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Supporting Information

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Supporting Information

Lewis acid catalysed asymmetric one-carbon ring-expansion of prochiral cyclobutanones

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Contents

1 General

Nuclear magnetic resonance (NMR) spectra were recorded by the analytical departments of the Organisch-Chemisches Institut at the Westfälische Wilhelms-Universität and of the Department Chemie at Johannes Gutenberg-Universität Mainz. Following spectrometers were used: An Avance II 400 (Bruker), a DD2 500 (Agilent), a DD2 600 (Agilent), an Avance III HD 300 (Bruker), an Avance III HD 400 (Bruker). Spectra were recorded at 26 °C (unless otherwise noted). Chemical shifts are reported in ppm with the solvent resonance as the internal standard (^{1}H NMR $CHCl_3$: δ = 7.26 ppm, C_6HD_5: δ = 7.16 ppm, $(CHD_2)(CD_3)SO$: δ = 2.50 ppm; ^{13}C NMR $CDCl_3$: δ = 77.16 ppm, C_6D_6: δ = 128.06 ppm, $(CD_3)_2SO$: δ = 39.5 ppm). The data is reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, br = broad, m = multiplet or combinations of these), coupling constants (Hz) and integration. Apparent multiplicity, which occurs as a result of accidental equality of coupling constants to magnetically non-equivalent protons, is marked as *app*.

Infrared (IR) spectra were obtained on a Perkin-Elmer 100 FT-IR spectrometer or on a Jasco FT/IR-4100 and are reported in wavenumbers (cm^{-1}). Bands are characterized as broad (br), strong (s), medium (m), and weak (w).

Melting points (M.P.) were measured on a Büchi B-545 and are reported uncorrected.

High Resolution Mass Spectrometry (HRMS) was performed by the analytical departments of the Organisch-Chemisches Institut at the Westfälische Wilhelms-Universität and of the Department Chemie at Johannes Gutenberg-Universität Mainz. Spectra were recorded on a Bruker Daltonics MicroTof, on a Thermo-Fisher Scientific Orbitrap LTQ XL or an Agilent G6545AQ-ToF. Signals are reported as mass to charge ratio *m/z*. GC-MS data was acquired using an Agilent 7890A Gas Chromatograph and an Agilent 5975 or 5975 VL MSD Inert Mass Selective Detector (EI) and is reported as *m/z* (relative intensity).

Optical rotations were measured on a Perkin-Elmer 241 polarimeter at 589 nm wavelength (sodium D-line) using a standard 10 cm cell (1 mL). Specific rotations, $[\alpha]_D^T$, are reported in degree mL/(g·dm) at the specific temperature. Concentrations (*c*) are given in grams per 100 mL of the specific solvent.

Analytical high-performance liquid chromatography (HPLC) measurements were performed on an Agilent 1100, an Agilent 1260 Infinity II or a Knauer system (Knauer HPLC Pump Smartline 1000 with degassing unit, Knauer Autosampler Smartline 3950, Knauer UV-detector Smartline 2550, Knauer RI-detector Smartline 2300). Separation was performed using Lux® i-Cellulose-5 (4.6 x 250 nm x 5 µm, Phenomenex Ltd.), Lux® Cellulose-1 (4.6 x 250 nm x 5 µm, Phenomenex Ltd.), Lux® Amylose-1 (4.6 x 250 nm x 5 µm, Phenomenex Ltd.), Lux® i-Amylose-3 (4.6 x 250 nm

x 5 µm, Phenomenex Ltd.), Reprosil Chiral-AMS (4.6 x 250 nm x 5 µm, Dr Maisch GmBH.) or Chiralpak® IF-3 (4.6 x 250 nm x 5 µm, Daicel Chiral Technologies).

Purification was performed either *via* standard column chromatography (FC) techniques using 60 M silica gel (0.04–0.063 mm, MACHEREY-NAGEL), 40-63 µm silica gel (VWR chemicals) or Geduran® Si 60 (0.04–0.063 mm, Millipore) or on an automated flash chromatography (AFC) system *Biotage Isolera One* utilizing *Biotage Sfär Silica D-Duo* 60 µm columns (5 g, 25 g, 100 g). Glass silica gel plates 60 F254 (Merck) were used for thin layer chromatography (TLC) using UV light (254/366 nm), $KMnO_4$ (1.5 g $KMnO_4$, 5 g $NaHCO_3$ and 5 mL NaOH 10% in 200 mL H_2O), CAM (0.5 g $Ce(NH_4)_2(NO_3)_6$ and 24.0 g of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, 28 mL H_2SO_4 in 200 mL H_2O) and PMA (10 g $H_3[P(Mo_3O_{10})_4]{\cdot}xH_2O$ in 100 mL EtOH) for detection.

Chemicals were purchased from *Alfa Aesar*, *Acros Organics*, *Sigma Aldrich*, *BLDpharm*, *FluoroChem*, *Carbolution* or *ABCR* and used as received. Scandium triflate was dried at 200 °C over P_2O_5 prior to use and stored in a glovebox. All work-up and purification procedures were carried out with pre-distilled technical grade solvents. Dry solvents were either dried with standard techniques or collected from a *MBraun MB SPS-800* (CH_2Cl_2, Et_2O, THF). A positive argon pressure was used to pass the solvents through the following columns:

CH_2Cl_2: 2 × MB-KOL-A

Et_2O: 1 × MB-KOL-A and 1 × MB-KOL MT2-250

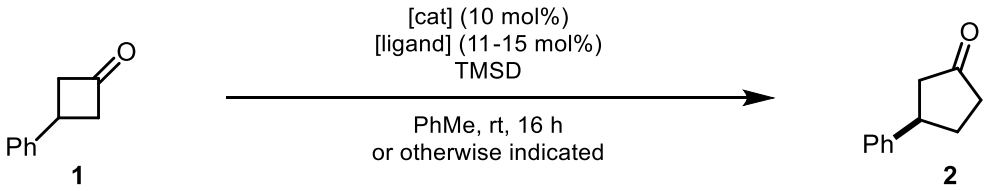
THF: 2 × MB-KOL MT2-150°C

All reactions involving air or moisture sensitive reagents were carried out in oven- (125 °C) and flame-dried glassware under argon or nitrogen atmosphere using standard *Schlenk* techniques. Reactions requiring heating were conducted using aluminium blocks as heating source.

2 Optimisation of reaction protocols

2.1 Optimisation of reaction conditions

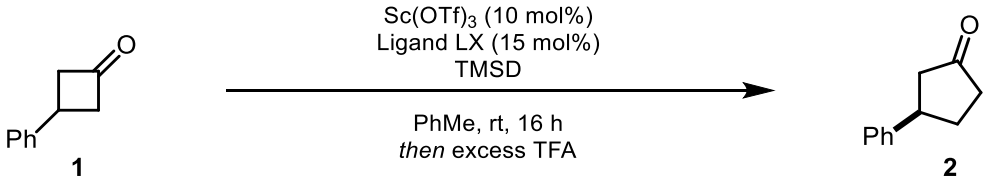
Table 1: Initial catalyst screening for the ring expansion of 3-phenylcyclobutanone (**1a**) with TMSD.



Entry	Catalyst system	Change to conditions	NMR yield	Yield	*er*
1	$Zn(OTf)_2$	-	-	-	-
2	$Cu(OTf)_2$	-	-	-	-
3	$Sc(OTf)_3$	-	78%	69%	-
4	$Hf(OTf)_4$	-	51%	n.d.	-
5	(**LS1**)Sc(III)	-	n.d.	40%	52:48
6	(*ent*-**L1a**)Sc(III)	-	74%	69%	40:60
7	(*ent*-**L1a**)Hf(IV)	-	70%	69%	49:51
8	(Salen)AlCl	20 mol% cat	<2%	n.d.	-
9	(**LS22**)AlMe	36 mol% cat, 18 mol% Ligand	Complex mixture	n.d.	-
10	chiral oxazoborolidinium ion[a]	−78 °C to rt	43%	n.d.	53:47

Reactions run on 0.1 mmol scale in dry solvent (0.1 M) under inert atmosphere using 1.1 eq. TMSD. NMR yields determined *via* ^{1}H NMR using mesitylen as internal standard. *er* determined *via* HPLC using chiral stationary phases.
[a] (*S*)-(−)-*o*-Tolyl-CBS-oxazaborolidinium bistriflimde, prepared according to a literature procedure.[1]

Table 2: Solvent screening for the ring expansion of 3-phenylcyclobutanone (**1a**) with TMSD.



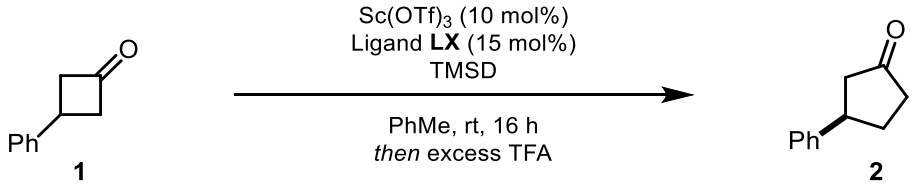
Entry	Ligand	Solvent	NMR yield	Yield	*er*
1	*ent*-**L1a**	PhMe	80%	77%	60:40
2	*ent*-**L1a**	Heptane	n.d.	60%	58:42
3	*ent*-**L1a**	EtOAc	82%	75%	55:45
4	*ent*-**L1a**	THF	83%	77%	52:48

Reactions run on 0.1 mmol scale in dry solvent (0.1 M) under inert atmosphere using 1.1 eq. TMSD. NMR yields determined *via* ^{1}H NMR using mesitylen as internal standard. *er* determined *via* HPLC using chiral stationary phases.

2.2 Ligand screening

The full details of the ligand screening are summarised in Table 3 with the structures of the corresponding ligands given in Figure 1 and Figure 2. Details on the ligand can be found in chapter 4.

Table 3: Result of the performed ligand screening for the ring expansion of cyclobutanone **1a** with TMSD.



Entry	Ligand	Yield	*er*	Entry	Ligand	Yield	*er*
1	*ent*-**L1a**	77%	40:60	**18**	*ent*-**LS7**	75%	39:61
2	**L1b**	53%	47:53	**19**	*ent*-**LS8**	81%	46:54
3	**L2a**	76%	51:49	**20**	**LS9**	71%	61:39
4	**L2b**	53%	53:47	**21**	**LS10**	49%	52:48
5	**L3a**	76%	63:37	**22**	**LS11**	77%	51:49
6	**L4a**	72%	64:36	**23**	**LS12**	52%	52:48
7	**L4b**	88%	67:33	**24**	**LS13**	41%	50:50
8	**L4c**	81%	67:33	**25**	**LS14**	76%	51:49
9	**LS1**	n.d.	52:48	**26**	**LS15**	29%	51:49
10	**LS2**	87%	62:38	**27**	**LS16**	74%	51:49
11	**LS3**	78%	52:48	**28**	**LS17**	77%	50:50
12	**LS4**	40%	56:44	**29**	**LS18**	n.d.	51:49
13	**LS5a**	87%	62:38	**30**	**LS19**	76%	51:49
14	**LS5b**	81%	62:38	**31**	**LS20**	69%	50:50
15	**LS5c**	78%	63:37	**32**	**LS21**	71%	50:50
16	**LS6a**	88%	51:49	**33**	**LS22**	69%	50:50
17	**LS6b**	78%	58:42	**34**	**LS23**	n.d.	51:49

Reactions run on 0.1 mmol scale in dry solvent (0.1 M) under inert atmosphere using 1.1 eq. TMSD. *er* determined *via* HPLC using chiral stationary phases.

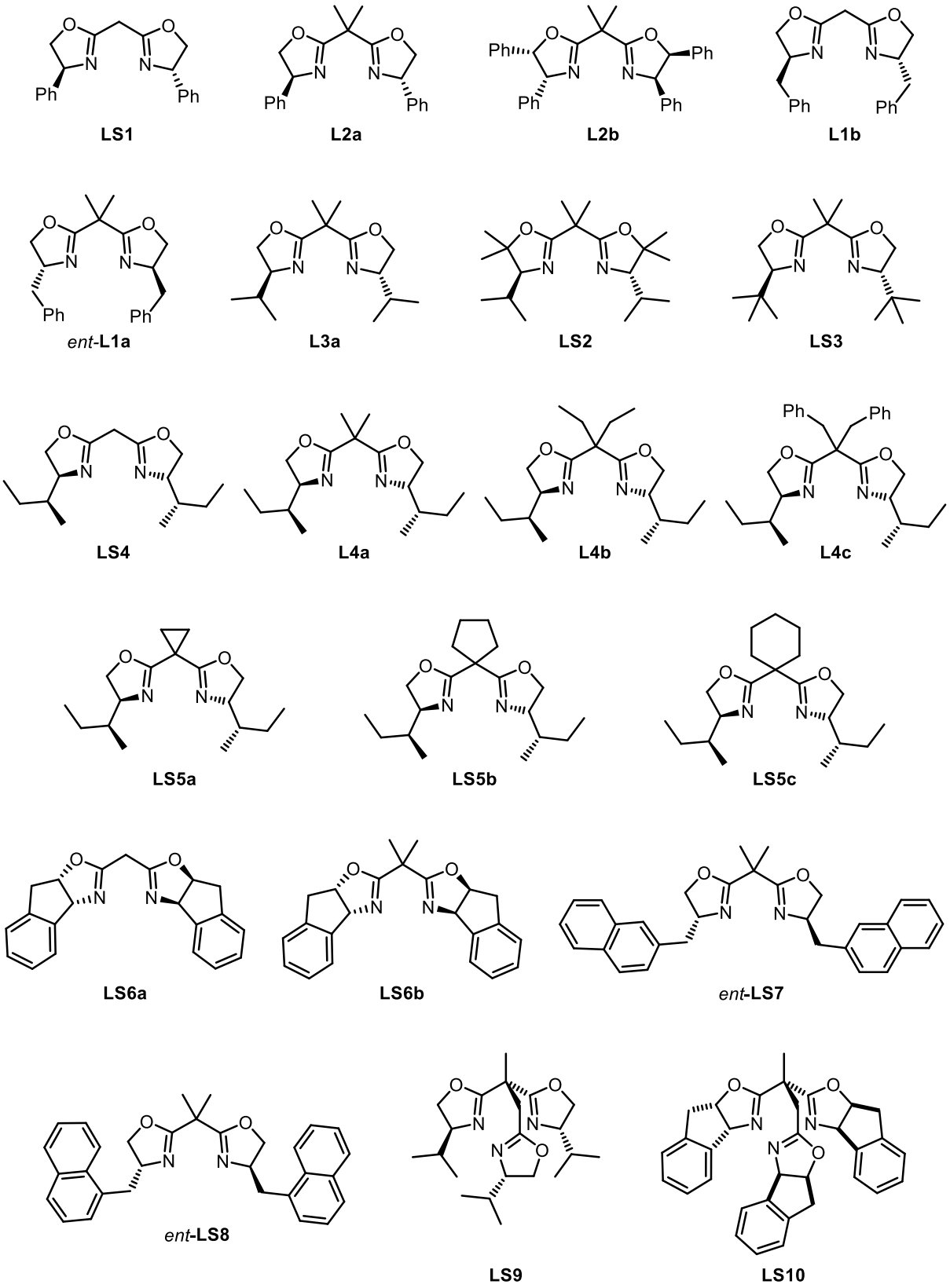


Figure 1: Structure of ligands elucidated in this study (part 1).

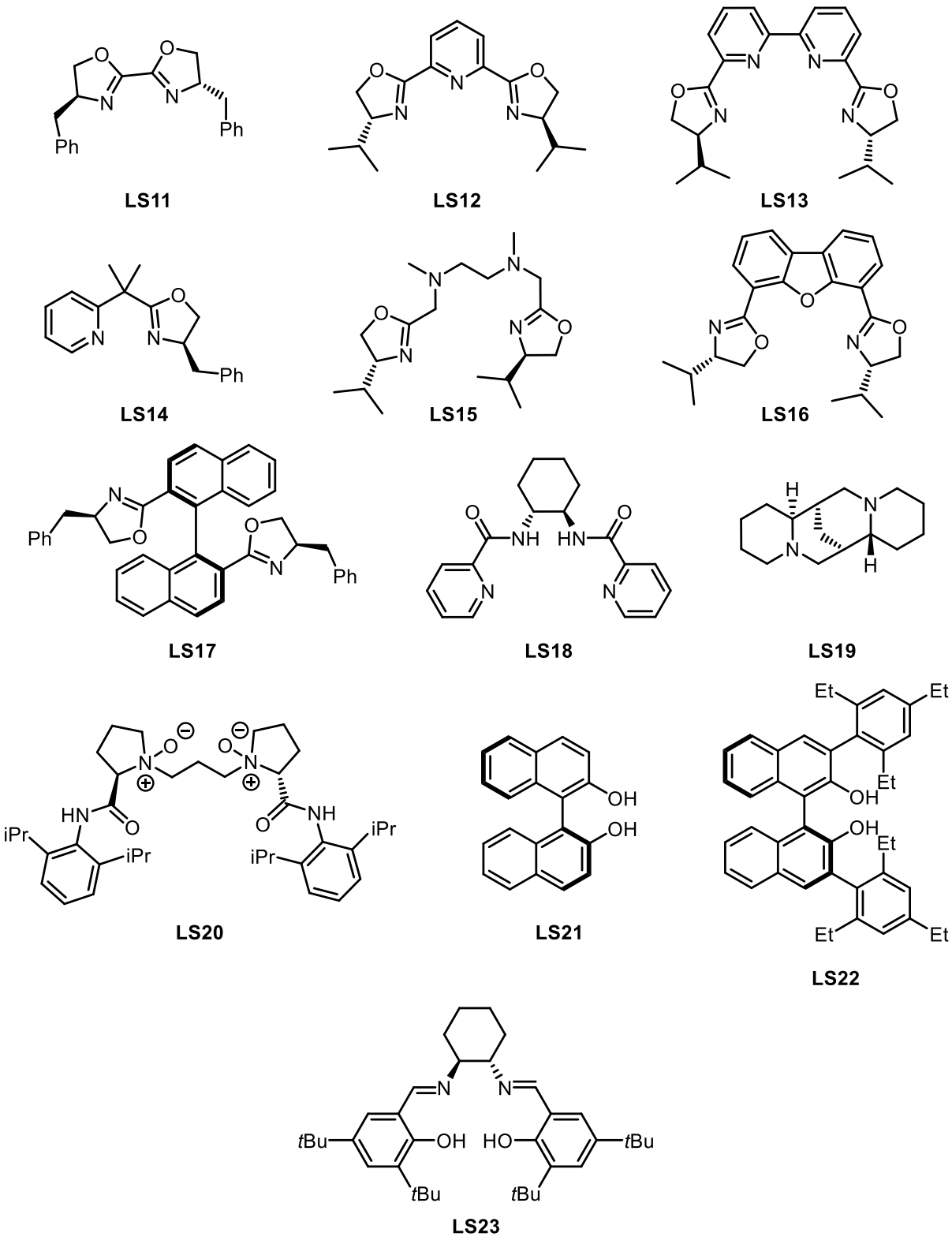


Figure 2: Structure of ligands elucidated in this study (part 2).

3 Synthesis of starting materials

3.1 General procedures

General Procedure A: [2+2] Cycloaddition of keteneiminium salt

Following a modified procedure by *Chernykh et al.*,[2] a Schlenk tube was charged with dimethylacetamide (1.20 eq.) in 1,2-dichloroethane (0.5 M). The reaction solution was kept at room temperature in a water bath. Tf_2O (2.00 eq.) was added dropwise and the reaction mixture was stirred at room temperature for 10 min. A solution of the corresponding alkene (1.00 eq.) and 2,6-lutidine (2.00 eq.) in 1,2-dichloroethane (2.0 M) was added dropwise to the reaction mixture, which was stirred at 90 °C for 8 h. The reaction was allowed to cool to room temperature and water (20 mL) was added. The reaction mixture was stirred at 90 °C for 16 h. The mixture was allowed to cool to room temperature and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The product was isolated *via* FC with the conditions given in the corresponding entry.

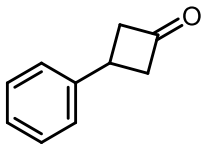
General Procedure B: [2+2] Cycloaddition of dichloroketene

Following a modified procedure by *Malkov et al.*,[3] a Schlenk flask was charged with Zn dust (6.00 eq.) and freshly distilled Et_2O (0.14 M with respect to the alkene). The corresponding alkene (1.00 eq.) was added to the suspension. The suspension was kept at room temperature in a water bath while a solution of trichloroacetyl chloride (2.50 eq.) and $POCl_3$ (1.10 eq.) in freshly distilled Et_2O (0.5 M with respect to the trichloroacetyl chloride) was added. The water bath was removed and the suspension was stirred at 40 °C for 8 h. After complete conversion, the suspension was allowed to cool down to room temperature and filtered through a pad of Celite® and washed with CH_2Cl_2. The solvents were removed under reduced pressure and the residue was taken up in CH_2Cl_2. The organic layer was washed with water (3 ×) and with an sat. aq. $NaHCO_3$ sol. (3 ×). The organic layer was dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The crude reaction mixture was used without further purification.

To a round flask the crude reaction mixture of the first reaction step and glacial acetic acid (0.1 M with respect to the alkene) were added. The solution was kept at 20 °C in a water bath and Zn dust (4.00 eq.) was slowly added. The suspension was heated to 80 °C and stirred for 16 h. The mixture was allowed to cool down to room temperature, filtered through a pad of Celite® and washed with CH_2Cl_2. The solvent was removed under reduced pressure. The residue was redissolved in CH_2Cl_2 (50 mL) and the organic layer was washed with an sat. aq. $NaHCO_3$ sol. (3 ×) and water (3 ×). The

organic layer was dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The product was obtained *via* FC with the conditions given in the corresponding entry.

3.2 Syntheses

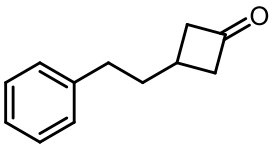


3-Phenylcyclobutanone [1a]

Following general procedure **A** using styrene (5.73 mL, 50.0 mmol, 1.00 eq.), dimethylacetamide (5.58 mL, 60.0 mmol, 1.20 eq.), Tf_2O (16.8 mL, 100 mmol, 2.00 eq.) and 2,6-lutidine (11.7 mL, 100 mmol, 2.00 eq.) the desired product was obtained *via* FC (pentane:Et_2O; 95:5 → 90:10) as colorless oil (5.29 g, 36.0 mmol, 72%).

