# Supplementary Information

## Biomimetic non-heme iron-catalyzed epoxidation of challenging terminal alkenes using aqueous $H_2O_2$ as an environmentally friendly oxidant

*Anja Fingerhut [a], Jorge Vargas-Caporali [b], Marco Antonio Leiva-Ramírez [b], Eusebio Juaristi [b,c,]* and Svetlana B. Tsogoeva [a,]**

[a] Department of Chemistry and Pharmacy, Institute of Organic Chemistry I and Interdisciplinary Center for Molecular Materials (ICMM), Friedrich-Alexander University Erlangen-Nürnberg, Nikolaus-Fiebiger-Straße 10, 91058 Erlangen, Germany. [b] Department of Chemistry, Centro de Investigación y de Estudios Avanzados, Av. Instituto Politécnico Nacional 2508, 07360 Ciudad de México, Mexico. [c] El Colegio Nacional, Donceles # 104, Centro Histórico, 06020 Ciudad de México, Mexico.

*E-Mail: juaristi@relaq.mx and svetlana.tsogoeva@fau.de

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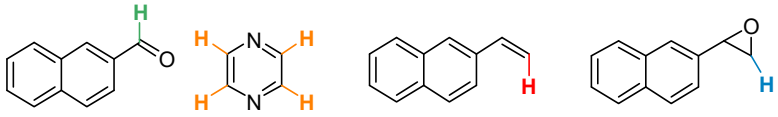
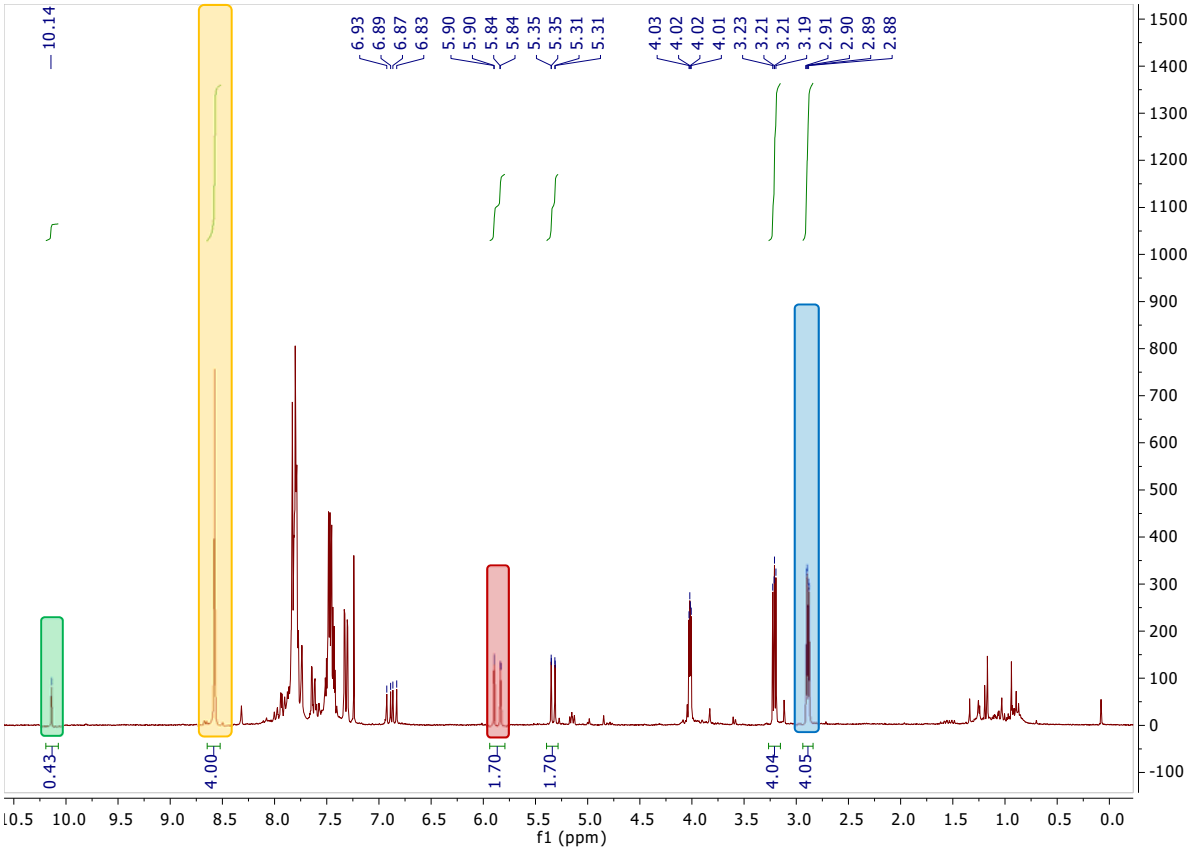
# 1 Determination of yield via $^1$H NMR using pyrazine as internal standard

**Exemplary: Table 2, Entry 1:**

$^1$H-NMR of reaction mixture after $SiO_2$-plug containing pyrazine as internal standard (m = 4.32 mg, n = 53.9 µmol)






1H (pyrazine) ≙ 53.9 µmol

1H (epoxide) ≙ 53.9 µmol x 4.05 = 218 µmol (n (epoxide))

→ yield = n (epoxide) / n (alkene) = 218 µmol / 500 µmol = 0.44 → 44%

## 2 Screening of reaction conditions for non-enantioselective epoxidation

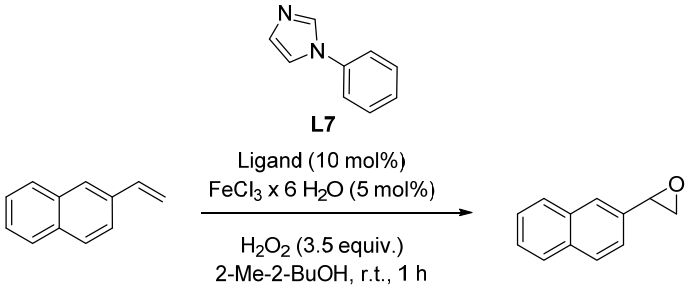



**Table 1.** Screening of reaction conditions.

| Entry | Modification of reaction conditions | yield [%][a)] |
|---|---|---|
| 1 | - | 53 |
| 2 | 1 h *in situ* catalyst generation (under inert conditions) | traces |
| 3 | 1 h *in situ* catalyst generation (not under inert conditions) | 54 |
| 4 | 1 h *in situ* catalyst generation and 5 mol% $CH_3CO_2H$ | 44 |
| 5 | 2 h reaction time and 2 h $H_2O_2$ addition. | 45 |
| 6 | 15°C | 22 |
| 7 | 0.05 M substrate | 42 |
| 8 | 0.2 M substrate | 25 |
| 9 | addition of $H_2O_2$ over 3 h period | 52 |
| 10 | 10 mol% catalyst loading | 55 |
| 11 | 0°C | 13 |
| 12 | 50°C | 27 |
| 13 | 1 h $H_2O_2$ addition plus 15 h stirring | 50 |
| 14 | 1 h $H_2O_2$ addition + 1 h stirring | 53 |
| 15 | + 5 mol% $H_2$Pydic | 19 |
| 16 | + 5 mol% mandelic acid | 26 |
| 17 | irradiation with cold light | 52 |

a) Determined via pyrazine as internal standard.

# 3 Screening of reaction conditions for enantioselective epoxidation

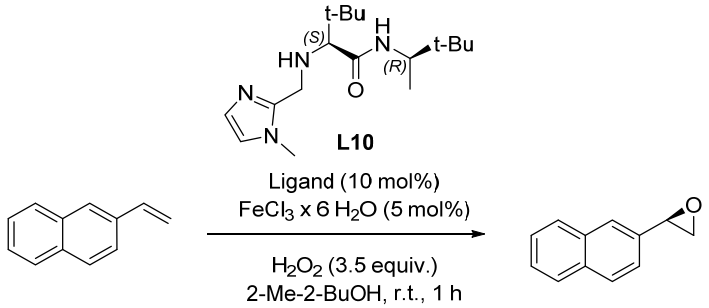



**Table 2**. Screening of reaction conditions.

| Entry | Modification of reaction conditions | yield [%][a)] | ee-value (*R*) [%] |
|---|---|---|---|
| 1 | - | 44 | 26 |
| 2 | 1 h *in situ* catalyst generation with air-bubbling | 42 | 24 |
| 3 | at 0°C | 23 | 36 |
| 4 | + 5 mol% mandelic acid | 32 | 27 |
| 5 | **L10** (5 mol%) | 31 | 26 |

a) Determined via pyrazine as internal standard.

# 4 Rearrangement of Epoxide

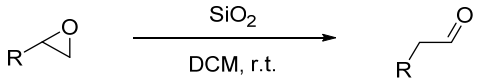
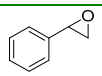
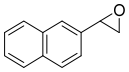
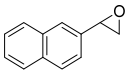
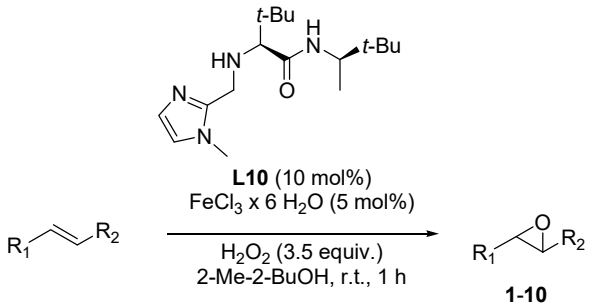



**Table 3.** First rearrangement attempts from epoxide towards corresponding aldehyde using $SiO_2$.

| Entry | Substrate | Time | Temperature | Yield [%] [c] |
|---|---|---|---|---|
| 1 [a), b)] |  | 5 h | reflux | 17 |
| 2 |  | 18 h | reflux | 34 |
| 3 [a)] |  | 18 h | r.t. | 29 |
| 4 [a)] |  | 2.5 h | reflux | 32 |

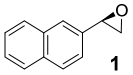
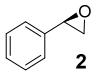
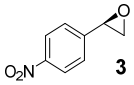
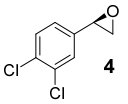
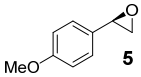
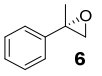
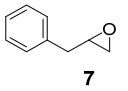
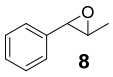
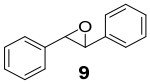
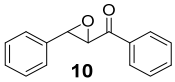
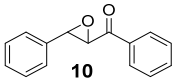
a) 3.33 g/mmol $SiO_2$; b) $CDCl_3$; c) Determined via pyrazine as internal standard.

## 5 Comparative Table




**1-10**

**Table 4.** Results obtained in this work contrasted with the results described in literature for non-heme iron-catalyzed epoxidation of the corresponding olefins.

| | | Results of this work | | Results described in literature | | |
|---|---|---|---|---|---|---|
| **Entry** | **Product** | **Yield** [a),b)] | **ee** [c)] | **Yield** [d)] | **ee** [d)] | **Ref.** |
| 1 |  **1** | 44 | 26 (*R*) | 40 | – | [1] |
| 2 |  **2** | 30 | 27 (*R*) | 84<br>30<br>15 | 8<br>–<br>– | [2]<br>[3]<br>[4] |
| 3 |  **3** | 14 | 29 (S) | 66<br>90 | –<br>– | [5]<br>[6] |
| 4 |  **4** | 25 | 25 (*R*) [e)] | – | – | – |
| 5 |  **5** | 5 [e)] | 14 (*R*) [e)] | 82<br>70 | –<br>– | [7]<br>[8] |
| 6 |  **6** | 22 | 16 (S) | 67 | 45 | [9] |
| 7 |  **7** | <5 [f)] | n.d. [g)] | 60 | – | [10] |
| 8 |  **8** | 32 | 50 | 32<br>49 | 19<br>– | [9]<br>[11] |
| 9 |  **9** | 27 | 16 (*R*) | 44<br>72 | –<br>– | [3]<br>[8] |
| 10 |  **10** | <5 | 27 (2*R*,3*S*) | 38 | 90 | [9] |
| 11 [h)] |  **10** | 7 | 51 (2*R*,3*S*) | – | – | – |

a) Yields determined via $^1$H NMR with pyrazine as internal standard. b) Results described in this work. c) ee values determined via chiral HPLC measurement. d) Results described in literature for non-heme iron-catalyzed epoxidation employing $H_2O_2$ and miscellaneous ligands and/or additives (see references for further details). e) ee value determined after derivatization: aminolysis with isopropylamine towards corresponding β-aminoalcohol. f) Detected via $^1$H-NMR and ESI-MS. g) n. d.: not determined. h) *in situ* catalyst generation with **L10** (5 mol%), $FeCl_3 \cdot 6H_2O$ (5 mol%), (*S*)-(+)-mandelic acid (15 mol%), 1.6 mL 2-Me-2-BuOH, followed by the addition of alkene (0.166 mmol) and 2 eq. $H_2O_2$ *via* syringe pump at r. t. (3 h reaction time).

**References ( see Table 4)**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2. Gelalcha, F. G.; Anilkumar, G.; Tse, M. K.; Bruckner, A.; Beller, M. Biomimetic Iron-Catalyzed Asymmetric Epoxidation of Aromatic Alkenes by Using Hydrogen Peroxide. *Chem. Eur. J*. **2008**, *14*, 7687-7698.
3. Park, H.; Ahn, H. M.; Jeong, H. Y.; Kim, C.; Lee, D. Non-heme iron catalysts for olefin epoxidation: conformationally rigid aryl–aryl junction to support amine/imine multidentate ligands. *Chem. Eur. J.* **2018**, *24*, 8632-8638.
4. Papastergiou, M.; Stathi, P.; Milaeva, E. R., Deligiannakis, Y.; Louloudi, M. Comparative study of the catalytic thermodynamic barriers for two homologous Mn- and Fe-non-heme oxidation catalysts. *J. Catal.* **2016**, *341*, 104-115.
5. Singh, K. K.; Tiwari, M. K.; Dhar, B. B.; Vanka, K.; Sen Gupta, S. Mechanism of oxygen atom transfer from $Fe^{V}(O)$ to olefins at room temperature. *Inorg. Chem.* **2015**, *54*, 6112-6121.
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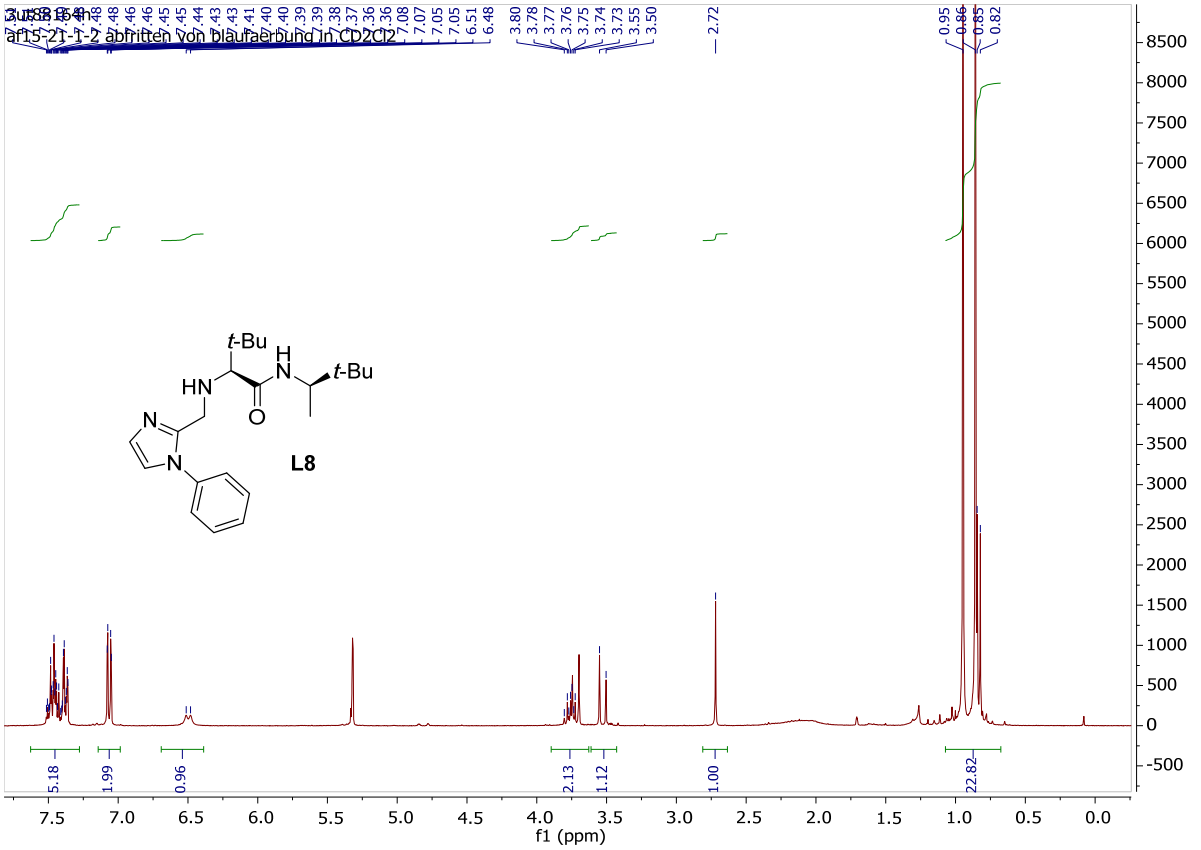
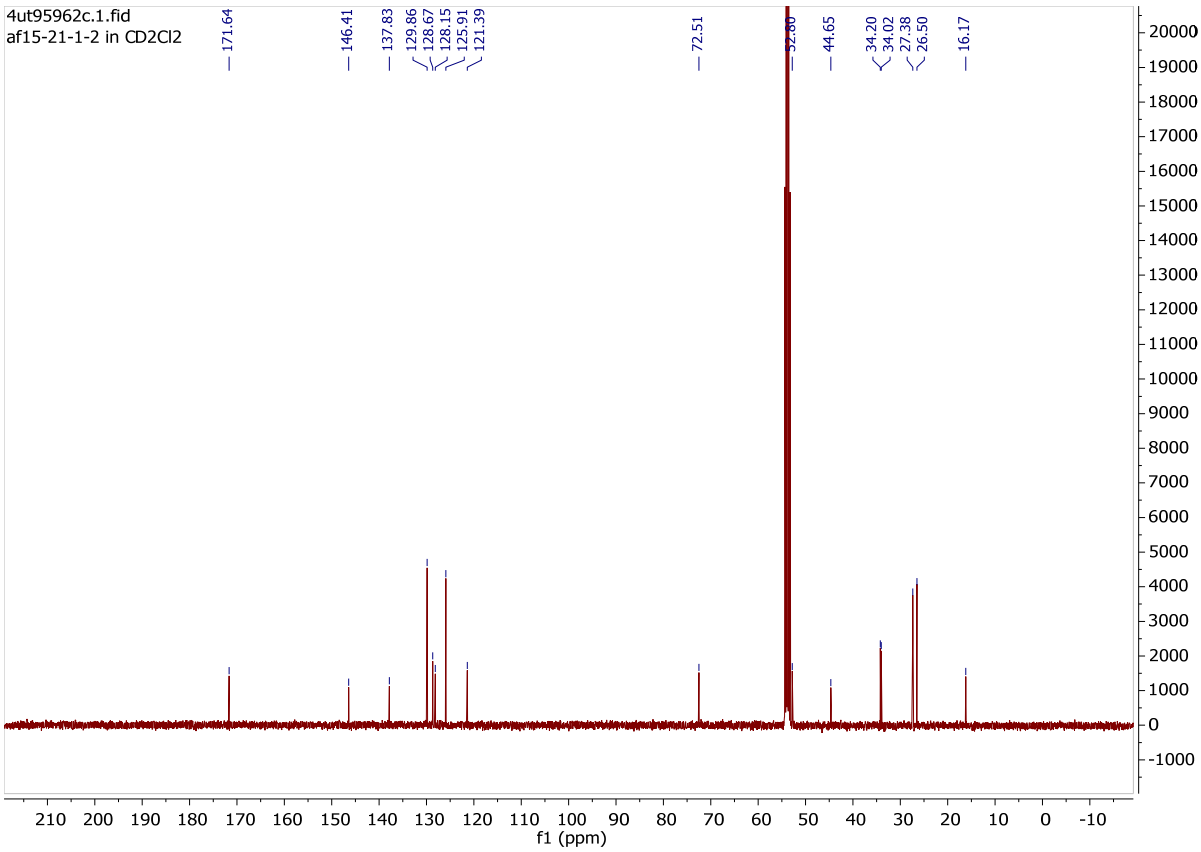
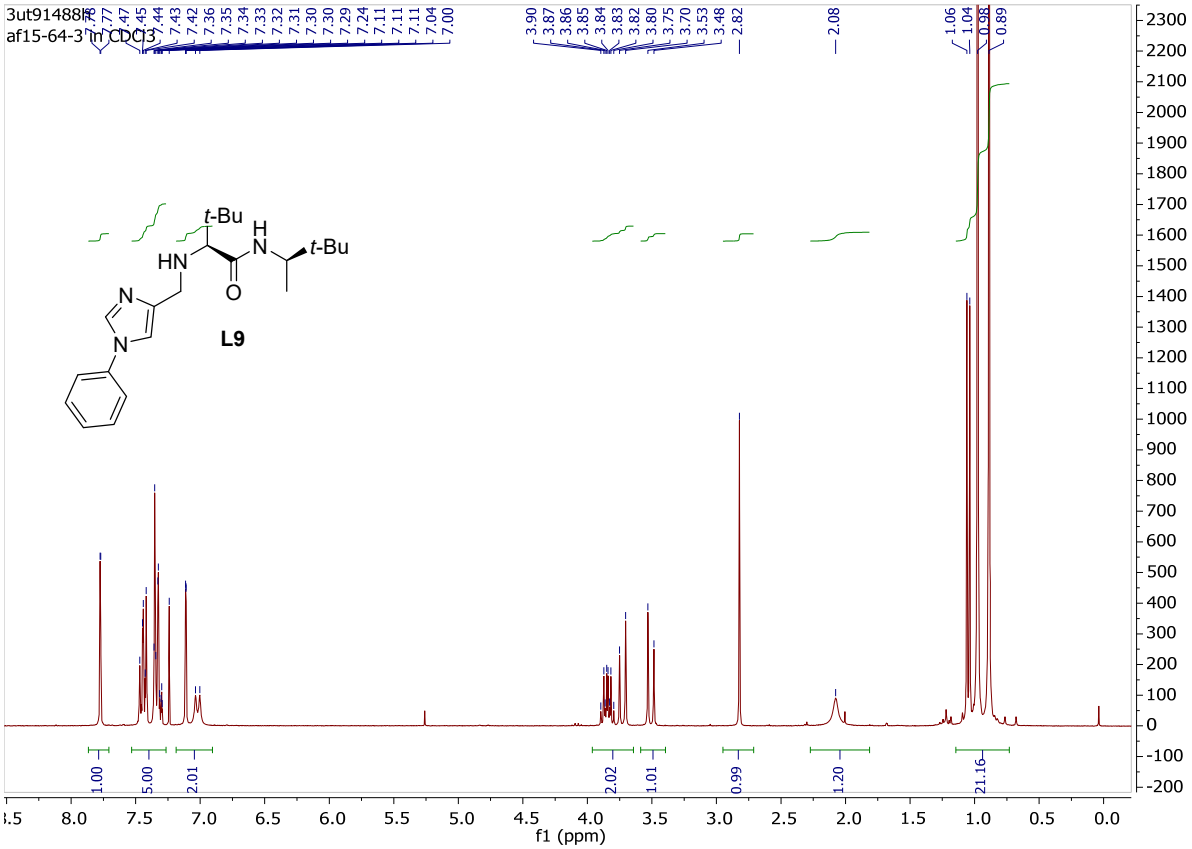
9. Cusso, O.; Garcia-Bosch, I.; Ribas, X.; Lloret-Fillol, J.; Costas, M. Asymmetric Epoxidation with $H_2O_2$ by Manipulating the Electronic Properties of Non-heme Iron Catalysts. *J. Am. Chem. Soc*. **2013**, *135*, 14871-14878.
10. Iron(III) aroylhydrazone complexes: Structure, electrochemical studies and catalytic activity in oxidation of olefins. *J. Mol. Catal. A – Chem.* **2009**, *304*, 139-146.
11. Moelands, M. A. H.; Schamhart, D. J.; Folkertsma, E.; Lutz, M.; Spek, A. L.; Klein Gebbink, R. J. M. Facial triad modeling using ferrous pyridinyl prolinate complexes: synthesis and catalytic applications. *Dalton Trans.* **2014**, *43*, 6769-6785.

