

## Supporting Information

### FINE CHEMICALS FROM A BIOMASS-DERIVED DICARBOXYLIC ACID: CHIRAL BISOXAZOLINES AND THEIR APPLICATION IN ENANTIOSELECTIVE DIELS-ALDER REACTIONS

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#### Table of Contents

1. General methods
2. General procedure for synthesis of chiral amido alcohol **3a-e** and **6**
3. General procedure for synthesis of chiral bisoxazolines **4a-e** and **7**
4. Copy of  $^1\text{H}$ ,  $^{13}\text{C}$  NMR spectrum.
5. Copy of HPLC spectrum.
6. X-ray structure and its parameters
7. References

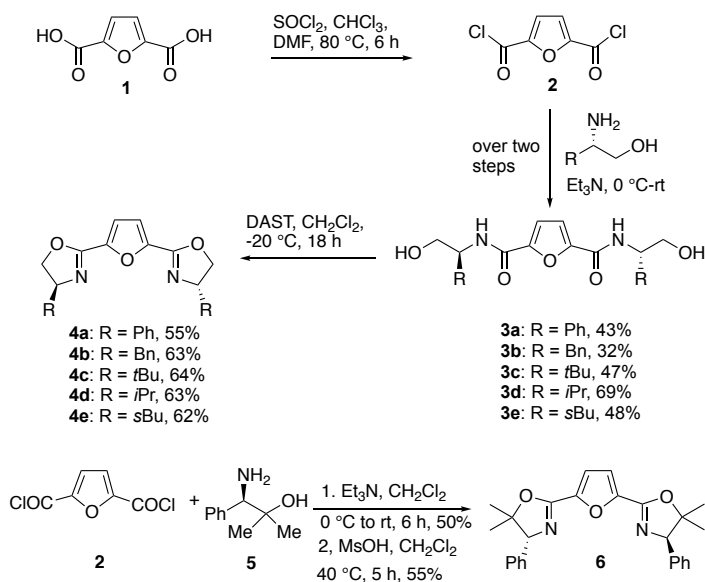
#### 1. General methods:

All commercially obtained reagents/solvents were used as received; chemicals were purchased from Alfa Aesar®, Sigma-Aldrich®, TCI America®, and were used as received without further purification. FDCA was synthesized according to literature procedure.<sup>1</sup> Zinc triflimide was prepared according to literature procedure.<sup>2</sup> Unless stated otherwise, reactions were conducted in oven-dried glassware under nitrogen atmosphere. Molecular sieves were dried under vacuum prior to use.  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra were recorded on Varian 400 MHz (100 MHz for  $^{13}\text{C}$ ) and on 500 MHz (125 MHz for  $^{13}\text{C}$ ) spectrometers. Data from the  $^1\text{H-NMR}$  spectroscopy are reported as chemical shift ( $\delta$  ppm) with the corresponding integration values. Coupling constants (J) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s (singlet), b (broad), d (doublet), t (triplet), q (quartet), and m (multiplet). Data for  $^{13}\text{C}$  NMR spectra are reported in terms of chemical shift ( $\delta$  ppm). High-resolution mass

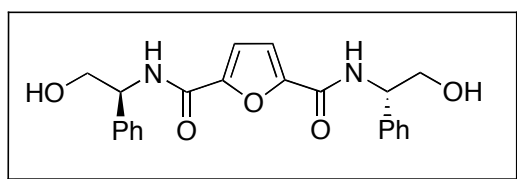
spectrum data in Electrospray Ionization mode were recorded on a Bruker – Daltronics® BioTof mass spectrometer in positive (ESI+) ion mode. HPLC analyses were carried out on Waters 515 HPLC pump and a 2487 dual  $\lambda$  absorbance detector connected to a PC with Empower workstation. Rotations were recorded on a JASCO-DIP-370 instrument. FT-IR spectra were recorded on a Nexus 470 FT-IR. Melting points were measured with a Fisher-Johns melting points apparatus and are uncorrected. When necessary, the compounds were purified by combiflash equipped with dual wavelength UV-Vis absorbance detector (Teledyne ISCO) using hexanes:ethyl acetate/CH<sub>2</sub>Cl<sub>2</sub>:MeOH as the mobile phase and Redisep® cartridge filled with silica (Teledyne ISCO) as stationary phase. In some cases, compounds were purified by column chromatography on silica gel (Sorbent Technologies®, silica gel standard grade: porosity 60 Å, particle size: 230 x 400 mesh, surface area: 500 – 600 m<sup>2</sup>/g, bulk density: 0.4 g/mL, pH range: 6.5 – 7.5).

## **2. General procedure for the synthesis of amido alcohols**

To a suspension of FDCA (3.20 mmol) in dry CHCl<sub>3</sub> (9 mL), thionyl chloride (11.04 mmol) and few drops of DMF were added at room temperature. Reaction mixture was stirred at reflux temperature for 6 h. It was then cooled and concentrated in vacuum. The crude product was used in the next step without further purification. To a solution of aminoalcohol (6.4 mmol) and triethylamine (12.8 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (20 mL), acid chloride **2** in CH<sub>2</sub>Cl<sub>2</sub> (6 mL) was added dropwise at 0° C. The reaction mixture was slowly warmed to room temperature and stirred for 12 h. It was diluted with CH<sub>2</sub>Cl<sub>2</sub> and washed with water, brine and dried over Na<sub>2</sub>SO<sub>4</sub>. Solvent was removed in vacuum and the crude compound was purified over silica gel column chromatography using MeOH/CH<sub>2</sub>Cl<sub>2</sub> as eluent.



**Synthesis of Ligands: *N,N'*-Bis((*S*)-2-hydroxy-1-phenylethyl)furan-2,5-dicarboxamide (3a):**



Yield: 43%

Yellow solid

mp: 122-125 °C.

$[\alpha]_D^{26} = -113.1$  (*c* 0.42, CHCl<sub>3</sub>)

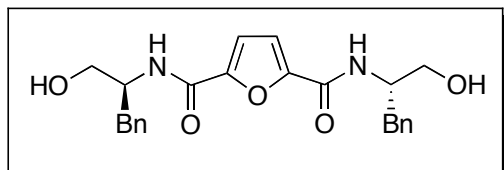
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.76 (bs, 2H), 3.98 (bs, 2H), 4.80 (bs, 2H), 5.29 (bs, 2H), 6.49 (bs, 2H), 7.19-7.31 (m, 10H), 8.29 (bs, 2H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 56.0, 65.1, 114.1, 126.7, 127.6, 128.5, 138.7, 147.6, 158.4.

IR (neat): 3427, 3315, 3027, 2941, 1645, 1594, 1295, 1077 cm<sup>-1</sup>.

HRMS: Calcd. for C<sub>22</sub>H<sub>22</sub>N<sub>2</sub>O<sub>5</sub>Na<sup>+</sup> 417.1421; Found 417.1414.

***N,N'*-Bis((*S*)-1-hydroxy-3-phenylpropan-2-yl)furan-2,5-dicarboxamide (3b):**



Yield: 32%

White solid

mp: 86-90 °C.

$[\alpha]_D^{26} = -114.6$  (*c* 0.2, CHCl<sub>3</sub>)

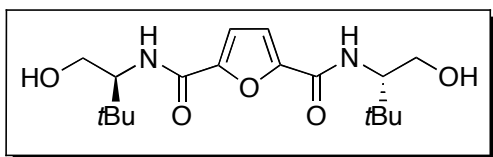
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 2.91 (m, 4H), 3.08 (bs, 2H), 3.62 (m, 2H), 3.82 (m, 2H), 4.33 (m, 2H), 6.84 (s, 2H), 6.88 (d, *J* = 8.4 Hz, 2H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>+CD<sub>3</sub>OD) δ 37.2 (d), 53.1 (d), 62.9, 115.0, 126.7, 128.7, 129.4, 138.0, 148.1 (d), 158.5 (d).

**IR** (neat): 3424, 3322, 3015, 2941, 1649, 1594, 1571, 1310, 1221 cm<sup>-1</sup>.

**HRMS**: Calcd. for C<sub>24</sub>H<sub>26</sub>N<sub>2</sub>O<sub>5</sub>Na+ 445.1734; Found 445.1736.

***N,N'*-Bis((*S*)-1-hydroxy-3,3-dimethylbutan-2-yl)furan-2,5-dicarboxamide (3c):**



Yield: 47%

White solid

mp: 222-224 °C.

[α]<sub>D</sub><sup>26</sup> = +21.0 (*c* 0.14, CHCl<sub>3</sub>)

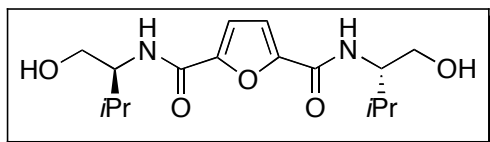
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 0.98 (s, 18H), 3.63 (m, 2H), 4.05 (m, 4H), 4.64 (m, 2H), 6.64 (s, 2H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub> + CD<sub>3</sub>OD) δ 26.7, 34.3, 59.7, 61.0, 114.6, 147.9, 159.5.

**IR** (neat): 3303, 2968, 1657, 1563 cm<sup>-1</sup>.

**HRMS**: Calcd. for C<sub>18</sub>H<sub>30</sub>N<sub>2</sub>O<sub>5</sub>Na+ 377.2047; Found 377.2041.

***N,N'*-Bis((*S*)-1-hydroxy-3-methylbutan-2-yl)furan-2,5-dicarboxamide (3d):**



Yield: 69%

White solid

mp: 92-96 °C.

[α]<sub>D</sub><sup>26</sup> = -9.5 (*c* 0.2, CHCl<sub>3</sub>)

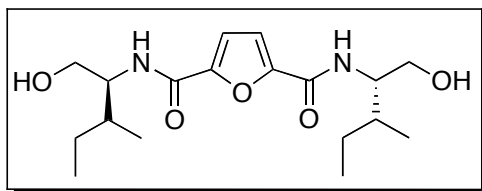
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 0.96 (m, 12H), 1.88 (m, 2H), 3.69 (m, 2H), 3.83 (m, 2H), 3.95 (m, 4H), 6.74 (s, 2H), 7.0 (d, *J* = 8.0 Hz, 2H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 19.1, 19.5, 29.6, 57.2 (d), 62.4 (d), 114.6, 148.0, 159.0 (d).

IR (neat): 3408, 3295, 3019, 2968, 1657, 1590, 1536, 1225  $\text{cm}^{-1}$ .

HRMS: Calcd. for  $\text{C}_{16}\text{H}_{26}\text{N}_2\text{O}_5\text{Na}^+$  349.1734; Found 349.1741.

***N*-((2*S*,3*R*)-1-Hydroxy-3-methylpentan-2-yl)-*N'*-((2*S*,3*S*)-1-hydroxy-3-methylpentan-2-yl)furan-2,5-dicarboxamide (3e):**



Yield: 48%

Yellow solid

mp: 94-98  $^{\circ}\text{C}$ .

$[\alpha]_{\text{D}}^{26} = -15.4$  (*c* 0.57,  $\text{CHCl}_3$ )

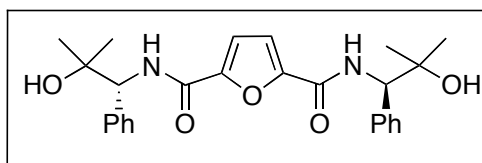
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.88 (t,  $J = 7.2$  Hz, 6H), 0.94 (d,  $J = 6.8$  Hz, 6H), 1.15 (m, 2H), 1.51 (m, 2H), 1.63 (m, 2H), 3.65 (m, 2H), 3.99 (m, 4H), 4.14 (bs, 2H), 6.68 (s, 2H), 7.14 (d,  $J = 8.8$  Hz, 2H).

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  11.4, 15.5, 25.8, 36.3, 56.1, 62.1, 114.0, 148.1, 158.7.

IR (neat): 3408, 3291, 3019, 2972, 1653, 1606, 1536, 1369  $\text{cm}^{-1}$ .

HRMS: Calcd. for  $\text{C}_{18}\text{H}_{30}\text{N}_2\text{O}_5\text{Na}^+$  377.2047; Found 377.2047.