Spectroscopic data was in agreement with that previously reported.[4]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 – 7.34 (m, 2H), 7.34 – 7.24 (m, 3H), 3.74 – 3.63 (m, 1H), 3.57 – 3.45 (m, 2H), 3.32 – 3.21 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)**: δ = 206.9, 143.7, 128.8, 126.7, 126.6, 54.8, 28.5.

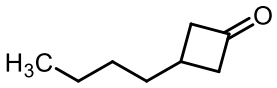


3-Phenethylcyclobutanone [1b]

Following modified general procedure **B** using 4-phenyl-1-butene (150 µL, 1.00 mmol, 1.00 eq.), zinc dust (392 mg, 6.00 mmol, 6.00 eq.) and trichloroacetyl chloride (280 µL, 2.50 mmol, 2.50 eq.) in the first step[1] and zinc dust (654 mg, 10.0 mmol, 10.0 eq.) in the second step[2] the desired product was obtained *via* FC (pentane:EtOAc; 95:5 → 90:10) as a colourless oil (108 mg, 0.620 mmol, 62%).

IR (neat): $\tilde{\nu}$ = 3567 (w), 3064 (w), 3026 (w), 2933 (w), 2850 (w), 2364 (w), 2342 (w), 1781 (s), 1604 (w), 1496 (w), 1455 (w), 1386 (w), 1102 (w), 1075 (w), 913 (w), 746 (m), 699 (s), 641 (m), 631 (m), 615 (s), 597 (s), 585 (m). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.34 – 7.27 (m, 2H, CH_{arom}), 7.25 – 7.13 (m, 3H, CH_{arom}), 3.20 – 3.08 (m, 2H, 2×CH_2), 2.76 – 2.62 (m, 4H, 4×CH_2), 2.38 (ttt, J = 8.7, 7.5, 6.2 Hz, 1H, CH), 1.96 – 1.88 (m, 2H, 2×CH_2). **^{13}C NMR (101 MHz, $CDCl_3$)**: δ = 208.3 (C_q), 141.5 (C_q), 128.6 (2×CH$_{arom}$), 128.5 (2×CH$_{arom}$), 126.1 (CH$_{arom}$), 52.6 (2×CH$_2$), 38.1 (CH$_2$), 34.7 (CH$_2$), 23.5 (CH$_3$). **HRMS (ESI)**: Calculated for $C_{12}H_{15}O^+$ [M+H]$^+$: 175.1118, found: 175.1117.

[1] [2+2] Cycloaddition performed at rt for 3 h without the addition of $POCl_3$.
[2] Reduction performed at 80 °C for 4 h.

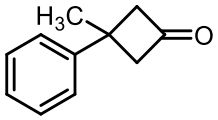


3-Butylcyclobutanone [1c]

Following general procedure **B** using 1-hexene (1.24 mL, 10.0 mmol, 1.00 eq.), zinc dust (3.92 g, 60.0 mmol, 6.00 eq.) and trichloroacetyl chloride (2.79 mL, 25.0 mmol, 2.50 eq.) in the first step and zinc dust (2.62 g, 40.0 mmol, 4.00 eq.) in the second step the desired product was obtained *via* FC (pentane:Et_2O; 95:5) as a colourless oil (471 mg, 3.70 mmol, 37%).

Spectroscopic data was in agreement with that previously reported.[5]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.22 – 3.07 (m, 2H), 2.72 – 2.60 (m, 2H), 2.42 – 2.28 (m, 1H), 1.58 *(app.* q, $J \approx 7.6$ Hz, 2H), 1.41 – 1.24 (m, 4H), 0.92 (t, J = 6.9 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)**: δ = 209.0, 52.7, 36.2, 30.6, 24.0, 22.6, 14.2.

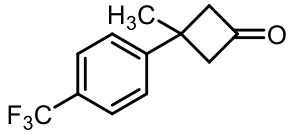


3-Methyl-3-phenylcyclobutanone [1d]

Following general procedure **A** using α-methylstyrene (3.25 mL, 25.0 mmol, 1.00 eq.), dimethylacetamide (2.79 mL, 30.0 mmol, 1.20 eq.), Tf_2O (8.41 mL, 50.0 mmol, 2.00 eq.) and 2,6-lutidine (5.83 mL, 50.0 mmol, 2.00 eq.) the desired product was obtained *via* AFC (CyHex:EtOAc; 100:0 → 80:20) as colorless oil (3.56 g, 22.3 mmol, 89%).

Spectroscopic data was in agreement with that previously reported.[6]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 – 7.34 (m, 2H), 7.34 – 7.24 (m, 3H), 3.74 – 3.63 (m, 1H), 3.57 – 3.45 (m, 2H), 3.32 – 3.21 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)**: δ = 206.9, 148.4, 128.7, 126.4, 125.8, 59.4, 34.1, 31.2.

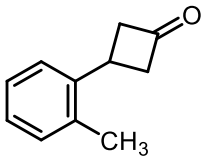


3-Methyl-3-(4-(trifluoromethyl)phenyl)cyclobutanone [1e]

Following general procedure **A** using 1-(prop-1-en-2-yl)-4-(trifluoromethyl)benzene (931 mg, 5.00 mmol, 1.00 eq.), dimethylacetamide (560 µL, 6.00 mmol, 1.20 eq.), Tf_2O (1.68 mL, 10.0 mmol, 2.00 eq.) and 2,6-lutidine (1.17 mL, 10.0 mmol, 2.00 eq.) the desired product was obtained *via* FC (pentane:Et_2O; 90:10) as colorless oil (621 mg, 2.72 mmol, 54%).

IR (neat): $\tilde{\nu}$ = 2962 (br), 2925 (br), 2871 (br), 1785 (s), 1619 (w), 1451 (w), 1411(w), 1389 (w), 1325 (s), 1300 (m), 1163 (m), 1108 (s), 1086 (s), 1064 (s), 1015 (m), 955 (w), 875 (w), 840 (m), 718 (w), 672 (w). **^{1}H NMR (599 MHz, $CDCl_3$)**: δ = 7.63 (d, J = 8.0 Hz, 2H, 2×CH_{arom}), 7.43 (d,

J = 8.0 Hz, 2H, 2×CH_{arom}), 3.51 – 3.44 (m, 2H, 2×CH_2), 3.20 – 3.13 (m, 2H, 2×CH_2), 1.63 (s, 3H, 3×CH_3). **^{13}C NMR (151 MHz, CDCl$_3$)**: δ = 205.5 (C_q), 152.3 (C_q), 128.9 (q, J = 32.5 Hz, C_q), 126.3 (2×CH$_{arom}$), 125.8 (q, J = 3.7 Hz, 2×CH$_{arom}$), 124.3 (q, J = 271.91 Hz, CF$_3$), 59.3 (2×CH$_2$), 34.3 (C_q), 31.0 (CH$_3$). **^{19}F NMR (377 MHz, CDCl$_3$)**: δ = −62.46. **HRMS (EI)**: Calculated for $C_{12}H_{11}F_3O^+$ [M]$^+$: 228.0756, found: 228.0760.



3-(2-Methylphenyl)cyclobutanone [1f]

Following general procedure **A** using 2-methylstyrene (2.18 mL, 17.0 mmol, 1.00 eq.), dimethylacetamide (1.90 mL, 20.4 mmol, 1.20 eq.), Tf_2O (5.72 mL, 34.0 mmol, 2.00 eq.) and 2,6-lutidine (3.96 mL, 34.0 mmol, 2.00 eq.) the desired product was obtained *via* FC (pentane:EtOAc; 95:5) as colorless oil (1.87 g, 11.7 mmol, 71%).

Spectroscopic data was in agreement with that previously reported.[7]

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.25 – 7.08 (m, 4H), 3.69 *(app.* p, $J \approx$ 8.3 Hz, 1H), 3.44 – 3.27 (m, 2H), 3.26 – 3.09 (m, 2H), 2.25 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)**: δ = 206.8, 140.8, 136.5, 130.6, 126.9, 126.4, 124.6, 53.1, 26.2, 20.1.

4 Synthesis of ligands

Following ligands were either commercially available or prepared according to literature procedures: **LS1**, *ent*-**L1a**, **L1b**,[8] **L2a**,[9] **L4a**,[10] **LS11**, **LS12**, **LS13**, **LS14**,[11] **LS16**,[12] **LS17**,[13] **LS19**, **LS20**,[14] **LS21**, **LS22**,[15] **LS23**.

4.1 General procedures

General procedure C: Bisamide formation

Following a modified procedure by *Evans et al.*[16], a flame dried Schlenk tube was charged with the corresponding aminoalcohol (2.00 eq.) and dry CH_2Cl_2 (0.8 M with respect to the aminoalcohol). The mixture was cooled to 0 °C and dry NEt_3 (5.00 eq.) were added. Then, a solution of the corresponding acid chloride (1.00 eq.) in dry CH_2Cl_2 (1.25 M) was added dropwise over 15 min. It was stirred at 0 °C for 30 min., before the reaction mixture was warmed to rt and stirred for 16 h. It was diluted with CH_2Cl_2 until all formed solids dissolved. It was washed with 1 M aq. HCl (1 ×). The aq. layer was extracted with CH_2Cl_2 (1 ×) and the combined org. phases were washed with sat. aq. $NaHCO_3$ sol. (1 ×). The aq. layer was extracted with CH_2Cl_2 (1 ×) and the combined org. phases were washed with brine (1 ×), dried over $MgSO_4$ filtered and concentrated *in vacuo*. The product was obtained *via* recrystallisation with the conditions given in the corresponding entry or was used without further purification.

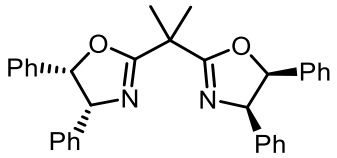
General procedure D: Synthesis of bis(oxazoline)-ligands

Following a modified procedure by *Bandini et al.*,[8] the corresponding bisamide (1.00 eq.) was suspended in dry CH_2Cl_2 (0.1 M with respect to the amide) in an oven dried Schlenk tube. The mixture was cooled to 0 °C and dry NEt_3 (5.0 eq.) was added. Then, mesyl chloride (2.50 eq.) was added dropwise. After complete addition the reaction mixture was stirred for 15 min at 0 °C before it was gradually warmed to rt and stirred for additional 16 h. Water was added and the phases were separated. The aq. layer was extracted with CH_2Cl_2 (4 ×). The combined org. phases were dried over $MgSO_4$, filtered and concentrated *in vacuo.* The residue was taken up in MeOH (0.1 M with respect to the amide). Sodium hydroxide (3.00 eq.) was added and the mixture was heated to reflux for 3 h. After cooling to rt the mixture was concentrated and water was added. It was extracted with CH_2Cl_2 (3 ×). The combined org. phases were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The product was obtained *via* FC, recrystallisation or distillation with the conditions given in the corresponding entry.

General procedure E: Alternative synthesis of bis(oxazoline)-ligands

In an oven dried Schlenk tube dimethyl malononitrile (1.00 eq.) was dissolved in dry PhMe (0.8 M with respect to the nitrile) and $Zn(OTf)_3$ (2.00 eq.) was added. The corresponding aminoalcohol (2.00 eq.) was added and the mixture was heated to 130 °C for 3 d. After cooling to rt, it was washed with sat. aq. $NaHCO_3$-sol. (1 ×) and brine (1 ×). The org. phase was dried over $MgSO_4$, filtered and concentrated *in vacuo*. The product was obtained *via* FC, recrystallisation or distillation with the conditions given in the corresponding entry.

4.2 Syntheses

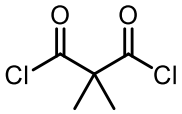


(4*R*,4'*R*,5*S*,5'*S*)-2,2'-(Propane-2,2-diyl)bis(4,5-diphenyl-4,5-dihydrooxazole) [L2b]

Following general procedure **E** using dimethyl malononitrile (90 mg, 0.96 mmol, 1.00 eq.), $Zn(OTf)_3$ (694 mg, 1.91 mmol, 2.00 eq.) and (1*S*,2*R*)-2-amino-1,2-diphenylethan-1-ol (407 mg, 1.91 mmol, 2.00 eq.) the desired product was obtained *via* FC (pentane:acetone; 80:20) as a yellow solid (212 mg, 0.436 mmol, 46%).

Spectroscopic data was in agreement with that previously reported.[17]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.02 (s, 10H), 6.96 (s, 10H), 5.97 (d, J = 10.1 Hz, 2H), 5.60 (d, J = 10.1 Hz, 2H), 1.93 (s, 6H). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 170.5, 137.6, 136.3, 128.0, 127.7, 127.5, 127.0, 126.7, 86.4, 73.9, 39.7, 24.9.

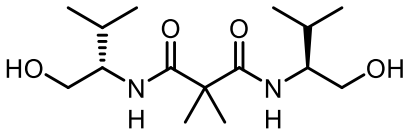


2,2-Dimethylmalonyl dichloride

Following a modified procedure by *Breising et al.*,[18] dimethylmalonic acid (1.00 g, 7.57 mmol, 1.00 eq.) was dissolved in dry CH_2Cl_2 (10 mL) under Ar-atmosphere. Then, DMF (60 µL, 0.76 mmol, 0.10 eq.) was added and the mixture was cooled to 0 °C. Oxalyl chloride (1.95 mL, 22.7 mmol, 3.00 eq.) was added *via* syringe pump over 20 min. After complete addition the reaction mixture was gradually warmed to rt and stirred for 16 h. The solvent was removed *in vacuo*. Distillation of the residue (Kugelrohr, 80 mbar, 77-85 °C) afforded the desired product as pale-yellow oil (1.16 g, 6.87 mmol, 91%).

Spectroscopic data was in agreement with that previously reported.[18]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.67 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)**: δ = 172.1, 69.2, 23.3.

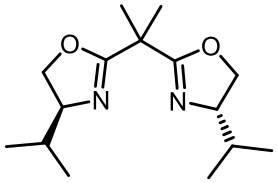


N^1,N^3-Bis((*S*)-1-hydroxy-3-methylbutan-2-yl)-2,2-dimethylmalonamide [S1]

Following general procedure **C** using L-valinol (586 mg, 5.00 mmol, 2.00 eq.), dry NEt_3 (1.73 mL, 12.5 mmol, 5.00 eq.) and 2,2-dimethylmalonyl dichloride (423 mg, 2.50 mmol, 1.00 eq.) the desired product was obtained as a colourless solid (620 mg, 2.05 mmol, 82%) and used without further purification.

Spectroscopic data was in agreement with that previously reported.[19]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.44 (d, J = 8.8 Hz, 2H), 3.86 – 3.68 (m, 4H), 3.52 (dd, J = 11.4, 7.2 Hz, 2H), 2.62 (br s, 2H), 1.80 (hept, J = 6.7 Hz, 2H), 1.49 (s, 6H), 0.98 – 0.72 (m, 12H). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 174.6, 63.5, 57.3, 50.3, 29.3, 23.9, 19.8, 18.9.

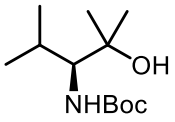


(4*S*,4'*S*)-2,2'-(Propane-2,2-diyl)bis(4-isopropyl-4,5-dihydrooxazole) [L3a]

Following general procedure **D** using amide **S1** (212 mg, 0.701 mmol, 1.00 eq.), dry NEt_3 (490 µL, 1.75 mmol, 5.00 eq.), mesyl chloride (140 µL, 3.50 mmol, 2.50 eq.) and NaOH (84.0 mg, 2.10 mmol, 3.00 eq.) the desired product was obtained *via* distillation (Kugelrohr, 1 mbar, 160 °C) as a colourless solid (173 mg, 0.650 mmol, 93%).

Spectroscopic data was in agreement with that previously reported.[20]

^{1}H NMR (400 MHz, $CDCl_3$): δ =4.20 (td, J = 7.7, 1.2 Hz, 2H), 4.03 – 3.93 (m, 4H), 1.85 – 1.75 (m, 2H), 1.51 (s, 6H), 0.91 (d, J = 6.8 Hz, 7H), 0.85 (d, J = 6.8 Hz, 6H). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 168.9, 71.6, 70.0, 38.7, 32.3, 24.6, 18.7, 17.5.



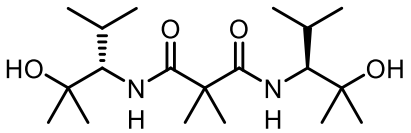
tert-Butyl (*S*)-(2-hydroxy-2,4-dimethylpentan-3-yl)carbamate [S2]

Following a procedure by *Xu et al.*,[21] Boc-L-valine methyl ester (1.40 g, 6.06 mmol, 1.00 eq.) was dissolved in dry THF (20 mL) in an oven dried Schlenk tube. It was cooled to −10 °C and methyl magnesium bromide solution (8.08 mL, 24.2 mmol, 3.00 eq., 3 M in Et_2O) was added dropwise. The mixture was gradually warmed to rt and stirred for 2 d. Then, sat. aq. $NaHCO_3$-sol. (10 mL) was added. The phases were separated and the aq. layer was extracted CH_2Cl_2 (3 × 10 mL). The

combined org. phases were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The desired product was obtained *via* AFC (CyHex:EtOAc; 90:10→70:30) as a colourless solid (1.15 g, 4.98 mmol, 82%).

Spectroscopic data was in agreement with that previously reported.[21]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.81 (d, *J* = 10.3 Hz, 1H), 3.44 – 3.33 (m, 1H), 2.10 (pd, *J* = 6.8, 2.6 Hz, 1H), 1.45 (s, 9H), 1.26 (s, 3H), 1.23 (s, 3H), 0.97 – 0.88 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)**: δ = 157.1, 79.2, 74.0, 61.9, 29.2, 28.6, 28.3, 27.2, 22.4, 17.0.



N^1,*N*^{3}-Bis((*S*)-2-hydroxy-2,4-dimethylpentan-3-yl)-2,2-dimethylmalonamide [S3]

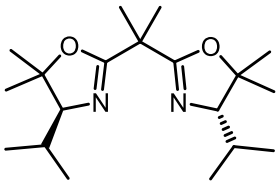
Following a procedure by *Xu et al.*,[21] amino alcohol **S2** (544 mg, 2.35 mmol, 1.00 eq.) was dissolved in MeOH (10 mL) and cooled to 0 °C. Then, conc. aq. HCl (1.18 mL, 14.1 mmol, 6.00 eq.) dissolved in MeOH (5 mL) was added dropwise. The mixture was warmed to rt and stirred for 16 h before a second portion of conc. aq. HCl (1.18 mL, 14.1 mmol, 6.00 eq.) dissolved in MeOH (5 mL) was added. It was stirred for additional 20 h. Then, it was cooled to 0 °C and NaOH (1.14 g, 28.2 mmol, 12.0 eq.) was added. After 15 min of stirring the formed precipitate was filtered off and the filter cake was washed with CH_2Cl_2. The filtrate was dried over $MgSO_4$, filtered and concentrated *in vacuo*. (*S*)-3-amino-2,4-dimethylpentan-2-ol was obtained *via* distillation (Kugelrohr, 45 mbar, 90–98 °C) as a colourless oil (252 mg, 1.92 mmol, 82%) and used in the next step.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.42 (d, *J* = 2.9 Hz, 1H), 1.93 (heptd, *J* = 6.9, 2.9 Hz, 1H), 1.20 (s, 3H), 1.12 (s, 3H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.89 (d, *J* = 6.8 Hz, 3H).

Following general procedure **C** using (*S*)-3-amino-2,4-dimethylpentan-2-ol (560 mg, 4.78 mmol, 2.00 eq.), dry NEt_3 (1.66 mL, 12.0 mmol, 5.00 eq.) and 2,2-dimethylmalonyl dichloride (404 mg, 2.39 mmol, 1.00 eq.) the desired product was obtained as an off-white solid (649 mg, 1.97 mmol, 82%) and used without further purification.

Spectroscopic data was in agreement with that previously reported.[22]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.99 (d, *J* = 9.8 Hz, 2H), 3.77 (dd, *J* = 9.8, 2.6 Hz, 2H), 2.13 (heptd, *J* = 6.8, 2.6 Hz, 2H), 1.56 (s, 6H), 1.24 (s, 6H), 1.18 (s, 7H), 0.93 (d, *J* = 6.8 Hz, 6H), 0.91 (d, *J* = 6.8 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)**: δ = 174.6, 74.0, 60.8, 50.1, 29.4, 28.3, 26.7, 24.6, 22.6, 17.0.

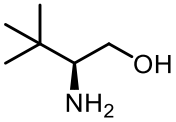


(4*S*,4'*S*)-2,2'-(Propane-2,2-diyl)bis(4-isopropyl-5,5-dimethyl-4,5-dihydrooxazole) [LS2]

According to a procedure by *Bennett et al.*,[22] an oven dried Schlenk tube was charged with 4 Å molecular sieves. Amide **S3** (81 mg, 0.23 mmol, 1.00 eq.) and dry CH_2Cl_2 (2 mL) were added followed by methanesulphonic acid (60 µL, 0.92 mmol, 4.00 eq.). Then, the mixture was heated to 40 °C for 3 h. After cooling to rt, sat. aq. $NaHCO_3$ sol. (2 mL) was added and the phases were separated. The aq. layer was extracted with CH_2Cl_2 (3 × 5 mL). The combined org. phases were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The desired product was obtained *via* FC (CH_2Cl_2:MeOH; 90:10) as a pale-yellow oil (52 mg, 0.16 mmol, 72%).

Spectroscopic data was in agreement with that previously reported.[22]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.30 (d, *J* = 6.6 Hz, 2H), 1.83 – 1.70 (m, 2H), 1.45 (d, *J* = 2.7 Hz, 6H), 1.33 (s, 6H), 1.28 (s, 6H), 0.98 (dd, *J* = 6.6, 1.2 Hz, 12H). **^{13}C NMR (101 MHz, $CDCl_3$)**: δ = 167.4, 86.3, 79.2, 38.6, 29.2, 29.1, 23.8, 21.4, 21.1, 19.5.

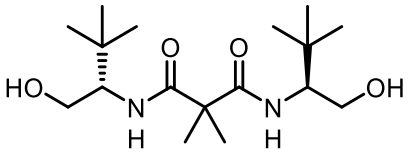


(*S*)-*tert*-Leucinol

According to a procedure by *McKennon et al.*,[23] *tert*-leucine (4.00 g, 30.5 mmol, 1.00 eq.) and $NaBH_4$ (2.77 g, 73.2 mmol, 2.40 eq.) were suspended in dry THF (80 mL). The mixture was cooled to 0 °C and a solution of iodine (7.74 g, 30.5 mmol, 1.00 eq.) in dry THF (30 mL) is added dropwise over 30 min. After complete addition, it was heated to reflux for 18 h. The reaction mixture was allowed to cool to rt and MeOH (20 mL) was added forming a clear solution. It was stirred for further 30 min before the solvent was removed *in vacuo*. The resulting white paste was dissolved in 20% aq. KOH solution (70 mL) and it was stirred for four hours. Thereafter, it was extracted with CH_2Cl_2 (3 × 50 mL). The combined org. layers were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified via distillation (Kugelrohr, 0.6 mbar, 65–85°C). The product was obtained as a colourless solid (2.96 g, 25.2 mmol, 84%).

