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Supplementary Material

Enantioselective Photochemical Rearrangements of Spirooxindole Epoxides Catalyzed by a Chiral Bifunctional Xanthone

Mark M. Maturi, Alexander Pöthig, Thorsten Bach*

Department Chemie and Catalysis Research Center (CRC), Technische Universität München, D-85747 Garching, Germany

***Correspondence to**: Department Chemie and Catalysis Research Center (CRC), Technische Universität München, D-85747 Garching, Germany. Fax: +49 (0)89 289 13315. E-mail: thorsten.bach@ch.tum.de

Content

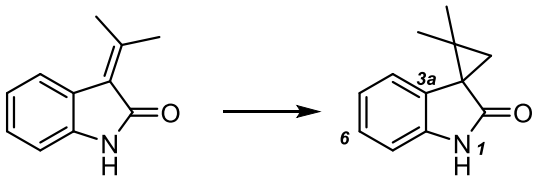
1. General Information

All reactions sensitive to air or moisture were carried out in flame-dried glassware under a positive pressure of argon using standard Schlenk techniques. Dry tetrahydrofuran (THF) was obtained from an MBraun MB-SPS 800 solvent purification system. Dry Acetonitril (MeCN, 99.9%, extra dry) was obtained from *Acros* and used without further purification. Trifluorotoluene ($PhCF_3$, 99%, anhydrous) and 1,3-bis(trifluoromethyl)benzene (hexafluoro-xylene, HFX, 99%) were purchased from *Sigma* and stored over molecular sieves (4 Å) under argon atmosphere for at least three days prior to use. Technical solvents [*n*-pentane (P), ethyl acetate (EA)] employed for preparative column chromatography were purified by distillation.

Flash chromatography was performed on silica gel 60 (230−400 mesh) with the eluent mixtures given for the corresponding procedures. Thin layer chromatography (**TLC**) was performed on silica coated glass plates (silica gel 60 F 254). Compounds were detected by UV (λ = 254 nm, 366 nm). **HPLC** analyses were performed using a *Dionex* system (P580 pump, ASI100 autosampler, STH 585, UVD 380 detector). Following chiral stationary phases were used: ChiralPak AD-H (250 x 4.6 mm), ChiralCell OJ-H (250 x 4.6 mm), Daicel Chemical Industries, with UV detection (λ = 210 or 254 nm) at 20 °C. Chiral **GC** analysis was performed using a *Agilent* GC System Typ HP 6890, hydrogen gas as mobile phase and a 2,3-dimethyl-6-TBDMS-β-cyclodextrine modified column as stationary phase. **IR** spectra were recorded on a *JASCO* IR-4100 (ATR), **^{1}H** and **^{13}C-NMR**-spectra were recorded on a *Bruker* spectrometer (AV-250, AV-360, AV-500, AVHD-300, AVHD-400 and AVHD-500). NMR spectra were calibrated to the respective residual solvent signals ($CHCl_3$ δ (^{1}H) = 7.26 ppm) and to the ^{13}C-D triplet (δ (^{13}C) = 77.16 ppm). For ^{1}H and ^{13}C-NMR, as well as nuclei labelling see Supplementary Material. Apparent multiplets which occur as a result of accidental equality of coupling constants to those of magnetically non-equivalent protons are marked as virtual (*virt.*). Multiplicities of ^{13}C-NMR signals due to ^{1}H-coupling were determined by DEPT and 2D HMQC experiments. HRMS data were recorded by electron spray ionization (ESI) on a *Thermo Finnigan* LTQ FT Ultra. **UV-Vis** spectra were recorded on a *Perkin-Elmer* Lambda 35 UV-Vis spectrometer. Optical rotations were recorded on a *Perkin-Elmer* 241 MC polarimeter and refer to the reported enantiomeric excess.

2. Synthetic Procedures and Analytical Data

2,2-Dimethylspiro[cyclopropane-1,3'-indolin]-2'-one (*rac*-**8**)



7a *rac*-**8**

$C_{12}H_{13}NO$
187.24 g/mol

Trimethylsulfoxonium iodine (139.6 mg, 635 µmol, 1.1 eq.) was added to a solution of NaH (60%, 15.2 mg, 635 µmol, 1.1 eq.) in DMSO (1.5 mL) at room temperature and stirred for 30 minutes. A solution of olefin **7a**[1] (100 mg, 577 µmol, 1.0 eq.) in THF (1.5 mL) was added drop wise. The reaction mixture was stirred at 50 °C for 15 hours, then poured onto ice/water (5 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The organic phase was dried with Na_2SO_4, filtered and the solvent removed in vacuo. Column chromatography (Ø = 2.5 cm, 10 g silica, P/EA = 8/2 → 7/3) afforded the title compound *rac*-**8** (84.0 mg, 449 µmol, 78%) as a white solid.

DC: R_f = 0.30 (P/EE 8/2, UV).

UV-Vis (CH_3CN, *c* = 1.0 mmol/L): λ (nm) = 295 (plateau, ε = 1360 $cm^{-1}M^{-1}$), 287 (ε = 1680 $cm^{-1}M^{-1}$), 255 (ε = 6680 $cm^{-1}M^{-1}$).

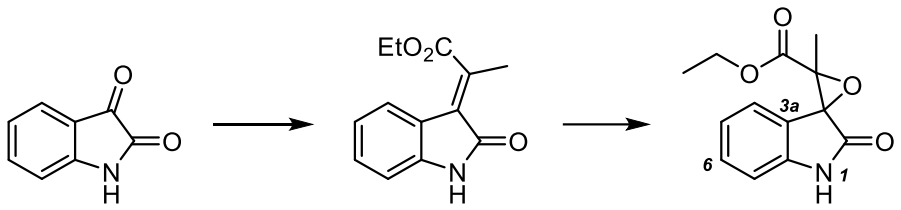
IR (ATR): ṽ (cm-1) = 3197 (br, NH), 2991 (w), 2924 (w), 1693 (s, C=O), 1660 (m), 1457 (m), 1360 (m), 1239 (w), 1098 (w), 822 (w), 727 (m).

^{1}H-NMR (250 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.06 (br s, 1H, NH), 7.22-7.14 (m, 1H, H-6), 7.01-6.96 (m, 2H, H4/H-7), 6.93 (*virt.* dt, $^3J \approx {}^3J$ = 7.7 Hz, ^4J = 0.8 Hz, 1H, H-5), 1.85 (d, ^2J = 4.8 Hz, 1H, C*H*H), 1.54 (d, ^2J = 4.8 Hz, 1H, CH*H*), 1.53 (s, 3H, CH_3), 1.40 (s, 3H, CH_3).

^{13}C-NMR (63 MHz, $CDCl_3$, 300 K): δ (ppm) = 178. (s, C-2), 141.2 (s, C-7a), 129.9 (s, C-3a), 126.4 (d, C-6), 122.0 (s, C-4), 121.3 (d, C-5), 109.4 (d, C-7), 37.3 (s, C-3), 33.4 (s, *C*$(CH_3)_2$), 32.1 (t, CH_2), 22.4 (q, CH_3), 19.6 (q, CH_3).

HRMS (ESI) ($C_{12}H_{13}NO$): ber.: $[(M + H)^+]$ 188.1070; gef.: $[(M + H)^+]$ 188.1070.

Ethyl 3'-methyl-2-oxospiro[indoline-3,2'-oxirane]-3'-carboxylate (*rac*-**9**)



rac-**9**

$C_{13}H_{13}NO_4$
247.25 g/mol

(Modified procedure for the literature known *N*-Boc protected derivative).[2] A solution of isatin (200 mg, 1.36 mmol, 1.0 eq.) in CH_2Cl_2 (15 mL) was treated with commercially available ethyl 2-(triphenyl-phosphanylidene)propanoate (739 mg, 2.04 mmol, 1.5 eq.) and stirred at room temperature for 18 hours. The reaction mixture was directly subjected to column chromatography (Ø = 2.5 cm, 30 g silica, P/EA = 9/1 → 7/3) to afford the easily separable E/Z-isomers as white solids (296 mg in total, 1.28 mmol, 94%, d.r. = 57/43). The isomers were individually characterized by ^{1}H-NMR, then combined and mixture was used for the next step.

The mixture of α,β-unsaturated oxindols (280 mg, 1.21 mmol, 1.0 eq.) was dissolved in ethanol (40 mL) and freshly powdered NaOH (121 mg, 3.03 mmol, 2.5 eq.) and aq. H_2O_2 (35%, 1.59 mL, 1.77 g, 18.2 mmol, 15 eq.) were added. The solution was stirred at room temperature for 16 hours. The excess of H_2O_2 was quenched by addition of MnO_2 and the mixture was stirred until gas evolution has ceased. All volatiles were removed in vacuo and the crude subjected to column chromatography (Ø = 5 cm, 30 g silica, P/EA = 90/10 → 85/15 → 80/20 → 70/30). The title compound *rac*-**10** (289 mg overall, 1.17 mmol, 96%) was obtained as white solid as a separable mixture of diastereoisomers (85.1 mg, and 204 mg, d.r. = 70/30).

TLC: R_f = 0.73, 0.59 (P/EE 1/1, UV).
UV-Vis (CH_3CN, *c* = 1.0 mmol/L): λ (nm) = 307 (ε = 1440 $cm^{-1}M^{-1}$), 250 (ε = 4570 $cm^{-1}M^{-1}$).

Major diastereoisomer

^{1}H-NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 9.09 (br s, 1H, NH), 7.35 (*virt.* td, $^3J \approx {}^3J$ = 7.7 Hz, ^4J = 1.3 Hz, 1H, H-6), 7.18 (br. d, ^3J = 7.8 Hz, 1H, H-4), 7.07 (*virt.* td, $^3J \approx {}^3J$ = 7.6 Hz, ^4J = 1.0 Hz, 1H, H-5), 6.99 (br. d, ^3J = 7.8 Hz, 1H, H-7), 4.36-4.26 (m, 2H, CH_2), 1.83 (s, 3H, CH_3), 1.33 (t, ^3J = 7.1 Hz, 3H, $CH_2C\mathit{H}_3$).

^{13}C-NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 172.8 (s, C-2), 168.0 (s, C=O), 143.1 (s, C-7a), 131.0 (d, C-6), 125.0 (d, C-4), 122.8 (d, C-5), 120.8 (s, C-3a), 111.5 (d, C-7), 66.8 (s, C-O), 64.4 (s, C-3), 62.0 (t, CH_2), 16.1 (q, CH_3), 14.2 (q, $CH_2\mathit{C}H_3$).

Minor diastereoisomer

^{1}H-NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.73 (br s, 1H, NH), 7.30 (*virt.* td, $^{3}J \approx {}^{3}J$ = 7.7 Hz, ^{4}J = 1.2 Hz, 1H, H-6), 7.13 (dd, ^{3}J = 7.6 Hz, ^{4}J = 1.2 Hz, 1H, H-4), 6.99 (*virt.* td, $^{3}J \approx {}^{3}J$ = 7.6 Hz, ^{4}J = 0.9 Hz, 1H, H-5), 6.94 (d, ^{3}J = 7.8 Hz, 1H, H-7), 4. 26 (q, ^{3}J = 7.1 Hz, 2H, CH_2), 1.98 (s, 3H, CH_3), 1.25 (t, ^{3}J = 7.1 Hz, 3H, $CH_2C\mathit{H}_3$).

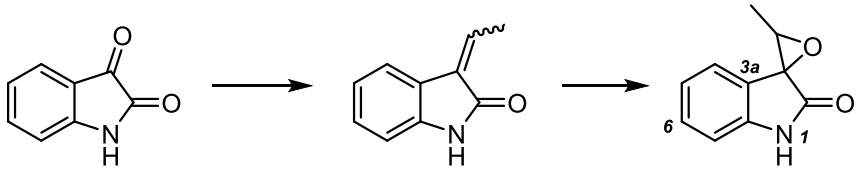
^{13}C-NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 172.7 (s, C-2), 167.9 (s, C=O), 142.1 (s, C-7a), 130.8 (d, C-6), 123.8 (d, C-3), 123.0 (d, C-5), 121.3 (s, C-3a), 111.0 (d, C-7), 67.7 (s, C-O), 62.7 (s, C-3), 62.3 (t, CH_2), 14.3 (q, CH_3), 13.8 (q, $CH_2\mathit{C}H_3$).

Following data was collected from the mixture.

IR (ATR): ṽ (cm-1) = 3328 (br, NH), 2980 (w), 2941 (w), 1741 (vs, C=O), 1724 (vs, C=O), 1619 (s), 1468 (m), 1293 (m), 1128 (m), 900 (w), 756 (w).

HRMS (ESI) ($C_{12}H_{13}NO_4$): ber.: $[(M + H)^+]$ 248.0917; gef.: $[(M + H)^+]$ 248.0919.

3'-Methylspiro[indoline-3,2'-oxiran]-2-one (*rac*-**10**)



rac-**10** $C_{10}H_9NO_2$ 175.19 g/mol

Following the procedure reported in the literature,[3] a solution of isatin (300 mg, 2.04 mmol, 1.0 eq.), propiophenone (271 µL, 274 mg, 2.04 mmol, 1.0 eq.) and freshly powdered KOH (50 mg. 891 µmol, 0.4 eq.) in an ethanol/water mixture (65/35) was stirred for 16 hours at room temperature. The reaction was quenched by addition of sat. NH_4Cl solution (15 mL) and the resulting mixture extracted with CH_2Cl_2 (4 × 30 mL). The organic phase was dried with Na_2SO_4, filtered and the solvent removed in vacuo. The crude product was obtained as yellow foam (300 mg, 1.07 mmol, 52%) and used without further purification.

Concentrated sulfuric acid (10 mL) was cooled to 0 °C and added to the crude product from the previous step. The solution was stirred for 15 minutes without cooling, then poured onto ice/water mixture (100 mL) and carefully neutralized with solid $NaHCO_3$. The aqueous solution was extracted with CH_2Cl_2 (4 × 50 mL), the organic phase dried with Na_2SO_4, filtered and the solvent removed in vacuo. The crude product, a yellow solid (162 mg, 1.02 mmol, 96%), was used without further purification.

The NMR data from the crude match the values reported in the literature.[3]

The crude α,β-unsaturated oxindol (70.0 mg, 440 µmol, 1.0 eq.) was dissolved in methanol (7 mL)

and freshly powdered NaOH (44.0 mg, 1.10 mmol, 2.5 eq.) and aq. H_2O_2 (35%, 680 µL, 754 mg, 6.60 mmol, 15 eq.) were added. The solution was stirred at room temperature for 16 hours. All volatiles were removed in vacuo and the crude subjected to column chromatography (Ø = 2.5 cm, 20 g silica, P/EA = 9/1 → 8/2 → 6/4). The title compound *rac*-**10** (67.6 mg, 386 µmol, 88%) was obtained as white solid as an inseparable mixture of diastereoisomers (d.r. = 67/33, determined from ^{1}H-NMR by integration of the aliphatic CH-group).

TLC: R_f = 0.64, 0.59 (P/EA 1/1, UV).
UV-Vis (CH_3CN, *c* = 1.0 mmol/L): λ (nm) = 300 (ε = 1470 $cm^{-1}M^{-1}$), 249 (ε = 5430 $cm^{-1}M^{-1}$).

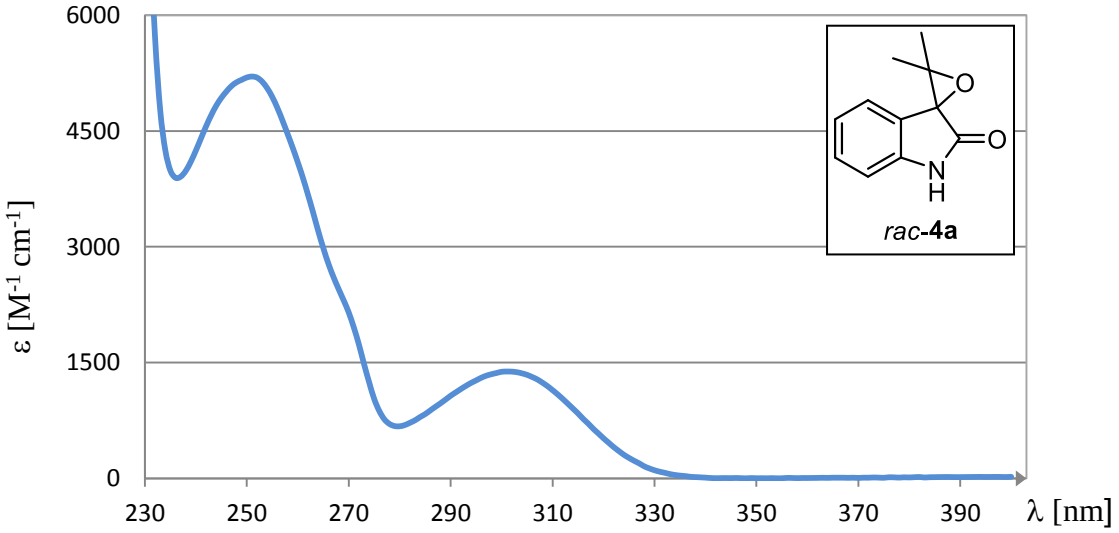
Major diastereoisomer:
^{1}H-NMR (250 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.62 (br. s, 1H, NH), 8.50 (*virt.* td, $^3J \approx {}^3J$ = 7.7 Hz, ^4J = 1.4 Hz, 1H, H-6), 7.19 (d, ^3J = 7.0 Hz, 1H, H-4), 7.07 (*virt.* td, $^3J \approx {}^3J$ = 7.5 Hz, ^4J = 0.8 Hz, 1H, H-5), 6.98 (d, ^3J = 7.8 Hz, 1H, H-7), 3.76 (q, ^3J = 5.3 Hz, 1H, CH), 1.61 (d, ^3J = 5.3 Hz, 1H, CH_3).

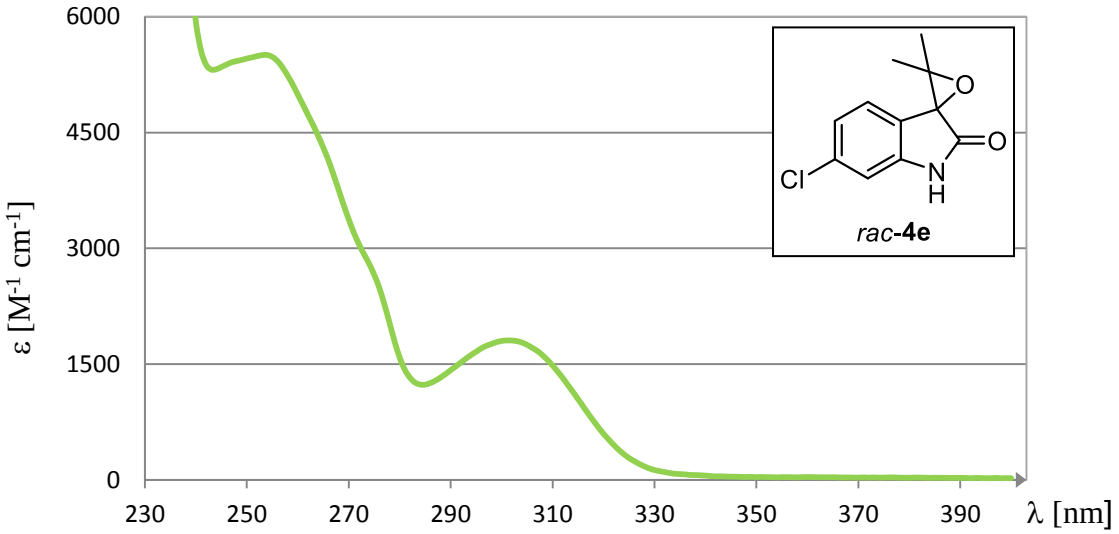
Minor diastereoisomer:
^{1}H-NMR (250 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.49 (br. s, 1H, NH), 7.33-7.27 (m, 1H, H-6)*, 7.12-7.03 (m, 2H, H-4/H-5)*, 6.94 (d, ^3J = 7.8 Hz, 1H, H-7), 3.75 (q, ^3J = 5.2 Hz, 1H, CH), 1.73 (d, ^3J = 5.23 Hz, 1H, CH_3).
* Signals overlap with the major diastereoisomer.

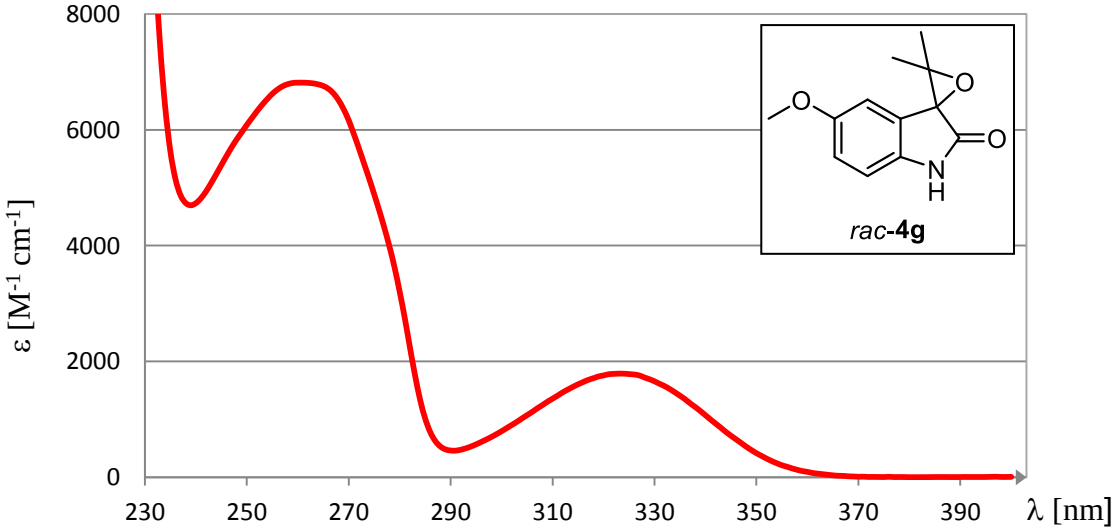
List of carbon signals. The unambiguous assignment from the mixture is not possible. Some of the signals from the major and minor diastereoisomer overlap and appear a single signal.
^{13}C-NMR (91 MHz, $CDCl_3$, 303 K): δ (ppm) = 175.0, 174.1, 142.6, 130.2, 130.1, 124.6, 124.5, 122.9, 122.8, 122.3, 122.1, 111.1, 110.7, 63.6, 61.6, 60.9, 13.8, 12.4.
IR (ATR): ṽ (cm-1) = 3328 (br, NH), 2981 (w), 2941 (w), 2913 (w), 1705 (vs, C=O), 1620 (s), 1455 (m), 1287 (m), 1122 (m), 911 (w), 755 (w).
HRMS (ESI) ($C_{10}H_9NO_2$): ber.: $[(M + H)^+]$ 176.0706; gef.: $[(M + H)^+]$ 176.0706.

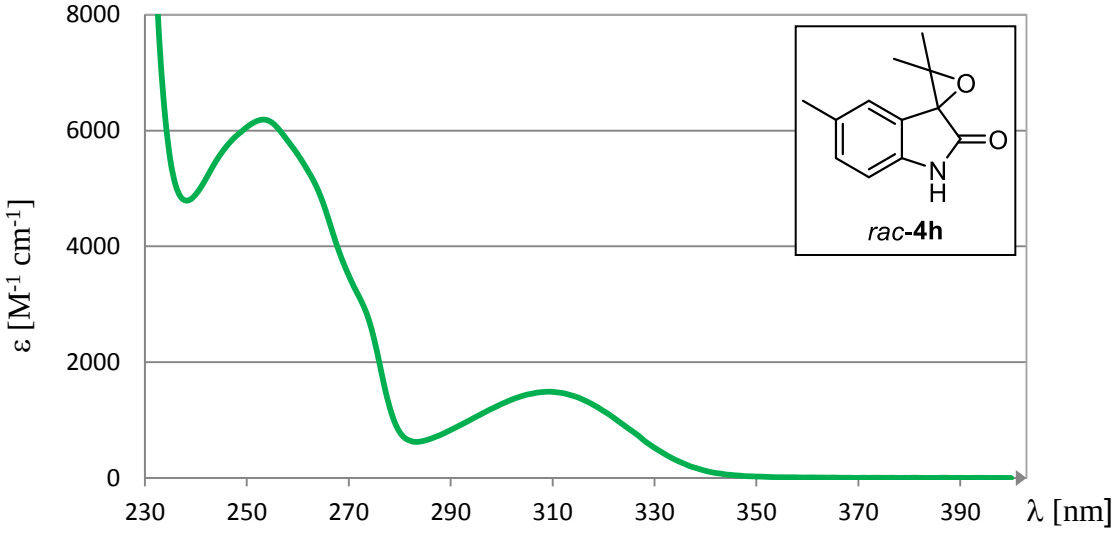
3. UV-Vis Spectra

All spectra were recorded at room temperature, *c* = 1mmol/L, d = 1 mm, in acetonitrile.





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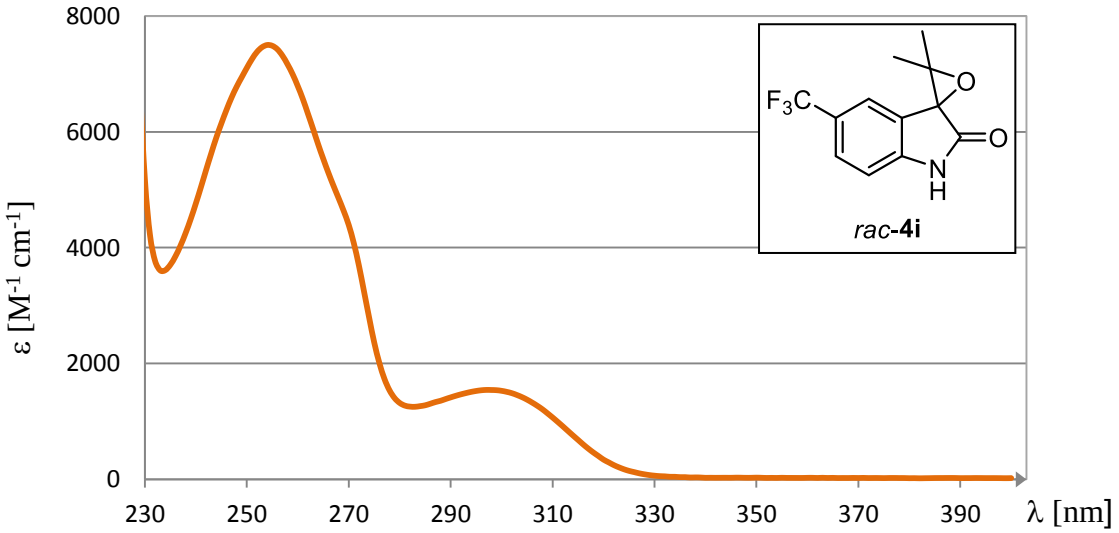
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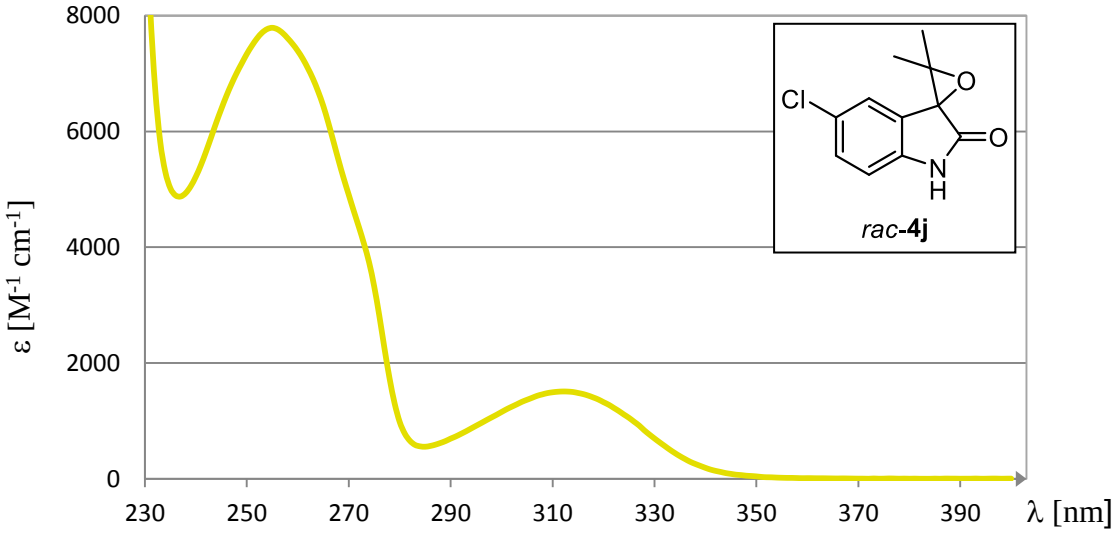
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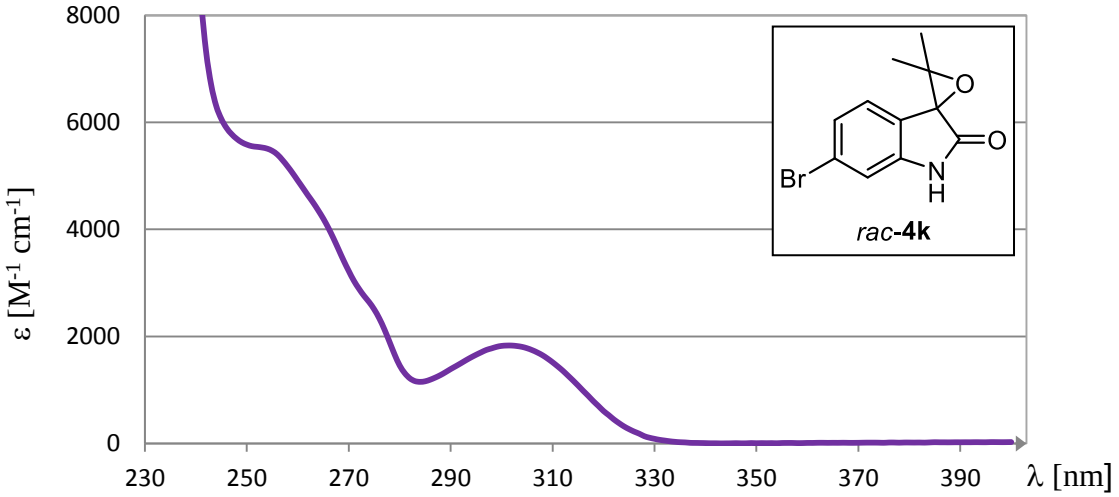
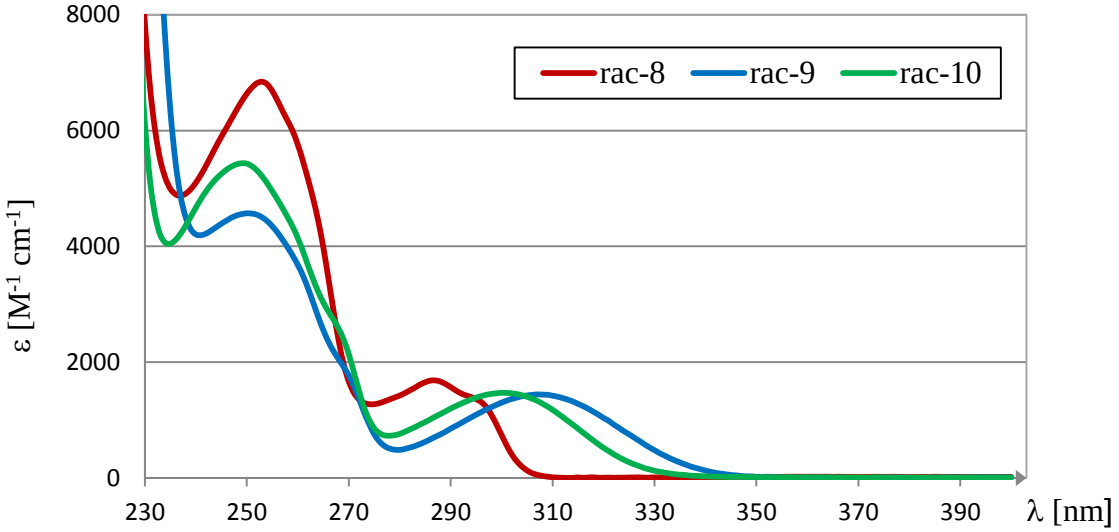
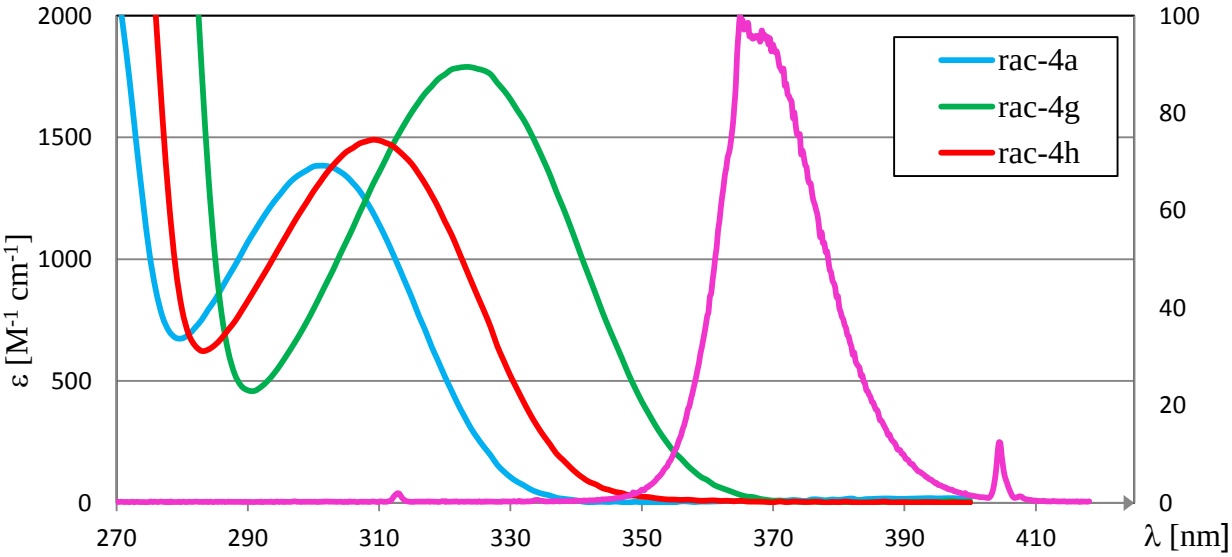




