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Convenient synthesis of furo[2,3-*c*][1,2]dioxoles from 1-aryl-2-allylalkane-1,3-diones

Alexander T. Zdvizhkov, Peter S. Radulov, Roman A. Novikov, Viktor A. Tafeenko, Vladimir V. Chernyshev, Alexey I. Ilovaisky, Alexander O. Terent'ev and Gennady I. Nikishin

Contents

General materials and methods

^{1}H and ^{13}C NMR spectra were recorded on Bruker AVANCE II 300 (300.1 and 75.5 MHz, respectively) spectrometer in $CDCl_3$. Assignments of ^{1}H and ^{13}C signals were made and the structures of the compounds were determined with the aid of 2D COSY, NOESY, editing-HSQC, HSQC-TOCSY, and HMBC spectra.

MeCN (HPLC grade) for ESI-HRMS experiments was ordered from Merck and used as supplied. All samples for ESI-HRMS experiments were prepared in 1.5 ml Eppendorf tubes. All plastic disposables (Eppendorf tubes and tips) used in sample preparation were washed with MeCN before use.

High resolution mass spectra were recorded on a Bruker maXis instrument equipped with electrospray ionization (ESI) ion source [S1,S2]. The all measurements were performed in a positive (+MS) ion mode (interface capillary voltage: 4500 V) with scan range *m*/*z*: 50 - 3000. External calibration of the mass spectrometer was performed with Electrospray Calibrant Solution (Fluka). A direct syringe injection was used for the all analyzed solutions in MeCN (flow rate: 3 μl min^{-1}). Nitrogen was used as nebulizer gas (0.4 bar) and dry gas (4.0 dm^3 min^{-1}); interface temperature was set at 180ºC. The all spectra were processed by using Bruker DataAnalysis 4.0 software package.

The molecular structure of **2b** was confirmed by X-ray structure determination. The single-crystal X-ray diffraction experiments for **2b** was carried out at room temperature using monochromated CuK_α radiation on a CAD-4 diffractometer (Nonius BV, The Netherlands) and STOE STADI-VARI Pilatus 100K diffractometer, respectively. The structures were solved with *SHELXS*[iii] and refined with *SHELXL* [S3]. All hydrogen atoms were located on a difference Fourier map, then placed in idealized positions (C-H 0.93-0.98 Å), and refined as riding with $U_{iso}(H)=1.2\text{-}1.5U_{eq}(C)$. The crystallographic data for **2b** are summarized in Table S1, and molecular structures drawn with DIAMOND [S4] are shown in Figure 1 (main article body).

The TLC analysis was carried out on standard silica gel chromatography plates. The melting points were determined on a Kofler hot-stage apparatus. Chromatography was performed on silica gel (0.060-0.200 mm, 60 A, CAS 7631-86-9).

Petroleum ether 40-70 (PE), Et_2O, MeCN, CH_2Cl_2, and ethyl acetate (EA) were distilled before use over the corresponding drying agents. The reagents I_2, $Na_2S_2O_3 \bullet 5H_2O$, and Na_2SO_4 were of chemical purity grade.

A solution of H_2O_2 was prepared by the extraction with diethyl ether from a 37% aqueous H_2O_2 solution followed by drying over $MgSO_4$ [S5].

Diketones **1a-c** were synthesized from commercially available diketones by the protocol described earlier [S6].

2-Allyl-1,3-diphenylpropane-1,3-dione ***1a*** [S6]

^{1}H NMR (300.15 MHz, $CDCl_3$): δ = 2.87 (t, *J* = 6.6 Hz, 2H, CH_2=CHC<u>H</u>$_2$C), 5.00-5.12 (m, 2H, C<u>H</u>$_2$=CH), 5.30 (t, 1H, *J* = 6.6 Hz, COC<u>H</u>CO), 5.80-5.94 (m, 1H CH_2=CH), 7.41-7.58 (m, 6H, Ph), 7.94-7.96 (m, 4H, Ph).

2-Allyl-1-(4-methylphenyl)butane-1,3-dione ***1b***

^{1}HNMR (300.15 MHz, $CDCl_3$): δ = 2.09 (s, 3H, CH_3CO), 2.37 (s, 3H, CH_3) 2.69 (t, *J* = 5.9 Hz, 2H, -CH_2-), 4.48 (t, *J* = 7.3 Hz, 1H, COC<u>H</u>CO), 4.97-5.07 (t, 2H, CH_2=), 5.70 (m, 1H, =CH-), 7.22-7.25 (m, 2H, Ph), 7.84-7.86 (m, 2H, Ph).

2-Allyl-1-phenylbutane-1,3-dione ***1c*** [S7]

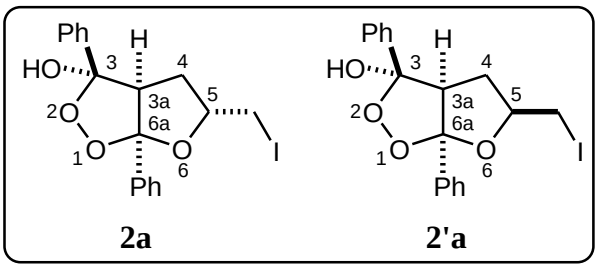
^{1}H NMR (300.15 MHz, $CDCl_3$): δ = 2.13 (s, 3H, CH_3), 2.73 (t, *J* = 6.6 Hz, 2H, CH_2=CHC<u>H</u>$_2$C), 4.54 (t, *J* = 6.6 Hz, 1H, COC<u>H</u>CO), 5.00-5.11 (m, 2H, C<u>H</u>$_2$=CH), 5.68-5.81 (m, 1H, CH_2=C<u>H</u>), 7.44-7.58 (m, 3H, Ph), 7.96-7.99 (m, 2H, Ph).

Reaction of 1-aryl-2-allylalkane-1,3-diones 1a-c with I_2 / H_2O_2 system.

Iodine (1.015 g, 4 mmol) and PMA (0.7301 g, 0.4 mmol) were dissolved in CH_2Cl_2 (10 ml), a 1.88 M ether solution of H_2O_2 (5.3 ml, 10 mmol) was added, and then diketone **1a-c** (2 mmol) was added with stirring at room temperature. The reaction mixture was stirred for one hour at room temperature. Petroleum ether (20 ml) and finely powdered $Na_2S_2O_3$•$5H_2O$ (3 g) were added, and the mixture was vigorously stirred until the solution turned colourless. The precipitate was filtered off and the solvents were evaporated on a rotary vacuum evaporator (10-15 Torr) at 15-20 °C. The products were isolated by silica gel column chromatography using PE-EA as the eluent (5:1, v/v).

