

An approach toward 17-arylsubstituted marginatafuran-type isospongian diterpenoids *via* a palladium-catalyzed Heck–Suzuki cascade reaction of 16-bromolambertianic acid

Yurii V. Kharitonov^a and Elvira E. Shults^{*a}

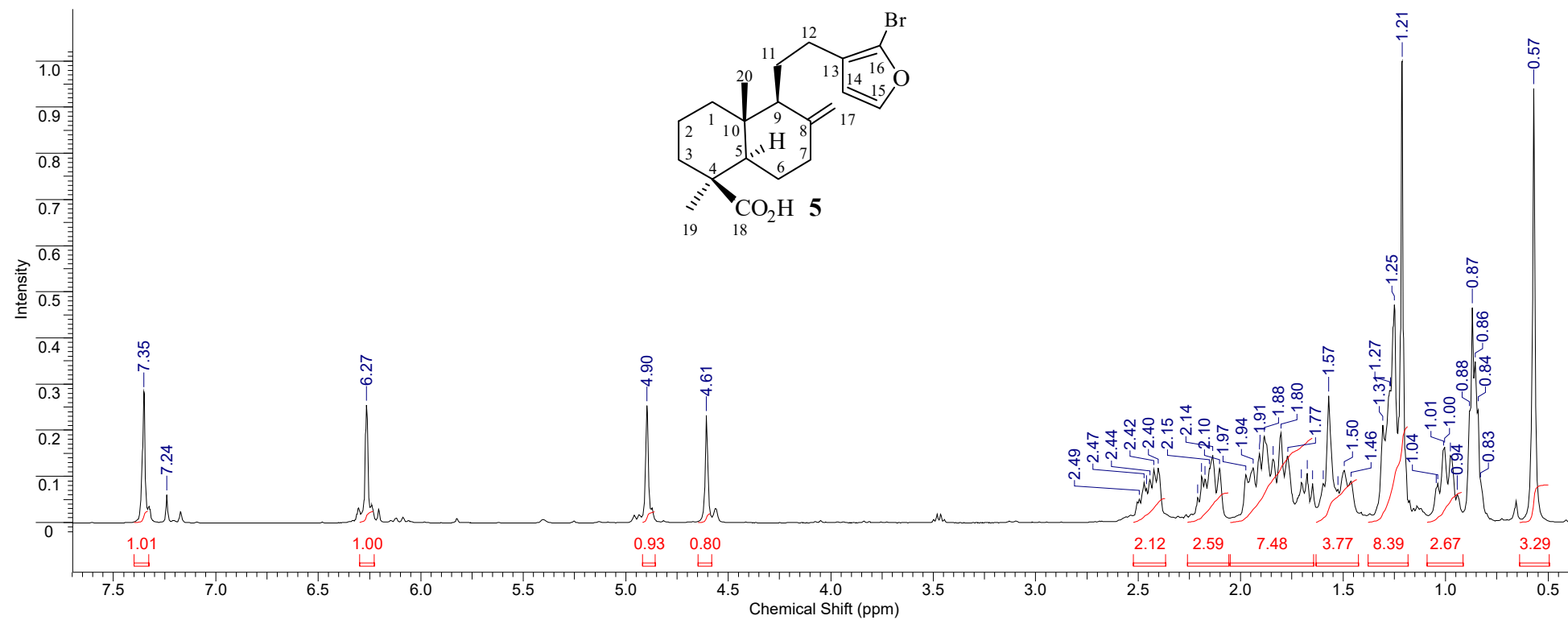
^aLaboratory of Medicinal Chemistry, Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, Lavrentyev Ave, 9, 630090 Novosibirsk, Russia;

E-mail: schultz@nioch.nsc.ru

Supporting Information

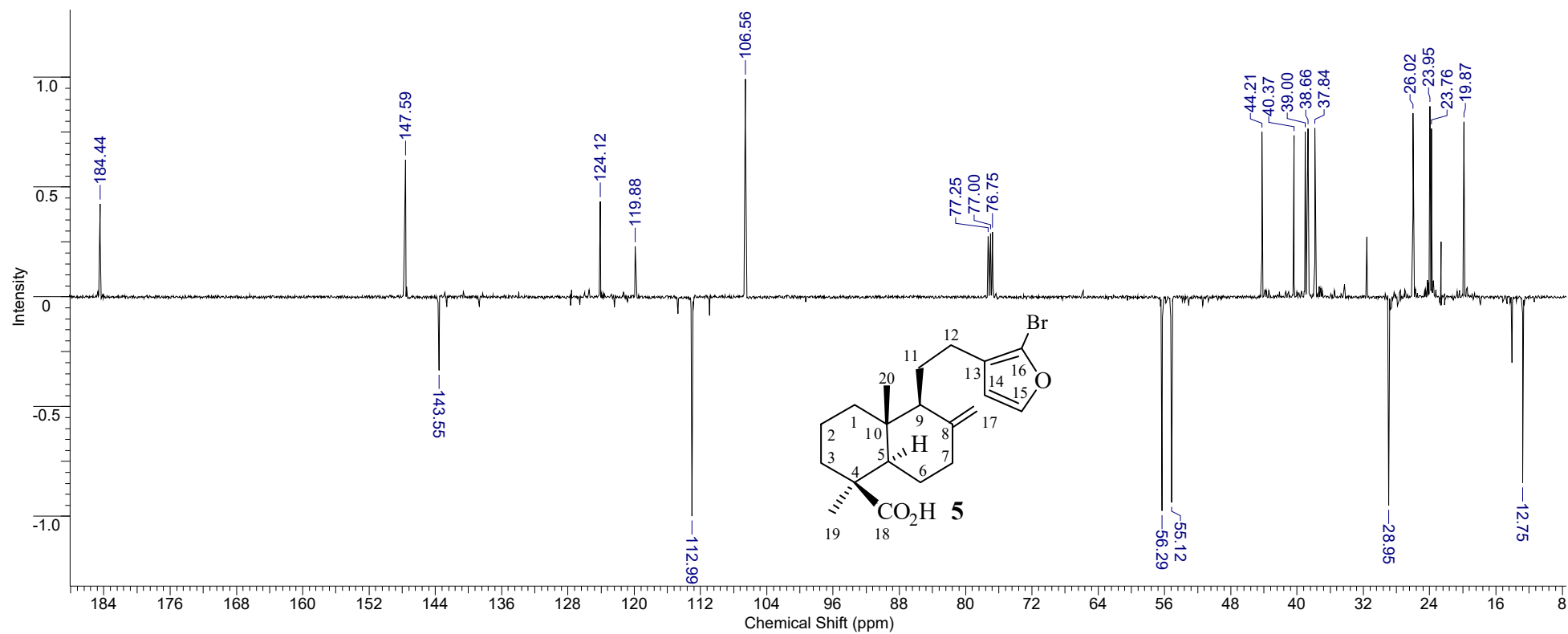
Figures S1-S46 NMR ¹H and ¹³C spectra of compounds **5**, **7a-j**, **8b,c,d,j**, **9-12**, **13a-c**, **14a**.

(1*S*,4*aR*,5*S*,8*aR*)-5-(2-(2-bromofuran-3-yl)ethyl)-1,4*a*-dimethyl-6-methylenedecahydronaphthalene-1-carboxylic acid (5**)** (¹H NMR, 400 MHz, CDCl₃)

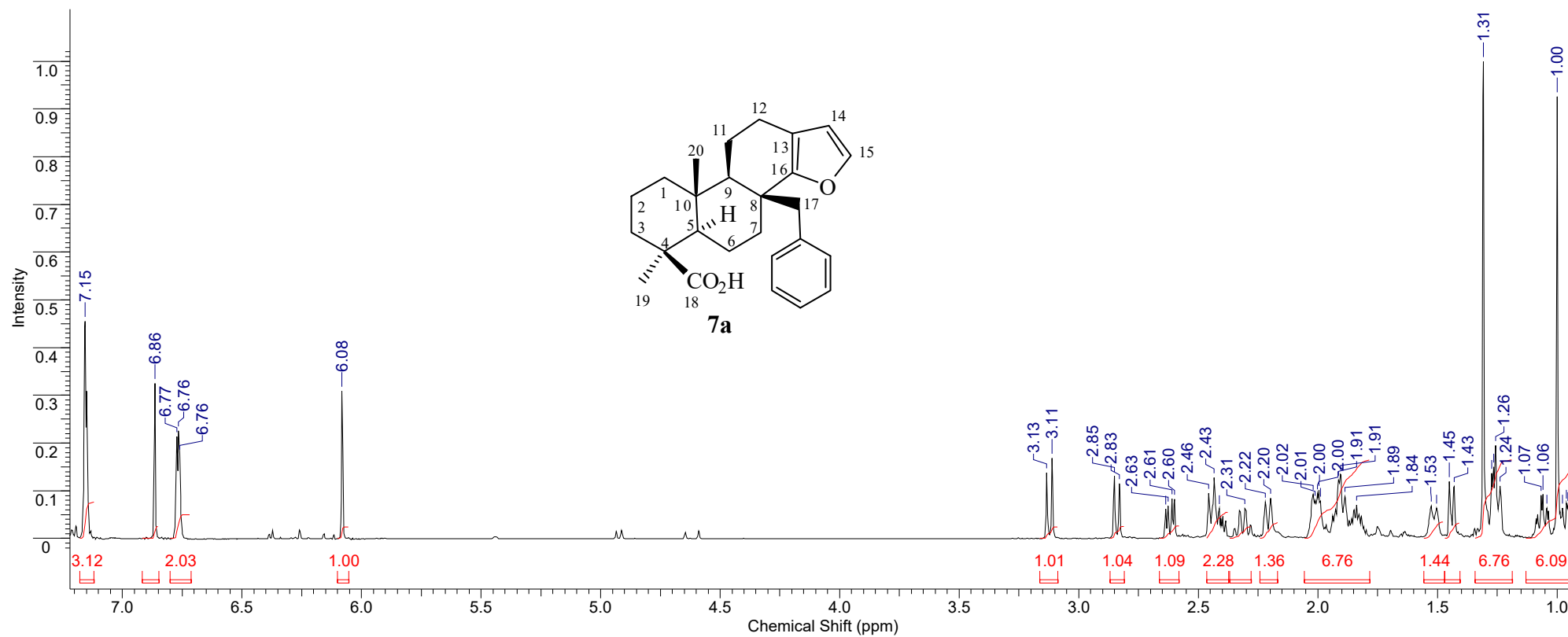


(1S,4aR,5S,8aR)-5-(2-(2-bromofuran-3-yl)ethyl)-1,4a-dimethyl-6-methylenedecahydronaphthalene-1-carboxylic acid (5).

(¹³C NMR, 126 MHz, CDCl₃)

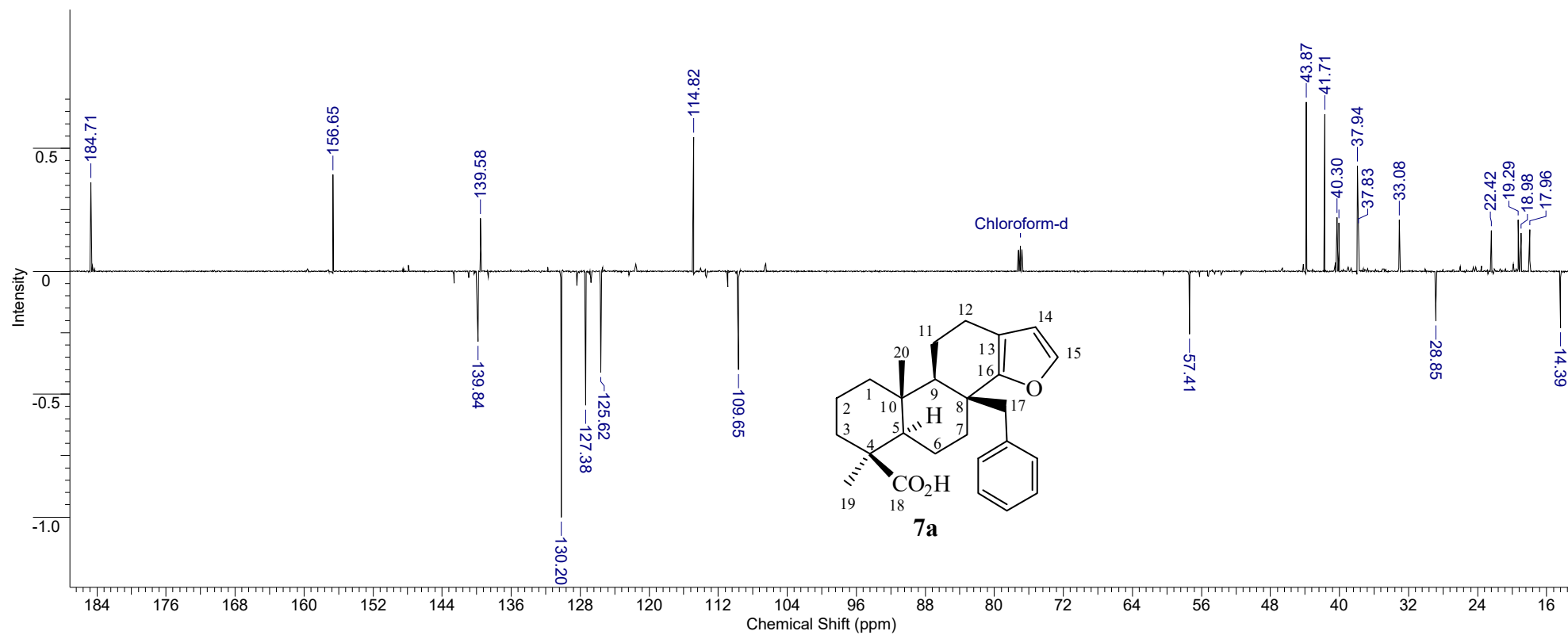


(3*b*S,5*a*R,6*S*,9*a*R,9*b*R)-3*b*-benzyl-6,9*a*-dimethyl-3*b*,4,5,5*a*,6,7,8,9,9*a*,9*b*,10,11-dodecahydrophenanthro[1,2-*b*]furan-6-carboxylic acid (7a**)** (^1H NMR, 600 MHz, CDCl_3)



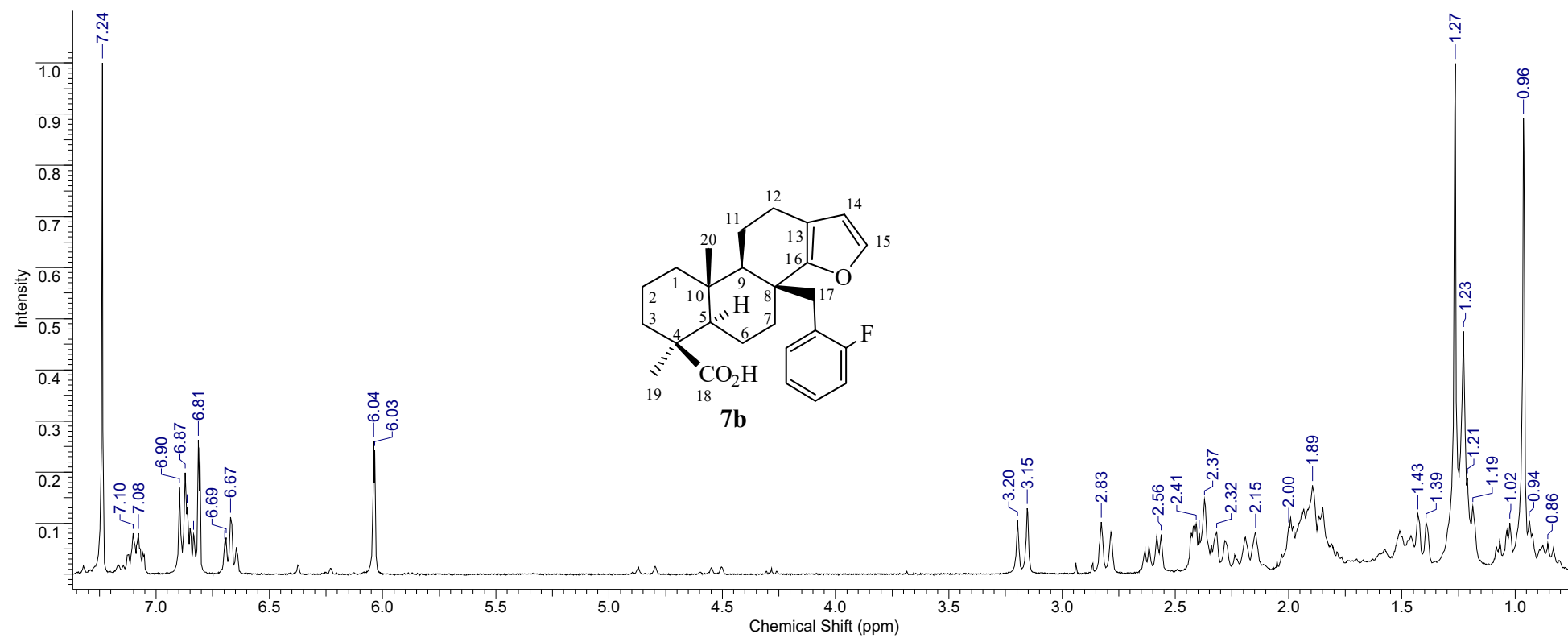
***(3bS,5aR,6S,9aR,9bR)*-3*b*-benzyl-6,9*a*-dimethyl-3*b*,4,5,5*a*,6,7,8,9,9*a*,9*b*,10,11-dodecahydrophenanthro[1,2-*b*]furan-6-carboxylic acid (**7a**)**

(¹³C NMR, 151 MHz, CDCl₃)



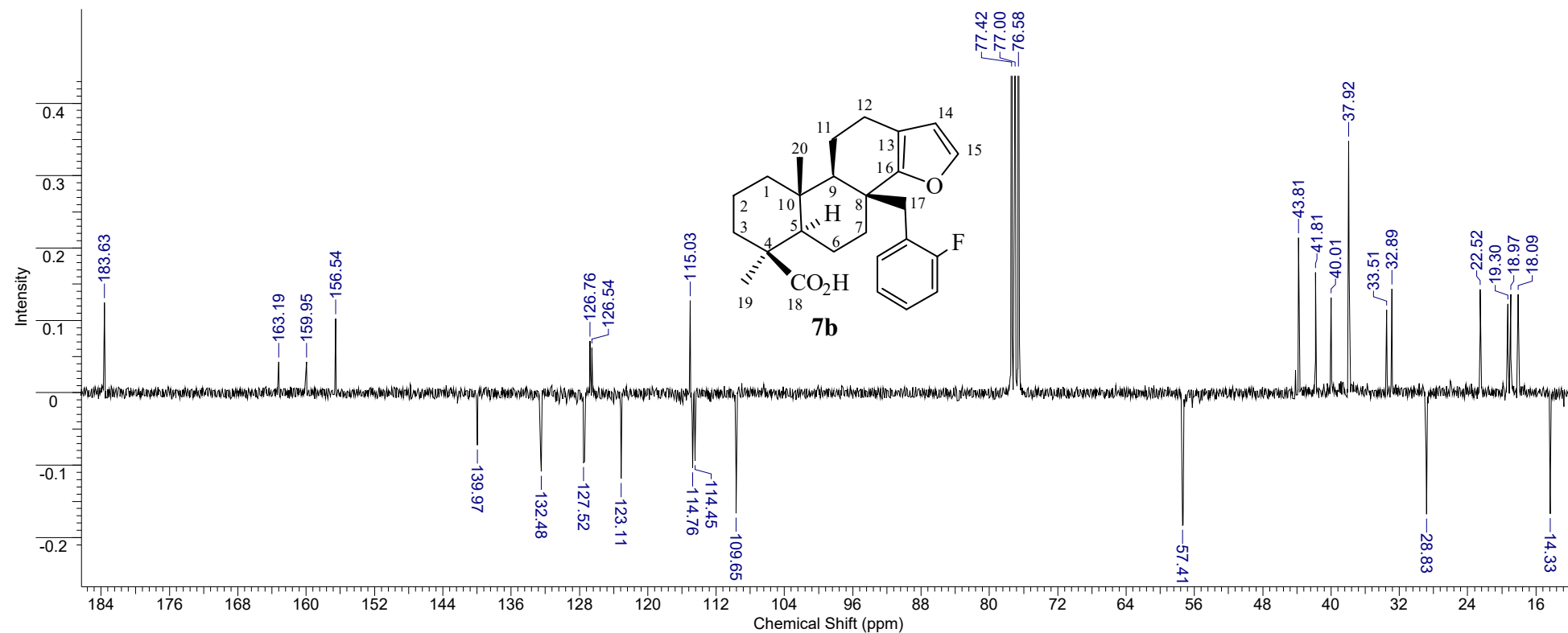
***(3bS,5aR,6S,9aR,9bR)*-3b-(2-fluorobenzyl)-6,9a-dimethyl-3b,4,5,5a,6,7,8,9,9a,9b,10,11-dodecahydrophenanthro[1,2-b]furan-6-carboxylic acid (**7b**)**

