Electronic Supplementary Material (ESI) for ChemComm.


# Formal [3+2] cycloaddition of vinylcyclopropan azlactones and enals using synergistic catalysis

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## Supporting Information

## General information

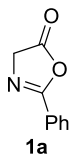
Chemicals and solvents were either purchased (puriss p.A.) from commercial suppliers or purified by standard techniques. For thin-layer chromatography (TLC), silica gel plates Merck 60 $F_{254}$ were used, and compounds were visualized by irradiation with UV light and/or by treatment with a solution of phosphomolybdenic acid (25 g), $Ce(SO_4)_2 \cdot H_2O$ (10 g), conc. $H_2SO_4$ (60 mL), and $H_2O$ (940 mL) followed by heating. Column chromatography was performed using silica gel Merck 60 (particle size 0.040–0.063 mm). $^1H$ NMR, $^{13}C$ NMR, 2D NMR were recorded with a Bruker DPX400 NMR. Chemical shifts (δ) are reported in ppm relative to residual solvent signals ($CHCl_3$, 7.26 ppm for $^1H$ NMR; $CDCl_3$, 77.16 ppm for $^{13}C$ NMR). HRMS were recorded using a LCQ Fleet spectrometer. Optical rotations were performed on an AU-Tomatica polarimeter, Autopol III. IR DRIFT spectras were recorded with Nicolet AVATAR 370 FT-IR in $cm^{-1}$. The HPLC analysis were performed on a LC20AD Shimadzu liquid chromatograph with SPD-M20A diode array detector with columns Daicel Chiralpak. Purifications by HPLC were performed under the following conditions: Agilent ZORBAX SBC18 column (5 µL, 9.4x150 mm); UV/Vis detection at $\lambda_{obs}$ = 210 and 254 nm; flow rate 4 mL/min, isocratic elution method Acetonitrile/$H_2O$ 50:50.

# 1. Starting material preparation

## 1.1. Preparation of azlactone derivatives 1a-b

Starting azlactone derivative **1a** was prepared according published procedure[1]. Spectral data correspond to data published in literature. [2] Starting material **1b** was prepared according published procedure.[3]

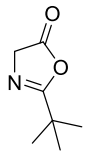
**2-Phenyloxazol-5(4H)-one (1a)**



**1a**

Yellowish solid, yield 80 %. $^1H$ NMR (400 MHz, $CDCl_3$) δ = 8.06 – 7.93 (m, 2H), 7.62 – 7.55 (m, 1H), 7.53 – 7.45 (m, 2H), 4.42 (s, 2H) ppm; $^{13}C$ NMR (101 MHz, $CDCl_3$) δ = 176.0, 163.7, 133.0, 129.0 (2C), 128.0 (2C), 126.0, 55.2 ppm.

**2-(*tert*-Butyl)oxazol-5(4H)-one (1b)**



**1b**

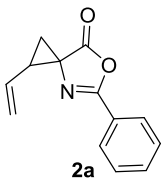
Yellow oil, yield 86 %. $^1H$ NMR (400 MHz, $CDCl_3$) δ = 4.14 (s, 2H), 1.25 (s, 9H) ppm. $^{13}C$ NMR (101 MHz, $CDCl_3$) δ = 176.7, 173.7, 54.6, 34.4, 26.8 (3C) ppm. HRMS (ESI) m/z calcd for $C_7H_{11}NO_2$ $[M]^+$ 141.0790, found 141.0788.

[1] Izumi, S., Kobayashi, Y., Takemoto, Y. *Org. Lett*. **2016**, *18*, 696.
[2] Chen, J., Shao, Y., Ma, L., Ma, M., Wan, X. *Org. Biomol. Chem*. **2016**, *14*, 10723.
[3] Hashimoto, M.; Matsumoto, M.; Terashima, S. *Tetrahedron* **2003**, *59*, 3041.

## 1.2. Preparation of vinylcyclopropane azlactone derivatives

Following published modified published procedure[4], to the (thio)azlactone derivatives **1a-c** (3.7 mmol, 1 equiv.) in dry THF (20 mL) was added (*E*)-1,4-dibromobut-2-ene (3.7 mmol, 1 equiv.) followed by addition of $Cs_2CO_3$ (9.3 mmol, 2.5 equiv.). Reaction mixture was then refluxed appropriate time to reach full conversion (TLC monitoring). Reaction mixture was then diluted with water (20 mL) and washed with $CHCl_3$ (3x20 mL). Combined organic phases were dried over $MgSO_4$, filtered and purified on silica yielding desired compounds **2a-b**.

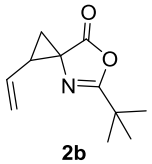
**5-Phenyl-1-vinyl-6-oxa-4-azaspiro[2.4]hept-4-en-7-one (2a)**



**2a**

Off-white solid, yield 65 %, m.p. 88.0 °C, $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.98 – 7.90 (m, 1H), 7.60 – 7.52 (m, 1H), 7.51 – 7.41 (m, 1H), 5.94 (ddd, $J_1$ = 17.1 Hz, $J_2$ = 10.4 Hz, $J_3$ = 9.2 Hz, 1H), 5.36 (ddd, $J_1$ = 17.1 Hz, $J_2$ = 1.4 Hz, $J_3$ = 0.6 Hz, 1H), 5.24 (ddd, $J_1$ = 10.4 Hz, $J_2$ = 1.5 Hz, $J_3$ =0.6 Hz, 1H), 2.92 – 2.83 (m, 1H), 2.24 (dd, $J_1$ = 9.3 Hz, $J_2$ = 5.3 Hz, 1H), 1.93 (dd, $J_1$ = 8.5 Hz, $J_2$ = 5.4 Hz, 1H) ppm; $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 176.0, 161.9, 132.5, 131.8, 129.0, 127.4, 126.2, 119.0, 53.7, 36.7, 25.5 ppm; IR (KBr): ν = 3088, 3067, 2992, 1811, 1628, 1320, 982 cm$^{-1}$; HRMS (ESI) m/z calcd for $C_{13}H_{12}NO_2$ $[M+H]^+$ 214,0863, found 214,0858.

**5-(*tert*-Butyl)-1-vinyl-6-oxa-4-azaspiro[2.4]hept-4-en-7-one (2b)**



**2b**

Transparent oil, yield 18 %, $^1$H NMR (400 MHz, $CDCl_3$) δ = 5.96 – 5.79 (m, 1H), 5.31 (d, *J* = 17.2 Hz, 1H), 5.18 (d, *J* = 10.4 Hz, 1H), 2.71 (q, *J* = 8.6 Hz, 1H), 2.07 (ddd, $J_1$ = 9.3, $J_2$ = 5.3 Hz, $J_3$ = 1.1 Hz, 1H), 1.74 (ddd, $J_1$ = 8.3 Hz, $J_2$ = 5.3 Hz, $J_3$ = 1.1 Hz, 1H), 1.27 (s, 9H) ppm; $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 176.7, 171.8, 131.9, 118.4, 52.5, 35.4, 34.3, 27.0, 24.8 (3C) ppm; IR (KBr): ν = 3085, 2980, 1805, 1646, 1368, 1234, 1156 cm$^{-1}$; HRMS (ESI) m/z calcd for $C_{11}H_{15}NO_2$ $[M]^+$ 193.1103, found 193.1105.

[4] Yin, J., Hyland, C. J. T. *J. Org. Chem*. **2015**, *80*, 6529.

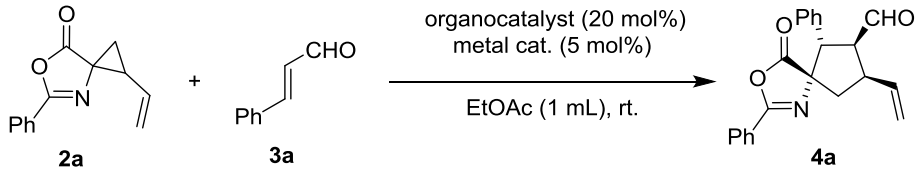
## 2. Asymmetric synthesis of spiro compounds

In a closed vial with EtOAc (1 mL) were added the organic catalyst 2-(diphenyl((trimethylsilyl)oxy)methyl)pyrrolidine (0.2 mmol, 0.2 equiv), corresponding α,β-unsaturated aldehyde **3** (0.1 mmol, 1 equiv), vinylcyclopropane azlactone derivative **2** (0.15 mmol, 1.5 equiv.), $Pd_2(dba)_3$ (0.05 mmol, 0.05 equiv.). The reaction mixture was stirred at room temperature and checked by $^1$H NMR. After full conversion crude mixture was purified by flash column chromatography (n-hexane/EtOAc) obtaining the desired product **4**.

## 3. Modified procedure for compounds 4k-m (derived from aliphatic enals)

In a closed vial with EtOAc (1 mL) were added the organic catalyst 2-(diphenyl((trimethylsilyl)oxy)methyl)pyrrolidine (0.2 mmol, 0.2 equiv), corresponding α,β-unsaturated aldehyde **3** (0.5 mmol, 5 equiv), vinylcyclopropane azlactone derivative **2** (0.10 mmol, 1.0 equiv.), $Pd_2(dba)_3$ (0.05 mmol, 0.05 equiv.). The reaction mixture was stirred at room temperature and checked by $^1$H NMR. After full conversion crude mixture was purified by flash column chromatography (n-hexane/EtOAc) to obtain the desired product **4**.

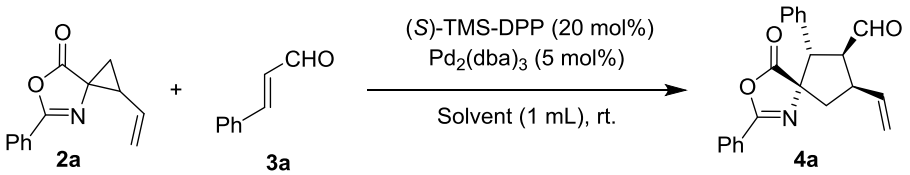
**Catalyst screening of corresponding catalytic reaction**




| Entry | Metal catalyst | Organocatalyst | Time (d) | Conversion (%) | Dr[a] | Yield (%) | ee (%)[b] |
|---|---|---|---|---|---|---|---|
| 1 | $Pd_2(dba)_3$ | (*S*)-TMS-DPP | 1 | 100 | 4:1 | 71 | 98/99 |
| 2 | $Pd_2(dba)_3$ | Joergensen | 7 | 0 | - | - | - |
| 3 | $Pd_2(dba)_3$ | MacMillan 1$^{st}$ gen. | 7 | 0 | - | - | - |
| 4 | $Pd_2(dba)_3$ | MacMillan 2$^{nd}$ gen. | 7 | 0 | - | - | - |
| 5 | $Pd_2(dba)_3$ | (*S*)-diphenylprolinol | 7 | 90 | 3:1 | 46 | 92/95 |
| 6 | $Pd_2(dba)_3$ | (*S*)-proline | 7 | 20 | 3:1 | 11 | 0/0 |
| 7 | $Pd(PPh_3)_4$ | (*S*)-TMS-DPP | 7 | >10 | - | - | - |
| 8 | $PdCl_2$ | (*S*)-TMS-DPP | 7 | 0 | - | - | - |
| 9 | $Pd(OAc)_2$ | (*S*)-TMS-DPP | 7 | 0 | - | - | - |
| 10 | $In(OTf)_3$ | (*S*)-TMS-DPP | 7 | 0 | - | - | - |

[a] determined by $^1$H NMR; [b] determined by Chiral HPLC

**Solvent screening of corresponding catalytic reaction**



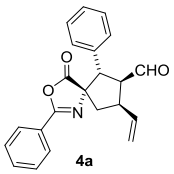

| Entry | Solvent | Time (d) | Conversion (%) | Dr[a] | Yield (%) | ee (%)[b] |
|---|---|---|---|---|---|---|
| 1 | EtOAc | 1 | 100 | 4:1 | 71 | 98/99 |
| 2 | MeCN | 4 | 100 | 2:1 | 68 | 96/97 |
| 3 | Toluene | 3 | 100 | 3:1 | 47 | 99/98 |
| 4 | DCM | 1 | 100 | 5:2 | 55 | 98/98 |
| 5 | MeOH | 7 | 100 | n.d. | n.d.* | n.d. |
| 6 | TBDME | 2 | 100 | 2:1 | 44 | 98/98 |
| 7 | THF | 3 | 100 | 2:1 | 68 | 99/99 |

[a] determined by $^{1}$H NMR; [b] determined by Chiral HPLC; * decomposition of starting material

## 4. Compound characterization

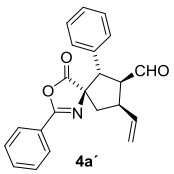
**(5*S*,6*S*,7*S*,8*R*)-4-Oxo-2,6-diphenyl-8-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7-carbaldehyde (4a) and (5*R*,6*S*,7*S*,8*R*)-4-Oxo-2,6-diphenyl-8-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7-carbaldehyde (4a´)**

Colorless oil, yield 71 %, dr =5:1(4a/4a´), *ee* 98/99 %; The ee was determined by HPLC analysis using Chiralpak IA column (90/10 heptane/i-PrOH, flow rate 1.0 ml/min, 25 °C; λ = 190 nm, 25 °C, **4a**: $t_{major}$ = 6.2 min; $t_{minor}$ = 7.6 min., **4a´**: $t_{minor}$ = 6.6 min., $t_{major}$ = 7.2 min.); IR (KBr): ν = 3058, 3028, 2857, 1820, 1652, 1293 $cm^{-1}$; $[\alpha]^{25}_{D}$ = +62.4 °, (0.71, $CHCl_3$); HRMS (ESI) m/z calcd for $C_{22}H_{19}NO_3$ $[M+Na]^+$ 368.1257, found . 368.1255.



4a

Compound **4a**: $^1$H NMR (400 MHz, $CDCl_3$) δ = 9.74 (d, *J* = 1.8 Hz, 1H), 7.85 – 7.79 (m, 2H), 7.55 – 7.51 (m, 1H), 7.45 – 7.38 (m, 2H), 7.25 – 7.14 (m, 5H), 5.97 – 5.86 (m, 1H), 5.30 (dd, $J_1$ = 17.4 Hz, $J_2$ = 1.2 Hz, 1H), 5.20 (dd, $J_1$ = 10.1 Hz, $J_2$ = 1.4 Hz, 1H), 4.20 (d, *J* = 10.6 Hz, 1H), 3.91 – 3.81 (m, 2H), 2.41 – 2.29 (m, 2H) ppm; $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 201.7, 179.0, 160.0, 136.9, 134.6, 132.8, 128.9 (2C), 128.8 (2C), 128.4 (2C), 128.0, 127.9 (2C), 125.6, 117.8, 78.1, 58.5, 54.8, 44.0, 43.1 ppm;

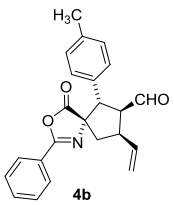


4a´

Compound **4a´**: $^1$H NMR (400 MHz, $CDCl_3$) δ = 9.74 (d, *J* = 1.8 Hz, 1H), 7.90 – 7.86 (m, 2H), 7.60 – 7.49 (m, 3H), 7.20 – 7.08 (m, 5H), 5.98 – 5.85 (m, 1H), 5.32 (d, *J* = 16.3 Hz, 1H), 5.21 (d, *J* = 10.0 Hz, 1H), 4.25 (d, *J* = 11.5 Hz, 1H), 4.07 (ddd, $J_1$ = 11.7, $J_2$ = 10.0 Hz, $J_3$ = 2.2 Hz, 1H), 3.90 – 3.82 (m, 1H), 2.48 (dd, $J_1$ = 13.8 Hz, $J_2$ =7.6 Hz, 1H)2.41 – 2.35 (m, 2H) ppm; $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 201.5, 178.9, 161.1, 137.0, 134.52, 133.0, 128.9 (2C), 128.8 (2C), 128.4 (2C), 128.1, 128.0, 127.9 (2C), 125.5, 117.9, 79.0, 55.8, 52.6, 42.6, 41.4 ppm;

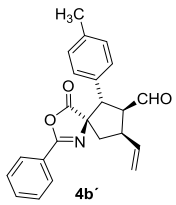
**(5*S*,6*S*,7*S*,8*R*)-4-Oxo-2-phenyl-6-(p-tolyl)-8-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7-carbaldehyde (4b) and (5*R*,6*S*,7*S*,8*R*)-4-Oxo-2-phenyl-6-(p-tolyl)-8-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7-carbaldehyde (4b´)**

Colorless oil, yield 72 %, dr 4:1 (4b/4b´), *ee* 98/96 %; The ee was determined by HPLC analysis using Chiralpak IA column (90/10 heptane/i-PrOH, flow rate 1.0 ml/min; λ = 190 nm, 25 °C, **4b**: $t_{major}$ = 5.7 min; $t_{minor}$ = 7.1 min., **4b´**: $t_{minor}$ = 6.4 min., $t_{major}$ = 7.5 min.); IR (KBr): ν = 3411, 3387, 3040, 2917, 1817, 1718, 1652, 1293 $cm^{-1}$; $[\alpha]^{25}_{D}$ = + 8.6 ° (0.35, $CHCl_3$); HRMS (ESI) m/z calcd for $C_{23}H_{21}NO_3$ $[M+Na]^+$ 382.1414, found . 382.1412.



4b

Compound **4b**: $^1$H NMR (400 MHz, $CDCl_3$) δ = 9.72 (d, *J* = 1.3 Hz, 1H), 7.87 – 7.83 (m, 2H), 7.57 – 7.49 (m, 1H), 7.48 – 7.41 (m, 2H), 7.11 (d, *J* = 7.8 Hz, 1H), 6.96 (d, *J* = 7.9 Hz, 2H), 5.97 – 5.84 (m, 1H), 5.28 (dt, $J_1$ = 16.8 Hz, $J_2$ = 1.1 Hz, 1H), 5.18 (dd, $J_1$ = 10.0 Hz, $J_2$ = 1.3 Hz, 1H), 4.16 (d, *J* = 10.6 Hz, 1H), 3.84-3.81 (m, 2H), 2.40 – 2.27 (m, 2H), 2.17 (s, 3H) ppm; $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 201.8, 179.0, 159.9, 137.6, 137.0, 132.8, 131.5, 129.1 (2C), 128.8 (2C), 128.8 (2C), 128.0 (2C), 125.7, 117.8, 78.2, 58.6, 54.5, 43.9, 43.2, 21.2 ppm.



4b´

Compound **4b´**: $^1$H NMR (400 MHz, $CDCl_3$) δ = 9.72 (d, *J* = 1.4 Hz, 1H), 7.90 – 7.87 (m, 2H), 7.56 – 7.50 (m, 1H), 7.47 – 7.38 (m, 2H), 7.07 (d, *J* = 8.2 Hz, 2H), 6.99 (d, *J* = 8.2

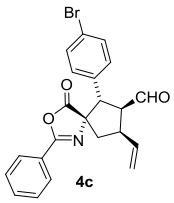
Hz, 2H), 5.99 – 5.87 (m, 1H), 5.31 (dt, $J_1$ = 16.9 Hz, $J_2$ = 1.0 Hz, 1H), 5.20 (d, $J$ = 10.0 Hz, 1H), 4.21 (d, $J$ = 11.6 Hz, 1H), 4.03 (ddd, $J_1$ = 11.7 Hz, $J_2$ = 9.9 Hz, $J_3$ =2.3 Hz, 1H), 3.86 – 3.80 (m, 1H), 2.47 (dd, $J_1$ = 13.8 Hz, $J_2$ = 7.6 Hz, 1H), 2.40 – 2.34 (m, 1H), 2.22 (s, 3H) ppm.$^{13}$C NMR (101 MHz, $CDCl_3$) δ = 201.6, 178.9, 161.0, 137.8, 137.0, 132.9, 131.4, 129.5 (2C), 128.9 (2C), 128.0 (2C), 127.9 (2C), 125.5, 117.9, 79.1, 55.9, 52.3, 42.7, 41.4, 21.2 ppm.

**(5*S*,6*S*,7*S*,8*R*)-6-(4-Bromophenyl)-4-oxo-2-phenyl-8-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7-carbaldehyde (4c) and (5*R*,6*S*,7*S*,8*R*)-6-(4-Bromophenyl)-4-oxo-2-phenyl-8-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7-carbaldehyde (4c´)**

Colorless oil, yield 64 %, dr 4:1 (4c/4c´), *ee* 98/97 %; The ee was determined by HPLC analysis using Chiralpak IA column (70/30 heptane/i-PrOH, flow rate 0.2 ml/min; λ = 190 nm, 25 °C, **4c**: $t_{major}$ = 25.0 min; $t_{minor}$ = 29.1 min., **4c´**: $t_{minor}$ = 27.2 min; $t_{major}$ = 31.3 min.); IR (KBr): ν = 3411, 3067, 2929, 2833, 1814, 1715, 1652, 1326 cm$^{-1}$; $[\alpha]^{25}_D$ = +38.1 °, (0.21, $CHCl_3$).

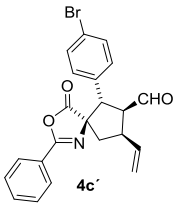
The diastereoisomers **4c** and **4c´** were separated by preparative HPLC due to prepare crystals for X-ray crystallography.

**(5*S*,6*S*,7*S*,8*R*)-6-(4-Bromophenyl)-4-oxo-2-phenyl-8-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7-carbaldehyde (4c)**




Compound **4c**: $^1$H NMR (400 MHz, $CDCl_3$) δ = 9.72 (d, $J$ = 1.8 Hz, 1H), 7.90 – 7.81 (m, 2H), 7.58 – 7.50 (m, 1H), 7.46 – 7.42 (m, 2H), 7.29 (d, $J$ = 8.5 Hz, 2H), 7.11 (d, $J$ = 8.5 Hz, 2H), 5.93 – 5.82 (m, 1H), 5.30 (dt, $J_1$ = 16.9 Hz, $J_2$ = 1.1 Hz, 1H), 5.20 (dd, $J_1$ = 10.1 Hz, $J_2$ = 1.3 Hz, 1H), 4.14 (d, $J$ = 10.4 Hz, 1H), 3.88 – 3.73 (m, 2H), 2.36 – 2.29 (m, 2H) ppm; $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 201.3, 178.7, 160.3, 136.7, 133.9, 133.1, 131.6 (2C), 130.7 (2C), 128.9 (2C), 128.0 (2C), 125.4, 122.1, 118.1, 77.8, 58.7, 53.9, 43.7, 43.3 ppm; $[\alpha]^{25}_D$ = +81.3 °, (0.46, $CHCl_3$); HRMS (ESI) m/z calcd for $C_{22}H_{18}BrNO_3$ $[M+H]^+$ 424.0542, found 424.0542.

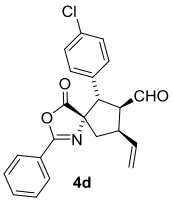
**(5*R*,6*S*,7*S*,8*R*)-6-(4-Bromophenyl)-4-oxo-2-phenyl-8-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7-carbaldehyde (4c´)**




Compound **4c´**: $^1$H NMR (400 MHz, $CDCl_3$) δ = 9.72 (d, $J$ = 1.8 Hz, 1H), 7.90 – 7.87 (m, 2H), 7.58 – 7.52 (m, 1H), 7.46 – 7.43 (m, 2H), 7.32 (d, $J$ = 8.5 Hz, 2H), 7.06 (d, $J$ = 8.5 Hz, 2H), 5.94 – 5.84 (m, 1H), 5.32 (d, $J$ = 15.7 Hz, 1H), 5.21 (d, $J$ = 10.5 Hz, 1H), 4.19 (d, $J$ = 11.5 Hz, 1H), 4.05-4.00 (m, 1H), 3.92 – 3.82 (m, 1H), 2.47 (dd, $J_1$ = 13.8 Hz, $J_2$ = 7.6 Hz, 1H), 2.51 – 2.33 (m, 1H) ppm; $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 201.1, 178.7, 161.3, 136.8, 133.8, 133.2, 131.9 (2C), 129.7 (2C), 129.0 (2C), 128.1 (2C), 125.3, 122.3, 118.2, 78.7, 55.8, 51.8, 42.4, 41.5 ppm; $[\alpha]^{25}_D$ = -39.7 °, (0.63, $CHCl_3$); HRMS (ESI) m/z calcd for $C_{22}H_{18}BrNO_3$ $[M+H]^+$ 424.0542, found 424.0541.

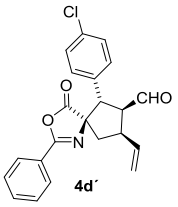
**(5*S*,6*S*,7*S*,8*R*)-6-(4-Chlorophenyl)-4-oxo-2-phenyl-8-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7-carbaldehyde (4d) and (5*R*,6*S*,7*S*,8*R*)-6-(4-Chlorophenyl)-4-oxo-2-phenyl-8-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7-carbaldehyde (4d´)**

Colorless oil, yield 74 %, dr 5:2 (4d/4d´), *ee* 99/98 %; The ee was determined by HPLC analysis using Chiralpak IA column (70/30 heptane/i-PrOH, flow rate 0.2 ml/min; λ = 190 nm, 25 °C, **4d**: $t_{major}$ = 24.4 min; $t_{minor}$ = 29.4 min., **4d´**: $t_{minor}$ = 26.6 min; $t_{major}$ = 30.6 min.); IR (KBr): ν = 3058, 2977, 2833, 2735, 1811, 1727, 1649, 1290 $cm^{-1}$; $[\alpha]^{25}_{D}$ = 0 °, (0.33, $CHCl_3$); HRMS (ESI) m/z calcd for $C_{22}H_{18}ClNO_3$ $[M+Na]^+$ 402.0867, found 402.0866.



4d

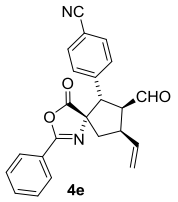
Compound **4d**: $^1$H NMR (400 MHz, $CDCl_3$) δ = 9.73 (d, *J* = 1.8 Hz, 1H), 7.88 – 7.82 (m, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.49 – 7.40 (m, 2H), 7.21 – 7.11 (m, 4H), 5.99 – 5.81 (m, 1H), 5.30 (d, *J* = 16.9 Hz, 1H), 5.20 (dd, $J_1$ = 10.1 Hz, $J_1$ = 1.3 Hz, 1H), 4.16 (d, *J* = 10.4 Hz, 1H), 3.88 – 3.74 (m, 2H), 2.37 – 2.27 (m, 2H) ppm; $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 201.3, 178.7, 160.2, 136.8, 133.9, 133.4, 133.1, 130.3 (2C), 128.9 (2C), 128.6 (2C), 128.0 (2C), 125.4, 118.1, 77.9, 58.7, 53.9, 43.7, 43.3 ppm.



4d´

Compound **4d´**: $^1$H NMR (400 MHz, $CDCl_3$) δ = 9.73 (d, *J* = 1.8 Hz, 1H), 7.88 – 7.82 (m, 2H), 7.57 – 7.52 (m, 1H), 7.49 – 7.40 (m, 3H), 7.21 – 7.11 (m, 4H), 5.99 – 5.81 (m, 1H), 5.32 (d, *J* = 16.9 Hz, 1H), 5.21 (d, *J* = 10.1 Hz, 1H), 4.20 (d, *J* = 11.5 Hz, 1H), 4.02 (ddd, $J_1$ = 11.6 Hz, $J_3$ = 10.0 Hz, $J_3$ = 2.0 Hz, 1H), 3.91 – 3.78 (m, 2H), 2.47 (dd, $J_1$ = 13.8 Hz, $J_2$ = 7.6 Hz, 1H), 2.40 – 2.29 (m, 1H) ppm; $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 201.1, 178.7, 161.2, 136.8, 134.0, 133.2, 133.2, 129.4 (2C), 129.0, 128.9, 128.1, 125.3, 118.1, 78.8, 55. 9, 51.8, 42.4, 41.4 ppm.

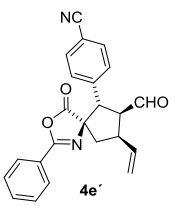
**4-((5*S*,6*S*,7*S*,8*R*)-7-Formyl-4-oxo-2-phenyl-8-vinyl-3-oxa-1-azaspiro[4.4]non-1-en-6-yl)benzonitrile (4e)**



4e

Colorless oil, yield 31 %, dr > 19:1, *ee* 85 %; The ee was determined by HPLC analysis using Chiralpak IA column (80/20 heptane/i-PrOH, flow rate 1.0 ml/min; λ = 190 nm, tmajor = 7.3 min; tminor = 10.1 min.); $^1$H NMR (400 MHz, $CDCl_3$) δ = 9.74 (d, *J* = 1.4 Hz, 1H), 7.86 – 7.80 (m, 2H), 7.60 – 7.53 (m, 1H), 7.49 – 7.42 (m, 4H), 7.38 – 7.33 (m, 2H), 5.86 (ddd, $J_1$ = 16.9 Hz, $J_2$ = 10.0 Hz, 8.7 Hz, 1H), 5.33 (dt, $J_1$ = 16.8 Hz, $J_2$ = 1.0 Hz, 1H), 5.23 (dd, $J_1$ = 10.1 Hz, $J_2$ = 1.3 Hz, 1H), 4.22 (d, *J* = 10.2 Hz, 1H), 3.95 – 3.81 (m, 2H), 2.33 (dd, $J_1$ = 7.9 Hz, $J_2$ = 2.1 Hz, 2H) ppm; $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 200.7, 178.4, 160.5, 140.6, 136.5, 133.3, 132.2 (2C), 129.8 (2C), 129.1 (2C), 127.9 (2C), 125.2, 118.6, 118.4, 111.9, 77.7, 58.6, 54.1, 43.7, 43.4 ppm; IR (KBr): ν = 3055, 2971, 2920, 2229, 1721, 1652 $cm^{-1}$; $[\alpha]^{25}_{D}$ = +49.3°, (0.34, $CHCl_3$); HRMS (ESI) m/z calcd for $C_{23}H_{18}N_2O_3$ $[M+H]^+$ 371.1390, found 371.1387.

**4-((5*R*,6*S*,7*S*,8*R*)-7-Formyl-4-oxo-2-phenyl-8-vinyl-3-oxa-1-azaspiro[4.4]non-1-en-6-yl)benzonitrile (4e´)**



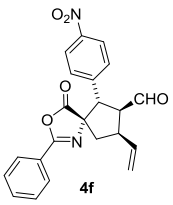
4e´

Colorless oil, yield 32 %, dr > 19:1, *ee* 97 %; The ee was determined by HPLC analysis using Chiralpak IC column (90/10 heptane/i-PrOH, flow rate 1.0 ml/min; λ = 204 nm, $t_{minor}$ = 9.3 min; $t_{major}$ = 24.6 min.); $^1$H NMR (400 MHz, $CDCl_3$) δ = 9.75 (d, *J* = 1.5 Hz, 1H), 7.87 (dd, $J_1$ = 8.4 Hz, $J_2$ = 1.4 Hz, 2H), 7.61 – 7.55 (m, 1H), 7.52 – 7.43 (m, 4H),

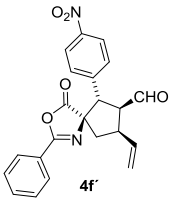
7.33 – 7.28 (m, 2H), 5.88 (ddd, $J_1$ = 16.9 Hz, $J_2$ = 10.0 Hz, $J_3$ = 9.2 Hz, 1H), 5.39 – 5.31 (m, 1H), 5.23 (dd, $J_1$ = 10.2 Hz, $J_2$ = 1.1 Hz, 1H), 4.26 (d, $J$ = 11.4 Hz, 1H), 4.08 (ddd, $J_1$ = 11.5 Hz, $J_2$ = 10.0 Hz, $J_3$ = 1.6 Hz, 1H), 3.95 – 3.81 (m, 1H), 2.49 (dd, J = 13.9, 7.6 Hz, 1H), 2.35 (dd, J = 13.9, 8.0 Hz, 1H) ppm; $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 200.5, 178.5, 161.5, 140.5, 136.6, 133.4, 132.5 (2C), 129.1 (2C), 128.9 (2C), 128.1 (2C), 125.1, 118.6, 118.4, 112.1, 78.7, 55.7, 52.2, 42.3, 41.6 ppm; IR (KBr): ν = 2959, 2929, 2917, 2851, 2232, 1811, 1715, 1652 cm$^{-1}$; $[\alpha]^{25}_D$ = -98.1 °, (0.26, $CHCl_3$); HRMS (ESI) m/z calcd for $C_{23}H_{18}N_2O_3$ $[M+H]^+$ 371.1390, found 371.1389.

**(5*S*,6*S*,7*S*,8*R*)-6-(4-Nitrophenyl)-4-oxo-2-phenyl-8-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7-carbaldehyde (4f) and (5*R*,6*S*,7*S*,8*R*)-6-(4-Nitrophenyl)-4-oxo-2-phenyl-8-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7-carbaldehyde (4f´)**

Colorless oil, yield 72 %, dr 4:1 (4f/4f´), *ee* 98/99 %; The ee was determined by HPLC analysis using Chiralpak IA column (90/10 heptane/i-PrOH, flow rate 1.0 ml/min; λ = 190 nm, 25 °C, **4f**: $t_{major}$ = 10.0 min; $t_{minor}$ = 13.2 min., **4f´**: $t_{minor}$ = 11.9 min; $t_{major}$ = 14.5 min.); IR (KBr): ν = 3073, 2974, 2851, 2735, 1814, 1724, 1652 cm$^{-1}$; HRMS (ESI) m/z calcd for $C_{22}H_{18}N_2O_5$ $[M+H]^+$ 391.1288, found 391.1289.

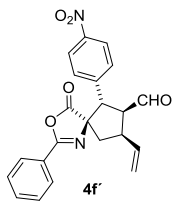



Compound **4f:** $^1$H NMR (400 MHz, $CDCl_3$) δ =9.78 – 9.73 (m, 1H), 8.03 (d, $J$ = 8.6 Hz, 1H), 7.86 – 7.82 (m, 1H), 7.61 – 7.52 (m, 1H), 7.49 – 7.41 (m, 4H), 5.96 – 5.81 (m, 1H), 5.39 – 5.30 (m, 1H), 5.24 (d, $J$ = 10.1 Hz, 1H), 4.28 (d, $J$ = 10.0 Hz, 1H), 3.97 – 3.83 (m, 2H), 2.41 – 2.31 (m, 2H) ppm; $^{13}$C NMR (101 MHz, $CDCl_3$) δ = ppm; $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 200.4, 178.3, 161.5, 147.7, 142.6, 136.5, 133.3, 130.0 (2C), 129.1 (2C), 128.1 (2C), 125.2, 123.6 (2C), 118.4, 77.65, 58.89, 53.75, 43.72, 43.58 ppm.




Compound **4f´:** $^1$H NMR (400 MHz, $CDCl_3$) δ = $^1$H NMR (400 MHz, $CDCl_3$) δ = 9.78 – 9.73 (m, 1H), 8.06 (d, $J$ = 8.6 Hz, 2H), 7.89 – 7.86 (m, 2H), 7.61 – 7.52 (m, 1H), 7.49 – 7.41 (m, 2H), 7.37 (d, $J$ = 8.5 Hz, 2H), 5.96 – 5.81 (m, 1H), 5.39 – 5.30 (m, 1H), 5.25 (d, J = 10.1 Hz, 1H), 4.32 (d, $J$ = 11.4 Hz, 1H), 4.12 (t, $J$ = 10.7 Hz, 1H), 3.97 – 3.83 (m, 1H), 2.51 (dd, $J_1$ = 13.8 Hz, $J_2$ = 7.6 Hz, 1H), 2.41 – 2.31 (m, 2H) ppm; $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 200.5, 178.5, 161.5, 147.7, 142.6, 136.6, 133.4, 129.1 (4C), 128.1 (2C), 125.0, 123. 9 (2C), 118.5, 78.7, 56.0, 52.0, 42.3, 41.7 ppm.

**(5*R*,6*S*,7*S*,8*R*)-6-(4-Nitrophenyl)-4-oxo-2-phenyl-8-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7-carbaldehyde (4f´)**

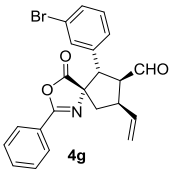



Colorless oil, yield 26 %, dr > 19:1, *ee* 98/99 %; The ee was determined by HPLC analysis using Chiralpak IA column (90/10 heptane/i-PrOH, flow rate 1.0 ml/min; λ = 190 nm, 25 °C, $t_{minor}$ = 11.9 min; $t_{major}$ = 14.5 min.); $^1$H NMR (400 MHz, $CDCl_3$) δ = 9.76 (d, $J$ = 1.4 Hz, 1H), 8.09 – 8.05 (m, 2H), 7.89 – 7.85 (m, 2H), 7.61 – 7.55 (m, 1H), 7.49 – 7.43 (m, 2H), 7.39 – 7.35 (m, 2H), 5.88 (dt, $J_1$ = 16.9 Hz, $J_2$ = 9.7 Hz, 1H), 5.35 (dt, $J_1$ = 16.9 Hz, $J_2$ = 1.1 Hz, 1H), 5.24 (dt, $J_1$ = 10.1 Hz, $J_2$ = 0.9 Hz, 1H), 4.32 (d, $J_1$ = 11.4 Hz, 1H), 4.12 (ddd, $J_1$ = 11.5 Hz, $J_2$ = 10.1 Hz, $J_3$ = 1.4 Hz, 1H), 3.91 (q, $J_1$ = 8.7 Hz, 1H), 2.51 (dd, $J_1$ = 13.9 Hz, $J_2$ = 7.6 Hz, 1H), 2.36 (dd, $J_1$ = 13.9 Hz, $J_2$ = 8.0 Hz, 1H) ppm; $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 200.5, 178.5, 161.5, 147.7, 142.6, 136.6, 133.4, 129.1 (4C), 128.1 (2C), 124.9, 123.9 (2C), 118.5, 78.7, 55.9,

51.9, 42.2, 41.6 ppm; IR (KBr): ν = 3073, 2974, 2851, 2735, 1814, 1724, 1652 $cm^{-1}$; $[\alpha]^{25}_{D}$ = -126.5°, (0.25, $CHCl_3$); HRMS (ESI) m/z calcd for $C_{22}H_{18}N_2O_5$ $[M+H]^+$ 391.1288, found 391.1289.

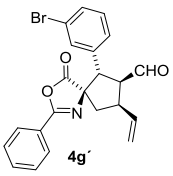
**(5*S*,6*S*,7*S*,8*R*)-6-(3-Bromophenyl)-4-oxo-2-phenyl-8-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7-carbaldehyde (4g) and (5*R*,6*S*,7*S*,8*R*)-6-(3-Bromophenyl)-4-oxo-2-phenyl-8-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7-carbaldehyde (4g´)**

Colorless oil, yield 60 %, dr 4:3 (4g/4g´), *ee* 97/91 %; The ee was determined by HPLC analysis using Chiralpak IA column (90/10 heptane/i-PrOH, flow rate 1.0 ml/min; λ = 190 nm, 25 °C, **4g**: $t_{major}$ = 6.3 min; $t_{minor}$ = 6.9 min., **4g´**: $t_{major}$ = 8.9 min; $t_{minor}$ = 9.6 min.); IR (KBr): ν =3067, 2983, 2956, 2926, 2854, 2824, 2732, 1817, 1721, 1652 $cm^{-1}$; $[\alpha]^{25}_{D}$ = -6.2 °, (0.81, $CHCl_3$); HRMS (ESI) m/z calcd for $C_{22}H_{18}BrNO_3$ $[M+H]^+$ 424.0543, found 424.0540.



4g

Compound **4g**: $^1$H NMR (400 MHz, $CDCl_3$) δ = 9.75 – 9.73 (m, 1H), 7.89 – 7.85 (m, 2H), 7.56 – 7.52 (m, 1H), 7.50 – 7.42 (m, 3H), 7.24 (ddd, $J_1$ = 7.9 Hz, $J_2$ = 2.0 Hz, $J_3$ = 1.1 Hz, 1H), 7.16 (dt, $J_1$ = 7.8 Hz, $J_2$ = 1.4 Hz, 1H), 7.03 (t, $J$ = 7.9 Hz, 1H), 5.95 – 5.80 (m, 1H), 5.33 (dt, $J_1$ = 16.9 Hz, $J_2$ = 1.1 Hz, 1H), 5.23 (dd, $J_1$ = 10.0 Hz, $J_2$ = 1.2 Hz, 1H), 4.15 (d, $J$ = 10.3 Hz, 1H), 3.93 – 3.74 (m, 2H), 2.39 – 2.29 (m, 2H) ppm; $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 201.1, 178. 7, 160.3, 137.3, 136.7, 133.1, 132.1, 131.2, 130.0, 128.9 (2C), 128.0 (2C), 127.9, 125.5, 122.3, 118.1, 77.8, 58.8, 54.1, 43.9, 43.2 ppm.

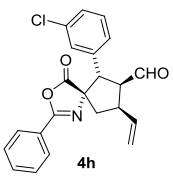


4g´

Compound **4g´**: $^1$H NMR (400 MHz, $CDCl_3$) δ = 9.75 – 9.73 (m, 1H), 7.90 – 7.86(m, 2H), 7.58 – 7.53 (m, 1H), 7.50 – 7.42 (m, 2H), 7.34 (t, J = 1.9 Hz, 1H), 7.30 (ddd, $J_1$ = 7.7 Hz, $J_2$ = 2.0 Hz, $J_3$ = 1.3 Hz, 1H), 7.12 (dt, $J_1$ = 7.8, $J_2$ = 1.5 Hz, 1H), 7.06 (t, $J$ = 7.8 Hz, 1H), 5.95 – 5.80 (m, 1H), 5.34 (dt, $J_1$ = 16.9 Hz, $J_2$ = 1.0 Hz, 1H), 5.24 (d, $J$ = 10.6 Hz, 1H), 4.19 (d, $J$ = 11.4 Hz, 1H), 4.03 (ddd, $J_1$ = 11.6 Hz, $J_2$ = 10.1 Hz, $J_3$ = 1.8 Hz, 1H), 3.92 – 3.84 (m, 1H), 2.46 (dd, $J_1$ = 13.8 Hz, $J_2$ = 7.5 Hz, 1H), 2.38 – 2.33 (m, 1H) ppm; $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 200.9, 178.6, 161.4, 137.2, 136.8, 133.1, 131.3, 131.2, 130.3, 129.0 (2C), 128.1 (2C), 126.7, 125.3, 122.8, 118.2, 78.8, 55.7, 52.0, 42.4, 41.5 ppm.

**(5*S*,6*S*,7*S*,8*R*)-6-(3-Chlorophenyl)-4-oxo-2-phenyl-8-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7-carbaldehyde (4h) and (5*R*,6*S*,7*S*,8*R*)-6-(3-Chlorophenyl)-4-oxo-2-phenyl-8-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7-carbaldehyde (4h)**

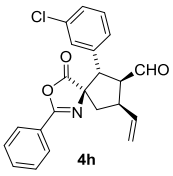
Colorless oil, yield 58 %, dr 2:1 (7h/7h´), *ee* 99/93 %; The ee was determined by HPLC analysis using Chiralpak IC column (90/10 heptane/i-PrOH, flow rate 0.1 ml/min; λ = 248 nm, 15 °C, **7h´**: $t_{major}$ = 68.2 min; $t_{minor}$ = 72.6 min., **7h**: $t_{major}$ = 78.2 min; $t_{minor}$ = 82.8 min.); IR (KBr): ν = 3047, 2980, 2926, 2851, 2744, 1817, 1721, 1652 $cm^{-1}$; $[\alpha]^{25}_{D}$ = +34.5 °, (0.29, $CHCl_3$); HRMS (ESI) m/z calcd for $C_{22}$H18$ClNO_3$ $[M+H]^+$ 380.1048, found 380.1045.



4h

Compound **7h**: $^1$H NMR (400 MHz, $CDCl_3$) δ = 9.74 (d, $J$ = 1.7 Hz, 1H), 7.87 – 7.83 (m, 2H), 7.56 – 7.51 (m, 1H), 7.48 – 7.41 (m, 2H), 7.15 – 7.06 (m, 3H), 5.94 – 5.83 (m, 1H),

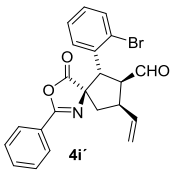
5.31 (d, *J* = 16.9 Hz, 1H), 5.21 (dd, $J_1$ = 10.0 Hz, $J_2$ = 1.3 Hz, 1H), 4.16 (d, *J* = 10.2 Hz, 1H), 3.89 – 3.77 (m, 2H), 2.35 – 2.28 (m, 2H) ppm; $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 201.1, 178.7, 160.3, 137.0, 136.7, 134.1, 133.0, 129.7, 129.1, 128.9 (2C), 128.2, 128.0 (2C), 127.4, 125.5, 118.1, 77.8, 58.7, 54.1, 43.9, 43.2 ppm.



4h

Compound **7h´**: $^1$H NMR (400 MHz, $CDCl_3$) δ = 9.74 (d, *J* = 1.7 Hz, 1H), 7.92 – 7.85 (m, 2H), 7.56 – 7.51 (m, 1H), 7.48 – 7.41 (m, 2H), 7.20 – 7.10 (m, 4H), 5.94 – 5.83 (m, 1H), 5.32 (dt, $J_1$ = 16.9 Hz, $J_2$ = 0.9 Hz, 1H), 5.25 – 5.17 (m, 1H), 4.20 (d, *J* = 11.4 Hz, 1H), 4.03 (ddd, $J_1$ = 11.5 Hz, $J_2$ = 10.1 Hz, $J_3$ = 1.9 Hz, 1H), 3.89 – 3.84 (m, 1H), 2.46 (dd, $J_1$ = 13.8 Hz, $J_2$ = 7.6 Hz, 1H), 2.38 – 2.33 (m, 1H) ppm; $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 200.9, 178.7, 161.3, 136.9, 136.8, 134.6, 133.1, 130.0, 129.0 (2C), 128.4, 128.3, 128.1 (2C), 126.3, 125.3, 118.1, 78.8, 55.8, 52.0, 42.4, 41.5 ppm.

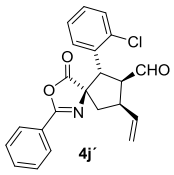
**(5*R*,6*S*,7*S*,8*R*)-6-(2-Bromophenyl)-4-oxo-2-phenyl-8-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7-carbaldehyde (4i´)**



4i´

Colorless oil, yield 45 %, dr > 19:1, *ee* 95 %; The ee was determined by HPLC analysis using Chiralpak IA column (90/10 heptane/i-PrOH, flow rate 1.0 ml/min; λ = 190 nm, 25 °C, $t_{major}$ = 7.3 min; $t_{minor}$ = 10.0 min.); $^1$H NMR (400 MHz, $CDCl_3$) δ = 9.75 (d, *J* = 2.5 Hz, 1H), 7.88 – 7.81 (m, 2H), 7.58 – 7.51 (m, 1H), 7.48 – 7.37 (m, 4H), 7.11 (td, $J_1$ = 7.6, $J_2$ = 1.4 Hz, 1H), 6.96 (ddd, $J_1$ = 8.0 Hz, $J_2$ = 7.3 Hz, $J_3$ = 1.7 Hz, 1H), 6.00 (ddd, $J_1$ = 16.9 Hz, $J_2$ = 10.1 Hz, $J_3$ = 8.9 Hz, 1H), 5.37 – 5.20 (m, 2H), 5.02 (d, *J* = 10.1 Hz, 1H), 3.88 – 3.78 (m, 1H), 3.70 (td, $J_1$ = 10.2, 2.5 Hz, 1H), 2.47 (dd, J = 13.4, 8.9 Hz, 1H), 2.34 (dd, J = 13.4, 7.2 Hz, 1H) ppm; $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 201.1, 178.5, 160.2, 136.4, 134.7, 133.3, 133.0, 131.1, 129.3, 128.9 (2C), 128.0 (2C), 126.8, 125.6, 125.6, 118.1, 76.7, 61.2, 51.9, 44.5, 43.7ppm; IR (KBr): ν = 3067, 2962, 2929, 2848, 2729, 1820, 1721, 1649 cm$^{-1}$; $[\alpha]^{25}_D$ = +144.1 °, (0.72, $CHCl_3$); HRMS (ESI) m/z calcd for $C_{22}H_{18}BrNO_3$ $[M+H]^+$ 424.0543, found 424.0539.

**(5*R*,6*S*,7*S*,8*R*)-6-(2-Chlorophenyl)-4-oxo-2-phenyl-8-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7-carbaldehyde (4j´)**

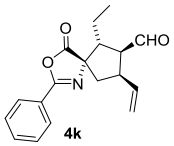


4j´

Colorless oil, yield 45 %, dr > 19:1, *ee* 89 %; The ee was determined by HPLC analysis using Chiralpak IA column (80/20 heptane/i-PrOH, flow rate 1.0 ml/min; λ = 190 nm, 25 °C, $t_{major}$ = 5.7 min; $t_{minor}$ = 7.2 min.); $^1$H NMR (400 MHz, $CDCl_3$) δ = 9.74 (d, *J* = 2.4 Hz, 1H), 7.86 – 7.81 (m, 2H), 7.57 – 7.50 (m, 1H), 7.45 – 7.37 (m, 3H), 7.30 – 7.23 (m, 1H), 7.09 – 7.01 (m, 2H), 5.99 (ddd, $J_1$ = 16.9 Hz, $J_1$ = 10.1 Hz, $J_1$ = 8.8 Hz, 1H), 5.37 – 5.19 (m, 2H), 5.00 (d, *J* = 10.1 Hz, 1H), 3.89 – 3.78 (m, 1H), 3.74 (td, $J_1$ = 10.2, $J_2$ = 2.4 Hz, 1H), 2.45 (dd, $J_1$ = 13.3 Hz, $J_2$ = 8.6 Hz, 1H), 2.34 (dd, $J_1$ = 13.4 Hz, $J_2$ = 7.2 Hz, 1H) ppm; $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 201.3, 178.7, 160.2, 136.4, 133.0, 132.8, 130.7, 129.9, 129.0, 128.9 (2C), 127.9 (2C), 126.2, 125.6, 118.1, 76.7, 60.6, 49.2, 44.4, 43.6 ppm; IR (KBr): ν = 3073, 2923, 2854, 1820, 1718, 1649 cm$^{-1}$; $[\alpha]^{25}_D$ = 137.3°, (0.63, $CHCl_3$); HRMS (ESI) m/z calcd for $C_{22}H_{18}ClNO_3$ $[M+H]^+$ 380.1048, found 380.1048.

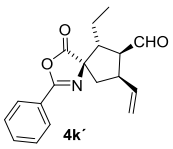
**(5*S*,6*S*,7*S*,8*R*)-6-Ethyl-4-oxo-2-phenyl-8-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7-carbaldehyde (4k) and (5*R*,6*S*,7*S*,8*R*)-6-Ethyl-4-oxo-2-phenyl-8-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7-carbaldehyde (4k´)**

Colorless oil, yield 69 %, dr 4:1 (4k/4k´), *ee* 98/95 %; The ee was determined by HPLC analysis using Chiralpak IC column (95/5 heptane/i-PrOH, flow rate 0.3 ml/min; λ = 190 nm, 25 °C, **4k´**: $t_{minor}$ = 20.5 min; $t_{major}$ = 21.6 min., **4k**: $t_{major}$ = 25.4 min; $t_{minor}$ = 36.8 min.; IR (KBr): ν = 3071, 2949, 2869, 1715, 1646, 1531, 1234 $cm^{-1}$; $[\alpha]^{25}_{D}$ = +5.6°, (0.67, $CHCl_3$); HRMS (ESI) m/z calcd for $C_{18}H_{20}NO_3$ $[M+H]^+$ 298.1438, found 298.1439.



4k

Compound **4k:** $^1$H NMR (400 MHz, $CDCl_3$) δ = 9.76 (d, *J* = 3.1 Hz, 1H), 8.06 – 7.96 (m, 2H), 7.64 – 7.54 (m, 1H), 7.54 – 7.45 (m, 2H), 5.85 (ddd, $J_1$ = 17.0 Hz, $J_2$ = 10.2 Hz, $J_3$ = 8.7 Hz, 1H), 5.25 – 5.18 (m, 1H), 5.15 (dt, $J_1$ = 10.2 Hz, $J_2$ = 1.2 Hz, 1H), 3.75 – 3.58 (m, 1H), 3.17 – 3.02 (m, 1H), 3.02 – 2.90 (m, 1H), 2.28 – 2.20 (m, 1H), 2.07 (dd, $J_1$ = 12.9 Hz, $J_2$ = 6.9 Hz, 1H), 1.45 – 1.21 (m, 2H), 0.75 (t, *J* = 7.5 Hz, 3H) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 202.6, 180.2, 160.3, 136.5, 133.0, 129.0 (2C), 128.1 (2C), 126.0, 117.5, 76.7, 59.3, 50.8, 44.8, 44.1, 22.8, 12.5 ppm.

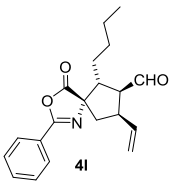


4k´

**Compound 4k´**: $^1$H NMR (400 MHz, $CDCl_3$) δ 9.75 (d, *J* = 3.1 Hz, 1H), 8.06 – 7.96 (m, 2H), 7.64 – 7.54 (m, 1H), 7.54 – 7.45 (m, 2H), 5.85 (ddd, $J_1$ =17.0 Hz, $J_2$ = 10.2 Hz, $J_3$ = 8.7 Hz, 1H), 5.25 – 5.18 (m, 1H), 5.15 (dt, $J_1$ = 10.2 Hz, $J_2$ = 1.2 Hz, 1H), 3.75 – 3.58 (m, 1H), 3.17 – 3.02 (m, 1H), 3.02 – 2.90 (m, 1H), 2.28 – 2.20 (m, 2H), 1.45 – 1.21 (m, 2H), 0.83 – 0.75 (m, 3H) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$) δ 202.6, 179.3, 161.1, 136.4, 133.0, 129.0 (2C), 128.1 (2C), 125.8, 117.6, 77.8, 58.4, 49.0, 43.0, 42.1, 23.0, 12.7 ppm.

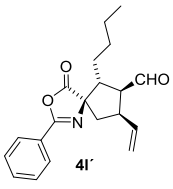
**(5*S*,6*S*,7*S*,8*R*)-6-Butyl-4-oxo-2-phenyl-8-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7-carbaldehyde (4l) and (5*R*,6*S*,7*S*,8*R*)-6-Butyl-4-oxo-2-phenyl-8-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7-carbaldehyde (4l´)**

Colorless oil, yield 78 %, dr 5:1 (4l/4l´), *ee* 98/83 %; The ee was determined by HPLC analysis using Chiralpak IC column (98/2 heptane/i-PrOH, flow rate 0.3 ml/min; λ = 222 nm, **4l´**: $t_{minor}$ = 19.5 min; $t_{major}$ = 21.6 min., **4l**: $t_{major}$ = 25.0 min; $t_{minor}$ = 29.2 min.; IR (KBr): ν = 3073, 2956, 2872, 1718, 1646, 1524, 1213 $cm^{-1}$; $[\alpha]^{25}_{D}$ = -14.9°, (0.24, $CHCl_3$); HRMS (ESI) m/z calcd for $C_{20}H_{23}NO_3$ $[M]^+$ 325.1678, found 325.1675.



4l

Compound **4l:** $^1$H NMR (400 MHz, $CDCl_3$) δ = 9.76 (d, *J* = 2.9 Hz, 1H), 8.05 – 7.98 (m, 2H), 7.63 – 7.56 (m, 1H), 7.55 – 7.46 (m, 2H), 5.91 – 5.78 (m, 1H), 5.21 (dt, $J_1$ = 17.0 Hz, $J_2$ = 1.2 Hz, 1H), 5.15 (dt, $J_1$ = 10.3 Hz, $J_2$ = 1.2 Hz, 1H), 3.75 – 3.57 (m, 1H), 3.19 – 2.96 (m, 2H), 2.33 – 2.15 (m, 2H), 1.36 – 1.23 (m, 4H), 1.23 – 1.03 (m, 2H), 0.77 (t, *J* = 7.3 Hz, 3H) ppm; $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 202.6, 180.1, 160.3, 136.5, 133.0, 129.0 (2C), 128.1 (2C), 125.9, 117.6, 77.4, 59.5, 49.0, 44.8, 44.1, 30.1, 29.4, 22.7, 13.9 ppm.

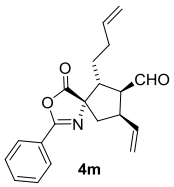


4l´

Compound **4l´**: $^1$H NMR (400 MHz, CDCl3) δ = 9.75 (d, J = 3.0 Hz), 8.05 – 7.98 (m, 2H), 7.63 – 7.56 (m, 1H), 7.55 – 7.46 (m, 2H), 5.91 – 5.78 (m, 1H), 5.21 (dt, J = 17.0, J‘ = 1.2 Hz, 1H), 5.15 (dt, J = 10.3, J‘ = 1.2 Hz, 1H), 3.75 – 3.57 (m, 1H), 3.19 – 2.96 (m, 2H), 2.33 – 2.15 (m, 1H), 2.07 (dd, J = 13.0, J‘ = 6.9 Hz, 1H), 1.36 – 1.23 (m, 4H), 1.23 –

1.03 (m, 2H), 0.83 – 0.76 (m, 3H) ppm. $^{13}$C NMR (101 MHz, CDCl3) δ = 202.6, 179.3, 158.3, 136.4, 133.0, 129.0 (2C), 128.1 (2C), 125.8, 117.6, 77.9, 58.6, 47.2, 43.1, 42.0, 30.2, 29.7, 22.7, 13.9 ppm.

**(5*S*,6*S*,7*S*,8*R*)-6-(But-3-en-1-yl)-4-oxo-2-phenyl-8-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7-carbaldehyde (4m)**

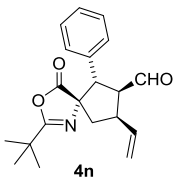


4m

Colorless oil, yield 50 %, dr 10:1, *ee* 92 %; The ee was determined by HPLC analysis using Chiralpak IA column (98/2 heptane/i-PrOH, flow rate 1.0 ml/min; λ = 235 nm, 25 °C, $t_{major}$ = 6.8 min; $t_{minor}$ = 7.6 min.); $^1$H NMR (400 MHz, $CDCl_3$) δ = 9.75 (d, *J* = 2.8 Hz, 1H), 8.05 – 7.99 (m, 2H), 7.63 – 7.56 (m, 1H), 7.54 – 7.48 (m, 2H), 5.84 (ddd, $J_1$ = 17.0 Hz, $J_2$ = 10.1 Hz, $J_3$ = 8.7 Hz, 1H), 5.69 – 5.56 (m, 1H), 5.27 – 5.11 (m, 2H), 4.94 – 4.84 (m, 2H), 3.66 (tt, $J_1$ = 9.5 Hz, $J_2$ = 7.2 Hz, 1H), 3.17 – 2.99 (m, 2H), 2.24 (dd, $J_1$ = 13.0 Hz, $J_2$ = 10.7 Hz, 1H), 2.07 (dd, $J_1$ = 12.9 Hz, $J_2$ = 6.8 Hz, 1H), 1.95 – 1.80 (m, 1H), 1.49 – 1.32 (m, 2H) ppm; $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 202.5, 179.9, 160.4, 137.3, 136.3, 133.1, 129.0 (2C), 128.2 (2C), 125.8, 117.7, 115.7, 76.8, 59.3, 48.2, 44.9, 44.0, 31.9, 29.1 ppm; IR (KBr): ν = 3070, 2929, 2857, 1814, 1718, 1649, 1299 cm$^{-1}$; $[\alpha]^{25}_D$ = +18.6 °, (0.3, $CHCl_3$); HRMS (ESI) m/z calcd for $C_{20}H_{21}NO_3$ $[M+Na]^+$ 346.1414, found 346.1415.

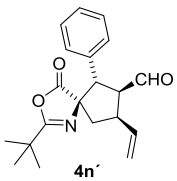
**(5*S*,6*S*,7*S*,8*R*)-2-(*tert*-Butyl)-4-oxo-6-phenyl-8-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7-carbaldehyde (4n) and (5*R*,6*S*,7*S*,8*R*)-2-(*tert*-Butyl)-4-oxo-6-phenyl-8-vinyl-3-oxa-1-azaspiro[4.4]non-1-ene-7-carbaldehyde (4n´)**

Colorless oil, yield 70 %, dr 2:1 (4n/4n´), *ee* 98/98 %; The ee was determined by HPLC analysis using Chiralpak IC column (98/2 heptane/i-PrOH, flow rate 1.0 ml/min; λ = 190 nm, 25 °C, **4n´**: $t_{major}$ = 8.5 min; $t_{minor}$ = 10.4 min., **4n**: $t_{minor}$ = 9.2 min; $t_{major}$ = 12.3 min.; IR (KBr): ν = 3428, 3028, 2977, 2869, 1814, 1718, 1661, 1284, 1204, 1141 cm$^{-1}$; $[\alpha]^{25}_D$ = -39.4 °, (0.55, $CHCl_3$); HRMS (ESI) m/z calcd for $C_{20}H_{23}NO_3$ $[M]^+$ 325.1678, found 325.1676.



