CH), 127.92 (CH), 83.83 (C), 68.58 (CH), 67.07 (CH₂), 66.64 (CH₂), 53.44 (CH₂), 24.88 (CH₃) 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, $T = 25^\circ\text{C}$) ketone 15.6 min, *R* and *S* isomers 12.3 min and 21.1 min. Configuration assigned by analogy with **9**.

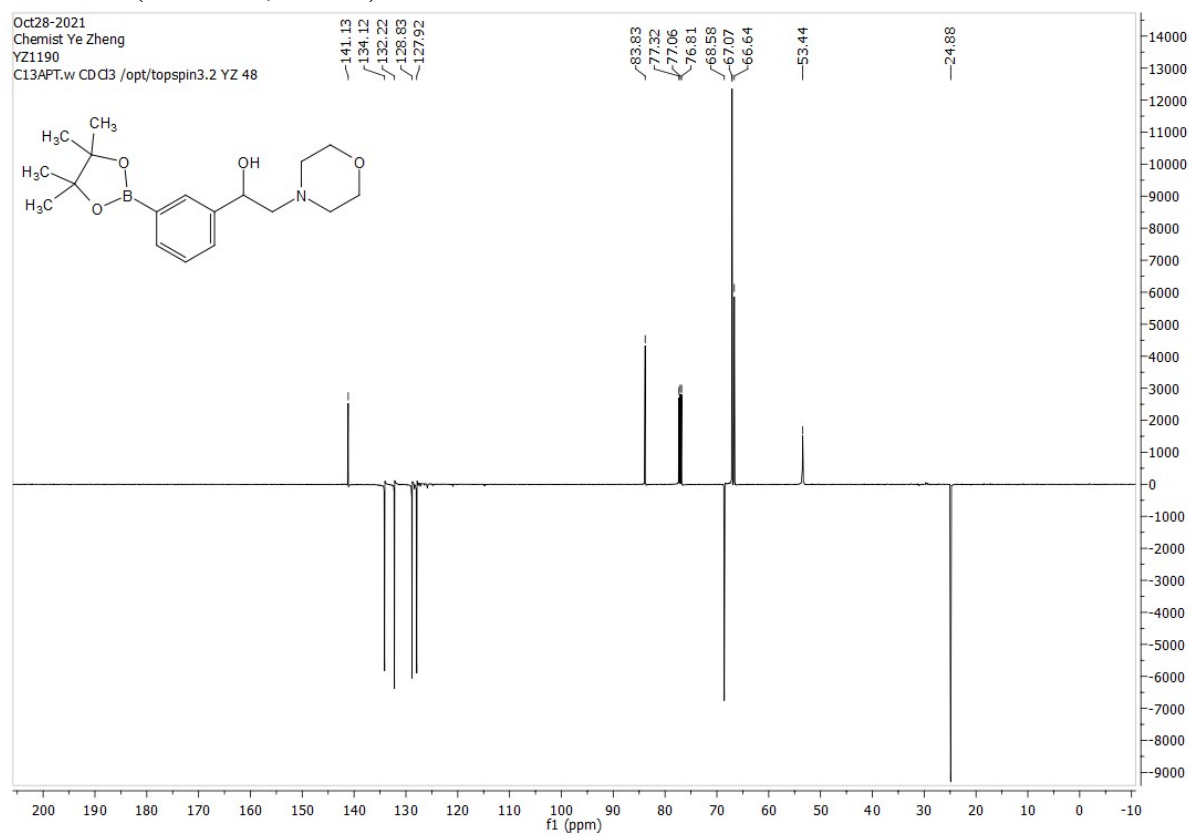
ATH of 2-morpholino-1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one:

(*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 stirred under a nitrogen atmosphere and followed by TLC (5:95 MeOH: DCM). After 72 hours, the reaction was quenched using saturated NaHCO₃ 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, $T = 25^\circ\text{C}$): $[\alpha]_D^{22} +62.0$ (c 0.300 in CHCl₃) 93% ee.

¹H NMR (500 MHz, CDCl₃)

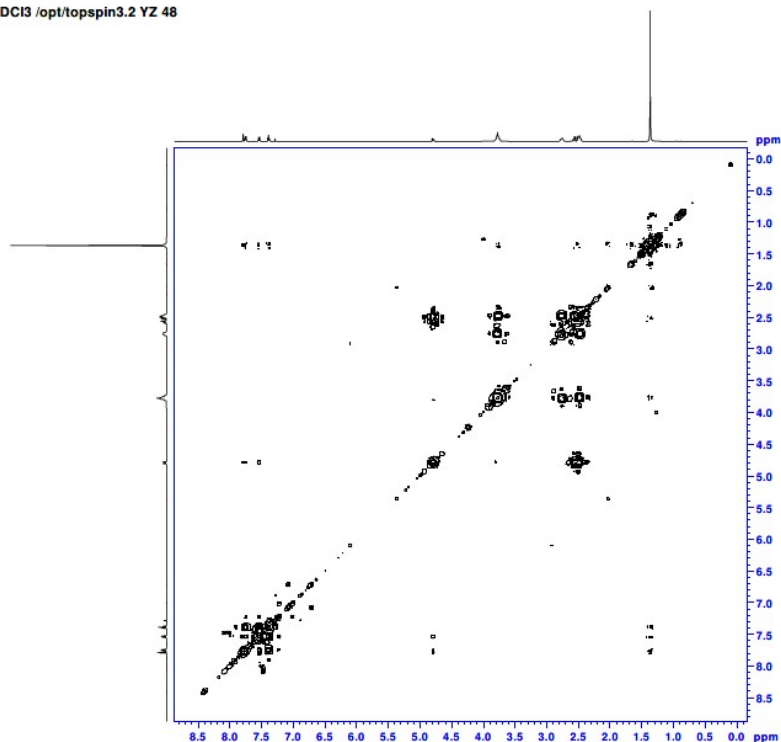


¹³C NMR (125 MHz, CDCl₃)



COSY (500 MHz, CDCl₃)

Chemist Ye Zheng
YZ1190
COSY.w CDCl₃ /opt/topspin3.2 YZ 48



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EXPNO     1
PROCNO    1

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===== GRADIENT CHANNEL =====
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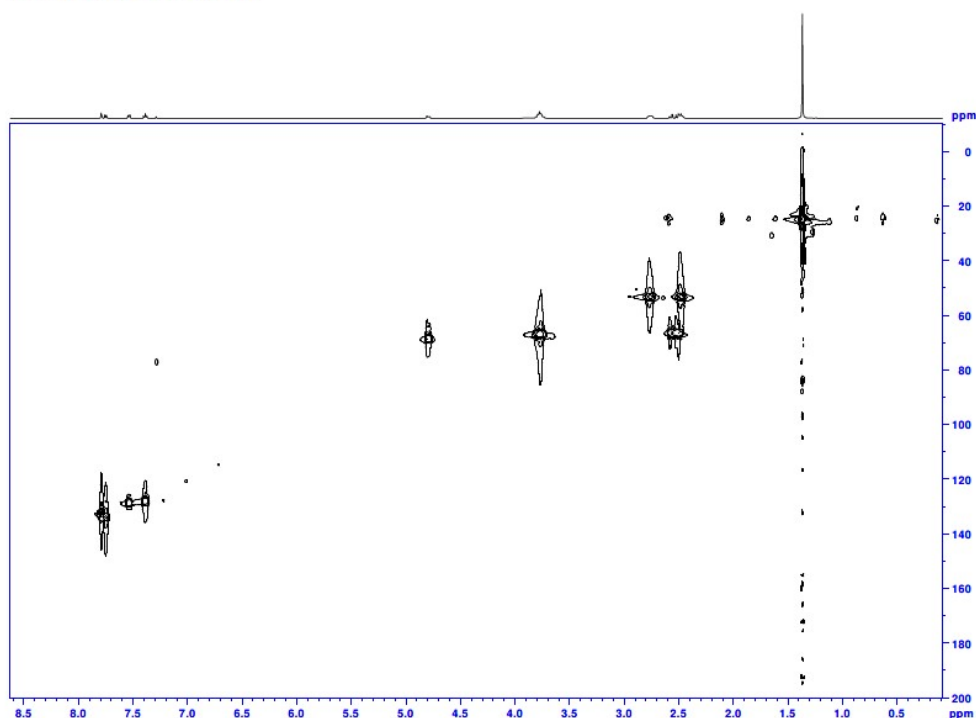
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F1 - Processing parameters
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HSQC (500 MHz, CDCl₃)

Chemist Ye Zheng
YZ1190
HSQC.w CDCl₃ /opt/topspin3.2 YZ 48



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Current Data Parameters
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EXPNO     1
PROCNO    1

F2 - Acquisition Parameters
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TE          300.2 K
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SF          500.132148 MHz
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P6          0.0000000 sec
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P8          0.0000000 sec
P9          0.0000000 sec
P10         1.5004997 sec

===== CHANNEL f1 =====
NUC1        13C
P1          9.10 usec
P2          34.20 usec
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===== GRADIENT CHANNEL =====
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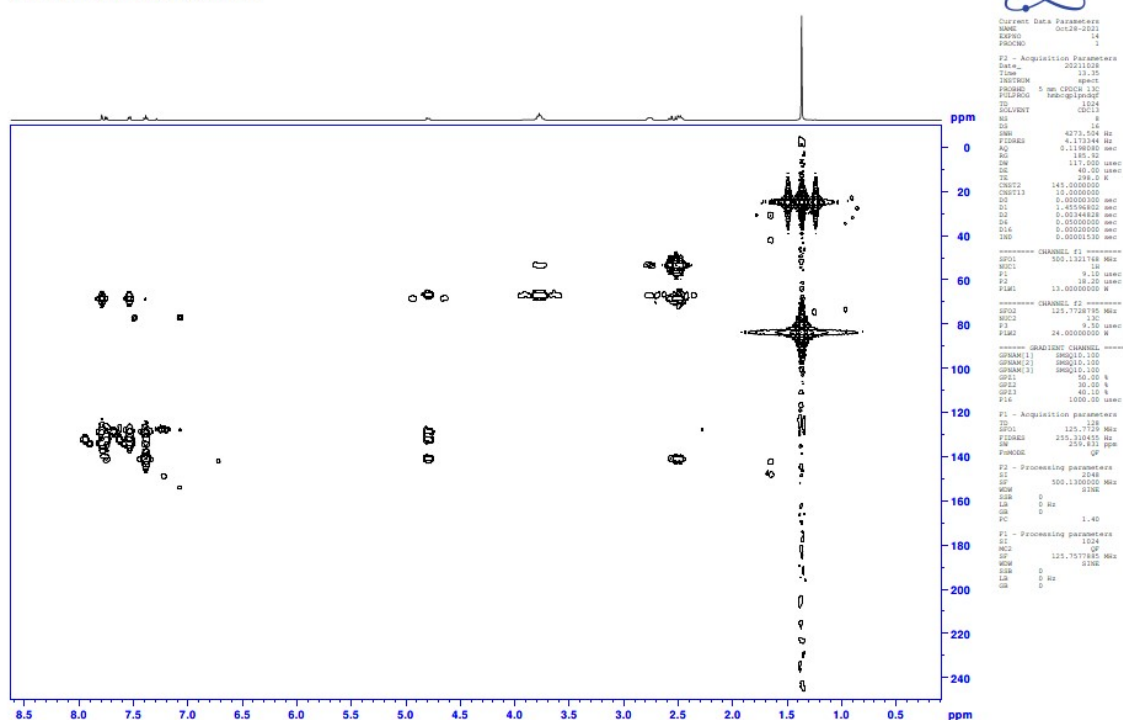
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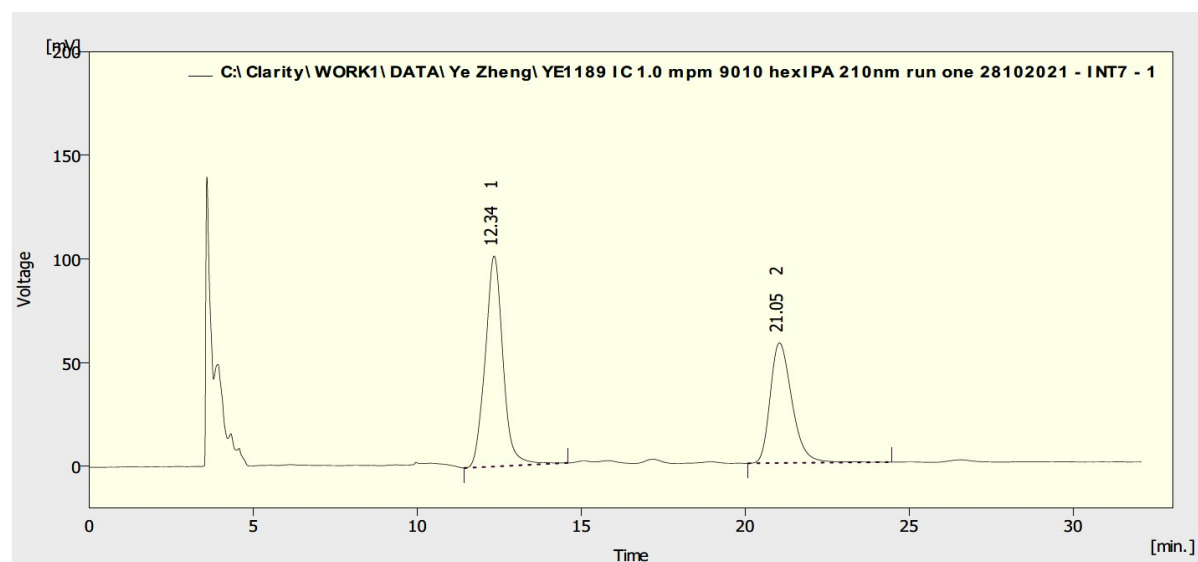
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HMBC (500 MHz, CDCl₃)

Chemist Ye Zheng
YZ1190
HMBC.w CDCl₃ /opt/topspin3.2 YZ 48



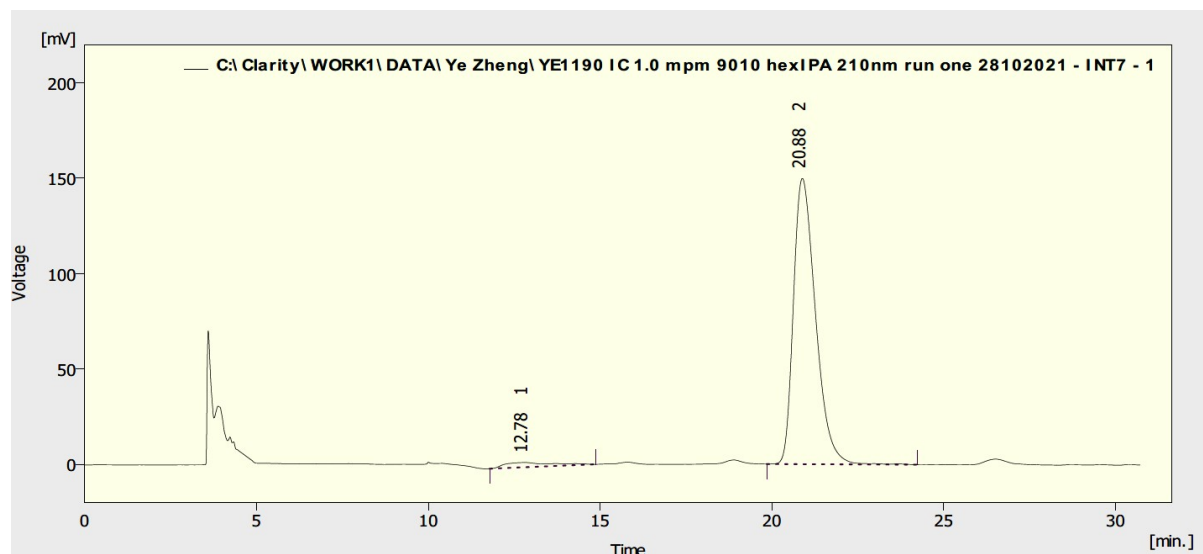
HPLC of racemic 2-morpholino-1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol **11**.



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		

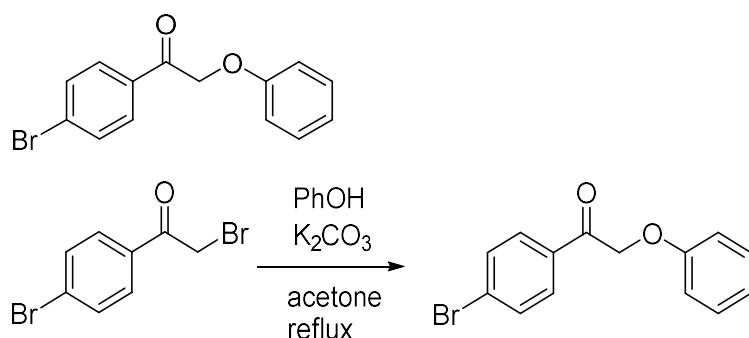
HPLC after ATH of 2-morpholino-1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one using (*R,R*)-3C-Tethered Ru(II)-TsDPEN catalyst **2** (after 72 hours, 100% conversion, 93% ee).



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.

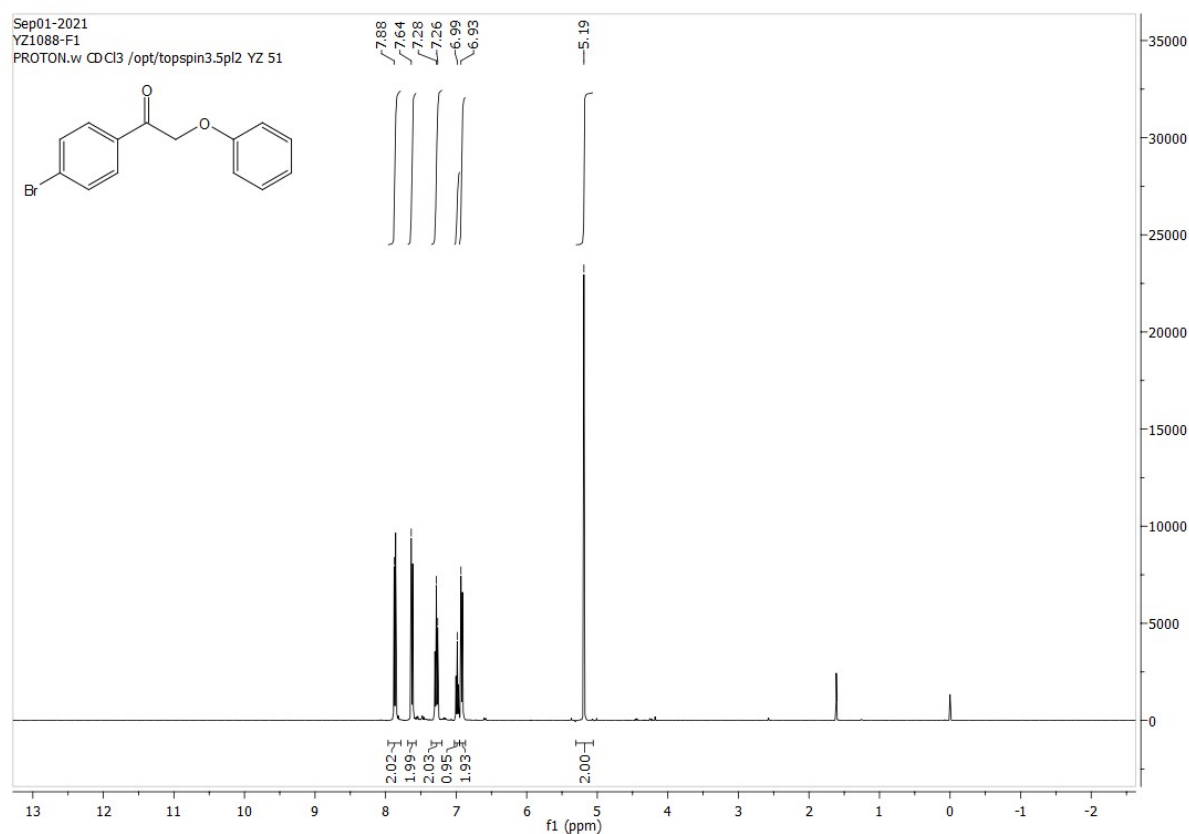


This compound has been reported and fully characterized. Reference: K. Gao, M. Xu, C. Cai, Y. Ding, J. Chen, B. Liu, Y. Xia, *Org. Lett.* 2020, **22**, 6055-6060.

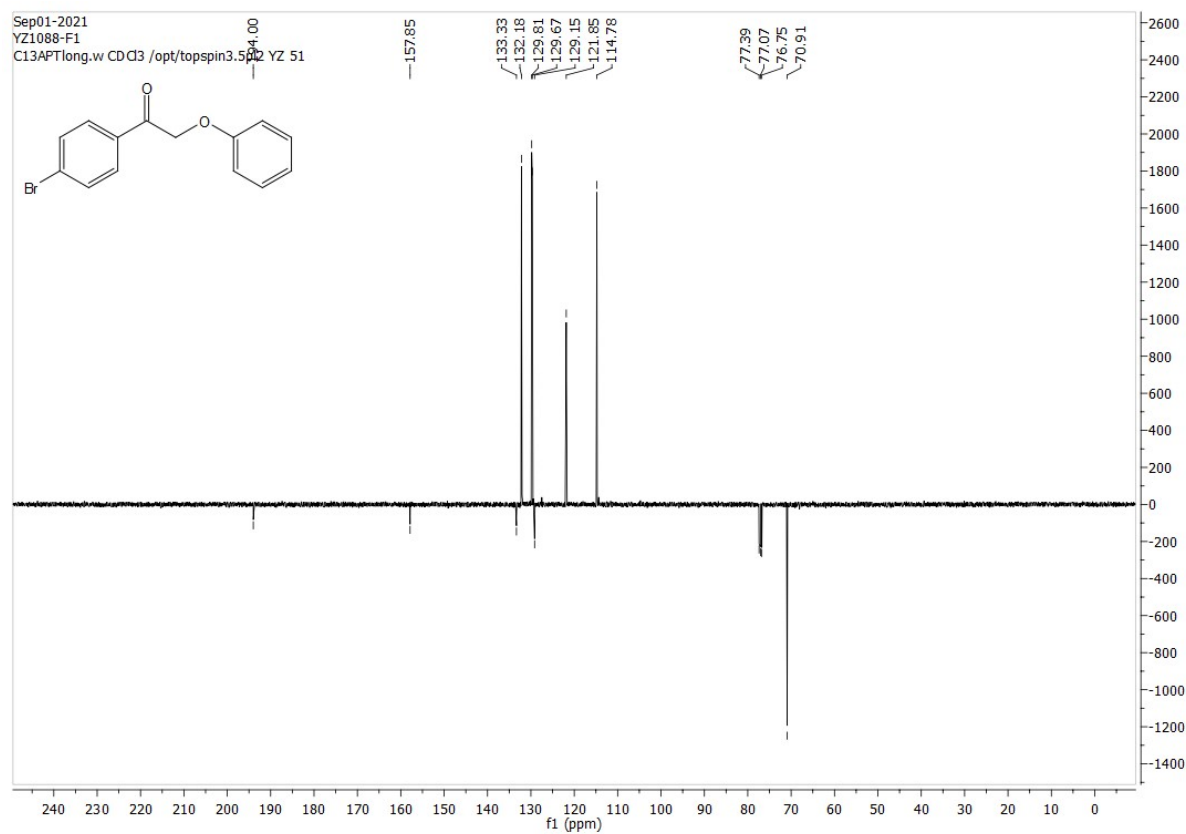
A round-bottom flask was charged with 2,4'-dibromoacetophenone (834 mg, 3.00 mmol), potassium carbonate (414 mg, 3.00 mmol), phenol (282 mg, 3.00 mmol) and acetone (2 mL). The reaction mixture was heated to reflux and left stirring under the nitrogen atmosphere overnight, followed by TLC (9:1 hexane: 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 (MgSO₄) 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: R_f ca 0.50 (9:1 hexane: EtOAc), strong UV and KMnO₄; δ_H (400 MHz, CDCl₃) 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, CH₂) ppm; δ_C (100 MHz, CDCl₃) 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 (CH₂) ppm; *m/z* (ES-API⁺) 313.0 (M⁺ + 23, 100%). Data matched that reported.

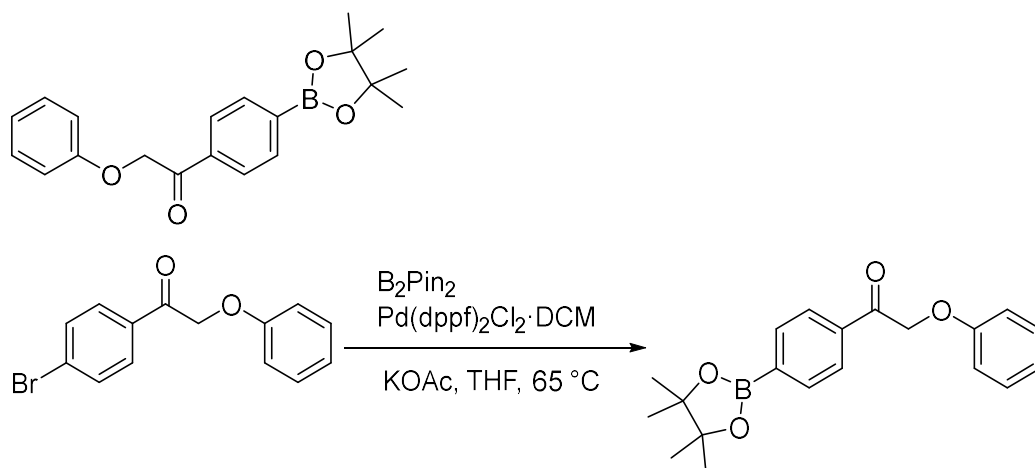
^1H NMR (400 MHz, CDCl_3)



^{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.

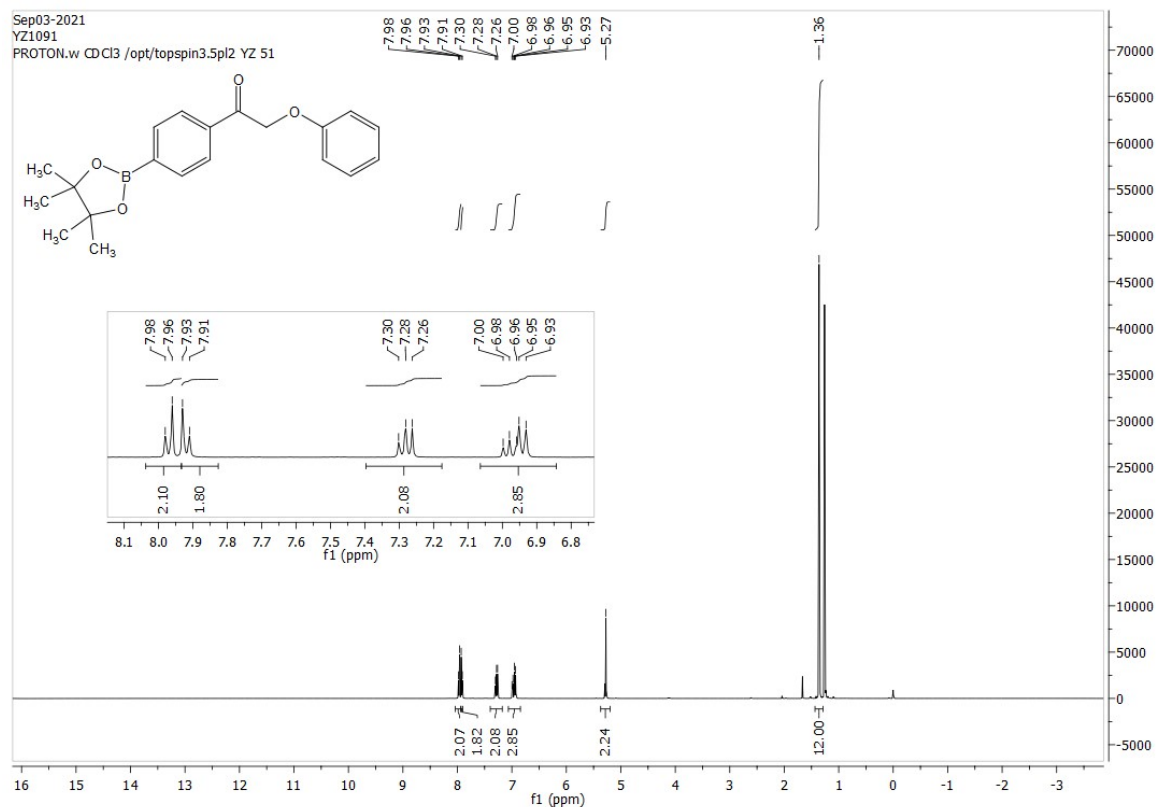


This compound is novel.

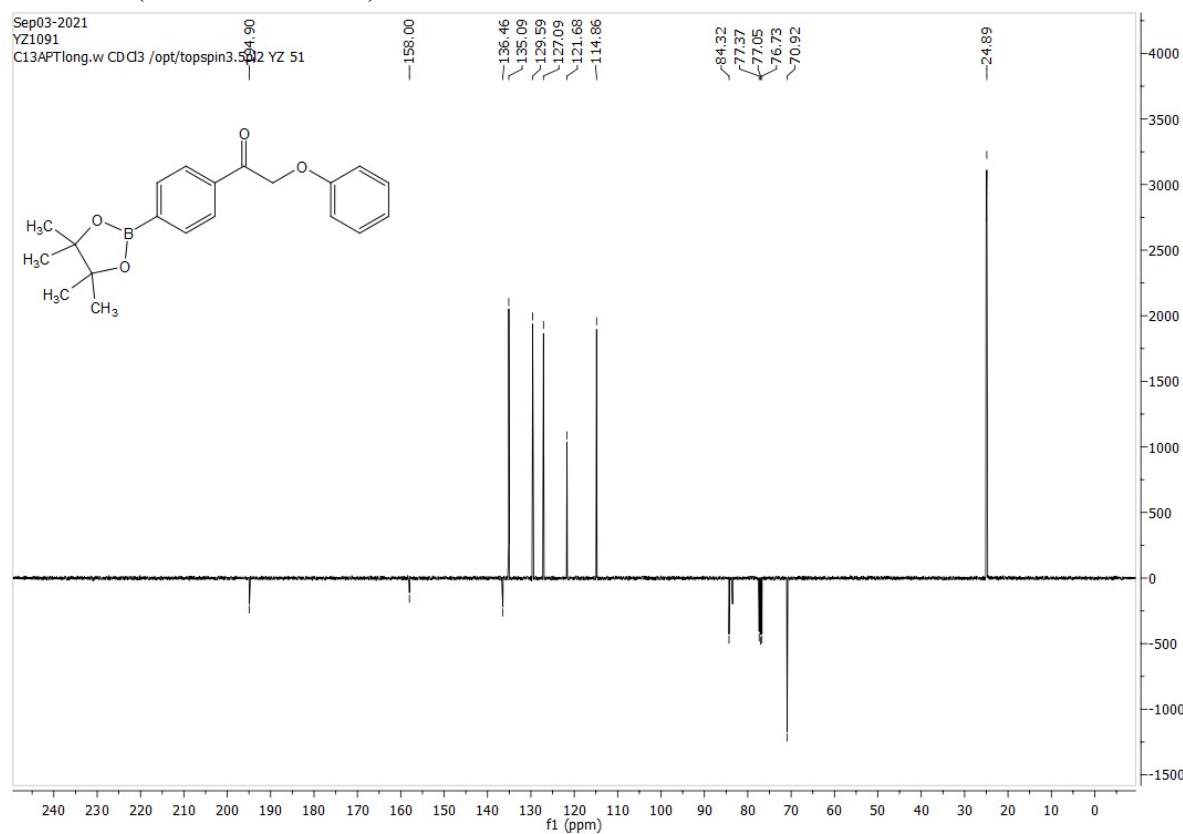
A round-bottom flask was charged with 1-(4-bromophenyl)-2-phenoxyethan-1-one (860 mg, 2.97 mmol), bis(pinacolato)diboron (904 mg, 3.56 mmol), potassium acetate (873 mg, 8.91 mmol), THF (15 mL) and $\text{Pd}(\text{dppf})_2\text{Cl}_2 \cdot \text{DCM}$ (122 mg, 0.149 mmol). The reaction mixture was heated 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: R_f ca 0.40 (9:1 hexane: EtOAc), strong UV and KMnO_4 ; HRMS: (found (ESI⁺): $[\text{M}+\text{H}]^+$, Calcd for $\text{C}_{20}\text{H}_{23}\text{BNaO}_4$ 361.1577; Found 361.1582; 2.2 ppm error; ν_{max} 2978, 2931, 1704, 1599, 1495, 1356, 1303, 1211, 1142, 1122, 1086, 961 cm^{-1} ; δ_{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; δ_{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 ($\text{M}^+ + 23$, 100%).

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

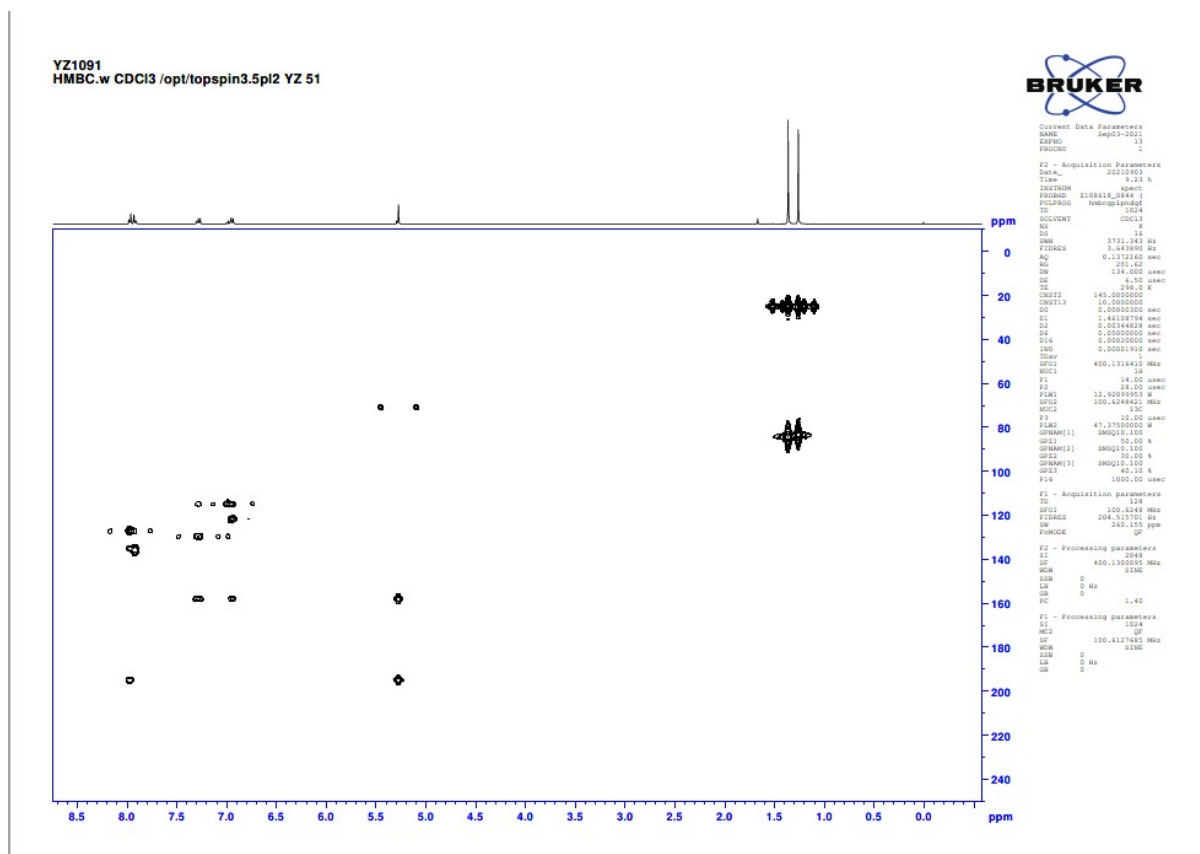
^1H NMR (400 MHz, CDCl_3)



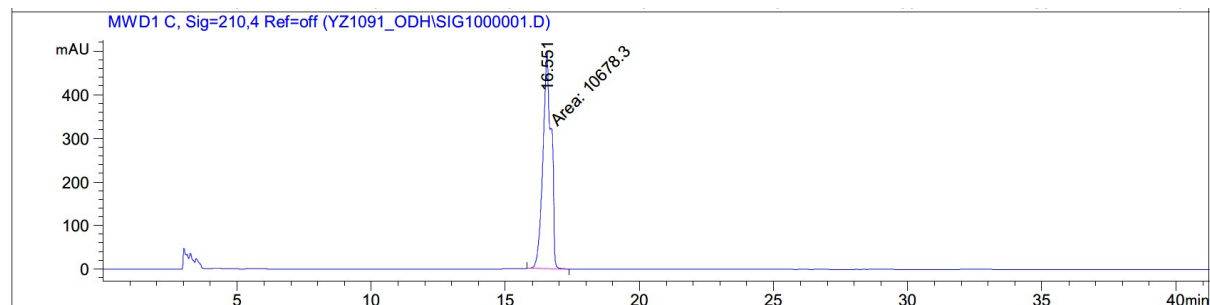
^{13}C NMR (100 MHz, CDCl_3)



COSY (400 MHz, CDCl_3)



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

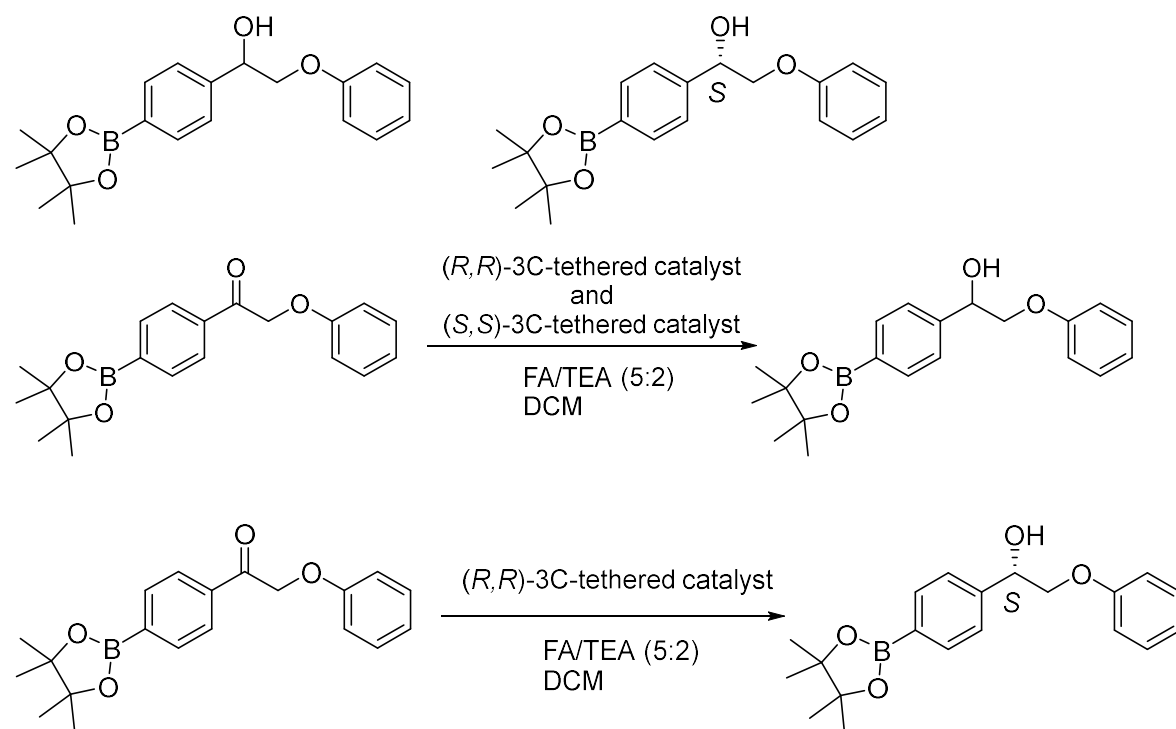


Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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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 μ mol, 0.5 mol%) and (*S,S*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (1.1 mg, 1.8 μ mol, 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 stirred under a nitrogen atmosphere and followed by TLC (4:1 hexane: EtOAc). After 72 hours, the reaction was quenched using saturated NaHCO₃ 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 0-20% 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: R_f ca 0.20 (4:1 hexane: EtOAc), strong UV and KMnO₄; HRMS: (found (ESI⁺): [M+H]⁺, Calcd for C₂₀H₂₅BNaO₄ 363.1741; Found 363.1738; 0.3 ppm error; ν_{max} 3461 (br), 2977, 2928, 1599, 1495,

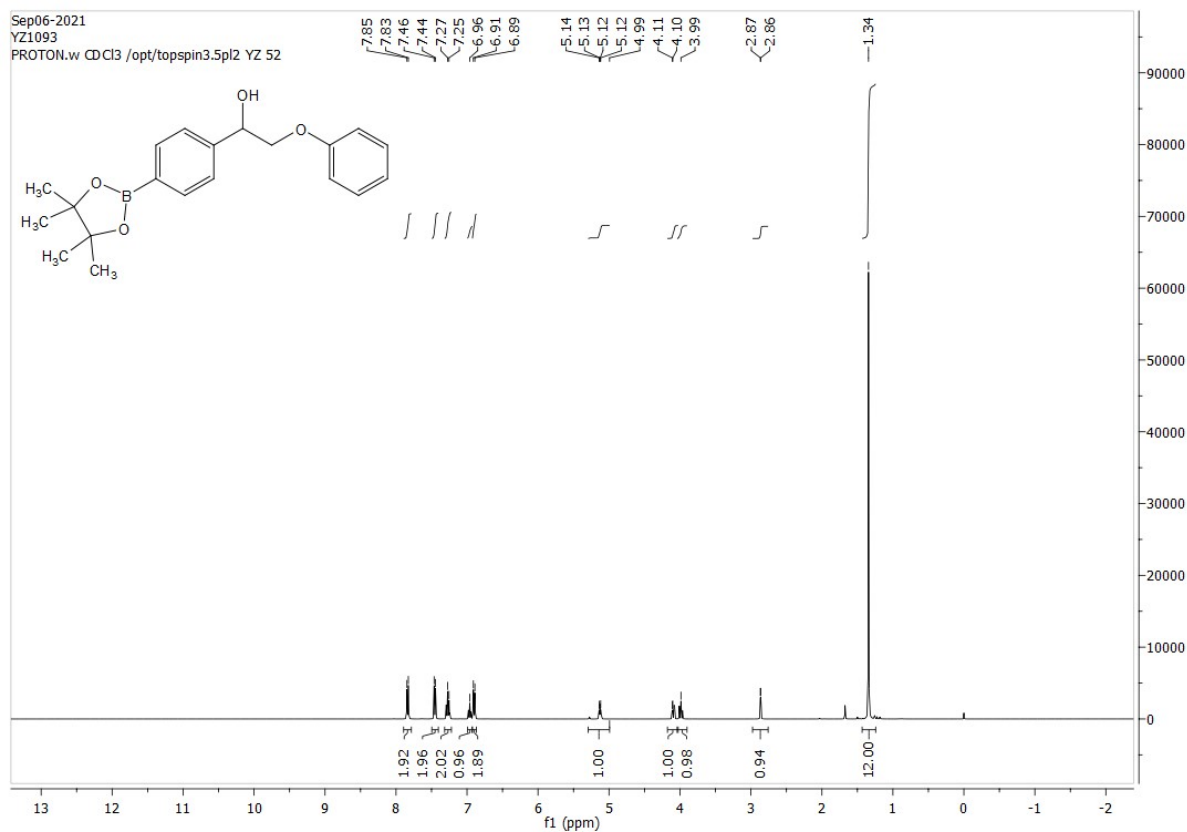
1397, 1357, 1241, 1141, 1086, 1019, 731 cm^{-1} ; δ_{H} (400 MHz, CDCl_3) 7.85 (2H, d, $J = 7.8$, ArH), 7.46 (2H, d, $J = 7.8$, ArH), 7.27 (2H, t, $J = 7.8$, ArH), 6.96 (1H, t, $J = 7.3$, ArH), 6.91 (2H, d, $J = 8.3$, ArH), 5.13 (1H, dd, $J = 6.1, 2.6$, ArCH), 4.10 (1H, dd, $J = 9.6, 3.1$, CH_2), 3.99 (1H, t, $J = 9.2$, CH_2), 2.87 (1H, d, $J = 2.6$, OH), 1.34 (12H, s, CH_3) ppm; δ_{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 ($\text{M}^+ + 23$, 100%).

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

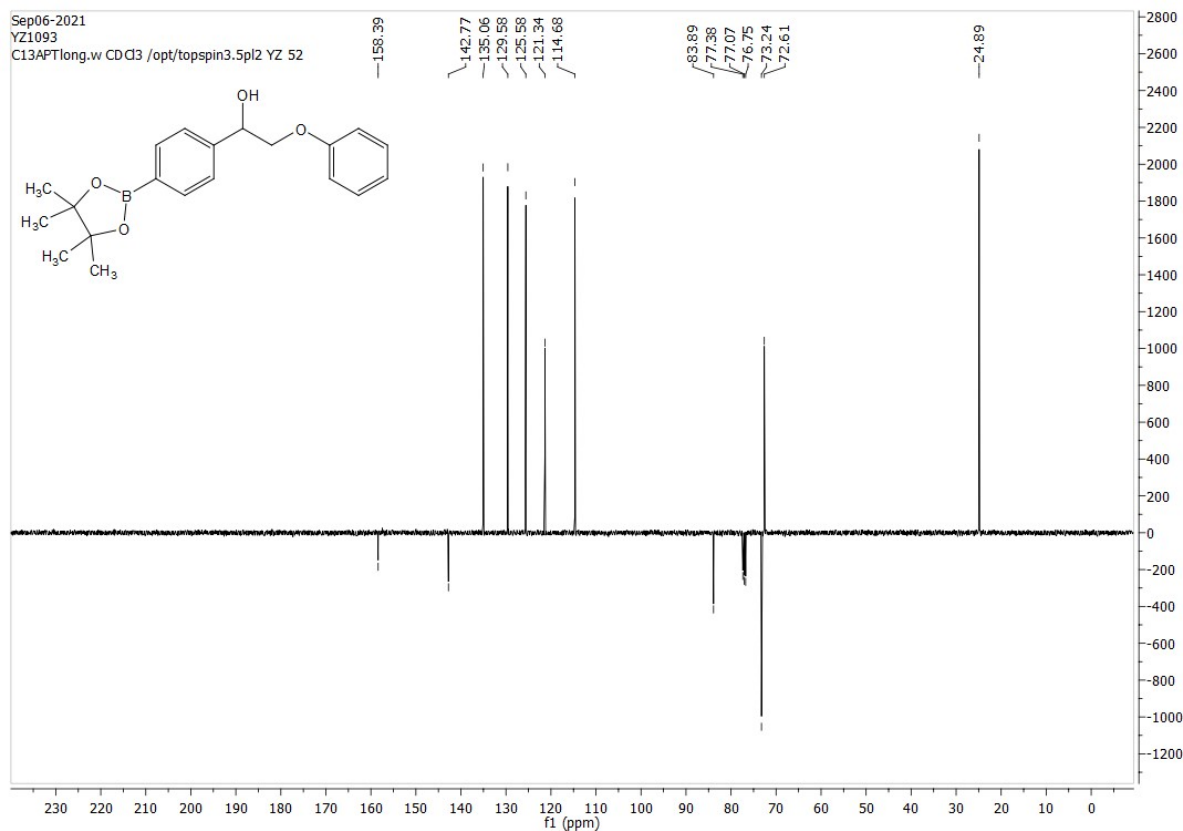
ATH of 2-phenoxy-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one:

(*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, $T = 25^\circ\text{C}$): $[\alpha]_{\text{D}}^{26} +31.3$ (c 0.408 in CHCl_3) 97% ee (*S* configuration, confirmed by methylation, as described below).

¹H NMR (400 MHz, CDCl₃)



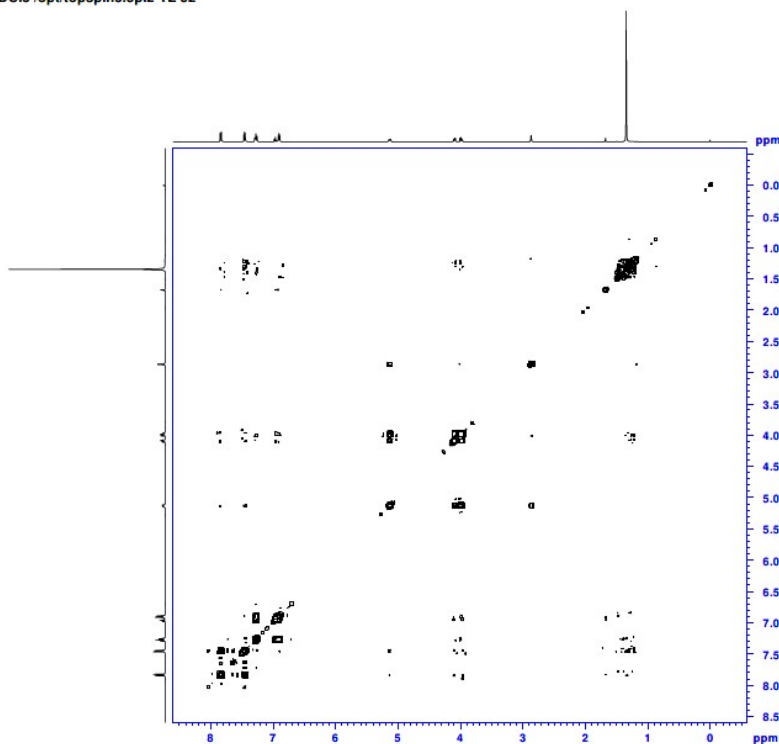
¹³C NMR (100 MHz, CDCl₃)



COSY (400 MHz, CDCl₃)

YZ1093
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YE1094 ODH 1.0 mpm 9505 hexIPA run one 06092021.pdf



Current Data Parameters
NAME Sep04-2021
EXPNO 22
PROCNO 1

F2 - Acquisition Parameters
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SOLVENT CDCl₃
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DS 4
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FIDRES 1.795152 Hz
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D12 0.0000000 sec
D13 0.0000000 sec
D16 0.0000000 sec
DRO 0.0000000 sec
TDav 1
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NUC1 13
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P7 10.00 %
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P9 1.40

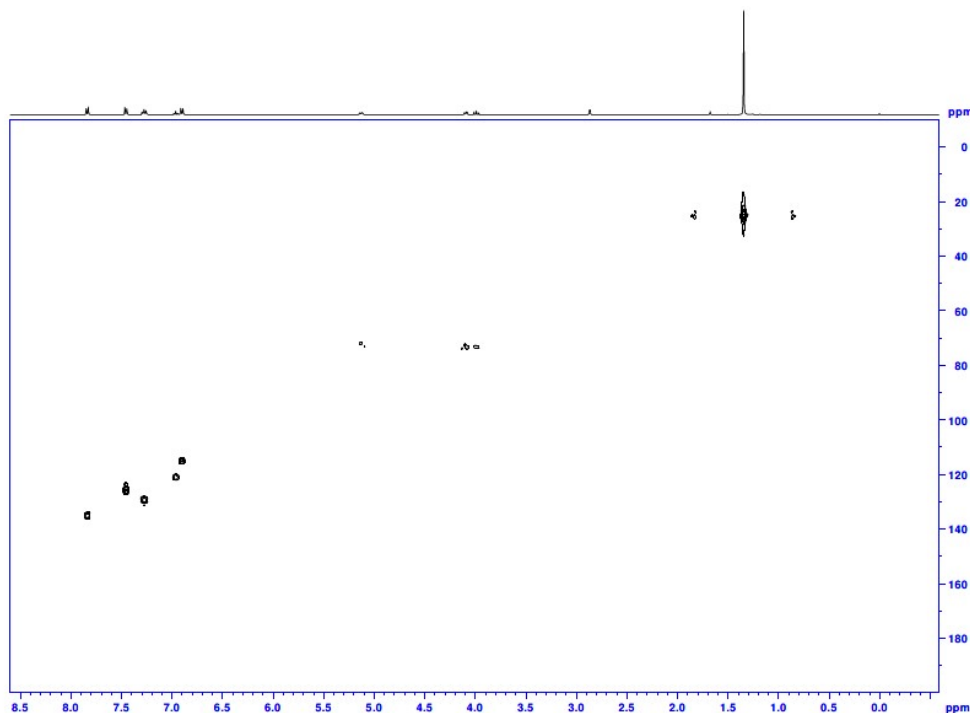
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F2 - Processing parameters
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WDW 0
SSB 0
LB 0 Hz
GB 0
PC 1.40

F1 - Processing parameters
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HSQC (400 MHz, CDCl₃)

YZ1093
HSQC.w CDCl₃ /opt/topspin3.5pl2 YZ 52



Current Data Parameters
NAME Sep04-2021
EXPNO 22
PROCNO 1

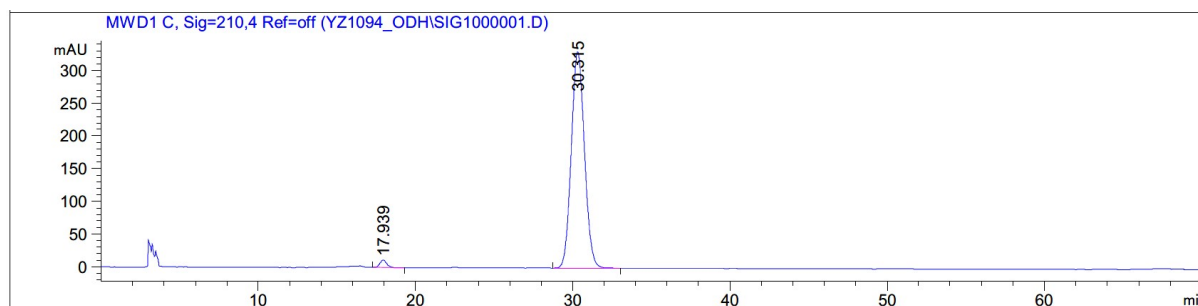
F2 - Acquisition Parameters
Date_ 20210904
Time 10:15 h
INSTRUM spect
PROBHD 1H/13C/15N
PULPROG zgpg30
SOLVENT CDCl₃
NS 4
DS 4
SWH 3676.471 Hz
FIDRES 1.795152 Hz
AQ 0.1785280 sec
RG 32.14
AQ 136.000 usec
DE 6.50 usec
TE 298.2 K
D0 0.0000000 sec
D1 1.9187895 sec
D11 0.0000000 sec
D12 0.0000000 sec
D13 0.0000000 sec
D16 0.0000000 sec
DRO 0.0000000 sec
TDav 1
SFO1 400.1314194 MHz
NUC1 13
P1 14.00 usec
P2 14.00 usec
P3 2500.00 usec
P4 12.9209953 M
P5 2.9239988 M
P6 10.00 %
P7 10.00 %
P8 1000.00 usec
P9 1.40

F1 - Acquisition parameters
TD 128
SFO1 400.1314 MHz
FIDRES 29.122417 Hz
SW 9.188 ppm
FWDDE 0

F2 - Processing parameters
SI 324
SF 400.1305170 MHz
WDW 0
SSB 0
LB 0 Hz
GB 0
PC 1.40

F1 - Processing parameters
SI 1024
SF 400.1305170 MHz
WDW 0
SSB 0
LB 0 Hz
GB 0
PC 1.40

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).

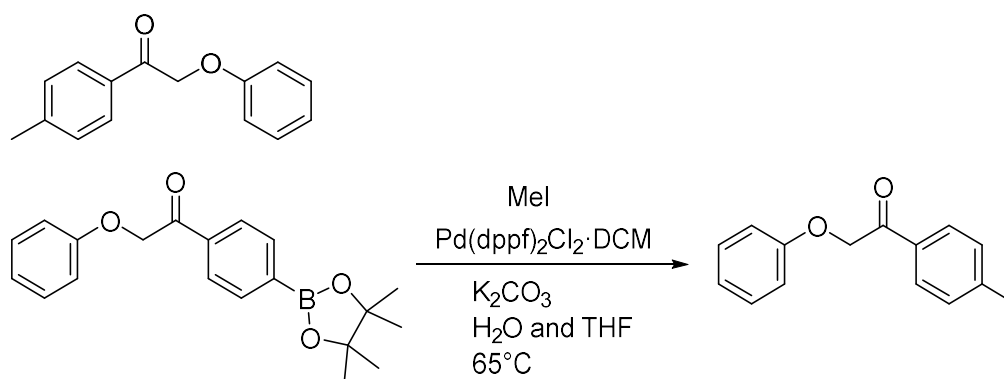


Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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

2-Phenoxy-1-(*p*-tolyl)ethan-1-one **20**.

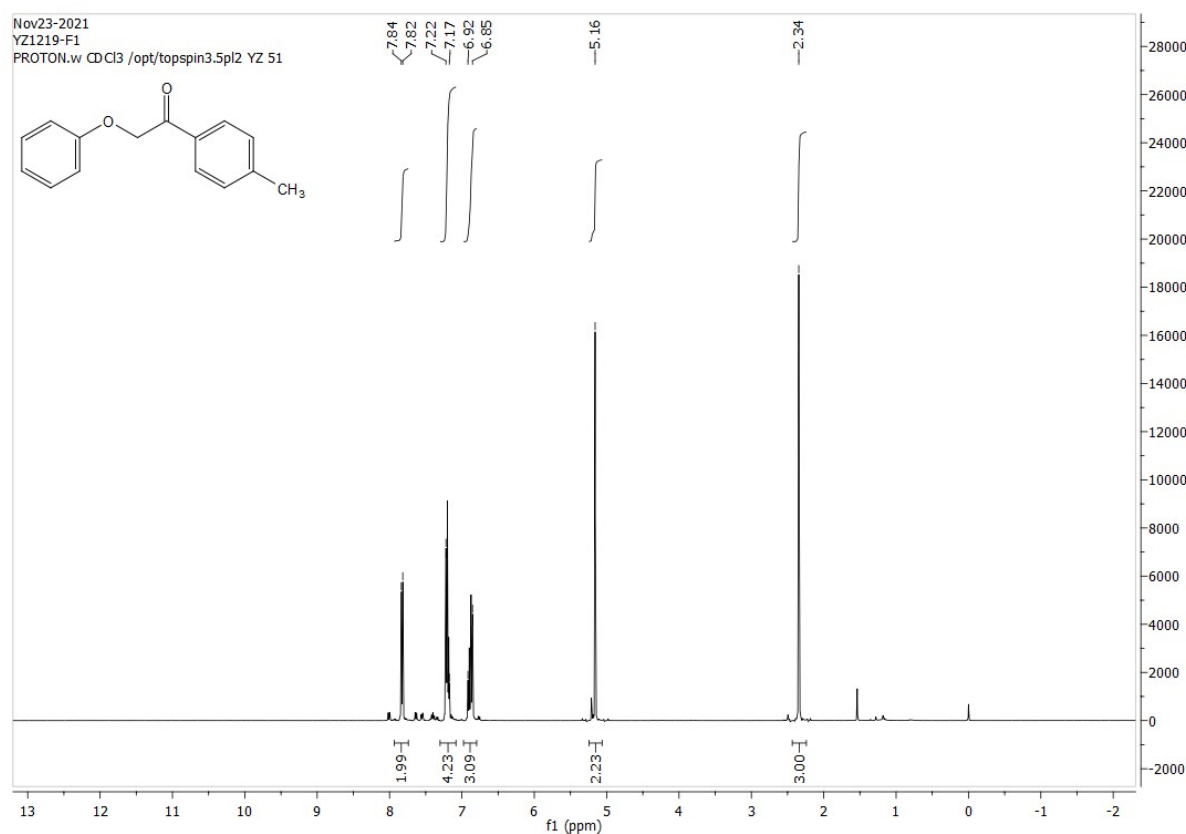


This compound has been reported and fully characterized: Y. Zhou, G. E. Klinger, E. L. Hegg, C. M. Saffron, J. E. Jackson, *J. Am. Chem. Soc.* 2020, **142**, 4037-4050.

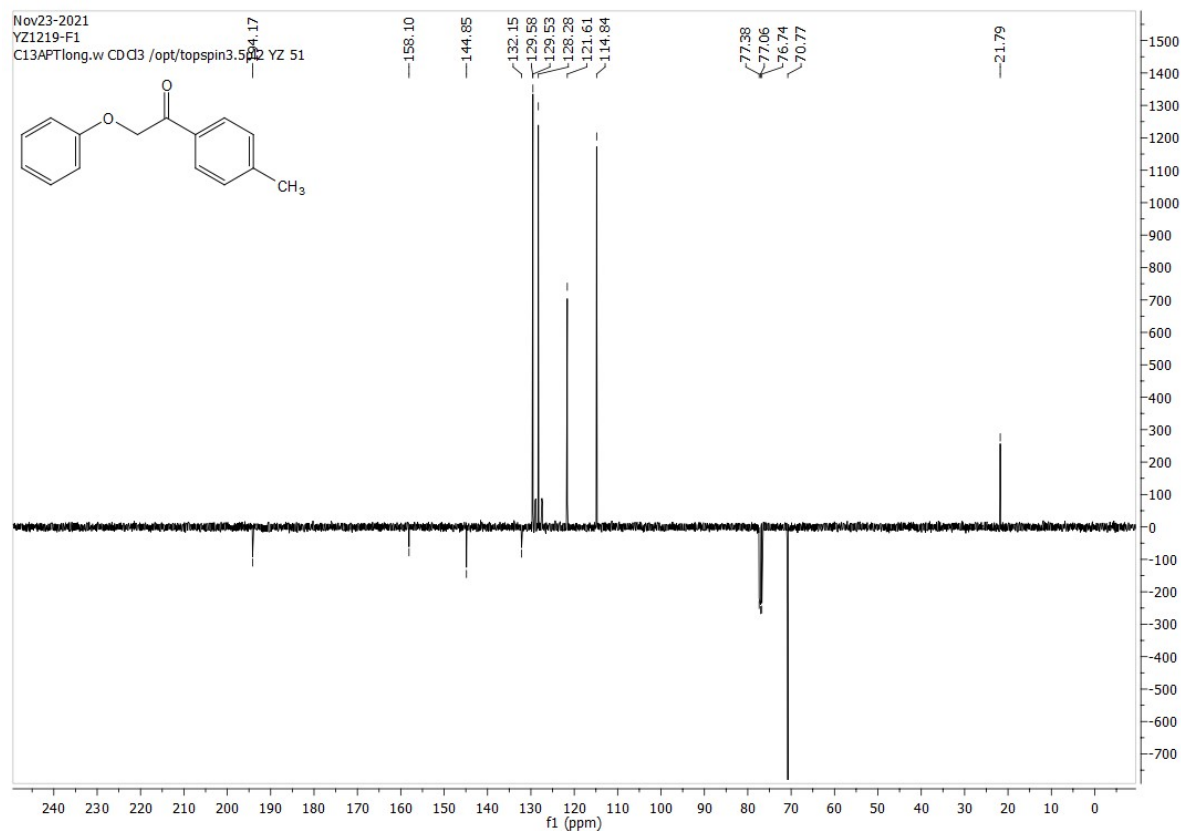
To a solution of 2-phenoxy-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one (680 mg, 2.00 mmol), iodomethane (568 mg, 4.00 mmol) and potassium carbonate (552 mg, 4.00 mmol) in THF (38 mL) was added Pd(dppf)₂Cl₂·DCM (81.7 mg, 0.100 mmol) and distilled water (0.258 mL). The reaction 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 (MgSO₄) 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: R_f ca 0.50 (9:1 hexane: EtOAc), strong UV and KMnO₄; δ_H (400 MHz, CDCl₃) 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, CH₂), 2.34 (3H, s, CH₃) ppm; δ_C (100 MHz, CDCl₃) 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 (CH₂), 21.19 (CH₃) 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:*i*PrOH 90:10, 1.0 mL/min, T = 25°C) ketone 15.8 min, *R* isomer 11.3 min and *S* isomer 20.4 min.

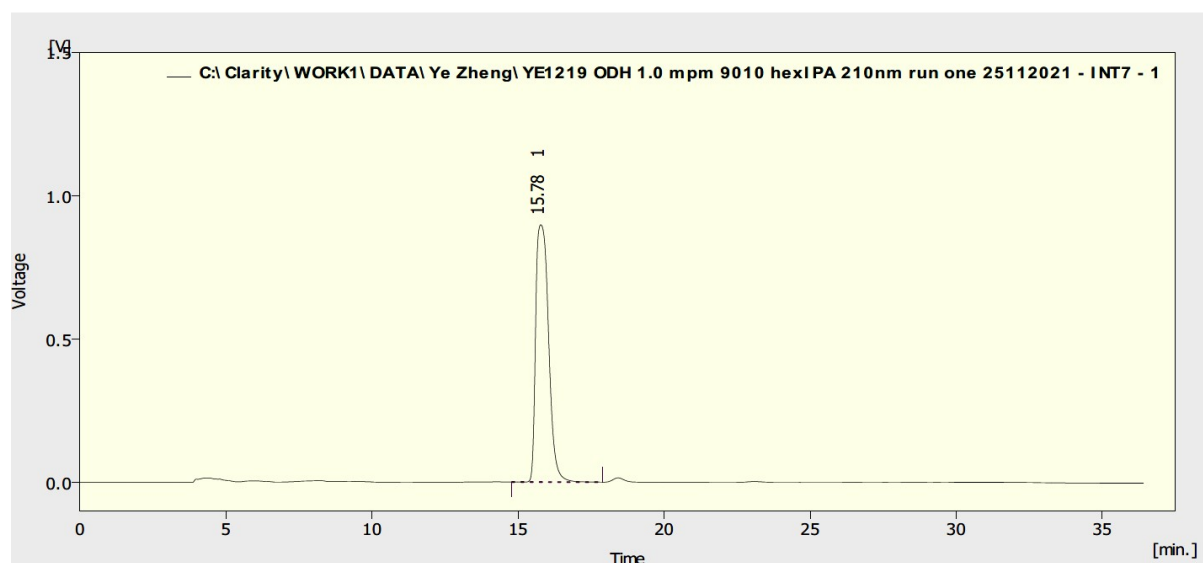
^1H NMR (400 MHz, CDCl_3)



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



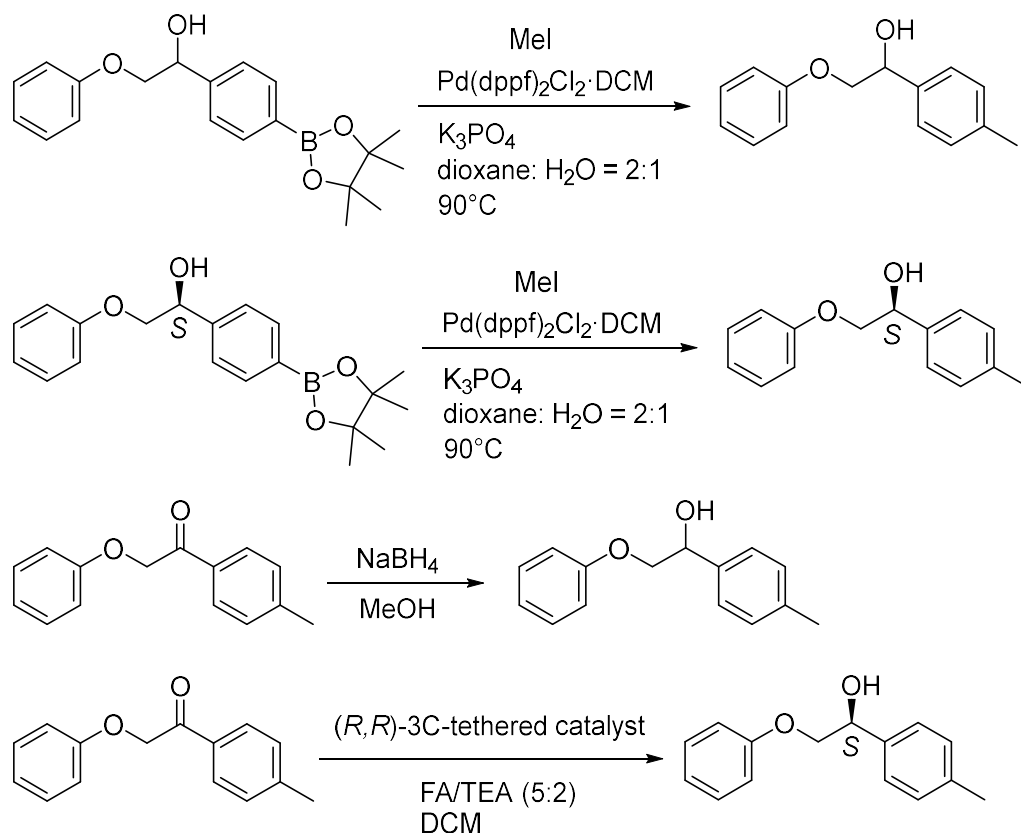
HPLC of 2-phenoxy-1-(p-tolyl)ethan-1-one **20**



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 $\text{Pd(dppf)}_2\text{Cl}_2 \cdot \text{DCM}$ (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: R_f ca 0.40 (9:1 hexane: EtOAc), strong UV and KMnO₄; δ_{H} (400 MHz, CDCl₃) 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, CH₂), 4.00 (1H, t, J = 9.2, CH₂), 2.73 (1H, s, OH), 2.36 (3H, s, CH₃) ppm; δ_{C} (100 MHz, CDCl₃) 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 (CH₂), 72.46 (CH), 21.19 (CH₃) 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)₂Cl₂·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 (MgSO₄) 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): $[\alpha]_{\text{D}}^{23}$ +113 (c 0.300 in CHCl₃) 96% ee (*S*) (lit. $[\alpha]_{\text{D}}^{20}$ +43 (c 1.2 in CHCl₃) 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 NaBH₄ reduction of ketone)

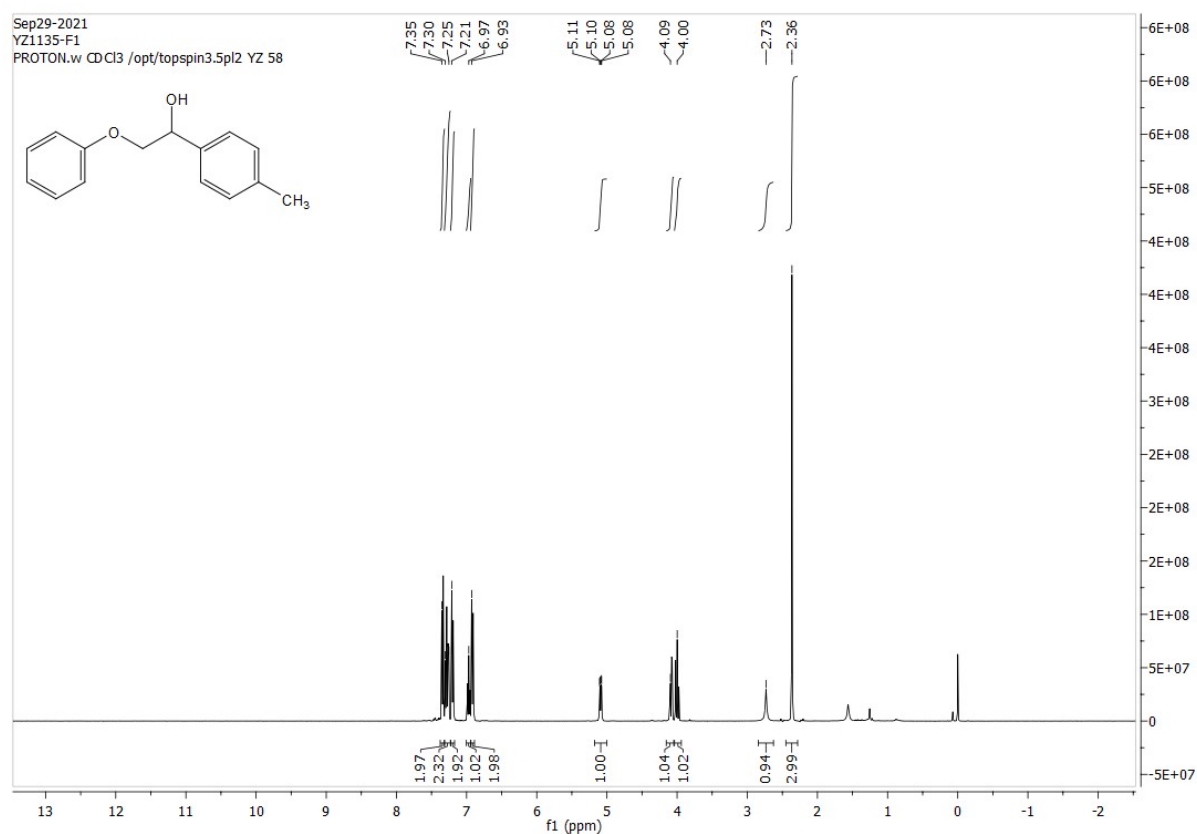
To a solution of 2-phenoxy-1-(*p*-tolyl)ethan-1-one **20** (50.0 mg, 0.221 mmol) in MeOH (1.1 mL) was added sodium borohydride (16.8 mg, 0.442 mmol). The reaction

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 × 20 mL), dried with MgSO₄, 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%).

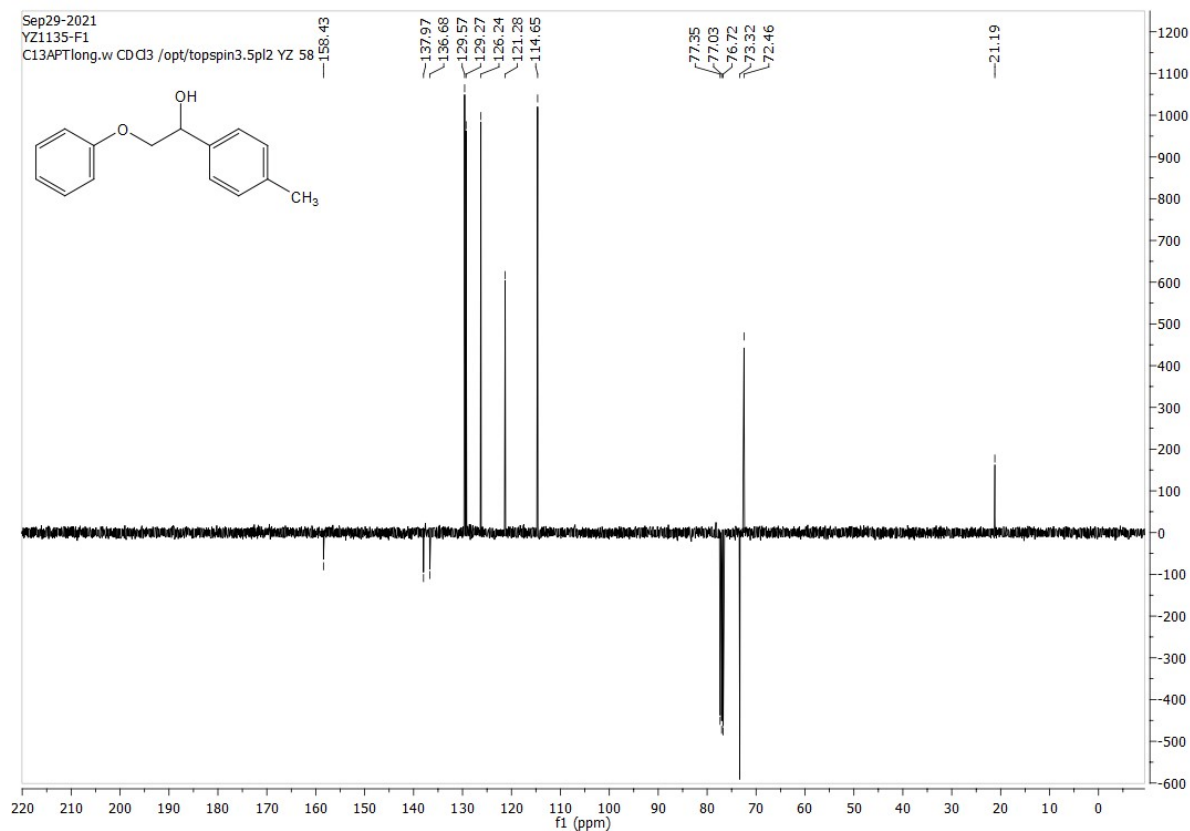
ATH of 2-phenoxy-1-(*p*-tolyl)ethan-1-one **20**.

(*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 stirred under a nitrogen atmosphere and followed by TLC (4:1 hexane: EtOAc). After 72 hours, the reaction was quenched using saturated NaHCO₃ 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 (MgSO₄) 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*).

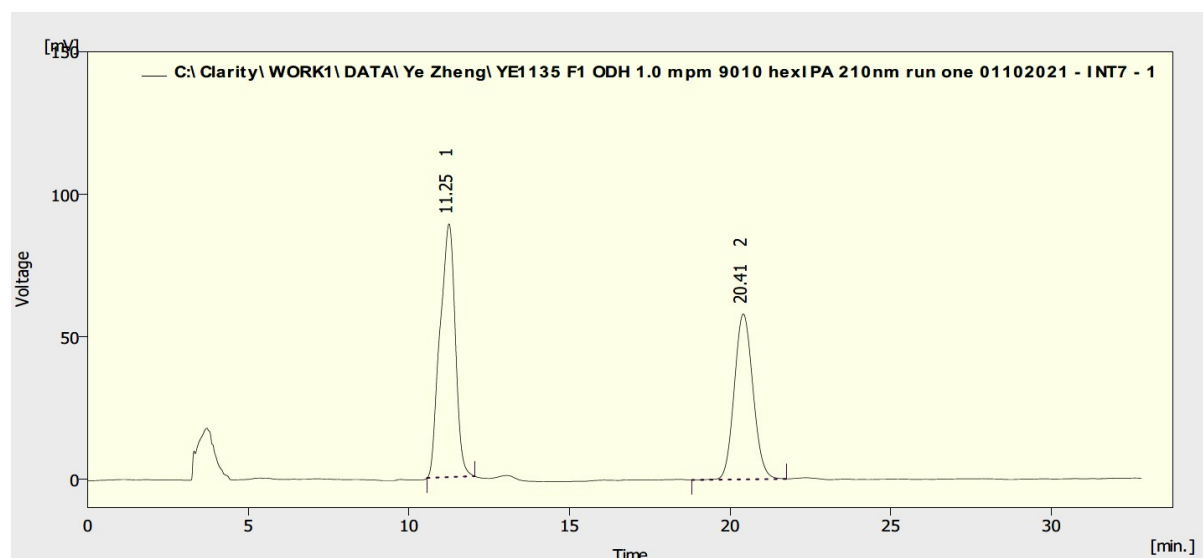
^1H NMR (400 MHz, CDCl_3)



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



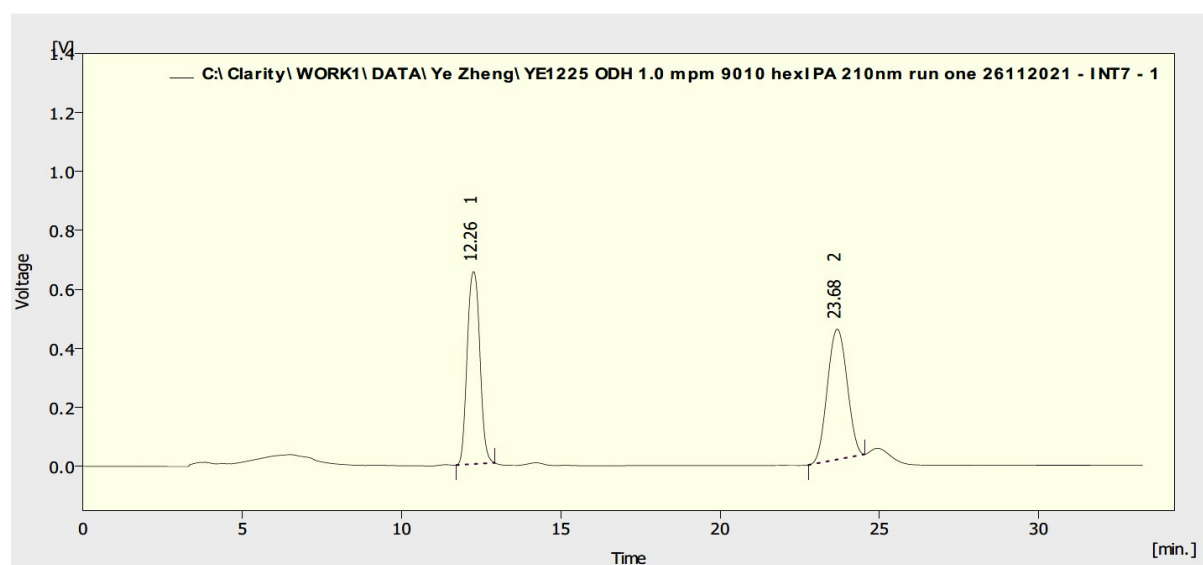
HPLC of racemic 2-phenoxy-1-(p-tolyl)ethan-1-ol **19** from coupling.