# 6 $^{1}$H NMR and $^{13}$C NMR spectra of new ligands

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HN
t-Bu
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N
L9
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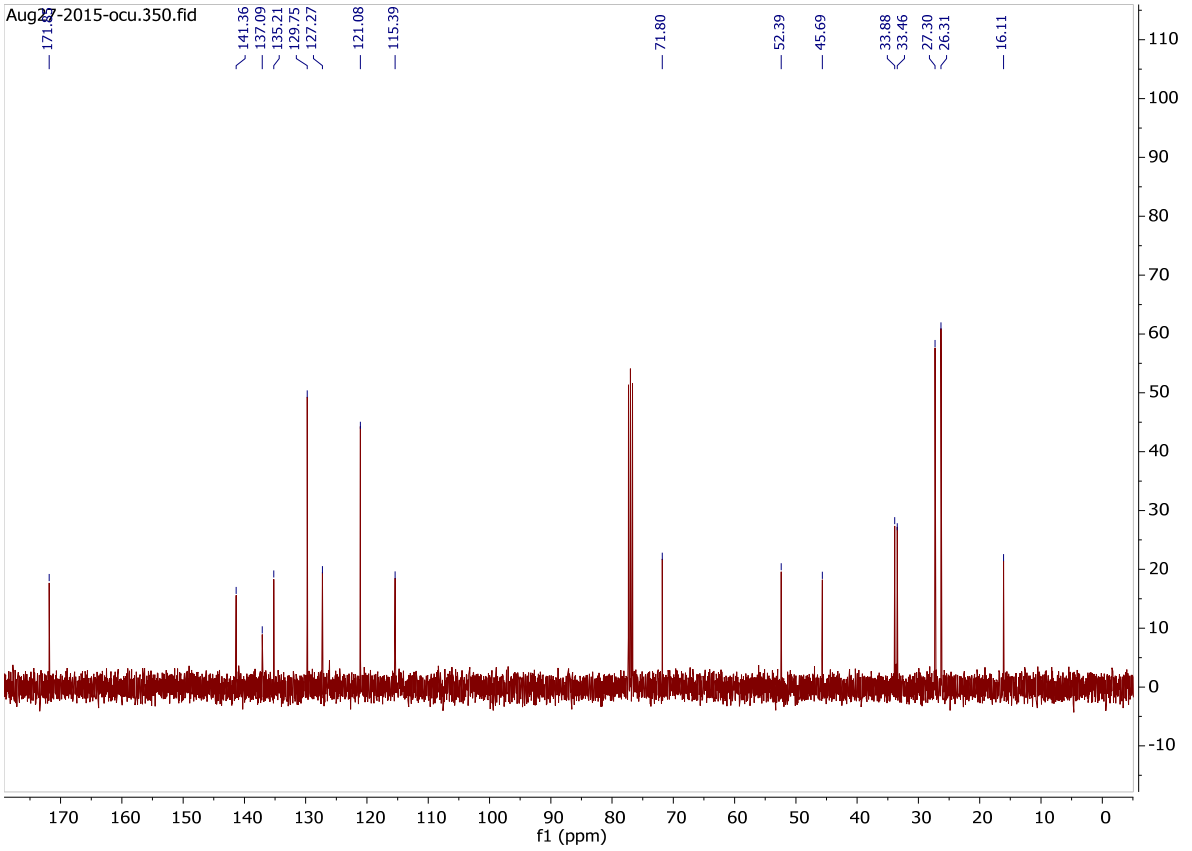
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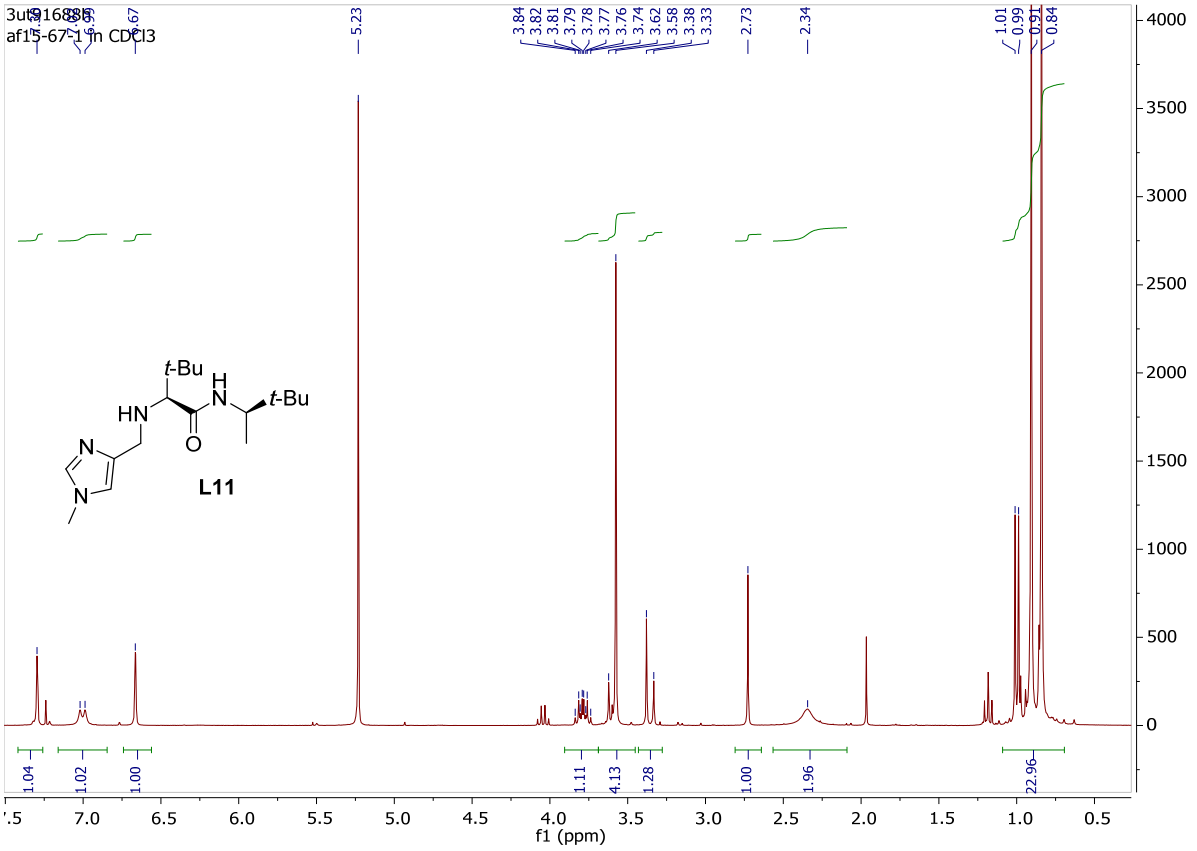
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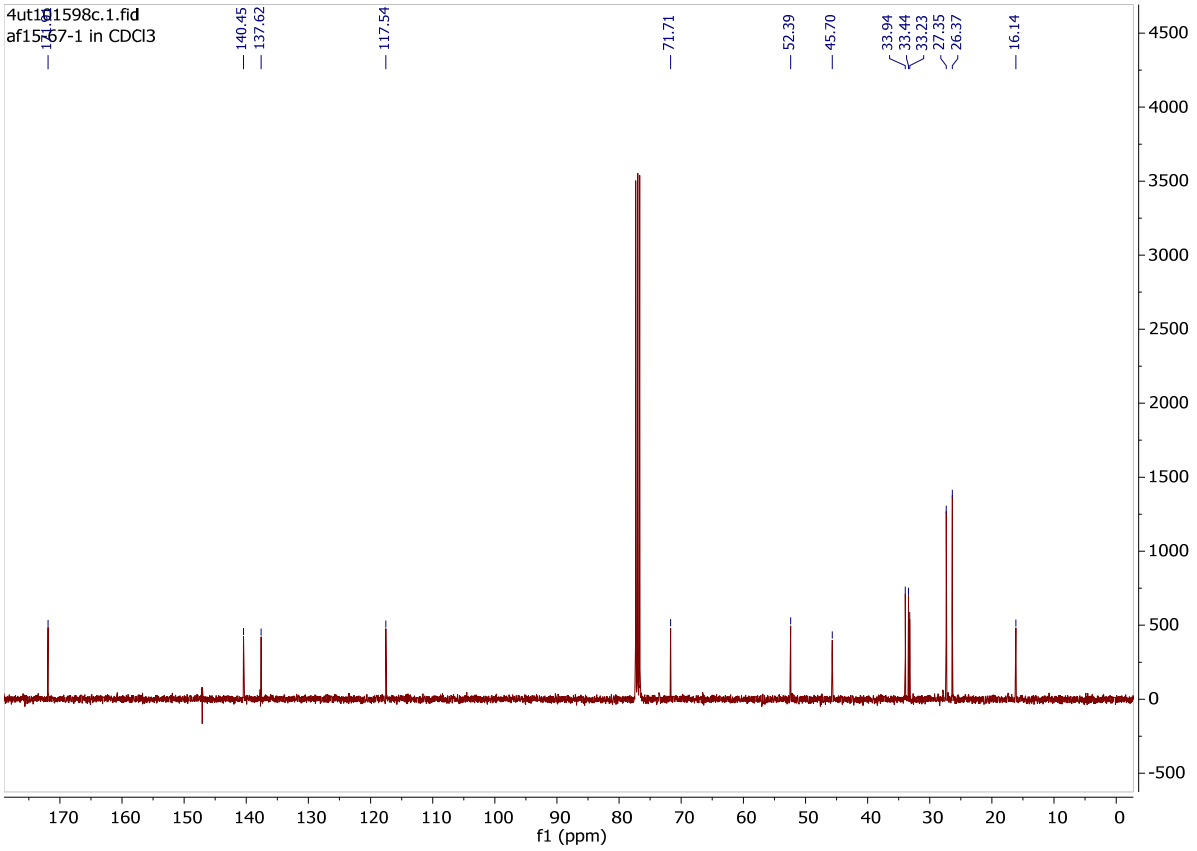
L11
f1 (ppm)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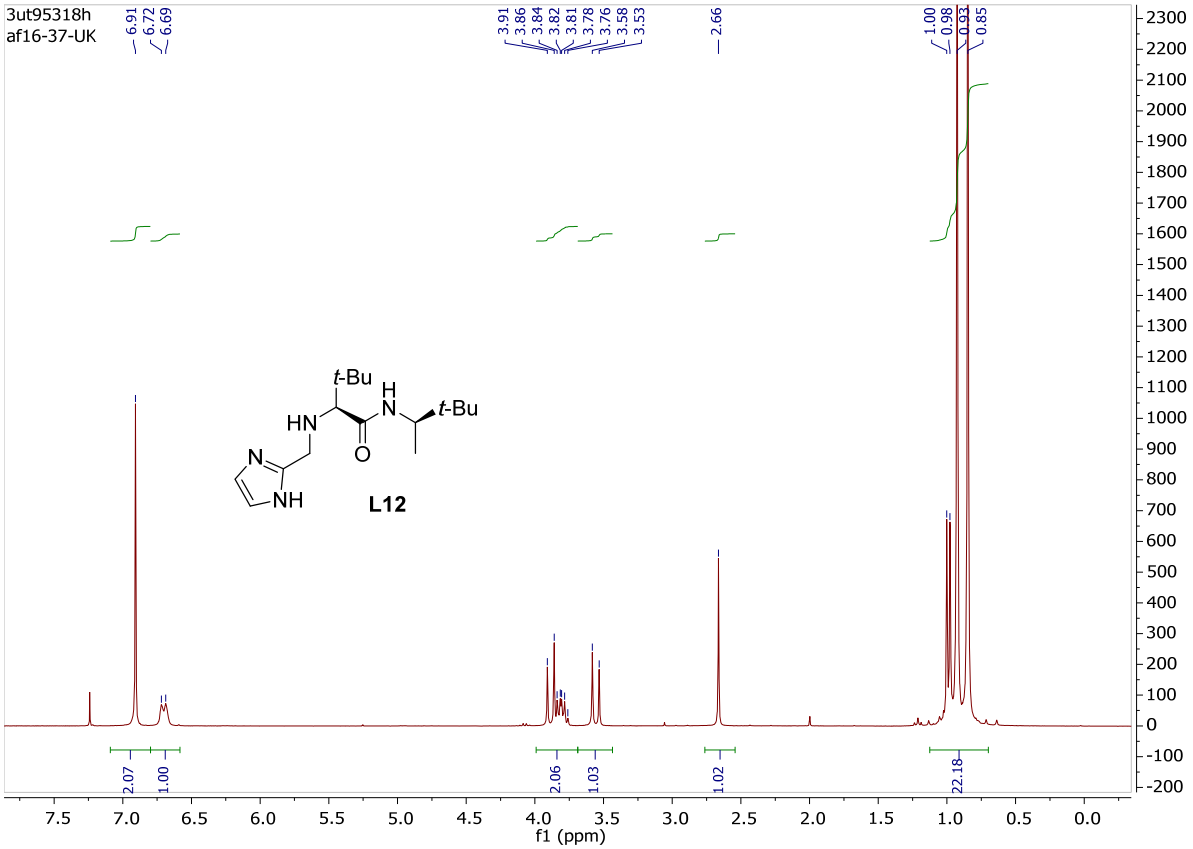
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3.58
3.53
2.66
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0.93
0.85
t-Bu
HN
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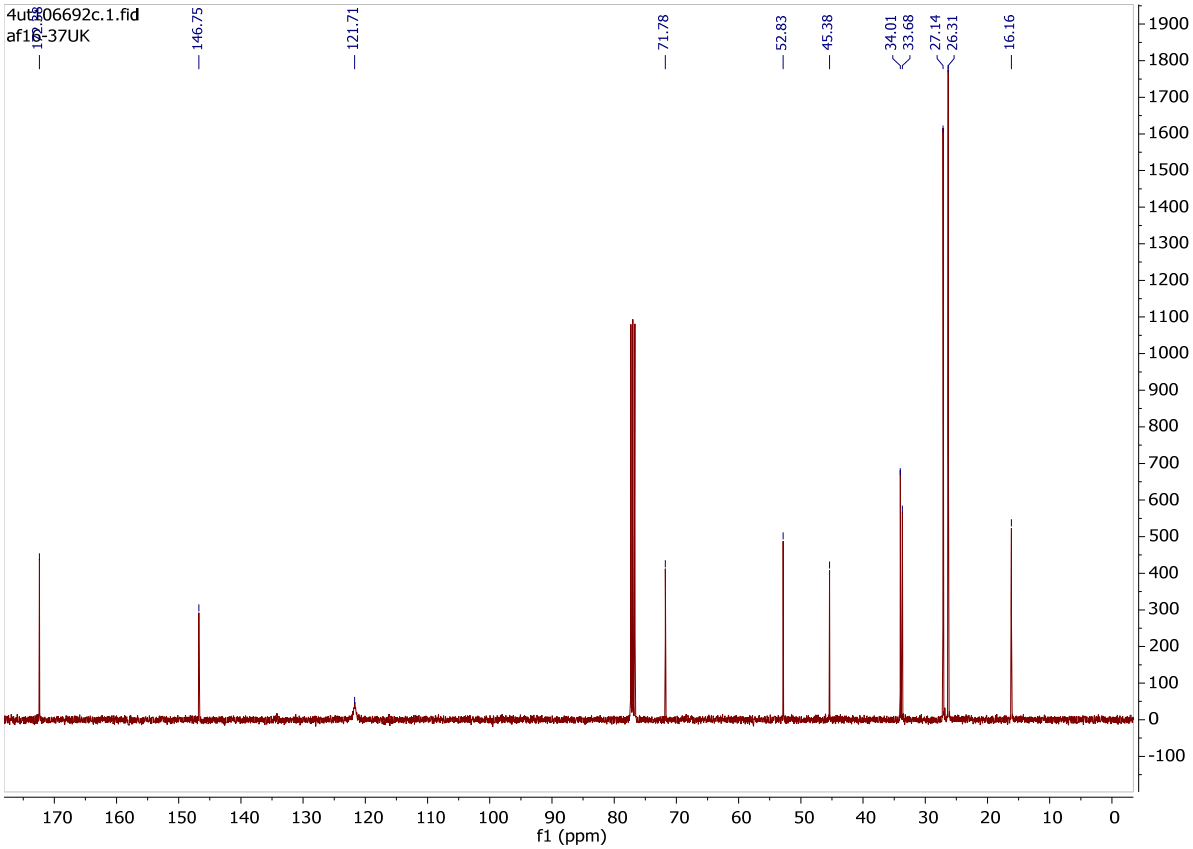
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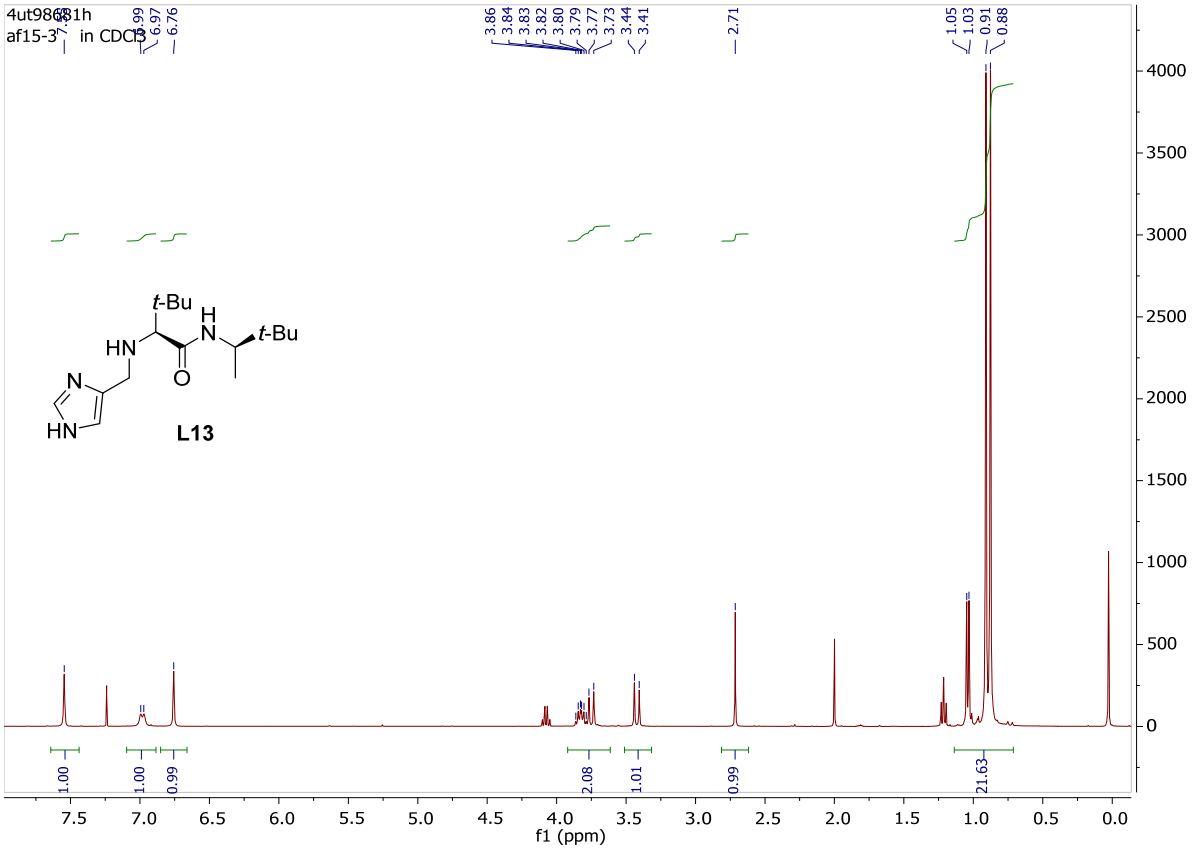
f1 (ppm)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6.97
6.76
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3.82
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3.79
3.77
3.73
3.44
3.41
2.71
1.05
1.03
0.91
0.88
t-Bu
HN