4n

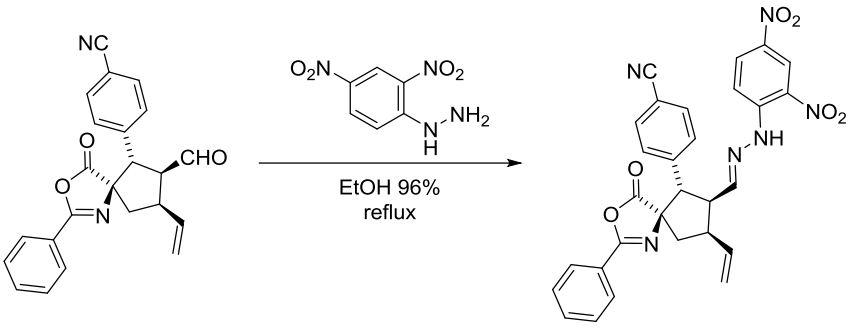
Compound **4n**: $^1$H NMR (400 MHz, $CDCl_3$) δ = 9.71 (d, *J* = 2.3 Hz, 1H), 7.26 – 7.11 (m, 5H), 5.97 – 5.80 (m, 1H), 5.27 (d, *J* = 16.9 Hz, 1H), 5.18 (dd, $J_1$ = 10.1, $J_2$ = 0.7 Hz, 1H), 4.12 – 3.96 (m, 1H), 3.85 – 3.67 (m, 2H), 2.41 – 2.13 (m, 2H), 0.94 (s, 9H) ppm; $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 201.4, 179.8, 169.5, 136.9, 134.4, 128.7 (2C), 128.0 (2C), 128.00, 117.5, 76.7, 57.6, 54.5, 43.9, 41.9, 33.7, 26.2 (3C) ppm.



4n´

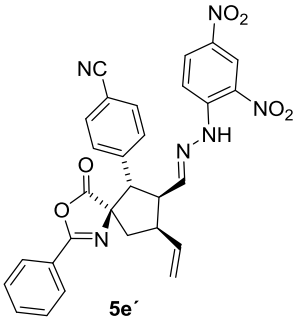
Compound **4n´**: $^1$H NMR (400 MHz, $CDCl_3$) δ = 9.69 (d, *J* = 2.1 Hz, 1H), 7.26 – 7.11 (m, 5H), 5.97 – 5.80 (m, 1H), 5.27 (d, *J* = 16.9 Hz, 1H), 5.17 (dd, $J_1$ = 10.0, $J_2$ = 0.7 Hz, 1H), 4.12 – 3.96 (m, 1H), 3.85 – 3.67 (m, 2H), 2.41 – 2.13 (m, 3H), 1.08 (s, 9H) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 201.2, 179.4, 171.2, 137.1, 134.3, 128.4 (2C), 128.00, 127.8 (2C), 117.5, 78.1, 55.0, 52.3, 42.2, 40.4, 33.8, 26.5 (3C) ppm.

## 5. Preparation of hydrazone



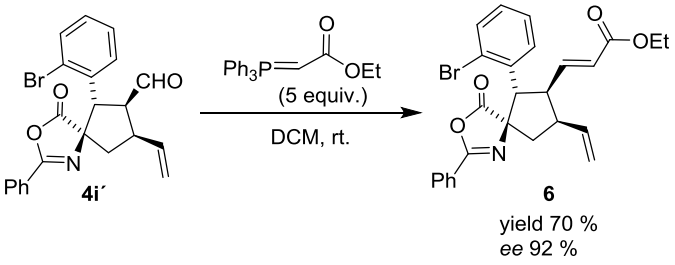

To the spirocompound **4e´** (0.1215 mmol, 45 mg, 1 equiv.) dissolved in EtOH (1ml) was added 2,4-dinitrophenylhydrazine (0.1215 mmol, 24 mg, 1 equiv.). Reaction mixture was refluxed until full conversion was reached (TLC monitoring). Desires product **5e´** was isolated by column chormatography in Hex/EtOAc (4:1) as yellow solid material (31 mg, 47 % yield).

**4-((5*R*,6*S*,7*S*,8*R*)-7-((*E*)-(2-(2,4-dinitrophenyl)hydrazineylidene)methyl)-4-oxo-2-phenyl-8-vinyl-3-oxa-1-azaspiro[4.4]non-1-en-6-yl)benzonitrile**



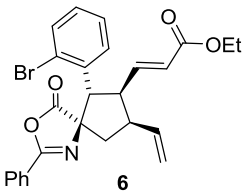

Yellow solid, yield 47 %, dr 20:1, *ee* 99 %; The ee was determined by HPLC analysis using Chiralpak IB column (80/20 heptane/i-PrOH, flow rate 1.0 ml/min; λ = 260 nm, 25 °C, $t_{major}$ = 30.5 min; $t_{minor}$ = 34.8 min; $^1$H NMR (400 MHz, $CDCl_3$) δ = 10.99 (s, 1H), 9.04 (d, *J* = 2.6 Hz, 1H), 8.23 (dd, $J_1$ = 9.5 Hz, $J_2$ = 2.4 Hz, 1H), 7.92 – 7.86 (m, 2H), 7.63 – 7.43 (m, 7H), 7.37 (d, *J* = 8.3 Hz, 2H), 6.11 – 5.93 (m, 1H), 5.29 (dd, $J_1$ = 24.5 Hz, $J_2$ = 13.6 Hz, 2H), 4.26 – 4.17 (m, 1H), 4.14 (d, *J* = 12.6 Hz, 1H), 3.67 – 3.56 (m, 1H), 2.65 (dd, $J_1$ = 14.2 Hz, $J_2$ = 8.0 Hz, 1H), 2.41 (dd, $J_1$ = 14.2 Hz, $J_2$ = 5.6 Hz, 1H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 178.6, 161.5, 149.3, 144.9, 140.4, 138.3, 137.4, 133.4, 132.5 (2C), 130.1, 129.3, 129.1 (2C), 129.1 (2C), 128.0 (2C), 125.1, 123.4, 118.4, 118.2, 116.3, 112.1, 78.8, 55.0, 46.8, 44.1, 41.1 ppm. IR (KBr): ν = 3303, 3106, 2959, 2229, 1811, 1649, 1619, 1518, 1422, 1332, 1281, 1222 $cm^{-1}$; $[\alpha]^{25}_D$ = + 4.5 ° (1.79, $CHCl_3$); HRMS (ESI) m/z calcd for $C_{29}H_{22}N_6O_6$ $[M+H]^+$ 551.1674, found 551.1674.

## 6. Wittig reaction of compound 4i´



To the spiro compound **4i´** (0.064 mmol, 27 mg, 1 equiv.) dissolved in DCM (2 mL) was added ylide reagent (0.32 mmol, 111 mg, 5 equiv.) under argon atmosphere. Reaction mixture was stirred at room temperature until full conversion was reached (TLC monitoring). Product **6** was isolated after silica separation as transparent oil (70 %).

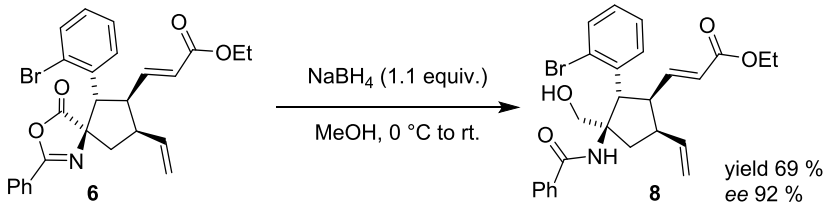
**Ethyl (*E*)-3-((5*R*,6*S*,7*S*,8*R*)-6-(2-bromophenyl)-4-oxo-2-phenyl-8-vinyl-3-oxa-1-azaspiro[4.4]non-1-en-7-yl)acrylate (6)**



**6**

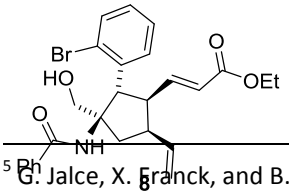
Colorless oil, yield 70 %, *ee* 92 %; The ee was determined by HPLC analysis using Chiralpak IA column (80/20 heptane/i-PrOH, flow rate 1.0 ml/min; λ = 190 nm, $t_{major}$ = 5.0 min; $t_{minor}$ = 6.5 min.); $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.87 – 7.80 (m, 2H), 7.57 – 7.50 (m, 1H), 7.48 – 7.39 (m, 4H), 7.12 (td, $J_1$ = 7.6 Hz, $J_2$ = 1.3 Hz, 1H), 6.95 (td, $J_1$ = 7.7 Hz, $J_2$ = 1.7 Hz, 1H), 6.88 (dd, $J_1$ = 15.6 Hz, $J_2$ = 8.8 Hz, 1H), 6.08 – 5.97 (m, 1H), 5.66 (dd, $J_1$ = 15.6 Hz, $J_2$ = 1.0 Hz, 1H), 5.25 – 5.16 (m, 2H), 4.51 (d, $J_1$ = 11.2 Hz, 1H), 4.12 (q, $J$ = 7.1 Hz, 2H), 3.69 – 3.58 (m, 1H), 3.52 – 3.39 (m, 1H), 2.52 – 2.37 (m, 2H), 1.24 (t, $J$ = 7.1 Hz, 3H) ppm; $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 179.3, 166.0, 160.0, 146.5, 137.7, 134.5, 133.1, 132.9, 131.0, 129.1, 128.9 (2C), 127.9 (2C), 126.8, 125.9, 125.8, 123.4, 117.1, 76.9, 76.7, 60.5, 56.2, 52.3, 46.0, 43.3, 14.3 ppm; IR (KBr): ν = 3067, 2983, 2956, 2932, 2857, 1739, 1718, 1667, 1652, cm$^{-1}$; $[\alpha]^{25}_D$ = +145.2 °, (0.3, $CHCl_3$); HRMS (ESI) m/z calcd for $C_{27}H_{28}BrNO_5$ $[M+Na]^+$ 548.1043, found 548.1034.

## 7. Azlactone ring opening with $NaBH_4$




According to modified procedure[5], to the compound **6** (0.09 mmol, 45 mg, 1 equiv.) in MeOH (2 mL) was added $NaBH_4$ (0.1 mmol, 3.3 mg, 1.1 equiv.) at 0 °C. Reaction was then stirred at room temperature until full conversion (TLC monitoring). Reaction mixture was then loaded on silica and desired product **8** was isolated as transparent oil (69 % yield).

**Ethyl (*E*)-3-((1*R*,2*S*,3*S*,5*R*)-3-benzamido-2-(2-bromophenyl)-3-(hydroxymethyl)-5 vinylcyclopentyl)acrylate (8)**



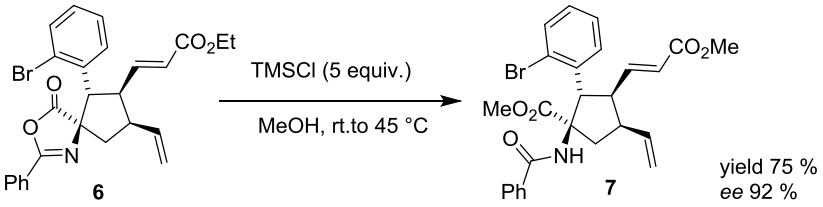
**8**

Colorless oil, yield 69 %, *ee* 92 %; The ee was determined by HPLC analysis using Chiralpak IA column (80/20 heptane/i-PrOH, flow rate 1.0 ml/min; λ = 190 nm, $t_{major}$ = 7.8 min; $t_{minor}$ = 8.7 min.); $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.65

[5] G. Jalce, X. Franck, and B. Figadère, *Eur. J. Org. Chem.* **2009**, 378.

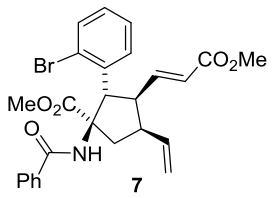
(dd, $J_1$ = 8.0 Hz, $J_2$ = 1.3 Hz, 1H), 7.58 – 7.52 (m, 2H), 7.51 – 7.43 (m, 1H), 7.41 – 7.30 (m, 4H), 7.16 (ddd, $J_1$ = 8.0 Hz, $J_2$ = 7.0 Hz, $J_3$ = 1.9 Hz, 1H), 6.78 (dd, $J_1$ = 15.7 Hz, $J_2$ = 8.4 Hz, 1H), 6.29 (s, 1H), 5.91 (ddd, $J_1$ = 16.9 Hz, $J_2$ = 10.3 Hz, $J_3$ = 8.5 Hz, 1H), 5.62 (dd, $J_1$ = 15.7 Hz, $J_2$ = 1.1 Hz, 1H), 5.19 – 5.08 (m, 2H), 4.10 (q, $J$ = 7.1 Hz, 2H), 4.07 (d, $J$ = 11.4 Hz, 1H), 3.95 (d, $J$ = 11.3 Hz, 1H), 3.82 (d, $J$ = 11.3 Hz, 1H), 3.69 (q, $J$ = 8.8 Hz, 1H), 3.27 (qd, $J_1$ = 8.1 Hz, $J_2$ = 4.9 Hz, 1H), 3.14 (dd, $J_1$ = 14.5 Hz, $J_2$ = 8.1 Hz, 1H), 2.22 (dd, $J_1$ = 14.5 Hz, $J_2$ = 5.0 Hz, 1H), 1.23 (t, $J$ = 7.1 Hz, 3H) ppm; $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 168.2, 166.2, 147.5, 138.4, 137.0, 135.1, 134.3, 131.8, 129.4, 128.8 (2C), 128.0, 126.9 (2C), 122.9, 116.6, 70.6, 67.9, 60.4, 55.4, 51.8, 45.6, 39.3, 29.8, 14.3 ppm; $[\alpha]^{25}_D$ = +134.7 °, (0.6, $CHCl_3$); HRMS (ESI) m/z calcd for $C_{26}H_{28}BrNO_4$ $[M+Na]^+$ 520.1094, found 520.1086.

## 8. Azlactone ring opening with TMSCl




Followed published precedure[6], to the compound **6** (0,04 mmol, 21 mg, 1 equiv.) in dry MeOH (1 mL) was added TMSCl (0.2 mmol, 26 µl, 5 equiv.) at room temperature under argon atmosphere. Reaction was then heated to 45 °C until full conversion was reached. Reaction mixture was then loaded on silica and desired product **7** was isolated as transparent oil (75 % yield).

**Methyl (1*R*,2*S*,3*S*,4*R*)-1-benzamido-2-(2-bromophenyl)-3-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)-4-vinylcyclopentane-1-carboxylate (7)**




Colorless oil, yield 75 %, *ee* 92 %; The ee was determined by HPLC analysis using Chiralpak IA column (90/10 heptane/i-PrOH, flow rate 1.0 ml/min; λ = 190 nm, tmajor = 16.9 min; tminor = 19.1 min.); $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.60 (dd, $J_1$ = 8.0 Hz, $J_2$ = 1.3 Hz, 1H), 7.57 – 7.52 (m, 2H), 7.51 – 7.43 (m, 1H), 7.42 – 7.34 (m, 3H), 7.30 (td, $J_1$ = 7.5 Hz, $J_2$ = 1.3 Hz, 1H), 7.13 (ddd, $J_1$ = 8.1 Hz, $J_2$ = 7.3 Hz, $J_3$ = 1.7 Hz, 1H), 6.80 (dd, $J_1$ = 15.8 Hz, $J_2$ = 8.3 Hz, 1H), 6.65 (s, 1H), 6.10 (ddd, $J_1$ = 16.9 Hz, $J_2$ = 10.2 Hz, $J_3$ =9.3 Hz, 1H), 5.64 (dd, $J_1$ = 15.8 Hz, $J_2$ = 1.1 Hz, 1H), 5.19 – 5.11 (m, 2H), 4.34 (d, $J$ = 11.9 Hz, 1H), 3.96 – 3.86 (m, 1H), 3.81 (s, 3H), 3.64 (s, 3H), 3.29 (dtd, $J_1$ = 12.1 Hz, $J_2$ = 8.3 Hz, $J_3$ = 4.0 Hz, 1H), 3.16 (dd, $J_1$ = 14.5 Hz, $J_2$ = 8.2 Hz, 1H), 2.77 (dd, $J_1$ = 14.5 Hz, $J_2$ = 4.0 Hz, 1H) ppm; $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 173.9, 167.6, 166.6, 147. 8, 138.0, 135.1, 134.5, 134.1, 131. 9, 129.7, 129.2, 128.7 (2C), 127.8, 126.8 (2C), 126.7, 122.6, 116.9, 67. 3, 56.2, 53.7, 51.7, 51.2, 46.8, 41.5 ppm; IR = 3419, 2950, 2923, 2854, 1727, 1667, 1652 $cm^{-1}$; $[\alpha]^{25}_D$ = +138.4 °, (0.6, $CHCl_3$); HRMS (ESI) m/z calcd for $C_{26}H_{26}BrNO_5$ $[M+Na]^+$ 534.0887, found 534.0880.

[7] M. Steurer, K. L. Jensen, D. Worgull, and K. A. Jørgensen, *Chem. Eur. J.* **2012**, *18*, 76.

## 9. Crystallographic data for 4c, 4c´ and 5e´

Crystallographic data for were collected on Bruker D8 VENTURE Kappa Duo PHOTON100 by IμS micro-focus sealed tube either with MoKα (0.71073) – **4c** or CuKα (λ= 1.54178) **4c´**, **5e´** radiation at a temperature of 120(2) K. The structures were solved by direct methods (XT)[7] and refined by full matrix least squares based on $F^2$ (SHELXL2018)[8]. The hydrogen atoms on carbon were fixed into idealized positions (riding model) and assigned temperature factors either $H_{iso}$(H) = 1.2 $U_{eq}$(pivot atom) or $H_{iso}$(H) = 1.5 $U_{eq}$ (pivot atom) for methyl moiety, the hydrogen atom in –N-H moiety was found on difference Fourier maps and refined under rigid body assumption with assigned temperature factors $H_{iso}$(H) = 1.2 $U_{eq}$(N(5)). The absolute structure determination was based on anomalous scattering either of Br or Cl atoms.

## Crystal data for compound 4c

$C_{22}H_{18}BrNO_3$, $M_r$ = 424.28; Monoclinic, $P2_1$, (No 4), $a$ = 12.1660 (6) Å, $b$ = 5.9496 (3) Å, $c$ = 13.4868 (6) Å, $\beta$ = 97.132 (2)°, $V$ = 968.66 (8) Å$^3$, Z = 2, $D_x$ = 1.455 Mg m$^{-3}$, Bar, colourless of dimensions 0.53 × 0.13 × 0.12 mm, multi-scan absorption correction (μ = 2.14 mm$^{-1}$), $T_{min}$ = 0.55, $T_{max}$ = 0.79; a total of 21861 measured reflections ($\theta_{max}$= 30.0˚), from which 5639 were unique ($R_{int}$ = 0.027) and 5293 observed according to the $I > 2\sigma(I)$ criterion. The refinement converged ($\Delta/\sigma_{max}$= 0.001) to $R$ = 0.029 for observed reflections and w$R(F^2)$ = 0.073, $GOF$ = 1.02 for 244 parameters and all 5639 reflections. The final difference map displayed no peaks of chemical significance ($\Delta\rho_{max}$ = 0.46, $\Delta\rho_{min}$ -0.62 e.Å$^{-3}$). Absolute structure parameter: -0.004 (4)[9]

Crystallographic data of compound **4c** have been deposited with Cambridge Crystallographic Data Centre: Deposit number: CCDC 1897667. Copies of the data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/ (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

[7] SHELXT: Sheldrick, G.M. (2015). *Acta Cryst*. **A71**, 3-8.
[8] SHELXL: Sheldrick, G.M. (2015). *Acta Cryst.* **C71**, 3-8.
[9] Parsons,S., Flack, H.D. and Wagner, T. (2013) *Acta Cryst*. **B69**, 249-259.

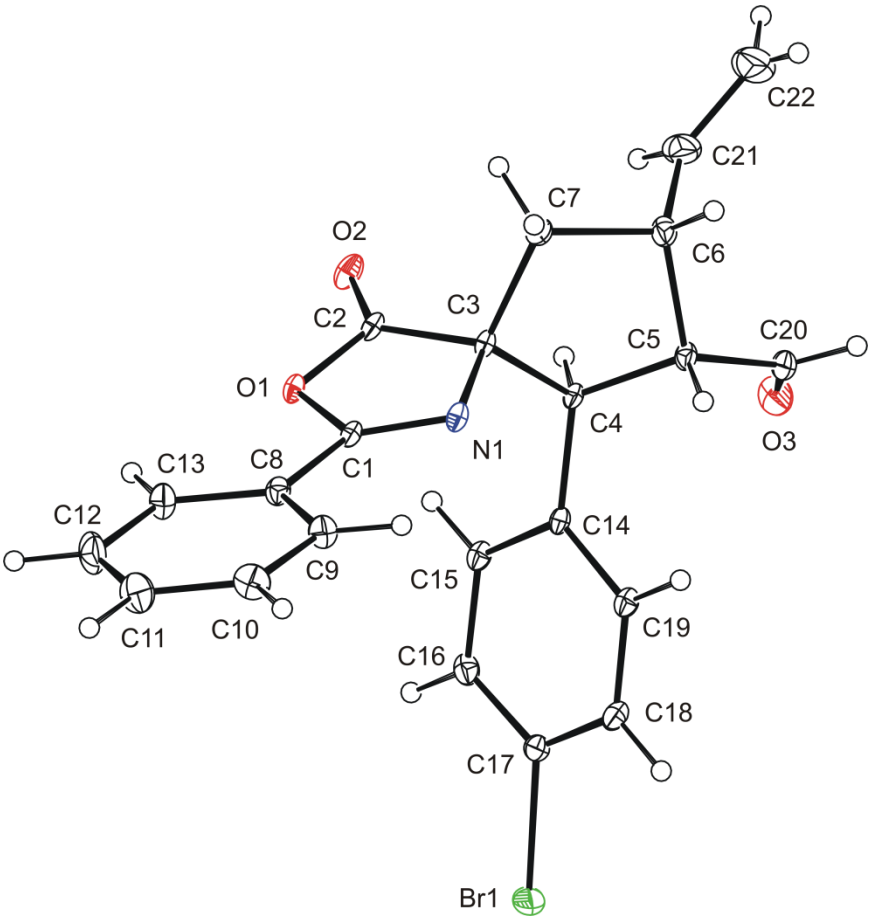



**Figure 1** View on the molecule of **4c** with atom numbering scheme witnessing S, S, S, R configuration on C3, C4, C5 and C6 respectively. The displacement ellipsoids are drawn on 30% probability level.

*Experimental details*

| Crystal data | |
|---|---|
| Chemical formula | $C_{22}H_{18}BrNO_3$ |
| $M_r$ | 424.28 |
| Crystal system, space group | Monoclinic, $P2_1$ |
| Temperature (K) | 120 |
| *a*, *b*, *c* (Å) | 12.1660 (6), 5.9496 (3), 13.4868 (6) |
| β (°) | 97.132 (2) |
| *V* (Å$^3$) | 968.66 (8) |
| *Z* | 2 |
| Radiation type | Mo *K*α |
| μ (mm$^{-1}$) | 2.14 |
| Crystal size (mm) | 0.53 × 0.13 × 0.12 |
| | |

| Data collection | |
|---|---|
| Diffractometer | Bruker D8 VENTURE Kappa Duo PHOTON 100 CMOS |
| Absorption correction | Multi-scan<br>*SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction |
| $T_{min}$, $T_{max}$ | 0.55, 0.79 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 21861, 5639, 5293 |
| $R_{int}$ | 0.027 |
| $(\sin \theta/\lambda)_{max}$ (Å$^{-1}$) | 0.705 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.029, 0.073, 1.02 |
| No. of reflections | 5639 |
| No. of parameters | 244 |
| No. of restraints | 1 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å$^{-3}$) | 0.46, -0.62 |
| Absolute structure | Flack x determined using 2219 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259). |
| Absolute structure parameter | -0.004 (4) |

Computer programs: Bruker Instrument Service vV6.2.9, *SAINT* V8.38A (Bruker AXS Inc., 2017), SHELXT 2014/5 (Sheldrick, 2014), *SHELXL2018*/1 (Sheldrick, 2018).

## References

Document origin: *publCIF* [Westrip, S. P. (2010). *J. Apply. Cryst.*, **43**, 920-925].

## Computing details

Data collection: Bruker Instrument Service vV6.2.9; cell refinement: *SAINT* V8.38A (Bruker AXS Inc., 2017); data reduction: *SAINT* V8.38A (Bruker AXS Inc., 2017); program(s) used to solve structure: SHELXT 2014/5 (Sheldrick, 2014); program(s) used to refine structure: *SHELXL2018*/1 (Sheldrick, 2018).

## Compound 4c

### *Crystal data*

| $C_{22}H_{18}BrNO_3$ | $F(000) = 432$ |
|---|---|
| $M_r = 424.28$ | $D_x = 1.455$ Mg m$^{-3}$ |

| | |
|---|---|
| Monoclinic, $P2_1$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| $a = 12.1660\ (6)$ Å | Cell parameters from 9889 reflections |
| $b = 5.9496\ (3)$ Å | $\theta = 2.4–30.0°$ |
| $c = 13.4868\ (6)$ Å | $\mu = 2.14$ mm$^{-1}$ |
| $\beta = 97.132\ (2)°$ | $T = 120$ K |
| $V = 968.66\ (8)$ Å$^3$ | Bar, colourless |
| $Z = 2$ | $0.53 \times 0.13 \times 0.12$ mm |

*Data collection*

| | |
|---|---|
| Bruker D8 VENTURE Kappa Duo PHOTON 100 CMOS diffractometer | 5639 independent reflections |
| Radiation source: IμS micro-focus sealed tube | 5293 reflections with $I > 2\sigma(I)$ |
| Quazar Mo multilayer optic monochromator | $R_{int} = 0.027$ |
| $\phi$ and $\omega$ scans | $\theta_{max} = 30.1°$, $\theta_{min} = 2.4°$ |
| Absorption correction: multi-scan *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction | $h = -17 \rightarrow 17$ |
| $T_{min} = 0.55$, $T_{max} = 0.79$ | $k = -8 \rightarrow 8$ |
| 21861 measured reflections | $l = -18 \rightarrow 18$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Hydrogen site location: inferred from neighbouring sites |
| Least-squares matrix: full | H-atom parameters constrained |
| $R[F^2 > 2\sigma(F^2)] = 0.029$ | $w = 1/[\sigma^2(F_o^2) + (0.0417P)^2 + 0.2993P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.073$ | $(\Delta/\sigma)_{max} = 0.001$ |
| $S = 1.02$ | $\Delta\rangle_{max} = 0.46$ e Å$^{-3}$ |
| 5639 reflections | $\Delta\rangle_{min} = -0.62$ e Å$^{-3}$ |
| 244 parameters | Absolute structure: Flack x determined using 2219 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259). |
| 1 restraint | Absolute structure parameter: -0.004 (4) |

*Special details*

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

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters*

*(Å$^2$) for compound 4c*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Br1 | 0.95829 (2) | 0.05391 (5) | 0.08161 (2) | 0.03541 (9) |
| O1 | 0.64816 (14) | 0.3775 (3) | 0.47114 (12) | 0.0154 (3) |
| O2 | 0.49042 (16) | 0.1877 (3) | 0.42238 (13) | 0.0226 (4) |
| O3 | 0.42563 (18) | 0.3430 (4) | 0.03057 (15) | 0.0317 (5) |
| N1 | 0.63798 (17) | 0.6687 (3) | 0.36124 (13) | 0.0147 (3) |
| C1 | 0.69038 (17) | 0.5789 (4) | 0.43883 (14) | 0.0135 (4) |
| C2 | 0.55045 (19) | 0.3427 (4) | 0.41080 (16) | 0.0159 (4) |
| C3 | 0.53944 (17) | 0.5289 (4) | 0.33330 (14) | 0.0140 (4) |
| C4 | 0.53202 (18) | 0.4307 (4) | 0.22569 (15) | 0.0131 (4) |
| H4 | 0.482290 | 0.296594 | 0.223856 | 0.016* |
| C5 | 0.46863 (19) | 0.6116 (4) | 0.16202 (16) | 0.0160 (4) |
| H5 | 0.519451 | 0.741081 | 0.154790 | 0.019* |
| C6 | 0.3764 (2) | 0.6886 (4) | 0.22479 (17) | 0.0216 (5) |
| H6 | 0.356809 | 0.849333 | 0.209737 | 0.026* |
| C7 | 0.4315 (2) | 0.6661 (4) | 0.33401 (17) | 0.0197 (4) |
| H7A | 0.380892 | 0.588366 | 0.374828 | 0.024* |
| H7AB | 0.448543 | 0.816703 | 0.363120 | 0.024* |
| C8 | 0.7877 (2) | 0.6621 (4) | 0.50307 (17) | 0.0172 (4) |
| C9 | 0.8326 (2) | 0.8719 (4) | 0.48427 (19) | 0.0218 (5) |
| H9 | 0.801952 | 0.957957 | 0.428229 | 0.026* |
| C10 | 0.9222 (2) | 0.9540 (5) | 0.5480 (2) | 0.0281 (5) |
| H10 | 0.952224 | 1.097437 | 0.535918 | 0.034* |
| C11 | 0.9682 (3) | 0.8272 (5) | 0.6293 (2) | 0.0333 (6) |
| H11 | 1.029863 | 0.883425 | 0.672176 | 0.040* |
| C12 | 0.9239 (3) | 0.6182 (5) | 0.6478 (2) | 0.0347 (7) |
| H12 | 0.955579 | 0.531014 | 0.703121 | 0.042* |
| C13 | 0.8333 (2) | 0.5375 (5) | 0.58542 (17) | 0.0251 (5) |
| H13 | 0.802177 | 0.395987 | 0.598946 | 0.030* |
| C14 | 0.64031 (18) | 0.3505 (4) | 0.19442 (15) | 0.0135 (4) |
| C15 | 0.6806 (2) | 0.1400 (4) | 0.22602 (17) | 0.0174 (4) |
| H15 | 0.641170 | 0.053757 | 0.269265 | 0.021* |
| C16 | 0.77724 (18) | 0.0530 (5) | 0.19565 (15) | 0.0200 (4) |
| H16 | 0.804104 | -0.090504 | 0.217977 | 0.024* |
| C17 | 0.8335 (2) | 0.1806 (4) | 0.13207 (17) | 0.0204 (4) |
| C18 | 0.7972 (2) | 0.3941 (4) | 0.10176 (18) | 0.0216 (5) |
| H18 | 0.837921 | 0.481697 | 0.060073 | 0.026* |
| C19 | 0.7009 (2) | 0.4777 (4) | 0.13307 (17) | 0.0182 (4) |
| H19 | 0.675699 | 0.623572 | 0.112509 | 0.022* |

| | | | | |
|---|---|---|---|---|
| C20 | 0.42053 (19) | 0.5336 (5) | 0.05963 (16) | 0.0221 (4) |
| H20 | 0.383889 | 0.641381 | 0.015192 | 0.027* |
| C21 | 0.2736 (2) | 0.5445 (8) | 0.20763 (19) | 0.0355 (6) |
| H21 | 0.281094 | 0.387929 | 0.220485 | 0.043* |
| C22 | 0.1748 (3) | 0.6223 (10) | 0.1761 (3) | 0.0629 (15) |
| H22A | 0.164623 | 0.778173 | 0.162599 | 0.075* |
| H22B | 0.113246 | 0.522990 | 0.166735 | 0.075* |

*Atomic displacement parameters (Å$^2$) for compound 4c*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Br1 | 0.02681 (12) | 0.0576 (2) | 0.02281 (12) | 0.01888 (14) | 0.00697 (8) | 0.00136 (14) |
| O1 | 0.0221 (8) | 0.0128 (7) | 0.0116 (7) | -0.0002 (6) | 0.0028 (6) | 0.0036 (6) |
| O2 | 0.0323 (10) | 0.0192 (8) | 0.0171 (8) | -0.0089 (7) | 0.0060 (7) | 0.0018 (6) |
| O3 | 0.0351 (11) | 0.0366 (11) | 0.0216 (9) | 0.0035 (9) | -0.0041 (8) | -0.0133 (8) |
| N1 | 0.0221 (9) | 0.0119 (8) | 0.0100 (8) | -0.0012 (7) | 0.0017 (7) | 0.0000 (7) |
| C1 | 0.0201 (9) | 0.0112 (9) | 0.0100 (8) | 0.0010 (8) | 0.0043 (6) | 0.0008 (8) |
| C2 | 0.0234 (11) | 0.0154 (10) | 0.0097 (9) | -0.0011 (8) | 0.0053 (8) | 0.0005 (7) |
| C3 | 0.0205 (9) | 0.0127 (9) | 0.0088 (7) | -0.0009 (8) | 0.0020 (6) | 0.0008 (8) |
| C4 | 0.0177 (10) | 0.0131 (9) | 0.0087 (8) | 0.0003 (7) | 0.0023 (7) | 0.0002 (7) |
| C5 | 0.0208 (10) | 0.0164 (10) | 0.0107 (9) | 0.0027 (7) | 0.0011 (7) | -0.0004 (7) |
| C6 | 0.0257 (12) | 0.0247 (12) | 0.0142 (10) | 0.0092 (9) | 0.0015 (9) | -0.0015 (9) |
| C7 | 0.0223 (11) | 0.0238 (11) | 0.0133 (9) | 0.0042 (9) | 0.0031 (8) | -0.0037 (9) |
| C8 | 0.0210 (10) | 0.0167 (10) | 0.0136 (9) | 0.0013 (8) | 0.0016 (8) | -0.0014 (8) |
| C9 | 0.0243 (12) | 0.0186 (11) | 0.0219 (11) | -0.0019 (9) | 0.0002 (9) | 0.0008 (9) |
| C10 | 0.0275 (13) | 0.0249 (12) | 0.0313 (13) | -0.0050 (10) | 0.0007 (11) | -0.0057 (11) |
| C11 | 0.0318 (14) | 0.0412 (16) | 0.0244 (14) | -0.0060 (12) | -0.0065 (11) | -0.0079 (12) |
| C12 | 0.0352 (14) | 0.0443 (18) | 0.0215 (12) | -0.0006 (12) | -0.0090 (11) | 0.0042 (11) |
| C13 | 0.0286 (11) | 0.0268 (12) | 0.0185 (9) | -0.0007 (12) | -0.0021 (8) | 0.0034 (11) |
| C14 | 0.0184 (10) | 0.0133 (9) | 0.0086 (9) | -0.0012 (8) | 0.0006 (7) | -0.0011 (7) |
| C15 | 0.0234 (11) | 0.0150 (9) | 0.0142 (9) | 0.0001 (8) | 0.0033 (8) | 0.0018 (8) |
| C16 | 0.0241 (10) | 0.0183 (9) | 0.0168 (9) | 0.0046 (11) | -0.0005 (7) | -0.0005 (11) |
| C17 | 0.0178 (10) | 0.0299 (12) | 0.0133 (9) | 0.0038 (9) | 0.0012 (8) | -0.0018 (9) |
| C18 | 0.0228 (11) | 0.0277 (12) | 0.0149 (10) | -0.0015 (9) | 0.0050 (8) | 0.0039 (9) |
| C19 | 0.0228 (11) | 0.0168 (10) | 0.0152 (10) | -0.0002 (8) | 0.0033 (8) | 0.0028 (8) |
| C20 | 0.0217 (9) | 0.0319 (13) | 0.0121 (8) | 0.0030 (11) | -0.0001 (7) | -0.0013 (11) |
| C21 | 0.0238 (11) | 0.0567 (17) | 0.0262 (11) | 0.0018 (16) | 0.0046 (9) | -0.0107 (17) |
| C22 | 0.0283 (15) | 0.124 (5) | 0.0357 (17) | 0.012 (2) | 0.0003 (13) | -0.005 (2) |

*Geometric parameters (Å, º) for compound 4c*

| | | | |
|---|---|---|---|
| Br1—C17 | 1.895 (2) | C9—C10 | 1.391 (4) |
| O1—C2 | 1.370 (3) | C9—H9 | 0.9500 |
| O1—C1 | 1.395 (3) | C10—C11 | 1.389 (4) |
| O2—C2 | 1.198 (3) | C10—H10 | 0.9500 |
| O3—C20 | 1.204 (4) | C11—C12 | 1.390 (5) |
| N1—C1 | 1.273 (3) | C11—H11 | 0.9500 |
| N1—C3 | 1.469 (3) | C12—C13 | 1.387 (4) |
| C1—C8 | 1.464 (3) | C12—H12 | 0.9500 |
| C2—C3 | 1.517 (3) | C13—H13 | 0.9500 |
| C3—C7 | 1.547 (3) | C14—C15 | 1.392 (3) |
| C3—C4 | 1.557 (3) | C14—C19 | 1.397 (3) |
| C4—C14 | 1.510 (3) | C15—C16 | 1.392 (3) |
| C4—C5 | 1.525 (3) | C15—H15 | 0.9500 |
| C4—H4 | 1.0000 | C16—C17 | 1.388 (4) |
| C5—C20 | 1.505 (3) | C16—H16 | 0.9500 |
| C5—C6 | 1.557 (3) | C17—C18 | 1.389 (4) |
| C5—H5 | 1.0000 | C18—C19 | 1.387 (3) |
| C6—C21 | 1.510 (4) | C18—H18 | 0.9500 |
| C6—C7 | 1.547 (3) | C19—H19 | 0.9500 |
| C6—H6 | 1.0000 | C20—H20 | 0.9500 |
| C7—H7A | 0.9900 | C21—C22 | 1.309 (5) |
| C7—H7AB | 0.9900 | C21—H21 | 0.9500 |
| C8—C13 | 1.392 (3) | C22—H22A | 0.9500 |
| C8—C9 | 1.398 (3) | C22—H22B | 0.9500 |
| | | | |
| C2—O1—C1 | 105.68 (16) | C10—C9—H9 | 120.2 |
| C1—N1—C3 | 106.43 (18) | C8—C9—H9 | 120.2 |
| N1—C1—O1 | 116.80 (19) | C11—C10—C9 | 120.3 (3) |
| N1—C1—C8 | 129.1 (2) | C11—C10—H10 | 119.9 |
| O1—C1—C8 | 114.07 (17) | C9—C10—H10 | 119.9 |
| O2—C2—O1 | 122.5 (2) | C10—C11—C12 | 120.1 (3) |
| O2—C2—C3 | 130.4 (2) | C10—C11—H11 | 120.0 |
| O1—C2—C3 | 107.14 (18) | C12—C11—H11 | 120.0 |
| N1—C3—C2 | 103.71 (16) | C13—C12—C11 | 119.8 (3) |
| N1—C3—C7 | 111.46 (19) | C13—C12—H12 | 120.1 |
| C2—C3—C7 | 112.54 (18) | C11—C12—H12 | 120.1 |
| N1—C3—C4 | 113.73 (17) | C12—C13—C8 | 120.5 (3) |
| C2—C3—C4 | 111.01 (18) | C12—C13—H13 | 119.8 |
| C7—C3—C4 | 104.63 (17) | C8—C13—H13 | 119.8 |
| C14—C4—C5 | 117.62 (18) | C15—C14—C19 | 118.5 (2) |

| | | | |
|---|---|---|---|
| C14—C4—C3 | 115.30 (18) | C15—C14—C4 | 119.00 (19) |
| C5—C4—C3 | 103.12 (17) | C19—C14—C4 | 122.48 (19) |
| C14—C4—H4 | 106.7 | C16—C15—C14 | 121.5 (2) |
| C5—C4—H4 | 106.7 | C16—C15—H15 | 119.3 |
| C3—C4—H4 | 106.7 | C14—C15—H15 | 119.3 |
| C20—C5—C4 | 114.27 (19) | C17—C16—C15 | 118.6 (2) |
| C20—C5—C6 | 111.43 (19) | C17—C16—H16 | 120.7 |
| C4—C5—C6 | 104.47 (18) | C15—C16—H16 | 120.7 |
| C20—C5—H5 | 108.8 | C16—C17—C18 | 121.2 (2) |
| C4—C5—H5 | 108.8 | C16—C17—Br1 | 118.9 (2) |
| C6—C5—H5 | 108.8 | C18—C17—Br1 | 119.82 (19) |
| C21—C6—C7 | 110.5 (2) | C19—C18—C17 | 119.2 (2) |
| C21—C6—C5 | 112.9 (2) | C19—C18—H18 | 120.4 |
| C7—C6—C5 | 103.62 (19) | C17—C18—H18 | 120.4 |
| C21—C6—H6 | 109.9 | C18—C19—C14 | 120.9 (2) |
| C7—C6—H6 | 109.9 | C18—C19—H19 | 119.5 |
| C5—C6—H6 | 109.9 | C14—C19—H19 | 119.5 |
| C6—C7—C3 | 107.94 (18) | O3—C20—C5 | 124.0 (2) |
| C6—C7—H7A | 110.1 | O3—C20—H20 | 118.0 |
| C3—C7—H7A | 110.1 | C5—C20—H20 | 118.0 |
| C6—C7—H7AB | 110.1 | C22—C21—C6 | 124.0 (4) |
| C3—C7—H7AB | 110.1 | C22—C21—H21 | 118.0 |
| H7A—C7—H7AB | 108.4 | C6—C21—H21 | 118.0 |
| C13—C8—C9 | 119.6 (2) | C21—C22—H22A | 120.0 |
| C13—C8—C1 | 120.3 (2) | C21—C22—H22B | 120.0 |
| C9—C8—C1 | 120.0 (2) | H22A—C22—H22B | 120.0 |
| C10—C9—C8 | 119.7 (2) | | |

Document origin: *publCIF* [Westrip, S. P. (2010). *J. Apply. Cryst.*, **43**, 920-925].

## Crystal data for compound 4c´

$C_{22}H_{18}BrNO_3$, $M_r$ = 424.28; Monoclinic, $P2_1$, (No 4), $a$ = 12.3124 (6) Å, $b$ = 6.3961 (3) Å, $c$ = 12.5551 (6) Å, $\beta$ = 90.017 (3)°, $V$ = 988.73 (8) Å$^3$, Z = 2, $D_x$ = 1.425 Mg m$^{-3}$, Plate, colourless of dimensions 0.36 × 0.17 × 0.03 mm, multi-scan absorption correction (μ = 3.01 mm$^{-1}$), $T_{min}$ = 0.68, $T_{max}$ = 0.91; a total of 13789 measured reflections ($\theta_{max}$= 65.6˚), from which 3381 were unique ($R_{int}$ = 0.060) and 2908 observed according to the $I > 2\sigma(I)$ criterion. The refinement converged ($\Delta/\sigma_{max}$= 0.001) to $R$ = 0.060 for observed reflections and w$R(F^2)$ = 0.153, *GOF* = 1.15 for 244 parameters and all 3381 reflections.

The final difference map displayed no peaks of chemical significance ($\Delta\rho_{max}$ = 0.61, $\Delta\rho_{min}$ -0.40 e.Å$^{-3}$). Absolute structure parameter: -0.02 (2)[9]

Crystallographic data of compound **4c´** have been deposited with Cambridge Crystallographic Data Centre: Deposit number: CCDC 1897668. Copies of the data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/ (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

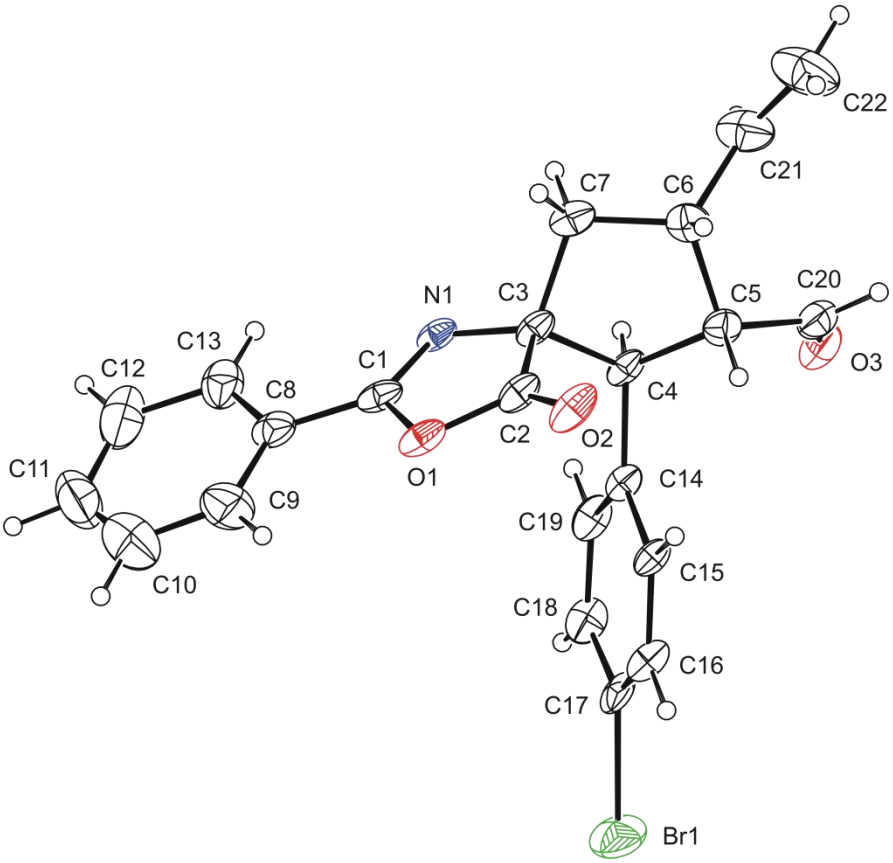



**Figure 2** View on the molecule of **4c´** with atom numbering scheme witnessing R, S, S, R configuration on C3, C4, C5 and C6 respectively. The displacement ellipsoids are drawn on 30% probability level.

*Experimental details*

| Crystal data | |
|---|---|
| Chemical formula | $C_{22}H_{18}BrNO_3$ |
| $M_r$ | 424.28 |
| Crystal system, space group | Monoclinic, $P2_1$ |
| Temperature (K) | 120 |
| *a*, *b*, *c* (Å) | 12.3124 (6), 6.3961 (3), 12.5551 (6) |
| β (°) | 90.017 (3) |

| | |
|---|---|
| $V$ (Å$^3$) | 988.73 (8) |
| $Z$ | 2 |
| Radiation type | Cu $K\alpha$ |
| μ (mm$^{-1}$) | 3.01 |
| Crystal size (mm) | 0.36 × 0.17 × 0.03 |
| | |
| Data collection | |
| Diffractometer | Bruker D8 VENTURE Kappa Duo PHOTON 100 CMOS |
| Absorption correction | Multi-scan<br>*SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction |
| $T_{min}$, $T_{max}$ | 0.68, 0.91 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 13789, 3381, 2908 |
| $R_{int}$ | 0.060 |
| (sin θ/λ)$_{max}$ (Å$^{-1}$) | 0.591 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.060, 0.153, 1.15 |
| No. of reflections | 3381 |
| No. of parameters | 244 |
| No. of restraints | 7 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å$^{-3}$) | 0.61, -0.40 |
| Absolute structure | Flack x determined using 1094 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259). |
| Absolute structure parameter | 0.02 (2) |

Computer programs: Bruker Instrument Service vV6.2.6, *SAINT* V8.38A (Bruker AXS Inc., 2017), SHELXT 2014/5 (Sheldrick, 2014), *SHELXL2018*/1 (Sheldrick, 2018).

## References

Document origin: *publCIF* [Westrip, S. P. (2010). *J. Apply. Cryst.*, **43**, 920-925].

## Computing details

Data collection: Bruker Instrument Service vV6.2.6; cell refinement: *SAINT* V8.38A (Bruker AXS Inc., 2017); data reduction: *SAINT* V8.38A (Bruker AXS Inc., 2017); program(s) used to solve structure: SHELXT 2014/5 (Sheldrick, 2014); program(s) used to refine structure: *SHELXL2018*/1 (Sheldrick, 2018).

## Compound 4c´

### *Crystal data*

| | |
|---|---|
| $C_{22}H_{18}BrNO_3$ | $F(000) = 432$ |
| $M_r = 424.28$ | $D_x = 1.425$ Mg m$^{-3}$ |
| Monoclinic, $P2_1$ | Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å |
| $a = 12.3124$ (6) Å | Cell parameters from 7483 reflections |
| $b = 6.3961$ (3) Å | $\theta = 3.5–64.0°$ |
| $c = 12.5551$ (6) Å | $\mu = 3.01$ mm$^{-1}$ |
| $\beta = 90.017$ (3)° | $T = 120$ K |
| $V = 988.73$ (8) Å$^3$ | Plate, colourless |
| $Z = 2$ | 0.36 × 0.17 × 0.03 mm |

### *Data collection*

| | |
|---|---|
| Bruker D8 VENTURE Kappa Duo PHOTON 100 CMOS diffractometer | 3381 independent reflections |
| Radiation source: IμS micro-focus sealed tube | 2908 reflections with $I > 2\sigma(I)$ |
| Helios Cu multilayer optic monochromator | $R_{int} = 0.060$ |
| $\phi$ and $\omega$ scans | $\theta_{max} = 65.6°$, $\theta_{min} = 3.5°$ |
| Absorption correction: multi-scan *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction | $h = -14\rightarrow14$ |
| $T_{min} = 0.68$, $T_{max} = 0.91$ | $k = -7\rightarrow7$ |
| 13789 measured reflections | $l = -14\rightarrow14$ |

### *Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Hydrogen site location: inferred from neighbouring sites |
| Least-squares matrix: full | H-atom parameters constrained |
| $R[F^2 > 2\sigma(F^2)] = 0.060$ | $w = 1/[\sigma^2(F_o^2) + (0.0609P)^2 + 1.4441P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.153$ | $(\Delta/\sigma)_{max} < 0.001$ |
| $S = 1.15$ | $\Delta\rangle_{max} = 0.61$ e Å$^{-3}$ |
| 3381 reflections | $\Delta\rangle_{min} = -0.40$ e Å$^{-3}$ |

| | |
|---|---|
| 244 parameters | Absolute structure: Flack x determined using 1094 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259). |
| 7 restraints | Absolute structure parameter: 0.02 (2) |

*Special details*

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

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$) for compound 4c´*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Br1 | 0.12302 (10) | -0.01069 (19) | 0.97134 (8) | 0.0792 (5) |
| O1 | 0.4624 (4) | 0.4469 (8) | 0.6350 (5) | 0.0447 (14) |
| O2 | 0.4060 (4) | 0.2470 (9) | 0.4983 (6) | 0.0541 (16) |
| O3 | -0.0250 (4) | 0.4567 (10) | 0.5033 (6) | 0.0558 (15) |
| N1 | 0.3520 (5) | 0.7282 (9) | 0.6212 (5) | 0.0361 (15) |
| C1 | 0.4314 (6) | 0.6451 (12) | 0.6691 (7) | 0.0415 (19) |
| C2 | 0.3950 (6) | 0.4025 (13) | 0.5498 (7) | 0.043 (2) |
| C3 | 0.3150 (6) | 0.5794 (11) | 0.5415 (7) | 0.0371 (18) |
| C4 | 0.1967 (5) | 0.5094 (11) | 0.5618 (6) | 0.0354 (16) |
| H4 | 0.152106 | 0.639112 | 0.569830 | 0.042* |
| C5 | 0.1633 (6) | 0.4071 (11) | 0.4566 (7) | 0.0414 (19) |
| H5 | 0.190962 | 0.260129 | 0.457526 | 0.050* |
| C6 | 0.2272 (6) | 0.5280 (13) | 0.3683 (7) | 0.046 (2) |
| H6 | 0.269950 | 0.424023 | 0.326125 | 0.056* |
| C7 | 0.3060 (7) | 0.6650 (14) | 0.4280 (7) | 0.050 (2) |
| H7A | 0.279430 | 0.811058 | 0.429397 | 0.060* |
| H7AB | 0.377899 | 0.662688 | 0.392826 | 0.060* |
| C8 | 0.4953 (7) | 0.7310 (14) | 0.7572 (8) | 0.048 (2) |
| C9 | 0.5699 (10) | 0.611 (2) | 0.8094 (12) | 0.089 (4) |
| H9 | 0.583992 | 0.472396 | 0.785505 | 0.106* |
| C10 | 0.6242 (15) | 0.688 (3) | 0.8956 (15) | 0.123 (6) |
| H10 | 0.674519 | 0.600935 | 0.932164 | 0.147* |
| C11 | 0.6074 (12) | 0.885 (3) | 0.9294 (11) | 0.105 (6) |
| H11 | 0.644456 | 0.934909 | 0.990691 | 0.126* |
| C12 | 0.5356 (10) | 1.015 (3) | 0.8745 (10) | 0.089 (4) |
| H12 | 0.526592 | 1.156983 | 0.895186 | 0.107* |

| | | | | |
|---|---|---|---|---|
| C13 | 0.4771 (8) | 0.9331 (16) | 0.7886 (8) | 0.060 (3) |
| H13 | 0.425212 | 1.016777 | 0.752255 | 0.072* |
| C14 | 0.1799 (5) | 0.3802 (11) | 0.6614 (6) | 0.0333 (17) |
| C15 | 0.2084 (6) | 0.1715 (11) | 0.6684 (6) | 0.0351 (17) |
| H15 | 0.238901 | 0.104643 | 0.607859 | 0.042* |
| C16 | 0.1940 (6) | 0.0587 (12) | 0.7595 (7) | 0.044 (2) |
| H16 | 0.215929 | -0.083599 | 0.762358 | 0.052* |
| C17 | 0.1478 (7) | 0.1513 (14) | 0.8471 (7) | 0.048 (2) |
| C18 | 0.1199 (7) | 0.3617 (14) | 0.8446 (7) | 0.051 (2) |
| H18 | 0.091224 | 0.428689 | 0.905942 | 0.061* |
| C19 | 0.1347 (6) | 0.4700 (14) | 0.7521 (6) | 0.0447 (18) |
| H19 | 0.113263 | 0.612558 | 0.749566 | 0.054* |
| C20 | 0.0418 (8) | 0.3975 (13) | 0.4394 (8) | 0.052 (2) |
| H20 | 0.016208 | 0.341368 | 0.373957 | 0.063* |
| C21 | 0.1539 (8) | 0.6436 (19) | 0.2932 (9) | 0.069 (3) |
| H21 | 0.109663 | 0.751829 | 0.321581 | 0.083* |
| C22 | 0.1469 (10) | 0.606 (3) | 0.1924 (11) | 0.100 (5) |
| H22A | 0.190028 | 0.498452 | 0.161493 | 0.120* |
| H22B | 0.098749 | 0.684819 | 0.149250 | 0.120* |

*Atomic displacement parameters (Å$^2$) for compound 4c´*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Br1 | 0.0933 (8) | 0.0831 (8) | 0.0613 (6) | -0.0218 (7) | 0.0267 (5) | 0.0170 (7) |
| O1 | 0.030 (2) | 0.026 (3) | 0.078 (4) | 0.008 (2) | 0.016 (3) | 0.014 (3) |
| O2 | 0.037 (3) | 0.037 (3) | 0.088 (5) | -0.003 (2) | 0.031 (3) | -0.006 (3) |
| O3 | 0.038 (3) | 0.038 (3) | 0.092 (4) | -0.004 (3) | 0.002 (3) | 0.006 (3) |
| N1 | 0.022 (3) | 0.028 (3) | 0.058 (4) | 0.001 (2) | 0.010 (3) | 0.012 (3) |
| C1 | 0.033 (4) | 0.036 (4) | 0.056 (5) | 0.001 (3) | 0.018 (4) | 0.016 (4) |
| C2 | 0.032 (4) | 0.037 (4) | 0.059 (5) | -0.006 (3) | 0.020 (4) | 0.002 (4) |
| C3 | 0.033 (4) | 0.021 (3) | 0.057 (5) | 0.001 (3) | 0.009 (4) | 0.002 (3) |
| C4 | 0.029 (3) | 0.016 (3) | 0.061 (4) | 0.004 (3) | 0.007 (3) | 0.002 (4) |
| C5 | 0.044 (4) | 0.027 (4) | 0.053 (5) | 0.005 (3) | -0.004 (4) | 0.002 (3) |
| C6 | 0.037 (4) | 0.049 (5) | 0.054 (5) | 0.011 (4) | 0.004 (4) | 0.009 (4) |
| C7 | 0.057 (5) | 0.036 (4) | 0.058 (5) | -0.001 (4) | 0.006 (4) | 0.011 (4) |
| C8 | 0.034 (4) | 0.052 (5) | 0.060 (6) | -0.005 (4) | 0.009 (4) | 0.018 (4) |
| C9 | 0.077 (8) | 0.086 (8) | 0.104 (10) | 0.006 (6) | -0.027 (8) | 0.033 (7) |
| C10 | 0.129 (14) | 0.125 (14) | 0.114 (13) | -0.006 (12) | -0.049 (11) | 0.025 (12) |
| C11 | 0.084 (9) | 0.169 (19) | 0.060 (7) | -0.038 (10) | -0.020 (7) | 0.011 (9) |
| C12 | 0.085 (8) | 0.106 (10) | 0.077 (7) | -0.041 (9) | 0.018 (7) | -0.028 (8) |
| C13 | 0.048 (5) | 0.068 (7) | 0.065 (6) | -0.010 (5) | 0.006 (4) | -0.004 (5) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C14 | 0.023 (3) | 0.027 (3) | 0.050 (5) | 0.003 (3) | 0.008 (3) | 0.001 (3) |
| C15 | 0.031 (4) | 0.029 (4) | 0.046 (4) | -0.005 (3) | 0.014 (3) | -0.002 (3) |
| C16 | 0.038 (4) | 0.029 (4) | 0.065 (6) | -0.002 (3) | 0.017 (4) | -0.001 (3) |
| C17 | 0.039 (4) | 0.050 (5) | 0.054 (5) | -0.026 (4) | 0.011 (4) | 0.002 (4) |
| C18 | 0.051 (5) | 0.050 (5) | 0.051 (5) | -0.007 (4) | 0.015 (4) | -0.011 (4) |
| C19 | 0.041 (4) | 0.031 (4) | 0.062 (5) | -0.001 (4) | 0.013 (4) | -0.013 (5) |
| C20 | 0.053 (5) | 0.039 (4) | 0.065 (6) | -0.009 (4) | -0.004 (5) | 0.010 (4) |
| C21 | 0.046 (5) | 0.091 (8) | 0.069 (7) | 0.015 (5) | 0.017 (5) | 0.030 (6) |
| C22 | 0.061 (7) | 0.162 (13) | 0.076 (8) | 0.026 (7) | 0.008 (6) | 0.047 (8) |

*Geometric parameters compound 4c´*

| | | | |
|---|---|---|---|
| Br1—C17 | 1.897 (9) | C9—C10 | 1.36 (2) |
| O1—C2 | 1.384 (11) | C9—H9 | 0.9500 |
| O1—C1 | 1.391 (10) | C10—C11 | 1.35 (2) |
| O2—C2 | 1.194 (10) | C10—H10 | 0.9500 |
| O3—C20 | 1.210 (11) | C11—C12 | 1.40 (2) |
| N1—C1 | 1.265 (10) | C11—H11 | 0.9500 |
| N1—C3 | 1.453 (10) | C12—C13 | 1.399 (15) |
| C1—C8 | 1.464 (13) | C12—H12 | 0.9500 |
| C2—C3 | 1.503 (11) | C13—H13 | 0.9500 |
| C3—C7 | 1.530 (12) | C14—C15 | 1.383 (10) |
| C3—C4 | 1.545 (10) | C14—C19 | 1.391 (10) |
| C4—C14 | 1.514 (10) | C15—C16 | 1.364 (11) |
| C4—C5 | 1.530 (11) | C15—H15 | 0.9500 |
| C4—H4 | 1.0000 | C16—C17 | 1.373 (12) |
| C5—C20 | 1.513 (13) | C16—H16 | 0.9500 |
| C5—C6 | 1.565 (12) | C17—C18 | 1.389 (13) |
| C5—H5 | 1.0000 | C18—C19 | 1.364 (13) |
| C6—C21 | 1.501 (13) | C18—H18 | 0.9500 |
| C6—C7 | 1.506 (13) | C19—H19 | 0.9500 |
| C6—H6 | 1.0000 | C20—H20 | 0.9500 |
| C7—H7A | 0.9900 | C21—C22 | 1.290 (18) |
| C7—H7AB | 0.9900 | C21—H21 | 0.9500 |
| C8—C9 | 1.365 (14) | C22—H22A | 0.9500 |
| C8—C13 | 1.370 (14) | C22—H22B | 0.9500 |
| | | | |
| C2—O1—C1 | 105.1 (6) | C10—C9—H9 | 119.8 |
| C1—N1—C3 | 107.1 (6) | C8—C9—H9 | 119.8 |
| N1—C1—O1 | 116.7 (8) | C11—C10—C9 | 120.9 (16) |
| N1—C1—C8 | 128.1 (8) | C11—C10—H10 | 119.5 |

| | | | |
|---|---|---|---|
| O1—C1—C8 | 115.2 (7) | C9—C10—H10 | 119.5 |
| O2—C2—O1 | 121.4 (8) | C10—C11—C12 | 120.0 (14) |
| O2—C2—C3 | 131.6 (9) | C10—C11—H11 | 120.0 |
| O1—C2—C3 | 106.9 (7) | C12—C11—H11 | 120.0 |
| N1—C3—C2 | 103.9 (6) | C11—C12—C13 | 118.8 (15) |
| N1—C3—C7 | 115.4 (6) | C11—C12—H12 | 120.6 |
| C2—C3—C7 | 112.4 (7) | C13—C12—H12 | 120.6 |
| N1—C3—C4 | 111.8 (6) | C8—C13—C12 | 119.4 (12) |
| C2—C3—C4 | 112.8 (6) | C8—C13—H13 | 120.3 |
| C7—C3—C4 | 100.9 (7) | C12—C13—H13 | 120.3 |
| C14—C4—C5 | 116.3 (6) | C15—C14—C19 | 116.6 (7) |
| C14—C4—C3 | 115.1 (6) | C15—C14—C4 | 123.0 (7) |
| C5—C4—C3 | 103.6 (6) | C19—C14—C4 | 120.4 (7) |
| C14—C4—H4 | 107.1 | C16—C15—C14 | 122.1 (7) |
| C5—C4—H4 | 107.1 | C16—C15—H15 | 119.0 |
| C3—C4—H4 | 107.1 | C14—C15—H15 | 119.0 |
| C20—C5—C4 | 114.0 (7) | C15—C16—C17 | 119.8 (8) |
| C20—C5—C6 | 114.6 (7) | C15—C16—H16 | 120.1 |
| C4—C5—C6 | 105.4 (6) | C17—C16—H16 | 120.1 |
| C20—C5—H5 | 107.5 | C16—C17—C18 | 120.1 (8) |
| C4—C5—H5 | 107.5 | C16—C17—Br1 | 119.3 (7) |
| C6—C5—H5 | 107.5 | C18—C17—Br1 | 120.5 (7) |
| C21—C6—C7 | 114.4 (8) | C19—C18—C17 | 118.6 (8) |
| C21—C6—C5 | 112.7 (7) | C19—C18—H18 | 120.7 |
| C7—C6—C5 | 105.0 (7) | C17—C18—H18 | 120.7 |
| C21—C6—H6 | 108.2 | C18—C19—C14 | 122.7 (8) |
| C7—C6—H6 | 108.2 | C18—C19—H19 | 118.6 |
| C5—C6—H6 | 108.2 | C14—C19—H19 | 118.6 |
| C6—C7—C3 | 107.6 (7) | O3—C20—C5 | 124.4 (9) |
| C6—C7—H7A | 110.2 | O3—C20—H20 | 117.8 |
| C3—C7—H7A | 110.2 | C5—C20—H20 | 117.8 |
| C6—C7—H7AB | 110.2 | C22—C21—C6 | 124.2 (11) |
| C3—C7—H7AB | 110.2 | C22—C21—H21 | 117.9 |
| H7A—C7—H7AB | 108.5 | C6—C21—H21 | 117.9 |
| C9—C8—C13 | 120.3 (11) | C21—C22—H22A | 120.0 |
| C9—C8—C1 | 120.8 (10) | C21—C22—H22B | 120.0 |
| C13—C8—C1 | 118.9 (8) | H22A—C22—H22B | 120.0 |
| C10—C9—C8 | 120.5 (15) | | |

Document origin: *publCIF* [Westrip, S. P. (2010). *J. Apply. Cryst.*, **43**, 920-925].