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		

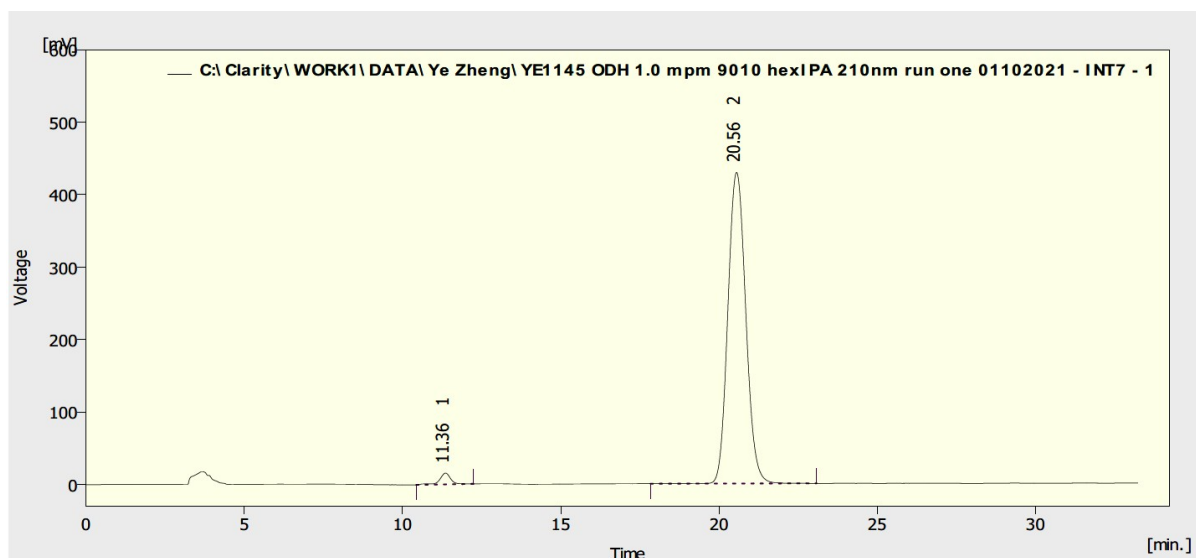
HPLC of racemic 2-phenoxy-1-(p-tolyl)ethan-1-ol **19** via reduction of **20** with NaBH₄.



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		

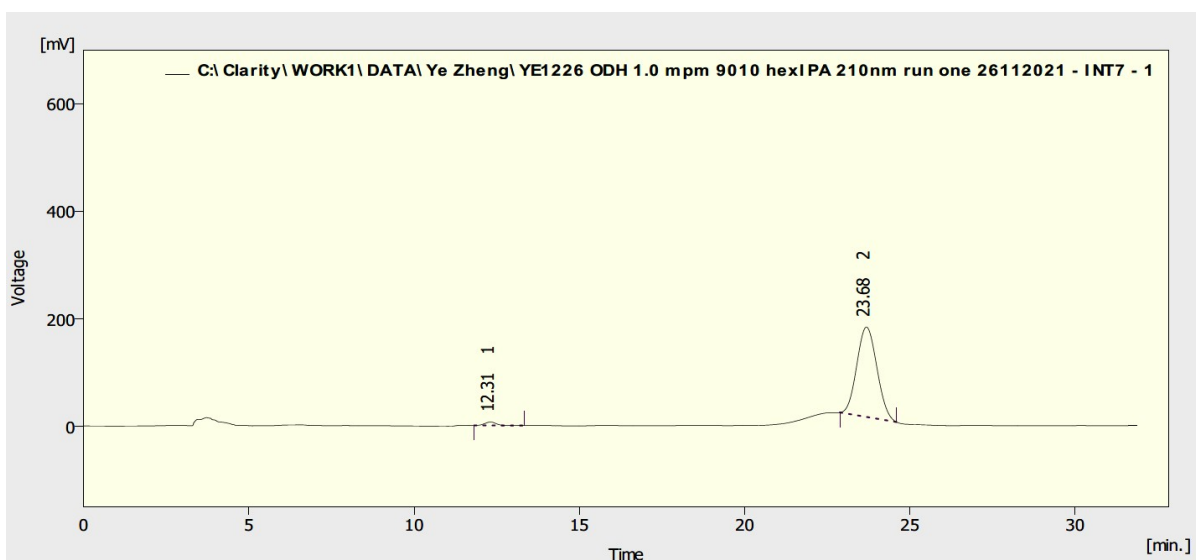
HPLC of (*S*)-2-phenoxy-1-(*p*-tolyl)ethan-1-ol **19** from coupling with (*S*)-**12** (96% ee, *S* configuration).



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		

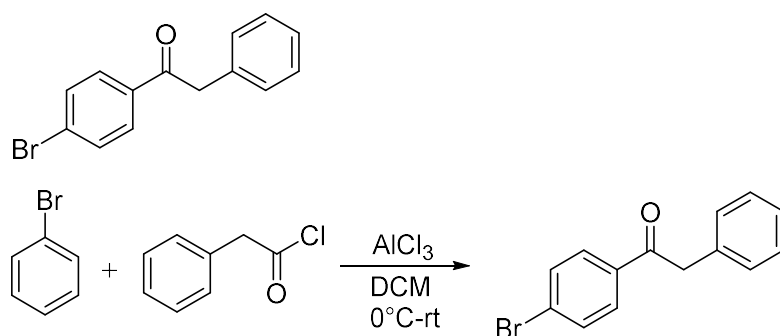
HPLC after ATH of 2-phenoxy-1-(*p*-tolyl)ethan-1-one **20** using (*R,R*)-3C-Tethered Ru(II)-TsDPEN catalyst **2** (after 72 hours, 100% conversion, 96% ee).



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		

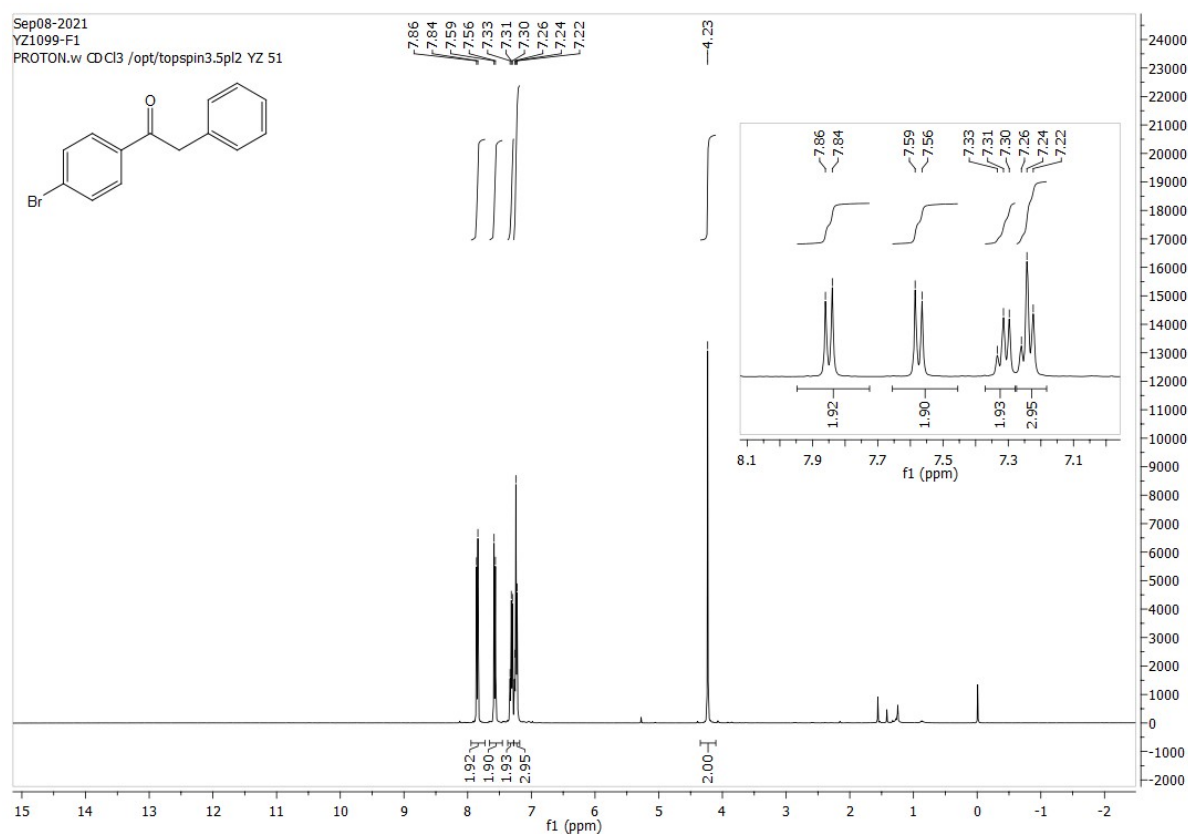
Compound name: 1-(4-Bromophenyl)-2-phenylethanone.



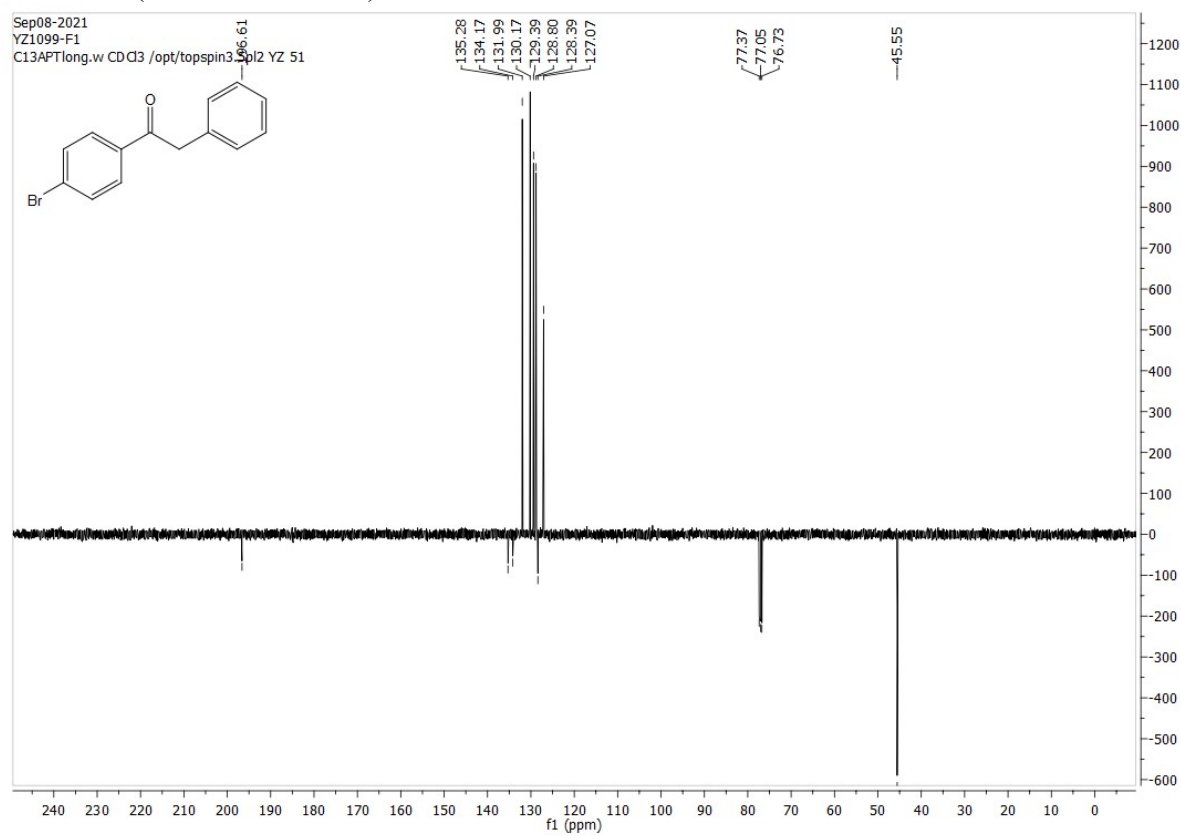
This compound has been reported and fully characterized: A. I. Khalaf, J. K. Huggan, C. J. Suckling, C. L. Gibson, K. Stewart, F. Giordani, M. P. Barrett, P. E. Wong, K. L. Barrack, W. N. Hunter, *J. Med. Chem.* 2014, **57**, 6479-6494.

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: R_f ca 0.70 (9:1 hexane: EtOAc), strong UV and KMnO_4 ; δ_{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; δ_{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 ($\text{M}^+ + 23$, 100%). Data matched that reported.

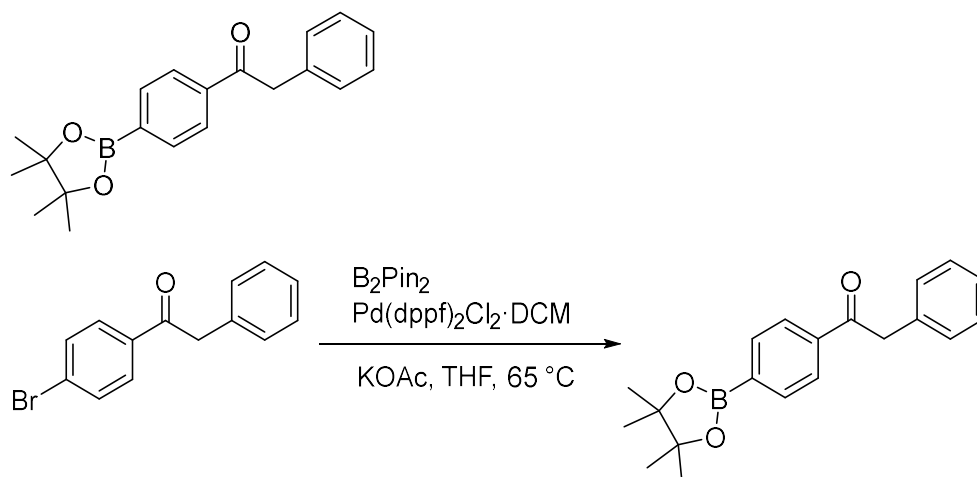
^1H NMR (400 MHz, CDCl_3)



^{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.

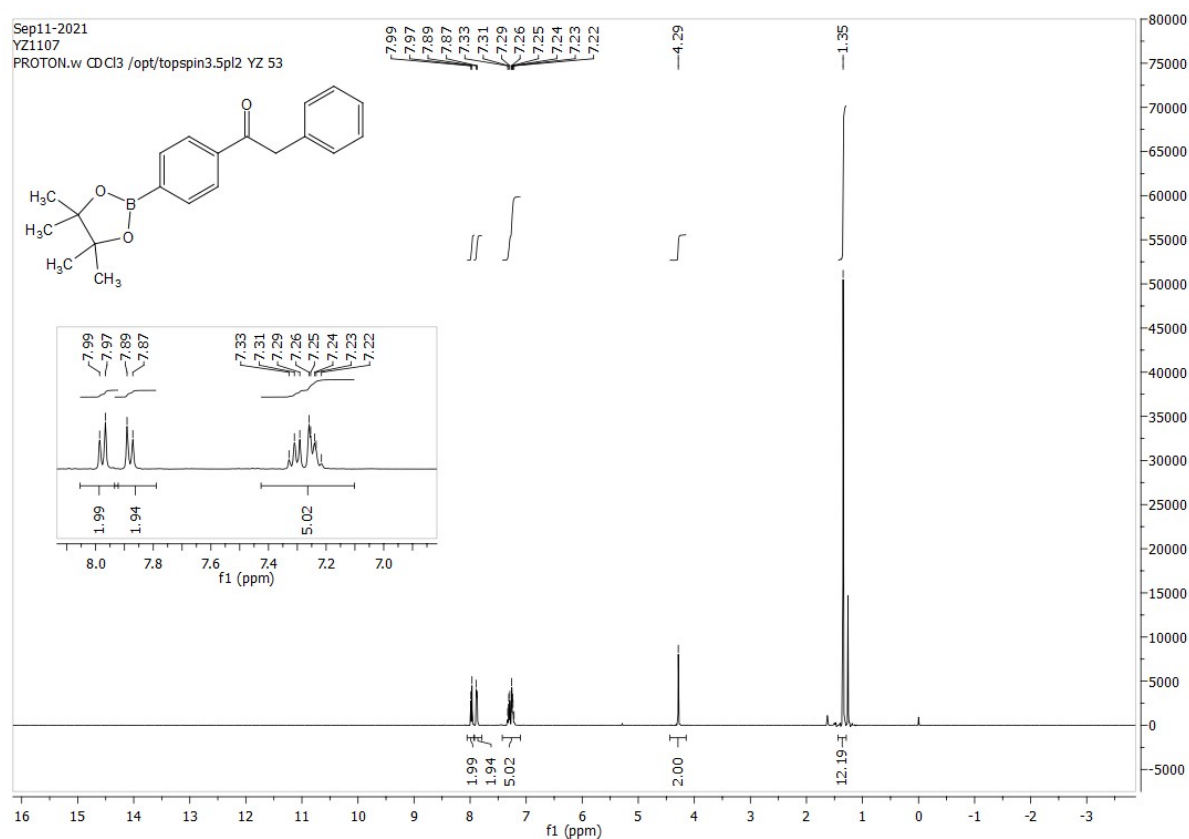


This compound has been reported and fully characterized: B. Lee, P. J. Chirik, *J. Am. Chem. Soc.* 2020, **142**, 2429-2437.

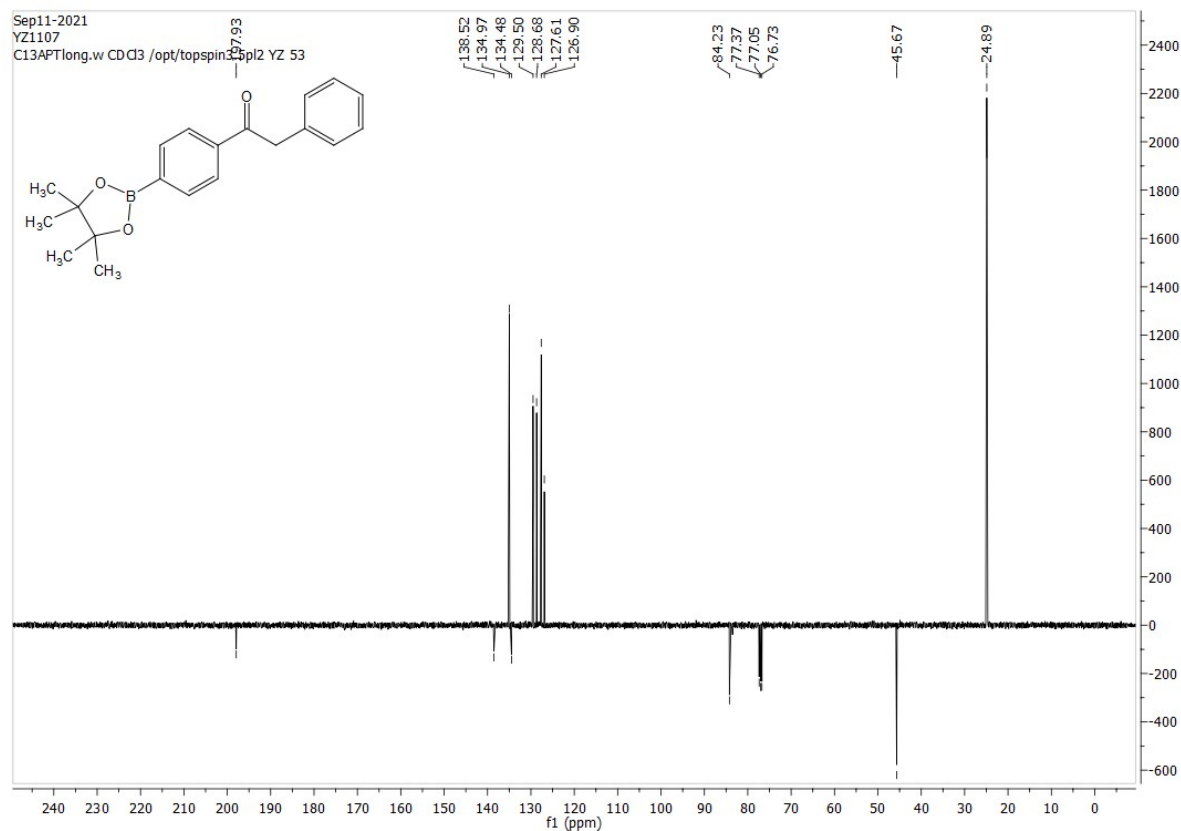
A round-bottom flask was charged with 1-(4-bromophenyl)-2-phenylethan-1-one (236 mg, 0.861 mmol), bis(pinacolato)diboron (262 mg, 1.03 mmol), potassium acetate (253 mg, 2.58 mmol), THF (4.3 mL) and $Pd(dppf)_2Cl_2 \cdot DCM$ (35.2 mg, 0.0431 mmol). The reaction mixture was heated to 65 °C and left stirring 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: R_f ca 0.70 (9:1 hexane: EtOAc), strong UV and $KMnO_4$; δ_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; δ_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, $T = 25^\circ C$) ketone 6.3 min, *R* and *S* isomers 6.2 min and 8.3 min.

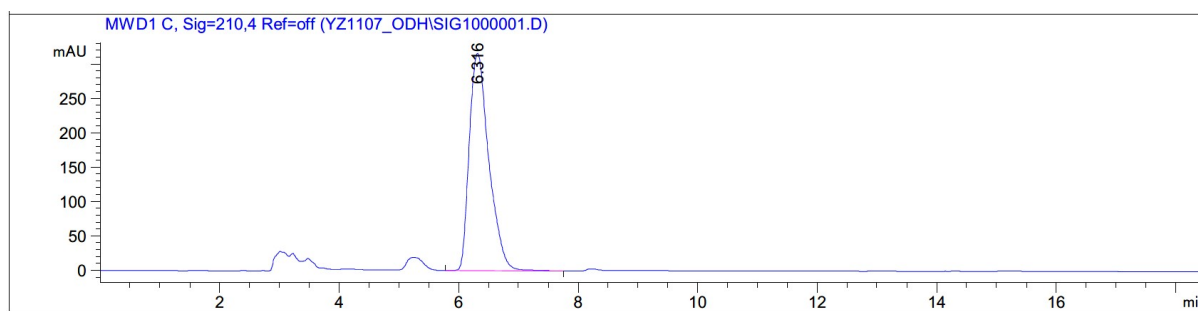
^1H NMR (400 MHz, CDCl_3)



^{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

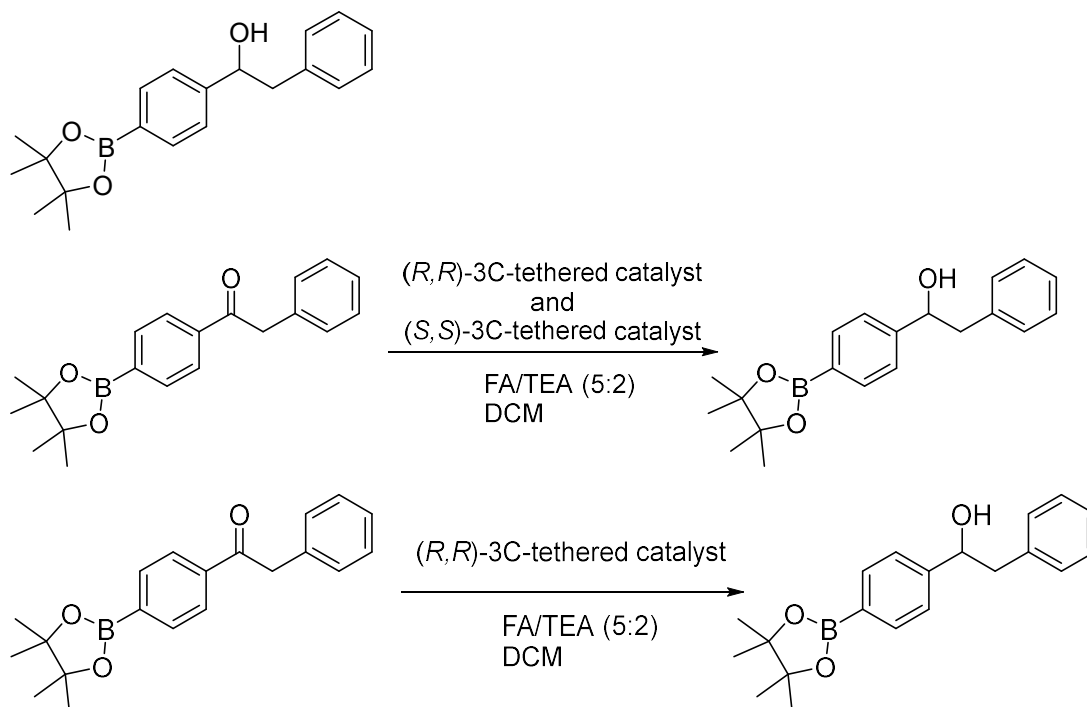


Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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 μ mol, 0.5 mol%) and (*S,S*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (0.38 mg, 0.62 μ mol, 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 stirred under a nitrogen atmosphere and followed by TLC (4:1 hexane: EtOAc). After 72 hours, the reaction was quenched using saturated NaHCO₃ 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 0-20% 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: R_f ca 0.20 (4:1 hexane: EtOAc), strong UV and KMnO₄; HRMS: (found (ESI⁺): [M+H]⁺, Calcd for C₂₀H₂₅BNaO₃ 347.1789; Found 347.1789; 1.1 ppm error; ν_{max} 3434 (br), 3036, 2920, 1467, 1455, 1398, 1319, 1231, 1164, 1088, 1018, 802 cm⁻¹; δ_{H} (500 MHz, CDCl₃) 7.80 (2H, d, *J* = 7.9, ArH),

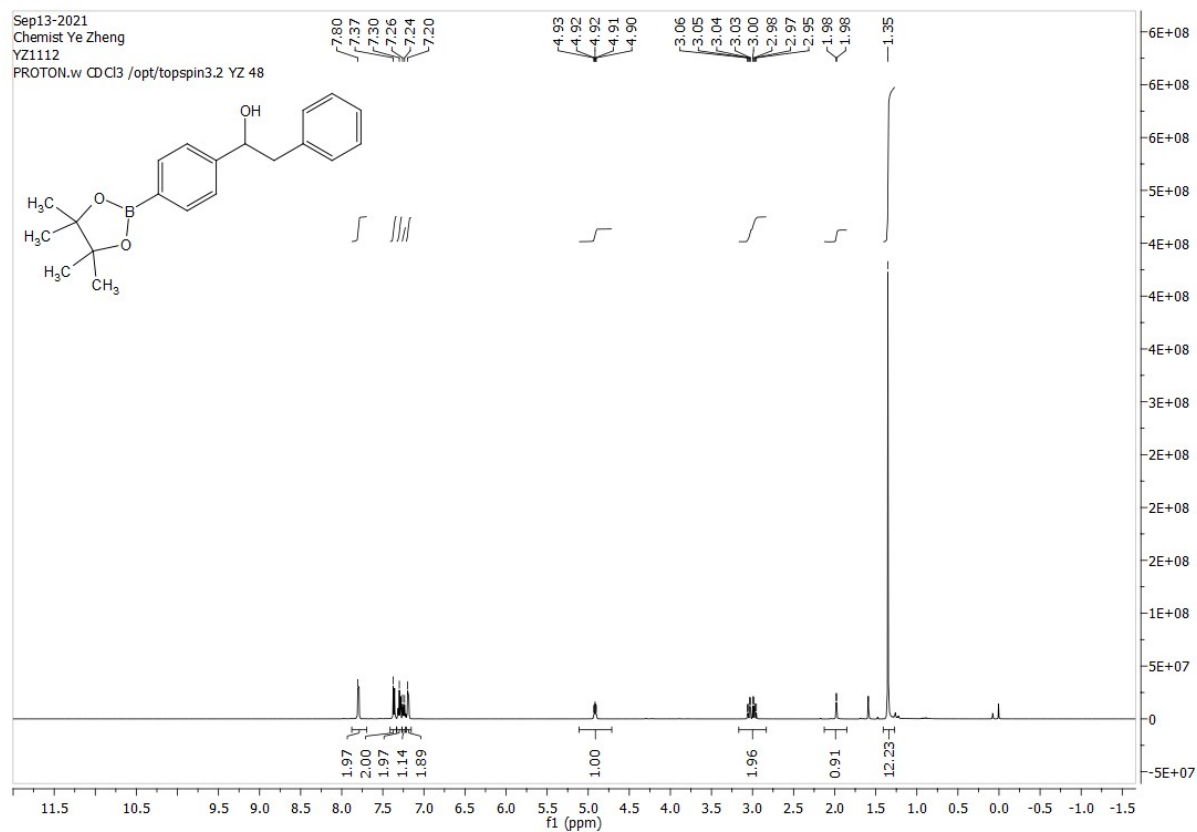
7.37 (2H, d, $J = 7.9$, ArH), 7.30 (2H, t, $J = 7.3$, ArH), 7.24 (1H, t, $J = 7.3$, ArH), 7.20 (2H, d, $J = 7.1$, ArH), 4.93-4.90 (1H, m, ArCH), 3.06-2.95 (2H, m, CH₂), 1.98 (1H, d, $J = 2.9$, OH), 1.35 (12H, s, CH₃) ppm; δ_c (125 MHz, CDCl₃) 136.96 (C), 137.89 (C), 134.95 (CH), 129.55 (CH), 128.54 (CH), 126.66 (CH), 125.22 (CH), 83.81 (C), 75.32 (CH), 46.05 (CH₂), 24.89 (CH₃) 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, $T = 25^\circ\text{C}$) ketone 6.3 min, *R* and *S* isomers 6.2 min and 8.3 min, configuration was assigned by analogy with **12**.

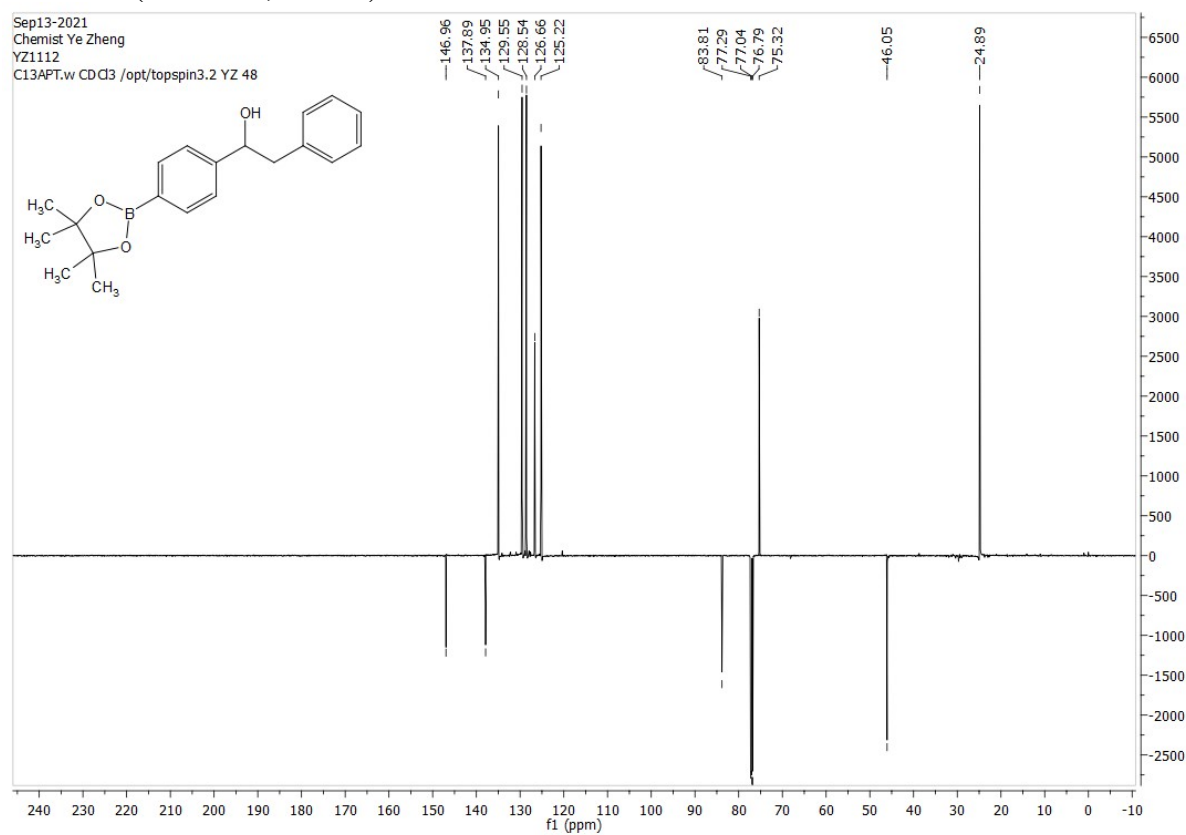
ATH of 2-phenyl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one:

(*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 stirred under a nitrogen atmosphere and followed by TLC (4:1 hexane: EtOAc). After 72 hours, the reaction was quenched using saturated NaHCO₃ 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 0-50% 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, $T = 25^\circ\text{C}$): $[\alpha]_D^{25} +0.75$ (c 0.400 in CHCl₃) 96% ee.

¹H NMR (500 MHz, CDCl₃)

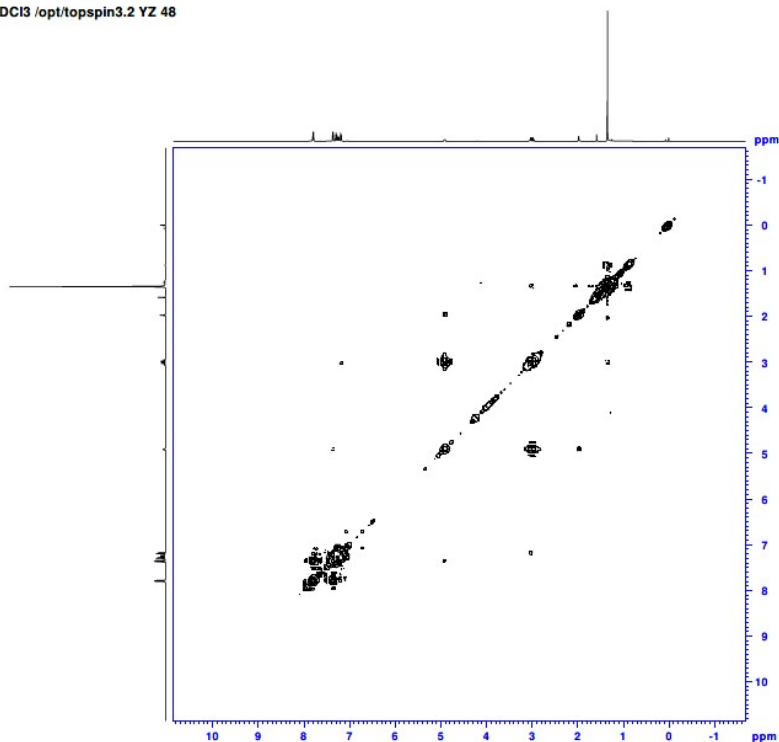


¹³C NMR (125 MHz, CDCl₃)



COSY (500 MHz, CDCl₃)

Chemist Ye Zheng
YZ1112
COSY.w CDCl₃ /opt/topspin3.2 YZ 48



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PROCNO    1

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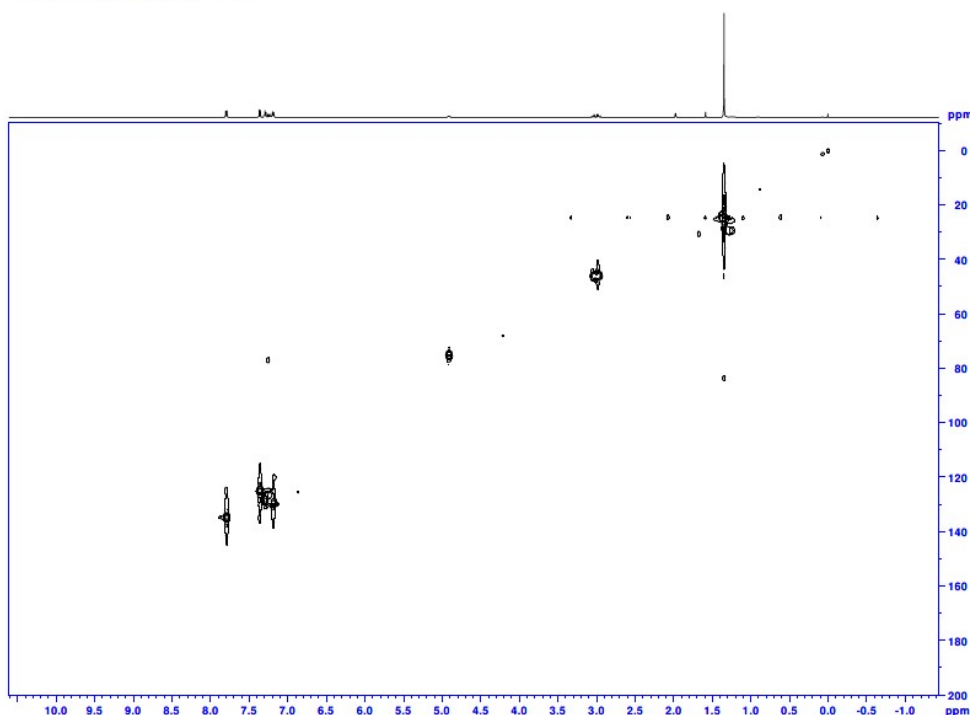
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HSQC (500 MHz, CDCl₃)

Chemist Ye Zheng
YZ1112
HSQC.w CDCl₃ /opt/topspin3.2 YZ 48



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P4         13.00000000 N
P5         1.50049997 N
P6         0.00000000 N

===== CHANNEL f1 =====
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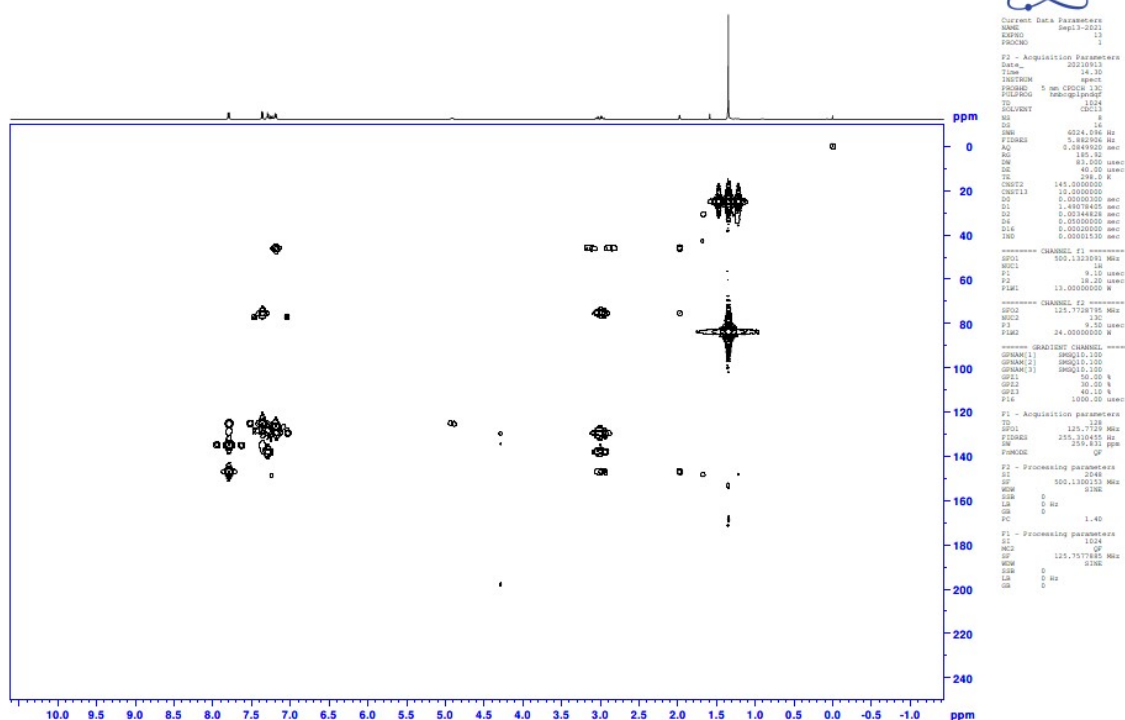
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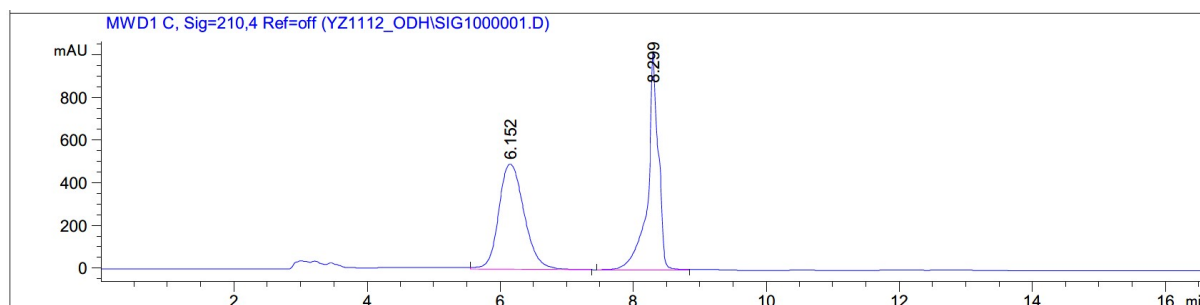
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HMBC (500 MHz, CDCl₃)

Chemist Ye Zheng
YZ1112



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

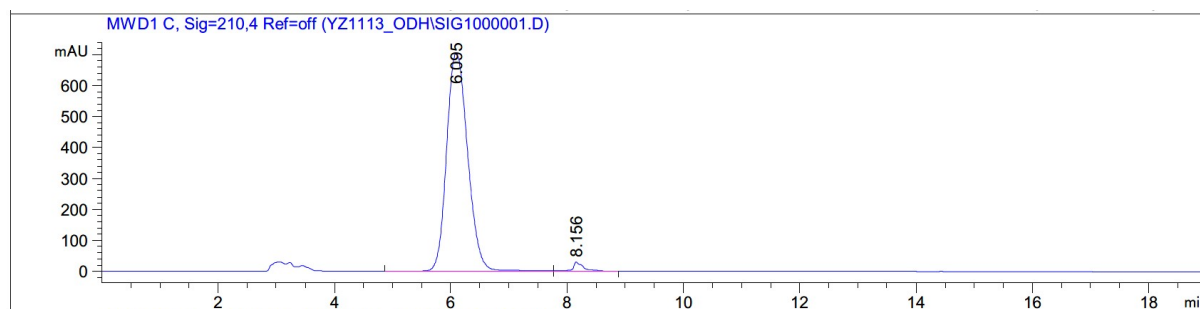


Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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).

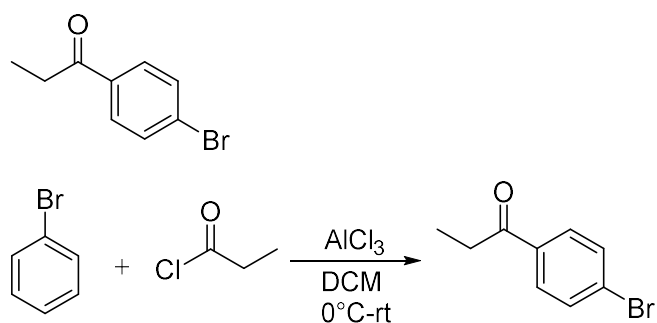


Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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

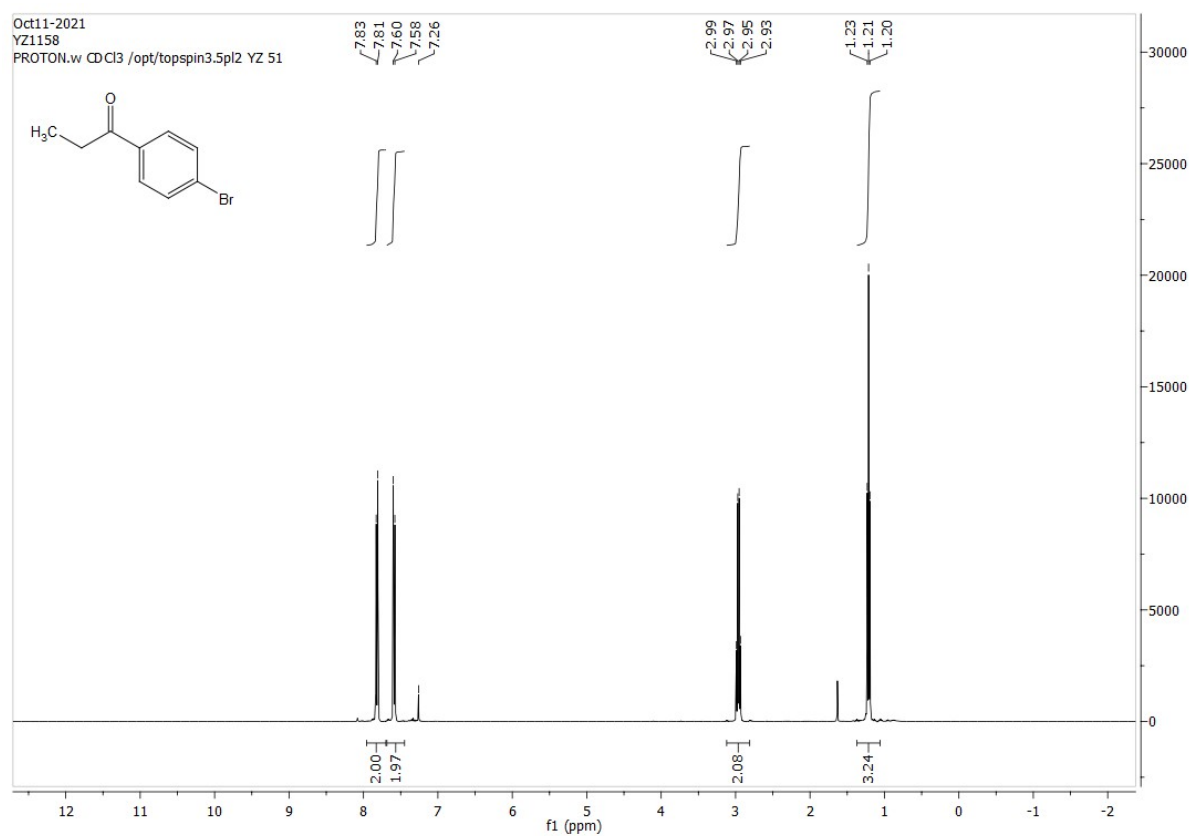
1-(4-Bromophenyl)propan-1-one.



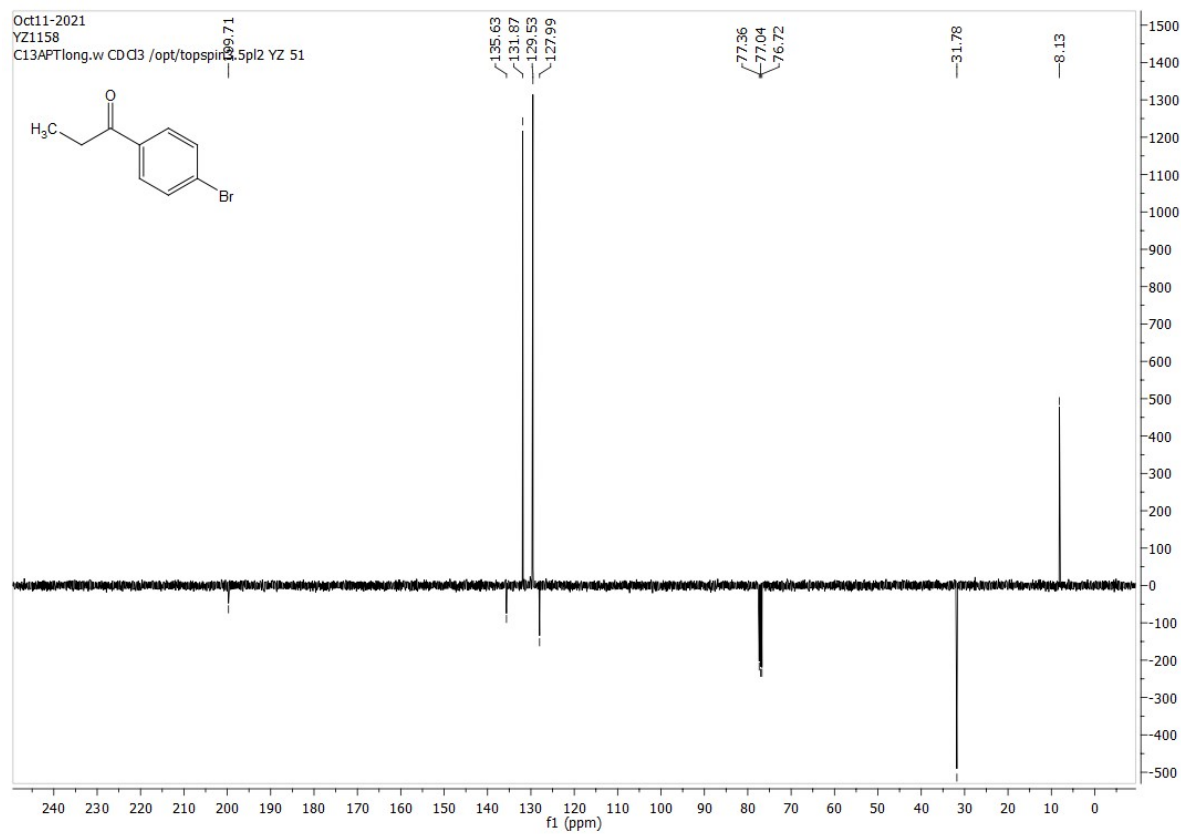
This compound has been reported and fully characterized: N. Rios-Lombardia, C. Vidal, M. Cocina, F. Moris, J. Garcia-Alvarez, J. Gonzalez-Sabin, *Chem. Commun.* 2015, **51**, 10937-10940.

To a solution of bromobenzene (318 mg, 2.00 mmol) was in DCM (1.2 mL) at 0 °C was added AlCl₃ (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 (MgSO₄) 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: R_f ca 0.70 (9:1 hexane: EtOAc), strong UV and KMnO₄; δ_H (400 MHz, CDCl₃) 7.83 (2H, d, *J* = 8.5, ArH), 7.60 (1H, d, *J* = 8.5, ArH), 2.97 (2H, q, *J* = 7.2, CH₂), 1.21 (3H, t, *J* = 7.2, CH₃) ppm; δ_C (100 MHz, CDCl₃) 199.71 (C), 135.63 (C), 131.87 (CH), 129.53 (CH), 127.99 (C), 31.78 (CH₂), 8.13 (CH₃) ppm. Data matched that reported.

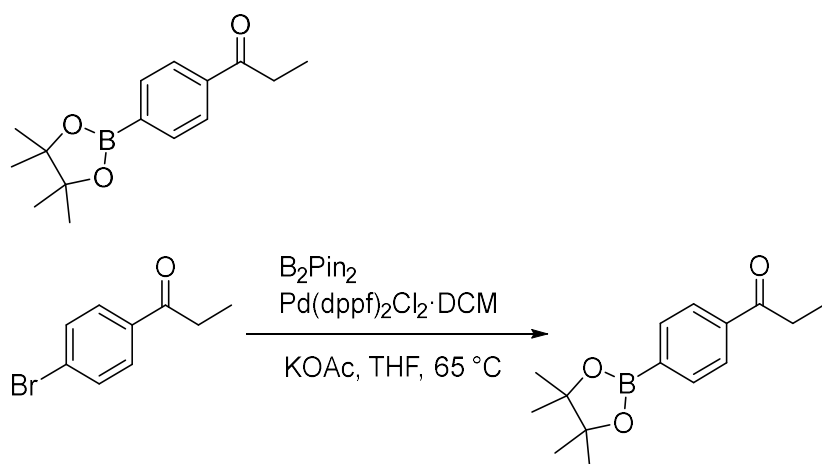
^1H NMR (400 MHz, CDCl_3)



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



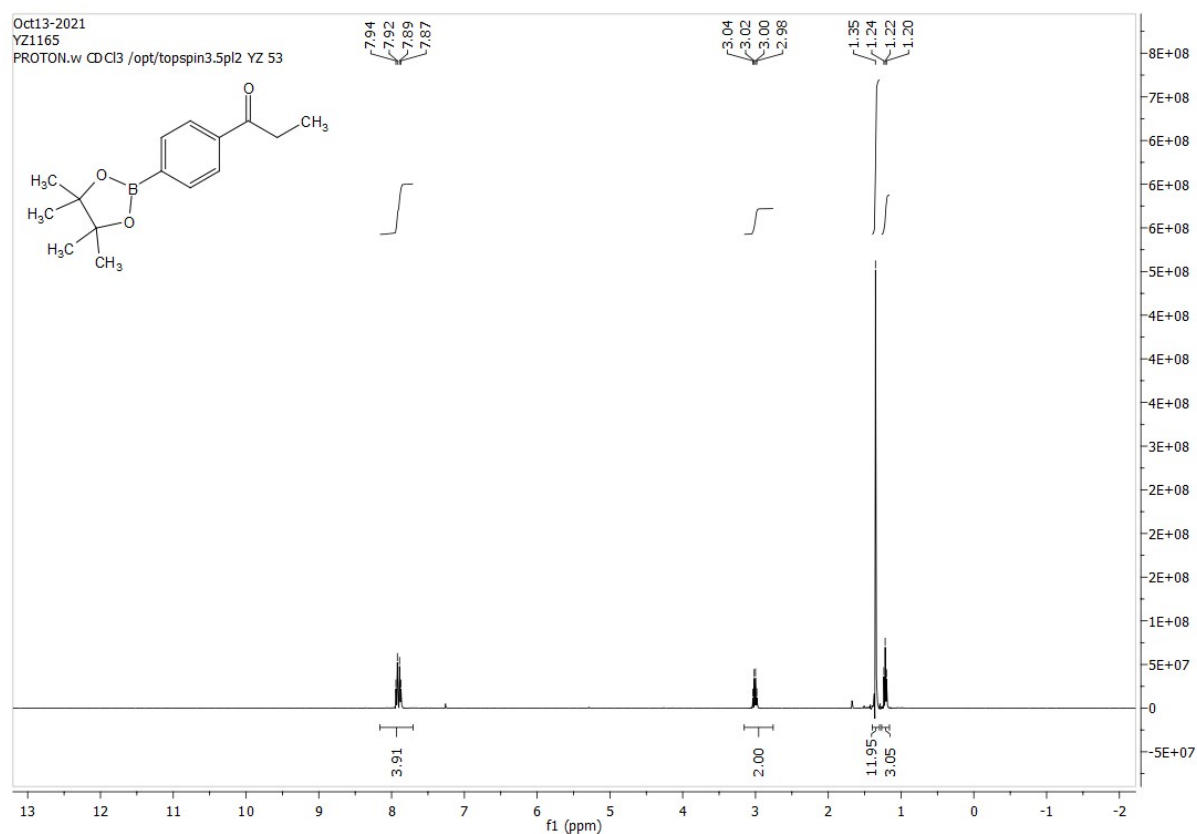
1-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propan-1-one.



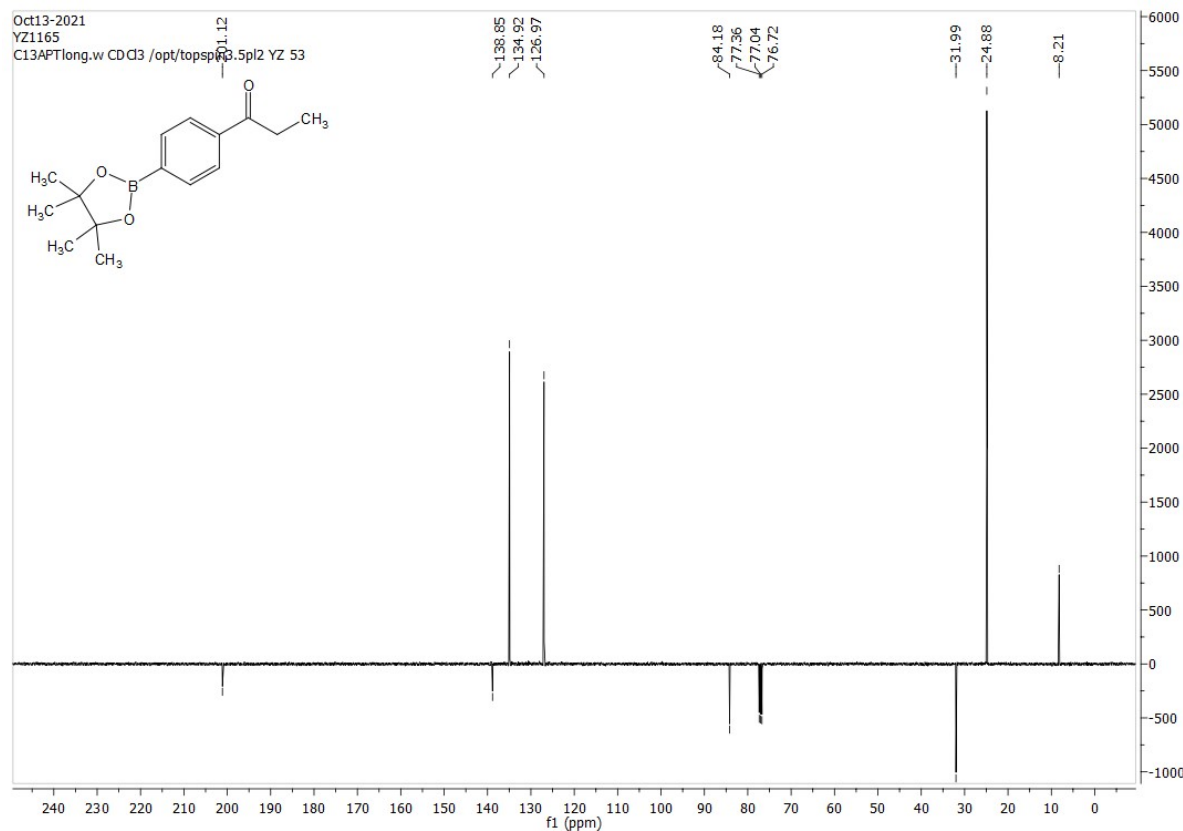
This compound has been reported and fully characterized: T. Kusakawa, Y. Kojima, F. Kannen, *Chem. Lett.* 2019, **48**, 1213-1216.

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 $Pd(dppf)_2Cl_2 \cdot DCM$ (157 mg, 0.192 mmol). The reaction mixture was heated to $65\text{ }^\circ C$ 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 ($3 \times 20\text{ mL}$), 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: R_f ca 0.50 (9:1 hexane: EtOAc), strong UV and $KMnO_4$; δ_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; δ_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 (ESI+) 283.1 ($M^+ + 23$, 100%). Data matched that reported.

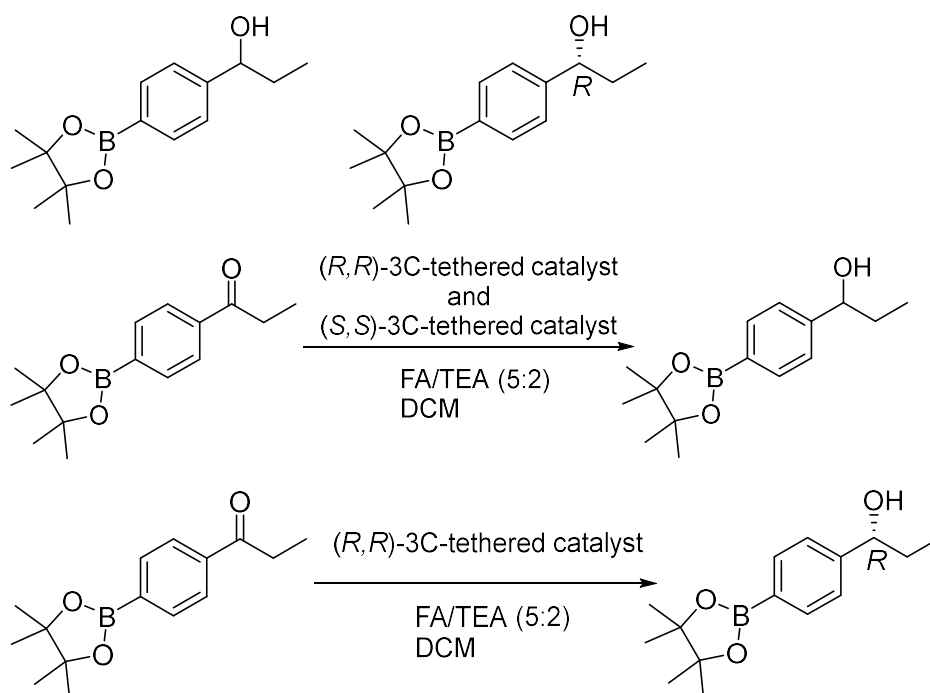
^1H NMR (400 MHz, CDCl_3)



^{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.

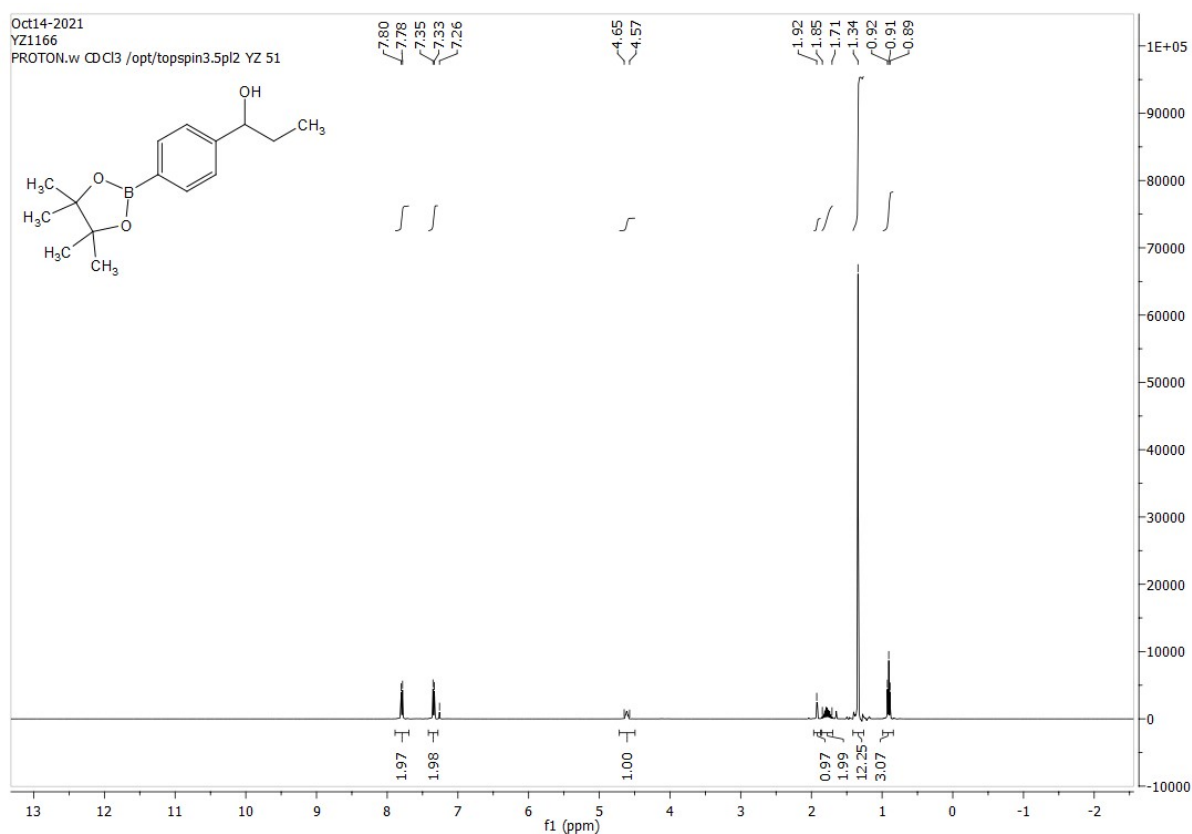
Synthesis of a racemic standard:

(*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 stirred 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: R_f ca 0.20 (9:1 hexane: EtOAc), strong UV and KMnO_4 ; Mp: 82°C; HRMS: (found (ESI+): $[\text{M}+\text{H}]^+$, Calcd for $\text{C}_{15}\text{H}_{23}\text{BNaO}_3$ 285.1632; Found 285.1632; 1.2 ppm error; ν_{max} 3258 (br), 2976, 2877, 1397, 1356, 1334, 1320, 1141, 1088, 1085, 1006, 962, 858 cm^{-1} ; δ_{H} (400 MHz, CDCl_3) 7.80 (2H, d, $J = 7.9$,

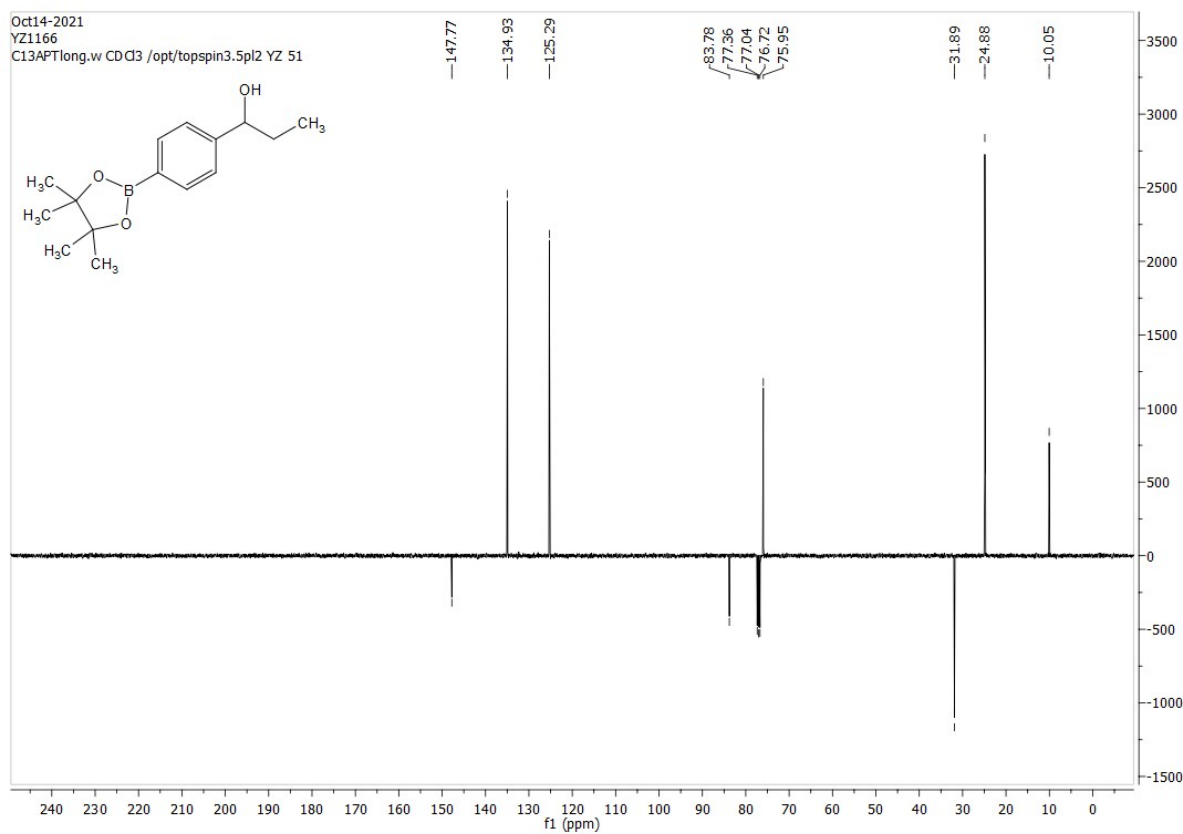
ArH), 7.35 (2H, d, $J = 7.9$, ArH), 4.65-4.57 (1H, m, ArCH), 1.92 (1H, d, $J = 3.3$, OH), 1.85-1.71 (2H, m, CH₂), 1.34 (12H, s, CH₃), 0.91 (3H, t, $J = 7.4$, CH₃) ppm; δ_C (100 MHz, CDCl₃) 147.77 (C), 134.93 (CH), 125.29 (CH), 83.79 (C), 79.95 (CH), 31.89 (CH₂), 24.88 (CH₃), 10.05 (CH₃) ppm; m/z (ES-API+) 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 μ mol, 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 stirred under a nitrogen atmosphere and followed by TLC (9:1 hexane: EtOAc). After 24 hours, the reaction was quenched using saturated NaHCO₃ 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 0-20% 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 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 CHCl₃), 94% ee, *S* configuration (ee and configuration were confirmed by comparison with compound after reaction with bromobenzene)

^1H NMR (400 MHz, CDCl_3)

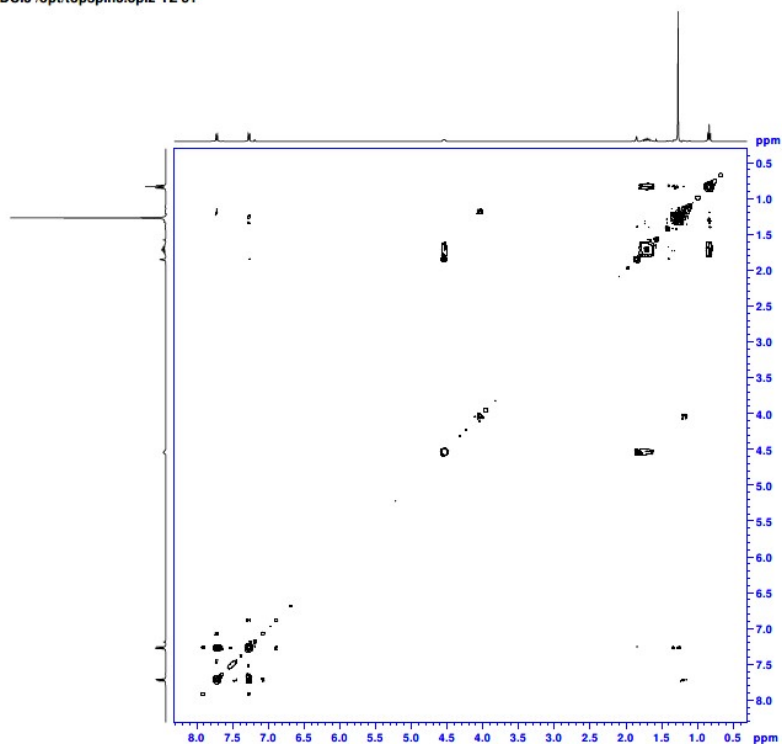


^{13}C NMR (100 MHz, CDCl_3)



COSY (400 MHz, CDCl₃)

YZ1166
COSY.w CDCl₃ /opt/topspin3.5pl2 YZ 51



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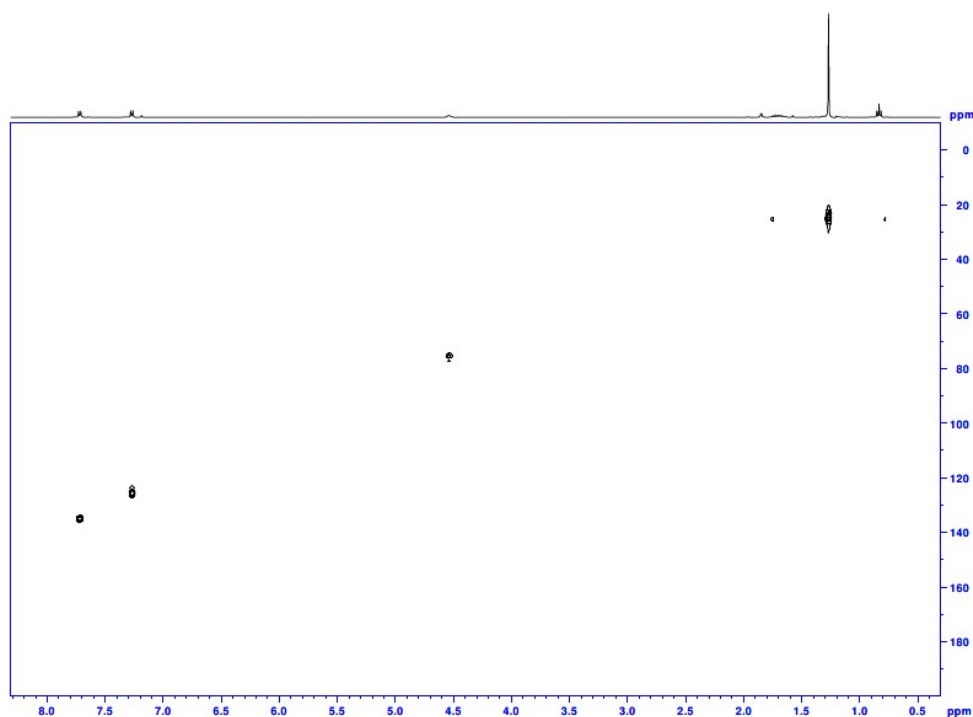
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F1 - Processing parameters
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GB 0
PC 1.40

HSQC (400 MHz, CDCl₃)

YZ1166
HSQC.w CDCl₃ /opt/topspin3.5pl2 YZ 51



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SW 4.100 usec
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D12 0.0000000 sec
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HMBC (400 MHz, CDCl₃)

YZ1166
HMBC.w CDCl₃ /opt/topspin3.5pl2 YZ 51



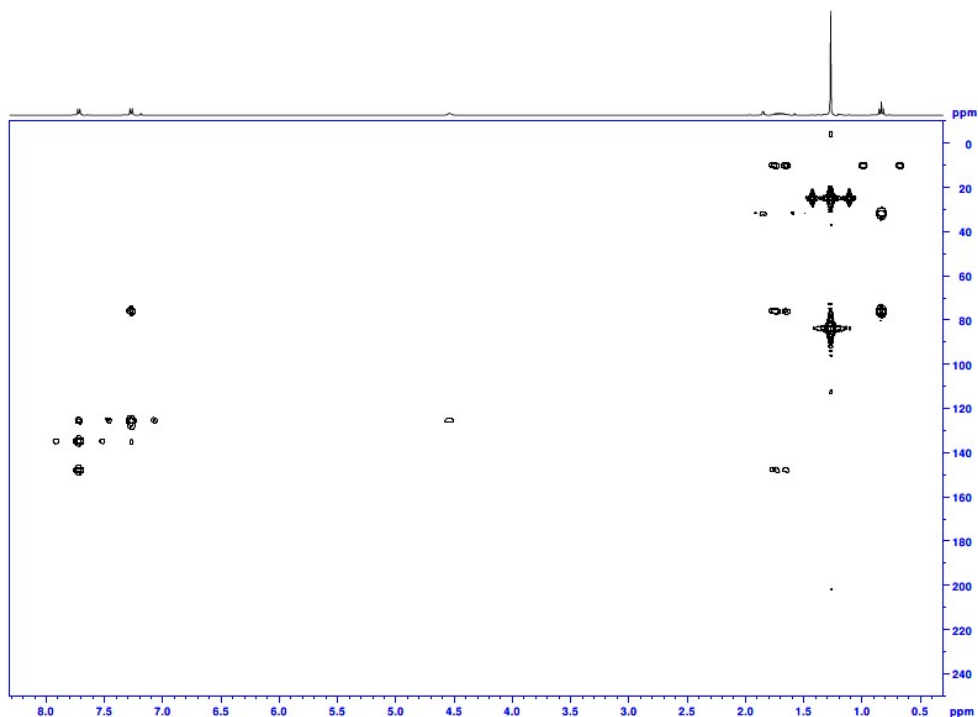
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EXPNO 13
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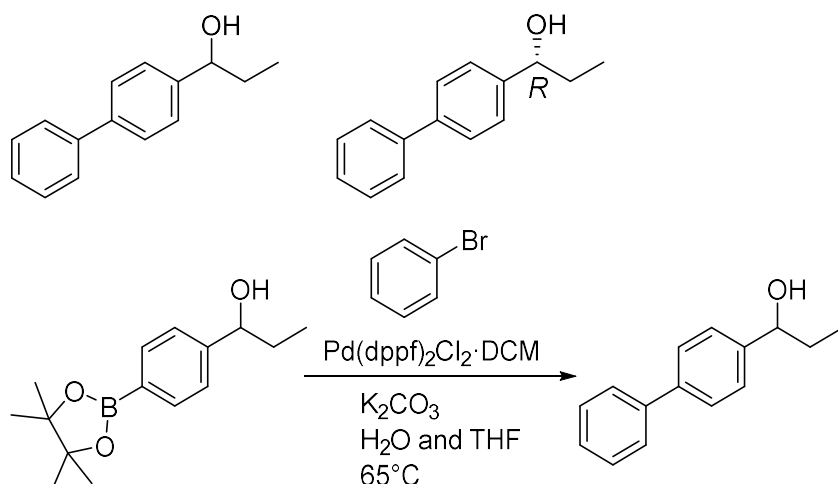
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F1 - Processing parameters
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Racemic and (*R*)-1-([1,1'-Biphenyl]-4-yl)propan-1-ol **21**.



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.

