Supporting Information (SI)

One-Pot Crabbé Homologation-Radical Cascade Cyclization with Memory of Chirality

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1. General Information

All reactions were performed under an argon atmosphere using freshly dried solvents. 1,4-Dioxane and Ethyl Acetate were used without any further distillation. THF was distilled over sodium benzophenone ketyl prior to use. Dry state adsorption conditions and purification were performed on silica gel 60 Å (70-230 mesh). Analytical thin layer chromatography was performed on pre-coated silica gel plates. Visualization was accomplished by UV (254 nm) and with phosphomolybdic acid in ethanol. Optical rotations were measured on a Perkin Elmer MC-241 polarimeter using a 10 cm path-length cell at 589 nm. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III spectrometer (400 MHz and 100 MHz, for ^{1}H and ^{13}C, respectively). Chemical shifts (δ) are reported in ppm and are relative to internal $CHCl_3$ (^{1}H, δ = 7.26) and $CDCl_3$ (^{13}C, δ = 77.16). Multiplicity is indicated by one or more of the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). The lists of coupling constants (*J*) correspond to the order of multiplicity assignment and are reported in Hertz (Hz). APT was used for ^{13}C spectra assignment. All melting points were uncorrected and were recorded in open capillary tubes using a Buchi melting point apparatus. High resolution mass spectra were obtained on QStar Elite (Applied Biosystems SCIEX).

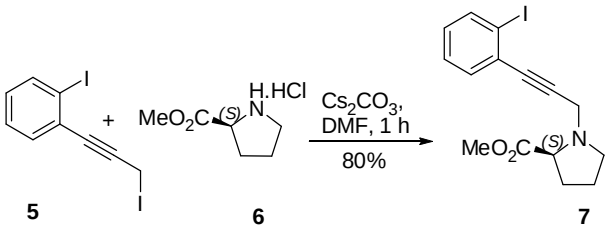
Purified compounds were analysed by chiral HPLC with double detection, with UV and circular dichroïsm (CD) detectors. The solvents for chiral chromatography (*n*-hexane, 2-PrOH, ethanol) were HPLC grade, they were degassed and filtered on a 0.45 µm membrane before use. The columns used are Chiralpak IA or AD-H (250*4.6 mm, amylose tris-(3,5-dimethylphenylcarbamate)), Chiralpak IB or OD-3 (250*4.6 mm, cellulose tris-(3,5-dimethylphenylcarbamate)), Chiralpak IC (250*4.6 mm, cellulose tris(3,5-dichlorophenylcarbamate)) and Lux-Cellulose-4 (250*4.6 mm, cellulose tris(4-chloro,3-methylphenylcarbamate)). Enantiomeric excesses were determined by integration of the peaks on the chromatograms obtained by UV detection at 230, 240 or 254 nm, and confirmed by circular dichroïsm detection at 254 nm. The sign given by the on-line circular dichroïsm detector for one enantiomer is the sign in the solvent used for the chromatographic separation. Retention times Rt in minutes, retention factors $k_i = (Rt_i$-

Rt_0)/Rt_0, enantioselectivity factor $\alpha = k_2/k_1$ and resolution are given. Rt_0 was determined by injection of tri-tertio-butyl benzene.

Iodides **15**, **16** and **17** were prepared according to our recently published procedures.[1] The syntheses of racemic starting materials and of rearranged products were achieved according to the procedures described for optically pure materials in the following. Unless otherwise stated all the yields are isolated yields of pure compounds.

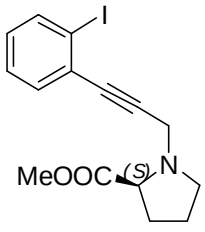
2. Synthesis of iodides 7, 10 and 14

2.1. (S)-Methyl 1-(3-(2-iodophenyl)prop-2-ynyl)pyrrolidine-2-carboxylate (7)



5 **6** **7**

1-Iodo-2-(3-iodoprop-1-ynyl)benzene **5**[1] (2.3 g, 6.25 mmol) was dissolved in DMF (15 mL) and Cs_2CO_3 (5.1 g, 15.63 mmol) was added followed by L-proline methyl ester hydrochloride **6** (1.24 g, 7.5 mmol), the reaction mixture was stirred for 1 h under argon, poured into water (30 mL), and then extracted with EtOAc (3 x 30 mL). The organic layer was washed with water (2 x 30 mL) and brine (30 mL) and dried over anhydrous sodium sulfate. After evaporation of the solvent, the residue was purified over a short pad of silica gel (pentane/EtOAc, 90/10) to afford **7** as brown oil (1.85 g, 80%).



$C_{15}H_{16}INO_2$
Mol. Wt.: 369.1975

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83 (1H, dd, *J*= 8.0 and 0.8, CH_{ar}), 7.43 (1H, dd, *J*= 7.8 and 1.5, CH_{ar}), 7.29 (1H, td, *J*= 7.6 and 1.0, CH_{ar}), 6.98 (1H, td, *J*= 7.8 and 1.8, CH_{ar}), 3.84 (2H, AB pattern, J_{AB}=17.6, Δν=19.6 Hz), 3.74 (3H, superimposed s, OCH_3), 3.74-3.69 (1H, m), 3.20-3.15 (1H, m), 2.98-2.96 (1H, m), 2.26-2.17 (1H, m), 2.07-1.83 (3H, m).

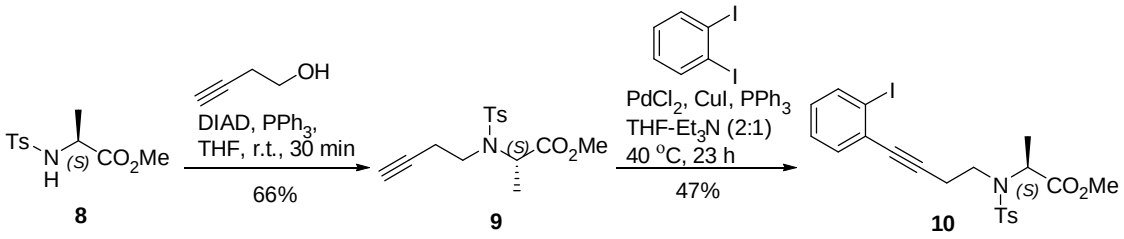
[1] M. Nechab, D. Campolo, J. Maury, P. Perfetti, N. Vanthuyne, D. Siri, M. P. Bertrand, *J. Am. Chem. Soc.*, **2010**, *132*, 14742.

^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.3 (CO), 138.8 (CH_{ar}), 133.0 (CH_{ar}), 129.8 (C_{ar}), 129.4 (CH_{ar}), 127.9 (CH_{ar}), 100.8 (C_{ar}), 88.5 (C≡C), 87.4 (C≡C), 62.7 (CH), 52.6 (CH_2), 52.2 (OCH_3), 42.2 (CH_2), 29.8 (CH_2), 23.6 (CH_2).

HRMS (ESI): m/z: calcd for $[M+H]^+$ $C_{15}H_{17}N_2OI$: 370.0299, found: 370.0299.

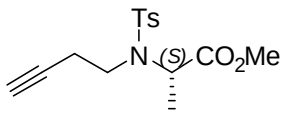
$[\alpha]_D^{25}$= -93.4 (c= 1.52, CH_2Cl_2)

2.2. (S)-Methyl 2-(N-(4-(2-iodophenyl)but-3-ynyl)-4-methylphenylsulfonamido)propanoate (10)



Synthesis of 9:

To a solution of (*S*)-methyl 2-(4-methylphenylsulfonamido)propanoate **8** (1.30 g, 5.05 mmol) and PPh_3 (2.65 g, 10.10 mmol) in THF (25mL) was added, at room temperature, a solution of 3-butyn-1-ol (535 mL, 7.07 mmol) in THF (5mL). Subsequently a solution of DIAD (2mL, 10.10 mmol) in THF (10 mL) was added slowly to the above solution. The reaction was monitored by TLC (dichloromethane/Et_2O: 98/2) and stopped after stirring for 30 min. The solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel (pentane/dichloromethane, 5/5 to 100% dichloromethane) to afford the compound **9** as a liquid (1.04 g, 66%).



$C_{15}H_{19}NO_4S$
Mol. Wt.: 309.3807

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69 (2H, d, *J*= 8.3, CH_{ar}), 7.29 (2H, d, *J*= 8.0, CH_{ar}), 4.63 (1H, q, *J*= 7.3, CH), 3.51 (3H, s, CH_3O), 3.45 (1H, ddd, *J*= 5.3, 10.3 and 15.3, CH_2N), 3.30 (1H, ddd, *J*= 5.3, 10.3 and 15.3, CH_2N), 2.70 (1H, dddd, J= 2.8, 5.3, 10.3 and 15.6, $CH_2C{\equiv}CH$), 2.52 (1H, dddd, J= 2.8, 5.8, 10.3 and 16.1, $CH_2C{\equiv}CH$), 2.42 (3H, s, CH_3), 2.00 (1H, t, *J*= 2.5, CH≡C), 1.43 (3H, d, *J*= 7.3, CH_3).

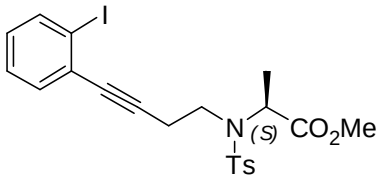
^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.9 (CO_2Me), 143.7 (C_{ar}), 136.7 (C_{ar}), 129.7 (2xCH_{ar}), 127.5 (2xCH_{ar}), 81.2 (C≡), 70.3 (CH≡), 55.5 (CHN), 52.2 (CH_3O), 44.6 (CH_2N), 21.6 (CH_3), 21.4 (CH_2), 17.0 (CH_3).

HRMS (ESI): m/z: calcd for $[M+H]^+$ $C_{15}H_{20}NO_4S$: 310.1108, found: 310.1108.

$[\alpha]_D^{25}$= -44 (c=1.15 , $CHCl_3$).

Synthesis of 10

To a solution of *o*-diiodobenzene (596 mg, 1.81 mmol) in a 2:1 mixture of THF:Et_3N (7.5 ml) was added $PdCl_2$ (6 mg, 0.04 mmol), CuI (2 mg, 0.07 mmol) and PPh_3 (38 mg, 0.14mmol). This mixture was stirred for 10 min at 40 °C. Then **9** (587 mg, 1.90 mmol) was added to the reaction mixture. The mixture was stirred for 23 h at 40 °C. Then, a 1M HCl solution (20 mL) was added to the reaction mixture and the latter was extracted with AcOEt (3 x 10 mL). After drying over MgSO4, and concentration in vacuo, crude **10** was purified by flash chromatography on silica gel (pentane/Et_2O, 100/0 to 80/20) to afford pure **10** as a yellow oil (439 mg, 47% (79% with respect to transformed diodobenzene, 41% of this starting material was recovered)).



$C_{21}H_{22}INO_4S$
Mol. Wt.: 511.3732

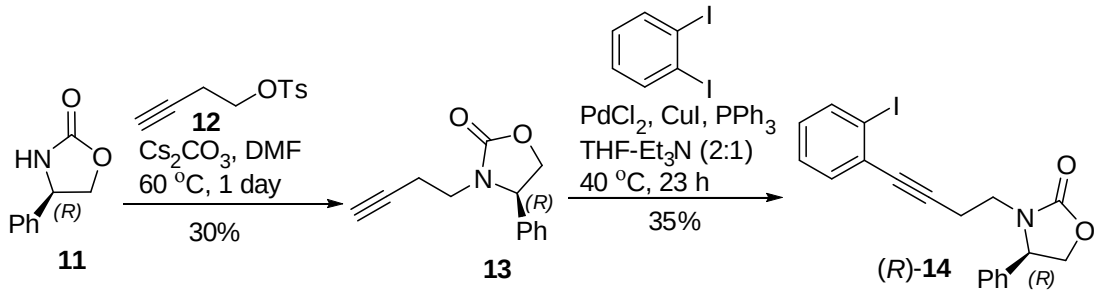
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82 (1H, dd, *J*= 0.7 and 8.0, CH_{ar}), 7.73 (2H, d, *J*= 8.3, CH_{ar}), 7.38 (1H, dd, *J*= 1.5 and 7.8, CH_{ar}), 7.29 (2H, d, *J*= 8.0, CH_{ar}), 7.25 (1H, superimposed dt, *J*= 1.0 and 7.5, CH_{ar}), 6.96 (1H, dt, *J*= 1.7 and 7.8, CH_{ar}), 4.67 (1H, q, *J*= 7.3, CH), 3.60 (1H, ddd, J= 5.3, 10.0 and 15.3, CH_2N), 3.53 (3H, s, CH_3O), 3.44 (1H, ddd, *J*= 6.0, 10.0 and 15.3, CH_2N), 2.97 (1H, ddd, *J*= 5.3, 10.0 and 15.3, $CH_2C{\equiv}C$), 2.81 (1H, ddd, *J*= 5.8, 10.0 and 16.0, $CH_2C{\equiv}C$), 2.42 (3H, s, CH_3), 1.49 (3H, d, *J*= 7.3, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.0 (CO_2Me), 143.7 (C_{ar}), 138.7 (CH_{ar}), 136.7 (C_{ar}), 132.6 (CH_{ar}), 129.9 (C_{ar}), 129.7 (2xCH_{ar}), 129.2 (CH_{ar}), 127.9 (CH_{ar}), 127.5 (2xCH_{ar}), 101.1 (C_{ar}), 91.0 (C≡C), 84.7 (C≡C), 55.6 (CHN), 52.3 (CH_3O), 44.6 (CH_2N), 22.5 (CH_2), 21.7 (CH_3), 17.1 (CH_3).

HRMS (ESI): m/z: calcd for $[M+NH_4]^+$ $C_{21}H_{26}N_2O_4SI$: 529.0653, found: 529.0647.

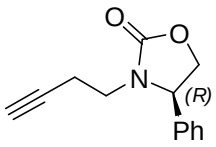
$[\alpha]_D^{25}$= not determined (non measurable because of opacity).

2.3. (R)-3-(4-(2-Iodophenyl)but-3-ynyl)-4-phenyloxazolidin-2-one (R-14)



Synthesis of 13:

To a solution of **11** (2 g, 12.2 mmol) and Cs_2CO_3 (20 g, 61.2 mmol) in DMF (40 mL) was added homopropargyl alcohol tosylated (**12**)[2] (5.50 g, 24.5 mmol). The reaction mixture was stirred at 60 °C for 4 h, then a first portion of **12** (5.50 g, 2.45 mmol) was added. After stirring for 5 h, a second portion of **10** (2.75 g, 12.2 mmol) was added. The reaction was stirred for an overall 1 day. After addition of a solution of HCl (1M), up to pH = 1, extraction with AcOEt and drying over $MgSO_4$, the solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel (pentane/AcOEt, 90/10 to 80/20). This led to **13** (780 mg, 30%) as an yellow oil.



$C_{13}H_{13}NO_2$
Mol. Wt.: 215.2478

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45-7.37 (3H, m, CH_{ar}), 7.32-7.29 (2H, m, CH_{ar}), 4.99 (1H, dd, *J*= 7.0 and 8.8, CH), 4.65 (1H, t, *J*= 8.8, CH), 4.13 (1H, dd, *J*= 7.0 and 8.5, CH), 3.62 (1H, dt, *J*= 14.0 and 7.0, CH_2N), 2.96 (1H, dt, *J*= 14.0 and 7.0, CH_2N); 2.46 (1H, dtd, *J*= 16.8, 7.0 and 2.8, $CH_2C{\equiv}CH$), 2.31 (1H, dtd, *J*= 16.8, 6.5 and 2.8, $CH_2C{\equiv}CH$), 2.00 (1H, t, *J*=2.8, $CH{\equiv}C$).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.3 (CO), 137.8 (C_{ar}), 129.5 ($2xCH_{ar}$), 129.4 (CH_{ar}), 127.2 ($2xCH_{ar}$), 81.2 ($C{\equiv}$), 70.4 ($CH{\equiv}$), 70.1 (CH_2O), 60.3 (CHN), 40.8 (NCH_2), 17.7 ($CH_2C{\equiv}C$).

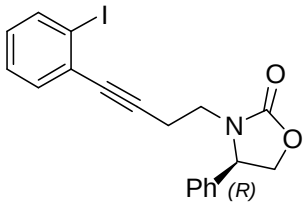
[2] For the synthesis of **12** see: A. Finaru, A. Berthault, T. Besson, G. Guillaumet and S. Berteina-Raboin, *Tetrahedron Letters*, 2002, **43**, 787.

HRMS (ESI): m/z: calcd for $[M+H]^+$ $C_{13}H_{14}NO_2$: 216.1019, found: 216.1018.

$[\alpha]_D^{25}$= -59 (c=0.9, $CHCl_3$).

Synthesis of R-14

Product (*R*)-**14** was prepared from (*R*)-**13** (780 mg, 3.62 mmol), according to the procedure already described for the synthesis of **10**, using diiodobenzene (1.19 g, 3.62 mmol), $PdCl_2$ (26 mg, 0.14 mmol), CuI (55 mg, 0.29 mmol) and PPh_3 (133 mg, 0.51 mmol) in a 2:1 mixture of THF:Et_3N. The reaction mixture was stirred for 17 h at 40 °C. After work-up, purification by liquid chromatography on silica gel (pentane/CH_2Cl_2, 90/10 to 100% CH_2Cl_2) led to 52 (527 mg, 35% (78% with respect to transformed diodobenzene, 55% of this starting material was recovered)) as a yellow oil.



$C_{19}H_{16}INO_2$
Mol. Wt.: 417.2403

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82 (1H, d, *J*= 7.8, CH_{ar}), 7.44-7.35 (4H, m, CH_{ar}), 7.33-7.28 (3H, m, CH_{ar}), 6.98 (1H, dt, *J*= 1.5 and 7.8, CH_{ar}), 5.11 (1H, dd, *J*= 6.8 and 8.8, CH), 4.67 (1H, t, *J*= 8.8, CH), 4.14 (1H, dd, *J*= 6.8 and 8.5, CH), 3.75 (1H, dt, *J*= 14.0 and 6.5, CH_2N), 3.07 (1H, dt, *J*= 14.0 and 6.5, CH_2N), 2.76 (1H, dt, *J*= 17.1 and 6.8, $CH_2C{\equiv}C$), 2.60 (1H, dt, J= 17.1 and 6.5, $CH_2C{\equiv}C$).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.3 (CO), 138.8 (CH_{ar}), 137.9(C_{ar}), 132.9 (CH_{ar}), 129.8 (C_{ar}), 129.5 (2xCH_{ar}), 129.4 (CH_{ar}), 129.3 (CH_{ar}); 128.0 (CH_{ar}), 127.2 (2xCH_{ar}), 100.8 (C_{ar}), 90.8 (C≡C), 84.5 (C≡C), 70.2 (CH_2O); 60.2 (CHN), 40.9 (CH_2N), 18.8 ($CH_2C{\equiv}C$).

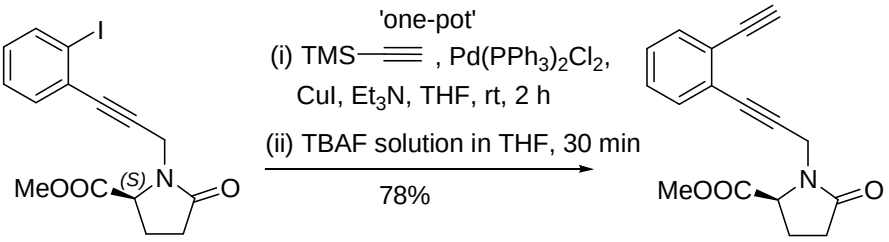
HRMS (ESI): m/z: calcd for $[M+H]^+$ $C_{19}H_{17}NO_2I$: 418.0299, found: 418.0298.

$[\alpha]_D^{25}$= -56 (c=0.6, $CHCl_3$).

(*S*)-**14** was prepared according to the same procedure.

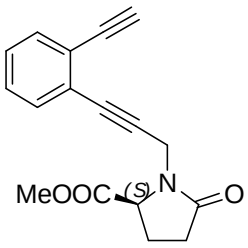
3. General one-pot protocol for the synthesis of enediynes 1a-f

3.1. (S)-Methyl 1-(3-(2-ethynylphenyl)prop-2-ynyl)-5-oxopyrrolidine-2-carboxylate (1a)



15 (S)-**1a**

Iodide **15**[1] (3 g, 7.83 mmol) in THF (75 mL), Et_3N (15 mL) was added and the reaction mixture was degassed with argon bubbling for 15 min. Then the catalyst, $Pd(PPh_3)_2Cl_2$ (110 mg, 2 mol%), and the co-catalyst, CuI (60 mg, 4 mol%), were added to the reaction mixture. After stirring for 10 min trimethylsilyl acetylene (1.66 mL, 11.74 mmol) was added and the reaction mixture was stirred for additional 2 h at room temperature. The conversion of the starting material was monitored by TLC. A solution of TBAF (12 mL of 1 M in THF, 12 mmol) was then added and the reaction mixture stirred further for 30 min. The reaction mixture was then passed through small celite bed, concentrated and the residue was purified by column chromatography on silica gel, using ethyl acetate/pentane (3:7) as eluent, to afford compound **1a** (1.72 g, 78% over 2 steps) as a brown liquid.



$C_{17}H_{15}NO_3$
Mol. Wt.: 281,3059

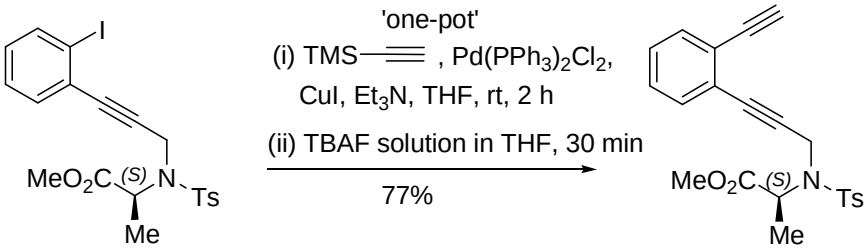
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48-7.45 (1H, m, CH_{ar}), 7.40-7.38 (1H, m, CH_{ar}), 7.29-7.25 (2H, m, CH_{ar}), 4.89 (1H, d, *J*= 17.8, CH_2N, A part of an AB pattern), 4.65-4.62 (1H, m, C**H**-CO_2Me), 4.02 (1H, d, *J*= 17.8, CH_2N, B part of an AB pattern), 3.75 (3H, s, CO_2CH_3), 3.31 (1H, s, C≡CH), 2.49-2.36 (3H, m, CH_2), 2.13-2.10 (1H, m, CH_2). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 174.5 (CO), 172.2 (CO), 132.6 (CH_{ar}), 132.1 (CH_{ar}), 128.6 (CH_{ar}), 128.3 (CH_{ar}), 125.4 (C_{ar}), 124.7 (C_{ar}), 86.7 (C≡C), 83.3 (C≡C), 82.2 (C≡C), 81.1 (≡CH), 58.4 (CH), 52.6 (OCH_3), 32.3 (CH_2N), 29.6 (CH_2), 22.9 (CH_2).

HRMS (ESI): m/z: calcd for $[M+H]^+$ $C_{17}H_{16}NO_3$: 282.1125, found: 282.1125.

Chiral HPLC separation of enantiomers: Chiralpak IC, hexane/ethanol 8/2, 1 mL/min, detection UV and CD 254 nm, Rt(*S*) = 13.41, Rt(*R*) = 14.78, k(*S*) = 3.47, k(*R*) = 3.93, α = 1.13 and Rs = 1.95. **ee = 96%**.

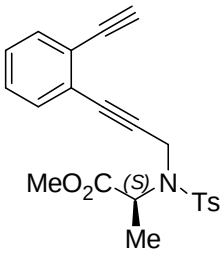
$[\alpha]_D^{25}$= +12.4 (c= 0.78, CH_2Cl_2).

3.2. (S)-*Methyl-2-(N-(3-(2-ethynylphenyl)prop-2-ynyl)-4-methylphenylsulfonamido) propanoate (1b)*



16 (S)-**1b**

Enediyne **1b** was prepared from compound **16**[1] (4.00 g, 8.04 mmol), $Pd(PPh_3)_2Cl_2$ (113 mg, 2 mol%), CuI (61.3 mg, 4 mol%), trimethylsilyl acetylene (1.7 mL, 12.06 mmol), Et_3N (20 mL) in THF (100 mL). The reaction mixture was stirred for 2 h. Deprotection was carried out with TBAF solution (1 M in THF) (12.5 mL, 12.5 mmol). The product was purified by column chromatography (20% ethyl acetate/pentane) to yield compound **1b** (2.45 g, 77% over 2 steps) as a brown liquid.



$C_{22}H_{21}NO_4S$
Mol. Wt.: 395,4714

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83 (2H, d, *J*= 8.3, CH_{ar}), 7.48 (1H, m, CH_{ar}), 7.29-7.23 (5H, m, CH_{ar}), 4.71 (1H, q, *J*= 7.3, C**H**CH_3), 4.64 (1H, d, *J*= 18.8, CH_2N, A part of an AB pattern), 4.41 (1H, d, *J*= 18.8, CH_2N, B part of an AB pattern), 3.65 (3H, s, CO_2CH_3), 3.24 (1H, s, ≡CH), 2.36 (3H, s, CH_3), 1.57 (3H, d, *J*= 7.3, CHC**H**$_3$).

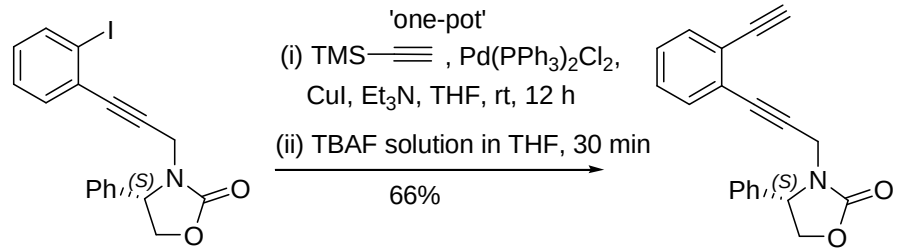
^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.0 (CO), 143.6 (C_{ar}), 137.3 (C_{ar}), 132.7 (CH_{ar}), 132.2 (CH_{ar}), 129.6 (2xCH_{ar}), 128.5 (CH_{ar}), 128.3 (CH_{ar}), 127.7 (2xCH_{ar}), 125.5 (C_{ar}), 124.6 (C_{ar}), 88.6 (C≡C), 83.0 (C≡C), 82.0 (C≡C), 81.1 (≡CH), 55.1 (**C**HCH$_3$), 52.4 (OCH_3), 35.2 (CH_2N), 21.6 (CH_3 of Ts), 16.5 (CH**C**H$_3$)

HRMS (ESI): m/z: calcd for $[M+H]^+$ $C_{22}H_{22}NO_4S$: 396.1264, found: 396.1264.

Chiral HPLC separation of enantiomers: Chiralcel OD-3, hexane/isopropanol 8/2, 1 mL/min, detection UV and CD 254 nm, Rt(*S*) = 12.04, Rt(*R*) = 13.00, k(*S*) = 3.01, k(*R*) = 3.33, α = 1.11 and Rs = 1.22. **ee = 99%**.

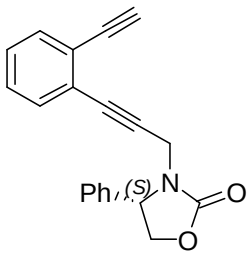
$[\alpha]_D^{25}$= -35.8 (c= 0.5, CH_2Cl_2).

3.3. (*S*)-*3-(3-(2-Ethynylphenyl)prop-2-ynyl)-4-phenyloxazolidin-2-one (S-1c)*



17 *(S)*-**1c**

Enediyne **1c** was prepared from compound **17**[1] (3.20 g, 7.94 mmol), $Pd(PPh_3)_2Cl_2$ (111.4 mg, 2 mol%), CuI (60.5 mg, 4 mol%), trimethylsilyl acetylene (1.68 mL, 11.90 mmol), Et_3N (16 mL) in THF (80 mL). The reaction mixture was stirred for 12 h. The deprotection was carried out with TBAF solution (1 M in THF) (12 mL, 12 mmol). The product was purified by column chromatography (20% ethyl acetate/pentane) to yield compound **1c** (1.57 g, 66% over 2 steps) as a brown liquid.



$C_{20}H_{15}NO_2$
Mol. Wt.: 301,3386

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38-7.36 (1H, m, CH_{ar}), 7.29-7.25 (6H, m, CH_{ar}), 7.17-7.12 (2H, m, CH_{ar}), 5.01 (1H, t, *J*= 8.3), 4.55 (1H, d, *J*= 17.8, CH_2N, A part of an AB pattern), 4.53 (1H, superimposed t, *J*= 8.8), 4.05 (1H, t, *J*= 8.0), 3.51 (1H, d, *J*= 17.8, CH_2N, B part of an AB pattern), 3.15 (1H, s, ≡CH).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.9 (CO), 136.9 (C_{ar}), 132.7 (CH_{ar}), 132.2 (CH_{ar}), 129.4 (2xCH_{ar}), 129.3 (CH_{ar}), 128.7 (CH_{ar}), 128.4 (CH_{ar}), 127.5 (2xCH_{ar}), 125.4 (C_{ar}), 124.8 (C_{ar}), 86.2 (C≡C), 83.5 (C≡C), 82.4 (C≡C), 81.2 (≡CH), 70.0 (OCH_2), 59.0 (CH), 33.1 (CH_2N).

HRMS (ESI): m/z: calcd for $[M+H]^+$ $C_{20}H_{16}NO_2$: 302.1176, found: 302.1176.

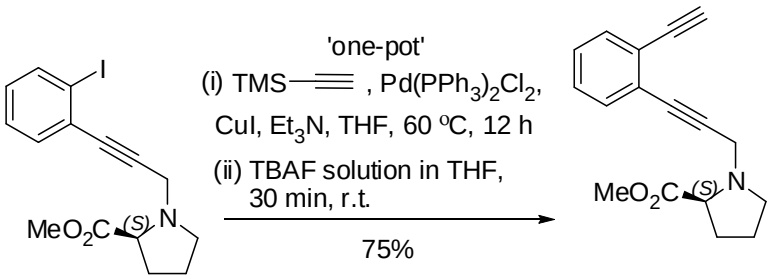
Chiral HPLC separation of enantiomers: Chiralpak IB, hexane/ethanol 9/1, 1 mL/min, detection UV 230 nm and CD 254 nm, Rt(*R*) = 9.63, Rt(*S*) = 10.61, k(*R*) = 2.21, k(*S*) = 2.54, α = 1.15. **ee = 99% for** (*S*) and **ee = 99.9% for** (*R*).

.

$[\alpha]_D^{25}$= +169.7 (c= 0.67, CH_2Cl_2) (*S*-isomer).

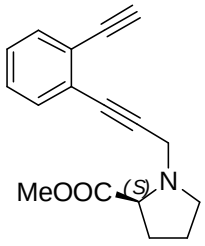
$[\alpha]_D^{25}$= -192.5 (c= 0.49, CH_2Cl_2) (*R*-isomer).

3.4. (S)-Methyl 1-(3-(2-ethynylphenyl)prop-2-ynyl)pyrrolidine-2-carboxylate (1d)



7 **1d**

Enediyne **1d** was prepared from compound **7** (1.80 g, 4.88 mmol), $Pd(PPh_3)_2Cl_2$ (68.5 mg, 2 mol%), CuI (37 mg, 4 mol%), trimethylsilyl acetylene (1 mL, 7.31 mmol), Et_3N (8 mL) in THF (20 mL). The reaction mixture was stirred for 12 h at 60 °C. The deprotection was carried out with TBAF solution (1 M in THF) (8 mL, 8 mmol). The product was purified by column chromatography (20% ethyl acetate/pentane) to yield compound **1d** (978 mg, 75% over 2 steps) as a brown liquid.



$C_{17}H_{17}NO_2$
Mol. Wt.: 267.3224

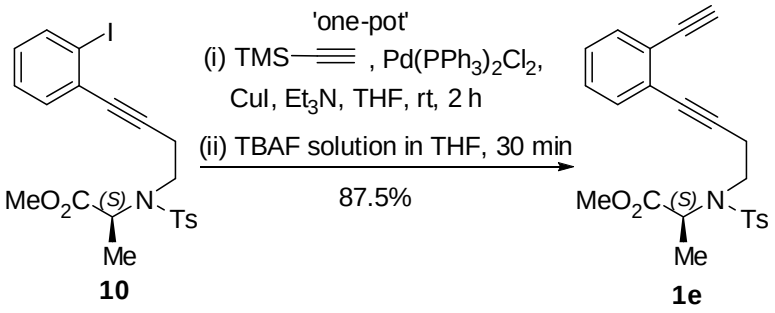
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49-7.47 (1H, m, CH_{ar}), 7.43-7.41 (1H, m, CH_{ar}), 7.29-7.22 (2H, m, CH_{ar}), 3.88 (2H, AB pattern, J_{AB}= 17.6, Δν= 22.3 Hz), 3.73 (3H, s, OCH_3), 3.67 (1H, dd, *J*= 6.5 and 9.0), 3.27 (1H, s, ≡CH), 3.12-3.08 (1H, m), 2.94-2.88 (1H, m), 2.22-2.13 (1H, m), 2.04-1.79 (3H, m). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 174.3 (CO), 132.7 (CH_{ar}), 132.1 (CH_{ar}), 128.6 (CH_{ar}), 127.9 (CH_{ar}), 126.3 (C_{ar}), 124.7 (C_{ar}), 88.6 (C≡C), 84.0 (C≡C), 82.6 (C≡C), 81.0 (CH≡), 62.5 (CH), 52.4 (CH_2), 52.1 (OCH_3), 42.2 (CH_2), 29.8 (CH_2), 23.5 (CH_2).

