

Supporting Information for:

## **Pd-Catalyzed Enantio- and Regioselective Formation of Allylic Aryl Ethers**

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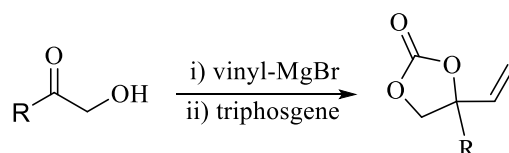
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## S2. General comments

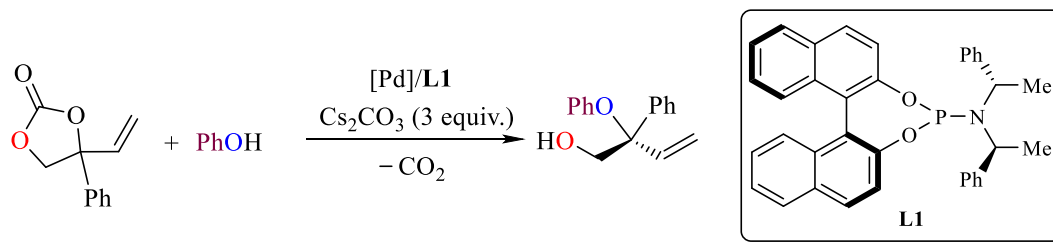
Commercially available phenols and solvents were purchased from Aldrich or TCI, and used without further purification. The palladium precursors and bases were purchased from Aldrich. Phosphoramidites **L1**, **L3-L6**, **L8-L12** were purchased from Aldrich or Strem; **L2**<sup>1</sup> and **L7**<sup>2</sup> were prepared according to previously reported procedures. All racemic allylic aryl ethers compounds were made using (*rac*)-**L1**. <sup>1</sup>H NMR, <sup>13</sup>C NMR, <sup>19</sup>F NMR spectra were recorded at room temperature on a Bruker AV-400 or AV-500 spectrometer and referenced to the residual deuterated solvent signals. All reported NMR values are given in parts per million (ppm). FT-IR measurements were carried out on a Bruker Optics FTIR Alpha spectrometer. Chiral high-performance liquid chromatography (HPLC) analysis, Mass spectrometric analyses and X-ray diffraction studies were performed by the Research Support Group at ICIQ.

## S2. Typical procedure for the preparation of cyclic vinyl-carbonates



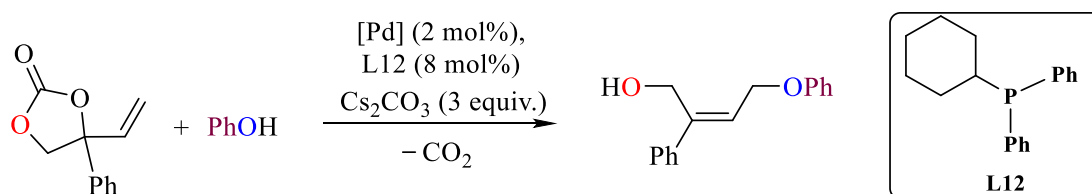
The vinyl-carbonates can be easily prepared according to a previous reported procedure with minor modifications.<sup>3</sup> To a solution of the respective hydroxy methyl ketone (5 mmol, 1 equiv) in THF (20 mL) was added vinyl magnesium bromide (1.0 M in THF, 2.5 equiv) at 0 °C. The reaction was stirred under an N<sub>2</sub> atmosphere at room temperature for 2 h. The reaction mixture was then quenched with saturated aqueous NH<sub>4</sub>Cl, and extracted with EtOAc. The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated affording a light yellow oil. To a solution of the latter in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) was added pyridine (20 mmol, 4 equiv) and triphosgene (2.5 mmol, 0.5 equiv) at 0 °C. The reaction was stirred under an N<sub>2</sub> atmosphere at room temperature for 2 h. The reaction mixture was then quenched with saturated aqueous NH<sub>4</sub>Cl, washed with H<sub>2</sub>O, and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The residue was purified by flash chromatography on silica to afford the corresponding carbonate.

### S3. Typical procedure for the formation of branched aryl ethers



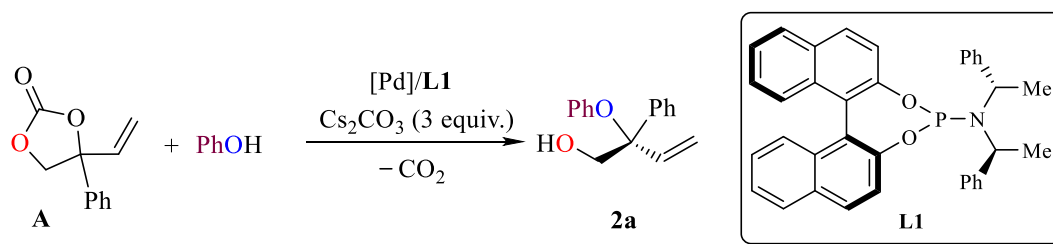
Carbonate (0.2 mmol, 0.038, 1 equiv) was combined with Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub> (0.0041 g, 2.0 mol%), **L1** (0.0086 g, 8.0 mol%) and phenol (0.0282 g, 1.5 equiv) in THF (0.30 mL) at room temperature in air. The reaction mixture was stirred at 0 °C for 36 h, after which the reaction mixture was mixed with 15 mL CH<sub>2</sub>Cl<sub>2</sub> and then washed with NaOH (0.1 N, 2 × 5 mL), brine (10 mL), dried (MgSO<sub>4</sub>), filtered and the solvent was removed in vacuo. The residue was subjected to flash column chromatography and the pure product was isolated (40.8 mg, 85%) (Hexane : EA = 50 : 1, R<sub>f</sub> = 0.15). The *ee* values were determined by HPLC equipped with a chiral column.

### S3. Typical procedure for the formation of linear aryl ethers.



Carbonate (0.2 mmol, 0.038, 1 equiv) was combined with Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub> (0.0041 g, 2.0 mol%), **L12** (0.0043 g, 8.0 mol%) and phenol (0.0282 g, 1.5 equiv) in THF (0.20 mL) at room temperature in air. The reaction mixture was stirred at room temperature for 12 h. Once the reaction had finished, the reaction mixture was purified by flash column chromatography (Hexane : EA = 10 : 1, R<sub>f</sub> = 0.2) and the pure product was isolated (45.5 mg, 95%).

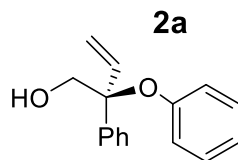
**S4: Typical procedure for the formation of 2a at a 1.1 mmol scale.**



Vinyl cyclic carbonate **A** (1.1 mmol, 0.209 g, 1 equiv) was combined with  $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$  (0.0226 g, 2.0 mol %), **L1** (0.0473 g, 8.0 mol %) and phenol (0.1551 g, 1.5 equiv) in THF (1.65 mL) at rt open to air. The reaction mixture was stirred at 0 °C for 36 h, after which the reaction mixture was mixed with 30 mL of  $\text{CH}_2\text{Cl}_2$  and then washed with NaOH (0.1 M,  $2 \times 10$  mL), brine (10 mL), dried over  $\text{MgSO}_4$  and filtered. The solvent was removed in vacuo. The residue was subjected to flash column chromatography (Hexane : EA = 50 : 1,  $R_f$  = 0.15), and the pure product **2a** was isolated (213.5 mg, 81%) with an *er* of 95:5 as determined by HPLC equipped with a chiral column).

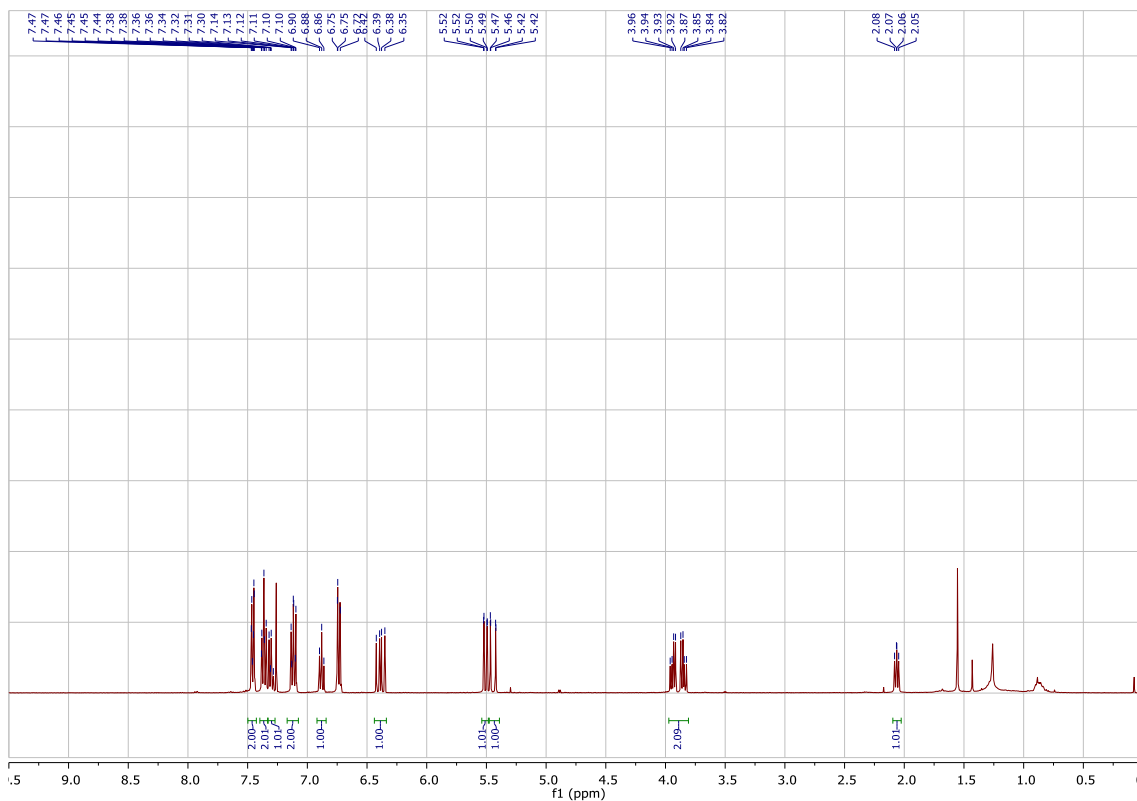
Cf. Scheme 3 in the main text: scale 0.20 mmol, yield of **2a** is 85%, *er* = 95:5.

## S5. IR, NMR spectra, HRMS and HPLC results



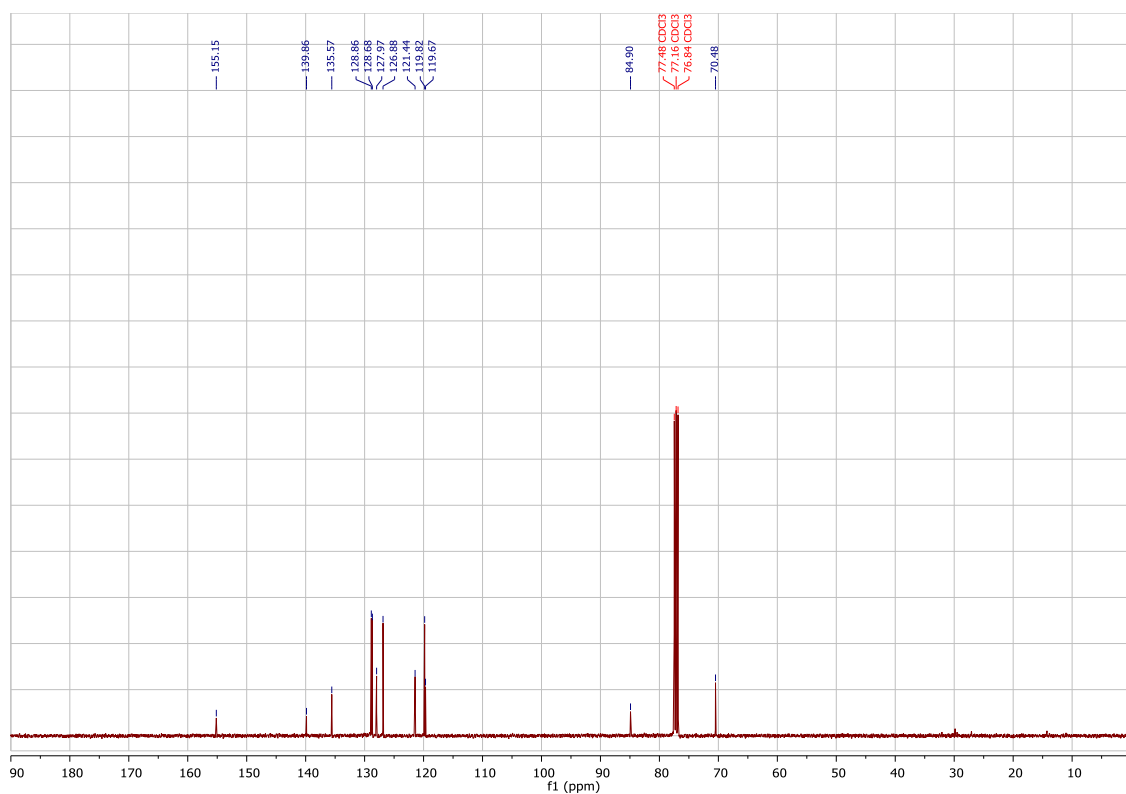
Scale: 0.2 mmol; isolated 40.8 mg (85% yield), light yellow oil, Hexane : EA = 50 : 1,  $R_f$  = 0.15

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ )



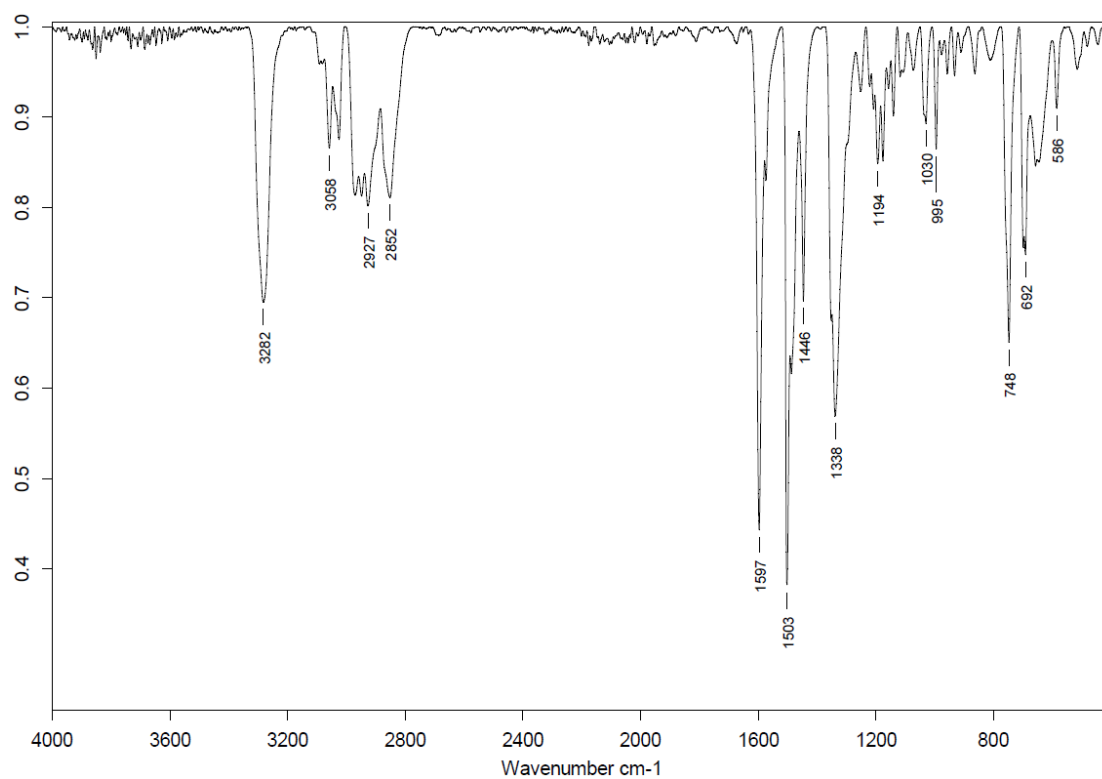
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50 – 7.43 (m, 2H), 7.40 – 7.33 (m, 2H), 7.33 – 7.27 (m, 1H), 7.17 – 7.07 (m, 2H), 6.88 (t,  $J$  = 7.4 Hz, 1H), 6.39 (dd,  $J$  = 17.5, 11.1 Hz, 1H), 5.51 (dd,  $J$  = 11.2, 1.0 Hz, 1H), 5.44 (dd,  $J$  = 17.5, 1.0 Hz, 1H), 3.97 – 3.81 (m, 2H), 2.06 (dd,  $J$  = 7.5, 6.3 Hz, 1H).

<sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>)



<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 155.15, 139.86, 135.57, 128.86, 128.68, 127.97, 126.88, 121.44, 119.82, 119.67, 84.90, 70.48.

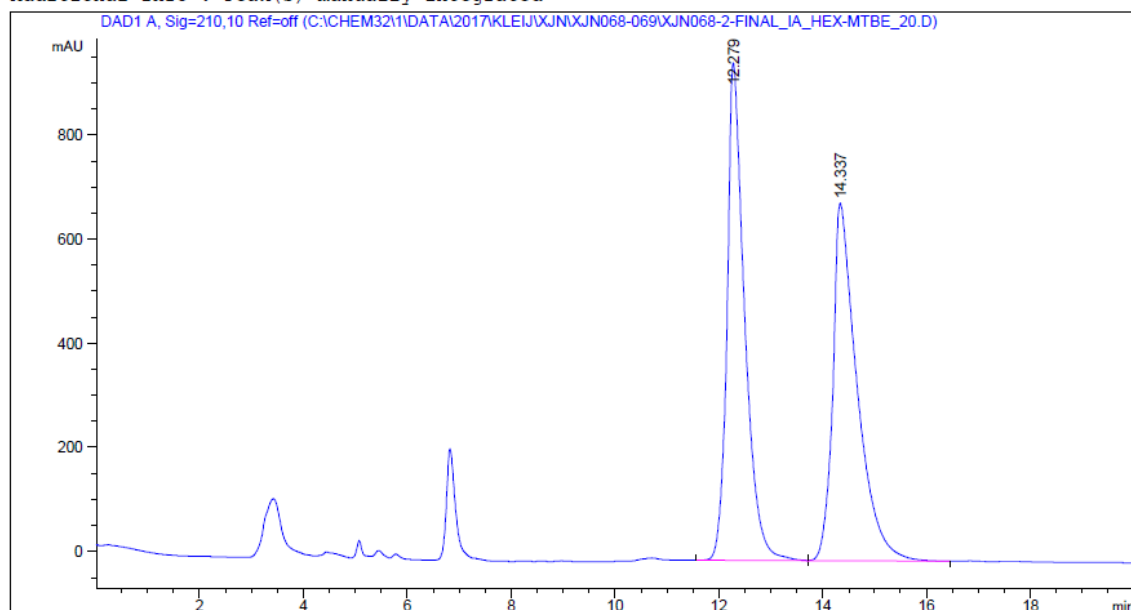
IR spectrum (neat)



HRMS (ESI<sup>+</sup>, MeOH): *m/z* calcd. 263.1043 (M + Na)<sup>+</sup>, found: 263.1043.

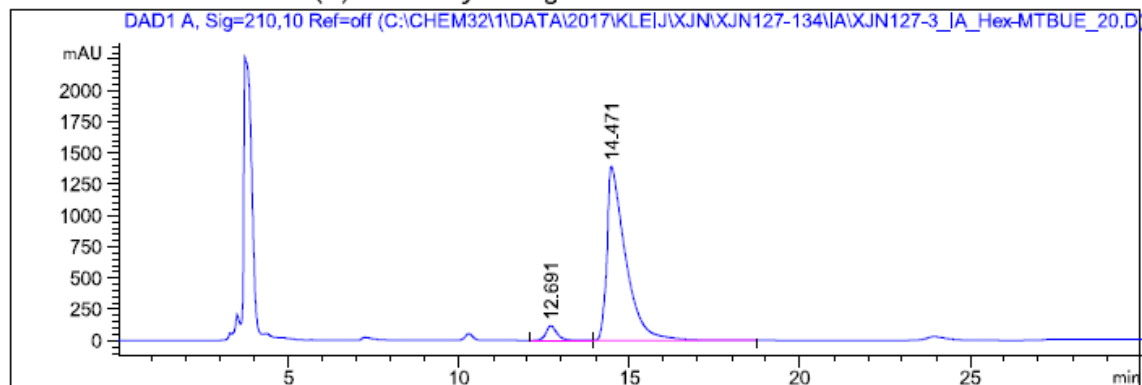
**HPLC conditions:** Chiralpak IA 250 × 4.6 mm, 5 μm, Hex/MTBE = 80 : 20, 1 mL/min; 95 : 5 *er*;  $[\alpha]_D^{25} = -56.03$  ( $c = 0.12$ , CHCl<sub>3</sub>). (Hex: hexane; MTBE: methyl *tert*-butyl ether)

Additional Info : Peak(s) manually integrated

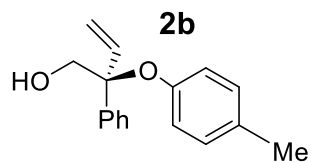


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 12.279        | BB   | 0.3362      | 2.24259e4    | 954.30103    | 50.1758 |
| 2      | 14.337        | BB   | 0.4587      | 2.22687e4    | 686.01563    | 49.8242 |

Additional Info : Peak(s) manually integrated

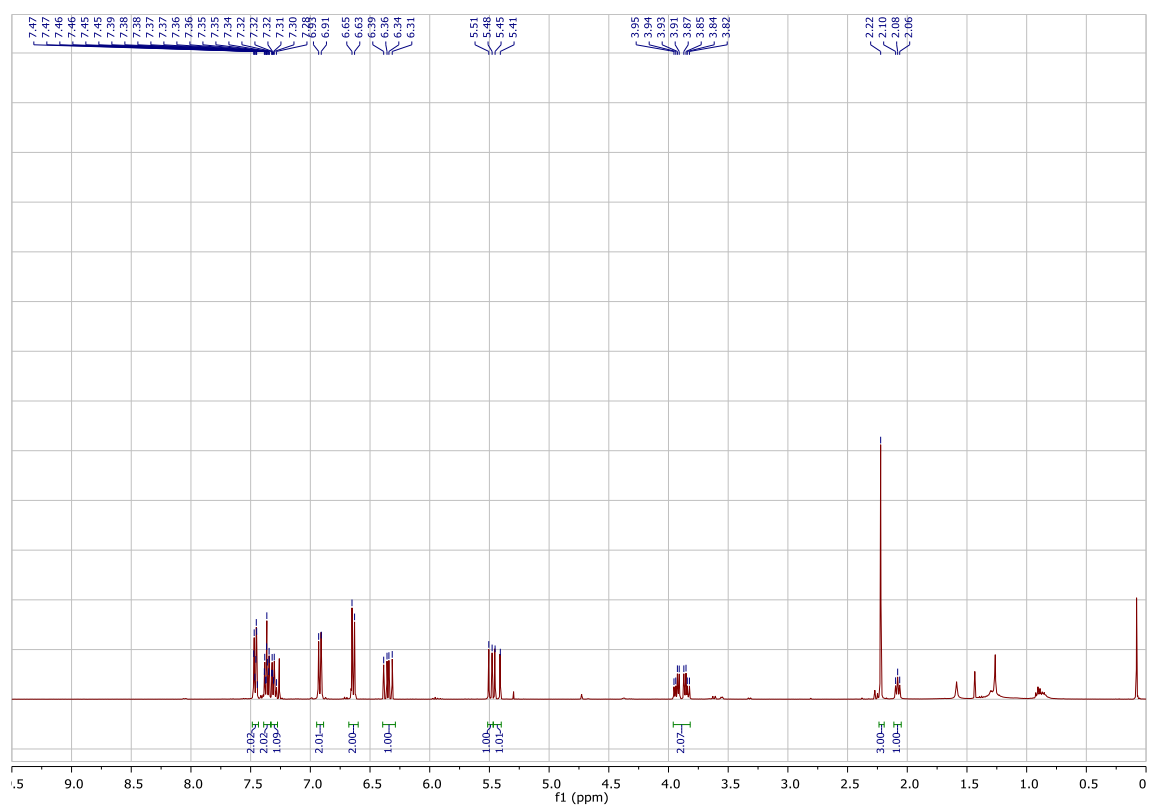


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 12.691        | BV   | 0.3372      | 2723.81982   | 118.92472    | 4.8827  |
| 2      | 14.471        | VB   | 0.5383      | 5.30613e4    | 1393.40503   | 95.1173 |



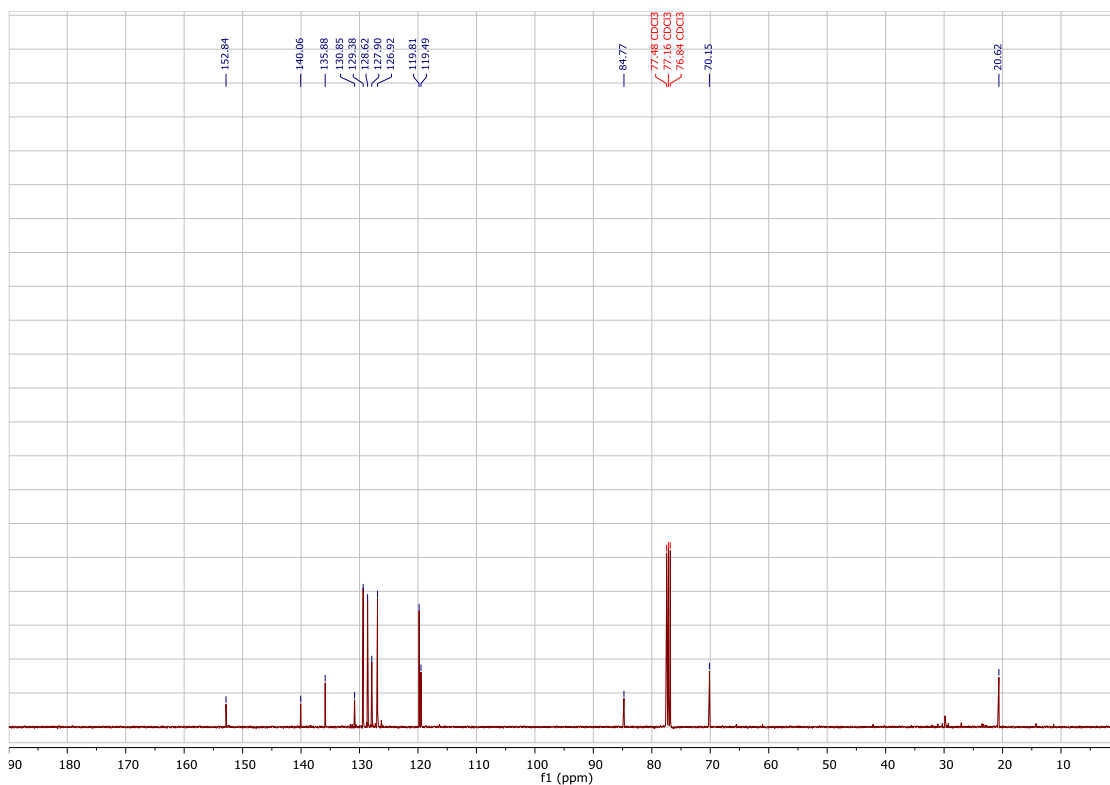
Scale: 0.2 mmol; isolated 43.5 mg (86% yield), light yellow oil, Hexane : EA = 50 : 1,  $R_f$  = 0.15

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ )



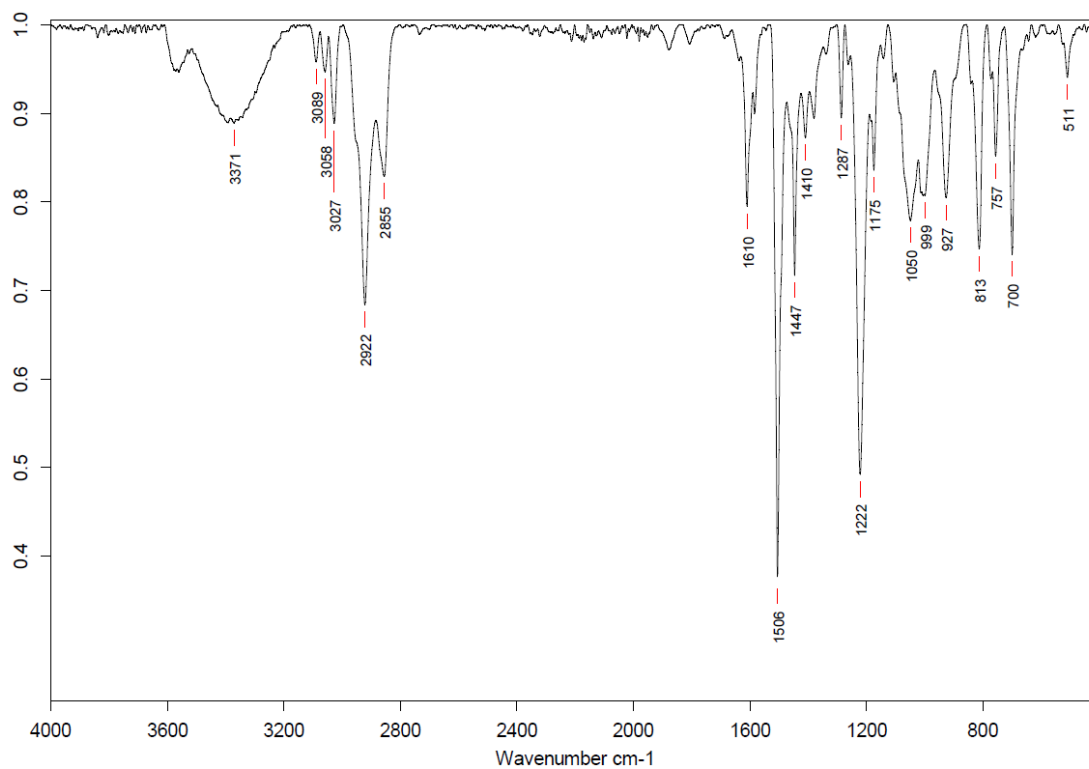
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 – 7.43 (m, 2H), 7.39 – 7.33 (m, 2H), 7.33 – 7.27 (m, 1H), 6.92 (d,  $J$  = 8.7 Hz, 2H), 6.64 (d,  $J$  = 8.6 Hz, 2H), 6.35 (dd,  $J$  = 17.5, 11.1 Hz, 1H), 5.49 (d,  $J$  = 11.1 Hz, 1H), 5.43 (d,  $J$  = 17.5 Hz, 1H), 3.96 – 3.82 (m, 2H), 2.22 (s, 3H), 2.08 (t,  $J$  = 6.8 Hz, 1H).

<sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>)



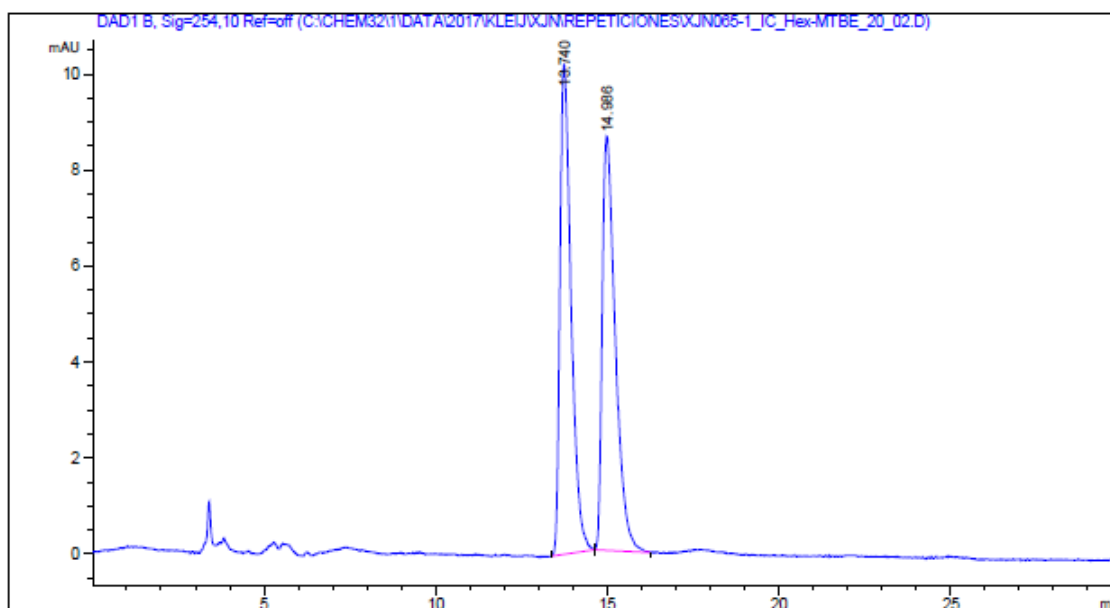
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  152.84, 140.06, 135.88, 130.85, 129.38, 128.62, 127.90, 126.92, 119.81, 119.49, 84.77, 70.15, 20.62.

IR spectrum (neat)



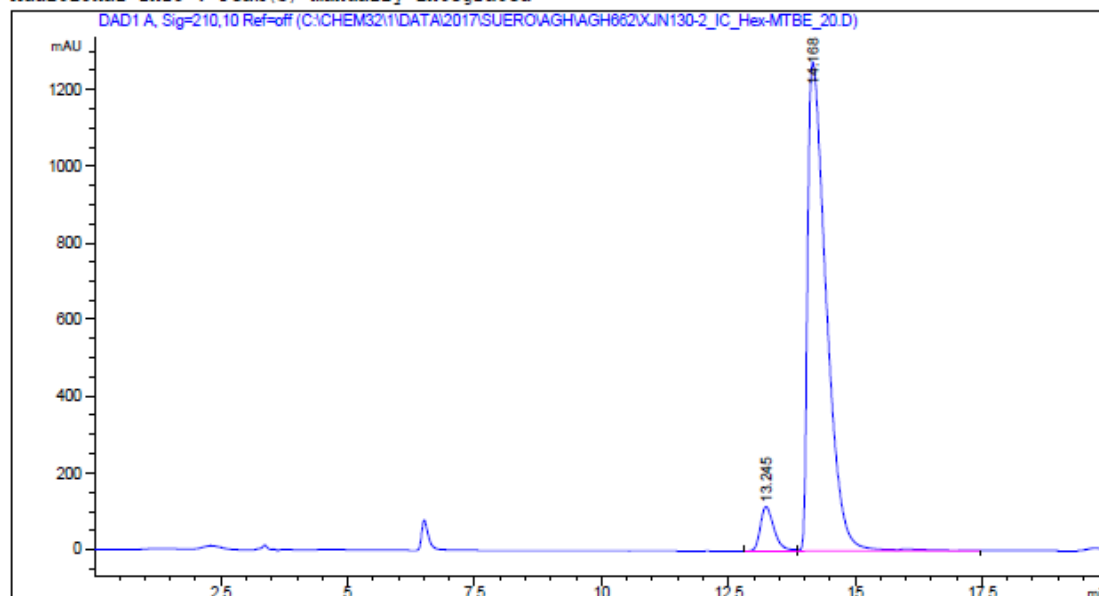
HRMS (ESI<sup>+</sup>, MeOH):  $m/z$  calcd. 277.1199 (M + Na)<sup>+</sup>, found: 277.1197.

**HPLC conditions:** Chiralpak IC 250 × 4.6 mm, 5 μm, Hex/MTBE = 80 : 20, 1 mL/min;  
94 : 6 *er*;  $[\alpha]_D^{25} = -46.21$  ( $c = 0.11$ , CHCl<sub>3</sub>).

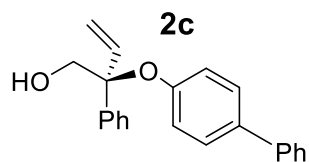


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 13.740        | BB   | 0.3426      | 230.06252    | 10.22144     | 50.1916 |
| 2      | 14.986        | BB   | 0.3924      | 228.30615    | 8.63555      | 49.8084 |

Additional Info : Peak(s) manually integrated

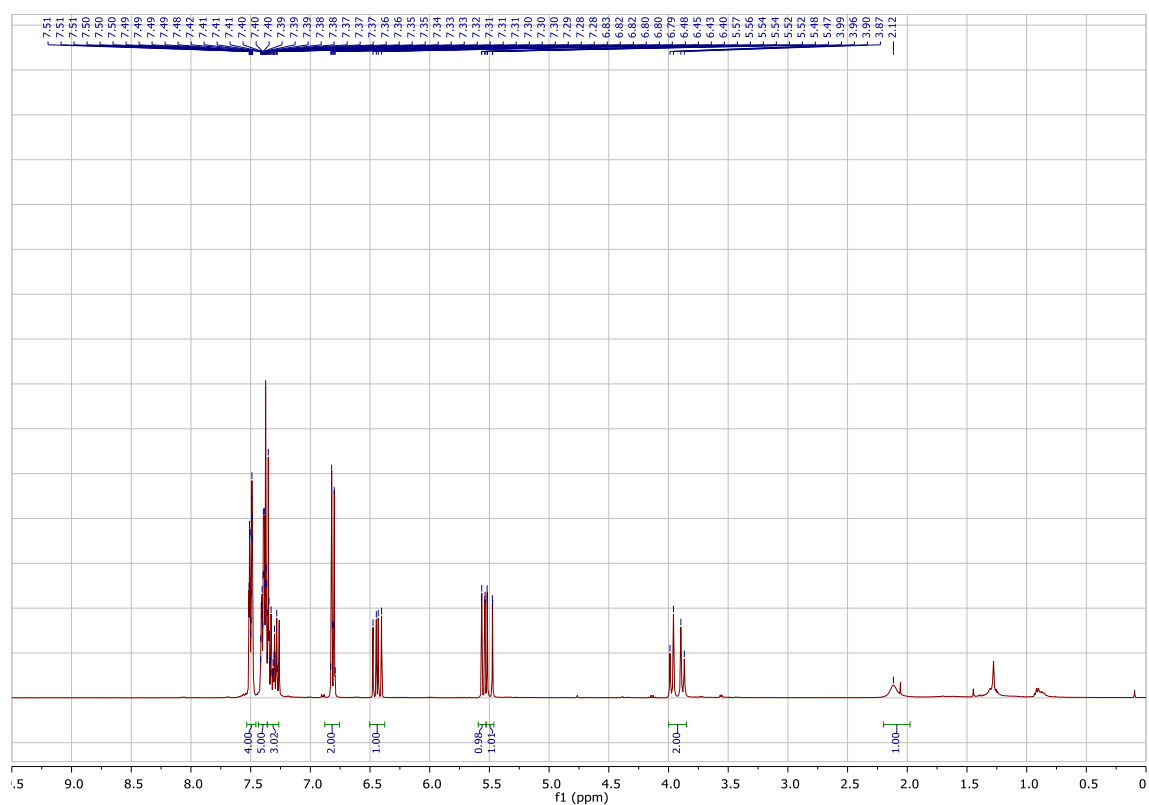


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 13.245        | BV   | 0.2856      | 2154.69971   | 115.53063    | 6.2254  |
| 2      | 14.168        | VV R | 0.3901      | 3.24567e4    | 1275.29614   | 93.7746 |



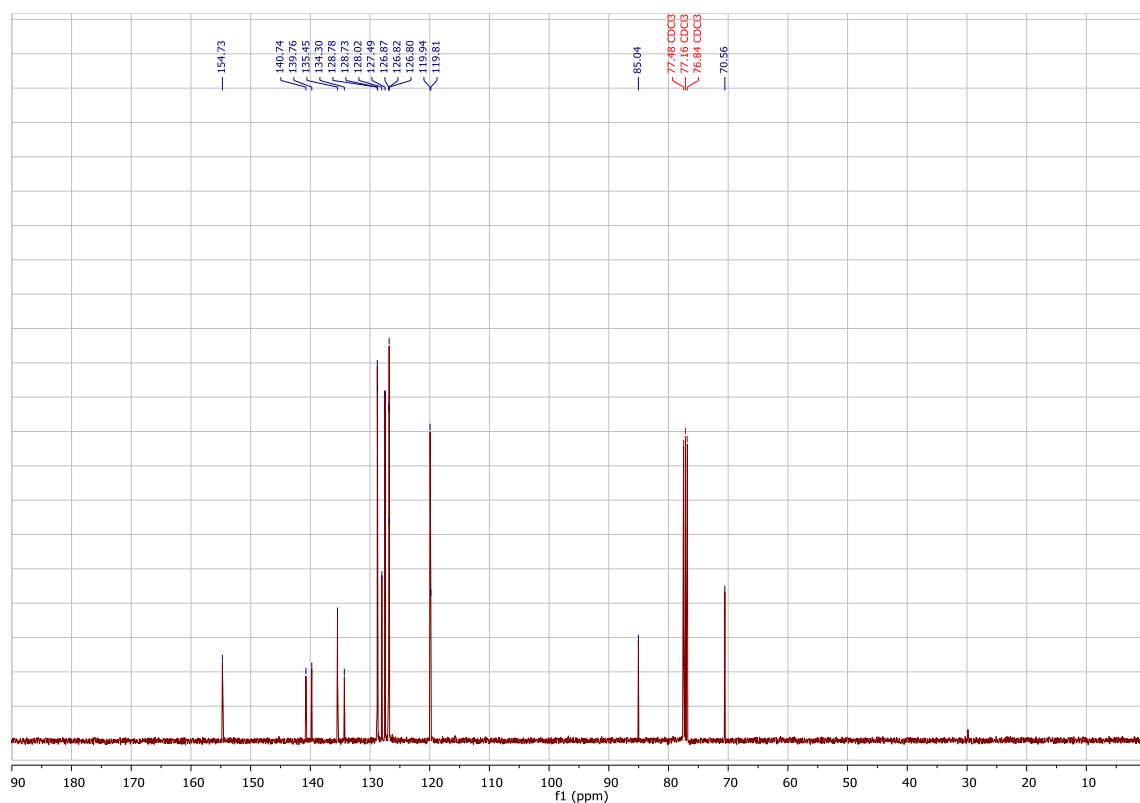
Scale: 0.2 mmol; isolated 37.0 mg (59% yield), light yellow solid, Hexane : EA = 50 : 1,  $R_f = 0.15$

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ )

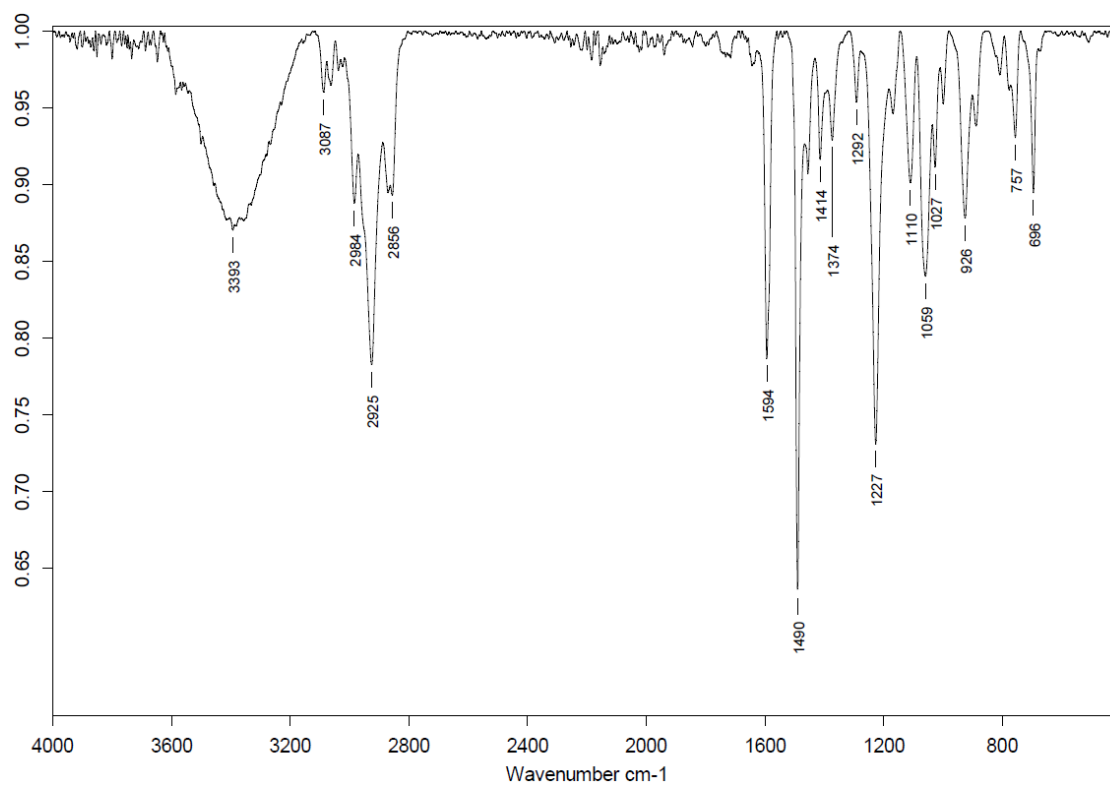


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53 – 7.46 (m, 4H), 7.43 – 7.36 (m, 5H), 7.36 – 7.26 (m, 3H), 6.88 – 6.76 (m, 2H), 6.44 (dd,  $J = 17.5, 11.1$  Hz, 1H), 5.55 (dd,  $J = 11.2, 1.0$  Hz, 1H), 5.50 (dd,  $J = 17.5, 1.0$  Hz, 1H), 4.00 – 3.85 (m, 2H), 2.12 (s, 1H).

<sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>)



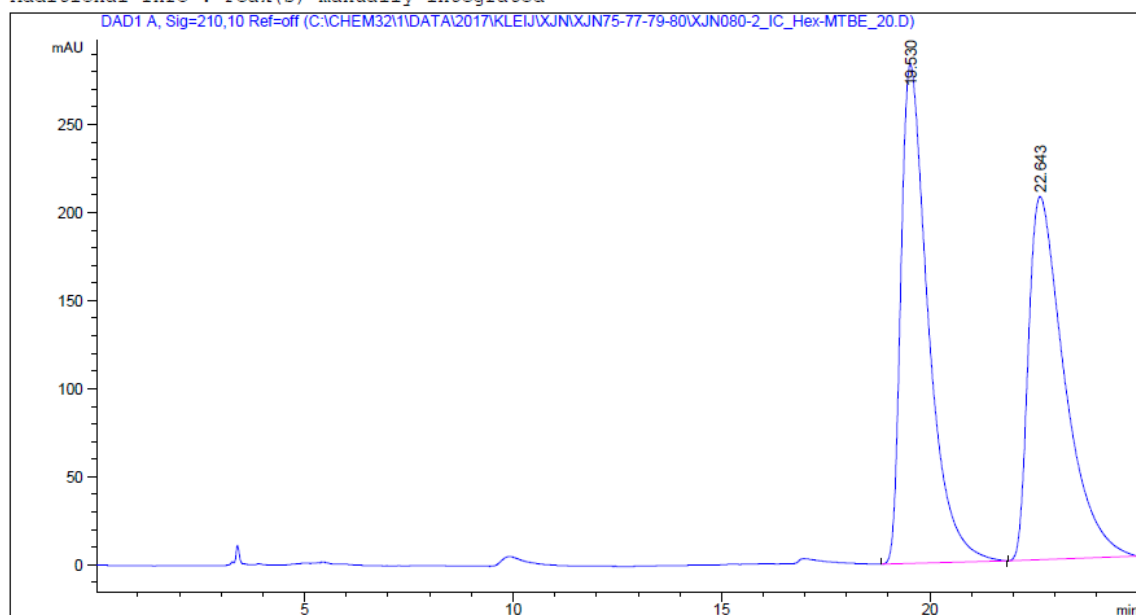
IR spectrum (neat)



**HRMS** (ESI<sup>+</sup>, MeOH): *m/z* calcd. 339.1356 (M + Na)<sup>+</sup>, found: 339.1365.

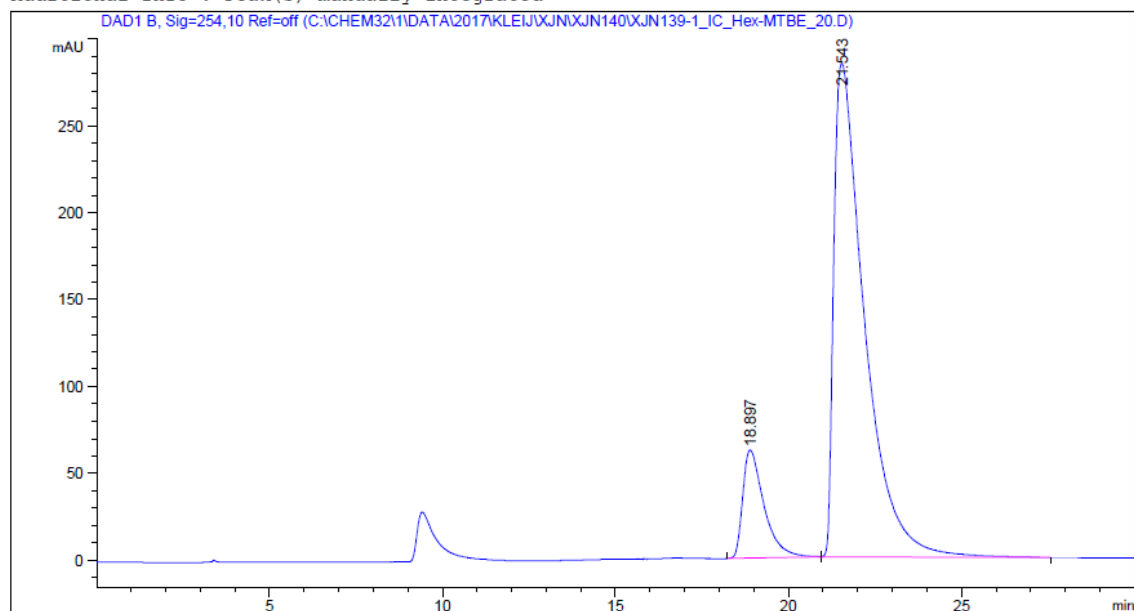
**HPLC conditions:** Chiralpak IC 250 × 4.6 mm, 5 μm, Hex/MTBE = 80 : 20, 1 mL/min;  
87 : 13 *er*;  $[\alpha]_D^{25} = -44.09$  ( $c = 0.10$ , CHCl<sub>3</sub>).

Additional Info : Peak(s) manually integrated

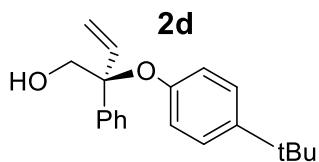


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 19.530        | BB   | 0.6850      | 1.28953e4    | 283.31763    | 51.0383 |
| 2      | 22.643        | BBA  | 0.9019      | 1.23706e4    | 206.20113    | 48.9617 |

Additional Info : Peak(s) manually integrated

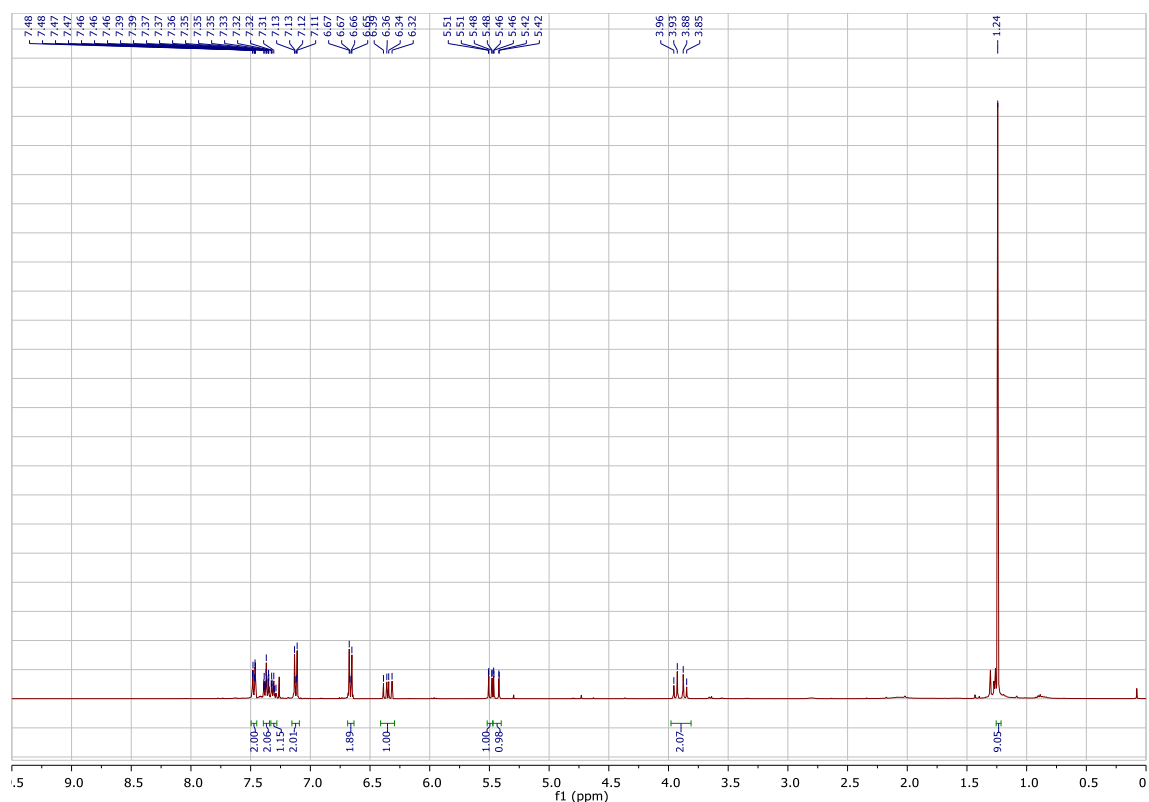


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 18.897        | BB   | 0.6361      | 2652.93579   | 62.13355     | 13.1756 |
| 2      | 21.543        | BB   | 0.9042      | 1.74822e4    | 283.99249    | 86.8244 |



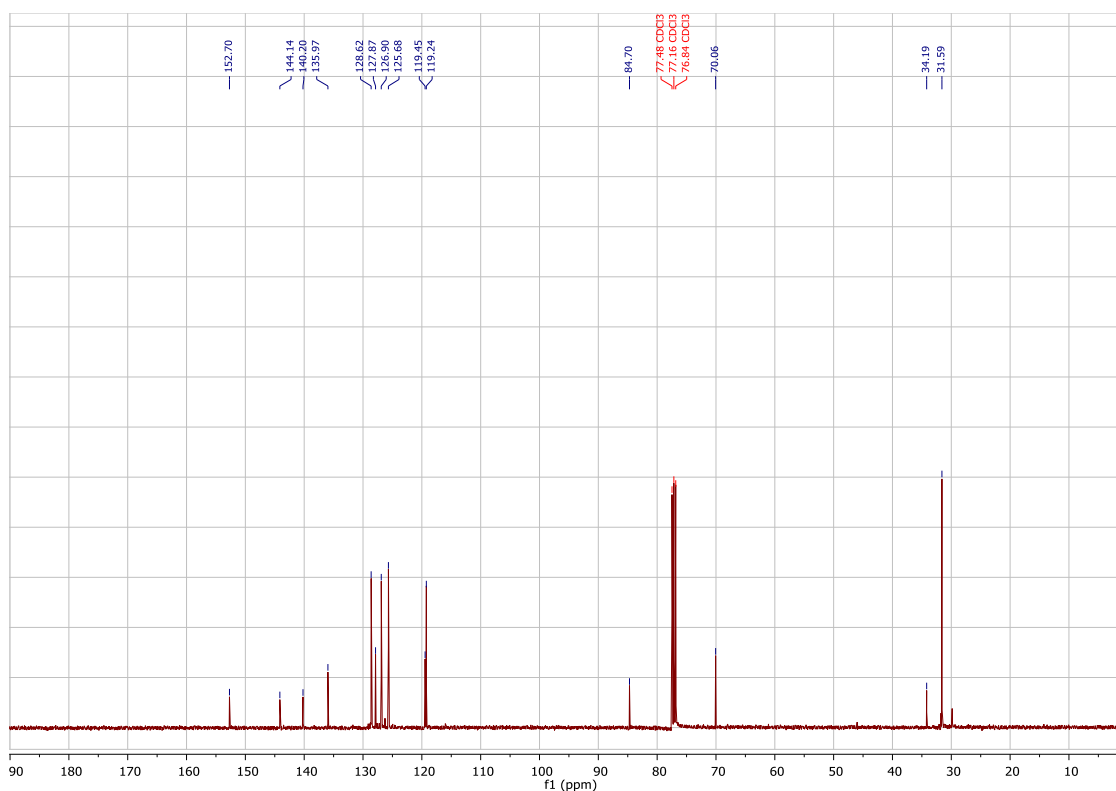
Scale: 0.2 mmol; isolated 47.9 mg (81% yield), light yellow oil, Hexane : EA = 50 : 1,  $R_f$  = 0.15

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ )



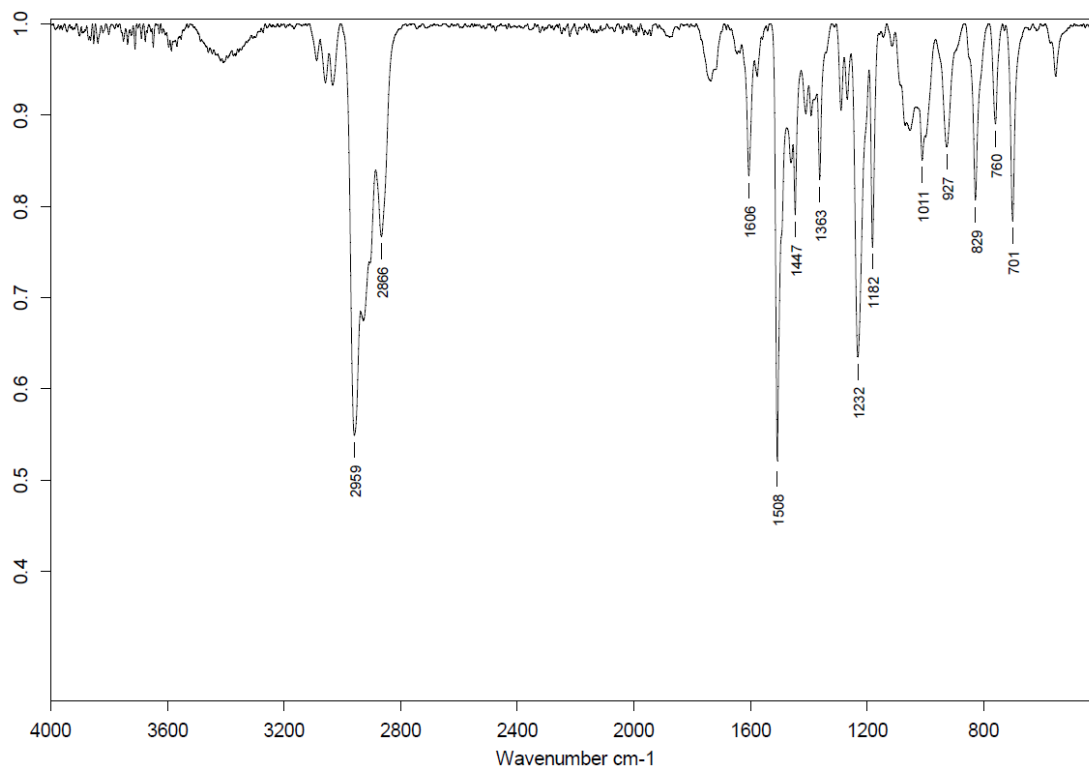
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50 – 7.45 (m, 2H), 7.39 – 7.34 (m, 2H), 7.33 – 7.28 (m, 1H), 7.15 – 7.09 (m, 2H), 6.69 – 6.63 (m, 2H), 6.35 (dd,  $J$  = 17.5, 11.2 Hz, 1H), 5.49 (dd,  $J$  = 11.1, 1.0 Hz, 1H), 5.44 (dd,  $J$  = 17.5, 1.1 Hz, 1H), 3.98 – 3.81 (m, 2H), 1.24 (s, 9H).

<sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>)



<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  152.70, 144.14, 140.20, 135.97, 128.62, 127.87, 126.90, 125.68, 119.45, 119.24, 84.70, 70.06, 34.19, 31.59.