***N,N'*-Bis((*R*)-2-hydroxy-2-methyl-1-phenylpropyl)furan-2,5-dicarboxamide 6a**



Yield: 50%

Yellow solid

mp: 125-128  $^{\circ}\text{C}$ .

$[\alpha]_{\text{D}}^{26} = +190.0$  (*c* 0.53,  $\text{CHCl}_3$ )

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.10 (s, 6H), 1.39 (s, 6H), 1.95 (bs, 2H), 4.94 (d,  $J = 8.0$  Hz, 1H), 7.06 (s, 2H), 7.26-7.42 (m, 12H).

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  27.1, 28.1, 61.7, 72.2, 115.2, 127.6, 128.1, 128.3, 139.1, 148.3, 157.6.

IR (neat): 3400, 3034, 2980, 1672, 1598, 1571, 1376, 1213, 1162  $\text{cm}^{-1}$ .

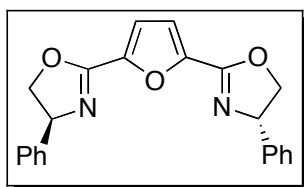
HRMS: Calcd. for  $\text{C}_{26}\text{H}_{30}\text{N}_2\text{O}_5\text{Na}^+$  473.2047; Found 473.2045.

**3. General procedure for the synthesis of chiral bisoxazolines:**

These compounds were synthesized according to literature procedure.<sup>3</sup> To a solution of amido alcohol **3** (1 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (10 mL), DAST was added dropwise at  $-20$   $^{\circ}\text{C}$ . Reaction mixture was stirred at same temperature for 18 h. Then 4 mL of aqueous 4N

ammonium hydroxide was added and the resulting solution was stirred for 15 min at -20 °C. Subsequently, the cooling bath was removed and 10 mL of water was added. Aqueous phase was the extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 X 20 mL) and the combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Solvent was removed in vacuum and crude compound was purified over silica gel chromatography using Hexane/EtOAc as eluent.

#### 2,5-Bis((S)-4-phenyl-4,5-dihydrooxazol-2-yl)furan (4a):



Yield: 55%

White solid

mp: 162-165 °C.

$[\alpha]_D^{26} = -80.3$  (c 0.5, CHCl<sub>3</sub>)

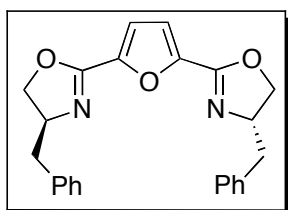
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.27 (m, 2H), 4.78 (m, 2H), 5.39 (m, 2H), 7.14 (s, 2H), 7.24-7.36 (m, 10H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 70.4, 75.2, 116.1, 126.9, 128, 129, 141.7, 144.9, 156.6.

IR (neat): 3058, 1668, 1516, 1357, 1205, 1112 cm<sup>-1</sup>.

HRMS: Calcd. for C<sub>22</sub>H<sub>18</sub>N<sub>2</sub>O<sub>3</sub>Na+ 381.1210; Found 381.1215.

#### 2,5-Bis((S)-4-benzyl-4,5-dihydrooxazol-2-yl)furan (4b):



Yield: 63%

White solid

mp: 140-144 °C.

$[\alpha]_D^{26} = +40.3$  (c 0.5, CHCl<sub>3</sub>)

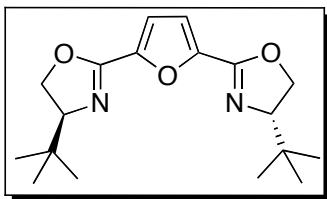
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 2.69 (dd, *J* = 13.6, 8.8 Hz, 2H), 3.21 (dd, *J* = 14.0, 5.2 Hz, 2H), 4.12 (m, 2H), 4.32 (m, 2H), 4.59 (m, 2H), 7.01 (s, 2H), 7.19-7.30 (m, 10H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 41.7, 68.2, 72.3, 115.7, 126.8, 128.8, 129.4, 137.8, 145.0, 155.9.

IR (neat): 3147, 2941, 1653, 1548, 1322, 1275, 1120 cm<sup>-1</sup>.

HRMS: Calcd. for C<sub>24</sub>H<sub>22</sub>N<sub>2</sub>O<sub>3</sub>Na+ 409.1523; Found 409.1529.

#### 2,5-Bis((S)-4-tert-butyl-4,5-dihydrooxazol-2-yl)furan (4c):



Yield: 64%

White solid

**mp:** 138-142 °C.

$[\alpha]_D^{26} = -72.6$  (*c* 0.1, CHCl<sub>3</sub>)

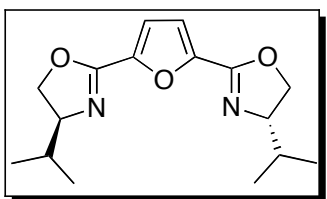
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.92 (s, 18H), 4.05 (m, 2H), 4.19 (m, 2H), 4.30 (m, 2H), 6.98 (s, 2H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 26.1, 34.2, 69.2, 76.6, 115.3, 144.9, 155.3.

**IR** (neat): 3139, 2968, 1660, 1365, 1221, 1120 cm<sup>-1</sup>.

**HRMS:** Calcd. for C<sub>18</sub>H<sub>26</sub>N<sub>2</sub>O<sub>3</sub>Na<sup>+</sup> 341.1836; Found 341.1828.

#### 2,5-Bis((*S*)-4-isopropyl-4,5-dihydrooxazol-2-yl)furan (4d):



Yield: 63%

White solid

**mp:** 98-102 °C.

$[\alpha]_D^{26} = -101.6$  (*c* 0.5, CHCl<sub>3</sub>)

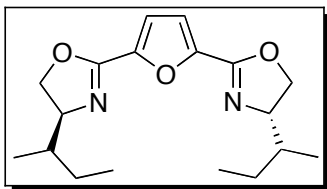
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.90 (d, *J* = 6.8 Hz, 6H), 1.0 (d, *J* = 6.8 Hz, 6H), 1.84 (m, 2H), 4.09 (m, 4H), 4.43 (m, 2H), 7.0 (s, 2H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 18.3, 19.0, 70.4, 73.0, 115.2, 144.9, 155.1.

**IR** (neat): 2964, 2921, 1680, 1653, 1365, 1310, 1112 cm<sup>-1</sup>.

**HRMS:** Calcd. for C<sub>16</sub>H<sub>22</sub>N<sub>2</sub>O<sub>3</sub>Na<sup>+</sup> 313.1523; Found 313.1521.

#### 2,5-Bis((*S*)-4-sec-butyl-4,5-dihydrooxazol-2-yl)furan (4e):



Yield: 62%

White solid

**m.p.:** 48-52 °C.

$[\alpha]_D^{26} = -64.0$  (*c* 0.5, CHCl<sub>3</sub>)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.82 (d, *J* = 6.4 Hz, 6H), 0.92 (t, *J* = 7.2 Hz, 6H), 1.21 (m, 2H), 1.55-1.70 (m, 6H), 4.09 (t, *J* = 8 Hz, 2H), 4.19 (m, 2H), 4.35 (m, 2H), 6.98 (s, 2H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 11.7, 14.6, 26.2, 39.2, 70.2, 71.6, 115.3, 144.9, 156.3.

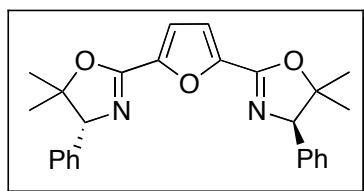
**IR** (neat): 2964, 2871, 1672, 1590, 1513, 1221, 1120 cm<sup>-1</sup>.

**HRMS:** Calcd. for C<sub>18</sub>H<sub>27</sub>N<sub>2</sub>O<sub>3</sub>+ 319.2016; Found 319.2031.

### Synthesis of chiral bioxazoline (6):

Methanesulfonic acid (5 mmol) was added dropwise to a solution of amido alcohol **6a** (1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL) at room temperature over a period of approximately 10 min and the reaction mixture was stirred at 40 °C for 5 h. Reaction mixture was then cooled and diluted with CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and washed with aqueous NaHCO<sub>3</sub>, water and brine. The organic layer was dried over anhydrous NaSO<sub>4</sub>. Solvent was removed in vacuum and crude compound was purified over silica gel chromatography using Hexane/EtOAc as eluent.

### 2,5-Bis((*R*)-5,5-dimethyl-4-phenyl-4,5-dihydrooxazol-2-yl)furan (6):



Yield: 55%

White solid

mp: 92-95 °C.

$[\alpha]_D^{26} = -51.7$  (*c* 0.475, CHCl<sub>3</sub>)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.92 (s, 6H), 1.62 (s, 6H), 5.01 (s, 2H), 7.12 (s, 2H), 7.19-7.30 (m, 10H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 23.9, 29.1, 78.5, 88.6, 115.8, 127.4, 127.8, 128.4, 138.5, 145.5, 155.9.

IR (neat): 3058, 2984, 2929, 1672, 1583, 1454, 1334, 1221, 1104 cm<sup>-1</sup>.

**HRMS:** Calcd. for C<sub>26</sub>H<sub>27</sub>N<sub>2</sub>O<sub>3</sub>+ 415.2016; Found 415.2023.

### General procedure for the asymmetric Diels-Alder reaction:

#### 3-((1*S*,2*S*,4*S*)-Bicyclo[2.2.1]hept-5-enecarbonyl)oxazolidin-2-one (8):

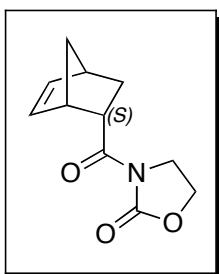
A mixture of ligand (0.033 mmol) and Lewis acid (0.030 mmol) in dichloromethane (2 mL) was stirred at room temperature for one hour. To the above solution 3-(2-propenoyl)-2-oxazolidinone **7** (0.10 mmol) and freshly distilled cyclopentadiene (1.0 mmol) was added at the temperature given in the tables. Reaction progress was monitored by TLC. After completion, the solvent was removed under reduced pressure and the residue was purified by flash chromatography to pure product. The endo/exo ratio was

determined by  $^1\text{H}$ NMR spectrum. The enantiomeric purity was evaluated on the basis of HPLC (81% ee).

(*endo*: *exo*) = 99:1

Yield: quantitative

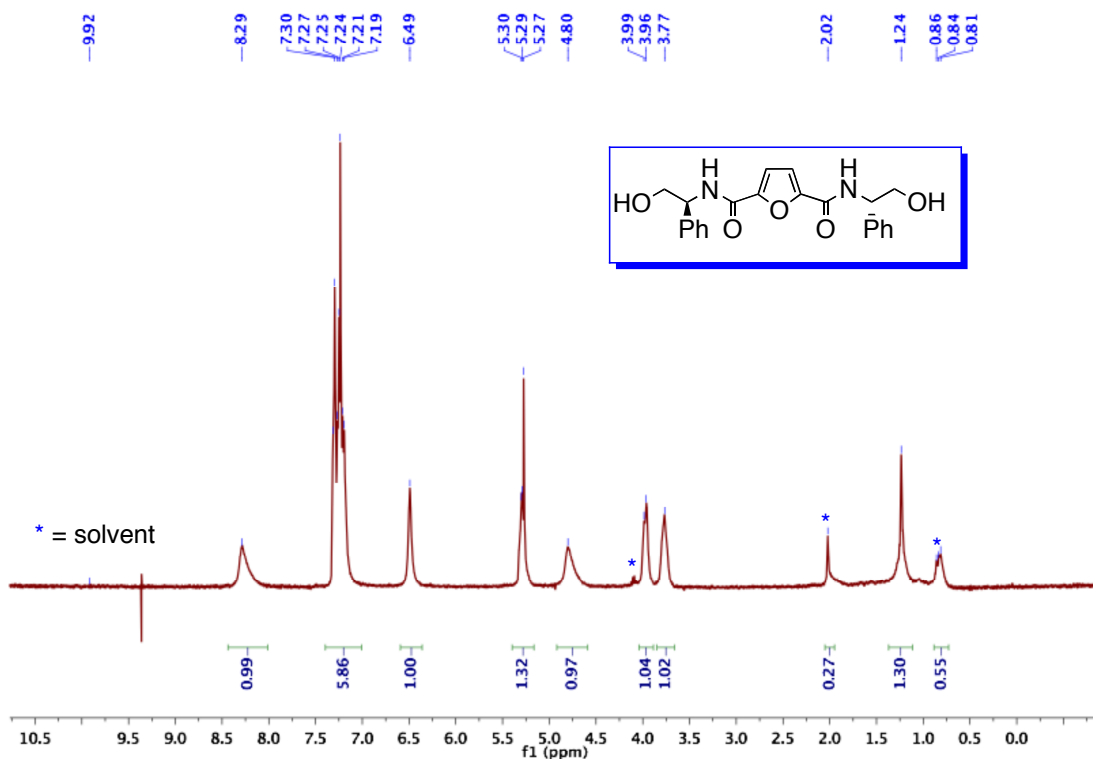
The HPLC analysis was performed on chiralcel OD-3 with hexanes/2-propanol (95:5) as eluent (0.6 mL/min),  $endo_{\text{major}}$   $t_R$  = 43.4 min,  $endo_{\text{minor}}$   $t_R$  = 47.5 min.