HRMS (ESI): m/z: calcd for $[M+H]^+$ $C_{17}H_{18}NO_2$: 268.1332, found: 268.1332.

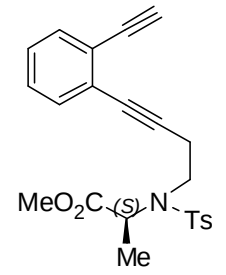
Chiral HPLC separation of enantiomers: Chiralpak ID, hexane/isopropanol 95/5, 1 mL/min, detection UV and CD 254 nm, Rt (S) = 7.27 Rt (R) = 7.97 and k(*S*) = 1.42, k(*R*) = 1.66, α = 1.17 and Rs = 2.49. **ee = 99%**.

$[\alpha]_D^{25}$= -106.5 (c= 0.81, CH_2Cl_2)

3.5. (S)-Methyl-2-(N-(3-(2-ethynylphenyl)prop-2-ynyl)-4-methylphenylsulfonamido)propanoate (1e)



Enediyne **1e** was prepared from compound **10** (1.00 g, 1.96 mmol), $Pd(PPh_3)_2Cl_2$ (28 mg, 2 mol%), CuI (15 mg, 4 mol%), trimethylsilyl acetylene (0.41 mL, 2.93 mmol), Et_3N (4 mL) in THF (10 mL). The reaction mixture was stirred for 2 h in room temperature. Deprotection was carried out with TBAF solution (1 M in THF) (3.0 mL, 3.00 mmol). The product was purified by column chromatography (20% ethyl acetate/pentane) to yield compound **1e** (700 mg, 87.5%) as a yellowish liquid.



$C_{23}H_{23}NO_4S$
Mol. Wt.: 409.4980

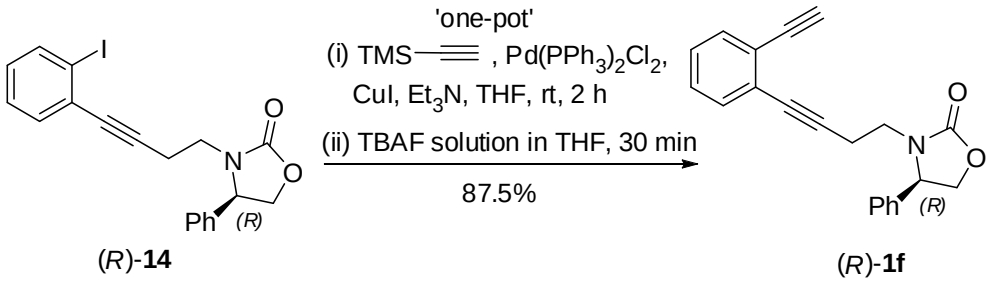
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 (2H, d, *J*= 8.3, CH_{ar}), 7.47 (1H, dd, *J*= 1.8 and 7.0, CH_{ar}), 7.38 (1H, dd, *J*= 1.5 and 7.3, CH_{ar}), 7.28 (2H, superimposed d, *J*= 8.3, CH_{ar}), 7.27-7.21 (2H, superimposed m, CH_{ar}), 4.66 (1H, q, *J*= 7.3, CHN), 3.58 (1H, ddd, *J*= 5.0, 9.8 and 15.8), 3.52 (3H, s, CH_3O), 3.42 (1H, ddd, *J*= 6.0, 9.8 and 15.8), 3.27 (1H, s, ≡CH), 2.95 (1H, ddd, *J*= 5.2, 9.8 and 16.8), 2.81 (1H, ddd, *J*= 6.0, 10.0 and 16.8), 2.41 (3H, s, CH_3), 1.48 (3H, d, *J*= 7.3, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 172.0 (CO_2Me), 143.7 (C_{ar}), 136.8 (C_{ar}), 132.7 (CH_{ar}), 132.0 (CH_{ar}), 129.7 (2xCH_{ar}), 128.6 (CH_{ar}), 127.7 (CH_{ar}), 127.5 (2xCH_{ar}), 126.5 (C_{ar}), 124.6 (C_{ar}), 91.3 (C≡C), 82.4 (C≡C), 81.0 (C≡C), 80.9 (≡CH), 55.6 (CHN), 52.3 (CH_3O), 44.8 (CH_2N), 22.5 (CH_2), 21.7 (CH_3), 17.1 (CH_3).

HRMS (ESI): m/z: calcd for $[M+H]^+$ $C_{23}H_{24}NO_4S$: 410.1421, found: 410.1426.

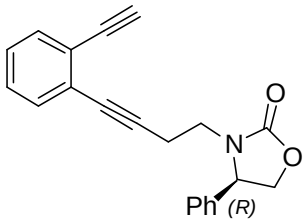
Chiral HPLC separation of enantiomers: Chiralpak IC, hexane/ethanol 7/3, 1 mL/min, detection UV and CD 254 nm, Rt (S) = 7.15, Rt (R) = 8.05 and k(*S*) = 1.38, k(*R*) = 1.68, α = 1.22 and Rs = 2.34.. **ee = 83%**.

$[\alpha]_D^{25}$= -24.2 (c= 0.64, CH_2Cl_2)

3.6. (R)-3-(4-(2-ethynylphenyl)but-3-ynyl)-4-phenyloxazolidin-2-one ((R)-1f)



Enediyne **1f** was prepared from compound **14** (280 mg, 0.67 mmol), $Pd(PPh_3)_2Cl_2$ (10 mg, 2 mol%), CuI (5 mg, 4 mol%), trimethylsilyl acetylene (0.19 mL, 1.34 mmol), Et_3N (2 mL) in THF (5 mL). The reaction mixture was stirred for 2 h in room temperature. Deprotection was carried out with TBAF solution (1 M in THF) (1.5 mL, 1.5 mmol). The product was purified by column chromatography (20% ethyl acetate/pentane) to yield compound **1f** (179 mg, 85%) as a yellowish liquid.



$C_{21}H_{17}NO_2$
Mol. Wt.: 315.3652

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48 (1H, dd, *J*= 2.0 and 7.0, CH_{ar}), 7.42-7.37 (4H, m, CH_{ar}), 7.32-7.23 (4H, m, CH_{ar}), 5.12 (1H, dd, *J*= 6.8 and 8.8, CH), 4.65 (1H, t, *J*= 8.8, CH), 4.13 (1H, dd, *J*= 6.8 and 8.5, CH), 3.73 (1H, dt, *J*= 14.0 and 6.5, CH_2N), 3.27 (1H, s, ≡CH), 3.05 (1H, dt, *J*= 13.8 and 6.5, CH_2N), 2.76 (1H, dt, *J*= 17.0 and 7.0, $CH_2C{\equiv}C$), 2.60 (1H, dt, J= 17.0 and 6.3, $CH_2C{\equiv}C$).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.3 (CO), 138.0 (C_{ar}), 132.8 (CH_{ar}), 132.2 (CH_{ar}), 129.5 (2xCH_{ar}), 129.3 (CH_{ar}), 128.7 (CH_{ar}), 129.3 (CH_{ar}); 127.9 (CH_{ar}), 127.3 (2xCH_{ar}), 126.3 (C_{ar}), 124.5 (C_{ar}), 91.1 (C≡C), 82.4 (C≡C), 80.9 (C≡C), 80.8 (C≡C), 70.1 (CH_2O); 60.3 (CHN), 40.9 (CH_2N), 18.8 ($CH_2C{\equiv}C$).

HRMS (ESI): m/z: calcd for $[M+H]^+$ $C_{21}H_{18}NO_2$: 316.1332, found: 316.1331.

Chiral HPLC separation of *R*-enantiomers: Chiralpak IC, hexane/ethanol 9/1, 1 mL/min, detection UV and CD 254 nm, Rt (S) = 14.73 Rt (R) = 13.07 and k(*R*) = 3.36, k(*S*) = 3.91, α = 1.16 and Rs = 3.52. **ee = 99.9%**.

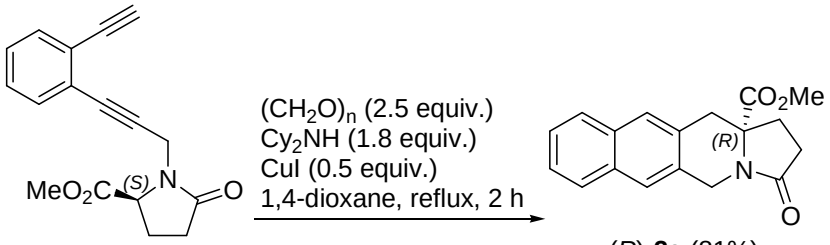
$[\alpha]_D^{25}$= -64.1 (c= 0.44, CH_2Cl_2)

Chiral HPLC separation of *S*-enantiomers: Chiralpak IC, hexane/ethanol 9/1, 1 mL/min, detection UV and CD 254 nm, Rt (S) = 14.73 Rt (R) = 13.07 and k(*S*) = 1.42, k(*R*) = 1.66, α = 1.17 and Rs = 4.24. **ee = 99.9%**.

$[\alpha]_D^{25}$= +59.4 (c= 0.87, CH_2Cl_2)

4. General One-Pot Crabbé Homologation-Radical Cascade Cyclization

4.1. Cyclization of (S)-1a

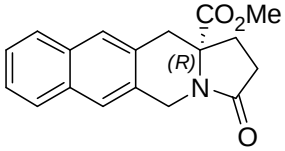


(*S*)-**1a**
ee = 96%

(*R*)-**2a** (81%)
ee = 95%

$(CH_2O)_n$ (27 mg, 0.89 mmol), CuI (34 mg, 0.18 mmol), 1,4-dioxane (1 mL), enediyne (*S*)-**1a** (100 mg, 0.36 mmol) and dicyclohexylamine (0.13 mL, 0.64 mmol) were added sequentially into an oven-dried reaction tube equipped with a reflux condenser under an argon atmosphere. The resulting mixture was stirred at reflux for 2 h. Solvent was evaporated under vacuo and redissolved in DCM, filtered, and the filtrate was concentrated and purified by column chromatography on silica gel using 1:1 ethyl acetate:pentane as eluent to afford the cyclized product (*R*)-**2a** (85 mg, 81%, ee= 95%).

(*R*)-Methyl 3-oxo-1,2,3,5,12,12a-hexahydrobenzo[*g*]pyrrolo [1,2-*b*]isoquinoline-12a-carboxylate (*R*-2a):



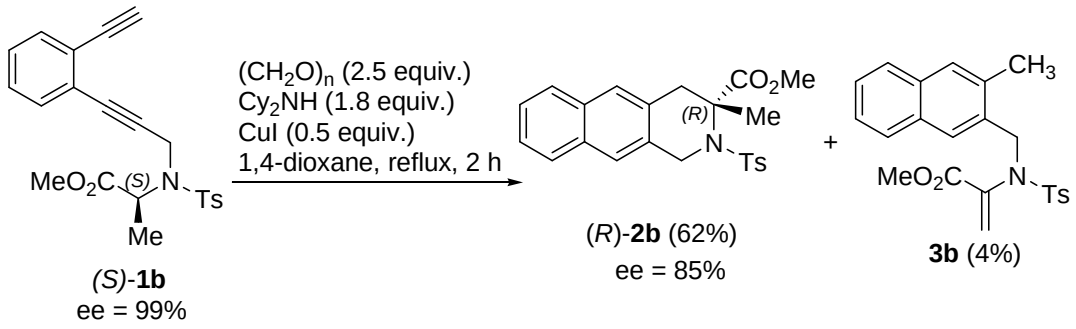
$C_{18}H_{17}NO_3$
Mol. Wt.: 295.3325

White solid, mp= 205.9 °C (acetonitrile); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.78-7.73 (2H, m, CH_{ar}), 7.64 (1H, s, CH_{ar}), 7.63 (1H, s, CH_{ar}), 7.46-7.41 (2H, m, CH_{ar}), 5.09 (1H, d, *J*= 17.3, CH_2N, A part of an AB pattern), 4.63 (1H, d, *J*= 17.3, CH_2N, B part of an AB pattern), 3.74 (1H, d, *J*= 15.3, CCH_2, A part of an AB pattern), 3.57 (3H, s, OCH_3), 3.08 (1H, d, *J*= 15.3, CCH_2, B part of an AB pattern), 2.64-2.47 (3H, m), 2.26-2.17 (1H, m).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.6 (CO), 173.4 (CO), 132.7 (C_{ar}), 132.4 (C_{ar}), 129.7 (C_{ar}), 129.3 (C_{ar}), 127.6 (CH_{ar}), 127.5 (CH_{ar}), 127.4 (CH_{ar}), 126.2 (CH_{ar}), 126.1 (CH_{ar}), 125.5 (CH_{ar}), 65.7 (C), 52.9 (OCH_3), 42.6 (CH_2), 40.0 (CH_2), 31.4 (CH_2), 29.7 (CH_2).
HRMS (ESI): m/z: calcd for $[M+H]^+$ $C_{18}H_{18}NO_3$: 296.1281, found: 296.1282.
Chiral HPLC separation of enantiomers: Chiralpak IB, hexane/ethanol 7/3, 1 mL/min, detection UV 230 nm and CD 254 nm, Rt (S) = 8.15 Rt (R) = 7.02 and k(*S*) = 1.72, k(*R*) = 1.34, α = 1.28 and Rs = 2.8. **ee = 95%** (ee = 99.9% after recrystallization).
$[\alpha]_D^{25}$ = -139.6 (c= 0.49, CH_2Cl_2)

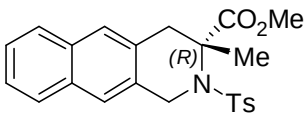
X-ray structure of (*R*)-2a

4.2. Cyclization of (S)-1b



Enediyne (*S*)-**1b** (100 mg, 0.25 mmol) was allowed to react with $(CH_2O)_n$ (19 mg, 0.63 mmol), CuI (24 mg, 0.13 mmol) and dicyclohexylamine (0.10 mL, 0.46 mmol) in refluxing 1,4-dioxane (1 mL) for 2 h. The products were purified by column chromatography on silica gel using 1:9 ethyl acetate:pentane as eluent to afford (*R*)-**2b** (64 mg, 62%, ee= 85%) and olefin **3b** (4.1 mg, 4%).

(*R*)-Methyl 3-methyl-2-tosyl-1,2,3,4-tetrahydrobenzo[*g*]isoquinoline-3-carboxylate (*R*-2b):



$C_{23}H_{23}NO_4S$
Mol. Wt.: 409.4980

Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ : 7.81-7.78 (2H, m, CH_{ar}),7.75 (2H, d, *J*= 8.3, CH_{ar}), 7.63 (1H, s, CH_{ar}), 7.54 (1H, s, CH_{ar}), 7.48-7.46 (2H, m, CH_{ar}), 7.23 (2H, d, *J*= 8.3, CH_{ar}), 4.55 (2H, s, CH_2), 3.82 (3H, s, OCH_3), 3.42 (1H, d, *J*= 14.6, CH_2, A part of an AB pattern), 3.02 (1H, d, *J*= 14.8, CH_2, B part of an AB pattern), 2.38 (3H, s, CH_3), 1.56 (3H, s, CH_3).

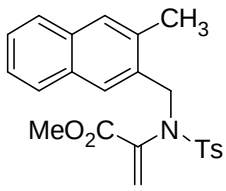
^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.8 (CO), 143.4 (C_{ar}), 138.3 (C_{ar}), 133.2 (C_{ar}), 132.6 (C_{ar}), 132.5 (C_{ar}), 131.4 (C_{ar}), 129.7 (2xCH_{ar}), 127.8 (CH_{ar}), 127.6 (CH_{ar}), 127.3 (2xCH_{ar}), 126.4 (CH_{ar}), 126.3 (CH_{ar}), 126.1 (CH_{ar}), 124.3 (CH_{ar}), 63.6 (C), 52.9 (OCH_3), 47.0 (CH_2), 42.1 (CH_2), 24.3 (CH_3), 21.6 (CH_3).

HRMS (ESI): m/z: calcd for $[M+H]^+$ $C_{23}H_{24}NO_4S$: 410.1421, found: 410.1420.

Chiral HPLC separation of enantiomers: Chiralpak IA, hexane/ethanol 7/3, 1 mL/min, detection UV 230 nm and CD 254 nm, Rt (S) = 12.07 Rt (R) = 8.67 and k(*S*) = 3.02, k(*R*) = 1.89, α = 1.60 and Rs = 6.77. **ee = 85%**.

$[\alpha]_D^{25}$ = +11.6 (c= 0.50, CH_2Cl_2)

Methyl 2-(4-methyl-*N*-((3-methylnaphthalen-2-yl)methyl) phenylsulfonamido)acrylate (3b):



$C_{23}H_{23}NO_4S$
Mol. Wt.: 409.4980

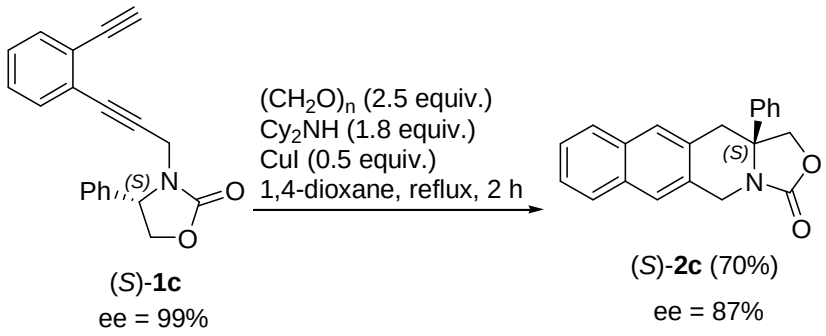
Colourless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.75 (2H, d, *J*= 8.3, CH_{ar}), 7.70 (1H, d, *J*= 8.0, CH_{ar}), 7.65 (1H, d, *J*= 7.8, CH_{ar}), 7.57 (1H, s, CH_{ar}), 7.48 (1H, s, CH_{ar}), 7.42-7.35 (2H, m, CH_{ar}), 7.32 (2H, d, *J*= 8.0, CH_{ar}), 6.15 (1H, s, =C**H_a**H_b), 5.66 (1H, s, =CH_a**H_b**), 4.79 (2H, s, CH_2N), 3.56 (3H, s, OCH_3), 2.54 (3H, s, CH_3), 2.45 (3H, s, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.2 (CO), 143.9 (C), 135.7 (C_{ar}), 135.5 (C_{ar}), 135.4 (C_{ar}), 133.5 (C_{ar}), 131.8 (C_{ar}), 131.6 (C_{ar}), 129.8 (CH_{ar}), 129.6 (2xCH_{ar}), 128.8 (CH_{ar}), 128.5 (=CH_2), 128.1 (2xCH_{ar}), 127.6 (CH_{ar}), 127.0 (CH_{ar}), 126.4 (CH_{ar}), 125.4 (CH_{ar}), 52.3 (OCH_3), 51.4 (CH_2N), 21.8 (CH_3), 19.6 (CH_3).

HRMS (ESI): m/z: calcd for $[M+NH_4]^+$ $C_{23}H_{27}N_2O_4S$: 427.1686, found: 427.1686.

4.3. Cyclization of (S)-1c

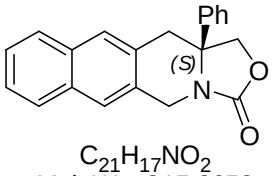
Enediyne (*S*)-**1c** (100 mg, 0.33 mmol) was allowed to react with $(CH_2O)_n$ (25 mg, 0.83 mmol), CuI (32 mg, 0.17 mmol) and dicyclohexylamine (0.12 mL, 0.60 mmol) in refluxing 1,4-dioxane (1 mL) for 2 h. The products were purified by column chromatography on silica gel using 3:7 ethyl acetate:pentane as eluent to afford (*S*)-**2c** (73 mg, 70%, ee= 87%).



(*S*)-**1c**
ee = 99%

(*S*)-**2c** (70%)
ee = 87%

(*S*)-12a-phenyl-12,12a-dihydro-1*H*-benzo[*g*]oxazolo [3,4-*b*]isoquinolin-3(5*H*)-one (*S*-2c):



$C_{21}H_{17}NO_2$
Mol. Wt.: 315.3652

White solid, mp= 243.3 °C (EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.75-7.73 (1H, m, CH_{ar}), 7.67 (1H, d, *J*= 7.3, CH_{ar}), 7.67 (1H, superimposed s, CH_{ar}), 7.49 (1H, s, CH_{ar}), 7.43-7.37 (4H, m, CH_{ar}), 7.33-7.28 (2H, m, CH_{ar}), 7.20 (1H, tt, *J*= 7.3 and 1.3, CH_{ar}), 5.17 (1H, d, *J*= 17.3, CH_2N, A part of an AB pattern), 4.45 (1H, d, J= 8.5, CH_2O, A part of an AB pattern), 4.42 (1H, d, *J*= 16.8, CH_2N, B part of an AB pattern), 4.31 (1H, d, J= 8.5, CH_2O, B part of an AB pattern), 3.79 (1H, d, J= 15.6, CH_2C, A part of an AB pattern), 3.51 (1H, d, J= 15.6, CH_2C, B part of an AB pattern).

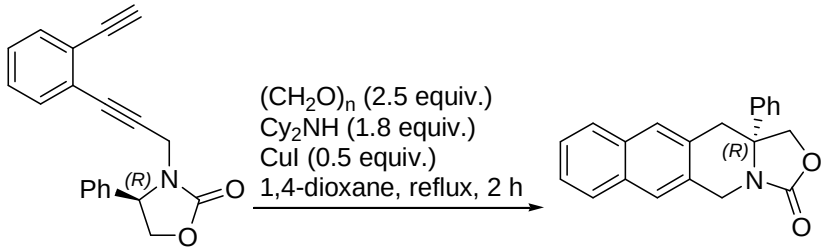
^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.0 (CO), 139.1 (C_{ar}), 132.5 (C_{ar}), 132.4 (C_{ar}), 130.2 (C_{ar}), 129.5 (2xCH_{ar}), 129.2 (C_{ar}), 128.3 (CH_{ar}), 127.8 (CH_{ar}), 127.4 (CH_{ar}), 127.3 (CH_{ar}), 126.2 (2xCH_{ar}), 126.1 (CH_{ar}), 126.0 (CH_{ar}), 125.0 (CH_{ar}), 76.5 (OCH_2), 62.2 (C), 42.4 (**C**H_2), 37.1 (CH_2).

HRMS (ESI): m/z: calcd for $[M+H]^+$ $C_{21}H_{18}NO_2$: 316.1332, found: 316.1332.

Chiral HPLC separation of enantiomers: Chiralpak IC, hexane/ethanol 7/3, 1 mL/min, detection UV 230 nm and CD 254 nm, Rt (S) = 15.26 Rt (R) = 17.37 and k(*S*) = 4.09, k(*R*) = 4.79, α = 1.17 and Rs = 2.60. **ee = 87%**.

$[\alpha]_D^{25}$ = +331.1 (c= 0.45, CH_2Cl_2)

4.4. Cyclization of (R)-1c



(*R*)-**1c**
ee = 99.9%

(*R*)-**2c** (70%)
ee = 90%

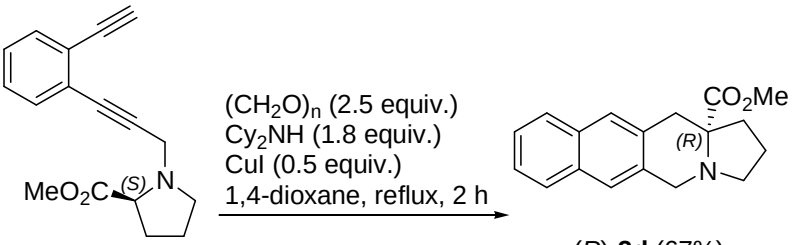
Enediyne (*R*)-**1c** (100 mg, 0.33 mmol) was allowed to react with $(CH_2O)_n$ (25 mg, 0.83 mmol), CuI (32 mg, 0.17 mmol) and dicyclohexylamine (0.12 mL, 0.60 mmol) in refluxing 1,4-dioxane (1 mL) for 2 h. The products were purified by column chromatography on silica gel using 3:7 ethyl acetate:pentane as eluent to afford (*R*)-**2c** (73 mg, 70%, ee= 90%) as white solid, mp= 231.3 °C (EtOAc).

HRMS (ESI): m/z: calcd for $[M+H]^+$ $C_{21}H_{18}NO_2$: 316.1332, found: 316.1332.

Chiral HPLC separation of enantiomers: Chiralpak IC, hexane/ethanol 7/3, 1 mL/min, detection UV 230 nm and CD 254 nm, Rt (S) = 15.26 Rt (R) = 17.37 and k(*S*) = 4.09, k(*R*) = 4.79, α = 1.17 and Rs = 2.60. **ee = 90%**.

$[\alpha]_D^{25}$ = -316.8 (c= 0.63, CH_2Cl_2)

4.5 Cyclization of (S)-1d

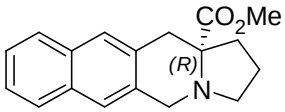


(*S*)-**1d**
ee = 99%

(*R*)-**2d** (67%)
ee = 97%

Enediyne (*S*)-**1d** (100 mg, 0.37 mmol) was allowed to react with $(CH_2O)_n$ (28 mg, 0.94 mmol), CuI (36 mg, 0.19 mmol) and dicyclohexylamine (0.13 mL, 0.67 mmol) in refluxing 1,4-dioxane (1 mL) for 2 h. The products were purified by column chromatography on silica gel using 2:8 ethyl acetate:pentane as eluent to afford (*R*)-**2d** (70 mg, 67%, ee= 97%) as white solid, mp= 116.3 °C (precipitated from ethyl acetate:pentane).

(*R*)-Methyl 1,2,3,5,12,12a-hexahydrobenzo[*g*]pyrrolo[1,2-*b*]isoquinolin-12a-carboxylate (*R*-2d):



$C_{18}H_{19}NO_2$
Mol. Wt.: 281.3490

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79-7.77 (2H, m, CH_{ar}), 7.62 (1H, s, CH_{ar}), 7.60 (1H, s, CH_{ar}), 7.44-7.42 (2H, m, CH_{ar}), 4.23 (1H, d, *J*= 15.1, A part of an AB pattern), 3.97 (1H, d, J= 15.0, A part of an AB pattern), 3.69 (3H, s, OCH_3), 3.36 (1H, d, *J*= 15.1, A part of an AB pattern), 3.16-3.12 (1H, m), 2.97 (1H, d, J= 15.0, B part of an AB pattern), 2.62 (1H, td, *J*= 8.5 and 5.8), 2.37-2.32 (1H, m), 1.87-1.80 (1H, m), 1.70-1.58 (2H, m).

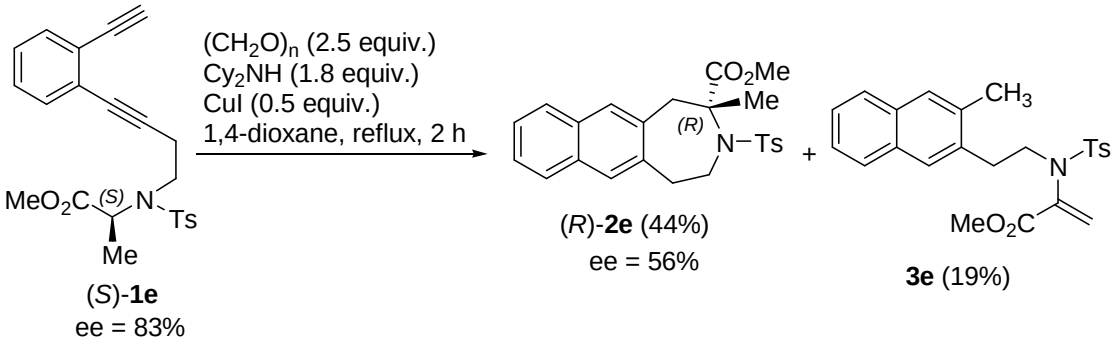
^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.3 (CO), 134.6 (C_{ar}), 133.1 (C_{ar}), 132.9 (C_{ar}), 132.4 (C_{ar}), 127.6 (CH_{ar}), 127.4 (CH_{ar}), 127.0 (CH_{ar}), 125.7 (CH_{ar}), 125.6 (CH_{ar}), 125.2 (CH_{ar}), 67.8 (C), 53.3 (**C**H_2), 52.3 (OCH_3), 51.0 (**C**H_2), 36.9 (**C**H_2), 36.8 (**C**H_2), 23.0 (**C**H_2).

HRMS (ESI): m/z: calcd for $[M+H]^+$ $C_{18}H_{20}NO_2$: 282.1489, found: 282.1490.

Chiral HPLC separation of enantiomers: Chiralpak AD-H, hexane/ethanol 95/5, 1 mL/min, detection UV 230 nm and CD 254 nm, Rt (S) = 8.96 Rt (R) = 11.13 and k(*S*) = 1.99, k(*R*) = 2.71, α = 1.36 and Rs = 3.96. **ee = 97%**.

$[\alpha]_D^{25}$ = +67.5 (c= 0.40, CH_2Cl_2)

4.6. Cyclization of (S)-1e



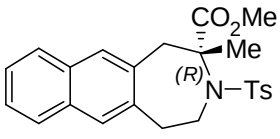
(*S*)-**1e**
ee = 83%

(*R*)-**2e** (44%)
ee = 56%

3e (19%)

Enediyne (*S*)-**1e** (100 mg, 0.24 mmol) was allowed to react with $(CH_2O)_n$ (18.3 mg, 0.61 mmol), CuI (23.3 mg, 0.12 mmol) and dicyclohexylamine (0.10 mL, 0.44 mmol) in refluxing 1,4-dioxane (1 mL) for 2 h. The products were purified by column chromatography on silica gel using 1:9 ethyl acetate:pentane as eluent to afford (*R*)-**2e** (45 mg, 44%, ee= 56%) and olefin **3e** (20 mg, 19%).

(*R*)-Methyl 2-methyl-3-tosyl-2,3,4,5-tetrahydro-1*H*-naphtho[2,3-*d*]azepine-2-carboxylate (*R*-2e):



$C_{24}H_{25}NO_4S$
Mol. Wt.: 423.5246

Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ : 7.80 (2H, d, *J*= 8.2, CH_{ar}), 7.76-7.72 (2H, m, CH_{ar}), 7.51 (1H, s, CH_{ar}), 7.50 (1H, s, CH_{ar}), 7.45-7.42 (2H, m, CH_{ar}), 7.24 (2H, d, *J*= 8.3, CH_{ar}), 3.81-3.74 (1H, m), 3.77 (3H, superimposed s, OCH_3), 3.67-3.52 (1H, m), 3.63 (1H, superimposed d, *J*= 15.6, A part of an AB pattern), 3.24-3.04 (2H, m), 3.14 (1H, superimposed d, *J*= 15.0, B part of an AB pattern), 2.40 (3H, s, CH_3), 1.54 (3H, s, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.4 (CO), 143.6 (C_{ar}), 137.9 (C_{ar}), 136.6 (C_{ar}), 133.3 (C_{ar}), 133.0 (C_{ar}), 132.3 (C_{ar}), 129.8 (CH_{ar}), 129.6 (2xCH_{ar}), 127.9 (2xCH_{ar}), 127.6

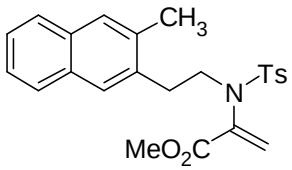
(CH_{ar}), 127.4 (CH_{ar}), 127.1 (CH_{ar}), 126.2 (CH_{ar}), 125.9 (CH_{ar}), 66.3 (C), 52.7 (OCH_3), 45.9 (CH_2), 44.2 (CH_2), 35.2 (CH_2), 22.1 (CH_3), 21.7 (CH_3).

HRMS (ESI): m/z: calcd for $[M+H]^+$ $C_{24}H_{26}NO_4S$: 424.1577, found: 424.1573.

Chiral HPLC separation of enantiomers: Chiralpak IB, hexane/ethanol 9/1, 1 mL/min, detection UV 230 nm and CD 254 nm, Rt (S) = 11.61 Rt (R) = 12.94 and k(*S*) = 2.87, k(*R*) = 3.31, α = 1.15 and Rs = 2.19. **ee = 56%**.