Experimental data for 2a-c and 3

5-Iodomethyl-3,6a-diphenyltetrahydro-3*H*-furo[2,3-*c*][1,2]dioxol-3-ol, 2a+2'a



Yellow oil, **2c:2'c** = 2:1. Yield 70 %. Rf 0.55 (1:5 EA/PE)
Elemental analysis:
Calculated for $C_{18}H_{17}IO_4$: % C 50.96; %H 4.04
found: % C 50.88; %H 4.01

HRMS-ESI: calculated 462.9803 [$C_{18}H_{17}IO_4$+K] found 462.9805 (Δ=0.4ppm)

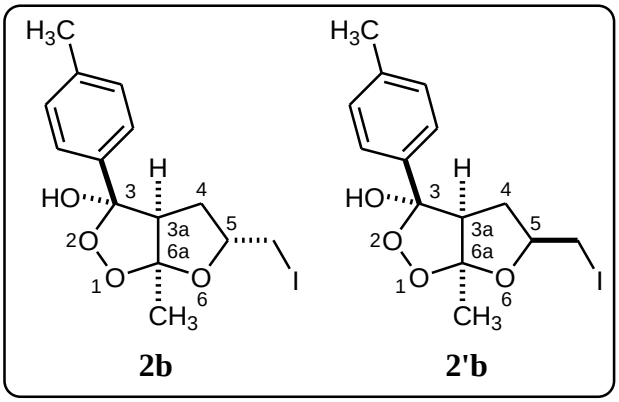
***rac*-(3*R*,3a*R*,5*R*,6a*R*)-5-Iodomethyl-3,6a-diphenyltetrahydro-3*H*-furo[2,3-*c*][1,2]dioxol-3-ol, 2a**

^{1}H NMR (300.15 MHz, $CDCl_3$): δ = 1.57 (dd, *J* = 13.6 Hz, 5.5 Hz, 1H, CH_2(4)), 1.76 (dd, *J* = 13.6 Hz, 10.5 Hz, 1H, CH_2(4)), 3.31-3.47 (m, 2H, CH_2I), 3.60-3.68 (m, 1H, CH(3a)), 4.28-4.41 (m, 1H, CH(5)), 7.36-7.95 (m, 10H, Ph).
^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 8.4 (CH_2I), 36.0 (CH_2(4)), 68.8 (CH(3a)), 78.4 (CH(5)), 109.0 (C(3)), 111.9 (C(6a)), 126.0, 127.3, 128.2, 128.8, 128.9, 129.4, 132.7, 135.7 (Ph).

***rac*-(3*R*,3a*R*,5*S*,6a*R*)-5-Iodomethyl-3,6a-diphenyltetrahydro-3*H*-furo[2,3-*c*][1,2]dioxol-3-ol, 2'a**

^{1}H NMR (300.15 MHz, $CDCl_3$): δ = 1.50 (dd, *J* = 13.5 Hz, 6.7 Hz, 1H, CH_2(4)), 2.05-2.19 (m, 1H, CH_2(4)), 3.40-3.47 (m, 2H, CH_2I), 3.77-3.82 (m, 1H, CH(3a)), 4.19-4.28 (m, 1H, CH(5)), 7.36-7.95 (m, 10H, Ph).
^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 7.3 (CH_2I), 36.0 (CH_2(4)), 68.8 (CH(3a)), 80.4 (CH(5)), 109.0 (C(3)), 111.9 (C(6a)), 126.0, 127.3, 128.2, 128.8, 128.9, 129.4, 132.7, 135.7 (Ph).

5-Iodomethyl-6a-methyl-3-(4-methylphenyl)tetrahydro-3*H*-furo[2,3-*c*][1,2]dioxol-3-ol, 2b+2'b



White crystals, **2b:2'b** = 2:1. Yield: 26 %.
m.p. 133-136°C. Rf: 0.54 (1/5 EA/PE).
Elemental analysis:
Calculated for $C_{14}H_{17}IO_4$: % C 44.70; %H 4.55
found: % C 44.69; %H 4.48.
HRMS-ESI: HRMS: calculated 394.0516 [$C_{14}H_{17}IO_4$+NH_4] found 394.0510 (Δ=1.5 ppm).

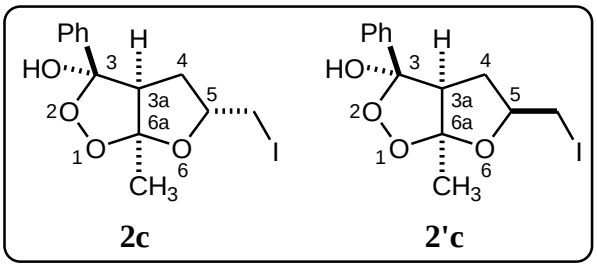
***rac*-(3*R*,3a*R*,5*R*,6a*S*)-5-iodomethyl-6a-methyl-3-(4-methylphenyl)tetrahydro-3*H*-furo[2,3-*c*][1,2]dioxol-3-ol, 2b**

^{1}H NMR (300.15 MHz, $CDCl_3$): δ = 1.57 (dd, *J* = 13.9 Hz, 7.9 Hz, 1H, CH_2(4)), 1.64 (dd, *J* = 13.9 Hz, 9.9 Hz, 1H, CH_2(4)) 1.74 (s, 3H, C(6a)CH_3), 2.37 (s, 3H, ArCH_3), 3.17-3.20 (m, 2H, CH_2I), 3.31-3.46 (m, 1H, CH(3a)), 4.08-4.15 (m, 1H, CH(5)), 7.19-7.37 (m, 4H, Ar).
^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 8.2 ((CH_2I), 16.8 (ArCH_3), 21.2 (C(6a)CH_3), 36.2 (CH_2(4)), 65.5 (CH (3a)), 77.8 (CH(5)), 108.9 (C(3)), 116.9 (C(6a)), 125.9, 126.1, 129.4, 139.3 (Ar).

