Electronic Supporting Information

Control of Azomethine Cycloaddition Stereochemistry by CF_3 Group: Structural Diversity of Fluorinated β-Proline Dimers

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Full reference [21] from the main text: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A. Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision D.01* **2013**, Gaussian, Inc., Wallingford CT.

GENERAL REMARKS

^{1}H NMR spectra were recorded on a Bruker AM-400, Agilent 400 MR, Bruker AVANCE III 600 MHz spectrometer for solutions in $CDCl_3$, DMSO-d_6 and toluene-d_8 with concentration of the samples 5 - 15 mM and tetramethylsilane (TMS) as internal standard. Assignment of ^{1}H and ^{13}C signals was obtained using the following 2D experiments: DQF-COSY, NOESY (350 ms mixing time), ROESY (300 ms mixing time), ^{13}C-^{1}H HSQC and ^{13}C-^{1}H HMBC.

Optical rotations were determined at 589 nm (sodium D line) by using a Perkin-Elmer-341 MC digital polarimeter and a Jasco DIP-360 polarimeter; $[\alpha]_D$-values are given in unit of 10 $deg^{-1}cm^2g^{-1}$.

NMR structural calculations

Interproton distance restraints for the structural calculations have been obtained from the analysis of the cross-peak volumes in ^{1}H-^{1}H ROESY spectra. The extracted distances have been divided into 4 ranges, with upper inter-proton limits of 2.5, 3.5, 4.5, and 5.5 Å. Total number of distant restraints was 31 for (*Z*)-**D-2b'**, 15 for (*E*)-**D-2b'**, 21 for (*Z*)-**D-2b"** and 25 for (*E*)-**D-2b"**. Structural calculations and refinements have been performed using the simulated annealing protocol of the restrained molecular dynamics method with CNS software package [1]. The initial topology parameters for the β-peptide dimers have been generated using the PRODRG server [2] and then manually verified and corrected. Final families of NMR structures contained 20 models with no restraint violation larger than 0.2 Å. Root mean square deviations (RMSD) of the coordinates of heavy atoms of the backbone of β-peptide dimers within the final families of calculated structures were between 0.01 and 0.08 Å.

References

(1) Brünger, A. T.; Adams, P. D.; Clore, G. M.; DeLano, W. L.; Gros, P.; Grosse-Kunstleve, R. W.; Jiang, J. S.; Kuszewski, J.; Nilges, M.; Pannu, N. S.; Read, R. J., Rice, L. M.; Simonson, T.; Warren, G. L. *Acta Crystallogr. D Biol. Crystallogr.* **1998**, *54*, 905-921.

(2) Schuttelkopf, A. W.; van Aalten, D. M. *Acta Crystallogr. D Biol. Crystallogr.* **2004**, *60*, 1355-1363.

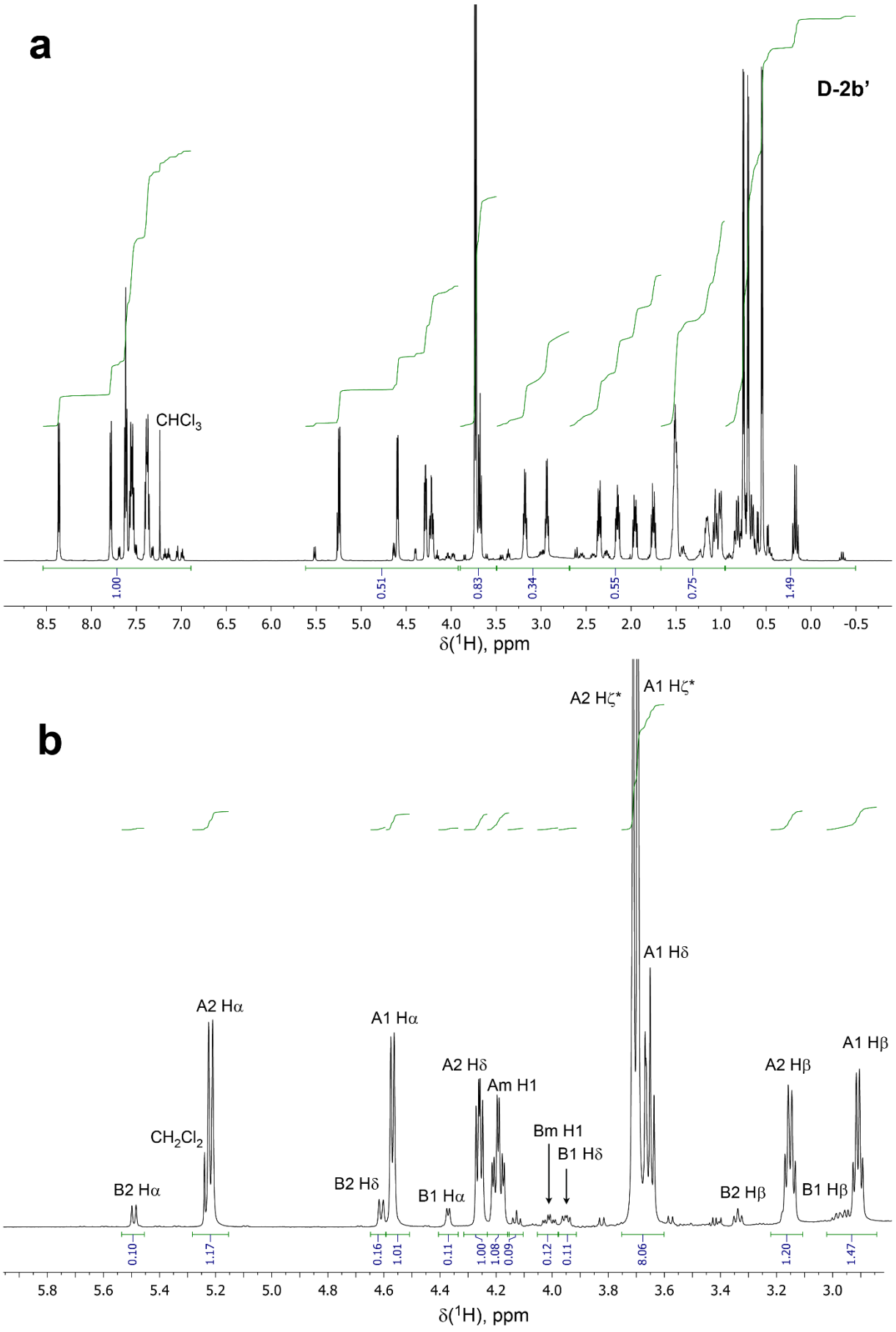


Figure S1. ^{1}H NMR spectrum (*a*) and its expanded fragment (*b*) of dimer **D-2b'** in $CDCl_3$ solution. A signals correspond to (*Z*)-isomer (91%) and B signals correspond to (*E*)-isomer (9%).

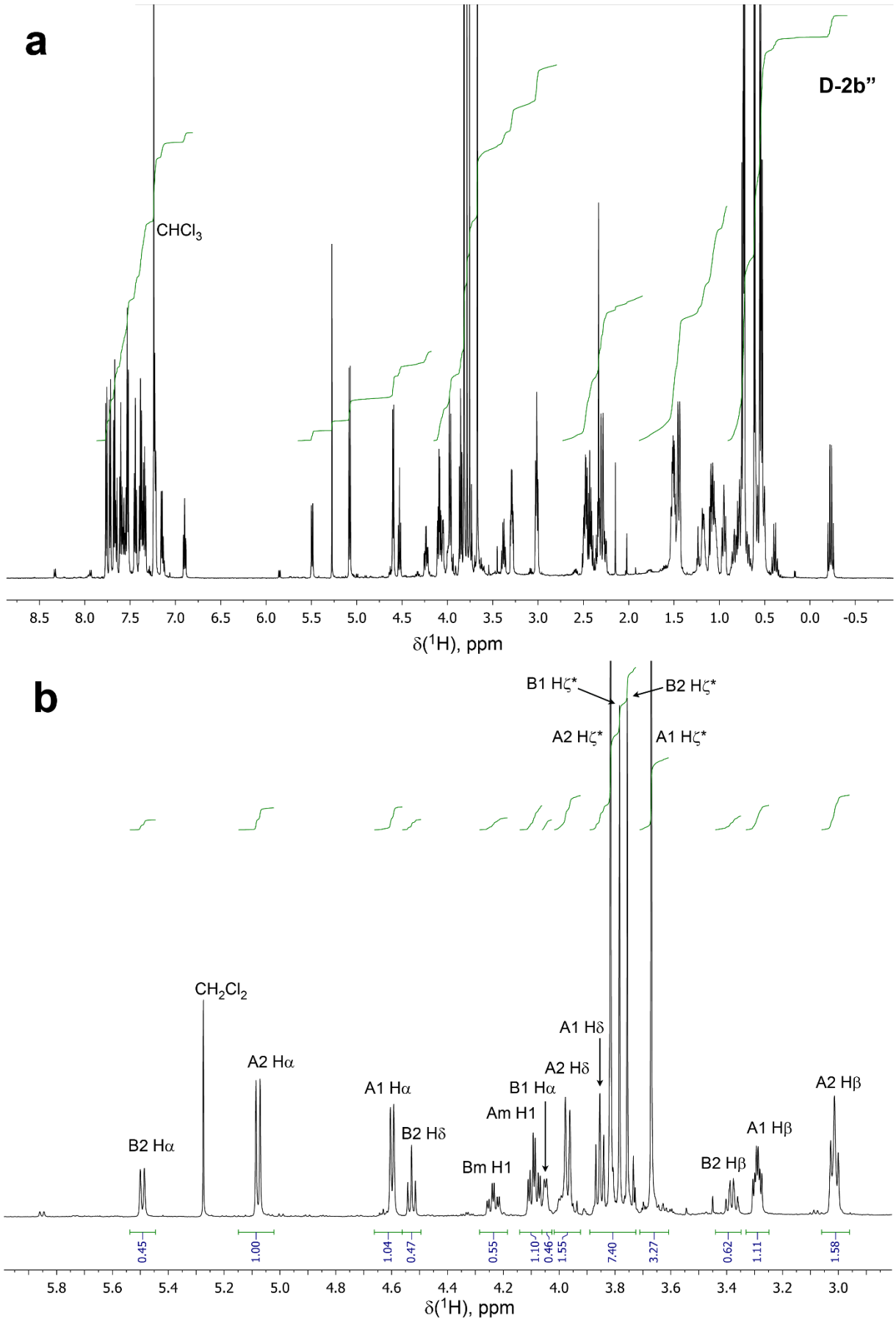


Figure S2. ^{1}H NMR spectrum (*a*) and its expanded fragment (*b*) of dimer **D-2b’’** in $CDCl_3$ solution. A signals correspond to (*E*)-isomer (68%) and B signals correspond to (*Z*)-isomer (32%).

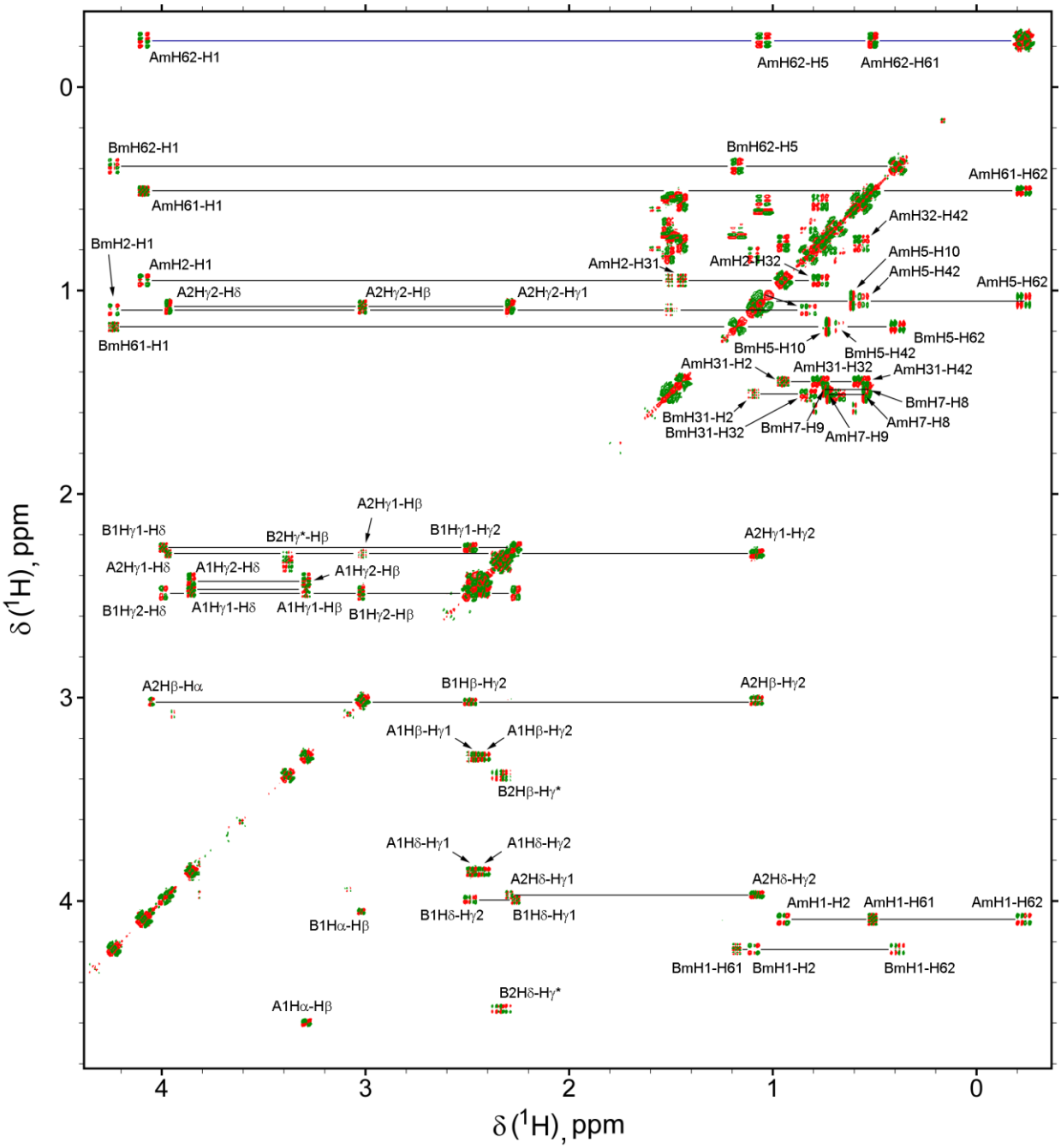


Figure S3. Fragment of DQF COSY spectrum of compound **D-2b''** in $CDCl_3$ solution. Resonance assignments, where signals A correspond to (*E*)-isomer (68%) and signals B correspond to (*Z*)-isomer (32%), are shown. A1, A2, B1 and B2 are β-proline residues, Am and Bm are D-menthyl groups. Horizontal lines connect resonances from the same spin systems.

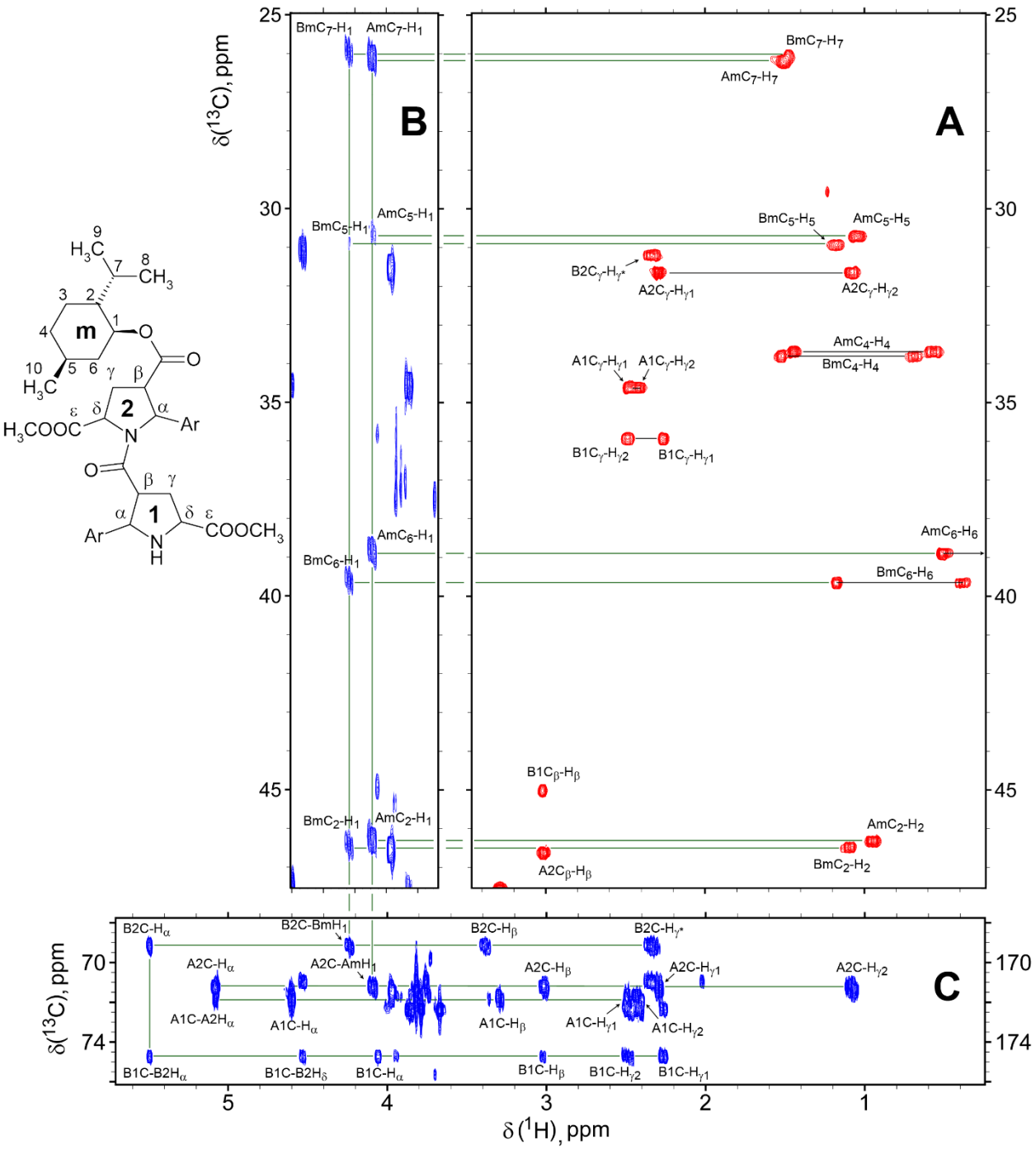


Figure S4. Fragments of ^{13}C-^{1}H HSQC (panel A) and 2D HMBC spectra (panels B and C) of compound **D-2b''** in $CDCl_3$ solution. Resonance assignments, where signals A correspond to (*E*)-isomer (68%) and signals B correspond to (*Z*)-isomer (32%), are shown. A1, A2, B1 and B2 are β-proline residues, Am and Bm are D-menthyl groups. Green lines show correlations between ^{1}H and ^{13}C resonances in HMBC and HSQC spectra. Assignment starts from H1 resonances of D-menthyl groups (panel B). They correlate to several menthyl ^{13}C signals (panel A), but also to the carbonyl ^{13}C resonances of residues A2 or B2 (panel C). Via correlation of these carbonyl groups to ^{1}H resonances of Hα, Hβ, Hγ and Hδ atoms one can connect pyrrolidine residues ***2*** and ***1***.

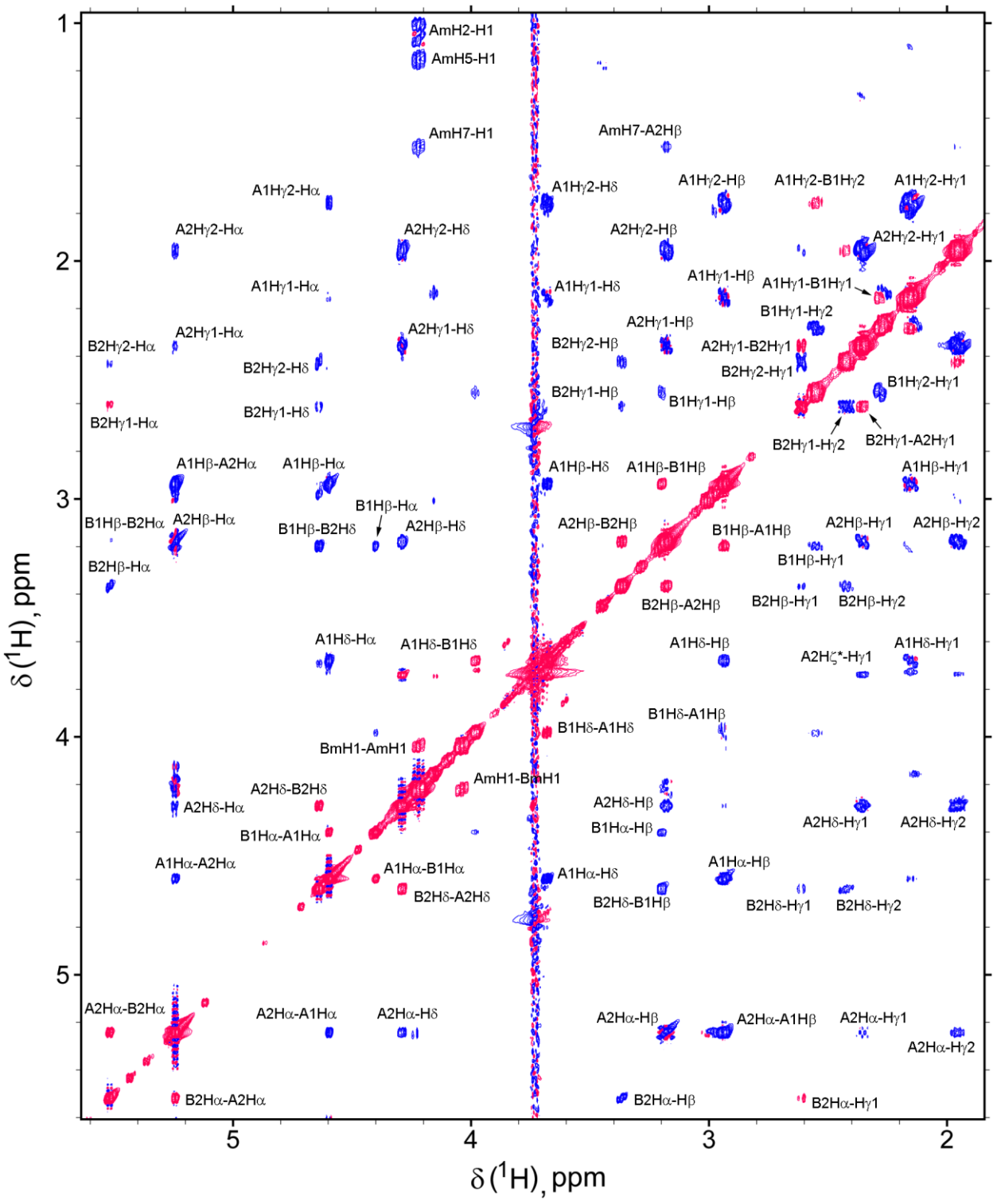


Figure S5. Fragment of 2D ROESY spectrum of compound **D-2b'**. Resonance assignments, where A signals correspond to (*Z*)-isomer (91%) and B signals correspond to (*E*)-isomer (9%), are shown.

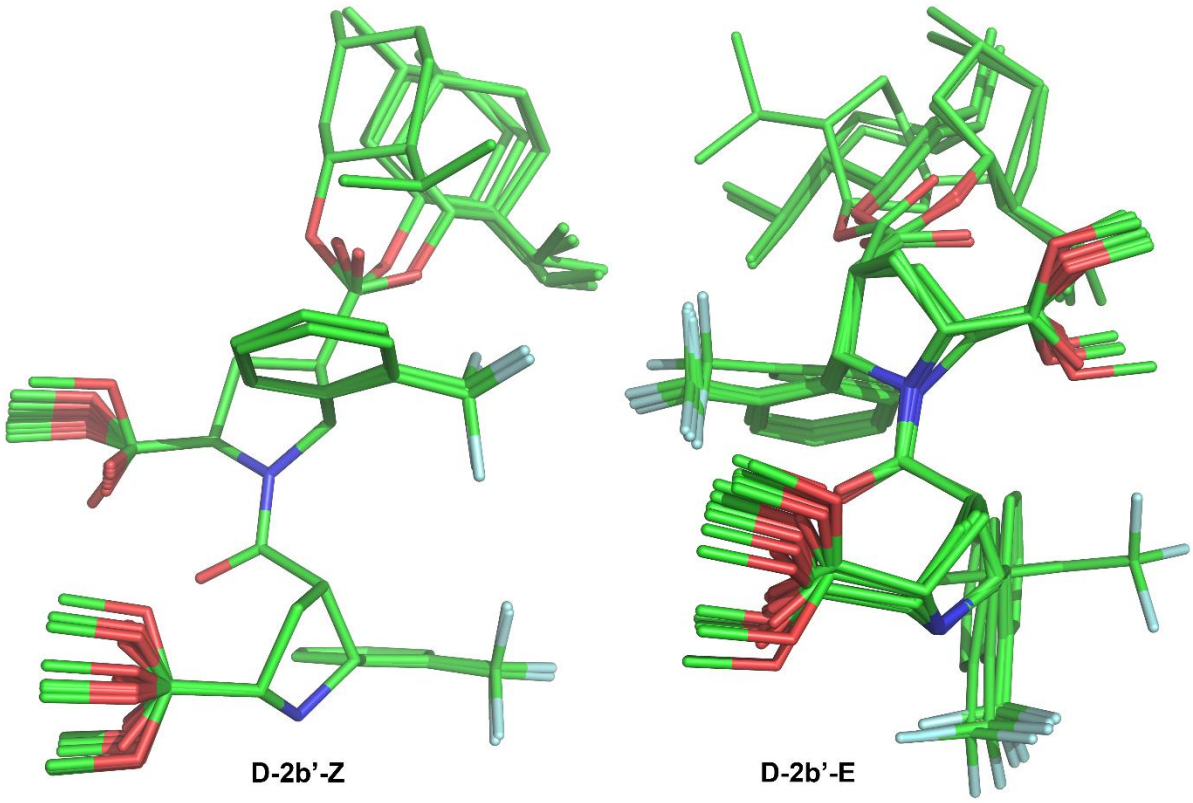


Figure S6. Families of NMR structures of dimer **D-2b'** in *Z*-form (left) and in *E*-form (right).