(¹H NMR, 400 MHz, CDCl₃)



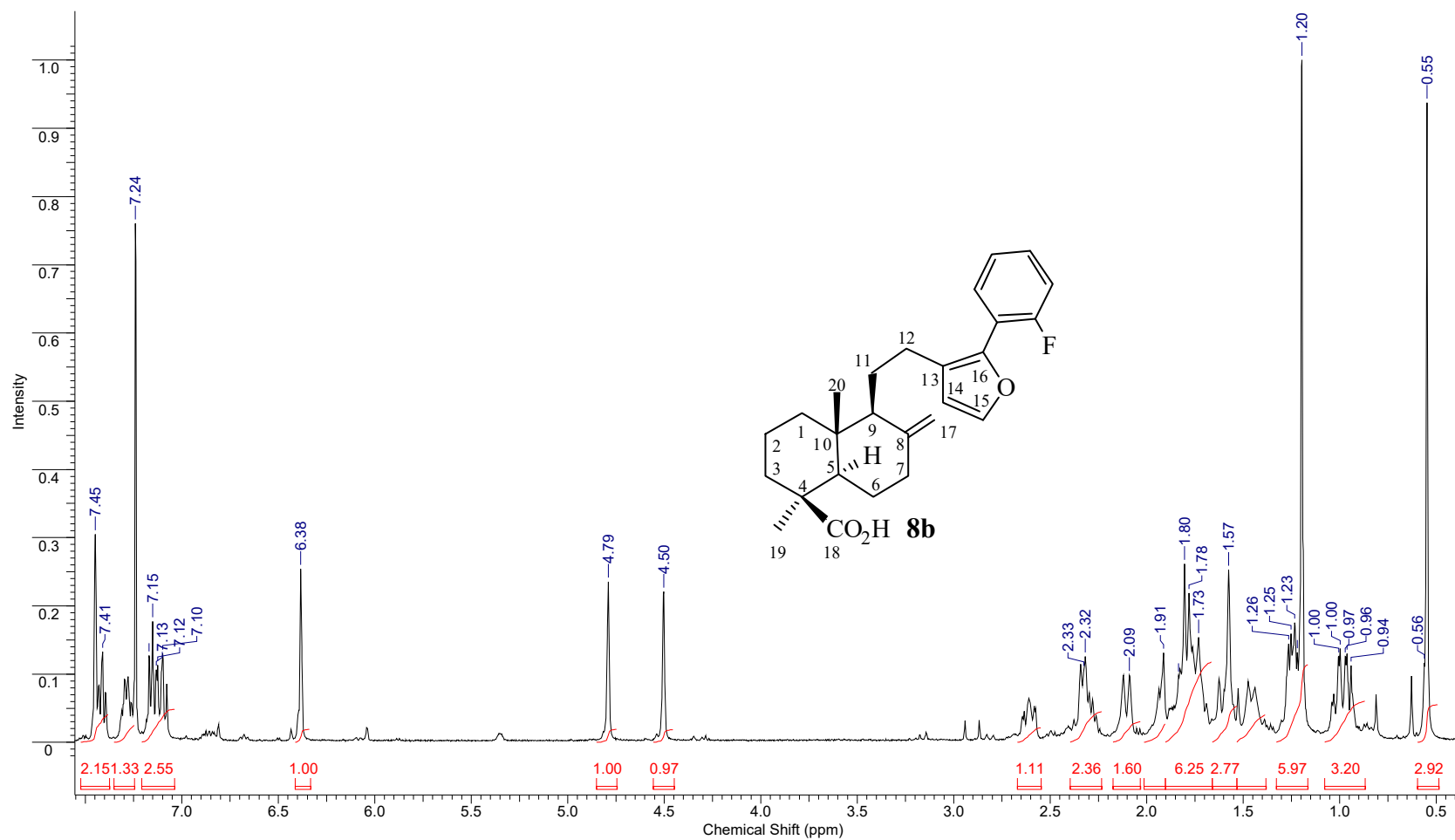
(3*bS*,5*aR*,6*S*,9*aR*,9*bR*)-3*b*-(2-fluorobenzyl)-6,9*a*-dimethyl-3*b*,4,5,5*a*,6,7,8,9,9*a*,9*b*,10,11-dodecahydrophenanthro[1,2-*b*]furan-6-carboxylic acid (7*b*)

(¹³C NMR, 75 MHz, CDCl₃)



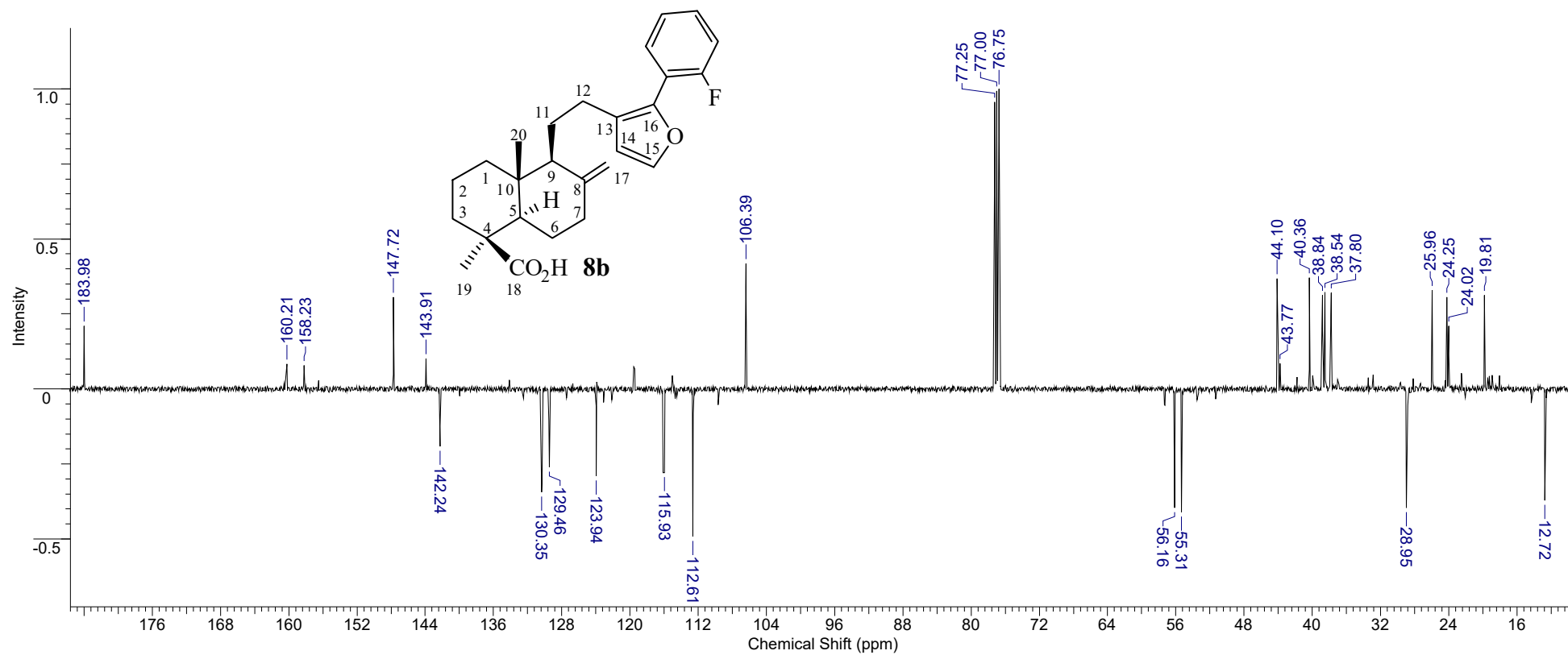
(1S,4aR,5S,8aR)-5-(2-(2-(2-fluorophenyl)furan-3-yl)ethyl)-1,4a-dimethyl-6-methylenedecahydronaphthalene-1-carboxylic acid (8b)

(¹H NMR, 400 MHz, CDCl₃)



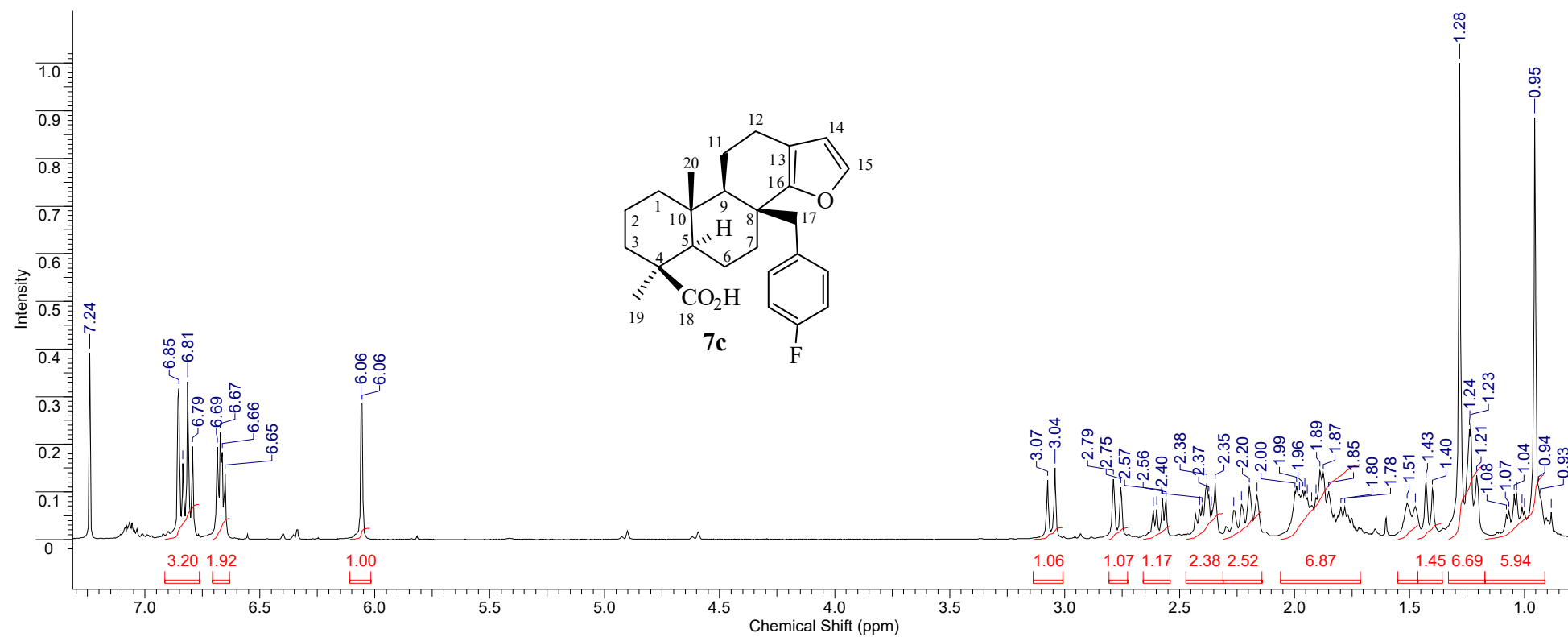
(1*S*,4*aR*,5*S*,8*aR*)-5-(2-(2-(2-fluorophenyl)furan-3-yl)ethyl)-1,4*a*-dimethyl-6-methylenedecahydronaphthalene-1-carboxylic acid (8b)

(¹³C NMR, 126 MHz, CDCl₃)



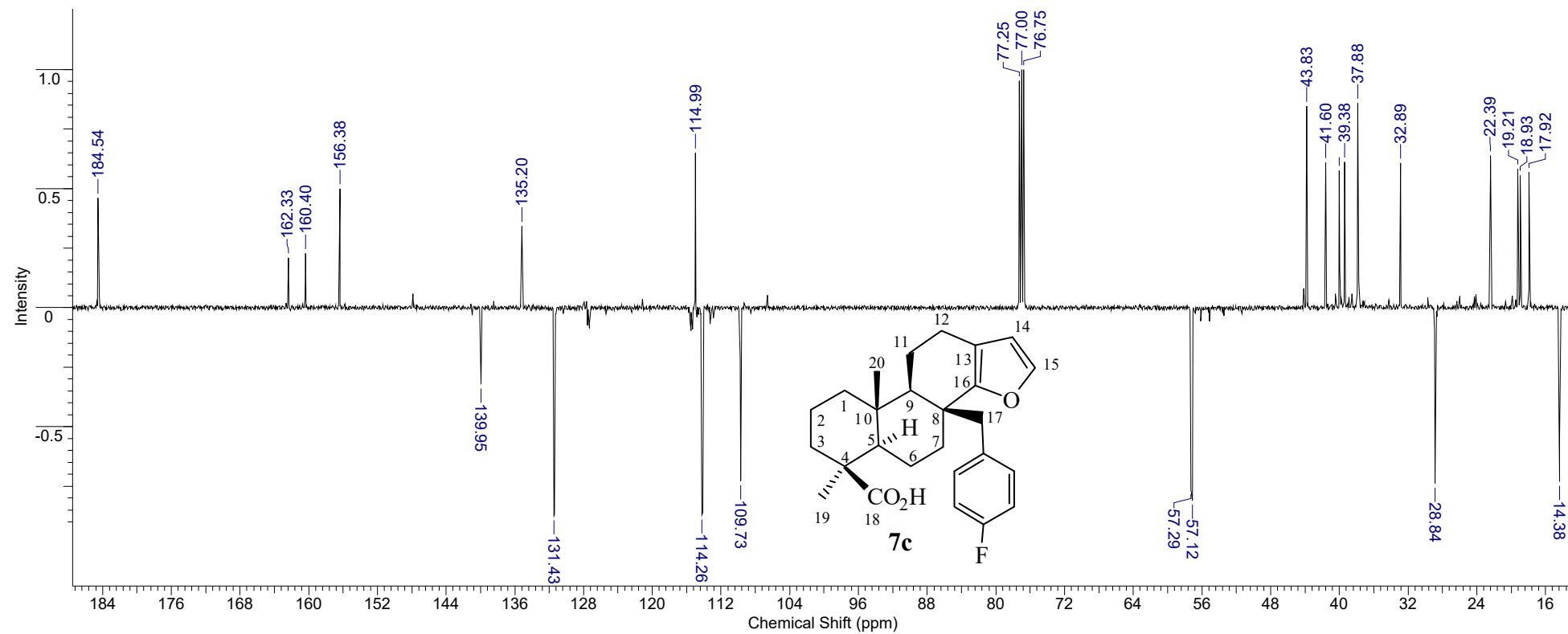
(3*bS*,5*aR*,6*S*,9*aR*,9*bR*)-3*b*-(4-fluorobenzyl)-6,9*a*-dimethyl-3*b*,4,5,5*a*,6,7,8,9,9*a*,9*b*,10,11-dodecahydrophenanthro[1,2-*b*]furan-6-carboxylic acid (7*c*)

(¹H NMR, 400 MHz, CDCl₃)



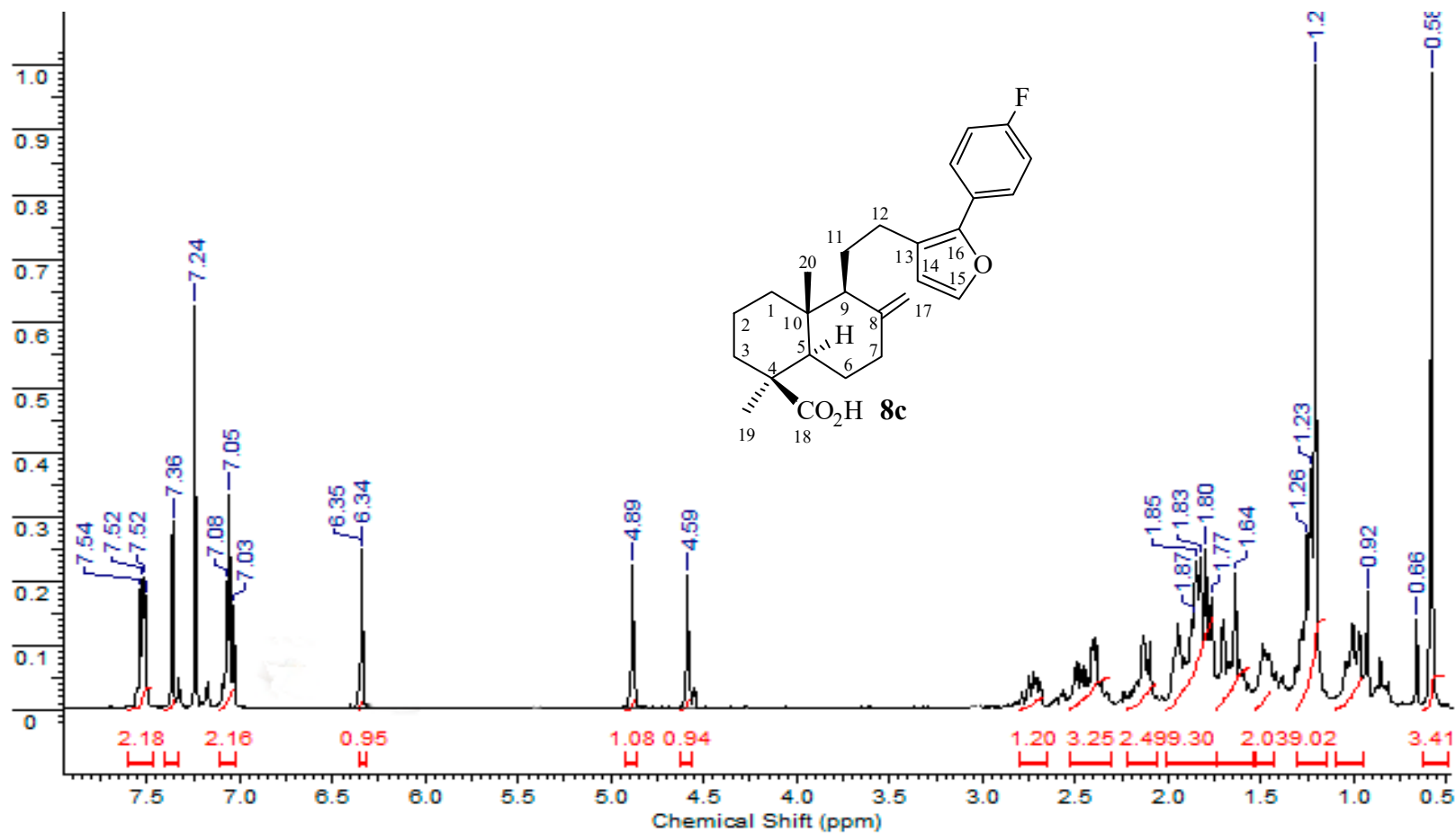
(3*b*S,5*a*R,6*S*,9*a*R,9*b*R)-3*b*-(4-fluorobenzyl)-6,9*a*-dimethyl-3*b*,4,5,5*a*,6,7,8,9,9*a*,9*b*,10,11-dodecahydrophenanthro[1,2-*b*]furan-6-carboxylic acid (7*c*)