H
N
t-Bu
O
N
HN
L13
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1.01
0.99
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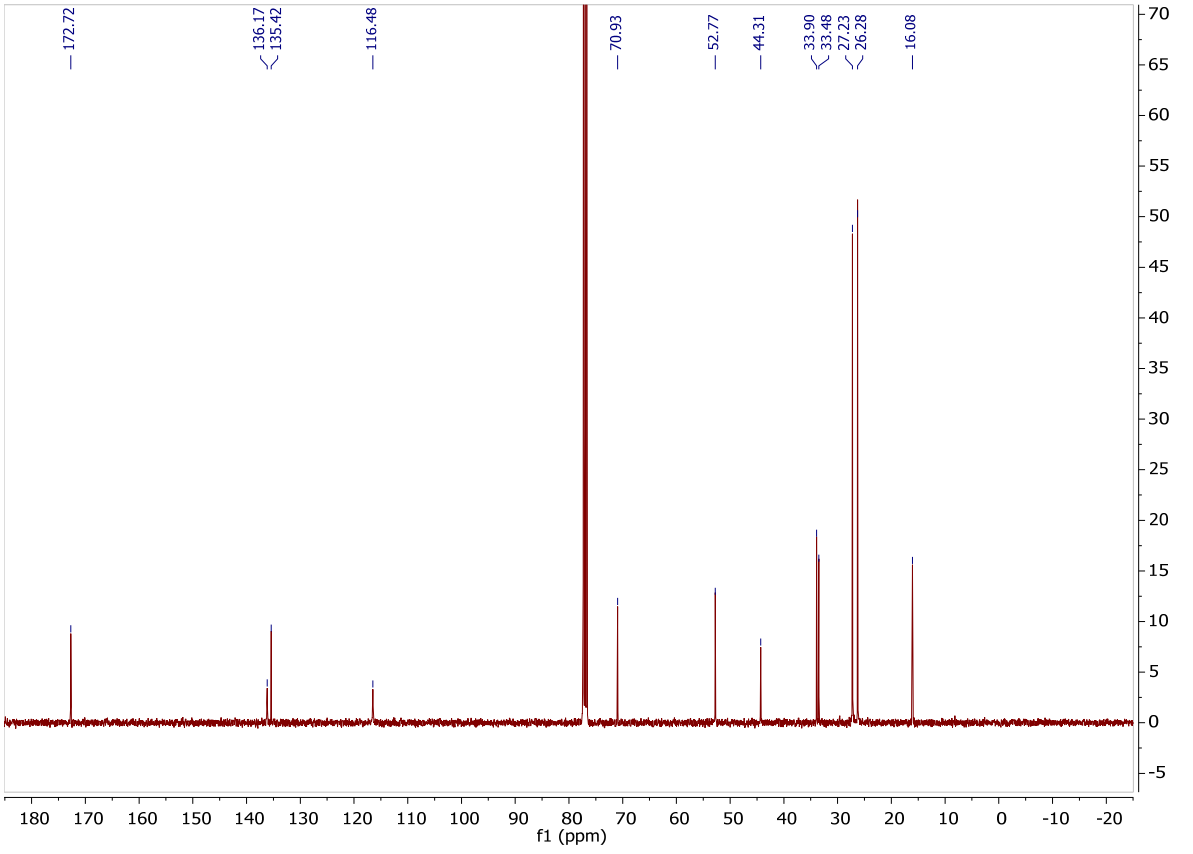
f1 (ppm)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136.17
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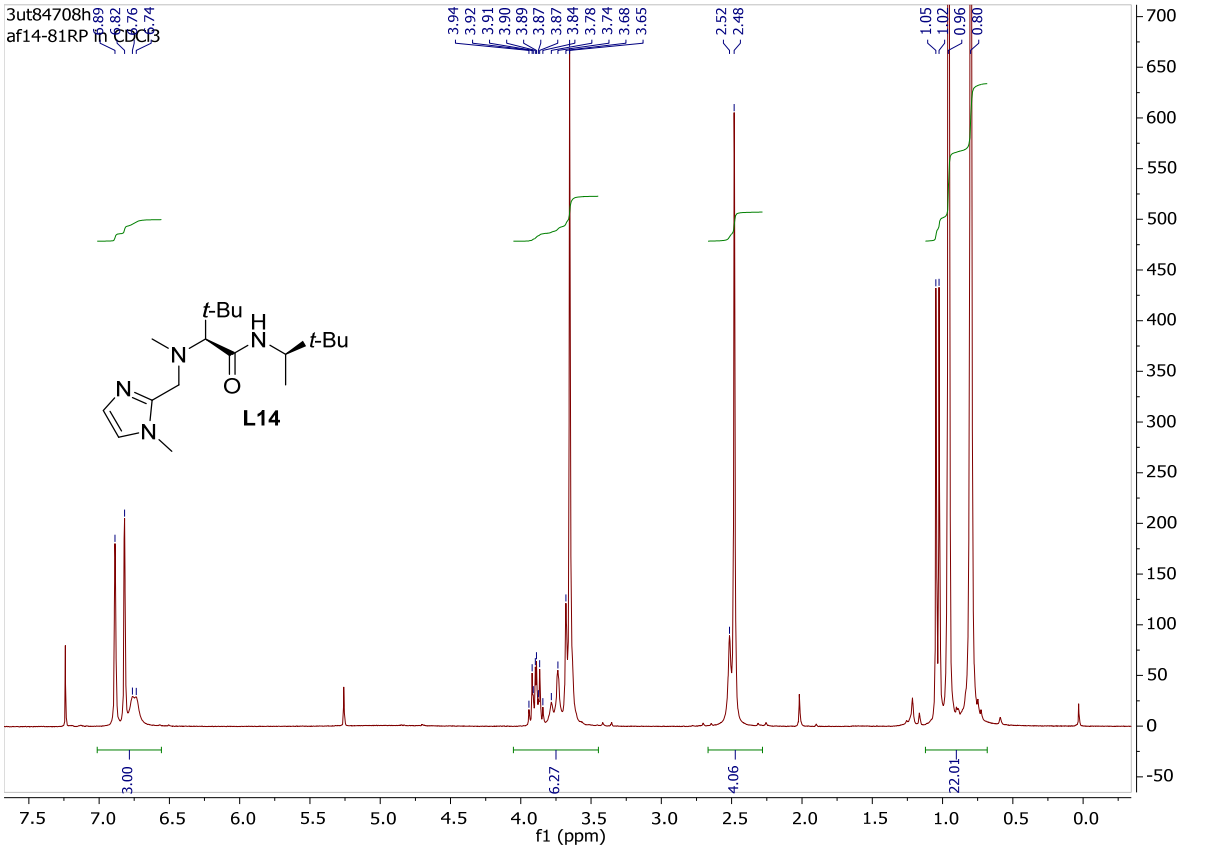
70.93
52.77
44.31
33.90
33.48
27.23
26.28
16.08
f1 (ppm)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3.74
3.68
3.65
2.52
2.48
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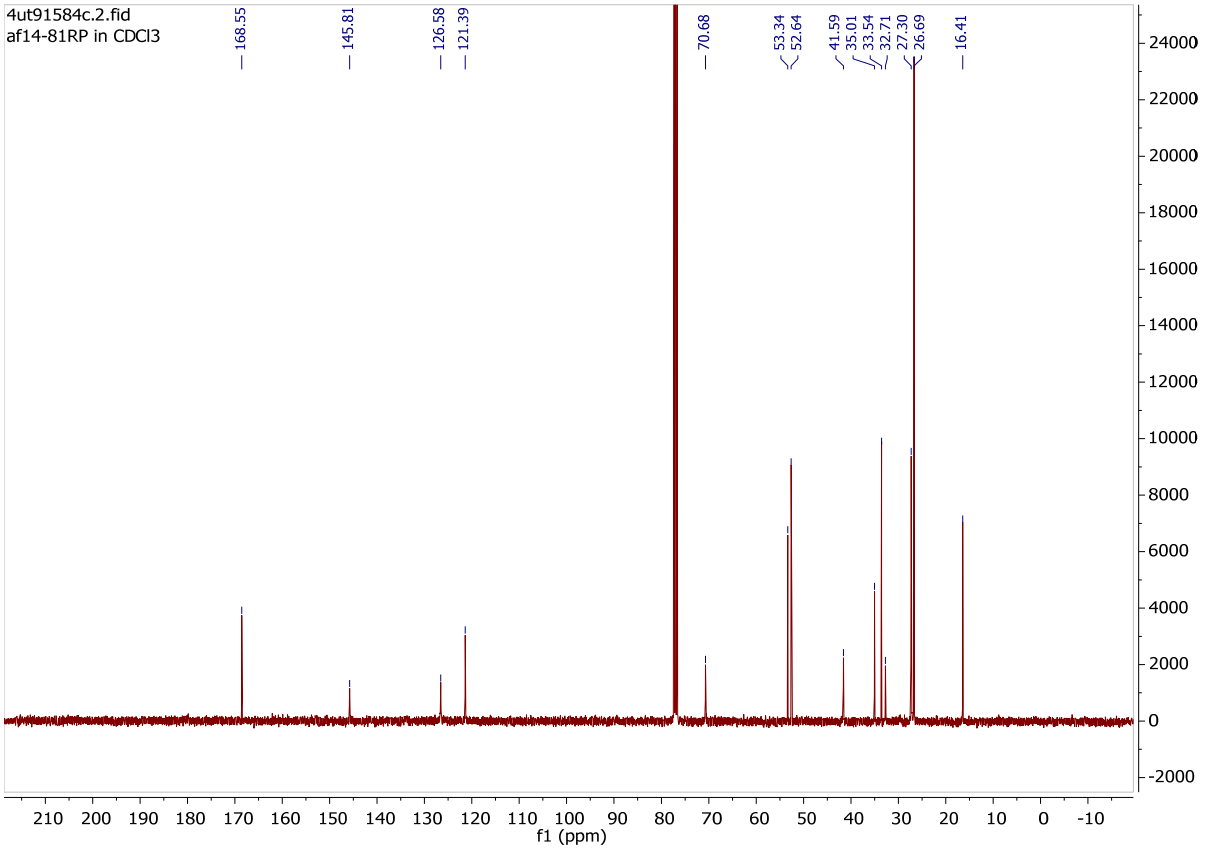
f1 (ppm)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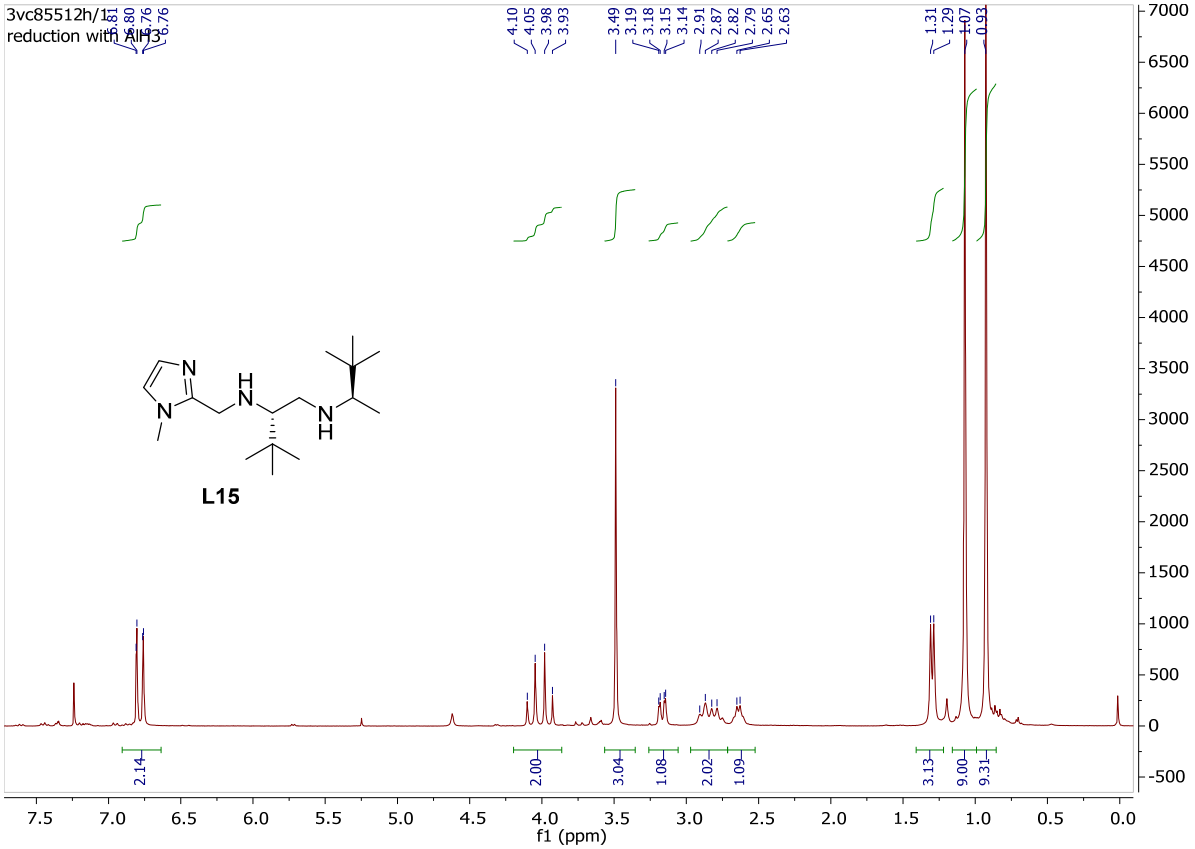
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6.76
4.10
4.05
3.98
3.93
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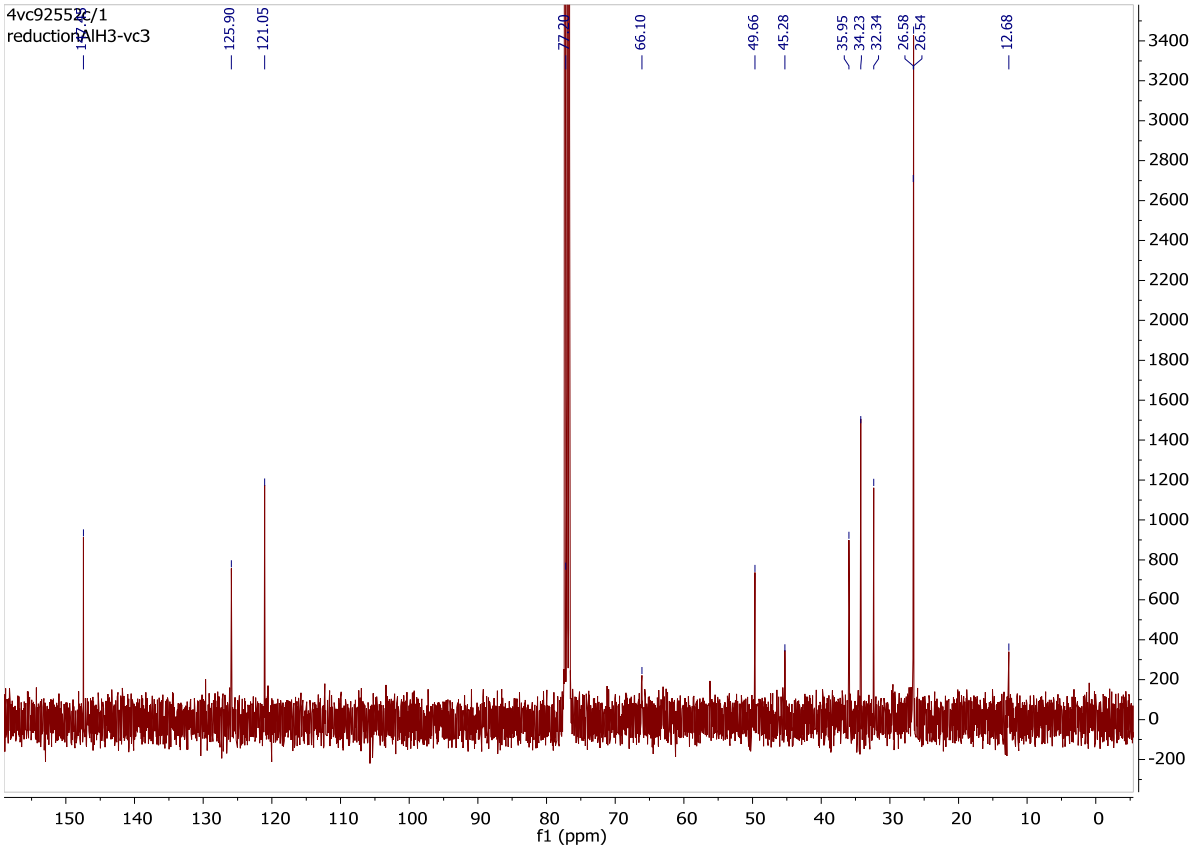
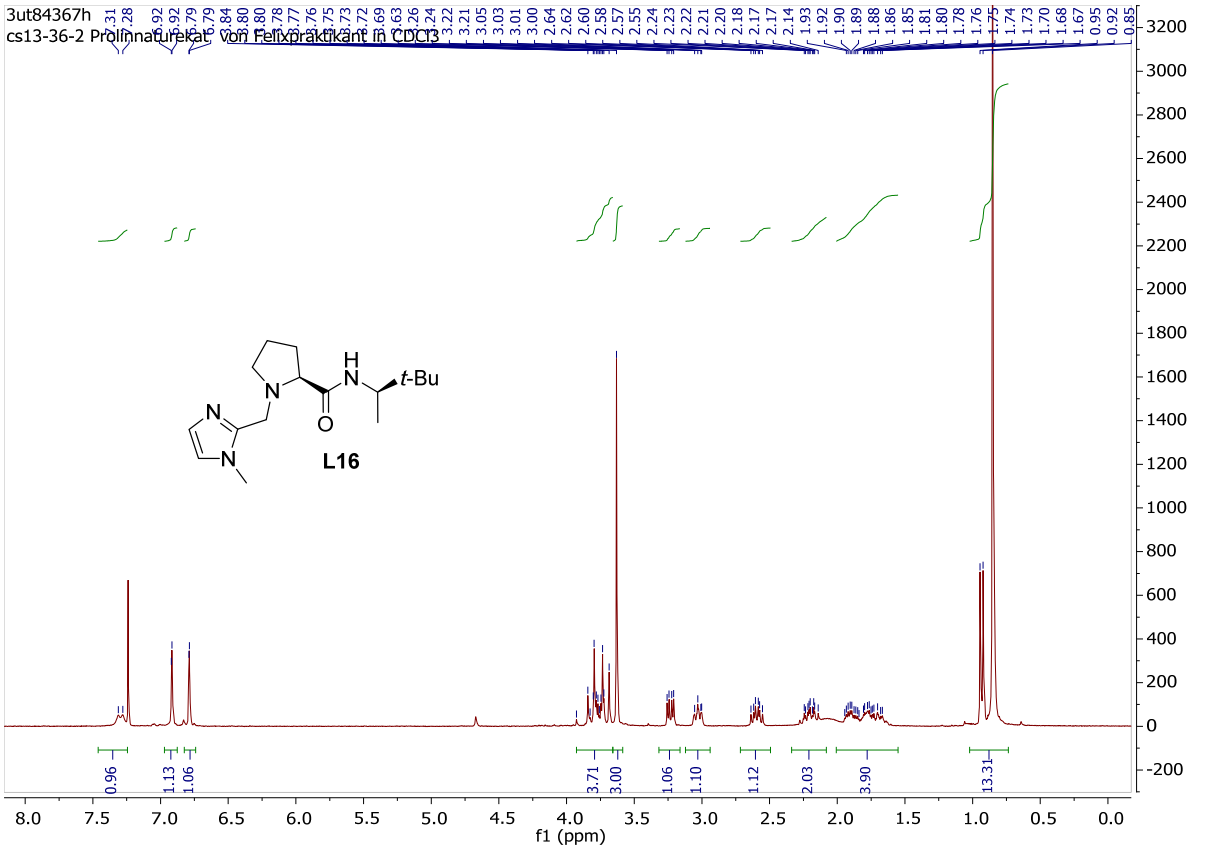
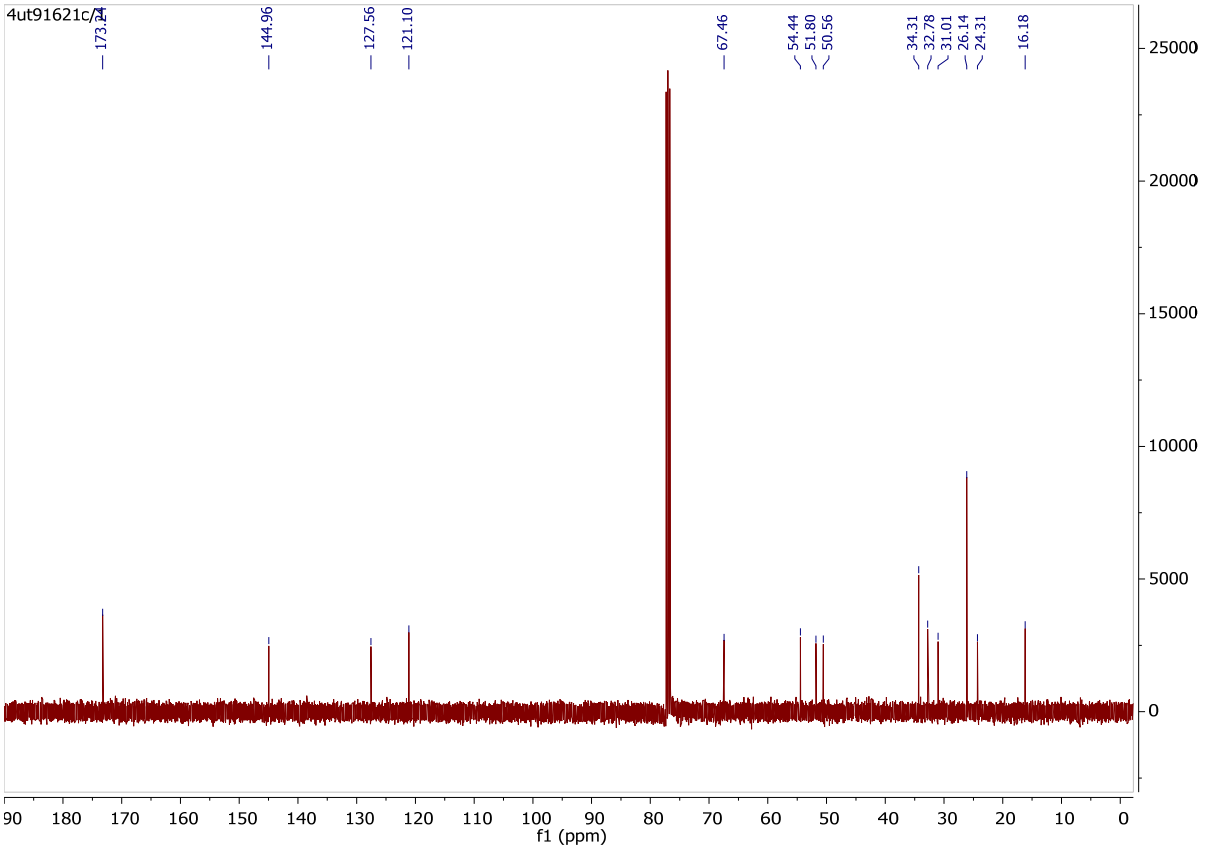
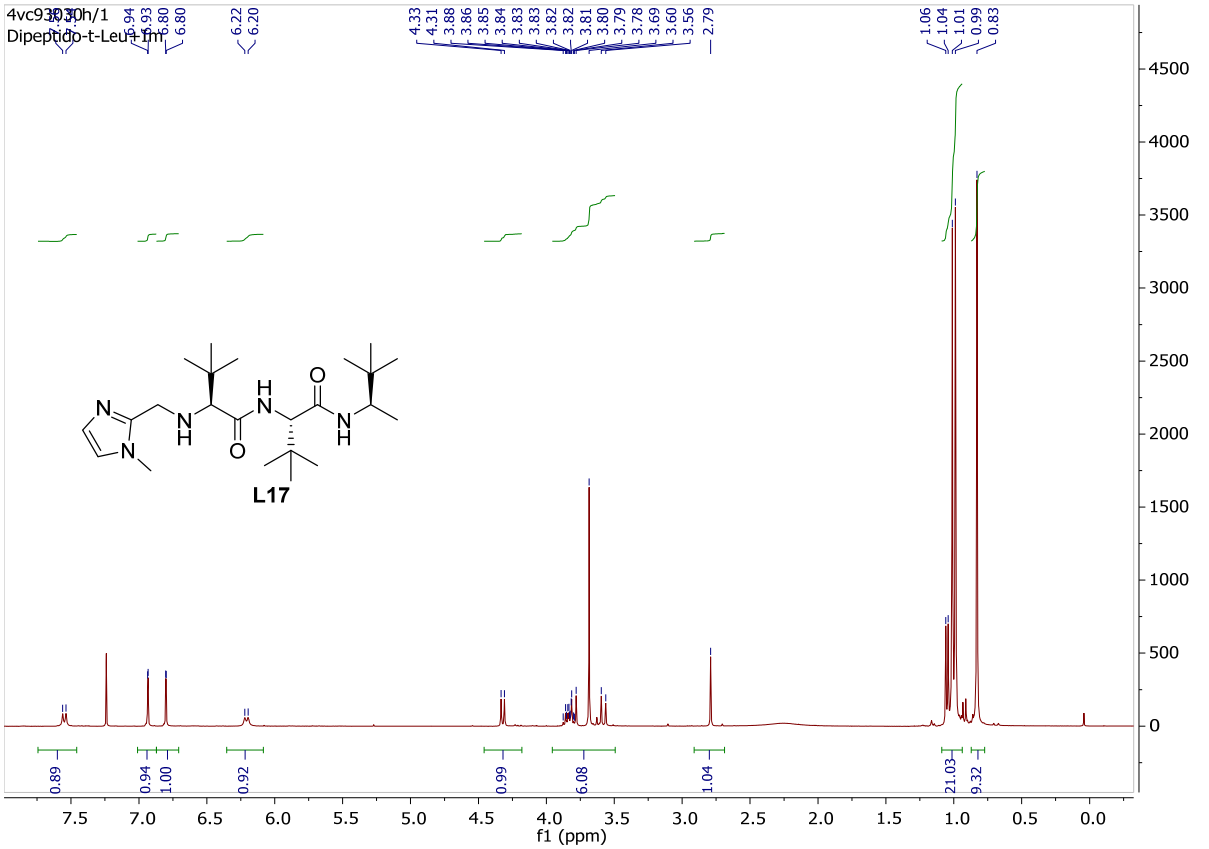
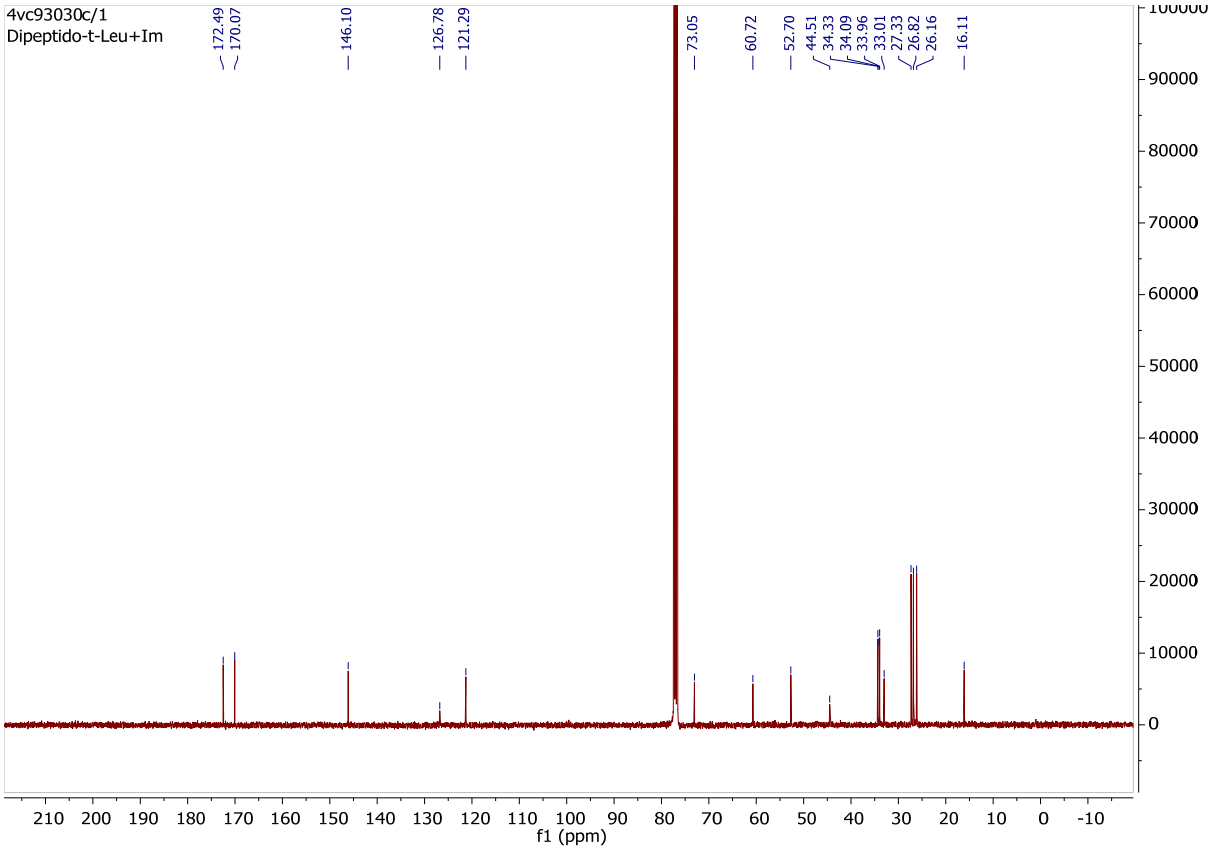
3.18
3.15
3.14
2.91
2.87
2.82
2.79
2.65
2.63
1.31
1.29
1.07
0.93
L15
2.14
2.00
3.04
1.08
2.02
1.09
3.13
9.00
9.31
f1 (ppm)