## Crystal data for compound 5e´

$2(C_{29}H_{22}N_6O_6)\cdot CH_2Cl_2$, $M_r$ = 1185.98; Triclinic, *P*1, (No 1), *a* = 11.0997 (8) Å, *b* = 11.2837 (8) Å, *c* = 22.4561 (16) Å, *α* = 95.057 (4)°, *β* = 95.843 (4)°, *γ* = 90.981 (4)°, *V* = 2786.1 (3) Å$^3$, Z = 2, $D_x$ = 1.414 Mg m$^{-3}$, Prism, yellow of dimensions 0.39 × 0.20 × 0.12 mm, multi-scan absorption correction (μ = 1.69 mm$^{-1}$), $T_{min}$ = 0.85, $T_{max}$ = 0.93; a total of 37346 measured reflections ($\theta_{max}$= 64.2˚), from which 16971 were unique ($R_{int}$ = 0.063) and 14507 observed according to the $I > 2\sigma(I)$ criterion. The refinement converged ($\Delta/\sigma_{max}$= 0.001) to *R* = 0.086 for observed reflections and w$R(F^2)$ = 0.244, *GOF* = 1.03 for 1531 parameters and all 16971 reflections. The final difference map displayed no peaks of chemical significance ($\Delta\rho_{max}$ = 0.51, $\Delta\rho_{min}$ -0.69 e.Å$^{-3}$). Absolute structure parameter: -0.01(4)[9]

Crystallographic data of compound **5e´** have been deposited with Cambridge Crystallographic Data Centre: Deposit number: CCDC 1897931. Copies of the data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/ (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

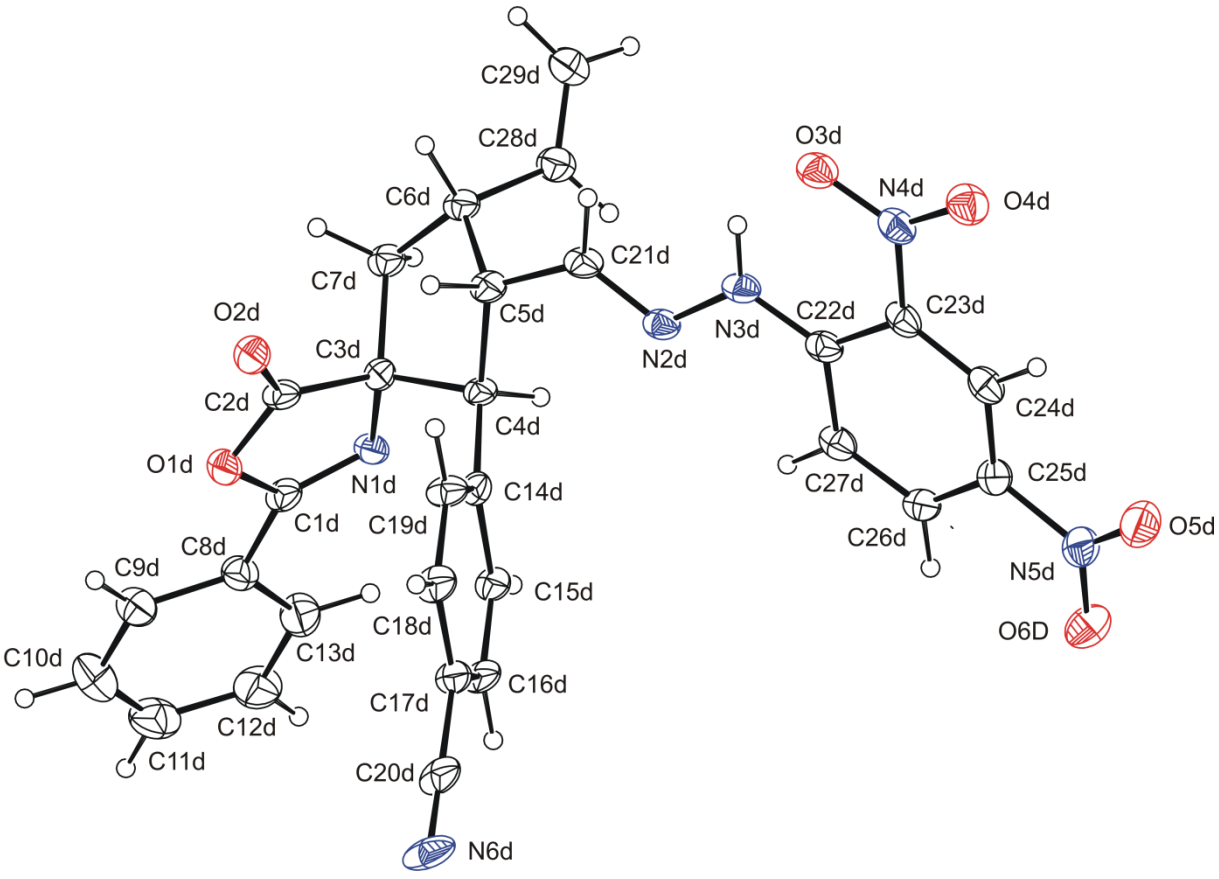



**Figure 3** View on the molecule of **5e´** with atom numbering scheme witnessing R, S, S, R configuration on C3, C4, C5 and C6 respectively. The displacement ellipsoids are drawn on 30% probability level.

*Experimental details*

| | |
|---|---|
| Crystal data | |
| Chemical formula | $2(C_{29}H_{22}N_6O_6)\cdot CH_2Cl_2$ |
| $M_r$ | 1185.98 |
| Crystal system, space group | Triclinic, *P*1 |
| Temperature (K) | 120 |
| *a*, *b*, *c* (Å) | 11.0997 (8), 11.2837 (8), 22.4561 (16) |
| α, β, γ (°) | 95.057 (4), 95.843 (4), 90.981 (4) |
| *V* (Å$^3$) | 2786.1 (3) |
| *Z* | 2 |
| Radiation type | Cu *K*α |
| μ (mm$^{-1}$) | 1.69 |
| Crystal size (mm) | 0.39 × 0.20 × 0.12 |
| | |
| Data collection | |
| Diffractometer | Bruker D8 VENTURE Kappa Duo PHOTON 100 CMOS |
| Absorption correction | Multi-scan<br>*SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction |
| $T_{min}$, $T_{max}$ | 0.85, 0.93 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 37346, 16971, 14507 |
| $R_{int}$ | 0.063 |
| $(\sin \theta/\lambda)_{max}$ (Å$^{-1}$) | 0.584 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S* | 0.086, 0.244, 1.03 |
| No. of reflections | 16971 |
| No. of parameters | 1531 |
| No. of restraints | 3 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å$^{-3}$) | 0.51, -0.69 |
| Absolute structure | Flack x determined using 5372 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259). |
| Absolute structure parameter | 0.01 (4) |

Computer programs: Bruker Instrument Service vV6.2.9, *SAINT* V8.38A (Bruker AXS Inc., 2017), SHELXT 2014/5 (Sheldrick, 2014), *SHELXL2018*/1 (Sheldrick, 2018).

***Table 2***

*Hydrogen-bond geometry (Å, °) for (fm56_vesely)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N3*A*—H3*A*···O3*A* | 0.88 | 1.97 | 2.591 (9) | 127 |
| N3*B*—H3*B*···O3*B* | 0.88 | 2.01 | 2.621 (9) | 125 |
| N3*B*—H3*B*···O3*C* | 0.88 | 2.63 | 3.420 (9) | 151 |
| N3*C*—H3*C*···O3*B* | 0.88 | 2.57 | 3.346 (9) | 148 |
| N3*C*—H3*C*···O3*C* | 0.88 | 2.02 | 2.622 (9) | 125 |
| N3*D*—H3*D*···O3*D* | 0.88 | 2.01 | 2.630 (9) | 126 |

## References

NOT FOUND

Document origin: *publCIF* [Westrip, S. P. (2010). *J. Apply. Cryst.*, **43**, 920-925].

## Computing details

Data collection: Bruker Instrument Service vV6.2.9; cell refinement: *SAINT* V8.38A (Bruker AXS Inc., 2017); data reduction: *SAINT* V8.38A (Bruker AXS Inc., 2017); program(s) used to solve structure: SHELXT 2014/5 (Sheldrick, 2014); program(s) used to refine structure: *SHELXL2018*/1 (Sheldrick, 2018).

## Compound 5e´

*Crystal data*

| $2(C_{29}H_{22}N_6O_6)\cdot CH_2Cl_2$ | $Z = 2$ |
|---|---|
| $M_r = 1185.98$ | $F(000) = 1228$ |
| Triclinic, *P*1 | $D_x = 1.414$ Mg m$^{-3}$ |
| $a = 11.0997$ (8) Å | Cu *K*α radiation, $\lambda = 1.54178$ Å |
| $b = 11.2837$ (8) Å | Cell parameters from 9901 reflections |
| $c = 22.4561$ (16) Å | $\theta = 3.9–63.9°$ |
| $\alpha = 95.057$ (4)° | $\mu = 1.69$ mm$^{-1}$ |
| $\beta = 95.843$ (4)° | $T = 120$ K |
| $\gamma = 90.981$ (4)° | Prism, yellow |
| $V = 2786.1$ (3) Å$^3$ | 0.39 × 0.20 × 0.12 mm |

*Data collection*

| | |
|---|---|
| Bruker D8 VENTURE Kappa Duo PHOTON 100 CMOS diffractometer | 16971 independent reflections |
| Radiation source: IμS micro-focus sealed tube | 14507 reflections with $I > 2\sigma(I)$ |
| Helios Cu multilayer optic monochromator | $R_{int} = 0.063$ |
| ϕ and ω scans | $\theta_{max} = 64.2°$, $\theta_{min} = 3.9°$ |
| Absorption correction: multi-scan *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction | $h = -12 \rightarrow 12$ |
| $T_{min} = 0.85$, $T_{max} = 0.93$ | $k = -12 \rightarrow 13$ |
| 37346 measured reflections | $l = -26 \rightarrow 26$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Hydrogen site location: inferred from neighbouring sites |
| Least-squares matrix: full | H-atom parameters constrained |
| $R[F^2 > 2\sigma(F^2)] = 0.086$ | $w = 1/[\sigma^2(F_o^2) + (0.1693P)^2 + 2.1102P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.244$ | $(\Delta/\sigma)_{max} < 0.001$ |
| $S = 1.03$ | $\Delta\rangle_{max} = 0.51$ e Å$^{-3}$ |
| 16971 reflections | $\Delta\rangle_{min} = -0.69$ e Å$^{-3}$ |
| 1531 parameters | Absolute structure: Flack x determined using 5372 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259). |
| 3 restraints | Absolute structure parameter: 0.01 (4) |

*Special details*

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

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$) for compound 5e´*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| O1A | -0.0715 (5) | 0.6795 (5) | 0.1071 (2) | 0.0382 (13) |
| O2A | -0.0460 (5) | 0.5518 (5) | 0.1783 (3) | 0.0394 (13) |
| O3A | 0.0722 (6) | 0.8422 (6) | 0.5481 (3) | 0.0452 (15) |
| O4A | 0.1731 (7) | 0.7886 (6) | 0.6283 (3) | 0.0520 (16) |

| | | | | |
|---|---|---|---|---|
| O5A | 0.3449 (7) | 0.4095 (7) | 0.6371 (3) | 0.0624 (19) |
| O6A | 0.3140 (6) | 0.2768 (6) | 0.5612 (3) | 0.0483 (15) |
| N1A | -0.1689 (6) | 0.8297 (6) | 0.1541 (3) | 0.0341 (14) |
| N2A | -0.0107 (6) | 0.6579 (6) | 0.3938 (3) | 0.0322 (14) |
| N3A | 0.0264 (6) | 0.6937 (6) | 0.4534 (3) | 0.0333 (15) |
| H3A | 0.006962 | 0.763846 | 0.469418 | 0.040* |
| N4A | 0.1302 (7) | 0.7663 (7) | 0.5768 (3) | 0.0379 (16) |
| N5A | 0.3004 (7) | 0.3760 (7) | 0.5861 (3) | 0.0412 (17) |
| N6A | 0.5074 (7) | 0.8912 (7) | 0.1946 (5) | 0.060 (2) |
| C1A | -0.1261 (7) | 0.7912 (8) | 0.1062 (4) | 0.0342 (17) |
| C2A | -0.0827 (7) | 0.6436 (8) | 0.1631 (4) | 0.0348 (17) |
| C3A | -0.1504 (7) | 0.7412 (7) | 0.1969 (3) | 0.0320 (16) |
| C4A | -0.0759 (7) | 0.7907 (7) | 0.2565 (3) | 0.0310 (16) |
| H4A | -0.110353 | 0.868793 | 0.269707 | 0.037* |
| C5A | -0.1092 (7) | 0.7009 (7) | 0.2999 (3) | 0.0316 (16) |
| H5A | -0.072155 | 0.623461 | 0.287724 | 0.038* |
| C6A | -0.2480 (7) | 0.6848 (8) | 0.2864 (4) | 0.0353 (17) |
| H6A | -0.273434 | 0.604141 | 0.296452 | 0.042* |
| C7A | -0.2698 (7) | 0.6911 (7) | 0.2170 (4) | 0.0336 (17) |
| H7AA | -0.289809 | 0.610901 | 0.196409 | 0.040* |
| H7AB | -0.337740 | 0.744006 | 0.206920 | 0.040* |
| C8A | -0.1264 (7) | 0.8455 (8) | 0.0498 (4) | 0.0375 (18) |
| C9A | -0.0937 (9) | 0.7836 (10) | -0.0026 (4) | 0.048 (2) |
| H9A | -0.068893 | 0.703490 | -0.002017 | 0.058* |
| C10A | -0.0974 (9) | 0.8387 (11) | -0.0555 (4) | 0.054 (3) |
| H10A | -0.073179 | 0.797057 | -0.090732 | 0.065* |
| C11A | -0.1360 (10) | 0.9534 (11) | -0.0571 (4) | 0.056 (3) |
| H11A | -0.140646 | 0.990145 | -0.093686 | 0.068* |
| C12A | -0.1679 (10) | 1.0153 (10) | -0.0057 (5) | 0.057 (3) |
| H12A | -0.193468 | 1.095096 | -0.006887 | 0.068* |
| C13A | -0.1631 (10) | 0.9621 (10) | 0.0478 (4) | 0.051 (2) |
| H13A | -0.184890 | 1.005545 | 0.083100 | 0.062* |
| C14A | 0.0561 (7) | 0.8125 (7) | 0.2491 (3) | 0.0299 (15) |
| C15A | 0.0887 (7) | 0.9163 (7) | 0.2246 (3) | 0.0309 (16) |
| H15A | 0.029477 | 0.974505 | 0.217304 | 0.037* |
| C16A | 0.2047 (7) | 0.9361 (7) | 0.2109 (4) | 0.0347 (17) |
| H16A | 0.224935 | 1.006402 | 0.193344 | 0.042* |
| C17A | 0.2923 (7) | 0.8524 (7) | 0.2230 (4) | 0.0346 (17) |
| C18A | 0.2619 (7) | 0.7497 (7) | 0.2496 (4) | 0.0368 (18) |
| H18A | 0.322289 | 0.693599 | 0.258929 | 0.044* |

| | | | | |
|---|---|---|---|---|
| C19A | 0.1463 (7) | 0.7299 (7) | 0.2620 (4) | 0.0339 (17) |
| H19A | 0.126374 | 0.659614 | 0.279674 | 0.041* |
| C20A | 0.4129 (8) | 0.8731 (8) | 0.2076 (5) | 0.044 (2) |
| C21A | -0.0675 (7) | 0.7339 (7) | 0.3643 (4) | 0.0342 (18) |
| H21A | -0.083110 | 0.810144 | 0.382947 | 0.041* |
| C22A | 0.0930 (6) | 0.6196 (7) | 0.4867 (3) | 0.0297 (16) |
| C23A | 0.1415 (7) | 0.6495 (7) | 0.5474 (4) | 0.0317 (17) |
| C24A | 0.2099 (7) | 0.5697 (8) | 0.5797 (4) | 0.0338 (17) |
| H24A | 0.243481 | 0.591746 | 0.619840 | 0.041* |
| C25A | 0.2277 (7) | 0.4589 (8) | 0.5526 (4) | 0.0344 (17) |
| C26A | 0.1822 (8) | 0.4257 (8) | 0.4936 (4) | 0.0358 (18) |
| H26A | 0.196964 | 0.348591 | 0.475613 | 0.043* |
| C27A | 0.1164 (8) | 0.5036 (8) | 0.4613 (4) | 0.0343 (17) |
| H27A | 0.085402 | 0.479673 | 0.420973 | 0.041* |
| C28A | -0.3217 (7) | 0.7774 (8) | 0.3173 (4) | 0.0400 (19) |
| H28A | -0.299032 | 0.858691 | 0.316260 | 0.048* |
| C29A | -0.4167 (9) | 0.7523 (10) | 0.3460 (4) | 0.050 (2) |
| H29A | -0.441596 | 0.671788 | 0.347804 | 0.060* |
| H29B | -0.459769 | 0.814800 | 0.364702 | 0.060* |
| O1B | 0.3763 (6) | 0.3263 (6) | 0.0996 (3) | 0.0478 (15) |
| O2B | 0.3049 (5) | 0.1677 (5) | 0.1403 (3) | 0.0404 (13) |
| O3B | 0.5456 (6) | 0.3820 (5) | 0.5337 (3) | 0.0404 (13) |
| O4B | 0.6258 (6) | 0.3194 (6) | 0.6158 (3) | 0.0445 (15) |
| O5B | 0.8048 (8) | -0.0590 (6) | 0.6198 (3) | 0.0597 (19) |
| O6B | 0.7900 (7) | -0.1830 (6) | 0.5403 (3) | 0.0542 (17) |
| N1B | 0.3806 (6) | 0.4721 (6) | 0.1757 (3) | 0.0362 (15) |
| N2B | 0.4482 (6) | 0.1966 (6) | 0.3791 (3) | 0.0311 (14) |
| N3B | 0.4877 (6) | 0.2328 (6) | 0.4384 (3) | 0.0316 (14) |
| H3B | 0.468327 | 0.302657 | 0.454848 | 0.038* |
| N4B | 0.5919 (6) | 0.3021 (6) | 0.5626 (3) | 0.0326 (15) |
| N5B | 0.7681 (7) | -0.0871 (7) | 0.5672 (3) | 0.0421 (17) |
| N6B | 0.9792 (7) | 0.1699 (7) | 0.1635 (4) | 0.0442 (17) |
| C1B | 0.4016 (8) | 0.4457 (8) | 0.1225 (4) | 0.0412 (19) |
| C2B | 0.3344 (7) | 0.2704 (7) | 0.1460 (4) | 0.0328 (17) |
| C3B | 0.3365 (7) | 0.3637 (7) | 0.1985 (4) | 0.0307 (16) |
| C4B | 0.4250 (7) | 0.3301 (7) | 0.2527 (3) | 0.0291 (15) |
| H4B | 0.441251 | 0.404707 | 0.280059 | 0.035* |
| C5B | 0.3486 (7) | 0.2460 (7) | 0.2864 (3) | 0.0294 (16) |
| H5B | 0.366997 | 0.161583 | 0.273914 | 0.035* |
| C6B | 0.2137 (7) | 0.2699 (7) | 0.2635 (3) | 0.0301 (16) |

| | | | | |
|---|---|---|---|---|
| H6B | 0.186364 | 0.200429 | 0.234189 | 0.036* |
| C7B | 0.2170 (7) | 0.3764 (7) | 0.2268 (3) | 0.0309 (16) |
| H7BA | 0.216524 | 0.451880 | 0.252854 | 0.037* |
| H7BB | 0.147158 | 0.373744 | 0.195582 | 0.037* |
| C8B | 0.4519 (9) | 0.5200 (9) | 0.0806 (4) | 0.048 (2) |
| C9B | 0.4601 (11) | 0.4805 (11) | 0.0213 (5) | 0.059 (3) |
| H9B | 0.428810 | 0.404057 | 0.005329 | 0.071* |
| C10B | 0.5157 (15) | 0.5556 (15) | -0.0151 (6) | 0.081 (4) |
| H10B | 0.518726 | 0.531773 | -0.056543 | 0.097* |
| C11B | 0.5656 (16) | 0.6629 (15) | 0.0092 (7) | 0.090 (5) |
| H11B | 0.607925 | 0.710359 | -0.015158 | 0.108* |
| C12B | 0.5559 (11) | 0.7034 (11) | 0.0675 (5) | 0.061 (3) |
| H12B | 0.590243 | 0.778693 | 0.083374 | 0.073* |
| C13B | 0.4957 (9) | 0.6336 (9) | 0.1031 (5) | 0.049 (2) |
| H13B | 0.484030 | 0.662979 | 0.143053 | 0.059* |
| C14B | 0.5470 (7) | 0.2885 (7) | 0.2357 (4) | 0.0330 (16) |
| C15B | 0.5722 (8) | 0.1716 (7) | 0.2214 (4) | 0.042 (2) |
| H15B | 0.512239 | 0.111780 | 0.224249 | 0.050* |
| C16B | 0.6836 (8) | 0.1384 (8) | 0.2028 (4) | 0.0412 (19) |
| H16B | 0.699010 | 0.057177 | 0.192112 | 0.049* |
| C17B | 0.7721 (7) | 0.2260 (8) | 0.2002 (4) | 0.0350 (17) |
| C18B | 0.7485 (8) | 0.3442 (8) | 0.2156 (4) | 0.0416 (19) |
| H18B | 0.809535 | 0.403733 | 0.214370 | 0.050* |
| C19B | 0.6366 (8) | 0.3758 (8) | 0.2328 (4) | 0.0412 (19) |
| H19B | 0.620460 | 0.457150 | 0.242631 | 0.049* |
| C20B | 0.8886 (8) | 0.1939 (8) | 0.1798 (4) | 0.0362 (18) |
| C21B | 0.3827 (7) | 0.2704 (7) | 0.3513 (4) | 0.0314 (16) |
| H21B | 0.356253 | 0.340290 | 0.372446 | 0.038* |
| C22B | 0.5574 (7) | 0.1580 (7) | 0.4708 (3) | 0.0296 (16) |
| C23B | 0.6060 (7) | 0.1862 (7) | 0.5312 (4) | 0.0306 (16) |
| C24B | 0.6740 (7) | 0.1068 (7) | 0.5634 (4) | 0.0316 (16) |
| H24B | 0.704272 | 0.127080 | 0.604237 | 0.038* |
| C25B | 0.6965 (7) | -0.0035 (7) | 0.5344 (4) | 0.0323 (17) |
| C26B | 0.6529 (7) | -0.0336 (7) | 0.4745 (4) | 0.0343 (17) |
| H26B | 0.671353 | -0.108551 | 0.455270 | 0.041* |
| C27B | 0.5838 (7) | 0.0439 (7) | 0.4432 (4) | 0.0320 (16) |
| H27B | 0.552989 | 0.021581 | 0.402679 | 0.038* |
| C28B | 0.1240 (8) | 0.2756 (9) | 0.3107 (4) | 0.042 (2) |
| H28B | 0.131513 | 0.218390 | 0.339381 | 0.051* |
| C29B | 0.0379 (8) | 0.3520 (9) | 0.3151 (4) | 0.045 (2) |

| | | | | |
|---|---|---|---|---|
| H29C | 0.027084 | 0.410732 | 0.287418 | 0.054* |
| H29D | -0.013985 | 0.348852 | 0.346131 | 0.054* |
| O1C | 0.6081 (6) | 0.7816 (6) | 0.8871 (3) | 0.0437 (14) |
| O2C | 0.6696 (5) | 0.6067 (5) | 0.8452 (3) | 0.0385 (13) |
| O3C | 0.4362 (5) | 0.5315 (5) | 0.4493 (3) | 0.0400 (13) |
| O4C | 0.3288 (5) | 0.5915 (5) | 0.3725 (3) | 0.0392 (13) |
| O5C | 0.1805 (8) | 0.9816 (7) | 0.3713 (3) | 0.064 (2) |
| O6C | 0.2044 (6) | 1.1040 (6) | 0.4510 (3) | 0.0490 (16) |
| N1C | 0.6124 (6) | 0.9014 (6) | 0.8120 (3) | 0.0345 (15) |
| N2C | 0.5185 (6) | 0.6984 (6) | 0.6090 (3) | 0.0306 (14) |
| N3C | 0.4886 (6) | 0.6728 (6) | 0.5480 (3) | 0.0322 (14) |
| H3C | 0.511524 | 0.605986 | 0.529778 | 0.039* |
| N4C | 0.3790 (6) | 0.6098 (6) | 0.4237 (3) | 0.0318 (14) |
| N5C | 0.2201 (7) | 1.0076 (7) | 0.4231 (3) | 0.0404 (17) |
| N6C | -0.0001 (7) | 0.6159 (7) | 0.8349 (4) | 0.0464 (18) |
| C1C | 0.5915 (8) | 0.8915 (8) | 0.8652 (4) | 0.0412 (19) |
| C2C | 0.6462 (8) | 0.7084 (8) | 0.8407 (3) | 0.0350 (18) |
| C3C | 0.6467 (7) | 0.7837 (7) | 0.7876 (3) | 0.0308 (16) |
| C4C | 0.5525 (7) | 0.7316 (7) | 0.7351 (3) | 0.0293 (15) |
| H4C | 0.538207 | 0.796092 | 0.707602 | 0.035* |
| C5C | 0.6220 (7) | 0.6345 (7) | 0.7009 (3) | 0.0316 (16) |
| H5C | 0.599834 | 0.556674 | 0.715581 | 0.038* |
| C6C | 0.7608 (7) | 0.6591 (7) | 0.7212 (3) | 0.0318 (16) |
| H6C | 0.788802 | 0.598048 | 0.748834 | 0.038* |
| C7C | 0.7654 (7) | 0.7813 (7) | 0.7583 (4) | 0.0327 (16) |
| H7CA | 0.836214 | 0.788321 | 0.789076 | 0.039* |
| H7CB | 0.769847 | 0.846917 | 0.731994 | 0.039* |
| C8C | 0.5492 (9) | 0.9845 (9) | 0.9079 (4) | 0.045 (2) |
| C9C | 0.5213 (10) | 1.0927 (9) | 0.8900 (5) | 0.056 (3) |
| H9C | 0.535175 | 1.110176 | 0.850564 | 0.067* |
| C10C | 0.4725 (16) | 1.1793 (13) | 0.9280 (7) | 0.088 (5) |
| H10C | 0.449615 | 1.253702 | 0.914150 | 0.105* |
| C11C | 0.458 (2) | 1.1557 (15) | 0.9848 (9) | 0.125 (9) |
| H11C | 0.422186 | 1.213030 | 1.010468 | 0.150* |
| C12C | 0.4962 (18) | 1.0483 (14) | 1.0068 (7) | 0.095 (5) |
| H12C | 0.494581 | 1.036027 | 1.048062 | 0.114* |
| C13C | 0.5352 (14) | 0.9622 (13) | 0.9674 (5) | 0.075 (3) |
| H13C | 0.553131 | 0.885922 | 0.980385 | 0.090* |
| C14C | 0.4318 (7) | 0.7002 (7) | 0.7542 (3) | 0.0306 (16) |
| C15C | 0.3942 (8) | 0.5842 (8) | 0.7631 (4) | 0.041 (2) |

| | | | | |
|---|---|---|---|---|
| H15C | 0.444709 | 0.519462 | 0.753911 | 0.050* |
| C16C | 0.2846 (8) | 0.5630 (8) | 0.7850 (4) | 0.042 (2) |
| H16C | 0.262537 | 0.484298 | 0.792341 | 0.050* |
| C17C | 0.2060 (7) | 0.6551 (7) | 0.7963 (4) | 0.0344 (17) |
| C18C | 0.2417 (8) | 0.7700 (8) | 0.7873 (4) | 0.044 (2) |
| H18C | 0.189498 | 0.834228 | 0.794914 | 0.053* |
| C19C | 0.3527 (8) | 0.7910 (8) | 0.7674 (4) | 0.0405 (19) |
| H19C | 0.376315 | 0.870548 | 0.762492 | 0.049* |
| C20C | 0.0929 (8) | 0.6324 (8) | 0.8185 (4) | 0.0382 (18) |
| C21C | 0.5875 (7) | 0.6240 (7) | 0.6345 (4) | 0.0339 (17) |
| H21C | 0.617777 | 0.560037 | 0.610424 | 0.041* |
| C22C | 0.4246 (6) | 0.7501 (7) | 0.5170 (3) | 0.0299 (16) |
| C23C | 0.3716 (7) | 0.7256 (7) | 0.4564 (3) | 0.0287 (16) |
| C24C | 0.3059 (7) | 0.8106 (7) | 0.4261 (3) | 0.0297 (16) |
| H24C | 0.272722 | 0.792630 | 0.385584 | 0.036* |
| C25C | 0.2899 (7) | 0.9190 (8) | 0.4551 (4) | 0.0329 (17) |
| C26C | 0.3353 (7) | 0.9466 (8) | 0.5145 (4) | 0.0347 (17) |
| H26C | 0.321212 | 1.022269 | 0.534259 | 0.042* |
| C27C | 0.4009 (7) | 0.8640 (8) | 0.5448 (4) | 0.0324 (17) |
| H27C | 0.431160 | 0.883956 | 0.585677 | 0.039* |
| C28C | 0.8427 (7) | 0.6557 (8) | 0.6709 (4) | 0.0352 (17) |
| H28C | 0.828626 | 0.710732 | 0.641412 | 0.042* |
| C29C | 0.9308 (8) | 0.5825 (9) | 0.6654 (4) | 0.042 (2) |
| H29E | 0.947345 | 0.526240 | 0.694108 | 0.051* |
| H29F | 0.978613 | 0.585098 | 0.632800 | 0.051* |
| O1D | 1.0594 (5) | 0.1420 (5) | 0.8978 (3) | 0.0393 (13) |
| O2D | 1.0292 (6) | -0.0120 (5) | 0.8271 (3) | 0.0414 (14) |
| O3D | 0.9485 (6) | 0.0053 (6) | 0.4559 (3) | 0.0440 (14) |
| O4D | 0.8650 (6) | 0.0715 (6) | 0.3749 (3) | 0.0496 (16) |
| O5D | 0.6787 (7) | 0.4467 (7) | 0.3767 (3) | 0.0586 (18) |
| O6D | 0.7105 (7) | 0.5747 (7) | 0.4553 (3) | 0.0577 (17) |
| N1D | 1.1608 (6) | 0.2780 (6) | 0.8505 (3) | 0.0318 (14) |
| N2D | 1.0167 (6) | 0.1702 (6) | 0.6165 (3) | 0.0339 (15) |
| N3D | 0.9904 (6) | 0.1478 (6) | 0.5553 (3) | 0.0349 (15) |
| H3D | 1.014956 | 0.081596 | 0.537105 | 0.042* |
| N4D | 0.8997 (7) | 0.0863 (7) | 0.4280 (3) | 0.0392 (16) |
| N5D | 0.7227 (7) | 0.4761 (7) | 0.4278 (4) | 0.0444 (18) |
| N6D | 0.4868 (8) | 0.3294 (7) | 0.7987 (5) | 0.062 (3) |
| C1D | 1.1156 (7) | 0.2546 (7) | 0.8985 (4) | 0.0351 (17) |
| C2D | 1.0692 (7) | 0.0870 (7) | 0.8422 (4) | 0.0338 (17) |

| | | | | |
|---|---|---|---|---|
| C3D | 1.1396 (7) | 0.1692 (7) | 0.8080 (3) | 0.0312 (16) |
| C4D | 1.0690 (7) | 0.1952 (7) | 0.7469 (3) | 0.0303 (16) |
| H4D | 1.108569 | 0.266312 | 0.732688 | 0.036* |
| C5D | 1.0998 (8) | 0.0858 (7) | 0.7068 (4) | 0.0352 (17) |
| H5D | 1.055037 | 0.016881 | 0.720159 | 0.042* |
| C6D | 1.2351 (7) | 0.0661 (8) | 0.7240 (4) | 0.0362 (18) |
| H6D | 1.250511 | -0.021194 | 0.720072 | 0.043* |
| C7D | 1.2583 (7) | 0.1140 (8) | 0.7905 (4) | 0.0362 (18) |
| H7DA | 1.324784 | 0.174851 | 0.796215 | 0.043* |
| H7DB | 1.281143 | 0.048647 | 0.815772 | 0.043* |
| C8D | 1.1160 (8) | 0.3323 (8) | 0.9533 (4) | 0.0394 (19) |
| C9D | 1.0797 (9) | 0.2905 (10) | 1.0061 (4) | 0.047 (2) |
| H9D | 1.051057 | 0.210576 | 1.005658 | 0.056* |
| C10D | 1.0855 (10) | 0.3638 (12) | 1.0580 (4) | 0.059 (3) |
| H10D | 1.062805 | 0.334217 | 1.093712 | 0.071* |
| C11D | 1.1237 (11) | 0.4799 (12) | 1.0589 (5) | 0.064 (3) |
| H11D | 1.126536 | 0.530845 | 1.095058 | 0.076* |
| C12D | 1.1585 (11) | 0.5238 (11) | 1.0071 (5) | 0.060 (3) |
| H12D | 1.184345 | 0.604685 | 1.008055 | 0.072* |
| C13D | 1.1558 (10) | 0.4510 (9) | 0.9548 (4) | 0.053 (2) |
| H13D | 1.180789 | 0.481009 | 0.919621 | 0.063* |
| C14D | 0.9411 (7) | 0.2230 (7) | 0.7529 (3) | 0.0314 (16) |
| C15D | 0.9115 (7) | 0.3350 (7) | 0.7778 (4) | 0.0330 (17) |
| H15D | 0.974008 | 0.394207 | 0.787259 | 0.040* |
| C16D | 0.7968 (7) | 0.3630 (7) | 0.7891 (4) | 0.0375 (18) |
| H16D | 0.780304 | 0.440165 | 0.806451 | 0.045* |
| C17D | 0.7033 (7) | 0.2774 (8) | 0.7751 (4) | 0.0373 (18) |
| C18D | 0.7290 (8) | 0.1649 (8) | 0.7505 (4) | 0.0411 (19) |
| H18D | 0.665714 | 0.106347 | 0.741246 | 0.049* |
| C19D | 0.8447 (7) | 0.1373 (7) | 0.7394 (4) | 0.0362 (17) |
| H19D | 0.860804 | 0.059757 | 0.722429 | 0.043* |
| C20D | 0.5816 (8) | 0.3065 (8) | 0.7882 (5) | 0.046 (2) |
| C21D | 1.0677 (8) | 0.0839 (7) | 0.6418 (4) | 0.0368 (18) |
| H21D | 1.085801 | 0.015136 | 0.617083 | 0.044* |
| C22D | 0.9283 (7) | 0.2246 (8) | 0.5231 (4) | 0.0343 (18) |
| C23D | 0.8849 (8) | 0.2008 (8) | 0.4610 (4) | 0.0357 (18) |
| C24D | 0.8177 (7) | 0.2830 (8) | 0.4306 (4) | 0.0375 (19) |
| H24D | 0.787061 | 0.264727 | 0.389677 | 0.045* |
| C25D | 0.7956 (8) | 0.3909 (8) | 0.4598 (4) | 0.0377 (19) |
| C26D | 0.8394 (7) | 0.4195 (8) | 0.5193 (4) | 0.0351 (18) |

| | | | | |
|---|---|---|---|---|
| H26D | 0.825451 | 0.495926 | 0.538353 | 0.042* |
| C27D | 0.9023 (7) | 0.3386 (8) | 0.5508 (4) | 0.0359 (18) |
| H27D | 0.929375 | 0.358554 | 0.592066 | 0.043* |
| C28D | 1.3186 (8) | 0.1296 (9) | 0.6866 (4) | 0.042 (2) |
| H28D | 1.297911 | 0.207176 | 0.676409 | 0.051* |
| C29D | 1.4180 (9) | 0.0838 (10) | 0.6674 (4) | 0.049 (2) |
| H29G | 1.441288 | 0.006375 | 0.676749 | 0.059* |
| H29H | 1.466203 | 0.128195 | 0.644148 | 0.059* |
| Cl1S | 0.2257 (4) | 0.8786 (6) | -0.06369 (17) | 0.1130 (16) |
| Cl2S | 0.2350 (5) | 0.8550 (4) | 0.06309 (16) | 0.1033 (14) |
| C1S | 0.1931 (12) | 0.9453 (15) | 0.0065 (7) | 0.083 (4) |
| H1SA | 0.237233 | 1.022934 | 0.015166 | 0.100* |
| H1SB | 0.105295 | 0.960065 | 0.005274 | 0.100* |
| Cl3S | 0.7726 (5) | 0.3339 (5) | 0.93689 (18) | 0.1039 (13) |
| Cl4S | 0.7597 (4) | 0.3867 (6) | 1.06397 (19) | 0.1127 (16) |
| C2S | 0.8006 (13) | 0.4375 (15) | 0.9981 (9) | 0.095 (5) |
| H2SA | 0.755217 | 0.510204 | 0.989980 | 0.114* |
| H2SB | 0.887966 | 0.459504 | 1.003455 | 0.114* |

*Atomic displacement parameters (Å$^2$) for compound 5e´*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1A | 0.046 (3) | 0.030 (3) | 0.040 (3) | 0.002 (2) | 0.013 (2) | 0.001 (2) |
| O2A | 0.047 (3) | 0.025 (3) | 0.047 (3) | -0.004 (3) | 0.011 (2) | 0.002 (2) |
| O3A | 0.059 (4) | 0.031 (3) | 0.043 (3) | 0.005 (3) | 0.004 (3) | -0.005 (3) |
| O4A | 0.071 (4) | 0.041 (4) | 0.042 (4) | -0.002 (3) | 0.003 (3) | -0.005 (3) |
| O5A | 0.074 (5) | 0.052 (5) | 0.060 (4) | 0.014 (4) | -0.005 (4) | 0.008 (3) |
| O6A | 0.056 (4) | 0.031 (4) | 0.058 (4) | 0.007 (3) | 0.011 (3) | 0.003 (3) |
| N1A | 0.041 (4) | 0.026 (4) | 0.036 (3) | 0.000 (3) | 0.006 (3) | 0.003 (3) |
| N2A | 0.035 (3) | 0.025 (4) | 0.038 (3) | -0.004 (3) | 0.008 (3) | 0.002 (3) |
| N3A | 0.040 (4) | 0.023 (4) | 0.039 (4) | 0.001 (3) | 0.017 (3) | -0.001 (3) |
| N4A | 0.044 (4) | 0.034 (4) | 0.036 (4) | -0.003 (3) | 0.012 (3) | -0.001 (3) |
| N5A | 0.045 (4) | 0.032 (4) | 0.047 (4) | -0.002 (3) | 0.009 (3) | 0.006 (3) |
| N6A | 0.038 (4) | 0.021 (4) | 0.125 (8) | -0.001 (3) | 0.029 (4) | 0.008 (4) |
| C1A | 0.026 (4) | 0.030 (5) | 0.046 (5) | -0.003 (3) | 0.006 (3) | 0.002 (3) |
| C2A | 0.037 (4) | 0.032 (5) | 0.037 (4) | -0.005 (3) | 0.007 (3) | 0.005 (3) |
| C3A | 0.036 (4) | 0.025 (4) | 0.036 (4) | 0.000 (3) | 0.007 (3) | 0.004 (3) |
| C4A | 0.043 (4) | 0.015 (4) | 0.037 (4) | -0.001 (3) | 0.012 (3) | 0.002 (3) |
| C5A | 0.039 (4) | 0.017 (4) | 0.040 (4) | -0.007 (3) | 0.010 (3) | 0.002 (3) |
| C6A | 0.039 (4) | 0.026 (4) | 0.042 (4) | -0.007 (3) | 0.016 (3) | 0.002 (3) |
| C7A | 0.031 (4) | 0.029 (4) | 0.042 (4) | -0.001 (3) | 0.011 (3) | 0.003 (3) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C8A | 0.034 (4) | 0.037 (5) | 0.042 (4) | -0.003 (3) | 0.009 (3) | 0.005 (4) |
| C9A | 0.048 (5) | 0.054 (6) | 0.044 (5) | 0.004 (4) | 0.009 (4) | 0.009 (4) |
| C10A | 0.046 (5) | 0.075 (8) | 0.043 (5) | 0.007 (5) | 0.016 (4) | 0.006 (5) |
| C11A | 0.062 (6) | 0.068 (8) | 0.041 (5) | -0.005 (5) | 0.005 (4) | 0.015 (5) |
| C12A | 0.069 (7) | 0.041 (6) | 0.062 (6) | -0.006 (5) | 0.005 (5) | 0.021 (5) |
| C13A | 0.071 (6) | 0.041 (6) | 0.042 (5) | 0.004 (5) | 0.006 (4) | 0.007 (4) |
| C14A | 0.033 (4) | 0.024 (4) | 0.033 (4) | 0.001 (3) | 0.009 (3) | 0.004 (3) |
| C15A | 0.035 (4) | 0.017 (4) | 0.042 (4) | 0.002 (3) | 0.008 (3) | 0.005 (3) |
| C16A | 0.040 (4) | 0.014 (4) | 0.051 (5) | 0.000 (3) | 0.012 (3) | 0.002 (3) |
| C17A | 0.033 (4) | 0.022 (4) | 0.049 (5) | 0.000 (3) | 0.012 (3) | -0.001 (3) |
| C18A | 0.037 (4) | 0.023 (4) | 0.052 (5) | 0.005 (3) | 0.005 (3) | 0.008 (3) |
| C19A | 0.038 (4) | 0.015 (4) | 0.050 (5) | 0.000 (3) | 0.007 (3) | 0.008 (3) |
| C20A | 0.037 (5) | 0.023 (5) | 0.073 (6) | -0.004 (3) | 0.015 (4) | 0.000 (4) |
| C21A | 0.041 (4) | 0.026 (4) | 0.038 (4) | -0.009 (3) | 0.017 (3) | 0.001 (3) |
| C22A | 0.024 (4) | 0.027 (4) | 0.040 (4) | -0.005 (3) | 0.015 (3) | 0.005 (3) |
| C23A | 0.029 (4) | 0.028 (4) | 0.040 (4) | -0.006 (3) | 0.016 (3) | 0.002 (3) |
| C24A | 0.030 (4) | 0.034 (5) | 0.038 (4) | -0.007 (3) | 0.011 (3) | 0.001 (3) |
| C25A | 0.032 (4) | 0.031 (5) | 0.044 (4) | 0.001 (3) | 0.015 (3) | 0.007 (3) |
| C26A | 0.040 (4) | 0.027 (4) | 0.042 (4) | -0.002 (3) | 0.016 (3) | 0.004 (3) |
| C27A | 0.040 (4) | 0.029 (4) | 0.035 (4) | -0.003 (3) | 0.012 (3) | 0.000 (3) |
| C28A | 0.035 (4) | 0.037 (5) | 0.048 (5) | -0.010 (3) | 0.014 (3) | -0.003 (4) |
| C29A | 0.044 (5) | 0.051 (6) | 0.056 (5) | -0.008 (4) | 0.020 (4) | -0.006 (4) |
| O1B | 0.072 (4) | 0.030 (4) | 0.044 (3) | -0.004 (3) | 0.025 (3) | 0.000 (3) |
| O2B | 0.049 (3) | 0.026 (4) | 0.047 (3) | -0.003 (2) | 0.013 (3) | -0.005 (2) |
| O3B | 0.052 (3) | 0.031 (3) | 0.038 (3) | 0.003 (3) | 0.003 (2) | 0.004 (2) |
| O4B | 0.060 (4) | 0.036 (4) | 0.035 (3) | 0.006 (3) | 0.002 (3) | -0.003 (2) |
| O5B | 0.088 (5) | 0.037 (4) | 0.049 (4) | 0.006 (3) | -0.014 (3) | 0.004 (3) |
| O6B | 0.073 (5) | 0.029 (4) | 0.059 (4) | 0.015 (3) | -0.004 (3) | 0.005 (3) |
| N1B | 0.041 (4) | 0.025 (4) | 0.045 (4) | -0.002 (3) | 0.015 (3) | 0.007 (3) |
| N2B | 0.029 (3) | 0.029 (4) | 0.036 (3) | -0.002 (3) | 0.007 (2) | 0.002 (3) |
| N3B | 0.031 (3) | 0.026 (4) | 0.038 (3) | 0.002 (3) | 0.006 (3) | 0.000 (3) |
| N4B | 0.033 (3) | 0.030 (4) | 0.036 (4) | 0.002 (3) | 0.008 (3) | 0.003 (3) |
| N5B | 0.055 (4) | 0.024 (4) | 0.048 (4) | -0.002 (3) | 0.002 (3) | 0.009 (3) |
| N6B | 0.039 (4) | 0.037 (4) | 0.057 (4) | -0.001 (3) | 0.006 (3) | 0.005 (3) |
| C1B | 0.053 (5) | 0.026 (5) | 0.046 (5) | -0.001 (4) | 0.013 (4) | 0.004 (4) |
| C2B | 0.037 (4) | 0.026 (5) | 0.038 (4) | 0.000 (3) | 0.015 (3) | 0.003 (3) |
| C3B | 0.029 (4) | 0.021 (4) | 0.044 (4) | -0.002 (3) | 0.008 (3) | 0.007 (3) |
| C4B | 0.030 (4) | 0.018 (4) | 0.039 (4) | -0.001 (3) | 0.008 (3) | -0.002 (3) |
| C5B | 0.032 (4) | 0.016 (4) | 0.040 (4) | 0.002 (3) | 0.007 (3) | 0.001 (3) |
| C6B | 0.029 (4) | 0.026 (4) | 0.036 (4) | 0.002 (3) | 0.006 (3) | 0.004 (3) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C7B | 0.032 (4) | 0.023 (4) | 0.040 (4) | 0.002 (3) | 0.011 (3) | 0.003 (3) |
| C8B | 0.054 (5) | 0.037 (5) | 0.056 (5) | -0.002 (4) | 0.021 (4) | 0.010 (4) |
| C9B | 0.076 (7) | 0.050 (7) | 0.055 (6) | 0.010 (5) | 0.024 (5) | 0.010 (5) |
| C10B | 0.106 (10) | 0.084 (11) | 0.063 (7) | 0.029 (8) | 0.036 (7) | 0.026 (7) |
| C11B | 0.121 (12) | 0.074 (11) | 0.087 (9) | -0.010 (8) | 0.041 (8) | 0.037 (8) |
| C12B | 0.069 (7) | 0.048 (7) | 0.071 (7) | -0.006 (5) | 0.025 (5) | 0.019 (5) |
| C13B | 0.056 (6) | 0.038 (6) | 0.056 (5) | -0.004 (4) | 0.013 (4) | 0.017 (4) |
| C14B | 0.036 (4) | 0.022 (4) | 0.043 (4) | -0.004 (3) | 0.010 (3) | 0.002 (3) |
| C15B | 0.034 (4) | 0.017 (4) | 0.076 (6) | -0.004 (3) | 0.018 (4) | -0.001 (4) |
| C16B | 0.039 (4) | 0.023 (4) | 0.062 (5) | -0.004 (3) | 0.012 (4) | -0.001 (4) |
| C17B | 0.026 (4) | 0.027 (4) | 0.052 (5) | -0.002 (3) | 0.007 (3) | 0.002 (3) |
| C18B | 0.034 (4) | 0.028 (5) | 0.062 (5) | -0.009 (3) | 0.007 (4) | 0.000 (4) |
| C19B | 0.043 (5) | 0.029 (5) | 0.052 (5) | -0.008 (3) | 0.009 (4) | -0.001 (4) |
| C20B | 0.035 (5) | 0.026 (4) | 0.048 (5) | -0.005 (3) | 0.007 (3) | 0.004 (3) |
| C21B | 0.025 (4) | 0.027 (4) | 0.044 (4) | 0.001 (3) | 0.009 (3) | 0.003 (3) |
| C22B | 0.027 (4) | 0.028 (4) | 0.036 (4) | -0.003 (3) | 0.011 (3) | 0.007 (3) |
| C23B | 0.032 (4) | 0.020 (4) | 0.043 (4) | -0.003 (3) | 0.018 (3) | 0.001 (3) |
| C24B | 0.028 (4) | 0.027 (4) | 0.041 (4) | -0.006 (3) | 0.009 (3) | 0.008 (3) |
| C25B | 0.031 (4) | 0.026 (4) | 0.042 (4) | 0.000 (3) | 0.008 (3) | 0.009 (3) |
| C26B | 0.040 (4) | 0.023 (4) | 0.041 (4) | -0.004 (3) | 0.011 (3) | 0.002 (3) |
| C27B | 0.033 (4) | 0.027 (4) | 0.038 (4) | -0.002 (3) | 0.007 (3) | 0.004 (3) |
| C28B | 0.049 (5) | 0.044 (6) | 0.036 (4) | 0.005 (4) | 0.010 (4) | 0.008 (4) |
| C29B | 0.039 (5) | 0.050 (6) | 0.048 (5) | 0.000 (4) | 0.016 (4) | -0.001 (4) |
| O1C | 0.061 (4) | 0.033 (4) | 0.040 (3) | 0.006 (3) | 0.018 (3) | 0.003 (2) |
| O2C | 0.048 (3) | 0.027 (3) | 0.044 (3) | 0.012 (2) | 0.013 (2) | 0.011 (2) |
| O3C | 0.043 (3) | 0.029 (3) | 0.047 (3) | 0.004 (2) | 0.005 (3) | -0.002 (3) |
| O4C | 0.049 (3) | 0.032 (3) | 0.037 (3) | -0.002 (2) | 0.006 (2) | 0.000 (2) |
| O5C | 0.094 (6) | 0.048 (5) | 0.046 (4) | 0.026 (4) | -0.012 (4) | -0.003 (3) |
| O6C | 0.065 (4) | 0.027 (4) | 0.055 (4) | 0.007 (3) | 0.007 (3) | 0.004 (3) |
| N1C | 0.042 (4) | 0.022 (4) | 0.040 (4) | 0.005 (3) | 0.013 (3) | -0.004 (3) |
| N2C | 0.028 (3) | 0.031 (4) | 0.035 (3) | -0.001 (3) | 0.013 (2) | 0.003 (3) |
| N3C | 0.031 (3) | 0.031 (4) | 0.035 (3) | 0.000 (3) | 0.009 (3) | -0.002 (3) |
| N4C | 0.039 (4) | 0.025 (4) | 0.032 (3) | -0.003 (3) | 0.009 (3) | 0.003 (3) |
| N5C | 0.048 (4) | 0.034 (4) | 0.040 (4) | 0.006 (3) | 0.004 (3) | 0.003 (3) |
| N6C | 0.038 (4) | 0.035 (4) | 0.067 (5) | 0.000 (3) | 0.011 (3) | -0.001 (3) |
| C1C | 0.052 (5) | 0.028 (5) | 0.045 (5) | 0.000 (4) | 0.011 (4) | 0.000 (4) |
| C2C | 0.046 (5) | 0.028 (5) | 0.032 (4) | 0.004 (3) | 0.009 (3) | 0.003 (3) |
| C3C | 0.043 (4) | 0.020 (4) | 0.030 (4) | 0.002 (3) | 0.008 (3) | -0.001 (3) |
| C4C | 0.038 (4) | 0.018 (4) | 0.034 (4) | 0.005 (3) | 0.005 (3) | 0.006 (3) |
| C5C | 0.039 (4) | 0.021 (4) | 0.037 (4) | 0.007 (3) | 0.011 (3) | 0.004 (3) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C6C | 0.044 (4) | 0.019 (4) | 0.035 (4) | 0.003 (3) | 0.011 (3) | 0.004 (3) |
| C7C | 0.033 (4) | 0.025 (4) | 0.042 (4) | 0.003 (3) | 0.011 (3) | 0.001 (3) |
| C8C | 0.053 (5) | 0.030 (5) | 0.053 (5) | -0.005 (4) | 0.020 (4) | -0.005 (4) |
| C9C | 0.070 (7) | 0.038 (6) | 0.063 (6) | -0.004 (5) | 0.030 (5) | -0.011 (5) |
| C10C | 0.128 (13) | 0.045 (8) | 0.096 (10) | 0.010 (7) | 0.050 (9) | -0.006 (7) |
| C11C | 0.21 (2) | 0.056 (10) | 0.125 (14) | -0.006 (11) | 0.117 (15) | -0.023 (9) |
| C12C | 0.152 (15) | 0.061 (9) | 0.078 (9) | -0.026 (9) | 0.061 (9) | -0.016 (7) |
| C13C | 0.108 (10) | 0.058 (8) | 0.059 (7) | 0.000 (7) | 0.028 (6) | -0.011 (5) |
| C14C | 0.036 (4) | 0.021 (4) | 0.036 (4) | 0.005 (3) | 0.009 (3) | 0.004 (3) |
| C15C | 0.039 (4) | 0.020 (4) | 0.067 (6) | 0.007 (3) | 0.017 (4) | 0.001 (4) |
| C16C | 0.042 (5) | 0.020 (4) | 0.065 (6) | -0.002 (3) | 0.015 (4) | 0.000 (4) |
| C17C | 0.036 (4) | 0.024 (4) | 0.044 (4) | 0.002 (3) | 0.007 (3) | 0.002 (3) |
| C18C | 0.033 (4) | 0.031 (5) | 0.070 (6) | 0.010 (3) | 0.013 (4) | 0.009 (4) |
| C19C | 0.038 (4) | 0.024 (5) | 0.063 (5) | 0.003 (3) | 0.009 (4) | 0.013 (4) |
| C20C | 0.041 (5) | 0.026 (5) | 0.046 (5) | 0.000 (3) | 0.006 (4) | -0.004 (3) |
| C21C | 0.040 (4) | 0.023 (4) | 0.039 (4) | 0.002 (3) | 0.009 (3) | -0.003 (3) |
| C22C | 0.027 (4) | 0.029 (4) | 0.036 (4) | -0.001 (3) | 0.015 (3) | 0.003 (3) |
| C23C | 0.036 (4) | 0.020 (4) | 0.031 (4) | -0.003 (3) | 0.011 (3) | 0.003 (3) |
| C24C | 0.026 (4) | 0.033 (5) | 0.031 (4) | -0.003 (3) | 0.009 (3) | 0.005 (3) |
| C25C | 0.025 (4) | 0.029 (4) | 0.048 (5) | -0.001 (3) | 0.014 (3) | 0.006 (3) |
| C26C | 0.032 (4) | 0.031 (5) | 0.042 (4) | -0.001 (3) | 0.014 (3) | 0.003 (3) |
| C27C | 0.036 (4) | 0.029 (4) | 0.032 (4) | -0.003 (3) | 0.006 (3) | 0.000 (3) |
| C28C | 0.039 (4) | 0.029 (5) | 0.039 (4) | 0.003 (3) | 0.011 (3) | 0.007 (3) |
| C29C | 0.036 (4) | 0.042 (5) | 0.051 (5) | -0.002 (4) | 0.019 (4) | 0.000 (4) |
| O1D | 0.049 (3) | 0.027 (3) | 0.045 (3) | -0.003 (2) | 0.019 (2) | 0.006 (2) |
| O2D | 0.053 (3) | 0.026 (3) | 0.047 (3) | -0.004 (3) | 0.014 (3) | 0.005 (2) |
| O3D | 0.051 (4) | 0.037 (4) | 0.043 (3) | 0.001 (3) | 0.011 (3) | -0.006 (3) |
| O4D | 0.060 (4) | 0.045 (4) | 0.043 (4) | -0.001 (3) | 0.007 (3) | -0.004 (3) |
| O5D | 0.076 (5) | 0.050 (5) | 0.049 (4) | 0.008 (4) | -0.001 (3) | 0.008 (3) |
| O6D | 0.066 (4) | 0.035 (4) | 0.070 (4) | 0.004 (3) | 0.003 (3) | 0.005 (3) |
| N1D | 0.034 (3) | 0.027 (4) | 0.036 (3) | 0.000 (3) | 0.012 (3) | 0.000 (3) |
| N2D | 0.035 (3) | 0.025 (4) | 0.043 (4) | -0.001 (3) | 0.014 (3) | -0.001 (3) |
| N3D | 0.037 (4) | 0.029 (4) | 0.038 (4) | 0.002 (3) | 0.010 (3) | -0.006 (3) |
| N4D | 0.039 (4) | 0.040 (5) | 0.039 (4) | -0.005 (3) | 0.014 (3) | 0.000 (3) |
| N5D | 0.044 (4) | 0.039 (5) | 0.052 (5) | -0.002 (3) | 0.011 (3) | 0.012 (4) |
| N6D | 0.044 (5) | 0.024 (4) | 0.125 (8) | 0.008 (3) | 0.034 (5) | 0.021 (4) |
| C1D | 0.036 (4) | 0.023 (4) | 0.048 (5) | 0.001 (3) | 0.008 (3) | 0.006 (3) |
| C2D | 0.034 (4) | 0.022 (4) | 0.047 (5) | 0.002 (3) | 0.010 (3) | 0.000 (3) |
| C3D | 0.042 (4) | 0.018 (4) | 0.035 (4) | -0.001 (3) | 0.009 (3) | 0.003 (3) |
| C4D | 0.036 (4) | 0.017 (4) | 0.039 (4) | 0.002 (3) | 0.012 (3) | 0.001 (3) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C5D | 0.045 (5) | 0.017 (4) | 0.044 (4) | -0.001 (3) | 0.012 (3) | -0.001 (3) |
| C6D | 0.036 (4) | 0.022 (4) | 0.053 (5) | 0.001 (3) | 0.018 (3) | 0.007 (3) |
| C7D | 0.034 (4) | 0.028 (4) | 0.049 (5) | 0.001 (3) | 0.011 (3) | 0.005 (3) |
| C8D | 0.045 (5) | 0.035 (5) | 0.038 (4) | 0.002 (4) | 0.010 (3) | 0.000 (3) |
| C9D | 0.047 (5) | 0.049 (6) | 0.045 (5) | 0.001 (4) | 0.011 (4) | 0.002 (4) |
| C10D | 0.056 (6) | 0.078 (9) | 0.042 (5) | -0.010 (5) | 0.010 (4) | -0.002 (5) |
| C11D | 0.066 (7) | 0.069 (9) | 0.051 (6) | 0.012 (6) | 0.003 (5) | -0.015 (5) |
| C12D | 0.079 (7) | 0.044 (6) | 0.052 (6) | 0.006 (5) | 0.002 (5) | -0.012 (5) |
| C13D | 0.072 (7) | 0.040 (6) | 0.047 (5) | -0.001 (5) | 0.010 (4) | 0.002 (4) |
| C14D | 0.040 (4) | 0.024 (4) | 0.032 (4) | 0.001 (3) | 0.006 (3) | 0.006 (3) |
| C15D | 0.039 (4) | 0.018 (4) | 0.043 (4) | -0.003 (3) | 0.008 (3) | 0.002 (3) |
| C16D | 0.040 (4) | 0.017 (4) | 0.057 (5) | 0.001 (3) | 0.012 (4) | 0.007 (3) |
| C17D | 0.034 (4) | 0.027 (4) | 0.054 (5) | 0.001 (3) | 0.016 (3) | 0.011 (4) |
| C18D | 0.040 (5) | 0.025 (5) | 0.058 (5) | -0.005 (3) | 0.008 (4) | 0.004 (4) |
| C19D | 0.032 (4) | 0.021 (4) | 0.055 (5) | -0.002 (3) | 0.009 (3) | -0.002 (3) |
| C20D | 0.041 (5) | 0.023 (5) | 0.079 (7) | -0.001 (4) | 0.016 (4) | 0.018 (4) |
| C21D | 0.047 (5) | 0.019 (4) | 0.044 (5) | -0.001 (3) | 0.014 (3) | -0.007 (3) |
| C22D | 0.029 (4) | 0.033 (5) | 0.043 (4) | -0.002 (3) | 0.014 (3) | 0.001 (3) |
| C23D | 0.039 (4) | 0.033 (5) | 0.036 (4) | -0.009 (3) | 0.016 (3) | -0.001 (3) |
| C24D | 0.033 (4) | 0.043 (5) | 0.038 (4) | -0.008 (3) | 0.012 (3) | 0.003 (4) |
| C25D | 0.038 (4) | 0.028 (5) | 0.051 (5) | -0.006 (3) | 0.017 (4) | 0.010 (4) |
| C26D | 0.036 (4) | 0.023 (4) | 0.049 (5) | -0.004 (3) | 0.017 (3) | 0.001 (3) |
| C27D | 0.039 (4) | 0.031 (5) | 0.039 (4) | -0.007 (3) | 0.014 (3) | -0.003 (3) |
| C28D | 0.043 (5) | 0.039 (5) | 0.049 (5) | 0.004 (4) | 0.015 (4) | 0.005 (4) |
| C29D | 0.055 (5) | 0.051 (6) | 0.044 (5) | 0.006 (4) | 0.016 (4) | 0.002 (4) |
| Cl1S | 0.084 (2) | 0.186 (5) | 0.071 (2) | 0.007 (3) | 0.0058 (17) | 0.023 (2) |
| Cl2S | 0.170 (4) | 0.072 (2) | 0.0633 (19) | -0.020 (2) | -0.007 (2) | 0.0045 (16) |
| C1S | 0.053 (7) | 0.091 (11) | 0.107 (10) | -0.012 (6) | 0.010 (6) | 0.018 (8) |
| Cl3S | 0.125 (3) | 0.111 (3) | 0.075 (2) | 0.010 (2) | 0.000 (2) | 0.017 (2) |
| Cl4S | 0.087 (2) | 0.166 (5) | 0.082 (2) | 0.016 (3) | 0.0059 (18) | -0.003 (3) |
| C2S | 0.053 (7) | 0.082 (11) | 0.148 (14) | 0.004 (7) | -0.008 (8) | 0.019 (9) |