(¹³C NMR, 126 MHz, CDCl₃)



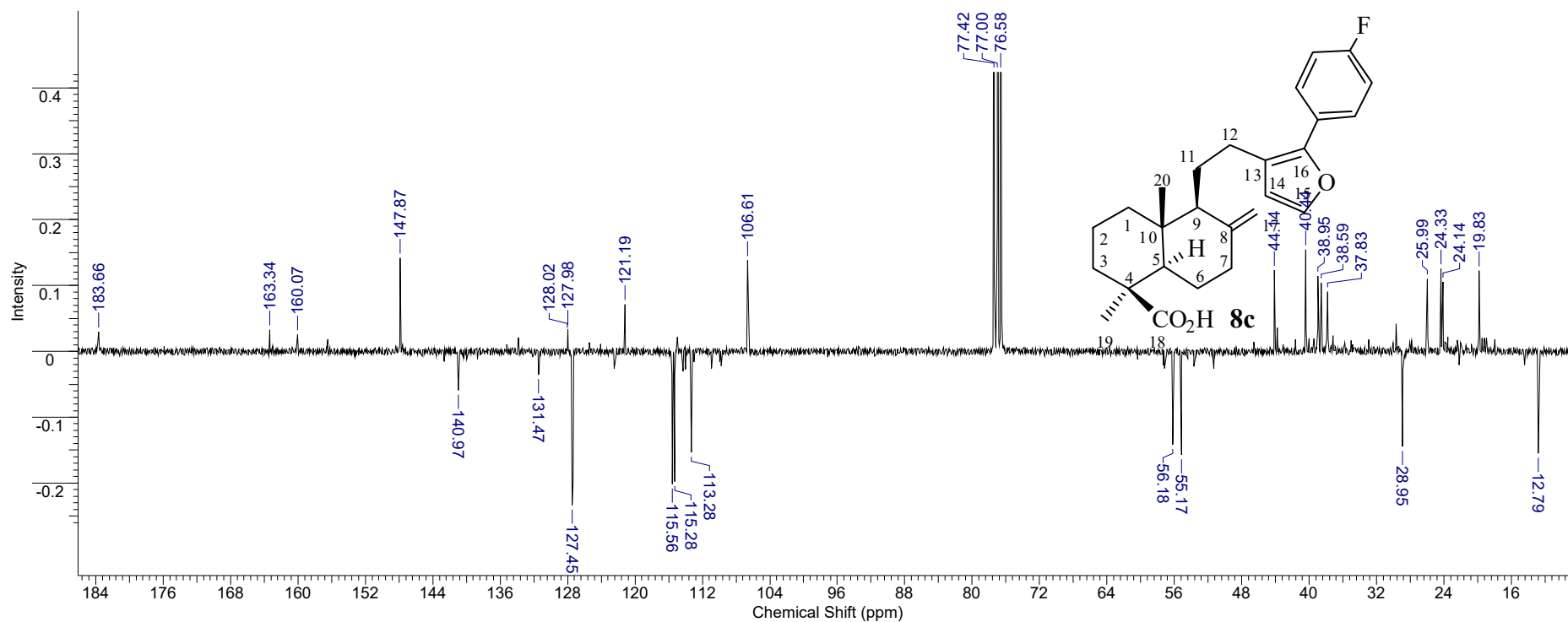
(1S,4aR,5S,8aR)-5-(2-(2-(5-fluorophenyl)furan-3-yl)ethyl)-1,4a-dimethyl-6-methylenedecahydronaphthalene-1-carboxylic acid (8c)

(¹H NMR, 400 MHz, CDCl₃)

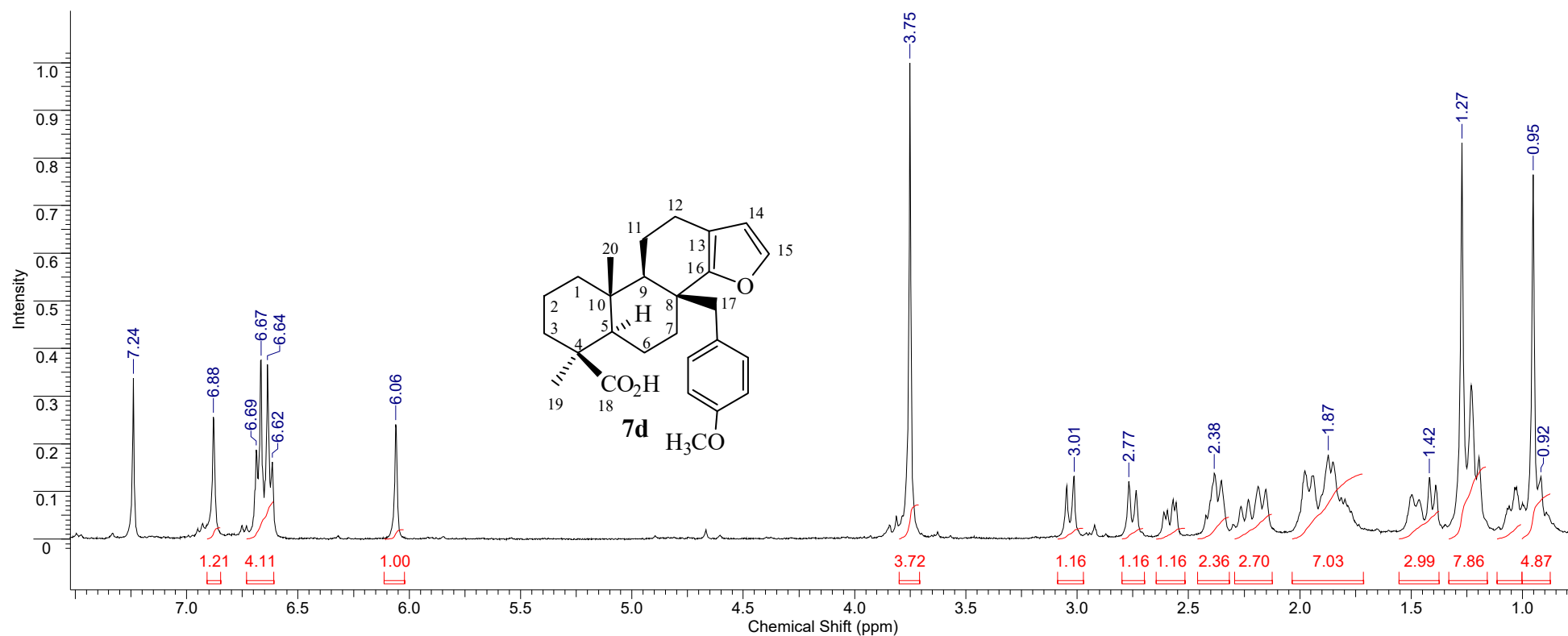


(1S,4aR,5S,8aR)-5-(2-(2-(5-fluorophenyl)furan-3-yl)ethyl)-1,4a-dimethyl-6-methylenedecahydronaphthalene-1-carboxylic acid (8c)

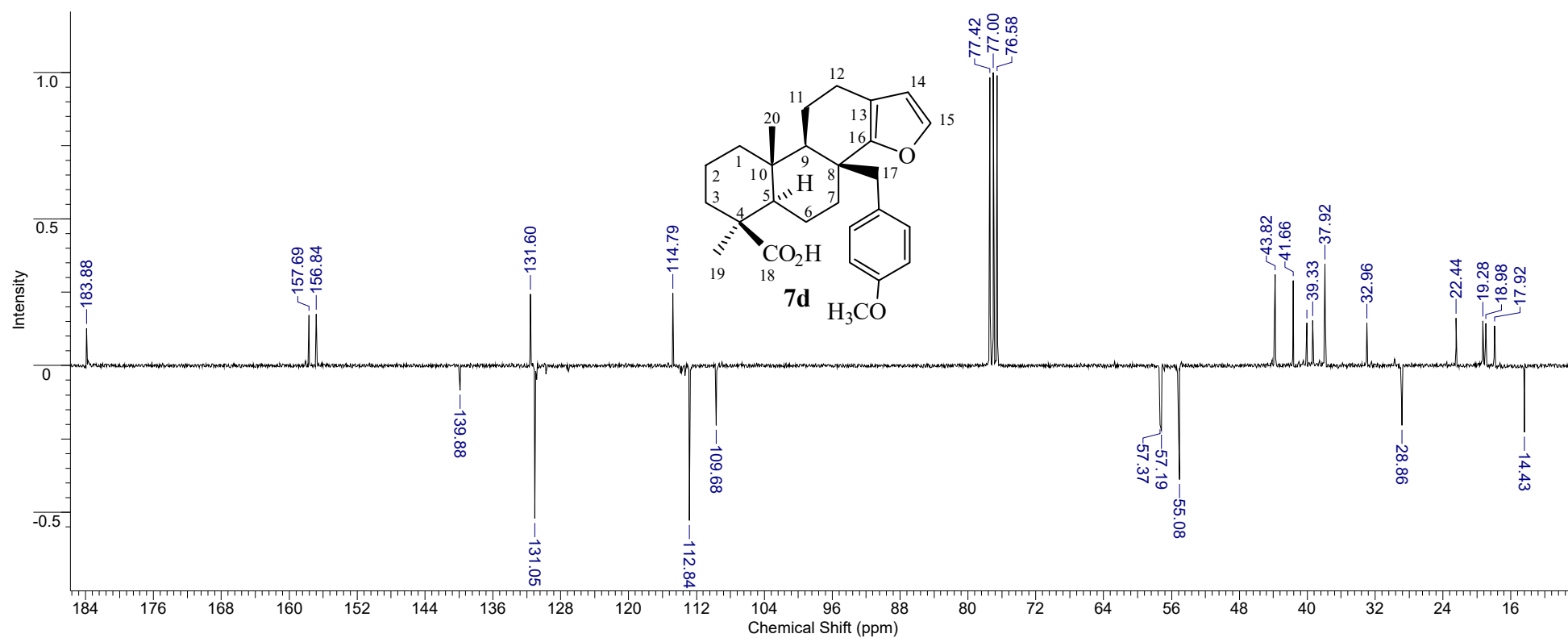
(^{13}C NMR, 75 MHz, CDCl_3)



***(3bS,5aR,6S,9aR,9bR)*-3b-(4-methoxybenzyl)-6,9a-dimethyl-3b,4,5,5a,6,7,8,9,9a,9b,10,11-dodecahydrophenanthro[1,2-b]furan-6-carboxylic acid**
(7d) (^1H NMR, 400 MHz, CDCl_3)

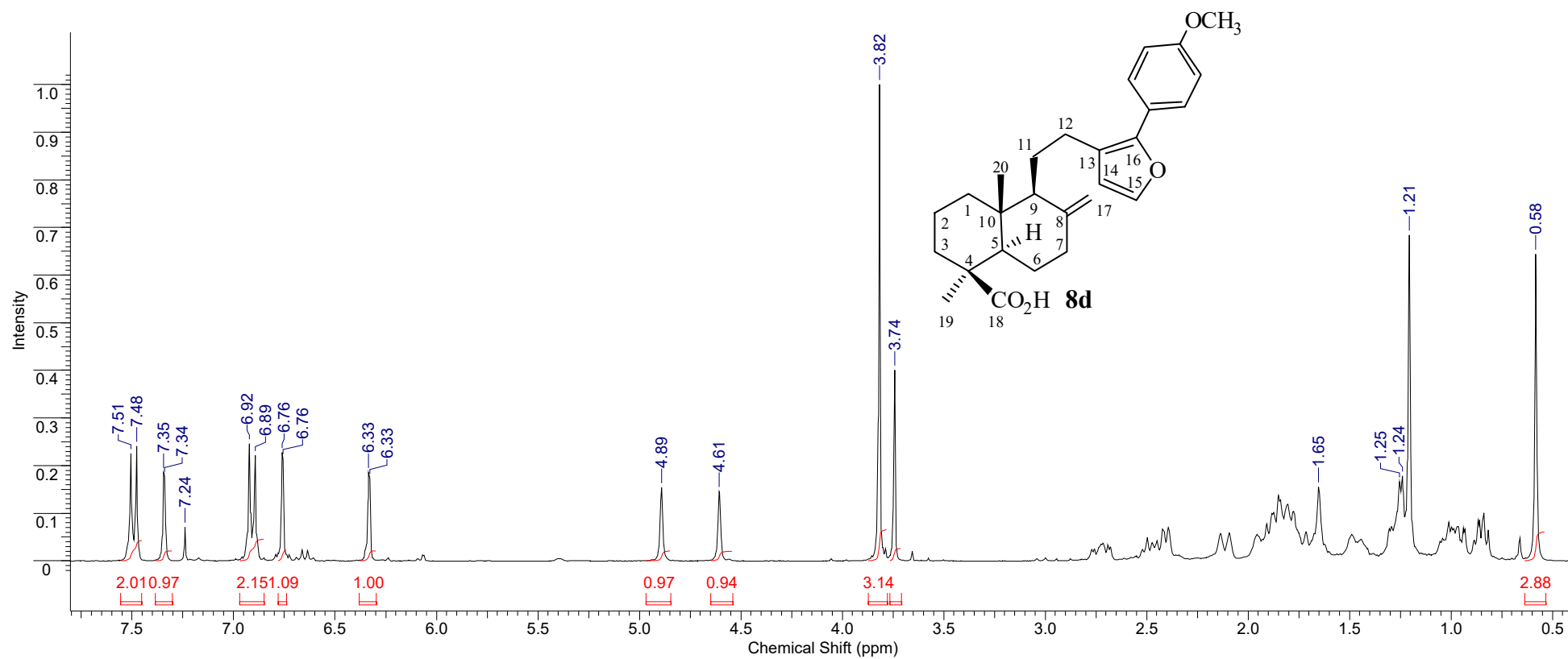


(3*bS*,5*aR*,6*S*,9*aR*,9*bR*)-3*b*-(4-methoxybenzyl)-6,9*a*-dimethyl-3*b*,4,5,5*a*,6,7,8,9,9*a*,9*b*,10,11-dodecahydrophenanthro[1,2-*b*]furan-6-carboxylic acid
(7d) (^{13}C NMR, 75 MHz, CDCl_3)



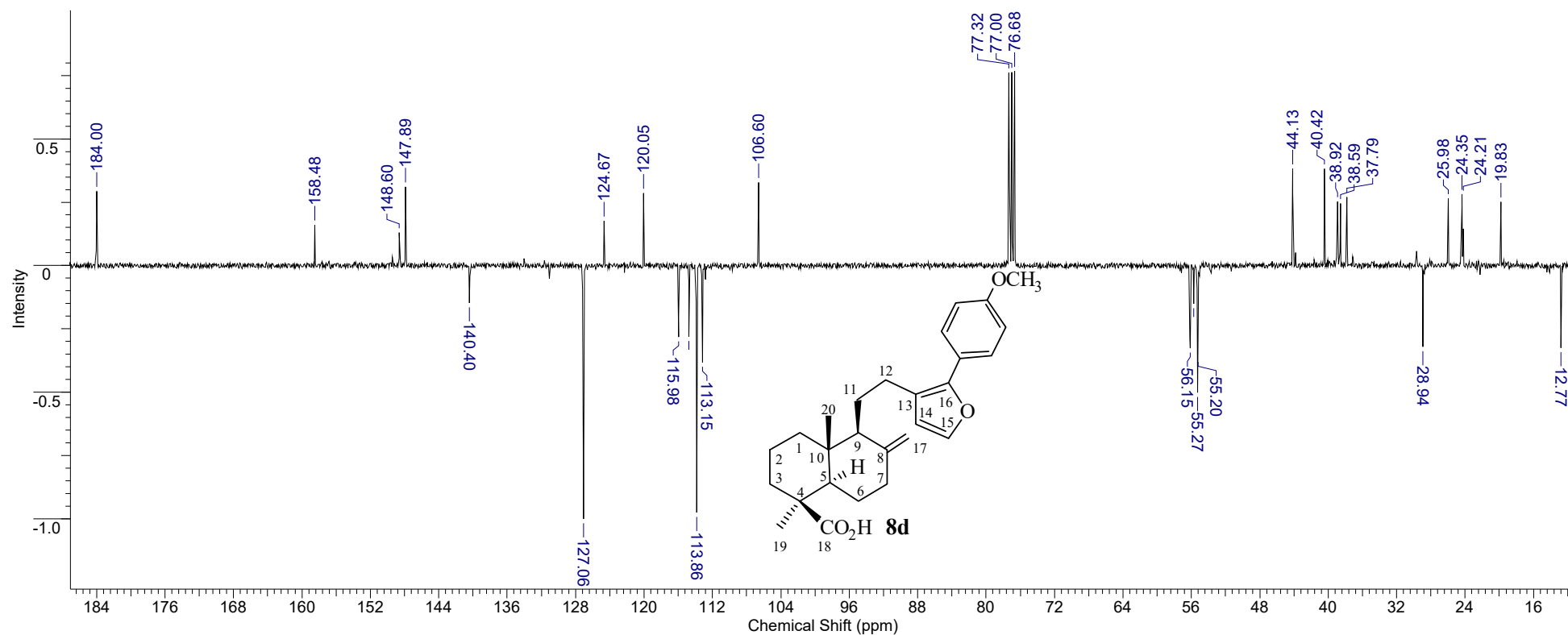
(1*S*,4*aR*,5*S*,8*aR*)-5-(2-(2-(4-methoxyphenyl)furan-3-yl)ethyl)-1,4*a*-dimethyl-6-methylenedecahydronaphthalene-1-carboxylic acid (8d**)**

(¹H NMR, 400 MHz, CDCl₃)



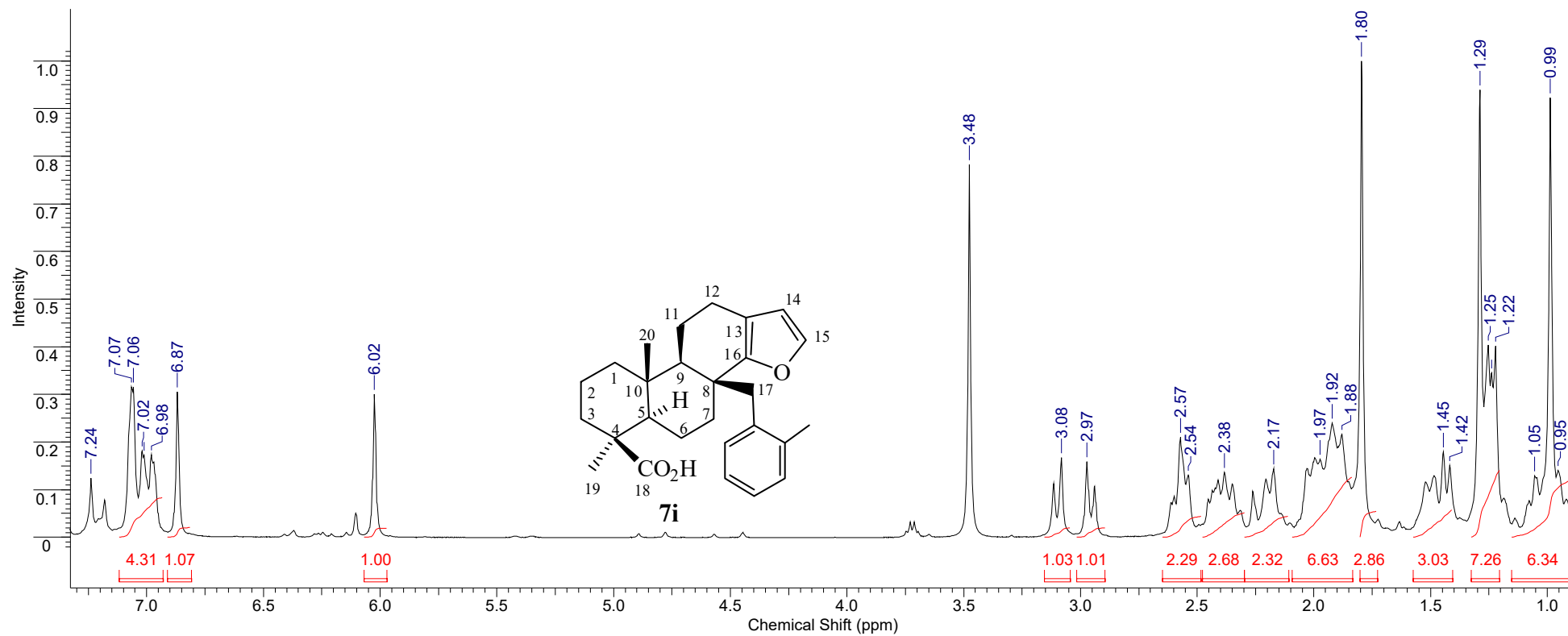
(1S,4aR,5S,8aR)-5-(2-(2-(4-methoxyphenyl)furan-3-yl)ethyl)-1,4a-dimethyl-6-methylenedecahydronaphthalene-1-carboxylic acid (8d)