4vc92552c/1
reduction AlH3-vc3
125.90
121.05
77.20
66.10
49.66
45.28
35.95
34.23
32.34
26.58
26.54
12.68
f1 (ppm)


3ut84367h
cs13-36-2 Prolinnatürekat von Felixpraktikant in CDCl3
L16
f1 (ppm)


4ut91621c/24
f1 (ppm)

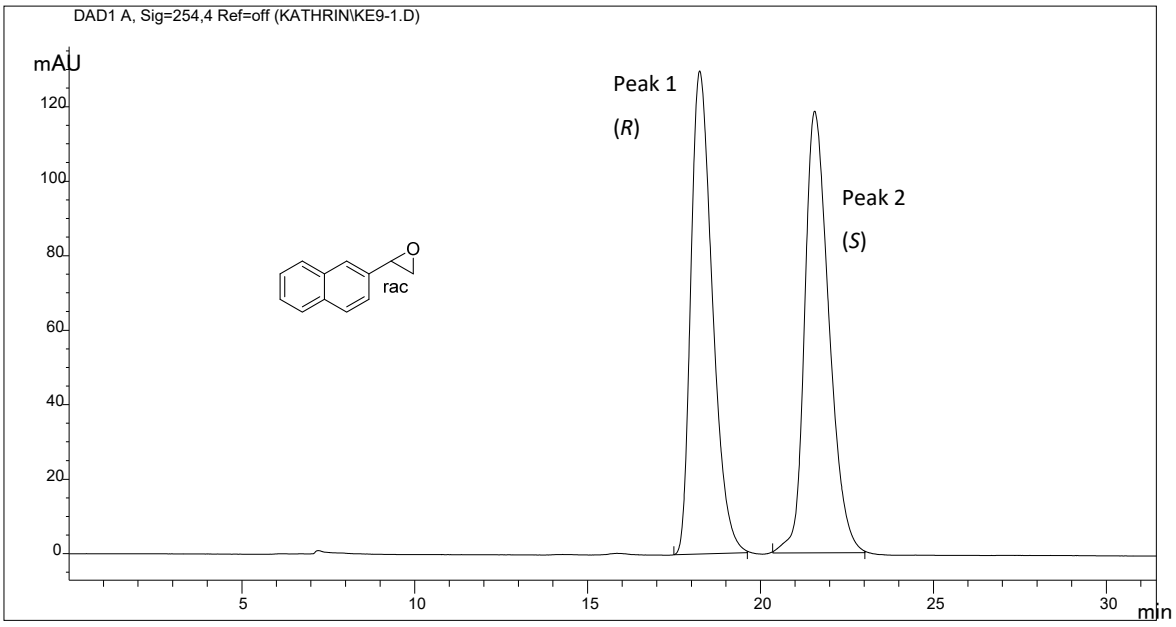

4vc93030h/1
Dipeptido-t-Leu+Im
9.94
6.93
6.80
6.80
6.22
6.20
4.33
4.31
3.88
3.86
3.85
3.84
3.83
3.83
3.82
3.82
3.81
3.80
3.79
3.78
3.69
3.60
3.56
2.79
1.06
1.04
1.01
0.99
0.83
L17
0.89
0.94
1.00
0.92
0.99
6.08
1.04
21.03
9.32
f1 (ppm)


4vc93030c/1
Dipeptido-t-Leu+Im
172.49
170.07
146.10
126.78
121.29
73.05
60.72
52.70
44.51
34.33
34.09
33.96
33.01
27.33
26.82
26.16
16.11
f1 (ppm)

# 7 HPLC chromatograms

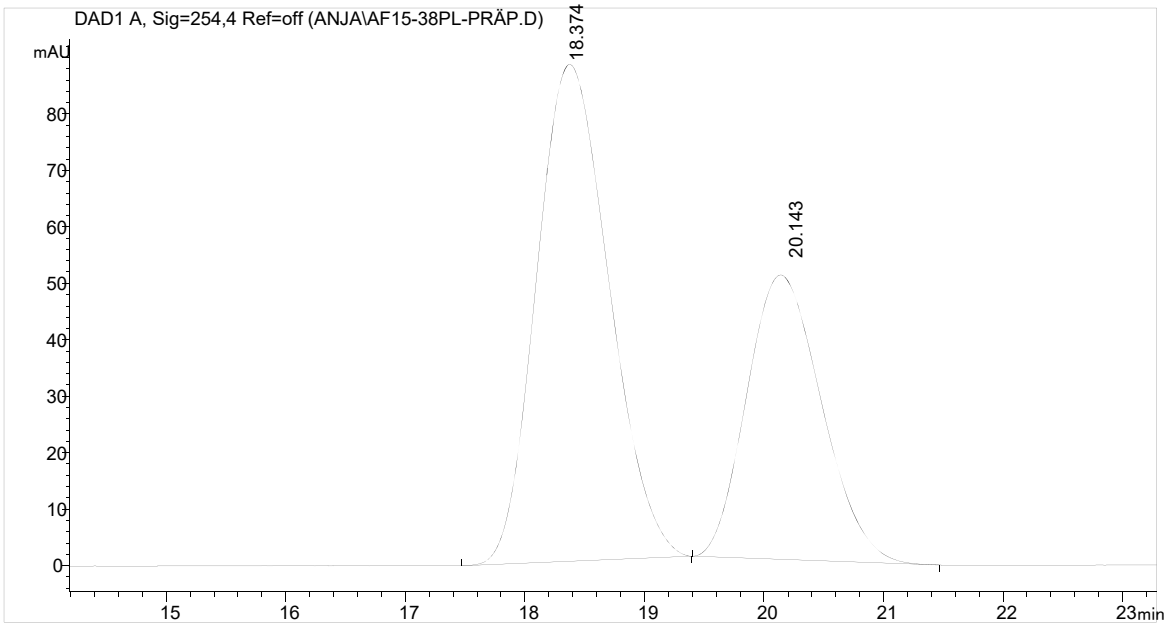
### 2-Naphthalen-2-yl-oxirane

**Chiral HPLC** (Daicel Chiralpak AS): *n*-hexane/*i*-PrOH 99:1, 0.5 ml/min flow rate, $\lambda$ = 254 nm;




| Peak | $t_R$ | Area | Area (%) |
|---|---|---|---|
| 1 | 18.236 | 5621.8 | 49.24 |
| 2 | 21.563 | 5796 | 50.76 |

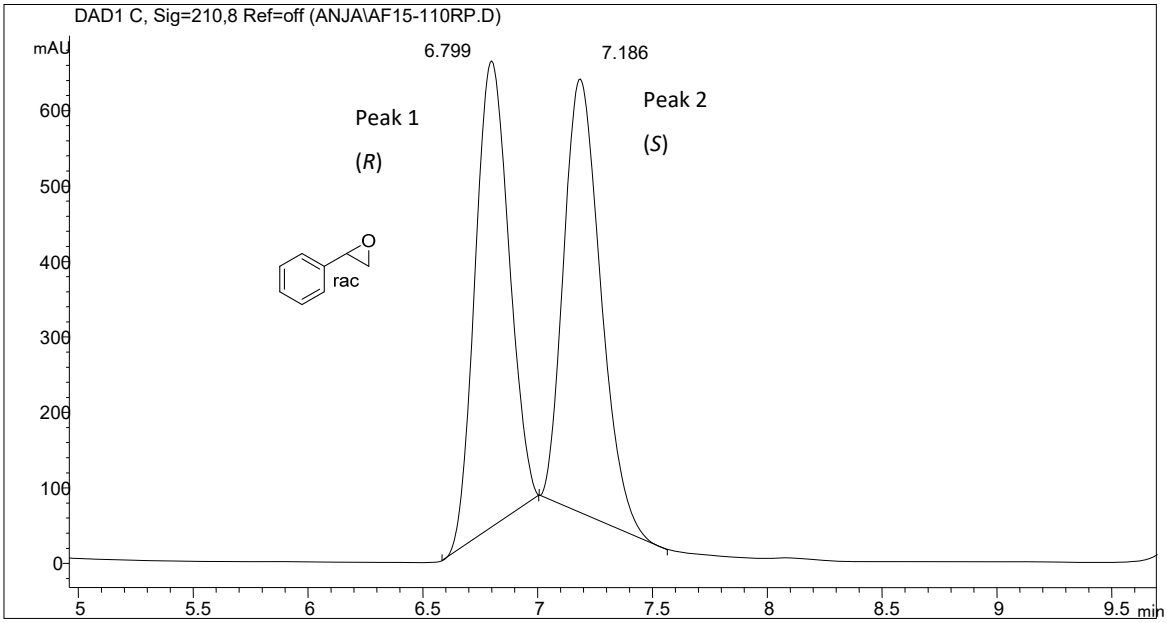
**See Entry 1, Table 2**




| Peak | $t_R$ | Area | Area (%) |
|---|---|---|---|
| 1 | 18.374 | 3715.3 | 62.867 |
| 2 | 20.143 | 2194.5 | 37.133 |

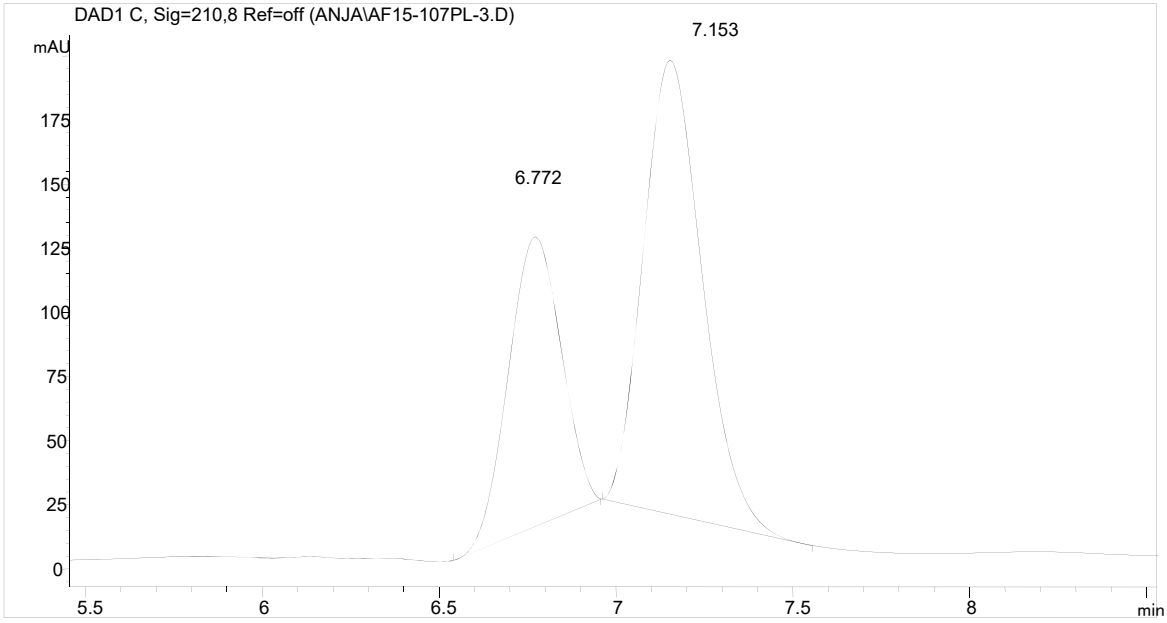
**2-Phenyloxirane**

**Chiral HPLC** (Macherey-Nagel OD): *n*-hexane/*i*-PrOH 99:1, 1.0 ml/min flow rate, $\lambda$ = 210 nm;




| Peak | $t_R$ | Area | Area (%) |
|---|---|---|---|
| 1 | 6.799 | 6357.5 | 49.627 |
| 2 | 7.186 | 6453 | 50.373 |

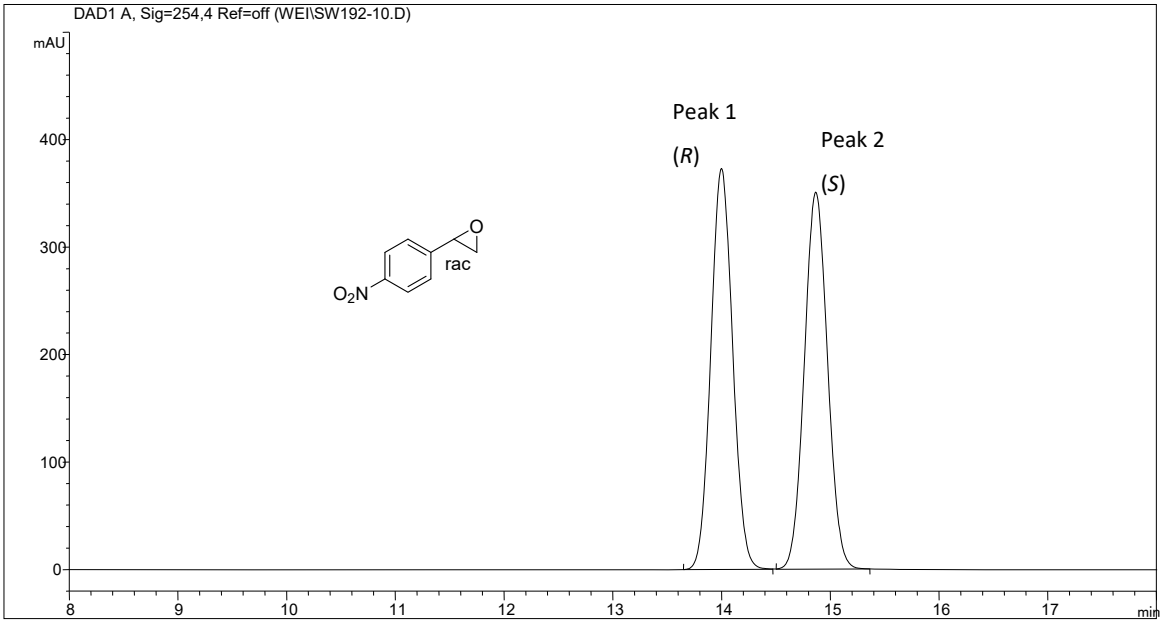
**See Entry 2, Table 2**




| Peak | $t_R$ | Area | Area (%) |
|---|---|---|---|
| 1 | 6.772 | 1174.8 | 36.338 |
| 2 | 7.153 | 2058.1 | 63.662 |

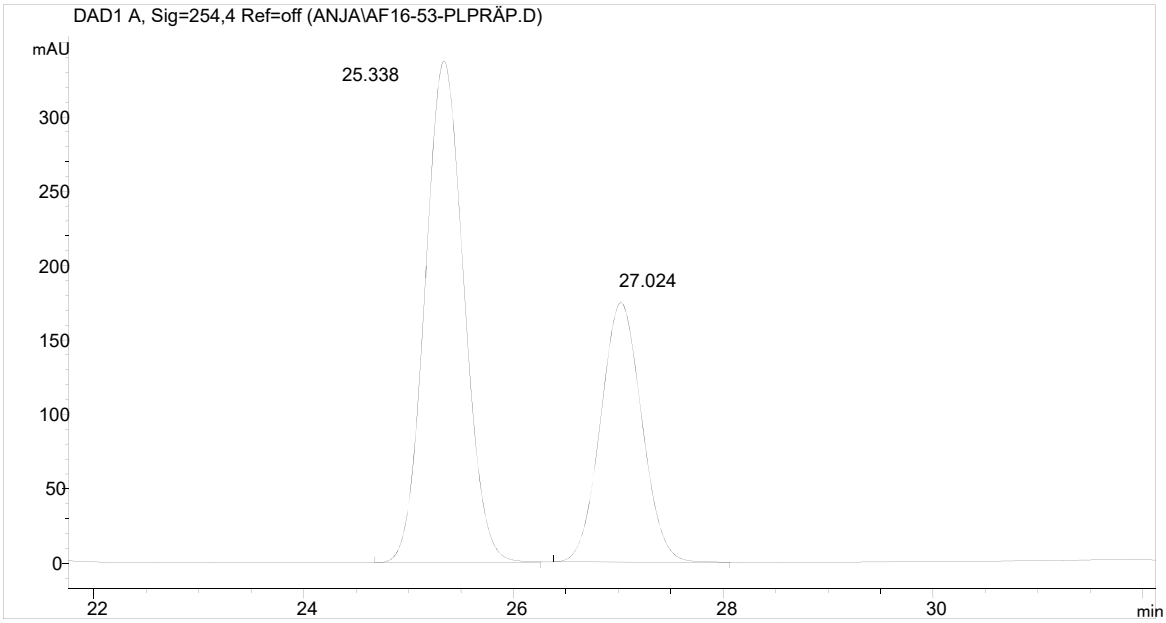
**2-(4-Nitro-phenyl)-oxirane**

**Chiral HPLC** (Daicel Chiralpak IC): *n*-hexane/*i*-PrOH 95:5, 1.0 ml/min flow rate, $\lambda$ = 254 nm;




| Peak | $t_R$ | Area | Area (%) |
|---|---|---|---|
| 1 | 13.998 | 360.44 | 49.94 |
| 2 | 14.865 | 339.40 | 50.06 |