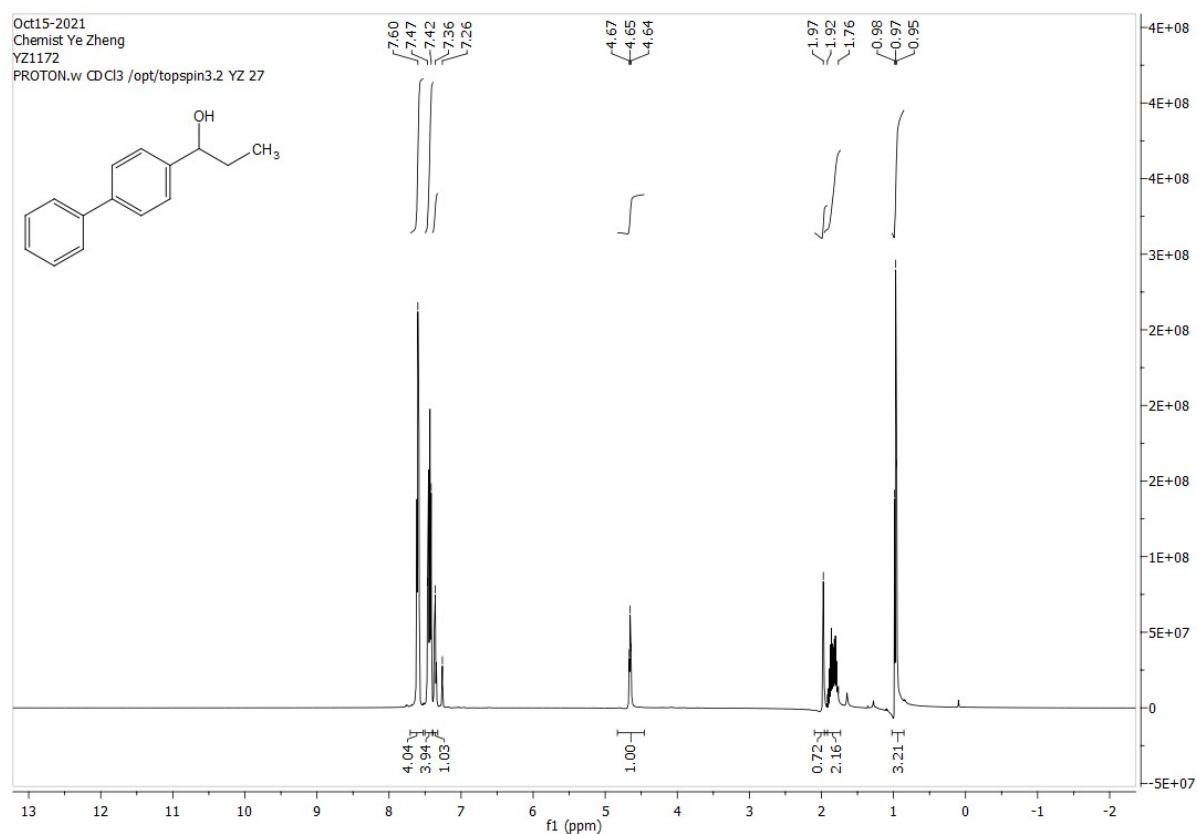
Racemic: To a solution of racemic 1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propan-1-ol **14** (90.0 mg, 0.344 mmol), bromobenzene (108 mg, 0.688 mmol) and potassium carbonate (94.9 mg, 0.688 mmol) in THF (6.7 mL) was added $\text{Pd(dppf)}_2\text{Cl}_2 \cdot \text{DCM}$ (14.1 mg, 0.0172 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: R_f ca 0.20 (9:1 hexane: EtOAc), strong UV and KMnO_4 ; δ_{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; δ_{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 ($\text{M}^+ + 23$, 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, $T = 25^\circ\text{C}$) *S* isomer 25.9 min

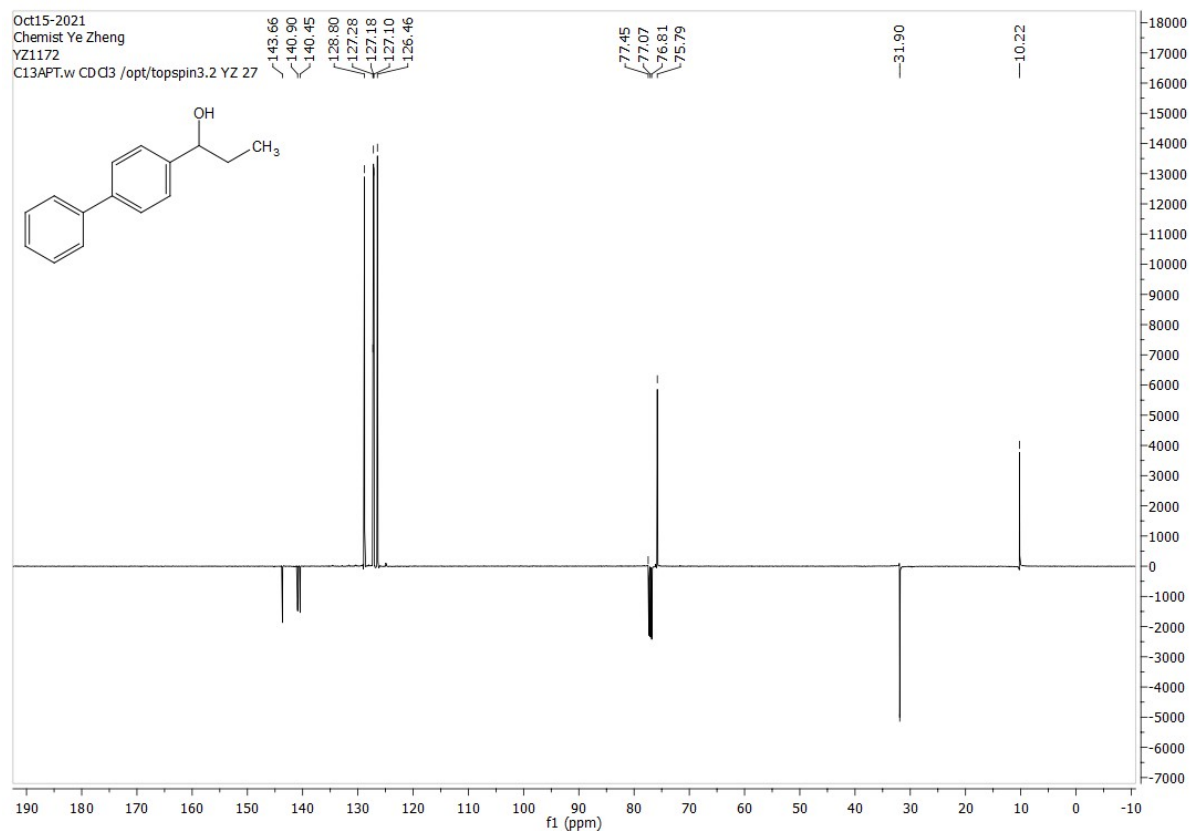
and *R* isomer 28.7 min. The same column and solvent combination was used in the reference above, permitting determination of the configuration of **21** and also of its precursor, **14**.

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)₂Cl₂·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 (MgSO₄) 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): [α]_D²³ +35.5 (c 0.300 in DCM) 94% ee (*R*) (lit. [α]_D²⁰ +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.

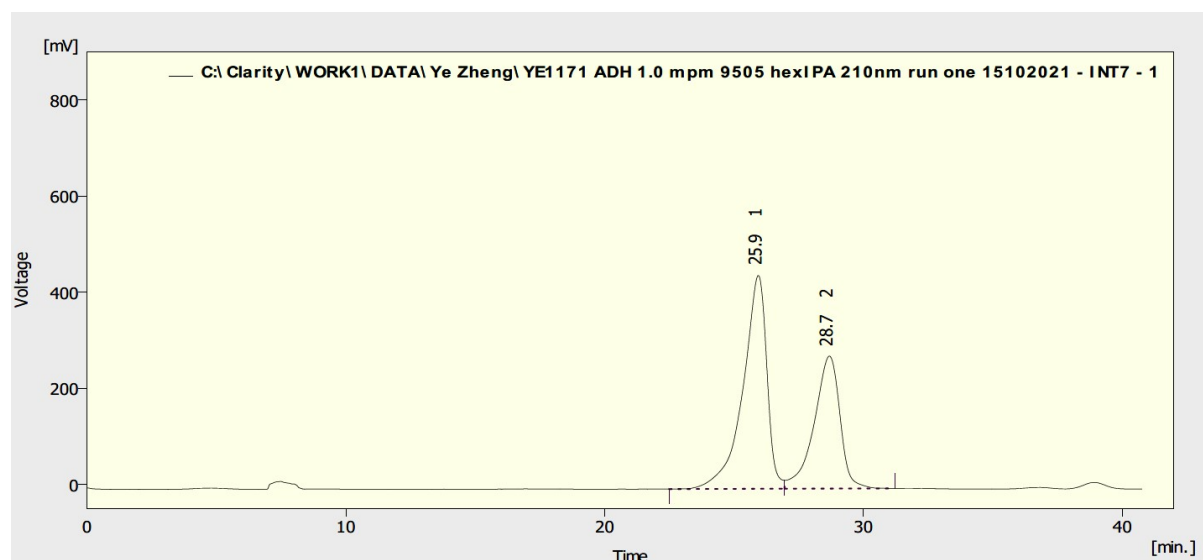
^1H NMR (500 MHz, CDCl_3)



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



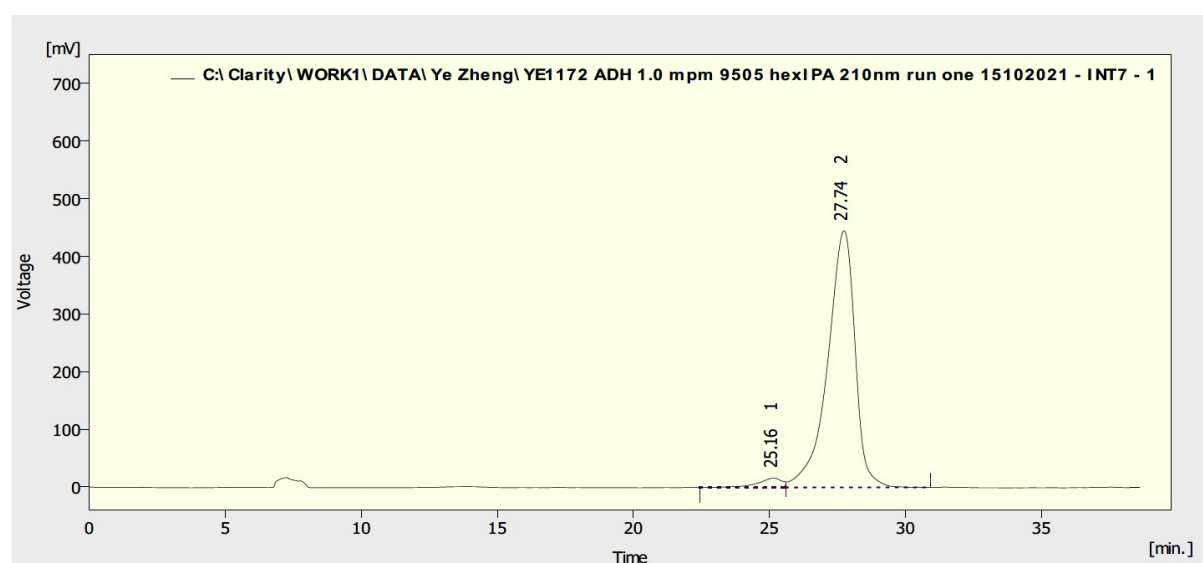
HPLC of racemic 1-([1,1'-biphenyl]-4-yl)propan-1-ol **21**.



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		

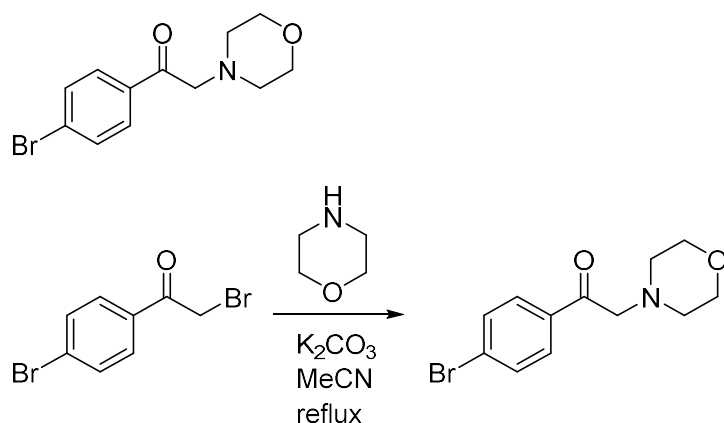
HPLC of (*R*)-1-([1,1'-biphenyl]-4-yl)propan-1-ol **21** (94% ee, *R* configuration)



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		

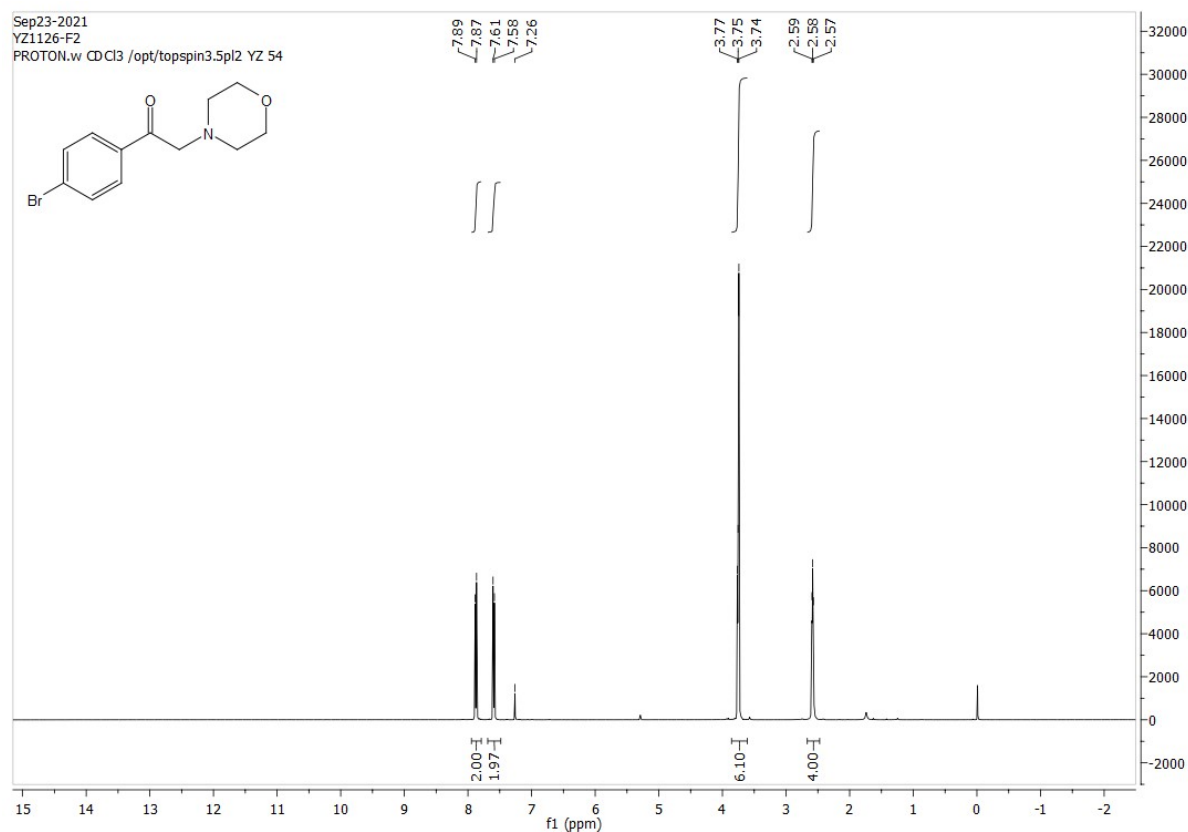
1-(4-Bromophenyl)-2-morpholinoethan-1-one.



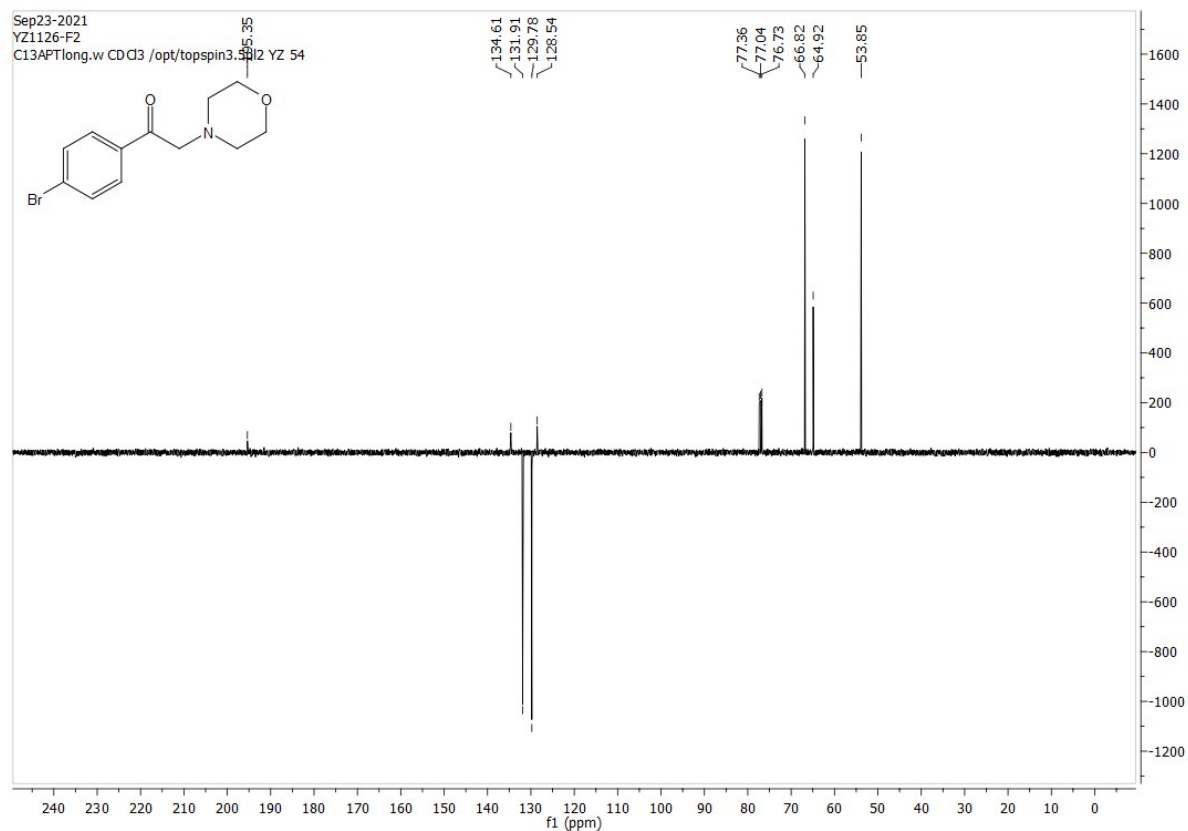
This compound has been reported and fully characterized: C. T. Bahner, E. Kite, F. Pierce, L. M. Rives, M. D. Pickens, C. Myers, *J. Am. Chem. Soc.* 1951, **73**, 4011-4013.

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). Et₂O (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with Et₂O (3 × 20 mL), and the combined organic layers were dried (MgSO₄) 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: R_f ca 0.20 (1:1 hexane: EtOAc), strong UV and KMnO₄; δ_H (400 MHz, CDCl₃) 7.89 (2H, d, *J* = 8.5, ArH), 7.61 (2H, d, *J* = 8.5, ArH), 3.77-3.74 (6H, m, CH₂), 2.59-2.57 (4H, m, CH₂) ppm; δ_C (100 MHz, CDCl₃) 195.35 (C), 134.61 (C), 131.91 (CH), 129.78 (CH), 128.54 (C), 66.82 (CH₂), 64.92 (CH₂), 53.85 (CH₂) ppm; *m/z* (ES-API⁺) 284.0 (M⁺ + 1, 100%). Data matched that reported.

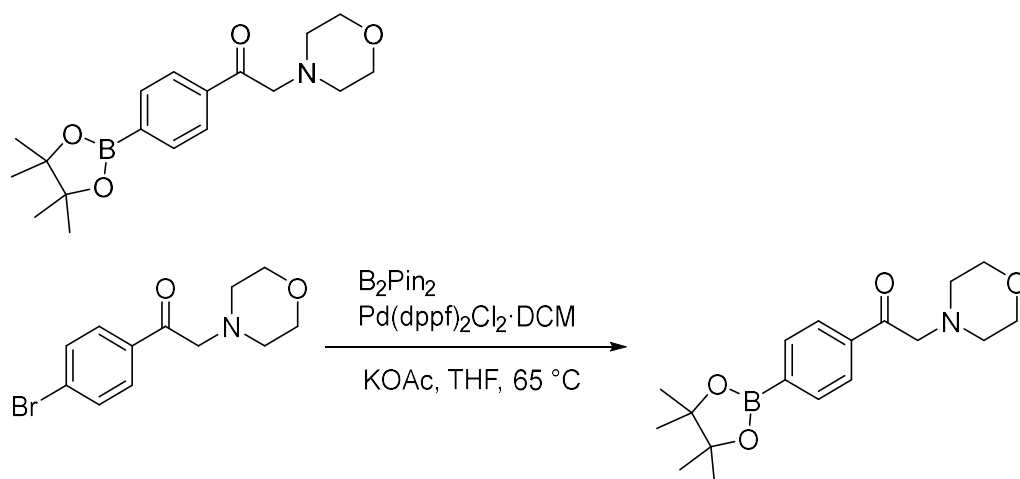
^1H NMR (400 MHz, CDCl_3)



^{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.



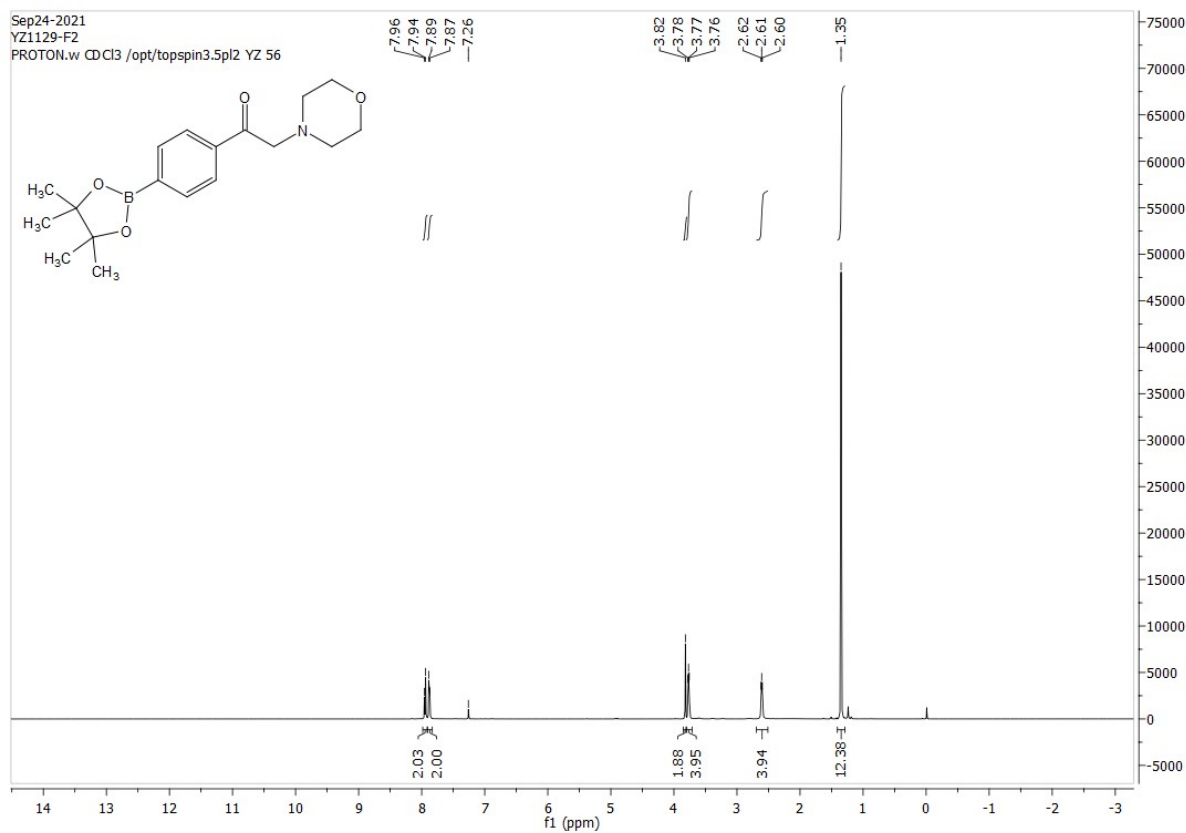
This compound is novel.

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).

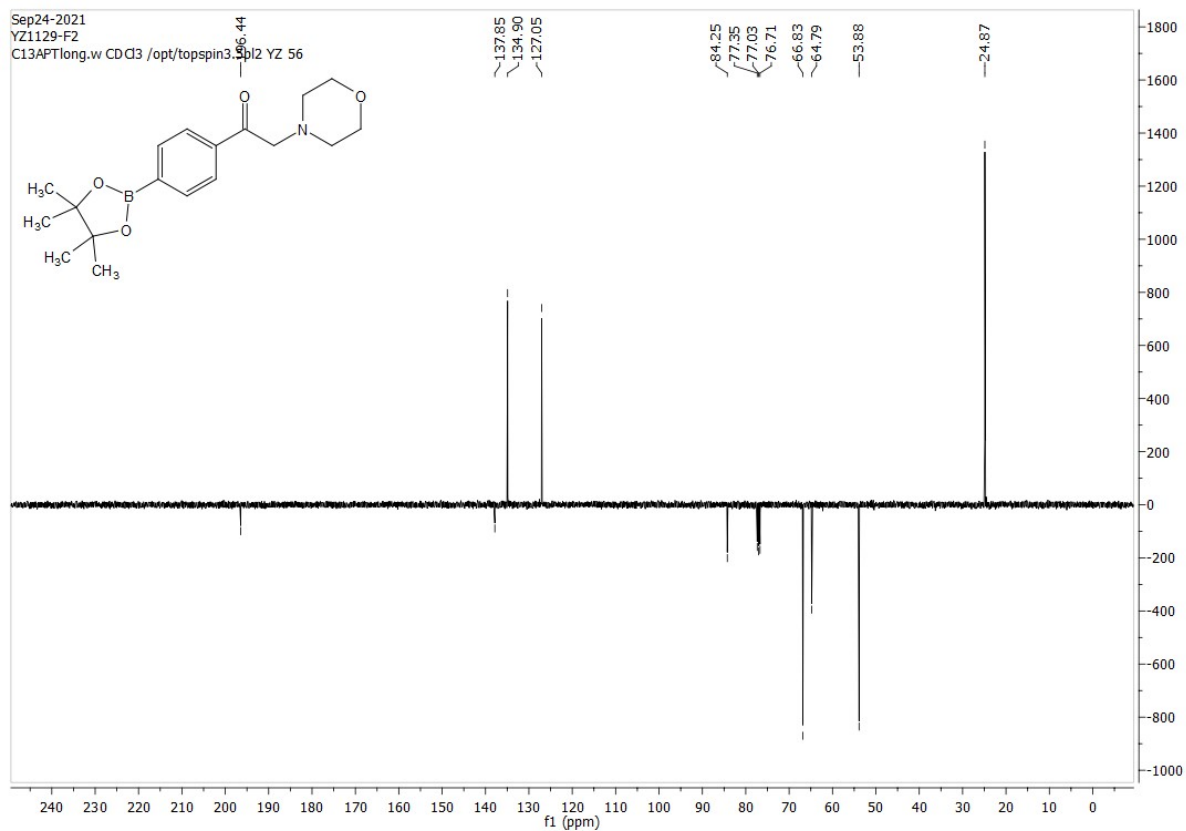
The reaction mixture was heated to 65 °C and left stirring under the nitrogen atmosphere overnight, followed by TLC (1:1 hexane: EtOAc). The mixture was quenched by distilled water (20 mL). EtOAc (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 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: R_f 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; ν_{max} 2977, 1697, 1508, 1452, 1397, 1357, 1217, 1142, 1115, 1088, 856 cm^{-1} ; δ_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; δ_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.

¹H NMR (400 MHz, CDCl₃)



¹³C NMR (100 MHz, CDCl₃)



YZ1129-F2
COSY.w CDC13 /opt/topspin3.5pl2 YZ 56

BRUKER

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PROCNO 1

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ppm

ppm

YZ1129-F2
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BRUKER

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YZ1129-F2
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BRUKER

Current Data Parameters
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EXPNO 23
PROCNO 1

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F1 - Processing parameters
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— C:\Clarity\WORK1\DATA\Ye Zheng\YE1129 IC 1.0 mpm 9010 hex\PA 210nm run one 27092021 - INT7 - 1

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3.5

1

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200

150

100

50

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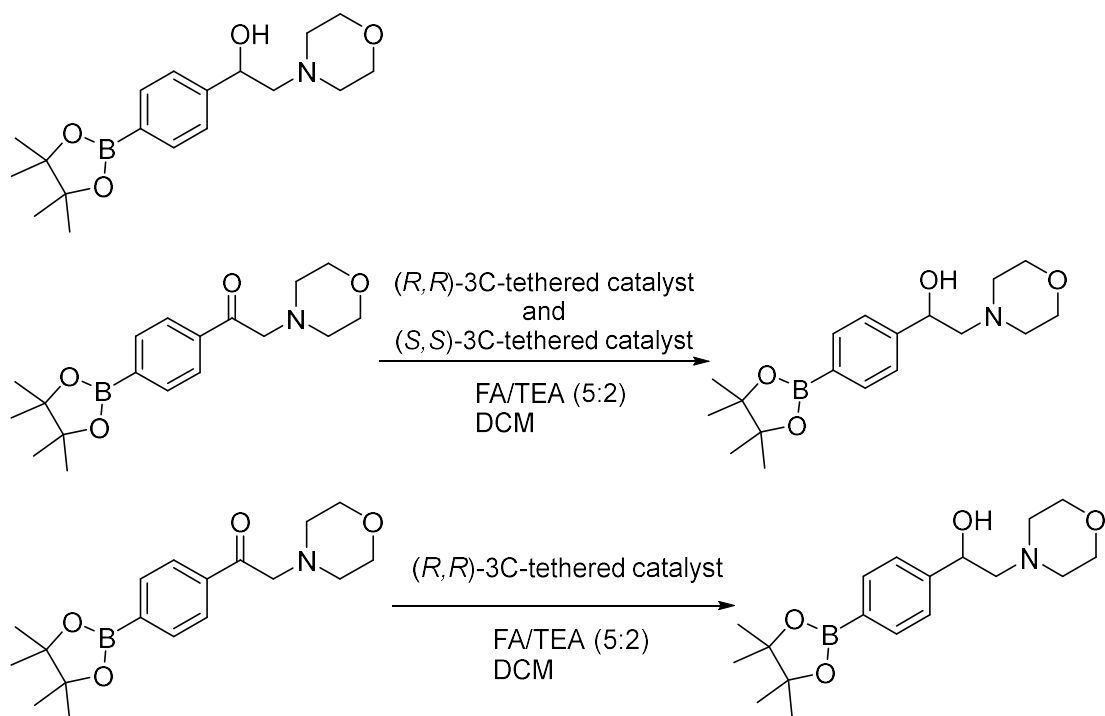
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Time [min.]

Voltage [mV]

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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 μ mol, 0.5 mol%) and (*S,S*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (0.75 mg, 1.2 μ mol, 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 stirred under a nitrogen atmosphere and followed by TLC (5:95 MeOH: DCM). After 72 hours, the reaction was quenched using saturated NaHCO₃ 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 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: R_f ca 0.20 (5:95 MeOH: DCM), strong UV and KMnO₄; HRMS: (found (ESI⁺): [M+H]⁺, Calcd for C₁₈H₂₉BNO₄ 334.2179; Found 334.2184; 2.5 ppm error; ν_{max} 3432 (br), 2973, 2854, 1391, 1356,

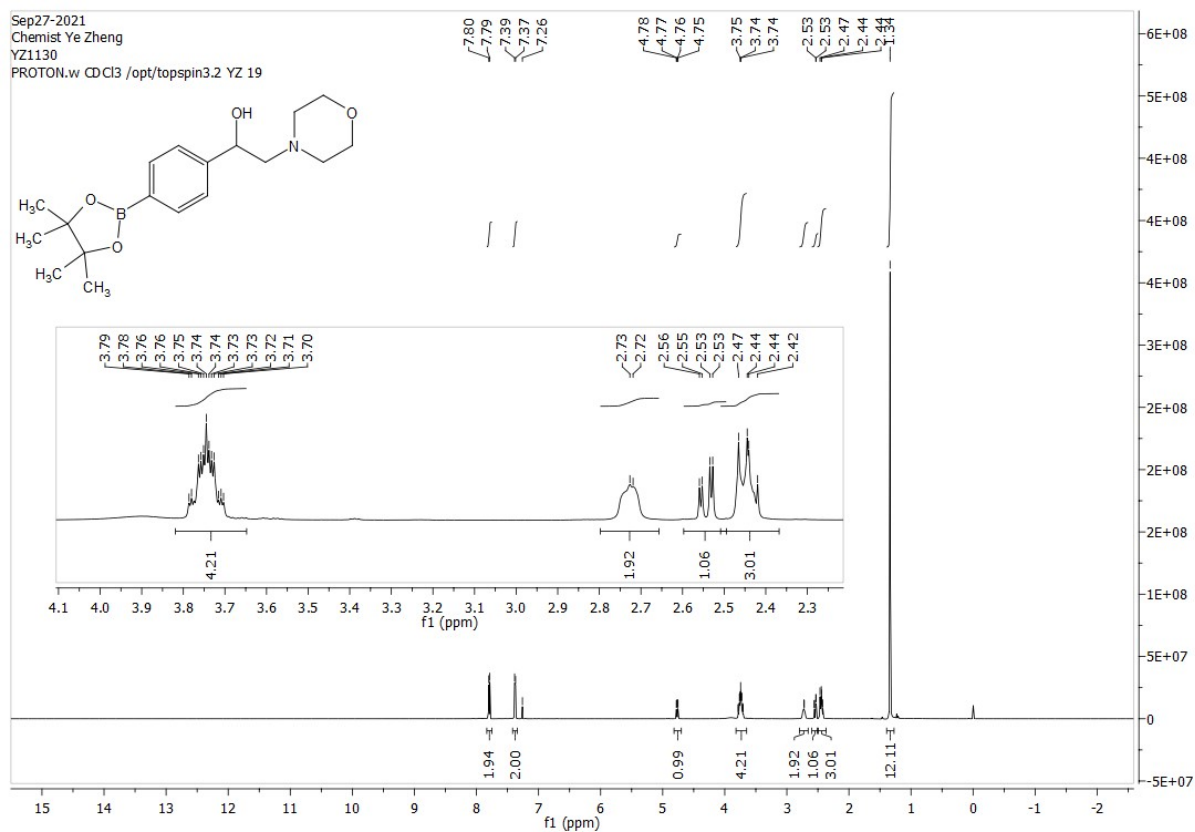
1319, 1144, 1113, 1086, 1070, 1016, 871 cm^{-1} ; δ_{H} (500 MHz, CDCl_3) 7.80 (2H, d, $J = 7.9$, ArH), 7.39 (2H, d, $J = 7.9$, ArH), 4.77 (1H, dd, $J = 10.3, 5.3$, ArCH), 3.79-3.70 (4H, m, CH_2), 2.73 (2H, d, $J = 3.8$, CH_2), 2.55 (1H, dd, $J = 12.5, 3.4$, CH_2), 2.47-2.42 (3H, m, CH_2), 1.34 (12H, s, CH_3) ppm; δ_{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 ($\text{M}^+ + 1$, 100%).

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

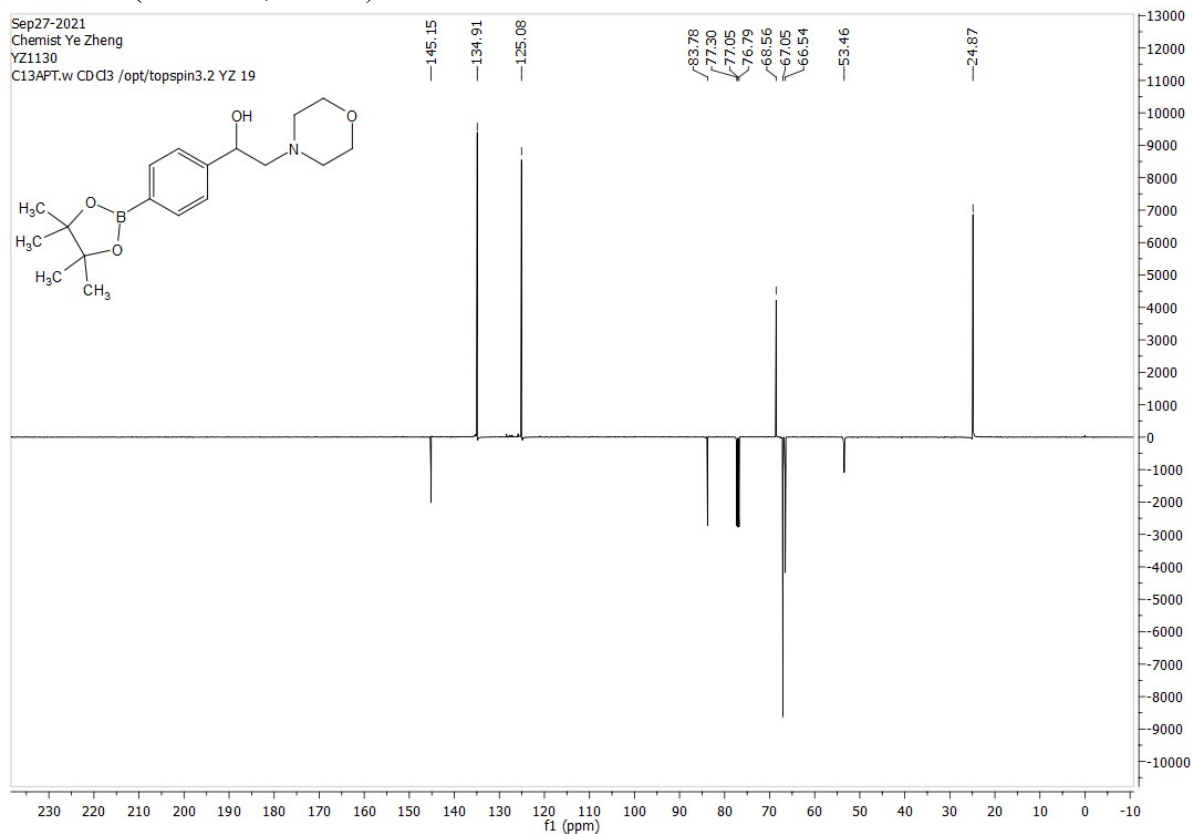
ATH of 2-morpholino-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one):

(*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 stirred 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, $T = 25^\circ\text{C}$): $[\alpha]_{\text{D}}^{24} +44.3$ (c 0.263 in CHCl_3) 99% ee.

^1H NMR (500 MHz, CDCl_3)

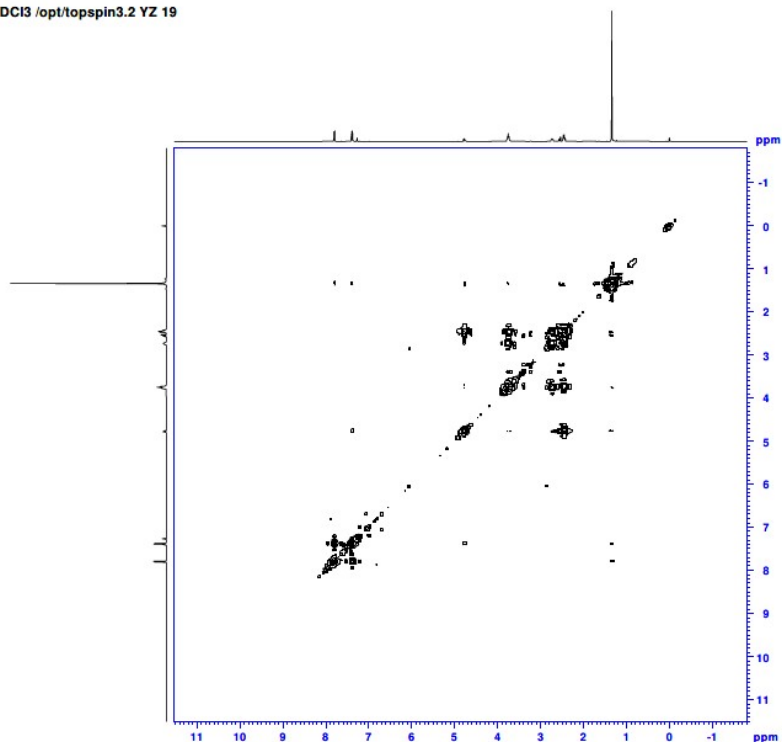


^{13}C NMR (125 MHz, CDCl_3)



COSY (500 MHz, CDCl₃)

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YZ1130
COSY.w CDCl₃ /opt/topspin3.2 YZ 19



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Current Data Parameters
NAME      Sep17-2021
EXPNO     1
PROCNO    1

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SOLVENT   CDCl3
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DS         4
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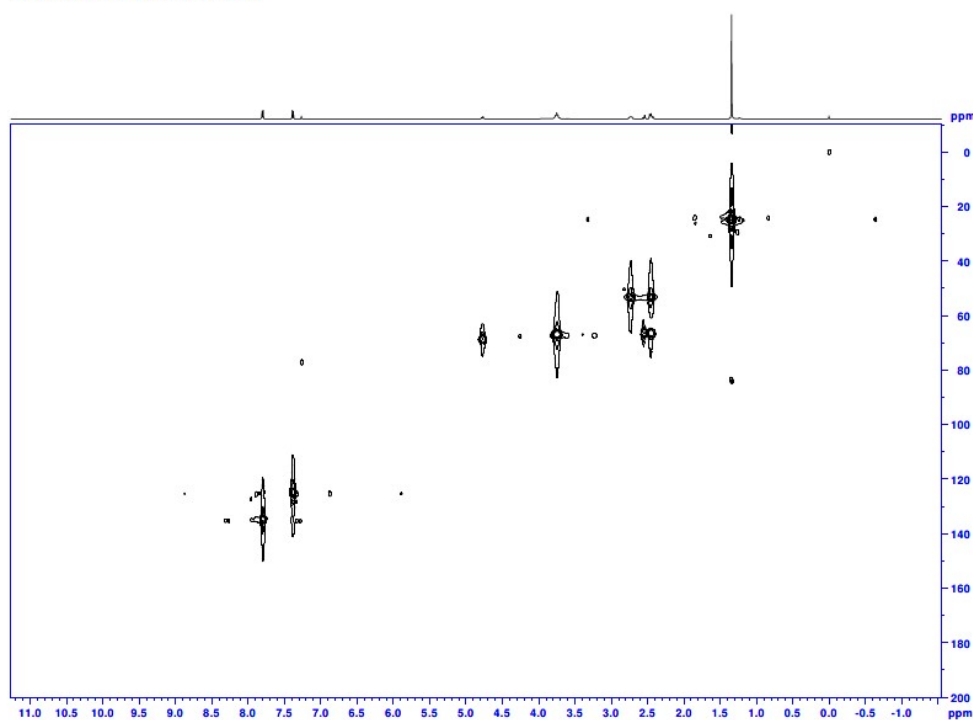
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F1 - Processing parameters
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HSQC (500 MHz, CDCl₃)

Chemist Ye Zheng
YZ1130
HSQC.w CDCl₃ /opt/topspin3.2 YZ 19



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Current Data Parameters
NAME      Sep17-2021
EXPNO     1
PROCNO    1

F2 - Acquisition Parameters
Date_     20210927
Time      17.48
INSTRUM   spect
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PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         2
DS         4
SWH        6410.481 Hz
FIDRES     0.1514000 Hz
AQ         0.1514000 sec
RG         327.41
DE         17.41
TE         300.2 K
DQ         40.00
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===== CHANNEL F1 =====
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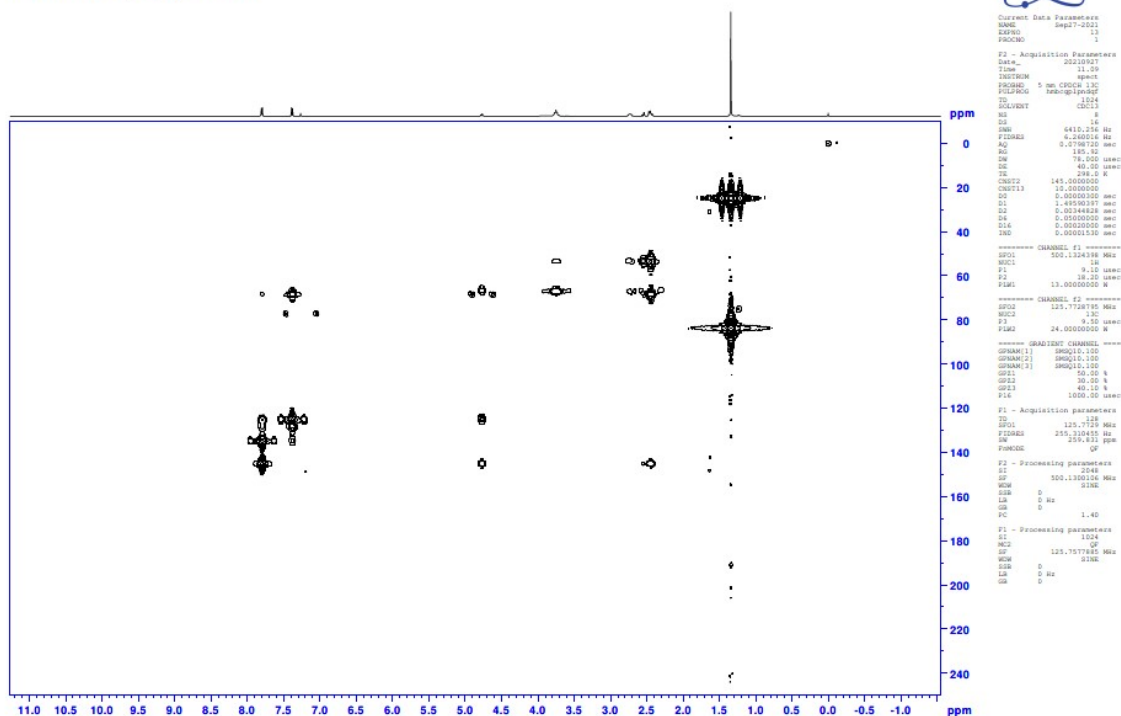
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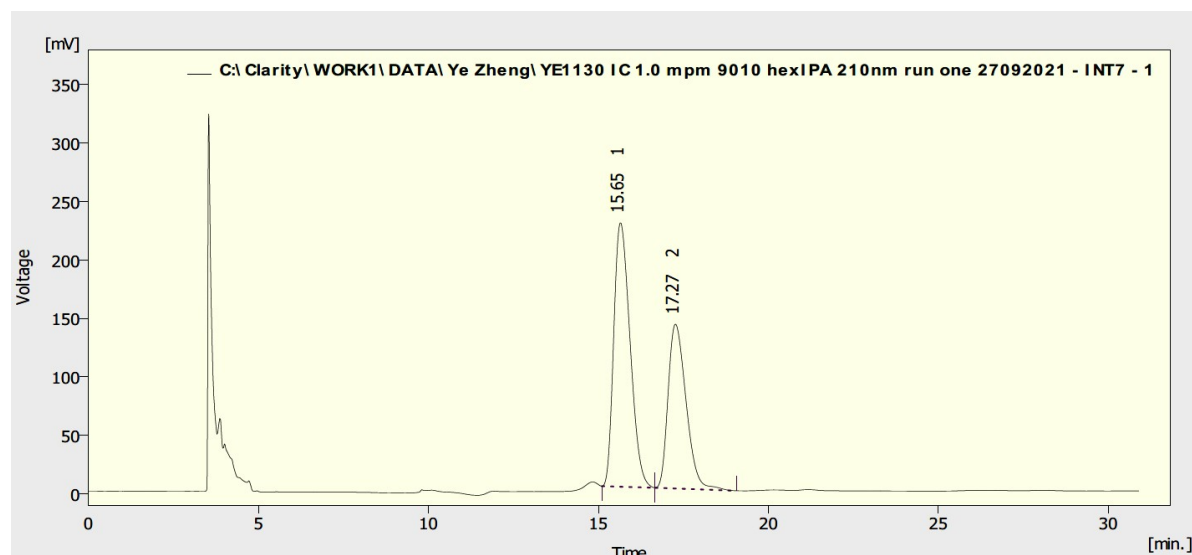
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HMBC (500 MHz, CDCl₃)

Chemist Ye Zheng
YZ1130
HMBC.w CDCl₃/opt/topspin3.2 YZ 19



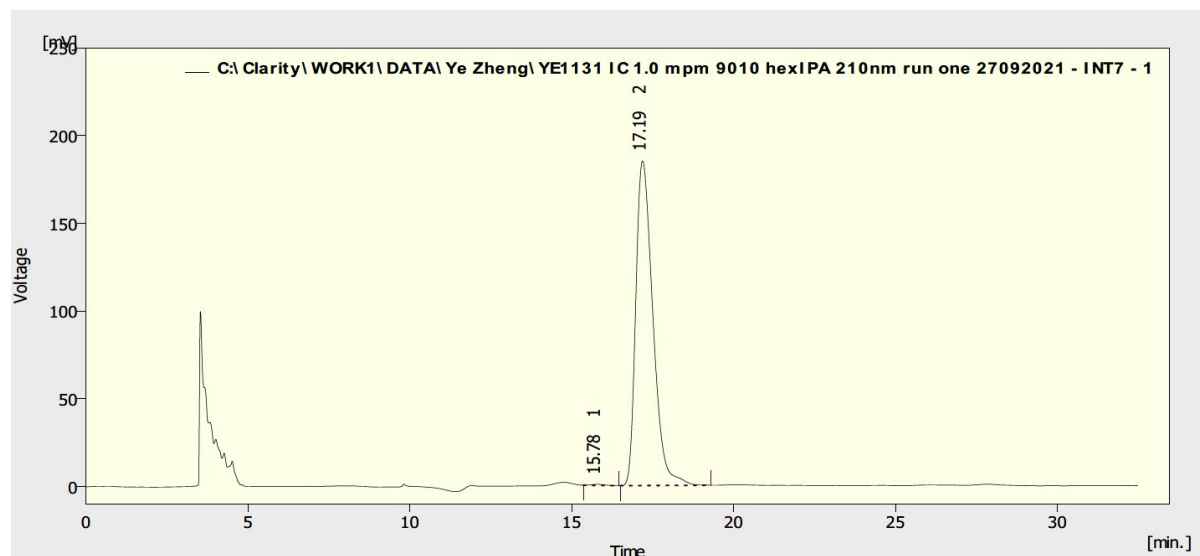
HPLC of racemic 2-morpholino-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol **15**.



Result Table (Uncal - C:\Clarity\WORK1\DATA\Ye Zheng\YE1130 IC 1.0 ppm 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		

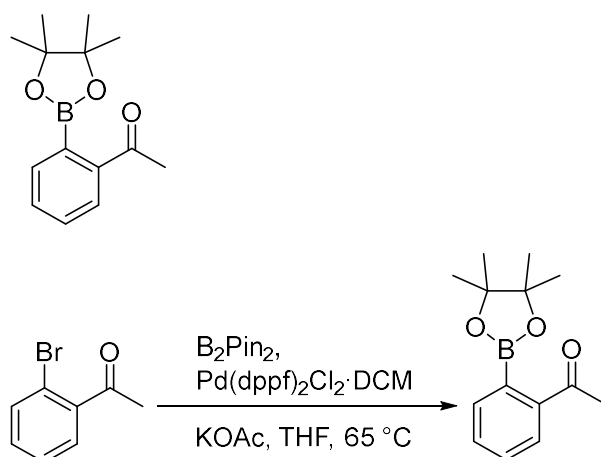
HPLC after ATH of 2-morpholino-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one using (*R,R*)-3C-Tethered Ru(II)-TsDPEN catalyst **2** (after 72 hours, 100% conversion, 99% ee).



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		

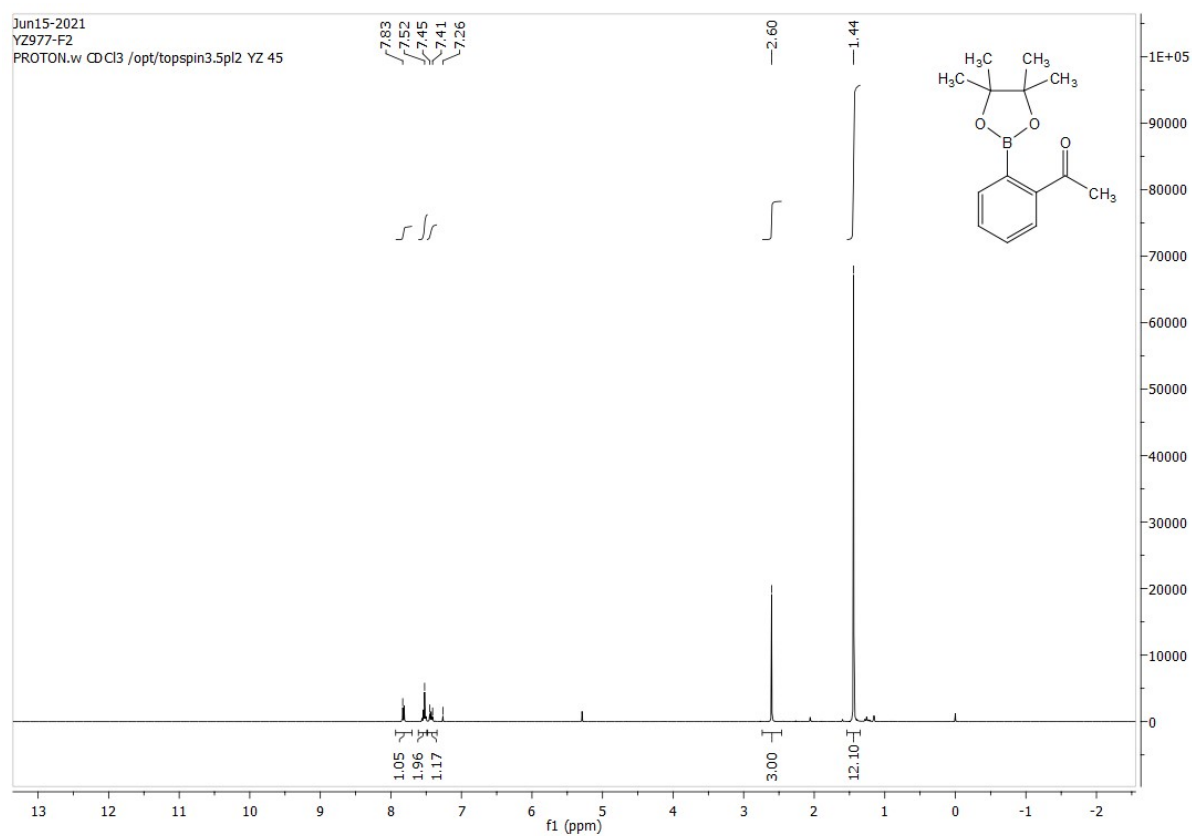
1-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one **16**.



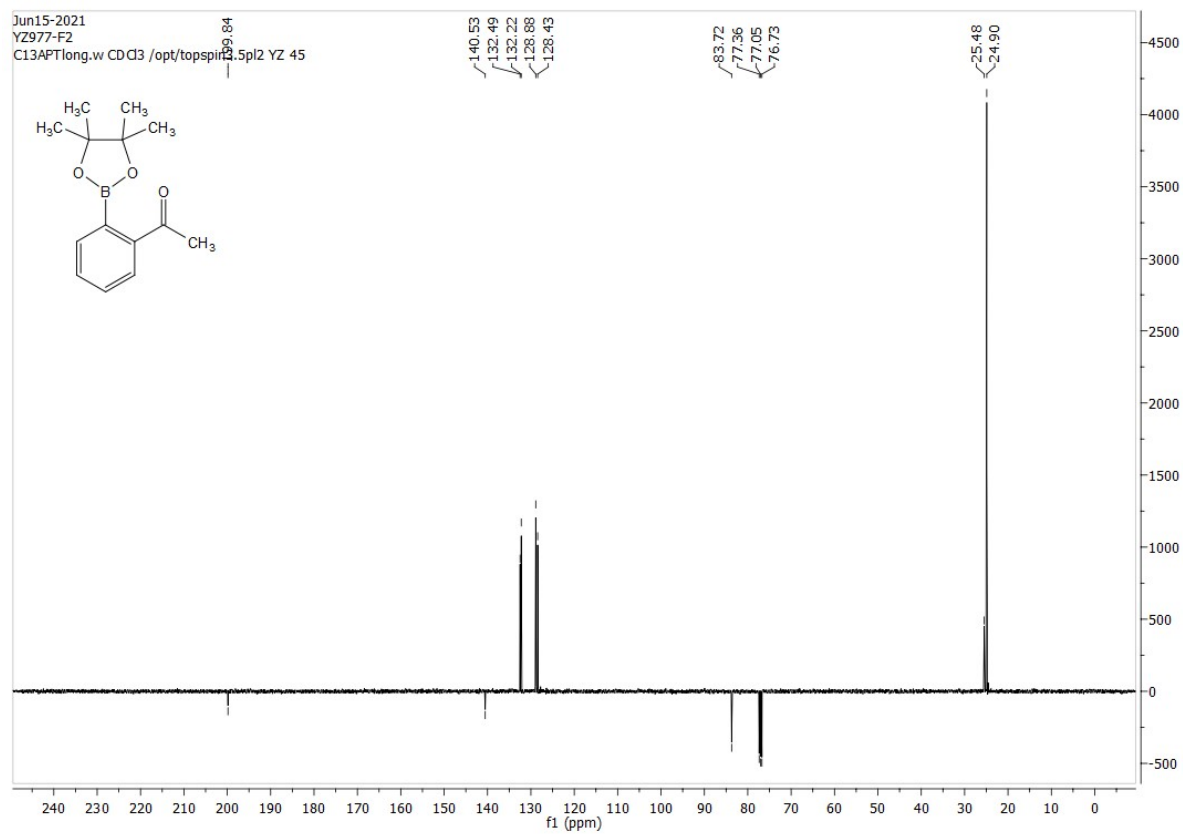
This compound has been reported and fully characterized: N. Su, T. Deng, D. J. Wink and T. G. Driver, *Org. Lett.* 2017, **19**, 3990-3993.

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)₂Cl₂·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 (MgSO₄) 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: R_f ca 0.50 (9:1 hexane: EtOAc), strong UV and KMnO₄; δ_H (400 MHz, CDCl₃) 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, CH₃), 1.44 (12H, s, CH₃) ppm; δ_C (100 MHz, CDCl₃) 199.84 (C), 140.53 (C), 132.49 (CH), 132.22 (CH), 128.88 (CH), 128.43 (CH), 83.72 (C), 25.48 (CH₃), 24.90 (CH₃) ppm. Data matched that reported.

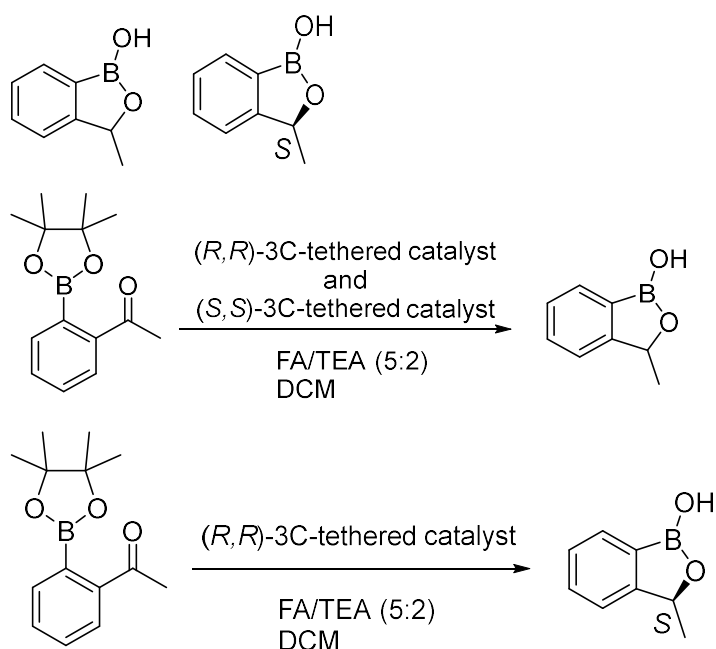
^1H NMR (400 MHz, CDCl_3)



^{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.

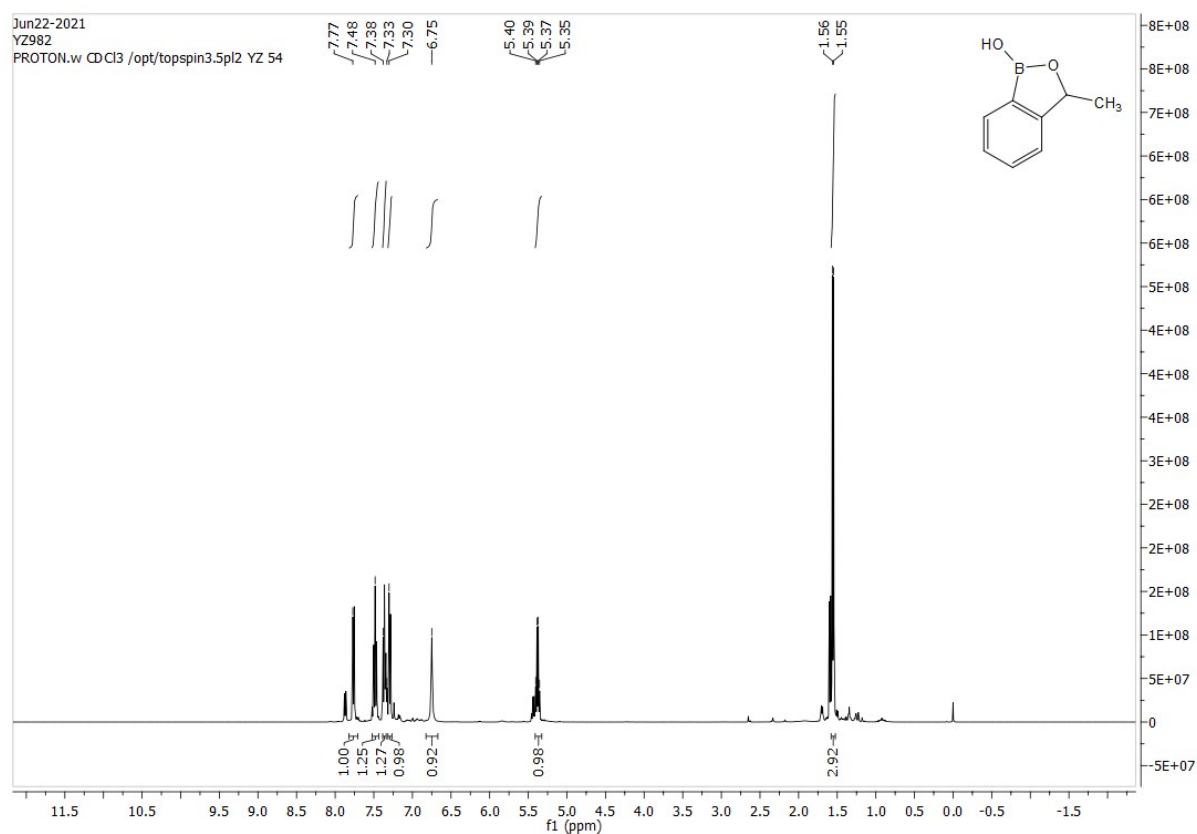
Synthesis of a racemic standard:

(*R,R*)-3C-Tethered Ru(II)-TsDPEN catalyst **2** (3.1 mg, 5.0 μ mol, 0.5 mol%) and (*S,S*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (3.1 mg, 5.0 μ mol, 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 stirred under a nitrogen atmosphere and followed by TLC (4:1 hexane: EtOAc). After 72 hours, the reaction was quenched using saturated NaHCO₃ 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 0-50% 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: R_f ca 0.20 (4:1 hexane: EtOAc), strong UV and KMnO₄; δ_{H} (400 MHz, CDCl₃) 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, CH₃) ppm; δ_{C} (100 MHz, CDCl₃) 158.01 (C), 131.19 (CH), 130.66

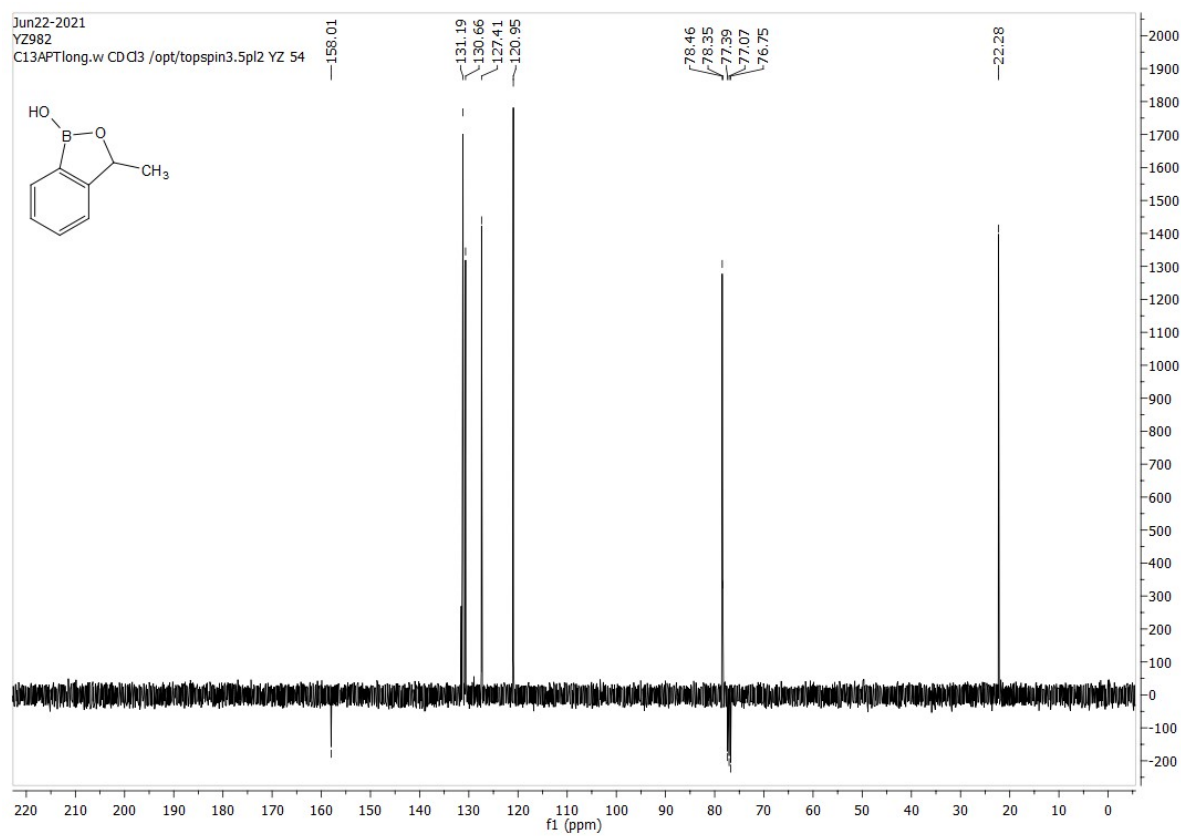
(CH), 127.41 (CH), 120.95 (CH), 78.46 (CH), 22.38 (CH₃) ppm. Data matched that reported.

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 NaHCO₃ 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 0-50% 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.

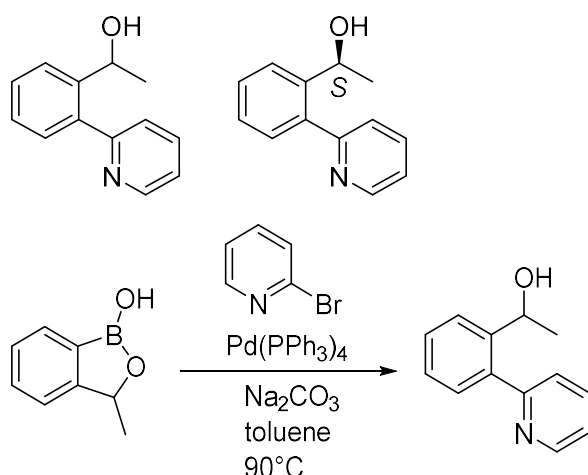
^1H NMR (400 MHz, CDCl_3)



^{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.

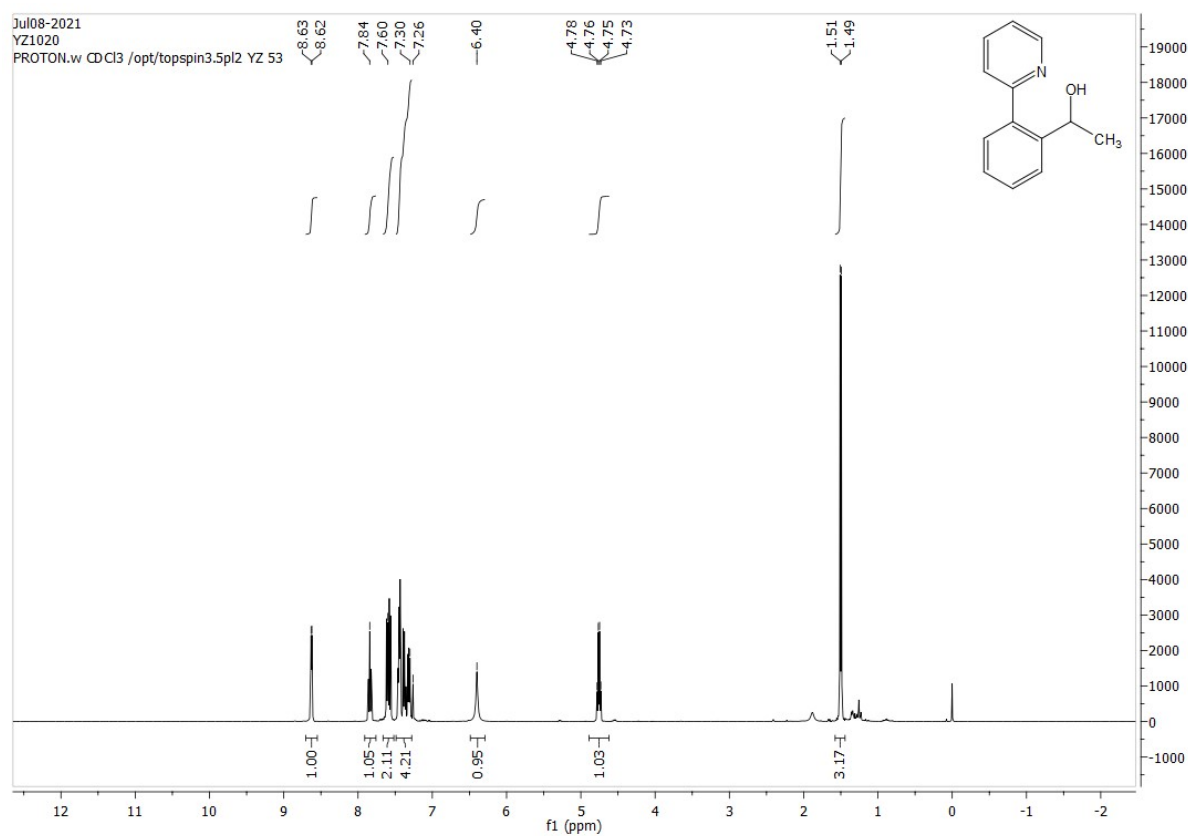
To a solution of $\text{Pd(PPh}_3)_4$ (70.5 mg, 0.0610 mmol) in toluene (7.3 mL) was added 2-bromopyridine (386 mg, 2.44 mmol), racemic 3-methylbenzo[*c*][1,2]oxaborol-1(3*H*)-ol **17** (180 mg, 1.22 mmol) and sodium carbonate (0.732 mL, 20% w/v). The reaction mixture was heated to 90 °C and left stirring 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: R_f ca 0.20 (2:1 hexane: EtOAc), strong UV and KMnO_4 ; δ_{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; δ_{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 ($\text{M}^+ + 23$, 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.

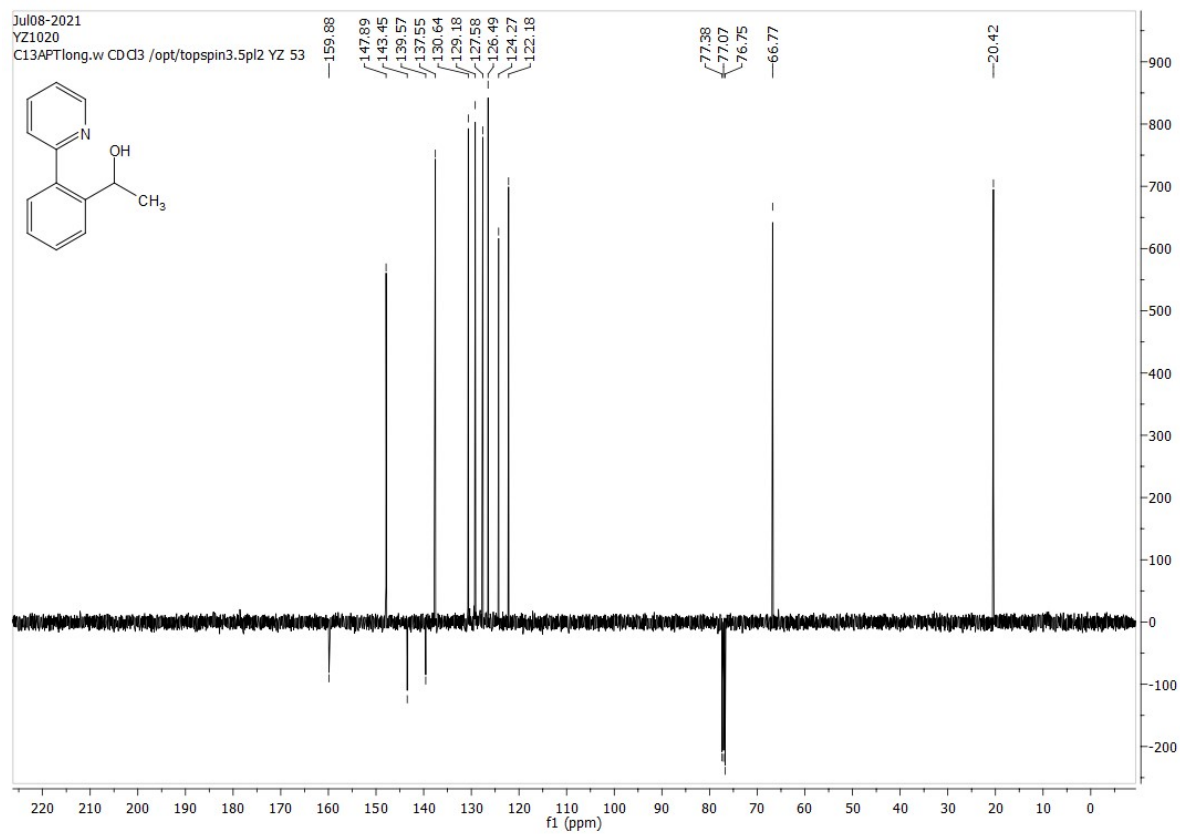
Asymmetric.

To a solution of Pd(PPh₃)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 (MgSO₄) 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); [α]_D²⁶ -11.4 (c 0.460 in CHCl₃) 31% ee (*S*) (lit. [α]_D²⁶ -14.3 (c 0.40 in CHCl₃) >99% ee (*S*)) Reference: E. Liardo, N. Rios-Lombardia, F. Moris, J. Gonzalez-Sabin, F. Rebolledo; *Eur. J. Org. Chem.* 2018, **23**, 3031-3035.

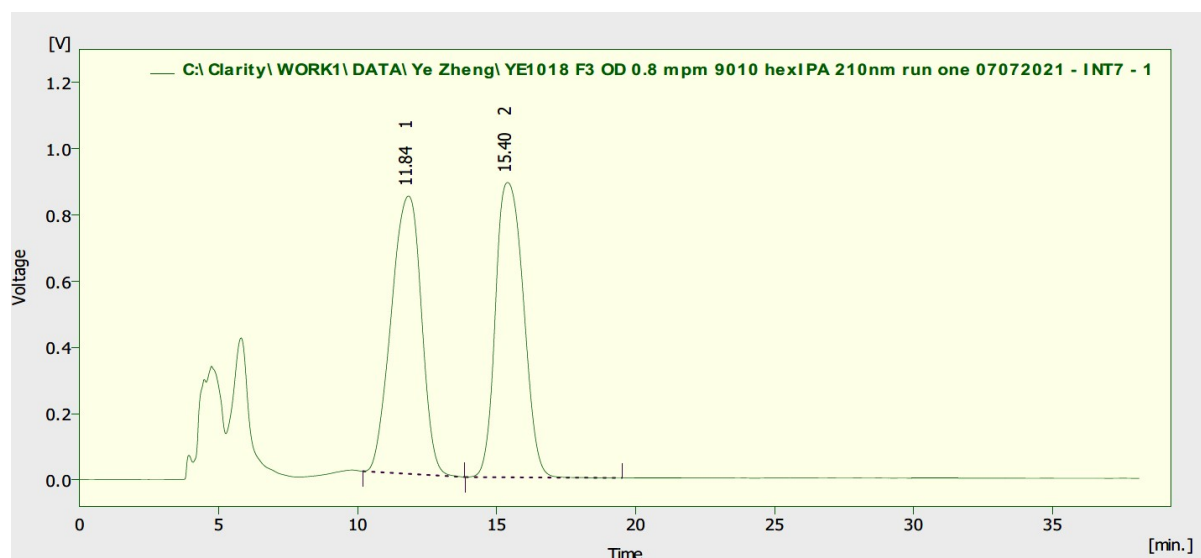
^1H NMR (400 MHz, CDCl_3)



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



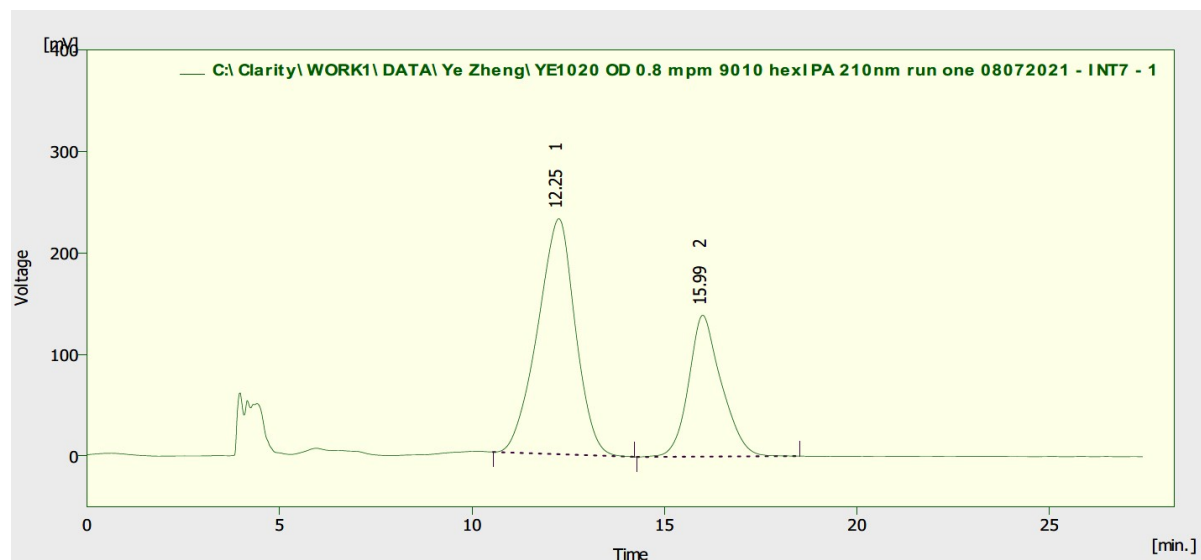
HPLC of racemic 1-(2-(pyridin-2-yl)phenyl)ethan-1-ol **18**.



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).

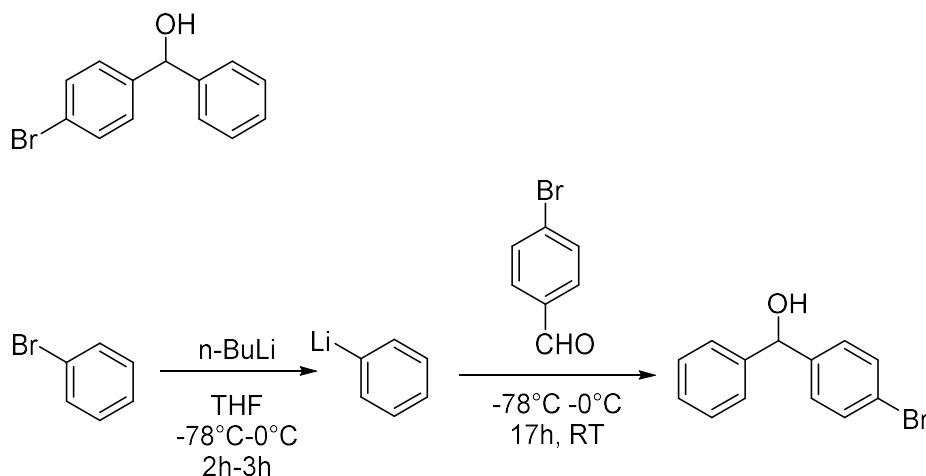


Result Table (Uncal - C:\Clarity\WORK1\DATA\Ye Zheng\YE1020 OD 0.8 mpm 9010 hexIPA 210nm run one 08072021 - INT7 - 1)

	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.