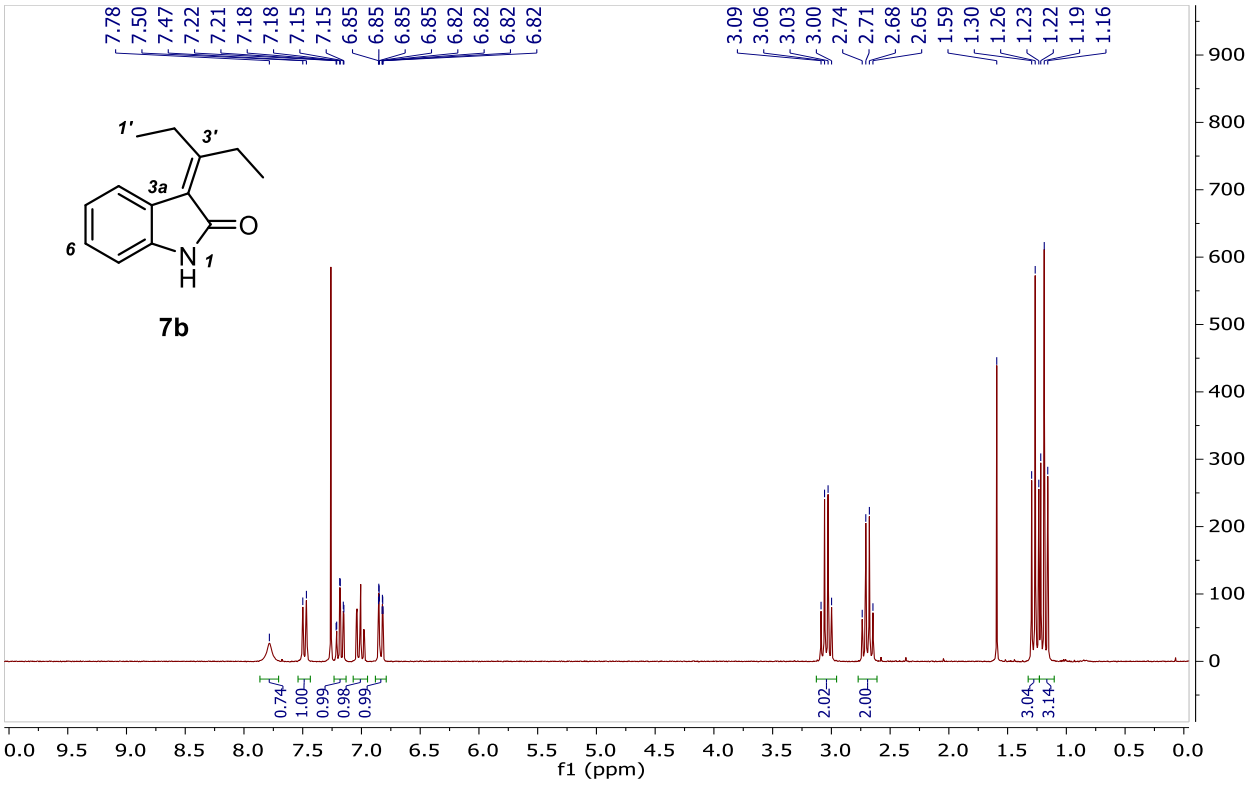


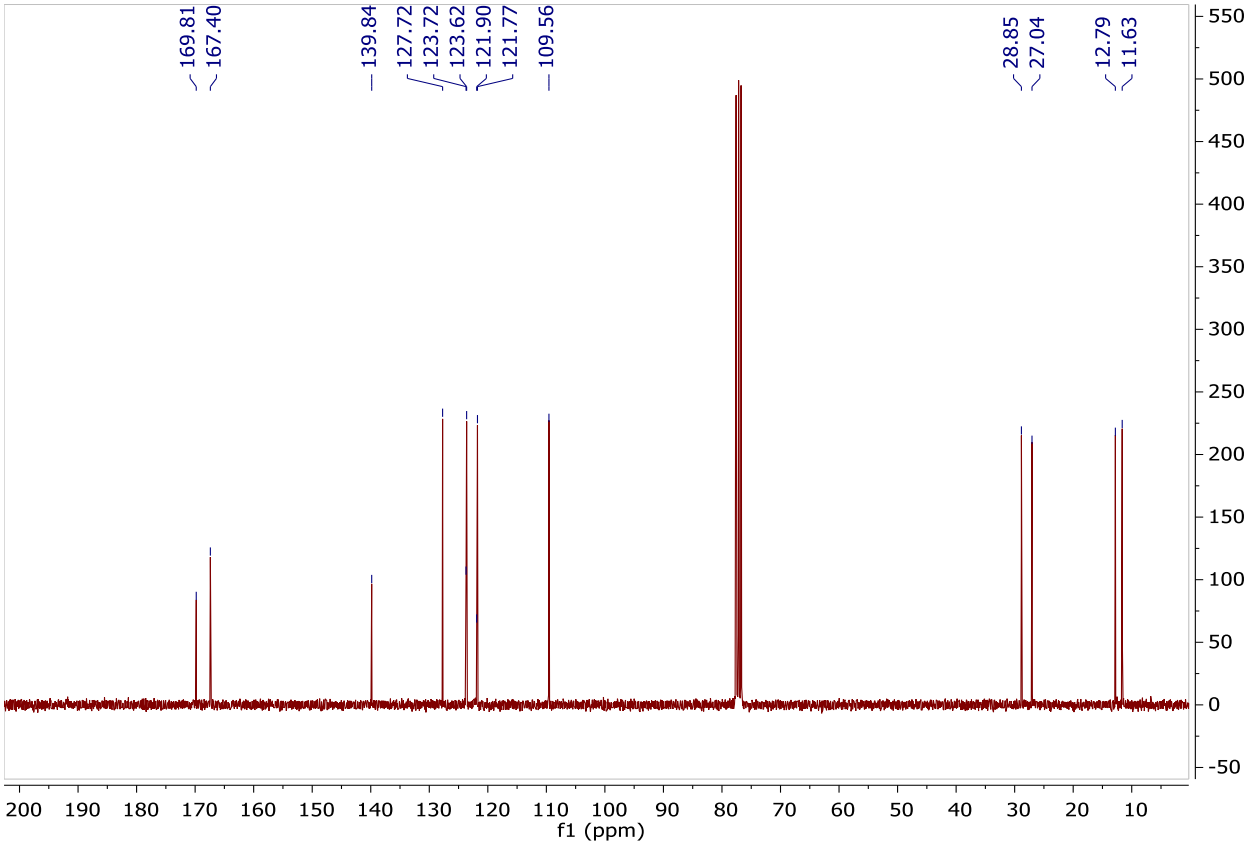
UV-Vis spectra of spirooxindol epoxides *rac*-**4a**, *rac*-**4g** and *rac*-**4h** in comparison to the normalized emission spectra of the light source (λ = 366 nm).[4]

4. NMR-Spectra of New Compounds

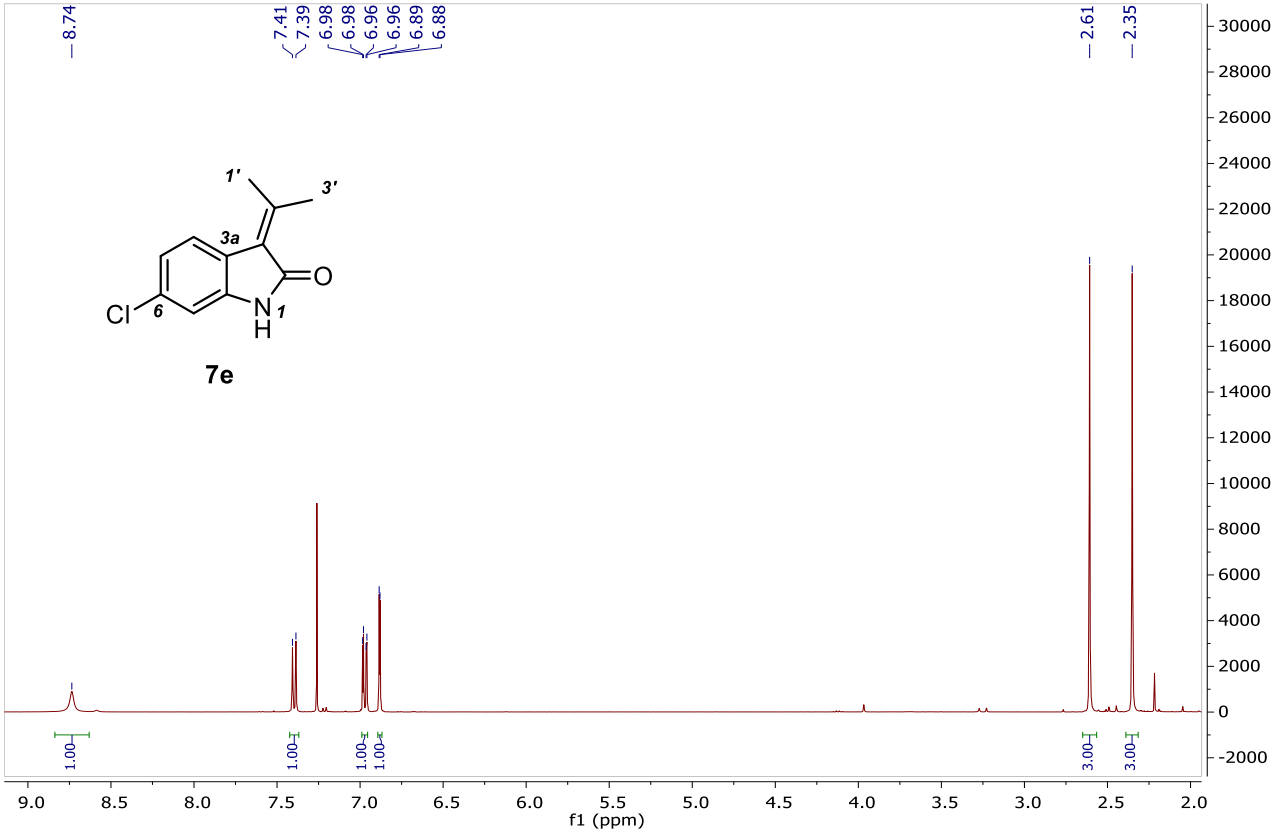
Order: Olefins, Spirooxindol Epoxides, 3-Acyl-indolin-2-ones.

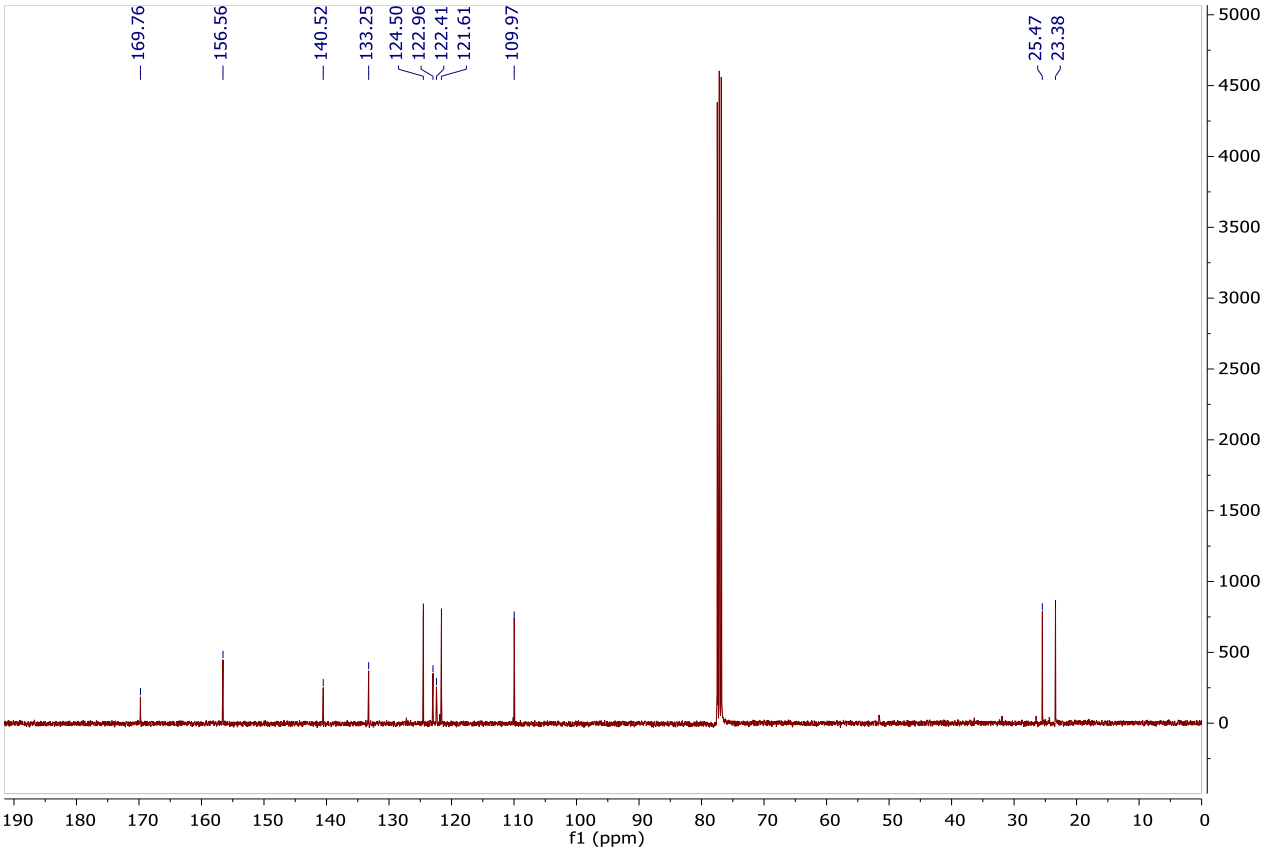
3-(Pentan-3-ylidene)indolin-2-one (7b)



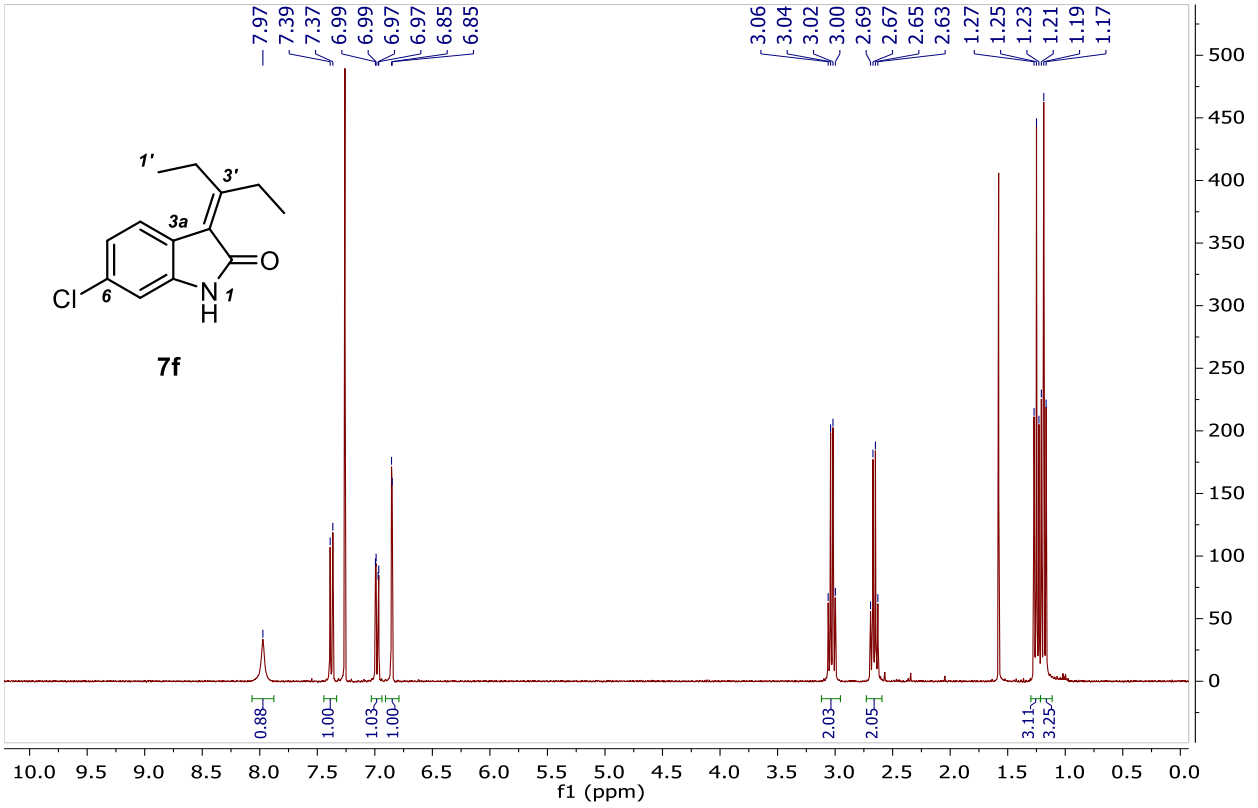


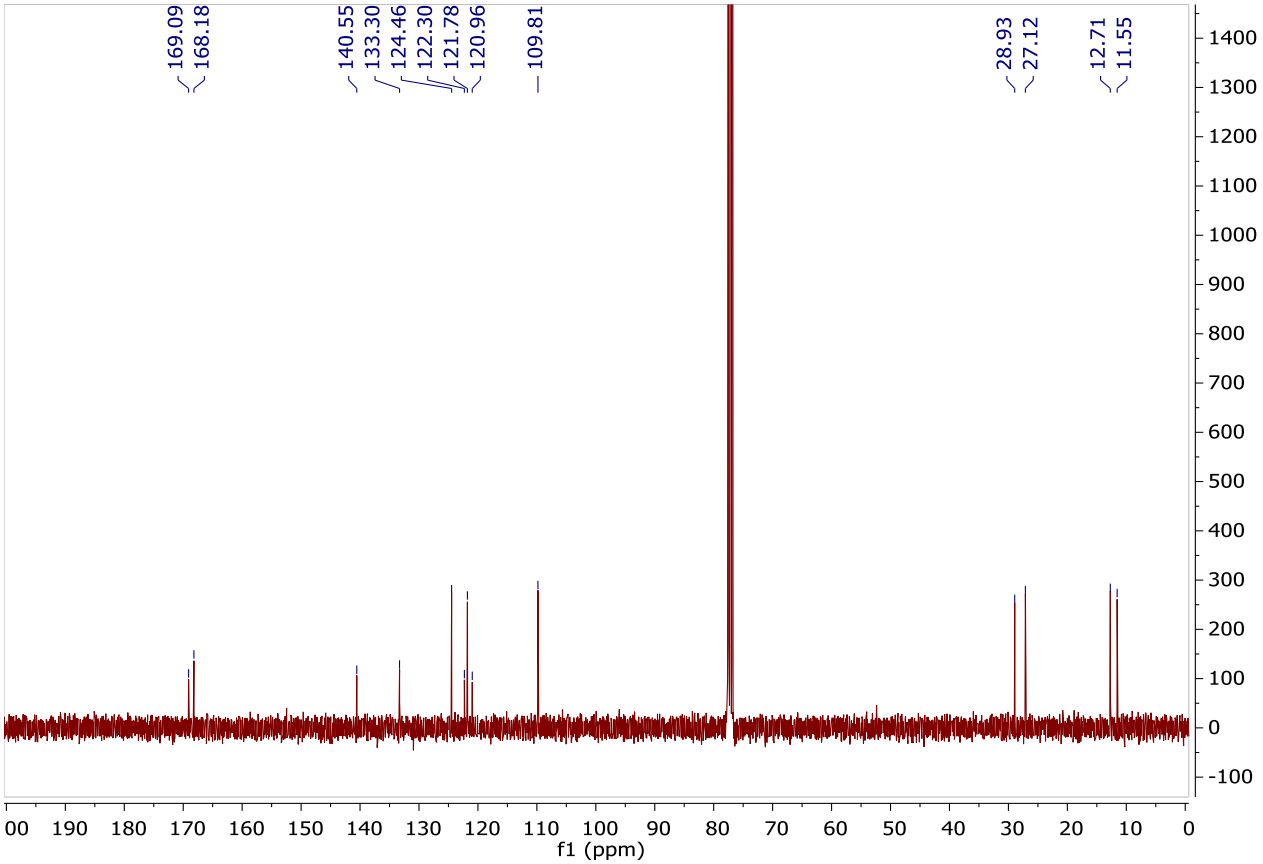
6-Chloro-3-(propan-2-ylidene)indolin-2-one (7e)



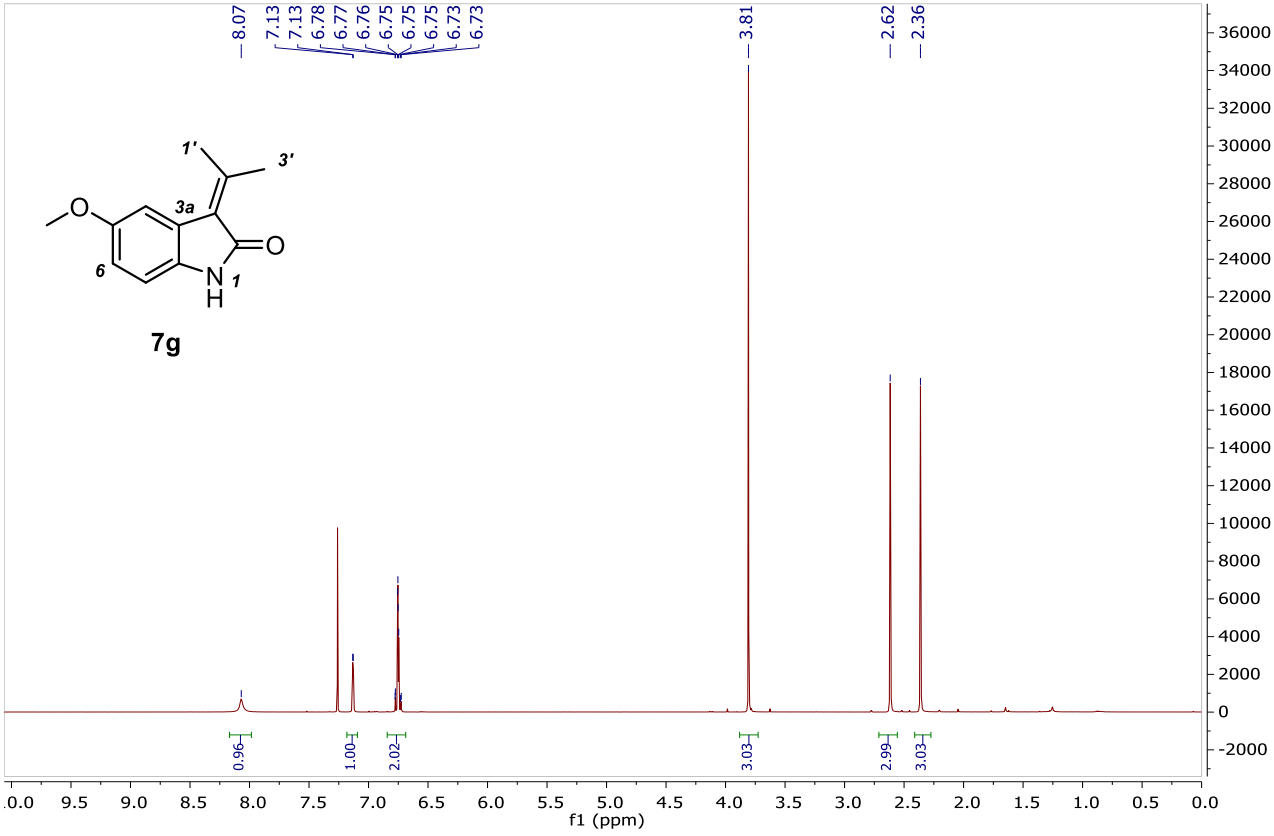


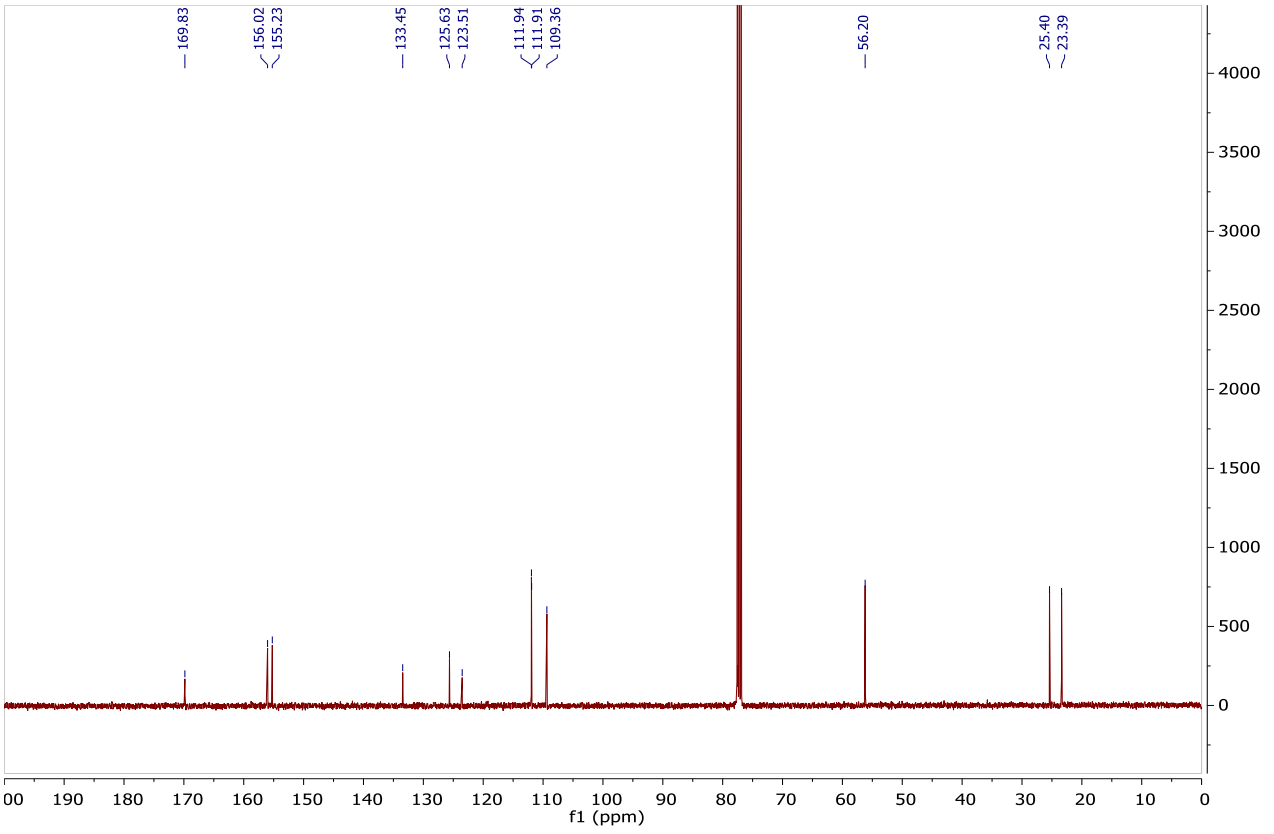
6-Chloro-3-(pentan-3-ylidene)indolin-2-one (7f)





5-Methoxy-3-(propan-2-ylidene)indolin-2-one (7g)





