



Supporting Information

for

A study on selective transformation of norbornadiene into fluorinated cyclopentane-fused isoxazolines

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Beilstein J. Org. Chem. **2021**, *17*, 2051–2066. [doi:10.3762/bjoc.17.132](https://doi.org/10.3762/bjoc.17.132)

Experimental section and NMR spectra

Experimental section

The experiments were performed in a manner analogous to reference [1].

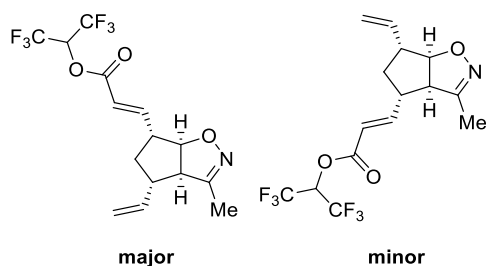
General procedure for ring-opening metathesis

To a solution of isoxazoline-fused derivative (100 mg) in anhydrous CH_2Cl_2 (15 mL), catalyst (3 mol %, see tables in the main manuscript) and ethylene were added from a bottle by bubbling, and the mixture was stirred for 2 hours at room temperature. The reaction was monitored by TLC and after completion, the catalyst was decomposed by adding a solution of NaHCO_3 (0.3 g) into the mixture of methanol (5 mL) and water (25 mL). The reaction mixture was stirred for 2 hours, then 20 mL water was added, and the two layers were separated. The aqueous phase was extracted with CH_2Cl_2 (3×30 mL), the combined organic phase was dried over Na_2SO_4 and concentrated under vacuum, and the crude product was purified by means of column chromatography on silica gel (*n*-hexane/EtOAc).

General procedure for cross-metathesis

To a solution of isoxazoline derivative (100 mg) in anhydrous CH_2Cl_2 (15 mL), Ru-based catalyst (3 mol %, see tables in the main manuscript) and fluorinated olefin **7a–h** (10 equiv) were added, and the mixture was stirred for 5 hours at reflux temperature. The reaction was monitored by TLC and after completion, the catalyst was decomposed by adding a solution of NaHCO_3 (0.3 g) into the mixture of methanol (5 mL) and water (25 mL). The reaction mixture was stirred for 2 hours, then 20 mL water was added, and the phases were separated. The aqueous phase was extracted with CH_2Cl_2 (3×10 mL). The combined organic phase was dried over Na_2SO_4 and concentrated under vacuum, and the crude product was purified by means of column chromatography on silica gel (*n*-hexane/EtOAc).

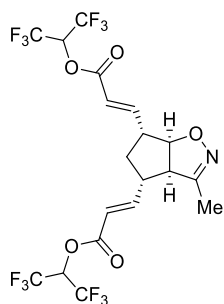
(E)-1,1,1,3,3,3-Hexafluoropropan-2-yl 3-((3a*R,4*S**,6*R**,6a*R**)-3-methyl-4-vinyl-4,5,6,6a-tetrahydro-3a*H*-cyclopenta[*d*]isoxazol-6-yl)acrylate** and **(E)-1,1,1,3,3,3-hexafluoropropan-2-yl 3-((3a*R**,4*S**,6*R**,6a*R**)-3-methyl-6-vinyl-4,5,6,6a-tetrahydro-3a*H*-cyclopenta[*d*]isoxazol-4-yl)acrylate, (±)-**8a** and (±)-**8b****



Best catalyst: G-2. Yield of (±)-**8a** and (±)-**8b**: 25% (53 mg); $R_f = 0.53$ (*n*-hexane/EtOAc 3:1); ratio of (±)-**8a** and (±)-**8b**: 2.5:1.

HRMS calcd. for $C_{15}H_{16}F_6NO_3^+$ ($[M+H]^+$): 372.1028, found: 372.1032.

(2*E*,2'*E*)-Bis(1,1,1,3,3,3-hexafluoropropan-2-yl) 3,3'-((3a*R,4*S**,6*R**,6a*R**)-3-methyl-4,5,6,6a-tetrahydro-3a*H*-cyclopenta[*d*]isoxazole-4,6-diyl)diacrylate, (±)-**8c****



Best catalyst: HG-2. Dark yellow oil; yield: 17% (54 mg); $R_f = 0.52$ (*n*-hexane/EtOAc 3:1).

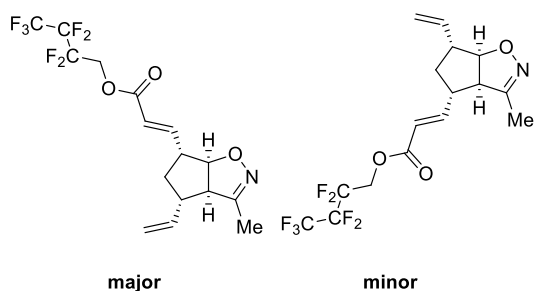
1H NMR (500 MHz, $CDCl_3$): $\delta = 1.63$ - 1.72 (dd, 1H, $J = 12$ Hz, CH_2); 2.02 (s, 3H, CH_3); 2.15 - 2.22 (m, 1H, CH_2); 2.87 - 2.96 (m, 2H, H-4 and H-6); 3.52 - 3.58 (m, 1H, H-3a); 4.88 - 4.94 (m, 1H, H-6a); 5.77 - 5.87 (m, 2H, $CH(CF_3)_2$); 6.04 - 6.11 (m, 2H, =CH); 7.11 - 7.25 (m, 2H, =CH).

^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 11.4, 36.9, 50.7, 60.5, 66.6$ (septett, $^2J_{C-F} = 34$ Hz, $CH(CF_3)_2$), 66.7 (septett, $^2J_{C-F} = 34$ Hz, $CH(CF_3)_2$), $88.6, 119.0, 119.6, 120.4$ (q, $^1J_{C-F} = 281$ Hz, CF_3), $151.6, 153.0, 155.6, 162.2, 162.3$.

^{19}F NMR (471 MHz, CDCl_3): δ = -73.2 (CF_3), -73.3 (CF_3).

HRMS calcd. for $\text{C}_{19}\text{H}_{16}\text{F}_{12}\text{NO}_5^+$ ($[\text{M}+\text{H}]^+$): 566.0831, found: 566.0830.

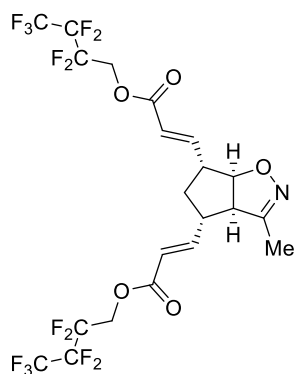
(E)-2,2,3,3,4,4,4-Heptafluorobutyl 3-((3a*R,4*S**,6*R**,6a*R**)-3-methyl-4-vinyl-4,5,6,6a-tetrahydro-3a*H*-cyclopenta[*d*]isoxazol-6-yl)acrylate** and **(E)-2,2,3,3,4,4,4-heptafluorobutyl 3-((3a*R**,4*S**,6*R**,6a*R**)-3-methyl-6-vinyl-4,5,6,6a-tetrahydro-3a*H*-cyclopenta[*d*]isoxazol-4-yl)acrylate, (±)-**9a** and (±)-**9b****



Best catalyst: G-2. Yield of (±)-**9a** and (±)-**9b**: 36% (82 mg); R_f = 0.46 (*n*-hexane/EtOAc 3:1); ratio of (±)-**9a** and (±)-**9b**: 2:1.

HRMS calcd. for $\text{C}_{16}\text{H}_{17}\text{F}_7\text{NO}_3^+$ ($[\text{M}+\text{H}]^+$): 404.1091, found: 404.1092.

(2*E*,2'*E*)-Bis(2,2,3,3,4,4,4-Heptafluorobutyl) 3,3'-((3a*R,4*S**,6*R**,6a*R**)-3-methyl-4,5,6,6a-tetrahydro-3a*H*-cyclopenta[*d*]isoxazole-4,6-diyl)diacrylate, (±)-**9c****



Best catalyst: HG-2. Yellow oil; yield: 34% (120 mg); R_f = 0.36 (*n*-hexane/EtOAc 3:1).

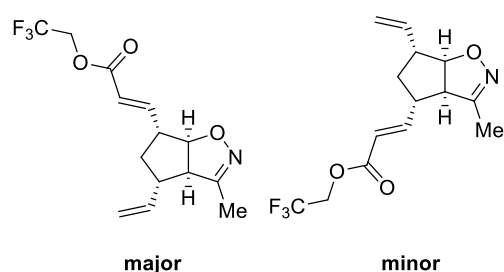
^1H NMR (500 MHz, CDCl_3): δ = 1.56-1.66 (m, 1H, CH_2); 1.99 (s, 3H, CH_3); 2.10-2.18 (m, 1H, CH_2); 2.82-2.92 (m, 2H, H-4 and H-6); 3.47-3.53 (m, 1H, H-3a); 4.58-4.71 (m, 4H, $\text{CH}_2(\text{CF}_2)_2\text{CF}_3$); 4.83-4.90 (m, 1H, H-6a); 5.97-6.04 (m, 2H, =CH); 6.99-7.13 (m, 2H, =CH).

^{13}C NMR (125 MHz, CDCl_3): δ = 11.4, 37.2, 46.6, 50.5, 59.4 (t, $J=27$ Hz, $\text{CH}_2(\text{CF}_2)_2\text{CF}_3$), 59.5 (t, $J=27$ Hz, $\text{CH}_2(\text{CF}_2)_2\text{CF}_3$), 60.7, 88.9, 100-120 (m, $\text{CF}_2\text{CF}_2\text{CF}_3$), 120.3, 120.8, 149.5, 150.8, 155.7, 163.9, 164.0.

^{19}F NMR (471 MHz, CDCl_3): δ = -80.87 (t, $J = 9$ Hz, CF_3), -80.89 (t, $J=9$ Hz, CF_3), -120.35 (m, $\text{CF}_2\text{CF}_2\text{CF}_3$), 127.58 (s, $\text{CF}_2\text{CF}_2\text{CF}_3$).

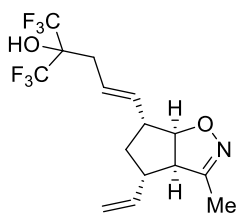
HRMS calcd. for $\text{C}_{21}\text{H}_{18}\text{F}_{14}\text{NO}_5^+$ ($[\text{M}+\text{H}]^+$): 630.0955, found: 630.0957.

(E)-2,2,2-Trifluoroethyl 3-((3a*R,4*S**,6*R**,6a*R**)-3-methyl-4-vinyl-4,5,6,6a-tetrahydro-3a*H*-cyclopenta-[*d*]isoxazol-6-yl)acrylate** and **(E)-2,2,2-trifluoroethyl 3-((3a*R**,4*S**,6*R**,6a*R**)-3-methyl-6-vinyl-4,5,6,6a-tetrahydro-3a*H*-cyclopenta[*d*]isoxazol-4-yl)acrylate, (±)-10a and (±)-10b**



Best catalyst: G-2. Yield of (±)-10a and (±)-10b: 23% (38 mg); R_f = 0.38 (*n*-hexane/EtOAc 3:1); ratio of (±)-10a and (±)-10b: 1.66:1; HRMS calcd. for $\text{C}_{14}\text{H}_{17}\text{F}_3\text{NO}_3^+$ ($[\text{M}+\text{H}]^+$): 304.1155, found: 304.1161.

(E)-1,1,1-Trifluoro-5-((3a*R,4*S**,6*R**,6a*R**)-3-methyl-4-vinyl-4,5,6,6a-tetrahydro-3a*H*-cyclopenta[*d*]isoxazol-6-yl)-2-(trifluoromethyl)pent-4-en-2-ol, (±)-11a**



Best catalyst: HG-2. White solid; yield: 15% (30 mg); R_f = 0.36 (*n*-hexane/EtOAc 4:1), mp. 108-109 °C.

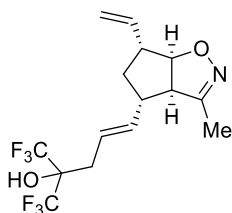
^1H NMR (500 MHz, CDCl_3): δ = 1.36-1.46 (m, 1H, CH_2); 1.92-2.01 (m, 4H, CH_2 and CH_3); 2.63-2.86 (m, 4H, H-4, H-6 and $\text{CH}_2\text{C}(\text{CF}_3)\text{OH}$); 3.33-3.41 (m, 1H, H-3a); 4.63-4.69 (m, 1H, H-6a); 4.77 (brs, 1H, OH); 5.06-5.20 (m, 2H, $=\text{CH}_2$); 5.57-5.66 (m, 1H, $=\text{CH}$); 5.69-5.75 (m, 1H, $=\text{CH}$); 5.77-5.87 (m, 1H, $=\text{CH}$).

^{13}C NMR (125 MHz, CDCl_3): δ = 11.1, 28.7, 45.8, 48.0, 60.5, 75.7 (septet, $^2J_{\text{C-F}} = 29$ Hz, $\text{C}(\text{CF}_3)_2\text{OH}$); 89.7, 115.5, 121.8, 122.9 (q, $^1J_{\text{C-F}} = 287$ Hz, CF_3); 123.3 (q, $^1J_{\text{C-F}} = 287$ Hz, CF_3); 136.1, 139.4, 157.8.

^{19}F NMR (471 MHz, CDCl_3): δ = -78.0 (CF_3), -75.3 (CF_3).

HRMS calcd. for $\text{C}_{15}\text{H}_{18}\text{F}_6\text{NO}_2^+$ ($[\text{M}+\text{H}]^+$): 358.1236, found: 358.1240.

(E)-1,1,1-Trifluoro-5-((3a*R,4*S**,6*R**,6a*R**)-3-methyl-6-vinyl-4,5,6,6a-tetrahydro-3a*H*-cyclopenta[*d*]isoxazol-4-yl)-2-(trifluoromethyl)pent-4-en-2-ol, (±)-11b**



Best catalyst: HG-2. Brown oil; yield: 26% (51 mg); R_f = 0.28 (*n*-hexane/EtOAc 4:1).

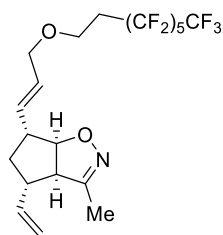
¹H NMR (500 MHz, CDCl₃): δ = 1.36-1.45 (m, 1H, CH₂); 1.92-2.01 (m, 4H, CH₂ and CH₃); 2.57-2.73 (m, 4H, H-4, H-6 and CH₂C(CF₃)₂OH); 3.31-3.38 (m, 1H, H-3a); 4.11 (brs, 1H, OH); 4.68-4.75 (m, 1H, H-6a); 5.05-5.18 (m, 2H, =CH₂); 5.54-5.92 (m, 3H, =CH).

¹³C NMR (125 MHz, CDCl₃): δ = 11.2, 33.8, 38.3, 48.3, 50.7, 60.9, 75.5 (septet, ²J_{C-F} = 29 Hz, C(CF₃)₂OH); 89.9, 115.4, 121.8, 123.0 (q, ¹J_{C-F} = 286 Hz, CF₃); 138.1, 139.7, 157.2.

¹⁹F NMR (471 MHz, CDCl₃): δ = -76.3 (CF₃), -76.5 (CF₃).

HRMS calcd. for C₁₅H₁₈F₆NO₂⁺ ([M+H]⁺): 358.1236, found: 358.1240.

(3aR*,4S*,6R*,6aR*)-3-Methyl-6-((E)-3-((3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-oxy)prop-1-en-1-yl)-4-vinyl-4,5,6,6a-tetrahydro-3aH-cyclopenta[d]isoxazole, (±)-12a



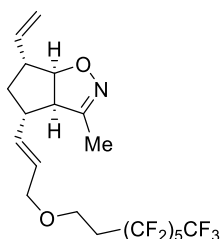
Best catalyst: HG-2. Brown oil; yield: 9% (30 mg); R_f = 0.36 (*n*-hexane/EtOAc 4:1).

¹H NMR (500 MHz, CDCl₃): δ = 1.37-1.46 (m, 1H, CH₂); 1.93-2.02 (m, 4H, CH₂ and CH₃); 2.37-2.47 (m, 2H, CH₂OCH₂CH₂C(CF₃)₂OH); 2.57-2.69 (m, 2H, H-4 and H-6); 3.28-3.34 (m, 1H, H-3a); 3.68-3.74 (t, 2H, *J* = 7 Hz, CH₂OCH₂CH₂C(CF₃)₂OH); 3.95-4.00 (m, 2H, CH₂OCH₂CH₂C(CF₃)₂OH); 4.68-4.75 (m, 1H, H-6a); 5.02-5.18 (m, 2H, =CH₂); 5.63-5.70 (m, 1H, =CH); 5.76-5.85 (m, 2H, =CH).

¹³C NMR (125 MHz, CDCl₃): δ = 11.4, 31.6 (t, ²J_{C-F} = 21 Hz, CH₂OCH₂CH₂C(CF₃)₂OH); 38.4, 48.4, 50.5, 61.0, 61.8 (t, ³J_{C-F} = 5 Hz, CH₂OCH₂CH₂C(CF₃)₂OH); 71.4, 90.1, 100-120 (m, C(CF₃)₂OH); 115.2, 126.9, 133.8, 139.9, 156.6.

¹⁹F NMR (471 MHz, CDCl₃): δ = -126.0 (CF₂); -123.5 (CF₂); -122.7 (CF₂); 121.7 (CF₂); -113.1 (CF₂); -80.8 (CF₃).

(3aR*,4S*,6R*,6aR*)-3-Methyl-4-((E)-3-((3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-oxy)prop-1-en-1-yl)-6-vinyl-3a,5,6,6a-tetrahydro-4H-cyclopenta[d]isoxazole, (±)-12b



Best catalyst: HG-2. Brown oil; yield: 6% (19 mg); R_f = 0.29 (*n*-hexane/EtOAc 4:1).

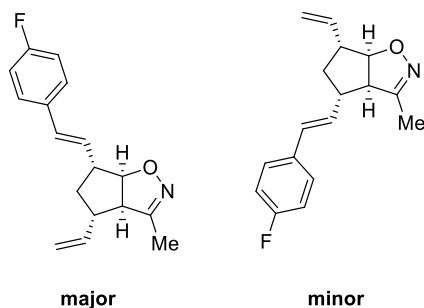
^1H NMR (500 MHz, CDCl_3): δ = 1.37-1.47 (m, 1H, CH_2); 1.94-2.02 (m, 4H, CH_2 and CH_3); 2.36-2.48 (m, 2H, $\text{CH}_2\text{OCH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3$); 2.59-2.69 (m, 2H, H-4 and H-6); 3.28-3.35 (m, 1H, H-3a); 3.69-3.75 (t, 2H, J = 7 Hz, $\text{CH}_2\text{OCH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3$); 3.97-4.00 (d, 2H, J = 5 Hz, $\text{CH}_2\text{OCH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3$); 4.70-4.76 (m, 1H, H-6a); 5.04-5.18 (m, 2H, $=\text{CH}_2$); 5.62-5.69 (m, 1H, $=\text{CH}$); 5.69-5.76 (m, 1H, $=\text{CH}$); 5.85-5.94 (m, 1H, $=\text{CH}$).

^{13}C NMR (125 MHz, CDCl_3): δ = 11.4, 31.6 (t, $^2J_{\text{C-F}}$ = 21 Hz, $\text{CH}_2\text{OCH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3$); 38.3, 47.0, 51.7, 61.2, 61.5 (t, $^3J_{\text{C-F}}$ = 5 Hz, $\text{CH}_2\text{OCH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3$); 71.1, 90.1, 100-120 (m, $(\text{CF}_2)_5\text{CF}_3$); 115.5, 126.7, 135.4, 138.2, 156.6.

^{19}F NMR (471 MHz, CDCl_3): δ = -126.0 (CF_2); -123.5 (CF_2); -122.7 (CF_2); 121.7 (CF_2); -113.1 (CF_2); -80.8 (CF_3).

HRMS calcd. for $\text{C}_{20}\text{H}_{21}\text{F}_{13}\text{NO}_2^+$ ($[\text{M}+\text{H}]^+$): 554.1359, found: 554.1358.

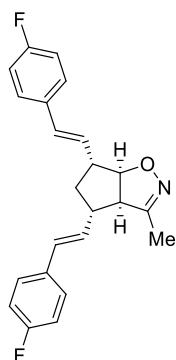
(3aR*,4S*,6R*,6aR*)-4-((E)-4-Fluorostyryl)-3-methyl-6-vinyl-4,5,6,6a-tetrahydro-3aH-cyclopenta-[d]isoxazole and (3aR*,4S*,6R*,6aR*)-6-((E)-4-fluorostyryl)-3-methyl-4-vinyl-4,5,6,6a-tetrahydro-3aH-cyclopenta[d]isoxazole, (±)-13a and (±)-13b



Best catalyst: G-2. Yield of (±)-13a and (±)-13b: 36% (55 mg); $R_f = 0.44$ (*n*-hexane/EtOAc 3:1); ratio of (±)-13a and (±)-13b: 1.4:1.

HRMS calcd. for $C_{17}H_{19}FNO^+$ ($[M+H]^+$): 272.1445, found: 272.1446.

(3aR*,4S*,6R*,6aR*)-4,6-Bis((E)-4-fluorostyryl)-3-methyl-4,5,6,6a-tetrahydro-3aH-cyclopenta[d]isoxazole, (±)-13c



Best catalyst: HG-2. Yellow oil; yield: 30% (61 mg); $R_f = 0.35$ (*n*-hexane/EtOAc 3:1).

1H NMR (500 MHz, $CDCl_3$): δ = 1.54-1.64 (dd, 1H, $J=12$ Hz, CH_2); 2.00 (s, 3H, CH_3); 2.07-2.14 (m, 1H, CH_2); 2.77-2.87 (m, 2H, H-4 and H-6); 3.40-3.46 (m, 1H, H-3a); 4.81-4.87 (m, 1H, H-6a); 6.07-6.14 (m, 1H, =CH); 6.15-6.22 (m, 1H, =CH); 6.44-6.51 (m, 2H, =CH); 6.95-7.04 (m, 4H, CH-Ar); 7.28-7.35 (m, 4H, CH-Ar).

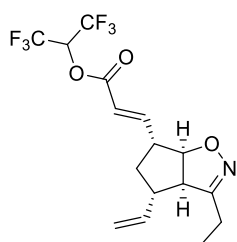
^{13}C NMR (125 MHz, $CDCl_3$): δ = 11.6, 39.2, 47.9, 51.3, 61.5, 90.3, 115.4 (d, $^2J_{C-F} = 19$ Hz); 115.6 (d, $^2J_{C-F} = 19$ Hz); 127.6 (d, $^3J_{C-F} = 7$ Hz); 127.6 (d, $^3J_{C-F} = 7$ Hz); 129.5, 129.6, 129.8,

131.3, 132.9 (d, $^4J_{C-F}$ = 3 Hz); 133.3 (d, $^4J_{C-F}$ = 3 Hz); 156.8, 162.2 (d, $^1J_{C-F}$ = 246 Hz), 162.4 (d, $^1J_{C-F}$ = 246 Hz).

^{19}F NMR (471 MHz, CDCl_3): δ = -114.33 (Ar-F), -114.93 (Ar-F).

HRMS calcd. for $\text{C}_{23}\text{H}_2\text{F}_2\text{NO}^+$ ($[\text{M}+\text{H}]^+$): 366.1664, found: 366.1669.

(E)-1,1,1,3,3,3-Hexafluoropropan-2-yl 3-((3a*R,4*S**,6*R**,6a*R**)-3-ethyl-4-vinyl-4,5,6,6a-tetrahydro-3a*H*-cyclopenta[*d*]isoxazol-6-yl)acrylate, ($\pm$)-14a**



Best catalyst: G-2. Pale yellow oil; yield: 16% (32 mg); R_f = 0.55 (*n*-hexane/EtOAc 3:1).

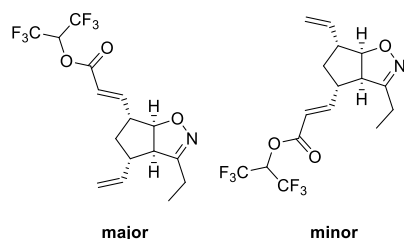
^1H NMR (500 MHz, CDCl_3): δ = 1.15-1.20 (t, 3H, J =7 Hz, CH_2CH_3); 1.48-1.57 (m, 1H, CH_2); 2.02-2.10 (m, 1H, CH_2); 2.19-2.29 (m, 1H, CH_2CH_3); 2.44-2.54 (m, 1H, CH_2CH_3); 2.65-2.75 (m, 1H, H-4); 2.79-2.89 (m, 1H, H-6); 3.43-3.50 (m, 1H, H-3a); 4.79-4.86 (m, 1H, H-6a); 5.07-5.20 (m, 2H, = CH_2); 5.76-5.86 (m, 2H, $\text{CH}(\text{CF}_3)_2$ and =CH); 6.01-6.07 (m, 1H, =CH); 7.19-7.24 (m, 1H, =CH).

^{13}C NMR (125 MHz, CDCl_3): δ = 10.6, 19.7, 37.9, 48.4, 50.9, 59.8, 66.5 (septett, J = 34 Hz, $\text{CH}(\text{CF}_3)_2$), 88.8, 116.0, 118.9, 120.49 (q, J = 282 Hz, CF_3), 139.2, 153.6, 161.4, 162.5.

^{19}F NMR (471 MHz, CDCl_3): δ = -73.2 (CF_3); -73.3 (CF_3).

HRMS calcd. for $\text{C}_{16}\text{H}_{18}\text{F}_6\text{NO}_3^+$ ($[\text{M}+\text{H}]^+$): 386.1185, found: 386.1190.

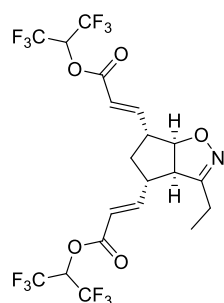
(E)-1,1,1,3,3,3-Hexafluoropropan-2-yl 3-((3aR*,4S*,6R*,6aR*)-3-ethyl-4-vinyl-4,5,6,6a-tetrahydro-3aH-cyclopenta[d]isoxazol-6-yl)acrylate and **(E)-1,1,1,3,3,3-hexafluoropropan-2-yl 3-((3aR*,4S*,6R*,6aR*)-3-ethyl-6-vinyl-4,5,6,6a-tetrahydro-3aH-cyclopenta[d]isoxazol-4-yl)acrylate, (±)-14a and (±)-14b**



Used catalyst: G-3. Yield of (±)-**14a** and (±)-**14b**: 13% (26 mg); $R_f = 0.55$ (*n*-hexane/EtOAc 3:1); ratio of (±)-**14a** and (±)-**14b**: 2:1.

HRMS calcd. for $C_{16}H_{18}F_6NO_3^+$ ($[M+H]^+$): 386.1185, found: 386.1190.

(2E,2'E)-bis(1,1,1,3,3,3-Hexafluoropropan-2-yl) 3,3'-((3aR*,4S*,6R*,6aR*)-3-ethyl-4,5,6,6a-tetrahydro-3aH-cyclopenta[d]isoxazole-4,6-diyl)diacrylate, (±)-14c



Best catalyst: HG-2. Pale yellow oil; yield: 27% (81 mg); $R_f = 0.54$ (*n*-hexane/EtOAc 3:1).

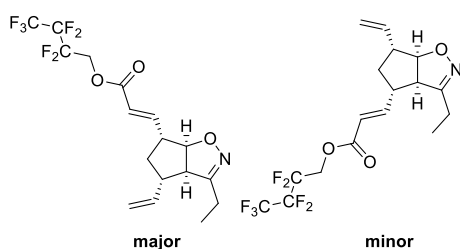
1H NMR (500 MHz, $CDCl_3$): $\delta = 1.17$ - 1.22 (m, 3H, CH_2CH_3); 1.61 - 1.70 (m, 1H, CH_2); 2.13 - 2.29 (m, 2H, CH_2 and CH_2CH_3); 2.42 - 2.52 (m, 1H, CH_2CH_3); 2.86 - 2.95 (m, 2H, H-4 and H-6); 2.56 - 2.63 (m, 1H, H-3a); 4.86 - 4.92 (m, 1H, H-6a); 5.76 - 5.86 (m, 2H, $CH(CF_3)_2$); 6.03 - 6.09 (m, 2H, =CH); 7.10 - 7.24 (m, 2H, =CH).

^{13}C NMR (125 MHz, CDCl_3): δ = 10.5, 19.8, 37.1, 46.6, 50.7, 59.5, 66.6 (septett, J = 35 Hz, $\text{CH}(\text{CF}_3)_2$); 66.7 (septett, J = 35 Hz, $\text{CH}(\text{CF}_3)_2$); 88.6, 119.0, 119.6, 120.5 (q, J = 286 Hz, CF_3); 151.7, 153.1, 160.1, 162.2, 162.3.

^{19}F NMR (471 MHz, CDCl_3): δ = -73.3 (CF_3); -73.2 (CF_3).

HRMS calcd. for $\text{C}_{20}\text{H}_{18}\text{F}_{12}\text{NO}_5^+$ ($[\text{M}+\text{H}]^+$): 580.0987, found: 580.0988.

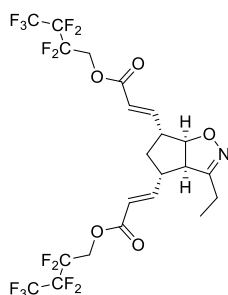
(E)-2,2,3,3,4,4,4-Heptafluorobutyl 3-((3aR*,4S*,6R*,6aR*)-3-ethyl-4-vinyl-4,5,6,6a-tetrahydro-3aH-cyclopenta[d]isoxazol-6-yl)acrylate and (E)-2,2,3,3,4,4,4-heptafluorobutyl 3-((3aR*,4S*,6R*,6aR*)-3-ethyl-6-vinyl-4,5,6,6a-tetrahydro-3aH-cyclopenta[d]isoxazol-4-yl)acrylate, ($\pm$)-15a and ($\pm$)-15b



Best catalyst: G-2. Yield of ($\pm$)-15a and ($\pm$)-15b: 34% (73 mg); R_f =0.54 (n -hexane/EtOAc, 3.1); ratio of ($\pm$)-15a and ($\pm$)-15b: 3.3:1.