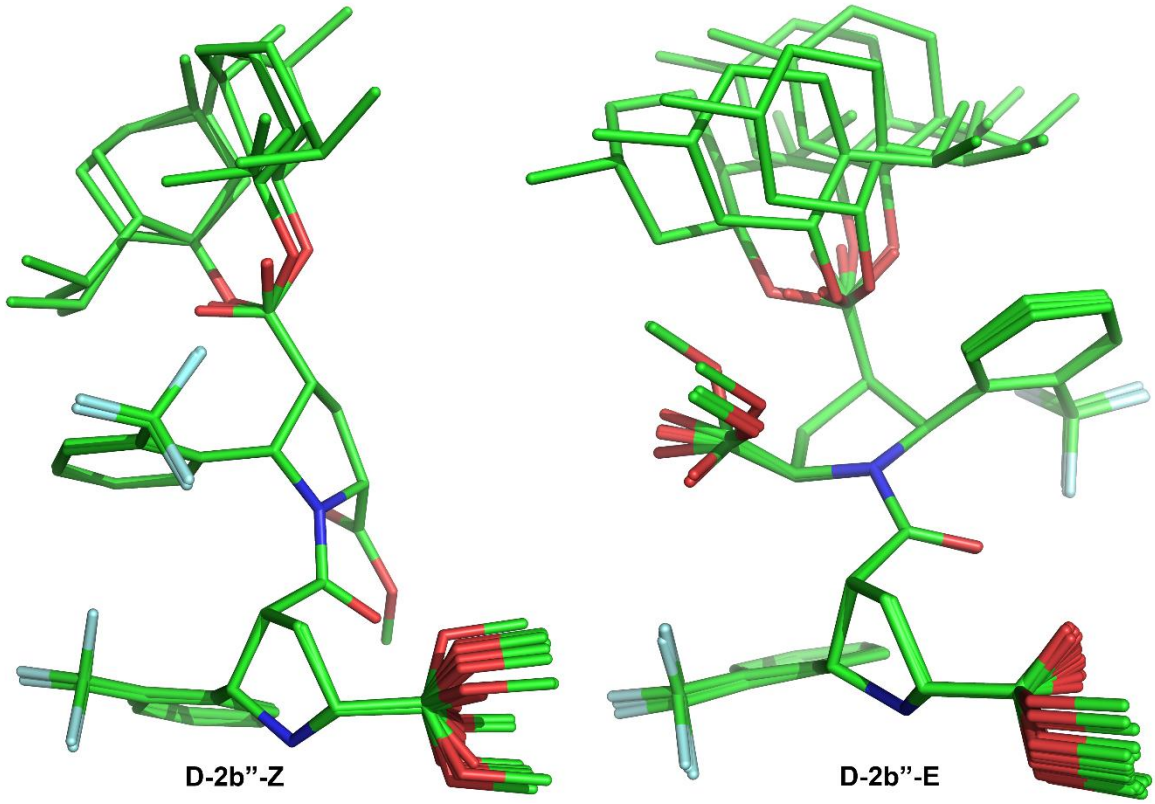


Figure S7. Families of NMR structures of dimer **D-2b"** in *Z*-form (left) and in *E*-form (right).

Table S1. Chemical shifts of fluorinated dimers.

Residue	Atom	Chemical shifts (^{1}H /^{13}C), ppm			
		(*Z*)-**D-2b'**	(*E*)-**D-2b'**	(*Z*)-**D-2b''**	(*E*)-**D-2b''**
	CO	- / 172.2	- / 173.3	- / 174.7	- / 171.8
	α	4.597 / 60.58	4.401 / 63.10	4.055 / 62.40	4.599 / 61.27
	β	2.936 / 47.03	3.197 / 45.65	3.021 / 45.02	3.291 / 47.54
	γ	2.152; 1.755/34.81	2.283; 2.551/35.97	2.263; 2.486/35.95	2.474; 2.421/34.62
	δ	3.679 / 59.53	3.981 / 59.85	3.996 / 59.43	3.856 / 59.95
	ε	- /172.8	- /172.2	- /172.3	- /172.4
1	ζ	3.724 / 52.08	3.722 / 52.07	3.785 / 52.29	3.670 / 52.05
	1	- / 137.6	- / 134.5	- / 134.1	- / 136.7
	2	- / 127.5	- / 128.1	- / 127.0	- / 128.0
	3	7.625 / 125.5	7.693 / 125.6	7.348 / 125.4	7.723 / 125.8
	4	7.371 / 127.6	7.382 / 127.1	7.376 / 127.3	7.445 / 128.2
	5	7.542 / 131.5	7.141 / 132.0	7.570 / 132.1	7.602 / 132.0
	6	7.785 / 129.4	7.319 / 128.8	7.651 / 129.4	7.674 / 129.1
	CO	- / 169.8	- / 171.0	- / 169.6	- / 171.3
	α	5.243 / 60.07	5.518 / 62.05	5.493 / 59.81	2.883 / 61.80
	β	3.180 / 48.67	4.195 / 47.16	3.382 / 49.16	3.016 / 46.61
	γ	2.356; 1.955/30.94	2.611; 2.423/32.90	2.334; 2.334/31.20	2.293; 1.079/31.65
	δ	4.290 / 59.65	4.639 / 60.29	4.530 / 59.47	3.528 / 59.25
	ε	- / 171.1	- / 170.9	- / 171.0	- / 171.4
2	ζ	3.739 / 52.18	3.529 / 52.41	3.758 / 52.20	2.331 / 52.59
	1	- / 137.0	- / 137.2	- / 136.4	- / 136.9
	2	- / 127.5	- / 126.9	- / 126.5	- / 126.9
	3	7.614 / 126.3	7.543 / 125.3	7.544 / 125.6	6.827 / 125.4
	4	7.393 / 128.2	7.183 / 126.4	7.233 / 127.6	7.205 / 126.9
	5	7.564 / 132.4	6.988 / 132.3	6.897 / 132.1	8.742 / 132.1
	6	8.362 / 129.8	7.044 / 128.0	7.331 / 129.3	7.763 / 128.0
	1	4.220 / 74.62	4.038 / 74.06	4.235 / 74.78	4.089 / 74.02
	2	1.066 / 46.38	0.908 / 46.27	1.095 / 46.47	0.951 / 46.31
	3	1.496; 0.817/ 23.13	1.431; 0.749/ 23.12	1.509; 0.825/ 23.14	1.445; 0.766/ 23.20
	4	1.506; 0.656/ 33.78	1.423; 0.539/ 33.68	1.520; 0.684/ 33.81	1.444; 0.566/ 33.70
	5	1.153 / 30.83	1.000 / 30.68	1.177 / 30.91	1.046 / 30.69
m	6	1.020; 0.169/ 39.23	0.465; -0.352/ 38.78	1.172; 0.386/ 39.64	0.511; -0.229/ 38.88
	7	1.519 / 26.04	1.494 / 26.02	1.483 / 26.03	1.508 / 26.15
	8	0.539 / 16.09	0.475 / 15.51	0.529 / 16.08	0.542 / 16.26
	9	0.749 / 20.48	0.717 / 20.45	0.746 / 20.52	0.726 / 20.41
	10	0.698 / 21.65	0.591 / 21.50	0.731 / 21.68	0.610 / 21.52

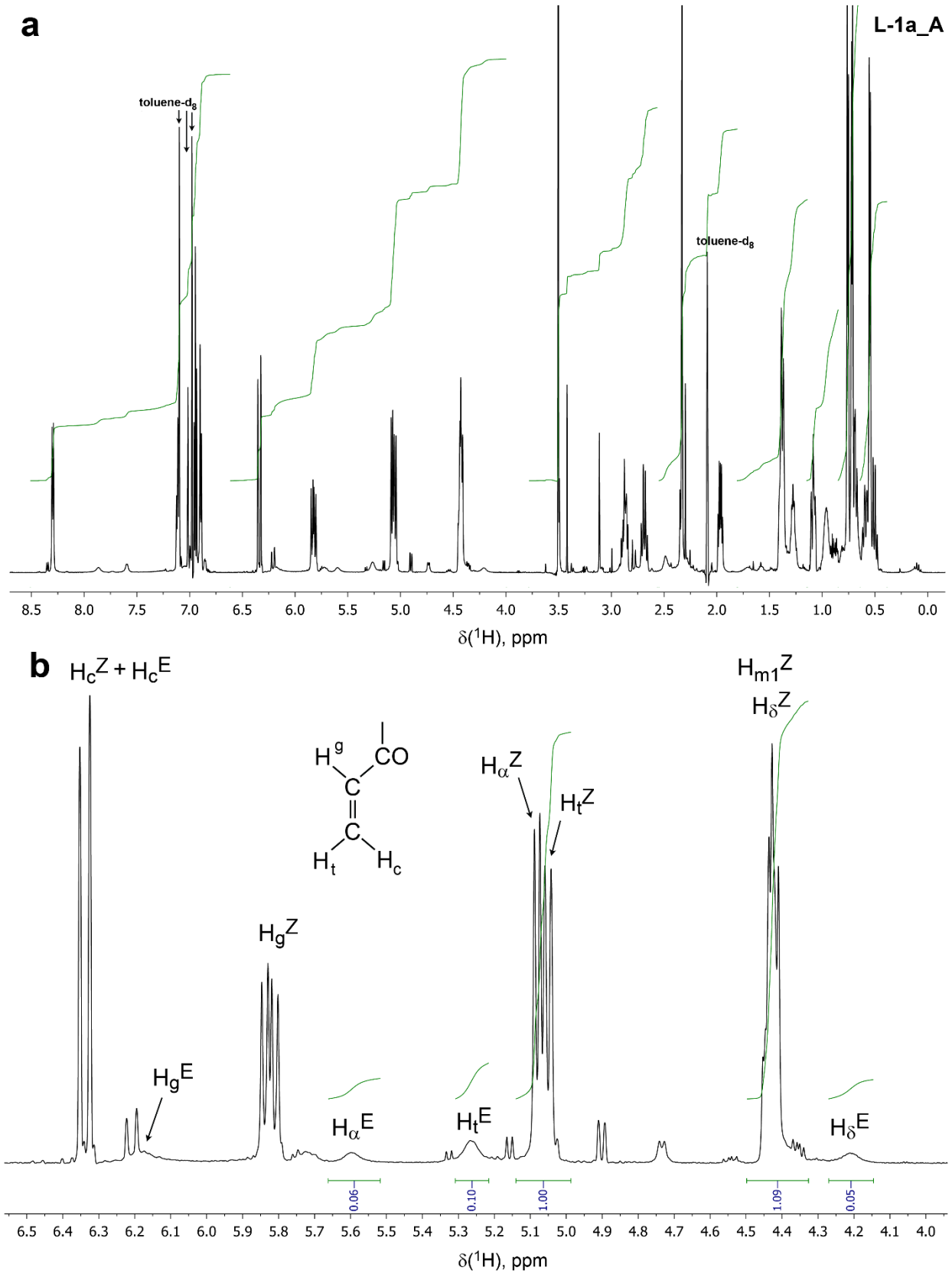


Figure S8. ^{1}H NMR spectrum (a) and its expanded fragment (b) of acrylamide **L-1a_A** in toluene-d_8. Content of *trans*-isomer (Z) is 90% and *cis*-isomer (E) is 10%.

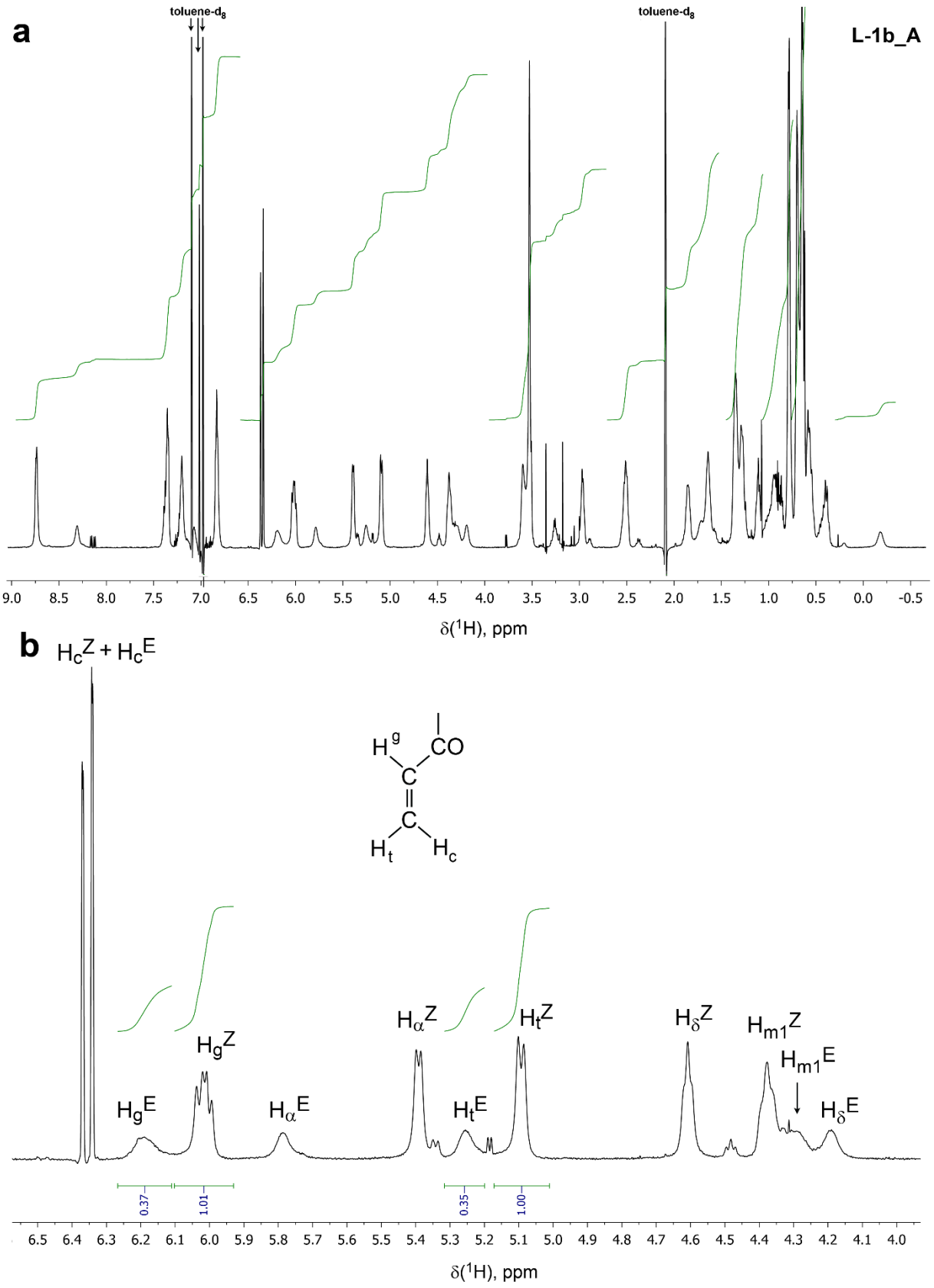


Figure S9. ^{1}H NMR spectrum (a) and its expanded fragment (b) of acrylamide **L-1b_A** in toluene-d_8. Content of *trans*-isomer (Z) is 74% and *cis*-isomer (E) is 26%.

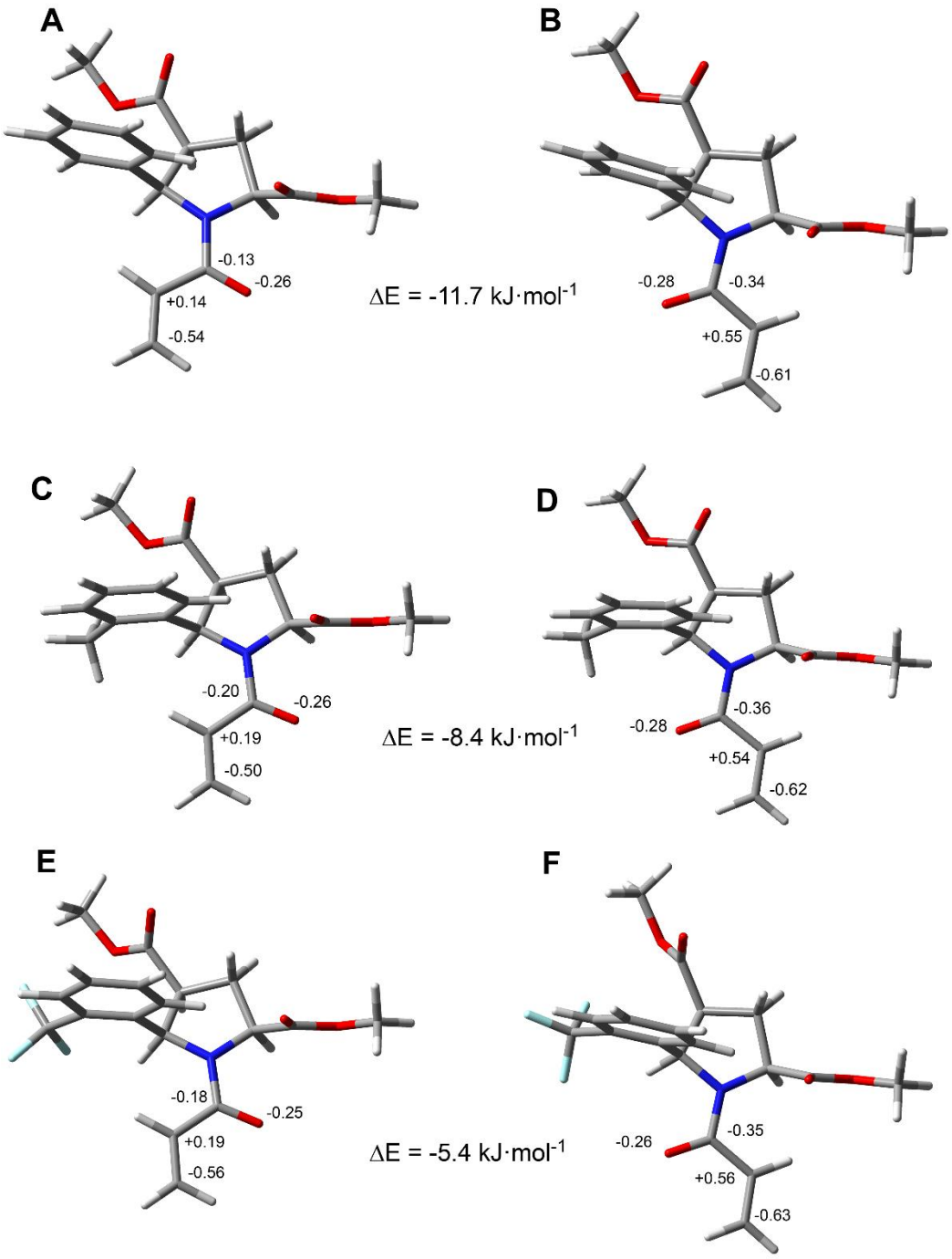


Figure S10. Structure of acrylamide derivatives **L-1_A** optimized using DFT quantum mechanics calculations. Shown are: *trans*-conformation of compound with no substitution in phenyl ring (***A***); *cis*-conformation of compound with no substitution in phenyl (***B***); *trans*-conformation of **L-1a_A** with *o*-CH_3 substitute (***C***); *cis*-conformation of **L-1a_A** (***D***); *trans*-conformation of **L-1b_A** with *o*-CF_3 substitute (***E***); *cis*-conformation of **L-1b_A** (***F***). Shown are Mulliken charges on the atoms of acrylamide fragment and calculated difference in energy of formation between *trans*- and *cis*-isomers ($\Delta E = E_{trans} - E_{cis}$).

Table S2. Chemical shifts of monomeric acrylamides.

Resi-due	Atom	Chemical shifts (^{1}H /^{13}C), ppm			
		trans-**L-1a_A**	*cis*-**L-1a_A**	*trans*-**L-1b_A**	*cis*-**L-1b_A**
a	1	5.825 / 128.0	6.197 / 126.2	6.019 / 127.7	6.189 / 128.9
	2c	6.338 / 127.7	6.334 / 127.6	6.356 / 128.2	6.354 / 127.8
	2t	5.047 / 127.7	5.264 / 127.6	5.094 / 128.2	5.257 / 127.8
1	α	5.080 / 58.25	5.596 / 60.75	5.394 / 59.58	5.789 / 61.93
	β	2.848 / 48.92	2.884 / 49.72	2.972 / 49.10	3.263 / 47.12
	γ	2.804; 1.946/ 29.44	2.739; 1.957 / 32.29	2.334; 2.334/30.91	2.293; 1.079/32.06
	δ	4.424 / 59.10	4.206 / 59.13	4.610 / 59.65	4.196 / 59.91
	ζ	3.505 / 51.36	3.421 / 51.46	3.576 / 51.69	3.530 / 51.46
	2	2.331 / 19.71	2.486 / 19.71	- / NA	- / NA
	3	6.899 / 130.1	6.921 / 130.7	7.363 / 125.2	7.391 / 125.1
	4	6.939 / 127.7	6.928 / 128.1	6.828 / 127.6	6.828 / 126.7
	5	7.106 / 126.9	6.939 / 126.8	7.206 / 132.6	7.084 / 132.0
	6	8.296 / 128.9	7.729 / 127.1	8.743 / 131.1	8.309 / 128.7
m	1	4.430 / 74.27	4.383 / 74.19	4.379 / 74.09	4.292 / 74.00
	2	1.085 / 46.65	1.007 / 46.36	1.115 / 46.66	1.011 / 46.52
	3	1.379; 0.705/ 23.01	1.333; 0.609/ 23.05	1.358; 0.696/ 23.20	1.303; 0.646/ 23.24
	4	1.379; 0.587/ 34.02	1.328; 0.525/ 33.96	1.344; 0.554/ 33.86	1.286; 0.430/ 33.78
	5	0.964 / 30.92	0.889 / 30.87	0.943 / 30.85	0.876 / 30.81
	6	1.308; 0.525/ 40.05	0.868; 0.095/ 39.33	1.284; 0.391/ 39.83	0.660; -0.180/ 39.00
	7	1.278 / 25.54	1.583 / 26.12	1.646 / 26.21	1.720 / 26.25
	8	0.549 / 15.86	0.676 / 16.09	0.648 / 16.07	0.595 / 15.53
	9	0.757 / 20.64	0.676 / 20.58	0.787 / 20.36	0.768 / 20.33
	10	0.717 / 21.68	0.659 / 21.66	0.701 / 21.61	0.578 / 21.52

X-RAY STUDIES

The molecule **D-3** comprises three substituted pyrrolidine rings linked by two amide group (Fig. S11). The chain is headed by (1*R*,2*S*,5*R*)-menthol group. All bond lengths and angles demonstrate ordinary values for organic compounds [1]. Both amide groups are planar within 0.027(2) Å and exhibit *Z*-configurations. All pyrrolidine cycles adopt an envelope conformation. Flap atoms C3, C20, and N3 are displaced from the base planes of other four atoms in pyrrolidine cycles by 0.581(4), 0.625(4), and 0.5699(4) Å, respectively. Terminal menthol ring adopts chair conformation with all substituents occupying equatorial positions. Of interest, amino group N3-H3 does not participate in any hydrogen bonding. The adjacent molecules in the structure are linked by weak van der Waals interactions only.

Experimental intensities were collected on a Bruker SMART APEX II diffractometer using graphite-monochoromated Mo*K*α radiation (λ = 0.71073 Å) at 183 K. The structure was solved by direct methods and refined by full matrix least-squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms [2]. All hydrogen atoms (except amino H3) were placed in calculated positions and refined using a riding model. Atom H3 was found from difference Fourier synthesis and refined isotropically. Absolute configuration was assigned according to synthetic procedures. Details of X-ray study are listed in Tables S3 and S4.

Crystallographic data (excluding structure factors) for the compound **D-3** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1474544. Copies of the data can be obtained free of charge on application to CCDC via www.ccdc.cam.ac.uk/data_request/cif.