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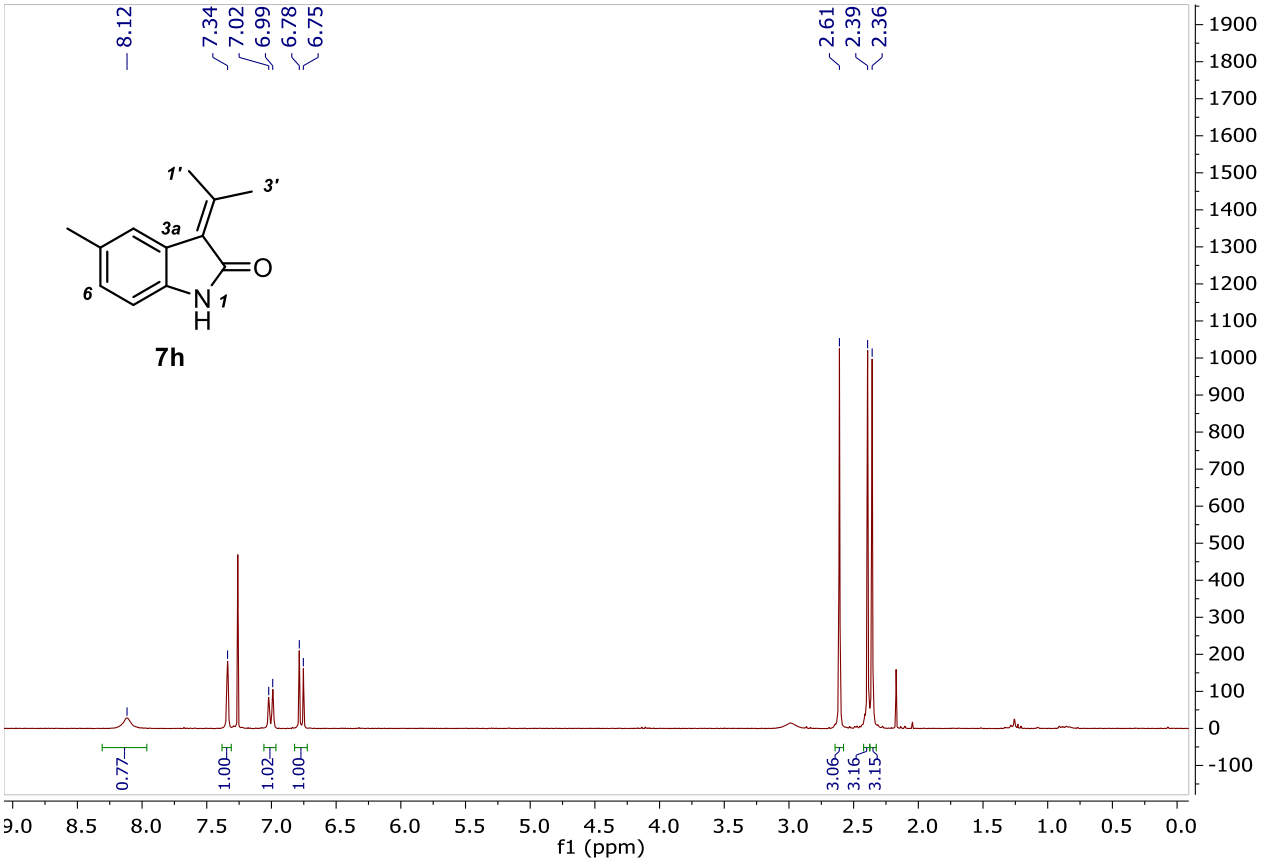
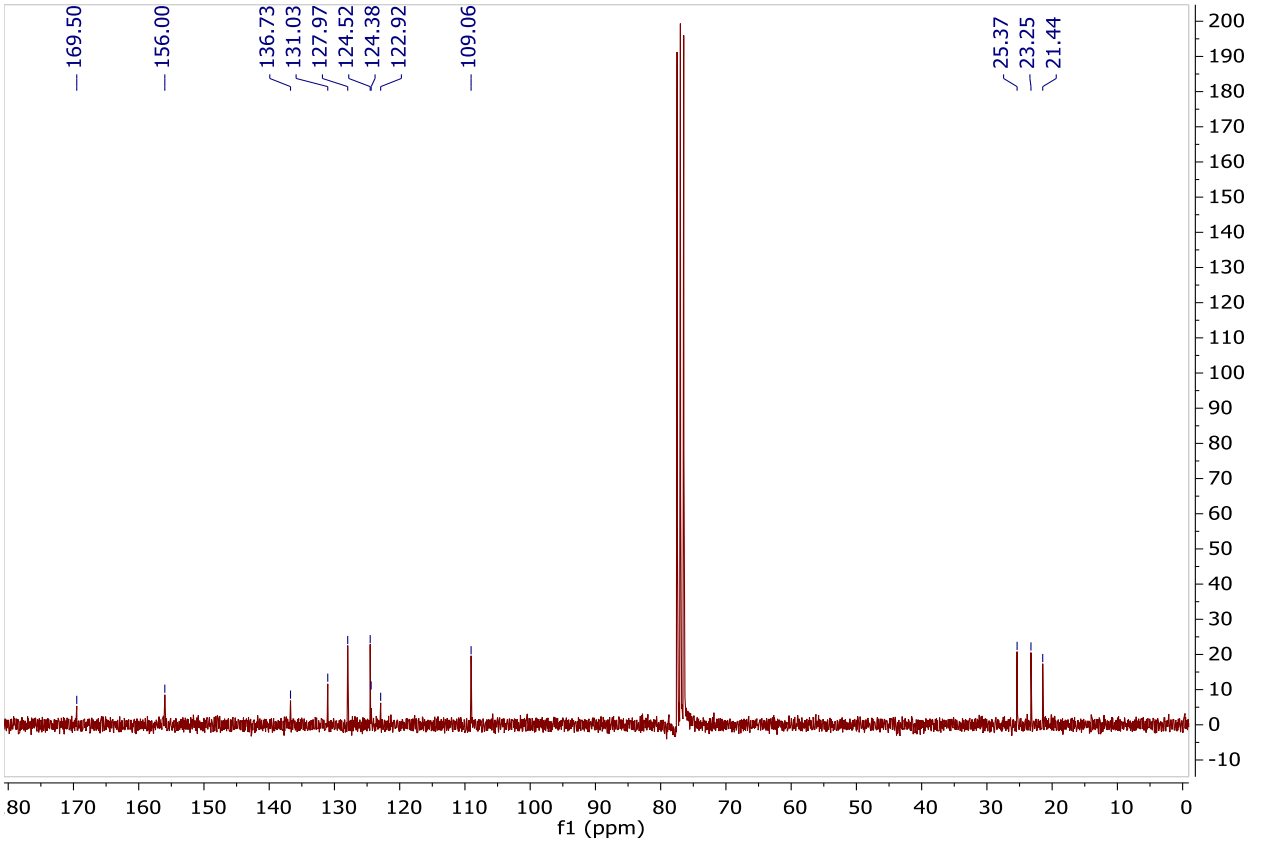
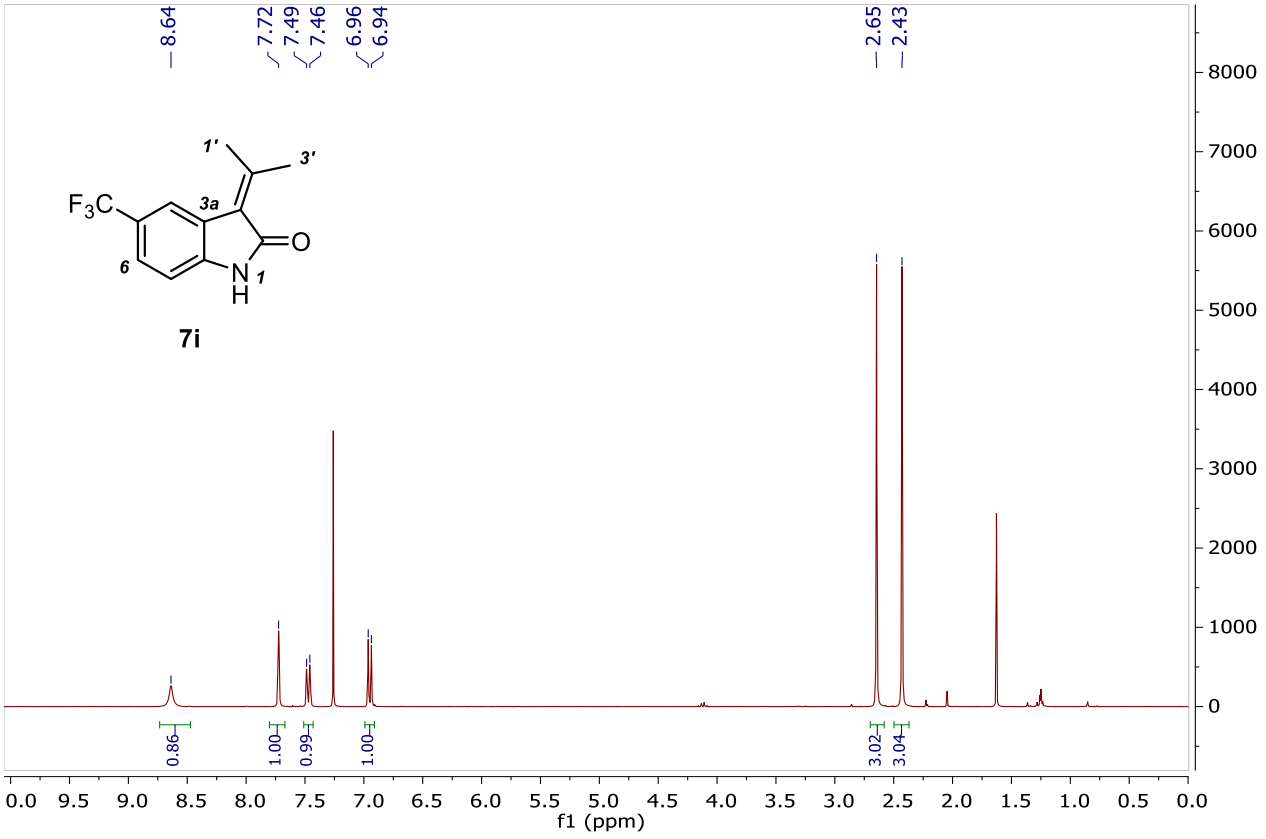
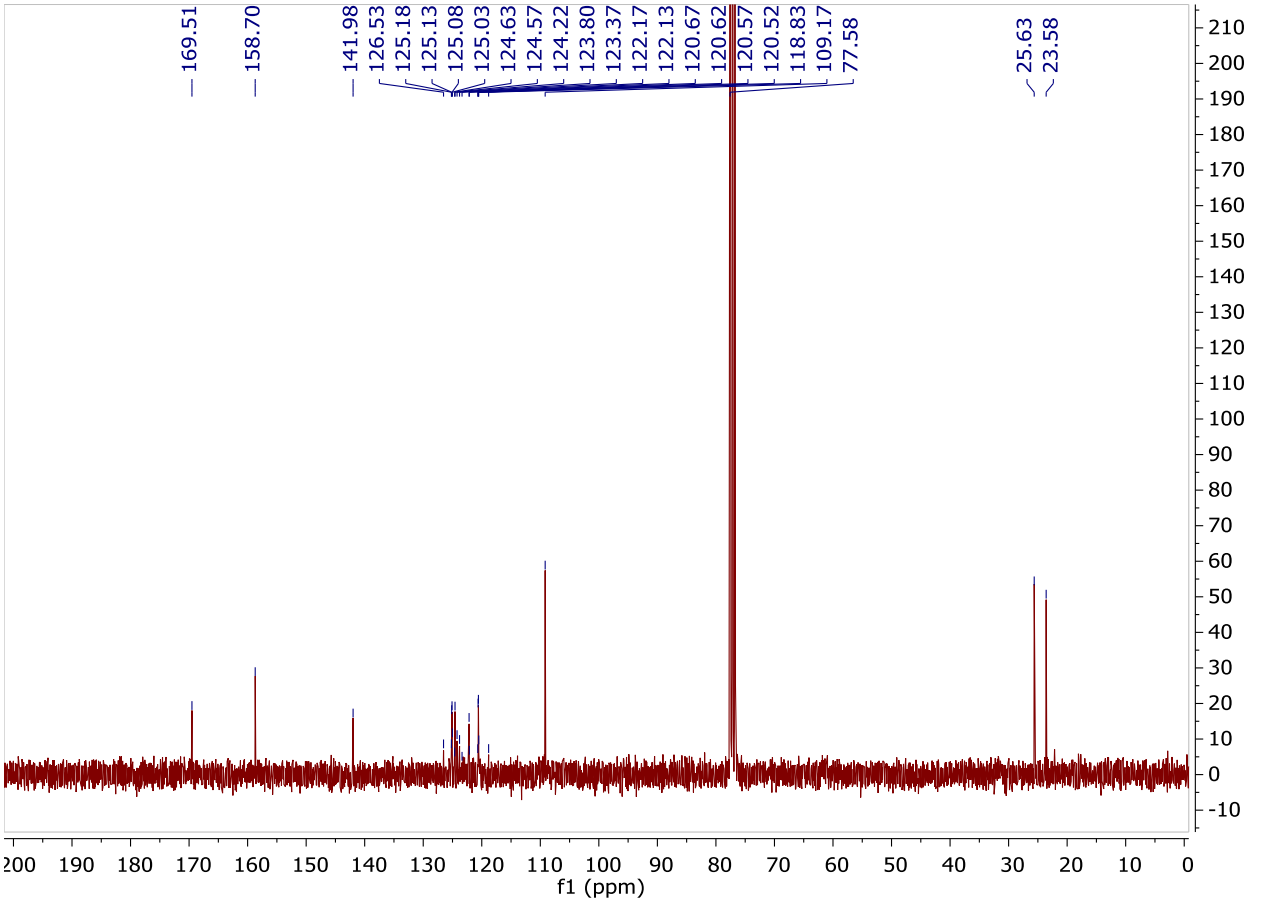


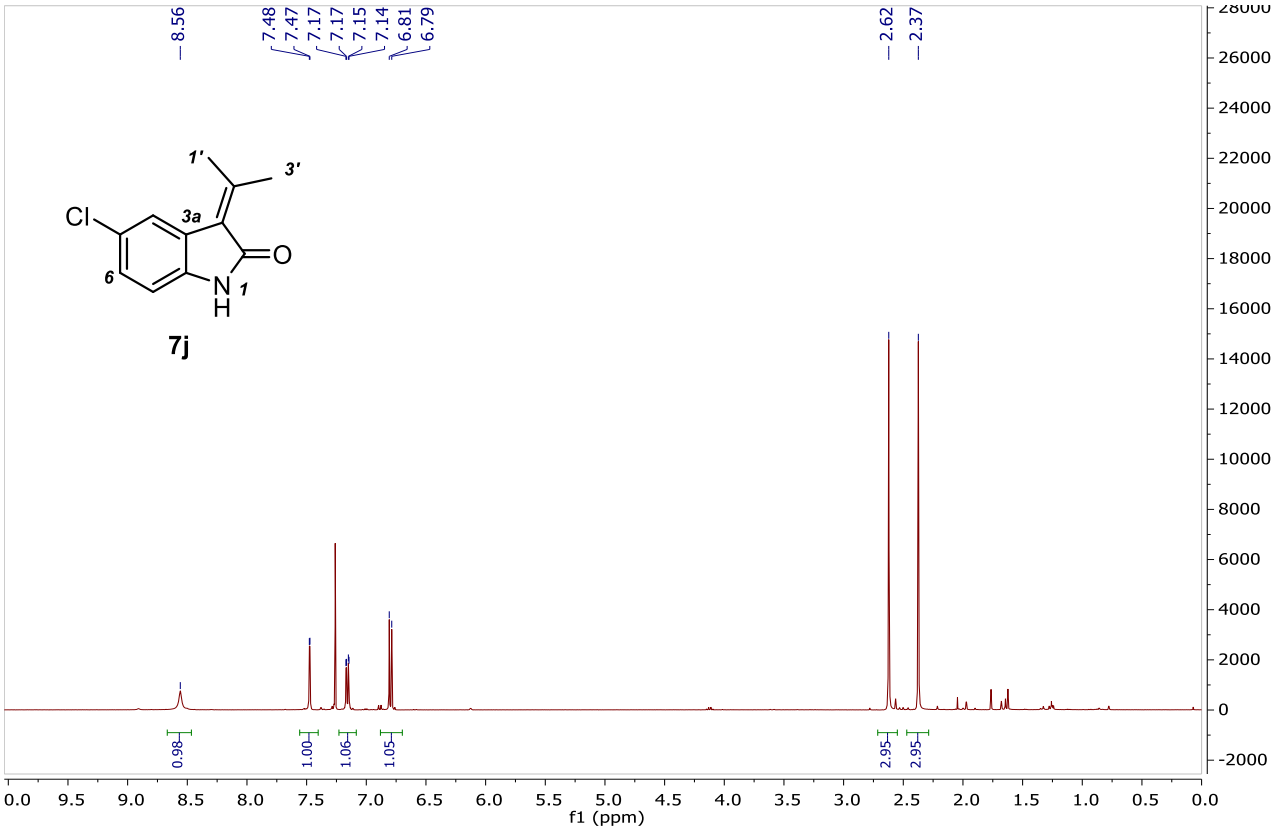


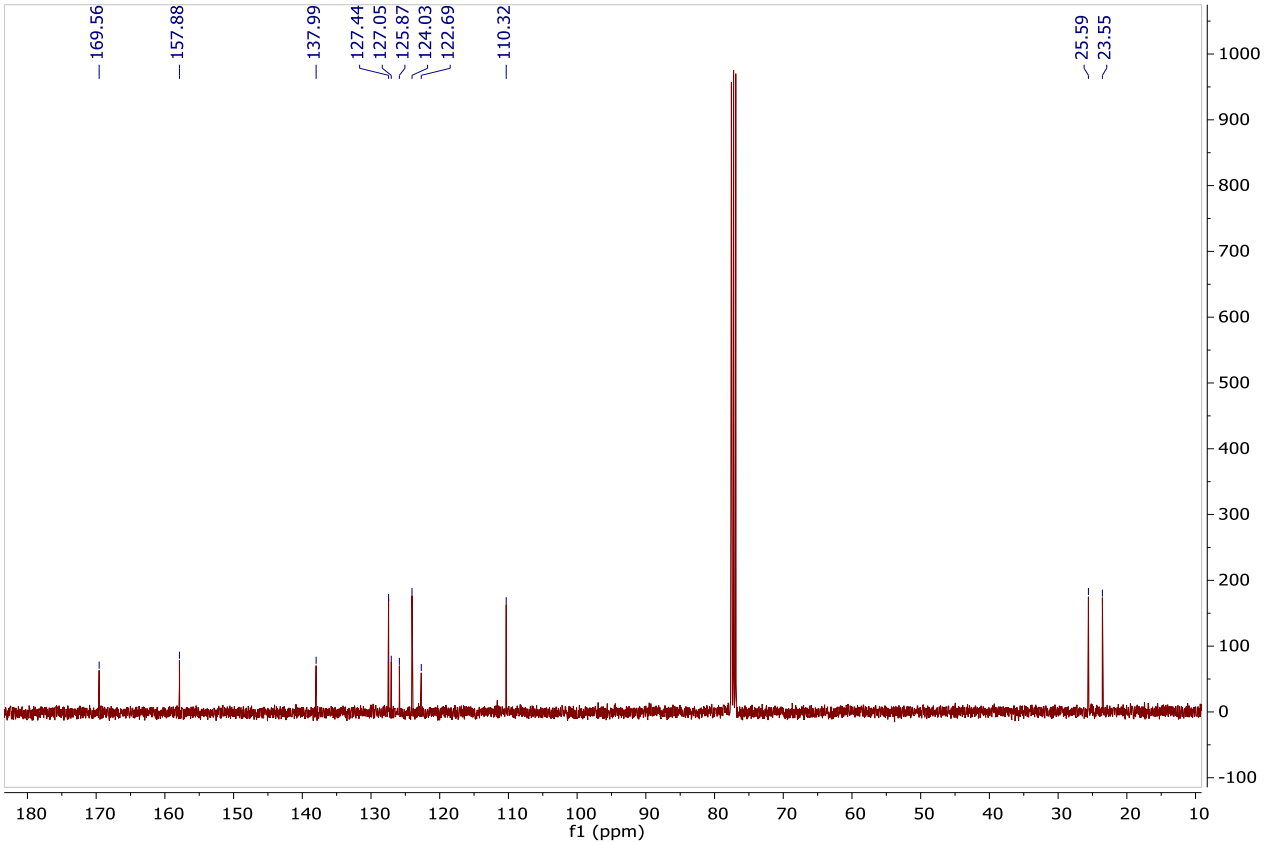
5-Trifluoromethyl-3-(propan-2-ylidene)indolin-2-one (7i)



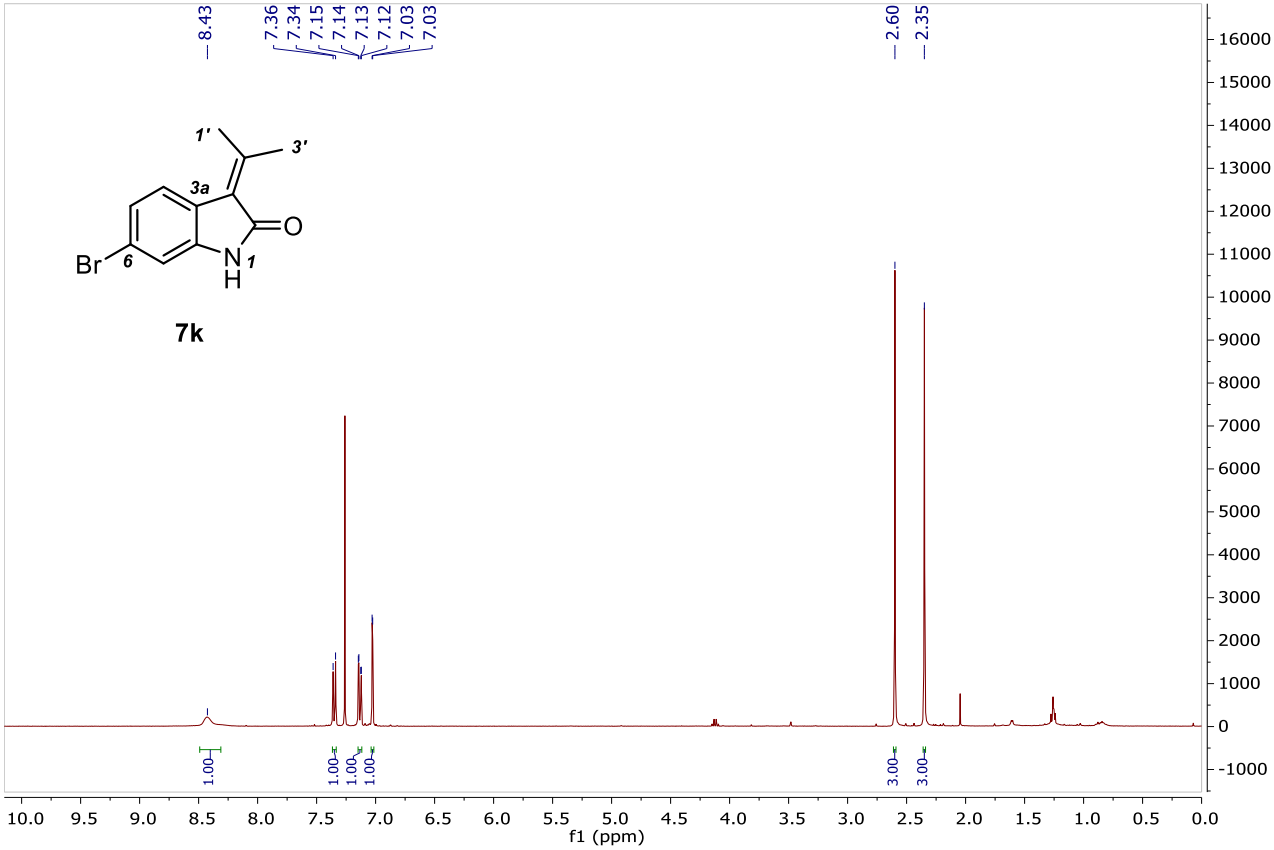


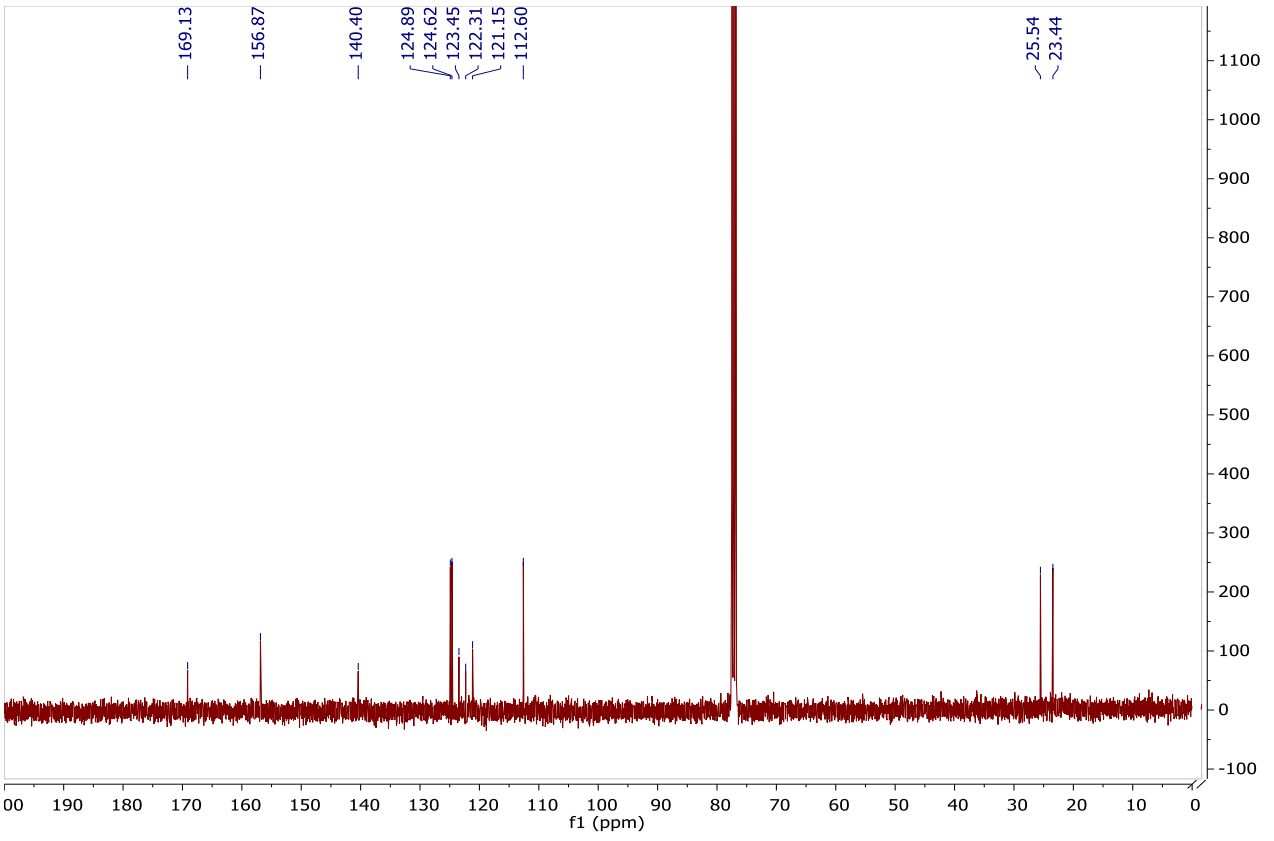
5-Chloro-3-(propan-2-ylidene)indolin-2-one (7j)



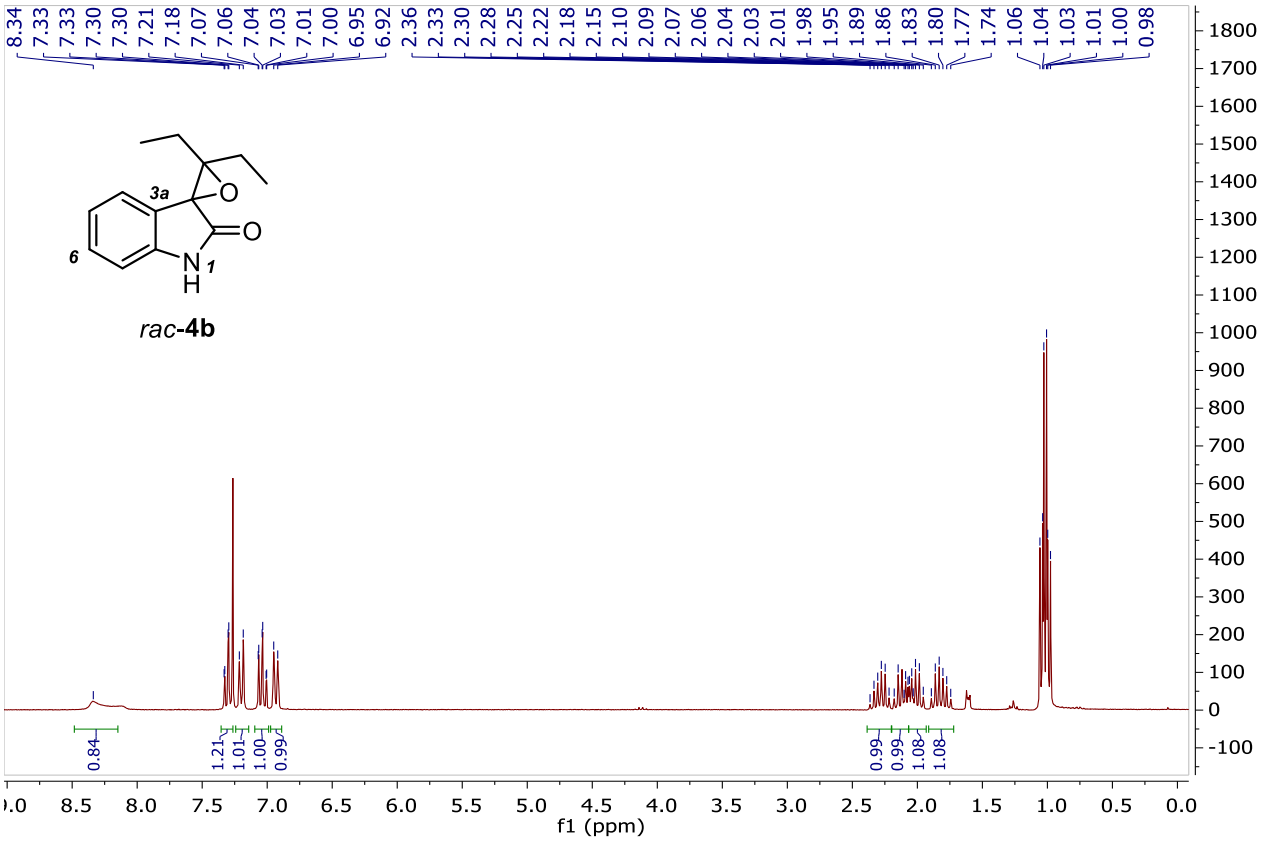


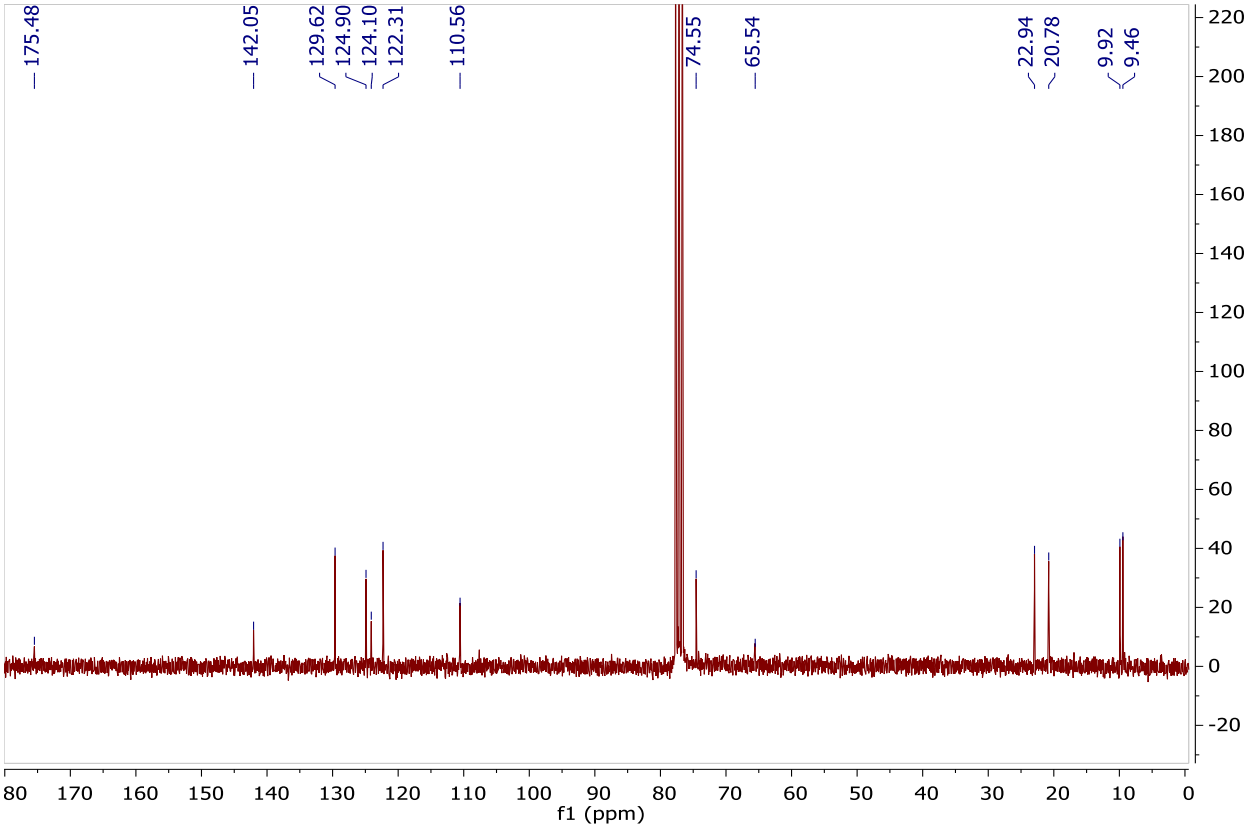
6-Bromo-3-(propan-2-ylidene)indolin-2-one (7k)



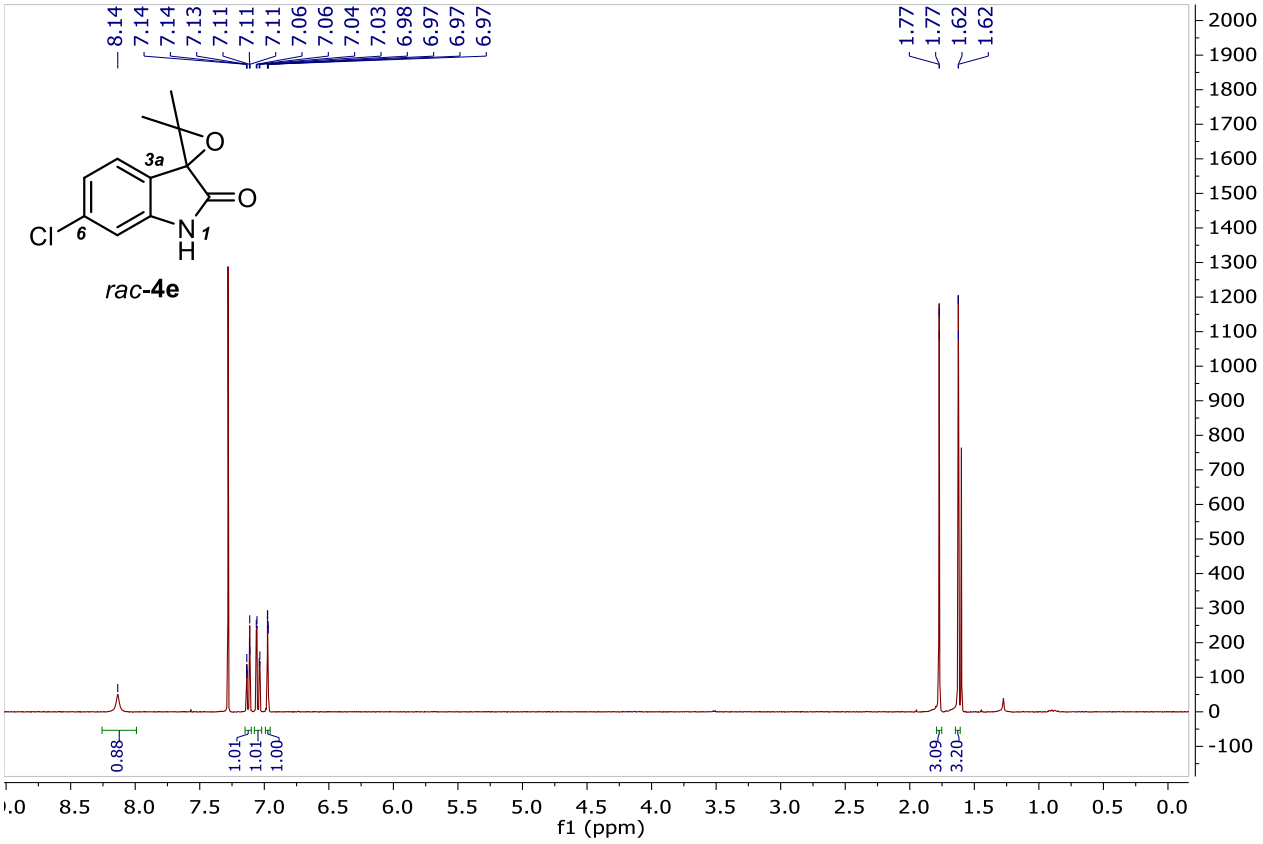


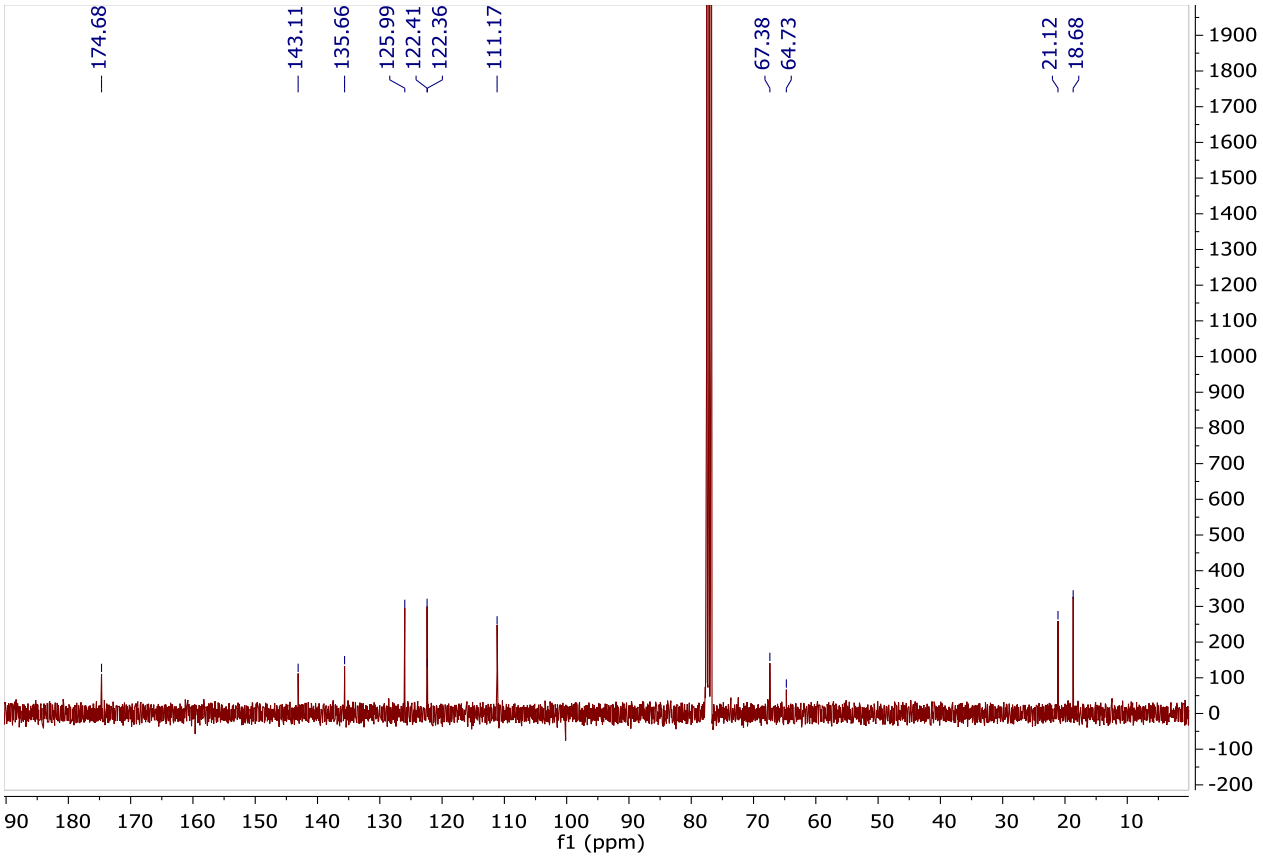
3',3'-Diethylspiro[indolin-3,2'oxidran]-2-one (*rac*-4b)