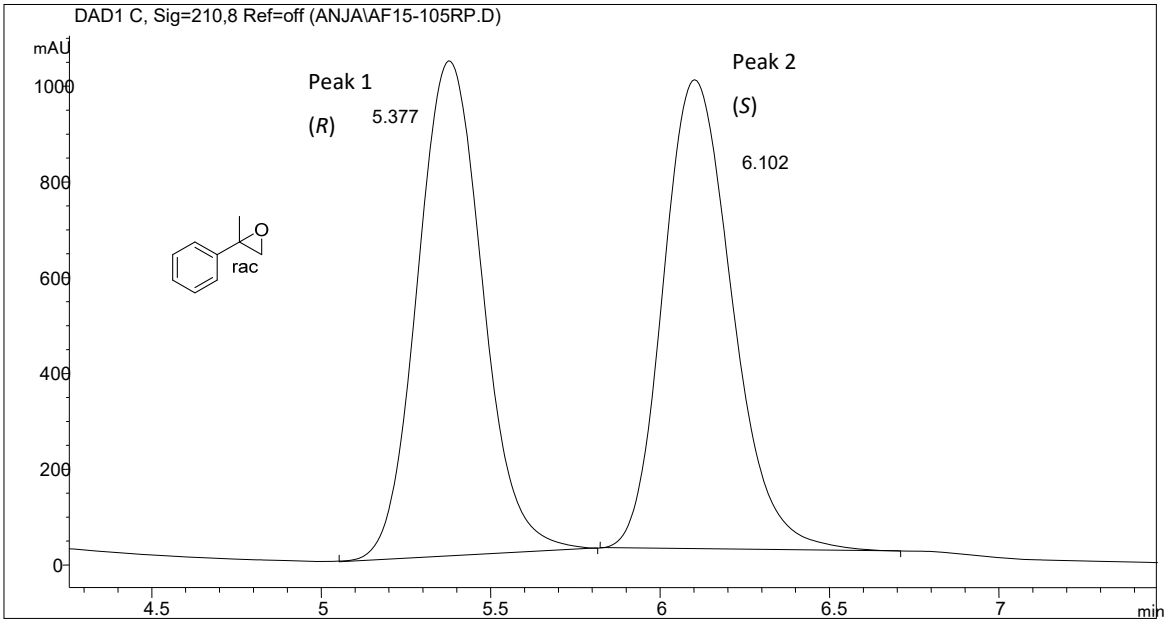
**See Entry 3, Table 2** (different retention behaviour due to pressure problems in HPLC system)




| Peak | $t_R$ | Area | Area (%) |
|---|---|---|---|
| 1 | 25.338 | 8679.2 | 64.625 |
| 2 | 27.024 | 4750.9 | 35.375 |

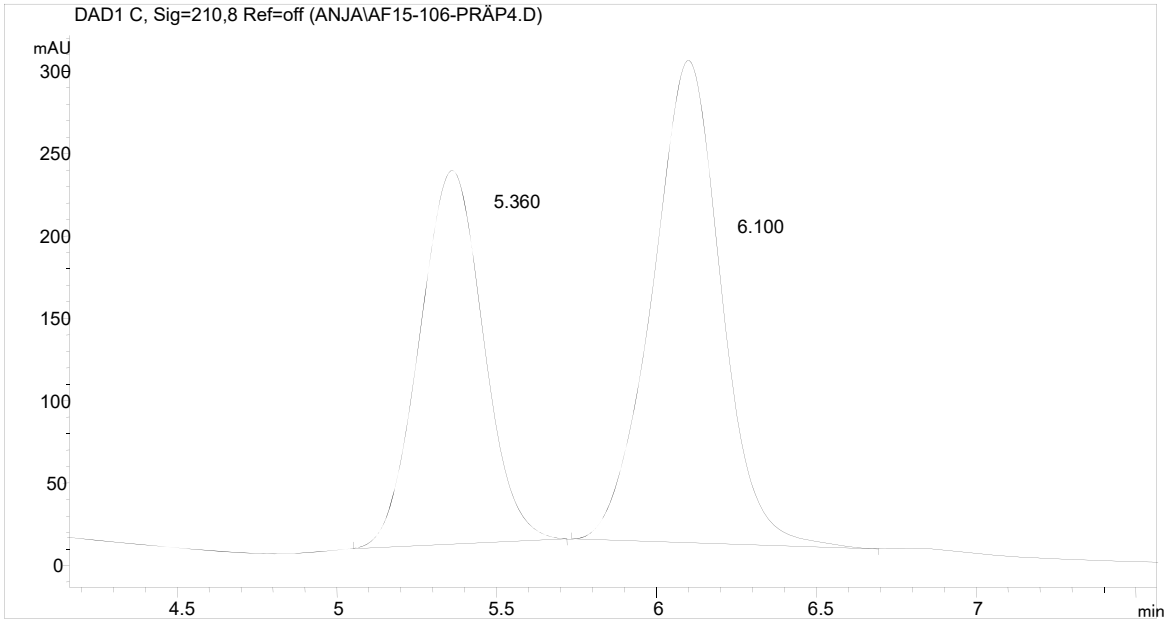
**2-Methyl-2-phenyloxirane**

**Chiral HPLC** (Macherey-Nagel OD): *n*-hexane/*i*-PrOH 99:1, 1.0 ml/min flow rate, $\lambda$ = 210 nm;




| Peak | $t_R$ | Area | Area (%) |
|---|---|---|---|
| 1 | 5.377 | 13850.2 | 50.000 |
| 2 | 6.102 | 13850 | 50.000 |

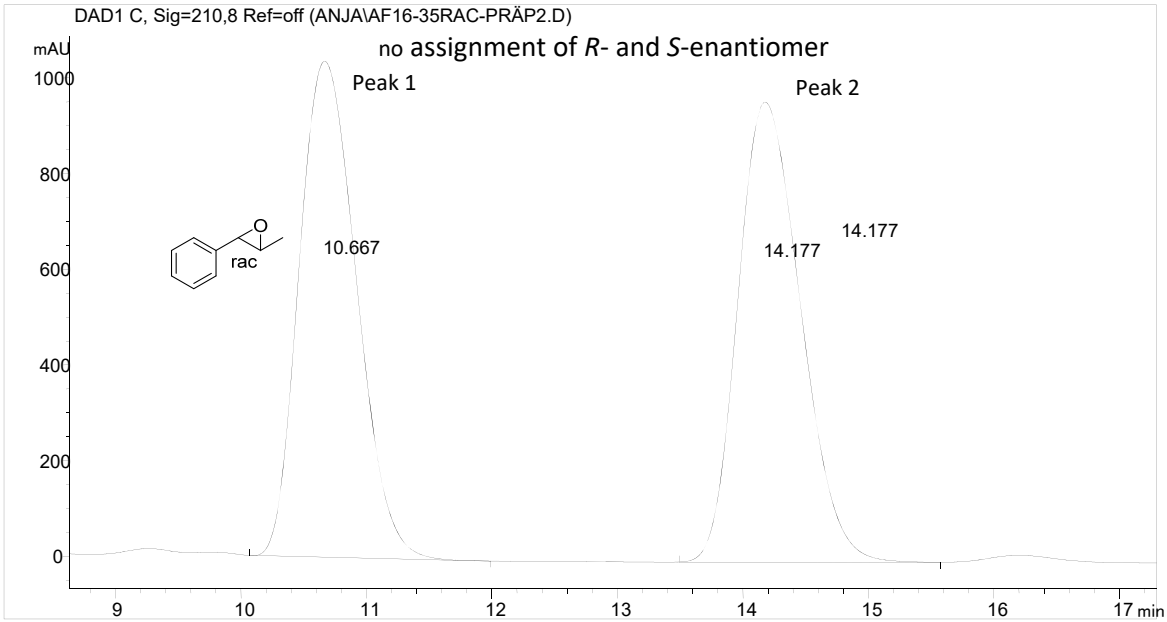
**See Entry 6, Table 2**




| Peak | $t_R$ | Area | Area (%) |
|---|---|---|---|
| 1 | 5.36 | 3153 | 41.812 |
| 2 | 6.1 | 4387.9 | 58.188 |

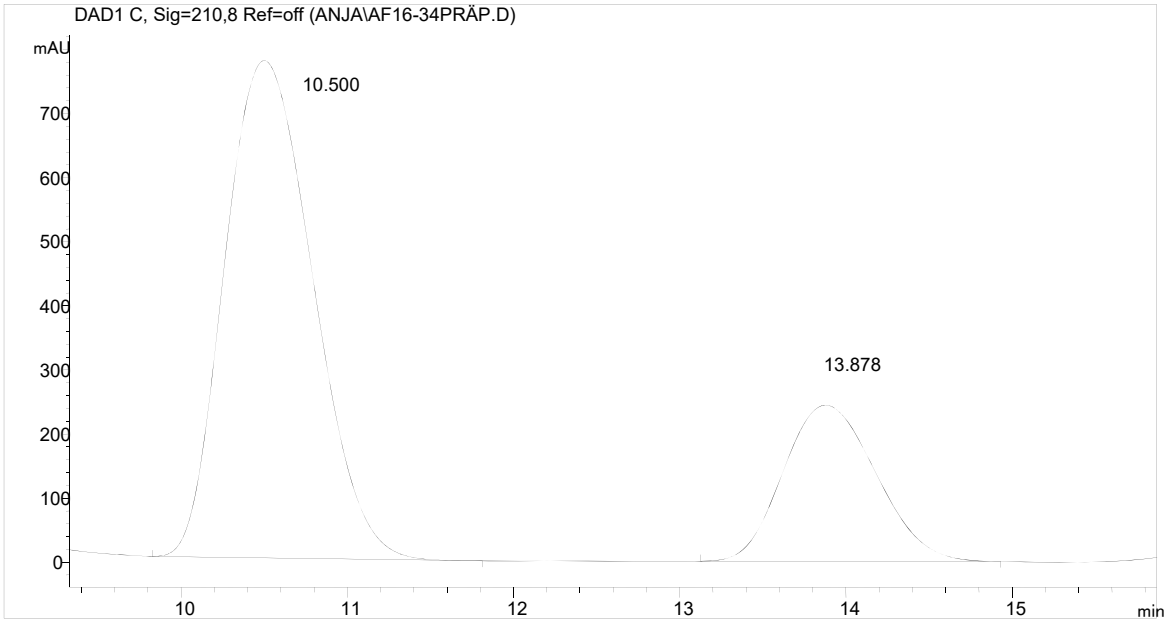
**2-Methyl-3-phenyloxirane**

**Chiral HPLC** (Daicel Chiralpak AS): *n*-hexane/*i*-PrOH 99:1, 0.5 ml/min flow rate, $\lambda$ = 210 nm;




| Peak | $t_R$ | Area | Area (%) |
|---|---|---|---|
| 1 | 10.667 | 32920.4 | 49.569 |
| 2 | 14.177 | 33493 | 50.431 |

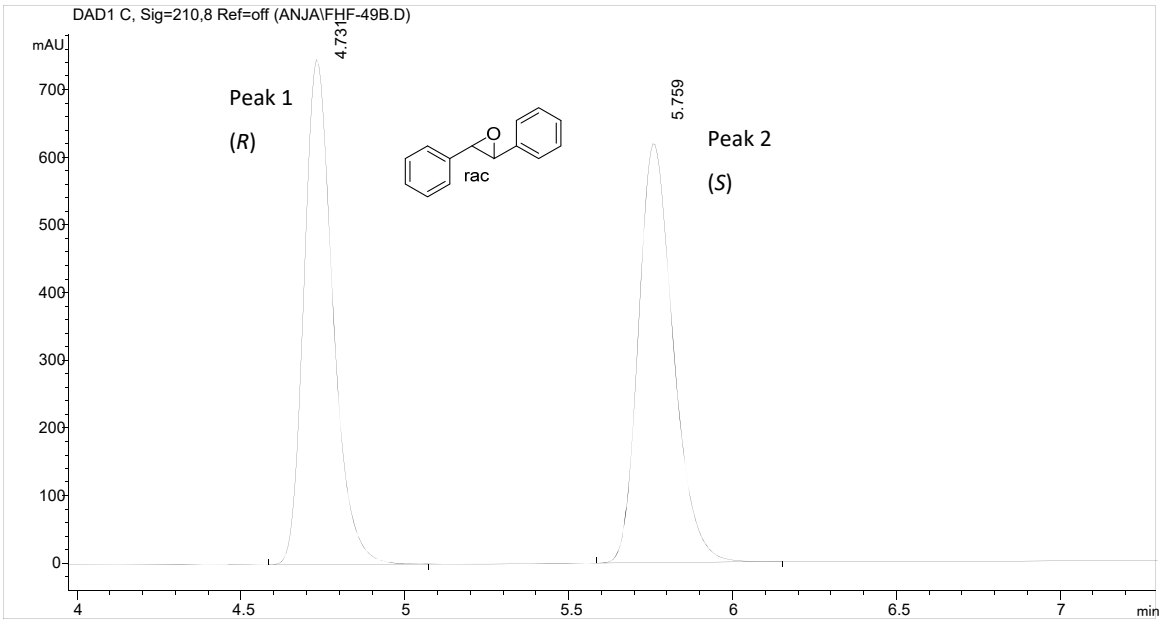
**See Entry 8, Table 2**




| Peak | $t_R$ | Area | Area (%) |
|---|---|---|---|
| 1 | 10.5 | 28623.3 | 75.183 |
| 2 | 13.878 | 9448.3 | 24.817 |

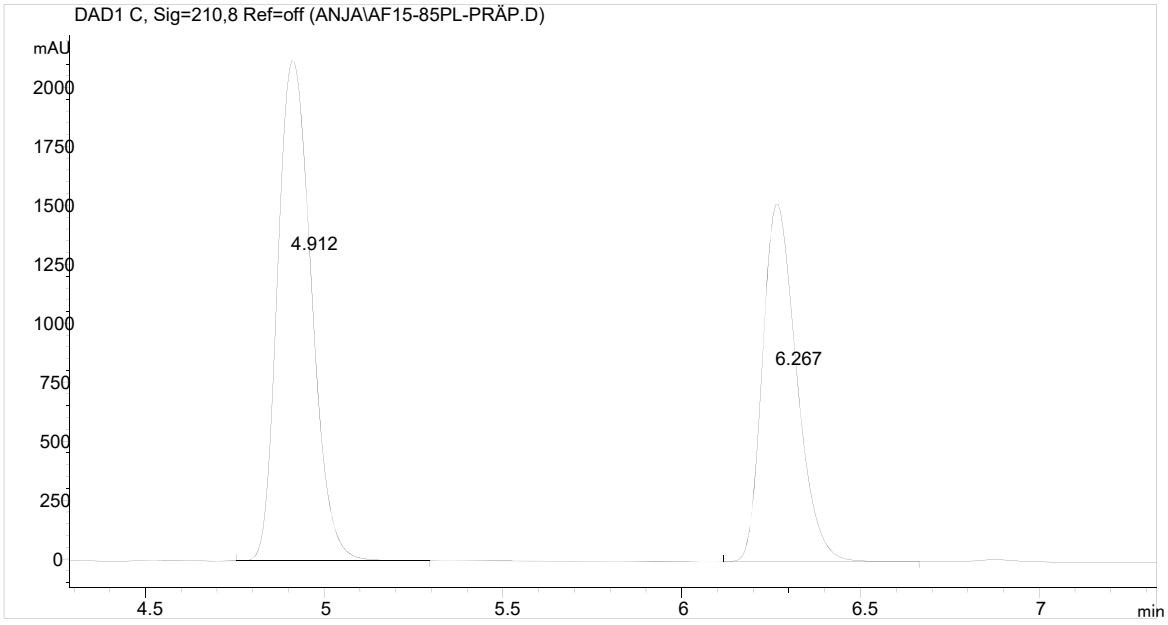
**2,3-Diphenyloxirane**

**Chiral HPLC** (Daicel Chiralpak IB): *n*-hexane/*i*-PrOH 92:8, 1.0 ml/min flow rate, $\lambda$ = 210 nm;




| Peak | $t_R$ | Area | Area (%) |
|---|---|---|---|
| 1 | 4.731 | 4576.1 | 49.973 |
| 2 | 5.759 | 4581.1 | 50.027 |

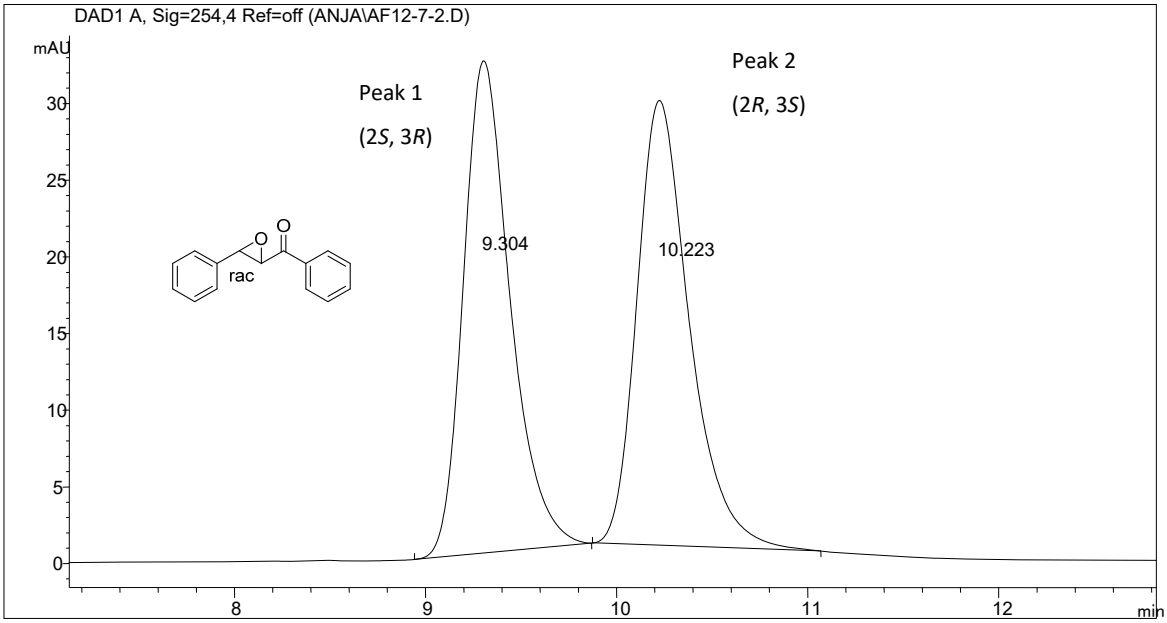
**See Entry 9, Table 2**




| Peak | $t_R$ | Area | Area (%) |
|---|---|---|---|
| 1 | 4.912 | 13954.8 | 58.083 |
| 2 | 6.267 | 10070.9 | 41.917 |

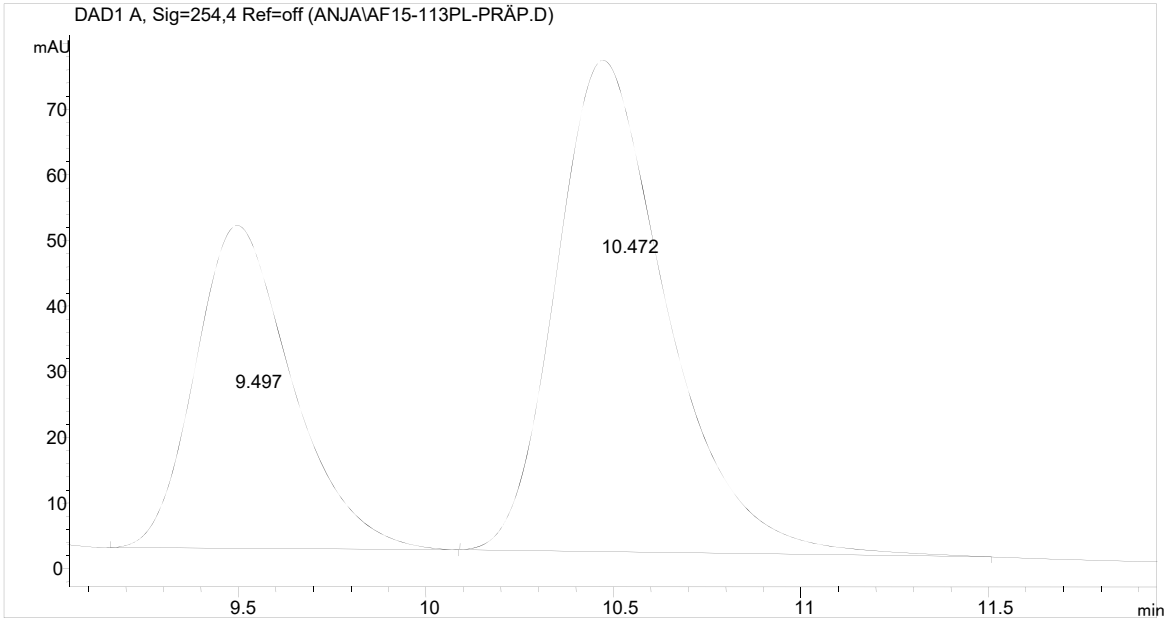
**Phenyl(3-phenyloxiran-2-yl)methanone**