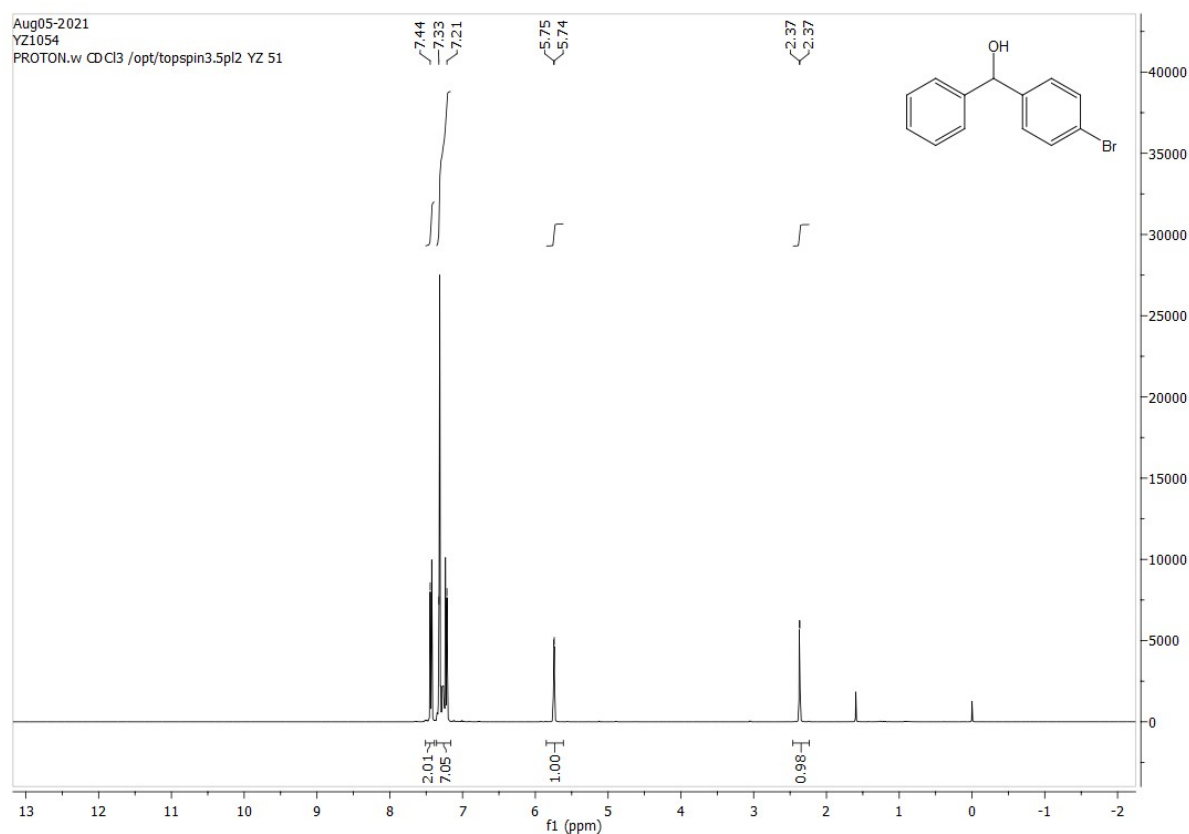
(4-Bromophenyl)(phenyl)methanol.



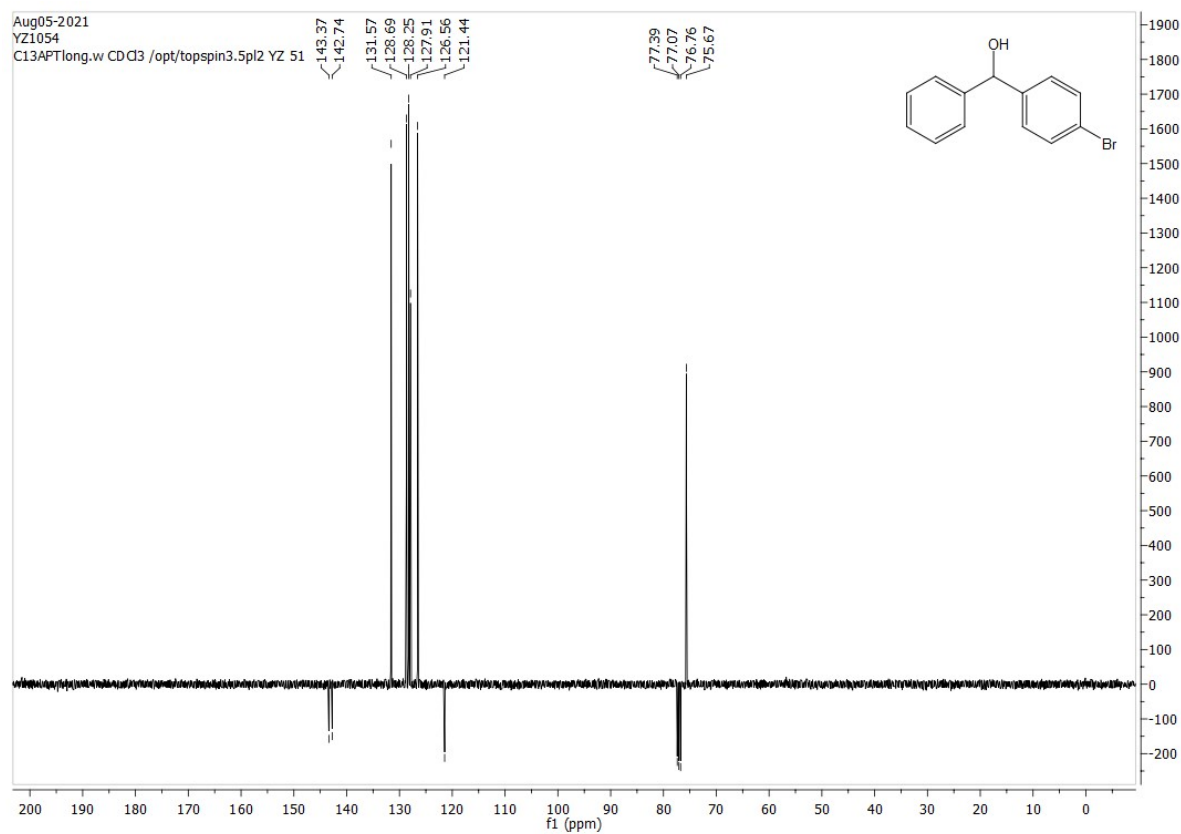
This compound has been reported and fully characterized: M. Das, D. F. O'Shea, *J. Org. Chem.* 2014, **79**, 5595-5607.

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 NH₄Cl 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 (MgSO₄) 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: R_f ca 0.20 (9:1 hexane: EtOAc), strong UV and KMnO₄; δ_H (400 MHz, CDCl₃) 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; δ_C (100 MHz, CDCl₃) 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.

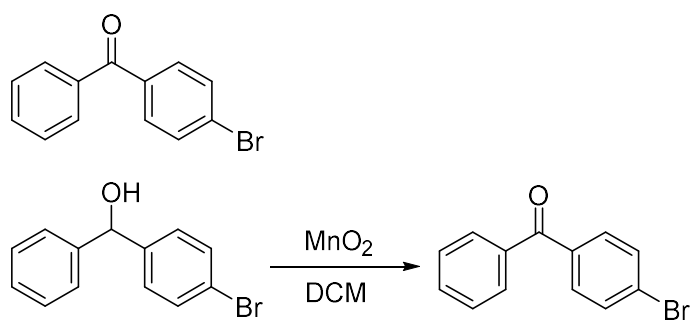
^1H NMR (400 MHz, CDCl_3)



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



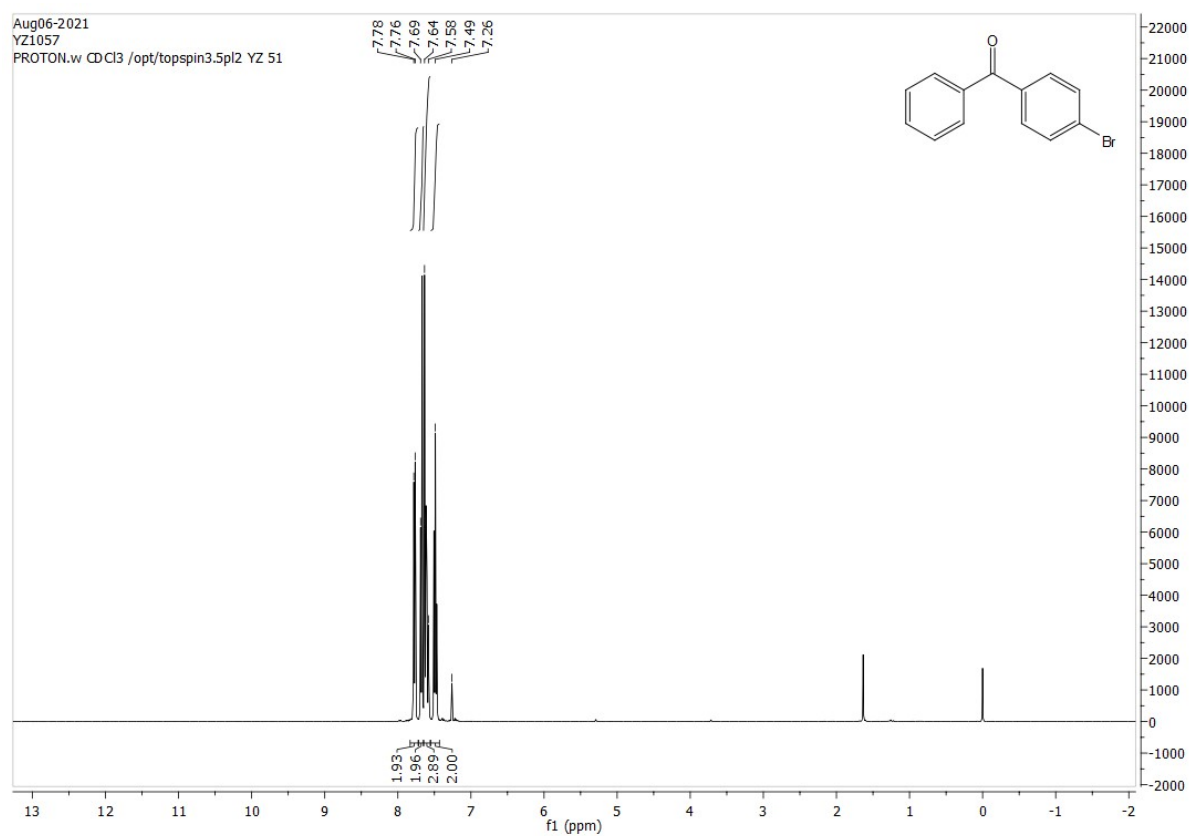
(4-Bromophenyl)(phenyl)methanone.



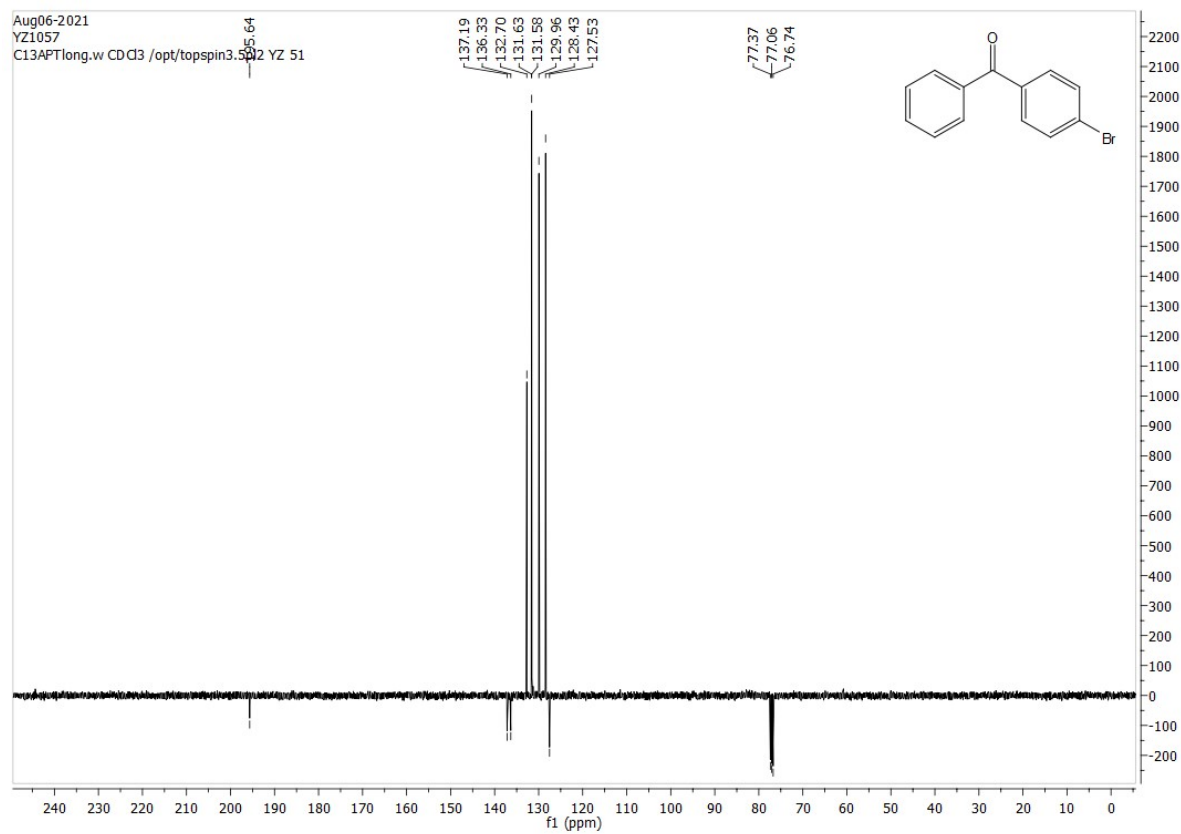
This compound has been reported and fully characterized: B. Skillinghaug, C. Skold, J. Rydfjord, F. Svensson, M. Behrends, J. Savmarker, P. J. R. Sjöberg, M. Larhed, *J. Org. Chem.* 2014, **79**, 12018-12032.

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: R_f ca 0.40 (9:1 hexane: EtOAc), strong UV and KMnO₄; δ_{H} (400 MHz, CDCl₃) 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; δ_{C} (100 MHz, CDCl₃) 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.

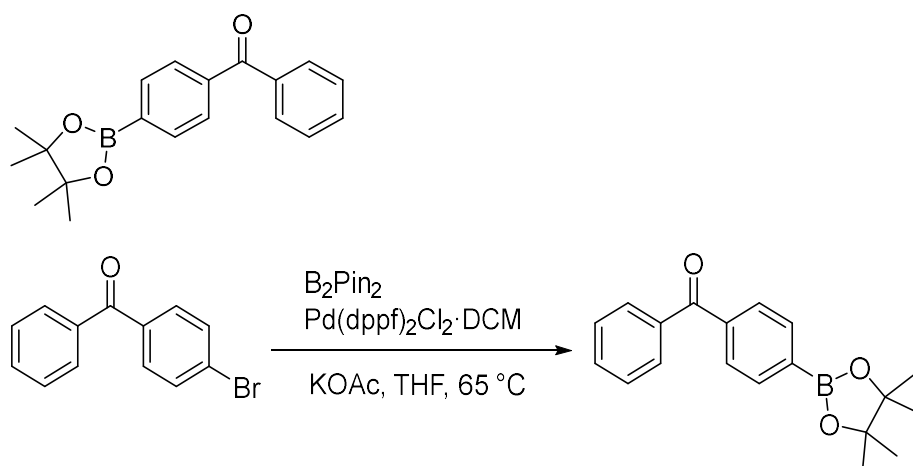
^1H NMR (400 MHz, CDCl_3)



^{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. Joksche, 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.

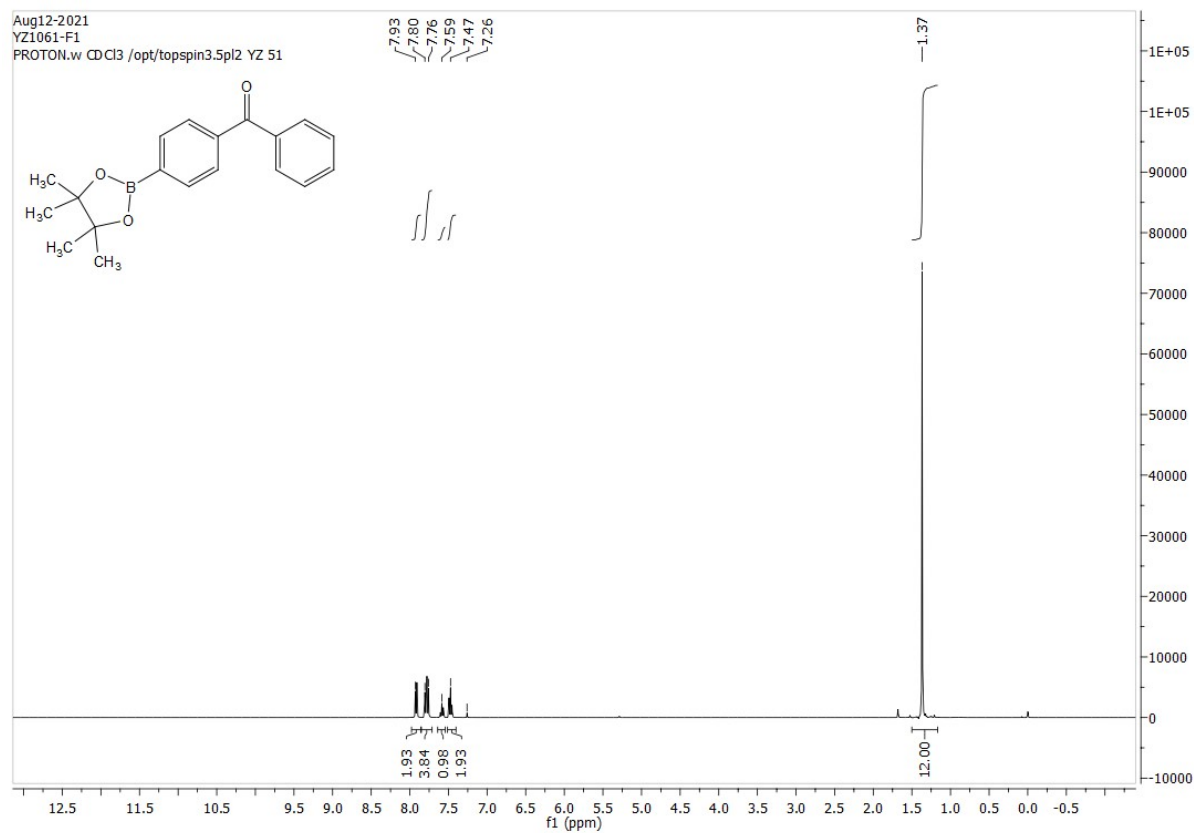
A round-bottom flask was charged with (4-bromophenyl)(phenyl)methanone (260 mg, 1.00 mmol), bis(pinacolato)diboron (305 mg, 1.20 mmol), potassium acetate (294 mg, 3.00 mmol), THF (5 mL) and $Pd(dppf)_2Cl_2 \cdot DCM$ (40.9 mg, 0.0500 mmol). The reaction mixture was heated to 65 °C and left stirring under 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: R_f ca 0.50 (4:1 hexane: EtOAc), strong UV and $KMnO_4$; δ_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; δ_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%).

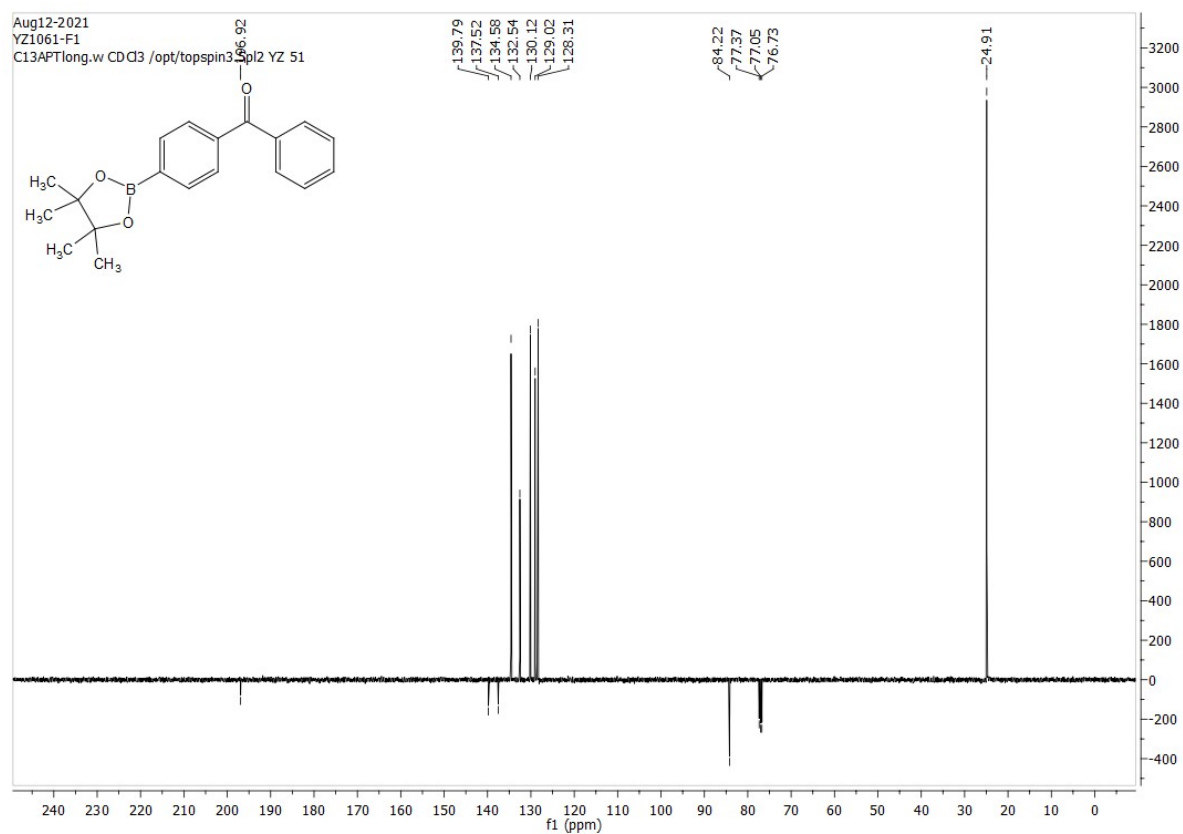
Data matched that reported.

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

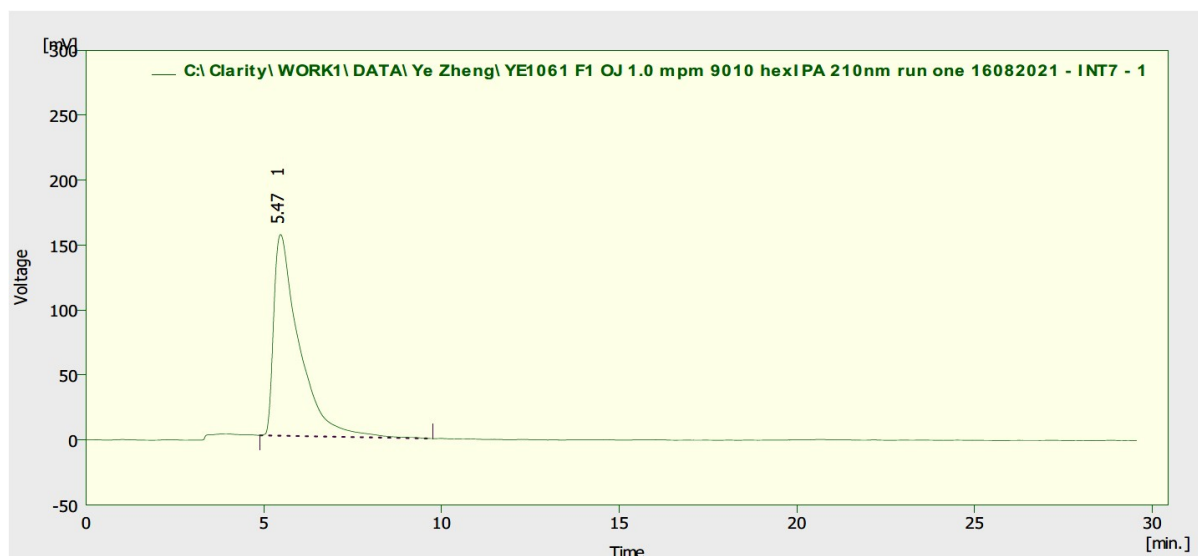
^1H NMR (400 MHz, CDCl_3)



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



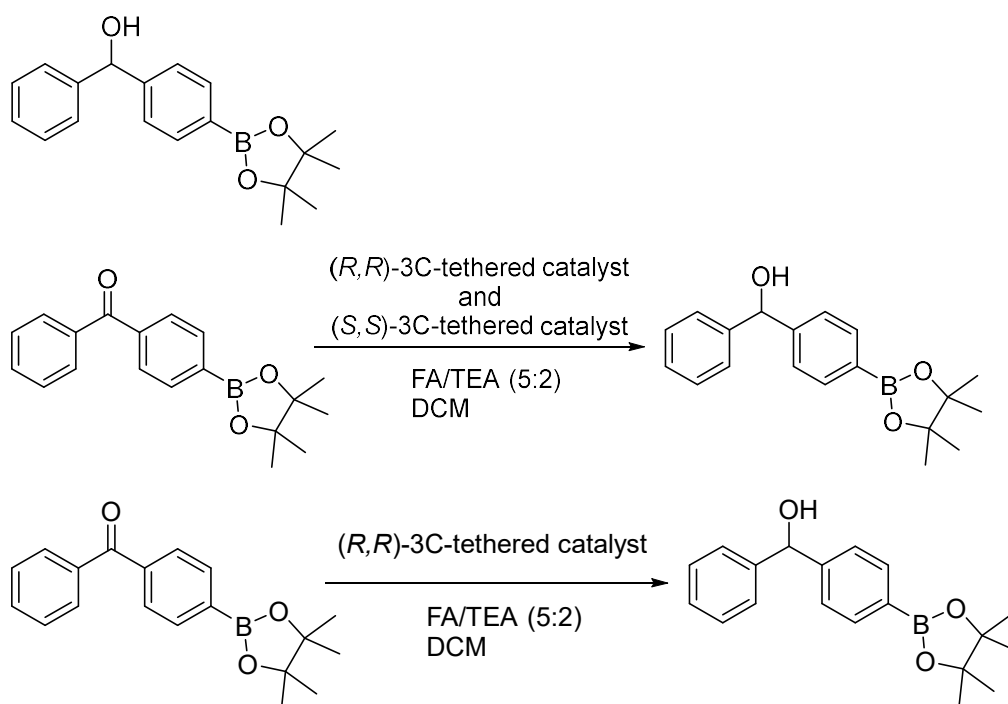
HPLC of phenyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone



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:

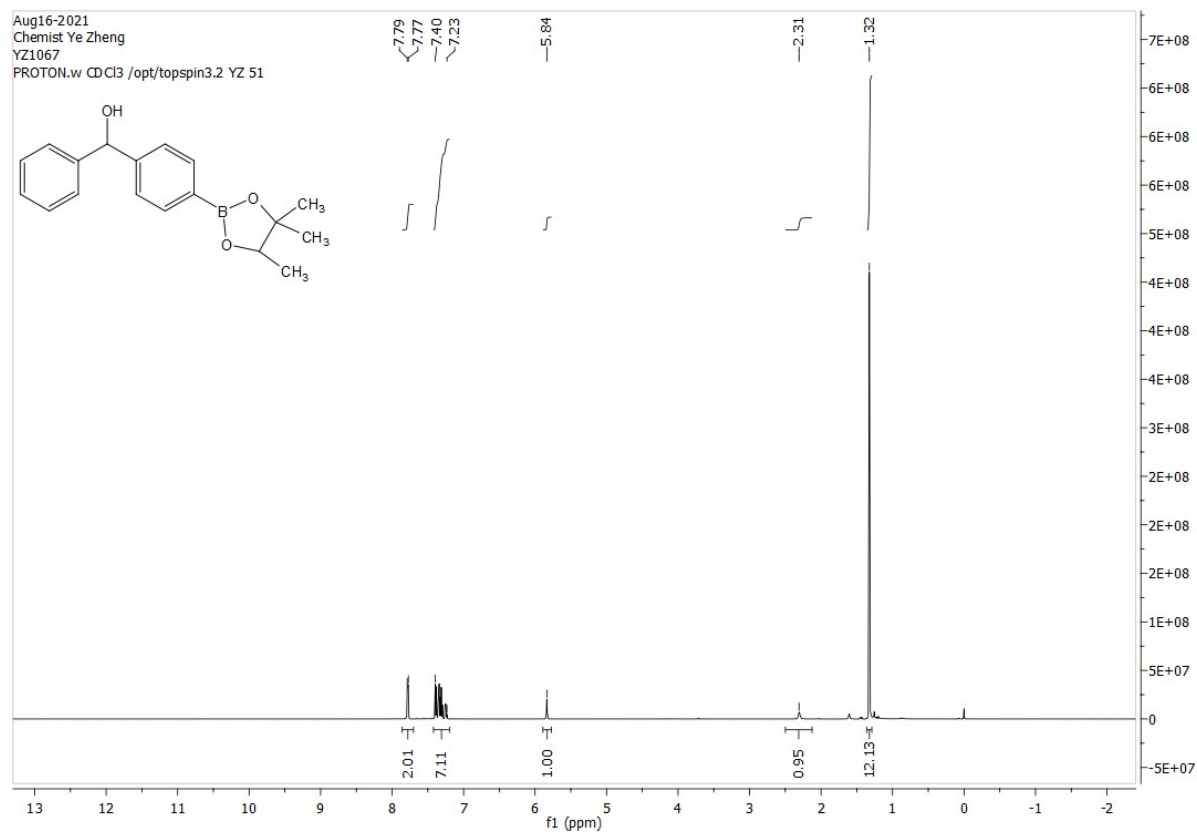
(*R,R*)-3C-Tethered Ru(II)-TsDPEN catalyst **2** (0.40 mg, 0.65 μ mol, 0.5 mol%) and (*S,S*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (0.40 mg, 0.65 μ mol, 0.5 mol%) were added to FA: TEA (5:2 azeotropic mixture, 0.18 mL) at rt and the mixture was stirred under a nitrogen atmosphere for 15 minutes; after 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 stirred under a nitrogen atmosphere and followed by TLC (9:1 hexane: EtOAc). After 72 hours, the reaction was quenched using saturated NaHCO₃ 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 0-50% 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: R_f ca 0.20 (9:1 hexane: EtOAc), strong UV and KMnO₄; δ_{H} (500 MHz, CDCl₃) 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, CH₃) ppm; δ_{C} (125 MHz, CDCl₃)

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 (CH₃) ppm; m/z (ES-API+) 333.2 (M⁺ + 23, 100%). Data matched that reported.

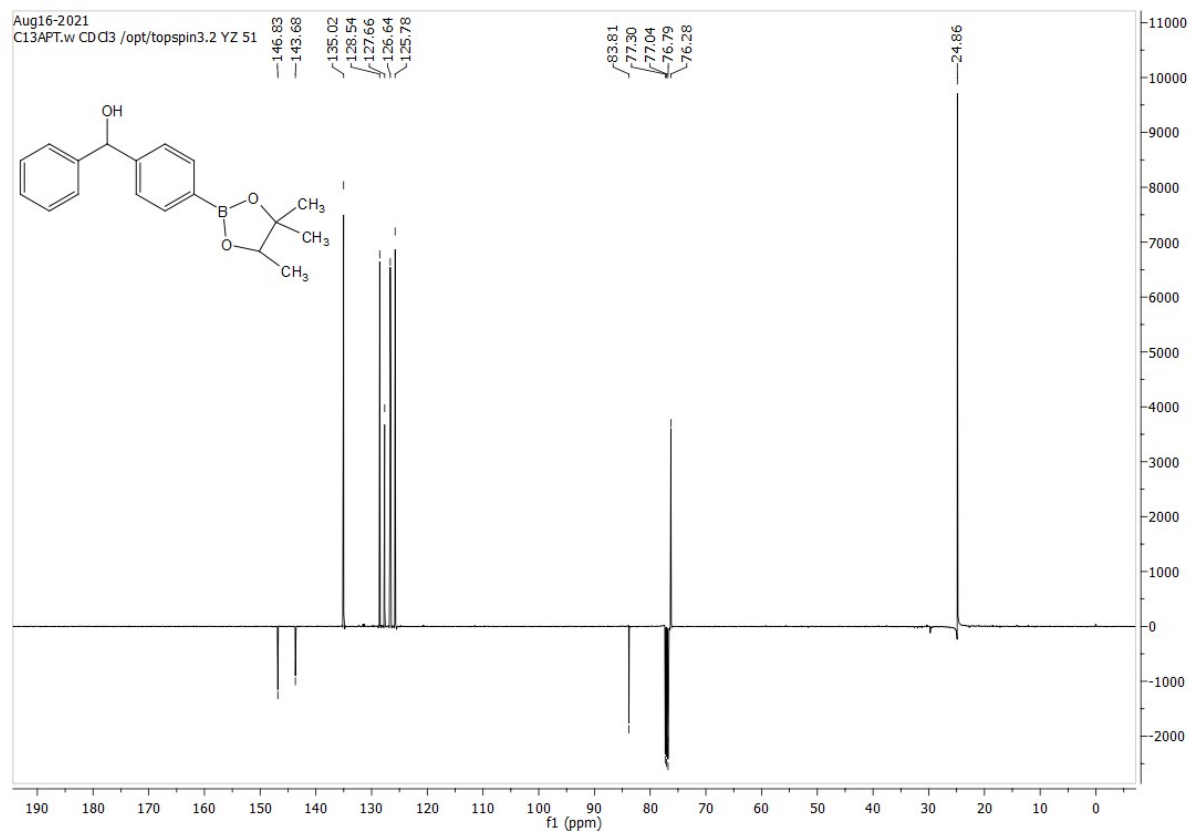
Enantiomeric excess and conversion determined by HPLC analysis (Chiralcel OJ, 30 cm x 6mm column, hexane:iPrOH 90:10, 1.0 mL/min, T = 25°C) ketone 5.5 min, *R* and *S* isomers 11.8 min and 18.8 min, configuration is not confirmed.

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 NaHCO₃ 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 0-50% 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.

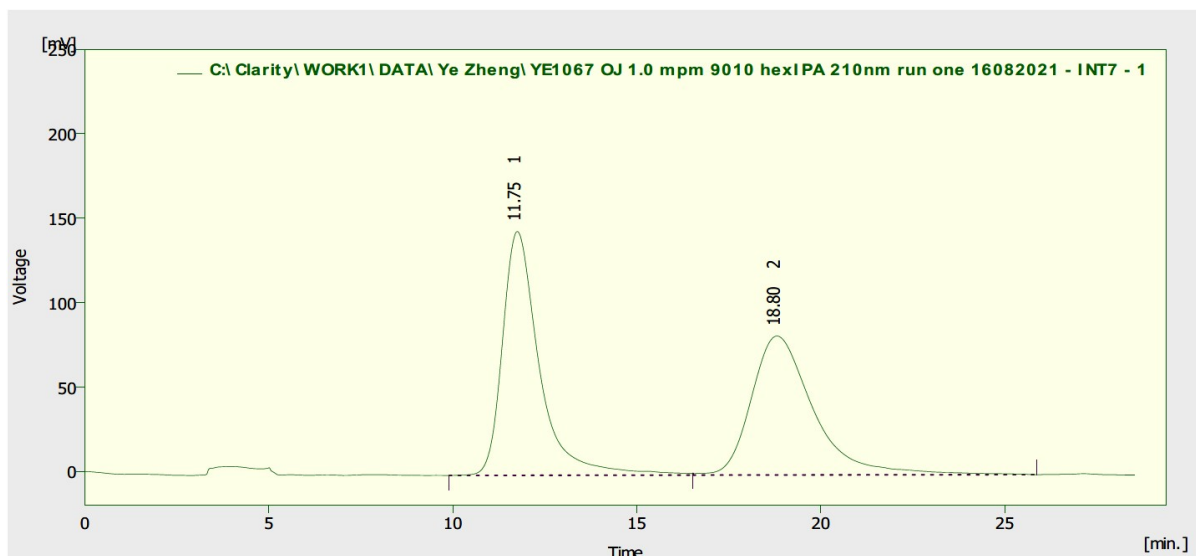
¹H NMR (500 MHz, CDCl₃)



¹³C NMR (125 MHz, CDCl₃)



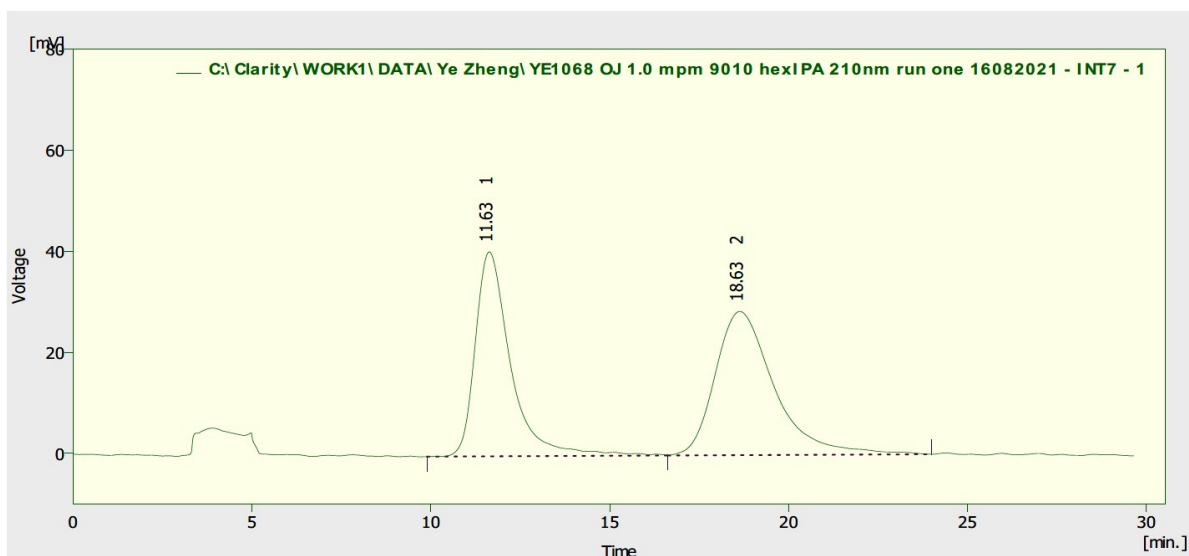
HPLC of racemic phenyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanol **22**



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		

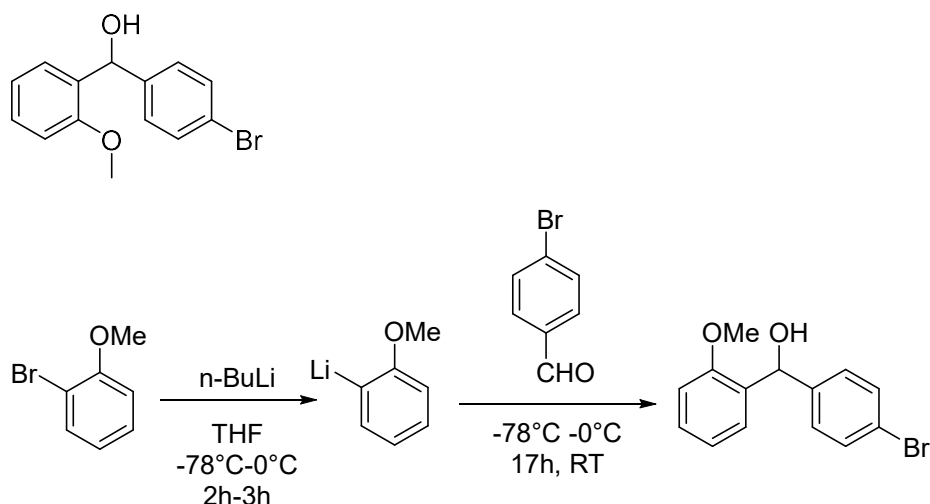
HPLC after ATH of phenyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone using (*R,R*)-3C-Tethered Ru(II)-TsDPEN catalyst **2** (after 72 hours, 100% conversion, 8% ee)



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		

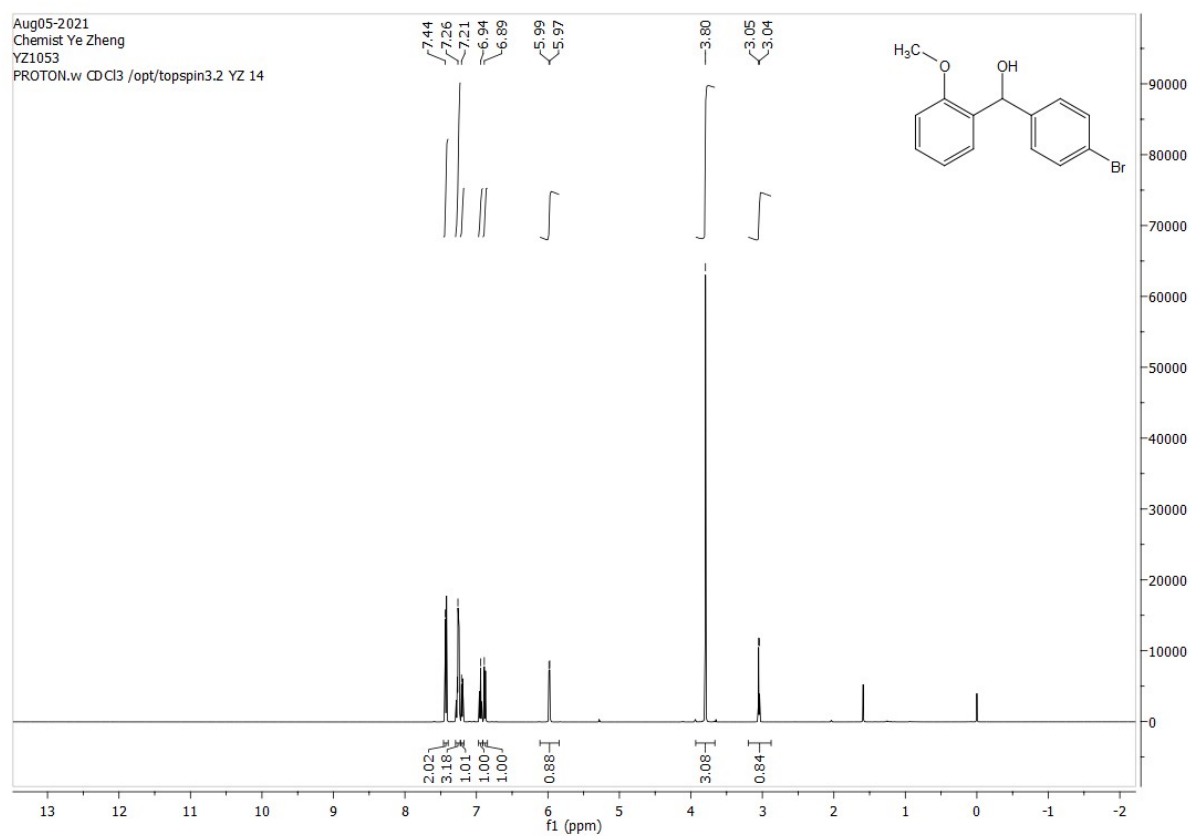
(4-Bromophenyl)(2-methoxyphenyl)methanol.



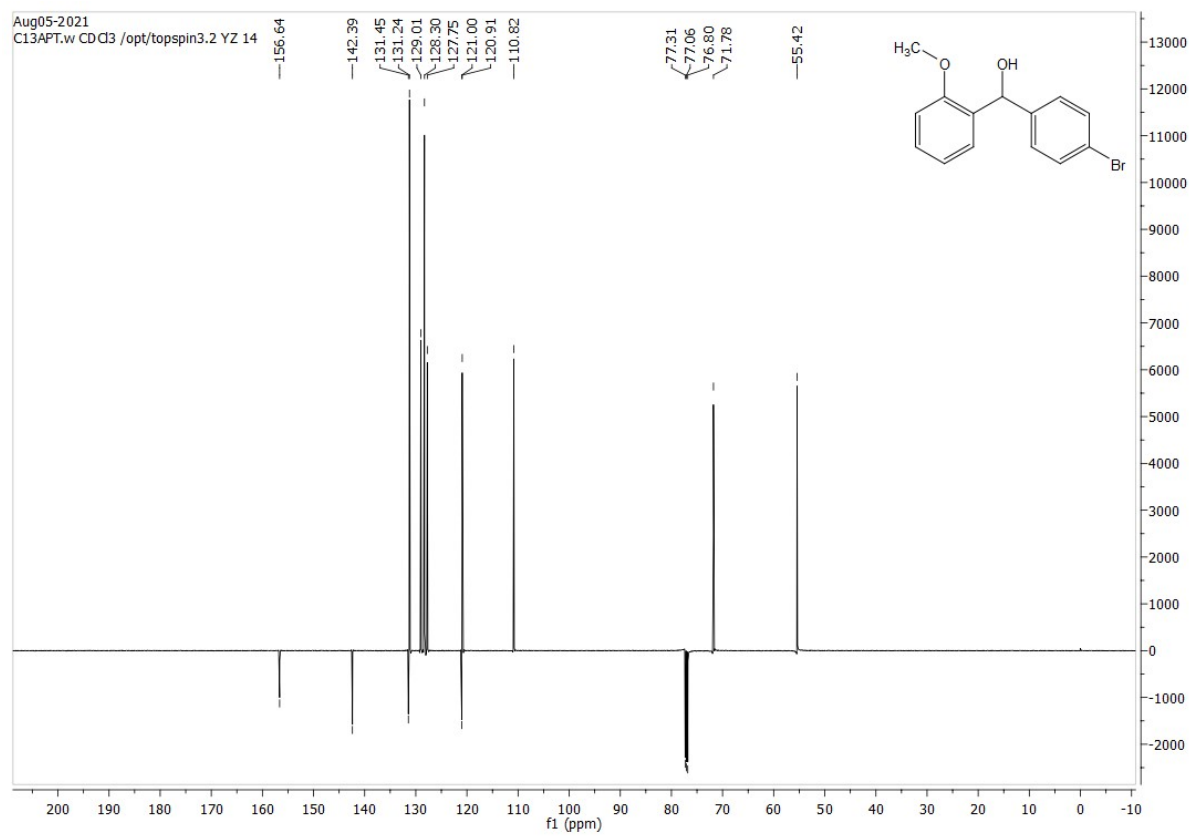
This compound is novel.

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 NH₄Cl 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 (MgSO₄) 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: R_f ca 0.20 (9:1 hexane: EtOAc), strong UV and KMnO₄; Mp: 75°C; HRMS: (found (ESI⁺): [M+H]⁺, Calcd for C₁₄H₁₃⁷⁹BrNaO₂ 314.9983; Found 314.9991; 2.7 ppm error); ν_{max} 3212 (br), 2998, 2938, 1587, 1485, 1462, 1437, 1279, 1240, 1184, 1046, 1029, 807, 751 cm⁻¹; δ_H (500 MHz, CDCl₃) 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, OCH₃), 3.05 (1H, d, *J* = 5.6, OH) ppm; δ_C (125 MHz, CDCl₃) 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 (CH₃) ppm; m/z (ES-API⁺) 315.0 (M⁺ + 23, 100%).

^1H NMR (500 MHz, CDCl_3)

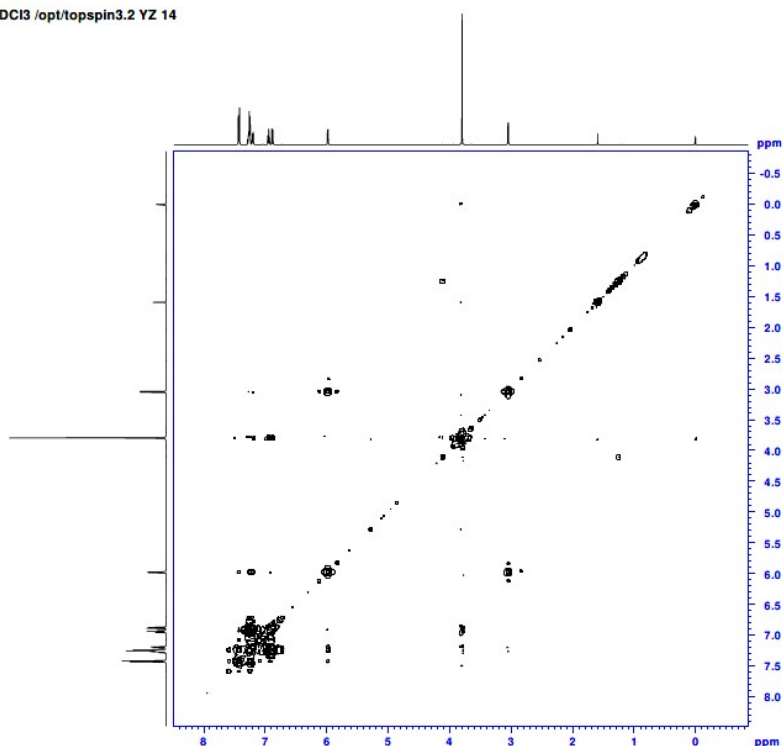


^{13}C NMR (125 MHz, CDCl_3)



COSY (500 MHz, CDCl₃)

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



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PROCNO    1

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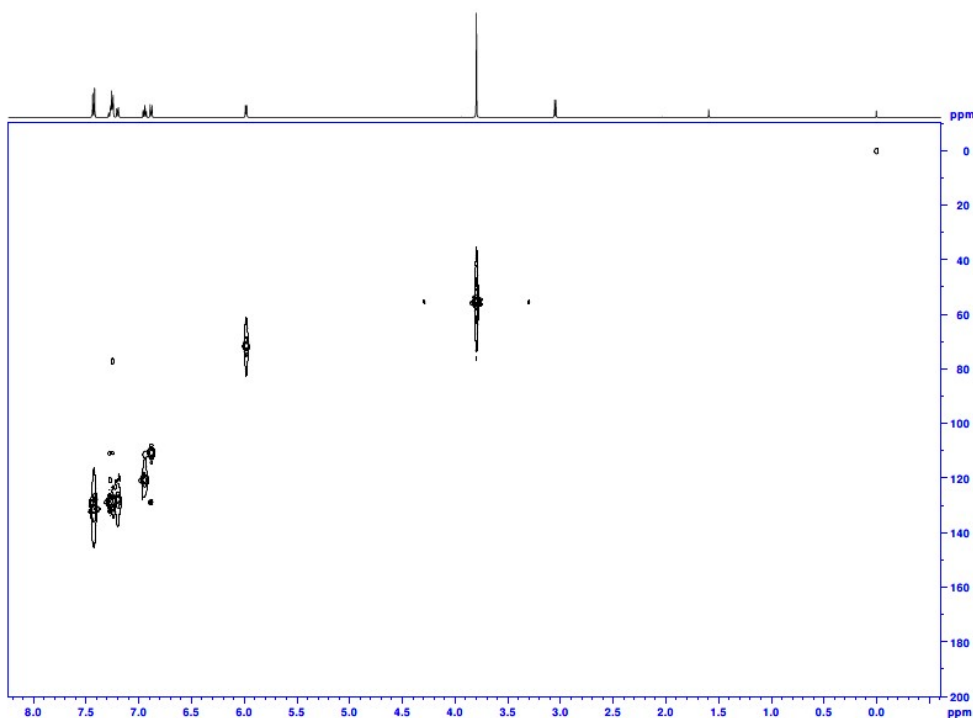
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HSQC (500 MHz, CDCl₃)

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



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PROCNO    1

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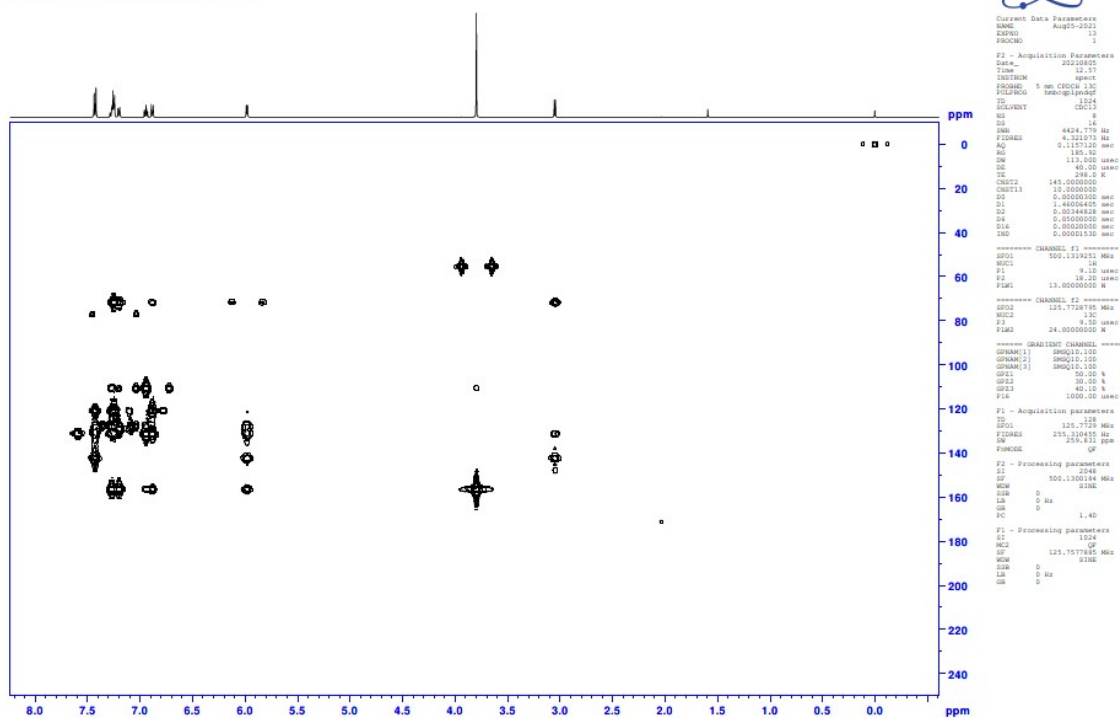
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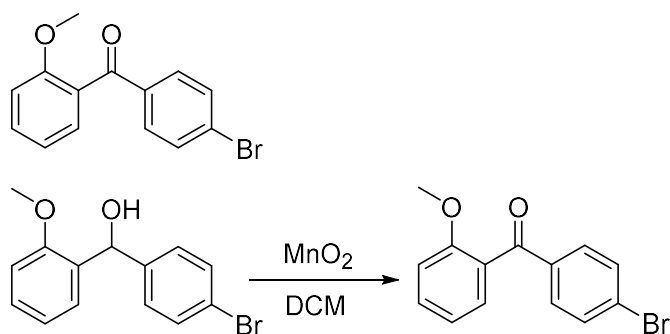
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HMBC (500 MHz, CDCl₃)

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



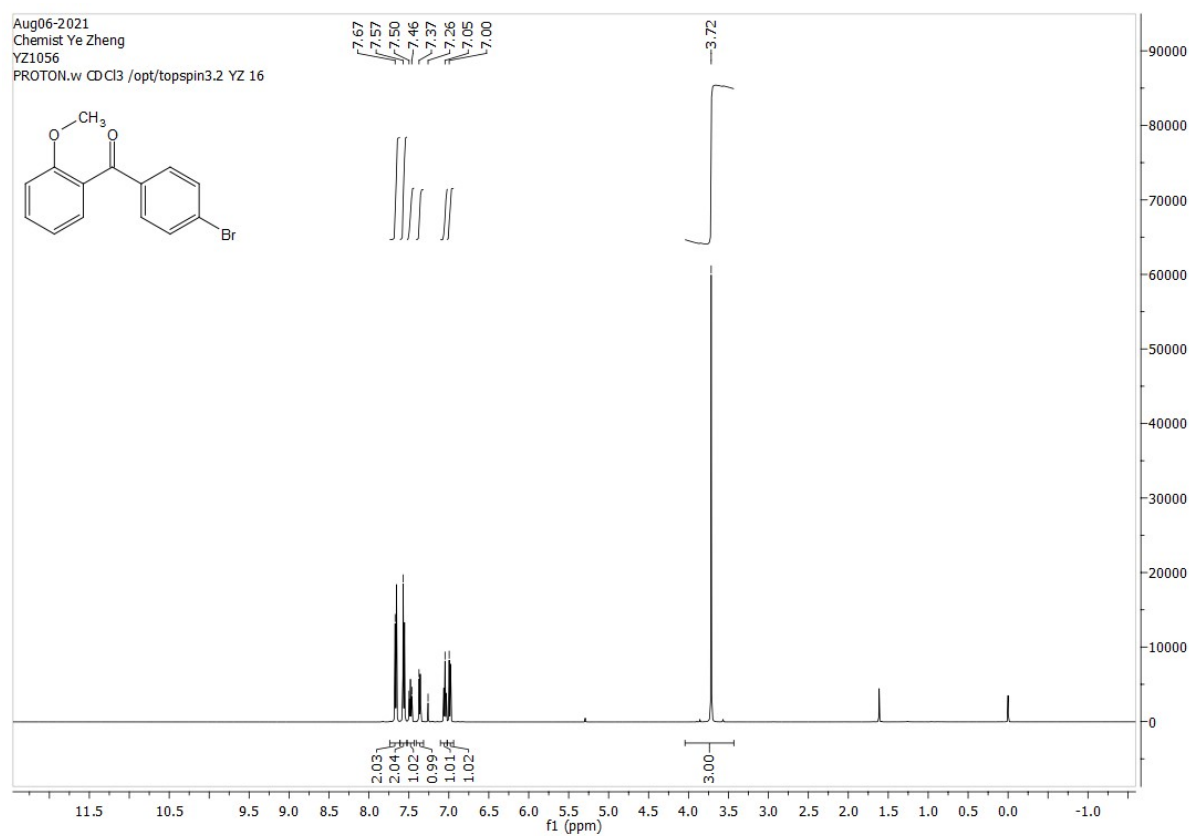
(4-Bromophenyl)(2-methoxyphenyl)methanone.



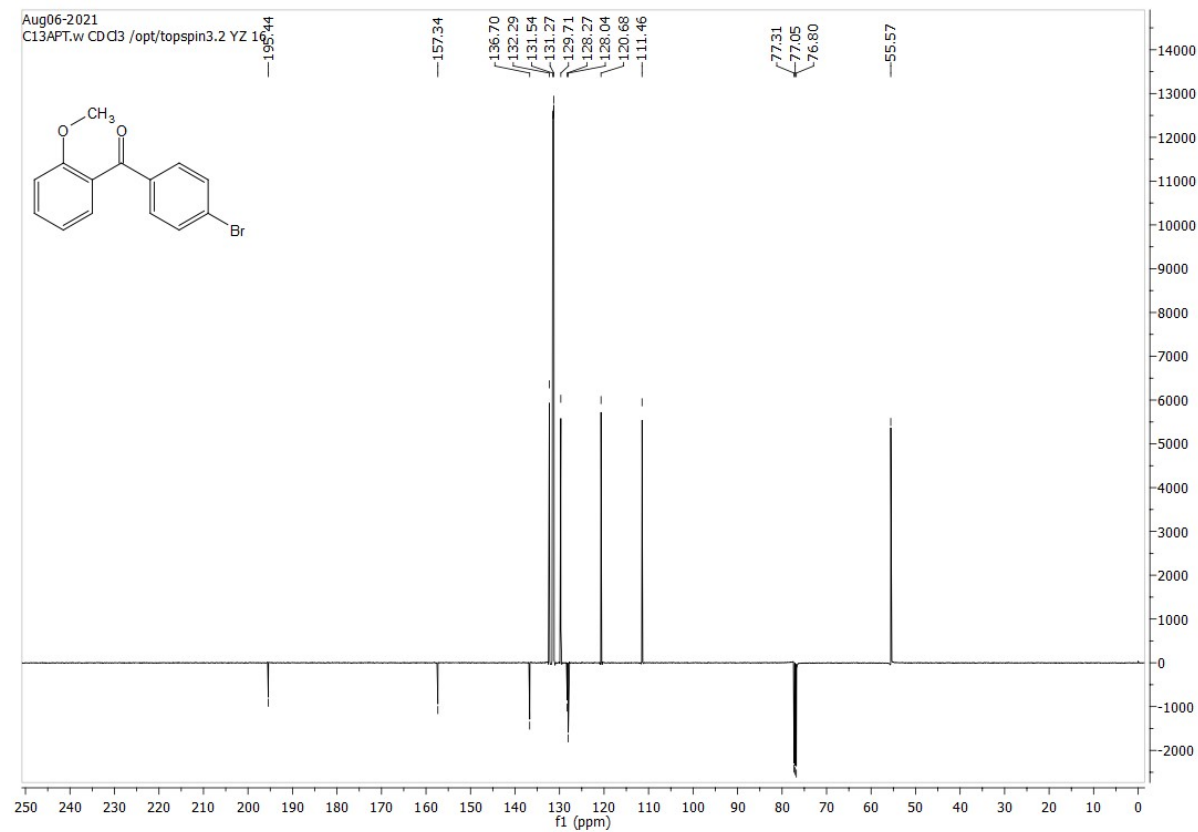
This compound is novel.

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: R_f ca 0.40 (9:1 hexane: EtOAc), strong UV and KMnO₄; Mp: 108°C; HRMS: (found (ESI⁺): [M+H]⁺, Calcd for C₁₄H₁₁⁷⁹BrNaO₂ 312.9831; Found 312.9835; 1.1 ppm error; ν_{max} 3091, 2979, 1658, 1599, 1580, 1482, 1451, 1294, 1241, 1065, 1011, 923, 729 cm⁻¹; δ_H (500 MHz, CDCl₃) 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, OCH₃) ppm; δ_C (125 MHz, CDCl₃) 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 (CH₃) ppm; m/z (ES-API⁺) 313.0 (M⁺ + 23, 100%).

^1H NMR (500 MHz, CDCl_3)



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



Chemist Ye Zheng
YZ1056
COSY.w CDC13 /opt/topspin3.2 YZ 16

BRUKER

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BRUKER

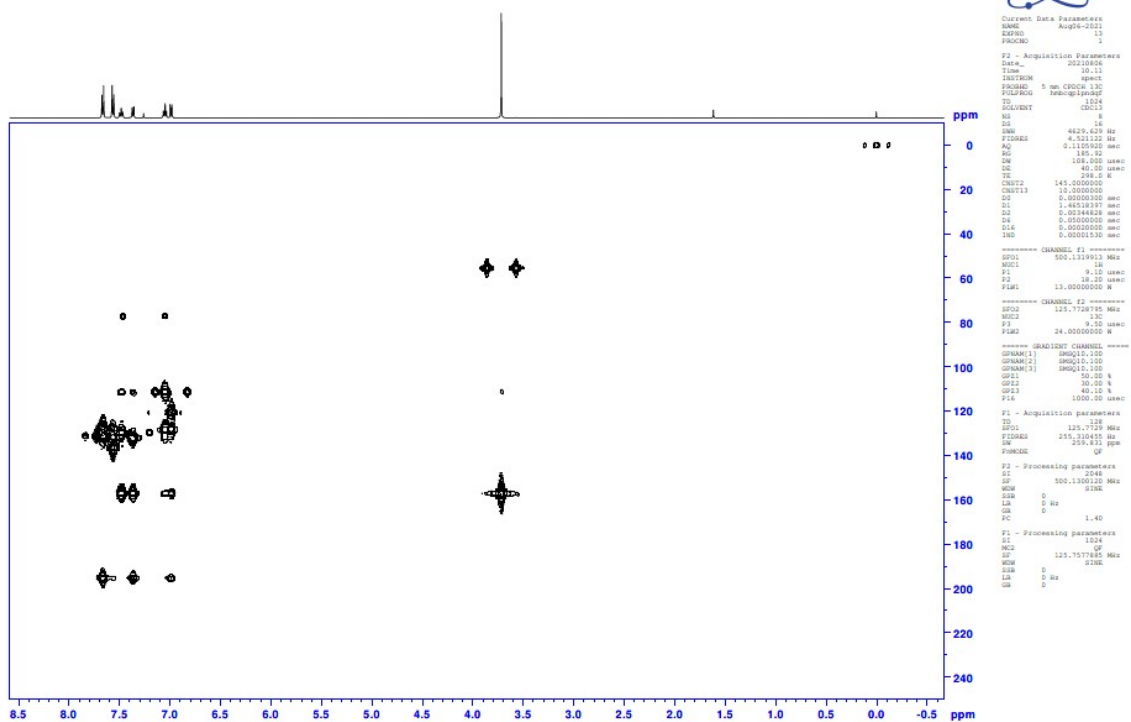
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SOLVENT CDCl3
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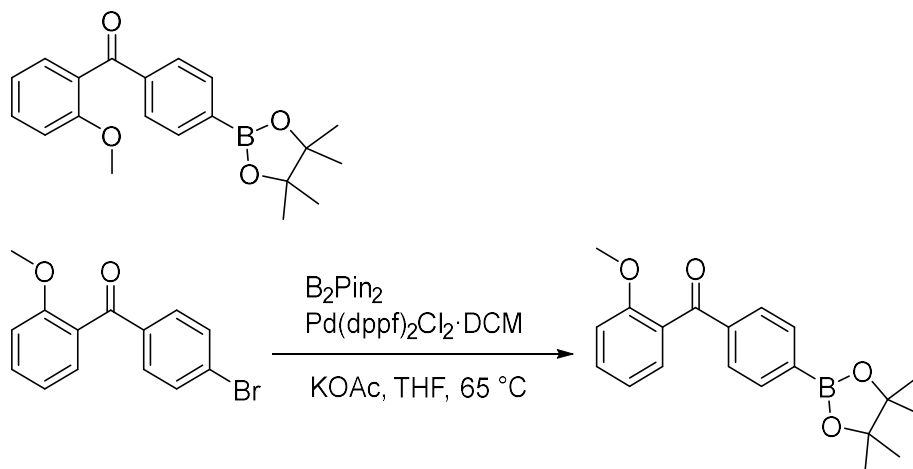
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P2JR 18.20 usec
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P2JV 18.2

HMBC (500 MHz, CDCl₃)

HMBC.w CDCl₃/opt/topspin3.2 YZ 16



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

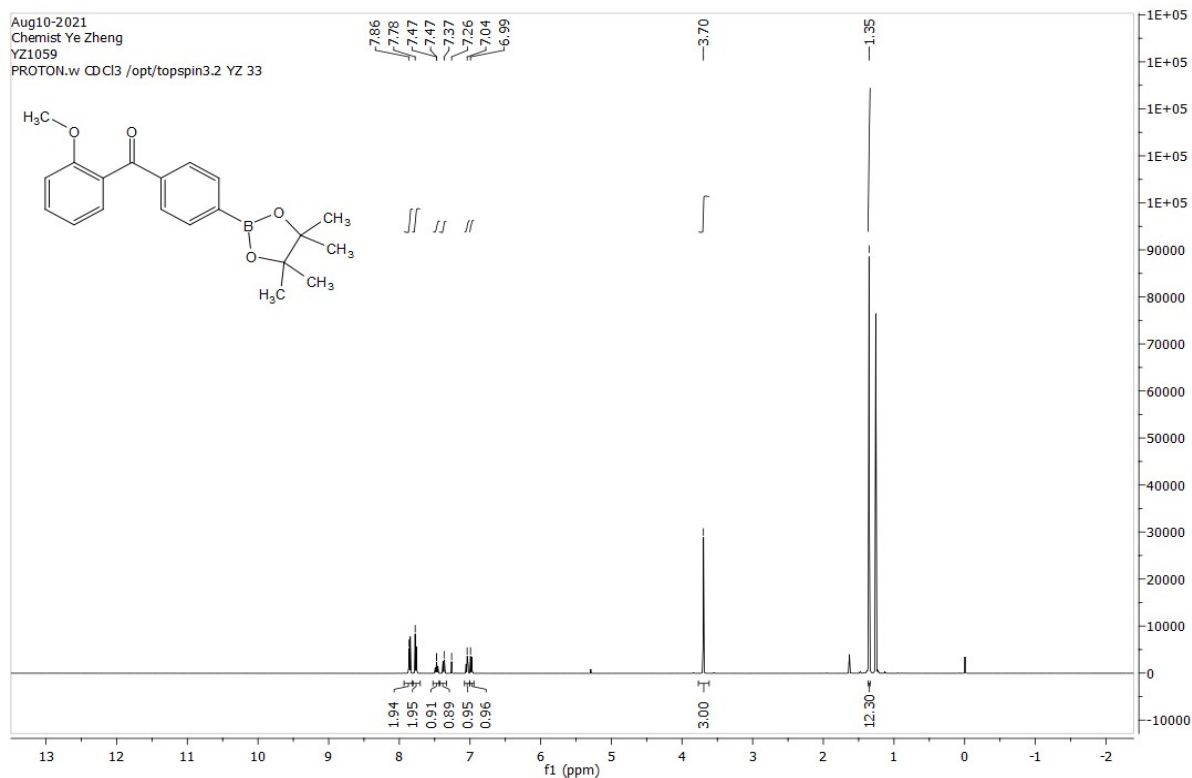


This compound is novel.

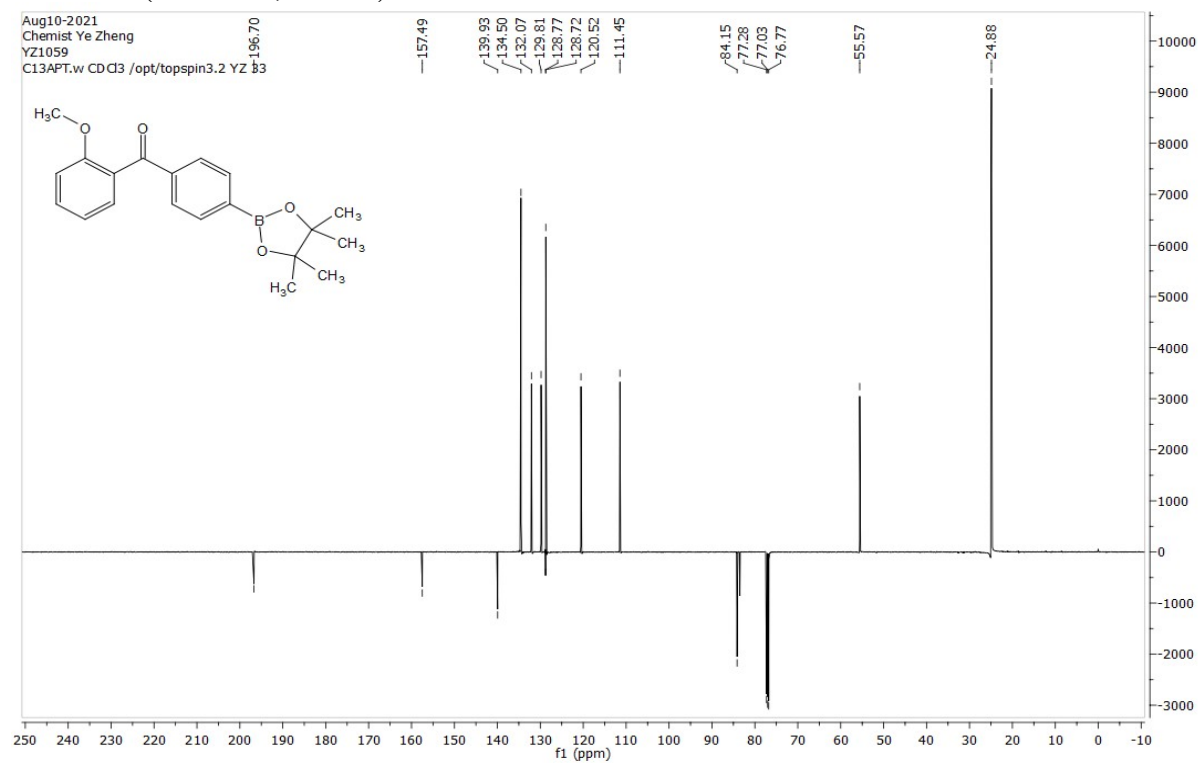
A round-bottom flask was charged with (4-bromophenyl)(2-methoxyphenyl)methanone (337 mg, 1.16 mmol), bis(pinacolato)diboron (353 mg, 1.39 mmol), potassium acetate (341 mg, 3.48 mmol), THF (7 mL) and $Pd(dppf)_2Cl_2 \cdot DCM$ (47.4 mg, 0.0580 mmol). The reaction mixture was heated to 65 °C and left stirring 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: R_f 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; ν_{max} 2973, 2929, 1662, 1596, 1505, 1484, 1359, 1265, 1207, 1136, 1088, 1024, 946, 848, 757 cm^{-1} ; δ_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; δ_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.