*Geometric parameters (Å, º) for compound 5e´*

| | | | |
|---|---|---|---|
| O1A—C2A | 1.371 (10) | O4C—N4C | 1.224 (9) |
| O1A—C1A | 1.409 (10) | O5C—N5C | 1.210 (10) |
| O2A—C2A | 1.185 (11) | O6C—N5C | 1.232 (10) |
| O3A—N4A | 1.263 (10) | N1C—C1C | 1.255 (11) |
| O4A—N4A | 1.210 (9) | N1C—C3C | 1.462 (10) |
| O5A—N5A | 1.225 (11) | N2C—C21C | 1.279 (11) |
| O6A—N5A | 1.226 (10) | N2C—N3C | 1.379 (9) |

| | | | |
|---|---|---|---|
| N1A—C1A | 1.263 (11) | N3C—C22C | 1.334 (11) |
| N1A—C3A | 1.449 (10) | N3C—H3C | 0.8800 |
| N2A—C21A | 1.266 (11) | N4C—C23C | 1.448 (11) |
| N2A—N3A | 1.383 (9) | N5C—C25C | 1.467 (11) |
| N3A—C22A | 1.350 (11) | N6C—C20C | 1.147 (12) |
| N3A—H3A | 0.8800 | C1C—C8C | 1.473 (13) |
| N4A—C23A | 1.434 (11) | C2C—C3C | 1.523 (11) |
| N5A—C25A | 1.455 (11) | C3C—C7C | 1.532 (11) |
| N6A—C20A | 1.138 (12) | C3C—C4C | 1.561 (11) |
| C1A—C8A | 1.455 (12) | C4C—C14C | 1.494 (11) |
| C2A—C3A | 1.533 (11) | C4C—C5C | 1.545 (10) |
| C3A—C4A | 1.555 (11) | C4C—H4C | 1.0000 |
| C3A—C7A | 1.555 (11) | C5C—C21C | 1.495 (11) |
| C4A—C14A | 1.510 (11) | C5C—C6C | 1.575 (12) |
| C4A—C5A | 1.532 (10) | C5C—H5C | 1.0000 |
| C4A—H4A | 1.0000 | C6C—C28C | 1.519 (11) |
| C5A—C21A | 1.485 (11) | C6C—C7C | 1.544 (11) |
| C5A—C6A | 1.545 (11) | C6C—H6C | 1.0000 |
| C5A—H5A | 1.0000 | C7C—H7CA | 0.9900 |
| C6A—C28A | 1.502 (12) | C7C—H7CB | 0.9900 |
| C6A—C7A | 1.561 (11) | C8C—C9C | 1.350 (16) |
| C6A—H6A | 1.0000 | C8C—C13C | 1.406 (16) |
| C7A—H7AA | 0.9900 | C9C—C10C | 1.394 (16) |
| C7A—H7AB | 0.9900 | C9C—H9C | 0.9500 |
| C8A—C13A | 1.387 (14) | C10C—C11C | 1.35 (2) |
| C8A—C9A | 1.399 (13) | C10C—H10C | 0.9500 |
| C9A—C10A | 1.385 (14) | C11C—C12C | 1.40 (3) |
| C9A—H9A | 0.9500 | C11C—H11C | 0.9500 |
| C10A—C11A | 1.372 (17) | C12C—C13C | 1.362 (19) |
| C10A—H10A | 0.9500 | C12C—H12C | 0.9500 |
| C11A—C12A | 1.377 (16) | C13C—H13C | 0.9500 |
| C11A—H11A | 0.9500 | C14C—C19C | 1.392 (11) |
| C12A—C13A | 1.386 (14) | C14C—C15C | 1.404 (12) |
| C12A—H12A | 0.9500 | C15C—C16C | 1.383 (13) |
| C13A—H13A | 0.9500 | C15C—H15C | 0.9500 |
| C14A—C15A | 1.395 (11) | C16C—C17C | 1.391 (12) |
| C14A—C19A | 1.405 (11) | C16C—H16C | 0.9500 |
| C15A—C16A | 1.373 (12) | C17C—C18C | 1.386 (13) |
| C15A—H15A | 0.9500 | C17C—C20C | 1.425 (13) |
| C16A—C17A | 1.391 (12) | C18C—C19C | 1.377 (13) |

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| C16A—H16A | 0.9500 | C18C—H18C | 0.9500 |
| C17A—C18A | 1.401 (12) | C19C—H19C | 0.9500 |
| C17A—C20A | 1.436 (12) | C21C—H21C | 0.9500 |
| C18A—C19A | 1.359 (12) | C22C—C27C | 1.420 (12) |
| C18A—H18A | 0.9500 | C22C—C23C | 1.429 (11) |
| C19A—H19A | 0.9500 | C23C—C24C | 1.397 (11) |
| C21A—H21A | 0.9500 | C24C—C25C | 1.357 (12) |
| C22A—C27A | 1.420 (12) | C24C—H24C | 0.9500 |
| C22A—C23A | 1.423 (11) | C25C—C26C | 1.384 (12) |
| C23A—C24A | 1.393 (12) | C26C—C27C | 1.377 (12) |
| C24A—C25A | 1.368 (12) | C26C—H26C | 0.9500 |
| C24A—H24A | 0.9500 | C27C—H27C | 0.9500 |
| C25A—C26A | 1.385 (12) | C28C—C29C | 1.299 (13) |
| C26A—C27A | 1.363 (13) | C28C—H28C | 0.9500 |
| C26A—H26A | 0.9500 | C29C—H29E | 0.9500 |
| C27A—H27A | 0.9500 | C29C—H29F | 0.9500 |
| C28A—C29A | 1.330 (13) | O1D—C2D | 1.360 (10) |
| C28A—H28A | 0.9500 | O1D—C1D | 1.404 (11) |
| C29A—H29A | 0.9500 | O2D—C2D | 1.202 (10) |
| C29A—H29B | 0.9500 | O3D—N4D | 1.253 (10) |
| O1B—C2B | 1.380 (10) | O4D—N4D | 1.212 (10) |
| O1B—C1B | 1.412 (11) | O5D—N5D | 1.215 (11) |
| O2B—C2B | 1.192 (10) | O6D—N5D | 1.239 (11) |
| O3B—N4B | 1.245 (9) | N1D—C1D | 1.280 (11) |
| O4B—N4B | 1.213 (9) | N1D—C3D | 1.486 (10) |
| O5B—N5B | 1.223 (10) | N2D—C21D | 1.282 (11) |
| O6B—N5B | 1.232 (10) | N2D—N3D | 1.375 (10) |
| N1B—C1B | 1.251 (11) | N3D—C22D | 1.334 (12) |
| N1B—C3B | 1.463 (10) | N3D—H3D | 0.8800 |
| N2B—C21B | 1.278 (11) | N4D—C23D | 1.451 (12) |
| N2B—N3B | 1.382 (9) | N5D—C25D | 1.458 (12) |
| N3B—C22B | 1.363 (11) | N6D—C20D | 1.131 (12) |
| N3B—H3B | 0.8800 | C1D—C8D | 1.447 (12) |
| N4B—C23B | 1.449 (10) | C2D—C3D | 1.511 (11) |
| N5B—C25B | 1.447 (11) | C3D—C7D | 1.539 (11) |
| N6B—C20B | 1.134 (11) | C3D—C4D | 1.563 (11) |
| C1B—C8B | 1.459 (13) | C4D—C14D | 1.476 (11) |
| C2B—C3B | 1.507 (11) | C4D—C5D | 1.527 (10) |
| C3B—C7B | 1.531 (10) | C4D—H4D | 1.0000 |
| C3B—C4B | 1.562 (11) | C5D—C21D | 1.466 (12) |

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| C4B—C14B | 1.516 (11) | C5D—C6D | 1.537 (12) |
| C4B—C5B | 1.556 (11) | C5D—H5D | 1.0000 |
| C4B—H4B | 1.0000 | C6D—C28D | 1.524 (12) |
| C5B—C21B | 1.469 (11) | C6D—C7D | 1.538 (12) |
| C5B—C6B | 1.568 (10) | C6D—H6D | 1.0000 |
| C5B—H5B | 1.0000 | C7D—H7DA | 0.9900 |
| C6B—C7B | 1.517 (11) | C7D—H7DB | 0.9900 |
| C6B—C28B | 1.524 (11) | C8D—C13D | 1.400 (15) |
| C6B—H6B | 1.0000 | C8D—C9D | 1.408 (13) |
| C7B—H7BA | 0.9900 | C9D—C10D | 1.364 (15) |
| C7B—H7BB | 0.9900 | C9D—H9D | 0.9500 |
| C8B—C9B | 1.381 (14) | C10D—C11D | 1.368 (19) |
| C8B—C13B | 1.396 (15) | C10D—H10D | 0.9500 |
| C9B—C10B | 1.404 (18) | C11D—C12D | 1.389 (18) |
| C9B—H9B | 0.9500 | C11D—H11D | 0.9500 |
| C10B—C11B | 1.37 (2) | C12D—C13D | 1.371 (15) |
| C10B—H10B | 0.9500 | C12D—H12D | 0.9500 |
| C11B—C12B | 1.36 (2) | C13D—H13D | 0.9500 |
| C11B—H11B | 0.9500 | C14D—C15D | 1.394 (11) |
| C12B—C13B | 1.383 (14) | C14D—C19D | 1.421 (12) |
| C12B—H12B | 0.9500 | C15D—C16D | 1.361 (12) |
| C13B—H13B | 0.9500 | C15D—H15D | 0.9500 |
| C14B—C15B | 1.371 (12) | C16D—C17D | 1.398 (12) |
| C14B—C19B | 1.398 (12) | C16D—H16D | 0.9500 |
| C15B—C16B | 1.392 (12) | C17D—C18D | 1.386 (13) |
| C15B—H15B | 0.9500 | C17D—C20D | 1.448 (12) |
| C16B—C17B | 1.390 (12) | C18D—C19D | 1.369 (12) |
| C16B—H16B | 0.9500 | C18D—H18D | 0.9500 |
| C17B—C18B | 1.384 (13) | C19D—H19D | 0.9500 |
| C17B—C20B | 1.456 (12) | C21D—H21D | 0.9500 |
| C18B—C19B | 1.381 (13) | C22D—C27D | 1.426 (12) |
| C18B—H18B | 0.9500 | C22D—C23D | 1.430 (12) |
| C19B—H19B | 0.9500 | C23D—C24D | 1.384 (13) |
| C21B—H21B | 0.9500 | C24D—C25D | 1.369 (13) |
| C22B—C23B | 1.414 (11) | C24D—H24D | 0.9500 |
| C22B—C27B | 1.427 (12) | C25D—C26D | 1.384 (13) |
| C23B—C24B | 1.387 (12) | C26D—C27D | 1.363 (13) |
| C24B—C25B | 1.391 (12) | C26D—H26D | 0.9500 |
| C24B—H24B | 0.9500 | C27D—H27D | 0.9500 |
| C25B—C26B | 1.393 (12) | C28D—C29D | 1.323 (13) |

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| C26B—C27B | 1.367 (12) | C28D—H28D | 0.9500 |
| C26B—H26B | 0.9500 | C29D—H29G | 0.9500 |
| C27B—H27B | 0.9500 | C29D—H29H | 0.9500 |
| C28B—C29B | 1.303 (14) | Cl1S—C1S | 1.761 (17) |
| C28B—H28B | 0.9500 | Cl2S—C1S | 1.730 (16) |
| C29B—H29C | 0.9500 | C1S—H1SA | 0.9900 |
| C29B—H29D | 0.9500 | C1S—H1SB | 0.9900 |
| O1C—C2C | 1.377 (10) | Cl3S—C2S | 1.722 (19) |
| O1C—C1C | 1.383 (11) | Cl4S—C2S | 1.73 (2) |
| O2C—C2C | 1.192 (10) | C2S—H2SA | 0.9900 |
| O3C—N4C | 1.245 (9) | C2S—H2SB | 0.9900 |
| | | | |
| C2A—O1A—C1A | 105.8 (6) | O4C—N4C—O3C | 122.1 (7) |
| C1A—N1A—C3A | 108.3 (7) | O4C—N4C—C23C | 119.7 (6) |
| C21A—N2A—N3A | 115.9 (7) | O3C—N4C—C23C | 118.1 (6) |
| C22A—N3A—N2A | 119.1 (7) | O5C—N5C—O6C | 123.8 (7) |
| C22A—N3A—H3A | 120.4 | O5C—N5C—C25C | 118.5 (7) |
| N2A—N3A—H3A | 120.4 | O6C—N5C—C25C | 117.7 (7) |
| O4A—N4A—O3A | 121.9 (7) | N1C—C1C—O1C | 117.5 (7) |
| O4A—N4A—C23A | 119.7 (7) | N1C—C1C—C8C | 127.3 (8) |
| O3A—N4A—C23A | 118.4 (7) | O1C—C1C—C8C | 115.2 (7) |
| O5A—N5A—O6A | 123.9 (8) | O2C—C2C—O1C | 122.7 (7) |
| O5A—N5A—C25A | 118.4 (8) | O2C—C2C—C3C | 131.2 (7) |
| O6A—N5A—C25A | 117.7 (7) | O1C—C2C—C3C | 106.1 (7) |
| N1A—C1A—O1A | 115.8 (7) | N1C—C3C—C2C | 103.8 (6) |
| N1A—C1A—C8A | 129.1 (8) | N1C—C3C—C7C | 115.0 (7) |
| O1A—C1A—C8A | 115.1 (7) | C2C—C3C—C7C | 114.2 (7) |
| O2A—C2A—O1A | 122.8 (8) | N1C—C3C—C4C | 111.3 (6) |
| O2A—C2A—C3A | 130.4 (7) | C2C—C3C—C4C | 110.0 (7) |
| O1A—C2A—C3A | 106.8 (7) | C7C—C3C—C4C | 102.5 (6) |
| N1A—C3A—C2A | 103.3 (6) | C14C—C4C—C5C | 118.9 (7) |
| N1A—C3A—C4A | 112.8 (7) | C14C—C4C—C3C | 114.1 (6) |
| C2A—C3A—C4A | 111.4 (6) | C5C—C4C—C3C | 104.2 (6) |
| N1A—C3A—C7A | 113.9 (6) | C14C—C4C—H4C | 106.3 |
| C2A—C3A—C7A | 111.3 (7) | C5C—C4C—H4C | 106.3 |
| C4A—C3A—C7A | 104.4 (6) | C3C—C4C—H4C | 106.3 |
| C14A—C4A—C5A | 118.8 (7) | C21C—C5C—C4C | 113.2 (6) |
| C14A—C4A—C3A | 112.6 (6) | C21C—C5C—C6C | 115.3 (6) |
| C5A—C4A—C3A | 101.9 (6) | C4C—C5C—C6C | 106.9 (6) |
| C14A—C4A—H4A | 107.7 | C21C—C5C—H5C | 107.0 |

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|---|---|---|---|
| C5A—C4A—H4A | 107.7 | C4C—C5C—H5C | 107.0 |
| C3A—C4A—H4A | 107.7 | C6C—C5C—H5C | 107.0 |
| C21A—C5A—C4A | 115.4 (6) | C28C—C6C—C7C | 112.6 (7) |
| C21A—C5A—C6A | 114.0 (6) | C28C—C6C—C5C | 115.7 (7) |
| C4A—C5A—C6A | 103.7 (6) | C7C—C6C—C5C | 104.2 (6) |
| C21A—C5A—H5A | 107.8 | C28C—C6C—H6C | 108.0 |
| C4A—C5A—H5A | 107.8 | C7C—C6C—H6C | 108.0 |
| C6A—C5A—H5A | 107.8 | C5C—C6C—H6C | 108.0 |
| C28A—C6A—C5A | 115.7 (7) | C3C—C7C—C6C | 104.1 (6) |
| C28A—C6A—C7A | 109.4 (7) | C3C—C7C—H7CA | 110.9 |
| C5A—C6A—C7A | 103.4 (6) | C6C—C7C—H7CA | 110.9 |
| C28A—C6A—H6A | 109.4 | C3C—C7C—H7CB | 110.9 |
| C5A—C6A—H6A | 109.4 | C6C—C7C—H7CB | 110.9 |
| C7A—C6A—H6A | 109.4 | H7CA—C7C—H7CB | 109.0 |
| C3A—C7A—C6A | 106.8 (6) | C9C—C8C—C13C | 118.8 (10) |
| C3A—C7A—H7AA | 110.4 | C9C—C8C—C1C | 120.2 (9) |
| C6A—C7A—H7AA | 110.4 | C13C—C8C—C1C | 121.0 (10) |
| C3A—C7A—H7AB | 110.4 | C8C—C9C—C10C | 121.4 (11) |
| C6A—C7A—H7AB | 110.4 | C8C—C9C—H9C | 119.3 |
| H7AA—C7A—H7AB | 108.6 | C10C—C9C—H9C | 119.3 |
| C13A—C8A—C9A | 119.0 (8) | C11C—C10C—C9C | 118.8 (15) |
| C13A—C8A—C1A | 118.6 (8) | C11C—C10C—H10C | 120.6 |
| C9A—C8A—C1A | 122.4 (8) | C9C—C10C—H10C | 120.6 |
| C10A—C9A—C8A | 120.2 (10) | C10C—C11C—C12C | 121.4 (12) |
| C10A—C9A—H9A | 119.9 | C10C—C11C—H11C | 119.3 |
| C8A—C9A—H9A | 119.9 | C12C—C11C—H11C | 119.3 |
| C11A—C10A—C9A | 120.2 (9) | C13C—C12C—C11C | 118.1 (14) |
| C11A—C10A—H10A | 119.9 | C13C—C12C—H12C | 120.9 |
| C9A—C10A—H10A | 119.9 | C11C—C12C—H12C | 120.9 |
| C10A—C11A—C12A | 120.1 (9) | C12C—C13C—C8C | 120.9 (14) |
| C10A—C11A—H11A | 120.0 | C12C—C13C—H13C | 119.5 |
| C12A—C11A—H11A | 120.0 | C8C—C13C—H13C | 119.5 |
| C11A—C12A—C13A | 120.5 (11) | C19C—C14C—C15C | 116.8 (7) |
| C11A—C12A—H12A | 119.8 | C19C—C14C—C4C | 119.0 (7) |
| C13A—C12A—H12A | 119.8 | C15C—C14C—C4C | 124.1 (7) |
| C12A—C13A—C8A | 120.1 (10) | C16C—C15C—C14C | 120.9 (7) |
| C12A—C13A—H13A | 120.0 | C16C—C15C—H15C | 119.5 |
| C8A—C13A—H13A | 120.0 | C14C—C15C—H15C | 119.5 |
| C15A—C14A—C19A | 118.4 (7) | C15C—C16C—C17C | 121.0 (8) |
| C15A—C14A—C4A | 118.2 (7) | C15C—C16C—H16C | 119.5 |

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|---|---|---|---|
| C19A—C14A—C4A | 123.2 (7) | C17C—C16C—H16C | 119.5 |
| C16A—C15A—C14A | 121.3 (7) | C18C—C17C—C16C | 118.6 (8) |
| C16A—C15A—H15A | 119.3 | C18C—C17C—C20C | 120.7 (7) |
| C14A—C15A—H15A | 119.3 | C16C—C17C—C20C | 120.7 (8) |
| C15A—C16A—C17A | 119.4 (7) | C19C—C18C—C17C | 120.0 (8) |
| C15A—C16A—H16A | 120.3 | C19C—C18C—H18C | 120.0 |
| C17A—C16A—H16A | 120.3 | C17C—C18C—H18C | 120.0 |
| C16A—C17A—C18A | 119.9 (7) | C18C—C19C—C14C | 122.6 (8) |
| C16A—C17A—C20A | 119.0 (8) | C18C—C19C—H19C | 118.7 |
| C18A—C17A—C20A | 121.2 (8) | C14C—C19C—H19C | 118.7 |
| C19A—C18A—C17A | 120.2 (7) | N6C—C20C—C17C | 177.8 (10) |
| C19A—C18A—H18A | 119.9 | N2C—C21C—C5C | 122.2 (7) |
| C17A—C18A—H18A | 119.9 | N2C—C21C—H21C | 118.9 |
| C18A—C19A—C14A | 120.7 (7) | C5C—C21C—H21C | 118.9 |
| C18A—C19A—H19A | 119.7 | N3C—C22C—C27C | 120.1 (7) |
| C14A—C19A—H19A | 119.7 | N3C—C22C—C23C | 124.4 (7) |
| N6A—C20A—C17A | 178.5 (11) | C27C—C22C—C23C | 115.4 (7) |
| N2A—C21A—C5A | 118.4 (7) | C24C—C23C—C22C | 121.8 (7) |
| N2A—C21A—H21A | 120.8 | C24C—C23C—N4C | 116.3 (7) |
| C5A—C21A—H21A | 120.8 | C22C—C23C—N4C | 121.9 (7) |
| N3A—C22A—C27A | 119.7 (7) | C25C—C24C—C23C | 119.5 (7) |
| N3A—C22A—C23A | 124.0 (7) | C25C—C24C—H24C | 120.2 |
| C27A—C22A—C23A | 116.4 (7) | C23C—C24C—H24C | 120.2 |
| C24A—C23A—C22A | 121.7 (7) | C24C—C25C—C26C | 121.3 (8) |
| C24A—C23A—N4A | 116.6 (7) | C24C—C25C—N5C | 119.2 (7) |
| C22A—C23A—N4A | 121.6 (7) | C26C—C25C—N5C | 119.4 (7) |
| C25A—C24A—C23A | 118.8 (8) | C27C—C26C—C25C | 119.8 (8) |
| C25A—C24A—H24A | 120.6 | C27C—C26C—H26C | 120.1 |
| C23A—C24A—H24A | 120.6 | C25C—C26C—H26C | 120.1 |
| C24A—C25A—C26A | 121.7 (8) | C26C—C27C—C22C | 122.0 (7) |
| C24A—C25A—N5A | 118.8 (8) | C26C—C27C—H27C | 119.0 |
| C26A—C25A—N5A | 119.5 (8) | C22C—C27C—H27C | 119.0 |
| C27A—C26A—C25A | 120.0 (8) | C29C—C28C—C6C | 124.3 (8) |
| C27A—C26A—H26A | 120.0 | C29C—C28C—H28C | 117.8 |
| C25A—C26A—H26A | 120.0 | C6C—C28C—H28C | 117.8 |
| C26A—C27A—C22A | 121.5 (8) | C28C—C29C—H29E | 120.0 |
| C26A—C27A—H27A | 119.2 | C28C—C29C—H29F | 120.0 |
| C22A—C27A—H27A | 119.2 | H29E—C29C—H29F | 120.0 |
| C29A—C28A—C6A | 123.9 (9) | C2D—O1D—C1D | 105.7 (6) |
| C29A—C28A—H28A | 118.0 | C1D—N1D—C3D | 106.1 (7) |

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|---|---|---|---|
| C6A—C28A—H28A | 118.0 | C21D—N2D—N3D | 113.8 (7) |
| C28A—C29A—H29A | 120.0 | C22D—N3D—N2D | 121.1 (7) |
| C28A—C29A—H29B | 120.0 | C22D—N3D—H3D | 119.5 |
| H29A—C29A—H29B | 120.0 | N2D—N3D—H3D | 119.5 |
| C2B—O1B—C1B | 105.8 (6) | O4D—N4D—O3D | 121.9 (7) |
| C1B—N1B—C3B | 107.3 (7) | O4D—N4D—C23D | 119.7 (8) |
| C21B—N2B—N3B | 115.5 (7) | O3D—N4D—C23D | 118.3 (7) |
| C22B—N3B—N2B | 118.5 (6) | O5D—N5D—O6D | 124.6 (8) |
| C22B—N3B—H3B | 120.7 | O5D—N5D—C25D | 118.7 (8) |
| N2B—N3B—H3B | 120.7 | O6D—N5D—C25D | 116.7 (8) |
| O4B—N4B—O3B | 121.8 (7) | N1D—C1D—O1D | 116.6 (7) |
| O4B—N4B—C23B | 119.8 (7) | N1D—C1D—C8D | 126.8 (8) |
| O3B—N4B—C23B | 118.4 (6) | O1D—C1D—C8D | 116.6 (7) |
| O5B—N5B—O6B | 123.3 (7) | O2D—C2D—O1D | 122.2 (7) |
| O5B—N5B—C25B | 118.6 (7) | O2D—C2D—C3D | 129.6 (7) |
| O6B—N5B—C25B | 118.1 (7) | O1D—C2D—C3D | 108.2 (7) |
| N1B—C1B—O1B | 116.1 (7) | N1D—C3D—C2D | 103.3 (6) |
| N1B—C1B—C8B | 129.3 (8) | N1D—C3D—C7D | 112.5 (6) |
| O1B—C1B—C8B | 114.5 (7) | C2D—C3D—C7D | 111.8 (6) |
| O2B—C2B—O1B | 121.8 (7) | N1D—C3D—C4D | 112.4 (6) |
| O2B—C2B—C3B | 131.8 (7) | C2D—C3D—C4D | 112.4 (7) |
| O1B—C2B—C3B | 106.4 (7) | C7D—C3D—C4D | 104.6 (6) |
| N1B—C3B—C2B | 104.4 (6) | C14D—C4D—C5D | 119.8 (7) |
| N1B—C3B—C7B | 114.7 (6) | C14D—C4D—C3D | 112.4 (6) |
| C2B—C3B—C7B | 115.1 (6) | C5D—C4D—C3D | 100.5 (6) |
| N1B—C3B—C4B | 110.0 (6) | C14D—C4D—H4D | 107.8 |
| C2B—C3B—C4B | 111.1 (6) | C5D—C4D—H4D | 107.8 |
| C7B—C3B—C4B | 101.8 (6) | C3D—C4D—H4D | 107.8 |
| C14B—C4B—C5B | 118.2 (6) | C21D—C5D—C4D | 118.5 (7) |
| C14B—C4B—C3B | 114.2 (6) | C21D—C5D—C6D | 113.1 (7) |
| C5B—C4B—C3B | 104.7 (6) | C4D—C5D—C6D | 105.4 (7) |
| C14B—C4B—H4B | 106.3 | C21D—C5D—H5D | 106.3 |
| C5B—C4B—H4B | 106.3 | C4D—C5D—H5D | 106.3 |
| C3B—C4B—H4B | 106.3 | C6D—C5D—H5D | 106.3 |
| C21B—C5B—C4B | 108.7 (6) | C28D—C6D—C5D | 113.8 (7) |
| C21B—C5B—C6B | 116.2 (6) | C28D—C6D—C7D | 110.3 (7) |
| C4B—C5B—C6B | 104.6 (6) | C5D—C6D—C7D | 104.8 (6) |
| C21B—C5B—H5B | 109.0 | C28D—C6D—H6D | 109.3 |
| C4B—C5B—H5B | 109.0 | C5D—C6D—H6D | 109.3 |
| C6B—C5B—H5B | 109.0 | C7D—C6D—H6D | 109.3 |

| | | | |
|---|---|---|---|
| C7B—C6B—C28B | 115.8 (7) | C6D—C7D—C3D | 106.7 (6) |
| C7B—C6B—C5B | 106.4 (6) | C6D—C7D—H7DA | 110.4 |
| C28B—C6B—C5B | 116.2 (6) | C3D—C7D—H7DA | 110.4 |
| C7B—C6B—H6B | 105.8 | C6D—C7D—H7DB | 110.4 |
| C28B—C6B—H6B | 105.8 | C3D—C7D—H7DB | 110.4 |
| C5B—C6B—H6B | 105.8 | H7DA—C7D—H7DB | 108.6 |
| C6B—C7B—C3B | 103.5 (6) | C13D—C8D—C9D | 118.8 (8) |
| C6B—C7B—H7BA | 111.1 | C13D—C8D—C1D | 119.8 (8) |
| C3B—C7B—H7BA | 111.1 | C9D—C8D—C1D | 121.4 (9) |
| C6B—C7B—H7BB | 111.1 | C10D—C9D—C8D | 120.5 (10) |
| C3B—C7B—H7BB | 111.1 | C10D—C9D—H9D | 119.7 |
| H7BA—C7B—H7BB | 109.0 | C8D—C9D—H9D | 119.7 |
| C9B—C8B—C13B | 120.1 (9) | C9D—C10D—C11D | 120.2 (10) |
| C9B—C8B—C1B | 122.4 (9) | C9D—C10D—H10D | 119.9 |
| C13B—C8B—C1B | 117.4 (9) | C11D—C10D—H10D | 119.9 |
| C8B—C9B—C10B | 118.6 (12) | C10D—C11D—C12D | 120.3 (10) |
| C8B—C9B—H9B | 120.7 | C10D—C11D—H11D | 119.8 |
| C10B—C9B—H9B | 120.7 | C12D—C11D—H11D | 119.8 |
| C11B—C10B—C9B | 120.0 (12) | C13D—C12D—C11D | 120.4 (11) |
| C11B—C10B—H10B | 120.0 | C13D—C12D—H12D | 119.8 |
| C9B—C10B—H10B | 120.0 | C11D—C12D—H12D | 119.8 |
| C12B—C11B—C10B | 121.6 (11) | C12D—C13D—C8D | 119.7 (10) |
| C12B—C11B—H11B | 119.2 | C12D—C13D—H13D | 120.2 |
| C10B—C11B—H11B | 119.2 | C8D—C13D—H13D | 120.2 |
| C11B—C12B—C13B | 119.2 (12) | C15D—C14D—C19D | 116.7 (7) |
| C11B—C12B—H12B | 120.4 | C15D—C14D—C4D | 119.9 (7) |
| C13B—C12B—H12B | 120.4 | C19D—C14D—C4D | 123.2 (7) |
| C12B—C13B—C8B | 120.1 (10) | C16D—C15D—C14D | 122.8 (8) |
| C12B—C13B—H13B | 119.9 | C16D—C15D—H15D | 118.6 |
| C8B—C13B—H13B | 119.9 | C14D—C15D—H15D | 118.6 |
| C15B—C14B—C19B | 119.0 (8) | C15D—C16D—C17D | 119.5 (8) |
| C15B—C14B—C4B | 123.6 (7) | C15D—C16D—H16D | 120.3 |
| C19B—C14B—C4B | 117.4 (7) | C17D—C16D—H16D | 120.3 |
| C14B—C15B—C16B | 121.5 (8) | C18D—C17D—C16D | 119.6 (8) |
| C14B—C15B—H15B | 119.3 | C18D—C17D—C20D | 120.9 (8) |
| C16B—C15B—H15B | 119.3 | C16D—C17D—C20D | 119.5 (8) |
| C17B—C16B—C15B | 119.0 (8) | C19D—C18D—C17D | 120.6 (8) |
| C17B—C16B—H16B | 120.5 | C19D—C18D—H18D | 119.7 |
| C15B—C16B—H16B | 120.5 | C17D—C18D—H18D | 119.7 |
| C18B—C17B—C16B | 120.0 (7) | C18D—C19D—C14D | 120.9 (8) |

| | | | |
|---|---|---|---|
| C18B—C17B—C20B | 119.9 (7) | C18D—C19D—H19D | 119.6 |
| C16B—C17B—C20B | 120.1 (8) | C14D—C19D—H19D | 119.6 |
| C19B—C18B—C17B | 120.2 (8) | N6D—C20D—C17D | 179.7 (13) |
| C19B—C18B—H18B | 119.9 | N2D—C21D—C5D | 123.5 (7) |
| C17B—C18B—H18B | 119.9 | N2D—C21D—H21D | 118.3 |
| C18B—C19B—C14B | 120.3 (8) | C5D—C21D—H21D | 118.3 |
| C18B—C19B—H19B | 119.9 | N3D—C22D—C27D | 119.6 (7) |
| C14B—C19B—H19B | 119.9 | N3D—C22D—C23D | 124.0 (8) |
| N6B—C20B—C17B | 179.3 (10) | C27D—C22D—C23D | 116.3 (8) |
| N2B—C21B—C5B | 119.3 (7) | C24D—C23D—C22D | 121.2 (8) |
| N2B—C21B—H21B | 120.4 | C24D—C23D—N4D | 116.5 (7) |
| C5B—C21B—H21B | 120.4 | C22D—C23D—N4D | 122.1 (8) |
| N3B—C22B—C23B | 123.8 (7) | C25D—C24D—C23D | 119.7 (8) |
| N3B—C22B—C27B | 119.2 (7) | C25D—C24D—H24D | 120.2 |
| C23B—C22B—C27B | 117.0 (7) | C23D—C24D—H24D | 120.2 |
| C24B—C23B—C22B | 122.4 (7) | C24D—C25D—C26D | 121.2 (8) |
| C24B—C23B—N4B | 115.6 (7) | C24D—C25D—N5D | 119.3 (8) |
| C22B—C23B—N4B | 122.0 (7) | C26D—C25D—N5D | 119.5 (8) |
| C23B—C24B—C25B | 118.2 (7) | C27D—C26D—C25D | 120.3 (8) |
| C23B—C24B—H24B | 120.9 | C27D—C26D—H26D | 119.8 |
| C25B—C24B—H24B | 120.9 | C25D—C26D—H26D | 119.8 |
| C24B—C25B—C26B | 121.3 (7) | C26D—C27D—C22D | 121.3 (8) |
| C24B—C25B—N5B | 119.0 (7) | C26D—C27D—H27D | 119.4 |
| C26B—C25B—N5B | 119.8 (7) | C22D—C27D—H27D | 119.4 |
| C27B—C26B—C25B | 120.4 (8) | C29D—C28D—C6D | 124.2 (9) |
| C27B—C26B—H26B | 119.8 | C29D—C28D—H28D | 117.9 |
| C25B—C26B—H26B | 119.8 | C6D—C28D—H28D | 117.9 |
| C26B—C27B—C22B | 120.7 (7) | C28D—C29D—H29G | 120.0 |
| C26B—C27B—H27B | 119.6 | C28D—C29D—H29H | 120.0 |
| C22B—C27B—H27B | 119.6 | H29G—C29D—H29H | 120.0 |
| C29B—C28B—C6B | 125.8 (8) | Cl2S—C1S—Cl1S | 110.9 (9) |
| C29B—C28B—H28B | 117.1 | Cl2S—C1S—H1SA | 109.5 |
| C6B—C28B—H28B | 117.1 | Cl1S—C1S—H1SA | 109.5 |
| C28B—C29B—H29C | 120.0 | Cl2S—C1S—H1SB | 109.5 |
| C28B—C29B—H29D | 120.0 | Cl1S—C1S—H1SB | 109.5 |
| H29C—C29B—H29D | 120.0 | H1SA—C1S—H1SB | 108.1 |
| C2C—O1C—C1C | 105.9 (6) | Cl3S—C2S—Cl4S | 113.0 (10) |
| C1C—N1C—C3C | 106.6 (7) | Cl3S—C2S—H2SA | 109.0 |
| C21C—N2C—N3C | 115.4 (7) | Cl4S—C2S—H2SA | 109.0 |
| C22C—N3C—N2C | 119.4 (7) | Cl3S—C2S—H2SB | 109.0 |

| | | | |
|---|---|---|---|
| C22C—N3C—H3C | 120.3 | Cl4S—C2S—H2SB | 109.0 |
| N2C—N3C—H3C | 120.3 | H2SA—C2S—H2SB | 107.8 |

*Hydrogen-bond geometry (Å, º) for compound 5e´*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N3*A*—H3*A*···O3*A* | 0.88 | 1.97 | 2.591 (9) | 127 |
| N3*B*—H3*B*···O3*B* | 0.88 | 2.01 | 2.621 (9) | 125 |
| N3*B*—H3*B*···O3*C* | 0.88 | 2.63 | 3.420 (9) | 151 |
| N3*C*—H3*C*···O3*B* | 0.88 | 2.57 | 3.346 (9) | 148 |
| N3*C*—H3*C*···O3*C* | 0.88 | 2.02 | 2.622 (9) | 125 |
| N3*D*—H3*D*···O3*D* | 0.88 | 2.01 | 2.630 (9) | 126 |

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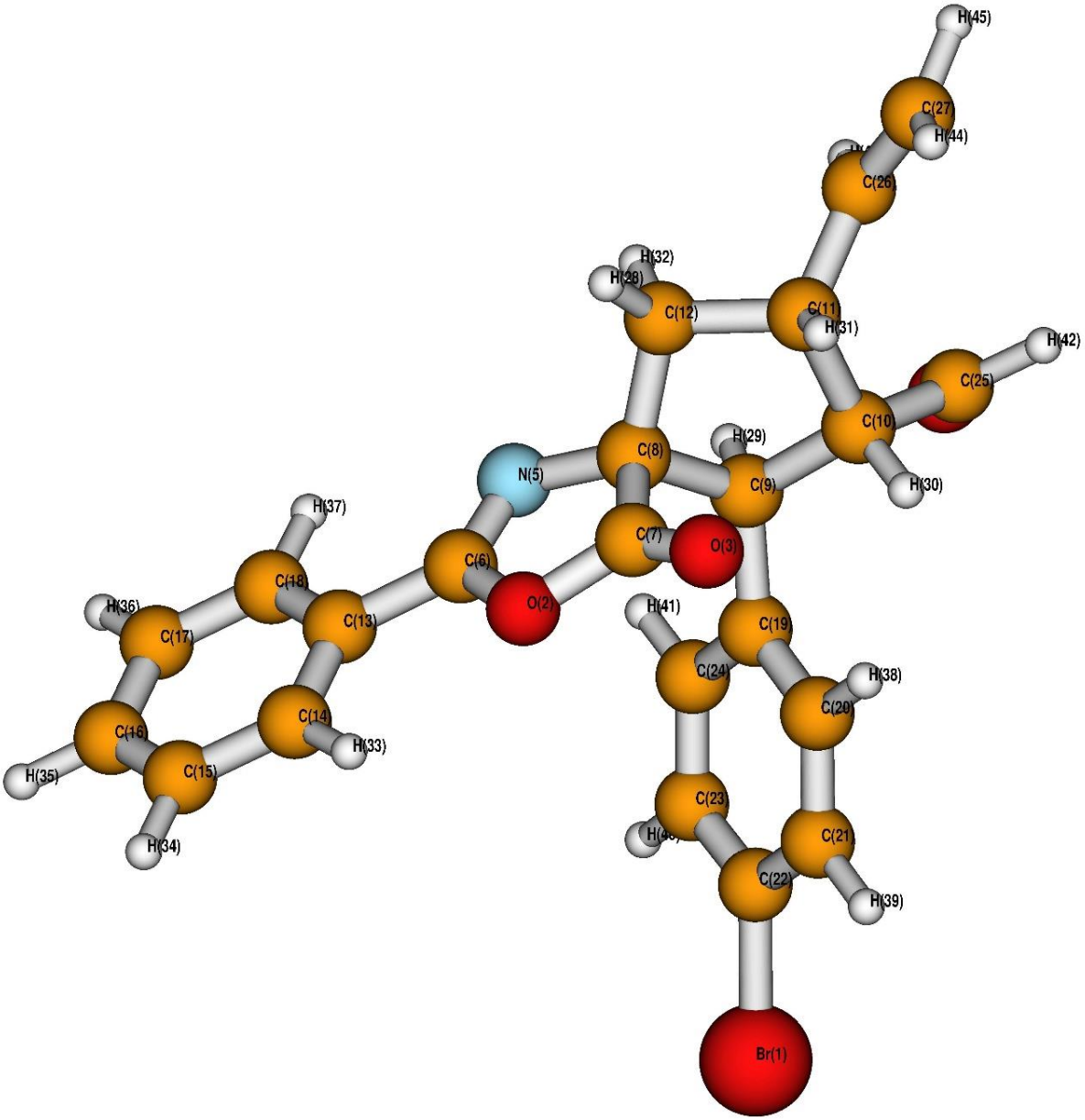
# 10. Computational studies

**Computational details**

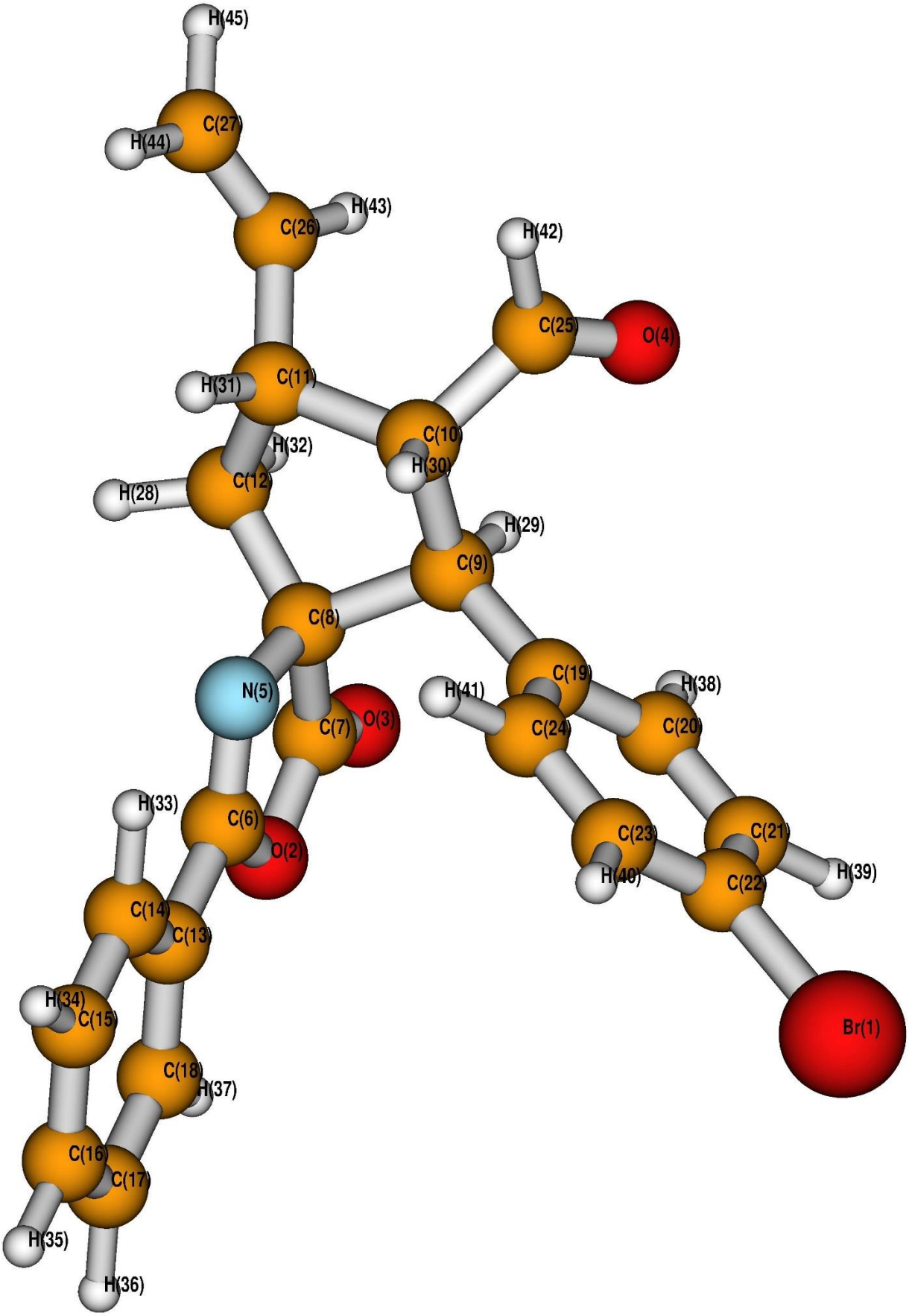
Computational studies of **4c** and **4c´** were carried out using Gaussian 16, Revision A.03.[i] Geometry optimizations employed the M11 functional[ii] and the 6-311+G(d,p) basis set on all atoms. Magnetic shielding constants were computed using the Gauge-Independent Atomic Orbital (GIAO) method[iii] by employing the HSEh1PBE functional[iv], the 6-311++G(3d,p) basis set for the bromium and the EPR-III basis set[v] for all other atoms of the optimized geometries. The solvent effects of chloroform were considered by employing the Polarizable Continuum Model.[vi]

**Atom labelling scheme and computed magnetic shieldings (isotropic values and anisotropy) for 4c**

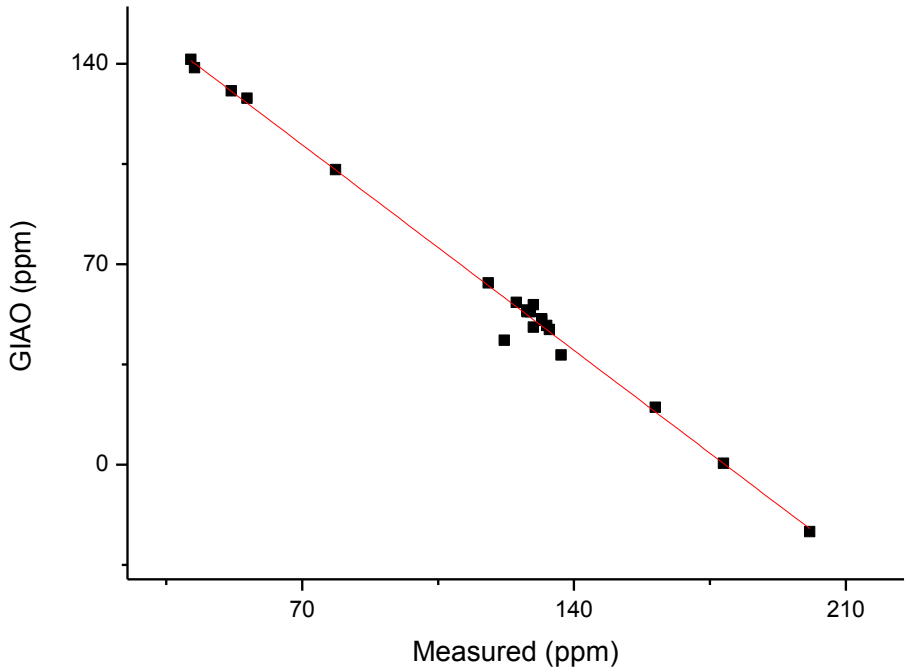


| | | | | | |
|---|---|---|---|---|---|
| 1 | Br | Isotropic = | 2031.6927 | Anisotropy = | 1352.6999 |
| 2 | O | Isotropic = | 9.4519 | Anisotropy = | 206.6257 |
| 3 | O | Isotropic = | -74.6858 | Anisotropy = | 630.8747 |
| 4 | O | Isotropic = | -334.1342 | Anisotropy = | 1076.3364 |
| 5 | N | Isotropic = | -13.4793 | Anisotropy = | 326.1122 |
| 6 | C | Isotropic = | 13.1321 | Anisotropy = | 81.4497 |
| 7 | C | Isotropic = | -6.3812 | Anisotropy = | 80.3267 |
| 8 | C | Isotropic = | 99.4478 | Anisotropy = | 7.6006 |
| 9 | C | Isotropic = | 122.5048 | Anisotropy = | 36.6521 |
| 10 | C | Isotropic = | 117.9886 | Anisotropy = | 36.4200 |
| 11 | C | Isotropic = | 132.8025 | Anisotropy = | 24.4803 |
| 12 | C | Isotropic = | 136.0188 | Anisotropy = | 40.9763 |
| 13 | C | Isotropic = | 50.0059 | Anisotropy = | 174.2649 |
| 14 | C | Isotropic = | 47.2960 | Anisotropy = | 198.4295 |
| 15 | C | Isotropic = | 46.1438 | Anisotropy = | 195.8184 |
| 16 | C | Isotropic = | 41.0054 | Anisotropy = | 201.8137 |
| 17 | C | Isotropic = | 46.0949 | Anisotropy = | 196.2215 |
| 18 | C | Isotropic = | 46.2135 | Anisotropy = | 197.2922 |
| 19 | C | Isotropic = | 39.2545 | Anisotropy = | 199.6105 |
| 20 | C | Isotropic = | 41.8059 | Anisotropy = | 168.0191 |
| 21 | C | Isotropic = | 43.5961 | Anisotropy = | 160.8996 |
| 22 | C | Isotropic = | 36.7581 | Anisotropy = | 118.9381 |
| 23 | C | Isotropic = | 44.8958 | Anisotropy = | 160.9014 |
| 24 | C | Isotropic = | 44.8998 | Anisotropy = | 191.0872 |
| 25 | C | Isotropic = | -33.6726 | Anisotropy = | 190.3998 |
| 26 | C | Isotropic = | 31.2464 | Anisotropy = | 167.0107 |
| 27 | C | Isotropic = | 57.5195 | Anisotropy = | 144.2961 |
| 28 | H | Isotropic = | 29.3050 | Anisotropy = | 7.7966 |
| 29 | H | Isotropic = | 27.1382 | Anisotropy = | 5.4265 |
| 30 | H | Isotropic = | 27.5376 | Anisotropy = | 5.2035 |
| 31 | H | Isotropic = | 27.3402 | Anisotropy = | 7.0285 |
| 32 | H | Isotropic = | 29.1482 | Anisotropy = | 6.6169 |
| 33 | H | Isotropic = | 22.6060 | Anisotropy = | 9.4625 |
| 34 | H | Isotropic = | 23.5537 | Anisotropy = | 5.9275 |
| 35 | H | Isotropic = | 23.5110 | Anisotropy = | 4.7108 |
| 36 | H | Isotropic = | 23.7061 | Anisotropy = | 5.2869 |
| 37 | H | Isotropic = | 23.4602 | Anisotropy = | 9.6548 |
| 38 | H | Isotropic = | 23.8749 | Anisotropy = | 8.5495 |
| 39 | H | Isotropic = | 23.9023 | Anisotropy = | 8.7395 |
| 40 | H | Isotropic = | 24.1896 | Anisotropy = | 9.7392 |
| 41 | H | Isotropic = | 23.9590 | Anisotropy = | 8.7535 |
| 42 | H | Isotropic = | 21.2772 | Anisotropy = | 5.3252 |
| 43 | H | Isotropic = | 25.3140 | Anisotropy = | 6.7716 |
| 44 | H | Isotropic = | 25.6912 | Anisotropy = | 7.0561 |
| 45 | H | Isotropic = | 25.9254 | Anisotropy = | 6.5688 |

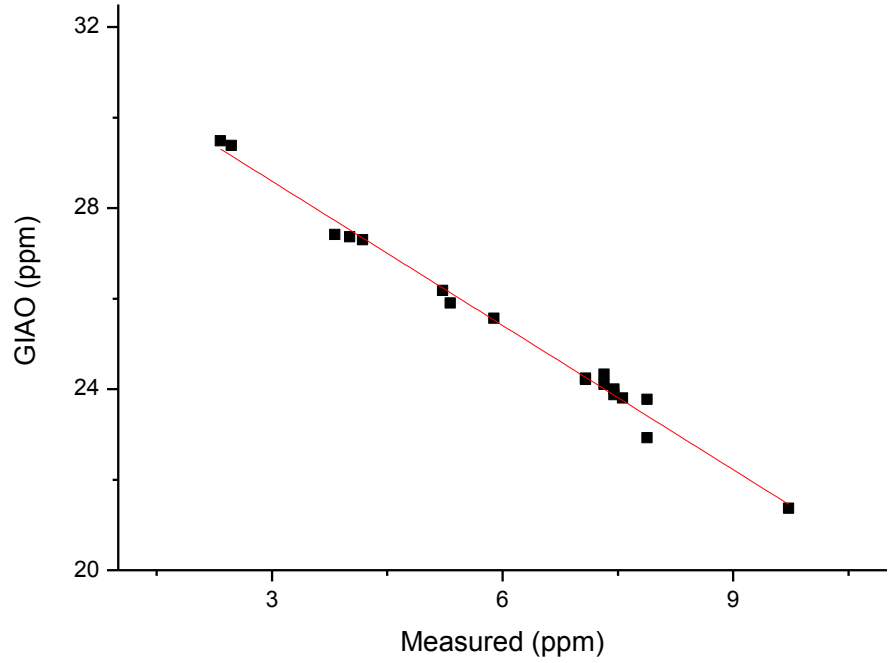
**Atom labelling scheme and computed magnetic shieldings (isotropic values and anisotropy) for 4c'**



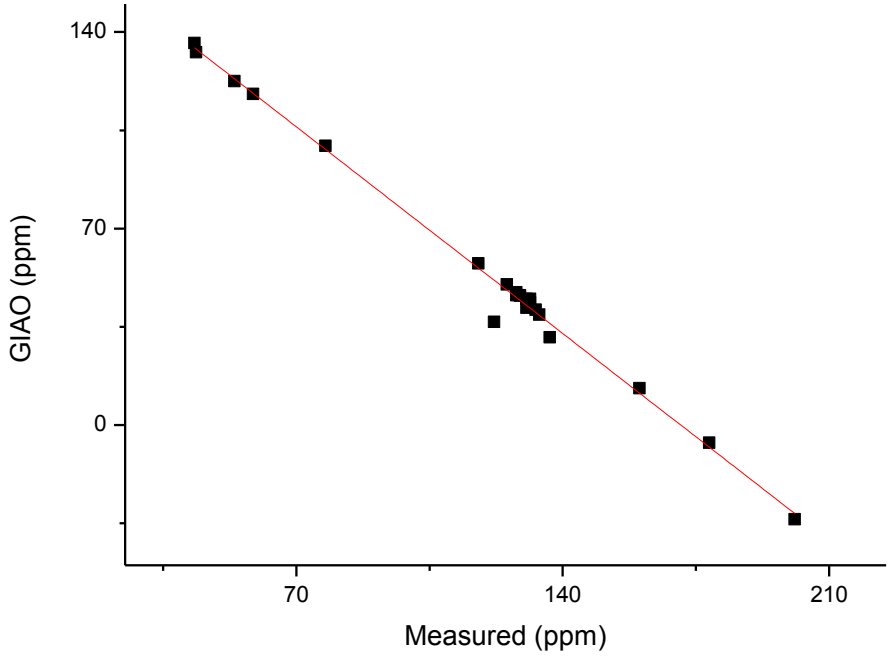
| | | | | | |
|---|---|---|---|---|---|
| 1 | Br | Isotropic = | 2034.3131 | Anisotropy = | 1360.4042 |
| 2 | O | Isotropic = | 16.6044 | Anisotropy = | 189.8274 |
| 3 | O | Isotropic = | -73.0280 | Anisotropy = | 608.0622 |
| 4 | O | Isotropic = | -325.1183 | Anisotropy = | 1064.0165 |
| 5 | N | Isotropic = | -8.5240 | Anisotropy = | 289.7751 |
| 6 | C | Isotropic = | 20.0258 | Anisotropy = | 80.6166 |
| 7 | C | Isotropic = | 0.4546 | Anisotropy = | 81.4048 |
| 8 | C | Isotropic = | 102.9876 | Anisotropy = | 14.8250 |
| 9 | C | Isotropic = | 130.5280 | Anisotropy = | 32.4947 |
| 10 | C | Isotropic = | 127.9674 | Anisotropy = | 33.9220 |
| 11 | C | Isotropic = | 138.6354 | Anisotropy = | 24.6054 |
| 12 | C | Isotropic = | 141.4835 | Anisotropy = | 41.4552 |
| 13 | C | Isotropic = | 56.6879 | Anisotropy = | 167.0575 |
| 14 | C | Isotropic = | 53.4443 | Anisotropy = | 189.7145 |
| 15 | C | Isotropic = | 53.4576 | Anisotropy = | 187.7867 |
| 16 | C | Isotropic = | 48.5445 | Anisotropy = | 192.7884 |
| 17 | C | Isotropic = | 53.3680 | Anisotropy = | 187.7878 |
| 18 | C | Isotropic = | 54.0031 | Anisotropy = | 191.5701 |
| 19 | C | Isotropic = | 47.1831 | Anisotropy = | 192.5850 |
| 20 | C | Isotropic = | 55.7923 | Anisotropy = | 179.4599 |
| 21 | C | Isotropic = | 50.3592 | Anisotropy = | 155.4647 |
| 22 | C | Isotropic = | 43.4801 | Anisotropy = | 115.2811 |
| 23 | C | Isotropic = | 50.9847 | Anisotropy = | 154.6520 |
| 24 | C | Isotropic = | 47.9920 | Anisotropy = | 167.1691 |
| 25 | C | Isotropic = | -23.4143 | Anisotropy = | 180.5575 |
| 26 | C | Isotropic = | 38.2441 | Anisotropy = | 159.2140 |
| 27 | C | Isotropic = | 63.5074 | Anisotropy = | 138.7815 |
| 28 | H | Isotropic = | 29.4859 | Anisotropy = | 7.5738 |
| 29 | H | Isotropic = | 27.2973 | Anisotropy = | 5.0060 |
| 30 | H | Isotropic = | 27.3678 | Anisotropy = | 5.6003 |
| 31 | H | Isotropic = | 27.4172 | Anisotropy = | 6.4021 |
| 32 | H | Isotropic = | 29.3857 | Anisotropy = | 7.0513 |
| 33 | H | Isotropic = | 23.7744 | Anisotropy = | 9.7626 |
| 34 | H | Isotropic = | 24.0028 | Anisotropy = | 5.5719 |
| 35 | H | Isotropic = | 23.8027 | Anisotropy = | 4.7057 |
| 36 | H | Isotropic = | 23.8758 | Anisotropy = | 5.7571 |
| 37 | H | Isotropic = | 22.9272 | Anisotropy = | 9.4909 |
| 38 | H | Isotropic = | 24.2109 | Anisotropy = | 10.1028 |
| 39 | H | Isotropic = | 24.1030 | Anisotropy = | 9.2854 |
| 40 | H | Isotropic = | 24.3306 | Anisotropy = | 8.9011 |
| 41 | H | Isotropic = | 24.2407 | Anisotropy = | 7.7408 |
| 42 | H | Isotropic = | 21.3670 | Anisotropy = | 5.2997 |
| 43 | H | Isotropic = | 25.5691 | Anisotropy = | 6.5888 |
| 44 | H | Isotropic = | 25.9031 | Anisotropy = | 7.0405 |
| 45 | H | Isotropic = | 26.1815 | Anisotropy = | 6.5381 |



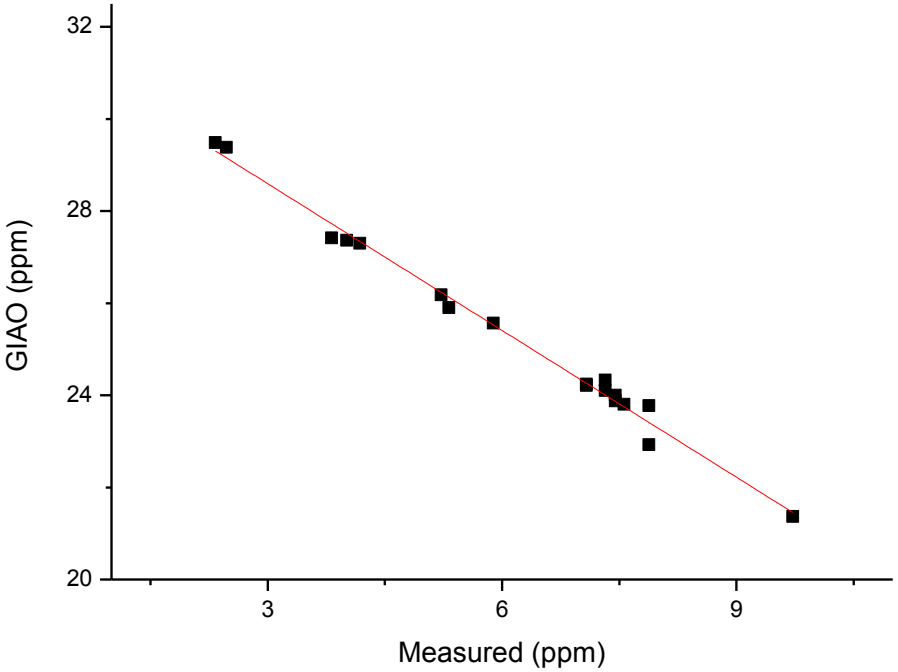

Correlation diagram of experimental NMR shifts for the carbon atoms of **4c** and their respective magnetic shielding constants computed by GIAO.