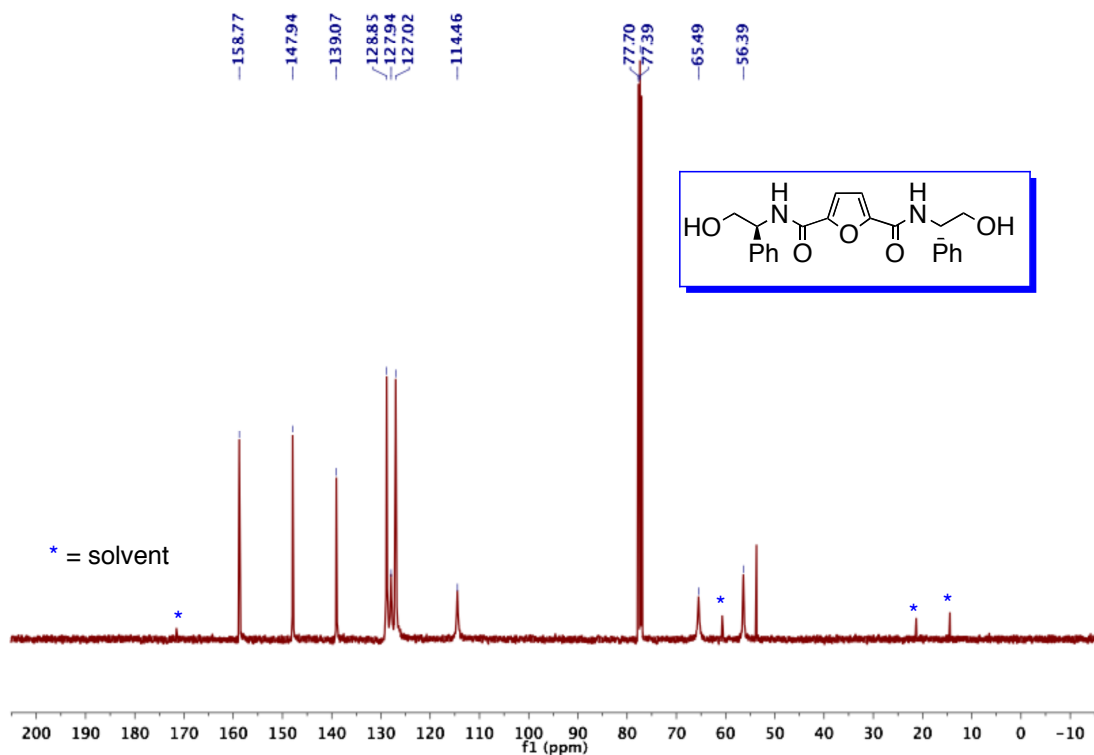
$[\alpha]_D^{26} = -77.5$  ( $c$  0.85,  $\text{CHCl}_3$ ); [Lit.<sup>4</sup>  $[\alpha]_{589} = -160$  ( $c$  0.83,  $\text{CHCl}_3$ ) for >98% ee (*endo*) product]

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.39 (m, 2H), 1.94 (m, 2H), 2.92 (bs, 1H), 3.28 (bs, 1H), 3.95 (m, 3H), 4.37 (m, 2H), 5.85 (dd,  $J = 6.0, 3.2$  Hz, 1H), 6.22 (dd,  $J = 5.6, 2.8$  Hz, 1H).

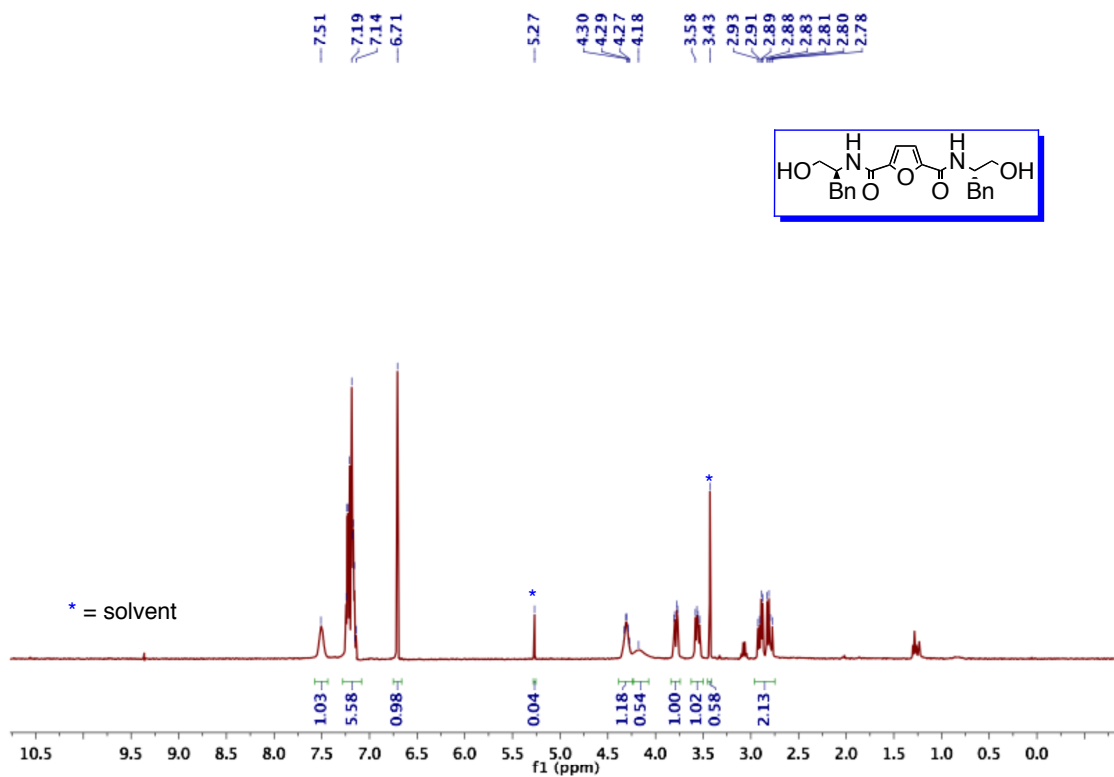
#### 4. Copy of $^1\text{H}$ and $^{13}\text{C}$ spectra:



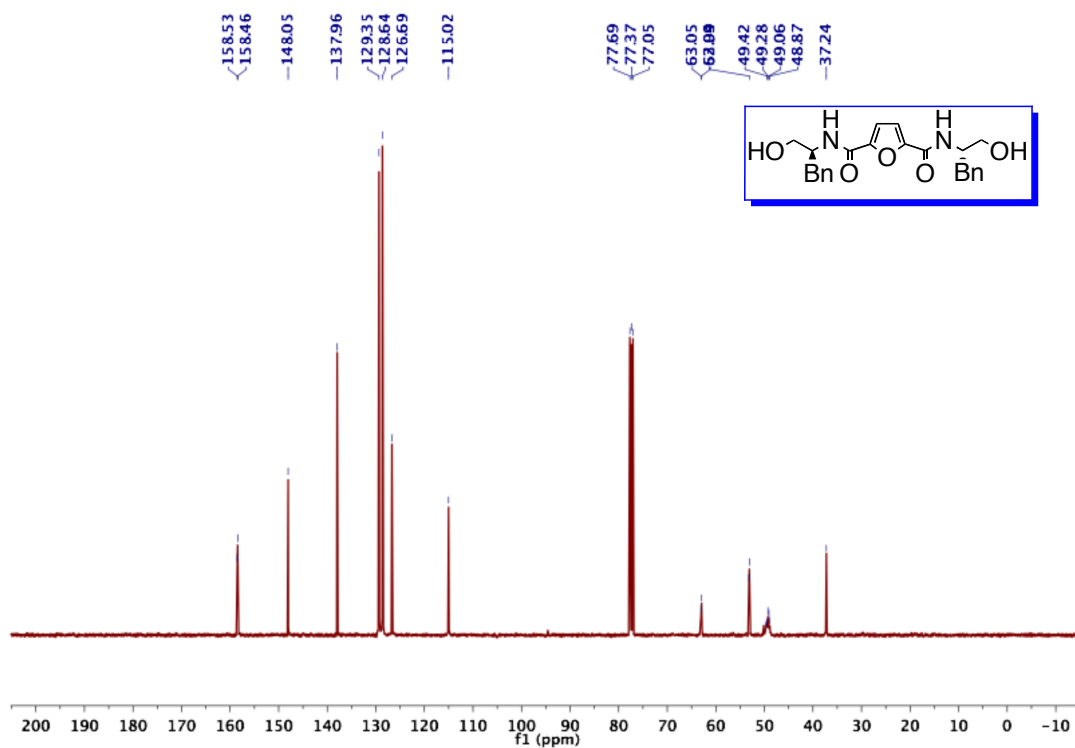
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **3a**



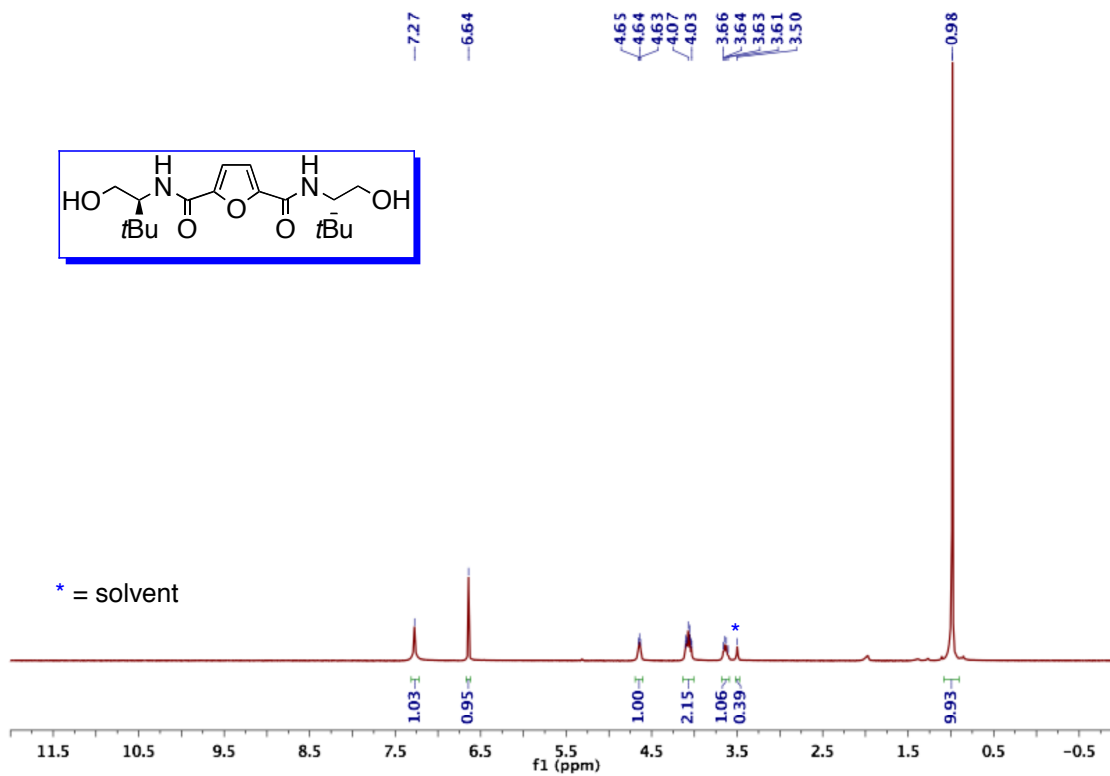
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of **3a**