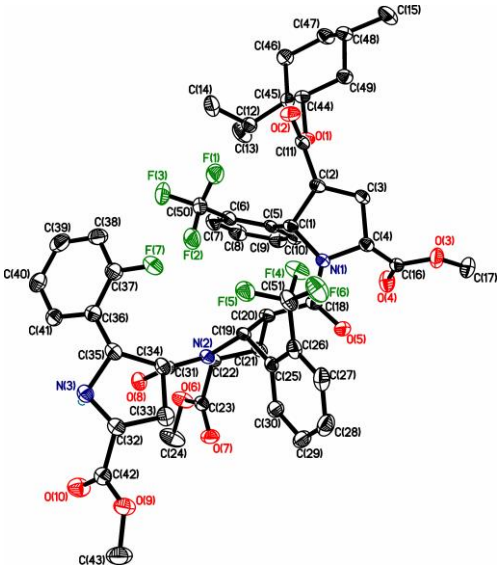
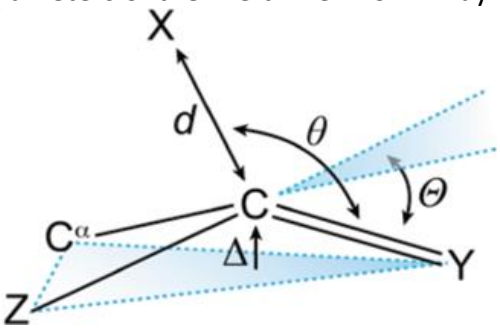


Figure S11. Molecular structure of **D-3**. Displacement ellipsoids are shown at 50 % probability level. Hydrogen atoms (except H3) are omitted for clarity.

Table S3. Crystallographic data and refinement details for compound **D-3**.

Formula	$C_{51}H_{56}F_7N_3O_{10}$
Formula weight	1003.99
Crystal size /mm^3	0.30×0.15×0.15
Crystal system	hexagonal
Space group	$P6_1$
Z	6
a /Å	12.5530(2)
c /Å	53.9500(16)
Volume /Å^3	7362.4(3)
Total reflections	108255
Unique data (R_{int})	5696 (0.0565)
ϑ /°	2.41 to 27.49
Data/restraints/parameters	5696 / 1 / 650
GoF on F^2	1.101
R_1 [I >2σ(I)]	0.0374
wR_2 (all data)	0.0868
Largest diff. peak and hole, e·Å^{-3}	0.185 / -0.142

Table S4. Conformational parameters of the **D-3** trimer from X-ray diffraction analysis.



X	**C**	**Z**	**Y**	**C$^\alpha$**	**d(Å)**	**θ(deg)**	**Δ(Å)**	**Θ(deg)**
O5	C16	O3	O4	C4	2.927(3)	86.8(2)	0.034(3)	4.0
O8	C23	O6	O7	C22	2.732(3)	95.2(2)	0.021(3)	2.5

References

(1) Allen, F.H. *Acta Cryst*. **2002**, *B58*, No 1, 380−388.

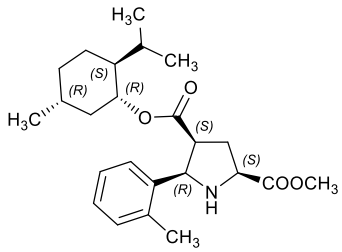
(2) Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, No 1, 112−122.

GENERAL PROCEDURES

General procedure for the synthesis of monomers L-1a, L-1b and D-1a [1]

A solution of triethylamine (TEA) (1.90 ml, 1.40 g, 14 mmol) in 15 ml of toluene was added dropwise to the mixture of corresponding iminoester ArCH=NCH$_2$COOR (11 mmol), AgOAc (2.50 g, 15 mmol), L-menthyl acrylate (or D-menthyl acrylate) (2.31 g, 11 mmol) in 75 ml of dry toluene under an inert atmosphere. Reaction flask was protected from the light with aluminium foil. Reaction mixture was stirred at room temperature for 12–48 h. Then the reaction mixture was filtered through Celite. Filtrate was washed with H_2O (50 ml) and saturated NH_4Cl solution (50 ml). Organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The crude products were purified by column chromatography on silica gel using hexane/AcOEt 3:1 as an eluent.

4-((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl) 2-methyl (2*S*,4*S*,5*R*)-5-(*o*-tolyl)pyrrolidine-2,4-dicarboxylate **L-1a**



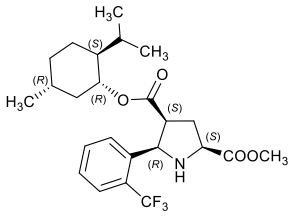
Yield 89 %, 0.870 g, white crystals, m. p. 75-77 °C, $[\alpha]_D^{25}$ +12.1° (*c* 1.33, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ −0.13 ÷ −0.04 (m, 1H), 0.62 (d, *J* 7.1 Hz, 3H), 0.65 (d, *J* 6.6 Hz, 3H), 0.64-0.69 (m, 1H), 0.74-0.77 (m, 1H), 0.80 (d, *J* 7.1 Hz, 3H), 0.83-0.91 (m, 1H), 1.03-1.19 (m, 2H), 1.48-1.53 (m, 2H), 1.62-1.70 (m, 1H), 2.36 (s, 3H), 2.41-2.48 (m, 2H), 2.81 (br.s, 1H), 3.34 (td, *J* 7.8, 5.5 Hz, 1H), 3.81 (s, 3H), 3.92 (t, *J* 8.3 Hz, 1H), 4.25 (td, *J* 10.9, 4.4 Hz, 1H), 4.57 (d, *J* 7.8 Hz, 1H), 7.07-7.17 (m, 3H), 7.37-7.39 (m, 1H).

^{13}C NMR (100 MHz, DMSO-d_6, 293 K): δ 16.32, 19.69, 20.65, 21.64, 23.29, 26.15, 30.88, 33.95, 34.22, 39.06, 46.58, 46.86, 52.23, 59.55, 62.71, 74.11, 125.61, 126.05, 127.33, 130.09, 135.94, 136.34, 172.56, 173.33.

Anal. Calcd for $C_{24}H_{35}NO_4$: C 71.79, H 8.79, N 3.49. Found:C 71.98, H 9.10, N 3.49.

4-((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl) 2-methyl (2*S*,4*S*,5*R*)-5-(2-(trifluoromethyl)-phenyl)pyrrolidine-2,4-dicarboxylate **L-1b**



Yield 88 %, 1.200 g, white crystals, m. p. 67-69 °C, $[\alpha]_D^{25}$ +3.9° (*c* 1.25, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ −0.14 (q, *J* 12.1 Hz, 1H), 0.55-0.62 (m, 1H), 0.62 (d, *J* 7.0 Hz, 3H), 0.64 (d, *J* 6.6 Hz, 3H), 0.71-0.78 (m, 1H), 0.78 (d, *J* 7.0 Hz, 3H), 0.81-0.89 (m, 1H), 1.01-1.20 (m, 2H), 1.47-1.52 (m, 2H), 1.62-1.71 (m, 1H), 2.39-2.44 (m, 1H), 2.48-2.55 (m, 1H), 2.61 (br.s, 1H), 3.31 (td, *J* 8.4, 6.6 Hz, 1H),

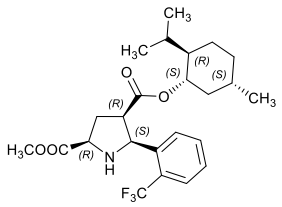
[1] Kudryavtsev, K. V.; Ivantcova, P. M.; Muhle-Goll, C.; Churakov, A. V.; Sokolov, M. N.; Dyuba, A. V.; Arutyunyan, A. M.; Howard, J. A. K.; Yu, C. C.; Guh, J. H.; Zefirov, N. S.; Bräse, S. *Org. Lett.* **2015**, *17*, 6178-6181.

3.79 (s, 3H), 3.91 (t, *J* 8.2 Hz, 1H), 4.24 (td, *J* 10.9, 4.5 Hz, 1H), 4.84 (d, *J* 8.6 Hz, 1H), 7.31 (t, *J* 7.7 Hz, 1H), 7.49 (t, *J* 7.7 Hz, 1H), 7.59 (d, *J* 7.7 Hz, 1H), 7.78 (d, *J* 7.7 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, 293 K): *δ* 16.36, 20.61, 21.71, 23.31, 26.18, 30.88, 33.38, 33.89, 39.35, 46.51, 48.55, 52.19, 59.44, 60.33, 74.13, 124.33 (q, *J* 250.8 Hz), 125.50, 125.7, 127.51, 128.99, 132.03, 138.40, 172.10, 173.37.

Anal. Calcd for $C_{24}H_{32}F_3NO_4$: C 63.28, H 7.08, N 3.07. Found: C 63.49, H 7.13, N 3.21.

4-((1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl) 2-methyl (2*R*,4*R*,5*S*)-5-(2-(trifluoromethyl)-phenyl)pyrrolidine-2,4-dicarboxylate **D-1b**



Yield 71 %, 3.900 g, white crystals, m. p. 67-69 °C, $[\alpha]_D^{25}$ −4.2° (*c* 1.31, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$, 293 K): *δ* −0.14 (q, *J* 12.1 Hz, 1H), 0.55-0.62 (m, 1H), 0.62 (d, *J* 7.0 Hz, 3H), 0.64 (d, *J* 6.6 Hz, 3H), 0.71-0.78 (m, 1H), 0.78 (d, *J* 7.0 Hz, 3H), 0.81-0.89 (m, 1H), 1.01-1.20 (m, 2H), 1.47-1.52 (m, 2H), 1.62-1.71 (m, 1H), 2.39-2.44 (m, 1H), 2.48-2.55 (m, 1H), 2.61 (br.s, 1H), 3.31 (td, *J* 8.4, 6.6 Hz, 1H), 3.79 (s, 3H), 3.93 (t, *J* 8.2 Hz, 1H), 4.24 (td, *J* 10.9, 4.5 Hz, 1H), 4.85 (d, *J* 8.6 Hz, 1H), 7.32 (t, *J* 7.7 Hz, 1H), 7.49 (t, *J* 7.7 Hz, 1H), 7.59 (d, *J* 7.7 Hz, 1H), 7.78 (d, *J* 7.7 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, 293 K): *δ* 16.36, 20.61, 21.71, 23.31, 26.18, 30.88, 33.38, 33.89, 39.35, 46.51, 48.55, 52.19, 59.44, 60.33, 74.13, 124.33 (q, *J* 250.8 Hz), 125.50, 125.7, 127.51, 128.99, 132.03, 138.40, 172.10, 173.37.

^{19}F NMR (376 MHz, $CDCl_3$, 293 K): *δ* −58.64 (s, minor rotamer), −58.46 (s, major rotamer).

Anal. Calcd for $C_{24}H_{32}F_3NO_4$: C 63.28, H 7.08, N 3.07. Found: C 63.57, H 7.13, N 3.21.

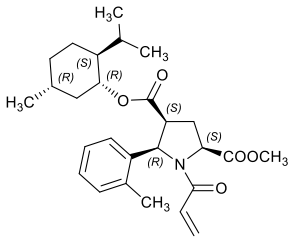
General procedure of cycloadditive oligomerization

Synthesis of acrylamides L-n_A and D-n_A from monomers L-1 and D-1 and dimer D-2b' [1]

TEA (1.16 ml, 0.84 g, 8.4 mmol) was added to a stirred solution of corresponding monomer or oligomer (5.2 mmol) in 70 ml of CH_2Cl_2 at 0 °C. Then acryloyl chloride (0.62 ml, 0.70 g, 7.8 mmol) was added dropwise to the reaction mixture under inert atmosphere. Cooling bath was removed after 15 min of completion of acryloyl chloride addition. The reaction mixture was stirred at rt for additional 24 h, then washed with H_2O (40 mL), brine (40 mL), dried over Na_2SO_4 and concentrated under reduced pressure. Acrylamides were isolated by column chromatography on silica gel using hexane/AcOEt from 3:1 to 1:2 as an eluent.

[1] Kudryavtsev, K. V.; Ivantcova, P. M.; Muhle-Goll, C.; Churakov, A. V.; Sokolov, M. N.; Dyuba, A. V.; Arutyunyan, A. M.; Howard, J. A. K.; Yu, C. C.; Guh, J. H.; Zefirov, N. S.; Bräse, S. *Org. Lett.* **2015**, *17*, 6178-6181.

4-((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl) 2-methyl (2*S*,4*S*,5*R*)-1-acryloyl-5-(*o*-tolyl)-pyrrolidine-2,4-dicarboxylate **L-1a_A**



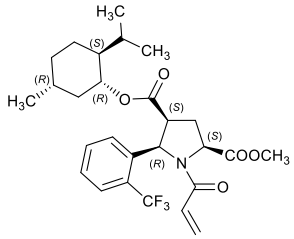
Yield 85 %, 0.910 g, white crystals, m.p. 78-80 °C, $[\alpha]_D^{25}$ −26.2° (*c* 0.90, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ 0.49 (d, *J* 7.0 Hz, 3H), 0.49-0.59 (m, 1H), 0.74 (d, *J* 7.0 Hz, 3H),0.76 (d, *J* 7.0 Hz, 3H), 0.83-0.93 (m, 2H), 1.13-1.19 (m, 2H), 1.25-1.35 (m, 2H), 1.53-1.58 (m, 2H), 2.44 (s, 3H), 2.40-2.46 (m, 1H), 2.66-2.75 (m, 1H), 3.54-3.60 (m, 1H), 3.85 (s, 3H), 4.33-4.39 (m, 1H), 4.54 (dd, *J* 10.0, 7.3 Hz, 1H), 5.51 (t, *J* 9.2 Hz, 2H), 5.87 (dd, *J* 16.6, 10.3 Hz, 1H), 6.29 (d, *J* 16.6 Hz, 1H), 7.08 (d, *J* 7.5 Hz, 1H), 7.16 (t, *J* 7.5 Hz, 1H), 7.23 (t, *J* 7.5 Hz, 1H), 7.94 (d, *J* 7.5 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-d_6, 293 K): δ 16.01, 19.99, 20.76, 21.80, 23.09, 25.73, 29.66, 31.09, 33.39, 39.85, 46.57, 49.05, 52.41, 58.72, 59.29, 75.21, 127.06, 127.49, 128.13, 128.39, 129.23, 130.40, 134.87, 137.03, 168.74, 171.95, 174.61.

Anal. Calcd for $C_{27}H_{37}NO_5$: C 71.18, H 8.19, N 3.07. Found: C 71.24, H 8.43, N 3.34.

4-((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl) 2-methyl (2*S*,4*S*,5*R*)-1-acryloyl-5-(2-(trifluoro-methyl)phenyl)pyrrolidine-2,4-dicarboxylate **L-1b_A**

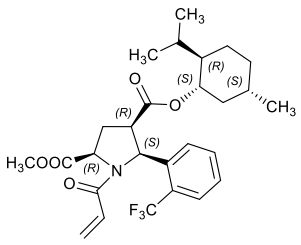


Yield 92 %, 1.000 g, white crystals, m.p. 127-129 °C, $[\alpha]_D^{20}$ −18.8° (*c* 1.05, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ 0.29-0.37 (m, 1H), 0.59 (d, *J* 7.0 Hz, 3H), 0.65-0.75 (m, 2H), 0.74 (d, *J* 6.6 Hz, 3H), 0.78 (d, *J* 7.0 Hz, 3H), 0.81-0.89 (m, 1H), 1.01-1.20 (m, 2H), 1.45-1.65 (m, 3H), 2.42-2.51 (m, 1H), 2.56-2.66 (m, 1H), 3.45-3.60 (m, 1H), 3.86-3.90 (m, 3H), 4.18-4.35 (m, 1H), 4.68-4.78 (m, 1H), 5.44-5.48 (m, 1H), 5.65-5.78 (m, 1H), 5.88-5.95 (m, 1H), 6.26-6.32 (m, 1H), 7.24-7.64 (m, 3H), 7.99-8.41 (m, 1H).

Anal. Calcd for $C_{27}H_{34}F_3NO_5$: C 63.64, H 6.73, N 2.75. Found: C 64.00, H 6.96, N 2.70.

4-((1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl) 2-methyl (2*R*,4*R*,5*S*)-1-acryloyl-5-(2-(trifluoro-methyl)phenyl)pyrrolidine-2,4-dicarboxylate **D-1b_A**



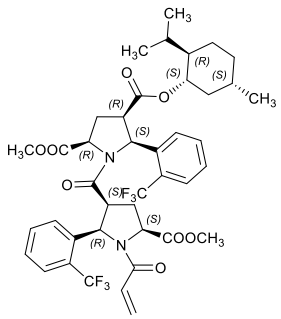
Yield 90 %, 5.700 g, white crystals, m.p. 127-129°C, $[\alpha]_D^{20}$ +19.2° (*c* 1.05, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ 0.29-0.37 (m, 1H), 0.59 (d, *J* 7.0 Hz, 3H), 0.65-0.75 (m, 2H), 0.74 (d, *J* 6.6 Hz, 3H), 0.78 (d, *J* 7.0 Hz, 3H), 0.81-0.89 (m, 1H), 1.01-1.20 (m, 2H), 1.45-1.65 (m, 3H), 2.42-2.51 (m, 1H), 2.56-2.66 (m, 1H), 3.45-3.60 (m, 1H), 3.86-3.90 (m, 3H), 4.18-4.35 (m, 1H), 4.68-4.78 (m, 1H), 5.44-5.48 (m, 1H), 5.65-5.78 (m, 1H), 5.89-5.95 (m, 1H), 6.26-6.32 (m, 1H), 7.24-7.65 (m, 3H), 7.99-8.41 (m, 1H).

^{19}F NMR (376 MHz, $CDCl_3$, 293 K): δ −58.99 (s, minor conformer), −57.94 (s, major conformer).

Anal. Calcd for $C_{27}H_{34}F_3NO_5$: C 63.64, H 6.73, N 2.75. Found: C 66.97, H 7.01, N 2.71.

4-((1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl) 2-methyl (2*R*,4*R*,5*S*)-1-((2*R*,3*S*,5*S*)-1-acryloyl-5-(methoxycarbonyl)-2-(2-(trifluoromethyl)phenyl)pyrrolidine-3-carbonyl)-5-(2-(trifluoromethyl)-phenyl)pyrrolidine-2,4-dicarboxylate **D-2b'_A**



Yield 94 %, 1.450 g, white crystals, m.p. 149-152 °C, $[\alpha]_D^{20}$ +47.4° (*c* 1.13, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$, 293 K): *δ* 0.28 (q, *J* 11.9 Hz, 1H), 0.60 (d, *J* 7.0 Hz, 3H), 0.65-0.74 (m, 1H), 0.75 (d, *J* 6.4 Hz, 3H), 0.80 (d, *J* 7.0 Hz, 3H), 0.81-0.91 (m, 1H), 1.07-1.15 (m, 2H), 1.15-1.25 (m, 1H), 1.53-1.65 (m, 3H), 1.65-1.71 (m, 1H), 2.29-2.38 (m, 1H), 2.38-2.48 (m, 1H), 2.50-2.58 (m, 1H), 3.05-3.12 (m, 1H), 3.52-3.58 (m, 1H), 3.71 (s, 3H), 3.75 (s, 3H), 3.92 (dd, *J* 11.7, 6.5 Hz, 1H), 4.28-4.35 (m, 1H), 4.45 (t, *J* 7.6 Hz, 1H), 5.47 (d, *J* 8.0 Hz, 1H), 5.52 (dd, *J* 10.4, 1.3 Hz, 1H), 5.70 (d, *J* 8.7 Hz, 1H), 5.92 (dd, *J* 16.6, 10.4 Hz, 1H), 6.28 (dd, *J* 16.6, 1.3 Hz, 1H), 7.40 (t, *J* 7.6 Hz, 1H), 7.47 (t, *J* 7.5 Hz, 1H), 7.58-7.67 (m, 3H), 7.69 (d, *J* 7.7 Hz, 1H), 8.32 (d, *J* 8.0 Hz, 1H), 8.41 (d, *J* 7.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, 293 K): *δ* 16.22, 20.64, 21.78, 23.29, 26.23, 31.02, 31.22, 31.46, 33.91, 39.68, 46.62, 47.00, 49.10, 52.34, 52.39, 58.60, 58.92, 59.59, 60.17, 74.96, 125.70, 126.08, 127.00, 128.21, 128.75, 129.85, 130.21, 131.36, 132.71, 133.01, 133.79, 137.90, 165.59, 168.39, 169.98, 171.25, 171.56.

Anal. Calcd for $C_{41}H_{46}F_6N_2O_8$: C 60.89, H 5.73, N 3.46. Found: C 61.14, H 5.86, N 3.31.

Synthesis of dimers L-2 and D-2 and trimer D-3 from acrylamides L-n_A and D-n_A

Procedure A [1]

A solution of TEA (0.39 ml, 0.28 g, 2.8 mmol) in 5 ml of toluene was added dropwise to the stirred mixture of corresponding iminoester ArCH=NCH$_2$COOR (2.2 mmol), AgOAc (0.50 g, 2.8 mmol), acrylamide **L-n_A** or **D-n_A** (1.9 mmol) in 40 ml of dry toluene under inert atmosphere. Reaction flask was protected from the light with aluminium foil. The reaction mixture was stirred at room temperature for 12–48 h. Then toluene was removed by evaporation under reduced pressure. The solid residue was suspended in 50 ml CH_2Cl_2 and the precipitate was removed by filtration. Organic phase was washed with 25 ml of water, 25 ml of brine and dried over Na_2SO_4, filtered and volatiles were evaporated under reduced pressure. The products were isolated by column chromatography on silica gel using hexane/AcOEt from 3:1 to 1:2 as an eluent.

Procedure B

Synthesis of AgOAc•2PPh$_3$ complex

Reaction flask has been protected from the light with aluminium foil. The mixture of AgOAc (0.50 g, 2.99 mmol) and PPh_3 (1.53 g, 5.99 mmol) in 10ml of toluene was stirred and heated until

[1] Kudryavtsev, K. V.; Ivantcova, P. M.; Muhle-Goll, C.; Churakov, A. V.; Sokolov, M. N.; Dyuba, A. V.; Arutyunyan, A. M.; Howard, J. A. K.; Yu, C. C.; Guh, J. H.; Zefirov, N. S.; Bräse, S. *Org. Lett.* **2015**, *17*, 6178-6181.

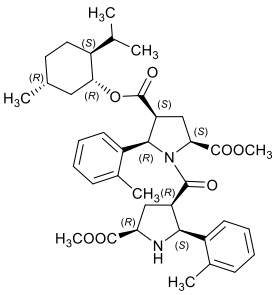
complete dissolution of the suspension, after that the reaction mixture was cooled to rt. Formed precipitate was filtered, dried on air, and finally redissolved in 100 ml DCM and filtered though Celite. Filtrate was concentrated under reduced pressure until starting of precipitation. White solid was filtered and dried on air. Yield 50 %, 1.00 g, m.p. 186-188 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ 1.99 (s, 3H), 7.27-7.44 (m, 30H).

Anal. Calcd for $C_{38}H_{33}AgO_2P_2$: C 66.00, H 4.81. Found: C 66.32, H 5.00.

For the production of dimers **L-2**, 132 mg (0.19 mmol) of AgOAc•2PPh_3 were used instead of equimolar amounts of AgOAc in *procedure A*. All other manipulations are the same as in the *procedure A*.

4-((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl) 2-methyl (2*S*,4*S*,5*R*)-1-((2*S*,3*R*,5*R*)-5-(methoxycarbonyl)-2-(*o*-tolyl)pyrrolidine-3-carbonyl)-5-(*o*-tolyl)pyrrolidine-2,4-dicarboxylate **L-2a'**



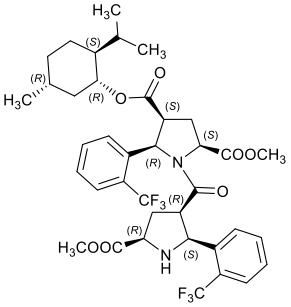
Yield 71 %, 0.540 g, (method A). Yield 93 %, 0.159 g (method B), white crystals, m.p. 163-165 °C, $[\alpha]_D^{25}$ −30.2° (*c* 0.45, MeOH).

^{1}H NMR (400 MHz, DMSO-d_6, 293 K): δ 0.37 (q, *J* 12.1 Hz, 1H), 0.46 (d, *J* 6.8 Hz, 3H), 0.67-0.73 (m, 1H), 0.71 (d, *J* 6.5 Hz, 3H), 0.74 (d, *J* 7.0 Hz, 3H), 0.80-0.89 (m, 2H), 1.05-1.08 (m, 1H), 1.23-1.32 (m, 1H), 1.47-1.53 (m, 2H), 1.90-1.97 (m, 3H), 2.06-2.08 (m, 1H), 2.31 (s, 3H), 2.42-2.46 (m, 1H), 2.46 (s, 3H), 2.70-2.74 (m, 1H), 2.78-2.88 (m, 1H), 3.63-3.68 (m, 1H), 3.67 (s, 3H), 3.68 (s, 3H), 3.95 (t, *J* 8.3 Hz, 1H), 4.07-4.13 (m, 1H), 4.44-4.52 (m, 2H), 7.09-7.18 (m, 4H), 7.21-7.30 (m, 3H), 7.75-7.77 (m, 1H).

^{13}C NMR (100 MHz, DMSO-d_6, 293 K): δ 16.23, 19.59, 20.53, 21.71, 22.88, 25.40, 28.64, 30.46, 33.54, 34.00, 39.17, 45.45, 46.06, 46.18, 47.72, 51.78, 51.93, 58.25, 58.80 (2C), 61.69, 74.07, 125.81, 125.94, 126.10, 126.24, 127.62, 127.72, 130.37, 130.48, 134.97, 135.28, 136.27, 136.83, 168.47, 171.55, 172.59, 173.28.

Anal. Calcd for $C_{38}H_{50}N_2O_7$: C 70.56, H 7.79, N 4.33. Found: C 70.72, H 8.02, N 4.32.