^1H NMR (500 MHz, CDCl_3)

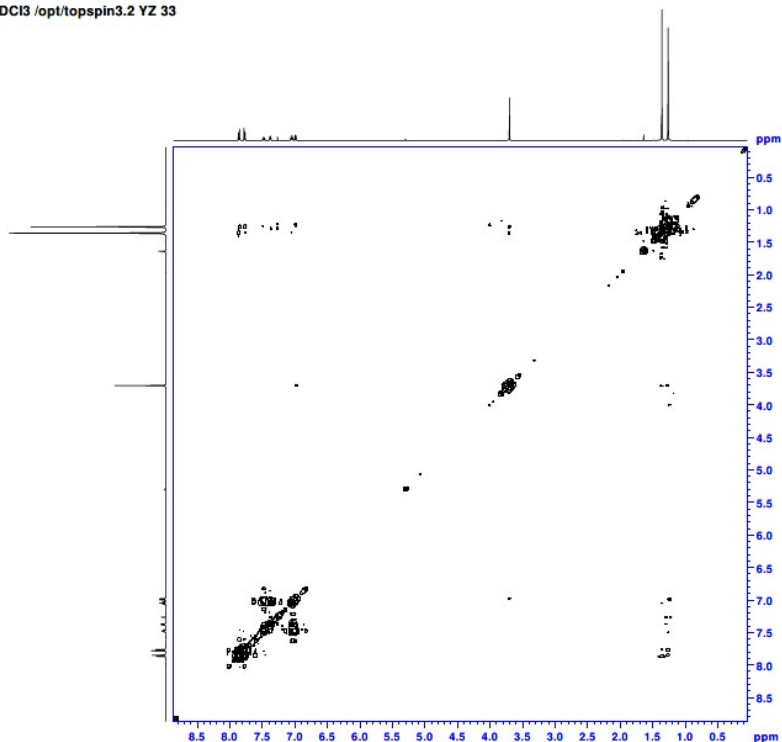


^{13}C NMR (125 MHz, CDCl_3)



COSY (500 MHz, CDCl₃)

Chemist Ye Zheng
YZ1059
COSY.w CDCl₃ /opt/topspin3.2 YZ 33



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PROCNO    1

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TE         298.2 K
DQ         0.0000000 sec
SFO1       500.1322707 MHz
NUC1       13C
P1         9.10 usec
P2         28.10 usec
P2F1       13.0000000 Hz
P1F1       1.5824997 Hz

===== CHANNEL F1 =====
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NUC1       13C
P1         9.10 usec
P2         28.10 usec
P2F1       13.0000000 Hz
P1F1       1.5824997 Hz

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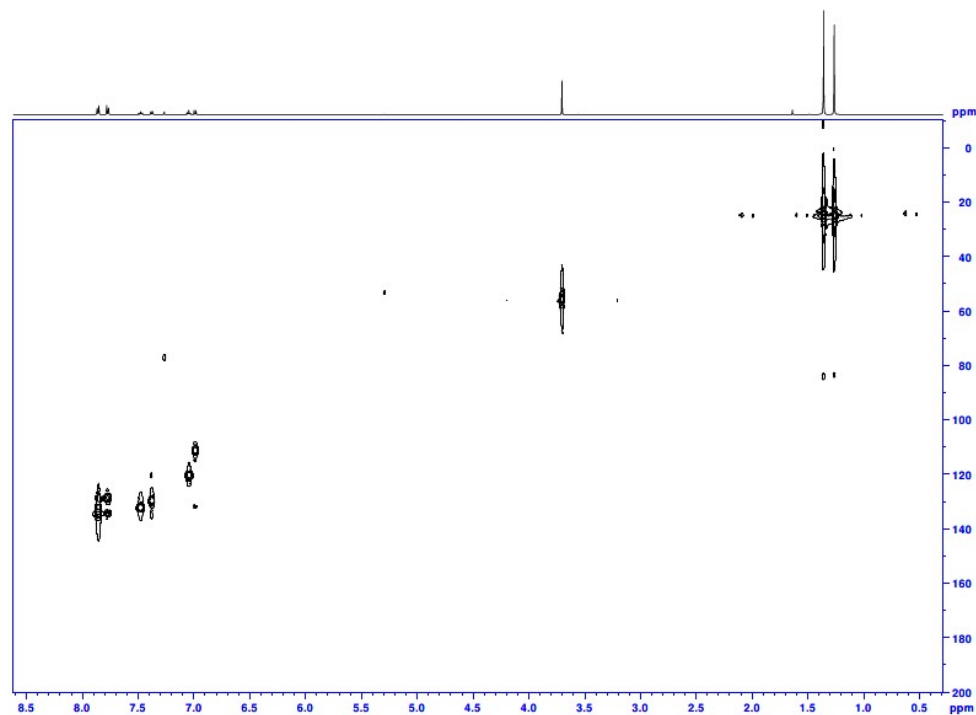
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F1 - Processing parameters
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WDW        EM
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LA         0 Hz
GB         0
PC         1.40
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HSQC (500 MHz, CDCl₃)

Chemist Ye Zheng
YZ1059
HSQC.w CDCl₃ /opt/topspin3.2 YZ 33



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Current Data Parameters
NAME      Aug10-2021
EXPNO     1
PROCNO    1

F2 - Acquisition Parameters
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Time      12.02
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DE         40.00 usec
TE         298.2 K
DQ         0.0000000 sec
SFO1       500.1322707 MHz
NUC1       13C
P1         9.10 usec
P2         28.10 usec
P2F1       13.0000000 Hz
P1F1       1.5824997 Hz

===== CHANNEL F1 =====
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NUC1       13C
P1         9.10 usec
P2         28.10 usec
P2F1       13.0000000 Hz
P1F1       1.5824997 Hz

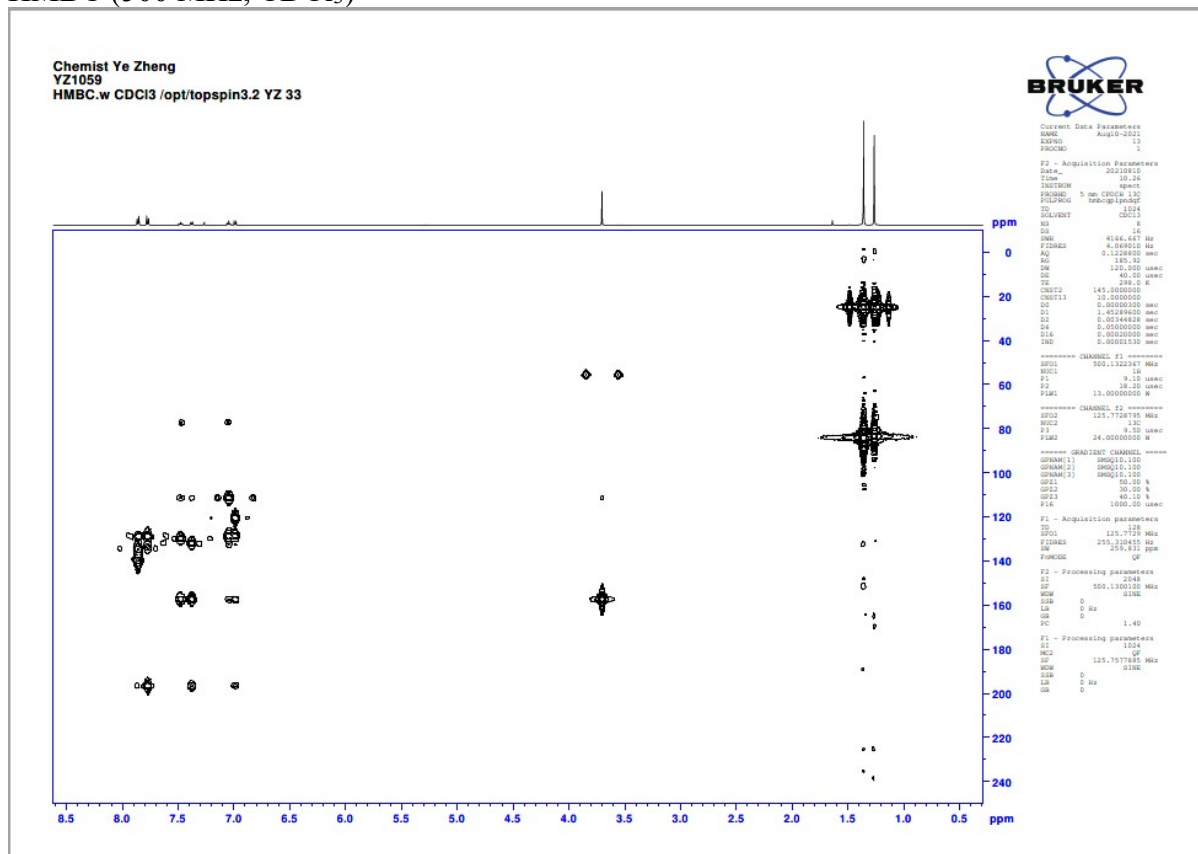
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P4PD2      0.5124600 Hz

===== GRADIENT CHANNEL =====
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OP1        60.10 Hz
OP2        1000.00 usec
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P2MODE     QF

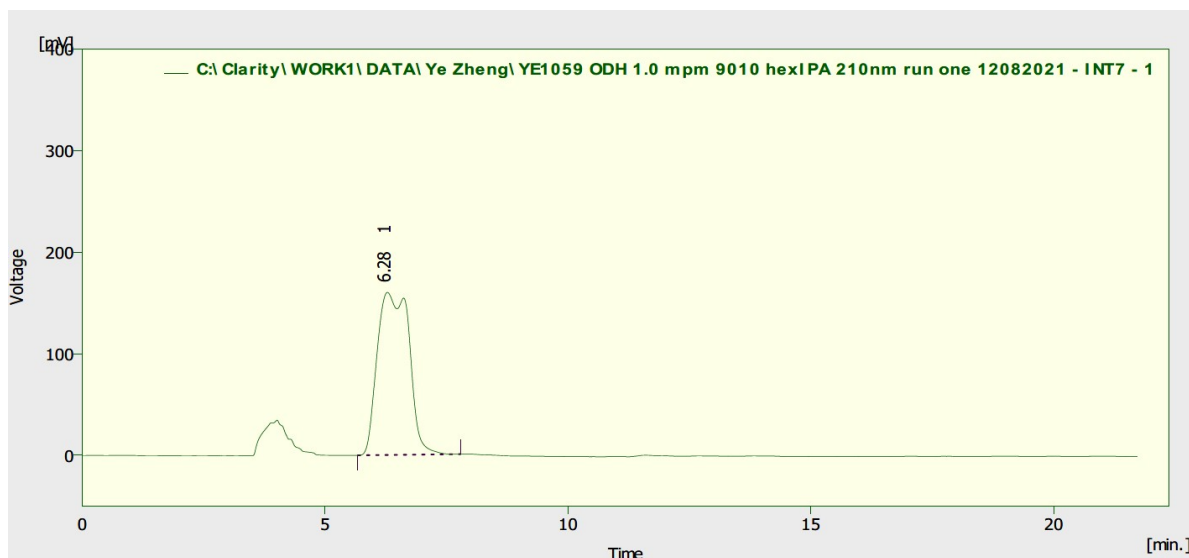
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F1 - Processing parameters
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SF         125.7577685 MHz
WDW        EM
SSB         0 Hz
LA         0 Hz
GB         0
PC         1.40
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HMBC (500 MHz, CDCl₃)



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

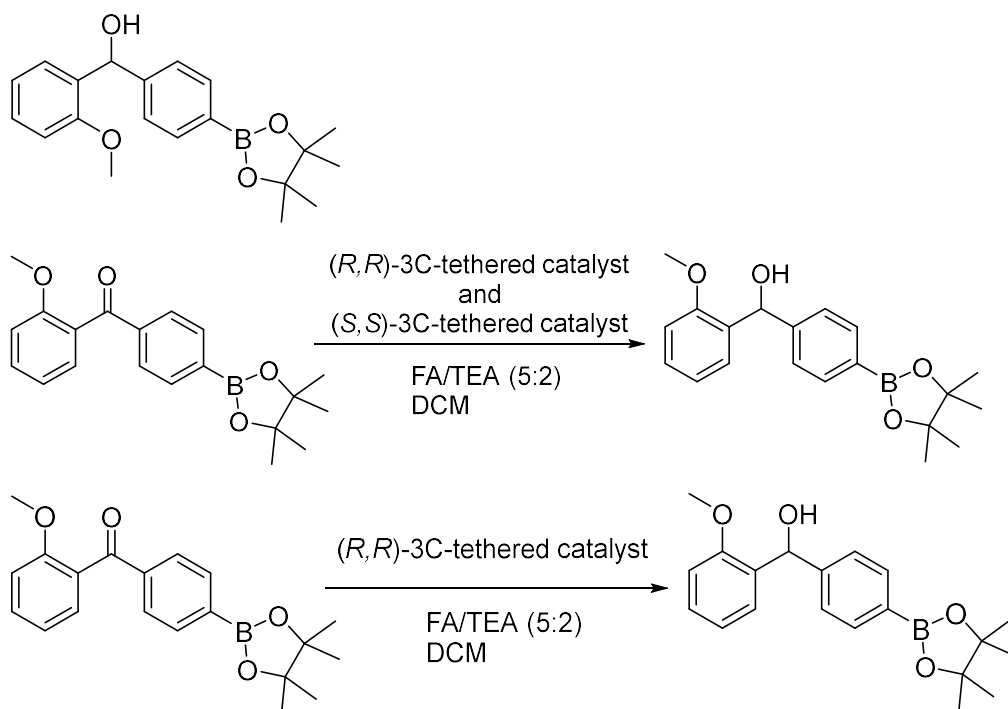


Result Table (Uncal - C:\Clarity\WORK1\DATA\Ye Zheng\YE1059 ODH 1.0 ppm 9010 hexIPA 210nm run one 12082021 - INT7 - 1)

	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 μ mol, 0.5 mol%) and (*S,S*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (0.738 mg, 1.19 μ mol, 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 stirred under a nitrogen atmosphere and followed by TLC (4:1 hexane: EtOAc). After 72 hours, the reaction was quenched using saturated NaHCO₃ 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 0-50% 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: R_f ca 0.20 (4:1 hexane: EtOAc), strong UV and KMnO₄; HRMS: (found (ESI⁺): [M+H]⁺, Calcd for C₂₀H₂₅BNaO₄ 363.1738; Found 363.1738; 1.0 ppm error; ν_{max} 3323 (br),

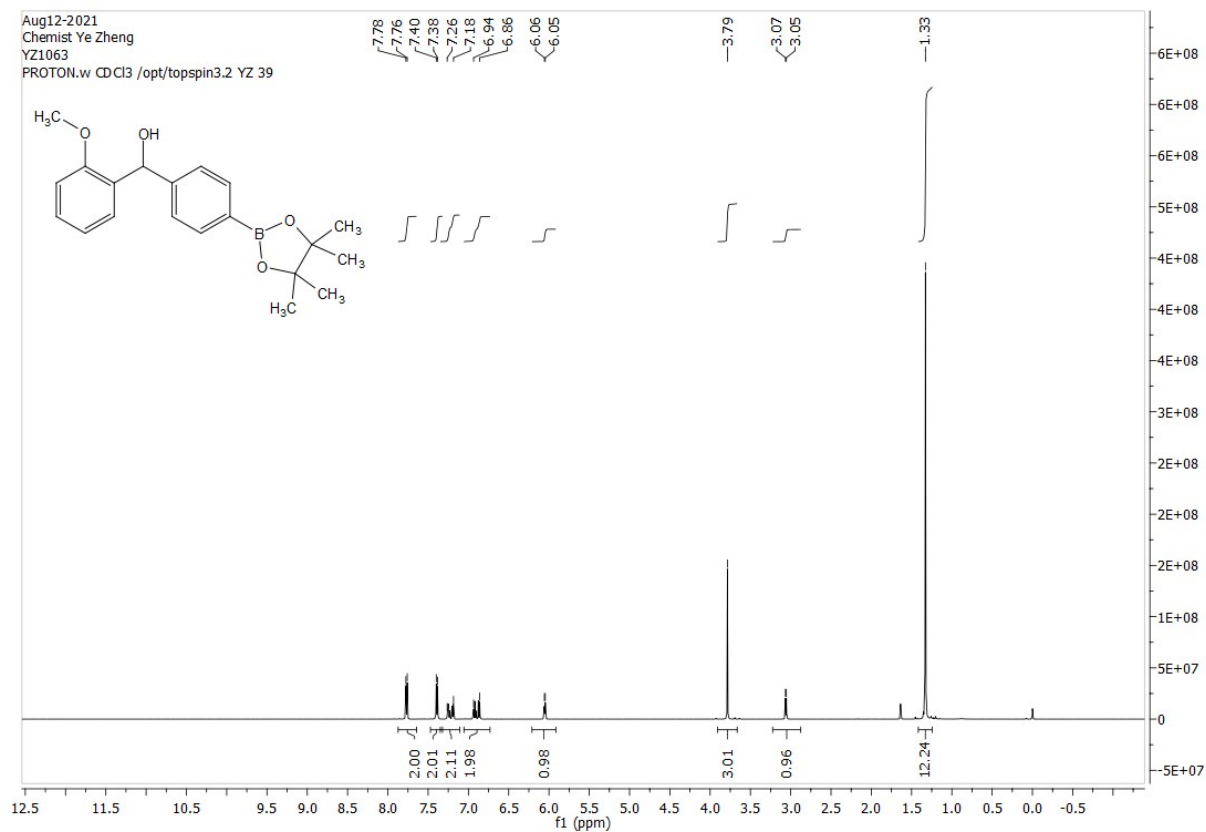
2978, 2936, 2837, 1611, 1489, 1463, 1298, 1240, 1164, 1048, 962 cm^{-1} ; δ_{H} (500 MHz, CDCl_3) 7.78 (2H, d, $J = 8.0$, ArH), 7.40 (2H, d, $J = 8.0$, ArH), 7.25-7.18 (2H, m, ArH), 6.94-6.86 (2H, m, ArH), 6.06 (1H, d, $J = 5.6$, ArCH), 3.79 (3H, s, OCH_3), 3.07 (1H, d, $J = 5.6$, OH), 1.33 (12H, s, CH_3) ppm; δ_{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 ($\text{M}^+ + 23$, 100%).

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

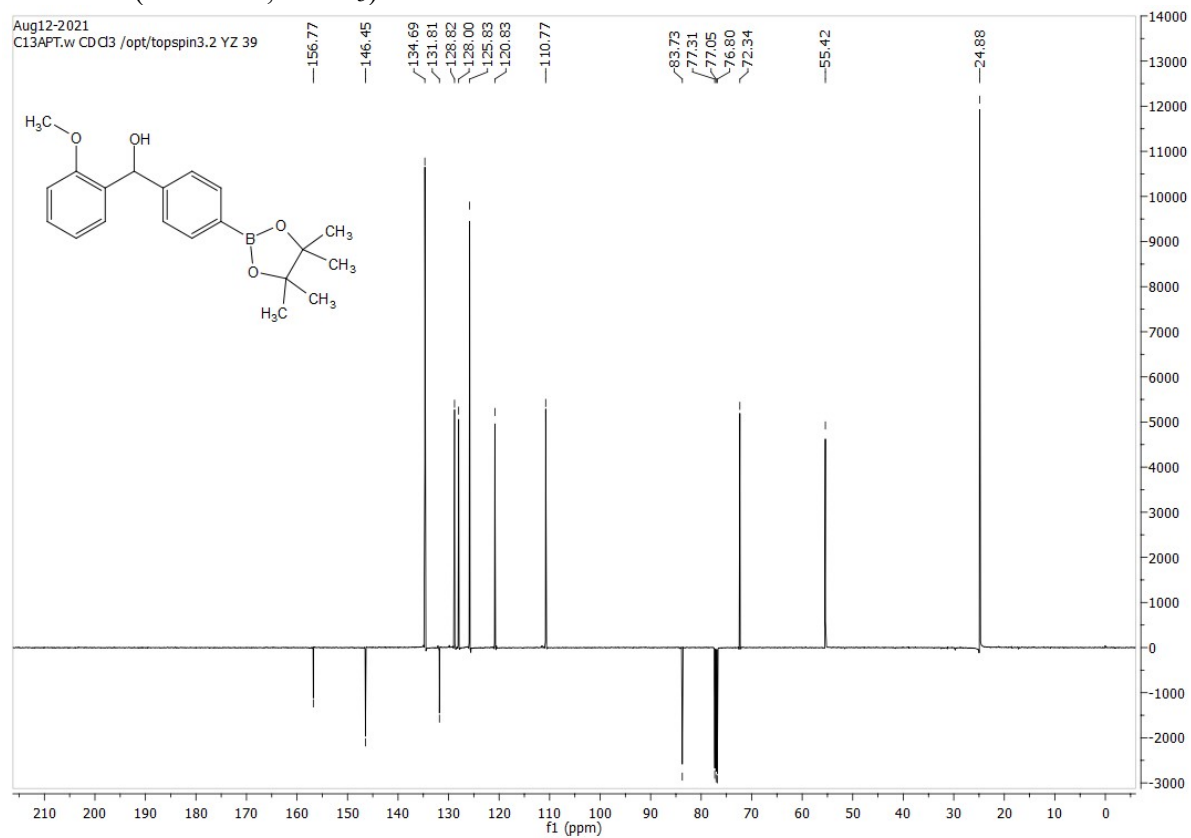
ATH of (2-methoxyphenyl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone.

(*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, $T = 25^\circ\text{C}$): $[\alpha]_{\text{D}}^{26} -27.1$ (c 0.376 in CHCl_3) 55% ee.

¹H NMR (500 MHz, CDCl₃)

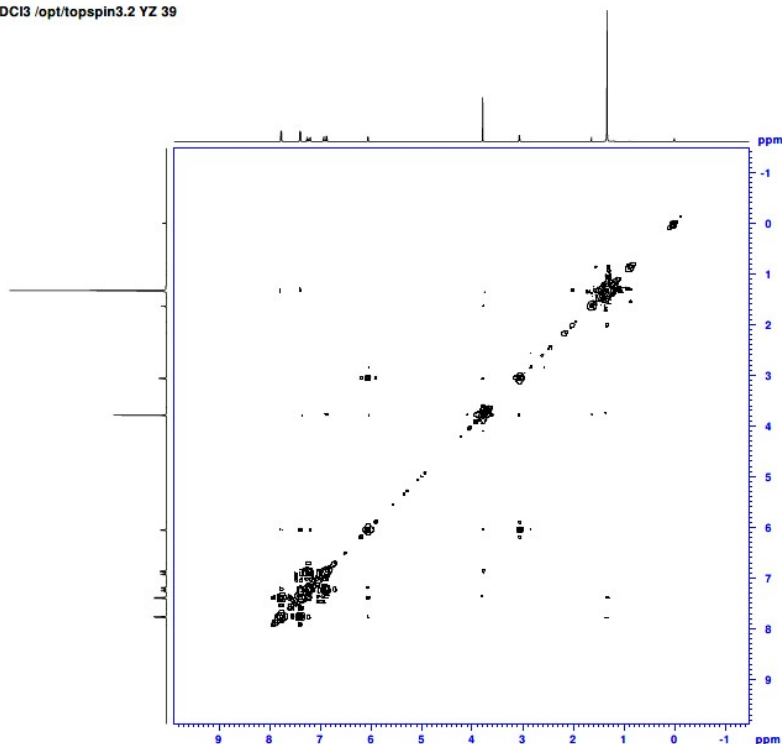


¹³C NMR (125 MHz, CDCl₃)



COSY (500 MHz, CDCl₃)

Chemist Ye Zheng
YZ1063
COSY.w CDCl₃ /opt/topspin3.2 YZ 39



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Current Data Parameters
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EXPNO    1
PROCNO    1

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P14        1000.00 usec

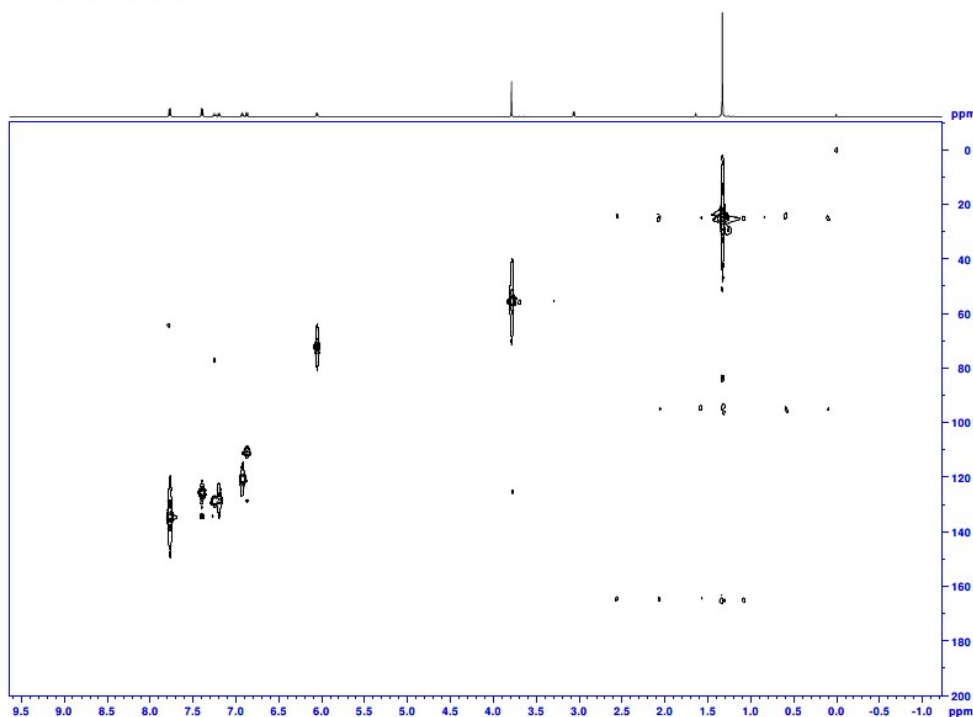
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PC         1.40
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HSQC (500 MHz, CDCl₃)

Chemist Ye Zheng
YZ1063
HSQC.w CDCl₃ /opt/topspin3.2 YZ 39



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NAME      Aug12-2021
EXPNO    1
PROCNO    1

F2 - Acquisition Parameters
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NS         1
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SWH        5681.818 Hz
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P12        2500.00 usec
P14        13.00000000 Hz
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===== CHANNEL f2 =====
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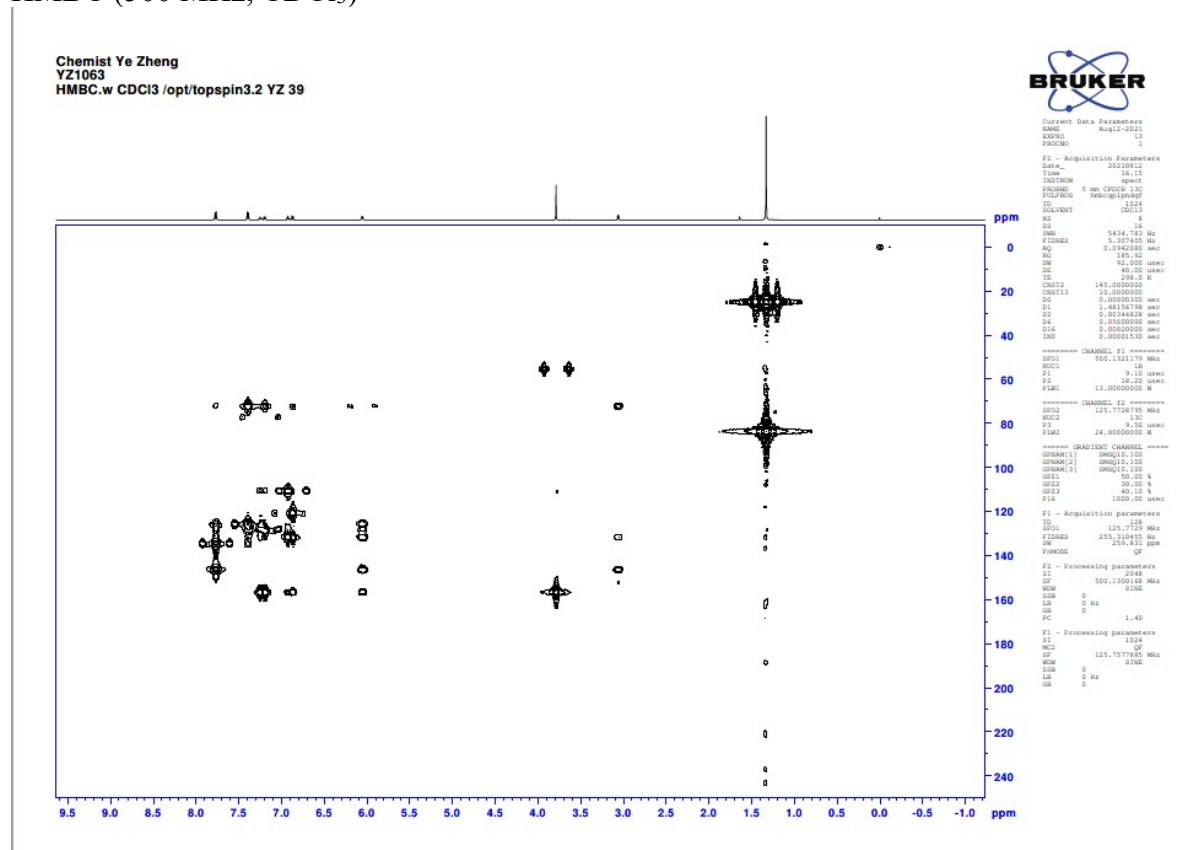
===== GRADIENT CHANNEL =====
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F1 - Acquisition parameters
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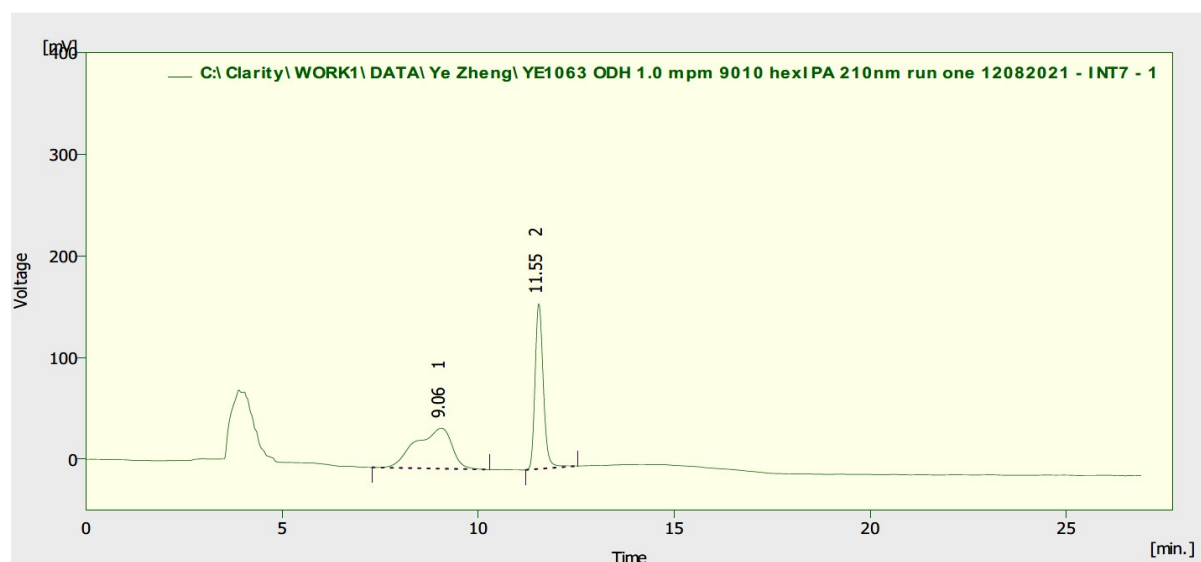
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F1 - Processing parameters
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HMBC (500 MHz, CDCl₃)



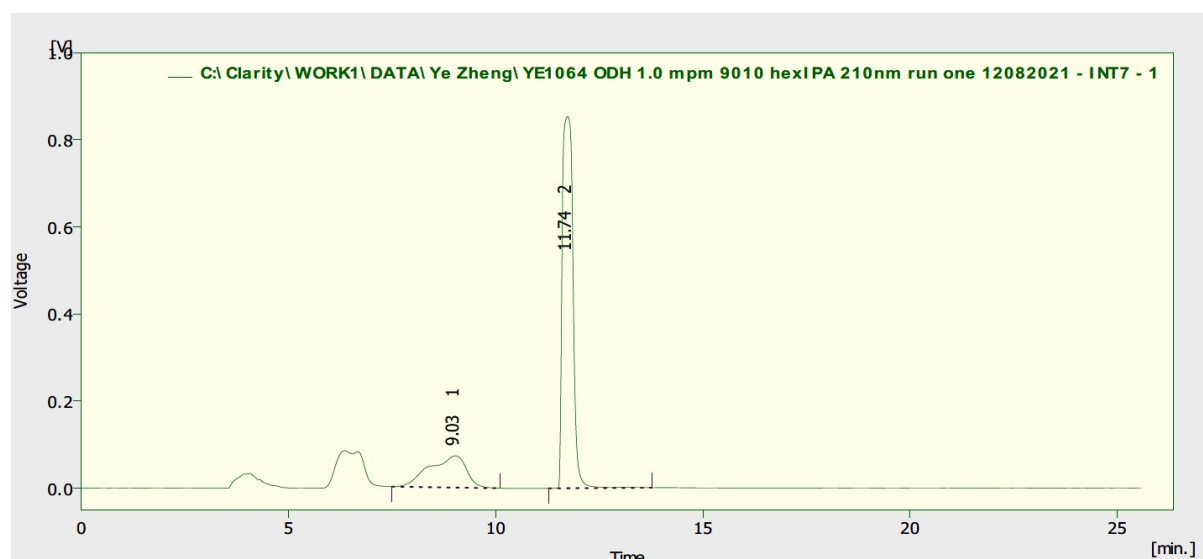
HPLC of racemic (2-methoxyphenyl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanol **23**.



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		

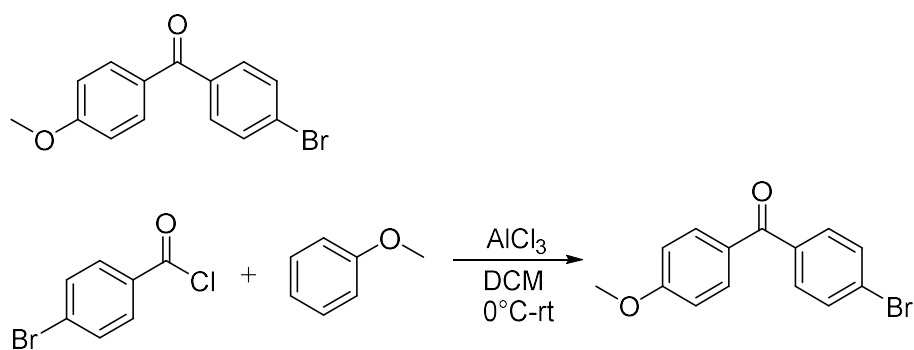
HPLC after ATH of (2-methoxyphenyl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone using (*R,R*)-3C-Tethered Ru(II)-TsDPEN catalyst **2** (after 72 hours, 100% conversion, 55% ee).



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		

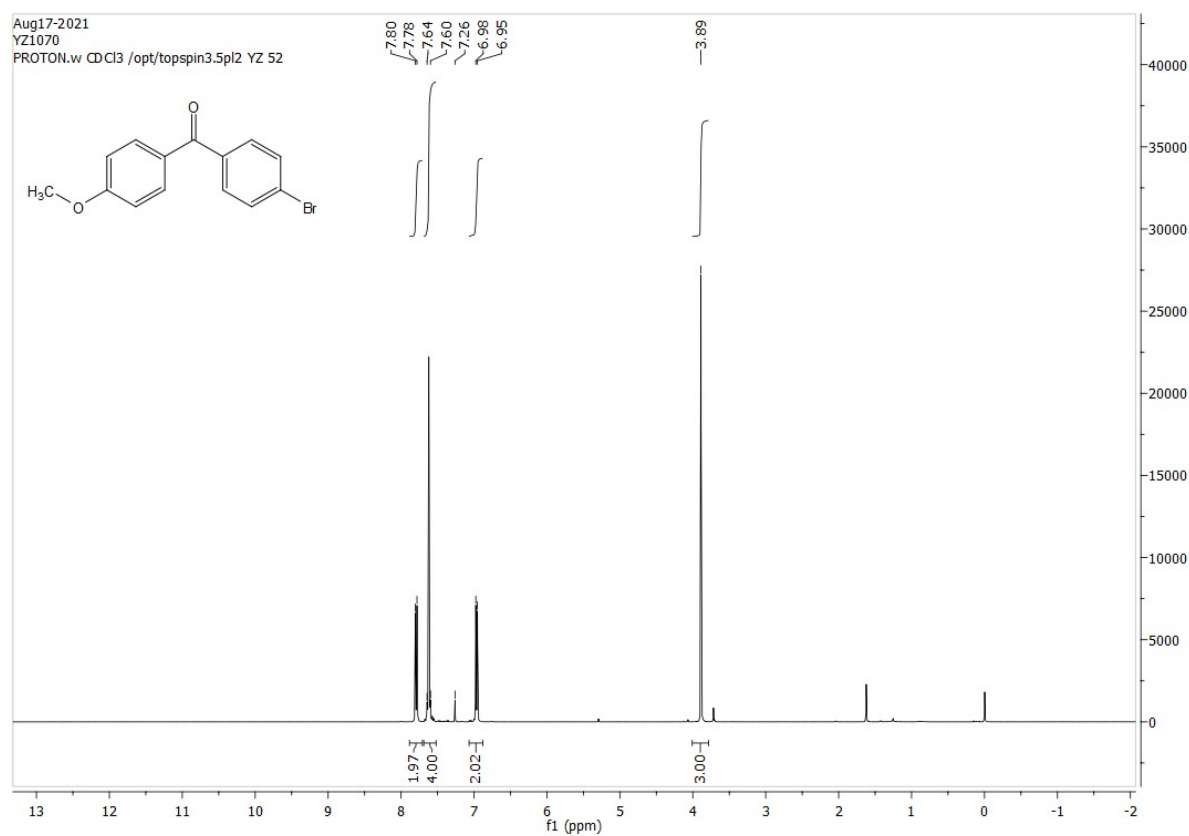
(4-Bromophenyl)(4-methoxyphenyl)methanone.



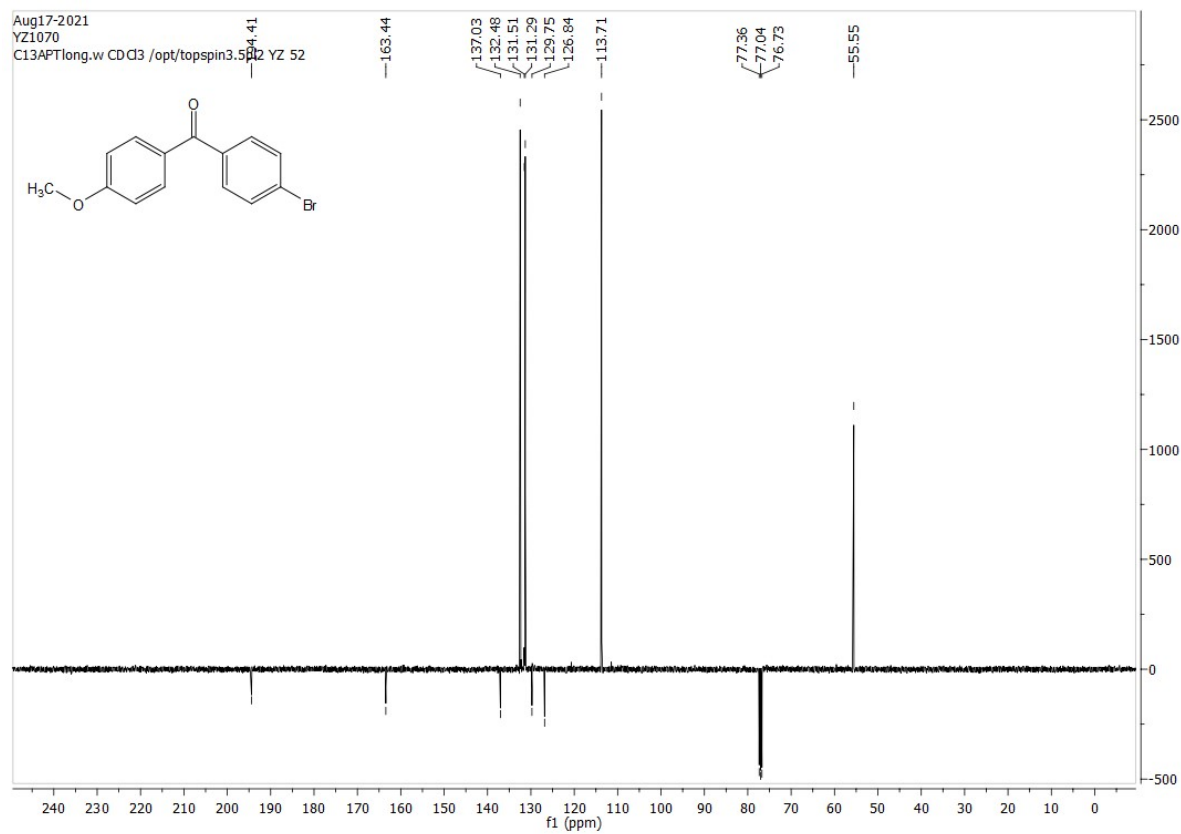
This compound has been reported and fully characterized: L. Dong, G.-R. Chen, X.-P. HeS. Vidal, *Org. Biomol. Chem.* 2019, **17**, 9251-9256.

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 AlCl₃ (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 (MgSO₄) 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: R_f ca 0.20 (9:1 hexane: EtOAc), strong UV and KMnO₄; δ_H (400 MHz, CDCl₃) 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, CH₃) ppm; δ_C (100 MHz, CDCl₃) 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 (CH₃) ppm; *m/z* (ES-API+) 331.0 (M⁺ + 23, 100%). Data matched that reported.

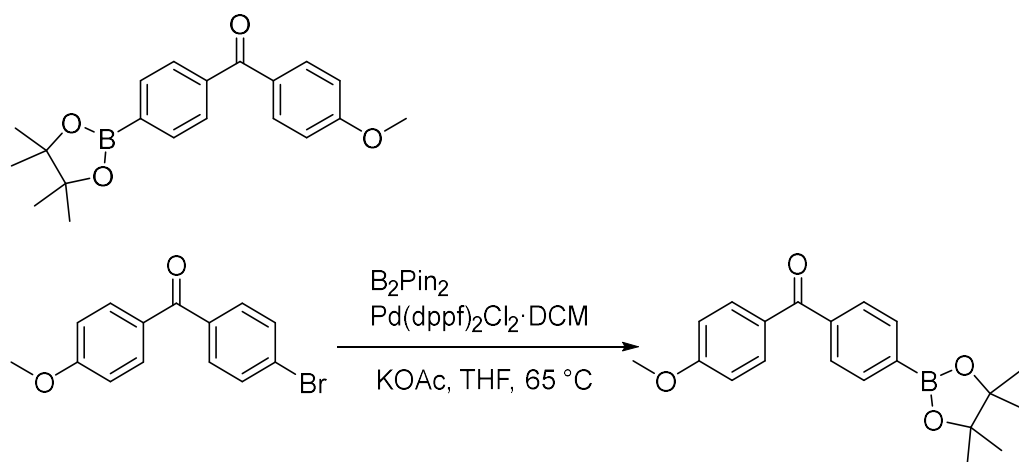
^1H NMR (400 MHz, CDCl_3)



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



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

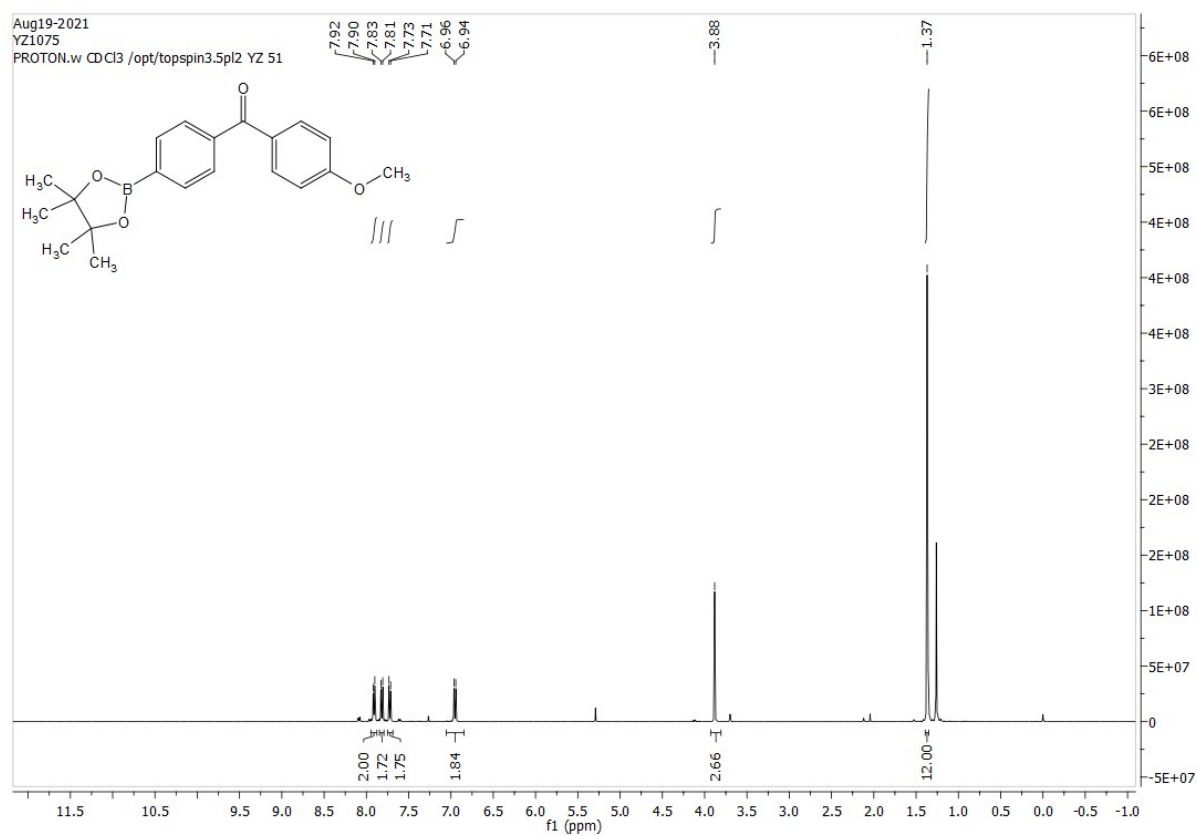


This compound is novel.

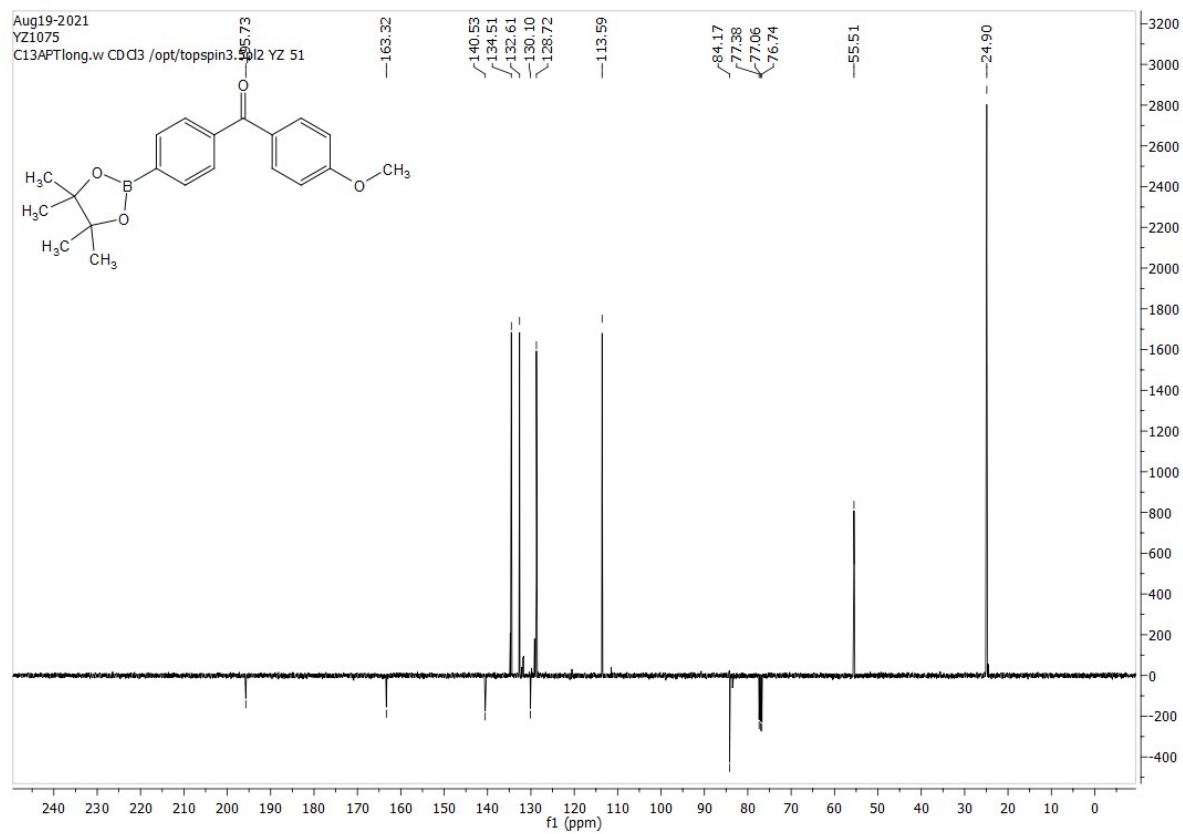
A round-bottom flask was charged with (4-bromophenyl)(4-methoxyphenyl)methanone (1.44 g, 4.97 mmol), bis(pinacolato)diboron (1.51 g, 5.96 mmol), potassium acetate (1.46 g, 14.9 mmol), THF (25 mL) and $Pd(dppf)_2Cl_2 \cdot DCM$ (203 mg, 0.249 mmol). The reaction mixture was heated to 65 °C and left stirring 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: R_f 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; ν_{max} 2976, 2931, 1649, 1597, 1504, 1396, 1255, 1123, 1085, 927, 821 cm^{-1} ; δ_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; δ_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.

^1H NMR (500 MHz, CDCl_3)

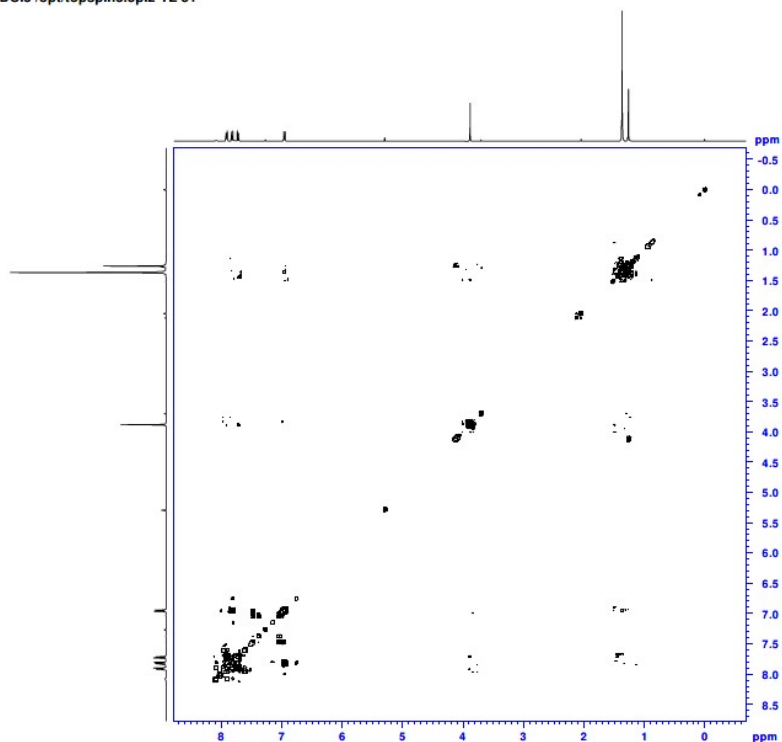


^{13}C NMR (125 MHz, CDCl_3)



COSY (500 MHz, CDCl₃)

YZ1075
COSY.w CDCl₃ /opt/topspin3.5pl2 YZ 51



Current Data Parameters
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EXPNO 1
PROCNO 1

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FIDRES 3781.819 Hz
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RG 384
SW 132.200 MHz
DE 4.50 dB
TE 300.2 K
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D12 0.00000000 sec
D13 0.00000000 sec
D14 0.00000000 sec
D15 0.00000000 sec
D16 0.00000000 sec
D17 0.00000000 sec
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P2 14.00 usec
P3 14.00 usec
P4 14.00 usec
P5 14.00 usec
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P7 14.00 usec
P8 14.00 usec
P9 14.00 usec
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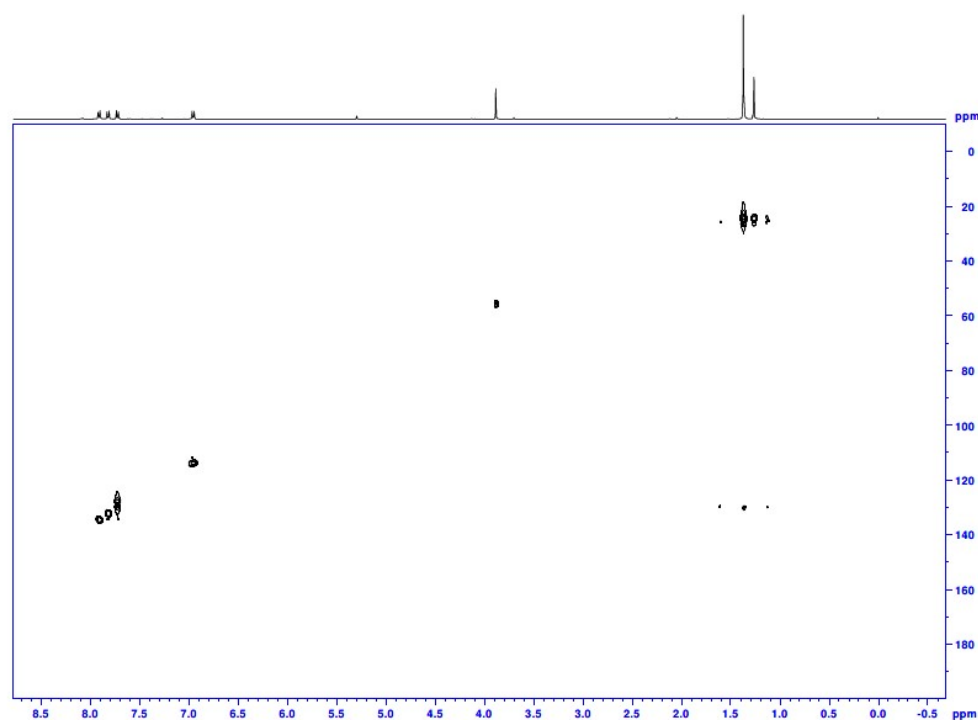
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RG 384
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D1 1.20000000 sec
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D14 0.00000000 sec
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D16 0.00000000 sec
D17 0.00000000 sec
TDav 400.1316268 MHz
NUC1 1H
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P2 14.00 usec
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P11 14.00 usec
P12 14.00 usec
P13 14.00 usec
P14 14.00 usec
P15 14.00 usec
P16 14.00 usec

F2 - Processing parameters
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WDW EM
SSB 0
LB 0 Hz
GB 0
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F1 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.40

HSQC (500 MHz, CDCl₃)

YZ1075
HSQC.w CDCl₃ /opt/topspin3.5pl2 YZ 51



Current Data Parameters
NAME Aug19-2021
EXPNO 1
PROCNO 1

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RG 384
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D12 0.00000000 sec
D13 0.00000000 sec
D14 0.00000000 sec
D15 0.00000000 sec
D16 0.00000000 sec
D17 0.00000000 sec
TDav 400.1316268 MHz
NUC1 1H
P1 14.00 usec
P2 14.00 usec
P3 14.00 usec
P4 14.00 usec
P5 14.00 usec
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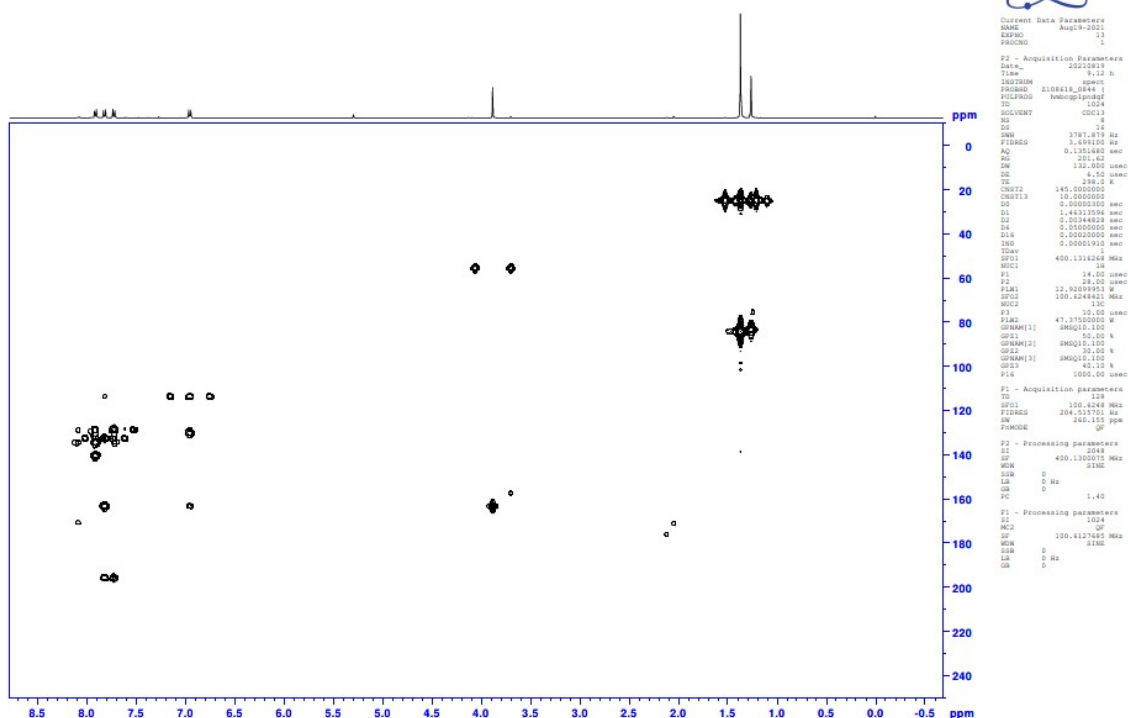
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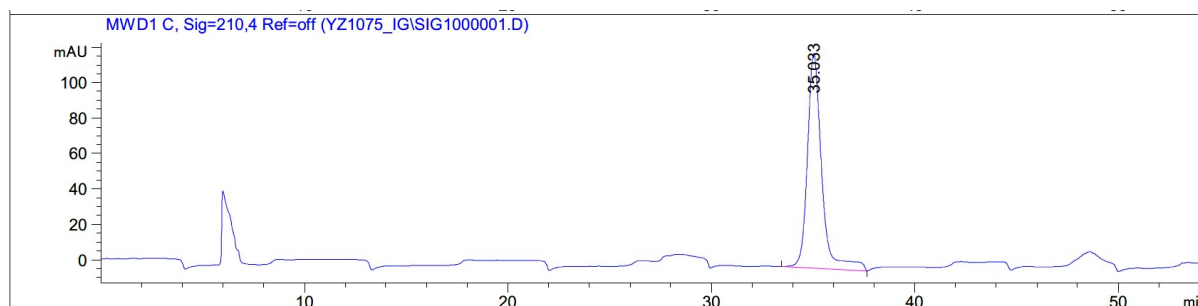
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HMBC (500 MHz, CDCl₃)

YZ1075
HMBC.w CDCl₃/opt/topspin3.5pl2 YZ 51



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



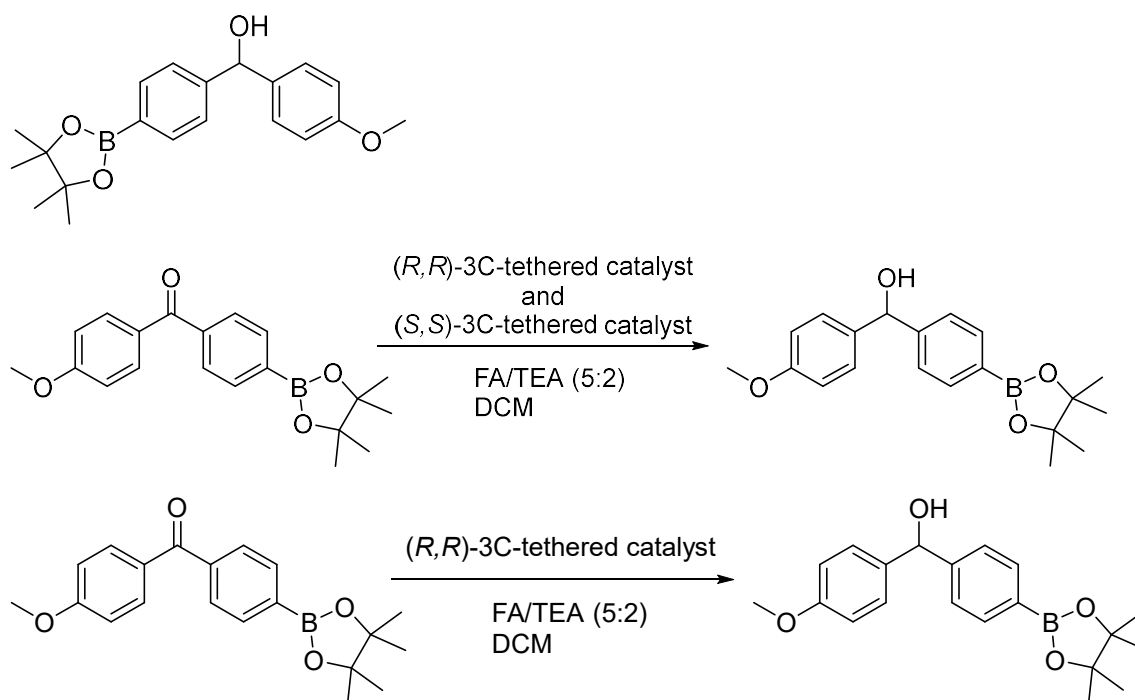
Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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Totals : 5954.32764 121.02700

(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:

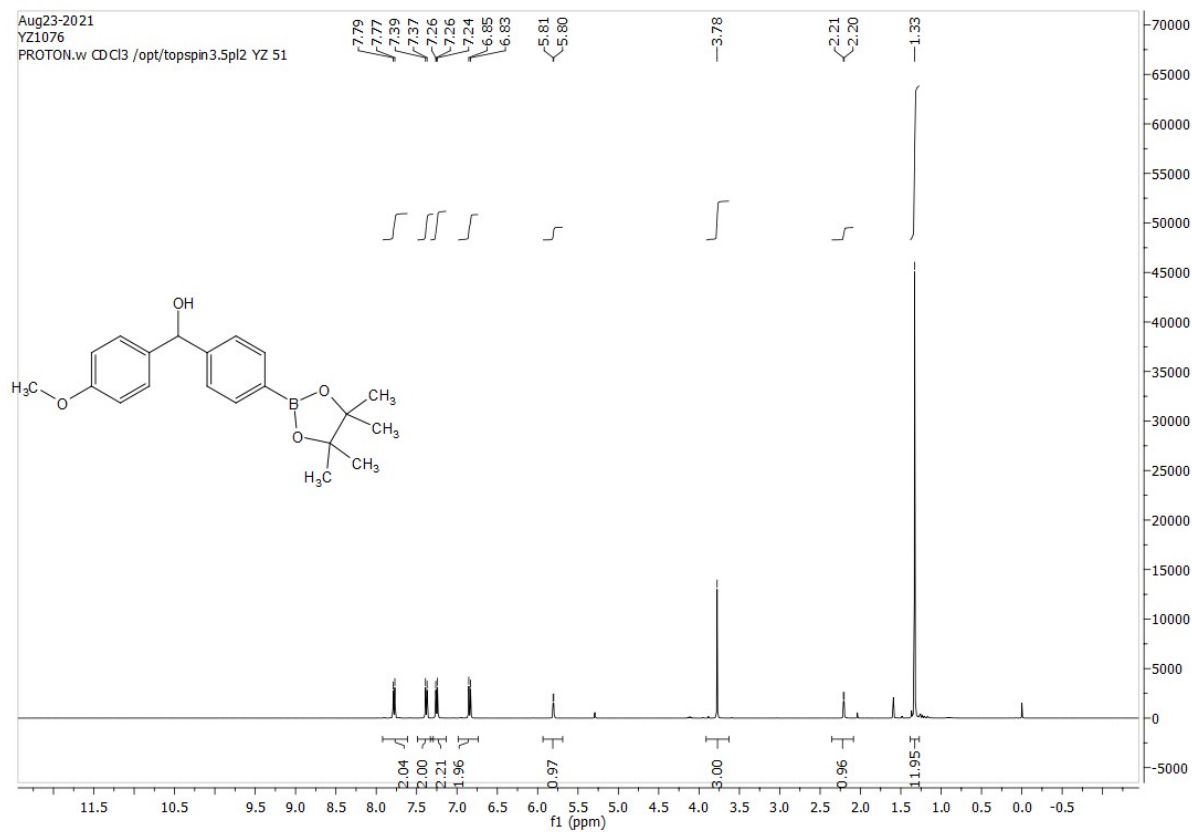
(R,R)-3C-Tethered Ru(II)-TsDPEN catalyst (0.74 mg, 1.2 μ mol, 0.5 mol%) and (S,S)-3C-tethered Ru(II)-TsDPEN catalyst (0.74 mg, 1.2 μ mol, 0.5 mol%) were added to FA: TEA (5:2 azeotropic mixture, 0.36 mL) at rt and the mixture was stirred under a nitrogen atmosphere for 15 minutes; after which a solution 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 stirred under a nitrogen atmosphere and followed by TLC (4:1 hexane: EtOAc). After 72 hours, the reaction was quenched using saturated NaHCO₃ 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 0-50% 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: R_f ca 0.40 (4:1 hexane: EtOAc), strong UV and KMnO₄; HRMS: (found (ESI⁺): [M+H]⁺, Calcd for C₂₀H₂₅BNaO₄ 363.1738; Found 363.1738; 1.0 ppm error; ν_{max} 3451 (br), 2977, 2933, 2836, 1611,

1510, 1397, 1318, 1245, 1169, 1141, 1085, 961 cm^{-1} ; δ_{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; δ_{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 ($\text{M}^+ + 23$, 100%).

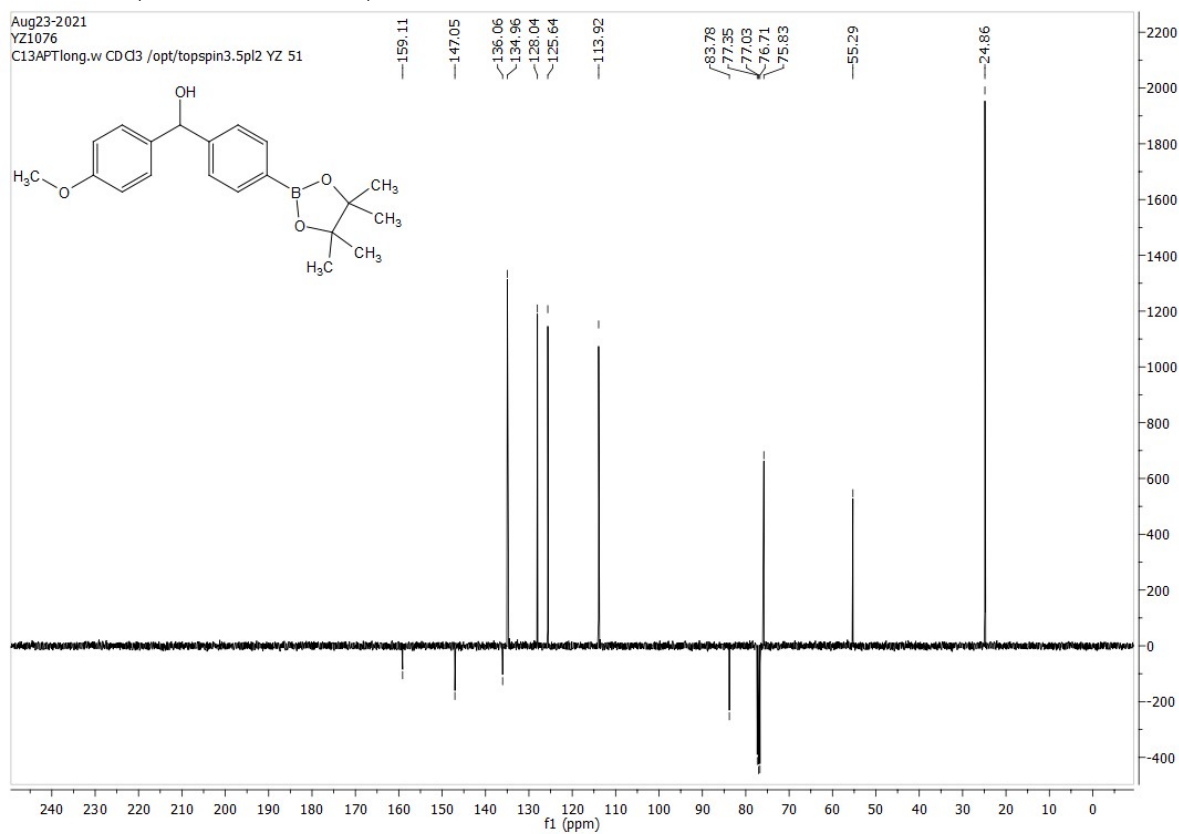
Enantiomeric excess and conversion determined by HPLC analysis (Chiralpak IG, 30 cm x 6mm column, hexane:iPrOH 95:5, 0.5 mL/min, $T = 25^\circ\text{C}$) ketone 35.0 min, *R* and *S* isomers 48.3 min and 52.5 min, configuration is not confirmed.

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, $T = 25^\circ\text{C}$): $[\alpha]_{\text{D}}^{26} -2.35$ (c 0.680 in CHCl_3) 20% ee.

¹H NMR (400 MHz, CDCl₃)

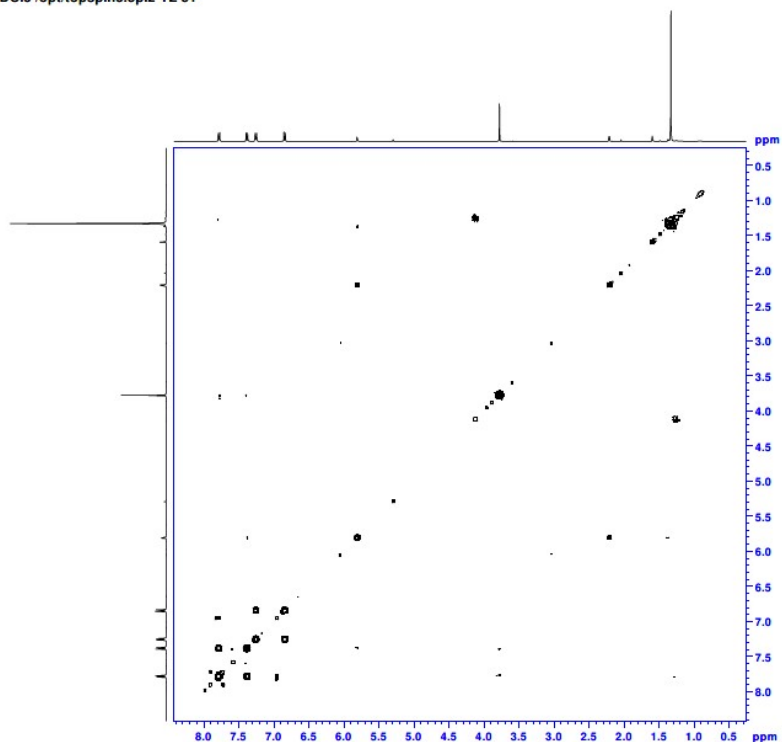


¹³C NMR (100 MHz, CDCl₃)



COSY (400 MHz, CDCl₃)

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



Current Data Parameters
NAME Aug13-2021
EXPNO 11
PROCNO 1

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FIDRES 0.1513440 Hz
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SQ 157.000 usec
DE 6.50 usec
TE 300.2 K
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D1 1.80000000 sec
D11 0.03000000 sec
D12 0.00000000 sec
D13 0.00000000 sec
D14 0.00000000 sec
D15 0.00000000 sec
TAcq 400.1317479 MHz
NUC1 1H
P1 14.00 usec
P2 14.00 usec
P3 250.00 usec
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GPR2 10.00 dB
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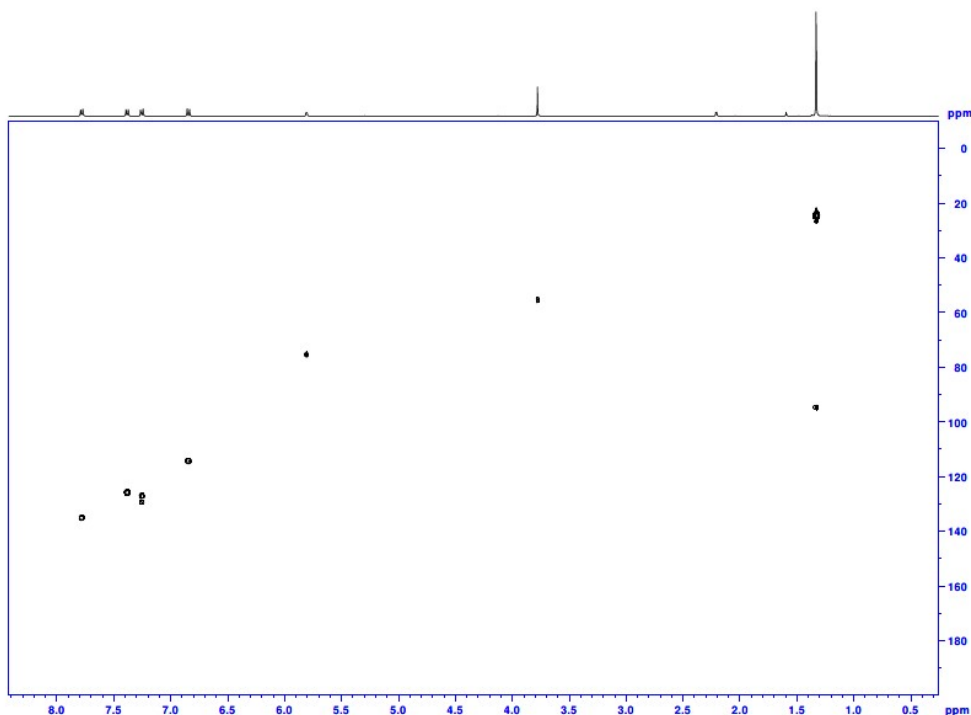
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F2 - Processing parameters
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F1 - Processing parameters
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WDW 0
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LB 0 Hz
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PC 1.40

HSQC (400 MHz, CDCl₃)

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



Current Data Parameters
NAME Aug13-2021
EXPNO 11
PROCNO 1

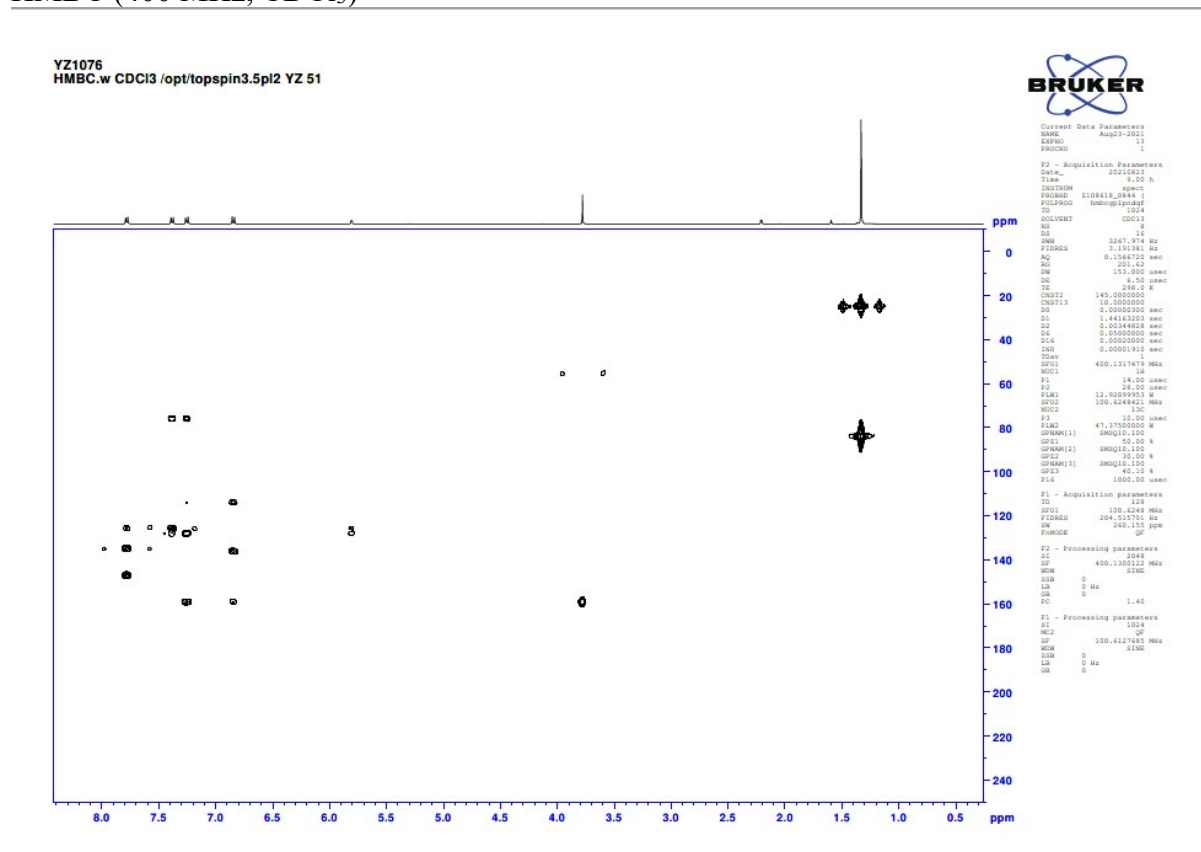
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DS 4
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FIDRES 0.1513440 Hz
AQ 0.3113440 sec
RG 64.18
SQ 157.000 usec
DE 6.50 usec
TE 300.2 K
D0 0.00000000 sec
D1 1.80000000 sec
D11 0.03000000 sec
D12 0.00000000 sec
D13 0.00000000 sec
D14 0.00000000 sec
D15 0.00000000 sec
TAcq 400.1317479 MHz
NUC1 1H
P1 14.00 usec
P2 14.00 usec
P3 250.00 usec
PL1 12.92099953 dB
PL12 2.81399953 dB
GPRAM[1] SMOUL1.100
GPR2 10.00 dB
P16 1000.00 usec

F1 - Acquisition parameters
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SF 400.1301222 MHz
WDW 0
SSB 0
LB 0 Hz
GB 0
PC 1.40

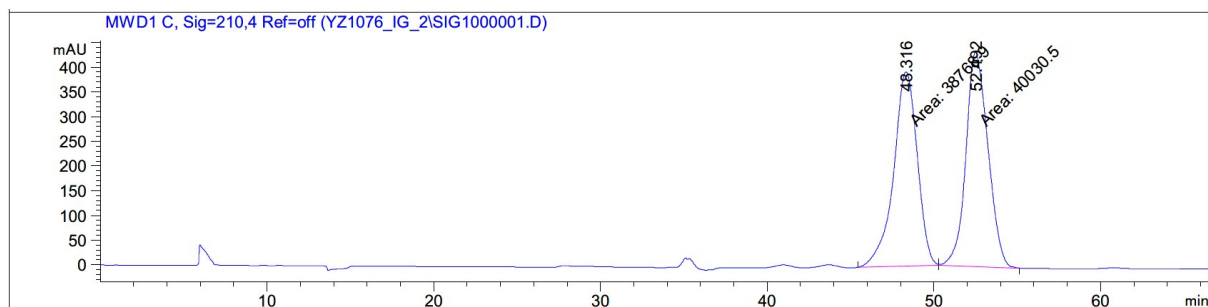
F2 - Processing parameters
SI 32768
SF 400.1301222 MHz
WDW 0
SSB 0
LB 0 Hz
GB 0
PC 1.40

F1 - Processing parameters
SI 32768
SF 400.1301222 MHz
WDW 0
SSB 0
LB 0 Hz
GB 0
PC 1.40

HMBC (400 MHz, CDCl₃)



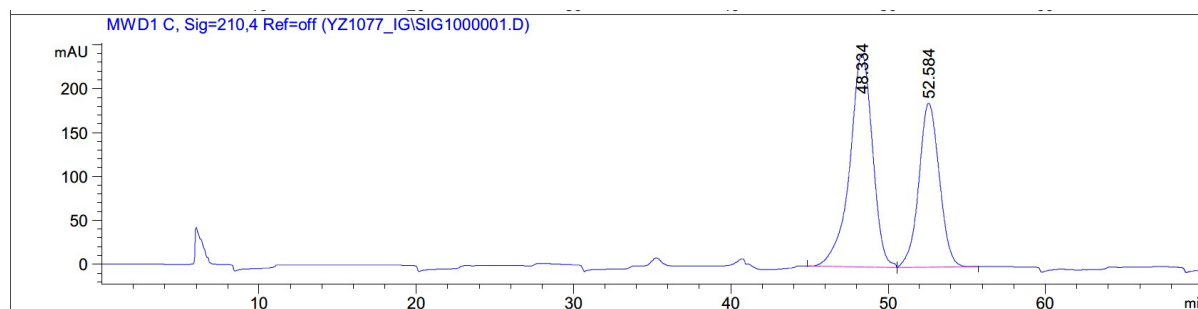
HPLC of racemic (4-methoxyphenyl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanol **24**.



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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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).

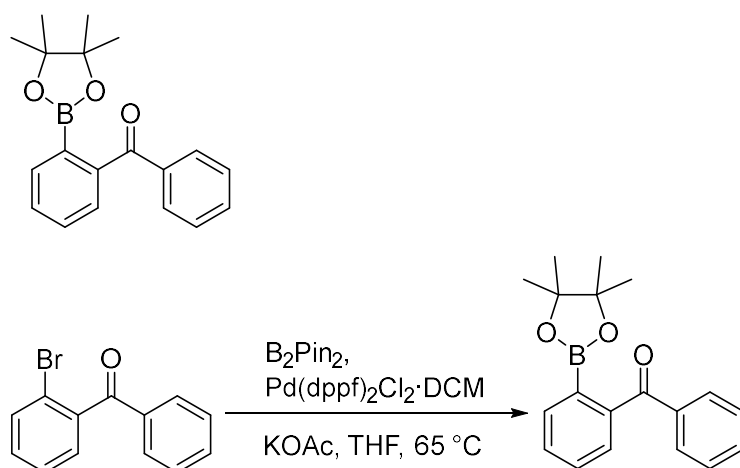


Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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.

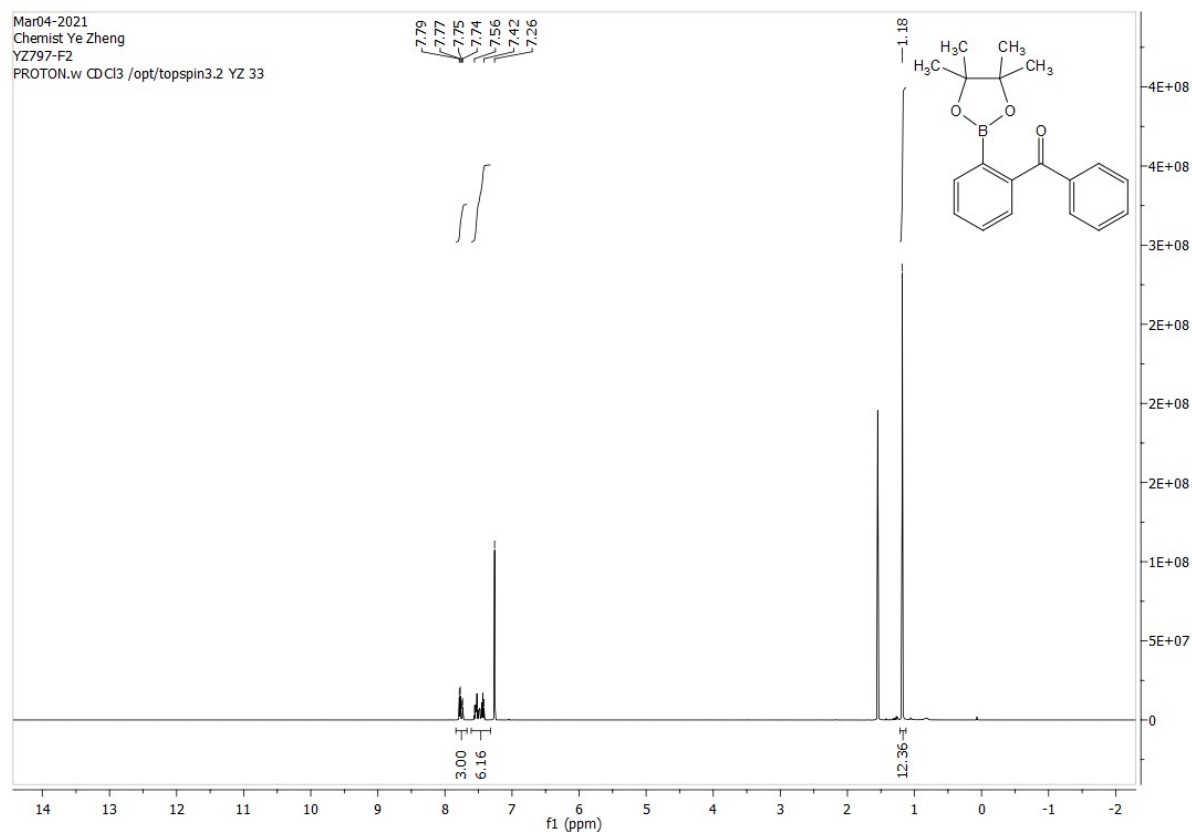


This compound has been reported and fully characterized: K. L. Billingsley, T. E. Barder and S. L. Buchwald, *Angew. Chem., Int. Ed.*, 2007, **46**, 55359-5363.