***rac*-(3*R*,3a*R*,5*S*,6a*S*)-5-iodomethyl-6a-methyl-3-(4-methylphenyl)tetrahydro-3*H*-furo[2,3-*c*][1,2]dioxol-3-ol, 2'b**

^{1}H NMR (300.15 MHz, $CDCl_3$): δ = 1.47 (dd, *J* = 13.5 Hz, 6.7 Hz, 1H, CH_2(4)), 1.72 (s, 3H, C(6a)CH_3), 2.02-2.16 (m, 1H, CH_2(4)), 2.37 (s, 3H, ArCH_3), 3.31-3.46 (m, 3H, CH(3a), CH_2I), 4.08-4.15 (m, 1H, CH(5)), 7.19-7.37 (m, 4H, Ar).
^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 8.2 ((CH_2I), 16.8 (ArCH_3), 22.0 (C(6a)CH_3), 34.7 (CH_2(4)), 65.4 (CH (3a)), 80.1 (CH(5)), 108.9 (C(3)), 116.9 (C(6a)), 125.9, 126.1, 129.4, 139.3 (Ar).

5-Iodomethyl-6a-methyl-3-phenyltetrahydro-3*H*-furo[2,3-*c*][1,2]dioxol-3-ol, 2c+2'c



Yield: 30 %, **2a:2'a** = 2:1. White crystals. m.p. 128-130°C. Rf 0.49 (1/5 EA/PE)
Elemental analysis:
Calculated for $C_{13}H_{15}IO_4$: % C 43.11; %H 4.17
found: % C 43.12; %H 4.15.
HRMS-ESI: calculated 384.9907 [$C_{13}H_{15}IO_4$+Na] found 384.9907 (Δ=0.0 ppm).

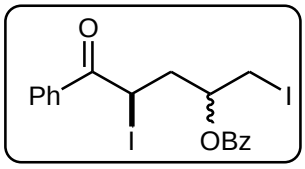
***rac*-(3*R*,3a*R*,5*R*,6a*S*)-5-iodomethyl-6a-methyl-3-phenyltetrahydro-3*H*-furo[2,3-*c*][1,2]dioxol-3-ol, 2c**

^{1}H NMR (300.15 MHz, $CDCl_3$): δ = 1.54 (dd, *J* = 13.1, 4.7 Hz, 1H, CH_2(4)), 1.66 (dd, *J* = 13.1, 10.1 Hz, 1H, CH_2(4)), 1.75 (s, 3H, CH_3), 3.05 (s, 1H, OH), 3.17-3.19 (m, 2H, CH_2I), 3.31-3.37 (m, 1H, CH(3a),), 4.11-4.18 (m, 1H, CH(5)), 7.39-7.48 (m, 5H, Ph).
^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 9.0 (CH_2I), 22.1 (CH_3), 36.2 (CH_2(4)), 65.7 (CH(3a)), 78.1 (CH(5)), 108.8 (C(3)), 117.0 (C(6a)), 126.0, 126.2, 128.8, 129.4, 137.1 (Ph).

***rac*-(3*R*,3a*R*,5*S*,6a*S*)-5-iodomethyl-6a-methyl-3-phenyltetrahydro-3*H*-furo[2,3-*c*][1,2]dioxol-3-ol, 2'c**

^{1}H NMR (300.15 MHz, $CDCl_3$): δ = 1.47 (dd, *J* = 13.6 Hz, 6.6 Hz, 1H, CH_2(4)), 1.72 (s, 3H, CH_3), 2.09 (ddd, *J* = 13.6 Hz, 10.6 Hz, 7.0 Hz, 1H, CH_2(4)), 3.07 (s, 1H, OH), 3.31-3.37 (m, 2H, CH_2I), 3.42-3.46 (m, 1H, CH(3a)), 4.11-4.18 (m, 1H, CH(5)), 7.39-7.48 (m, 5H, Ph).
^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 8.2 (CH_2I), 21.3 (CH_3), 34.7 (CH_2(4)), 65.6 (CH(3a)), 80.1 (CH(5)), 108.8 (C(3)), 117.0 (C(6a)), 126.0, 126.2, 128.8, 129.4, 137.1 (Ph).

3-Iodo-1-iodomethyl-4-oxo-4-phenylbutyl benzoate 3 (mixture of diastereomers) [S8]



Yellow oil.
^{1}H NMR (300.15 MHz, $CDCl_3$): δ = 2.61-2.72, 2.93-3.02 (both m, total 2H, CHICH_2CHCH_2I), 3.43-3.61 (m, 2H, CH_2I), 4.86-4.90, 5.21-

5.26 (both m, total 1H, CHO), 5.45-5.50 (m, 1H, CHI), 7.37-7.45 (m, 4H, Ar), 7.50-7.61 (m, 2H, Ar), 7.91-8.02 (m, 4H, Ar).