HRMS calcd. for $\text{C}_{17}\text{H}_{18}\text{F}_7\text{NO}_3^+$ ($[\text{M}+\text{H}]^+$): 418.1247, found: 418.1249.

(2E,2'E)-bis(2,2,3,3,4,4,4-Heptafluorobutyl) 3,3'-((3aR*,4S*,6R*,6aR*)-3-ethyl-4,5,6,6a-tetrahydro-3aH-cyclopenta[d]isoxazole-4,6-diyl)diacrylate, ($\pm$)-15c



Best catalyst: HG-2. Yellow oil; yield: 42% (140 mg); R_f = 0.52 (n -hexane/EtOAc 3:1).

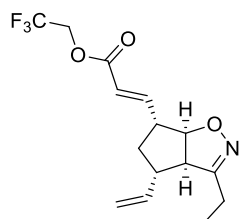
^1H NMR (500 MHz, CDCl_3): δ = 1.15-1.20 (t, 3H, J = 7 Hz, CH_3); 1.57-1.65 (m, 1H, CH_2); 2.09-2.16 (m, 1H, CH_2); 2.18-2.27 (m, 1H, CH_2); 2.41-2.54 (m, 1H, CH_2); 2.82-2.91 (m, 2H, H-4 and H-6); 3.53-3.59 (m, 1H, H-3a); 4.60-4.70 (m, 4H, $\text{CH}_2(\text{CF}_2)_2\text{CF}_3$); 4.84-4.89 (m, 1H, H-6a); 5.96-6.03 (m, 2H, =CH); 6.98-7.05 (m, 1H, =CH); 7.05-7.12 (m, 1H, =CH).

^{13}C NMR (125 MHz, CDCl_3): δ = 10.4, 19.7, 37.3, 46.6, 50.5, 59.4 (t, J = 27 Hz, $\text{CH}_2(\text{CF}_2)_2\text{CF}_3$); 59.5 (t, J = 27 Hz, $\text{CH}_2(\text{CF}_2)_2\text{CF}_3$); 59.6, 88.8, 100-120 (m, $\text{CF}_2\text{CF}_2\text{CF}_3$); 120.3, 120.8, 149.5, 150.9, 160.2, 163.9, 164.1.

^{19}F NMR (471 MHz, CDCl_3): δ = -80.86 (t, J = 9 Hz, CF_3); -80.87 (t, J = 9 Hz, CF_3); -120.4 (m, $\text{CF}_2\text{CF}_2\text{CF}_3$); -127.6 (s, $\text{CF}_2\text{CF}_2\text{CF}_3$).

HRMS calcd. for $\text{C}_{22}\text{H}_{20}\text{F}_{14}\text{NO}_5^+$ ($[\text{M}+\text{H}]^+$): 644.1112, found: 644.1117.

(E)-2,2,2-Trifluoroethyl 3-((3aR*,4S*,6R*,6aR*)-3-ethyl-4-vinyl-4,5,6,6a-tetrahydro-3aH-cyclopenta[d]isoxazol-6-yl)acrylate, ($\pm$)-16a



Used catalyst: HG-2. Yellow oil; yield: 7% (12 mg); R_f = 0.54 (n -hexane/EtOAc, 3:1).

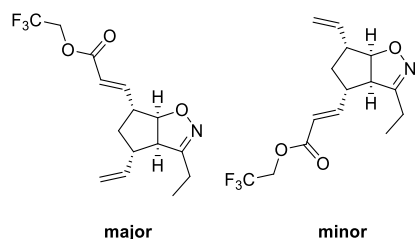
^1H NMR (500 MHz, CDCl_3): δ = 1.15-1.19 (t, 3H, J = 7 Hz, CH_3); 1.46-1.54 (m, 1H, CH_2); 2.00-2.06 (m, 1H, CH_2); 2.18-2.30 (m, 1H, CH_2); 2.42-2.53 (m, 1H, CH_2); 2.63-2.72 (m, 1H, CH_2); 2.76-2.84 (m, 1H, CH_2); 2.43-3.49 (m, 1H, H-4); 4.48-4.57 (m, 2H, CH_2CF_3); 5.07-5.20 (m, 2H, =CH₂); 5.76-5.85 (m, 1H, =CH); 5.97-5.02 (m, 1H, =CH); 7.04-7.15 (m, 1H, =CH).

^{13}C NMR (125 MHz, CDCl_3): δ = 10.6, 19.7, 37.9, 48.5, 50.7, 59.8, 60.3 (q, J = 37 Hz, CH_2CF_3); 88.9, 115.9, 120.3, 123.0 (q, J = 277 Hz, CF_3); 139.4, 150.6, 161.4, 164.3.

^{19}F NMR (471 MHz, CDCl_3): δ = -73.7 (CF_3).

HRMS calcd. for $\text{C}_{15}\text{H}_{19}\text{F}_3\text{NO}_3^+$ ($[\text{M}+\text{H}]^+$): 318.1311, found: 318.1311.

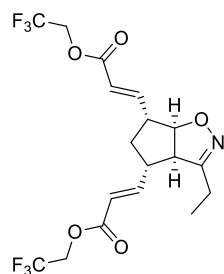
(E)-2,2,2-Trifluoroethyl 3-((3aR*,4S*,6R*,6aR*)-3-ethyl-4-vinyl-4,5,6,6a-tetrahydro-3aH-cyclopenta[d]isoxazol-6-yl)acrylate and **(E)-2,2,2-trifluoroethyl 3-((3aR*,4S*,6R*,6aR*)-3-ethyl-6-vinyl-4,5,6,6a-tetrahydro-3aH-cyclopenta[d]isoxazol-4-yl)acrylate, (±)-16a and (±)-16b**



Best catalyst: G-2. Yield of (±)-**16a** and (±)-**16b**: 34% (56 mg); $R_f = 0.54$ (*n*-hexane/EtOAc 3:1); ratio of (±)-**16a** and (±)-**16b**: 2.5:1.

HRMS calcd. for $C_{16}H_{18}F_6NO_3^+$ ($[M+H]^+$): 318.1311, found: 318.1311.

(2E,2'E)-bis(2,2,2-Trifluoroethyl) 3,3'-((3aR*,4S*,6R*,6aR*)-3-ethyl-4,5,6,6a-tetrahydro-3aH-cyclopenta[d]isoxazole-4,6-diyl)diacrylate, (±)-16c



Best catalyst: HG-2. Yellow oil; yield: 52% (120 mg); $R_f = 0.36$ (*n*-hexane/EtOAc 3:1).

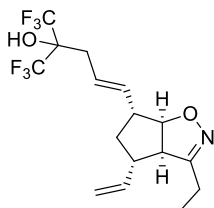
1H NMR (500 MHz, $CDCl_3$): $\delta = 1.16$ -1.21 (t, 3H, $J = 7$ Hz, CH_3); 1.57-1.66 (m, 1H, CH_2); 2.09-2.17 (m, 1H, CH_2); 2.18-2.27 (m, 1H, CH_2); 2.42-2.51 (m, 1H, CH_2); 2.82-2.90 (m, 2H, H-4 and H-6); 3.54-3.60 (m, 1H, H-3a); 4.49-4.57 (m, 4H, CH_2CF_3); 4.84-4.89 (m, 1H, H-6a); 5.98-6.04 (m, 2H, =CH); 6.99-7.06 (m, 1H, =CH); 7.06-7.13 (m, 1H, =CH).

^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 10.5, 19.8, 37.3, 46.6, 50.5, 59.6, 60.4$ (q, $J = 37$ Hz, CH_2CF_3); 60.5 (q, $J = 37$ Hz, CH_2CF_3); 88.8, 120.4, 120.9, 122.9 (q, $J = 277$ Hz, CF_3); 123.0 (q, $J = 277$ Hz, CF_3); 149.5, 150.9, 160.3, 163.9, 164.1.

^{19}F NMR (471 MHz, CDCl_3): $\delta = -73.8$ (CF_3); -73.7 (CF_3).

HRMS calcd. for $\text{C}_{18}\text{H}_{20}\text{F}_6\text{NO}_5^+$ ($[\text{M}+\text{H}]^+$): 444.1240, found: 444.1244.

(E)-5-((3a*R,4*S**,6*R**,6a*R**)-3-Ethyl-4-vinyl-4,5,6,6a-tetrahydro-3a*H*-cyclopenta[*d*]isoxazol-6-yl)-1,1,1-trifluoro-2-(trifluoromethyl)pent-4-en-2-ol, ($\pm$)-17a**



Best catalyst: G-2. Yellow oil; yield: 34% (20 mg); $R_f = 0.34$ (*n*-hexane/EtOAc 4:1).

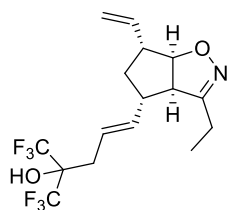
^1H NMR (500 MHz, CDCl_3): $\delta = 1.14$ -1.19 (t, 3H, $J = 7$ Hz, CH_3); 1.36-1.45 (m, 1H, CH_2); 1.92-1.98 (m, 1H, CH_2); 2.20-2.29 (m, 1H, CH_2); 2.46-2.56 (m, 1H, CH_2); 2.64-2.86 (m, 4H, H-4, H-6 and $\text{CH}_2\text{C}(\text{CF}_3)_2\text{OH}$); 3.41-3.48 (m, 1H, H-3a), 4.62-4.68 (m, 1H, H-6a); 4.72 (brs, 1H, OH); 5.06-5.19 (m, 2H, $=\text{CH}_2$); 5.57-5.65 (m, 1H, $=\text{CH}$); 5.69-5.75 (m, 1H, $=\text{CH}$); 5.77-5.87 (m, 1H, $=\text{CH}$).

^{13}C NMR (125 MHz, CDCl_3): $\delta = 10.5, 19.5, 28.7, 38.7, 45.8, 48.0, 59.3, 75.7$ (septet, $^2J_{\text{C-F}} = 29$ Hz, $\text{C}(\text{CF}_3)_2\text{OH}$); 89.6, 115.5, 121.7, 123.0 (q, $^1J_{\text{C-F}} = 287$ Hz, CF_3); 123.2 (q, $^1J_{\text{C-F}} = 287$ Hz, CF_3); 126.6, 136.2, 139.6, 162.2.

^{19}F NMR (471 MHz, CDCl_3): $\delta = -78.0$ (CF_3); -75.3 (CF_3).

HRMS calcd. for $\text{C}_{16}\text{H}_{20}\text{F}_6\text{NO}_2^+$ ($[\text{M}+\text{H}]^+$): 372.1392, found: 372.1397.

(E)-5-((3aR*,4S*,6R*,6aR*)-3-Ethyl-6-vinyl-4,5,6,6a-tetrahydro-3aH-cyclopenta[d]isoxazol-4-yl)-1,1,1-trifluoro-2-(trifluoromethyl)pent-4-en-2-ol, (±)-17b



Best catalyst: G-2. Yellow oil; yield: 11% (65 mg); $R_f = 0.32$ (*n*-hexane/EtOAc, 4:1).

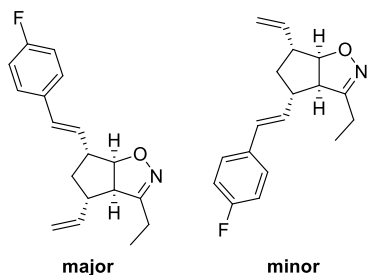
^1H NMR (500 MHz, CDCl_3): $\delta = 1.12$ -1.19 (m, 3H, CH_3); 1.36-1.45 (m, 1H, CH_2); 1.93-2.00 (m, 1H, CH_2); 2.17-2.29 (m, 1H, CH_2); 2.42-2.53 (m, 1H, CH_2); 2.57-2.74 (m, 4H, H-4, H-6 and $\text{CH}_2(\text{CF}_3)_2\text{OH}$); 3.36-3.47 (m, 1H, H-3a); 3.76 (brs, 1H, OH); 4.63-4.76 (m, 1H, H-6a); 5.03-5.19 (m, 2H, $=\text{CH}_2$); 5.52-5.64 (m, 1H, $=\text{CH}$); 5.73-5.86 (m, 2H, $=\text{CH}$).

^{13}C NMR (125 MHz, CDCl_3): $\delta = 10.5, 19.5, 33.8, 38.4, 48.2, 50.6, 59.6, 75.5$ (septet, $^2J_{\text{C-F}} = 29$ Hz, $\text{CH}_2(\text{CF}_3)_2\text{OH}$); 89.7, 115.4, 120.9, 123.0 (q, $^1J_{\text{C-F}} = 286$ Hz, CF_3); 138.1, 139.8, 161.7.

^{19}F NMR (471 MHz, CDCl_3): $\delta = -76.5$ (CF_3); -76.3 (CF_3).

HRMS calcd. for $\text{C}_{16}\text{H}_{20}\text{F}_6\text{NO}_2^+$ ($[\text{M}+\text{H}]^+$): 372.1392, found: 372.1398.

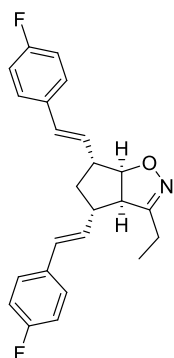
(3aR*,4S*,6R*,6aR*)-3-Ethyl-4-((E)-4-fluorostyryl)-6-vinyl-4,5,6,6a-tetrahydro-3aH-cyclopenta[d]isoxazole and (3aR*,4S*,6R*,6aR*)-3-ethyl-6-((E)-4-fluorostyryl)-4-vinyl-4,5,6,6a-tetrahydro-3aH-cyclopenta[d]isoxazole, (±)-19a and (±)-19b



Best catalyst: G-2. Yield of (±)-**19a** and (±)-**19b**: 37% (55 mg); $R_f = 0.53$ (*n*-hexane/EtOAc 3:1); ratio of (±)-**19a** and (±)-**19b**: 2:1.

HRMS calcd. for $\text{C}_{18}\text{H}_{20}\text{F}_6\text{NO}_5^+$ ($[\text{M}+\text{H}]^+$): 286.1601, found: 286.1603.

(3aR*,4S*,6R*,6aR*)-3-Ethyl-4,6-bis((E)-4-fluorostyryl)-4,5,6,6a-tetrahydro-3aH-cyclopenta[d]isoxazole, (±)-19c



Best catalyst: HG-2. White solid; yield: 38% (76 mg); $R_f = 0.45$ (*n*-hexane/EtOAc 3:1), mp. 96-97 °C.

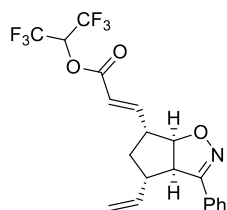
^1H NMR (500 MHz, CDCl_3): $\delta = 1.16\text{-}1.20$ (t, 3H, $J=7$ Hz, CH_3); 1.55-1.64 (m, 1H, CH_2); 2.06-2.13 (m, 1H, CH_2); 2.23-2.32 (m, 1H, CH_2); 2.48-2.57 (m, 1H, CH_2); 2.77-2.86 (m, 2H, H-4 and H-6); 3.48-3.54 (m, 1H, H-3a); 4.82-4.86 (m, 1H, H-6a); 6.07-6.13 (m, 1H, =CH); 6.16-6.22 (m, 1H, =CH); 6.44-6.47 (m, 1H, =CH); 6.47-6.50 (m, 1H, =CH).

^{13}C NMR (125 MHz, CDCl_3): $\delta = 10.7, 19.9, 39.3, 47.9, 51.3, 60.2, 90.2, 115.4$ (d, $^2J_{\text{C-F}} = 20$ Hz); 115.6 (d, $^2J_{\text{C-F}} = 20$ Hz); 127.6 (d, $^3J_{\text{C-F}} = 5$ Hz); 127.6 (d, $^3J_{\text{C-F}} = 5$ Hz); 129.5, 129.6, 129.8, 131.4, 132.9 (d, $^4J_{\text{C-F}} = 3$ Hz); 133.3 (d, $^4J_{\text{C-F}} = 3$ Hz); 162.2 (d, $^1J_{\text{C-F}} = 246$ Hz); 162.3 (d, $^1J_{\text{C-F}} = 246$ Hz).

^{19}F NMR (471 MHz, CDCl_3): $\delta = -114.9$ (Ar-F), -114.3 (Ar-F).

HRMS calcd. for $\text{C}_{24}\text{H}_{24}\text{F}_2\text{NO}^+$ ($[\text{M}+\text{H}]^+$): 380.1820, found: 380.1824.

(E)-1,1,1,3,3,3-Hexafluoropropan-2-yl 3-((3a*R,4*S**,6*R**,6a*R**)-3-phenyl-4-vinyl-4,5,6,6a-tetrahydro-3a*H*-cyclopenta[*d*]isoxazol-6-yl)acrylate, (±)-20a**



Best catalyst: G-3. Colorless oil; yield: 30% (55 mg); $R_f = 0.42$ (*n*-hexane/EtOAc 7:1).

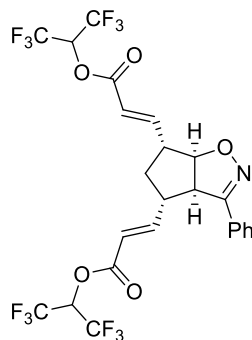
^1H NMR (500 MHz, CDCl_3): $\delta = 1.58\text{--}1.66$ (m, 1H, CH_2); 2.09–2.17 (m, 1H, CH_2); 2.79–2.87 (m, 1H, H-4); 2.93–3.01 (m, 1H, H-6); 3.97–4.03 (m, 1H, H-3a); 5.04–5.11 (m, 2H, H-6a and $=\text{CH}_2$); 5.14–5.18 (m, 1H, $=\text{CH}_2$); 5.79–5.95 (m, 2H, $\text{CH}(\text{CF}_3)_2$ and $=\text{CH}$); 6.06–6.12 (m, 1H, $=\text{CH}$); 7.23–7.30 (m, 1H, $=\text{CH}$); 7.35–7.43 (m, 3H, Ar-H); 7.66–7.70 (m, 2H, Ar-H).

^{13}C NMR (125 MHz, CDCl_3): $\delta = 37.9, 48.3, 50.3, 57.9, 66.5$ (septett, $^2J_{\text{C-F}} = 35$ Hz, $\text{CH}(\text{CF}_3)_2$); 90.4, 116.7, 119.1, 120.5 (q, $^1J_{\text{C-F}} = 281$ Hz, CF_3); 127.7, 128.4, 128.6, 130.2, 139.9, 152.9, 159.0, 162.5.

^{19}F NMR (471 MHz, CDCl_3): $\delta = -73.2$ (CF_3).

HRMS calcd. for $\text{C}_{20}\text{H}_{18}\text{F}_6\text{NO}_3^+$ ($[\text{M}+\text{H}]^+$): 434.1185, found: 434.1189.

(2*E*,2'*E*)-Bis(1,1,1,3,3,3-hexafluoropropan-2-yl) 3,3'-((3a*R,4*S**,6*R**,6a*R**)-3-phenyl-4,5,6,6a-tetrahydro-3a*H*-cyclopenta[*d*]isoxazole-4,6-diyl)diacrylate, (±)-20c**



Best catalyst: HG-2. White solid; yield: 38% (100 mg); $R_f = 0.39$ (*n*-hexane/EtOAc 7:1), mp. 112–113 °C.

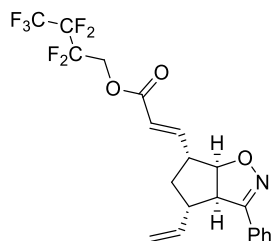
^1H NMR (500 MHz, CDCl_3): δ = 1.71-1.80 (m, 1H, CH_2); 2.18-2.25 (m, 1H, CH_2); 2.94-3.03 (m, 1H, H-4); 3.03-3.11 (m, 1H, H-6); 4.09-4.15 (m, 1H, H-3a); 5.10-5.16 (m, 1H, H-6a); 5.78-5.94 (m, 3H, $\text{CH}(\text{CF}_3)_2$ and $=\text{CH}$); 6.09-6.15 (m, 1H, $=\text{CH}$); 7.17-7.29 (m, 2H, $=\text{CH}$); 7.34-7.47 (m, 3H, Ar-H); 7.54-7.60 (m, 2H, Ar-H).

^{13}C NMR (125 MHz, CDCl_3): δ = 37.3, 47.3, 50.3, 57.8, 66.6 (septett, $^2J_{\text{C-F}}$ = 35 Hz, $\text{CH}(\text{CF}_3)_2$); 66.7 (septett, $^2J_{\text{C-F}}$ = 35 Hz, $\text{CH}(\text{CF}_3)_2$); 90.2, 119.8, 120.3 (q, $^1J_{\text{C-F}}$ = 282 Hz, CF_3); 127.5, 127.7, 128.8, 130.7, 151.6, 153.3, 158.1, 162.1, 162.2.

^{19}F NMR (471 MHz, CDCl_3): δ = -73.2 (CF_3); -73.3 (CF_3).

HRMS calcd. for $\text{C}_{24}\text{H}_{18}\text{F}_{12}\text{NO}_5^+$ ($[\text{M}+\text{H}]^+$): 628.0987, found: 628.0987.

(E)-2,2,3,3,4,4,4-Heptafluorobutyl 3-((3a*R,4*S**,6*R**,6a*R**)-3-phenyl-4-vinyl-4,5,6,6a-tetrahydro-3a*H*-cyclopenta[*d*]isoxazol-6-yl)acrylate, ($\pm$)-21a**



Best catalyst: G-2. Yellow oil; yield: 27% (53 mg); R_f = 0.38 (*n*-hexane/EtOAc 7:1).

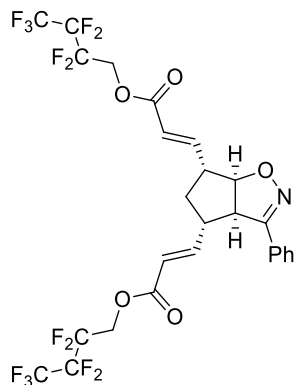
^1H NMR (500 MHz, CDCl_3): δ = 1.55-1.65 (m, 1H, CH_2); 2.07-2.15 (m, 1H, CH_2); 2.77-2.86 (m, 1H, H-4); 2.90-2.99 (m, 1H, H-6); 3.95-4.02 (m, 1H, H-3a); 4.60-4.71 (m, 2H, $\text{CH}_2(\text{CF}_2)_2\text{CF}_3$); 5.01-5.17 (m, 3H, H-6a and $=\text{CH}_2$); 5.83-5.96 (m, 1H, $=\text{CH}$); 5.99-6.06 (m, 1H, CH); 7.10-7.18 (m, 1H, $=\text{CH}$); 7.34-7.43 (m, 3H, Ar-H); 7.64-7.71 (m, 2H, Ar-H).

^{13}C NMR (125 MHz, CDCl_3): δ = 37.9, 48.3, 50.1, 57.8, 59.3 (t, $^2J_{\text{C-F}}$ = 27 Hz, $\text{CH}_2(\text{CF}_2)_2\text{CF}_3$); 90.6, 116.5, 100-120 (m, $\text{CF}_2\text{CF}_2\text{CF}_3$); 120.4, 127.7, 128.4, 128.6, 130.1, 140.1, 150.6, 159.0, 164.3.

^{19}F NMR (471 MHz, CDCl_3): δ = -80.86 (t, J = 9 Hz, CF_3); -80.85 (t, J = 9 Hz, CF_3); -120.4 (m, $\text{CF}_2\text{CF}_2\text{CF}_3$); -127.6 (s, $\text{CF}_2\text{CF}_2\text{CF}_3$).

HRMS calcd. for $C_{21}H_{19}F_7NO_3^+$ ($[M+H]^+$): 466.1247, found: 466.1253.

(2*E*,2'*E*)-Bis(2,2,3,3,4,4,4-heptafluorobutyl) 3,3'-((3*aR,4*S**,6*R**,6*aR**)-3-phenyl-4,5,6,6a-tetrahydro-3*aH*-cyclopenta[*d*]isoxazole-4,6-diyl)diacrylate, ($\pm$)-21c**



Best catalyst: HG-2. Yellow solid; yield: 37% (108 mg); R_f = 0.31 (*n*-hexane/EtOAc 7:1), mp. 69-70 °C.

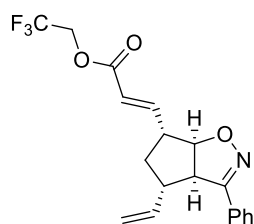
1H NMR (500 MHz, $CDCl_3$): δ = 1.65-1.75 (m, 1H, CH_2); 2.14-2.21 (m, 1H, CH_2); 2.92-3.07 (m, 2H, H-4 and H-6); 4.05-4.11 (m, 1H, H-3a); 4.54-4.74 (m, 4H, $CH_2(CF_2)CF_3$); 5.07-5.13 (m, 1H, H-6a); 5.82-5.87 (m, 1H, =CH); 6.02-6.07 (m, 1H, =CH); 7.06-7.15 (m, 2H, =CH); 7.35-7.44 (m, 3H, Ar-H); 7.54-7.59 (m, 2H, Ar-H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 37.4, 46.9, 50.1, 59.4 (t, $^2J_{C-F}$ = 27 Hz, $CH_2(CF_2)_2CF_3$); 90.4, 100-120 (m, $CF_2CF_2CF_3$); 120.9, 121.0, 127.4, 127.9, 128.8, 130.5, 149.4, 151.3, 158.2, 164.0.

^{19}F NMR (471 MHz, $CDCl_3$): δ = -80.82 (t, J = 9 Hz, CF_3); -80.84 (t, J = 9 Hz, CF_3); -120.4 (m, $CF_2CF_2CF_3$); -127.6 (s, $CF_2CF_2CF_3$).

HRMS calcd. for $C_{26}H_{20}F_{14}NO_5^+$ ($[M+H]^+$): 692.1112, found: 692.1119.

(E)-2,2,2-Trifluoroethyl 3-((3aR*,4S*,6R*,6aR*)-3-phenyl-4-vinyl-4,5,6,6a-tetrahydro-3aH-cyclopenta[d]isoxazol-6-yl)acrylate, (±)-22a



Best catalyst: G-2. Pale yellow oil; yield: 37% (57 mg); R_f = 0.33 (*n*-hexane/EtOAc 7:1).

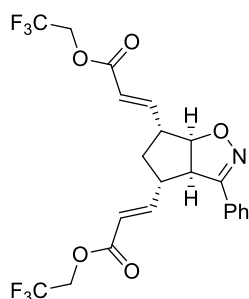
^1H NMR (500 MHz, CDCl_3): δ = 1.59-1.66 (m, 1H, CH_2); 2.10-2.17 (m, 1H, CH_2); 2.80-2.88 (m, 1H, H-4); 2.92-3.01 (m, 1H, H-6); 3.97-4.05 (m, 1H, H-3a); 4.52-4.62 (m, 2H, CH_2CF_3); 5.03-5.21 (m, 3H, H-6a and $=\text{CH}_2$); 5.87-5.97 (m, 1H, $=\text{CH}$); 6.03-6.09 (m, 1H, $=\text{CH}$); 7.14-7.21 (m, 1H, CH); 7.37-7.47 (m, 3H, Ar-H); 7.68-7.73 (m, 2H, Ar-H).

^{13}C NMR (125 MHz, CDCl_3): δ = 37.9, 48.3, 50.1, 57.8, 60.4 (q, $^2J_{\text{C-F}}$ = 37 Hz, CH_2CF_3); 90.6, 116.5, 120.5, 123.0 (q, $^1J_{\text{C-F}}$ = 277 Hz, CF_3); 127.7, 128.4, 128.6, 130.1, 140.1, 150.5, 159.0, 164.3.

^{19}F NMR (471 MHz, CDCl_3): δ = -73.7 (CF_3).

HRMS calcd. for $\text{C}_{19}\text{H}_{19}\text{F}_3\text{NO}_3^+$ ($[\text{M}+\text{H}]^+$): 366.1311, found: 366.1316.

(2E,2'E)-Bis(2,2,2-trifluoroethyl) 3,3'-((3aR*,4S*,6R*,6aR*)-3-phenyl-4,5,6,6a-tetrahydro-3aH-cyclopenta[d]isoxazole-4,6-diyl)diacrylate, (±)-22c



Best catalyst: HG-2. Yellow oil; yield: 48% (99 mg); R_f = 0.41 (*n*-hexane/EtOAc 5:1).

^1H NMR (500 MHz, CDCl_3): δ = 1.68-1.78 (m, 1H, CH_2); 2.16-2.23 (m, 1H, CH_2); 2.94-3.09 (m, 2H, H-4 and H-6); 4.08-4.13 (m, 1H, H-3a), 4.51-4.64 (m, 4H, CH_2CF_3); 5.09-5.15 (m, 1H,

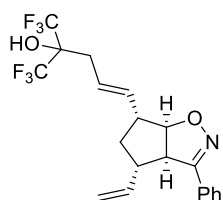
H-6a); 5.85-5.92 (m, 1H, =CH); 6.04-6.10 (m, 1H, =CH); 7.08-7.19 (m, 2H, =CH); 7.37-7.47 (m, 3H, Ar-H); 7.57-7.62 (m, 2H, Ar-H).

^{13}C NMR (125 MHz, CDCl_3): δ = 37.4, 46.9, 50.1, 57.6, 59.9, 60.42 (q, $^2J_{\text{C-F}}$ = 37 Hz, CH_2CF_3); 60.45 (q, $^2J_{\text{C-F}}$ = 37 Hz, CH_2CF_3); 90.4, 120.9, 122.54 (q, $^1J_{\text{C-F}}$ = 277 Hz, CF_3); 122.59 (q, $^1J_{\text{C-F}}$ = 277 Hz, CF_3); 127.4, 127.9, 128.8, 129.0, 130.5, 149.3, 151.3, 158.2, 164.0, 164.1.

^{19}F NMR (471 MHz, CDCl_3): δ = -73.77 (CF_3); -73.77 (CF_3).

HRMS calcd. for $\text{C}_{22}\text{H}_{20}\text{F}_6\text{NO}_5^+$ ($[\text{M}+\text{H}]^+$): 492.1240, found: 492.1247.