$[\alpha]_D^{25}$ = -10.4 (c= 0.48, CH_2Cl_2)

Methyl 2-(4-methyl-*N*-(2-(3-methylnaphthalen-2-yl)ethyl) phenylsulfonamido)acrylate (3e):



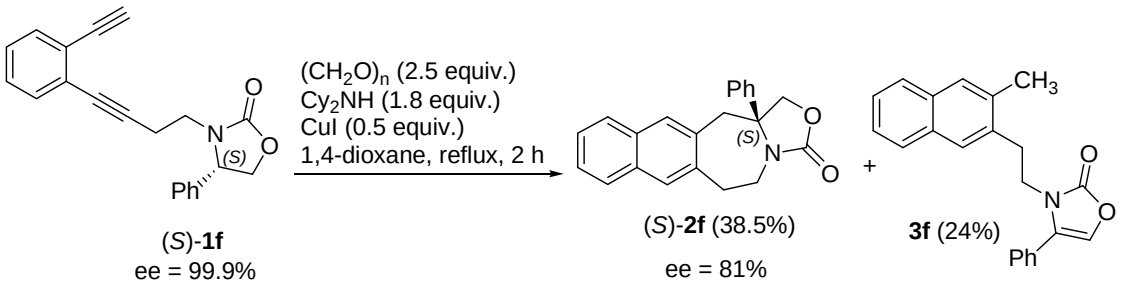
$C_{24}H_{25}NO_4S$
Mol. Wt.: 423.5246

Colourless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.72-7.69 (2H, m, CH_{ar}), 7.66 (2H, d, *J*= 8.3, CH_{ar}), 7.57 (1H, s, CH_{ar}), 7.52 (1H, s, CH_{ar}), 7.40-7.38 (2H, m, CH_{ar}), 7.21 (2H, d, *J*= 8.3, CH_{ar}), 6.45 (1H, s, =C**H$_a$**H$_b$), 5.81 (1H, s, =CH$_a$**H$_b$**), 3.67 (3H, s, OCH_3), 3.64-3.60 (2H, m, CH_2N), 3.03-2.99 (2H, m, CH_2), 2.42 (3H, s, CH_3), 2.39 (3H, s, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.4 (CO), 143.7 (C), 136.2 (C_{ar}), 136.1 (C_{ar}), 135.1 (C_{ar}), 134.7 (C_{ar}), 132.8 (C_{ar}), 132.3 (C_{ar}), 129.5 (2xCH_{ar}), 128.5 (=CH_2), 128.4 (CH_{ar}), 128.1 (CH_{ar}), 127.8 (2xCH_{ar}), 127.2 (CH_{ar}), 127.0 (CH_{ar}), 125.7 (CH_{ar}), 125.4 (CH_{ar}), 52.6 (OCH_3), 49.7 (CH_2N), 33.1 (CH_2), 21.7 (CH_3), 19.8 (CH_3).

HRMS (ESI): m/z: calcd for $[M+H]^+$ $C_{24}H_{26}NO_4S$: 424.1577, found: 424.1576.

4.7. Cyclization of (S)-1f



(*S*)-**1f**
ee = 99.9%

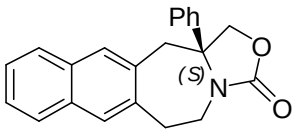
(*S*)-**2f** (38.5%)
ee = 81%

3f (24%)

Enediyne (*S*)-**1f** (100 mg, 0.32 mmol) was allowed to react with $(CH_2O)_n$ (24 mg, 0.79 mmol), CuI (30 mg, 0.16 mmol) and dicyclohexylamine (0.11 mL, 0.57 mmol) in

refluxing 1,4-dioxane (1 mL) for 2 h. The products were purified by column chromatography on silica gel using 2:8 ethyl acetate:pentane as eluent to afford (*S*)-**2f** (40 mg, 38.5%, ee= 81%) and olefin **3f** (25 mg, 24%).

(*S*)-13a-phenyl-5,6,13,13a-tetrahydronaphtho[2,3-*d*]oxazolo[3,4-*a*]azepin-3(1*H*)-one (*S*-2f):



$C_{22}H_{19}NO_2$
Mol. Wt.: 329.3918

Yellowish oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.77-7.75 (1H, m, CH_{ar}), 7.72-7.70 (1H, m, CH_{ar}), 7.68 (1H, s, CH_{ar}), 7.54 (1H, s, CH_{ar}), 7.43-7.41 (2H, m, CH_{ar}), 7.34-7.33 (4H, m, CH_{ar}), 7.22-7.20 (1H, m, CH_{ar}), 4.35 (1H, d, *J*= 8.3, A part of an AB pattern), 4.29-4.26 (1H, m), 4.11 (1H, d, J= 8.3, B part of an AB pattern), 3.74 (1H, d, *J*= 14.6, A part of an AB pattern), 3.63 (1H, d, J= 14.0, B part of an AB pattern), 3.21-3.18 (2H, m), 3.03-2.99 (1H, m).

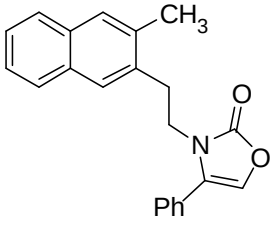
^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.2 (CO), 133.7 (C_{ar}), 133.0 (C_{ar}), 132.6 (C_{ar}), 129.4 (2xCH_{ar}), 128.2 (CH_{ar}), 128.0 (CH_{ar}), 127.3 (2xCH_{ar}), 127.2 (CH_{ar}), 126.2 (CH_{ar}), 126.0 (CH_{ar}), 125.9 (2xCH_{ar}), 76.0 (OCH_2), 65.3 (C), 44.4 (CH_2N), 40.9 (CH_2), 33.6 (CH_2).

Due to unexplained low intensity (slow relaxation time) of aliphatic carbons, the spectra was assigned from 2D HSQC sequence which allowed unambiguous measurement of chemical shifts.

HRMS (ESI): m/z: calcd for $[M+H]^+$ $C_{22}H_{20}NO_2$: 330.1489, found: 330.1488.

Chiral HPLC separation of enantiomers: Chiralpak IA, hexane/ethanol 7/3, 1 mL/min, detection UV 230 nm and CD 254 nm, Rt (S) = 10.61 Rt (R) = 12.85 and k(*S*) = 2.54, k(*R*) = 3.28, α = 1.30 and Rs = 4.17. **ee = 81%**.

$[\alpha]_D^{25}$ = +98.4 (c= 0.94, CH_2Cl_2)



$C_{22}H_{19}NO_2$
Mol. Wt.: 329.3918

3-(2-(3-Methylnaphthalen-2-yl)ethyl-4-phenyloxazol-2(3*H*)-one (3f):

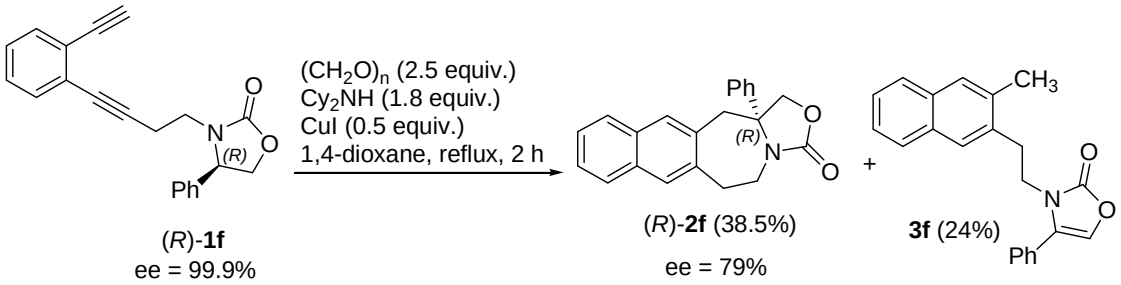
White solid, mp= 97.8 °C (precipitated from ethyl acetate:pentane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.69-7.64 (2H, m, CH_{ar}), 7.47 (1H, s, CH_{ar}), 7.41-7.38 (3H, m, CH_{ar}), 7.38 (1H, superimposed s, CH_{ar}), 7.31 (2H, t, *J*= 7.3, CH_{ar}), 7.02 (2H, d, *J*= 7.0, CH_{ar}), 6.72 (1H, s, CH=), 3.89 (2H, t, *J*= 7.3, CH_2N), 3.01

(2H, t, *J*= 7.3, CH_2), 2.17 (3H, s, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.2 (CO), 134.6 (C_{ar}), 134.5 (C_{ar}), 132.9 (C_{ar}), 132.4 (C_{ar}), 129.9 (C_{ar}), 129.6 (CH_{ar}), 129.0 (2xCH_{ar}), 128.7 (2xCH_{ar}), 128.5 (CH_{ar}), 128.4 (CH_{ar}), 127.2 (CH_{ar}), 126.9 (CH_{ar}), 126.4 (C=), 125.8 (CH_{ar}), 125.4 (CH_{ar}), 123.9 (CH=), 42.5 (**C**H_2), 32.3 (CH_2), 19.4 (CH_3).

HRMS (ESI): m/z: calcd for $[M+H]^+$ $C_{22}H_{20}NO_2$: 330.1489, found: 330.1488.

4.8. Cyclization of (R)-1f



Enediyne (*R*)-**1f** (100 mg, 0.32 mmol) was allowed to react with $(CH_2O)_n$ (24 mg, 0.79 mmol), CuI (30 mg, 0.16 mmol) and dicyclohexylamine (0.11 mL, 0.57 mmol) in refluxing 1,4-dioxane (1 mL) for 2 h. The products were purified by column chromatography on silica gel using 2:8 ethyl acetate:pentane as eluent to afford (*R*)-**2f** (40 mg, 38.5%, ee= 79%) as yellowish oil and olefin **3f** (25 mg, 24%).

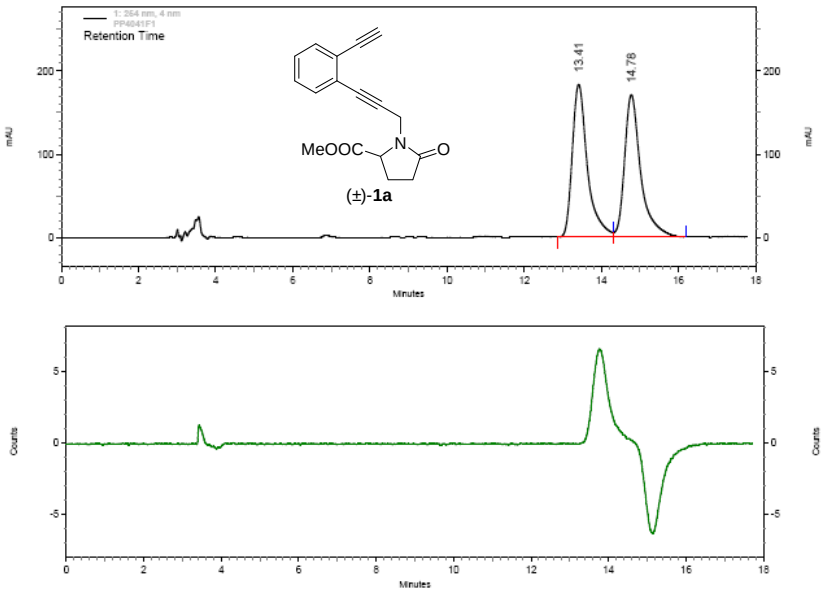
HRMS (ESI) of (*R*)-2f: m/z: calcd for $[M+H]^+$ $C_{22}H_{20}NO_2$: 330.1489, found: 330.1488.

Chiral HPLC separation of enantiomers: Chiralpak IA, hexane/ethanol 7/3, 1 mL/min, detection UV 230 nm and CD 254 nm, Rt (S) = 10.61 Rt (R) = 12.85 and k(*S*) = 2.54, k(*R*) = 3.28, α = 1.30 and Rs = 4.17. **ee = 79%**.

$[\alpha]_D^{25}$ = -112.0 (c= 0.44, CH_2Cl_2).

5. HPLC spectra

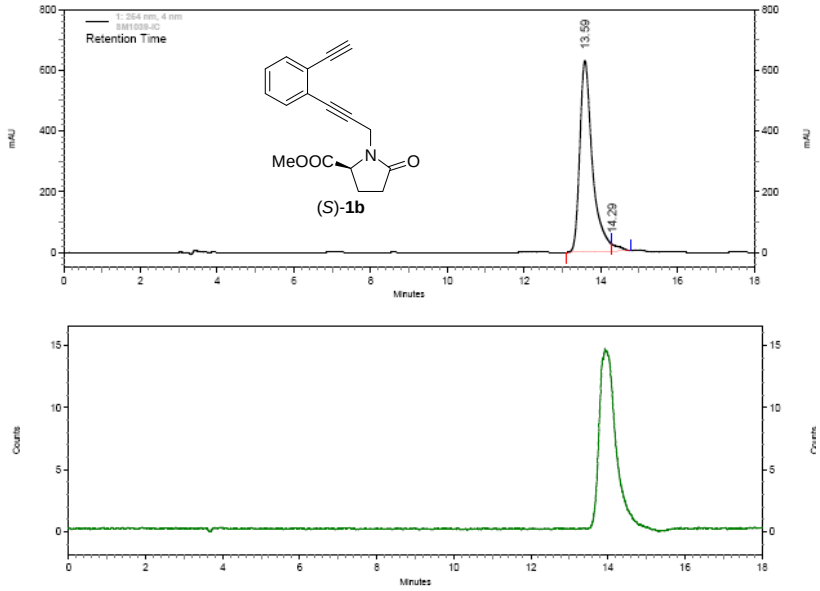
Method description : Chiralpak IC, Hexane/Ethanol 80/20, 1 ml/min, DAD and CD 254nm



1: 254 nm, 4 nm
Results

Retention Time	Area	Area %	Capacity factor	Relative RT	Resolution (USP)
13.41	20094701	50.08	3.47	1.00	0.00
14.78	20031024	49.92	3.93	1.13	1.95
Totals	40125725	100.00			

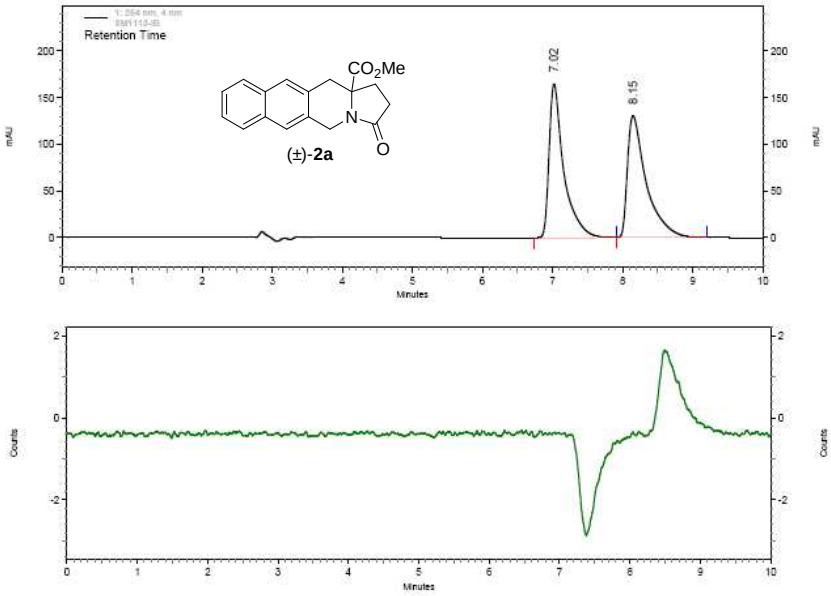
Method description : Chiralpak IC, Hexane/Ethanol 80/20, 1 ml/min, DAD and CD 254nm



1: 254 nm, 4 nm
Results

Retention Time	Area	Area %	Capacity factor	Relative RT	Resolution (USP)
13.59	57357318	98.01	3.53	1.00	0.00
14.29	1164461	1.99	3.76	1.07	0.00
Totals	58521779	100.00			

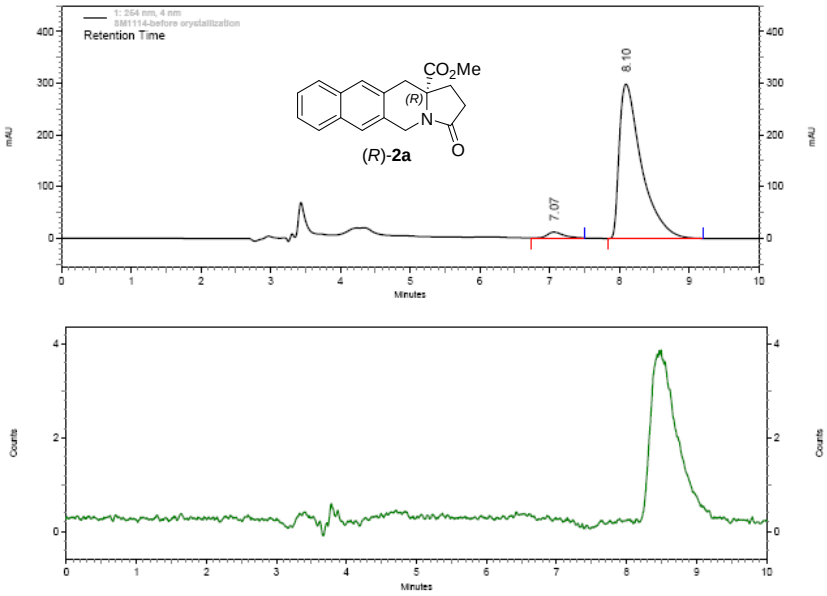
Method description : Chiralpak IB, Hexane/Ethanol 70/30, 1 ml/min, DAD and CD 254nm



1: 254 nm, 4 nm
Results

Retention Time	Area	Area %	Capacity factor	Relative RT	Resolution (USP)
7.02	9582229	49.57	1.34	1.00	0.00
8.15	9747416	50.43	1.72	1.28	2.80
Totals	19329645	100.00			

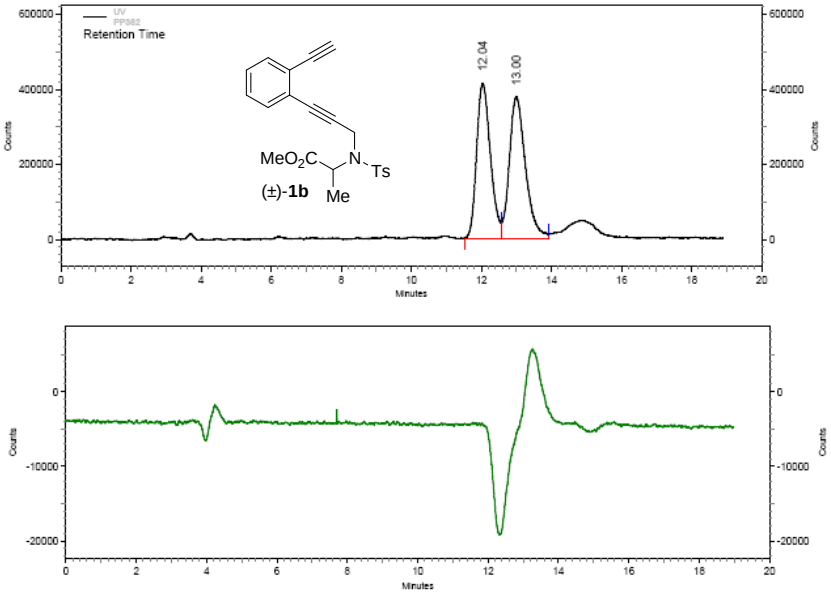
Method description : Chiralpak IB, Hexane/Ethanol 70/30, 1 ml/min, DAD and CD 254nm



1: 254 nm, 4 nm
Results

Retention Time	Area	Area %	Capacity factor	Relative RT	Resolution (USP)
7.07	713204	2.63	1.36	1.00	0.00
8.10	26422255	97.37	1.70	1.25	2.16
Totals	27135459	100.00			

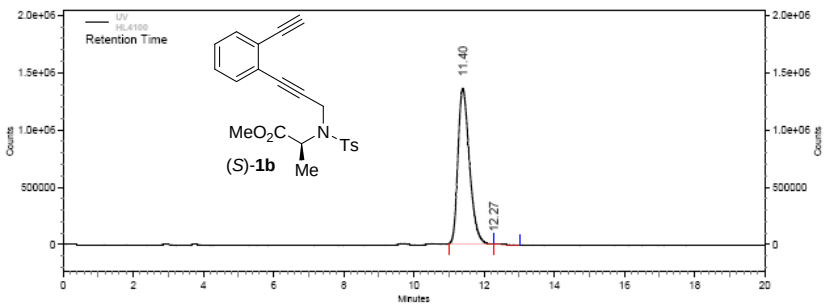
Method description : Chiralcel OD-3, Hexane/Isopropanol 80/20, 1 ml/min, UV 254 nm et CD254

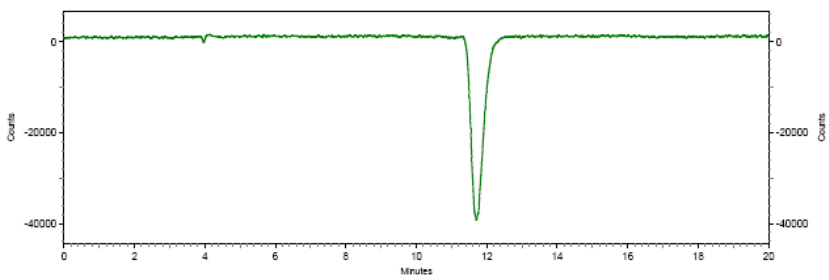


UV Results

Retention Time	Area	Area %	Capacity factor	Relative RT	Resolution (USP)
12.04	11238193	48.27	3.01	1.00	0.00
13.00	12044119	51.73	3.33	1.11	1.22
Totals	23282312	100.00			

Method description : Chiralcel OD-3, Hexane/Isopropanol 80/20, 1 ml/min, UV 254 nm et CD254nm

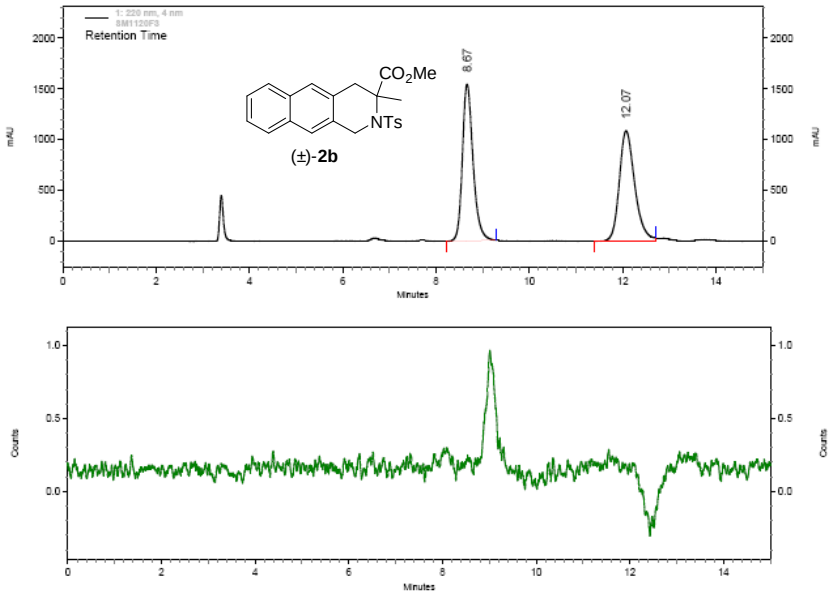




UV Results

Retention Time	Area	Area %	Capacity factor	Relative RT	Resolution (USP)
11.40	30928864	99.59	2.80	1.00	0.00
12.27	126057	0.41	3.09	1.10	0.95
Totals	31054921	100.00			

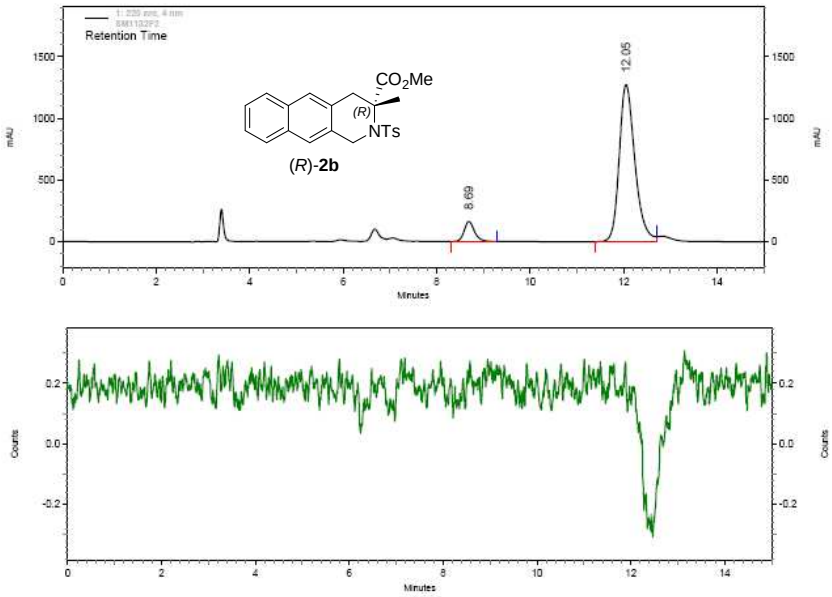
Method description : Chiralpak IA, Hexane/Ethanol 70/30, 1 ml/min, DAD and CD 254nm



1: 220 nm, 4 nm
Results

Retention Time	Area	Area %	Capacity factor	Relative RT	Resolution (USP)
8.67	98018933	49.34	1.89	1.00	0.00
12.07	100660532	50.66	3.02	1.60	6.77
Totals	198679465	100.00			

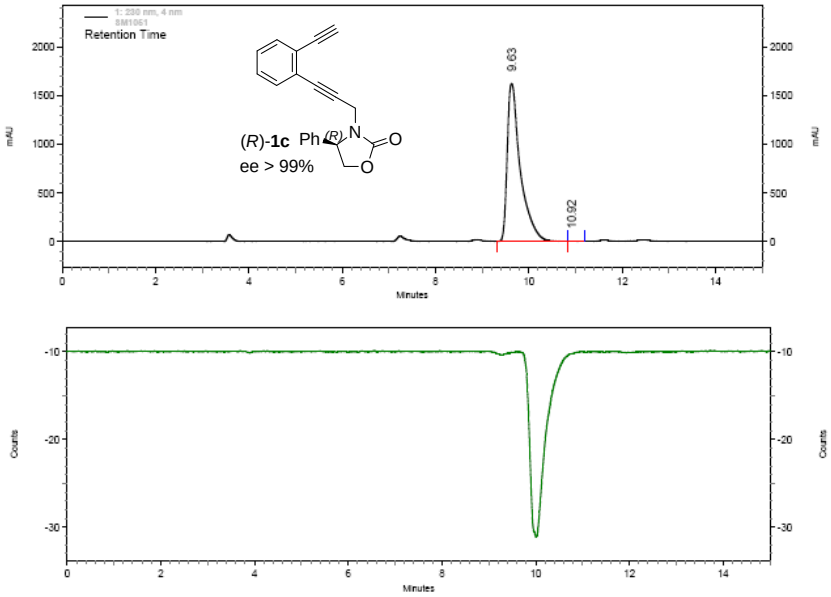
Method description : Chiralpak IA, Hexane/Ethanol 70/30, 1 ml/min, DAD and CD 254nm



1: 220 nm, 4 nm
Results

Retention Time	Area	Area %	Capacity factor	Relative RT	Resolution (USP)
8.69	9959234	7.73	1.90	1.00	0.00
12.05	118884616	92.27	3.02	1.59	6.72
Totals	128843850	100.00			

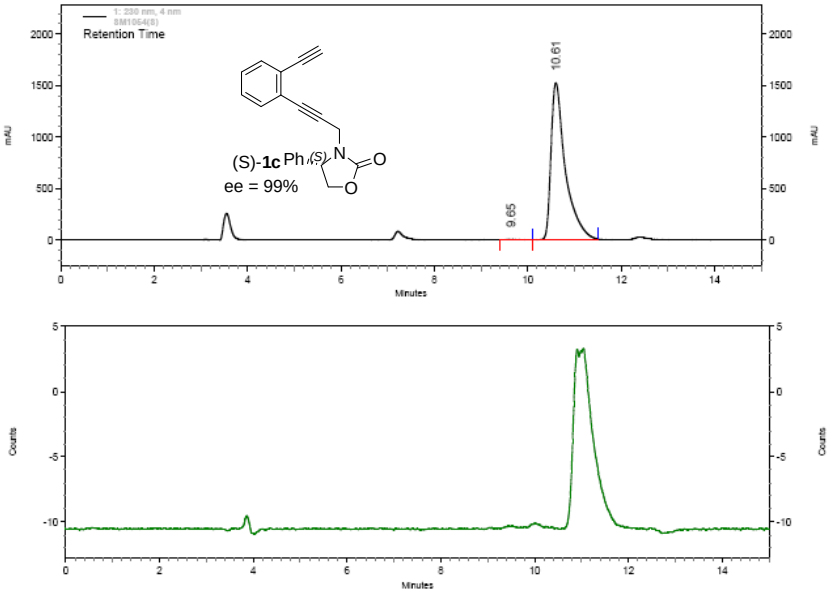
Method description : Chiralpak IB, Hexane/Ethanol 90/10, 1 ml/min, DAD and CD 254nm



1: 230 nm, 4 nm
Results

Retention Time	Area	Area %	Capacity factor	Relative RT	Resolution (USP)
9.63	126895659	99.96	2.21	1.00	0.00
10.92	52369	0.04	2.64	1.19	2.02
Totals	126948028	100.00			

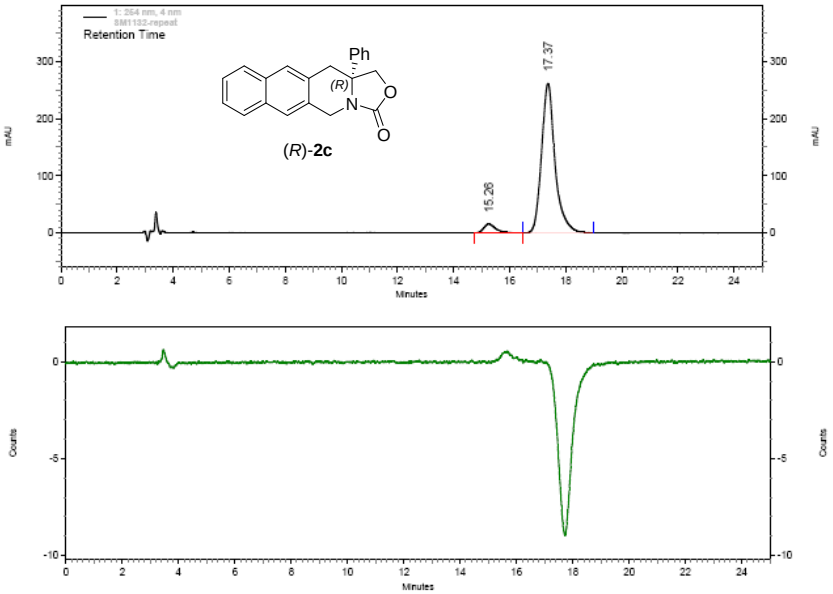
Method description : Chiralpak IB, Hexane/Ethanol 90/10, 1 ml/min, DAD and CD 254nm



1: 230 nm, 4 nm
Results

Retention Time	Area	Area %	Capacity factor	Relative RT	Resolution (USP)
9.65	458194	0.35	2.22	1.00	0.00
10.61	130666955	99.65	2.54	1.14	2.07
Totals	131125149	100.00			

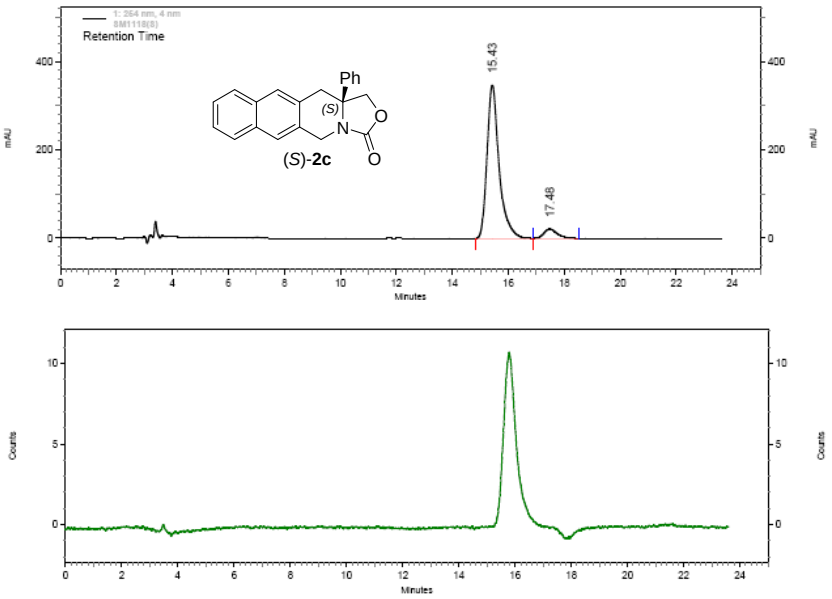
Method description : Chiralpak IC, Hexane/Ethanol 70/30, 1 ml/min, DAD and CD 254nm



1: 254 nm, 4 nm
Results

Retention Time	Area	Area %	Capacity factor	Relative RT	Resolution (USP)
15.26	1829061	4.97	4.09	1.00	0.00
17.37	34938562	95.03	4.79	1.17	2.64
Totals	36767623	100.00			

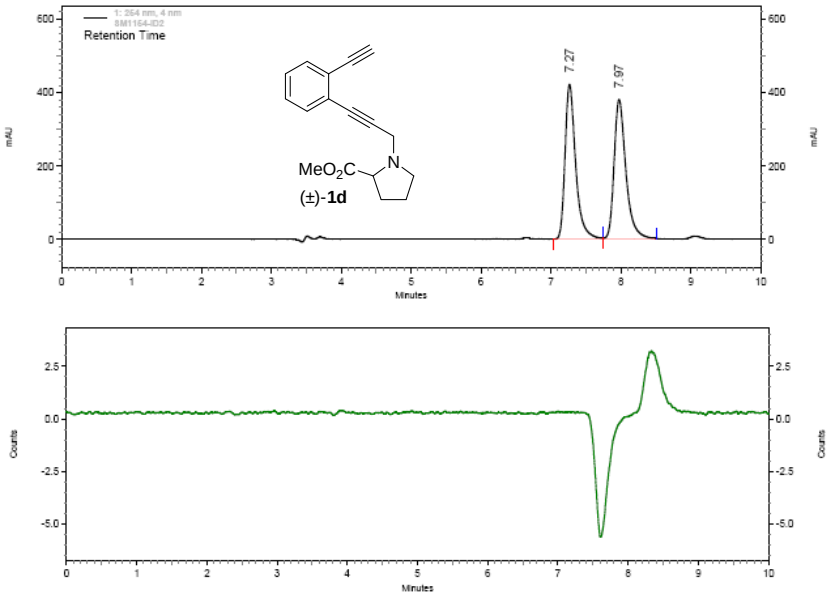
Method description : Chiralpak IC, Hexane/Ethanol 70/30, 1 ml/min, DAD and CD 254nm