References

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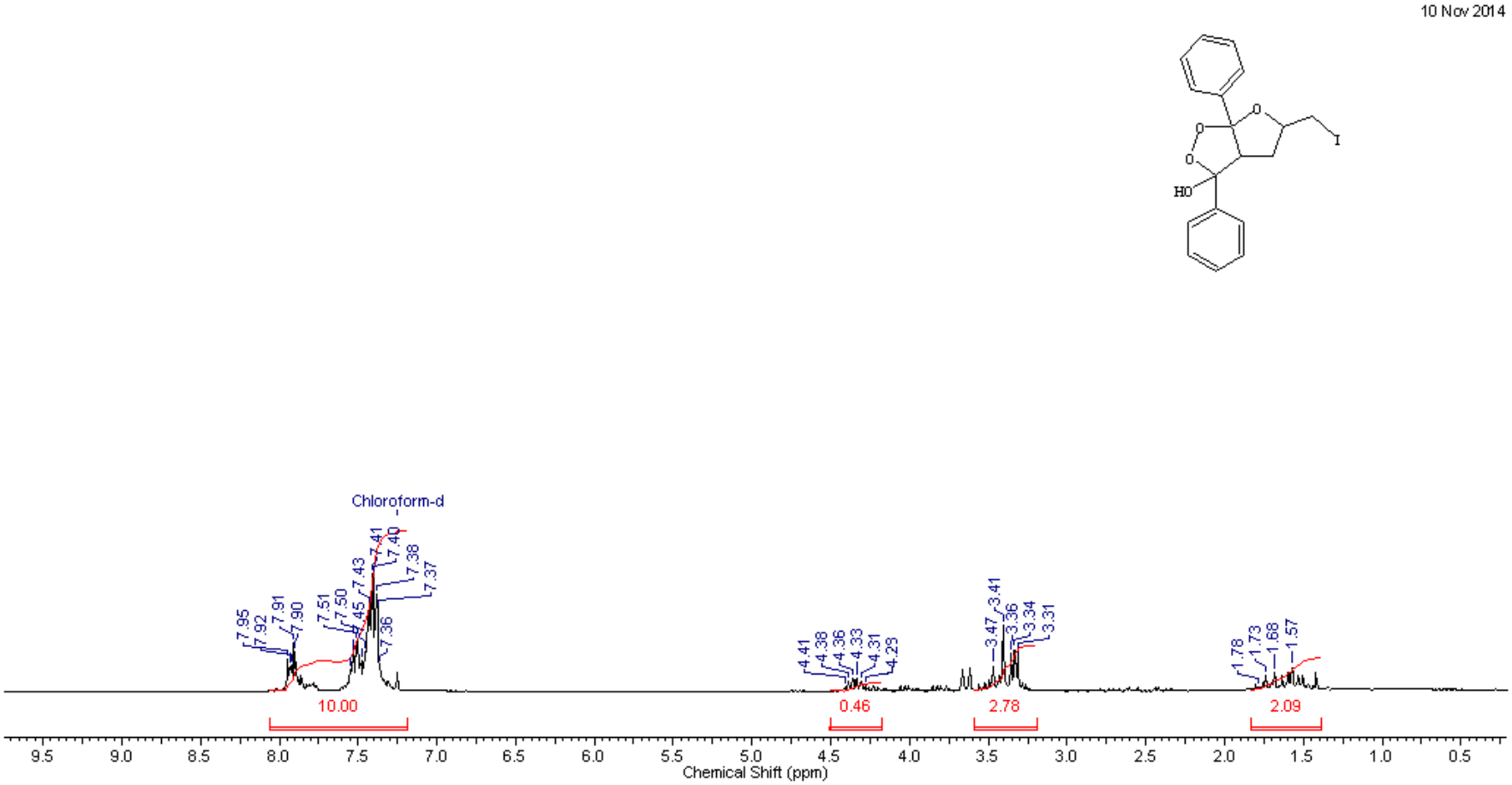
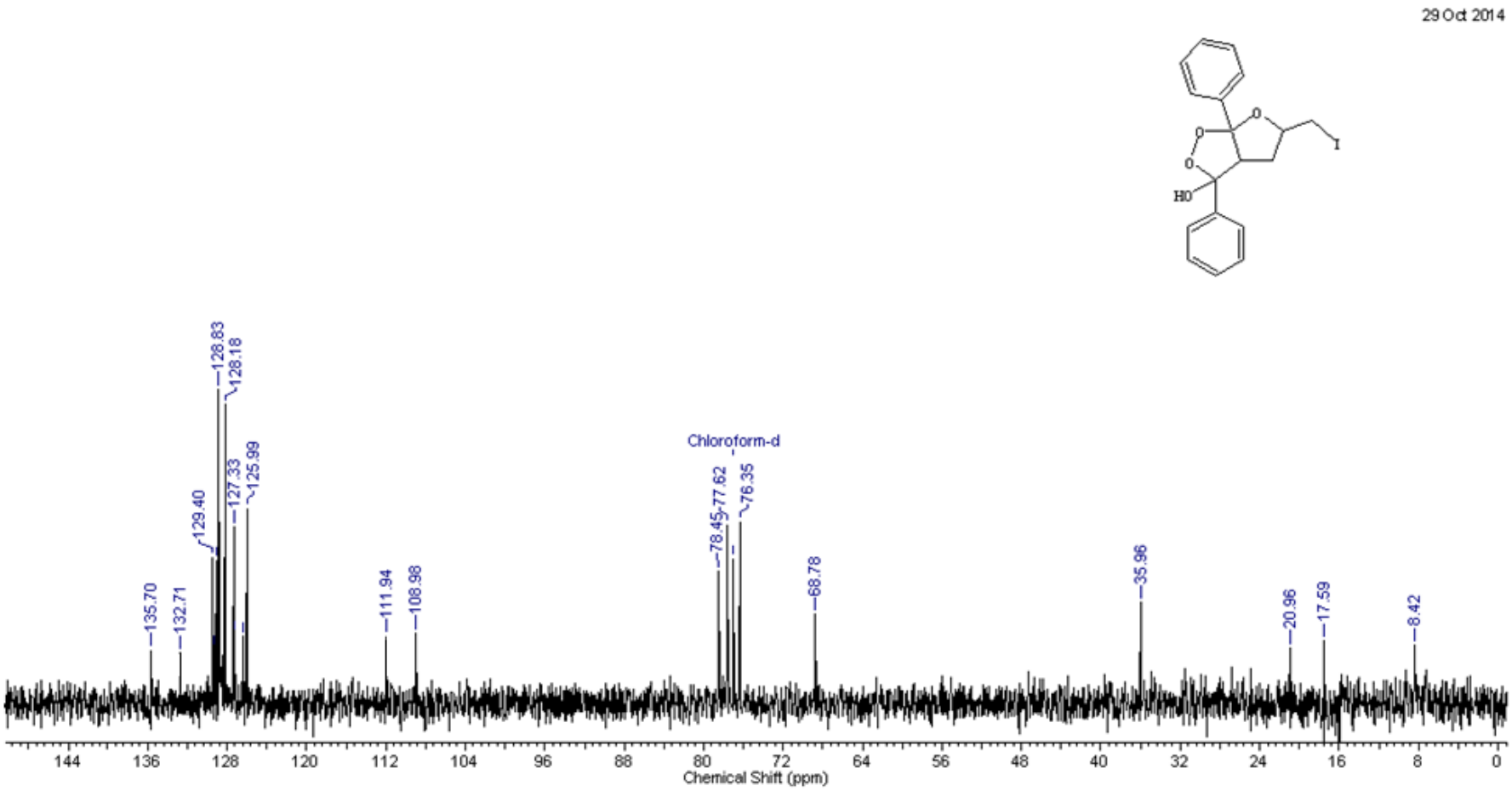
[S7] W. Yang, L. Huang, H. Liu, W. Wang and H. Li, *Chem. Commun.*, 2013, **49**, 4667.