(E)-1,1,1-Trifluoro-5-((3a*R,4*S**,6*R**,6a*R**)-3-phenyl-4-vinyl-4,5,6,6a-tetrahydro-3a*H*-cyclopenta[*d*]isoxazol-6-yl)-2-(trifluoromethyl)pent-4-en-2-ol, ($\pm$)-23a**



Best catalyst: G-2. Brown oil; yield: 54% (95 mg); R_f = 0.45 (*n*-hexane/EtOAc 4:1).

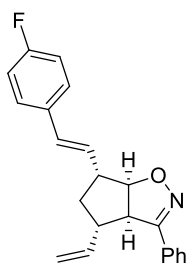
^1H NMR (500 MHz, CDCl_3): δ = 1.44-1.55 (m, 1H, CH_2); 1.99-2.08 (m, 1H, CH_2); 2.69-2.85 (m, 4H, H-4, H-6 and $\text{CH}_2(\text{CF}_3)_2\text{OH}$); 3.47 (brs, 1H, OH); 3.88-3.97 (m, 1H, H-3a); 4.91-4.98 (m, 1H, H-6a); 5.01-5.17 (m, 2H, = CH_2); 5.57-5.70 (m, 1H, =CH); 5.77-5.97 (m, 2H, =CH); 7.32-7.43 (m, 3H, Ar-H); 2.64-2.71 (m, 2H, Ar-H).

^{13}C NMR (125 MHz, CDCl_3): δ = 33.7, 38.4, 48.2, 50.1, 57.6, 75.2 (septet, $^2J_{\text{C-F}}$ = 29 Hz, $\text{CH}_2(\text{CF}_3)_2\text{OH}$); 91.4, 116.0, 121.0 122.9 (q, $^1J_{\text{C-F}}$ = 287 Hz, CF_3); 127.6, 128.5, 128.6, 130.0, 138.7, 140.6, 159.1.

^{19}F NMR (471 MHz, CDCl_3): δ = -76.5 (CF_3); -76.4 (CF_3).

HRMS calcd. for $\text{C}_{20}\text{H}_{20}\text{F}_6\text{NO}_2^+$ ($[\text{M}+\text{H}]^+$): 420.1393, found: 420.1392.

(3aR*,4S*,6R*,6aR*)-6-((E)-4-Fluorostyryl)-3-phenyl-4-vinyl-4,5,6,6a-tetrahydro-3aH-cyclopenta[d]isoxazole, (±)-25a



Best catalyst: G-2. White solid; yield: 28% (39 mg); R_f = 0.39 (*n*-hexane/EtOAc 7:1), mp. 57-58 °C.

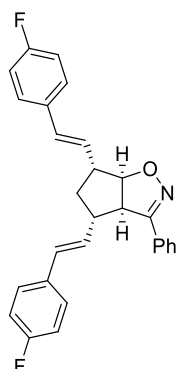
^1H NMR (500 MHz, CDCl_3): δ = 1.55-1.64 (m, 1H, CH_2); 2.07-2.14 (m, 1H, CH_2); 2.74-2.85 (m, 1H, H-4); 2.85- 2.95 (m, 1H, H-6); 3.91-3.97 (m, 1H, H-3a); 5.00-5.14 (m, 3H, H-6a and $=\text{CH}_2$); 5.88-5.98 (m, 1H, $=\text{CH}$); 6.15-6.22 (m, 1H, $=\text{CH}$); 6.46-6.53 (m, 1H, $=\text{CH}$); 6.96-7.02 (m, 2H, Ar-H); 7.26-7.40 (m, 5H, Ar-H); 7.66-7.72 (m, 2H, Ar-H).

^{13}C NMR (125 MHz, CDCl_3): δ = 38.7, 48.4, 50.6, 57.7, 91.9, 115.4 (d, $^2J_{\text{C-F}}$ = 21 Hz); 115.8, 127.65 (d, $^3J_{\text{C-F}}$ = 7 Hz); 127.66; 128.4, 128.8, 129.6, 129.8, 133.3 (d, $^4J_{\text{C-F}}$ = 3 Hz); 140.8, 159.1, 162.2 (d, $^1J_{\text{C-F}}$ = 246 Hz).

^{19}F NMR (471 MHz, CDCl_3): δ = -114.9 (Ar-F).

HRMS calcd. for $\text{C}_{22}\text{H}_{21}\text{FNO}^+$ ($[\text{M}+\text{H}]^+$): 334.1601, found: 334.1603.

(3aR*,4S*,6R*,6aR*)-4,6-Bis((E)-4-fluorostyryl)-3-phenyl-4,5,6,6a-tetrahydro-3aH-cyclopenta[d]isoxazole, (±)-25c



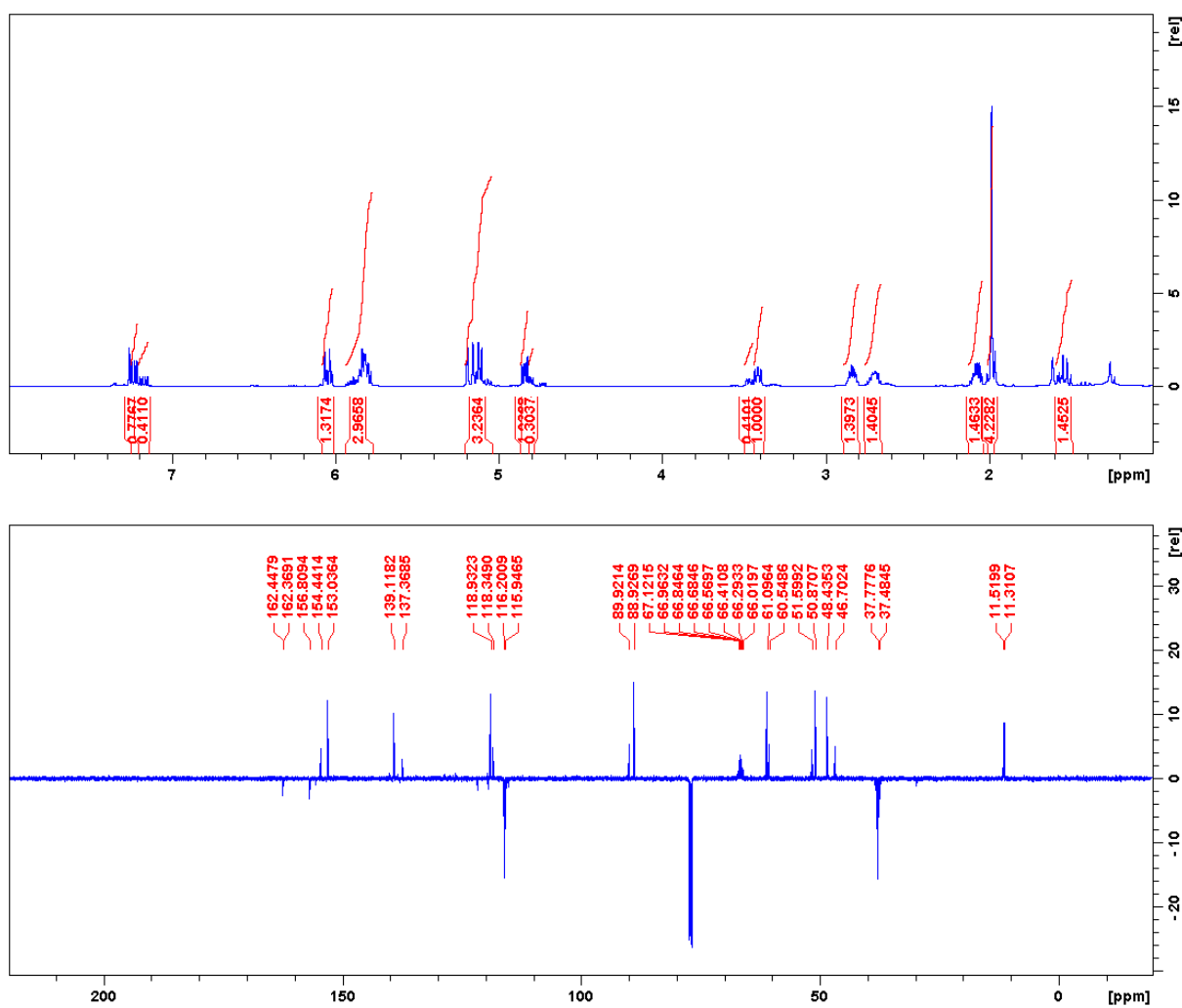
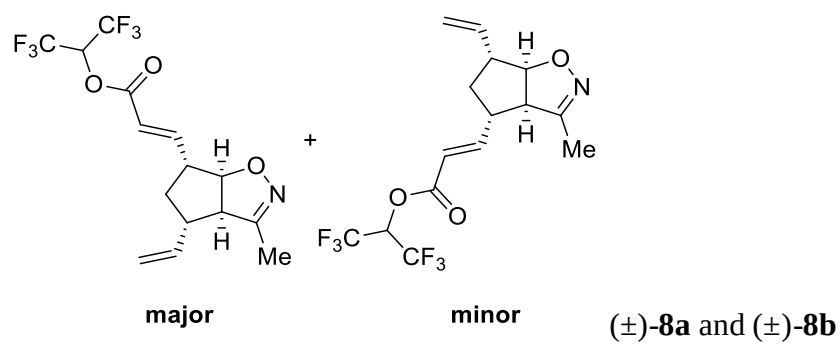
Best catalyst: G-2. White solid; yield: 49% (88 mg); R_f = 0.52 (*n*-hexane/EtOAc 5:1), mp. 163-164 °C.

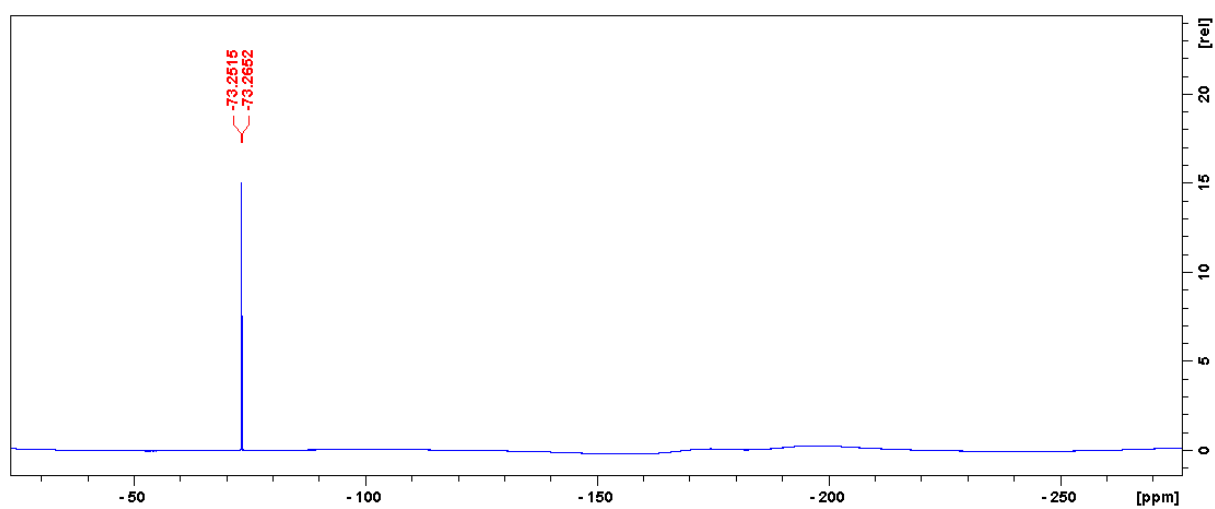
^1H NMR (500 MHz, CDCl_3): δ = 1.63-1.73 (m, 1H, CH_2); 2.11-2.19 (m, 1H, CH_2); 2.86-2.99 (m, 2H, H-4 and H-6); 3.97-4.04 (m, 1H, H-3a); 5.04-5.10 (m, 1H, H-6a); 6.13-6.26 (m, 2H, =CH); 6.27-6.34 (m, 1H, =CH); 6.48-6.54 (m, 1H, =CH); 6.95-7.05 (m, 4H, Ar-H); 7.26-7.40 (m, 7H, Ar-H); 7.66-7.73 (m, 2H, Ar-H).

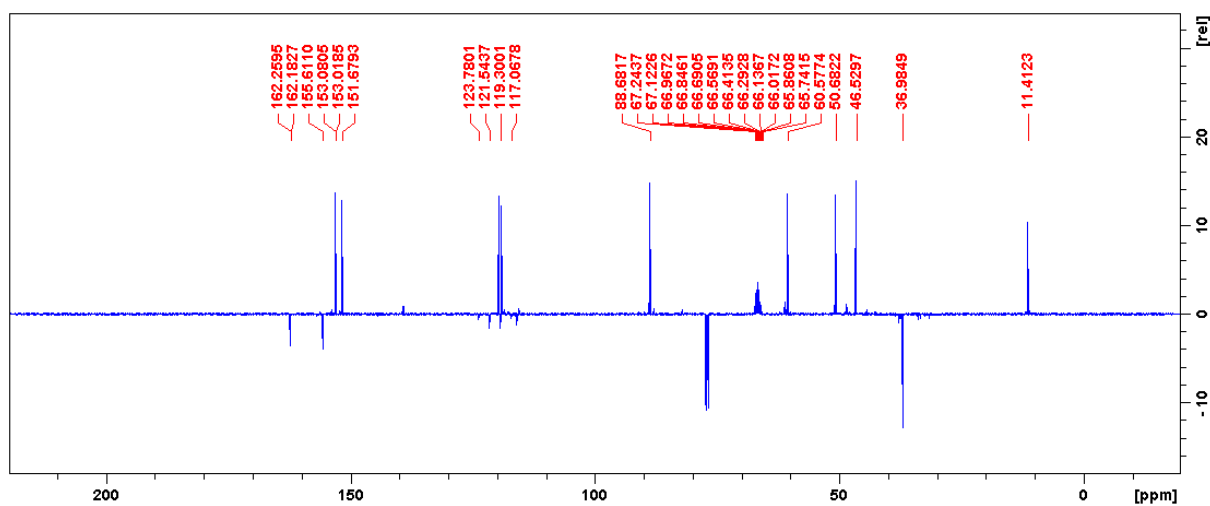
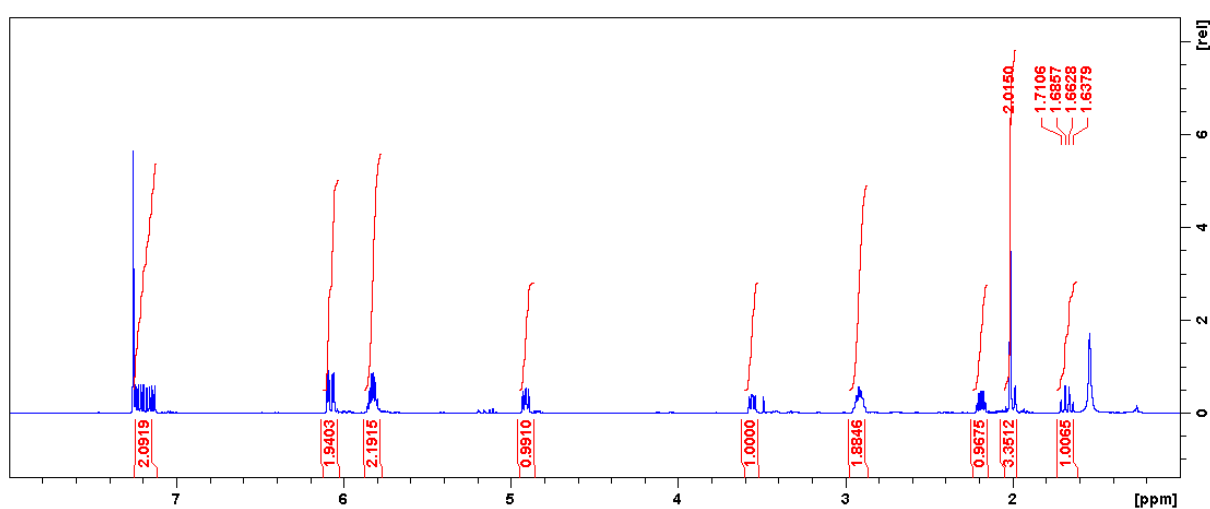
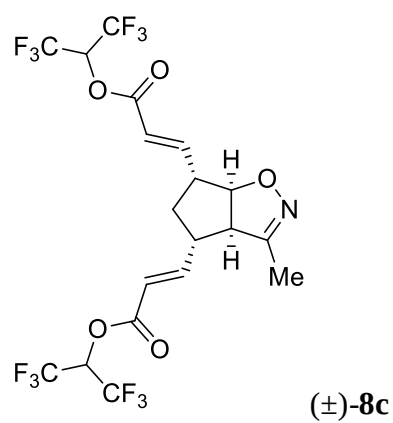
^{13}C NMR (125 MHz, CDCl_3): δ = 39.1, 48.1, 50.7, 58.3, 91.8, 115.4 (d, $^2J_{\text{C-F}}$ = 16 Hz); 115.5 (d, $^2J_{\text{C-F}}$ = 16 Hz); 127.6 (d, $^3J_{\text{C-F}}$ = 8 Hz); 127.8; 128.5, 128.8, 129.5, 129.9 (d, $^3J_{\text{C-F}}$ = 8 Hz); 130.3, 132.0, 133.0 (d, $^4J_{\text{C-F}}$ = 3 Hz); 133.3 (d, $^4J_{\text{C-F}}$ = 3 Hz); 159.0, 162.2 (d, $^1J_{\text{C-F}}$ = 247 Hz); 162.3 (d, $^1J_{\text{C-F}}$ = 247 Hz).

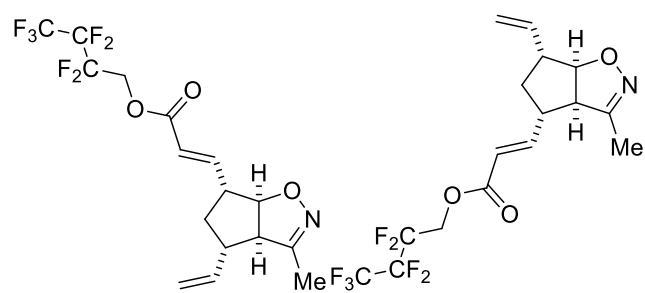
^{19}F NMR (471 MHz, CDCl_3): δ = -114.7 (Ar-F); -114.3 (Ar-F).

HRMS calcd. for $\text{C}_{28}\text{H}_{24}\text{F}_2\text{NO}^+$ ($[\text{M}+\text{H}]^+$): 428.1820, found: 428.1825.





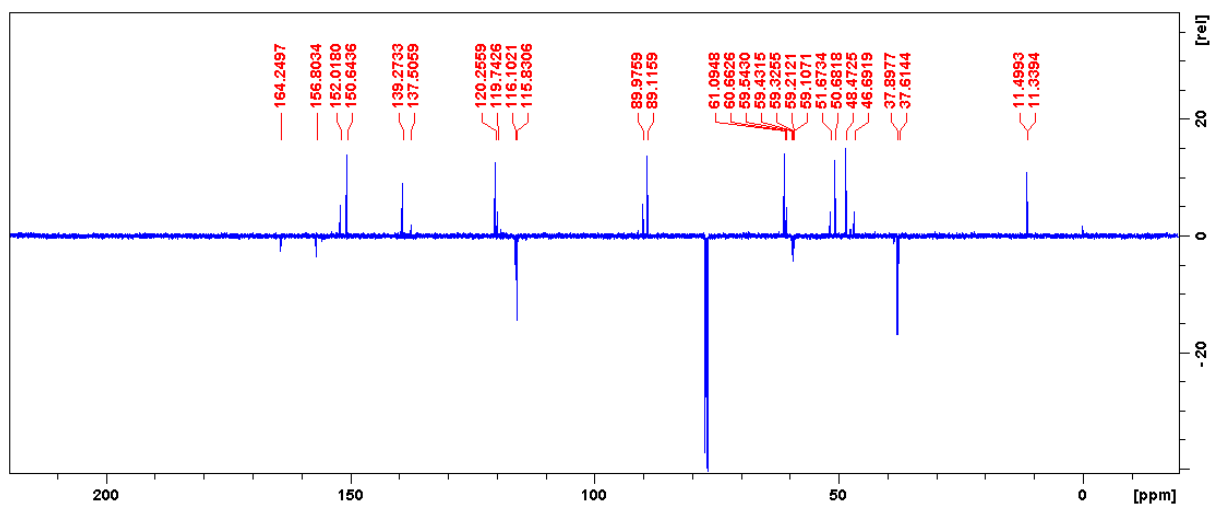
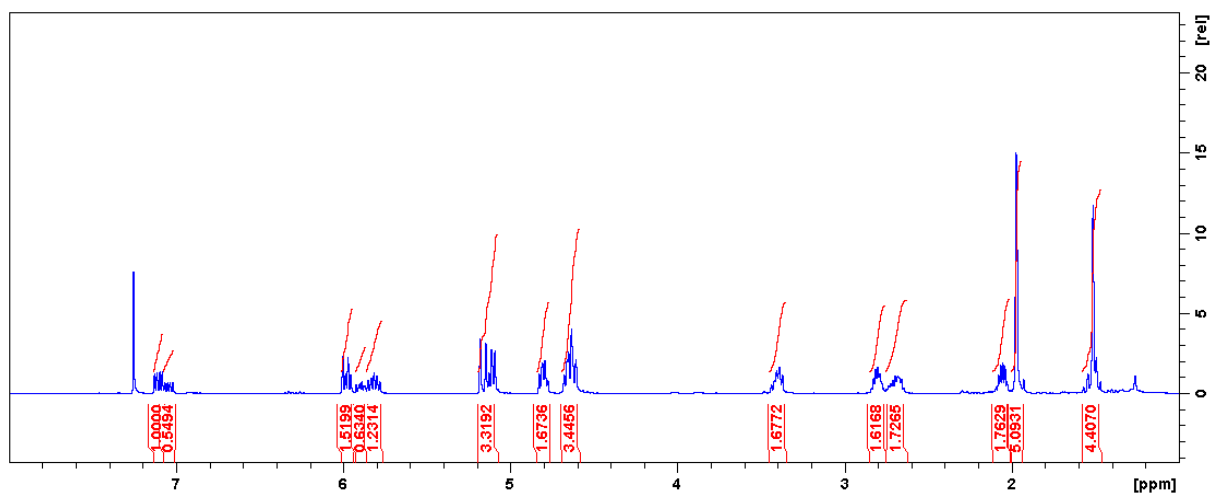


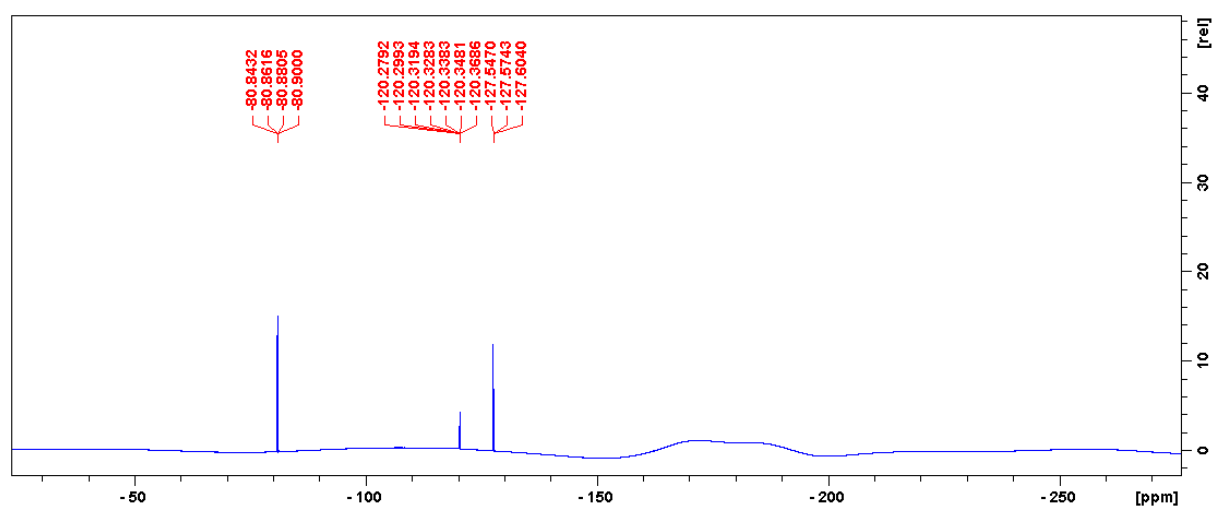


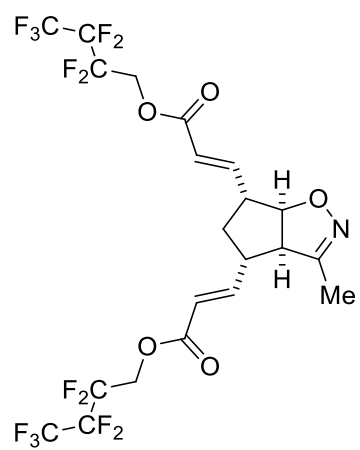
major

minor

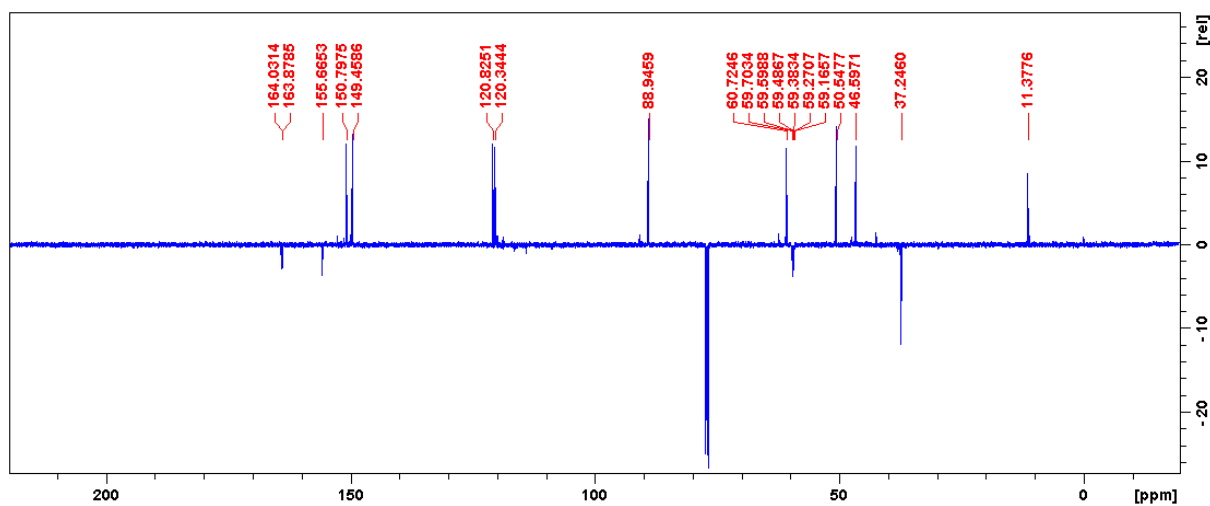
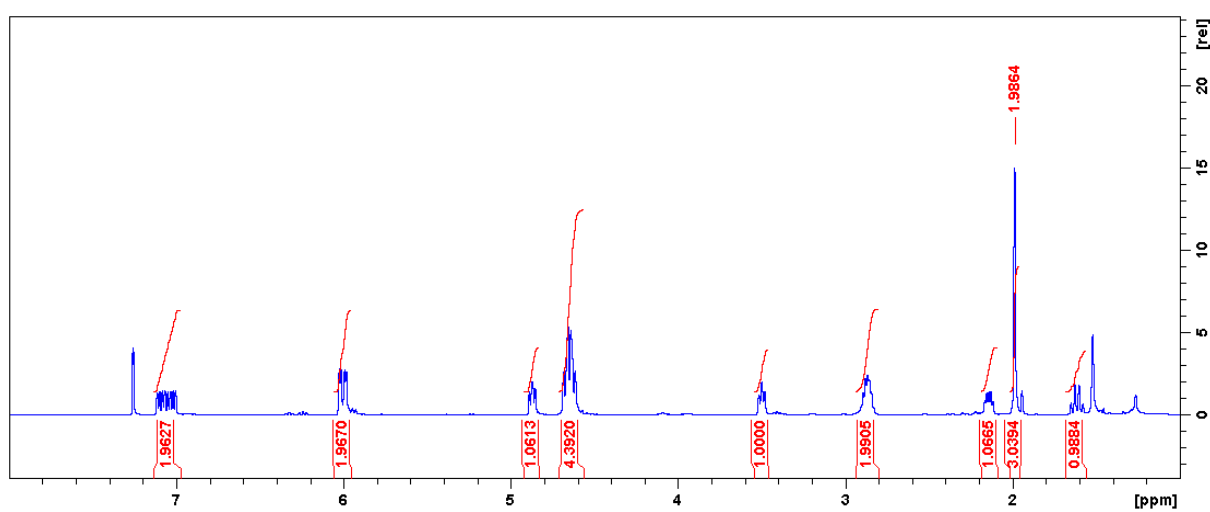
(±)-9a and (±)-9b