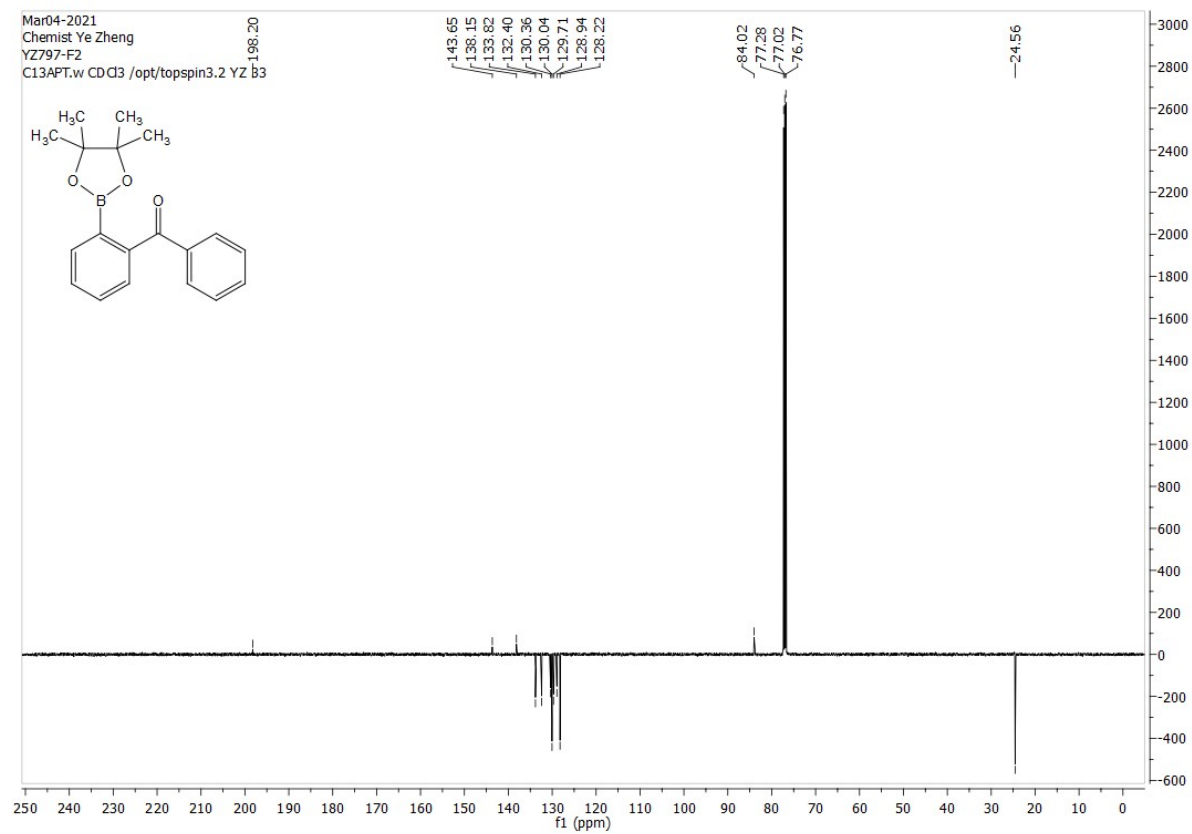
A round-bottom flask was charged with 2-bromobenzophenone (130 mg, 0.500 mmol), bis(pinacolato)diboron (152 mg, 0.600 mmol), potassium acetate (147 mg, 1.50 mmol), THF (3.2 mL) and $Pd(dppf)_2Cl_2 \cdot DCM$ (20.4 mg, 0.0250 mmol). The reaction mixture was heated to 65 °C and left stirring under the 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: R_f ca 0.50 (9:1 hexane: EtOAc), strong UV and $KMnO_4$; δ_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; δ_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, $T = 25^\circ C$) ketone 5.4 min, *R* and *S* isomers 4.2 min and 5.5 min.

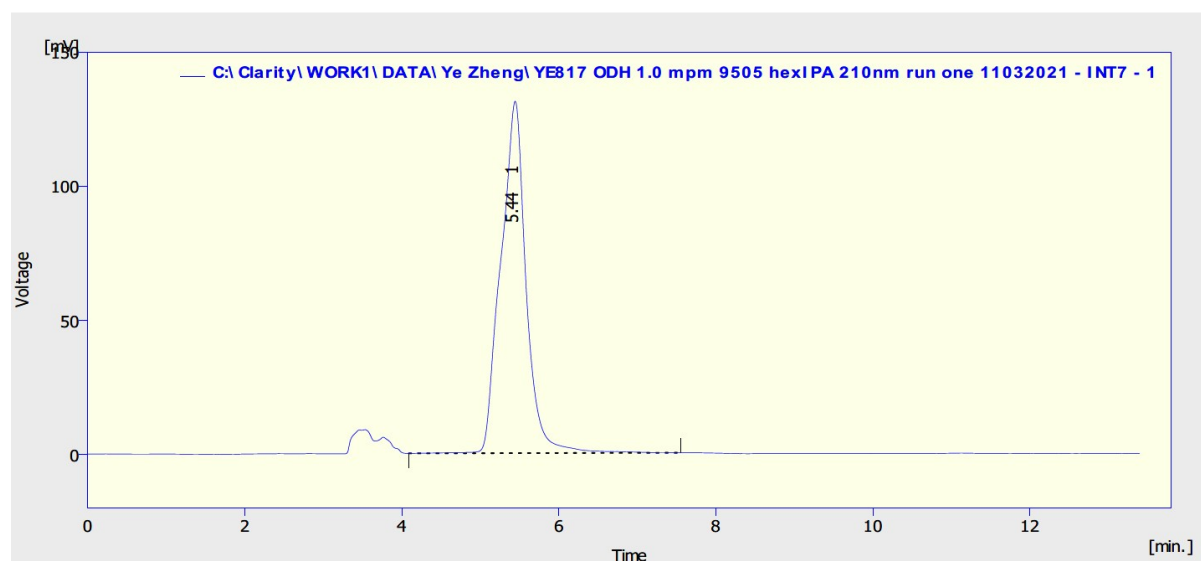
^1H NMR (500 MHz, CDCl_3)



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



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

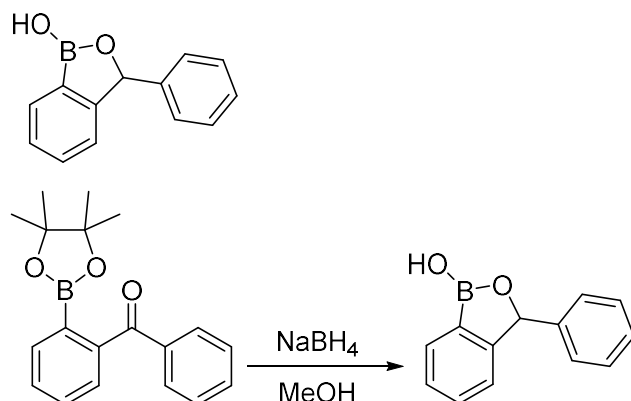


Result Table (Uncal - C:\Clarity\WORK1\DATA\Ye Zheng\YE817 ODH 1.0 mpm 9505 hexIPA 210nm run one 11032021 - INT7 - 1)

	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.

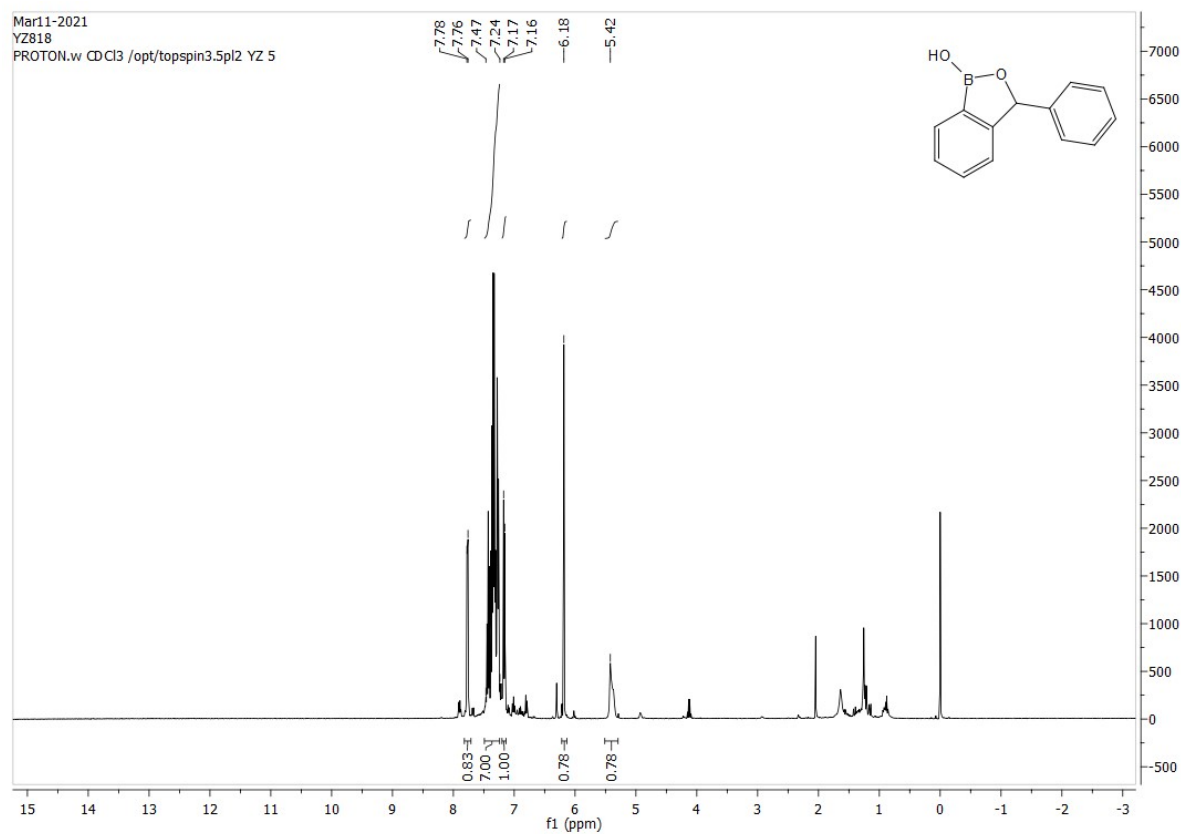
To a solution of phenyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone (153 mg, 0.497 mmol) in MeOH (2.5 mL) was added sodium borohydride (37.8 mg, 0.994 mmol). The reaction was stirred for 4 hours. TLC (9:1 hexane: EtOAc) after this time indicated full conversion. Distilled water (20 mL) was added, and the mixture was extracted with EtOAc (3 × 20 mL), dried with MgSO₄. 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: R_f ca 0.20 (9:1 hexane: EtOAc), strong UV and KMnO₄; δ_{H} (400 MHz, CDCl₃) 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; δ_{C} (100 MHz, CDCl₃) 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.

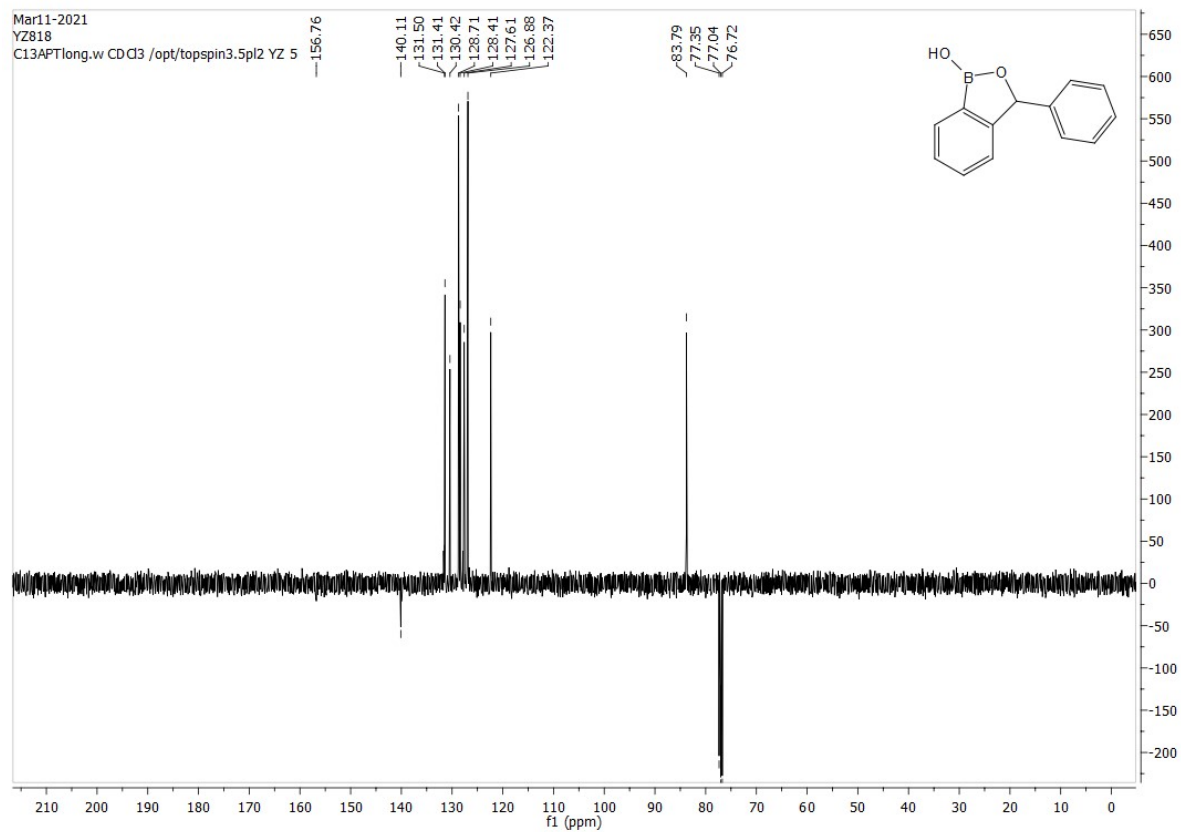
ATH of phenyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone).

(*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 stirred under a nitrogen atmosphere, followed by TLC (9:1 hexane: EtOAc). After 72 hours, the reaction was quenched using saturated NaHCO₃ 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 0-50% 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; [α]_D¹⁷ +2.29 (c 0.940 in CHCl₃) 23% ee.

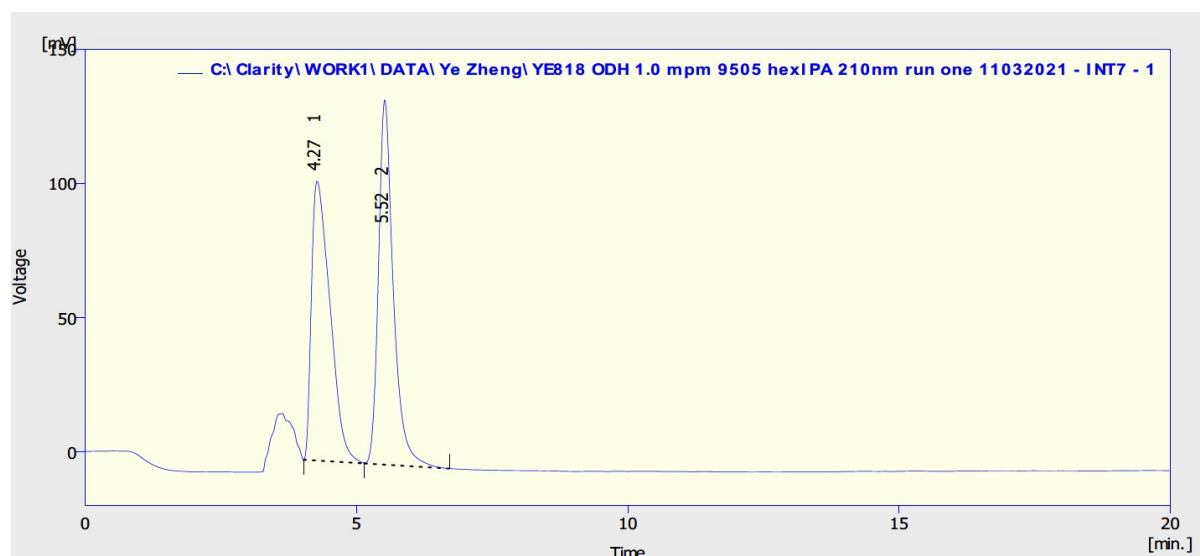
^1H NMR (400 MHz, CDCl_3)



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



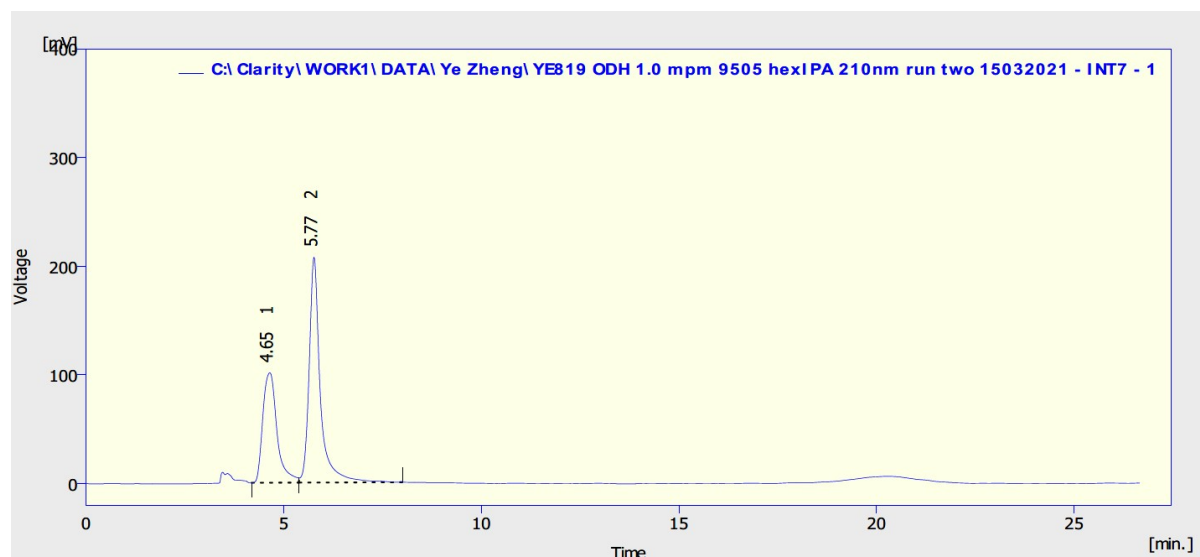
HPLC of racemic phenylbenzo[c][1,2]oxaborol-1(3H)-ol **25**.



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		

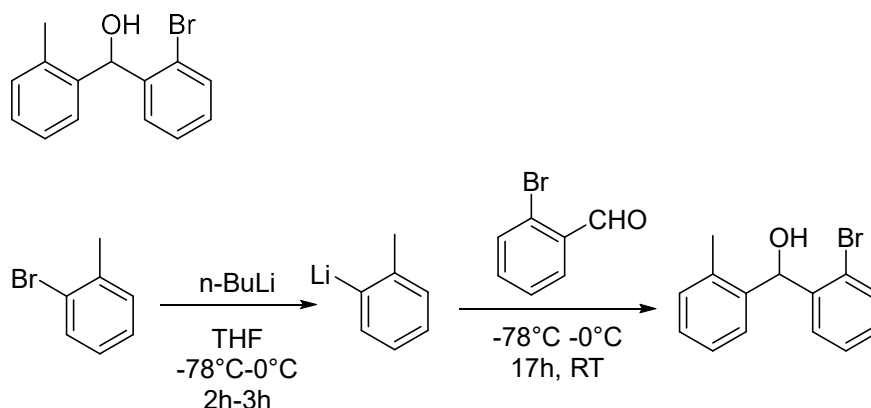
HPLC after ATH of phenyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone using (*R,R*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (after 72 hours, 100% conversion, 23% ee)



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		

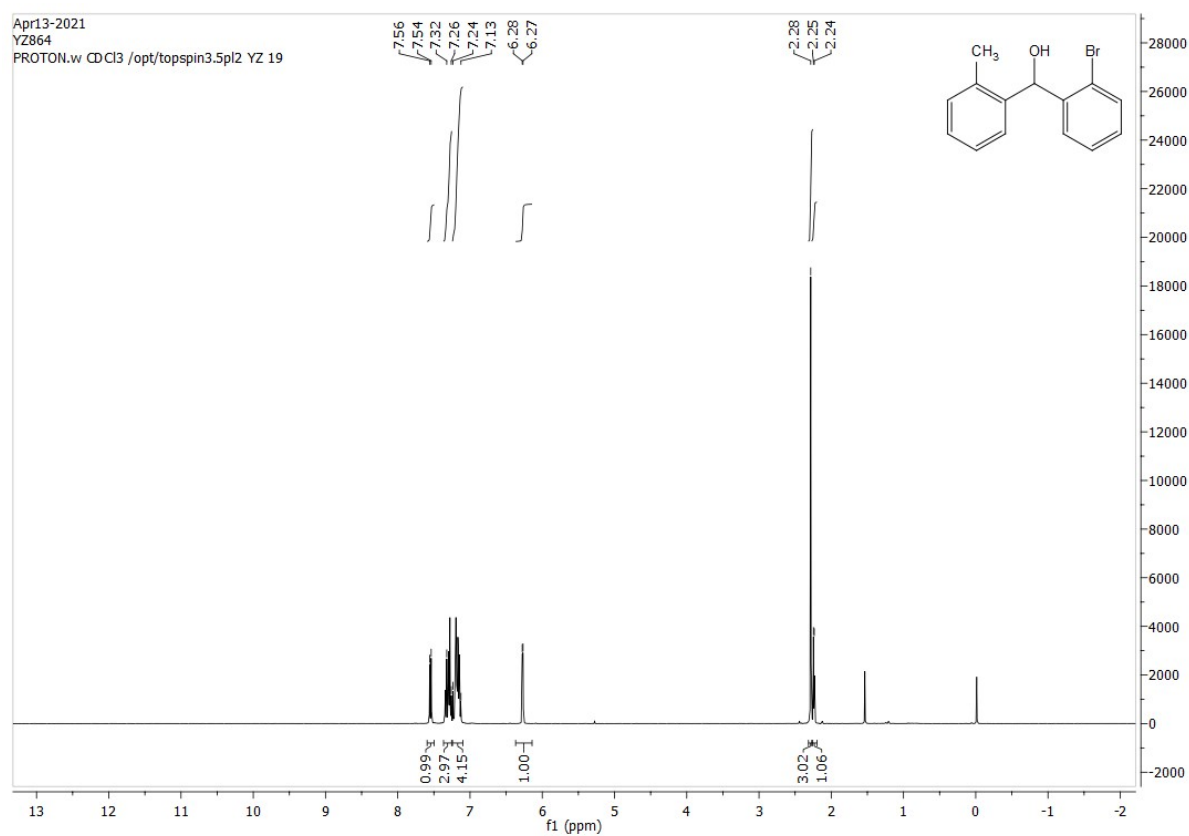
(2-Bromophenyl)(o-tolyl)methanol.



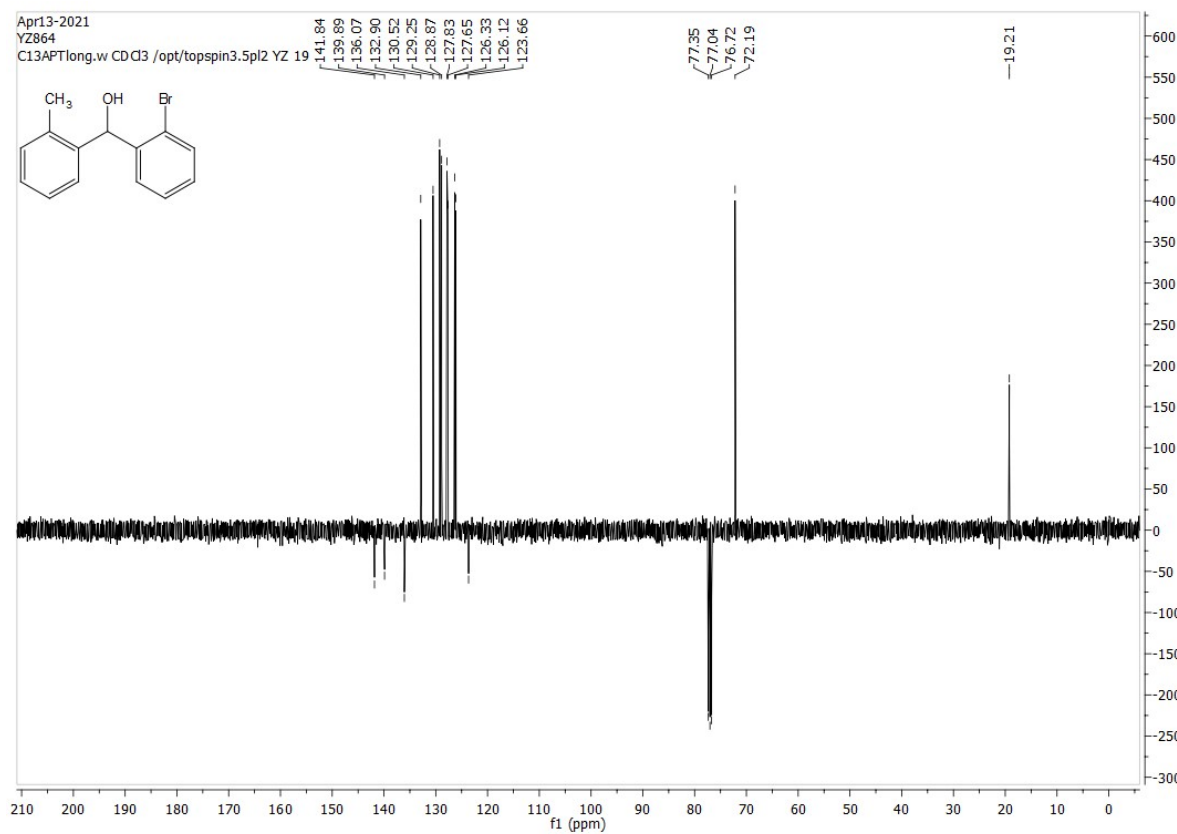
This compound has been reported and fully characterized: Yuan-Xi Liao, Chun-Hui Xing, Matthew Israel, Qiao-Sheng Hu, *Tetrahedron Letters*, 2011, **52**, 3324-3328

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 NH₄Cl 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 (MgSO₄) 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: R_f ca 0.30 TLC (9:1 hexane: EtOAc)., strong UV and KMnO₄; δ_H (400 MHz, CDCl₃) 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, ArCHOH), 2.28 (3H, s, CH₃), 2.25 (1H, d, *J* = 4.5, ArCHOH) ppm; δ_C (100 MHz, CDCl₃) 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 (CH₃) ppm.

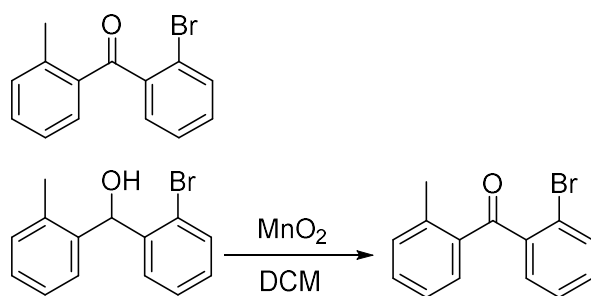
^1H NMR (400 MHz, CDCl_3)



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



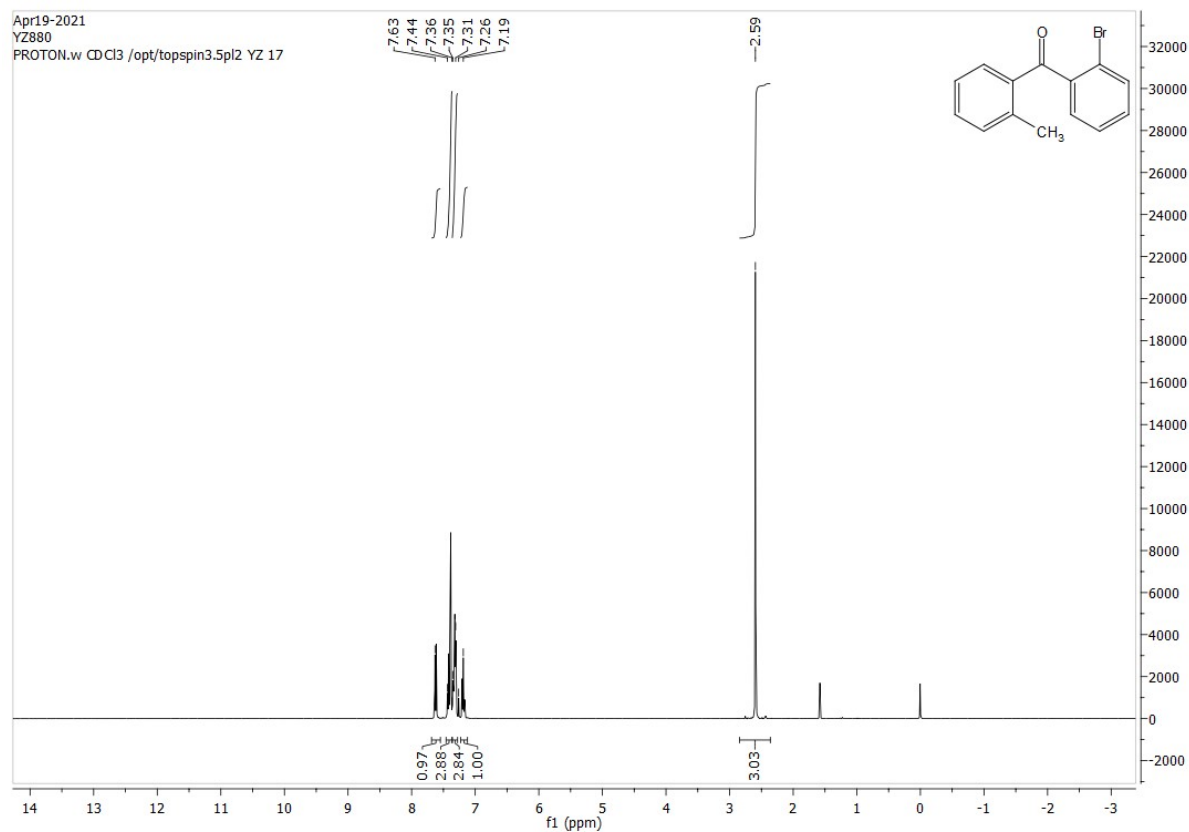
(2-Bromophenyl)(*o*-tolyl)methanone.



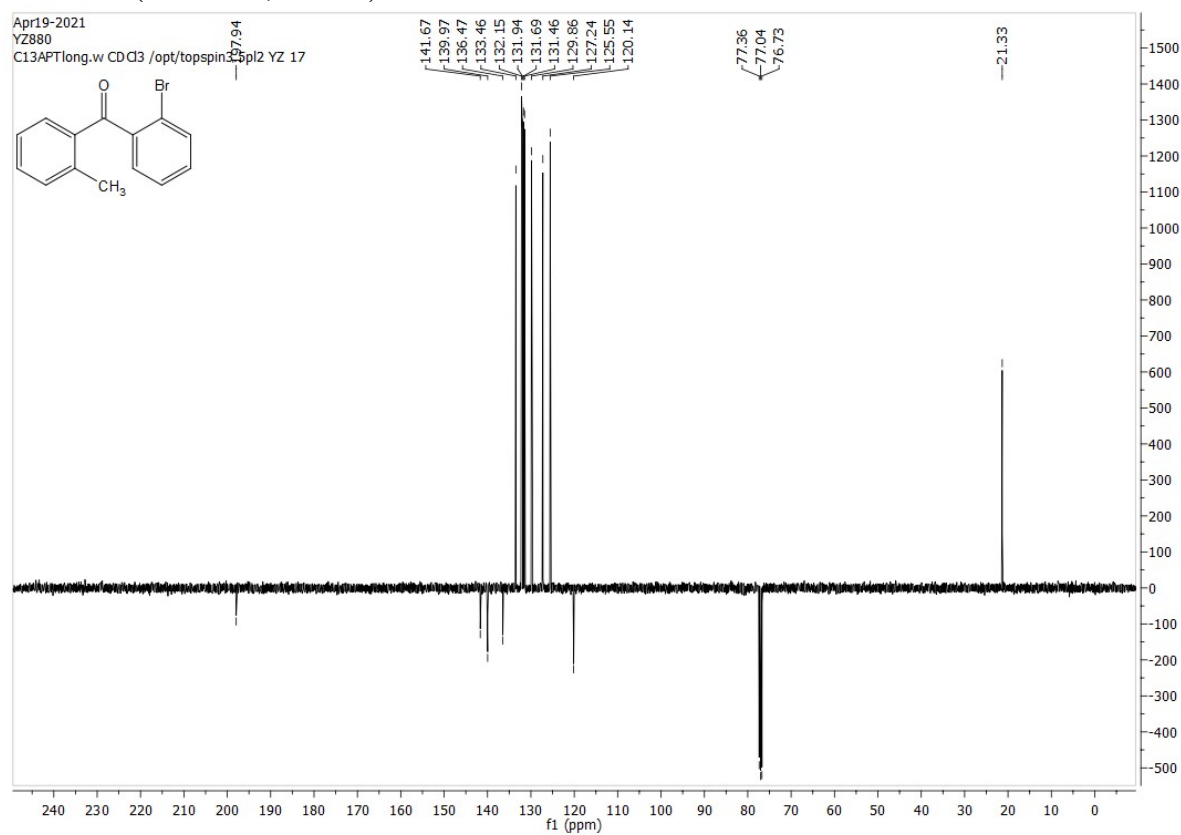
This compound has been reported and fully characterized: P. Sharma, S. Rohilla and N. Jain, *J. Org. Chem.*, 2017, **82**, 1105-1113.

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: R_f ca 0.50 (9:1 hexane: EtOAc), strong UV and KMnO₄; δ_{H} (400 MHz, CDCl₃) 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, CH₃) ppm; δ_{C} (100 MHz, CDCl₃) 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 (CH₃) ppm. Data matched that reported.

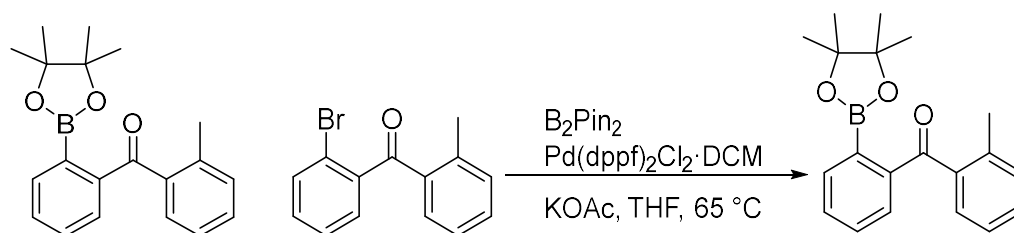
^1H NMR (400 MHz, CDCl_3)



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



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

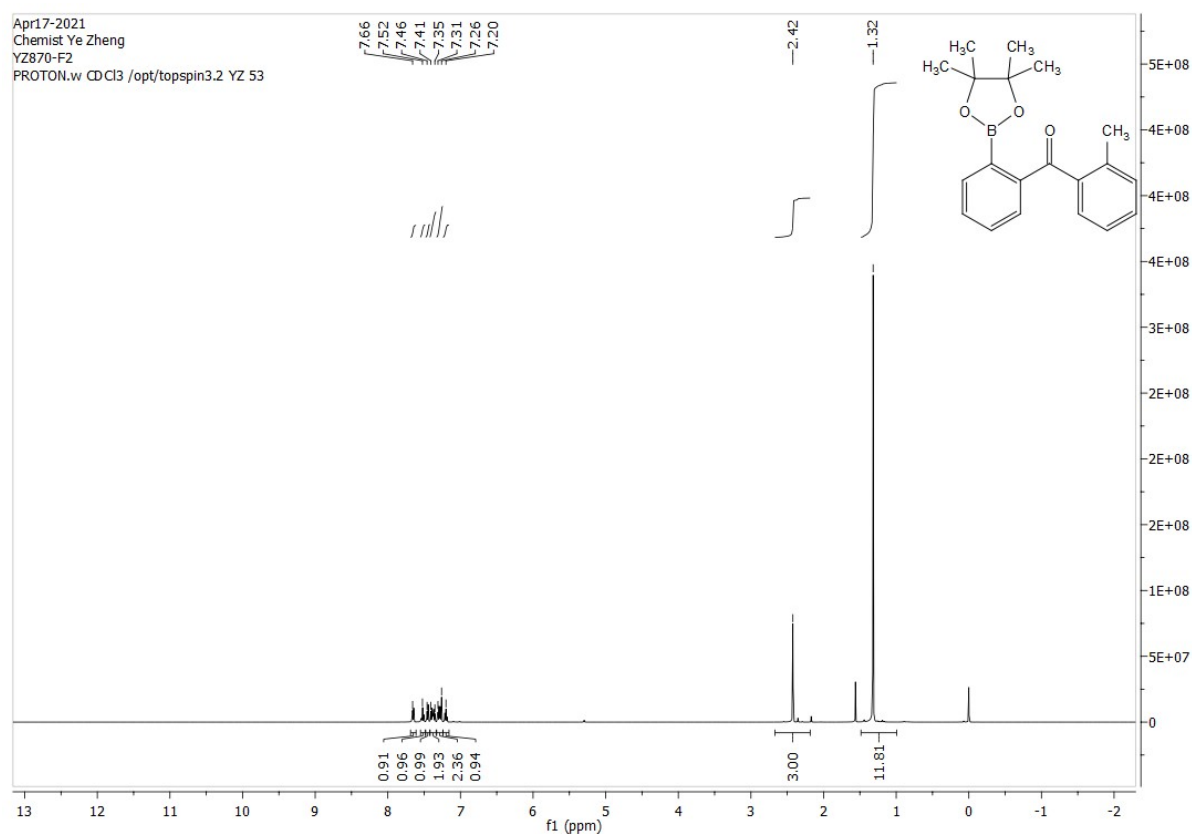


This compound is novel.

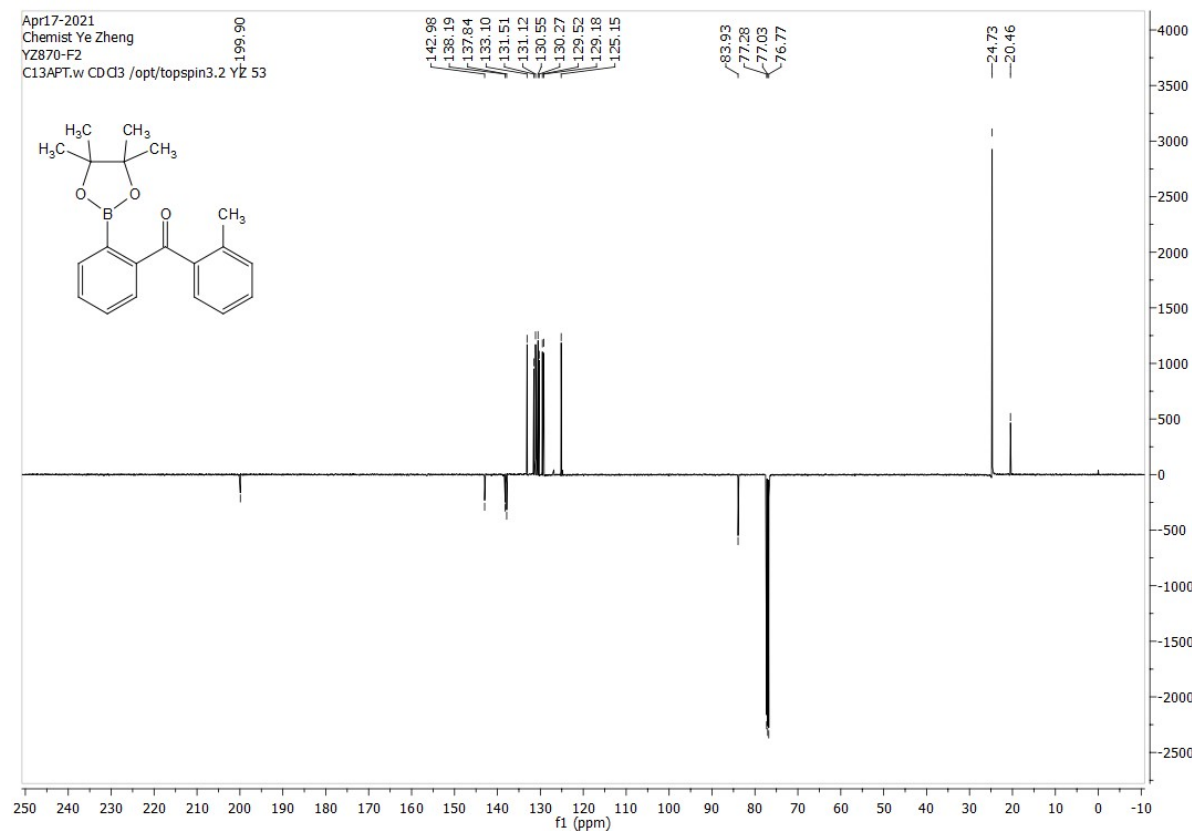
A round-bottom flask was charged with (2-bromophenyl)(*o*-tolyl)methanone (706 mg, 2.58 mmol), bis(pinacolato)diboron (787 mg, 3.10 mmol), potassium acetate (759 mg, 7.74 mmol), THF (16 mL) and $Pd(dppf)_2Cl_2 \cdot DCM$ (105 mg, 0.129 mmol). The reaction mixture was heated to 65 °C and left stirring 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: R_f 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); ν_{max} 2972, 2926, 1649, 1561, 1370, 1340, 1301, 1267, 1254, 1144, 1108, 1069, 1033, 932, 855, 751 cm^{-1} ; δ_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; δ_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 (ESI-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.

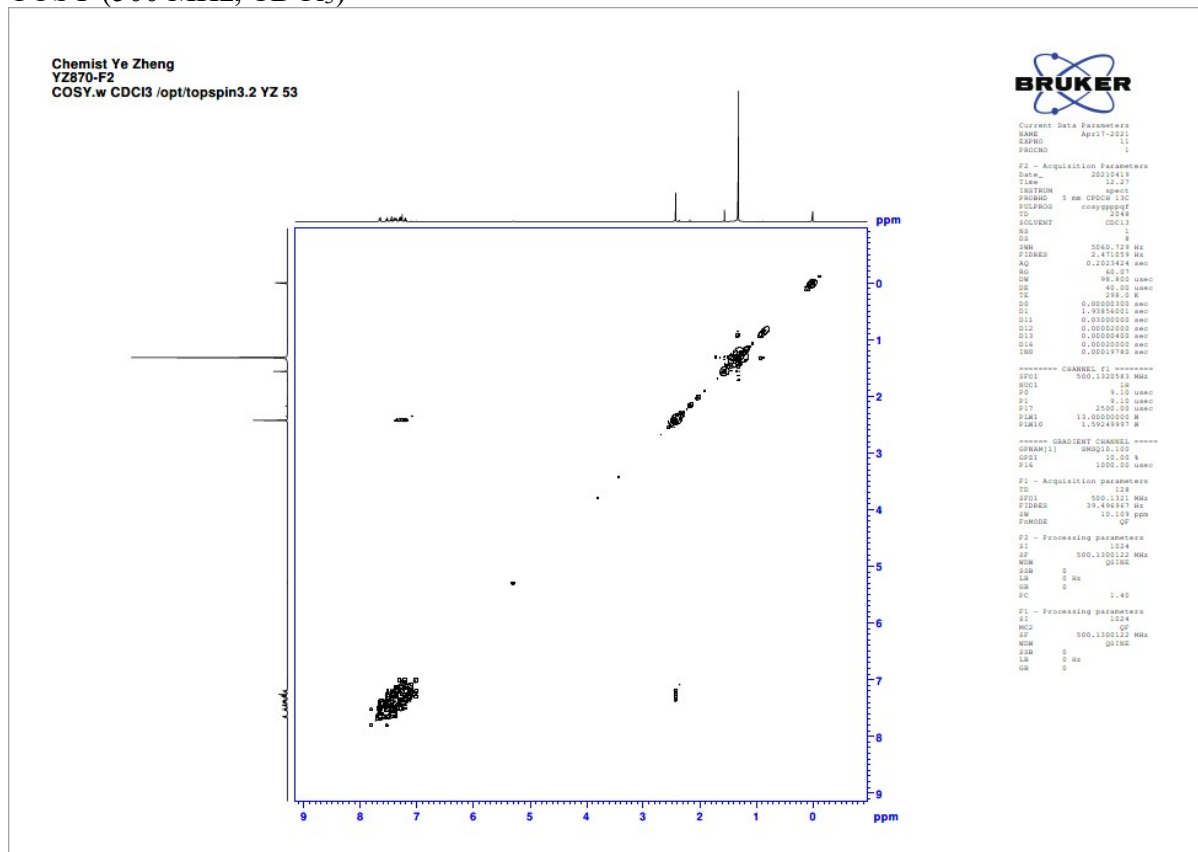
^1H NMR (500 MHz, CDCl_3)



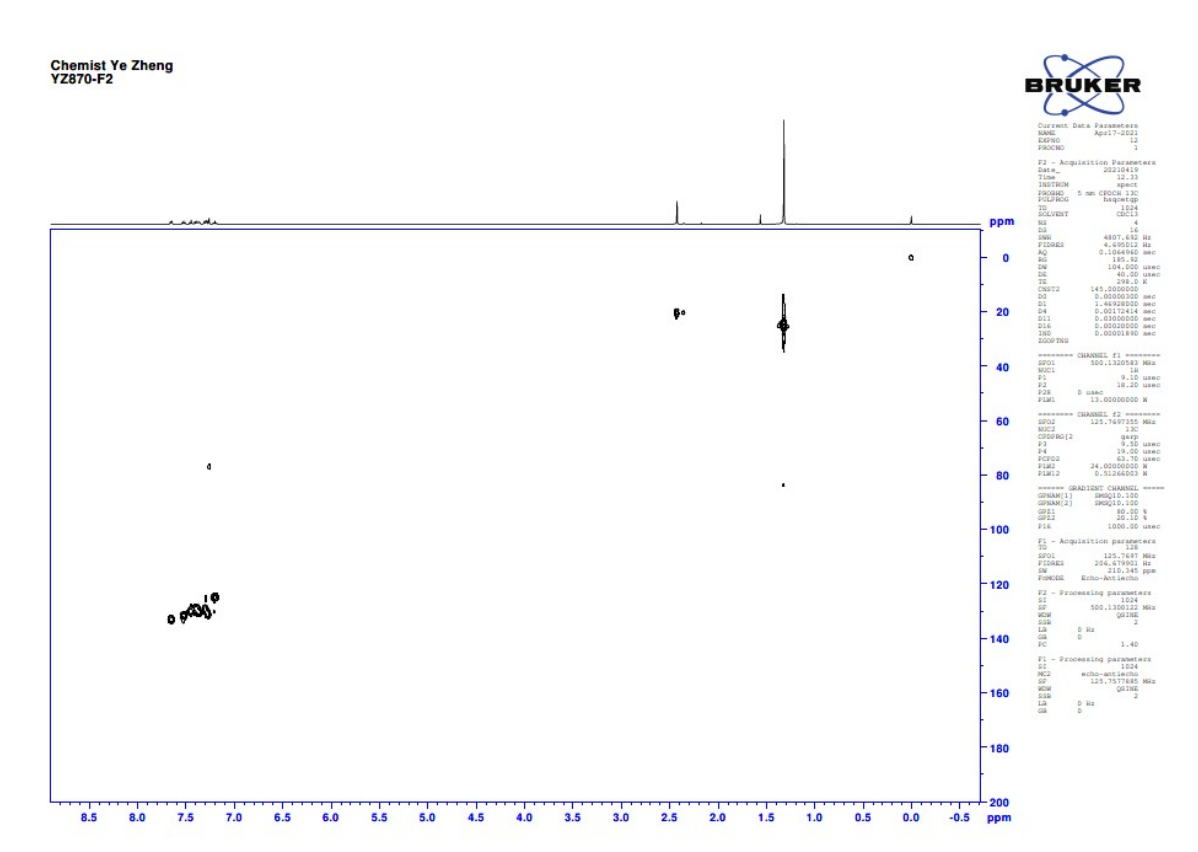
^{13}C NMR (125 MHz, CDCl_3)



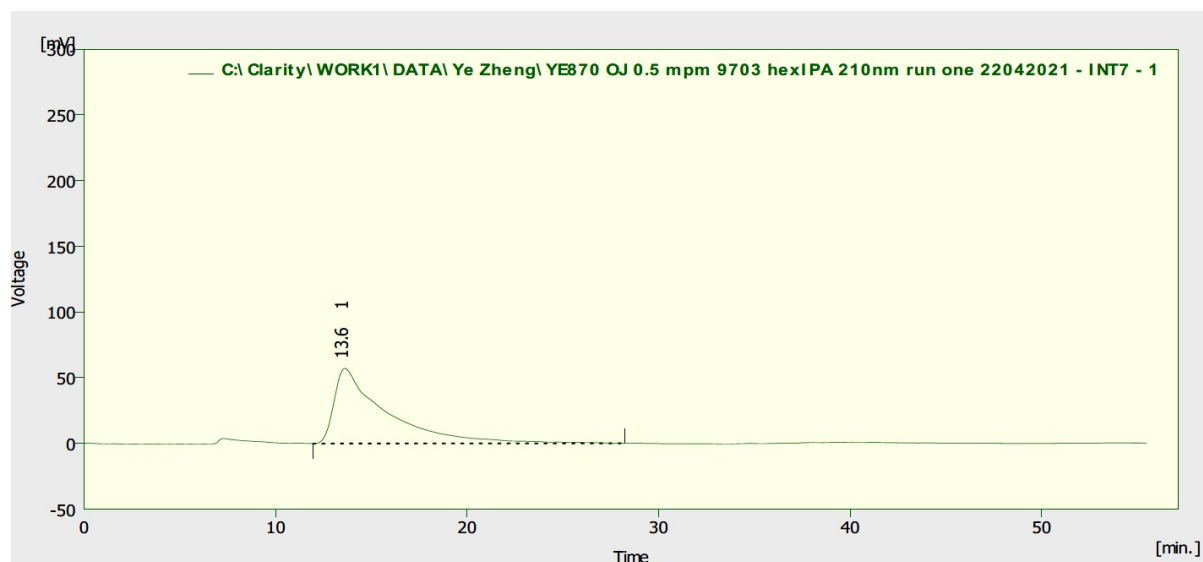
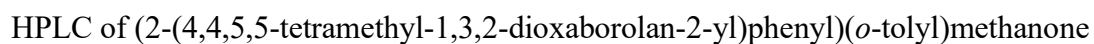
COSY (500 MHz, CDCl₃)



HSQC (500 MHz, CDCl₃)



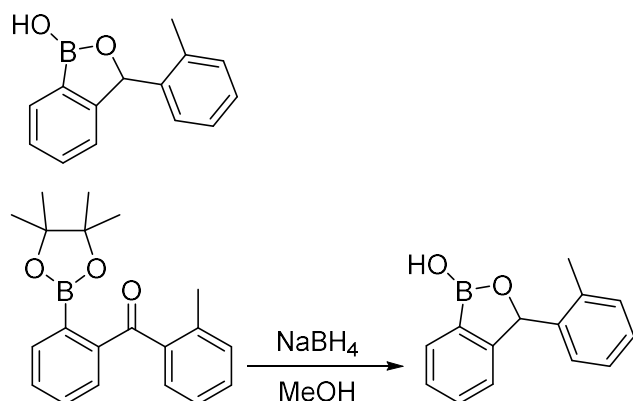
Chemist Ye Zheng
YZ870-F2
HMBC.w CDCl3 /opt/topspin3.2 YZ 53



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(3*H*)-ol **26**.



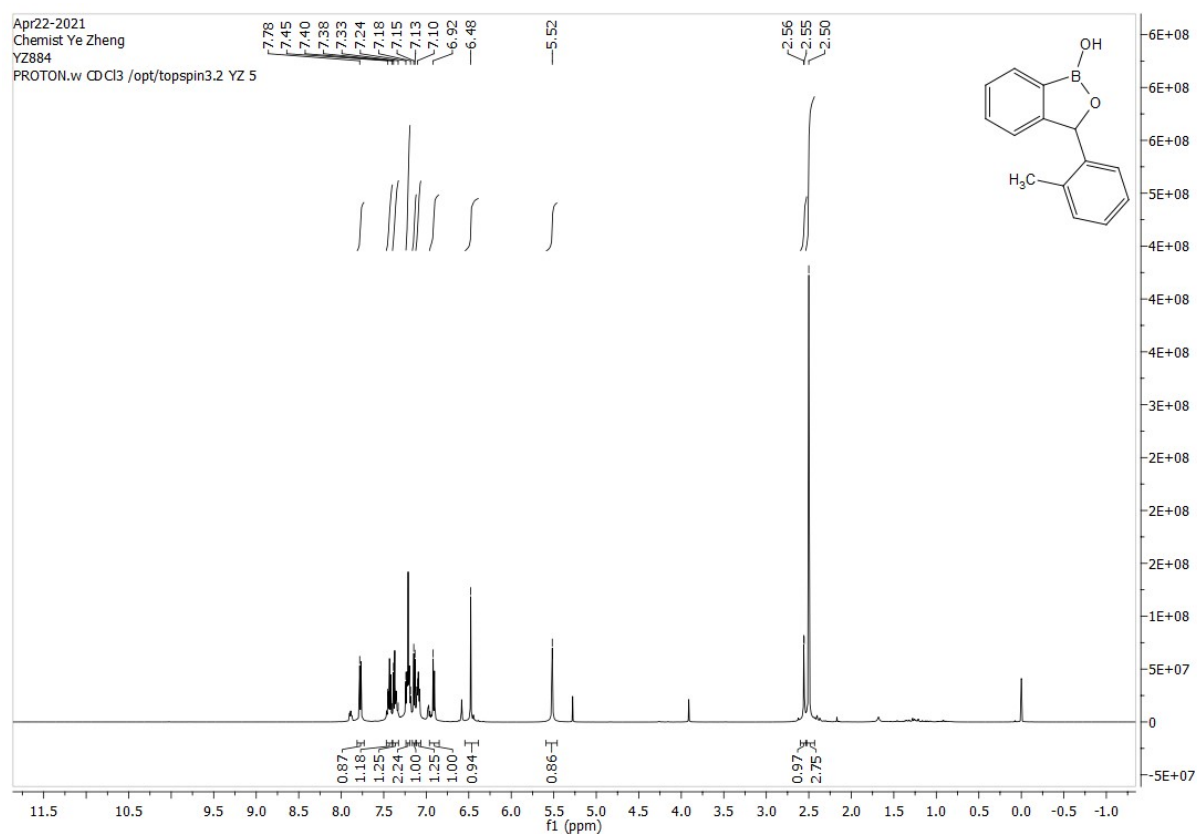
This compound is novel.

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 × 20 mL), dried with MgSO₄. 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(3*H*)-ol **26** as a white solid (103 mg, 0.460 mmol, 60%). TLC: R_f ca 0.20 (4:1 hexane: EtOAc), strong UV and KMnO₄; Mp: 121 °C; HRMS: (found (ESI⁺): [M+H]⁺, Calcd for C₁₄H₁₃BNaO₂ 247.0913; Found 247.0901; -3.9 ppm error); ν_{max} 3381 (br), 3020, 2975, 1604, 1489, 1382, 1344, 1287, 1143, 1108, 1080, 974, 757, 732 cm⁻¹; δ_H (500 MHz, CDCl₃) 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, CH₃) ppm; δ_C (125 MHz, CDCl₃) 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 (CH₃) ppm. m/z (ES-API⁺) 247.1 (M⁺ + 23, 100%).

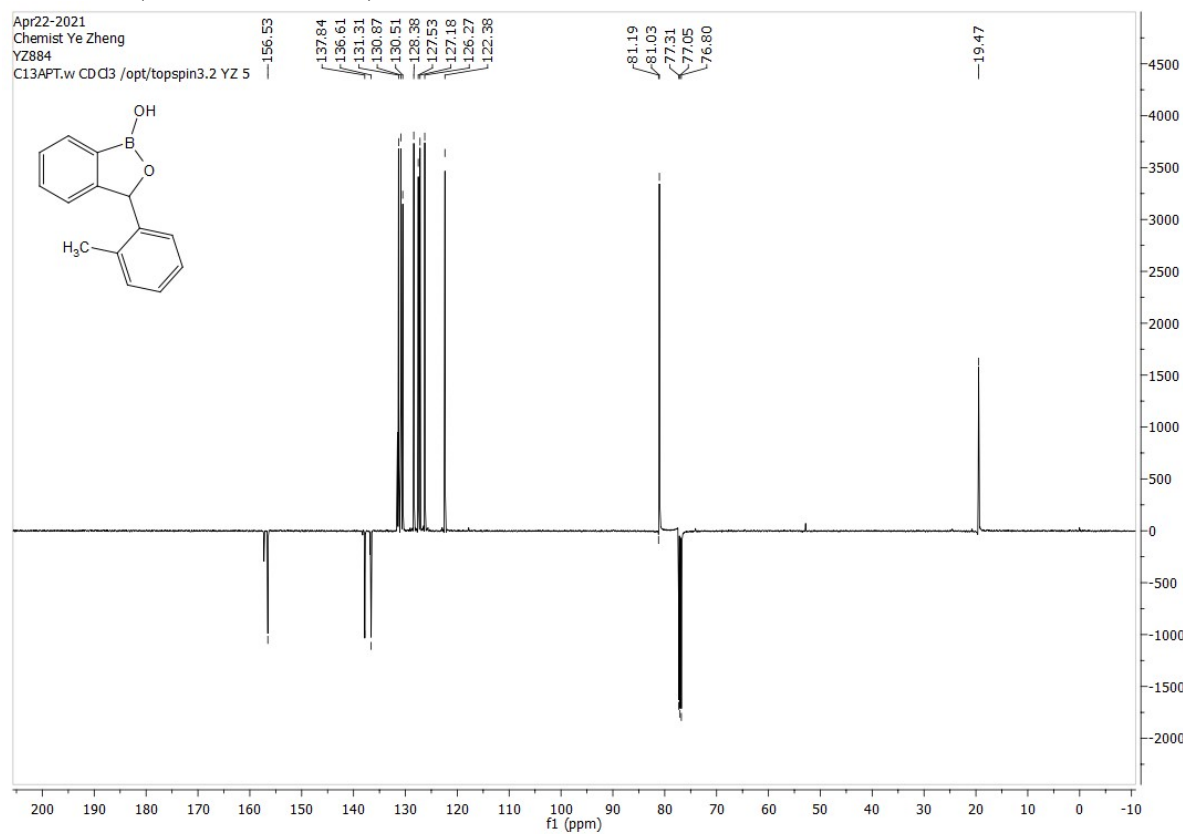
Enantiomeric excess and conversion determined by HPLC analysis (Chiralcel OJ, 30 cm x 6mm column, hexane:iPrOH 97:3, 0.5 mL/min, T = 25°C) ketone 13.6 min, *R* and *S* isomers 14.9 min and 19.0 min, configuration is not confirmed.

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 stirred under a nitrogen atmosphere, followed by TLC (4:1 hexane: EtOAc). After 72 hours, the reaction was quenched using saturated NaHCO₃ 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 0-50% 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

^1H NMR (500 MHz, CDCl_3)

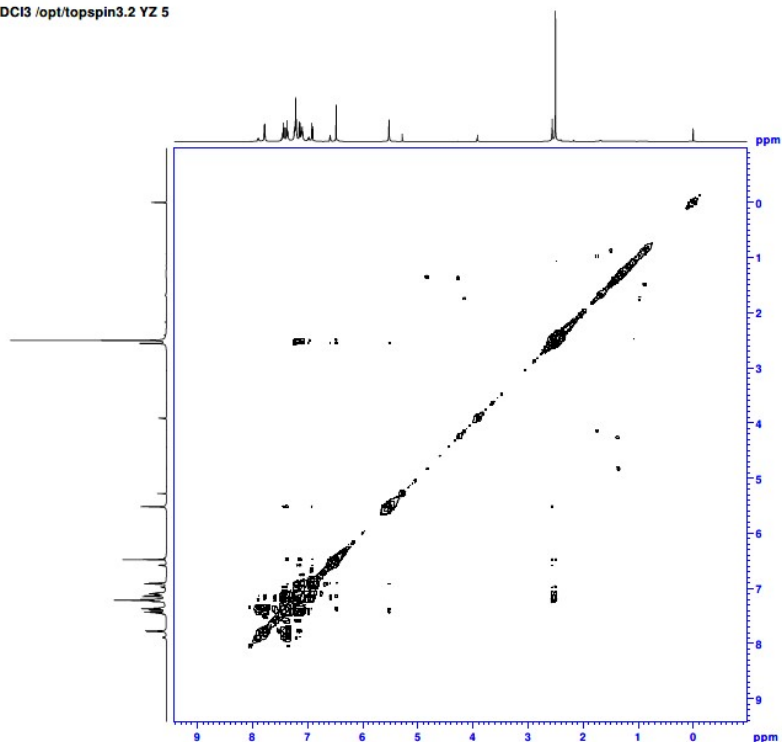


^{13}C NMR (125 MHz, CDCl_3)



COSY (500 MHz, CDCl₃)

Chemist Ye Zheng
YZ884
COSY.w CDCl₃ /opt/topspin3.2 YZ 5



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EXPNO     11
PROCNO    1

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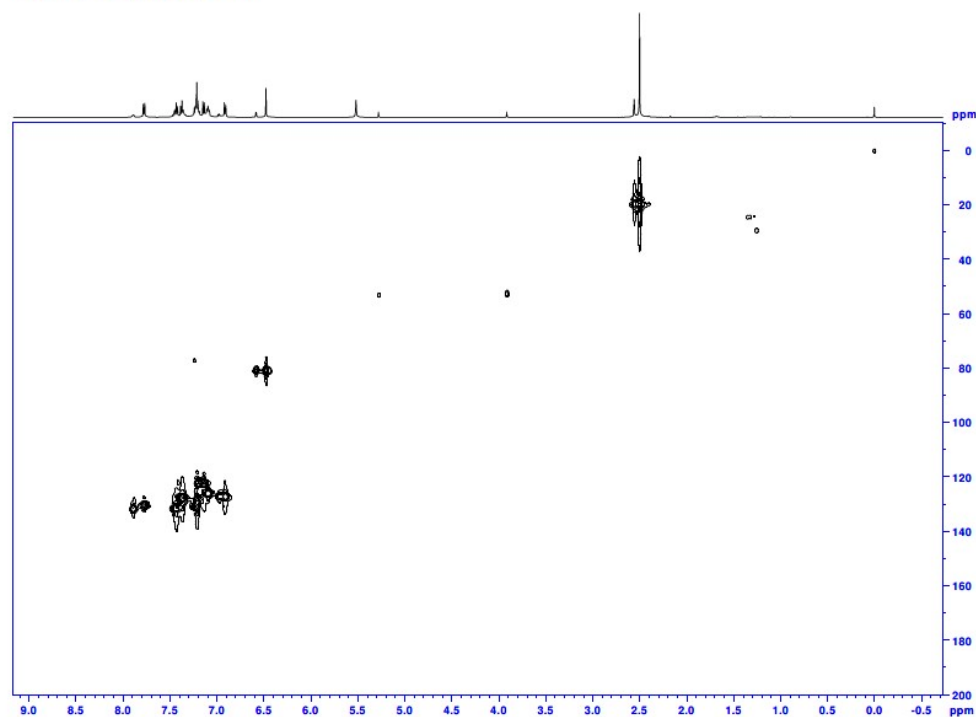
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F1 - Processing parameters
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HSQC (500 MHz, CDCl₃)

Chemist Ye Zheng
YZ884
HSQC.w CDCl₃ /opt/topspin3.2 YZ 5



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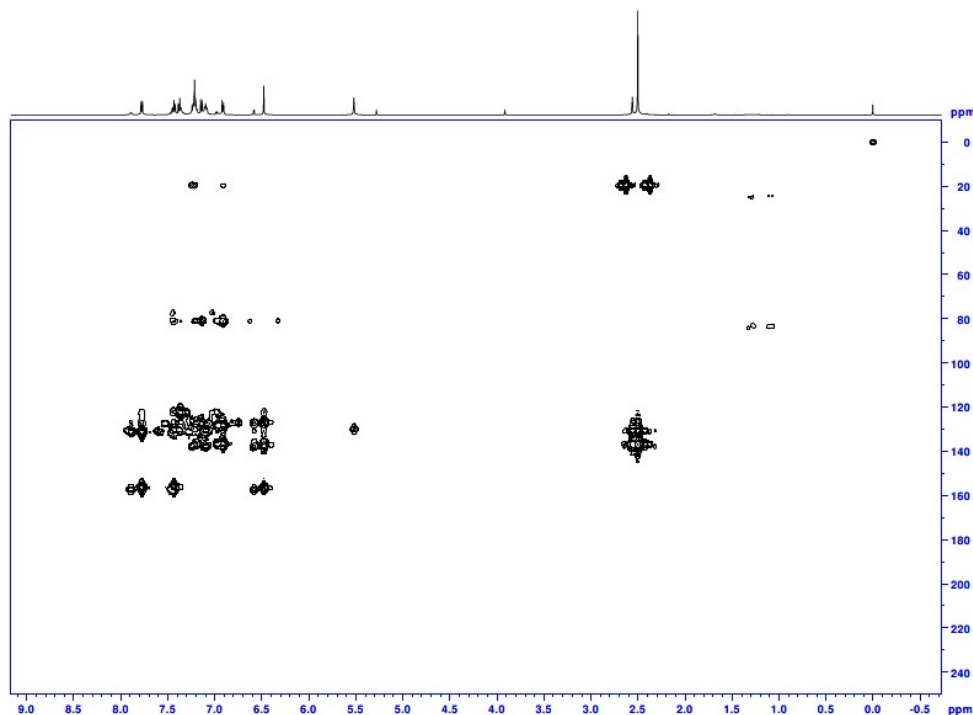
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HMBC (500 MHz, CDCl₃)

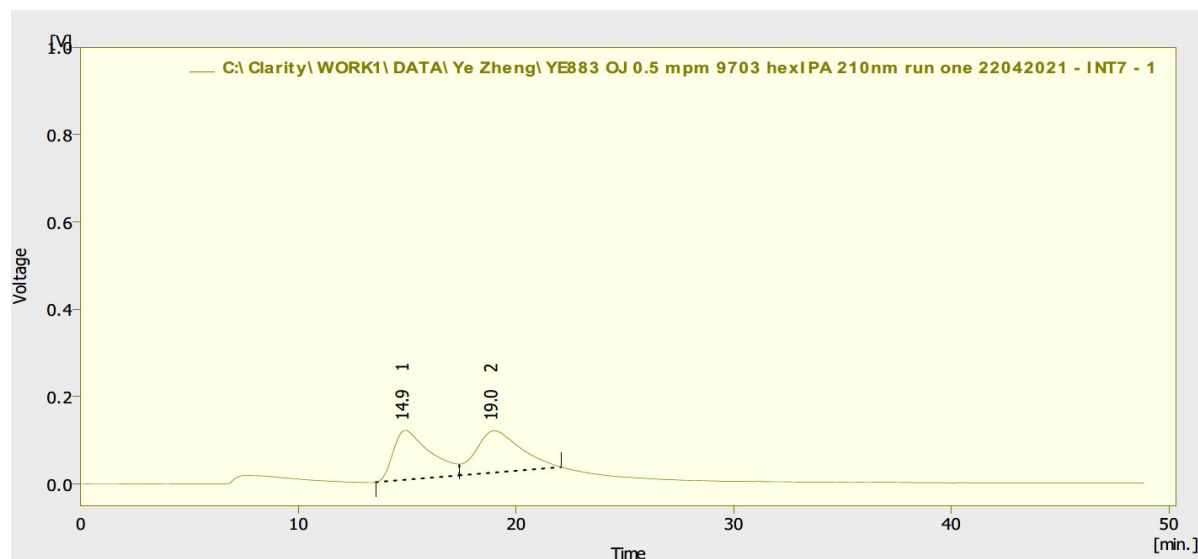
Chemist Ye Zheng
YZ884
HMBC.w CDCl₃ /opt/topspin3.2 YZ 5



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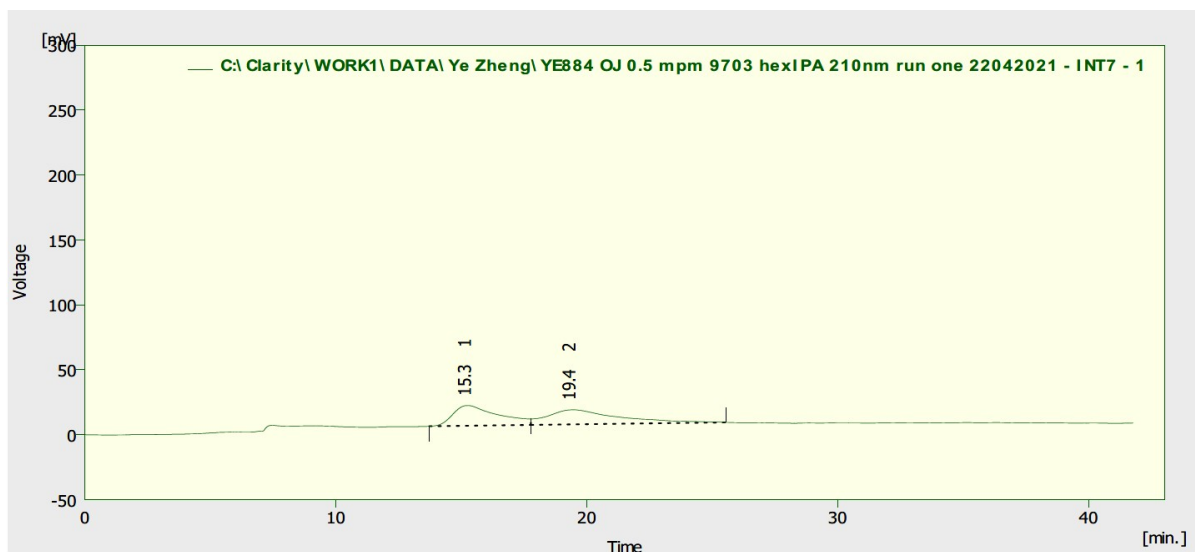
HPLC of racemic 3-(*o*-Tolyl)benzo[*c*][1,2]oxaborol-1(3*H*)-ol **26**



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		

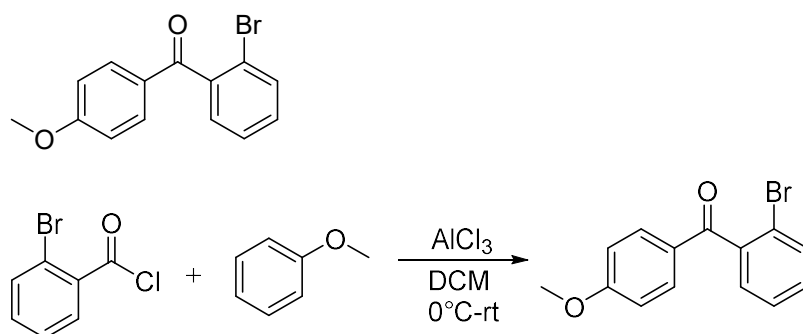
HPLC after ATH of (2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)(*o*-tolyl)methanone using (*R,R*)-3C-tethered Ru(II)-TsDPEN catalyst **2** (after 72 hours, 100% conversion, 6% ee).



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.

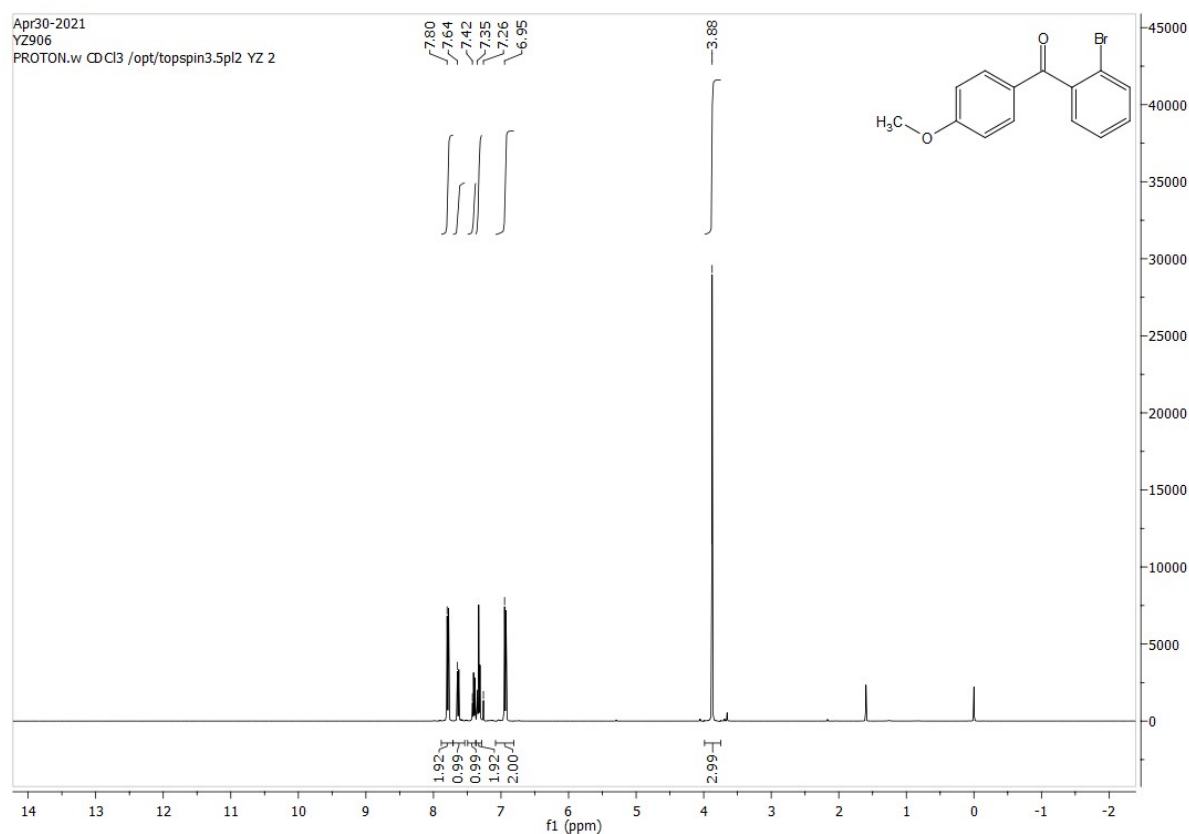


This compound has been reported and fully characterized: F. Ling, H. Hou, J. Chen, S. Nian, X. Yi, Z. Wang, D. Song and W. Zhong, *Org. Lett.* 2019, **21**, 3937-3941.

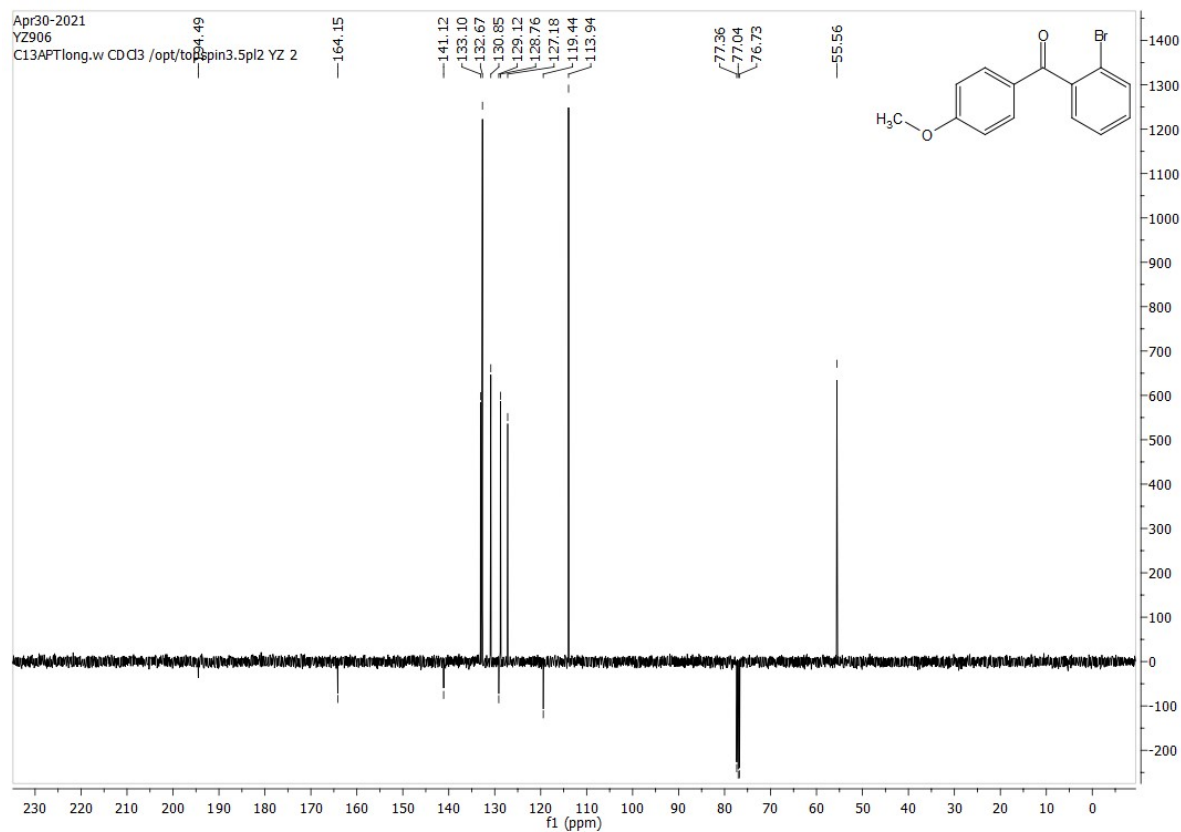
To a solution of 2-bromobenzoyl chloride (438 mg, 2.00 mmol) was in DCM (10 mL) at 0°C was added dropwise anisole (281 mg, 2.60 mmol). The reaction mixture was then stirred under a nitrogen atmosphere for 30 minutes, after which AlCl_3 (319 mg, 2.40 mmol) was added. The reaction mixture was left stirring 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: R_f ca 0.50 (9:1 hexane: EtOAc), strong UV and KMnO_4 ; δ_{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; δ_{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 ($\text{M}^+ + 23$, 100%). Data matched that reported.