Correlation diagram of experimental NMR shifts for the hydrogen atoms of **4c** and their respective magnetic shielding constants computed by GIAO.




Correlation diagram of experimental NMR shifts for the carbon atoms of **4c'** and their respective magnetic shielding constants computed by GIAO.

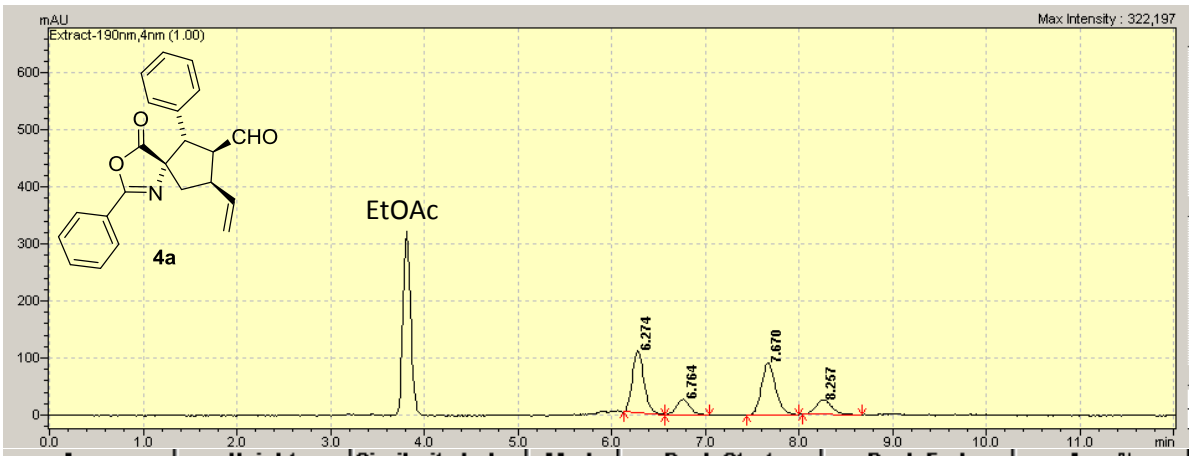



Correlation diagram of experimental NMR shifts for the hydrogen atoms of **4c** and their respective magnetic shielding constants computed by GIAO.

## 11. Chiral HPLC analysis

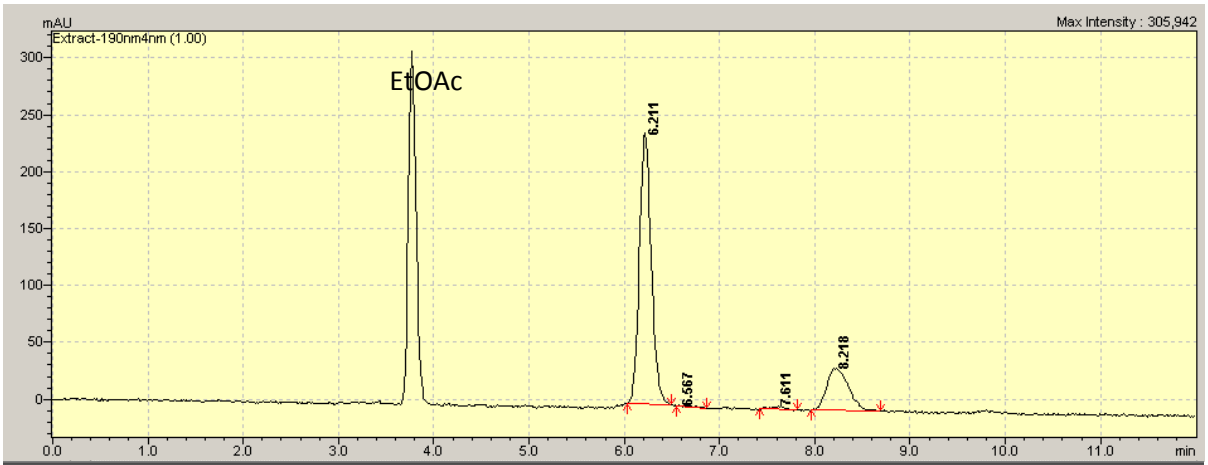
**Racemate – 4a and 4a´**

Column IA (heptane:i-ProOH 90:10, 1 mL flow, 25 °C)




| Area | Height | Similarity Index | Mark | Peak Start | Peak End | Area% |
|---|---|---|---|---|---|---|
| 933133 | 108520 | 0.000000 | | 6.133 | 6.571 | 38.3604 |
| 266459 | 27576 | 0.000000 | | 6.571 | 7.051 | 10.9539 |
| 974615 | 91211 | 0.000000 | | 7.445 | 8.000 | 40.0658 |
| 258332 | 24203 | 0.000000 | | 8.096 | 8.459 | 10.6199 |

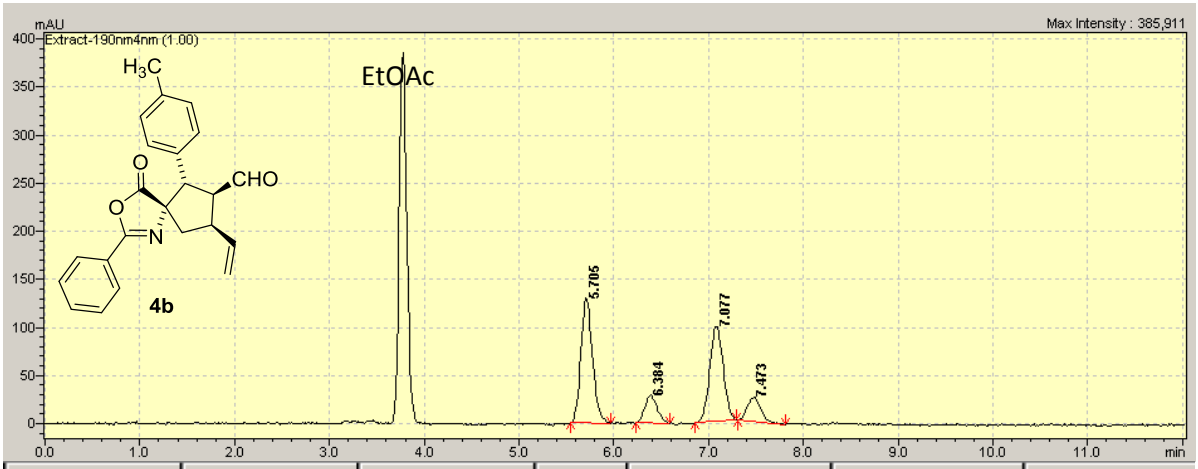
**Chiral – 4a and 4a´**




| Area | Height | Similarity Index | Mark | Peak Start | Peak End | Area% |
|---|---|---|---|---|---|---|
| 2066168 | 237555 | 0.000000 | | 6.027 | 6.496 | 76.9871 |
| 9146 | 963 | 0.000000 | | 6.549 | 6.869 | 0.3408 |
| 18141 | 2764 | 0.000000 | | 7.424 | 7.819 | 0.6759 |
| 590329 | 36610 | 0.000000 | | 7.957 | 8.693 | 21.9961 |

**Racemate – 4b and 4b´**

Column IA (heptane:*i*-ProOH 90:10, 1 mL flow, 25 °C)

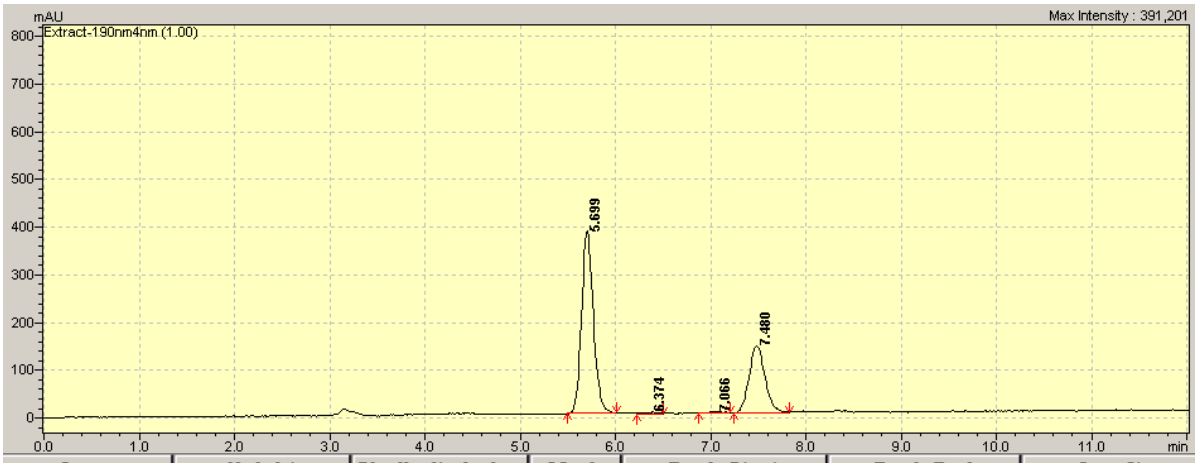






| Area | Height | Similarity Index | Mark | Peak Start | Peak End | Area% |
|---|---|---|---|---|---|---|
| 1003770 | 125028 | 0.000000 | | 5.579 | 5.888 | 40.3921 |
| 257989 | 28972 | 0.000000 | | 6.240 | 6.592 | 10.3816 |
| 980619 | 98777 | 0.000000 | | 6.859 | 7.296 | 39.4605 |
| 242688 | 25164 | 0.000000 | | 7.307 | 7.808 | 9.7658 |

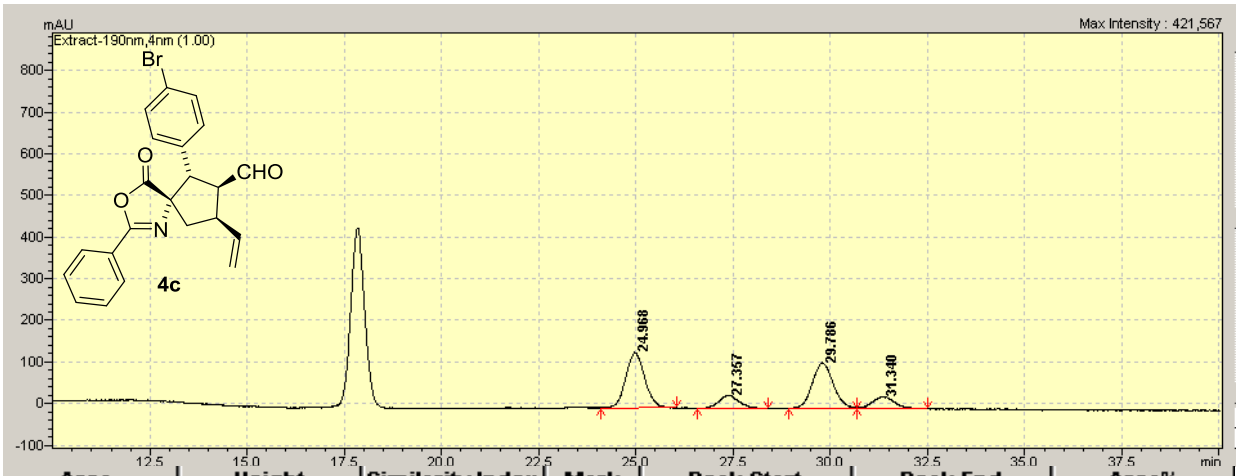
**Chiral – 4b and 4b´**




| Area | Height | Similarity Index | Mark | Peak Start | Peak End | Area% |
|---|---|---|---|---|---|---|
| 3293406 | 380975 | 0.000000 | | 5.493 | 6.016 | 66.4238 |
| 29752 | 3376 | 0.000000 | | 6.219 | 6.507 | 0.6001 |
| 31483 | 3225 | 0.000000 | | 6.869 | 7.200 | 0.6350 |
| 1603527 | 140652 | 0.000000 | | 7.243 | 7.829 | 32.3411 |

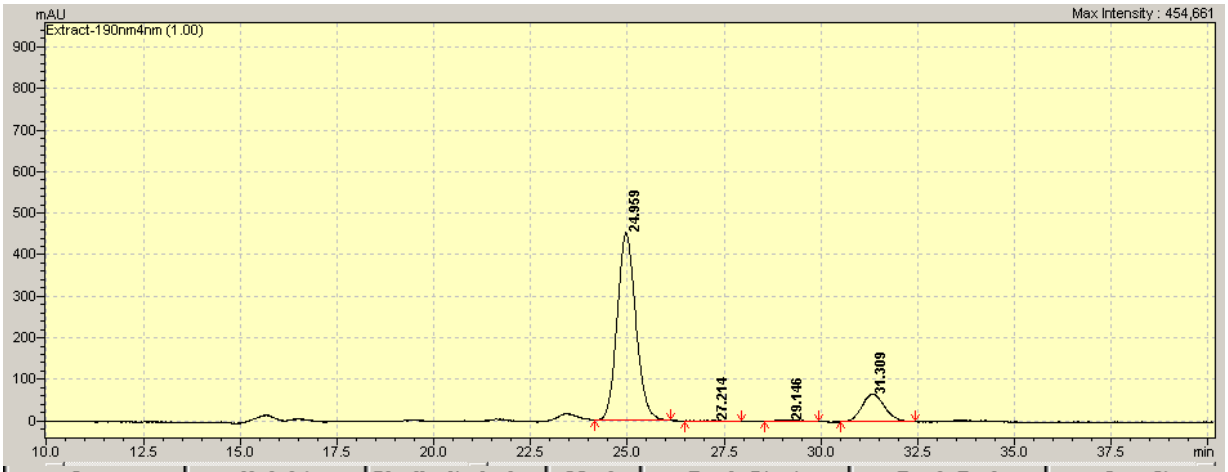
**Racemate – 4c and 4c´**

Column IA (heptane:*i*-PrOH 70:30, 0.2 mL flow, 25 °C)




| Area | Height | Similarity Index | Mark | Peak Start | Peak End | Area% |
|---|---|---|---|---|---|---|
| 4080512 | 128446 | 0.000000 | | 24.427 | 25.653 | 39.3002 |
| 1119056 | 31520 | 0.000000 | | 26.592 | 28.405 | 10.7778 |
| 4101480 | 109729 | 0.000000 | | 28.917 | 30.667 | 39.5022 |
| 1081880 | 28812 | 0.000000 | V | 30.667 | 32.491 | 10.4198 |

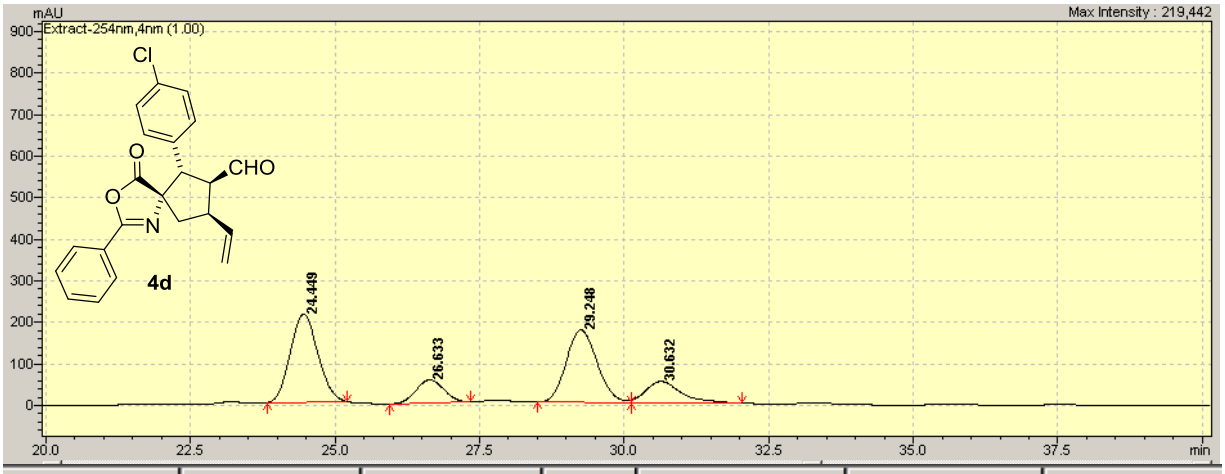
**Chiral – 4c and 4c´**




| Area | Height | Similarity Index | Mark | Peak Start | Peak End | Area% |
|---|---|---|---|---|---|---|
| 15111964 | 453139 | 0.000000 | | 24.160 | 26.400 | 83.5909 |
| 75684 | 2601 | 0.000000 | | 26.816 | 27.872 | 0.4186 |
| 134951 | 3805 | 0.000000 | | 28.587 | 29.941 | 0.7465 |
| 2755887 | 67107 | 0.000000 | | 30.571 | 32.491 | 15.2440 |

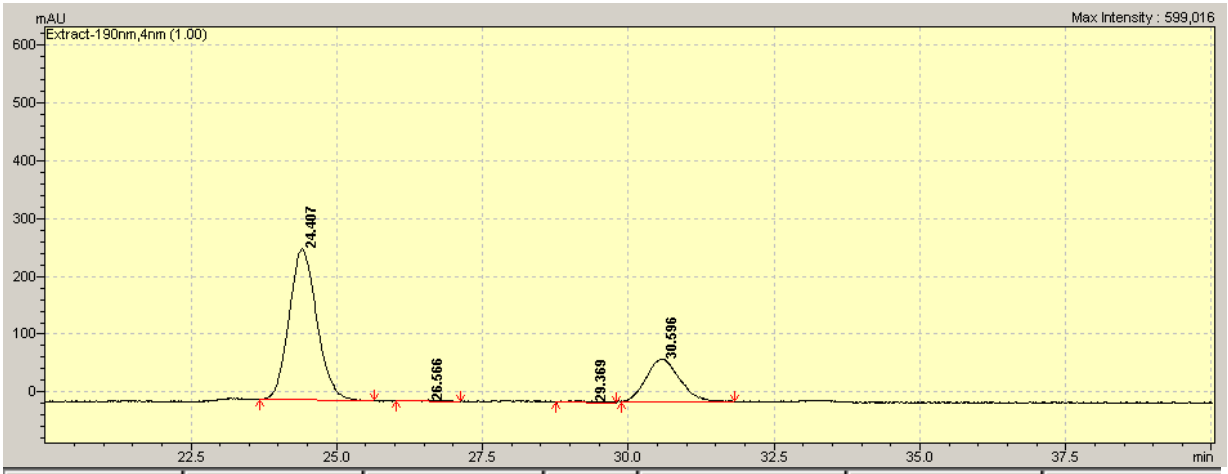
**Racemate – 4d and 4d´**

Column IA (heptane:*i*-PrOH, 70:30, 0.2 mL flow, 25 °C)




| Area | Height | Similarity Index | Mark | Peak Start | Peak End | Area% |
|---|---|---|---|---|---|---|
| 6578820 | 204969 | 0.000000 | | 23.947 | 25.120 | 38.4041 |
| 1864433 | 55492 | 0.000000 | | 25.941 | 27.349 | 10.8837 |
| 6482728 | 174838 | 0.000000 | | 28.512 | 30.123 | 37.8431 |
| 2204539 | 51483 | 0.000000 | V | 30.123 | 32.032 | 12.8691 |

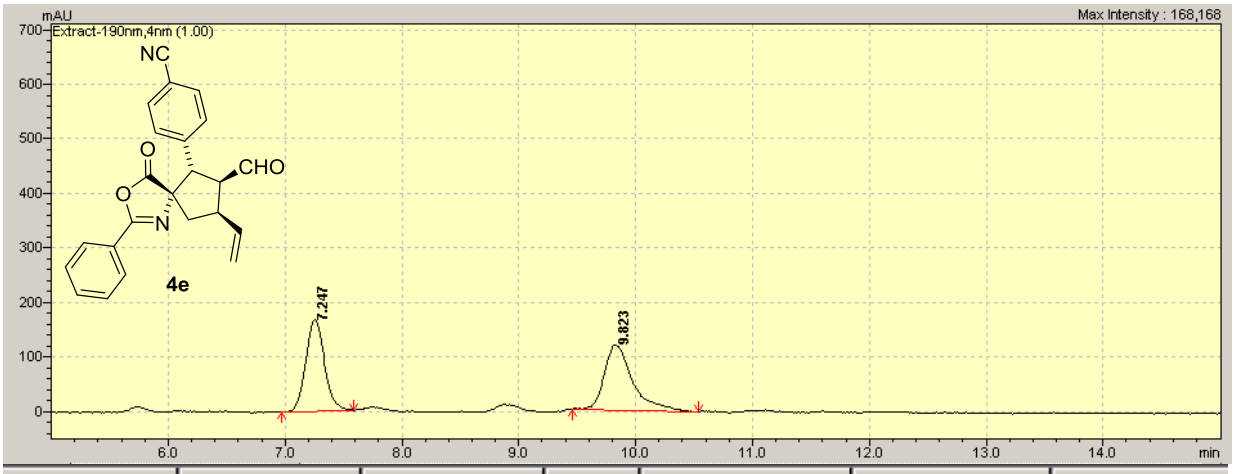
**Chiral – 4d and 4d´**




| Area | Height | Similarity Index | Mark | Peak Start | Peak End | Area% |
|---|---|---|---|---|---|---|
| 8705437 | 262247 | 0.000000 | | 23.680 | 25.643 | 74.1802 |
| 29803 | 2189 | 0.000000 | | 26.027 | 27.115 | 0.2540 |
| 61173 | 2315 | 0.000000 | | 28.757 | 29.803 | 0.5213 |
| 2939114 | 74052 | 0.000000 | | 29.888 | 31.819 | 25.0446 |

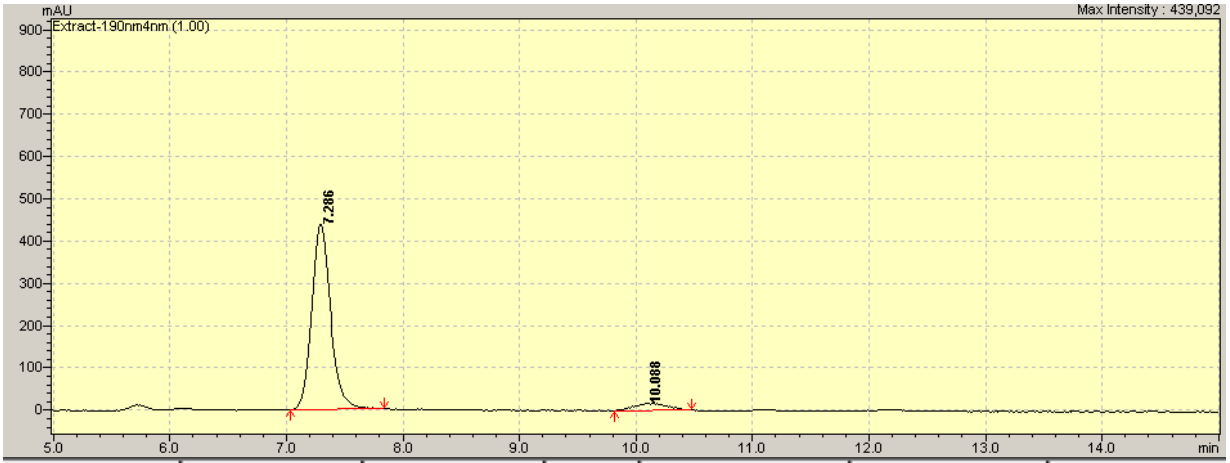
**Racemate – 4e**

Column IA (heptane:*i*-PrOH, 80:20, 1 mL flow, 25 °C)




| Area | Height | Similarity Index | Mark | Peak Start | Peak End | Area% |
|---|---|---|---|---|---|---|
| 1873694 | 167997 | 0.000000 | | 6.965 | 7.584 | 50.7445 |
| 1818716 | 116481 | 0.000000 | | 9.579 | 10.325 | 49.2555 |

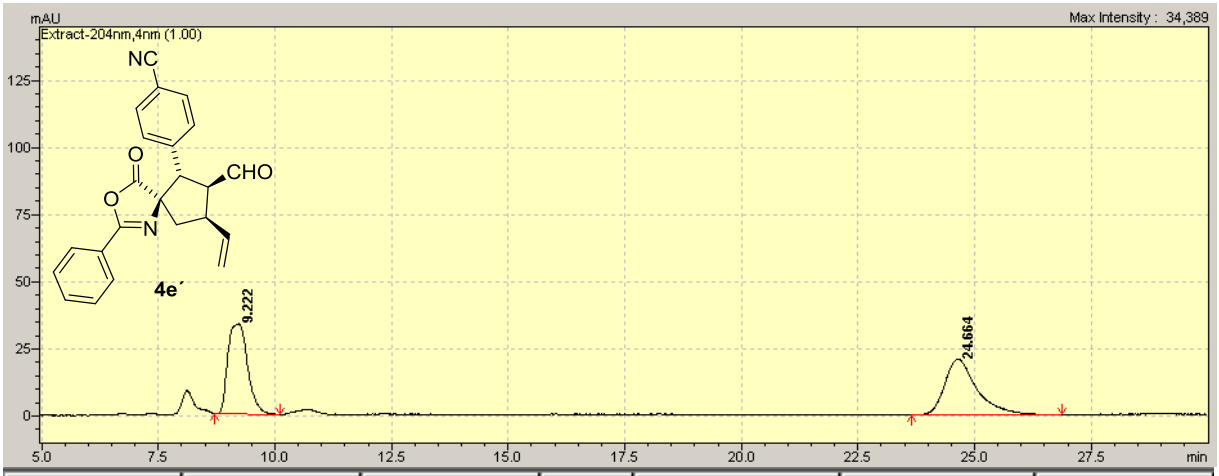
**Chiral – 4e**




| Area | Height | Similarity Index | Mark | Peak Start | Peak End | Area% |
|---|---|---|---|---|---|---|
| 4890796 | 436404 | 0.000000 | | 7.029 | 7.840 | 93.9061 |
| 317381 | 16160 | 0.000000 | | 9.813 | 10.475 | 6.0939 |

**Racemate – 4e´**

Column IC (heptane:*i*-PrOH, 90:10, 1 mL flow, 25 °C)



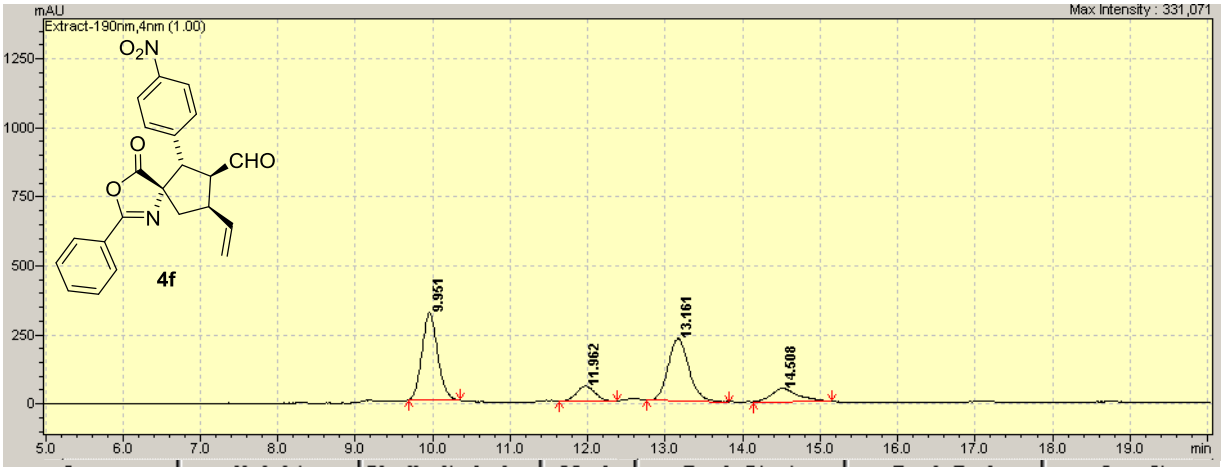

| Area | Height | Similarity Index | Mark | Peak Start | Peak End | Area% |
|---|---|---|---|---|---|---|
| 985879 | 33597 | 0.000000 | | 8.715 | 10.101 | 49.5783 |
| 1002651 | 20775 | 0.000000 | | 23.648 | 26.880 | 50.4217 |

**Chiral – 4e´**


| Area | Height | Similarity Index | Mark | Peak Start | Peak End | Area% |
|---|---|---|---|---|---|---|
| 23382 | 1275 | 0.000000 | | 8.885 | 9.824 | 1.3575 |
| 1698982 | 36852 | 0.000000 | | 23.360 | 26.987 | 98.6425 |

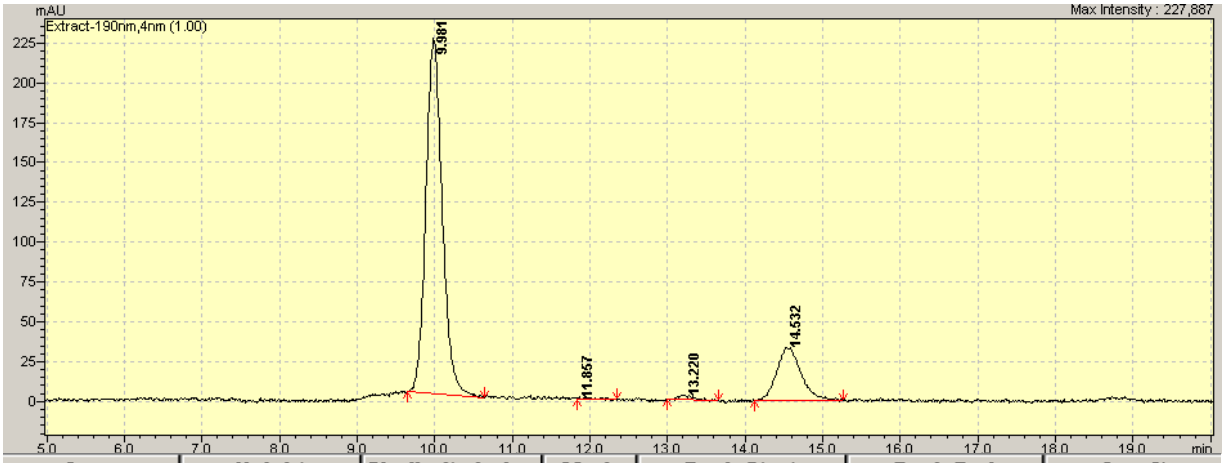
**Racemate – 4f and 4f´**

Column IA (heptane:*i*-PrOH, 90:10, 1 mL flow, 25 °C)



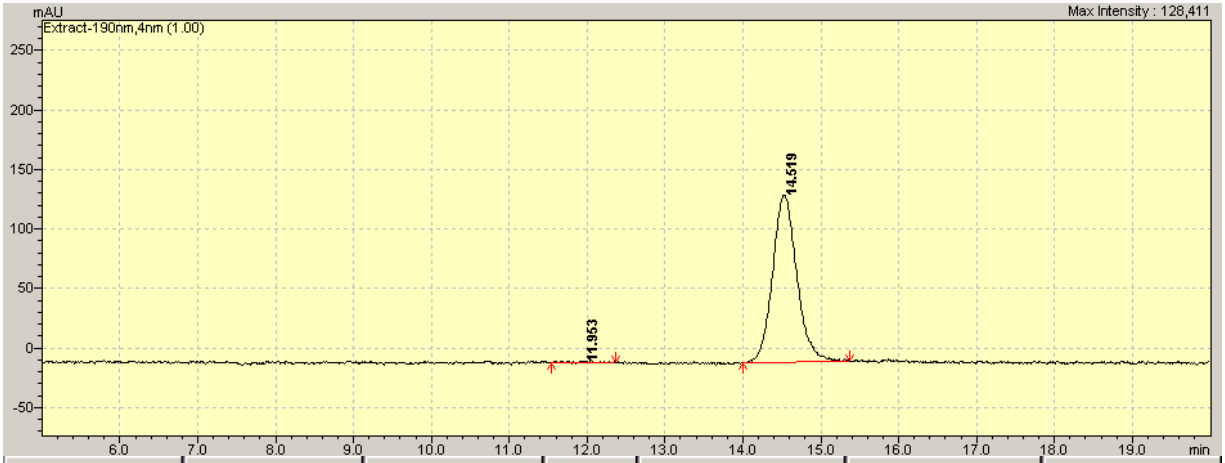

| Area | Height | Similarity Index | Mark | Peak Start | Peak End | Area% |
|---|---|---|---|---|---|---|
| 4239531 | 309870 | 0.000000 | | 9.728 | 10.304 | 41.5747 |
| 874870 | 54228 | 0.000000 | | 11.627 | 12.373 | 8.5794 |
| 4185631 | 225829 | 0.000000 | | 12.757 | 13.824 | 41.0462 |
| 897344 | 43221 | 0.000000 | | 14.208 | 14.987 | 8.7998 |

**Chiral – 4f and 4f´**




| Area | Height | Similarity Index | Mark | Peak Start | Peak End | Area% |
|---|---|---|---|---|---|---|
| 3271520 | 222764 | 0.000000 | | 9.653 | 10.645 | 81.2266 |
| 4085 | 1123 | 0.000000 | | 11.840 | 12.352 | 0.1014 |
| 35034 | 2830 | 0.000000 | | 13.003 | 13.653 | 0.8698 |
| 717009 | 33178 | 0.000000 | | 14.123 | 15.264 | 17.8022 |

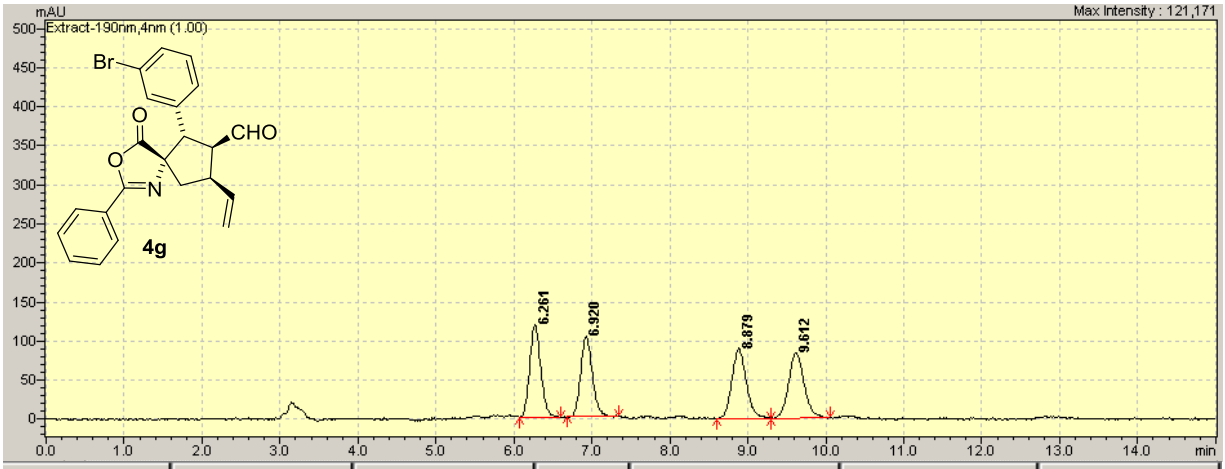
**Chiral – 4f´**




| Area | Height | Similarity Index | Mark | Peak Start | Peak End | Area% |
|---|---|---|---|---|---|---|
| 9994 | 1209 | 0.000000 | | 11.541 | 12.373 | 0.3288 |
| 3029784 | 140041 | 0.000000 | | 14.005 | 15.371 | 99.6712 |

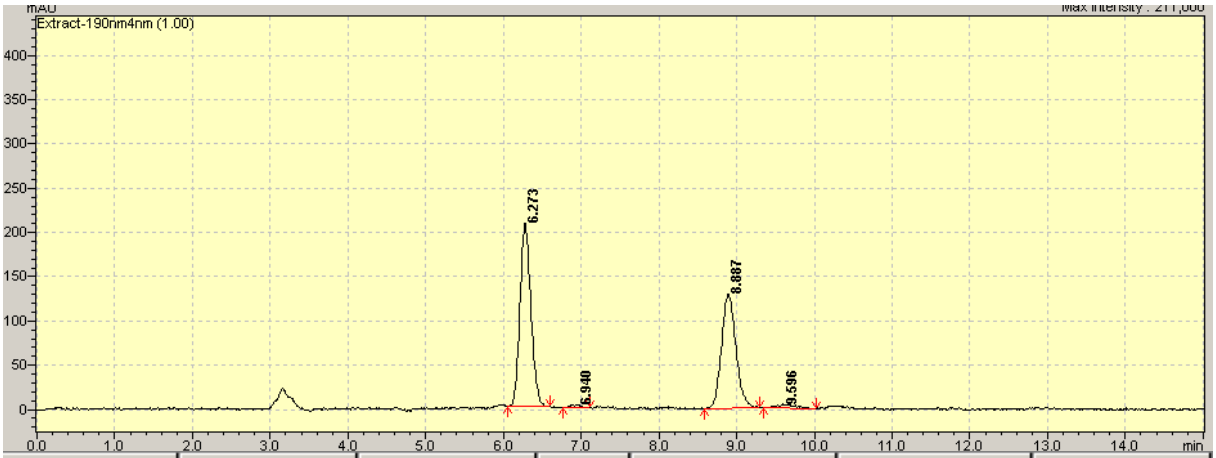
**Racemate – 4g and 4g´**

Column IA (heptane:*i*-PrOH 90:10, 1 mL flow, 25 °C)




| Area | Height | Similarity Index | Mark | Peak Start | Peak End | Area% |
|---|---|---|---|---|---|---|
| 1167140 | 118592 | 0.000000 | | 6.069 | 6.603 | 25.6947 |
| 1067635 | 103211 | 0.000000 | | 6.688 | 7.339 | 23.5041 |
| 1154262 | 90299 | 0.000000 | | 8.608 | 9.301 | 25.4111 |
| 1153307 | 83105 | 0.000000 | V | 9.301 | 10.059 | 25.3901 |

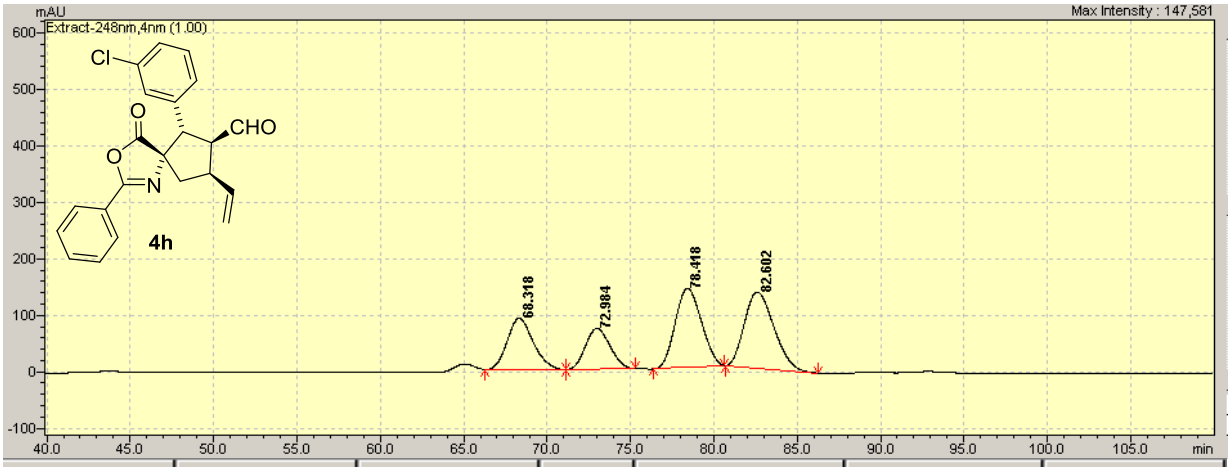
**Chiral – 4g and 4g´**




| Area | Height | Similarity Index | Mark | Peak Start | Peak End | Area% |
|---|---|---|---|---|---|---|
| 2015065 | 207087 | 0.000000 | | 6.059 | 6.603 | 53.1421 |
| 32387 | 3713 | 0.000000 | | 6.763 | 7.115 | 0.8541 |
| 1662126 | 129659 | 0.000000 | | 8.587 | 9.301 | 43.8342 |
| 82266 | 4764 | 0.000000 | | 9.344 | 10.016 | 2.1695 |

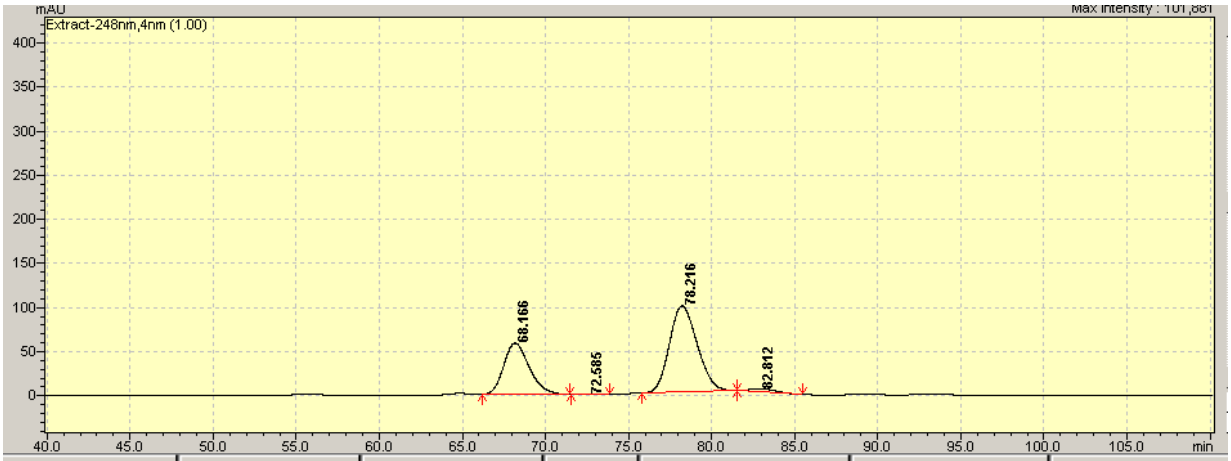
**Racemate – 4h and 4h´**

Column IC (heptane: *i*-PrOH, 90:10, 0.1 mL flow, 15 °C)




| Area | Height | Similarity Index | Mark | Peak Start | Peak End | Area% |
|---|---|---|---|---|---|---|
| 7681198 | 80317 | 0.000000 | | 67.040 | 70.283 | 16.3371 |
| 7424167 | 72187 | 0.000000 | | 71.125 | 75.328 | 15.7904 |
| 15309238 | 139796 | 0.000000 | | 76.341 | 80.651 | 32.5610 |
| 16602436 | 134825 | 0.000000 | | 80.725 | 86.251 | 35.3115 |

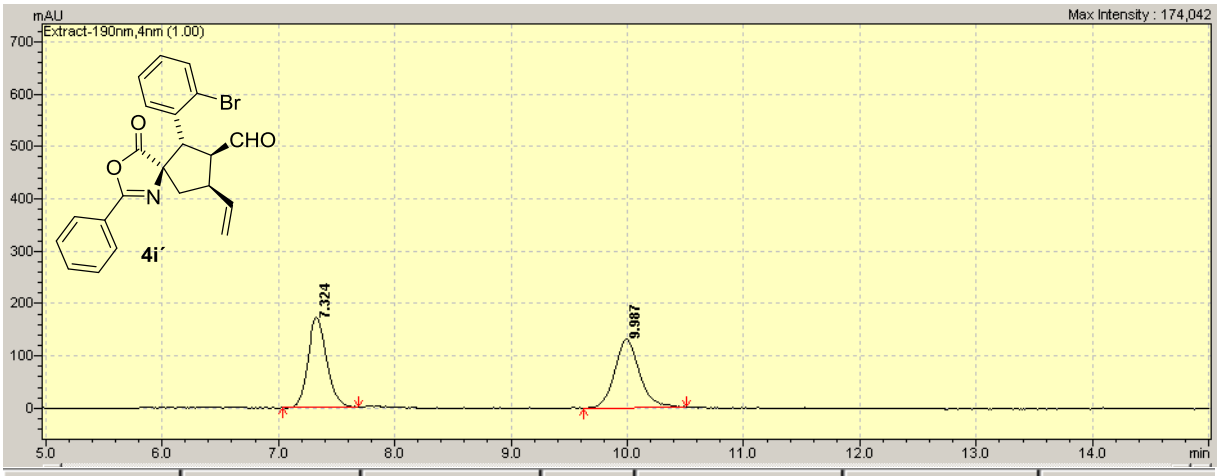
**Chiral – 4h and 4h´**




| Area | Height | Similarity Index | Mark | Peak Start | Peak End | Area% |
|---|---|---|---|---|---|---|
| 6235655 | 58139 | 0.000000 | | 66.219 | 71.499 | 34.6330 |
| 9262 | 169 | 0.000000 | | 71.509 | 73.867 | 0.0514 |
| 11339026 | 97543 | 0.000000 | | 75.829 | 81.568 | 62.9773 |
| 420989 | 3816 | 0.000000 | | 81.568 | 85.461 | 2.3382 |

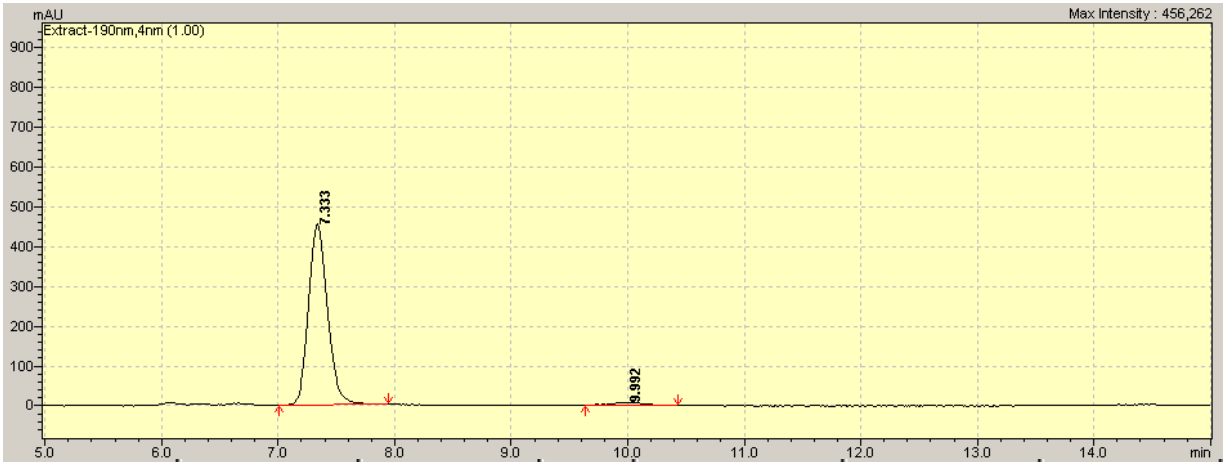
**Racemate – 4i´**

Column IA (heptane:*i*-PrOH 90:10, 1 mL flow, 25 °C)




| Area | Height | Similarity Index | Mark | Peak Start | Peak End | Area% |
|---|---|---|---|---|---|---|
| 1903335 | 171482 | 0.000000 | | 7.040 | 7.691 | 49.0802 |
| 1974673 | 132363 | 0.000000 | | 9.621 | 10.507 | 50.9198 |

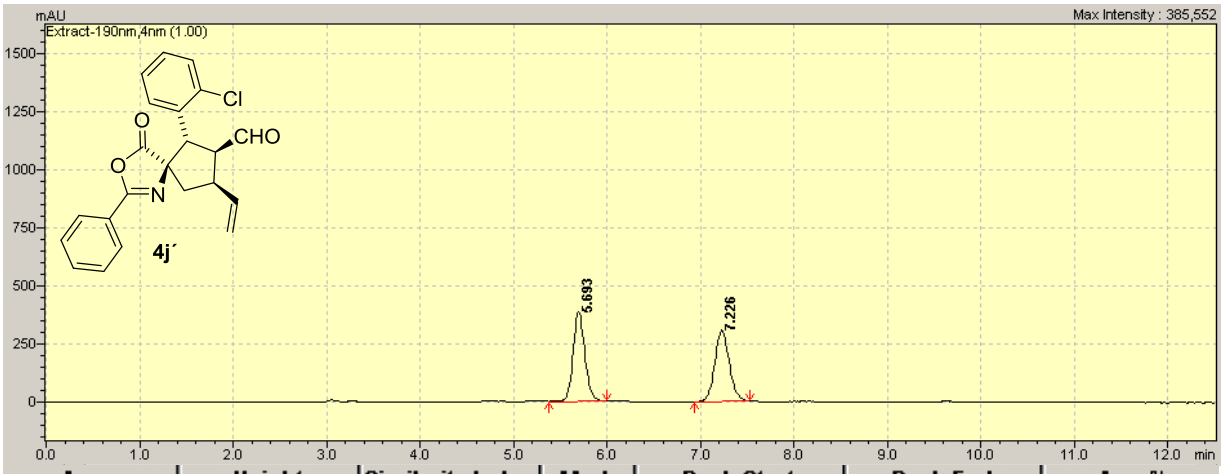
**Chiral – 4i´**




| Area | Height | Similarity Index | Mark | Peak Start | Peak End | Area% |
|---|---|---|---|---|---|---|
| 5034754 | 453575 | 0.000000 | | 7.008 | 7.947 | 97.0954 |
| 150613 | 7459 | 0.000000 | | 9.632 | 10.432 | 2.9046 |

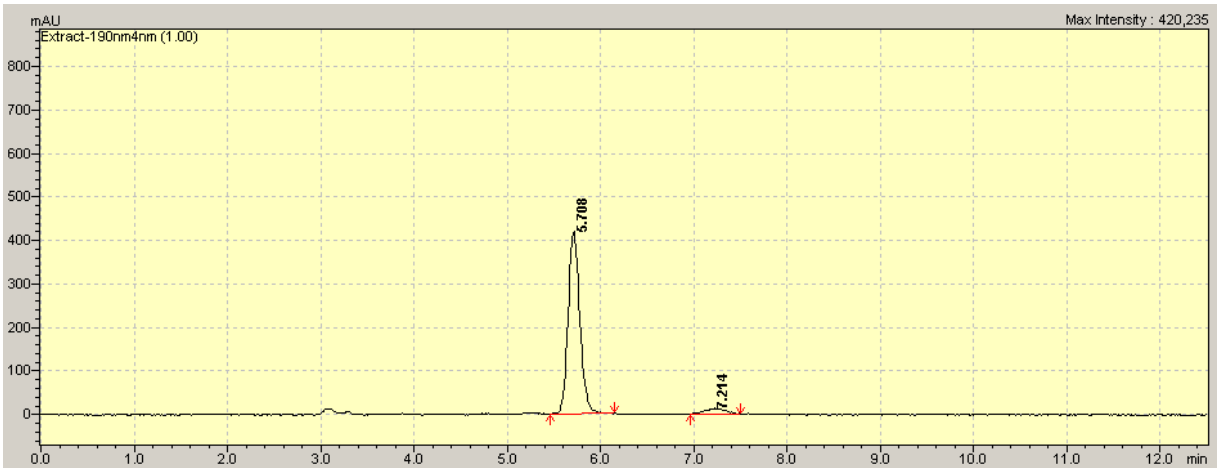
**Racemate – 4j´**

Column IA (heptane:*i*-PrOH, 80:20, 1 mL flow, 25 °C)




| Area | Height | Similarity Index | Mark | Peak Start | Peak End | Area% |
|---|---|---|---|---|---|---|
| 3372929 | 382557 | 0.000000 | | 5.376 | 6.005 | 50.3889 |
| 3320858 | 306638 | 0.000000 | | 6.944 | 7.531 | 49.6111 |

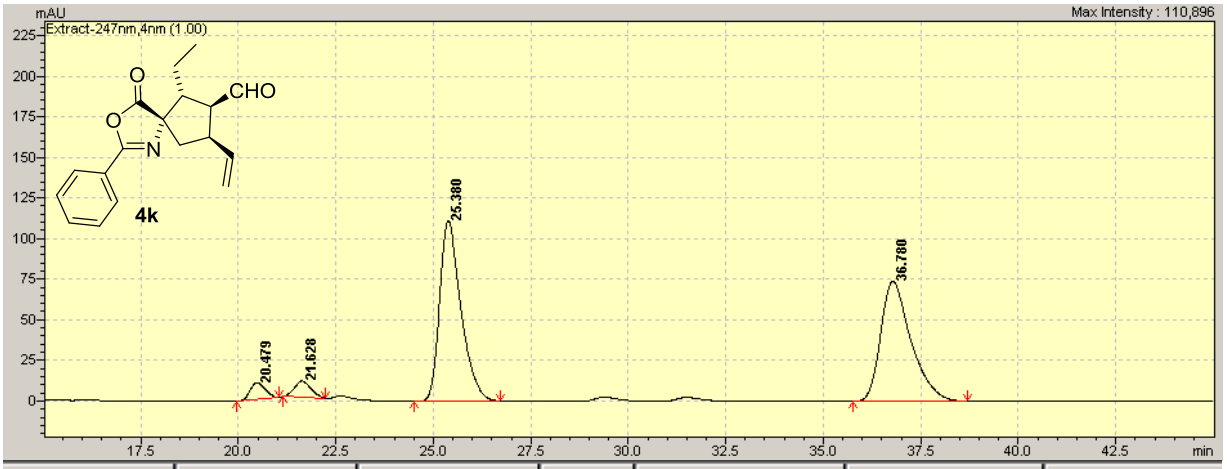
**Chiral – 4j´**




| Area | Height | Similarity Index | Mark | Peak Start | Peak End | Area% |
|---|---|---|---|---|---|---|
| 3672881 | 418301 | 0.000000 | | 5.461 | 6.155 | 94.9200 |
| 196567 | 13074 | 0.000000 | | 6.965 | 7.499 | 5.0800 |

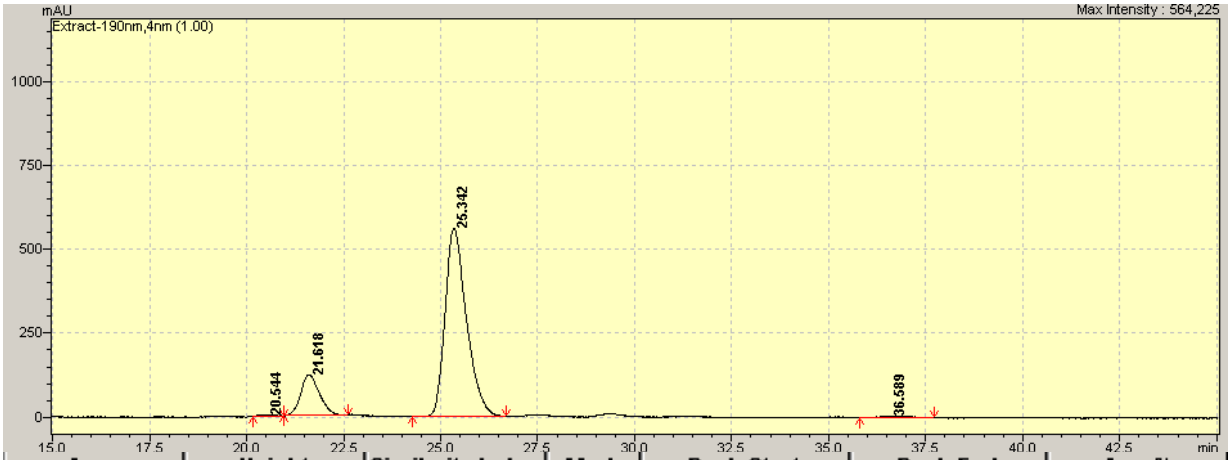
**Racemate – 4k and 4k´**

Column IC (heptane:*i*-PrOH, 95:5, 0.3 mL flow, 25 °C)




| Area | Height | Similarity Index | Mark | Peak Start | Peak End | Area% |
|---|---|---|---|---|---|---|
| 272904 | 10214 | 0.000000 | | 19.968 | 21.045 | 3.2013 |
| 299193 | 10039 | 0.000000 | | 21.141 | 22.240 | 3.5097 |
| 3949232 | 108212 | 0.000000 | | 24.875 | 26.389 | 46.3271 |
| 4003333 | 74242 | 0.000000 | | 35.776 | 38.688 | 46.9618 |

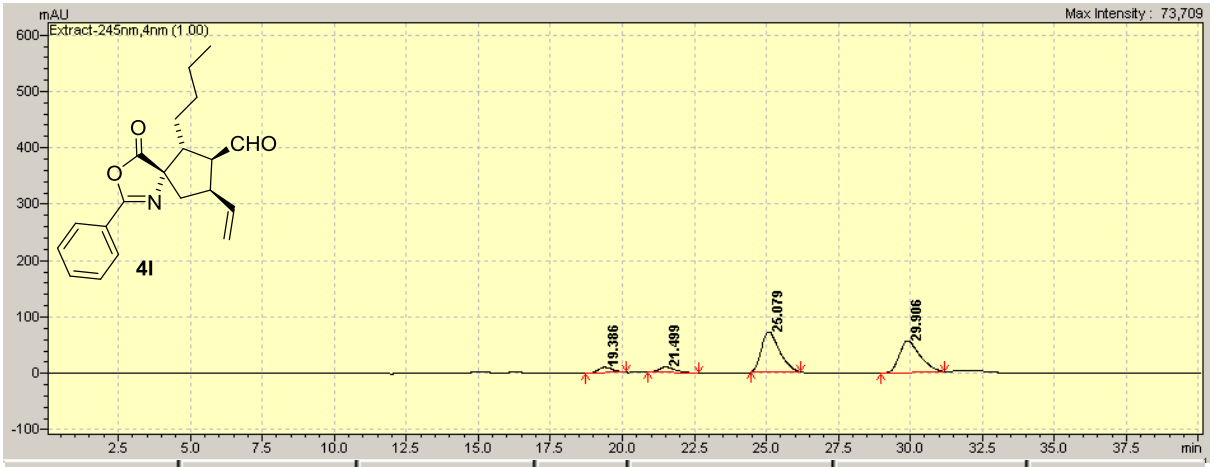
**Chiral – 4k and 4k´**




| Area | Height | Similarity Index | Mark | Peak Start | Peak End | Area% |
|---|---|---|---|---|---|---|
| 127682 | 5415 | 0.000000 | | 20.149 | 20.949 | 0.4928 |
| 4001449 | 121005 | 0.000000 | | 20.960 | 22.613 | 15.4441 |
| 21521934 | 562434 | 0.000000 | | 24.288 | 26.699 | 83.0664 |
| 258235 | 5836 | 0.000000 | | 35.808 | 37.717 | 0.9967 |

