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Supporting Information

for

Diversity-oriented synthesis of 17-spirosteroids

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General experimental details, compound descriptions, ^{1}H and ^{13}C NMR spectra

Content

General experimental methods

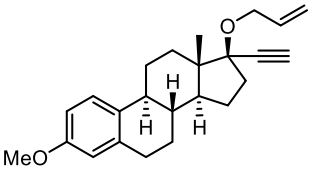
All reactions were carried out in oven-dried vessels under an atmosphere of argon in anhydrous solvents. Dry toluene was distilled in the presence of the sodium/benzophenone couple before use. Dry DMF was purchased (Aldrich). Reactions under microwave conditions were carried out in an Anton Paar Monowave 300 apparatus (850) equipped with an infrared external temperature sensor for temperature monitoring and a stirrer. Sealed microwave tubes were utilized for microwave experiments. Reactions were monitored by TLC on Merck silica gel 60 F254 aluminum sheets, using UV absorption then vanillin-H_2SO_4 (1% vanillin in ethanol + 2% H_2SO_4) or basic permanganate (1% $KMnSO_4$ + 15% Na_2CO_3 in water). The products were purified by flash silica gel column chromatography (Geduran silica gel Si 60, 40-63 µm). NMR spectra were recorded on Bruker 400 or 600 MHz Avance III spectrometers. Chemical shifts (δ) are quoted in ppm with internal calibration from the residual solvent peak ($CHCl_3$: 7.27, 77.0 ppm for ^1H and ^{13}C NMR, respectively). The following abbreviations are used to designate multiplicities: *s* = singlet, *d* = doublet, *t* = triplet, *q* = quadruplet, *m* = multiplet, *quint* = quintet, *br* = broad. High resolution mass spectra (HRMS) of synthesized compounds were measured on a Qq-ToF spectrometer using electrospray ionization (ESI). Infrared spectra were recorded on a Shimadzu 8400S FTIR spectrometer. Specific rotations were recorded on a Perkin Elmer 341 polarimeter at 20 °C. Melting points were measured on a Büchi B-545 apparatus.

General procedures

See the experimental part of the article.

Compound description

17-*O*-Allylmestranol (5a)



White powder (66% from **1** following procedure A).

M.p. = 67-69 °C.

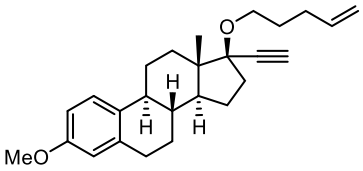
[α]$_D^{20}$ = +10 ($CHCl_3$, *c* 0.1).

^{1}H NMR (600 MHz, $CDCl_3$) δ ppm: 0.91 (*s*, 3H), 1.31-1.54 (*m*, 4H), 1.72-1.90 (*m*, 4H), 1.97-2.07 (*m*, 2H), 2.18-2.37 (*m*, 3H), 2.61 (*s*, 1H), 2.79-2.91 (*m*, 2H), 3.77 (*s*, 3H), 4.16 (*m*, 2H), 5.12 (*m*, 1H), 5.29 (*m*, 1H), 5.89-5.98 (*m*, 1H), 6.64 (*d*, J = 2.8 Hz, 1H), 6.72 (*dd*, J = 2.8, 8.6 Hz, 1H), 7.22 (*d*, J = 8.6 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ ppm: 12.8, 22.8, 26.5, 27.2, 29.8, 34.1, 37.2, 39.2, 43.5, 47.7, 49.5, 55.2, 66.7, 75.7, 85.0, 85.2, 111.5, 113.8, 115.7, 126.4, 132.6, 135.4, 137.9, 157.4.

HRMS (ESI+) *m/z*: calculated for $C_{24}H_{31}O_2^+$ [MH^+]: 351.2319; found: 351.2321.

17-*O*-(4-Penten-1-yl)mestranol (5b)



White powder (51% from **1** following procedure A).

M.p. = 52 °C.

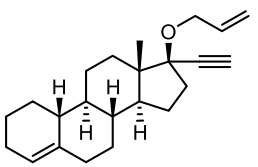
[α]$_D^{20}$ = +10 ($CHCl_3$, *c* 0.1).

^{1}H NMR (600 MHz, $CDCl_3$) δ ppm: 0.88 (*s*, 3H), 1.33-1.53 (*m*, 4H), 1.61-1.71 (m, 2H), 1.74-1.83 (*m*, 3H), 1.86-1.90 (m, 1H), 1.97-2.02 (*m*, 2H), 2.12-2.17 (m, 2H), 2.22-2.27 (*m*, 2H), 2.31-2.35 (m, 1H), 2.58 (*s*, 1H), 2.82-2.90 (*m*, 2H), 3.55 (*pseudo dt*, J = 6.6, 8.8 Hz, 1H), 3.67 (*pseudo dt*, J = 6.2, 8.8 Hz, 1H), 3.78 (*s*, 3H), 4.95-4.98 (*m*, 1H), 5.02-5.05 (*m*, 1H), 5.81-5.88 (*m*, 1H), 6.63 (*d*, J = 2.8 Hz, 1H), 6.72 (*dd*, J = 2.8, 8.5 Hz, 1H), 7.22 (*d*, J = 8.5 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ ppm: 12.7, 22.8, 26.5, 27.2, 29.4, 29.8, 30.5, 34.1, 37.0, 39.2, 43.5, 47.6, 49.4, 55.2, 64.7, 75.3, 84.9, 85.4, 111.5, 113.8, 114.5, 126.4, 132.7, 138.0, 138.6, 157.4.

HRMS (EI+) *m/z*: calculated for $C_{26}H_{34}O_2^+$ [M^+]: 378.2559; found: 378.2556.

17-*O*-Allyllynestrenol (6a)



White powder (93% from **2** following procedure A).

M.p. = 80 °C.

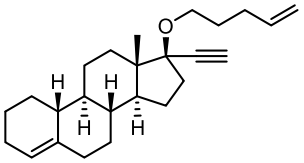
[α]$_D^{20}$ = +16 ($CHCl_3$, *c* 0.1).

^{1}H NMR (600 MHz, $CDCl_3$) δ ppm: 0.70 (*ddd*, J = 4.0, 10.6, 22.1 Hz, 1H), 0.84-0.96 (*m,* 4H), 1.05-1.42 (*m,* 6H), 1.51-1.61 (*ddd,* J = 7.6, 11.6, 11.6 Hz, 1H), 1.63-2.05 (*m,* 11H), 2.17-2.27 (*m,* 2H), 2.57 (*s,* 1H), 4.11 (*ddt*, J = 5.2, 12.6, 1.6 Hz, 1H), 4.17 (*ddt*, J = 5.2, 12.6, 1.6 Hz, 1H), 5.13 (*dq*, J = 1.6, 10.4 Hz, 1H), 5.29 (*dq*, J = 1.8, 17.2 Hz, 1H), 5.38-5.41 (*brs*, 1H), 5.94 (*ddt*, 5.2, 10.4, 17.2 Hz, 1H).

NMR ^{13}C (150 MHz, $CDCl_3$) δ ppm: 12.9, 22.1, 23.0, 25.5, 26.2, 28.8, 31.7, 34.1, 35.5, 37.1, 41.4, 42.0, 47.5, 49.5, 49.9, 66.6, 75.5, 85.1, 85.2, 115.7, 119.9, 135.4, 140.3.

HRMS (ESI+) *m/z*: calculated for $C_{23}H_{32}ONa^+$ [MNa^+]: 347.2345; found: 347.2332.

17-*O*-(4-Penten-1-yl)lynestrenol (6b)



Brown resin (49% from **2** following procedure A).

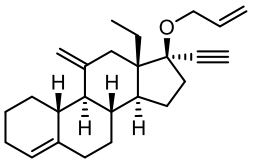
$[\alpha]_D^{20}$ = +18 ($CHCl_3$, *c* 0.1).

^{1}H NMR (600 MHz, $CDCl_3$) δ ppm: 0.70 (*ddd*, J = 4.0, 10.8, 21.8 Hz, 1H), 0.83-0.93 (*m*, 5H), 1.08-1.24 (*m*, 3H) 1.27-1.40 (*m*, 3H), 1.52-1.58 (m, 2H), 1.62-1.71 (*m*, 4H), 1.78 (*dt*, J = 4.4, 12.8 Hz, 1H), 1.82-1.86 (m, 1H), 1.90-2.03 (*m*, 5H), 2.11-2.16 (m, 2H), 2.16-2.22 (*m*, 2H), 2.53 (*s*, 1H), 3.49-3.53 (*m*, 1H), 3.63 (*dt*, J = 8.8, 6.2 Hz, 1H), 4.94-4.97 (*m*, 1H), 5.01-5.04 (*dq*, J = 17.0, 1.7 Hz, 1H), 5.39 (*brs*, 1H), 5.80-5.87 (*m*, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ ppm: 12.8, 22.1, 22.9, 25.5, 26.2, 28.8, 29.4, 30.5, 31.7, 34.0, 35.5, 37.0, 41.4, 42.0, 47.5, 49.4, 49.9, 64.7, 75.1, 84.9, 114.5, 119.9, 138.7, 140.4, 157.4.

HRMS (ESI+) *m/z*: calculated for $C_{25}H_{36}ONa^+$ [MNa^+]: 375.2658; found: 375.2642.

17-*O*-Allyldesogestrel (7)



Beige powder (58% from **3** following procedure A).

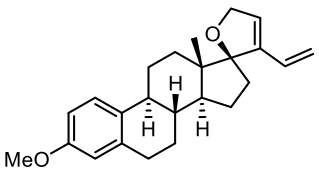
M.p. = 70 °C.

$[\alpha]_D^{20}$ = +50 ($CHCl_3$, *c* 0.1).

^{1}H NMR (600 MHz, $CDCl_3$) δ ppm: 0.83-0.98 (*m*, 2H), 1.04 (*t*, J = 7.4 Hz, 3H), 1.12-1.19 (*m*, 1H), 1.31-1.48 (*m*, 6H), 1.61-1.69 (*m*, 3H), 1.88 (*ddd*, J = 12.7, 10.4, 7.6 Hz, 1H), 1.92-1.99 (*m*, 3H), 2.11 (*ddd*, J = 13.6, 12.1, 3.6 Hz, 1H), 2.18-2.29 (*m*, 4H), 2.34-2.36 (*d*, J = 12.3 Hz, 1H), 2.61 (*s*, 1H), 2.66 (*d*, J = 12.5 Hz, 1H), 4.08 (*ddt*, J = 12.7, 5.0, 1.6 Hz, 1H), 4.20 (ddt, J = 12.7, 5.1, 1.6 Hz, 1H), 4.77 (*brs*, 1H), 4.97 (*m*, 1H), 5.12 (*ddd*, J = 10.5, 3.3, 1.5 Hz, 1H), 5.29 (*dq*, J = 17.2, 1.8 Hz, 1H), 5.47 (*m*, 1H), 5.92 (*ddt*, J = 17.2, 10.3, 5.2 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ ppm: 9.0, 20.2, 21.88, 21.95, 25.7, 29.1, 29.7, 31.7, 35.5, 36.6, 37.2, 41.4, 42.5, 51.0, 51.8, 54.7, 66.9, 75.9, 85.11, 86.4, 108.4, 115.5, 121.2, 135.3, 140.0, 147.7.

(2'*S*,8*R*,9*S*,13*S*,14*S*)-3-Methoxy-13-methyl-3'-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-5'*H*-spiro[cyclopenta[*a*]phenanthrene-17,2'-furan] (8a)



White powder (70% from **5a** following procedure B).

M.p. = 128-129 °C.

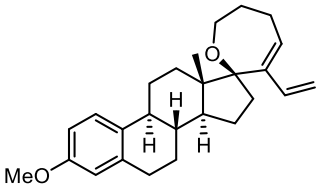
[α]$_D^{20}$ = +9 ($CHCl_3$, *c* 0.1).

^{1}H NMR (600 MHz, $CDCl_3$) δ ppm : 0.96 (*s*, 3H), 1.28-1.39 (*m*, 1H), 1.42-1.60 (*m*, 6H), 1.69-1.79 (*m*, 1H), 1.87-1.94 (*m*, 1H), 1.95-2.07 (*m*, 2H), 2.07-2.14 (*m*, 1H), 2.21-2.27 (*m*, 1H), 2.76-2.93 (*m*, 2H), 3.77 (*s*, 3H), 4.53 (*s*, 2H), 5.13 (*dd*, J = 1.8, 10.8 Hz, 1H), 5.50 (*dd*, J = 1.8, 17.2 Hz, 1H), 5.96 (*s*, 1H), 6.18-6.29 (*m*, 1H), 6.62 (*d*, J = 2.7 Hz, 1H), 6.69 (*dd*, J = 2.7, 8.5 Hz, 1H), 7.17 (*d*, J = 8.5 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ ppm : 15.4, 23.7, 26.4, 27.4, 29.9, 32.6, 34.4, 39.3, 43.7, 47.6, 49.4, 55.2, 72.7, 99.9, 111.4, 113.7, 116.1, 122.6, 126.3, 131.2, 132.7, 134.0, 144.4, 157.4.

HRMS (ESI+) *m/z*: calculated for $C_{24}H_{31}O_2^+$ [MH^+]: 351.2319; found: 351.2318.

(2'*S*,8*R*,9*S*,13*S*,14*S*)-3-Methoxy-13-methyl-3'-vinyl-6,6',7,7',8,9,11,12,13,14,15,16-dodecahydro-5'*H*-spiro[cyclopenta[*a*]phenanthrene-17,2'-oxepine] (8b)



White powder (67% from **5b** following procedure B).

M.p. = 168 °C.

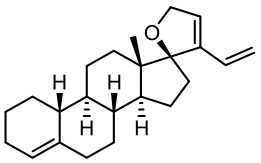
[α]$_D^{20}$ = +14.6 ($CHCl_3$, *c* 0.1).

^{1}H NMR (600 MHz, $CDCl_3$) δ ppm : 0.96 (*s*, 3H), 1.25-1.32 (*m*, 1H), 1.45-1.60 (*m*, 5H), 1.66-1.73 (*m*, 2H), 1.80-1.94 (*m*, 5H), 2.06 (*dt*, J = 4.0, 11.5 Hz, 1H), 2.21-2.29 (*m*, 2H), 2.72 (*pseudo hept.*, J = 6.5 Hz, 1H), 2.79-2.88 (*m*, 2H), 3.60 (*ddd*, J = 6.4, 11.6, 11.6 Hz, 1H), 3.77 (*s*, 3H, OCH_3), 3.77-3.80 (m, 1H), 4.84 (*dd*, J = 2.0, 10.5 Hz, 1H), 5.28 (*dd*, J = 2.0, 16.4 Hz, 1H,), 6.05 (*dd*, J = 6.7, 8.9 Hz, 1H), 6.28 (dd, J = 10.5, 16.4 Hz, 1H), 6.61 (*d*, J = 2.7 Hz, 1H), 6.69 (*dd*, J = 2.7, 8.5 Hz, 1H), 7.18 (*d*, J = 8.5 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ ppm : 14.9, 22.5, 24.1, 26.3, 26.35, 27.6, 29.8, 32.5, 34.0, 39.2, 43.6, 48.7, 48.9, 55.2, 61.7, 95.3, 111.3, 112.7, 113.7, 126.2, 126.4, 132.9, 137.9, 140.4, 143.5, 157.3.

HRMS (ESI+) *m/z*: calculated for $C_{26}H_{35}O_2^+$ [MH^+]: 379.2632; found: 379.2635.

(2'*S*,8*R*,9*S*,10*R*,13*S*,14*S*)-13-Methyl-3'-vinyl-1,2,3,6,7,8,9,10,11,12,13,14,15,16-tetradecahydro-5'*H*-spiro[cyclopenta[*a*]phenanthrene-17,2'-furan] (9a)



White powder (76% from **6a** following procedure B).

M.p. = 60 °C.

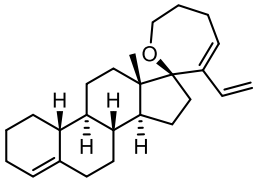
[α]$_D^{20}$ = +205 ($CHCl_3$, *c* 0.1).

^{1}H NMR (600 MHz, $CDCl_3$) δ ppm : 0.57 (*ddd*, J = 4.2, 10.6, 21.7 Hz, 1H), 0.83-0.91 (*ddd*, J = 3.9, 12.8, 24.7 Hz, 1H), 0.96 (*s,* 3H), 1.04-1.11 (*m*, 1H), 1.17 (*ddd*, J = 3.3, 12.2, 24.7 Hz, 1H), 1.21-1.45 (*m,* 6H), 1.62-1.80 (*m,* 5H), 1.86-2.06 (*m,* 6H), 2.16-2.24 (*m,* 1H), 4.43-4.59 (*m,* 2H), 5.09 (*dd*, J = 1.9, 10.8 Hz, 1H), 5.39 (*brs,* 1H), 5.47 (*dd*, J = 1.8, 17.2 Hz, 1H), 5.93 (*s,* 1H), 6.18 (*dd*, J = 10.8, 17.2 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ ppm: 15.5, 22.1, 23.8, 25.5, 26.0, 28.8, 31.8, 32.6, 34.4, 35.5, 41.6, 42.0, 47.5, 49.4, 50.1, 72.6, 99.9, 115.9, 119.9, 122.4, 131.2, 140.2, 144.5.

HRMS (ESI+) *m/z*: calculated for $C_{23}H_{33}O^+$ [MH^+]: 325.2526; found: 325.2515.

(2'*S*,8*R*,9*S*,10*R*,13*S*,14*S*)-13-Methyl-3'-vinyl-1,2,3,6,6',7,7',8,9,10,11,12,13,14,15,16-hexadecahydro-5'*H*-spiro[cyclopenta[*a*]phenanthrene-17,2'-oxepine] (9b)



Colorless resin (80% from **6b** following procedure B).

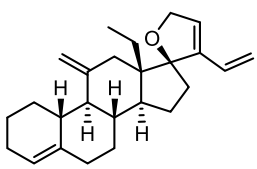
[α]$_D^{20}$ = +126 ($CHCl_3$, *c* 0.1).

^{1}H NMR (600 MHz, $CDCl_3$) δ ppm : 0.52 (*ddd*, J = 4.3, 10.9, 21.6 Hz, 1H), 0.78-0.90 (*m*, 3H), 0.96 (*s*, 3H), 1.02-1.09 (*m*, 2H), 1.14-1.28 (*m*, 2H), 1.30-1.50 (*m*, 4H), 1.50-1.62 (*m*, 2H), 1.63-1.69 (*m*, 3H), 1.84-2.02 (*m*, 6H), 2.17-2.23 (*m*, 2H), 2.68 (*ddd*, J = 6.5, 12.8, 19.3 Hz, 1H), 3.57 (*ddd*, J = 6.3, 11.2, 12.0 Hz, 1H), 3.76 (*dd*, J = 8.0, 12.2 Hz, 1H), 4.79 (*dd*, J = 2.1, 10.5 Hz, 1H), 5.24 (*dd*, J = 2.1, 16.5 Hz, 1H), 5.38 (*brs*, 1H), 6.01 (*dd*, J = 6.5, 8.9 Hz, 1H), 6.23 (*dd*, J = 10.4, 16.5 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ ppm: 15.0, 22.1, 22.4, 24.2, 25.5, 26.0, 26.3, 28.8, 31.9, 32.5, 34.0, 35.5, 41.4, 42.0, 48.6, 48.8, 50.1, 61.6, 95.4, 112.6, 119.7, 126.2, 140.4, 140.7, 143.5.

HRMS (ESI+) *m/z*: calculated for $C_{25}H_{37}O^+$ [MH^+]: 353.2839; found: 353.2854.

(2'*S*,8*S*,9*S*,10*R*,13*S*,14*S*)-13-Ethyl-11-methylene-3'-vinyl-1,2,3,6,7,8,9,10,11,12,13,14,15,16-tetradecahydro-5'*H*-spiro[cyclopenta[*a*]phenanthrene-17,2'-furan] (10)



Colorless resin (82% from **7** following procedure A).

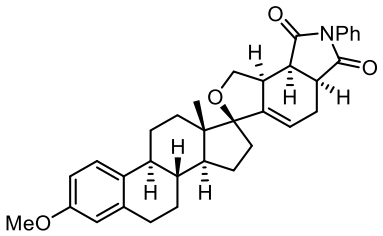
^{1}H NMR (600 MHz, $CDCl_3$) δ ppm: 0.87-0.94 (*m*, 1H), 1.04 (*t*, J = 7.2 Hz, 3H), 1.06-1.12 (*m*, 1H), 1.20-1.24 (*m*, 1H), 1.26 (*brs*, 1H), 1.36-1.49 (*m*, 4H), 1.57-1.64 (*m*, 3H), 1.70 (*dq*, J = 12.3, 3.4 Hz, 1H), 1.77 (*d*, J = 12.3 Hz, 1H), 1.93-1.98 (*m*, 3H), 2.00-2.08

(*m*, 2H), 2.18-2.26 (*m*, 3H), 2.35 (*d*, J = 12.3 Hz, 1H), 4.46 (*d*, J = 13.6 Hz, 1H), 4.51 (*dt*, J = 13.6, 1.8 Hz, 1H), 4.73 (*brs*, 1H), 4.92 (*m*, 1H), 5.13 (*dd*, J = 10.7, 1.7 Hz, 1H), 5.46-5.51 (*m*, 2H), 5.98 (*brs*, 1H), 6.23 (*ddq*, J = 17.2, 10.8, 1.3 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ ppm: 9.1, 21.4, 22.0, 22.8, 25.7, 29.1, 31.8, 35.1, 35.5, 36.6, 40.5, 42.6, 51.4, 52.4, 54.8, 72.2, 100.4, 108.1, 116.3, 121.2, 122.8, 131.0, 140.1, 144.7, 148.0.

HRMS (ESI+) *m/z*: calculated for $C_{25}H_{35}O^+$ [MH^+]: 351.2682; found: 351.2692.

(3'*S*,5a'*S*,8*R*,8a'*R*,8b'*S*,9*S*,13*S*,14*S*)-3-Methoxy-13-methyl-7'-phenyl-1',5',5a',6,7,8,8b',9,11,12,13,14,15,16-tetradecahydrospiro[cyclopenta[*a*]phenanthrene-17,3'-furo[3,4-*e*]isoindole]-6',8'(7'*H*,8a'*H*)-dione (16a)



Pale brown powder (83% from **5a** following procedure C).

M.p. = 107-108 °C

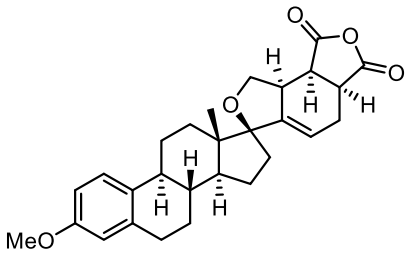
[α]$_D^{20}$ = +15 ($CHCl_3$, *c* 0.1).

NMR ^{1}H (600 MHz, $CDCl_3$) δ ppm : 0.97 (*s*, 3H), 1.29-1.55 (*m*, 6H), 1.63-1.75 (*m*, 3H), 1.86-1.95 (*m*, 1H), 2.09-2.31 (*m*, 4H), 2.81-2.94 (*m*, 3H), 3.00-3.08 (*m*, 1H), 3.33 (*td*, J = 1.8, 6.0 Hz, 1H), 3.40 (*t*, J = 8.5 Hz, 1H), 3.78 (*s*, 3H), 4.03-4.07 (*dd*, J = 7.8, 9.6 Hz, 1H), 4.73 (*dd*, J = 2.1, 9.6 Hz, 1H), 5.74-5.79 (*m*, 1H), 6.64 (*d*, J = 2.8 Hz, 1H), 6.71 (*dd*, J = 2.8, 8.6 Hz, 1H), 7.16 (*d*, J = 8.6 Hz, 1H), 7.19-7.22 (*m*, 2H), 7.36 (*tt*, J = 1.2, 6.8 Hz, 1H), 7.43 (*t*, J = 7.5 Hz, 2H).

NMR ^{13}C (150 MHz, $CDCl_3$) δ ppm : 13.6, 22.9, 25.1, 26.6, 27.2, 29.8, 35.1, 35.3, 39.1, 39.9, 40.8, 41.2, 43.4, 47.1, 49.1, 55.2, 65.8, 94.7, 111.5, 113.7, 117.0, 126.2, 126.4 (2C), 128.5, 129.0 (2C), 131.9, 132.4, 137.9, 151.4, 157.4, 176.2, 178.4.

HRMS (ESI+) *m/z*: calculated for $C_{34}H_{38}NO_4^+$ [MH^+]: 524.2795; found: 524.2811.

(3*S*,5a*S*,8a*R*,8b*S*,8'*R*,9'*S*,13'*S*,14'*S*)-3'-Methoxy-13'-methyl-5,5a,6',7',8',9',11',12',13',14',15',16'-dodecahydro-1*H*-spiro[benzo[1,2-*c*:3,4-*c*']difuran-3,17'-cyclopenta[*a*]phenanthrene]-6,8(8a*H*,8b*H*)-dione (16b)



White powder (10% from **5a** following procedure C).

M.p. = 220 °C

[α]$_D^{20}$ = +13 ($CHCl_3$, *c* 0.1).

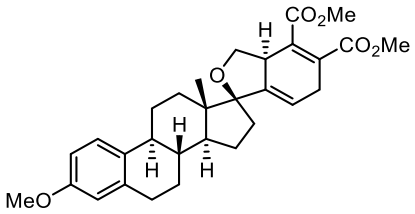
NMR ^{1}H (600 MHz, $CDCl_3$) δ ppm: 0.95 (*s*, 3H), 1.29-1.38 (*m*, 2H), 1.39-1.54 (*m*, 4H), 1.63-1.76 (*m*, 3H), 1.88-1.94 (*m*, 1H), 2.07-2.17 (*m*, 2H), 2.18-2.23 (*m*, 1H), 2.27-2.31 (*m*, 1H), 2.76-2.80 (*m*, 1H), 2.82-2.88 (*m*, 2H), 2.93 (*ddd*, J = 1.7, 7.4, 15.2 Hz, 1H), 3.43-3.44 (*m*, 1H), 3.54 (*dd*, J = 8.0, 9.6 Hz, 1H), 3.78 (*s*, 3H), 4.06 (*dd*, J = 8.1, 9.9

Hz, 1H), 4.54 (*dd*, J = 2.6, 9.8 Hz, 1H), 5.79 (*dt*, J = 3.1, 7.2 Hz, 1H), 6.63 (*d*, J = 2.8 Hz, 1H), 6.70 (*dd*, J = 2.8, 8.6 Hz, 1H), 7.15 (*d*, J = 8.6 Hz, 1H).

NMR ^{13}C (150 MHz, $CDCl_3$) δ ppm: 13.6, 22.9, 25.1, 26.5, 27.2, 29.8, 34.7, 35.0, 39.0, 40.1 (2C), 42.0, 43.4, 47.2, 49.0, 55.2, 65.7, 94.8, 111.5, 113.7, 116.5, 126.2, 132.3, 137.9, 152.0, 157.5, 170.7, 174.0.

HRMS (ESI+) *m/z*: calculated for $C_{28}H_{33}O_5^+$ [MH^+]: 449.2323; found: 449.2334.

(1'*S*,3a'*R*,8*R*,9*S*,13*S*,14*S*)-Dimethyl 3-methoxy-13-methyl-3a',6,6',7,8,9,11,12,13,14,15,16-dodecahydro-3'*H*-spiro[cyclopenta[*a*]phenanthrene-17,1'-isobenzofuran]-4',5'-dicarboxylate (16c)



White solid (73% from **5a** following procedure C).

M.p. = 63.6 °C

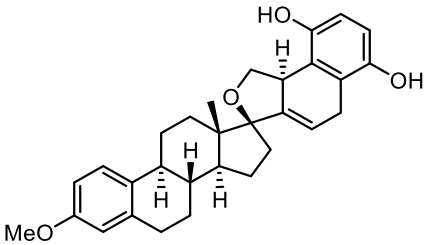
[α]$_D^{20}$ = +8 ($CHCl_3$, *c* 0.1).

NMR ^{1}H (600 MHz, $CDCl_3$) δ ppm : 0.92 (*s,* 3H), 1.20-1.26 (*m*, 1H), 1.29-1.39 (*m*, 1H), 1.43-1.51 (*m,* 4H), 1,61-1,65 (*m,* 1H), 1.70-1.75 (*m,* 1H), 1.90-1.95 (*m,* 2H), 2.07-2.15 (*m,* 2H), 2.21-2.29 (*m,* 1H), 2.80-2.93 (*m*, 2H), 3.16-3.24 (*m,* 2H), 3.43-3.57 (*m,* 2H), 3.78 (*s*, 3H), 3.80 (*s*, 3H), 3.81 (*s*, 3H), 4.23 (*t*, J = 7.1 Hz, 1H), 5.55 (*m*, 1H), 6.63 (*d*, J = 2.8 Hz, 1H), 6.71 (*dd*, J = 2.8, 8.6 Hz, 1H), 7.18 (*d*, J = 8.7 Hz, 1H).

NMR ^{13}C (150 MHz, $CDCl_3$) δ ppm: 14.1, 22.9, 26.2, 27.3, 29.6, 29.9, 32.8, 36.2, 39.2, 41.3, 43.7, 46.6, 48.5, 52.3, 52.4, 55.2, 68.8, 94.1, 111.5, 113.8, 115.0, 126.3, 132.1, 132.6, 135.1, 138.0, 144.5, 157.4, 167.4, 168.4.

HRMS (ESI+) *m/z*: calculated for $C_{30}H_{37}O_6^+$ [MH^+]: 493.2585; found: 493.2599.

(3'*S*,8*R*,9*S*,9b'*R*,13*S*,14*S*)-3-Methoxy-13-methyl-5',6,7,8,9,9b',11,12,13,14,15,16-dodecahydro-1'*H*-spiro[cyclopenta[*a*]phenanthrene-17,3'-naphtho[1,2-*c*]furan]-6',9'-diol (16d)



White powder (61% from **5a** following procedure C).

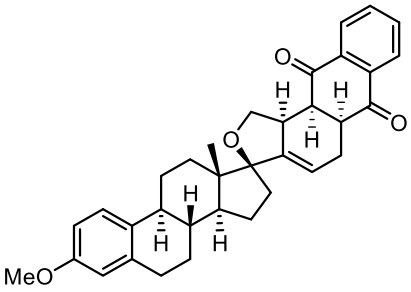
[α]$_D^{20}$ = +14 ($CHCl_3$, *c* 0.1).

M.p. = 116-118 °C

NMR ^{1}H (400 MHz, $CDCl_3$) δ ppm : 0.98 (*s*, 3H), 1.26-1.60 (*m*, 6H), 1.67-1.79 (*m*, 2H), 1.92-2.03 (*m*, 2H), 2.11-2.26 (*m*, 3H), 2.82-2.94 (*m*, 2H), 3.34 (*dd*, J = 7.8, 21.4 Hz, 1H), 3.51-3.60 (*m*, 2H), 3.73-3.83 (*m*, 4H), 4.81 (*t*, J = 7.8 Hz, 1H), 5.24 (br. *s,* 1H), 5.45 (br. *s,* 1H), 5.70-5.74 (*m*, 1H), 6.47 (*d*, J = 8.5 Hz, 1H), 6.54 (*d*, J = 8.5 Hz, 1H), 6.64 (*d*, J = 2.7 Hz, 1H), 6.70 (*dd*, J = 2.7, 8.5 Hz, 1H), 7.19 (*d*, J = 8.5 Hz, 1H).

NMR ^{13}C (150 MHz, $CDCl_3$) δ ppm : 14.2, 23.0, 25.5, 26.4, 26.9, 27.4, 29.9, 33.0, 36.3, 39.3, 40.0, 43.7, 46.5, 48.4, 55.2, 70.5, 93.4, 111.4, 112.8, 112.9, 113.7, 116.0, 122.7, 123.1, 132.8, 138.0, 145.2, 146.8, 147.6, 157.4.

(3*S*,5a*S*,8'*R*,9'*S*,11a*R*,11b*S*,13'*S*,14'*S*)-3'-Methoxy-13'-methyl-5,5a,6',7',8',9',11',12',13',14',15',16'-dodecahydro-1*H*-spiro[anthra[1,2-*c*]furan-3,17'-cyclopenta[*a*]phenanthrene]-6,11(11a*H*,11b*H*)-dione (16e)



White amorphous solid (91% from **5a** following procedure C).

[α]$_D^{20}$ = +36 ($CHCl_3$, *c* 0.1).

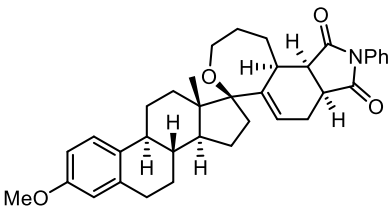
M.p. = 129.4 °C

NMR ^{1}H (400 MHz, $CDCl_3$) δ ppm : 0.96 (*s,* 3H), 1.30-1.38 (*m*, 2H), 1.43-1.53 (*m,* 4H), 1.62 (*dt*, 3.2, 11.7 Hz, 1H), 1.67-1.71 (*m*, 1H), 1.89-1.97 (*m,* 2H), 2.11-2.21 (*m*, 2H), 2.24-2.32 (*m*, 2H), 2.55-2.60 (*m*, 1H), 2.82-2.91 (*m*, 2H), 2.95-3.00 (*m*, 1H), 3.36 (*ddd*, J = 4.7, 6.6, 10.9 Hz, 1H), 3.70 (*t*, J = 5.1 Hz, 1H), 3.78 (*s*, 3H), 4.00 (*dd*, J = 7.9, 9.1 Hz, 1H), 4.38 (*t*, J = 8.1 Hz, 1H), 5.44 (*q*, J = 3.5 Hz, 1H), 6.63 (*d*, J = 2.7 Hz, 1H), 6.71 (*dd*, J = 2.7, 8.5 Hz, 1H), 7.19 (*d*, J = 8.5 Hz, 1H), 7.73-7.76 (*m*, 2H), 7.96-7.94 (*m*, 2H).

NMR ^{13}C (150 MHz, $CDCl_3$) δ ppm : 14.2, 23.0, 26.4, 26.5, 27.3, 29.9, 33.3, 35.4, 39.2, 41.6, 43.6, 46.6, 46.8, 48.5, 48.8, 55.2, 66.7, 94.7, 111.4, 113.7, 115.1, 126.3, 126.5, 127.0, 132.7 (2C^q), 134.1, 134.5, 135.6, 138.0, 146.3, 157.4, 196.4, 198.7.

HRMS (ESI+) *m/z*: calculated for $C_{34}H_{37}O_4^+$ [MH^+]: 509.2686; found: 509.2706.

(3a'*S*,6'*S*,8*R*,9*S*,10a'*S*,10b'*R*,13*S*,14*S*)-3-Methoxy-13-methyl-2'-phenyl-3a',4',6,7,8,8',9,9',10',10a',11,12,13,14,15,16-hexadecahydrospiro[cyclopenta[*a*]phenanthrene-17,6'-oxepino[4,3-*e*]isoindole]-1',3'(2'*H*,10b'*H*)-dione (16f)



White powder (14% from **5b**, isolated from a mixture of several stereoisomeric cycloadducts, global yield: 65%).

M.p. = 280 °C

[α]$_D^{20}$ = –9 ($CHCl_3$, *c* 0.1).

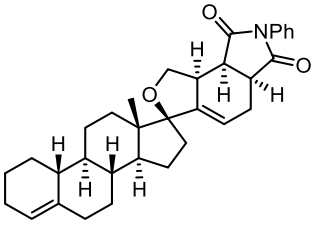
NMR ^{1}H (600 MHz, $CDCl_3$) δ ppm : 0.97 (*s*, 3H), 1.03 (*dt*, J = 3.9, 12.4 Hz, 1H), 1.11-1.18 (*m*, 1H), 1.31-1.57 (*m*, 7H), 1.66-1.76 (*m*, 3H), 1.88-1.92 (*m*, 1H), 1.94-1.99 (*m*, 1H), 2.06-2.12 (*m*, 2H), 2.23-2.27 (*m*, 1H), 2.51 (*ddd*, J = 2.2, 8.1, 17.5 Hz, 1H), 2.82-2.91 (*m*, 3H), 3.25-3.34 (*m*, 4H), 3.78 (*s*, 3H), 3.79-3.82 (*m*, 1H), 5.70 (*dd*, J = 2.0, 7.2

Hz, 1H), 6.63 (*d*, J = 2.6 Hz, 1H), 6.71 (*dd*, J = 2.6, 8.6 Hz, 1H), 7.18 (*d*, J = 8.6 Hz, 1H), 7.30-7.33 (*m*, 2H), 7.40-7.43 (*m*, 1H), 7.48-7.51 (*m*, 2H).

NMR ^{13}C (150 MHz, $CDCl_3$) δ ppm: 14.5, 22.2, 23.3, 26.3, 27.4, 28.1, 29.8 (2C), 34.0, 35.0, 37.8, 38.7, 39.2, 43.7, 44.1, 47.4, 48.2, 55.2, 65.5, 92.2, 111.4, 113.8, 123.6, 126.2, 126.4 (2C), 128.6, 129.2 (2C), 131.9, 132.5, 137.9, 149.2, 157.4, 178.1, 179.5.

HRMS (ESI+) *m/z*: calculated for $C_{36}H_{42}NO_4^+$ [MH^+]: 552.3108; found: 552.3122.

(3'*S*,5a'*S*,8*R*,8a'*R*,8b'*S*,9*S*,10*R*,13*S*,14*S*)-13-Methyl-7'-phenyl-1,1',2,3,5',5a',6,7,8,8b',9,10,11,12,13,14,15,16-octadecahydrospiro[cyclopenta[*a*]phenanthrene-17,3'-furo[3,4-*e*]isoindole]-6',8'(7'*H*,8a'*H*)-dione (17a)



Brown powder (84% from **6a** following procedure C).

M.p. = 249 °C.

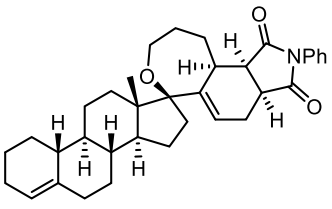
[α]$_D^{20}$ = –50 ($CHCl_3$, *c* 0.1).

^{1}H NMR (600 MHz, $CDCl_3$) δ ppm : 0.57-0.64 (*m*, 1H), 0.83-0.92 (*m*, 1H), 0.96 (*s,* 3H), 1.02-1.11 (*m,* 1H), 1.14-1.24 (*m,* 3H), 1.27-1.39 (*m,* 3H), 1.52-1.58 (m, 2H), 1.60-1.64 (*m*, 1H), 1.64-1.78 (*m,* 4H), 1.85-2.03 (*m,* 4H), 2.10 (*ddd*, J = 2.9, 11.3, 14.0 Hz, 1H), 2.17-2.26 (*m,* 2H), 2.76-2.83 (*m,* 1H), 3.00 (*ddd*, J = 2.0, 7.4, 14.7 Hz, 1H), 3.30 (*ddd*, J = 1.9, 6.0, 8.4 Hz, 1H), 3.37 (*t*, J = 8.4 Hz, 1H), 4.01 (*dd*, J = 7.7, 9.5 Hz, 1H), 4.69 (*dd*, *J* = 2.3, 9.6 Hz, 1H), 5.37-5.41 (*m*, 1H), 5.68 (*ddd*, *J* = 3.2, 7.3, 7.3 Hz, 1H), 7.15-7.21 (*m,* 2H), 7.32-7.37 (*m,* 1H), 7.39-7.44 (*m,* 2H).

NMR ^{13}C (150 MHz, $CDCl_3$) δ ppm: 13.6, 22.0, 23.1, 25.0, 25.5, 26.2, 28.7, 31.7, 35.0, 35.2, 35.4, 39.9, 40.8, 41.2, 41.8, 47.0, 49.1, 49.9, 65.8, 94.7, 116.7, 119.9, 126.4 (3C), 128.5, 129.0 (2C), 131.9, 140.2, 151.4, 176.2, 178.4.

HRMS (ESI+) *m/z*: calculated for $C_{33}H_{40}NO_3^+$ [MH^+]: 498.3003; found: 498.2988.

(3a'*S*,6'*S*,8*R*,9*S*,10*R*,10a'*S*,10b'*R*,13*S*,14*S*)-13-Methyl-2'-phenyl-1,2,3,3a',4',6,7,8,8',9,9',10,10',10a',11,12,13,14,15,16-icosahydrospiro[cyclopenta[*a*]phenanthrene-17,6'-oxepino[4,3-*e*]isoindole]-1',3'(2'*H*,10b'*H*)-dione (17b)



White powder (10% from **6b**, isolated from a mixture of several stereoisomeric cycloadducts, global yield: 48%).

M.p. = 194 °C

[α]$_D^{20}$ = +6 ($CHCl_3$, *c* 0.1).

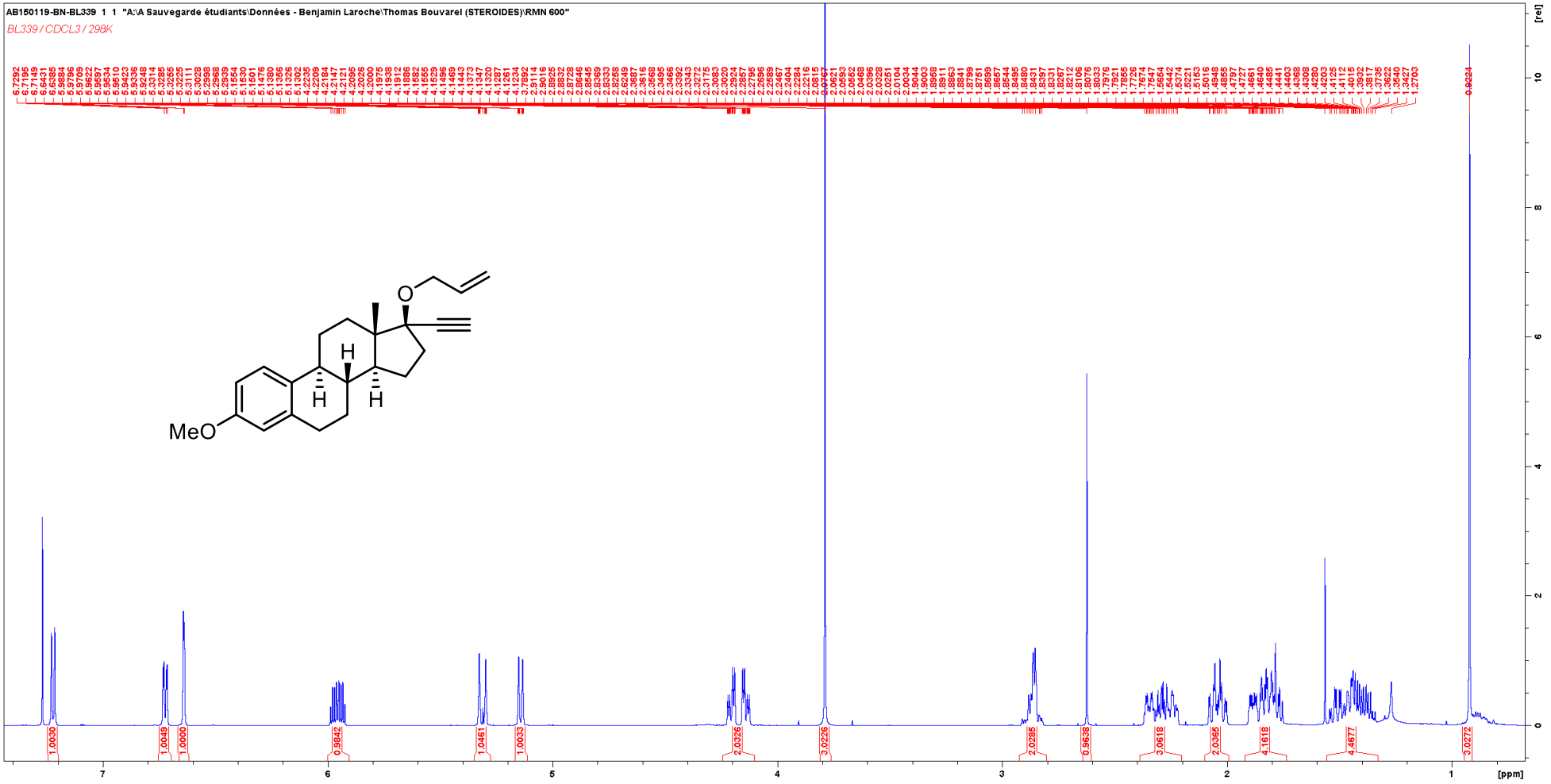
NMR ^{1}H (600 MHz, $CDCl_3$) δ ppm: 0.36 (*ddd*, J = 4.4, 10.9, 22.2 Hz, 1H), 0.50 (*dt*, J = 4.3, 12.7 Hz, 1H), 0.78-0.87 (*m*, 2H), 0.88 (*s,* 3H), 0.97-1.04 (*m*, 1H), 1.08 (*ddd,* J = 8.0, 11.7, 11.7 Hz, 1H), 1.19 (*ddd*, J = 2.9, 11.0, 21.6 Hz, 1H), 1.27-1.35 (*m,* 3H), 1.41-

1.45 (*m*, 1H), 1.51-1.56 (*m*, 2H), 1.59-1.67 (*m,* 4H), 1.73-1.78 (*m,* 1H), 1.82-1.99 (*m,* 7H), 2.19 (*ddd*, J = 2.6, 3.8, 13.7 Hz, 1H), 2.47 (*ddd,* J = 2.0, 8.1, 16.6 Hz, 1H), 2.97 (*ddd*, J = 1.1, 7.3, 16.5 Hz, 1H), 3.13 (*dd*, J = 0.5, 9.9 Hz, 1H), 3.20-3.25 (*m*, 2H), 3.29-3.33 (*m*, 1H), 3.78-3.82 (*m*, 1H), 5.37 (*brs*, 1H), 5.56 (*dd*, *J* = 2.2, 7.4 Hz, 1H), 7.27-7.29 (*m*, 2H), 7.34-7.37 (*m*, 1H), 7.41-7.44 (*m*, 2H).

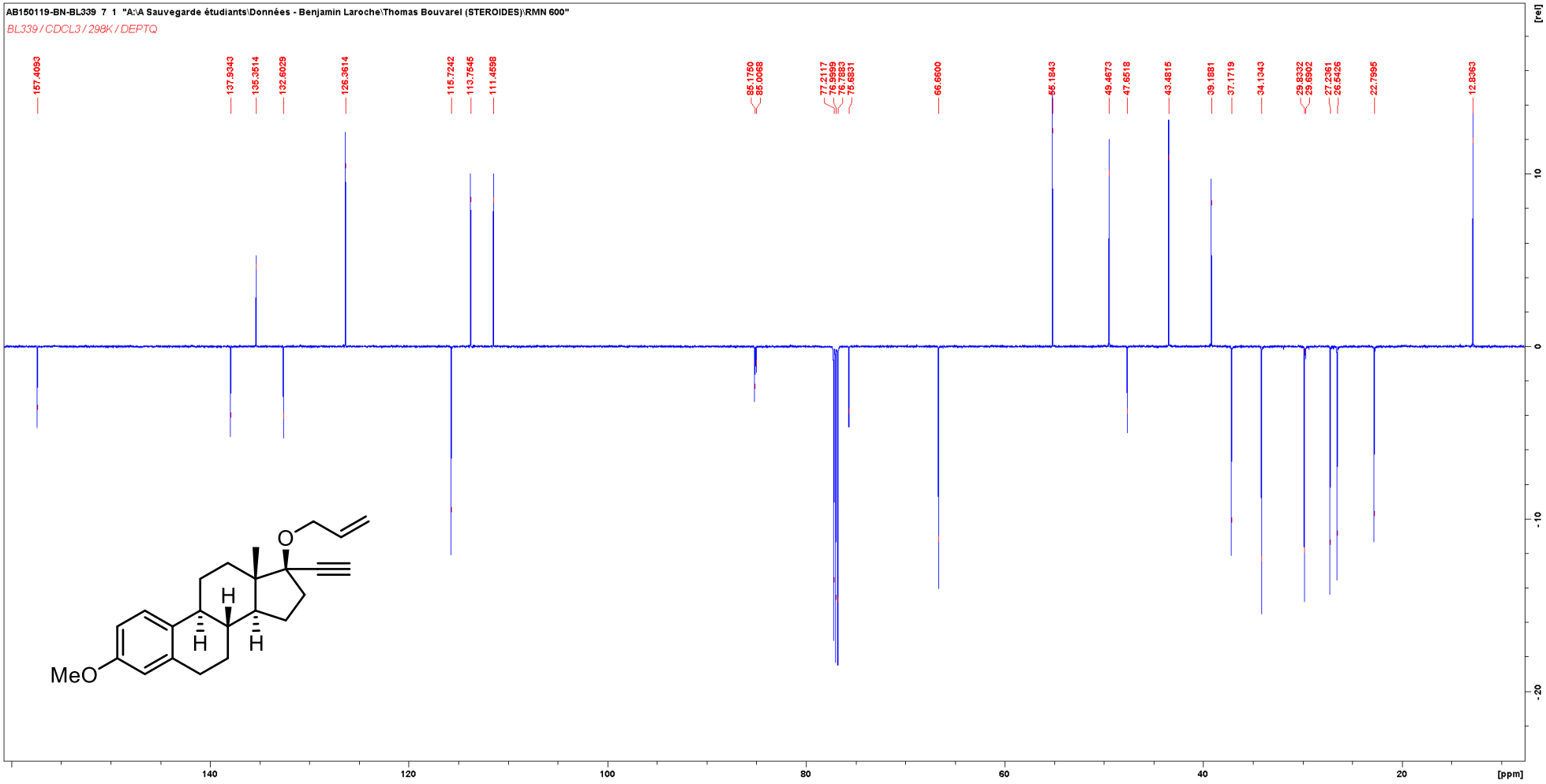
NMR ^{13}C (150 MHz, $CDCl_3$) δ ppm : 14.7, 22.2, 23.0, 23.6, 25.6, 28.5, 29.6, 31.7, 34.0, 35.5, 36.1, 37.3, 37.6, 38.9, 41.5, 42.0, 47.3, 47.7, 48.4, 49.8, 65.5, 92.3, 119.8, 123.1, 125.9 (3C), 128.3, 129.1 (2C), 132.1, 140.3, 149.2, 178.5, 179.3.