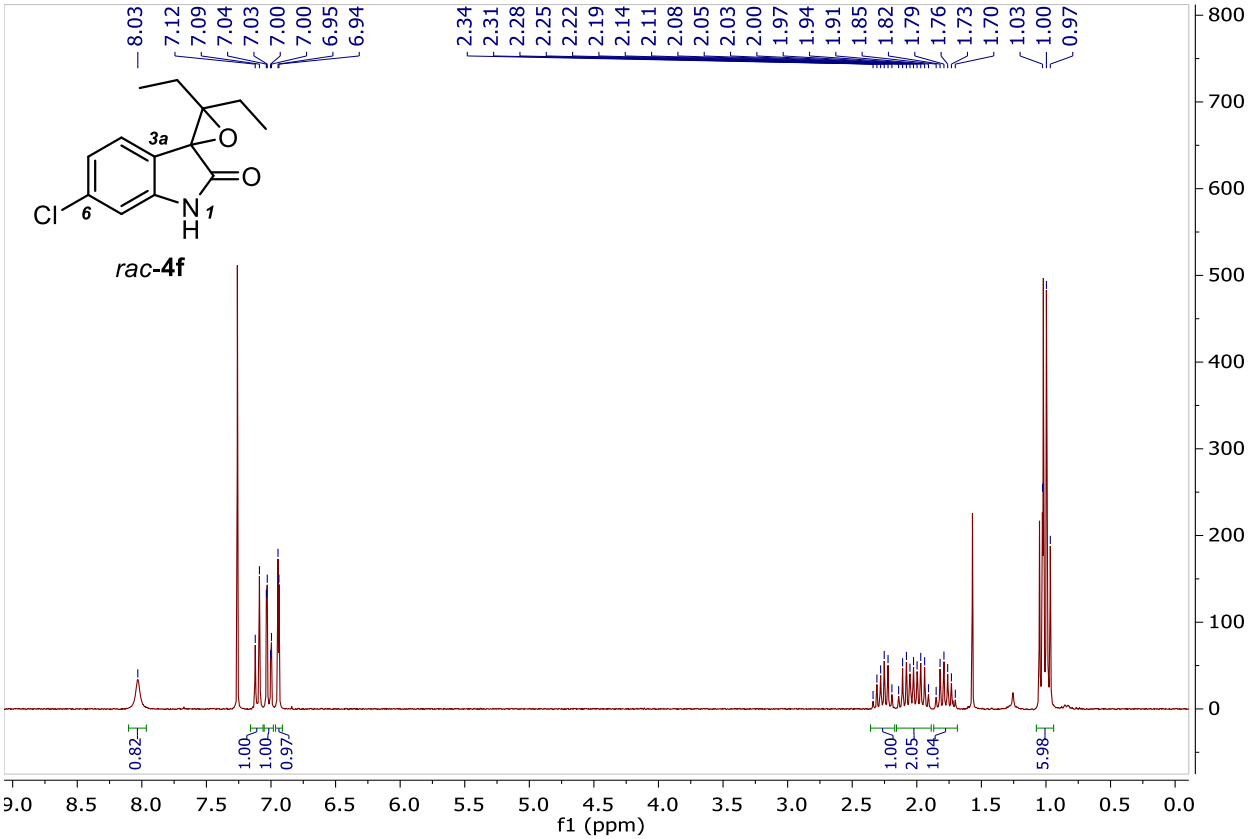


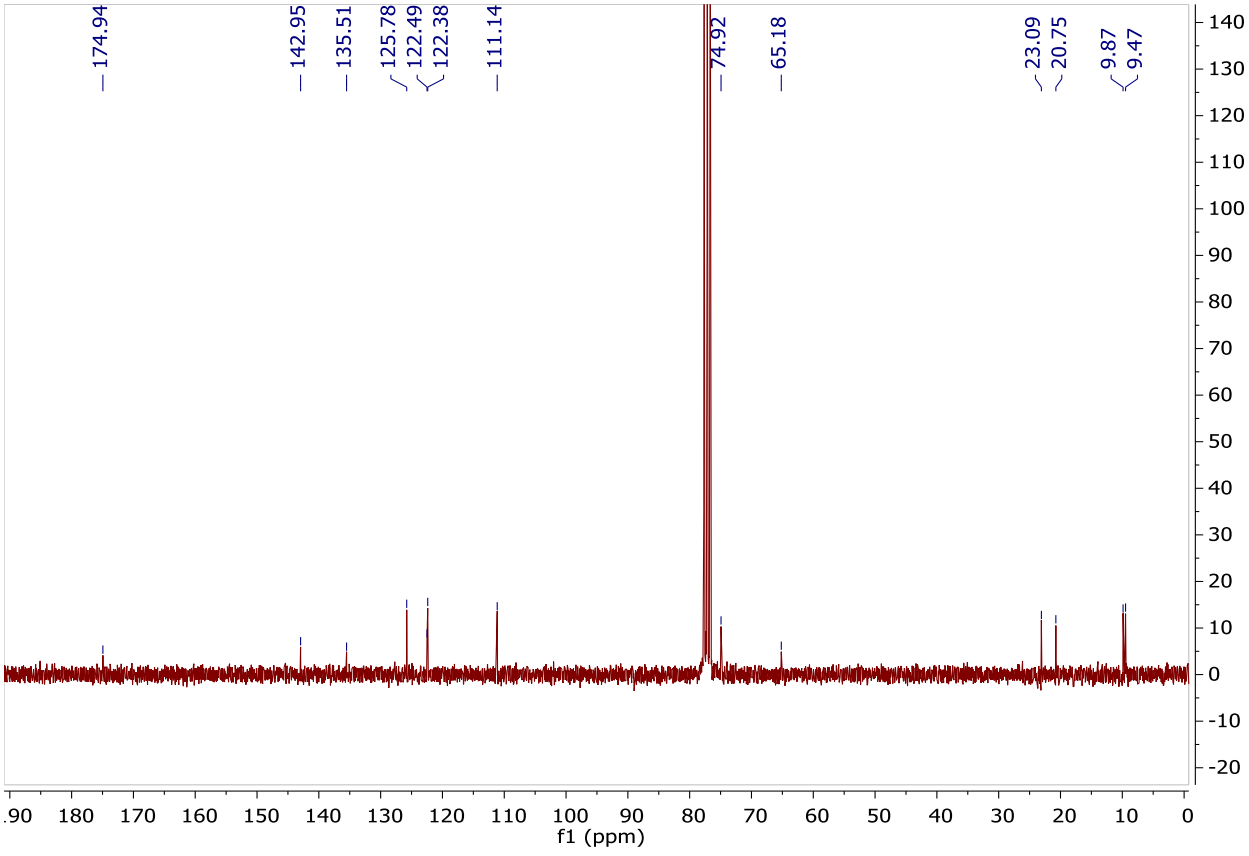
6-Chloro-3',3'-dimethylspiro[indolin-3,2'-oxiran]-2-one (*rac*-4e)



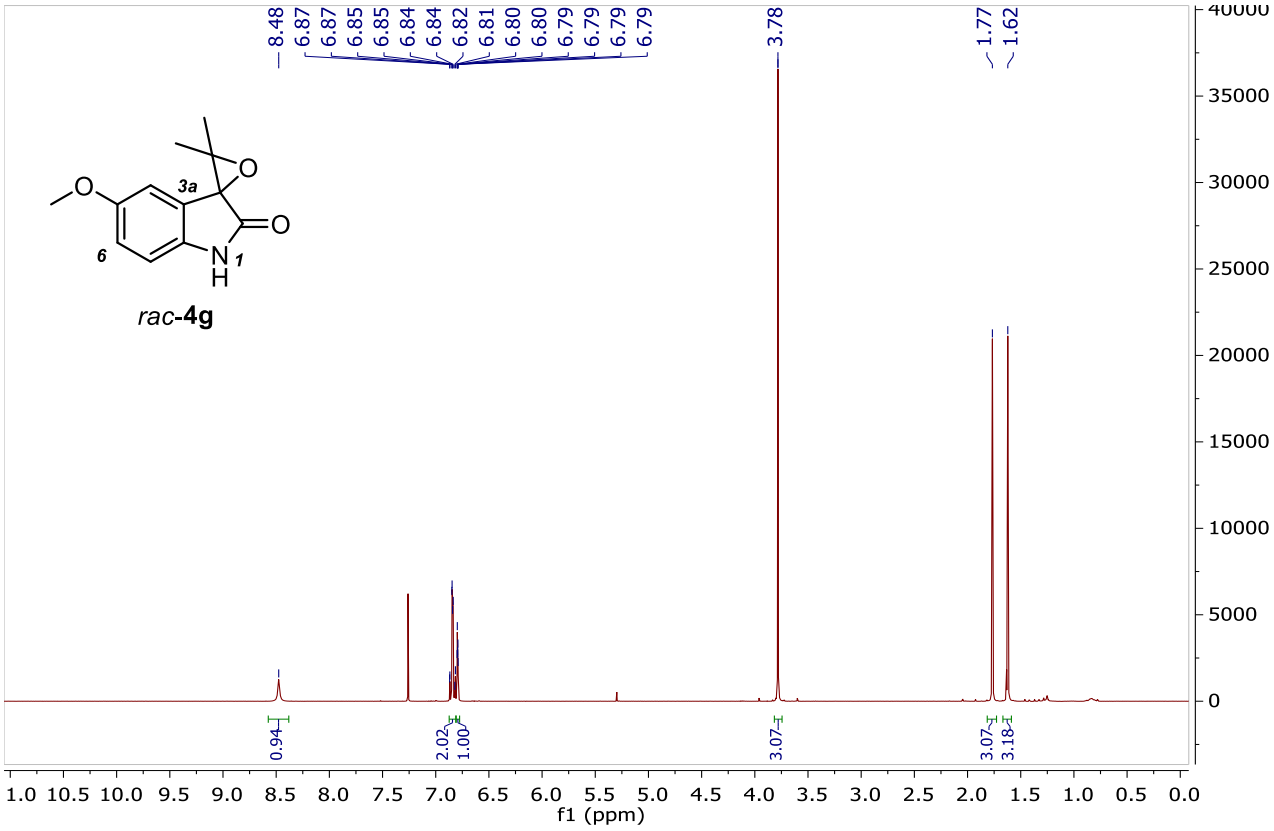


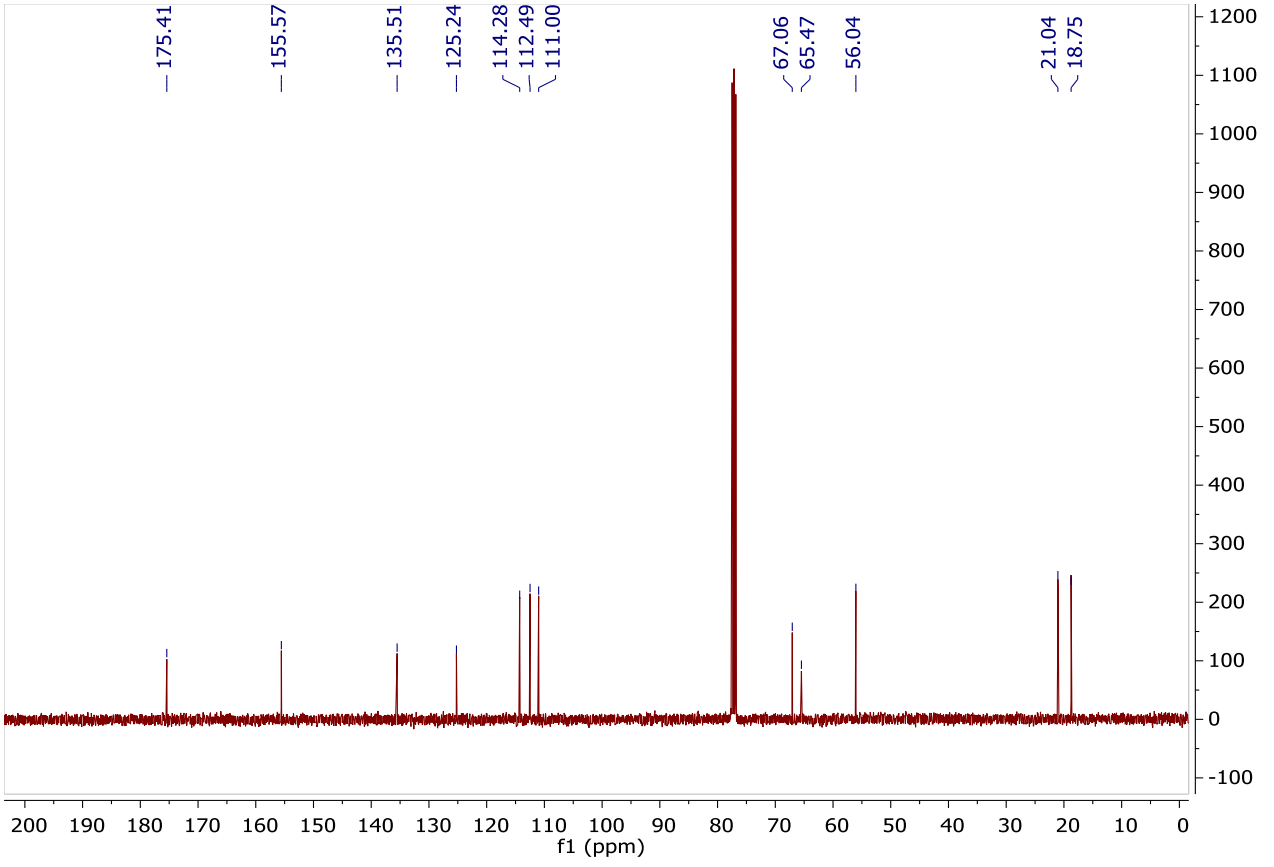
6-Chloro-3',3'-diethylspiro[indolin-3,2'-oxiran]-2-one (*rac*-4f)



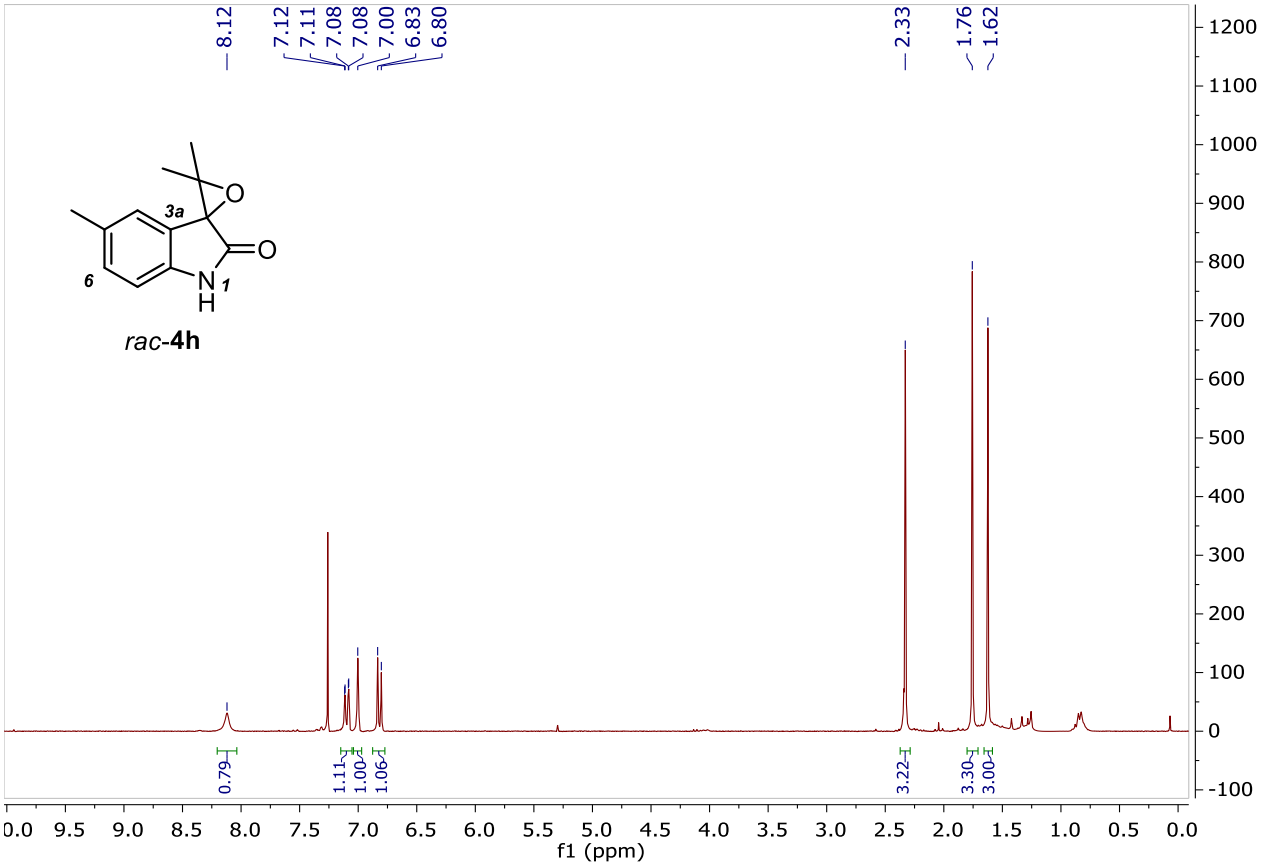


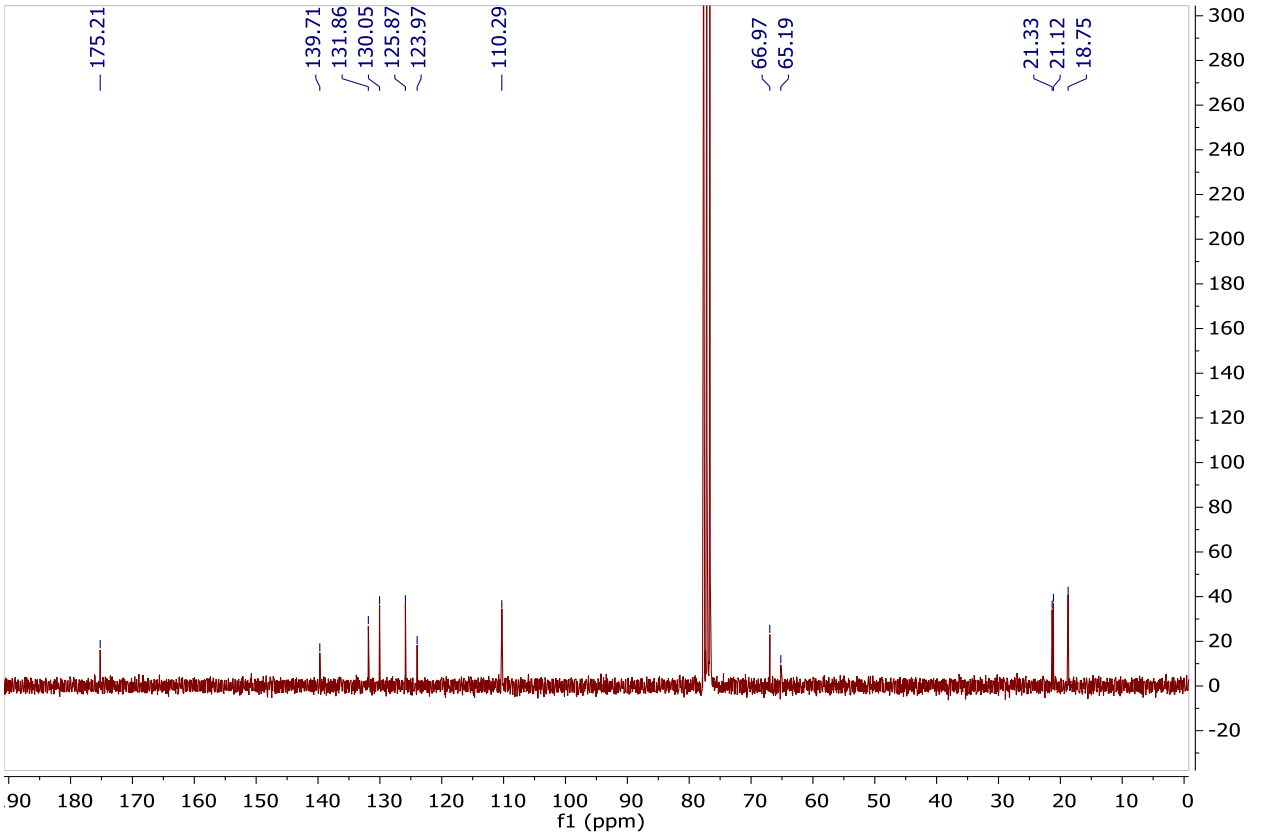
5-Methoxy-3',3'-dimethylspiro[indolin-3,2'-oxiran]-2-one (*rac*-4g)



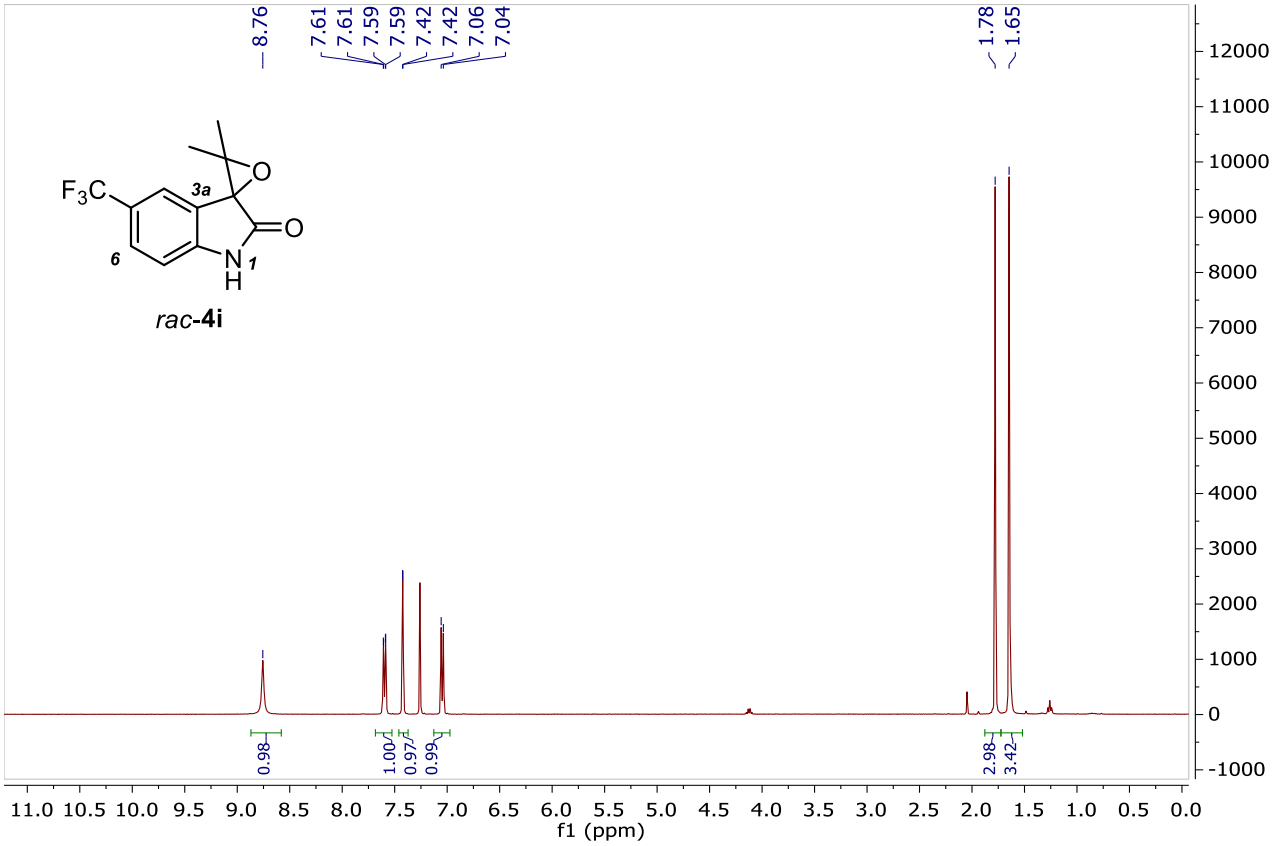


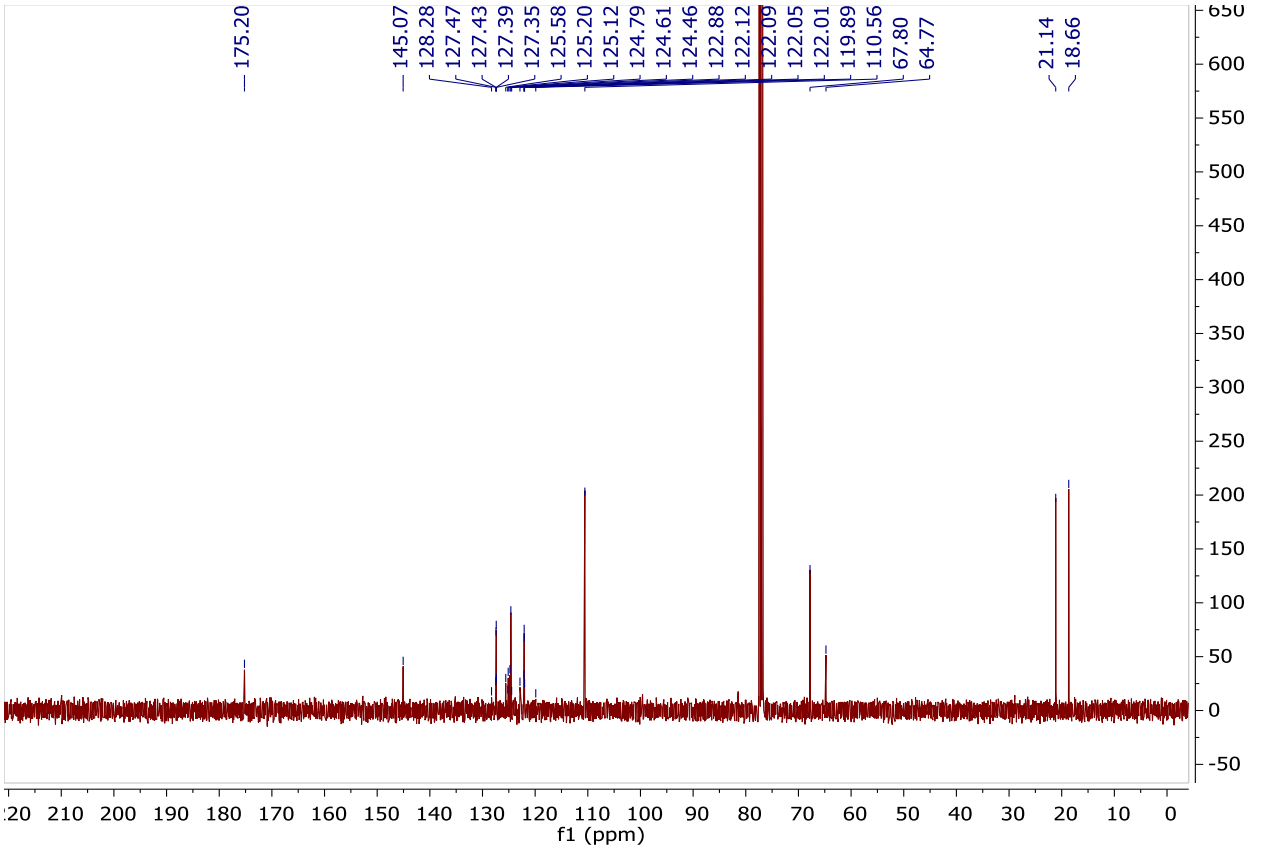
5-Methyl-3',3'-dimethylspiro[indolin-3,2'-oxiran]-2-one (*rac*-4h)



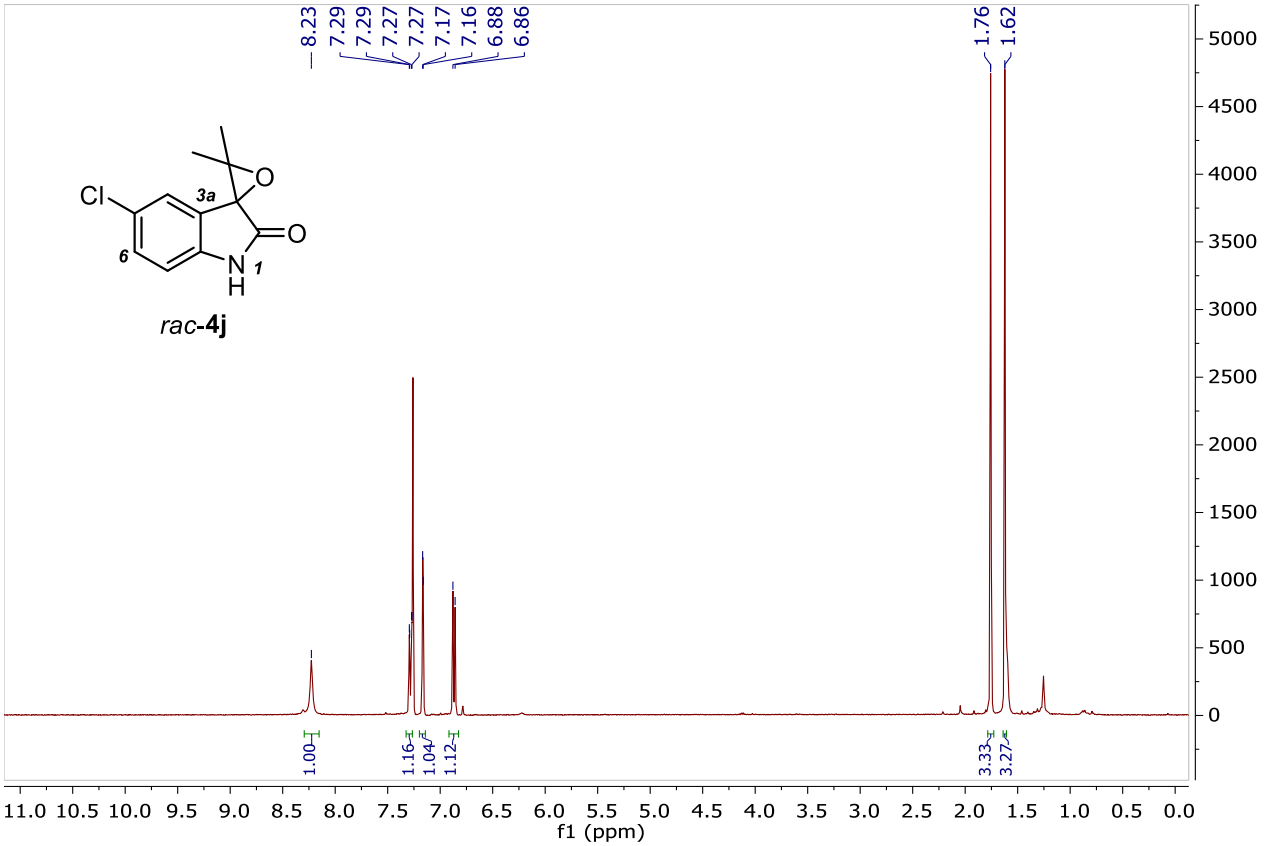


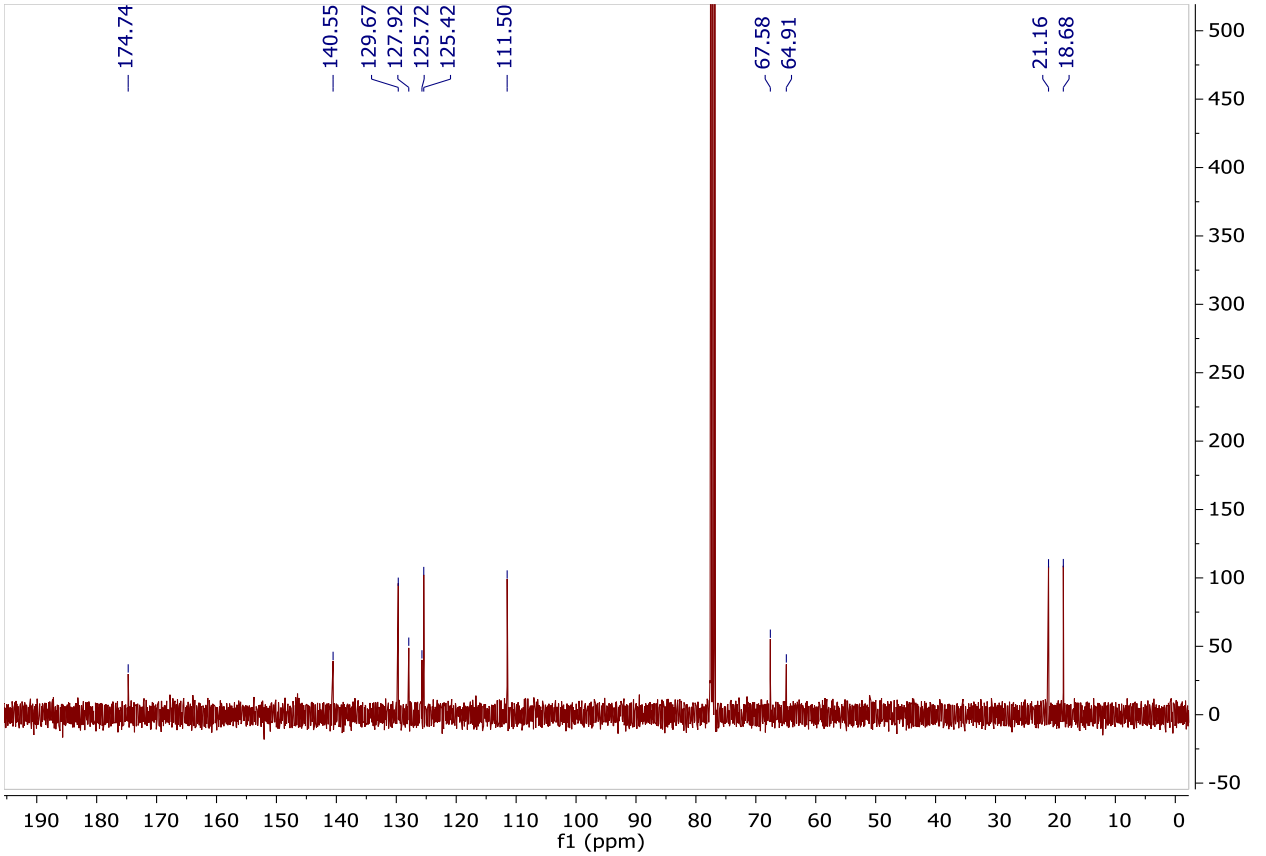
5-Trifluoromethyl-3',3'-dimethylspiro[indolin-3,2'-oxiran]-2-one (*rac*-4i)