1: 254 nm, 4 nm
Results

Retention Time	Area	Area %	Capacity factor	Relative RT	Resolution (USP)
15.43	41773029	93.44	4.14	1.00	0.00
17.48	2930447	6.56	4.83	1.16	2.50
Totals	44703476	100.00			

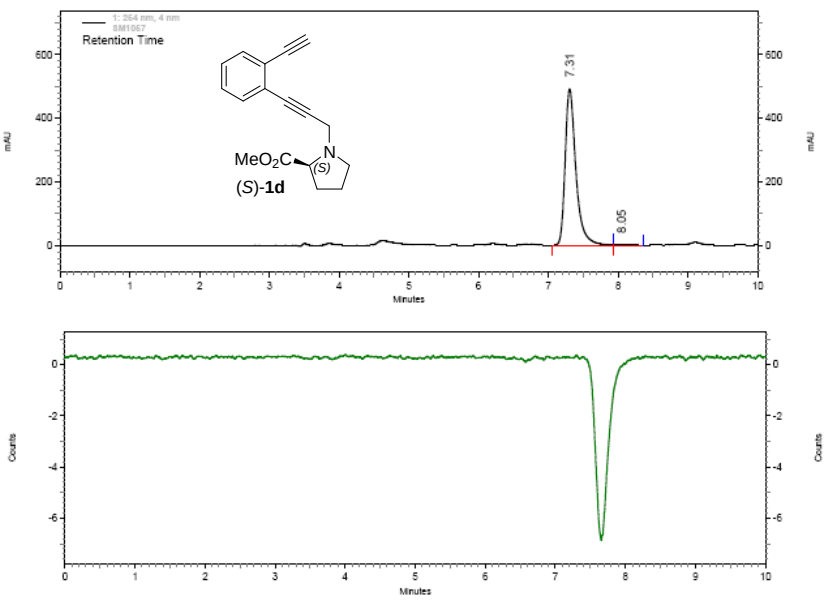
Method description : Chiralpak ID, Hexane/isopropanol 95/5, 1 ml/min, DAD and CD 254nm



1: 254 nm, 4 nm
Results

Retention Time	Area	Area %	Capacity factor	Relative RT	Resolution (USP)
7.27	17843427	50.09	1.42	1.00	0.00
7.97	17776006	49.91	1.66	1.17	2.49
Totals	35619433	100.00			

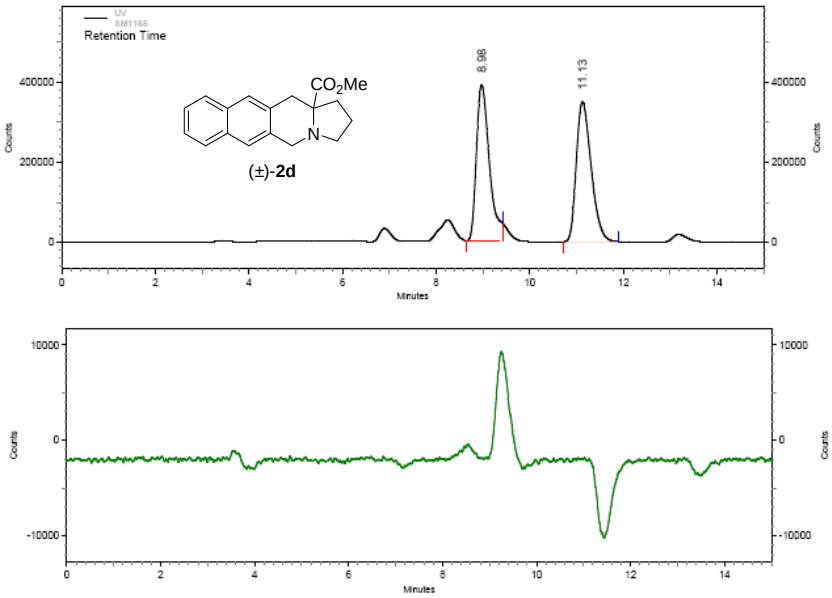
Method description : Chiralpak ID, Hexane/isopropanol 95/5, 1 ml/min, DAD and CD 254nm



1: 254 nm, 4 nm
Results

Retention Time	Area	Area %	Capacity factor	Relative RT	Resolution (USP)
7.31	21021659	99.56	1.44	1.00	0.00
8.05	92206	0.44	1.68	1.17	2.24
Totals	21113865	100.00			

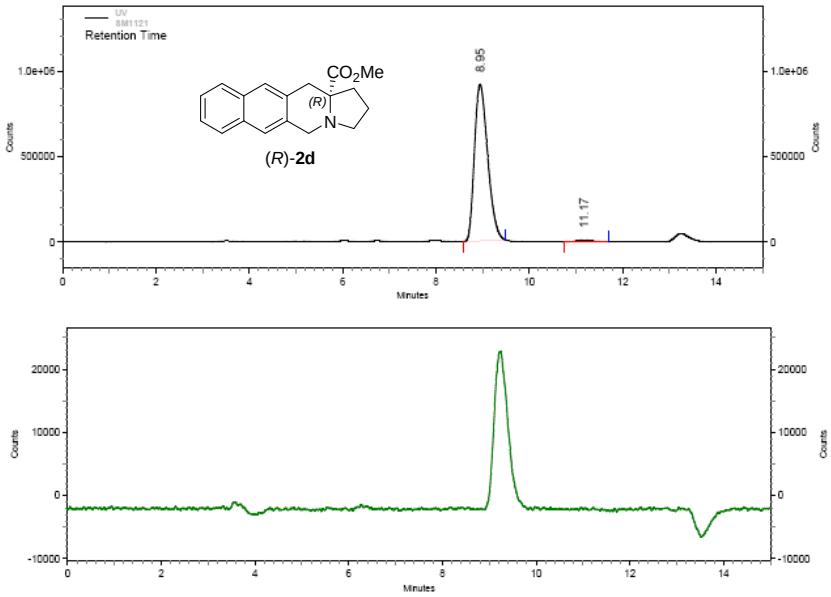
Method description : Chiralpak AD-H, Hexane/ethanol 95/5, 1 ml/min, UV 254 nm et CD254nm



UV Results

Retention Time	Area	Area %	Capacity factor	Relative RT	Resolution (USP)
8.98	7454862	49.26	1.99	1.00	0.00
11.13	7677729	50.74	2.71	1.36	3.96
Totals	15132591	100.00			

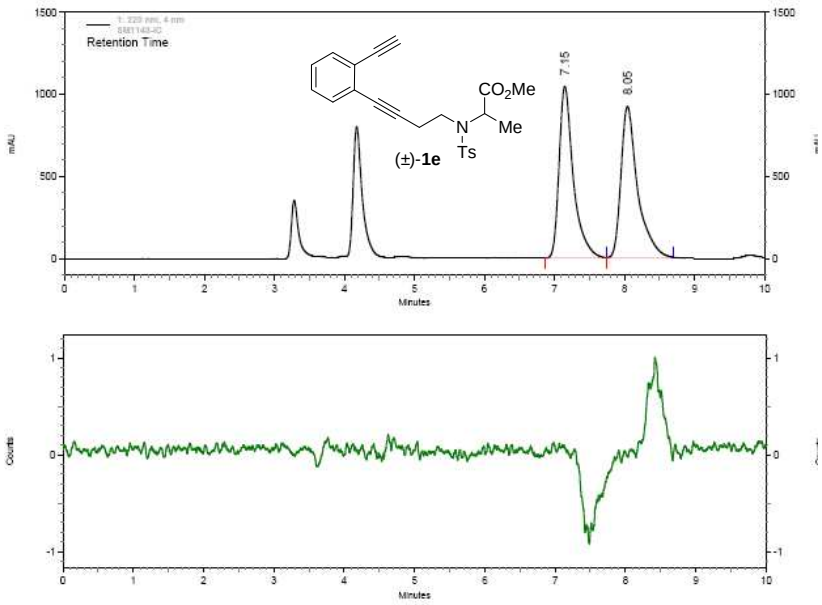
Method description : Chiralpak AD-H, Hexane/ethanol 95/5, 1 ml/min, UV 254 nm et CD254nm



UV Results

Retention Time	Area	Area %	Capacity factor	Relative RT	Resolution (USP)
8.95	18031114	98.67	1.98	1.00	0.00
11.17	242399	1.33	2.72	1.37	3.91
Totals	18273513	100.00			

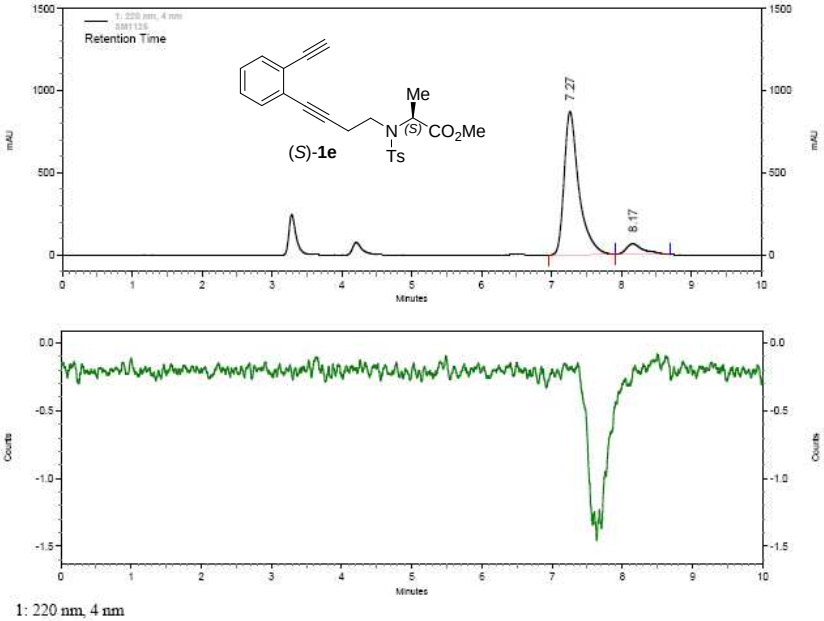
Method description : Chiralpak IC, Hexane/Ethanol 70/30, 1 ml/min, DAD and CD 254nm



1: 220 nm, 4 nm
Results

Retention Time	Area	Area %	Capacity factor	Relative RT	Resolution (USP)
7.15	59157081	49.29	1.38	1.00	0.00
8.05	60867611	50.71	1.68	1.22	2.34
Totals	120024692	100.00			

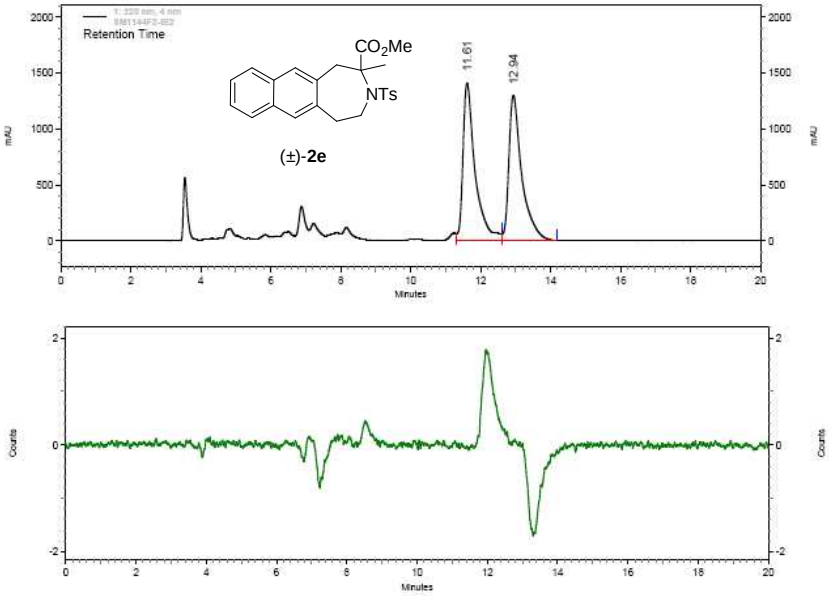
Method description : Chiralpak IC, Hexane/Ethanol 70/30, 1 ml/min, DAD and CD 254nm



1: 220 nm, 4 nm
Results

Retention Time	Area	Area %	Capacity factor	Relative RT	Resolution (USP)
7.27	51199432	91.68	1.42	1.00	0.00
8.17	4647165	8.32	1.72	1.21	2.28
Totals	55846597	100.00			

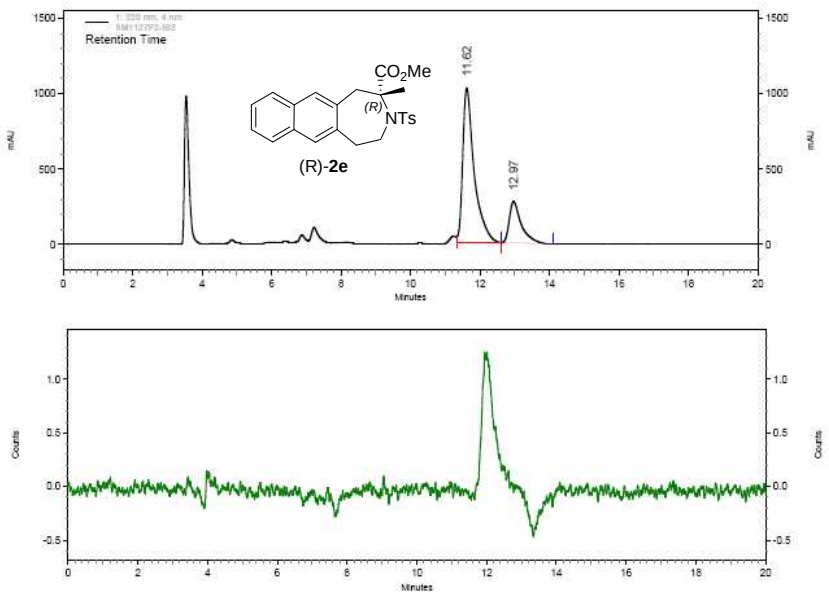
Method description : Chiralpak IB, Hexane/Ethanol 90/10, 1 ml/min, DAD and CD 254nm



1: 220 nm, 4 nm
Results

Retention Time	Area	Area %	Capacity factor	Relative RT	Resolution (USP)
11.61	134626830	50.29	2.87	1.00	0.00
12.94	133054508	49.71	3.31	1.15	2.19
Totals	267681338	100.00			

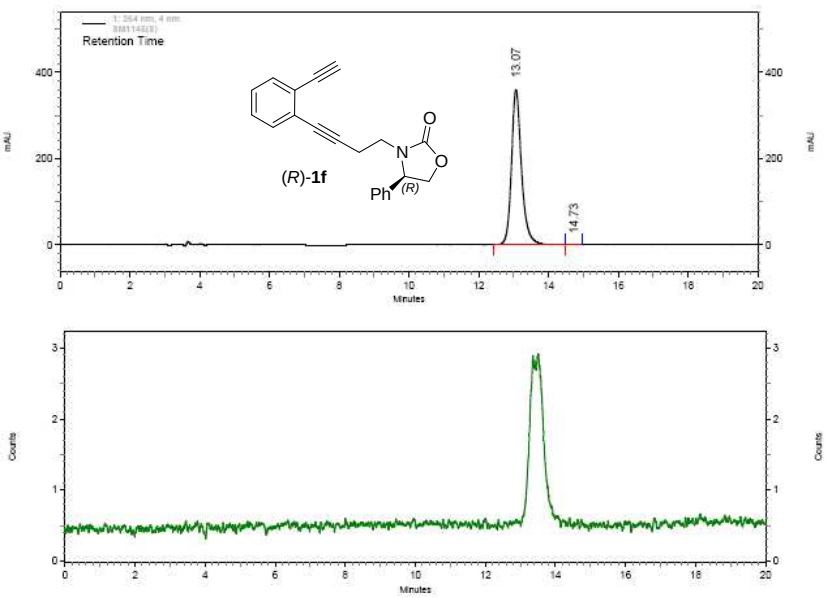
Method description : Chiralpak IB, Hexane/Ethanol 90/10, 1 ml/min, DAD and CD 254nm



1: 220 nm, 4 nm
Results

Retention Time	Area	Area %	Capacity factor	Relative RT	Resolution (USP)
11.62	94369637	78.07	2.87	1.00	0.00
12.97	26514513	21.93	3.32	1.16	2.31
Totals	120884150	100.00			

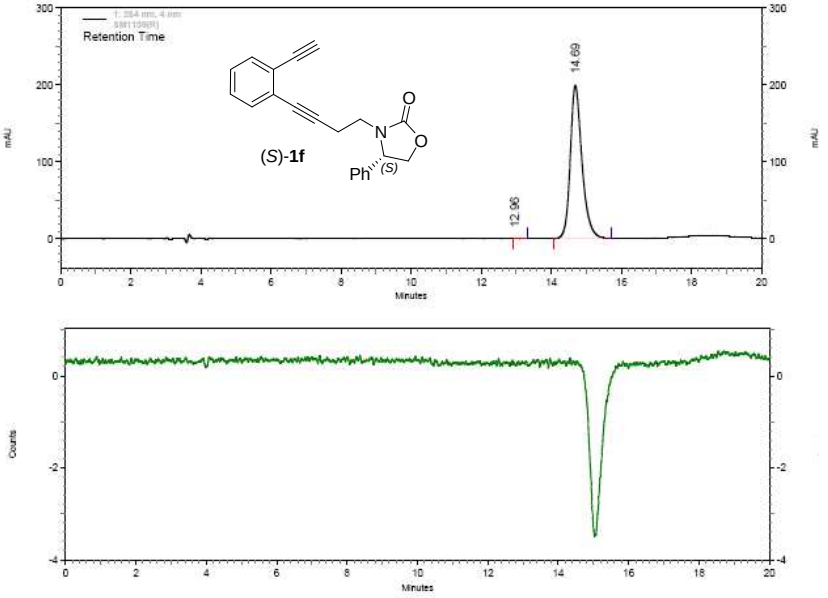
Method description : Chiralpak IA, Hexane/Ethanol 90/10, 1 ml/min, DAD and CD 254nm



1: 254 nm, 4 nm
Results

Retention Time	Area	Area %	Capacity factor	Relative RT	Resolution (USP)
13.07	28792775	99.97	3.36	1.00	0.00
14.73	8794	0.03	3.91	1.16	3.52
Totals	28801569	100.00			

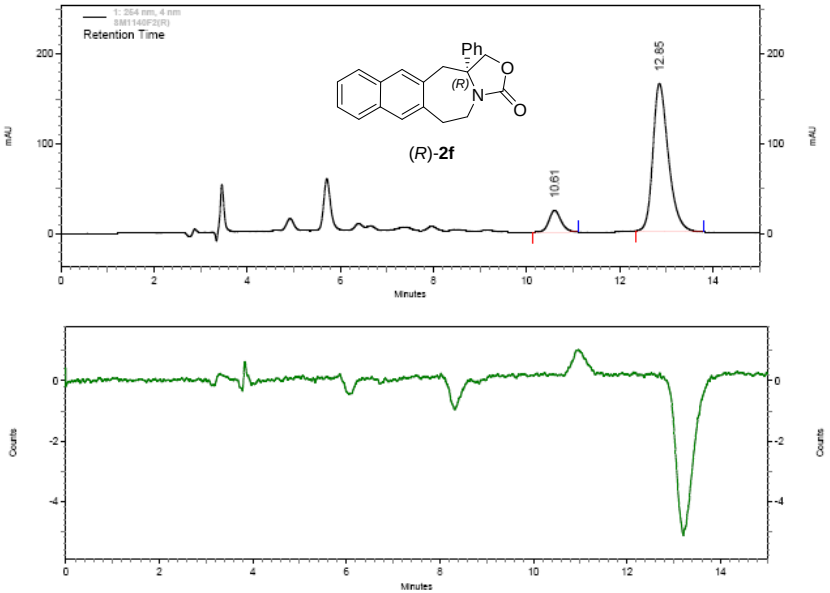
Method description : Chiralpak IA, Hexane/Ethanol 90/10, 1 ml/min, DAD and CD 254nm



1: 254 nm, 4 nm
Results

Retention Time	Area	Area %	Capacity factor	Relative RT	Resolution (USP)
12.96	8714	0.05	3.32	1.00	0.00
14.69	18528265	99.95	3.90	1.17	4.24
Totals	18536979	100.00			

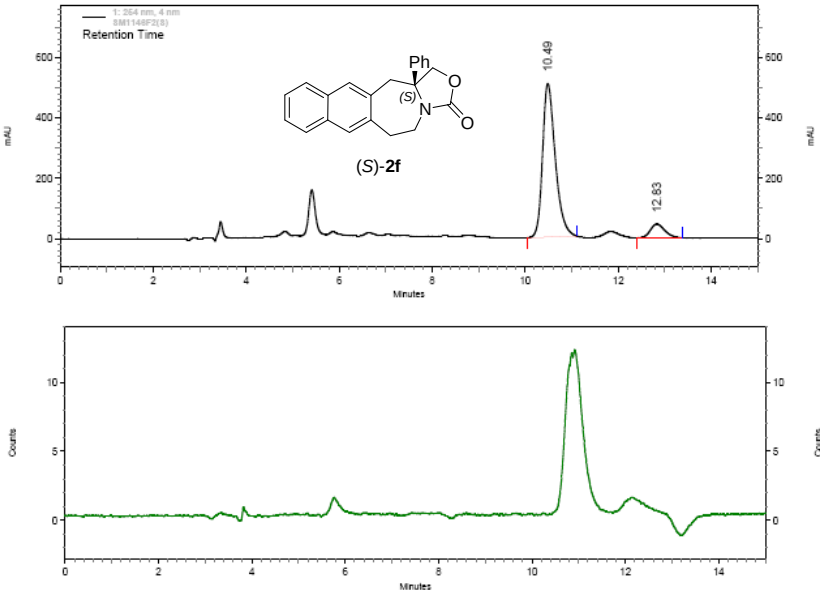
Method description : Chiralpak IA, Hexane/Ethanol 70/30, 1 ml/min, DAD and CD 254nm



1: 254 nm, 4 nm
Results

Retention Time	Area	Area %	Capacity factor	Relative RT	Resolution (USP)
10.61	1746352	10.31	2.54	1.00	0.00
12.85	15191332	89.69	3.28	1.30	4.17
Totals	16937684	100.00			

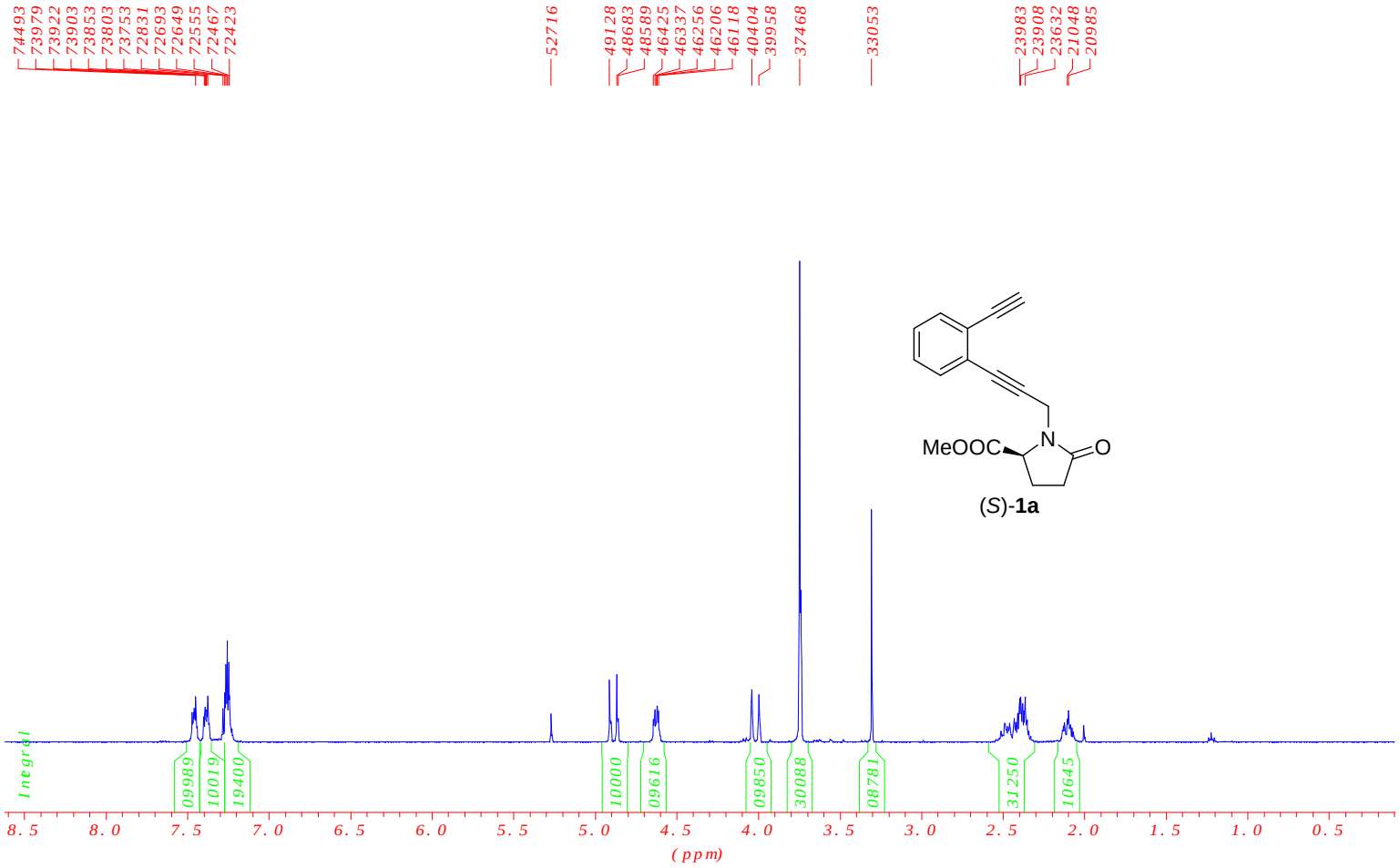
Method description : Chiralpak IA, Hexane/Ethanol 70/30, 1 ml/min, DAD and CD 254nm

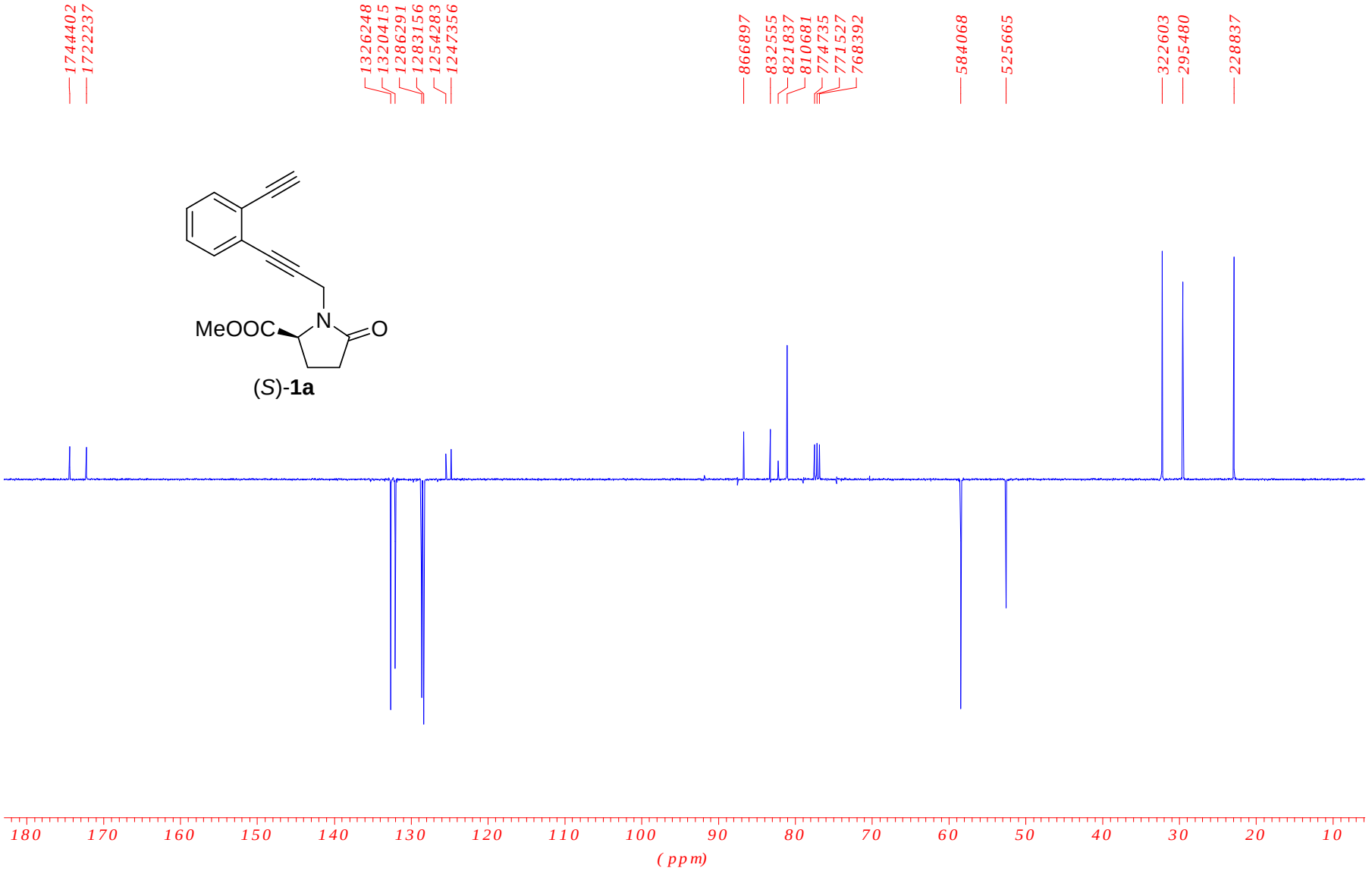


1: 254 nm, 4 nm
Results

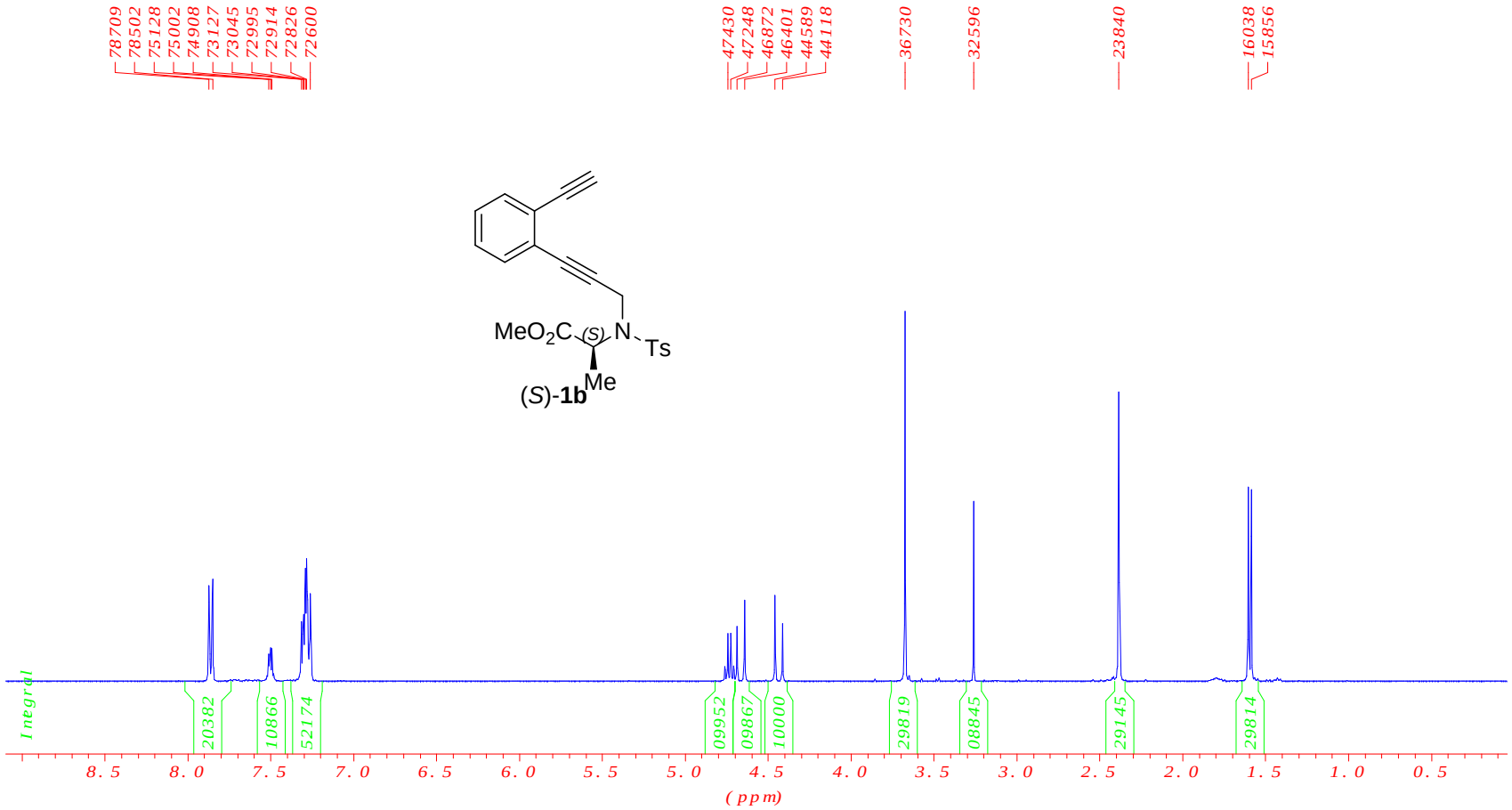
Retention Time	Area	Area %	Capacity factor	Relative RT	Resolution (USP)
10.49	38560089	90.73	2.50	1.00	0.00
12.83	3941121	9.27	3.28	1.31	4.39
Totals	42501210	100.00			