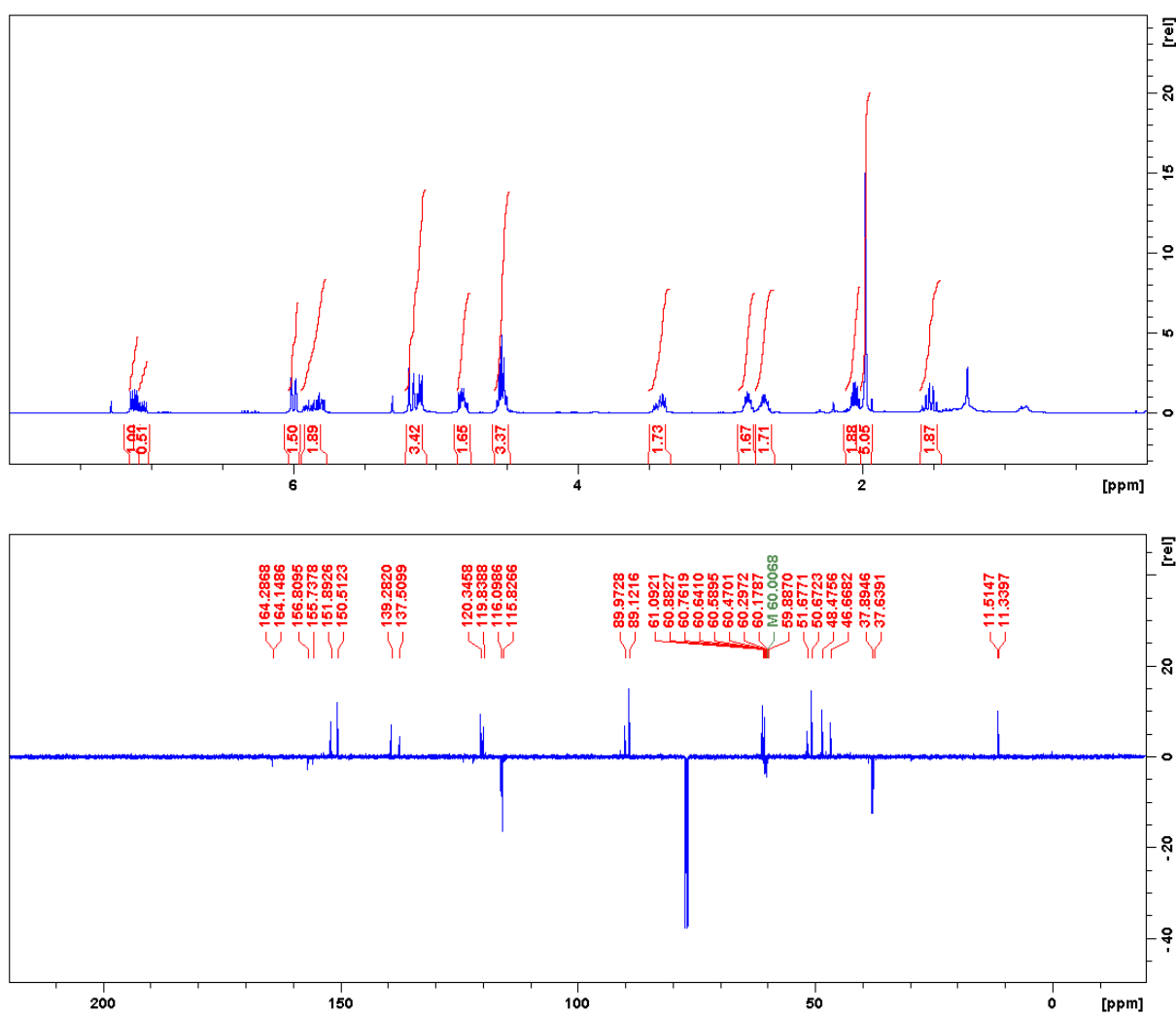
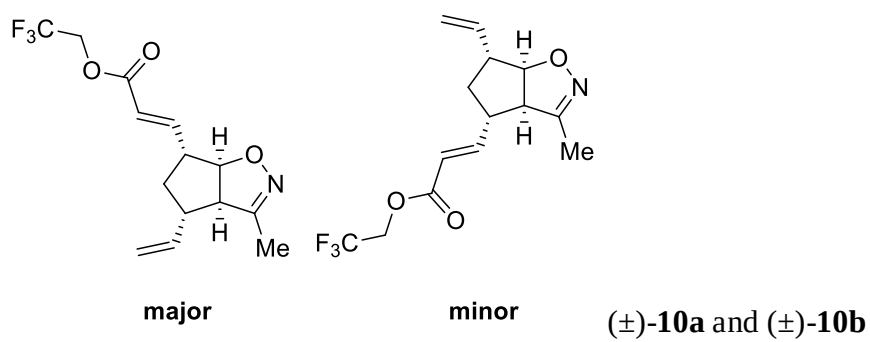


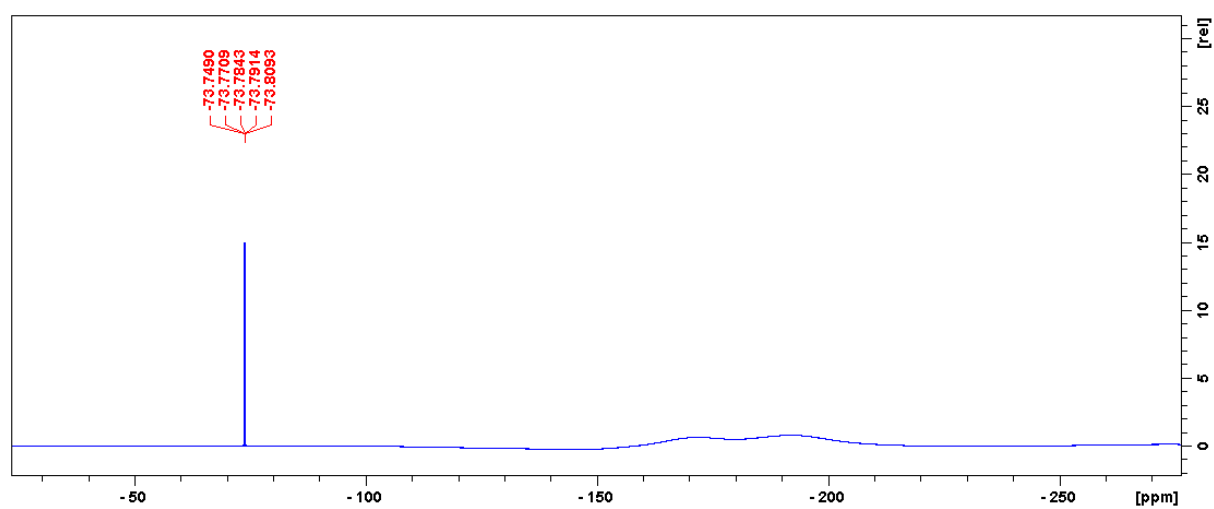


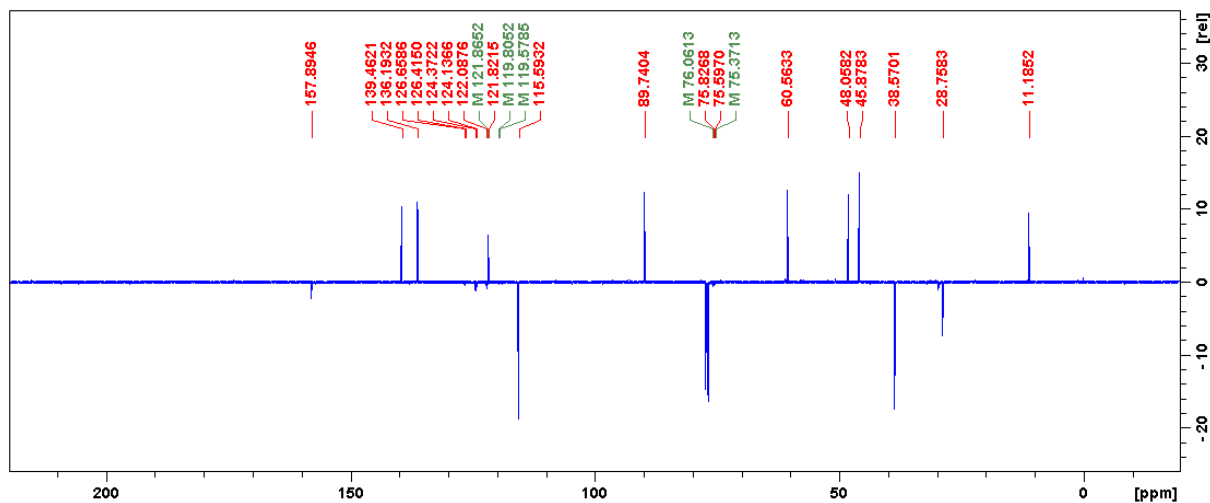
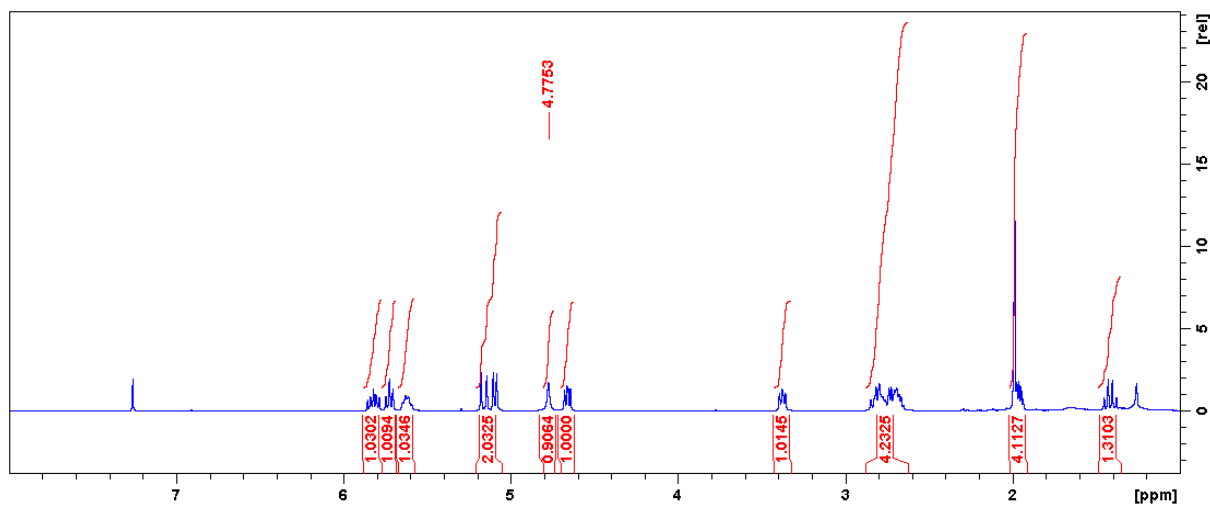
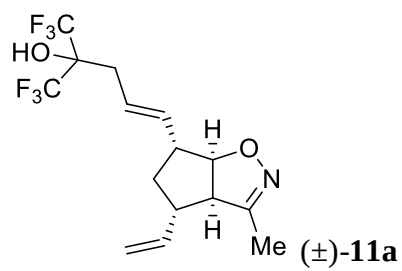


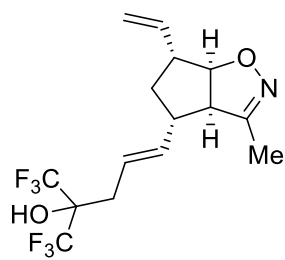
(±)-9c



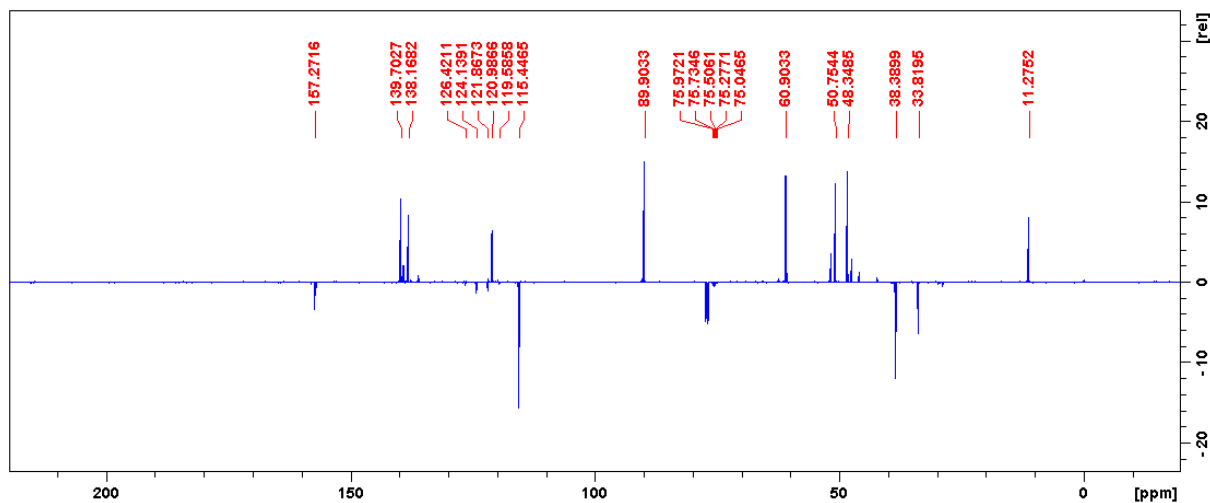
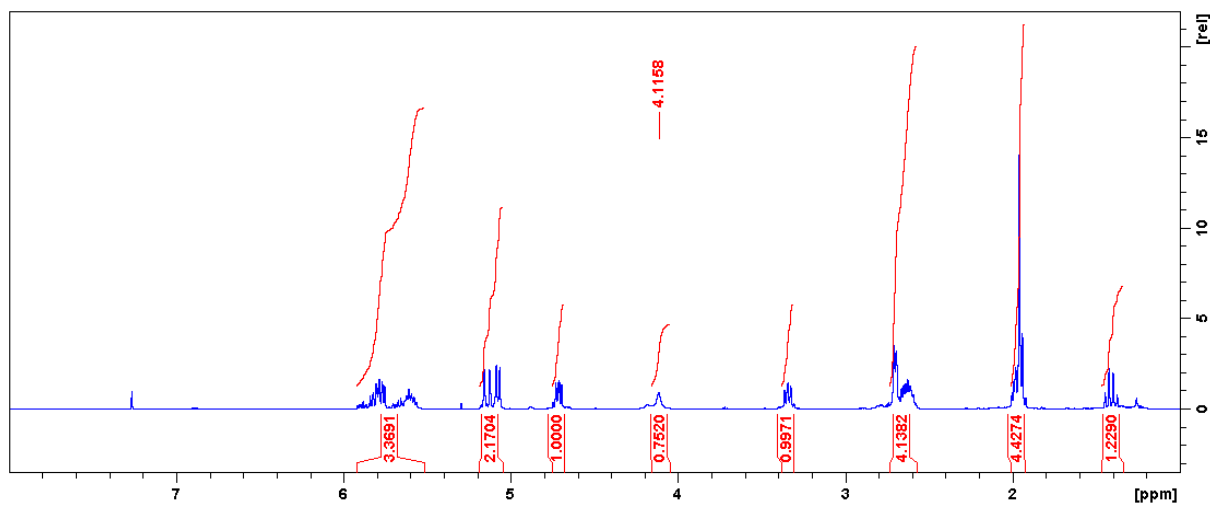


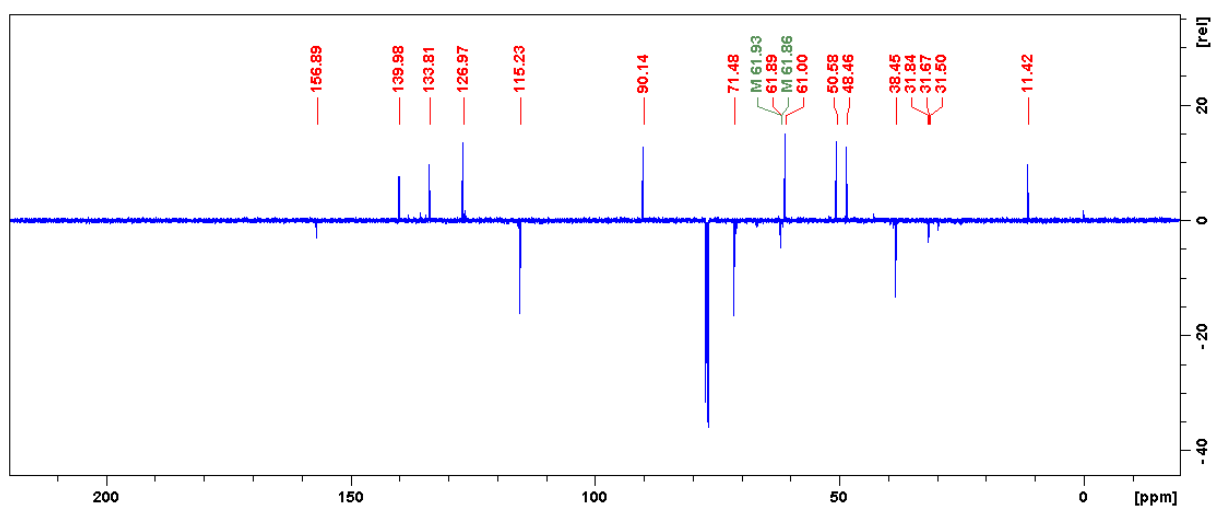
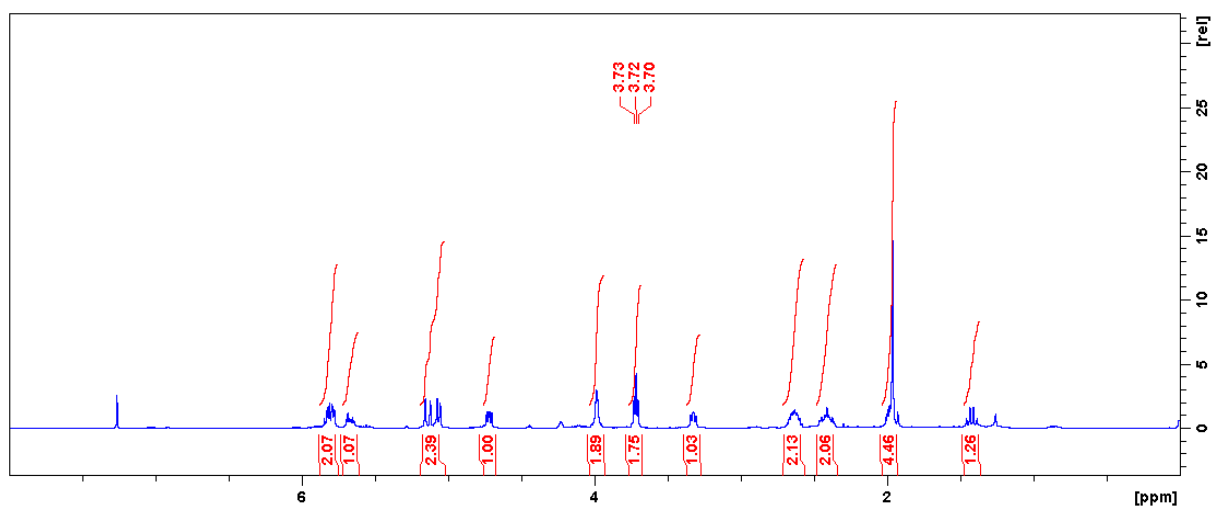
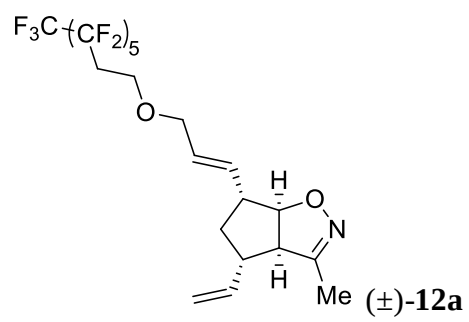


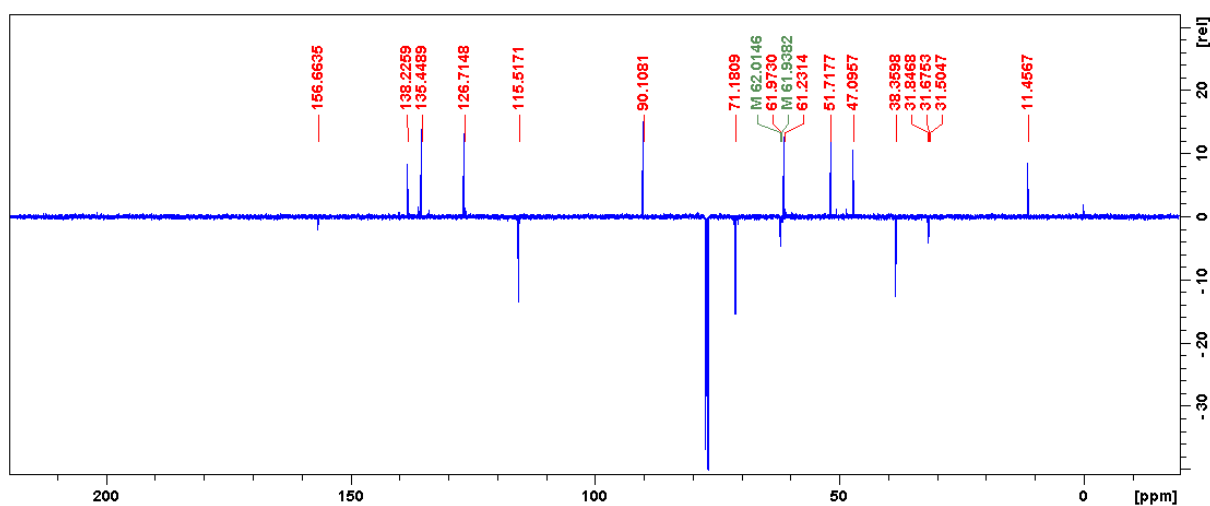
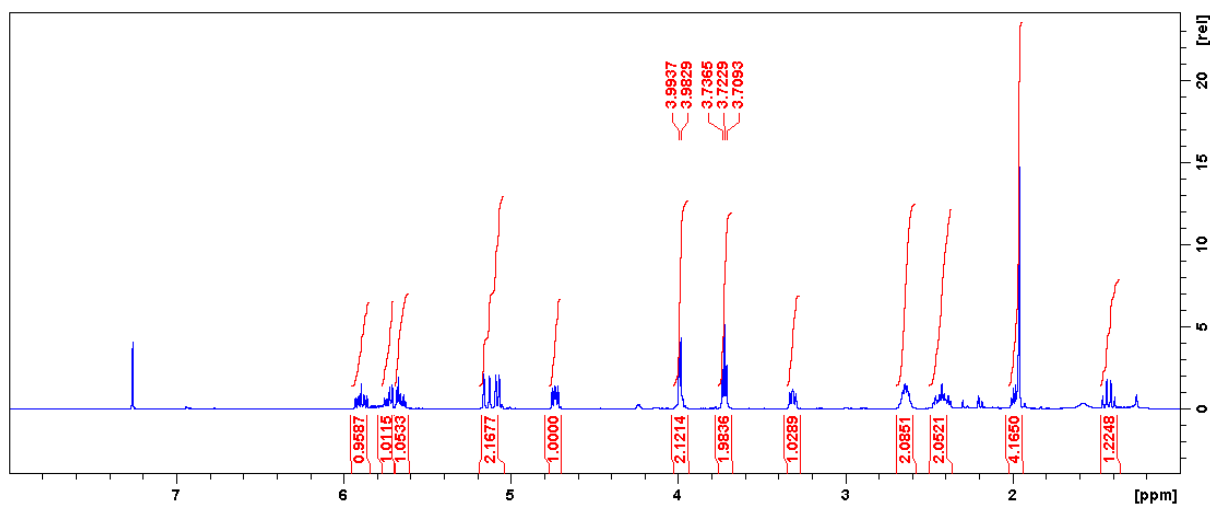
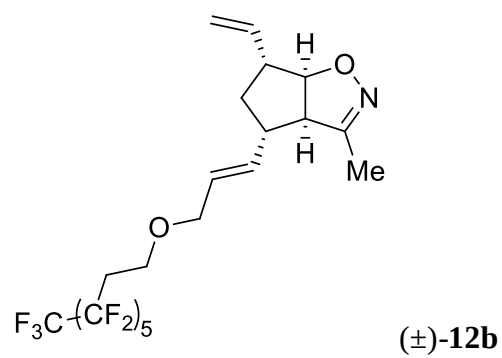


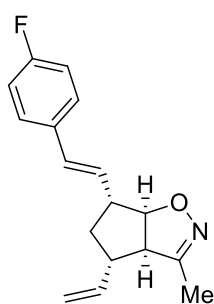


(±)-11b

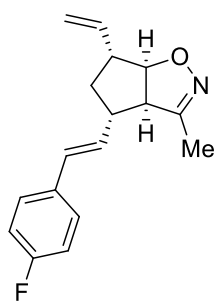








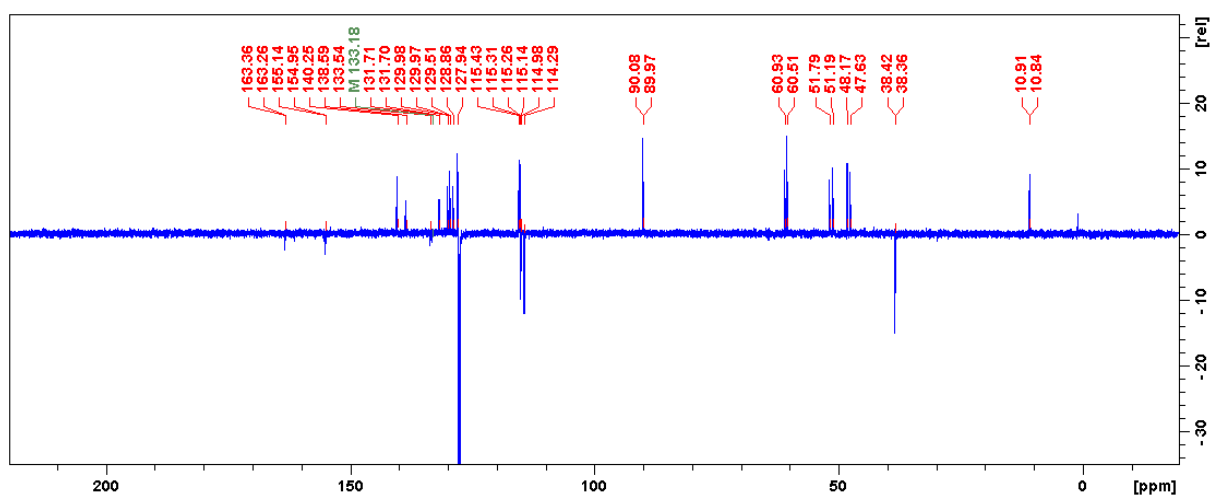
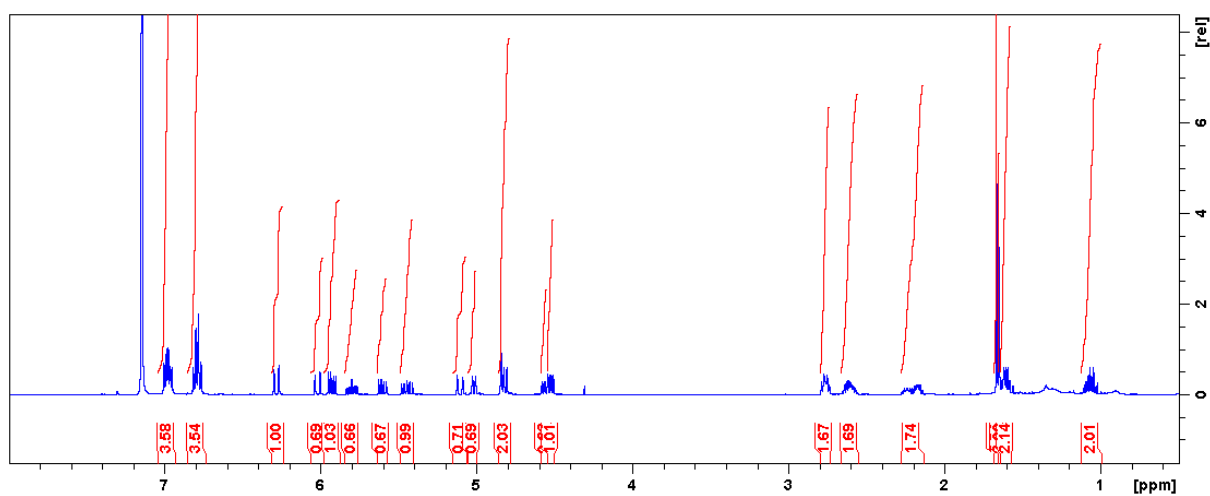
major