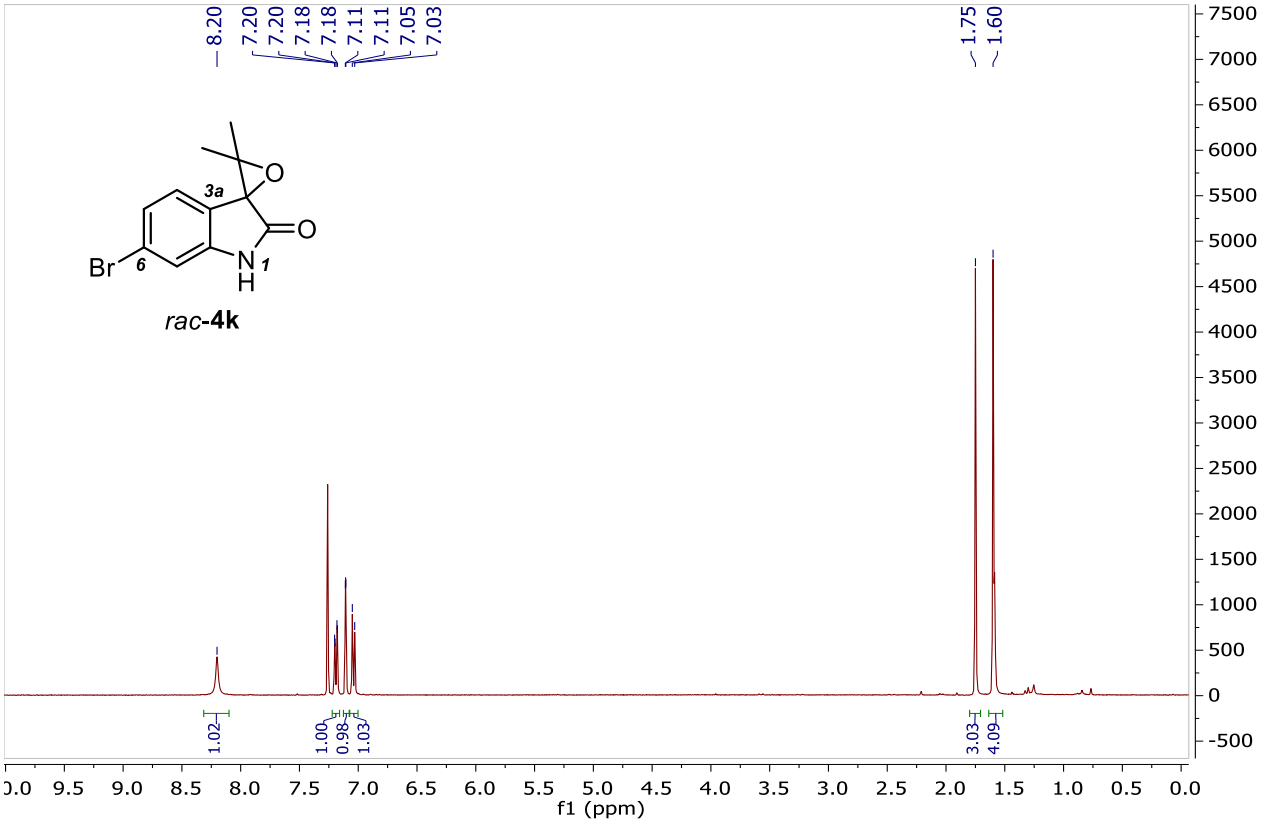


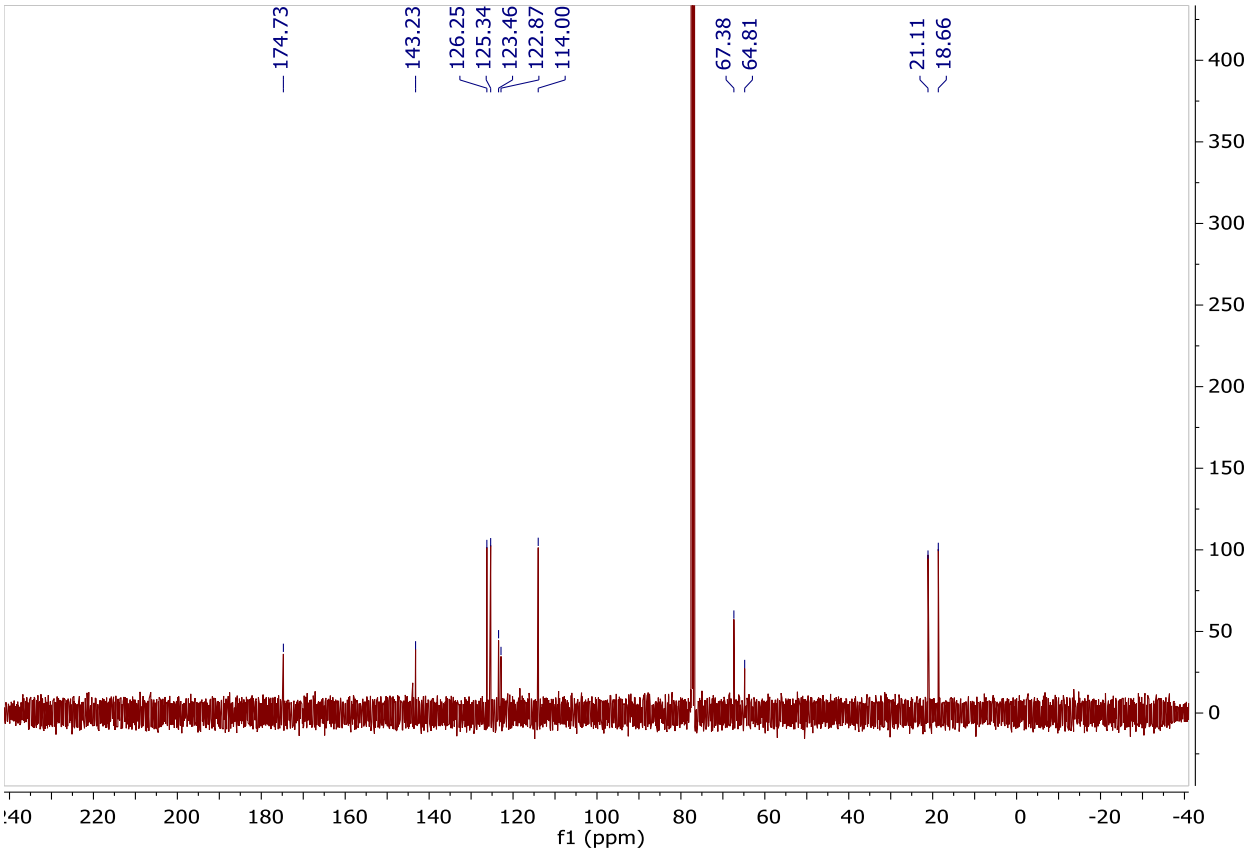
5-Chloro-3',3'-dimethylspiro[indolin-3,2'-oxiran]-2-one (*rac*-4j)



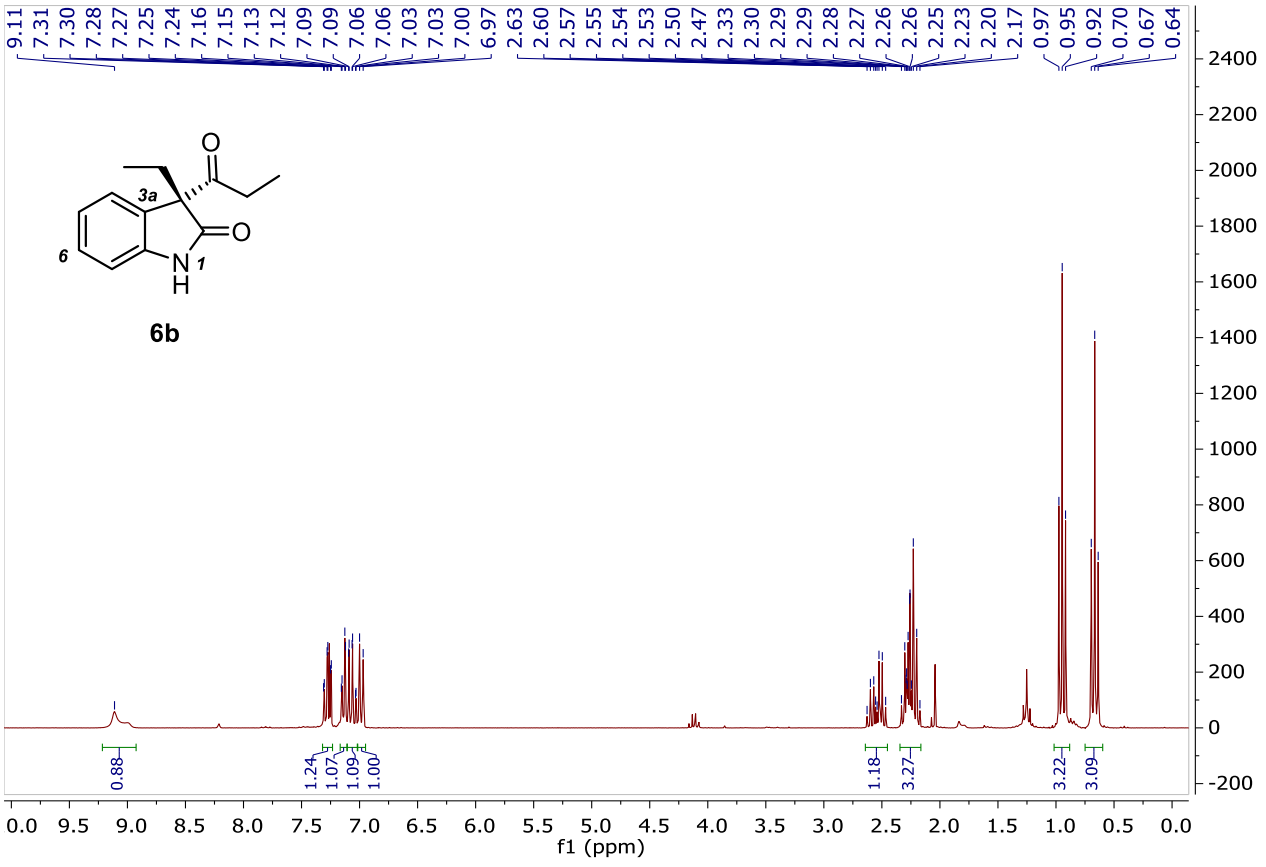


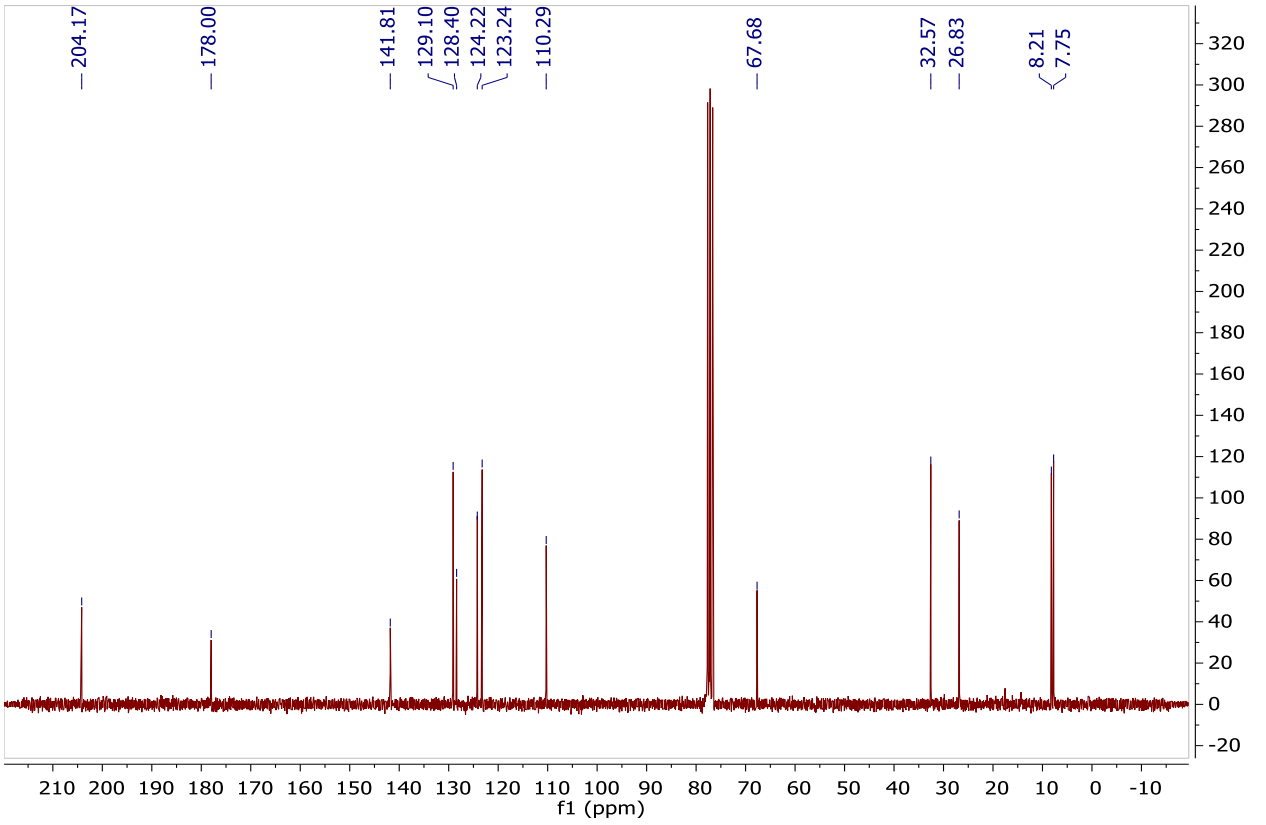
6-Bromo-3',3'-dimethylspiro[indolin-3,2'-oxiran]-2-one (*rac*-4k)



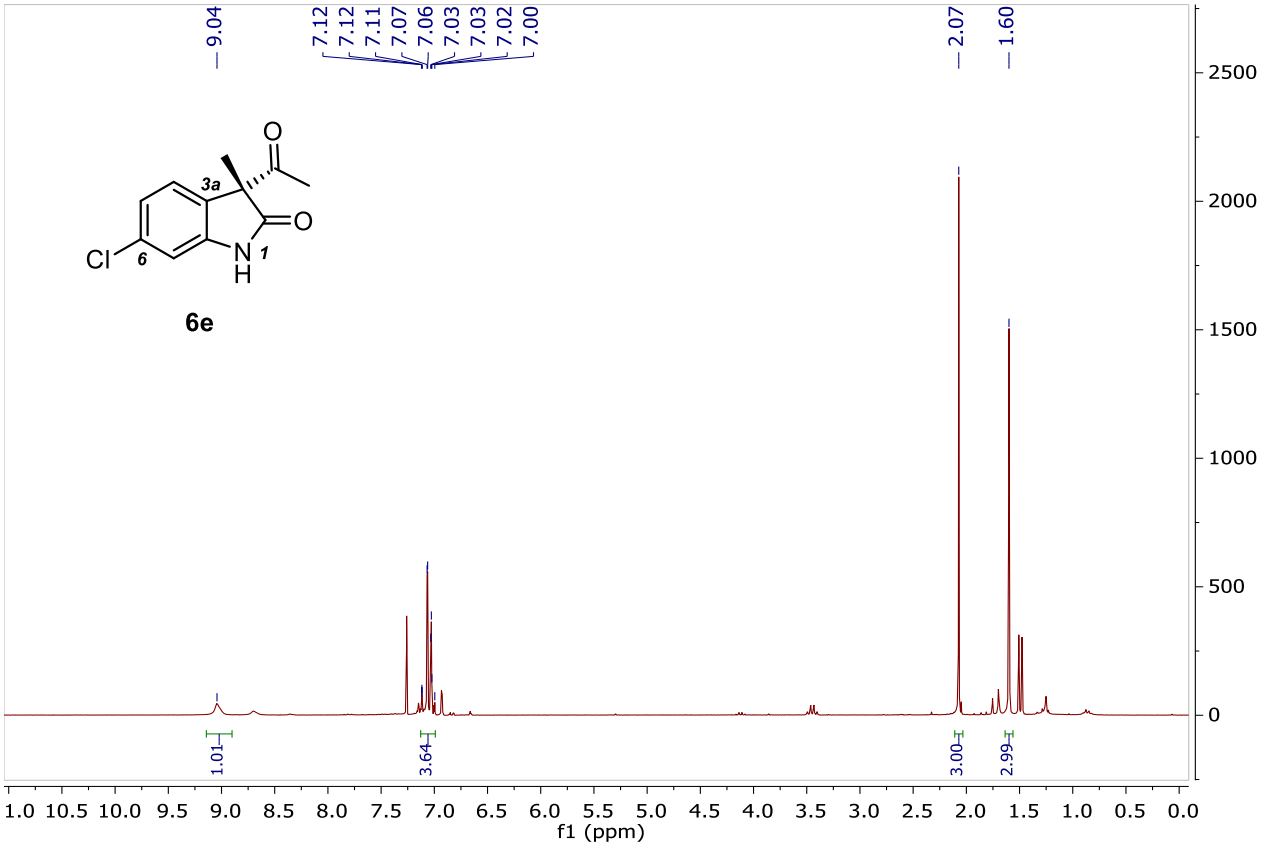


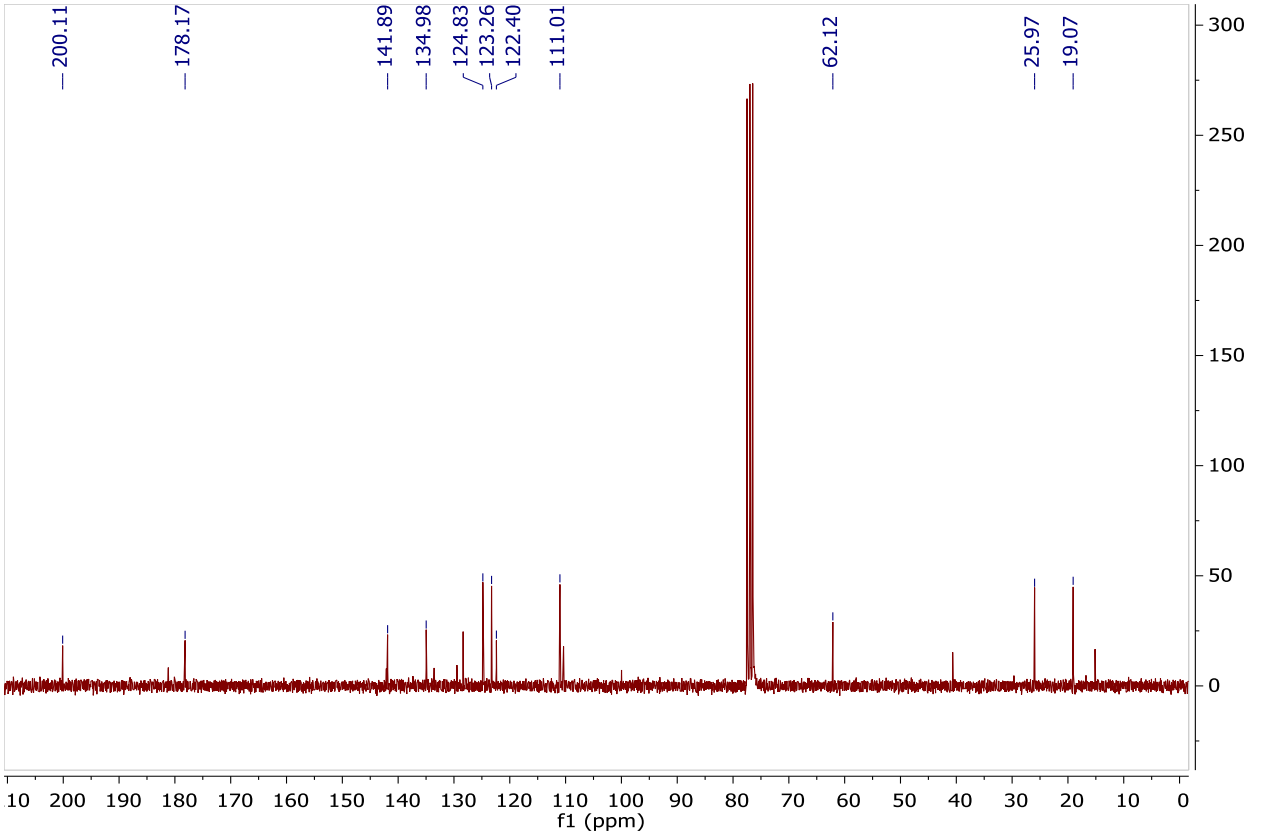
(*R*)-3-Ethyl-3-propionylindolin-2-one (6b)



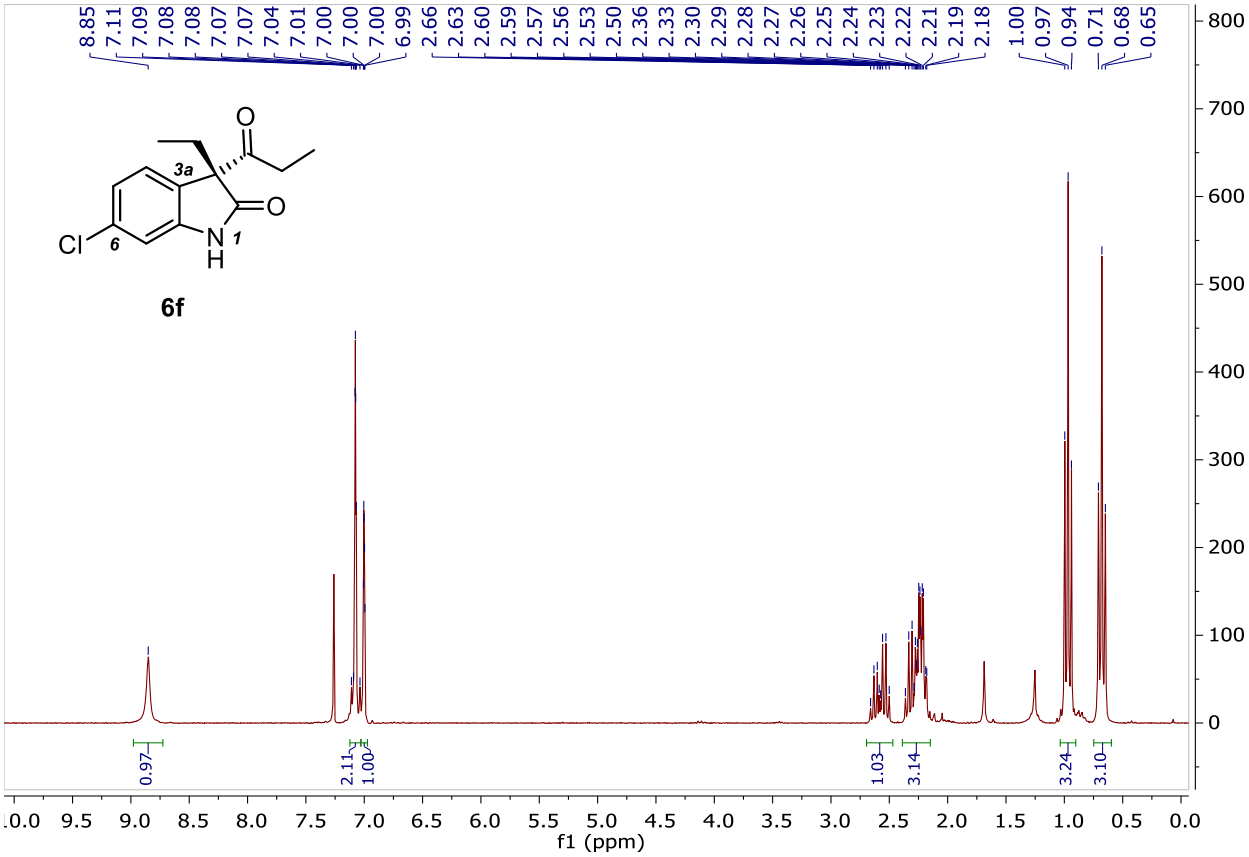


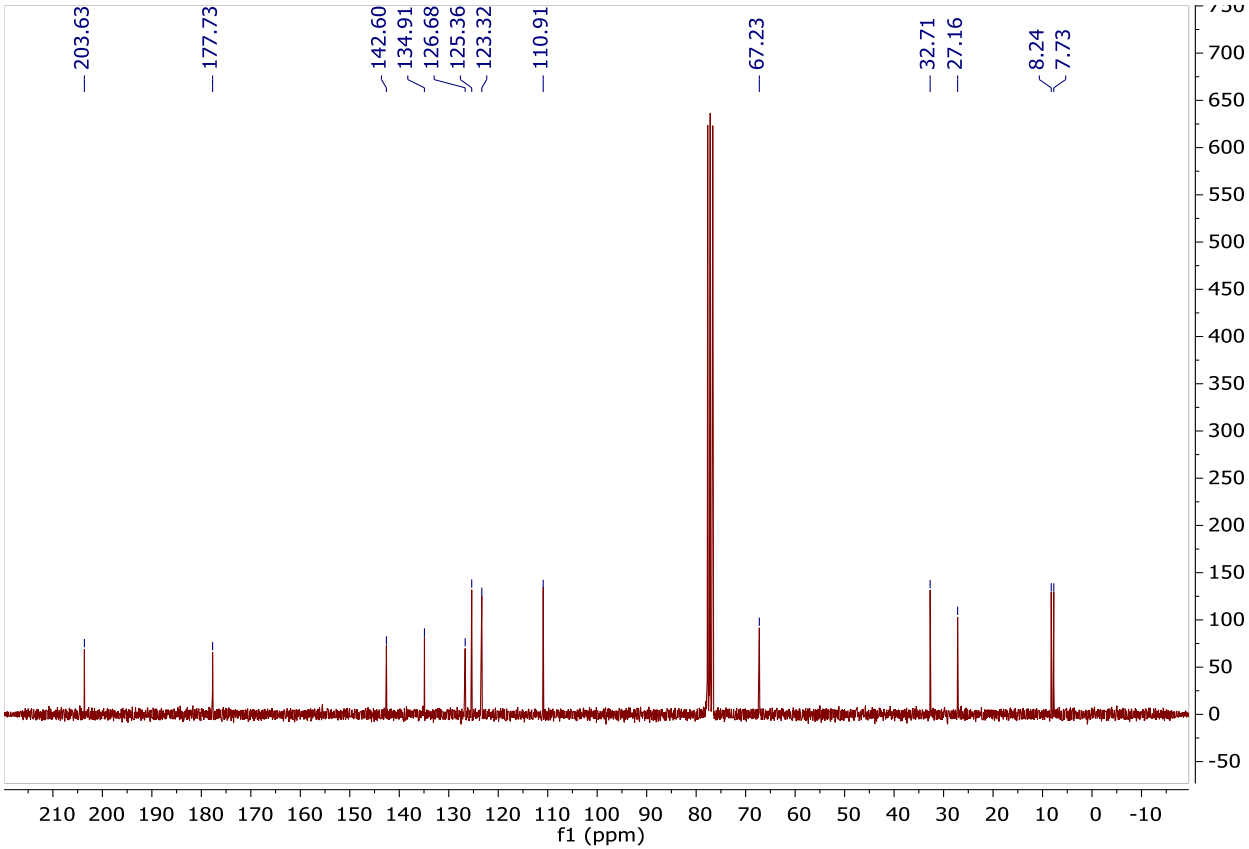
(*R*)-3-Acetyl-6-chloro-3-methylindolin-2-on (6e)



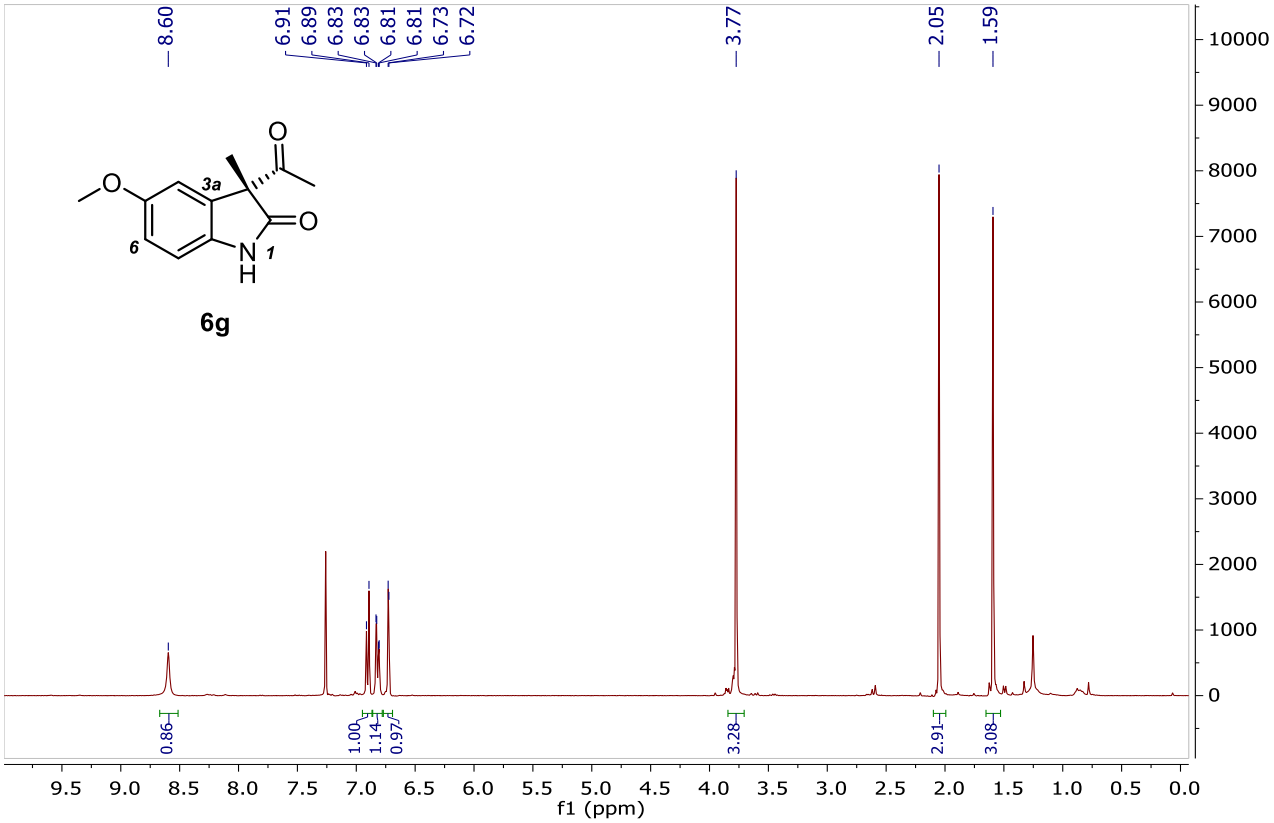


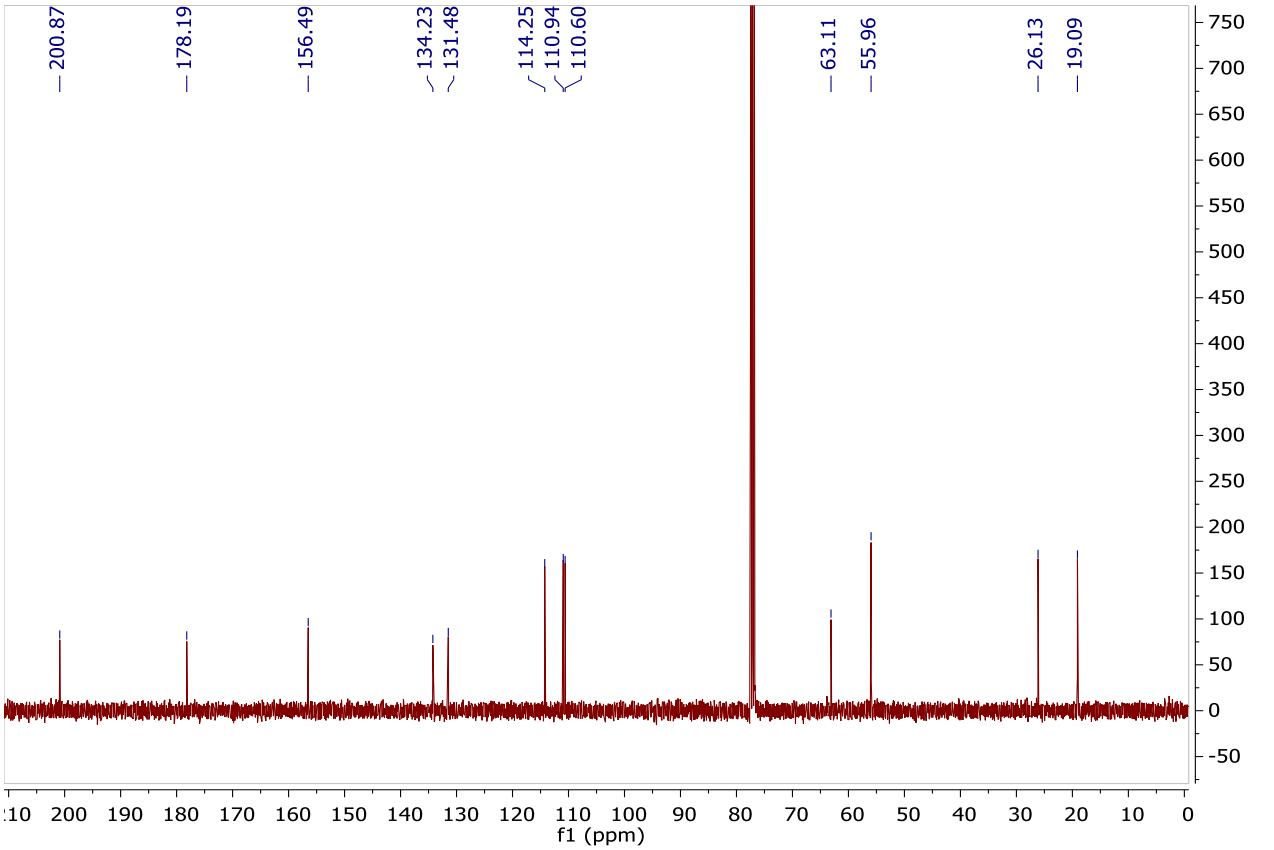
(*R*)-6-Chloro-3-ethyl-3-propionylindolin-2-on3 (6f)