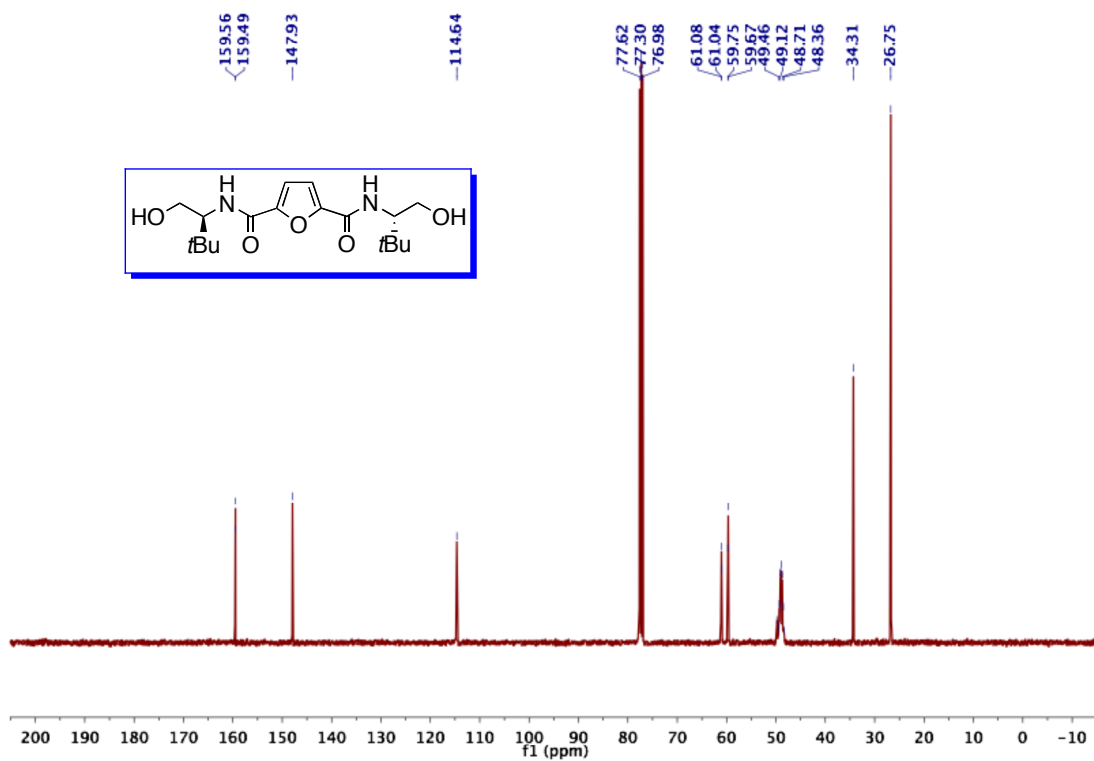
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **3b**



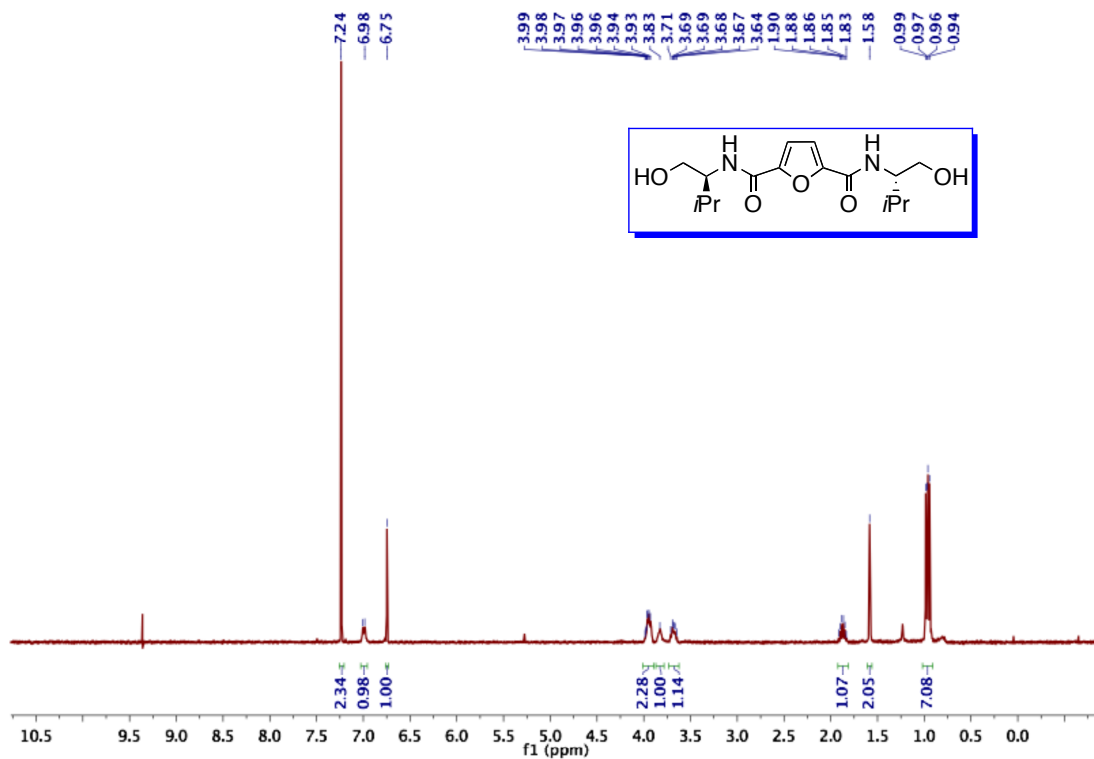
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3+\text{CD}_3\text{OD}$ ) spectrum of **3b**



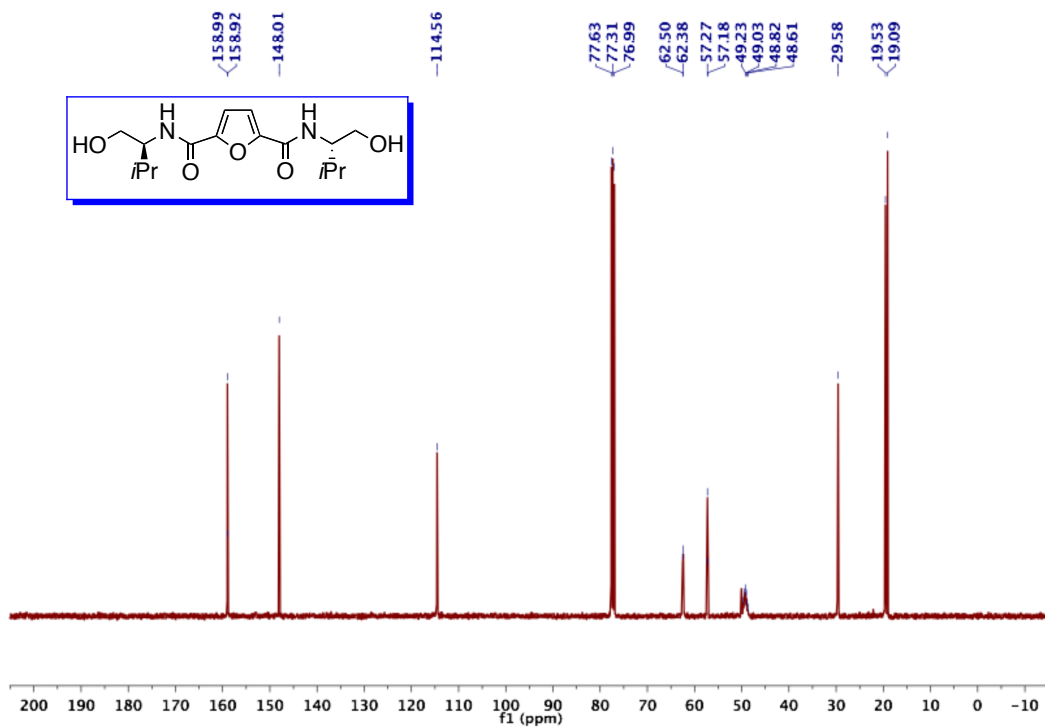
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **3c**



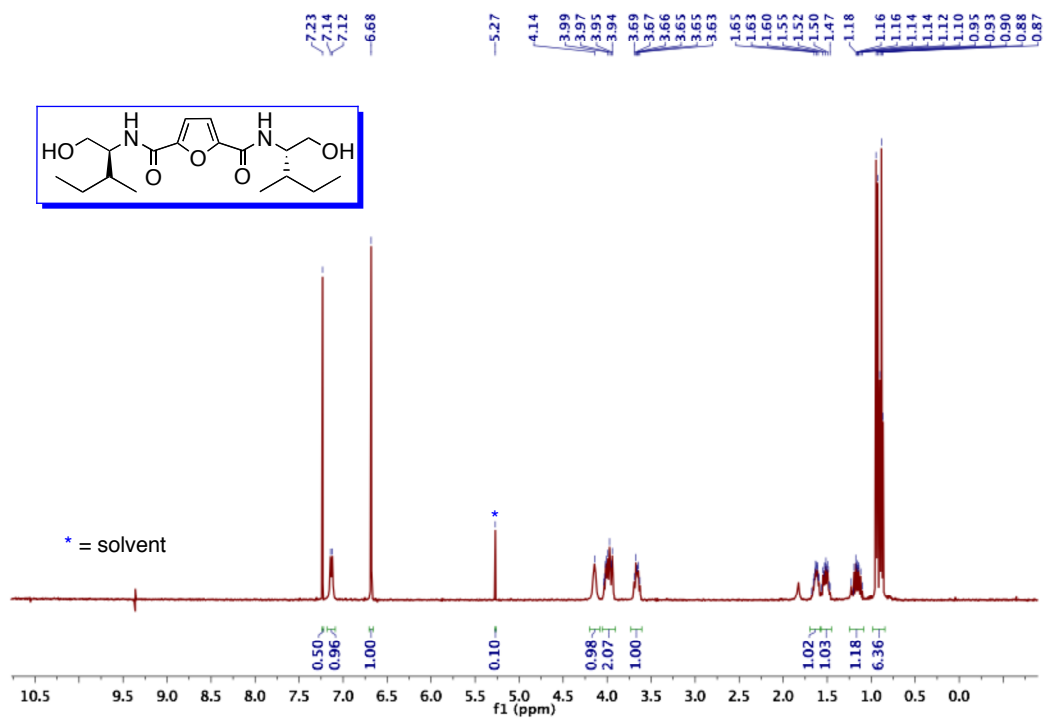
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3 + \text{CD}_3\text{OD}$ ) spectrum of **3c**