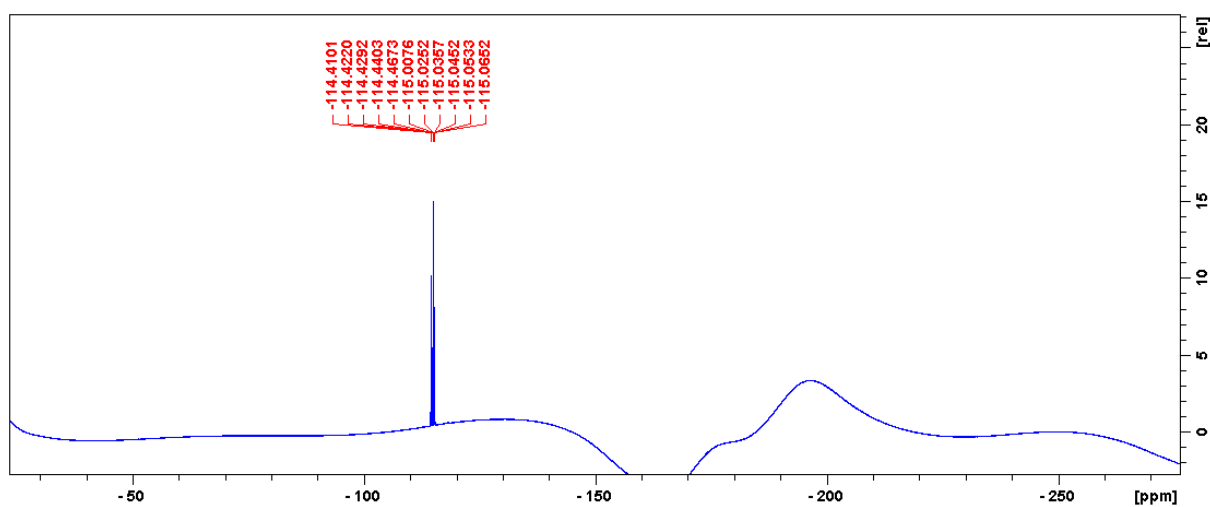
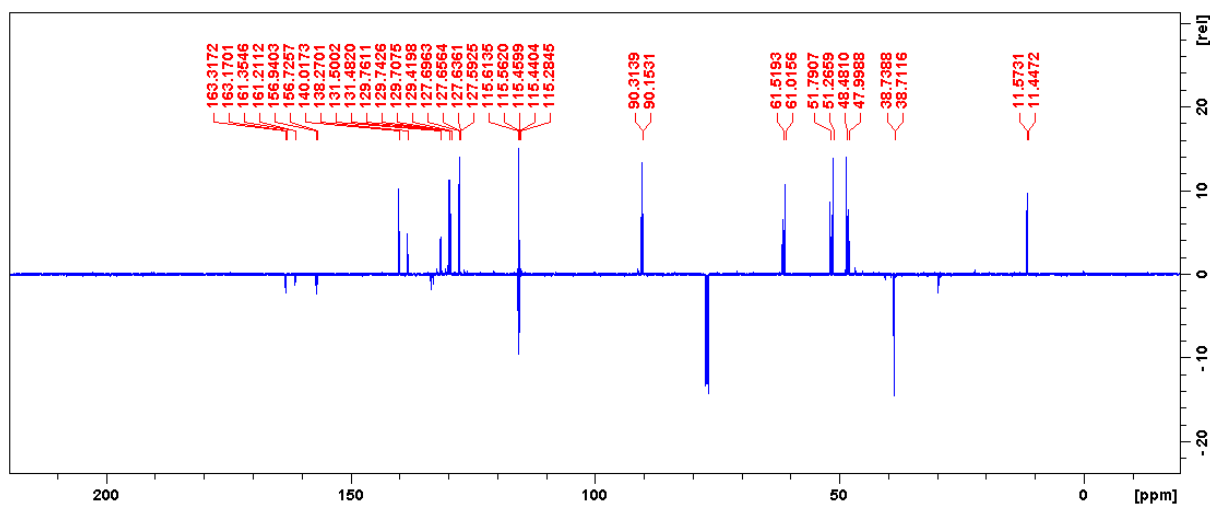
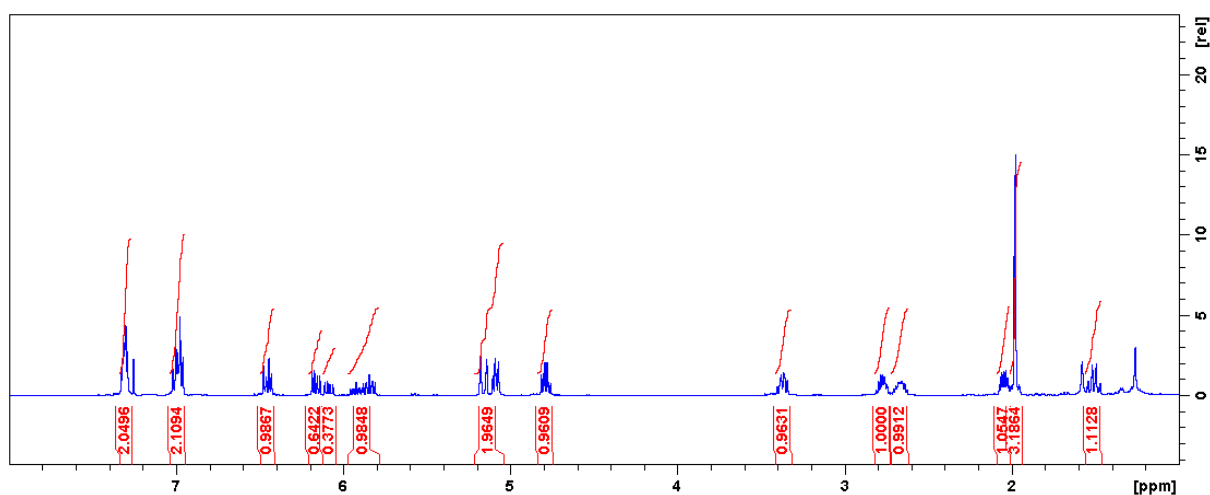
minor

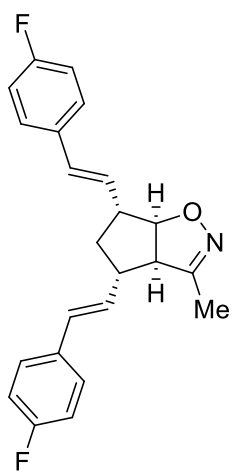
(±)-13a and (±)-13b

Spectra in D₆-benzene:

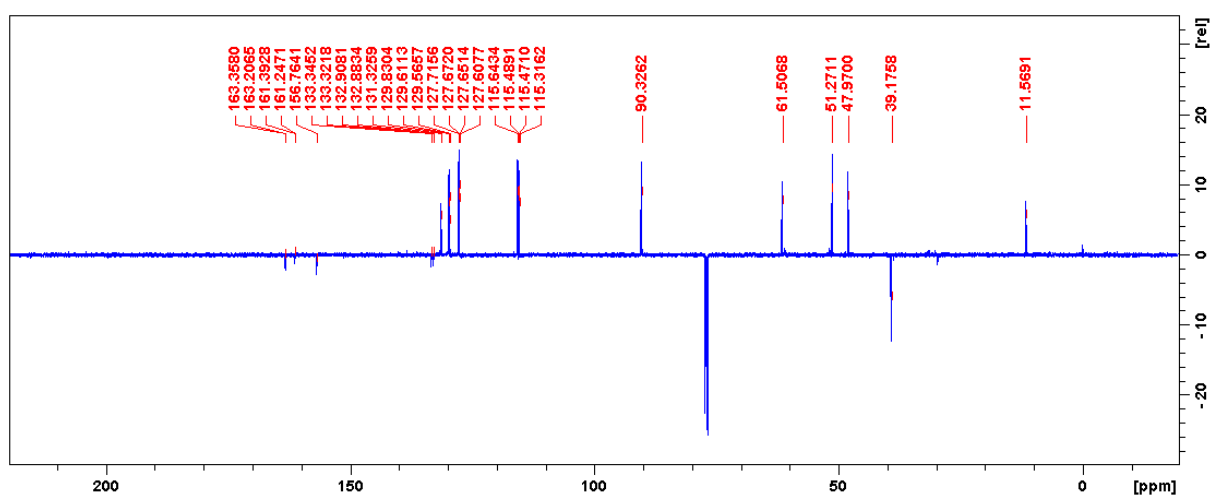
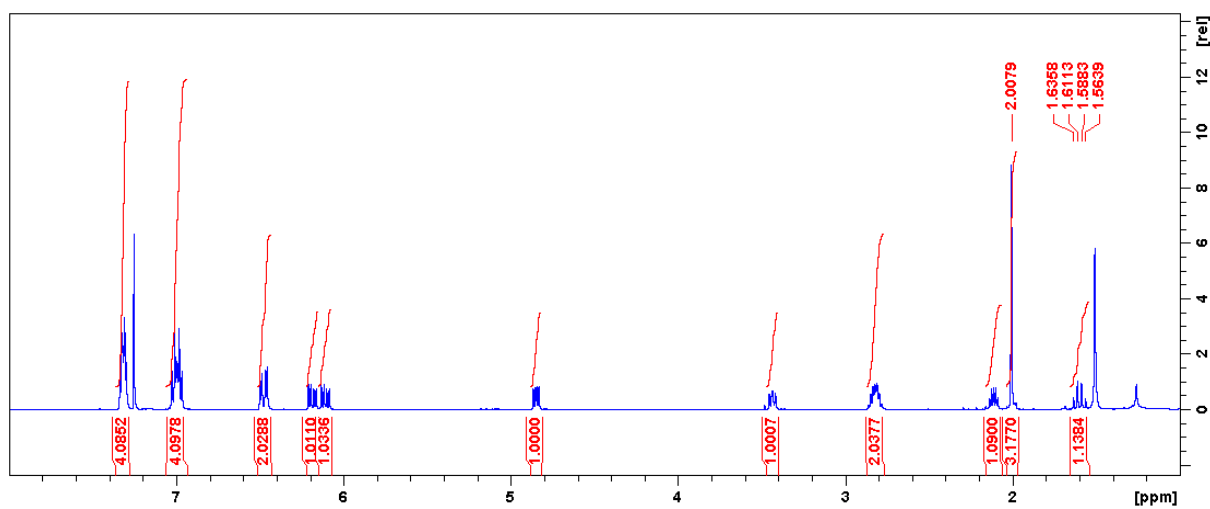


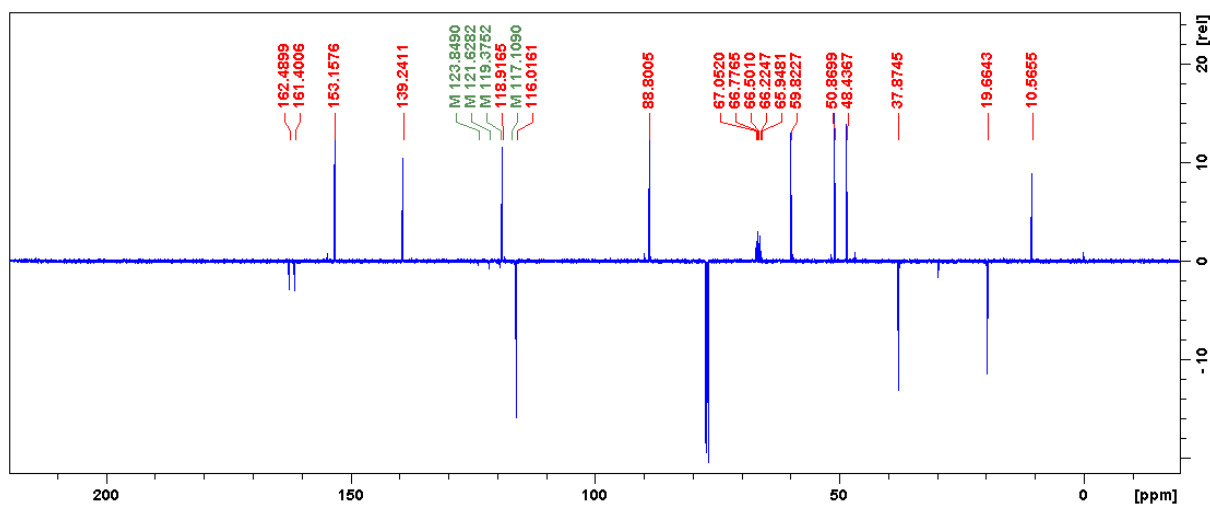
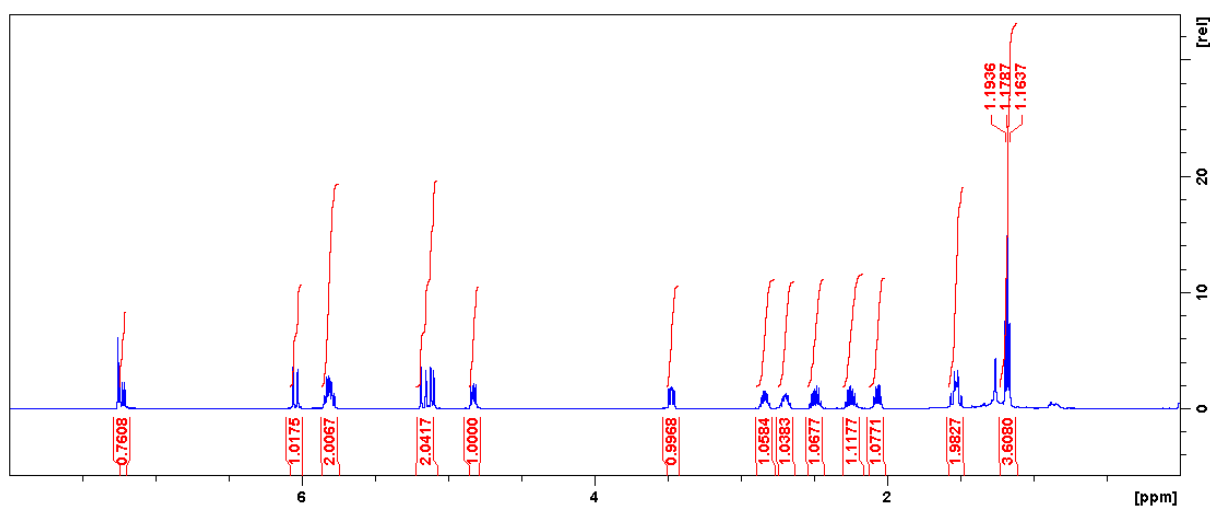
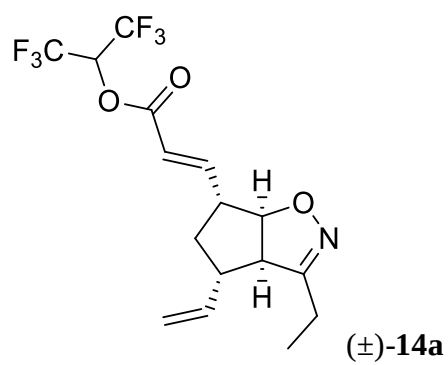
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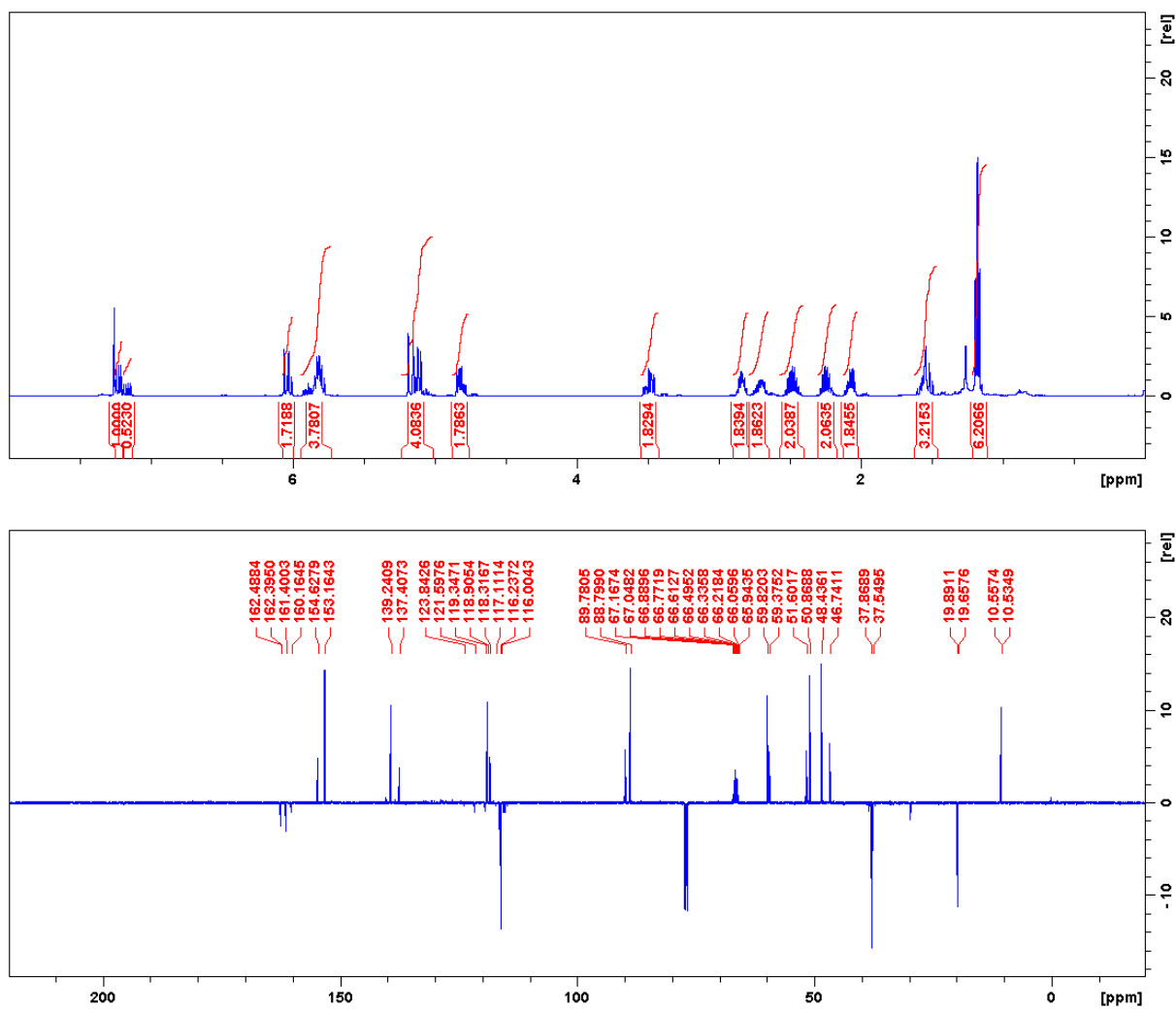
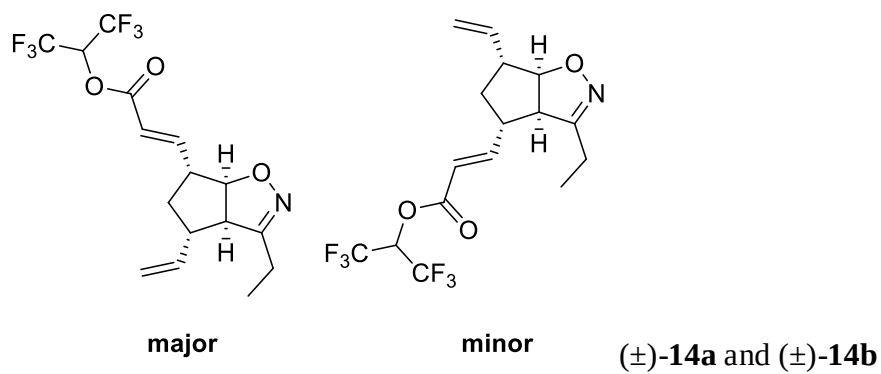


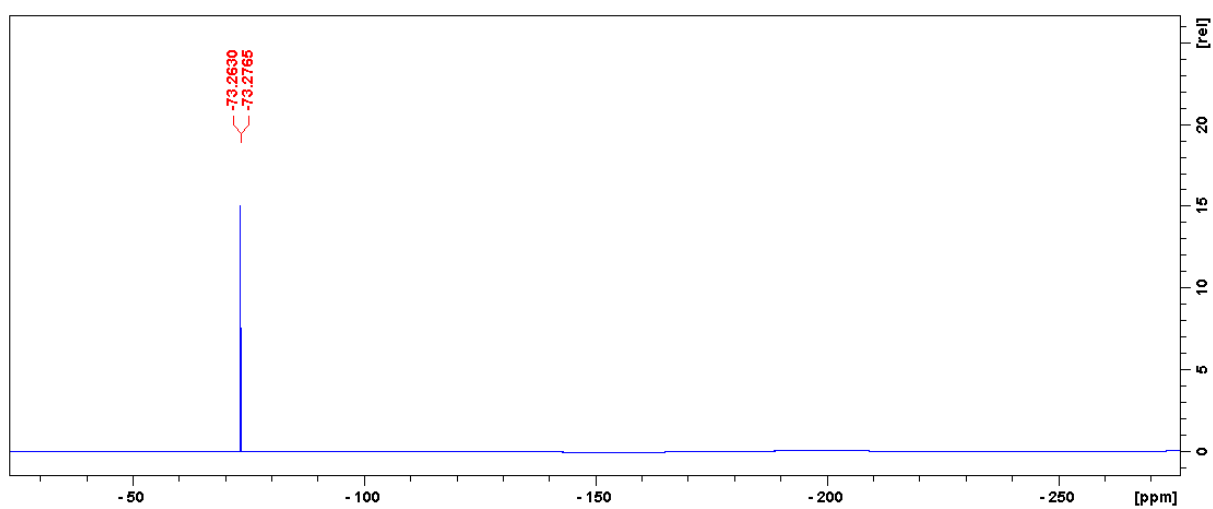


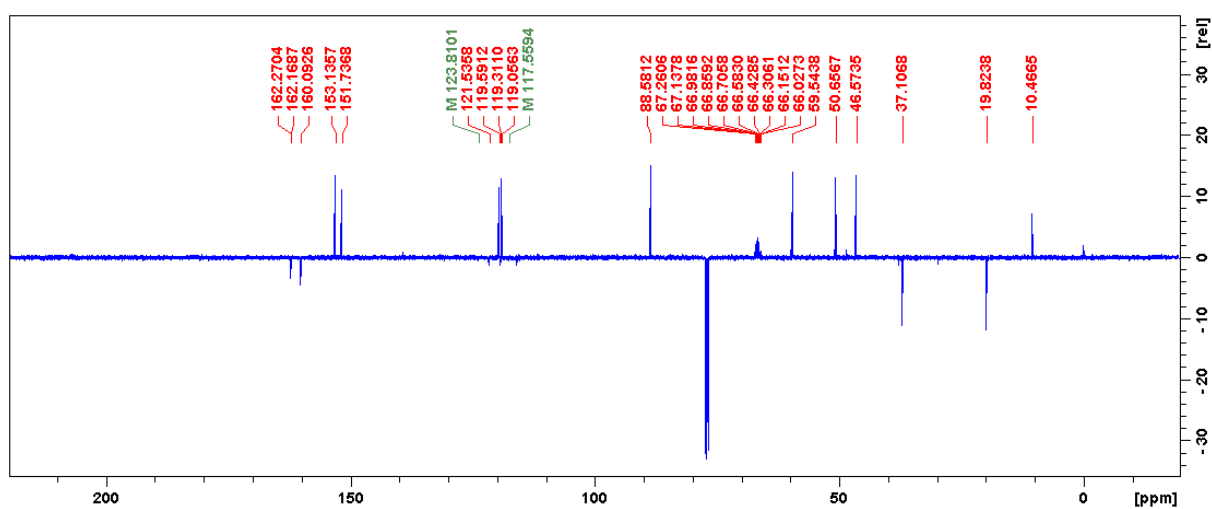
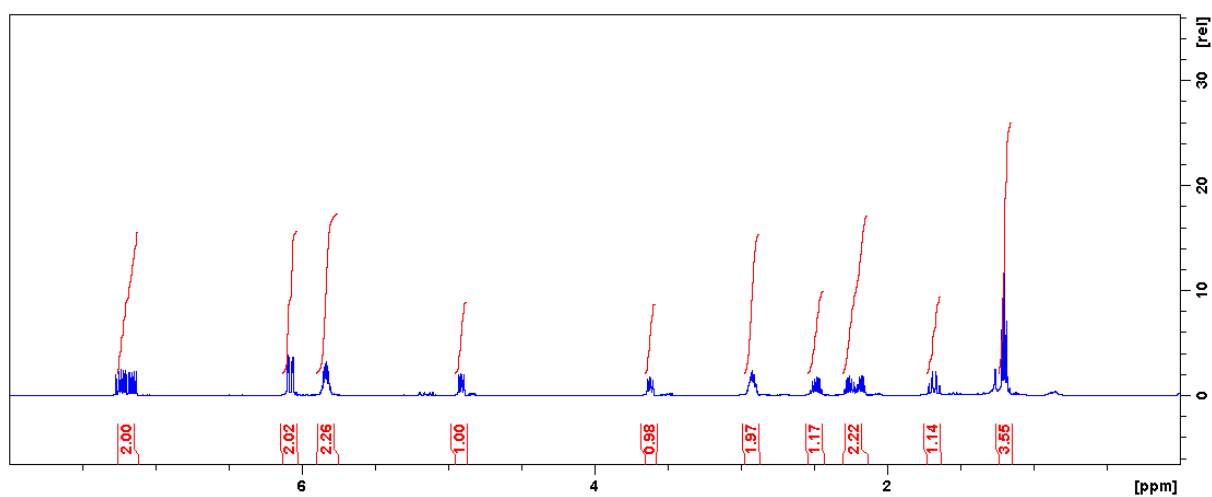
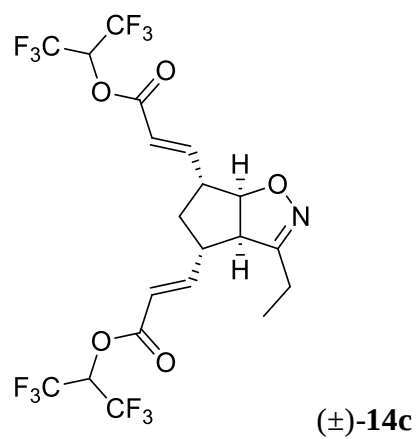
(±)-13c

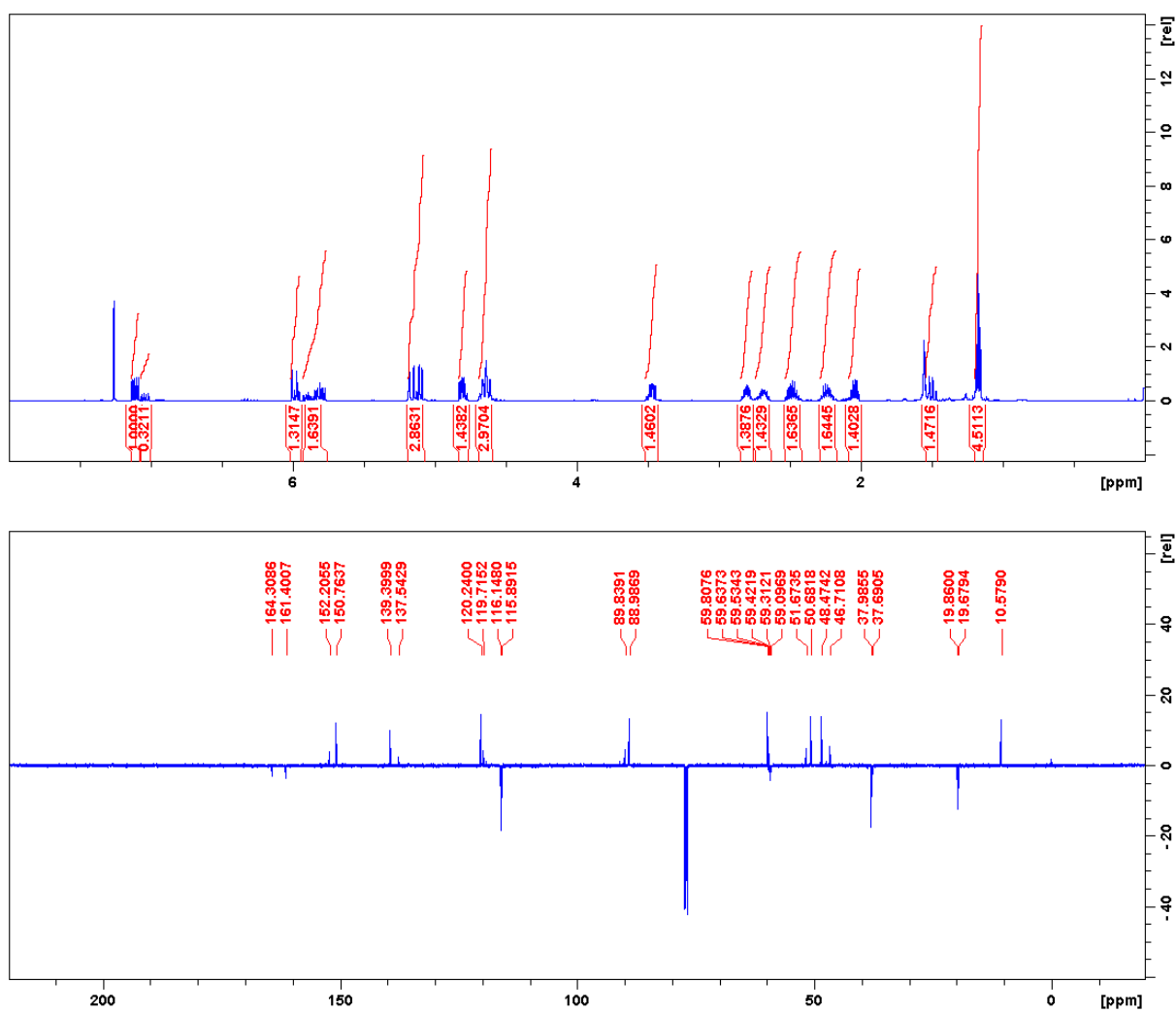
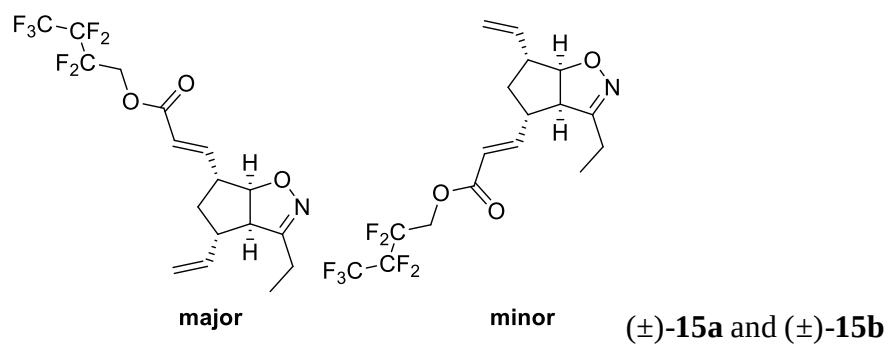