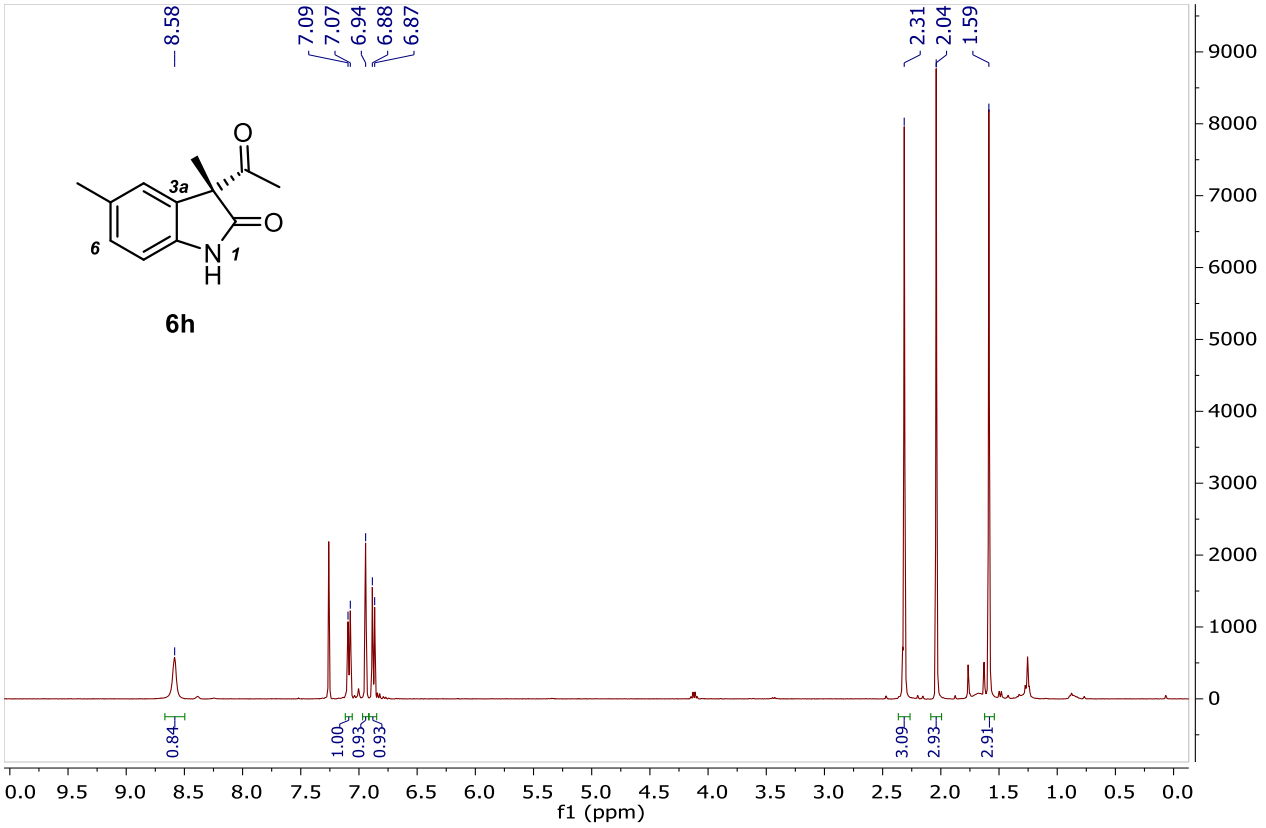


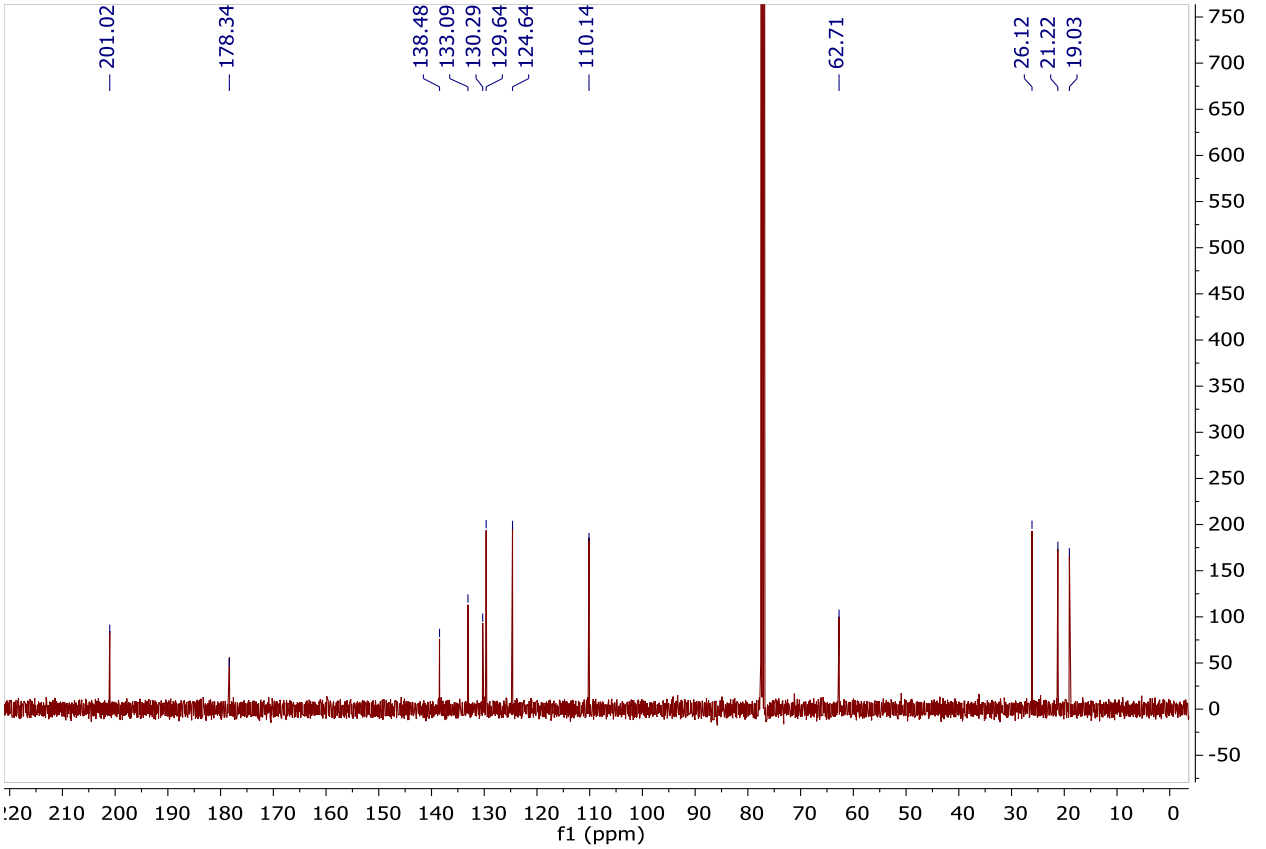
(*R*)-3-Acetyl-5-methoxy-3-methylindolin-2-one (6g)



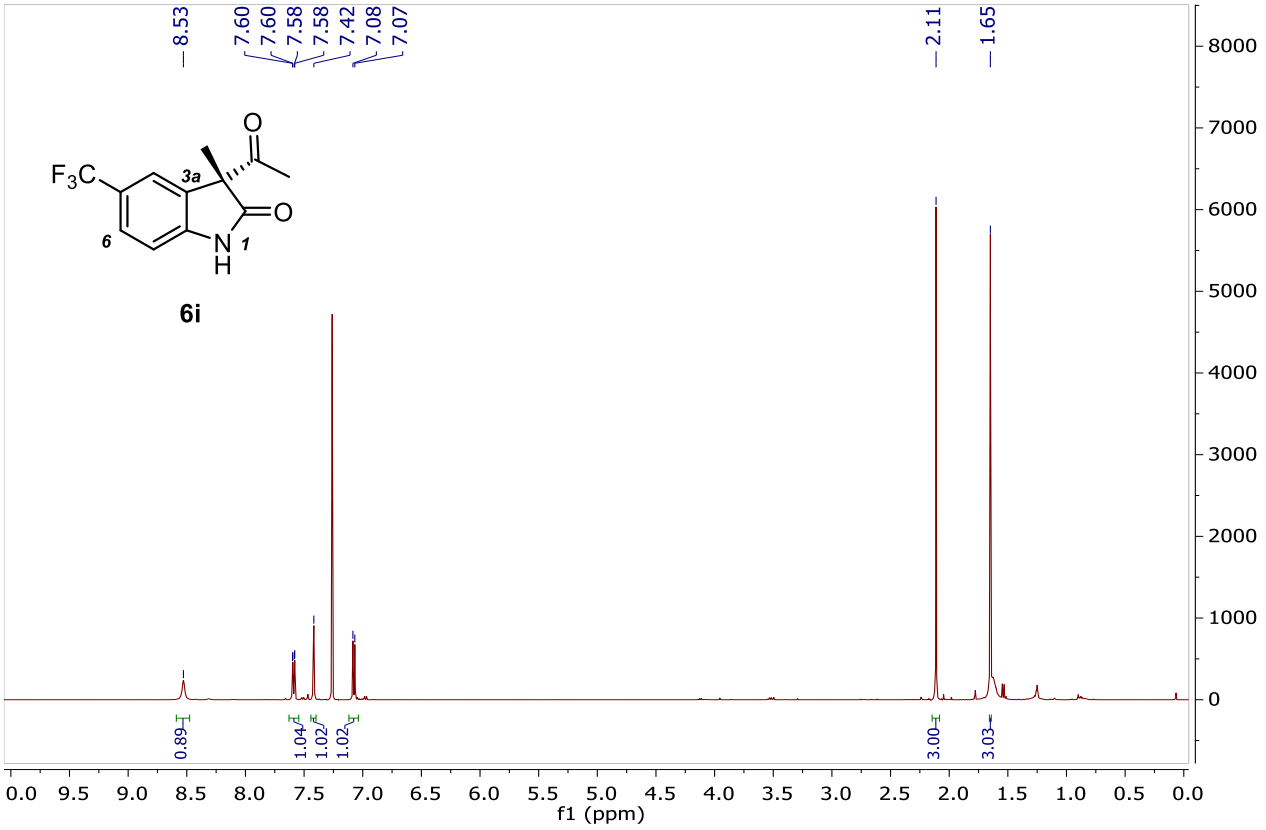


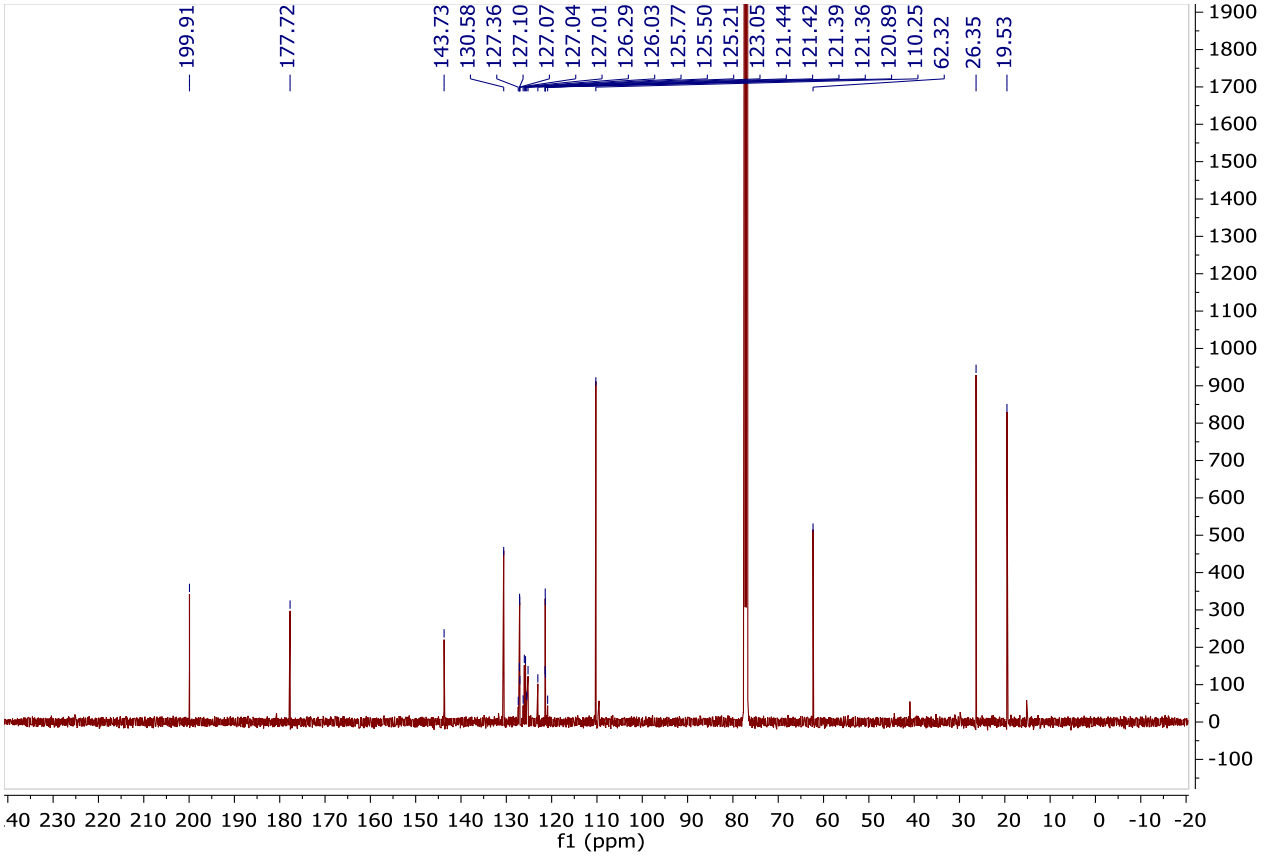
(*R*)-3-Acetyl-3,5-dimethylindolin-2-one (6h):



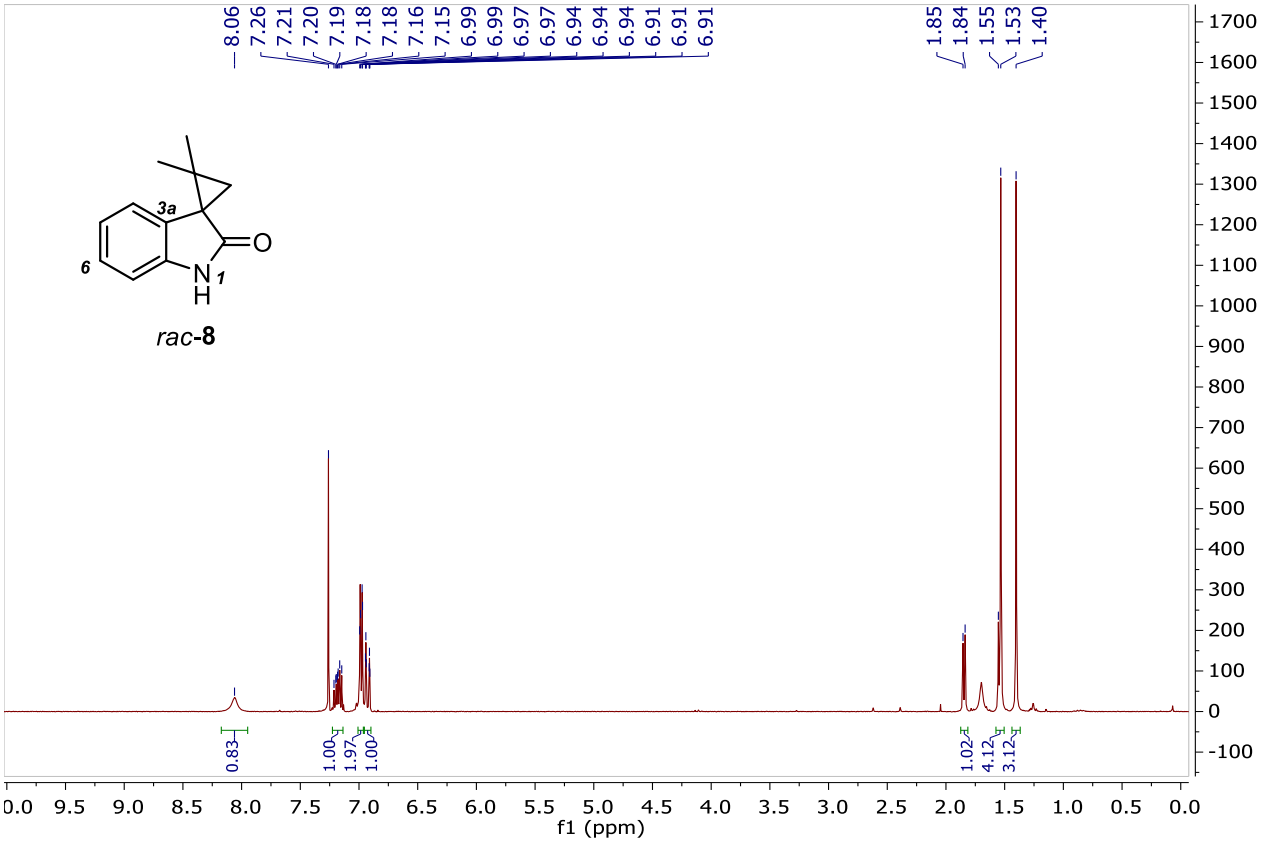


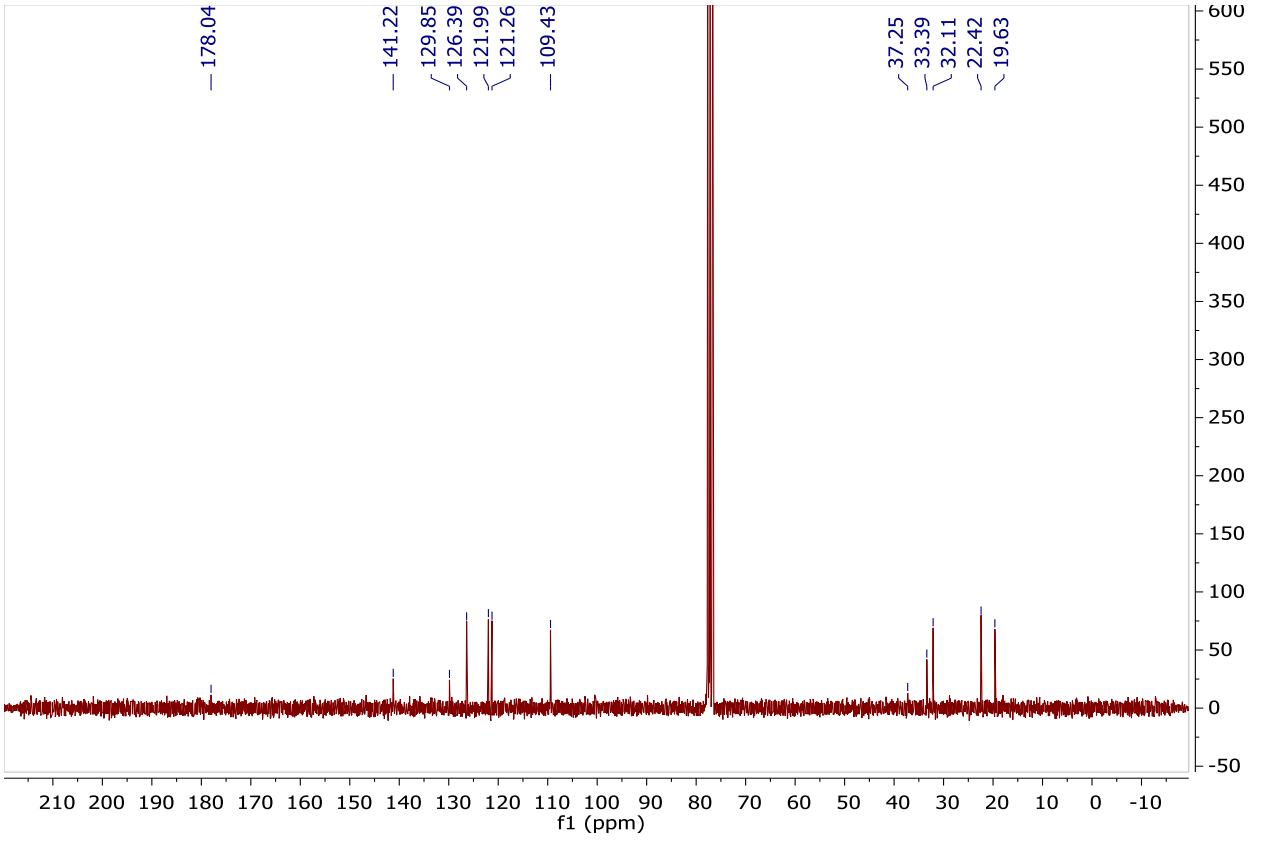
(*R*)-3-Acetyl-3-methyl-5-(trifluoromethyl)indolin-2-one (6i)



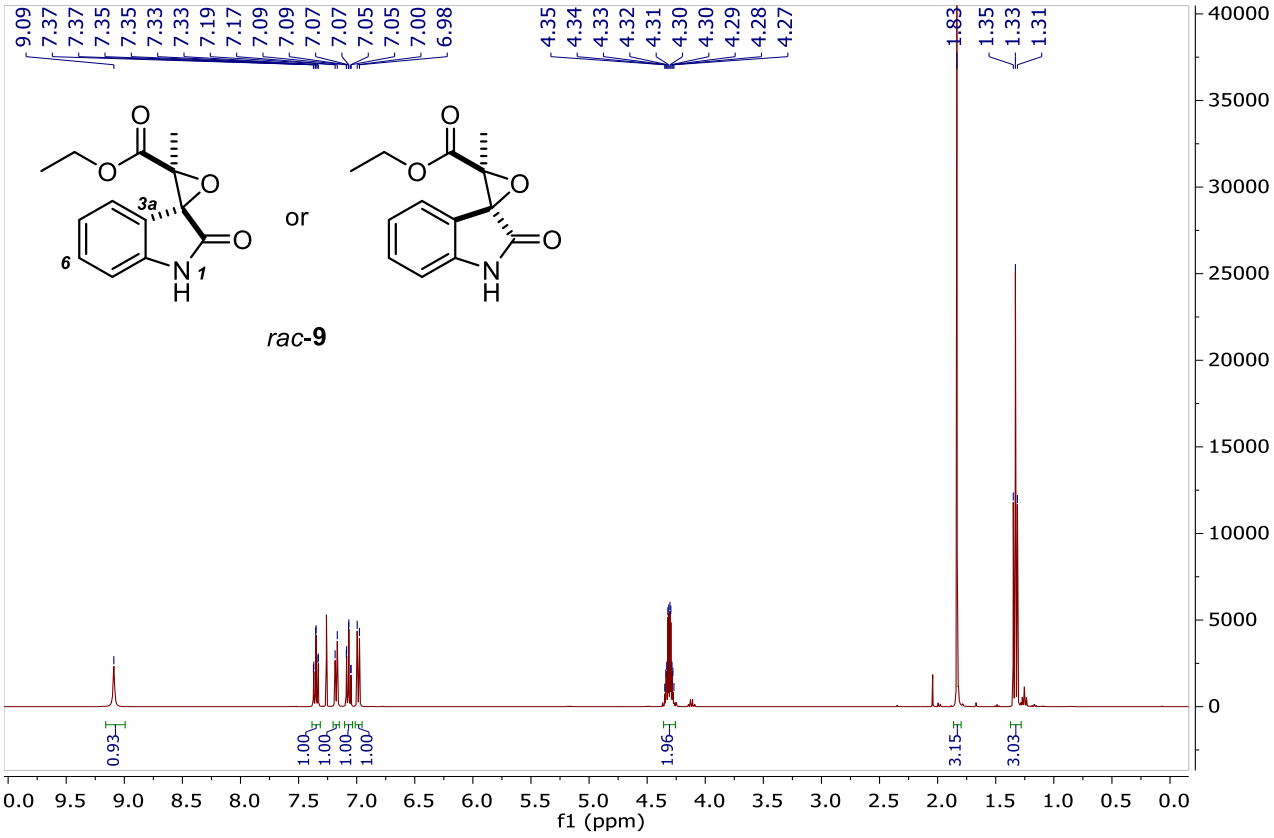


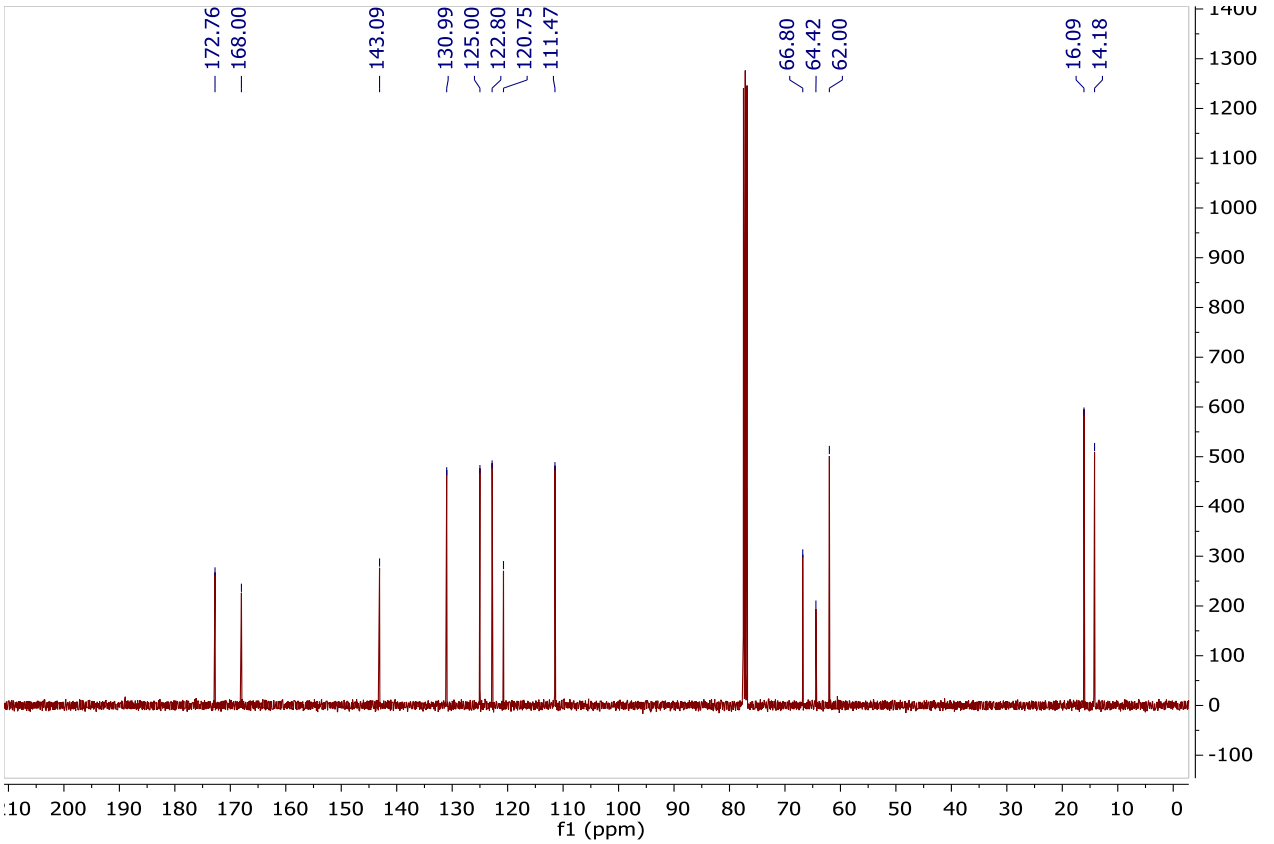
2,2-Dimethylspiro[cyclopropane-1,3'-indolin]-2'-one (*rac*-**8**)



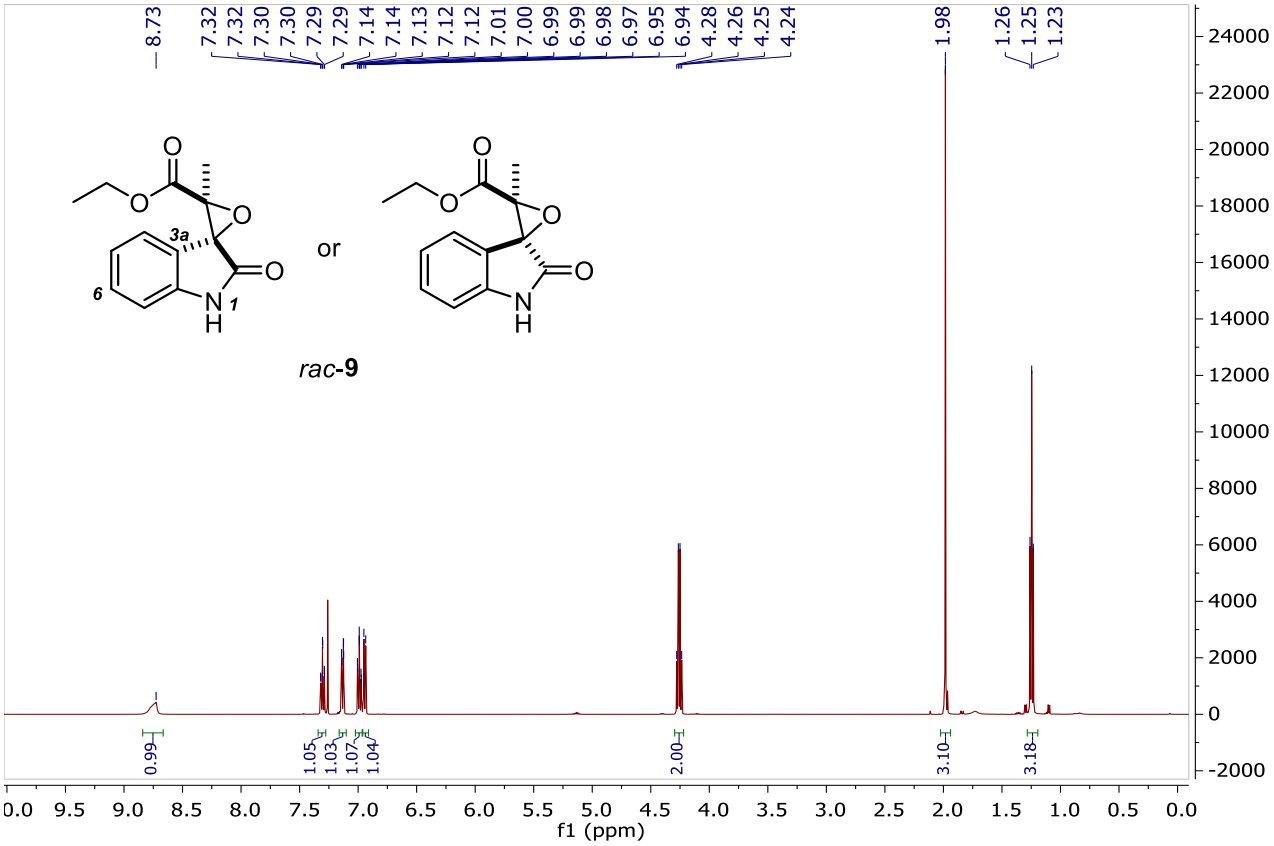


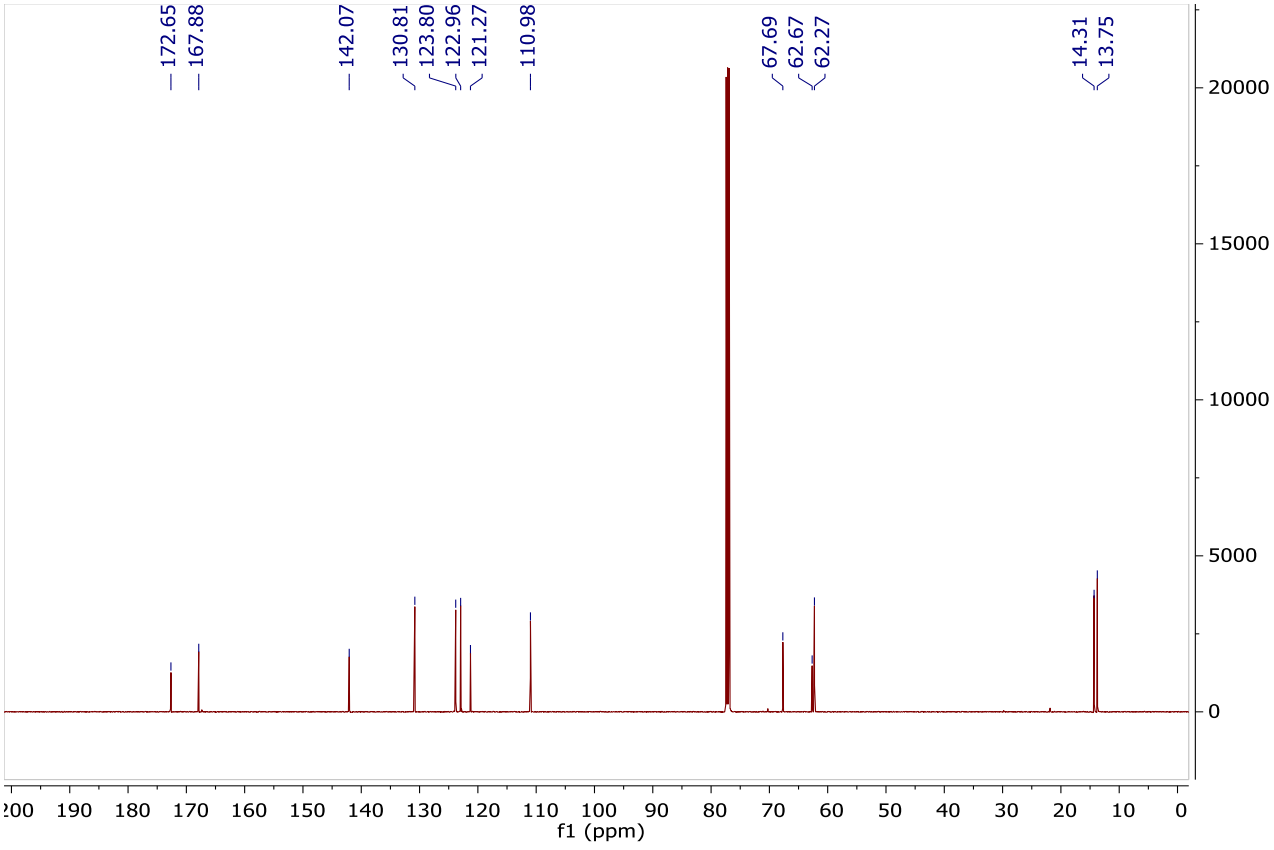
Ethyl 3'-methyl-2-oxospiro[indoline-3,2'-oxirane]-3'-carboxylate (*rac*-**9**) (major diastereomer)