Spectroscopic data was in agreement with that previously reported.[24]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.70 (dd, *J* = 10.2, 3.9 Hz, 1H), 3.20 (t, *J* = 10.2 Hz, 1H), 2.51 (dd, *J* = 10.2, 3.9 Hz, 1H), 1.90 (s, 3H), 0.89 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)**: δ = 62.4, 61.8, 33.2, 26.4.

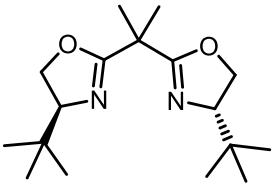


N^1,N^3-Bis((*S*)-1-hydroxy-3,3-dimethylbutan-2-yl)-2,2-dimethylmalonamide [S4]

Following general procedure **C** using (*S*)-*tert*-leucinol (560 mg, 4.78 mmol, 2.00 eq.), dry NEt_3 (1.66 mL, 12.0 mmol, 5.00 eq.) and 2,2-dimethylmalonyl dichloride (404 mg, 2.39 mmol, 1.00 eq.) the desired product was obtained as a colourless solid (649 mg, 1.97 mmol, 82%) and used without further purification.

Spectroscopic data was in agreement with that previously reported.[16]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.43 (d, *J* = 9.6 Hz, 2H), 3.93 – 3.80 (m, 4H), 3.51 – 3.29 (m, 2H), 1.51 (s, 6H), 0.93 (s, 18H). **^{13}C NMR (101 MHz, $CDCl_3$)**: δ = 175.0, 62.5, 59.7, 50.4, 33.6, 26.9, 23.9.

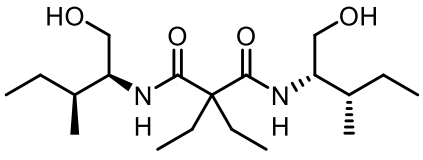


(4*S*,4'*S*)-2,2'-(Propane-2,2-diyl)bis(4-(*tert*-butyl)-4,5-dihydrooxazole) [LS3]

Following general procedure **D** using amide **S4** (628 mg, 1.90 mmol, 1.00 eq.), dry NEt_3 (1.32 mL, 9.50 mmol, 5.00 eq.), mesyl chloride (370 µL, 4.75 mmol, 2.50 eq.) and NaOH (228 mg, 5.70 mmol, 3.00 eq.) the desired product was obtained as a pale-yellow oil (491 mg, 1.67 mmol, 88%). No further purification was required.

Spectroscopic data was in agreement with that previously reported.[16,24]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.21 – 3.98 (m, 4H), 3.83 (dd, *J* = 10.0, 6.9 Hz, 2H), 1.50 (s, 6H), 0.86 (s, 18H). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 168.7, 75.4, 69.1, 38.7, 34.0, 25.7, 24.5.



N^1,N^3-Bis((2*S*,3*S*)-1-hydroxy-3-methylpentan-2-yl)-2,2-diethylmalonamide [S5]

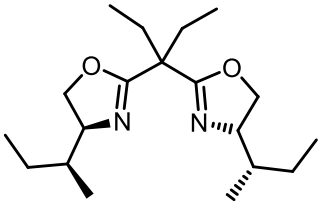
Following a modified procedure by *Breising et al.*,[18] diethylmalonic acid (801 mg, 5.00 mmol, 1.00 eq.) was dissolved in dry CH_2Cl_2 (7 mL) under Ar-atmosphere. Then, DMF (40 µL, 0.50 mmol, 0.10 eq.) was added and the mixture was cooled to 0 °C. Oxalyl chloride (1.29 mL, 15.0 mmol, 3.00 eq.) was added *via* syringe pump over 20 min. After complete addition the reaction mixture was gradually warmed to rt and stirred for 16 h. The solvent was removed *in vacuo*. Distillation of

the residue (Kugelrohr, 60 mbar, 110 °C) afforded diethylmalonyl dichloride as colourless oil (791 mg, 4.02 mmol, 80%), which was used in the next step.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.17 (q, J = 7.6 Hz, 2H), 0.91 (t, J = 7.6 Hz, 3H).

Following general procedure **C** using L-isoleucinol (938 mg, 8.00 mmol, 2.00 eq.), dry NEt_3 (2.77 mL, 20.0 mmol, 5.00 eq.) and 2,2-diethylmalonyl dichloride (788 mg, 4.00 mmol, 1.00 eq.) the desired product was obtained as a colourless solid (1.38 g, 3.84 mmol, 96%) and used without further purification.

M.P.: 128–129 °C. **IR (neat)**: $\tilde{\nu}$ = 3350 (w), 2968 (w), 2880 (w), 2360 (w), 1654 (w), 1522 (w), 1461 (w), 1385 (w), 1216 (m), 1075 (w), 1049 (w), 753 (s), 667 (w), 624 (w). **^{1}H NMR (599 MHz, $CDCl_3$)**: δ = 6.84 (d, J = 8.6 Hz, 2H, 2×N*H*), 3.87 (qd, J = 7.3, 3.1 Hz, 2H, 2×C*H*), 3.78 – 3.69 (m, 2H, 2×CH_2), 3.59 – 3.53 (m, 2H, 2×CH_2), 3.39 (br s, 2H, 2×O*H*), 2.03 – 1.83 (m, 4H, 4×CH_2), 1.68 – 1.55 (m, 2H, 2×C*H*), 1.55 – 1.41 (m, 2H, 2×CH_2), 1.21 – 1.08 (m, 2H, 2×CH_2), 0.92 (d, J = 6.8 Hz, 6H, 6×CH_3), 0.89 (t, J = 7.4 Hz, 6H, 6×CH_3), 0.86 (t, J = 7.5 Hz, 6H, 6×CH_3). **^{13}C NMR (151 MHz, $CDCl_3$)**: δ = 173.9 (2×C_q), 63.8 (2×CH$_2$), 58.6 (C_q), 56.1 (2×CH), 35.6 (2×CH), 27.5 (2×CH$_2$), 25.6 (2×CH$_2$), 15.8 (2×CH$_3$), 11.2 (2×CH$_3$), 8.9 (2×CH$_3$). **HRMS (ESI)**: Calculated for $C_{19}H_{38}N_2O_4Na^+$ [M+Na]$^+$: 381.2724, found: 381.2418.

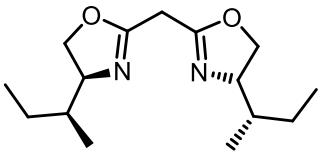


(4*S*,4'*S*)-2,2'-(Pentane-3,3-diyl)bis(4-((*S*)-*sec*-butyl)-4,5-dihydrooxazole) [L4b]

Following general procedure **D** using amide **S5** (1.36 g, 3.80 mmol, 1.00 eq.), dry NEt_3 (2.65 mL, 19.0 mmol, 5.00 eq.), mesyl chloride (0.74 mL, 9.50 mmol, 2.50 eq.) and NaOH (456 mg, 11.4 mmol, 3.00 eq.) the desired product was obtained as a pale-yellow oil (1.15 g, 3.56 mmol, 94%). No further purification was required.

Spectroscopic data was in agreement with that previously reported.[25]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.19 – 4.06 (m, 4H), 3.97 – 3.90 (m, 2H), 2.08 – 1.88 (m, 4H), 1.74 – 1.60 (m, 2H), 1.50 – 1.36 (m, 2H), 1.25 – 1.08 (m, 2H), 0.91 (t, J = 7.4 Hz, 7H), 0.87 – 0.76 (m, 12H). **^{13}C NMR (101 MHz, $CDCl_3$)**: δ = 167.3, 70.4, 69.0, 46.7, 38.7, 26.4, 25.2, 14.1, 11.9, 8.4.

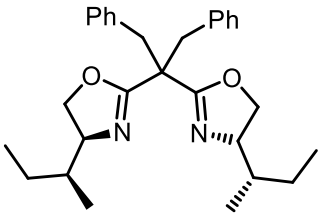


Bis((*S*)-4-((*S*)-*sec*-butyl)-4,5-dihydrooxazol-2-yl)methane [LS4]

According to a procedure by *Synder et at.*,[26] diethyl malonimidate dihydrochloride (1.16 g, 5.00 mmol, 1.00 eq.) and L-isoleucinol (1.33 g, 10.5 mmol, 2.10 eq.) were dissolved in CH_2Cl_2 (50 mL) and stirred at 40 °C for 24 h. Then, the mixture was poured into water (100 mL) and it was extracted with CH_2Cl_2 (4 × 25 mL). The combined org. phases were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The desired product was obtained *via* FC (CH_2Cl_2:MeOH; 95:5) as a yellow oil (622 mg, 2.24 mmol, 47%).

Spectroscopic data was in agreement with that previously reported.[27]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.30 – 4.16 (m, 2H), 4.10 – 3.95 (m, 4H), 3.33 (s, 2H), 1.68 – 1.42 (m, 4H), 1.23 – 1.10 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 6H), 0.81 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)**: δ = 161.6, 70.8, 70.1, 38.9, 28.5, 26.0, 14.2, 11.4.



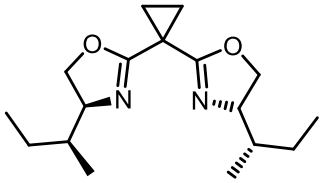
(4*S*,4'*S*)-2,2'-(1,3-Diphenylpropane-2,2-diyl)bis(4-((*S*)-*sec*-butyl)-4,5-dihydro-oxazole) [L4c]

Following a modified procedure by *Barnes et al.*,[28] bis(oxazoline) **LS4** (133 mg, 0.500 mmol, 1.00 eq.) was dissolved in dry THF (2.5 mL) in a flame dried Schlenk tube and placed in a cold water bath. Benzyl bromide (120 µL, 1.03 mmol, 2.05 eq.) was added followed by dropwise addition of LiHMDS (0.51 mL, 0.51 mmol, 1.02 eq., 1.0 M in PhMe). The mixture was stirred for 1 h remaining the temperature below 25 °C. Then, a second portion of LiHMDS (0.83 mL, 0.83 mmol, 1.70 eq., 1.0 M in PhMe) was added dropwise over 30 min *via* syringe pump. The reaction mixture was then stirred at rt for 16 h. Sat. aq. NH_4Cl-sol. (5 mL) was added. The phases were separated and the aq. layer was extracted with EtOAc (3 × 10 mL). The combined org. phases were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The desired product was obtained *via* FC (pentane:Et_2O; 100:0 → 0:100) as a yellow oil (196 mg, 0.438 mmol, 88%).

Spectroscopic data was in agreement with that previously reported.[29]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 – 7.18 (m, 10H), 4.21 – 4.09 (m, 2H), 4.07 – 3.95 (m, 2H), 3.95 – 3.85 (m, 2H), 3.39 (d, *J* = 14.1 Hz, 2H), 3.24 (d, *J* = 14.2 Hz, 2H), 1.61 – 1.49 (m, 2H), 1.49 – 1.38

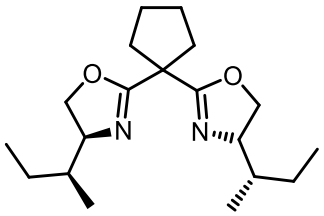
(m, 2H), 1.18 – 1.03 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 6H), 0.74 (d, *J* = 6.8 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)**: δ = 166.2, 137.1, 130.6, 128.1, 126.7, 70.7, 69.4, 48.3, 39.2, 38.9, 26.4, 14.3, 11.8.



(4*S*,4'*S*)-2,2'-(Cyclopropane-1,1-diyl)bis(4-((*S*)-*sec*-butyl)-4,5-dihydrooxazole) [LS5a]

Following a modified procedure by *Hofstra et al.*,[28] sodium hydride (174 mg, 4.34 mmol, 3.00 eq., 60% on mineral oil) was suspended in dry THF (6 mL) in a flame dried Schlenk tube and cooled to 0 °C. Bis(oxazoline) **LS4** (385 mg, 1.45 mmol, 1.00 eq.) dissolved in dry THF (5 mL) was added dropwise. The mixture was stirred at 0 °C for 30 min before it was allowed to warm to rt. Then, dibromoethane (190 µL, 2.17 mmol, 1.50 eq.) was added slowly and the reaction mixture was heated to 50 °C for 16 h. After cooling to rt water was added. The phases were separated and the aq. layer was extracted with CH_2Cl_2 (3 × 10 mL). the combined org. phases were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The desired product was obtained *via* FC (Et_2O:CH_2Cl_2:MeOH; 88:10:2) as a pale-yellow resin (88 mg, 0.30 mmol, 21%).

IR (neat): $\tilde{\nu}$ = 3342 (w), 2967 (m), 2929 (w), 2877 (w), 1709 (w), 1659 (s), 1556 (m), 1463 (w), 1382 (w), 1260 (w), 1216 (w), 1120 (m), 1035 (w), 980 (w), 850 (w), 802 (w), 753 (s), 666 (w), 646 (w), 625 (w), 616 (w), 594 (w), 584 (w). **^{1}H NMR (599 MHz, $CDCl_3$)**: δ = 4.25 – 4.15 (m, 2H, 2×CH_2), 4.06 – 3.97 (m, 4H, 2×CH_2, 2×CH), 1.65 – 1.54 (m, 2H, 2×CH), 1.51 – 1.44 (m, 2H, 2×CH_2), 1.44 – 1.41 (m, 2H, 2×CH_2), 1.36 – 1.30 (m, 2H, 2×CH_2), 1.18 – 1.09 (m, 2H, 2×CH_2), 0.89 (t, *J* = 7.4 Hz, 6H, 2×CH_3), 0.78 (d, *J* = 6.8 Hz, 6H, 2×CH_3). **^{13}C NMR (151 MHz, $CDCl_3$)**: δ = 165.5 (2×C_q), 70.4 (2×*C*H), 69.9 (2×*C*H_2), 38.9 (2×*C*H), 26.1 (2×*C*H_2), 18.4 (C_q), 15.4 (2×*C*H_2), 14.1 (2×*C*H_3), 11.8 (2×*C*H_3). **HRMS (ESI)**: Calculated for $C_{17}H_{28}N_2O_2Na^+$ $[M+Na]^+$: 315.2043, found: 315.2029. **Optical Rotaion**: $[\alpha]_D^{25}$ = −80.8 (*c* = 1.00, $CHCl_3$).

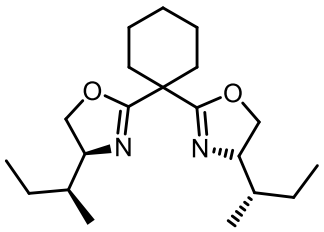


(4*S*,4'*S*)-2,2'-(Cyclopentane-1,1-diyl)bis(4-((*S*)-*sec*-butyl)-4,5-dihydrooxazole) [LS5b]

Following a modified procedure by *Barnes et al.*,[28] bis(oxazoline) **LS4** (266 mg, 1.00 mmol, 1.00 eq.) was dissolved in dry THF (5 mL) in a flame dried Schlenk tube and placed in a cold water

bath. Dibromobutane (240 µL, 2.05 mmol, 2.05 eq.) was added followed by dropwise addition of LiHMDS (1.02 mL, 1.02 mmol, 1.02 eq., 1.0 M in PhMe). The mixture was stirred for 1 h remaining the temperature below 25 °C. Then, a second portion of LiHMDS (1.70 mL, 1.70 mmol, 1.70 eq., 1.0 M in PhMe) was added dropwise over 30 min *via* syringe pump. The reaction mixture was then stirred at rt for 16 h. Sat. aq. NH_4Cl-sol. (5 mL) was added. The phases were separated and the aq. layer was extracted with EtOAc (3 × 20 mL). The combined org. phases were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The desired product was obtained as a yellow oil (234 mg, 0.730 mmol, 73%). No further purification was required.

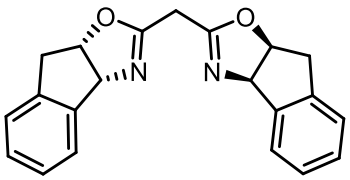
IR (neat): $\tilde{\nu}$ = 3399 (w), 2962 (s), 2876 (m), 2358 (w), 2340 (w), 2328 (w), 1736 (w), 1656 (s), 1523 (m), 1463 (m), 1380 (w), 1357 (w), 1248 (m), 1155 (m), 1060 (w), 1003 (m), 964 (m), 907 (w), 761 (w), 747 (w). **^{1}H NMR (500 MHz, $CDCl_3$)**: δ = 4.18 (dd, J = 9.7, 8.0 Hz, 2H, 2×CH_2), 4.08 (ddd, J = 9.7, 7.2, 5.1 Hz, 2H, 2×CH), 3.98 (dd, J = 8.0, 7.2 Hz, 2H, 2×CH_2), 2.38 – 2.28 (m, 2H, 2×CH_2), 2.21 – 2.09 (m, 2H, 2×CH_2), 1.79 – 1.69 (m, 4H, 4×CH_2), 1.69 – 1.58 (m, 2H, 2×CH), 1.48 – 1.36 (m, 2H, 2×CH_2), 1.20 – 1.10 (m, 2H, 2×CH_2), 0.90 (t, J = 7.5 Hz, 6H, 6×CH_3), 0.78 (d, J = 6.8 Hz, 6H, 6×CH_3). **^{13}C NMR (126 MHz, $CDCl_3$)**: δ = 168.2 (2×C_q), 70.2 (2×CH), 69.6 (2×CH$_2$), 49.2 (C_q), 38.7 (2×CH), 35.6 (2×CH$_2$), 26.2 (2×CH$_2$), 25.1 (2×CH$_2$), 13.9 (2×CH$_3$), 11.9 (2×CH$_3$). **HRMS (ESI)**: Calculated for $C_{17}H_{28}N_2O_2Na^+$ $[M+Na]^+$: 343.2356, found: 343.2352. **Optical rotation**: $[\alpha]_D^{25}$ = −64.9 (c = 1.00, $CHCl_3$).



(4*S*,4'*S*)-2,2'-(Cyclohexane-1,1-diyl)bis(4-((*S*)-*sec*-butyl)-4,5-dihydrooxazole) [LS5c]

Following a modified procedure by *Barnes et al.*,[28] bis(oxazoline) **LS4** (175 mg, 0.655 mmol, 1.00 eq.) was dissolved in dry THF (3.3 mL) in a flame dried Schlenk tube and placed in a cold water bath. Dibromopentane (180 µL, 1.34 mmol, 2.05 eq.) was added followed by dropwise addition of LiHMDS (0.67 mL, 0.67 mmol, 1.02 eq., 1.0 M in PhMe). The mixture was stirred for 1 h remaining the temperature below 25 °C. Then, a second portion of LiHMDS (1.09 mL, 1.09 mmol, 1.70 eq., 1.0 M in PhMe) was added dropwise over 30 min *via* syringe pump. The reaction mixture was then stirred at rt for 16 h. Sat. aq. NH_4Cl-sol. (5 mL) was added. The phases were separated and the aq. layer was extracted with EtOAc (3 × 15 mL). The combined org. phases were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The desired product was obtained *via* FC (pentane:Et_2O; 50:50) as a yellow oil (165 mg, 0.493 mmol, 75%).

IR (neat): $\tilde{\nu}$ = 3400 (m), 2957 (s), 2928 (s), 2878 (m), 1739 (w), 1655 (s), 1518 (m), 1463 (m), 1379 (w), 1348 (w), 1228 (m), 1211 (m), 1128 (m), 1057 (m), 1047 (m), 1034 (m), 1013 (w), 1002 (w), 979 (s), 955 (w), 941 (w), 906 (w), 894 (w). **^{1}H NMR (500 MHz, $CDCl_3$)**: δ = 4.18 – 4.07 (m, 4H, 2×CH_2, 2×CH), 3.99 – 3.93 (m, 2H, 2×CH_2), 2.12 – 2.04 (m, 2H, 2×CH_2), 2.01 – 1.93 (m, 2H, 2×CH_2), 1.72 – 1.65 (m, 2H, 2×CH), 1.65 – 1.57 (m, 2H, 2×CH_2), 1.56 – 1.47 (m, 1H, 2×CH_2), 1.47 – 1.37 (m, 4H, 4×CH_2), 1.21 – 1.09 (m, 2H, 2×CH_2), 0.91 (t, J = 7.4 Hz, 6H, 6×CH_3), 0.80 (d, J = 6.8 Hz, 6H, 6×CH_3). **^{13}C NMR (126 MHz, $CDCl_3$)**: δ = 167.6 (2×C_q), 70.4 (2×CH), 69.0 (2×CH$_2$), 43.3 (C_q), 38.7 (2×CH), 32.8 (2×CH$_2$), 26.3 (2×CH$_2$), 25.6 (CH$_2$), 22.8 (2×CH$_2$), 14.0 (2×CH$_3$), 11.9 (2×CH$_3$). **HRMS (ESI)**: Calculated for $C_{17}H_{28}N_2O_2Na^+$ [M+Na]$^+$: 357.2513, found: 357.2509. **Optical rotation**: $[\alpha]_D^{25}$ = −61.5 (c = 1.00, $CHCl_3$).

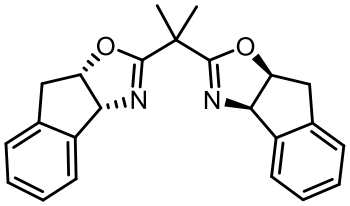


Bis((3a*R*,8a*S*)-3a,8a-dihydro-8-indeno[1,2-*d*]oxazol-2-yl)methane [LS6a]

According to a procedure by *Synder et at.*,[26] diethyl malonimidate dihydrochloride (578 mg, 2.50 mmol, 1.00 eq.) and (1*R*,2*S*)-1-amino-2,3-dihydro-1H-inden-2-ol (783 mg, 5.52 mmol, 2.10 eq.) were dissolved in CH_2Cl_2 (25 mL) and stirred at 40 °C for 18 h. Then, the mixture was poured into water (50 mL) and it was extracted with CH_2Cl_2 (4 × 10 mL). The combined org. phases were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The desired product was obtained *via* recrystallisation from hot *i*PrOH as white needles (478 mg, 1.45 mmol, 56%).