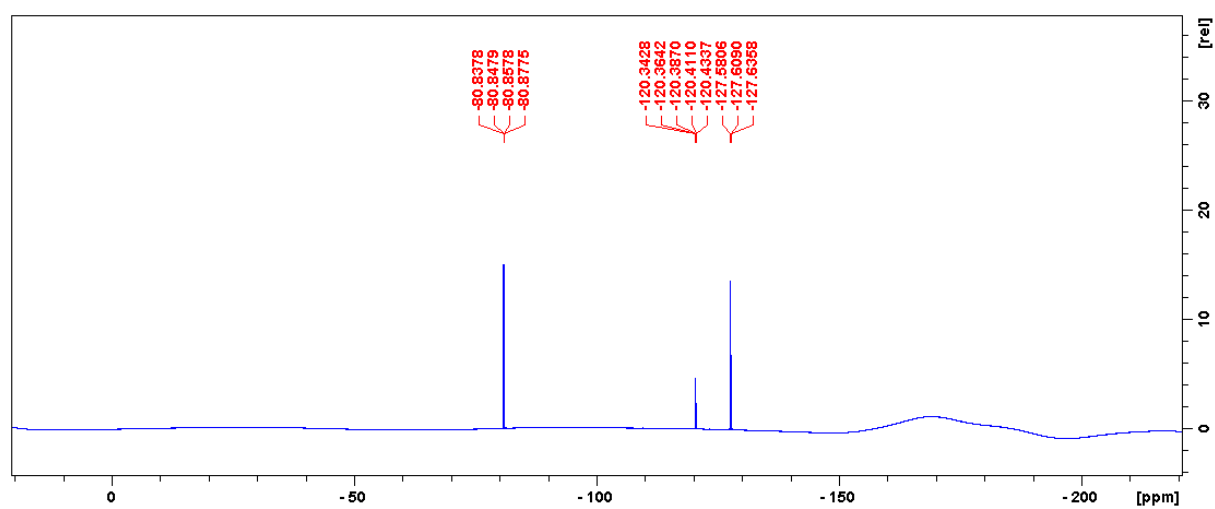


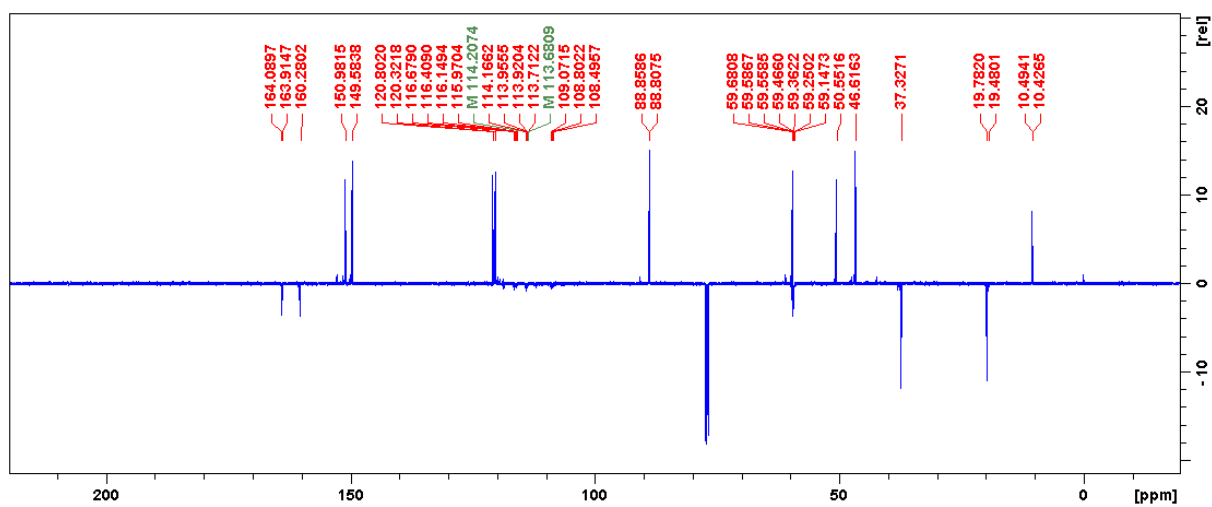
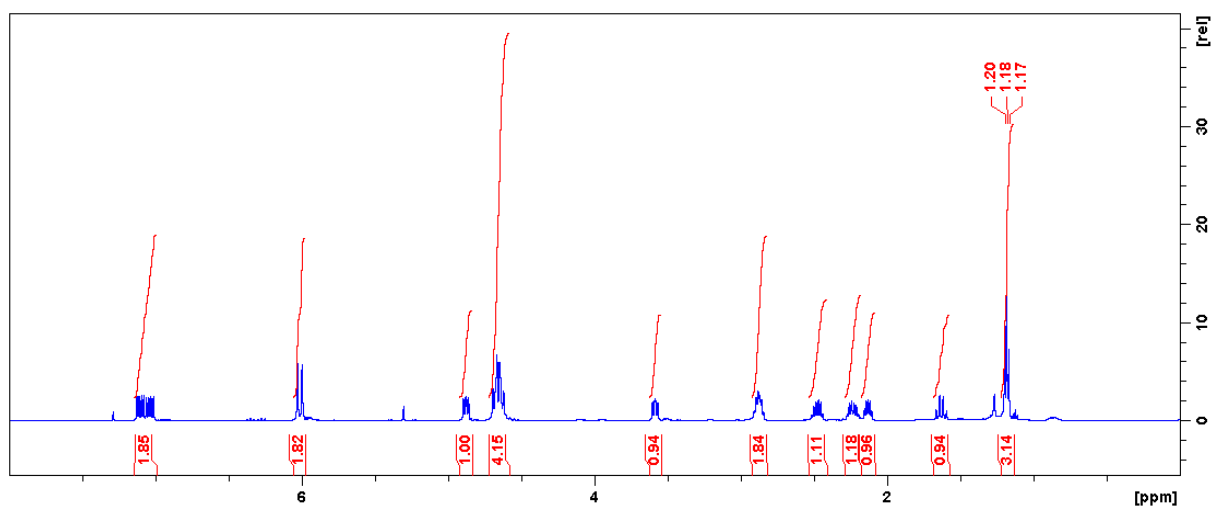
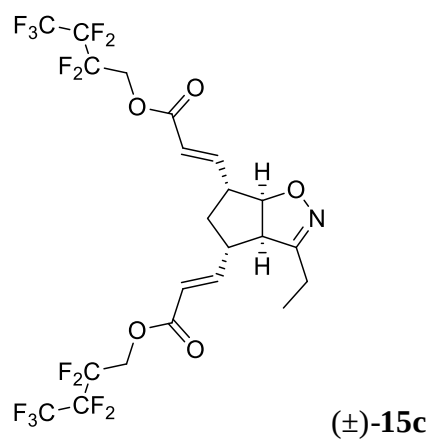


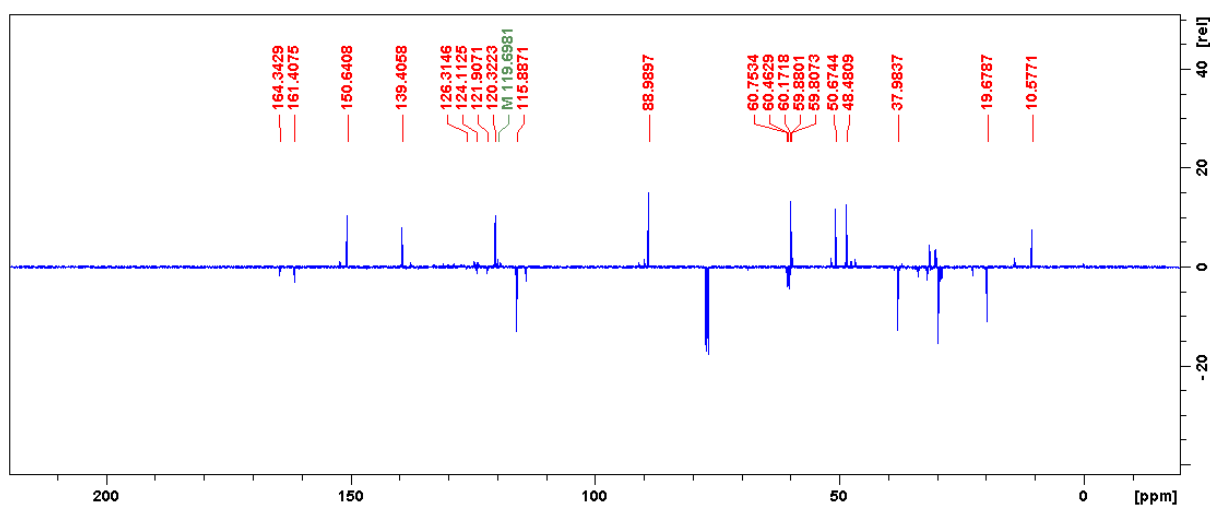
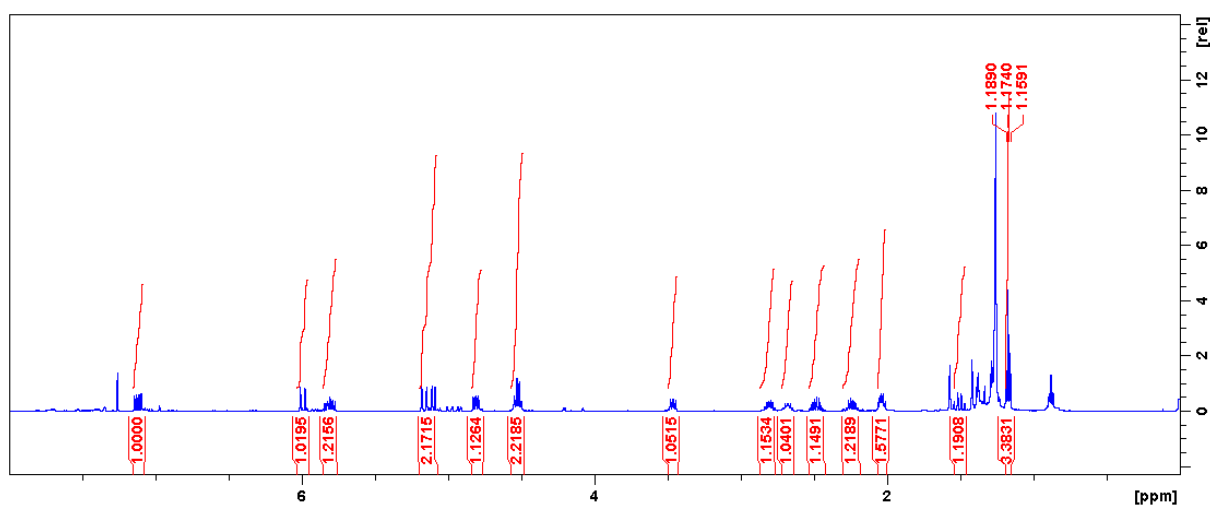
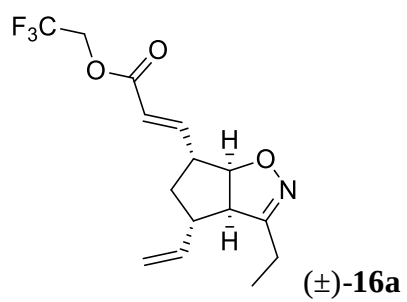


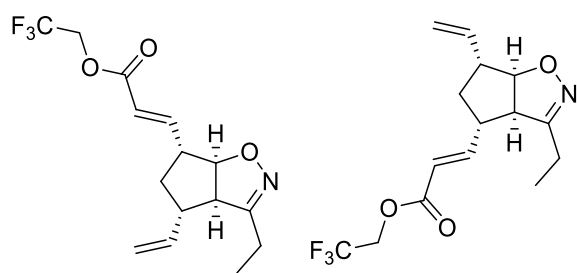








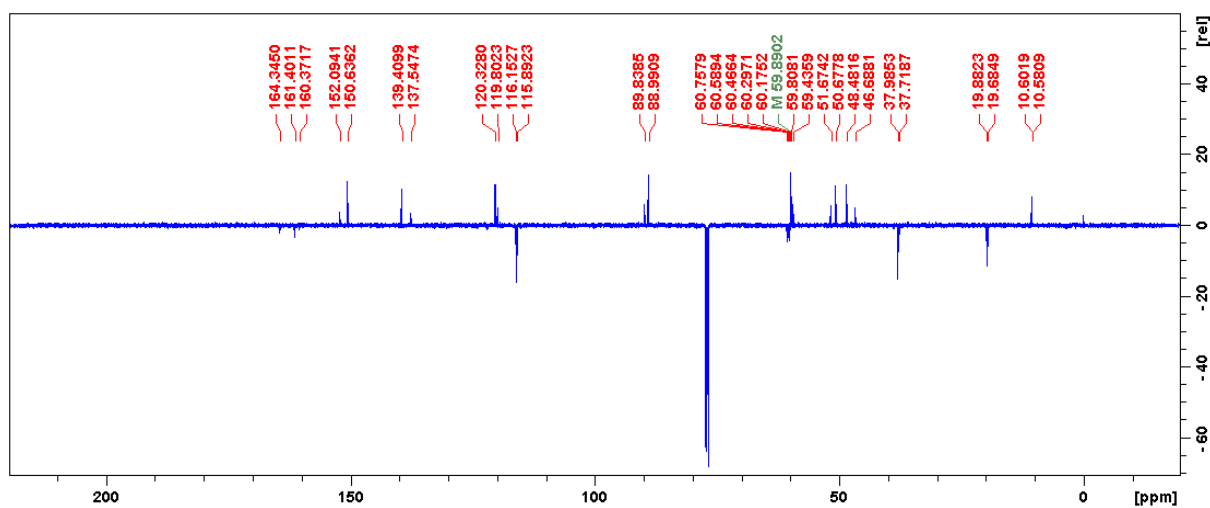
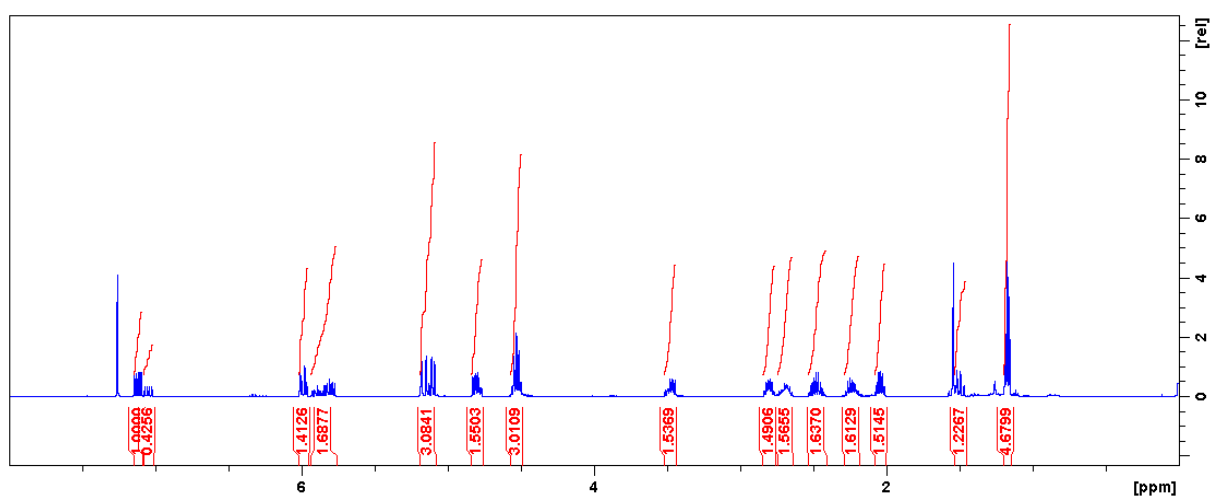


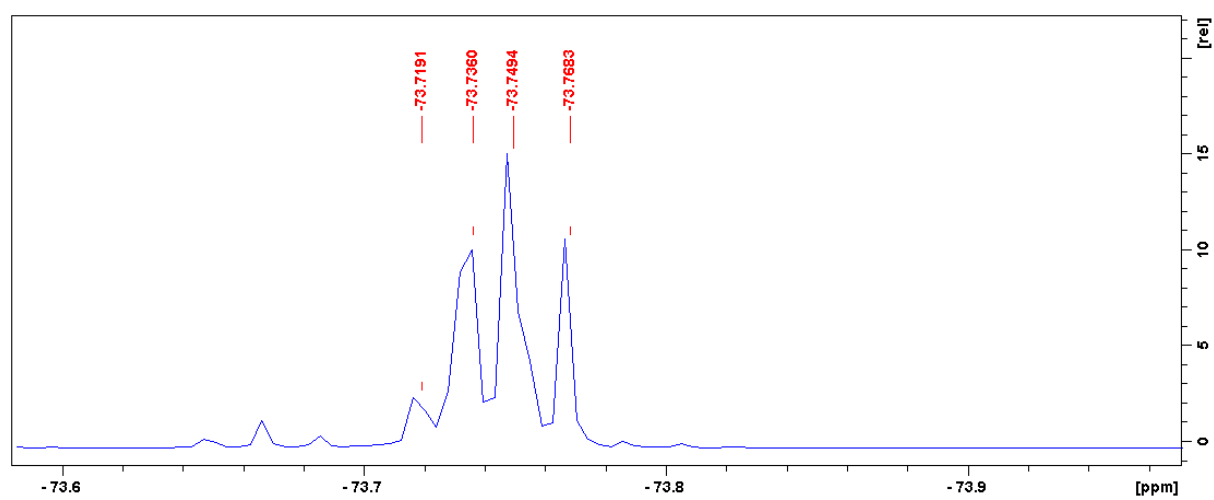


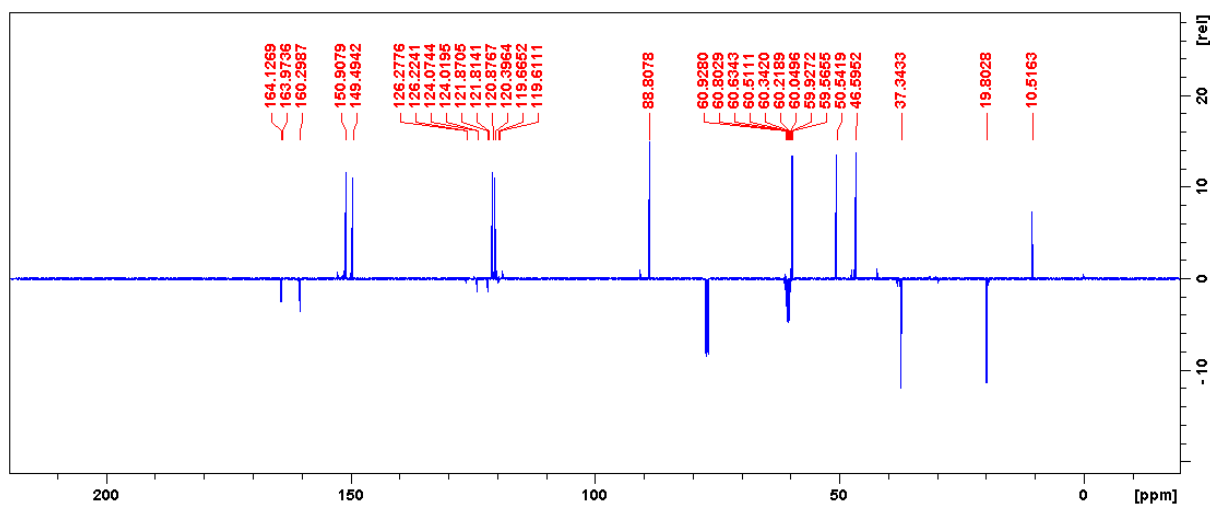
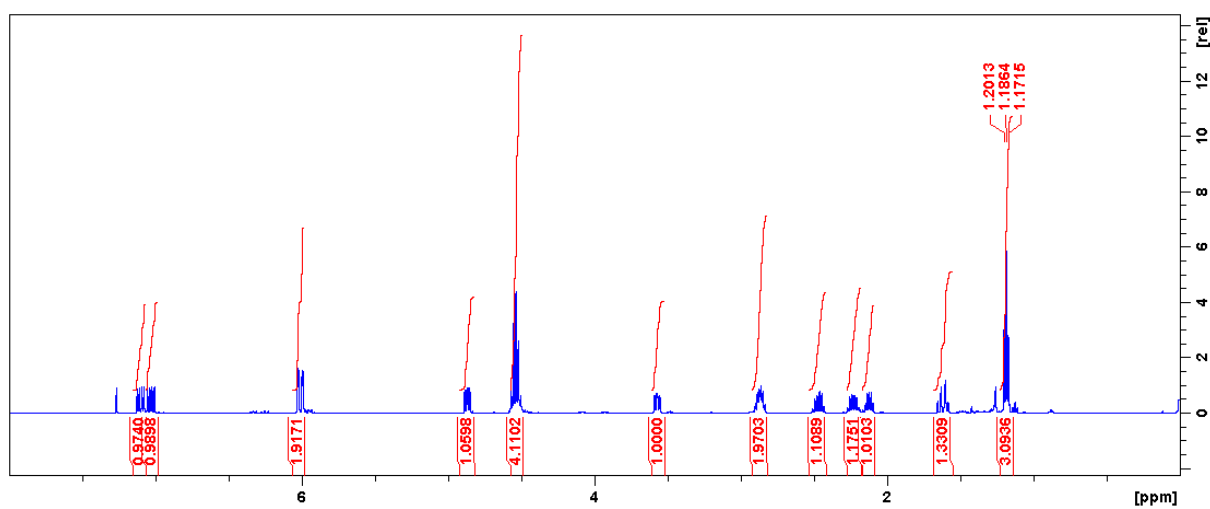
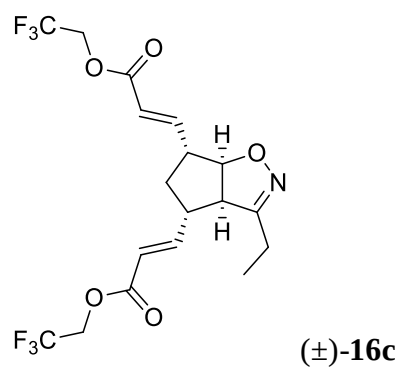
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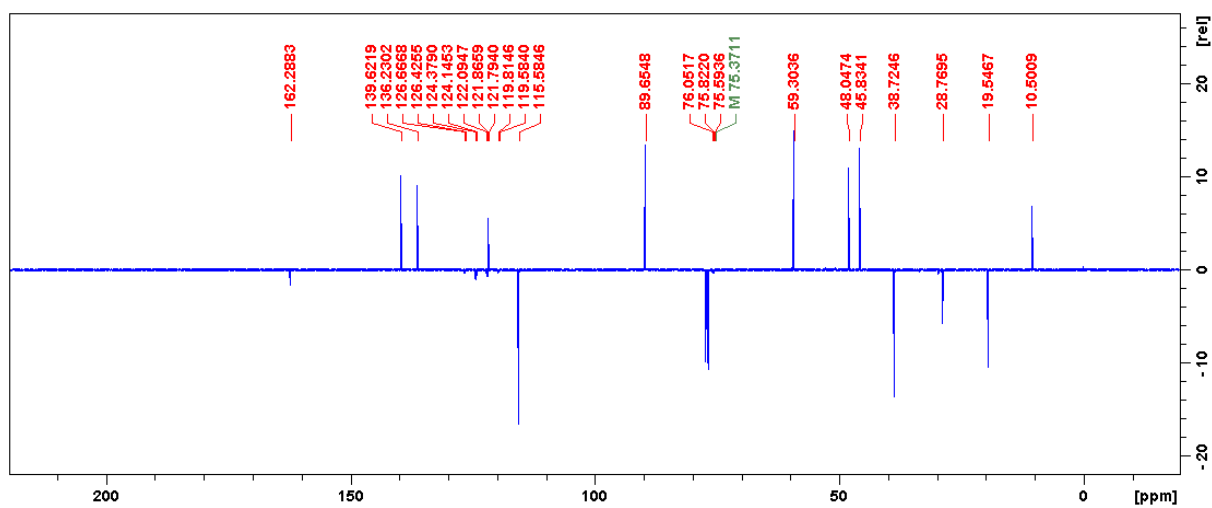
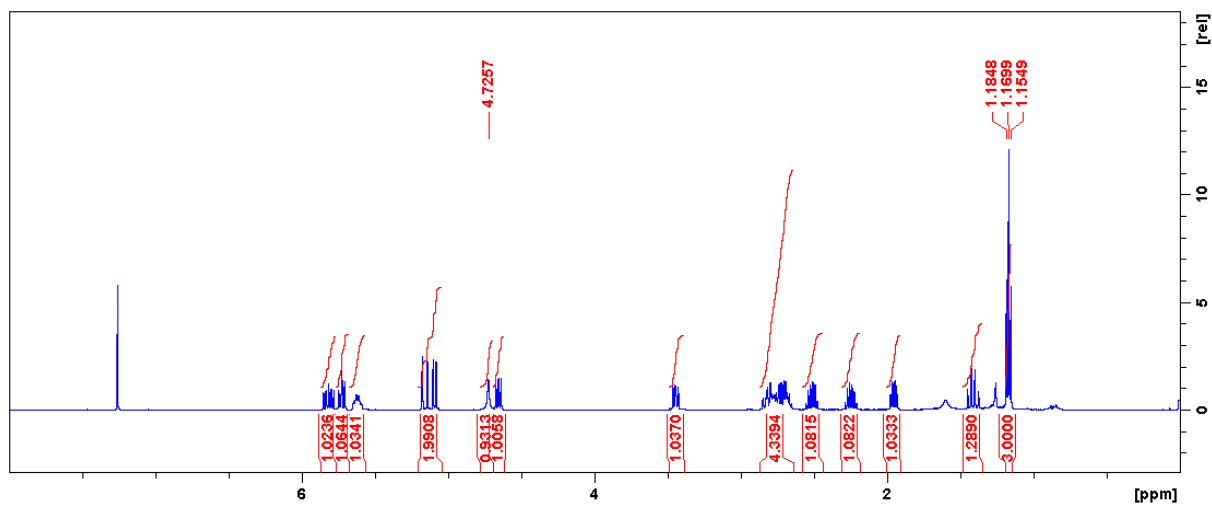
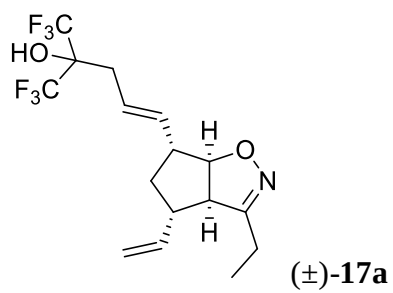
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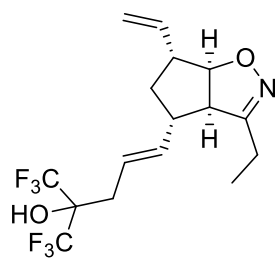
(±)-16a and (±)-16b



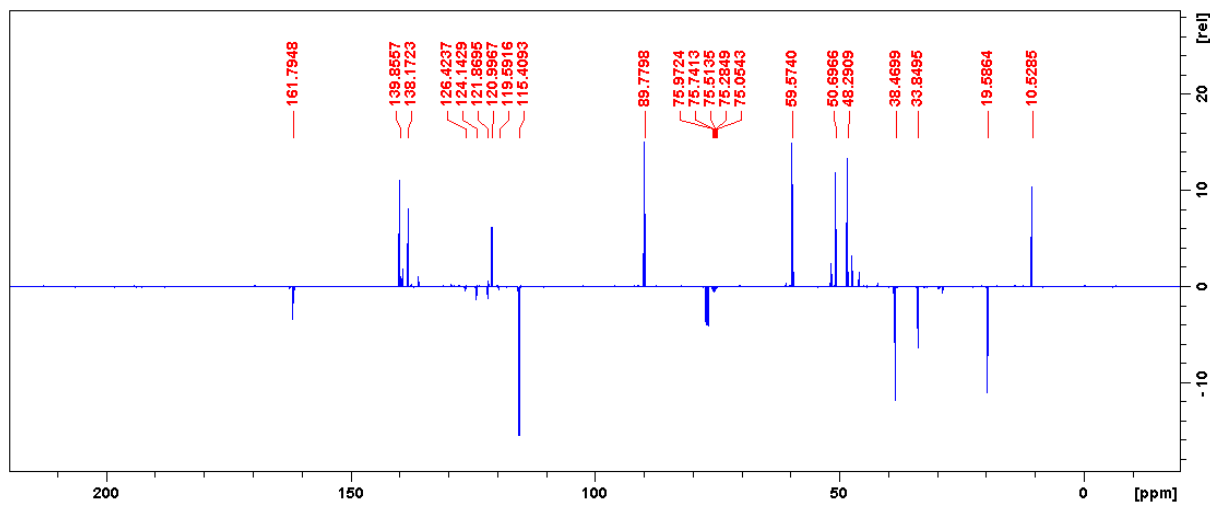
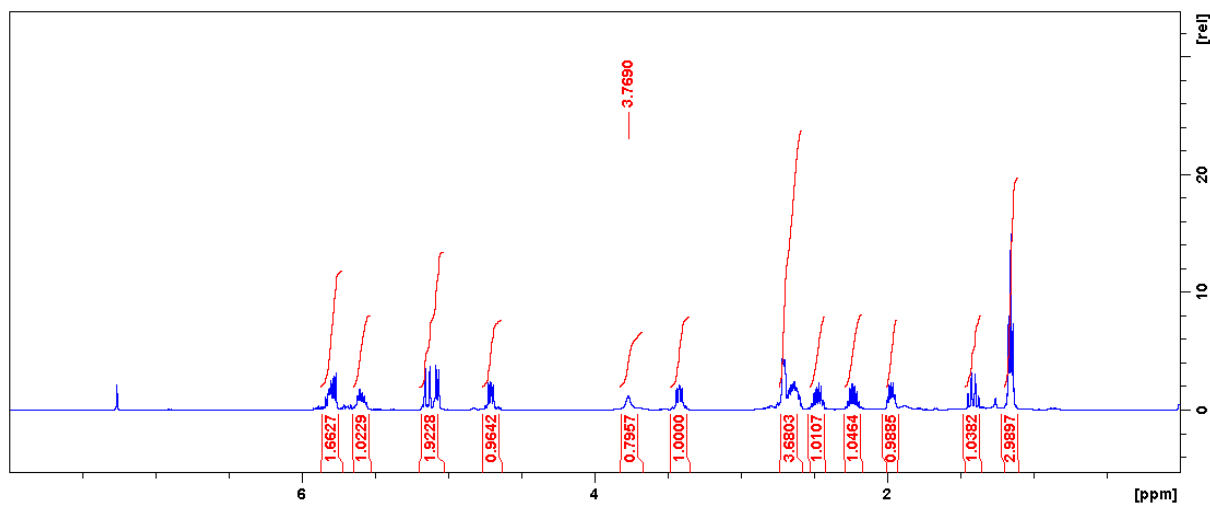