[S8] A. T. Zdvizhkov, A. O. Terent'ev, P. S. Radulov, R. A. Novikov, V. A. Tafeenko, V. V. Chernyshev, A. I. Ilovaisky, D. O. Levitsky, F. Fleury and G. I. Nikishin, *Terahedron Lett.*, 2016, **57**, 949.

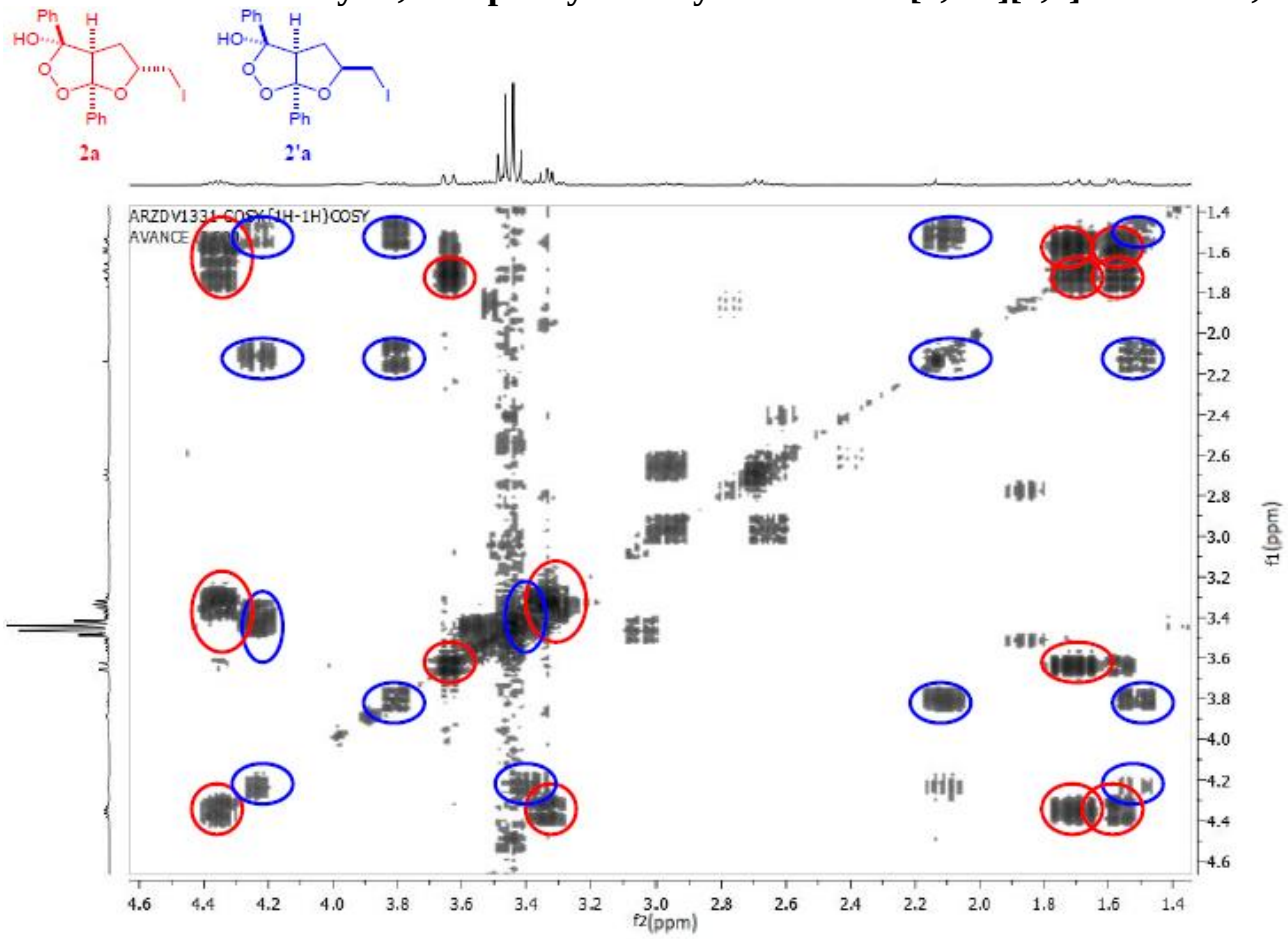
^{1}H NMR of 5-iodomethyl-3,6a-diphenyltetrahydro-3*H*-furo[2,3-*c*][1,2]dioxol-3-ol, 2a+2'a