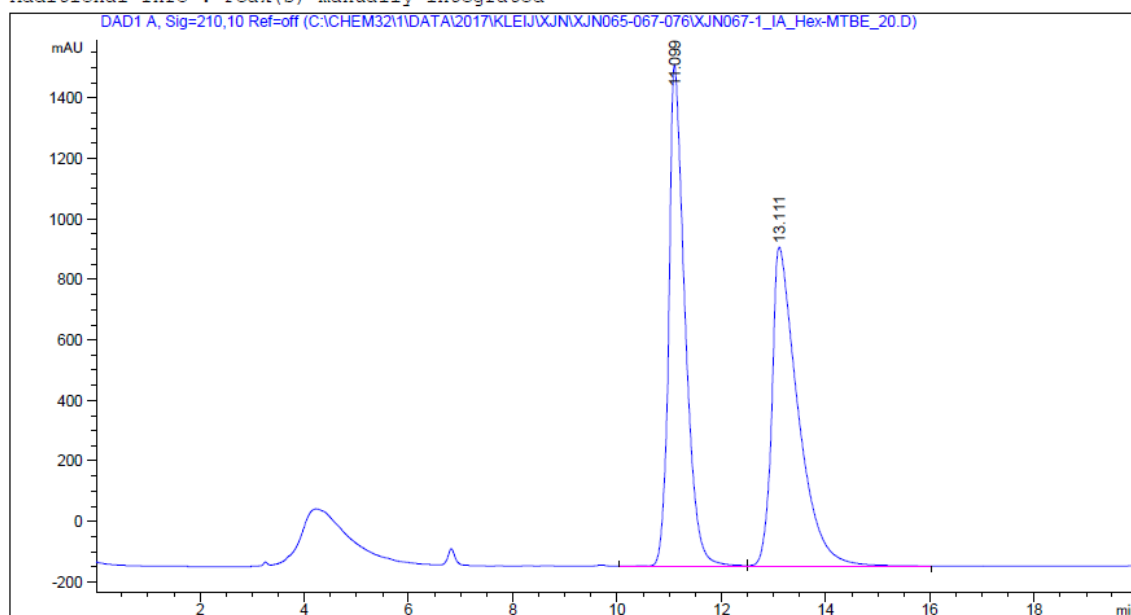
IR spectrum (neat)



HRMS (ESI<sup>+</sup>, MeOH):  $m/z$  calcd. 319.1669 (M + Na)<sup>+</sup>, found: 319.1668.

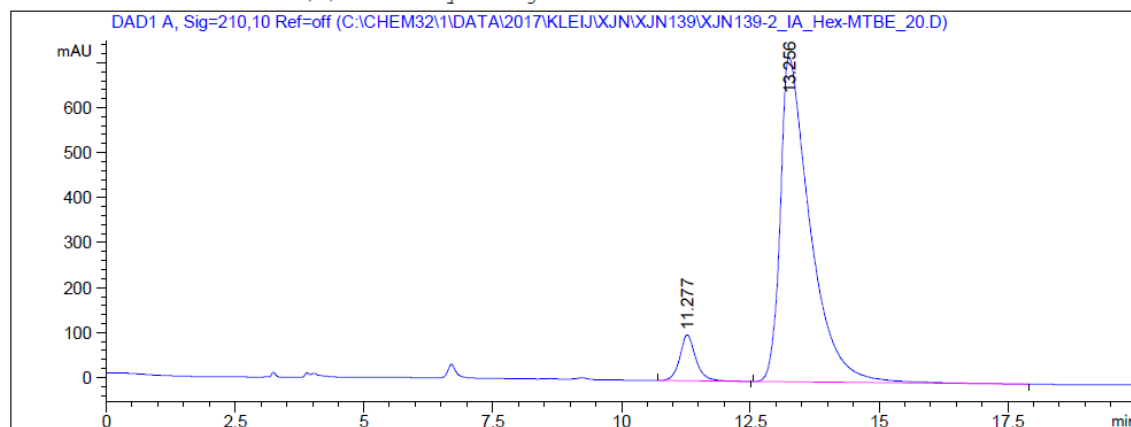
**HPLC conditions:** Chiralpak IA 250 × 4.6 mm, 5 μm, Hex/MTBE = 80 : 20, 1 mL/min;  
93 : 7 *er*;  $[\alpha]_D^{25} = -31.72$  ( $c = 0.10$ , CHCl<sub>3</sub>).

Additional Info : Peak(s) manually integrated

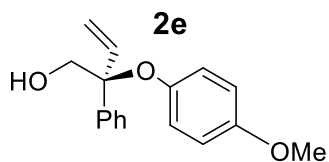


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 11.099        | VV R | 0.3155      | 3.57627e4    | 1657.73132   | 49.4024 |
| 2      | 13.111        | VB   | 0.4991      | 3.66279e4    | 1054.78235   | 50.5976 |

Additional Info : Peak(s) manually integrated

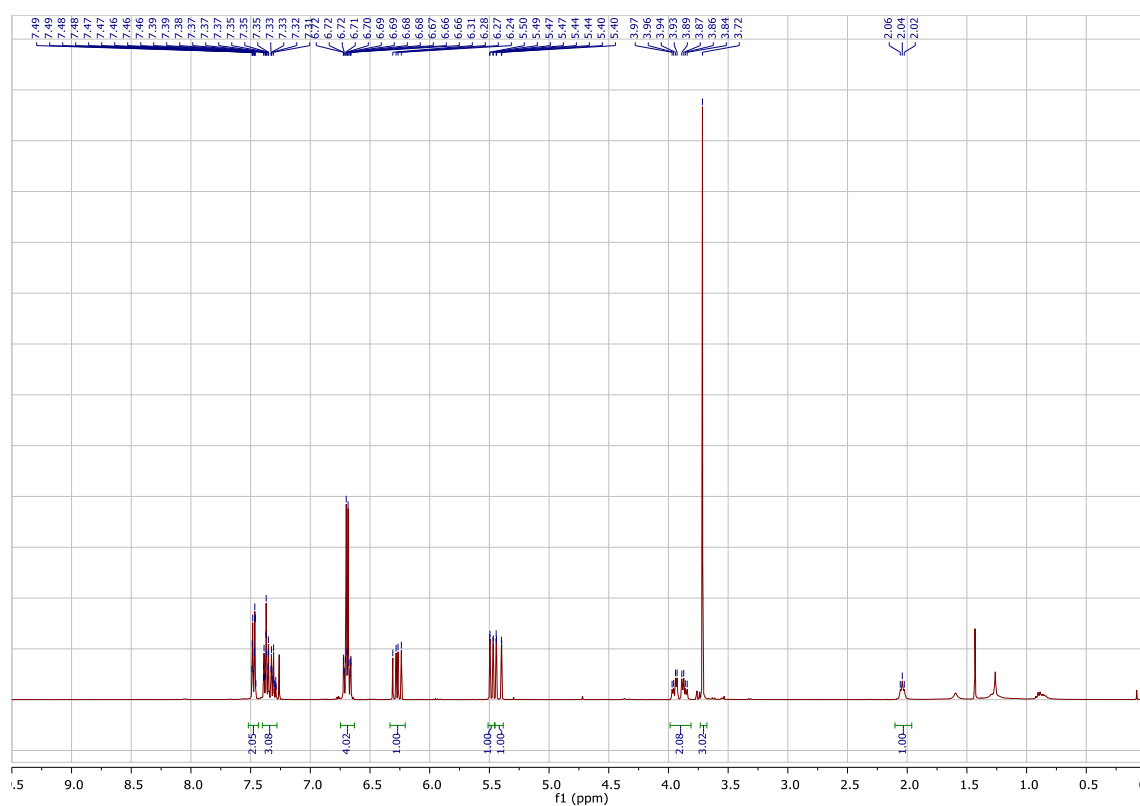


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 11.277        | BB   | 0.3170      | 2191.47070   | 101.87803    | 7.0105  |
| 2      | 13.256        | BB   | 0.5803      | 2.90682e4    | 721.05310    | 92.9895 |



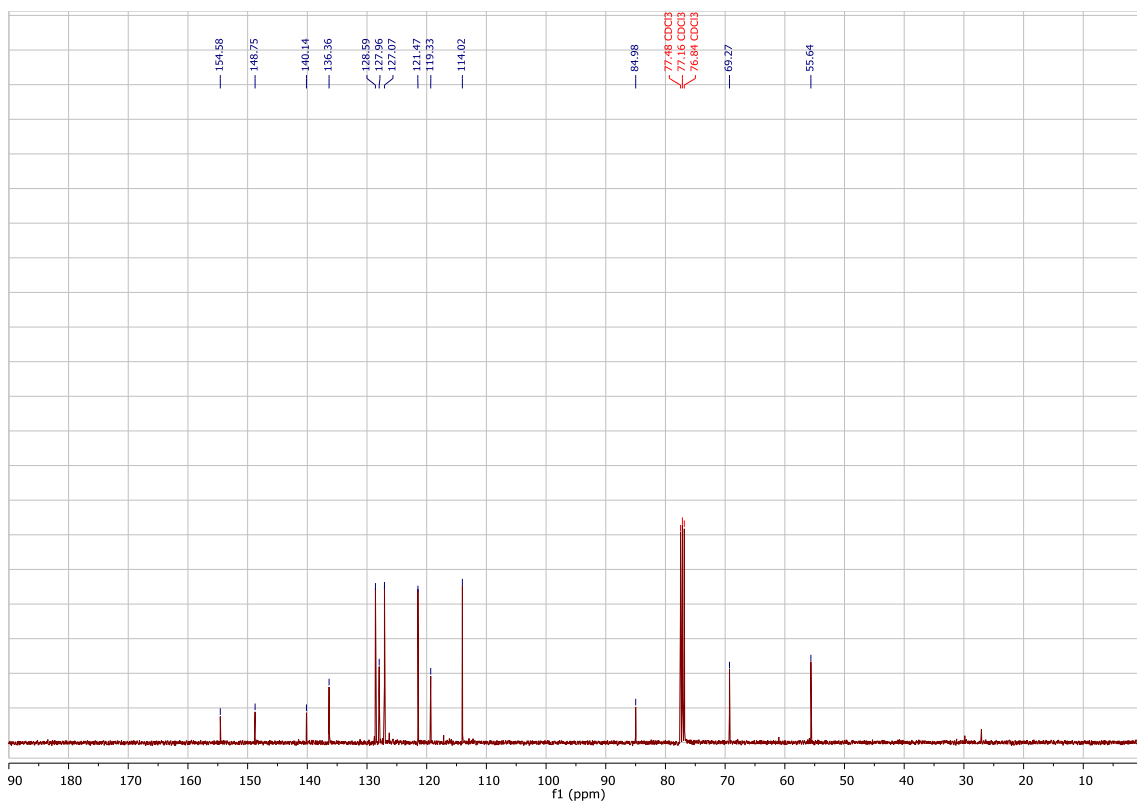
Scale: 0.2 mmol; isolated 45.5 mg (85% yield), light yellow oil, Hexane : EA = 50 : 1,  $R_f$  = 0.15

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ )



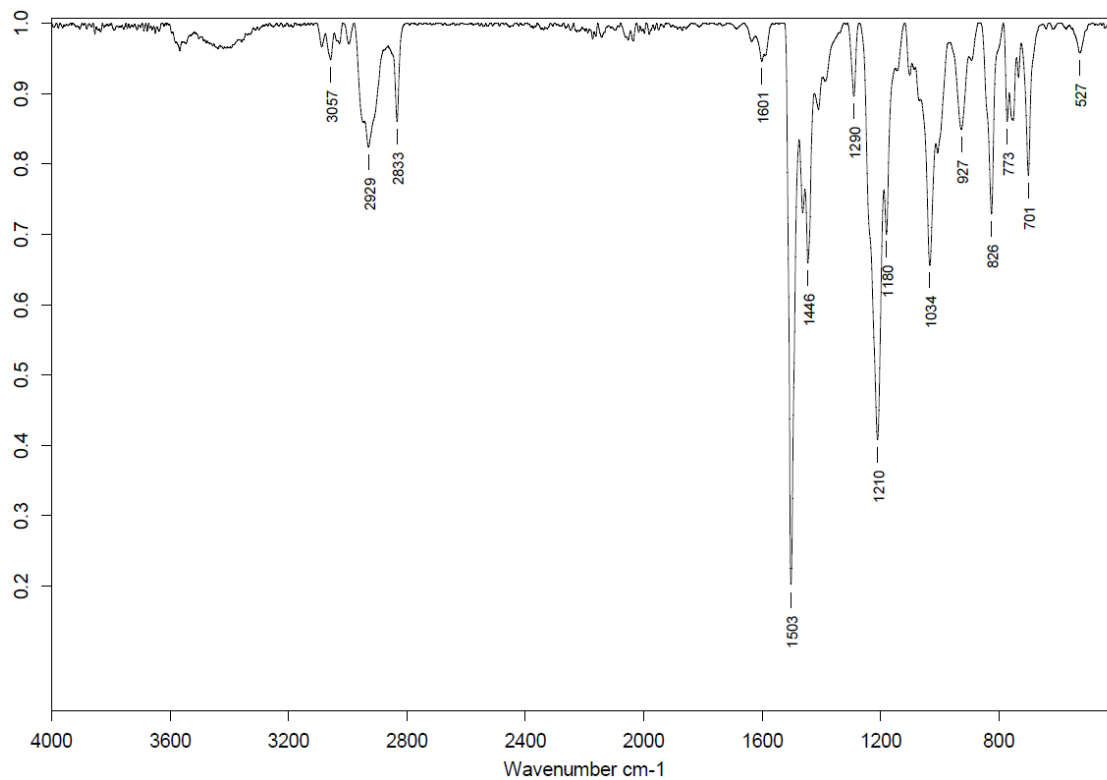
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 – 7.43 (m, 2H), 7.40 – 7.28 (m, 3H), 6.75 – 6.63 (m, 4H), 6.27 (dd,  $J$  = 17.6, 11.1 Hz, 1H), 5.48 (dd,  $J$  = 11.1, 1.1 Hz, 1H), 5.42 (dd,  $J$  = 17.6, 1.1 Hz, 1H), 3.99 – 3.81 (m, 2H), 3.72 (s, 3H), 2.04 (t,  $J$  = 6.7 Hz, 1H).

<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>)



<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 154.58, 148.75, 140.14, 136.36, 128.59, 127.96, 127.07, 121.47, 119.33, 114.02, 84.98, 69.27, 55.64.

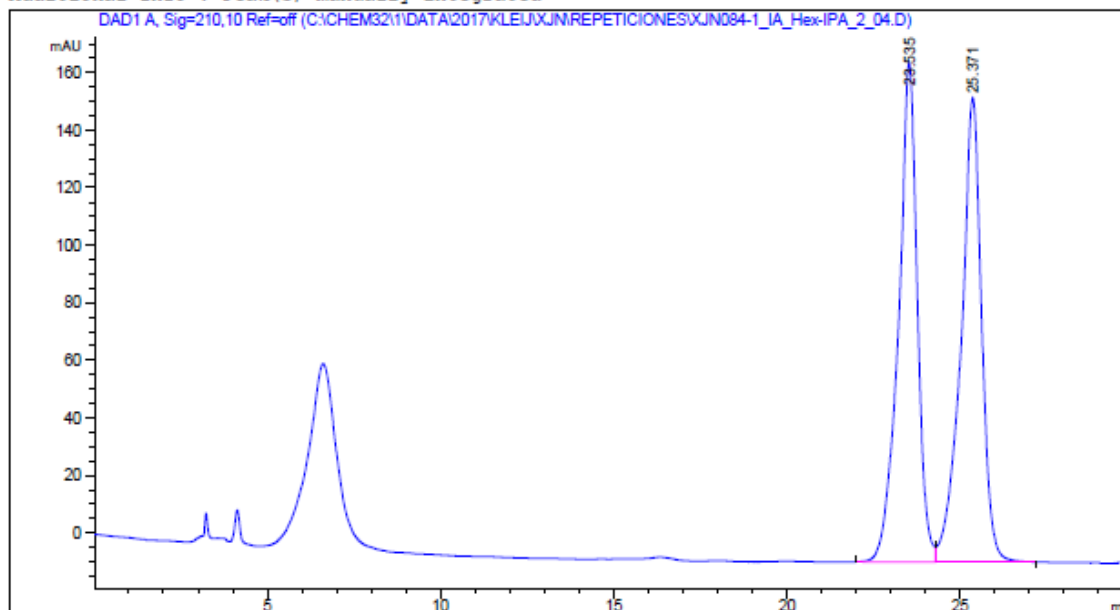
IR spectrum (neat)



HRMS (ESI<sup>+</sup>, MeOH): *m/z* calcd. 293.1148 (M + Na)<sup>+</sup>, found: 293.1155.

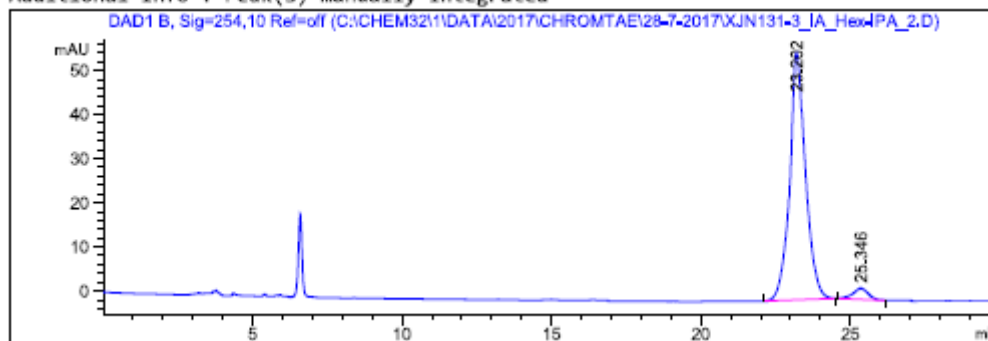
**HPLC conditions:** Chiralpak IA 250 × 4.6 mm, 5 μm, Hex/IPA = 98 : 2, 1 mL/min; 96 : 4 *er*;  $[\alpha]_{\text{D}}^{25} = -39.25$  ( $c = 0.11$ , CHCl<sub>3</sub>).

Additional Info : Peak(s) manually integrated

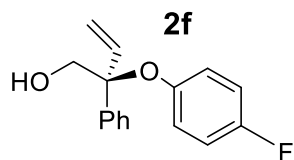


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 23.535        | BV   | 0.5443      | 6552.61328   | 173.61475    | 49.6331 |
| 2      | 25.371        | VB   | 0.5925      | 6649.49854   | 161.46825    | 50.3669 |

Additional Info : Peak(s) manually integrated

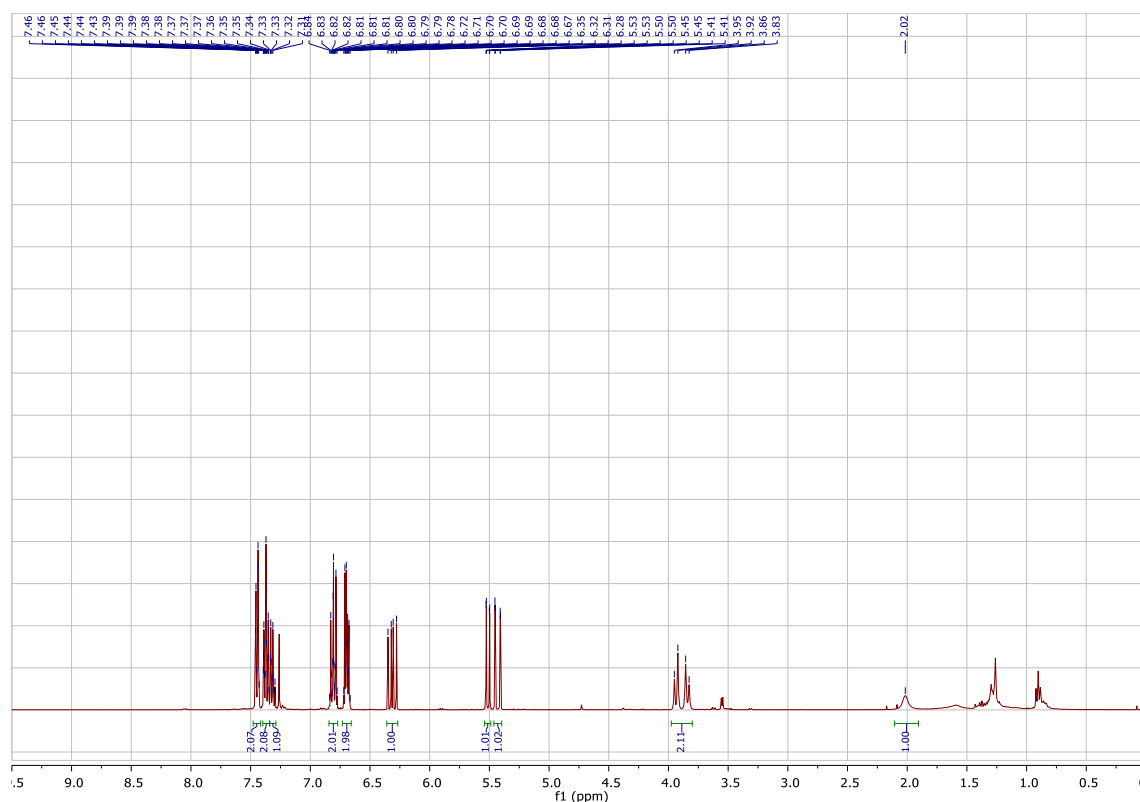


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 23.202        | BB   | 0.5320      | 2062.57007   | 55.96486     | 95.8979 |
| 2      | 25.346        | BB   | 0.4544      | 88.22784     | 2.53289      | 4.1021  |



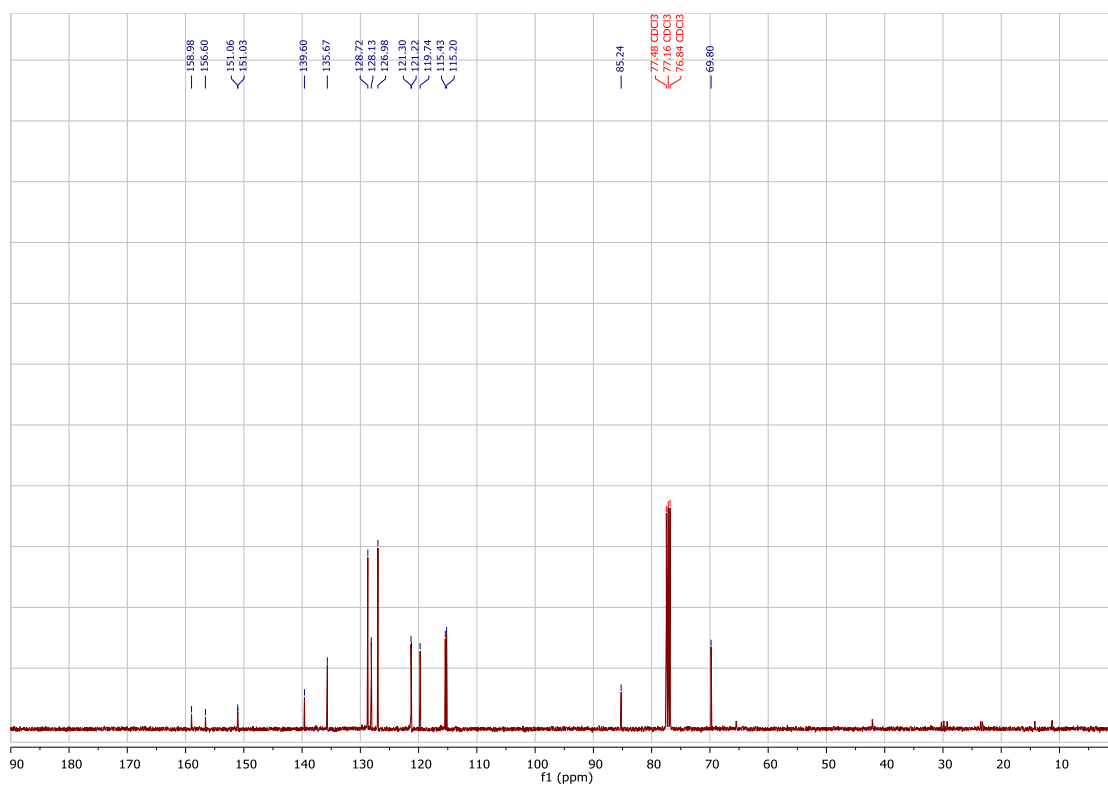
Scale: 0.2 mmol; isolated 39.0 mg (76% yield), light yellow oil, Hexane : EA = 50 : 1,  $R_f$  = 0.15

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ )



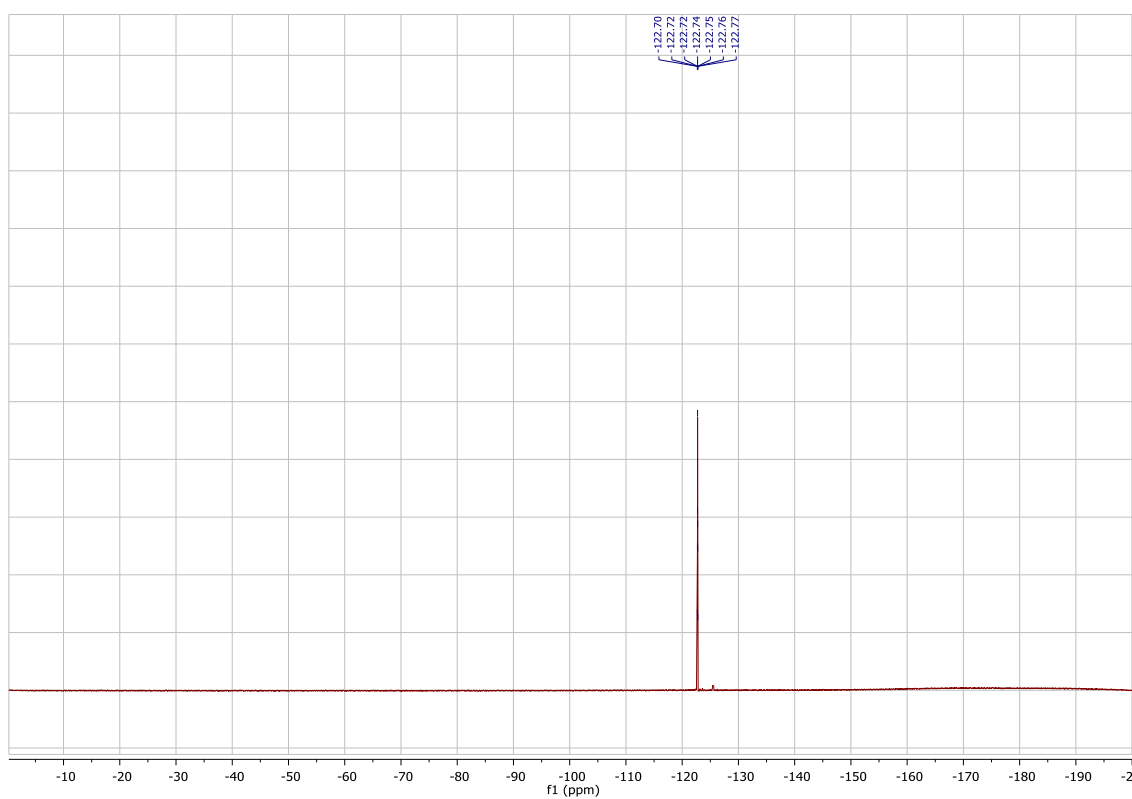
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 – 7.42 (m, 2H), 7.40 – 7.34 (m, 2H), 7.34 – 7.29 (m, 1H), 6.84 – 6.77 (m, 2H), 6.73 – 6.66 (m, 2H), 6.31 (dd,  $J$  = 17.5, 11.1 Hz, 1H), 5.51 (dd,  $J$  = 11.1, 1.0 Hz, 1H), 5.43 (dd,  $J$  = 17.5, 1.0 Hz, 1H), 3.98 – 3.80 (m, 2H), 2.02 (s, 1H).

$^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ )



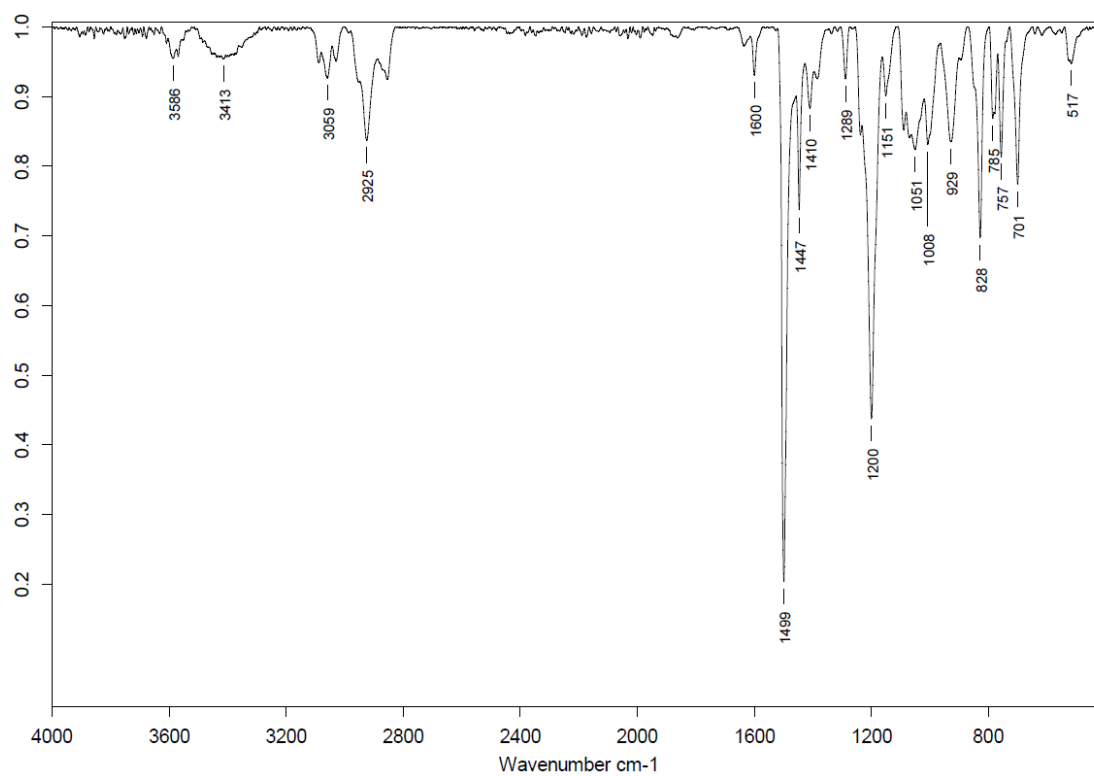
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.98, 156.60, 151.06, 151.03, 139.60, 135.67, 128.72, 128.13, 126.98, 121.30, 121.22, 119.74, 115.43, 115.20, 85.24, 69.80.

$^{19}\text{F}$  NMR spectrum ( $\text{CDCl}_3$ )



$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -122.74 (tt,  $J = 8.5, 4.6$  Hz).

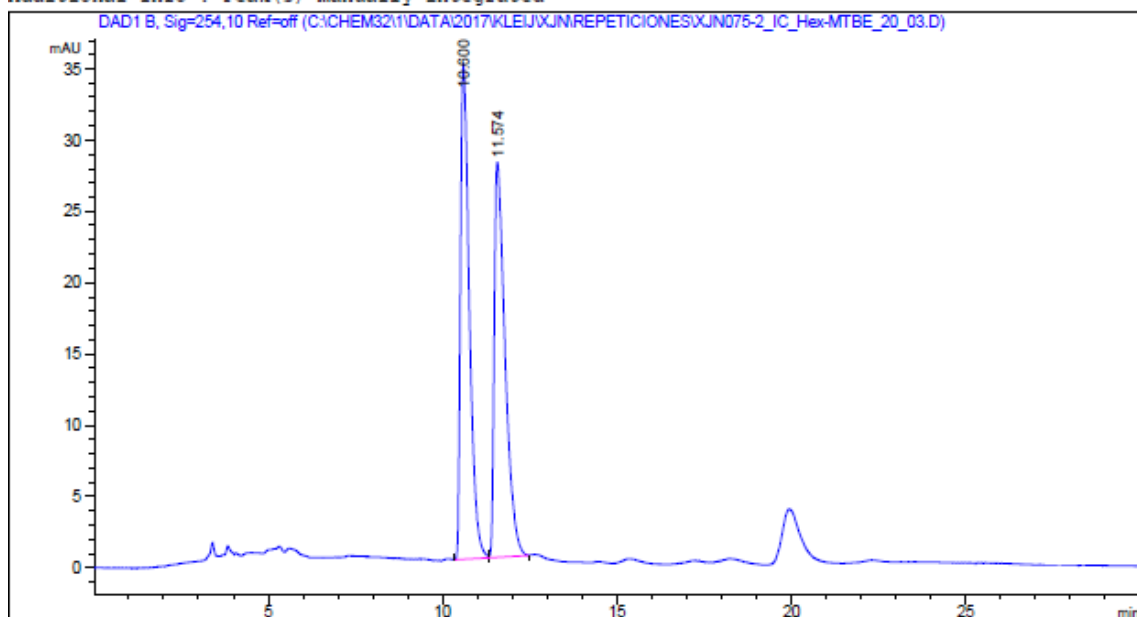
IR spectrum (neat)



**HRMS** (ESI+, MeOH):  $m/z$  calcd. 281.0948 ( $M + Na$ )<sup>+</sup>, found: 281.0942.

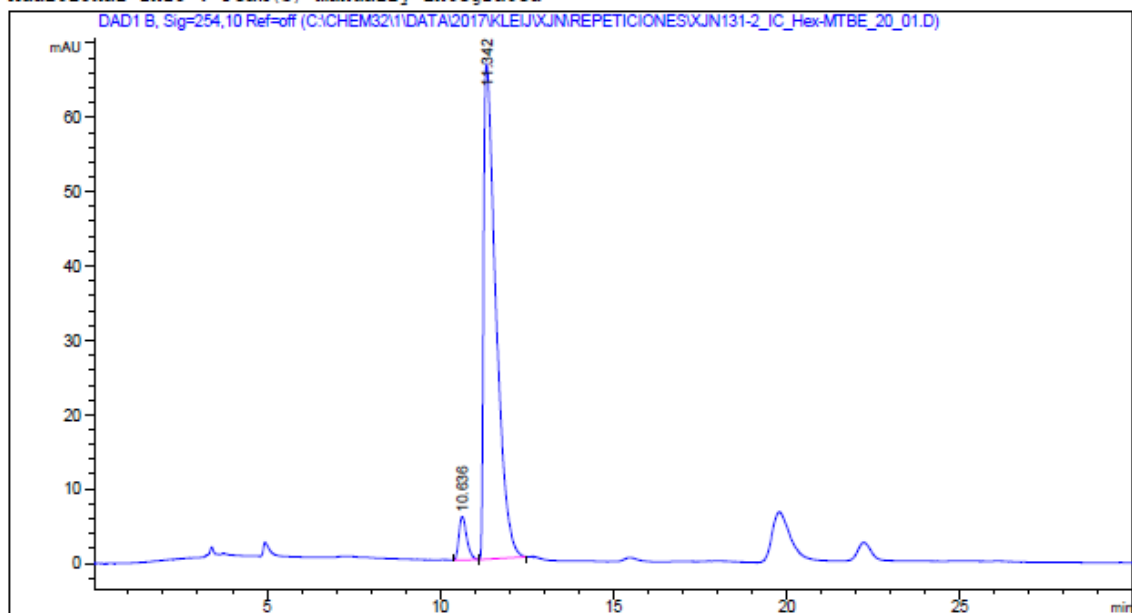
**HPLC conditions:** Chiralpak IC 250 × 4.6 mm, 5 μm, Hex/MTBE = 80 : 20, 1 mL/min;  
95 : 5 *er*;  $[\alpha]_D^{25} = -44.70$  ( $c = 0.10$ , CHCl<sub>3</sub>).

Additional Info : Peak(s) manually integrated

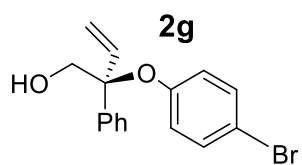


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 10.600        | BV   | 0.2653      | 610.44183    | 34.69475     | 50.4617 |
| 2      | 11.574        | VB   | 0.3260      | 599.27106    | 27.73917     | 49.5383 |

Additional Info : Peak(s) manually integrated

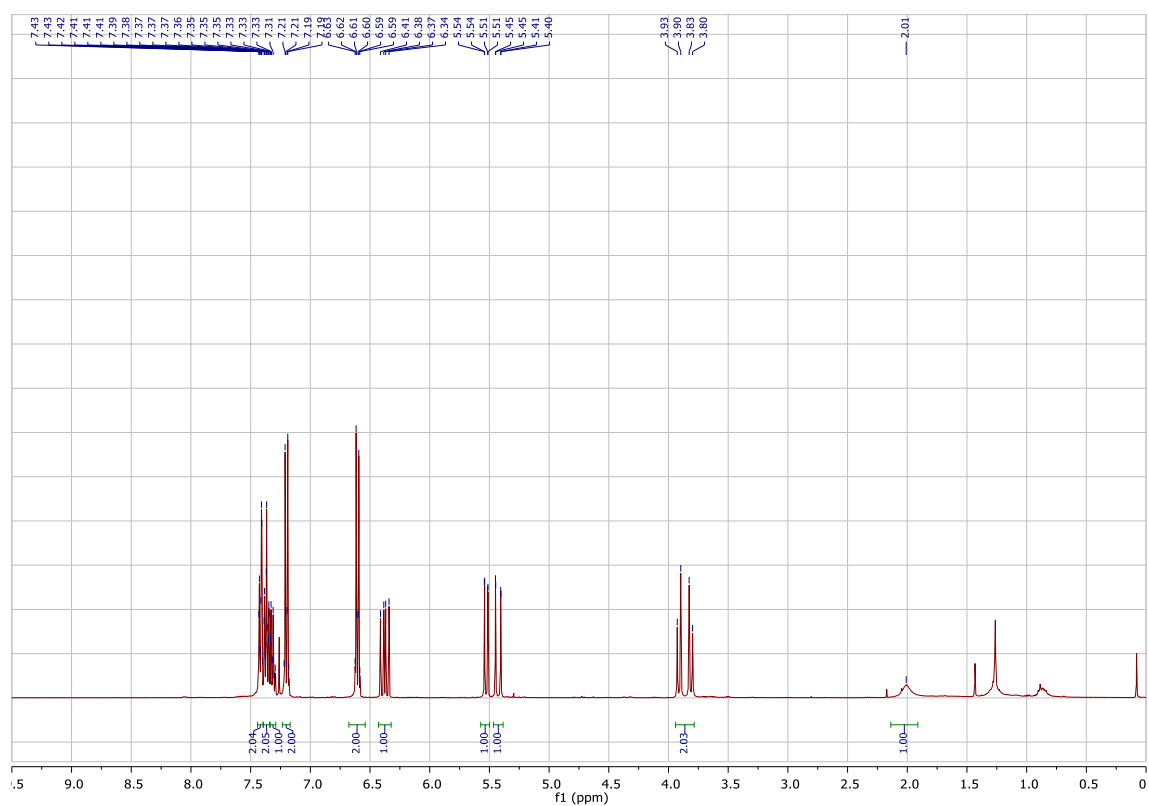


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 10.636        | BB   | 0.2384      | 90.91647     | 5.81561      | 5.2699  |
| 2      | 11.342        | BB   | 0.3620      | 1634.28052   | 66.65661     | 94.7301 |



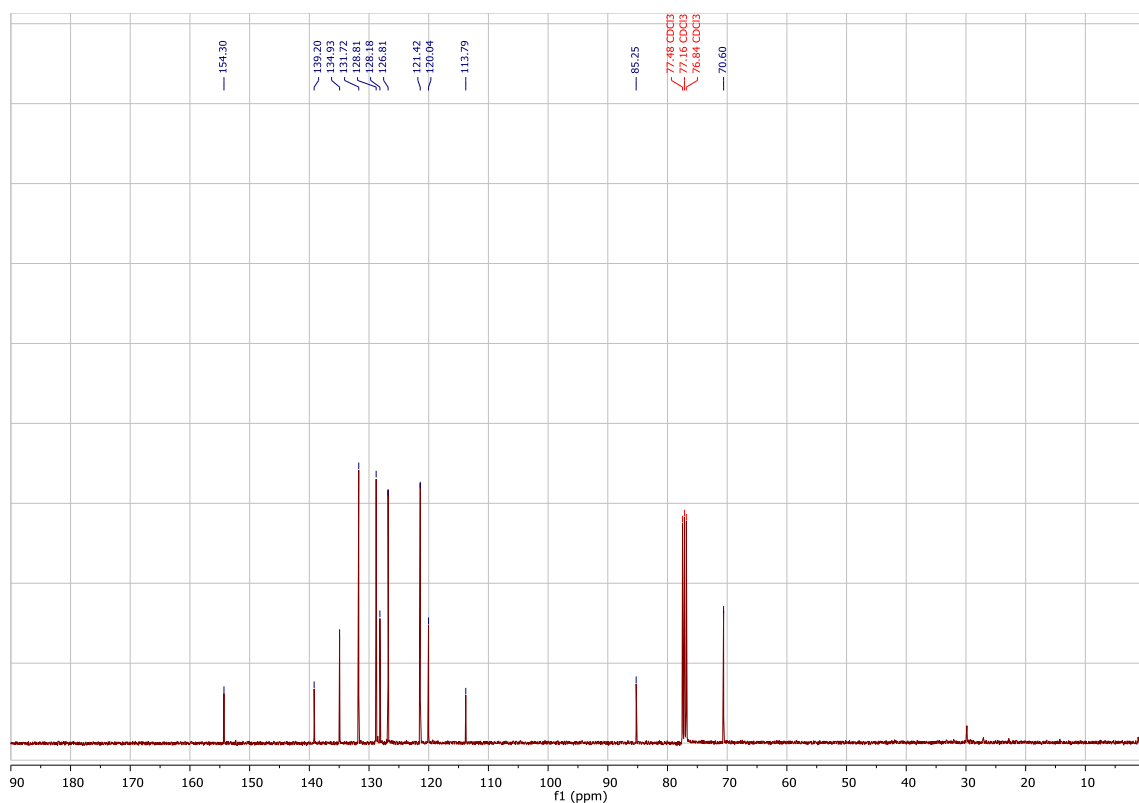
Scale: 0.2 mmol; isolated 52.7 mg (83% yield), light yellow oil, Hexane : EA = 50 : 1,  $R_f$  = 0.15

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ )

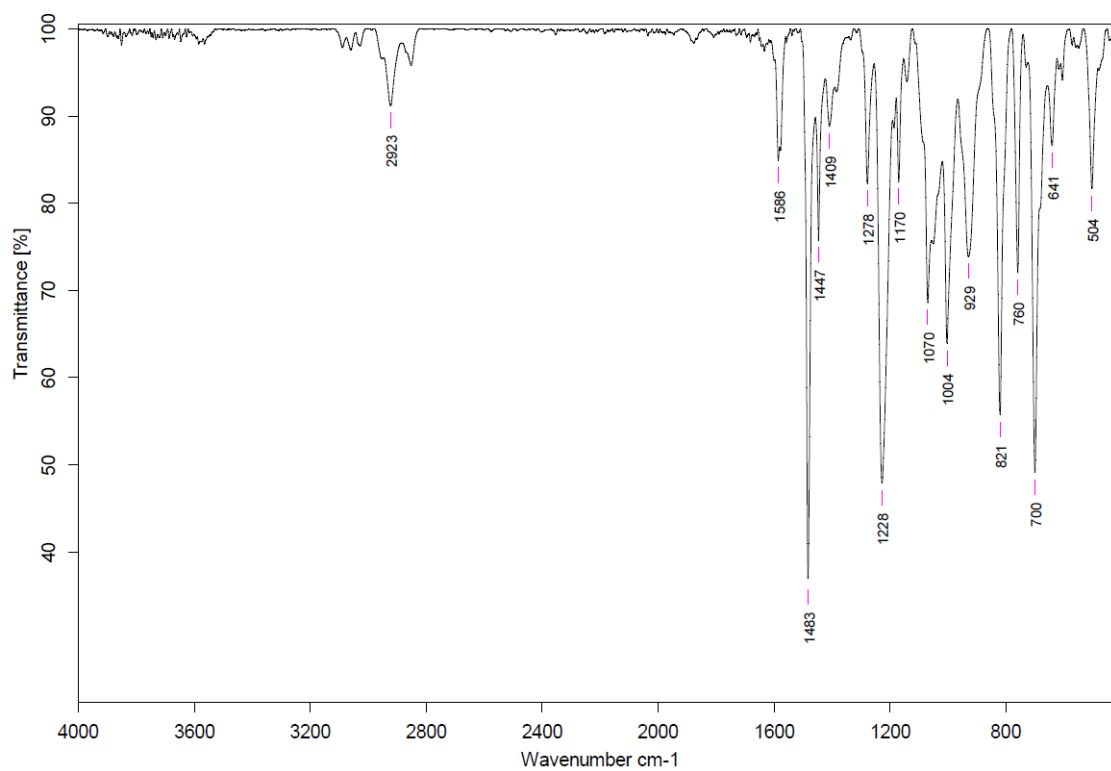


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 – 7.40 (m, 2H), 7.39 – 7.34 (m, 2H), 7.34 – 7.29 (m, 1H), 7.23 – 7.17 (m, 2H), 6.68 – 6.54 (m, 2H), 6.38 (dd,  $J$  = 17.5, 11.2 Hz, 1H), 5.53 (dd,  $J$  = 11.1, 0.9 Hz, 1H), 5.43 (dd,  $J$  = 17.5, 0.9 Hz, 1H), 3.94 – 3.78 (m, 2H), 2.01 (s, 1H).

<sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>)



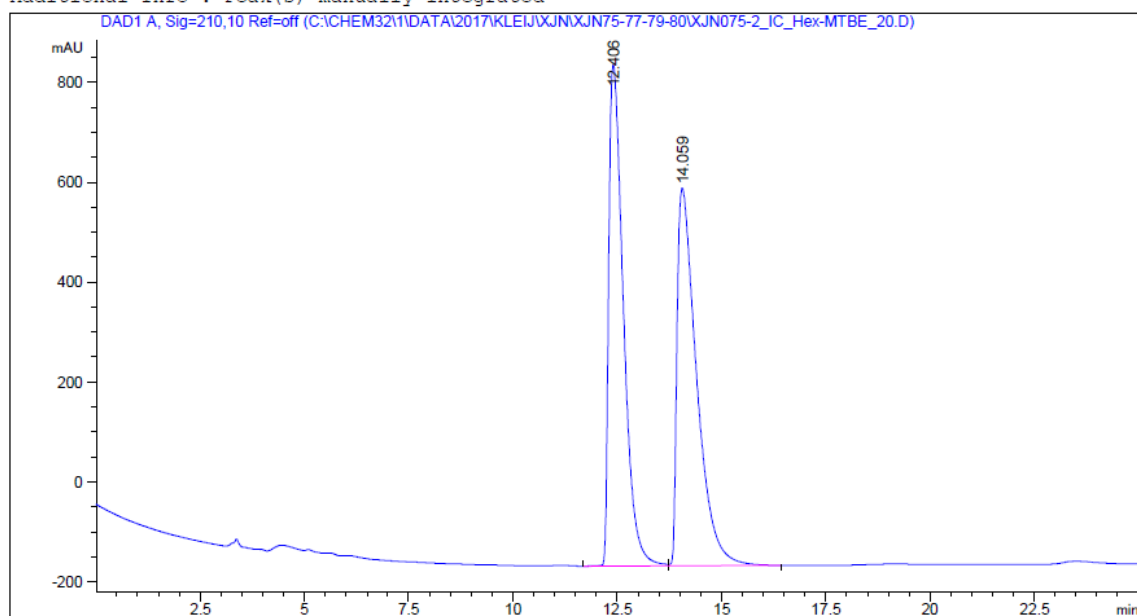
IR spectrum (neat)



HRMS (ESI<sup>+</sup>, MeOH): *m/z* calcd. 341.0148 (M + Na)<sup>+</sup>, found: 341.0145.

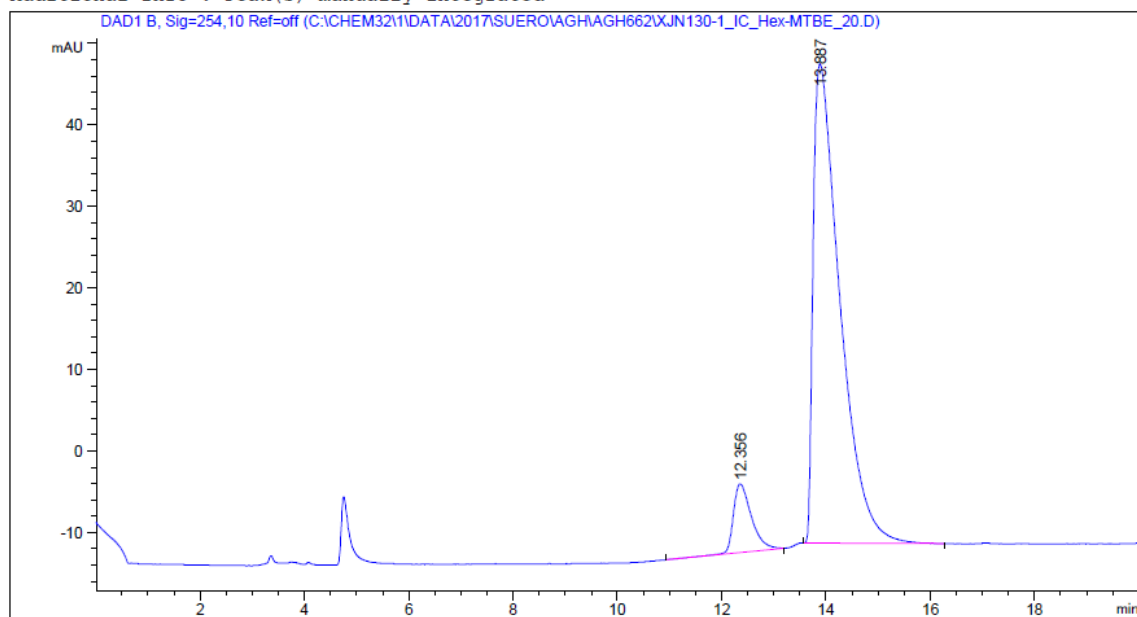
**HPLC conditions:** Chiralpak IC 250 × 4.6 mm, 5 μm, Hex/MTBE = 80 : 20, 1 mL/min;  
91 : 9 *er*;  $[\alpha]_D^{25} = -40.73$  ( $c = 0.09$ , CHCl<sub>3</sub>).

Additional Info : Peak(s) manually integrated

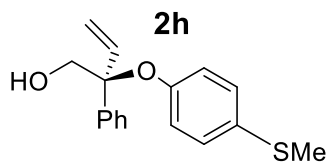


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 12.406        | BV   | 0.3783      | 2.44396e4    | 1003.01770   | 49.8384 |
| 2      | 14.059        | VB   | 0.4875      | 2.45981e4    | 756.26312    | 50.1616 |

Additional Info : Peak(s) manually integrated

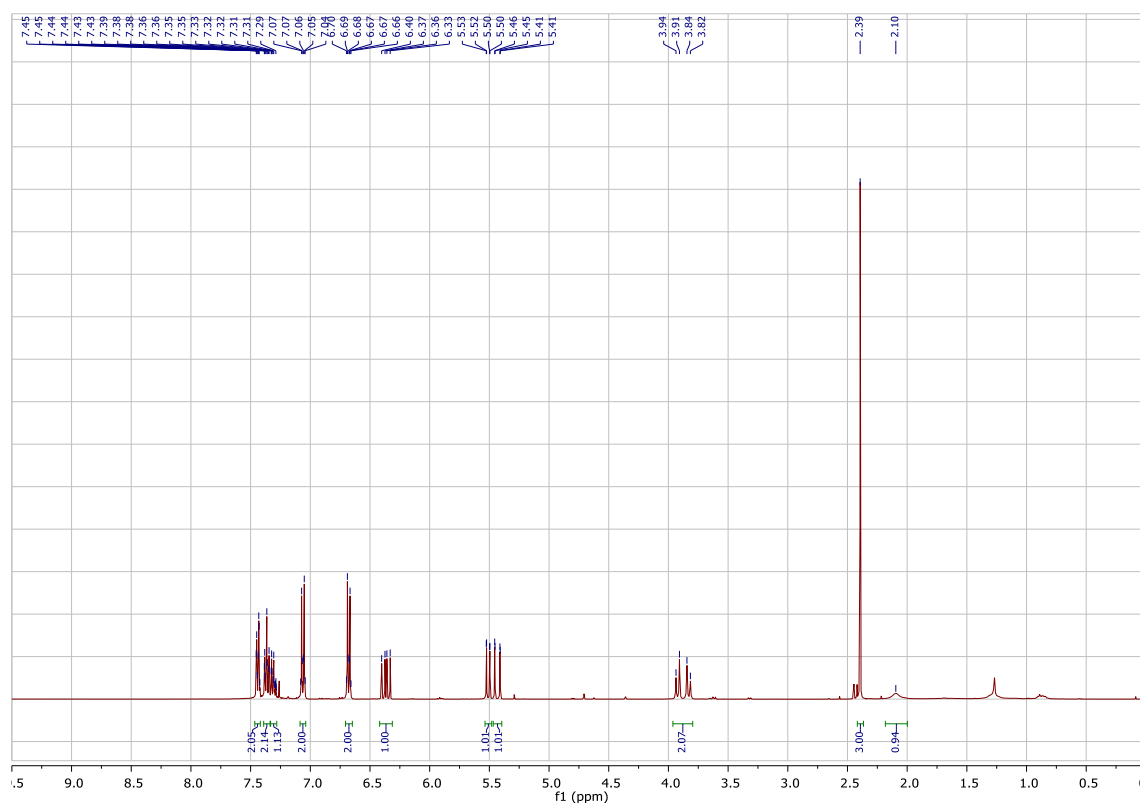


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 12.356        | BB   | 0.3629      | 202.63643    | 8.41640      | 8.8105  |
| 2      | 13.887        | BB   | 0.5260      | 2097.29761   | 58.81979     | 91.1895 |



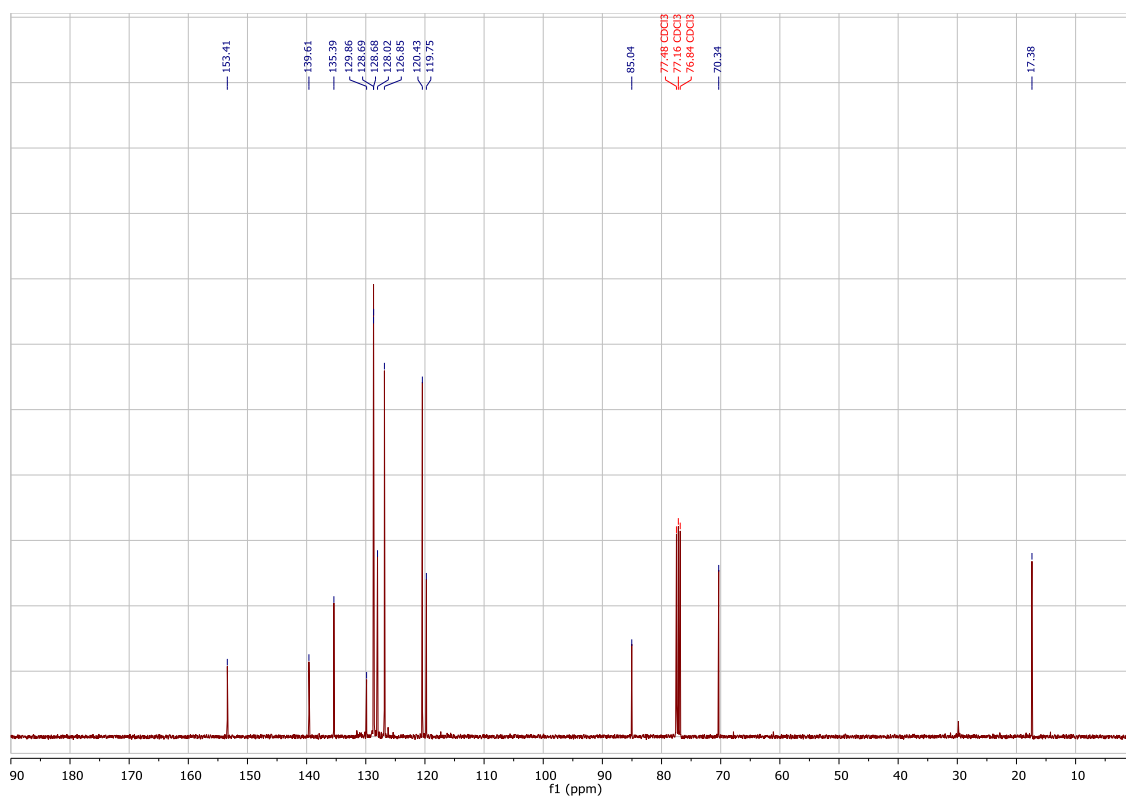
Scale: 0.2 mmol; isolated 45.7 mg (80% yield), light yellow solid, Hexane : EA = 50 : 1,  $R_f = 0.15$

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ )



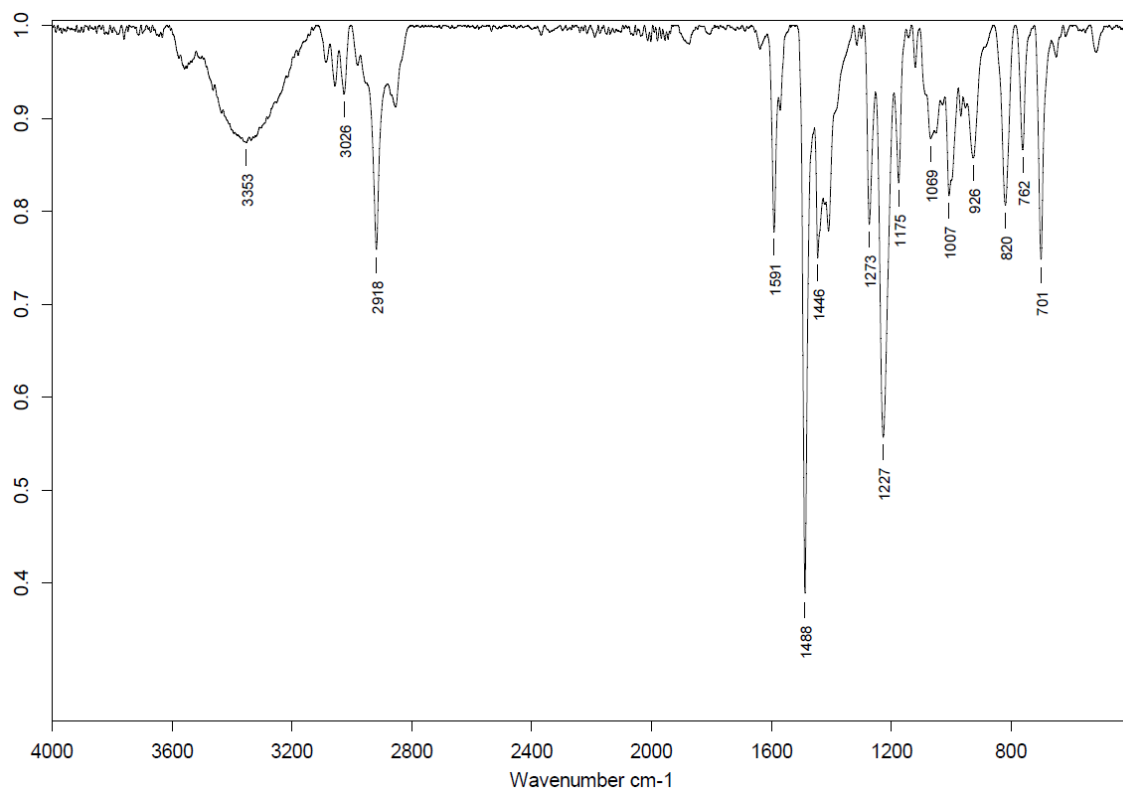
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 – 7.42 (m, 2H), 7.39 – 7.34 (m, 2H), 7.33 – 7.28 (m, 1H), 7.09 – 7.04 (m, 2H), 6.70 – 6.65 (m, 2H), 6.37 (dd,  $J = 17.5, 11.1$  Hz, 1H), 5.51 (dd,  $J = 11.1, 1.0$  Hz, 1H), 5.43 (dd,  $J = 17.5, 1.0$  Hz, 1H), 3.96 – 3.80 (m, 2H), 2.39 (s, 3H), 2.10 (s, 1H).

$^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ )



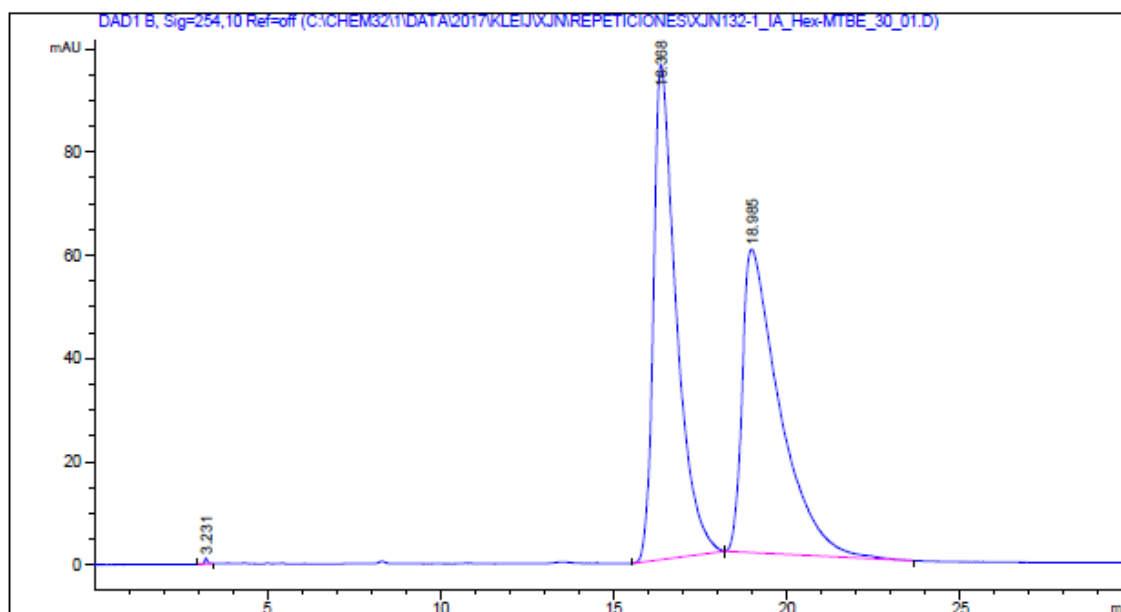
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  153.41, 139.61, 135.39, 129.86, 128.69, 128.68, 128.02, 126.85, 120.43, 119.75, 85.04, 70.34, 17.38.