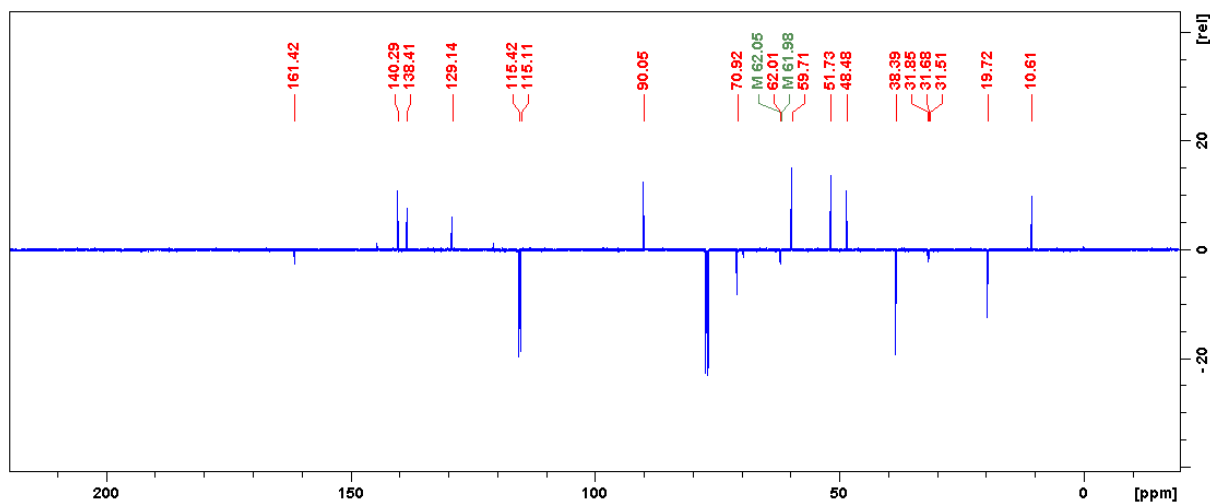
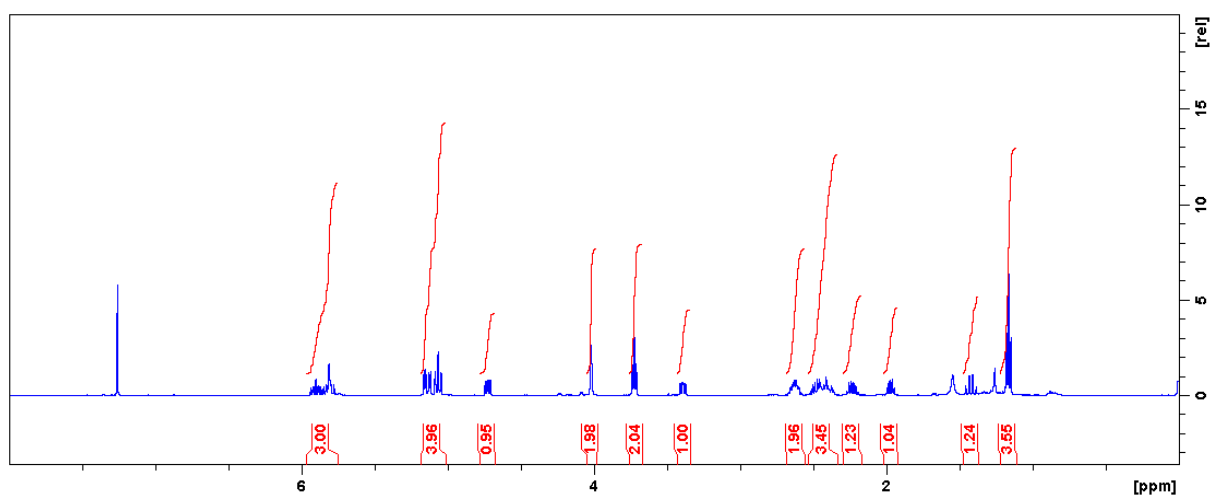
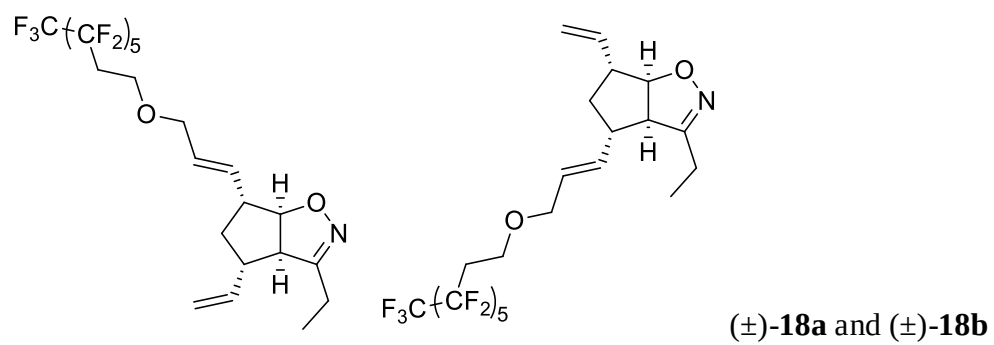


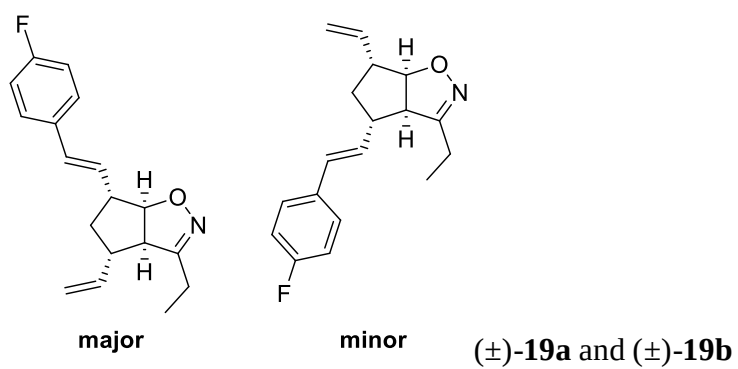




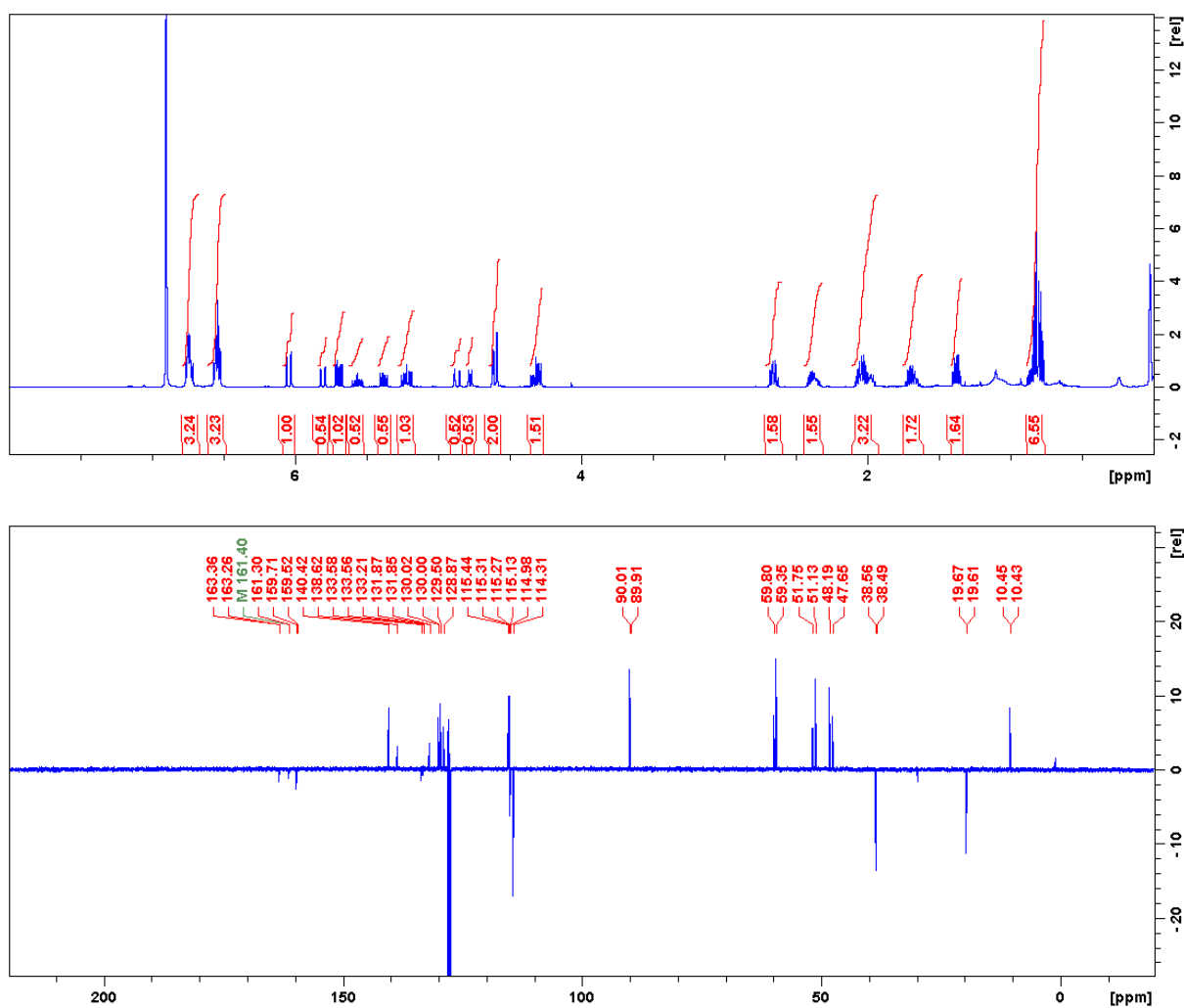
(±)-17b



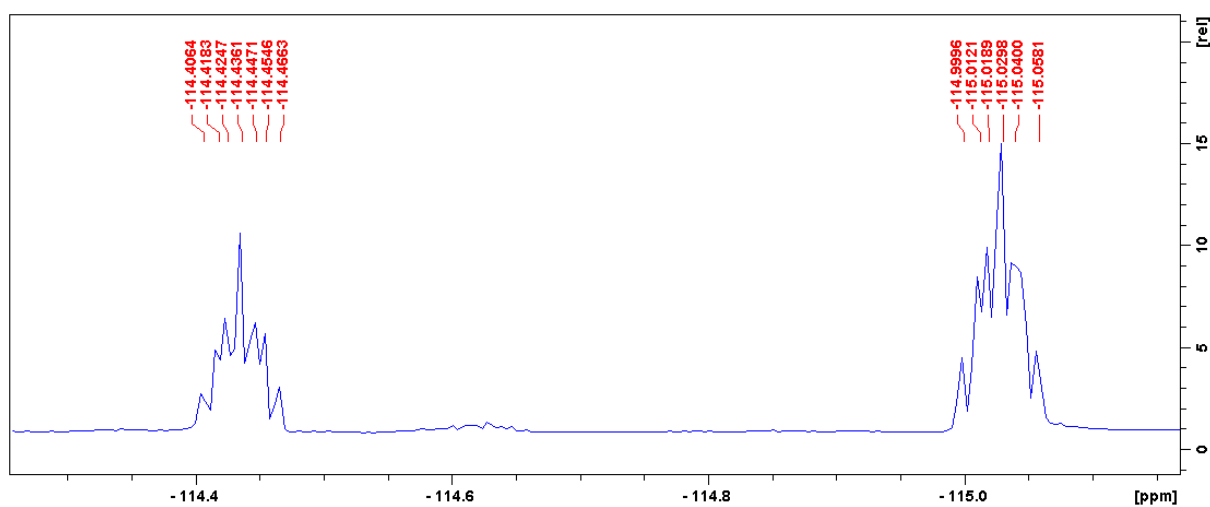
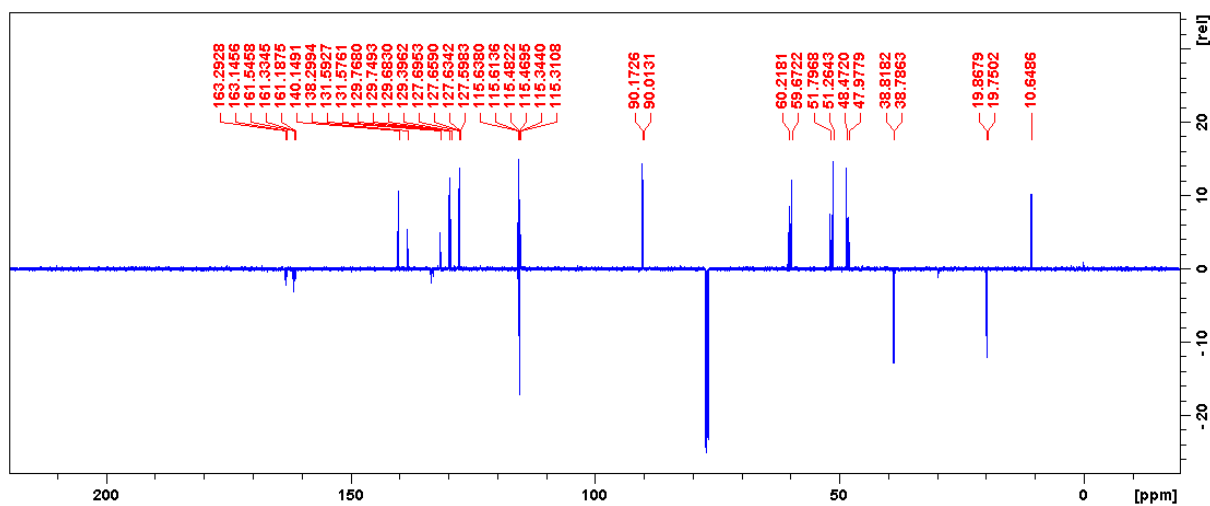
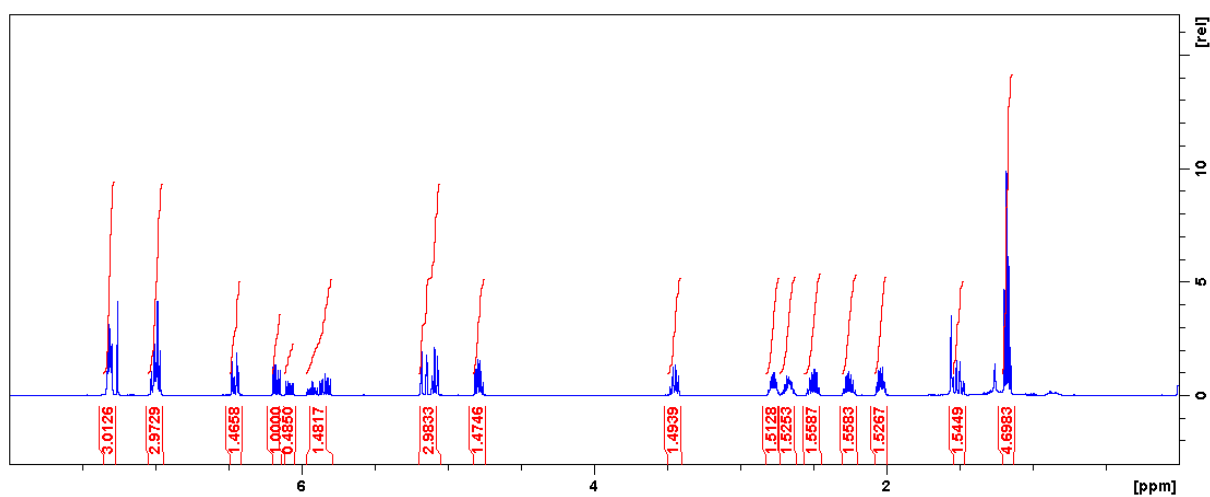


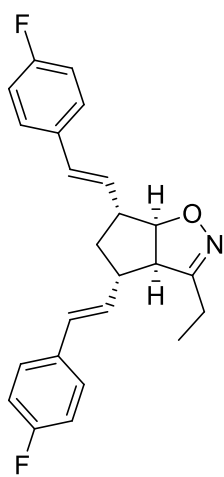


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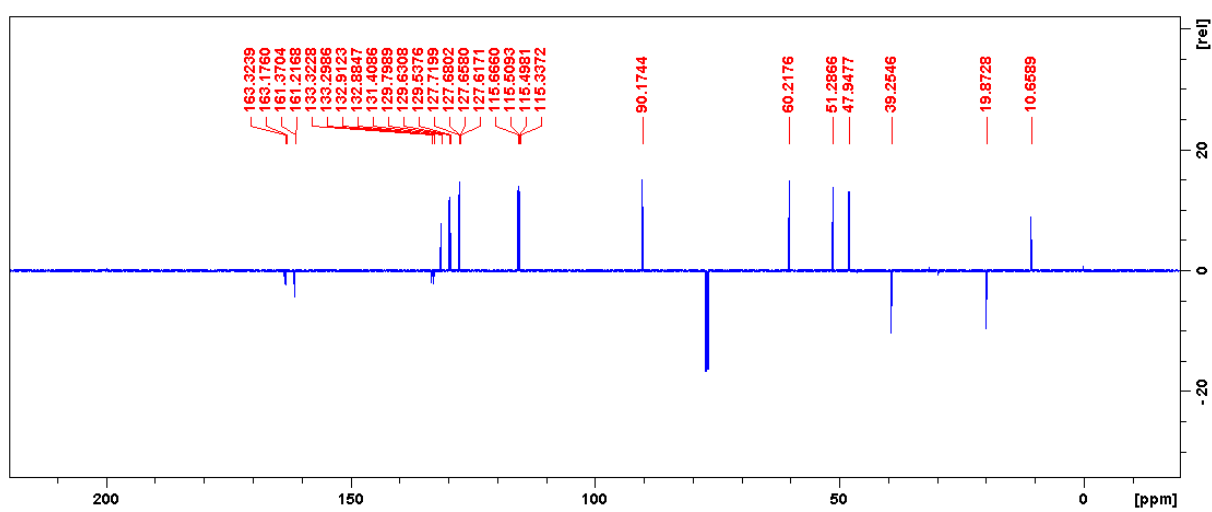
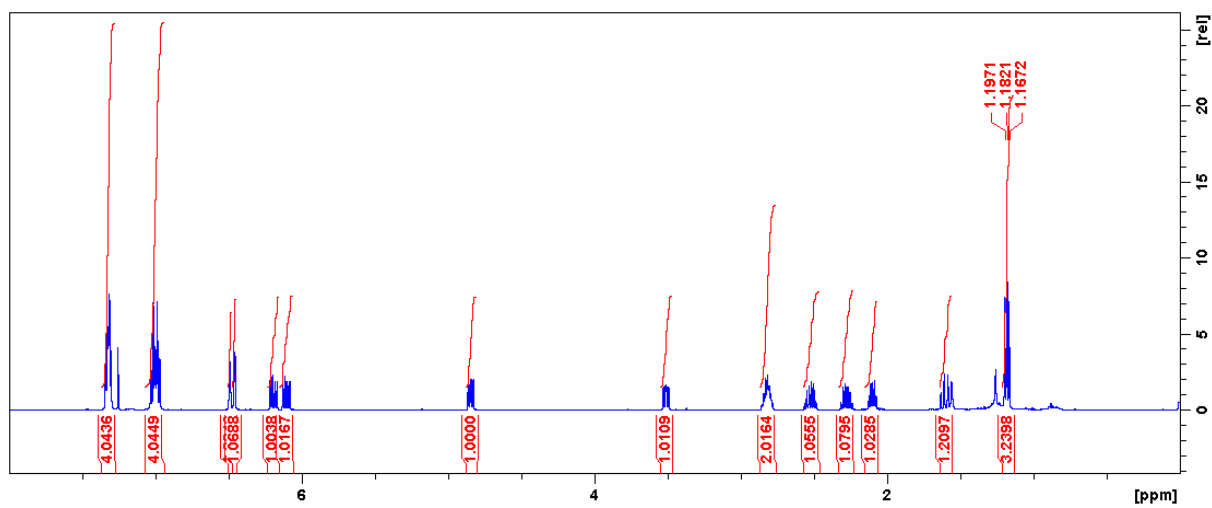


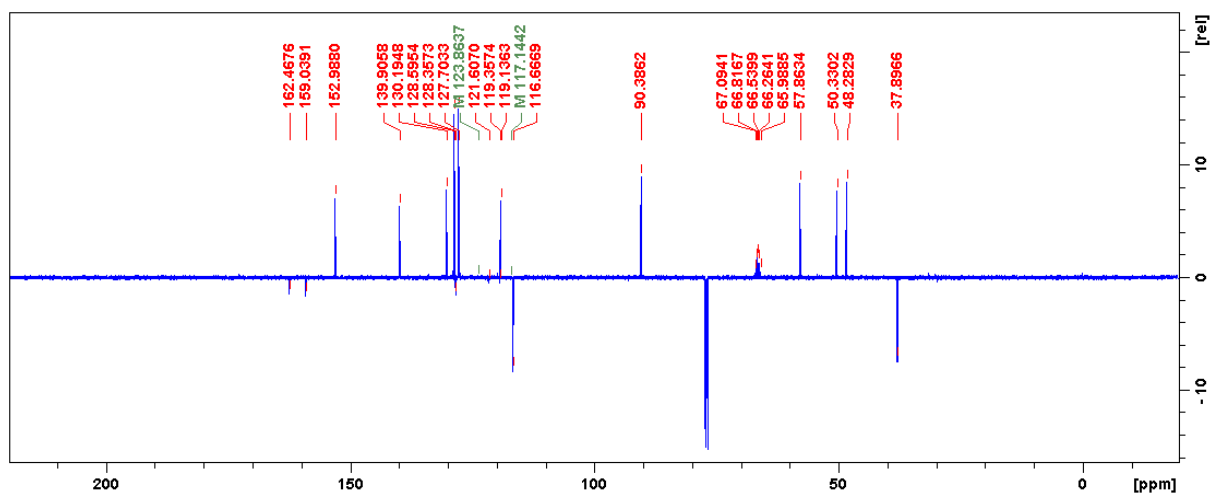
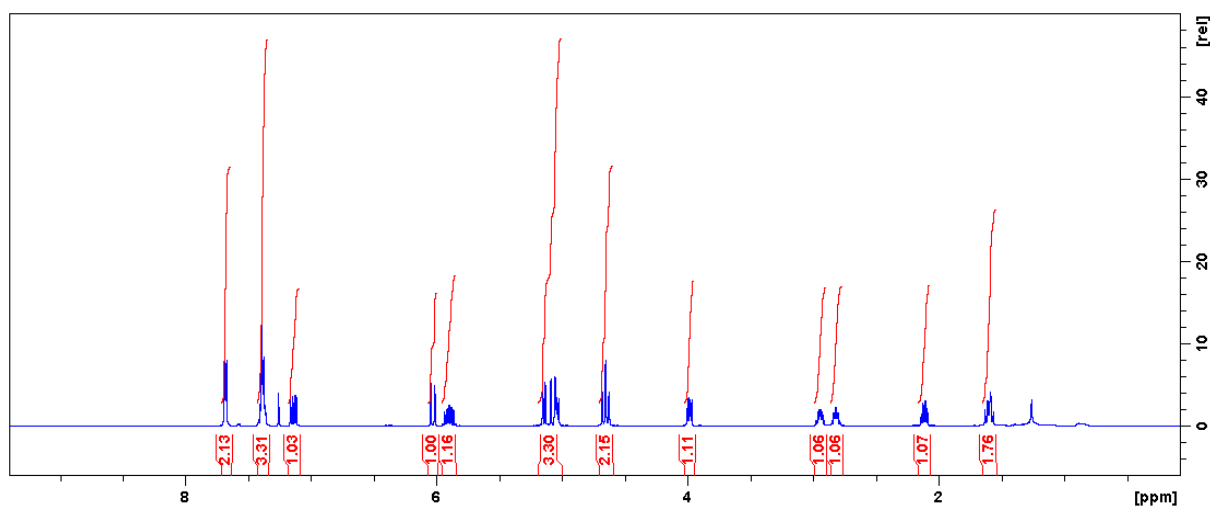
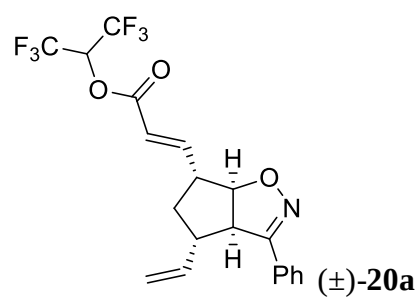
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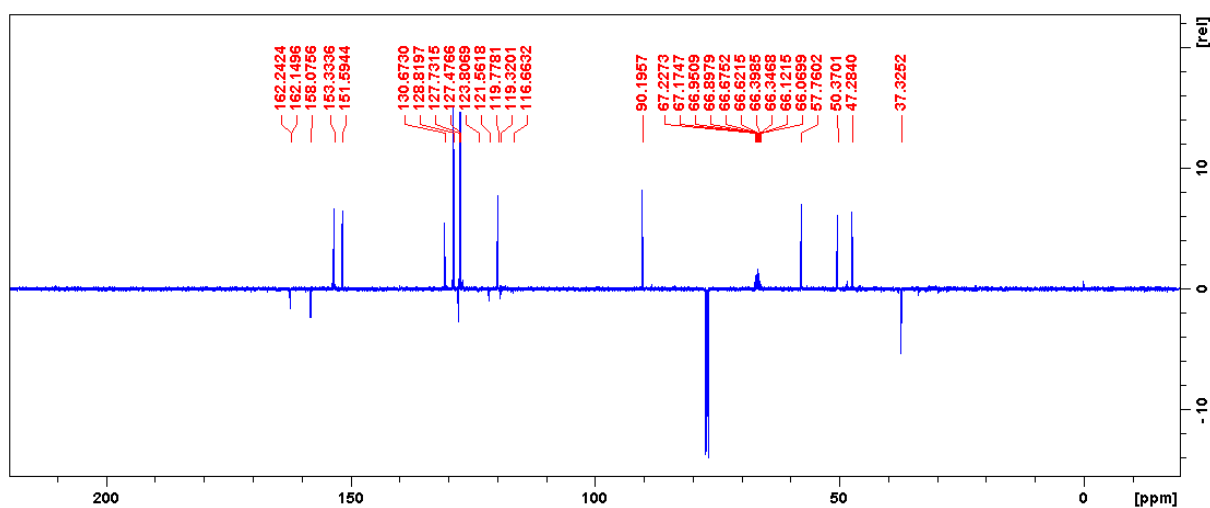
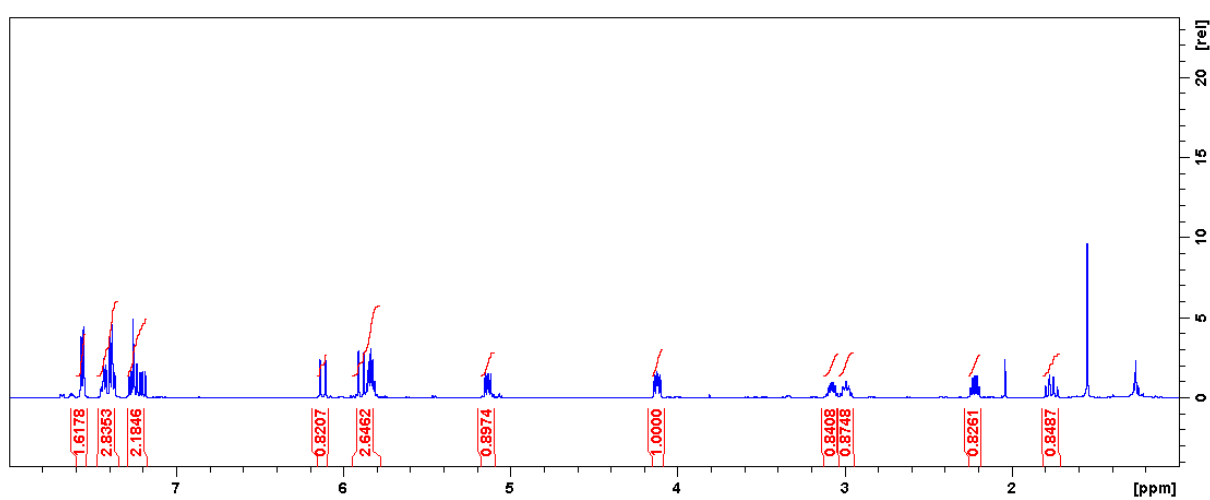
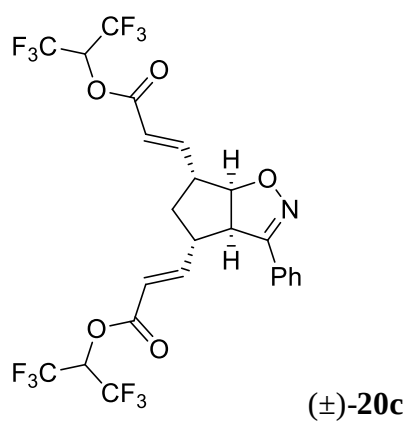