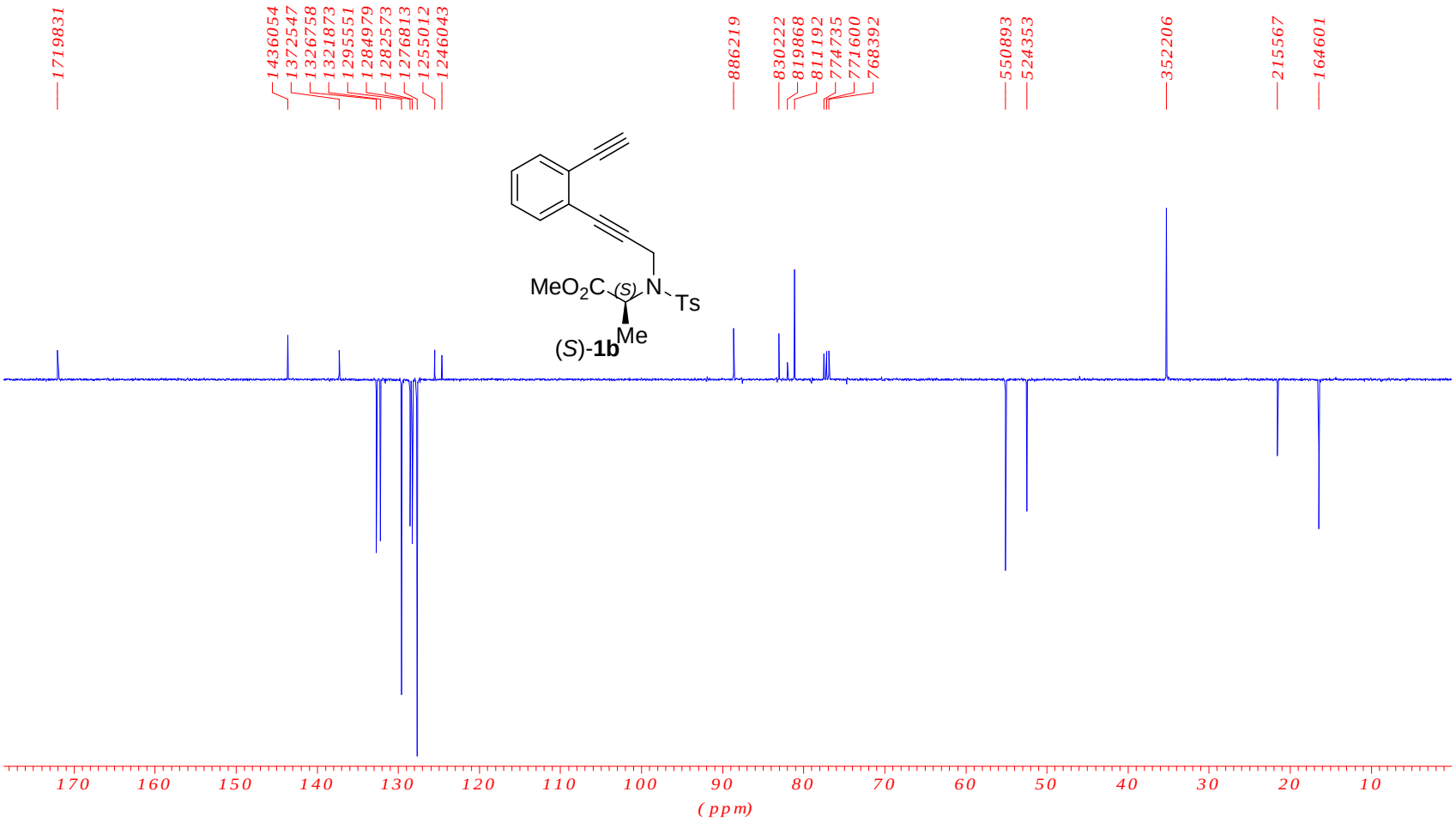
6. NMR spectra

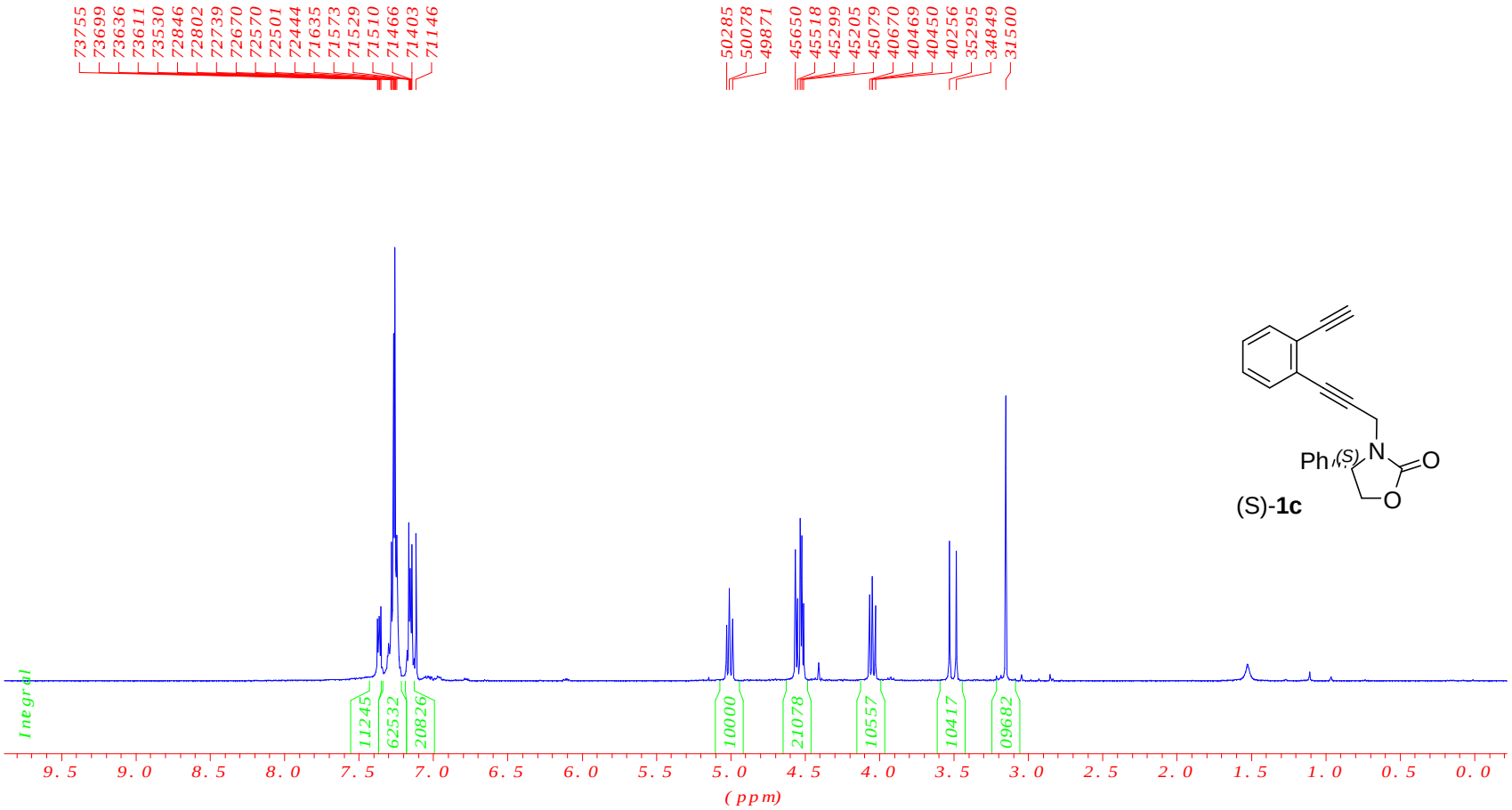


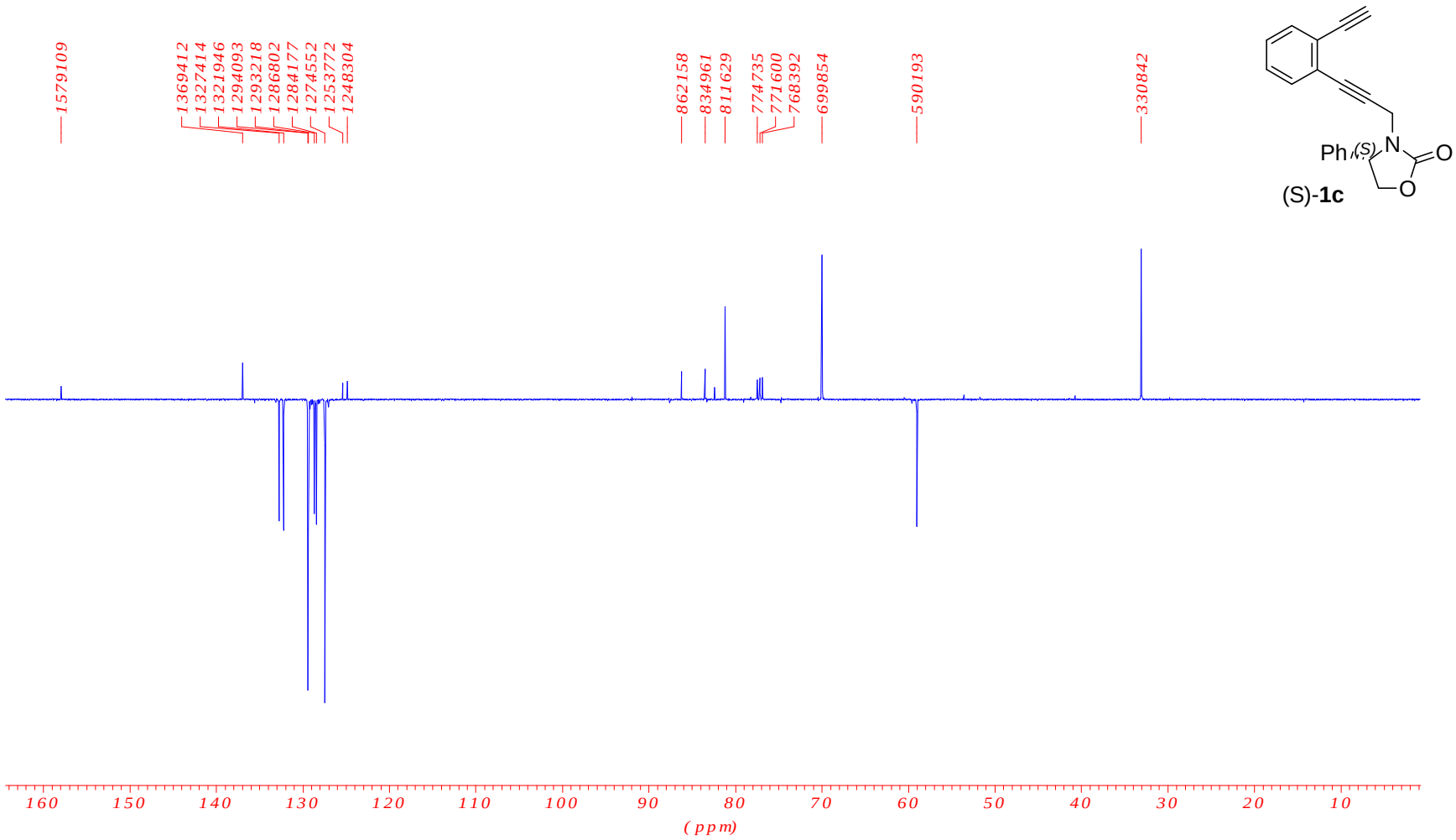


(*S*)-**1a**








1579109
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1253772
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811629
774735
771600
768392
699854
590193
330842
Ph
(S)
N
O
O
(S)-1c
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150
140
130
120
110
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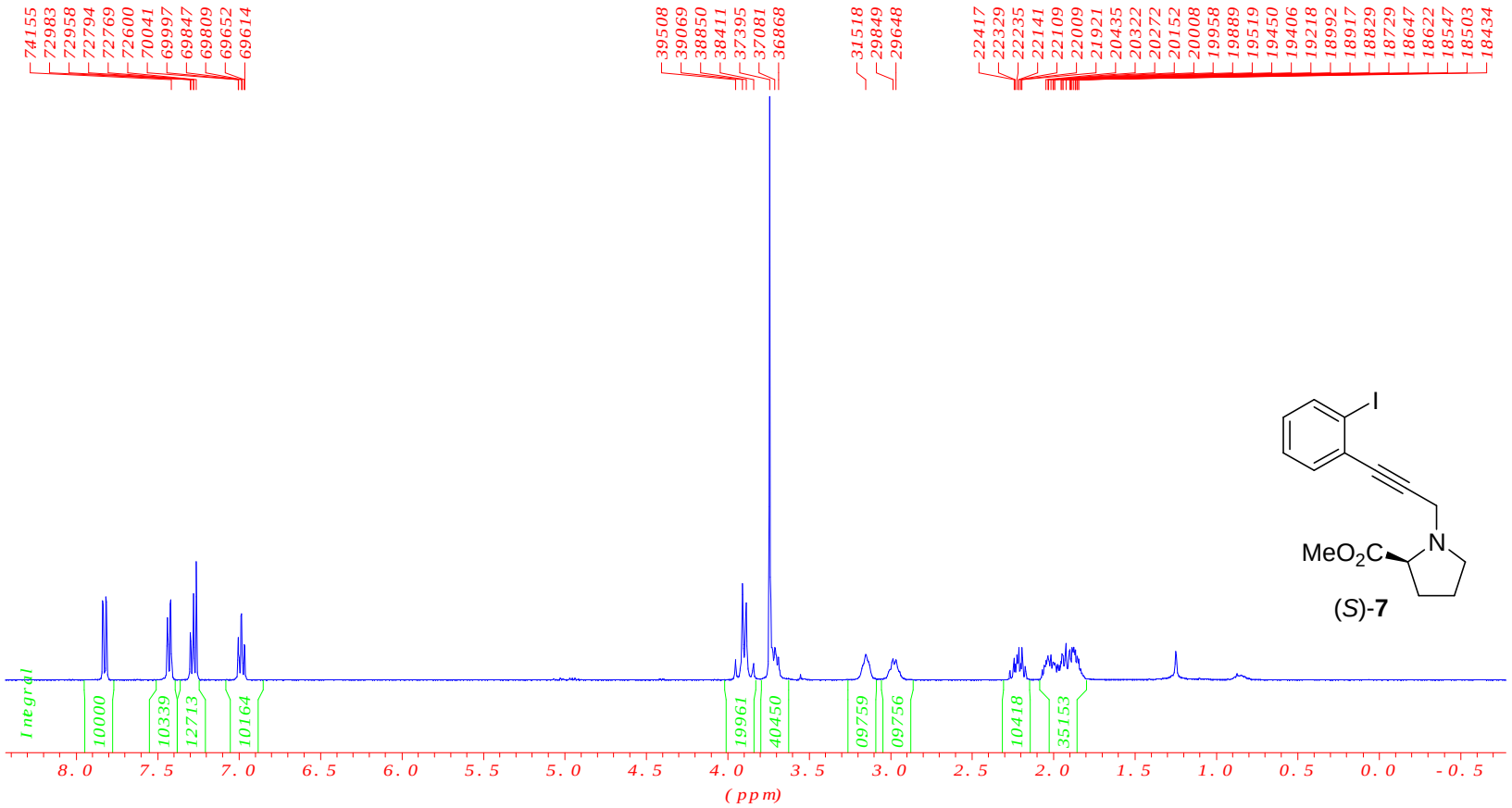
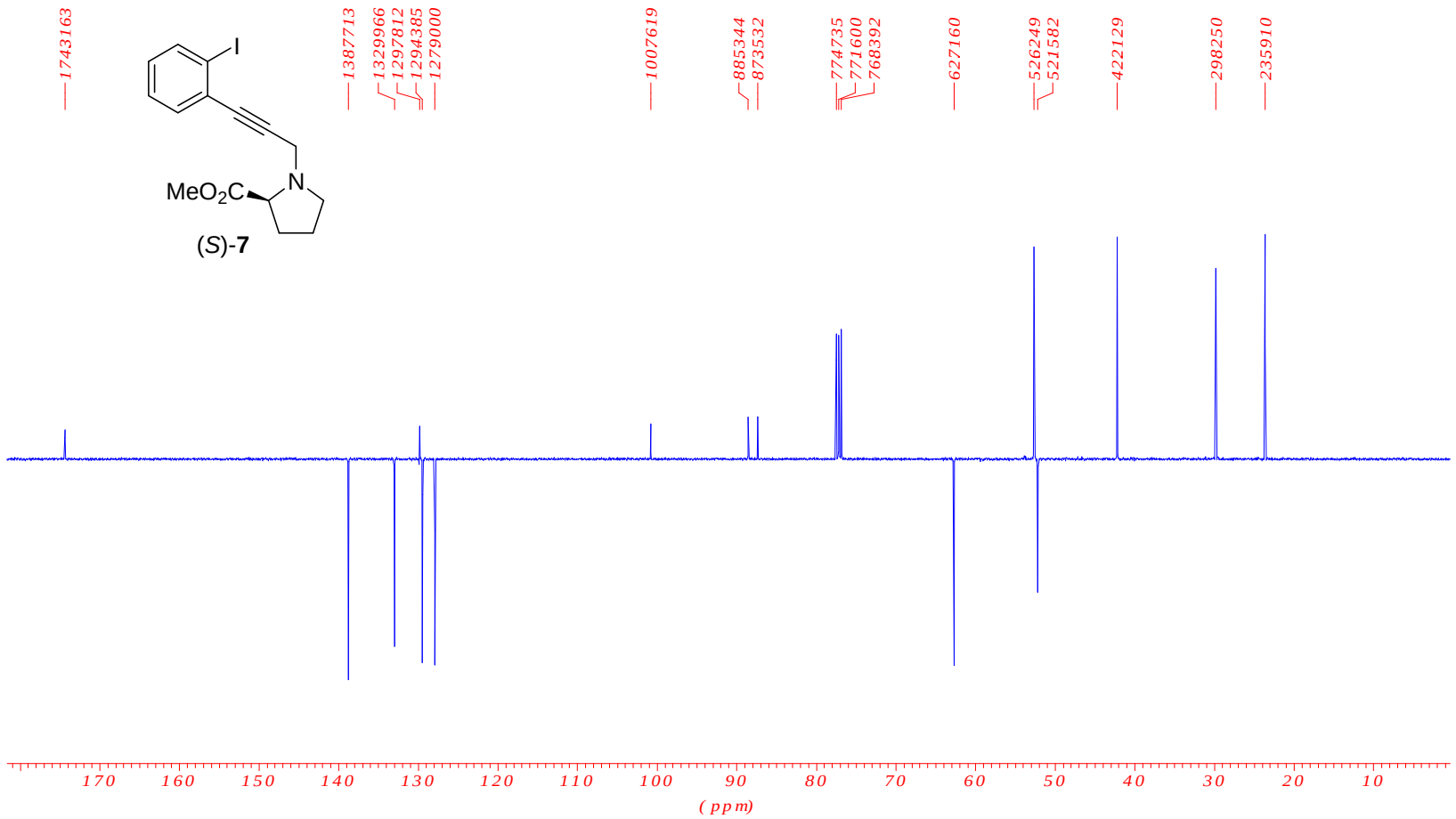
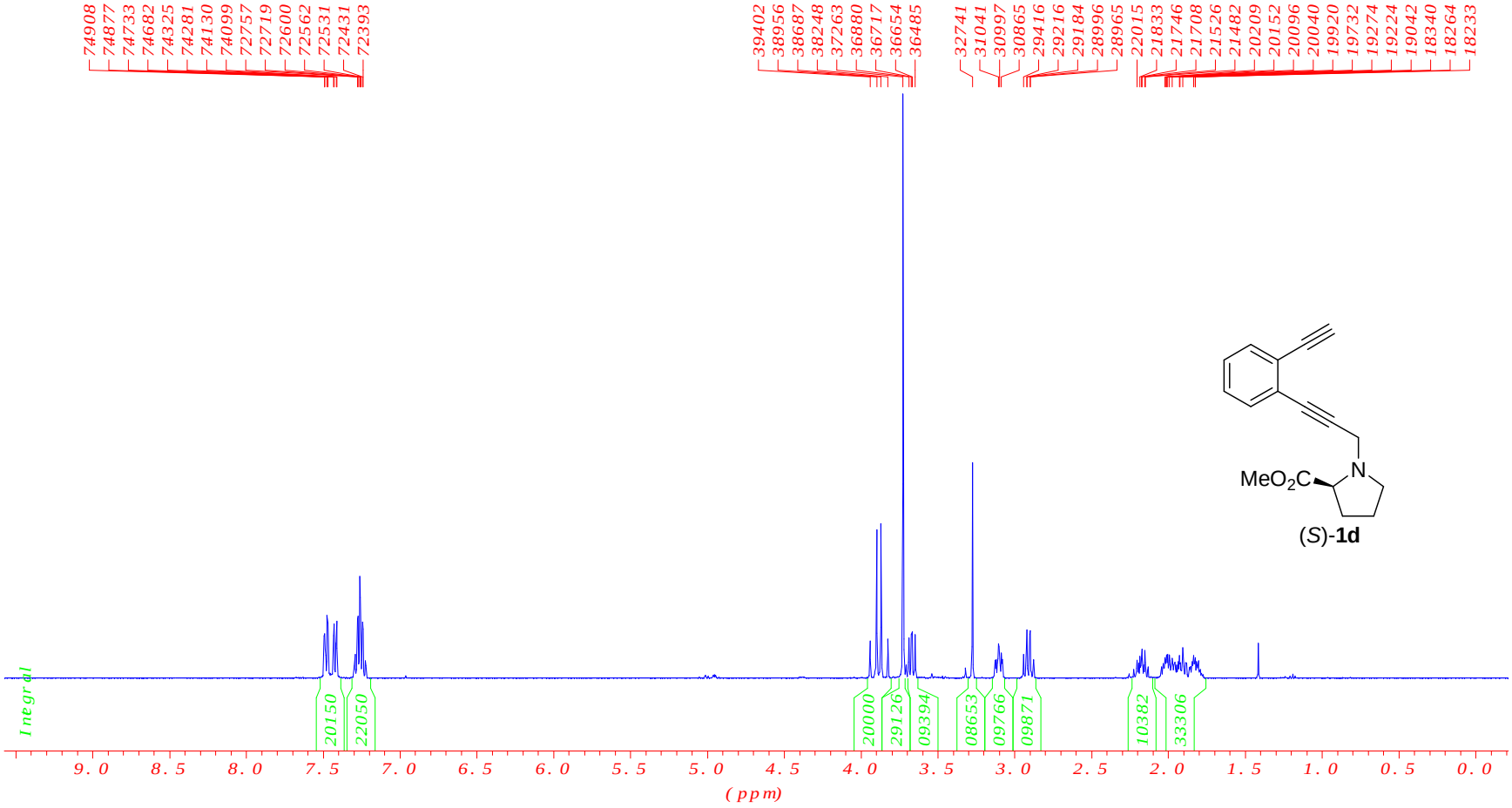
70
60
50
40
30
20
10
(ppm)