Spectroscopic data was in agreement with that previously reported.[26]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 – 7.43 (m, 2H), 7.28 – 7.22 (m, 6H), 5.57 (d, J = 7.9 Hz, 2H), 5.34 (ddd, J = 8.2, 7.0, 1.8 Hz, 2H), 3.39 (dd, J = 18.0, 7.0 Hz, 2H), 3.26 (d, J = 1.0 Hz, 2H), 3.16 (dd, J = 18.0, 1.7 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)**: δ = 162.1, 141.7, 139.8, 128.6, 127.6, 125.6, 125.4, 83.7, 76.7, 39.8, 28.8.



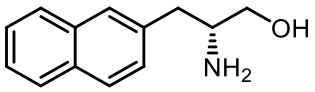
(3a*R*,3a'*R*,8a*S*,8a'*S*)-2,2'-(Propane-2,2-diyl)bis(3a,8a-dihydro-8*H*-indeno[1,2-d]-oxazole) [LS6b]

Following general procedure **E** using dimethyl malononitrile (47 mg, 0.50 mmol, 1.00 eq.), $Zn(OTf)_3$ (364 mg, 1.00 mmol, 2.00 eq.) and (1*R*,2*S*)-1-amino-2,3-dihydro-1H-inden-2-ol (149 mg,

1.00 mmol, 2.00 eq.) the desired product was obtained *via* recrystallisation from hot EtOH as an off-white solid (115 mg, 0.320 mmol, 64%).

Spectroscopic data was in agreement with that previously reported.[30]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 – 7.46 (m, 2H), 7.32 – 7.18 (m, 6H), 5.54 – 5.49 (m, 2H), 5.34 – 5.20 (m, 2H), 3.30 (dd, *J* = 17.9, 7.1 Hz, 2H), 3.05 – 2.85 (m, 2H), 1.42 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)**: δ = 169.3, 142.0, 139.9, 128.5, 127.5, 125.8, 125.2, 83.3, 76.6, 39.8, 38.6, 24.0.

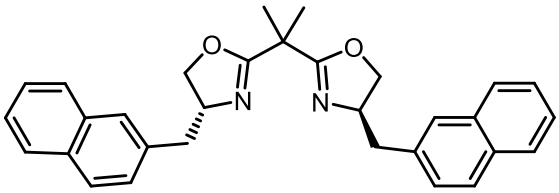


(*R*)-2-Amino-3-(naphthalen-2-yl)propan-1-ol [S6]

According to a procedure by *Slattery et at.*,[31] $LiAlH_4$ (380 mg, 10.0 mmol, 5.00 eq.) was suspended in dry THF (40 mL) and cooled to 0 °C. (*R*)-3-(2-Naphthyl)-alanine (431 mg, 2.00 mmol, 1.00 eq.) was added in small portions. After complete addition, the mixture was stirred at 0 °C for 1 h and afterwards heated to 66 °C for 16 h. After cooling to rt, water (0.5 mL) was added dropwise followed by aq. NaOH (10%, 0.5 mL) and additional water (1.5 mL). The mixture was stirred until a white suspension was observed. The mixture was filtered, the precipitate collected and heated to reflux in THF for 1 h. It was filtered again and the combined filtrates were concentrated. The residue was taken up in CH_2Cl_2 (40 mL) and washed with brine (40 mL). The aq. layer was extracted with CH_2Cl_2 (30 mL) and the combined org. phases were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The desired product was obtained as an off-white solid (402 mg, 2.00 mmol, 99%) and used without further purification.

Spectroscopic data was in agreement with that previously reported.[31]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87 – 7.73 (m, 4H), 7.68 – 7.59 (m, 1H), 7.53 – 7.39 (m, 2H), 7.32 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.98 (d, *J* = 0.8 Hz, 0H), 3.68 (dd, *J* = 10.6, 3.9 Hz, 1H), 3.44 (dd, *J* = 10.6, 7.1 Hz, 1H), 3.30 – 3.18 (m, 1H), 2.96 (dd, *J* = 13.5, 5.3 Hz, 1H), 2.71 (dd, *J* = 13.5, 8.6 Hz, 1H), 2.00 (br s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 135.8, 133.6, 132.4, 128.5, 127.9, 127.8, 127.6, 127.6, 126.3, 125.7, 65.9, 54.3, 40.6.



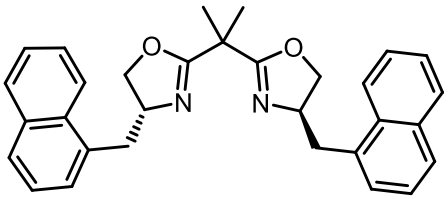
(4*R*,4'*R*)-2,2'-(Propane-2,2-diyl)bis(4-(naphthalen-2-ylmethyl)-4,5-dihydrooxazole) [*ent*-LS7]

Following general procedure **E** using dimethyl malononitrile (94 mg, 1.00 mmol, 1.00 eq.), $Zn(OTf)_3$ (727 mg, 2.00 mmol, 2.00 eq.) and aminoalcohol **S6** (403 mg, 2.00 mmol, 2.00 eq.) the

desired product was obtained *via* FC (pentane:EtOAc; 50:50 → 0:100) and crystallisation from $CHCl_3$/MeOH as a white solid (289 mg, 0.625 mmol, 63%).

Spectroscopic data was in agreement with that previously reported.[31]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.86 – 7.70 (m, 6H), 7.62 (d, *J* = 1.8 Hz, 2H), 7.52 – 7.39 (m, 4H), 7.33 (dd, *J* = 8.4, 1.7 Hz, 2H), 4.60 – 4.41 (m, 2H), 4.13 (dd, *J* = 9.3, 8.5 Hz, 2H), 4.00 (dd, *J* = 8.5, 7.0 Hz, 2H), 3.24 (dd, *J* = 13.7, 4.7 Hz, 2H), 2.83 (dd, *J* = 13.7, 8.4 Hz, 2H), 1.47 (s, 6H). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 169.6, 135.3, 133.6, 132.3, 128.1, 128.0, 128.0, 127.7, 127.6, 126.2, 125.6, 72.1, 67.0, 41.5, 38.7, 24.3.



(4*R*,4'*R*)-2,2'-(Propane-2,2-diyl)bis(4-(naphthalen-1-ylmethyl)-4,5-dihydrooxazole) [*ent*-LS8]

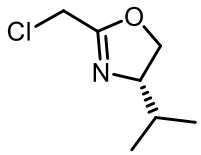
According to a procedure by *Slattery et at.*,[31] $LiAlH_4$ (380 mg, 10.0 mmol, 5.00 eq.) was suspended in dry THF (40 mL) and cooled to 0 °C. (*R*)-3-(1-Naphthyl)-alanine (431 mg, 2.00 mmol, 1.00 eq.) was added in small portions. After complete addition, the mixture was stirred at 0 °C for 1 h and afterwards heated to 66 °C for 16 h. After cooling to rt, water (0.5 mL) was added dropwise followed by aq. NaOH (10%, 0.5 mL) and additional water (1.5 mL). The mixture was stirred until a white suspension was observed. The mixture was filtered, the precipitate collected and heated to reflux in THF for 1 h. It was filtered again and the combined filtrates were concentrated. The residue was taken up in CH_2Cl_2 (40 mL) and washed with brine (40 mL). The aq. layer was extracted with CH_2Cl_2 (30 mL) and the combined org. phases were dried over $MgSO_4$, filtered and concentrated *in vacuo*. (*R*)-2-Amino-3-(naphthalen-1-yl)propan-1-ol was obtained as brown solid (388 mg, 1.93 mmol, 96%) and used without further purification.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.11 – 7.99 (m, 1H), 7.90 – 7.84 (m, 1H), 7.75 (dt, *J* = 8.2, 1.1 Hz, 1H), 7.57 – 7.47 (m, 2H), 7.46 – 7.39 (m, 1H), 7.34 (dd, *J* = 7.0, 1.3 Hz, 1H), 3.71 (dd, *J* = 10.6, 3.7 Hz, 1H), 3.49 (dd, *J* = 10.6, 6.5 Hz, 1H), 3.38 – 3.25 (m, 2H), 3.03 – 2.89 (m, 1H), 1.93 (br s, 3H).

Following general procedure **E** using dimethyl malononitrile (86 mg, 0.91 mmol, 1.00 eq.), $Zn(OTf)_3$ (661 mg, 1.82 mmol, 2.00 eq.) and (*R*)-2-Amino-3-(naphthalen-1-yl)propan-1-ol (367 mg, 1.82 mmol, 2.00 eq.) the desired product was obtained *via* FC (CH_2Cl_2:MeOH; 97:3 and Et_2O:pentane; 80:20 → 100:0) as a brown resin (283 mg, 0.612 mmol, 67%).

IR (neat): $\tilde{\nu}$ = 3003 (w), 2360 (w), 2336 (w), 1653 (m), 1510 (w), 1396 (w), 1357 (w), 1259 (w), 1216 (w), 1148 (w), 1119 (w), 973 (w), 930 (w), 749 (s), 667 (w). **^{1}H NMR (599 MHz, $CDCl_3$)**: δ = 8.17 – 8.13 (m, 2H, 2×CH_{arom}), 7.85 (dd, *J* = 8.0, 1.6 Hz, 2H, 2×CH_{arom}), 7.75 (d, *J* = 8.2 Hz, 2H,

2×CH_{arom}), 7.52 (ddd, J = 8.4, 6.8, 1.6 Hz, 2H, 2×CH_{arom}), 7.49 (ddd, J = 8.1, 6.8, 1.4 Hz, 2H, 2×CH_{arom}), 7.40 (dd, J = 8.2, 7.0 Hz, 2H, 2×CH_{arom}), 7.34 – 7.31 (m, 2H, 2×CH_{arom}), 4.61 (dtd, J = 9.4, 7.9, 4.6 Hz, 2H, 2×CH), 4.12 – 4.08 (m, 4H, 4×CH_2), 3.69 (dd, J = 14.1, 4.7 Hz, 2H, 2×CH_2), 2.96 (dd, J = 14.1, 9.4 Hz, 2H, 2×CH_2), 1.51 (s, 6H, 6×CH_3). **^{13}C NMR (151 MHz, $CDCl_3$)**: δ = 169.7 (2×C_q), 134.1 (2×C_q), 134.0 (2×C_q), 132.3 (2×C_q), 128.9 (2×CH$_{arom}$), 127.6 (2×CH$_{arom}$), 127.3 (2×CH$_{arom}$), 126.1 (2×CH$_{arom}$), 125.8 (2×CH$_{arom}$), 125.5 (2×CH$_{arom}$), 124.2 (2×CH$_{arom}$), 72.4 (2×CH$_2$), 66.4 (2×CH$_2$), 38.8 (2×CH$_2$), 38.8 (C_q), 24.4 (2×CH$_3$). **HRMS (ESI)**: Calculated for $C_{17}H_{28}N_2O_2Na^+$ $[M+Na]^+$: 485.2120, found: 485.2192. **Optical rotation**: $[\alpha]_D^{25}$ = +19.8 (c = 1.00, $CHCl_3$).



(*S*)-2-(Chloromethyl)-4-isopropyl-4,5-dihydrooxazole [S7]

A solution of chloroacetonitrile (4.17 mL, 66.0 mmol, 1.00 eq.) and EtOH (4.24 mL, 72.6 mmol, 1.10 eq.) in dry Et_2O (10 mL) was cooled to −10 °C. Then, $HCl_{(g)}$ was bubbled through the solution until a white precipitation was observed. The suspension was degassed with argon before the solids were collected *via* filtration and washed with cold Et_2O, affording ethyl 2-chloroacetimidate hydrochloride as a white solid. Additional crops of the product were obtained from precipitation of the motherliquor in the cold (7.16 g, 45.3 mmol, 69% in total).

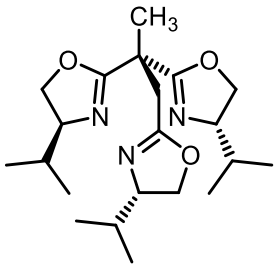
^{1}H NMR (400 MHz, DMSO-d_6): δ = 4.37 (s, 2H), 4.16 (q, J = 7.1 Hz, 2H), 1.21 (t, J = 7.1 Hz, 3H).

According to a procedure by *Ye et at.*,[32] ethyl 2-chloroacetimidate hydrochloride (869 mg, 5.50 mmol, 1.10 eq.) was suspended in dry CH_2Cl_2 (15 mL) and L-valinol (516 mg, 5.00 mmol, 1.00 eq.) was added. The mixture was cooled to 0 °C and NEt_3 (0.76 mL, 5.5 mmol, 1.10 eq.) was added. The reaction mixture was gradually warmed to rt and stirred for 16 h. The solvent was removed *in vacuo* and the residue was extracted with EtOAc (3 × 20 mL). The combined org. phases were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The desired product was obtained *via* FC (pentane:EtOAc; 80:20) as a colourless oil (432 mg, 2.68 mmol, 53%).

Spectroscopic data was in agreement with that previously reported.[32]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.35 (dd, J = 9.7, 8.4 Hz, 1H), 4.11 (s, 2H), 4.10 – 4.01 (m, 1H), 4.01 – 3.92 (m, 1H), 1.84 – 1.70 (m, J = 6.7 Hz, 1H), 0.97 (d, J = 6.7 Hz, 3H), 0.89 (d, J = 6.8 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.5, 72.5, 71.3, 36.5, 32.5, 18.8, 18.2.



(4*S*,4'*S*,4''*S*)-2,2',2''-(Propane-1,2,2-triyl)tris(4-isopropyl-4,5-dihydrooxazole) [LS9]

According to a procedure by *Synder et at.*,[26] diethyl malonimidate dihydrochloride (578 mg, 2.50 mmol, 1.00 eq.) and L-valinol (774 mg, 7.50 mmol, 3.00 eq.) were dissolved in CH_2Cl_2 (25 mL) and stirred at 40 °C for 18 h. Then, the mixture was poured into water (50 mL) and it was extracted with CH_2Cl_2 (4 × 10 mL). The combined org. phases were dried over $MgSO_4$, filtered and concentrated *in vacuo*. Bis((*S*)-4-isopropyl-4,5-dihydrooxazol-2-yl)methane was obtained *via* distillation (Kugelrohr, 2 mbar, 160 °C) as a colourless oil (278 mg, 1.17 mmol, 47%) and used in the next step.

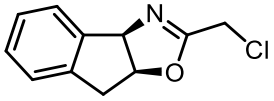
Spectroscopic data was in agreement with that previously reported.[27]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.26 (dd, *J* = 9.4, 8.0 Hz, 2H), 4.02 – 3.96 (m, 2H), 3.96 – 3.89 (m, 2H), 3.37 – 3.31 (m, 2H), 1.82 – 1.68 (m, *J* = 6.7 Hz, 2H), 0.94 (d, *J* = 6.8 Hz, 6H), 0.86 (d, *J* = 6.8 Hz, 6H).

According to a procedure by *Rendina et at.*,[33] the bis(oxazoline) (278 mg, 1.17 mmol, 1.00 eq.) obtained in the first step was added to a suspension of sodium hydride (49.0 mg, 1.23 mmol, 1.05 eq.) in dry THF (5 mL). The mixture was heated to 50 °C for 30 min then allowed to cool to rt. Methyl iodide (70.0 µL, 1.17 mmol, 1.00 eq.) dissolved in dry THF (1 mL) was added dropwise. It was stirred for 30 min before a second portion of sodium hydride (49.0 mg, 1.23 mmol, 1.05 eq.) was added. The mixture was stirred for another 30 min. Then, oxazoline **S7** (226 mg, 1.40 mmol, 1.20 eq.) was added and it was stirred for 18 h. The reaction mixture was poured in sat. aq. $NaHCO_3$-sol. (10 mL), the phases were separated and the aq. layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined org. phases were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The desired product was obtained *via* FC (pentane:EtOAc:MeOH; 50:50:0→0:95:5) as a colourless oil (317 mg, 0.839 mmol, 72%).

Spectroscopic data was in agreement with that previously reported.[34]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.26 – 4.08 (m, 3H), 4.05 – 3.78 (m, 6H), 3.11 – 3.02 (m, 1H), 2.98 – 2.88 (m, 1H), 1.86 – 1.66 (m, 2H), 1.59 (s, 3H), 1.02 – 0.74 (m, 18H). **^{13}C NMR (101 MHz, $CDCl_3$)**: δ = 167.1, 163.8, 72.3, 72.1, 71.7, 70.5, 70.1, 69.9, 41.0, 35.1, 32.7, 32.5, 32.3, 21.4, 19.0, 19.0, 18.7, 18.3, 18.2, 18.0, 17.5.



(3a*R*,8a*S*)-2-(Chloromethyl)-3a,8a-dihydro-8*H*-indeno[1,2-*d*]oxazole [S8]

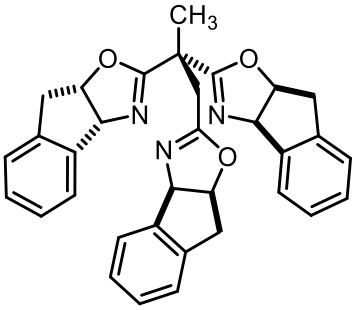
A solution of chloroacetonitrile (4.17 mL, 66.0 mmol, 1.00 eq.) and EtOH (4.24 mL, 72.6 mmol, 1.10 eq.) in dry Et_2O (10 mL) was cooled to −10 °C. Then, $HCl_{(g)}$ was bubbled through the solution until a white precipitation was observed. The suspension was degassed with argon before the solids were collected *via* filtration and washed with cold Et_2O, affording ethyl 2-chloroacetimidate hydrochloride as a white solid. Additional crops of the product were obtained from precipitation of the motherliquor in the cold (7.16 g, 45.3 mmol, 69% in total).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 4.37 (s, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 3H).

According to a procedure by *Ye et al.*,[32] ethyl 2-chloroacetimidate hydrochloride (869 mg, 5.50 mmol, 1.10 eq.) was suspended in dry CH_2Cl_2 (20 mL) and (1*R*,2*S*)-1-amino-2,3-dihydro-1H-inden-2-ol (746 mg, 5.00 mmol, 1.00 eq.) was added. The mixture was cooled to 0 °C and NEt_3 (0.76 mL, 5.5 mmol, 1.10 eq.) was added. The reaction mixture was gradually warmed to rt and stirred for 16 h. The solvent was removed *in vacuo* and the residue was extracted with EtOAc (3 × 20 mL). The combined org. phases were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The desired product was obtained *via* FC (pentane:EtOAc:MeOH; 79:19:2) as a colourless oil (720 mg, 3.47 mmol, 69%).

Spectroscopic data was in agreement with that previously reported.[32]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 – 7.45 (m, 1H), 7.34 – 7.23 (m, 4H), 5.61 (dd, *J* = 8.0, 0.9 Hz, 1H), 5.50 – 5.42 (m, 1H), 4.10 (dd, *J* = 13.0, 0.8 Hz, 1H), 4.04 (dd, *J* = 13.0, 0.7 Hz, 1H), 3.46 (ddd, *J* = 18.1, 7.0, 0.9 Hz, 1H), 3.29 (dd, *J* = 18.1, 1.6 Hz, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 163.0, 141.0, 140.0, 128.8, 127.6, 125.5, 125.4, 84.4, 76.7, 39.6, 36.5.



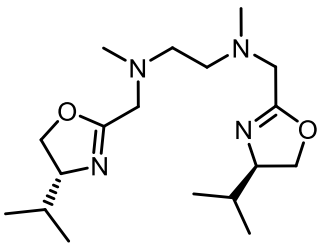
(3a*R*,3a'*R*,3a''*R*,8a*S*,8a'*S*,8a''*S*)-2,2',2''-(Propane-1,2,2-triyl)tris(3a,8a-dihydro-8*H*-indeno[1,2-d]oxazole) [LS10]

According to a procedure by *Rendina et at.*,[33] the bis(oxazoline) **LS6a** (278 mg, 1.17 mmol, 1.00 eq.) was added to a suspension of sodium hydride (49.0 mg, 1.23 mmol, 1.05 eq.) in dry THF (5 mL). The mixture was heated to 50 °C for 30 min then allowed to cool to rt. Methyl iodide

(70.0 µL, 1.17 mmol, 1.00 eq.) dissolved in dry THF (1 mL) was added dropwise. It was stirred for 30 min before a second portion of sodium hydride (49.0 mg, 1.23 mmol, 1.05 eq.) was added. The mixture was stirred for another 30 min. Then, oxazoline **S8** (226 mg, 1.40 mmol, 1.20 eq.) was added and it was stirred for 18 h. The reaction mixture was poured in sat. aq. $NaHCO_3$-sol. (10 mL), the phases were separated and the aq. layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined org. phases were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The desired product was obtained *via* FC (EtOAc:MeOH; 90:10→85:15) and crystallisation from $CHCl_3$/MeOH as a colourless solid (389 mg, 0.755 mmol, 59%).

Spectroscopic data was in agreement with that previously reported.[35]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 (d, *J* = 6.9 Hz, 1H), 7.47 – 7.41 (m, 1H), 7.36 – 7.31 (m, 1H), 7.30 – 7.13 (m, 9H), 5.57 (d, *J* = 8.0 Hz, 1H), 5.49 (d, *J* = 7.9 Hz, 1H), 5.32 – 5.24 (m, 1H), 5.19 (d, *J* = 8.0 Hz, 1H), 5.14 (ddd, *J* = 8.3, 7.0, 1.8 Hz, 1H), 4.11 – 4.04 (m, 1H), 3.31 (ddd, *J* = 17.0, 9.5, 7.1 Hz, 2H), 3.13 – 2.74 (m, 6H), 1.45 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)**: δ = 167.6, 167.2, 164.2, 142.1, 142.0, 141.7, 140.5, 139.7, 139.7, 128.5, 128.3, 127.4, 127.4, 127.3, 125.7, 125.7, 125.4, 125.2, 125.1, 83.5, 83.5, 82.6, 76.6, 76.5, 76.1, 40.8, 39.9, 39.8, 39.6, 34.9, 21.1.