IR spectrum (neat)



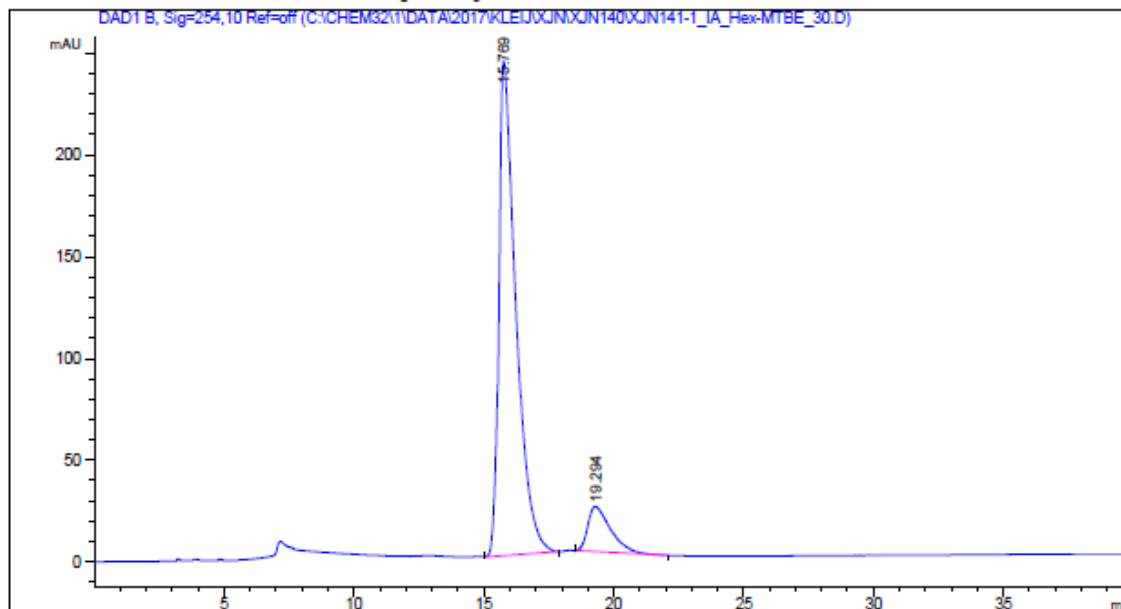
HRMS (ESI $^{+}$ , MeOH):  $m/z$  calcd. 309.0920 ( $\text{M} + \text{Na}$ ) $^{+}$ , found: 309.0921.

**HPLC conditions:** Chiralpak IA 250 × 4.6 mm, 5 μm, Hex/MTBE = 70 : 30, 1 mL/min;  
89 : 11 *er*;  $[\alpha]_D^{25} = -33.99$  (*c* = 0.12, CHCl<sub>3</sub>).

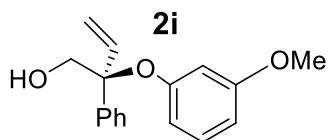


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 3.231         | BB   | 0.0837      | 6.32915      | 1.15846      | 0.0720  |
| 2      | 16.368        | BB   | 0.6603      | 4393.03076   | 95.93186     | 49.9414 |
| 3      | 18.985        | BB   | 1.0219      | 4397.01514   | 58.83359     | 49.9867 |

Additional Info : Peak(s) manually integrated

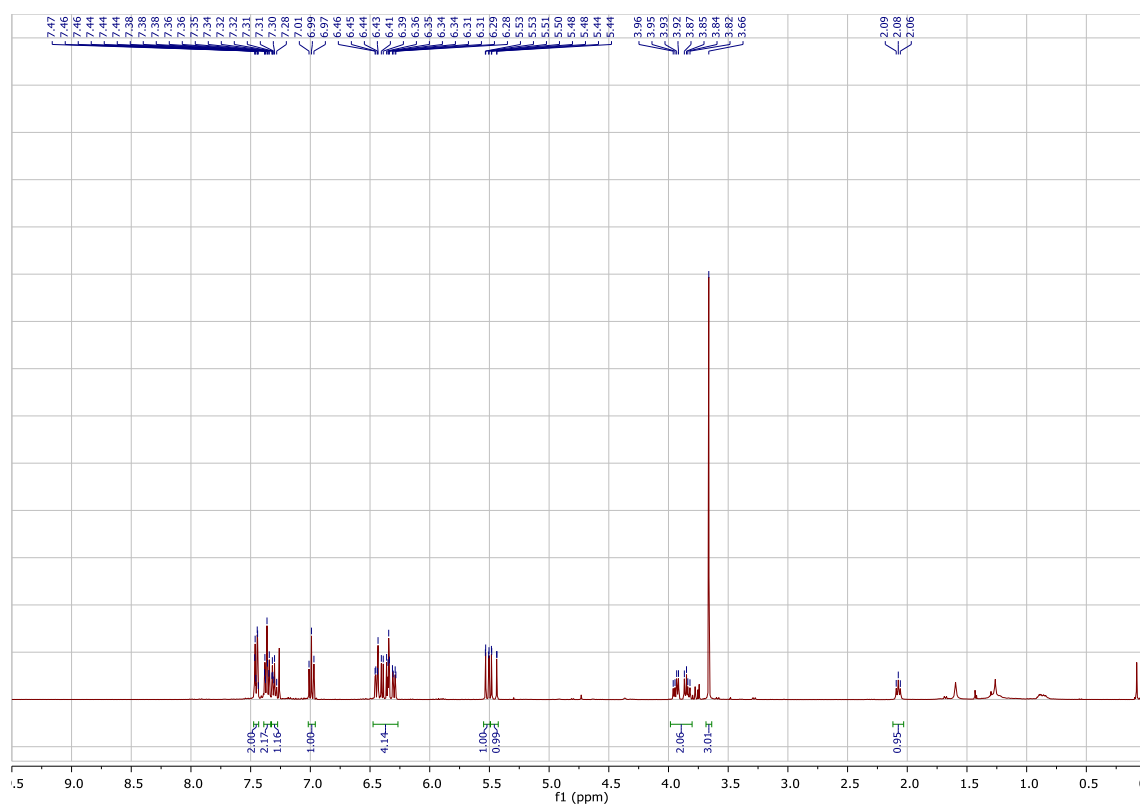


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 15.769        | BB   | 0.6479      | 1.10365e4    | 242.97923    | 88.9968 |
| 2      | 19.294        | BB   | 0.8642      | 1364.50171   | 22.22851     | 11.0032 |



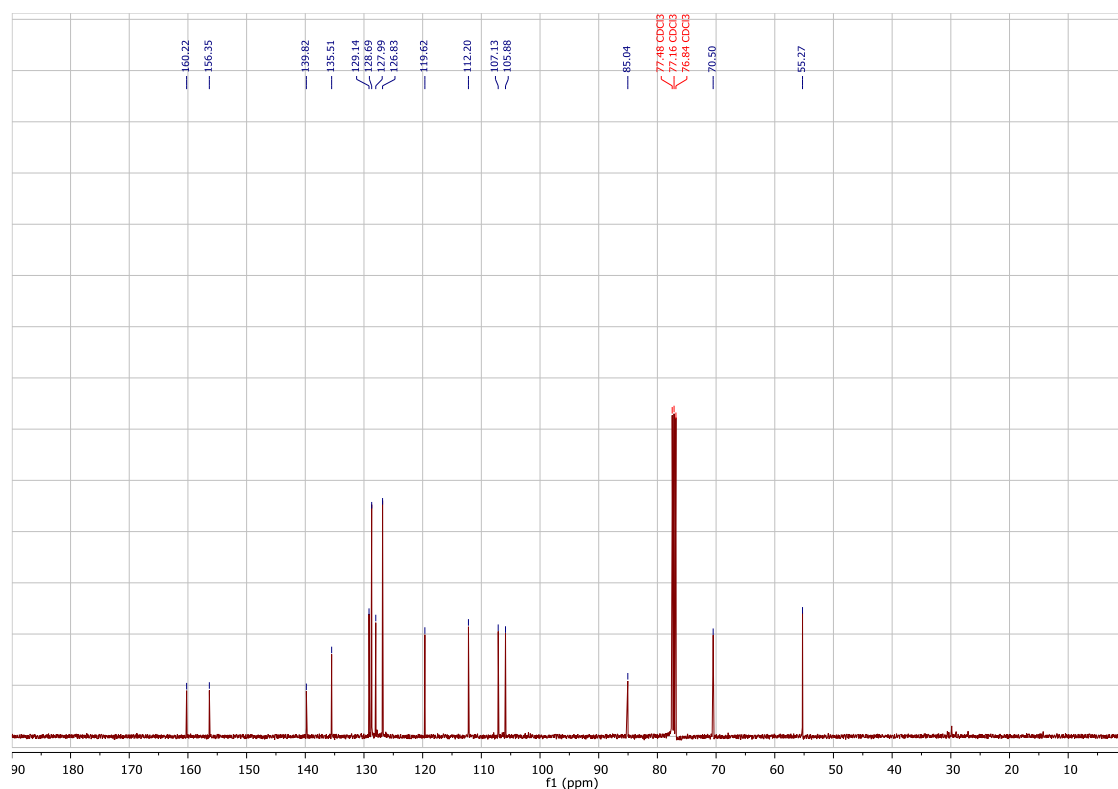
Scale: 0.2 mmol; isolated 41 mg (76% yield), light yellow oil, Hexane : EA = 50 : 1,  $R_f$  = 0.15

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ )



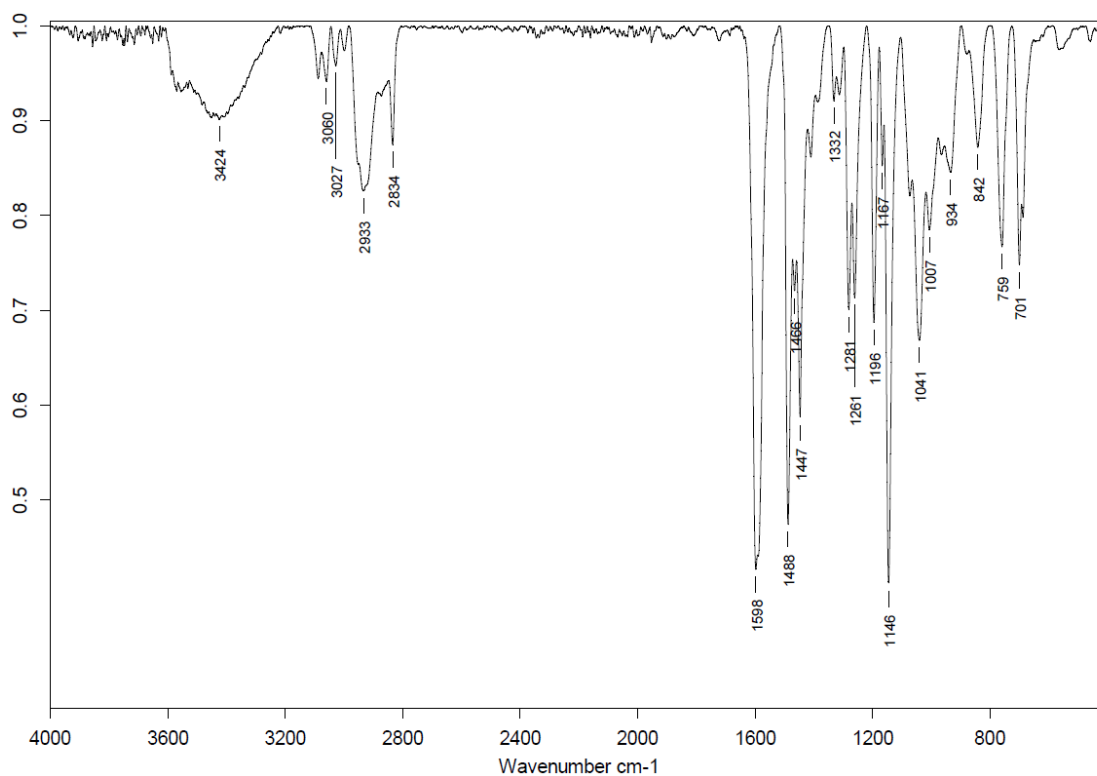
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 (m, 2H), 7.39 – 7.33 (m, 2H), 7.33 – 7.27 (m, 1H), 6.99 (t,  $J$  = 8.2 Hz, 1H), 6.47 – 6.27 (m, 4H), 5.52 (dd,  $J$  = 11.1, 1.0 Hz, 1H), 5.46 (dd,  $J$  = 17.5, 1.0 Hz, 1H), 3.98 – 3.80 (m, 2H), 3.66 (s, 3H), 2.08 (t,  $J$  = 6.9 Hz, 1H).

<sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>)



<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  160.22, 156.35, 139.82, 135.51, 129.14, 128.69, 127.99, 126.83, 119.62, 112.20, 107.13, 105.88, 85.04, 70.50, 55.27.

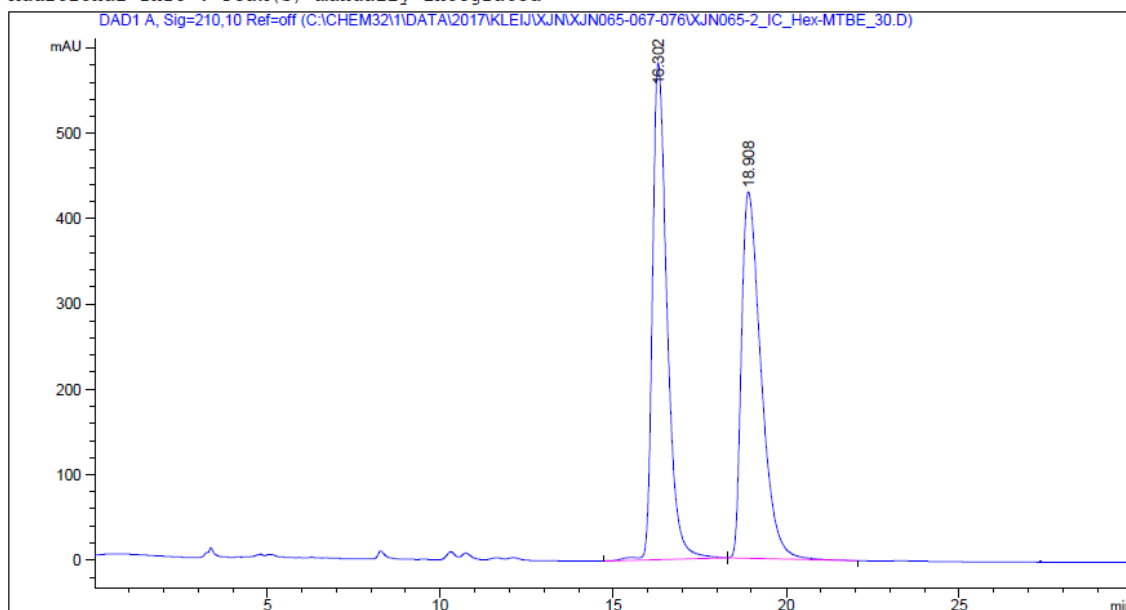
IR spectrum (neat)



HRMS (ESI<sup>+</sup>, MeOH):  $m/z$  calcd. 293.1157 (M + Na)<sup>+</sup>, found: 293.1148.

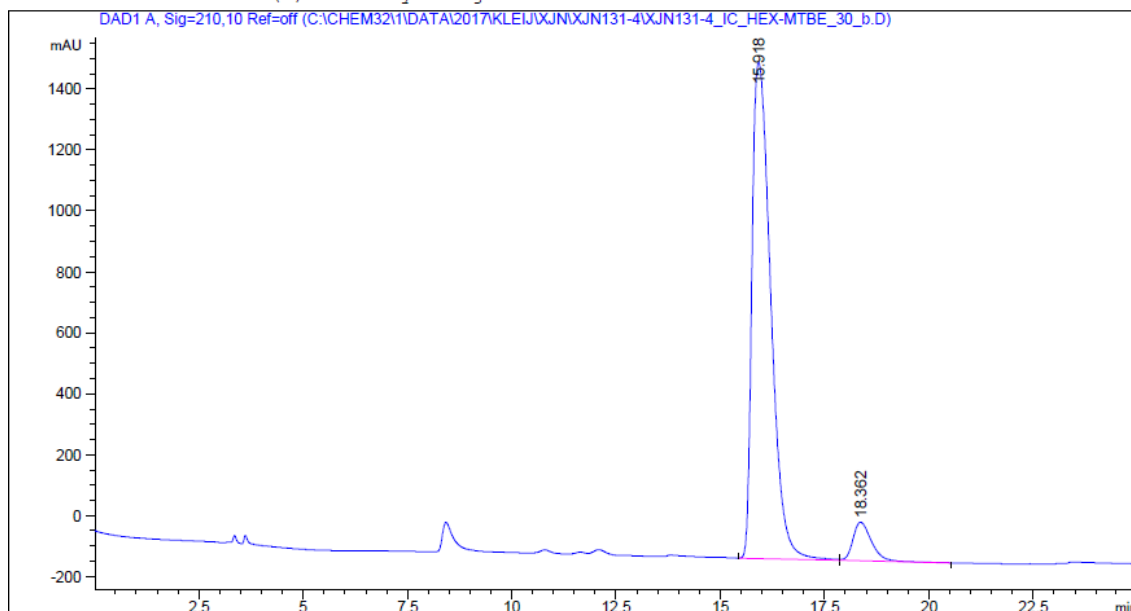
**HPLC conditions:** Chiralpak IC 250 × 4.6 mm, 5 μm, Hex/MTBE = 70 : 30, 1 mL/min;  
93 : 7 *er*;  $[\alpha]_D^{25} = -38.13$  ( $c = 0.10$ , CHCl<sub>3</sub>).

Additional Info : Peak(s) manually integrated

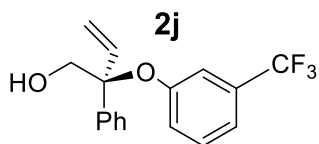


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 16.302        | BB   | 0.4488      | 1.70972e4    | 581.85236    | 50.3448 |
| 2      | 18.908        | BB   | 0.6020      | 1.68630e4    | 429.51129    | 49.6552 |

Additional Info : Peak(s) manually integrated

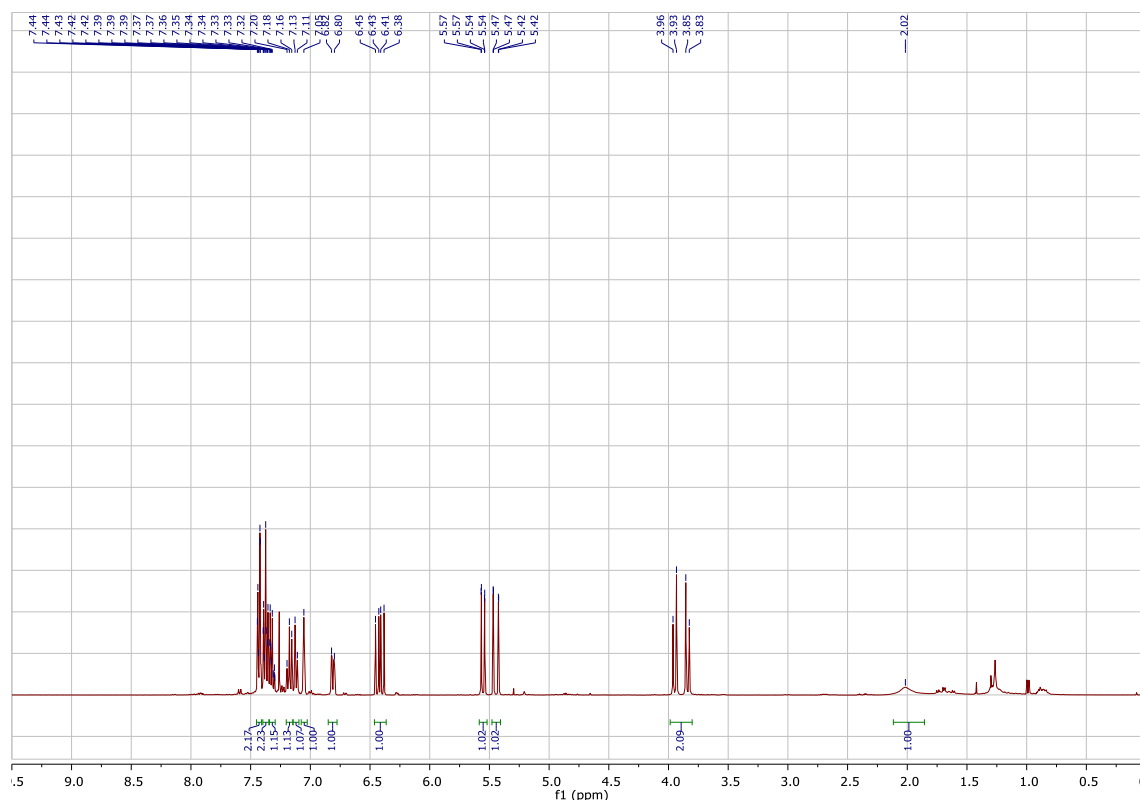


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 15.918        | BV   | 0.4887      | 5.06374e4    | 1628.62683   | 92.8431 |
| 2      | 18.362        | VB   | 0.4712      | 3903.44067   | 126.79259    | 7.1569  |



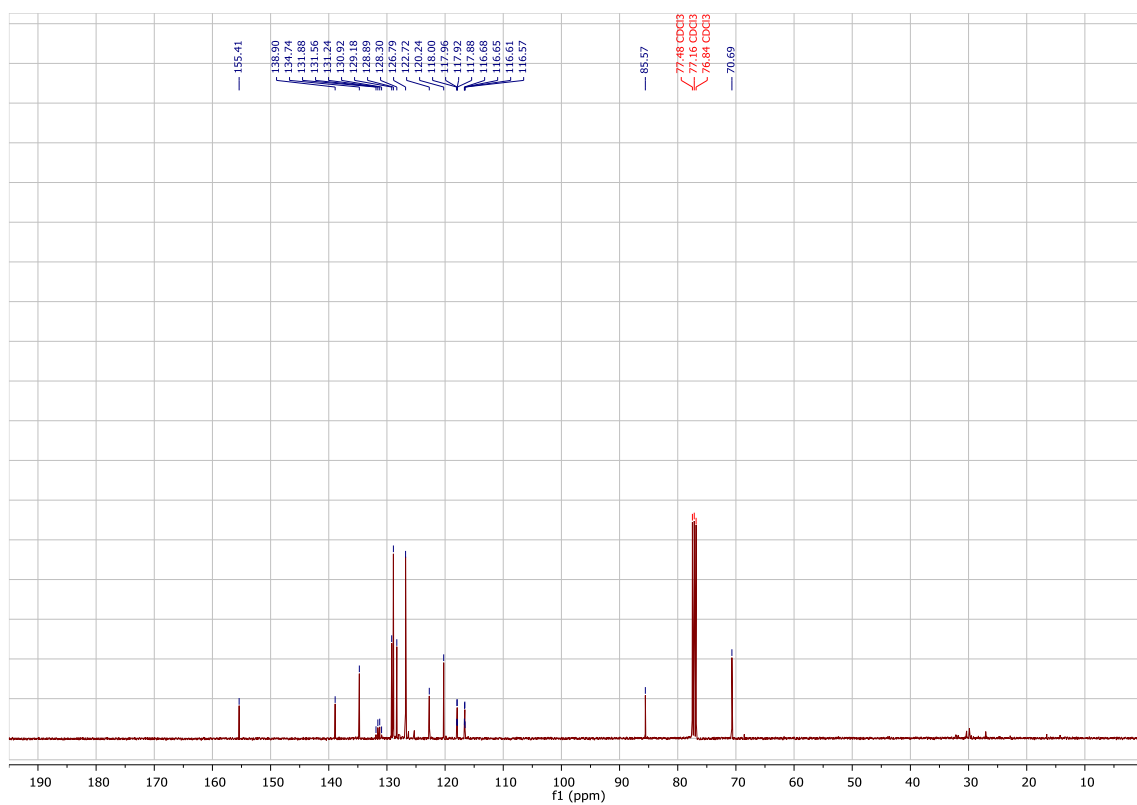
Scale: 0.2 mmol; isolated 35.7 mg (58% yield), light yellow oil, Hexane : EA = 50 : 1,  $R_f$  = 0.15

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ )



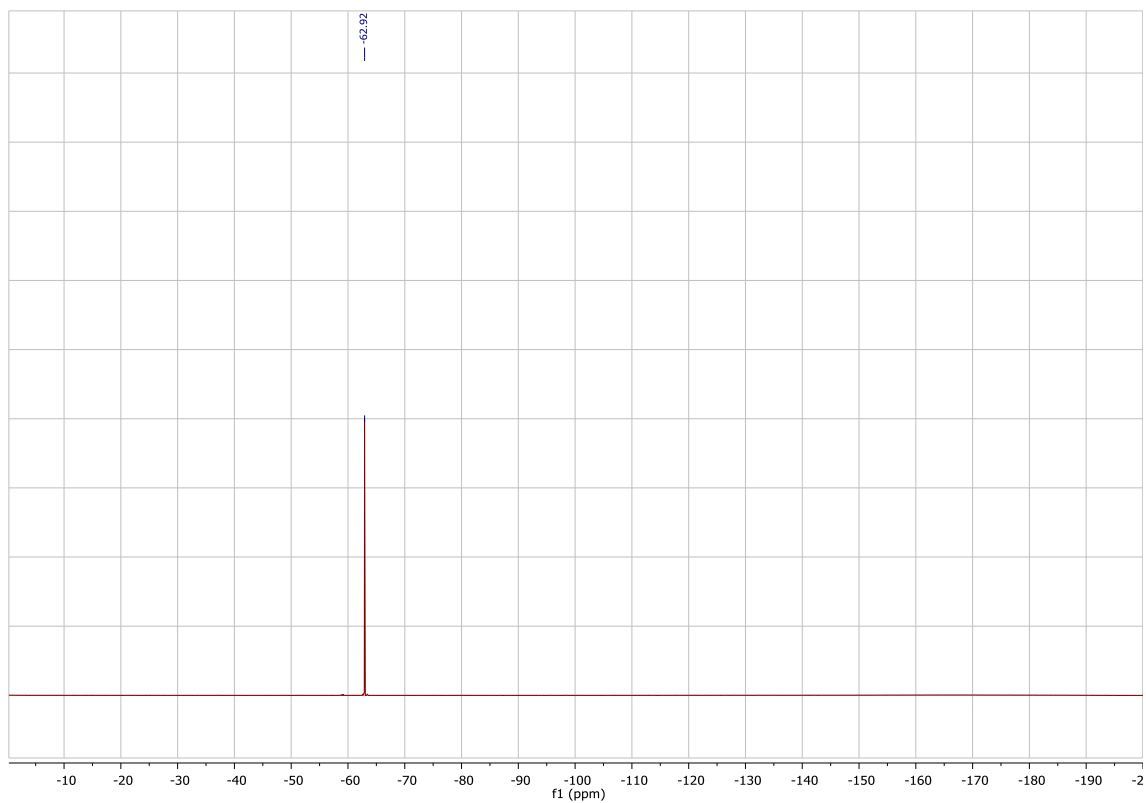
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 (m, 2H), 7.40 – 7.35 (m, 2H), 7.34 – 7.29 (m, 1H), 7.18 (t,  $J$  = 7.9 Hz, 1H), 7.12 (d,  $J$  = 7.7 Hz, 1H), 7.05 (s, 1H), 6.81 (d,  $J$  = 9.6 Hz, 1H), 6.42 (dd,  $J$  = 17.5, 11.1 Hz, 1H), 5.55 (dd,  $J$  = 11.1, 0.9 Hz, 1H), 5.45 (dd,  $J$  = 17.5, 0.9 Hz, 1H), 3.99 – 3.80 (m, 2H), 2.02 (s, 1H).

$^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ )



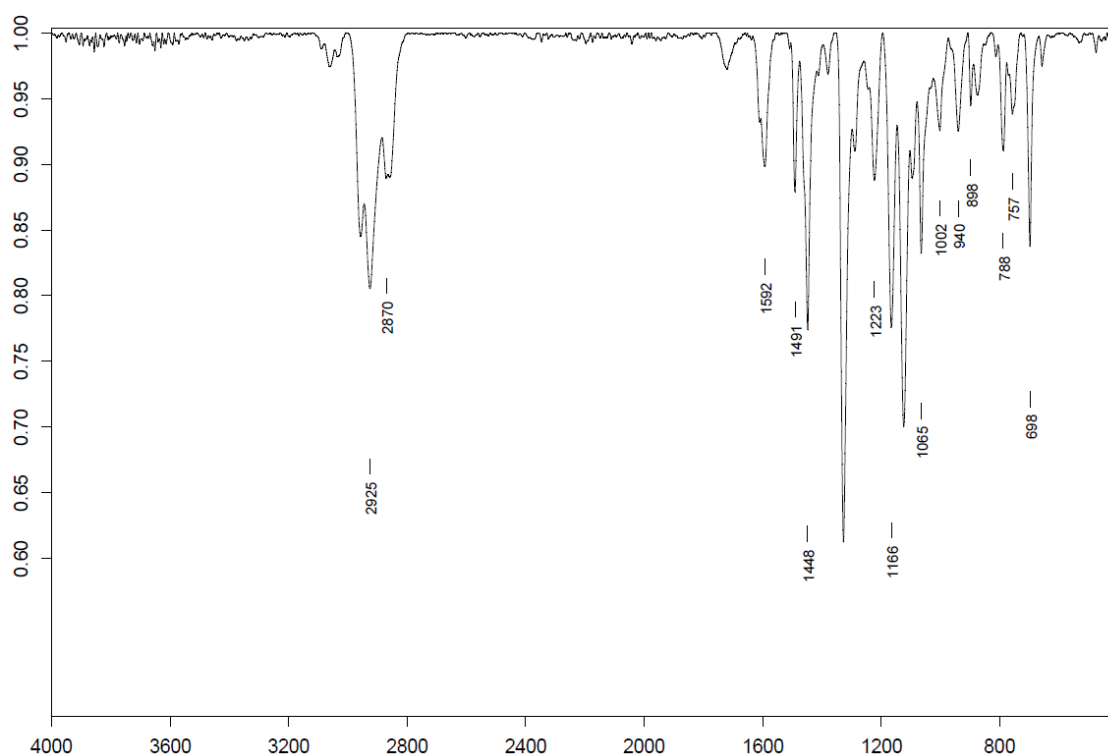
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  155.41, 138.90, 134.74, 131.40 (q,  $J = 32.32$  Hz), 129.18, 128.89, 128.30, 126.79, 122.72, 120.24, 117.94 (q,  $J = 4.04$  Hz), 116.63 (q,  $J = 4.04$  Hz), 85.57, 70.69.

$^{19}\text{F}$  NMR spectrum ( $\text{CDCl}_3$ )



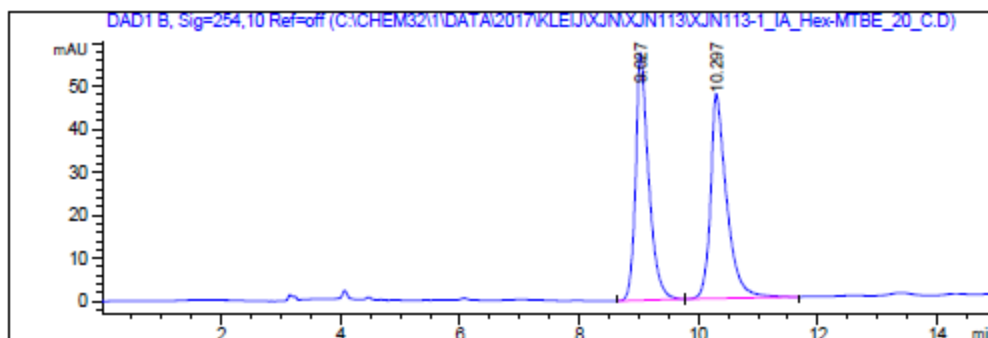
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.92.

IR spectrum (neat)



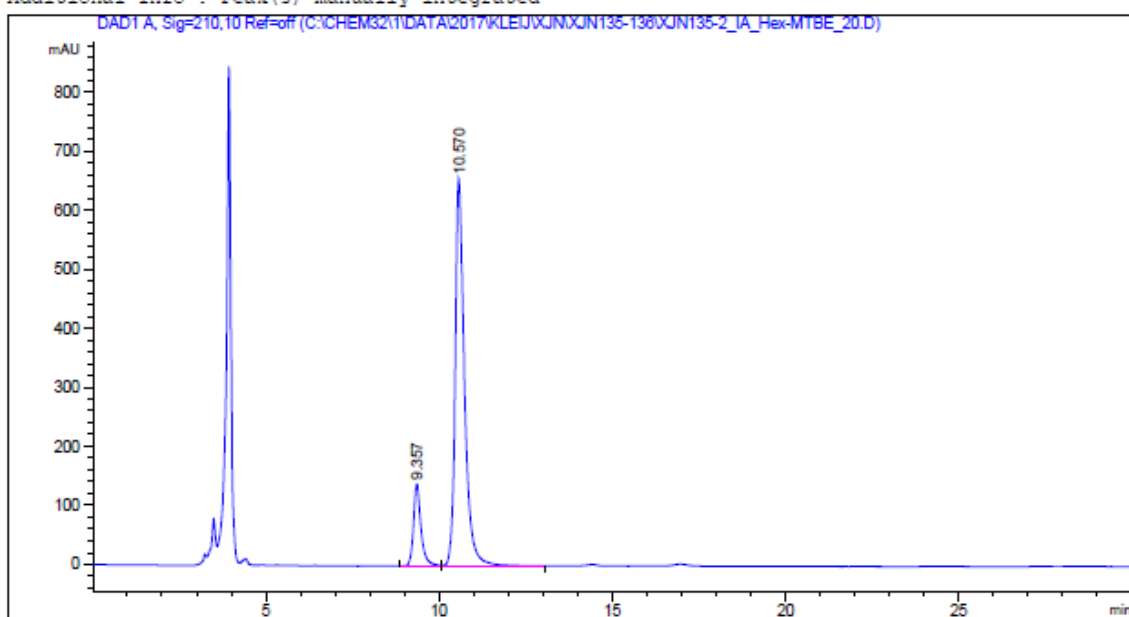
**HRMS** (ESI<sup>+</sup>, MeOH):  $m/z$  calcd. 331.0916 ( $M + Na$ )<sup>+</sup>, found: 331.0922.

**HPLC conditions:** Chiralpak IA 250 × 4.6 mm, 5 μm, Hex/MTBE = 80 : 20, 1 mL/min;  
85 : 15 *er*;  $[\alpha]_D^{25} = -43.10$  ( $c = 0.11$ , CHCl<sub>3</sub>).

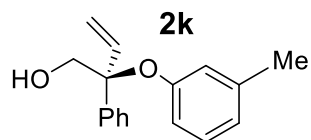


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 9.027         | BB   | 0.2214      | 872.97479    | 57.40595     | 49.3845 |
| 2      | 10.297        | BB   | 0.2695      | 894.73419    | 47.56058     | 50.6155 |

Additional Info : Peak(s) manually integrated

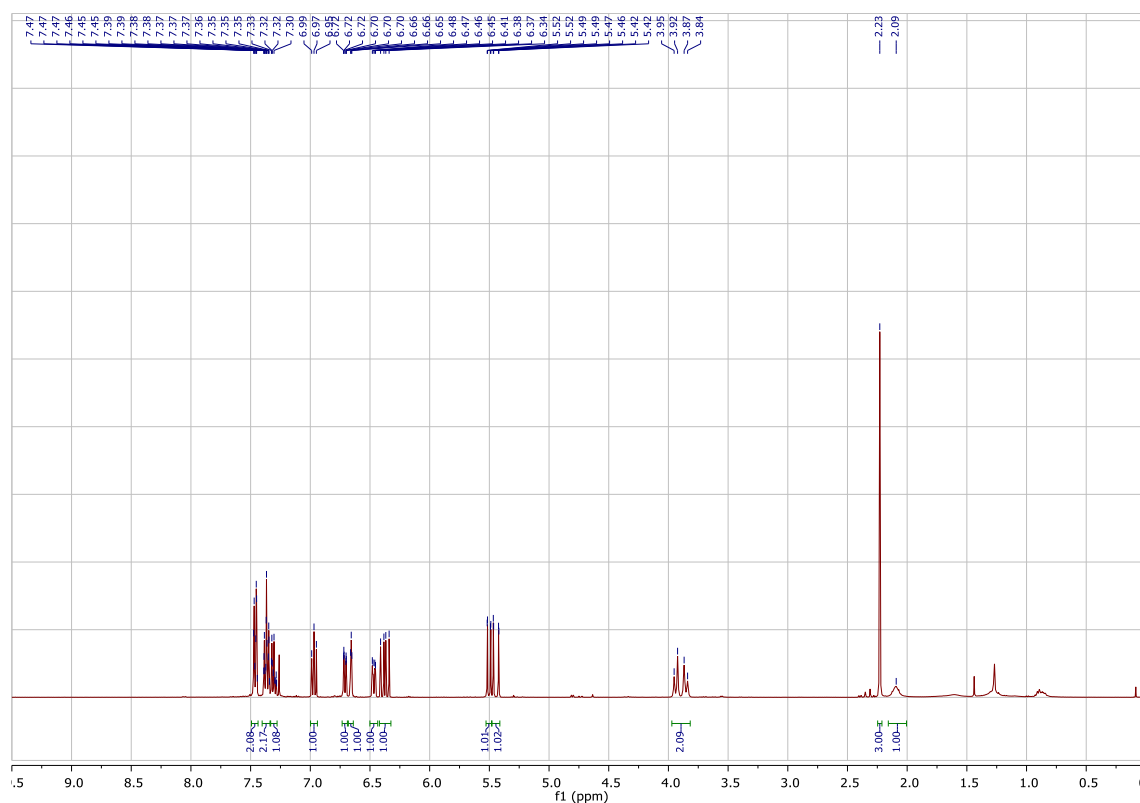


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 9.357         | BV   | 0.2197      | 2099.95581   | 139.46379    | 14.6686 |
| 2      | 10.570        | VB   | 0.2691      | 1.22160e4    | 656.40436    | 85.3314 |



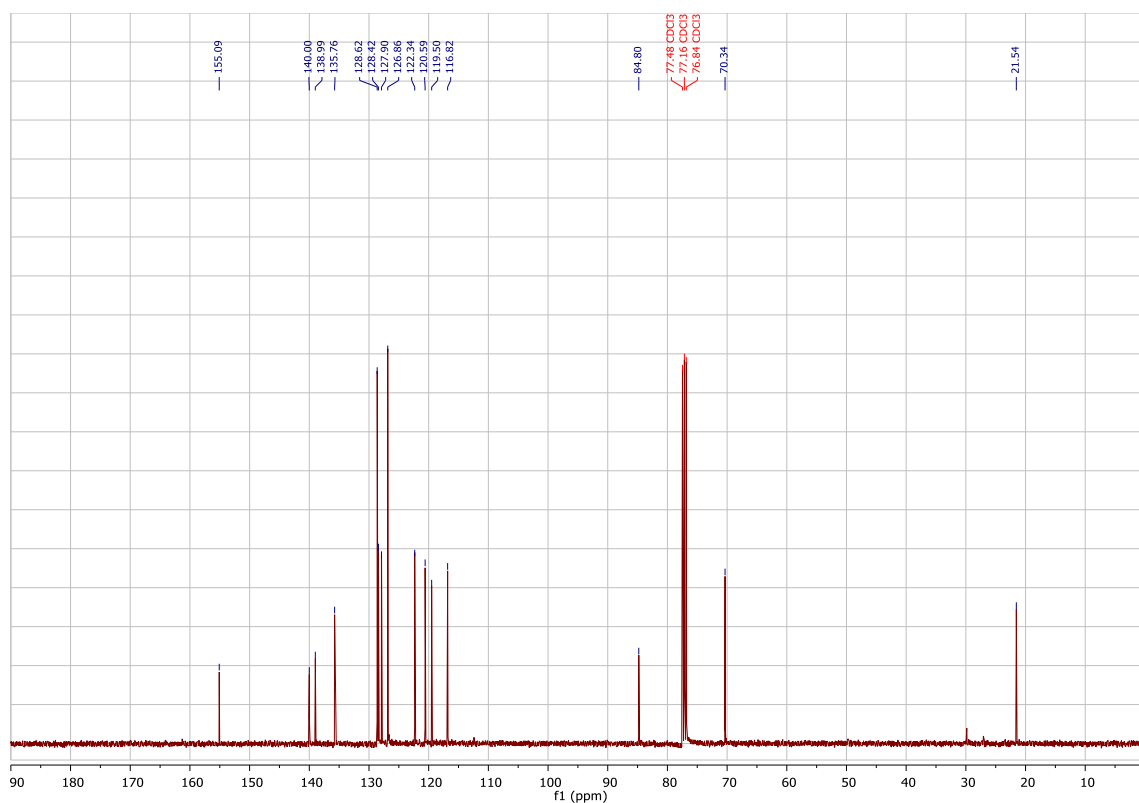
Scale: 0.2 mmol; isolated 42.6 mg (84% yield), light yellow oil, Hexane : EA = 50 : 1,  $R_f$  = 0.15

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ )



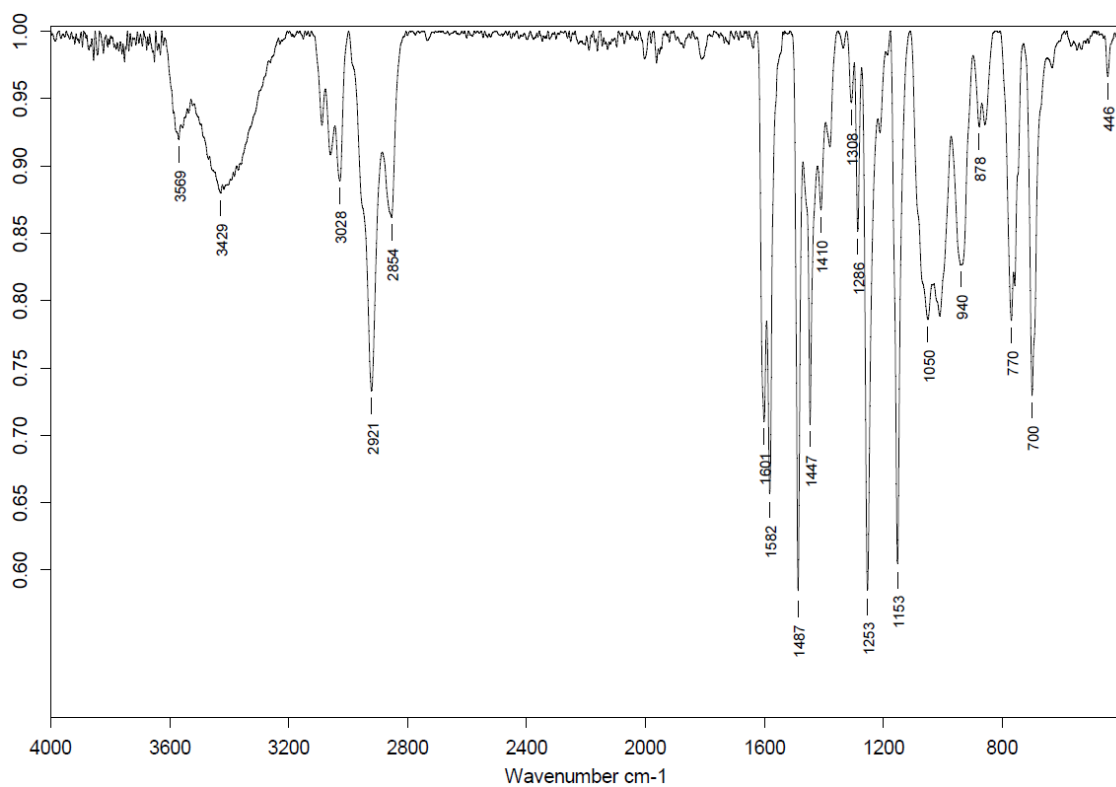
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 – 7.44 (m, 2H), 7.40 – 7.34 (m, 2H), 7.33 – 7.28 (m, 1H), 6.97 (t,  $J$  = 7.9 Hz, 1H), 6.71 (m, 1H), 6.66 (t,  $J$  = 2.0 Hz, 1H), 6.47 (dd,  $J$  = 8.2, 2.4 Hz, 1H), 6.38 (dd,  $J$  = 17.5, 11.1 Hz, 1H), 5.50 (dd,  $J$  = 11.1, 1.0 Hz, 1H), 5.44 (dd,  $J$  = 17.5, 1.0 Hz, 1H), 3.97 – 3.82 (m, 2H), 2.23 (s, 3H), 2.09 (s, 1H).

$^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ )



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  155.09, 140.00, 138.99, 135.76, 128.62, 128.42, 127.90, 126.86, 122.34, 120.59, 119.50, 116.82, 84.80, 70.34, 21.54.

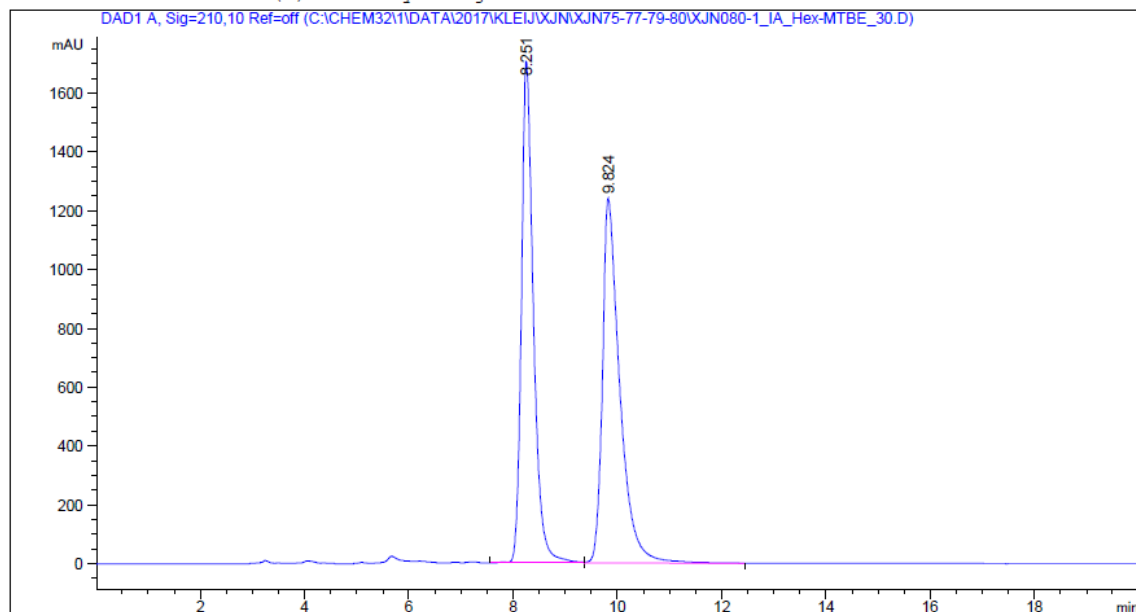
IR spectrum (neat)



HRMS (ESI+, MeOH):  $m/z$  calcd. 277.1199 ( $\text{M} + \text{Na}$ ) $^+$ , found: 277.1186.

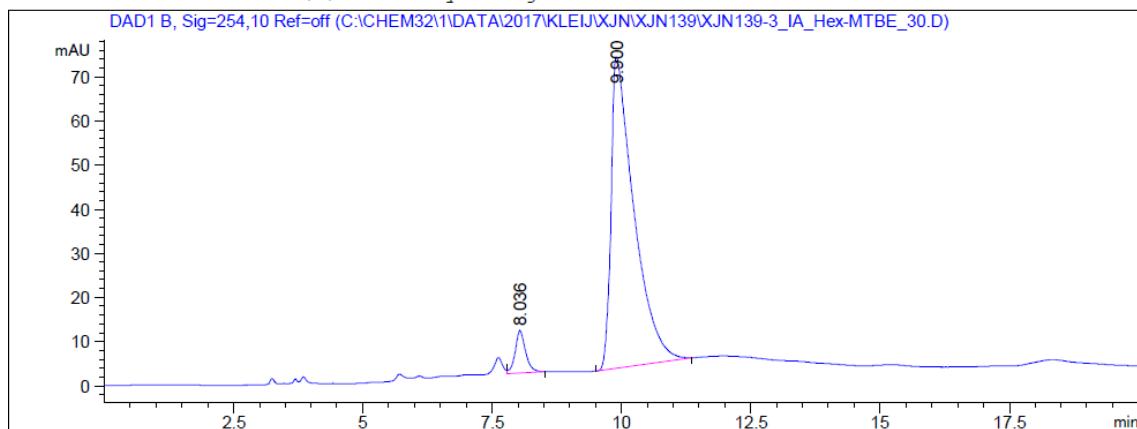
**HPLC conditions:** Chiralpak IA 250 × 4.6 mm, 5 μm, Hex/MTBE = 70 : 30, 1 mL/min;  
94 : 6 *er*;  $[\alpha]_D^{25} = -40.14$  ( $c = 0.11$ , CHCl<sub>3</sub>).

Additional Info : Peak(s) manually integrated

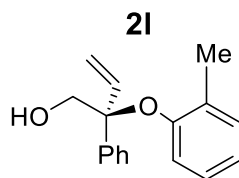


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 8.251         | VV R | 0.2370      | 2.73893e4    | 1705.96655   | 48.8045 |
| 2      | 9.824         | VB   | 0.3343      | 2.87311e4    | 1240.05713   | 51.1955 |

Additional Info : Peak(s) manually integrated

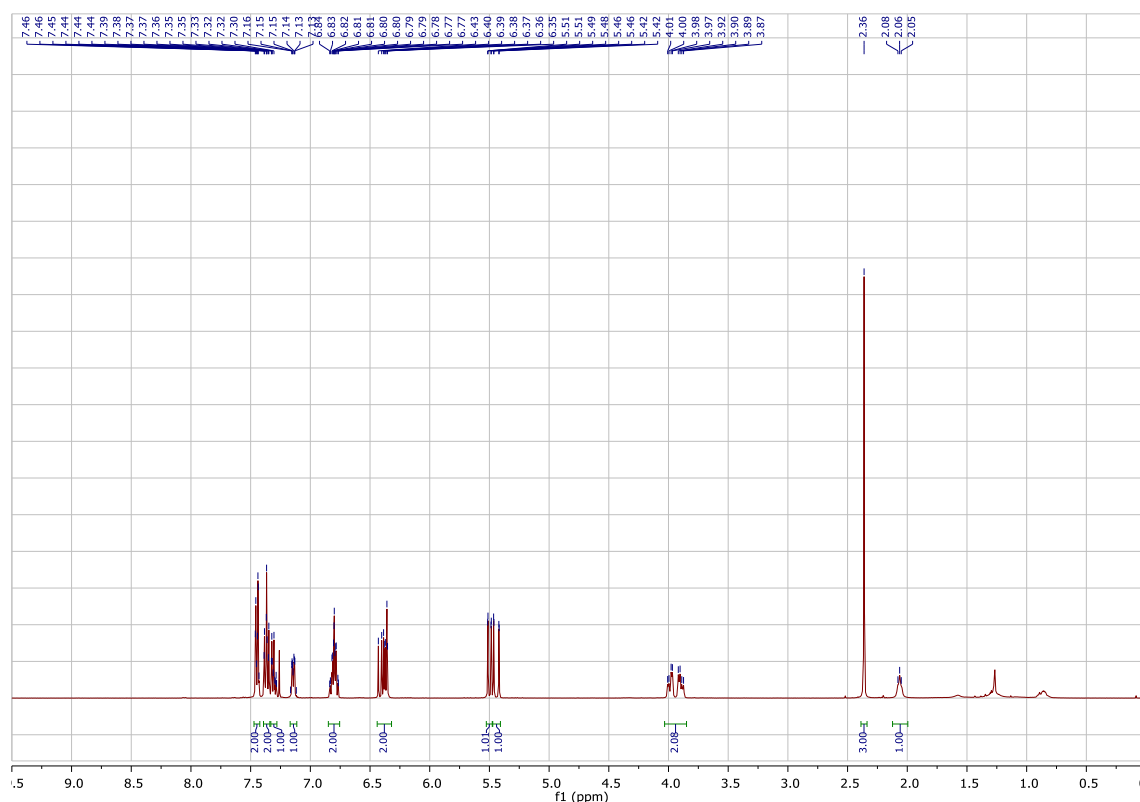


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 8.036         | VB   | 0.2069      | 134.32574    | 9.61825      | 5.8234  |
| 2      | 9.900         | BB   | 0.4288      | 2172.34546   | 70.63331     | 94.1766 |



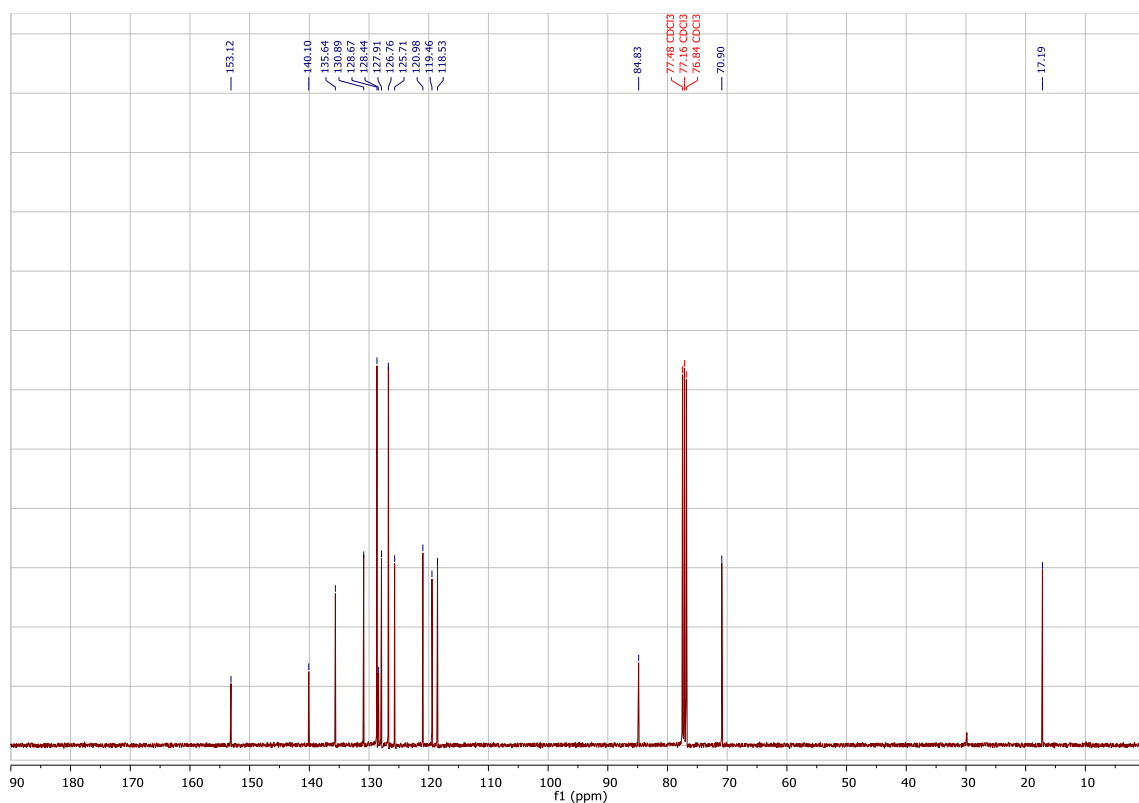
Scale: 0.2 mmol; isolated 44.2 mg (87% yield), light yellow oil, Hexane : EA = 50 : 1,  $R_f$  = 0.15

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ )



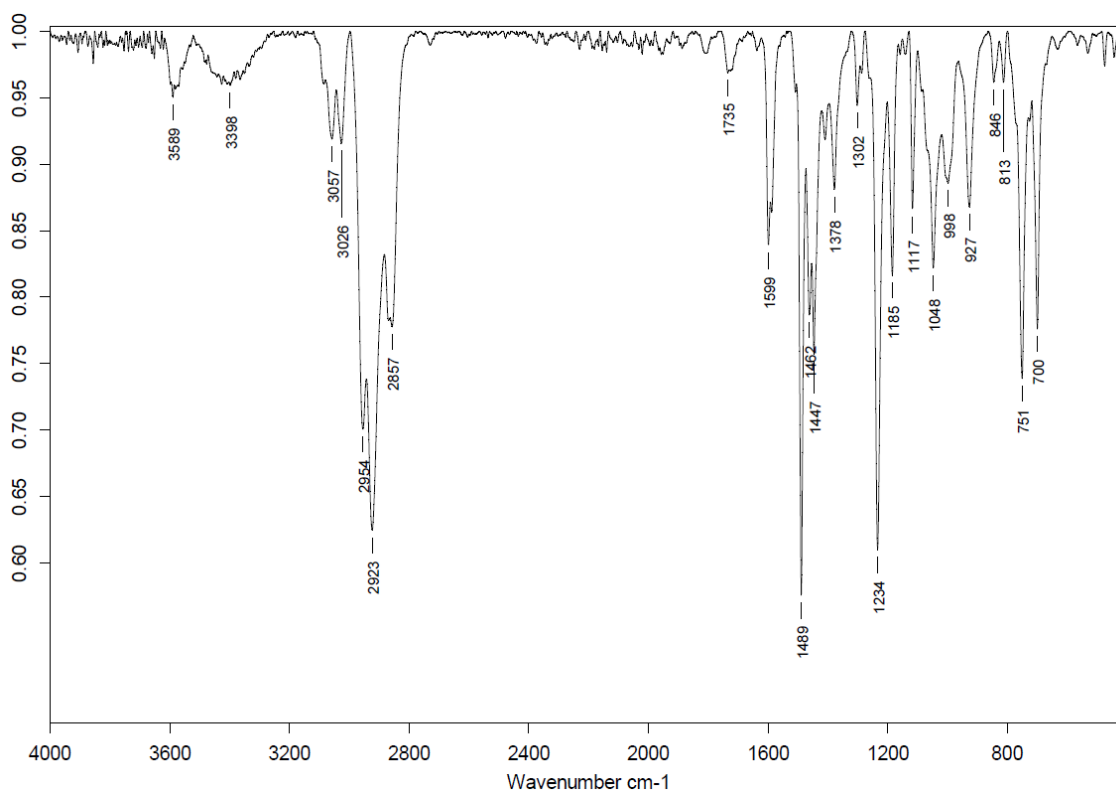
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 – 7.42 (m, 2H), 7.37 (m, 2H), 7.33 – 7.28 (m, 1H), 7.17 – 7.11 (m, 1H), 6.85 – 6.75 (m, 2H), 6.44 – 6.32 (m, 2H), 5.50 (dd,  $J$  = 11.1, 1.0 Hz, 1H), 5.44 (dd,  $J$  = 17.5, 1.0 Hz, 1H), 4.03 – 3.85 (m, 2H), 2.36 (s, 3H), 2.06 (t,  $J$  = 5.6 Hz, 1H).

$^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ )



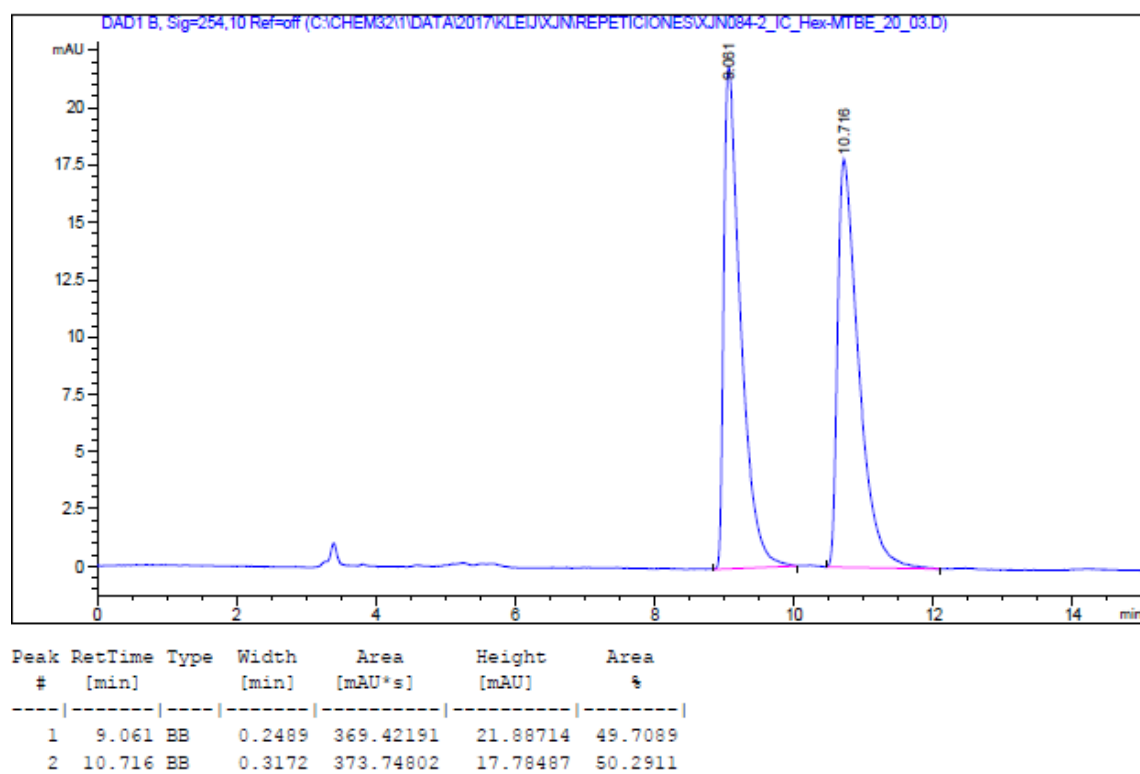
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  153.12, 140.10, 135.64, 130.89, 128.67, 128.44, 127.91, 126.76, 125.71, 120.98, 119.46, 118.53, 84.83, 70.90, 17.19.