**Chiral HPLC** (Macherey-Nagel OD): *n*-hexane/*i*-PrOH 90:10, 1.0 ml/min flow rate, $\lambda$ = 245 nm;



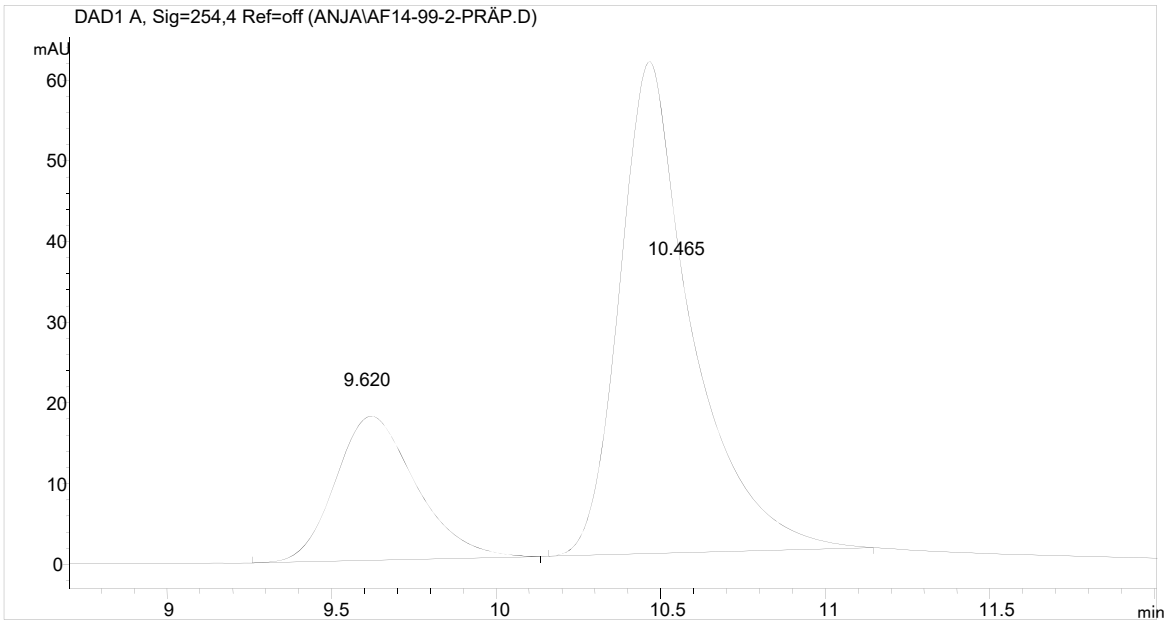

| Peak | $t_R$ | Area | Area (%) |
|---|---|---|---|
| 1 | 9.304 | 547.6 | 49.702 |
| 2 | 10.223 | 554.1 | 50.298 |

**See Entry 10, Table 2**



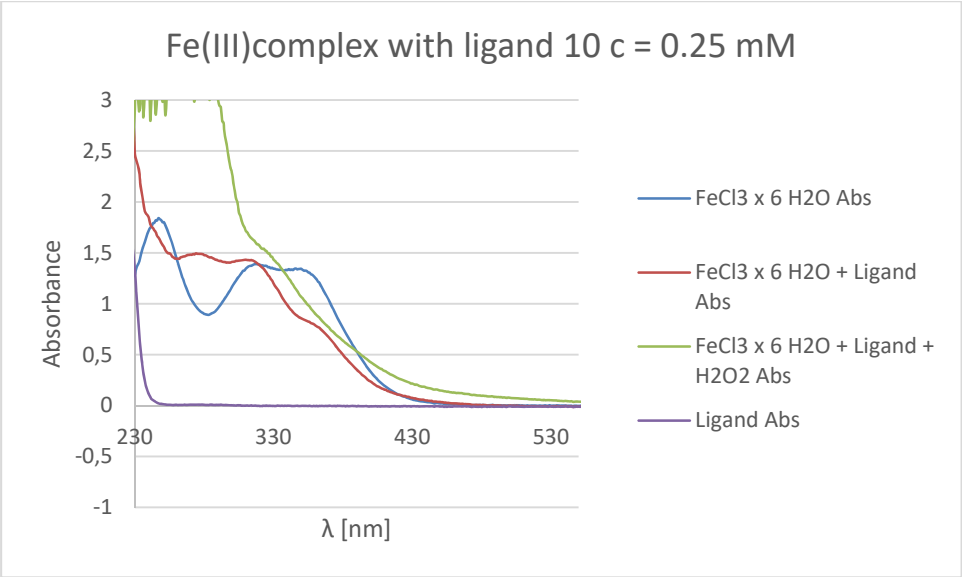

| Peak | $t_R$ | Area | Area (%) |
|---|---|---|---|
| 1 | 9.497 | 884.6 | 36.474 |
| 2 | 10.472 | 1540.7 | 63.526 |

**See Entry 11, Table 2**

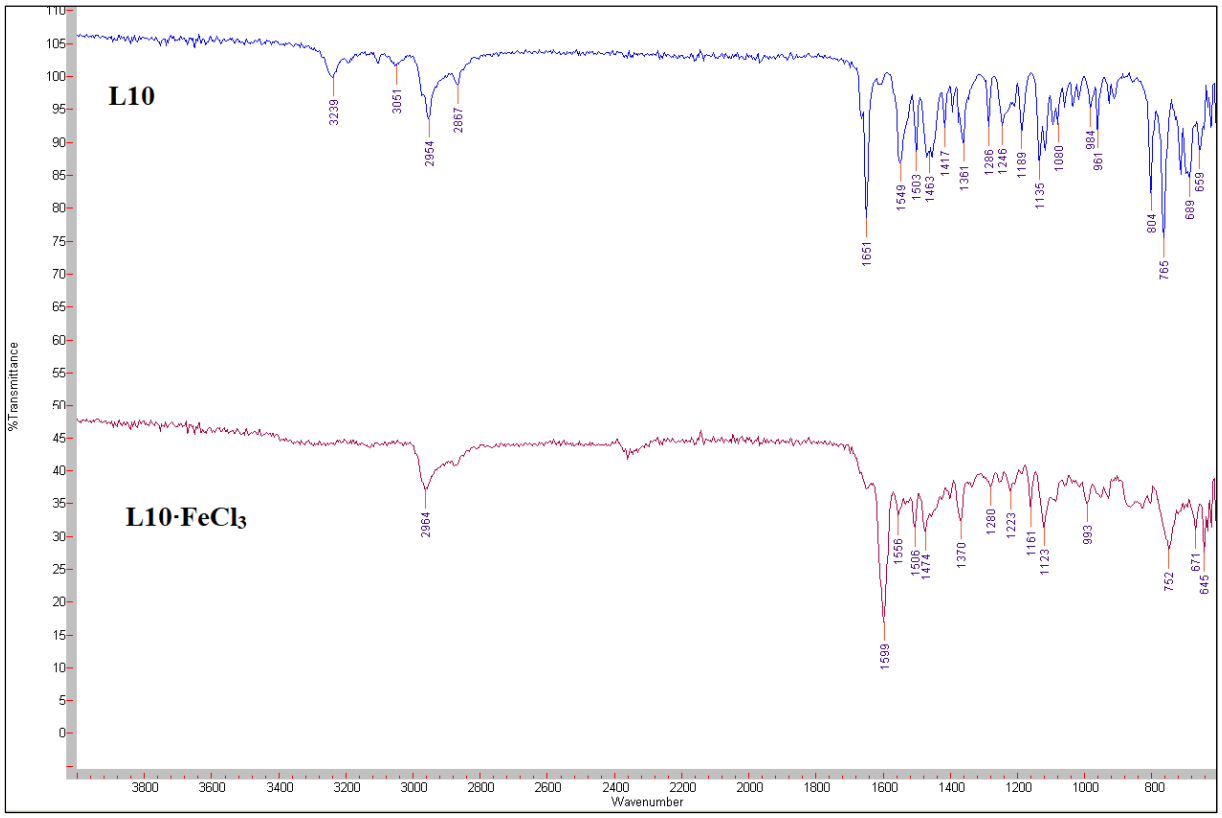


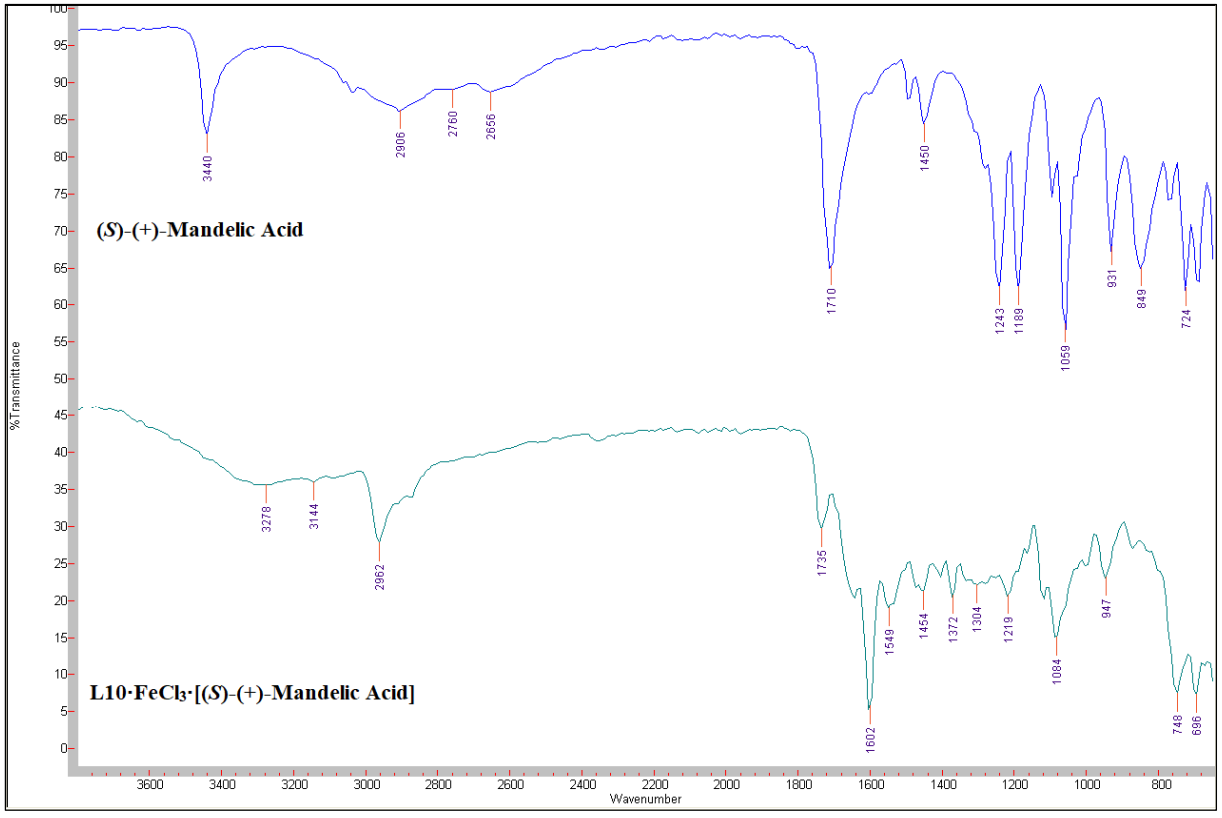

| Peak | $t_R$ | Area | Area (%) |
|---|---|---|---|
| 1 | 9.62 | 304.5 | 24.589 |
| 2 | 10.465 | 934 | 75.411 |

## 8 Investigation of Fe(III) complex via UV-Vis spectroscopy



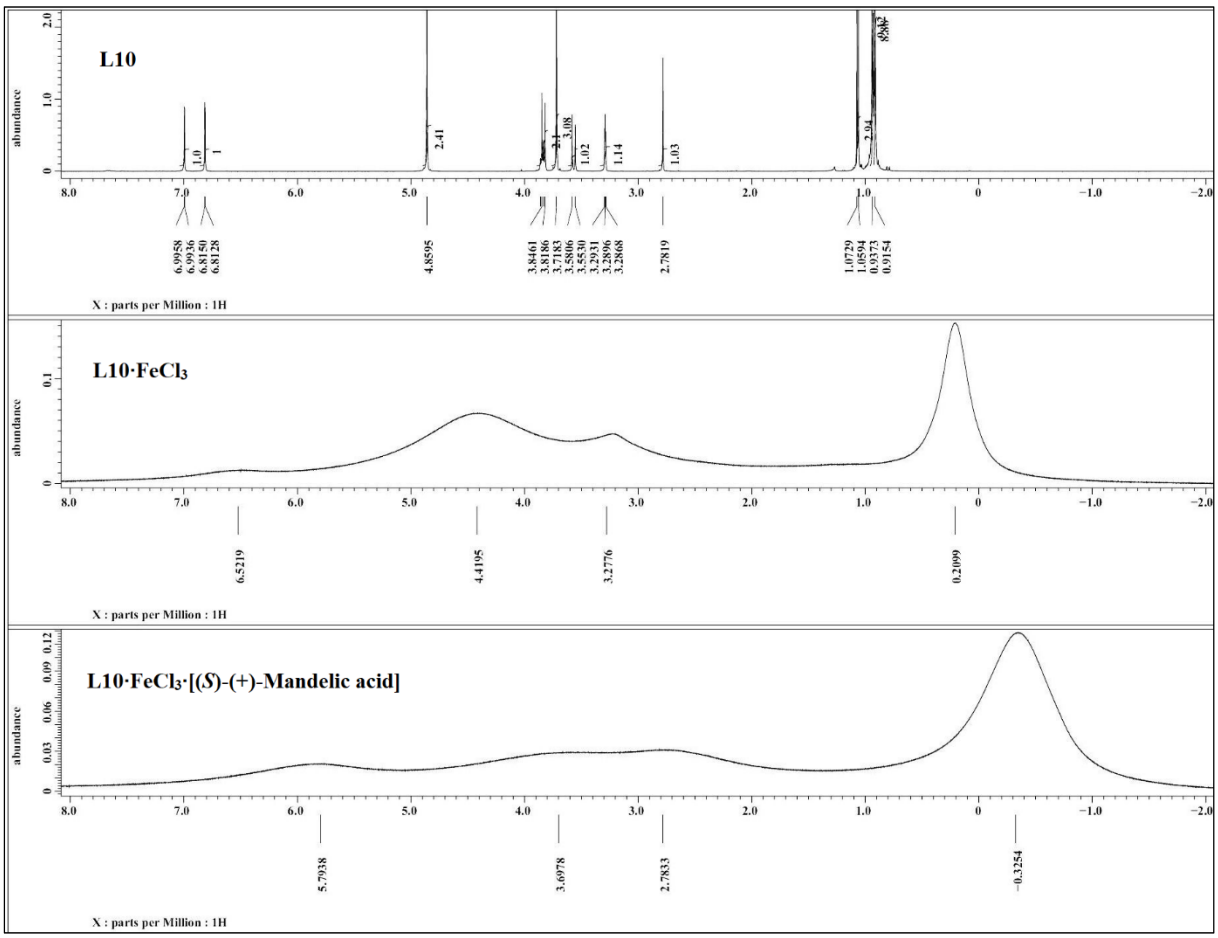
# 9 Infrared Experiments of Fe(III) complex



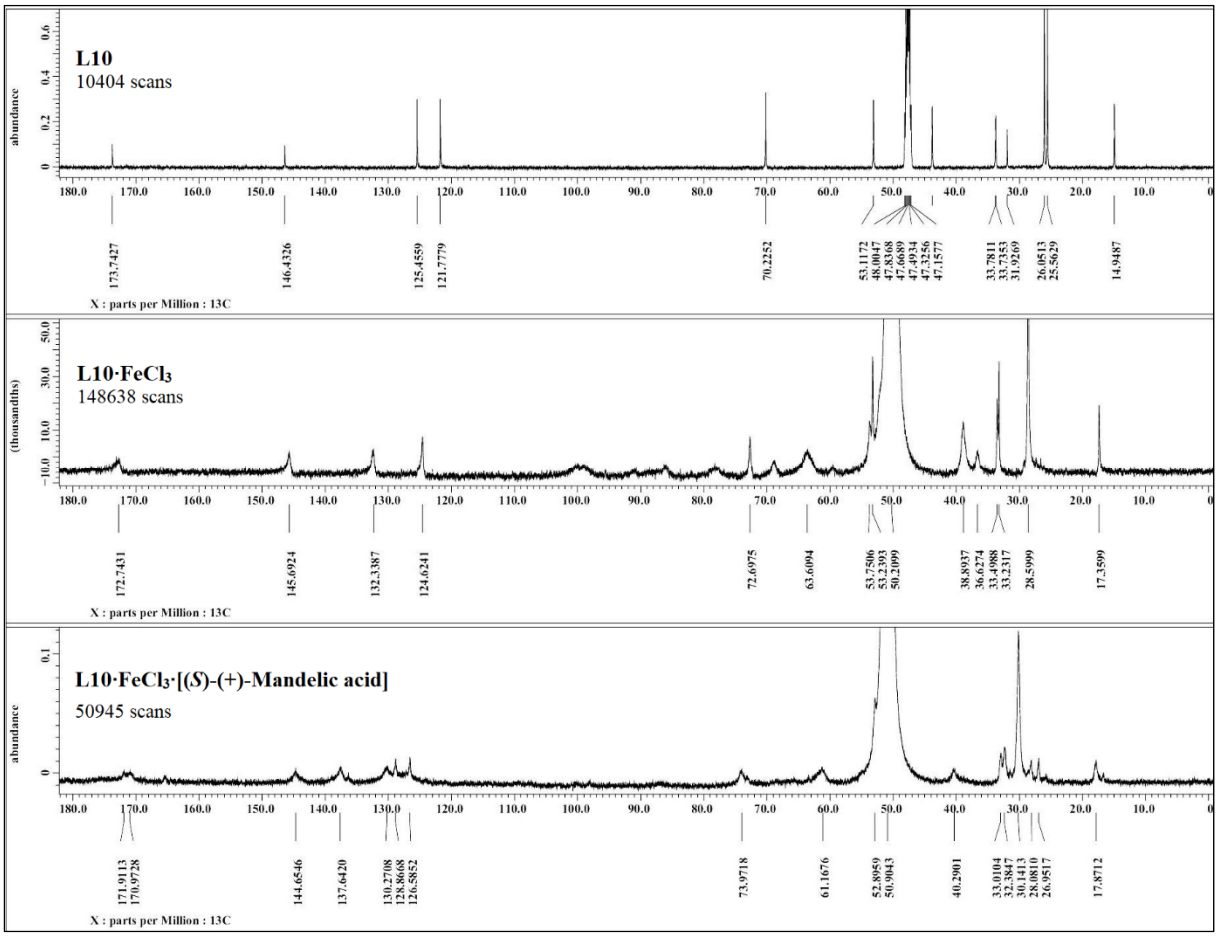



# 9 NMR Experiments of Fe(III) complex (Jeol ECA 500)

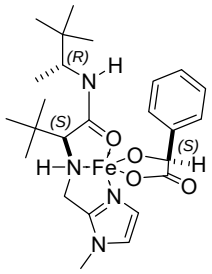
**$^1$H, 500 MHz, methanol-$d_3$**



## $^{13}C$, 125.765 MHz, methanol-$d_3$



## 10 MS-ESI Experiment of Fe(III) complex




$C_{25}H_{38}FeN_4O_4$
Mol. Wt.: 514.4386

## 11 X-Ray Crystallographic Data

### (*S*,*R*)-**V-(d)**

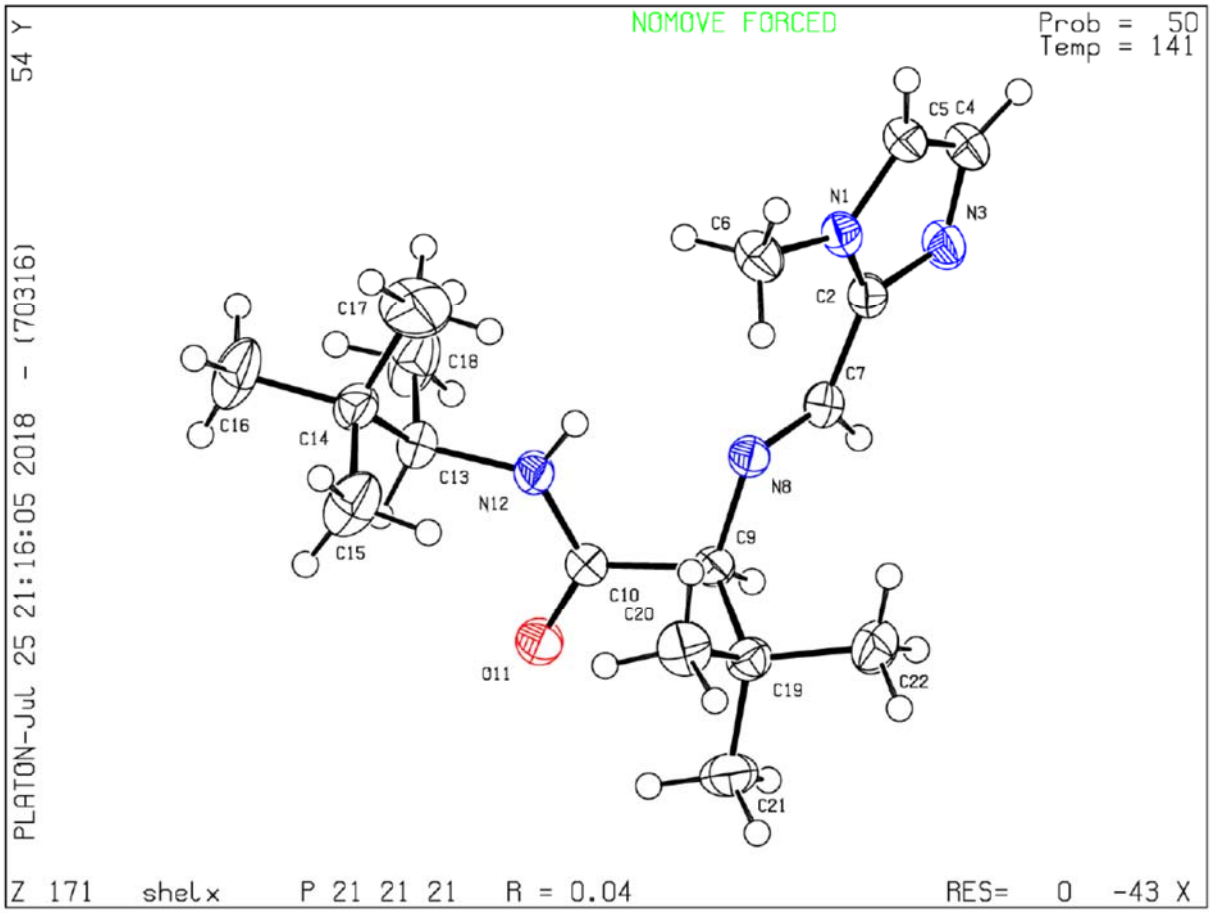



**Table A**

Experimental details

| | |
|---|---|
| Crystal data | |
| Chemical formula | $C_{17}H_{30}N_4O$ |
| $M_r$ | 306.45 |
| Crystal system, space group | Orthorhombic, $P2_12_12_1$ |
| Temperature (K) | 141 |
| $a$, $b$, $c$ (Å) | 6.9534 (3), 14.0923 (5), 18.9394 (7) |
| $V$ (Å$^3$) | 1855.86 (12) |
| $Z$ | 4 |
| Radiation type | Cu $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 0.55 |
| Crystal size (mm) | 0.45 × 0.39 × 0.26 |
| | |
| Data collection | |
| Diffractometer | Bruker D8 VENTURE |
| Absorption correction | Multi-scan<br>*SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction |
| $T_{min}$, $T_{max}$ | 0.677, 0.754 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 12734, 3632, 3452 |
| $R_{int}$ | 0.035 |
| (sin $\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.618 |

**Table A**

Experimental details

| | |
|---|---|
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.038, 0.096, 1.09 |
| No. of reflections | 3632 |
| No. of parameters | 216 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.23, −0.18 |
| Absolute structure | Refined as an inversion twin. |
| Absolute structure parameter | 0.1 (4) |

Computer programs: Bruker *APEX3* software, *SAINT* V8.38A integration software, *SORTAV* (Blessing, 1995), *SHELXS2013* (Sheldrick, 2008),
*SHELXL2018*/3 (Sheldrick, 2018), *ORTEP-3 for Windows* (Farrugia, 2012), *WinGX* publication routines (Farrugia, 2012).