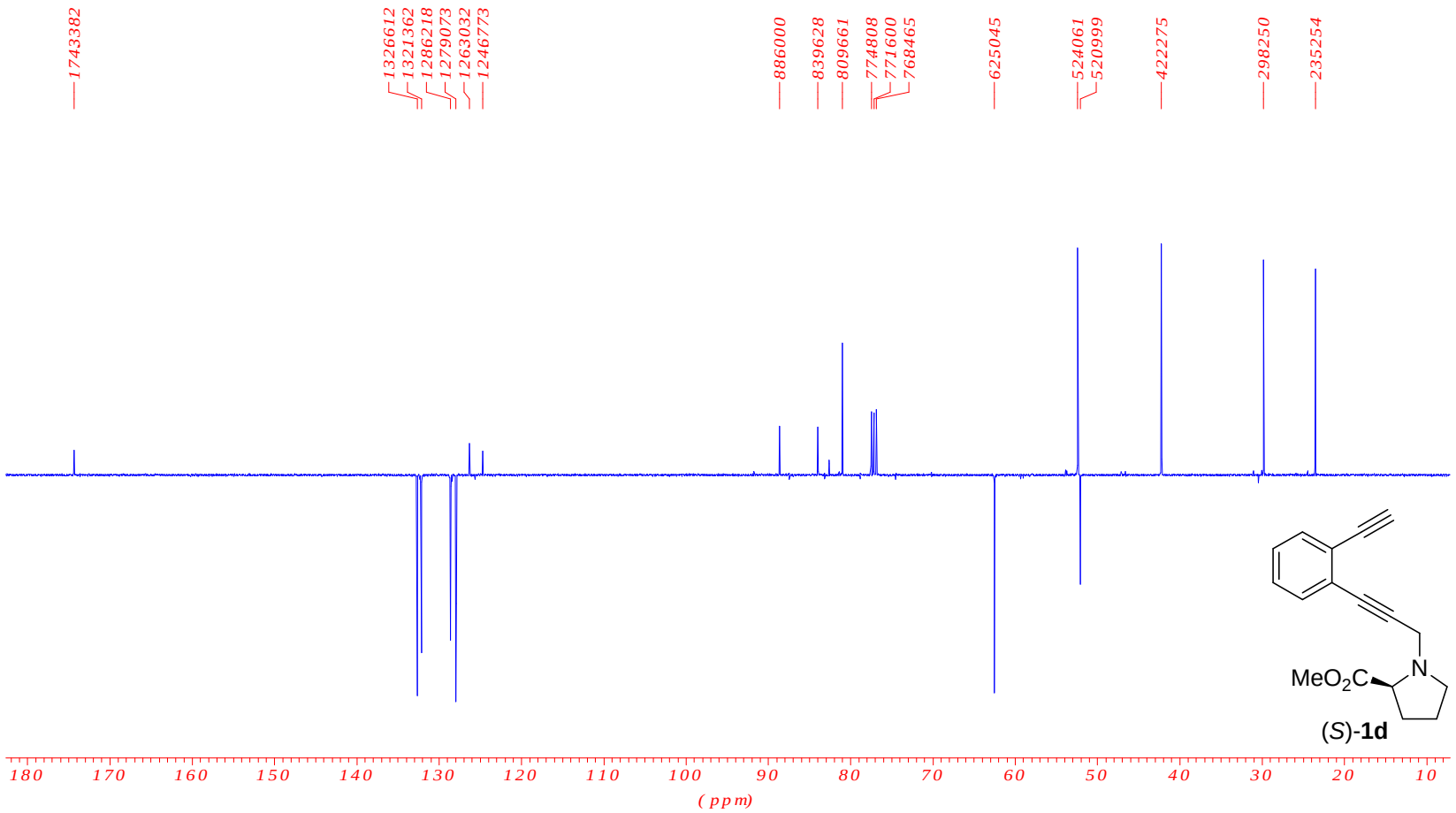


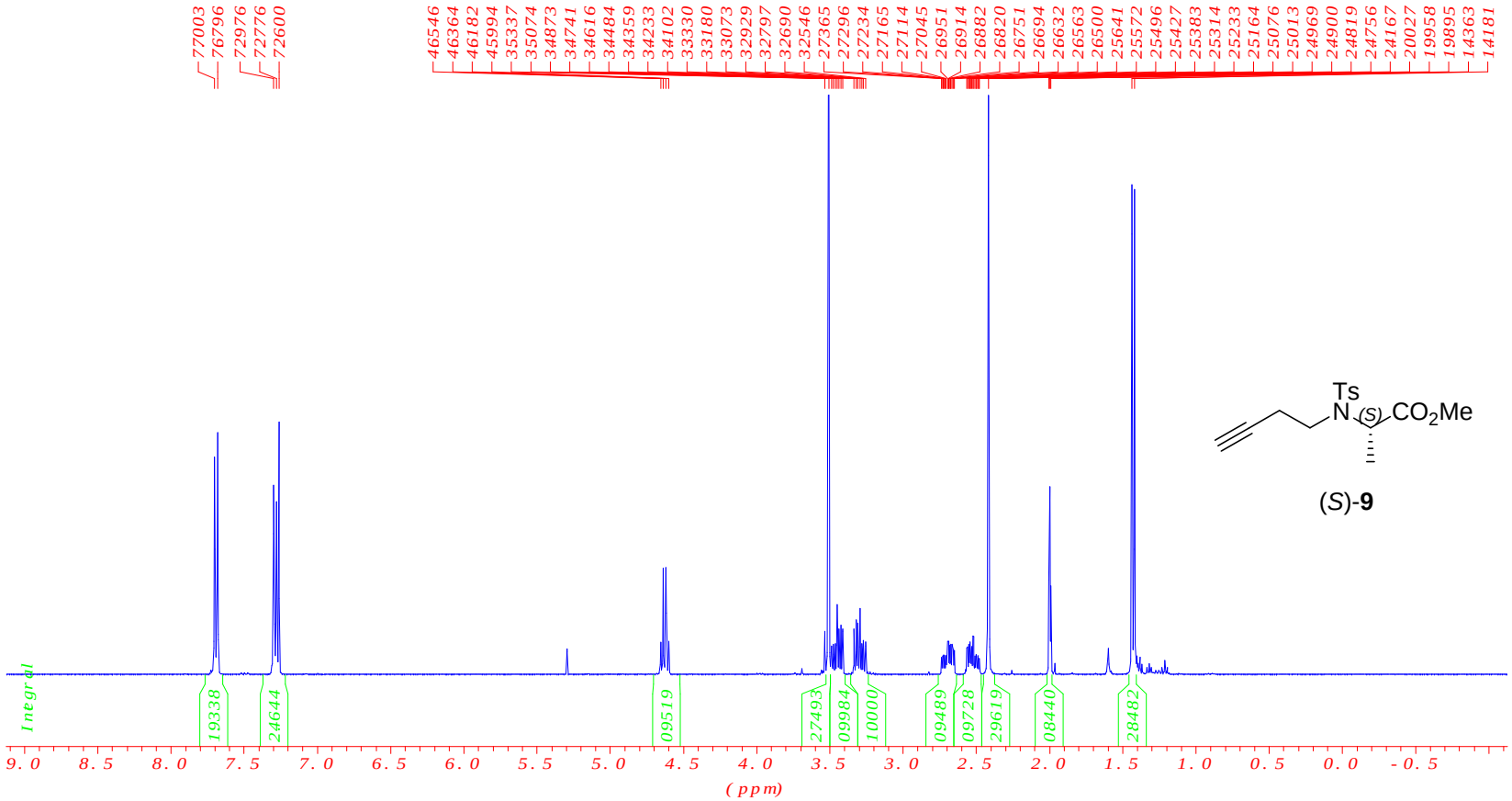
(*S*)-**7**



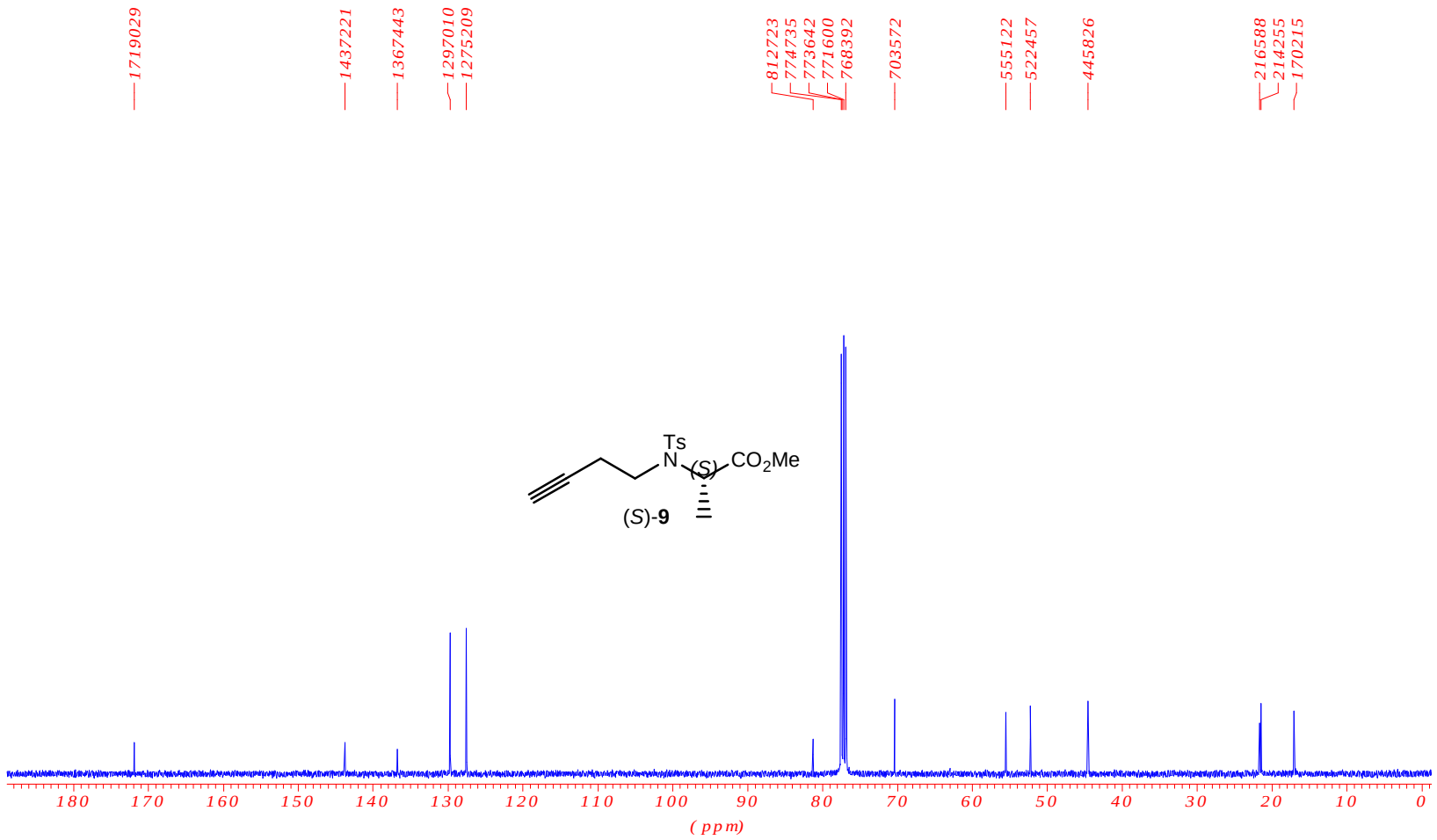


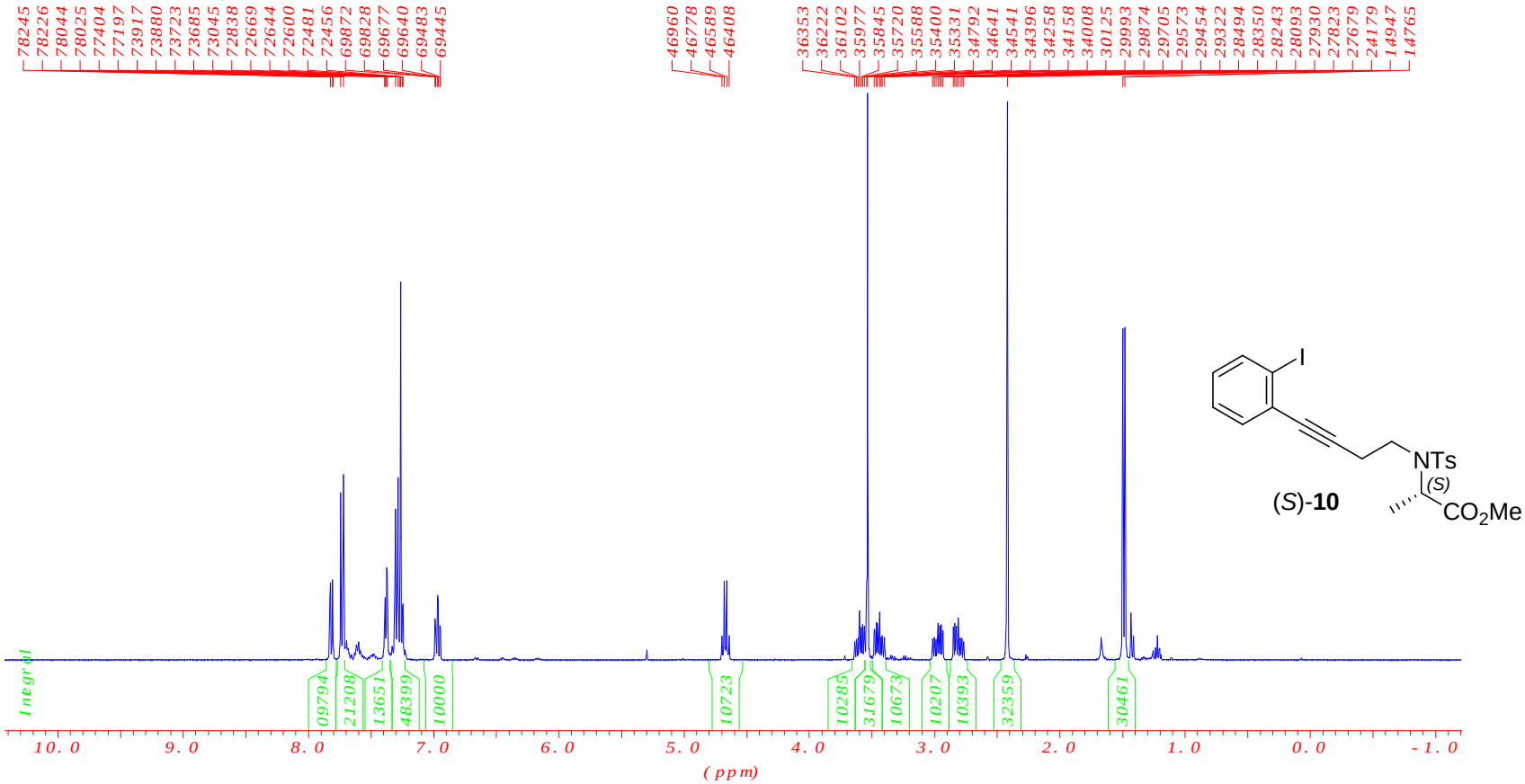
(*S*)-**1d**

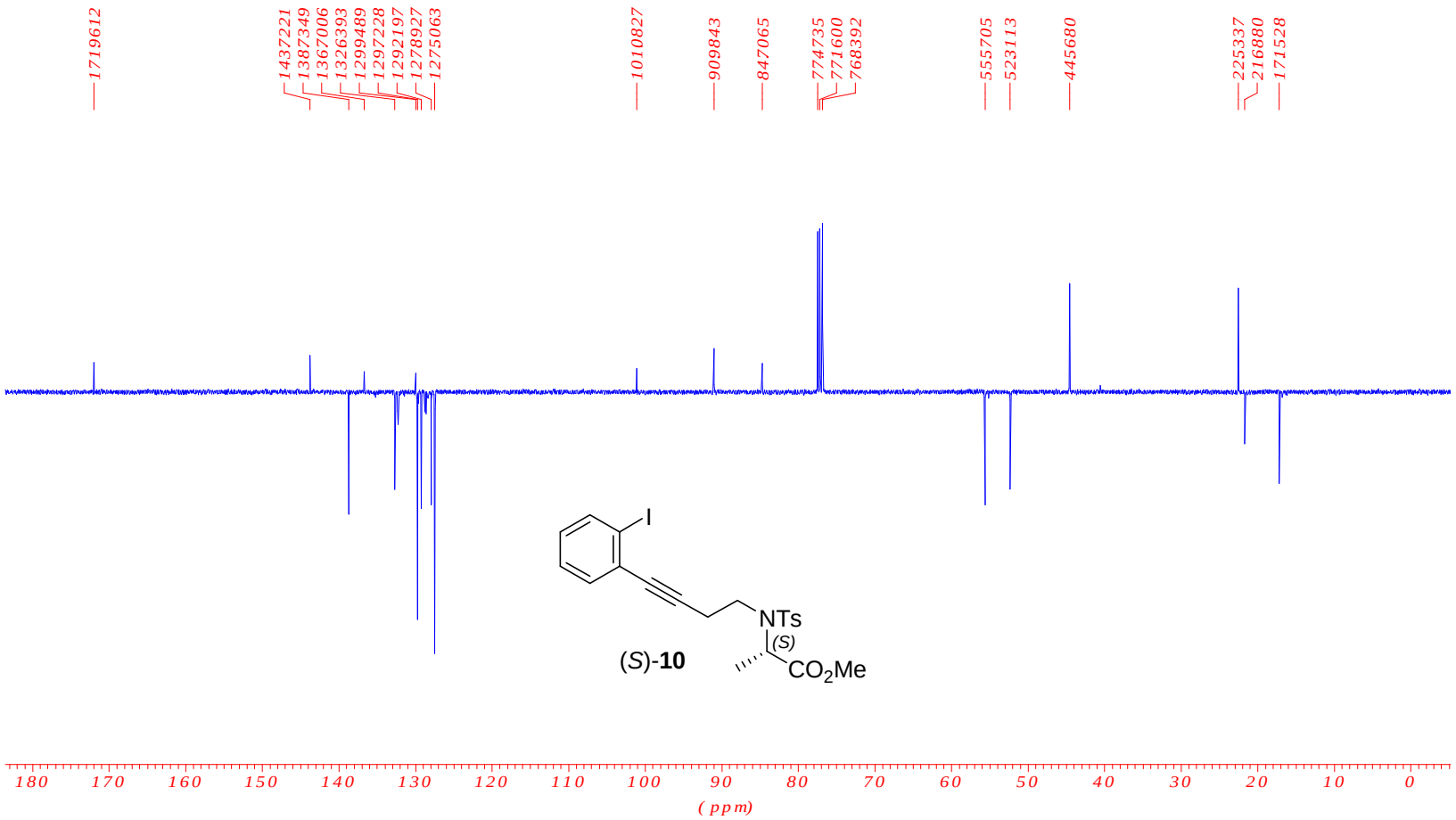


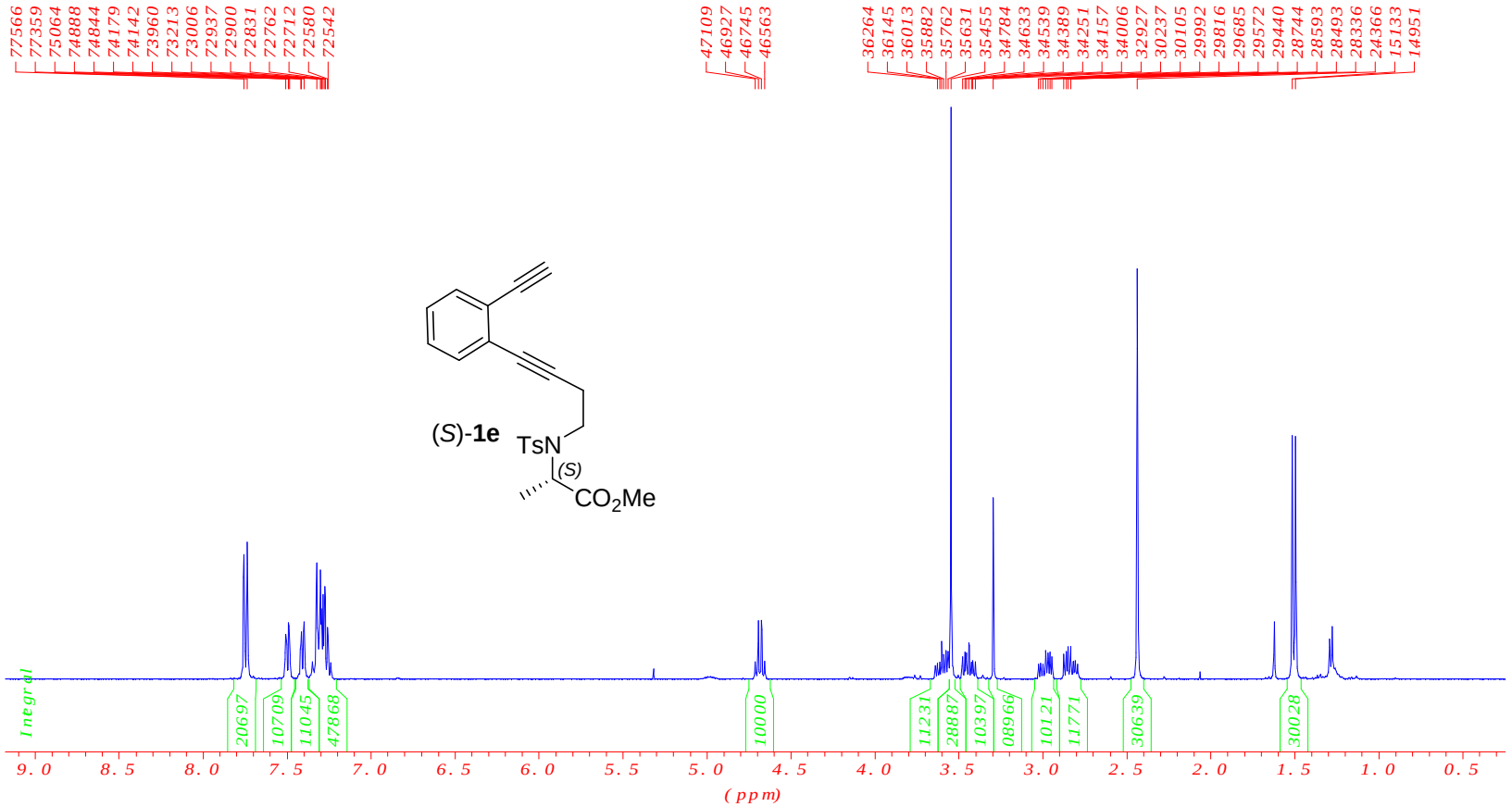


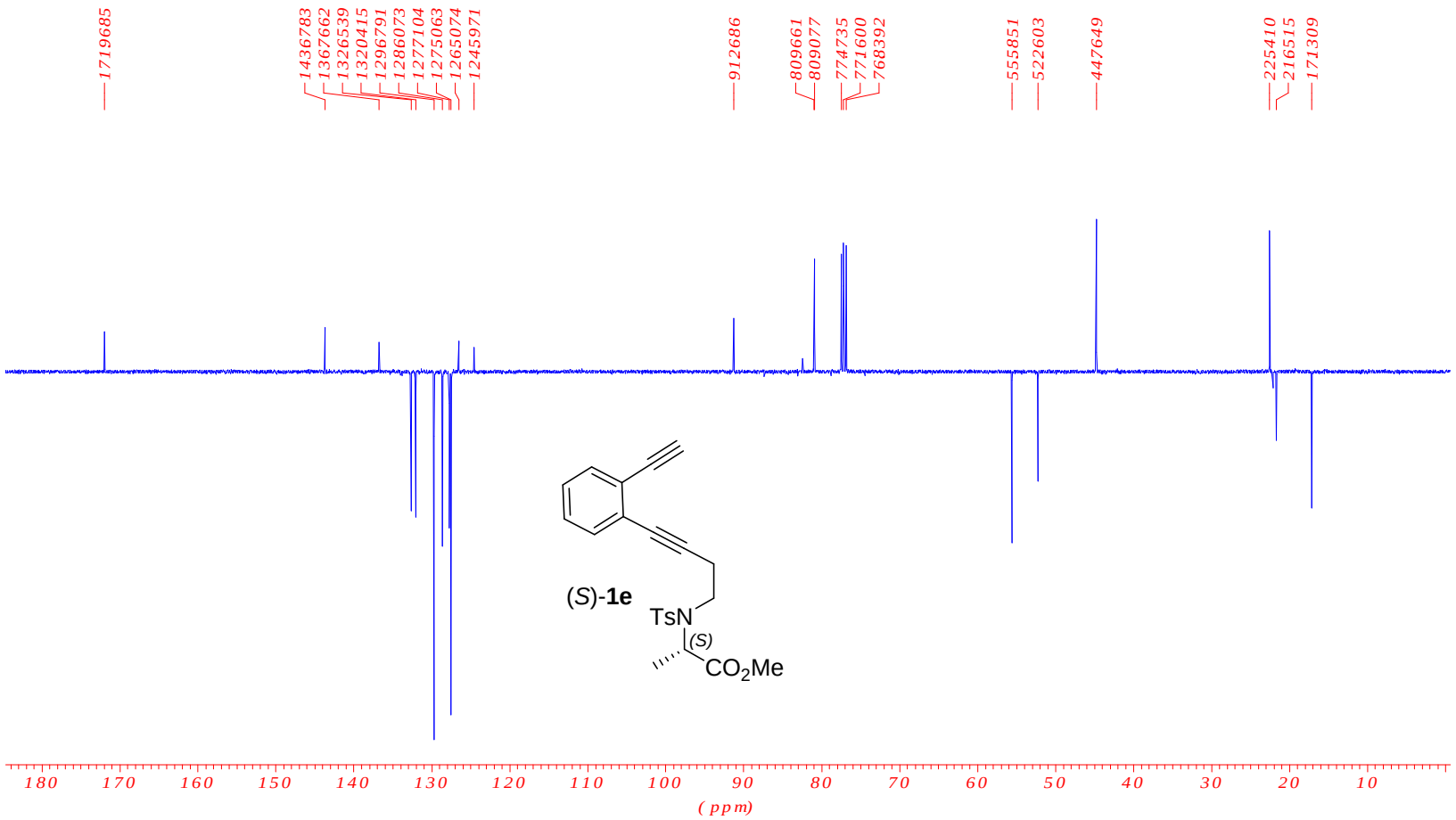
(*S*)-**9**

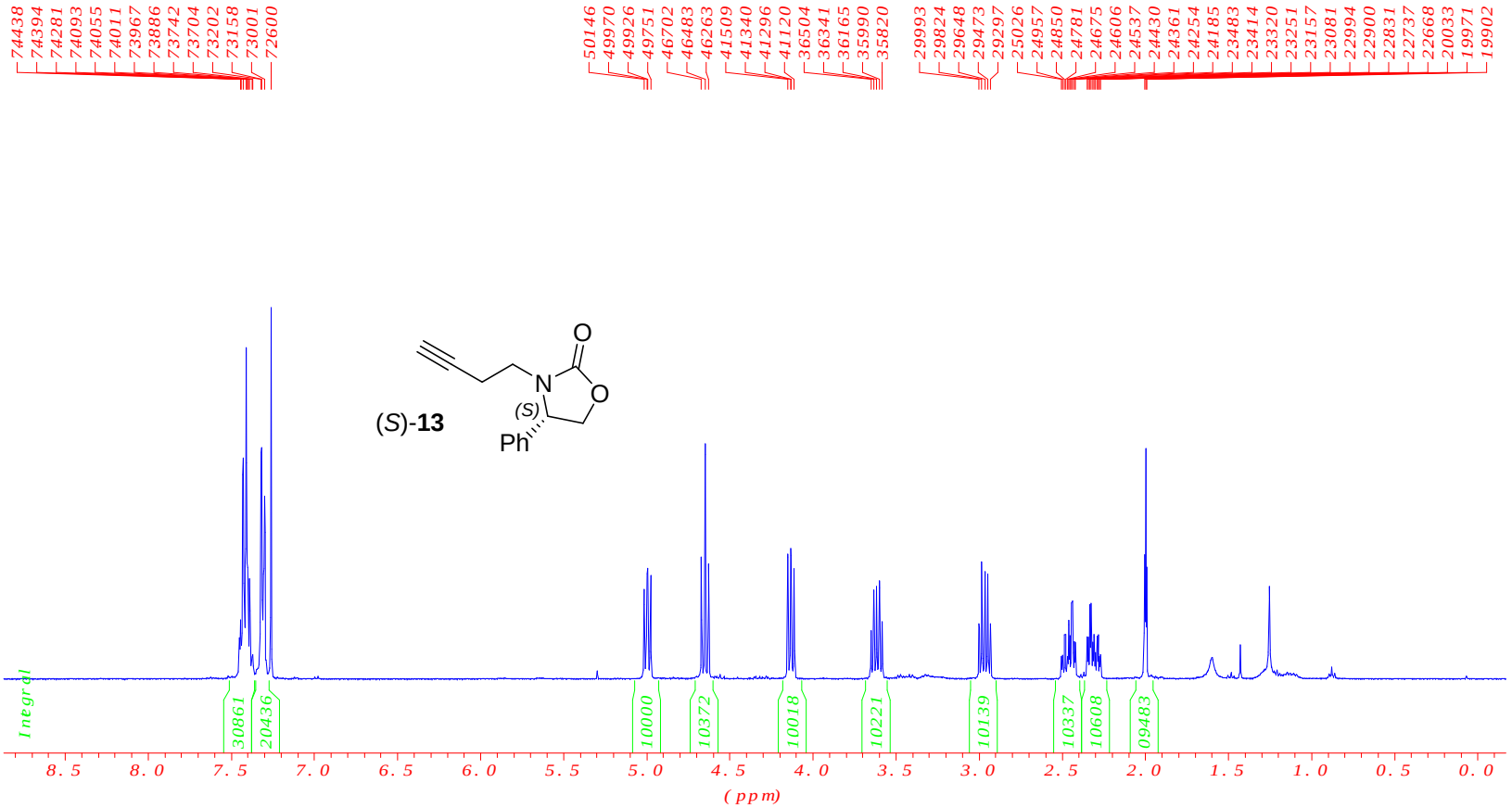


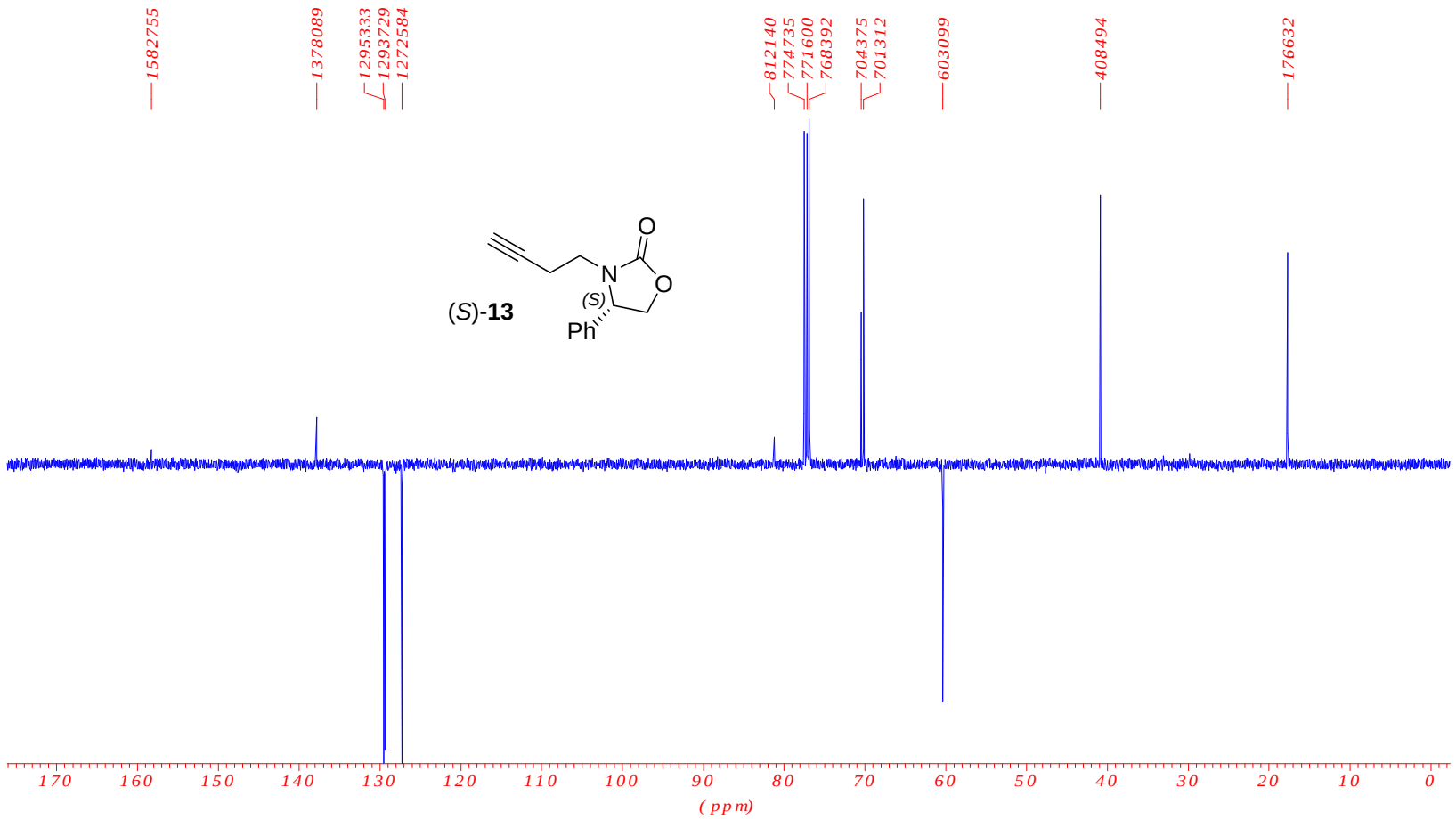


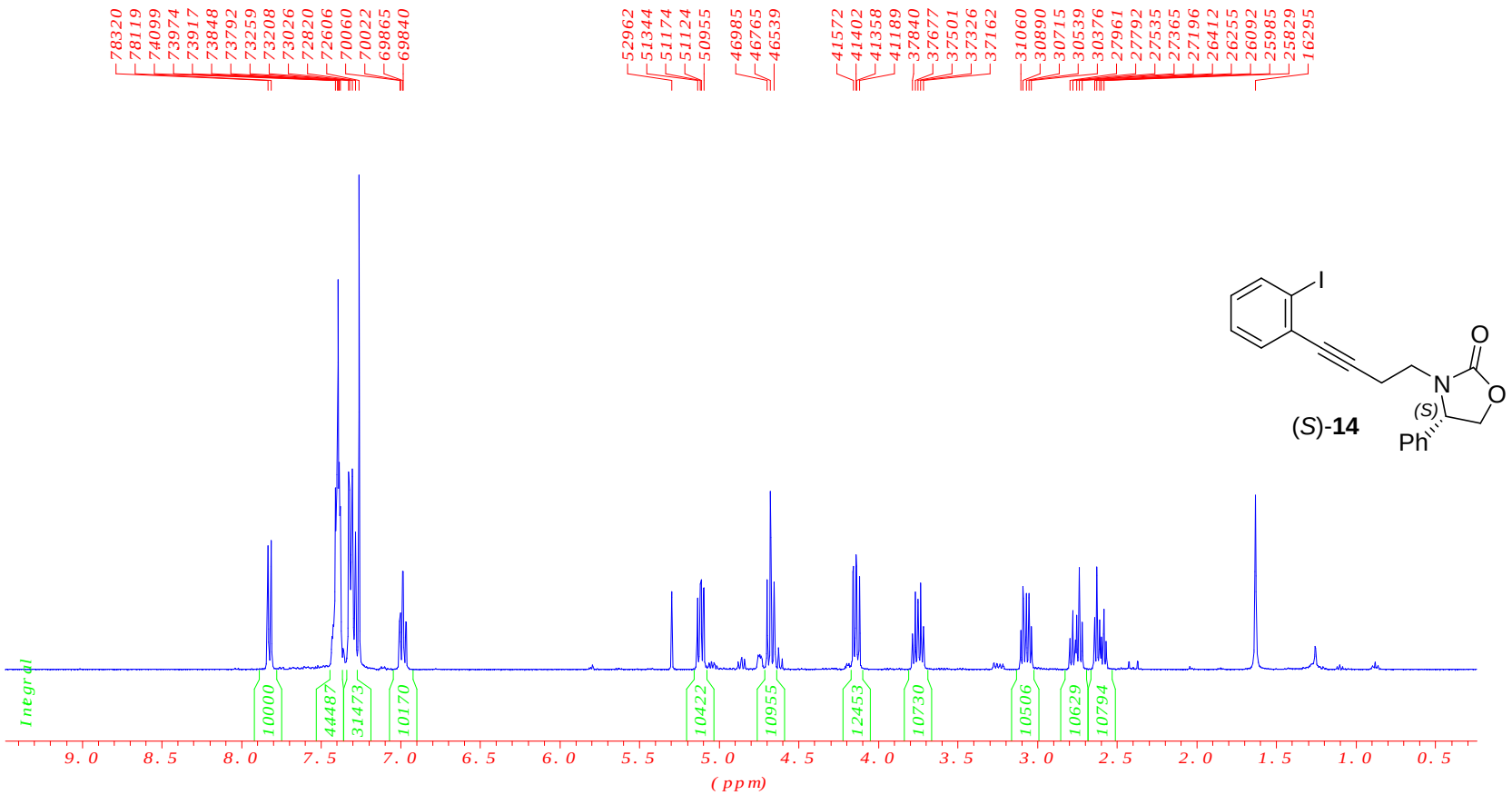




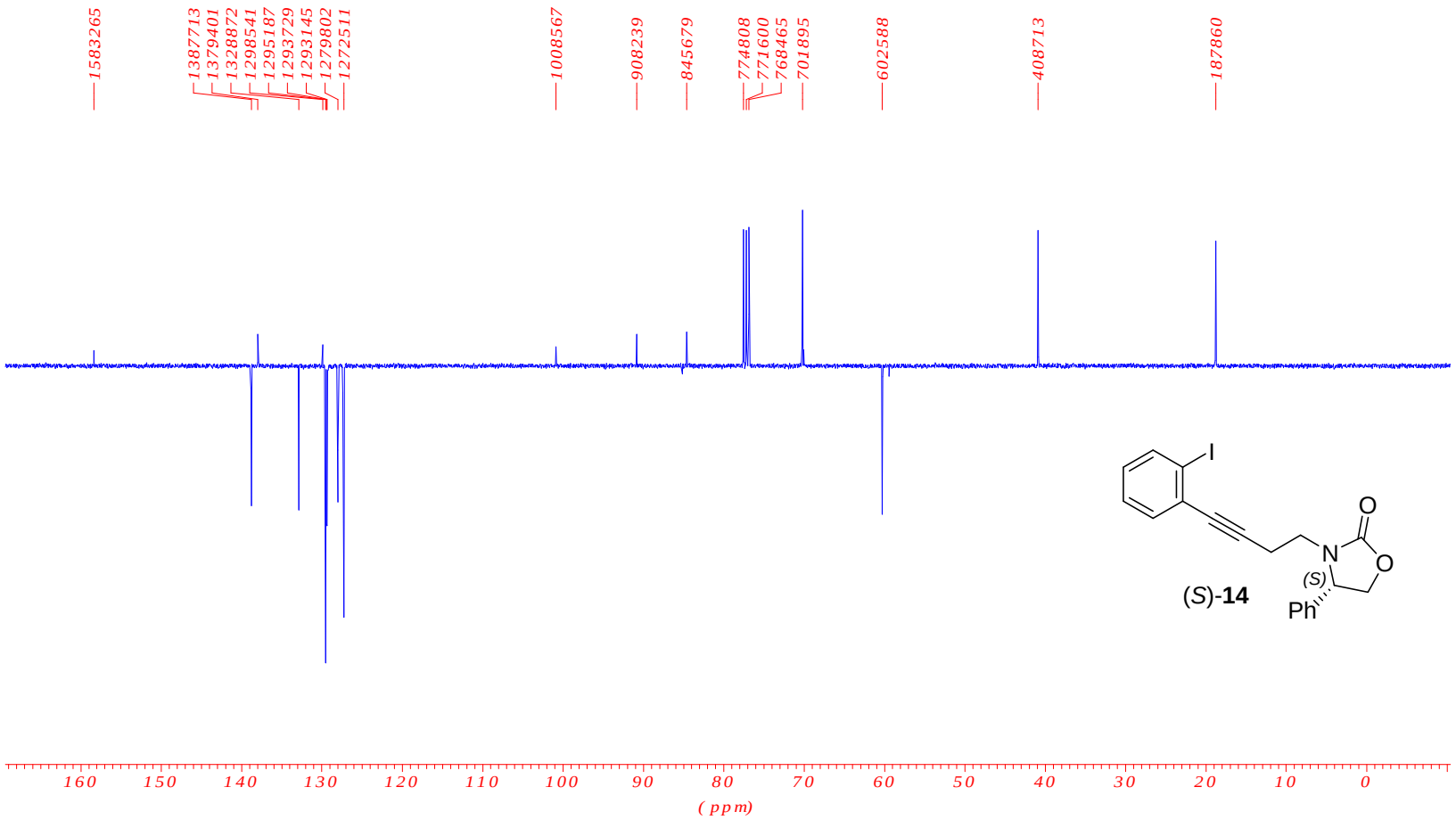