IR spectrum (neat)

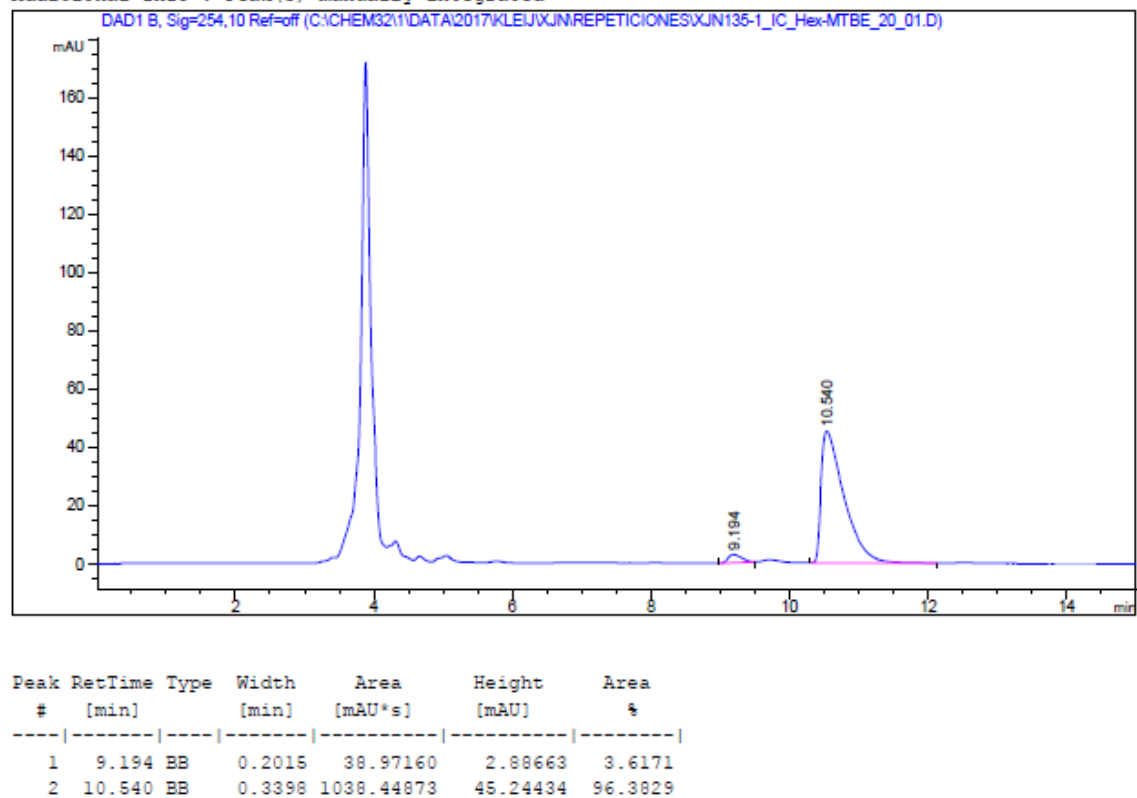


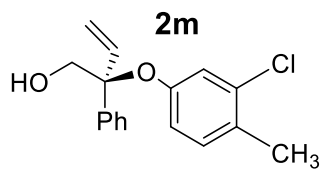
HRMS (ESI $^{+}$ , MeOH):  $m/z$  calcd. 277.1199 ( $\text{M} + \text{Na}$ ) $^{+}$ , found: 277.1199.

**HPLC conditions:** Chiralpak IC 250 × 4.6 mm, 5 μm, Hex/MTBE = 80 : 20, 1 mL/min;  
96 : 4 *er*;  $[\alpha]_D^{25} = -41.26$  ( $c = 0.10$ , CHCl<sub>3</sub>).



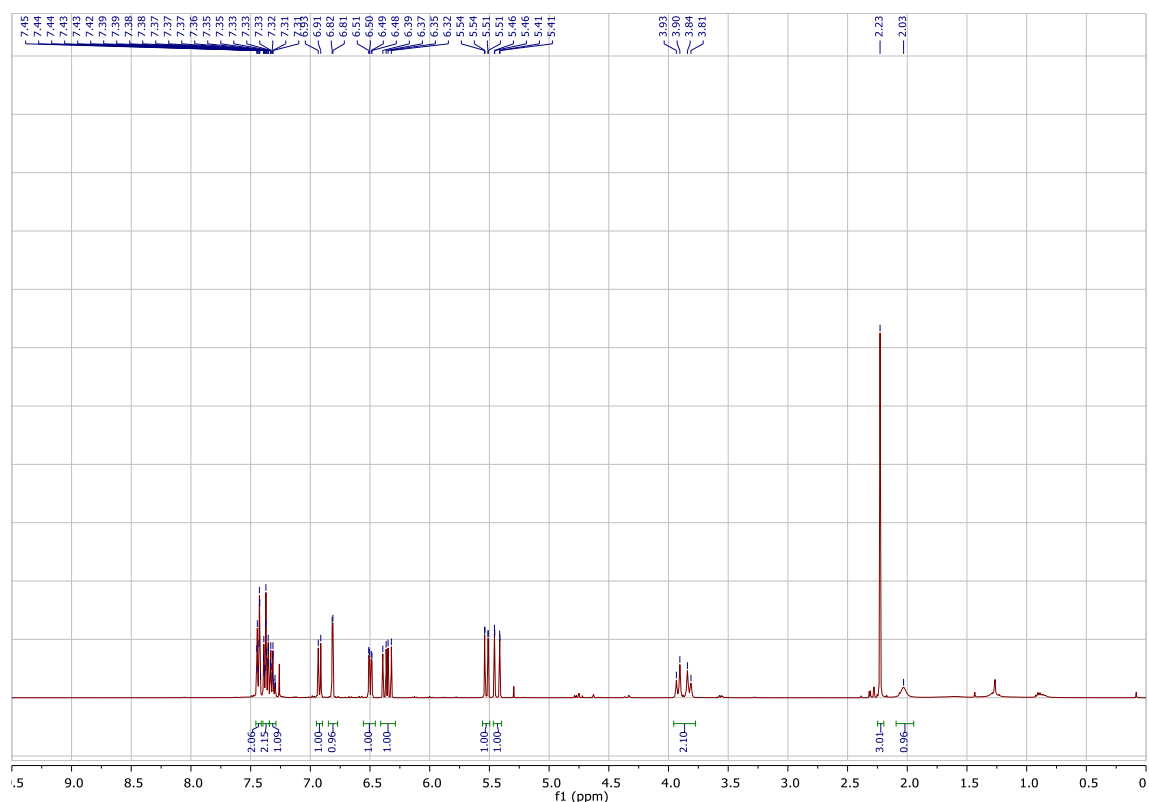
Additional Info : Peak(s) manually integrated





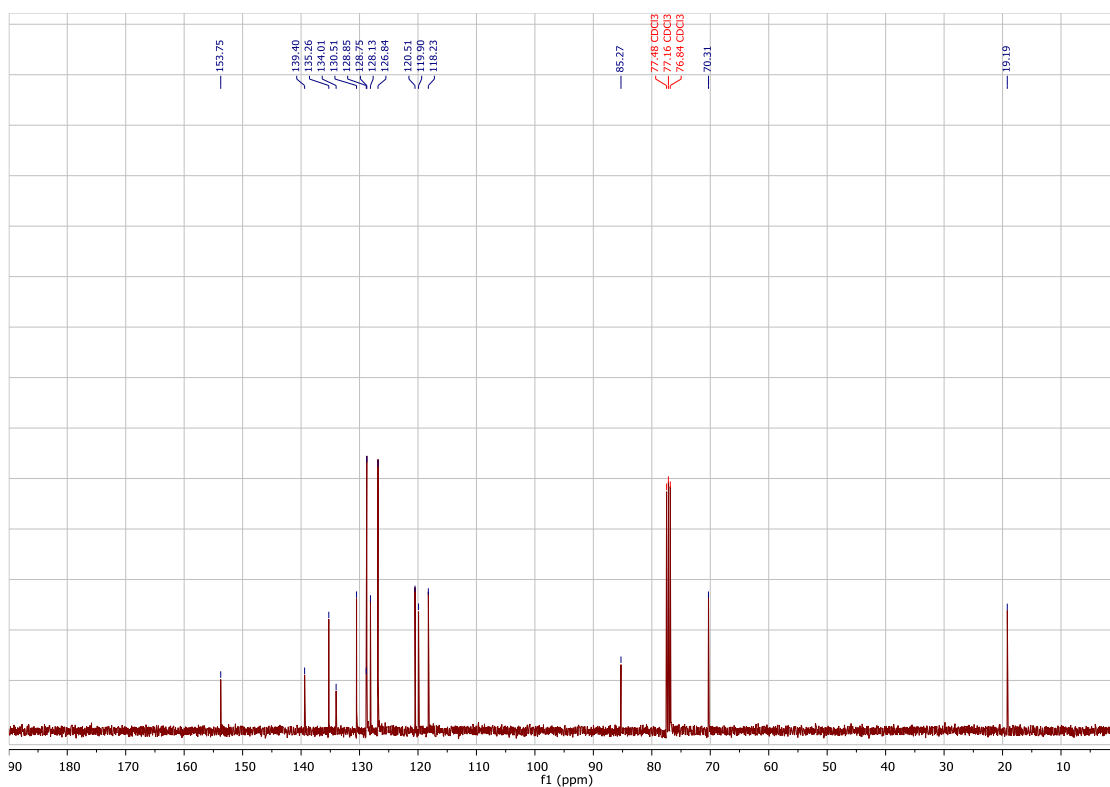
Scale: 0.2 mmol; isolated 41.0 mg (72% yield), light yellow solid, Hexane : EA = 50 : 1,  $R_f = 0.15$

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ )



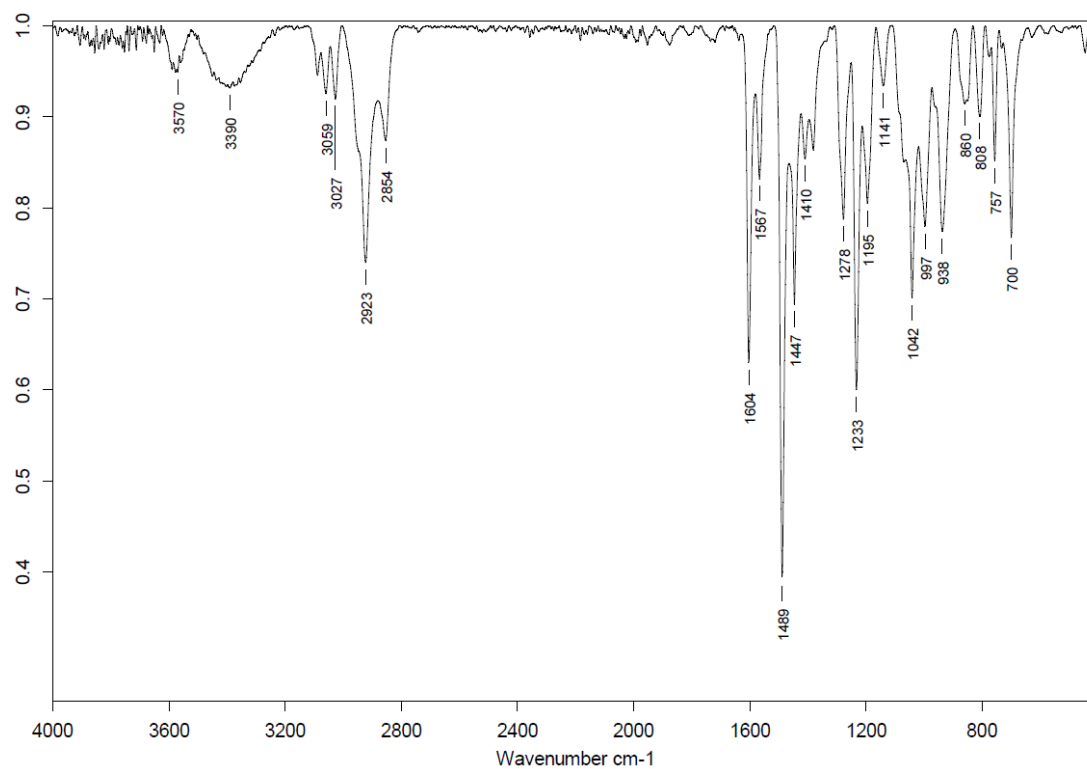
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 – 7.41 (m, 2H), 7.37 (m, 2H), 7.34 – 7.29 (m, 1H), 6.92 (d,  $J = 8.4$  Hz, 1H), 6.81 (d,  $J = 2.5$  Hz, 1H), 6.50 (dd,  $J = 8.4, 2.5$  Hz, 1H), 6.36 (dd,  $J = 17.5, 11.1$  Hz, 1H), 5.52 (dd,  $J = 11.1, 1.0$  Hz, 1H), 5.43 (dd,  $J = 17.5, 1.0$  Hz, 1H), 3.96 – 3.77 (m, 2H), 2.23 (s, 3H), 2.03 (s, 1H).

<sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>)



<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  153.75, 139.40, 135.26, 134.01, 130.51, 128.85, 128.75, 128.13, 126.84, 120.51, 119.90, 118.23, 85.27, 70.31, 19.19.

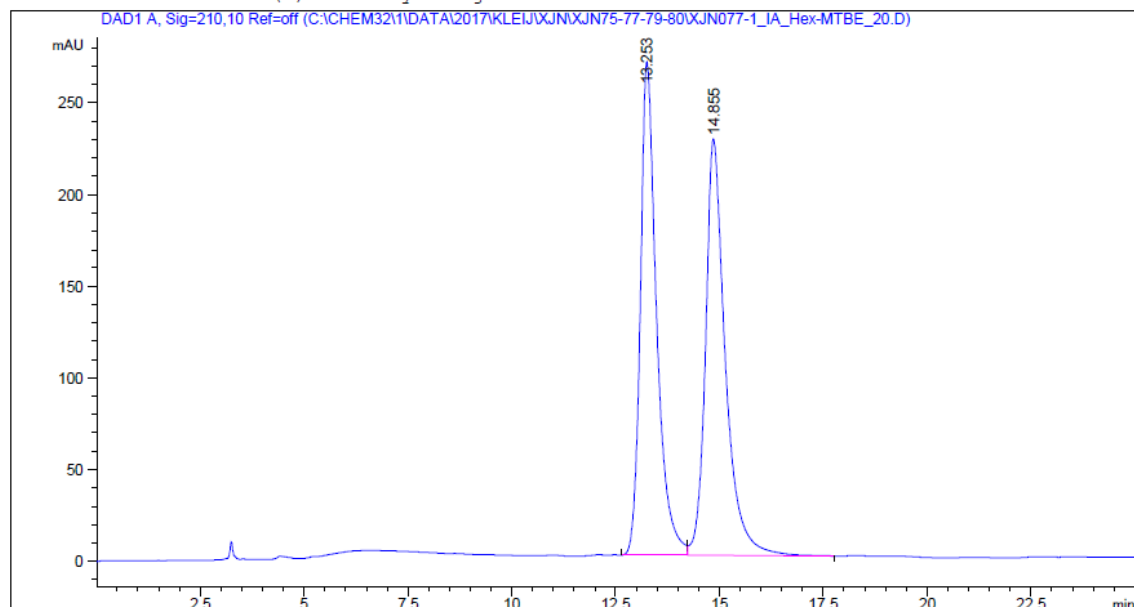
IR spectrum (neat)



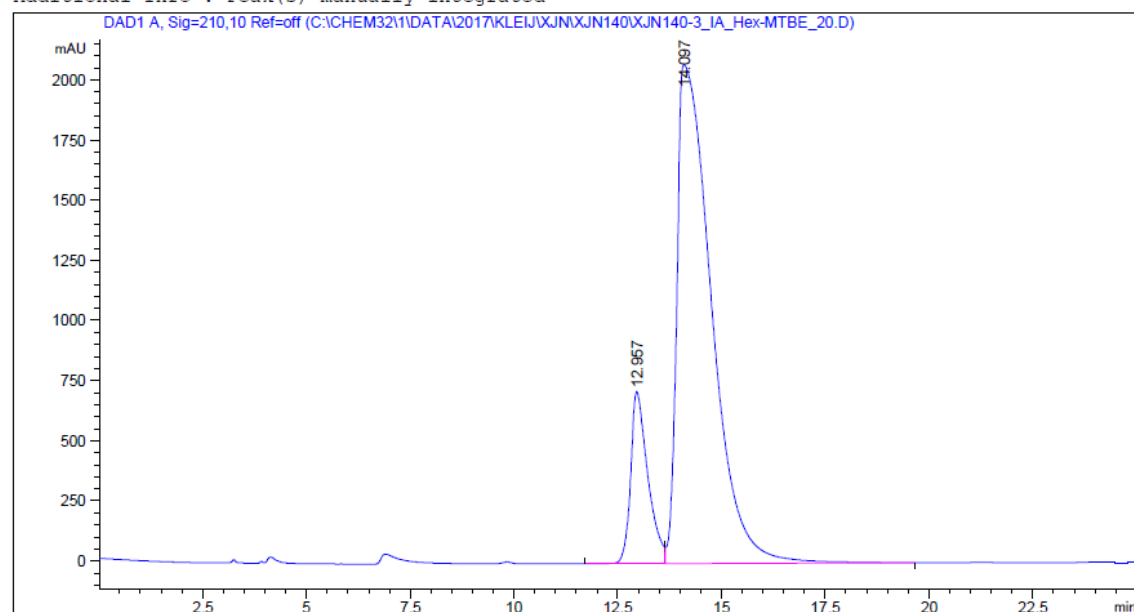
HRMS (ESI<sup>+</sup>, MeOH):  $m/z$  calcd. 311.0809 (M + Na)<sup>+</sup>, found: 311.0801.

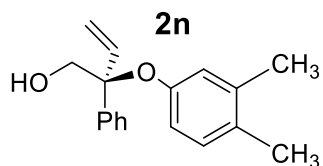
**HPLC conditions:** Chiralpak IA 250 × 4.6 mm, 5 μm, Hex/MTBE = 80 : 20, 1 mL/min;  
85 : 15 *er*;  $[\alpha]_D^{25} = -43.90$  ( $c = 0.13$ , CHCl<sub>3</sub>).

Additional Info : Peak(s) manually integrated



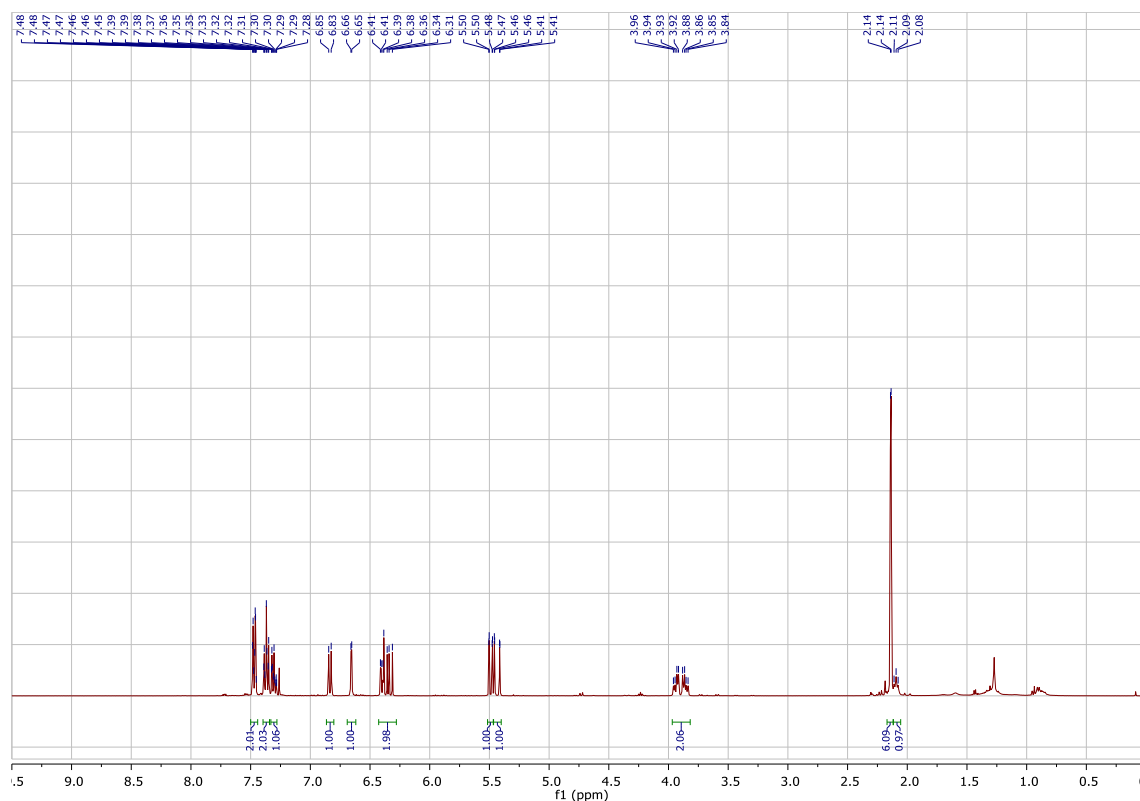
Additional Info : Peak(s) manually integrated





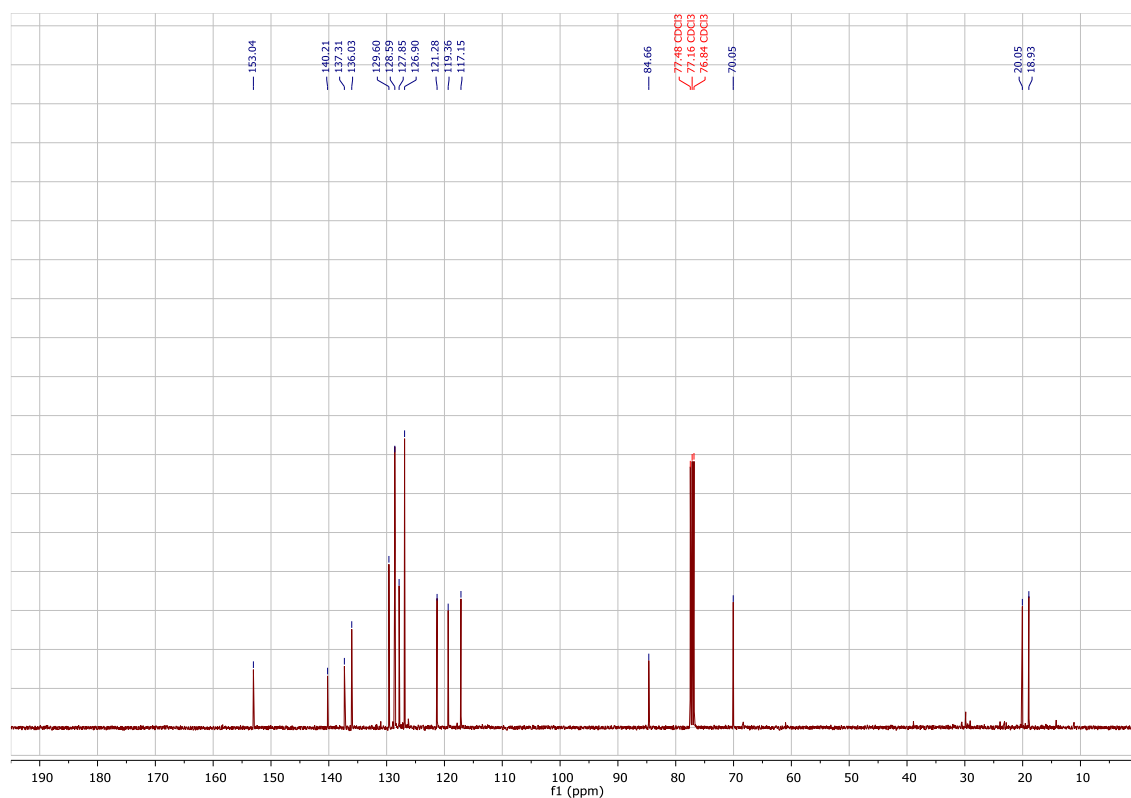
Scale: 0.2 mmol; isolated 42.8 mg (80% yield), light yellow oil, Hexane : EA = 50 : 1,  $R_f$  = 0.15

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ )

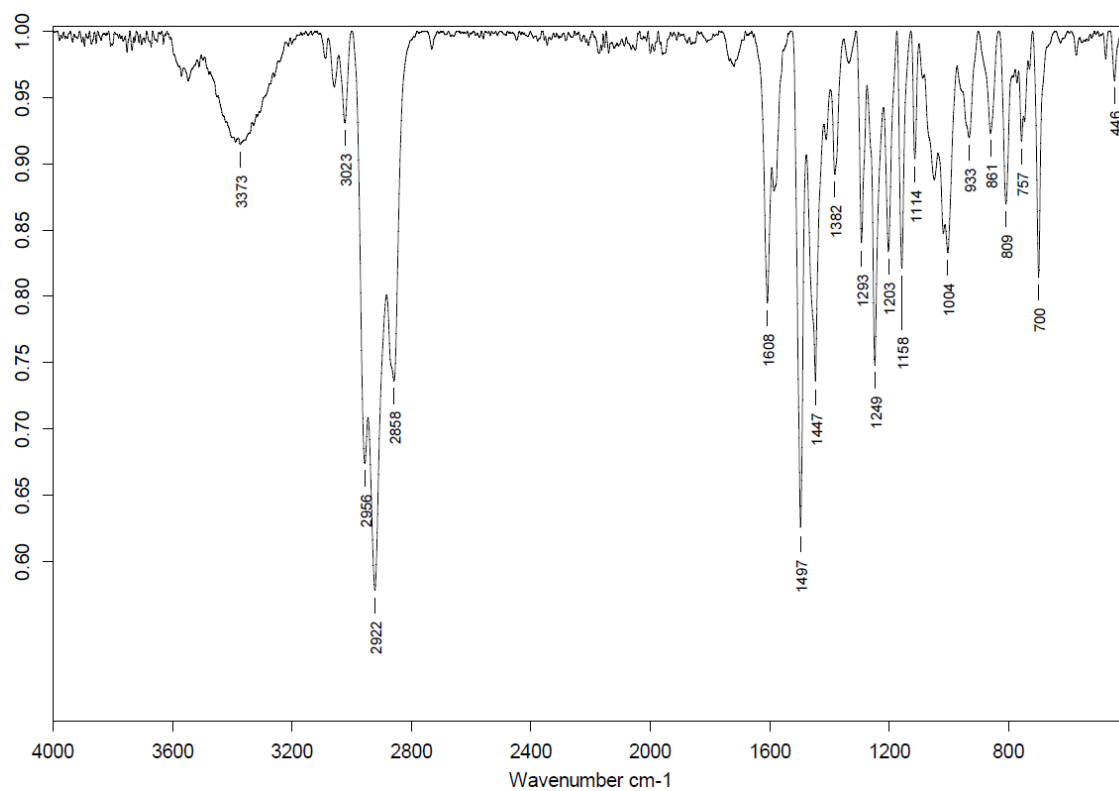


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50 – 7.44 (m, 2H), 7.40 – 7.34 (m, 2H), 7.33 – 7.28 (m, 1H), 6.84 (d,  $J$  = 8.3 Hz, 1H), 6.66 (d,  $J$  = 2.7 Hz, 1H), 6.43 – 6.28 (m, 2H), 5.49 (dd,  $J$  = 11.1, 1.1 Hz, 1H), 5.44 (dd,  $J$  = 17.5, 1.1 Hz, 1H), 3.97 – 3.82 (m, 2H), 2.14 (d,  $J$  = 2.1 Hz, 6H), 2.09 (t,  $J$  = 6.8 Hz, 1H).

$^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ )



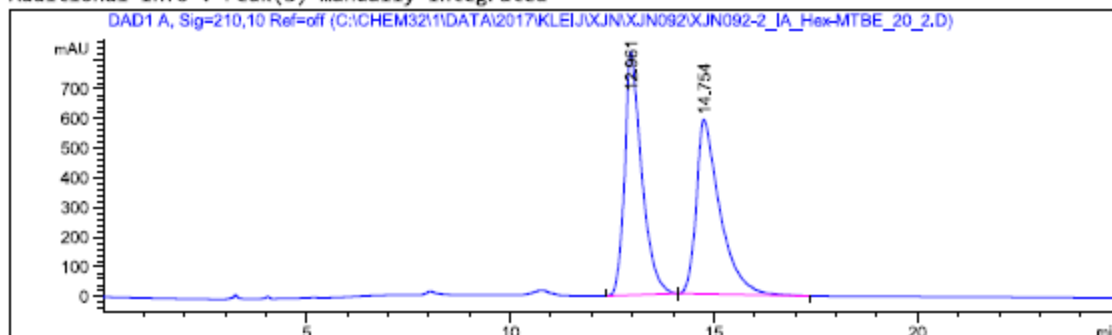
IR spectrum (neat)



**HRMS** (ESI<sup>+</sup>, MeOH):  $m/z$  calcd. 291.1356 ( $\text{M} + \text{Na}$ )<sup>+</sup>, found: 291.1355.

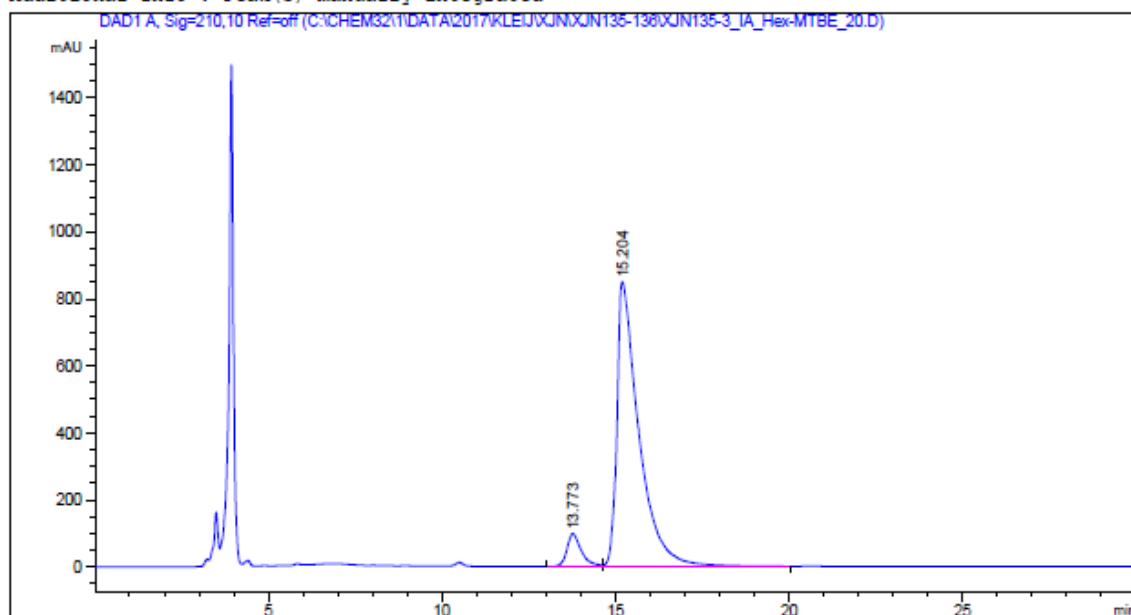
**HPLC conditions:** Chiralpak IA 250 × 4.6 mm, 5 μm, Hex/MTBE = 80 : 20, 1 mL/min; 93 : 7 *er*;  $[\alpha]_D^{25} = -39.95$  ( $c = 0.12$ , CHCl<sub>3</sub>).

Additional Info : Peak(s) manually integrated

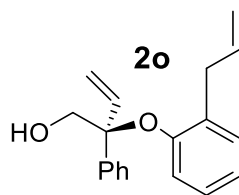


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 12.961        | BB   | 0.4224      | 2.40954e4    | 821.00067    | 50.2627 |
| 2      | 14.754        | BB   | 0.5762      | 2.38435e4    | 589.14026    | 49.7373 |

Additional Info : Peak(s) manually integrated

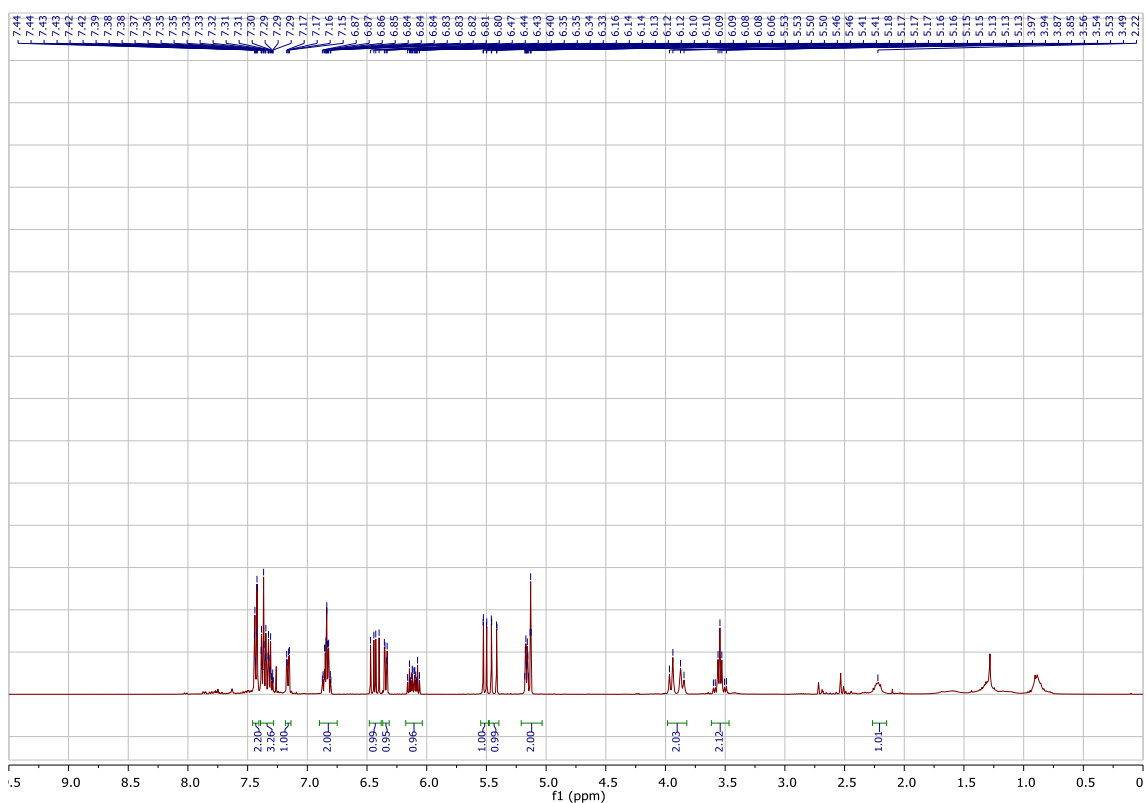


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 13.773        | BV   | 0.4232      | 2840.13110   | 98.26805     | 7.0650  |
| 2      | 15.204        | VB   | 0.6227      | 3.73600e4    | 850.18097    | 92.9350 |



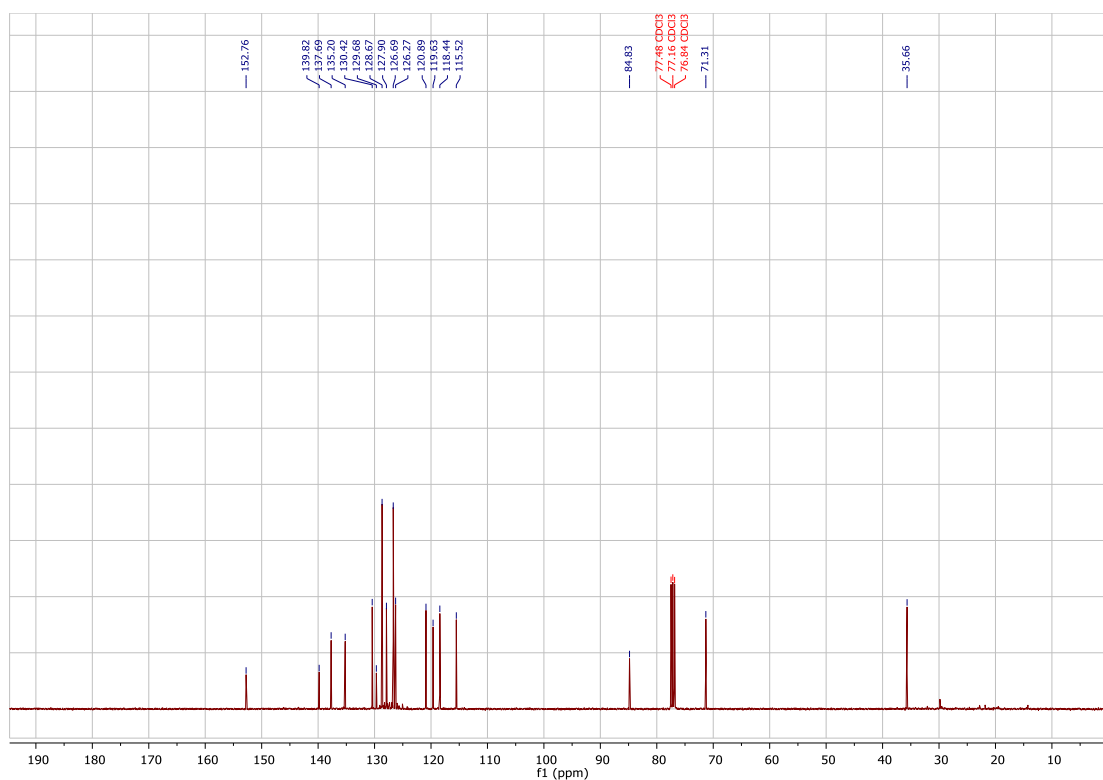
Scale: 0.2 mmol; isolated 43.7 mg (78% yield), light yellow oil, Hexane : EA = 50 : 1,  $R_f$  = 0.15

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ )



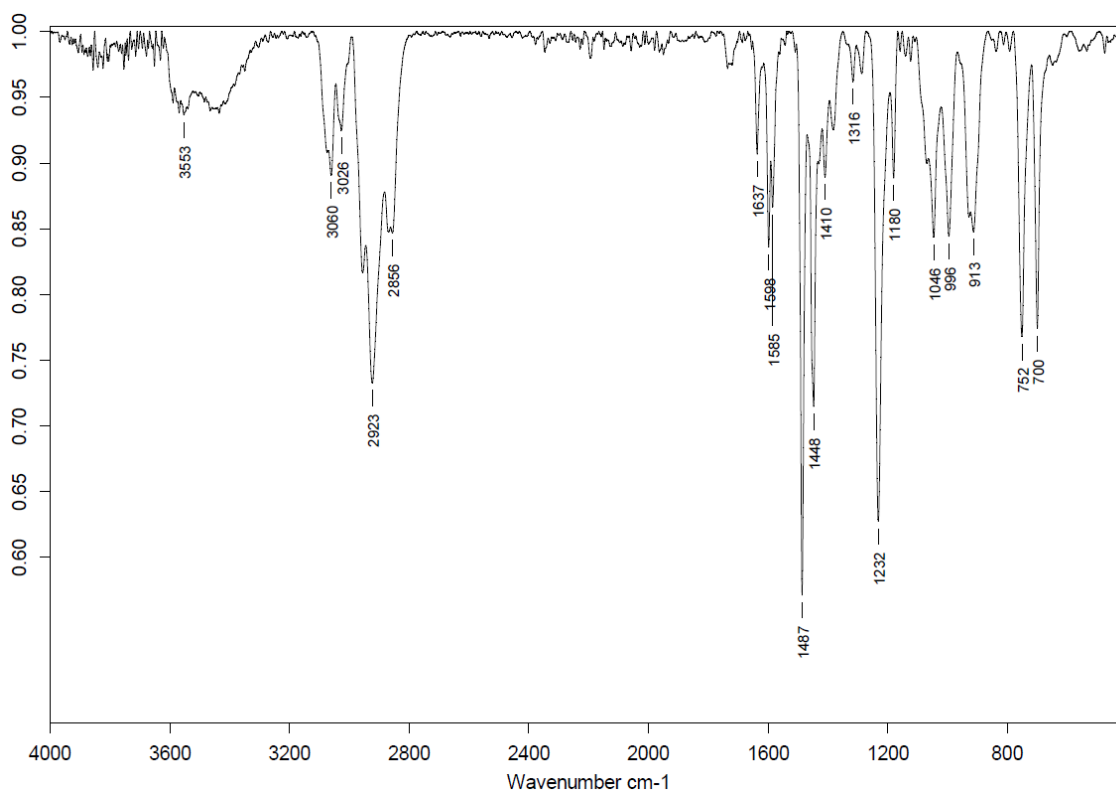
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 – 7.41 (m, 2H), 7.39 – 7.28 (m, 3H), 7.16 (dd,  $J$  = 6.8, 2.4 Hz, 1H), 6.90 – 6.75 (m, 2H), 6.43 (dd,  $J$  = 17.5, 11.2 Hz, 1H), 6.34 (dd,  $J$  = 7.6, 1.8 Hz, 1H), 6.11 (ddt,  $J$  = 15.7, 11.0, 6.3 Hz, 1H), 5.51 (dd,  $J$  = 11.2, 1.0 Hz, 1H), 5.44 (dd,  $J$  = 17.5, 1.0 Hz, 1H), 5.21 – 5.03 (m, 2H), 3.98 – 3.82 (m, 2H), 3.62 – 3.47 (m, 2H), 2.22 (s, 1H).

<sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>)



<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  152.76, 139.82, 137.69, 135.20, 130.42, 129.68, 128.67, 127.90, 126.69, 126.27, 120.89, 119.63, 118.44, 115.52, 84.83, 71.31, 35.66.

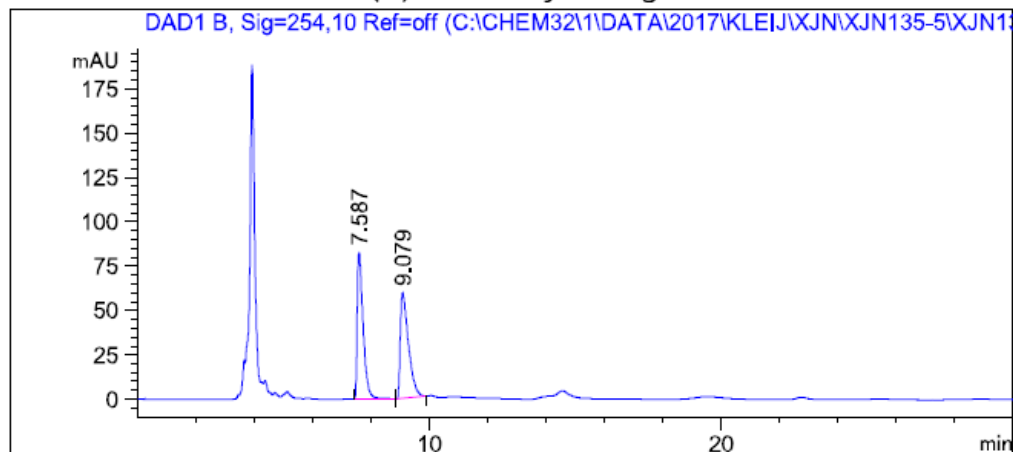
IR spectrum (neat)



HRMS (ESI<sup>+</sup>, MeOH):  $m/z$  calcd. 303.1356 (M + Na)<sup>+</sup>, found: 303.1352.

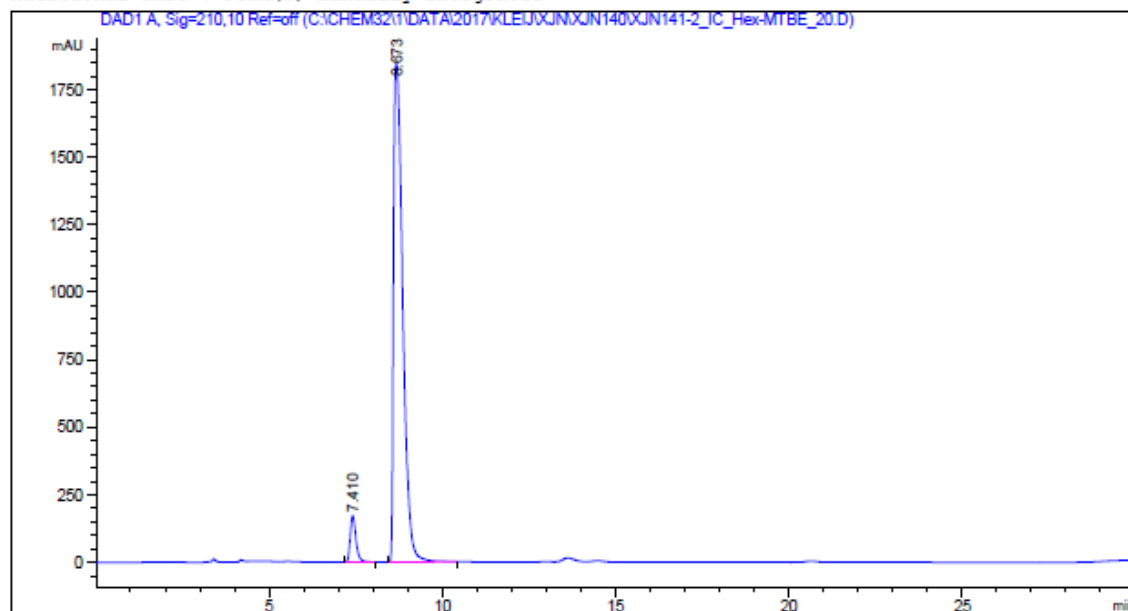
**HPLC conditions:** Chiralpak IC 250 × 4.6 mm, 5 μm, Hex/MTBE = 80 : 20, 1 mL/min;  
94.5 : 5.5 *er*;  $[\alpha]_D^{25} = -70.28$  (*c* = 0.12, CHCl<sub>3</sub>).

Additional Info : Peak(s) manually integrated

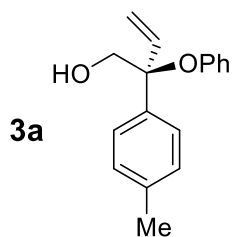


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 7.587         | BB   | 0.2099      | 1164.79968   | 82.91244     | 50.4167 |
| 2      | 9.079         | BB   | 0.2905      | 1145.54321   | 59.53025     | 49.5833 |

Additional Info : Peak(s) manually integrated

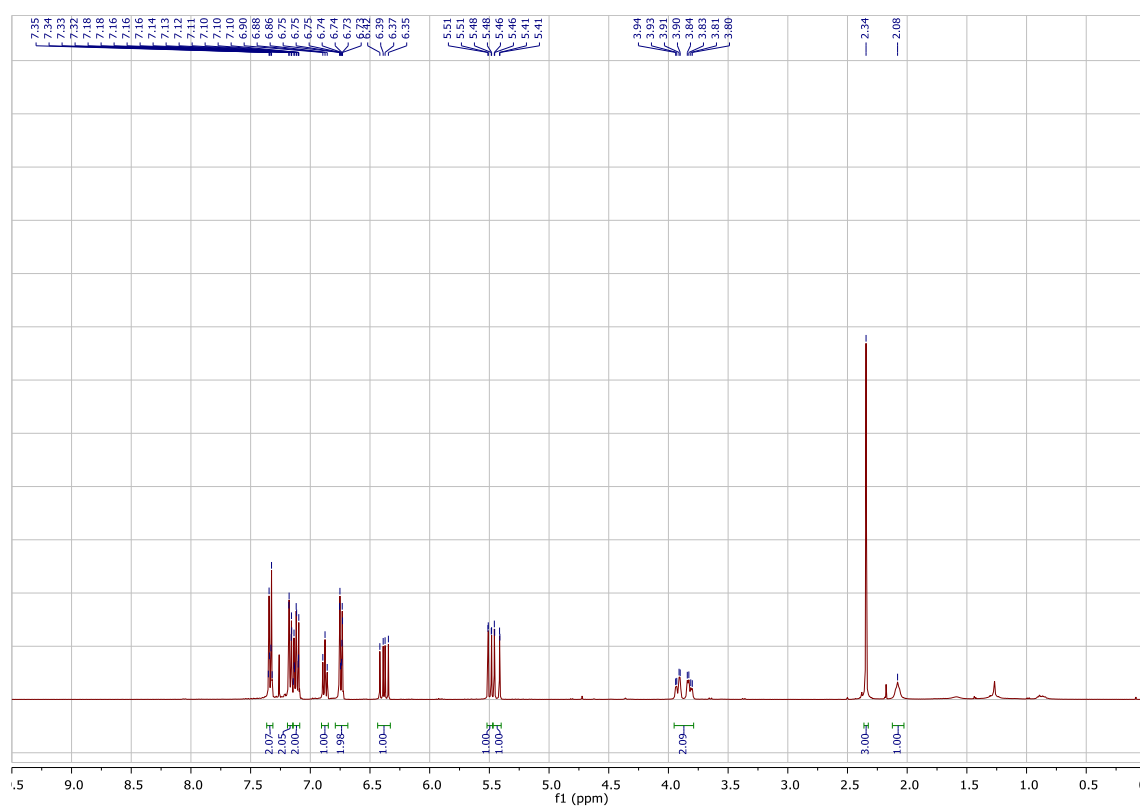


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 7.410         | BB   | 0.1729      | 1948.24023   | 171.06516    | 5.4703  |
| 2      | 8.673         | BB   | 0.2846      | 3.36668e4    | 1847.68799   | 94.5297 |



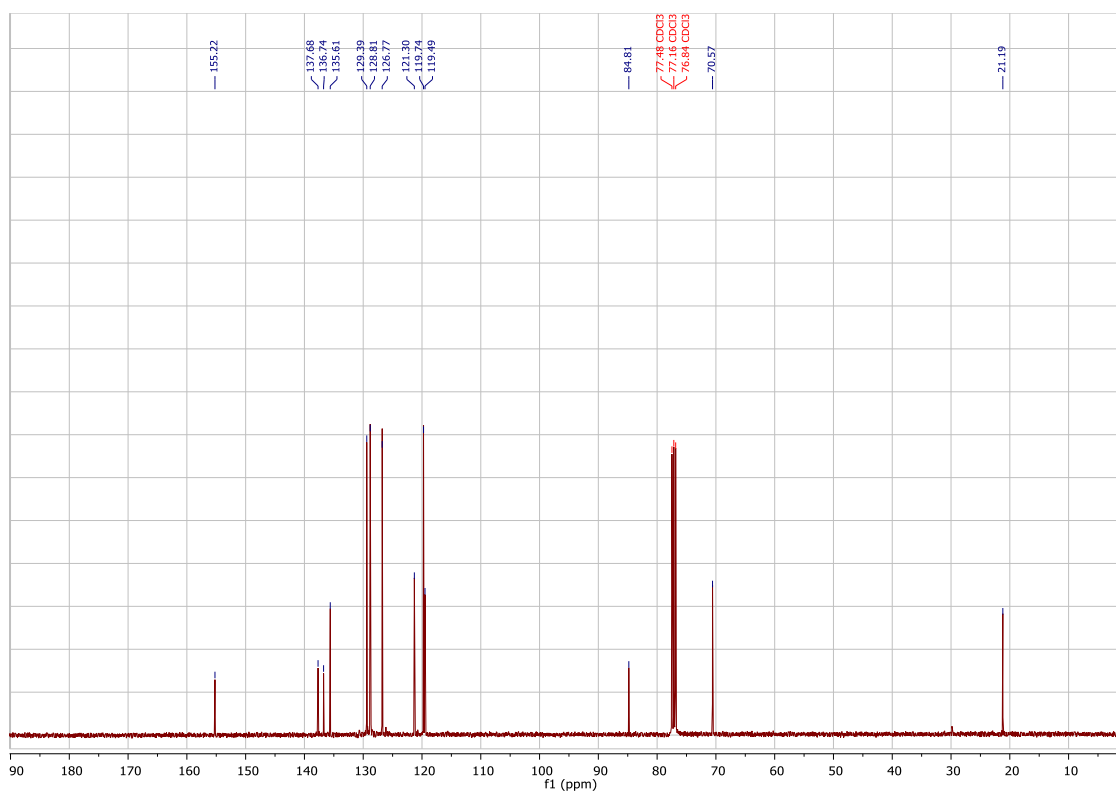
Scale: 0.2 mmol; isolated 43.2 mg (85% yield), light yellow solid, Hexane : EA = 50 : 1,  $R_f = 0.15$

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ )



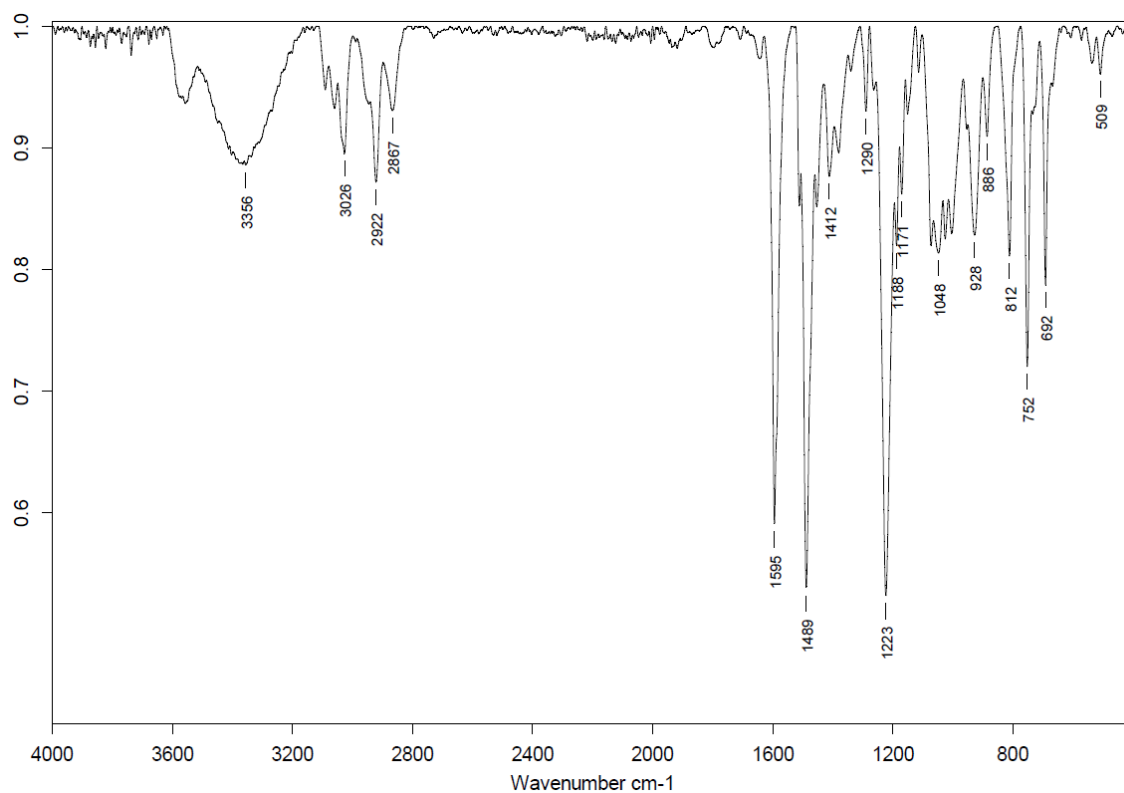
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 – 7.31 (m, 2H), 7.19 – 7.15 (m, 2H), 7.14 – 7.09 (m, 2H), 6.88 (t,  $J = 7.3$  Hz, 1H), 6.79 – 6.69 (m, 2H), 6.38 (dd,  $J = 17.5, 11.1$  Hz, 1H), 5.50 (dd,  $J = 11.1, 1.0$  Hz, 1H), 5.44 (dd,  $J = 17.5, 1.1$  Hz, 1H), 3.87 (m, 2H), 2.34 (s, 3H), 2.08 (s, 1H).

<sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>)



<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  155.22, 137.68, 136.74, 135.61, 129.39, 128.81, 126.77, 121.30, 119.74, 119.49, 84.81, 70.57, 21.19.

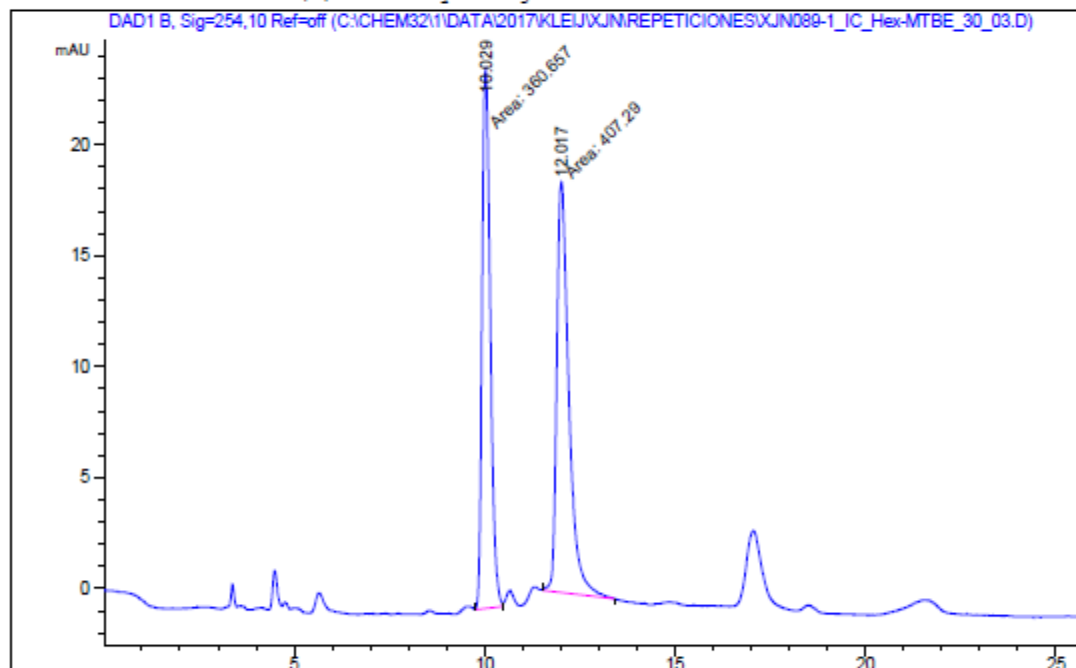
IR spectrum (neat)



HRMS (ESI<sup>+</sup>, MeOH):  $m/z$  calcd. 277.1199 (M + Na)<sup>+</sup>, found: 277.1193.

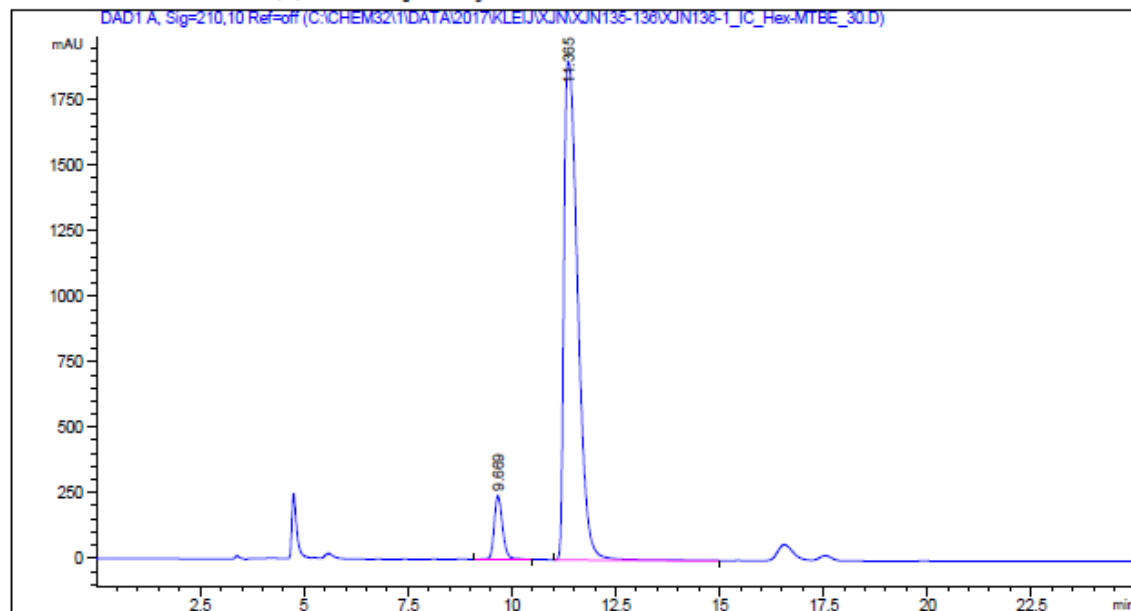
**HPLC conditions:** Chiralpak IC 250 × 4.6 mm, 5 μm, Hex/MTBE = 70 : 30, 1 mL/min; 93 : 7 *er*;  $[\alpha]_D^{25} = -38.01$  ( $c = 0.12$ , CHCl<sub>3</sub>).