HRMS (ESI+) *m/z*: calculated for $C_{35}H_{44}NO_3^+$ [MH^+]: 526.3316; found: 526.3334.

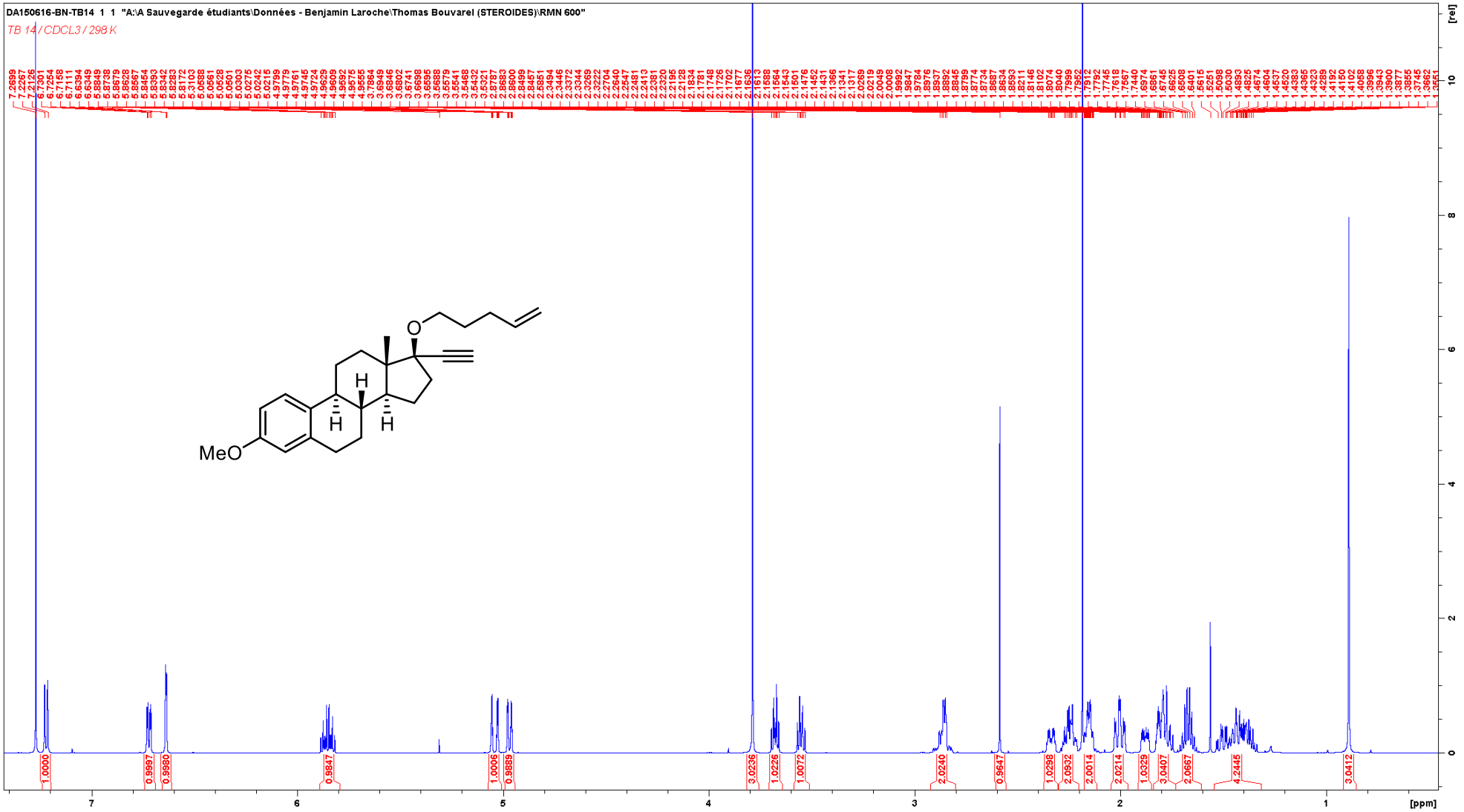
17-*O*-Allylmestranol (5a): ^{1}H NMR (600 MHz, $CDCl_3$)



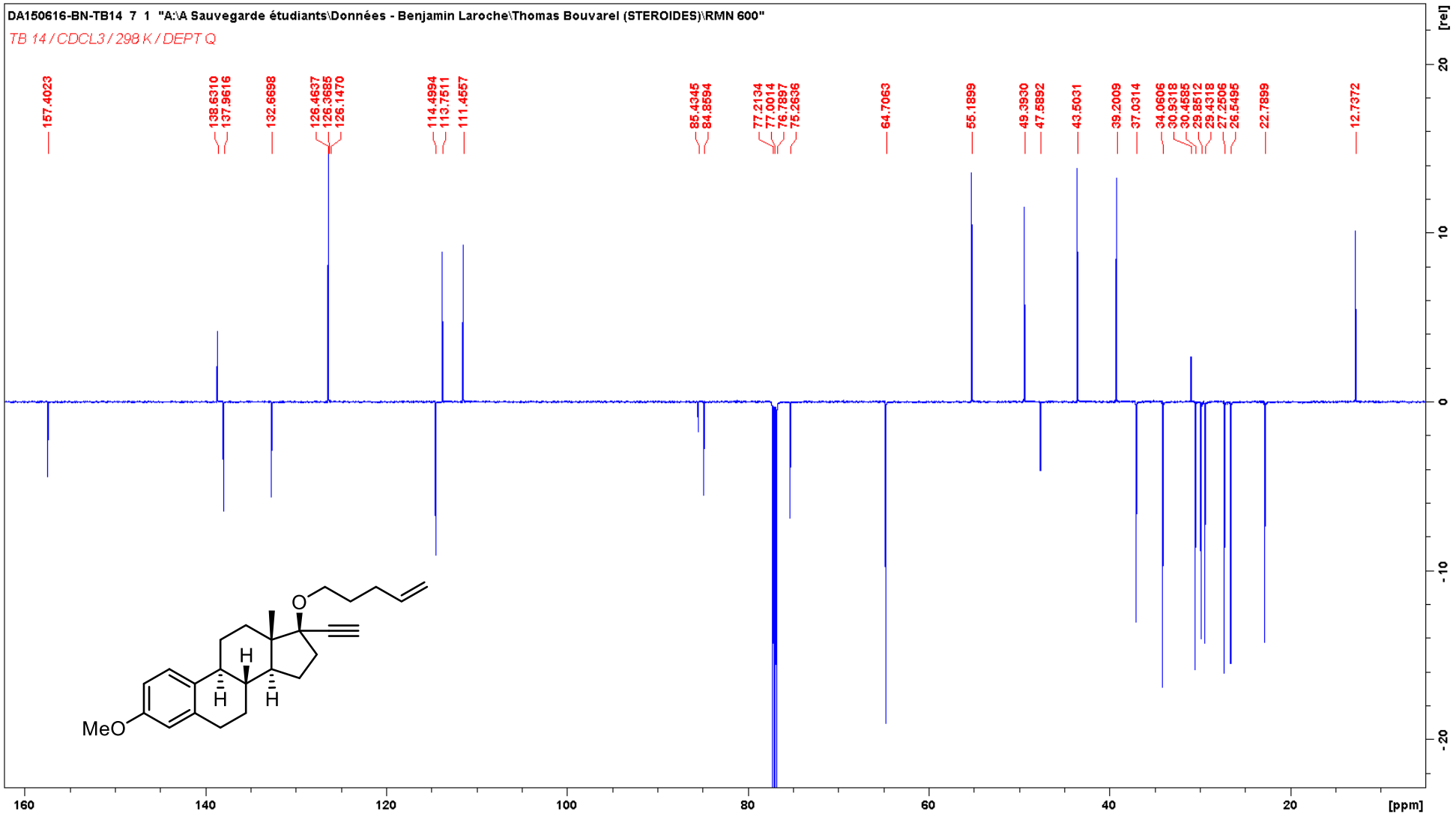
17-*O*-Allylmestranol (5a): ^{13}C NMR (150 MHz, $CDCl_3$)



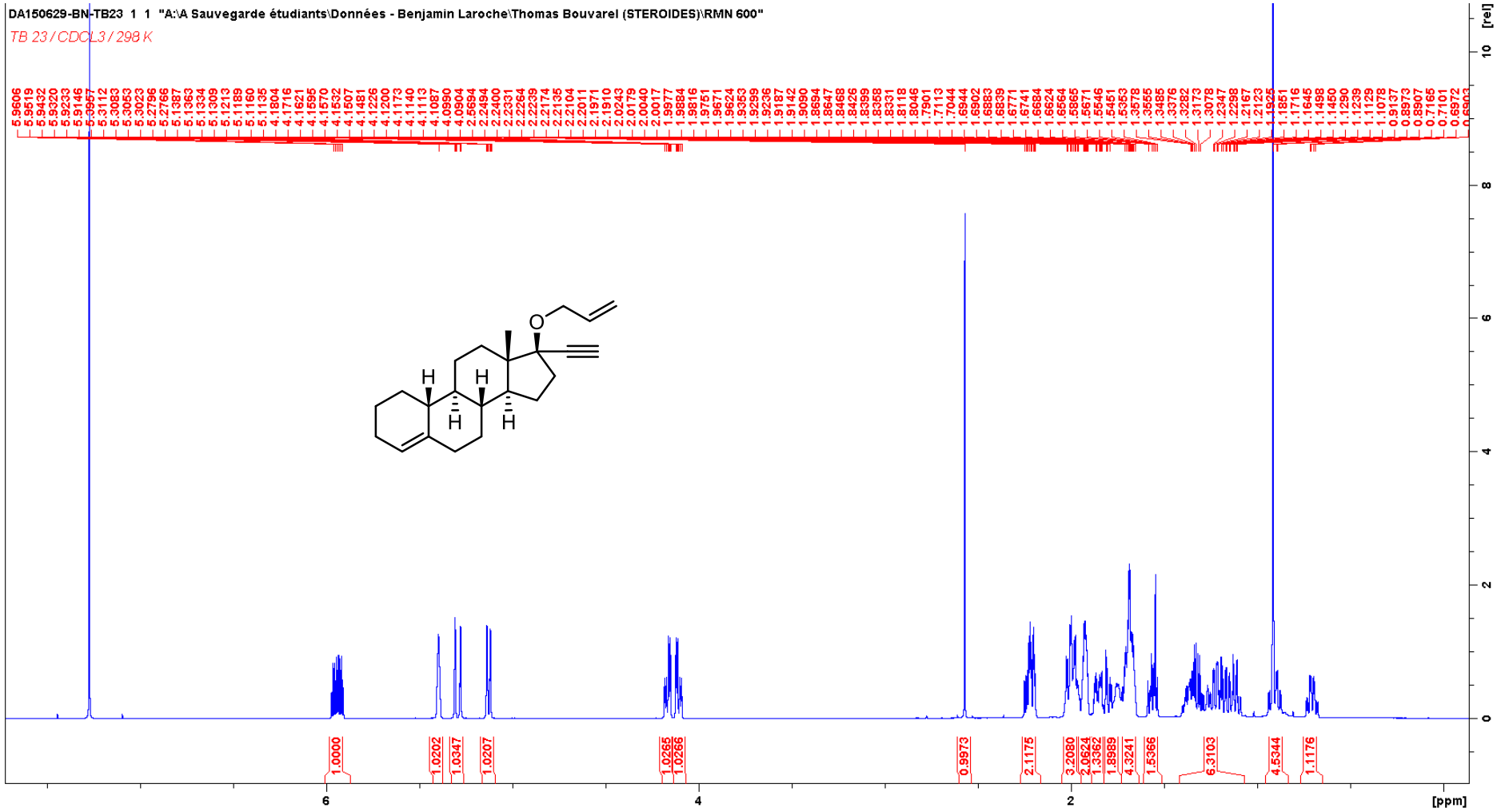
17-*O*-(4-Penten-1-yl)mestranol (5b): ^{1}H NMR (600 MHz, $CDCl_3$)



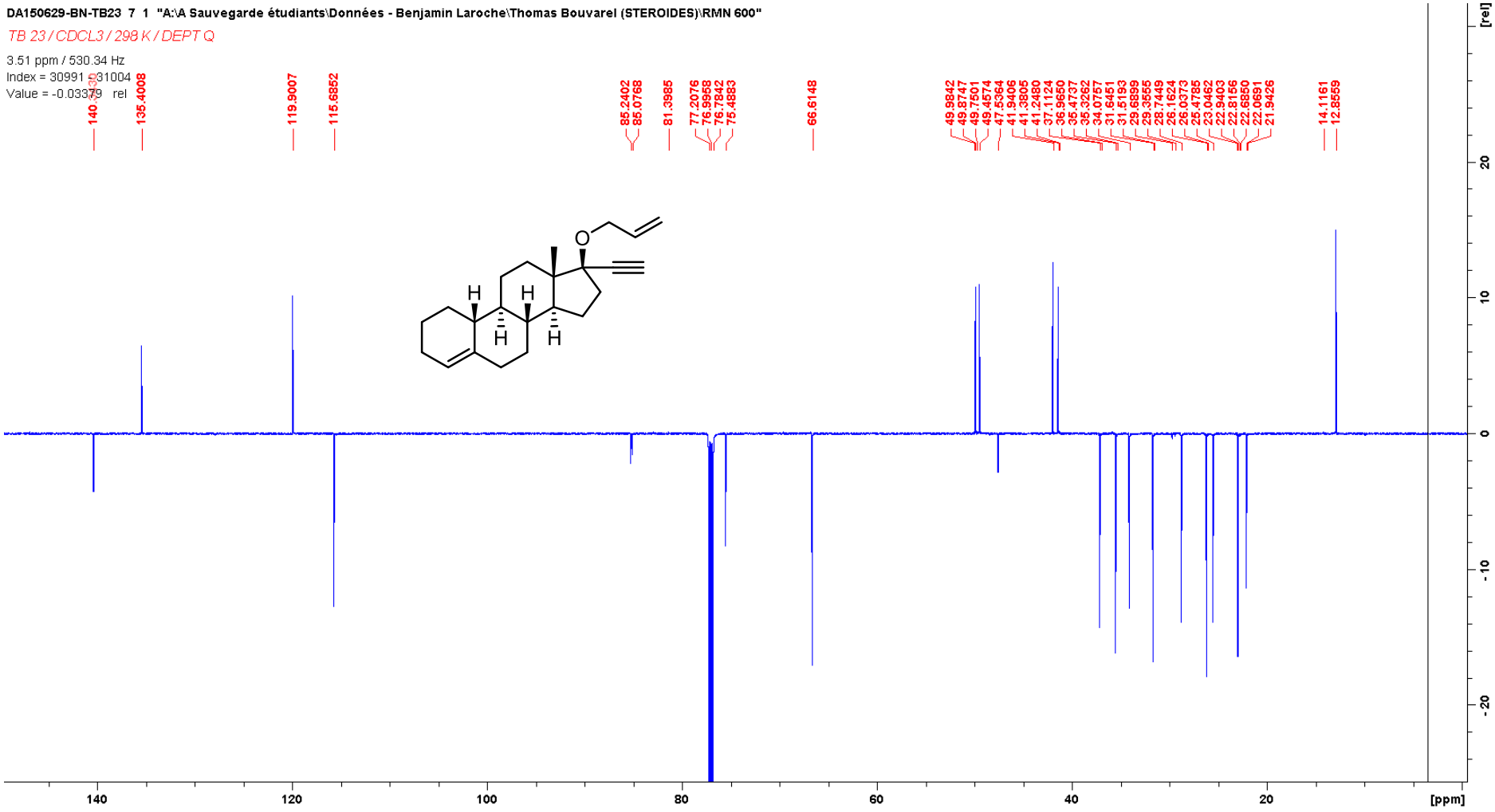
17-*O*-(4-Penten-1-yl)mestranol (5b): ^{13}C NMR (150 MHz, $CDCl_3$)



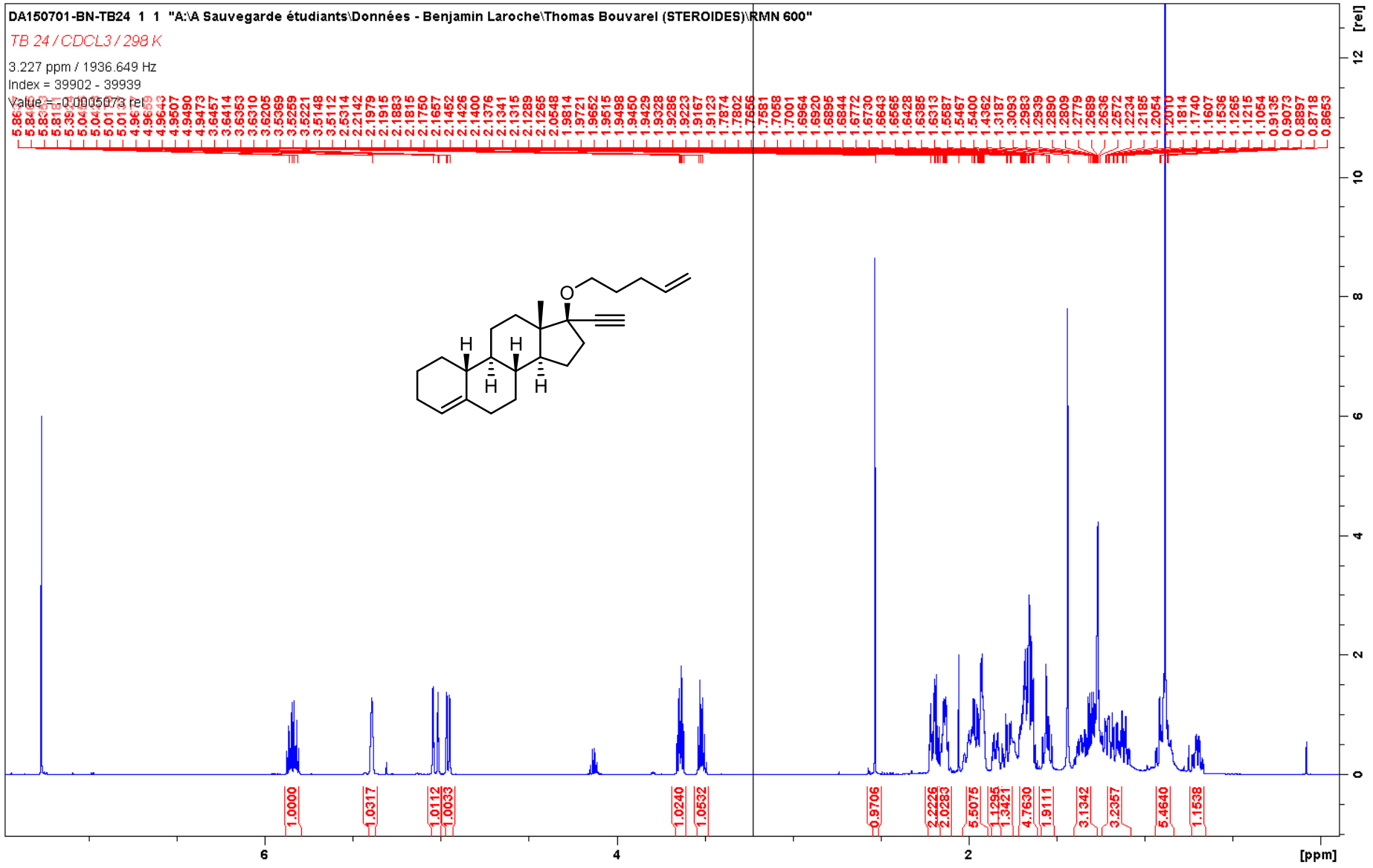
17-*O*-Allyllynestrenol (6a): ^{1}H NMR (600 MHz, $CDCl_3$)



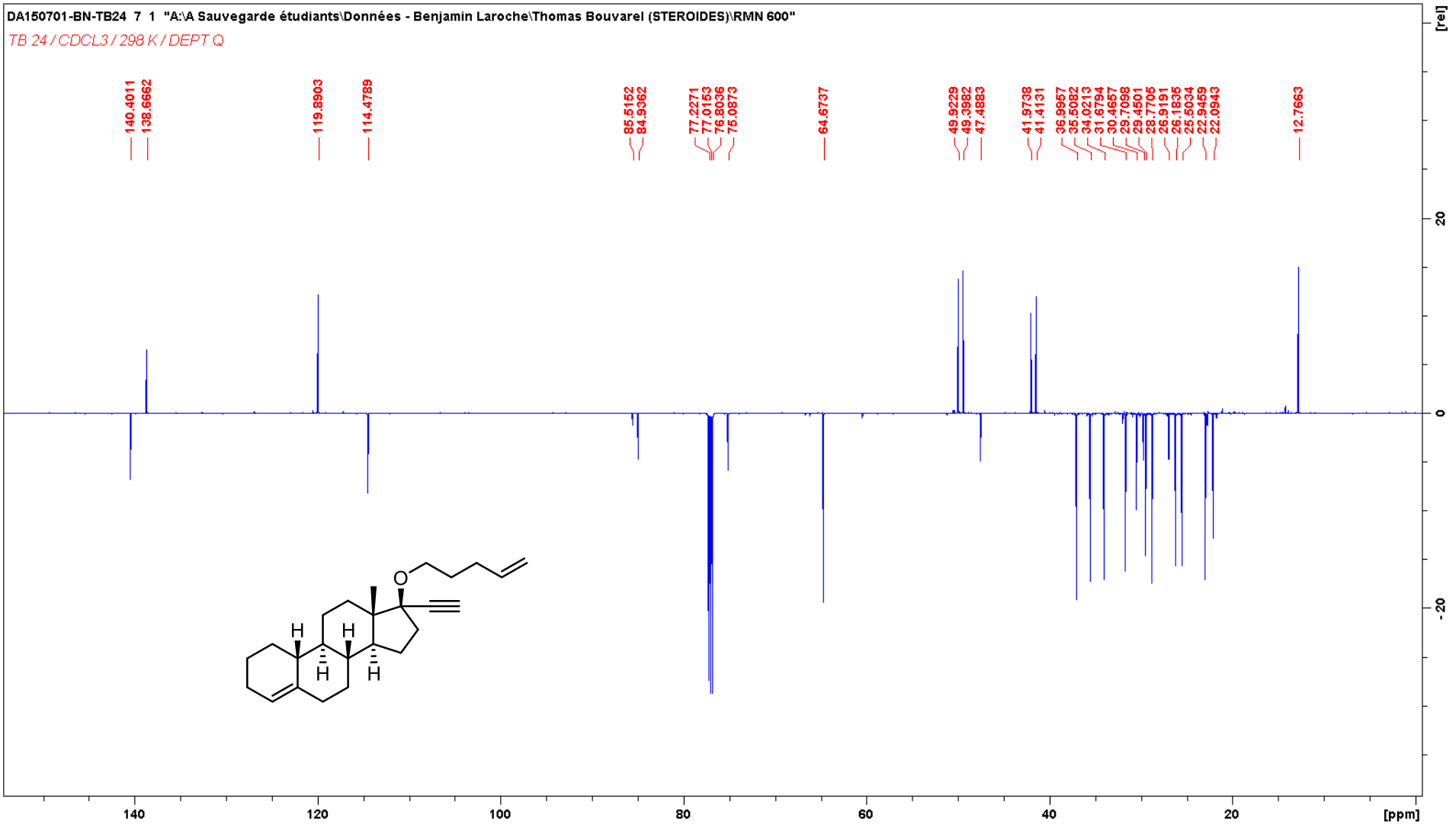
17-*O*-Allyllynestrenol (6a): ^{13}C NMR (150 MHz, $CDCl_3$)



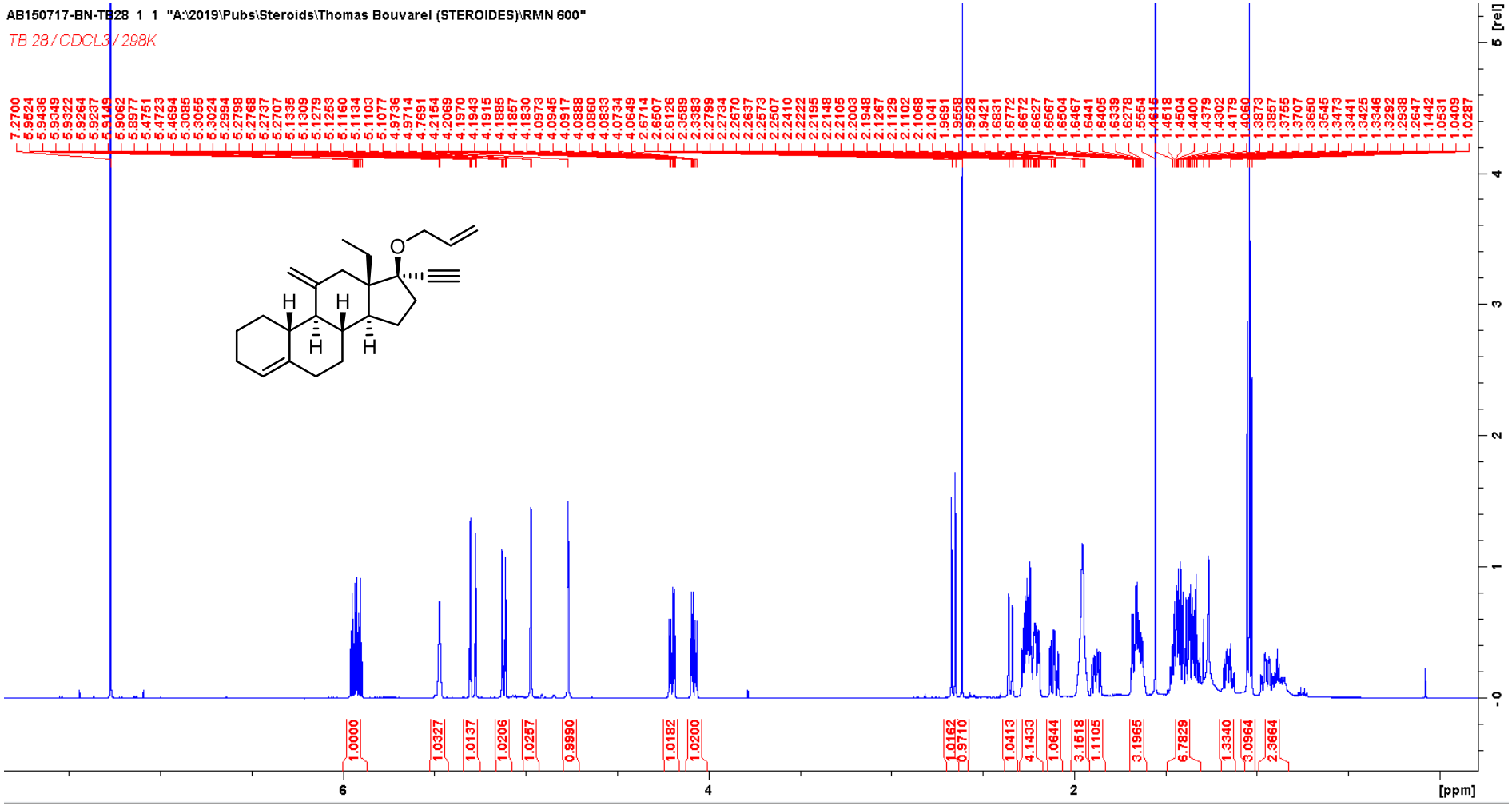
17-*O*-(4-Penten-1-yl)lynestrenol (6b): ^{1}H NMR (600 MHz, $CDCl_3$)



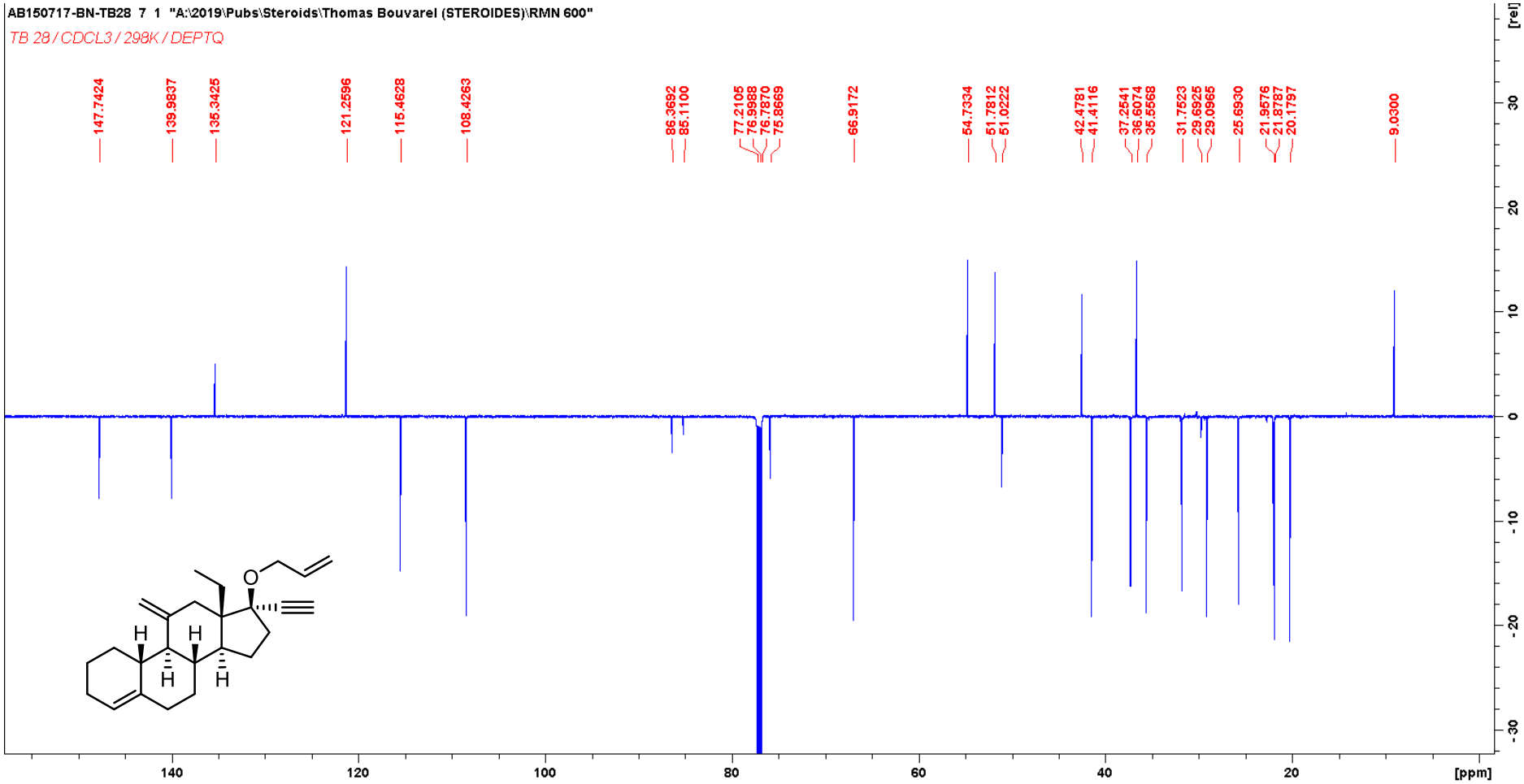
17-*O*-(4-Penten-1-yl)lynestrenol (6b): ^{13}C NMR (150 MHz, $CDCl_3$)



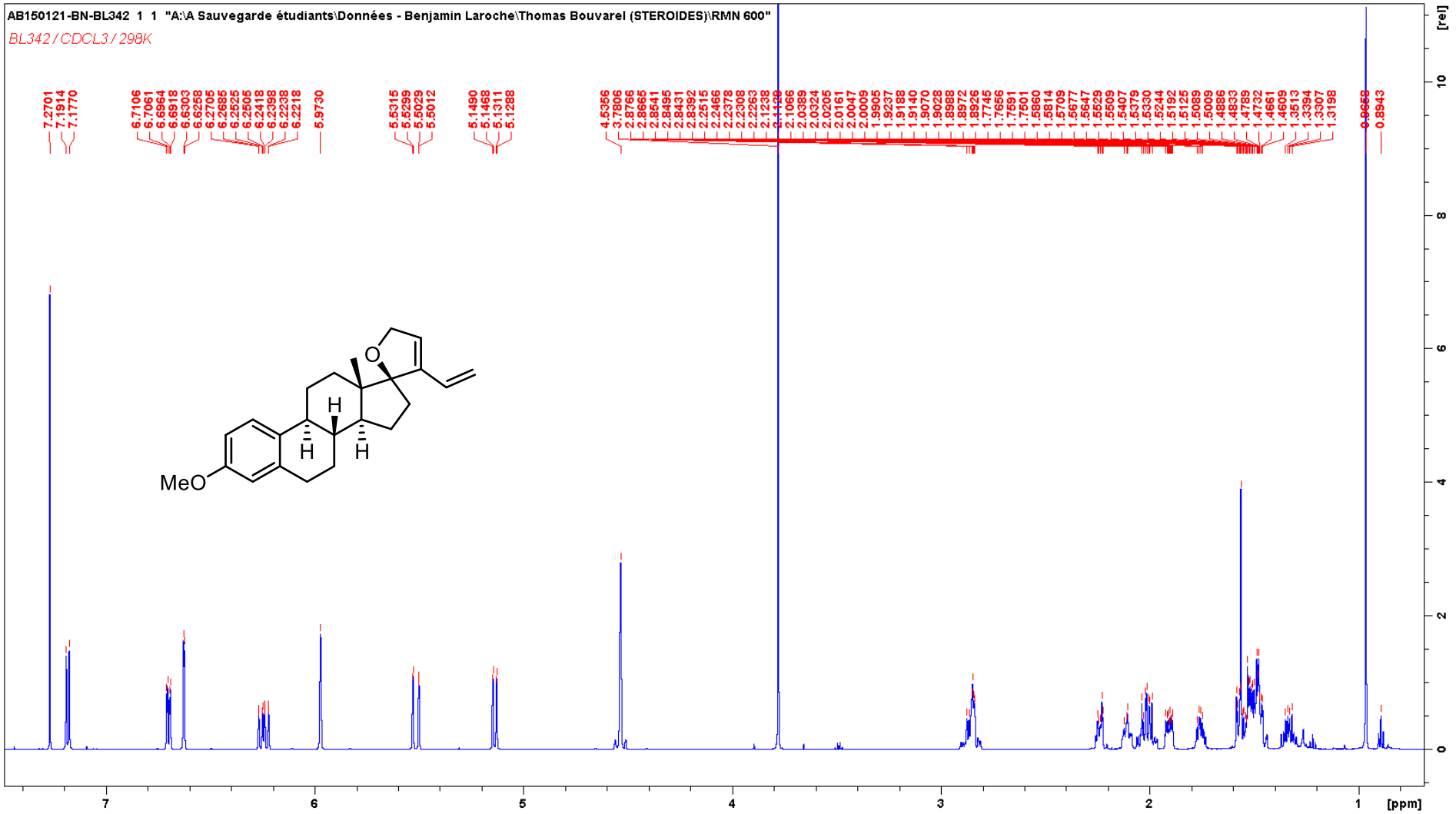
17-*O*-Allyldesogestrel (7): ^{1}H NMR (600 MHz, $CDCl_3$)



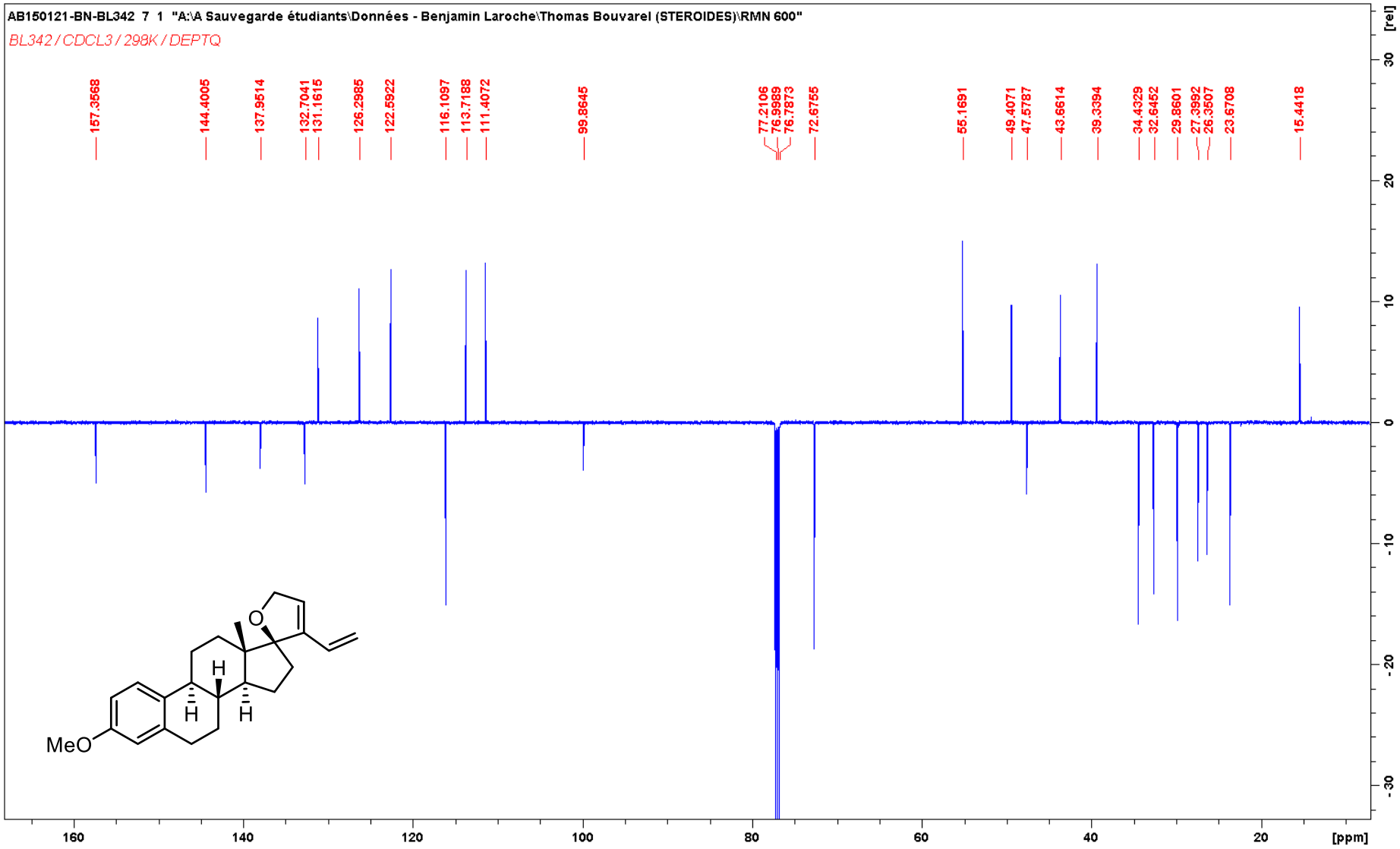
17-*O*-Allyldesogestrel (7): ^{13}C NMR (150 MHz, $CDCl_3$)



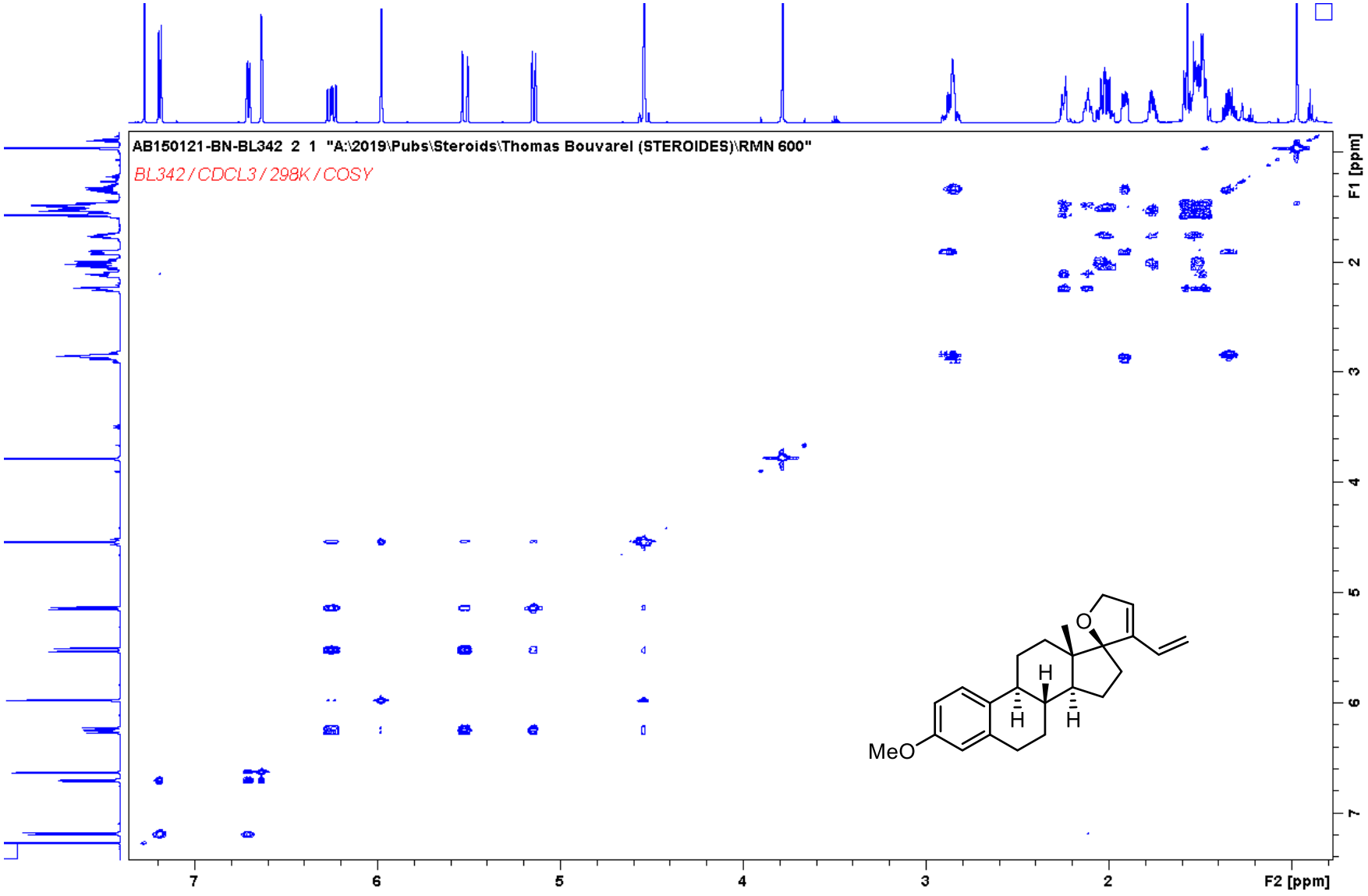
(2'*S*,8*R*,9*S*,13*S*,14*S*)-3-Methoxy-13-methyl-3'-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-5'*H*-spiro[cyclopenta[*a*]phenanthrene-17,2'-furan] (8a): ^{1}H NMR (600 MHz, $CDCl_3$)



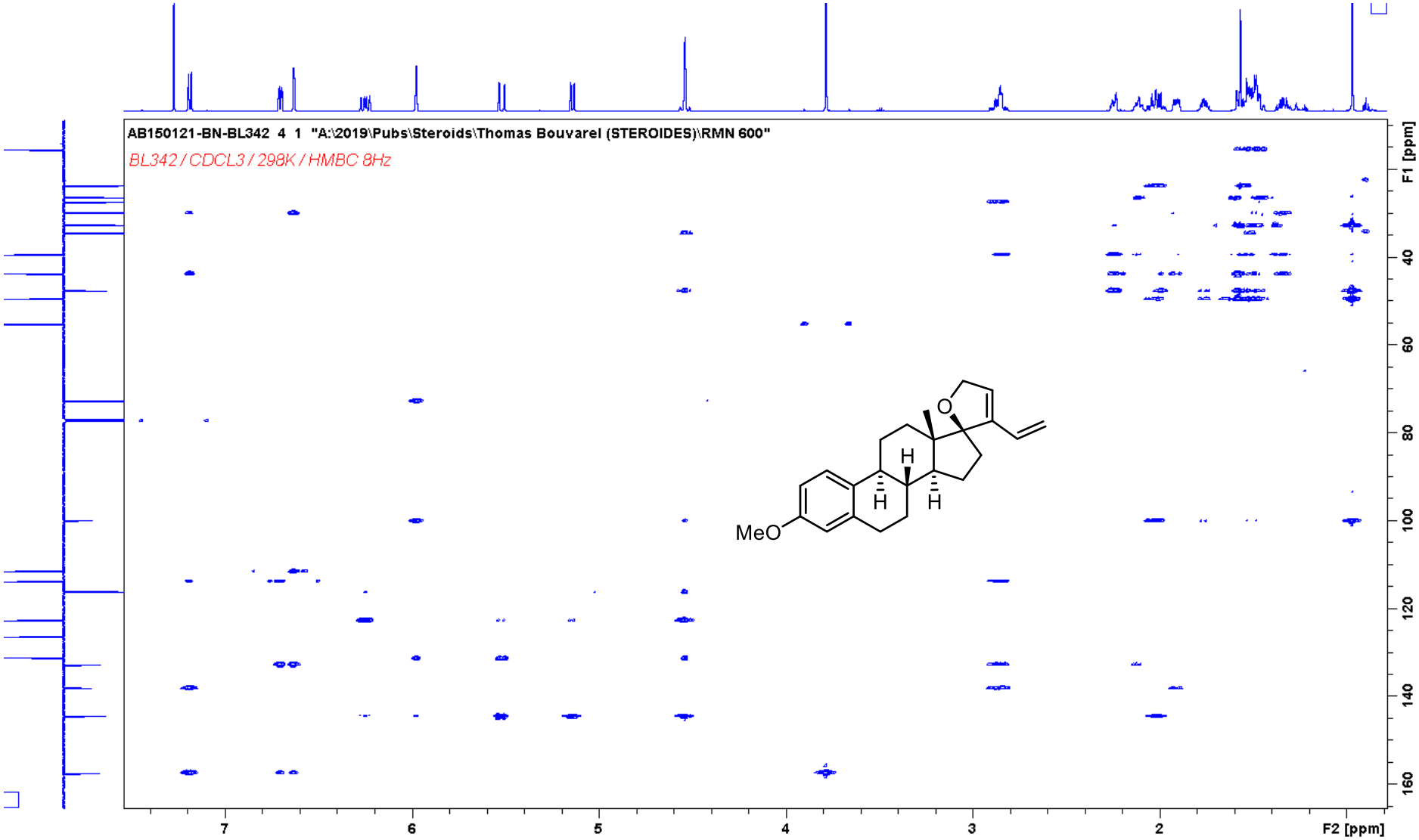
(2'*S*,8*R*,9*S*,13*S*,14*S*)-3-Methoxy-13-methyl-3'-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-5'*H*-spiro[cyclopenta[*a*]phenanthrene-17,2'-furan](8a): ^{13}C NMR (150 MHz, $CDCl_3$)



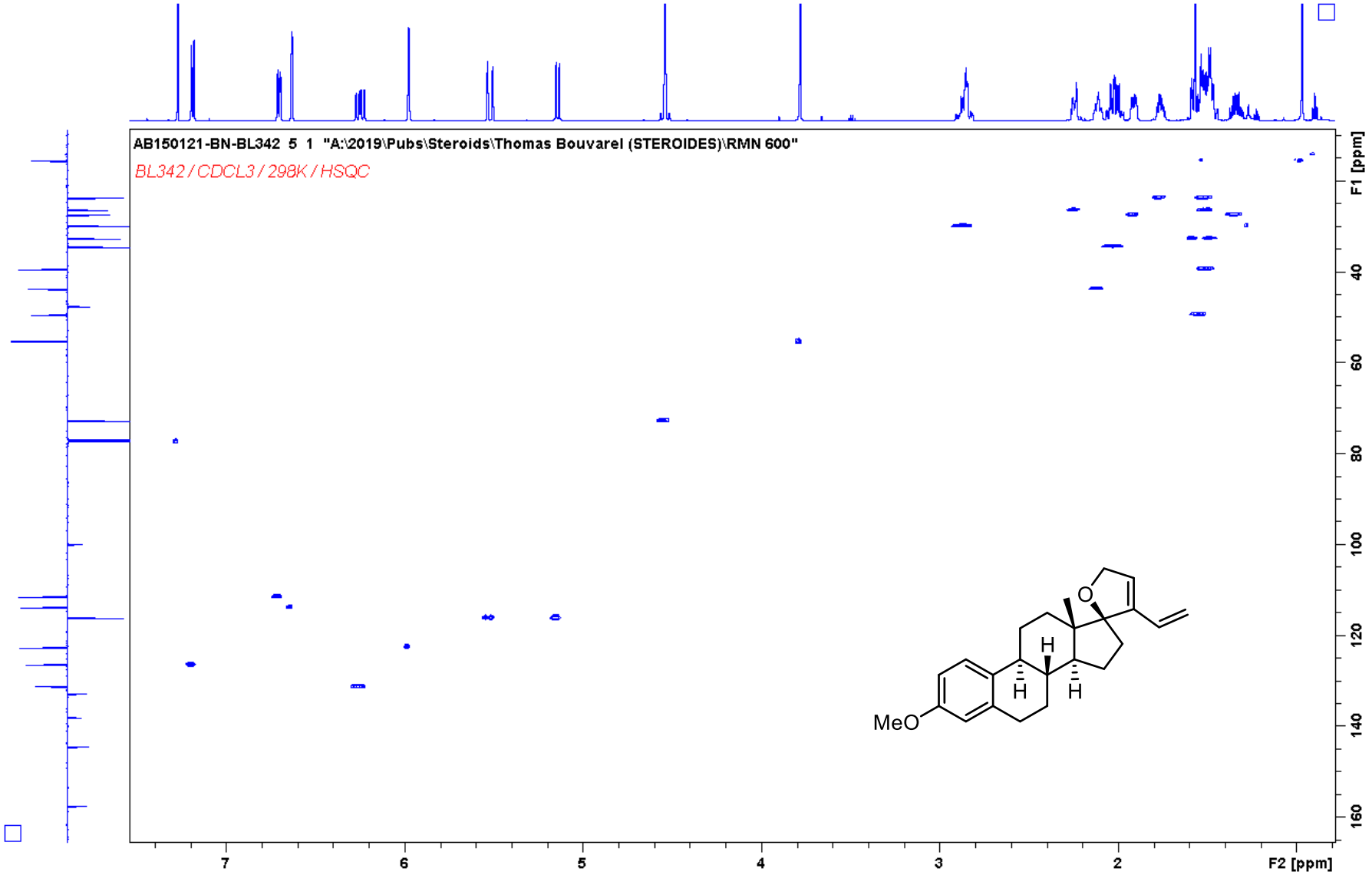
(2'*S*,8*R*,9*S*,13*S*,14*S*)-3-Methoxy-13-methyl-3'-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-5'*H*-spiro[cyclopenta[*a*]phenanthrene-17,2'-furan] (8a): COSY NMR (600 MHz, $CDCl_3$)