4-((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl) 2-methyl (2*S*,4*S*,5*R*)-1-((2*S*,3*R*,5*R*)-5-(methoxycarbonyl)-2-(2-(trifluoromethyl)phenyl)pyrrolidine-3-carbonyl)-5-(2-(trifluoromethyl)-phenyl)pyrrolidine-2,4-dicarboxylate **L-2b'**



Yield 47 %, 0.284 g (method A). Yield 44 %, 0.223 g (method B), white crystals, m.p. 81-83 °C, $[\alpha]_D^{20}$ +9.3° (*c* 1.13, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ (*Z*-conformer) 0.18 (q, *J* 12.0 Hz, 1H), 0.56 (d, *J* 7.0 Hz, 3H), 0.65-0.70 (m, 1H), 0.71 (d, *J* 6.2 Hz, 3H), 0.77 (d, *J* 7.0 Hz, 3H), 0.78-0.88 (m, 1H), 1.00-1.21 (m, 2H), 1.42-1.57 (m, 2H), 1.76 (ddd, *J* 13.9, 8.0, 7.8 Hz, 1H), 1.93-2.00 (m, 1H), 2.13-2.20 (m, 1H), 2.34-2.40 (m, 1H), 2.95 (q, *J* 6.9 Hz, 1H), 3.17-3.22 (m, 1H), 3.67-3.74 (m, 2H), 3.74 (s, 3H), 3.75 (s, 3H), 4.23 (td, *J* 10.8, 4.3 Hz, 1H), 4.30 (dd, *J* 8.6, 5.5 Hz, 1H), 4.61 (d, *J* 7.0 Hz, 1H), 5.26 (d, *J* 8.6 Hz, 1H), 7.39 (q, *J* 7.4 Hz, 2H), 7.56 (q, *J* 7.8 Hz, 2H), 7.62-7.65 (m, 2H), 7.79 (d, *J* 8.2 Hz, 1H), 8.38 (d, *J* 7.8 Hz, 1H). δ (*E*-conformer) −0.39 ÷ −0.30 (m, 1H), 0.60 (d, *J* 7.0 Hz, 3H),

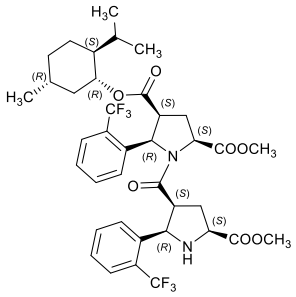
0.63 (d, *J* 6.6 Hz, 3H), 0.71-0.78 (m, 2H), 0.78 (d, *J* 7.0 Hz, 3H), 1.00-1.21 (m, 3H), 1.42-1.57 (m, 3H), 2.29-2.31 (m, 1H), 2.41-2.64 (m, 3H), 3.36-3.40 (m, 1H), 3.55-3.57 (m, 1H), 3.69 (s, 3H), 3.71 (s, 3H), 3.97 (dd, *J* 9.6, 6.0 Hz, 1H), 4.05 (td, *J* 10.8, 4.3 Hz, 1H), 4.39 (d, *J* 6.0 Hz, 1H), 4.60 (d, *J* 9.2 Hz, 1H), 5.53 (d, *J* 9.0 Hz, 1H), 6.98-7.02 (m, 1H), 7.05-7.07 (m, 1H), 7.13-7.21 (m, 2H), 7.33-7.35 (m, 1H), 7.51-7.61 (m, 2H), 7.69-7.71 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, 293 K): *δ* 16.21, 20.59, 21.76, 23.26, 26.16, 30.95, 31.05, 33.88, 34.88, 39.39, 46.49, 47.13, 48.76, 52.18, 52.28, 59.61, 59.75, 60.23, 60.73, 74.24, 125.59, 125.65, 126.32, 126.38, 127.69, 128.32, 129.60, 130.02, 131.63, 132.53, 137.27, 137.70, 170.08, 171.32, 172.41, 172.99. Signals of CF_3-groups did not accumulate.

^{19}F NMR (376 MHz, $CDCl_3$, 293 K): *δ* −58.89 (s, *E*-conformer); −58.31 (s, *E*-conformer); −58.21 (q, *J* 5.5 Hz, *Z*-conformer), −57.52 (q, *J* 5.5 Hz, *Z*-conformer).

Anal. Calcd for $C_{38}H_{44}F_6N_2O_7$: C 60.47, H 5.88, N 3.71. Found: C 60.80, H 6.12, N 3.75.

4-((1*R*,2S,5*R*)-2-isopropyl-5-methylcyclohexyl) 2-methyl (2*S*,4*S*,5*R*)-1-((2*R*,3*S*,5*S*)-5-(methoxycarbonyl)2-(2-(trifluoromethyl)phenyl)pyrrolidine-3-carbonyl)-5-(2-(trifluoromethyl)-phenyl)pyrrolidine-2,4-dicarboxylate **L-2b''**



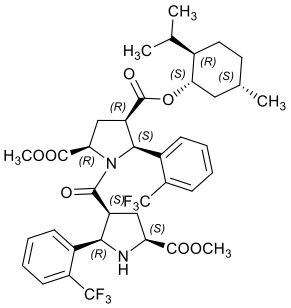
Yield 38%, 0.230 g (method A). Yield 27 %, 0.137 g (method B), white crystals, m.p. 73-75 °C, $[\alpha]_D^{20}$ +49.0° (*c* 1.1, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$, 293 K): *δ* (*E*-conformer) −0.24 ÷ −0.15 (m, 1H), 0.52-0.58 (m, 1H), 0.58 (d, *J* 7.0 Hz, 3H), 0.65 (d, *J* 6.6 Hz, 3H), 0.71-0.78 (m, 1H), 0.76 (d, *J* 7.0 Hz, 3H), 0.81-0.89 (m, 1H), 1.07-1.16 (m, 2H), 1.47-1.52 (m, 4H), 2.25-2.37 (m, 2H), 2.43-2.55 (m, 2H), 3.03-3.07 (m, 1H), 3.30-3.35 (m, 1H), 3.71 (s, 3H), 3.85 (s, 3H), 3.85-3.90 (m, 1H), 3.95-4.05 (m, 1H), 4.12 (td, *J* 10.9, 4.4 Hz, 1H), 4.63 (d, *J* 8.6 Hz, 1H), 5.11 (d, *J* 8.6 Hz, 1H), 7.24-7.28 (m, 1H), 7.37-7.50 (m, 2H), 7.55-7.66 (m, 2H), 7.68-7.81 (m, 3H). *δ* (*Z*-conformer) 0.39-0.48 (m, 1H), 0.52-0.58 (m, 1H), 0.57 (d, *J* 7.0 Hz, 3H), 0.63 (d, *J* 6.6 Hz, 3H), 0.71-0.78 (m, 1H), 0.78 (d, *J* 7.0 Hz, 3H), 0.93-1.02 (m, 2H), 1.07-1.16 (m, 1H), 1.20-1.24 (m, 2H), 1.47-1.52 (m, 2H), 2.25-2.37 (m, 2H), 2.43-2.55 (m, 2H), 3.03-3.07 (m, 1H), 3.38-3.44 (m, 1H), 3.79 (s, 3H), 3.81 (s, 3H), 3.95-4.05 (m, 2H), 4.28 (td, *J* 10.9, 4.0 Hz, 1H), 4.56 (t, *J* 8.2 Hz, 1H), 5.53 (d, *J* 8.8 Hz, 1H), 6.94 (t, *J* 7.8 Hz, 1H), 7.37-7.50 (m, 2H), 7.55-7.66 (m, 2H), 7.68-7.81 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, 293 K): *δ* (*E*-conformer) 16.26, 20.41, 21.52, 23.20, 26.15, 30.69, 31.65, 33.70, 34.62, 38.88, 46.31, 46.61, 47.54, 52.05, 52.59, 59.25, 59.95, 61.27, 61.80, 74.02, 125.40, 125.80, 126.90 (2C), 128.00 (2C), 128.20, 129.10, 132.00, 132.10, 136.70, 136.90, 171.30, 171.40, 171.80, 172.40. Signals of CF_3-groups did not accumulate. *δ* (*Z*-conformer) 16.08, 20.52, 21.68, 23.14, 26.03, 30.91, 31.20, 33.81, 35.95, 39.64, 45.02, 46.47, 49.16, 52.20, 52.29, 59.43, 59.47, 59.81, 62.40, 74.78, 125.40, 125.60, 126.50, 127.00, 127.30, 127.60, 129.30, 129.40, 132.10 (2C), 134.10, 136.40, 169.60, 171.00, 172.30, 174.70. Signals of CF_3-groups did not accumulate.

Anal. Calcd for $C_{38}H_{44}F_6N_2O_7$: C 60.47, H 5.88, N 3.71. Found: C 60.65, H 5.90, N 3.65.

4-((1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl) 2-methyl (2*R*,4*R*,5*S*)-1-((2*R*,3*S*,5*S*)-5-(methoxycarbonyl)-2-(2-(trifluoromethyl)phenyl)pyrrolidine-3-carbonyl)-5-(2-(trifluoromethyl)-phenyl)pyrrolidine-2,4-dicarboxylate **D-2b'**



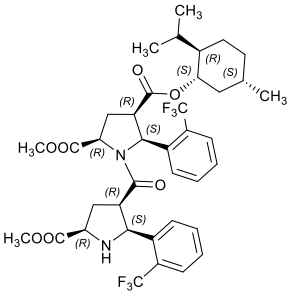
Yield 53%, 1.450 g (method A), white crystals, m.p. 81-83°C, $[\alpha]_D^{20}$ −5.5°. (*c* 0.46, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$, 293 K): *δ* (*Z*-conformer) 0.18 (q, *J* 12.0 Hz, 1H), 0.56 (d, *J* 7.0 Hz, 3H), 0.65-0.70 (m, 1H), 0.71 (d, *J* 6.2 Hz, 3H), 0.77 (d, *J* 7.0 Hz, 3H), 0.78-0.88 (m, 1H), 1.00-1.21 (m, 2H), 1.42-1.57 (m, 2H), 1.76 (ddd, *J* 13.9, 8.0, 7.8 Hz, 1H), 1.93-2.00 (m, 1H), 2.13-2.20 (m, 1H), 2.34-2.40 (m, 1H), 2.95 (q, *J* 6.9 Hz, 1H), 3.17-3.22 (m, 1H), 3.67-3.74 (m, 2H), 3.74 (s, 3H), 3.75 (s, 3H), 4.23 (td, *J* 10.8, 4.3 Hz, 1H), 4.30 (dd, *J* 8.6, 5.5 Hz, 1H), 4.61 (d, *J* 7.0 Hz, 1H), 5.26 (d, *J* 8.6 Hz, 1H), 7.39 (q, *J* 7.4 Hz, 2H), 7.56 (q, *J* 7.8 Hz, 2H), 7.62-7.65 (m, 2H), 7.79 (d, *J* 8.2 Hz, 1H), 8.38 (d, *J* 7.8 Hz, 1H). *δ* (*E*-conformer) −0.39 ÷ −0.30 (m, 1H), 0.60 (d, *J* 7.0 Hz, 3H), 0.63 (d, *J* 6.6 Hz, 3H), 0.71-0.78 (m, 2H), 0.78 (d, *J* 7.0 Hz, 3H), 1.00-1.21 (m, 3H), 1.42-1.57 (m, 3H), 2.29-2.31 (m, 1H), 2.41-2.64 (m, 3H), 3.36-3.40 (m, 1H), 3.55-3.57 (m, 1H), 3.69 (s, 3H), 3.71 (s, 3H), 3.97 (dd, *J* 9.6, 6.0 Hz, 1H), 4.05 (td, *J* 10.8, 4.3 Hz, 1H), 4.39 (d, *J* 6.0 Hz, 1H), 4.60 (d, *J* 9.2 Hz, 1H), 5.53 (d, *J* 9.0 Hz, 1H), 6.98-7.02 (m, 1H), 7.05-7.07 (m, 1H), 7.13-7.21 (m, 2H), 7.33-7.35 (m, 1H), 7.51-7.61 (m, 2H), 7.69-7.71 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, 293 K): *δ* 16.21, 20.59, 21.76, 23.26, 26.16, 30.95, 31.05, 33.88, 34.88, 39.39, 46.49, 47.13, 48.76, 52.18, 52.28, 59.61, 59.75, 60.23, 60.73, 74.24, 125.59, 125.65, 126.32, 126.38, 127.69, 128.32, 129.60, 130.02, 131.63, 132.53, 137.27, 137.70, 170.08, 171.32, 172.41, 172.99. Signals of CF_3-groups did not accumulate.

Anal. Calcd for $C_{38}H_{44}F_6N_2O_7$: C 60.47, H 5.88, N 3.71. Found: C 60.76, H 6.19, N 3.43.

4-((1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl) 2-methyl (2*R*,4*R*,5*S*)-1-((2*S*,3*R*,5*R*)-5-(methoxy-carbonyl)-2-(2-(trifluoromethyl)phenyl)pyrrolidine-3-carbonyl)-5-(2-(trifluoromethyl)phenyl)-pyrrolidine-2,4-dicarboxylate **D-2b''**



Yield 42%, 1.149 g (method A), white crystals, m.p. 73-75 °C, $[\alpha]_D^{20}$ −48.5° (*c* 1.13, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$, 293 K): *δ* (*E*-conformer) −0.27 ÷ −0.18 (m, 1H), 0.48-0.54 (m, 1H), 0.56 (d, *J* 7.0 Hz, 3H), 0.61 (d, *J* 6.6 Hz, 3H), 0.69-0.74 (m, 1H), 0.72 (d, *J* 7.0 Hz, 3H), 0.78-0.85 (m, 1H), 1.04-1.12 (m, 2H), 1.43-1.61 (m, 4H), 2.21-2.33 (m, 2H), 2.39-2.51 (m, 2H), 2.81 (br.s, 1H), 2.99-3.03 (m, 1H), 3.27-3.31 (m, 1H), 3.67 (s, 3H), 3.82 (s, 3H), 3.81-3.86 (m, 1H), 3.91-4.01 (m, 1H), 4.09 (td, *J* 10.9, 4.4 Hz, 1H), 4.57-4.63 (m, 1H), 5.08 (d, *J* 8.6 Hz, 1H), 7.21-7.24 (m, 1H), 7.33-7.46 (m, 2H), 7.51-7.62 (m, 2H), 7.65-7.78 (m, 3H). *δ* (*Z*-conformer) 0.36-0.45 (m, 1H), 0.48-0.54 (m, 1H), 0.55 (d, *J* 7.0 Hz, 3H), 0.61 (d, *J* 6.6 Hz, 3H), 0.68-0.74 (m, 1H), 0.74 (d, *J* 7.0 Hz, 3H), 0.92-0.98 (m, 2H), 1.04-1.13 (m, 1H), 1.18-1.24 (m, 2H), 1.47-1.52 (m, 2H), 2.23-2.33 (m, 2H), 2.43-2.50 (m,

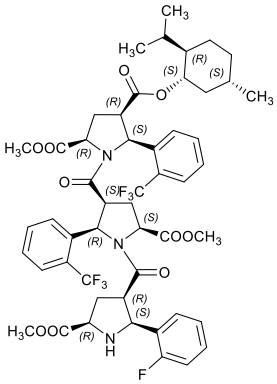
2H), 2.99-3.03 (m, 1H), 3.34-3.40 (m, 1H), 3.75 (s, 3H), 3.78 (s, 3H), 3.91-4.01 (m, 2H), 4.24 (td, *J* 10.9, 4.0 Hz, 1H), 4.52 (t, *J* 8.2 Hz, 1H), 5.50 (d, *J* 8.8 Hz, 1H), 6.91 (t, *J* 7.8 Hz, 1H), 7.34-7.46 (m, 2H), 7.52-7.62 (m, 2H), 7.65-7.78 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, 293 K): *δ* (*E*-conformer) 16.26, 20.41, 21.52, 23.20, 26.15, 30.69, 31.65, 33.70, 34.62, 38.88, 46.31, 46.61, 47.54, 52.05, 52.59, 59.25, 59.95, 61.27, 61.80, 74.02, 125.40, 125.80, 126.90 (2C), 128.00 (2C), 128.20, 129.10, 132.00, 132.10, 136.70, 136.90, 171.30, 171.40, 171.80, 172.40. Signals of CF_3-groups did not accumulate. *δ* (*Z*-conformer) 16.08, 20.52, 21.68, 23.14, 26.03, 30.91, 31.20, 33.81, 35.95, 39.64, 45.02, 46.47, 49.16, 52.20, 52.29, 59.43, 59.47, 59.81, 62.40, 74.78, 125.40, 125.60, 126.50, 127.00, 127.30, 127.60, 129.30, 129.40, 132.10 (2C), 134.10, 136.40, 169.60, 171.00, 172.30, 174.70. Signals of CF_3-groups did not accumulate.

^{19}F NMR (376 MHz, DMSO-d_6, 293 K): *δ* −57.87 (s, *Z*-conformer); −57.50 (s, *E*-conformer); −56.72 (s, *E*-conformer), −56.32 (s, *Z*-conformer).

Anal. Calcd for $C_{38}H_{44}F_6N_2O_7$: C 60.47, H 5.88, N 3.71. Found: C 60.75, H 6.11, N 3.64.

4-((1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl) 2-methyl (2*R*,4*R*,5*S*)-1-((2*R*,3*S*,5*S*)-1-((2*S*,3*R*,5*R*)-2-(2-fluorophenyl)-5-(methoxycarbonyl)pyrrolidine-3-carbonyl)-5-(methoxycarbonyl)-2-(2-(trifluoromethyl)phenyl)pyrrolidine-3-carbonyl)-5-(2-(trifluoromethyl)phenyl)pyrrolidine-2,4-dicarboxylate **D-3**



Yield 96%, 1.290 g, white crystals, m.p. 132-134 °C, $[\alpha]_D^{20}$ −24.3° (*c* 0.97, MeOH).

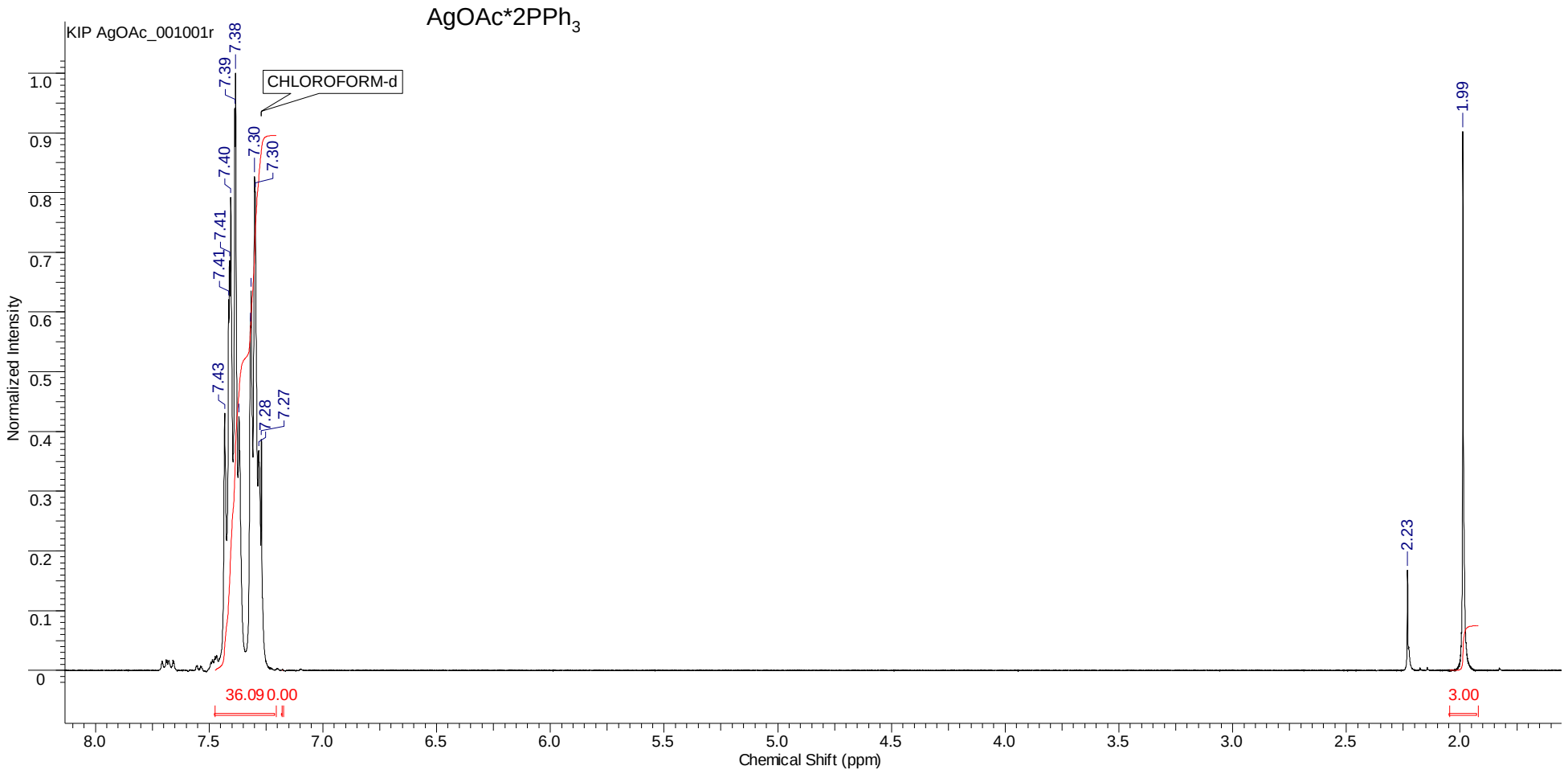
^{1}H NMR (400 MHz, $CDCl_3$, 293 K): *δ* 0.25-0.34 (m, 1H), 0.60 (d, *J* 7.0 Hz, 3H), 0.68-0.74 (m, 1H), 0.76 (d, *J* 6.5 Hz, 3H), 0.81 (d, *J* 7.0 Hz, 3H), 0.81-0.91 (m, 1H), 1.09-1.24 (m, 3H), 1.46-1.63 (m, 4H), 1.74 (ddd, *J* 13.3, 8.8, 5.8 Hz, 1H), 2.13-2.22 (m, 1H), 2.36-2.44 (m, 1H), 2.48-2.55 (m, 1H), 3.05-3.15 (m, 2H), 3.50-3.61 (m, 3H), 3.63 (s, 3H), 3.69 (s, 3H), 3.70 (s, 3H), 4.28-4.35 (m, 2H), 4.42 (dd, *J* 8.6, 6.4 Hz, 1H), 5.56 (d, *J* 8.3 Hz, 1H), 5.75 (d, *J* 8.9 Hz, 1H), 6.98 (dd, *J* 10.5, 8.4 Hz, 1H), 7.08 (td, *J* 7.5, 1.1 Hz, 1H), 7.18-7.22 (m, 1H), 7.40-7.51 (m, 3H), 7.59-7.64 (m, 3H), 7.68 (d, *J* 7.5 Hz, 1H), 8.31 (d, *J* 7.9 Hz, 1H), 8.37 (d, *J* 7.9 Hz, 1H).

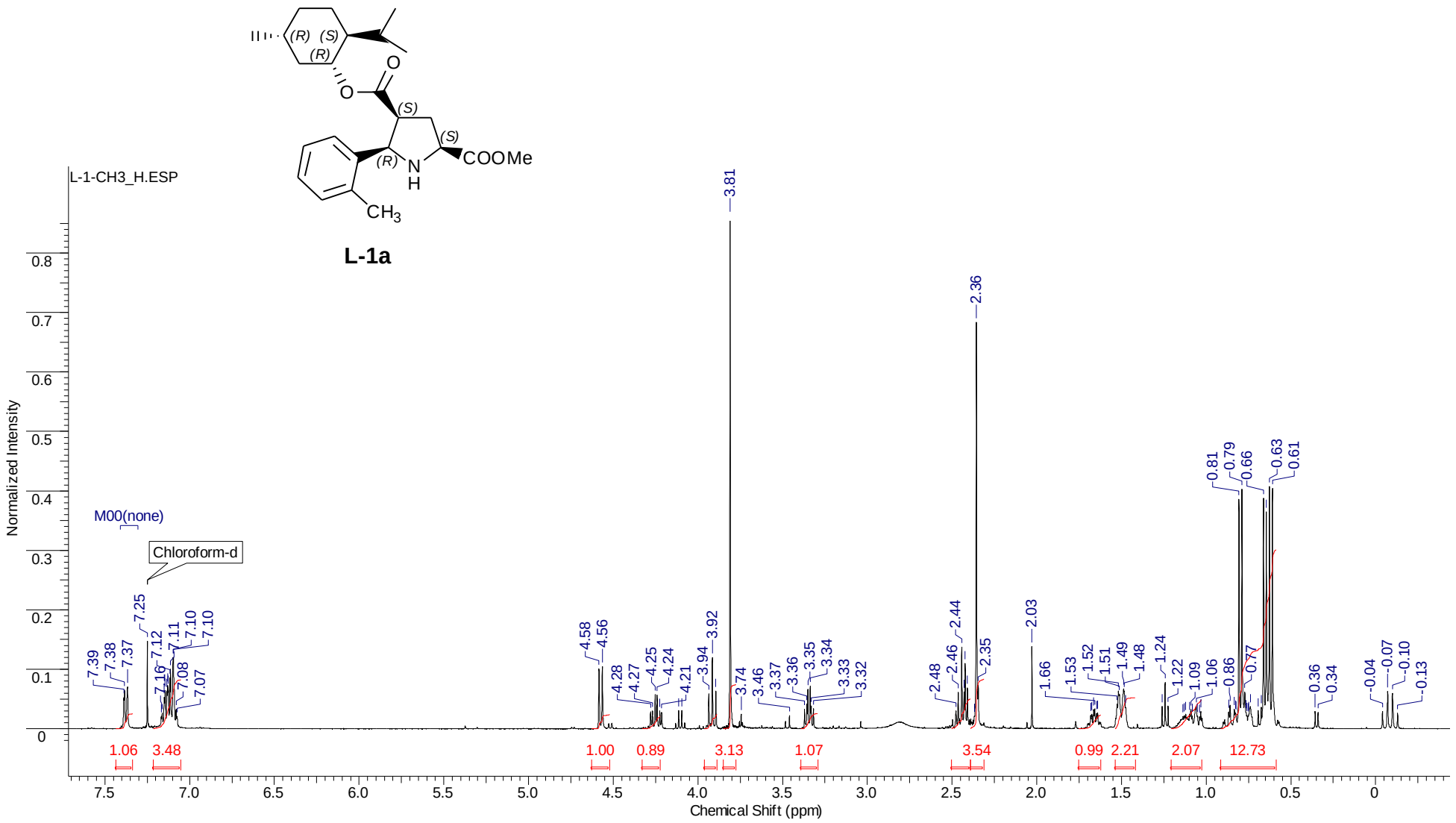
^{13}C NMR (100 MHz, $CDCl_3$, 293 K): *δ* 16.18, 20.63, 21.78, 23.23, 26.17, 30.98, 31.18, 31.80, 33.87, 35.73, 39.62, 45.79, 46.57, 46.69, 49.11, 52.09, 52.22, 52.29, 58.39, 59.06, 59.54, 59.61, 59.67, 60.12, 74.88, 114.43 (d, *J* 22.0 Hz), 124.17, 125.68, 125.91, 125.97, 127.25 (q), 127.39 (q), 128.09, 128.29, 128.33, 128.45, 128.53, 128.67, 130.22, 131.28, 132.43, 132.82, 137.73, 138.59, 159.34 (d, *J* 159.3 Hz, *C*-F), 168.62, 170.03, 171.16, 171.42, 172.70, 172.78.