Additional Info : Peak(s) manually integrated

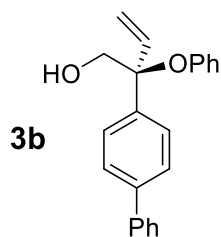


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 10.029        | MM   | 0.2467      | 360.65744    | 24.36497     | 46.9638 |
| 2      | 12.017        | MM   | 0.3665      | 407.28979    | 18.52077     | 53.0362 |

Additional Info : Peak(s) manually integrated

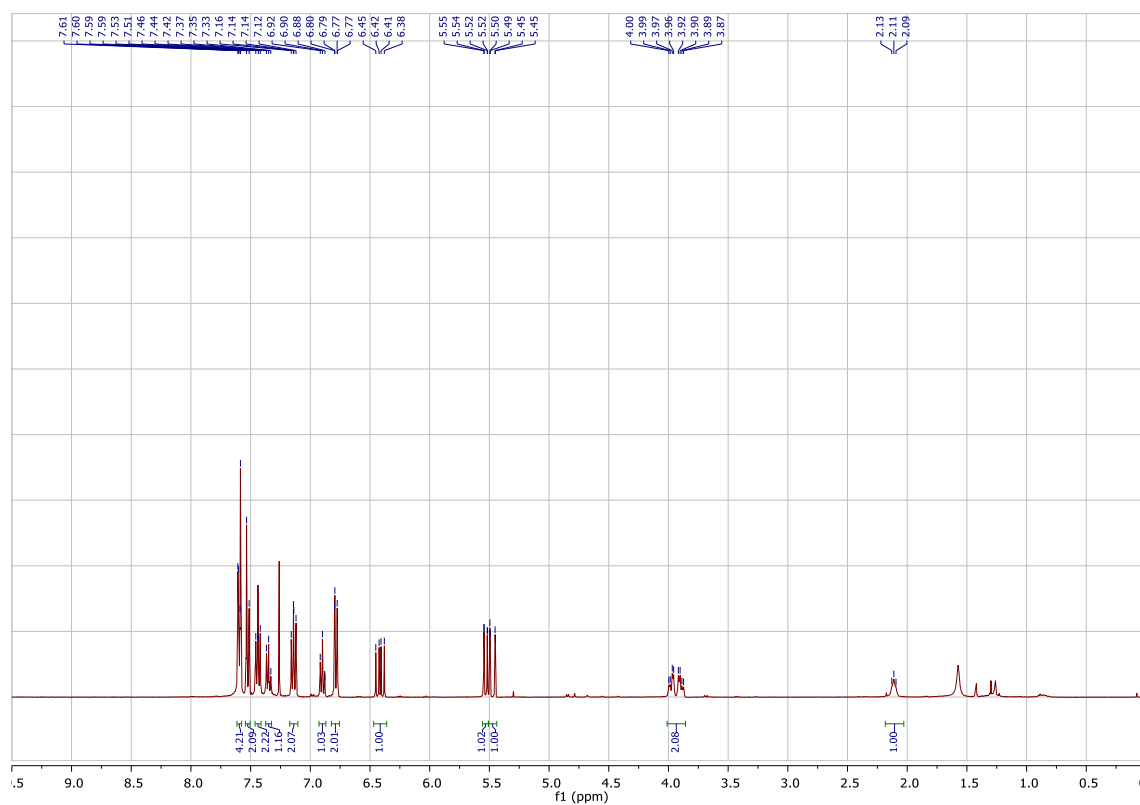


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 9.669         | BB   | 0.2137      | 3418.67285   | 243.69025    | 7.2626  |
| 2      | 11.365        | BB   | 0.3634      | 4.36535e4    | 1904.31519   | 92.7374 |



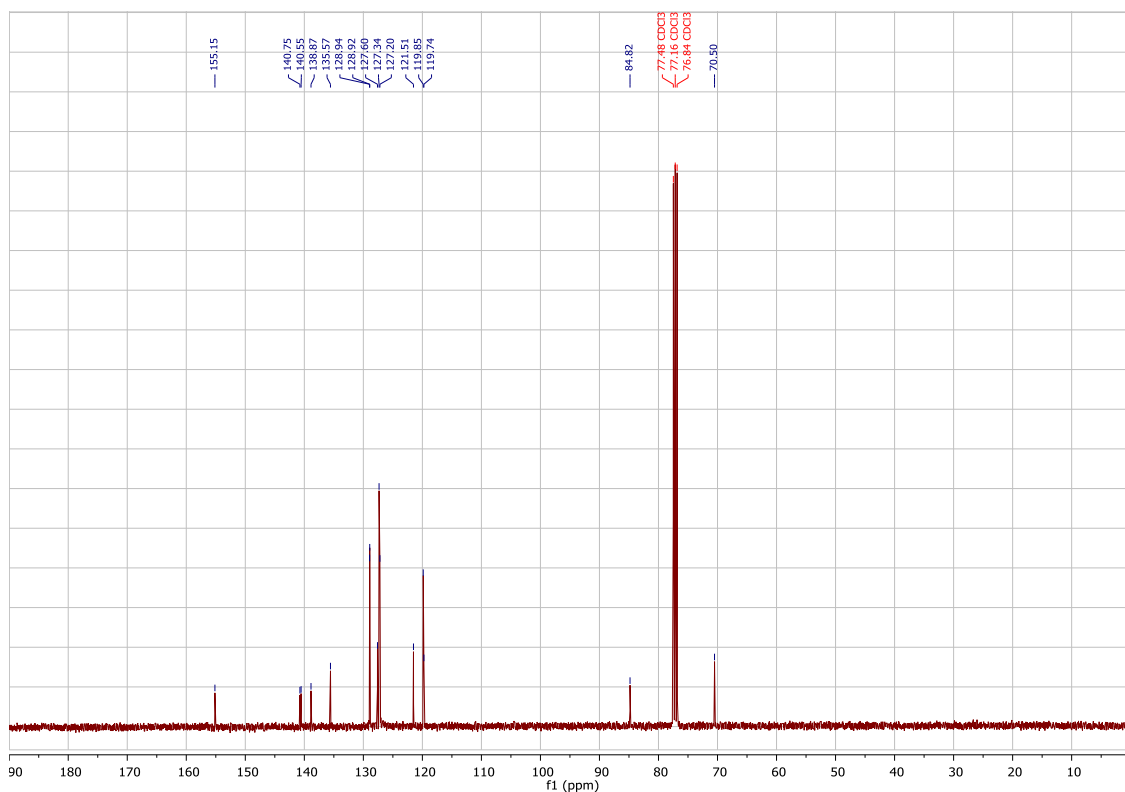
Scale: 0.2 mmol; isolated 45.5 mg (72% yield), yellow solid, Hexane : EA = 50 : 1,  $R_f$  = 0.15

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ )



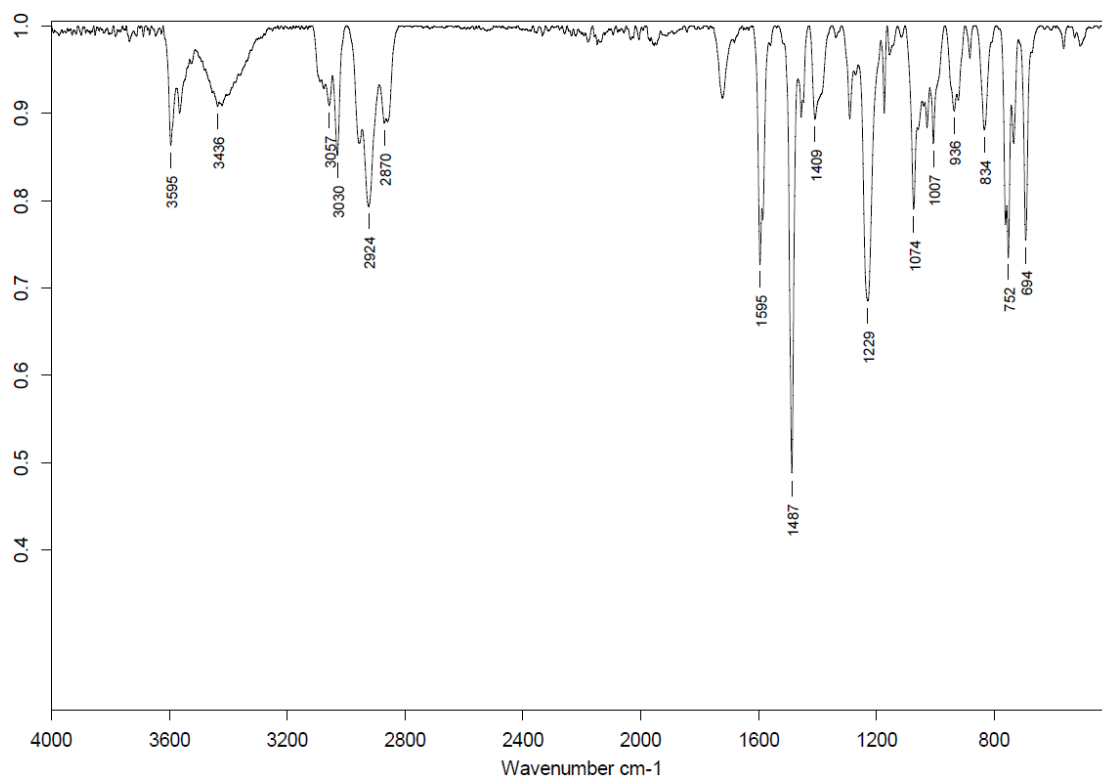
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61 – 7.58 (m, 4H), 7.52 (d,  $J$  = 8.6 Hz, 2H), 7.46 – 7.41 (m, 2H), 7.35 (t,  $J$  = 7.3 Hz, 1H), 7.14 (m, 2H), 6.90 (t,  $J$  = 7.9 Hz, 1H), 6.78 (m, 2H), 6.42 (dd,  $J$  = 17.5, 11.1 Hz, 1H), 5.53 (dd,  $J$  = 11.2, 1.0 Hz, 1H), 5.47 (dd,  $J$  = 17.5, 1.0 Hz, 1H), 4.01 – 3.86 (m, 2H), 2.12 (d,  $J$  = 6.9 Hz, 1H).

<sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>)



<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  155.15, 140.75, 140.55, 138.87, 135.57, 128.94, 128.92, 127.60, 127.34, 127.20, 121.51, 119.85, 119.74, 84.82, 70.50.

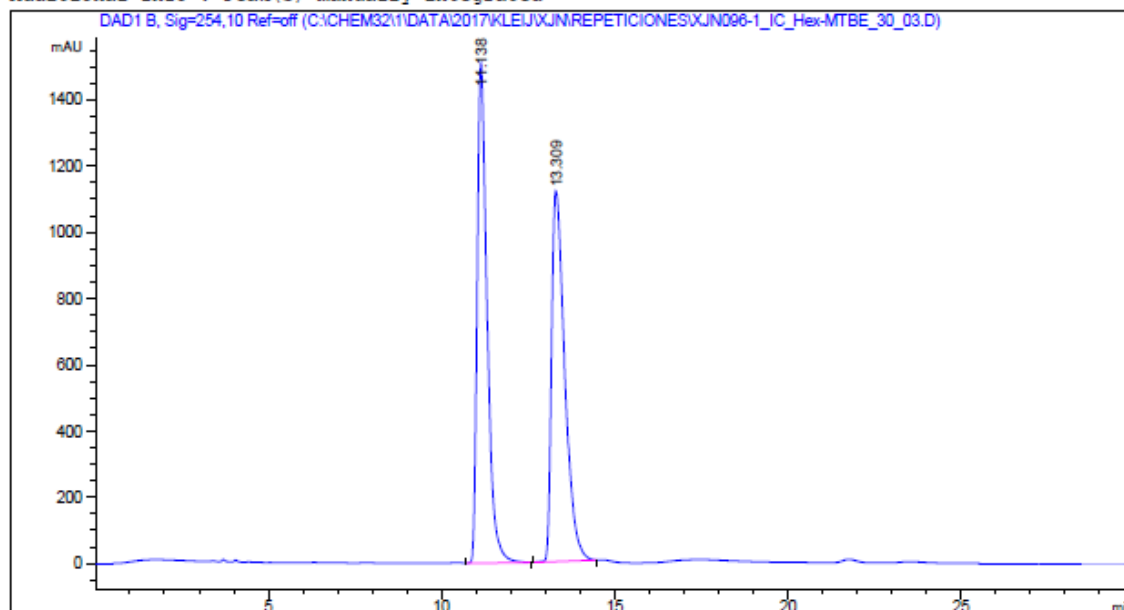
IR spectrum (neat)



HRMS (ESI<sup>+</sup>, MeOH):  $m/z$  calcd. 339.1356 (M + Na)<sup>+</sup>, found: 339.1363.

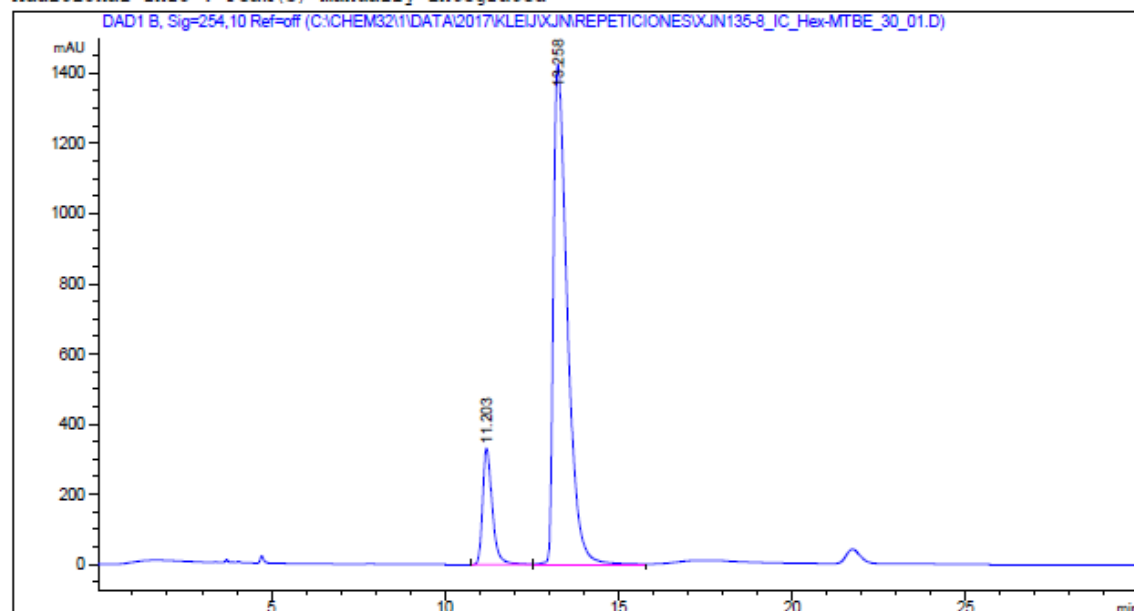
**HPLC conditions:** Chiralpak IC 250 × 4.6 mm, 5 μm, Hex/MTBE = 70 : 30, 1 mL/min;  
86: 14 *er*;  $[\alpha]_D^{25} = -29.27$  ( $c = 0.11$ , CHCl<sub>3</sub>).

Additional Info : Peak(s) manually integrated

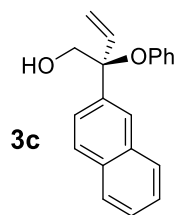


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 11.138        | BB   | 0.3054      | 3.01609e4    | 1507.87073   | 50.4730 |
| 2      | 13.309        | BB   | 0.4029      | 2.95956e4    | 1117.77344   | 49.5270 |

Additional Info : Peak(s) manually integrated

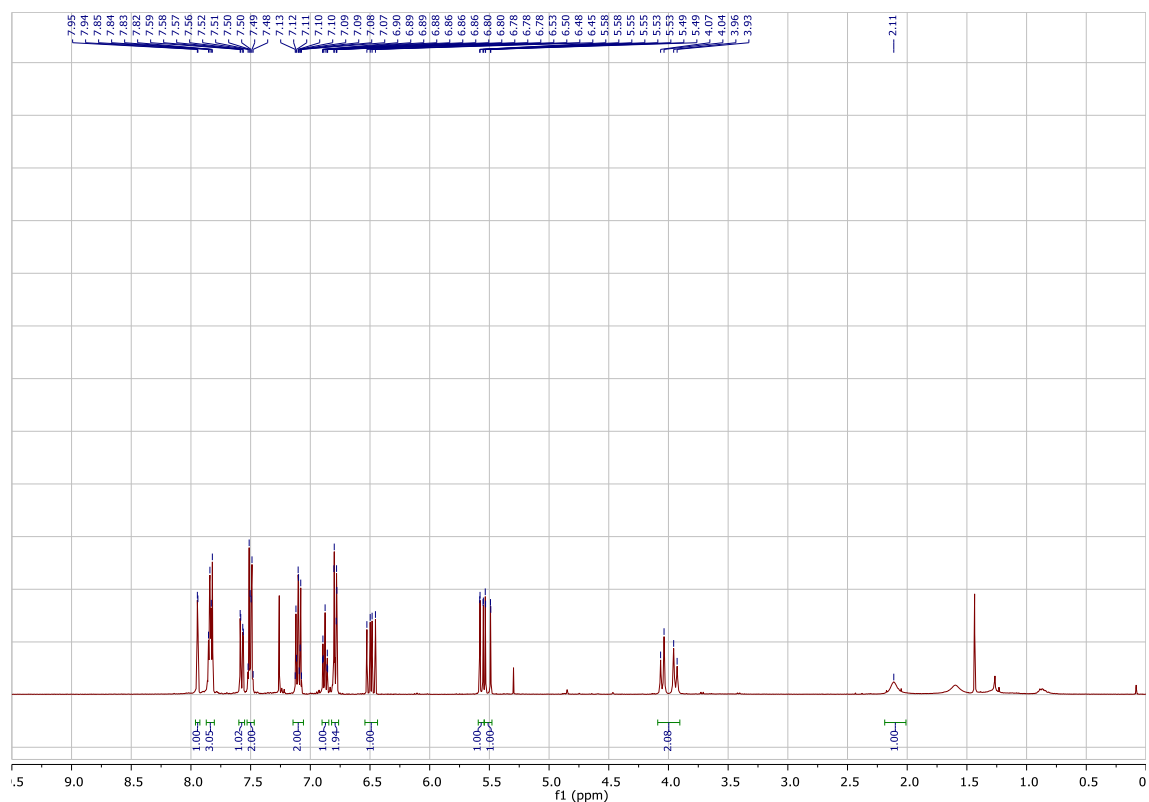


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 11.203        | BB   | 0.2954      | 6399.44287   | 331.20605    | 13.9429 |
| 2      | 13.258        | BB   | 0.4215      | 3.94981e4    | 1424.50488   | 86.0571 |



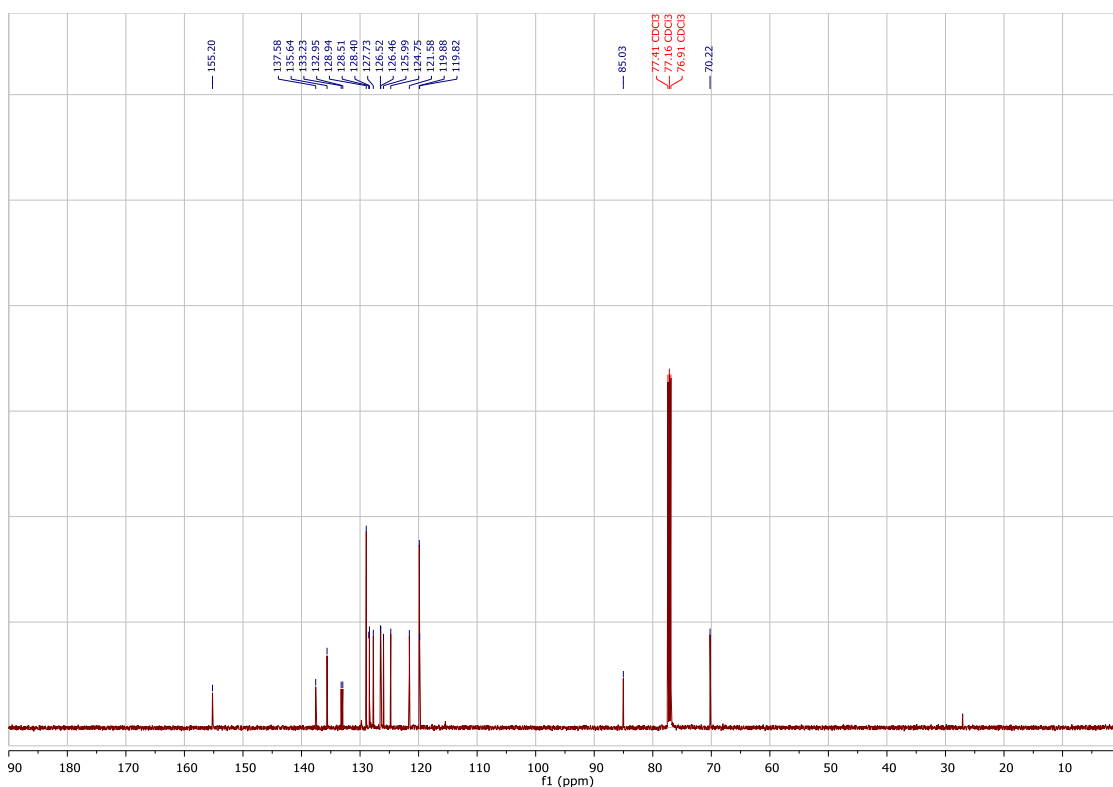
Scale: 0.2 mmol; isolated 33.6 mg (58% yield), light yellow solid, Hexane : EA = 50 : 1,  $R_f = 0.15$

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ )



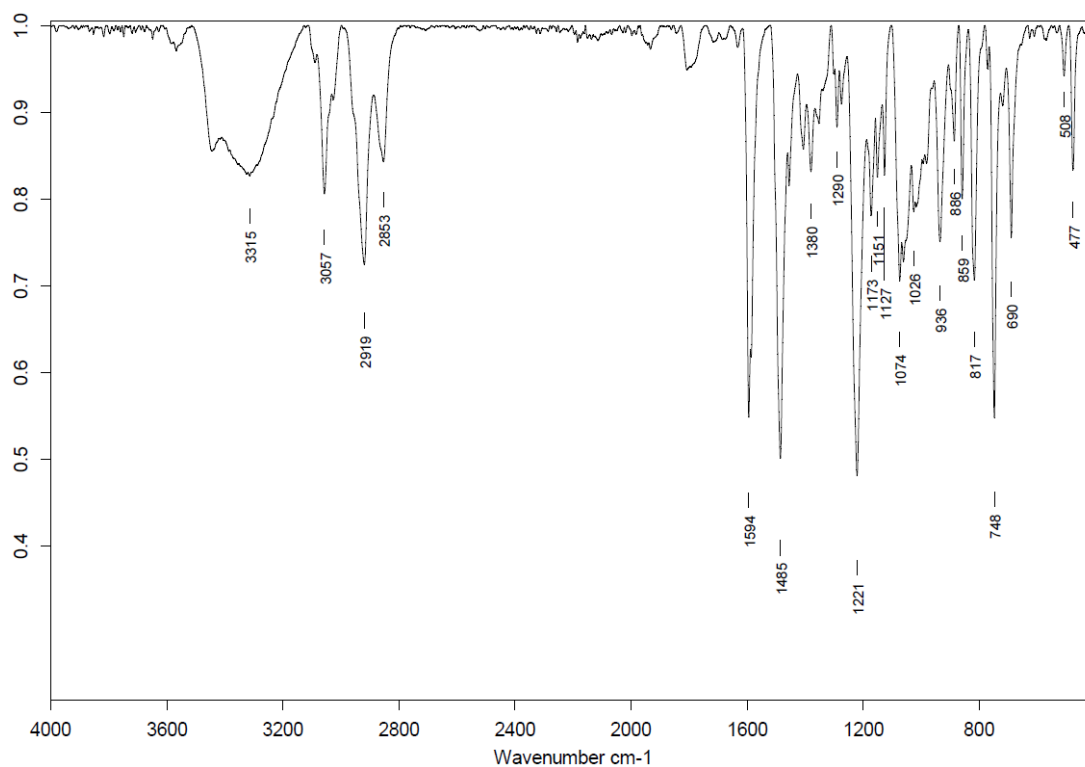
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (d,  $J = 1.8$  Hz, 1H), 7.84 (m, 3H), 7.57 (m, 1H), 7.50 (m, 2H), 7.10 (m, 2H), 6.90 – 6.84 (m, 1H), 6.82 – 6.76 (m, 2H), 6.49 (dd,  $J = 17.5, 11.1$  Hz, 1H), 5.57 (dd,  $J = 11.1, 1.0$  Hz, 1H), 5.51 (dd,  $J = 17.5, 1.0$  Hz, 1H), 4.09 – 3.90 (m, 2H), 2.11 (s, 1H).

<sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>)



<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  155.20, 137.58, 135.64, 133.23, 132.95, 128.94, 128.51, 128.40, 127.73, 126.52, 126.46, 125.99, 124.75, 121.58, 119.88, 119.82, 85.03, 70.22.

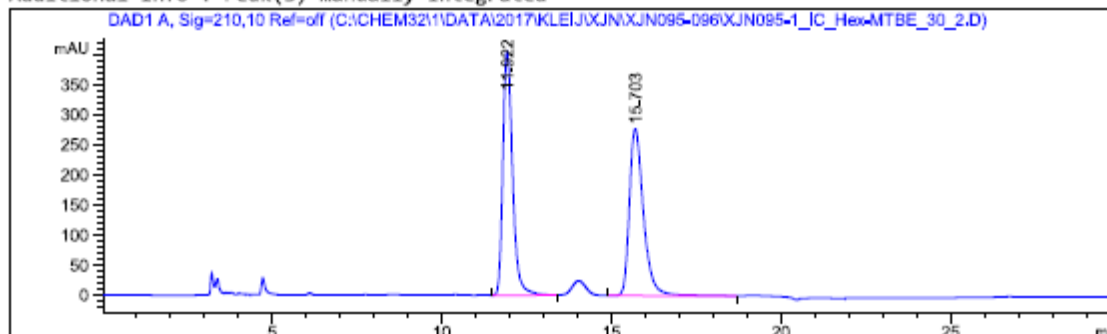
IR spectrum (neat)



HRMS (ESI<sup>+</sup>, MeOH):  $m/z$  calcd. 313.1199 (M + Na)<sup>+</sup>, found: 313.1202.

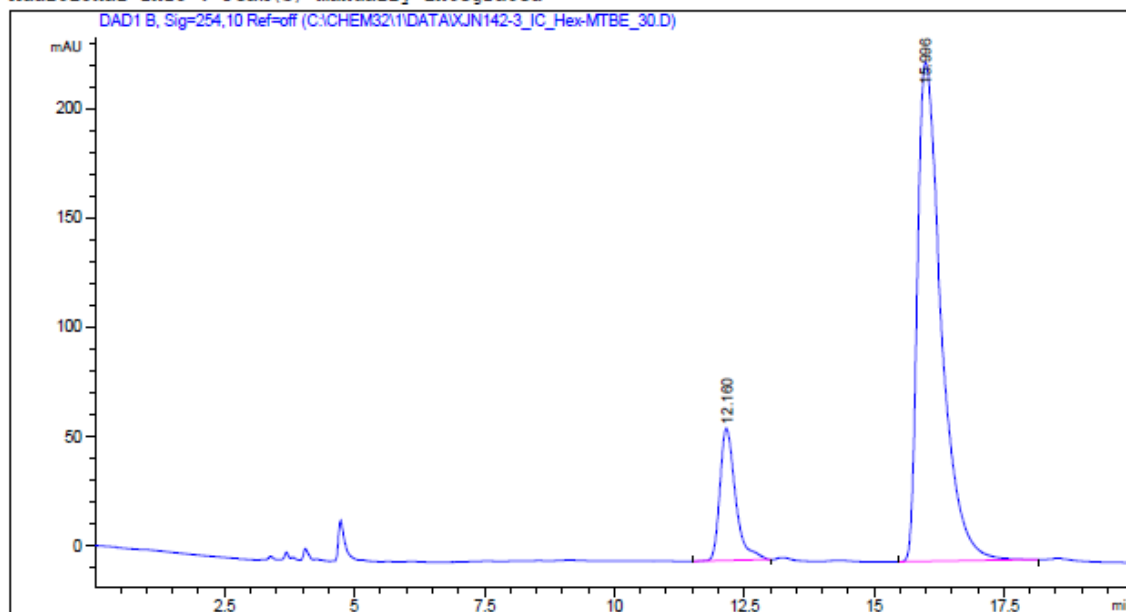
**HPLC conditions:** Chiralpak IC 250 × 4.6 mm, 5 μm, Hex/MTBE = 70 : 30, 1 mL/min;  
85 : 15 *er*;  $[\alpha]_D^{25} = -51.92$  ( $c = 0.12$ , CHCl<sub>3</sub>).

Additional Info : Peak(s) manually integrated

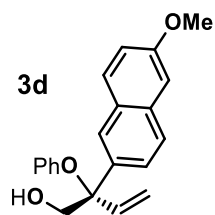


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 11.922        | BB   | 0.3032      | 8022.47070   | 404.73987    | 50.1476 |
| 2      | 15.703        | BB   | 0.4403      | 7975.26123   | 276.63397    | 49.8524 |

Additional Info : Peak(s) manually integrated

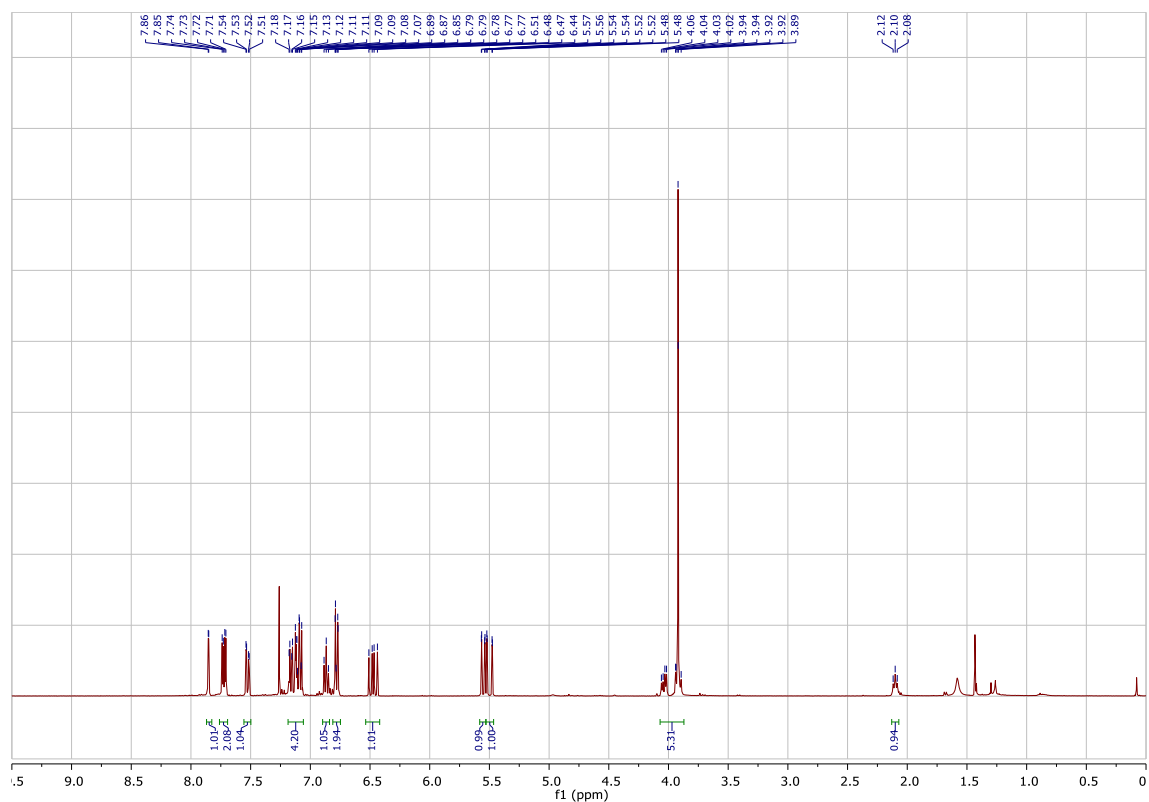


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 12.160        | BB   | 0.3194      | 1272.73230   | 60.50556     | 14.9878 |
| 2      | 15.996        | BB   | 0.4610      | 7219.05713   | 228.23291    | 85.0122 |



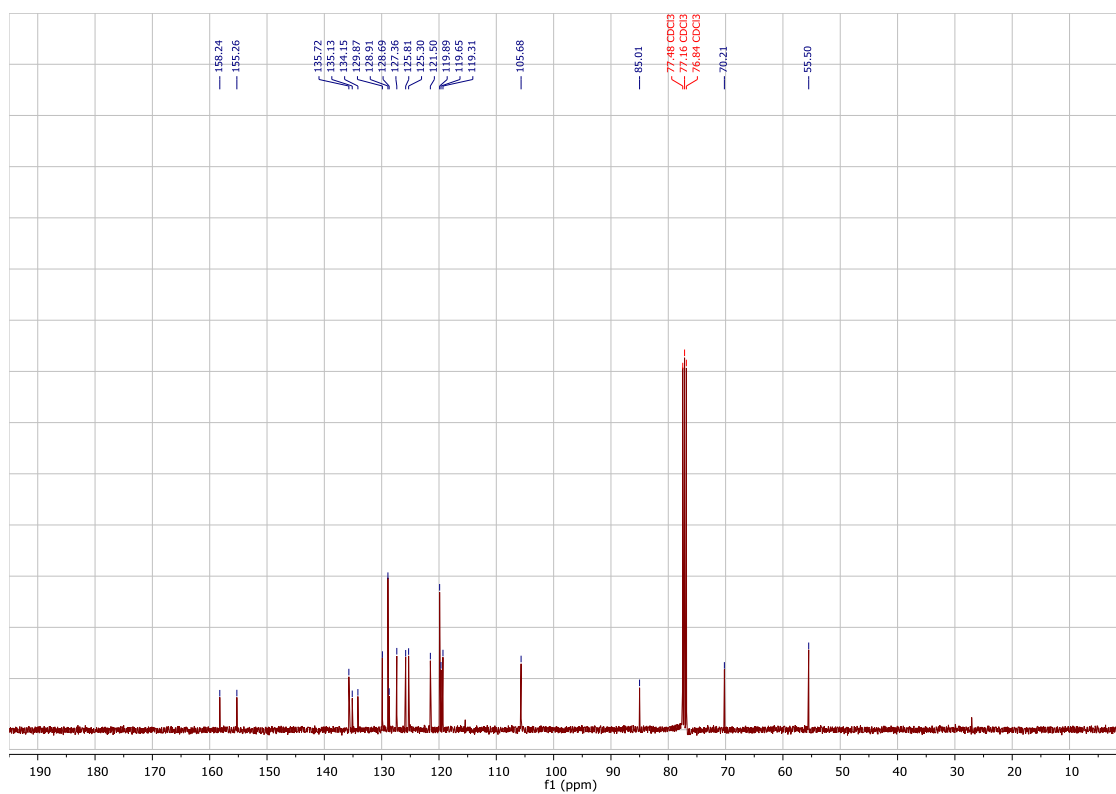
Scale: 0.2 mmol; isolated 48.0 mg (75% yield), light yellow solid, Hexane : EA = 20 : 1,  $R_f = 0.15$

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ )



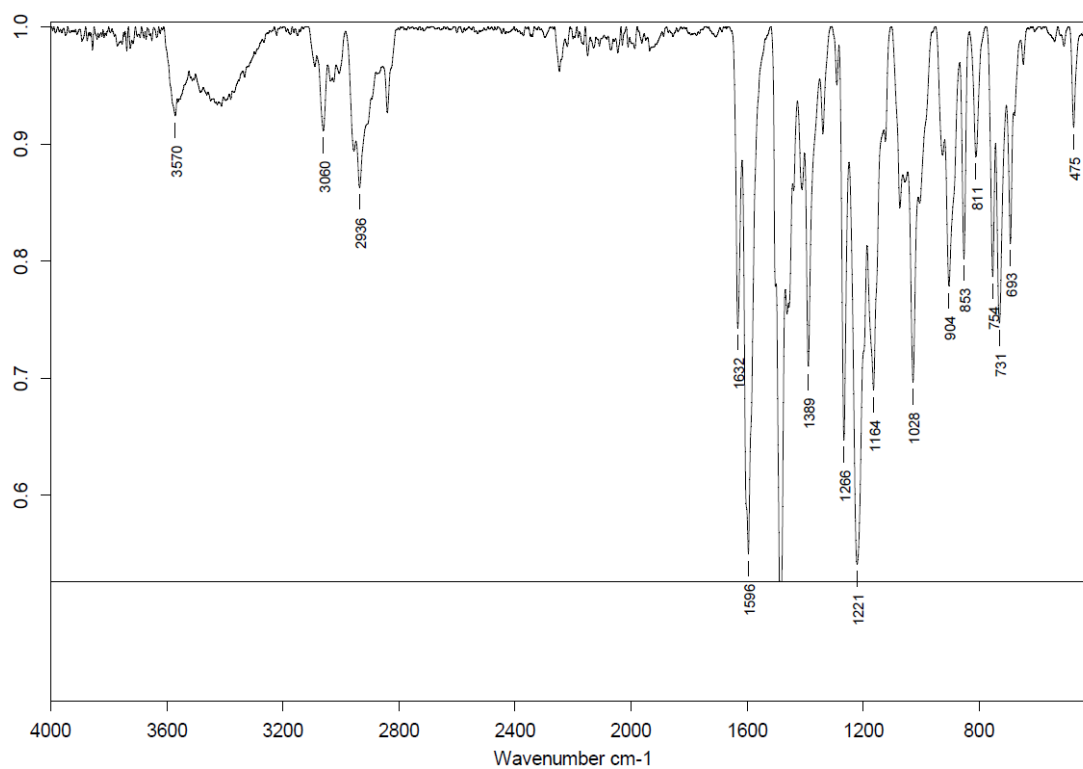
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (d,  $J = 1.7$  Hz, 1H), 7.72 (m, 2H), 7.53 (m, 1H), 7.19 – 7.06 (m, 4H), 6.87 (t,  $J = 7.4$  Hz, 1H), 6.78 (m, 2H), 6.47 (dd,  $J = 17.5, 11.1$  Hz, 1H), 5.55 (dd,  $J = 11.1, 1.0$  Hz, 1H), 5.50 (dd,  $J = 17.5, 1.0$  Hz, 1H), 4.07 – 3.87 (m, 5H), 2.10 (t,  $J = 6.9$  Hz, 1H).

$^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ )



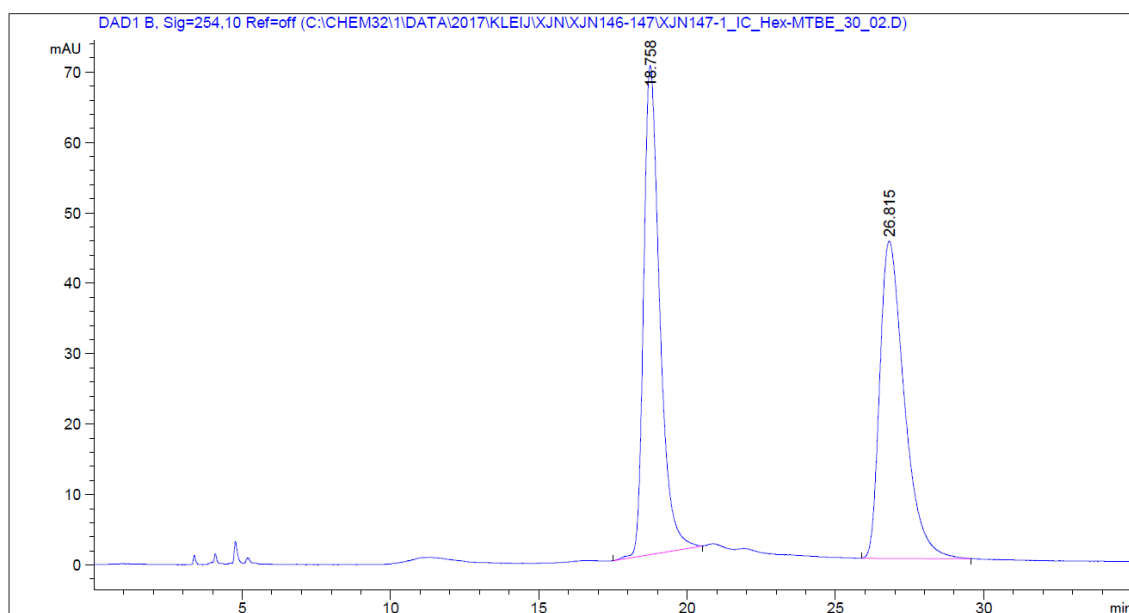
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.24, 155.26, 135.72, 135.13, 134.15, 129.87, 128.91, 128.69, 127.36, 125.81, 125.30, 121.50, 119.89, 119.65, 119.31, 105.68, 85.01, 70.21, 55.50.

IR spectrum (neat)

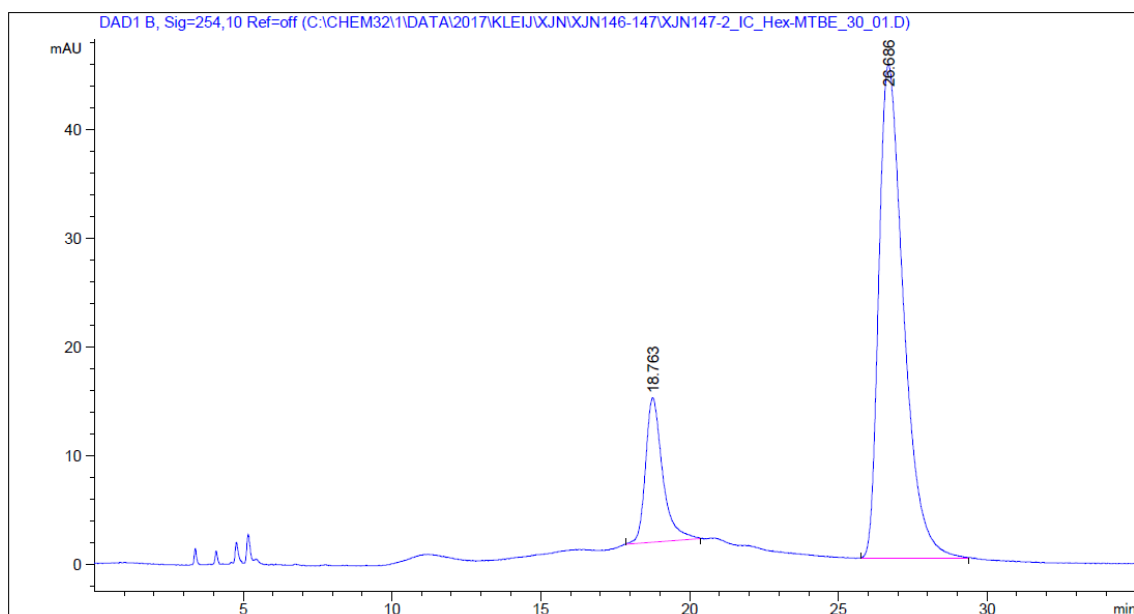


HRMS (ESI+, MeOH):  $m/z$  calcd. 343.1305 ( $\text{M} + \text{Na}$ ) $^+$ , found: 343.1303.

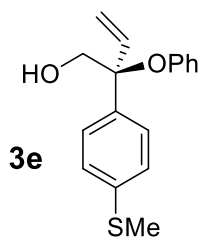
**HPLC conditions:** Chiralpak IC 250 × 4.6 mm, 5 μm, Hex/MTBE = 70 : 30, 1 mL/min;  
83 : 17 *er*;  $[\alpha]_D^{25} = -55.49$  ( $c = 0.11$ , CHCl<sub>3</sub>).



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 18.758        | BB   | 0.5713      | 2619.39697   | 69.55901     | 50.3424 |
| 2      | 26.815        | BB   | 0.8768      | 2583.76416   | 45.06886     | 49.6576 |

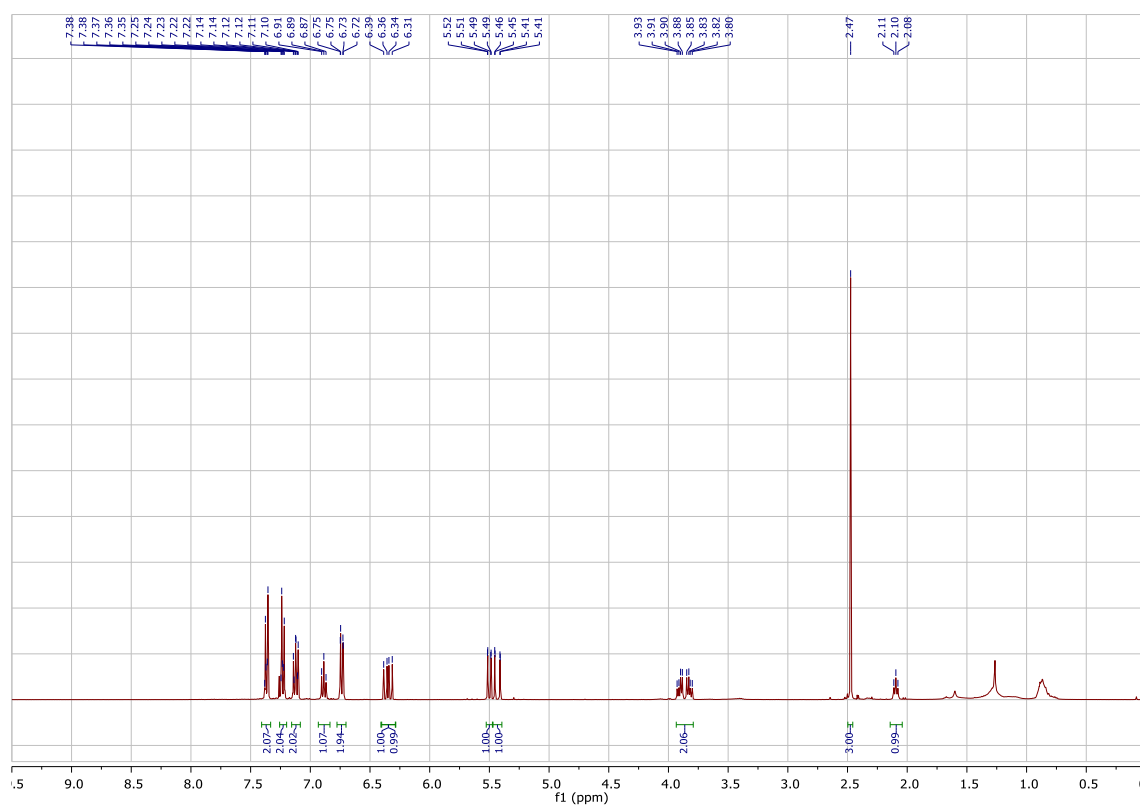


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 18.763        | BB   | 0.5905      | 529.19904    | 13.29073     | 16.7911 |
| 2      | 26.686        | BB   | 0.8619      | 2622.45801   | 45.40374     | 83.2089 |



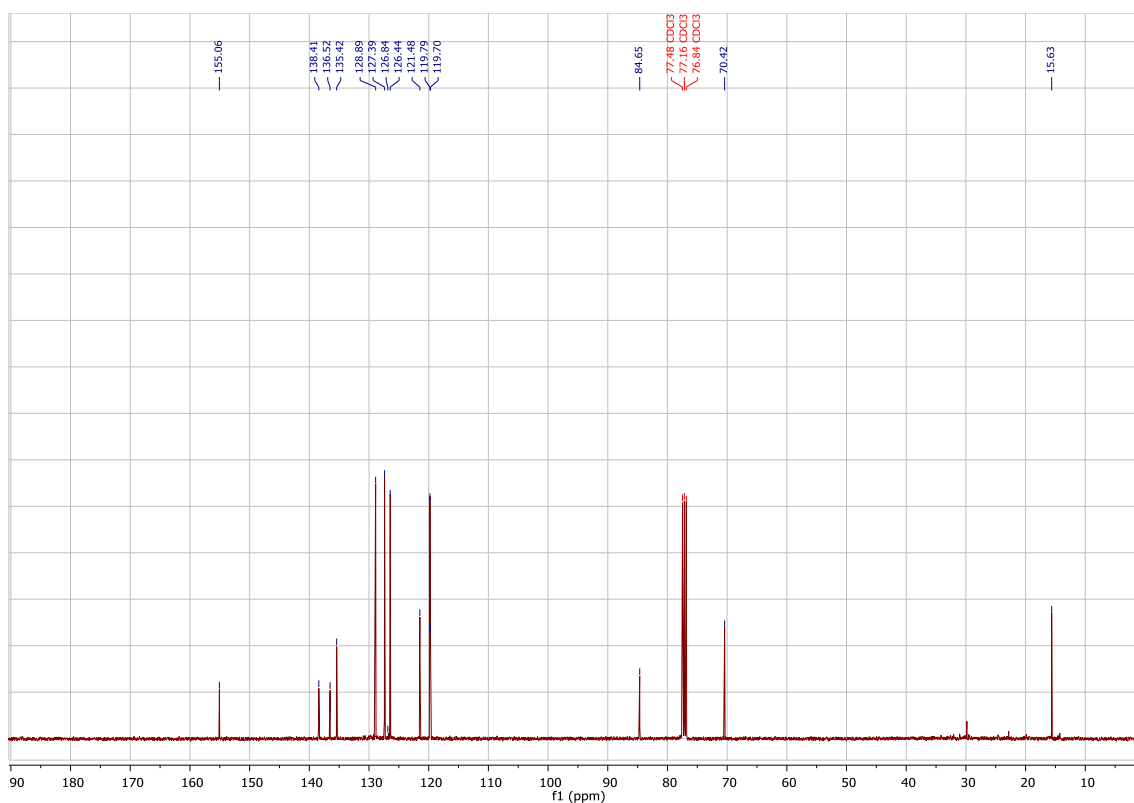
Scale: 0.2 mmol; isolated 46.3 mg (81% yield), light yellow solid, Hexane : EA = 50 : 1,  $R_f = 0.15$

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ )



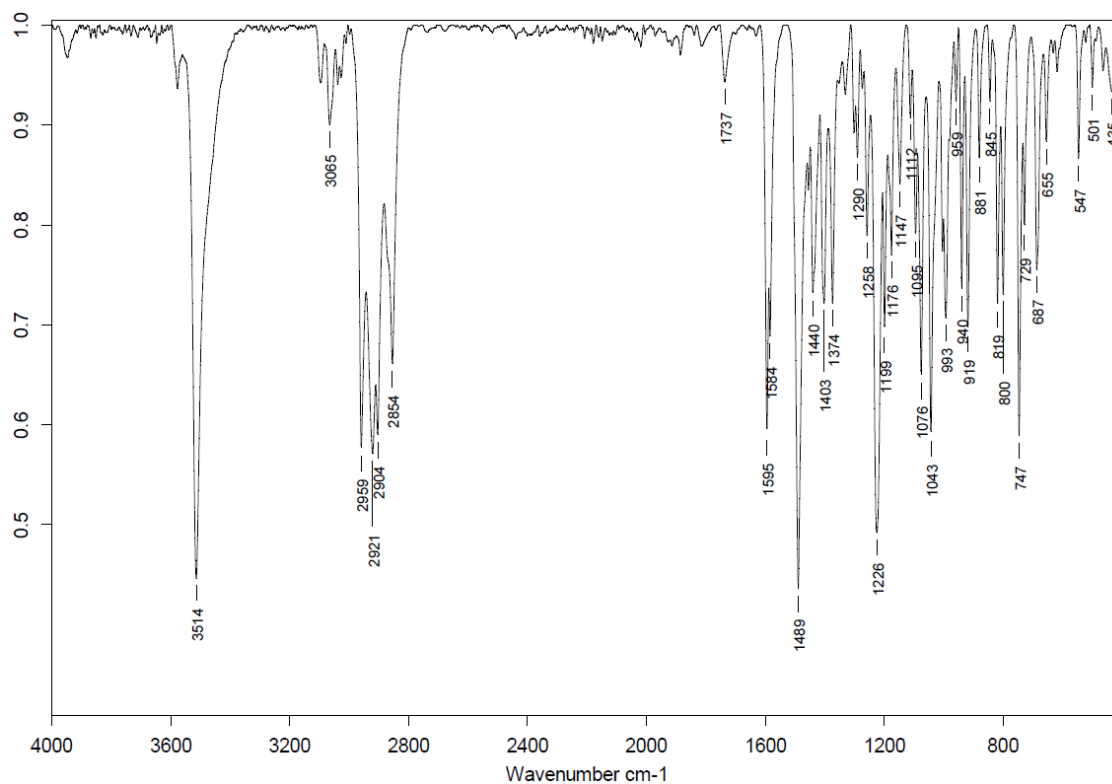
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41 – 7.33 (m, 2H), 7.26 – 7.20 (m, 2H), 7.16 – 7.08 (m, 2H), 6.89 (t,  $J = 7.4$  Hz, 1H), 6.74 (dd,  $J = 8.7, 1.0$  Hz, 2H), 6.35 (dd,  $J = 17.5, 11.1$  Hz, 1H), 5.50 (dd,  $J = 11.1, 1.0$  Hz, 1H), 5.43 (dd,  $J = 17.5, 1.0$  Hz, 1H), 3.93 – 3.79 (m, 2H), 2.47 (s, 3H), 2.09 (t,  $J = 6.9$  Hz, 1H).

<sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>)



<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  155.06, 138.41, 136.52, 135.42, 128.89, 127.39, 126.44, 121.48, 119.79, 119.70, 84.65, 70.42, 15.63.

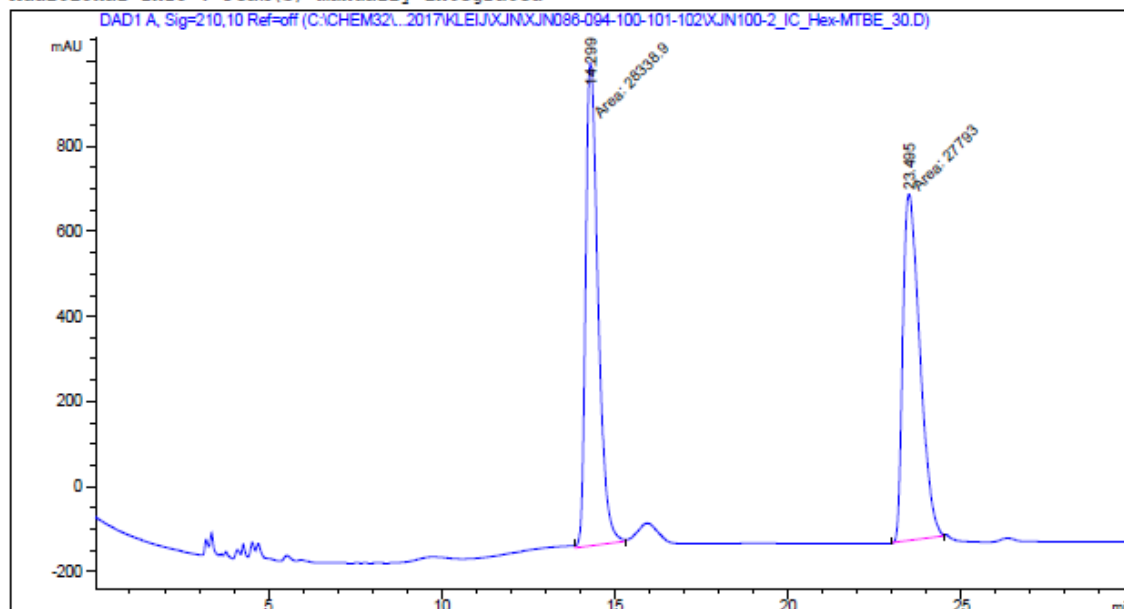
IR spectrum (neat)



HRMS (ESI<sup>+</sup>, MeOH):  $m/z$  calcd. 309.0920 (M + Na)<sup>+</sup>, found: 309.0917.

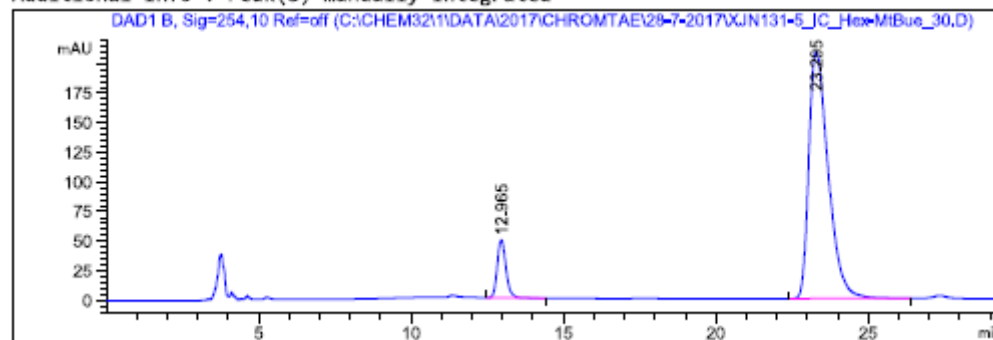
**HPLC conditions:** Chiralpak IC 250 × 4.6 mm, 5 μm, Hex/MTBE = 70 : 30, 1 mL/min; 90.5 : 9.5 *er*;  $[\alpha]_D^{25} = -36.48$  (*c* = 0.10, CHCl<sub>3</sub>).