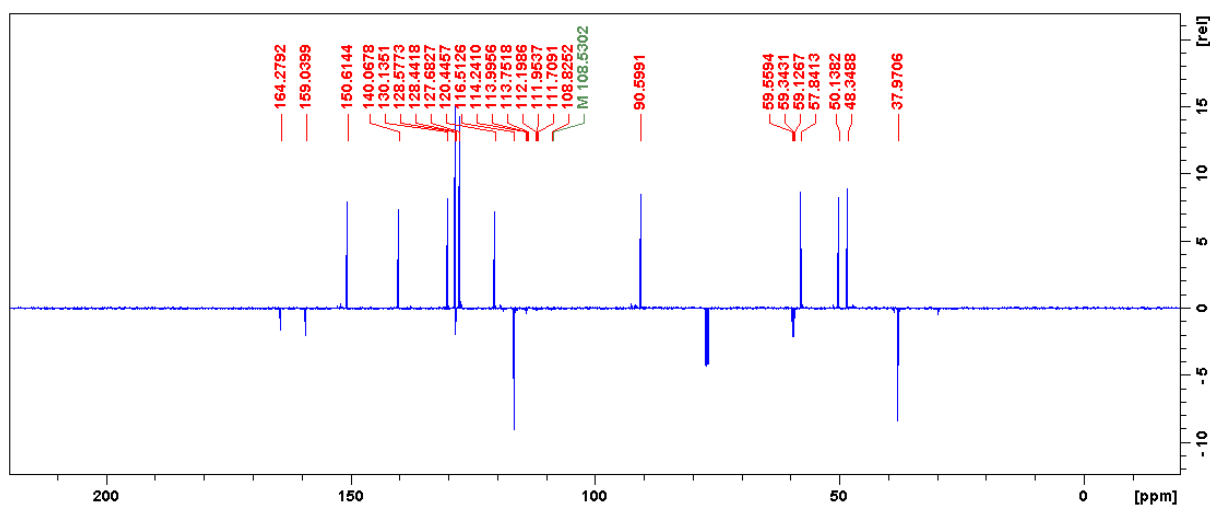
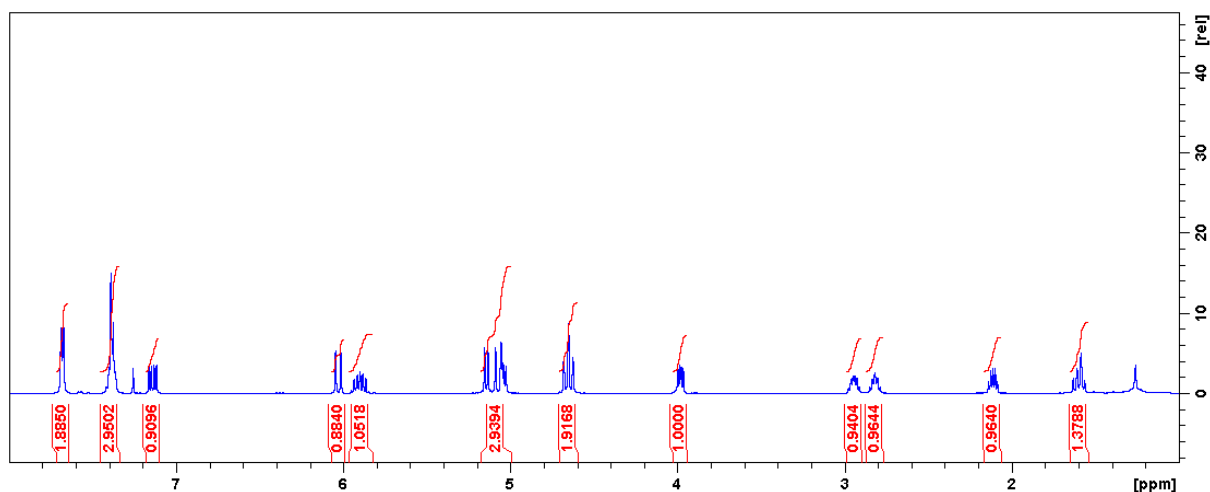
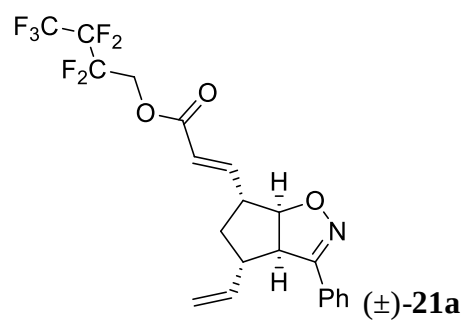


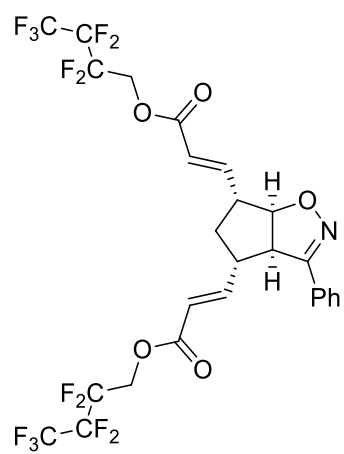
(±)-19c



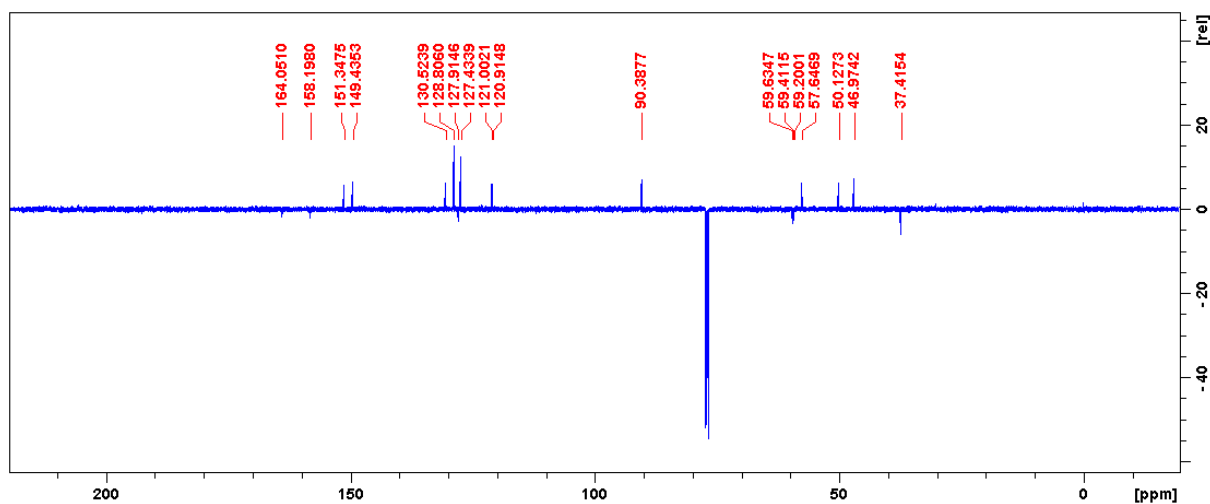
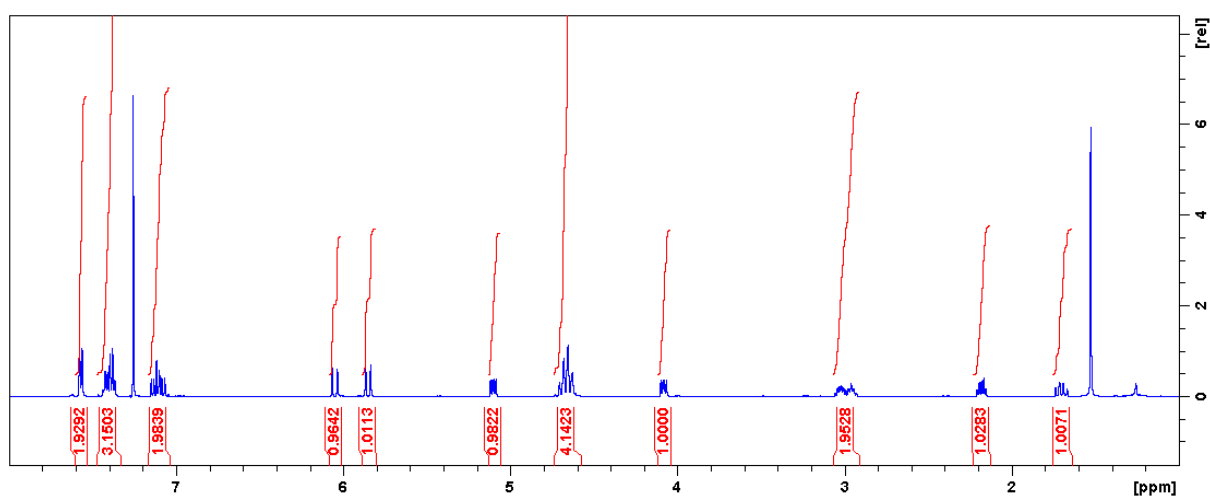


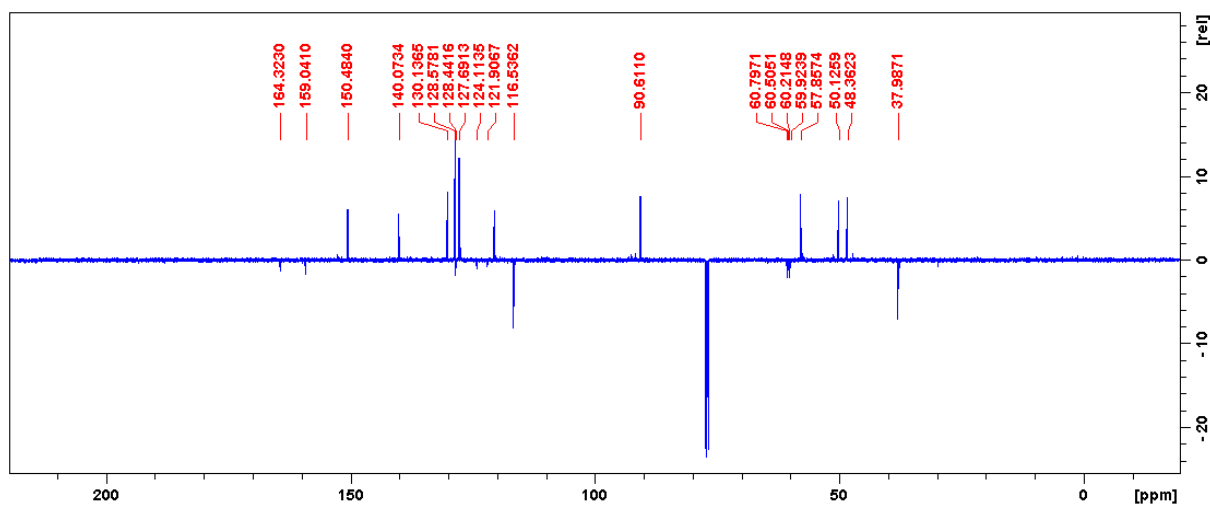
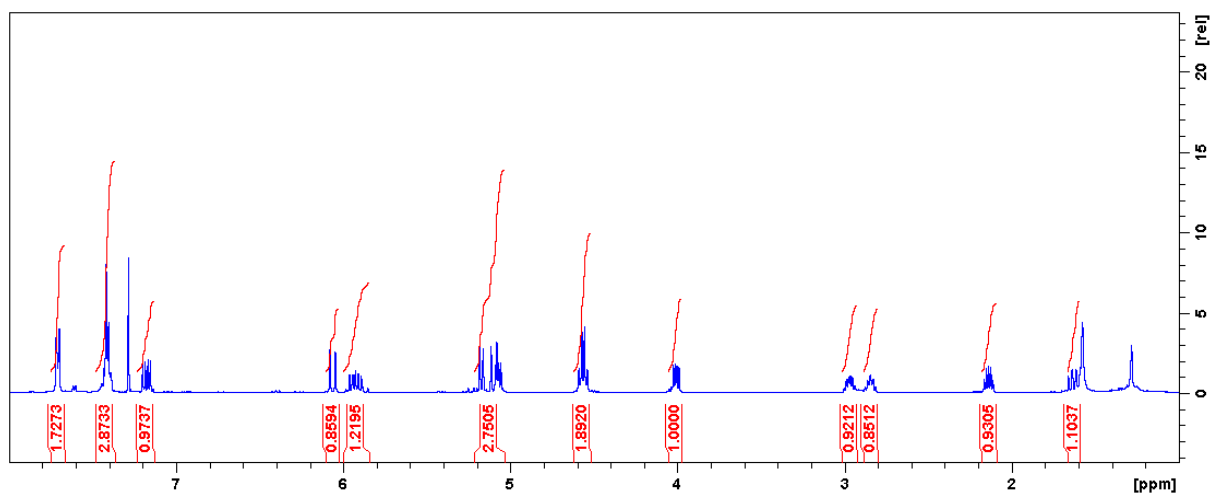
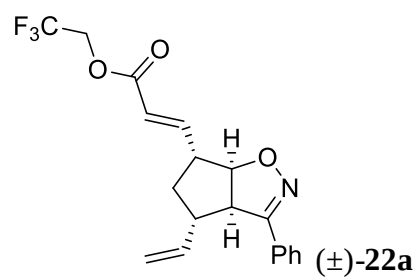


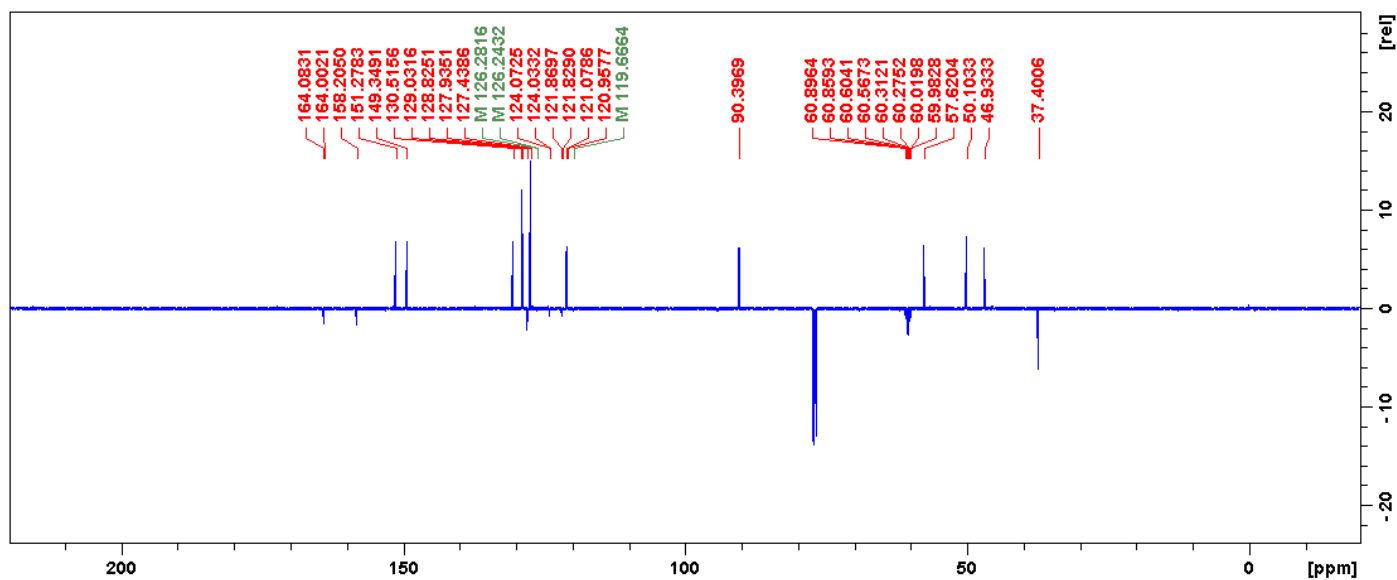
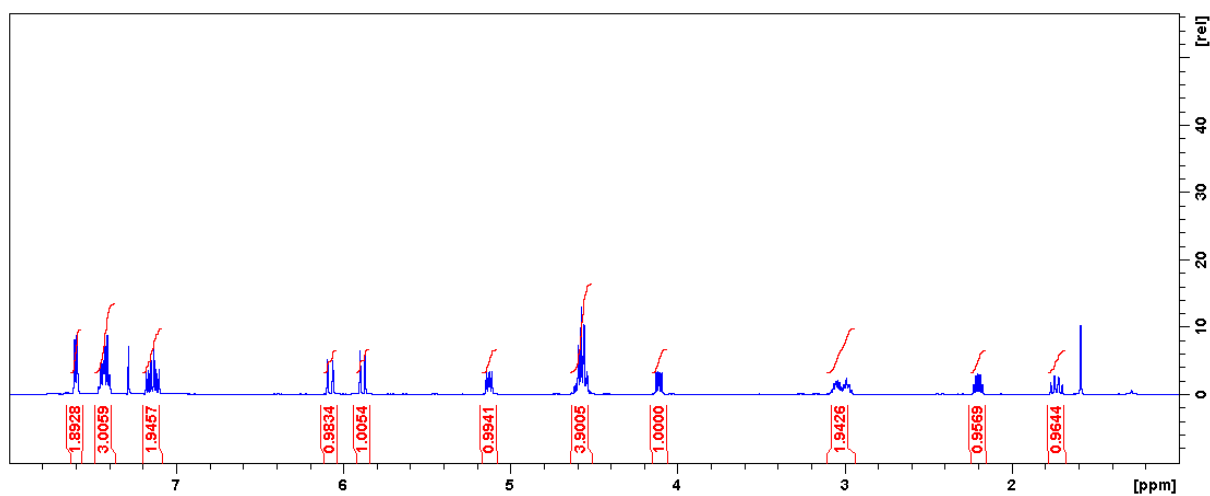
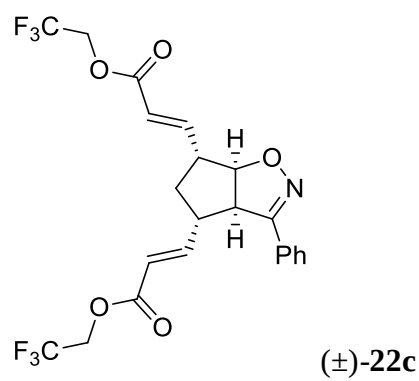


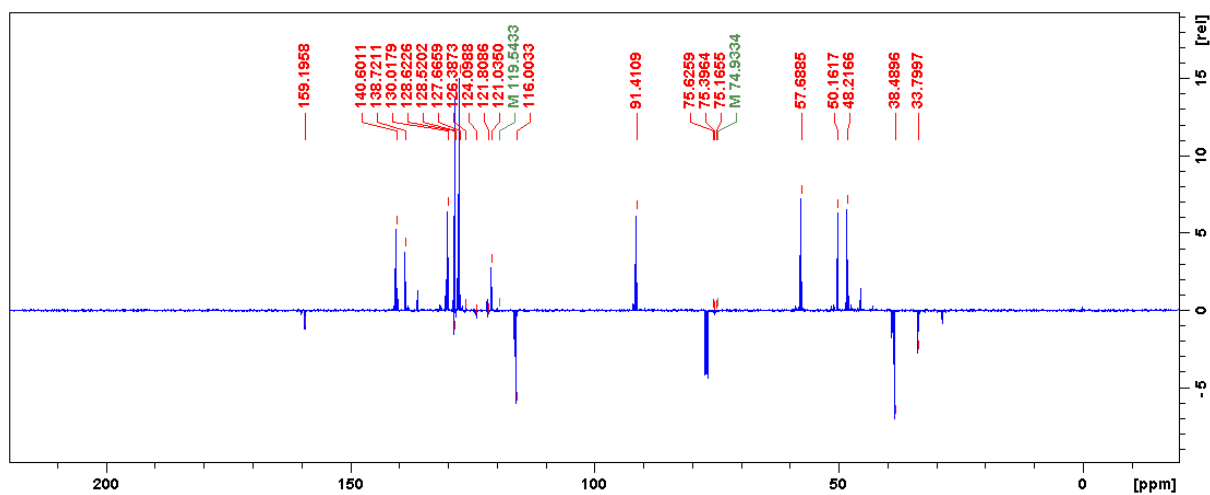
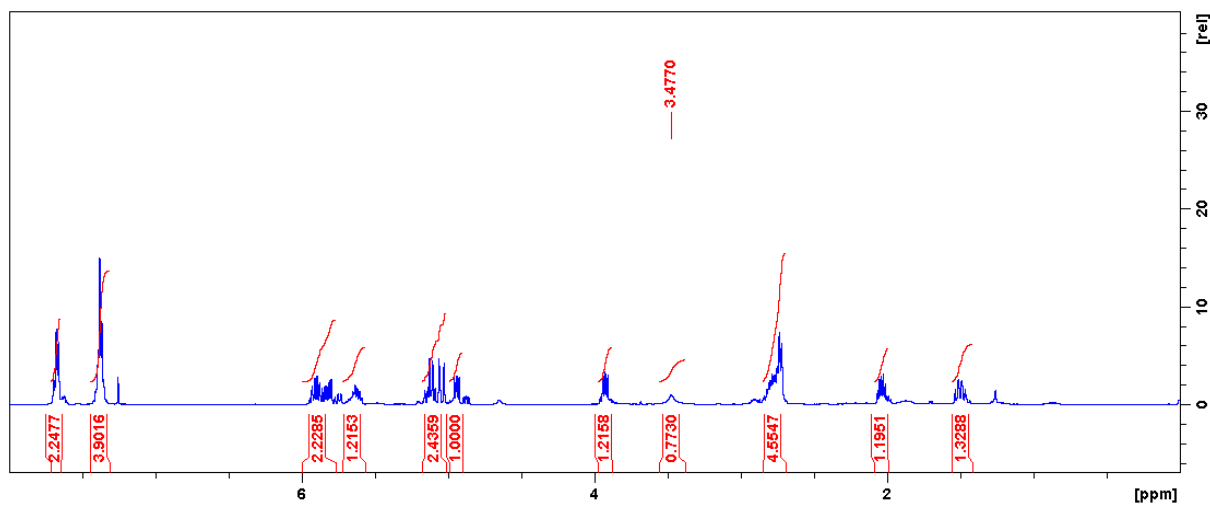
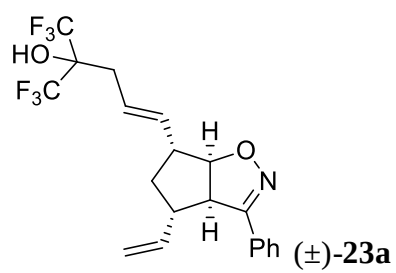


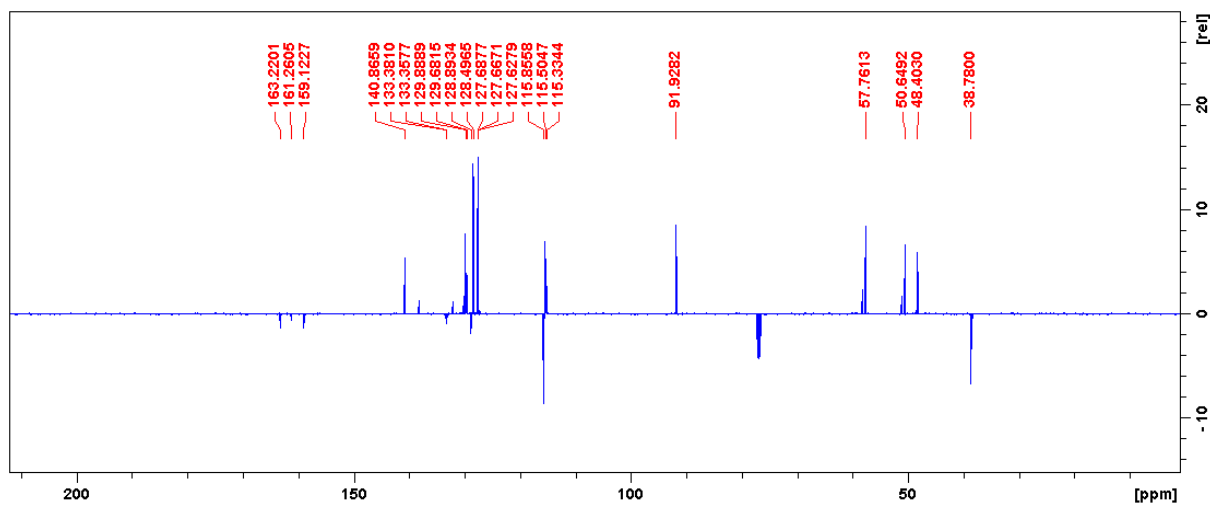
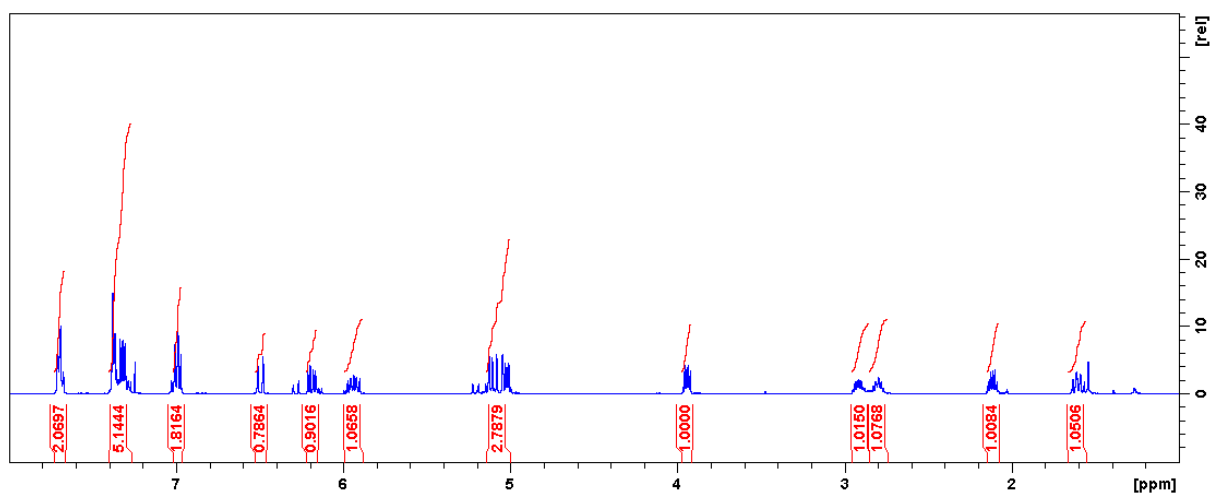
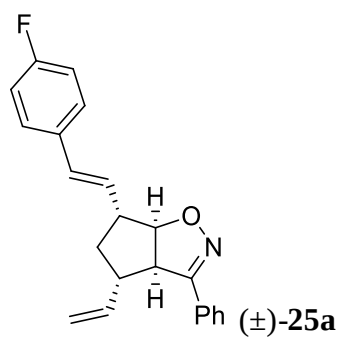
(±)-21c

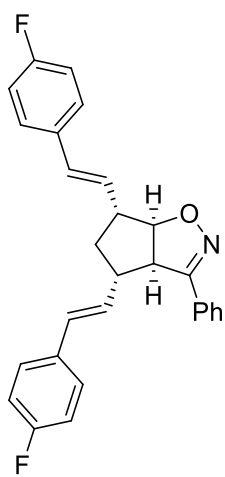




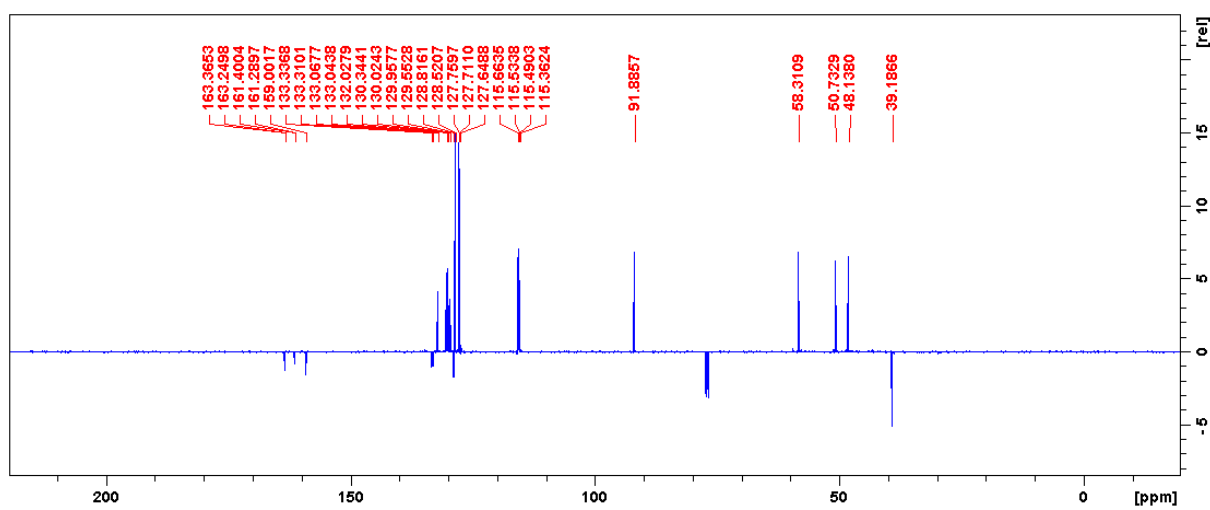
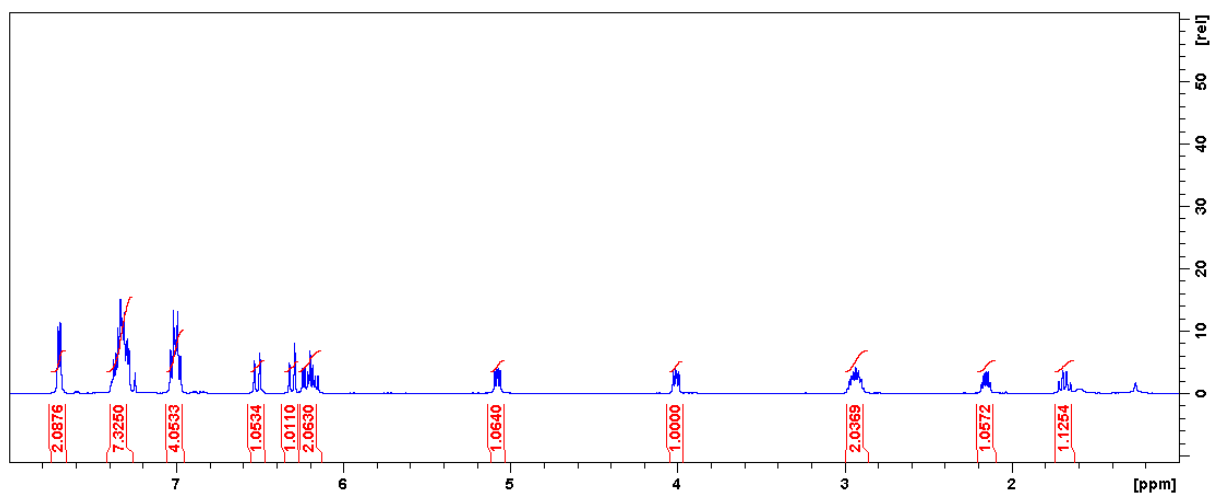








(±)-25c



References

1. Benke, Z.; Remete, A. M.; Semghouli, A.; Kiss, L. *Asian J. Org. Chem.* **2021**, *10*, 1184–1191. doi:10.1002/ajoc.202100147