**Table B**

Hydrogen-bond geometry (Å, º)

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C4—H4···O11$^{i}$ | 0.95 | 2.45 | 3.356 (2) | 159 |
| C6—H6*A*···N8 | 0.98 | 2.55 | 3.027 (2) | 110 |
| C6—H6*C*···O11$^{ii}$ | 0.98 | 2.54 | 3.482 (2) | 162 |
| N12—H12···N8 | 0.83 (3) | 2.12 (2) | 2.597 (2) | 117 (2) |

Symmetry codes: (i) −*x*+1/2, −*y*+1, *z*+1/2; (ii) −*x*+3/2, −*y*+1, *z*+1/2.

## Computing details

Data collection: Bruker *APEX3* software; cell refinement: *SAINT* V8.38A integration software; data reduction: *SORTAV* (Blessing, 1995); program(s) used to solve structure: *SHELXS2013* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2018*/3 (Sheldrick, 2018); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 2012).

## (shelx)

*Crystal data*

| | |
|---|---|
| $C_{17}H_{30}N_4O$ | $F(000) = 672$ |
| $M_r = 306.45$ | $D_x = 1.097$ Mg m$^{-3}$ |
| Orthorhombic, $P2_12_12_1$ | Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å |
| Hall symbol: P 2ac 2ab | Cell parameters from 9103 reflections |
| $a = 6.9534$ (3) Å | $\theta = 3.9$–$72.3°$ |
| $b = 14.0923$ (5) Å | $\mu = 0.55$ mm$^{-1}$ |
| $c = 18.9394$ (7) Å | $T = 141$ K |
| $V = 1855.86$ (12) Å$^3$ | Block, colourless |
| $Z = 4$ | 0.45 × 0.39 × 0.26 mm |

*Data collection*

| | |
|---|---|
| Bruker D8 VENTURE diffractometer | 12734 measured reflections |
| | 3632 independent reflections |
| Radiation source: sealed x-ray microsource | 3452 reflections with $I > 2\sigma(I)$ |
| Multilayer mirrors monochromator | $R_{int} = 0.035$ |
| φ or ω oscillation scans | $\theta_{max} = 72.3°$, $\theta_{min} = 3.9°$ |
| Absorption correction: multi-scan SADABS2016/2 - Bruker AXS area detector scaling and absorption correcti | $h = -8 \rightarrow 8$ |
| | $k = -17 \rightarrow 16$ |
| | $l = -22 \rightarrow 23$ |
| $T_{min} = 0.677$, $T_{max} = 0.754$ | |

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.096$
$S = 1.09$
3632 reflections
216 parameters
0 restraints
0 constraints
Primary atom site location: dual
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F^2) + (0.0536P)^2 + 0.1847P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.23$ e Å$^{-3}$
$\Delta\rho_{min} = -0.18$ e Å$^{-3}$
Absolute structure: Refined as an inversion twin.
Absolute structure parameter: 0.1 (4)

*Special details*

*Geometry*. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.
*Refinement*. Refined as a 2-component inversion twin.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C2 | 0.3729 (3) | 0.51502 (13) | 0.81217 (10) | 0.0274 (4) |
| C4 | 0.2396 (3) | 0.48785 (15) | 0.91227 (11) | 0.0371 (4) |
| H4 | 0.144996 | 0.478742 | 0.947808 | 0.045* |
| C5 | 0.4333 (3) | 0.48187 (15) | 0.92274 (10) | 0.0338 (4) |
| H5 | 0.496783 | 0.46861 | 0.96604 | 0.041* |
| C6 | 0.7258 (3) | 0.49392 (16) | 0.84670 (10) | 0.0352 (4) |
| H6A | 0.763954 | 0.544904 | 0.814422 | 0.053* |
| H6B | 0.75851 | 0.432403 | 0.825763 | 0.053* |
| H6C | 0.793877 | 0.501301 | 0.891665 | 0.053* |
| C7 | 0.3917 (3) | 0.53921 (13) | 0.73808 (10) | 0.0272 (4) |
| C9 | 0.5455 (3) | 0.56919 (12) | 0.63061 (9) | 0.0247 (4) |
| H9 | 0.408052 | 0.573869 | 0.61549 | 0.03* |
| C10 | 0.6423 (2) | 0.48977 (13) | 0.58749 (9) | 0.0248 (3) |
| C13 | 0.8078 (3) | 0.33434 (13) | 0.59699 (10) | 0.0300 (4) |
| H13 | 0.818462 | 0.342356 | 0.544672 | 0.036* |
| C14 | 1.0118 (3) | 0.31556 (14) | 0.62544 (11) | 0.0331 (4) |
| C15 | 1.1452 (3) | 0.39353 (17) | 0.59928 (16) | 0.0516 (6) |
| H15A | 1.272017 | 0.386047 | 0.621168 | 0.077* |
| H15B | 1.091777 | 0.455574 | 0.611966 | 0.077* |
| H15C | 1.157823 | 0.389187 | 0.547843 | 0.077* |
| C16 | 1.0829 (3) | 0.22042 (17) | 0.59710 (18) | 0.0551 (7) |
| H16A | 1.069924 | 0.219389 | 0.545578 | 0.083* |
| H16B | 1.00607 | 0.169023 | 0.61759 | 0.083* |
| H16C | 1.21828 | 0.211756 | 0.609928 | 0.083* |
| C17 | 1.0160 (5) | 0.3147 (3) | 0.70620 (14) | 0.0720 (9) |
| H17A | 1.145193 | 0.297563 | 0.722449 | 0.108* |
| H17B | 0.922929 | 0.268148 | 0.723832 | 0.108* |
| H17C | 0.98247 | 0.377843 | 0.72406 | 0.108* |
| C18 | 0.6634 (3) | 0.25497 (17) | 0.61048 (17) | 0.0544 (7) |
| H18A | 0.711664 | 0.195721 | 0.589983 | 0.082* |
| H18B | 0.539995 | 0.271339 | 0.588671 | 0.082* |
| H18C | 0.645806 | 0.246831 | 0.66146 | 0.082* |
| C19 | 0.6426 (3) | 0.66769 (13) | 0.61868 (10) | 0.0303 (4) |
| C20 | 0.8590 (3) | 0.66265 (16) | 0.63368 (12) | 0.0403 (5) |

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| H20A | 0.880126 | 0.634832 | 0.680459 | 0.06* |
| H20B | 0.913638 | 0.726724 | 0.632361 | 0.06* |
| H20C | 0.921503 | 0.623174 | 0.597792 | 0.06* |
| C21 | 0.6082 (4) | 0.70108 (16) | 0.54278 (12) | 0.0447 (5) |
| H21A | 0.672692 | 0.657792 | 0.509924 | 0.067* |
| H21B | 0.660107 | 0.765247 | 0.536865 | 0.067* |
| H21C | 0.469829 | 0.701575 | 0.532976 | 0.067* |
| C22 | 0.5494 (3) | 0.73969 (15) | 0.66897 (12) | 0.0417 (5) |
| H22A | 0.576565 | 0.721556 | 0.717924 | 0.062* |
| H22B | 0.41006 | 0.740513 | 0.661321 | 0.062* |
| H22C | 0.602216 | 0.802981 | 0.659783 | 0.062* |
| N1 | 0.5181 (2) | 0.49860 (11) | 0.85900 (8) | 0.0280 (3) |
| N3 | 0.2014 (2) | 0.50889 (13) | 0.84311 (9) | 0.0339 (4) |
| N8 | 0.5499 (2) | 0.54364 (11) | 0.70524 (8) | 0.0257 (3) |
| N12 | 0.7308 (2) | 0.42302 (12) | 0.62562 (8) | 0.0286 (3) |
| O11 | 0.6345 (2) | 0.48868 (10) | 0.52280 (7) | 0.0374 (3) |
| H7 | 0.267 (3) | 0.5536 (16) | 0.7145 (12) | 0.033 (6)* |
| H12 | 0.721 (3) | 0.4291 (17) | 0.6690 (13) | 0.035 (6)* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C2 | 0.0268 (8) | 0.0257 (8) | 0.0299 (8) | 0.0000 (7) | 0.0033 (7) | −0.0030 (7) |
| C4 | 0.0392 (10) | 0.0389 (10) | 0.0331 (9) | 0.0029 (9) | 0.0128 (8) | 0.0010 (9) |
| C5 | 0.0422 (10) | 0.0336 (9) | 0.0257 (9) | 0.0024 (9) | 0.0059 (8) | −0.0005 (8) |
| C6 | 0.0261 (9) | 0.0481 (12) | 0.0315 (9) | 0.0003 (8) | −0.0005 (7) | −0.0014 (9) |
| C7 | 0.0244 (9) | 0.0268 (8) | 0.0303 (9) | 0.0020 (7) | −0.0002 (7) | −0.0024 (7) |
| C9 | 0.0223 (8) | 0.0281 (8) | 0.0236 (8) | 0.0020 (7) | −0.0017 (6) | 0.0016 (7) |
| C10 | 0.0229 (7) | 0.0267 (8) | 0.0250 (8) | −0.0016 (7) | −0.0014 (6) | −0.0008 (7) |
| C13 | 0.0301 (10) | 0.0266 (9) | 0.0333 (9) | 0.0043 (7) | 0.0007 (7) | −0.0022 (8) |
| C14 | 0.0295 (9) | 0.0306 (9) | 0.0393 (10) | 0.0049 (8) | 0.0009 (8) | 0.0036 (8) |
| C15 | 0.0342 (11) | 0.0348 (11) | 0.0858 (18) | −0.0030 (10) | 0.0005 (12) | 0.0015 (12) |
| C16 | 0.0311 (11) | 0.0326 (11) | 0.102 (2) | 0.0059 (9) | 0.0098 (12) | −0.0033 (12) |
| C17 | 0.0647 (18) | 0.105 (3) | 0.0463 (14) | 0.0288 (18) | −0.0145 (13) | 0.0212 (16) |
| C18 | 0.0322 (11) | 0.0338 (11) | 0.097 (2) | 0.0000 (9) | 0.0089 (12) | −0.0044 (12) |
| C19 | 0.0337 (10) | 0.0264 (9) | 0.0309 (9) | 0.0000 (8) | −0.0005 (8) | 0.0011 (7) |
| C20 | 0.0350 (11) | 0.0392 (11) | 0.0467 (11) | −0.0094 (9) | 0.0005 (9) | −0.0035 (10) |
| C21 | 0.0614 (15) | 0.0350 (10) | 0.0377 (11) | −0.0012 (10) | 0.0006 (10) | 0.0097 (9) |
| C22 | 0.0489 (12) | 0.0280 (9) | 0.0481 (12) | 0.0027 (9) | 0.0043 (10) | −0.0035 (9) |
| N1 | 0.0289 (7) | 0.0285 (8) | 0.0267 (7) | 0.0000 (6) | 0.0027 (6) | −0.0030 (6) |
| N3 | 0.0307 (8) | 0.0362 (9) | 0.0348 (8) | 0.0010 (7) | 0.0082 (7) | −0.0013 (7) |
| N8 | 0.0268 (7) | 0.0265 (7) | 0.0237 (7) | 0.0018 (6) | −0.0009 (6) | −0.0004 (6) |
| N12 | 0.0326 (8) | 0.0302 (8) | 0.0229 (7) | 0.0076 (7) | −0.0012 (6) | −0.0013 (6) |
| O11 | 0.0494 (8) | 0.0394 (8) | 0.0235 (6) | 0.0102 (7) | −0.0039 (6) | −0.0009 (6) |

*Geometric parameters*

*Bond lengths (Å)*

| | | | |
|---|---|---|---|
| C2—N3 | 1.331 (2) | C14—C17 | 1.530 (3) |
| C2—N1 | 1.364 (2) | C15—H15A | 0.98 |
| C2—C7 | 1.450 (2) | C15—H15B | 0.98 |
| C4—C5 | 1.363 (3) | C15—H15C | 0.98 |
| C4—N3 | 1.369 (3) | C16—H16A | 0.98 |

*Bond lengths (Å)*

| | | | |
|---|---|---|---|
| C4—H4 | 0.95 | C16—H16B | 0.98 |
| C5—N1 | 1.364 (2) | C16—H16C | 0.98 |
| C5—H5 | 0.95 | C17—H17A | 0.98 |
| C6—N1 | 1.464 (2) | C17—H17B | 0.98 |
| C6—H6A | 0.98 | C17—H17C | 0.98 |
| C6—H6B | 0.98 | C18—H18A | 0.98 |
| C6—H6C | 0.98 | C18—H18B | 0.98 |
| C7—N8 | 1.265 (2) | C18—H18C | 0.98 |
| C7—H7 | 1.00 (2) | C19—C21 | 1.531 (3) |
| C9—N8 | 1.459 (2) | C19—C20 | 1.533 (3) |
| C9—C10 | 1.540 (2) | C19—C22 | 1.535 (3) |
| C9—C19 | 1.560 (3) | C20—H20A | 0.98 |
| C9—H9 | 1 | C20—H20B | 0.98 |
| C10—O11 | 1.227 (2) | C20—H20C | 0.98 |
| C10—N12 | 1.336 (2) | C21—H21A | 0.98 |
| C13—N12 | 1.464 (2) | C21—H21B | 0.98 |
| C13—C18 | 1.525 (3) | C21—H21C | 0.98 |
| C13—C14 | 1.540 (3) | C22—H22A | 0.98 |
| C13—H13 | 1 | C22—H22B | 0.98 |
| C14—C15 | 1.521 (3) | C22—H22C | 0.98 |
| C14—C16 | 1.527 (3) | N12—H12 | 0.83 (3) |

*Bond Angles (°)*

| | | | |
|---|---|---|---|
| N3—C2—N1 | 111.45 (16) | C14—C16—H16C | 109.5 |
| N3—C2—C7 | 121.50 (17) | H16A—C16—H16C | 109.5 |
| N1—C2—C7 | 127.03 (16) | H16B—C16—H16C | 109.5 |
| C5—C4—N3 | 110.12 (17) | C14—C17—H17A | 109.5 |
| C5—C4—H4 | 124.9 | C14—C17—H17B | 109.5 |
| N3—C4—H4 | 124.9 | H17A—C17—H17B | 109.5 |
| C4—C5—N1 | 106.73 (18) | C14—C17—H17C | 109.5 |
| C4—C5—H5 | 126.6 | H17A—C17—H17C | 109.5 |
| N1—C5—H5 | 126.6 | H17B—C17—H17C | 109.5 |
| N1—C6—H6A | 109.5 | C13—C18—H18A | 109.5 |
| N1—C6—H6B | 109.5 | C13—C18—H18B | 109.5 |
| H6A—C6—H6B | 109.5 | H18A—C18—H18B | 109.5 |
| N1—C6—H6C | 109.5 | C13—C18—H18C | 109.5 |
| H6A—C6—H6C | 109.5 | H18A—C18—H18C | 109.5 |
| H6B—C6—H6C | 109.5 | H18B—C18—H18C | 109.5 |
| N8—C7—C2 | 124.48 (17) | C21—C19—C20 | 109.96 (19) |
| N8—C7—H7 | 121.9 (13) | C21—C19—C22 | 108.27 (17) |
| C2—C7—H7 | 113.6 (13) | C20—C19—C22 | 109.26 (18) |
| N8—C9—C10 | 108.98 (14) | C21—C19—C9 | 109.99 (16) |
| N8—C9—C19 | 110.54 (14) | C20—C19—C9 | 110.90 (16) |
| C10—C9—C19 | 112.38 (15) | C22—C19—C9 | 108.40 (16) |
| N8—C9—H9 | 108.3 | C19—C20—H20A | 109.5 |
| C10—C9—H9 | 108.3 | C19—C20—H20B | 109.5 |
| C19—C9—H9 | 108.3 | H20A—C20—H20B | 109.5 |
| O11—C10—N12 | 123.46 (17) | C19—C20—H20C | 109.5 |
| O11—C10—C9 | 121.30 (16) | H20A—C20—H20C | 109.5 |
| N12—C10—C9 | 115.23 (15) | H20B—C20—H20C | 109.5 |
| N12—C13—C18 | 108.88 (17) | C19—C21—H21A | 109.5 |

*Bond Angles (°)*

| | | | |
|---|---|---|---|
| N12—C13—C14 | 110.73 (16) | C19—C21—H21B | 109.5 |
| C18—C13—C14 | 114.94 (17) | H21A—C21—H21B | 109.5 |
| N12—C13—H13 | 107.3 | C19—C21—H21C | 109.5 |
| C18—C13—H13 | 107.3 | H21A—C21—H21C | 109.5 |
| C14—C13—H13 | 107.3 | H21B—C21—H21C | 109.5 |
| C15—C14—C16 | 108.80 (18) | C19—C22—H22A | 109.5 |
| C15—C14—C17 | 108.6 (2) | C19—C22—H22B | 109.5 |
| C16—C14—C17 | 109.8 (2) | H22A—C22—H22B | 109.5 |
| C15—C14—C13 | 108.88 (17) | C19—C22—H22C | 109.5 |
| C16—C14—C13 | 109.04 (18) | H22A—C22—H22C | 109.5 |
| C17—C14—C13 | 111.64 (19) | H22B—C22—H22C | 109.5 |
| C14—C15—H15A | 109.5 | C2—N1—C5 | 106.52 (16) |
| C14—C15—H15B | 109.5 | C2—N1—C6 | 129.38 (15) |
| H15A—C15—H15B | 109.5 | C5—N1—C6 | 124.04 (16) |
| C14—C15—H15C | 109.5 | C2—N3—C4 | 105.17 (17) |
| H15A—C15—H15C | 109.5 | C7—N8—C9 | 118.07 (16) |
| H15B—C15—H15C | 109.5 | C10—N12—C13 | 124.71 (16) |
| C14—C16—H16A | 109.5 | C10—N12—H12 | 115.1 (17) |
| C14—C16—H16B | 109.5 | C13—N12—H12 | 119.1 (17) |
| H16A—C16—H16B | 109.5 | | |

*Torsion Angles (°)*

| | | | |
|---|---|---|---|
| N3—C4—C5—N1 | −0.5 (2) | C10—C9—C19—C22 | −174.58 (15) |
| N3—C2—C7—N8 | −178.00 (19) | N3—C2—N1—C5 | −0.4 (2) |
| N1—C2—C7—N8 | 3.9 (3) | C7—C2—N1—C5 | 177.86 (18) |
| N8—C9—C10—O11 | 170.40 (17) | N3—C2—N1—C6 | 176.74 (19) |
| C19—C9—C10—O11 | −66.7 (2) | C7—C2—N1—C6 | −5.0 (3) |
| N8—C9—C10—N12 | −8.7 (2) | C4—C5—N1—C2 | 0.5 (2) |
| C19—C9—C10—N12 | 114.21 (18) | C4—C5—N1—C6 | −176.78 (19) |
| N12—C13—C14—C15 | −64.0 (2) | N1—C2—N3—C4 | 0.1 (2) |
| C18—C13—C14—C15 | 172.1 (2) | C7—C2—N3—C4 | −178.29 (18) |
| N12—C13—C14—C16 | 177.39 (18) | C5—C4—N3—C2 | 0.3 (2) |
| C18—C13—C14—C16 | 53.5 (3) | C2—C7—N8—C9 | −179.87 (16) |
| N12—C13—C14—C17 | 55.9 (3) | C10—C9—N8—C7 | −122.76 (17) |
| C18—C13—C14—C17 | −68.0 (3) | C19—C9—N8—C7 | 113.26 (18) |
| N8—C9—C19—C21 | −170.77 (17) | O11—C10—N12—C13 | −8.3 (3) |
| C10—C9—C19—C21 | 67.2 (2) | C9—C10—N12—C13 | 170.72 (16) |
| N8—C9—C19—C20 | 67.4 (2) | C18—C13—N12—C10 | −98.8 (2) |
| C10—C9—C19—C20 | −54.6 (2) | C14—C13—N12—C10 | 133.88 (19) |
| N8—C9—C19—C22 | −52.6 (2) | | |

## L10

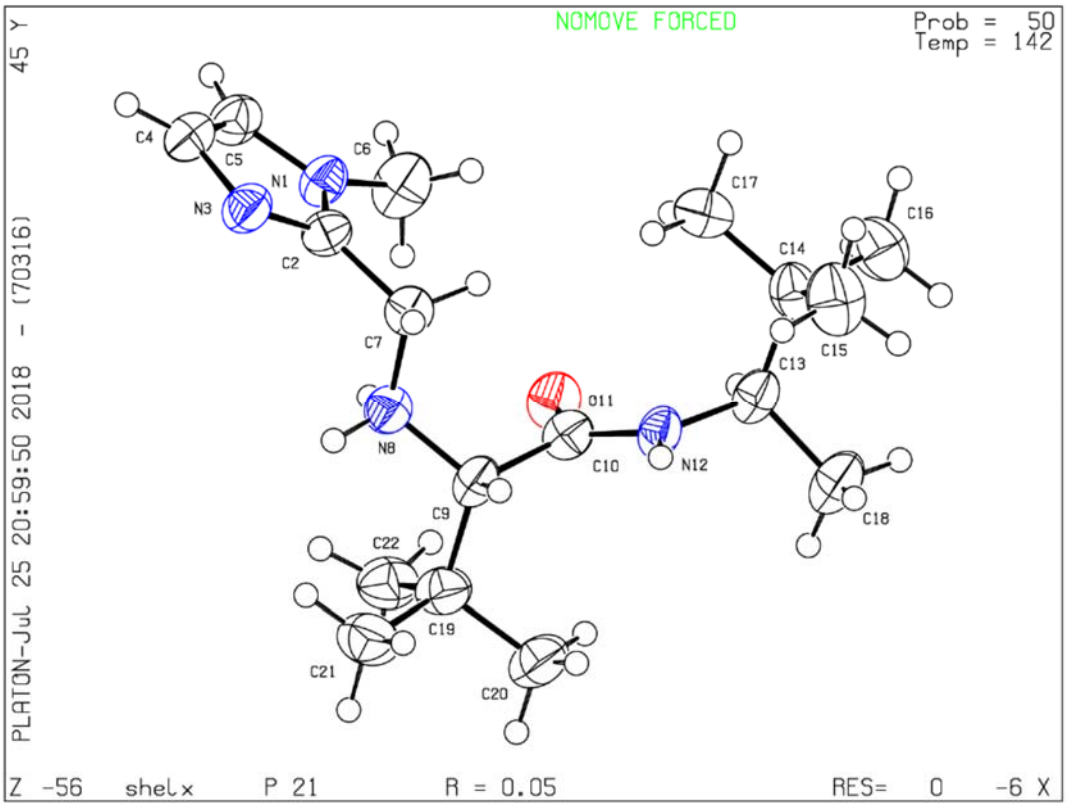



**Table A**

Experimental details

| | |
|---|---|
| Crystal data | |
| Chemical formula | $C_{17}H_{33}N_4O$ |
| $M_r$ | 309.47 |
| Crystal system, space group | Monoclinic, $P2_1$ |
| Temperature (K) | 142 |
| $a$, $b$, $c$ (Å) | 8.0138 (5), 13.0776 (8), 9.4290 (6) |
| $\beta$ (°) | 108.996 (4) |
| $V$ (Å$^3$) | 934.36 (10) |
| $Z$ | 2 |
| Radiation type | Cu $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 0.55 |
| Crystal size (mm) | 0.32 × 0.17 × 0.11 |
| | |
| Data collection | |
| Diffractometer | Bruker D8 VENTURE |
| Absorption correction | Multi-scan<br>*SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction |
| $T_{min}$, $T_{max}$ | 0.575, 0.752 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 12600, 2823, 2188 |
| $R_{int}$ | 0.085 |
| $\theta_{max}$ (°) | 61.4 |
| (sin $\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.570 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.053, 0.136, 1.05 |

**Table A**

Experimental details

| | |
|---|---|
| No. of reflections | 2823 |
| No. of parameters | 212 |
| No. of restraints | 1 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.14, −0.36 |
| Absolute structure | Flack x determined using 788 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259). |
| Absolute structure parameter | 0.2 (3) |

Computer programs: Bruker *APEX3* software, *SAINT* V8.38A integration software, *SORTAV* (Blessing, 1995), *SHELXS2013* (Sheldrick, 2008), *SHELXL2018*/3 (Sheldrick, 2018), *ORTEP* for Windows (Farrugia, 2012), *WinGX* publication routines (Farrugia, 2012).