Additional Info : Peak(s) manually integrated

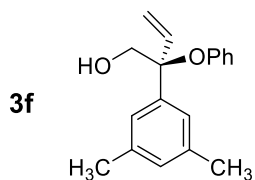


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 14.299        | MM   | 0.4159      | 2.83389e4    | 1135.74902   | 50.4862 |
| 2      | 23.495        | MM   | 0.5687      | 2.77930e4    | 814.59003    | 49.5138 |

Additional Info : Peak(s) manually integrated

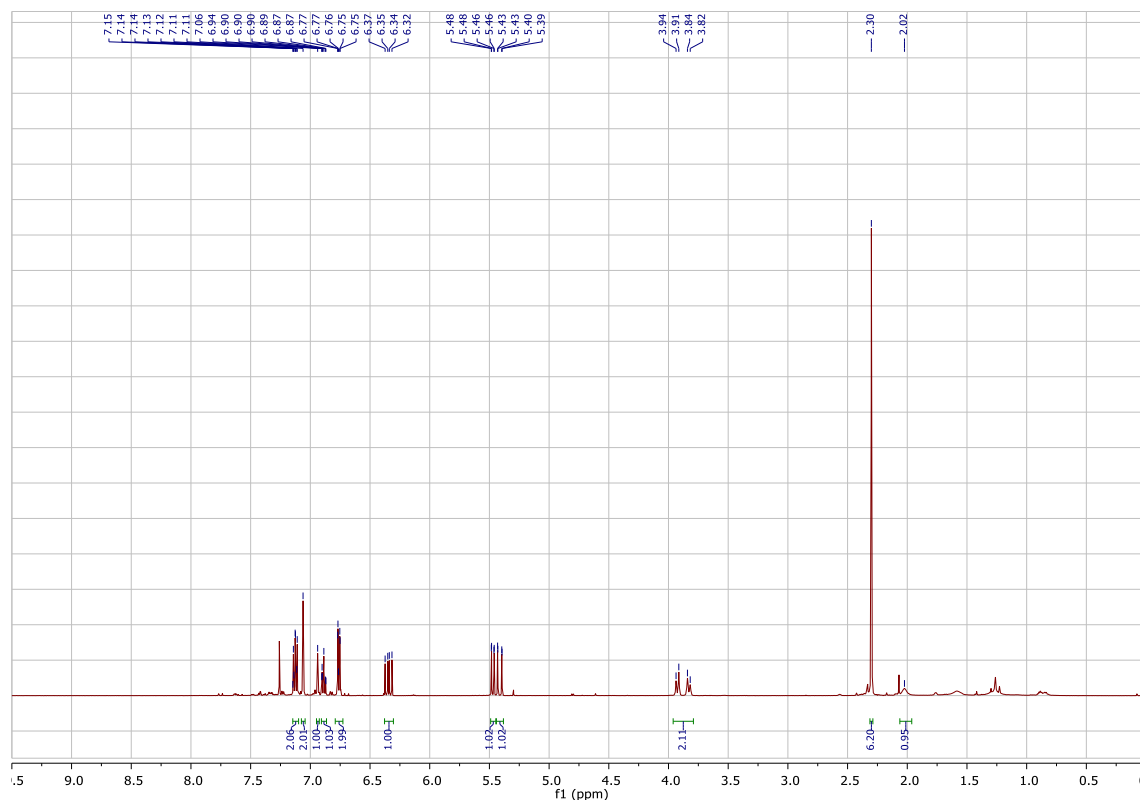


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 12.965        | BB   | 0.3022      | 961.42004    | 48.72560     | 9.4434  |
| 2      | 23.295        | BB   | 0.6787      | 9219.40625   | 208.18417    | 90.5566 |



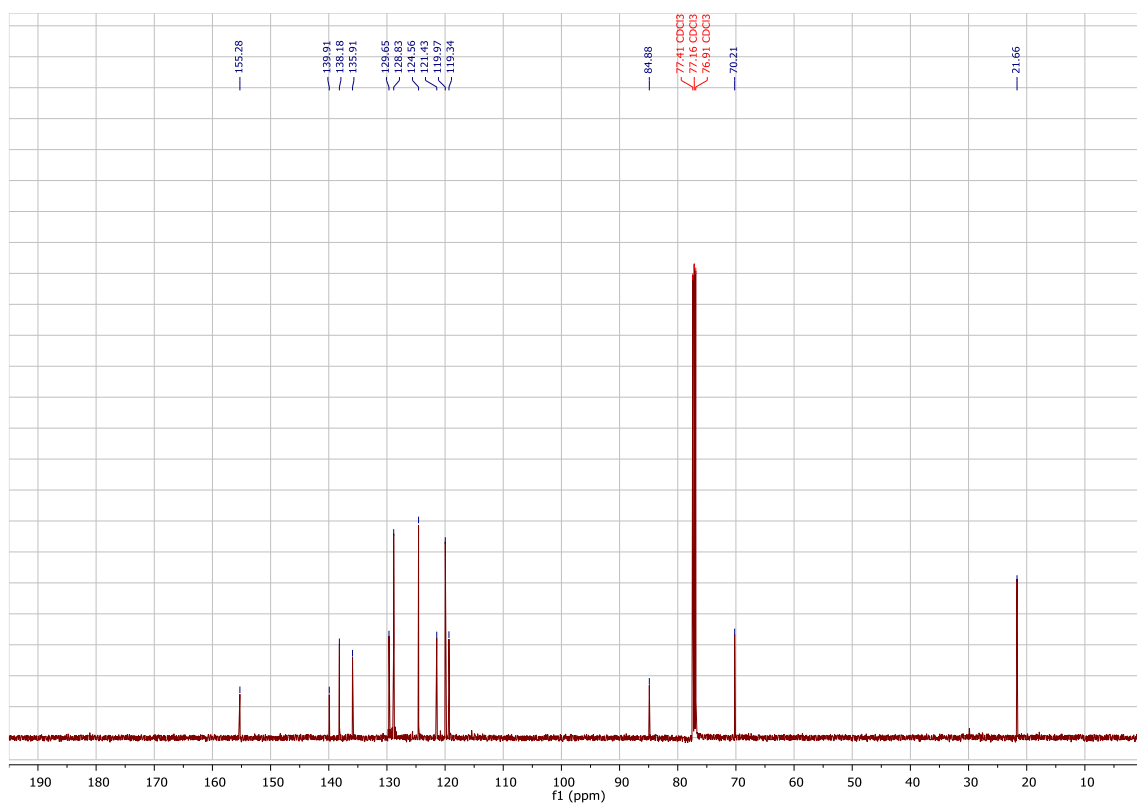
Scale: 0.2 mmol; isolated 30.5 mg (57% yield), yellow solid, Hexane : EA = 50 : 1,  $R_f$  = 0.15

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ )



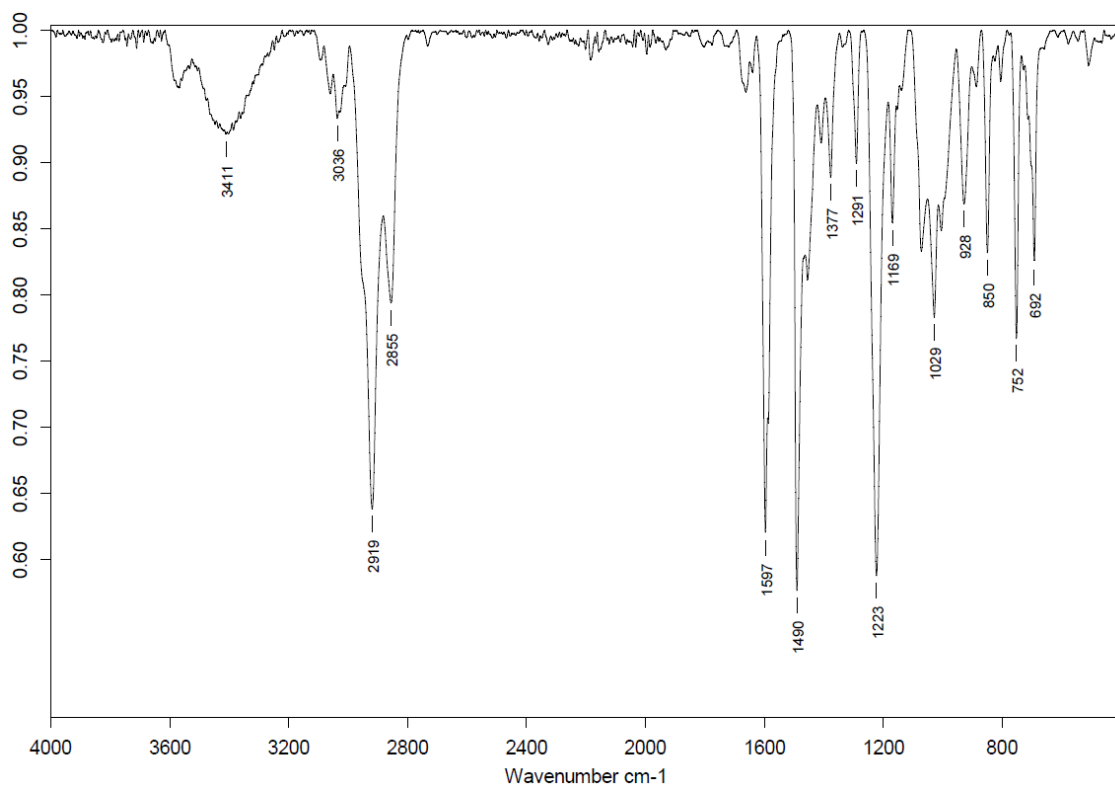
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.15 – 7.10 (m, 2H), 7.06 (s, 2H), 6.94 (s, 1H), 6.91 – 6.86 (m, 1H), 6.79 – 6.73 (m, 2H), 6.34 (dd,  $J$  = 17.6, 11.1 Hz, 1H), 5.47 (dd,  $J$  = 11.1, 1.0 Hz, 1H), 5.41 (dd,  $J$  = 17.6, 1.0 Hz, 1H), 3.96 – 3.79 (m, 2H), 2.30 (s, 6H), 2.02 (s, 1H).

<sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>)



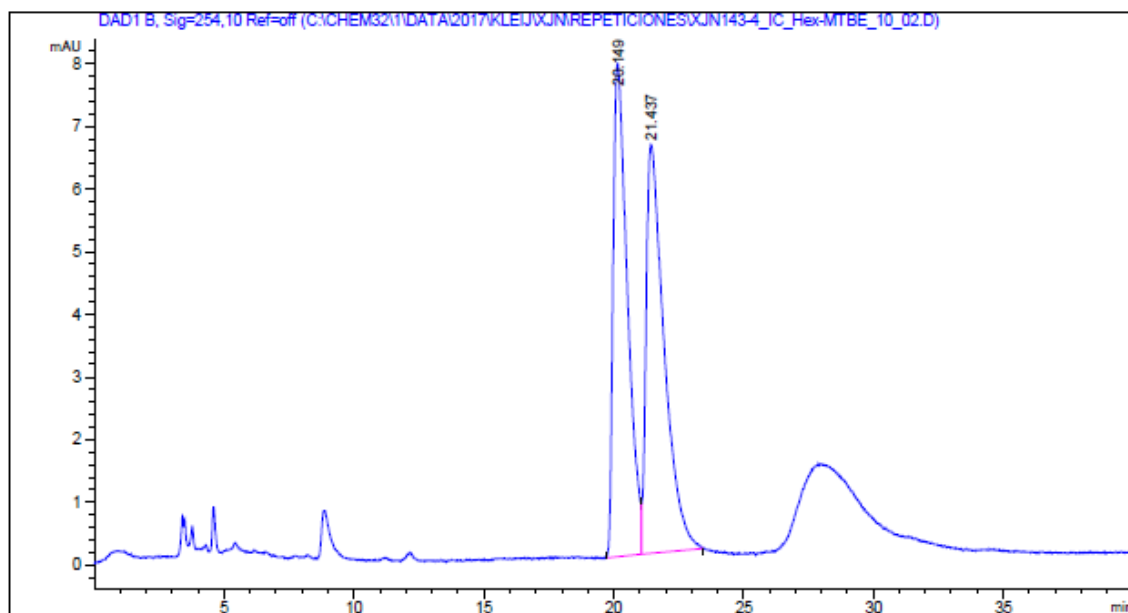
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  155.28, 139.91, 138.18, 135.91, 129.65, 128.83, 124.56, 121.43, 119.97, 119.34, 84.88, 70.21, 21.66.

IR spectrum (neat)



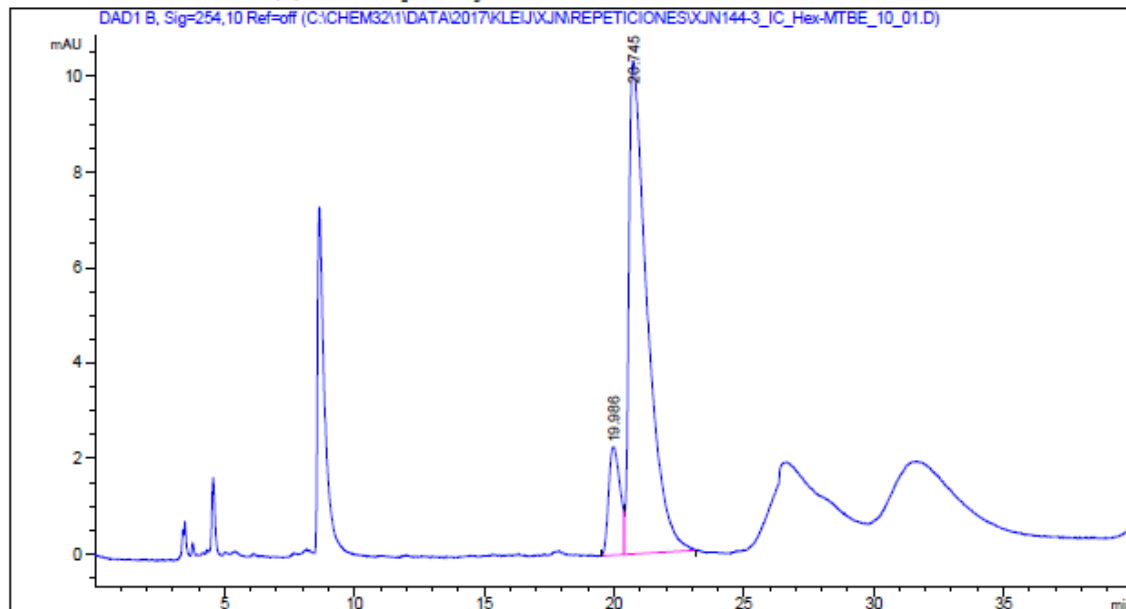
HRMS (ESI<sup>+</sup>, MeOH):  $m/z$  calcd. 291.1356 (M + Na)<sup>+</sup>, found: 291.1361.

**HPLC conditions:** Chiralpak IC 250 × 4.6 mm, 5 μm, Hex/MTBE = 80 : 20, 1 mL/min;  
88 : 12 *er*;  $[\alpha]_D^{25} = +3.1$  (*c* = 0.07, CHCl<sub>3</sub>).

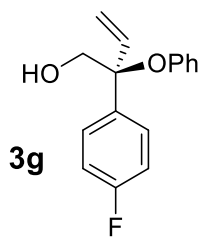


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 20.149        | BV   | 0.5286      | 299.43106    | 7.85807      | 48.7049 |
| 2      | 21.437        | VB   | 0.6344      | 315.35565    | 6.51896      | 51.2951 |

Additional Info : Peak(s) manually integrated

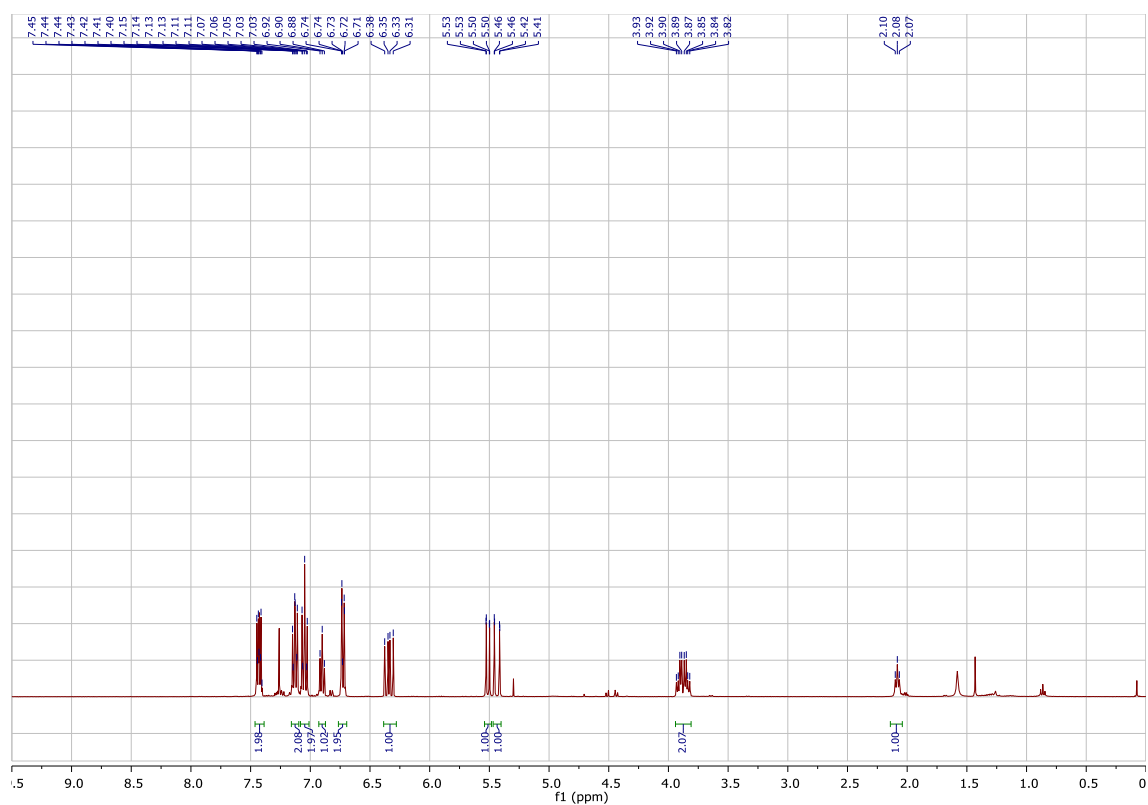


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 19.986        | BV   | 0.3913      | 69.15713     | 2.25822      | 11.9634 |
| 2      | 20.745        | VB   | 0.6576      | 508.91318    | 10.31584     | 88.0366 |



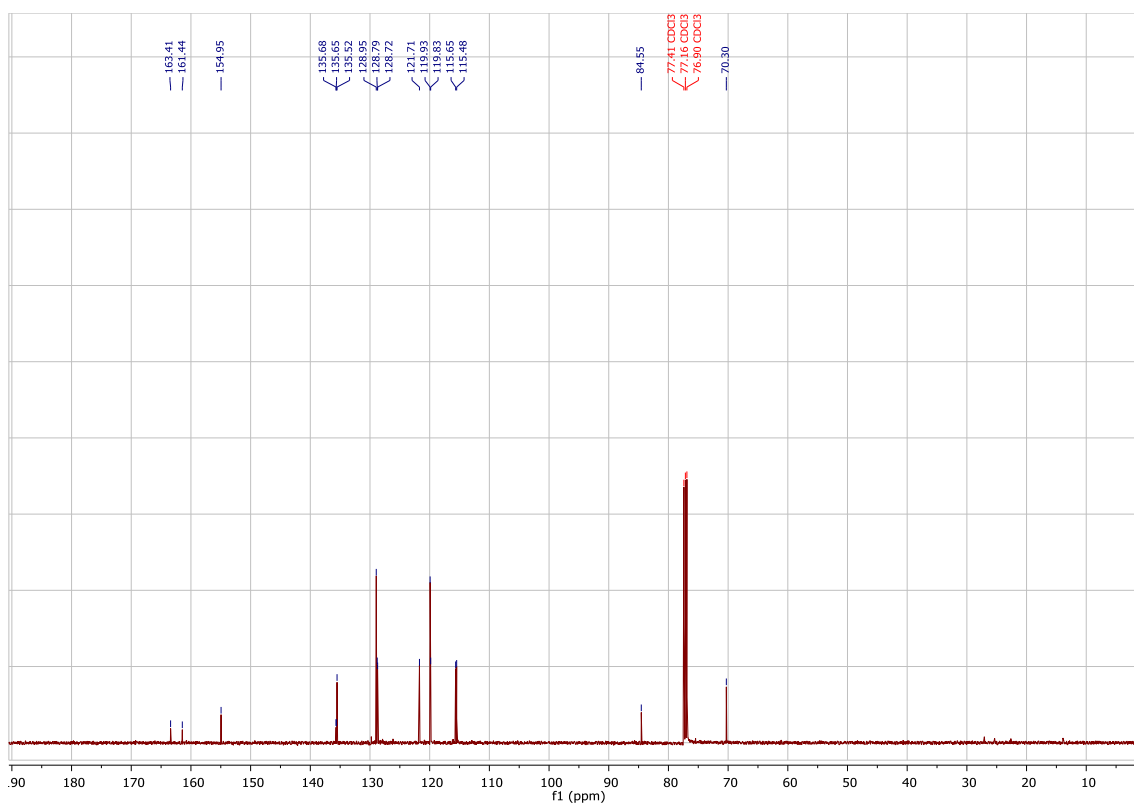
Scale: 0.2 mmol; isolated 42.8 mg (83% yield), white solid, Hexane : EA = 50 : 1,  $R_f$  = 0.15

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ )



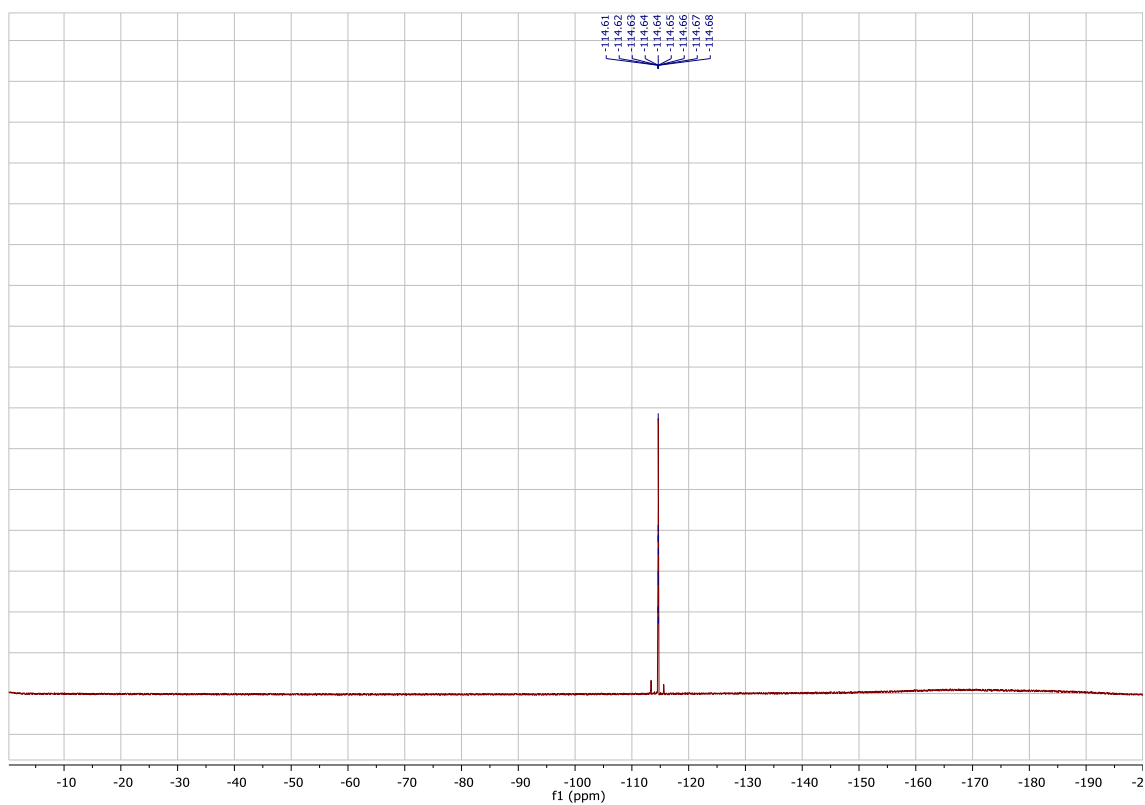
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 – 7.39 (m, 2H), 7.16 – 7.10 (m, 2H), 7.08 – 7.01 (m, 2H), 6.90 (t,  $J$  = 7.4 Hz, 1H), 6.76 – 6.69 (m, 2H), 6.34 (dd,  $J$  = 17.5, 11.1 Hz, 1H), 5.54 – 5.41 (m, 2H), 3.94 – 3.81 (m, 2H), 2.08 (t,  $J$  = 6.9 Hz, 1H).

$^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ )



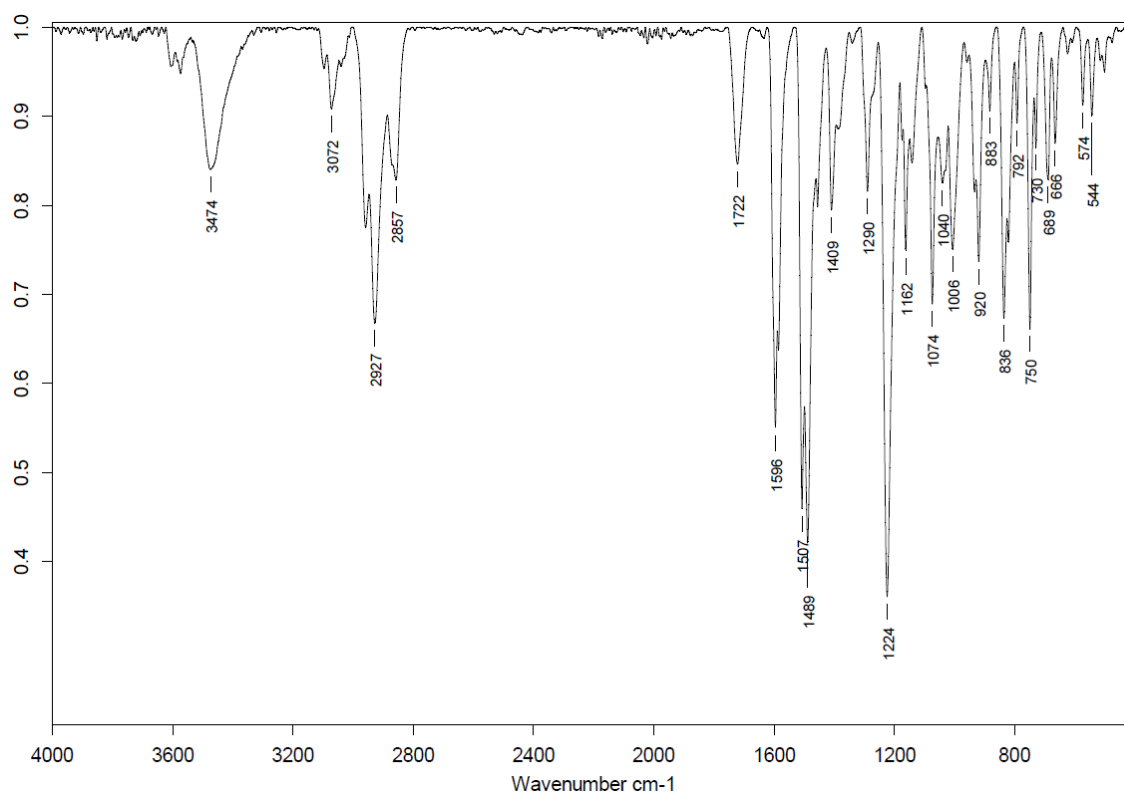
$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  163.41, 161.44, 154.95, 135.68, 135.65, 135.52, 128.95, 128.79, 128.72, 121.71, 119.93, 119.83, 115.65, 115.48, 84.55, 70.30.

$^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ )



$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -114.64 (tt,  $J = 8.5, 5.2$  Hz).

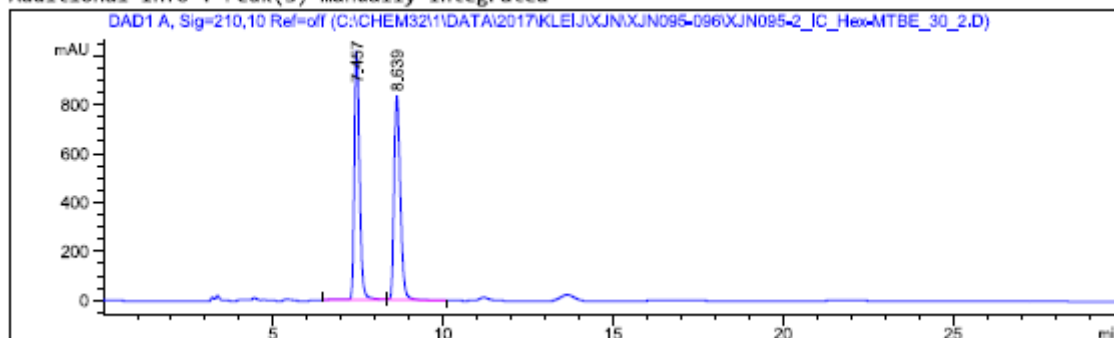
IR spectrum (neat)



**HRMS** (ESI<sup>+</sup>, MeOH): *m/z* calcd. 281.0948 (M + Na)<sup>+</sup>, found: 281.0957.

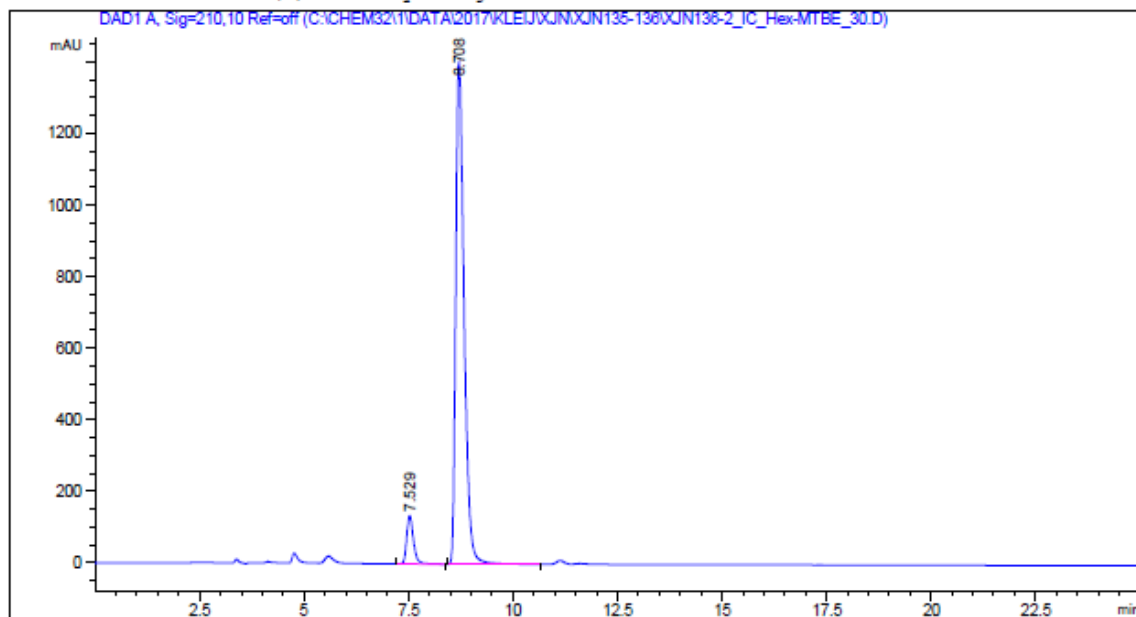
**HPLC conditions:** Chiralpak IC 250 × 4.6 mm, 5 μm, Hex/MTBE = 70 : 30, 1 mL/min;  
93 : 7 *er*;  $[\alpha]_D^{25} = -40.14$  ( $c = 0.13$ , CHCl<sub>3</sub>).

Additional Info : Peak(s) manually integrated

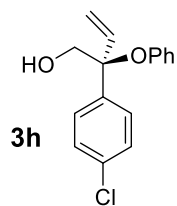


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 7.457         | BB   | 0.1617      | 1.07189e4    | 1010.75592   | 50.4827 |
| 2      | 8.639         | BB   | 0.1955      | 1.05139e4    | 831.71912    | 49.5173 |

Additional Info : Peak(s) manually integrated

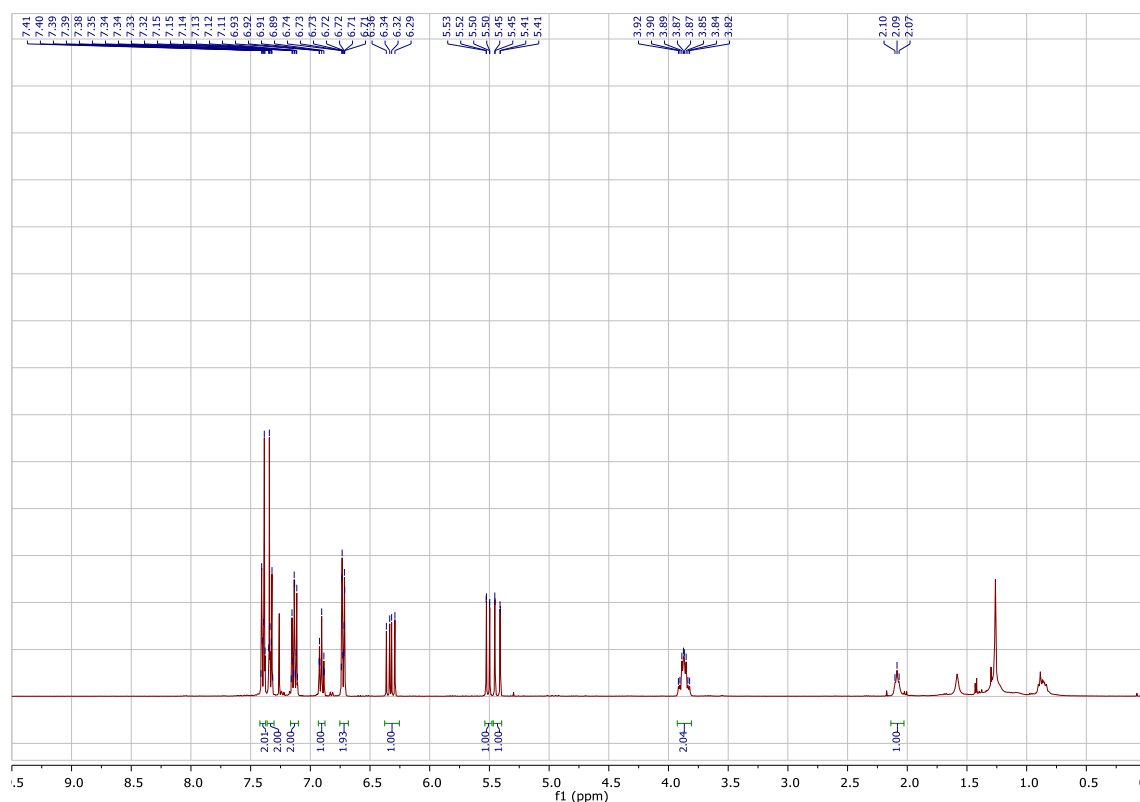


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 7.529         | BB   | 0.1704      | 1508.91357   | 134.99863    | 7.1503  |
| 2      | 8.708         | BB   | 0.2171      | 1.95940e4    | 1401.91418   | 92.8497 |



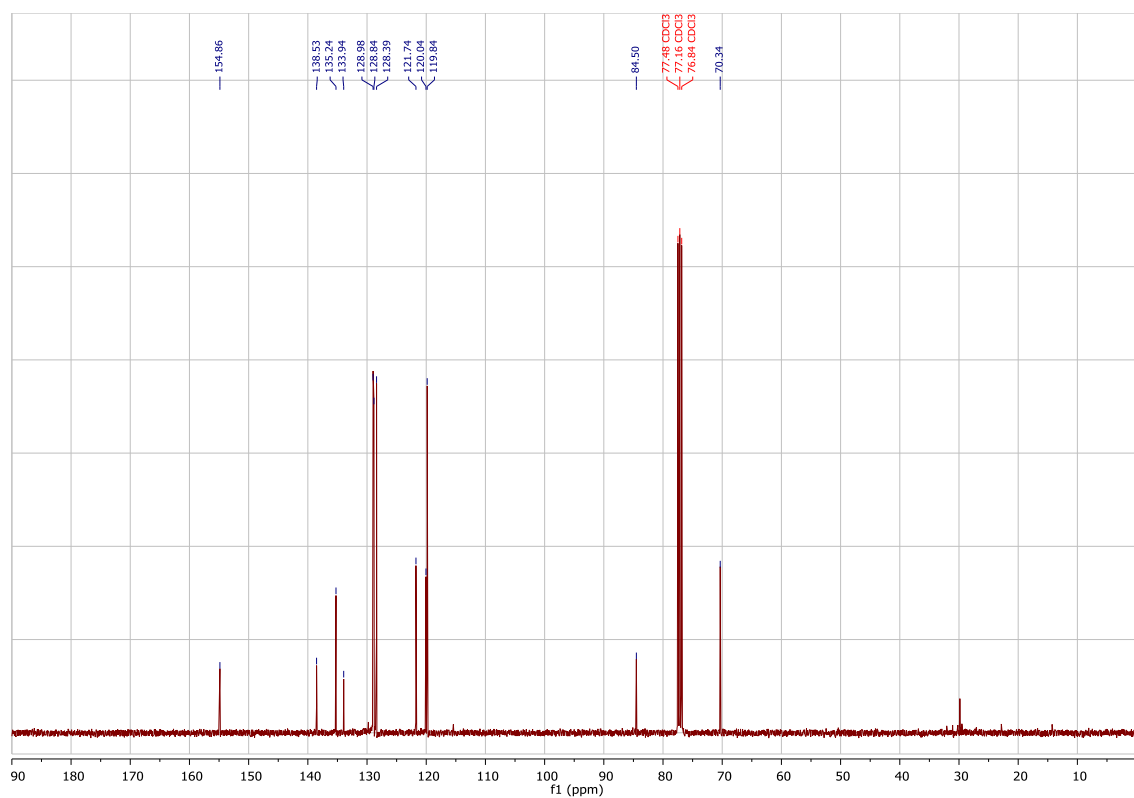
Scale: 0.2 mmol; isolated 34.5 mg (63% yield), light yellow oil, Hexane : EA = 50 : 1,  $R_f$  = 0.15

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ )



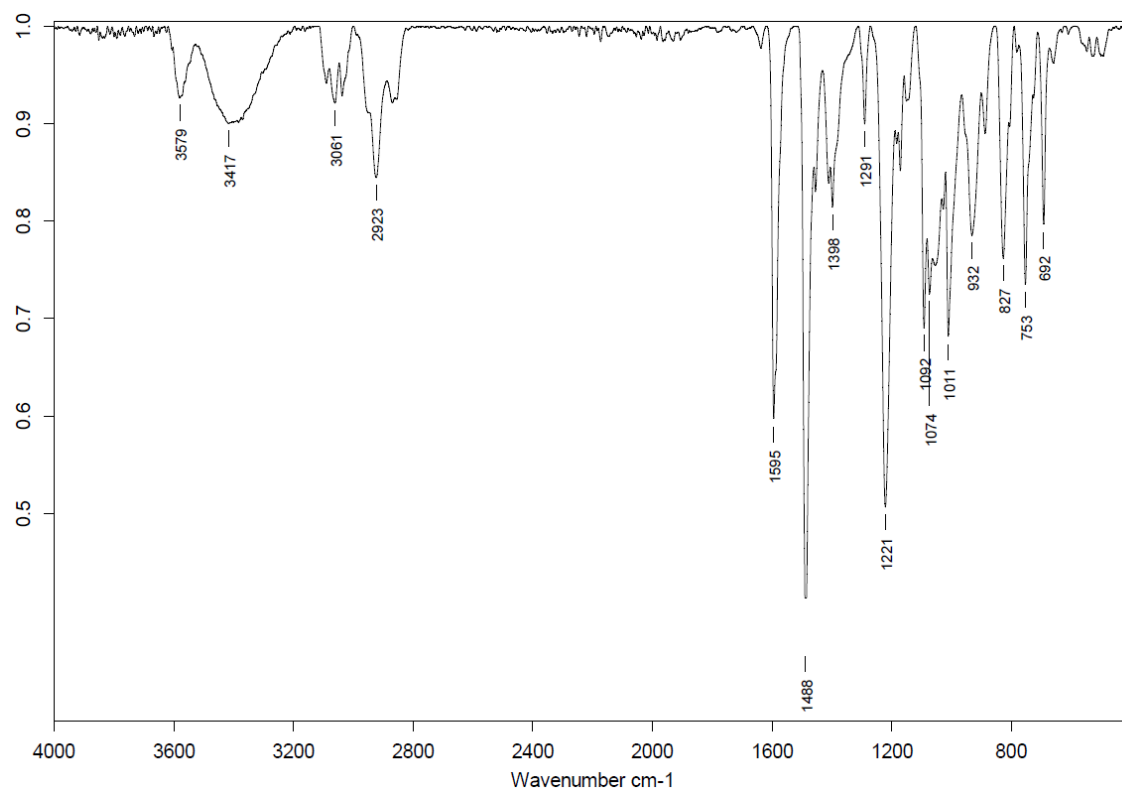
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 – 7.37 (m, 2H), 7.36 – 7.30 (m, 2H), 7.17 – 7.10 (m, 2H), 6.93 – 6.88 (m, 1H), 6.75 – 6.68 (m, 2H), 6.33 (dd,  $J$  = 17.5, 11.1 Hz, 1H), 5.51 (dd,  $J$  = 11.1, 0.9 Hz, 1H), 5.43 (dd,  $J$  = 17.5, 0.9 Hz, 1H), 3.87 (qd,  $J$  = 11.6, 5.4 Hz, 2H), 2.09 (t,  $J$  = 6.9 Hz, 1H).

<sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>)



<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 154.86, 138.53, 135.24, 133.94, 128.98, 128.84, 128.39, 121.74, 120.04, 119.84, 84.50, 70.34.

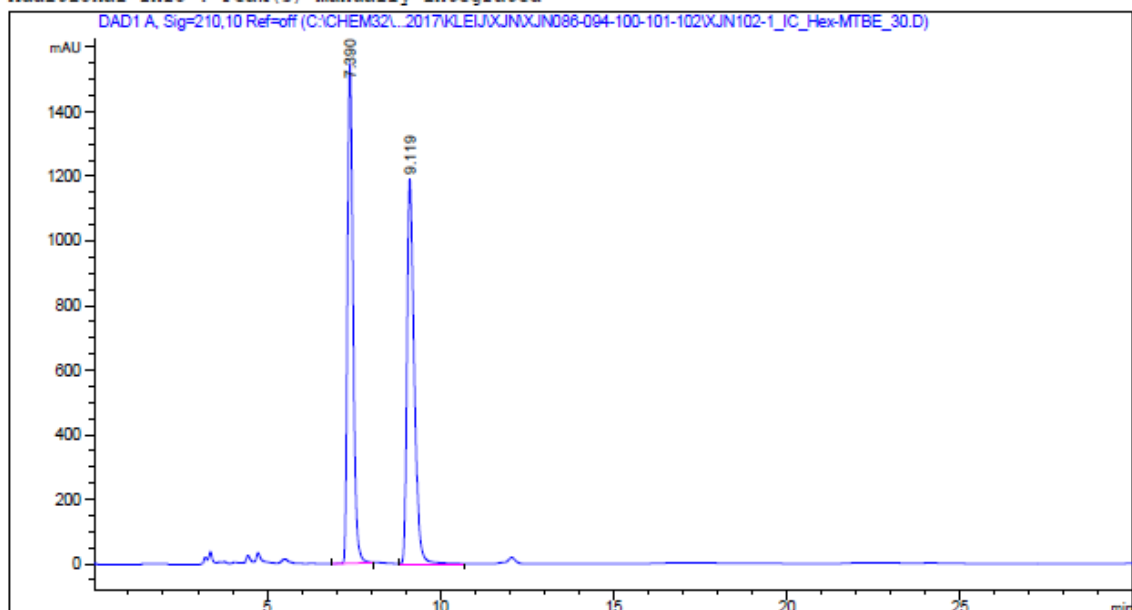
IR spectrum (neat)



**HRMS** (ESI<sup>+</sup>, MeOH): *m/z* calcd. 297.0653 (M + Na)<sup>+</sup>, found: 297.0662.

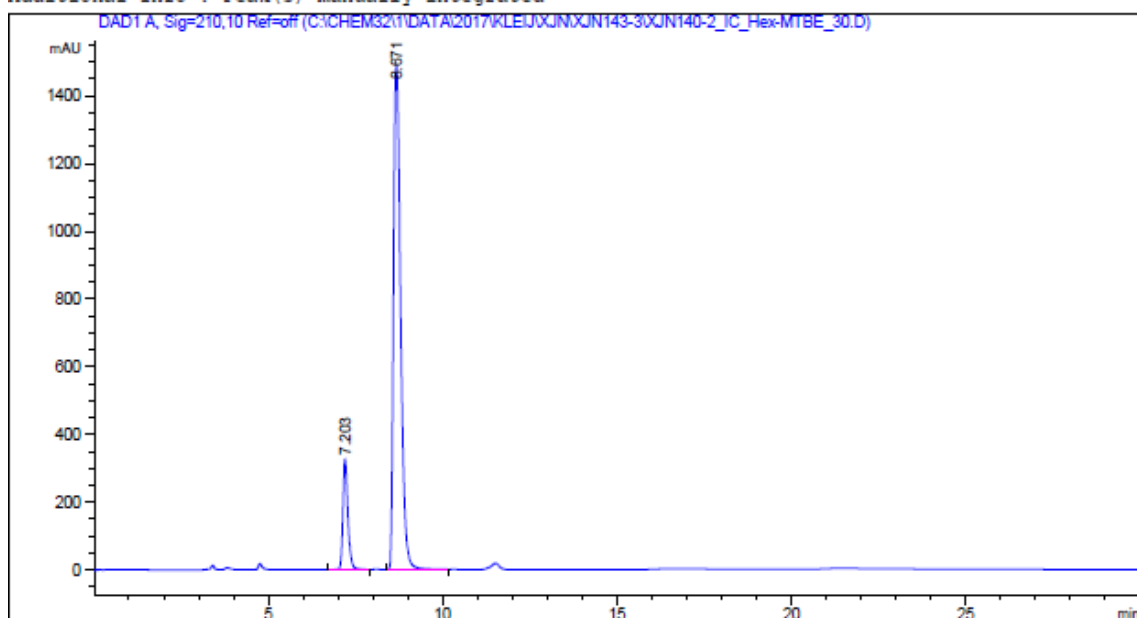
**HPLC conditions:** Chiralpak IC 250 × 4.6 mm, 5 μm, Hex/MTBE = 70 : 30, 1 mL/min;  
86 : 14 *er*;  $[\alpha]_D^{25} = -38.00$  ( $c = 0.09$ , CHCl<sub>3</sub>).

Additional Info : Peak(s) manually integrated

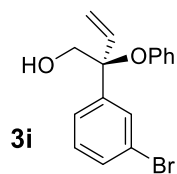


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 7.390         | BB   | 0.1707      | 1.70563e4    | 1545.73035   | 49.2974 |
| 2      | 9.119         | BB   | 0.2254      | 1.75425e4    | 1194.12488   | 50.7026 |

Additional Info : Peak(s) manually integrated

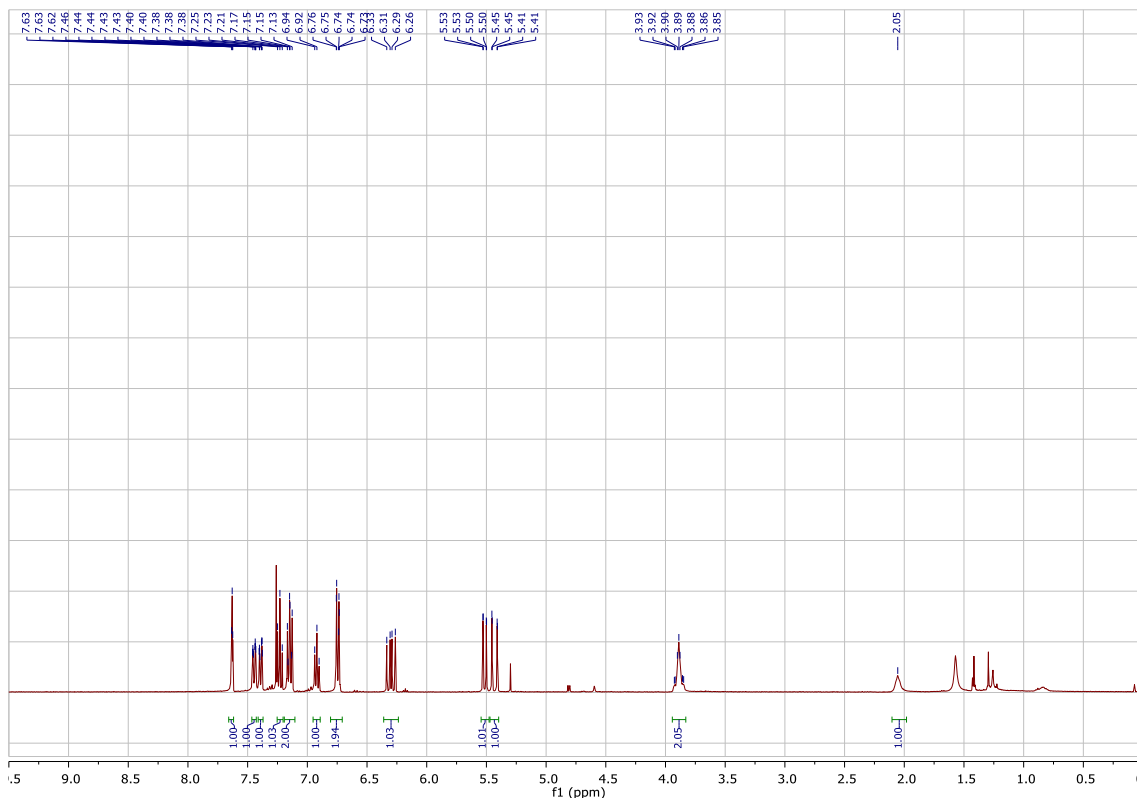


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 7.203         | BB   | 0.1570      | 3324.09351   | 325.69645    | 13.8170 |
| 2      | 8.671         | BB   | 0.2147      | 2.07339e4    | 1486.62756   | 86.1830 |



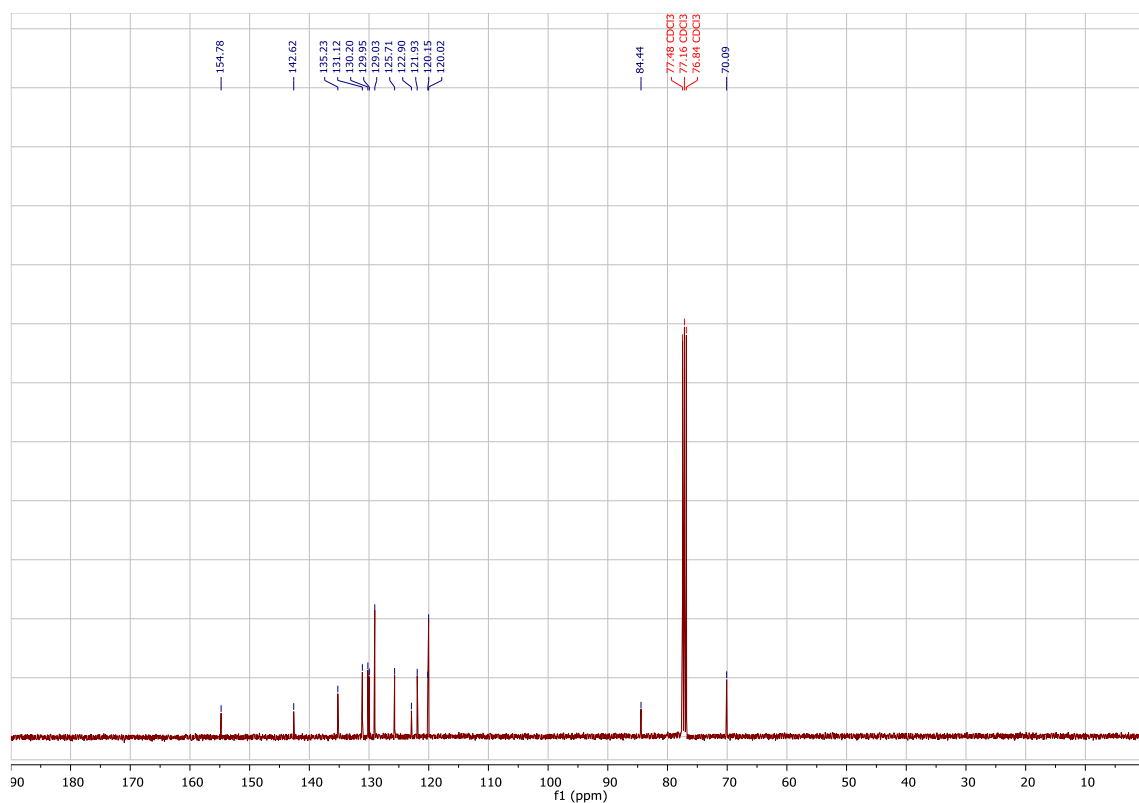
Scale: 0.2 mmol; isolated 31.1 mg (49% yield), yellow solid, Hexane : EA = 50 : 1,  $R_f$  = 0.15

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ )



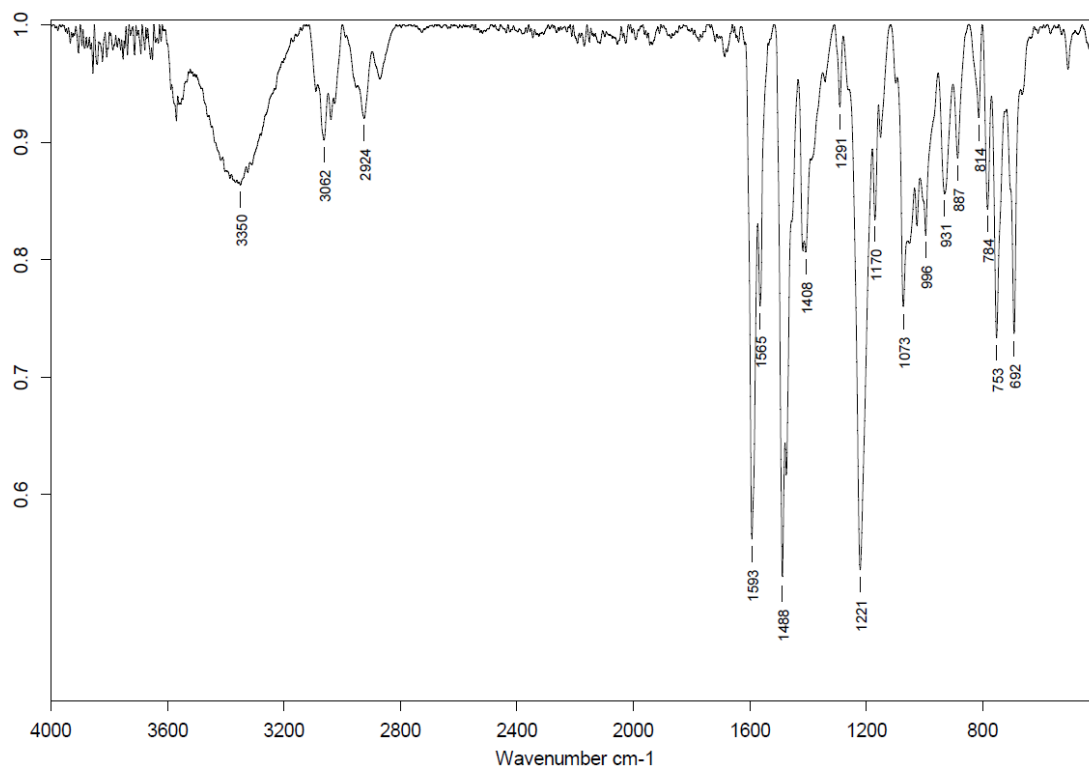
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 (t,  $J$  = 1.8 Hz, 1H), 7.45 (m, 1H), 7.39 (m, 1H), 7.23 (m, 1H), 7.19 – 7.10 (m, 2H), 6.92 (t,  $J$  = 7.4 Hz, 1H), 6.81 – 6.71 (m, 2H), 6.30 (dd,  $J$  = 17.5, 11.1 Hz, 1H), 5.51 (dd,  $J$  = 11.1, 0.9 Hz, 1H), 5.43 (dd,  $J$  = 17.5, 0.9 Hz, 1H), 3.88 (q,  $J$  = 8.4, 6.7 Hz, 2H), 2.05 (s, 1H).

<sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>)



<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  154.78, 142.62, 135.23, 131.12, 130.20, 129.95, 129.03, 125.71, 122.90, 121.93, 120.15, 120.02, 84.44, 70.09.

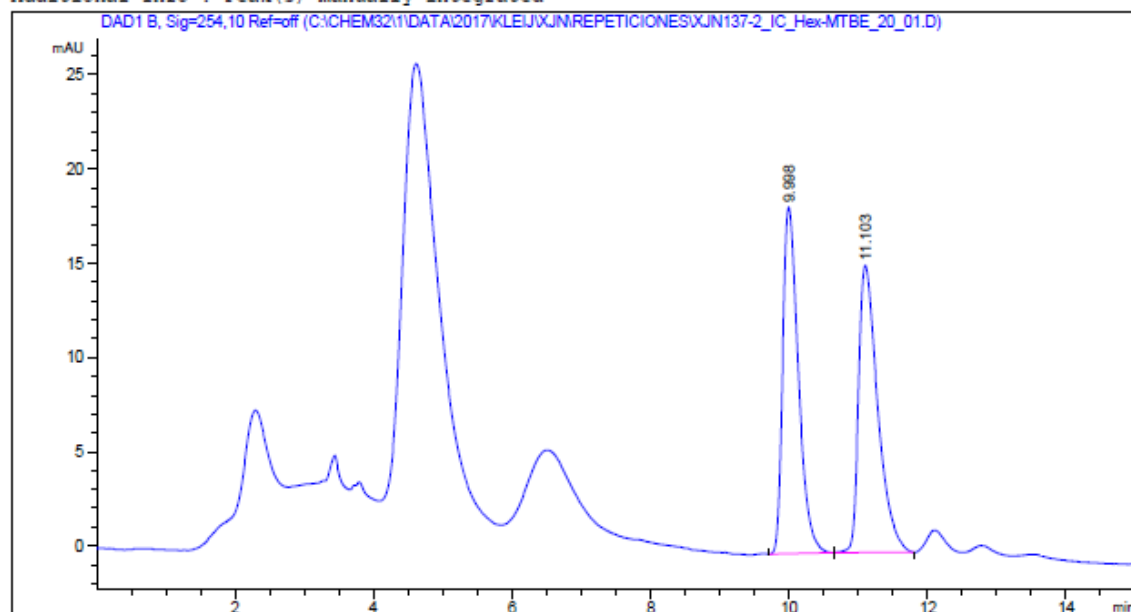
IR spectrum (neat)



HRMS (ESI<sup>+</sup>, MeOH):  $m/z$  calcd. 341.0148 (M + Na)<sup>+</sup>, found: 341.0143.

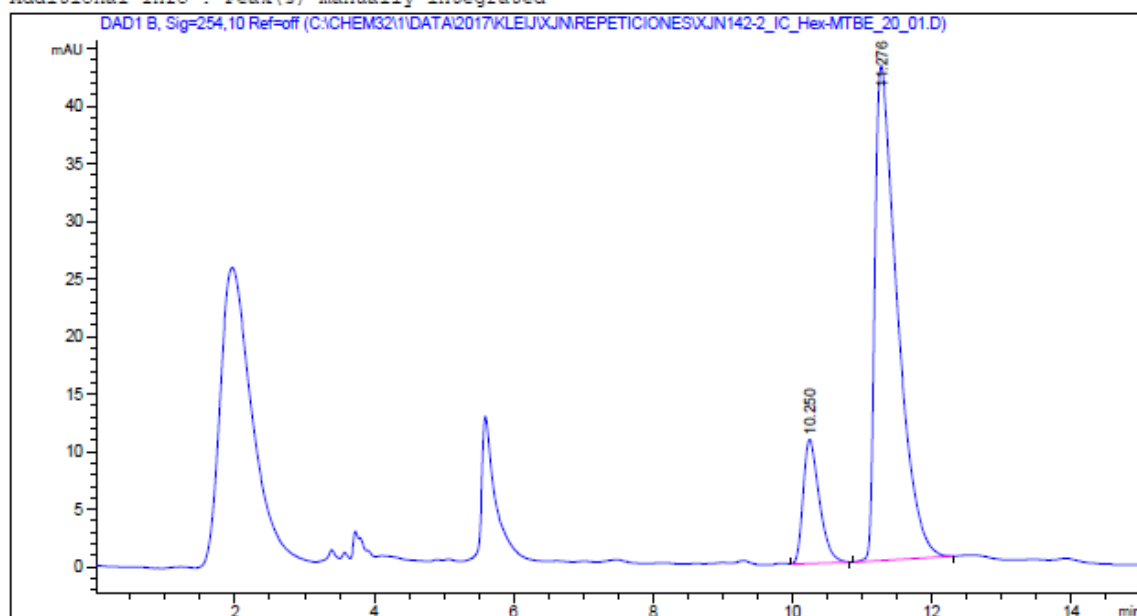
**HPLC conditions:** Chiralpak IC 250 x 4.6 mm, 5  $\mu$ m, Hex/MTBE = 80 : 20, 1 mL/min;  
85 : 15 *er*;  $[\alpha]_D^{25} = -26.16$  ( $c = 0.10$ ,  $\text{CHCl}_3$ ).