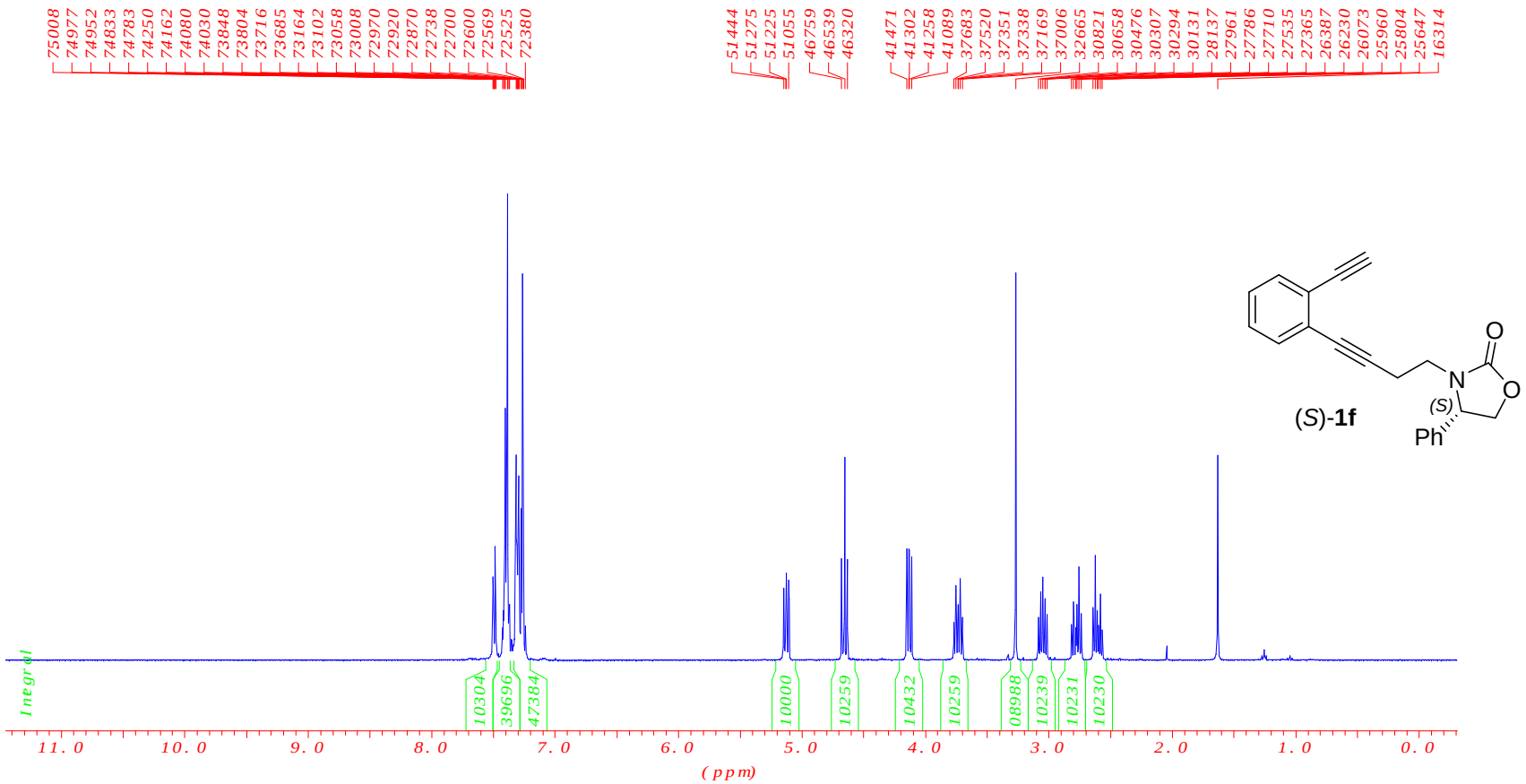


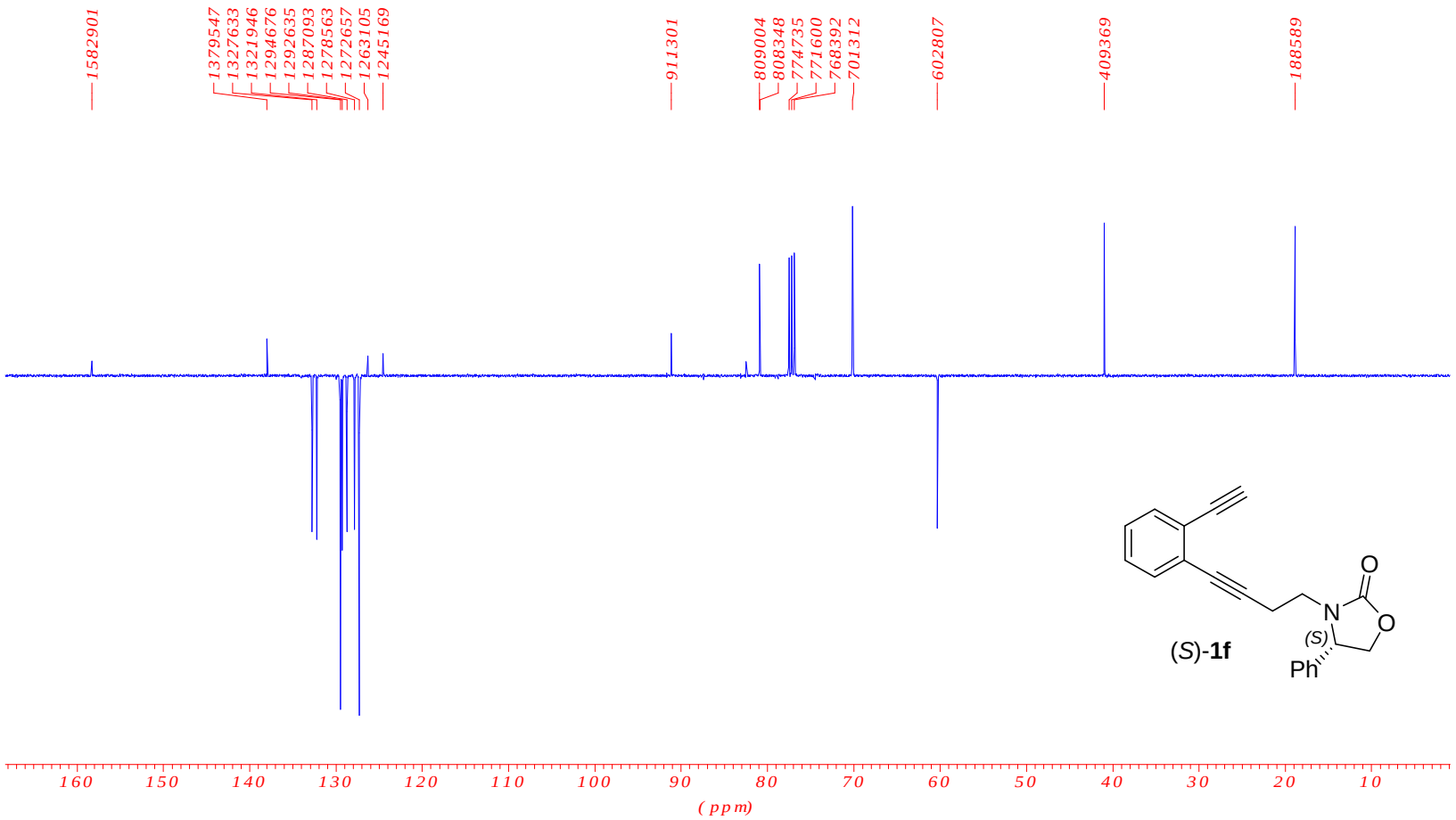




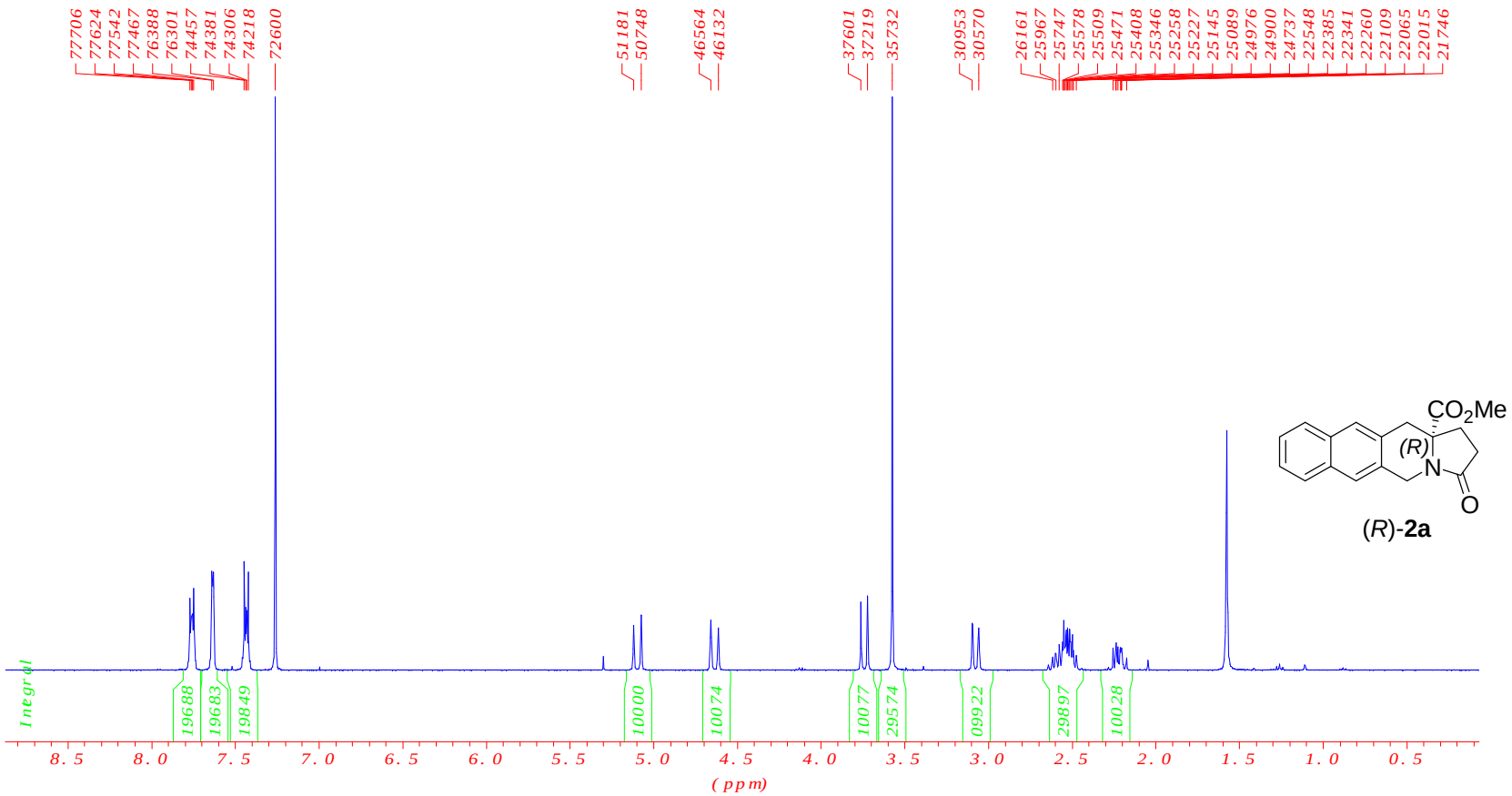
(*S*)-**14**



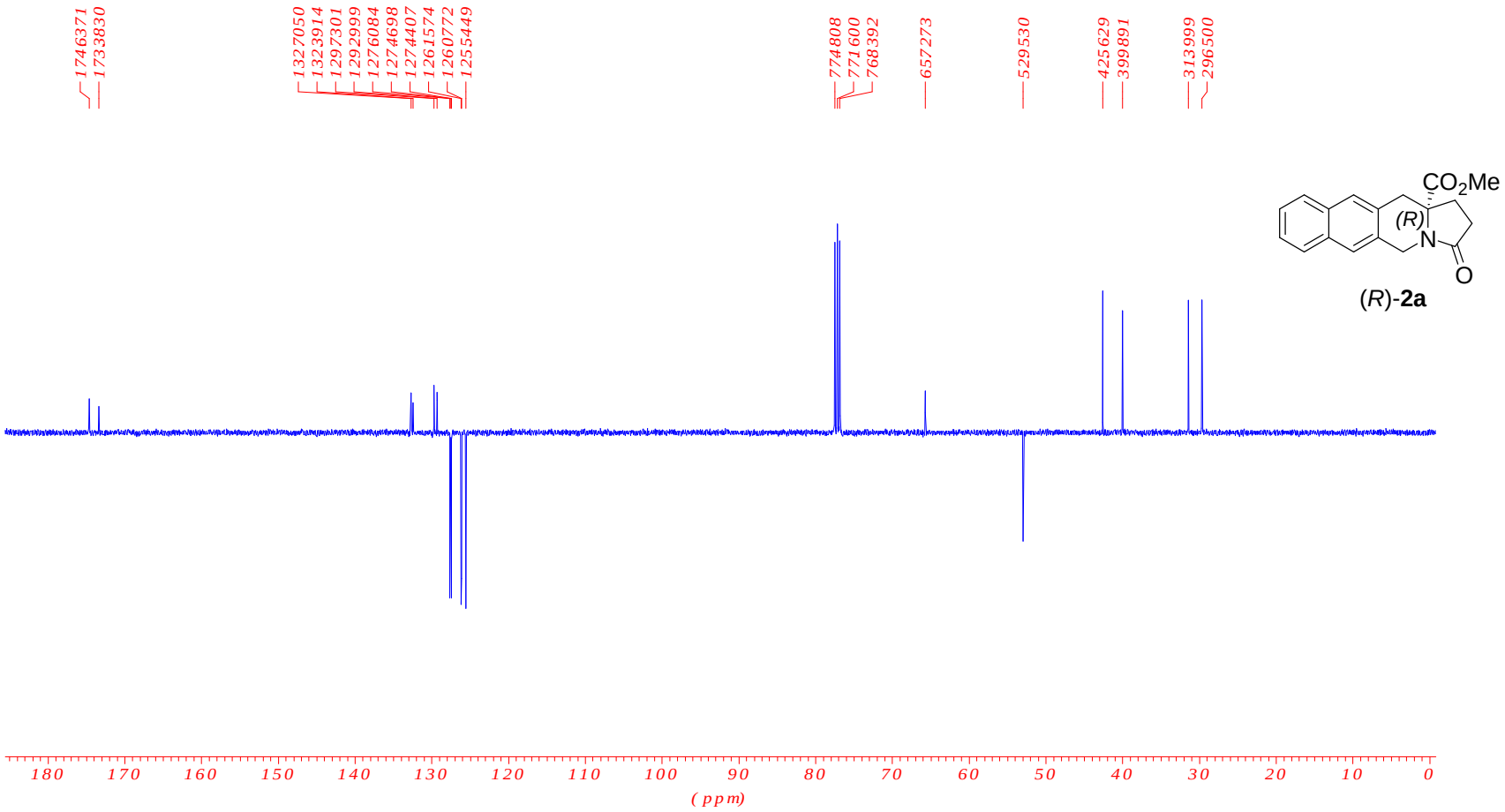




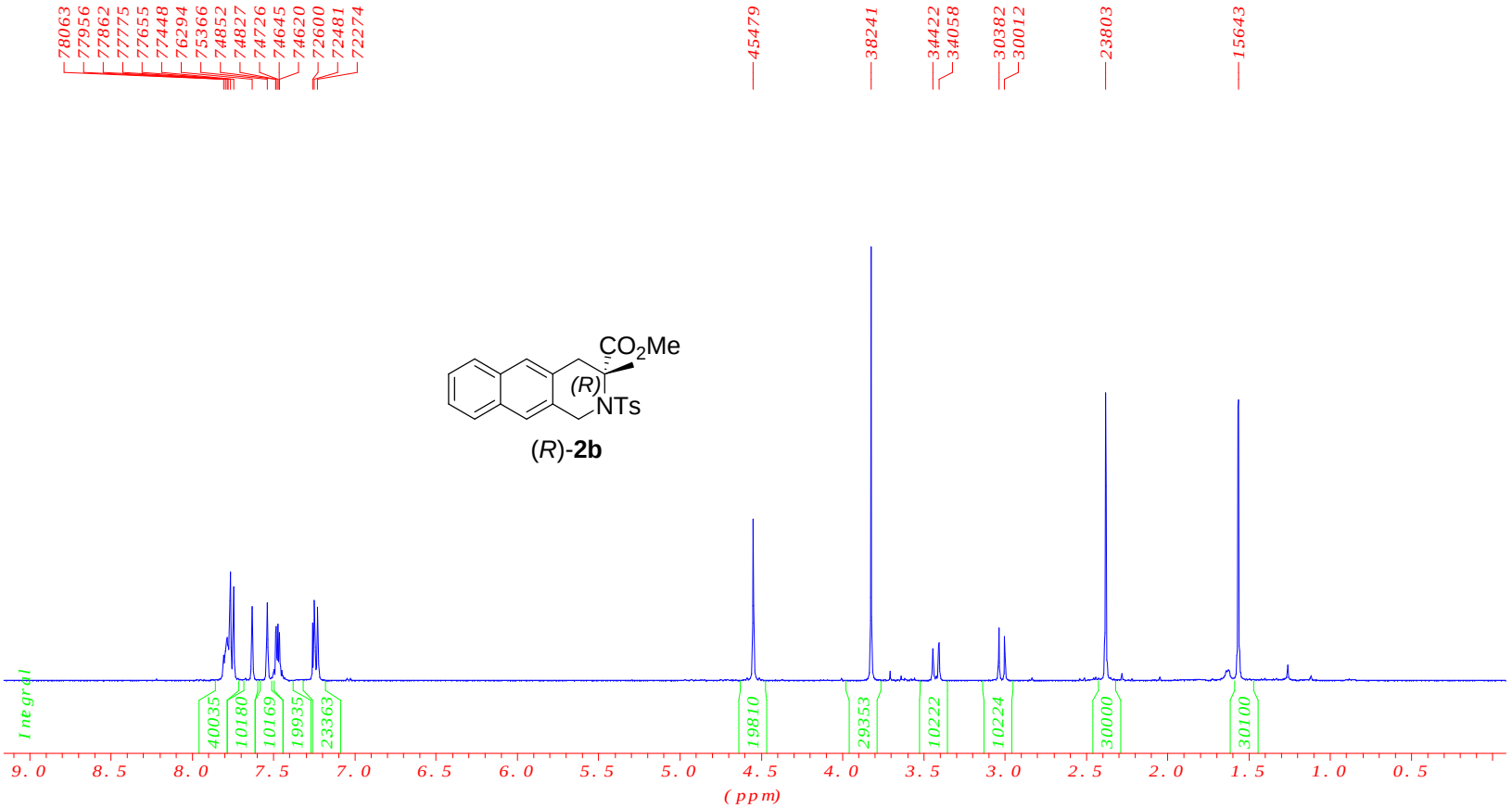
(*S*)-**1f**

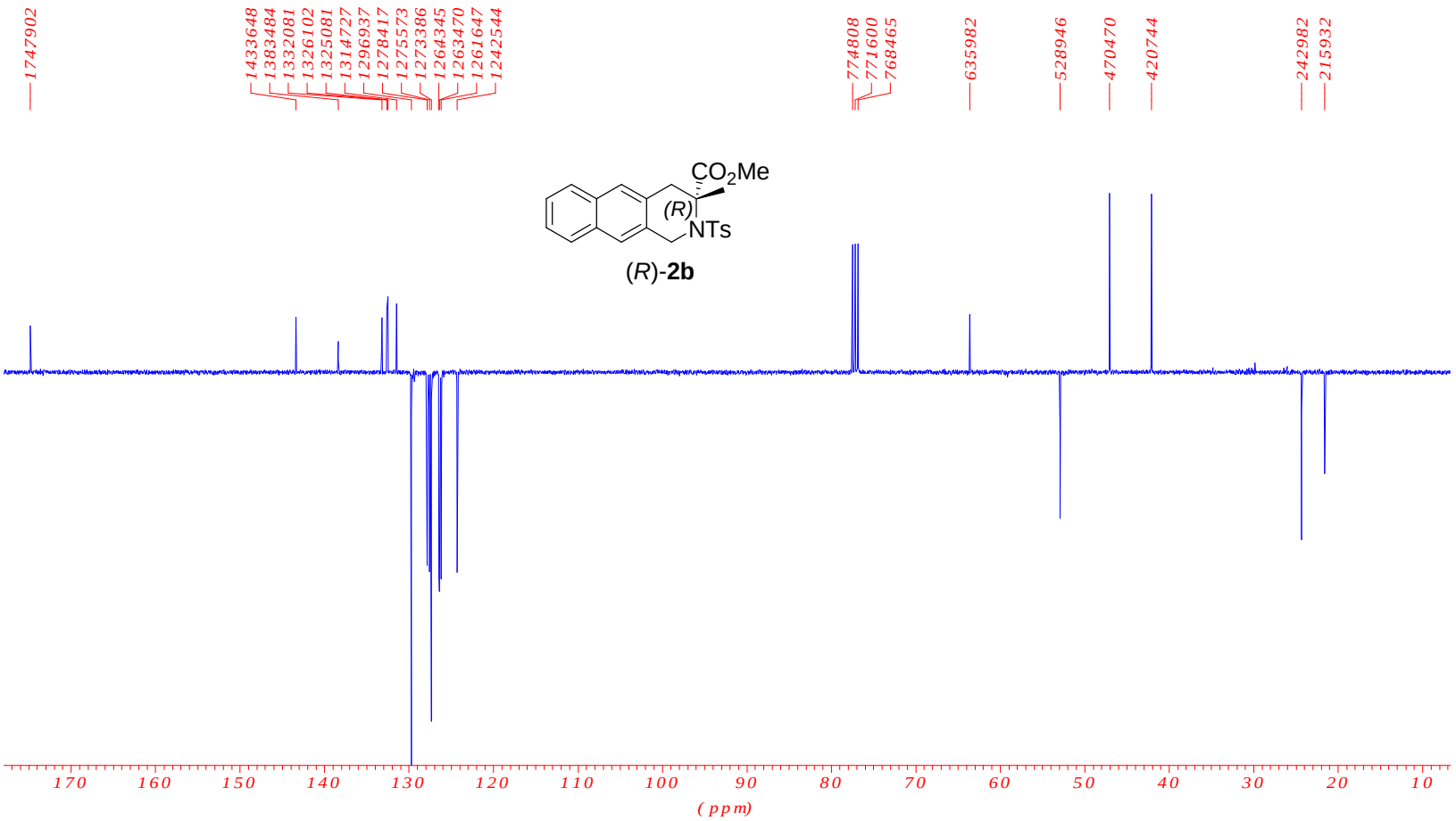


(*R*)-**2a**

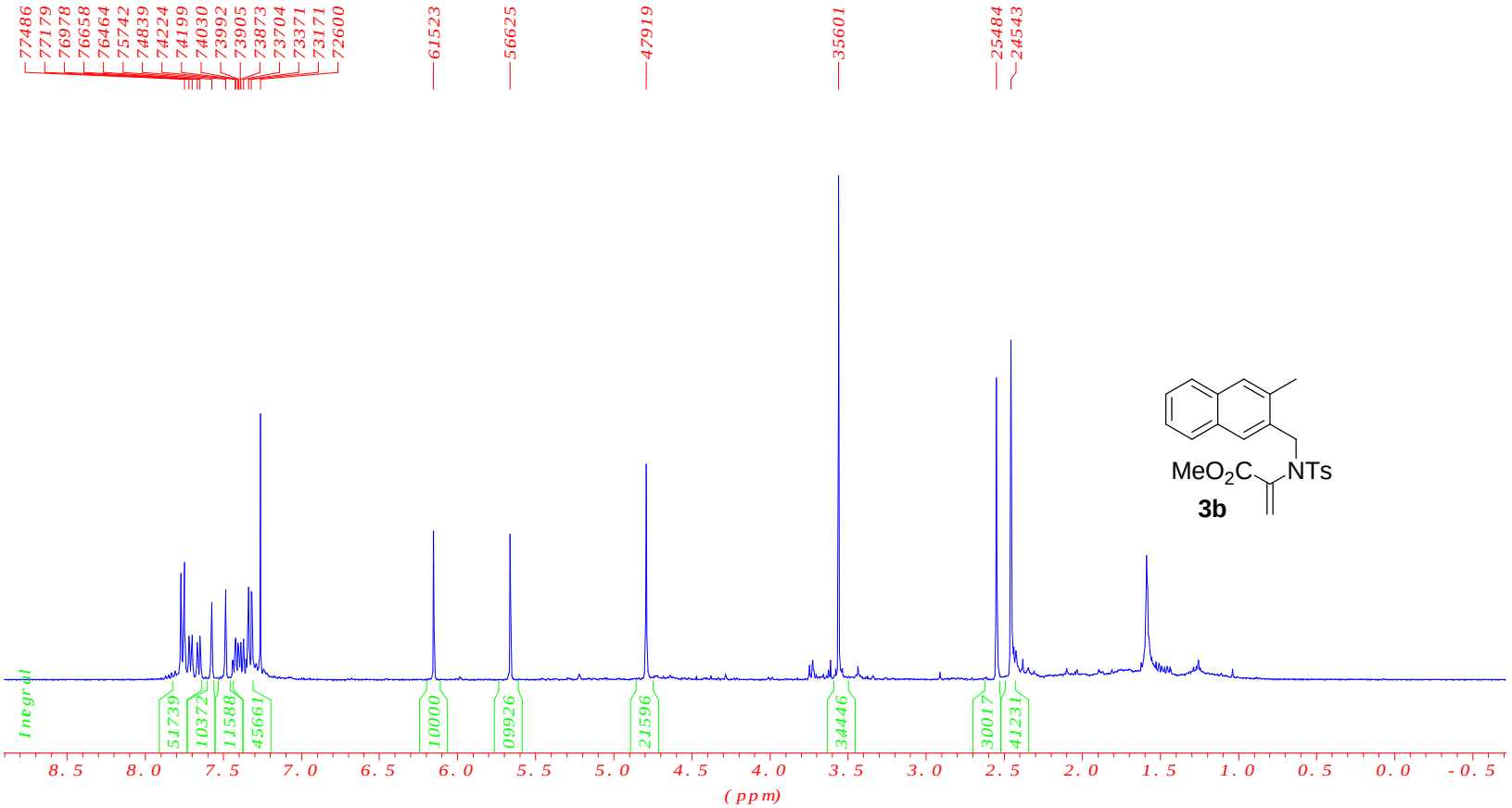


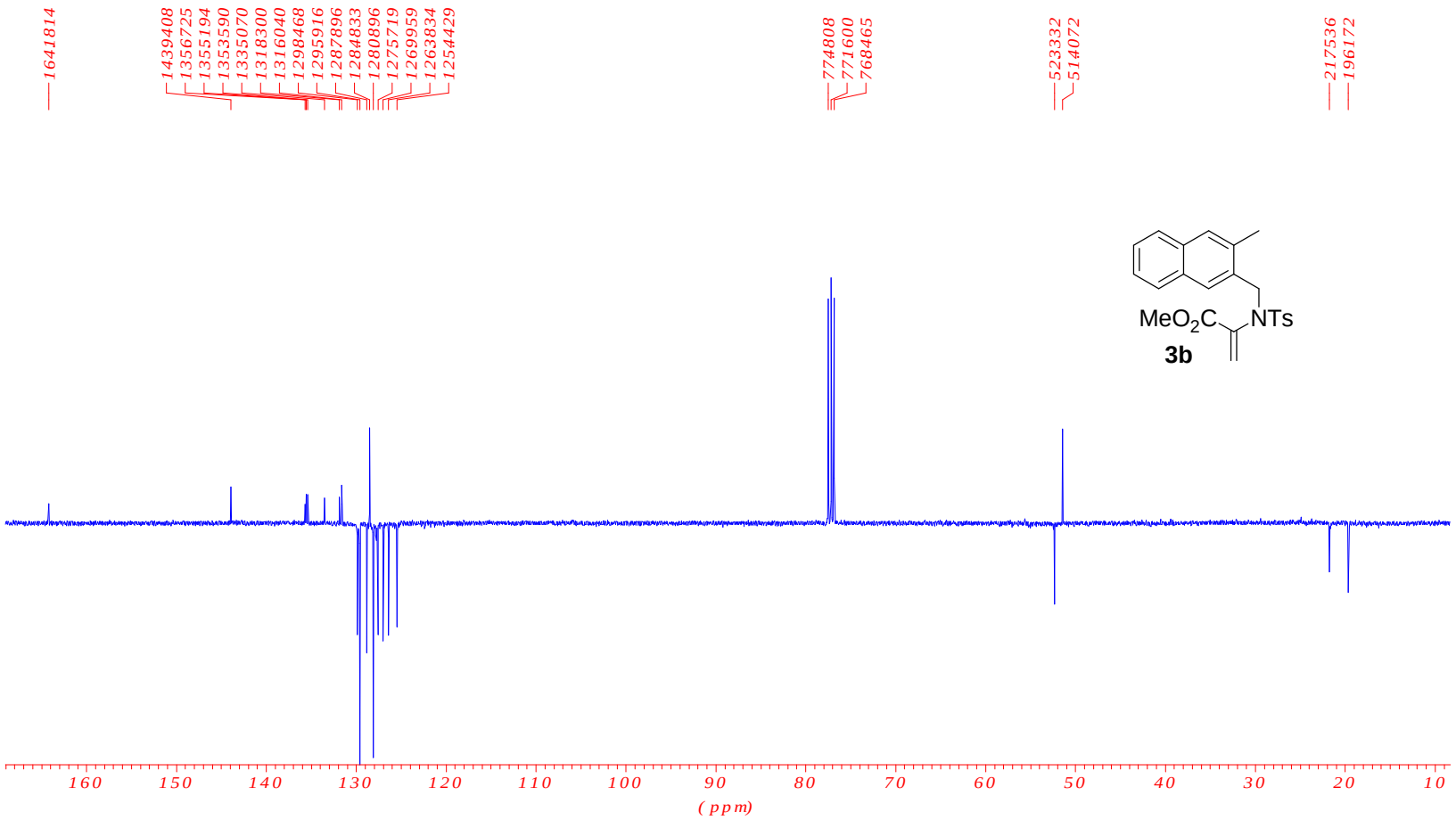
(*R*)-**2a**

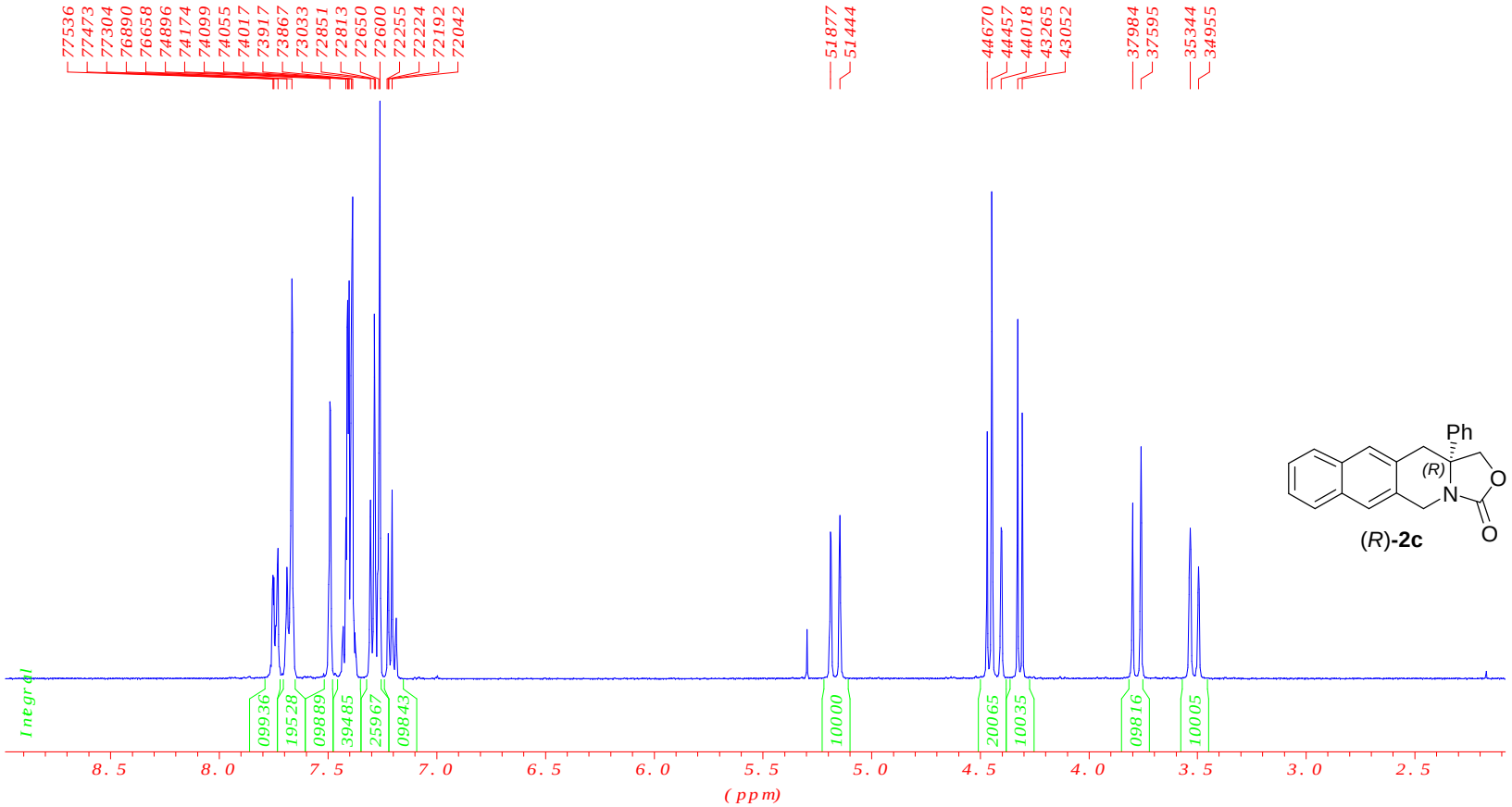




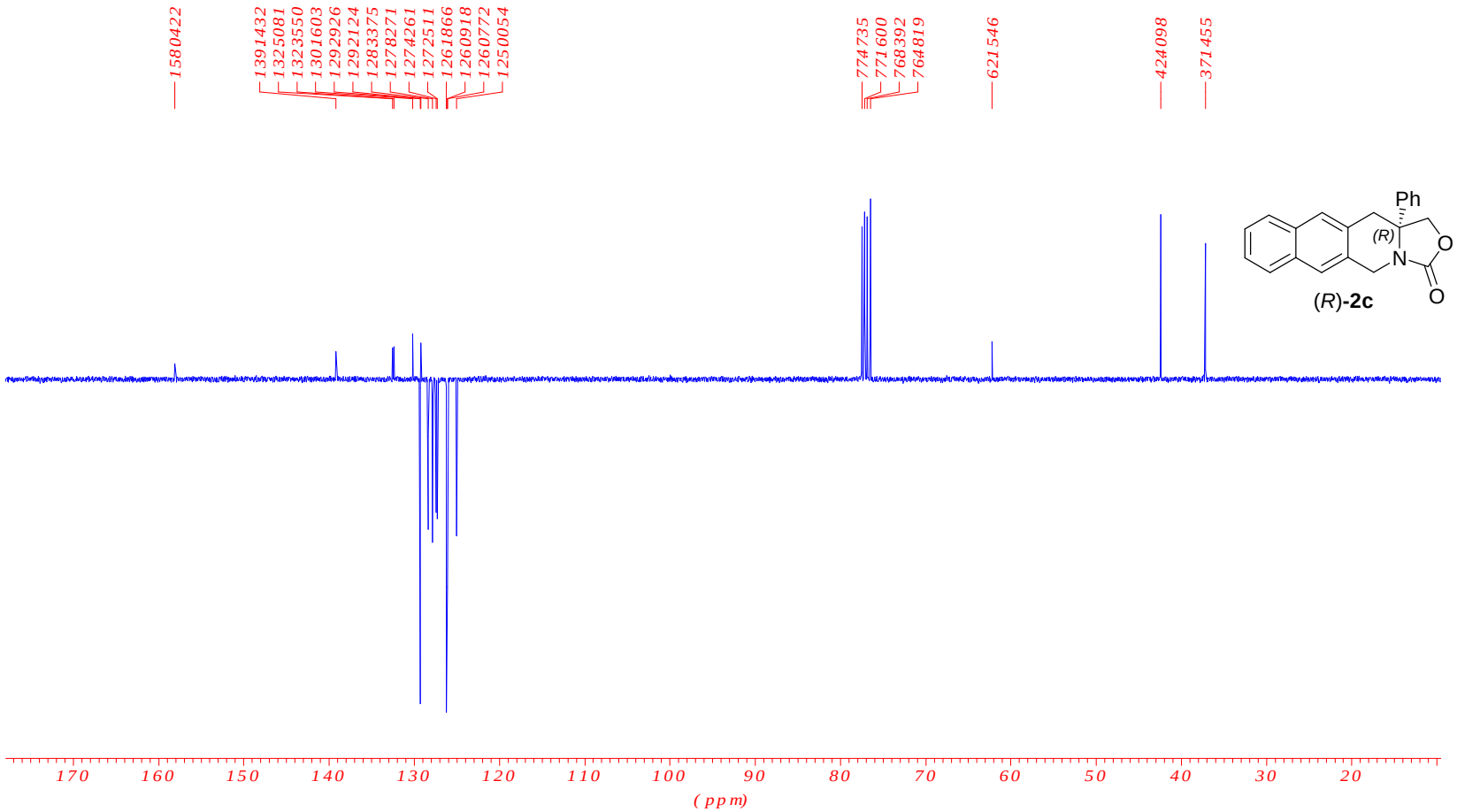