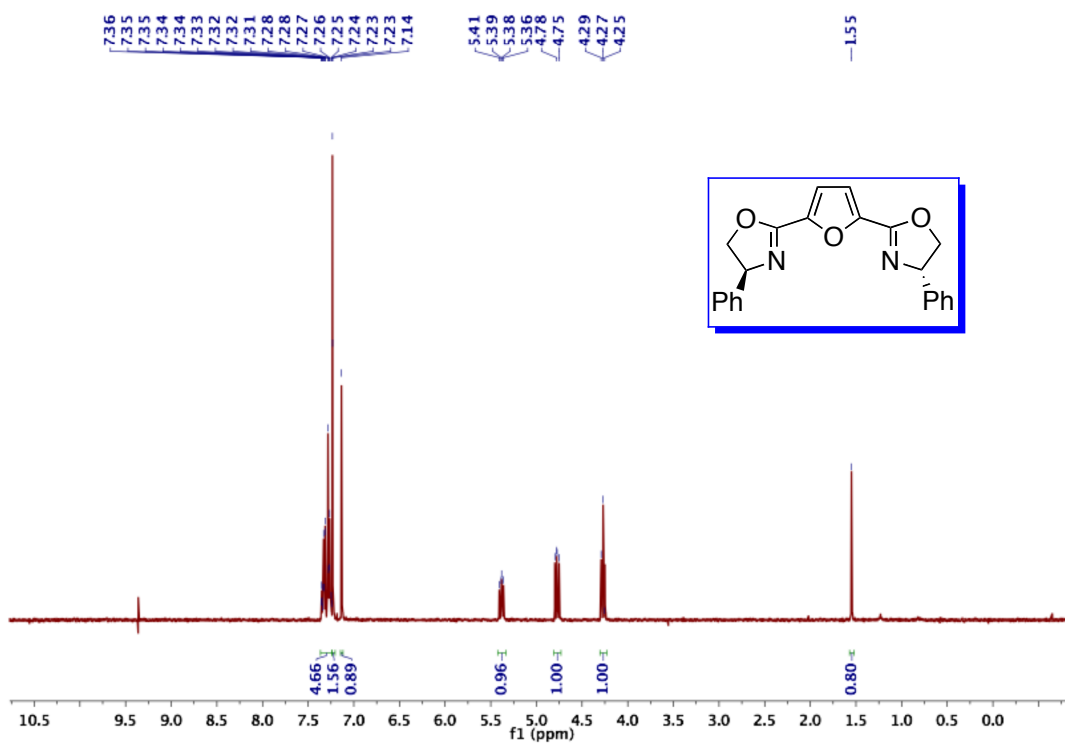
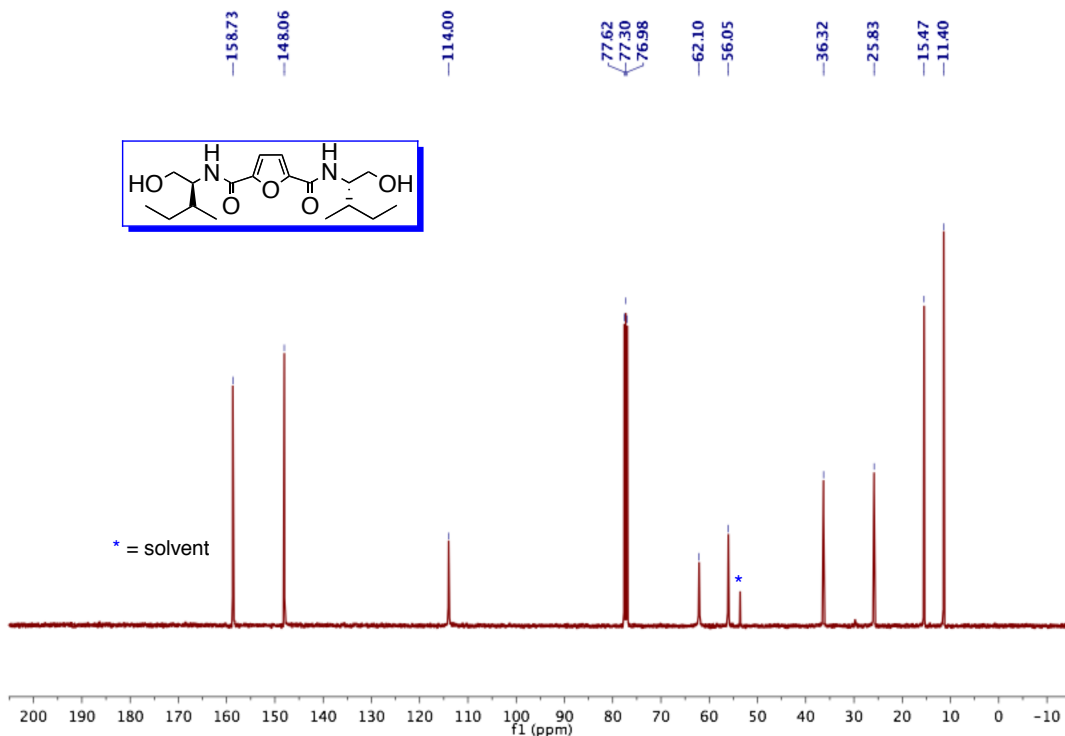
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **3d**

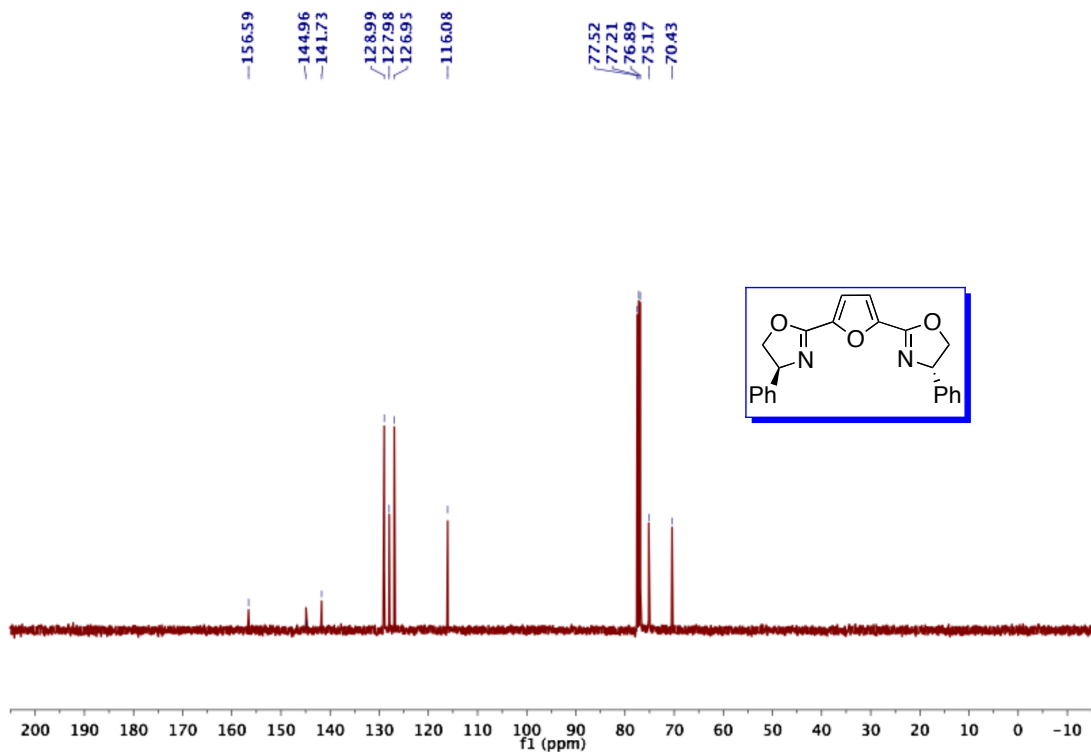


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>+CD<sub>3</sub>OD) spectrum of **3d**

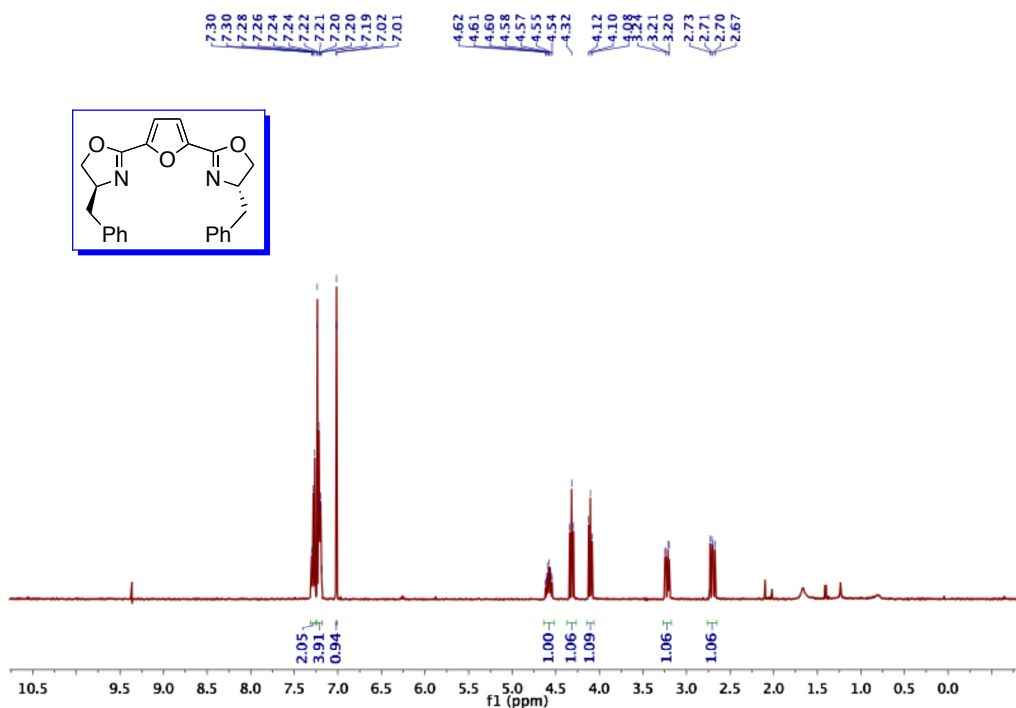


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **3e**

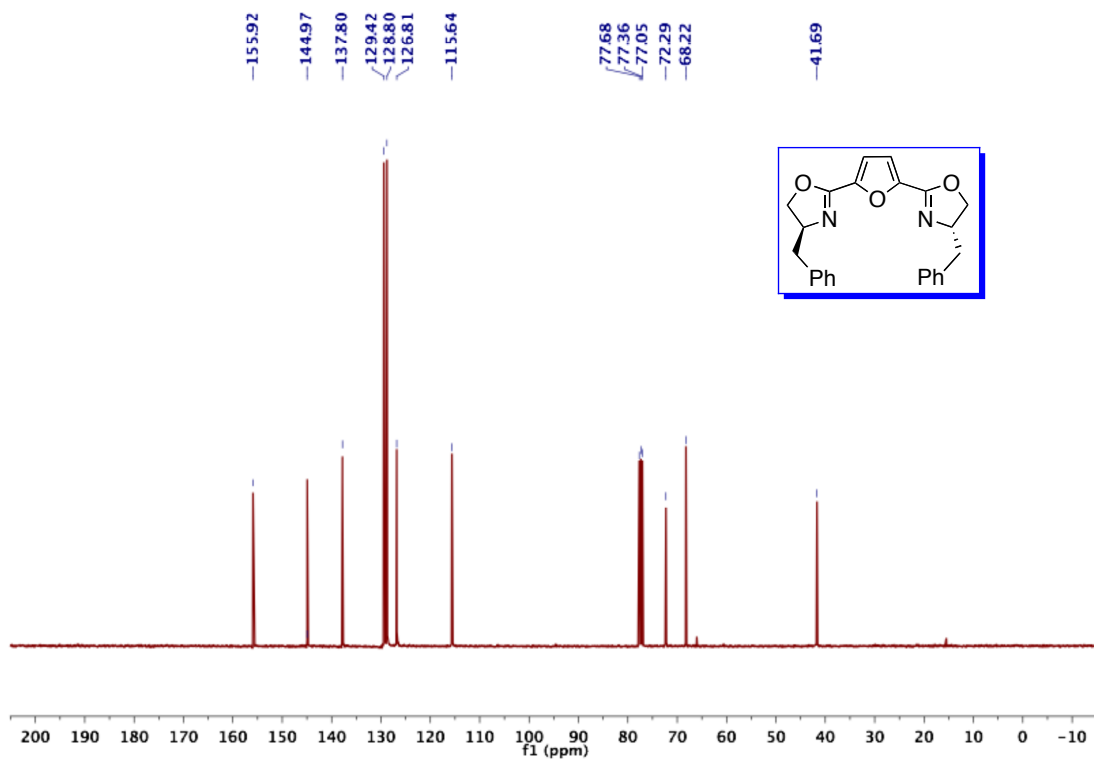




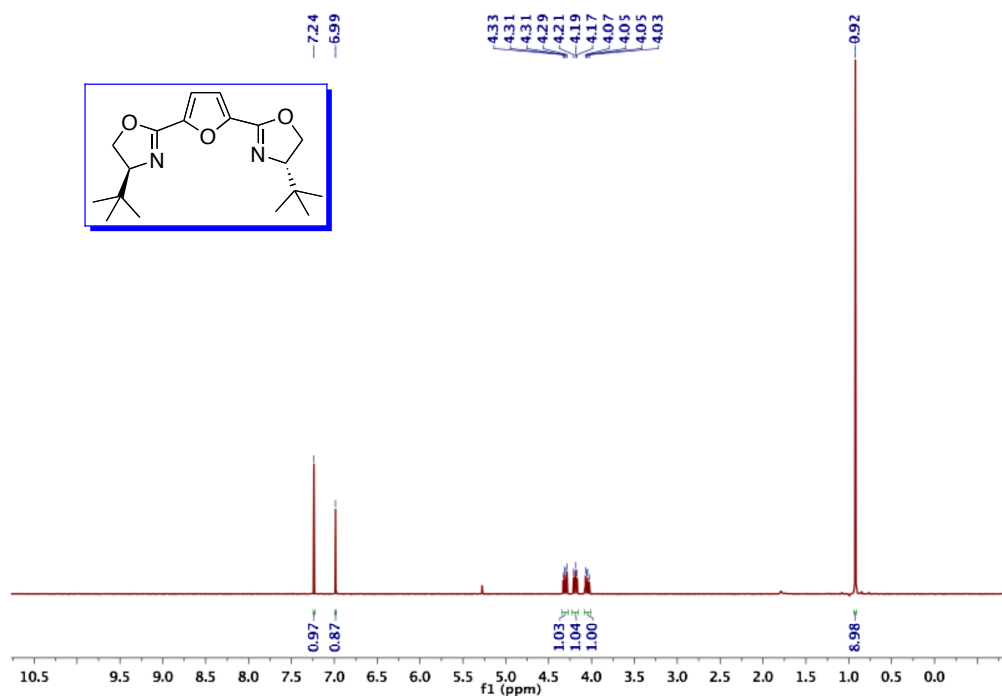
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of **4a**