Additional Info : Peak(s) manually integrated

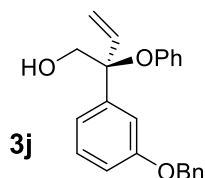


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 9.998         | BB   | 0.2387      | 287.77426    | 18.37293     | 49.6360 |
| 2      | 11.103        | BB   | 0.2918      | 291.99509    | 15.21965     | 50.3640 |

Additional Info : Peak(s) manually integrated

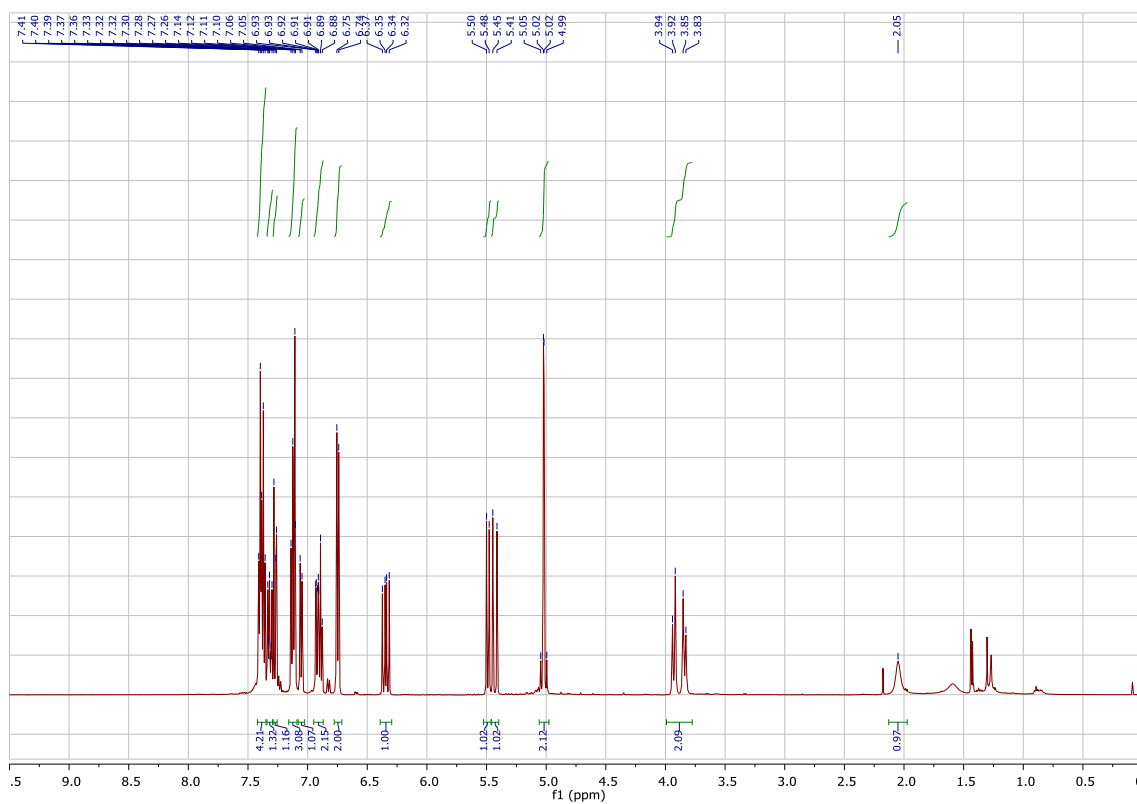


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 10.250        | BB   | 0.2485      | 174.01523    | 10.77020     | 15.3657 |
| 2      | 11.276        | BB   | 0.3284      | 958.47876    | 42.95053     | 84.6343 |



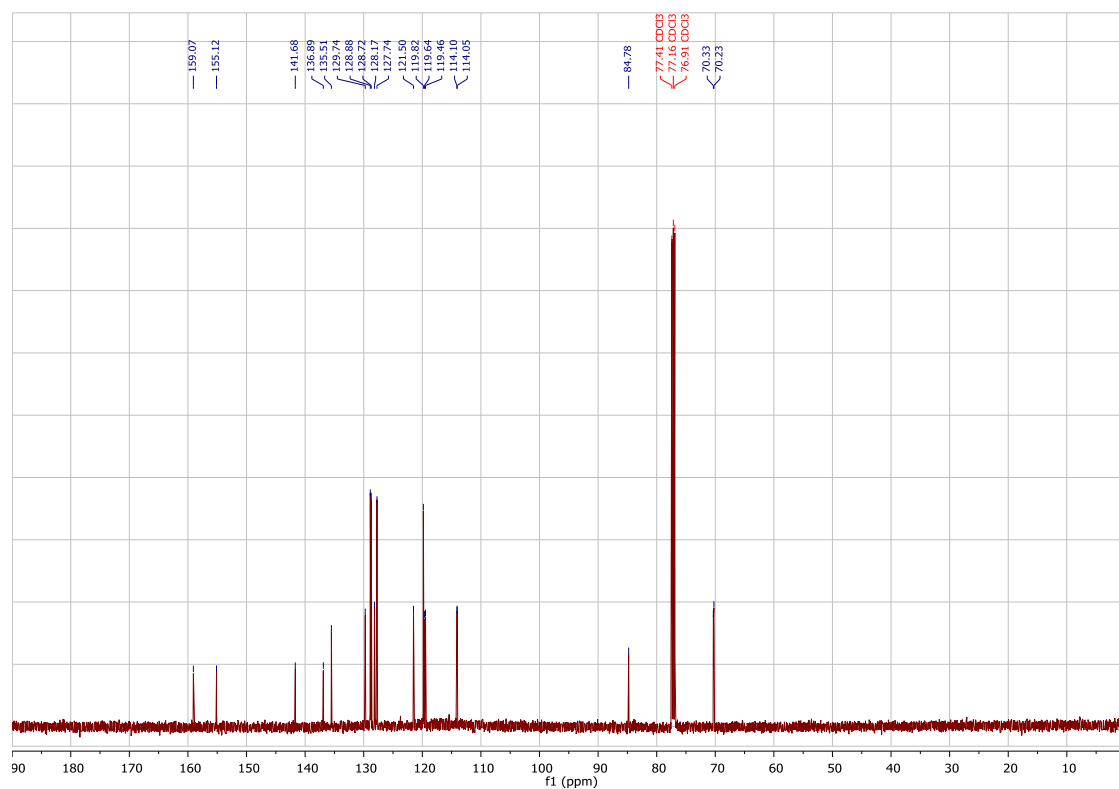
Scale: 0.2 mmol; isolated 47.0 mg (68% yield), light yellow solid, Hexane : EA = 50 : 1,  $R_f = 0.10$

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ )



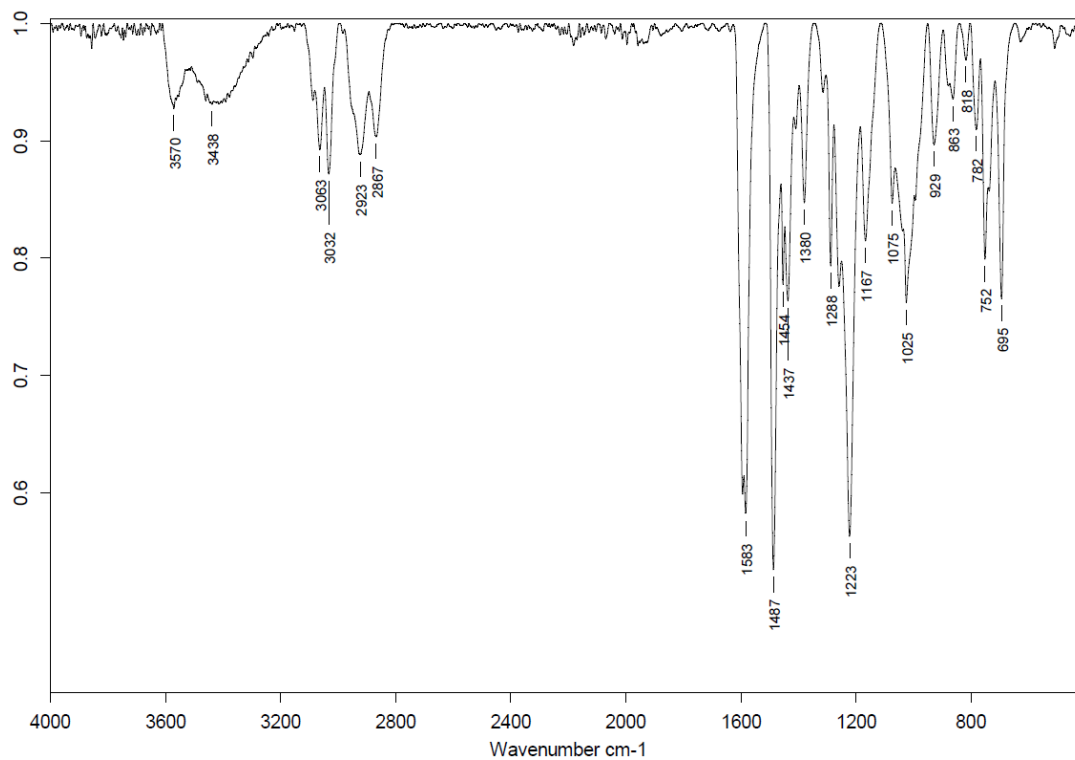
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41 (m, 4H), 7.37 – 7.32 (m, 1H), 7.32 – 7.28 (m, 1H), 7.19 – 7.12 (m, 3H), 7.08 (d,  $J = 7.8$  Hz, 1H), 6.98 – 6.90 (m, 2H), 6.77 (d,  $J = 7.9$  Hz, 2H), 6.37 (dd,  $J = 17.5, 11.1$  Hz, 1H), 5.52 (d,  $J = 11.1$  Hz, 1H), 5.46 (d,  $J = 17.5$  Hz, 1H), 5.05 (d,  $J = 2.3$  Hz, 2H), 4.02 – 3.80 (m, 2H), 2.08 (s, 1H).

<sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>)



<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  159.07, 155.12, 141.68, 136.89, 135.51, 129.74, 128.88, 128.72, 128.17, 127.74, 121.50, 119.82, 119.64, 119.46, 114.10, 114.05, 84.78, 70.33, 70.23.

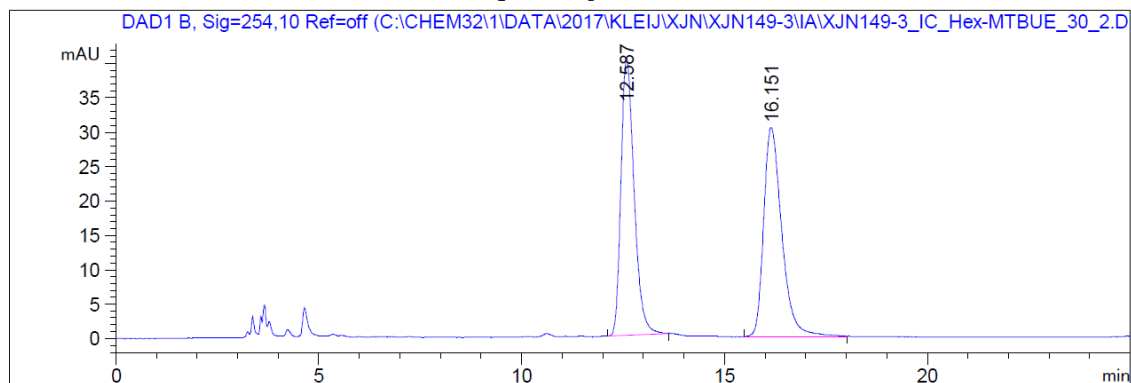
IR spectrum (neat)



HRMS (ESI<sup>+</sup>, MeOH):  $m/z$  calcd. 369.1461 (M + Na)<sup>+</sup>, found: 369.1463.

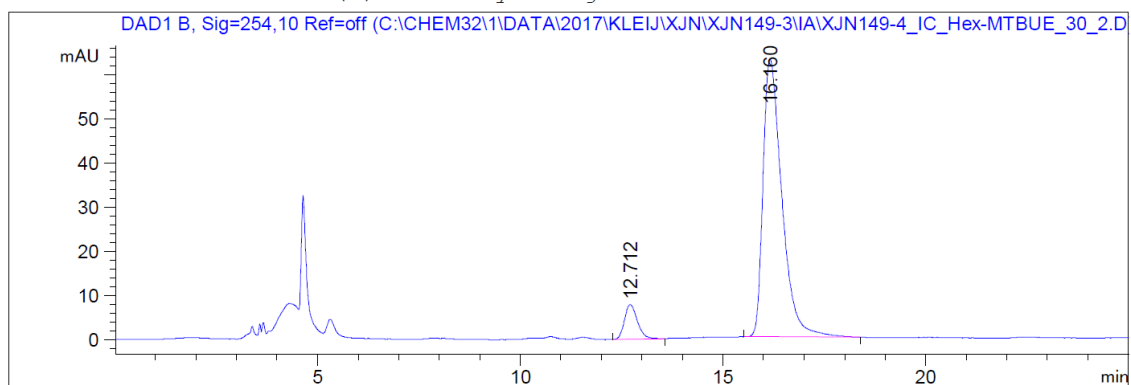
**HPLC conditions:** Chiralpak IC 250 × 4.6 mm, 5 μm, Hex/MTBE = 70 : 30, 1 mL/min;  
92 : 8 er;  $[\alpha]_D^{25} = -36.06$  ( $c = 0.10$ , CHCl<sub>3</sub>).

Additional Info : Peak(s) manually integrated

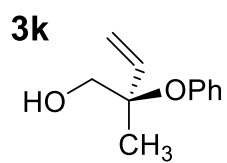


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 12.587        | BB   | 0.3434      | 904.14587    | 40.35524     | 49.0357 |
| 2      | 16.151        | BB   | 0.4668      | 939.70599    | 30.38390     | 50.9643 |

Additional Info : Peak(s) manually integrated

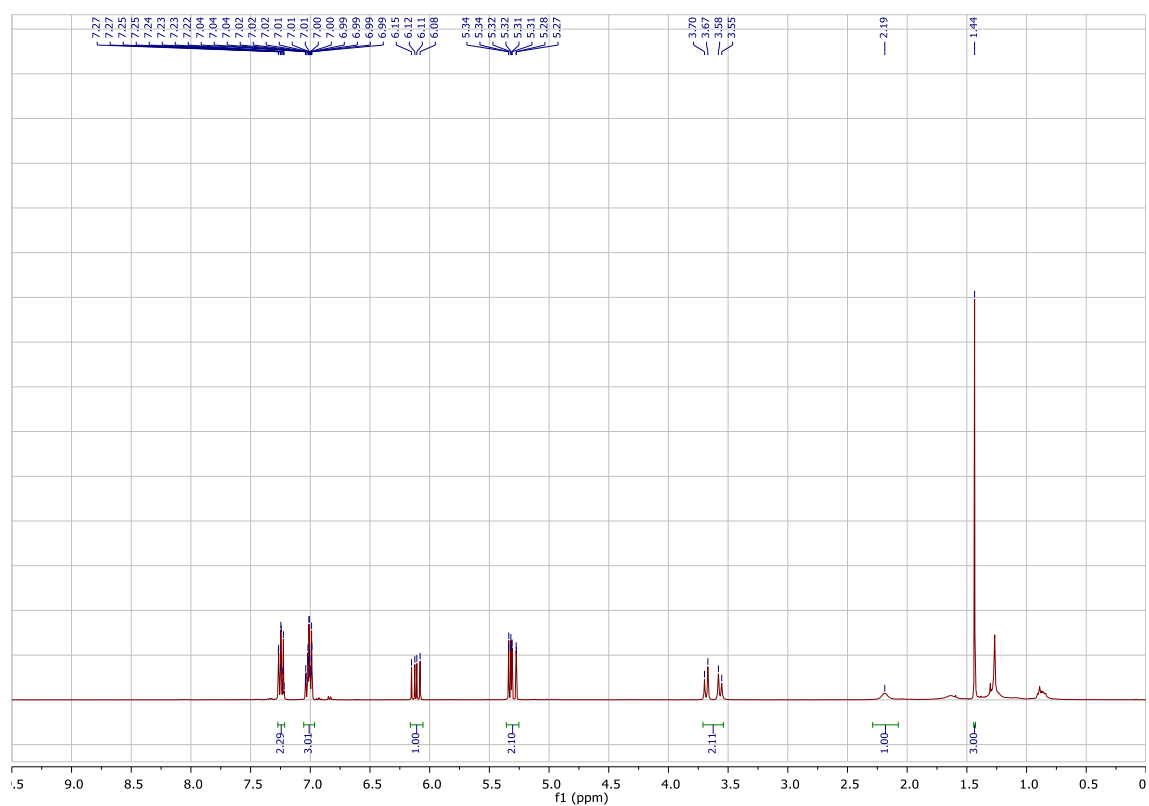


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 12.712        | BB   | 0.3329      | 175.26665    | 7.89767      | 7.9127  |
| 2      | 16.160        | BB   | 0.4903      | 2039.75000   | 62.90194     | 92.0873 |



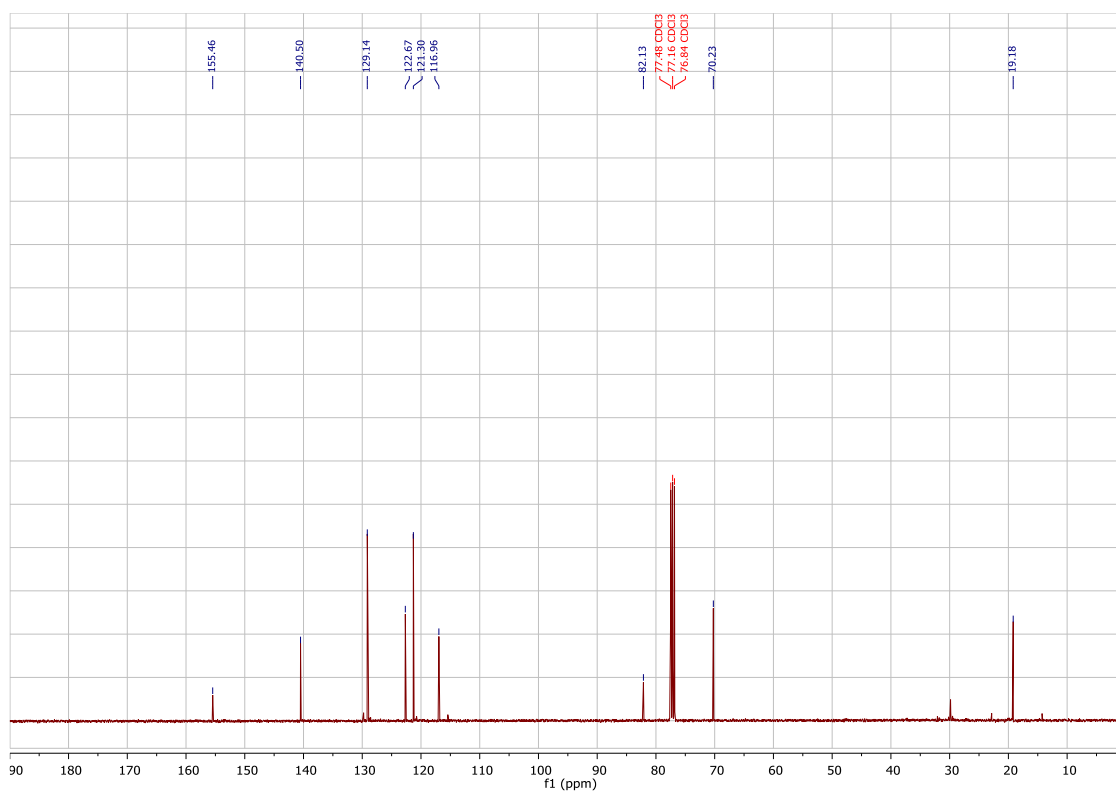
Scale: 0.2 mmol; isolated 29.5 mg (83% yield), light yellow oil, Hexane : EA = 50 : 1,  $R_f$  = 0.15

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ )



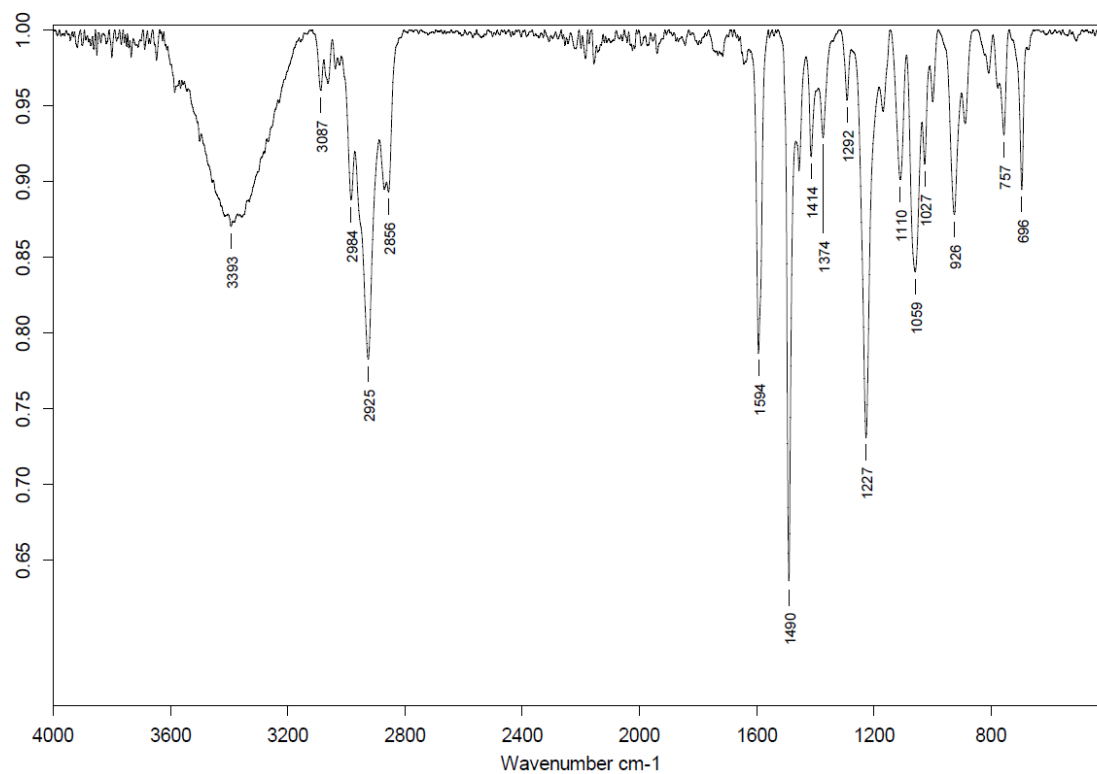
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25 (m, 2H), 7.01 (m, 3H), 6.12 (dd,  $J$  = 17.6, 11.1 Hz, 1H), 5.36 – 5.25 (m, 2H), 3.71 – 3.54 (m, 2H), 2.19 (s, 1H), 1.44 (s, 3H).

$^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ )



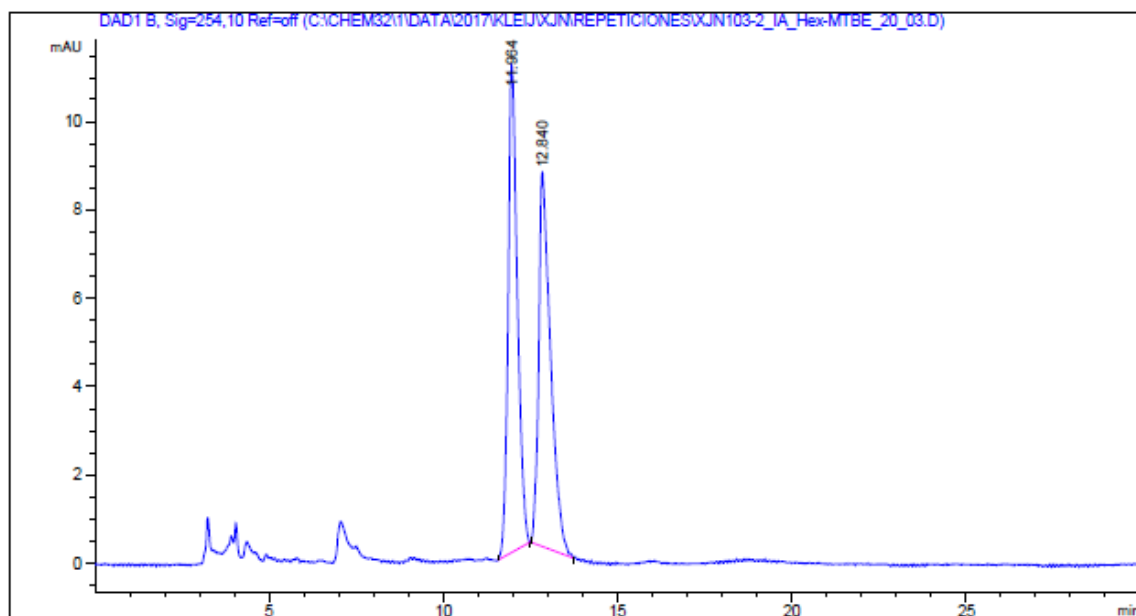
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  155.46, 140.50, 129.14, 122.67, 121.30, 116.96, 82.13, 70.23, 19.18.

IR spectrum (neat)



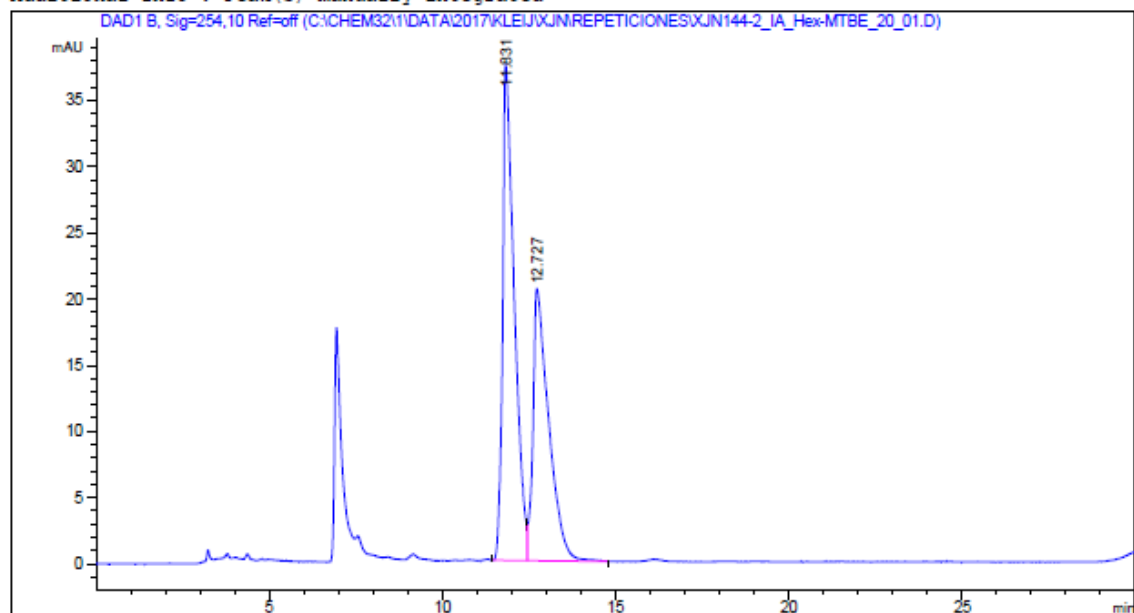
HRMS (ESI $^{+}$ , MeOH):  $m/z$  calcd. 201.0886 ( $\text{M} + \text{Na}$ ) $^{+}$ , found: 201.0883.

**HPLC conditions:** Chiralpak IA 250 × 4.6 mm, 5 μm, Hex/MTBE = 80:20, 1 mL/min; 57.5 : 42.5 *er*;  $[\alpha]_D^{25} = -1.22$  ( $c = 0.09$ , CHCl<sub>3</sub>).

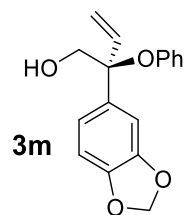


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 11.964        | BB   | 0.2664      | 203.28680    | 11.06008     | 50.2305 |
| 2      | 12.840        | BB   | 0.3232      | 201.42107    | 8.47600      | 49.7695 |

Additional Info : Peak(s) manually integrated

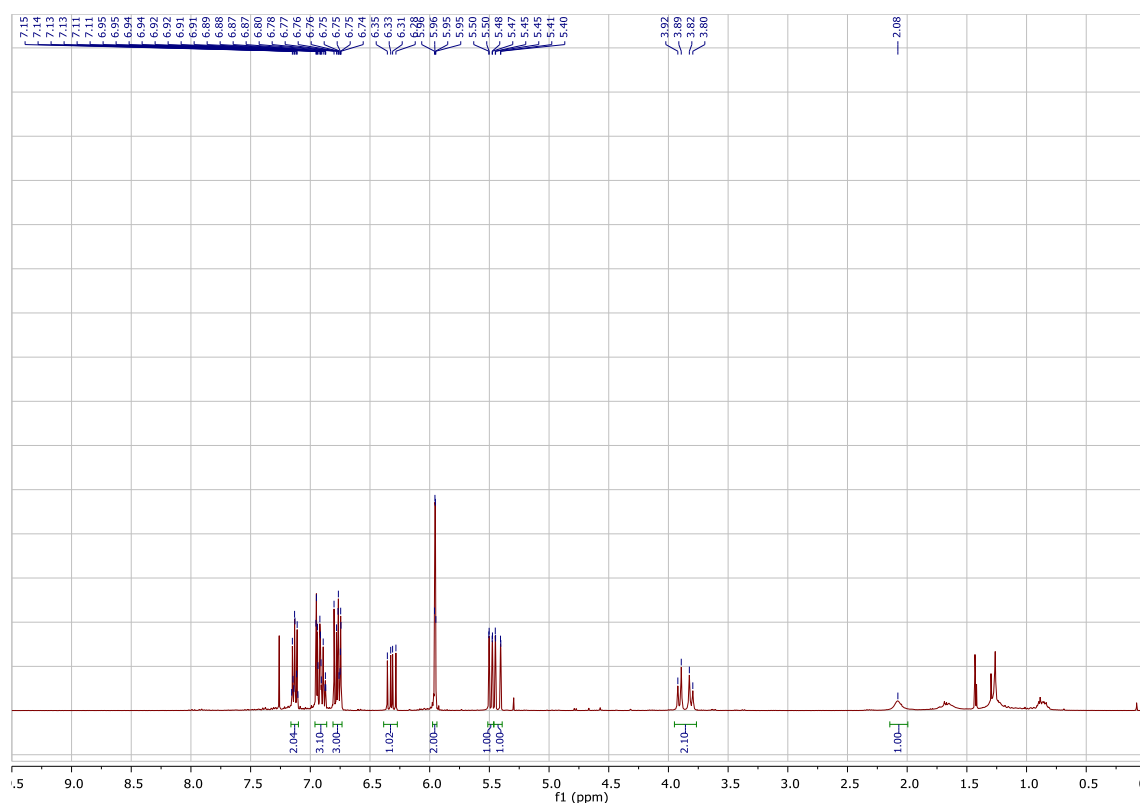


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 11.831        | BV   | 0.3293      | 878.45435    | 37.50002     | 57.5500 |
| 2      | 12.727        | VB   | 0.4297      | 647.96582    | 20.55854     | 42.4500 |



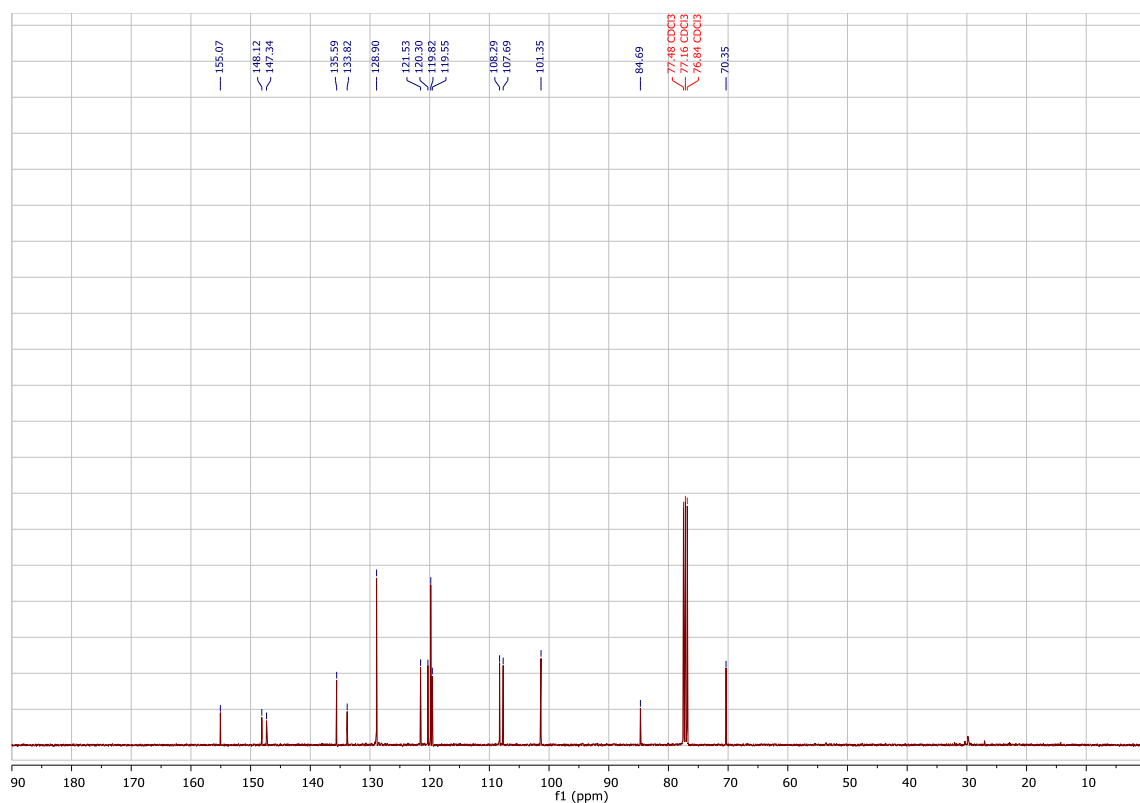
Scale: 0.2 mmol; isolated 43.7 mg (77% yield), light yellow solid, Hexane : EA = 50 : 1,  $R_f = 0.15$

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ )



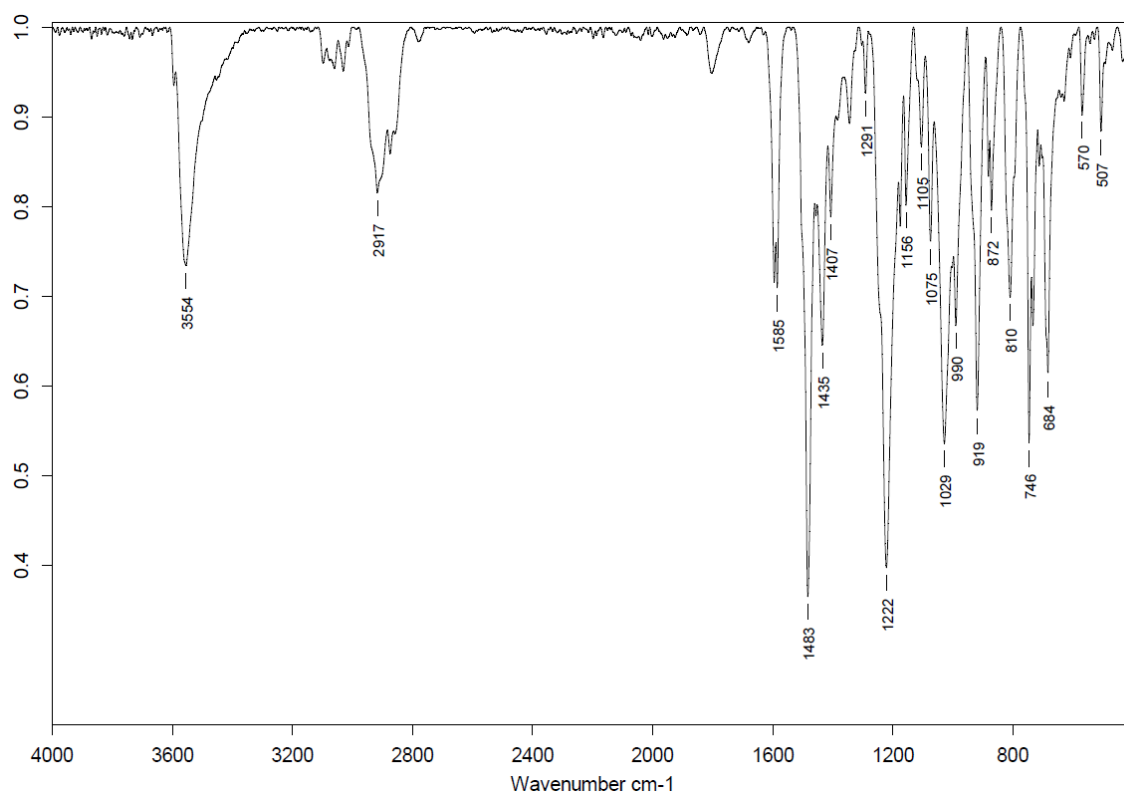
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.13 (m, 2H), 6.96 – 6.86 (m, 3H), 6.81 – 6.73 (m, 3H), 6.32 (dd,  $J = 17.5, 11.1$  Hz, 1H), 5.95 (q,  $J = 1.4$  Hz, 2H), 5.49 (dd,  $J = 11.1, 1.0$  Hz, 1H), 5.43 (dd,  $J = 17.5, 1.0$  Hz, 1H), 3.95 – 3.77 (m, 2H), 2.08 (s, 1H).

<sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>)



<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 155.07, 148.12, 147.34, 135.59, 133.82, 128.90, 121.53, 120.30, 119.82, 119.55, 108.29, 107.69, 101.35, 84.69, 70.35.

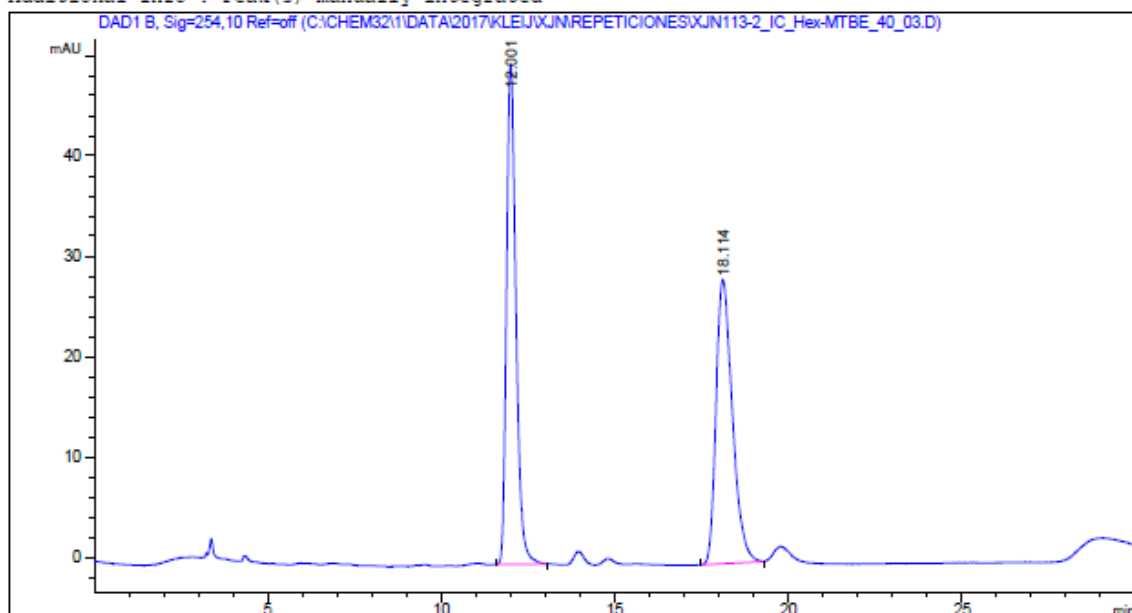
IR spectrum (neat)



HRMS (ESI<sup>+</sup>, MeOH): *m/z* calcd. 307.0941 (M + Na)<sup>+</sup>, found: 307.0940.

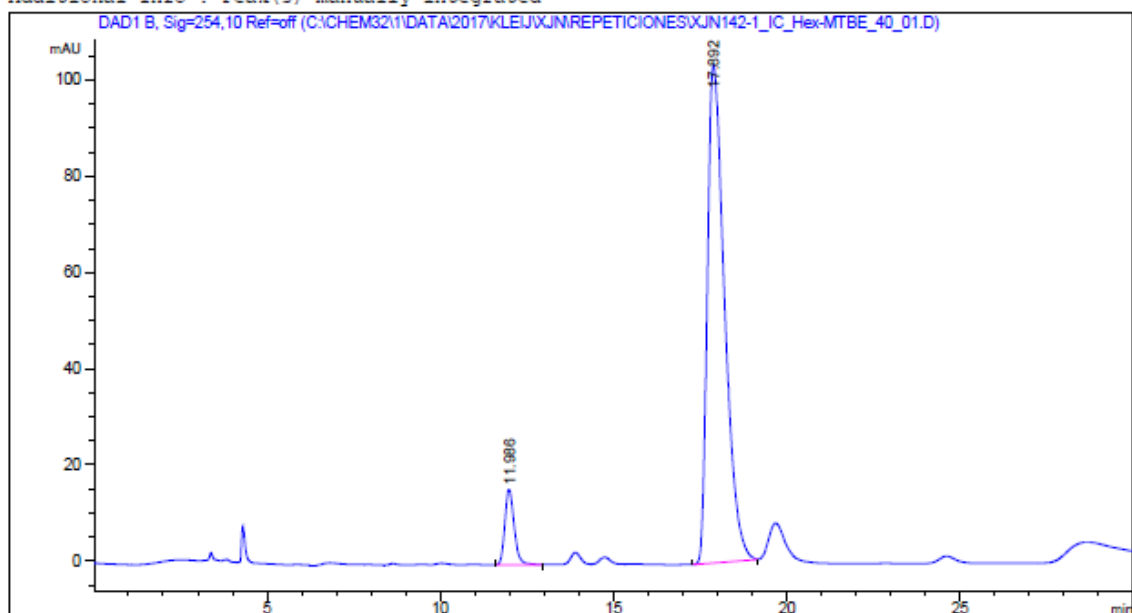
**HPLC conditions:** Chiralpak IC 250 × 4.6 mm, 5 μm, Hex/MTBE = 60 : 40, 1 mL/min;  
92 : 8 er;  $[\alpha]_D^{25} = -45.14$  ( $c = 0.12$ ,  $\text{CHCl}_3$ ).

Additional Info : Peak(s) manually integrated

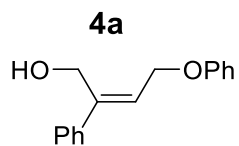


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 12.001        | BB   | 0.2898      | 937.01239    | 49.73335     | 50.3473 |
| 2      | 18.114        | BB   | 0.5031      | 924.08386    | 28.29279     | 49.6527 |

Additional Info : Peak(s) manually integrated

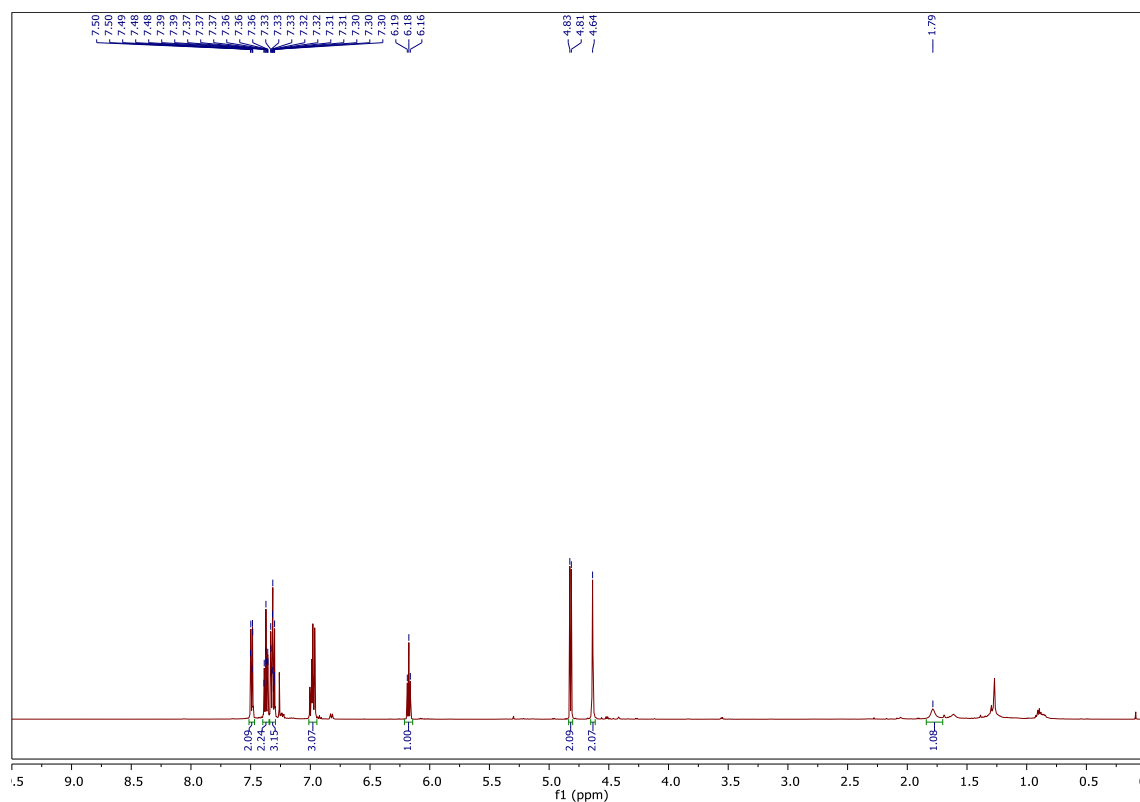


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 11.986        | BB   | 0.2861      | 293.98517    | 15.72703     | 7.6229  |
| 2      | 17.892        | BB   | 0.5279      | 3562.62305   | 103.42551    | 92.3771 |



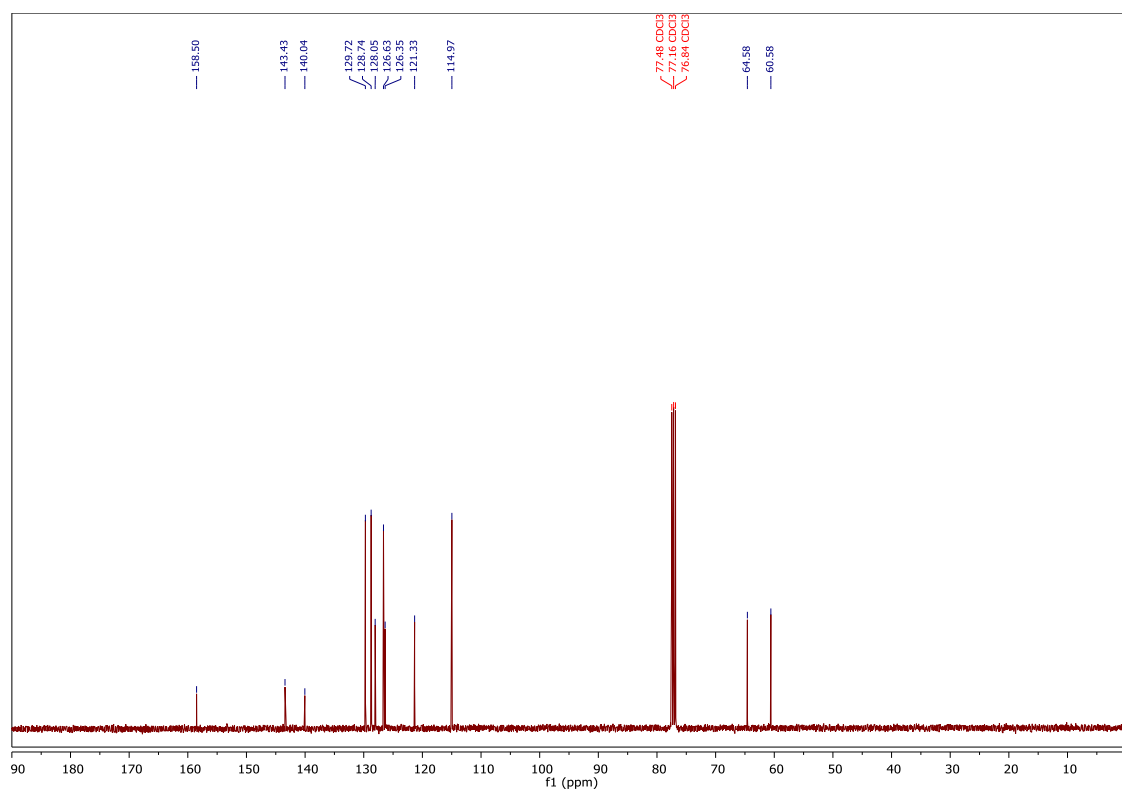
Scale: 0.2 mmol; isolated 45.5 mg (95% yield), light yellow oil, Hexane : EA = 10 : 1,  $R_f$  = 0.2

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ )



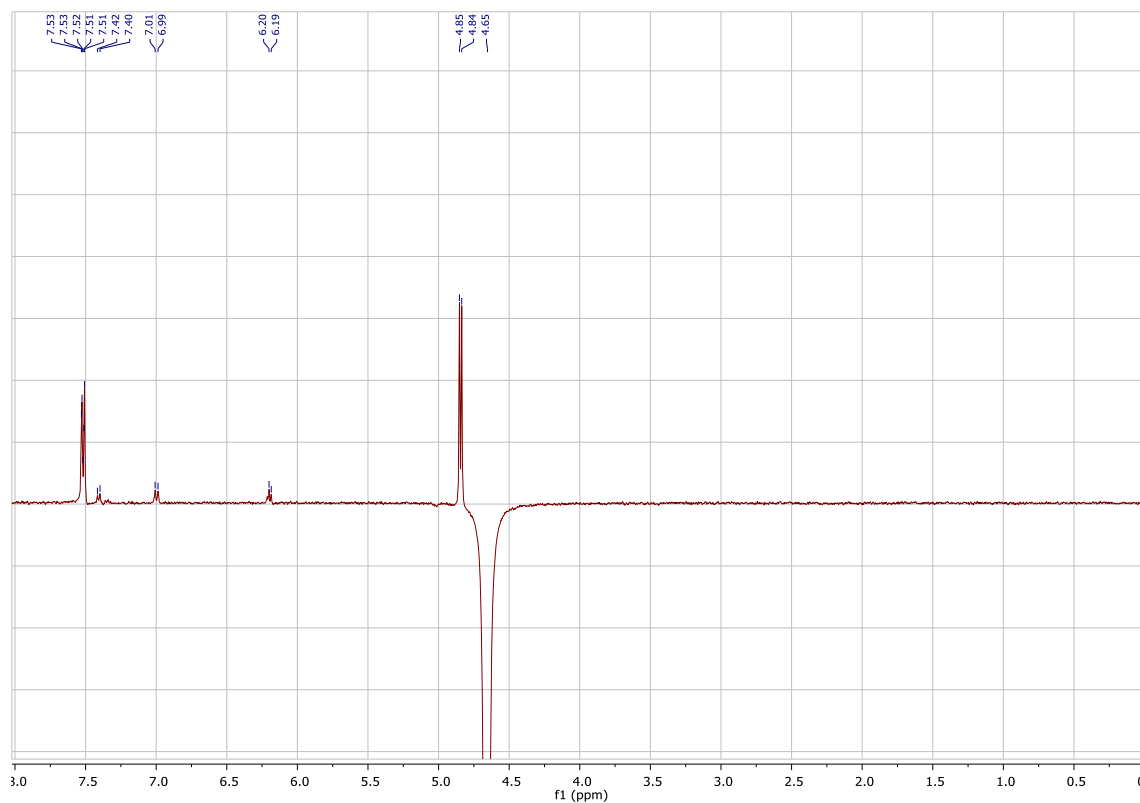
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51 – 7.47 (m, 2H), 7.40 – 7.35 (m, 2H), 7.34 – 7.29 (m, 3H), 7.01 – 6.95 (m, 3H), 6.18 (t,  $J$  = 6.4 Hz, 1H), 4.82 (d,  $J$  = 6.4 Hz, 2H), 4.64 (s, 2H), 1.79 (s, 1H).

$^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ )

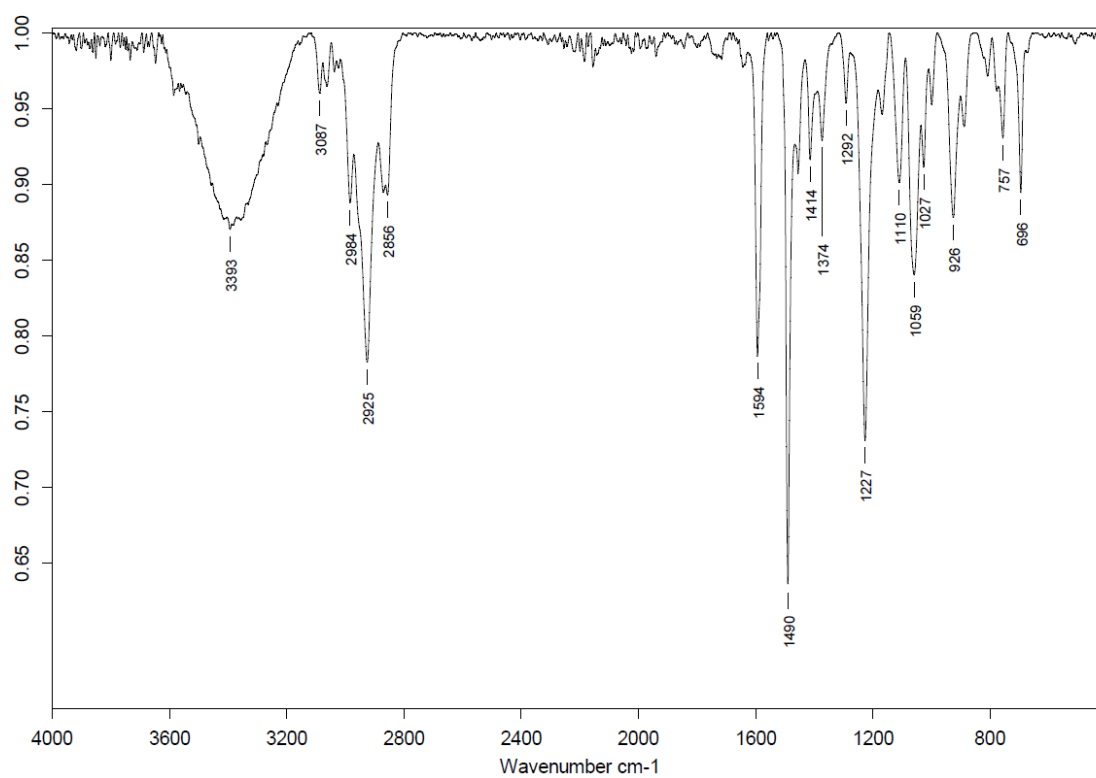


$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.50, 143.43, 140.04, 129.72, 128.74, 128.05, 126.63, 126.35, 121.33, 114.97, 77.48, 77.16, 76.84, 64.58, 60.58.

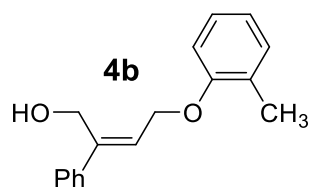
$^1\text{H}$ -Selective 1D NOESY ( $\text{CDCl}_3$ )



IR spectrum (neat)

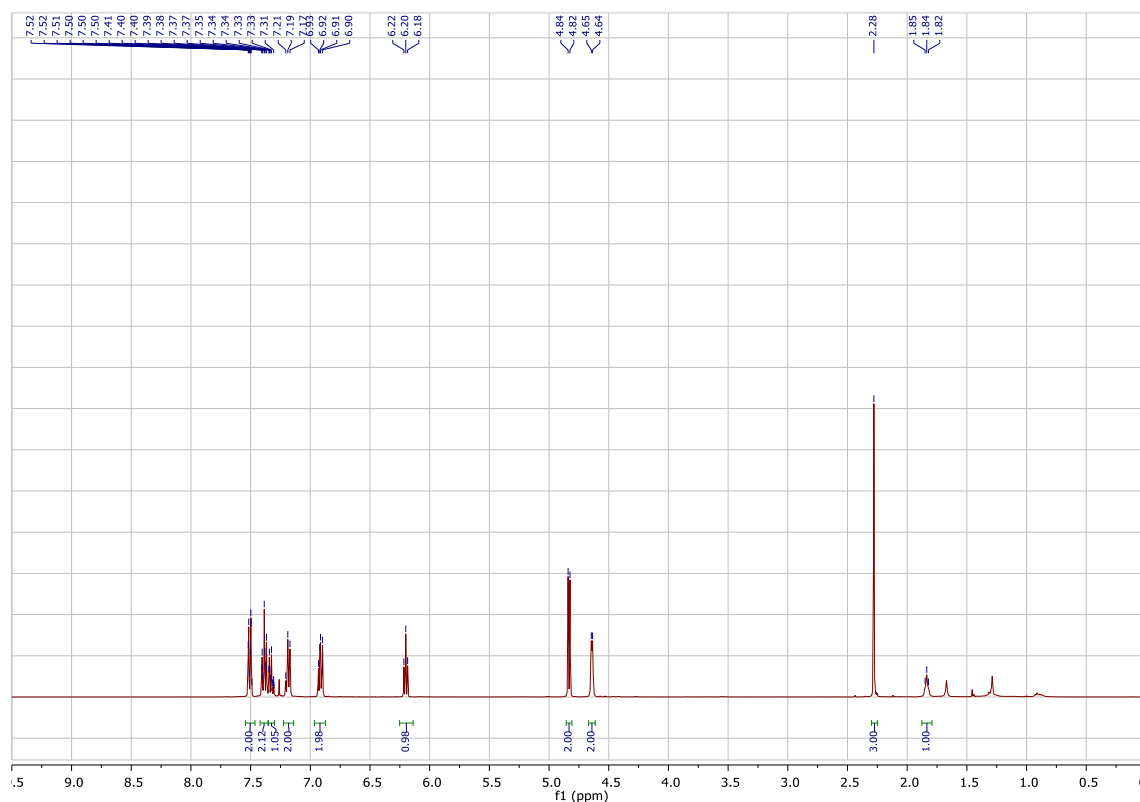


**HRMS** (ESI<sup>+</sup>, MeOH):  $m/z$  calcd. 263.1043 ( $M + Na$ )<sup>+</sup>, found: 263.1042.



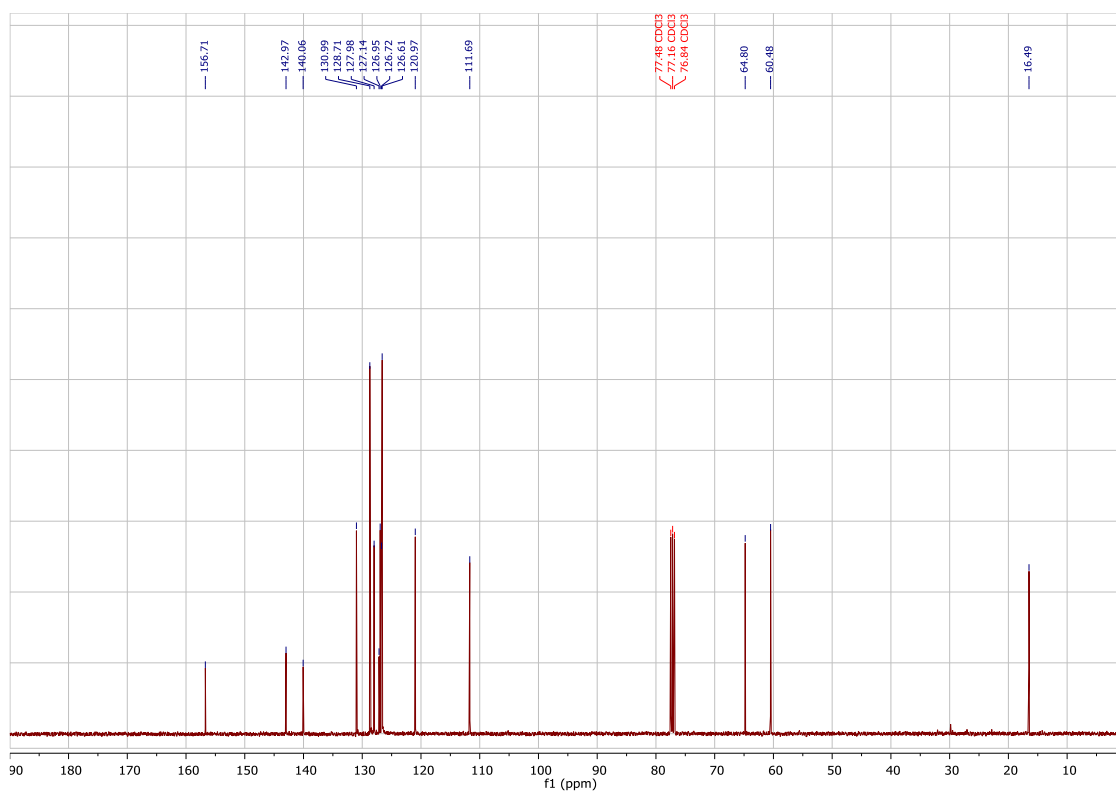
Scale: 0.2 mmol; isolated 46.2 mg (91% yield), light yellow liquid, Hexane : EA = 10 : 1,  $R_f = 0.2$

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ )



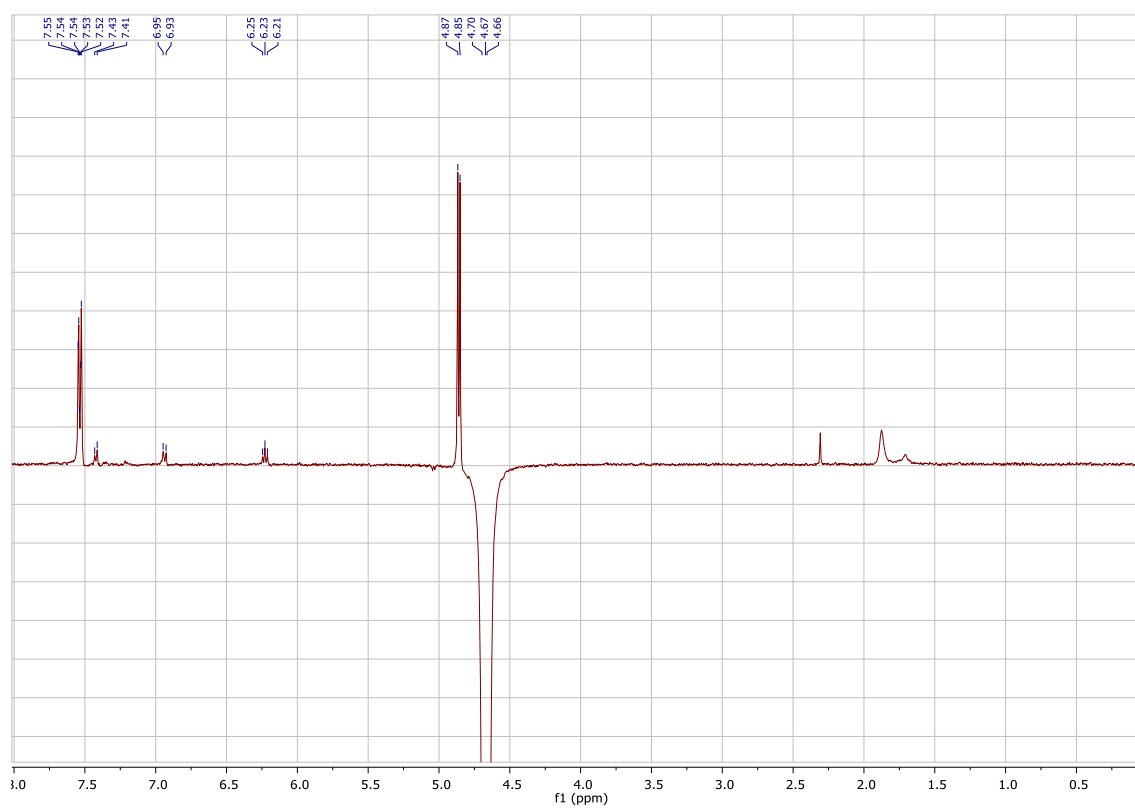
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 – 7.46 (m, 2H), 7.42 – 7.35 (m, 2H), 7.35 – 7.30 (m, 1H), 7.19 (t,  $J = 7.0$  Hz, 2H), 6.97 – 6.87 (m, 2H), 6.20 (t,  $J = 6.3$  Hz, 1H), 4.83 (d,  $J = 6.3$  Hz, 2H), 4.64 (d,  $J = 4.3$  Hz, 2H), 2.28 (s, 3H), 1.84 (t,  $J = 5.5$  Hz, 1H).