(*R*)-**2b**

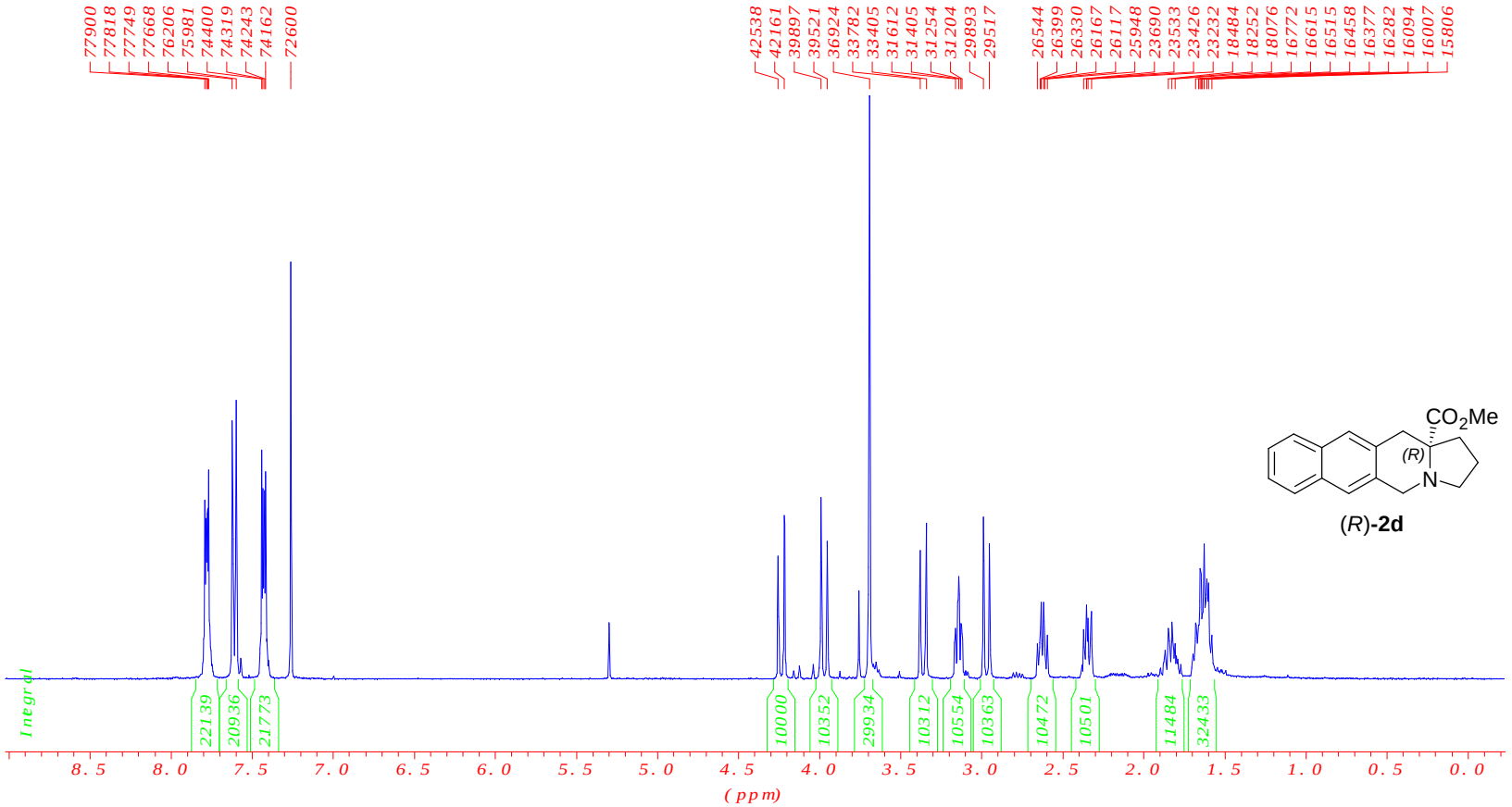




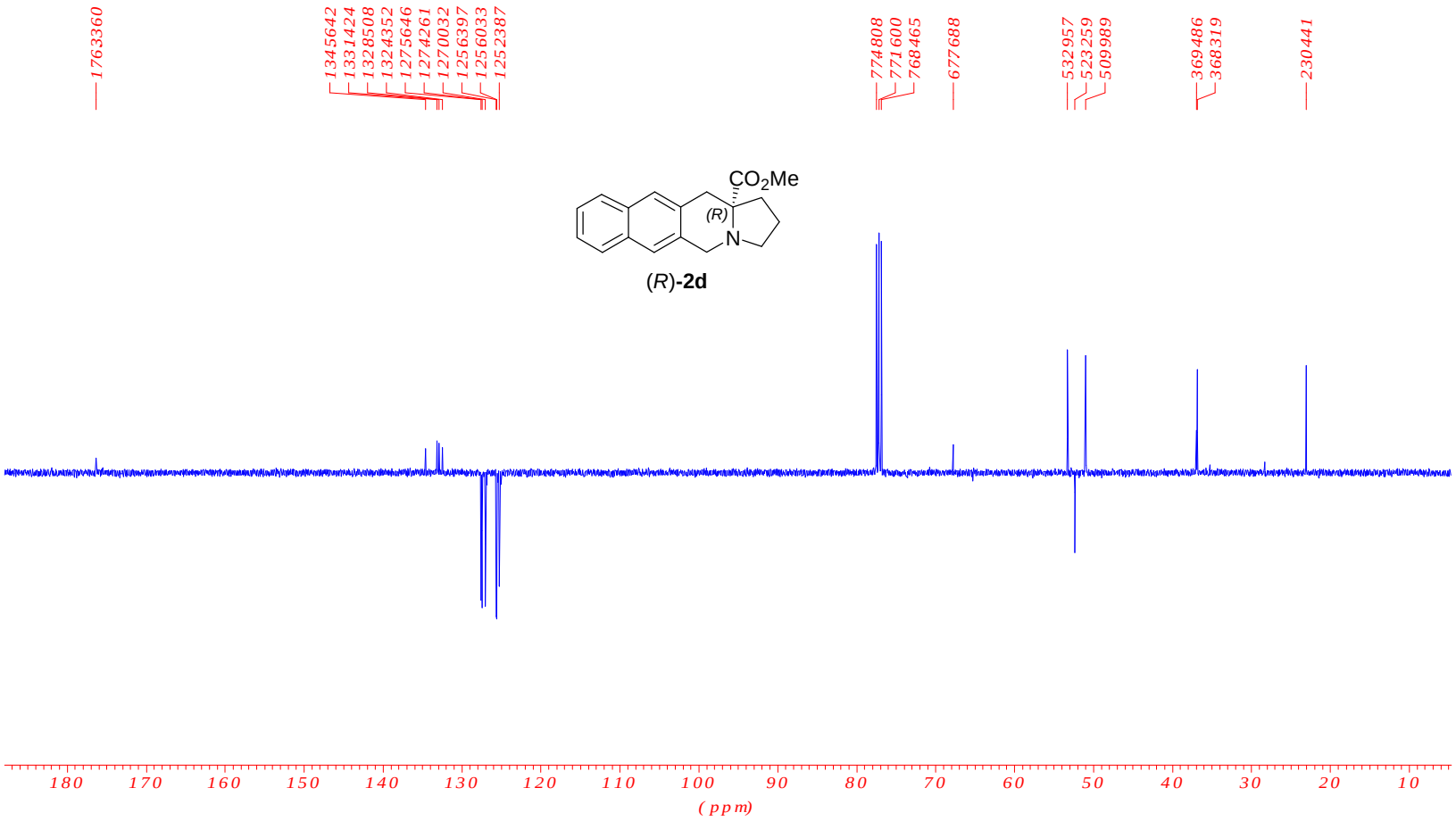


(*R*)-**2c**

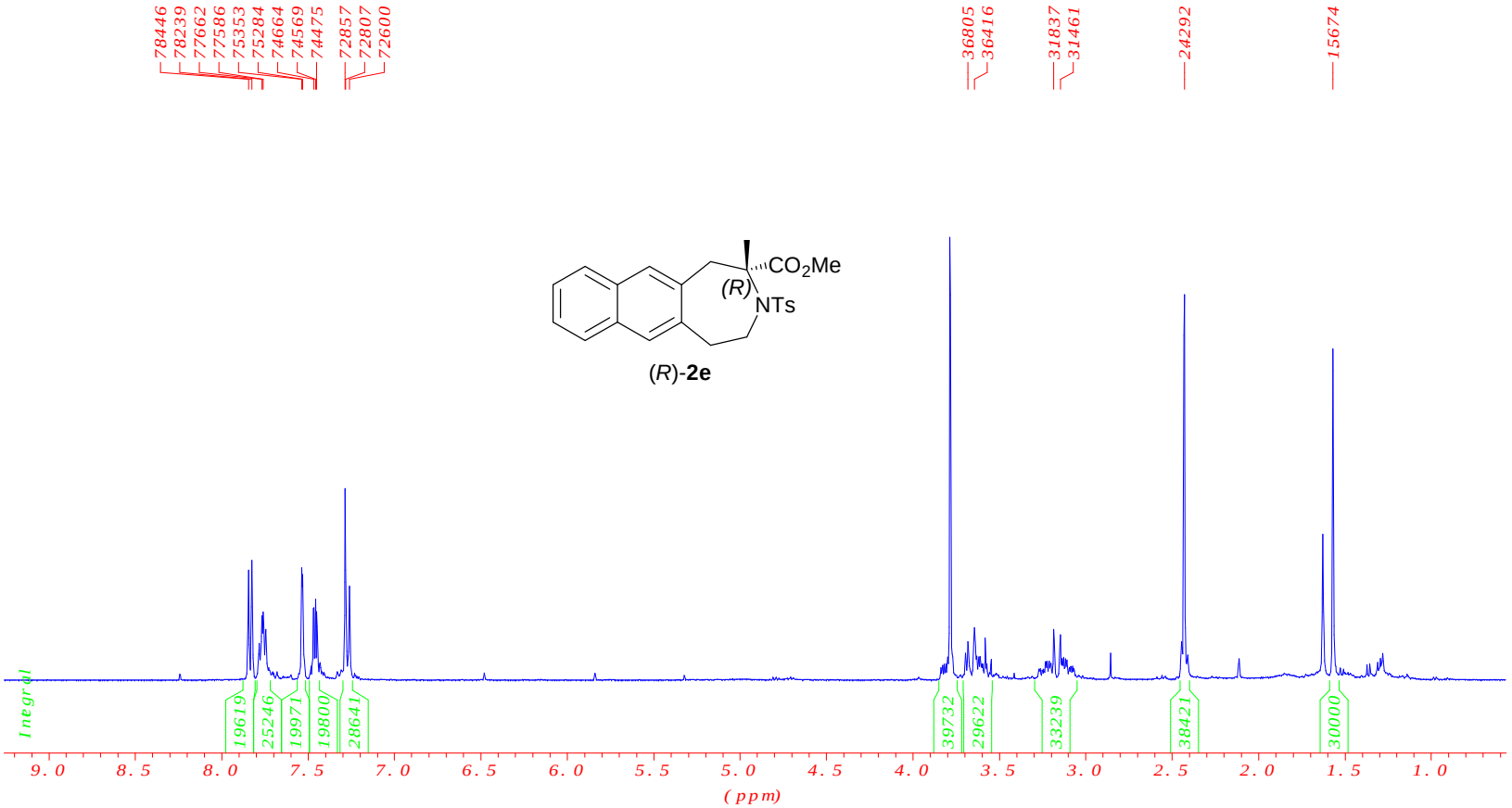


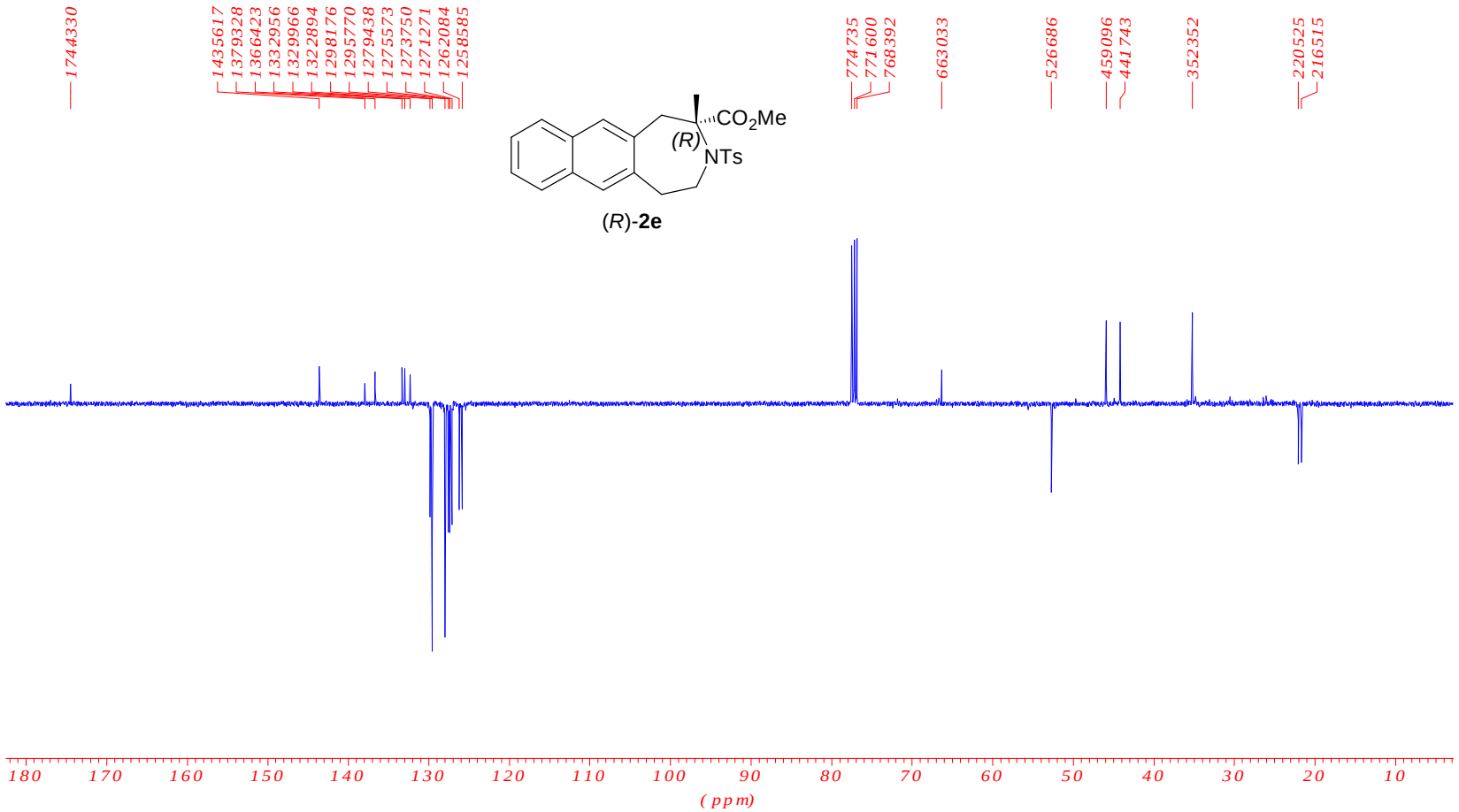


(*R*)-**2d**

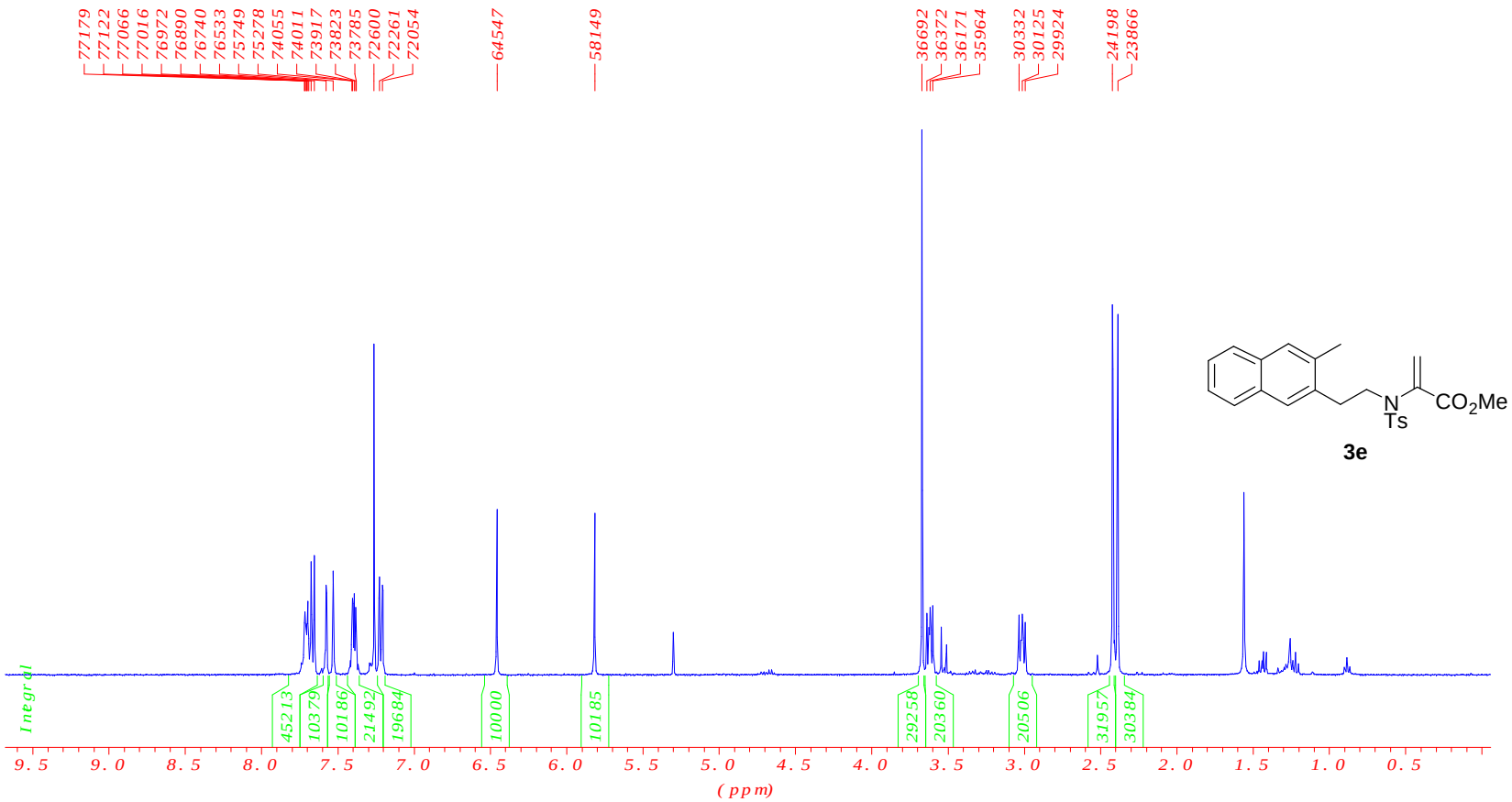


(*R*)-**2d**

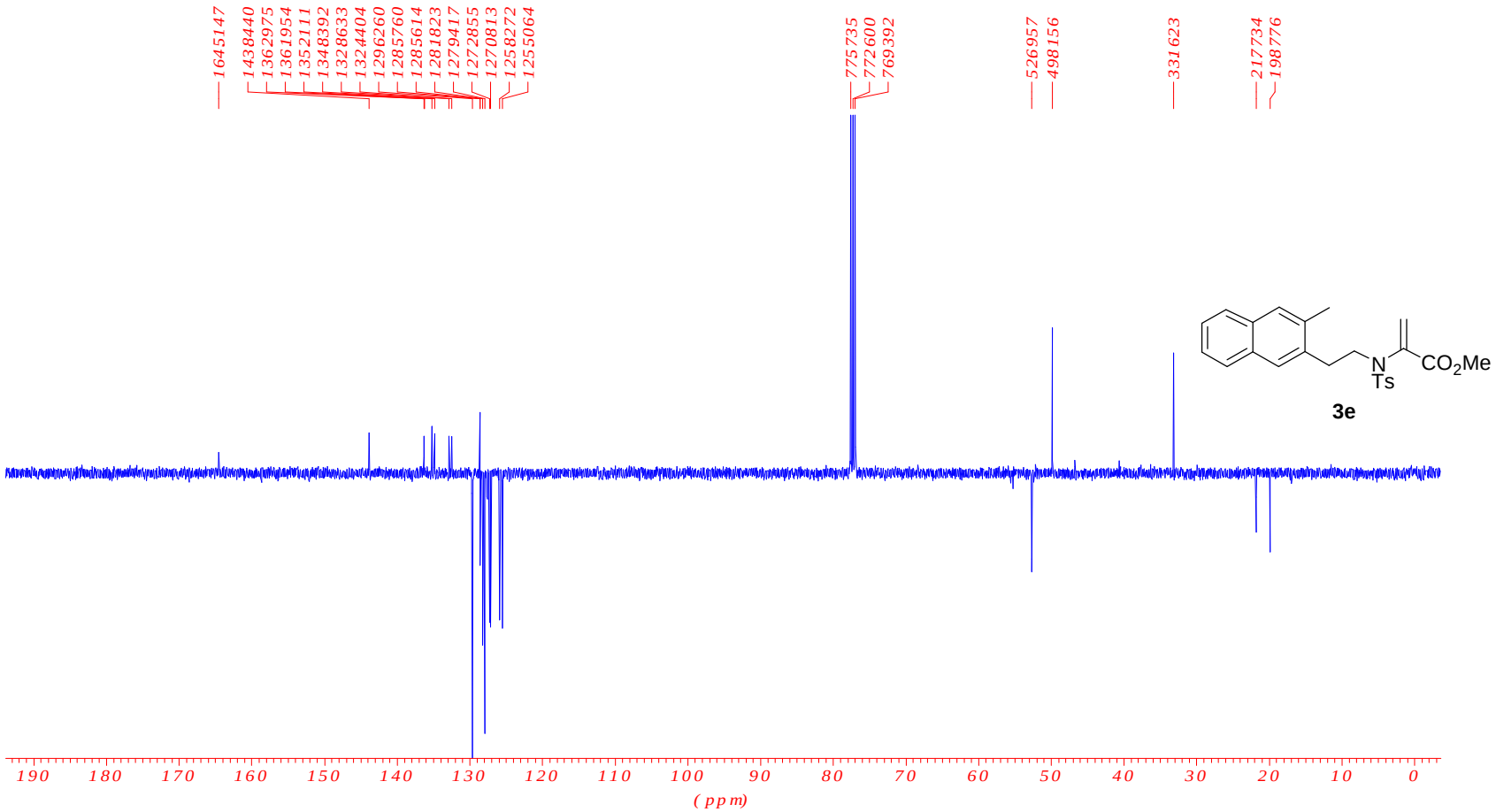




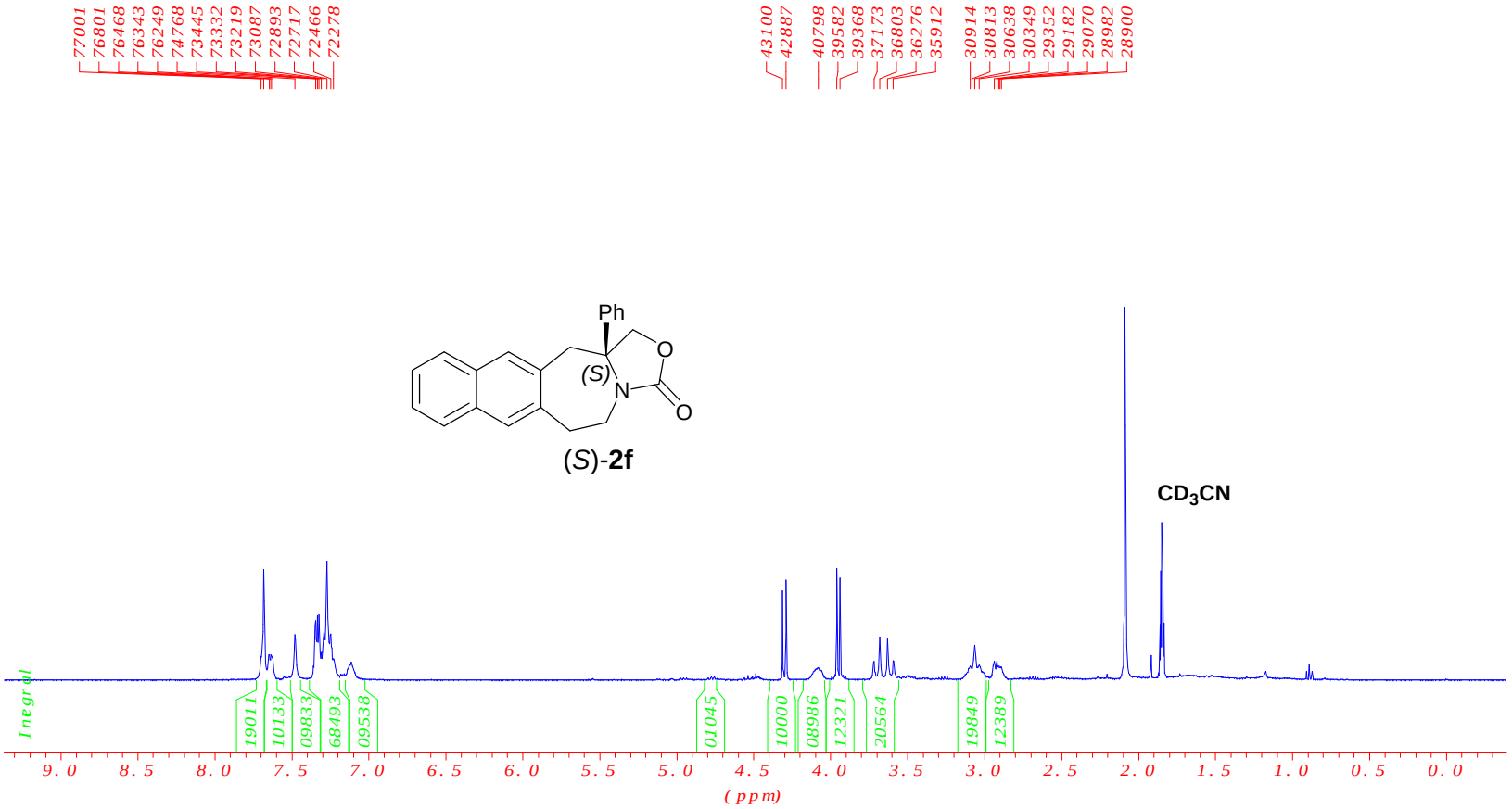
(*R*)-**2e**



3e

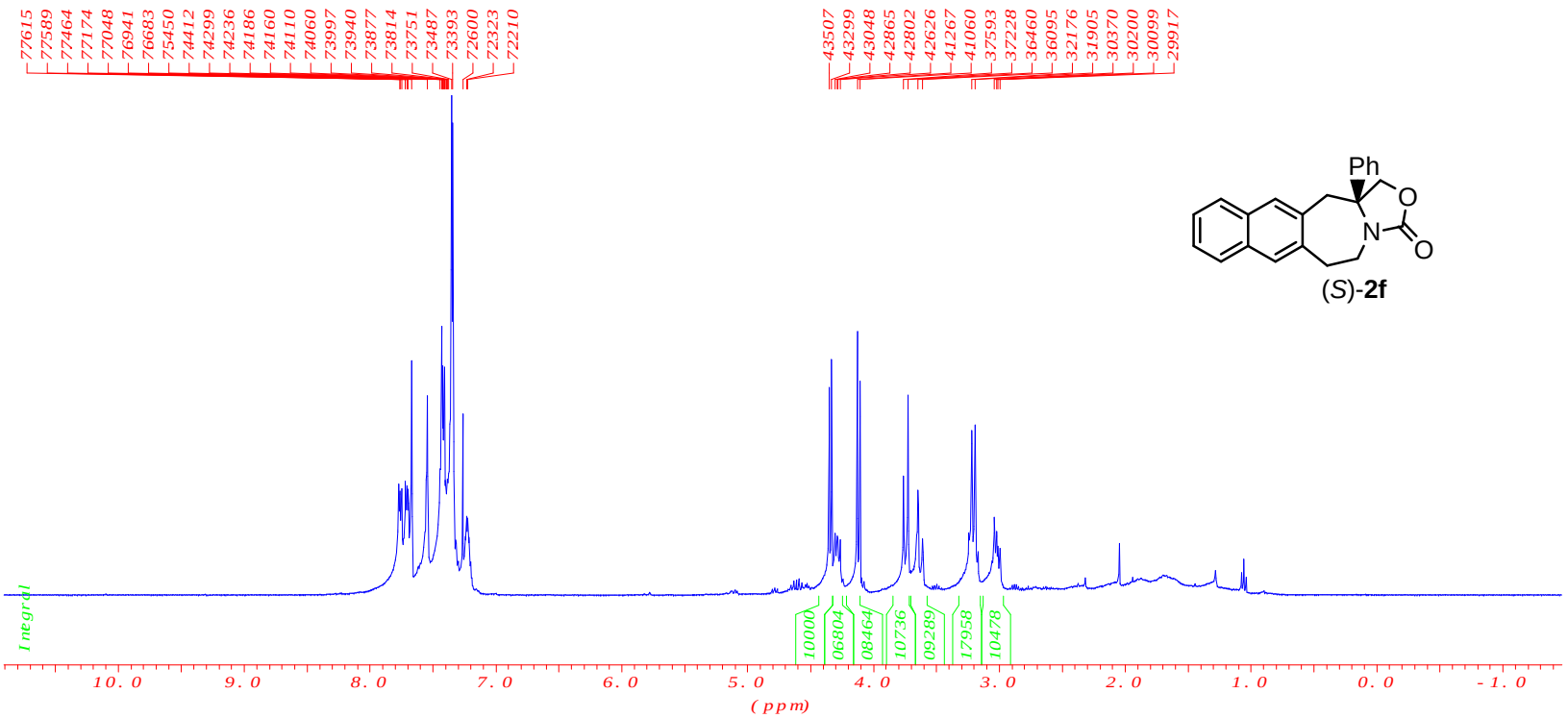


HNMR in CD_3CN



(*S*)-**2f**

HNMR in $CDCl_3$



(*S*)-**2f**

HSQC