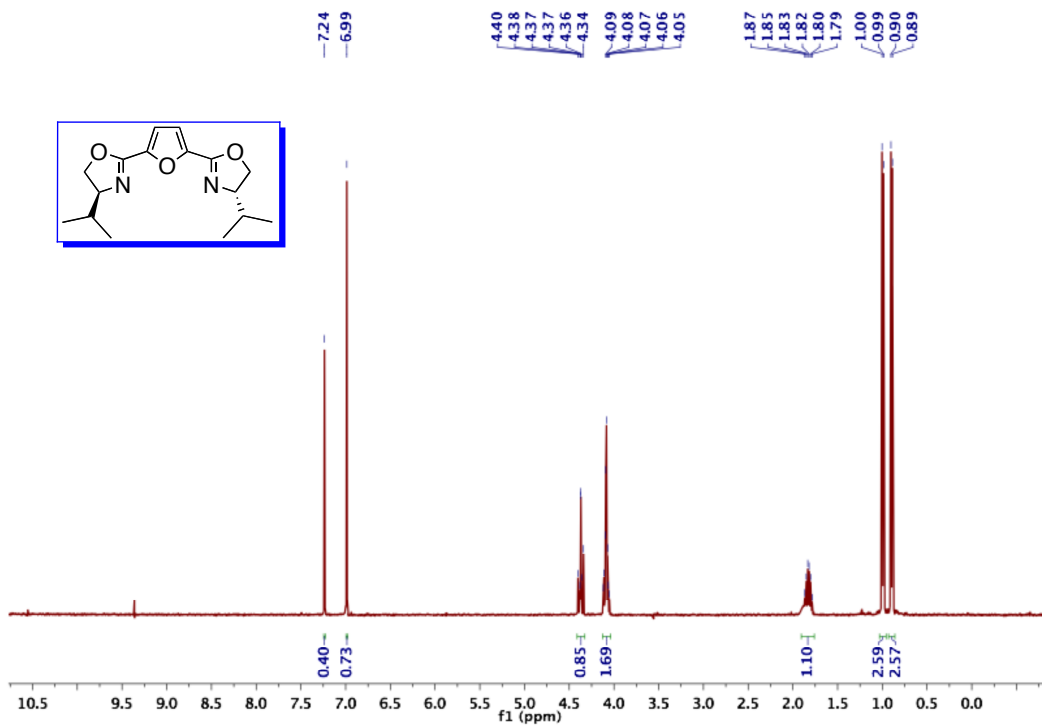
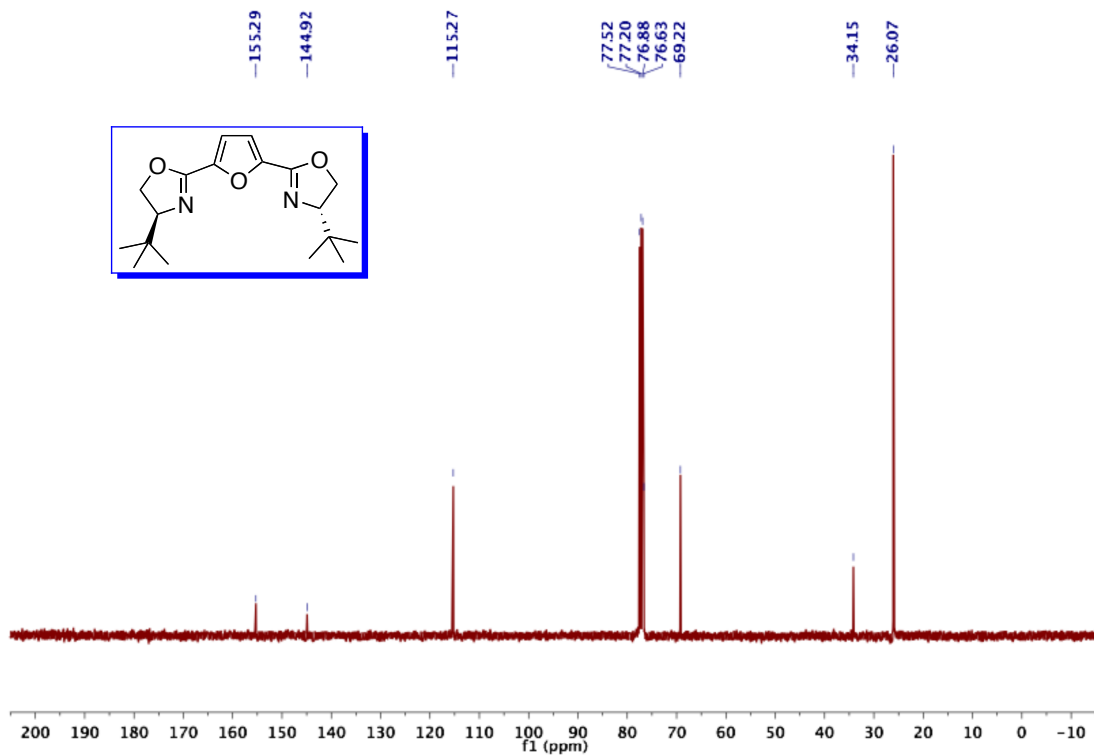
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **4b**

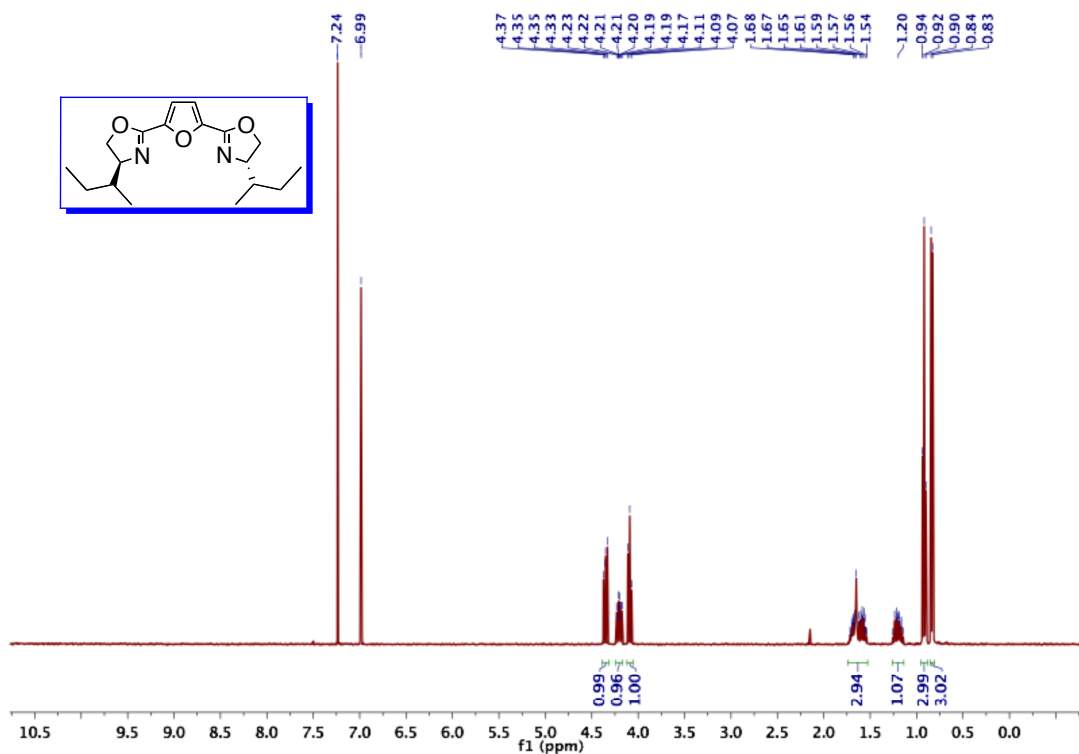
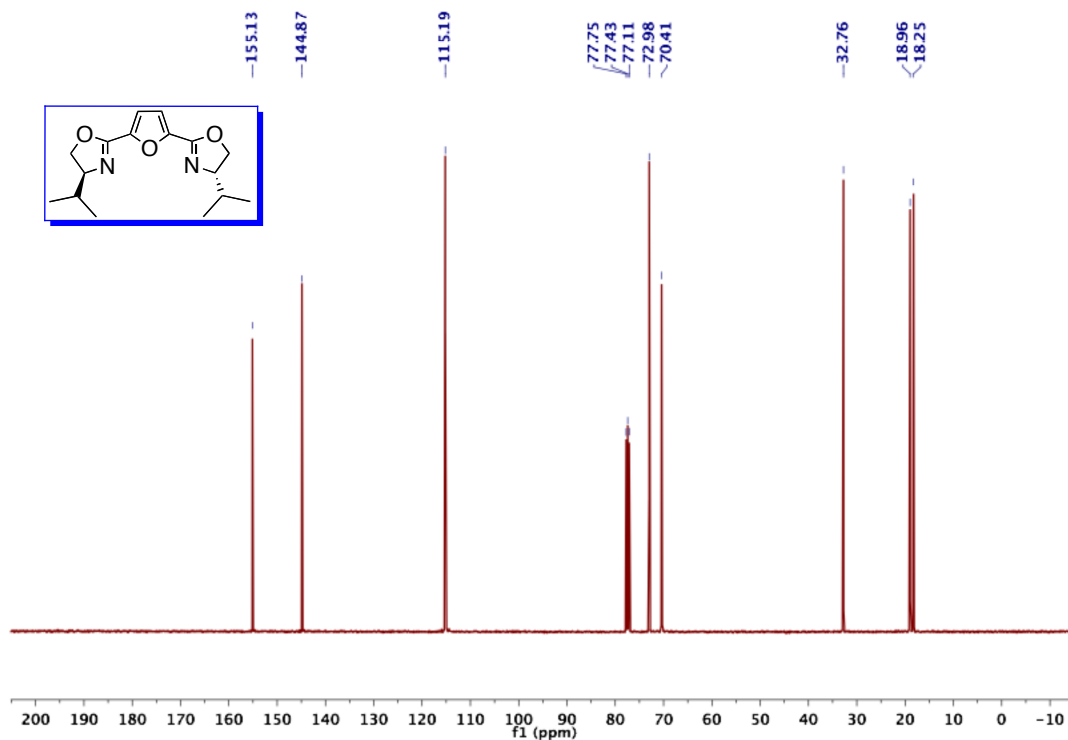