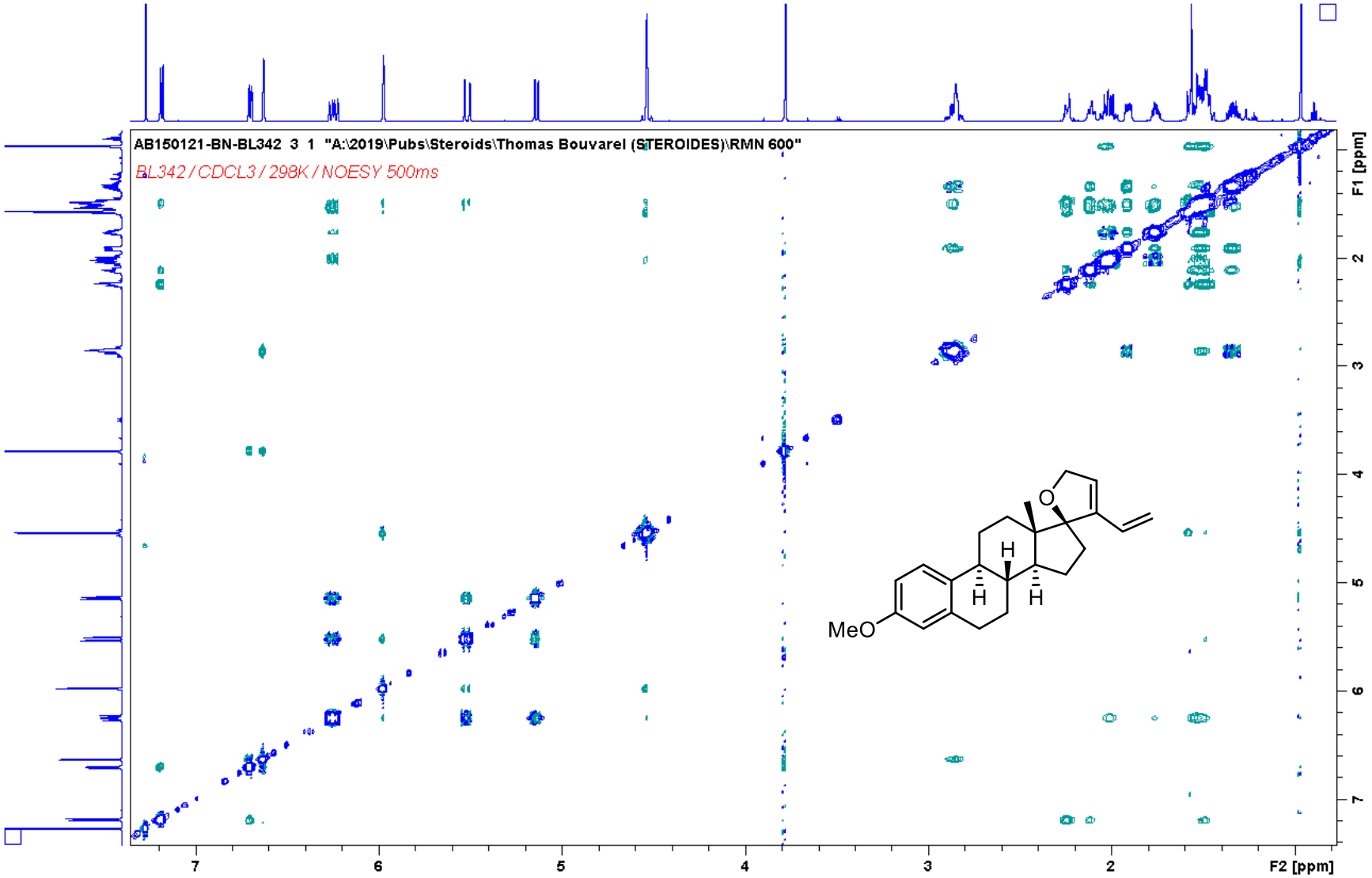
(2'*S*,8*R*,9S,13*S*,14*S*)-3-Methoxy-13-methyl-3'-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-5'*H*-spiro[cyclopenta[*a*]phenanthrene-17,2'-furan] (8a): HMBC NMR (600 MHz, $CDCl_3$)



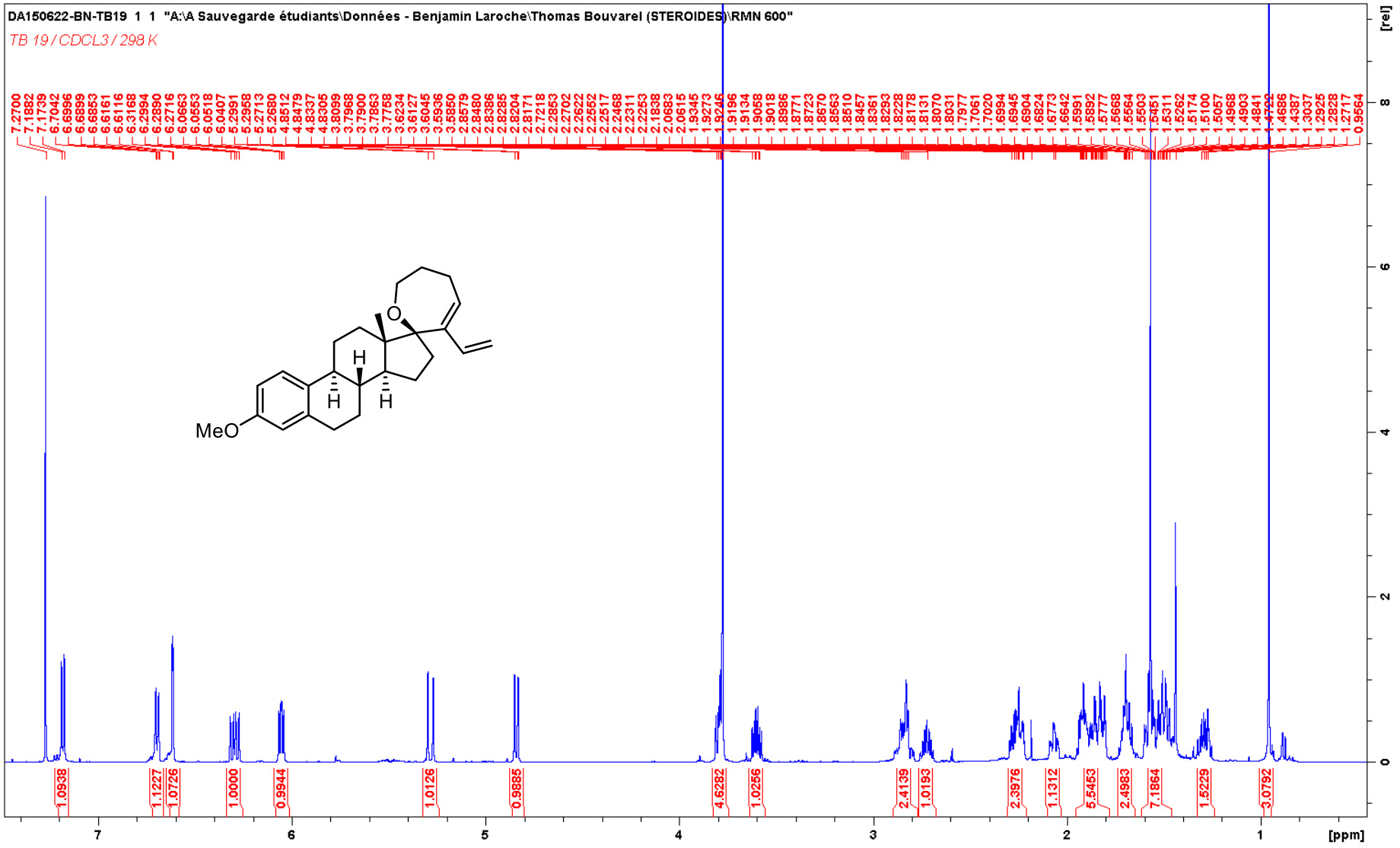
(2'*S*,8*R*,9*S*,13*S*,14*S*)-3-Methoxy-13-methyl-3'-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-5'*H*-spiro[cyclopenta[*a*]phenanthrene-17,2'-furan] (8a): HSQC NMR (600 MHz, $CDCl_3$)



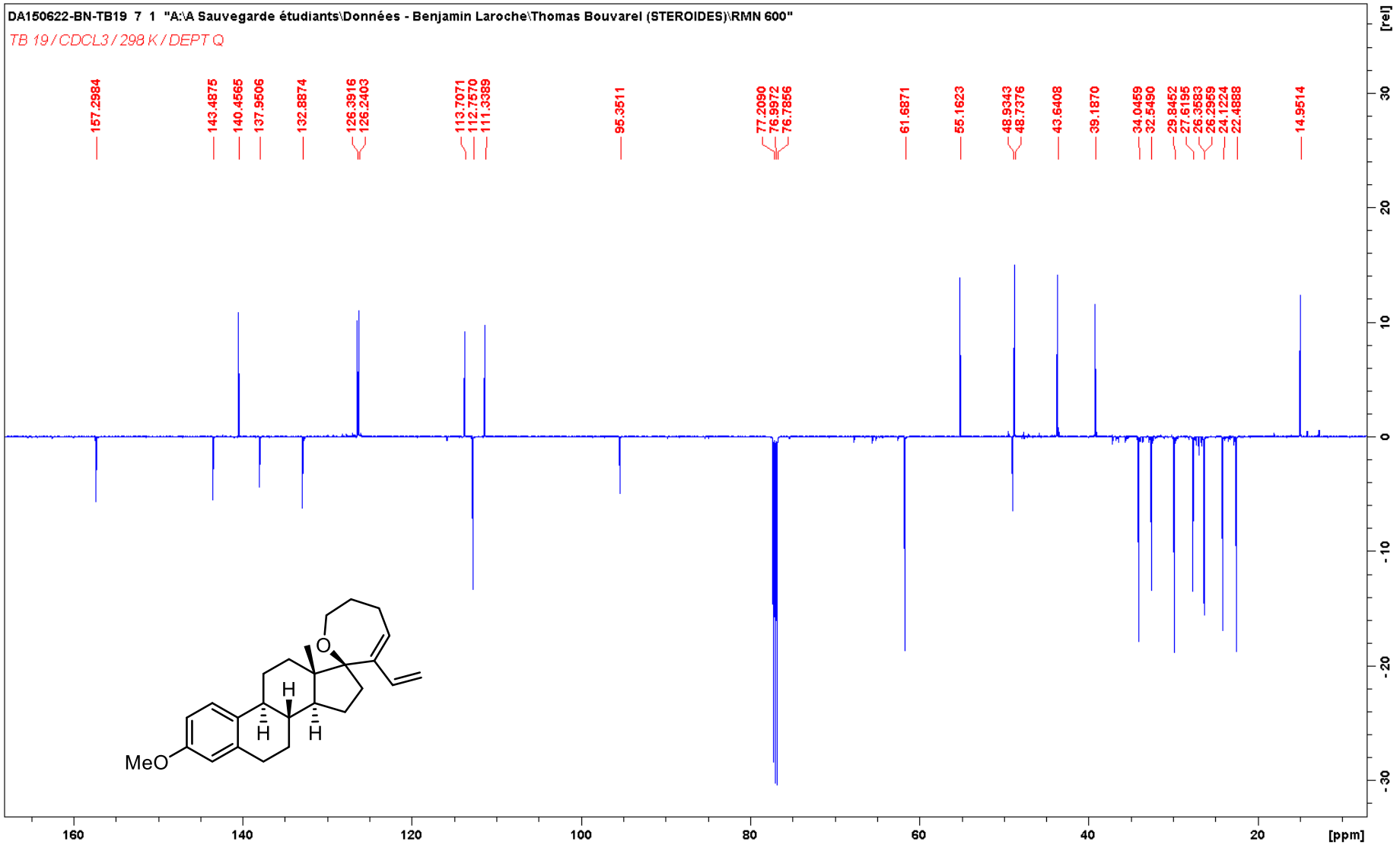
(2'*S*,8*R*,9*S*,13*S*,14*S*)-3-Methoxy-13-methyl-3'-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-5'*H*-spiro[cyclopenta[*a*]phenanthrene-17,2'-furan] (8a): NOESY NMR (600 MHz, $CDCl_3$)



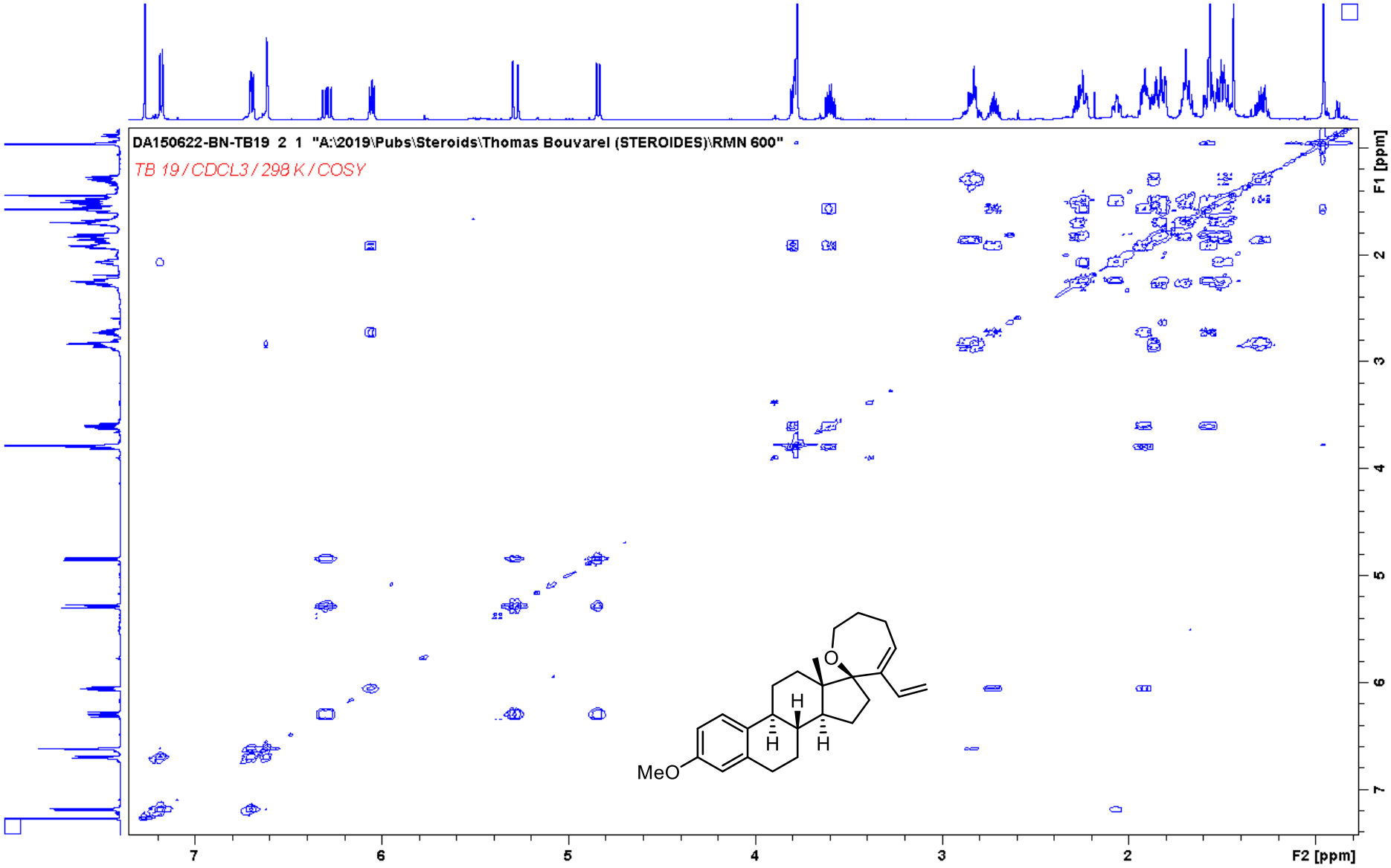
(2'*S*,8*R*,9*S*,13*S*,14*S*)-3-Methoxy-13-methyl-3'-vinyl-6,6',7,7',8,9,11,12,13,14,15,16-dodecahydro-5'*H*-spiro[cyclopenta[*a*]phenanthrene-17,2'-oxepine](8b): ^{1}H NMR (600 MHz, $CDCl_3$)



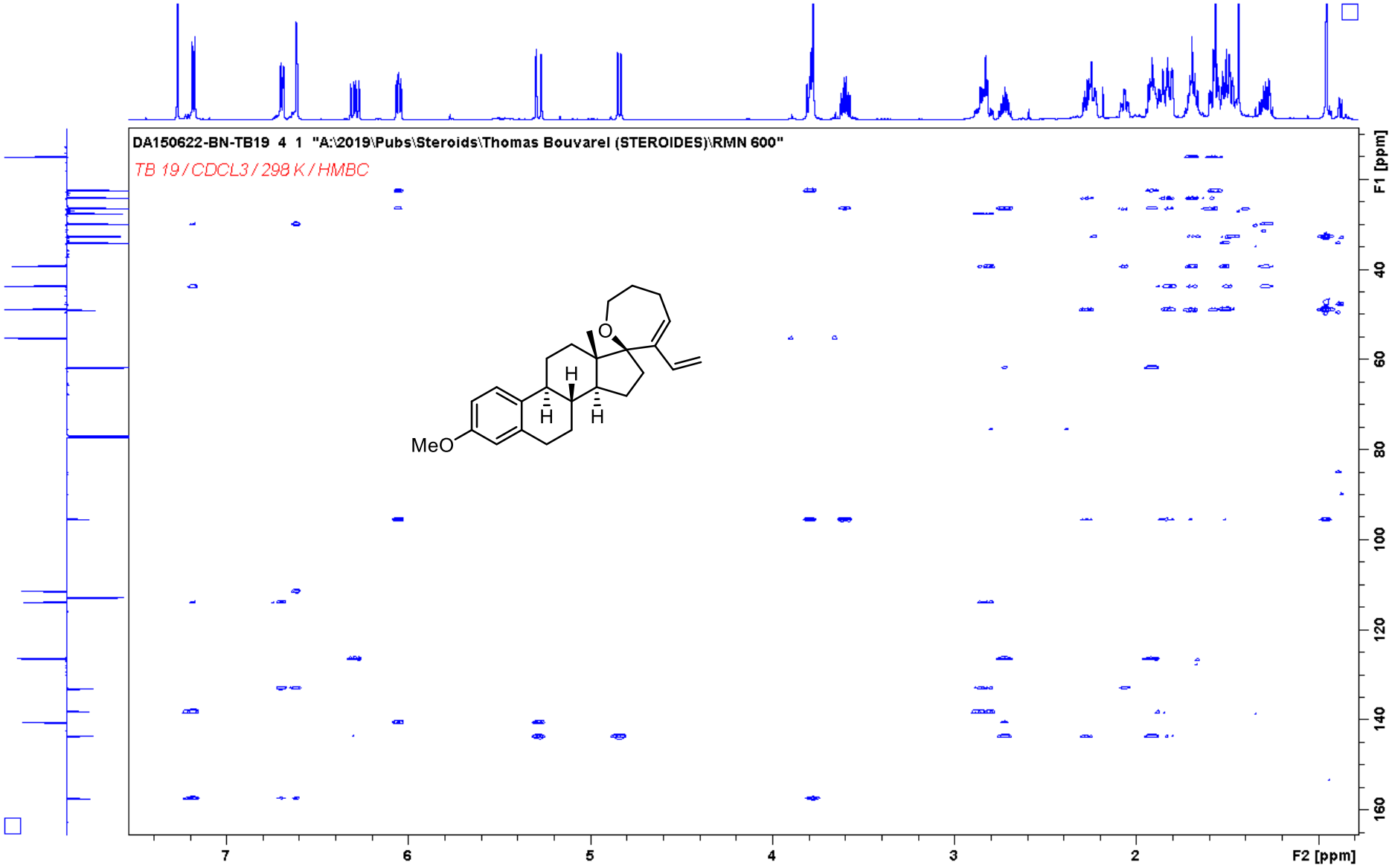
(2'*S*,8*R*,9*S*,13*S*,14*S*)-3-Methoxy-13-methyl-3'-vinyl-6,6',7,7',8,9,11,12,13,14,15,16-dodecahydro-5'*H*-spiro[cyclopenta[*a*]phenanthrene-17,2'-oxepine] (8b): ^{13}C NMR (150 MHz, $CDCl_3$)



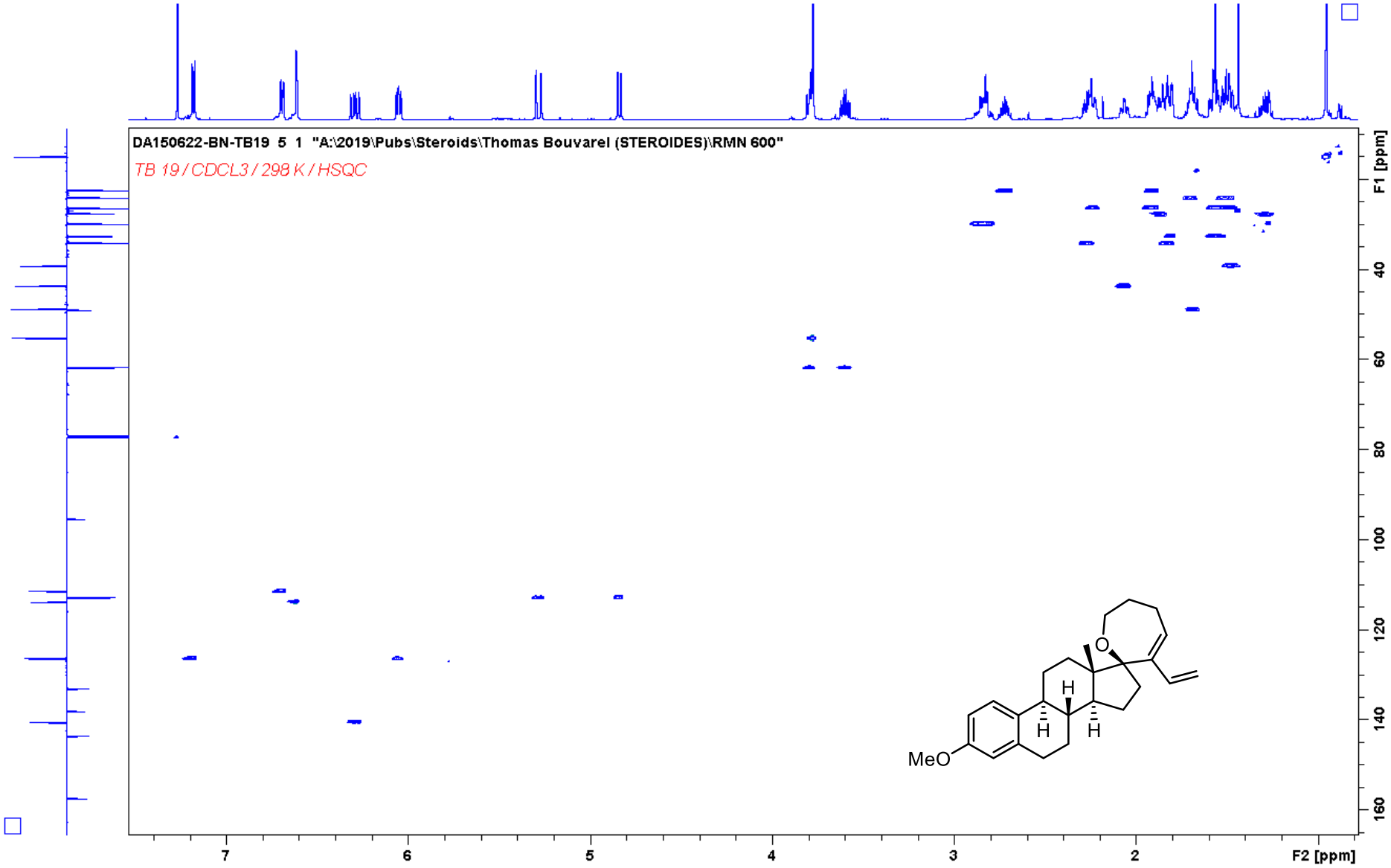
(2'*S*,8*R*,9*S*,13*S*,14*S*)-3-Methoxy-13-methyl-3'-vinyl-6,6',7,7',8,9,11,12,13,14,15,16-dodecahydro-5'*H*-spiro[cyclopenta[*a*]phenanthrene-17,2'-oxepine](8b): COSY NMR (600 MHz, $CDCl_3$)



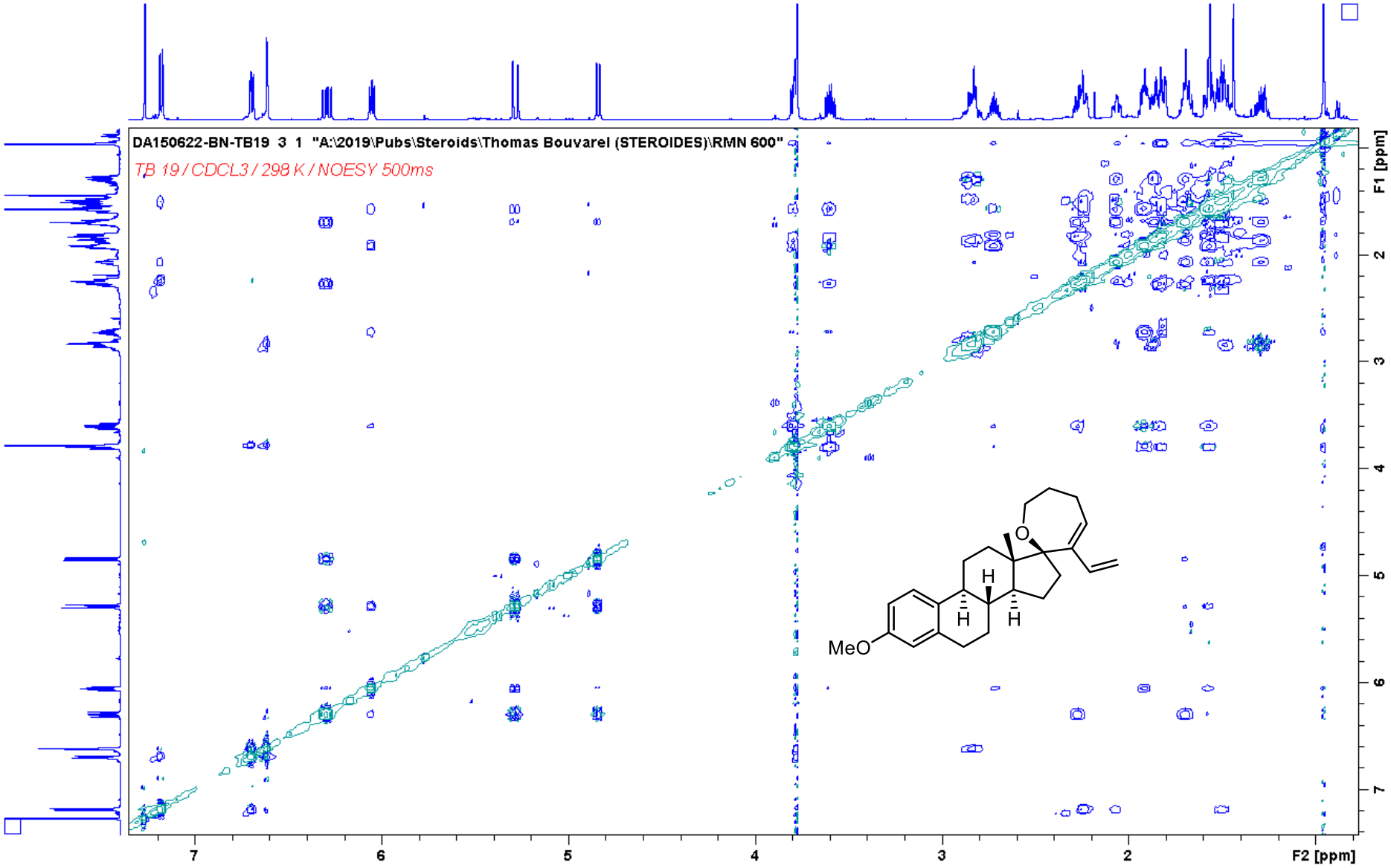
(2'*S*,8*R*,9*S*,13*S*,14*S*)-3-Methoxy-13-methyl-3'-vinyl-6,6',7,7',8,9,11,12,13,14,15,16-dodecahydro-5'*H*-spiro[cyclopenta[*a*]phenanthrene-17,2'-oxepine](8b): HMBC NMR (600 MHz, $CDCl_3$)



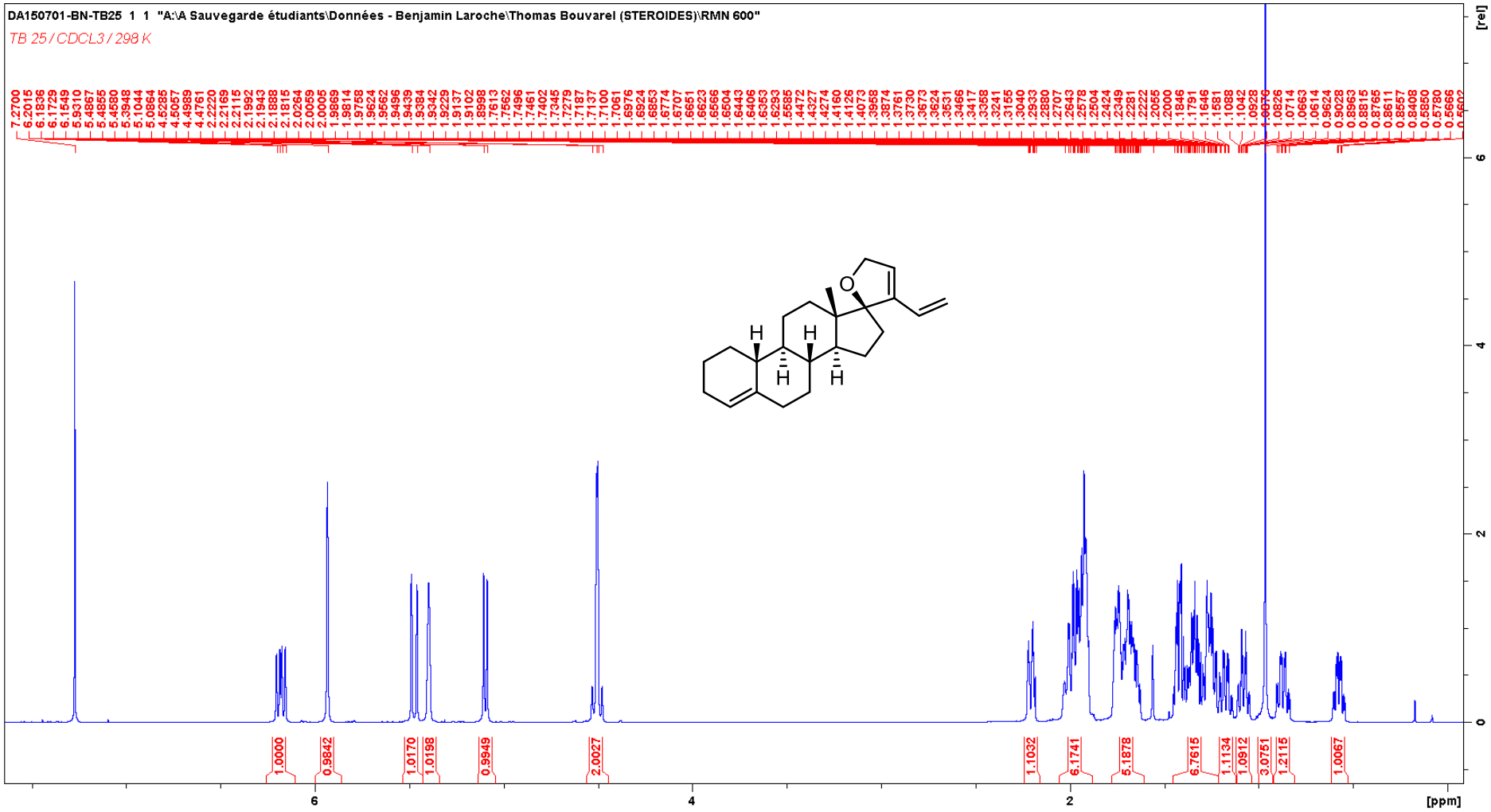
(2'*S*,8*R*,9*S*,13*S*,14*S*)-3-Methoxy-13-methyl-3'-vinyl-6,6',7,7',8,9,11,12,13,14,15,16-dodecahydro-5'*H*-spiro[cyclopenta[*a*]phenanthrene-17,2'-oxepine](8b): HSQC NMR (600 MHz, $CDCl_3$)



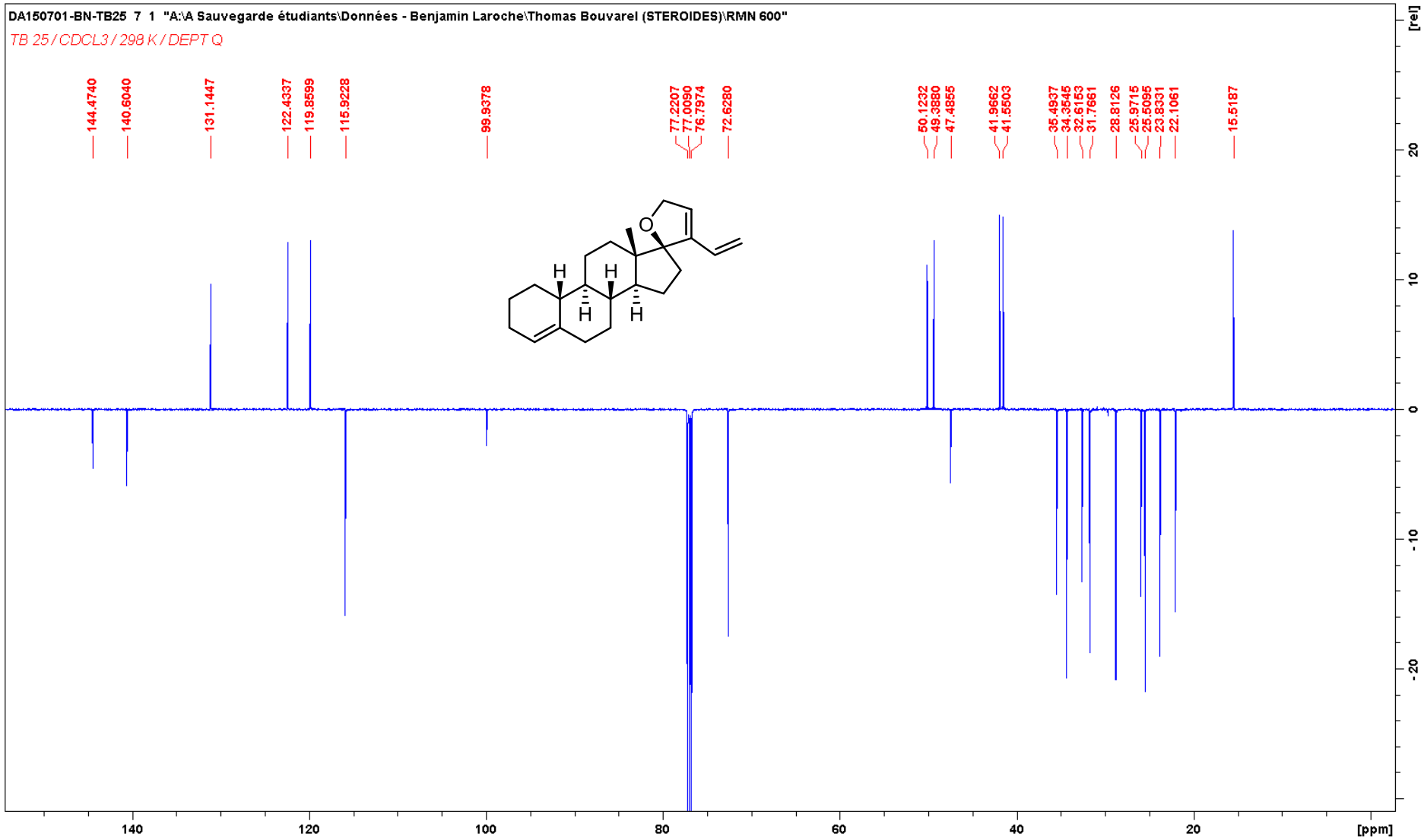
(2'*S*,8*R*,9*S*,13*S*,14*S*)-3-Methoxy-13-methyl-3'-vinyl-6,6',7,7',8,9,11,12,13,14,15,16-dodecahydro-5'*H*-spiro[cyclopenta[*a*]phenanthrene-17,2'-oxepine](8b): NOESY NMR (600 MHz, $CDCl_3$)



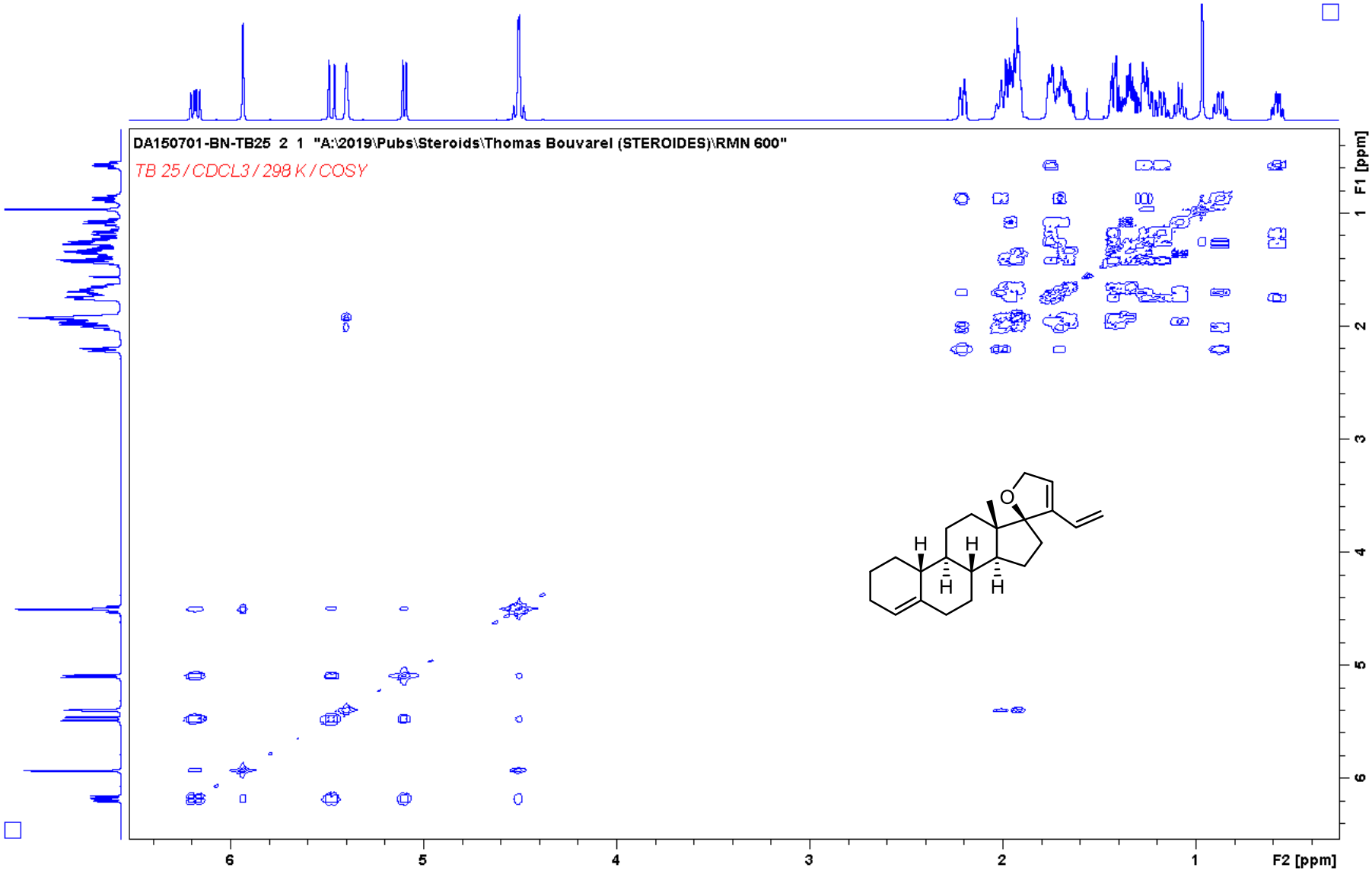
(2'*S*,8*R*,9*S*,10*R*,13*S*,14*S*)-13-Methyl-3'-vinyl-1,2,3,6,7,8,9,10,11,12,13,14,15,16-tetradecahydro-5'*H*-spiro[cyclopenta[*a*]phenanthrene-17,2'-furan] (9a): ^{1}H NMR (600 MHz, $CDCl_3$)



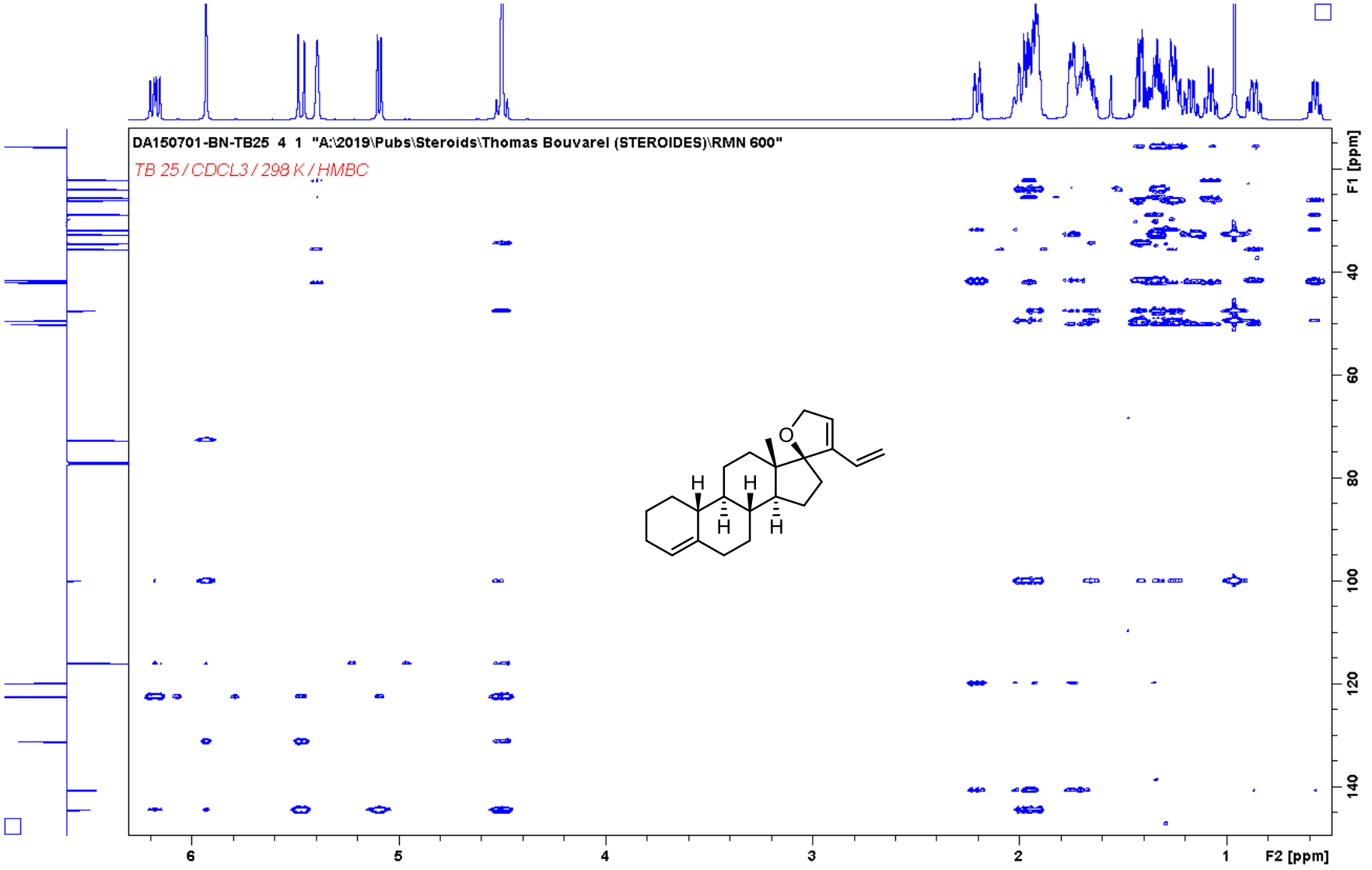
(2'*S*,8*R*,9*S*,10*R*,13*S*,14*S*)-13-Methyl-3'-vinyl-1,2,3,6,7,8,9,10,11,12,13,14,15,16-tetradecahydro-5'*H*-spiro[cyclopenta[*a*]phenanthrene-17,2'-furan] (9a): ^{13}C NMR (150 MHz, $CDCl_3$)



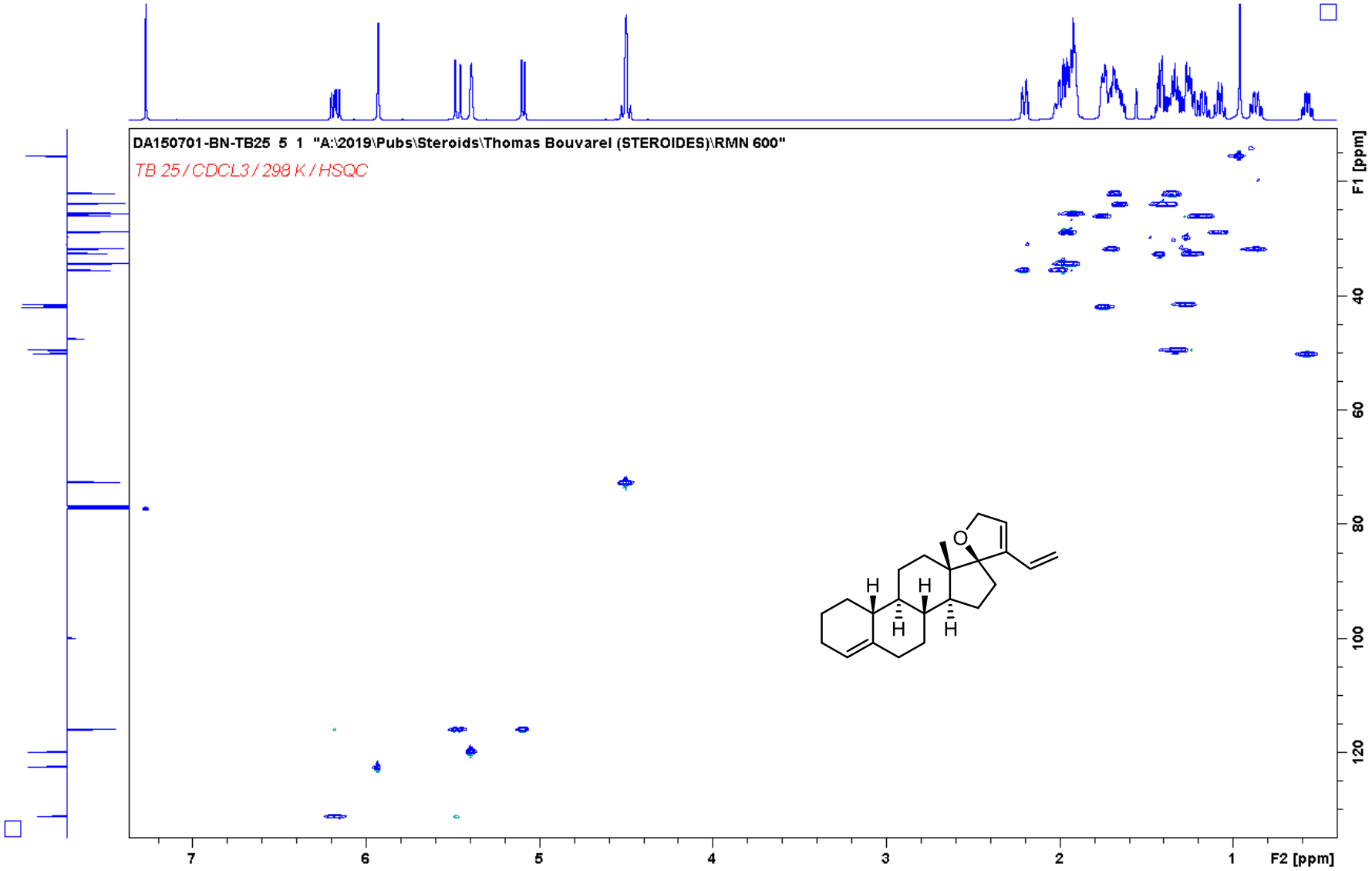
(2'*S*,8*R*,9*S*,10*R*,13*S*,14*S*)-13-Methyl-3'-vinyl-1,2,3,6,7,8,9,10,11,12,13,14,15,16-tetradecahydro-5'*H*-spiro[cyclopenta[*a*]phenanthrene-17,2'-furan] (9a): COSY NMR (600 MHz, $CDCl_3$)