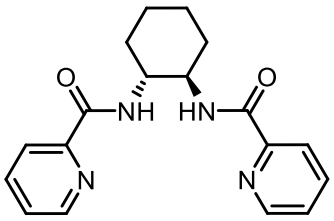


N^1-(((*R*)-4-Isopropyl-4,5-dihydrooxazol-2-yl)methyl)-*N*^{2}-(((*S*)-4-isopropyl-4,5-dihydrooxazol-2-yl)methyl)-*N*^{1},*N*^{2}-dimethylethane-1,2-diamine [LS15]

According to a procedure by *Guillemot et at.*,[36] oxazoline **S7** (647 mg, 4.00 mmol, 2.00 eq.) was dissolved in dry MeCN (5 mL) in an oven dried Schlenk tube. *N*,*N*'-dimethylethylendiamine (200 µL, 2.00 mmol, 1.00 eq.) and K_2CO_3 (1.22 g, 8.80 mmol, 4.40 eq.) were added and the mixture was heated to 82 °C for 3 h. After cooling to rt, the solids were filtered off and the filtrate was and concentrated *in vacuo*. The desired product was obtained *via* distillation (Kugelrohr, 0.15 mbar, 160 °C) as a pale-yellow resin (396 mg, 1.17 mmol, 59%).

Spectroscopic data was in agreement with that previously reported.[36]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.27 – 4.19 (m, 2H), 3.99 – 3.84 (m, 4H), 3.31 – 3.25 (m, 4H), 2.62 (s, 4H), 2.33 (s, 6H), 0.94 (d, *J* = 6.8 Hz, 6H), 0.87 (d, *J* = 6.8 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)**: δ = 164.5, 72.2, 70.1, 54.9, 54.4, 42.9, 32.3, 18.9, 18.3.



N,*N*'-((1*R*,2*R*)-Cyclohexane-1,2-diyl)dipicolinamide [LS18]

(1*R*,2*R*)-1,2-diaminocyclohexane (571 mg, 5.00 mmol, 1.00 eq.) and 2-picolinic acid (1.54 g, 12.5 mmol, 2.50 eq.) were dissolved in CH_2Cl_2 (25 mL). Then, 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride (2.88 g, 15.0 mmol, 3.00 eq.) and DMAP (122 mg, 1.00 mmol, 0.20 eq.) were added and it was stirred at rt for 32 h. Then, 1 M aq. HCl (20 mL) was added. The phases were separated and the aq. layer extracted with CH_2Cl_2 (3 × 15 mL). The combined org. phases were washed with 1 M aq. NaOH (2 × 10 mL) and brine (10 mL). The org. layer was dried over $MgSO_4$, filtered and concentrated *in vacuo*. The desired product was obtained *via* recrystallisation from hot EtOH as colourless needles (825 mg, 2.54 mmol, 51%).

Spectroscopic data was in agreement with that previously reported.[37]

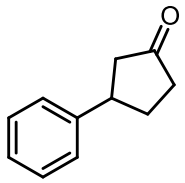
^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.48 (ddd, *J* = 4.8, 1.7, 0.9 Hz, 2H), 8.33 – 8.15 (m, 2H), 8.03 (dt, *J* = 7.8, 1.1 Hz, 2H), 7.70 (td, *J* = 7.7, 1.7 Hz, 2H), 7.36 – 7.26 (m, 2H), 4.14 – 3.98 (m, 2H), 2.27 – 2.09 (m, 2H), 1.92 – 1.67 (m, 2H), 1.54 – 1.31 (m, 4H). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 164.6, 149.8, 148.2, 137.1, 126.0, 122.1, 53.3, 32.7, 24.9.

5 Synthesis of cyclopentanones

5.1 Preparation of racemic material

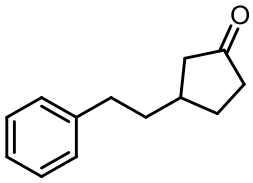
General procedure F: Scandium catalysed ring expansion

In an flame-dried tube, $Sc(OTf)_3$ (0.10 eq.) was suspended in dry PhMe (0.1 M) under Argon-atmosphere. The corresponding cyclobutanone (1.00 eq.) was added and it was stirred for 15 min at rt. Then, TMSD (0.6 M in hex, 1.30 eq.) was added and the mixture was stirred at rt for 16 h. Thereafter, an excess amount of TFA (6.50 eq.) was added and the solvent was removed *in vacuo*. The desired product was obtained *via* FC with the conditions given in the corresponding entry.



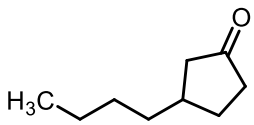
rac-3-Phenylcyclopentanone (*rac*-2a)

According to general procedure **F**, using 3-phenylcyclobutanone (14.6 mg, 0.100 mmol, 1.00 eq.), $Sc(OTf)_3$ (4.9 mg, 10 µmol, 0.10 eq.) and TMSD (0.22 mL, 0.13 mmol, 0.6 M in hex, 1.32 eq.), the product was obtained *via* FC (CH_2Cl_2) as a colourless oil (11.1 mg, 69.3 µmol, 69%).
Spectroscopic data was in agreement with that previously reported.[38]
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.31 (m, 2H), 7.30–7.22 (m, 3H), 3.49–3.37 (m, 1H), 2.68 (dd, *J* = 18.0, 7.3, 1H), 2.54–2.40 (m, 2H), 2.40–2.25 (m, 2H), 2.09–1.92 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)**: δ = 218.5, 143.2, 128.8, 126.9, 126.9, 45.9, 42.4, 39.0, 31.3.



rac-3-Phenethylcyclopentanone (*rac*-2b)

According to general procedure **F**, using 3-phenethylcyclobutanone (17.4 mg, 0.100 mmol, 1.00 eq.), $Sc(OTf)_3$ (4.9 mg, 10 µmol, 0.10 eq.) and TMSD (0.22 mL, 0.13 mmol, 0.6 M in hex, 1.32 eq.), the product was obtained *via* FC (CH_2Cl_2) as a colourless oil (15.7 mg, 83.4 µmol, 83%).
Spectroscopic data was in agreement with that previously reported.[39]
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.27 (m, 2H), 7.20 (m, 3H), 2.67 (t, *J* = 7.8, 2H), 2.47–2.38 (m, 1H), 2.37–2.26 (m, 1H), 2.24–2.09 (m, 3H), 1.89–1.73 (m, 3H), 1.63–1.50 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)**: δ = 219.6, 141.9, 128.5, 128.3, 126.0, 45.2, 38.6, 37.4, 36.6, 34.2, 29.5.

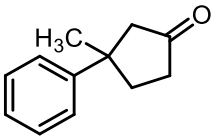


rac-3-Butylcyclopentanone (*rac*-2c)

According to general procedure **F**, using 3-butylcyclobutanone (12.6 mg, 0.100 mmol, 1.00 eq.), $Sc(OTf)_3$ (4.9 mg, 10 µmol, 0.10 eq.) and TMSD (0.22 mL, 0.13 mmol, 0.6 M in hex, 1.32 eq.), the product was obtained *via* FC (CH_2Cl_2) as a colourless oil (10.0 mg, 71.3 µmol, 71%).

Spectroscopic data was in agreement with that previously reported.[40]

^{1}H NMR (300 MHz, CDCl3): δ = 2.44–2.23 (m, 2H), 2.23–2.04 (m, 3H), 1.87–1.69 (m, 1H), 1.58–1.16 (m, 7H), 0.96–0.78 (m, 3H). **^{13}C NMR (75 MHz, CDCl3)**: δ = 220.3, 45.5, 38.7, 37.3, 35.5, 30.2, 29.7, 22.9, 14.2.

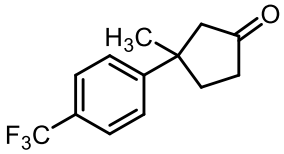


rac-3-Methyl-3-phenylcyclopentanone (*rac*-2d)

According to general procedure **F**, using 3-methyl-3-phenylcyclobutan-1-one (16.0 mg, 0.100 mmol, 1.00 eq.), $Sc(OTf)_3$ (4.9 mg, 10 µmol, 0.10 eq.) and TMSD (0.22 mL, 0.13 mmol, 0.6 M in hex, 1.32 eq.), the product was obtained *via* FC (pentane:EtOAc; 95:5) as a colourless oil (12.0 mg, 68.9 µmol, 69%).

Spectroscopic data was in agreement with that previously reported.[41]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.27 (m, 4H), 7.27–7.21 (m, 1H), 2.66 (d, *J* = 17.6, 1H), 2.48 (d, *J* = 17.6, 1H), 2.45–2.34 (m, 2H), 2.34–2.22 (m, 2H), 1.39 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)**: δ = 218.7, 148.6, 128.7, 126.5, 125.6, 52.4, 44.0, 36.9, 35.9, 29.5.

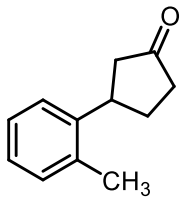


rac-3-Methyl-3-[4-(trifluoromethyl)phenyl]cyclopentanone (*rac*-2e)

According to general procedure **F**, using 3-methyl-3-[4-(trifluoromethyl)phenyl]cyclobutanone (22.8 mg, 0.100 mmol, 1.00 eq.), $Sc(OTf)_3$ (4.9 mg, 10 µmol, 0.10 eq.) and TMSD (0.22 mL, 0.13 mmol, 0.6 M in hex, 1.32 eq.), the product was obtained *via* FC (pentane:EtOAc; 95:5) as a yellow oil (16.0 mg, 66.1 µmol, 66%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (*app.* d, *J* = 8.2 Hz, 2H), 7.40 (*app.* d, *J* = 8.2 Hz, 2H), 2.64 (d, *J* = 17.5 Hz, 1H), 2.51 (dt, *J* = 17.7, 1.3 Hz, 1H), 2.52–2.34 (m, 2H), 2.35–2.25 (m, 2H), 1.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 217.6, 152.5, 128.7 (q, J = 32.6 Hz), 125.9, 125.6 (q, J = 3.9 Hz), 124.13 (q, J = 272.0 Hz), 51.9, 44.0, 36.6, 35.6, 29.3.



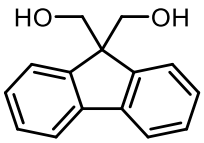
rac-3-(2-Methylphenyl)cyclopentanone (*rac*-2f)

According to general procedure **F**, using 3-(2-methylphenyl)cyclobutanone (16.0 mg, 0.100 mmol, 1.00 eq.), $Sc(OTf)_3$ (4.9 mg, 10 µmol, 0.10 eq.) and TMSD (0.22 mL, 0.13 mmol, 0.6 M in hex, 1.32 eq.), the product was obtained *via* FC (CH_2Cl_2) as a colourless oil (11.0 mg, 63.1 µmol, 63%).

Spectroscopic data was in agreement with that previously reported.[42]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25–7.12 (m, 4H), 3.68–3.55 (m, 1H), 2.69–2.59 (m, 1H), 2.55–2.40 (m, 1H), 2.40 (s, 3H), 2.37–2.22 (m, 3H), 2.06–1.95 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)**: δ = 218.9, 141.1, 136.1, 130.8, 126.7, 126.5, 124.9, 45.5, 38.7, 38.5, 30.2, 19.8.

5.2 Derivatisation of non-UV/vis-active β-substituted cyclopentanones for the determination of their *er*

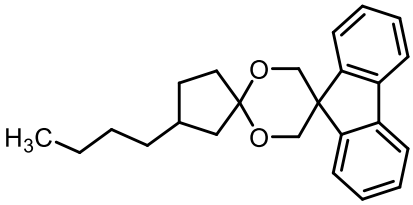


[9-(Hydroxymethyl)-9-fluorenyl]methanol [S9]

Paraformaldehyde (249 mg, 8.30 mmol, 2.77 eq.) and sodium ethoxide (53 mg, 0.78 mmol, 0.26 eq.) were suspended in a mixture of DMSO (1.5 mL), ethanol (0.5 mL) and toluene (1 mL). The mixture was cooled to 0 °C and a solution of fluorene (499 mg, 3.00 mmol, 1.00 eq.) in DMSO (1.5 mL) was added. It was stirred at 0 °C for 30 min before it was gradually warmed to rt and stirred for additional 16 h. Then, it was acidified to pH ≈ 1 by addition of conc. aq. HCl (10 drops) and diluted with water (10 mL). The phases were separated and the aqueous phase was extracted with EtOAc (3 × 5 mL). The combined organic fractions were washed successively with water (2 × 5 mL) and Brine (5 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was obtained *via* recrystallisation (from EtOH, then from PhMe) as colourless solid (281 mg, 1.24 mmol, 41%).

Spectroscopic data was in agreement with that previously reported.[43]

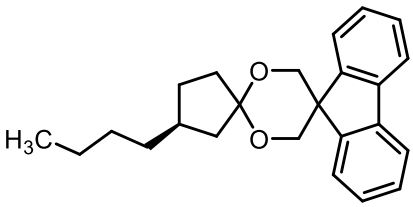
^{1}H NMR (400 MHz, DMSO): δ = 7.82 (d, *J* = 7.5 Hz, 2H), 7.60 (d, *J* = 7.4 Hz, 2H), 7.44–7.24 (m, 4H), 4.87 (t, *J* = 5.3 Hz, 2H), 3.71 (d, *J* = 5.3 Hz, 4H); **^{13}C NMR (101 MHz, DMSO)**: δ = 147.6, 140.4, 127.2, 126.6, 125.2, 119.8, 63.8, 57.5.



rac-3-Butyldispiro[cyclopentane-1,2'-[1,3]dioxane-5',9''-fluorene] [*rac*-S10]

In a tube containing activated 4 Å molecular sieves, 3-butylcyclopentanone (***rac*-2c**) (10.0 mg, 71.3 µmol, 1.00 eq.), diol **S9** (45 mg, 0.20 mmol, 2.80 eq.) and *p*-toluenesulphonic acid monohydrate (1.9 mg, 10 µmol, 0.14 eq.) were suspended in dry PhMe (1 mL). The mixture was stirred at 120 °C for 16 h. After cooling to rt, it was poured into water and diluted with Et_2O (5 mL). The org. layer was washed with water and brine, dried over $MgSO_4$, filtered and the solvent was removed *in vacuo*. The residue was taken up in CH_2Cl_2 and filtered through a silica plug which was eluted with CH_2Cl_2. The product was obtained *via* FC (pentane:EtOAc; 97:3) as a colourless solid (10.0 mg, 29 µmol, 41%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.88 – 7.70 (m, 4H), 7.41 (td, *J* = 7.5, 1.3 Hz, 2H), 7.34 (tt, *J* = 7.4, 1.2 Hz, 2H), 3.99 (d, *J* = 3.7, 4H), 2.55 (dd, *J* = 13.1, 7.4, 1H), 2.43 – 2.27 (m, 1H), 2.23 – 2.02 (m, 2H), 2.02 – 1.90 (m, 1H), 1.67 (dd, *J* = 13.1, 10.0, 1H), 1.53 – 1.28 (m, 7H), 0.98 – 0.87 (m, 3H).



3-Butyldispiro[cyclopentane-1,2'-[1,3]dioxane-5',9''-fluorene] [S10]

In a tube containing activated 4 Å molecular sieves, 3-butylcyclopentanone (**2c**) (4.0 mg, 29 µmol, 1.00 eq.), diol **S9** (13 mg, 57 µmol, 2.00 eq.) and *p*-toluenesulphonic acid monohydrate (1.0 mg, 5.2 µmol, 0.18 eq.) were suspended in dry PhMe (1 mL). The mixture was stirred at 120 °C for 16 h. After cooling to rt, it was poured into water and diluted with Et_2O (5 mL). The org. layer was washed with water and brine, dried over $MgSO_4$, filtered and the solvent was removed *in vacuo*. The residue was taken up in CH_2Cl_2 and filtered through a silica plug which was eluted with CH_2Cl_2. The product was obtained *via* FC (pentane:EtOAc; 97:3) as a colourless solid (3.0 mg, 8.6 µmol, 30%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 – 7.72 (m, 4H), 7.41 (td, *J* = 7.3, 1.2 Hz, 2H), 7.33 (tt, *J* = 7.4, 1.3 Hz, 2H), 3.98 (d, *J* = 5.2 Hz, 4H), 2.55 (dd, *J* = 13.1, 7.5 Hz, 1H), 2.39 – 2.27 (m, 1H), 2.21 – 2.06

(m, 1H), 2.00 – 1.91 (m, 1H), 1.66 (dd, *J* = 13.1, 10.1 Hz, 1H), 1.49 – 1.28 (m, 7H), 0.99 – 0.82 (m, 3H).

The enantiomeric purity of 82:18 *er* was established by HPLC analysis using a chiral column (Lux® Amylose 1 column, rt, 1 mL/min, 99,5:0,5 hexane:iPrOH, 254 nm, t_R(major) = 13.1 min, t_R(minor) = 19.8 min).

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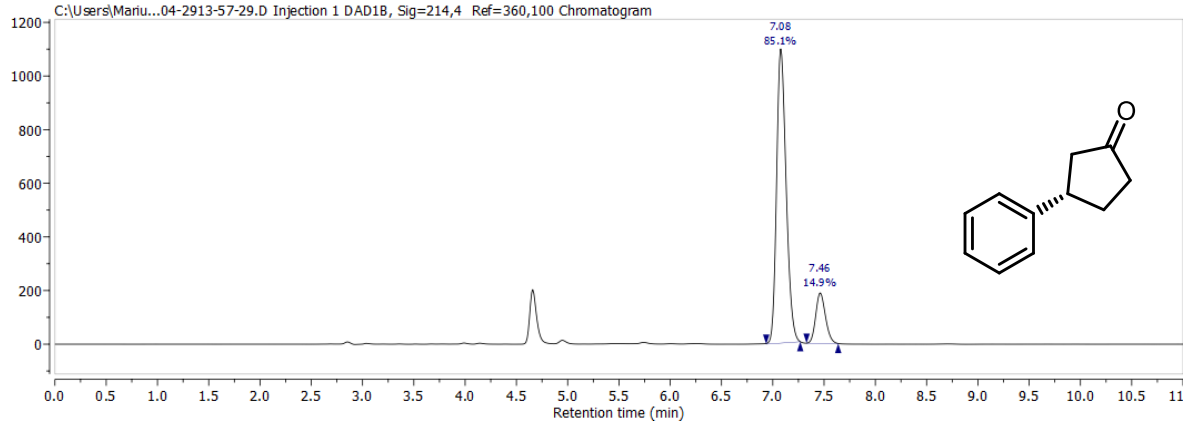
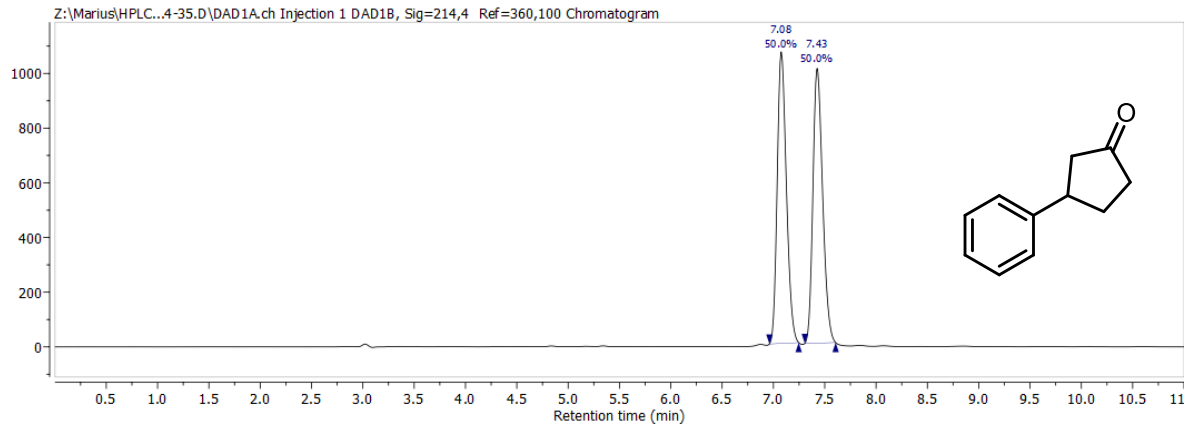
7 HPLC chromatograms

[2a]



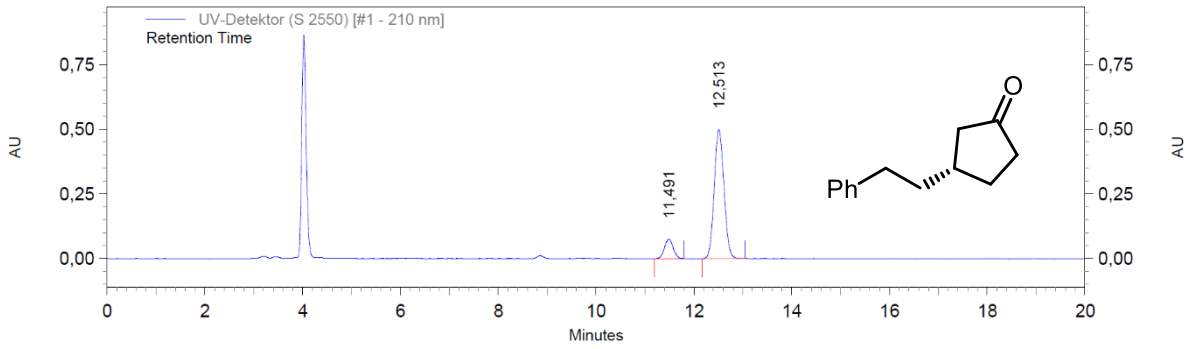
Retention Time	Area	Area %
7.078	70672.915	85.10
7.463	12378.226	14.90

[*rac*-2a]



Retention Time	Area	Area %
7.076	66302.853	50.03
7.426	66227.619	49.97

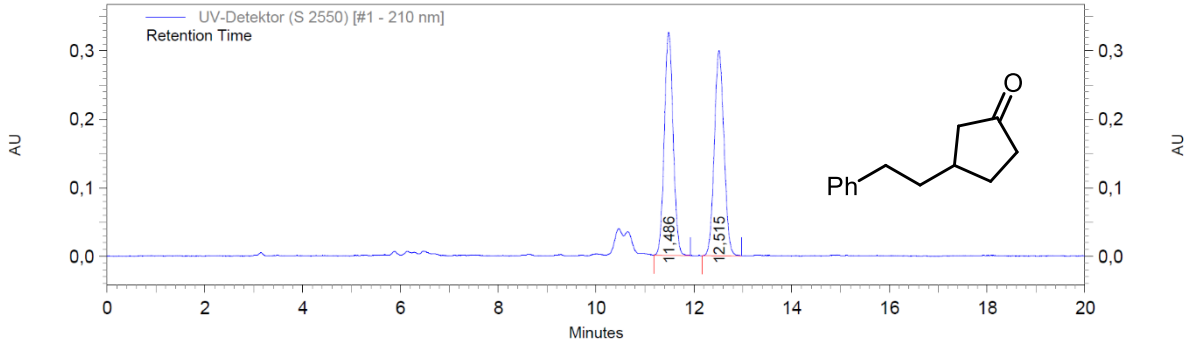
[2b]