(¹³C NMR, 75 MHz, CDCl₃)



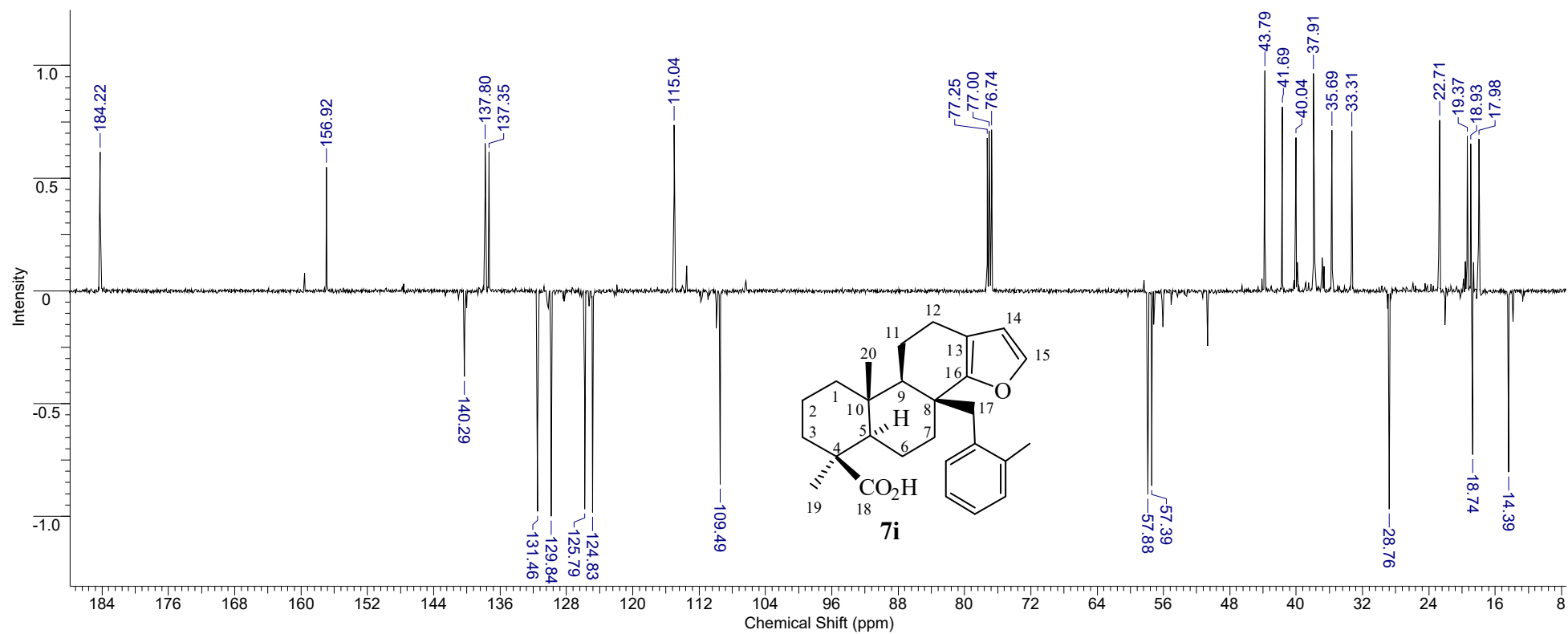
(5aR,6S,9aR,9bR)-6,9a-dimethyl-3b-(2-methylbenzyl)-3b,4,5,5a,6,7,8,9,9a,9b,10,11-dodecahydrophenanthro[1,2-b]furan-6-carboxylic acid (7i)

(¹H NMR, 400 MHz, CDCl₃)



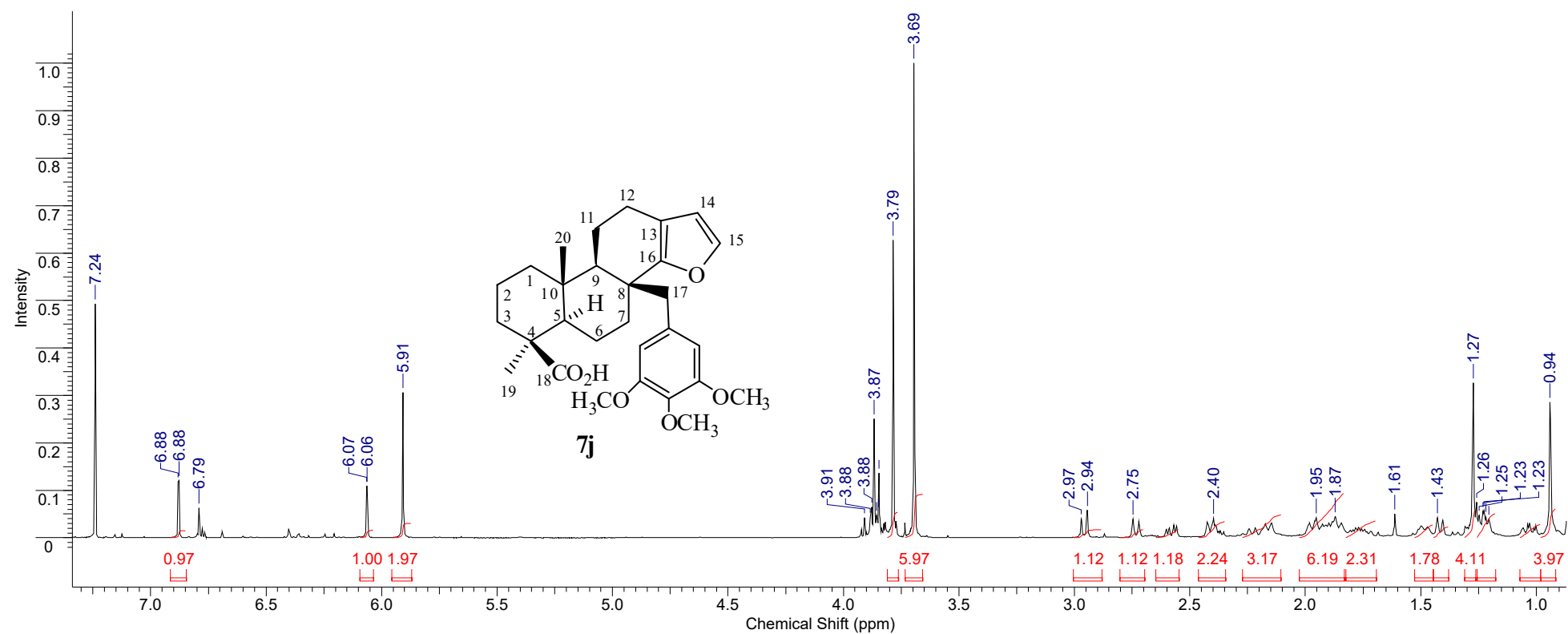
(5aR,6S,9aR,9bR)-6,9a-dimethyl-3b-(2-methylbenzyl)-3b,4,5,5a,6,7,8,9,9a,9b,10,11-dodecahydrophenanthro[1,2-b]furan-6-carboxylic acid (7i)

(¹³C NMR, 126 MHz, CDCl₃)

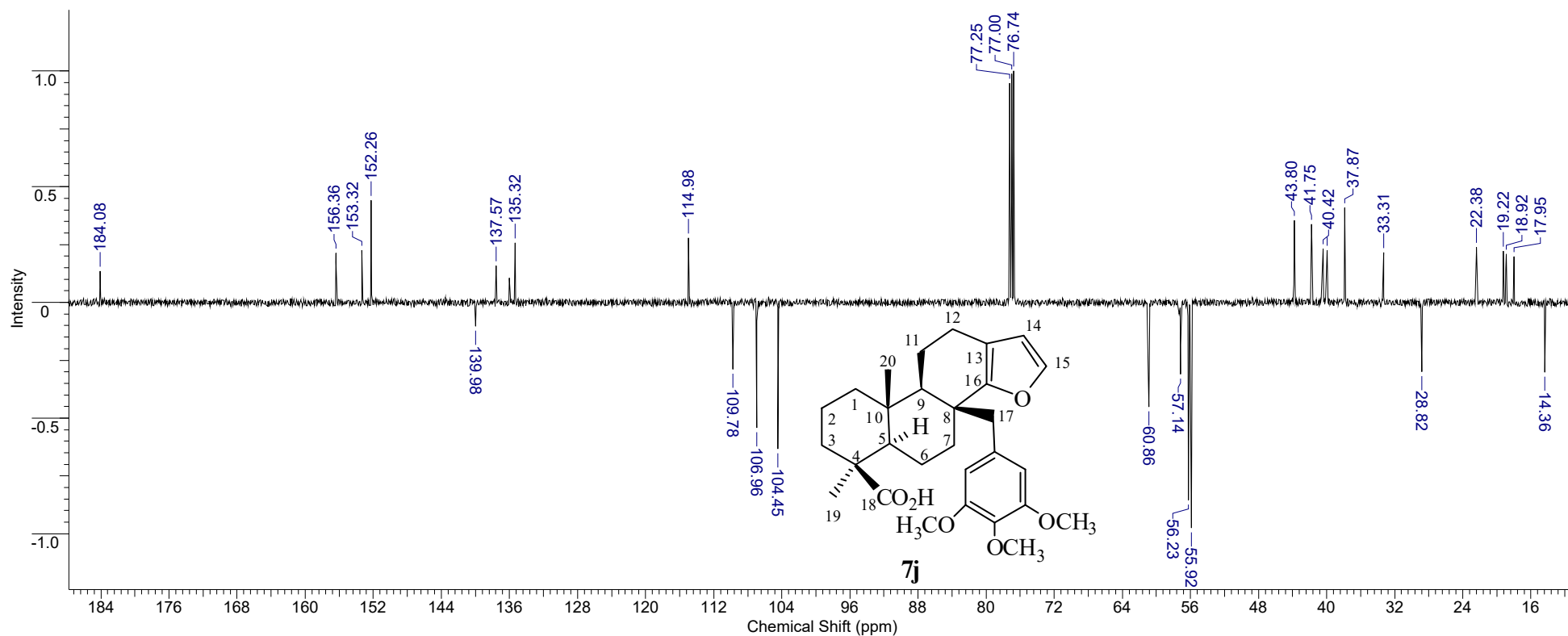


(5aR,6S,9aR,9bR)-6,9a-dimethyl-3b-(3,4,5-trimethoxybenzyl)-3b,4,5,5a,6,7,8,9,9a,9b,10,11-dodecahydrophenanthro[1,2-b]furan-6-carboxylic acid

(7j) (^1H NMR, 300 MHz, CDCl_3)

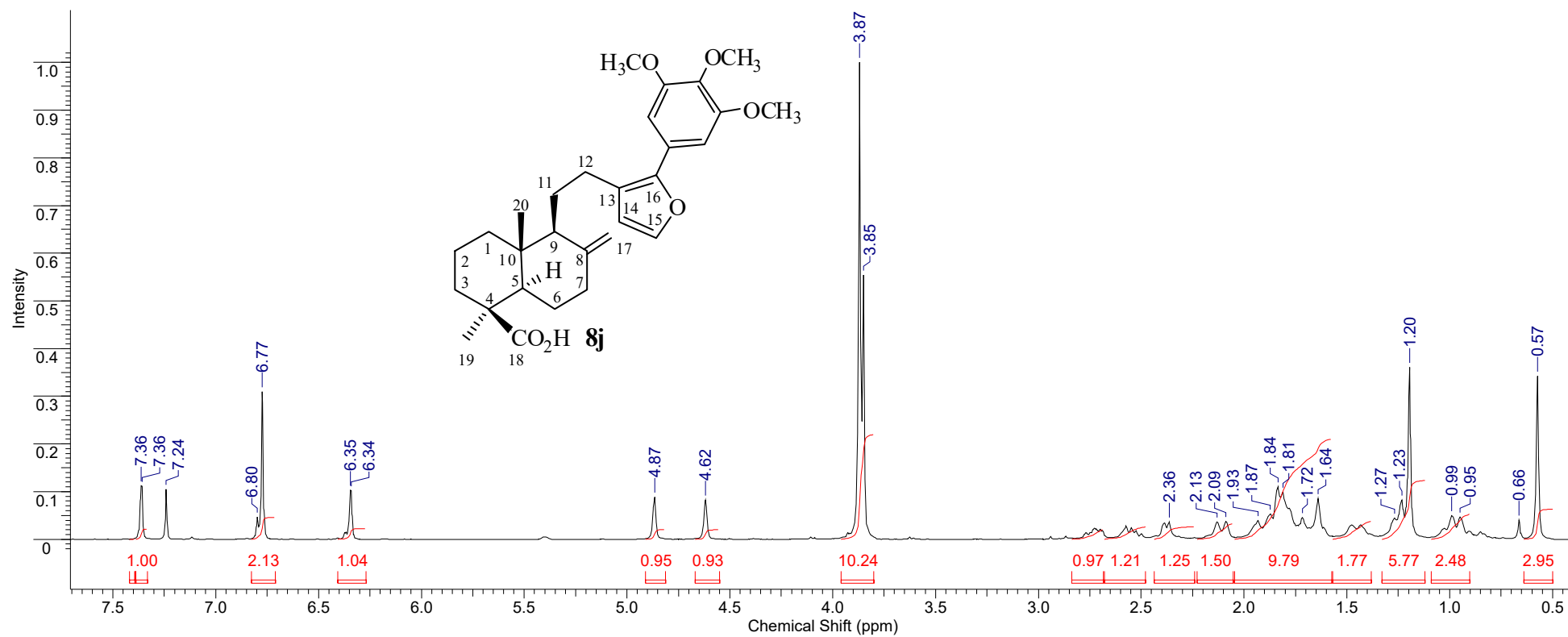


(5aR,6S,9aR,9bR)-6,9a-dimethyl-3b-(3,4,5-trimethoxybenzyl)-3b,4,5,5a,6,7,8,9,9a,9b,10,11-dodecahydrophenanthro[1,2-b]furan-6-carboxylic acid
(7j) (^{13}C NMR, 126 MHz, CDCl_3)



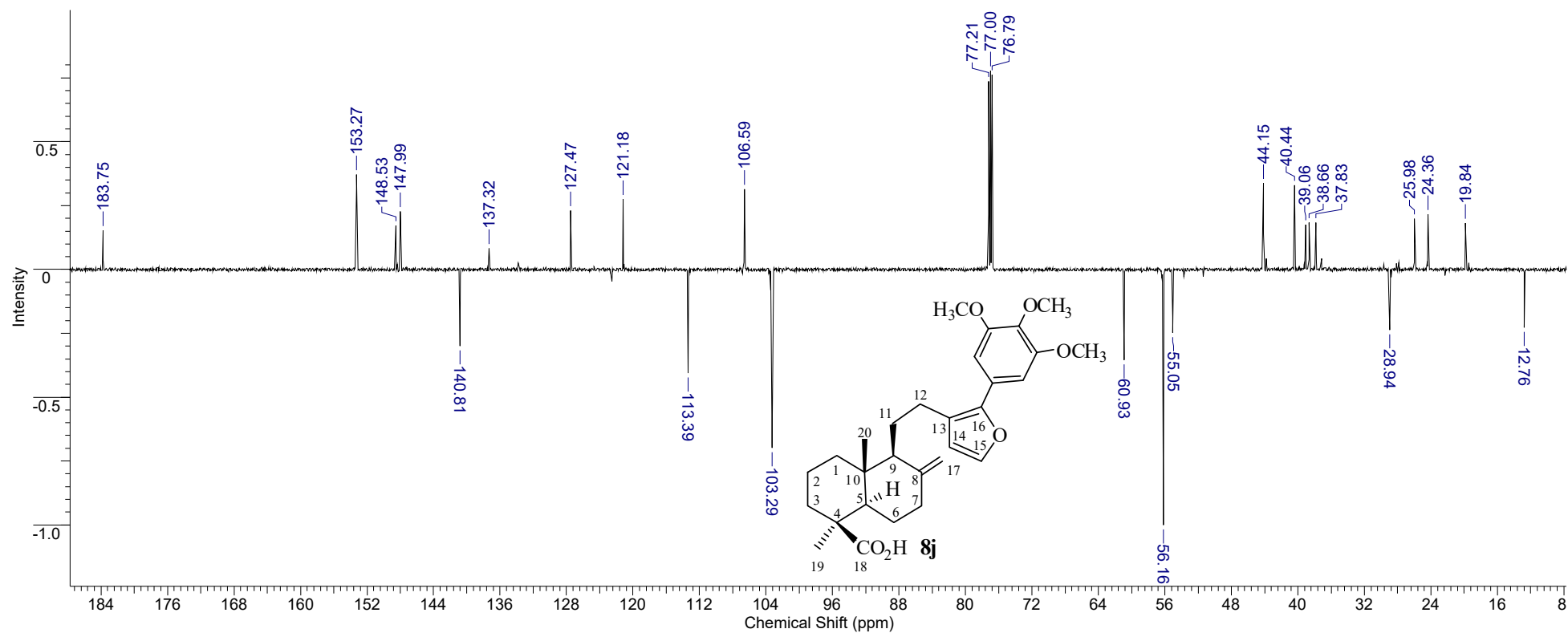
***(1S,4aR,5S,8aR)*-1,4a-dimethyl-6-methylene-5-(2-(2-(3,4,5-trimethoxyphenyl)furan-3-yl)ethyl)decahydronaphthalene-1-carboxylic acid (**8j**)**

(¹H NMR, 300 MHz, CDCl₃)