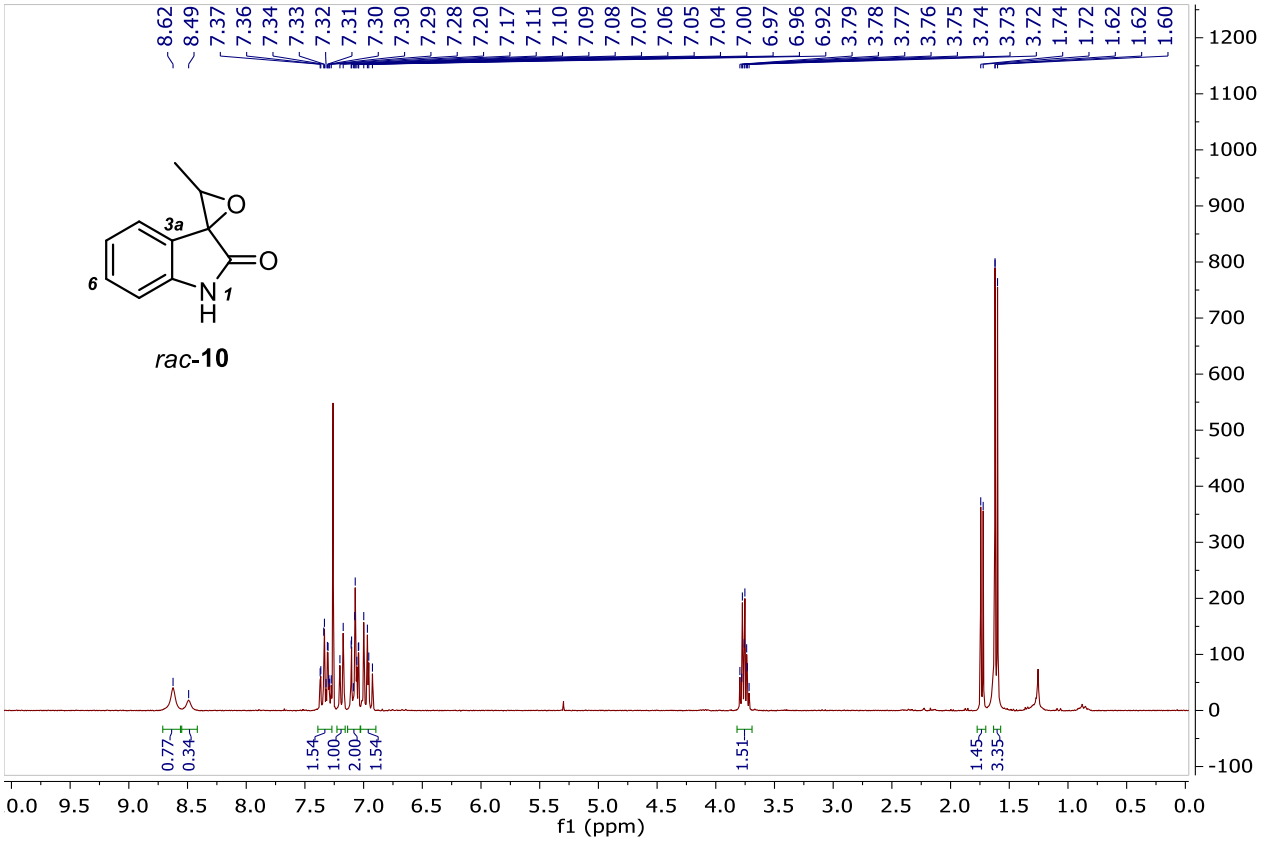


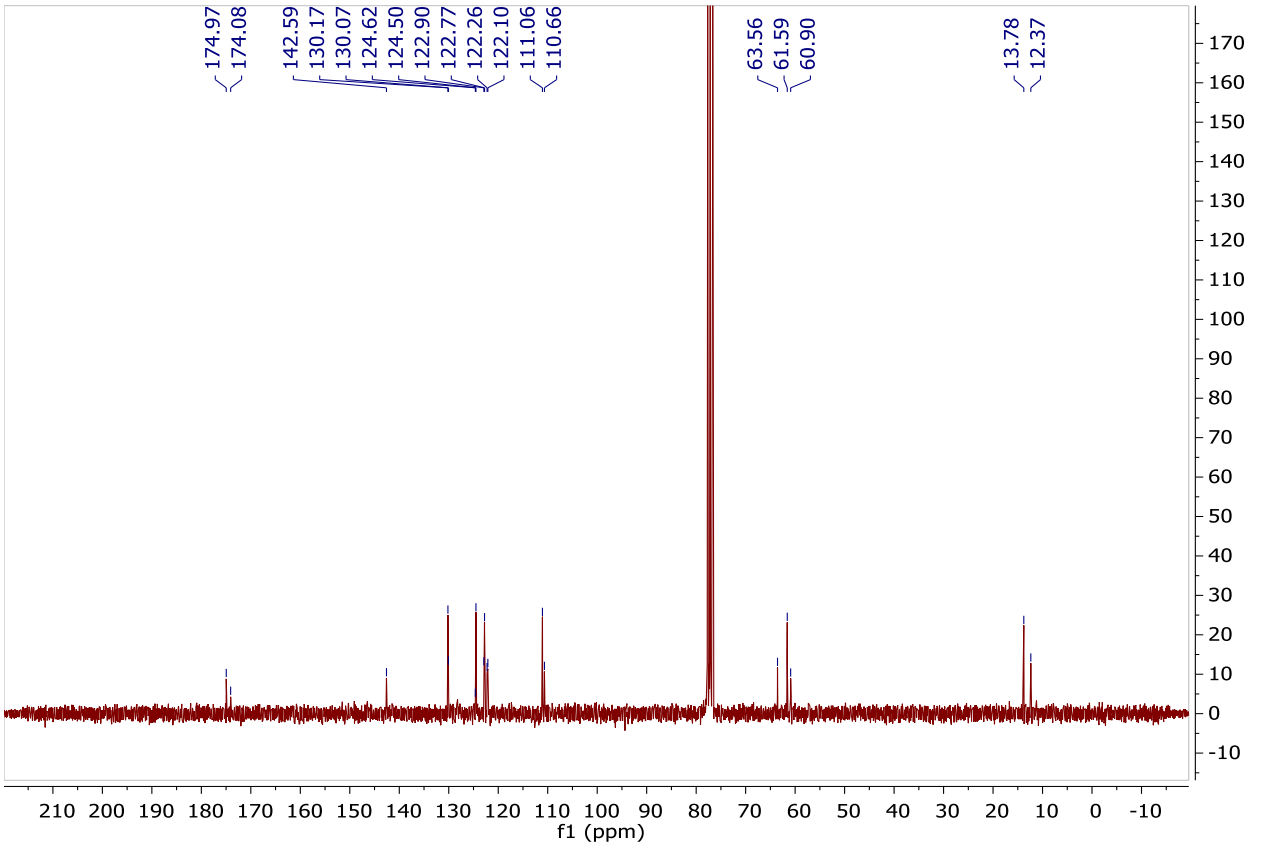
Ethyl 3'-methyl-2-oxospiro[indoline-3,2'-oxirane]-3'-carboxylate (*rac*-**9**) (minor diastereomer)





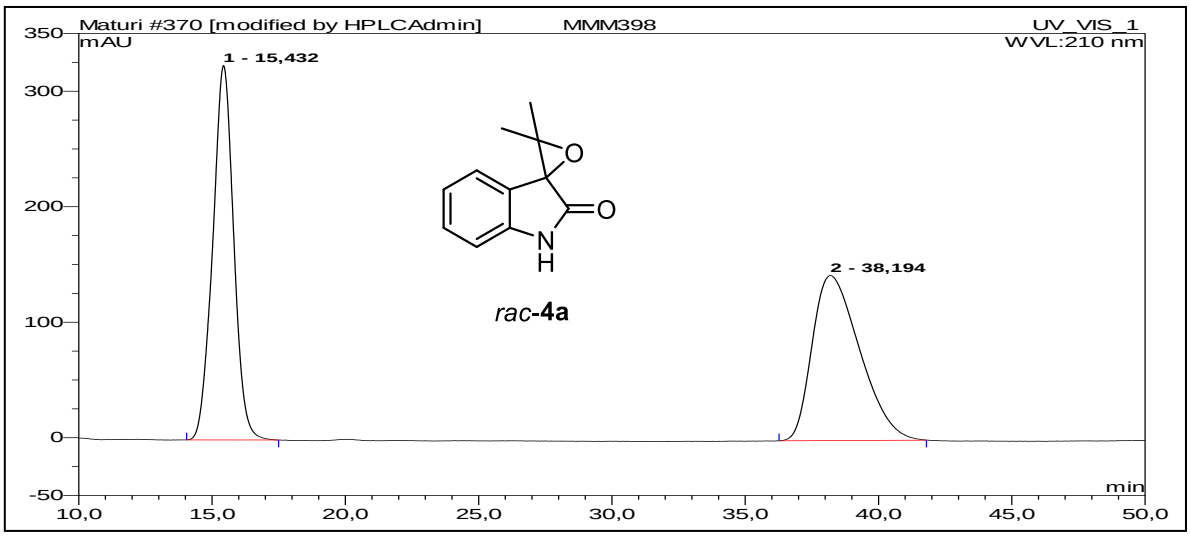
3'-Methylspiro[indoline-3,2'-oxiran]-2-one (*rac*-**10**)

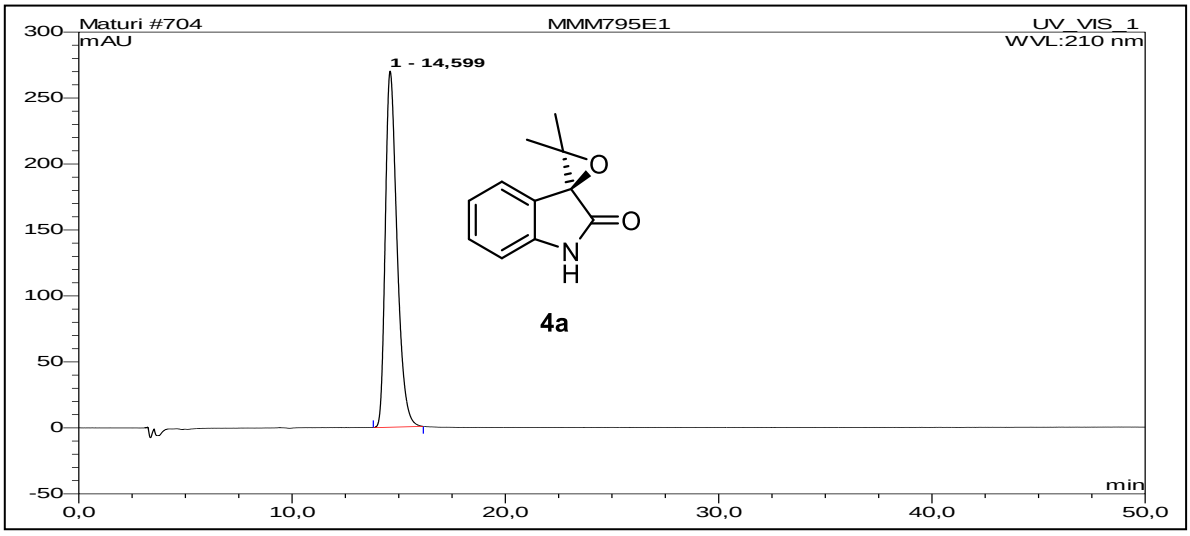


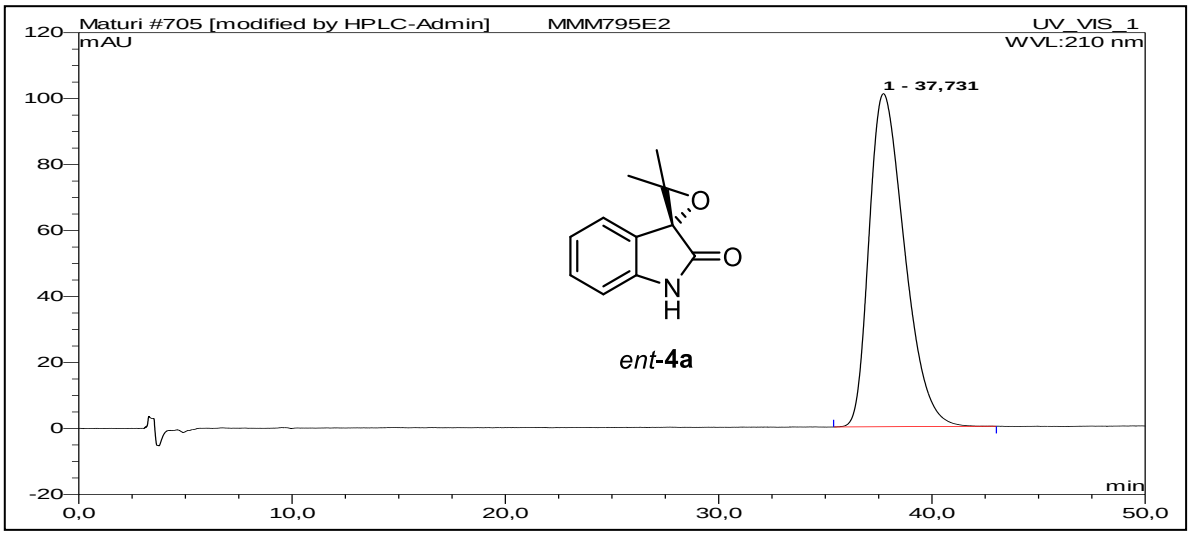


5. Representative HPLC and GLC Traces

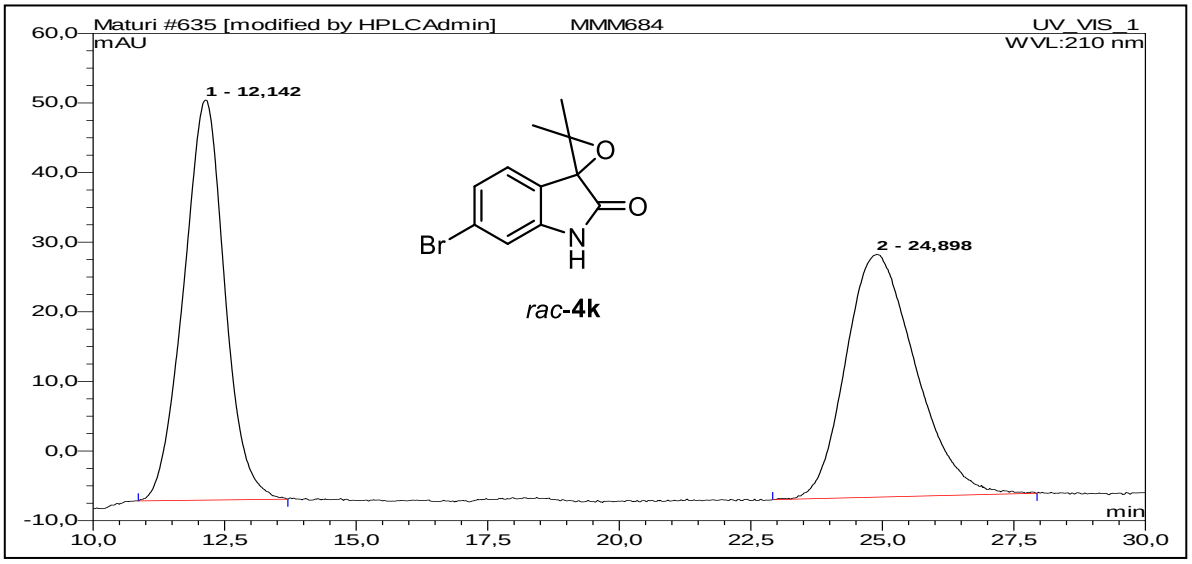
3',3'-Dimethylspiro[indolin-3,2'-oxiran]-2-one (*rac*-4a)

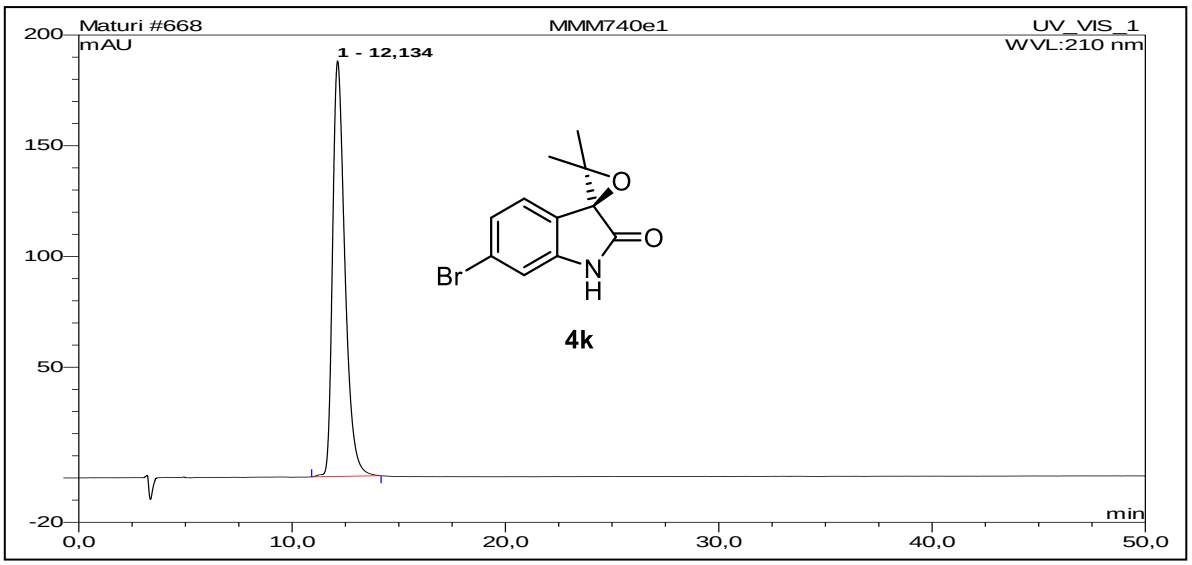


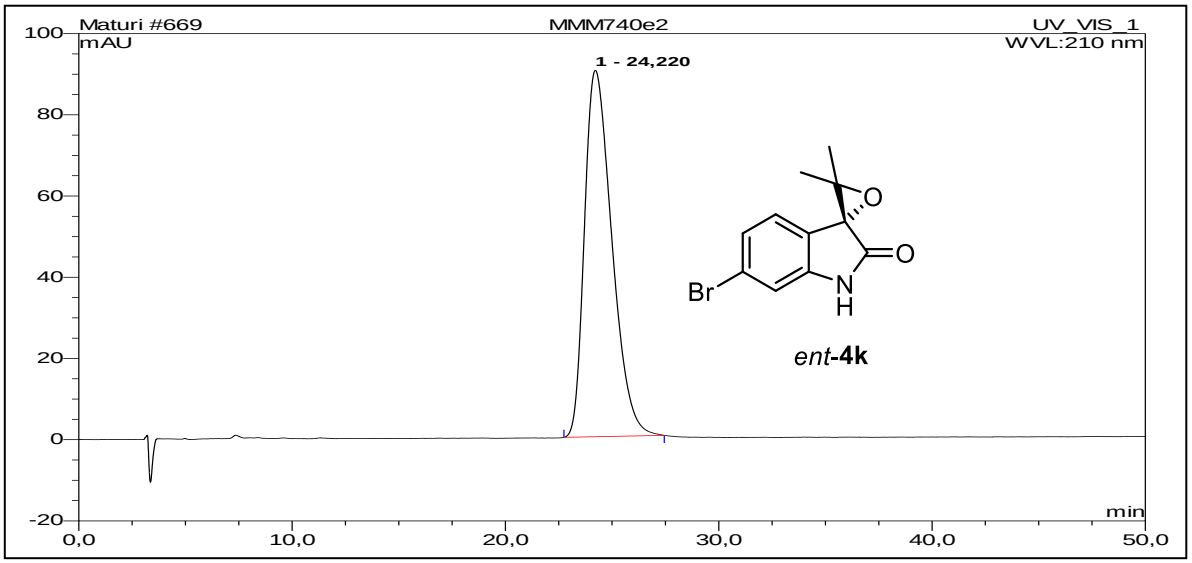




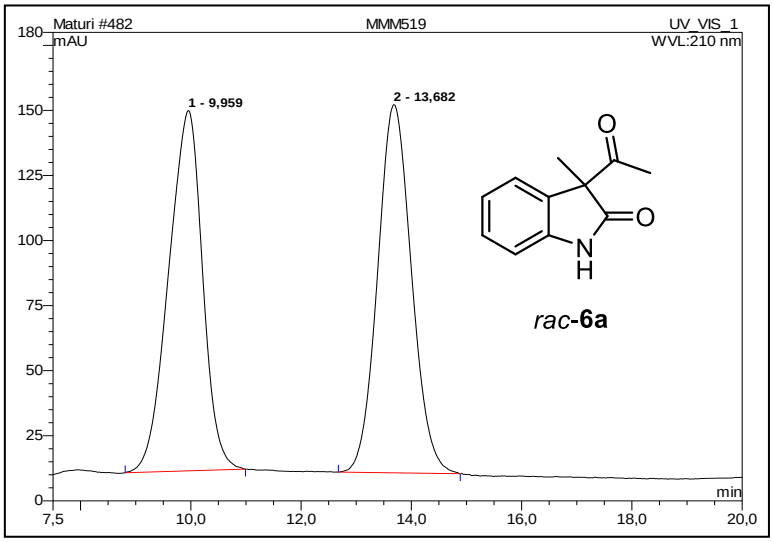
6-Bromo-3',3'-dimethylspiro[indolin-3,2'-oxiran]-2-one (*rac*-**4k**)

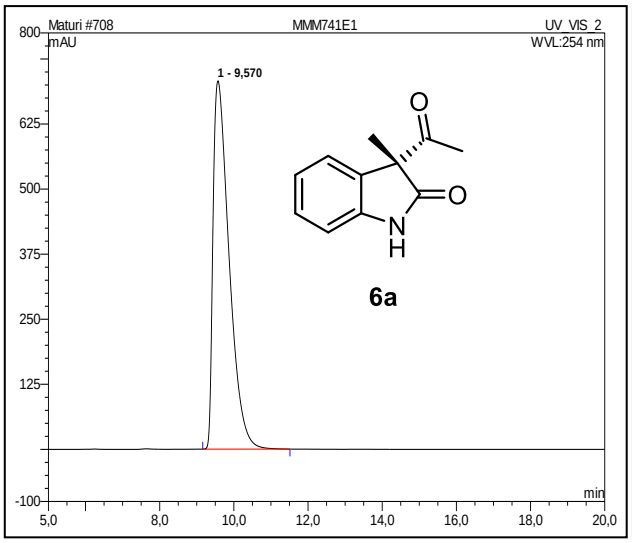


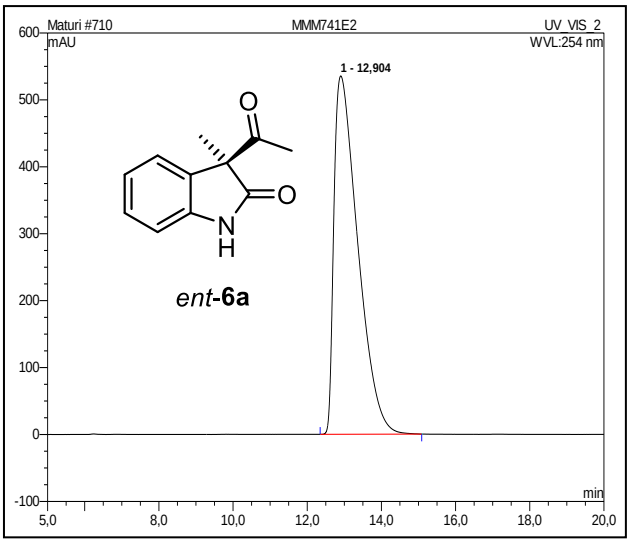


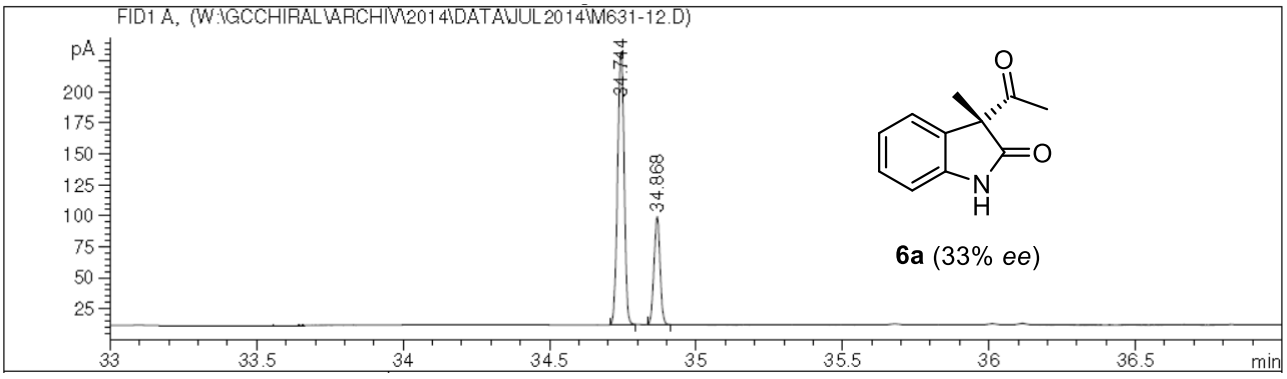


(*R*)-3-Acetyl-3-methylindolin-2-on (6a)

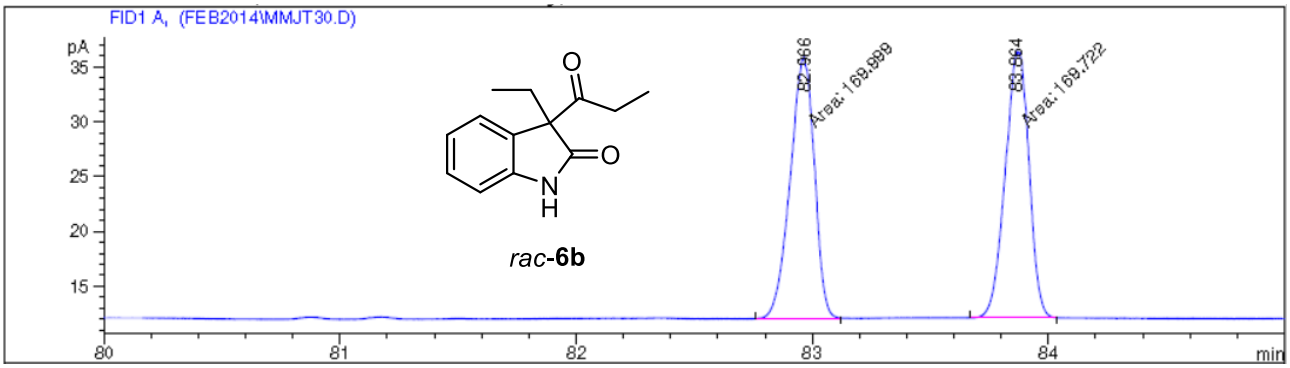


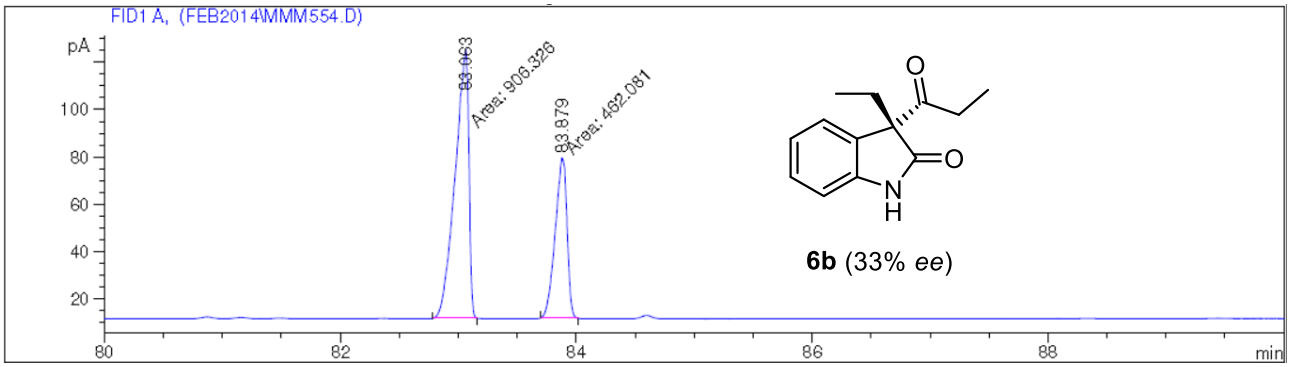




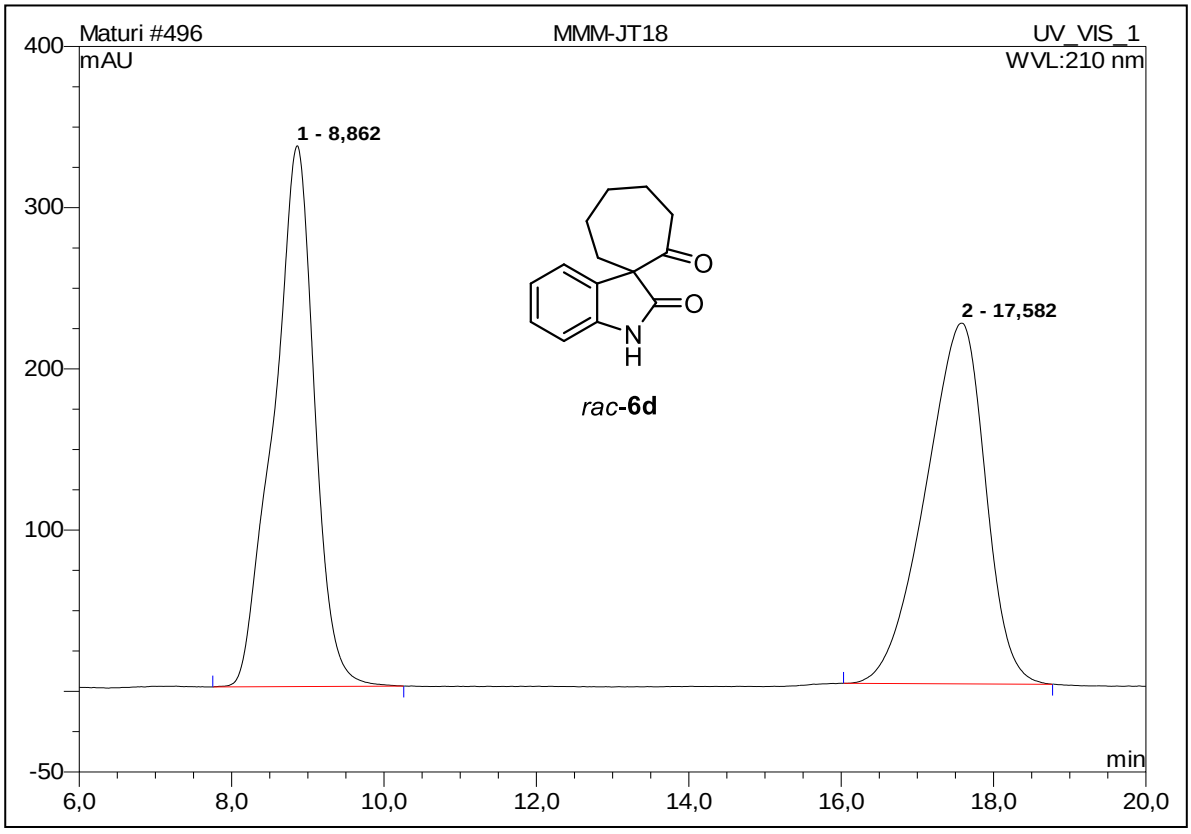


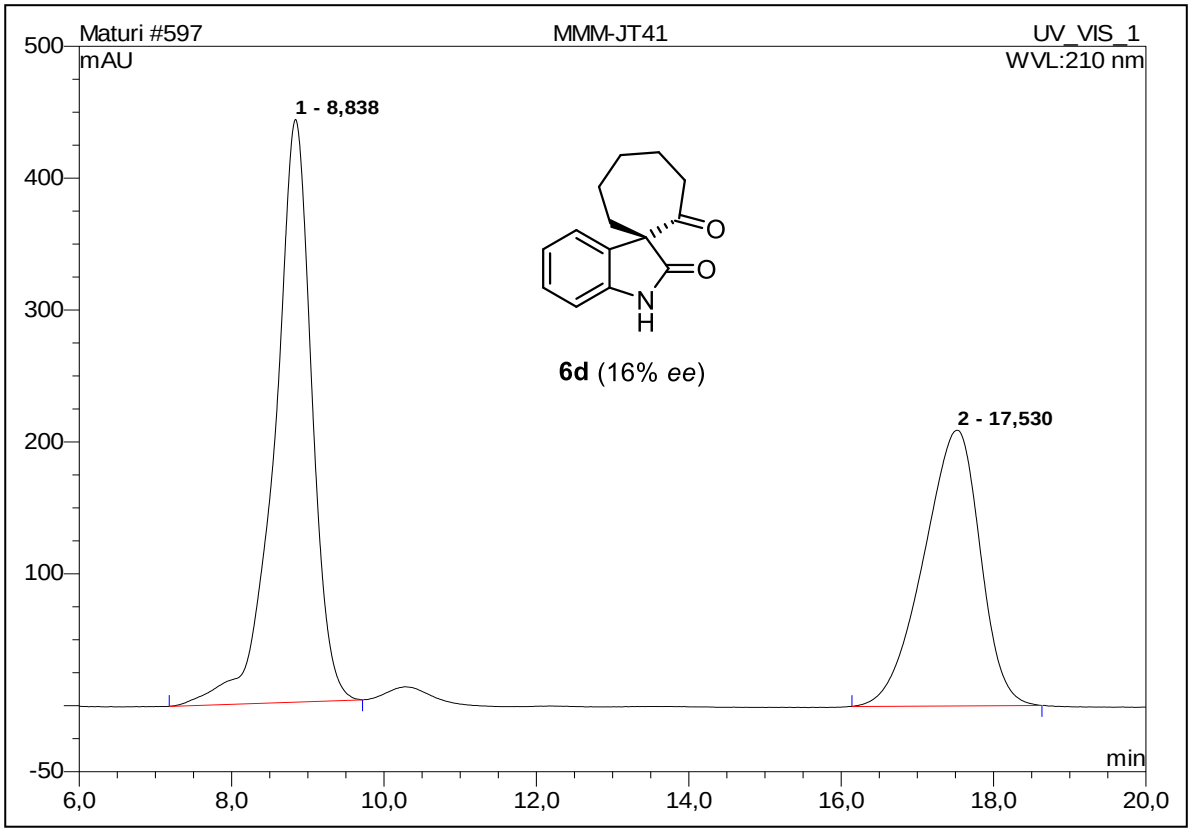
(*R*)-3-Ethyl-3-propionylindolin-2-one (6b)