UV-Detektor (S 2550) [#1 - 210 nm] Results

Retention Time	Area	Area %
11,491	935916	11,97
12,513	6882966	88,03

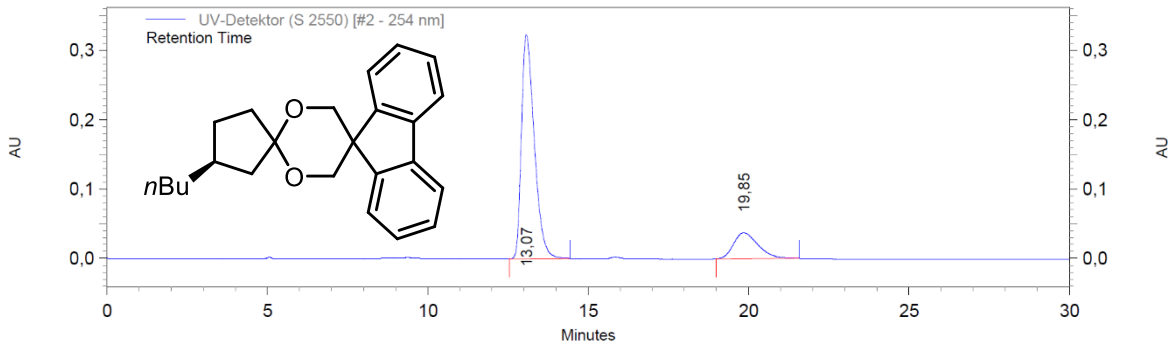
[*rac*-2b]



UV-Detektor (S 2550) [#1 - 210 nm] Results

Retention Time	Area	Area %
11,486	4084702	49,85
12,515	4108519	50,15

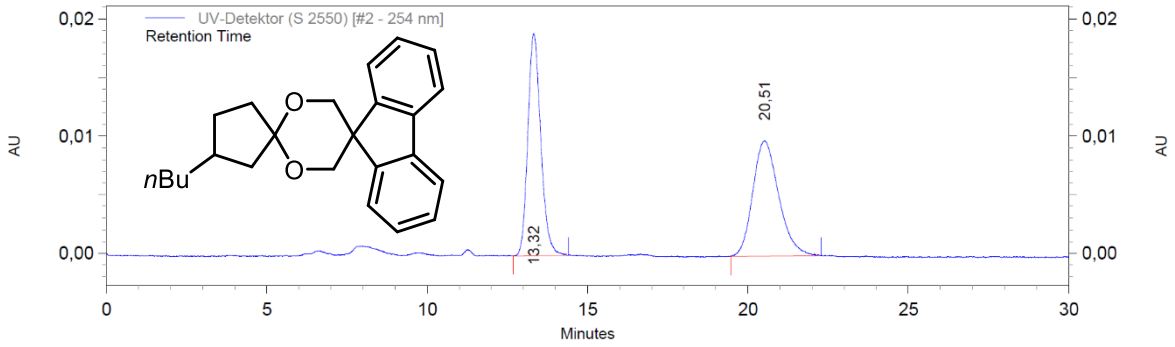
[S10]



UV-Detektor (S 2550) [#2 - 254 nm] Results

Retention Time	Area	Area %
13,072	8948684	81,88
19,854	1980187	18,12

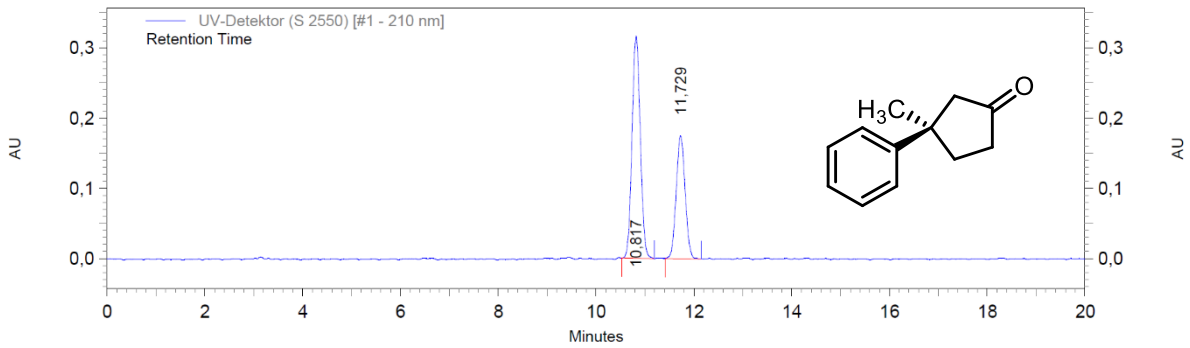
[*rac*-S10]



UV-Detektor (S 2550) [#2 - 254 nm] Results

Retention Time	Area	Area %
13,321	533269	49,14
20,514	551884	50,86

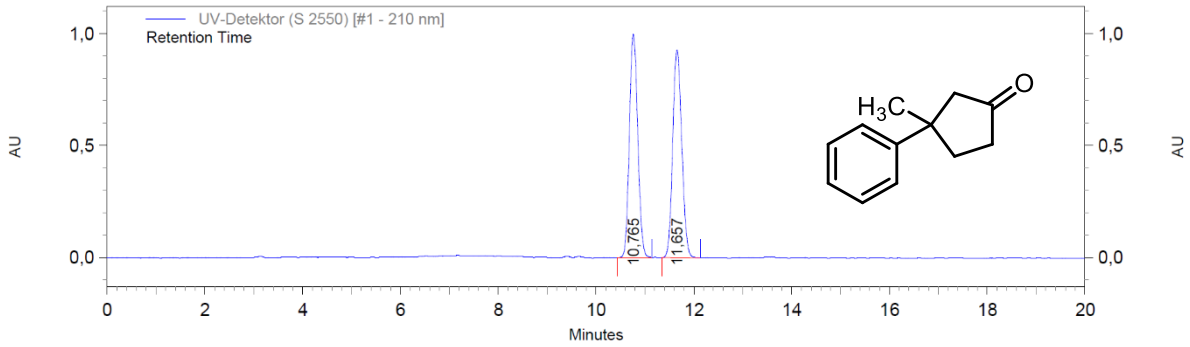
[2d]



UV-Detektor (S 2550) [#1 - 210 nm] Results

Retention Time	Area	Area %
10,817	3724644	62,67
11,729	2218816	37,33

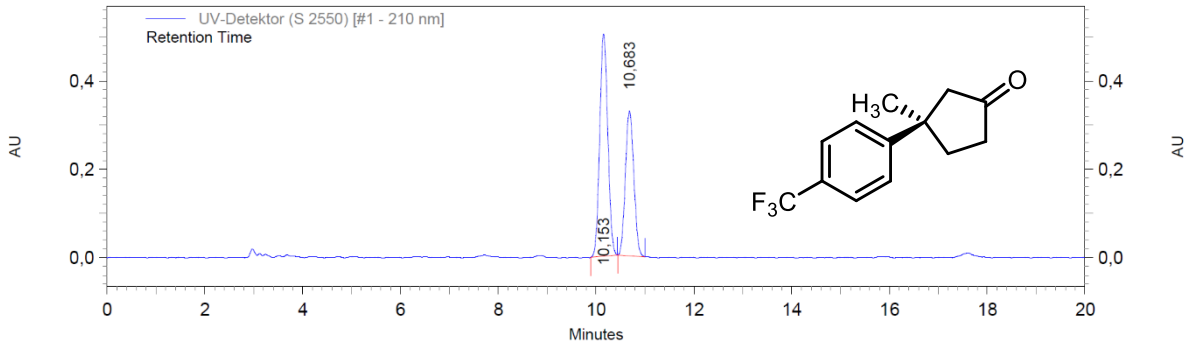
[*rac*-2d]



UV-Detektor (S 2550) [#1 - 210 nm] Results

Retention Time	Area	Area %
10,765	11834750	49,85
11,657	11907863	50,15

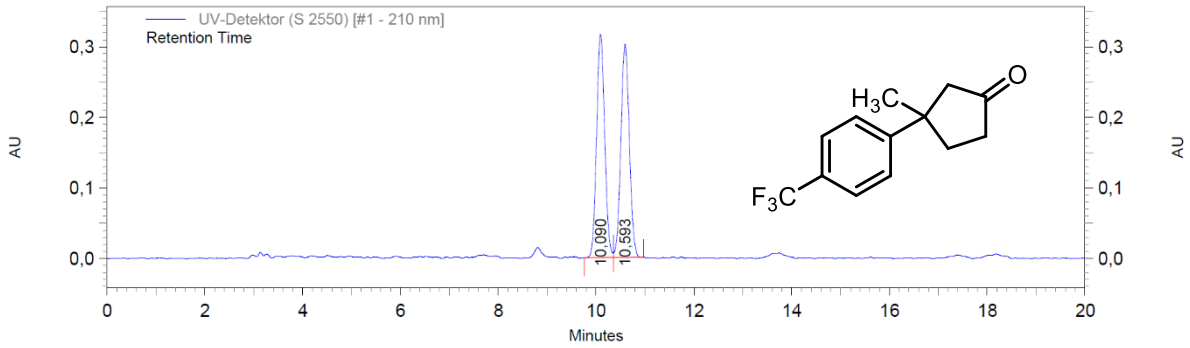
[2e]



UV-Detektor (S 2550) [#1 - 210 nm] Results

Retention Time	Area	Area %
10,153	5765152	59,33
10,683	3951986	40,67

[*rac*-2e]

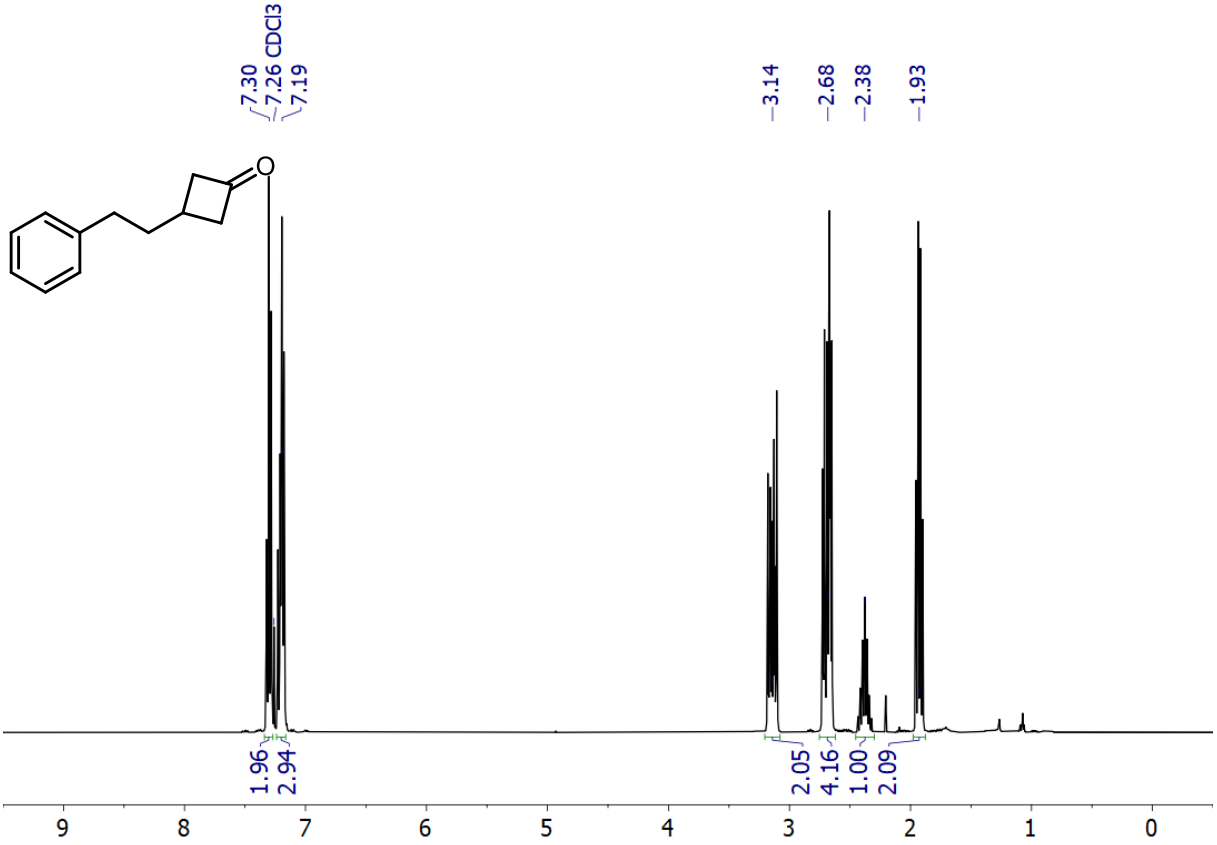


UV-Detektor (S 2550) [#1 - 210 nm] Results

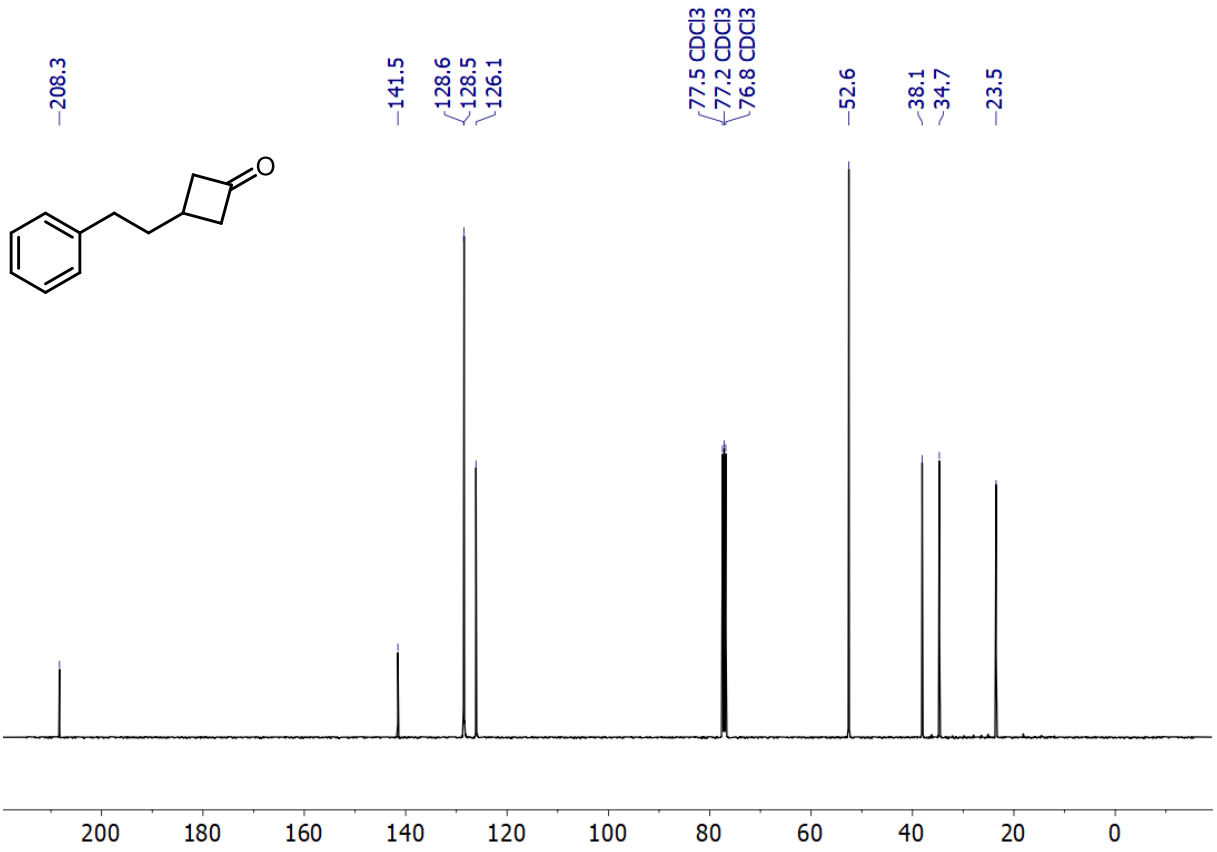
Retention Time	Area	Area %
10,090	3647426	49,90
10,593	3662364	50,10