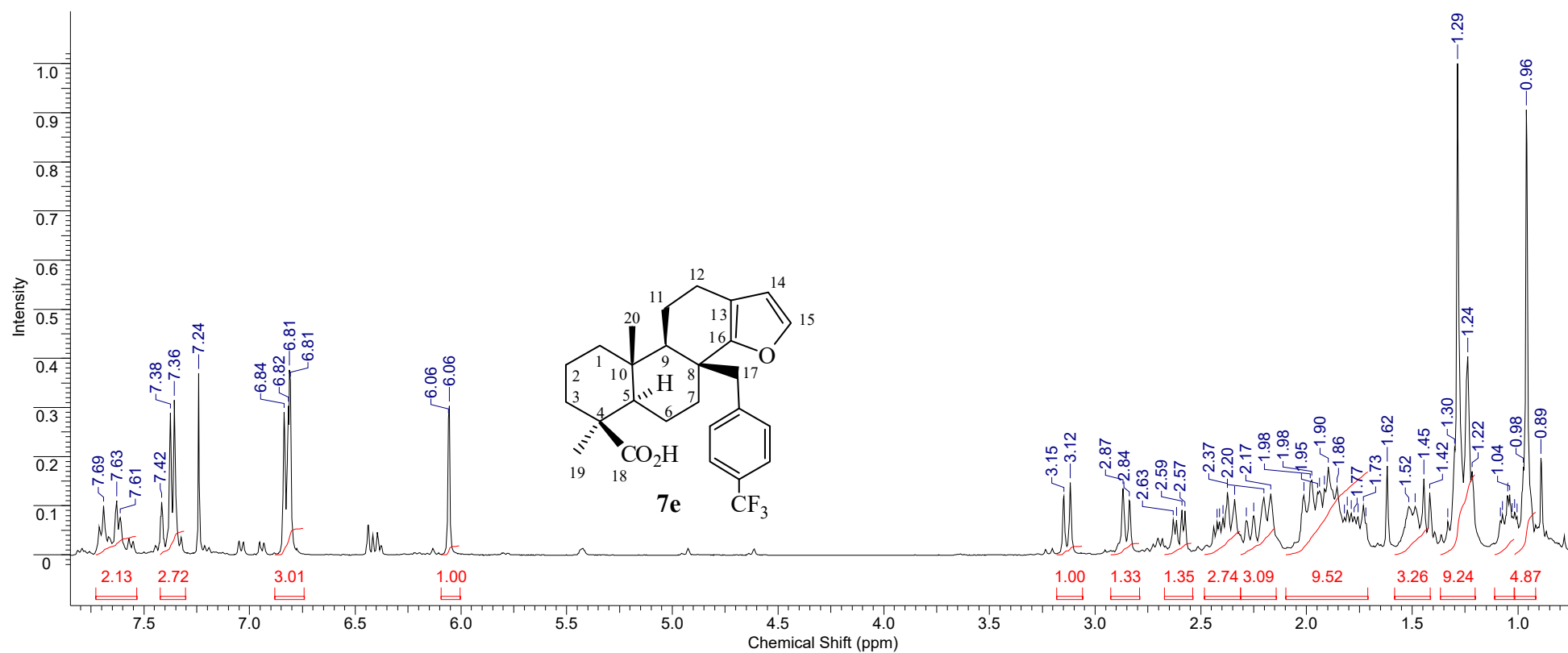


(1S,4aR,5S,8aR)-1,4a-dimethyl-6-methylene-5-(2-(2-(3,4,5-trimethoxyphenyl)furan-3-yl)ethyl)decahydronaphthalene-1-carboxylic acid (8j)

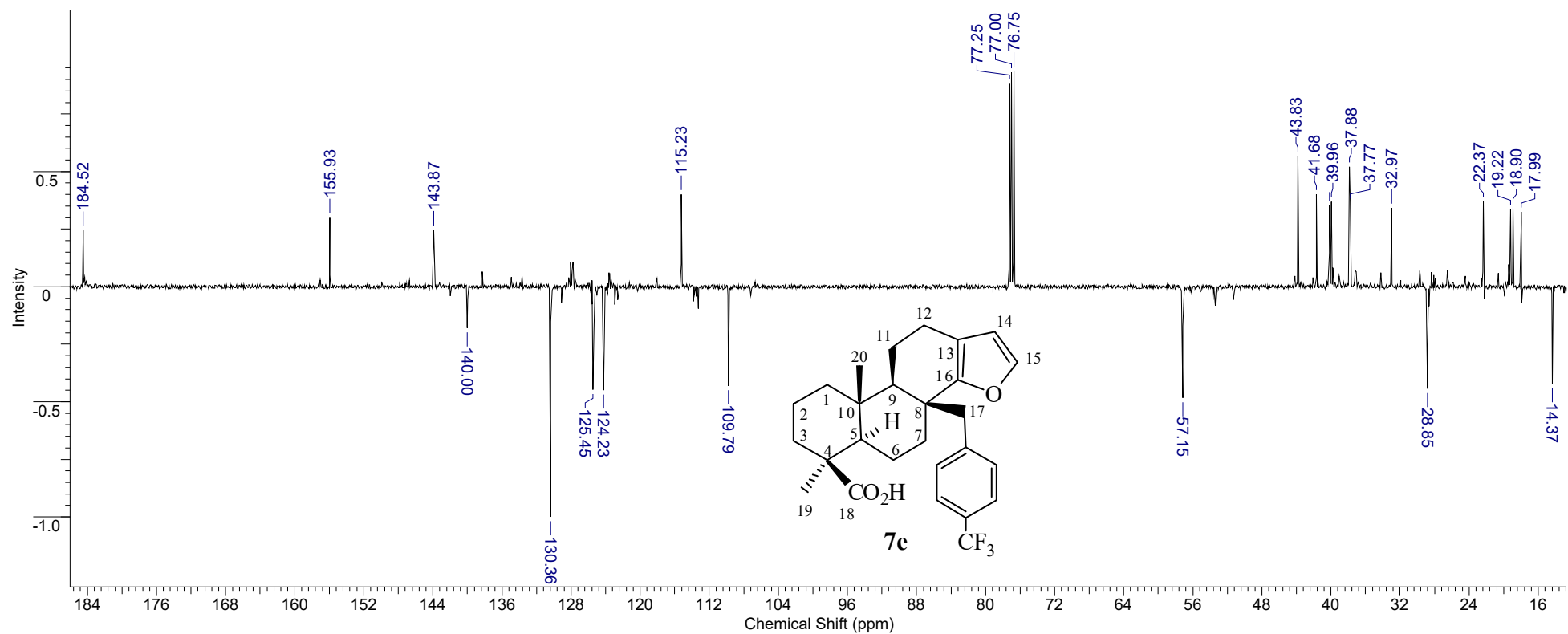
(¹³C NMR, 151 MHz, CDCl₃)



***(5aR,6S,9aR,9bR)*-6,9a-dimethyl-3b-(4-(trifluoromethyl)benzyl)-3b,4,5,5a,6,7,8,9,9a,9b,10,11-dodecahydrophenanthro[1,2-b]furan-6-carboxylic acid (**7e**)** (¹H NMR, 400 MHz, CDCl₃)

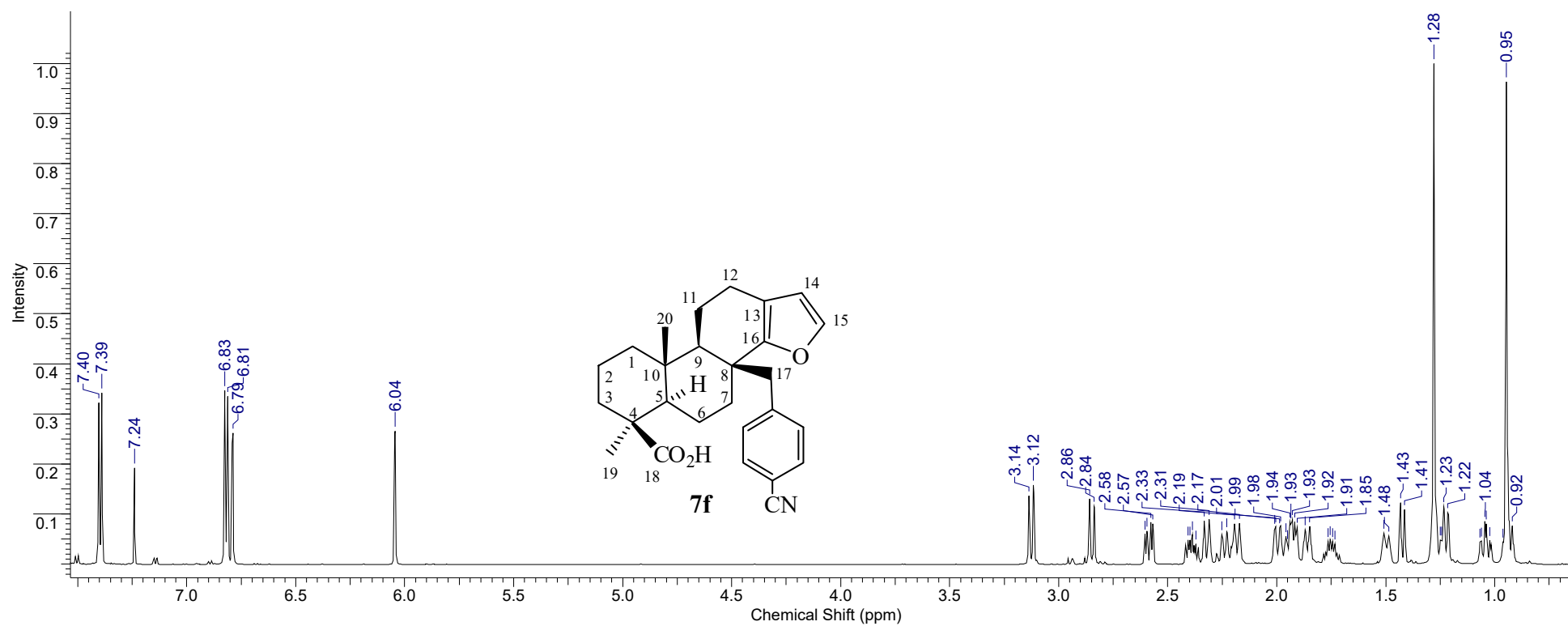


***(5aR,6S,9aR,9bR)*-6,9a-dimethyl-3b-(4-(trifluoromethyl)benzyl)-3b,4,5,5a,6,7,8,9,9a,9b,10,11-dodecahydrophenanthro[1,2-b]furan-6-carboxylic acid (7e)** (^{13}C NMR, 126 MHz, CDCl_3)



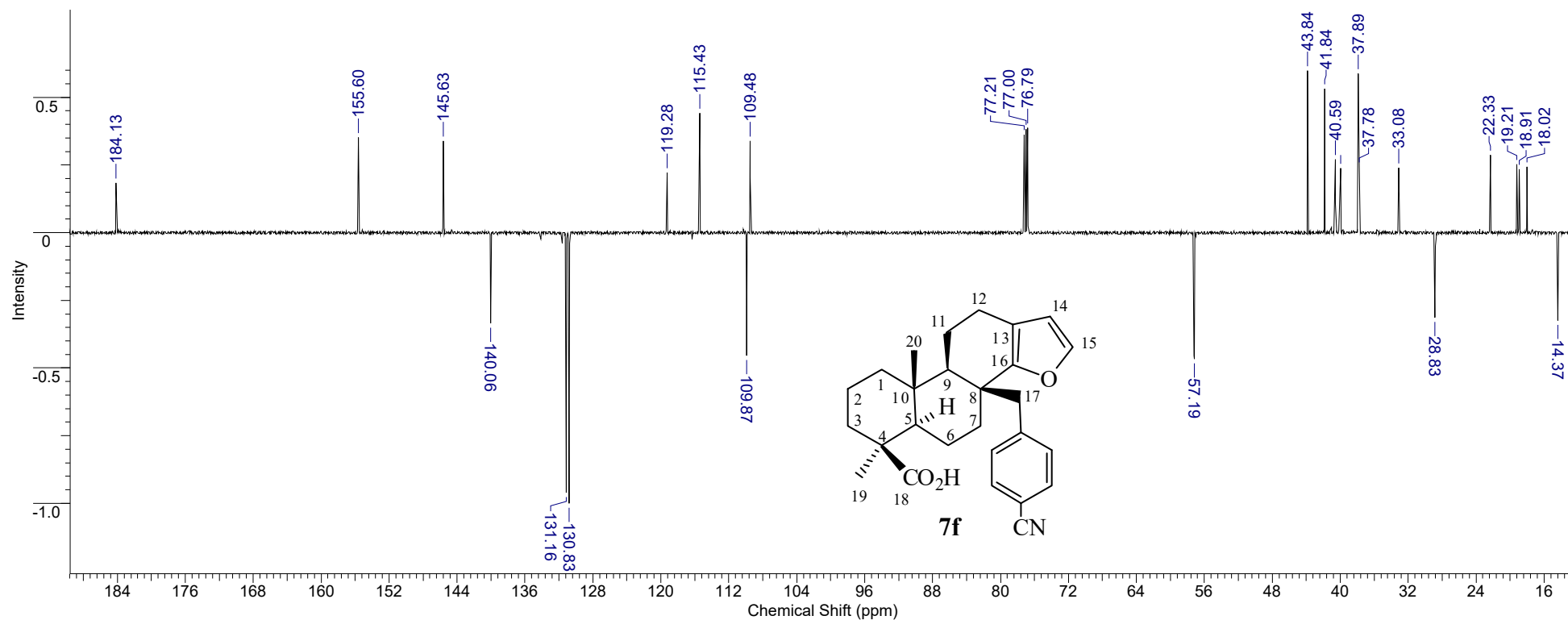
(3bS,5aR,6S,9aR,9bR)-3b-(4-cyanobenzyl)-6,9a-dimethyl-3b,4,5,5a,6,7,8,9,9a,9b,10,11-dodecahydrophenanthro[1,2-b]furan-6-carboxylic acid (7f)

(¹H NMR, 600 MHz, CDCl₃)



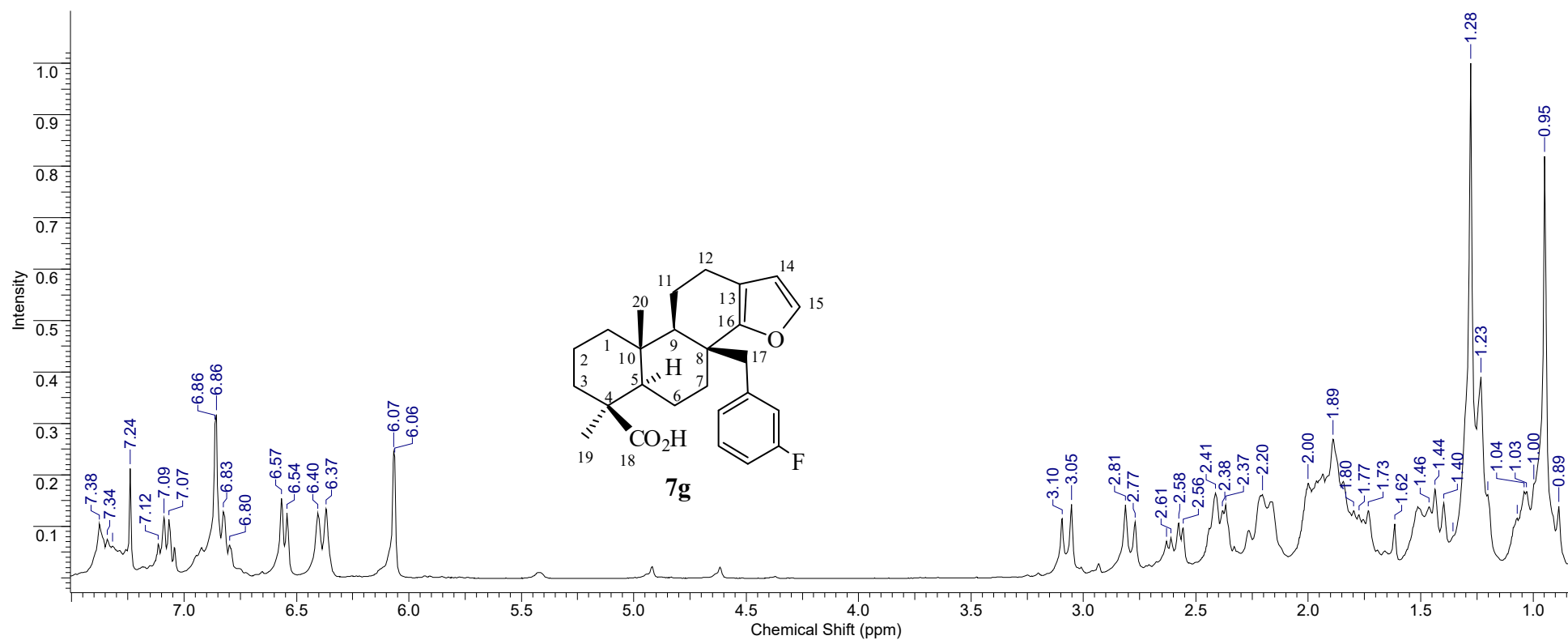
(3*bS*,5*aR*,6*S*,9*aR*,9*bR*)-3*b*-(4-cyanobenzyl)-6,9*a*-dimethyl-3*b*,4,5,5*a*,6,7,8,9,9*a*,9*b*,10,11-dodecahydrophenanthro[1,2-*b*]furan-6-carboxylic acid (7*f*)

(¹³C NMR, 151 MHz, CDCl₃)



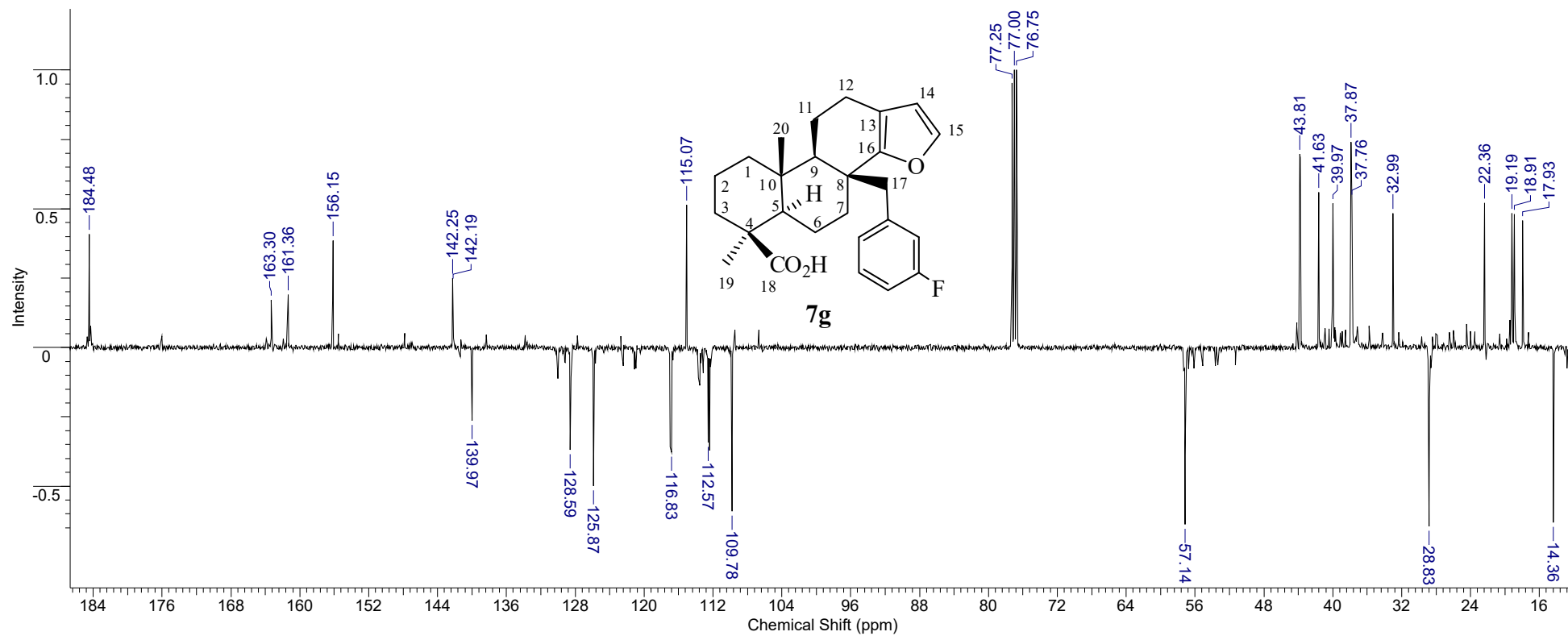
(3*bS*,5*aR*,6*S*,9*aR*,9*bR*)-3*b*-(3-fluorobenzyl)-6,9*a*-dimethyl-3*b*,4,5,5*a*,6,7,8,9,9*a*,9*b*,10,11-dodecahydrophenanthro[1,2-*b*]furan-6-carboxylic acid (7g)

(¹H NMR, 300 MHz, CDCl₃)