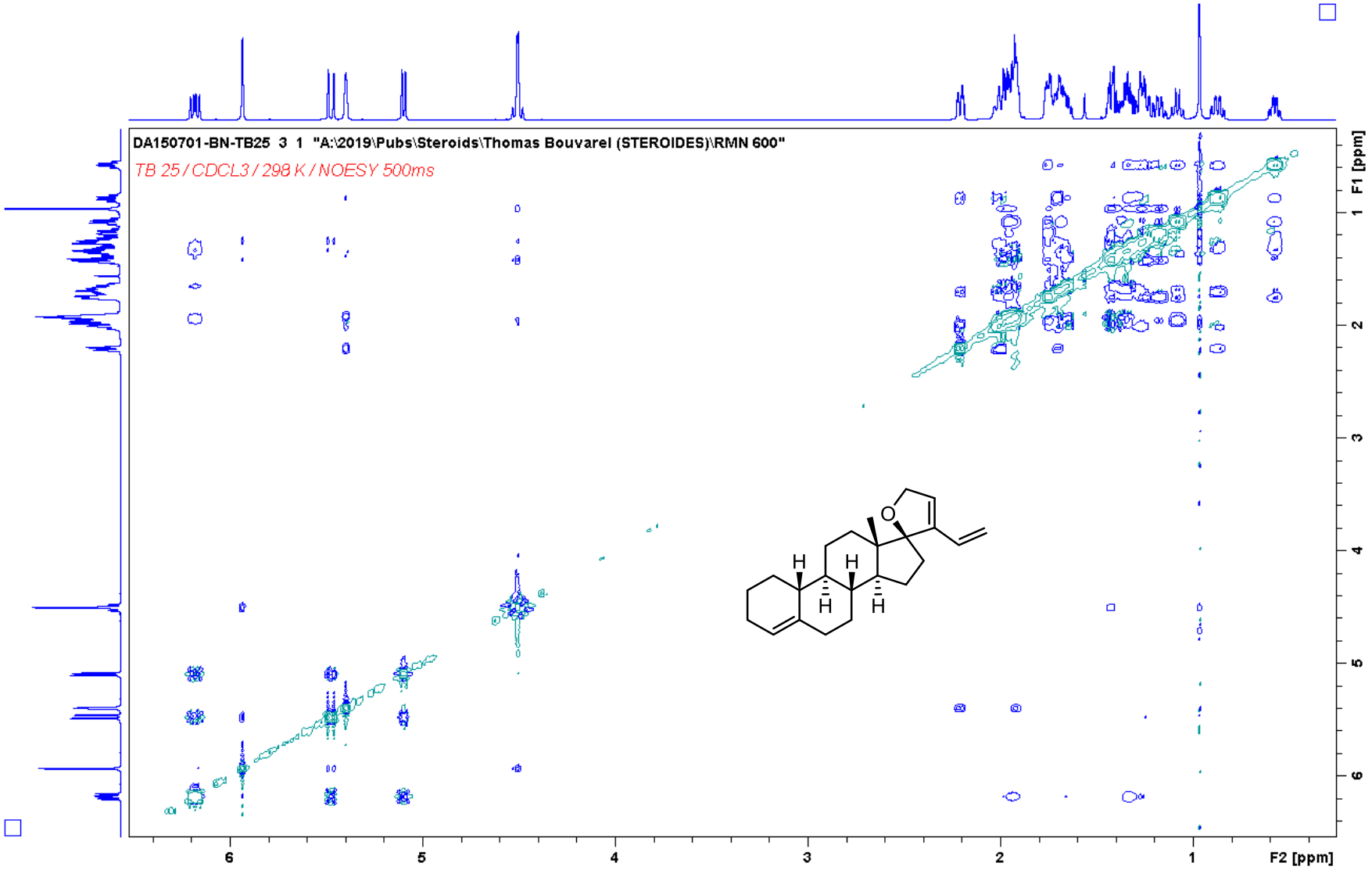
(2'*S*,8*R*,9*S*,10*R*,13*S*,14*S*)-13-Methyl-3'-vinyl-1,2,3,6,7,8,9,10,11,12,13,14,15,16-tetradecahydro-5'*H*-spiro[cyclopenta[*a*]phenanthrene-17,2'-furan] (9a): HMBC NMR (600 MHz, $CDCl_3$)



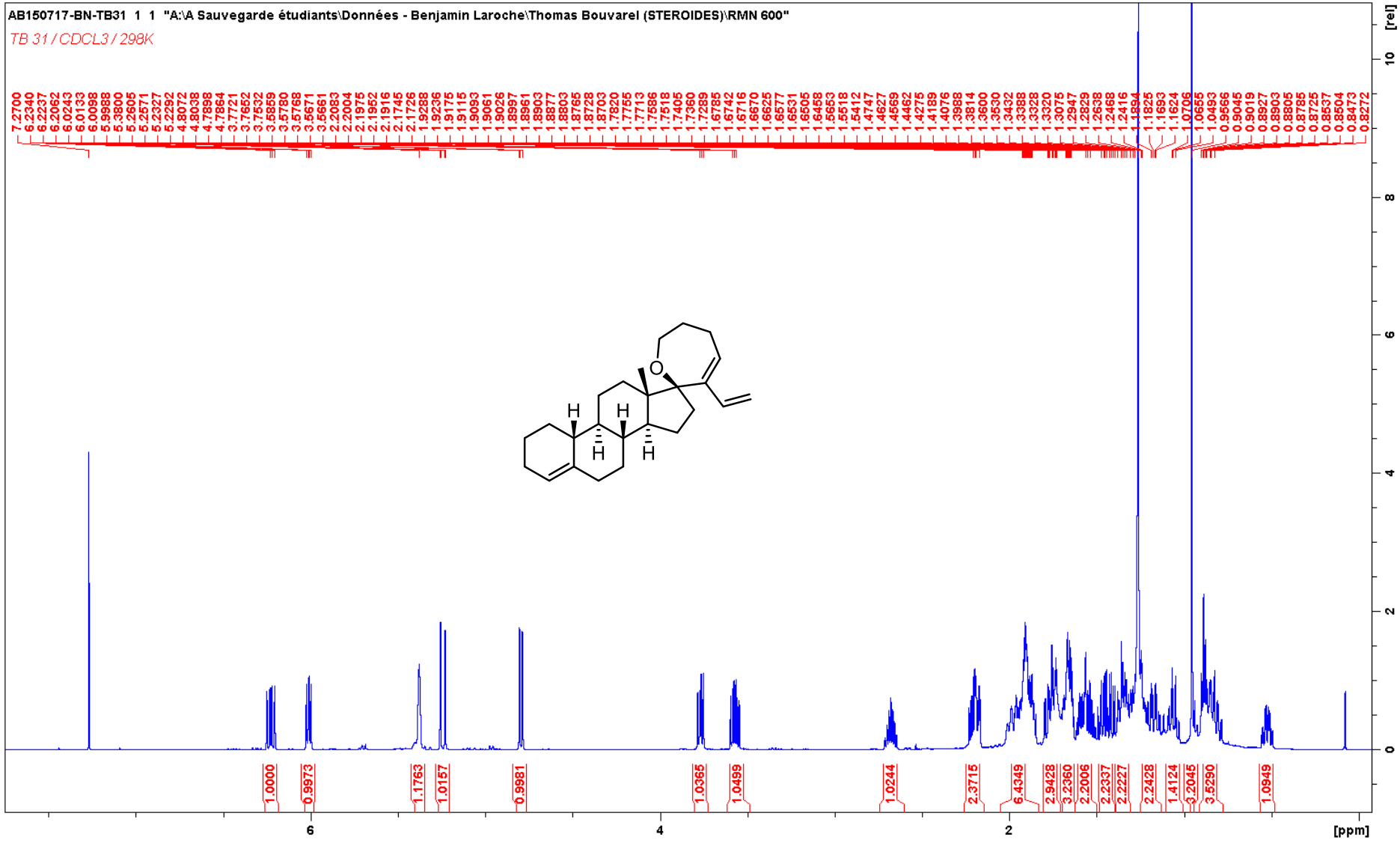
(2'*S*,8*R*,9*S*,10*R*,13*S*,14*S*)-13-Methyl-3'-vinyl-1,2,3,6,7,8,9,10,11,12,13,14,15,16-tetradecahydro-5'*H*-spiro[cyclopenta[*a*]phenanthrene-17,2'-furan] (9a): HSQC NMR (600 MHz, $CDCl_3$)



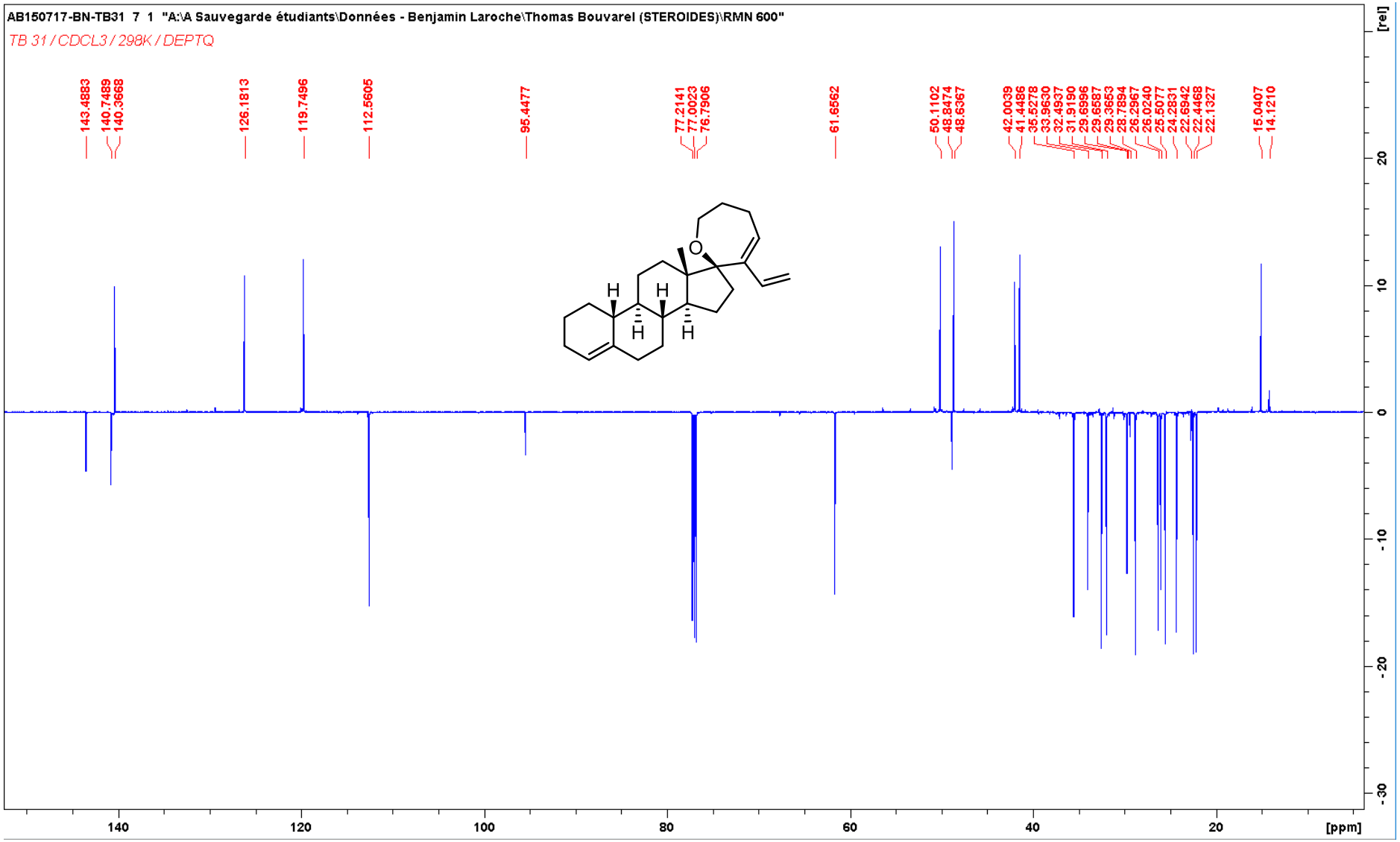
(2'*S*,8*R*,9*S*,10*R*,13*S*,14*S*)-13-Methyl-3'-vinyl-1,2,3,6,7,8,9,10,11,12,13,14,15,16-tetradecahydro-5'*H*-spiro[cyclopenta[*a*]phenanthrene-17,2'-furan] (9a): NOESY NMR (600 MHz, $CDCl_3$)



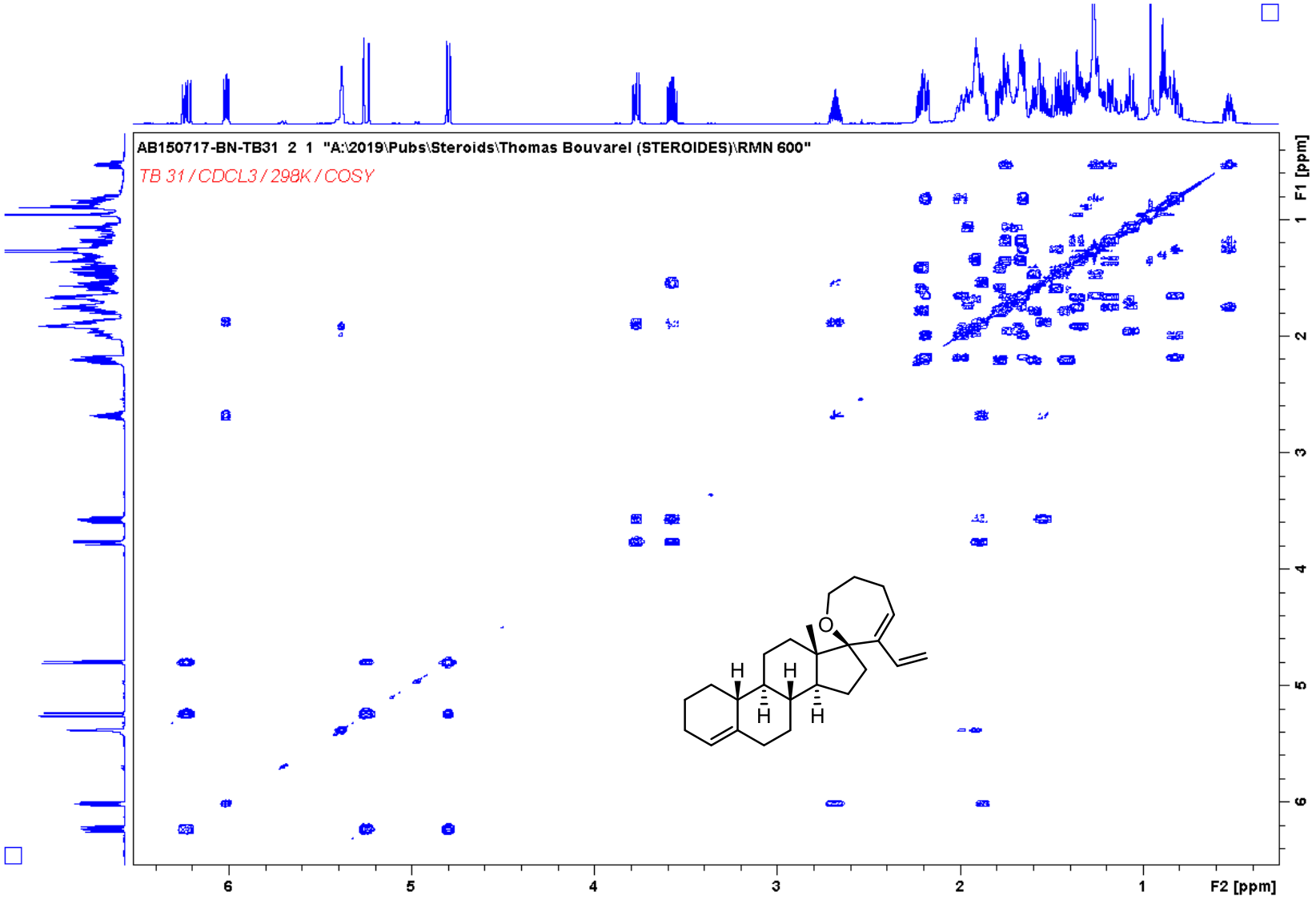
(2'*S*,8*R*,9*S*,10*R*,13*S*,14*S*)-13-Methyl-3'-vinyl-1,2,3,6,6',7,7',8,9,10,11,12,13,14,15,16-hexadecahydro-5'*H*-spiro[cyclopenta[*a*]phenanthrene-17,2'-oxepine] (9b): ^{1}H NMR (600 MHz, $CDCl_3$)



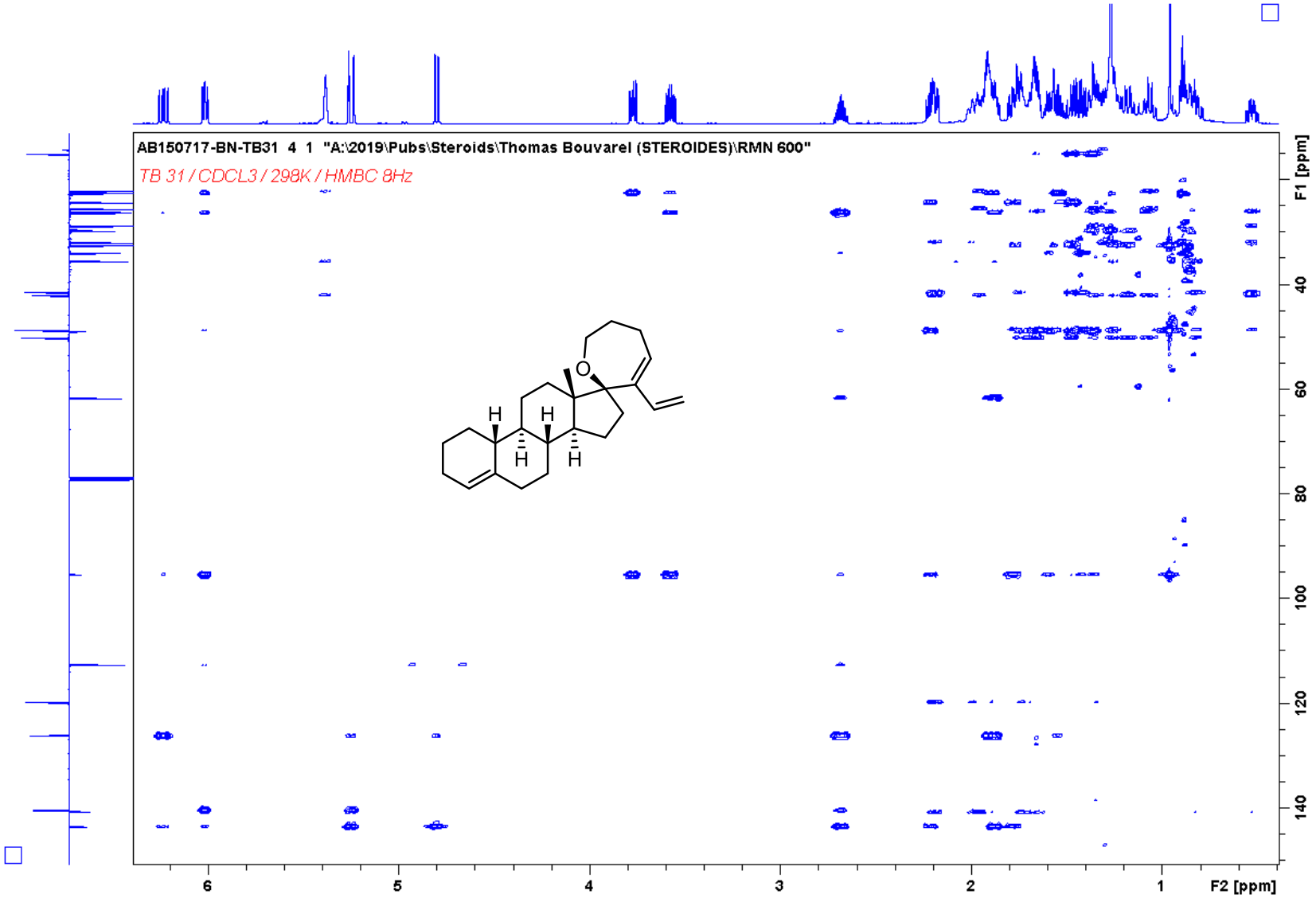
(2'*S*,8*R*,9*S*,10*R*,13*S*,14*S*)-13-Methyl-3'-vinyl-1,2,3,6,6',7,7',8,9,10,11,12,13,14,15,16-hexadecahydro-5'*H*-spiro[cyclopenta[*a*]phenanthrene-17,2'-oxepine] (9b): ^{13}C NMR (150 MHz, $CDCl_3$)



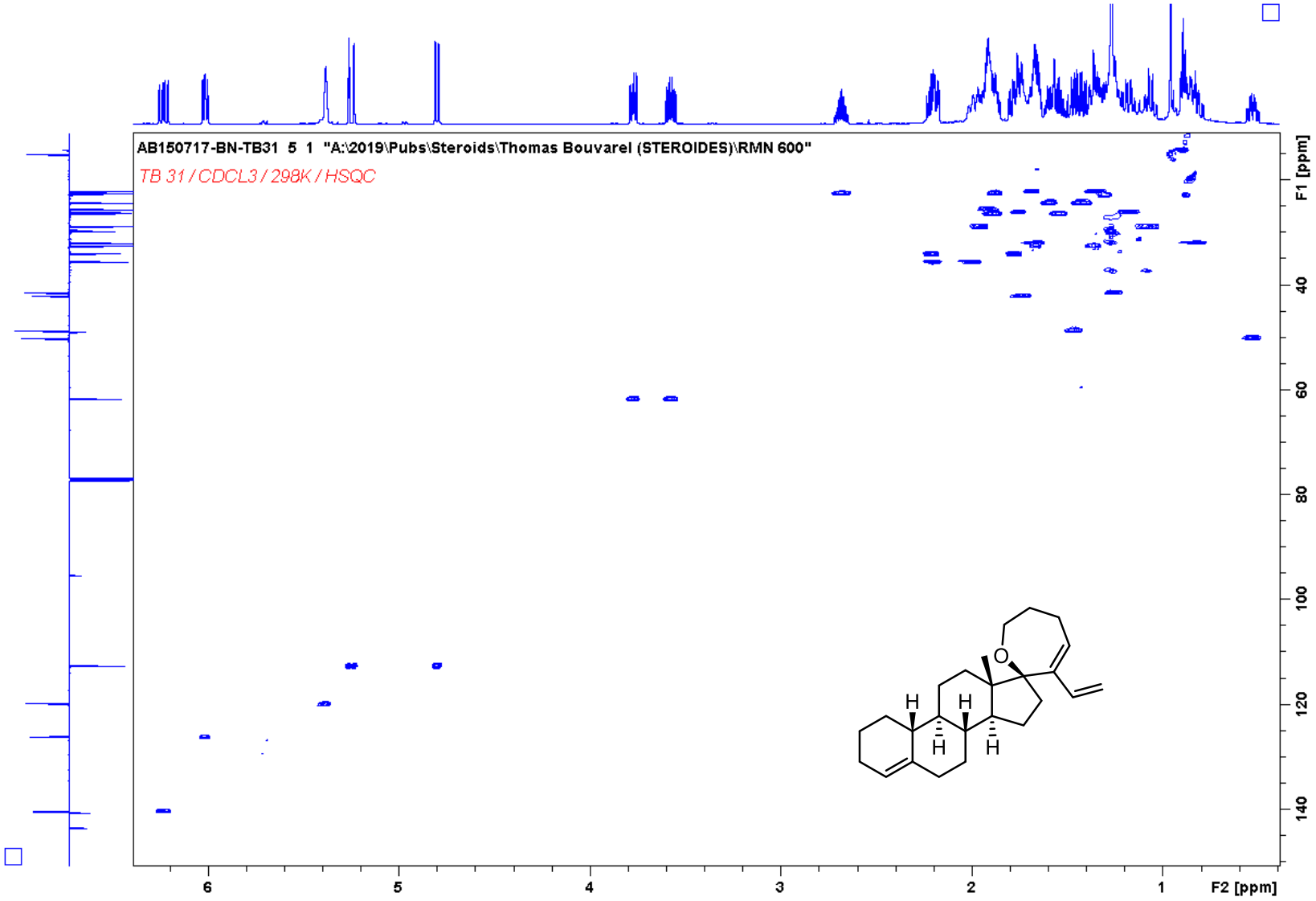
(2'*S*,8*R*,9*S*,10*R*,13*S*,14*S*)-13-Methyl-3'-vinyl-1,2,3,6,6',7,7',8,9,10,11,12,13,14,15,16-hexadecahydro-5'*H*-spiro[cyclopenta[*a*]phenanthrene-17,2'-oxepine] (9b): COSY NMR (600 MHz, $CDCl_3$)



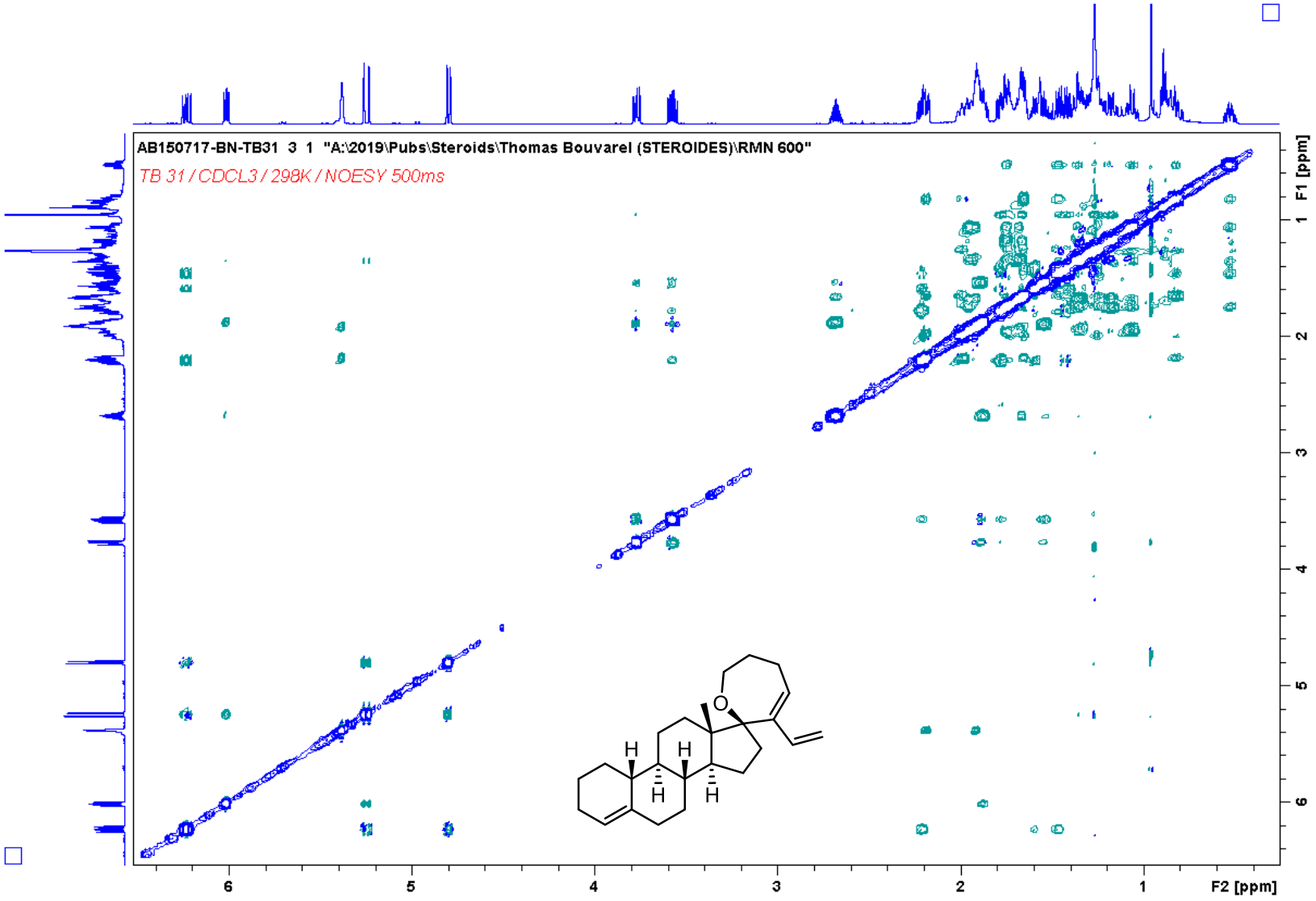
(2'*S*,8*R*,9*S*,10*R*,13*S*,14*S*)-13-Methyl-3'-vinyl-1,2,3,6,6',7,7',8,9,10,11,12,13,14,15,16-hexadecahydro-5'*H*-spiro[cyclopenta[*a*]phenanthrene-17,2'-oxepine] (9b): HMBC NMR (600 MHz, $CDCl_3$)



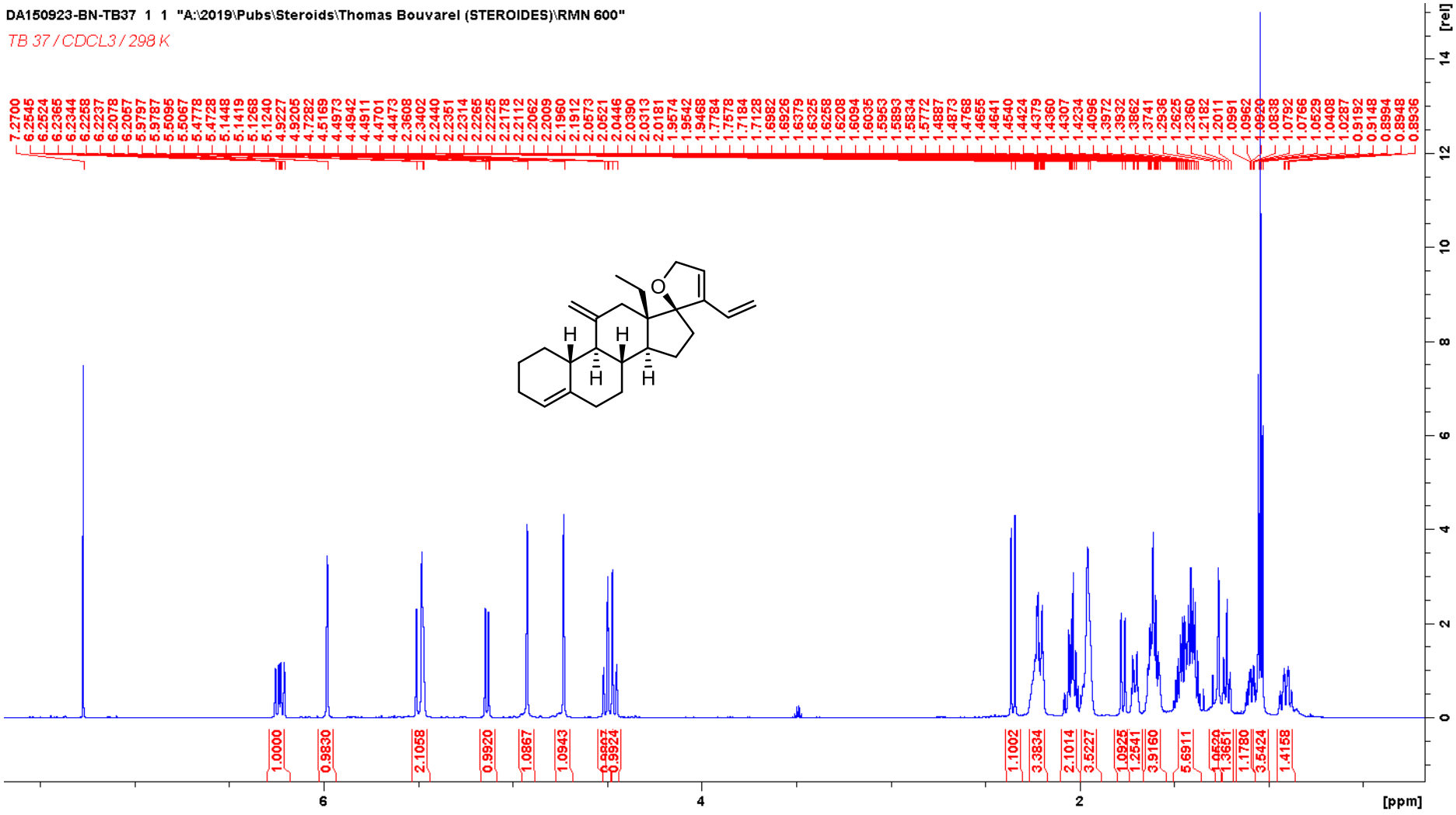
(2'*S*,8*R*,9*S*,10*R*,13*S*,14*S*)-13-Methyl-3'-vinyl-1,2,3,6,6',7,7',8,9,10,11,12,13,14,15,16-hexadecahydro-5'*H*-spiro[cyclopenta[a]phenanthrene-17,2'-oxepine] (9b): HSQC NMR (600 MHz, $CDCl_3$)



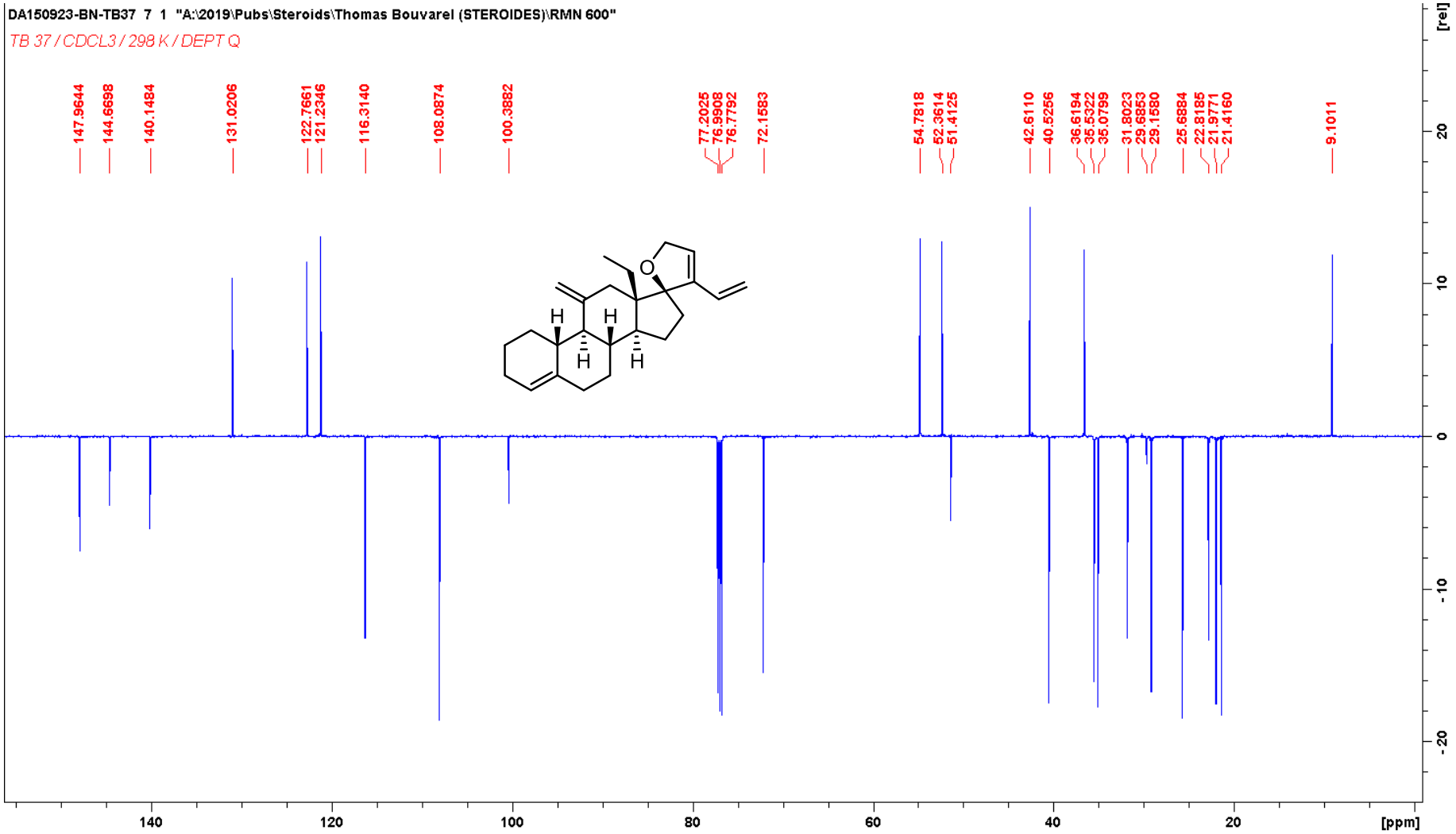
(2'*S*,8*R*,9*S*,10*R*,13*S*,14*S*)-13-Methyl-3'-vinyl-1,2,3,6,6',7,7',8,9,10,11,12,13,14,15,16-hexadecahydro-5'*H*-spiro[cyclopenta[*a*]phenanthrene-17,2'-oxepine] (9b): NOESY NMR (600 MHz, $CDCl_3$)



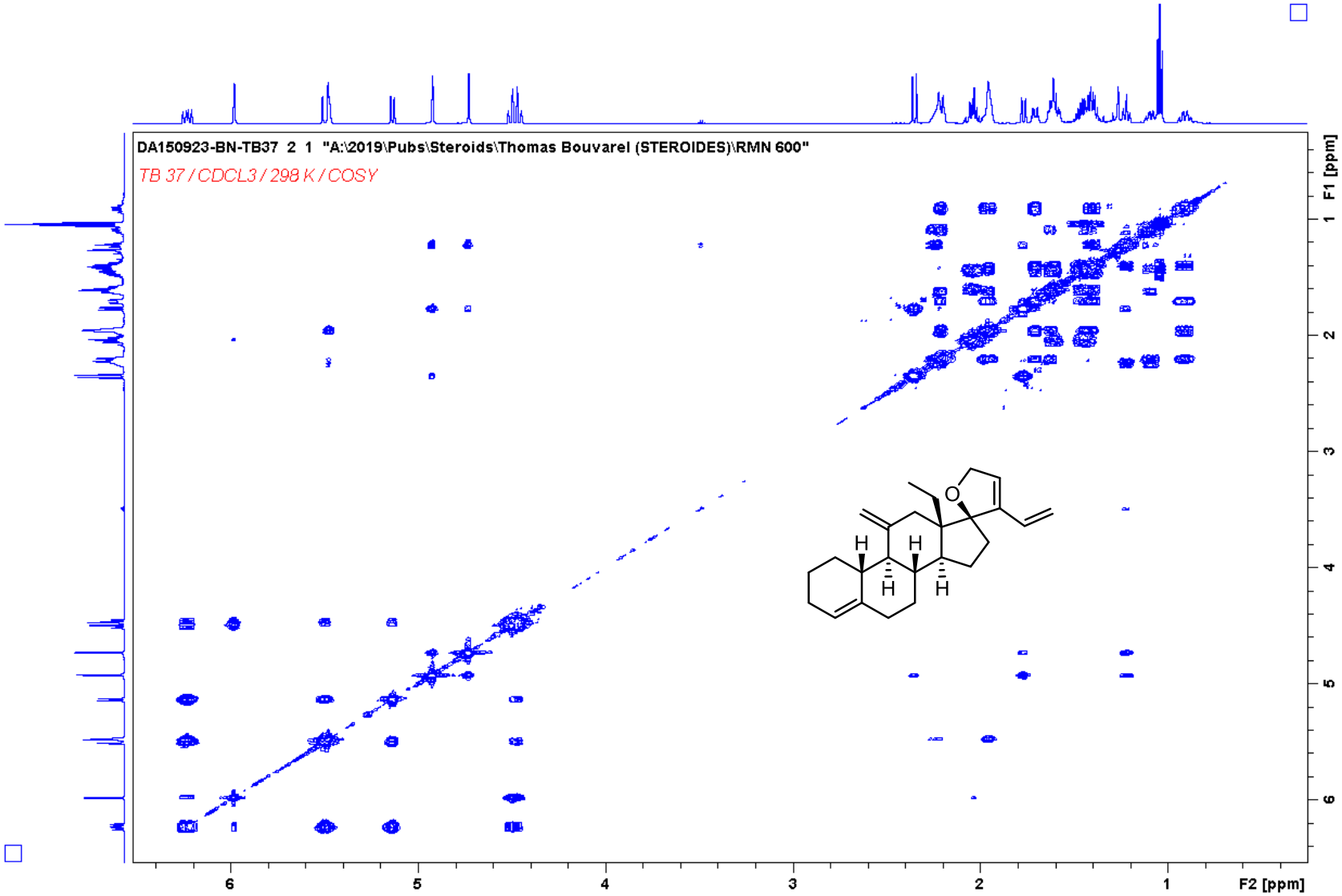
(8*R*,9*S*,13*S*,14*S*,17*R*)-3-Methoxy-13-methyl-3'-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-5'*H*,6'*H*,7'*H*-spiro[cyclopenta[*a*]phenanthrene-17,2'-oxepin] (10): ^{1}H NMR (600 MHz, $CDCl_3$)



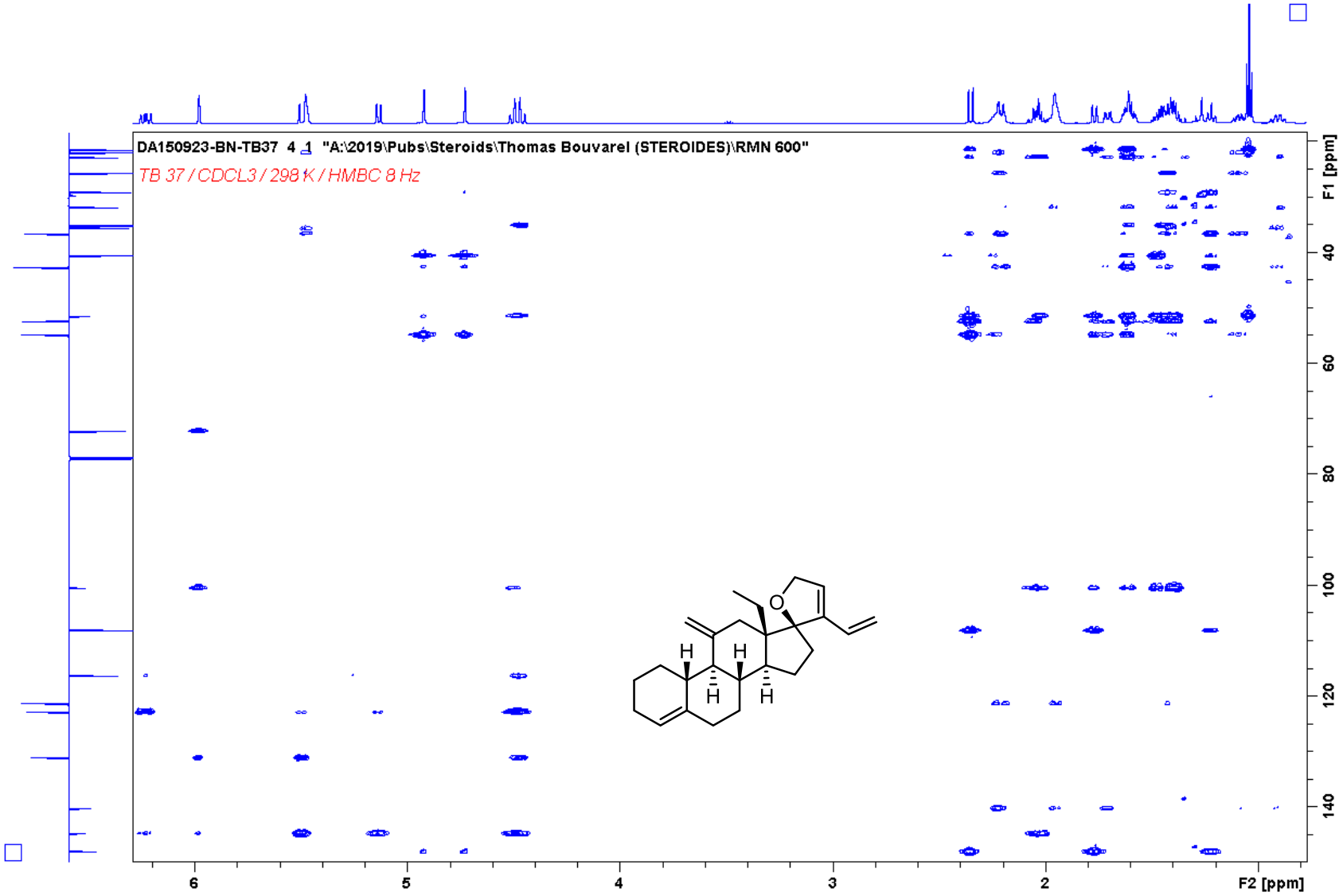
(8*R*,9*S*,13*S*,14*S*,17*R*)-3-Methoxy-13-methyl-3'-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-5'*H*,6'*H*,7'*H*-spiro[cyclopenta[*a*]phenanthrene-17,2'-oxepin] (10): ^{13}C NMR (150 MHz, $CDCl_3$)



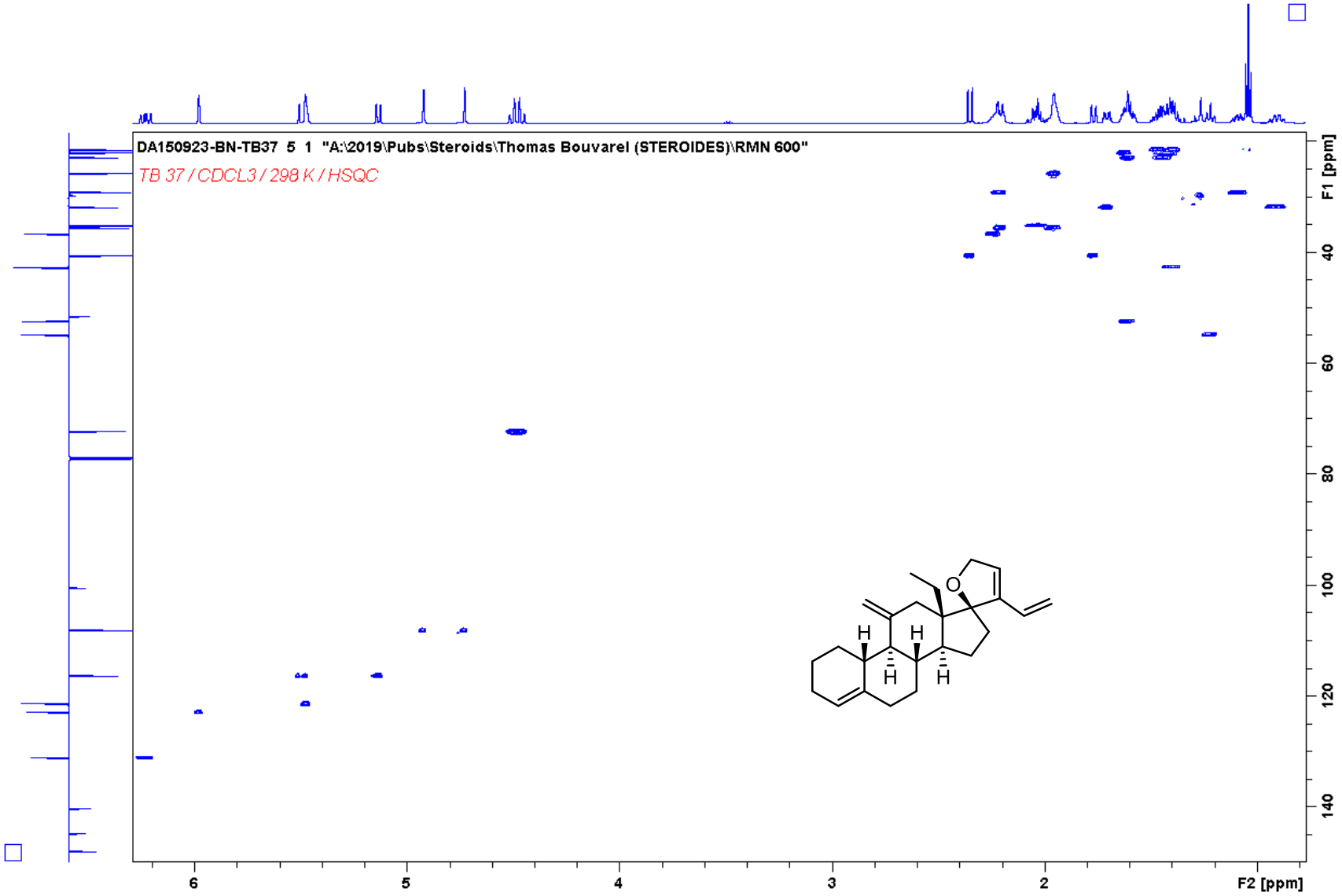
(8*R*,9*S*,13*S*,14*S*,17*R*)-3-Methoxy-13-methyl-3'-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-5'*H*,6'*H*,7'*H*-spiro[cyclopenta[*a*]phenanthrene-17,2'-oxepin] (10): COSY NMR (600 MHz, $CDCl_3$)