^{19}F NMR (376 MHz, $CDCl_3$, 293 K): *δ* −119.18 (s, 1F), −58.45 (d, *J* 8.9 Hz, 3F), −58.17 (d, *J* 8.9 Hz, 3F).

Anal. Calcd for $C_{51}H_{56}F_7N_3O_{10}$: C 61.01, H 5.62, N 4.19. Found: C 61.29, H 5.31, N 4.18.

^{1}H AND ^{13}C SPECTRA OF SYNTHESIZED COMPOUNDS

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O
O
(S)
(S)
(R)
N
H
COOMe
CH3
L-1a
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Chloroform-d
Chemical Shift (ppm)
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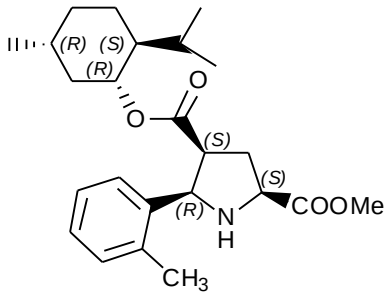
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(S)
(R)
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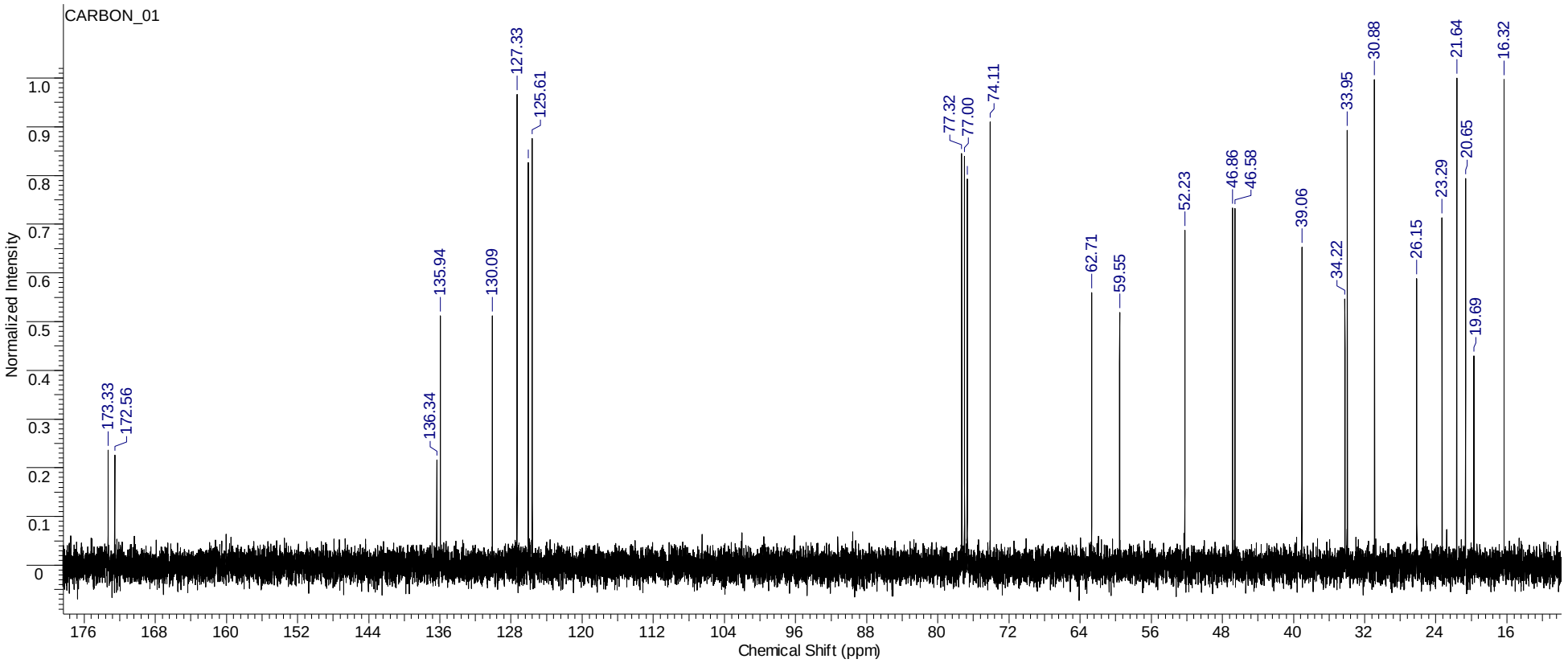
O
(S)
(S)
(R)
N
H
COOMe
CH3

L-1a


CARBON_01
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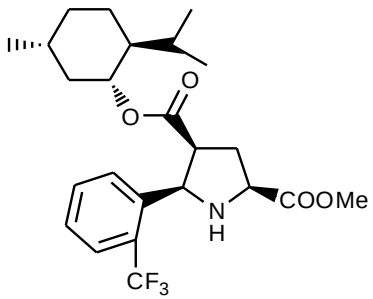
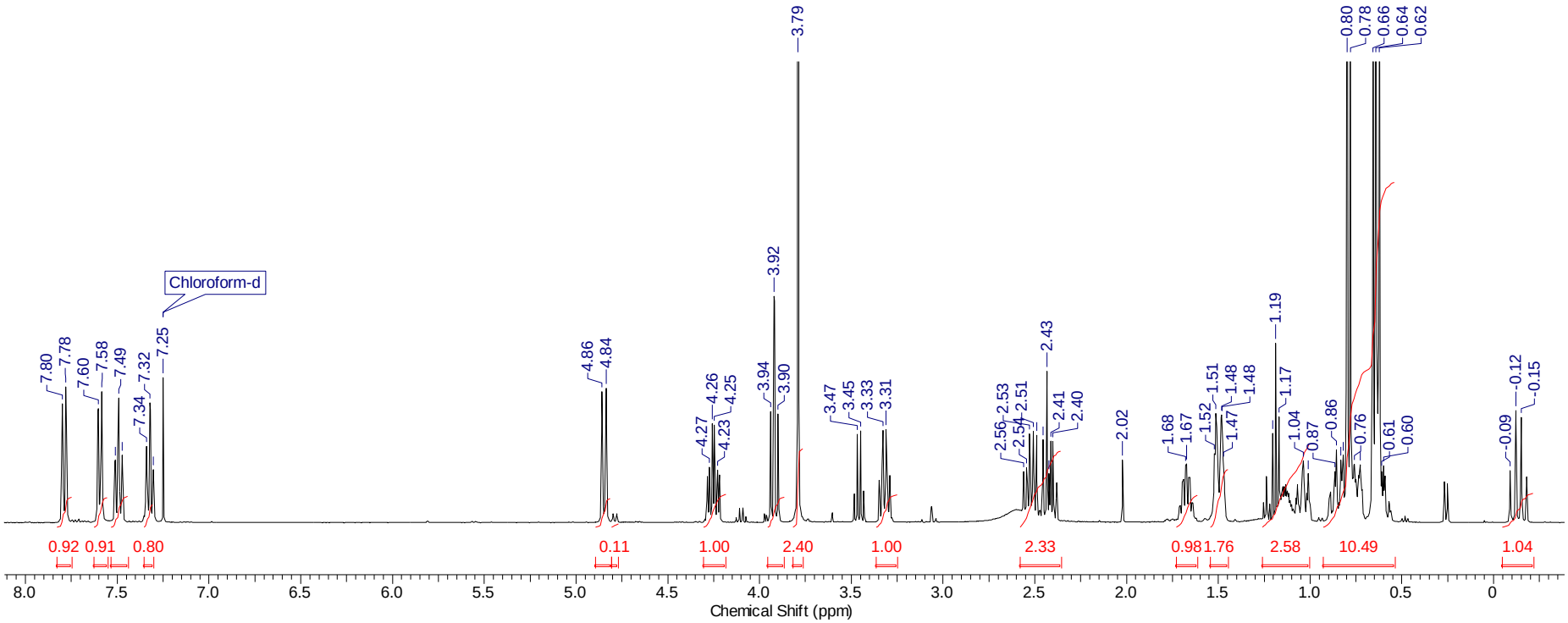
Chemical Shift (ppm)


O
O
COOMe
N
H
CF3

L-1b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0.91
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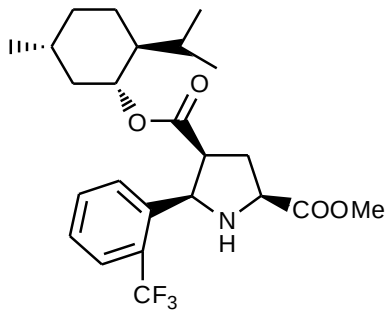
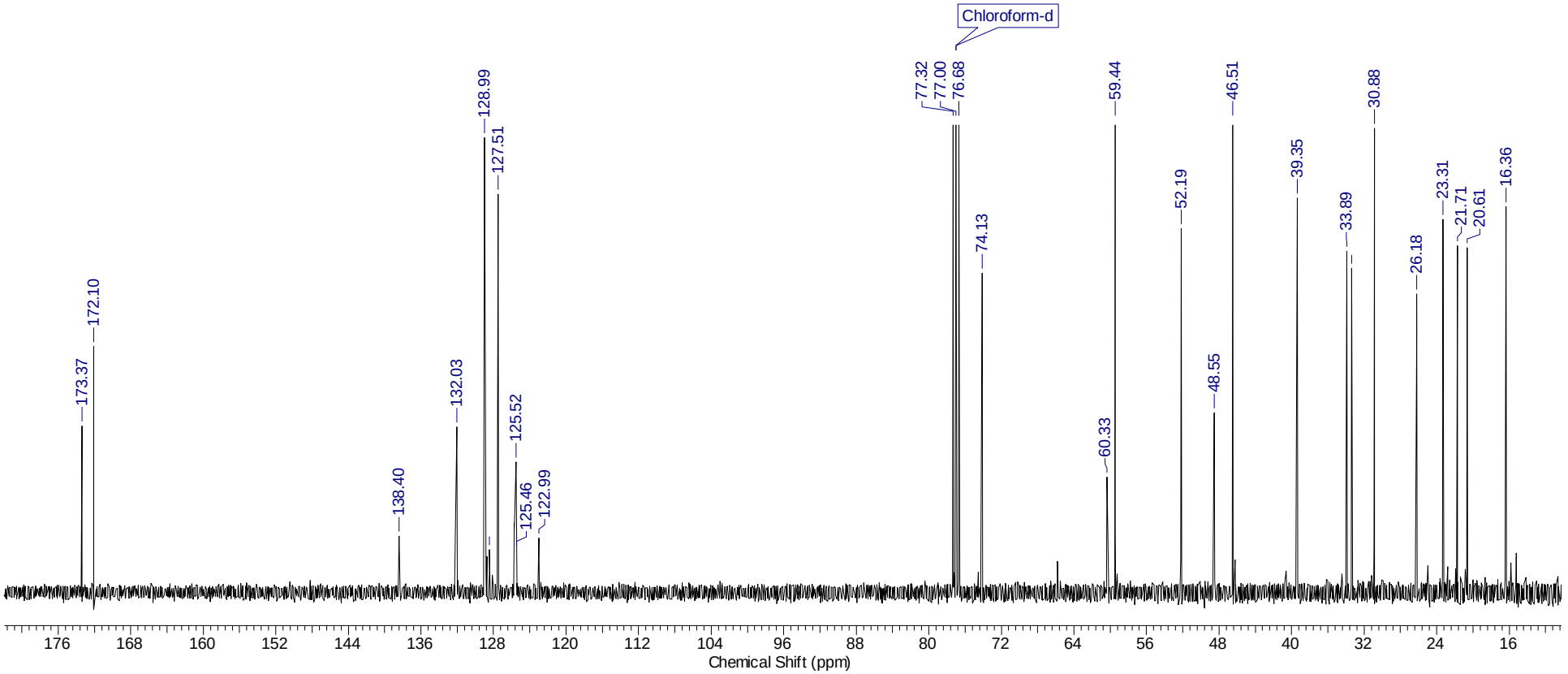
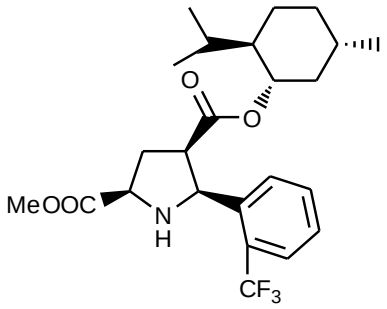
10.49
1.04
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

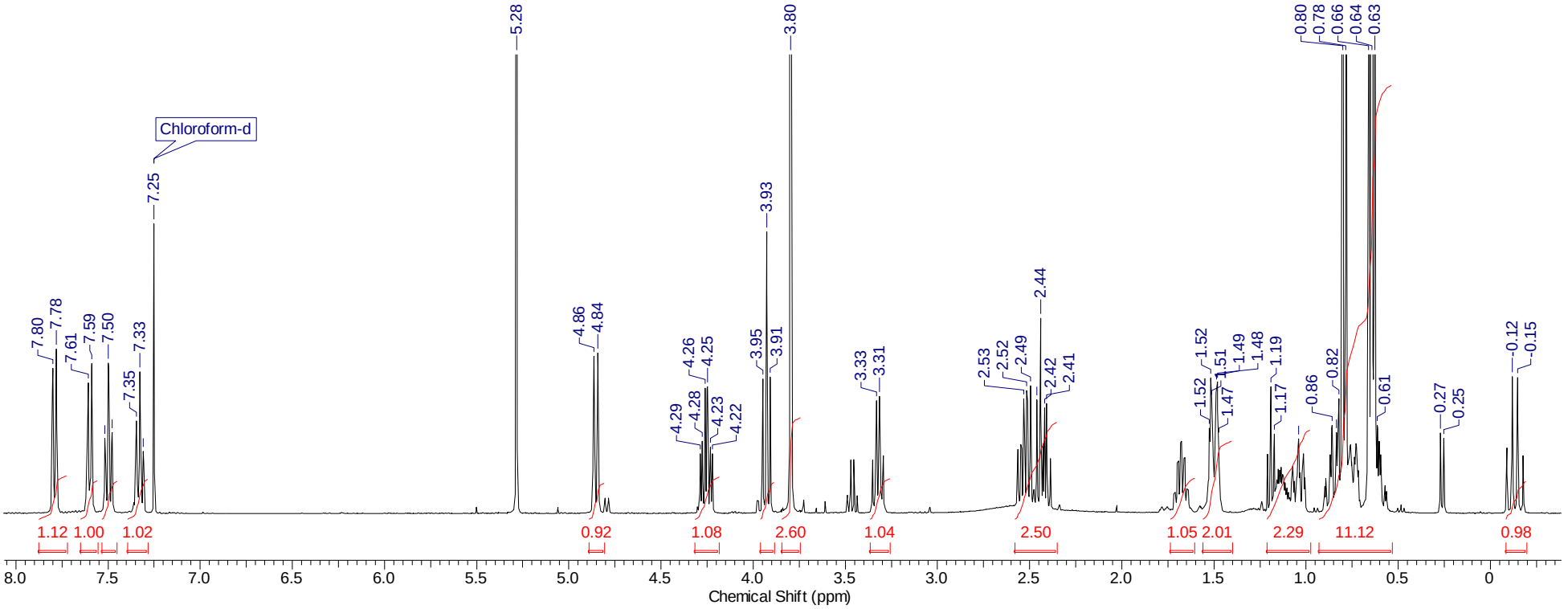

O
O
N
H
COOMe
CF3

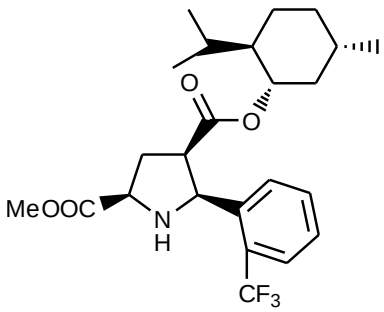
L-1b


Chloroform-d
77.32
77.00
76.68
128.99
127.51
74.13
59.44
46.51
52.19
39.35
33.89
30.88
26.18
23.31
21.71
20.61
16.36
173.37
172.10
138.40
132.03
125.52
125.46
122.99
60.33
48.55
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
Chemical Shift (ppm)

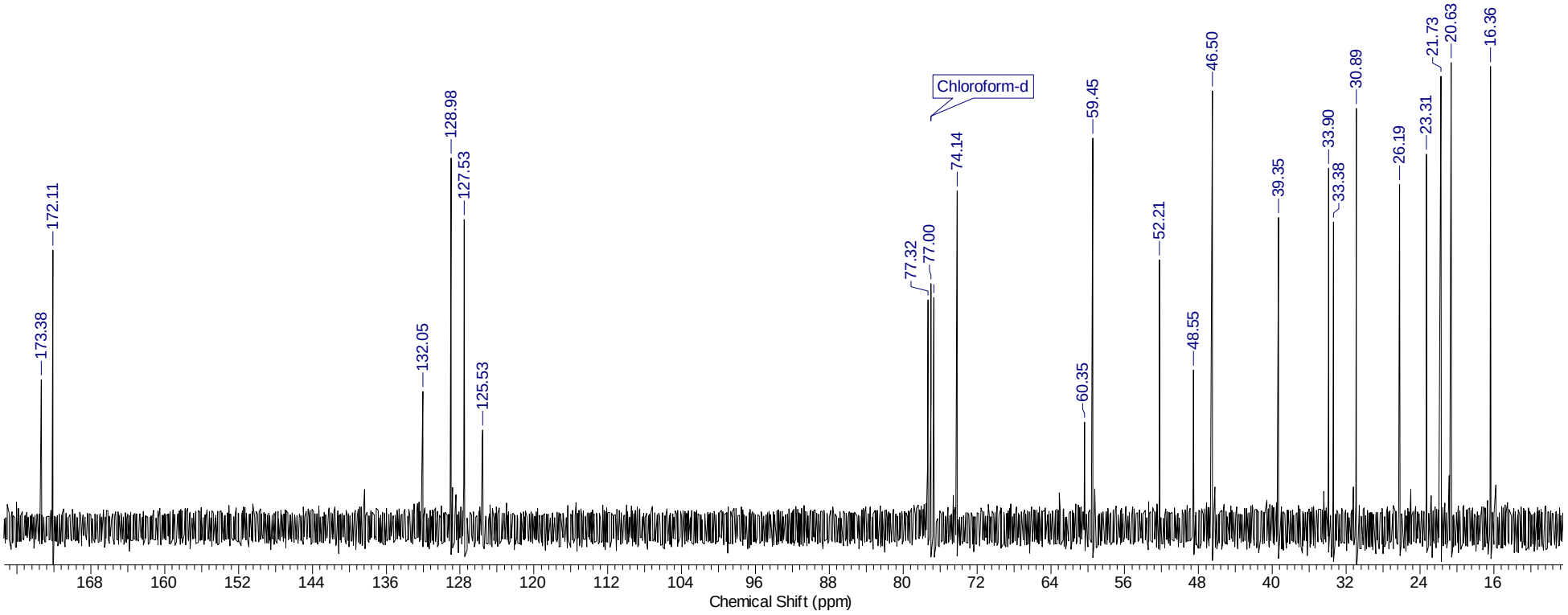

O
O
MeOOC
N
H
CF3

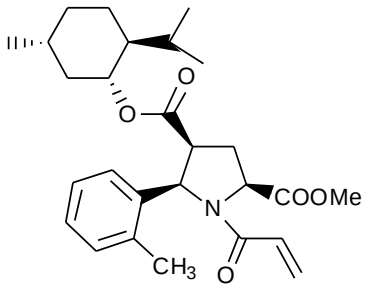
D-1b


Chloroform-d
7.80
7.78
7.61
7.59
7.50
7.35
7.33
7.25
5.28
4.86
4.84
4.29
4.28
4.26
4.25
4.23
4.22
3.95
3.93
3.91
3.80
3.33
3.31
2.53
2.52
2.49
2.44
2.42
2.41
1.52
1.52
1.51
1.49
1.48
1.47
1.19
1.17
0.86
0.82
0.80
0.78
0.66
0.64
0.63
0.61
0.27
0.25
0.12
0.15
1.12
1.00
1.02
0.92
1.08
2.60
1.04
2.50
1.05
2.01
2.29
11.12
0.98
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

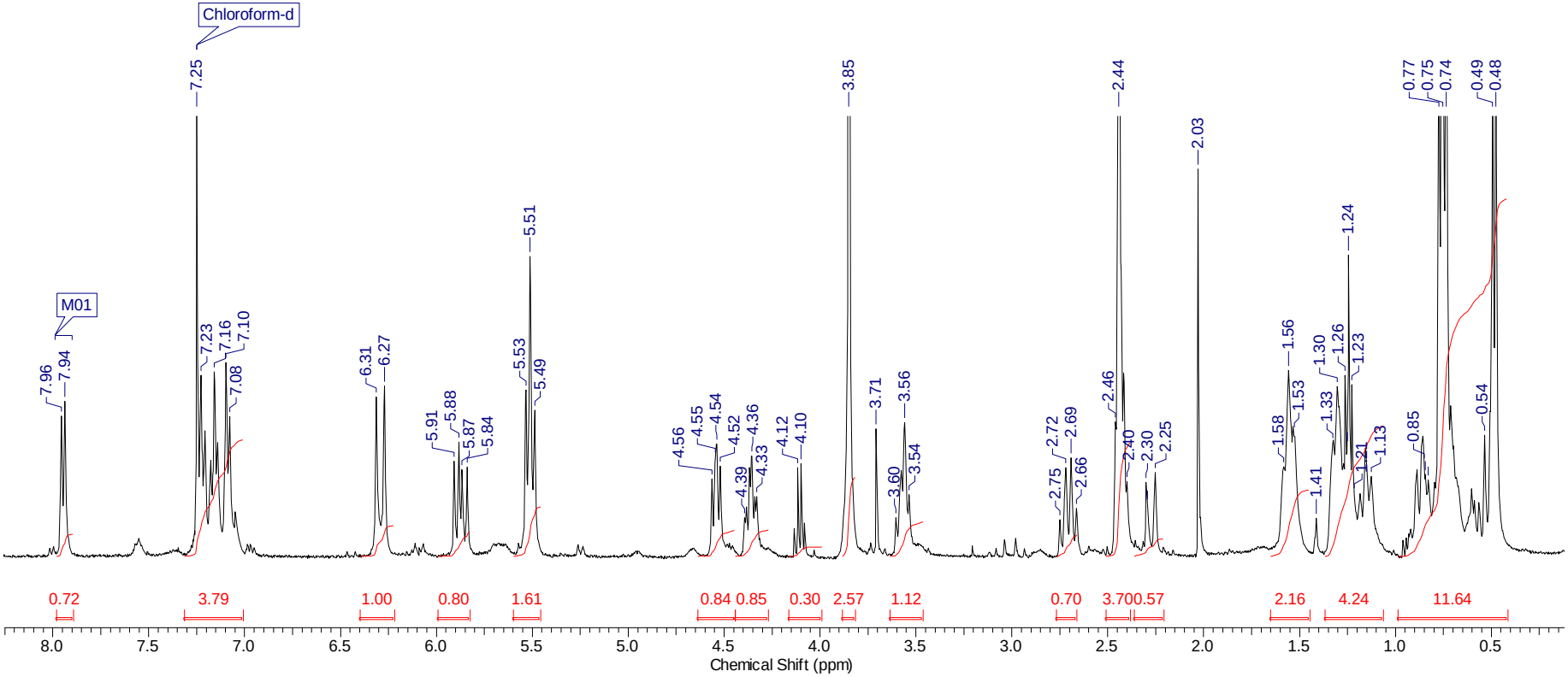

O
O
MeOOC
N
H
CF3

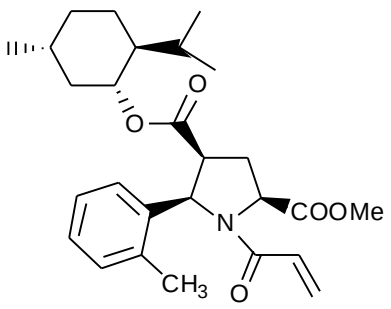
D-1b


173.38
172.11
132.05
128.98
127.53
125.53
77.32
77.00
Chloroform-d
74.14
60.35
59.45
52.21
48.55
46.50
39.35
33.90
33.38
30.89
26.19
23.31
21.73
20.63
16.36
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
Chemical Shift (ppm)