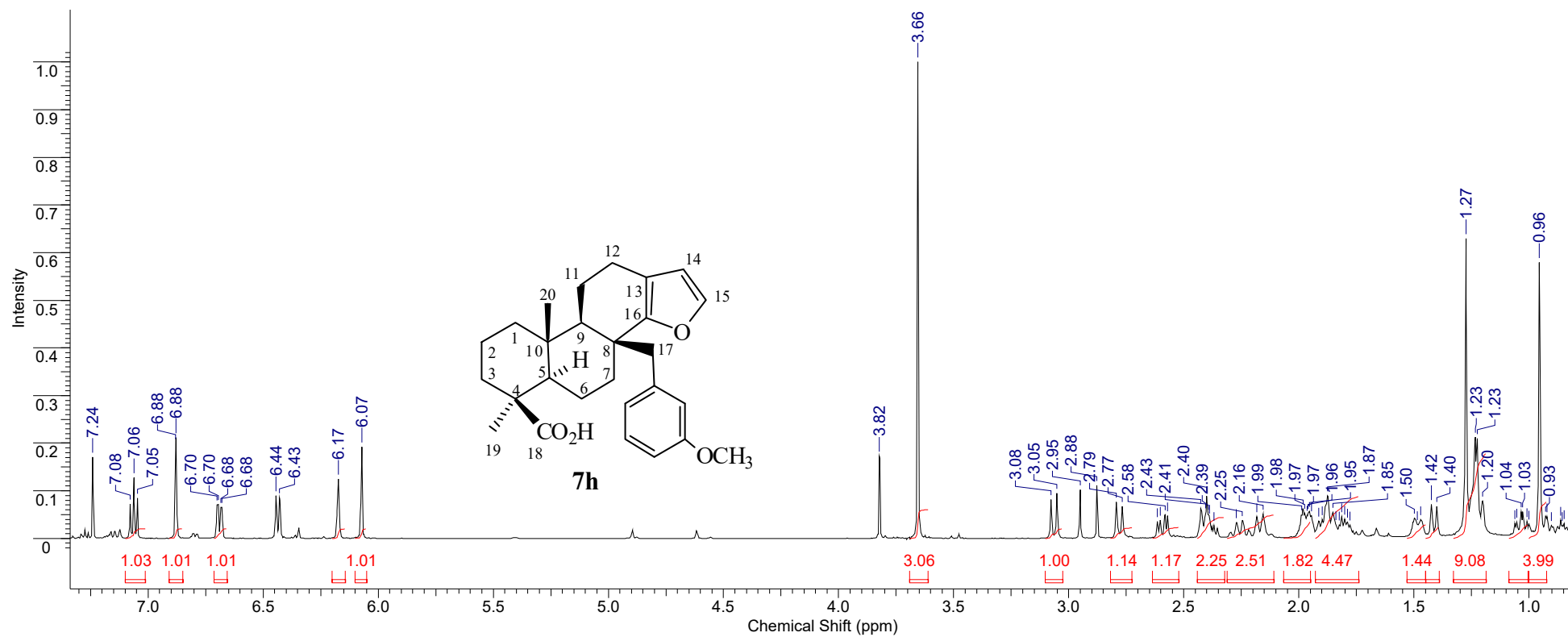


(3bS,5aR,6S,9aR,9bR)-3b-(3-fluorobenzyl)-6,9a-dimethyl-3b,4,5,5a,6,7,8,9,9a,9b,10,11-dodecahydrophenanthro[1,2-b]furan-6-carboxylic acid (7g)

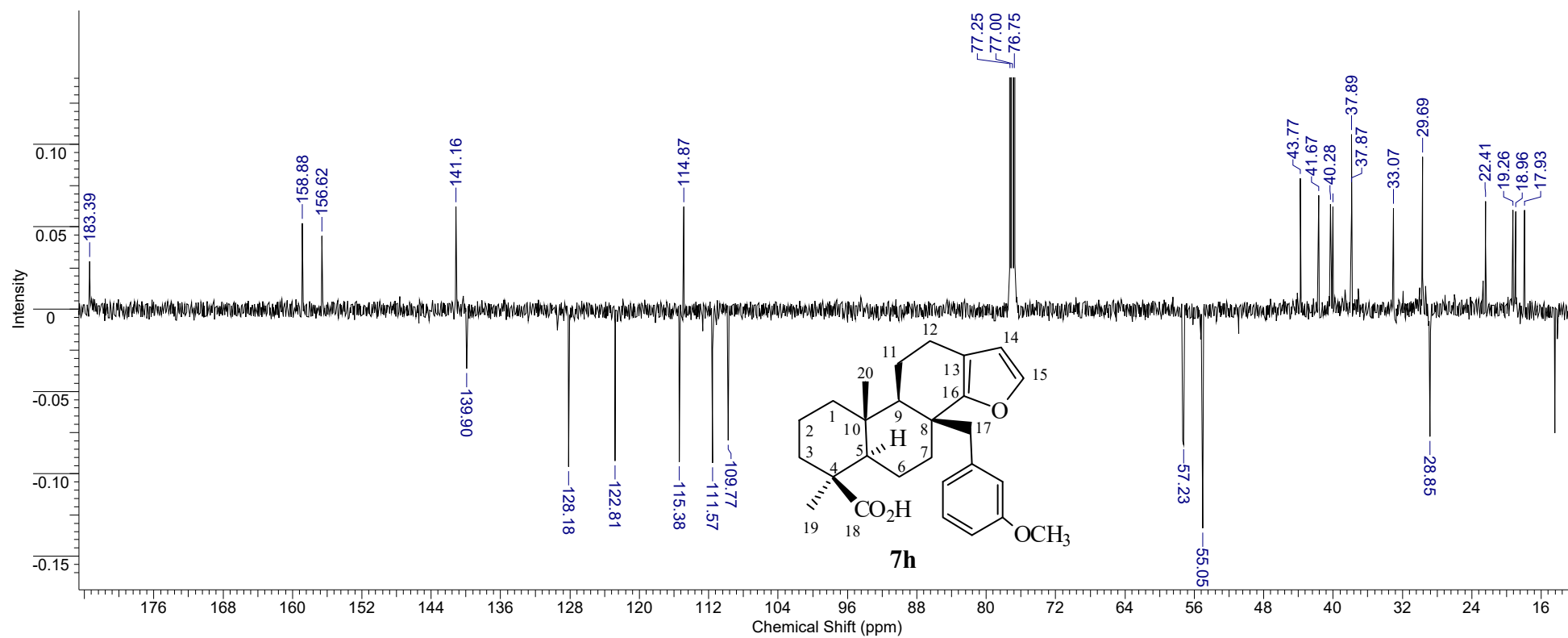
(^{13}C NMR, 126 MHz, CDCl_3)



(3*bS*,5*aR*,6*S*,9*aR*,9*bR*)-3*b*-(3-methoxybenzyl)-6,9*a*-dimethyl-3*b*,4,5,5*a*,6,7,8,9,9*a*,9*b*,10,11-dodecahydrophenanthro[1,2-*b*]furan-6-carboxylic acid
(7h) (¹H NMR, 500 MHz, CDCl₃)

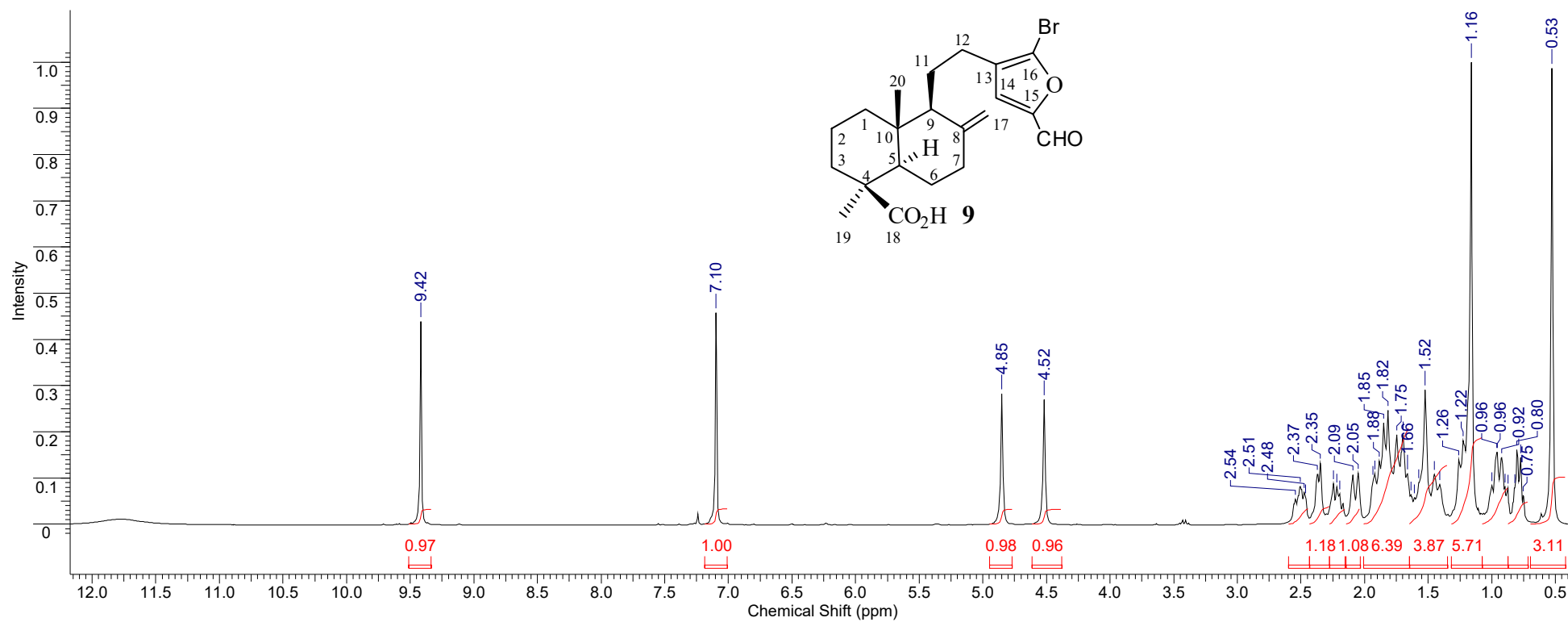


(3*bS*,5*aR*,6*S*,9*aR*,9*bR*)-3*b*-(3-methoxybenzyl)-6,9*a*-dimethyl-3*b*,4,5,5*a*,6,7,8,9,9*a*,9*b*,10,11-dodecahydrophenanthro[1,2-*b*]furan-6-carboxylic acid
(7h) (^{13}C NMR, 126 MHz, CDCl_3)



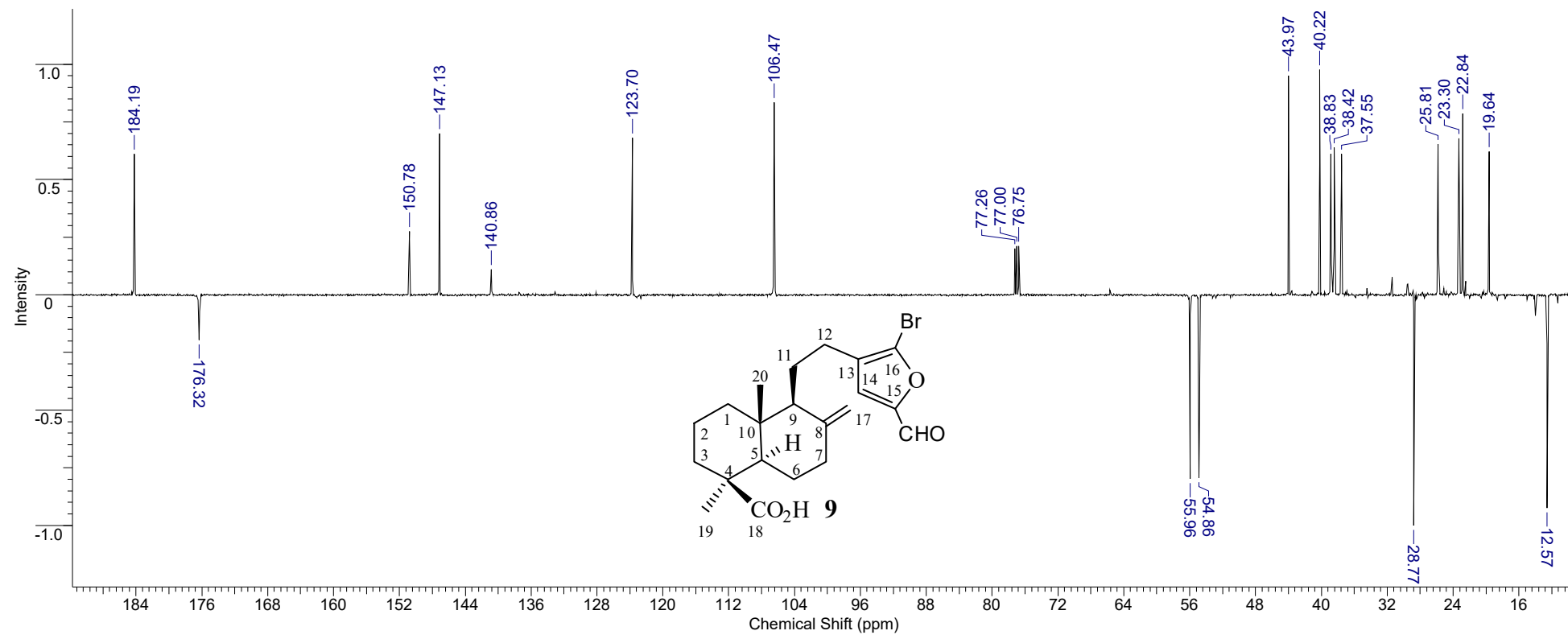
***(1S,4aR,5S,8aR)*-5-(2-(2-bromo-5-formylfuran-3-yl)ethyl)-1,4a-dimethyl-6-methylenedecahydronaphthalene-1-carboxylic acid (**9**)**

(¹H NMR, 300 MHz, CDCl₃)



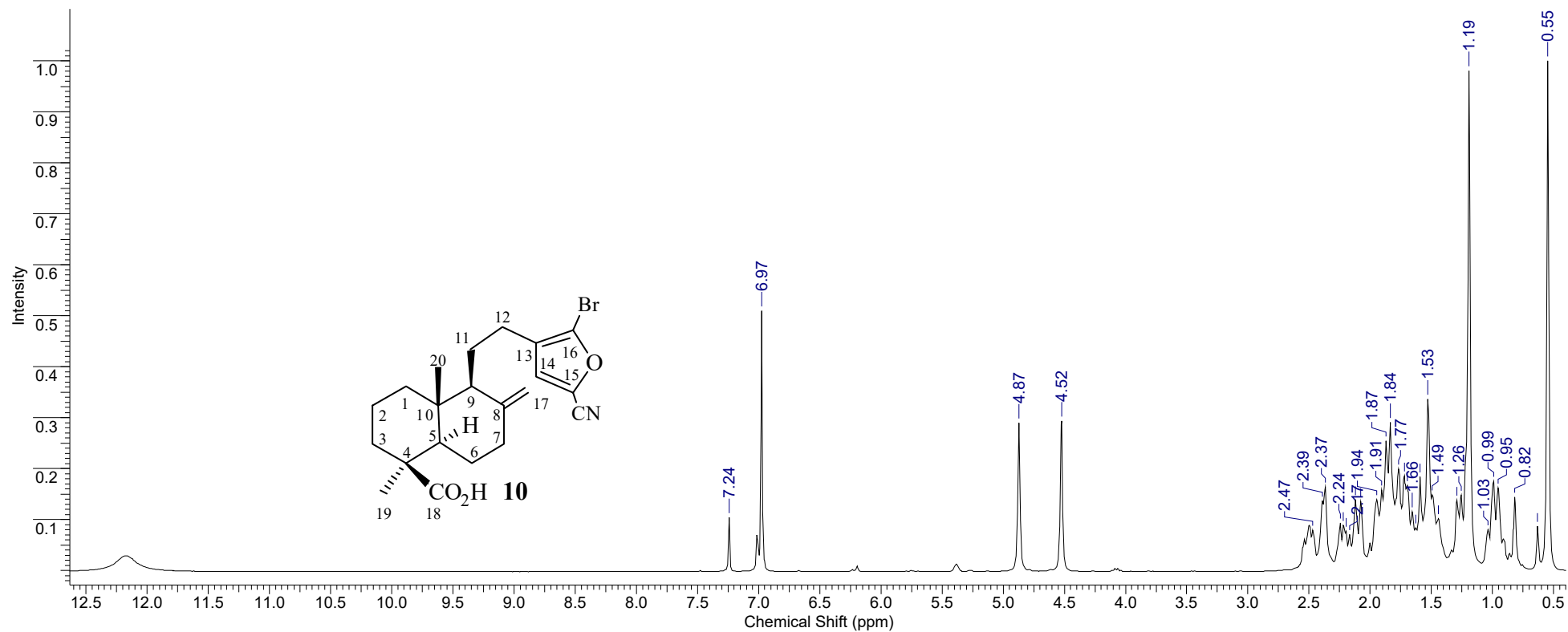
(1S,4aR,5S,8aR)-5-(2-(2-bromo-5-formylfuran-3-yl)ethyl)-1,4a-dimethyl-6-methylenedecahydronaphthalene-1-carboxylic acid (9)

(¹³C NMR, 126 MHz, CDCl₃)



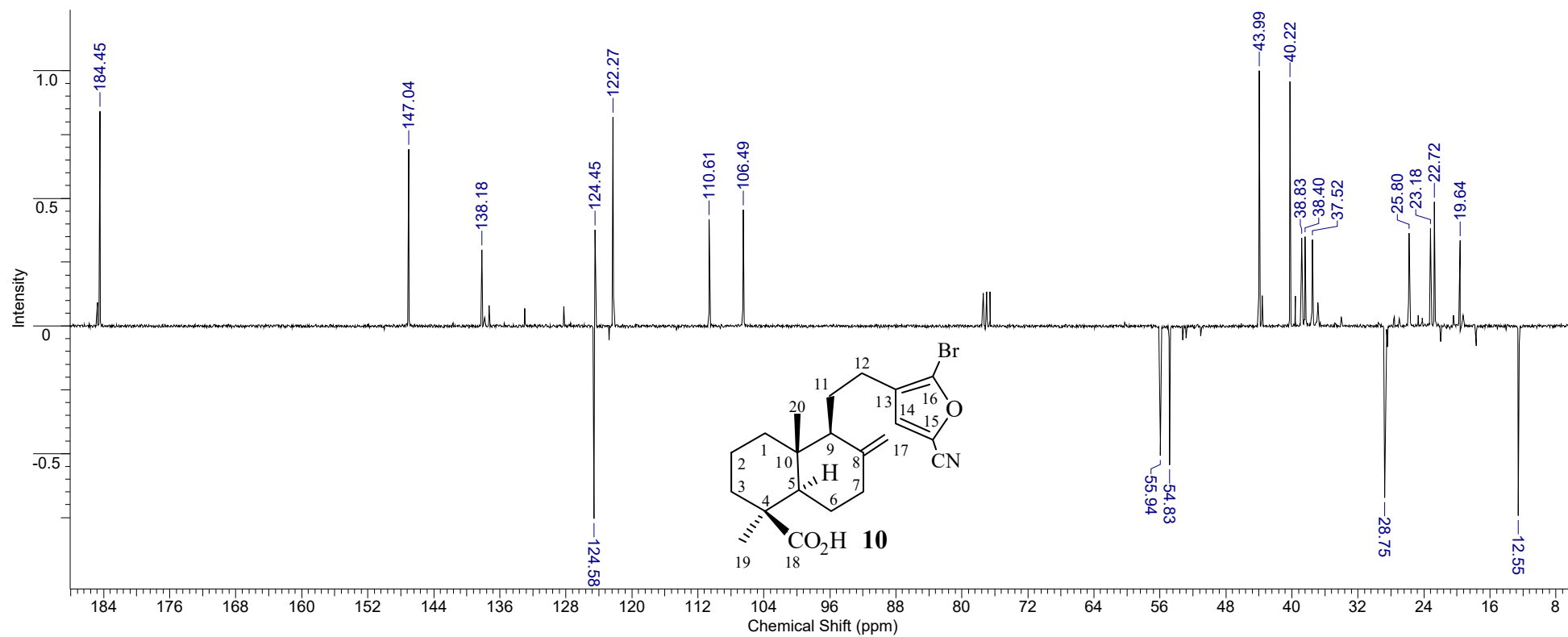
***(1S,4aR,5S,8aR)*-5-(2-(2-bromo-5-cyanofuran-3-yl)ethyl)-1,4a-dimethyl-6-methylenedecahydronaphthalene-1-carboxylic acid (10)**