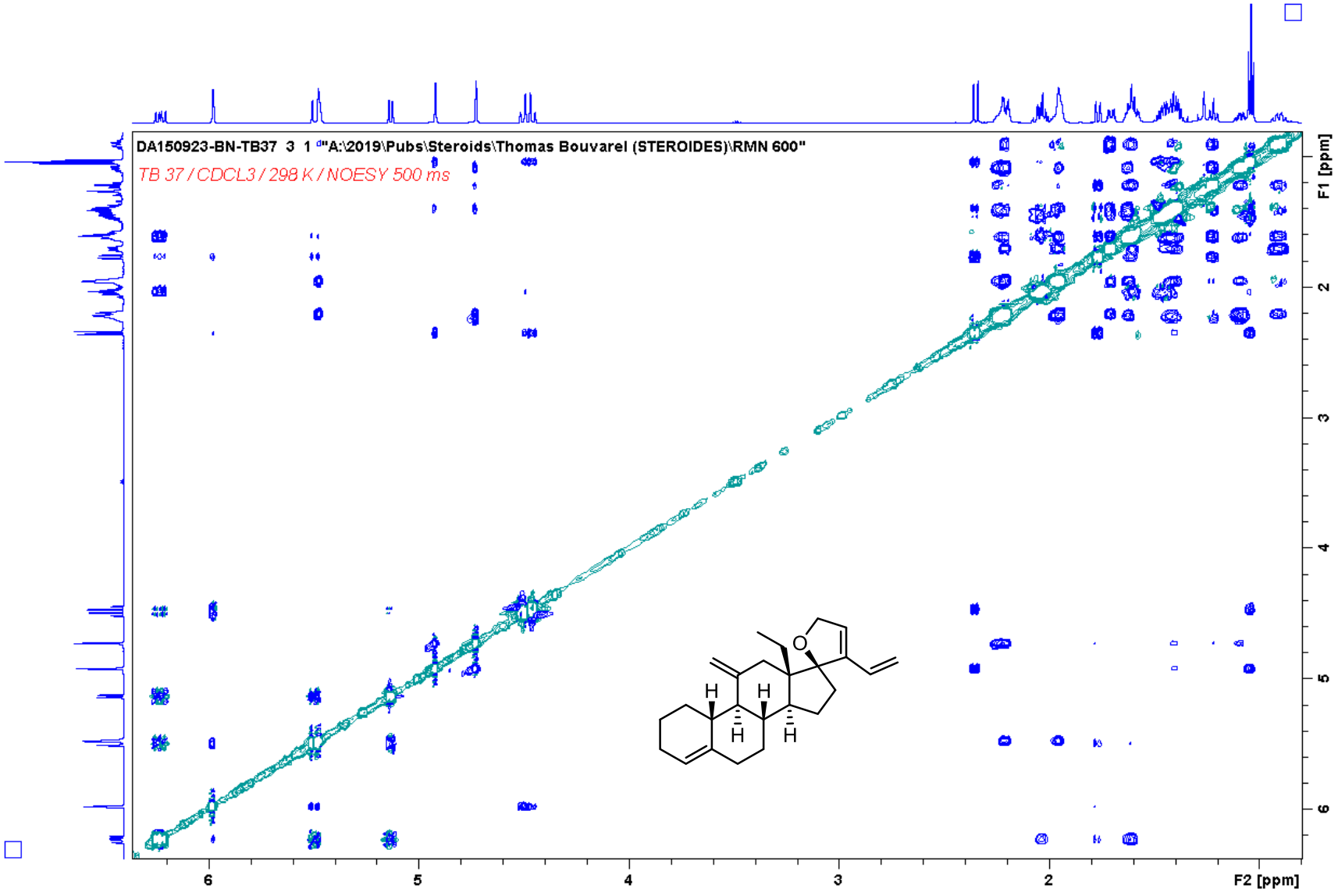
(8*R*,9*S*,13*S*,14*S*,17*R*)-3-Methoxy-13-methyl-3'-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-5'*H*,6'*H*,7'*H*-spiro[cyclopenta[*a*]phenanthrene-17,2'-oxepin] (10): HMBC NMR (600 MHz, $CDCl_3$)



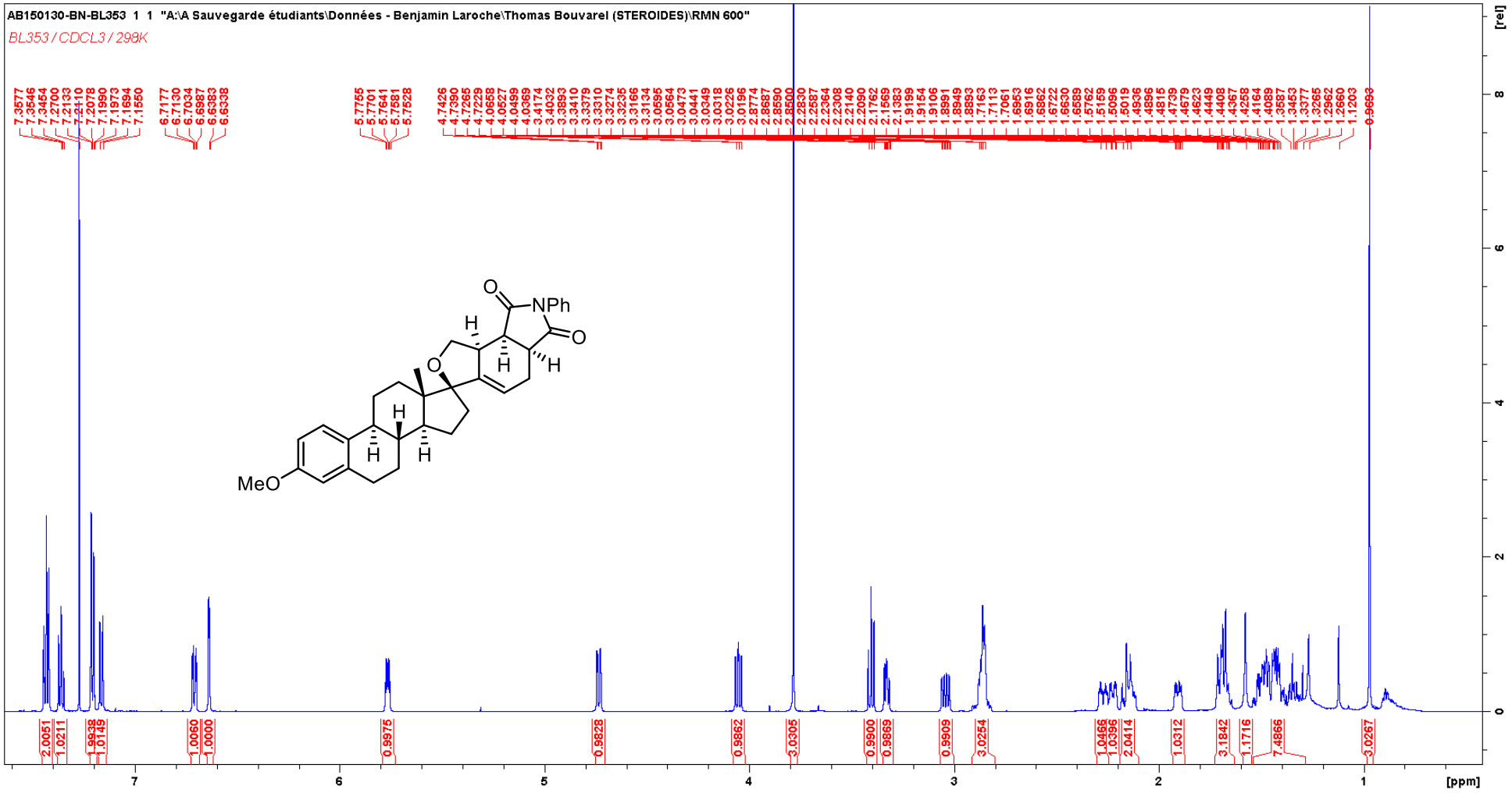
(8*R*,9*S*,13*S*,14*S*,17*R*)-3-Methoxy-13-methyl-3'-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-5'*H*,6'*H*,7'*H*-spiro[cyclopenta[*a*]phenanthrene-17,2'-oxepin] (10): HSQC NMR (600 MHz, $CDCl_3$)



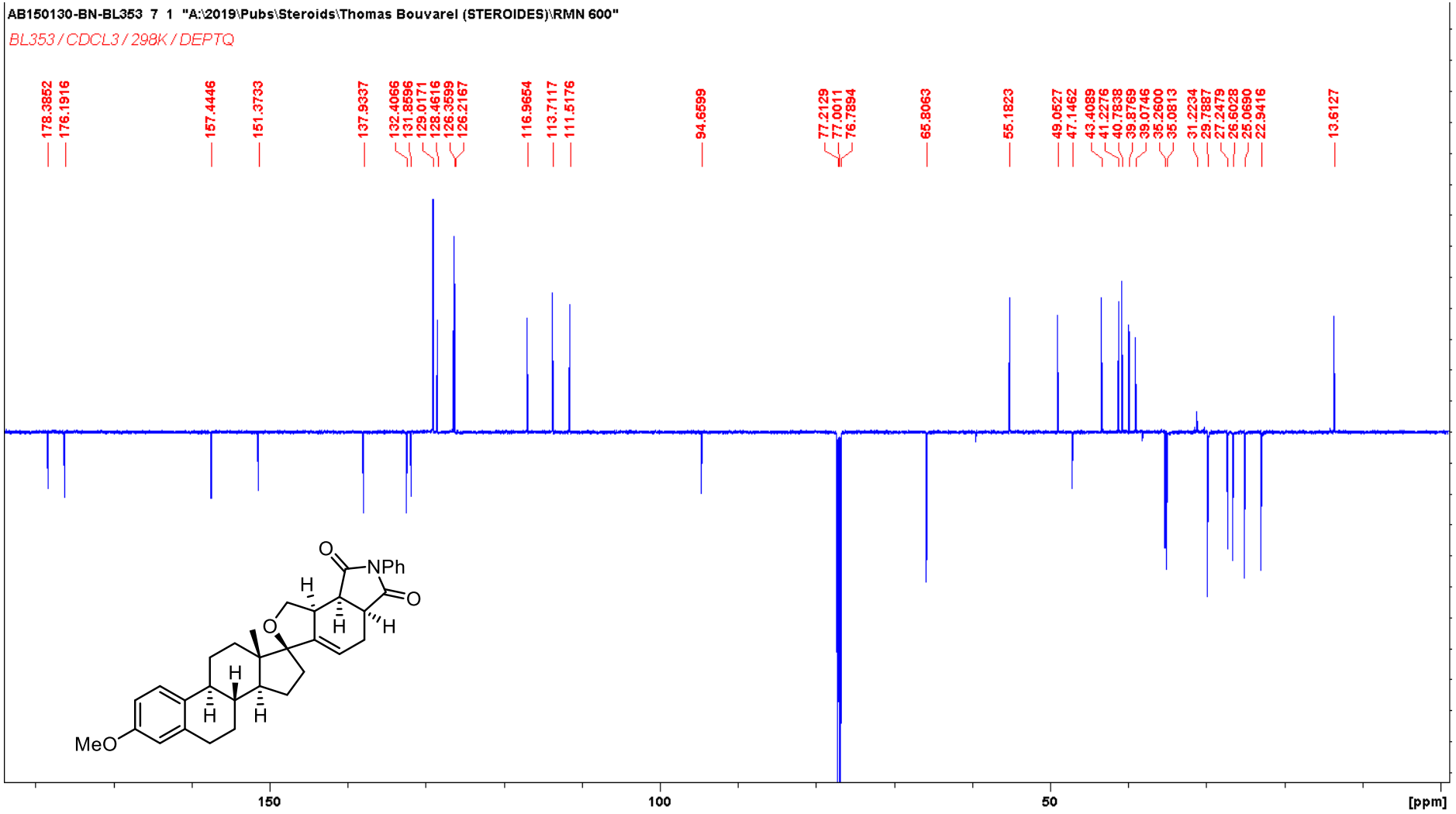
(8*R*,9*S*,13*S*,14*S*,17*R*)-3-Methoxy-13-methyl-3'-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-5'*H*,6'*H*,7'*H*-spiro[cyclopenta[*a*]phenanthrene-17,2'-oxepin] (10): NOESY NMR (600 MHz, $CDCl_3$)



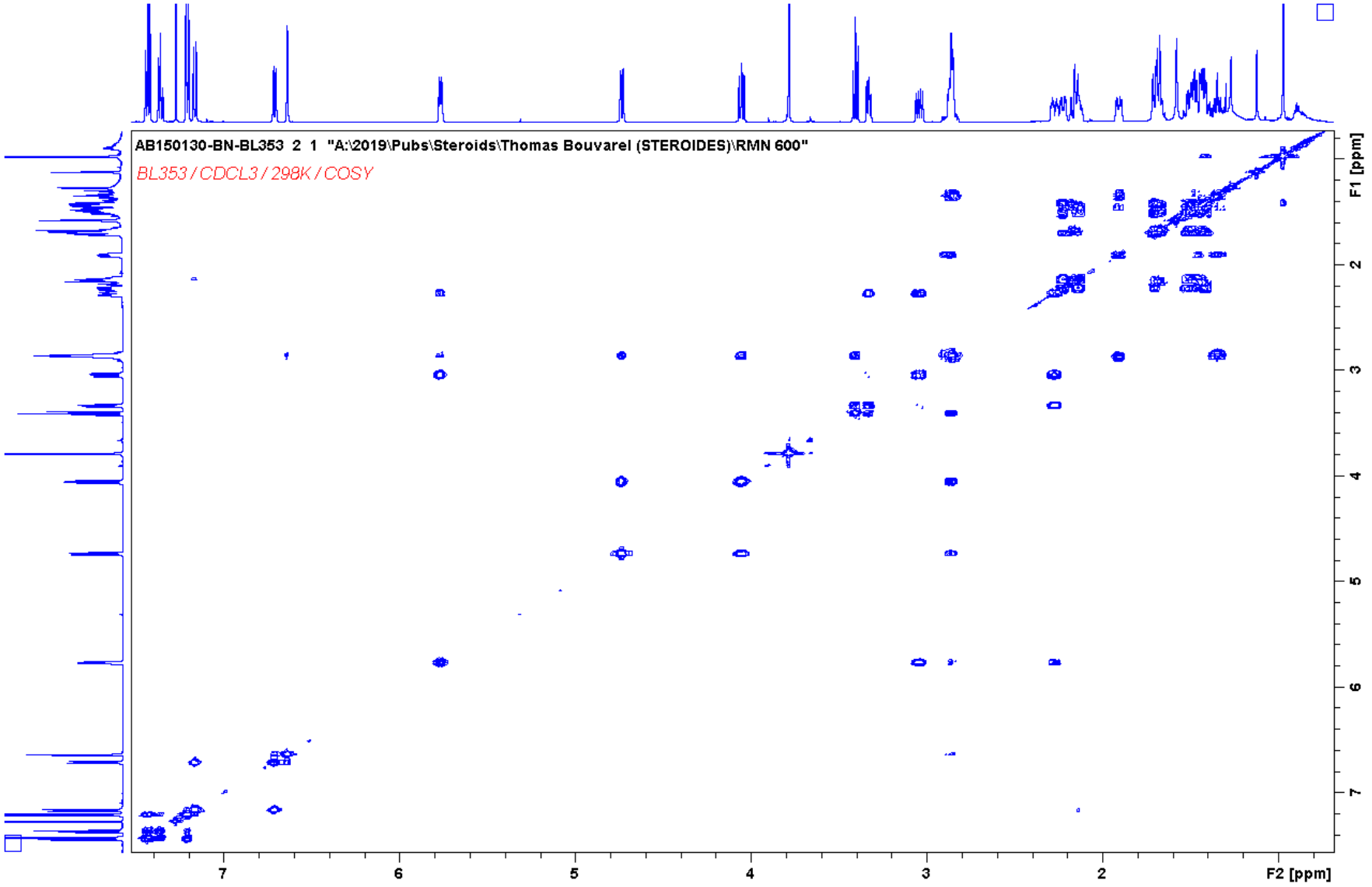
(3'S,5a'S,8R,8a'R,8b'S,9S,13S,14S)-3-Methoxy-13-methyl-7'-phenyl-1',5',5a',6,7,8,8b',9,11,12,13,14,15,16-tetradecahydrospiro[cyclopenta[*a*]phenanthrene-17,3'-furo[3,4-*e*]isoindole]-6',8'(7'*H*,8a'*H*)-dione (16a): ^{1}H NMR (600 MHz, $CDCl_3$)



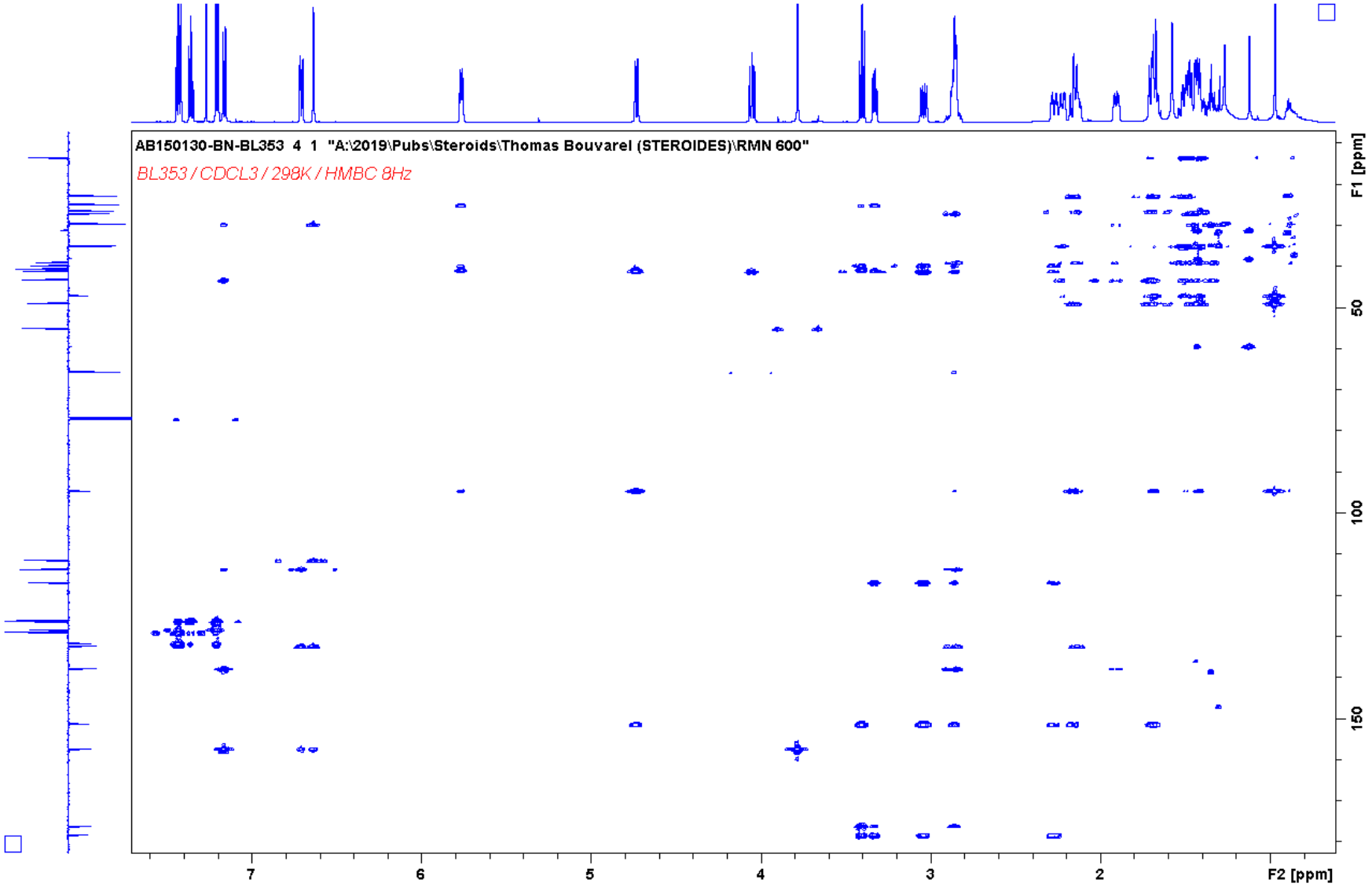
(3'*S*,5a'*S*,8*R*,8a'*R*,8b'*S*,9*S*,13*S*,14*S*)-3-Methoxy-13-methyl-7'-phenyl-1',5',5a',6,7,8,8b',9,11,12,13,14,15,16-tetradecahydrospiro[cyclopenta[*a*]phenanthrene-17,3'-furo[3,4-*e*]isoindole]-6',8'(7'*H*,8a'*H*)-dione (16a): ^{13}C NMR (150 MHz, $CDCl_3$)



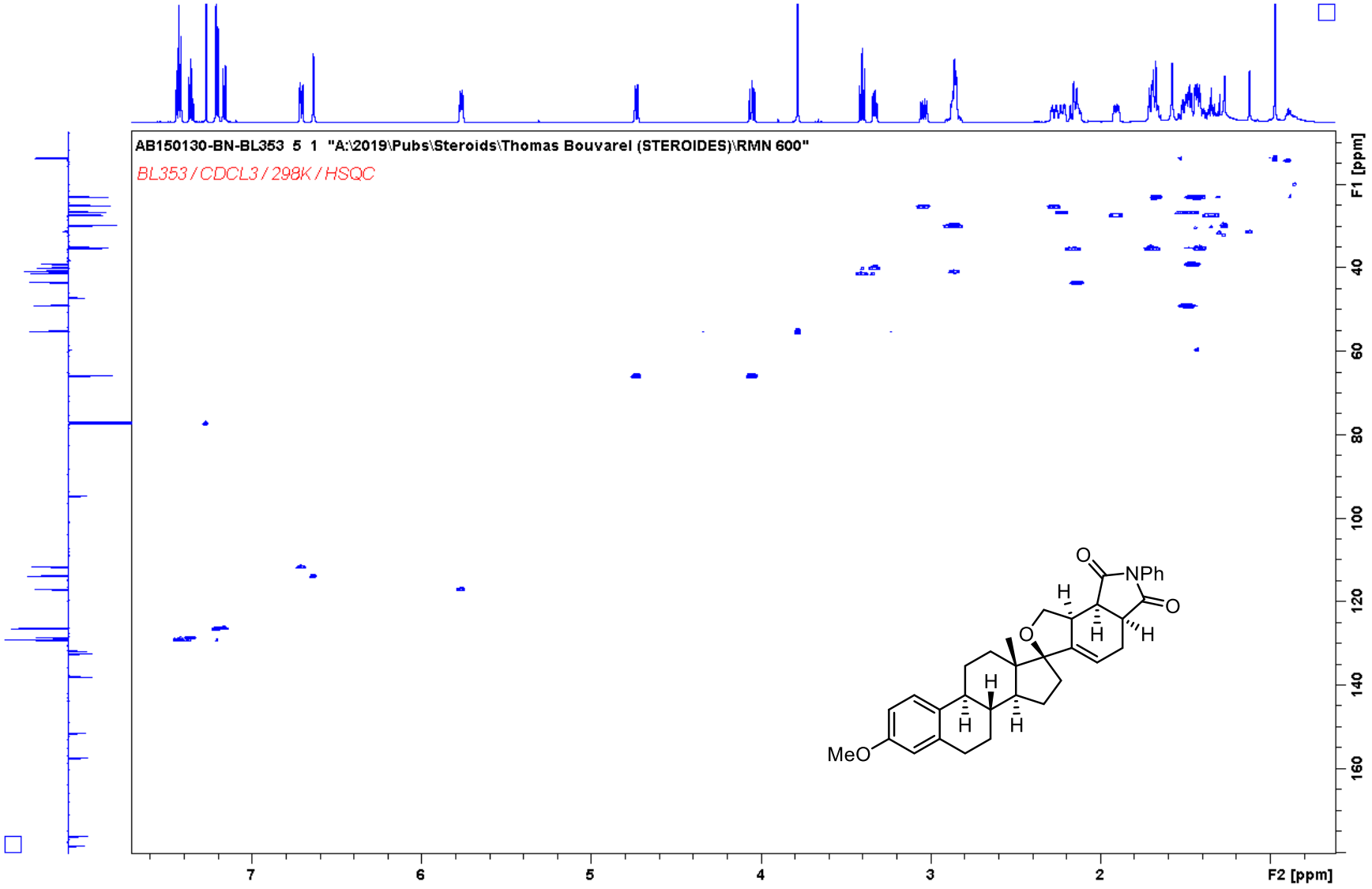
(3'*S*,5a'*S*,8*R*,8a'*R*,8b'*S*,9*S*,13*S*,14*S*)-3-Methoxy-13-methyl-7'-phenyl-1',5',5a',6,7,8,8b',9,11,12,13,14,15,16-tetradecahydrospiro[cyclopenta[*a*]phenanthrene-17,3'-furo[3,4-*e*]isoindole]-6',8'(7'H,8a'*H*)-dione (16a): COSY NMR (600 MHz,



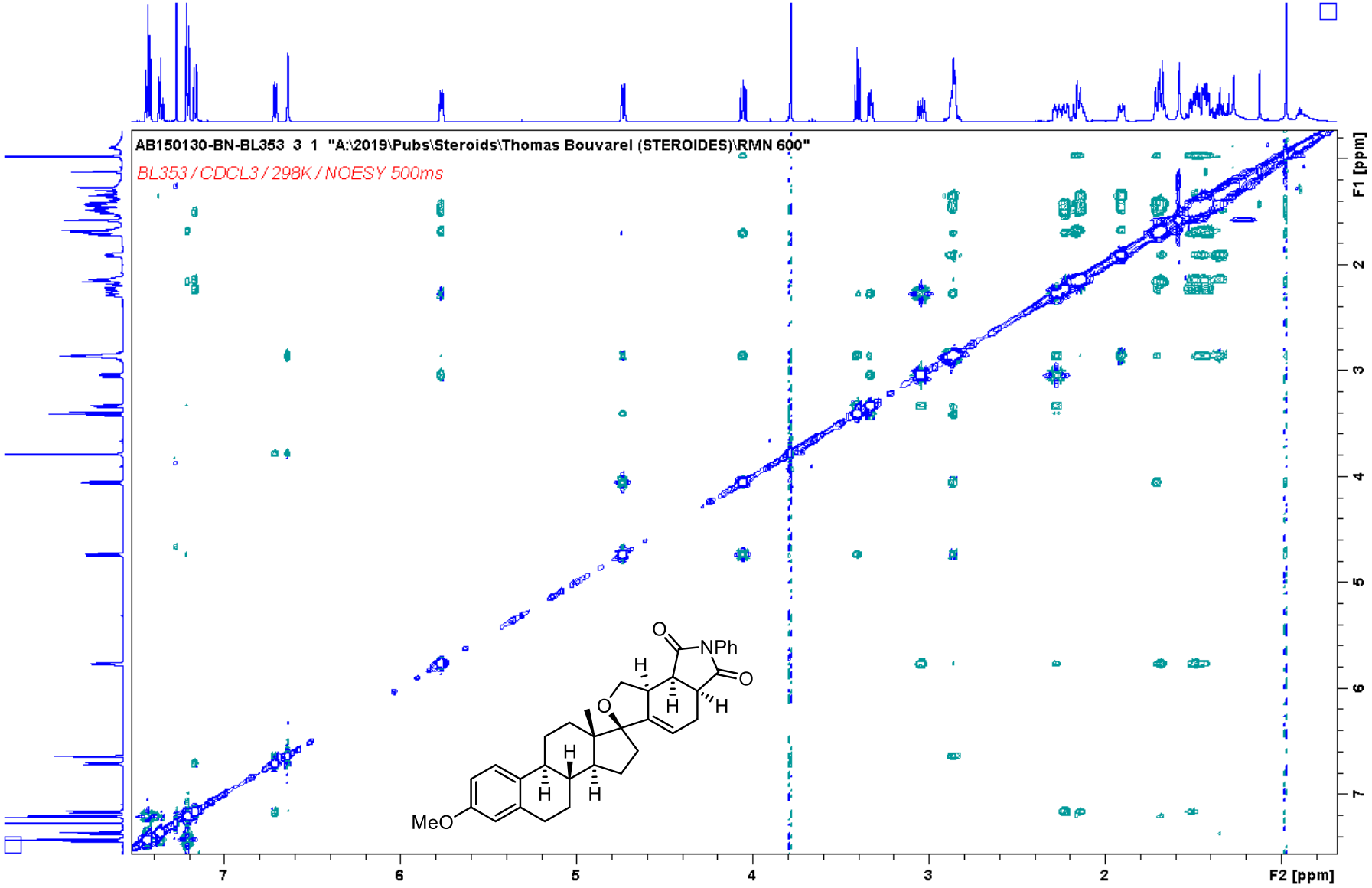
(3'*S*,5a'*S*,8*R*,8a'*R*,8b'*S*,9*S*,13*S*,14*S*)-3-Methoxy-13-methyl-7'-phenyl-1',5',5a',6,7,8,8b',9,11,12,13,14,15,16-tetradecahydrospiro[cyclopenta[*a*]phenanthrene-17,3'-furo[3,4-*e*]isoindole]-6',8'(7'*H*,8a'*H*)-dione (16a): HMBC NMR (600 MHz,



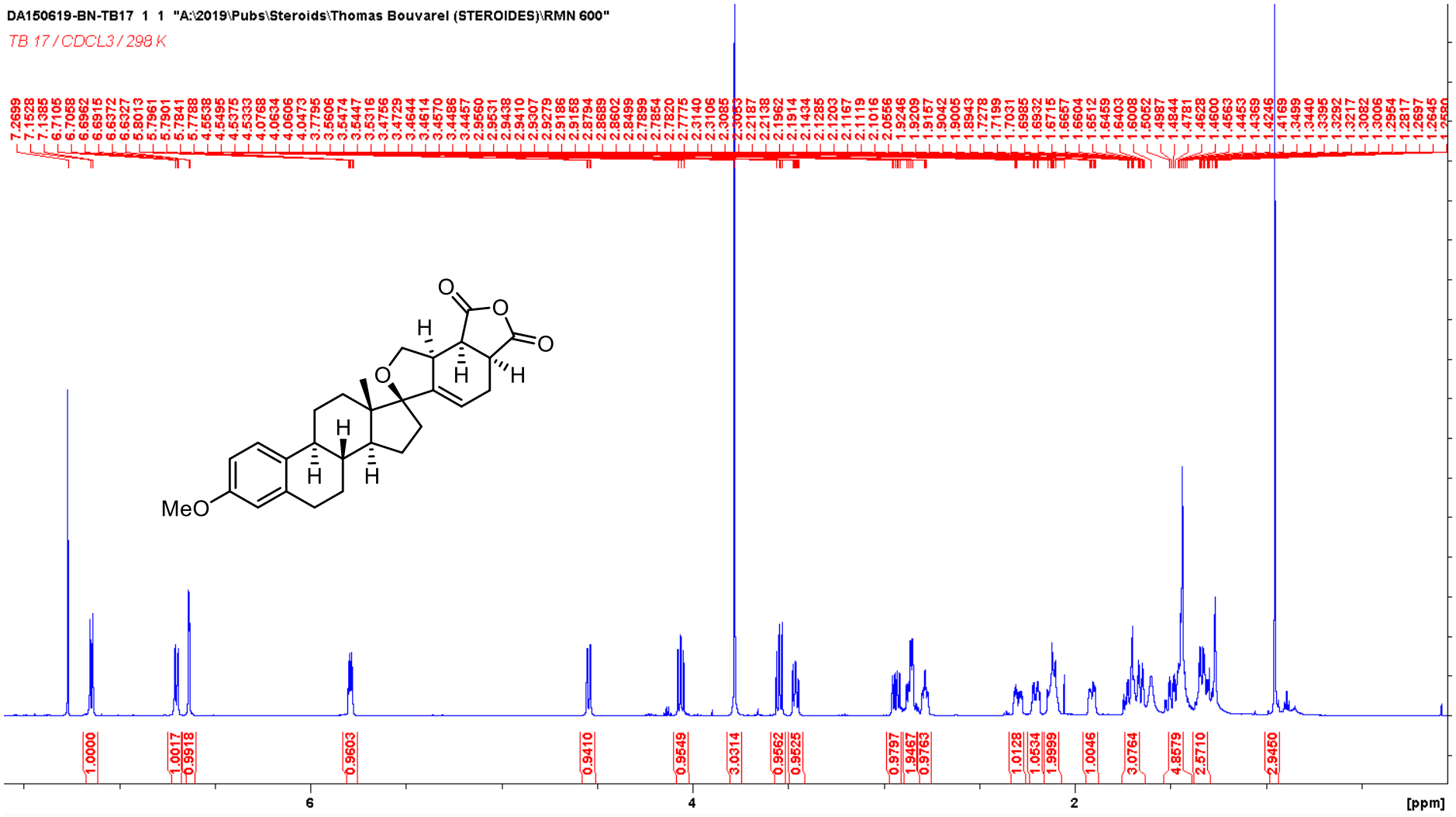
(3'*S*,5a'*S*,8*R*,8a'*R*,8b'*S*,9*S*,13*S*,14*S*)-3-Methoxy-13-methyl-7'-phenyl-1',5',5a',6,7,8,8b',9,11,12,13,14,15,16-tetradecahydrospiro[cyclopenta[*a*]phenanthrene-17,3'-furo[3,4-*e*]isoindole]-6',8'(7'*H*,8a'*H*)-dione (16a): HSQC NMR (600 MHz,



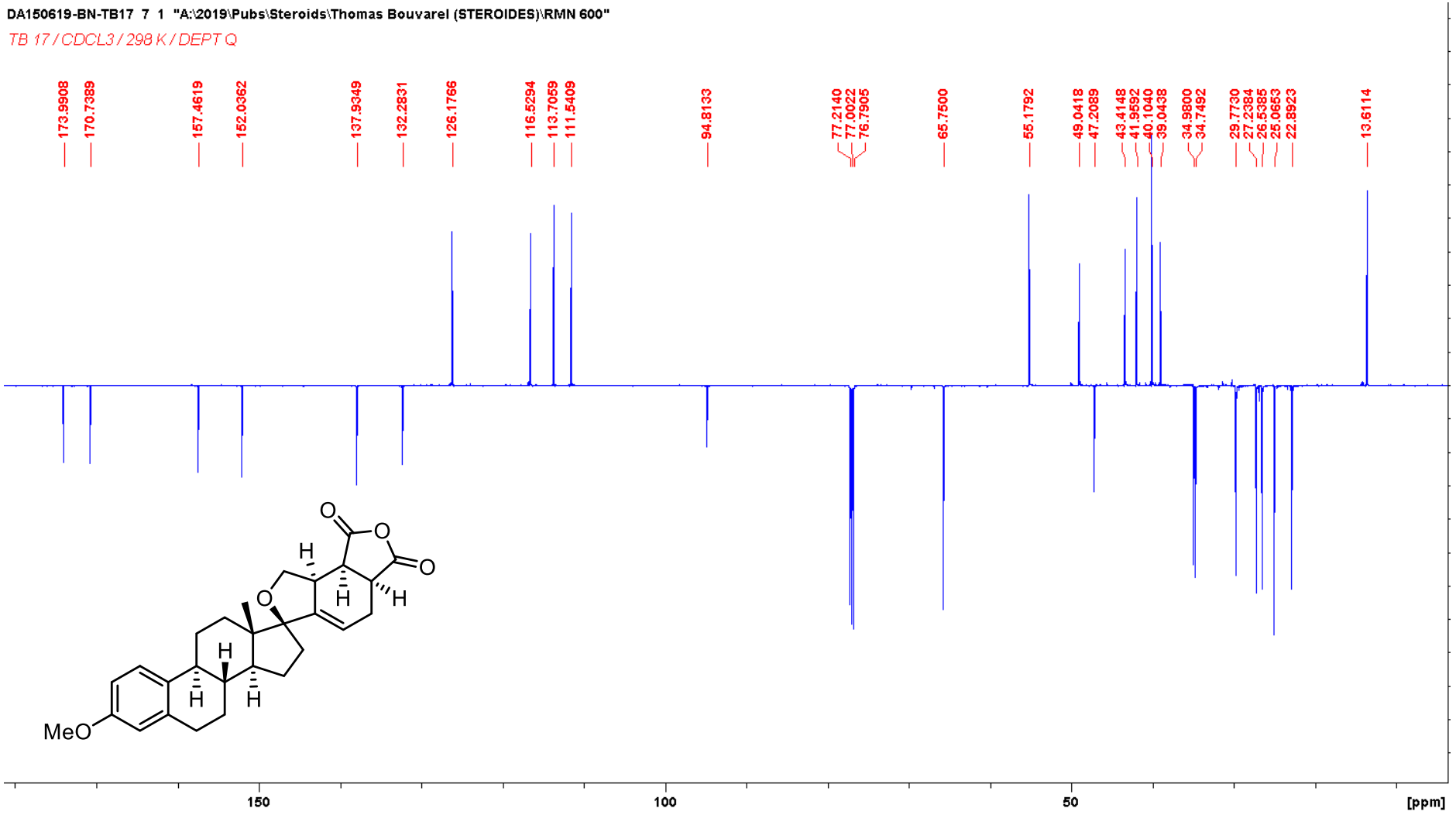
(3'*S*,5a'*S*,8*R*,8a'*R*,8b'*S*,9*S*,13*S*,14*S*)-3-Methoxy-13-methyl-7'-phenyl-1',5',5a',6,7,8,8b',9,11,12,13,14,15,16-tetradecahydrospiro[cyclopenta[*a*]phenanthrene-17,3'-furo[3,4-*e*]isoindole]-6',8'(7'*H*,8a'*H*)-dione (16a): NOESY NMR (600 MHz,



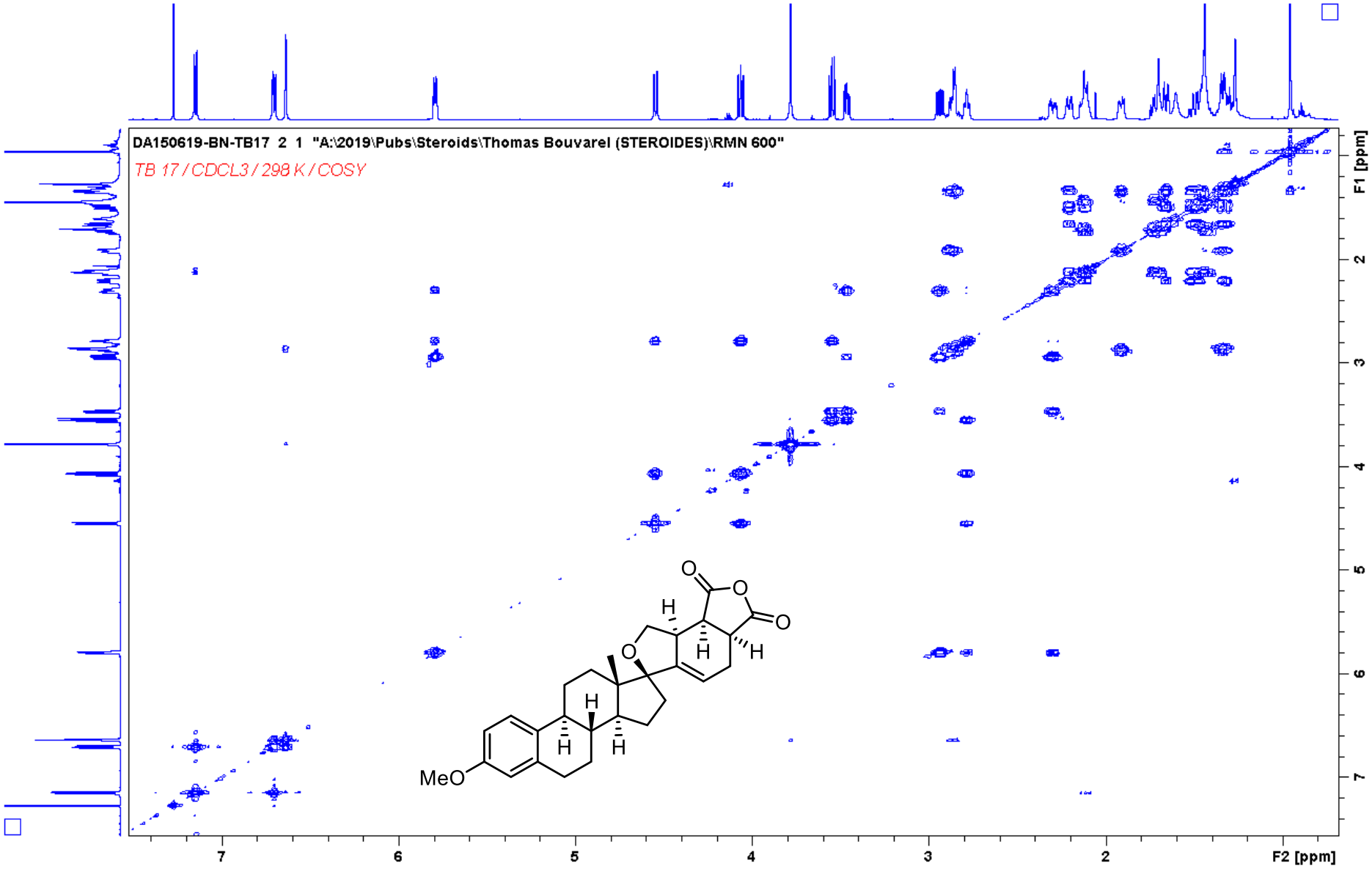
(3*S*,5a*S*,8a*R*,8b*S*,8'*R*,9'*S*,13'*S*,14'*S*)-3'-Methoxy-13'-methyl-5,5a,6',7',8',9',11',12',13',14',15',16'-dodecahydro-1*H*-spiro[benzo[1,2-*c*:3,4-*c*']difuran-3,17'-cyclopenta[*a*]phenanthrene]-6,8(8a*H*,8b*H*)-dione (16b): ^{1}H NMR (600 MHz, $CDCl_3$)



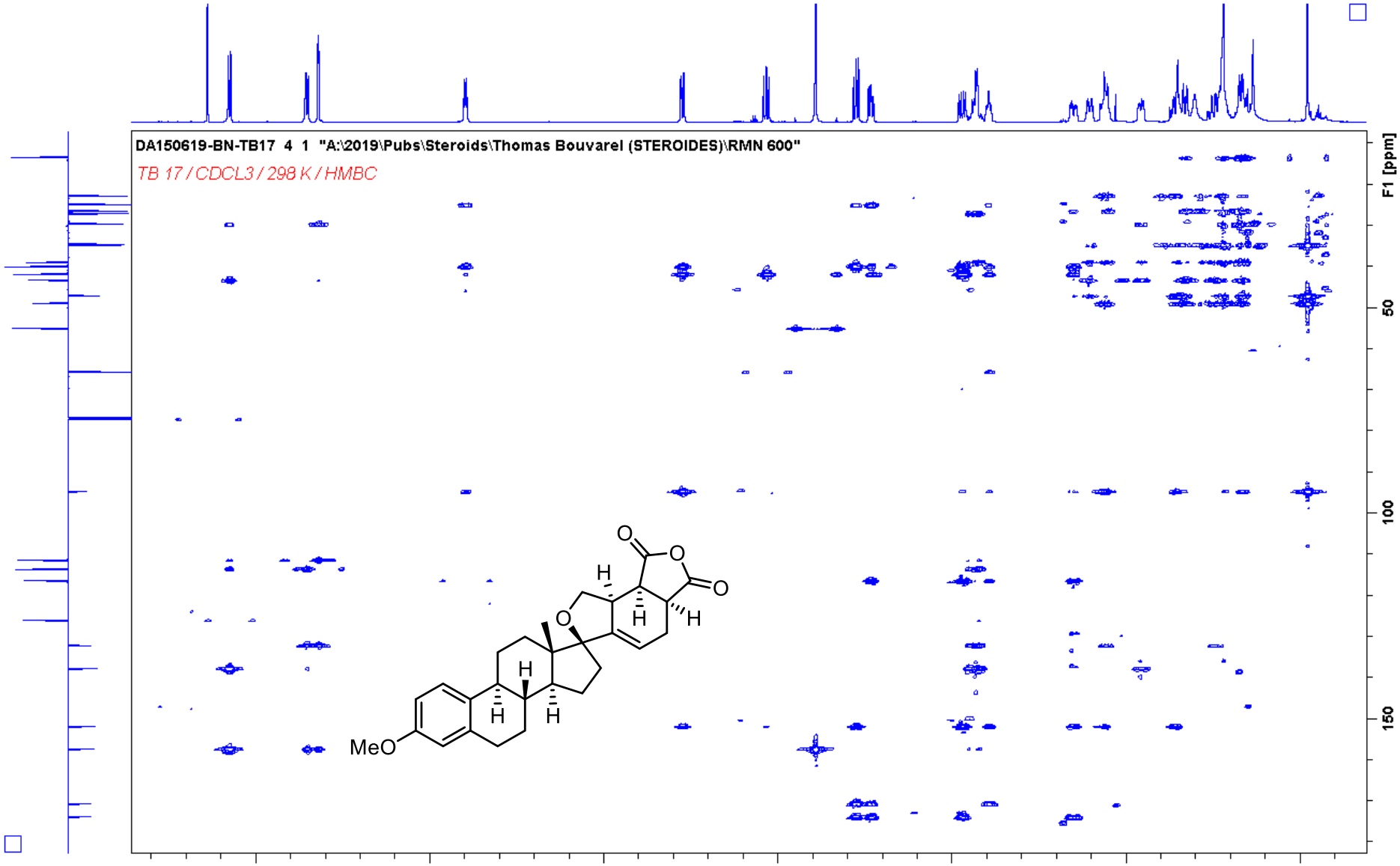
(3*S*,5a*S*,8a*R*,8b*S*,8'*R*,9'*S*,13'*S*,14'*S*)-3'-Methoxy-13'-methyl-5,5a,6',7',8',9',11',12',13',14',15',16'-dodecahydro-1*H*-spiro[benzo[1,2-*c*:3,4-*c*']difuran-3,17'-cyclopenta[*a*]phenanthrene]-6,8(8a*H*,8b*H*)-dione (16b): ^{13}C NMR (150 MHz, $CDCl_3$)



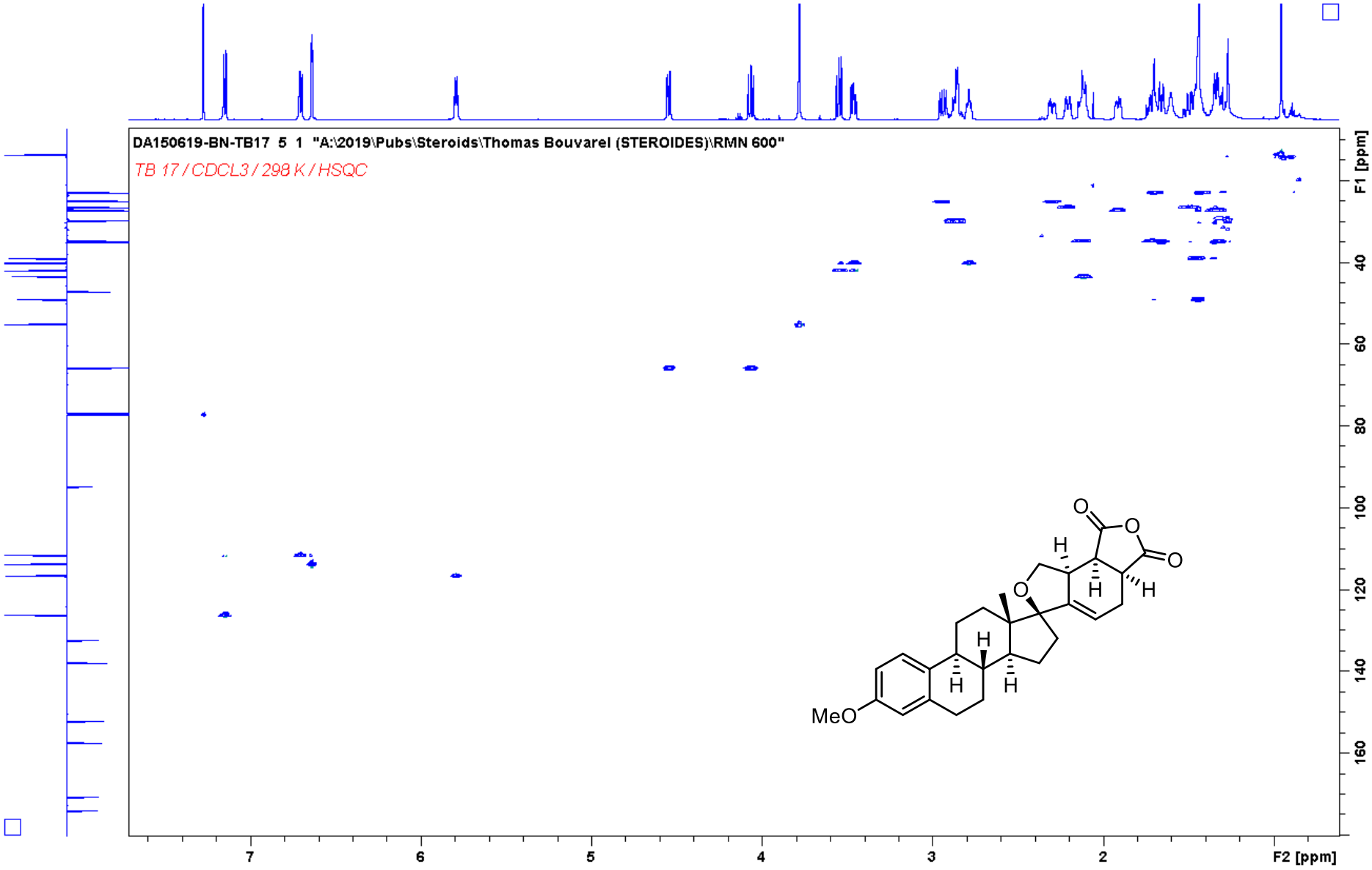
(3*S*,5a*S*,8a*R*,8b*S*,8'*R*,9'*S*,13'*S*,14'*S*)-3'-Methoxy-13'-methyl-5,5a,6',7',8',9',11',12',13',14',15',16'-dodecahydro-1*H*-spiro[benzo[1,2-*c*:3,4-*c*']difuran-3,17'-cyclopenta[*a*]phenanthrene]-6,8(8a*H*,8b*H*)-dione (16b): COSY NMR (600 MHz, $CDCl_3$)