8 ^{1}H, ^{13}C and ^{19}F NMR spectra of unknown compounds

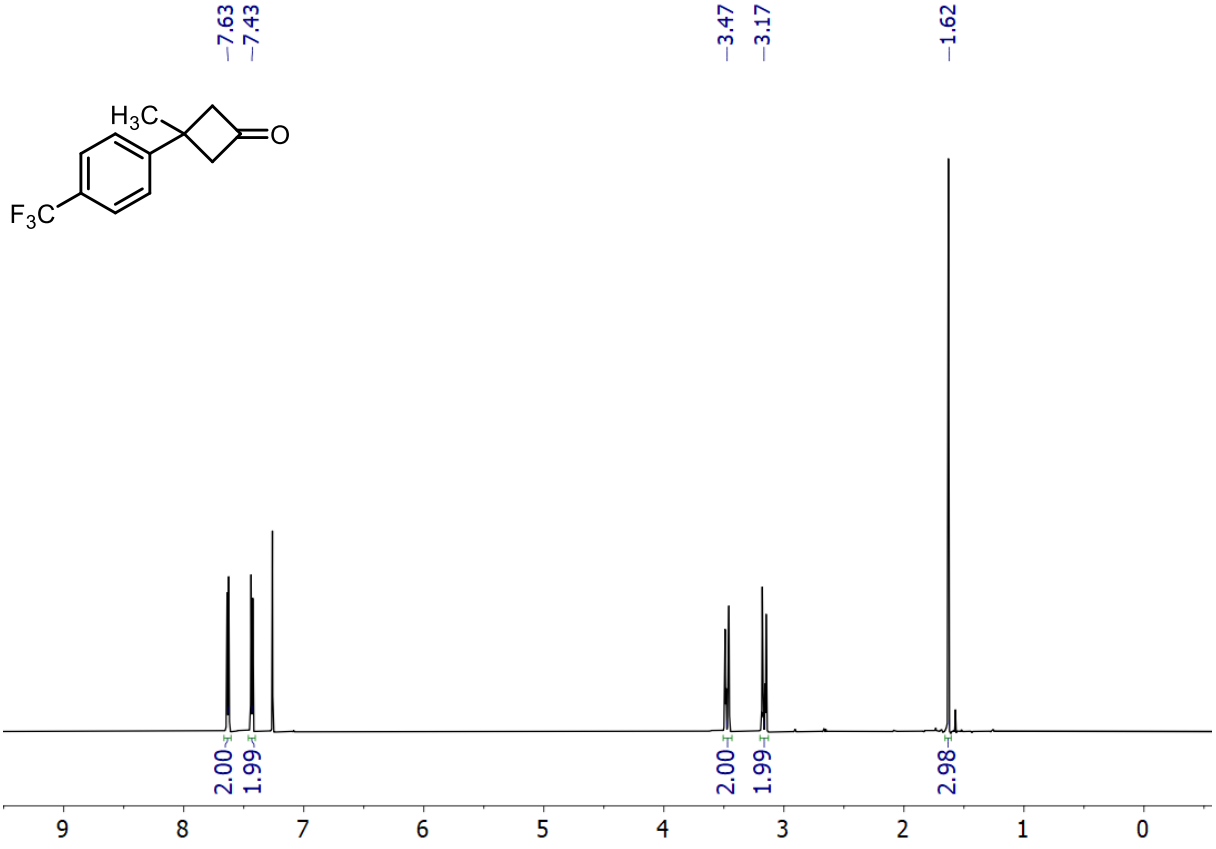
[1b], ^{1}H, $CDCl_3$, 400 MHz



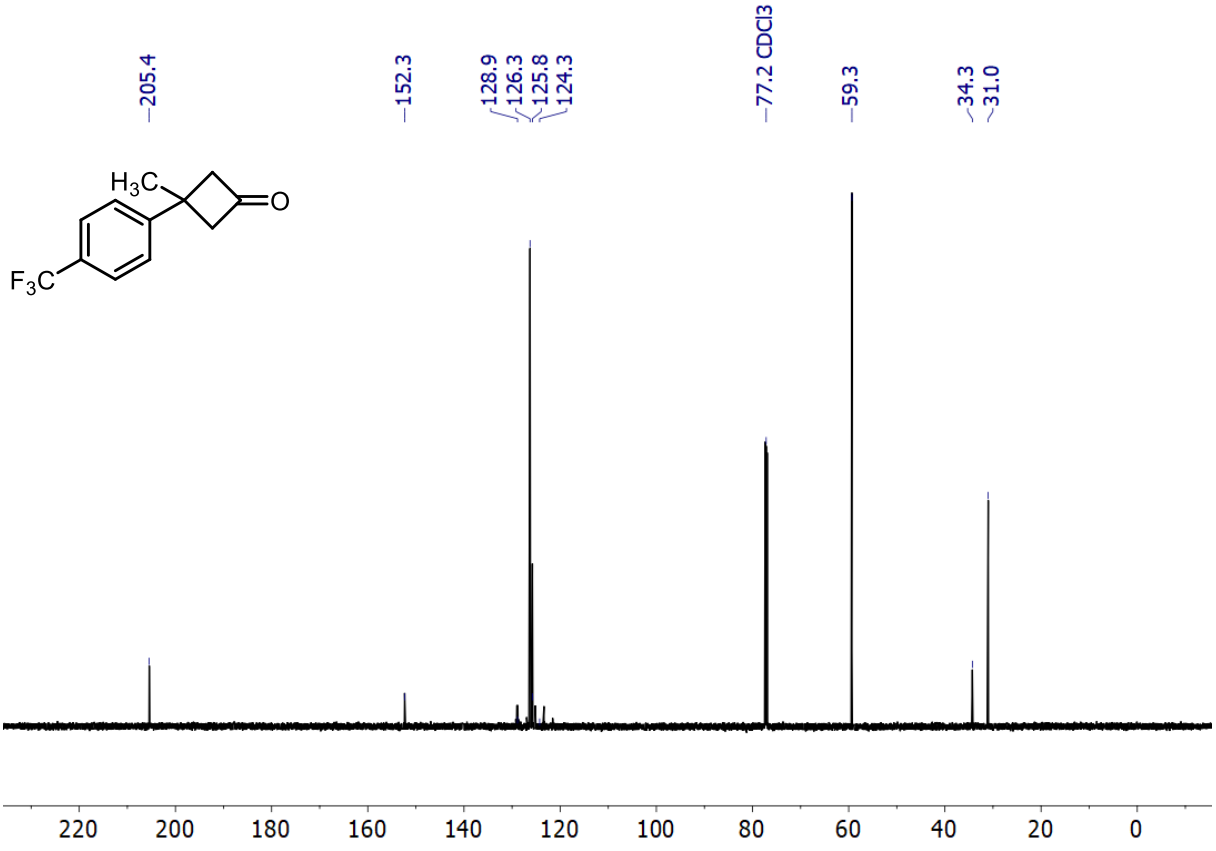
[1b], ^{13}C, $CDCl_3$, 101 MHz



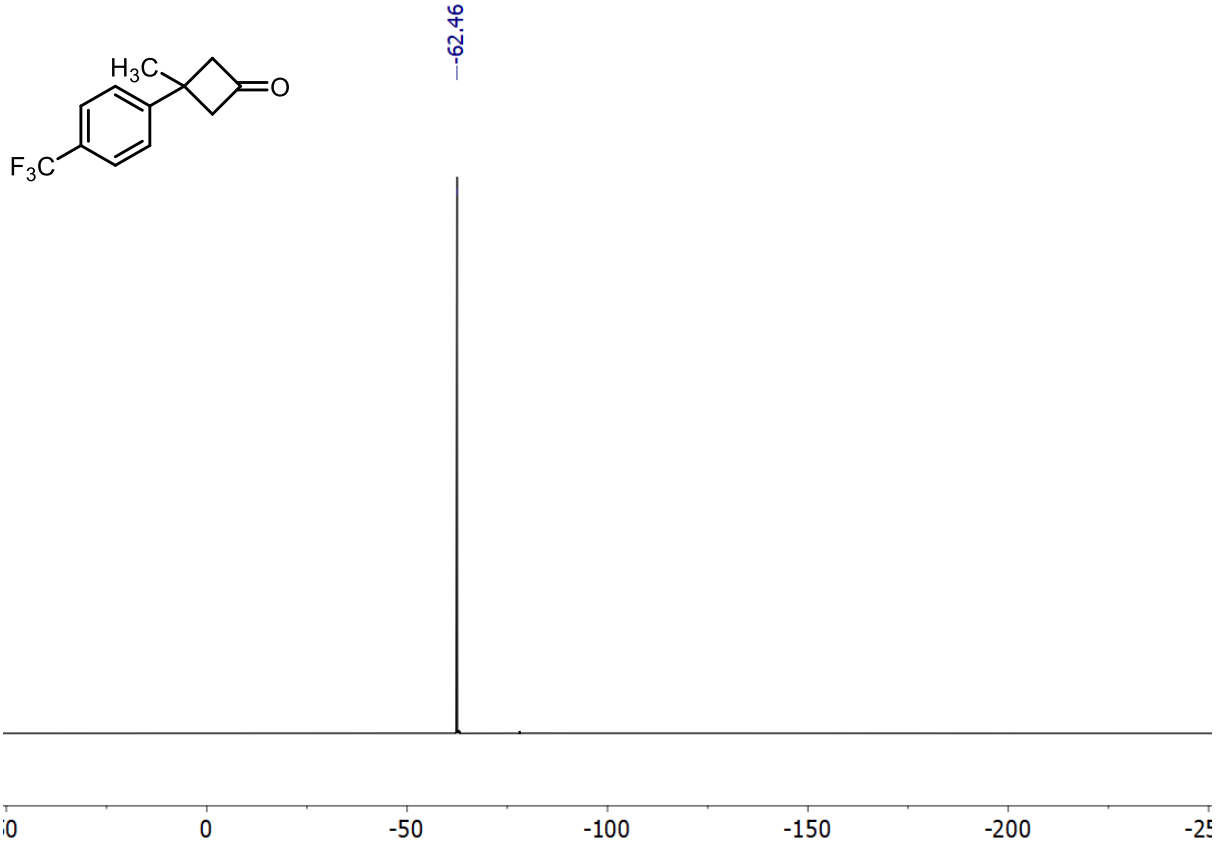
[1e], ^{1}H, $CDCl_3$, 599 MHz



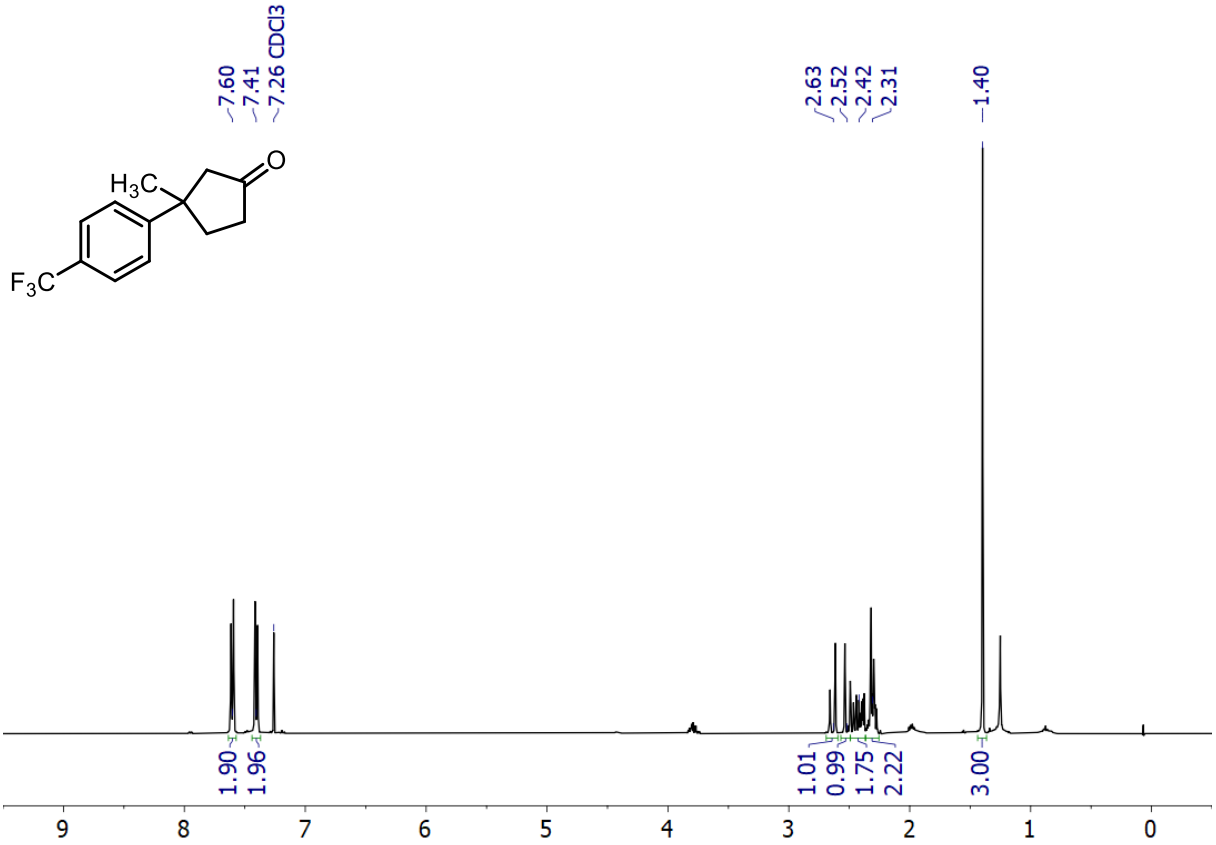
[1e], ^{13}C, $CDCl_3$, 151 MHz



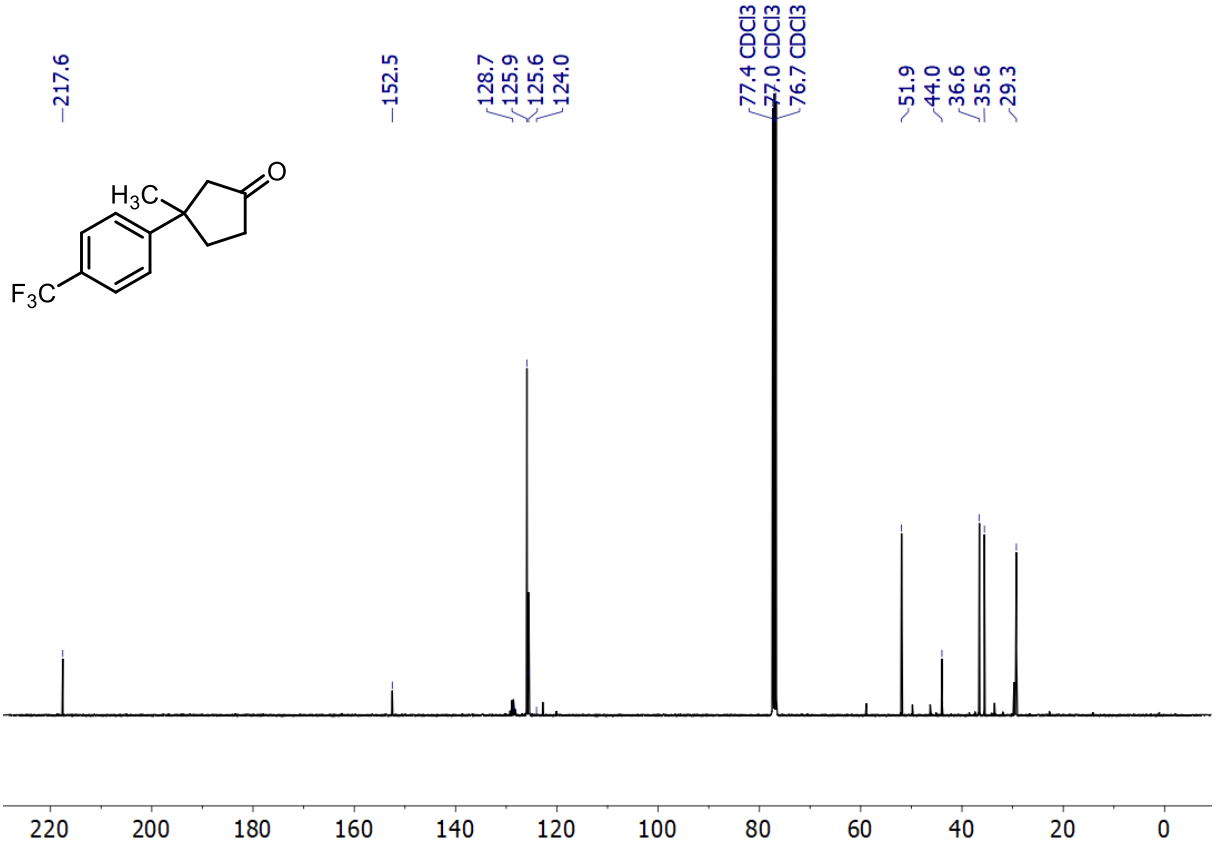
[1e], ^{19}F, $CDCl_3$, 377 MHz



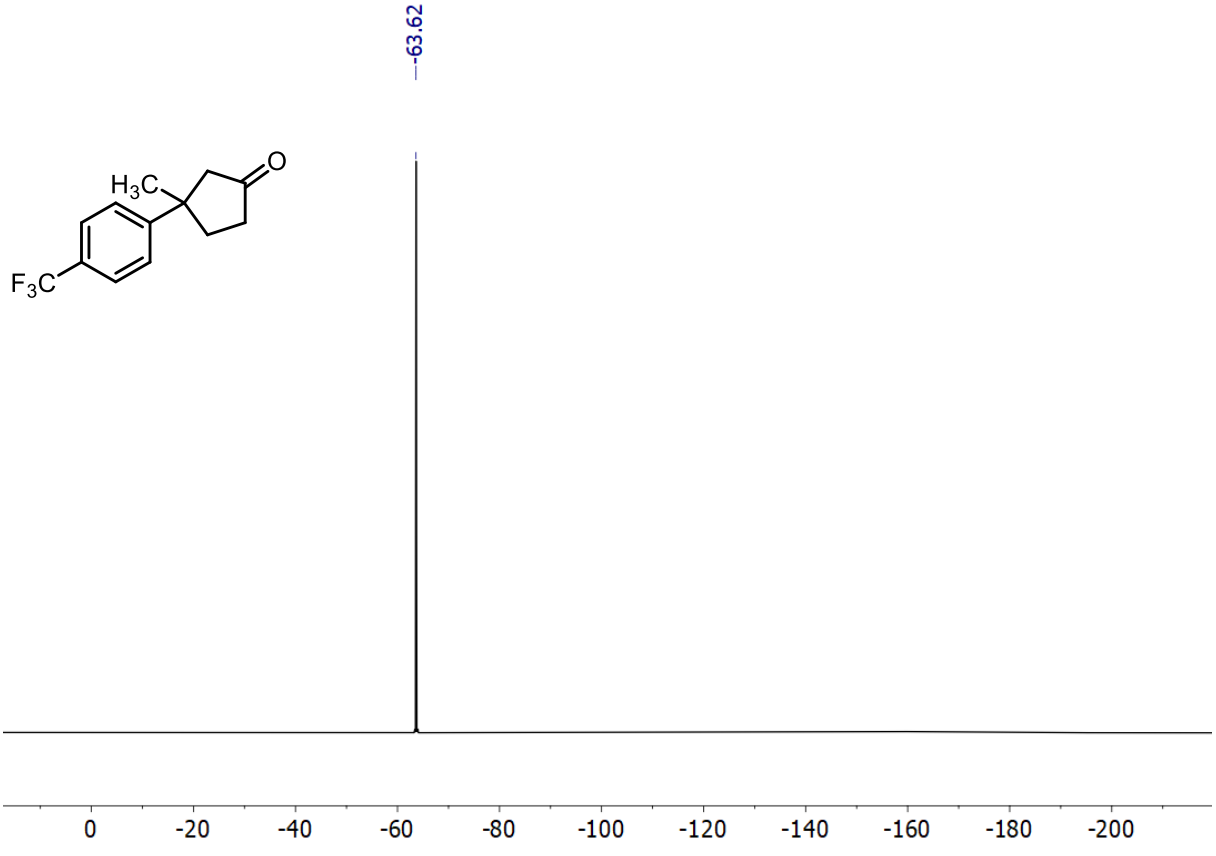
[2e], ^{1}H, $CDCl_3$, 400 MHz



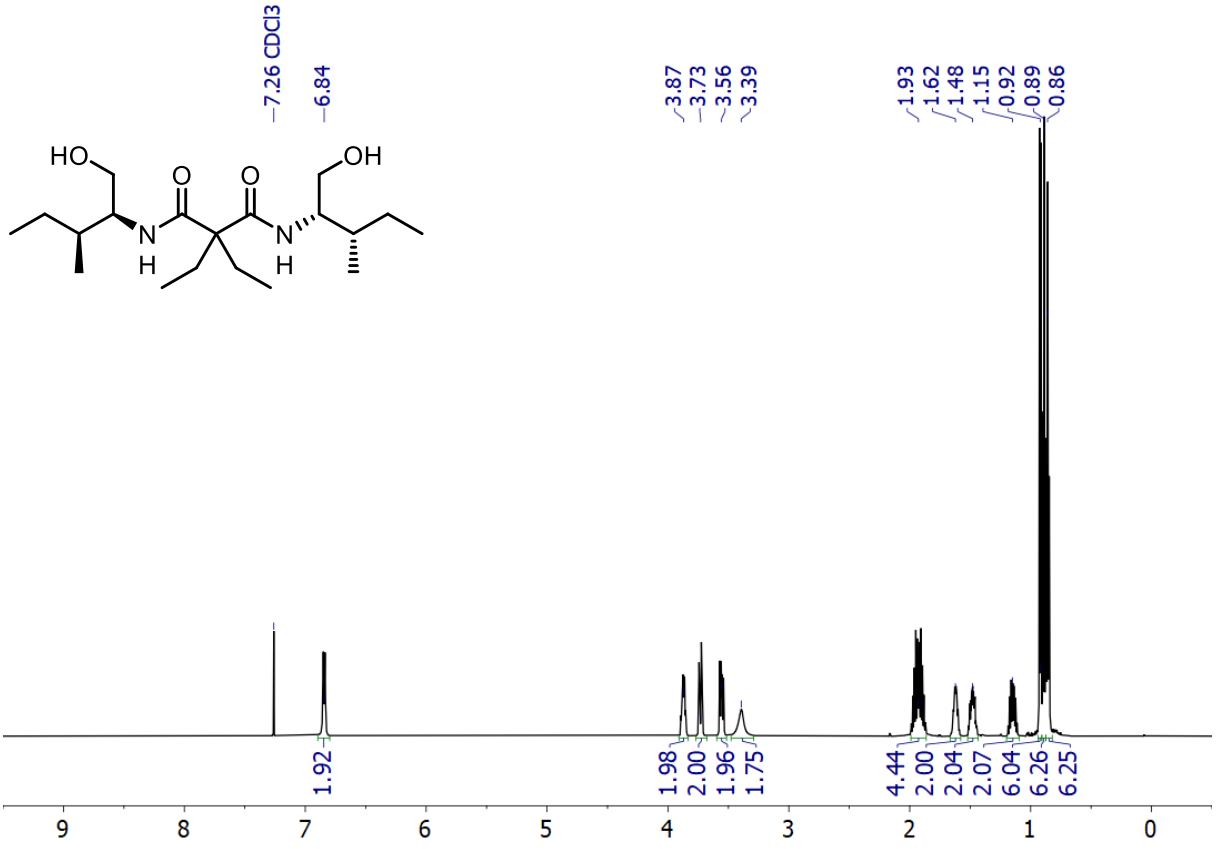
[2e], ^{13}C, $CDCl_3$, 101 MHz



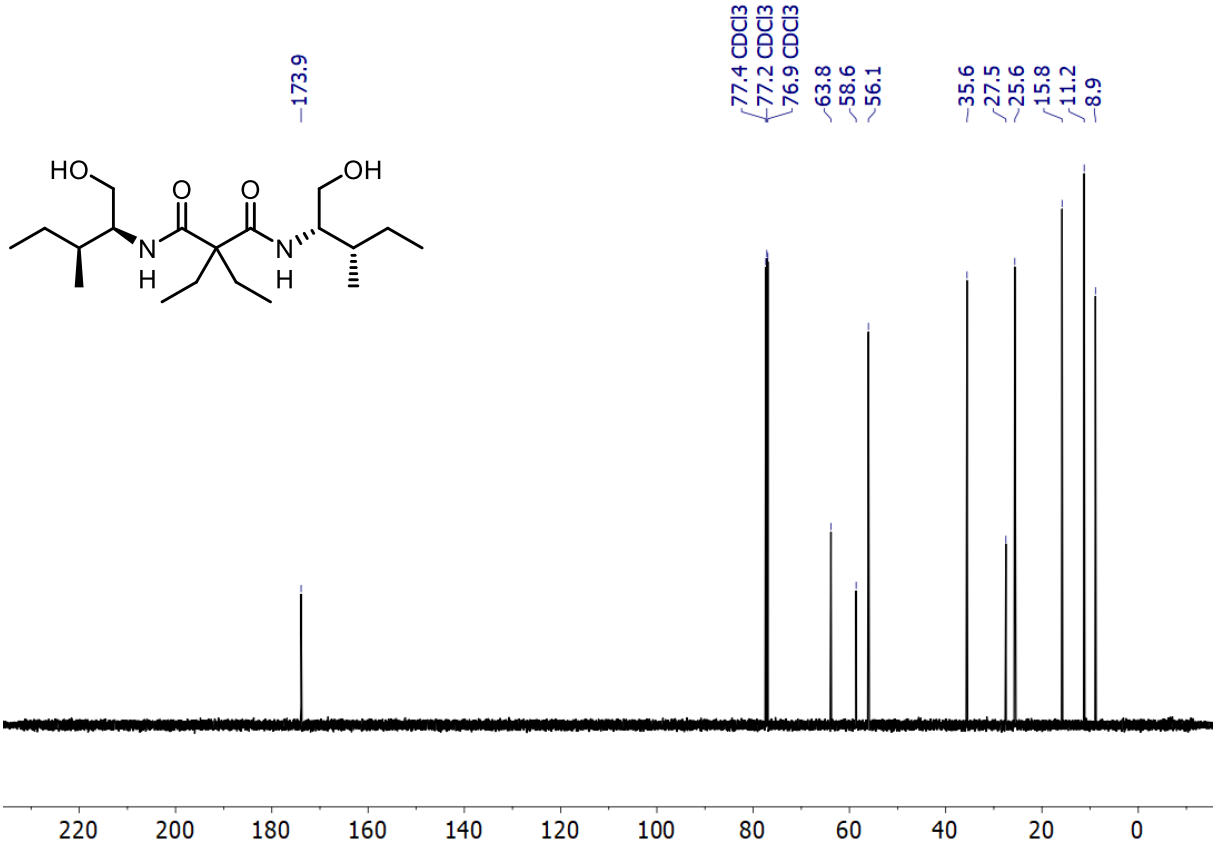
[2e], ^{19}F, $CDCl_3$, 377 MHz