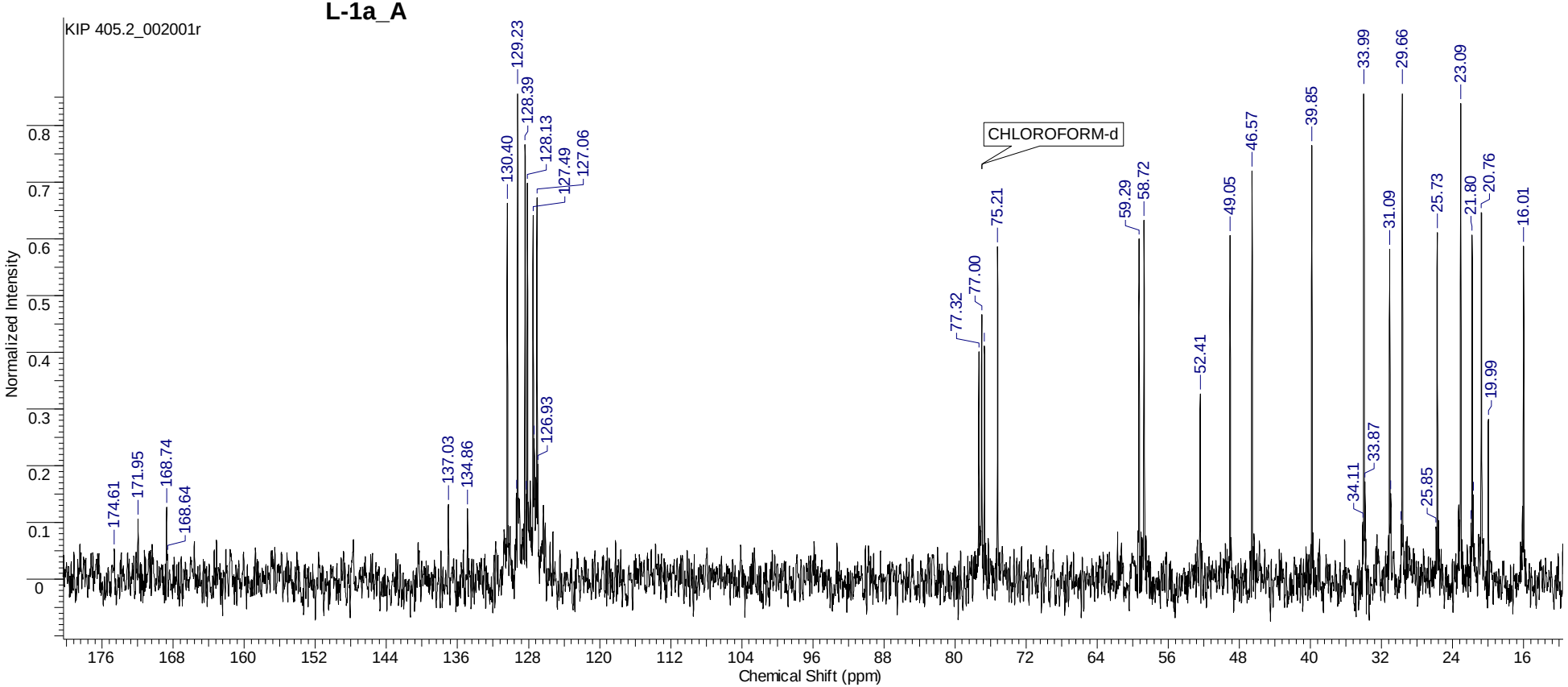

O
O
COOMe
N
CH3
O

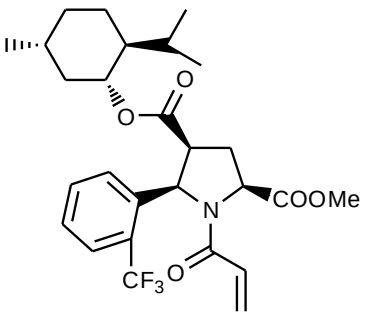
L-1a_A


Chloroform-d
M01
7.96
7.94
7.25
7.23
7.16
7.10
7.08
6.31
6.27
5.91
5.88
5.87
5.84
5.53
5.51
5.49
4.56
4.55
4.54
4.52
4.39
4.36
4.33
4.12
4.10
3.85
3.71
3.60
3.56
3.54
2.75
2.72
2.69
2.66
2.46
2.44
2.40
2.30
2.25
2.03
1.58
1.56
1.53
1.41
1.33
1.30
1.26
1.24
1.23
1.21
1.13
0.85
0.77
0.75
0.74
0.54
0.49
0.48
0.72
3.79
1.00
0.80
1.61
0.84
0.85
0.30
2.57
1.12
0.70
3.70
0.57
2.16
4.24
11.64
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

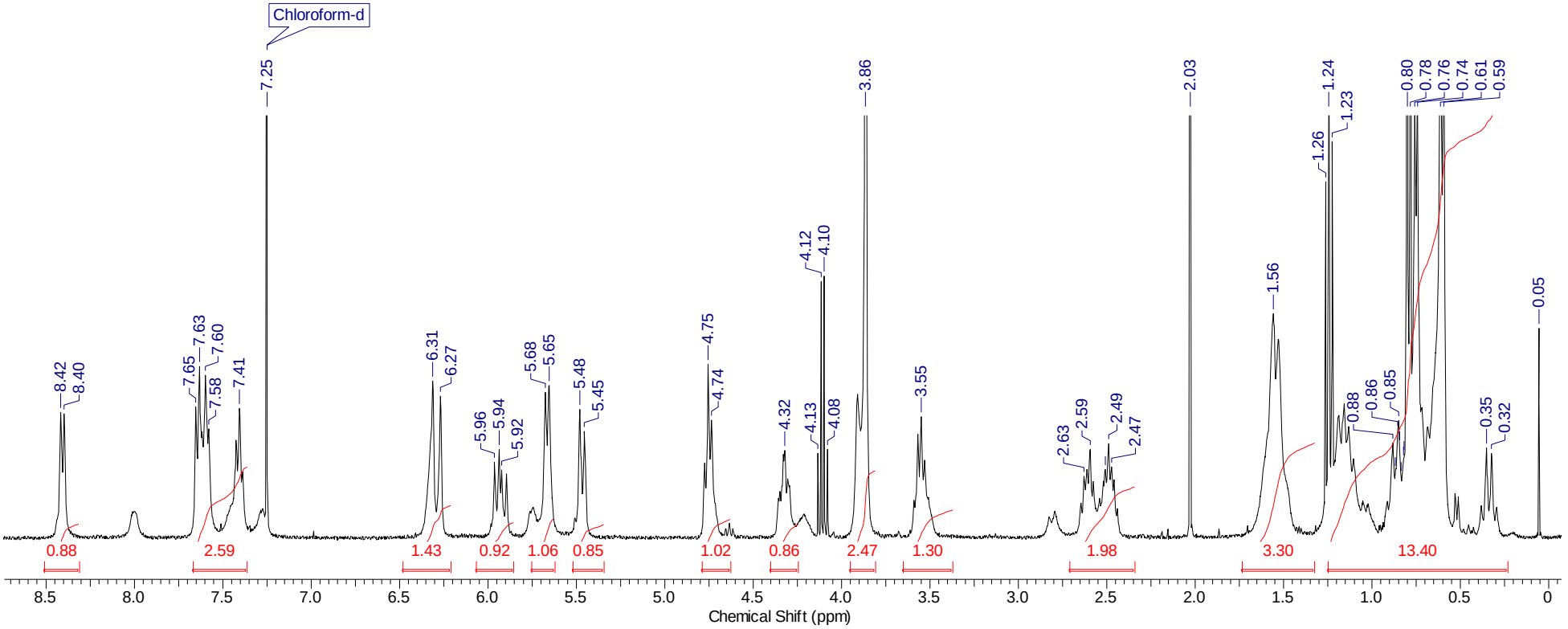

O
O
COOMe
N
CH3
O

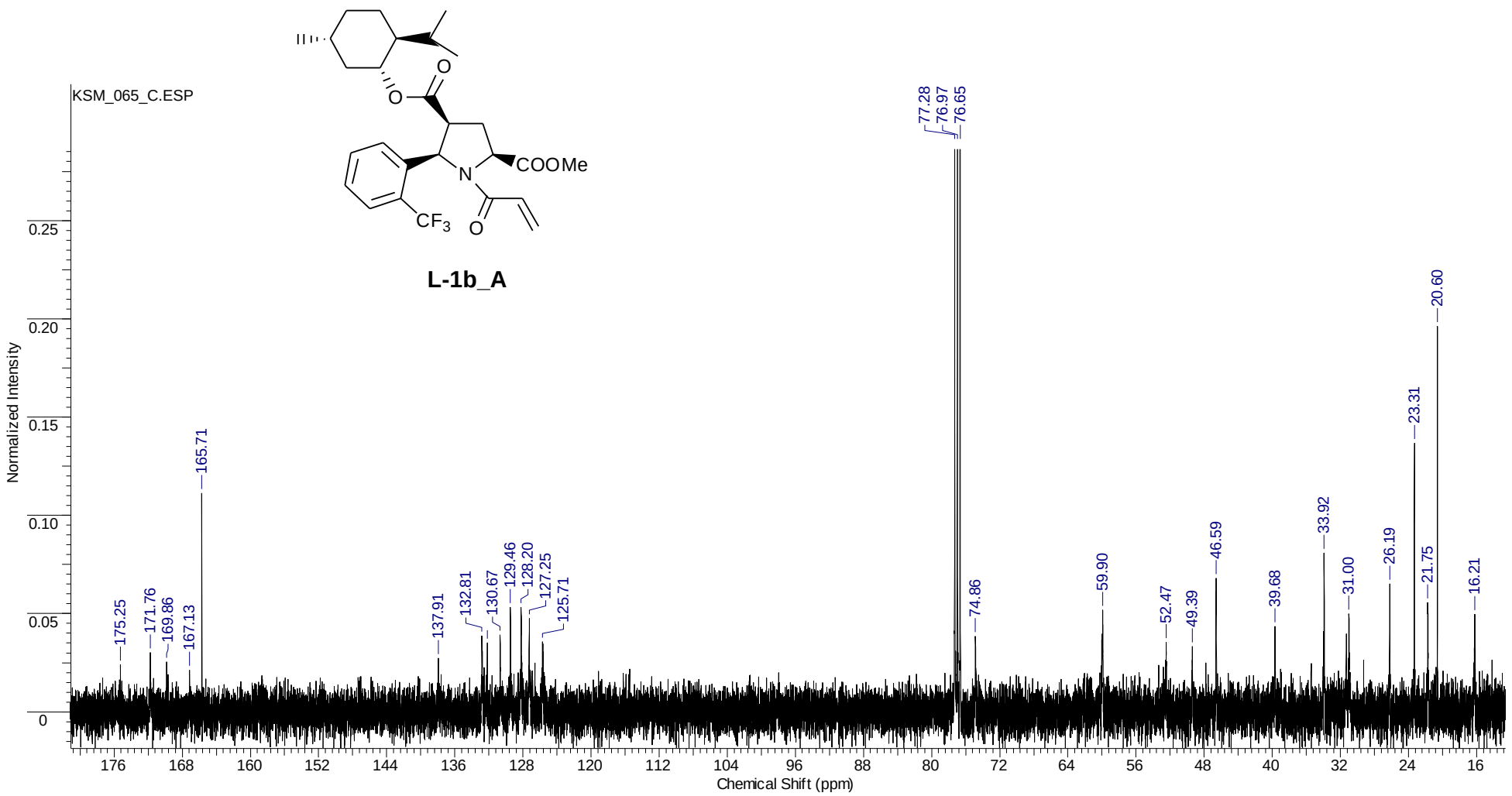
L-1a_A

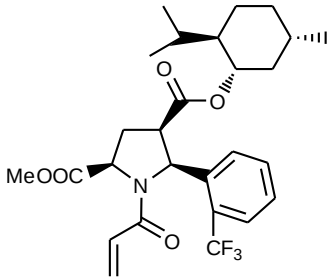

KIP 405.2_002001r
Normalized Intensity
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
174.61
171.95
168.74
168.64
137.03
134.86
130.40
129.23
128.39
128.13
127.49
127.06
126.93
77.32
77.00
75.21
CHLOROFORM-d
59.29
58.72
52.41
49.05
46.57
39.85
34.11
33.87
33.99
31.09
29.66
25.85
25.73
23.09
21.80
20.76
19.99
16.01
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
Chemical Shift (ppm)


O
O
COOMe
N
CF3
O

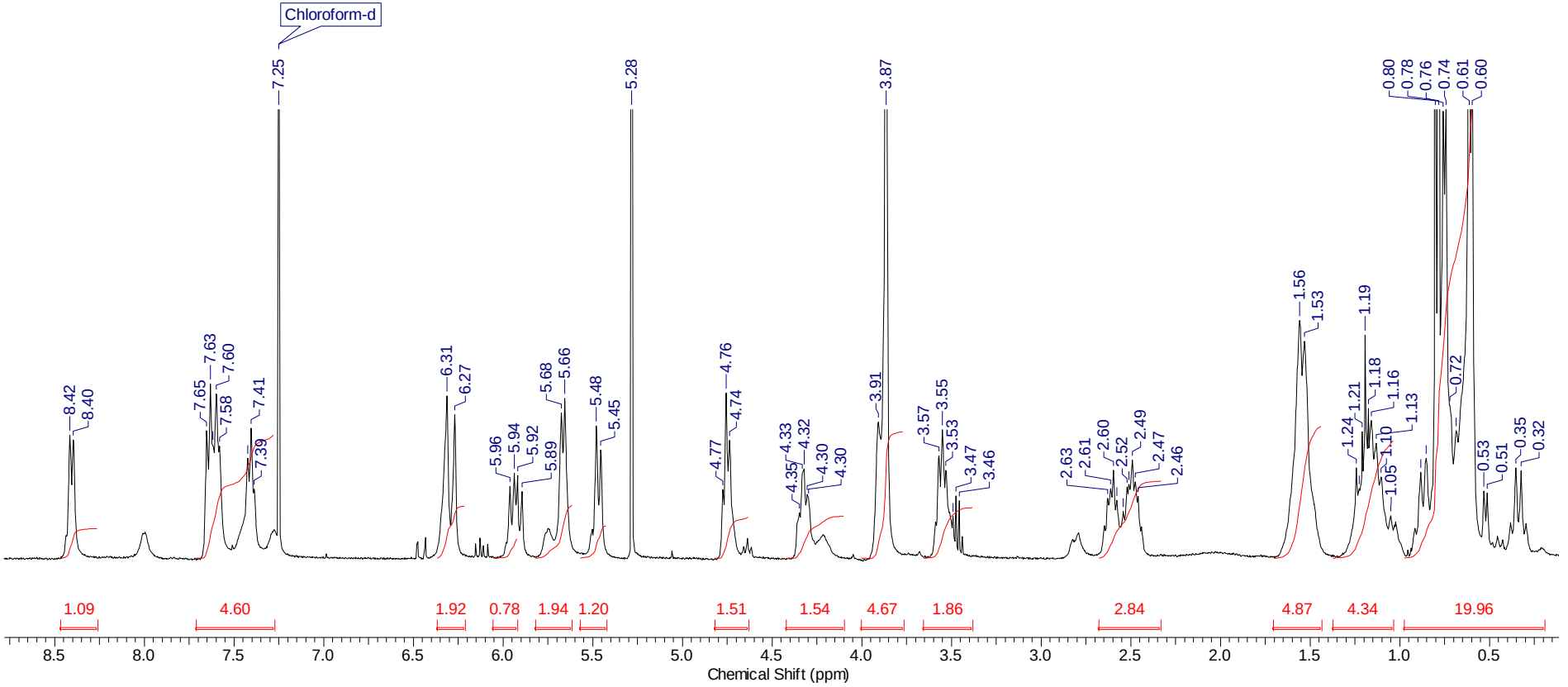
L-1b_A

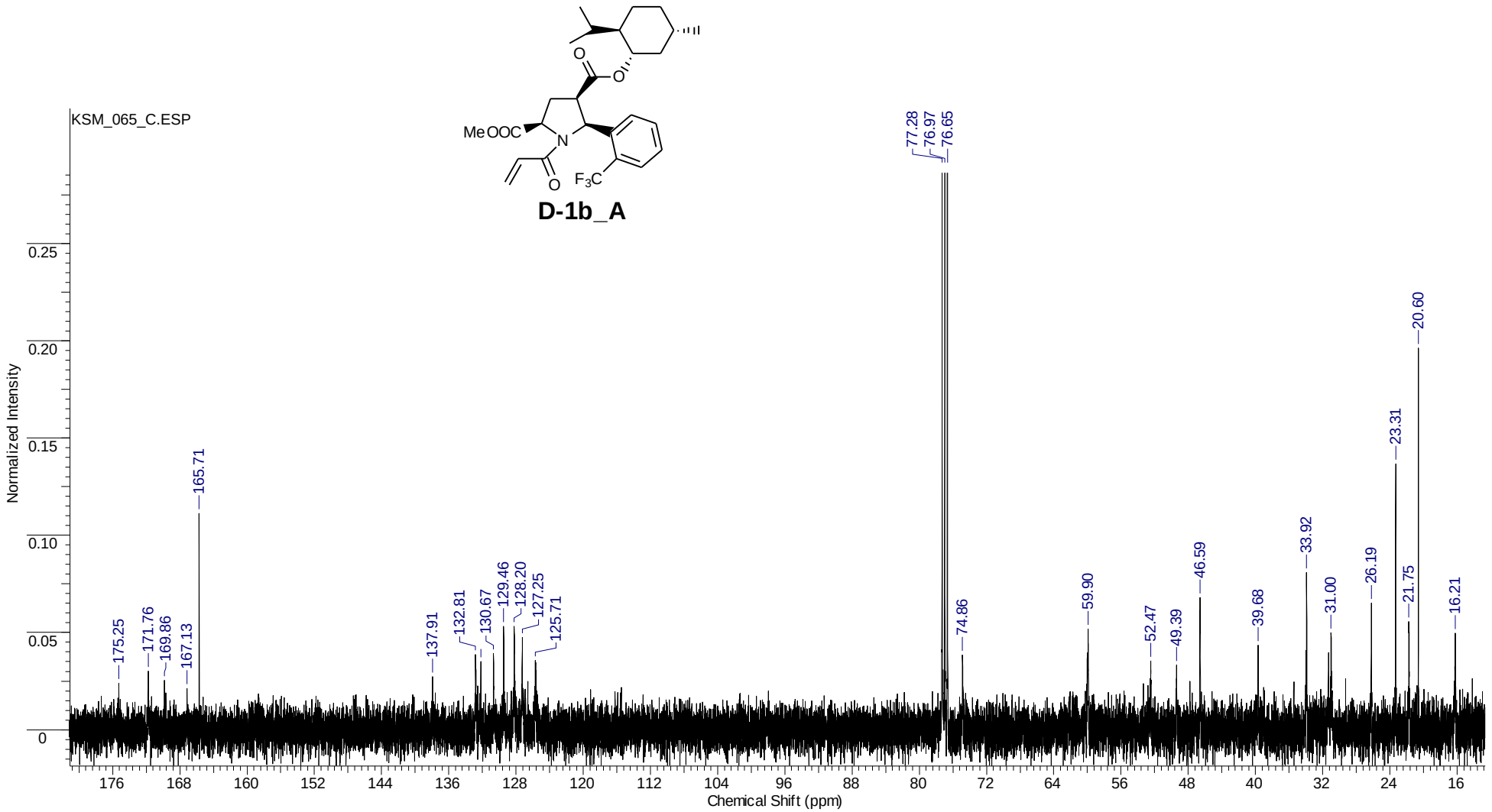

Chloroform-d
7.25
8.42
8.40
7.65
7.63
7.60
7.58
7.41
6.31
6.27
5.96
5.94
5.92
5.68
5.65
5.48
5.45
4.75
4.74
4.32
4.13
4.12
4.10
4.08
3.86
3.55
2.63
2.59
2.49
2.47
2.03
1.56
1.26
1.24
1.23
0.88
0.86
0.85
0.80
0.78
0.76
0.74
0.61
0.59
0.35
0.32
0.05
0.88
2.59
1.43
0.92
1.06
0.85
1.02
0.86
2.47
1.30
1.98
3.30
13.40
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

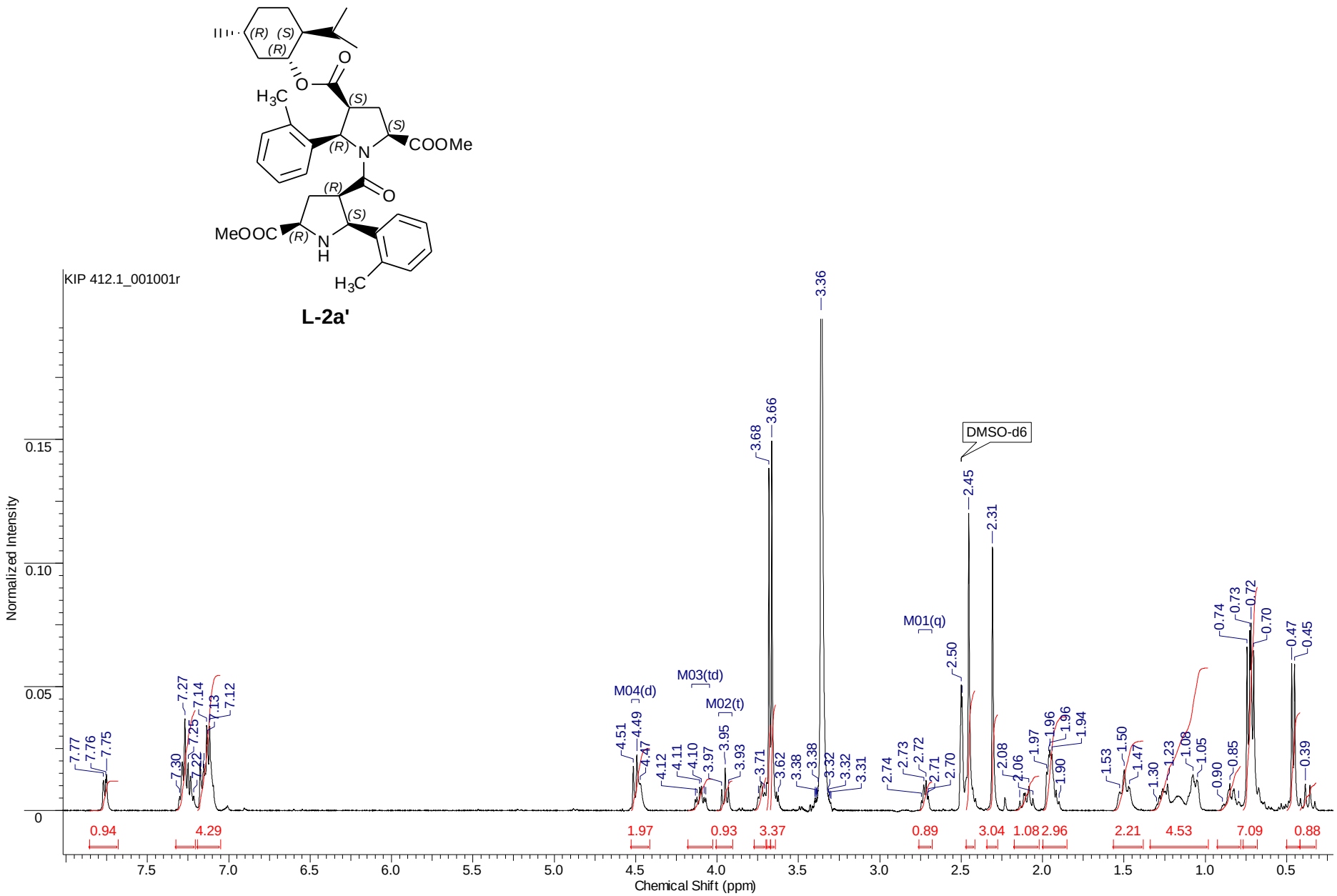

KSM_065_C.ESP
O
O
COOMe
N
CF3
O
L-1b_A
Normalized Intensity
0.25
0.20
0.15
0.10
0.05
0
175.25
171.76
169.86
167.13
165.71
137.91
132.81
130.67
129.46
128.20
127.25
125.71
77.28
76.97
76.65
74.86
59.90
52.47
49.39
46.59
39.68
33.92
31.00
26.19
23.31
21.75
20.60
16.21
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
Chemical Shift (ppm)