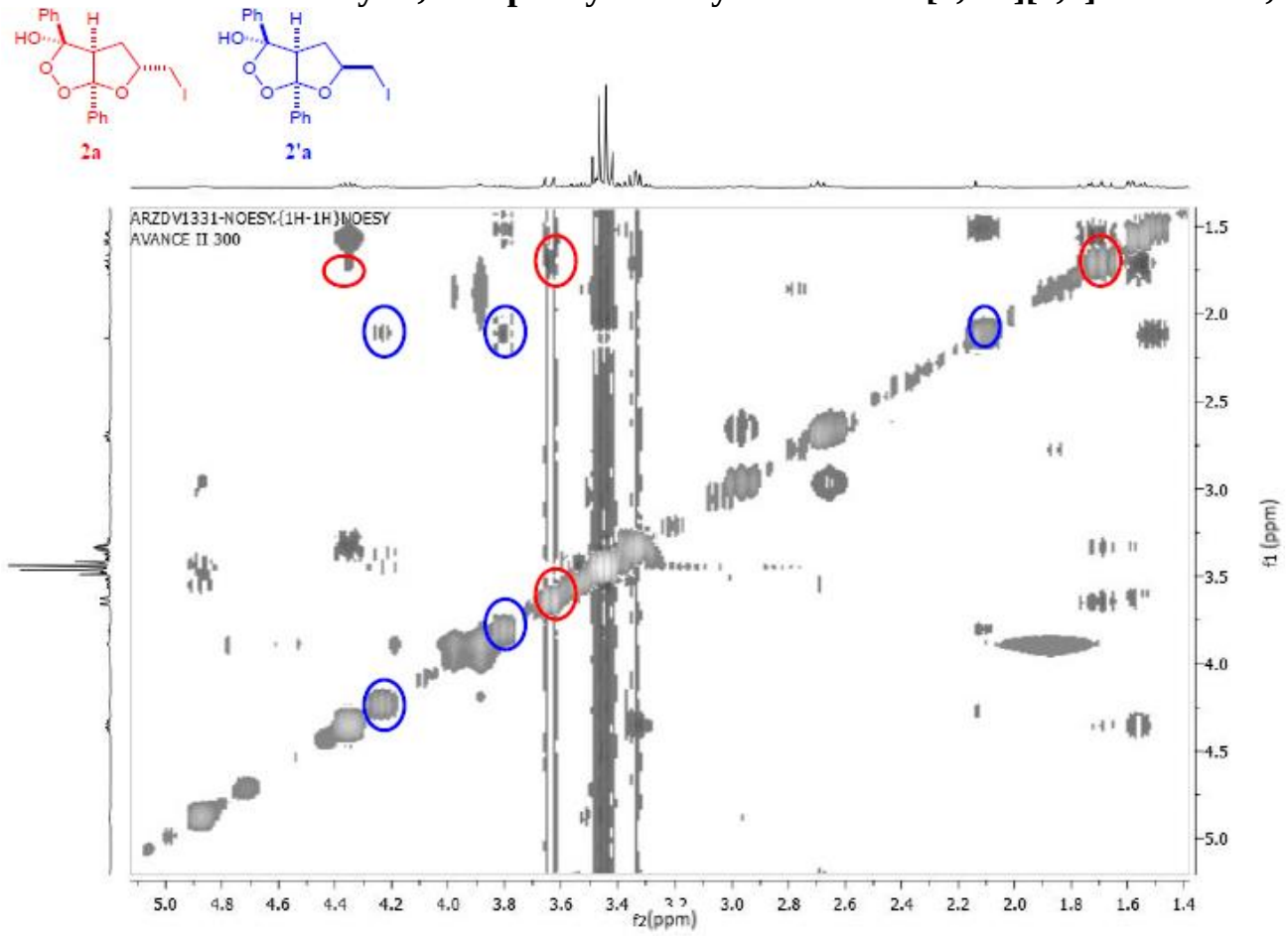
^{13}C NMR of 5-iodomethyl-3,6a-diphenyltetrahydro-3*H*-furo[2,3-*c*][1,2]dioxol-3-ol, 2a+2'a



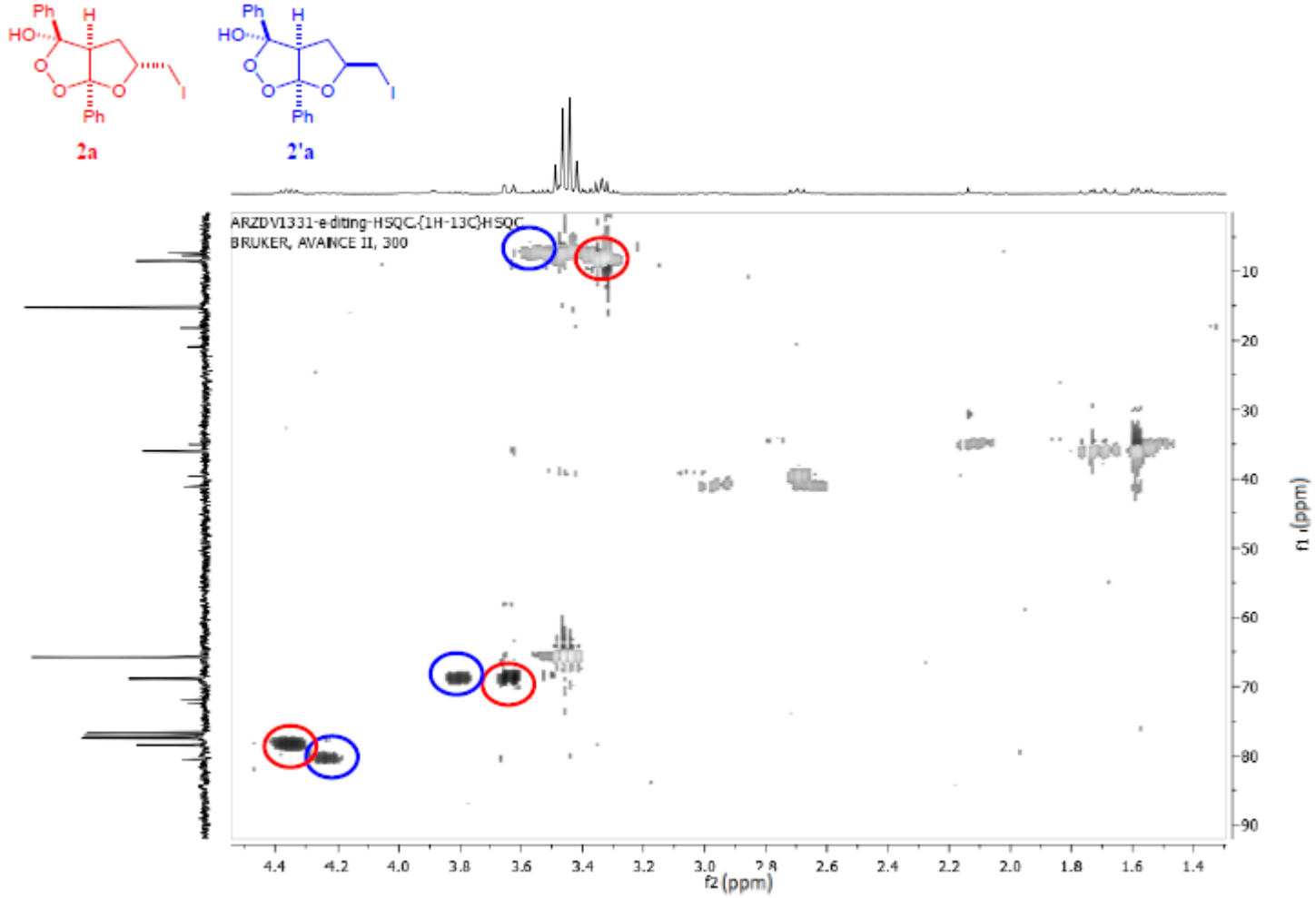
COSY of 5-iodomethyl-3,6a-diphenyltetrahydro-3*H*-furo[2,3-*c*][1,2]dioxol-3-ol, 2a+2'a