$^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ )

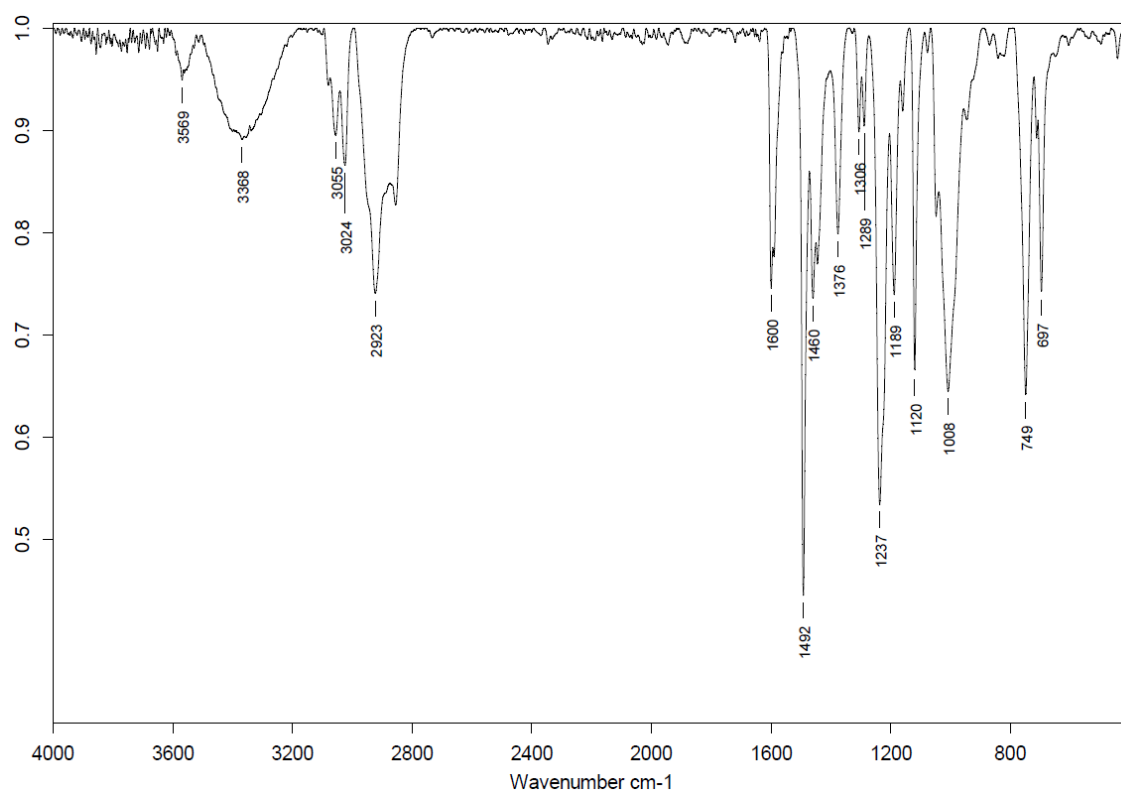


$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  156.71, 142.97, 140.06, 130.99, 128.71, 127.98, 127.14, 126.95, 126.72, 126.61, 120.97, 111.69, 64.80, 60.48, 16.49.

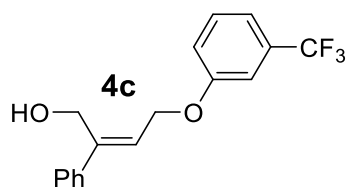
$^1\text{H}$ -Selective 1D NOESY ( $\text{CDCl}_3$ )



IR spectrum (neat)

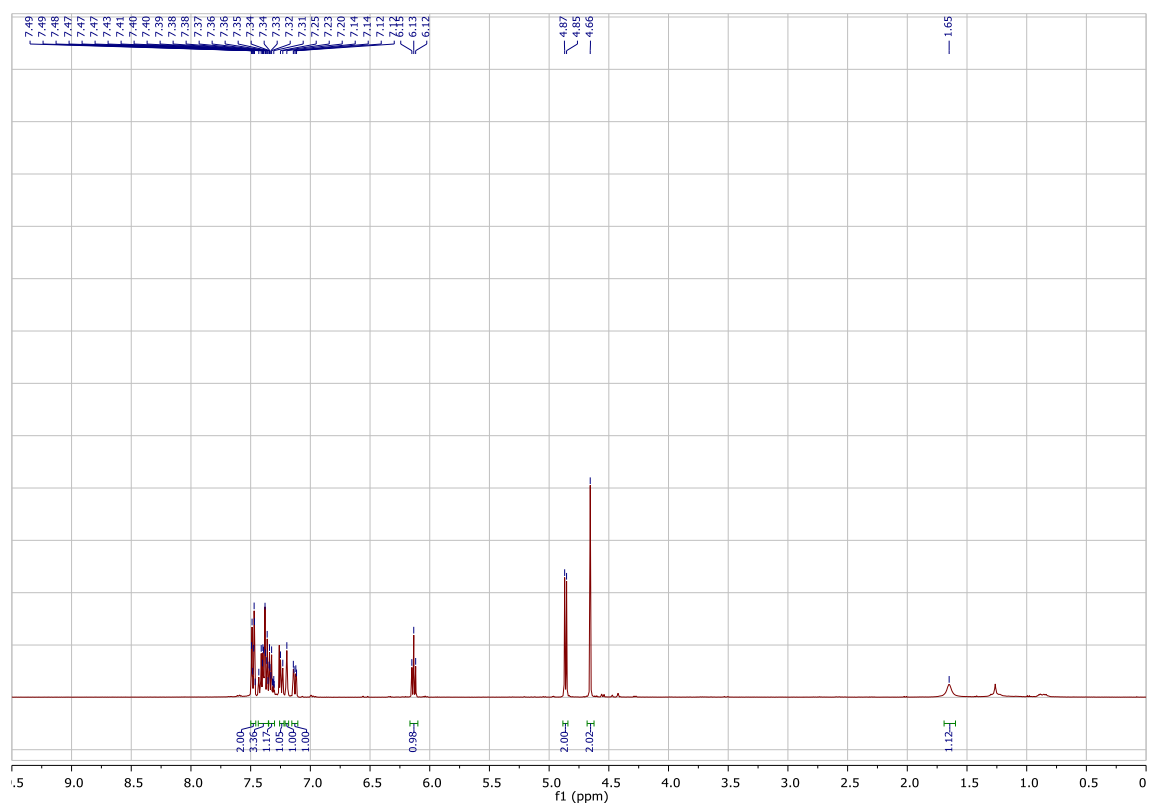


**HRMS** (ESI<sup>+</sup>, MeOH): *m/z* calcd. 277.1199 (M + Na)<sup>+</sup>, found: 277.1186.



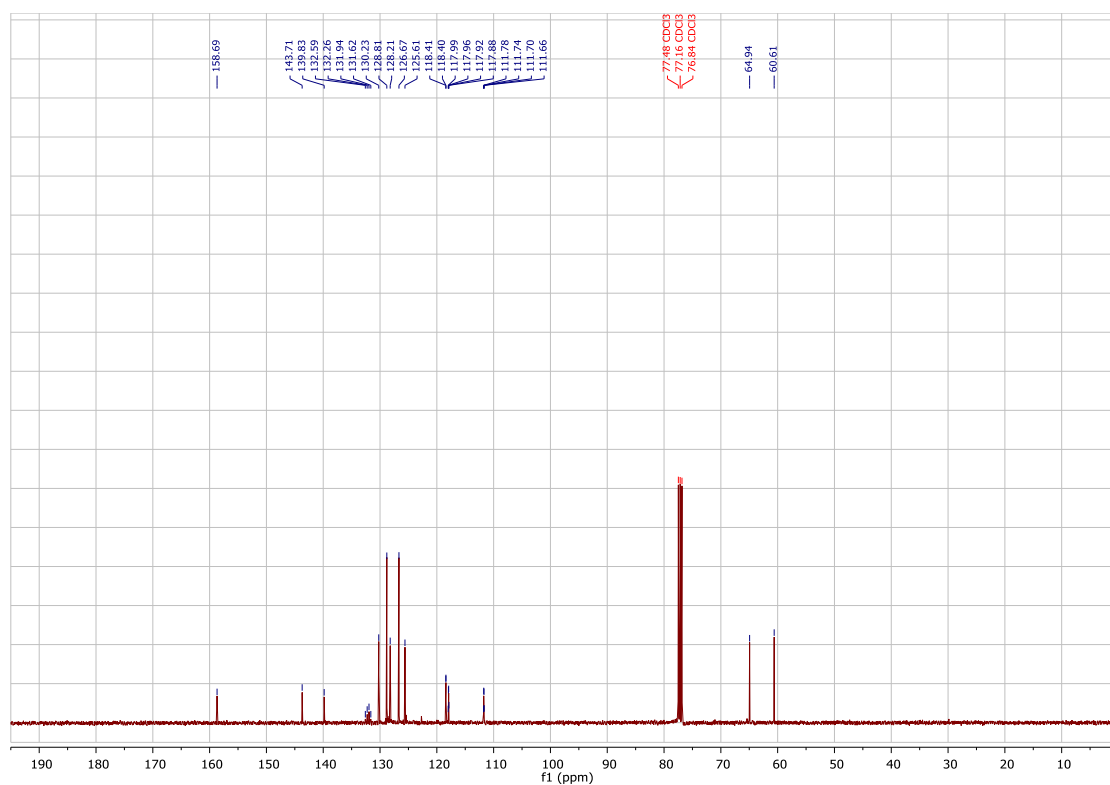
Scale: 0.2 mmol; isolated 40.0 mg (65% yield), yellow solid, Hexane : EA = 10 : 1,  $R_f$  = 0.2

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ )



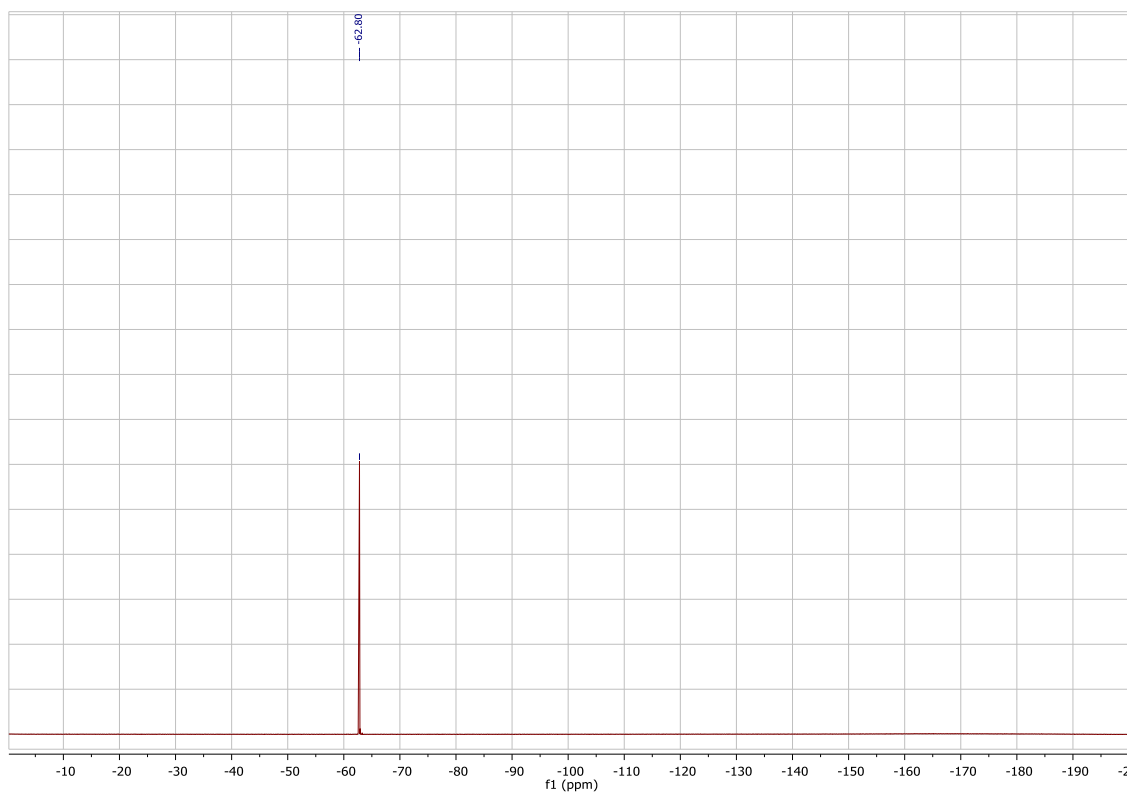
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50 – 7.46 (m, 2H), 7.44 – 7.35 (m, 3H), 7.35 – 7.30 (m, 1H), 7.24 (d,  $J$  = 7.7 Hz, 1H), 7.20 (s, 1H), 7.13 (m, 1H), 6.13 (t,  $J$  = 6.4 Hz, 1H), 4.86 (d,  $J$  = 6.4 Hz, 2H), 1.65 (s, 1H).

$^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ )



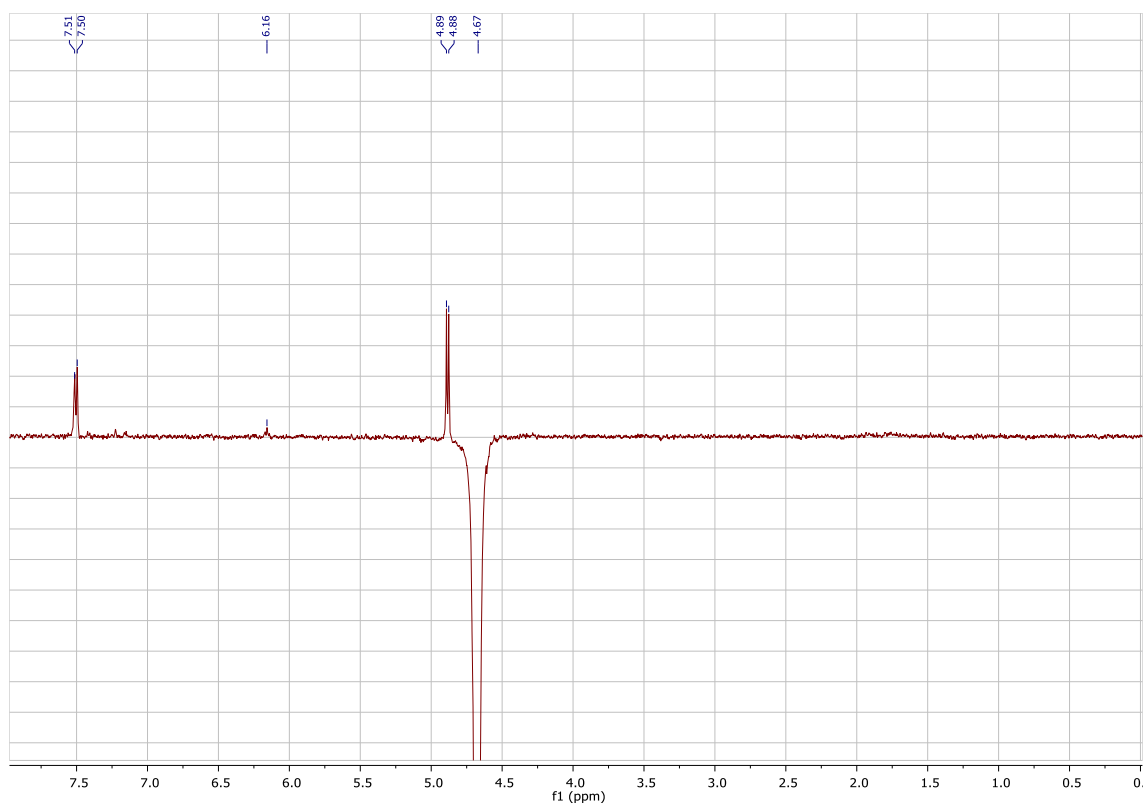
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.69, 143.71, 139.83, 132.1 (q,  $J = 32.32$  Hz), 130.22, 128.80, 128.21, 126.67, 125.61, 118.41, 118.40, 117.94 (q,  $J = 4.04$  Hz), 111.72 (q,  $J = 4.04$  Hz), 64.93, 60.61.

$^{19}\text{F}$  NMR spectrum ( $\text{CDCl}_3$ )

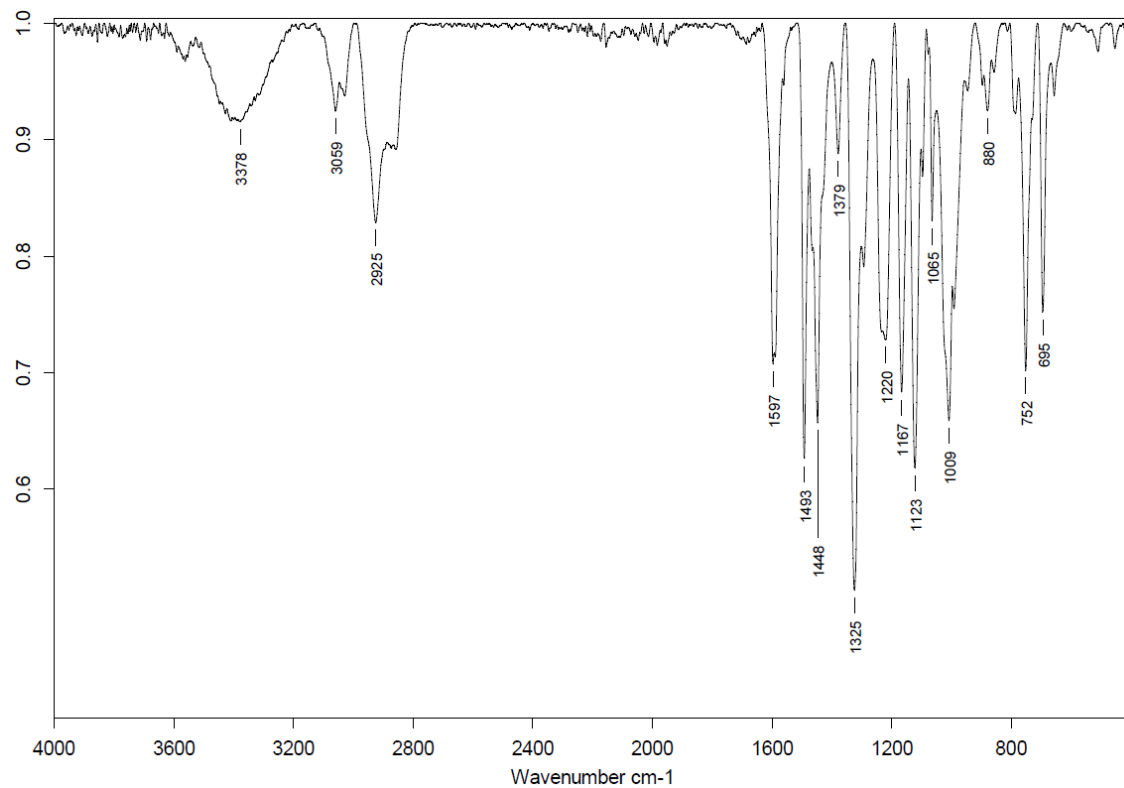


$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.80.

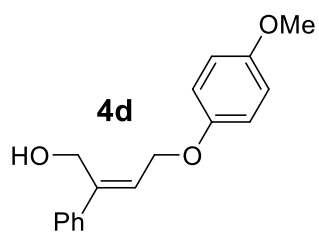
<sup>1</sup>H-Selective 1D NOESY (CDCl<sub>3</sub>)



IR spectrum (neat)

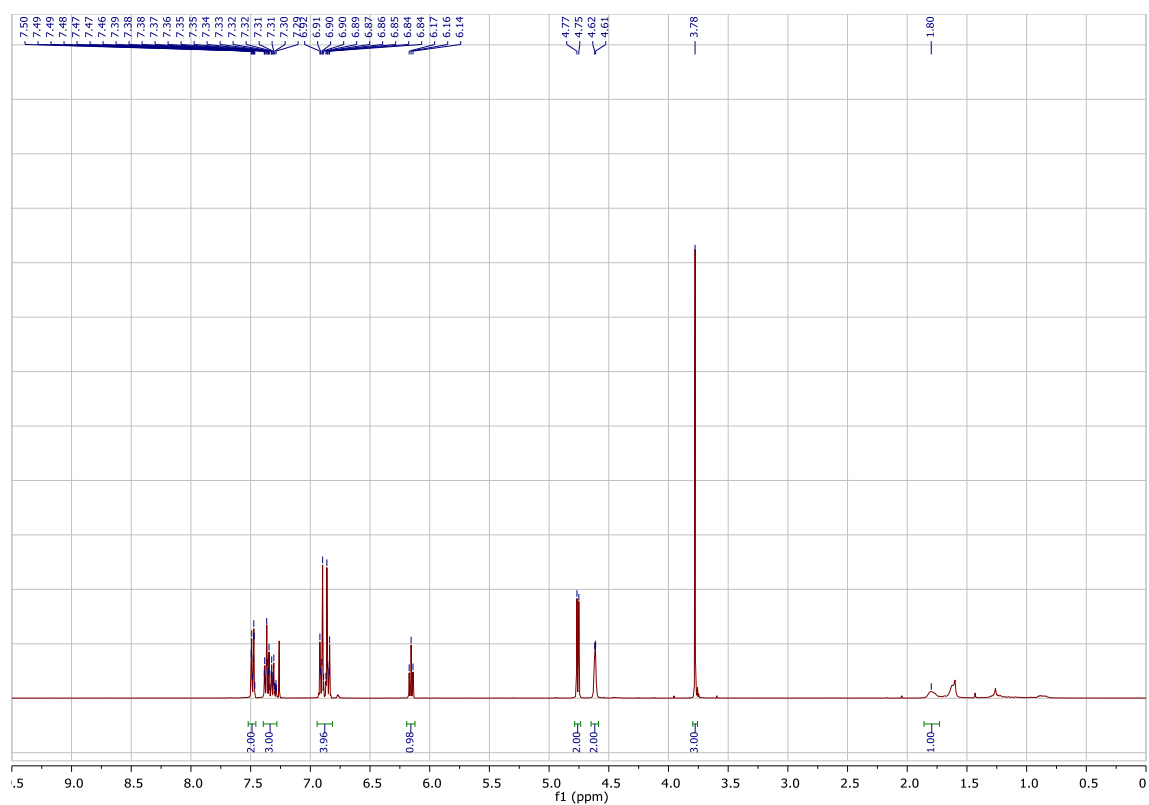


**HRMS** (ESI<sup>+</sup>, MeOH): *m/z* calcd. 331.0916 (M + Na)<sup>+</sup>, found: 331.0916.



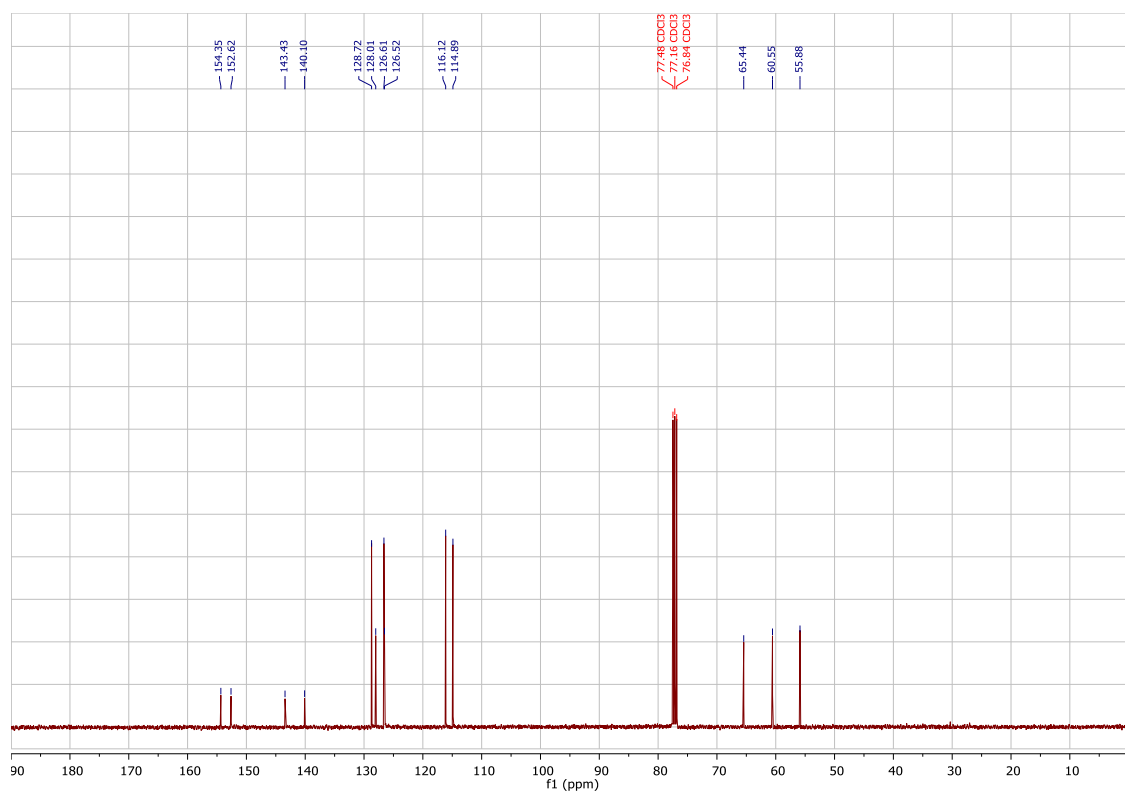
Scale: 0.2 mmol; isolated 52.9 mg (98% yield), white solid, Hexane : EA = 10 : 1,  $R_f$  = 0.2

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ )



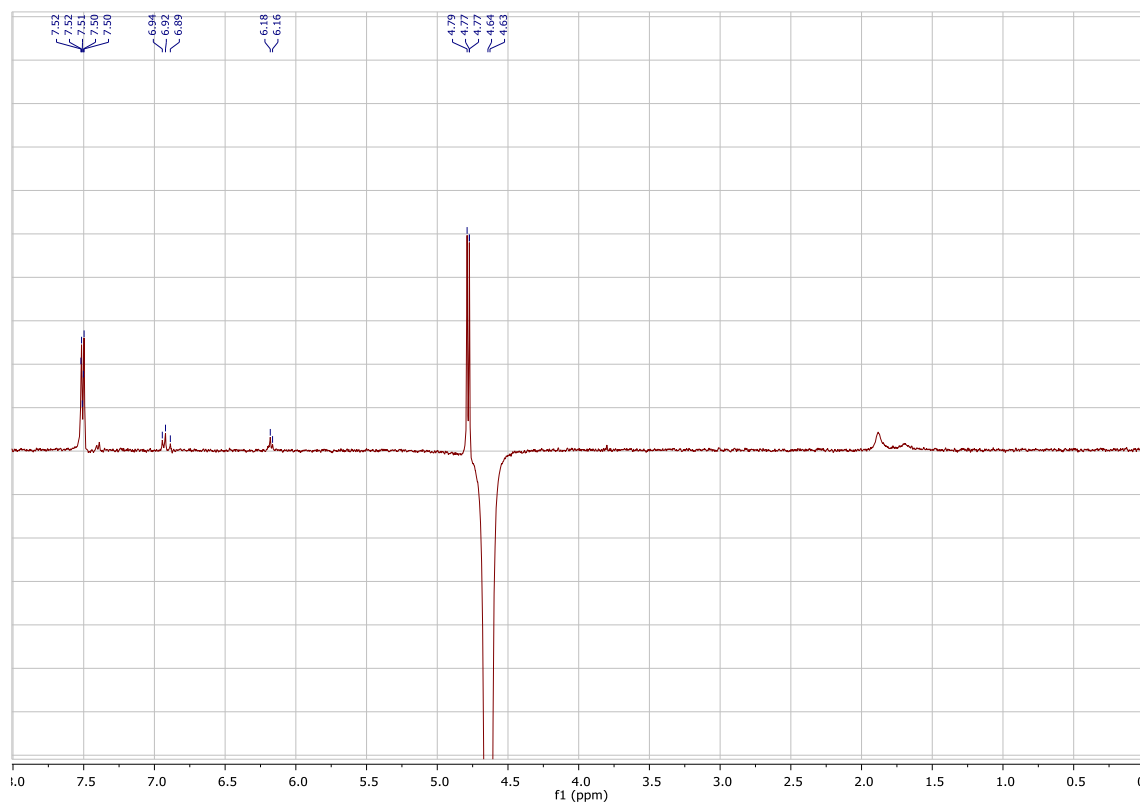
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 – 7.46 (m, 2H), 7.39 – 7.28 (m, 3H), 6.94 – 6.81 (m, 4H), 6.16 (t,  $J$  = 6.4 Hz, 1H), 4.76 (d,  $J$  = 6.4 Hz, 2H), 4.61 (d,  $J$  = 2.9 Hz, 2H), 3.78 (s, 3H), 1.80 (s, 1H).

$^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ )

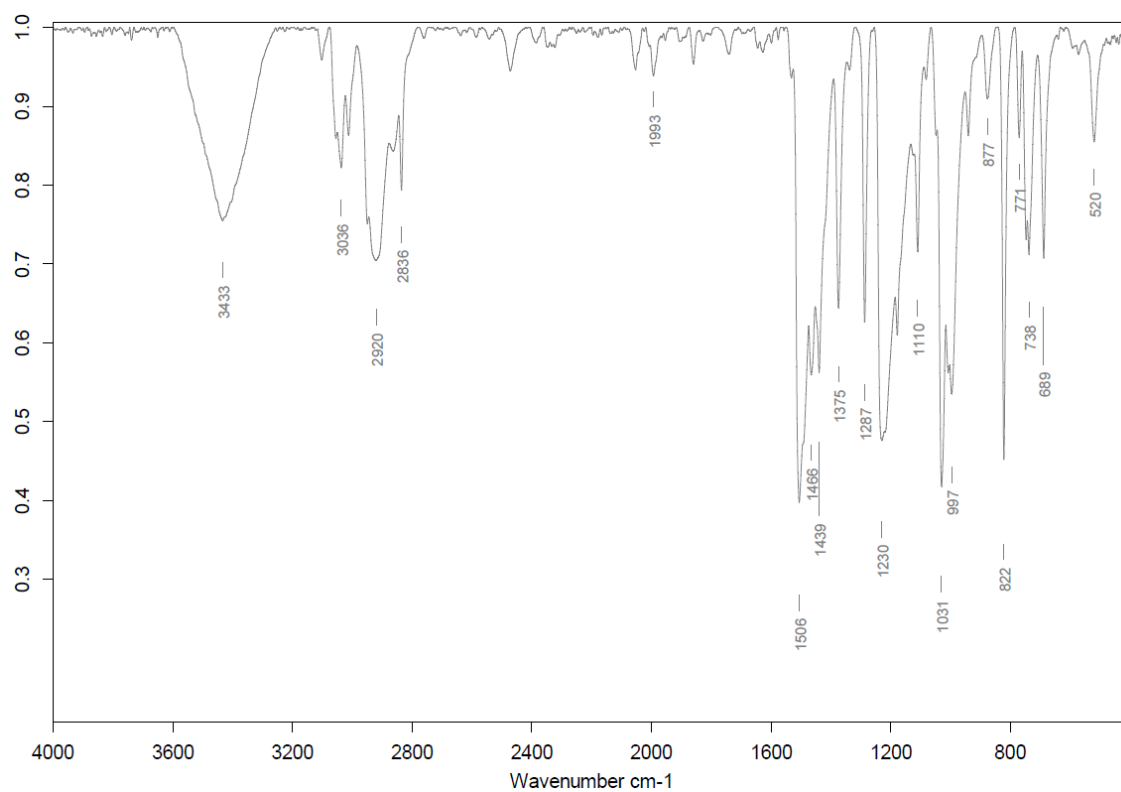


$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  154.35, 152.62, 143.43, 140.10, 128.72, 128.01, 126.61, 126.52, 116.12, 114.89, 65.44, 60.55, 55.88.

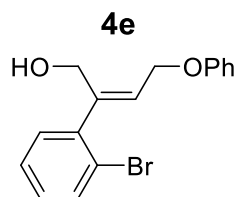
$^1\text{H}$ -Selective 1D NOESY ( $\text{CDCl}_3$ )



IR spectrum (neat)

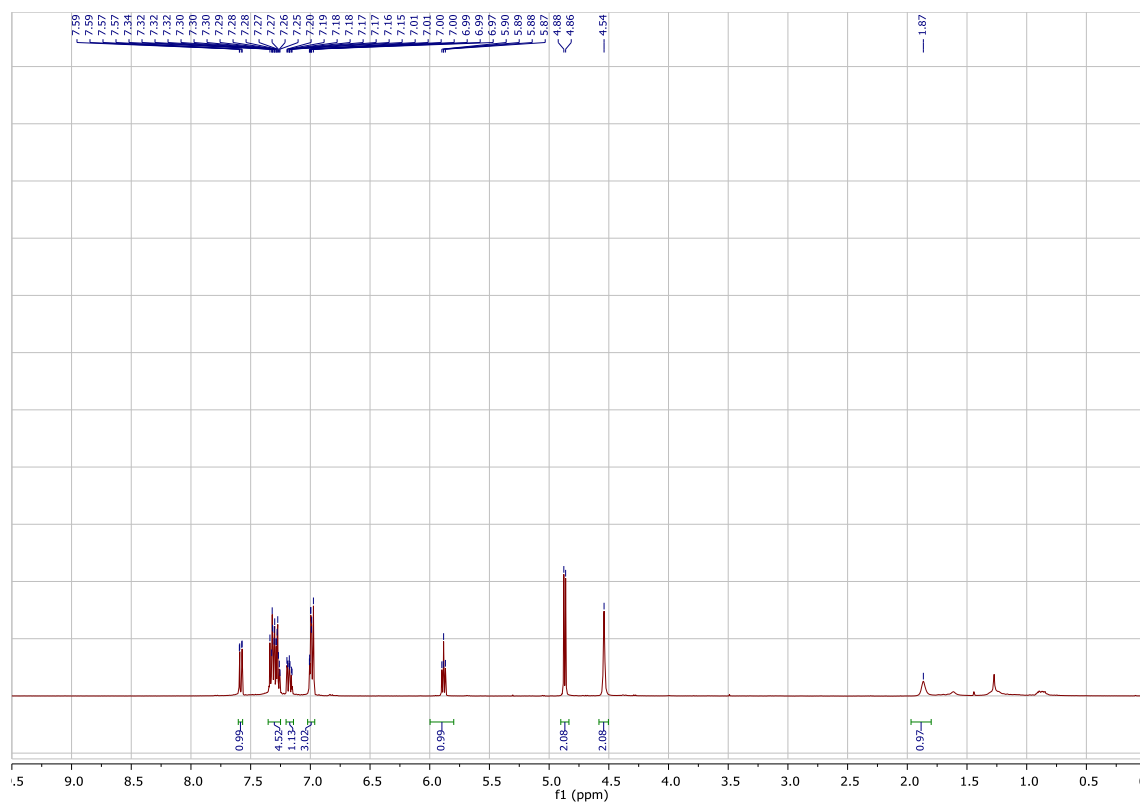


**HRMS (ESI<sup>+</sup>, MeOH):** *m/z* calcd. 293.1148 (M + Na)<sup>+</sup>, found: 293.1137.



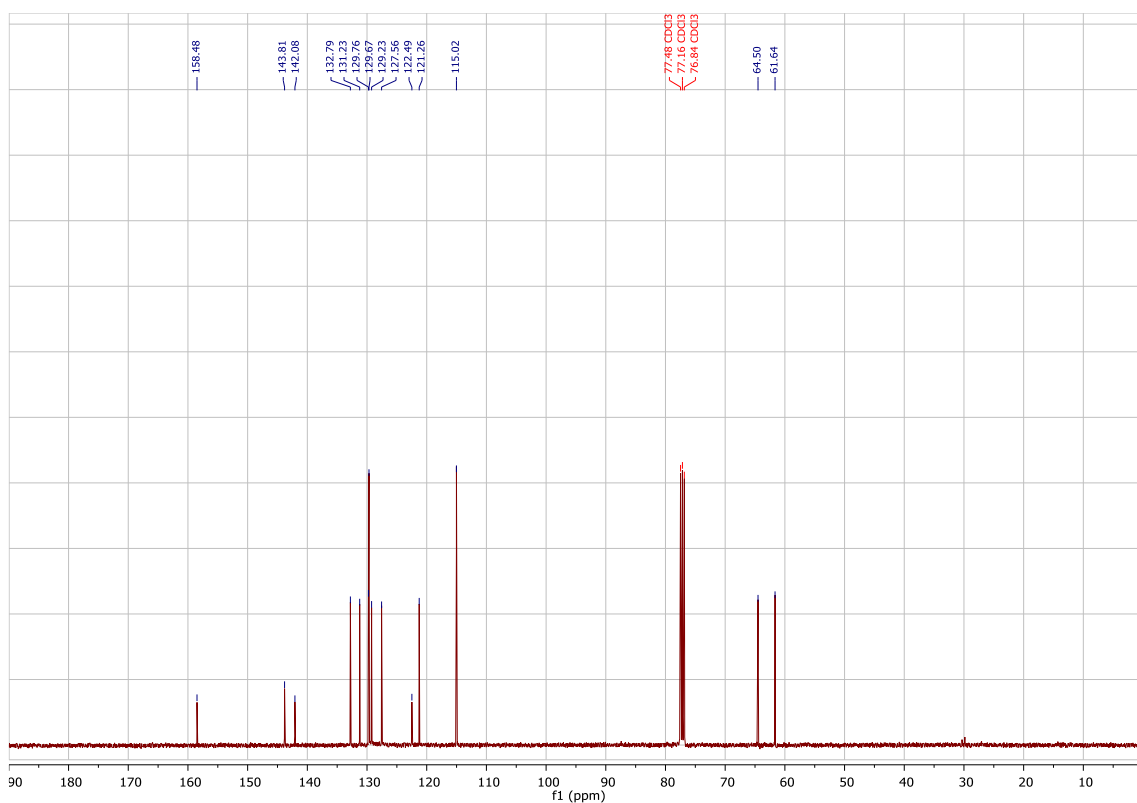
Scale: 0.2 mmol; isolated 45.8 mg (72% yield), white solid, Hexane : EA = 10 : 1,  $R_f$  = 0.2

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ )



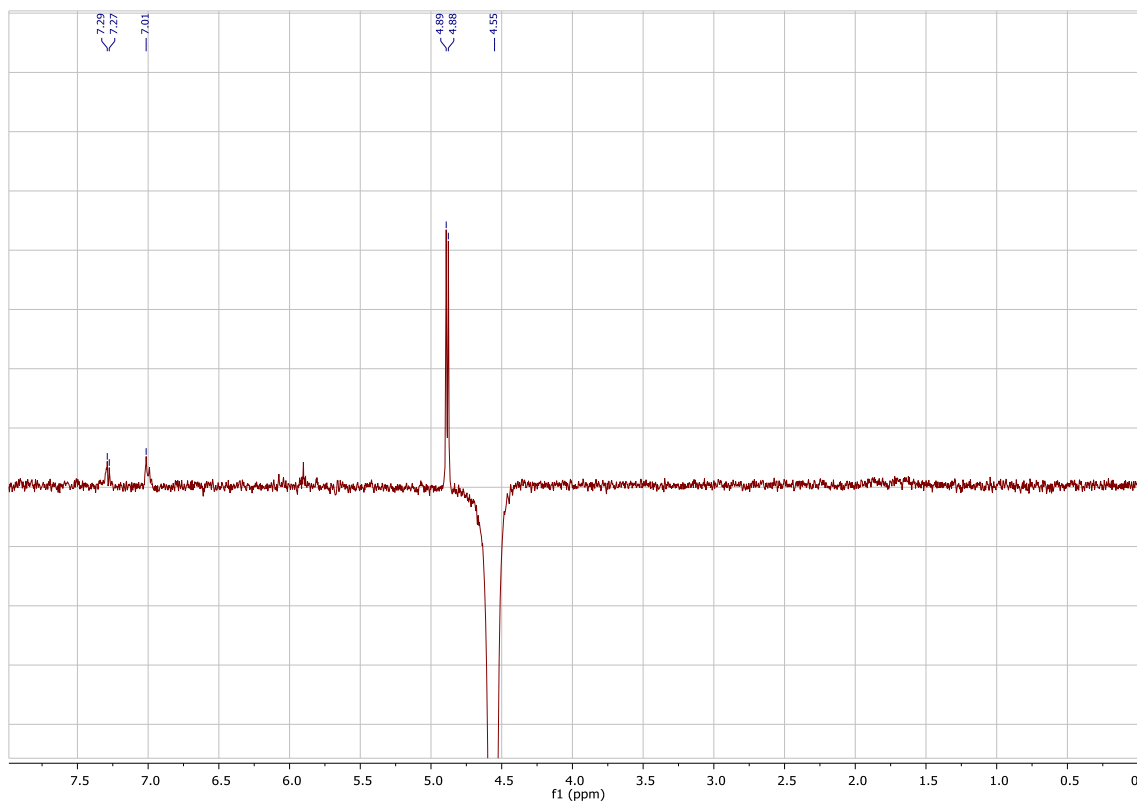
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 (dd,  $J$  = 8.0, 1.2 Hz, 1H), 7.35 – 7.25 (m, 5H), 7.20 – 7.14 (m, 1H), 7.02 – 6.96 (m, 3H), 5.88 (t,  $J$  = 6.0 Hz, 1H), 4.87 (d,  $J$  = 6.1 Hz, 2H), 4.54 (s, 2H), 1.87 (s, 1H).

$^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ )

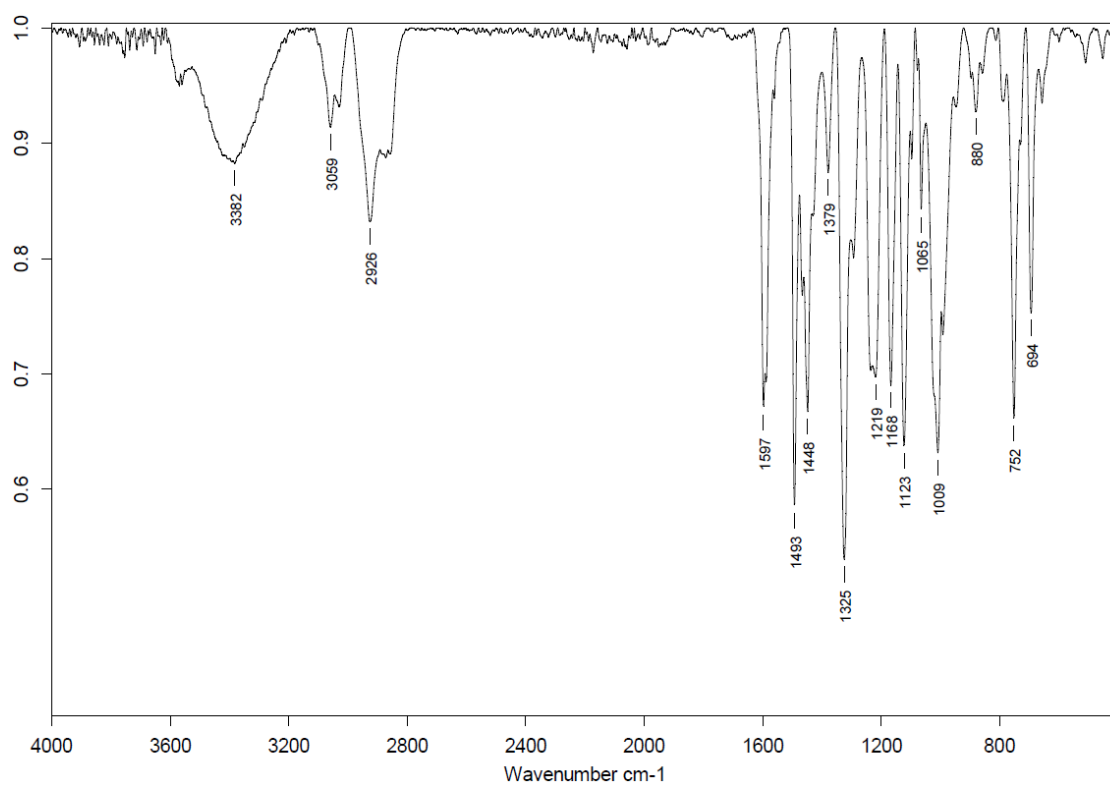


$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.48, 143.81, 142.08, 132.79, 131.23, 129.76, 129.67, 129.23, 127.56, 122.49, 121.26, 115.02, 64.50, 61.64.

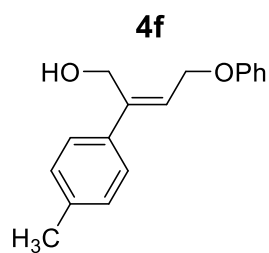
$^1\text{H}$ -Selective 1D NOESY ( $\text{CDCl}_3$ )



IR spectrum (neat)

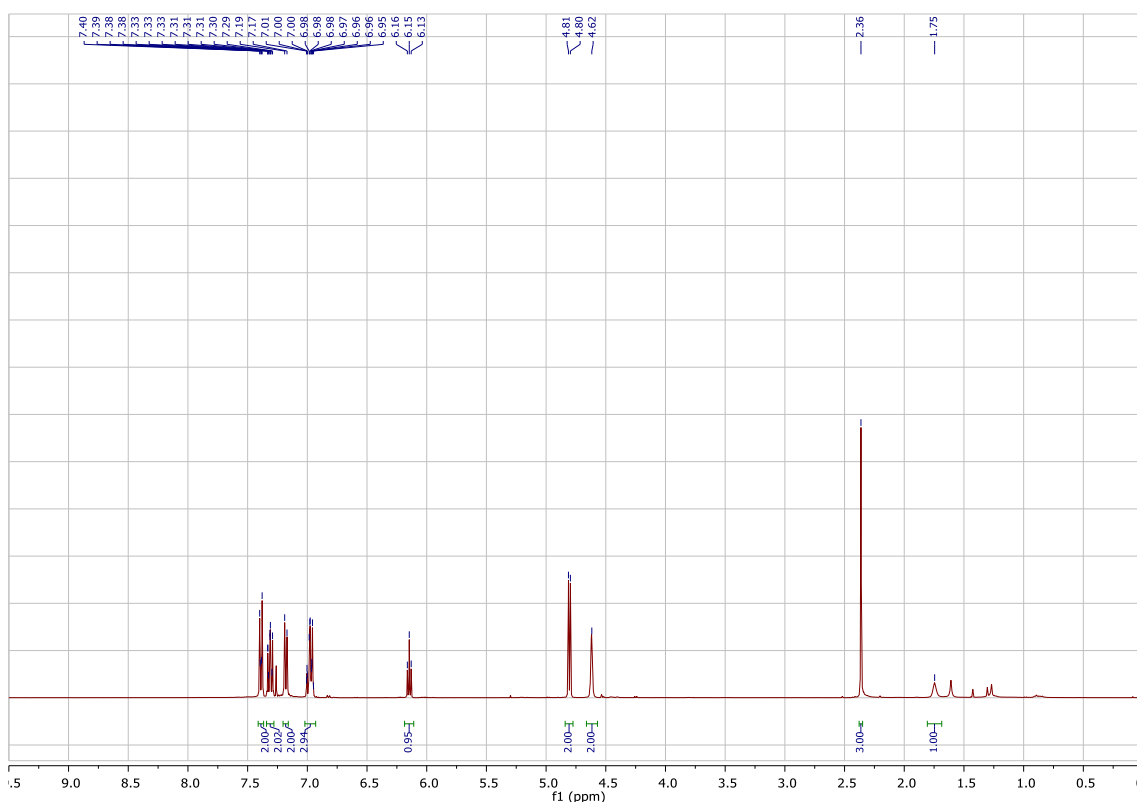


**HRMS** (ESI<sup>+</sup>, MeOH): *m/z* calcd. 341.0148 (M + Na)<sup>+</sup>, found: 341.0133.



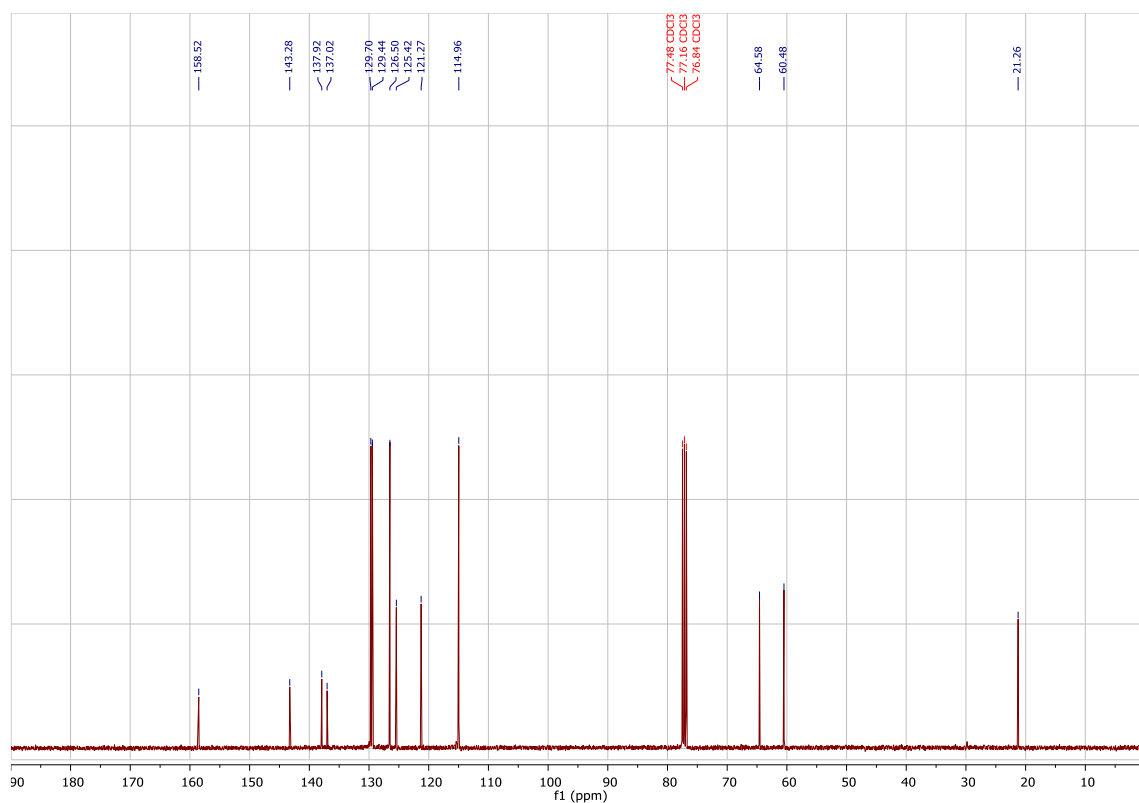
Scale: 0.2 mmol; isolated 41.1 mg (81% yield), yellow oil, Hexane : EA = 10 : 1,  $R_f$  = 0.2

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ )



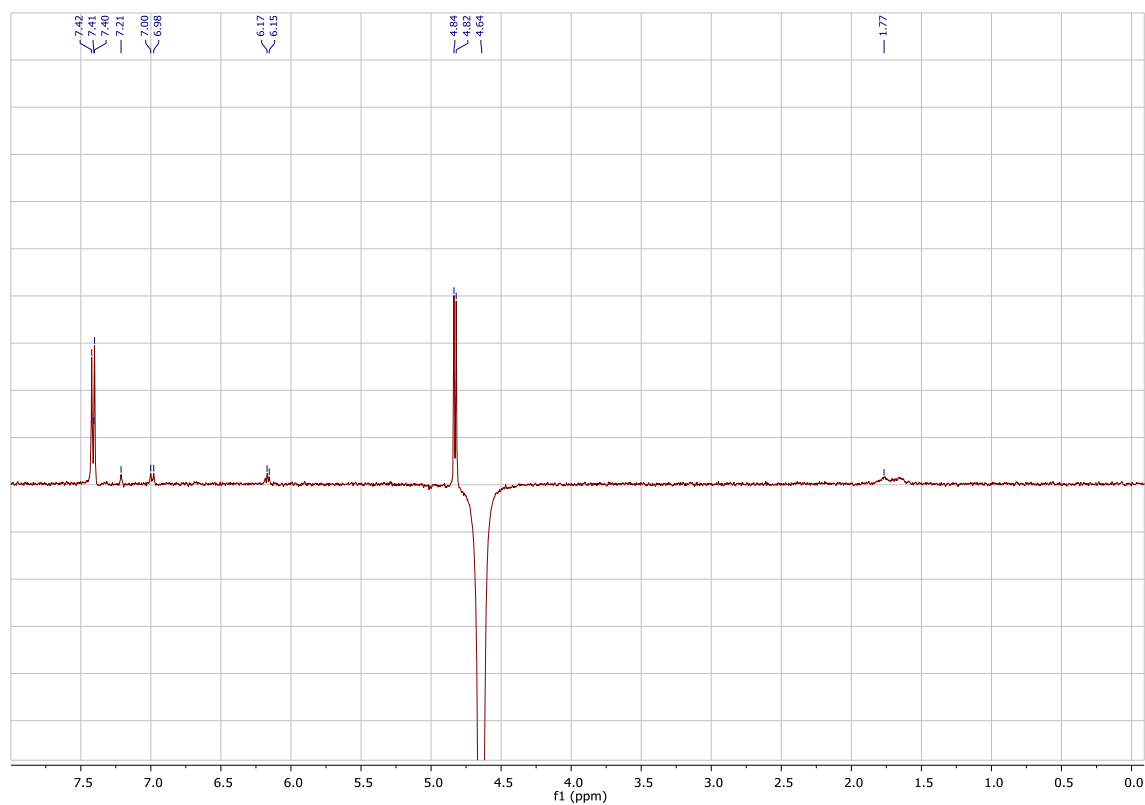
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41 – 7.37 (m, 2H), 7.34 – 7.28 (m, 2H), 7.18 (d,  $J$  = 7.8 Hz, 2H), 7.02 – 6.93 (m, 3H), 6.15 (t,  $J$  = 6.4 Hz, 1H), 4.80 (d,  $J$  = 6.4 Hz, 2H), 4.62 (s, 2H), 2.36 (s, 3H), 1.75 (s, 1H).

$^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ )

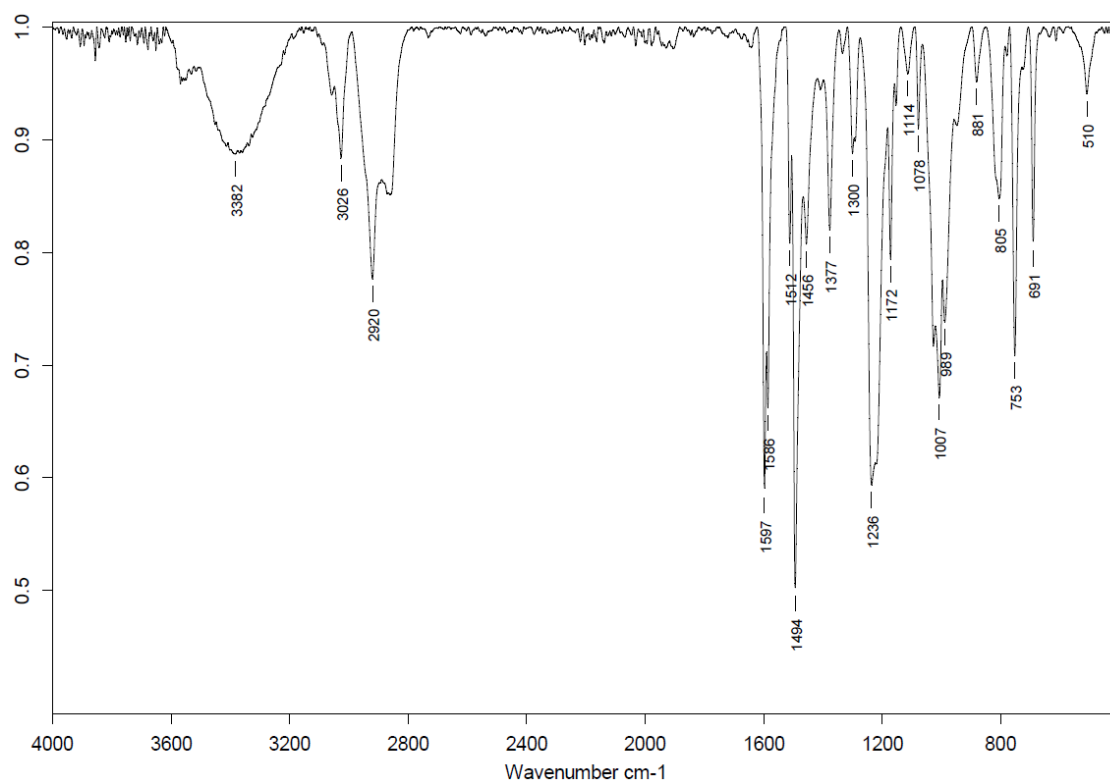


$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.52, 143.28, 137.92, 137.02, 129.70, 129.44, 126.50, 125.42, 121.27, 114.96, 64.58, 60.48, 21.26.

$^1\text{H}$ -Selective 1D NOESY ( $\text{CDCl}_3$ )

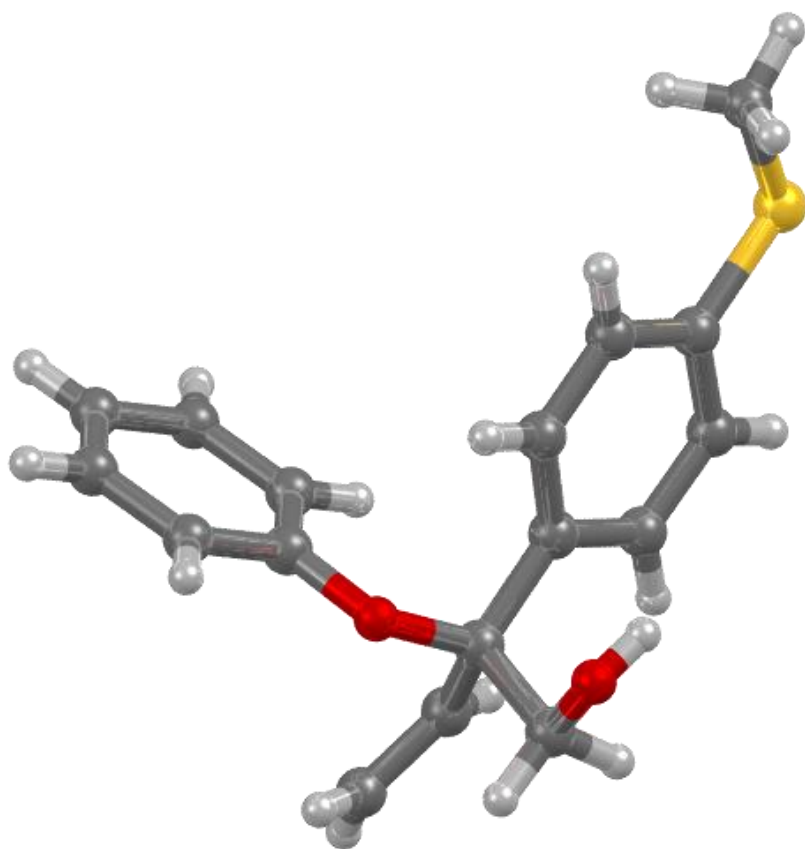


IR spectrum (neat)



**HRMS** (ESI<sup>+</sup>, MeOH): *m/z* calcd. 277.1199 (M + Na)<sup>+</sup>, found: 277.1195.

**S107. X-ray molecular structure of compound 3e**



## S108. References

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- (2) Polet, D.; Alexakis, A.; Tissot-Croset, K.; Corminboeuf, C.; Ditrich, K. *Chem. Eur. J.* **2006**, *12*, 3596-3609.
- (3) (a) Khan, A.; Zheng, R.; Kan, Y.; Ye, J.; Xing, J.; Zhang, Y. J. *Angew. Chem. Int. Ed.* **2014**, *53*, 6439-6442. (b) Khan, A.; Yang, L.; Xu, J.; Jin, L. Y.; Zhang, Y. J. *Angew. Chem. Int. Ed.* **2014**, *53*, 11257-11260. (c) Khan, A.; Xing, J.; Zhao, J.; Kan, Y.; Zhang, W.; Zhang, Y. J. *Chem. Eur. J.* **2015**, *21*, 120-124; (d) Yang, L.; Khan, A.; Zheng, R.; Jin, L. Y.; Zhang, Y. J. *Org. Lett.* **2015**, *17*, 6230-6233. (e) Guo, W.; Martínez-Rodríguez, L.; Martin, E.; Escudero-Adán, E. C.; Kleij, A. W. *Angew. Chem. Int. Ed.* **2016**, *55*, 11037-11040.