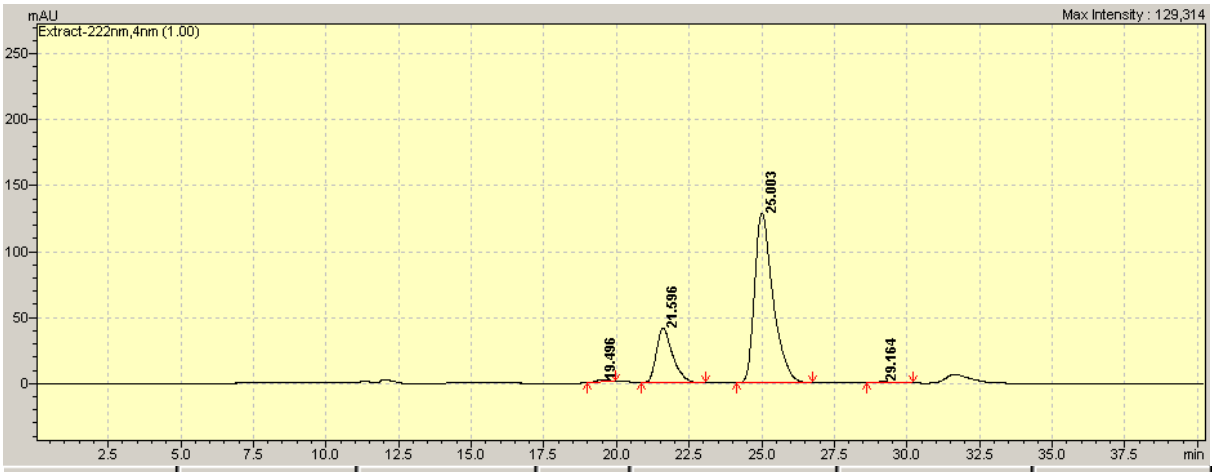
**Racemate – 4l and 4l´**

Column IC (heptane:*i*-PrOH, 98:2, 0.3 mL flow, 25 °C)




| Area | Height | Similarity Index | Mark | Peak Start | Peak End | Area% |
|---|---|---|---|---|---|---|
| 344144 | 9765 | 0.000000 | | 18.709 | 20.139 | 5.2669 |
| 330414 | 8921 | 0.000000 | | 20.907 | 22.667 | 5.0567 |
| 3093917 | 71166 | 0.000000 | | 24.480 | 26.187 | 47.3502 |
| 2765644 | 55955 | 0.000000 | | 28.992 | 31.189 | 42.3262 |

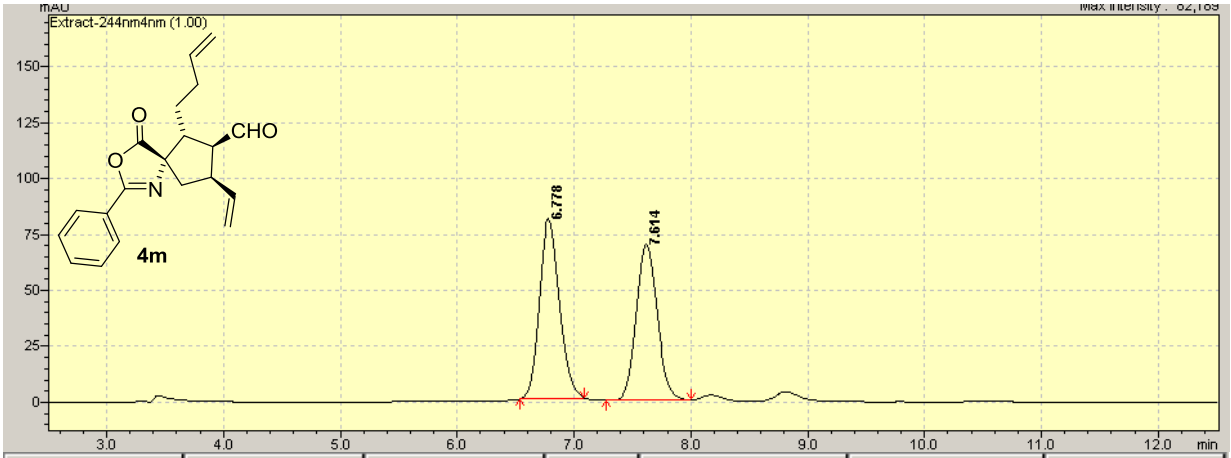
**Chiral – 4l and 4l´**




| Area | Height | Similarity Index | Mark | Peak Start | Peak End | Area% |
|---|---|---|---|---|---|---|
| 46198 | 1597 | 0.000000 | | 18.997 | 19.947 | 0.6261 |
| 1609161 | 41294 | 0.000000 | | 20.864 | 23.083 | 21.8096 |
| 5679680 | 128791 | 0.000000 | | 24.149 | 26.763 | 76.9792 |
| 43166 | 990 | 0.000000 | | 28.597 | 30.219 | 0.5851 |

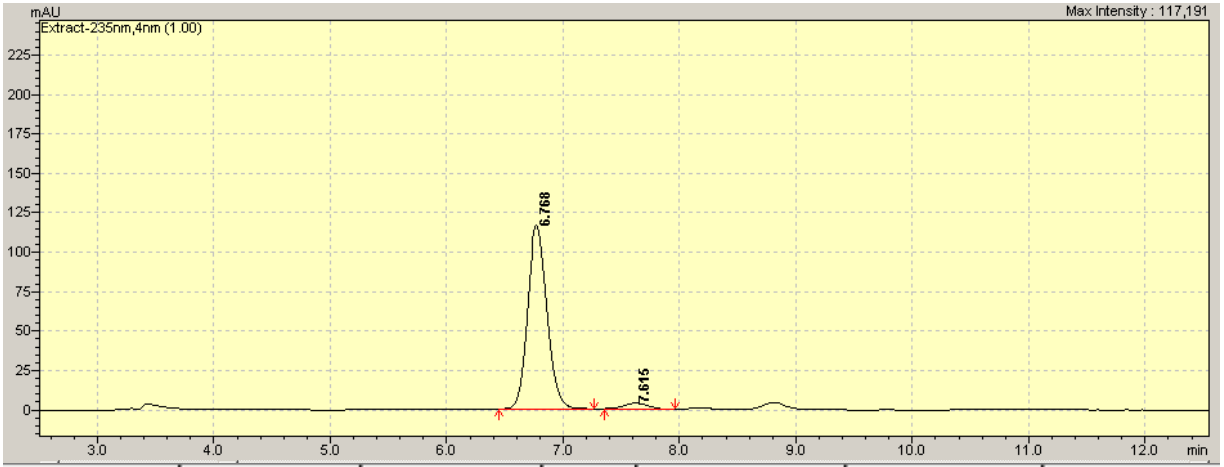
**Racemate – 4m**

Column IA (heptane:*i*-PrOH, 98:2, 1 mL flow, 25 °C)




| Area | Height | Similarity Index | Mark | Peak Start | Peak End | Area% |
|---|---|---|---|---|---|---|
| 837710 | 75419 | 0.000000 | | 6.624 | 7.029 | 49.3384 |
| 860175 | 69532 | 0.000000 | | 7.275 | 8.000 | 50.6616 |

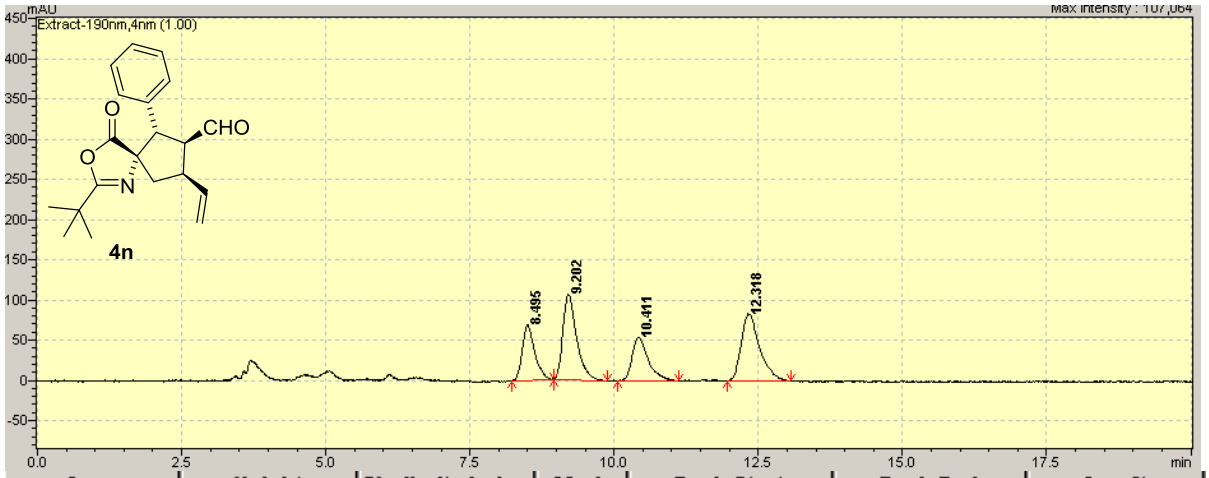
**Chiral – 4m**




| Area | Height | Similarity Index | Mark | Peak Start | Peak End | Area% |
|---|---|---|---|---|---|---|
| 1351865 | 116460 | 0.000000 | | 6.453 | 7.264 | 96.1921 |
| 53515 | 3707 | 0.000000 | | 7.360 | 7.968 | 3.8079 |

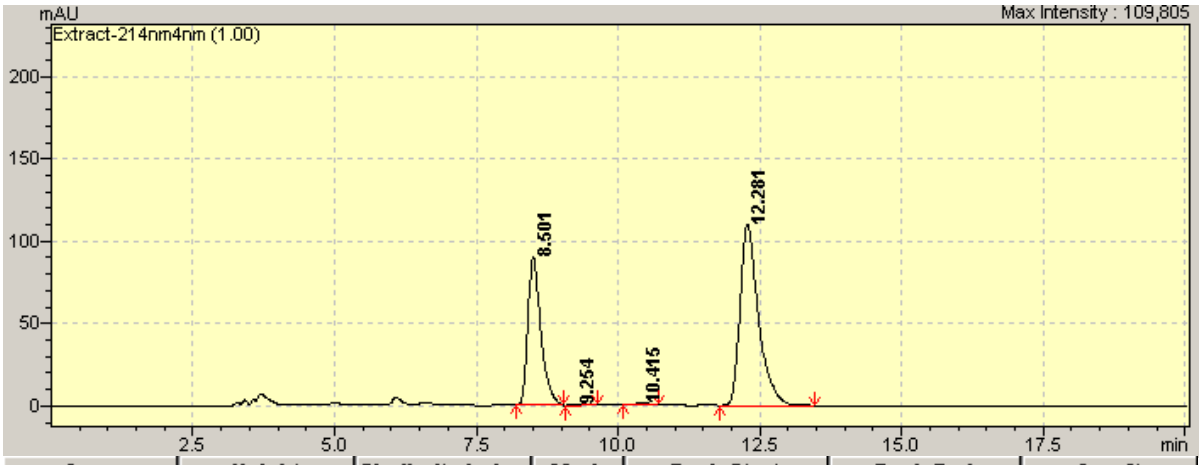
**Racemate – 4n and 4n´**

Column IC (heptane:*i*-PrOH, 98:2, 1.0 mL flow, 25 °C)




| Area | Height | Similarity Index | Mark | Peak Start | Peak End | Area% |
|---|---|---|---|---|---|---|
| 1063891 | 70262 | 0.000000 | | 8.235 | 8.949 | 18.4535 |
| 1760199 | 106618 | 0.000000 | | 8.949 | 9.888 | 30.5311 |
| 1079801 | 54502 | 0.000000 | | 10.059 | 11.115 | 18.7295 |
| 1861366 | 83847 | 0.000000 | | 11.957 | 13.077 | 32.2859 |

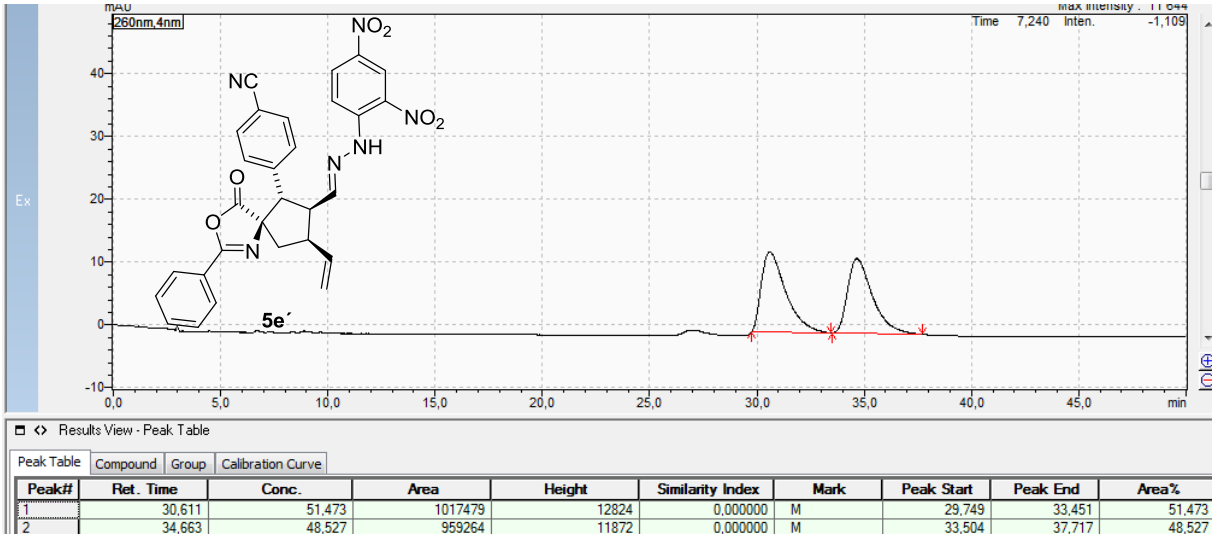
**Chiral – 4n and 4n´**




| Area | Height | Similarity Index | Mark | Peak Start | Peak End | Area% |
|---|---|---|---|---|---|---|
| 1433308 | 90170 | 0.000000 | | 8.192 | 9.035 | 36.3822 |
| 12096 | 689 | 0.000000 | | 9.056 | 9.653 | 0.3070 |
| 17328 | 1228 | 0.000000 | | 10.080 | 10.720 | 0.4398 |
| 2476858 | 109509 | 0.000000 | | 11.797 | 13.472 | 62.8710 |

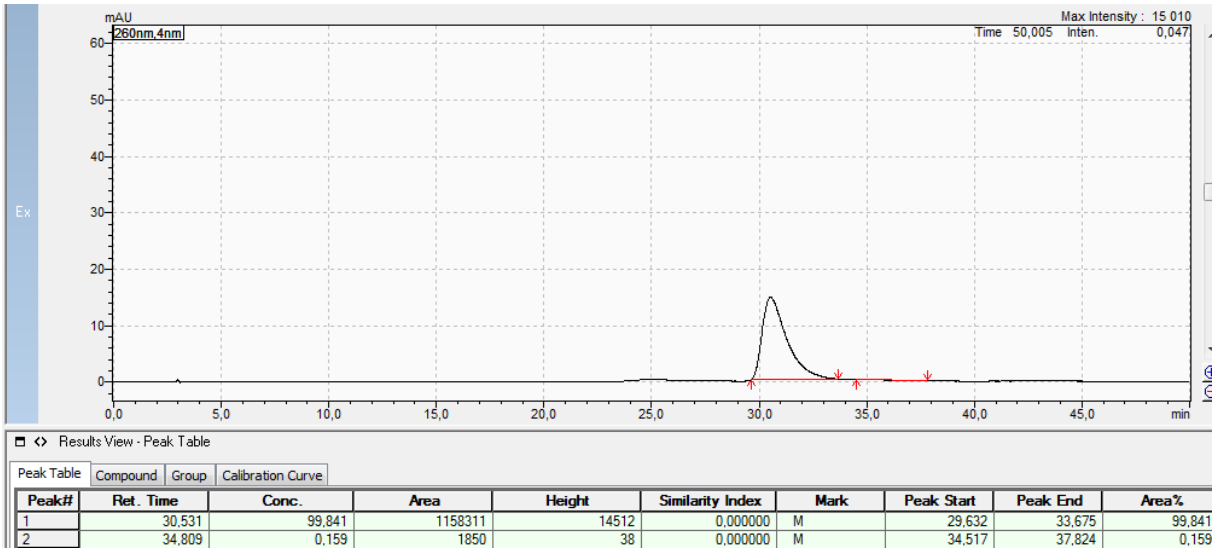
**Racemate – 5e´**

Column IB (heptane:i-PrOH, 80:20, 1 mL flow, 25 °C)




| Peak# | Ret. Time | Conc. | Area | Height | Similarity Index | Mark | Peak Start | Peak End | Area% |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 30,611 | 51,473 | 1017479 | 12824 | 0,000000 | M | 29,749 | 33,451 | 51,473 |
| 2 | 34,663 | 48,527 | 959264 | 11872 | 0,000000 | M | 33,504 | 37,717 | 48,527 |

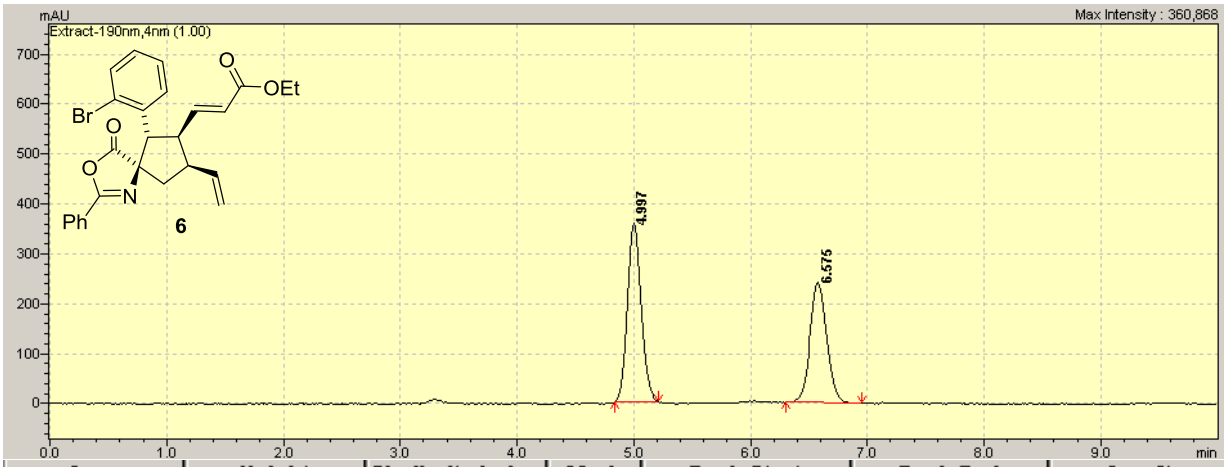
**Chiral – 5e´**




| Peak# | Ret. Time | Conc. | Area | Height | Similarity Index | Mark | Peak Start | Peak End | Area% |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 30,531 | 99,841 | 1158311 | 14512 | 0,000000 | M | 29,632 | 33,675 | 99,841 |
| 2 | 34,809 | 0,159 | 1850 | 38 | 0,000000 | M | 34,517 | 37,824 | 0,159 |

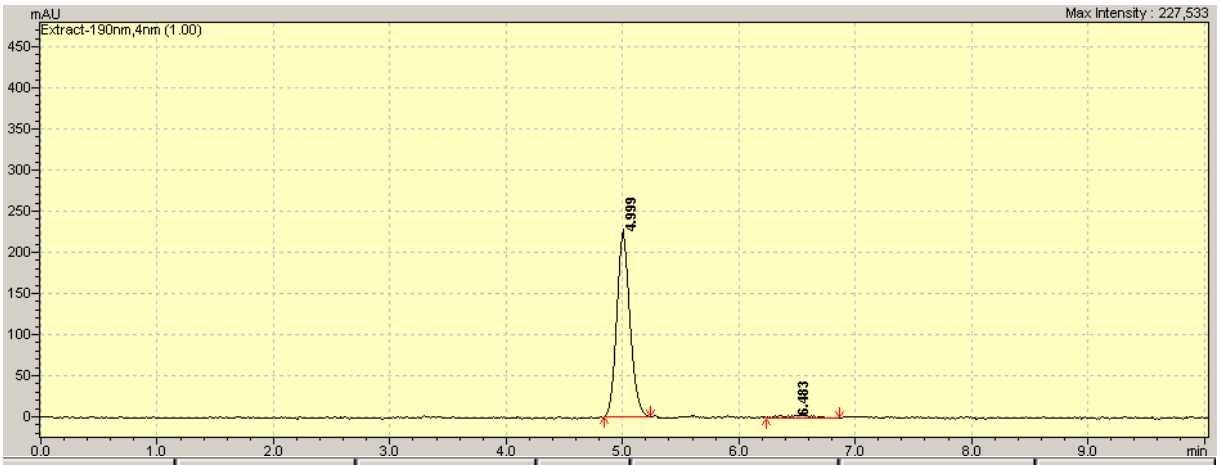
**Racemate – 6**

Column IA (heptane:*i*-PrOH, 80:20, 1 mL flow, 25 °C)




| Area | Height | Similarity Index | Mark | Peak Start | Peak End | Area% |
|---|---|---|---|---|---|---|
| 2365752 | 329270 | 0.000000 | | 4.896 | 5.152 | 49.4999 |
| 2413550 | 241355 | 0.000000 | | 6.304 | 6.955 | 50.5001 |

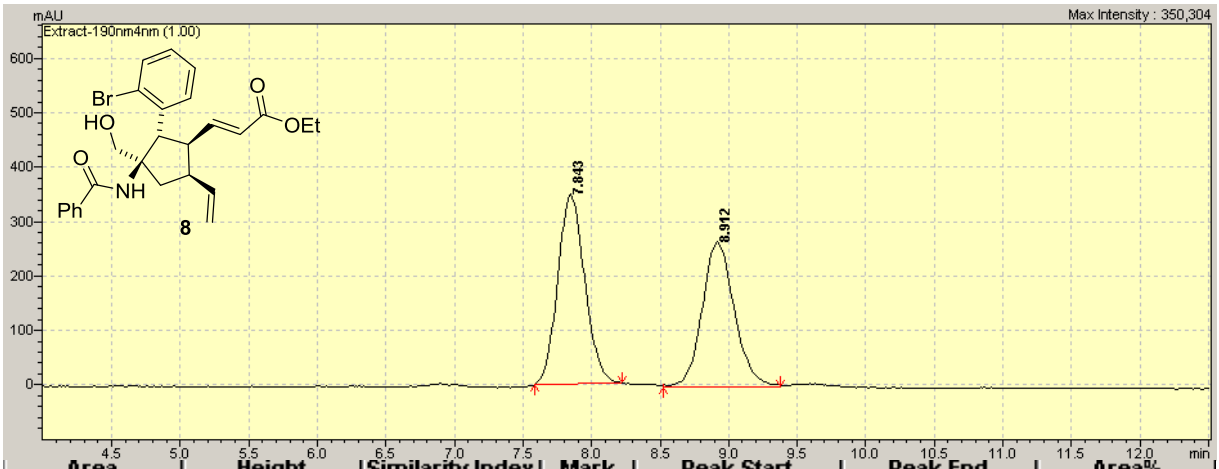
**Chiral – 6**




| Area | Height | Similarity Index | Mark | Peak Start | Peak End | Area% |
|---|---|---|---|---|---|---|
| 1849360 | 227234 | 0.000000 | | 4.843 | 5.237 | 96.3812 |
| 69437 | 3810 | 0.000000 | | 6.240 | 6.869 | 3.6188 |

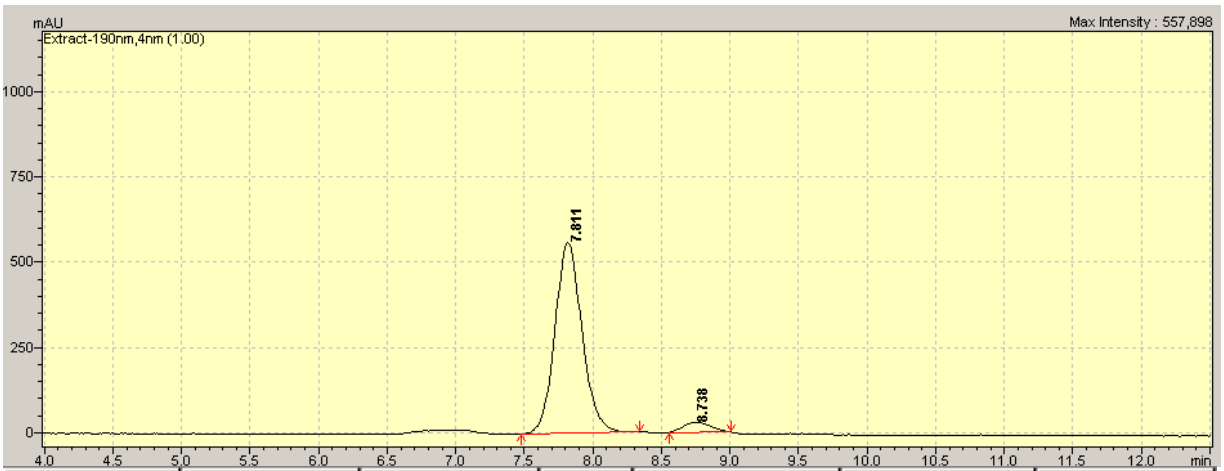
**Racemate – 8**

Column IA (heptane:*i*-PrOH 80:20, 1 mL flow, 25 °C)




| Area | Height | Similarity Index | Mark | Peak Start | Peak End | Area% |
|---|---|---|---|---|---|---|
| 4415571 | 338000 | 0.000000 | | 7.627 | 8.128 | 50.1278 |
| 4393063 | 266913 | 0.000000 | | 8.523 | 9.376 | 49.8722 |

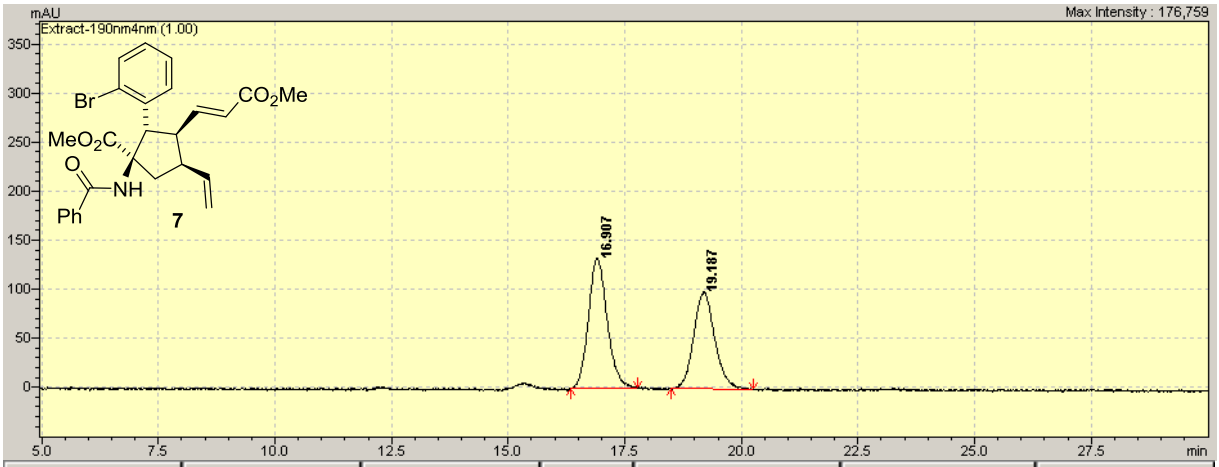
**Chiral – 8**




| Area | Height | Similarity Index | Mark | Peak Start | Peak End | Area% |
|---|---|---|---|---|---|---|
| 7654837 | 559192 | 0.000000 | | 7.477 | 8.341 | 95.8996 |
| 327297 | 25025 | 0.000000 | | 8.597 | 9.003 | 4.1004 |

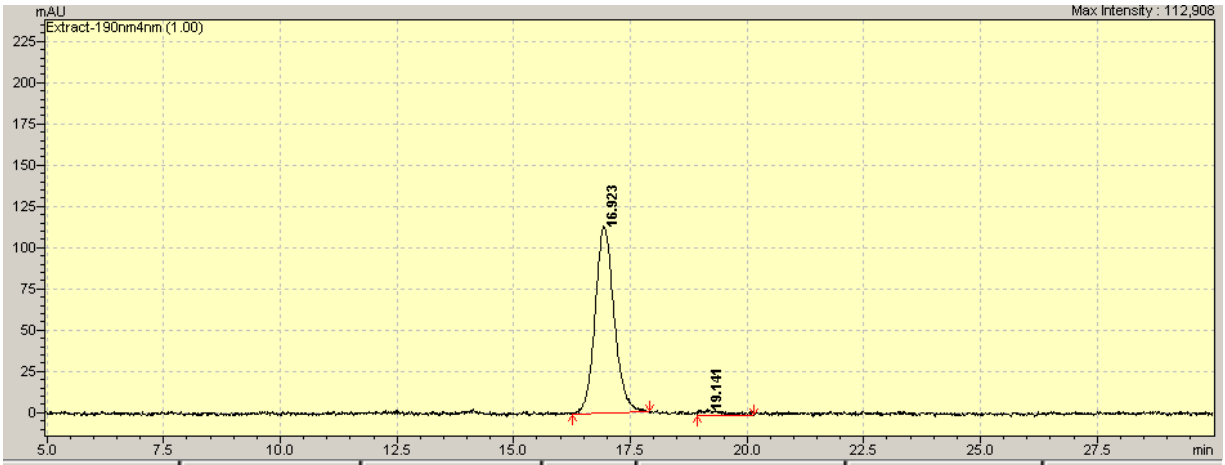
**Racemate – 7**

Column IA (heptane:*i*-PrOH 90:10, 1 mL flow, 25 °C)



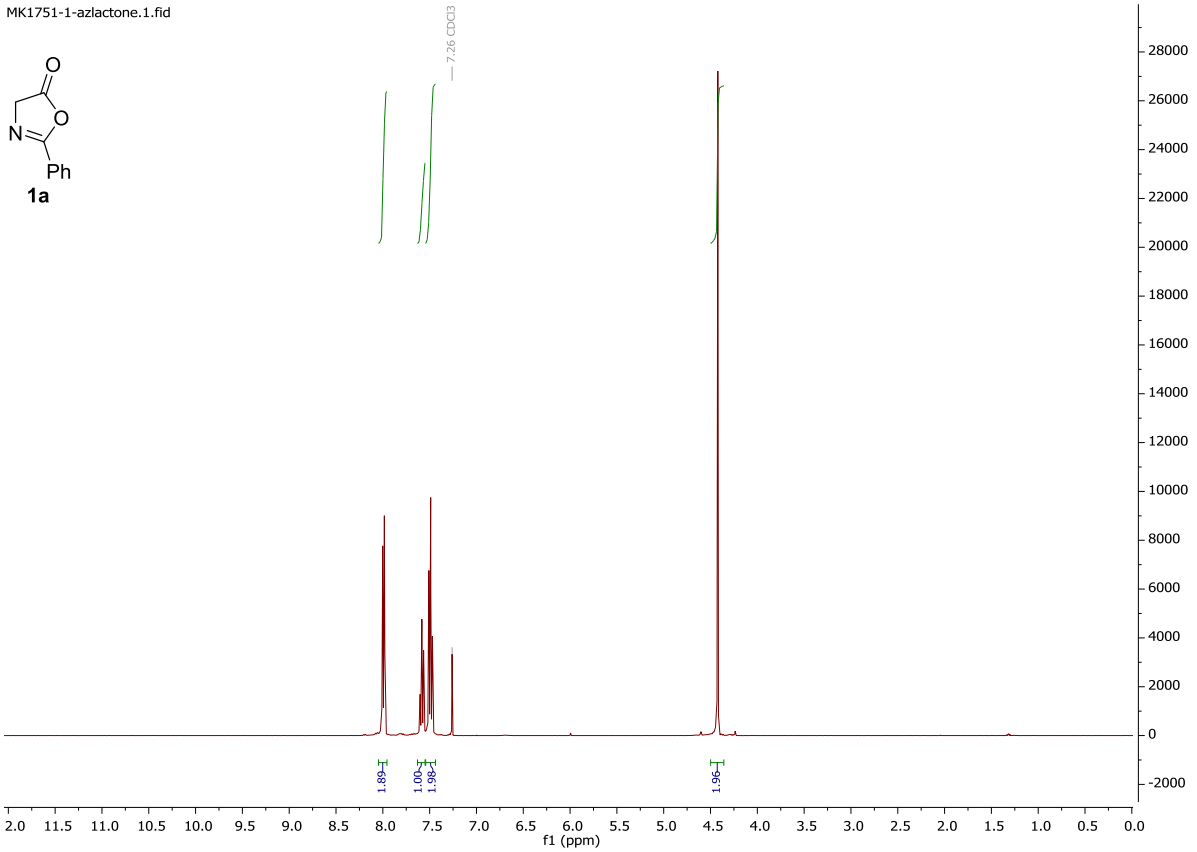

| Area | Height | Similarity Index | Mark | Peak Start | Peak End | Area% |
|---|---|---|---|---|---|---|
| 3173613 | 124723 | 0.000000 | | 16.512 | 17.461 | 50.5922 |
| 3099322 | 99422 | 0.000000 | | 18.496 | 20.256 | 49.4078 |

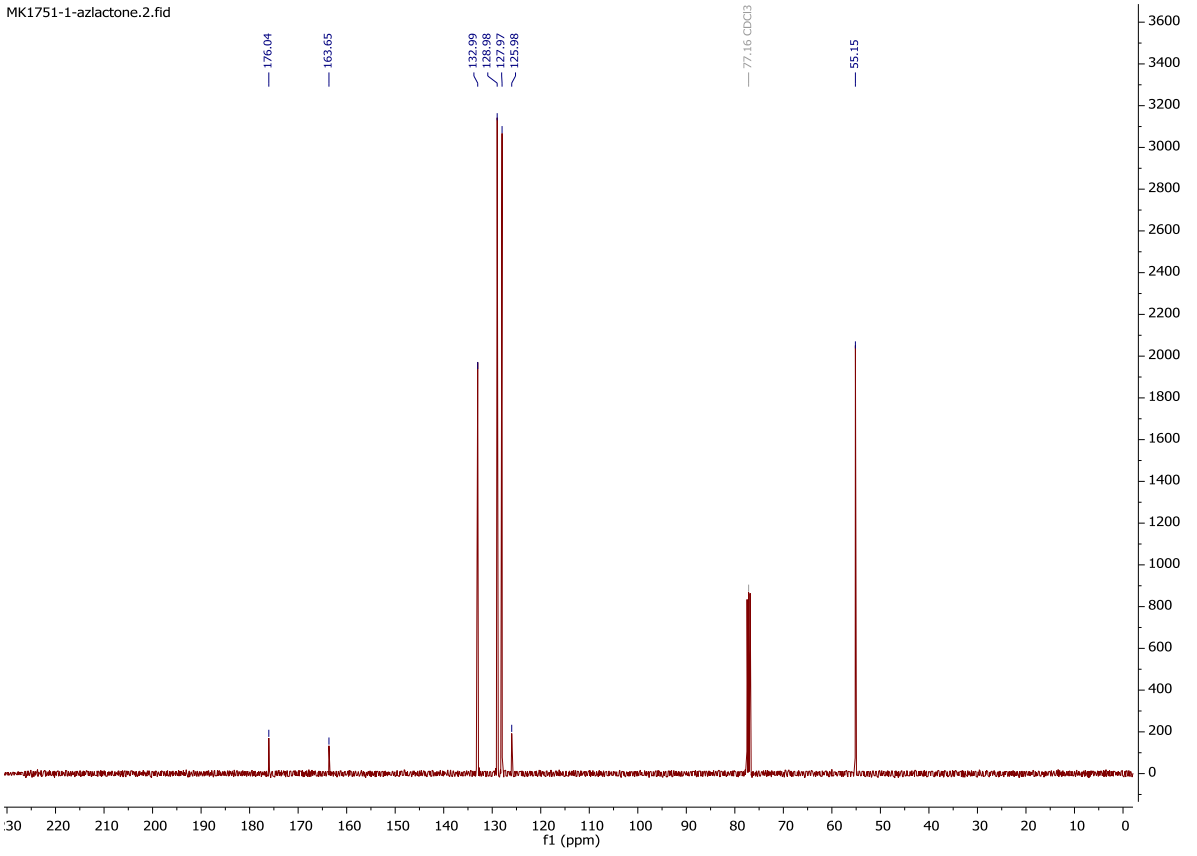
**Chiral – 7**



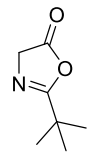

| Area | Height | Similarity Index | Mark | Peak Start | Peak End | Area% |
|---|---|---|---|---|---|---|
| 3216430 | 113223 | 0.000000 | | 16.267 | 17.909 | 96.5492 |
| 114959 | 3330 | 0.000000 | | 18.933 | 20.160 | 3.4508 |

# 12. NMR spectra



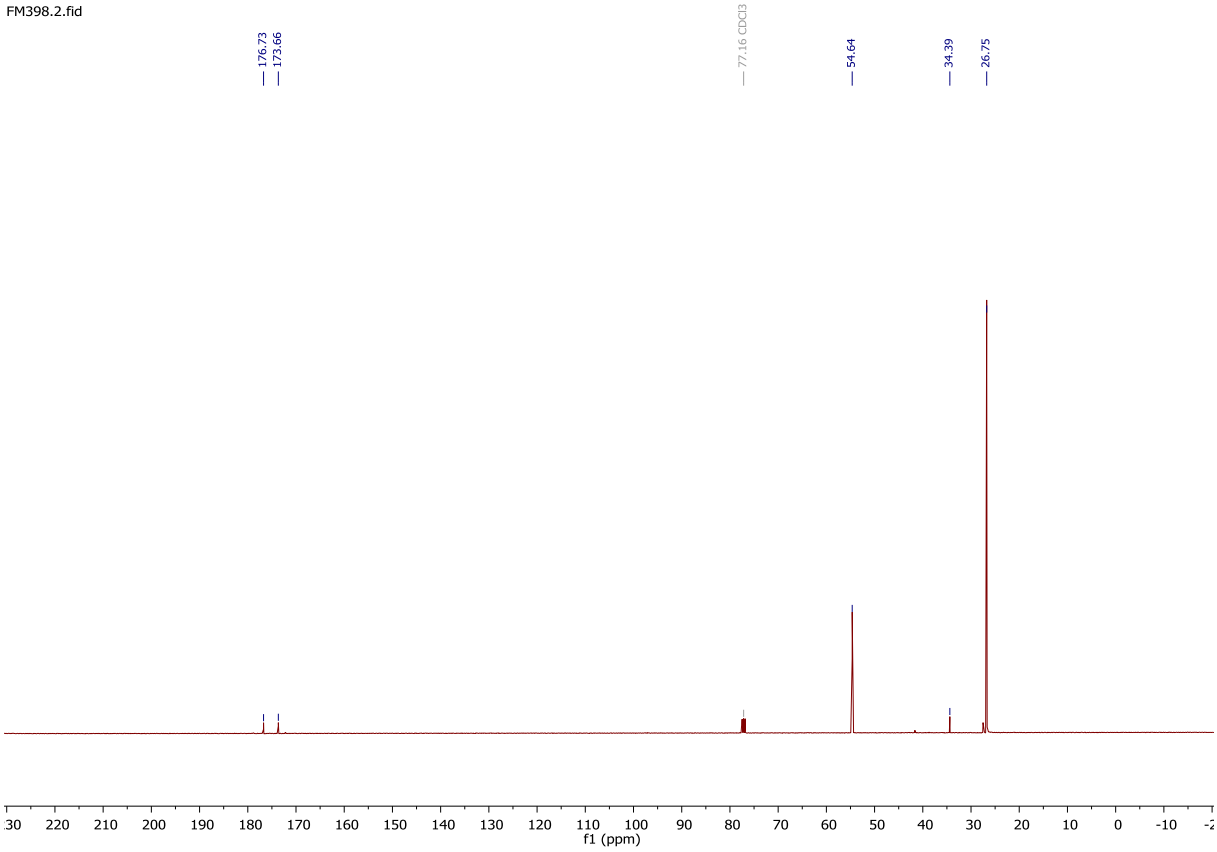
FM398.1.fid

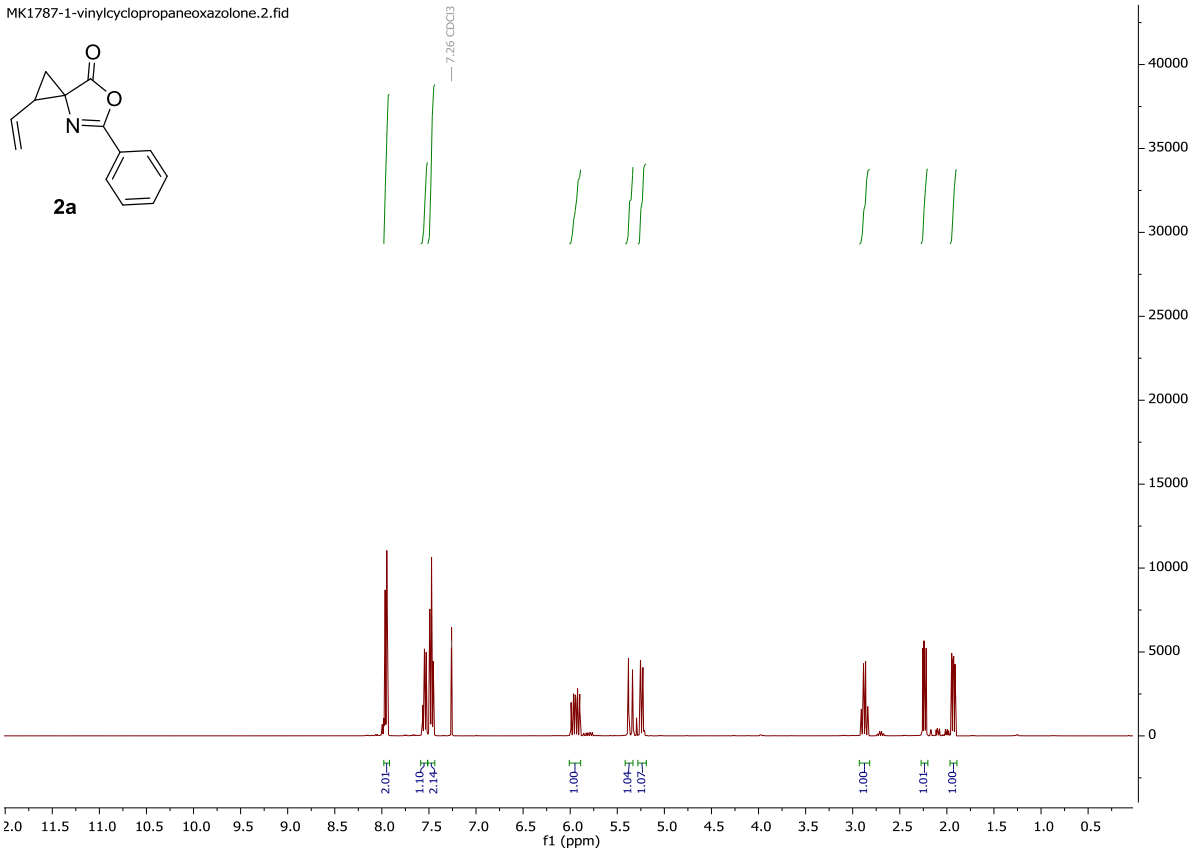


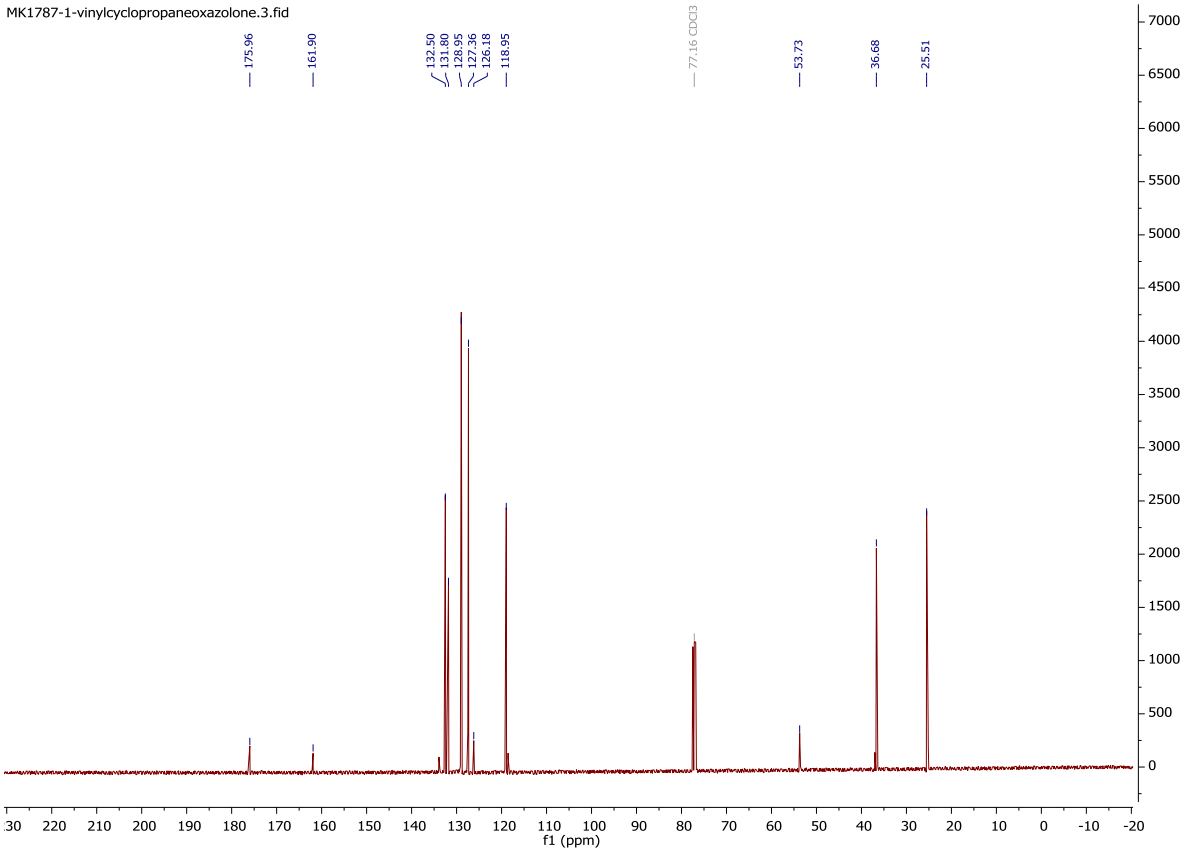
**1b**



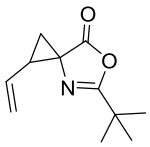

FM398.2.fid




MK1787-1-vinylcyclopropaneoxazolone.2.fid
7.26 CDCl3
2a
2.01
1.10
2.14
1.00
1.04
1.07
1.00
1.01
1.00
f1 (ppm)


MK1787-1-vinylcyclopropaneoxazolone.3.fid
175.96
161.90
132.50
131.80
128.95
127.36
126.18
118.95
77.16 CDCl3
53.73
36.68
25.51
f1 (ppm)

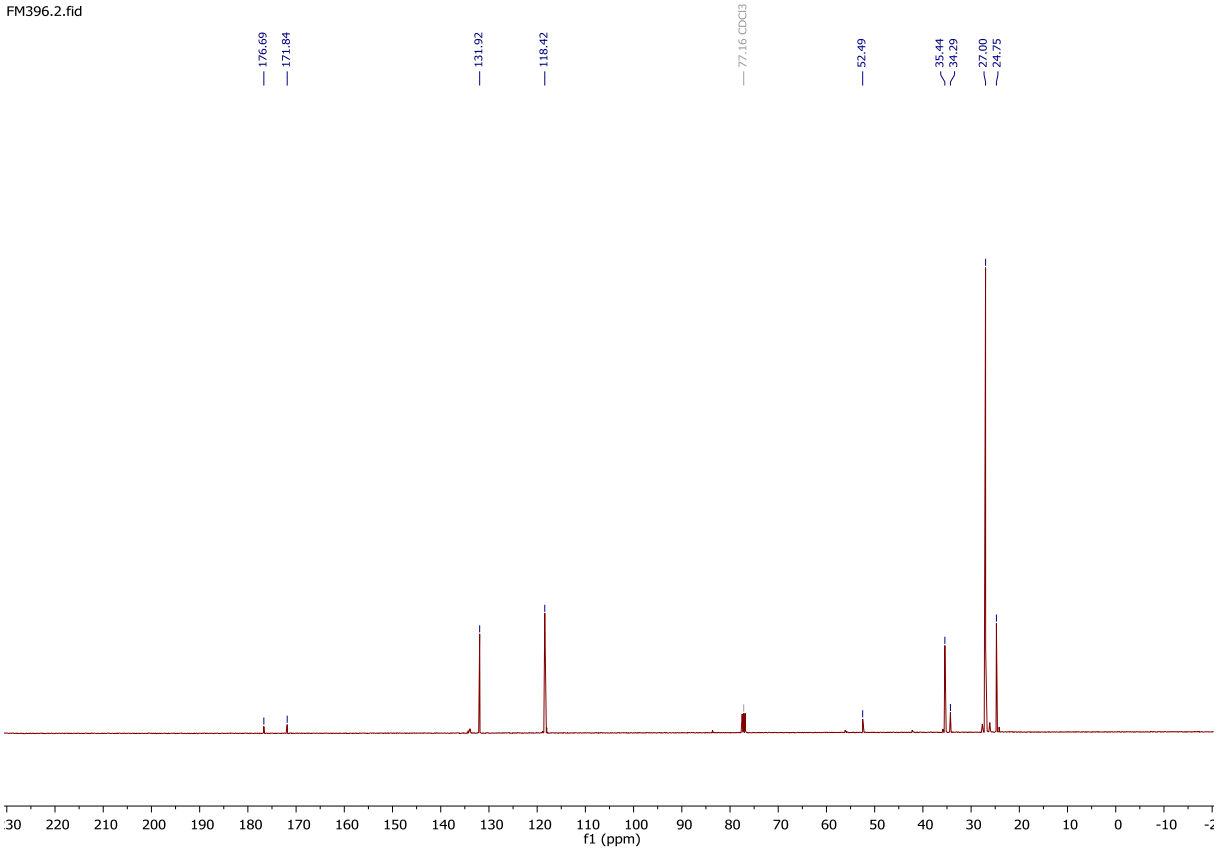
FM396.1.fid

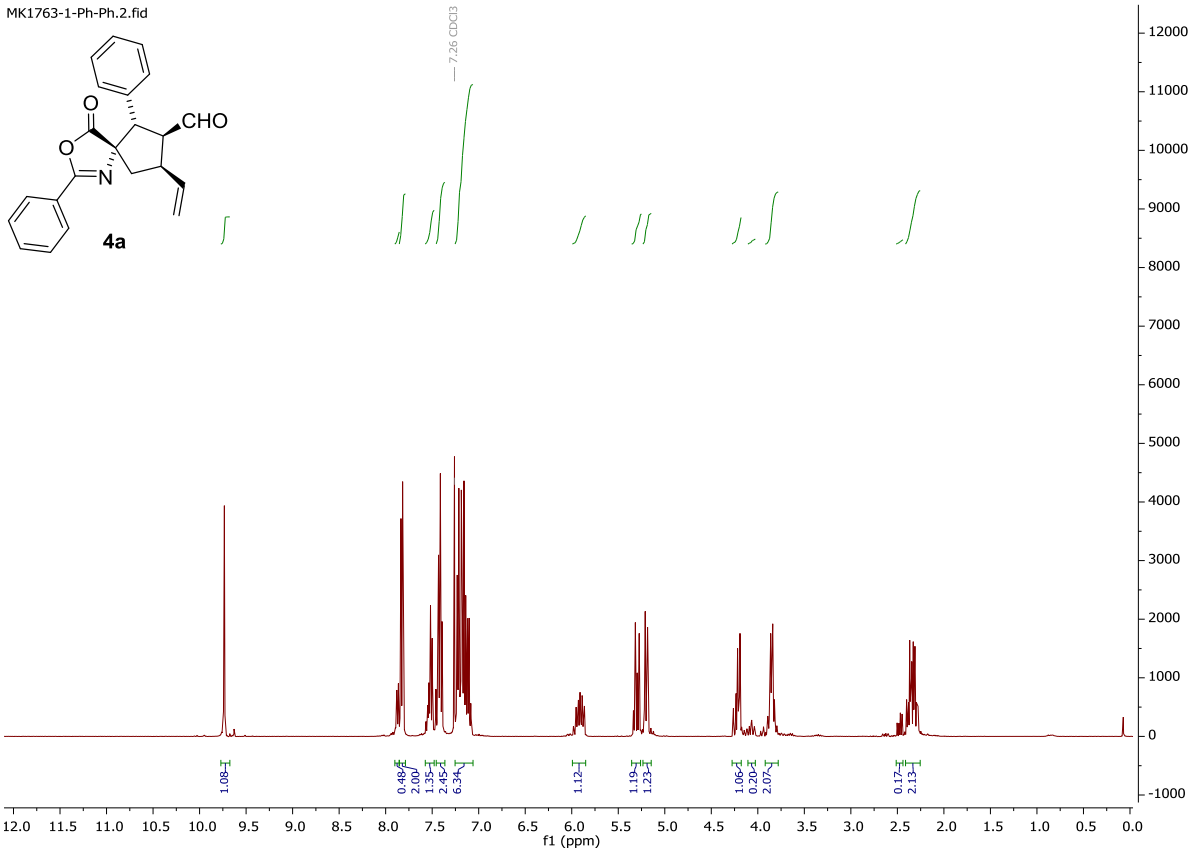


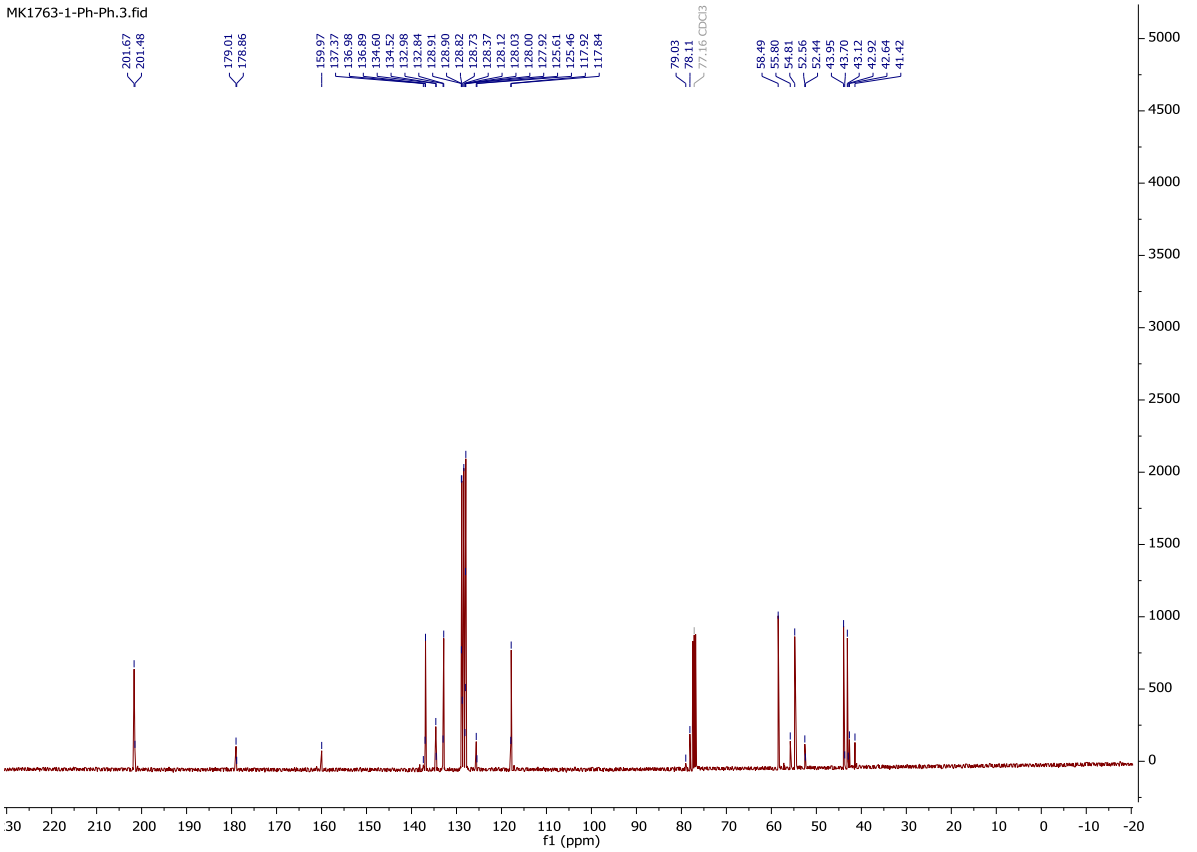
**2b**

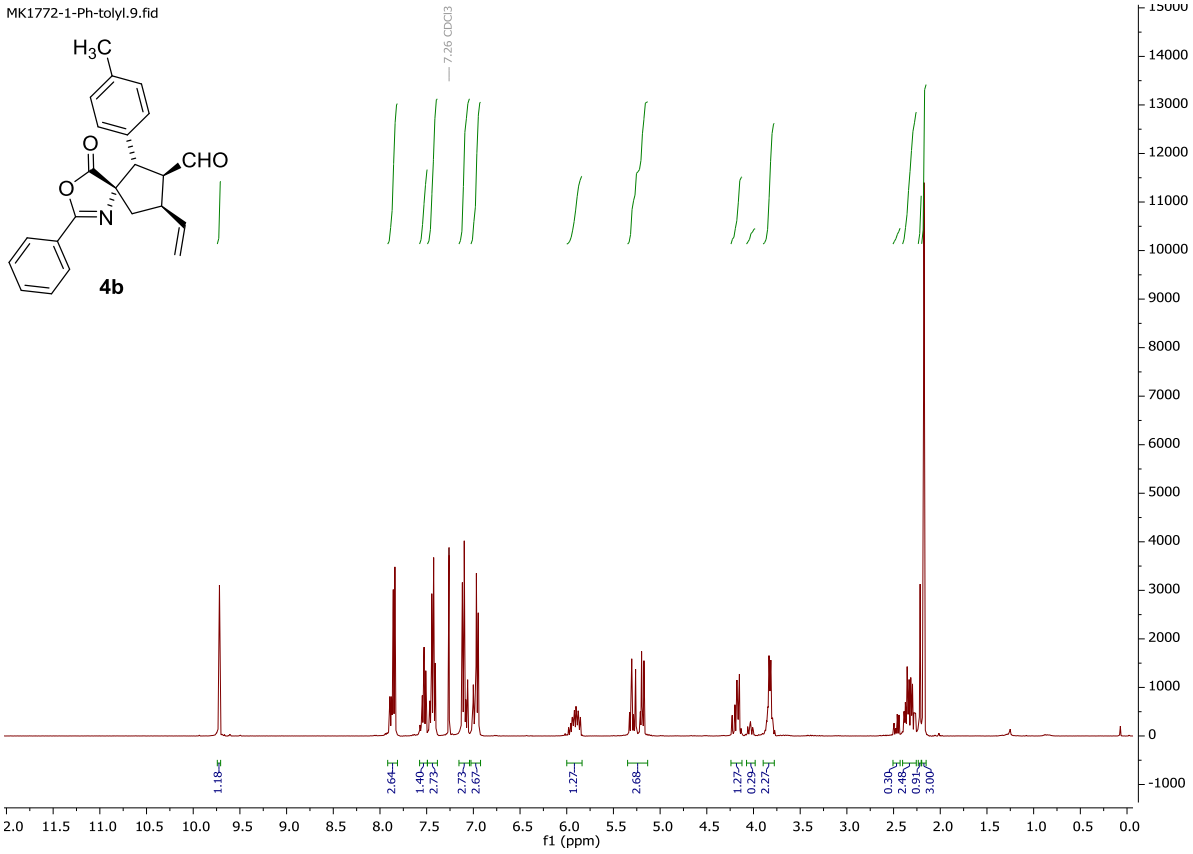


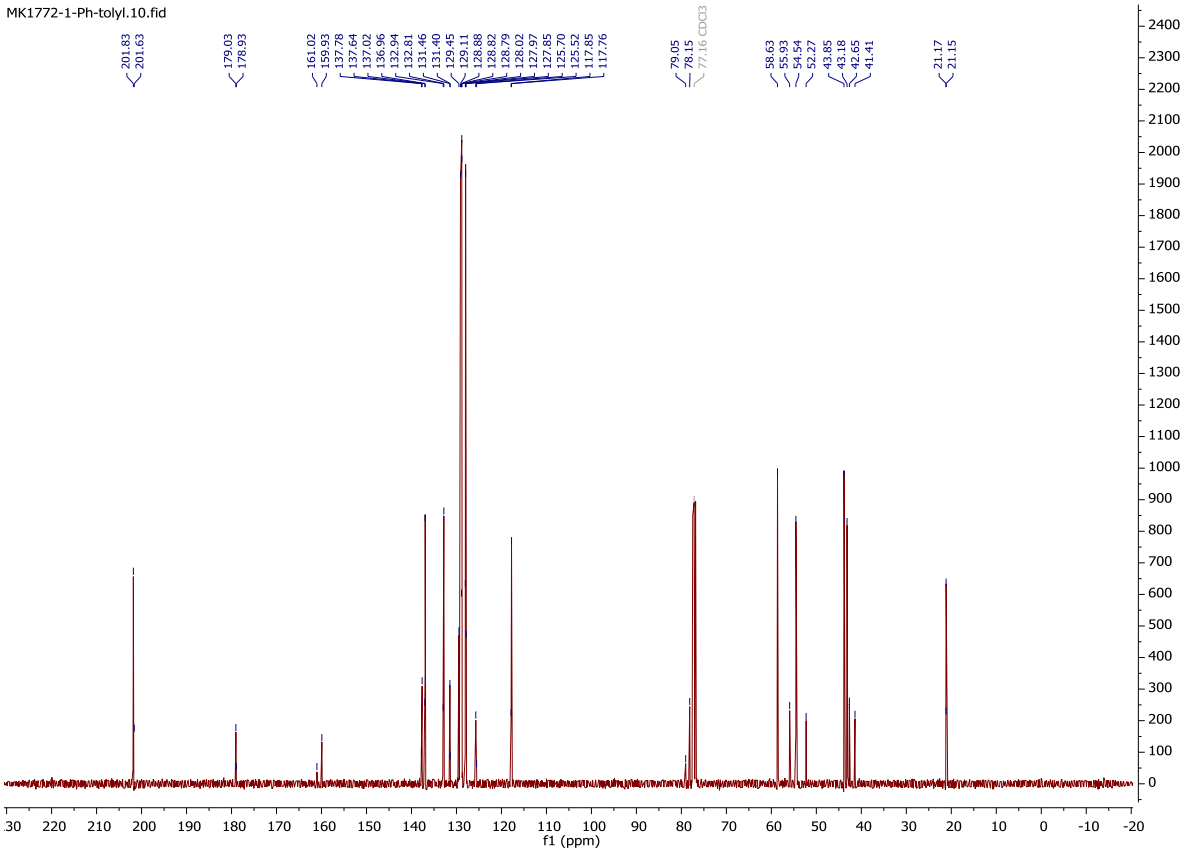

FM396.2.fid

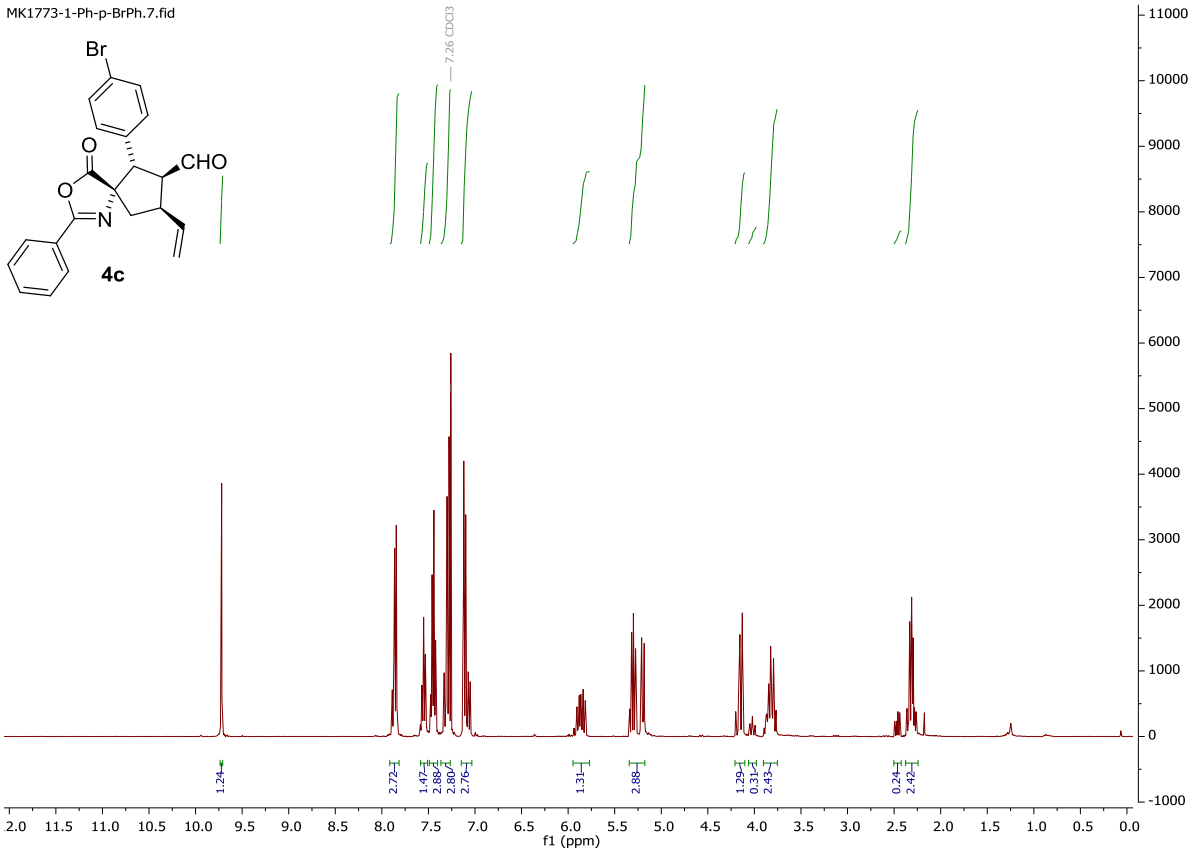


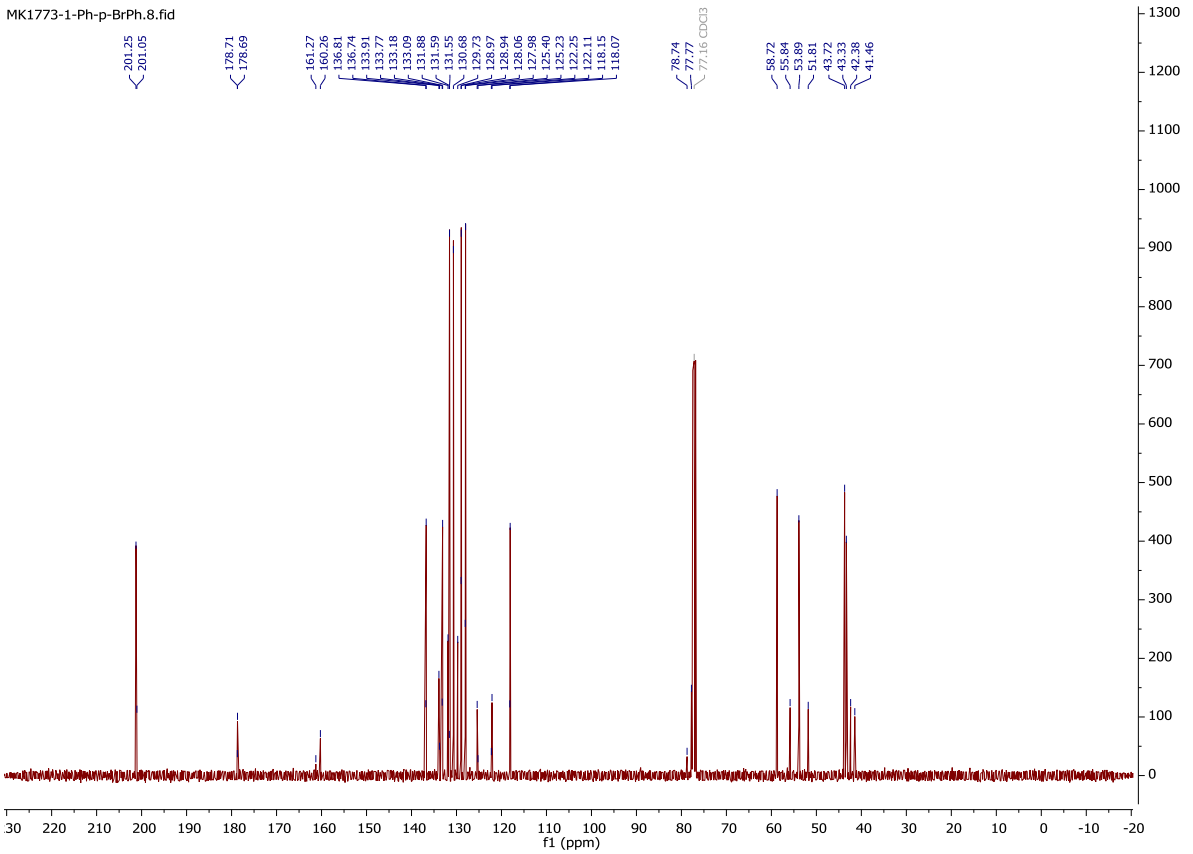

MK1763-1-Ph-Ph.2.fid
CHO
O
O
N
4a
7.26 CDCl3
f1 (ppm)