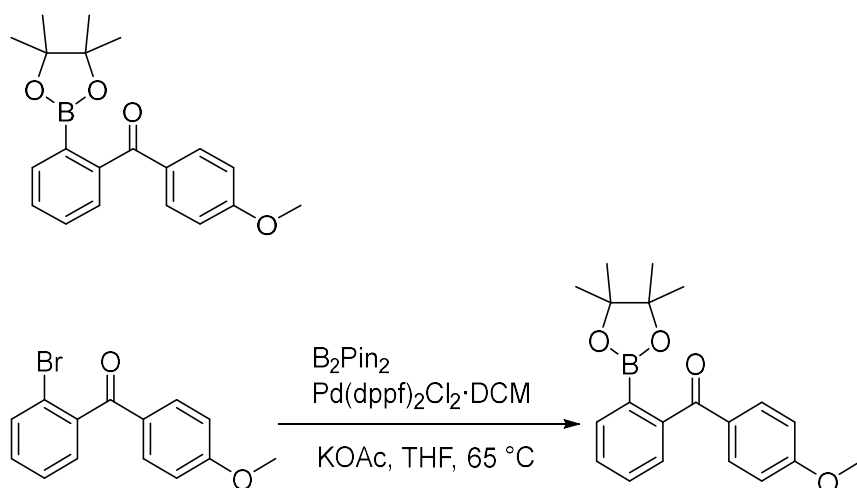
^1H NMR (400 MHz, CDCl_3)



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



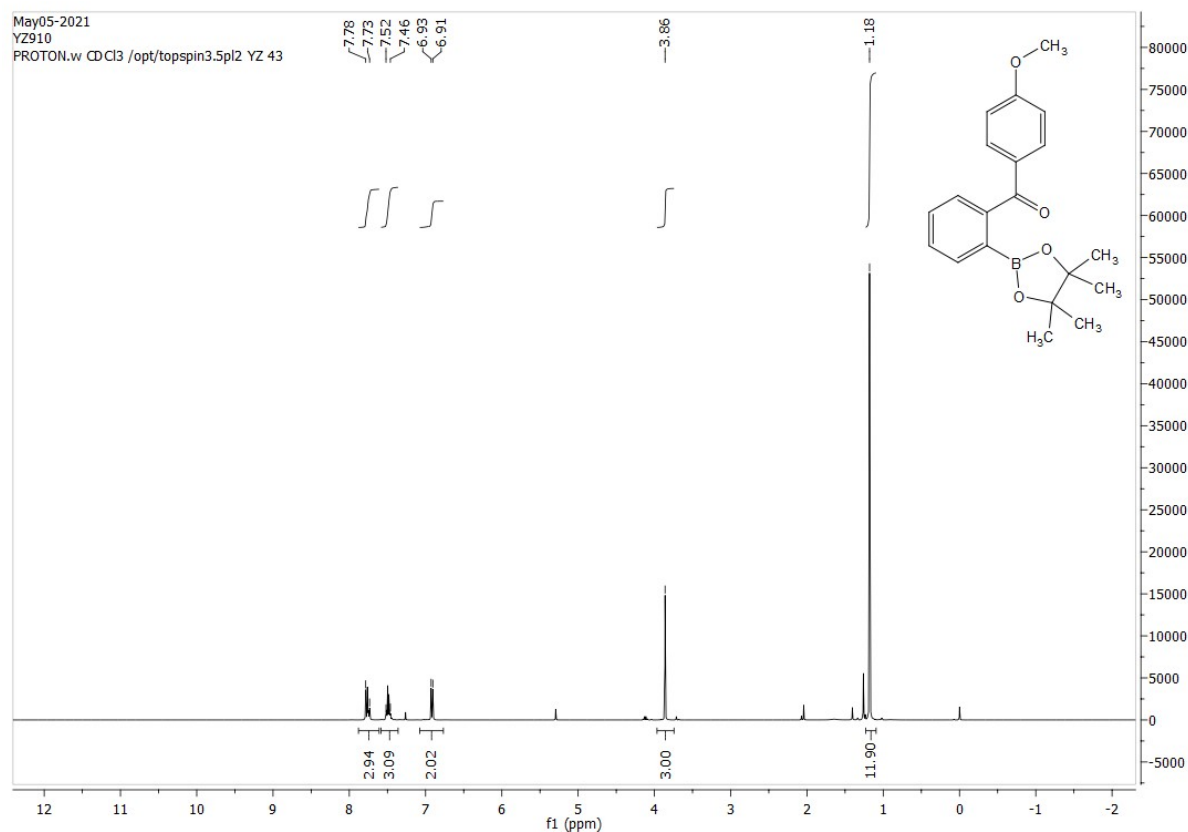
(4-Methoxyphenyl)(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone.



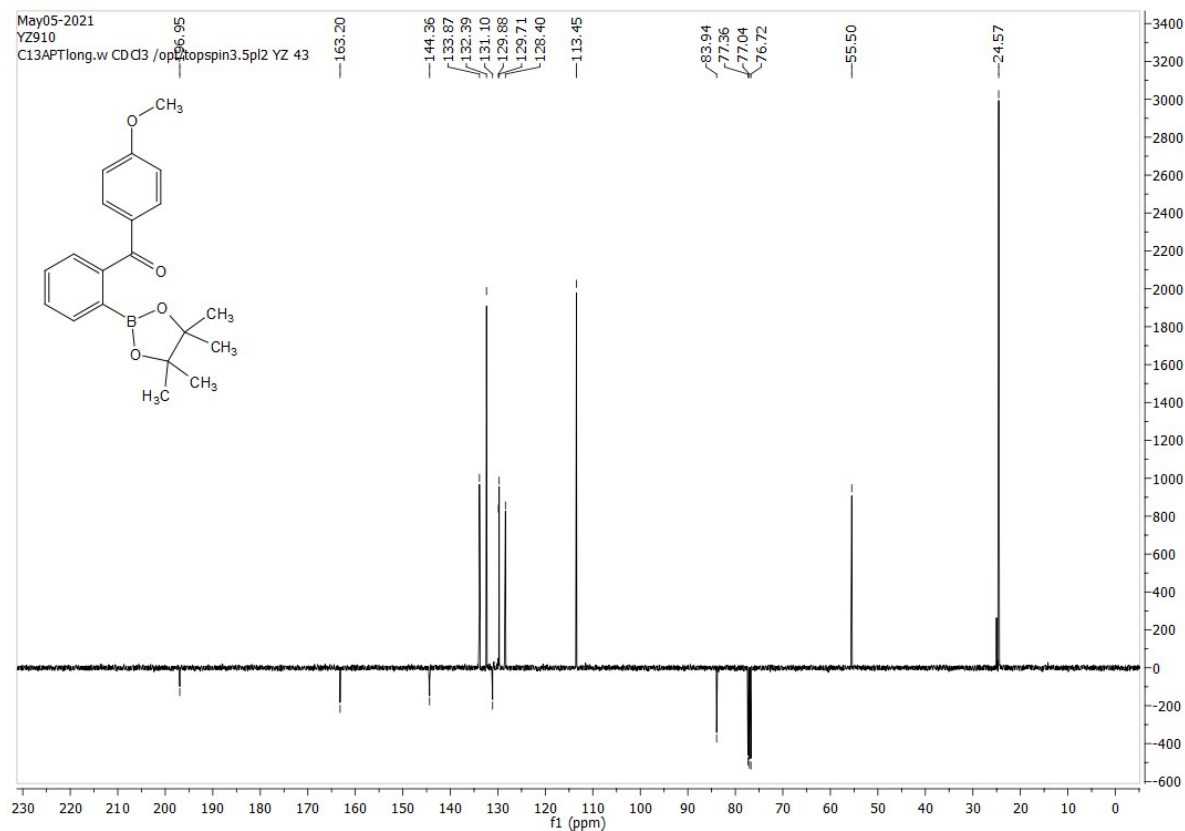
This compound is novel.

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 $Pd(dppf)_2Cl_2 \cdot DCM$ (90.7 mg, 0.111 mmol). The reaction mixture was heated to $65\text{ }^\circ C$ 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 ($3 \times 20\text{ mL}$), 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: R_f 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); ν_{max} 2977, 2933, 1656, 1596, 1563, 1348, 1213, 1114, 1096, 1028, 932, 855, 753 cm^{-1} ; δ_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; δ_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, $T = 25^\circ C$) ketone 17.1 min, *R* and *S* isomers 4.4 min and 5.9 min, configuration is not confirmed.

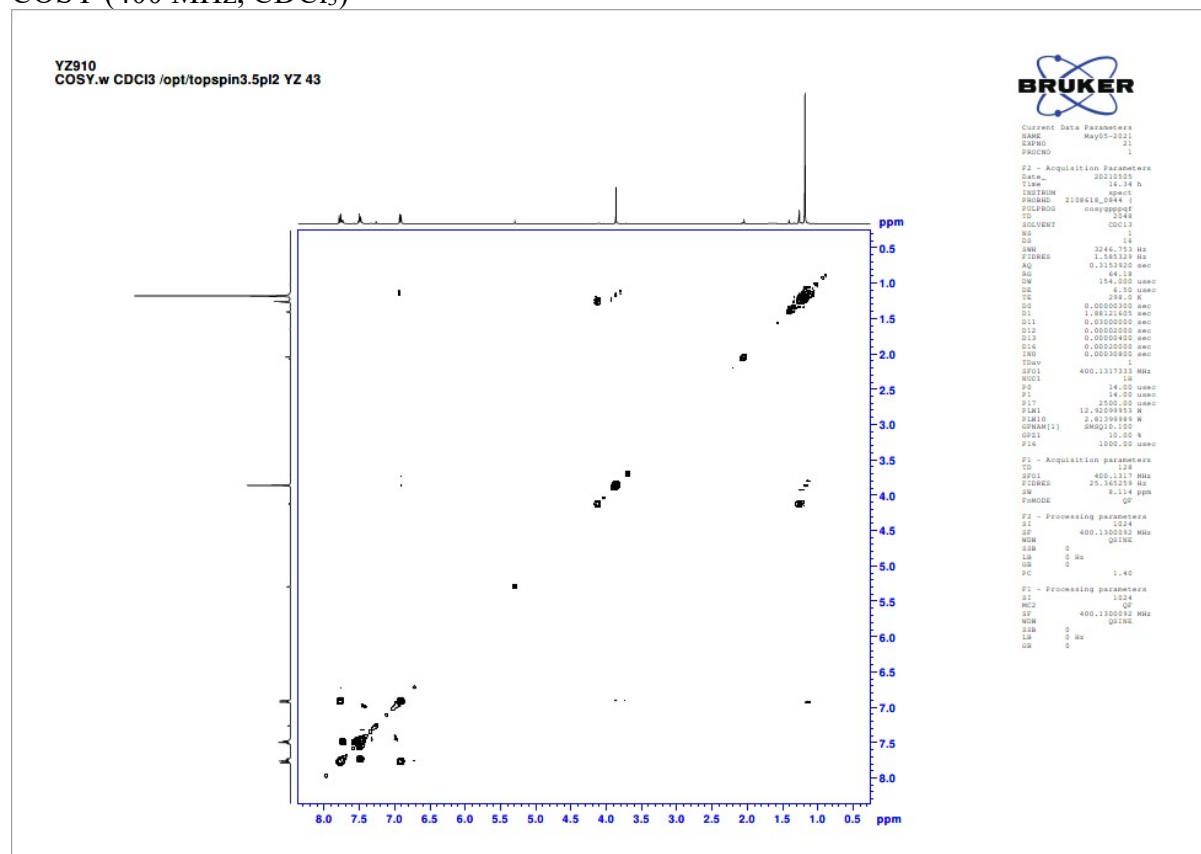
^1H NMR (400 MHz, CDCl_3)



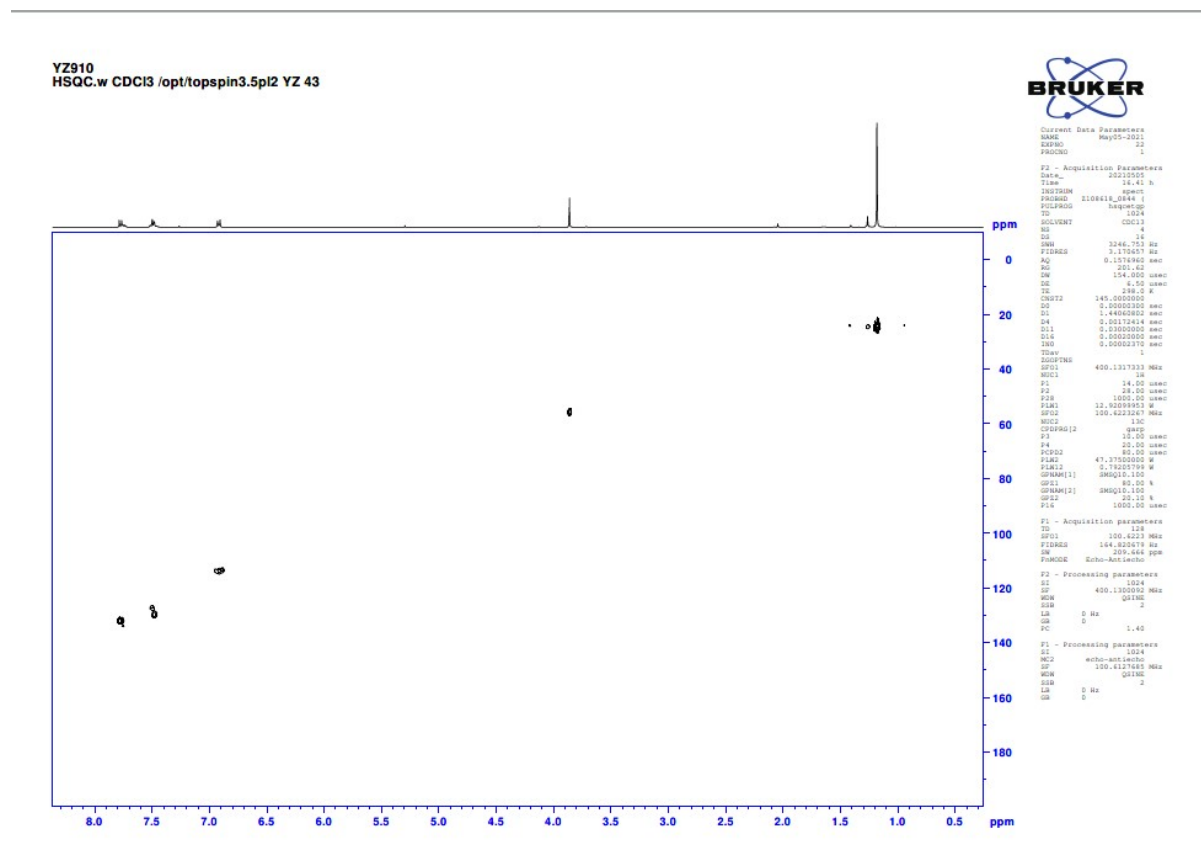
^{13}C NMR (100 MHz, CDCl_3)



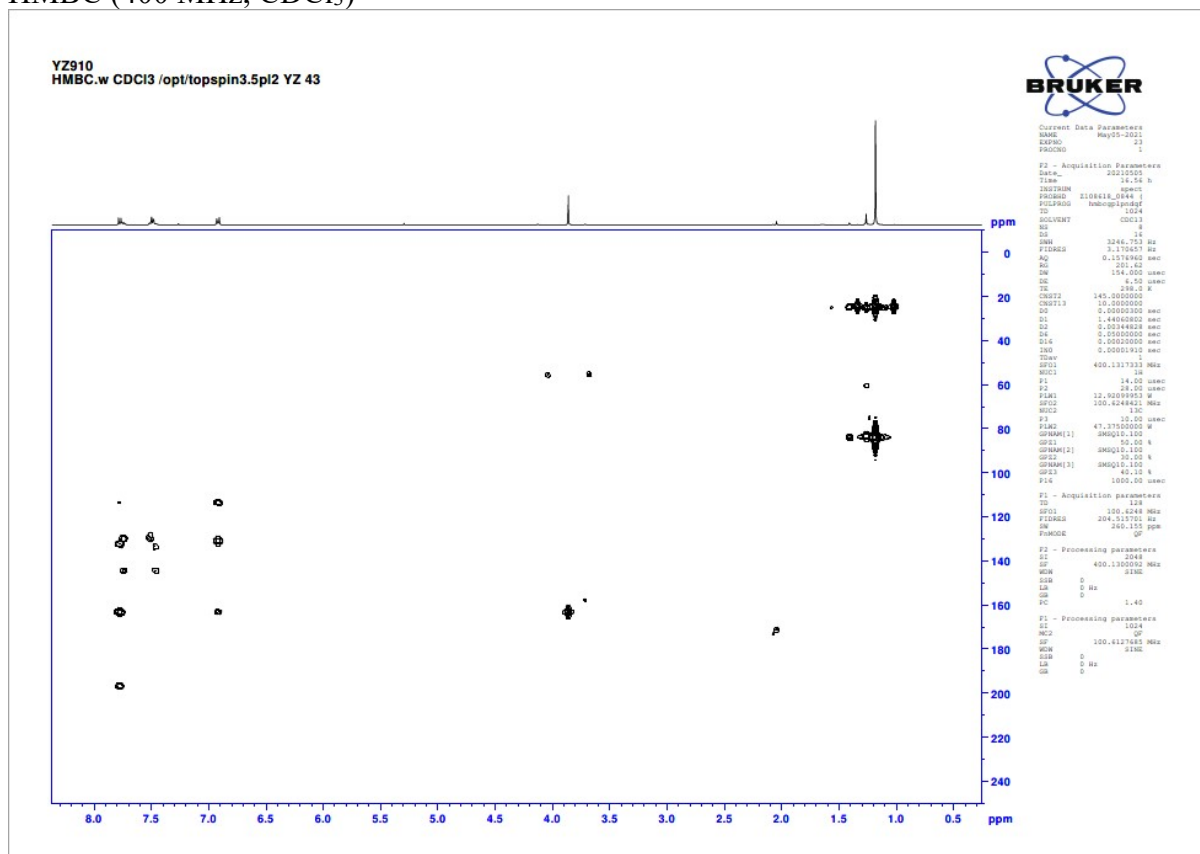
COSY (400 MHz, CDCl₃)



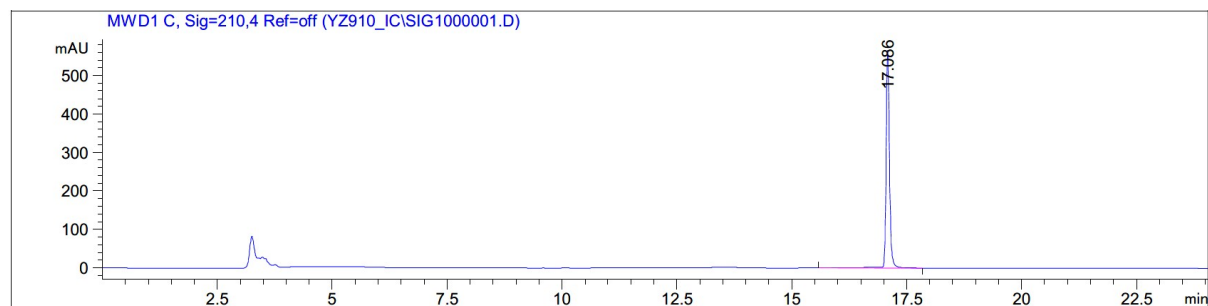
HSQC (400 MHz, CDCl₃)



HMBC (400 MHz, CDCl₃)



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

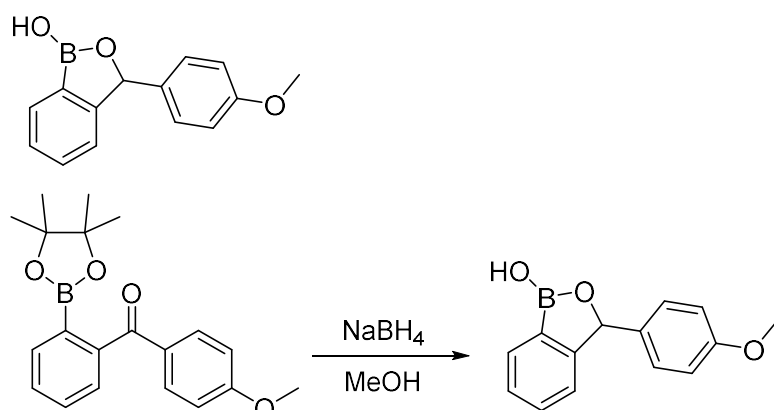


Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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Totals : 2923.16113 566.39697

3-(4-Methoxyphenyl)benzo[*c*][1,2]oxaborol-1(3*H*)-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 × 20 mL), dried with MgSO₄.

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(3*H*)-ol **27** as a white solid (61.6 mg, 0.256 mmol, 35%).

TLC: R_f ca 0.20 (4:1 hexane: EtOAc), strong UV and KMnO₄; Mp: 99 °C; HRMS: (found (ESI⁺): [M+H]⁺, Calcd for C₁₄H₁₃BNaO₃ 263.0857; Found 263.0850; -1.5 ppm error); ν_{max} 3358 (br), 1607, 1509, 1476, 1420, 1276, 1254, 1172, 1025, 951, 819, 739 cm⁻¹; δ_H (400 MHz, CDCl₃) 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, CH₃) ppm; δ_C (100 MHz, CDCl₃) 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 (CH₃) 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.

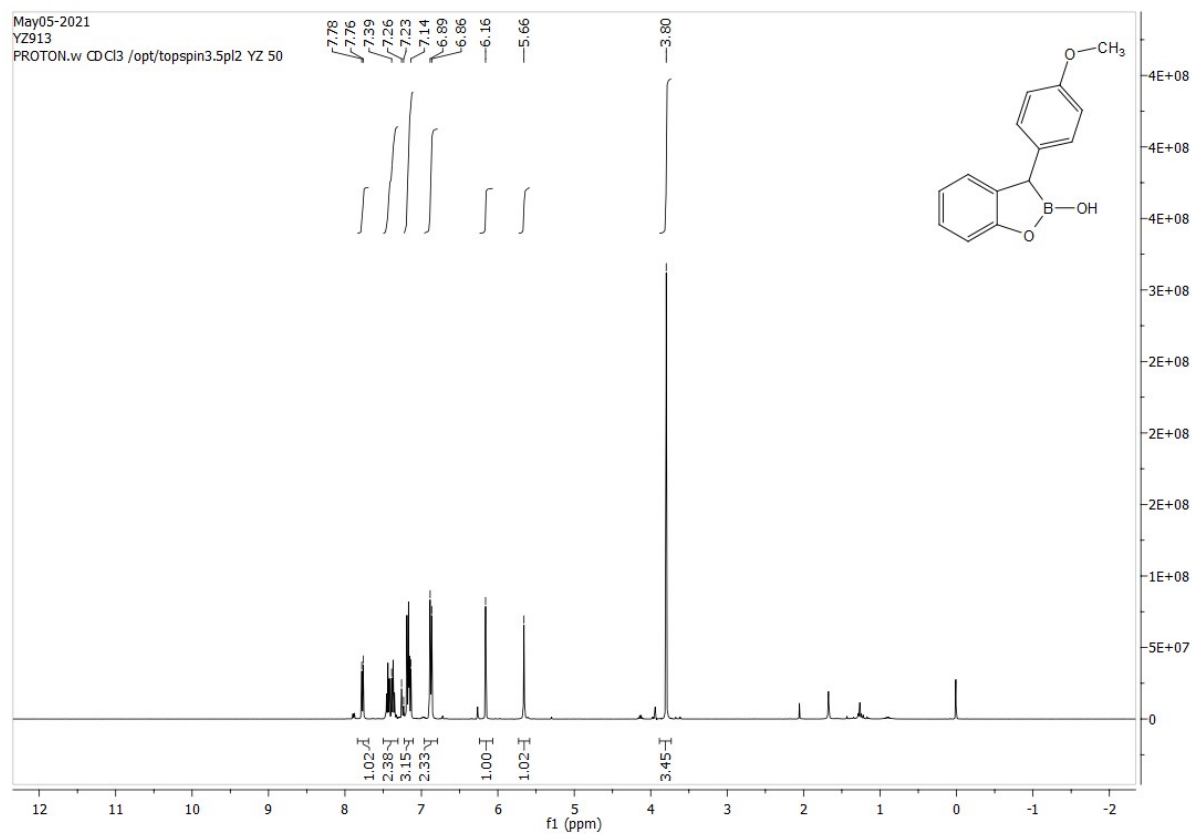
ATH of (4-methoxyphenyl)(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone.

(*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 NaHCO₃ 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 0-50% ethyl acetate in hexane to give 3-(4-methoxyphenyl)benzo[*c*][1,2]oxaborol-1(3*H*)-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; [α]_D²⁵ +2.79 (c 0.179 in CHCl₃) 23% ee

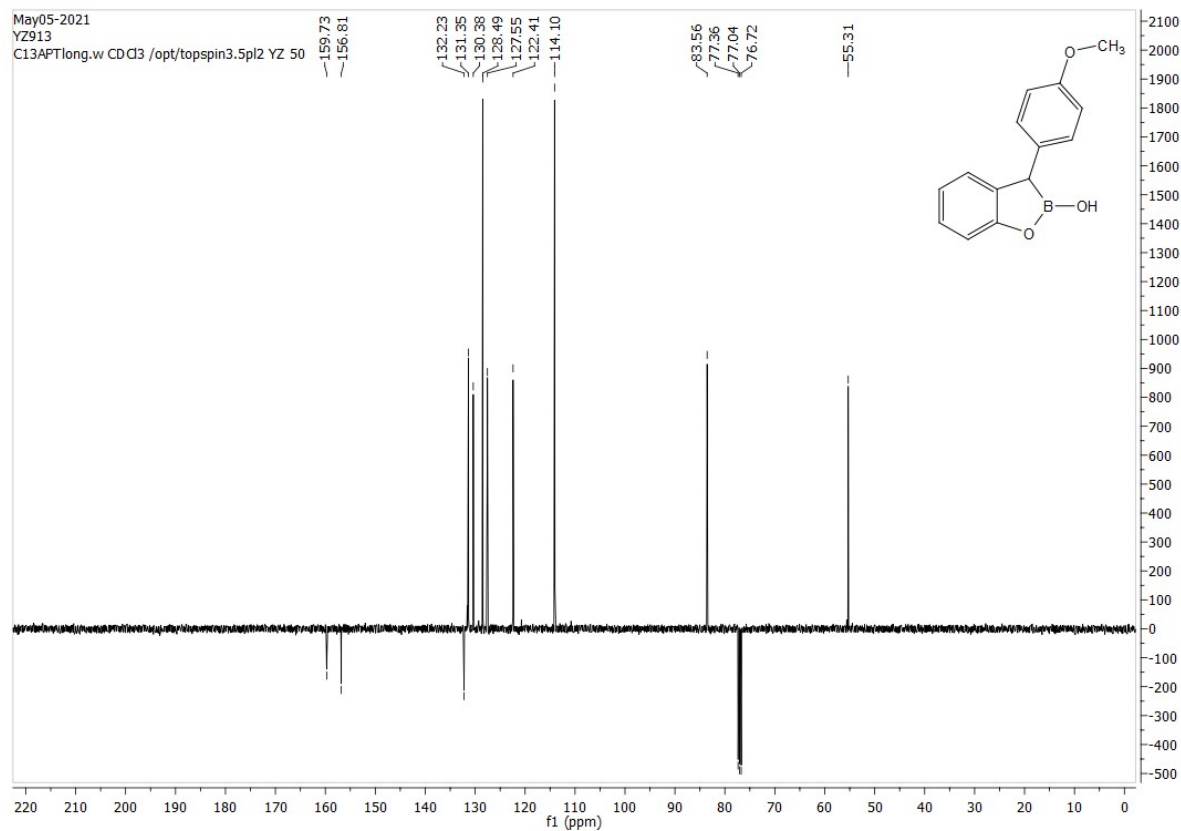
A control reaction in the absence of catalyst was carried out:

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 NaHCO₃ 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. NMR indicated that no product was formed.

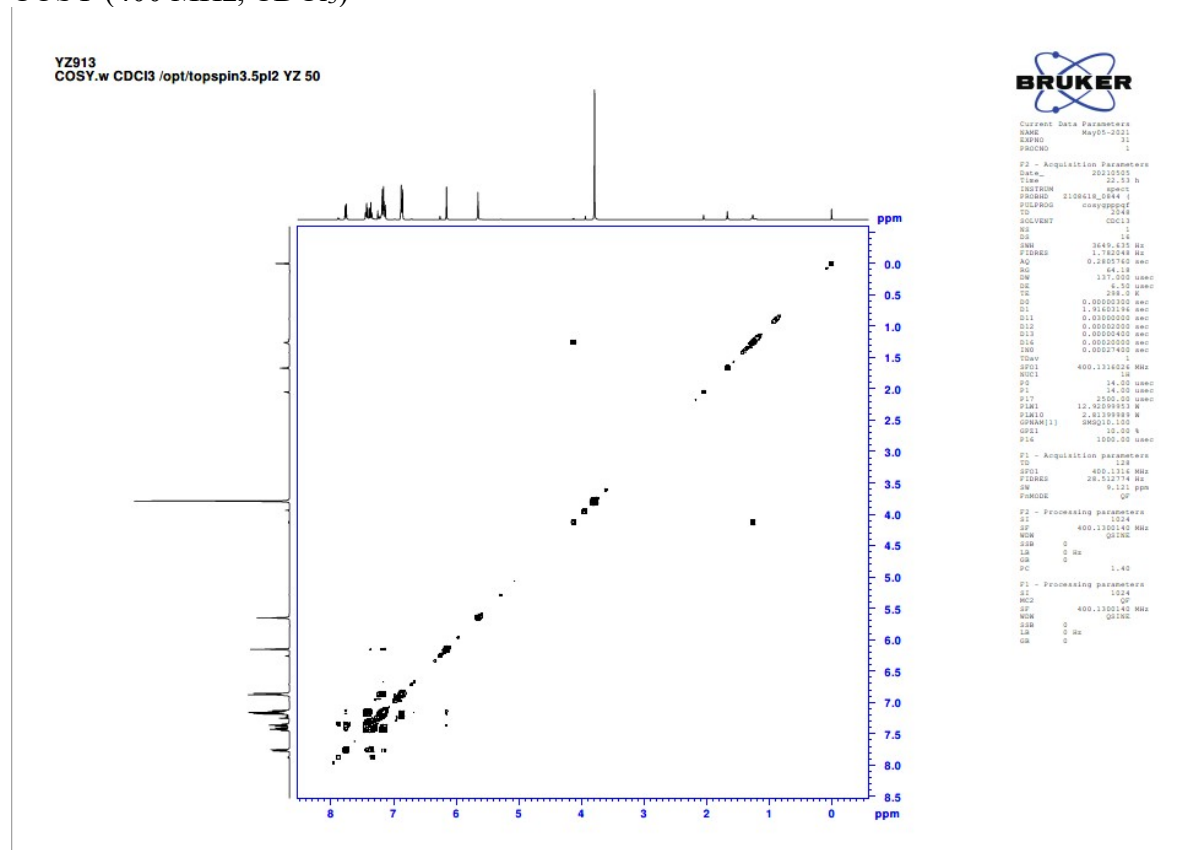
^1H NMR (400 MHz, CDCl_3)



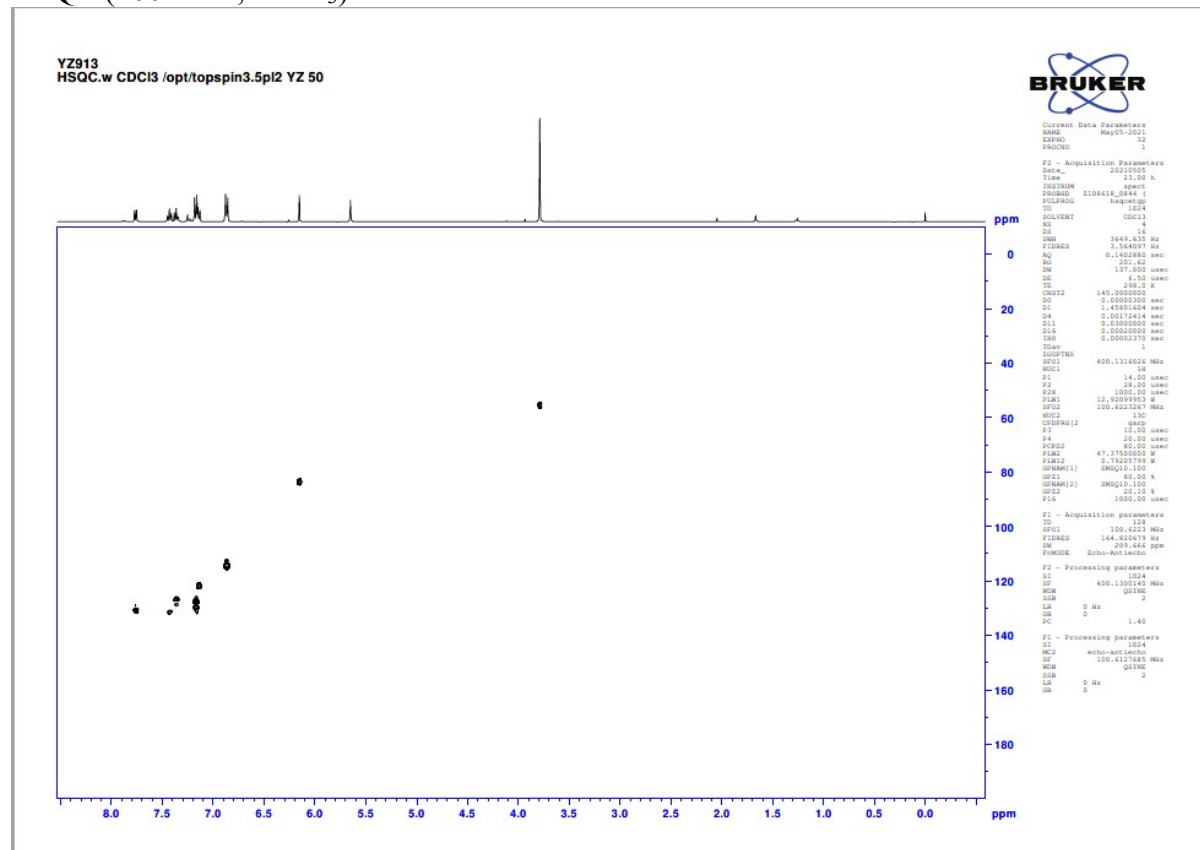
^{13}C NMR (100 MHz, CDCl_3)



COSY (400 MHz, CDCl₃)



HSQC (400 MHz, CDCl₃)



YZ913
HMBC.w CDCI3 /opt/topspin3.5pl2 YZ 50

Current Data Parameters
NAME YZ913-001
EXPNO 31
PROCNO 1

F2 - Acquisition Parameters
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Time 23:15 N
INSTRUM spect
PROBHD Z108618_0044_1
PULPROG hmcgpprog4
PC 10.4
FIDRES 0.0013
AQ 0.0013

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NUC2 1H
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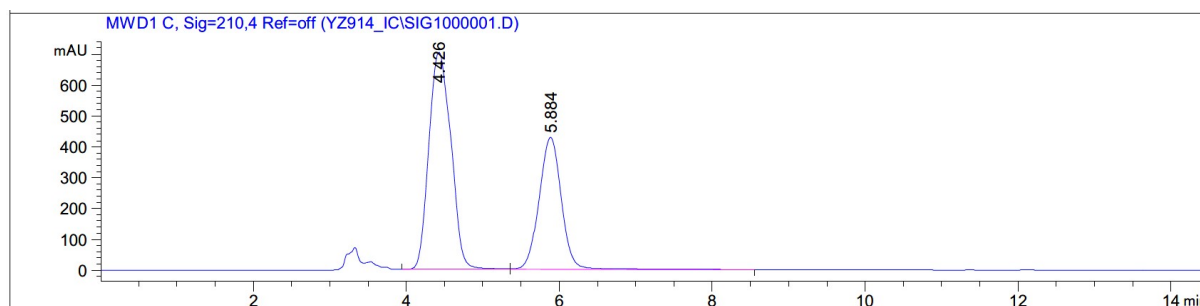
MWD1 C, Sig=210,4 Ref=off (YZ913_IC_2\SIG1000001.D)

Chromatogram showing two peaks at retention times 4.354 and 5.758 minutes. The y-axis is labeled mAU and ranges from 0 to 1000. The x-axis is labeled 'min' and ranges from 0 to 30.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.354	BB	0.2994	2.44836e4	1203.34912	51.3163
2	5.758	BB	0.3099	2.32276e4	1168.52063	48.6837

S189

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).

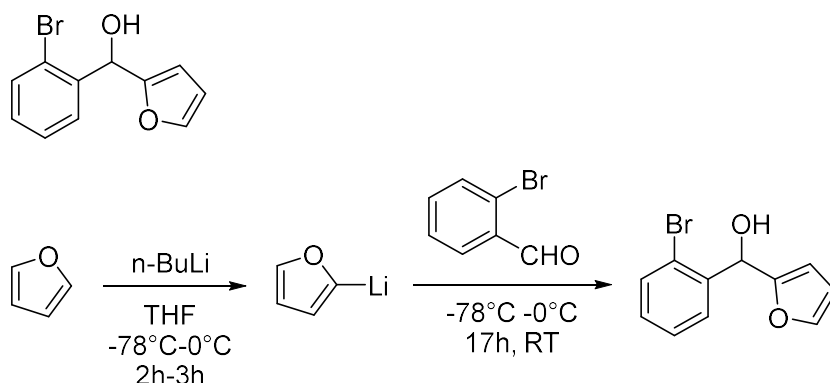


Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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

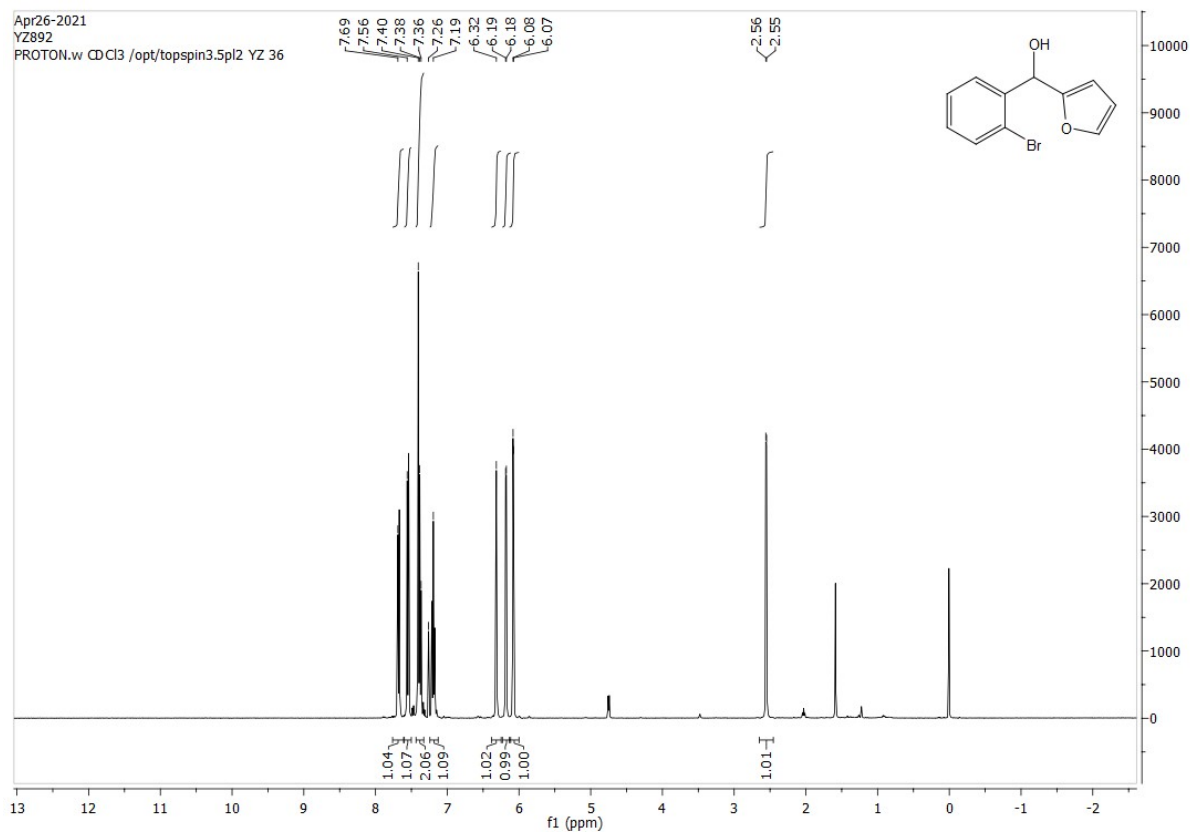
(2-Bromophenyl)(furan-2-yl)methanol.



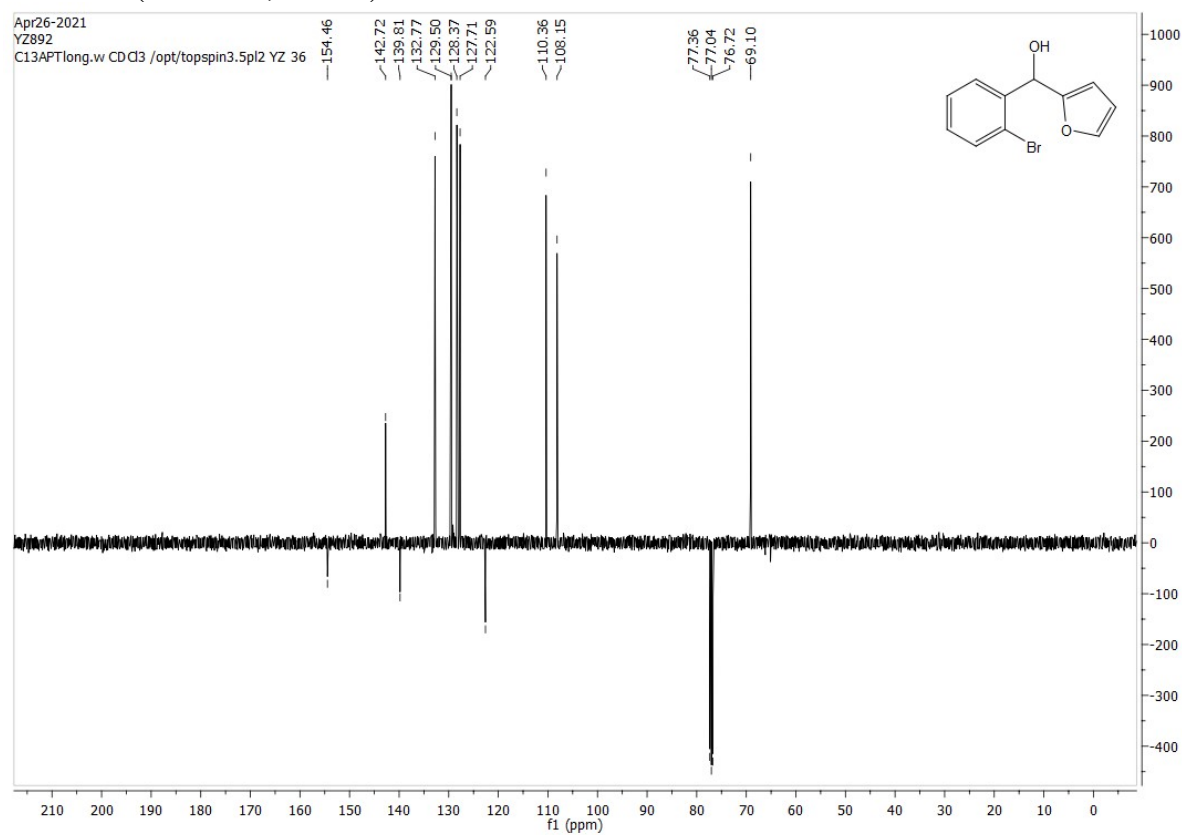
This compound has been reported and fully characterized: M. Tang, Y. Kong, B. Chu and D. Feng, *Adv. Synth. Catal.* 2016, **358**, 926-939.

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 NH₄Cl 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 (MgSO₄) 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: R_f ca 0.30 (9:1 hexane: EtOAc), strong UV and KMnO₄; δ_H (400 MHz, CDCl₃) 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, ArCHOH), 2.56 (1H, d, *J* = 4.0, ArCHOH) ppm; δ_C (100 MHz, CDCl₃) 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.

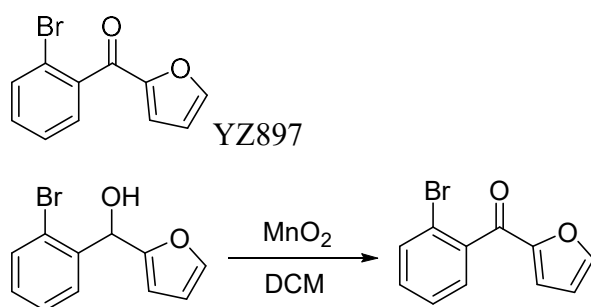
^1H NMR (400 MHz, CDCl_3)



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



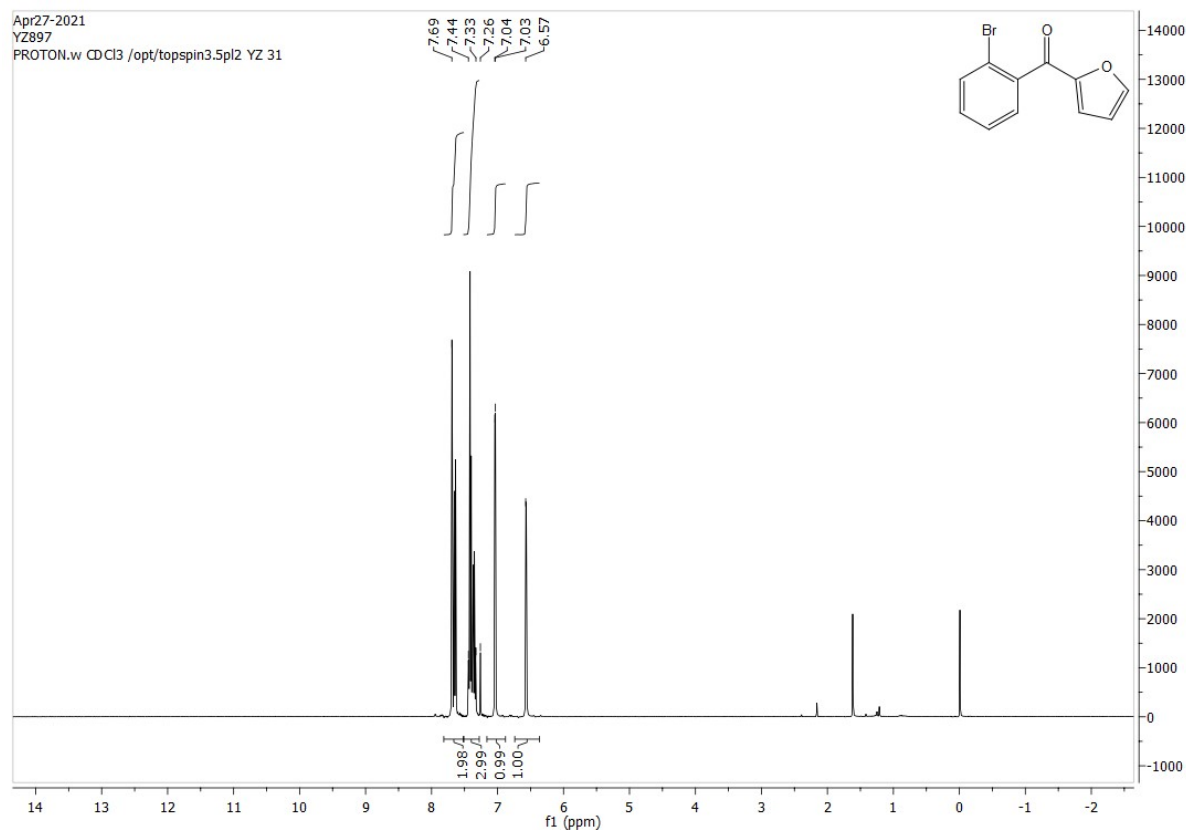
(2-Bromophenyl)(furan-2-yl)methanone.



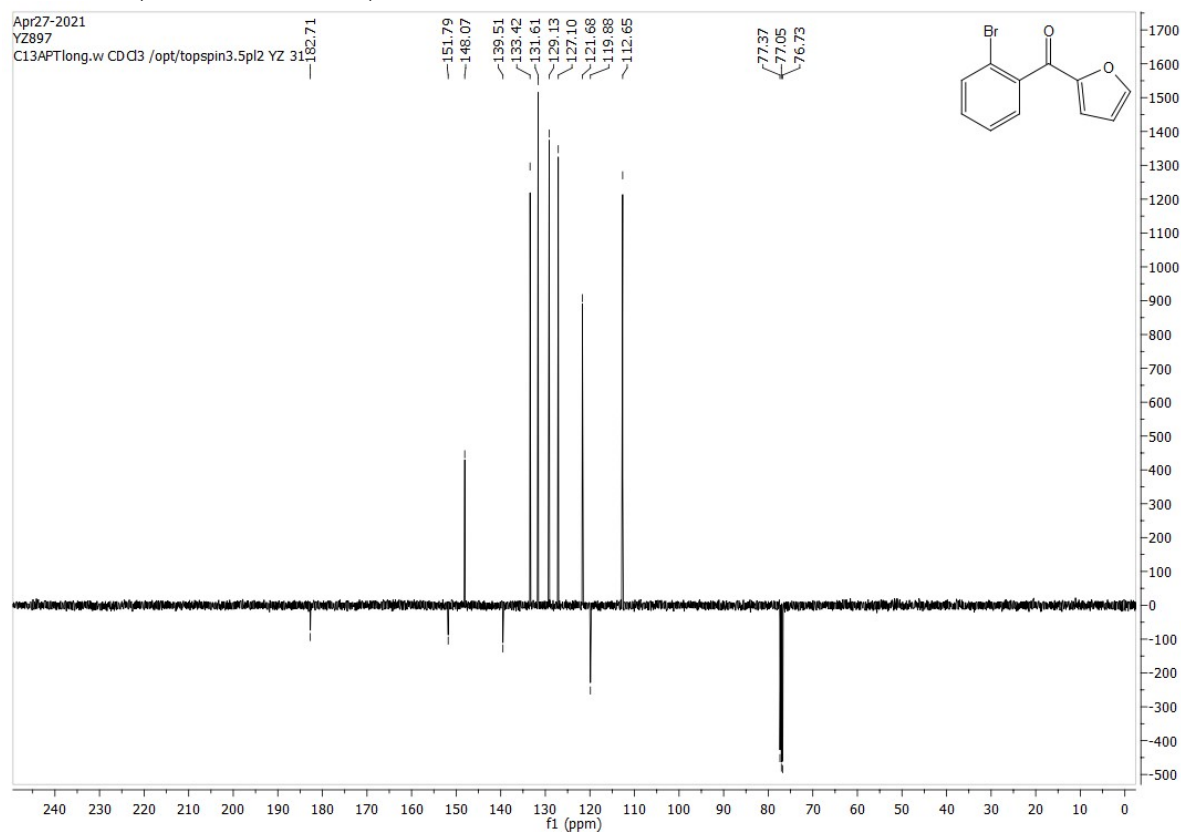
This compound has been reported but not fully characterized: M. Tang, Y. Kong, B. Chu and D. Feng, *Adv. Synth. Catal.* 2016, **358**, 926-939.

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: R_f ca 0.50 (9:1 hexane: EtOAc), strong UV and KMnO₄; HRMS: (found (ESI⁺): [M+Na]⁺, Calcd for C₁₁H₇⁷⁹BrNaO₂ 272.9501; Found 272.9495; -2.4 ppm error); ν_{max} 3130, 1652, 1561, 1457, 1390, 1298, 1150, 1018, 956, 743, 68 cm⁻¹; δ_H (400 MHz, CDCl₃) 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; δ_C (100 MHz, CDCl₃) 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%).

^1H NMR (400 MHz, CDCl_3)



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



YZ897
COSY.w CDC13 /opt/topspin3.5pl2 YZ 31

Current Data Parameters
NAME Apr7-2021
EXPRO 41
PROCNO 1

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Date_ 20210427
Time 21.14 h
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PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 16
DS 14
SWH 3676.471 Hz
FIDRES 1.795152 Hz
AQ 0.2785280 sec
RG 64.18
DW 136.500 usec
DE 4.10 usec
TE 300.2 K
D0 0.0000000 sec
D1 1.9180797 sec
D11 0.0300000 sec
D12 0.0000000 sec
D13 0.0000400 sec
D14 0.0000000 sec
DRO 0.0002700 sec
TDSP 1
SFO1 400.1315416 MHz
NUC1 1H
P0 14.00 usec
P1 14.00 usec
P17 2550.00 usec
P1810 12.42599513 s
P1815 2.8109988 s
GPRM(1) SMOUL 1.20
OP1 10.00 s
P14 1600.00 usec

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SFO1 400.13154 MHz
FIDRES 28.72427 Hz
SW 9.184 ppm
P0MODE QF

F2 - Processing parameters
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SF 400.1300712 MHz
WDW QF
SS 0
LB 0 Hz
GB 0
PC 1.40

F1 - Processing parameters
SI 1024
SF 400.1300712 MHz
WDW QF
SS 0
LB 0 Hz
GB 0
PC 1.40

YZ897
HSQC.w CDCI3 /opt/topspin3.5pl2 YZ 31

Current Data Parameters
NAME: YZ897
EXPNO: 42
PROCNO: 1

F2 - Acquisition Parameters
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Time: 22:42 h
INSTRUM: spect
PROBHD: EBOB1H-5mm
PULPROG: zgpg30
SOLVENT: cdcl3

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SD: 4
SWH: 3876.471 Hz
F2RES: 0.130240 Hz
AQ: 0.130240 sec
RG: 255.42
SW: 138.000 usec
DE: 6.50 usec
TE: 300.2 K
CSTRT: 145.0000000
DO: 0.0000300 sec
AL: 1.4750400 sec
DA: 0.0012414 sec
S1: 0.0000000 sec
S14: 0.0000000 sec
S16: 0.0000237 sec

TD: 65536
SFOFMS: 400.131954 MHz
NUC1: 13C
P1: 14.00 usec
P2: 28.00 usec
P3: 1000.00 usec
P1M1: 12.9209953 MHz
SFO1: 100.6212417 MHz
NUC2: 1H
CPOBPG2: zgpg2
P4: 30.00 usec
P5: 20.00 usec
PCPD2: 47.3750000 MHz
P1M2: 5.7007979 MHz
SFO2: 500.1360491 MHz
SFO1M2: 500.1360491 MHz
P6: 10.00 usec
P7: 1000.00 usec

F1 - Acquisition parameters
TD: 132
SFO1: 100.6212417 MHz
F2RES: 100.6212417 Hz
SW: 205.464 ppm
PULPROG: zgpg30

F2 - Processing parameters
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SF: 400.1319571 MHz
WDW: gauss
SSB: 0
LB: 0 Hz
GB: 0
PC: 1.40

F1 - Processing parameters
SI: 1024
MC2: echo-ant-echo
SF: 100.6127683 MHz
WDW: gauss
SSB: 0
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GB: 0

YZ897
HMBC.w CDCI3 /opt/topspin3.5pl2 YZ 31

Current Data Parameters
NAME Apr17-2021
EXPNO 43
PROCNO 1

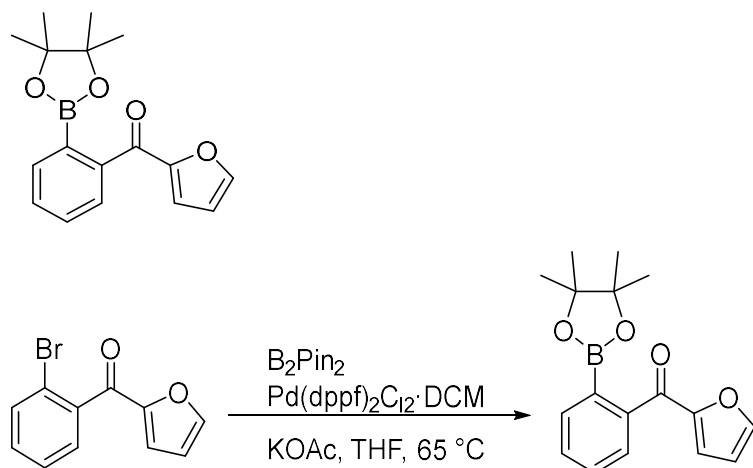
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DE 4.50 usec
TE 300.2 K
CMT2 145.00000000
CMT13 10.00000000
DS 0.00000000 usec
D2 0.00344928 usec
D4 0.00000000 usec
D14 0.00000000 usec
TMS 0.00001912 usec
TD0 400.131816 Mhz
NUC1 13
P1 14.00 usec
P2 28.00 usec
PL1 12.92099901 W
PL2 100.424941 Mhz
NUC2 13C
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P4 47.37020000 Mhz
GPM1 50.00 A
GPM2 50.00 A
GPM3 50.00 A
P14 100.00 usec

F1 - Acquisition parameters
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AQ 204.51701 Mhz
RG 360.153 ppm
FWDEN 0

F2 - Processing parameters
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WDW 0
SSB 0 Mhz
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PC 1.40

F1 - Processing parameters
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WDW 0
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GB 0

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

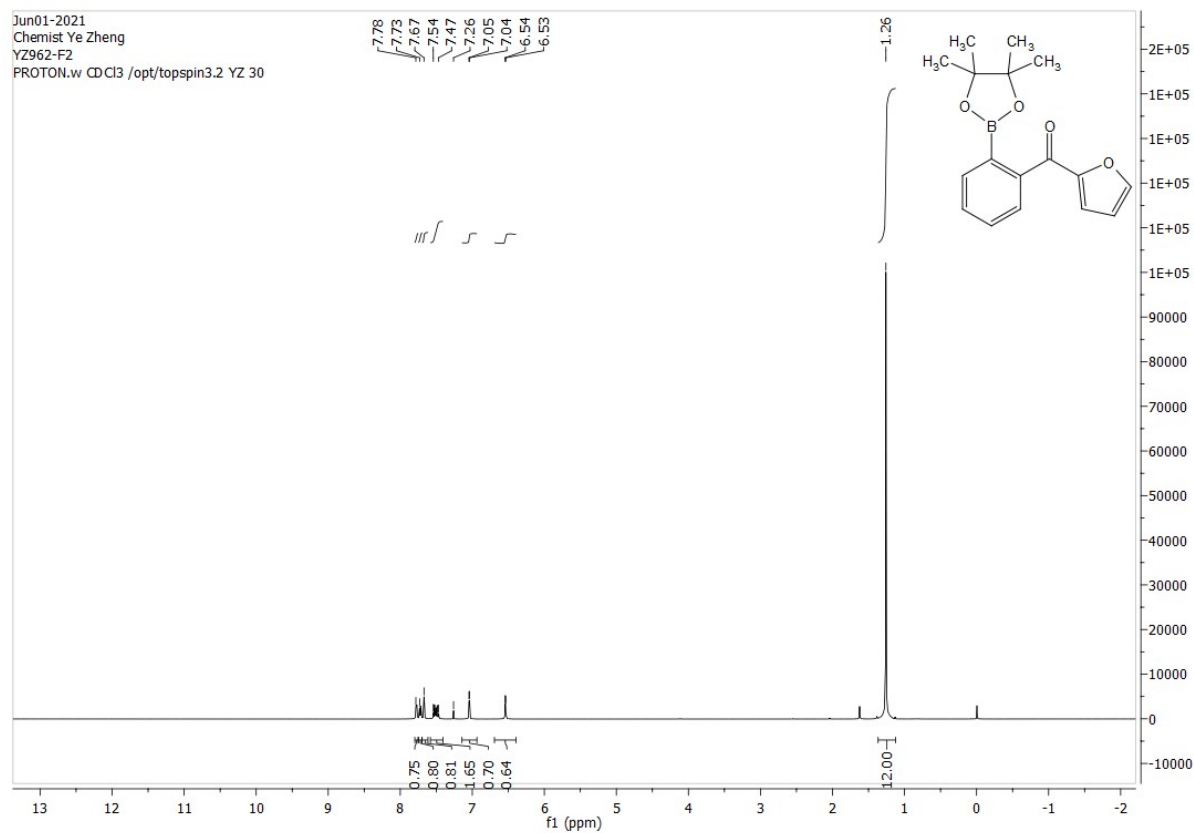


This compound is novel.

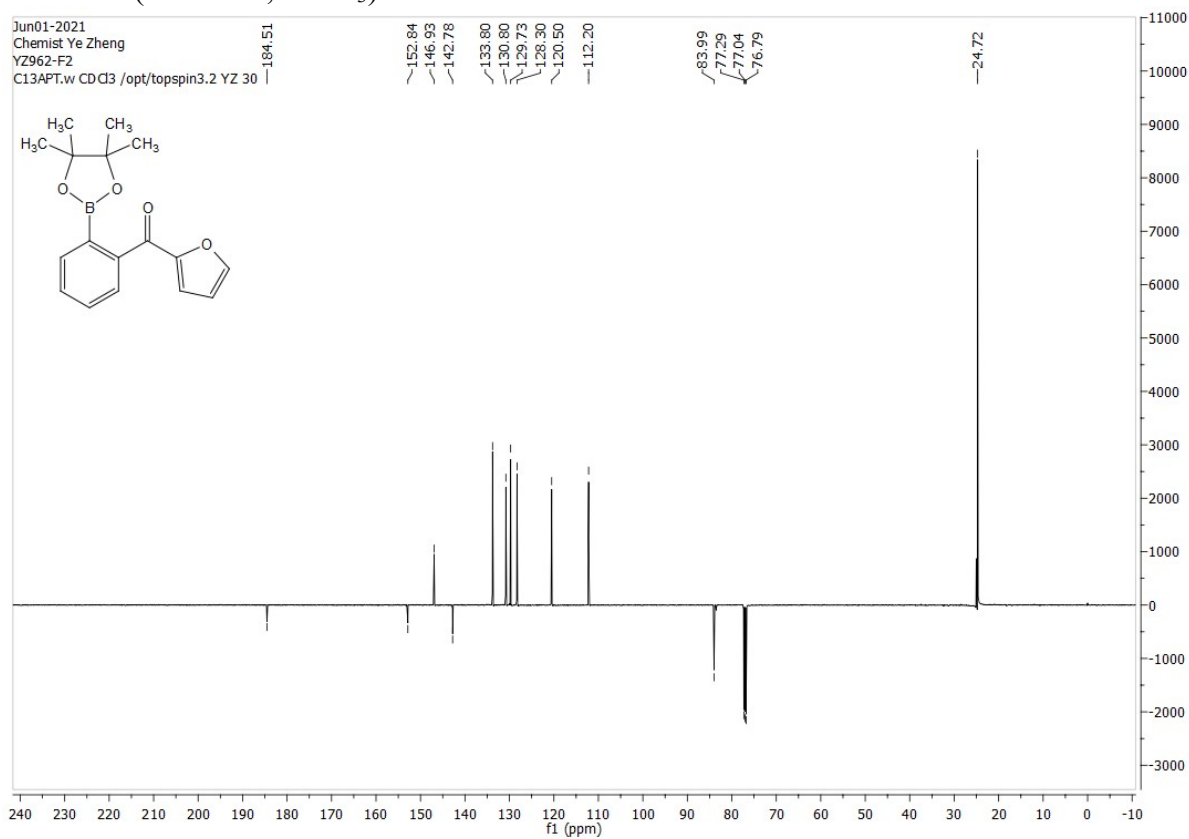
A round-bottom flask was charged with (2-bromophenyl)(furan-2-yl)methanone (560 mg, 2.25 mmol), bis(pinacolato)diboron (686 mg, 2.70 mmol), potassium acetate (662 mg, 6.75 mmol), THF (14 mL) and $Pd(dppf)_2Cl_2 \cdot DCM$ (92.3 mg, 0.113 mmol). The reaction mixture was heated to 65 °C and left stirring 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: R_f 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); ν_{max} 2978, 1653, 1564, 1462, 1346, 1304, 1143, 1037 cm^{-1} ; δ_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; δ_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, $T = 25^\circ C$) ketone 19.6 min, *R* and *S* isomers 6.7 min and 13.3 min.

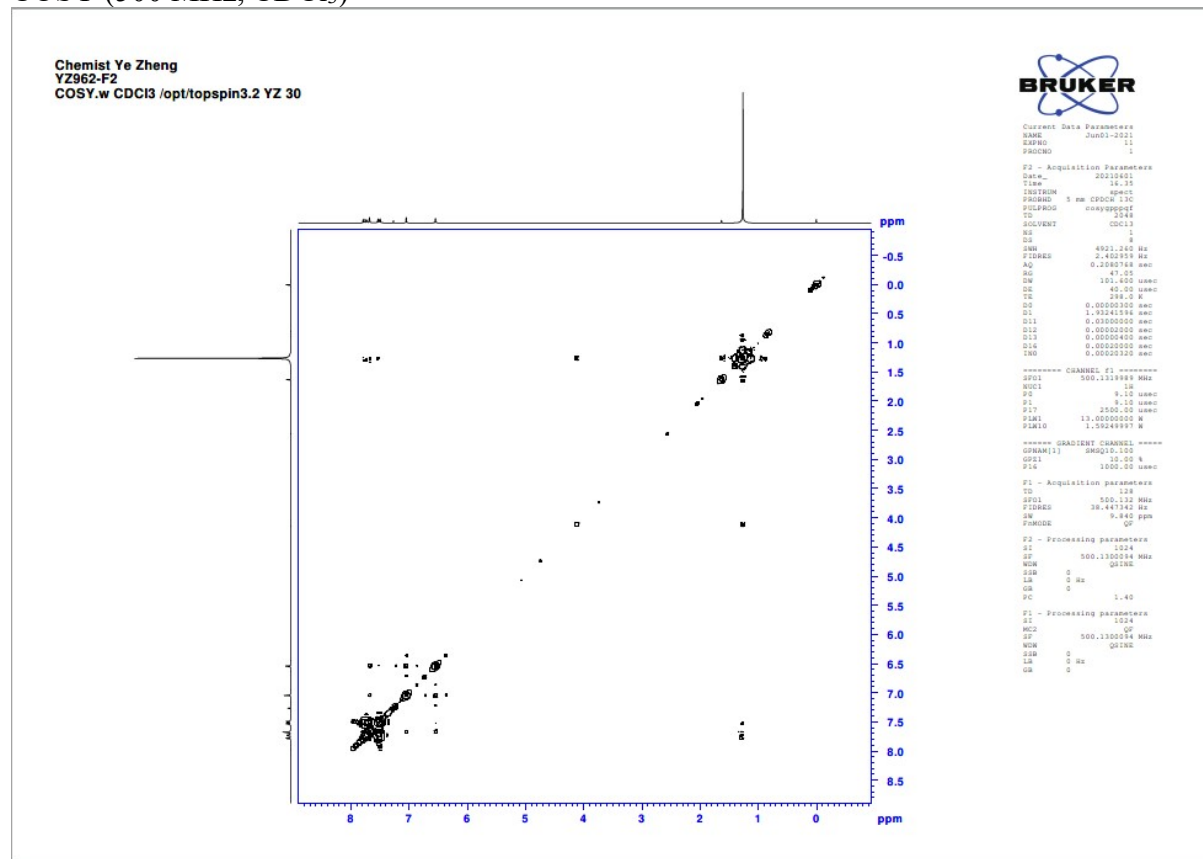
¹H NMR (500 MHz, CDCl₃)



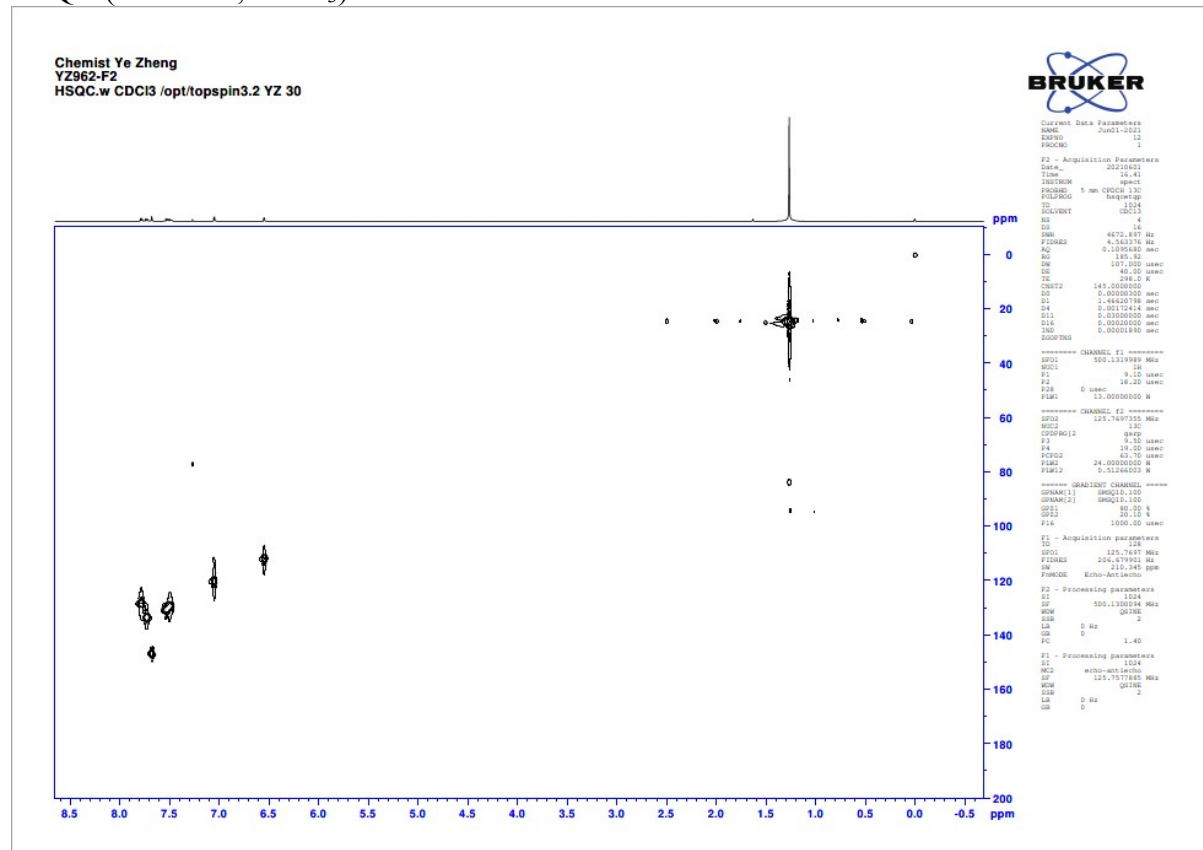
¹³C NMR (125 MHz, CDCl₃)



COSY (500 MHz, CDCl₃)

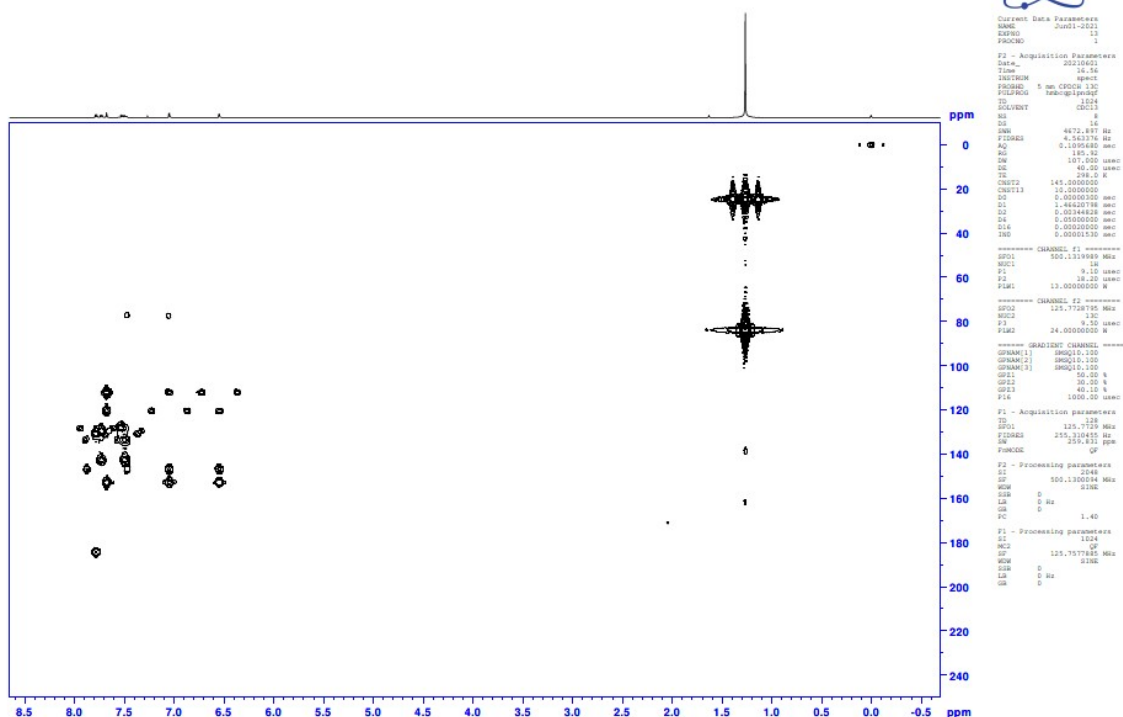


HSQC (500 MHz, CDCl₃)

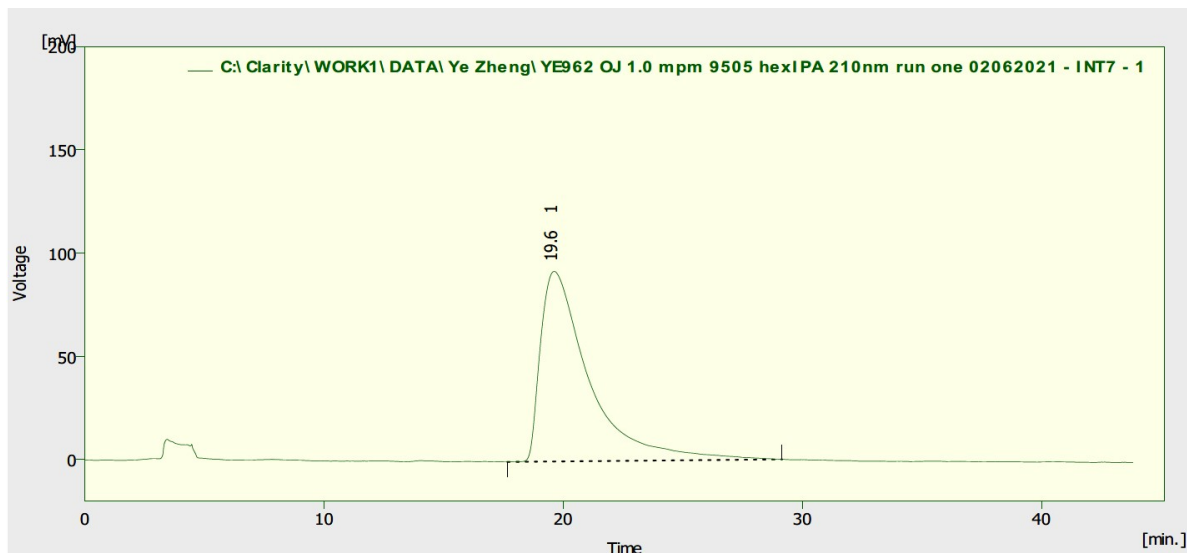


HMBC (500 MHz, CDCl₃)

Chemist Ye Zheng
YZ962-F2
HMBC.w CDCl₃ /opt/topspin3.2 YZ 30



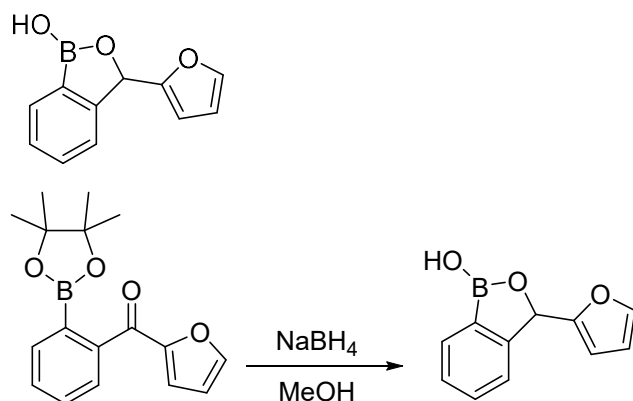
HPLC of furan-2-yl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone



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.

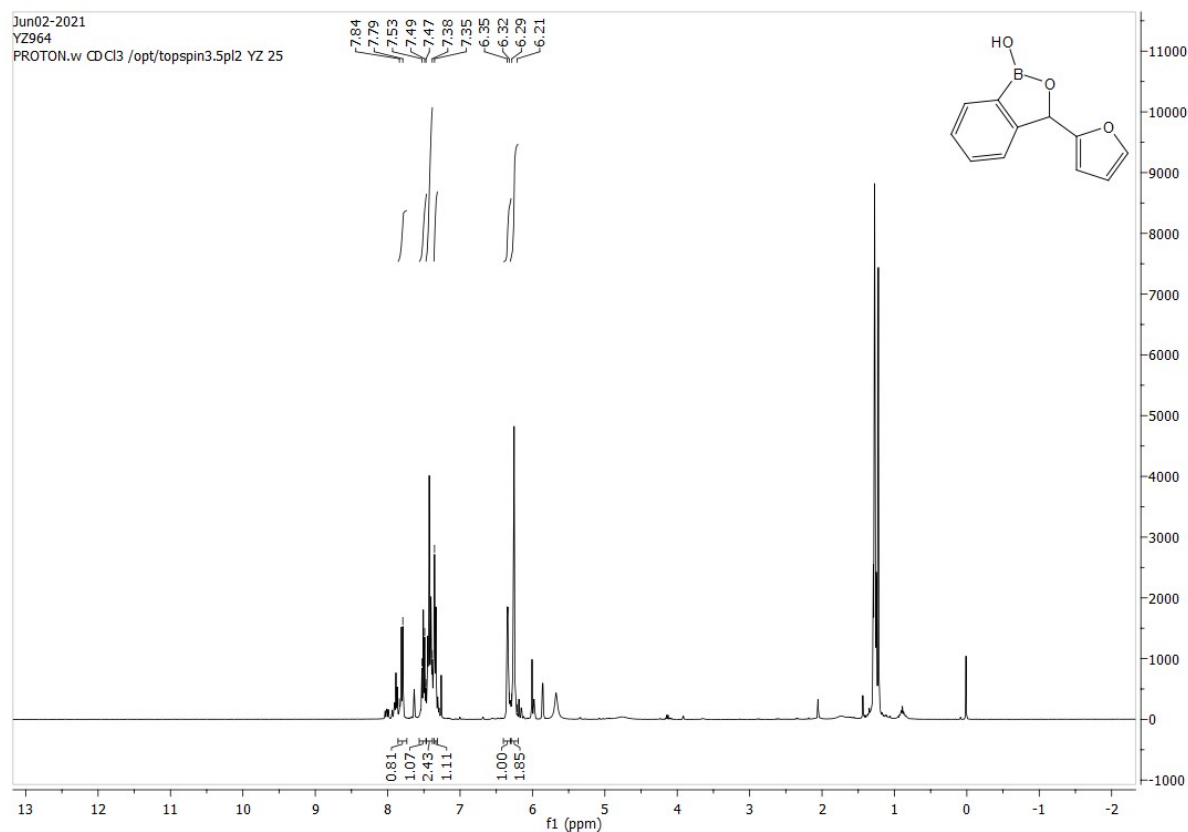
To a solution of furan-2-yl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone (120 mg, 0.403 mmol) in MeOH (2.5 mL) was added sodium borohydride (30.6 mg, 0.806 mmol). The reaction was stirred for 4 hours. TLC (1:1 hexane: EtOAc) after this time indicated full conversion. Distilled water (20 mL) was added, and the mixture was extracted with EtOAc (3 × 20 mL), dried with MgSO₄. 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: R_f ca 0.20 (1:1 hexane: EtOAc), strong UV and KMnO₄; δ_H (400 MHz, CDCl₃) 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; δ_C (100 MHz, CDCl₃) 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 6 mm 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.