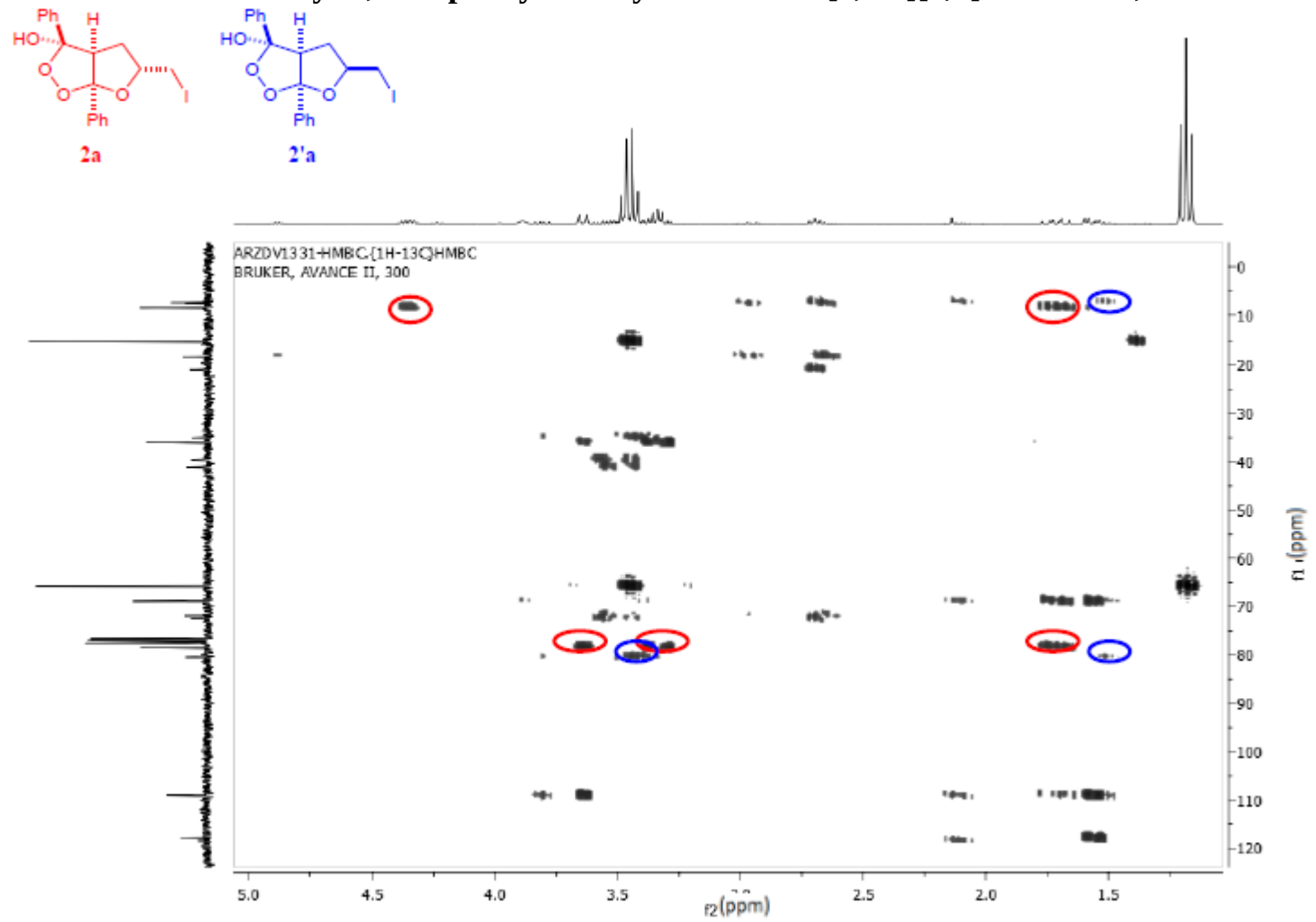
NOESY of 5-iodomethyl-3,6a-diphenyltetrahydro-3*H*-furo[2,3-*c*][1,2]dioxol-3-ol, 2a+2'a



HSQC of 5-iodomethyl-3,6a-diphenyltetrahydro-3*H*-furo[2,3-*c*][1,2]dioxol-3-ol, 2a+2'a



HMBC of 5-iodomethyl-3,6a-diphenyltetrahydro-3*H*-furo[2,3-*c*][1,2]dioxol-3-ol, 2a+2'a



HRMS-ESI of 5-iodomethyl-3,6a-diphenyltetrahydro-3*H*-furo[2,3-*c*][1,2]dioxol-3-ol, 2a+2'a