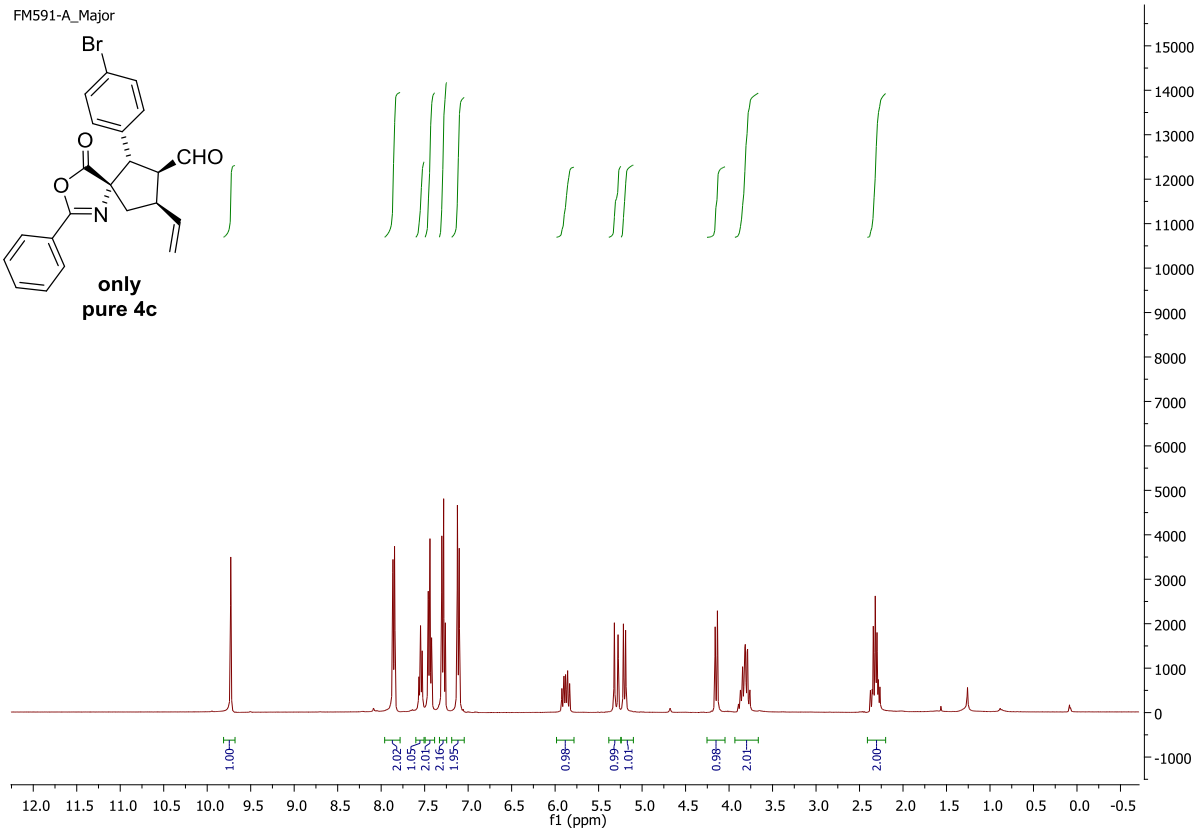

MK1763-1-Ph-Ph.3.fid
201.67
201.48
179.01
178.86
159.97
137.37
136.98
136.89
134.60
134.52
132.98
132.84
128.91
128.90
128.82
128.73
128.37
128.12
128.03
128.00
127.92
125.61
125.46
117.92
117.84
79.03
78.11
77.16 CDCl3
58.49
55.80
54.81
52.56
52.44
43.95
43.70
43.12
42.92
42.64
41.42
f1 (ppm)

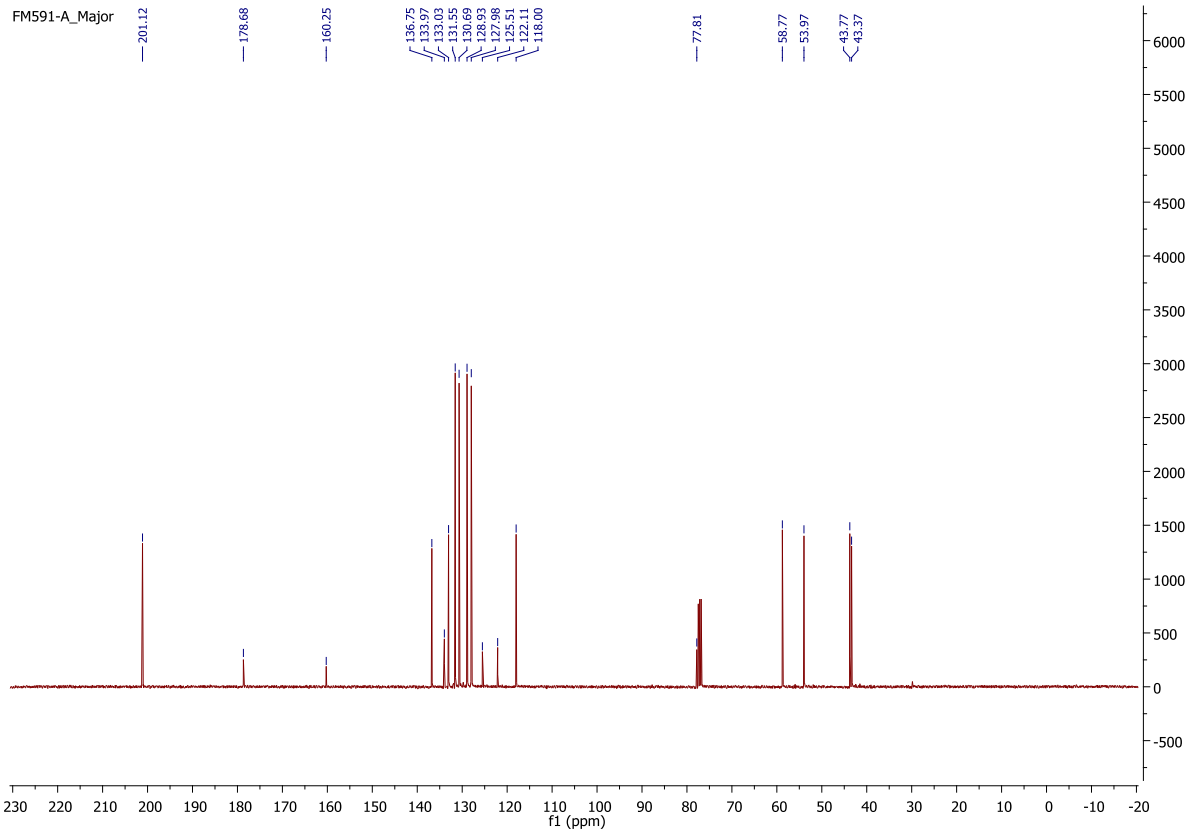

MK1772-1-Ph-tolyl.9.fid
H3C
O
CHO
O
N
4b
7.26 CDCl3
1.18
2.64
1.40
2.73
2.73
2.67
1.27
2.68
1.27
0.29
2.27
0.30
2.48
0.91
3.00
f1 (ppm)

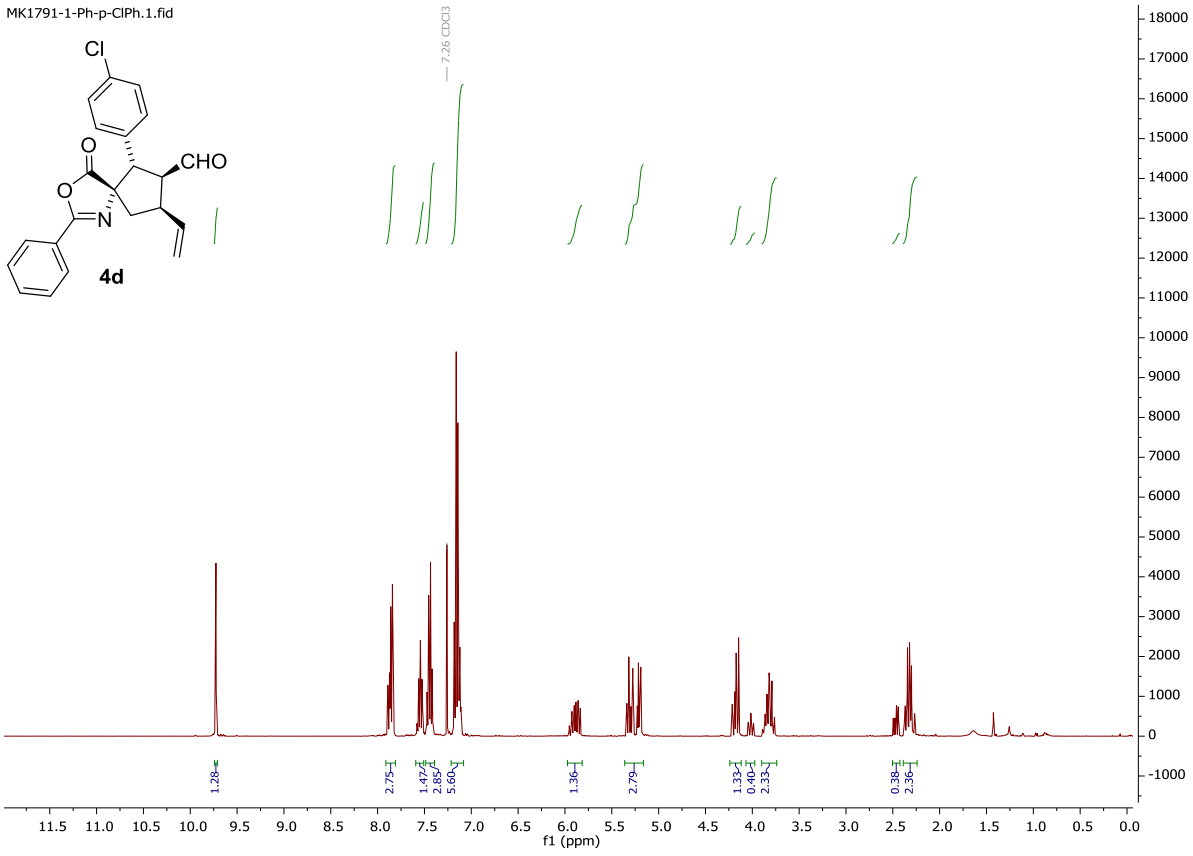

MK1772-1-Ph-tolyl.10.fid
201.83
201.63
179.03
178.93
161.02
159.93
137.78
137.64
137.02
136.96
132.94
132.81
131.46
131.40
129.45
129.11
128.88
128.82
128.79
128.02
127.97
127.85
125.70
125.52
117.85
117.76
79.05
78.15
77.16 CDCl3
58.63
55.93
54.54
52.27
43.85
43.18
42.65
41.41
21.17
21.15
f1 (ppm)

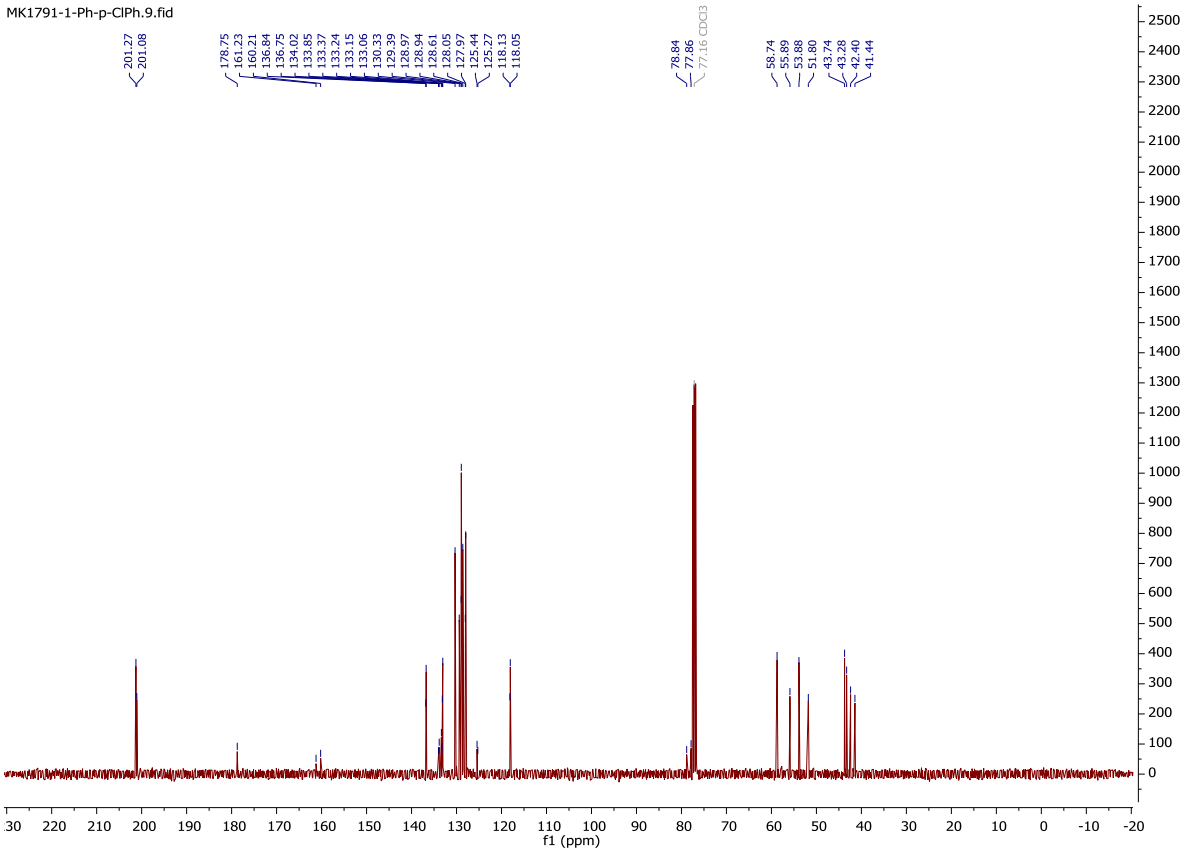

MK1773-1-Ph-p-BrPh.7.fid
Br
O
O
N
CHO
4c
7.26 CDCl3
1.24
2.72
1.47
2.88
2.80
2.76
1.31
2.88
1.29
0.31
2.43
0.24
2.42
f1 (ppm)

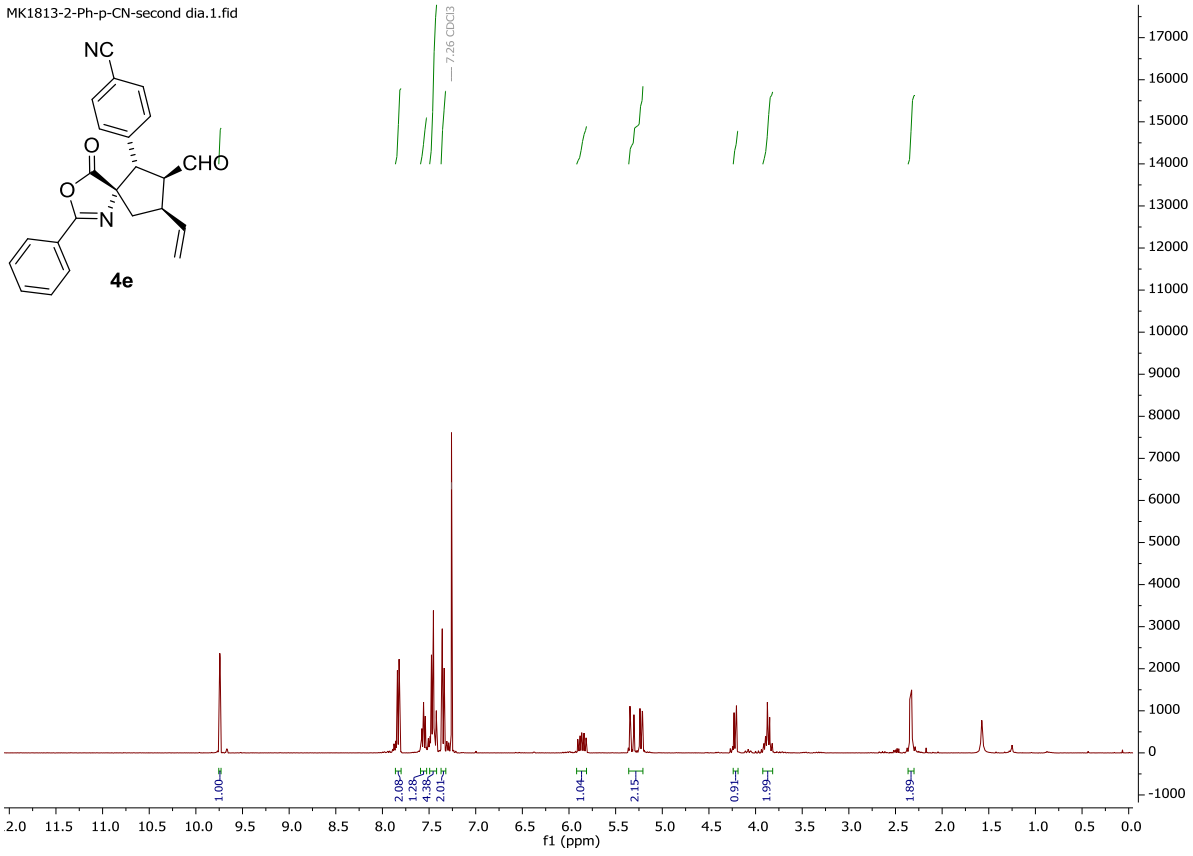

MK1773-1-Ph-p-BrPh.8.fid
201.25
201.05
178.71
178.69
161.27
160.26
136.81
136.74
133.91
133.77
133.18
133.09
131.88
131.59
131.55
130.68
129.73
128.97
128.94
128.06
127.98
125.40
125.23
122.25
122.11
118.15
118.07
78.74
77.77
77.16 CDCl3
58.72
55.84
53.89
51.81
43.72
43.33
42.38
41.46
f1 (ppm)

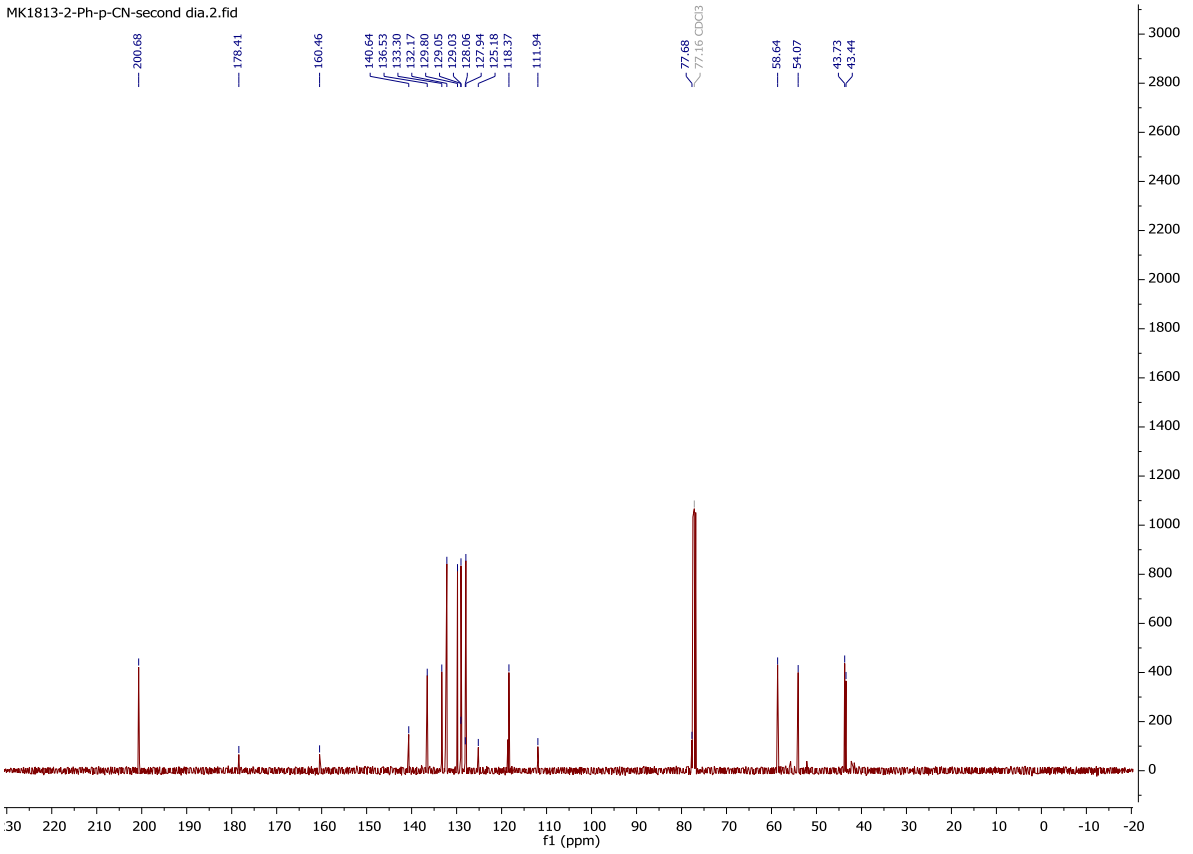

FM591-A_Major
Br
O
O
N
CHO
only
pure 4c
1.00
2.02
1.05
2.01
2.16
1.95
0.98
0.99
1.01
0.98
2.01
2.00
f1 (ppm)

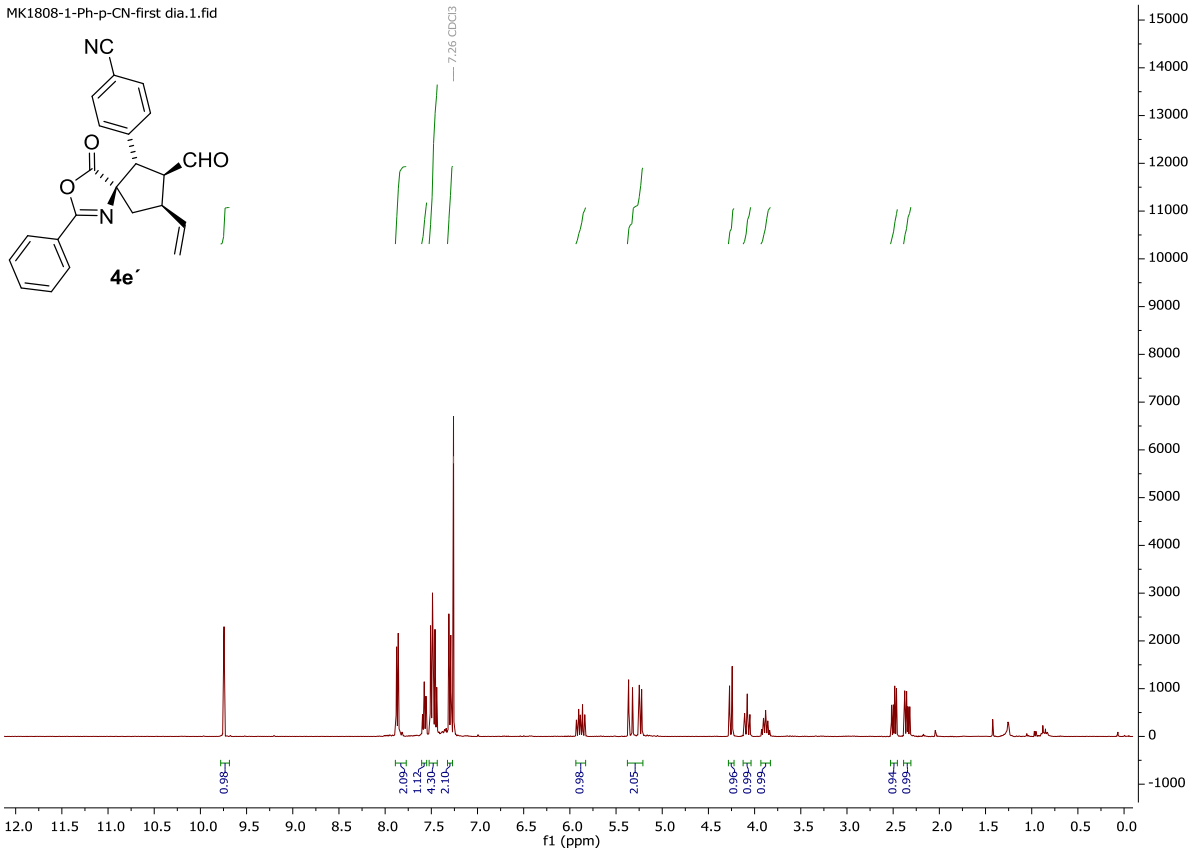

FM591-A_Major
201.12
178.68
160.25
136.75
133.97
133.03
131.55
130.69
128.93
127.98
125.51
122.11
118.00
77.81
58.77
53.97
43.77
43.37
f1 (ppm)

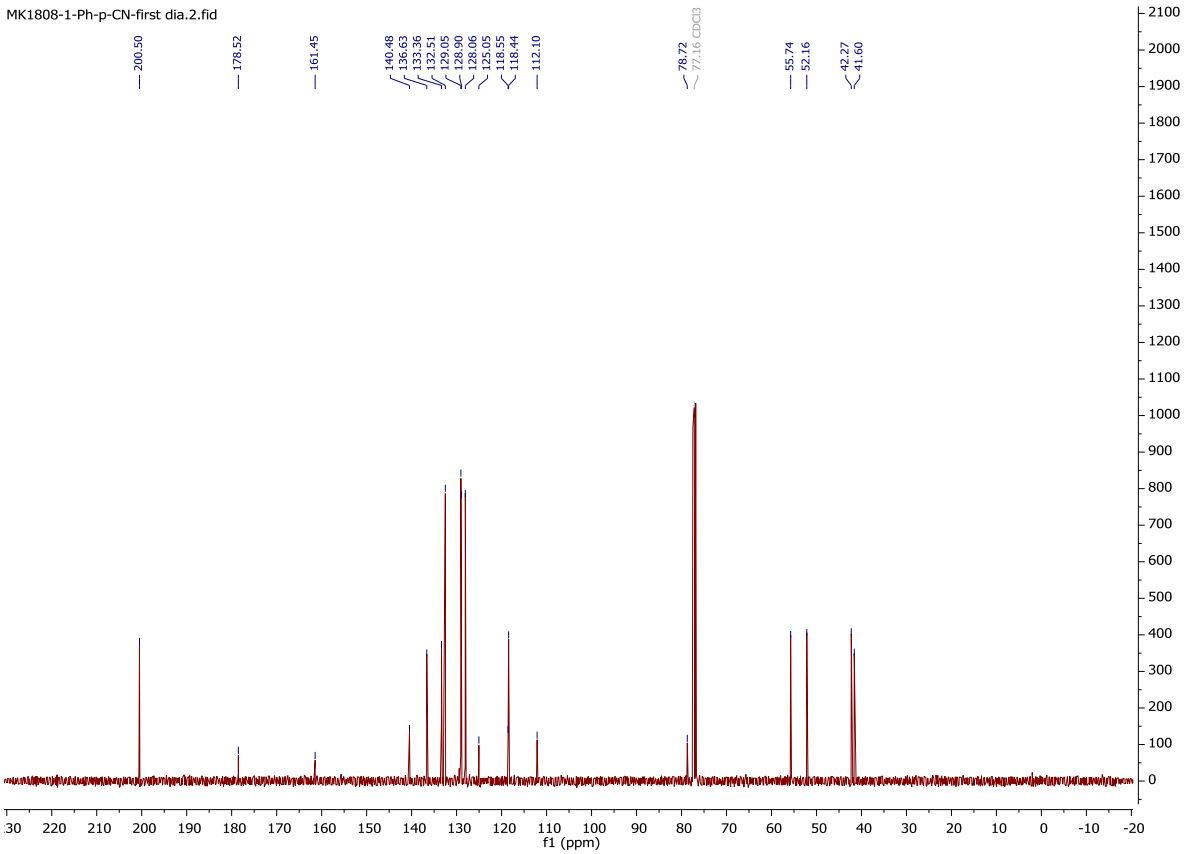

MK1791-1-Ph-p-ClPh.1.fid
Cl
O
CHO
O
N
4d
7.26 CDCl3
1.28
2.75
1.47
2.85
5.60
1.36
2.79
1.33
0.40
2.33
0.38
2.36
f1 (ppm)

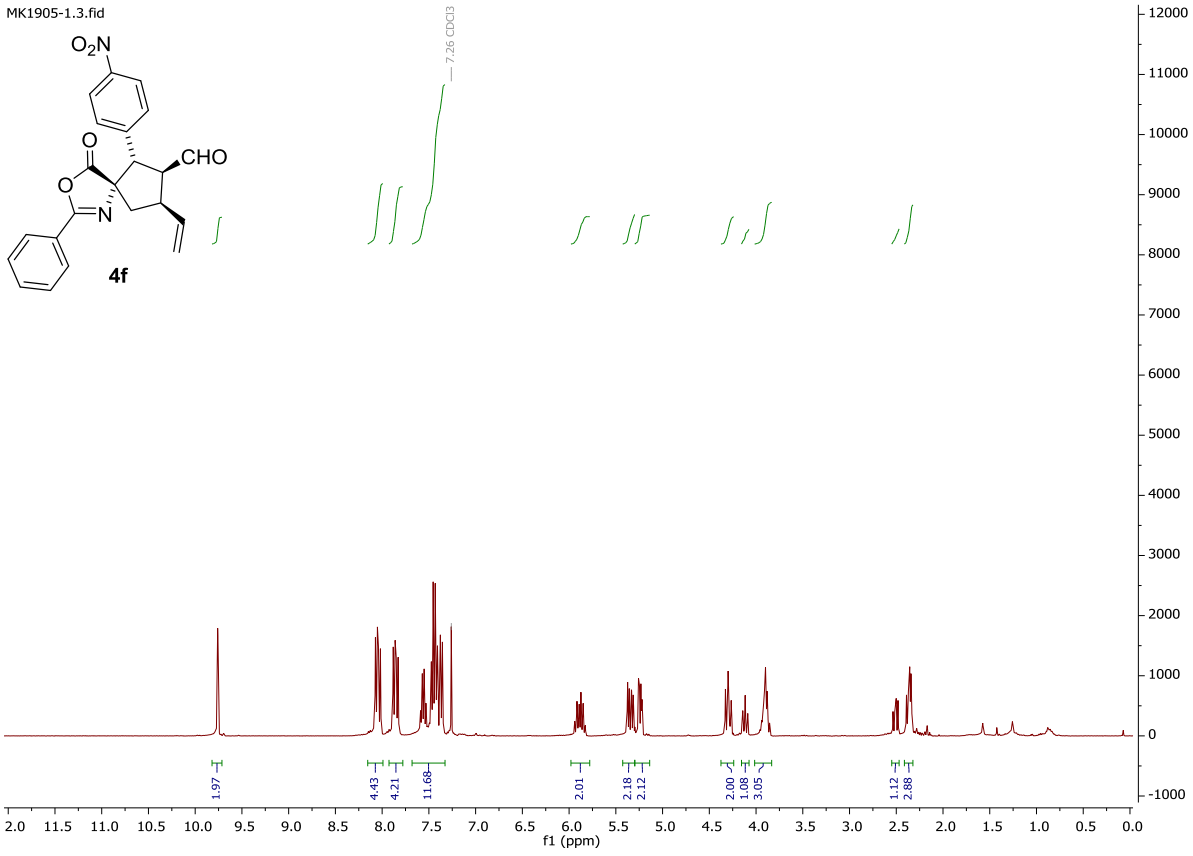

MK1791-1-Ph-p-ClPh.9.fid
201.27
201.08
178.75
161.23
160.21
136.84
136.75
134.02
133.85
133.37
133.24
133.15
133.06
130.33
129.39
128.97
128.94
128.61
128.05
127.97
125.44
125.27
118.13
118.05
78.84
77.86
77.16 CDCl3
58.74
55.89
53.88
51.80
43.74
43.28
42.40
41.44
f1 (ppm)

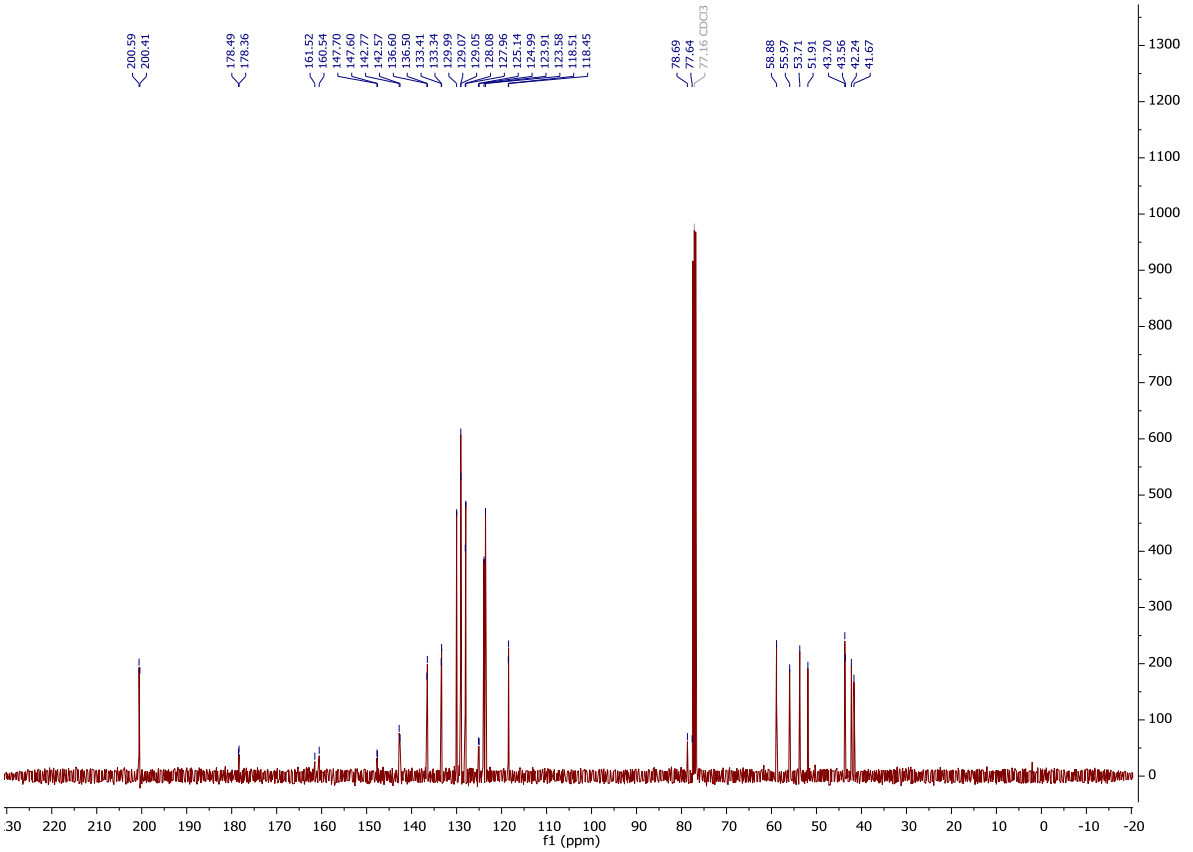

MK1813-2-Ph-p-CN-second dia.1.fid
NC
O
CHO
O
N
4e
7.26 CDCl3
1.00
2.08
1.28
4.38
2.01
1.04
2.15
0.91
1.99
1.89
f1 (ppm)


MK1813-2-Ph-p-CN-second dia.2.fid
200.68
178.41
160.46
140.64
136.53
133.30
132.17
129.80
129.05
129.03
128.06
127.94
125.18
118.37
111.94
77.68
77.16 CDCl3
58.64
54.07
43.73
43.44
f1 (ppm)

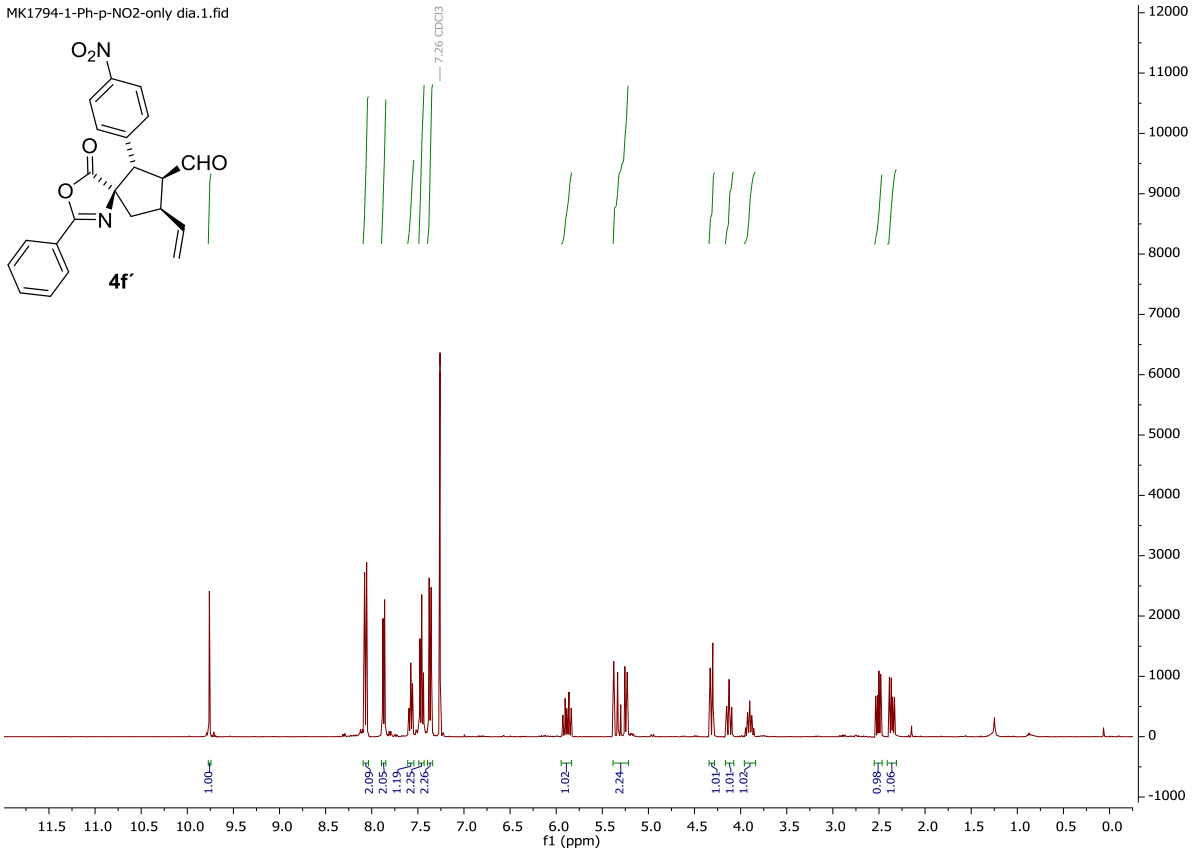

MK1808-1-Ph-p-CN-first dia.1.fid
NC
O
CHO
O
N
4e´
7.26 CDCl3
0.98
2.09
1.12
4.30
2.10
0.98
2.05
0.96
0.99
0.99
0.94
0.99
f1 (ppm)

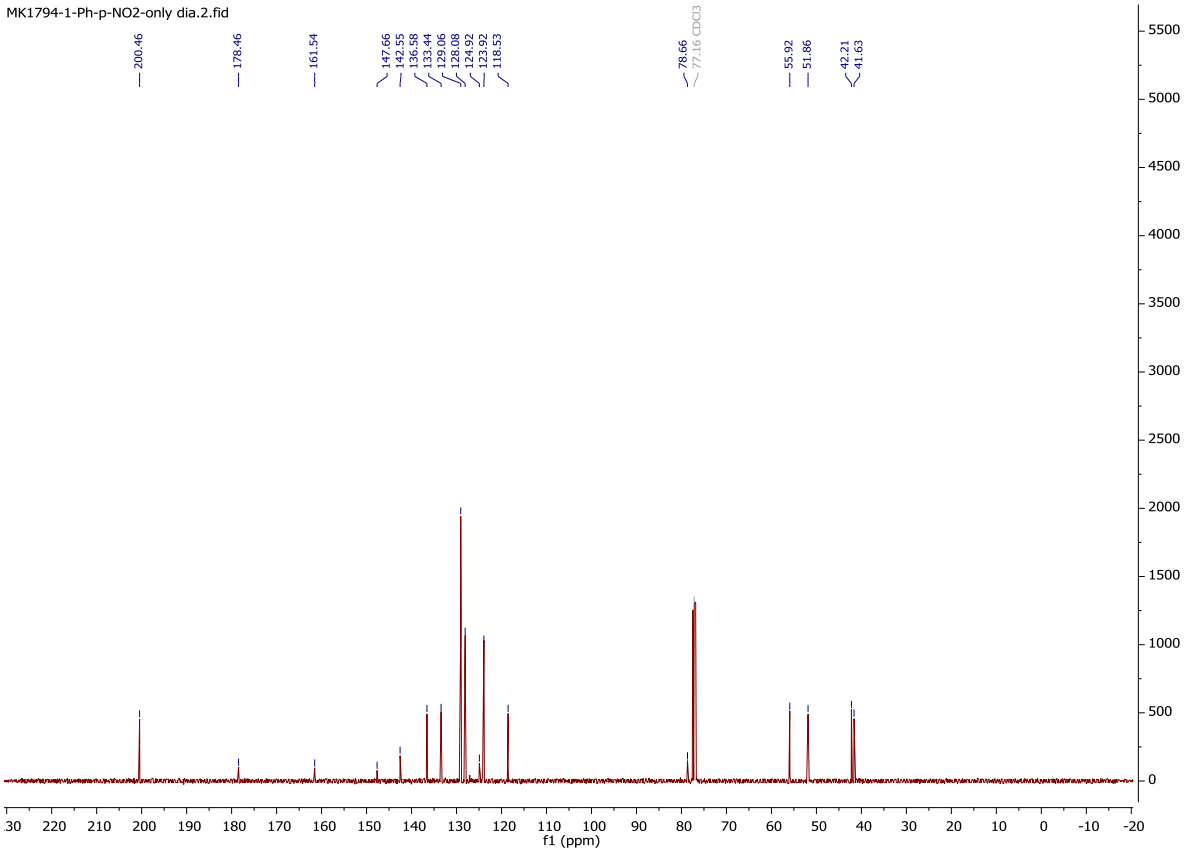

MK1808-1-Ph-p-CN-first dia.2.fid
200.50
178.52
161.45
140.48
136.63
133.36
132.51
129.95
128.90
128.06
125.05
118.55
118.44
112.10
78.72
77.16 CDCl3
55.74
52.16
42.27
41.60
f1 (ppm)

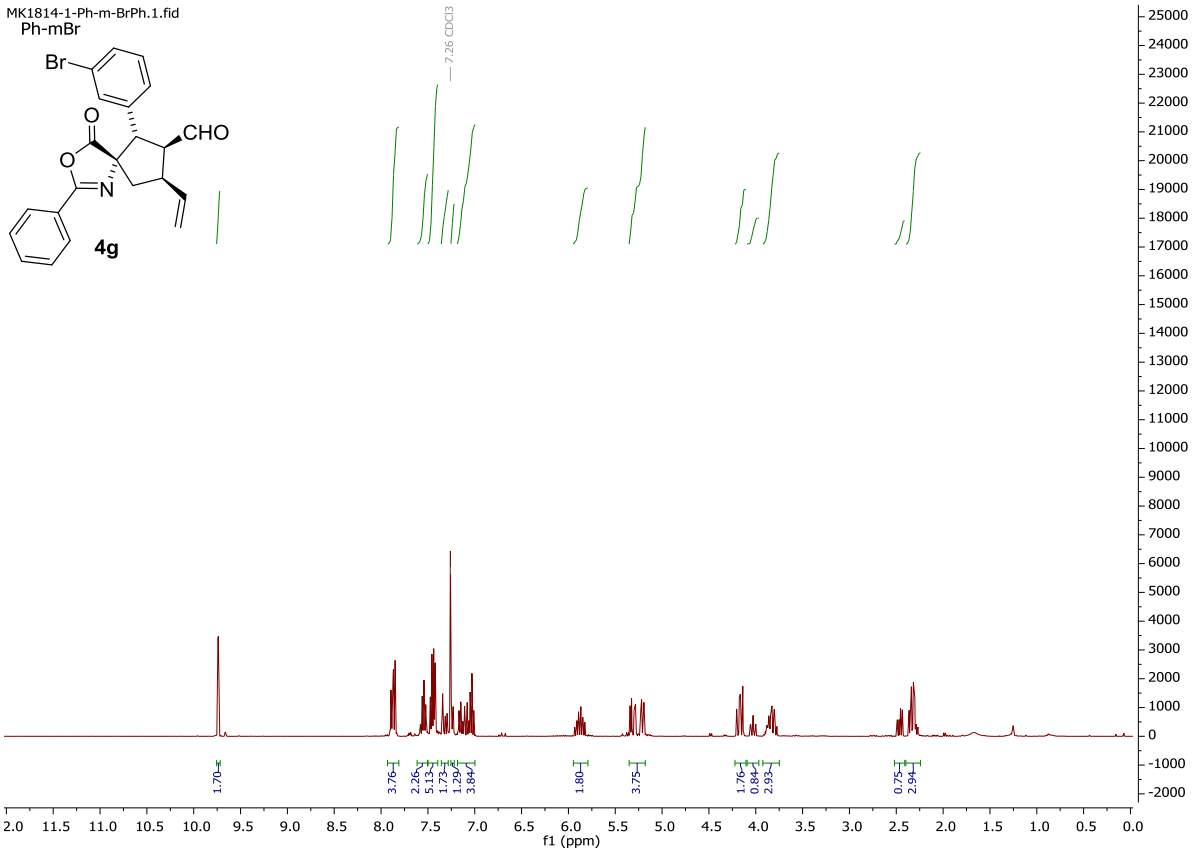


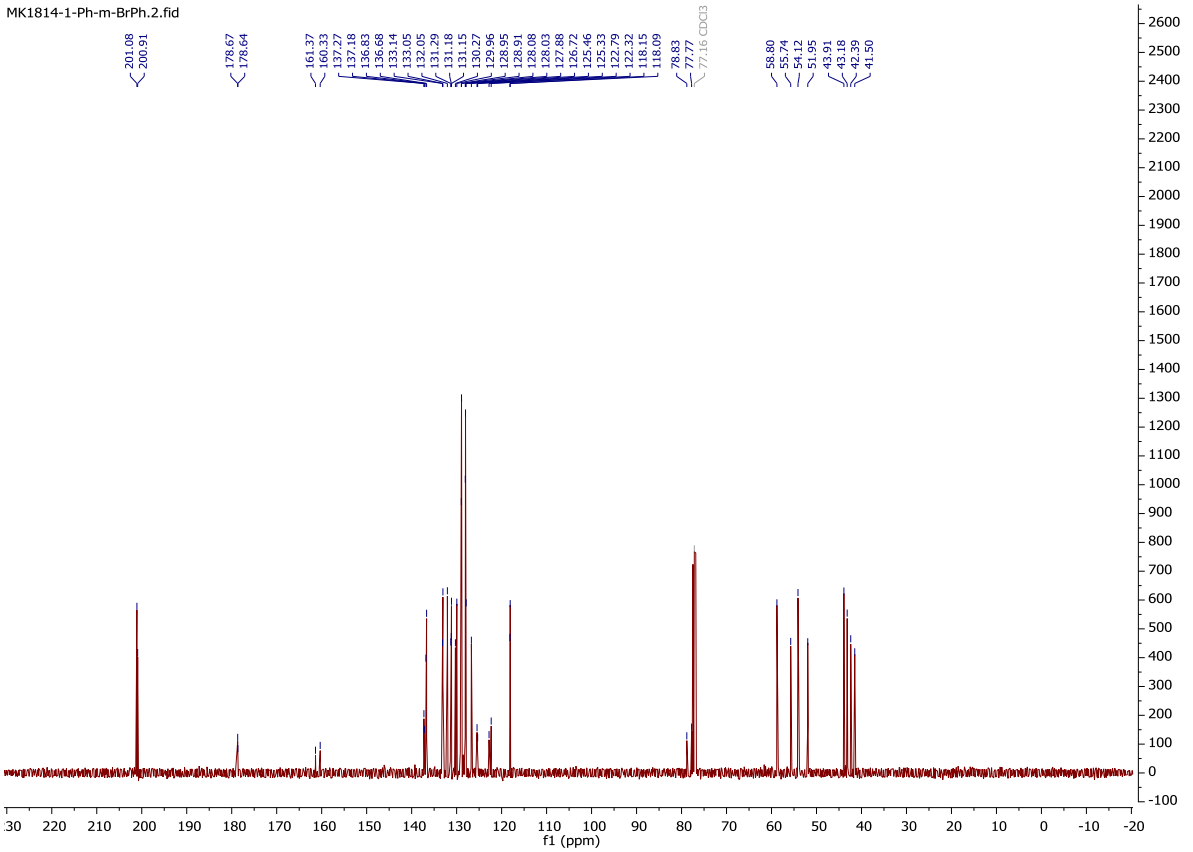



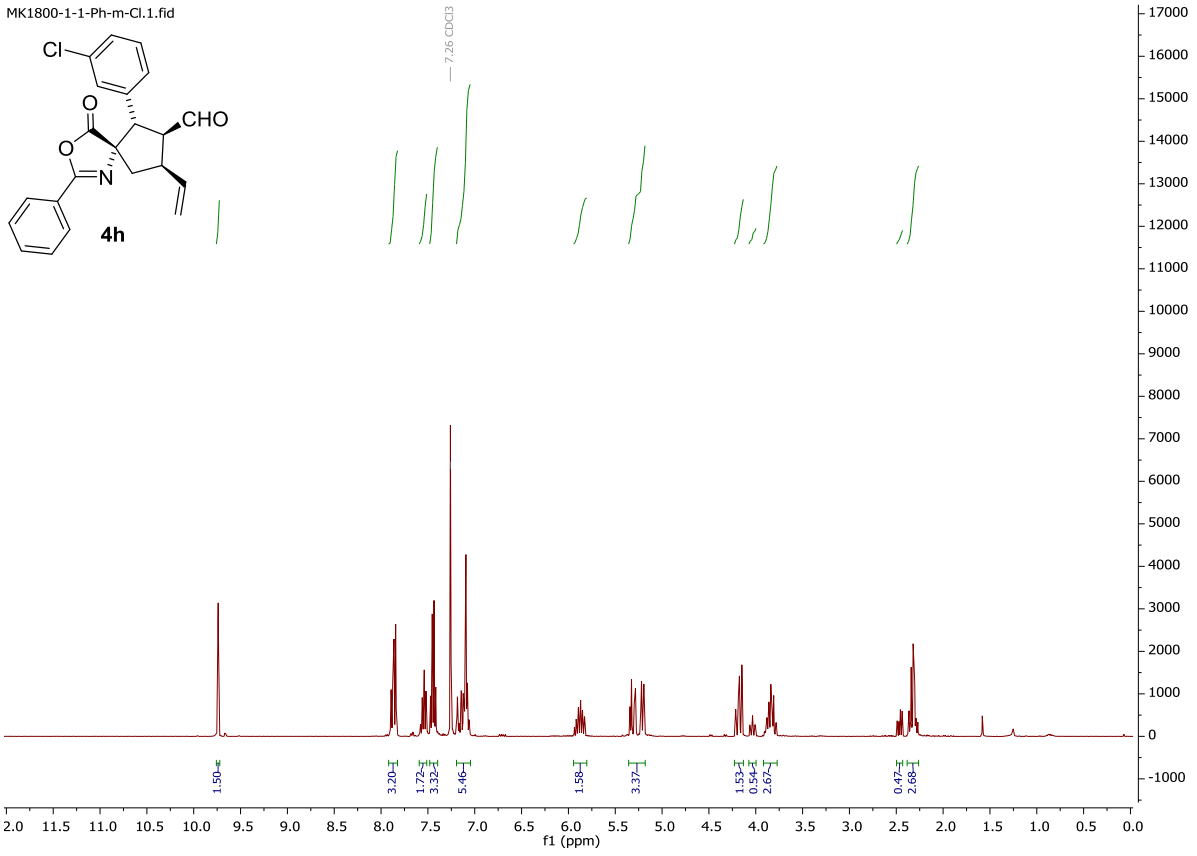

Minor diastereoizomer

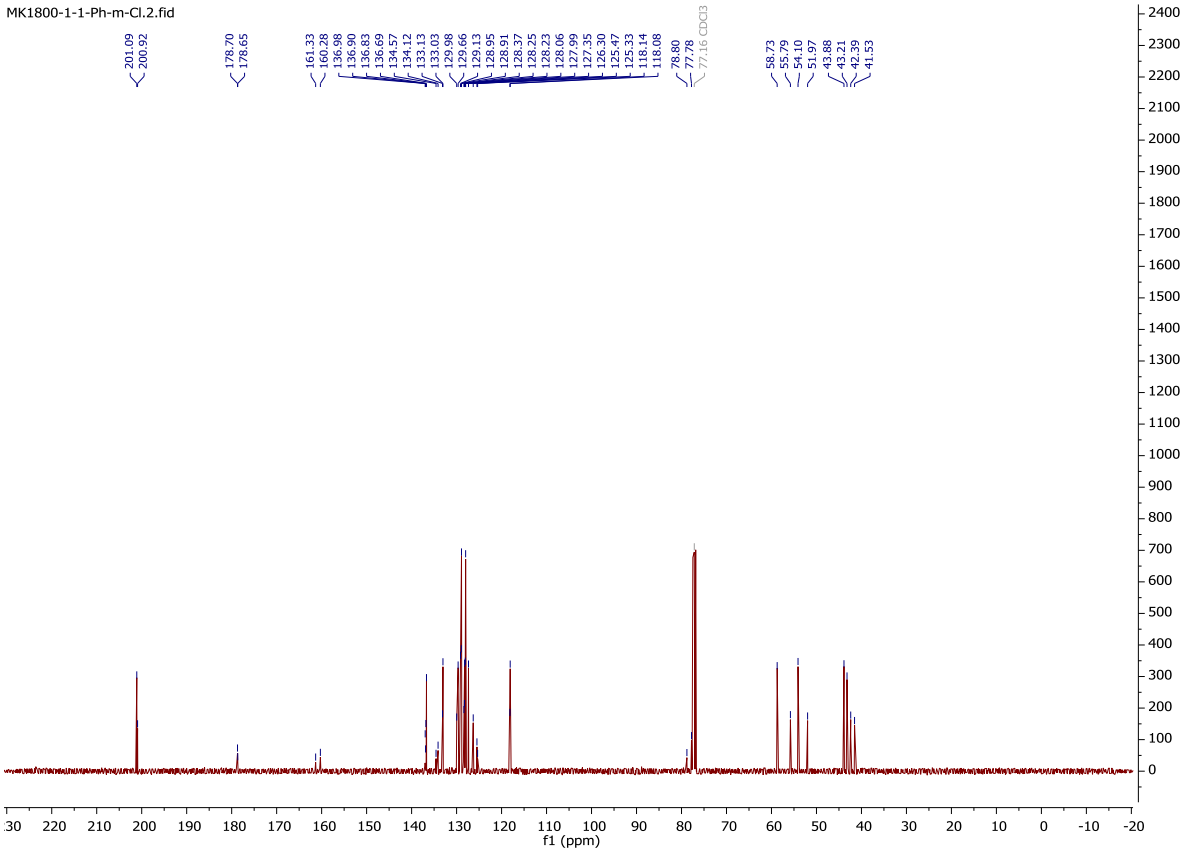

MK1794-1-Ph-p-NO2-only dia.1.fid
$O_2N$
O
CHO
O
N
4f´
7.26 CDCl3
1.00
2.09
2.05
1.19
2.25
2.26
1.02
2.24
1.01
1.01
1.02
0.98
1.06
f1 (ppm)