(¹H NMR, 300 MHz, CDCl₃)



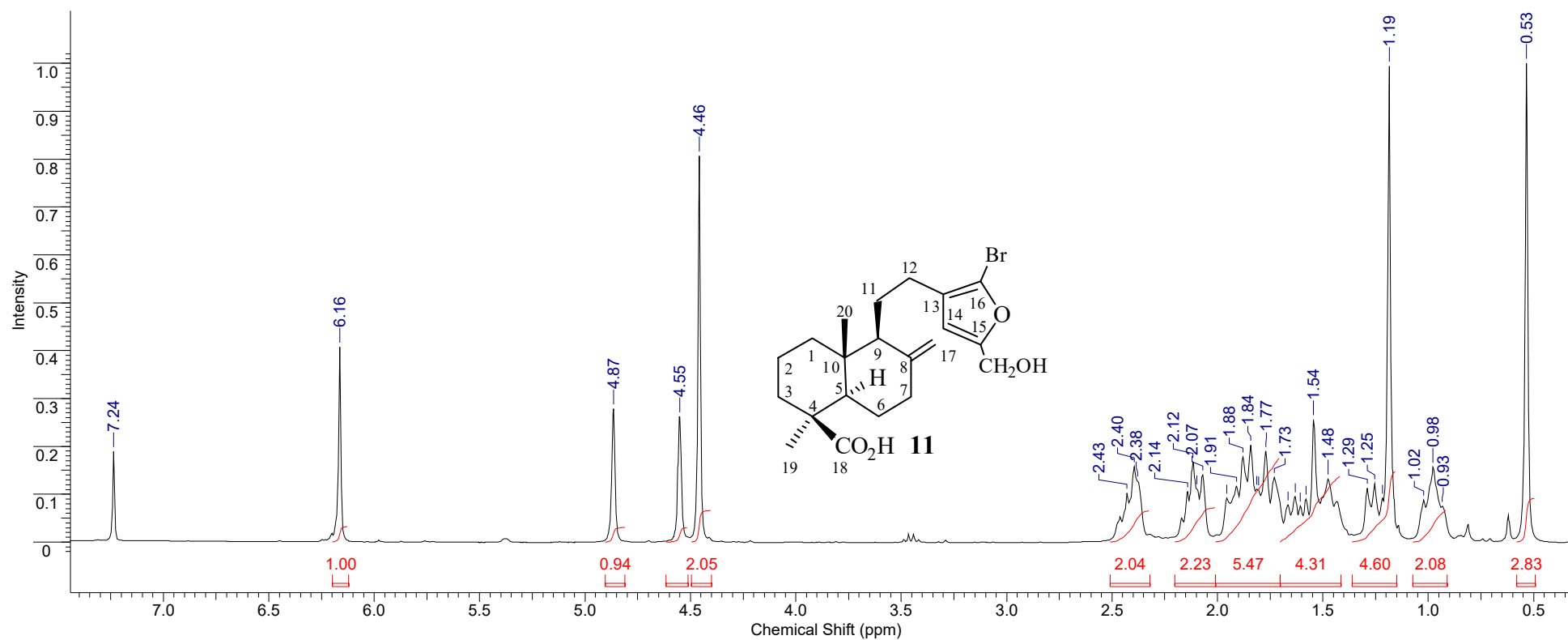
(1S,4aR,5S,8aR)-5-(2-(2-bromo-5-cyanofuran-3-yl)ethyl)-1,4a-dimethyl-6-methylenedecahydronaphthalene-1-carboxylic acid (10)

(¹³C NMR, 75 MHz, CDCl₃)



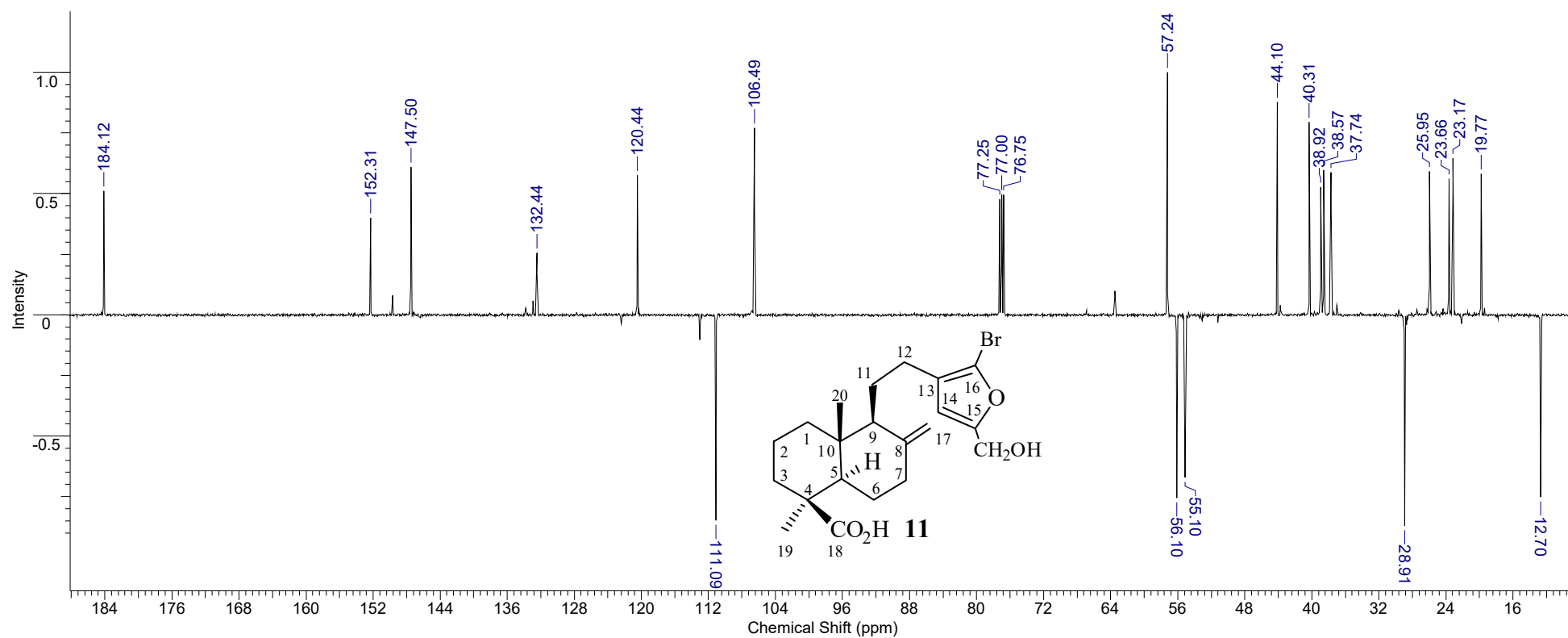
***(1S,4aR,5S,8aR)*-5-(2-(2-bromo-5-(hydroxymethyl)furan-3-yl)ethyl)-1,4a-dimethyl-6-methylenedecahydronaphthalene-1-carboxylic acid (**11**)**

(¹H NMR, 300 MHz, CDCl₃)



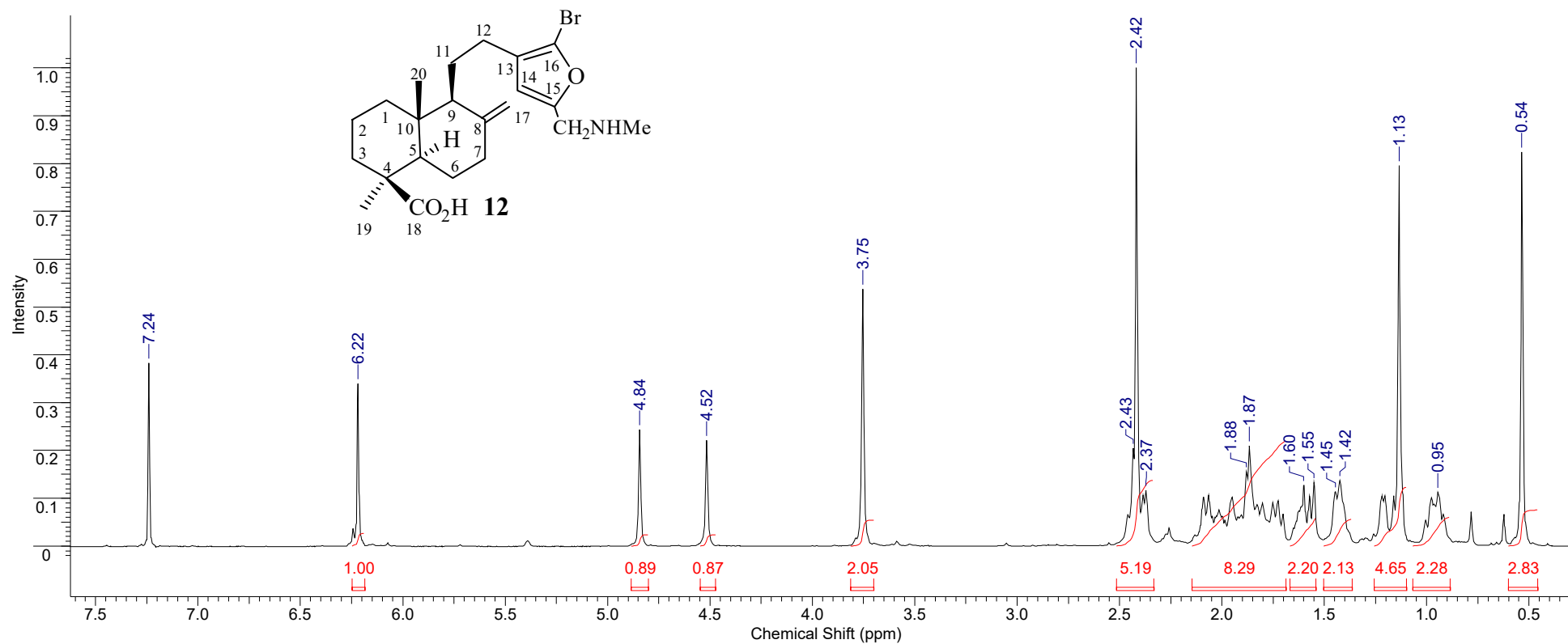
(1S,4aR,5S,8aR)-5-(2-(2-bromo-5-(hydroxymethyl)furan-3-yl)ethyl)-1,4a-dimethyl-6-methylenedecahydronaphthalene-1-carboxylic acid (11)

(^{13}C NMR, 126 MHz, CDCl_3)

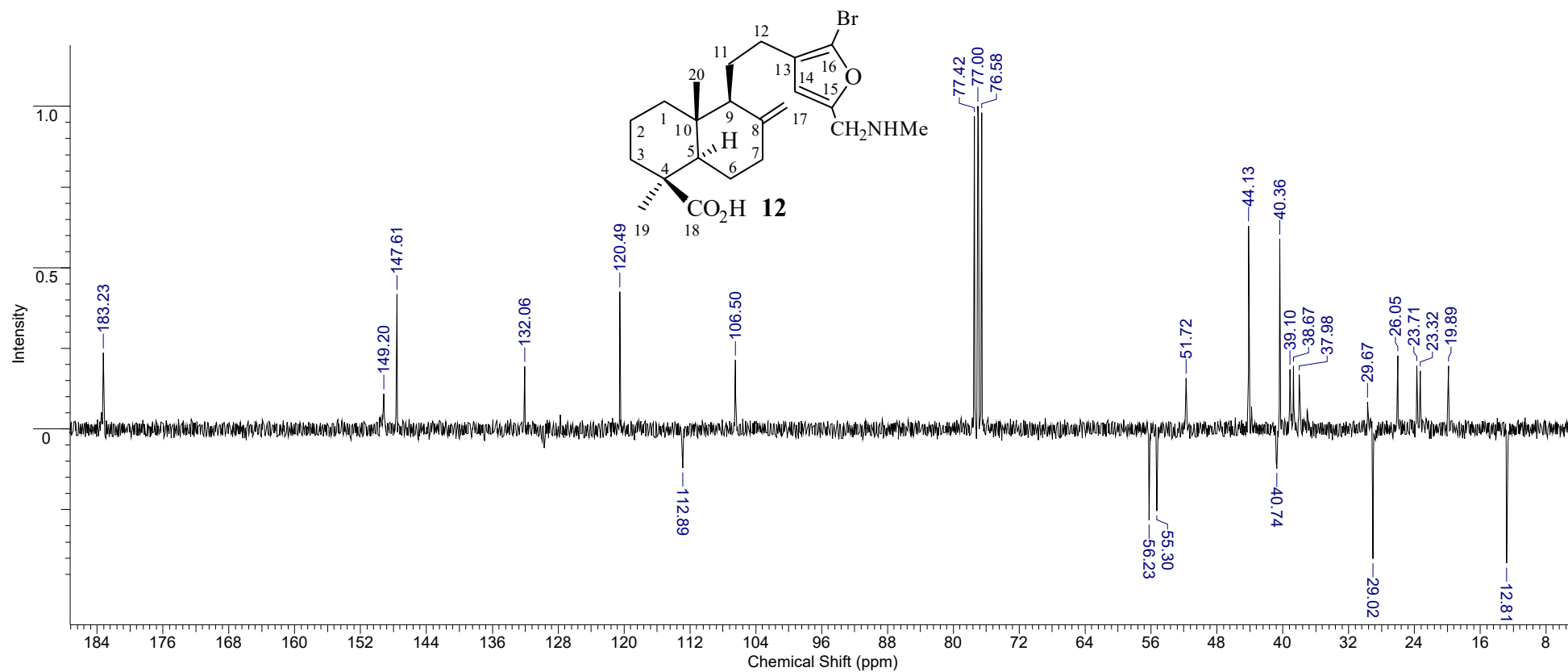


(1*S*,4*aR*,5*S*,8*aR*)-5-(2-(2-bromo-5-((methylamino)methyl)furan-3-yl)ethyl)-1,4*a*-dimethyl-6-methylenedecahydronaphthalene-1-carboxylic acid

(12) (¹H NMR, 500 MHz, CDCl₃)

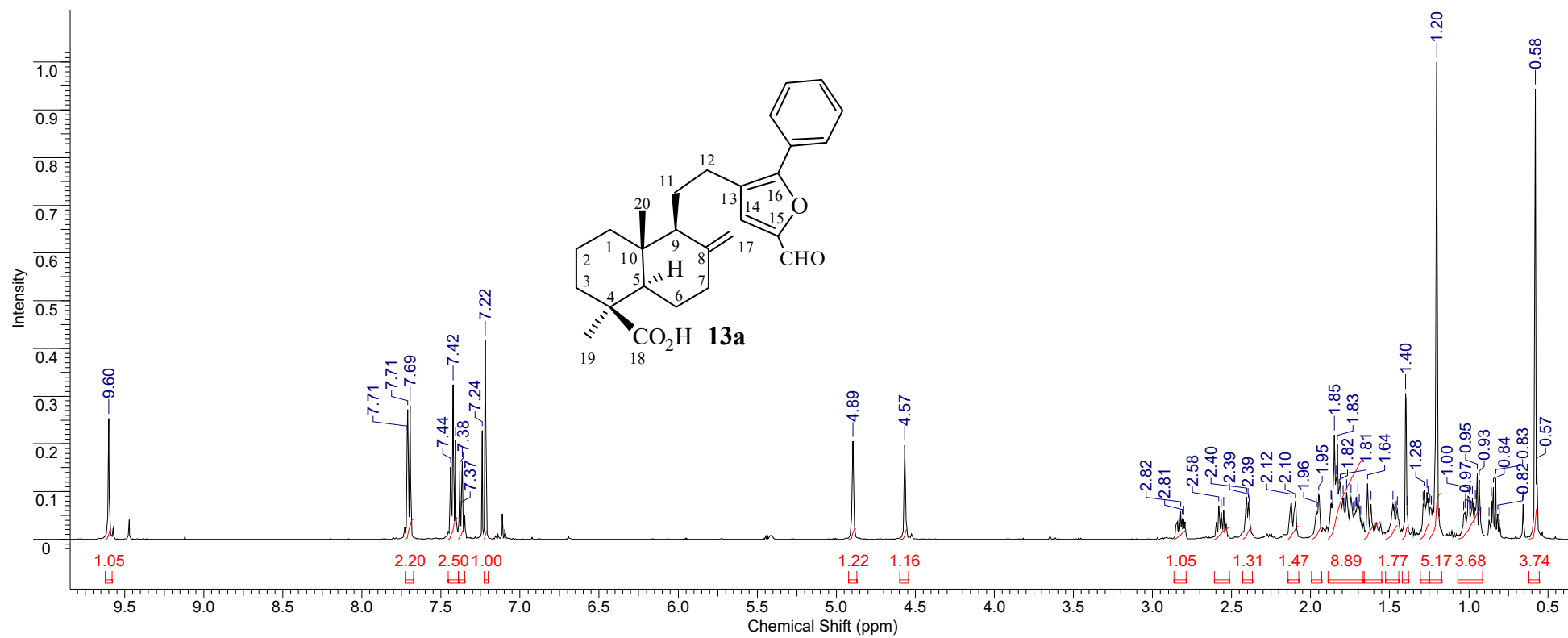


(1*S*,4*aR*,5*S*,8*aR*)-5-(2-(2-bromo-5-((methylamino)methyl)furan-3-yl)ethyl)-1,4*a*-dimethyl-6-methylenedecahydronaphthalene-1-carboxylic acid
(12) (^{13}C NMR, 75 MHz, CDCl_3)