**Table B**

Hydrogen-bond geometry (Å, º)

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C5—H5···O11$^{i}$ | 0.95 | 2.54 | 3.461 (6) | 162 |
| N12—H12···N3$^{ii}$ | 1.00 (6) | 2.12 (6) | 3.112 (6) | 173 (5) |

Symmetry codes: (i) −*x*, *y*+1/2, −*z*; (ii) −*x*+1, *y*−1/2, −*z*+1.

## Computing details

Data collection: Bruker *APEX3* software; cell refinement: *SAINT* V8.38A integration software; data reduction: *SORTAV* (Blessing, 1995); program(s) used to solve structure: *SHELXS2013* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2018*/3 (Sheldrick, 2018); molecular graphics: *ORTEP* for Windows (Farrugia, 2012); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 2012).

## (shelx)

*Crystal data*

$C_{17}H_{33}N_4O$
$M_r$ = 309.47
Monoclinic, $P2_1$
Hall symbol: P2yb
$a$ = 8.0138 (5) Å
$b$ = 13.0776 (8) Å
$c$ = 9.4290 (6) Å
$\beta$ = 108.996 (4)°
$V$ = 934.36 (10) Å$^3$
$Z$ = 2

$F(000)$ = 342
$D_x$ = 1.1 Mg m$^{-3}$
Cu $K\alpha$ radiation, $\lambda$ = 1.54178 Å
Cell parameters from 4408 reflections
$\theta$ = 5.0–61.0°
$\mu$ = 0.55 mm$^{-1}$
$T$ = 142 K
Nedle, yellow
0.32 × 0.17 × 0.11 mm

*Data collection*

Bruker D8 VENTURE
diffractometer
Radiation source: sealed x-ray microsource
Graphite monochromator
$\varphi$ or $\omega$ oscillation scans
Absorption correction: multi-scan
*SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction
$T_{min}$ = 0.575, $T_{max}$ = 0.752

12600 measured reflections
2823 independent
reflections 2188
reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.085
$\theta_{max}$ = 61.4°, $\theta_{min}$ = 5.0°
$h$ = −9→9
$k$ = −14→14
$l$ = −10→10

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.136$
$S = 1.05$
2823 reflections
212 parameters
1 restraint
0 constraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o{}^2) + (0.0604P)^2 + 0.2044P]$
where $P = (F_o{}^2 + 2F_c{}^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.14$ e Å$^{-3}$
$\Delta\rho_{min} = -0.36$ e Å$^{-3}$
Extinction correction: *SHELXL2018*/3 (Sheldrick 2018), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.015 (2)
Absolute structure: Flack x determined using 788 quotients [(I+)-(I-)]/[(I+)+(I-)]
(Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
Absolute structure parameter: 0.2 (3)

*Special details*

*Geometry*. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C2 | 0.3348 (6) | 0.6980 (4) | 0.3103 (5) | 0.0382 (11) |
| C4 | 0.3312 (7) | 0.8611 (4) | 0.2862 (6) | 0.0462 (13) |
| H4 | 0.35655 | 0.931443 | 0.307661 | 0.055* |
| C5 | 0.2177 (7) | 0.8236 (4) | 0.1544 (6) | 0.0455 (13) |
| H5 | 0.150157 | 0.861998 | 0.069571 | 0.055* |
| C6 | 0.1311 (8) | 0.6446 (4) | 0.0569 (6) | 0.0610 (16) |
| H6A | 0.071904 | 0.679762 | −0.038017 | 0.092* |
| H6B | 0.043321 | 0.608073 | 0.089694 | 0.092* |
| H6C | 0.216946 | 0.595744 | 0.04262 | 0.092* |
| C7 | 0.3643 (6) | 0.5916 (4) | 0.3689 (5) | 0.0402 (12) |
| H7A | 0.375645 | 0.545345 | 0.289401 | 0.048* |
| H7B | 0.475741 | 0.588434 | 0.454325 | 0.048* |
| C9 | 0.2174 (7) | 0.4479 (3) | 0.4451 (5) | 0.0399 (12) |
| H9 | 0.33545 | 0.428946 | 0.517268 | 0.048* |
| C10 | 0.1924 (7) | 0.3884 (4) | 0.2987 (5) | 0.0411 (12) |
| C13 | 0.2989 (7) | 0.2483 (3) | 0.1769 (6) | 0.0441 (13) |
| H13 | 0.182689 | 0.263213 | 0.099002 | 0.053* |
| C14 | 0.4412 (6) | 0.2703 (4) | 0.1042 (5) | 0.0466 (12) |
| C15 | 0.6244 (8) | 0.2388 (5) | 0.2048 (7) | 0.0696 (18) |
| H15A | 0.712189 | 0.259567 | 0.158441 | 0.104* |
| H15B | 0.628447 | 0.164366 | 0.217997 | 0.104* |
| H15C | 0.650458 | 0.272049 | 0.30275 | 0.104* |
| C16 | 0.3938 (8) | 0.2135 (5) | −0.0458 (6) | 0.0645 (17) |
| H16A | 0.274134 | 0.232295 | −0.108318 | 0.097* |
| H16B | 0.399434 | 0.139552 | −0.027595 | 0.097* |
| H16C | 0.477638 | 0.232147 | −0.097413 | 0.097* |
| C17 | 0.4435 (8) | 0.3847 (4) | 0.0725 (6) | 0.0594 (16) |
| H17A | 0.489048 | 0.422025 | 0.167537 | 0.089* |
| H17B | 0.323367 | 0.407958 | 0.01827 | 0.089* |
| H17C | 0.519617 | 0.397686 | 0.011484 | 0.089* |
| C18 | 0.2916 (9) | 0.1377 (4) | 0.2241 (6) | 0.0618 (16) |

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| H18A | 0.277223 | 0.092684 | 0.137794 | 0.093* |
| H18B | 0.191415 | 0.128578 | 0.260932 | 0.093* |
| H18C | 0.401311 | 0.120407 | 0.303971 | 0.093* |
| C19 | 0.0762 (7) | 0.4195 (4) | 0.5182 (5) | 0.0473 (13) |
| C20 | 0.0639 (8) | 0.3039 (4) | 0.5296 (7) | 0.0593 (15) |
| H20A | −0.015704 | 0.286892 | 0.586023 | 0.089* |
| H20B | 0.181366 | 0.275884 | 0.581448 | 0.089* |
| H20C | 0.018026 | 0.274557 | 0.428684 | 0.089* |
| C21 | 0.1366 (9) | 0.4653 (5) | 0.6773 (6) | 0.0627 (17) |
| H21A | 0.141411 | 0.540003 | 0.670733 | 0.094* |
| H21B | 0.254068 | 0.439047 | 0.733583 | 0.094* |
| H21C | 0.052905 | 0.44613 | 0.728686 | 0.094* |
| C22 | −0.1051 (7) | 0.4627 (5) | 0.4306 (6) | 0.0557 (15) |
| H22A | −0.193409 | 0.435466 | 0.472006 | 0.084* |
| H22B | −0.135983 | 0.442913 | 0.32489 | 0.084* |
| H22C | −0.102243 | 0.537427 | 0.438568 | 0.084* |
| N1 | 0.2217 (5) | 0.7193 (3) | 0.1702 (5) | 0.0412 (10) |
| N3 | 0.4031 (5) | 0.7818 (3) | 0.3831 (4) | 0.0442 (10) |
| N8 | 0.2189 (5) | 0.5574 (3) | 0.4178 (5) | 0.0420 (11) |
| H8A | 0.22442 | 0.591095 | 0.503666 | 0.05* |
| H8B | 0.115367 | 0.57492 | 0.346681 | 0.05* |
| N12 | 0.3115 (6) | 0.3156 (3) | 0.3053 (5) | 0.0415 (10) |
| O11 | 0.0704 (4) | 0.4108 (3) | 0.1833 (4) | 0.0496 (10) |
| H12 | 0.410 (8) | 0.308 (5) | 0.402 (7) | 0.080 (19)* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C2 | 0.037 (3) | 0.038 (3) | 0.037 (3) | −0.002 (2) | 0.009 (2) | 0.003 (2) |
| C4 | 0.054 (3) | 0.036 (3) | 0.050 (3) | 0.000 (2) | 0.018 (3) | 0.006 (2) |
| C5 | 0.047 (3) | 0.043 (3) | 0.044 (3) | 0.007 (2) | 0.011 (2) | 0.011 (2) |
| C6 | 0.070 (4) | 0.053 (4) | 0.043 (3) | −0.002 (3) | −0.004 (3) | −0.002 (3) |
| C7 | 0.040 (3) | 0.040 (3) | 0.038 (3) | 0.000 (2) | 0.009 (2) | 0.000 (2) |
| C9 | 0.048 (3) | 0.030 (3) | 0.036 (3) | 0.000 (2) | 0.005 (2) | 0.001 (2) |
| C10 | 0.042 (3) | 0.039 (3) | 0.039 (3) | −0.003 (2) | 0.008 (2) | 0.001 (2) |
| C13 | 0.052 (3) | 0.032 (3) | 0.040 (3) | 0.000 (2) | 0.004 (2) | −0.001 (2) |
| C14 | 0.048 (3) | 0.048 (3) | 0.040 (3) | 0.005 (3) | 0.010 (2) | −0.005 (2) |
| C15 | 0.064 (4) | 0.073 (5) | 0.064 (4) | 0.012 (3) | 0.010 (3) | −0.008 (3) |
| C16 | 0.073 (4) | 0.073 (5) | 0.046 (3) | −0.001 (3) | 0.018 (3) | −0.012 (3) |
| C17 | 0.068 (4) | 0.061 (4) | 0.059 (3) | −0.004 (3) | 0.035 (3) | 0.003 (3) |
| C18 | 0.090 (4) | 0.036 (3) | 0.048 (3) | −0.002 (3) | 0.007 (3) | 0.001 (3) |
| C19 | 0.052 (3) | 0.047 (3) | 0.043 (3) | −0.010 (3) | 0.016 (2) | 0.001 (2) |
| C20 | 0.073 (4) | 0.043 (4) | 0.061 (4) | −0.010 (3) | 0.021 (3) | 0.006 (3) |
| C21 | 0.077 (4) | 0.068 (4) | 0.050 (3) | −0.016 (3) | 0.030 (3) | −0.007 (3) |
| C22 | 0.047 (3) | 0.061 (4) | 0.061 (4) | −0.004 (3) | 0.021 (3) | 0.006 (3) |
| N1 | 0.044 (2) | 0.034 (3) | 0.041 (2) | 0.0030 (18) | 0.0081 (19) | 0.0042 (18) |
| N3 | 0.052 (2) | 0.035 (2) | 0.045 (2) | −0.005 (2) | 0.0149 (19) | 0.000 (2) |
| N8 | 0.046 (3) | 0.037 (3) | 0.043 (2) | −0.0019 (18) | 0.015 (2) | −0.0006 (18) |
| N12 | 0.052 (3) | 0.030 (2) | 0.037 (2) | 0.001 (2) | 0.009 (2) | −0.0033 (17) |
| O11 | 0.051 (2) | 0.048 (2) | 0.041 (2) | 0.0042 (17) | 0.0036 (17) | 0.0014 (17) |

*Geometric parameters*

*Bond lengths (Å)*

| | | | |
|---|---|---|---|
| C2—N3 | 1.314 (6) | C15—H15A | 0.98 |
| C2—N1 | 1.366 (6) | C15—H15B | 0.98 |

*Bond lengths (Å)*

| | | | |
|---|---|---|---|
| C2—C7 | 1.488 (7) | C15—H15C | 0.98 |
| C4—C5 | 1.369 (7) | C16—H16A | 0.98 |
| C4—N3 | 1.378 (6) | C16—H16B | 0.98 |
| C4—H4 | 0.95 | C16—H16C | 0.98 |
| C5—N1 | 1.372 (6) | C17—H17A | 0.98 |
| C5—H5 | 0.95 | C17—H17B | 0.98 |
| C6—N1 | 1.455 (6) | C17—H17C | 0.98 |
| C6—H6A | 0.98 | C18—H18A | 0.98 |
| C6—H6B | 0.98 | C18—H18B | 0.98 |
| C6—H6C | 0.98 | C18—H18C | 0.98 |
| C7—N8 | 1.456 (6) | C19—C20 | 1.520 (8) |
| C7—H7A | 0.99 | C19—C22 | 1.527 (7) |
| C7—H7B | 0.99 | C19—C21 | 1.540 (7) |
| C9—N8 | 1.456 (6) | C20—H20A | 0.98 |
| C9—C10 | 1.539 (7) | C20—H20B | 0.98 |
| C9—C19 | 1.550 (7) | C20—H20C | 0.98 |
| C9—H9 | 1 | C21—H21A | 0.98 |
| C10—O11 | 1.238 (5) | C21—H21B | 0.98 |
| C10—N12 | 1.335 (6) | C21—H21C | 0.98 |
| C13—N12 | 1.473 (6) | C22—H22A | 0.98 |
| C13—C18 | 1.521 (7) | C22—H22B | 0.98 |
| C13—C14 | 1.537 (7) | C22—H22C | 0.98 |
| C13—H13 | 1 | N8—H8A | 0.91 |
| C14—C15 | 1.522 (7) | N8—H8B | 0.91 |
| C14—C17 | 1.528 (8) | N12—H12 | 1.00 (6) |
| C14—C16 | 1.532 (7) | | |

*Bond Angles (°)*

| | | | |
|---|---|---|---|
| N3—C2—N1 | 111.6 (4) | H16A—C16—H16C | 109.5 |
| N3—C2—C7 | 126.7 (4) | H16B—C16—H16C | 109.5 |
| N1—C2—C7 | 121.7 (4) | C14—C17—H17A | 109.5 |
| C5—C4—N3 | 110.1 (5) | C14—C17—H17B | 109.5 |
| C5—C4—H4 | 124.9 | H17A—C17—H17B | 109.5 |
| N3—C4—H4 | 124.9 | C14—C17—H17C | 109.5 |
| C4—C5—N1 | 105.8 (5) | H17A—C17—H17C | 109.5 |
| C4—C5—H5 | 127.1 | H17B—C17—H17C | 109.5 |
| N1—C5—H5 | 127.1 | C13—C18—H18A | 109.5 |
| N1—C6—H6A | 109.5 | C13—C18—H18B | 109.5 |
| N1—C6—H6B | 109.5 | H18A—C18—H18B | 109.5 |
| H6A—C6—H6B | 109.5 | C13—C18—H18C | 109.5 |
| N1—C6—H6C | 109.5 | H18A—C18—H18C | 109.5 |
| H6A—C6—H6C | 109.5 | H18B—C18—H18C | 109.5 |
| H6B—C6—H6C | 109.5 | C20—C19—C22 | 109.5 (5) |
| N8—C7—C2 | 111.0 (4) | C20—C19—C21 | 109.0 (5) |
| N8—C7—H7A | 109.4 | C22—C19—C21 | 109.0 (5) |
| C2—C7—H7A | 109.4 | C20—C19—C9 | 110.1 (4) |
| N8—C7—H7B | 109.4 | C22—C19—C9 | 112.0 (4) |
| C2—C7—H7B | 109.4 | C21—C19—C9 | 107.2 (4) |
| H7A—C7—H7B | 108 | C19—C20—H20A | 109.5 |
| N8—C9—C10 | 110.2 (4) | C19—C20—H20B | 109.5 |
| N8—C9—C19 | 111.3 (4) | H20A—C20—H20B | 109.5 |
| C10—C9—C19 | 112.1 (4) | C19—C20—H20C | 109.5 |
| N8—C9—H9 | 107.7 | H20A—C20—H20C | 109.5 |
| C10—C9—H9 | 107.7 | H20B—C20—H20C | 109.5 |
| C19—C9—H9 | 107.7 | C19—C21—H21A | 109.5 |
| O11—C10—N12 | 123.8 (5) | C19—C21—H21B | 109.5 |

*Bond Angles (°)*

| | | | |
|---|---|---|---|
| O11—C10—C9 | 120.3 (5) | H21A—C21—H21B | 109.5 |
| N12—C10—C9 | 115.8 (4) | C19—C21—H21C | 109.5 |
| N12—C13—C18 | 109.1 (4) | H21A—C21—H21C | 109.5 |
| N12—C13—C14 | 113.1 (4) | H21B—C21—H21C | 109.5 |
| C18—C13—C14 | 114.4 (5) | C19—C22—H22A | 109.5 |
| N12—C13—H13 | 106.6 | C19—C22—H22B | 109.5 |
| C18—C13—H13 | 106.6 | H22A—C22—H22B | 109.5 |
| C14—C13—H13 | 106.6 | C19—C22—H22C | 109.5 |
| C15—C14—C17 | 108.5 (5) | H22A—C22—H22C | 109.5 |
| C15—C14—C16 | 110.0 (5) | H22B—C22—H22C | 109.5 |
| C17—C14—C16 | 108.1 (4) | C2—N1—C5 | 107.0 (4) |
| C15—C14—C13 | 112.1 (5) | C2—N1—C6 | 126.1 (4) |
| C17—C14—C13 | 109.2 (4) | C5—N1—C6 | 126.8 (4) |
| C16—C14—C13 | 108.9 (4) | C2—N3—C4 | 105.6 (4) |
| C14—C15—H15A | 109.5 | C9—N8—C7 | 114.3 (4) |
| C14—C15—H15B | 109.5 | C9—N8—H8A | 108.7 |
| H15A—C15—H15B | 109.5 | C7—N8—H8A | 108.7 |
| C14—C15—H15C | 109.5 | C9—N8—H8B | 108.7 |
| H15A—C15—H15C | 109.5 | C7—N8—H8B | 108.7 |
| H15B—C15—H15C | 109.5 | H8A—N8—H8B | 107.6 |
| C14—C16—H16A | 109.5 | C10—N12—C13 | 122.1 (4) |
| C14—C16—H16B | 109.5 | C10—N12—H12 | 117 (4) |
| H16A—C16—H16B | 109.5 | C13—N12—H12 | 120 (4) |
| C14—C16—H16C | 109.5 | | |

*Torsion Angles (°)*

| | | | |
|---|---|---|---|
| N3—C4—C5—N1 | −0.7 (6) | C10—C9—C19—C21 | 168.3 (4) |
| N3—C2—C7—N8 | 99.0 (5) | N3—C2—N1—C5 | −0.5 (6) |
| N1—C2—C7—N8 | −77.9 (5) | C7—C2—N1—C5 | 176.8 (5) |
| N8—C9—C10—O11 | −50.8 (6) | N3—C2—N1—C6 | 176.3 (5) |
| C19—C9—C10—O11 | 73.7 (6) | C7—C2—N1—C6 | −6.3 (7) |
| N8—C9—C10—N12 | 127.4 (5) | C4—C5—N1—C2 | 0.7 (6) |
| C19—C9—C10—N12 | −108.1 (5) | C4—C5—N1—C6 | −176.1 (5) |
| N12—C13—C14—C15 | 70.0 (6) | N1—C2—N3—C4 | 0.1 (5) |
| C18—C13—C14—C15 | −55.8 (6) | C7—C2—N3—C4 | −177.1 (5) |
| N12—C13—C14—C17 | −50.2 (5) | C5—C4—N3—C2 | 0.4 (6) |
| C18—C13—C14—C17 | −176.0 (4) | C10—C9—N8—C7 | −63.2 (5) |
| N12—C13—C14—C16 | −168.0 (4) | C19—C9—N8—C7 | 171.8 (4) |
| C18—C13—C14—C16 | 66.2 (6) | C2—C7—N8—C9 | 167.0 (4) |
| N8—C9—C19—C20 | 173.8 (4) | O11—C10—N12—C13 | −5.5 (8) |
| C10—C9—C19—C20 | 49.9 (6) | C9—C10—N12—C13 | 176.3 (4) |
| N8—C9—C19—C22 | 51.7 (5) | C18—C13—N12—C10 | −121.9 (5) |
| C10—C9—C19—C22 | −72.2 (5) | C14—C13—N12—C10 | 109.5 (5) |
| N8—C9—C19—C21 | −67.8 (5) | | |