MK1794-1-Ph-p-NO2-only dia.2.fid
200.46
178.46
161.54
147.66
142.55
136.58
133.44
129.06
128.08
124.92
123.92
118.53
78.66
77.16 CDCl3
55.92
51.86
42.21
41.63
f1 (ppm)

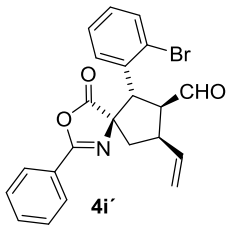

MK1814-1-Ph-m-BrPh.1.fid
Ph-mBr
Br
O
O
N
CHO
4g
7.26 CDCl3
1.70
3.76
2.26
5.13
1.73
1.29
3.84
1.80
3.75
1.76
0.84
2.93
0.75
2.94
f1 (ppm)


MK1814-1-Ph-m-BrPh.2.fid
201.08
200.91
178.67
178.64
161.37
160.33
137.27
137.18
136.83
136.68
133.14
133.05
132.05
131.29
131.18
131.15
130.27
129.96
128.95
128.91
128.08
128.03
127.88
126.72
125.46
125.33
122.79
122.32
118.15
118.09
78.83
77.77
77.16 CDCl3
58.80
55.74
54.12
51.95
43.91
43.18
42.39
41.50
f1 (ppm)


MK1800-1-1-Ph-m-Cl.1.fid
Cl
O
O
N
CHO
4h
7.26 CDCl3
1.50
3.20
1.72
3.32
5.46
1.58
3.37
1.53
0.54
2.67
0.47
2.68
f1 (ppm)


MK1800-1-1-Ph-m-Cl.2.fid
201.09
200.92
178.70
178.65
161.33
160.28
136.98
136.90
136.83
136.69
134.57
134.12
133.13
133.03
129.98
129.66
129.13
128.95
128.91
128.37
128.25
128.23
128.06
127.99
127.35
126.30
125.47
125.33
118.14
118.08
78.80
77.78
77.16 CDCl3
58.73
55.79
54.10
51.97
43.88
43.21
42.39
41.53
f1 (ppm)

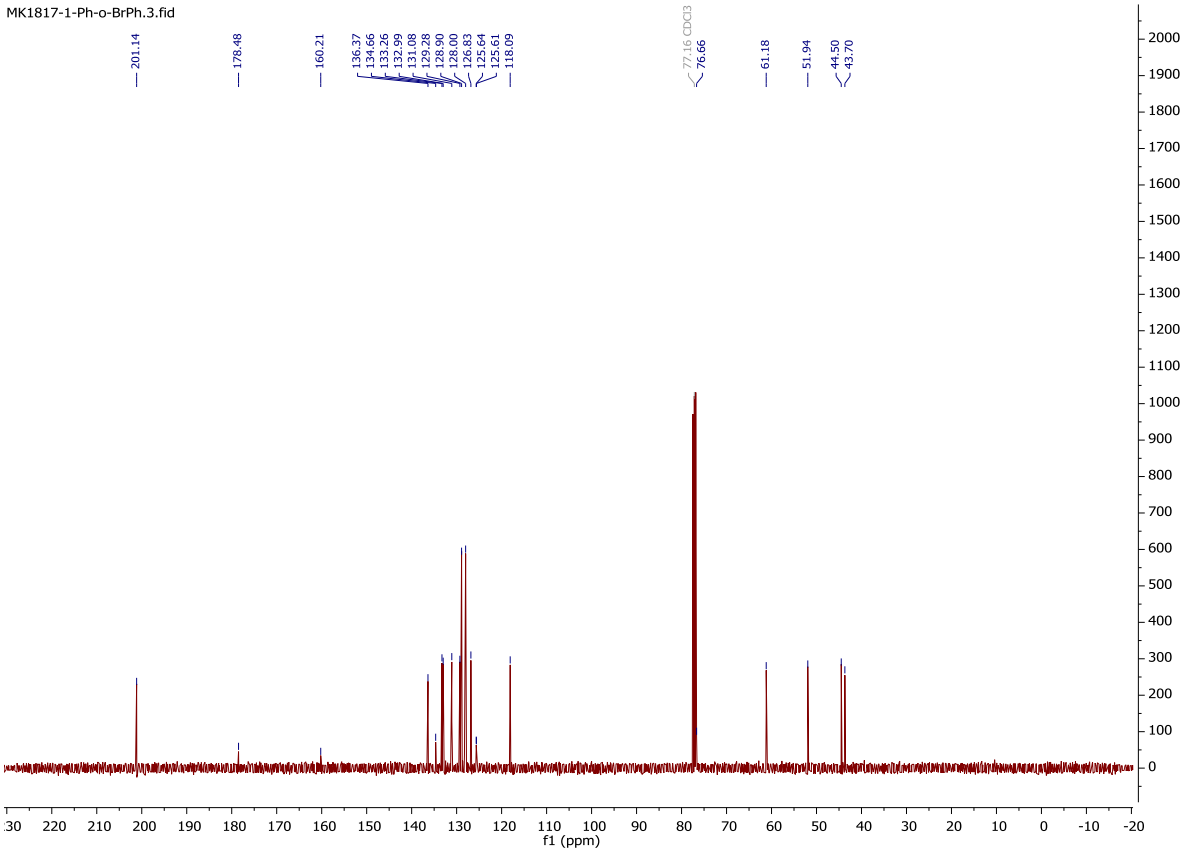
MK1817-1-Ph-o-BrPh.2.fid

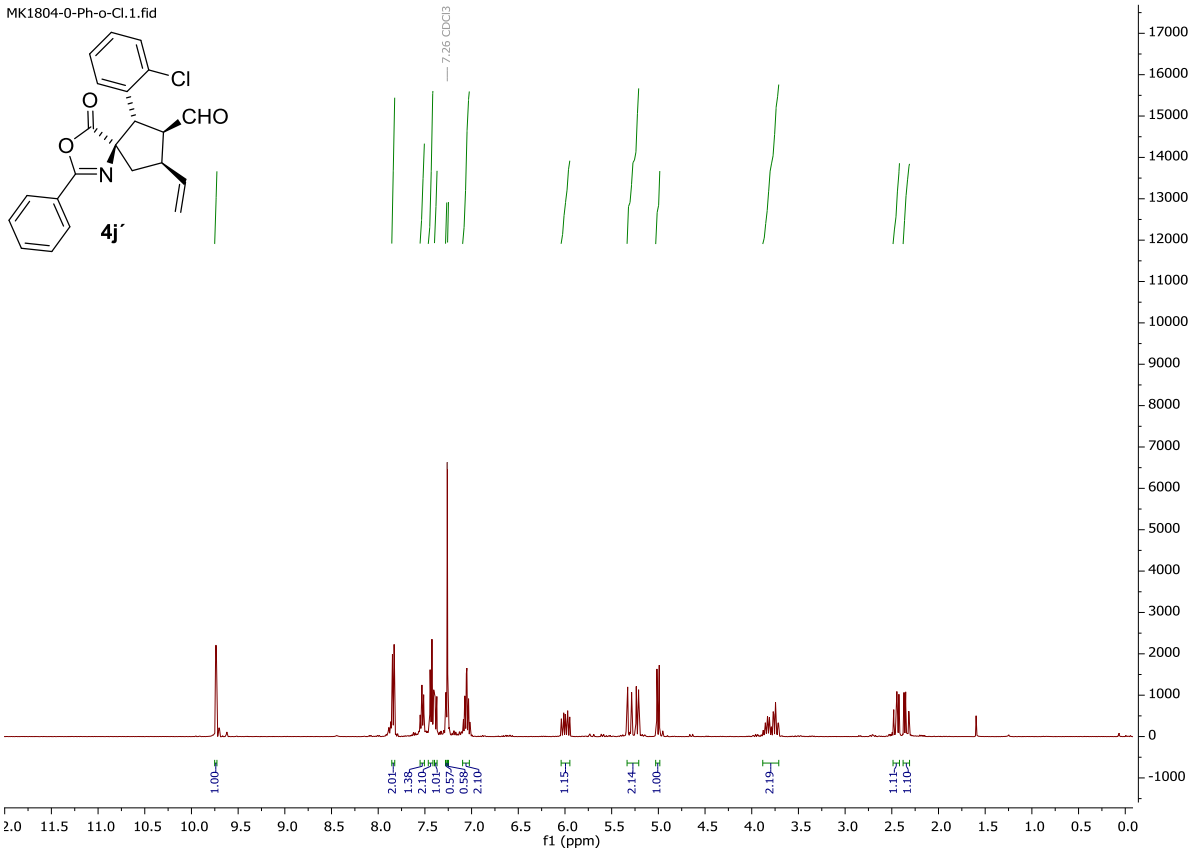


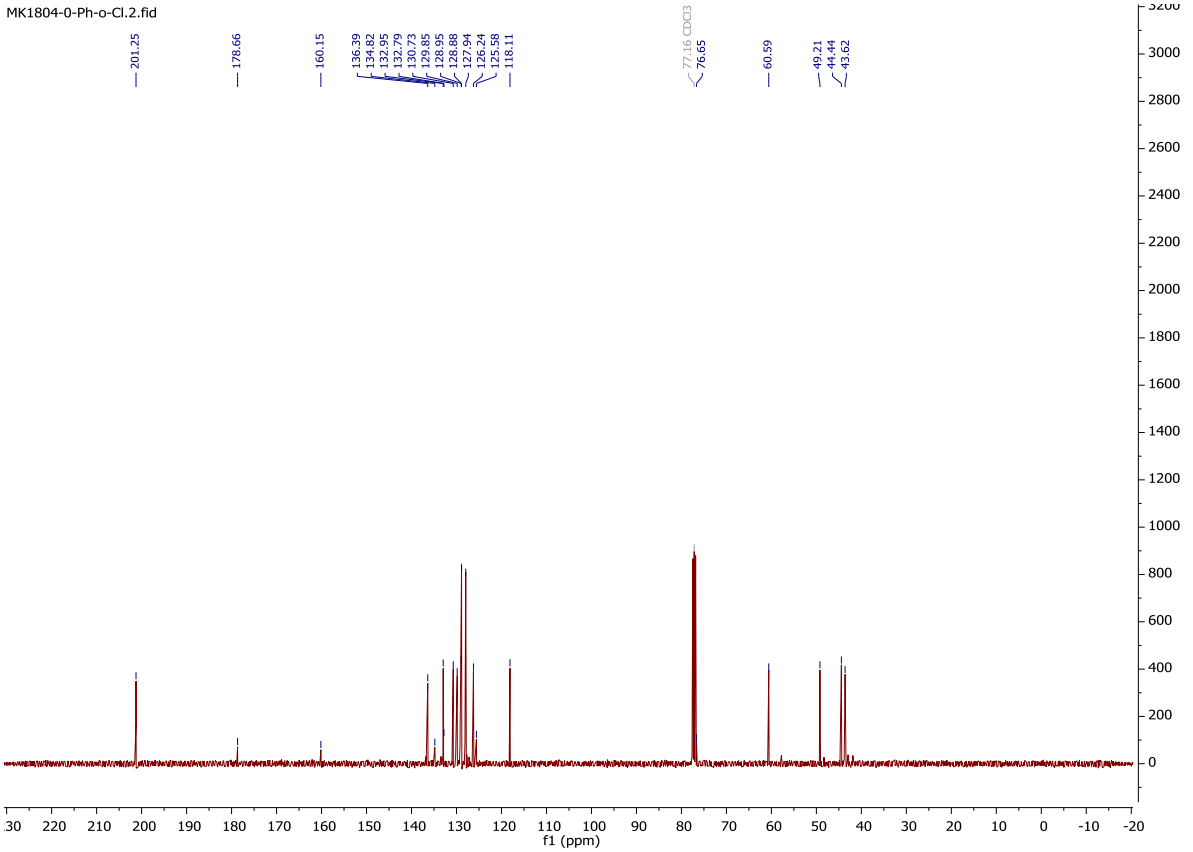

**4i´**

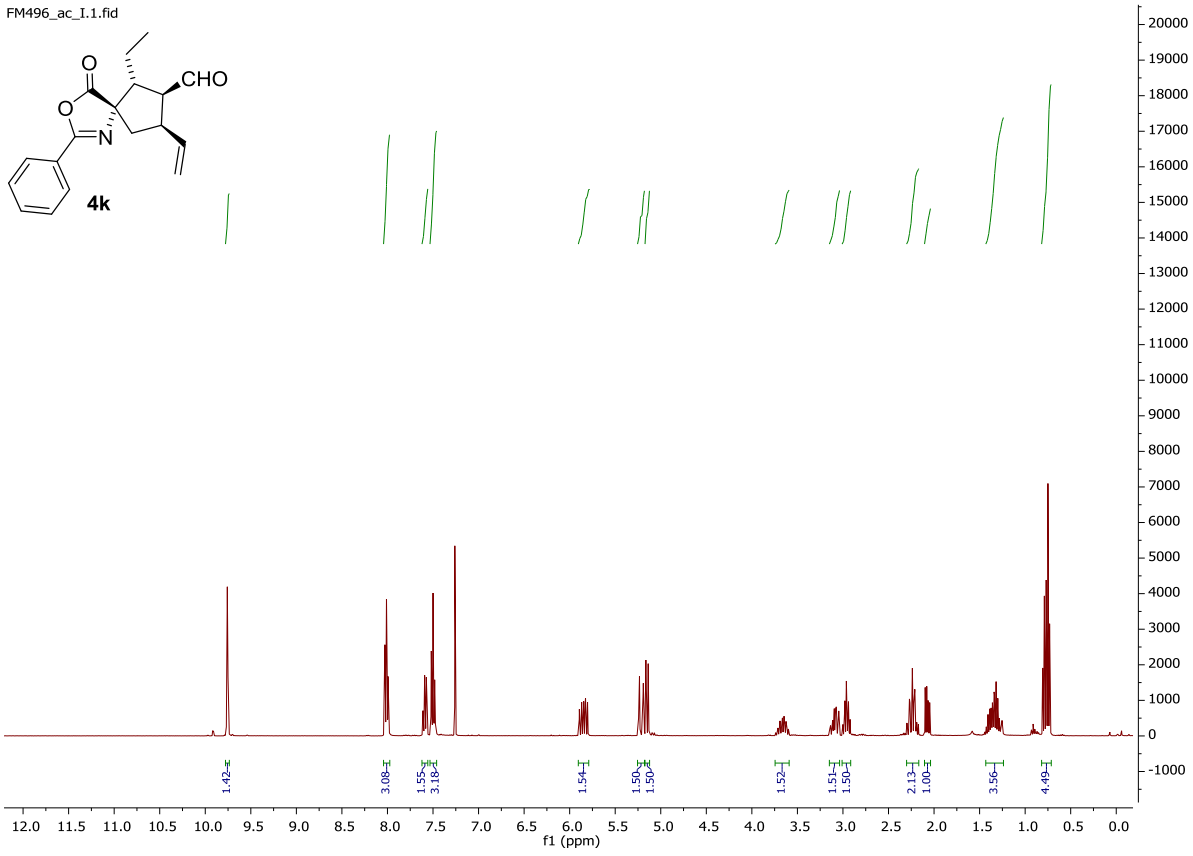


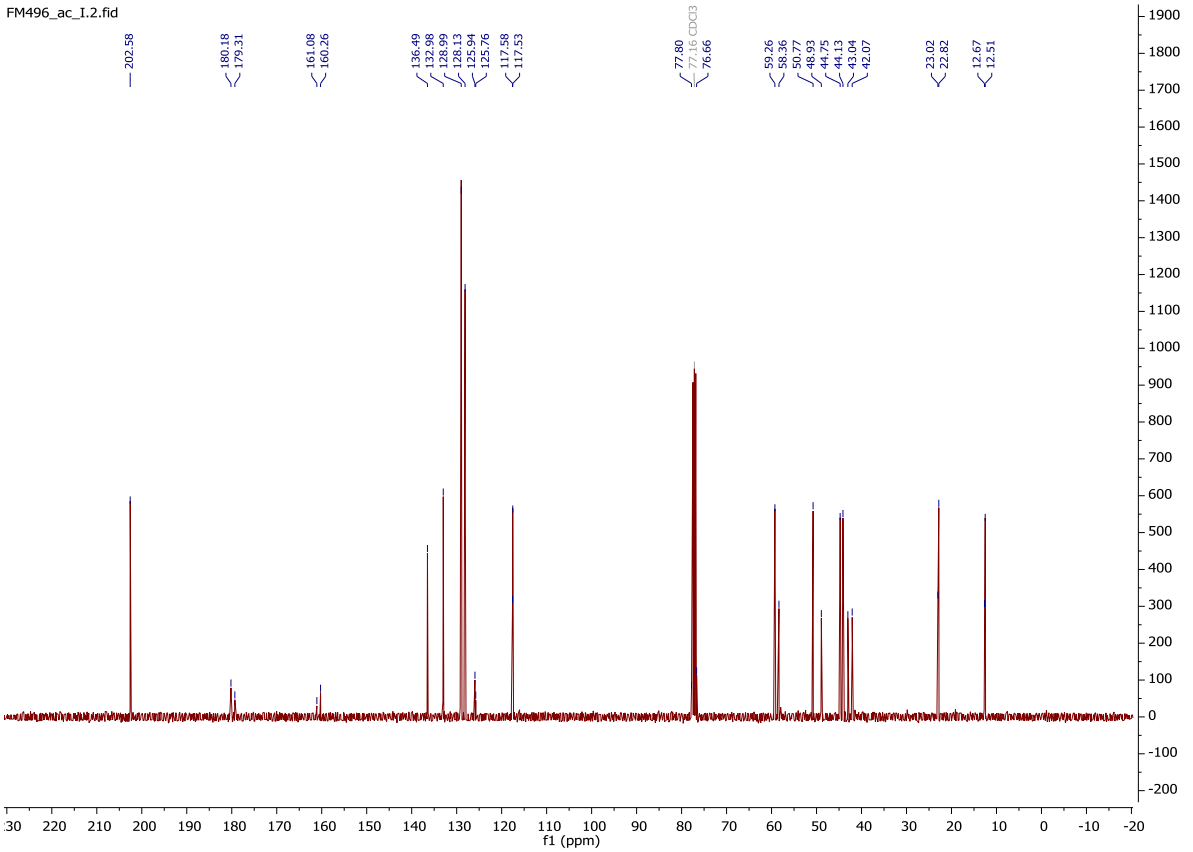

MK1817-1-Ph-o-BrPh.3.fid

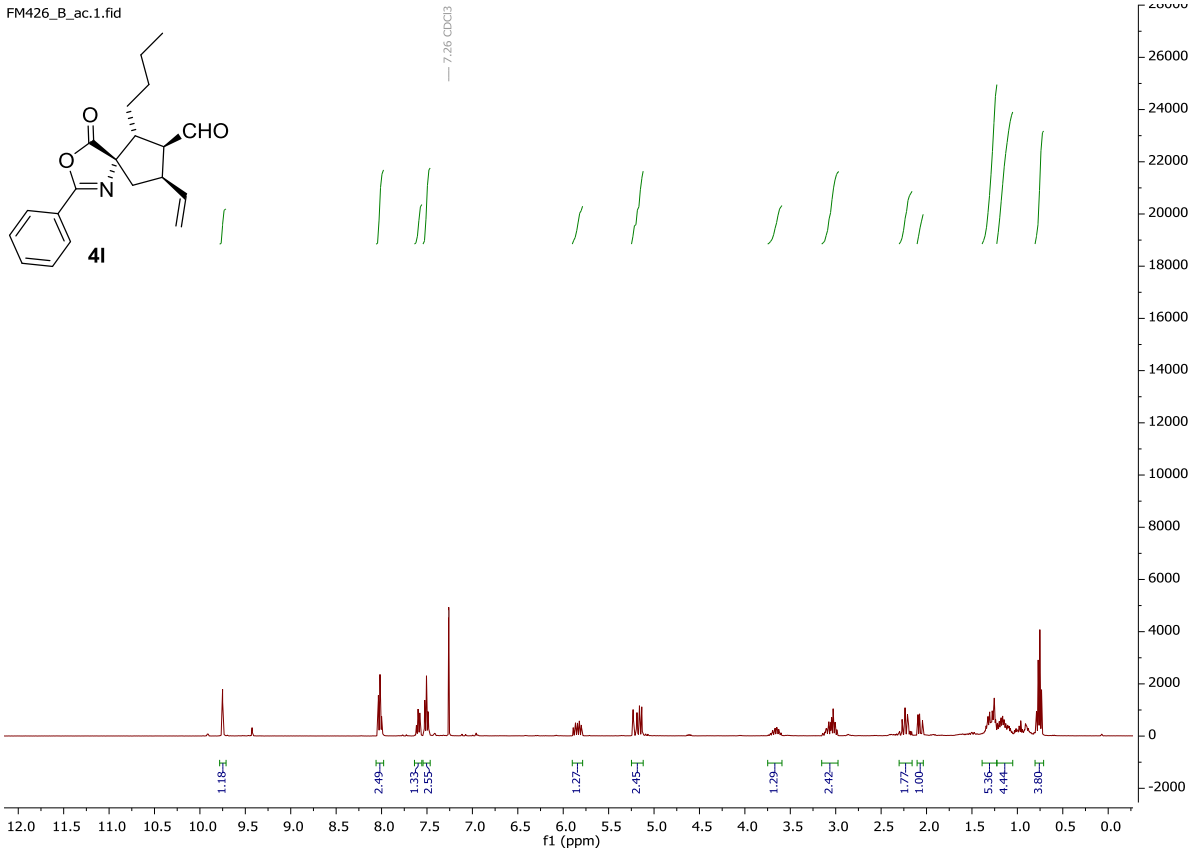


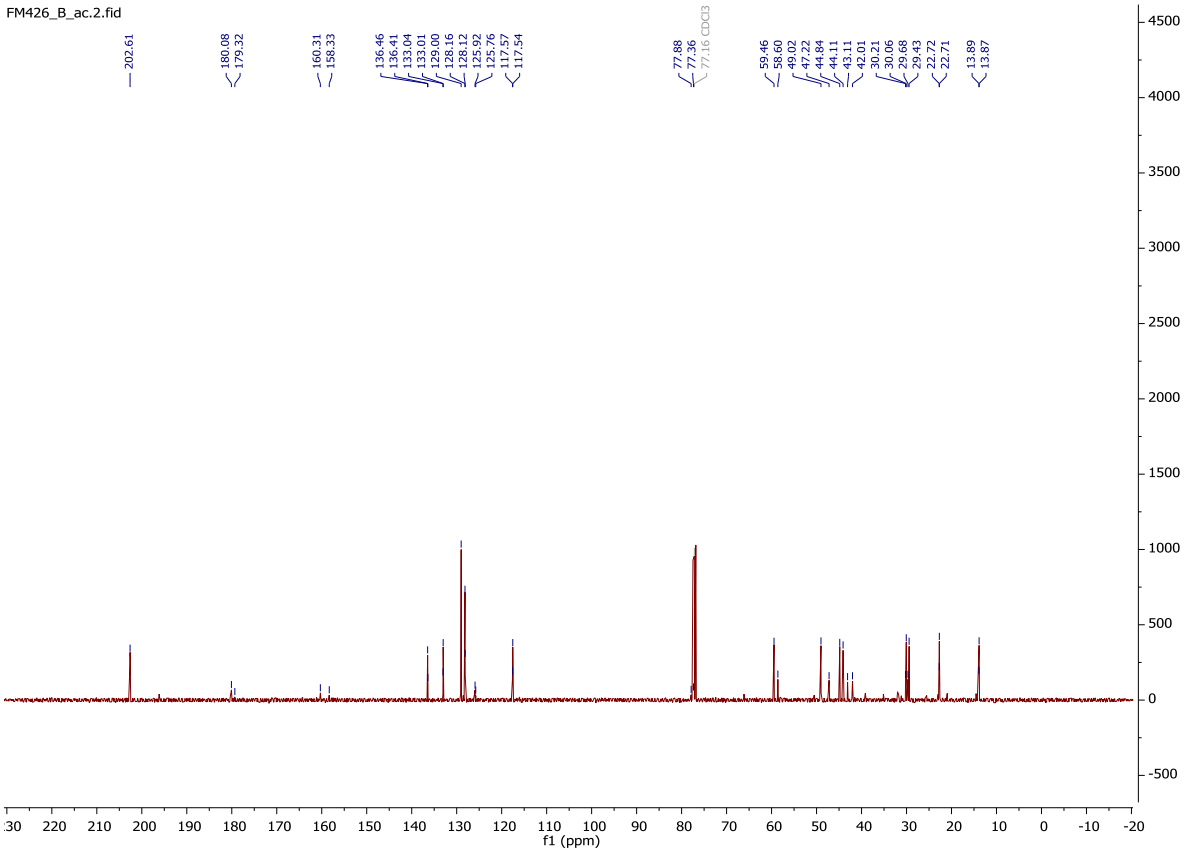

MK1804-0-Ph-o-Cl.1.fid
Cl
O
CHO
O
N
4j´
7.26 CDCl3
1.00
2.01
1.38
2.10
1.01
0.57
0.58
2.10
1.15
2.14
1.00
2.19
1.11
1.10
f1 (ppm)

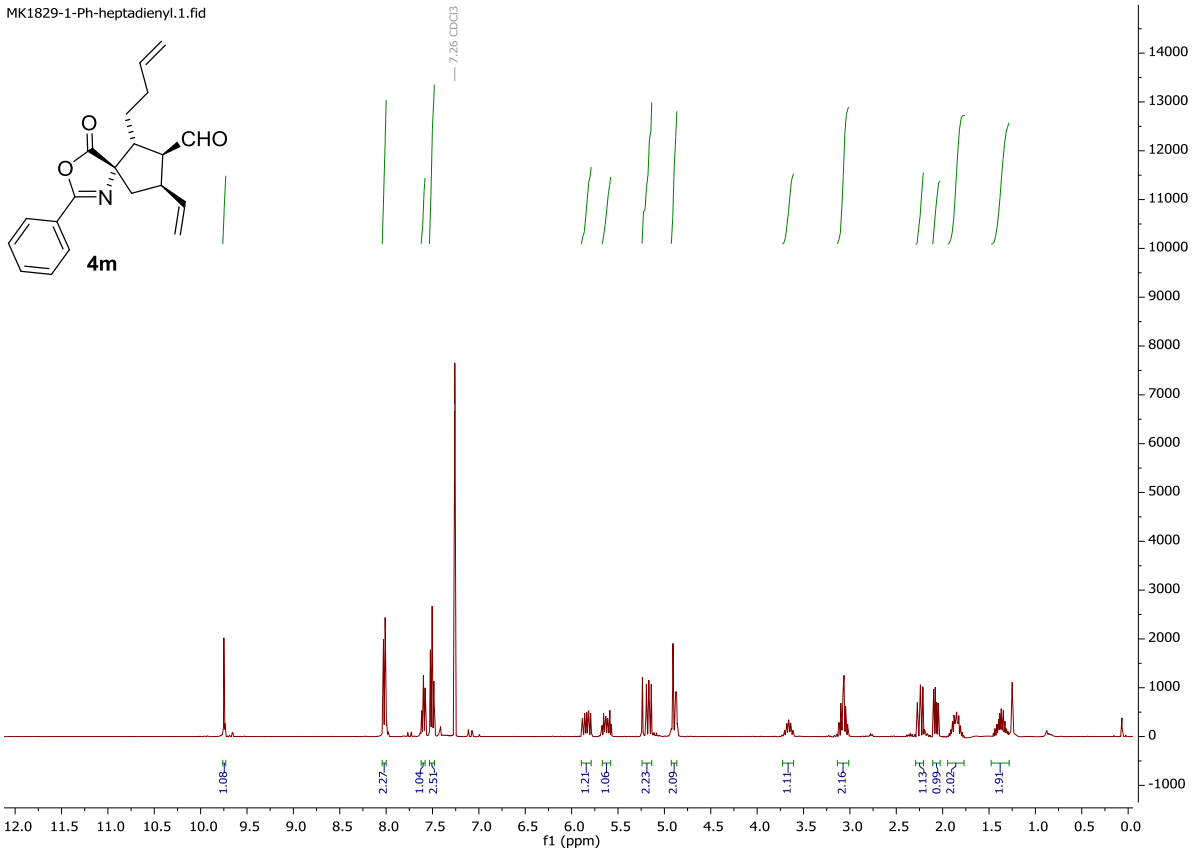

MK1804-0-Ph-o-Cl.2.fid
201.25
178.66
160.15
136.39
134.82
132.95
132.79
130.73
129.85
128.95
128.88
127.94
126.24
125.58
118.11
77.16 CDCl3
76.65
60.59
49.21
44.44
43.62
f1 (ppm)

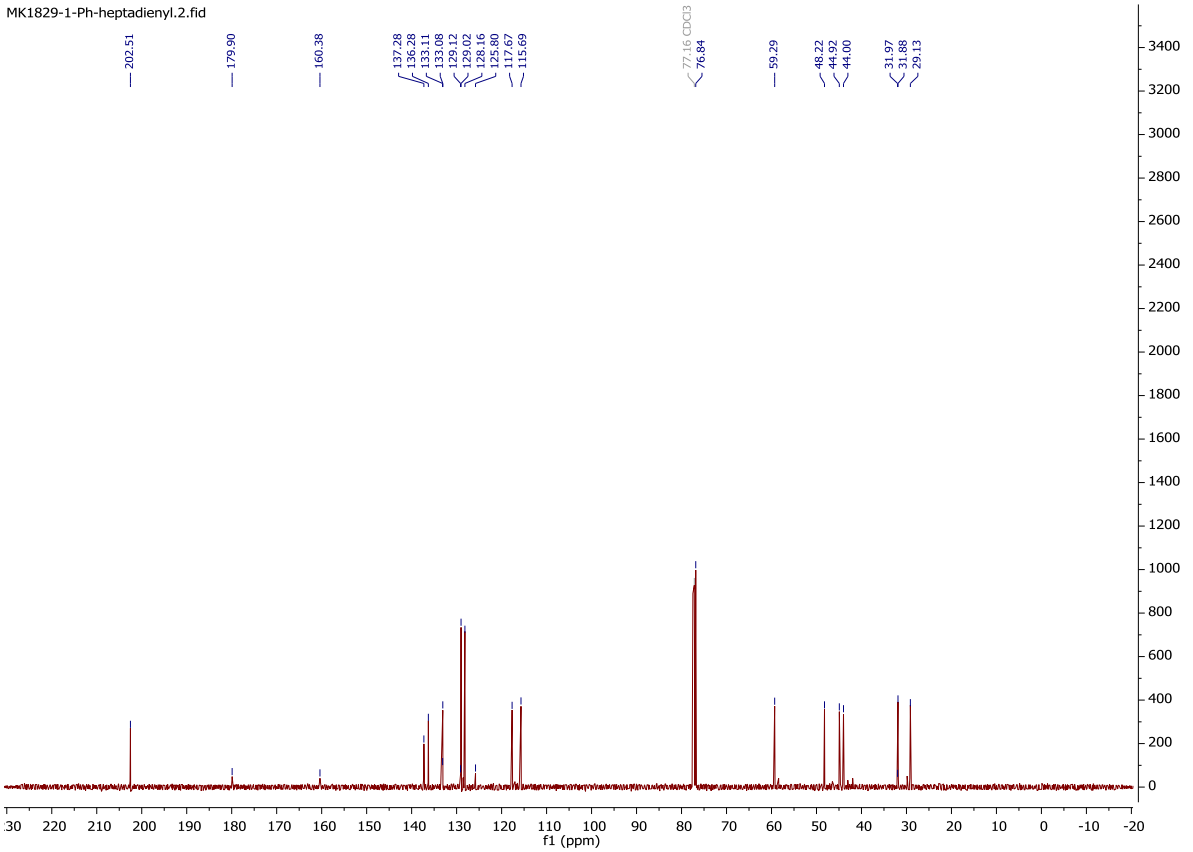

FM496_ac_I.1.fid
O
O
N
CHO
4k
1.42
3.08
1.55
3.18
1.54
1.50
1.50
1.52
1.51
1.50
2.13
1.00
3.56
4.49
f1 (ppm)


FM496_ac_I.2.fid
202.58
180.18
179.31
161.08
160.26
136.49
132.98
128.99
128.13
125.94
125.76
117.58
117.53
77.80
77.16 CDCl3
76.66
59.26
58.36
50.77
48.93
44.75
44.13
43.04
42.07
23.02
22.82
12.67
12.51
f1 (ppm)

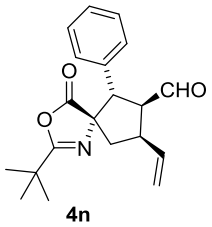

FM426_B_ac.1.fid
7.26 CDCl3
O
CHO
O
N
4l
1.18
2.49
1.33
2.55
1.27
2.45
1.29
2.42
1.77
1.00
5.36
4.44
3.80
f1 (ppm)


FM426_B_ac.2.fid
202.61
180.08
179.32
160.31
158.33
136.46
136.41
133.04
133.01
129.00
128.16
128.12
125.92
125.76
117.57
117.54
77.88
77.36
77.16 CDCl3
59.46
58.60
49.02
47.22
44.84
44.11
43.11
42.01
30.21
30.06
29.68
29.43
22.72
22.71
13.89
13.87
f1 (ppm)


MK1829-1-Ph-heptadienyl.1.fid
7.26 CDCl3
O
O
N
CHO
4m
1.08
2.27
1.04
2.51
1.21
1.06
2.23
2.09
1.11
2.16
1.13
0.99
2.02
1.91
f1 (ppm)


MK1829-1-Ph-heptadienyl.2.fid
202.51
179.90
160.38
137.28
136.28
133.11
133.08
129.12
129.02
128.16
125.80
117.67
115.69
77.16 CDCl3
76.84
59.29
48.22
44.92
44.00
31.97
31.88
29.13
f1 (ppm)

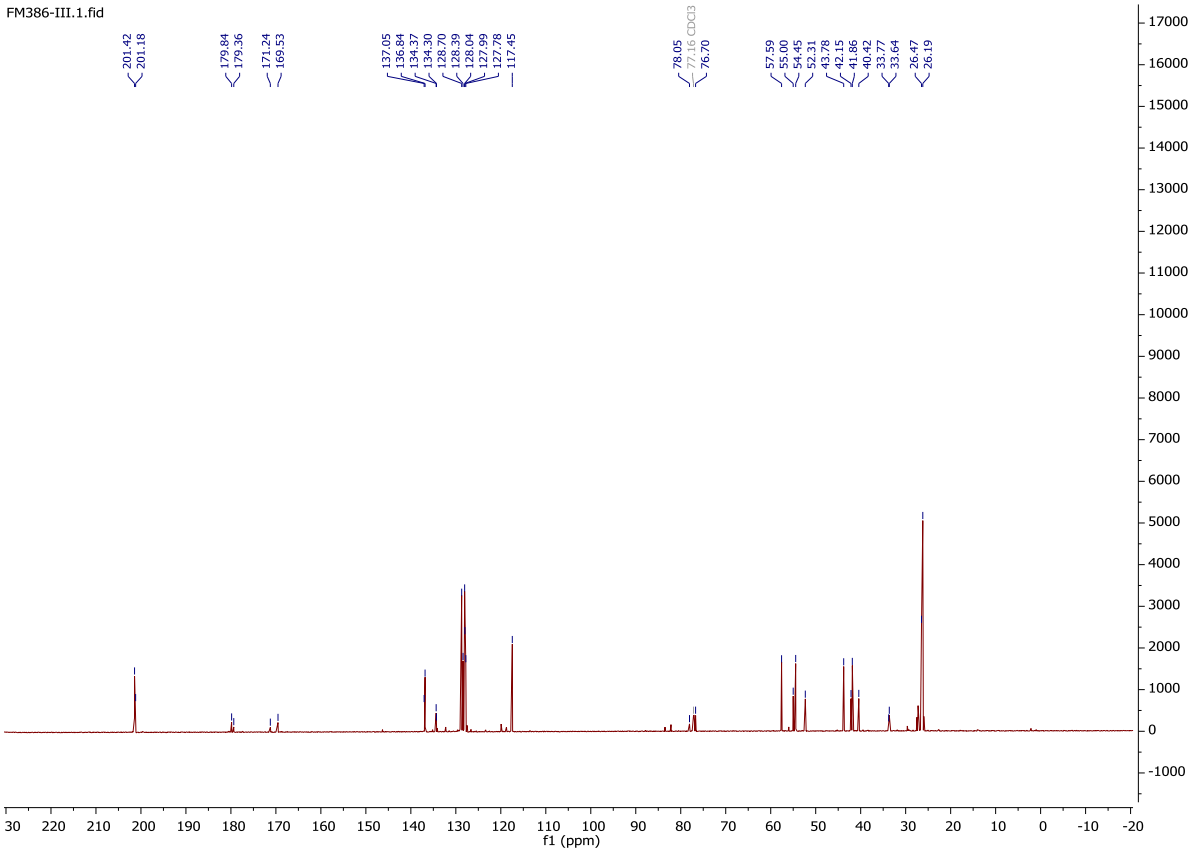
FM386-I_p2.1.fid

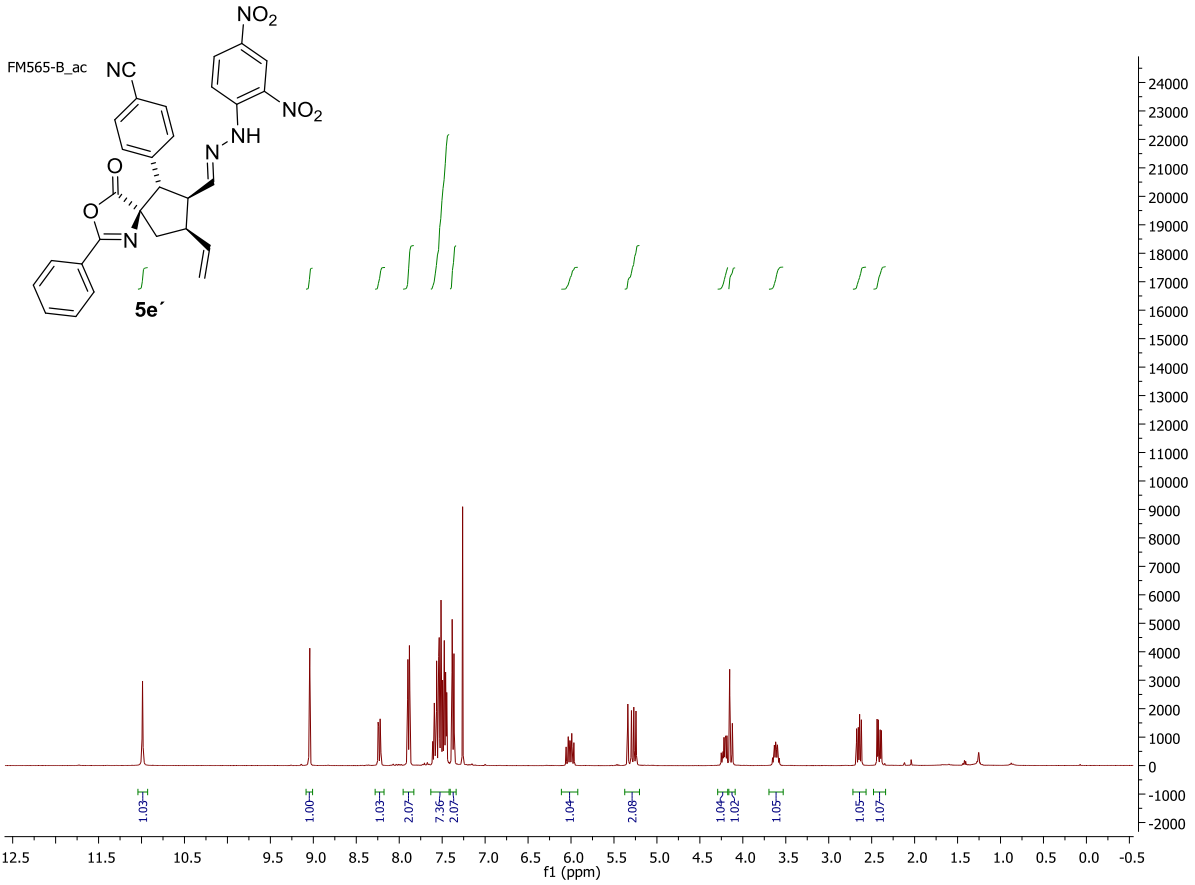


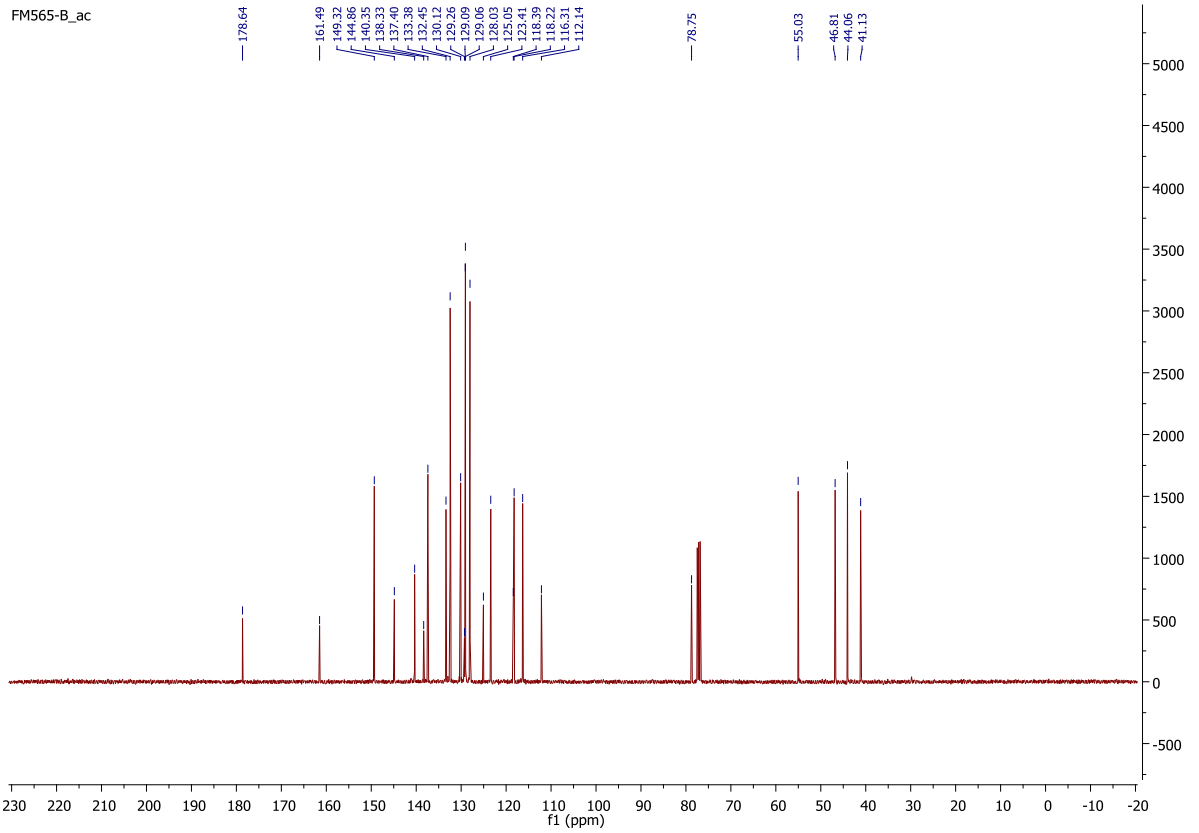

**4n**



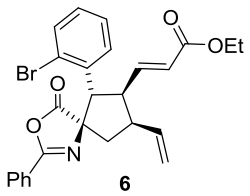

FM386-III.1.fid




FM565-B_ac
NC
NO2
NO2
NH
N
O
O
N
5e´
1.03
1.00
1.03
2.07
7.36
2.07
1.04
2.08
1.04
1.02
1.05
1.05
1.07
f1 (ppm)


FM565-B_ac
178.64
161.49
149.32
144.86
140.35
138.33
137.40
133.38
132.45
130.12
129.26
129.09
129.06
128.03
125.05
123.41
118.39
118.22
116.31
112.14
78.75
55.03
46.81
44.06
41.13
f1 (ppm)

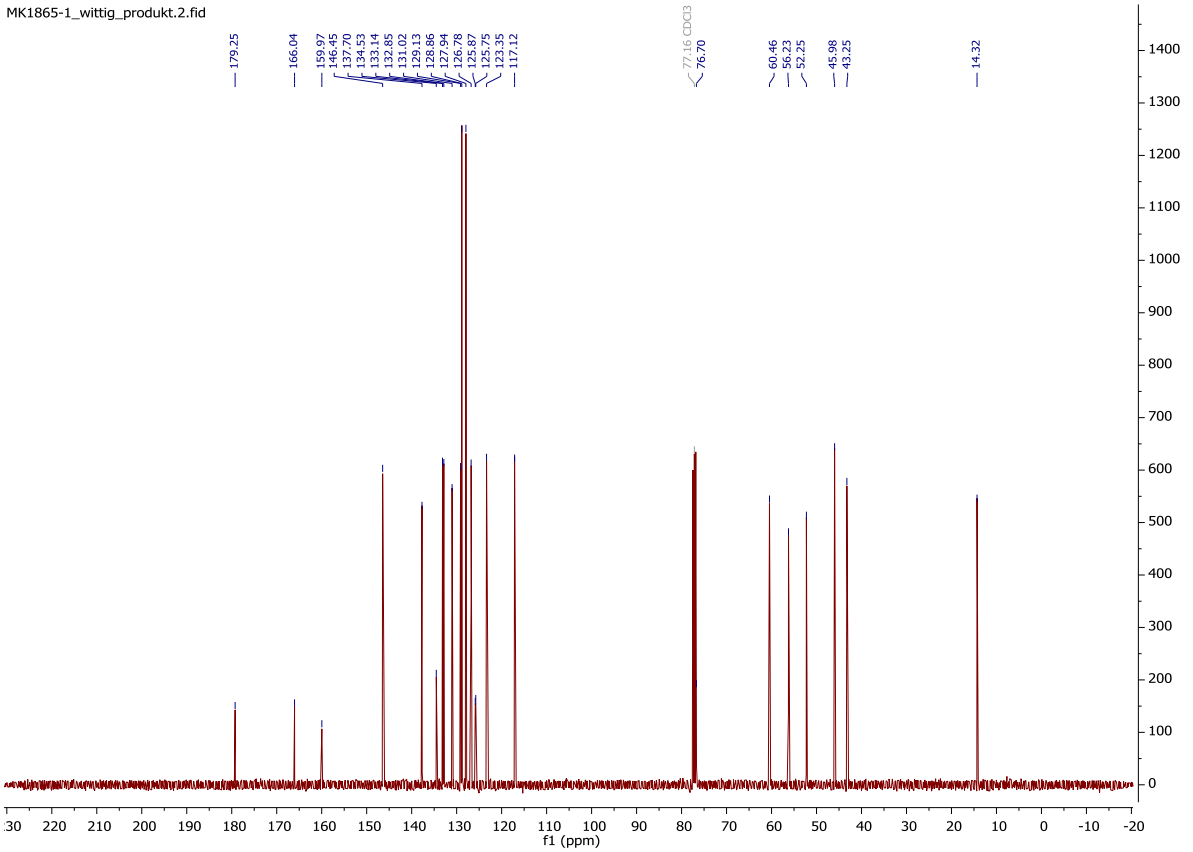
MK1865-1_wittig_produkt.1.fid



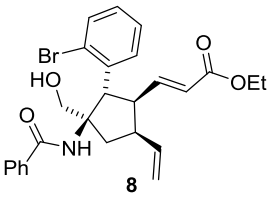

**6**




MK1865-1_wittig_produkt.2.fid



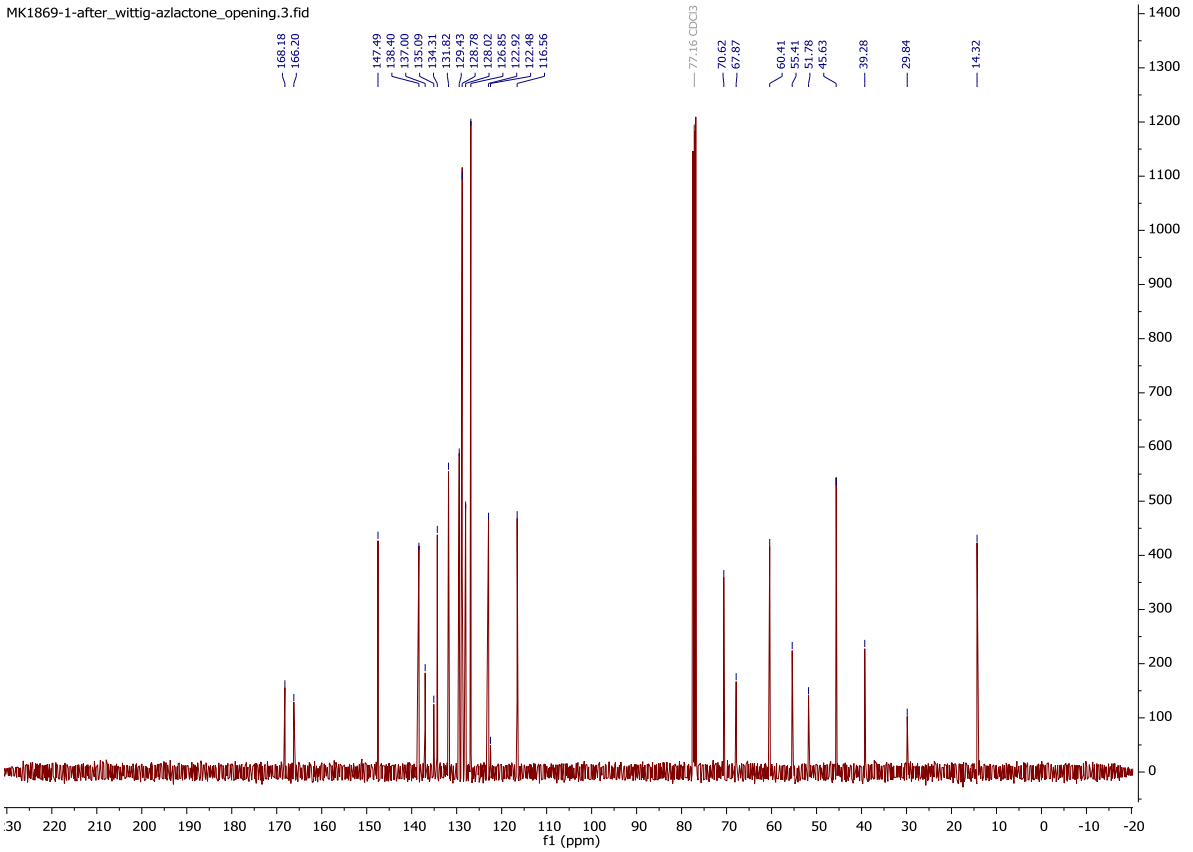
MK1869-1-after_wittig-azlactone_opening.2.fid

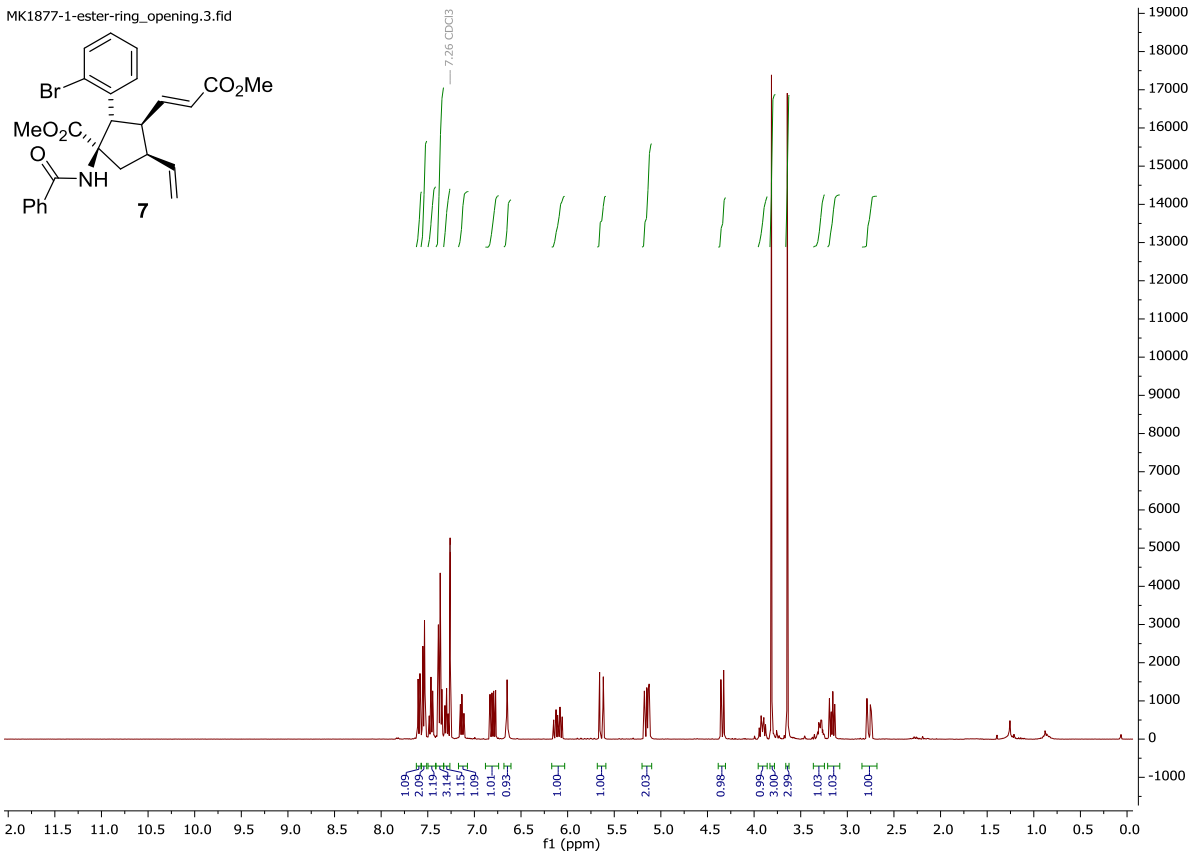


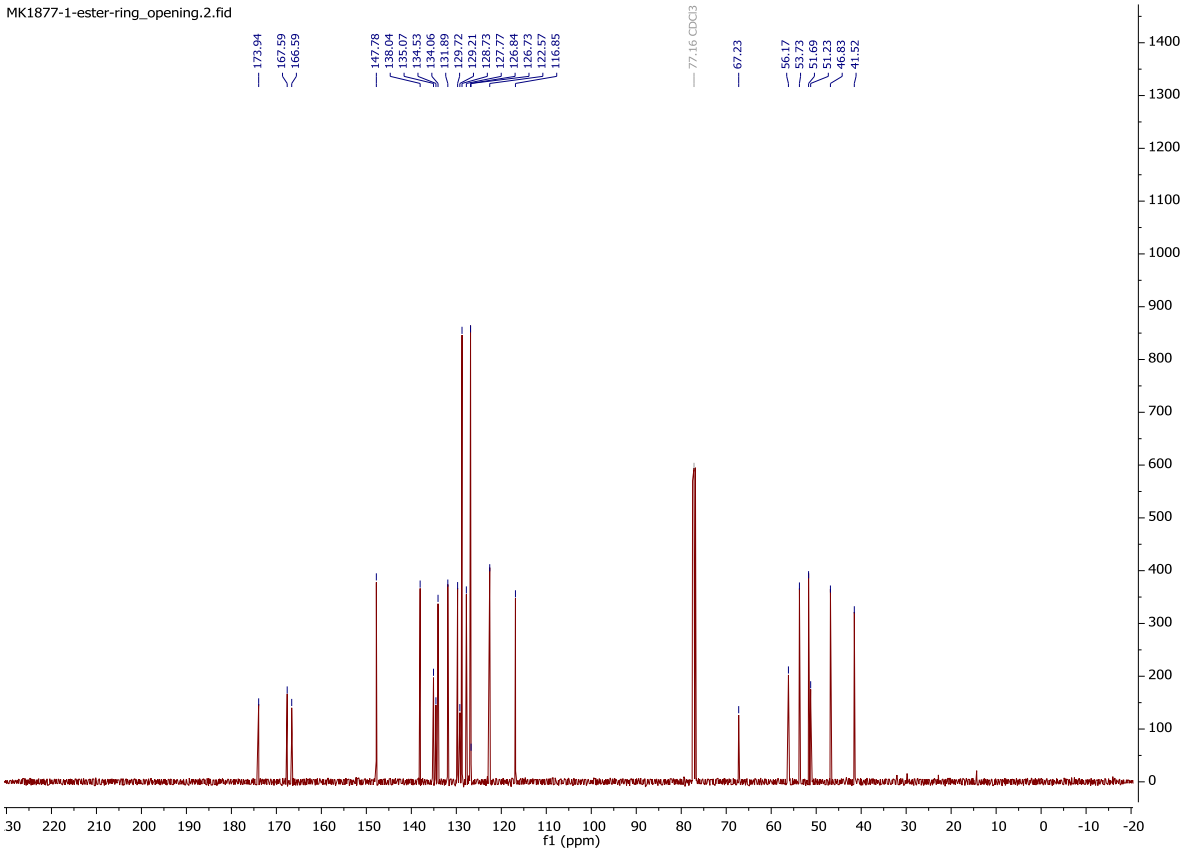

**8**




MK1869-1-after_wittig-azlactone_opening.3.fid




MK1877-1-ester-ring_opening.3.fid
Br
CO2Me
MeO2C
O
NH
Ph
7
7.26 CDCl3
1.09
2.09
1.19
3.14
1.15
1.09
1.01
0.93
1.00
1.00
2.03
0.98
0.99
3.00
2.99
1.03
1.03
1.00
f1 (ppm)


MK1877-1-ester-ring_opening.2.fid
173.94
167.59
166.59
147.78
138.04
135.07
134.06
131.99
129.72
129.21
128.73
127.77
126.84
126.73
122.57
116.85
77.16 CDCl3
67.23
56.17
53.73
51.69
51.23
46.83
41.52
f1 (ppm)

[i] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

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