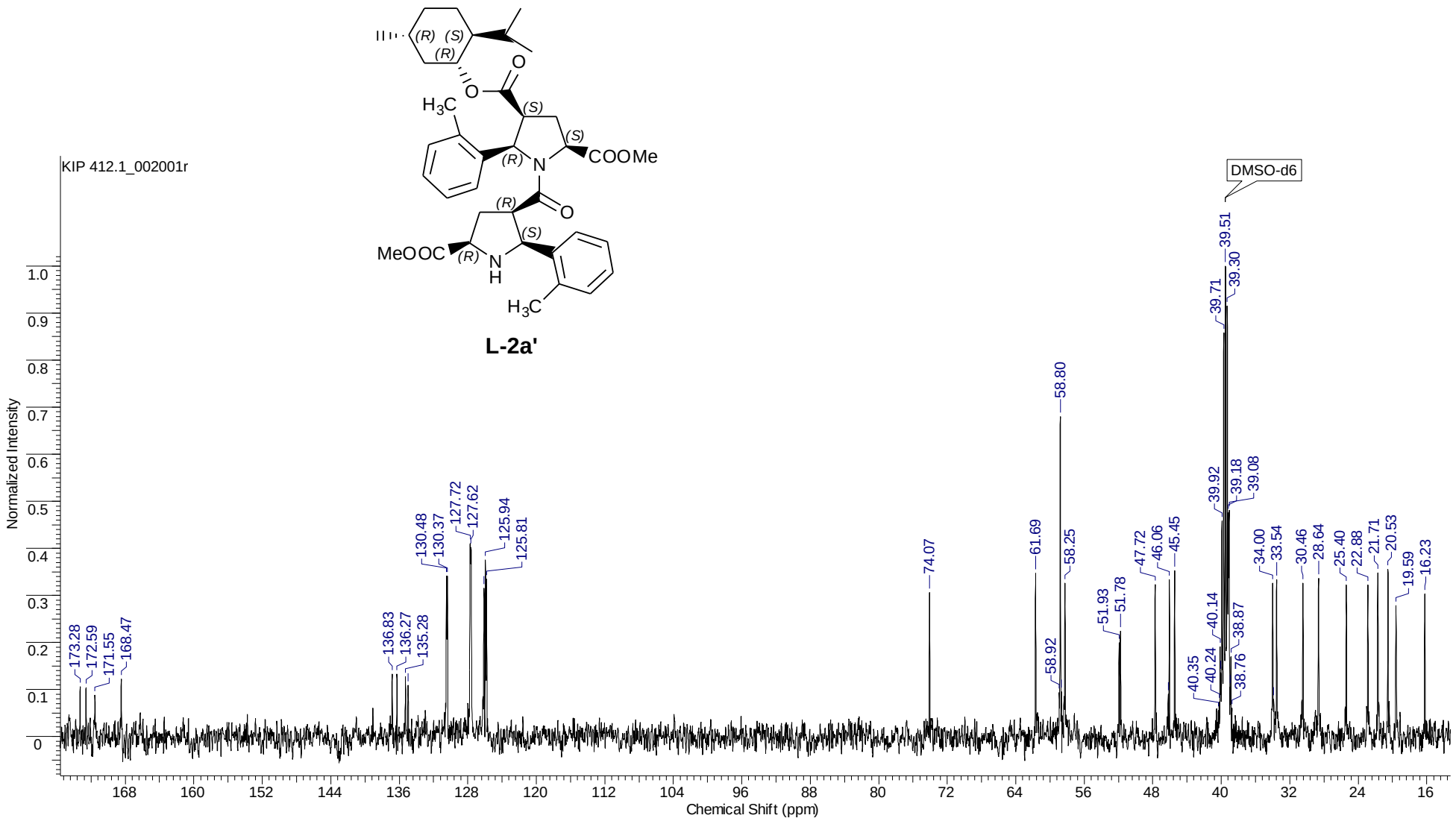

MeOOC
N
O
O
O
O
CF3

D-1b_A

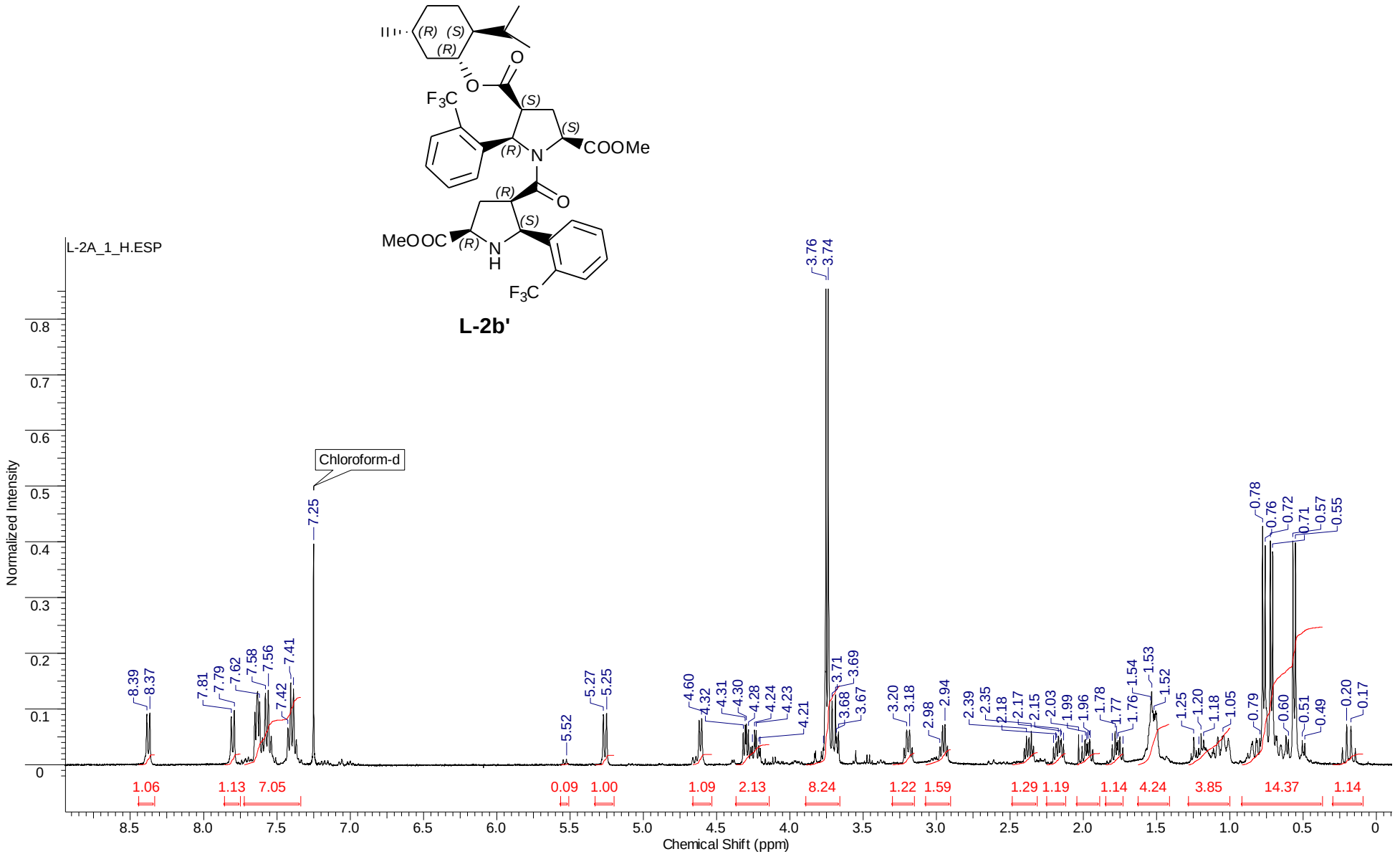

Chloroform-d
8.42
8.40
7.65
7.63
7.60
7.58
7.41
7.39
7.25
6.31
6.27
5.96
5.94
5.92
5.89
5.68
5.66
5.48
5.45
5.28
4.77
4.76
4.74
4.35
4.33
4.32
4.30
4.30
3.91
3.87
3.57
3.55
3.53
3.47
3.46
2.63
2.61
2.60
2.52
2.49
2.47
2.46
1.56
1.53
1.24
1.21
1.19
1.18
1.16
1.13
1.10
1.05
0.80
0.78
0.76
0.74
0.72
0.61
0.60
0.53
0.51
0.35
0.32
1.09
4.60
1.92
0.78
1.94
1.20
1.51
1.54
4.67
1.86
2.84
4.87
4.34
19.96
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

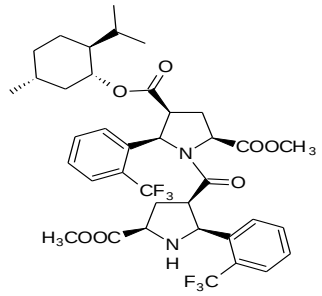

KSM_065_C.ESP
MeOOC
N
O
O
O
O
F3C
D-1b_A
Normalized Intensity
0.25
0.20
0.15
0.10
0.05
0
175.25
171.76
169.86
167.13
165.71
137.91
132.81
130.67
129.46
128.20
127.25
125.71
77.28
76.97
76.65
74.86
59.90
52.47
49.39
46.59
39.68
33.92
31.00
26.19
23.31
21.75
20.60
16.21
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
Chemical Shift (ppm)


KIP 412.1_001001r
L-2a'
Normalized Intensity
Chemical Shift (ppm)
DMSO-d6
M01(q)
M02(t)
M03(td)
M04(d)
0.94
4.29
1.97
0.93
3.37
0.89
3.04
1.08
2.96
2.21
4.53
7.09
0.88


KIP 412.1_002001r
DMSO-d6
Normalized Intensity
Chemical Shift (ppm)
173.28
172.59
171.55
168.47
136.83
136.27
135.28
130.48
130.37
127.72
127.62
125.94
125.81
74.07
61.69
58.80
58.92
58.25
51.93
51.78
47.72
46.06
45.45
40.35
40.24
40.14
39.92
39.71
39.51
39.30
39.18
39.08
38.87
38.76
34.00
33.54
30.46
28.64
25.40
22.88
21.71
20.53
19.59
16.23

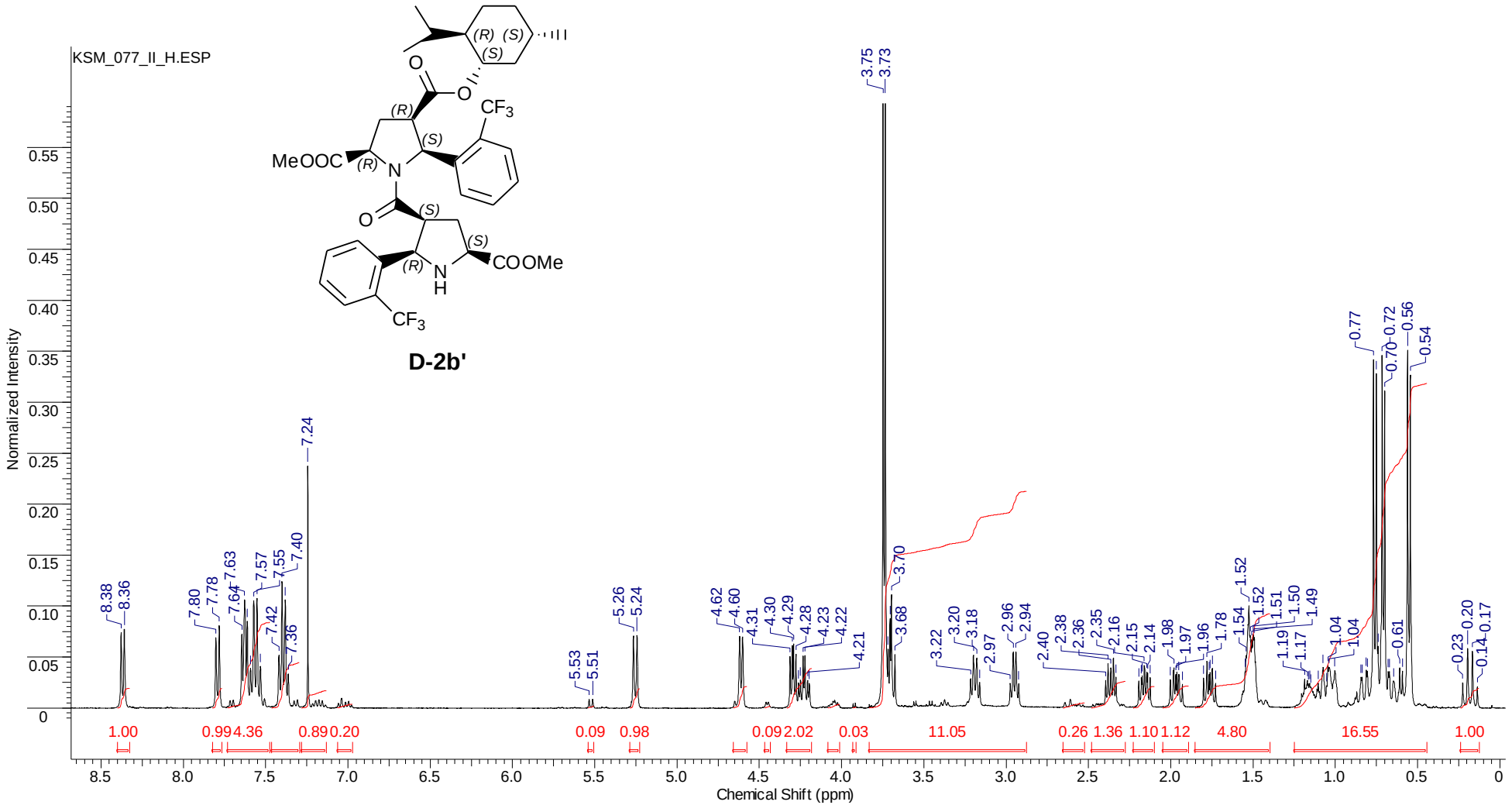
L-2a'

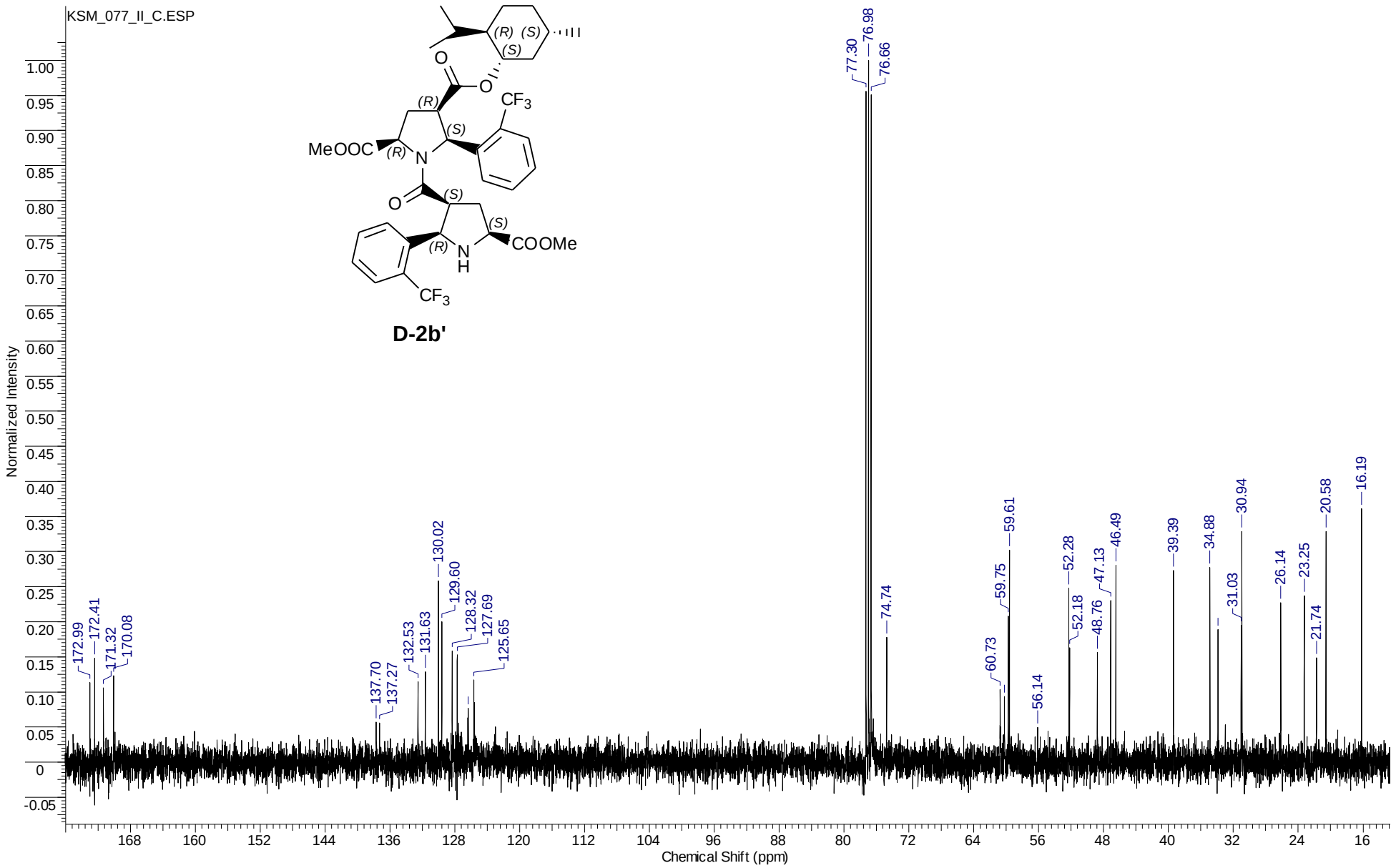

L-2A_1_H.ESP
Chloroform-d
Normalized Intensity
Chemical Shift (ppm)
L-2b'

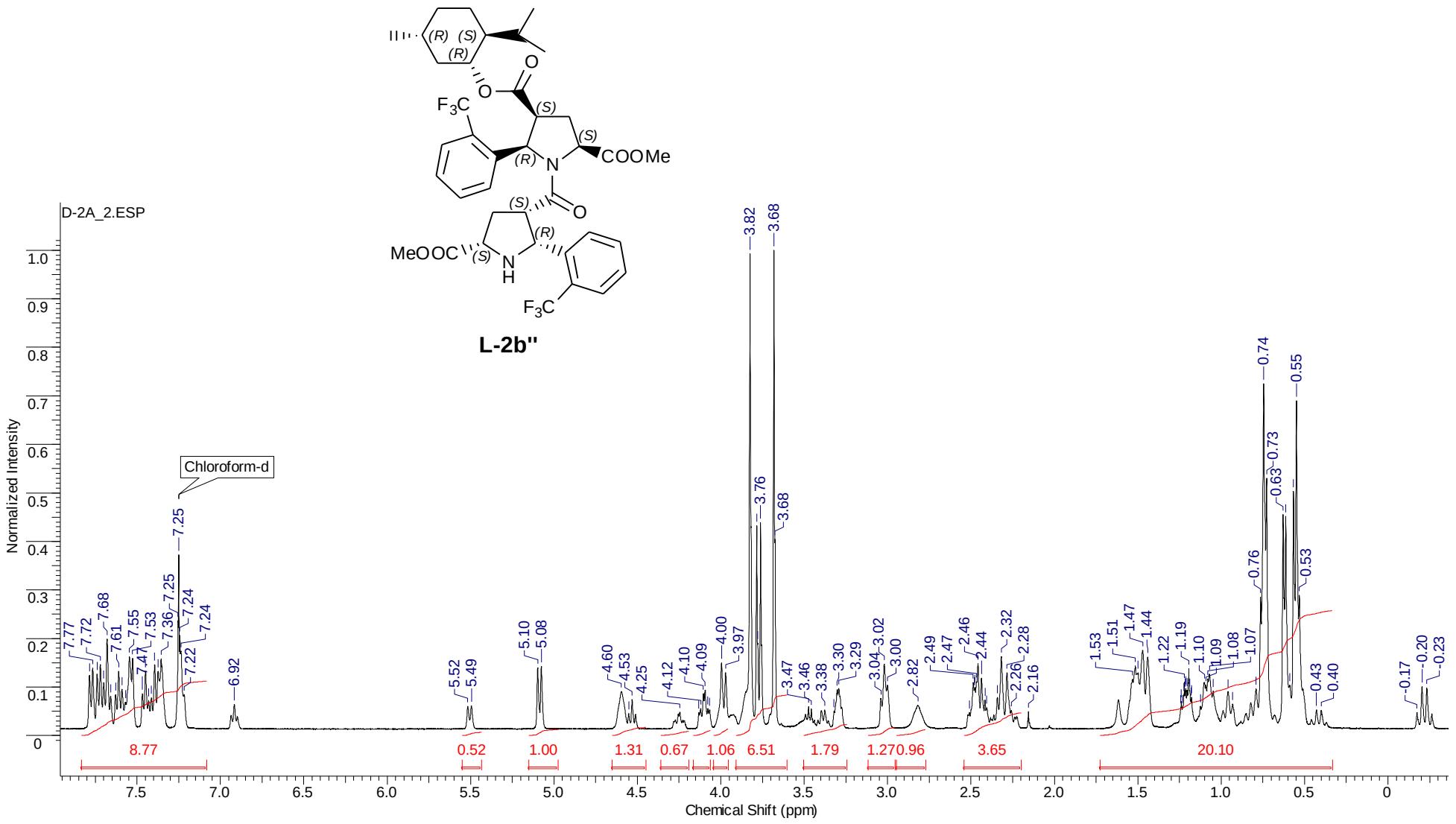

O
O
COOCH3
N
CF3
O
H3COOC
N
H
F3C

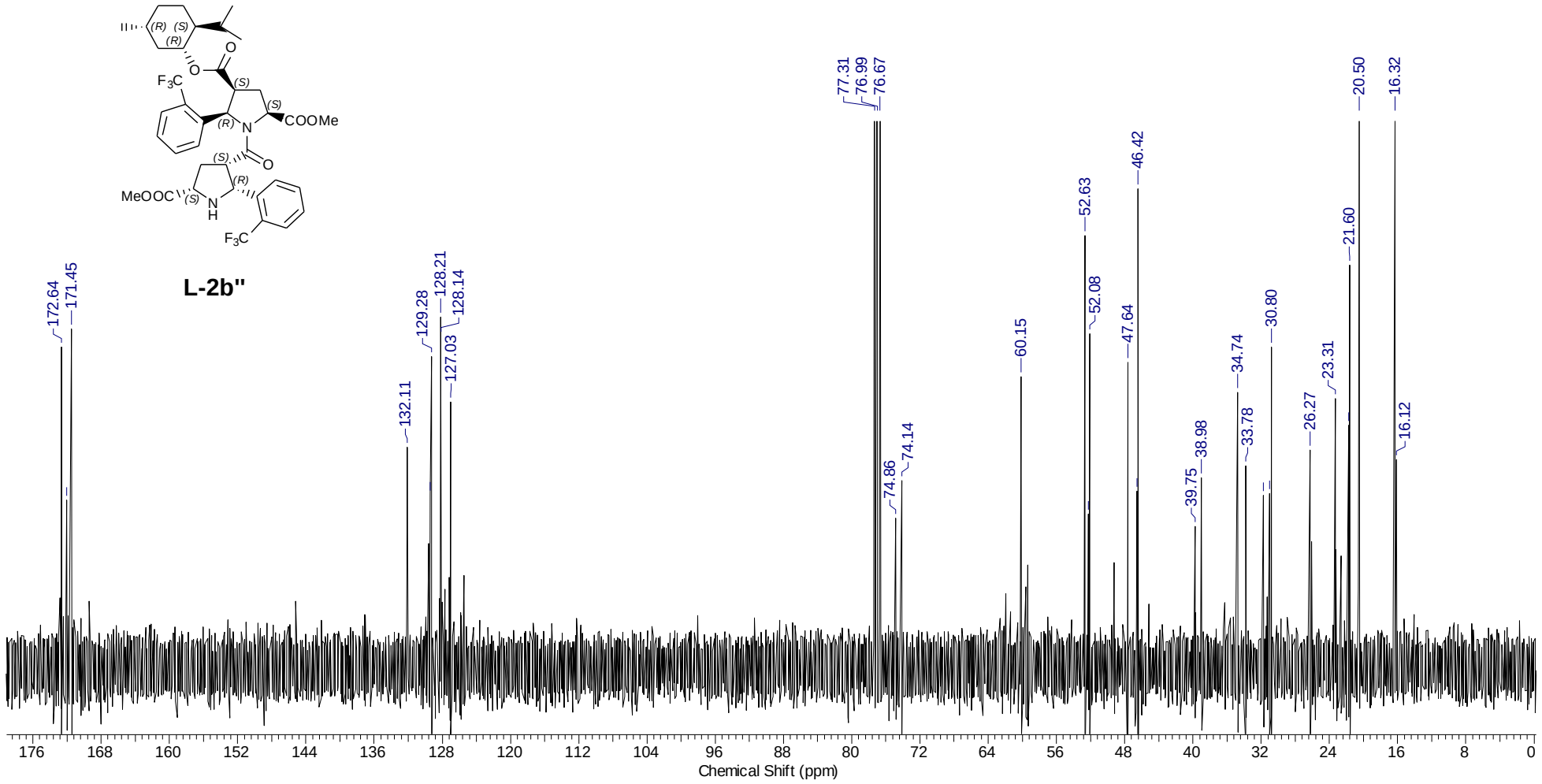
L-2b'