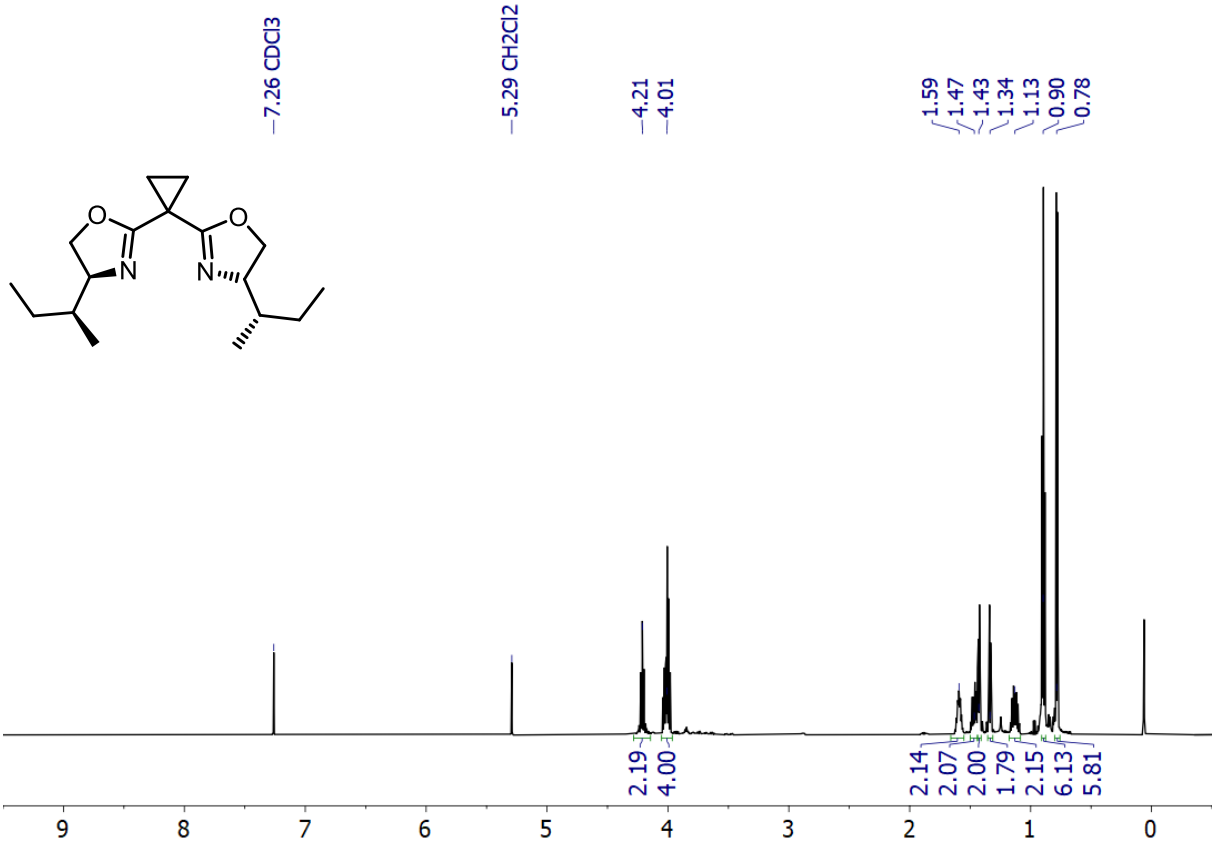
[S5], ^{1}H, $CDCl_3$, 599 MHz



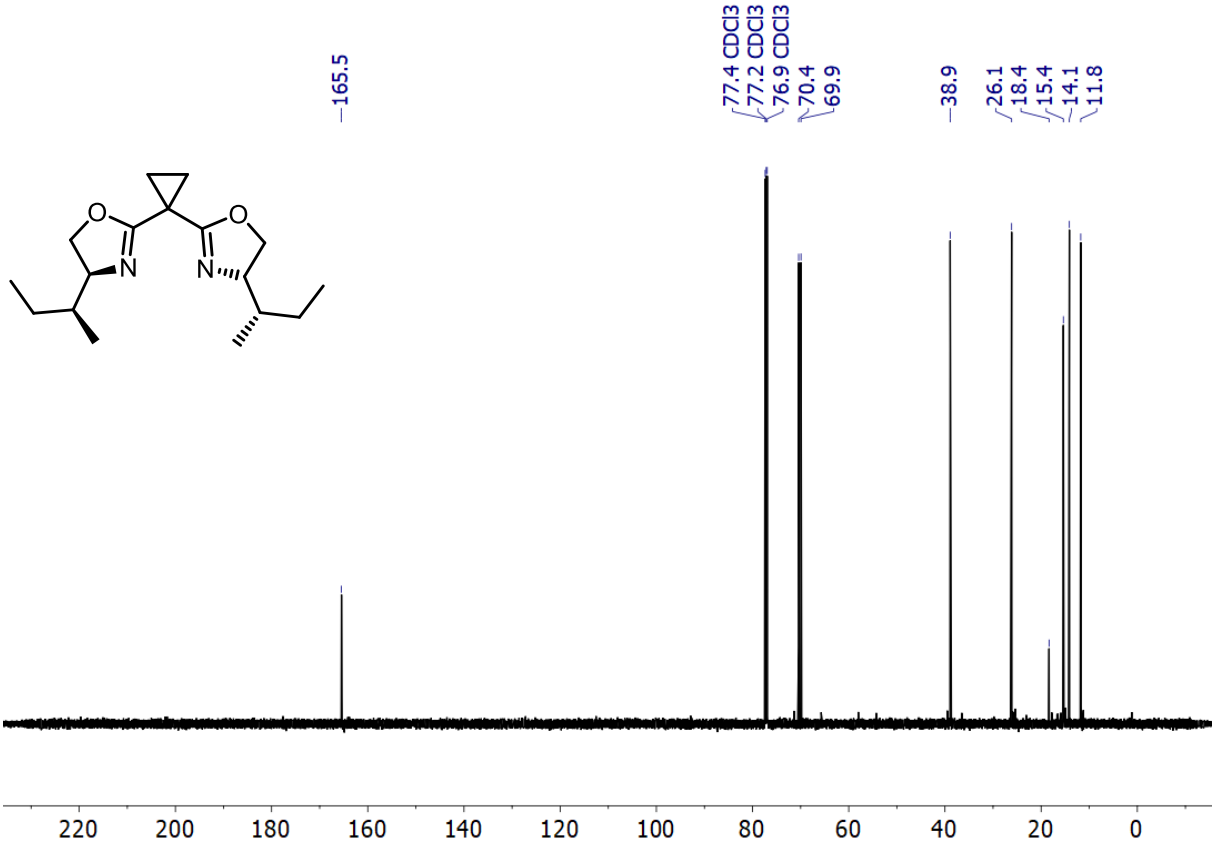
[S5], ^{13}C, $CDCl_3$, 151 MHz



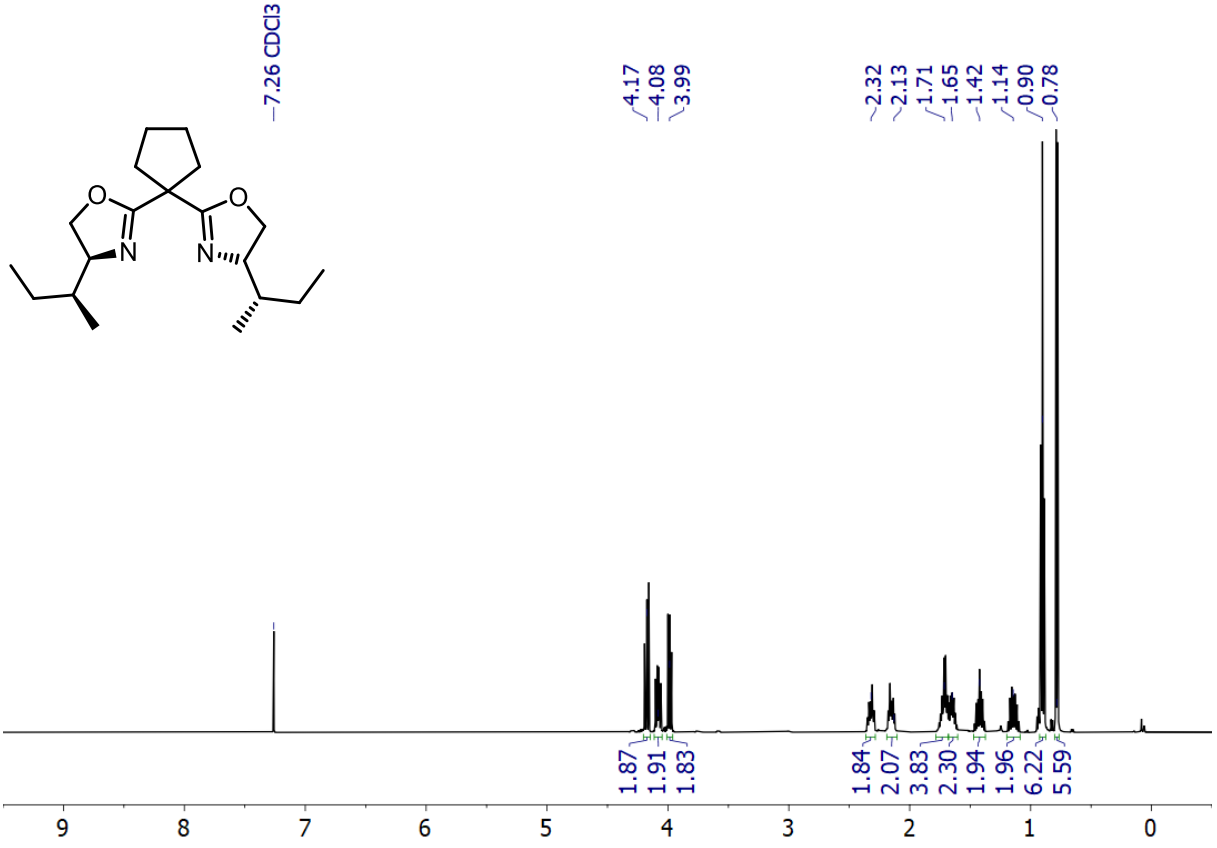
[LS5a], ^{1}H, $CDCl_3$, 599 MHz



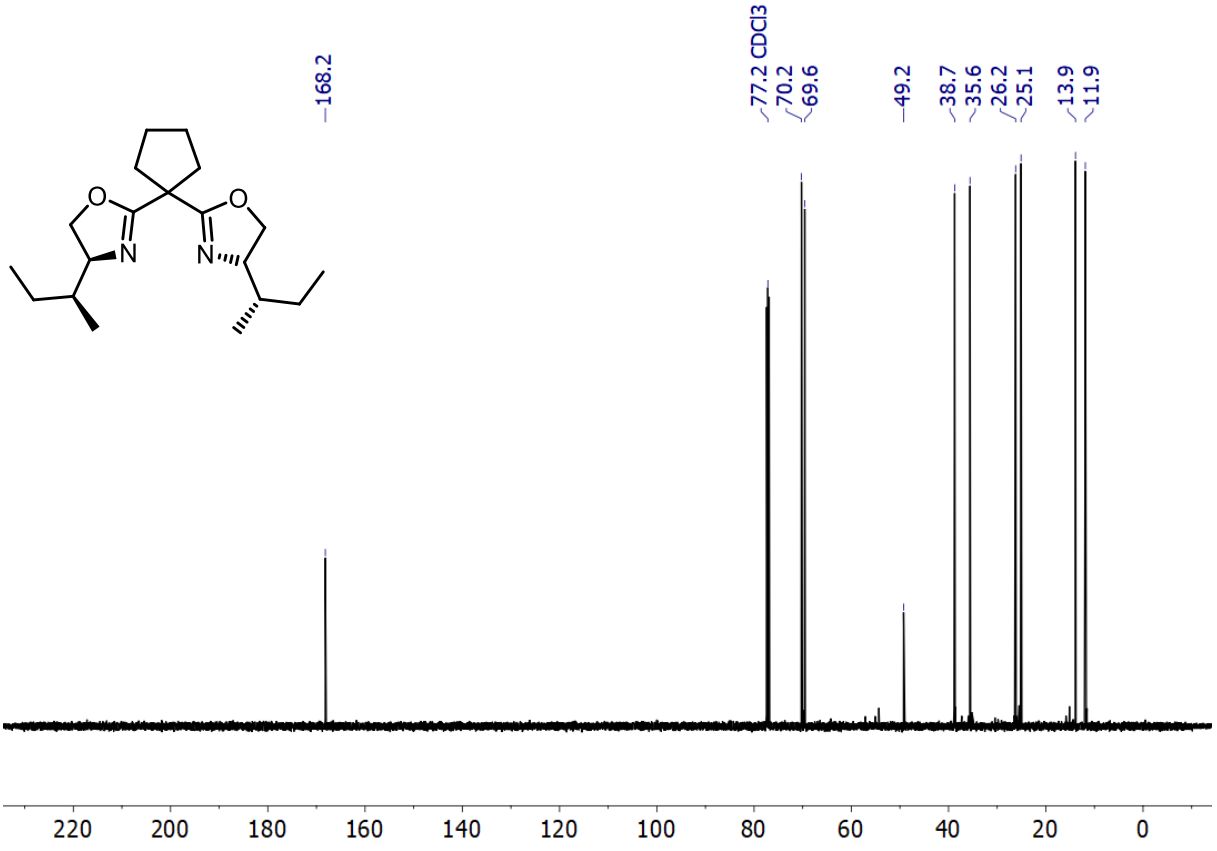
[LS5a], ^{13}C, $CDCl_3$, 151 MHz



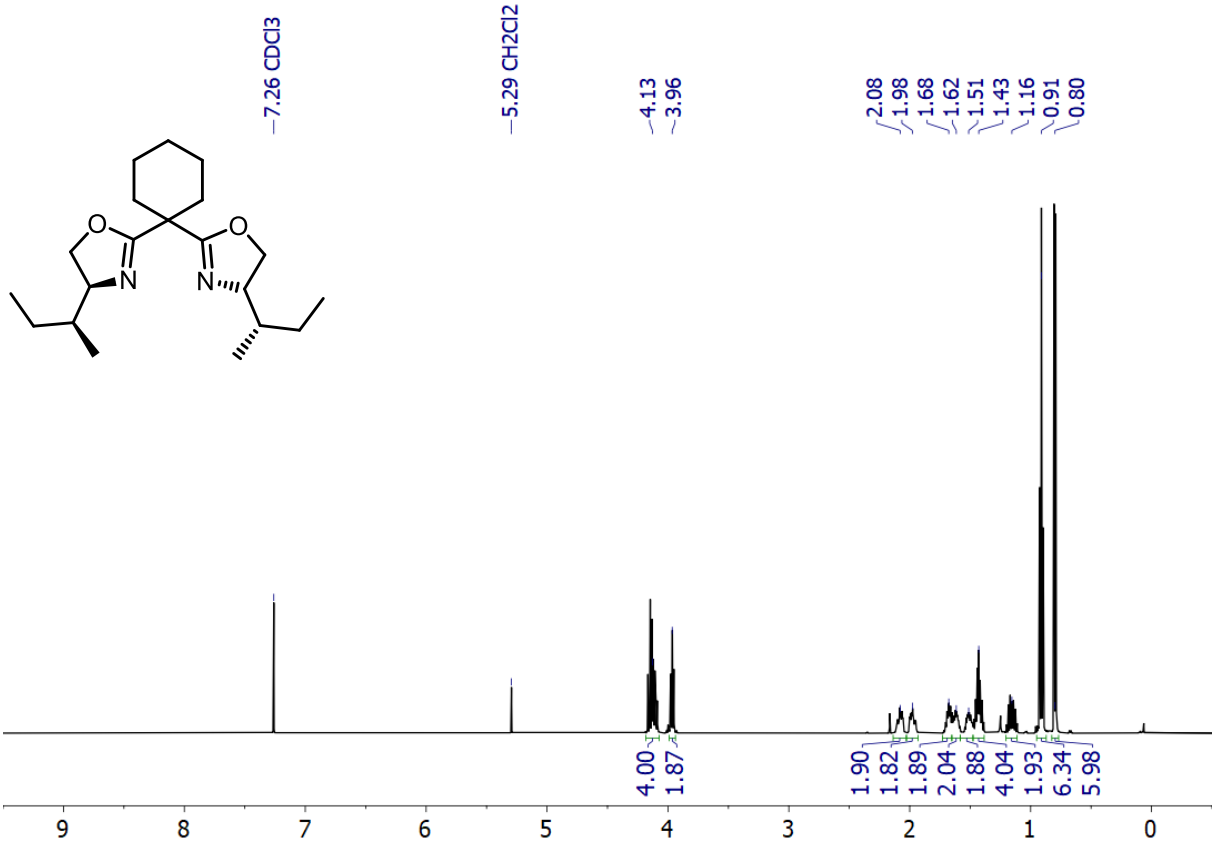
[LS5b], ^{1}H, $CDCl_3$, 500 MHz



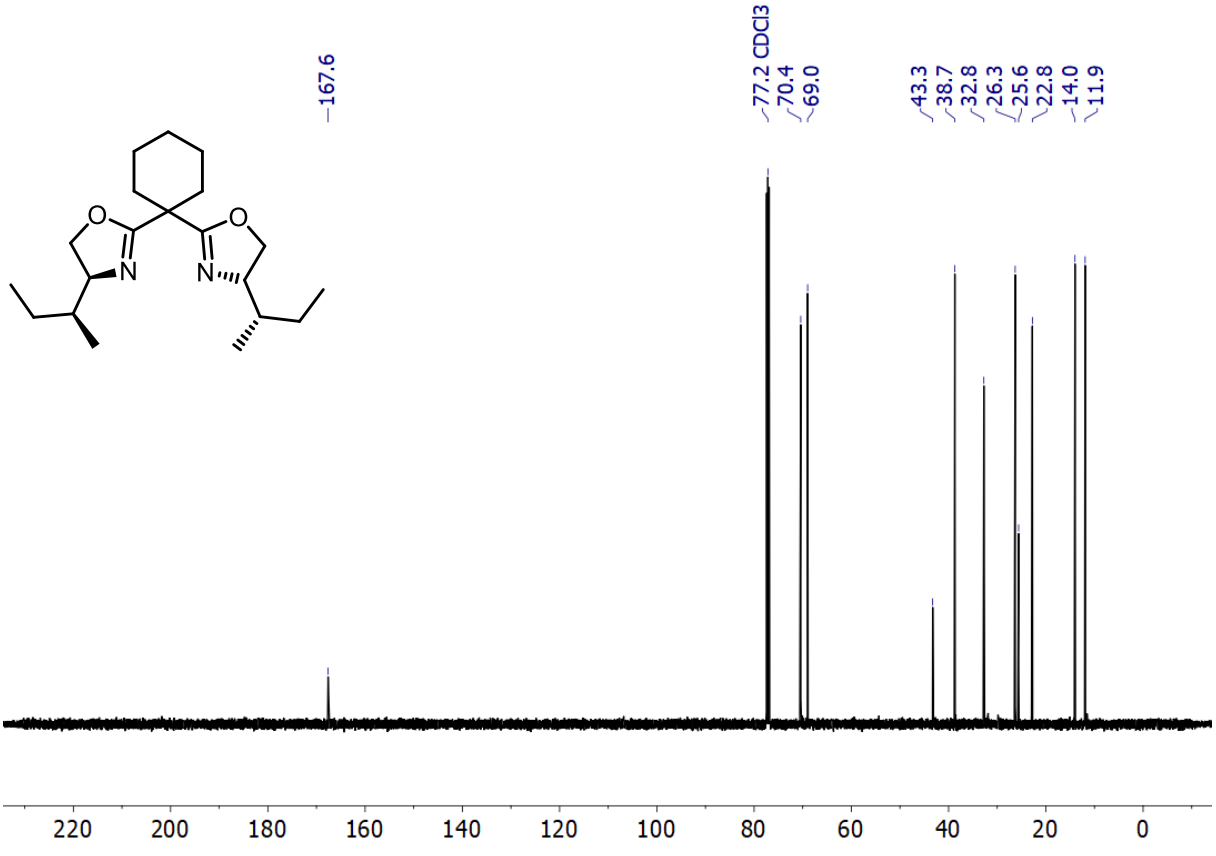
[LS5b], ^{13}C, $CDCl_3$, 126 MHz



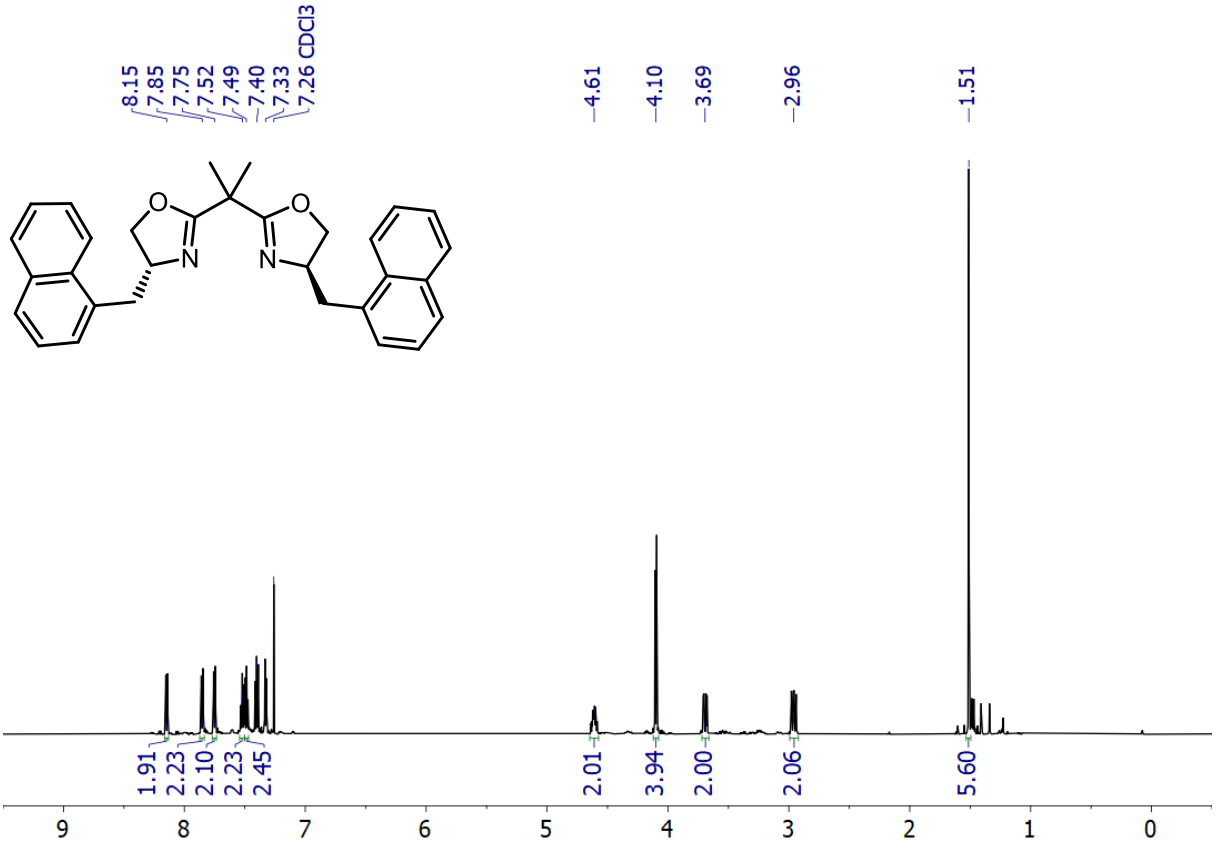
[LS5c], ^{1}H, $CDCl_3$, 500 MHz



[LS5c], ^{13}C, $CDCl_3$, 126 MHz



[LS8], ^{1}H, $CDCl_3$, 599 MHz



[LS8], ^{13}C, $CDCl_3$, 151 MHz