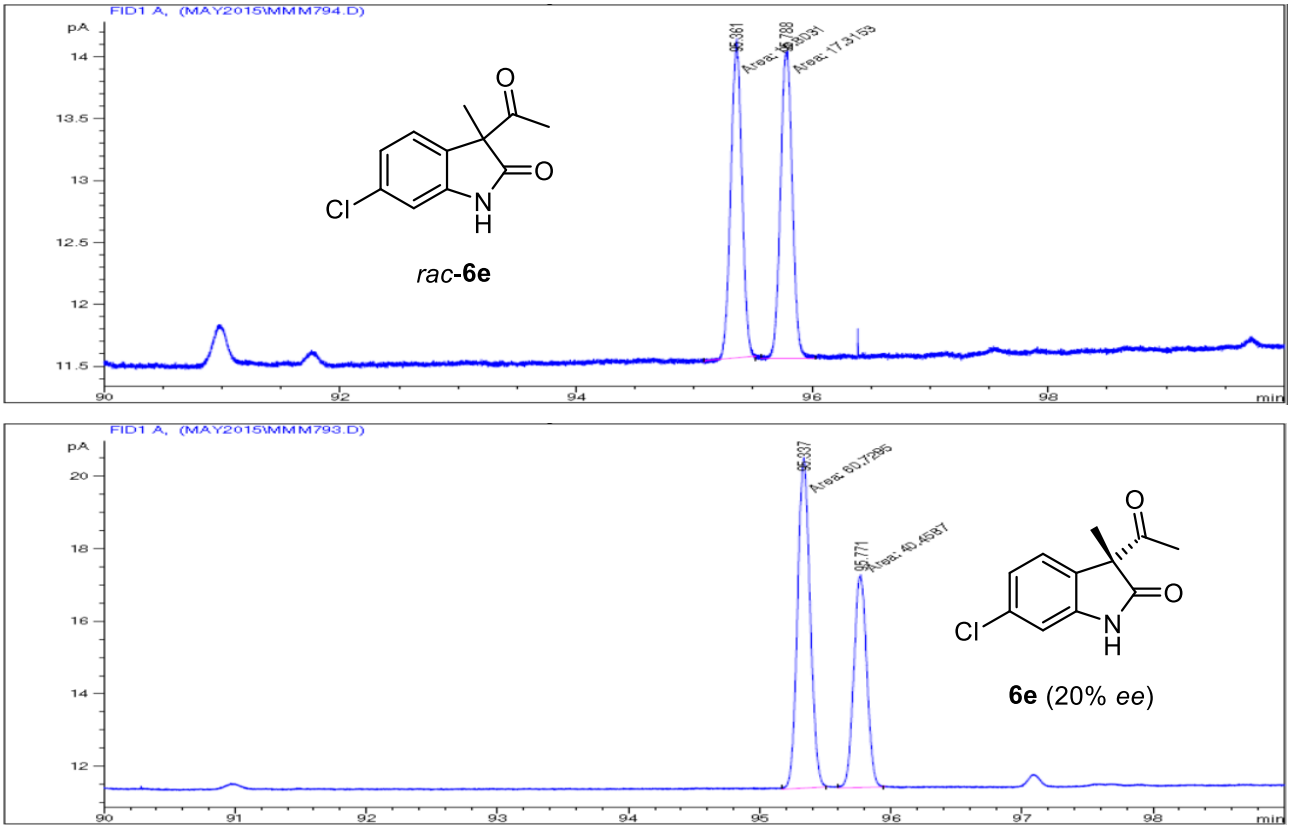


(*R*)-Spiro[cycloheptane-1,3'-indolin]-2,2'-dione (6d)

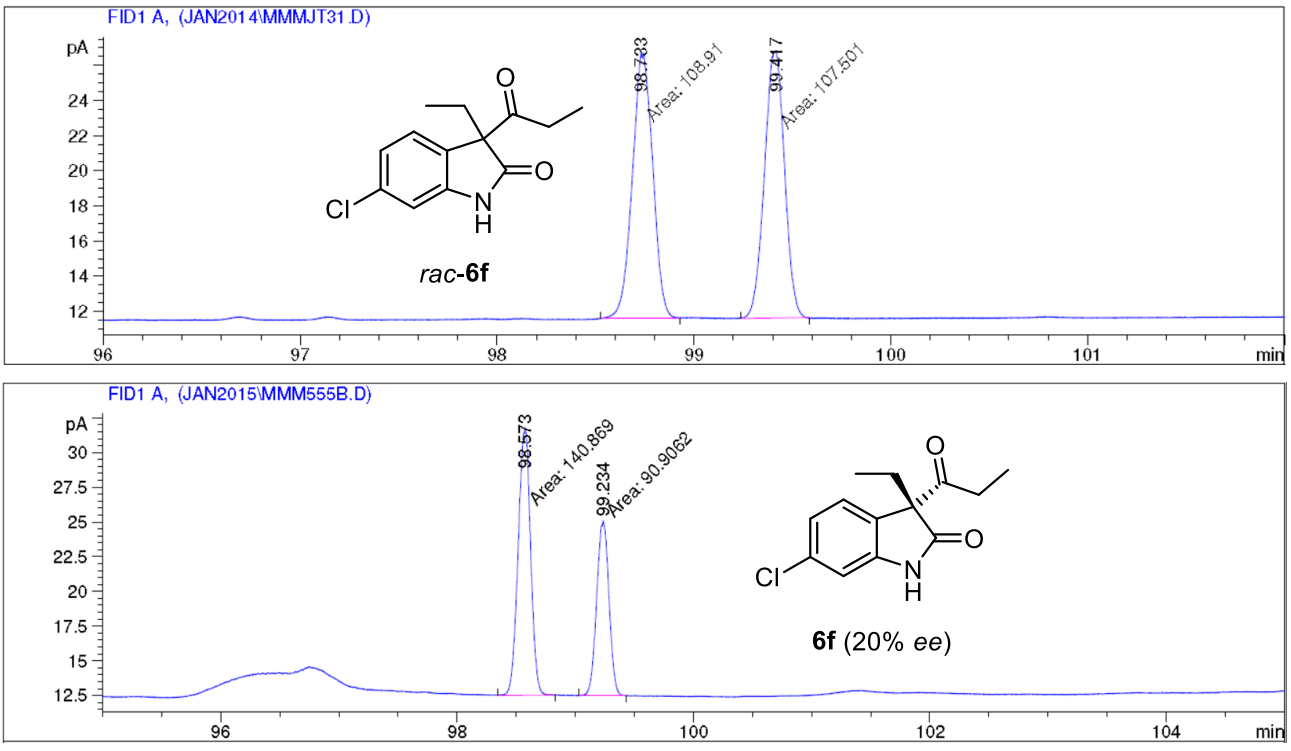




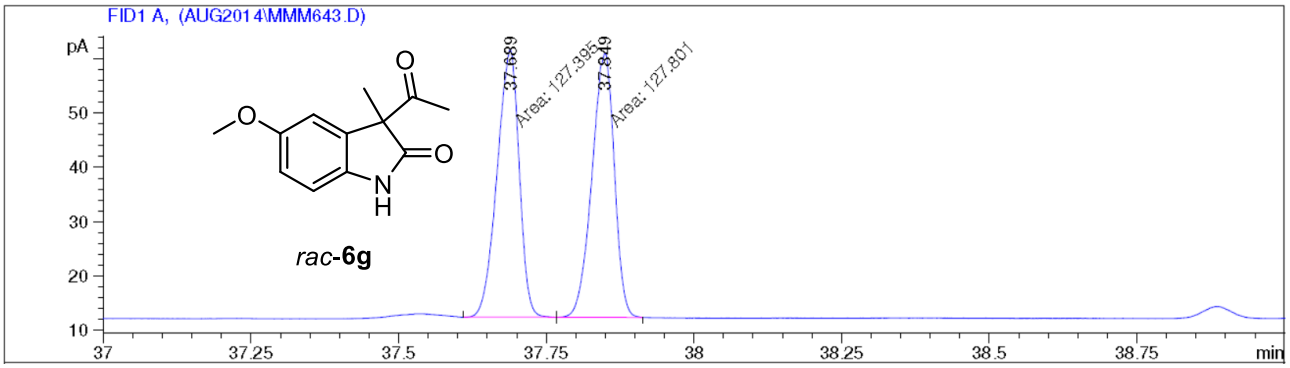
(*R*)-3-Acetyl-6-chloro-3-methylindolin-2-on (6e)

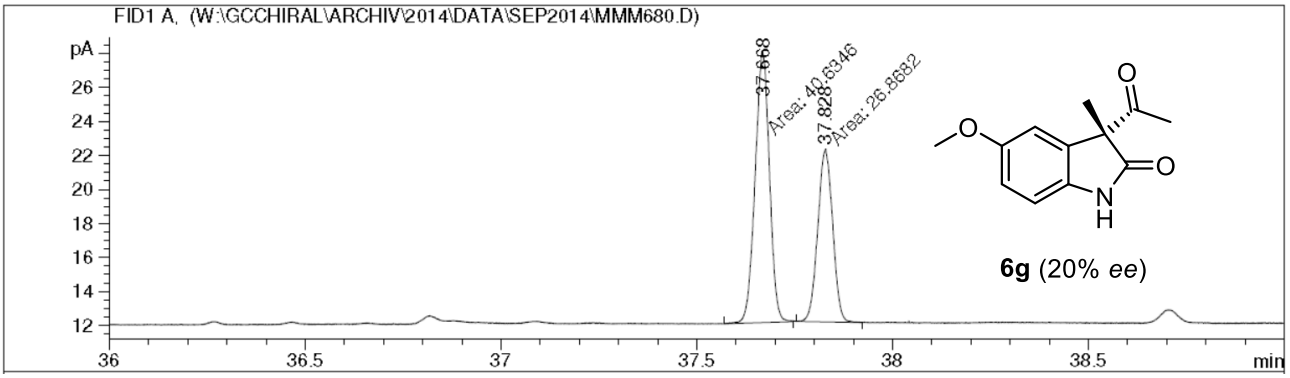


(*R*)-6-Chloro-3-ethyl-3-propionylindolin-2-on3 (6f)

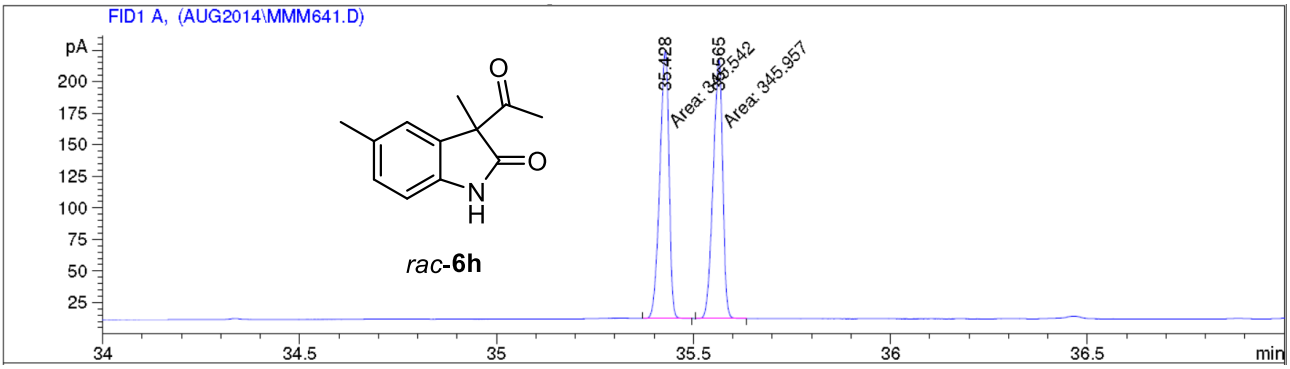


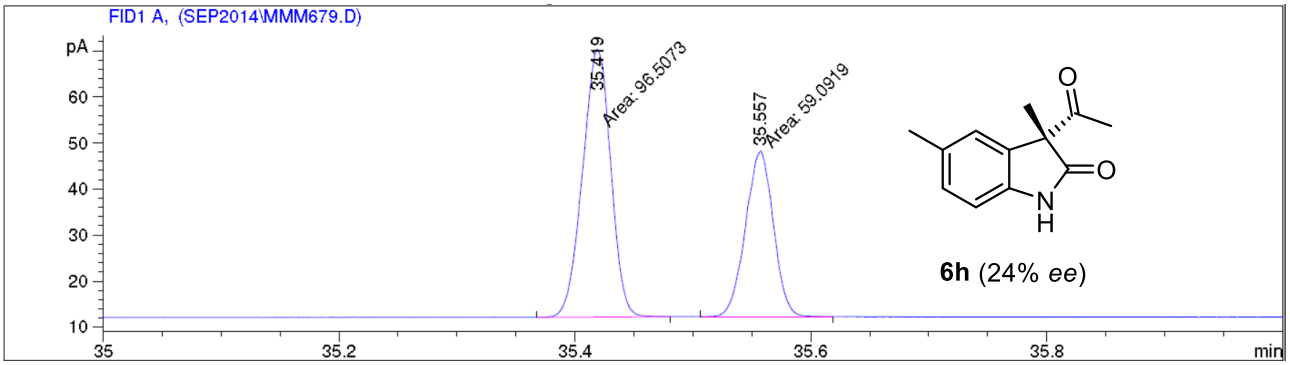
(*R*)-3-Acetyl-5-methoxy-3-methylindolin-2-one (6g)



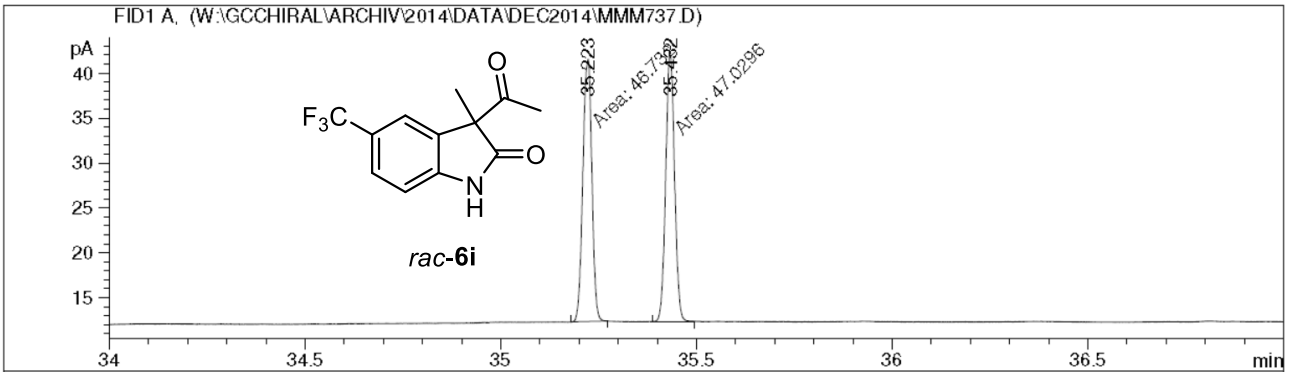


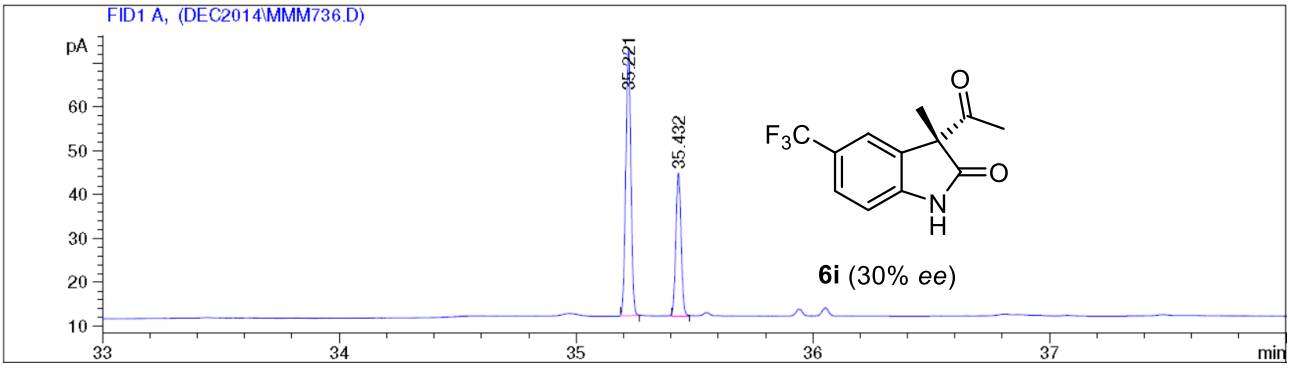
(*R*)-3-Acetyl-3,5-dimethylindolin-2-one (6h)





(*R*)-3-Acetyl-3-methyl-5-(trifluoromethyl)indolin-2-one (6i)

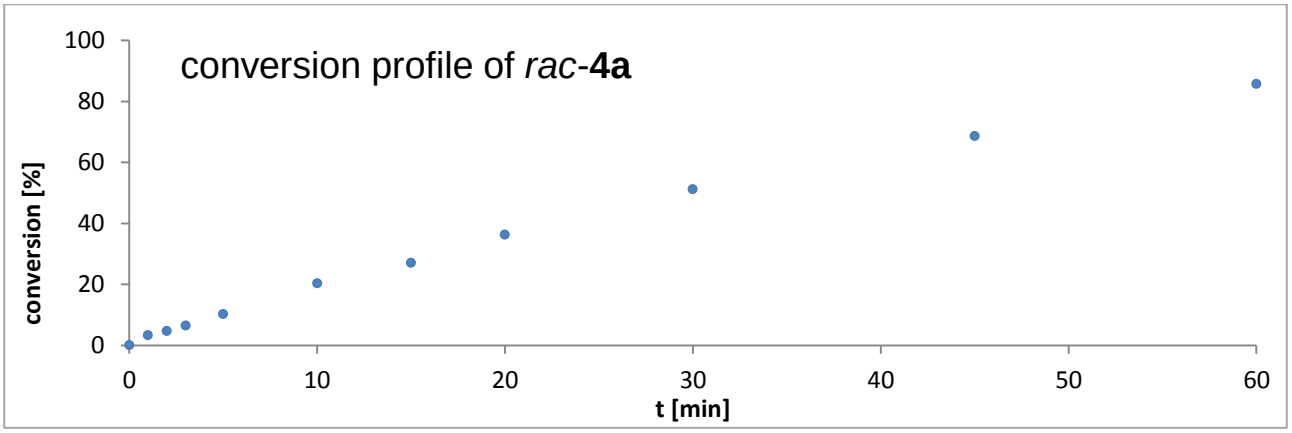


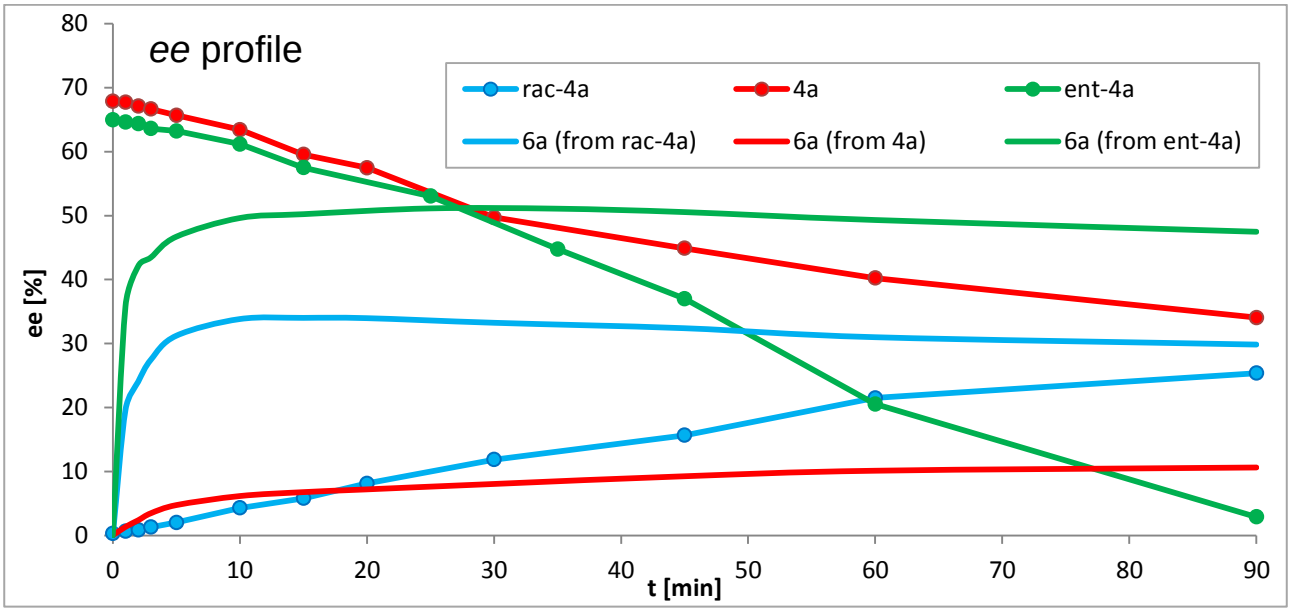


6. Conversion and *ee* Profile

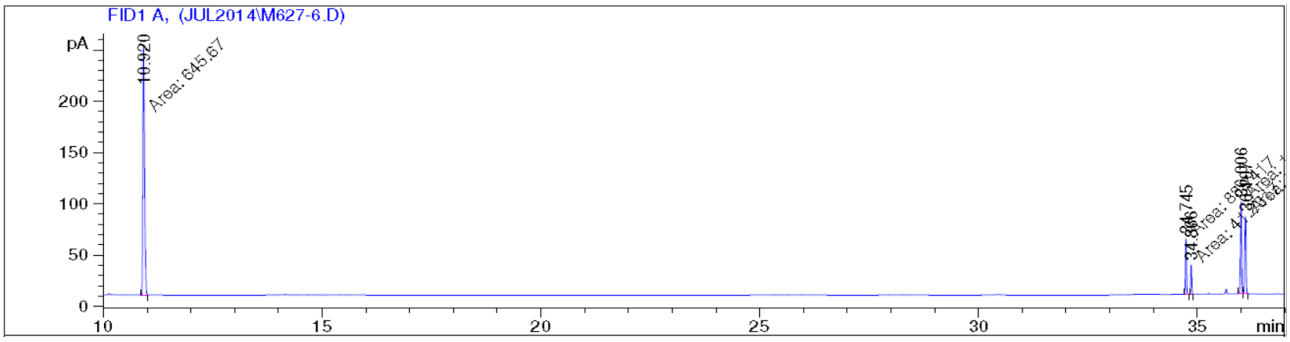
GC-calibration was performed with ^{n}dodecane (t_R = 10.9 min) as internal standard.

Chiral GLC Temperature program: 60 C° (1 min), 5 °C/min → 160 °C (10 min), 15 °C/min → 220 °C (20 min). Reaction conditions: substrate (18.9 mg. 100 µmmol, 1.0 eq.), chiral xanthone **1** (1.04 mg, 2.50 µmol, 2.5 mol%) in HFX/$PhCF_3$ (2/1, 10 mL), –65 °C, λ = 366 nm.





Chiral GC trace: t_R (min) = 10.9 (^{n}dodecane), 34.7 (**6a**), 34.9 (*ent*-**6a**), 36.0 (**4a**), 36.1 (*ent*-**4a**).



7. Literature

[1] W. C. Anthony, *J.* Org. *Chem.* **1966**, *31*, 77-81.

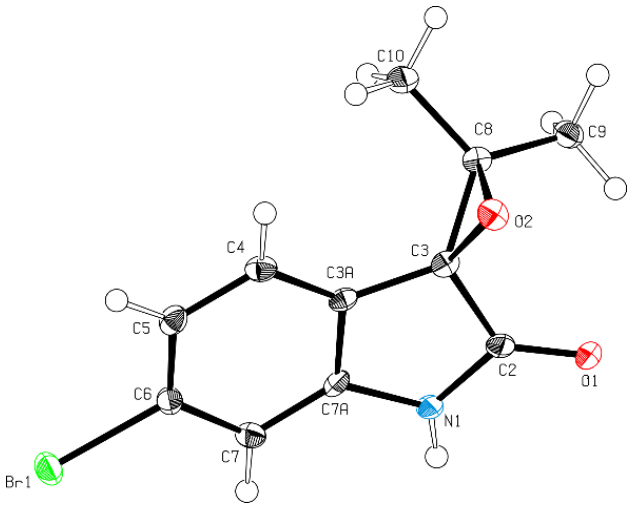
[2] A. Quintavalla, F. Lanza, E. Montroni, M. Lombardo, C. Trombini, *J. Org. Chem.*, **2013**, *78*, 12049-12064.

[3] P. López-Alvarado, C. Avendaño, *Synthesis* **2002**, 104-110.

[4] M. M. Maturi, M. Wenninger, R. Alonso, A. Bauer, A. Pöthig, E. Riedle, T. Bach, *Chem. Eur. J.* **2013**, *19*, 7461-7472.

8. Crystallographic Data

Crystal Structure Report for MatMa2 (CCDC 1400715)



A clear colourless block-like specimen of $C_{11}H_{10}BrNO_2$, approximate dimensions 0.077 mm x 0.092 mm x 0.546 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker Kappa APEX II CCD system equipped with a graphite monochromator and a Mo fine-focus tube (λ = 0.71073 Å).

A total of 2499 frames were collected. The total exposure time was 13.88 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 13506 reflections to a maximum θ angle of 27.38° (0.77 Å resolution), of which 2295 were independent (average redundancy 5.885, completeness = 99.9%, R_{int} = 3.95%) and 2120 (92.37%) were greater than $2\sigma(F^2)$. The final cell constants of a = 9.9552(6) Å, b = 4.1540(3) Å, c = 12.7102(8) Å, β = 105.482(3)°, volume = 506.54(6) $Å^3$, are based upon the refinement of the XYZ-centroids of 5595 reflections above 20 σ(I) with 4.641° < 2θ < 54.70°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.464. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.2170 and 0.7460.

The structure was solved and refined using the Bruker SHELXTL Software Package in conjunction with SHELXLE, using the space group P 1 21 1, with Z = 2 for the formula unit, $C_{11}H_{10}BrNO_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 141 variables converged at R1 = 2.30%, for the observed data and wR2 = 4.86% for all data. The goodness-of-fit was 1.041. The largest peak in the final difference electron density synthesis was 0.300 $e^-/Å^3$ and the largest hole was -0.320 $e^-/Å^3$ with an RMS deviation of 0.061 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.758 g/cm^3 and F(000), 268 e^-.

Table S1. Sample and crystal data for ZhoFa2.

Identification code	MatMa2 AP7301-123
Chemical formula	$C_{11}H_{10}BrNO_2$
Formula weight	268.11
Temperature	123(2) K
Wavelength	0.71073 Å
Crystal size	0.077 x 0.092 x 0.546 mm

Crystal habit	clear colourless block	
Crystal system	monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 9.9552(6) Å	α = 90°
	b = 4.1540(3) Å	β = 105.482(3)°
	c = 12.7102(8) Å	γ = 90°
Volume	506.54(6) $Å^3$	
Z	2	
Density (calculated)	1.758 g/cm^3	
Absorption coefficient	4.034 mm^{-1}	
F(000)	268	

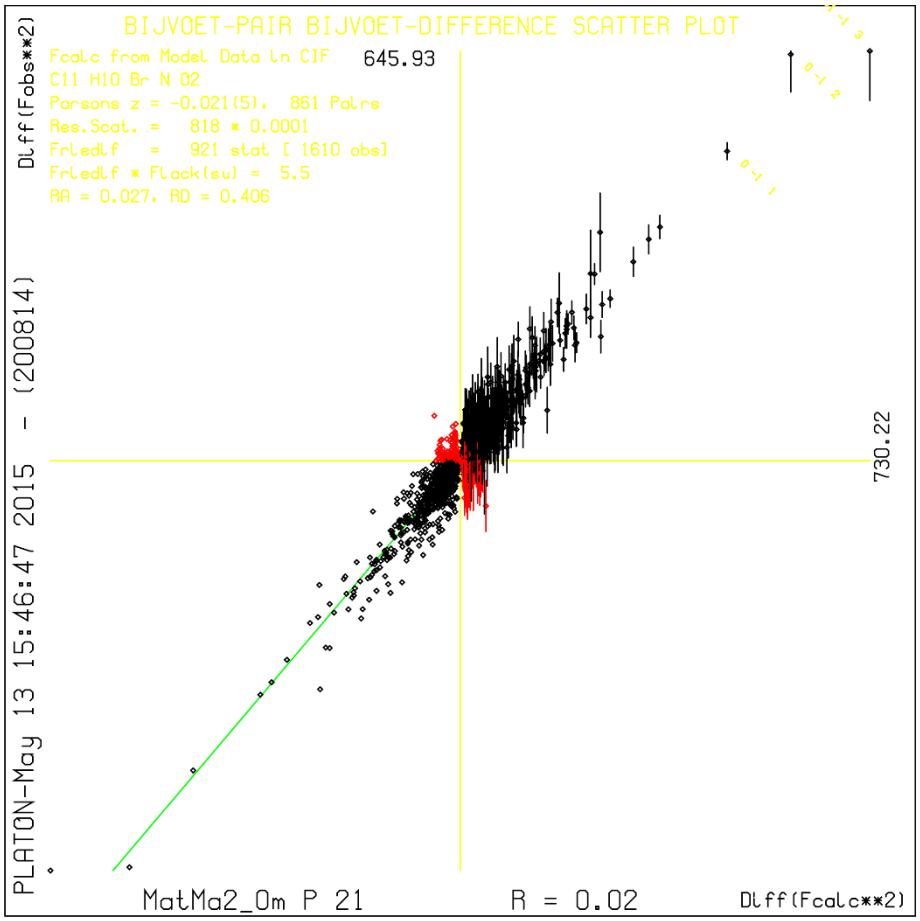
Table S2. Data collection and structure refinement for ZhoFa2.

Diffractometer	Bruker Kappa APEX II CCD
Radiation source	fine-focus tube, Mo
Theta range for data collection	2.12 to 27.38°
Index ranges	-12<=h<=12, -5<=k<=5, -16<=l<=16
Reflections collected	13506
Independent reflections	2295 [R(int) = 0.0395]
Coverage of independent reflections	99.9%
Absorption correction	multi-scan
Max. and min. transmission	0.7460 and 0.2170
Structure solution technique	direct methods
Structure solution program	SHELXS-97 (Sheldrick, 2008)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2014 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	2295 / 1 / 141
Goodness-of-fit on F^2	1.041
Final R indices	2120 data; I>2σ(I) R1 = 0.0230, wR2 = 0.0476
	all data R1 = 0.0265, wR2 = 0.0486
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0253P)^2+0.0260P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.300 and -0.320 $eÅ^{-3}$
R.M.S. deviation from mean	0.061 $eÅ^{-3}$

Absolute Structure determination

The absolute configuration of the compound is confirmed by use of the anomalous dispersion effect. The resulting FLACK parameter (x = -0.022(6), SHELXL2014) and PARSONs parameter (z = -0.021(5), SHELXL2014) indicated that the absolute structure had been correctly assigned. Additionally, the absolute structure parameter y (Hooft, Straver & Spek, 2008) was calculated using PLATON (Spek, 2010). The resulting value was y = -0.023(5), and the P2(true)/P3(true)

probabilities were 1.0, each supporting the correct assignment of the absolute configuration.



Space Group	P21
Wavelength	0.71073
Flack x	-0.022(6)
Parsons z ..	-0.021(5)
Bijvoet Pairs	987
Coverage ...	100
DlffCalcMax.	730.22
Outlier Crit	1460.45
Scatter Plot	
Sigma Crit..	0.25
Select Pairs	835
Number Plus	723
Number Minus	112
Slope	1.044
Student-T Prob. Plot	
Sample Size.	977
Corr. Coeff.	0.999
Intercept ..	0.224
Slope	0.955
Bayesian Statistics	
Student_T Nu	100
Select Pairs	987
Theta_Min ..	5.18
Theta_Max ..	27.38
P2(true)....	1.000
P3(true)....	1.000
P3(rac-twin)	0.0E+00
P3(false) ..	0.0E+00
G	1.0459
G (su)	0.0104
Hooft y ...	-0.023(5)