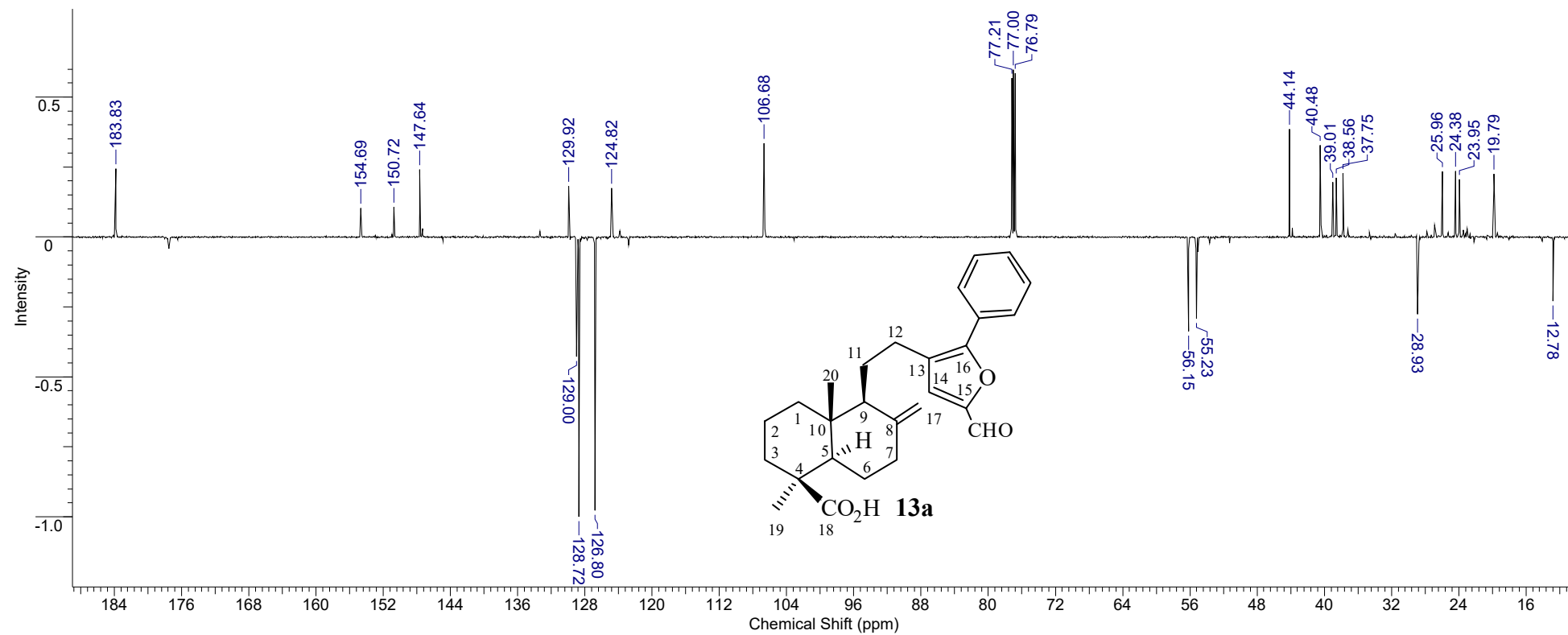
(1*S*,4*aR*,5*S*,8*aR*)-5-(2-(5-formyl-2-phenylfuran-3-yl)ethyl)-1,4*a*-dimethyl-6-methylenedecahydronaphthalene-1-carboxylic acid (13a)

(¹H NMR, 500 MHz, CDCl₃)



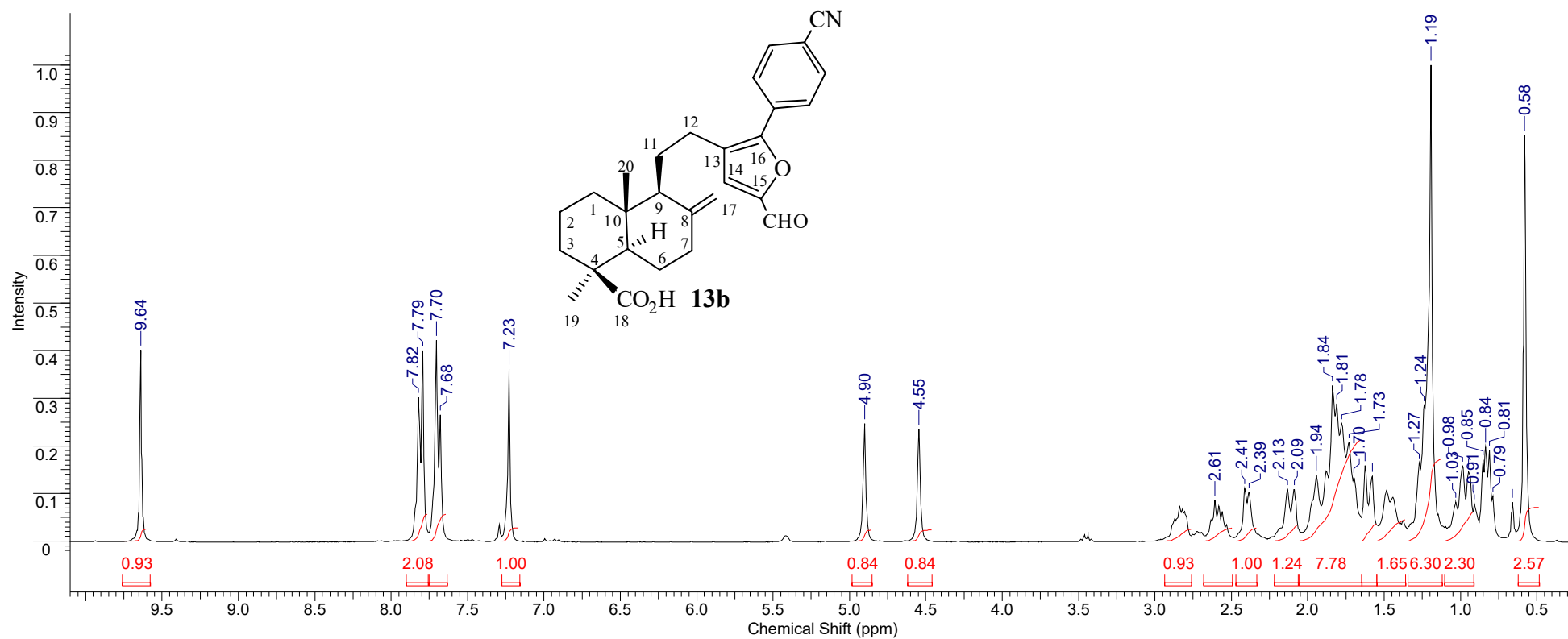
(1*S*,4*aR*,5*S*,8*aR*)-5-(2-(5-formyl-2-phenylfuran-3-yl)ethyl)-1,4*a*-dimethyl-6-methylenedecahydronaphthalene-1-carboxylic acid (13a)

(¹³C NMR, 151 MHz, CDCl₃)



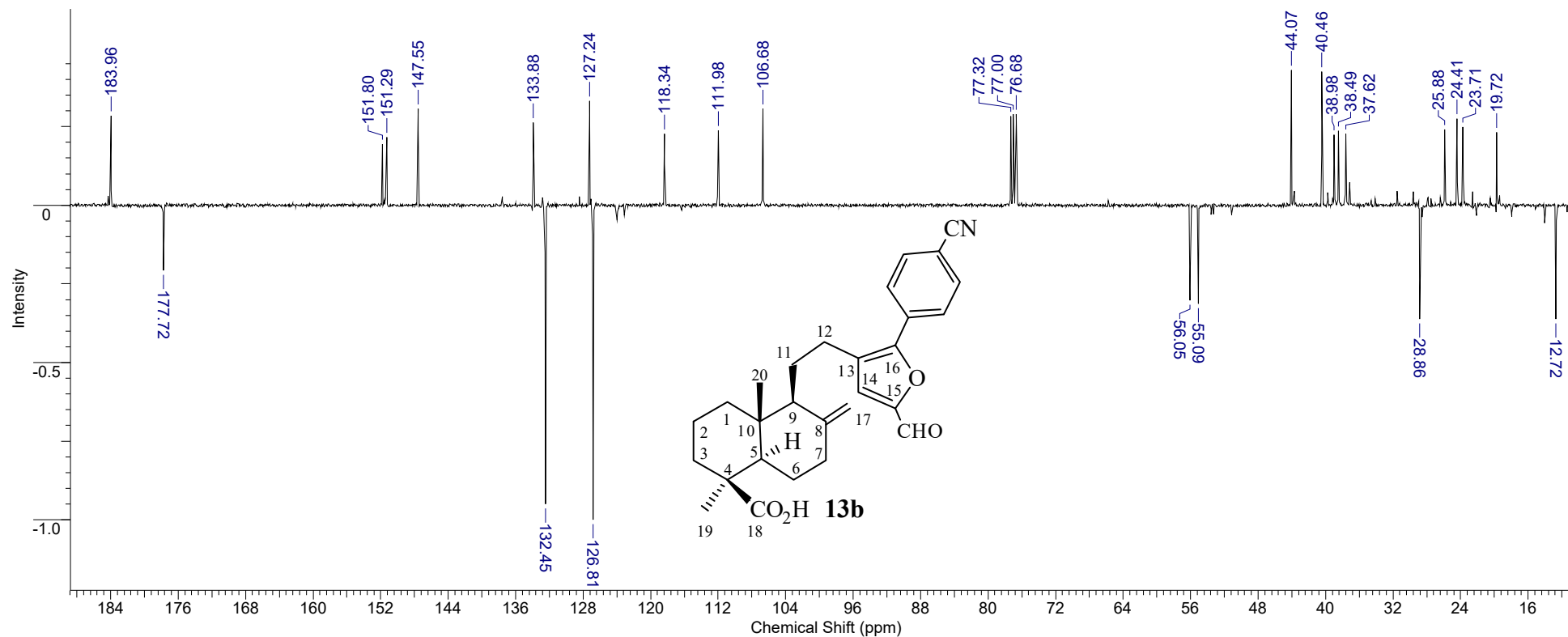
(1*S*,4*aR*,5*S*,8*aR*)-5-(2-(2-(4-cyanophenyl)-5-formylfuran-3-yl)ethyl)-1,4*a*-dimethyl-6-methylenedecahydronaphthalene-1-carboxylic acid (13b)

(¹H NMR, 300 MHz, CDCl₃)



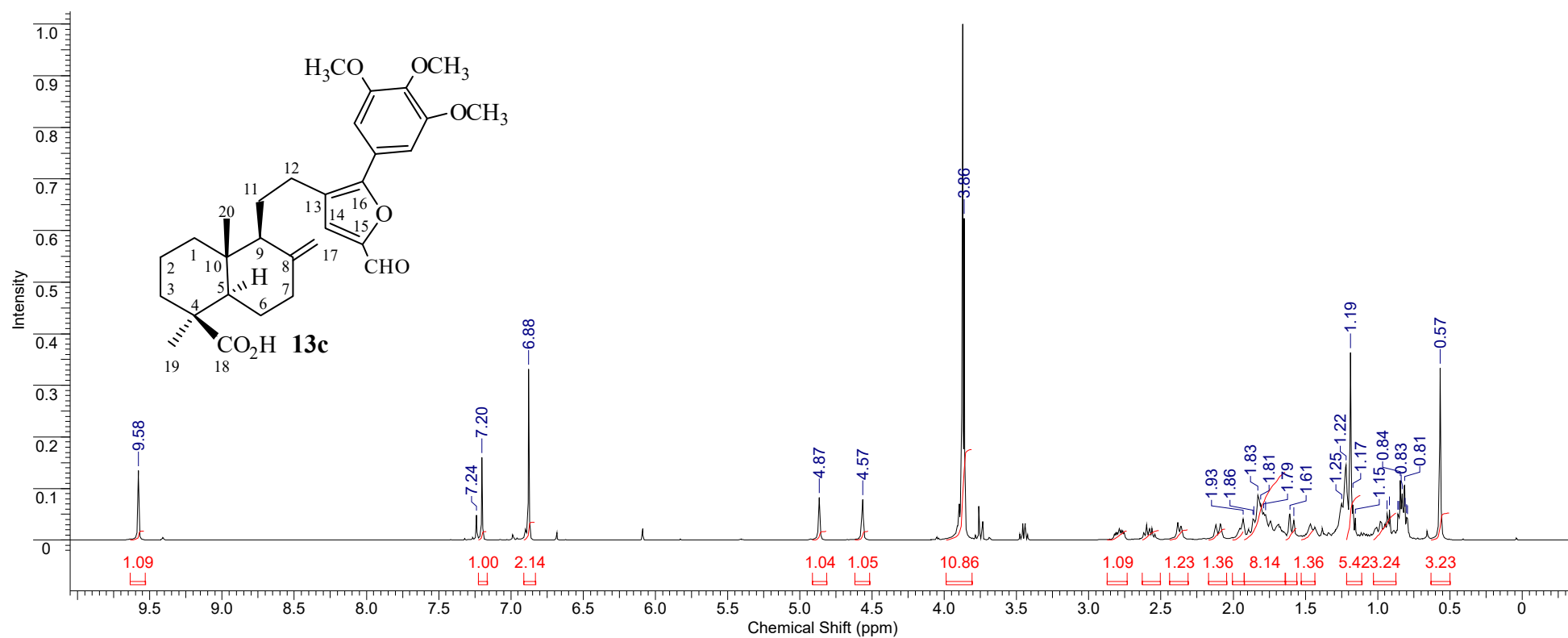
(1*S*,4*aR*,5*S*,8*aR*)-5-(2-(2-(4-cyanophenyl)-5-formylfuran-3-yl)ethyl)-1,4*a*-dimethyl-6-methylenedecahydronaphthalene-1-carboxylic acid (13b)

(¹³C NMR, 101 MHz, CDCl₃)

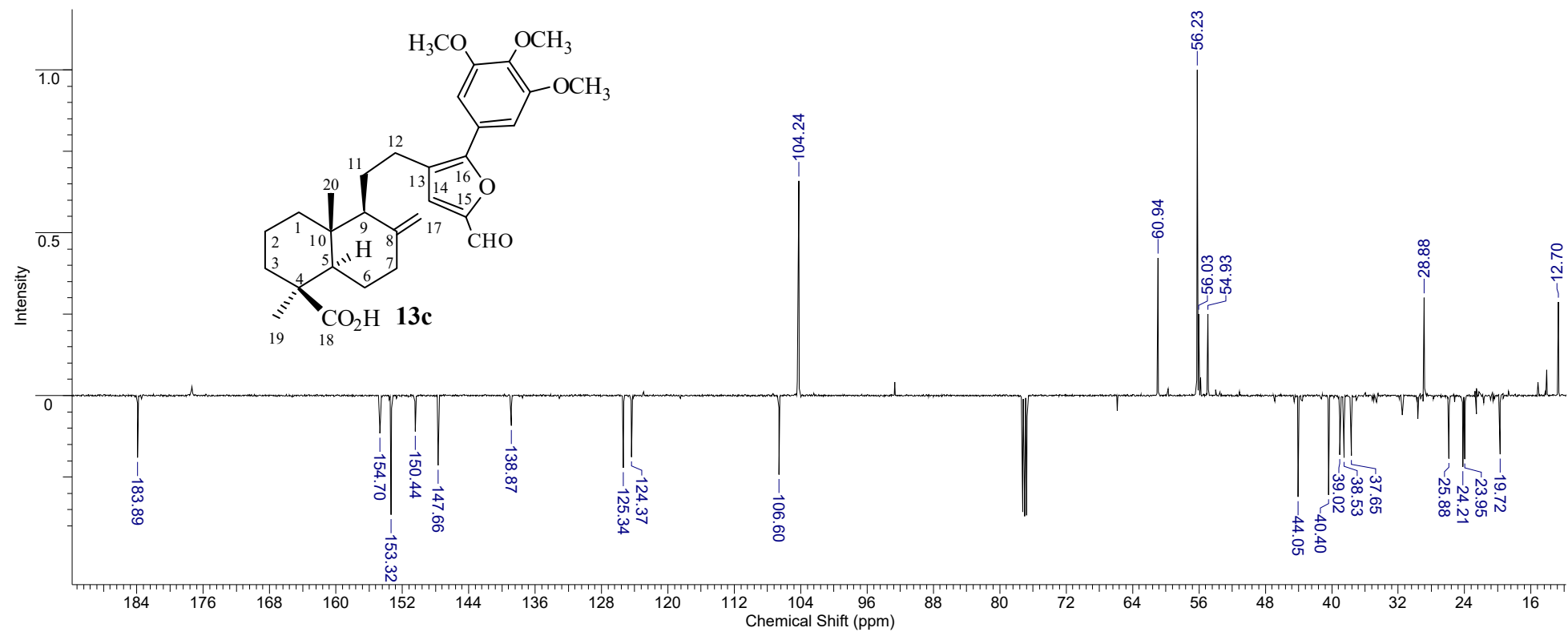


(1S,4aR,5S,8aR)-5-(2-(5-formyl-2-(3,4,5-trimethoxyphenyl)furan-3-yl)ethyl)-1,4a-dimethyl-6-methylenedecahydronaphthalene-1-carboxylic acid

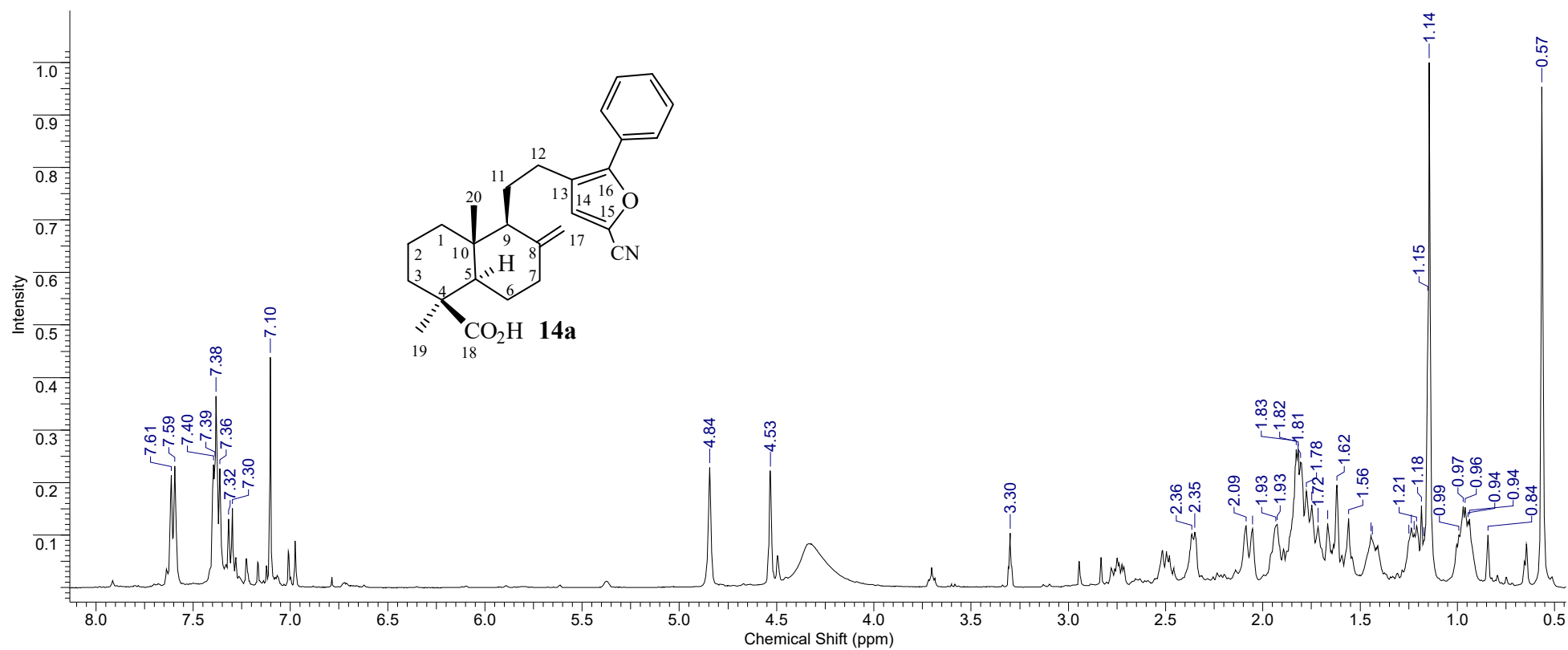
(13c) (^1H NMR, 400 MHz, CDCl_3)



(1S,4aR,5S,8aR)-5-(2-(5-formyl-2-(3,4,5-trimethoxyphenyl)furan-3-yl)ethyl)-1,4a-dimethyl-6-methylenedecahydronaphthalene-1-carboxylic acid
(13c) (¹³C NMR, 126 MHz, CDCl₃)



(1*S*,4*aR*,5*S*,8*aR*)-5-(2-(5-cyano-2-phenylfuran-3-yl)ethyl)-1,4*a*-dimethyl-6-methylenedecahydronaphthalene-1-carboxylic acid (14a**)** (¹H NMR, 400 MHz, CDCl₃)



(1S,4aR,5S,8aR)-5-(2-(5-cyano-2-phenylfuran-3-yl)ethyl)-1,4a-dimethyl-6-methylenedecahydronaphthalene-1-carboxylic acid (14a)

(¹³C NMR, 126 MHz, CDCl₃)