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of **4b**

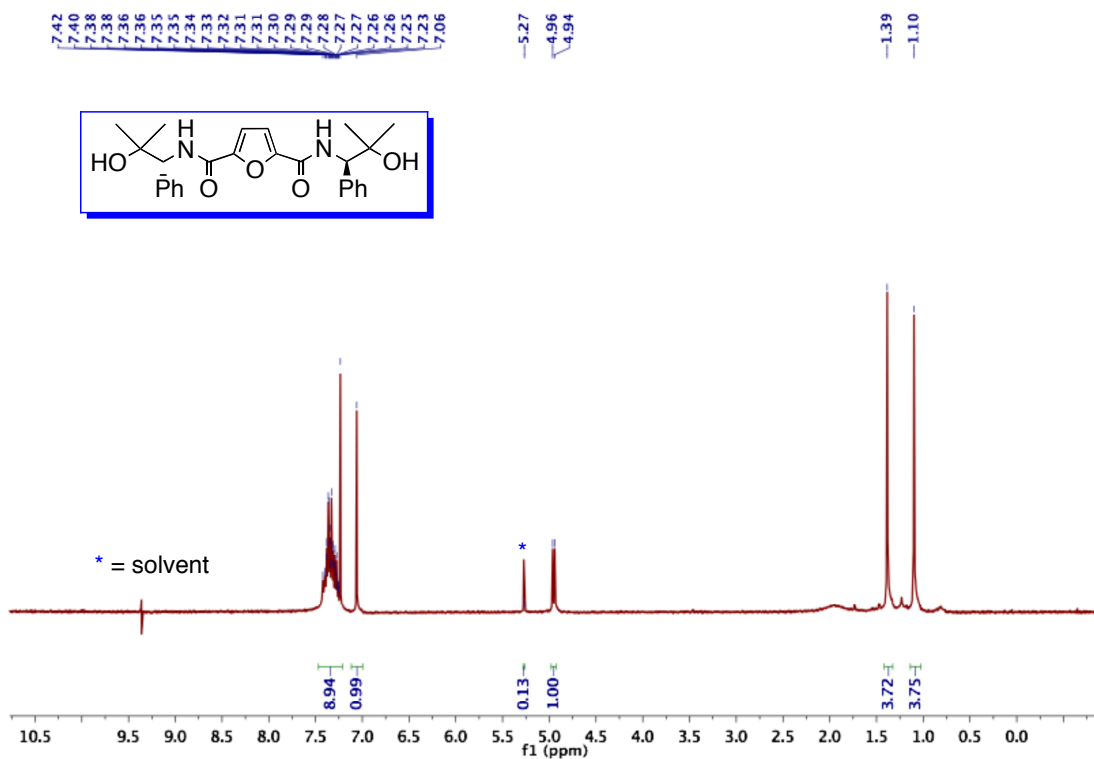
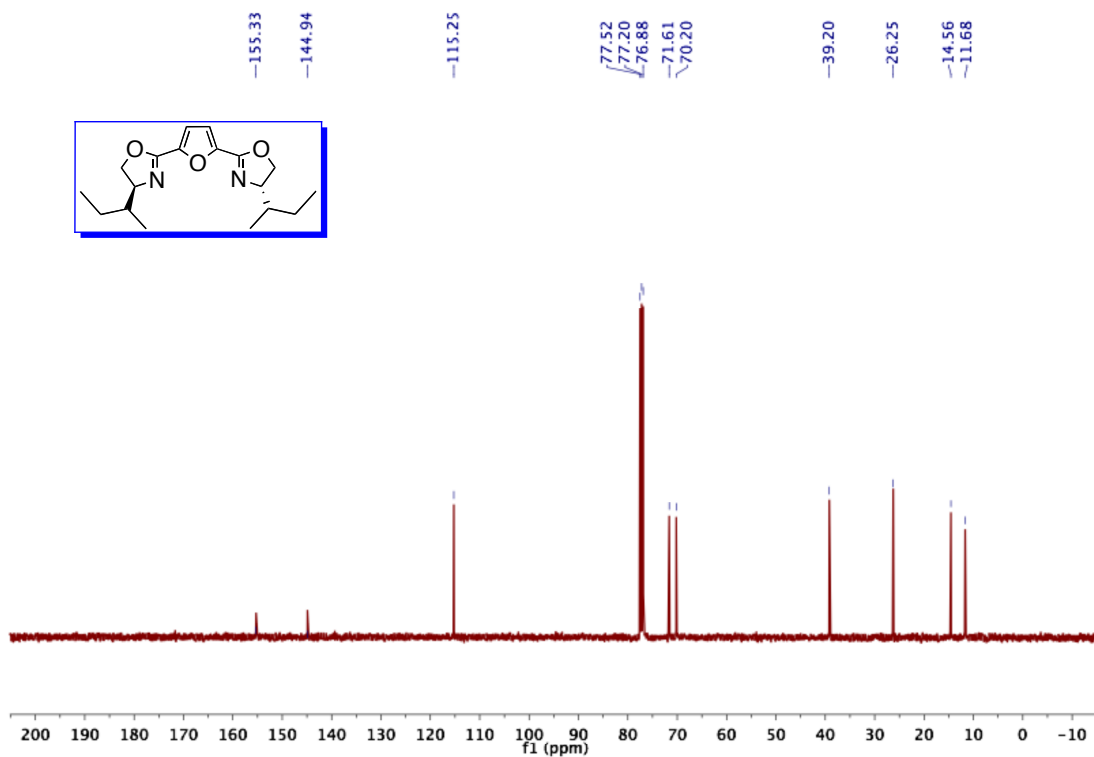


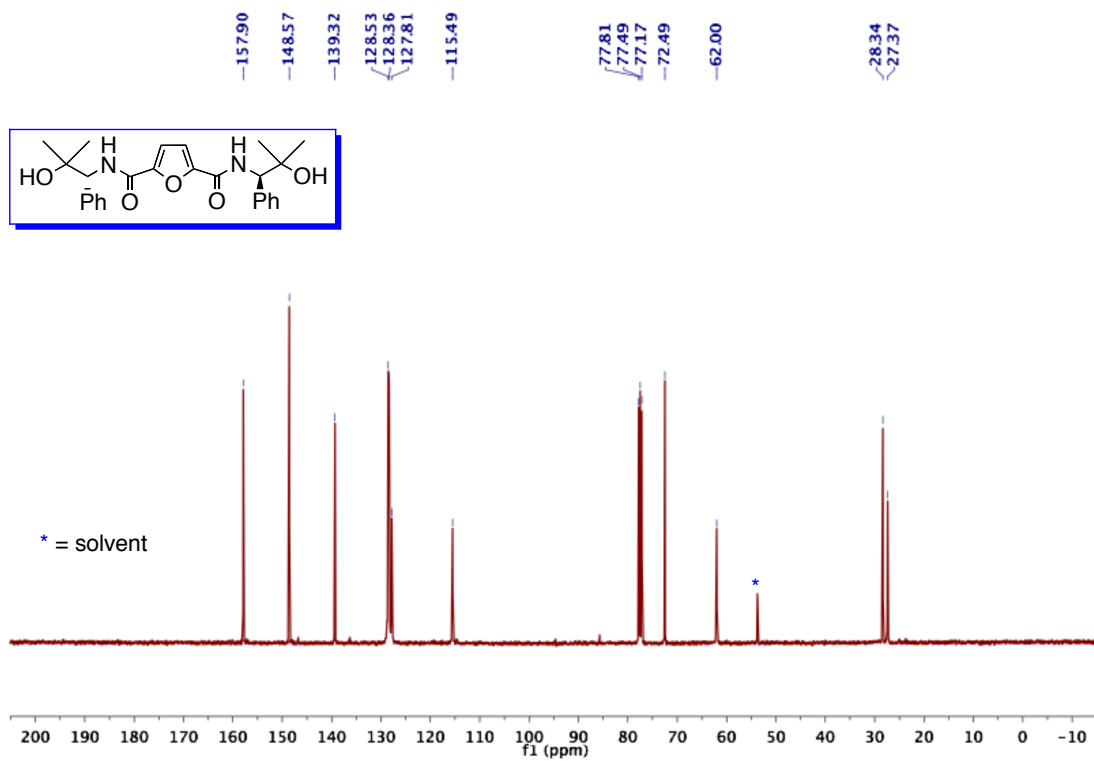
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **4c**



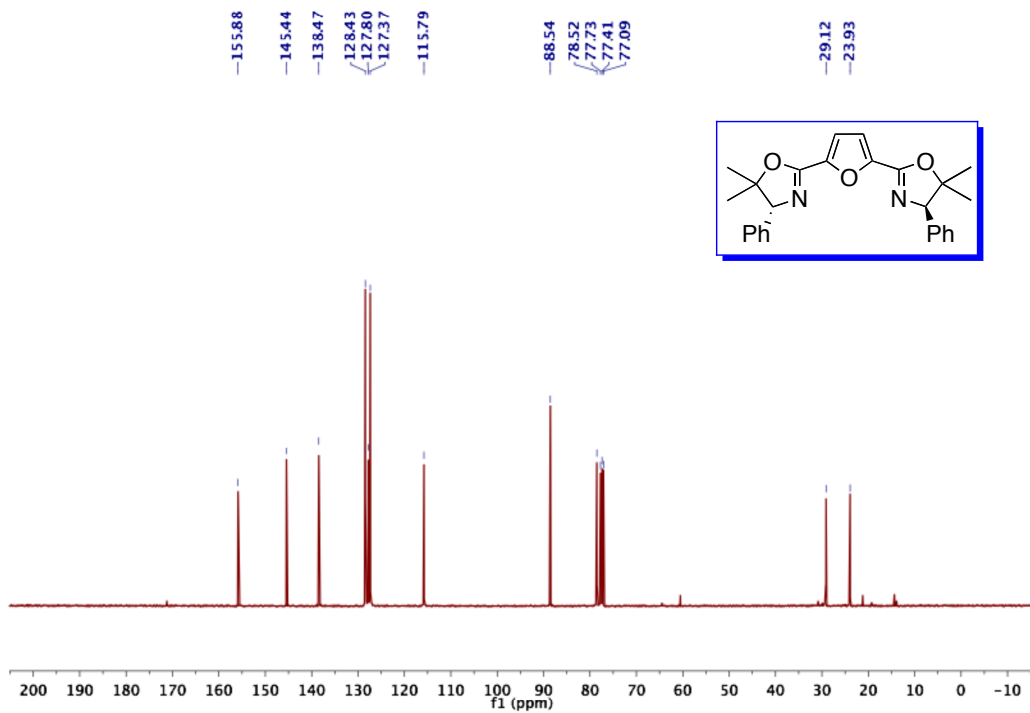
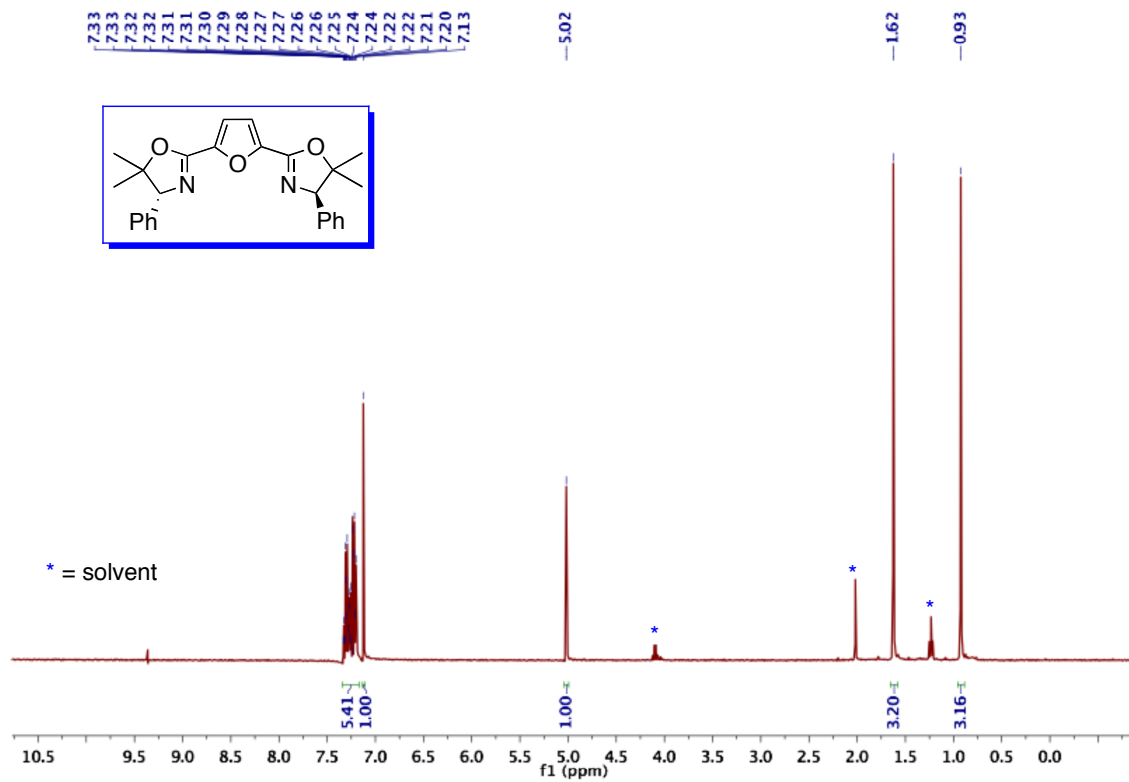