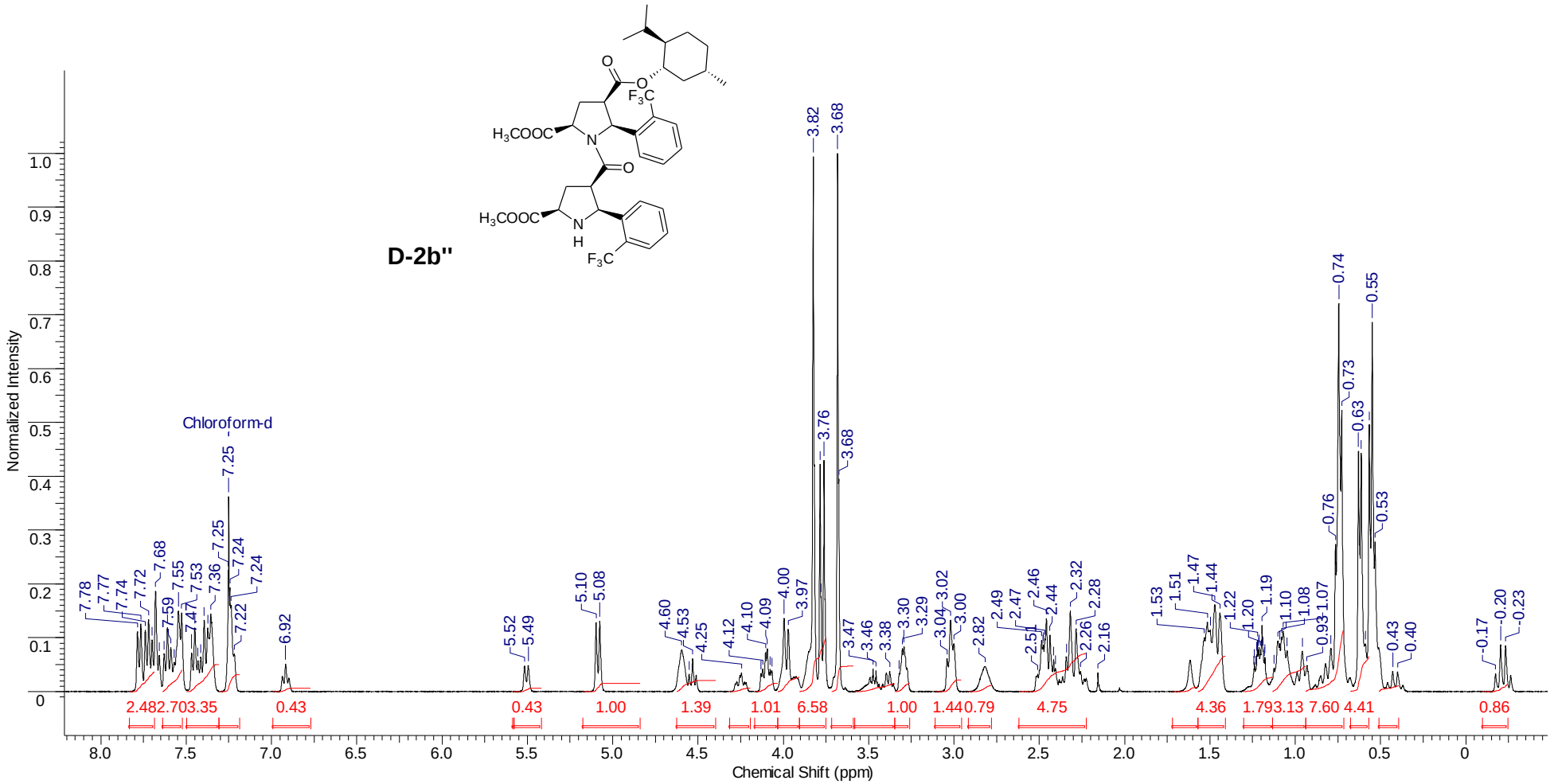
77.30
76.98
76.66
172.99
172.41
171.32
170.08
137.70
137.27
132.53
131.63
130.02
129.60
128.32
127.69
125.65
74.74
60.73
59.75
59.61
56.14
52.28
48.76
47.13
46.49
39.39
34.88
33.88
30.94
26.14
23.25
21.74
20.58
16.19
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
Chemical Shift (ppm)

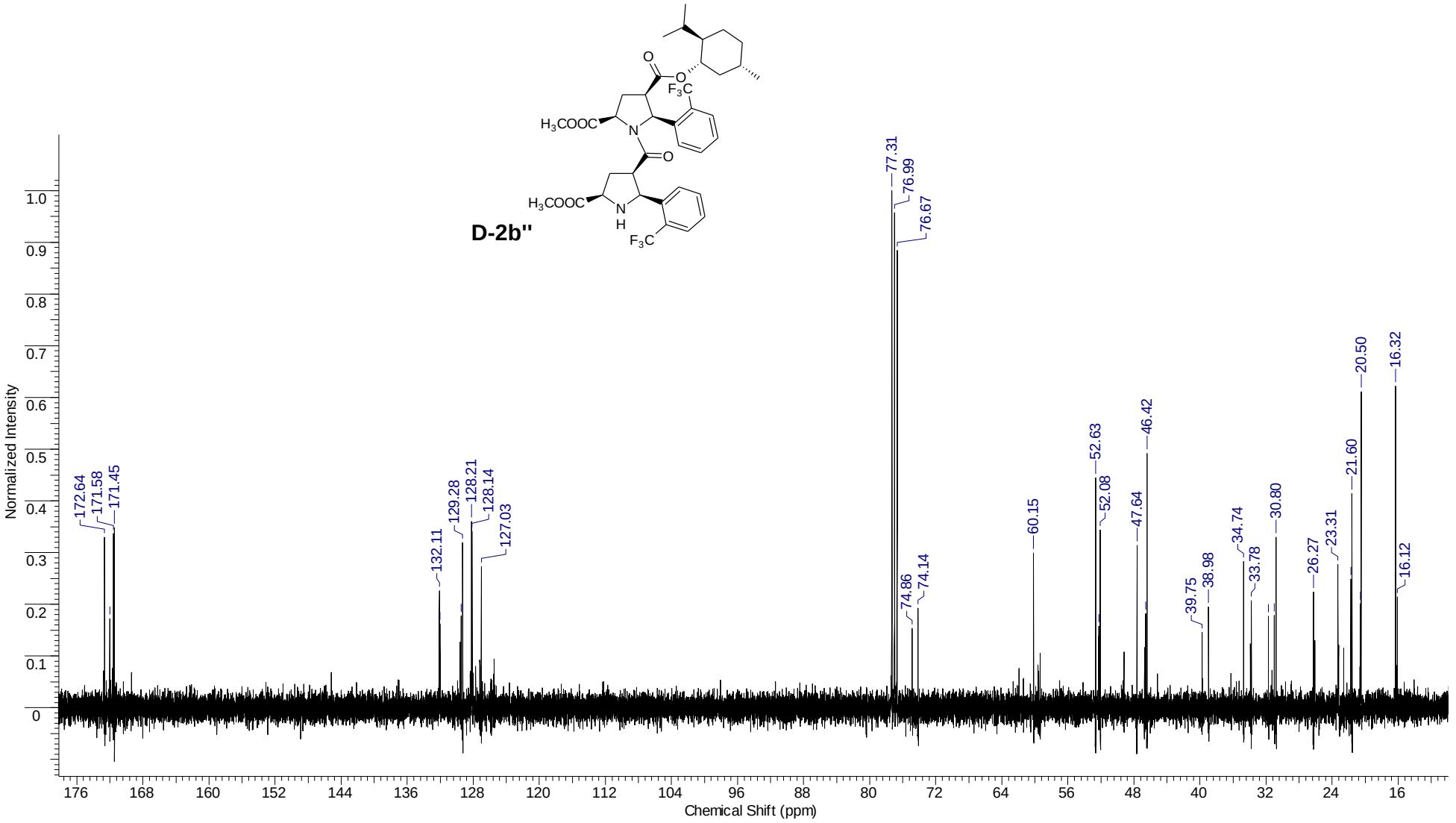

KSM_077_II_H.ESP
D-2b'
Normalized Intensity
Chemical Shift (ppm)

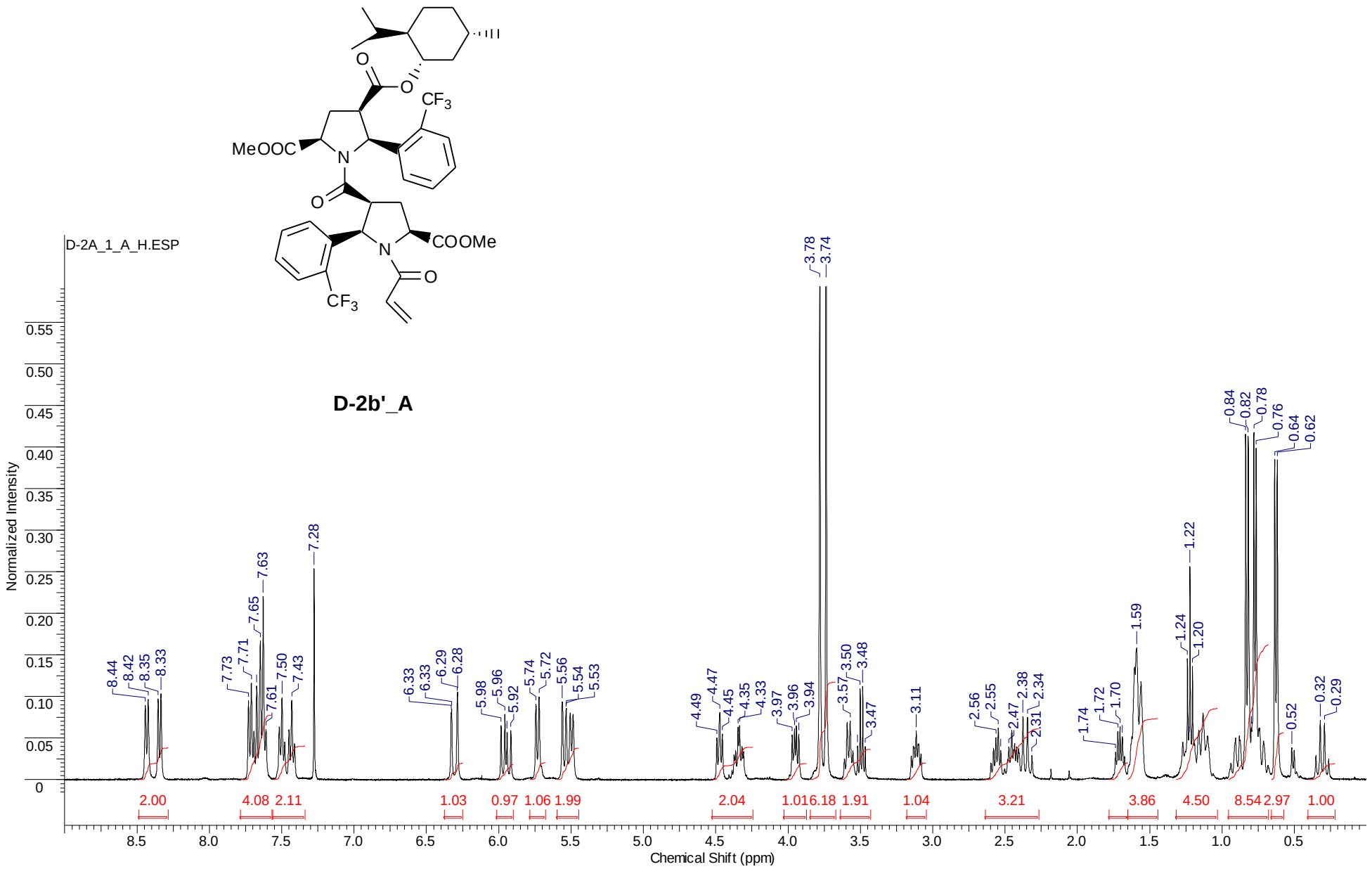

KSM_077_II_C.ESP
Normalized Intensity
Chemical Shift (ppm)
MeOOC
COOMe
CF3
CF3
D-2b'
172.99
172.41
171.32
170.08
137.70
137.27
132.53
131.63
130.02
129.60
128.32
127.69
125.65
77.30
76.98
76.66
74.74
60.73
59.75
59.61
56.14
52.28
52.18
48.76
47.13
46.49
39.39
34.88
31.03
30.94
26.14
23.25
21.74
20.58
16.19

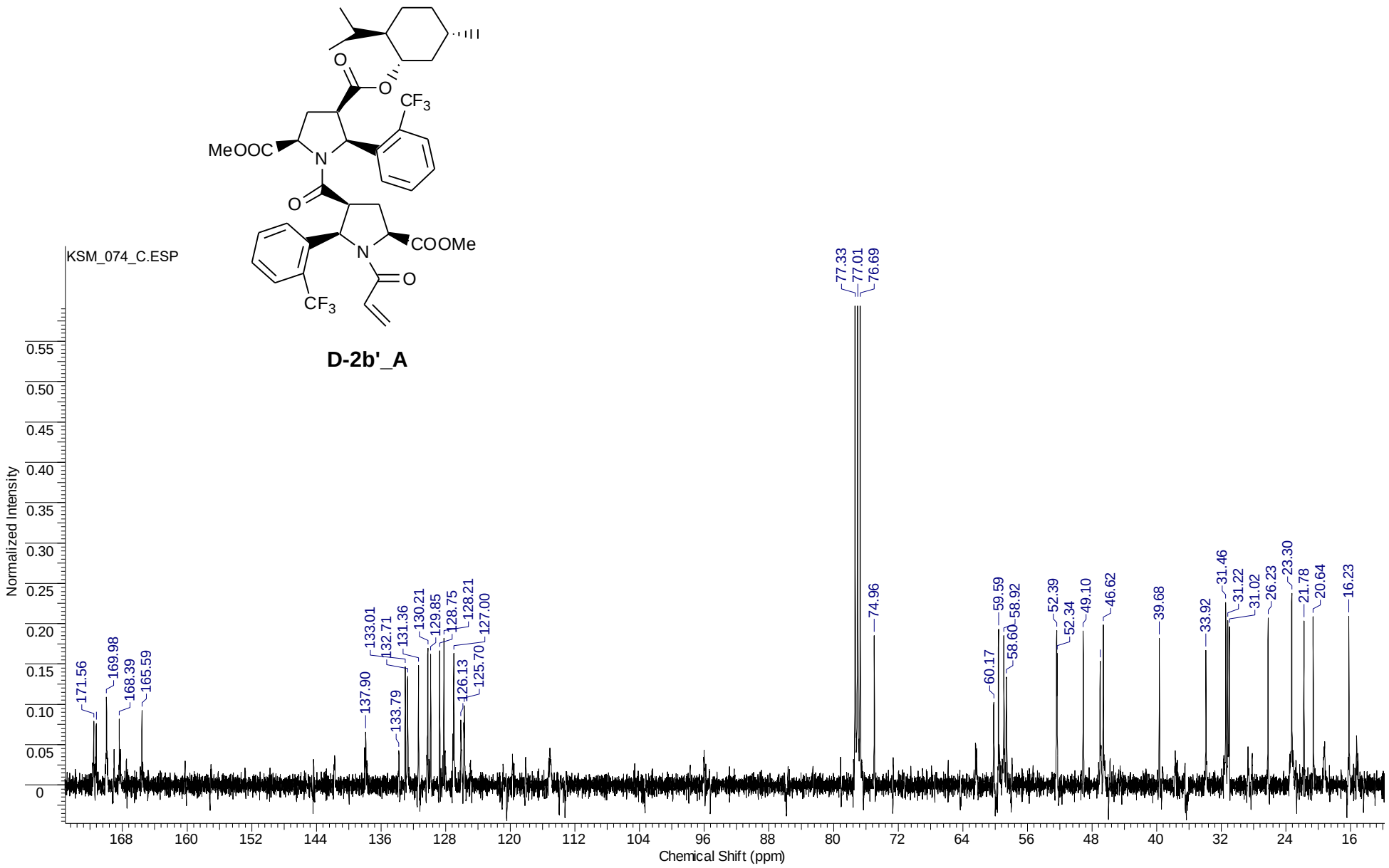

D-2A_2.ESP
Chloroform-d
Normalized Intensity
Chemical Shift (ppm)
L-2b''

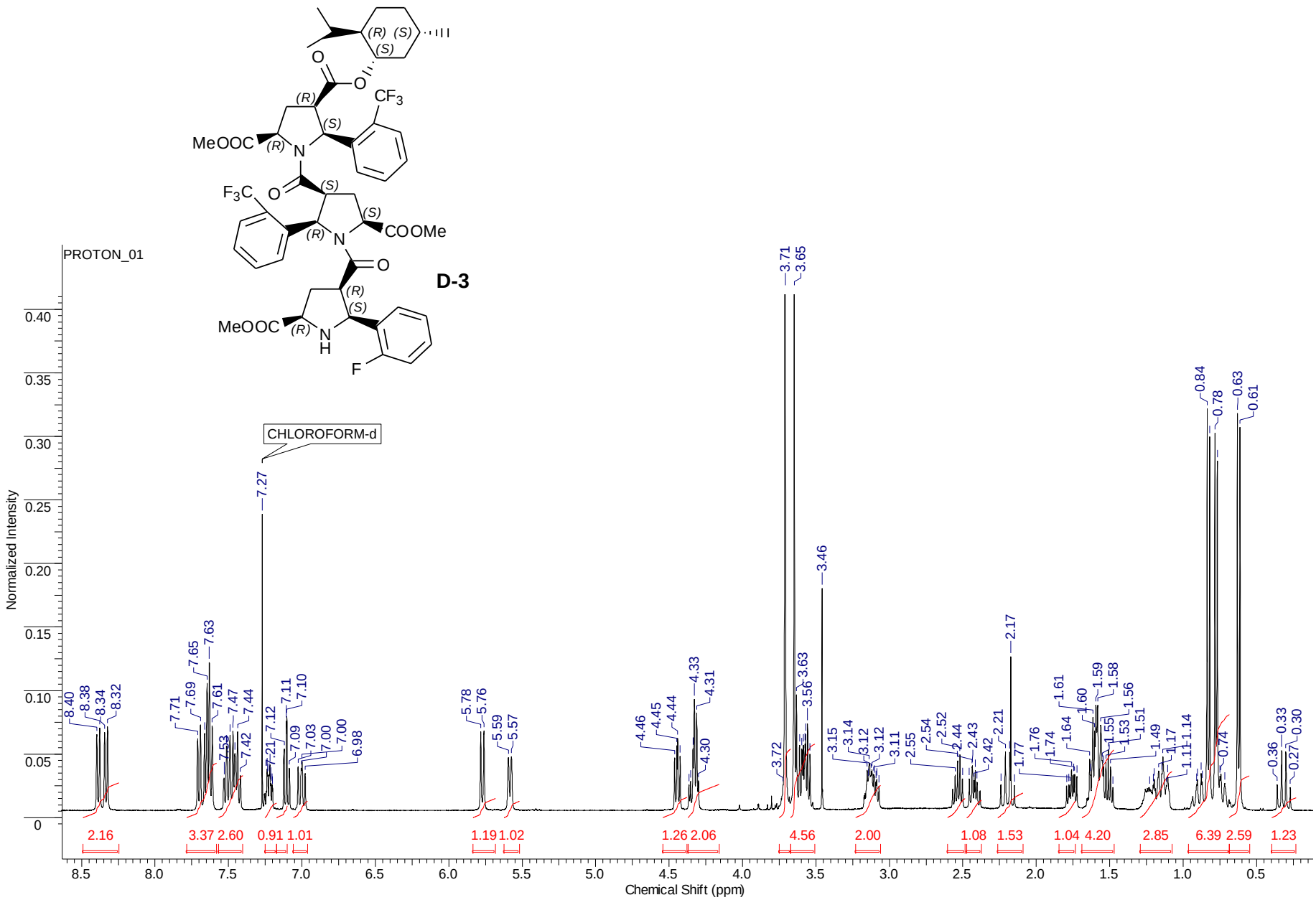

L-2b''
172.64
171.45
132.11
129.28
128.21
128.14
127.03
77.31
76.99
76.67
74.86
74.14
60.15
52.63
52.08
47.64
46.42
39.75
38.98
34.74
33.78
30.80
26.27
23.31
21.60
20.50
16.32
16.12
Chemical Shift (ppm)

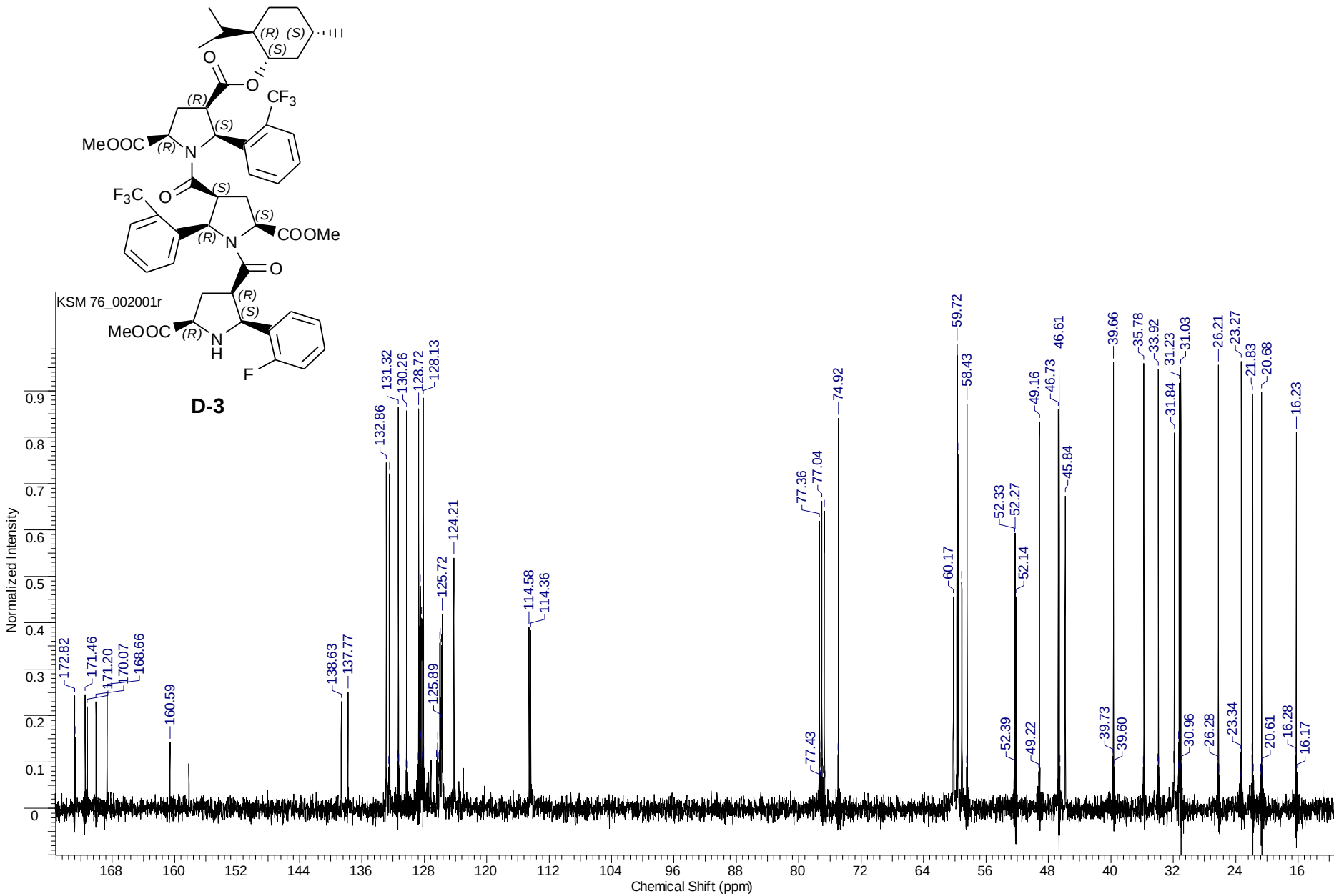

D-2b''
Chloroform-d
Normalized Intensity
Chemical Shift (ppm)


D-2b''
Normalized Intensity
Chemical Shift (ppm)
172.64
171.58
171.45
132.11
129.28
128.21
128.14
127.03
77.31
76.99
76.67
74.86
74.14
60.15
52.63
52.08
47.64
46.42
39.75
38.98
34.74
33.78
30.80
26.27
23.31
21.60
20.50
16.32
16.12


D-2A_1_A_H.ESP
MeOOC
COOMe
CF3
CF3
O
O
N
N
O
O
O
D-2b'_A
Normalized Intensity
Chemical Shift (ppm)
8.44
8.42
8.35
8.33
7.73
7.71
7.65
7.63
7.61
7.50
7.43
7.28
6.33
6.33
6.29
6.28
5.98
5.96
5.92
5.74
5.72
5.56
5.54
5.53
4.49
4.47
4.45
4.35
4.33
3.97
3.96
3.94
3.78
3.74
3.57
3.50
3.48
3.47
3.11
2.56
2.55
2.47
2.38
2.34
2.31
1.74
1.72
1.70
1.59
1.24
1.22
1.20
0.84
0.82
0.78
0.76
0.64
0.62
0.52
0.32
0.29
2.00
4.08
2.11
1.03
0.97
1.06
1.99
2.04
1.01
6.18
1.91
1.04
3.21
3.86
4.50
8.54
2.97
1.00


KSM_074_C.ESP
MeOOC
COOMe
CF3
CF3
D-2b'_A
Normalized Intensity
Chemical Shift (ppm)
171.56
169.98
168.39
165.59
137.90
133.79
133.01
132.71
131.36
130.21
129.85
128.75
128.21
127.00
126.13
125.70
77.33
77.01
76.69
74.96
60.17
59.59
58.60
58.92
52.39
52.34
49.10
46.62
39.68
33.92
31.46
31.22
31.02
26.23
23.30
21.78
20.64
16.23


PROTON_01
D-3
CHLOROFORM-d
Normalized Intensity
Chemical Shift (ppm)
2.16
3.37 2.60
0.91 1.01
1.19 1.02
1.26 2.06
4.56
2.00
1.08
1.53
1.04 4.20
2.85
6.39 2.59
1.23


KSM 76_002001r
D-3
Normalized Intensity
Chemical Shift (ppm)
172.82
171.46
171.20
170.07
168.66
160.59
138.63
137.77
132.86
131.32
130.26
128.72
128.13
125.89
125.72
124.21
114.58
114.36
77.43
77.36
77.04
74.92
60.17
59.72
58.43
52.39
52.33
52.27
52.14
49.22
49.16
46.73
46.61
45.84
39.73
39.66
39.60
35.78
33.92
31.84
31.23
31.03
30.96
26.28
26.21
23.34
23.27
21.83
20.68
20.61
16.28
16.23
16.17