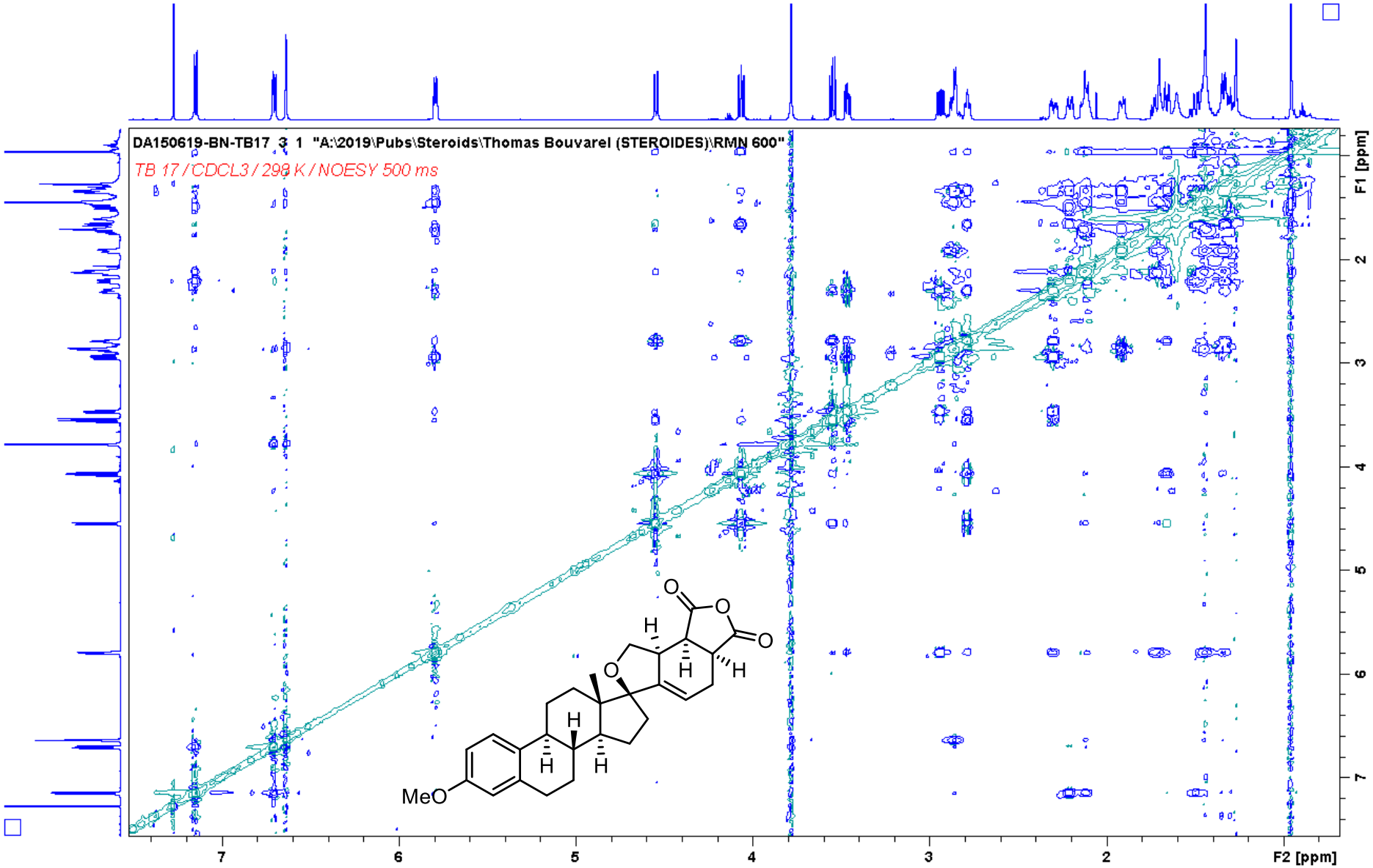
(3*S*,5a*S*,8a*R*,8b*S*,8'*R*,9'*S*,13'*S*,14'*S*)-3'-Methoxy-13'-methyl-5,5a,6',7',8',9',11',12',13',14',15',16'-dodecahydro-1*H*-spiro[benzo[1,2-*c*:3,4-*c*']difuran-3,17'-cyclopenta[*a*]phenanthrene]-6,8(8a*H*,8b*H*)dione (16b): HMBC NMR (600 MHz, $CDCl_3$)



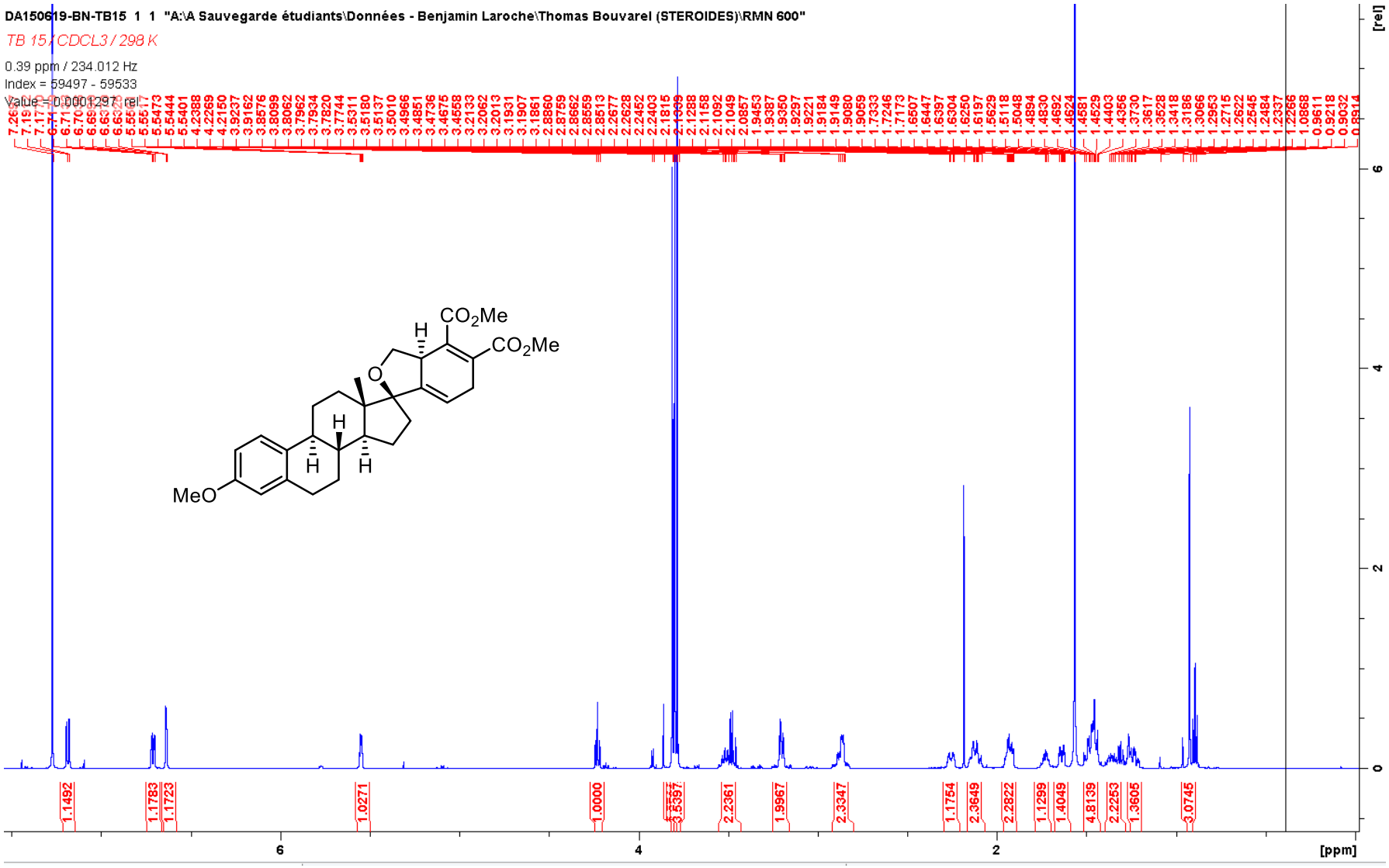
(3*S*,5a*S*,8a*R*,8b*S*,8'*R*,9'*S*,13'*S*,14'*S*)-3'-Methoxy-13'-methyl-5,5a,6',7',8',9',11',12',13',14',15',16'-dodecahydro-1*H*-spiro[benzo[1,2-*c*:3,4-*c*']difuran-3,17'-cyclopenta[*a*]phenanthrene]-6,8(8a*H*,8b*H*)-dione (16b): HSQC NMR (600 MHz, $CDCl_3$)



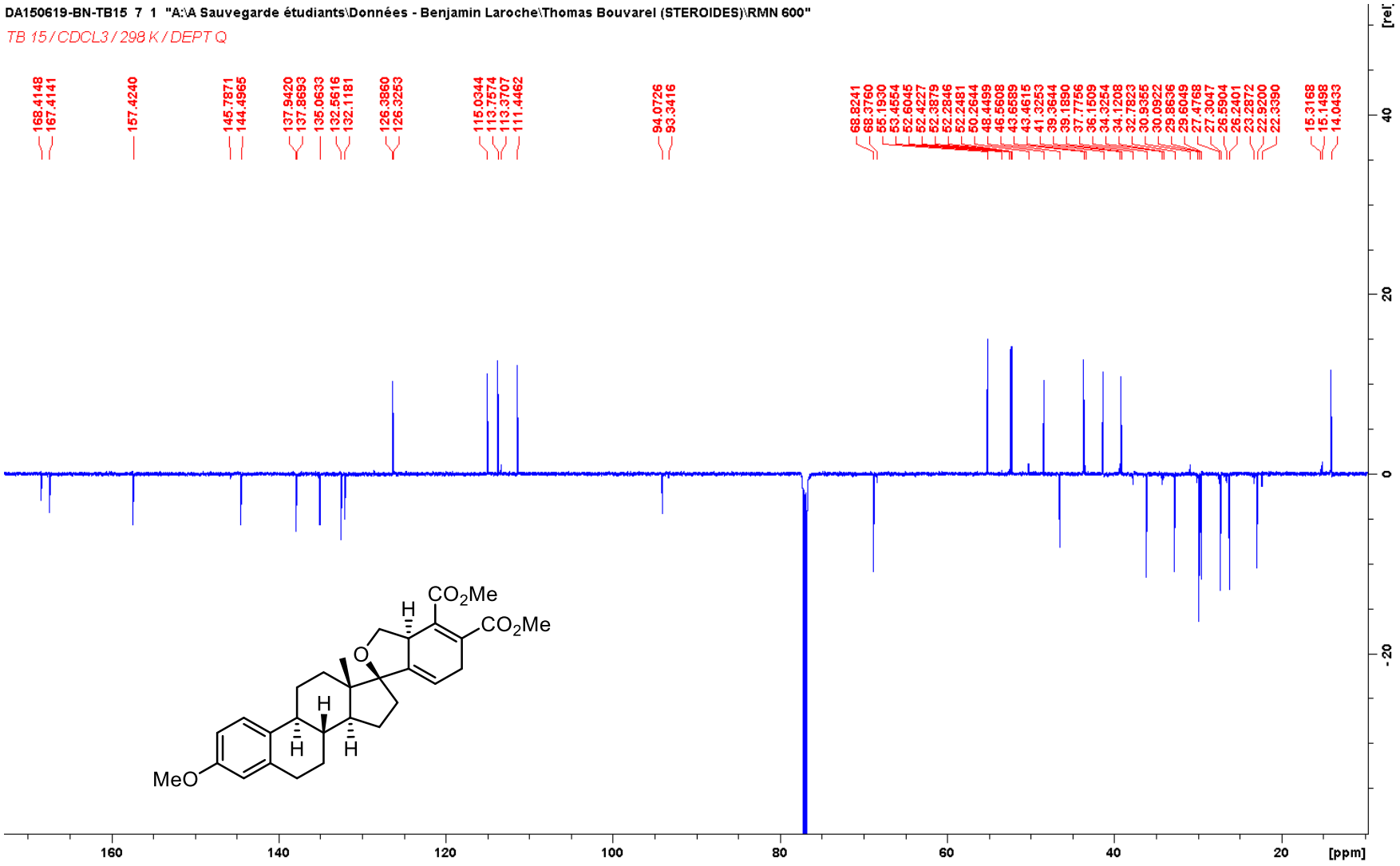
(3*S*,5a*S*,8a*R*,8b*S*,8'*R*,9'*S*,13'*S*,14'*S*)-3'-Methoxy-13'-methyl-5,5a,6',7',8',9',11',12',13',14',15',16'-dodecahydro-1*H*-spiro[benzo[1,2-*c*:3,4-*c*']difuran-3,17'-cyclopenta[*a*]phenanthrene]-6,8(8a*H*,8b*H*)dione (16b): NOESY NMR (600 MHz, $CDCl_3$)



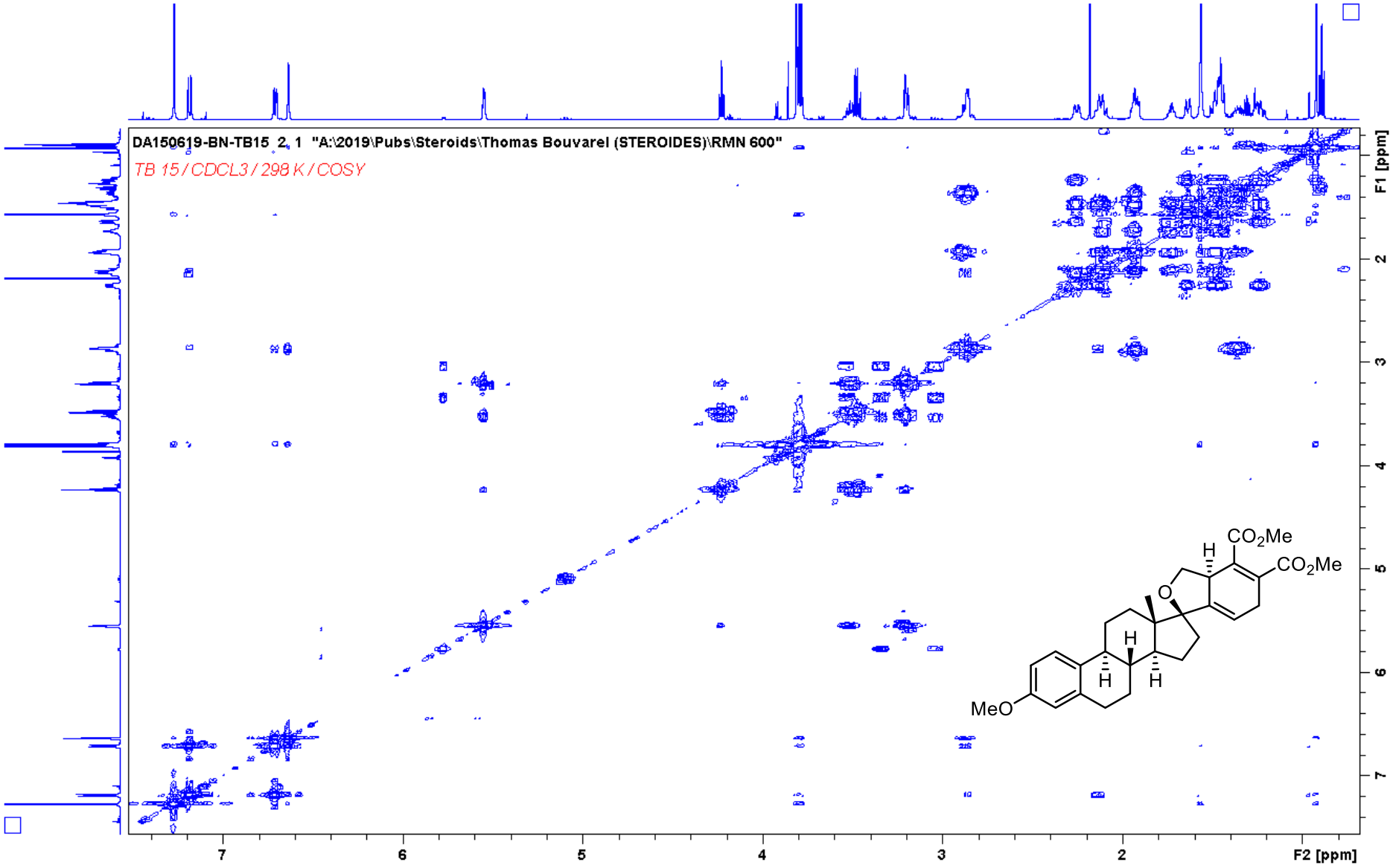
(1'*S*,3a'*R*,8*R*,9*S*,13*S*,14*S*)-dimethyl 3-methoxy-13-methyl-3a',6,6',7,8,9,11,12,13,14,15,16-dodecahydro-3'*H*-spiro[cyclopenta[*a*]phenanthrene-17,1'-isobenzofuran]-4',5'-dicarboxylate (16c): ^{1}H NMR (600 MHz, $CDCl_3$)



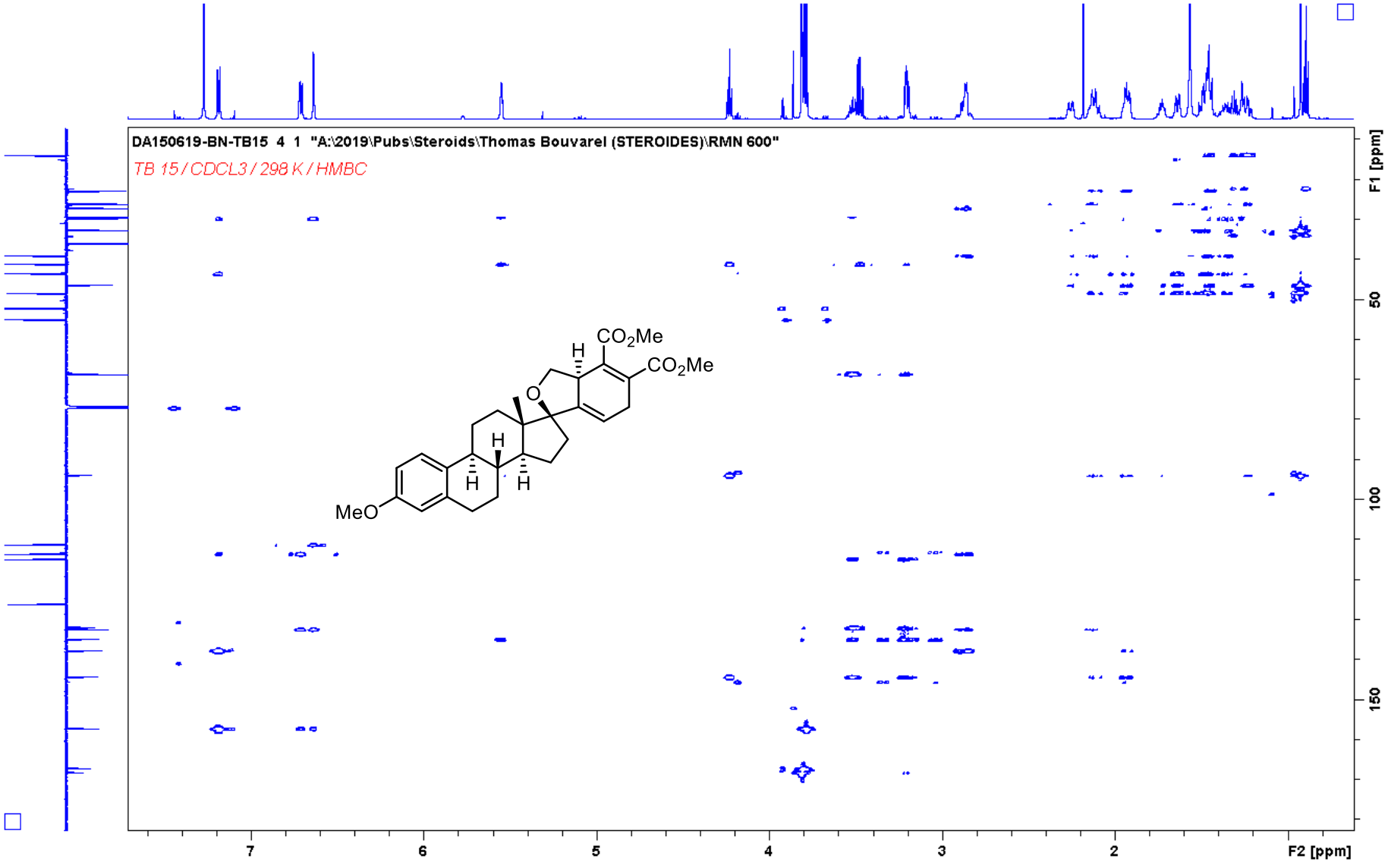
(1'*S*,3a'*R*,8*R*,9*S*,13*S*,14*S*)-Dimethyl 3-methoxy-13-methyl-3a',6,6',7,8,9,11,12,13,14,15,16-dodecahydro-3'*H*-spiro[cyclopenta[*a*]phenanthrene-17,1'-isobenzofuran]-4',5'-dicarboxylate (16c): ^{13}C NMR (150 MHz, $CDCl_3$)



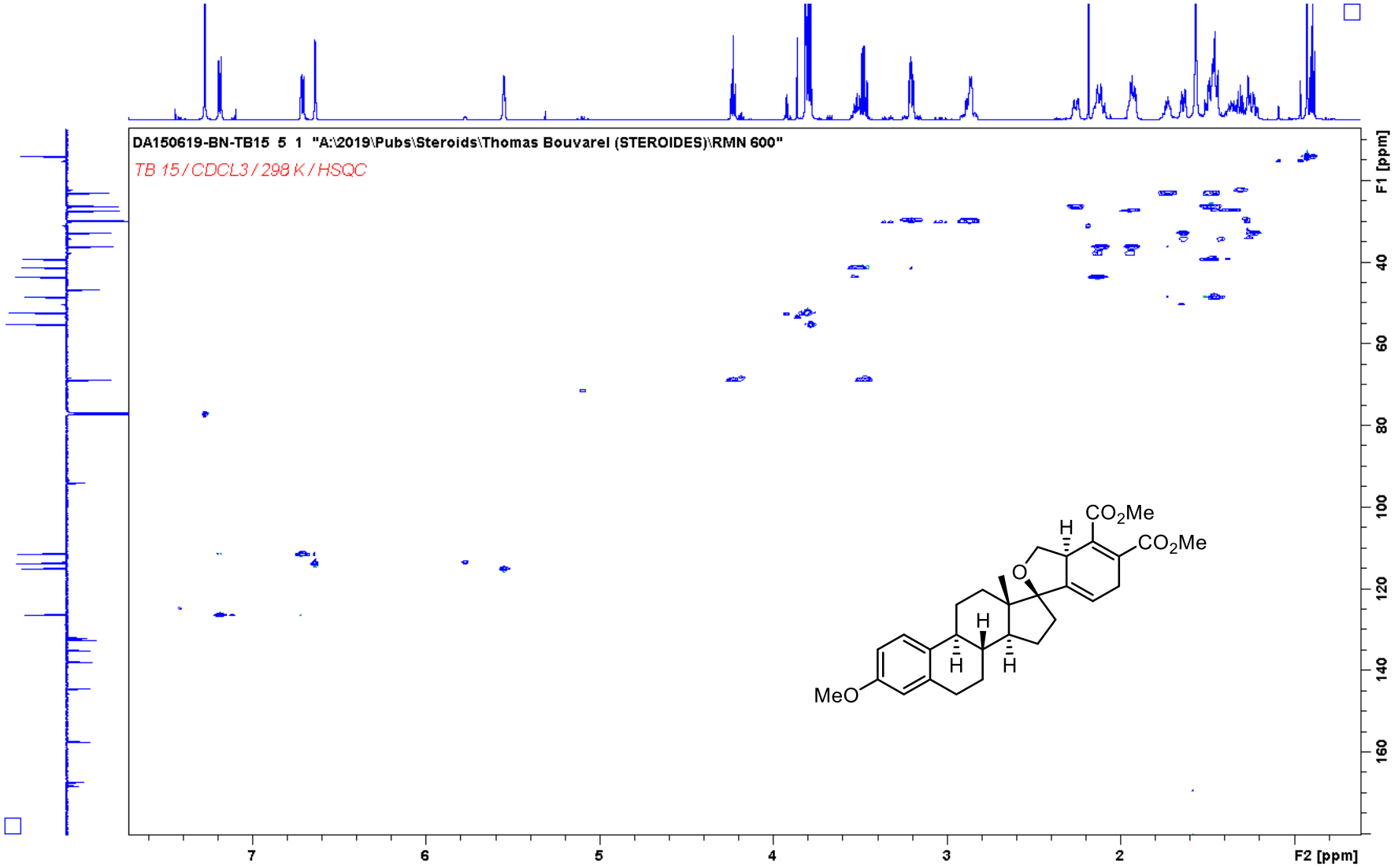
(1'*S*,3a'*R*,8*R*,9*S*,13*S*,14*S*)-Dimethyl 3-methoxy-13-methyl-3a',6,6',7,8,9,11,12,13,14,15,16-dodecahydro-3'*H*-spiro[cyclopenta[*a*]phenanthrene-17,1'-isobenzofuran]-4',5'-dicarboxylate (16c): COSY NMR (600 MHz, $CDCl_3$)



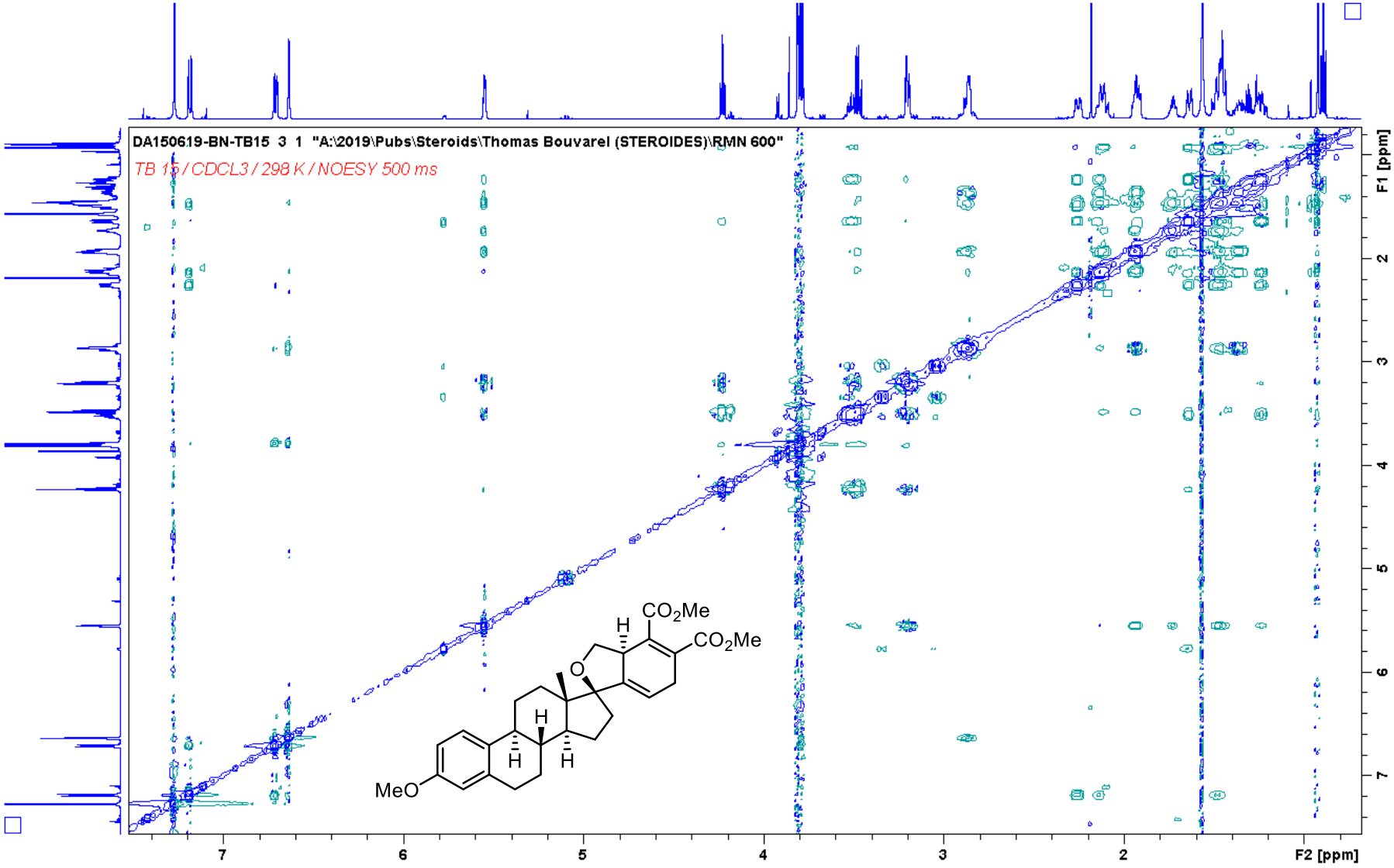
(1'*S*,3a'*R*,8*R*,9*S*,13*S*,14*S*)-Dimethyl 3-methoxy-13-methyl-3a',6,6',7,8,9,11,12,13,14,15,16-dodecahydro-3'*H*-spiro[cyclopenta[*a*]phenanthrene-17,1'-isobenzofuran]-4',5'-dicarboxylate (16c): HMBC NMR (600 MHz, $CDCl_3$)



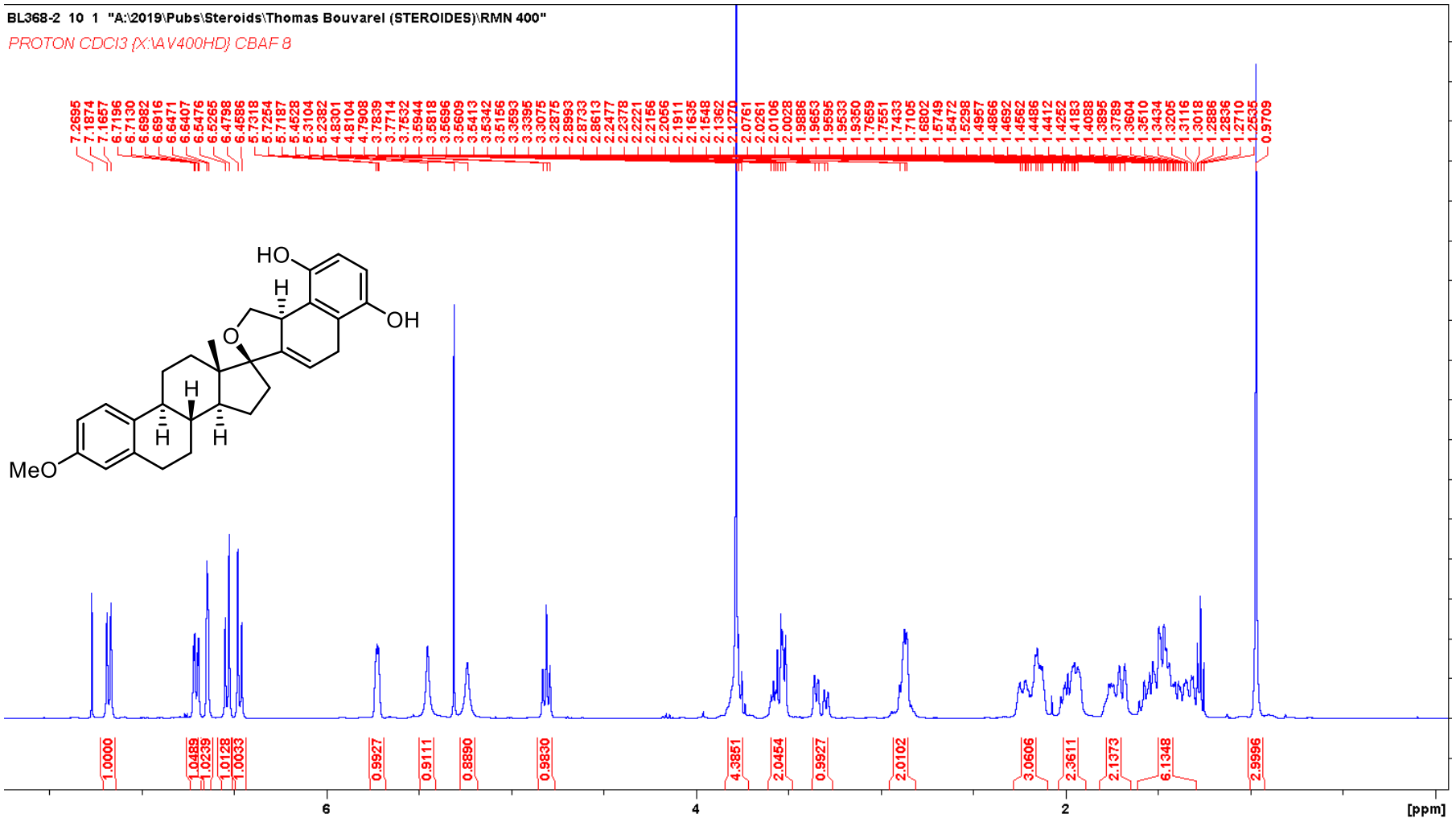
(1'*S*,3a'*R*,8*R*,9*S*,13*S*,14*S*)-Dimethyl 3-methoxy-13-methyl-3a',6,6',7,8,9,11,12,13,14,15,16-dodecahydro-3'*H*-spiro[cyclopenta[*a*]phenanthrene-17,1'-isobenzofuran]-4',5'-dicarboxylate (16c): HSQC NMR (600 MHz, $CDCl_3$)



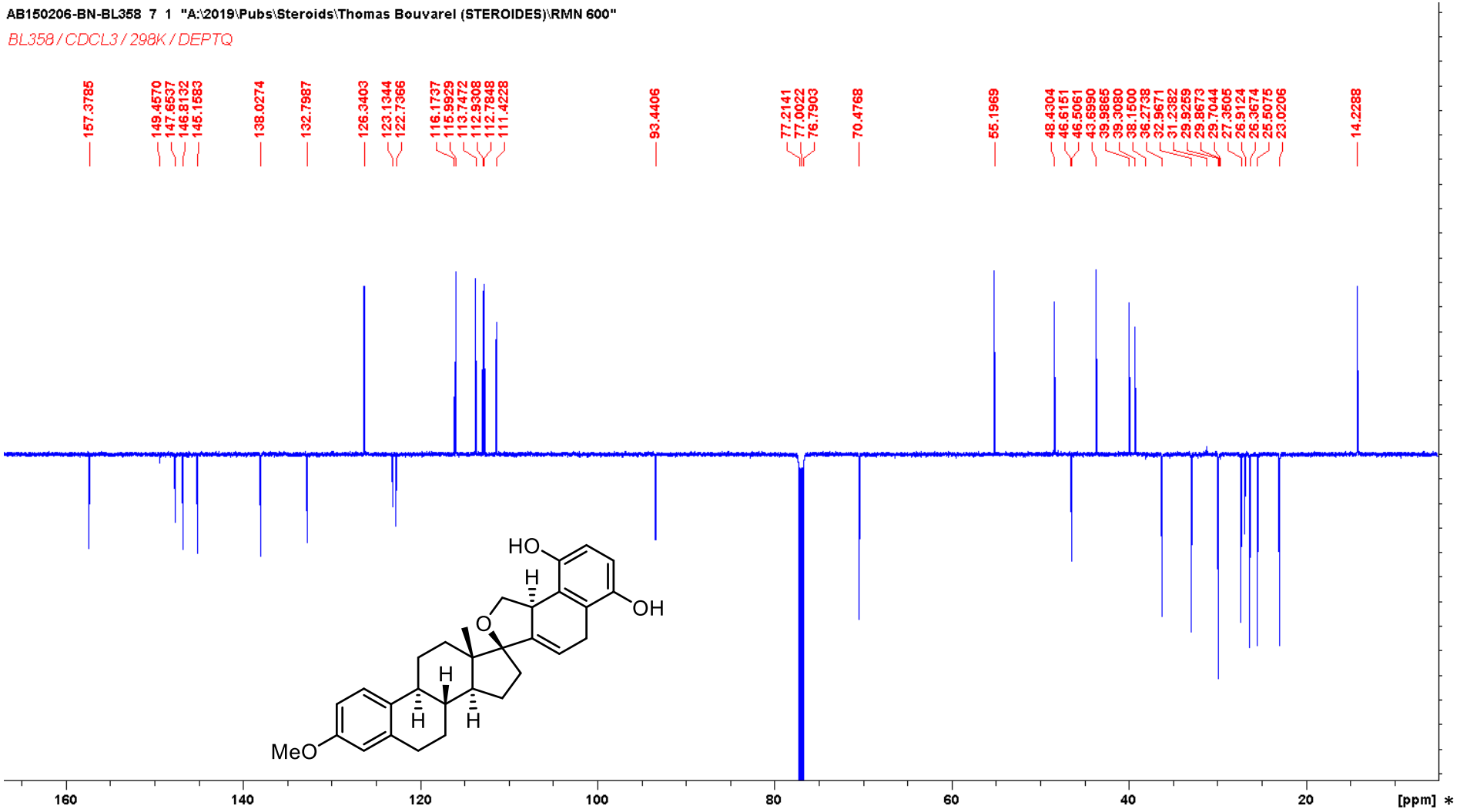
(1'*S*,3a'*R*,8*R*,9*S*,13*S*,14*S*)-Dimethyl 3-methoxy-13-methyl-3a',6,6',7,8,9,11,12,13,14,15,16-dodecahydro-3'*H*-spiro[cyclopenta[*a*]phenanthrene-17,1'-isobenzofuran]-4',5'-dicarboxylate (16c): NOESY NMR (600 MHz, $CDCl_3$)



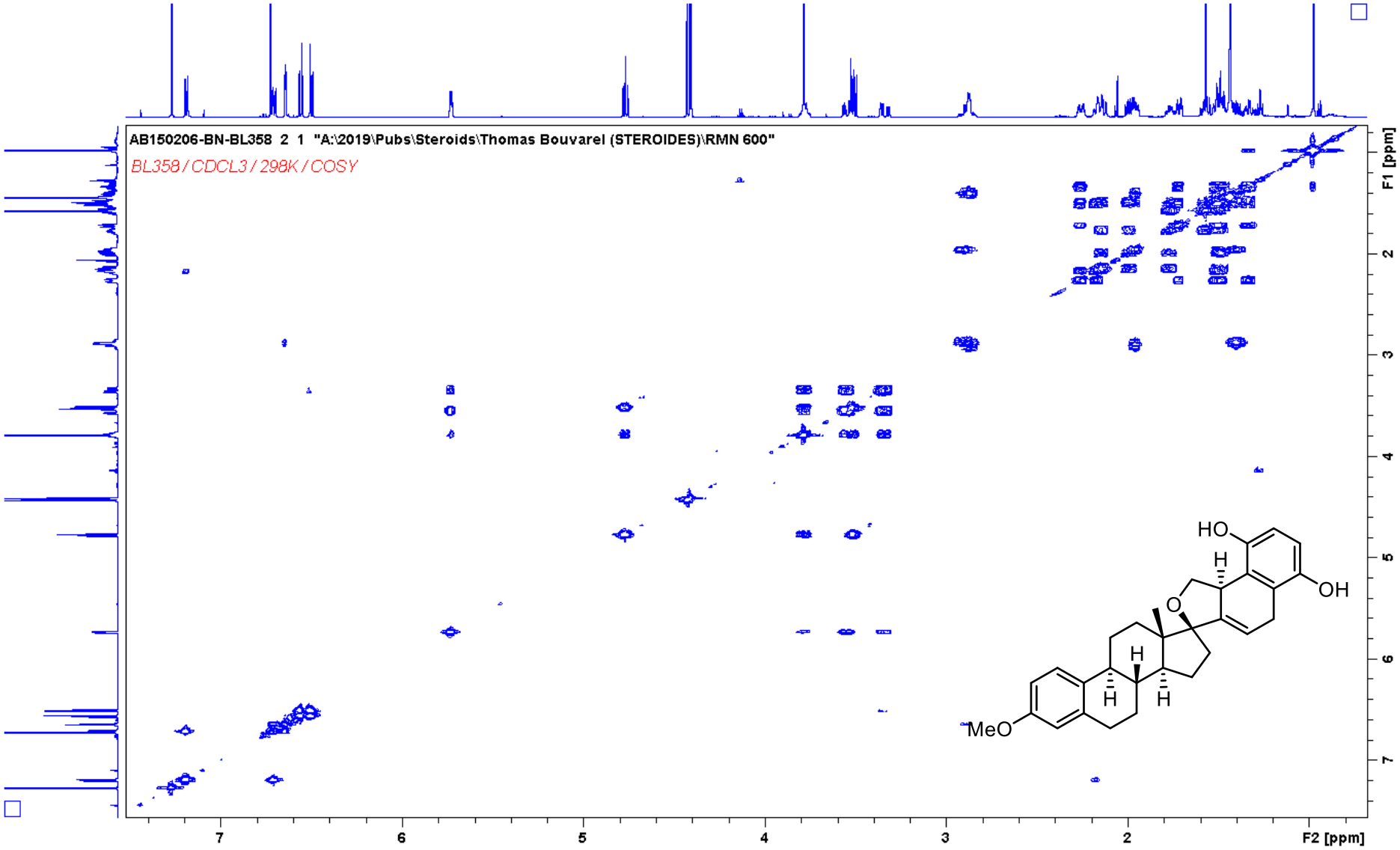
(3'*S*,8*R*,9*S*,9b'*R*,13*S*,14*S*)-3-Methoxy-13-methyl-5',6,7,8,9,9b',11,12,13,14,15,16-dodecahydro-1'*H*-spiro[cyclopenta[*a*]phenanthrene-17,3'-naphtho[1,2-*c*]furan]-6',9'-diol (16d): ^{1}H NMR (400 MHz, $CDCl_3$)



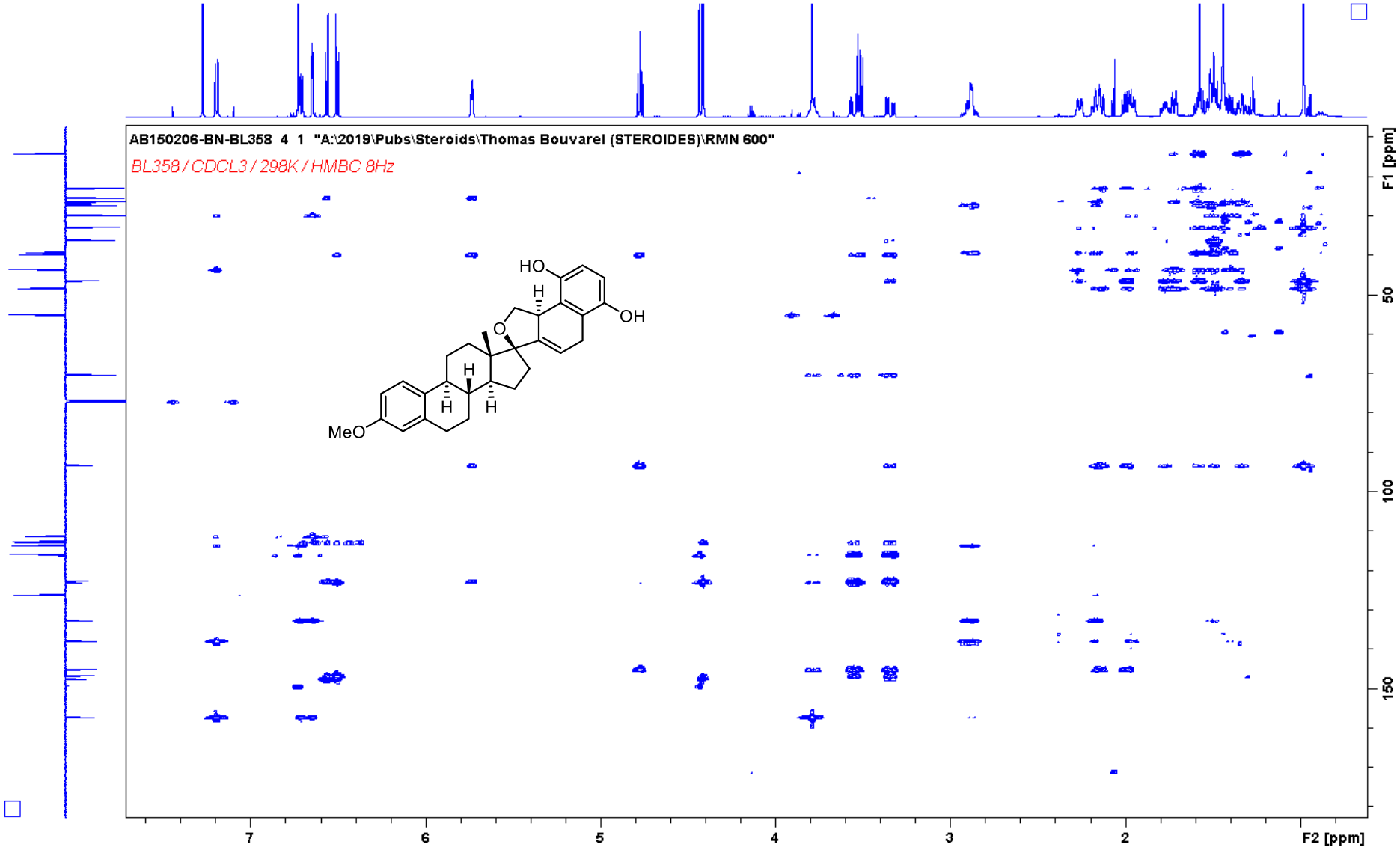
(3'*S*,8*R*,9*S*,9b'*R*,13*S*,14*S*)-3-Methoxy-13-methyl-5',6,7,8,9,9b',11,12,13,14,15,16-dodecahydro-1'*H*-spiro[cyclopenta[*a*]phenanthrene-17,3'-naphtho[1,2-*c*]furan]-6',9'-diol (16d): ^{13}C NMR (150 MHz, $CDCl_3$)



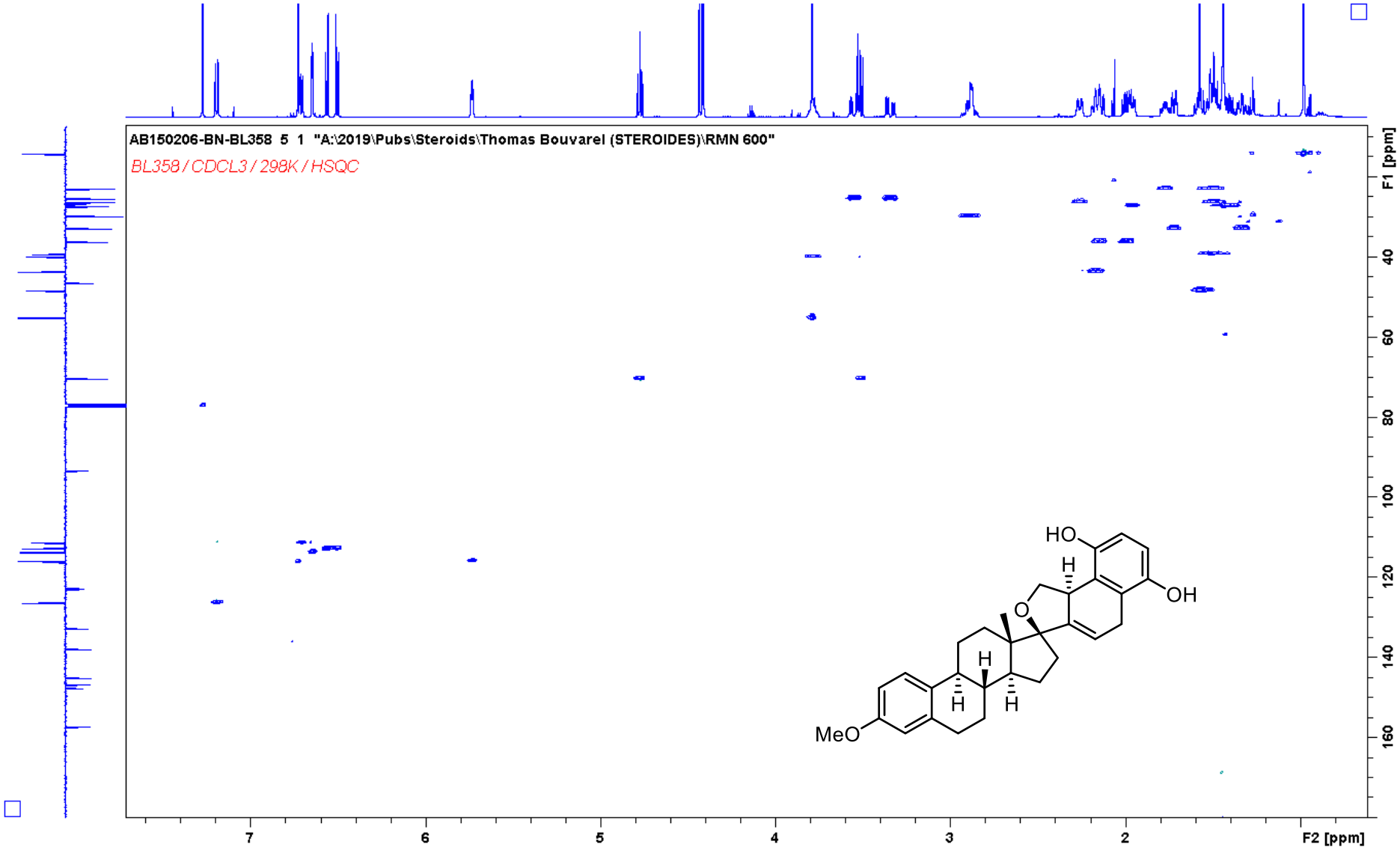
(3'*S*,8*R*,9*S*,9b'*R*,13*S*,14*S*)-3-Methoxy-13-methyl-5',6,7,8,9,9b',11,12,13,14,15,16-dodecahydro-1'*H*-spiro[cyclopenta[*a*]phenanthrene-17,3'-naphtho[1,2-*c*]furan]-6',9'-diol (16d): COSY NMR (600 MHz, $CDCl_3$)