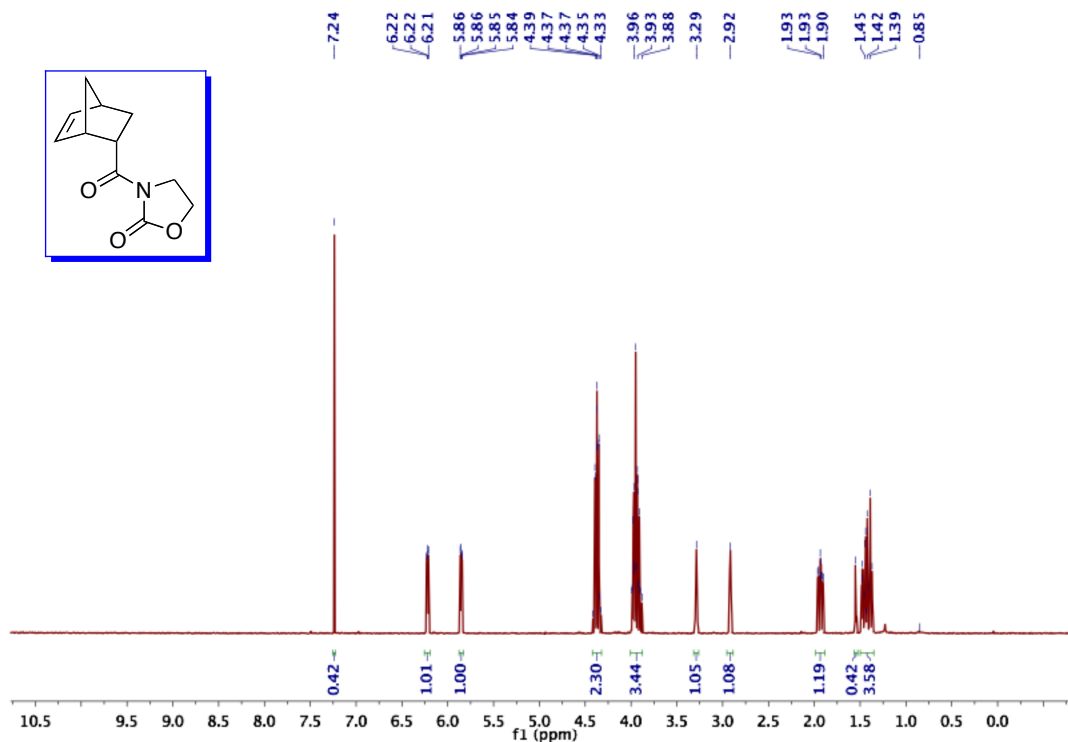
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **4e**





<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **6a**

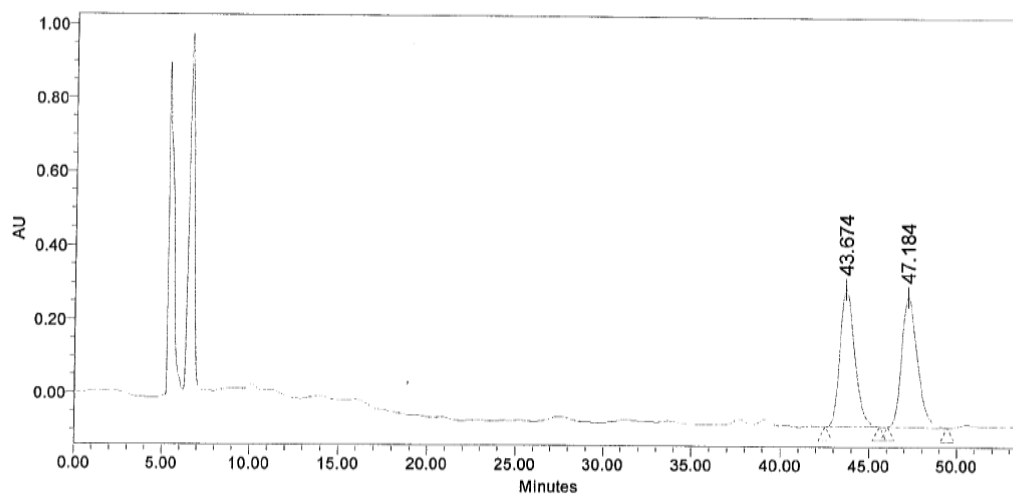




<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of 8

### 5. Copy of HPLC spectrum:

HPLC spectrum of compound 8 (Racemic)

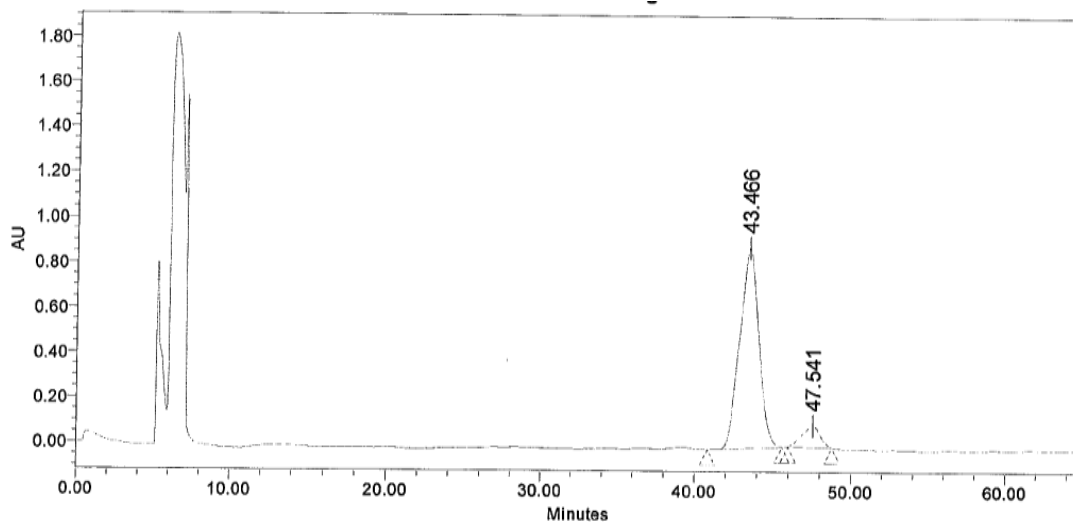


Peak Results

Name	RT	Area	% Area
1	43.674	21812700	49.55
2	47.184	22207759	50.45

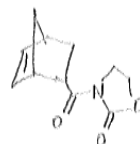
P. ...

## HPLC spectrum of compound **8** (Chiral)



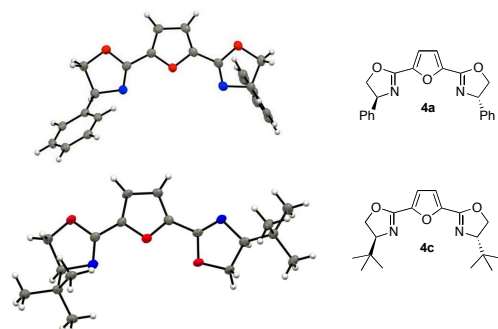
**Peak Results**

Name	RT	Area	% Area
1	43.466	75570184	90.59
2	47.541	7849377	9.41



## 6. X-ray structures and structural parameters:

Structure determination: Single crystal X-ray diffraction data of the compounds **4a** and **4c** were collected on a Bruker Apex Duo diffractometer with a Apex 2 CCD area detector at  $T = 100\text{K}$ . Cu radiation was used. Details of data collection and refinement are given in the table below.



**Structural parameters of compound 4a:**

<b>Formula</b>	C <sub>22</sub> H <sub>18</sub> N <sub>2</sub> O <sub>3</sub>
<b>FW</b>	358.38
<b>cryst. size_max [mm]</b>	0.19
<b>cryst. size_mid [mm]</b>	0.13
<b>cryst. size_min [mm]</b>	0.08
<b>cryst. system</b>	Orthorhombic
<b>Space Group, Z</b>	P2(1)2(1)2(1), 12
<b>a [Å]</b>	5.7959(2)
<b>b [Å]</b>	15.0832(4)
<b>c [Å]</b>	59.8997(17)
<b>V [Å<sup>3</sup>]</b>	5236.5(3)
<b>ρ<sub>calc</sub> [g/cm<sup>3</sup>]</b>	1.364
<b>μ [mm<sup>-1</sup>]</b>	0.744
<b>Radiation Type</b>	Cu
<b>F(000)</b>	2256
<b>no of measured refl.</b>	41458
<b>no of unique refl.</b>	9300
<b>no of unique refl. (I ≥ 2σ)</b>	9250
<b>Theta range for data collection</b>	3.02 to 68.05 deg.
<b>R1/wR2 (I ≥ 2σ) [%]</b>	3.30/7.98
<b>R1/wR2 (all data) [%]</b>	3.31/7.99
<b>CCDC number</b>	1040226

**Structural parameters of compound 4c:**

<b>Formula</b>	C <sub>18</sub> H <sub>26</sub> N <sub>2</sub> O <sub>3</sub>
<b>FW</b>	318.41
<b>cryst. size_max [mm]</b>	0.24
<b>cryst. size_mid [mm]</b>	0.21
<b>cryst. size_min [mm]</b>	0.10
<b>cryst. system</b>	Orthorhombic

<b>Space Group, Z</b>	P2(1)2(1)2(1), 4
<b>a [Å]</b>	5.8439(2)
<b>b [Å]</b>	12.2991(5)
<b>c [Å]</b>	23.6950(10)
<b>V [Å<sup>3</sup>]</b>	1703.07(12)
<b><math>\rho_{\text{calc}}</math> [g/cm<sup>3</sup>]</b>	1.242
<b><math>\mu</math> [mm<sup>-1</sup>]</b>	0.680
<b>Radiation Type</b>	Cu
<b>F(000)</b>	688
<b>no of measured refl.</b>	9123
<b>no of unique refl.</b>	2880
<b>no of unique refl. (<math>I \geq 2\sigma</math>)</b>	2836
<b>Theta range for data collection</b>	7.48 to 66.72 deg.
<b>R1/wR2 (<math>I \geq 2\sigma</math>)<sup>a</sup> [%]</b>	4.97/14.12
<b>R1/wR2 (all data) [%]</b>	5.01/14.15
<b>CCDC number</b>	1040227

## 7. References:

<sup>1</sup> (a) Binder, J. B.; Raines, R. T. *J. Am. Chem.* **2009**, *131*, 1979-1985. (b) Miura, T.; Kakinuma, H.; Kawano, T.; Matsuhisa, H. (Canon Kabushiki Kaisha) U.S. Patent 7411078, 2008.

<sup>2</sup> Sibi, M. P.; Petrovic, G. *Tetrahedron: Asymmetry* **2003**, *14*, 2879-2882.

<sup>3</sup> Iserloh, U.; Oderaotoshi, Y.; Kanemasa, S.; Curran, D. P. *Organic Syntheses*, **2003**, *80*, 46.

<sup>4</sup> Evans, D. A.; Miller, S. J.; Lectka, T.; Matt, P. von *J. Am. Chem. Soc.* **1999**, *121*, 7559-7573.