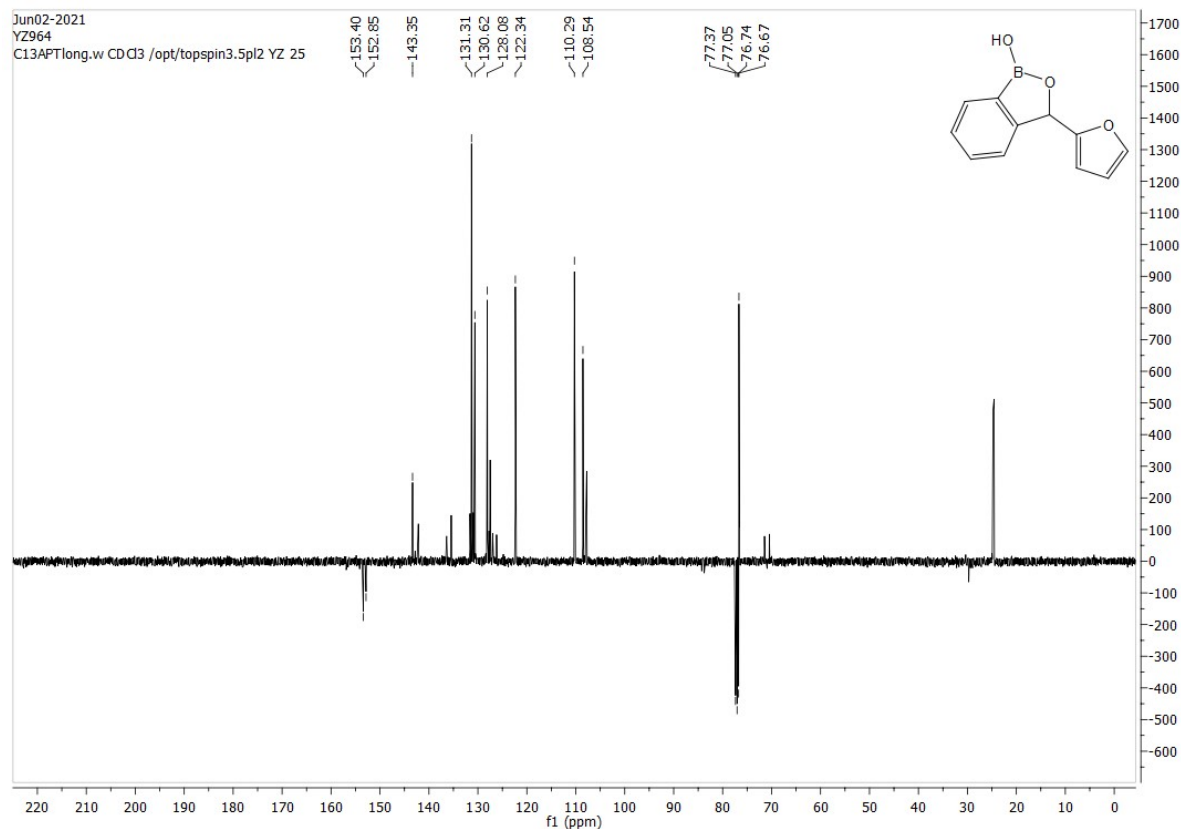
ATH of furan-2-yl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone.

(*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 stirred under a nitrogen atmosphere, followed by TLC (1:1 hexane: EtOAc). After 72 hours, the reaction was quenched using saturated NaHCO₃ 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 0-50% 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

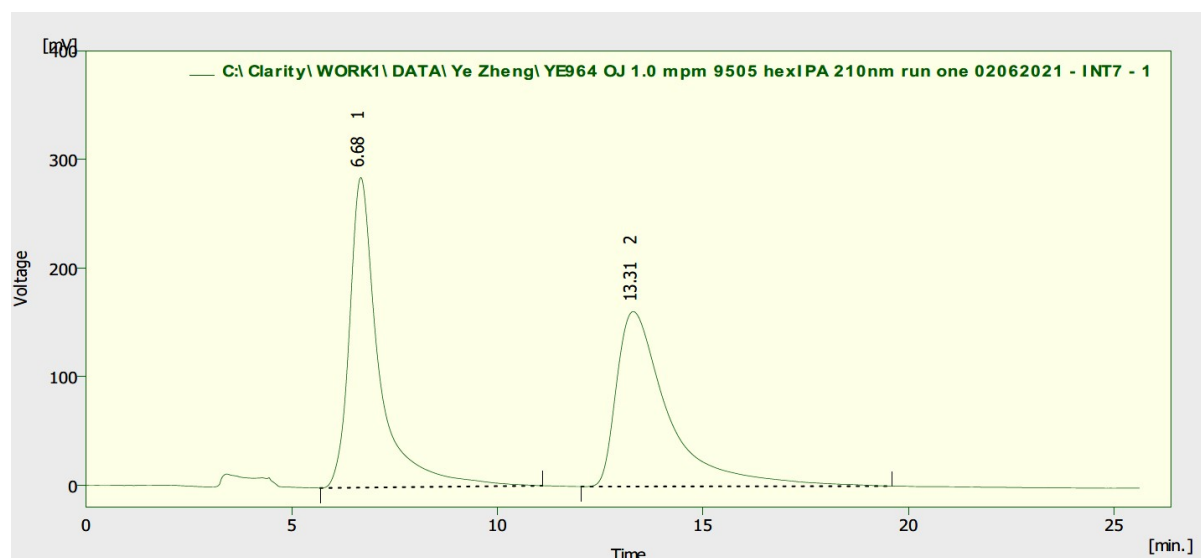
^1H NMR (400 MHz, CDCl_3)



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



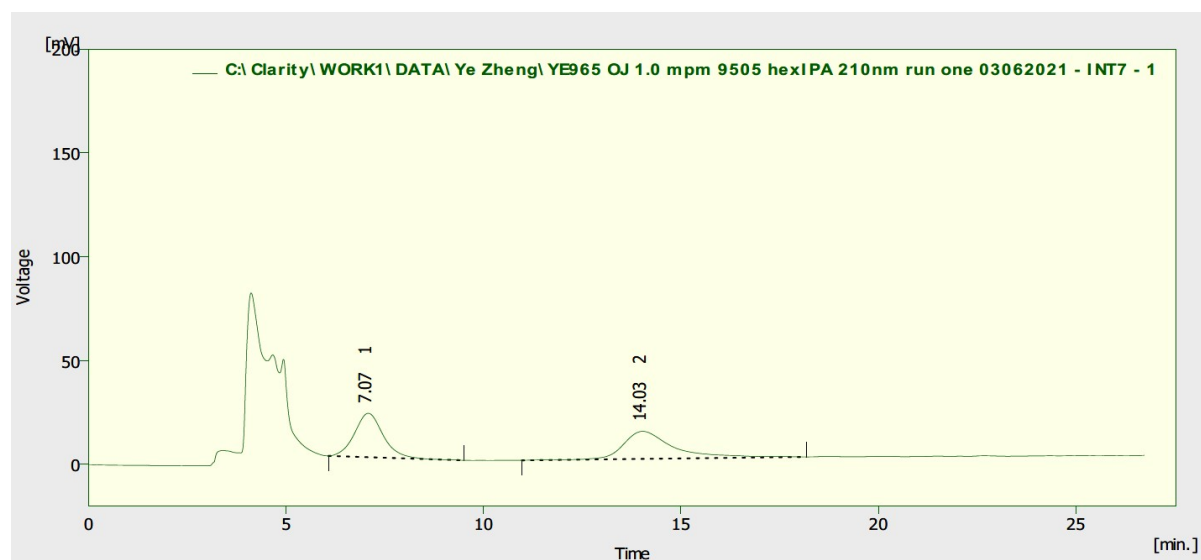
HPLC of racemic 3-(furan-2-yl)benzo[c][1,2]oxaborol-1(3*H*)-ol **28**.



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)

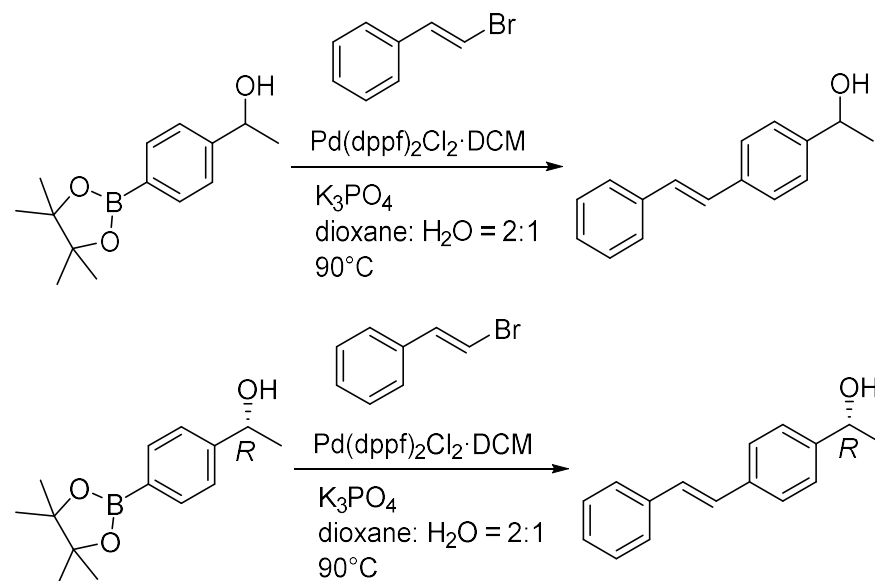


Result Table (Uncal - C:\Clarity\WORK1\DATA\Ye Zheng\YE965 OJ 1.0 mpm 9505 hexIPA 210nm run one 03062021 - INT7 - 1)

	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.

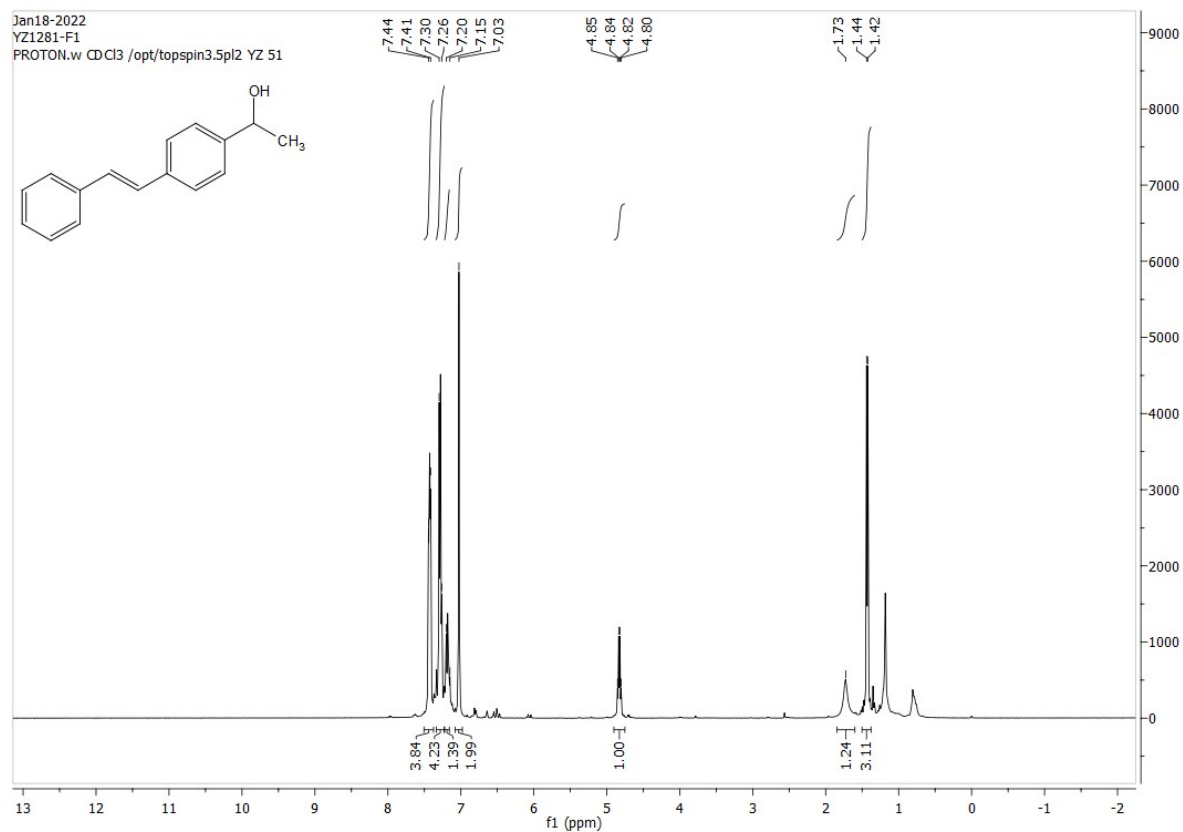
Racemic: To a solution of racemic 1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol **7** (52.0 mg, 0.210 mmol), β -bromostyrene (57.6 mg, 0.315 mmol) and tripotassium phosphate (134 mg, 0.630 mmol) in dioxane (1 mL) and distilled water (0.5 mL) was added $\text{Pd(dppf)}_2\text{Cl}_2 \cdot \text{DCM}$ (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: R_f ca 0.30 (4:1 hexane: EtOAc), strong UV and KMnO_4 ; δ_{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; δ_{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 ($\text{M}^+ + 23$, 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.

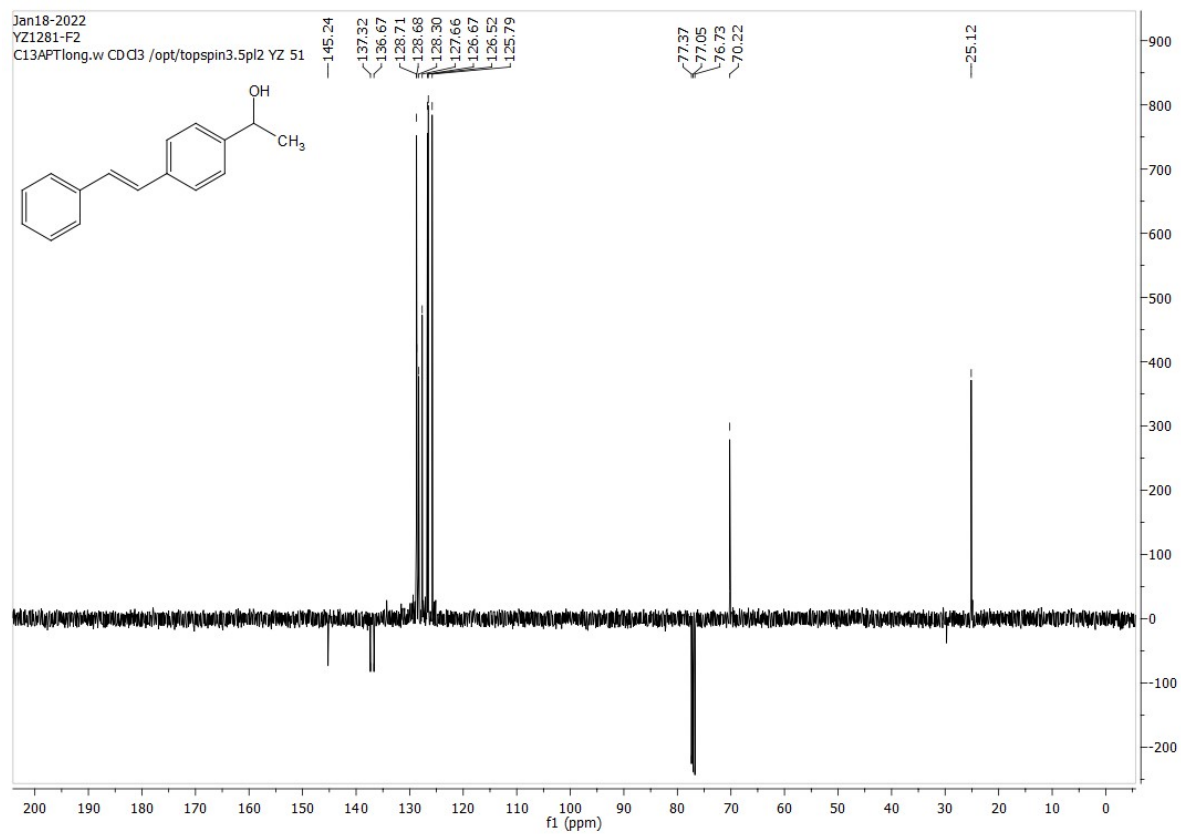
Asymmetric:

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)₂Cl₂·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 (MgSO₄) 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): [α]_D³⁰ +35 (c 0.180 in CHCl₃) 98% ee (*R*).

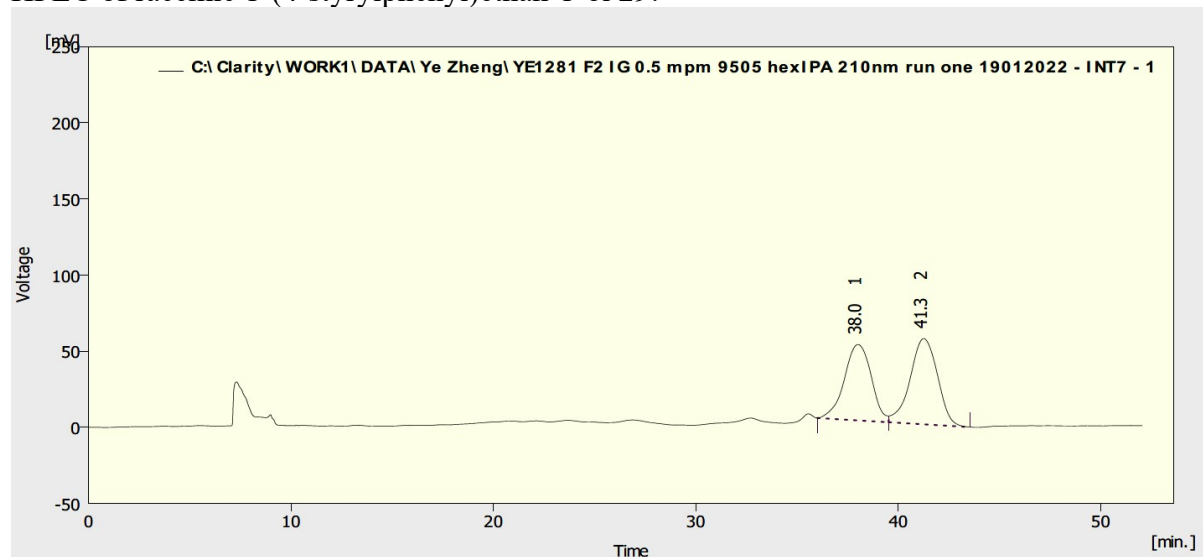
¹H NMR (400 MHz, CDCl₃)



¹³C NMR (100 MHz, CDCl₃)



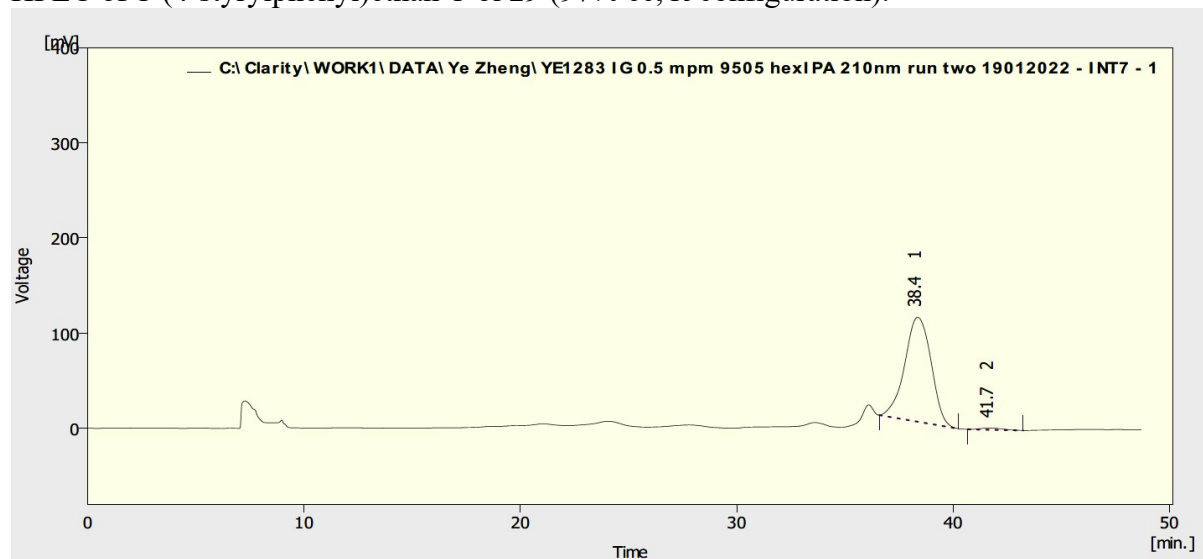
HPLC of racemic 1-(4-styrylphenyl)ethan-1-ol **29**.



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		

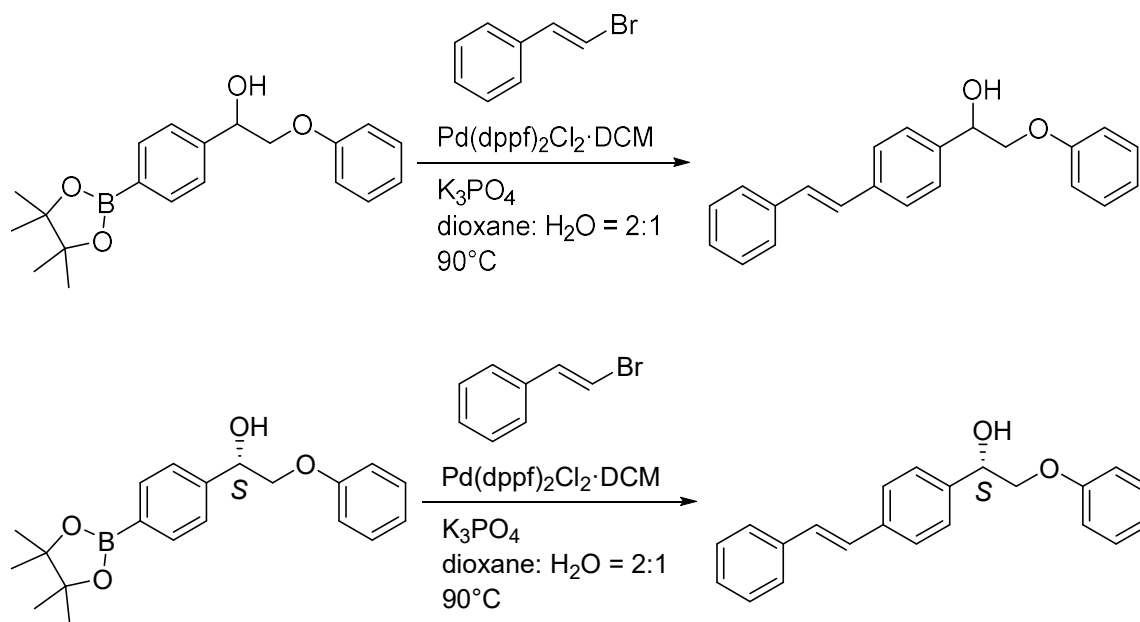
HPLC of 1-(4-styrylphenyl)ethan-1-ol **29** (97% ee, *R* configuration).



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 $\text{Pd(dppf)}_2\text{Cl}_2\cdot\text{DCM}$ (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 \times 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: R_f ca 0.40 (4:1 hexane: EtOAc), strong UV and KMnO_4 ; Mp: 128 °C; HRMS: (found (ESI⁺): $[\text{M}+\text{H}]^+$, Calcd for $\text{C}_{22}\text{H}_{20}\text{NaO}_2$ 339.1353; Found 339.1356; 0.8 ppm error; ν_{max} 3393 (br), 3055, 3024, 2922, 2868, 1598, 1586, 1493, 1449, 1239, 1172, 1076, 1037, 1017 cm^{-1} ; δ_{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),

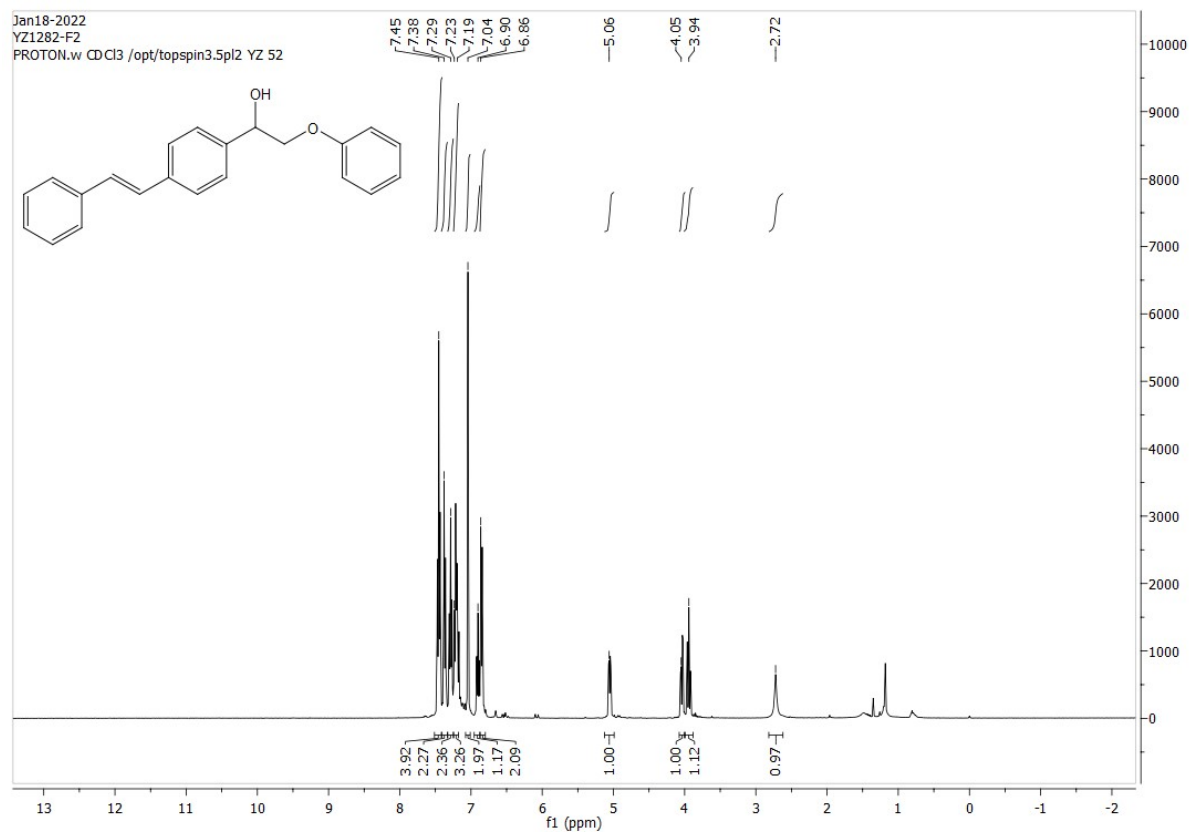
6.90 (1H, t, $J = 7.3$, ArH), 6.86 (2H, d, $J = 8.2$, ArH), 5.06 (1H, dd, $J = 8.7, 2.7$, ArCH), 4.05 (1H, dd, $J = 9.6, 3.0$, CH₂), 3.94 (1H, t, $J = 9.2$, CH₂), 2.72 (1H, s, OH) ppm; δ_c (100 MHz, CDCl₃) 158.39 (C), 138.99 (C), 137.36 (C), 137.23 (C), 129.61 (CH), 129.05 (CH), 128.74 (CH), 128.18 (CH), 127.76 (CH), 126.70 (CH), 126.68 (CH), 126.57 (CH), 121.37 (CH), 114.68 (CH), 73.20 (CH₂), 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, $T = 25^\circ\text{C}$) *R* isomer 14.9 min and *S* isomer 21.2 min.

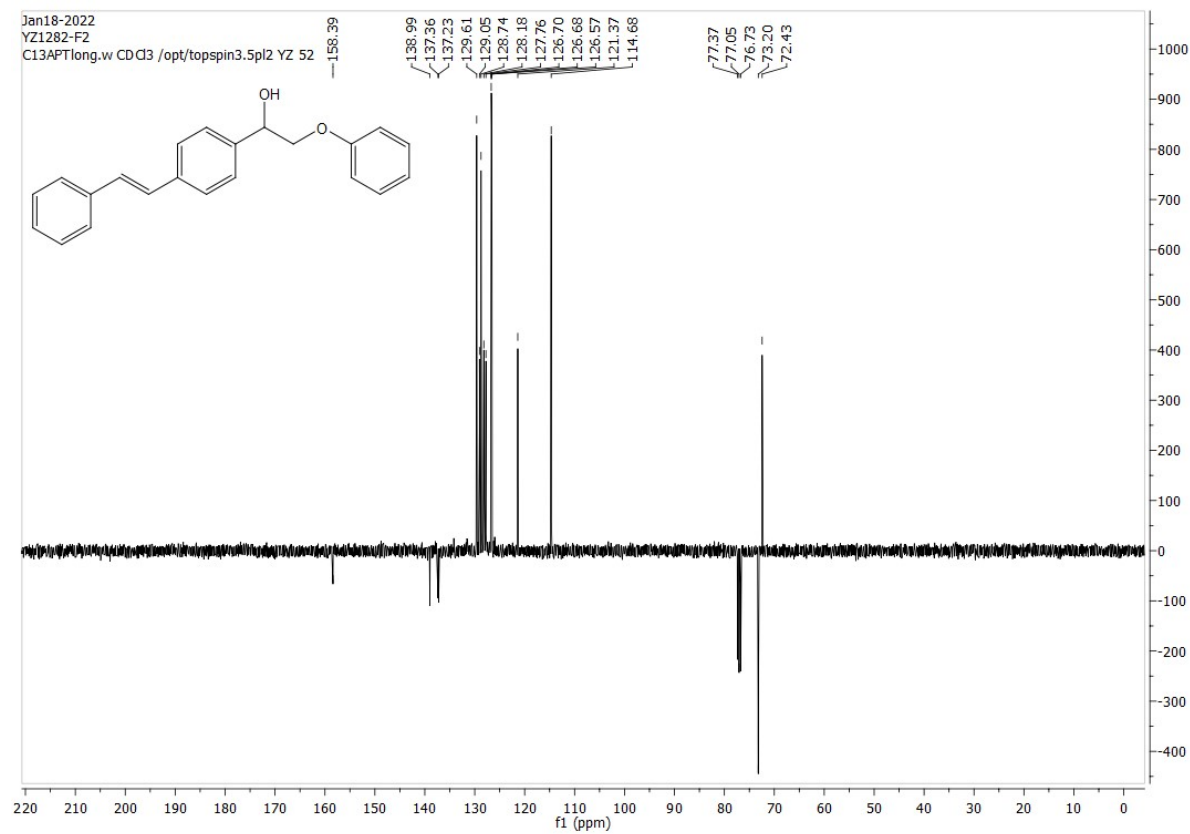
Asymmetric:

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** (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)₂Cl₂·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 (MgSO₄) 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, $T = 25^\circ\text{C}$): $[\alpha]_D^{30} +43.3$ (c 0.187 in CHCl₃) 96% ee (*S*)

¹H NMR (400 MHz, CDCl₃)

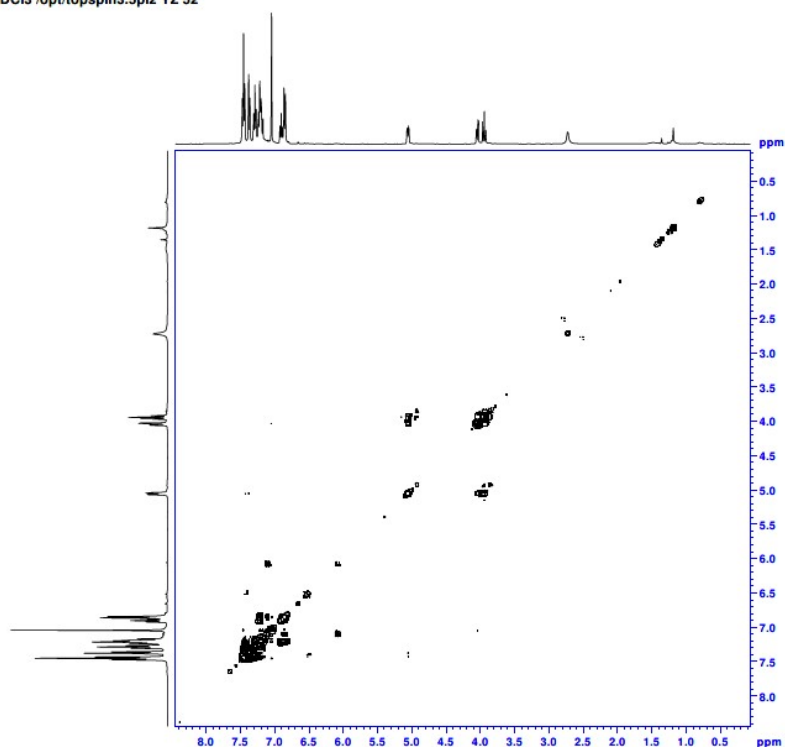


¹³C NMR (100 MHz, CDCl₃)



COSY (400 MHz, CDCl₃)

YZ1282-F2
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PROCNO 1

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D13 0.0000000 sec
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SFO1 400.1317487 MHz
NUC1 1H
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P2 14.00 usec
P3 2500.00 usec
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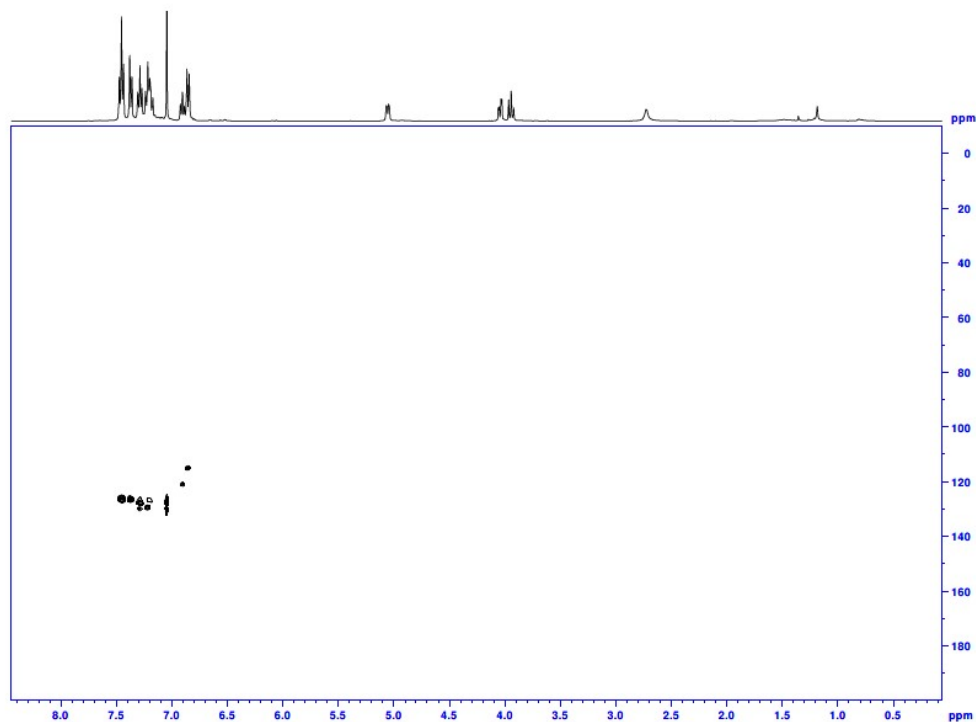
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F1 - Processing parameters
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WDW 0
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PC 0

HSQC (400 MHz, CDCl₃)

YZ1282-F2
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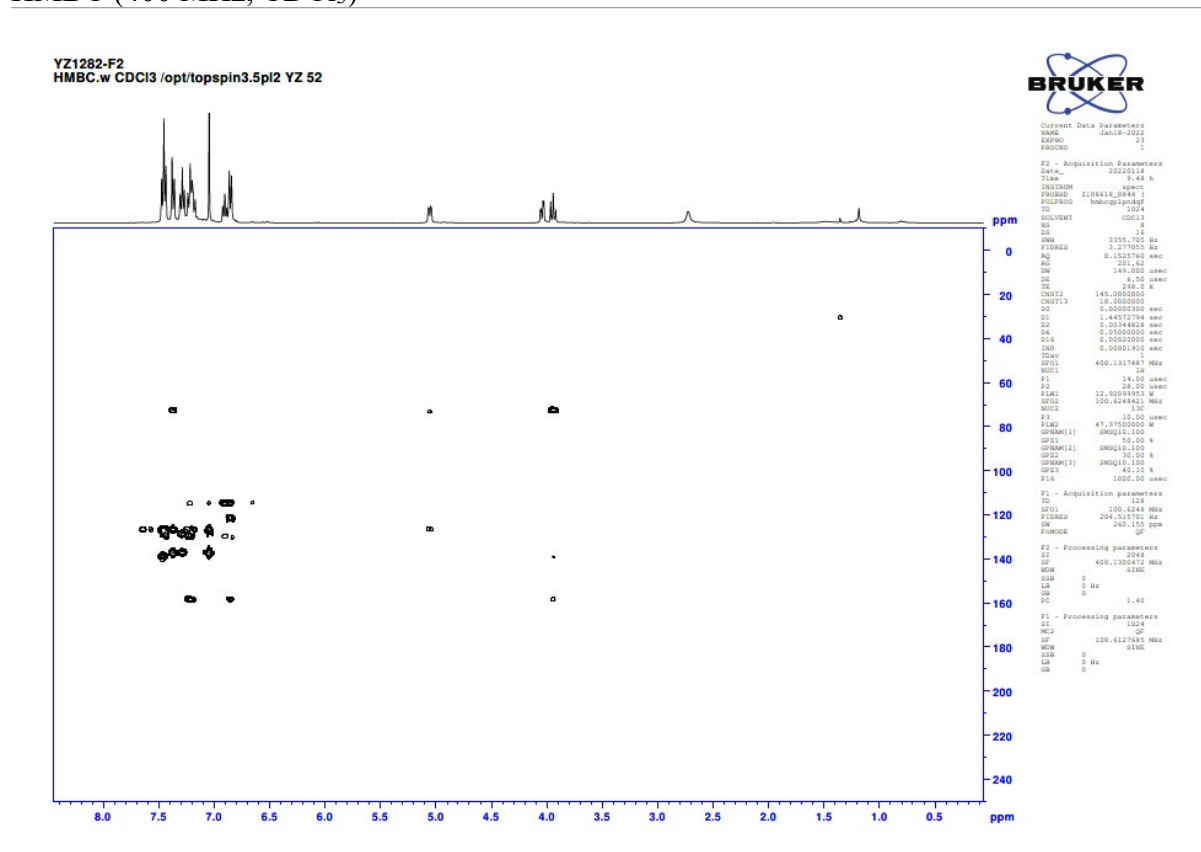
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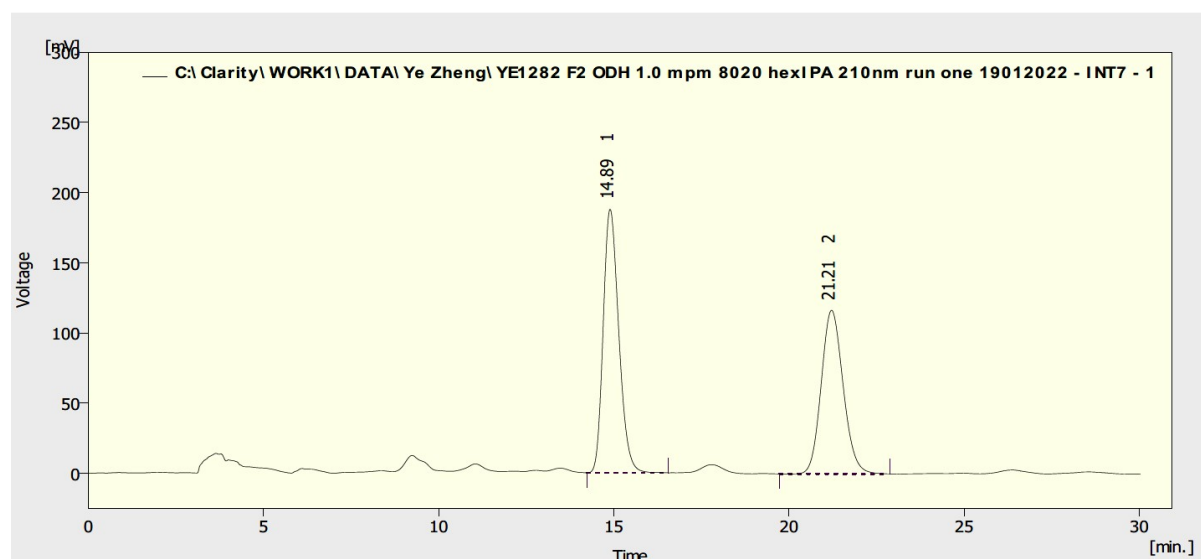
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HMBC (400 MHz, CDCl₃)



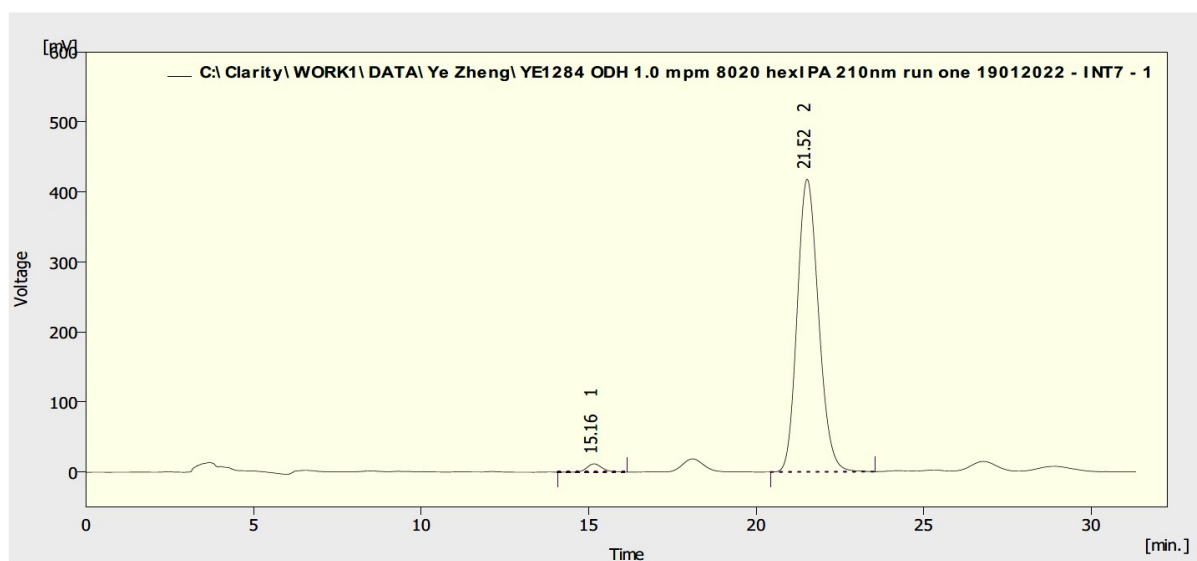
HPLC of racemic 2-phenoxy-1-(4-styrylphenyl)ethan-1-ol **30**.



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		

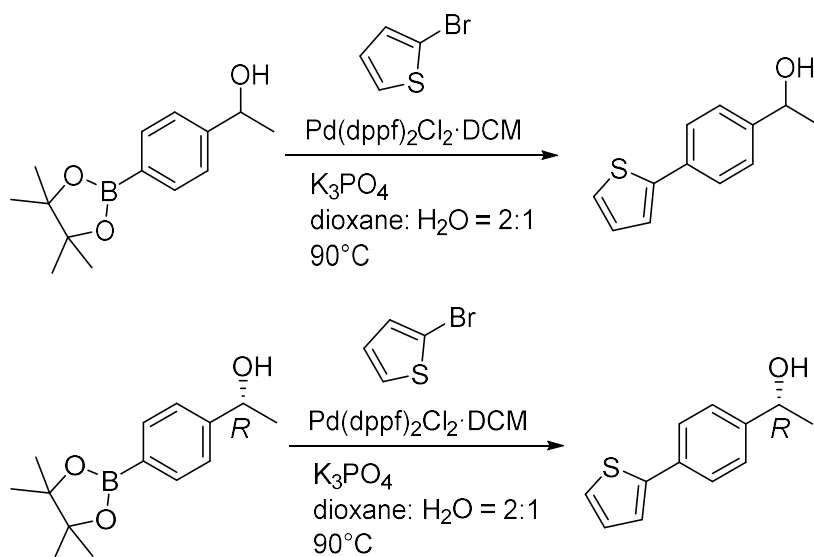
HPLC of 2-phenoxy-1-(4-styrylphenyl)ethan-1-ol (96% ee, *S* configuration) **30**.



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:

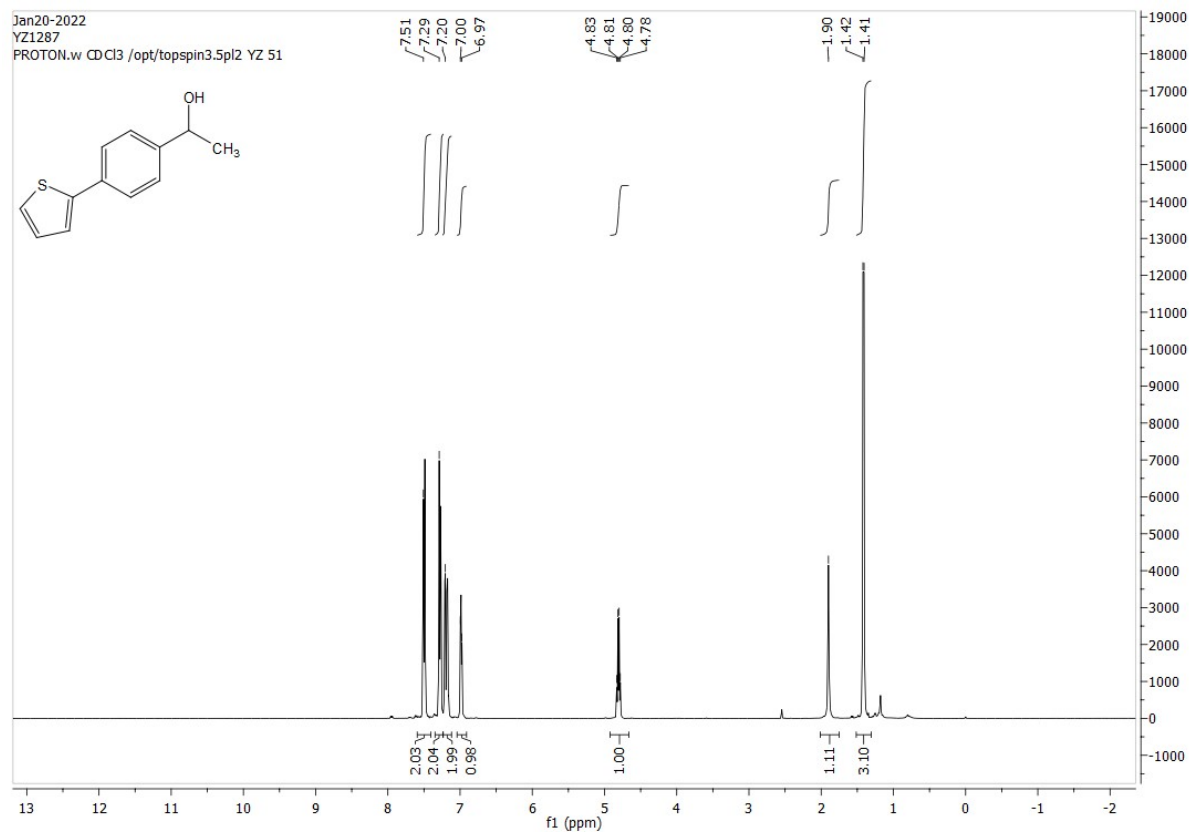
To a solution of racemic 1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol **7** (89.0 mg, 0.359 mmol), 2-bromothiophene (87.9 mg, 0.539 mmol) and tripotassium phosphate (229 mg, 1.08 mmol) in dioxane (1.8 mL) and distilled water (0.9 mL) was added $\text{Pd(dppf)}_2\text{Cl}_2 \cdot \text{DCM}$ (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: R_f ca 0.40 (4:1 hexane: EtOAc), strong UV and KMnO_4 ; Mp: 80°C ; HRMS: (found (ESI⁺): $[\text{M}+\text{H}]^+$, Calcd for $\text{C}_{12}\text{H}_{12}\text{NaO}_2\text{S}$ 227.0508; Found 227.0501; -3.2 ppm error; ν_{max} 3269 (br), 3100, 3067, 2969, 1426, 1406, 1256, 1208, 1070, 1004, 815, 685 cm^{-1} ; δ_{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; δ_{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 (CH₃) 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.

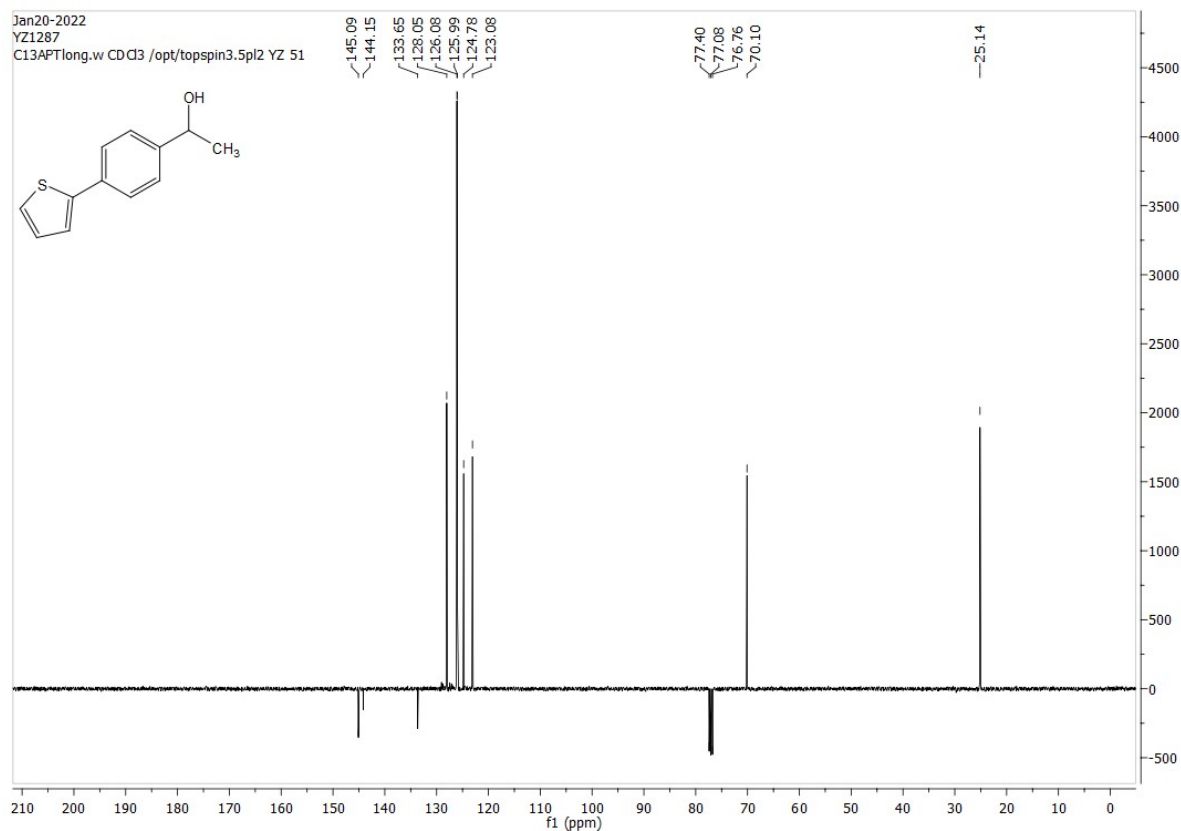
Asymmetric.

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)₂Cl₂·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 (MgSO₄) 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): [α]_D²⁶ +30.7 (c 0.176 in CHCl₃) 94% ee (*R*).

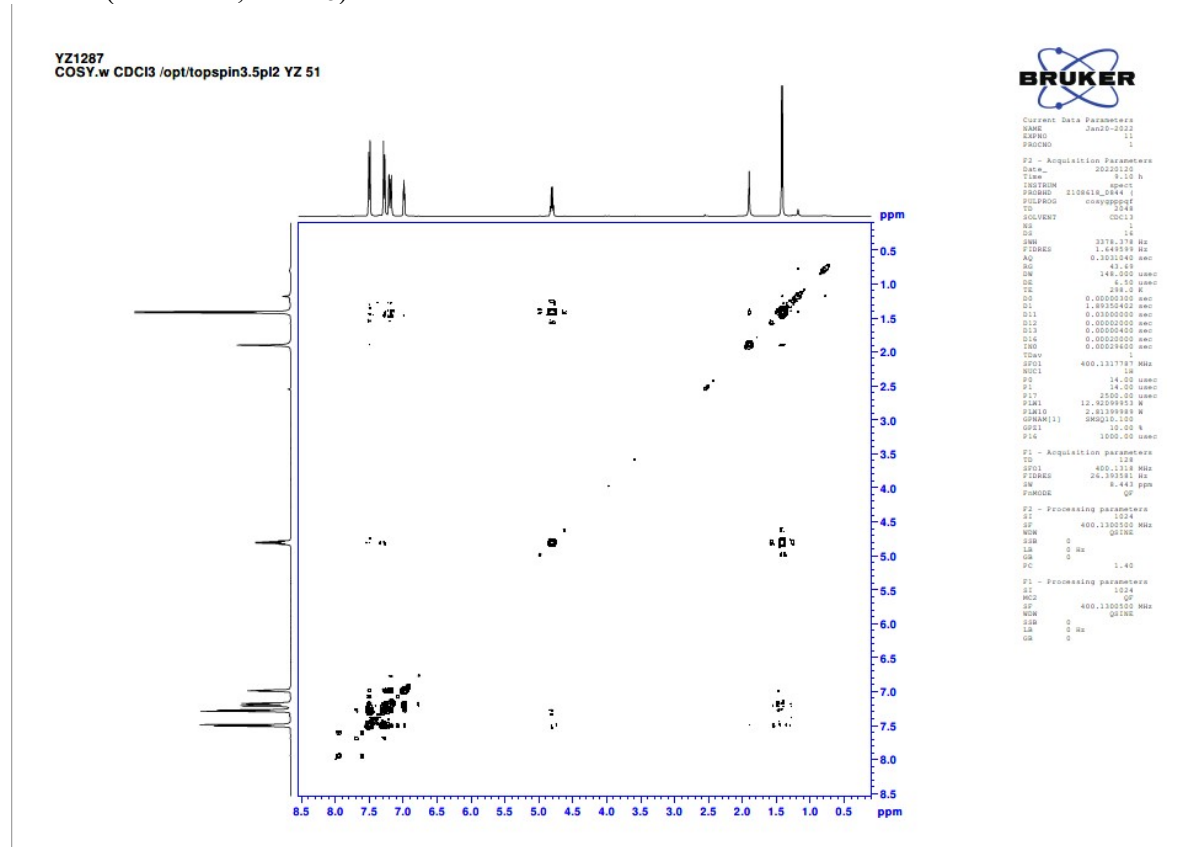
¹H NMR (400 MHz, CDCl₃)



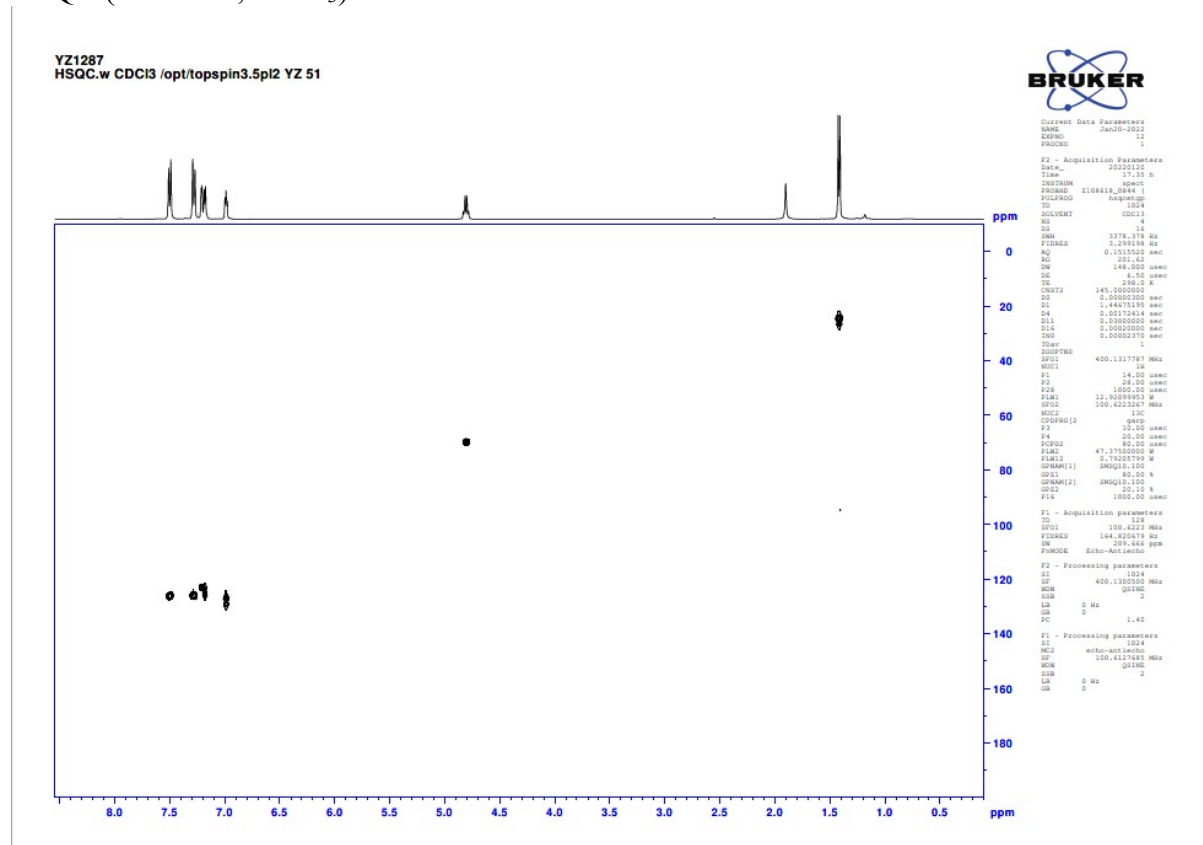
¹³C NMR (100 MHz, CDCl₃)



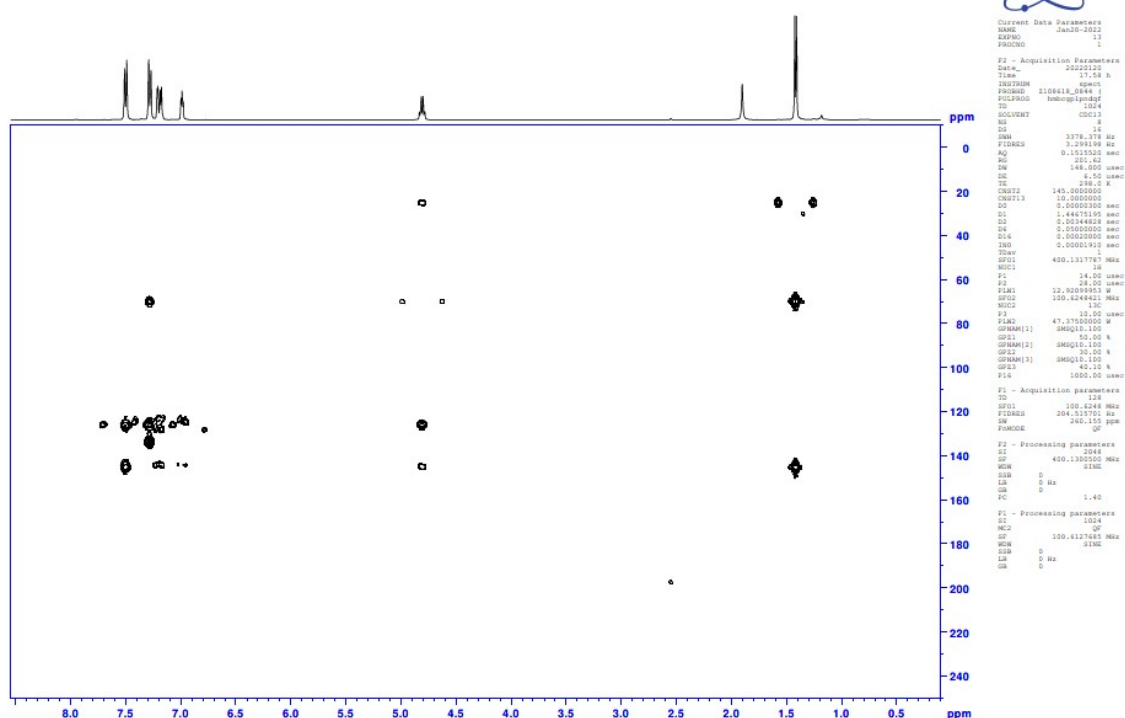
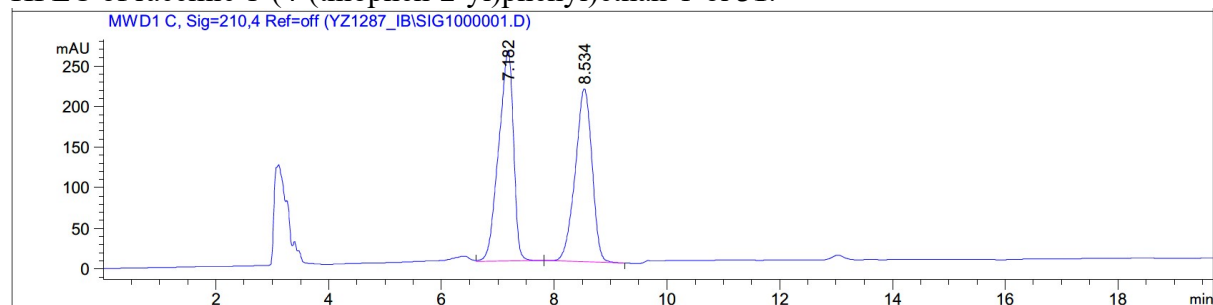
COSY (400 MHz, CDCl₃)



HSQC (400 MHz, CDCl₃)



HMBC (400 MHz, CDCl₃)

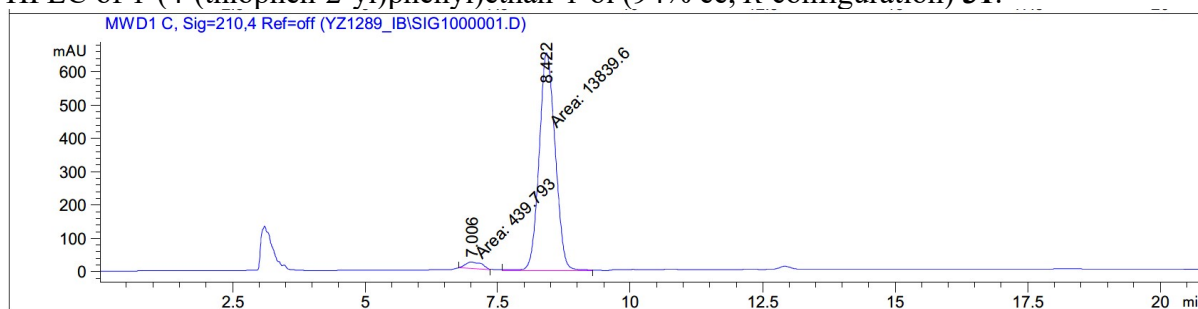
HPLC of racemic 1-(4-(thiophen-2-yl)phenyl)ethan-1-ol **31**.

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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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**.

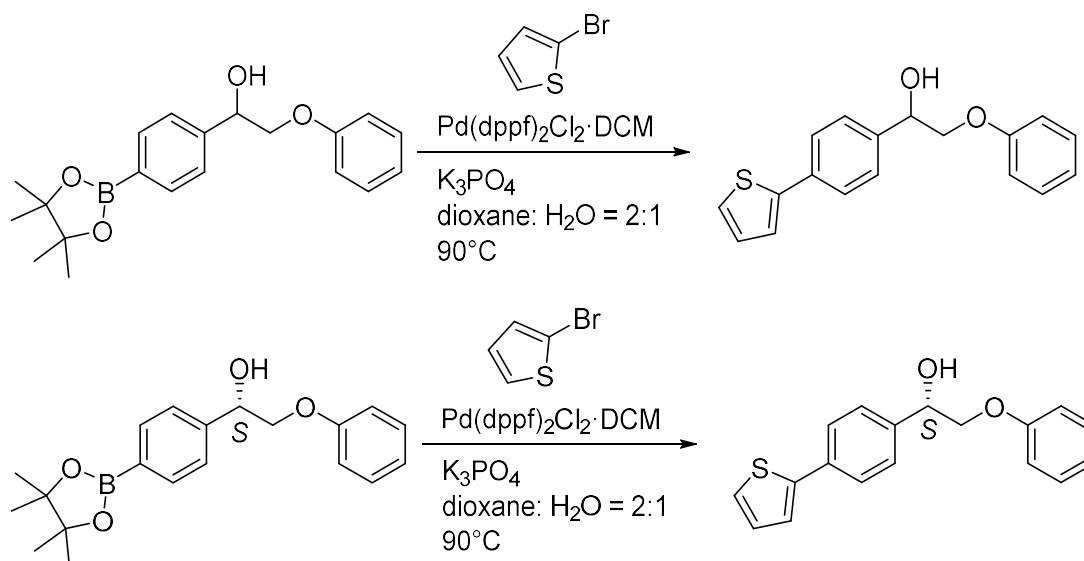


Signal 2: MWD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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

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)₂Cl₂·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 (MgSO₄) 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: R_f ca 0.40 (4:1 hexane: EtOAc), strong UV and KMnO₄; Mp: 104 °C; HRMS: (found (ESI⁺): [M+H]⁺, Calcd for C₁₈H₁₆NaO₂S 319.0759; Found 319.0763; 1.3 ppm error; ν_{max} 3382 (br), 3104, 3066, 3027, 2922, 2868, 1597, 1586, 1493, 1453, 1300, 1290, 1239, 1078, 1037, 1017 816, 751, 688 cm⁻¹; δ_H (400 MHz, CDCl₃) 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, CH₂), 3.93 (1H, t, *J* =

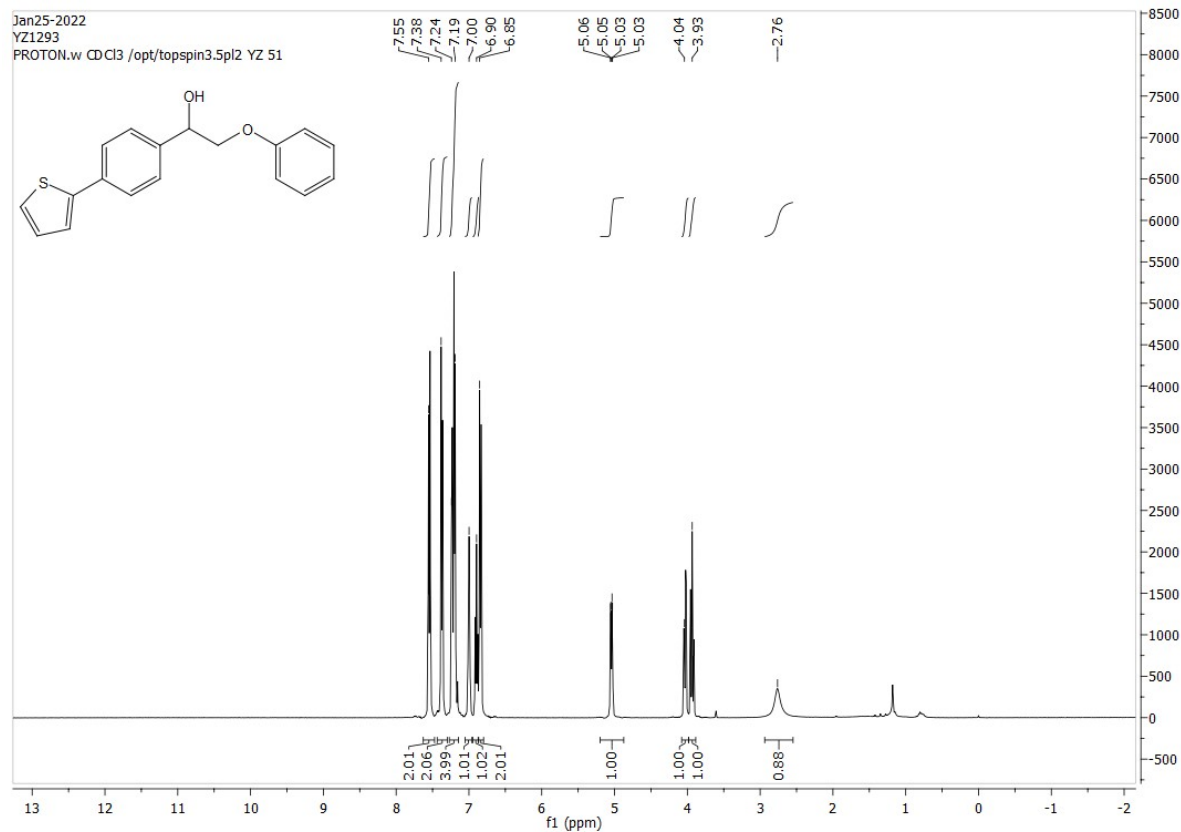
9.1, CH₂), 2.76 (1H, s, OH) ppm; δ_c (100 MHz, CDCl₃) 158.38 (C), 143.97 (C), 138.89 (C), 134.36 (C), 129.62 (CH), 128.10 (CH), 126.89 (CH), 126.12 (CH), 125.00 (CH), 123.30 (CH), 121.40 (CH), 114.69 (CH), 73.18 (CH₂), 72.34 (CH) ppm; m/z (ES-API+) 319.1 ($M^+ + 23$, 100%).

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.

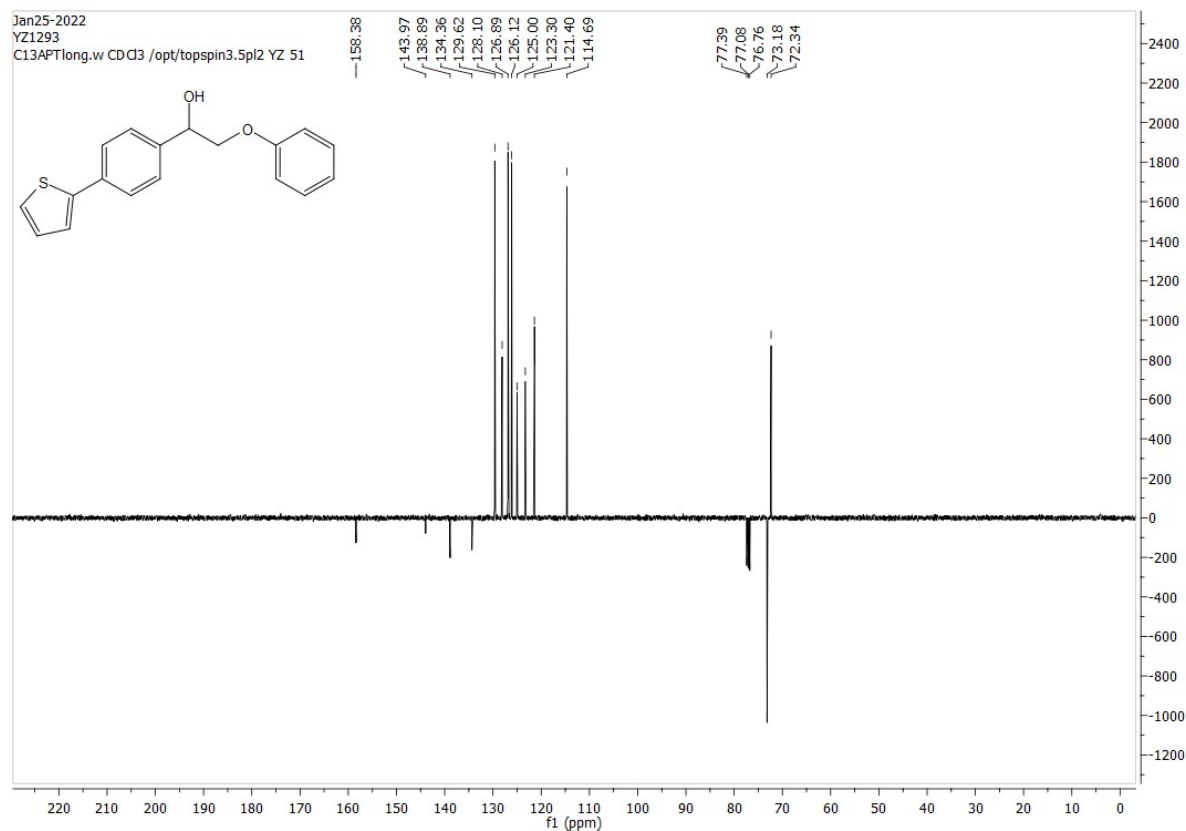
Asymmetric.

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)₂Cl₂·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 (MgSO₄) 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 CHCl₃) 96% ee (*S*)

^1H NMR (400 MHz, CDCl_3)

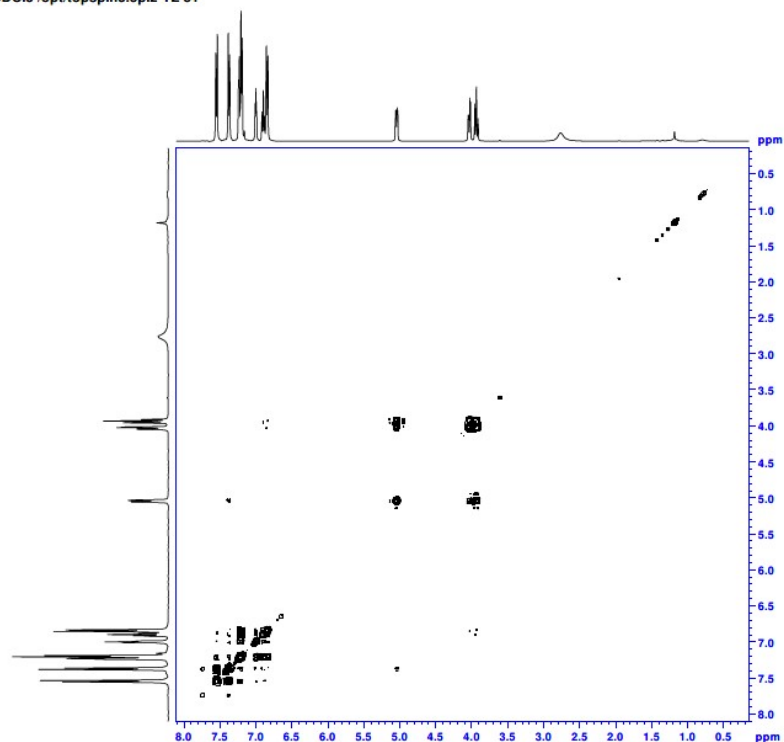


^{13}C NMR (100 MHz, CDCl_3)



COSY (400 MHz, CDCl₃)

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



Current Data Parameters
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EXPNO 11
PROCNO 1

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FIDRES 1.555334 Hz
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RG 49.97
SW 157.0000 sec
DE 4.10 sec
TE 298.2 K
D0 0.0000300 sec
D1 1.8750700 sec
D11 0.0300000 sec
D12 0.0000000 sec
D13 0.0000000 sec
D16 0.0000000 sec
DRO 0.0000000 sec
TD0 400.1317022 MHz
NUC1 1H
NUC2 1H
P1 14.00 sec
P2 14.00 sec
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P16 1000.00 sec

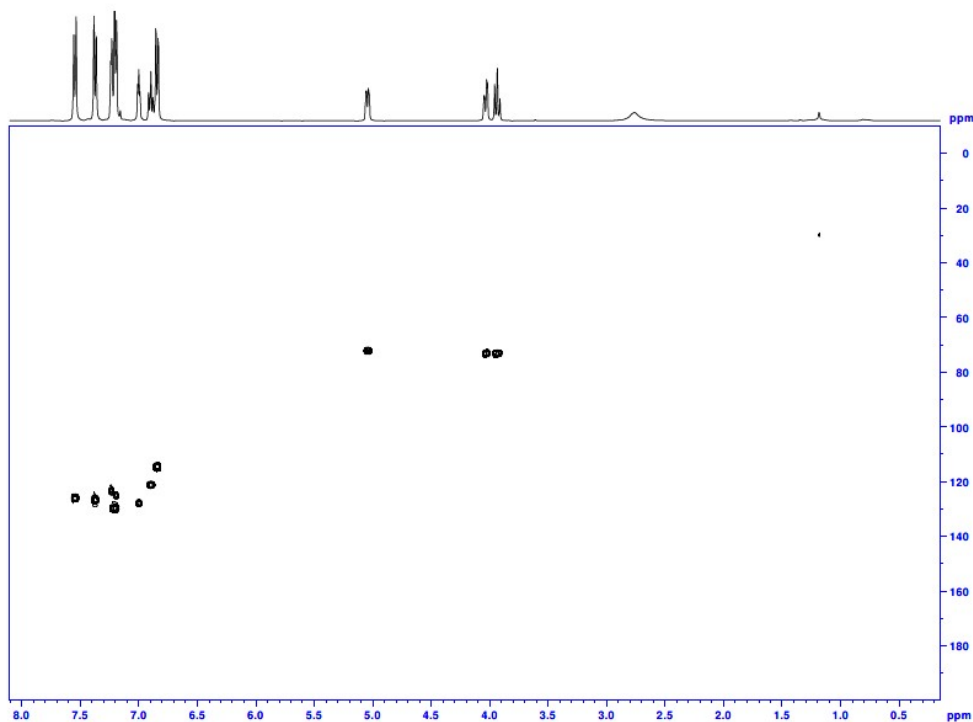
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FIDRES 1.555334 Hz
SW 157.0000 sec
PULPROG zgpg30

F2 - Processing parameters
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SF 400.1317022 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.40

F1 - Processing parameters
SI 32768
SF 400.1317022 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0

HSQC (400 MHz, CDCl₃)

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



Current Data Parameters
NAME Jan25-2022
EXPNO 12
PROCNO 1

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AQ 0.3215140 sec
RG 49.97
SW 157.0000 sec
DE 4.10 sec
TE 298.2 K
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D1 1.8750700 sec
D11 0.0300000 sec
D12 0.0017244 sec
D13 0.0000000 sec
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DRO 0.0000000 sec
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NUC1 1H
NUC2 13C
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P2 28.00 sec
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GRAB[1] SMOUL1.100
GR1 20.10 Hz
P16 1000.00 sec

F1 - Acquisition parameters
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FIDRES 1.54800078 Hz
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F2 - Processing parameters
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WDW EM
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LB 0 Hz
GB 0
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F1 - Processing parameters
SI 32768
SF 400.6223 MHz
WDW EM
SSB 0
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YZ1293
HMBC.w CDC13 /opt/topspin3.5pl2 YZ 51

BRUKER

Current Data Parameters
Date_ 20220115
Time 9:50 A
F2 - Acquisition Parameters
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FIDRES 3.110079 Hz
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DE 6.50 usec
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CHET13 10.0000000
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SFO 0.00000000 sec
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DM 240.155 ppm
FWDGDE 0F
F2 - Processing parameters
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MWD1 C, Sig=210,4 Ref=off (YZ1293_IB_2\SIG1000001.D)

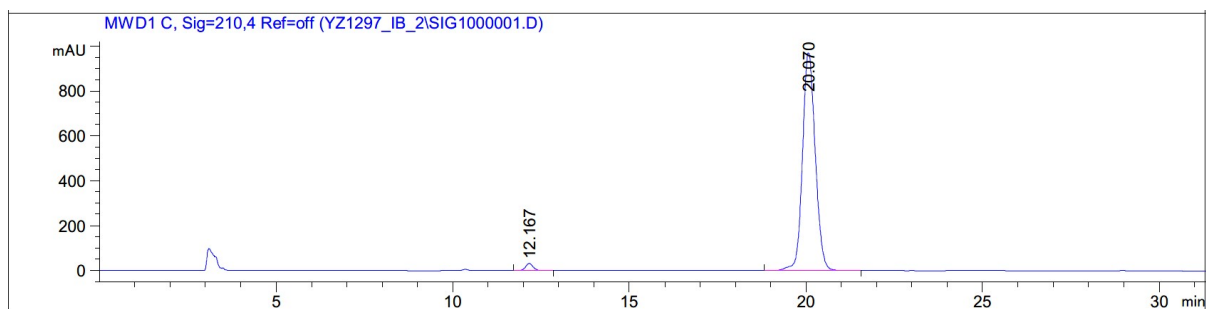
The chromatogram displays two prominent peaks. The first peak is at a retention time of 12.013 minutes, reaching a maximum absorbance of approximately 1100 mAU. The second peak is at 19.891 minutes, reaching a maximum absorbance of approximately 800 mAU. The baseline is stable with minor noise and small peaks around 3 and 18 minutes.

Retention Time (min)	Approximate mAU
12.013	1100
19.891	800

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.013	VV	0.2309	1.94369e4	1296.40540	49.1425
2	19.891	BB	0.3835	2.01152e4	810.63892	50.8575

S225

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



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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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