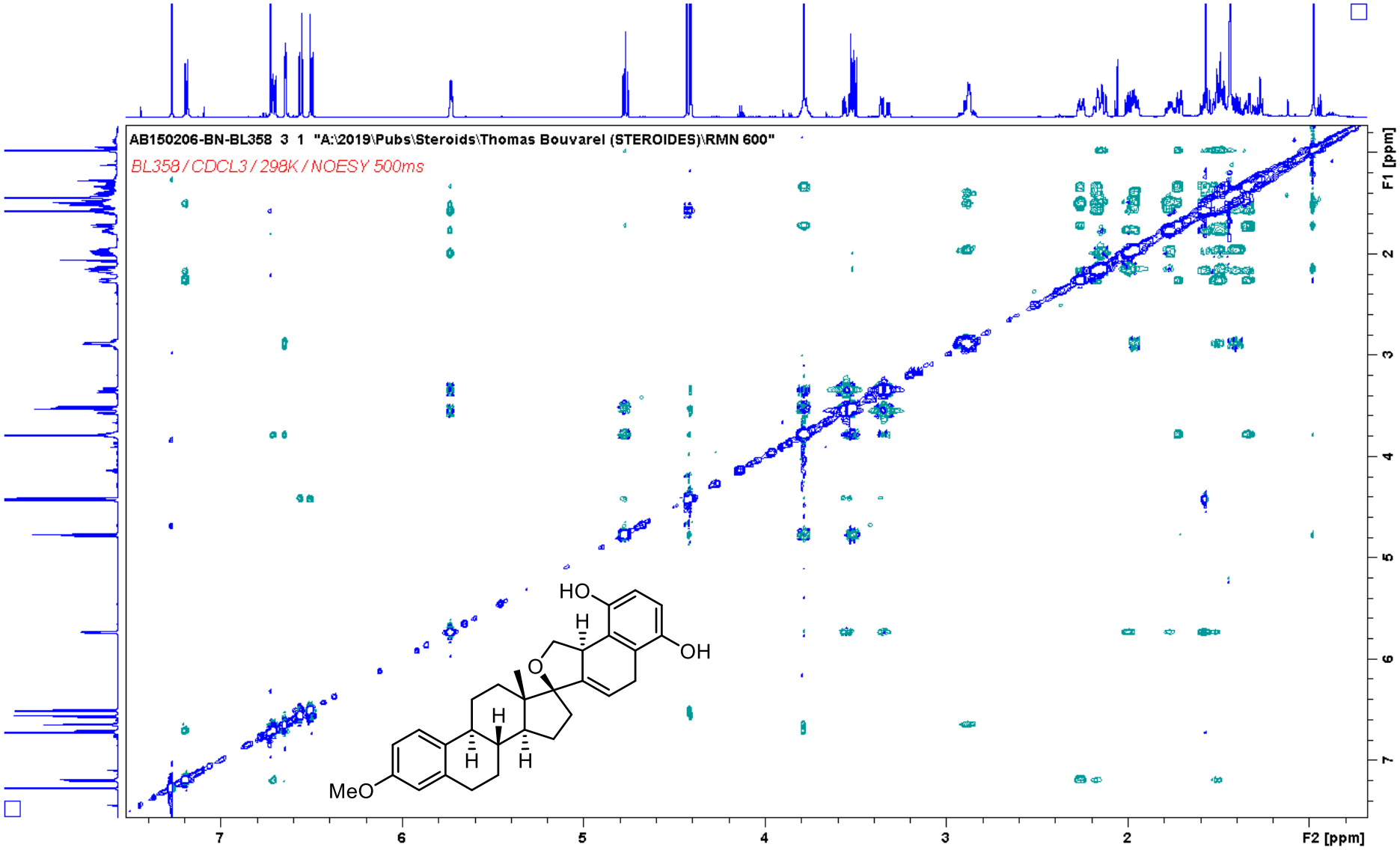
(3'*S*,8*R*,9*S*,9b'*R*,13*S*,14*S*)-3-Methoxy-13-methyl-5',6,7,8,9,9b',11,12,13,14,15,16-dodecahydro-1'*H*-spiro[cyclopenta[*a*]phenanthrene-17,3'-naphtho[1,2-*c*]furan]-6',9'-diol (16d): HMBC NMR (600 MHz, $CDCl_3$)



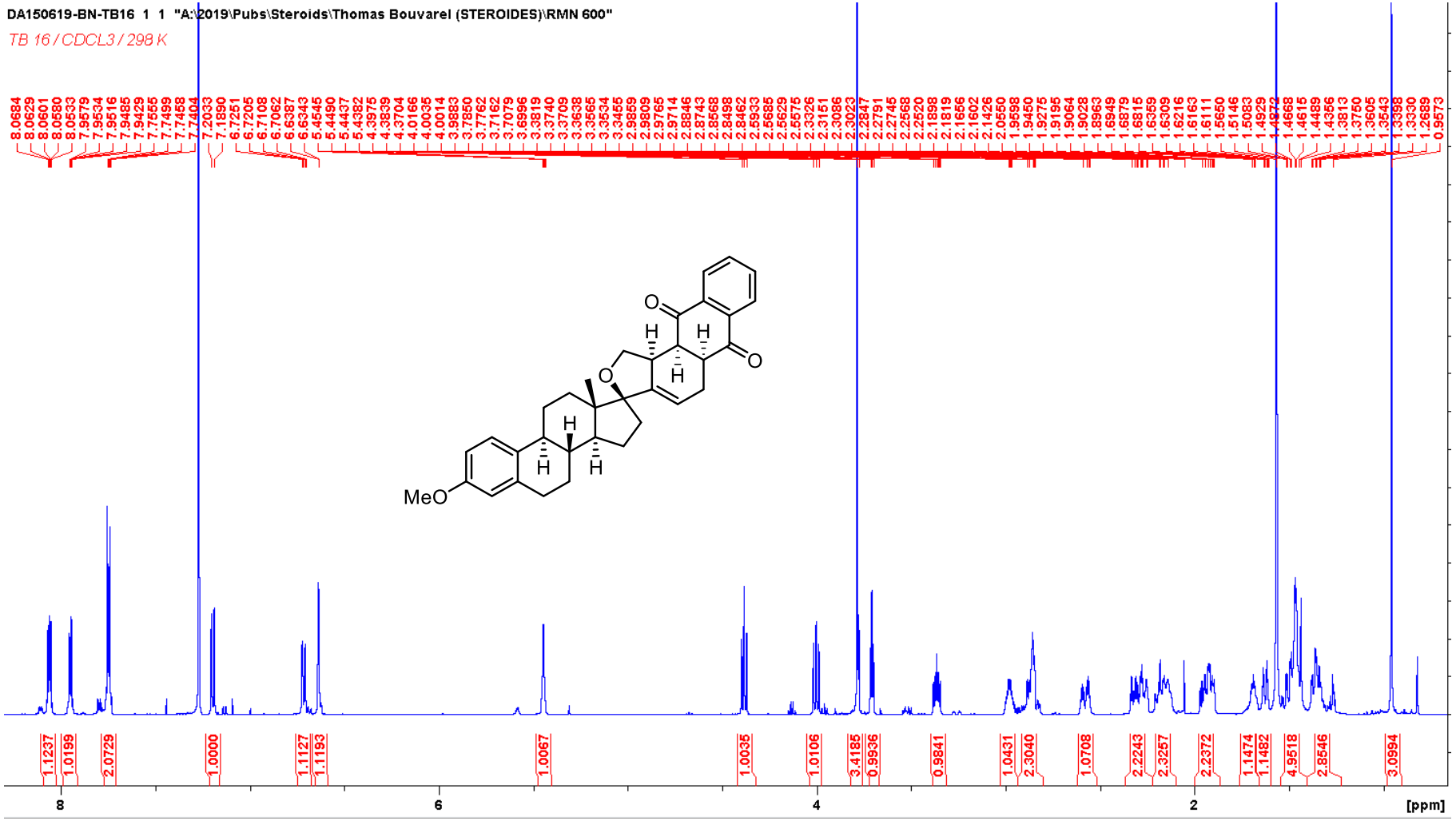
(3'*S*,8*R*,9*S*,9b'*R*,13*S*,14*S*)-3-Methoxy-13-methyl-5',6,7,8,9,9b',11,12,13,14,15,16-dodecahydro-1'*H*-spiro[cyclopenta[*a*]phenanthrene-17,3'-naphtho[1,2-*c*]furan]-6',9'-diol (16d): HSQC NMR (600 MHz, $CDCl_3$)



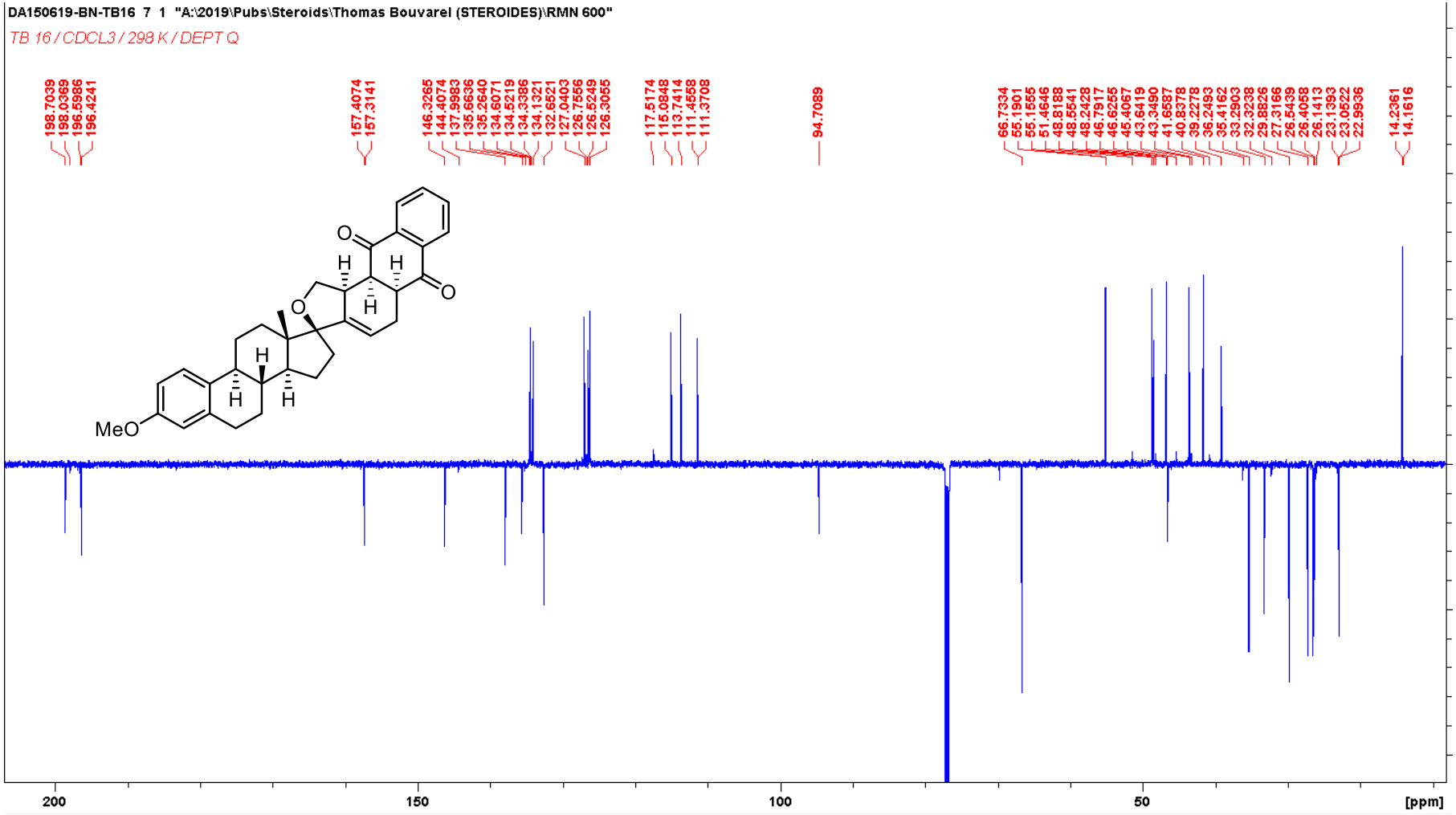
(3'*S*,8*R*,9*S*,9b'*R*,13*S*,14*S*)-3-Methoxy-13-methyl-5',6,7,8,9,9b',11,12,13,14,15,16-dodecahydro-1'*H*-spiro[cyclopenta[*a*]phenanthrene-17,3'-naphtho[1,2-*c*]furan]-6',9'-diol (16d): NOESY NMR (600 MHz, $CDCl_3$)



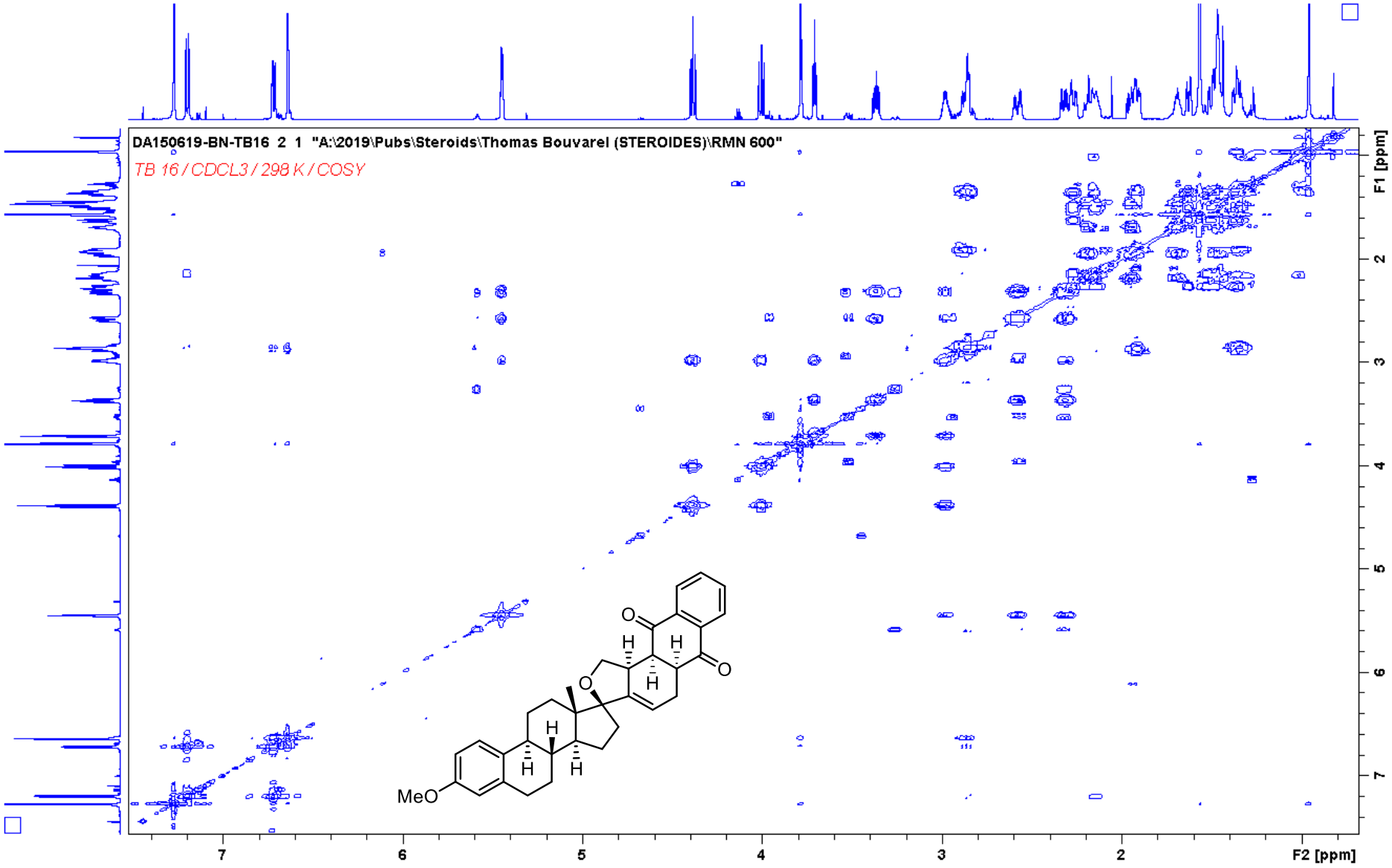
(3*S*,5a*S*,8'*R*,9'*S*,11a*R*,11b*S*,13'*S*,14'*S*)-3'-Methoxy-13'-methyl-5,5a,6',7',8',9',11',12',13',14',15',16'-dodecahydro-1*H*-spiro[anthra[1,2-*c*]furan-3,17'-cyclopenta[*a*]phenanthrene]-6,11-(11a*H*,11b*H*)dione (16e): ^{1}H NMR (600 MHz, $CDCl_3$)



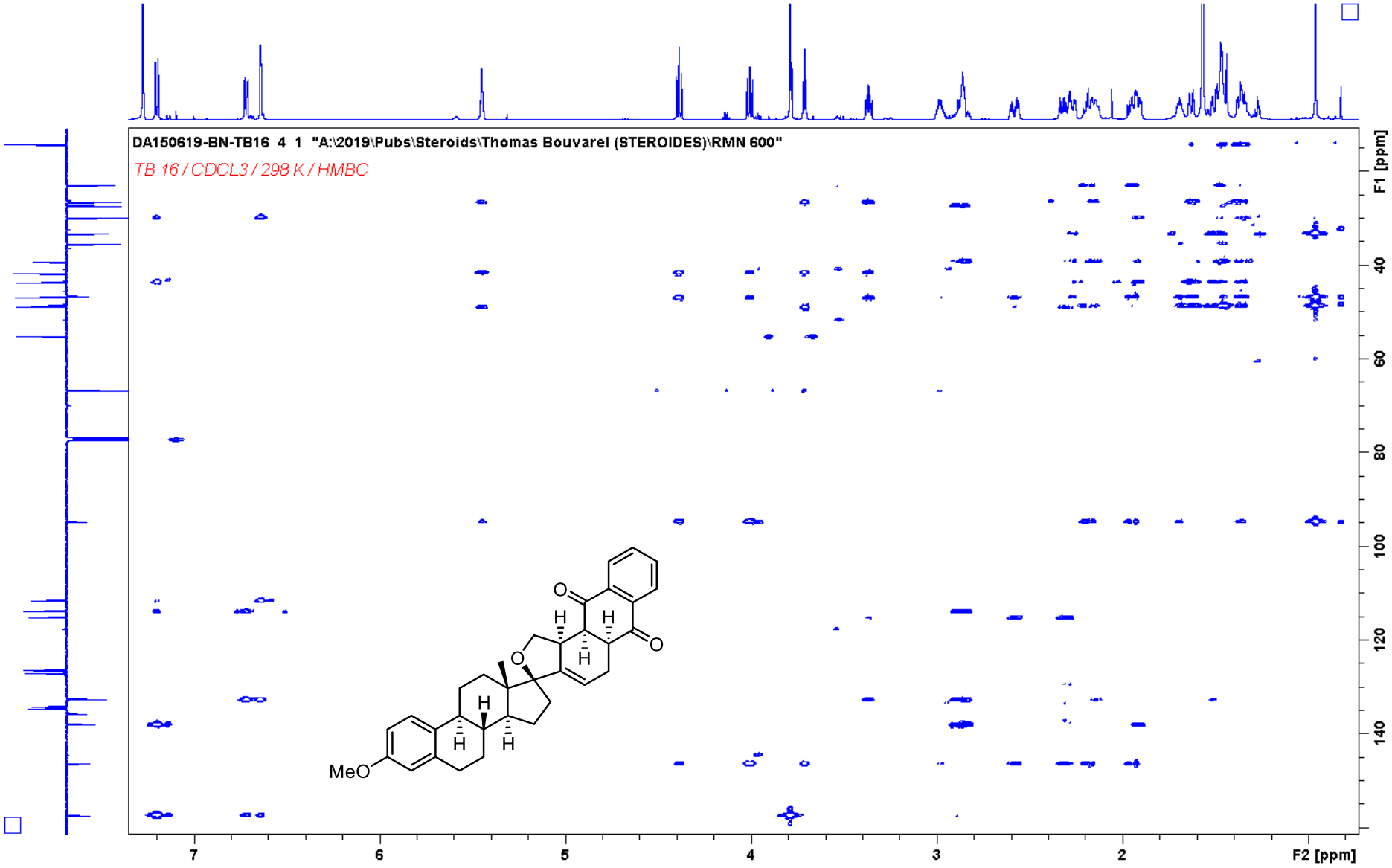
(3*S*,5a*S*,8'*R*,9'*S*,11a*R*,11b*S*,13'*S*,14'*S*)-3'-Methoxy-13'-methyl-5,5a,6',7',8',9',11',12',13',14',15',16'-dodecahydro-1*H*-spiro[anthra[1,2-*c*]furan-3,17'-cyclopenta[*a*]phenanthrene]-6,11-(11a*H*,11b*H*)dione (16e): ^{13}C NMR (150 MHz, $CDCl_3$)



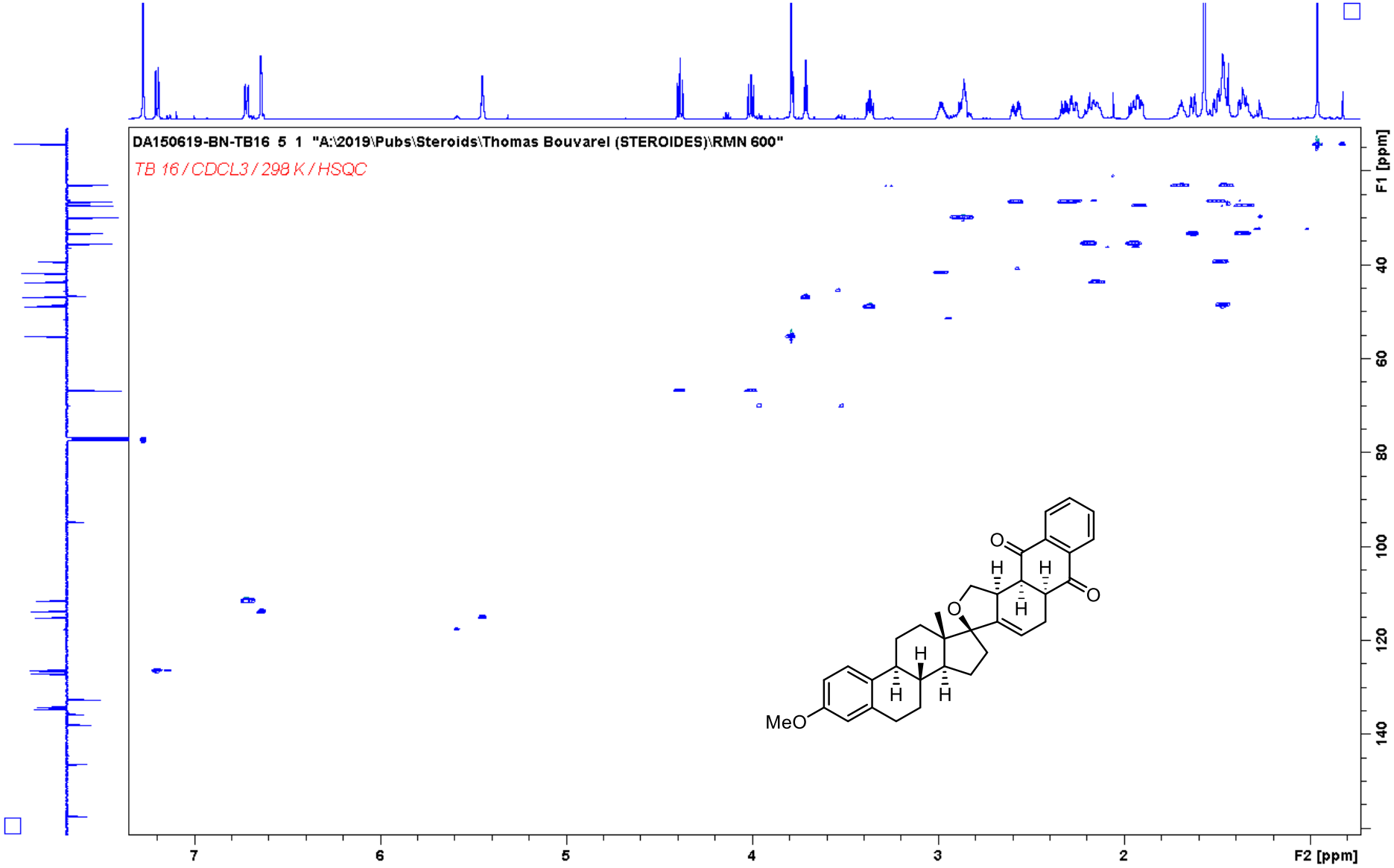
(3*S*,5a*S*,8'*R*,9'S,11a*R*,11b*S*,13'*S*,14'*S*)-3'-Methoxy-13'-methyl-5,5a,6',7',8',9',11',12',13',14',15',16'-dodecahydro-1*H*-spiro[anthra[1,2-*c*]furan-3,17'-cyclopenta[*a*]phenanthrene]-6,11-(11a*H*,11b*H*)dione (16e): COSY NMR (600 MHz, $CDCl_3$)



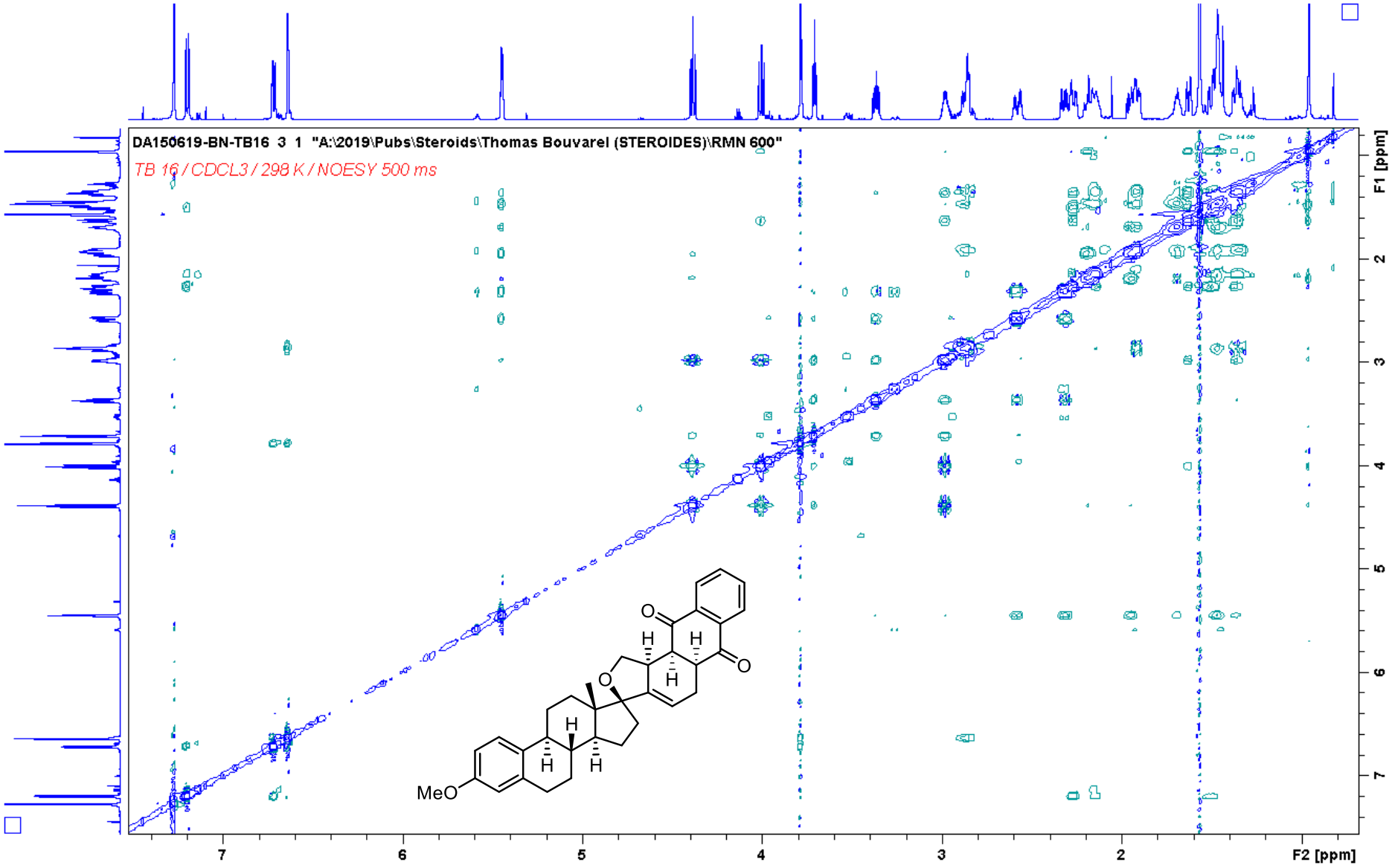
(3*S*,5a*S*,8'*R*,9'*S*,11a*R*,11b*S*,13'*S*,14'*S*)-3'-Methoxy-13'-methyl-5,5a,6',7',8',9',11',12',13',14',15',16'-dodecahydro-1*H*-spiro[anthra[1,2-*c*]furan-3,17'-cyclopenta[*a*]phenanthrene]-6,11-(11aH,11b*H*)dione (16e): HMBC NMR (600 MHz, $CDCl_3$)



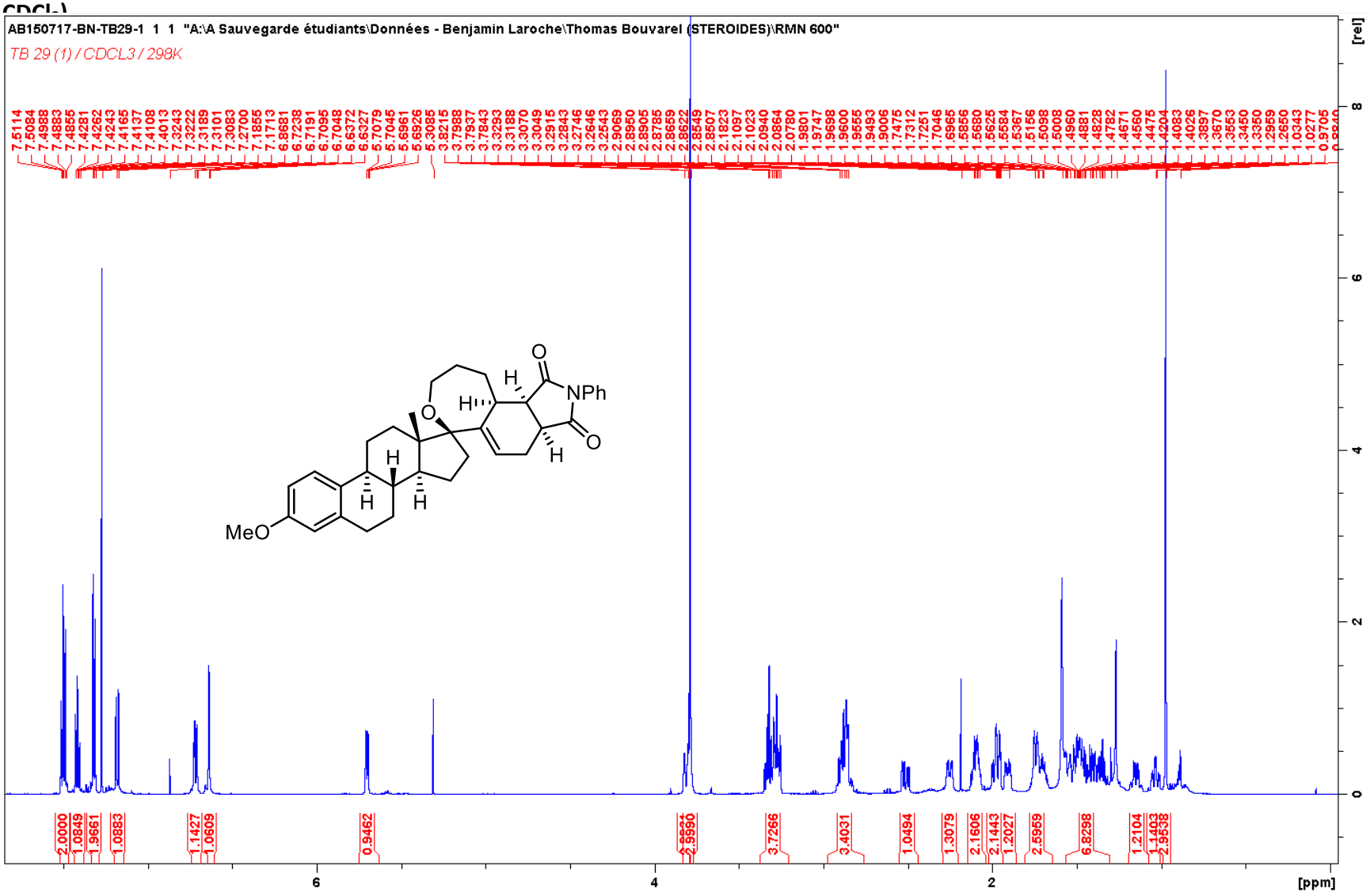
(3*S*,5a*S*,8'i,9'*S*,11a*R*,11b*S*,13'*S*,14'i)-3'-Methoxy-13'-methyl-5,5a,6',7',8',9',11',12',13',14',15',16'-dodecahydro-1*H*-spiro[anthra[1,2-*c*]furan-3,17'-cyclopenta[*a*]phenanthrene]-6,11-(11a*H*,11b*H*)dione (16e): HSQC NMR (600 MHz, $CDCl_3$)



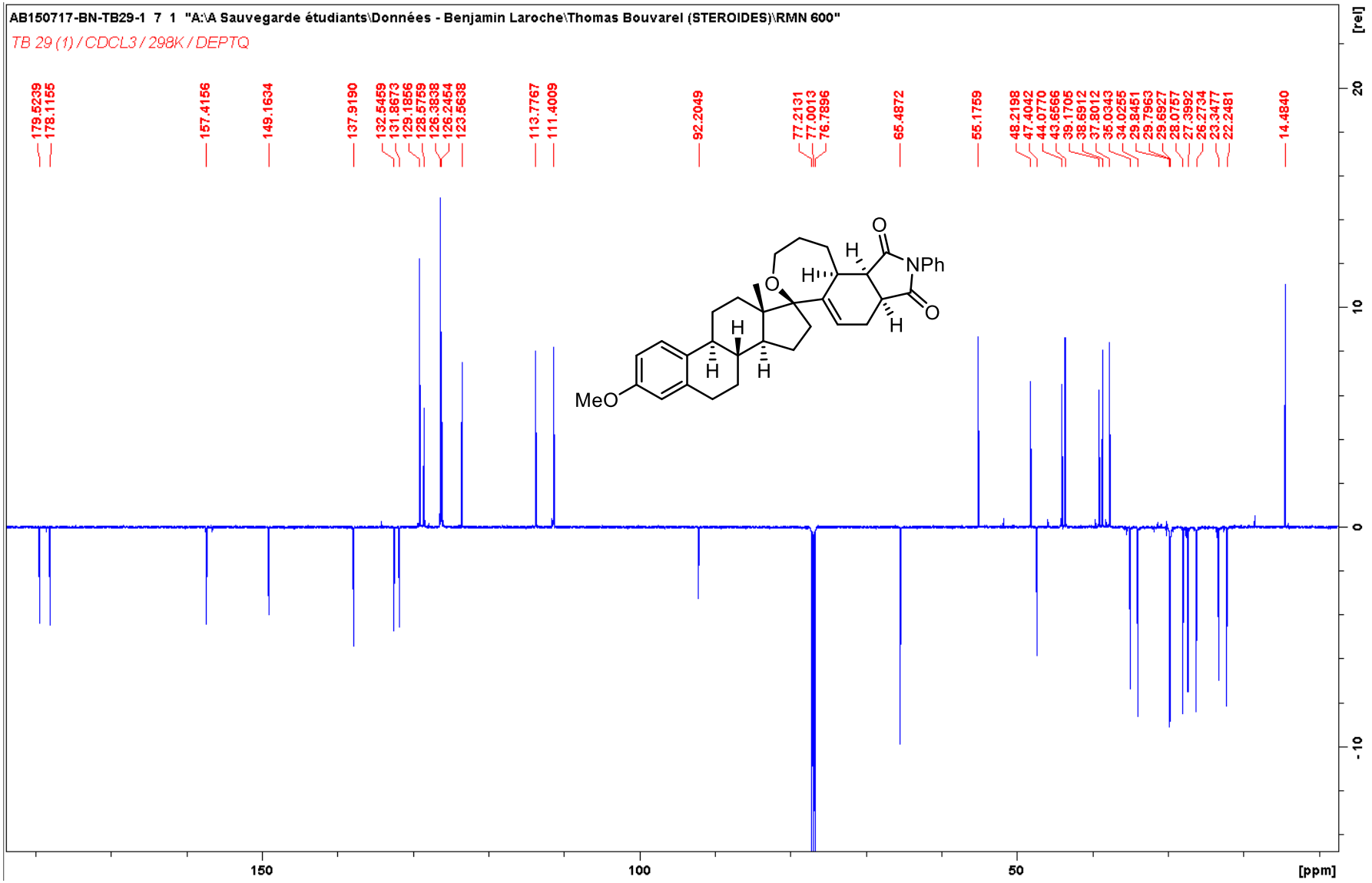
(3*S*,5a*S*,8'*R*,9'*S*,11a*R*,11b*S*,13'*S*,14'*S*)-3'-Methoxy-13'-methyl-5,5a,6',7',8',9',11',12',13',14',15',16'-dodecahydro-1*H*-spiro[anthra[1,2-*c*]furan-3,17'-cyclopenta[*a*]phenanthrene]-6,11-(11a*H*,11b*H*)dione (16e): NOESY NMR (600 MHz, $CDCl_3$)



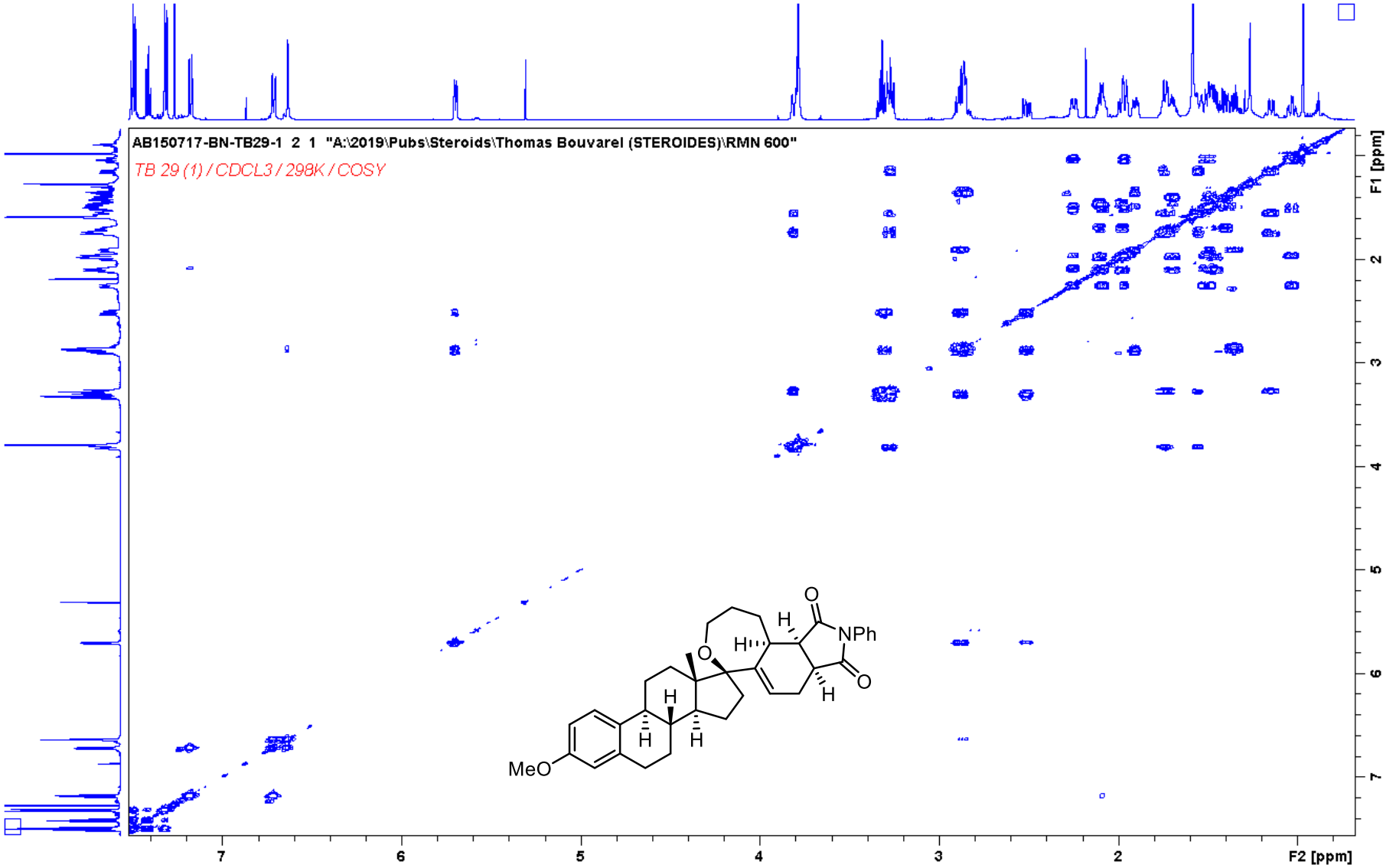
(3a'*S*,6'*S*,8*R*,9*S*,10a'*S*,10b'*R*,13*S*,14*S*)-3-Methoxy-13-methyl-2'-phenyl-3a',4',6,7,8,8',9,9',10',10a',11,12,13,14,15,16-hexadecahydrospiro[cyclopenta[*a*]phenanthrene-17,6'-oxepino[4,3-*e*]isoindole]-1',3'(2'H,10b'*H*)-dione (16f): ^{1}H NMR (600 MHz, CDCl$_3$)



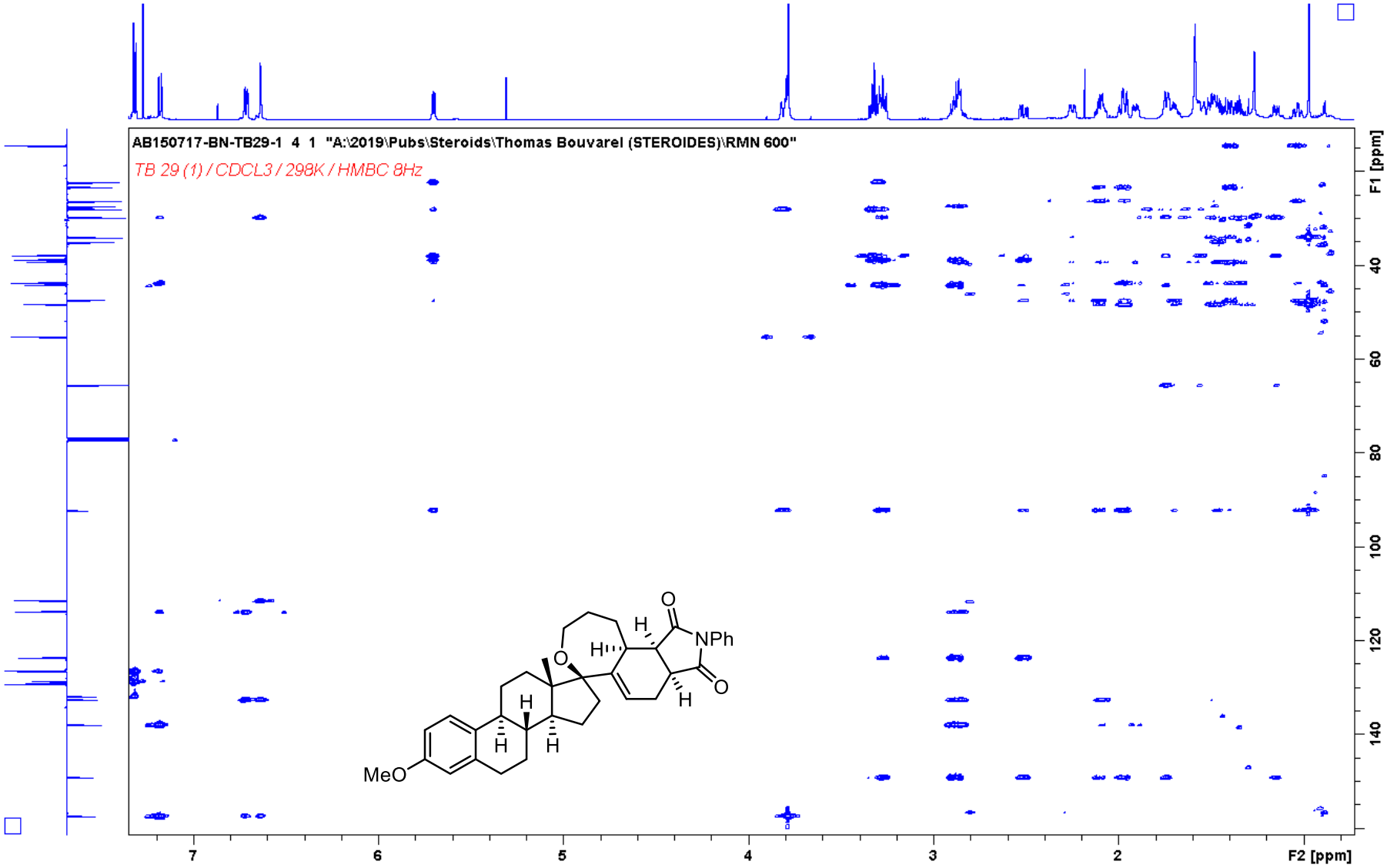
(3a'*S*,6'*S*,8*R*,9*S*,10a'*S*,10b'*R*,13*S*,14*S*)-3-Methoxy-13-methyl-2'-phenyl-3a',4',6,7,8,8',9,9',10',10a',11,12,13,14,15,16-hexadecahydrospiro[cyclopenta[*a*]phenanthrene-17,6'-oxepino[4,3-*e*]isoindole]-1',3'-(2'*H*,10b'*H*)dione (16f): ^{13}C NMR (150 MHz, $CDCl_3$)



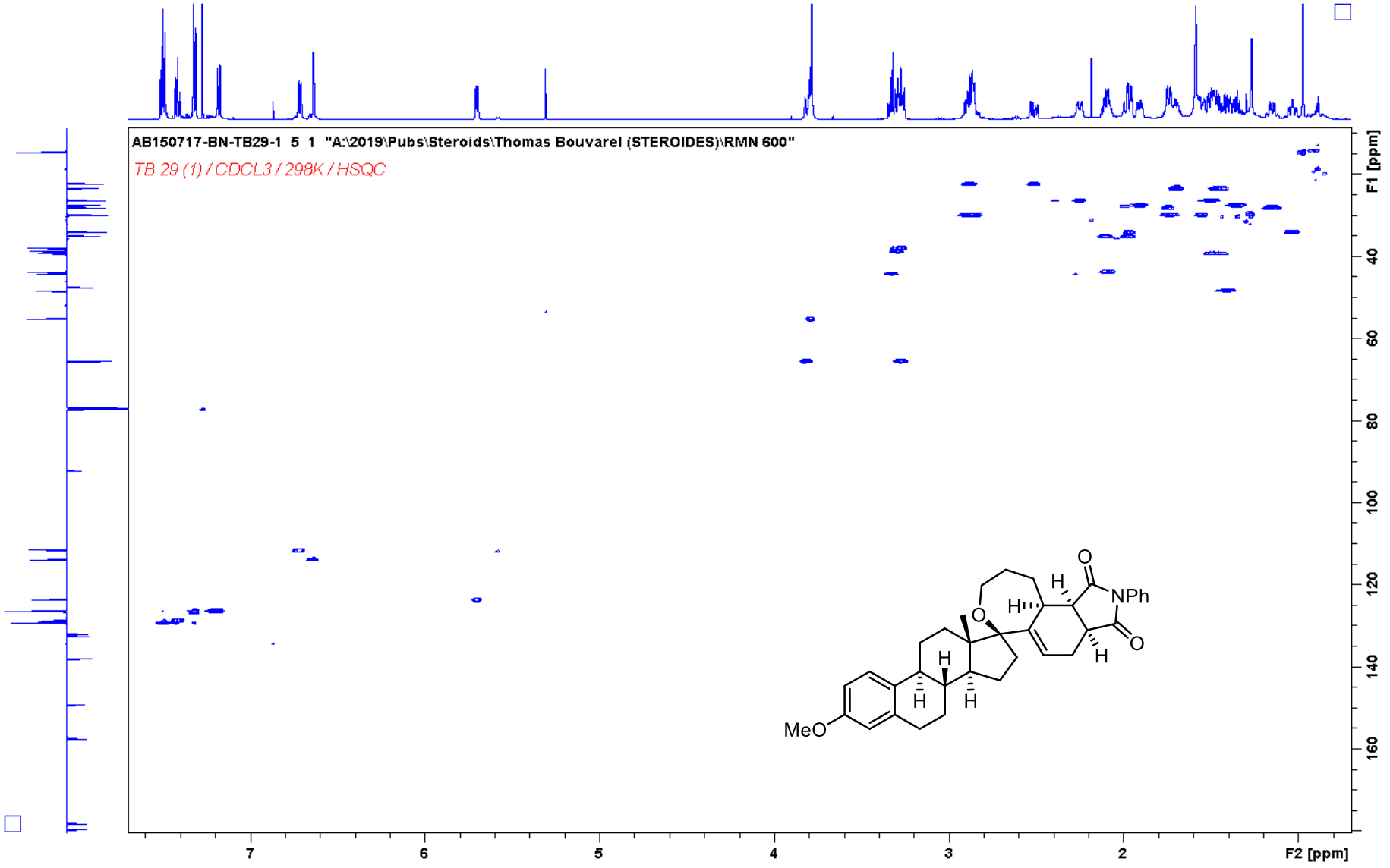
(3a'*S*,6'*S*,8*R*,9*S*,10a'*S*,10*b*'R,13*S*,14*S*)-3-Methoxy-13-methyl-2'-phenyl-3a',4',6,7,8,8',9,9',10',10a',11,12,13,14,15,16-hexadecahydrospiro[cyclopenta[*a*]phenanthrene-17,6'-oxepino[4,3-*e*]isoindole]-1',3'-(2'*H*,10b'*H*)dione (16f): COSY NMR (600 MHz, $CDCl_3$)



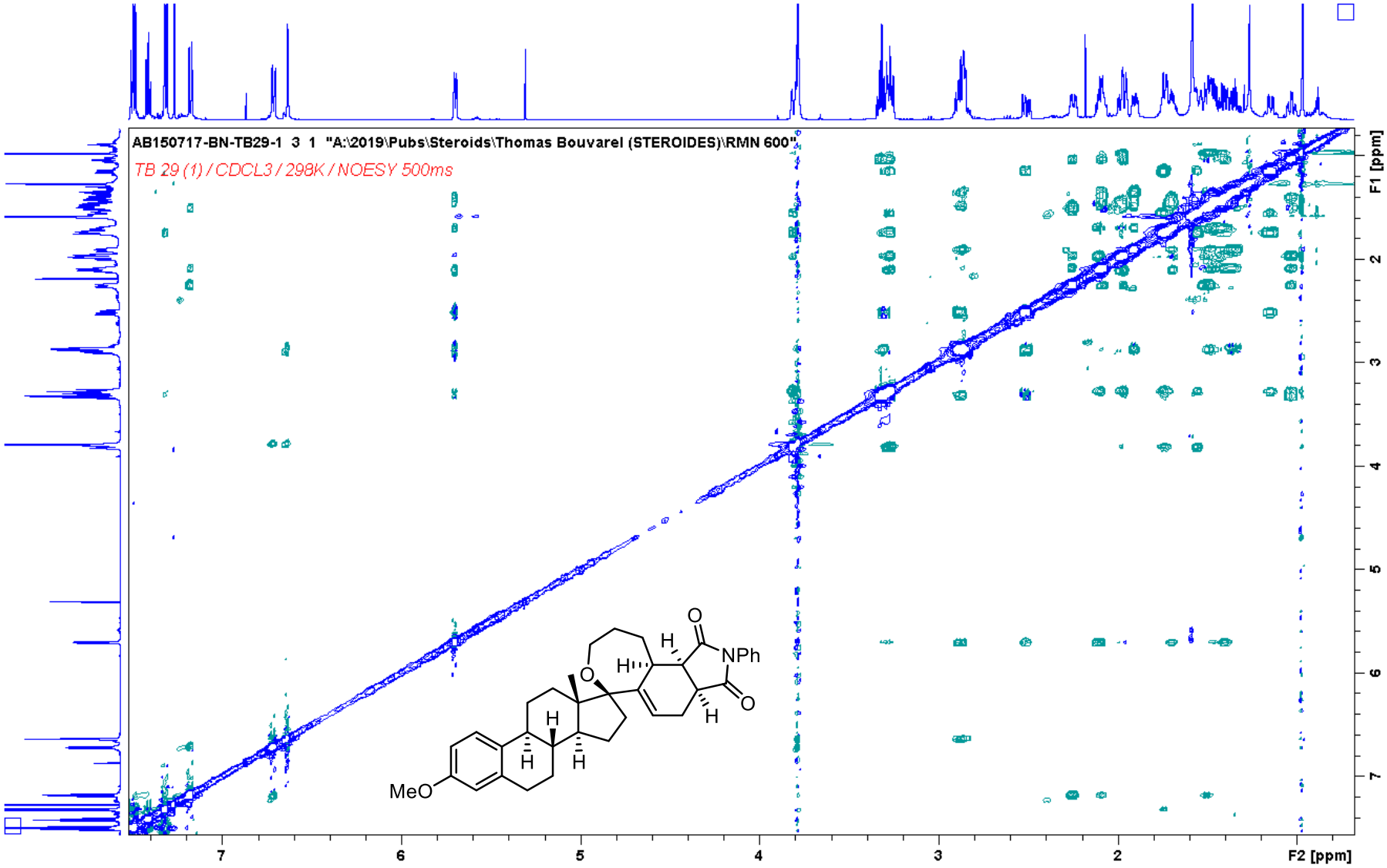
(3a'*S*,6'*S*,8*R*,9*S*,10a'*S*,10b'*R*,13*S*,14*S*)-3-Methoxy-13-methyl-2'-phenyl-3a',4',6,7,8,8',9,9',10',10a',11,12,13,14,15,16-hexadecahydrospiro[cyclopenta[*a*]phenanthrene-17,6'-oxepino[4,3-*e*]isoindole]-1',3'-(2'*H*,10b'*H*)dione (16f): HMBC NMR (600 MHz, $CDCl_3$)



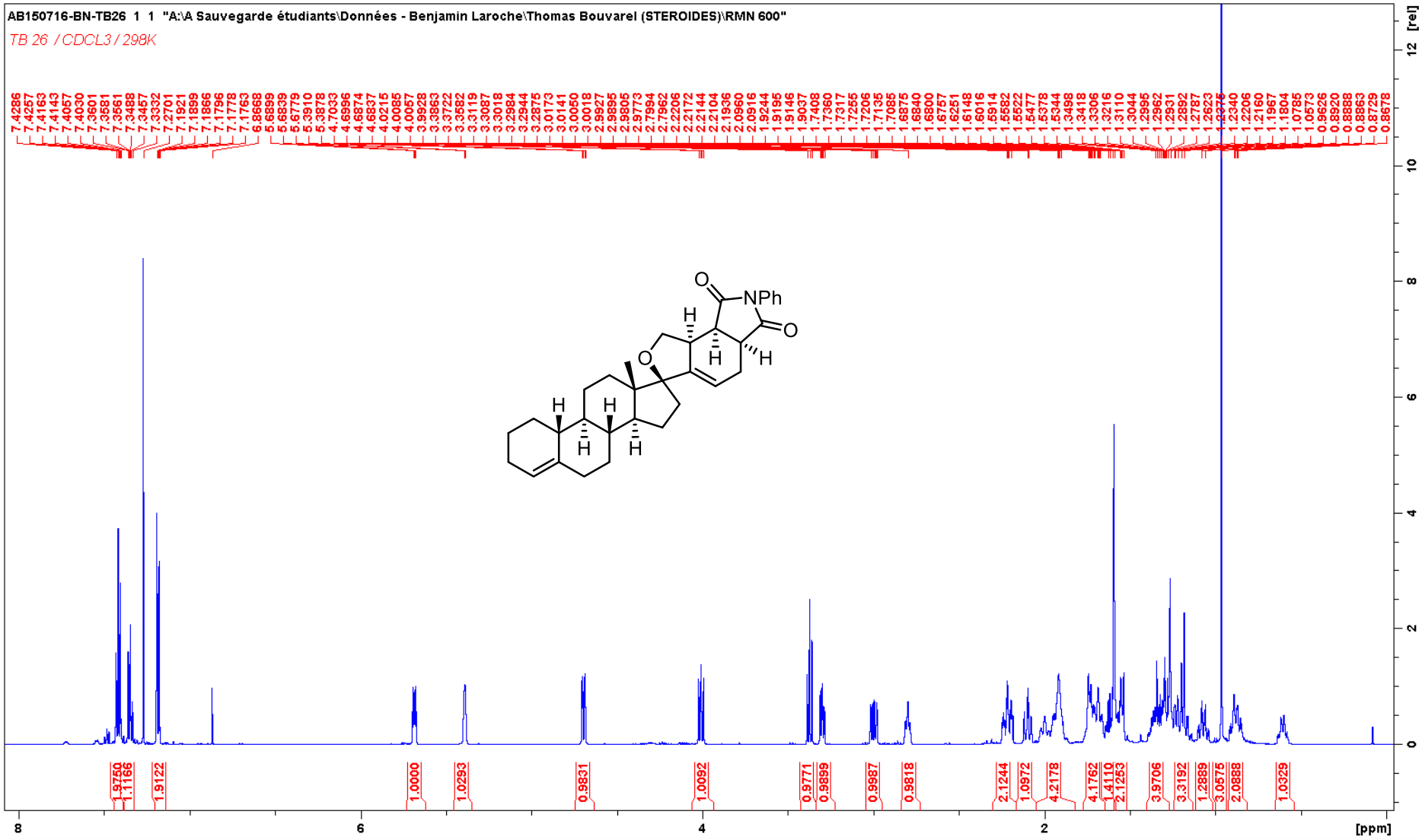
(3a'*S*,6'*S*,8*R*,9*S*,10a'*S*,10b'*R*,13*S*,14*S*)-3-Methoxy-13-methyl-2'-phenyl-3a',4',6,7,8,8',9,9',10',10a',11,12,13,14,15,16-hexadecahydrospiro[cyclopenta[*a*]phenanthrene-17,6'-oxepino[4,3-*e*]isoindole]-1',3'-(2'*H*,10b'*H*)dione (16f): HSQC NMR (600 MHz, $CDCl_3$)



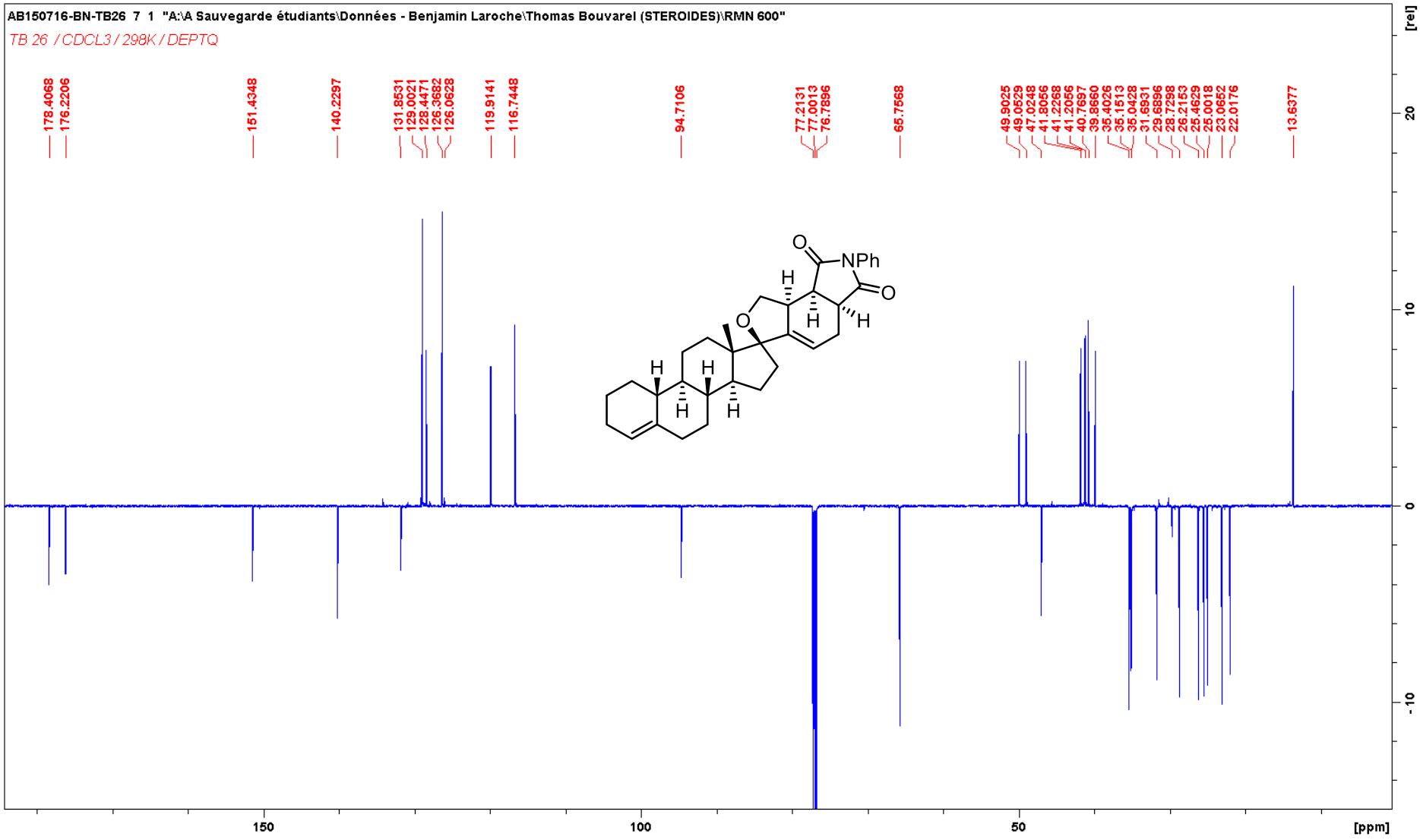
(3a'*S*,6'*S*,8*R*,9*S*,10a'*S*,10b'*R*,13*S*,14*S*)-3-Methoxy-13-methyl-2'-phenyl-3a',4',6,7,8,8',9,9',10',10a',11,12,13,14,15,16-hexadecahydrospiro[cyclopenta[*a*]phenanthrene-17,6'-oxepino[4,3-*e*]isoindole]-1',3'-(2'*H*,10b'*H*)dione (16f): NOESY NMR (600 MHz, $CDCl_3$)



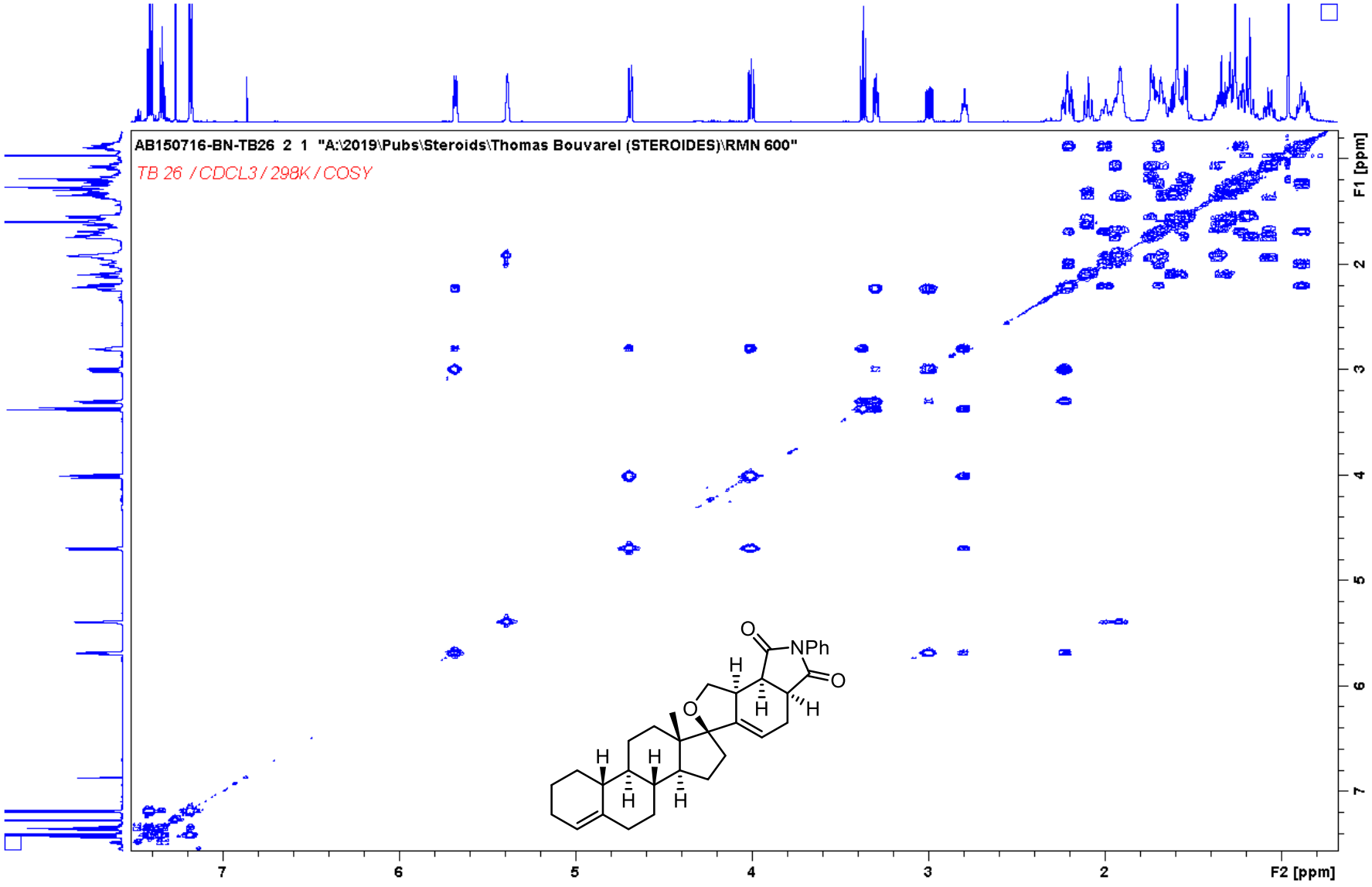
(3'*S*,5a'*S*,8*R*,8a'*R*,8b'*S*,9*S*,10*R*,13*S*,14*S*)-13-Methyl-7'-phenyl-1,1',2,3,5',5a',6,7,8,8b',9,10,11,12,13,14,15,16-octadecahydrospiro[cyclopenta[*a*]phenanthrene-17,3'-furo[3,4-*e*]isoindole]-6',8'-(7'*H*,8a'*H*)dione (17a): ^{1}H NMR (600 MHz, $CDCl_3$)



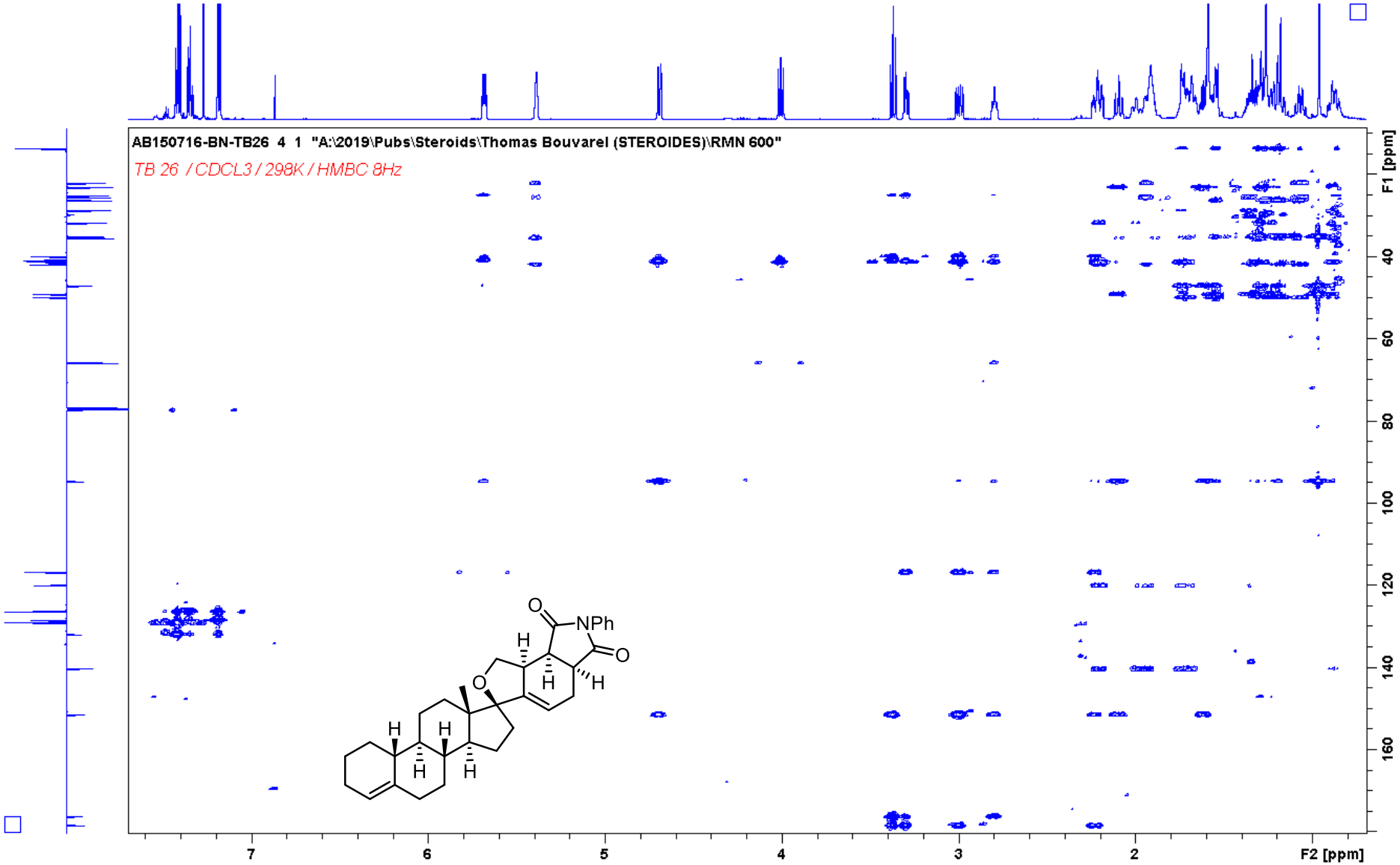
(3'*S*,5a'*S*,8*R*,8a'*R*,8b'*S*,9*S*,10*R*,13*S*,14*S*)-13-Methyl-7'-phenyl-1,1',2,3,5',5a',6,7,8,8b',9,10,11,12,13,14,15,16-octadecahydrospiro[cyclopenta[*a*]phenanthrene-17,3'-furo[3,4-*e*]isoindole]-6',8'-(7'*H*,8a'*H*)dione (17a): ^{13}C NMR (150 MHz, $CDCl_3$)



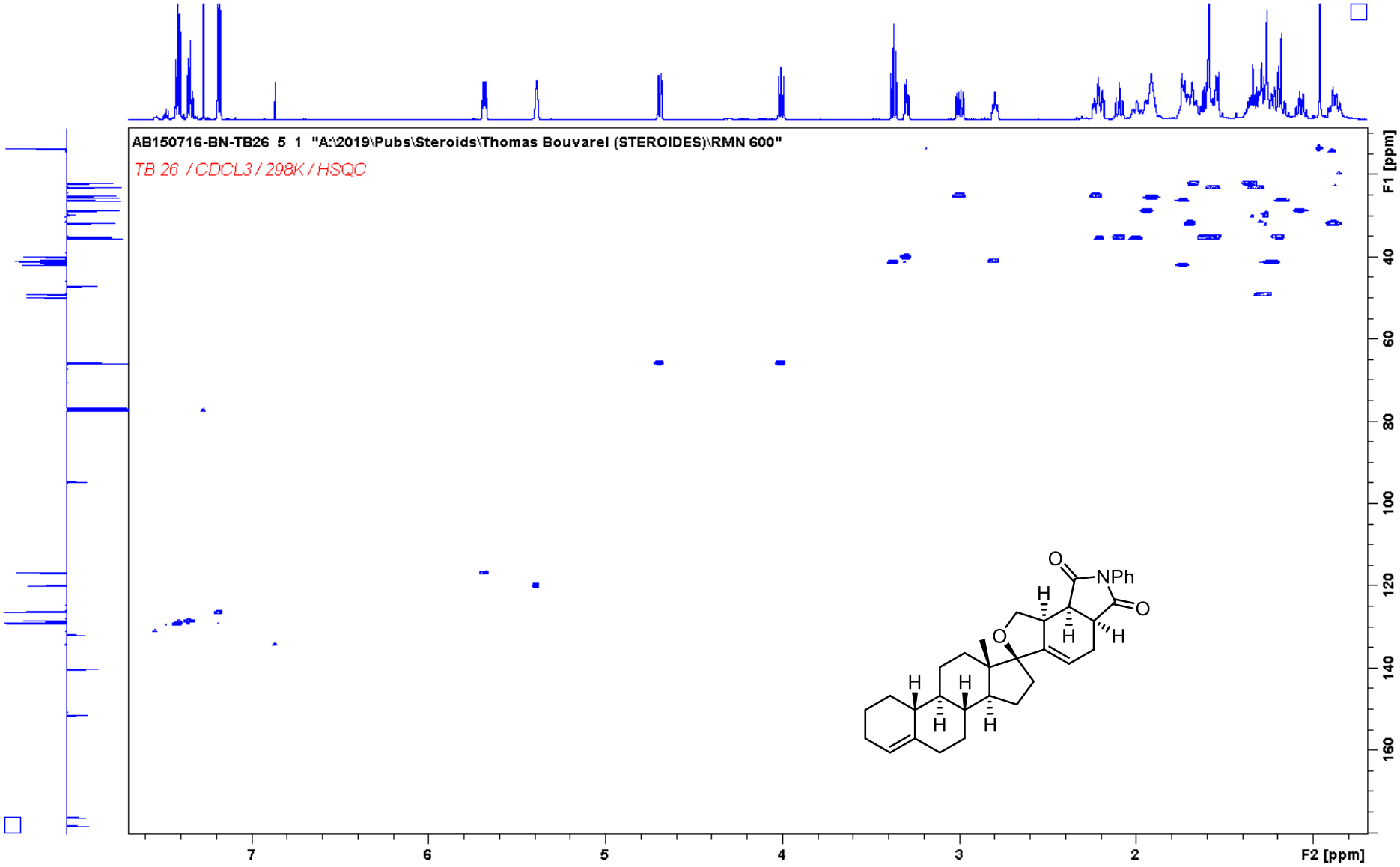
(3'*S*,5a'*S*,8*R*,8a'*R*,8b'*S*,9*S*,10*R*,13*S*,14*S*)-13-Methyl-7'-phenyl-1,1',2,3,5',5a',6,7,8,8b',9,10,11,12,13,14,15,16-octadecahydrospiro[cyclopenta[*a*]phenanthrene-17,3'-furo[3,4-*e*]isoindole]-6',8'-(7'*H*,8a'*H*)dione (17a): COSY NMR (600 MHz, $CDCl_3$)



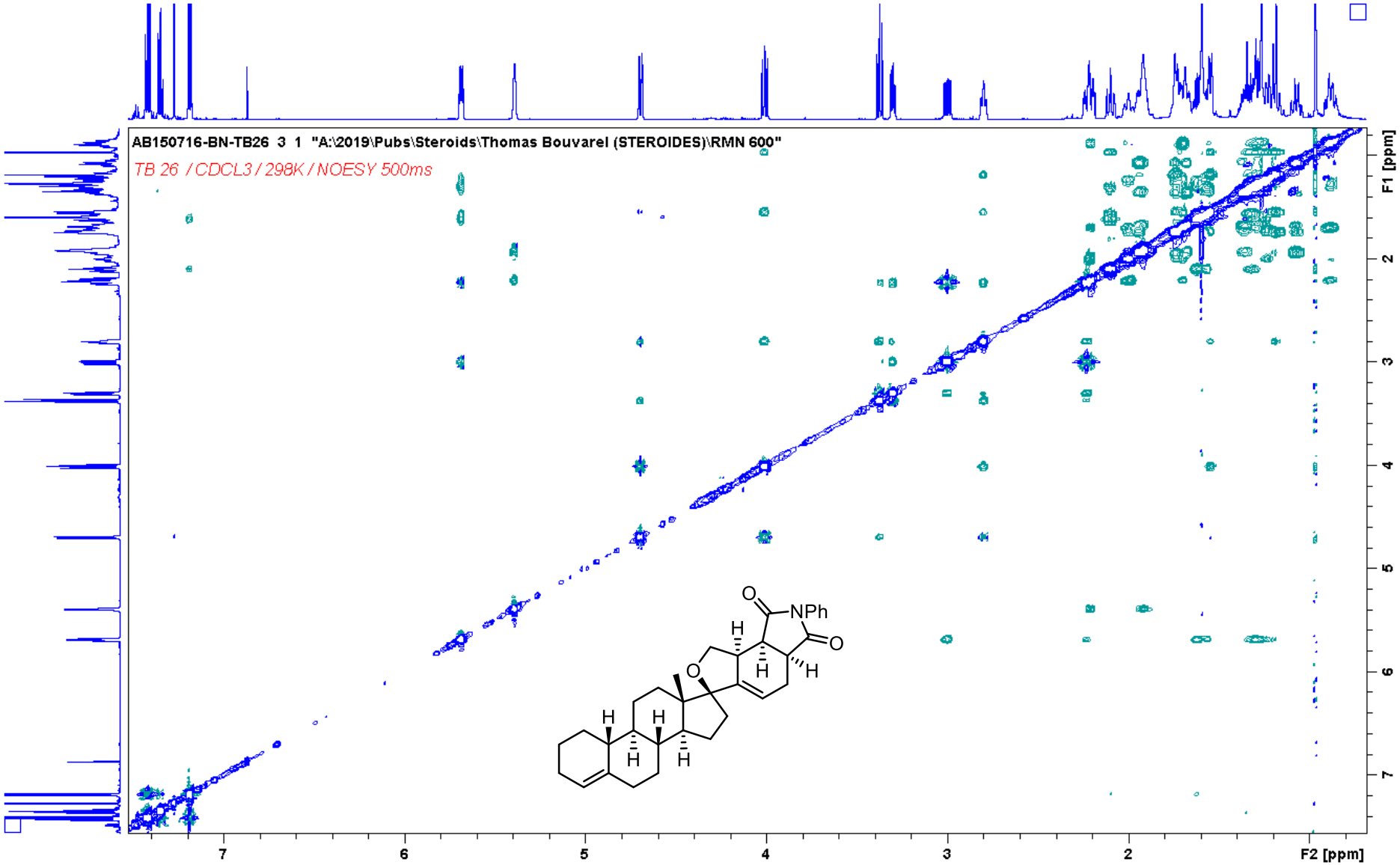
(3'*S*,5a'*S*,8*R*,8a'*R*,8b'*S*,9*S*,10*R*,13*S*,14*S*)-13-Methyl-7'-phenyl-1,1',2,3,5',5a',6,7,8,8b',9,10,11,12,13,14,15,16-octadecahydrospiro[cyclopenta[*a*]phenanthrene-17,3'-furo[3,4-*e*]isoindole]-6',8'(-7'*H*,8a'*H*)dione (17a): HMBC NMR (600 MHz, $CDCl_3$)



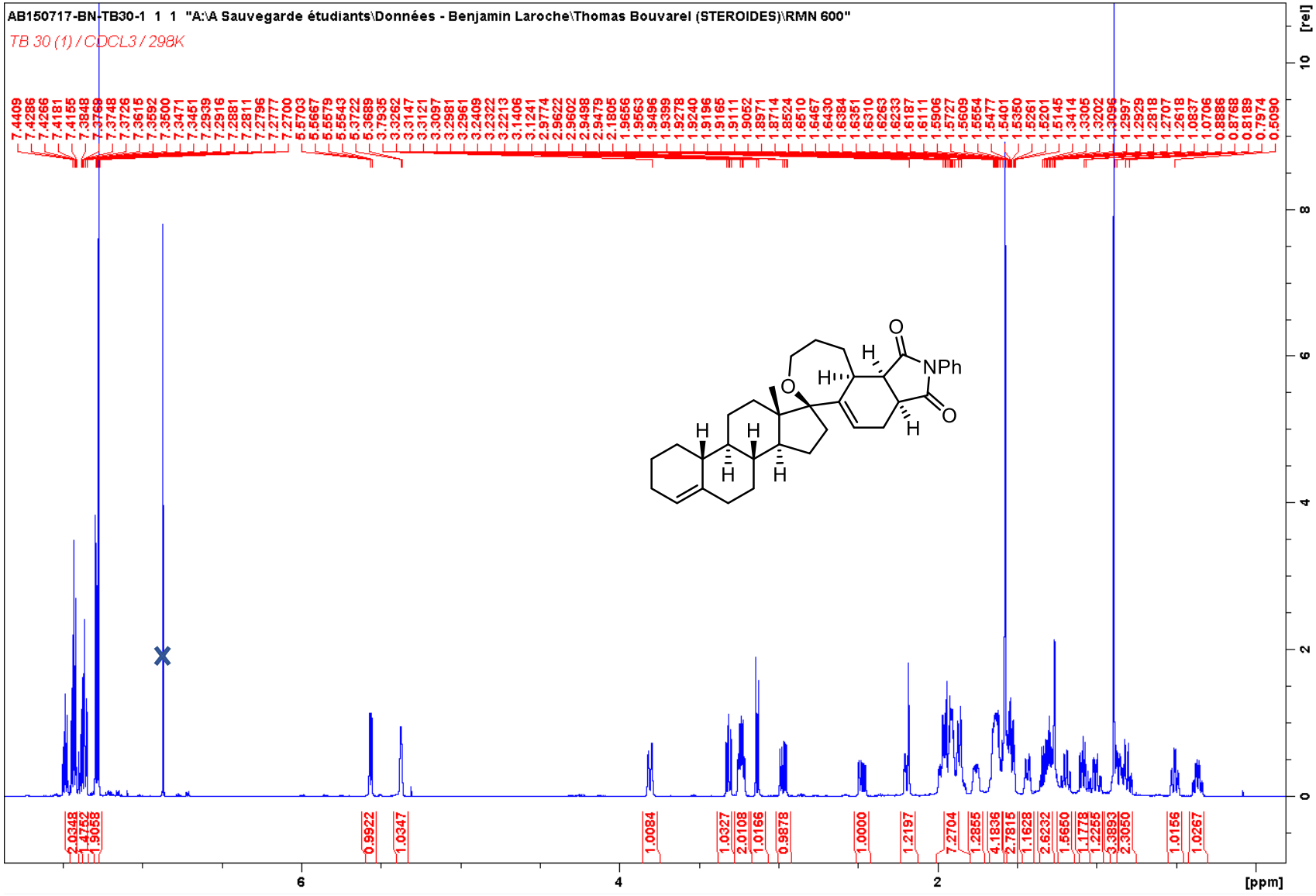
(3'*S*,5a'*S*,8*R*,8a'*R*,8b'*S*,9*S*,10*R*,13*S*,14*S*)-13-Methyl-7'-phenyl-1,1',2,3,5',5a',6,7,8,8b',9,10,11,12,13,14,15,16-octadecahydrospiro[cyclopenta[*a*]phenanthrene-17,3'-furo[3,4-*e*]isoindole]-6',8'-(7'*H*,8a'*H*)dione (17a): HSQC NMR (600 MHz, $CDCl_3$)



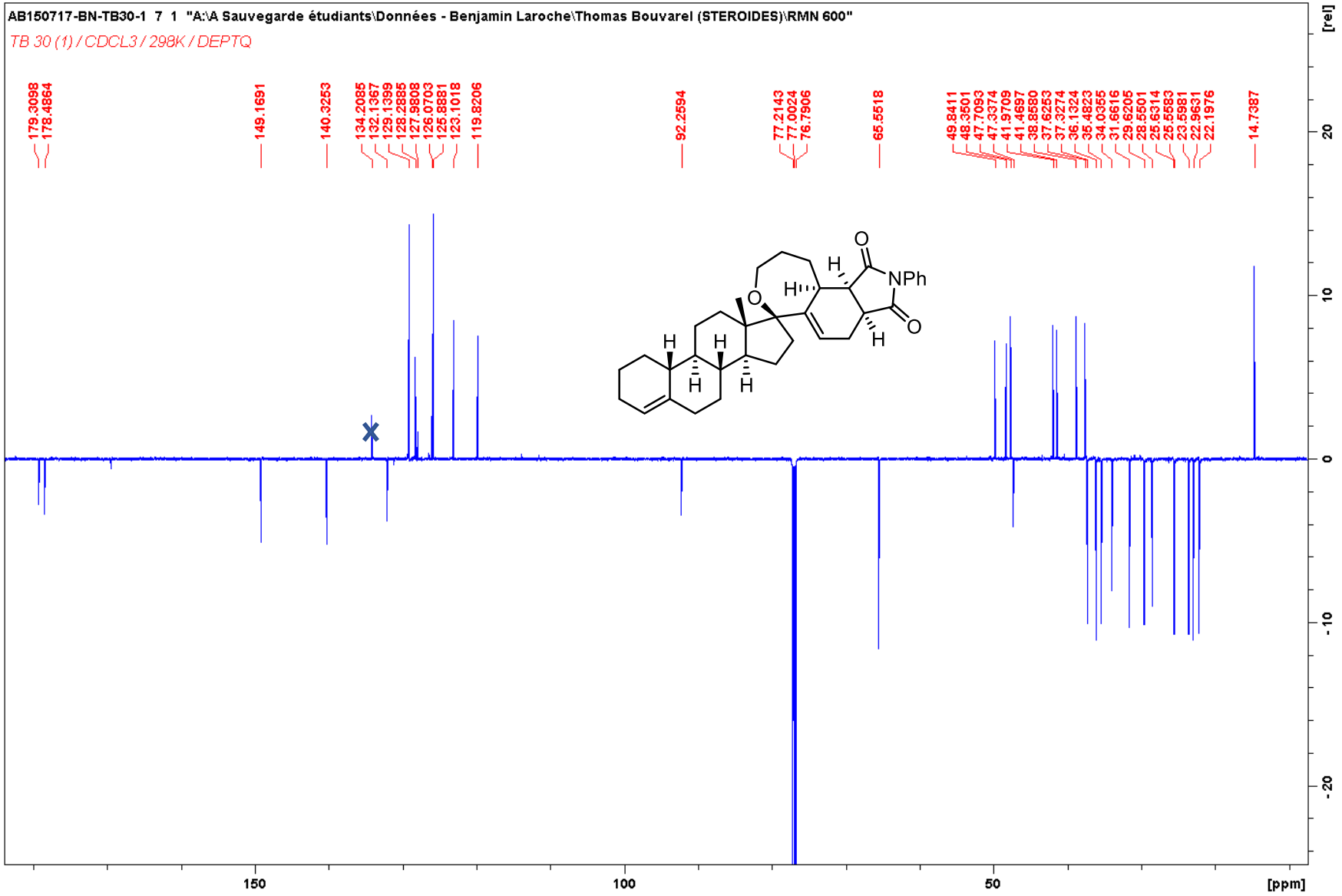
(3'*S*,5a'*S*,8*R*,8a'*R*,8b'*S*,9*S*,10*R*,13*S*,14*S*)-13-Methyl-7'-phenyl-1,1',2,3,5',5a',6,7,8,8b',9,10,11,12,13,14,15,16-octadecahydrospiro[cyclopenta[*a*]phenanthrene-17,3'-furo[3,4-*e*]isoindole]-6',8'(7'H,8a'*H*)dione (17a): NOESY NMR (600 MHz, $CDCl_3$)



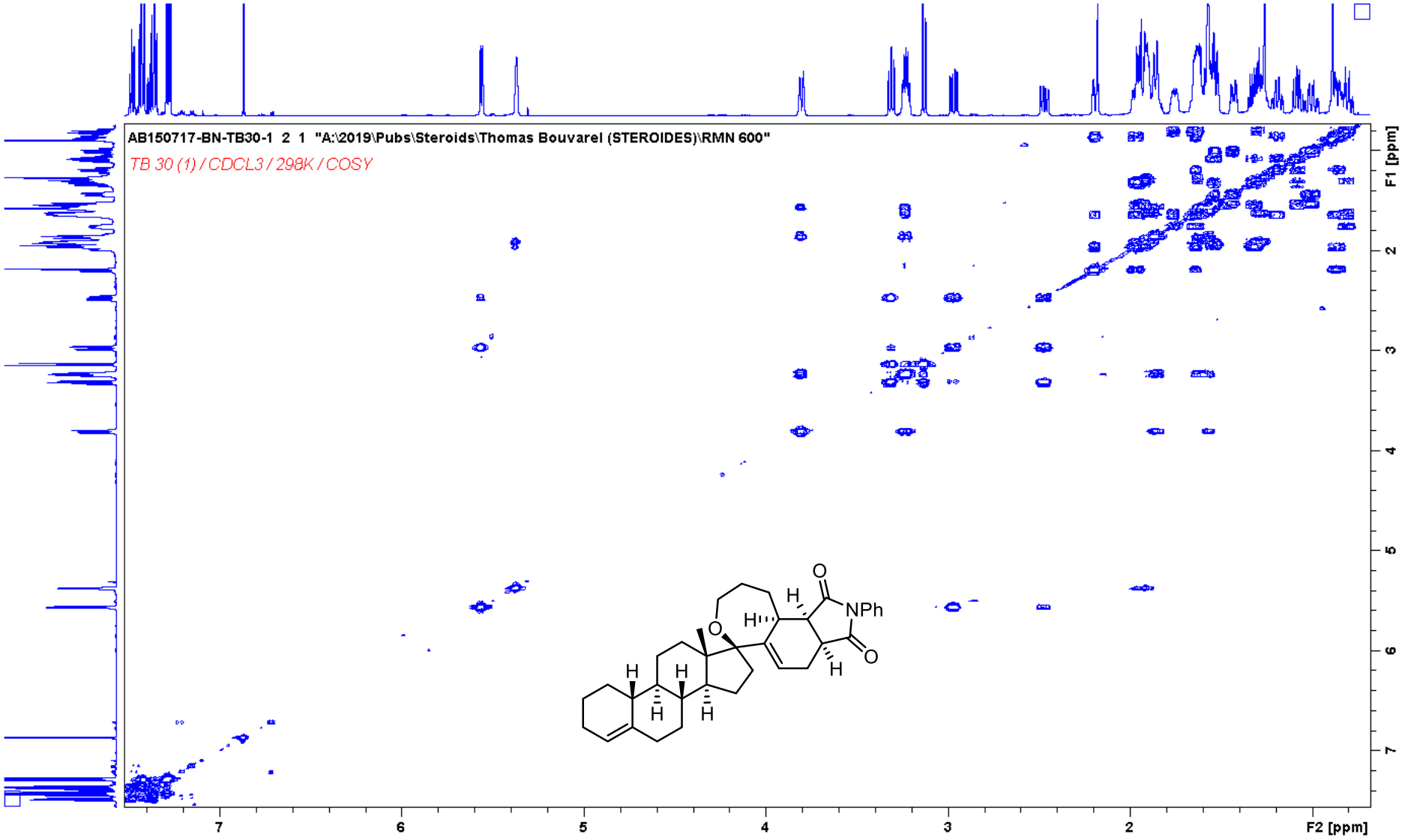
(3a'*S*,6'*S*,8*R*,9*S*,10*R*,10a'*S*,10b'*R*,13*S*,14*S*)-13-Methyl-2'-phenyl-1,2,3,3a',4',6,7,8,8',9,9',10,10',10a',11,12,13,14,15,16-icosahydrospiro[cyclopenta[*a*]phenanthrene-17,6'-oxepino[4,3-*e*]isoindole]-1',3'-(2'*H*,10b'*H*)dione (17b): ^{1}H NMR (600 MHz, $CDCl_3$)



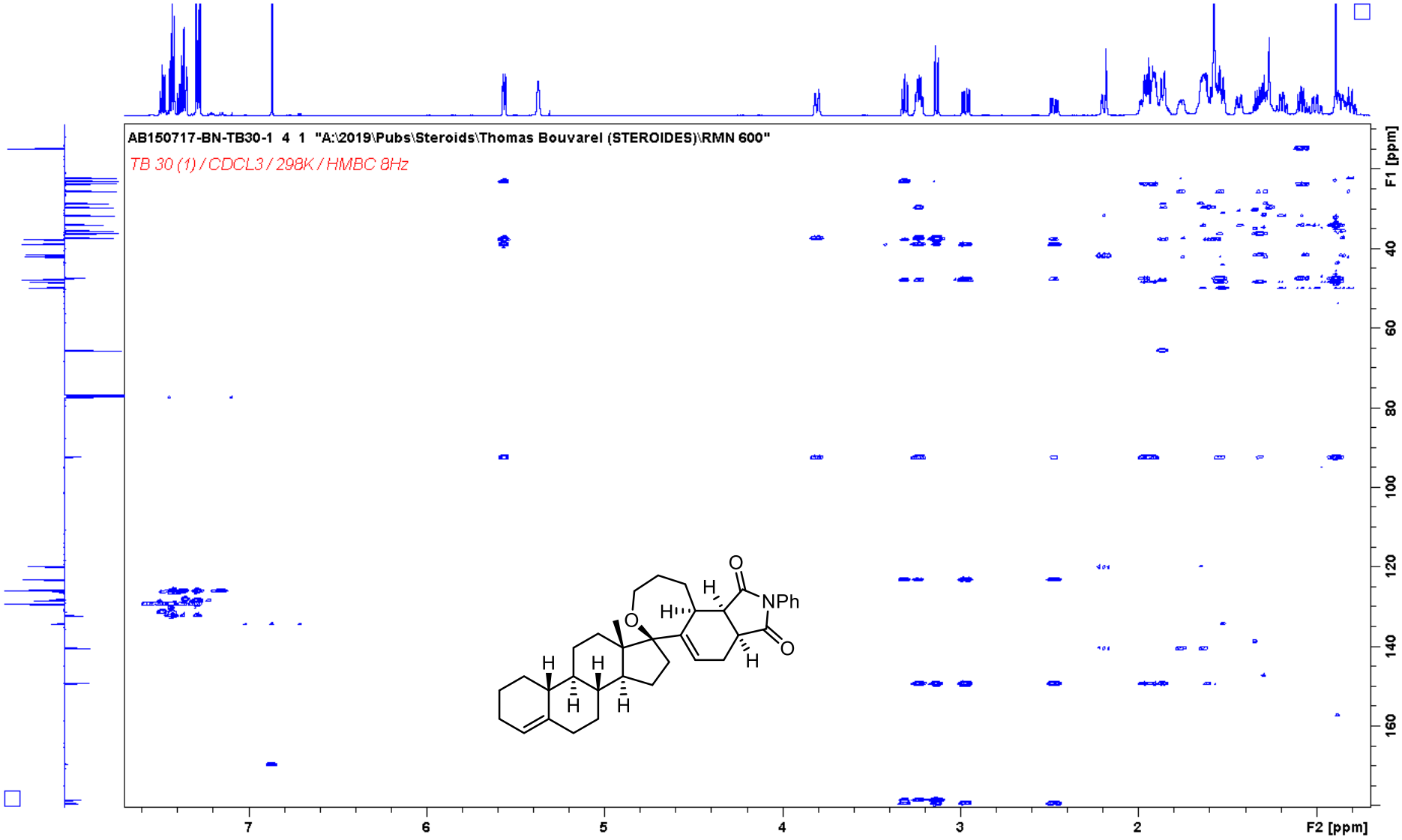
(3a'*S*,6'*S*,8*R*,9*S*,10*R*,10a'*S*,10b'*R*,13*S*,14*S*)-13-Methyl-2'-phenyl-1,2,3,3a',4',6,7,8,8',9,9',10,10',10a',11,12,13,14,15,16-icosahydrospiro[cyclopenta[*a*]phenanthrene-17,6'-oxepino[4,3-*e*]isoindole]-1',3'-(2'*H*,10b'*H*)dione (17b): ^{13}C NMR (150 MHz, $CDCl_3$)



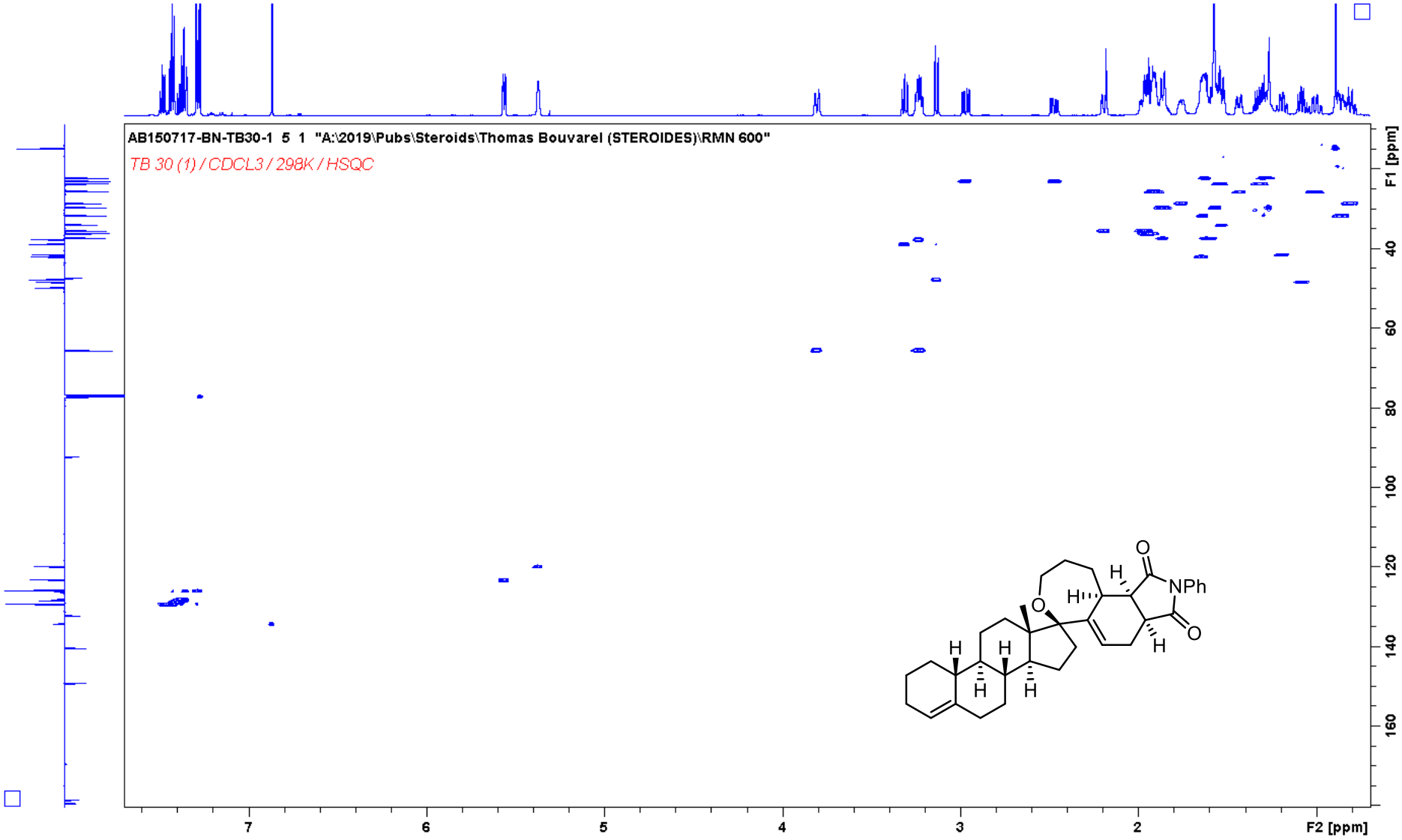
(3a'*S*,6'*S*,8*R*,9*S*,10*R*,10a'*S*,10b'*R*,13*S*,14*S*)-13-Methyl-2'-phenyl-1,2,3,3a',4',6,7,8,8',9,9',10,10',10a',11,12,13,14,15,16-icosahydrospiro[cyclopenta[*a*]phenanthrene-17,6'-oxepino[4,3-*e*]isoindole]-1',3'-(2'*H*,10b'*H*)dione (17b): COSY NMR (600 MHz, $CDCl_3$)



(3a'S,6'S,8R,9S,10R,10a'S,10b'R,13S,14S)-13-Methyl-2'-phenyl-1,2,3,3a',4',6,7,8,8',9,9',10,10',10a',11,12,13,14,15,16-icosahydrospiro[cyclopenta[*a*]phenanthrene-17,6'-oxepino[4,3-*e*]isoindole]-1',3'-(2'H,10b'H)dione (17b): HMBC NMR (600 MHz, $CDCl_3$)



(3a'*S*,6'*S*,8*R*,9*S*,10*R*,10a'*S*,10b'*R*,13*S*,14*S*)-13-Methyl-2'-phenyl-1,2,3,3a',4',6,7,8,8',9,9',10,10',10a',11,12,13,14,15,16-icosahydrospiro[cyclopenta[*a*]phenanthrene-17,6'-oxepino[4,3-*e*]isoindole]-1',3'-(2'*H*,10b'*H*)dione (17b): HSQC NMR (600 MHz, $CDCl_3$)



(3a'*S*,6'*S*,8*R*,9*S*,10*R*,10a'*S*,10b'*R*,13*S*,14*S*)-13-Methyl-2'-phenyl-1,2,3,3a',4',6,7,8,8',9,9',10,10',10a',11,12,13,14,15,16-icosahydrospiro[cyclopenta[*a*]phenanthrene-17,6'-oxepino[4,3-*e*]isoindole]-1',3'(2'*H*,10b'*H*)-dione (17b): NOESY NMR (600 MHz, $CDCl_3$)