Display Report

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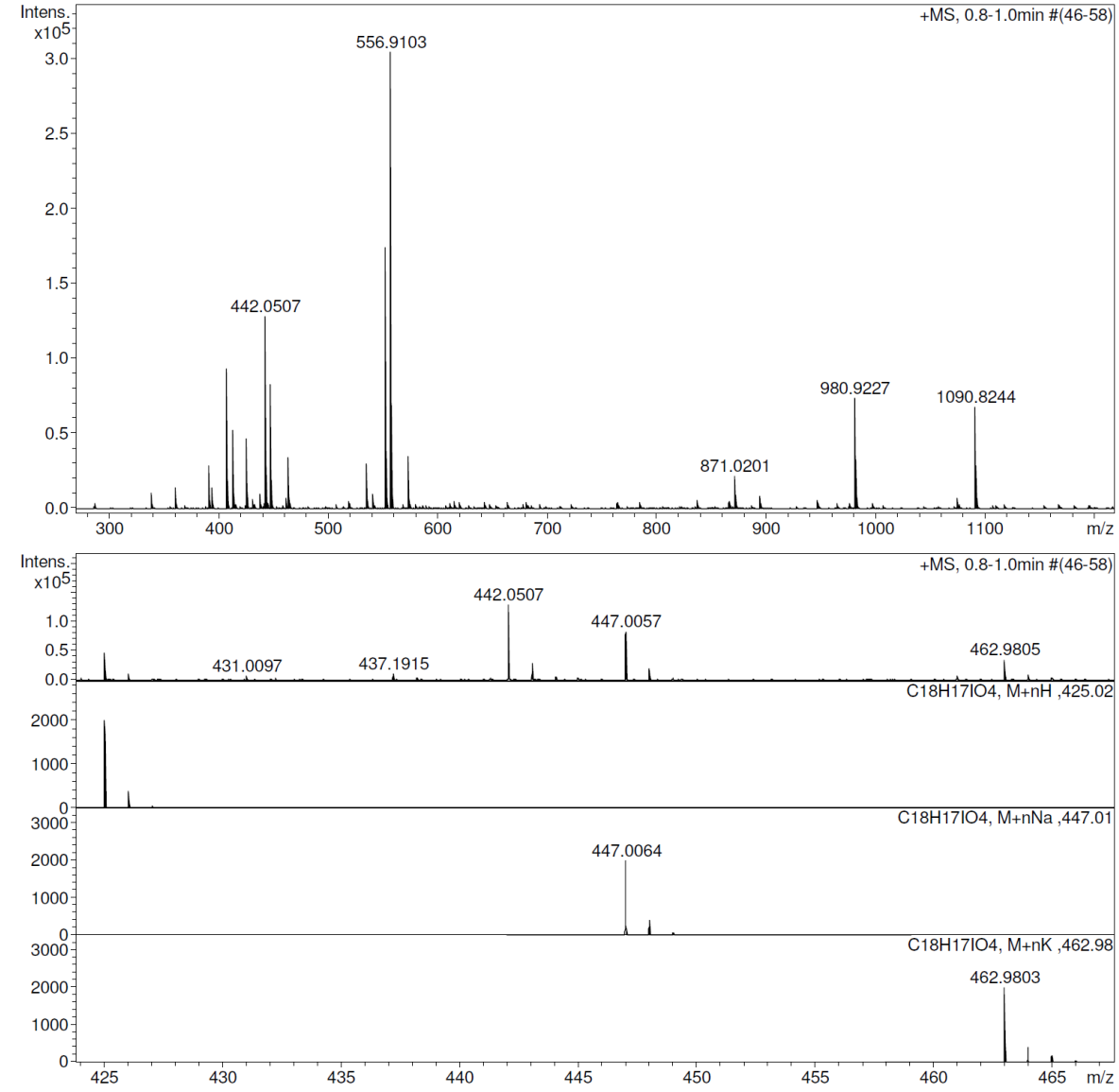
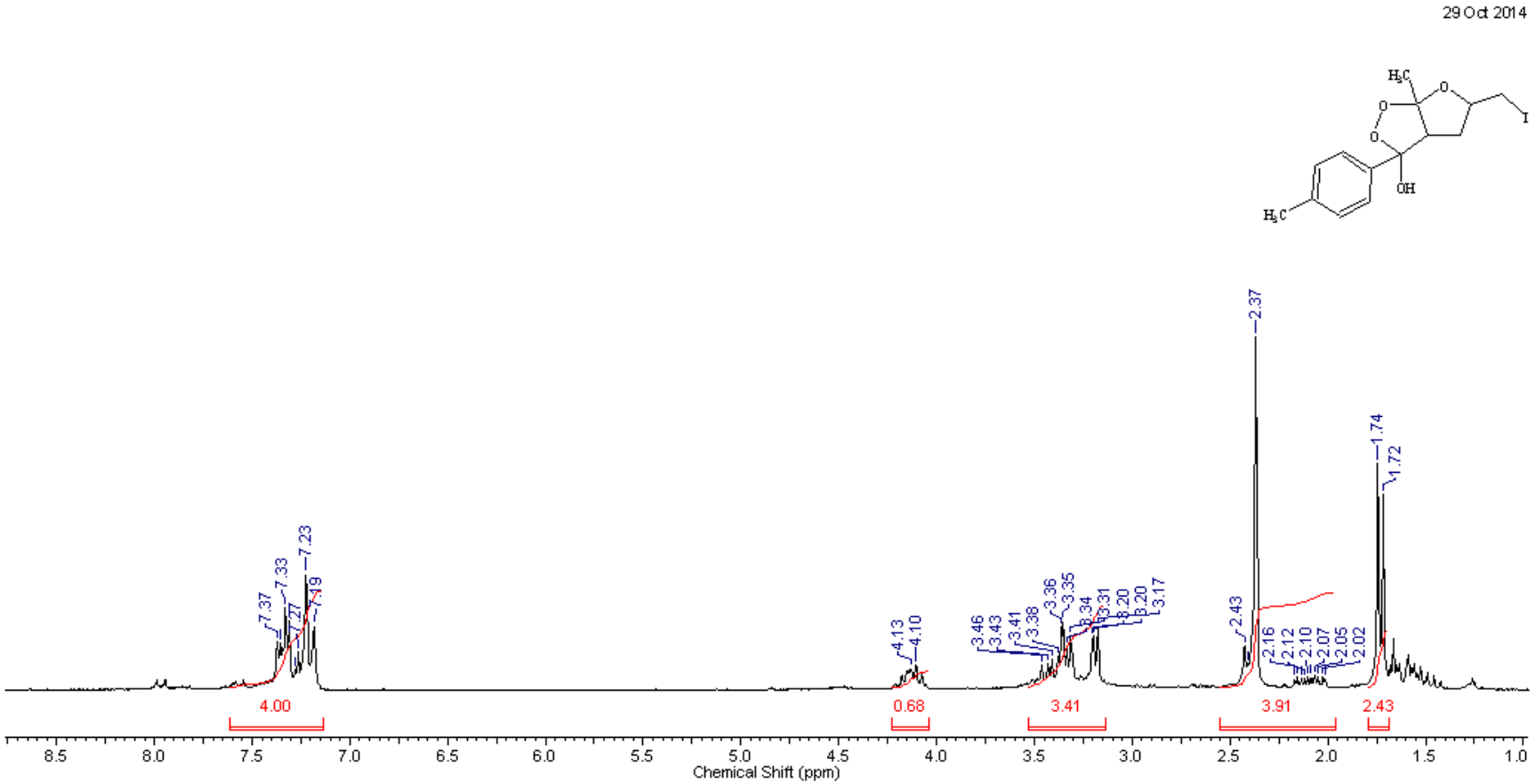
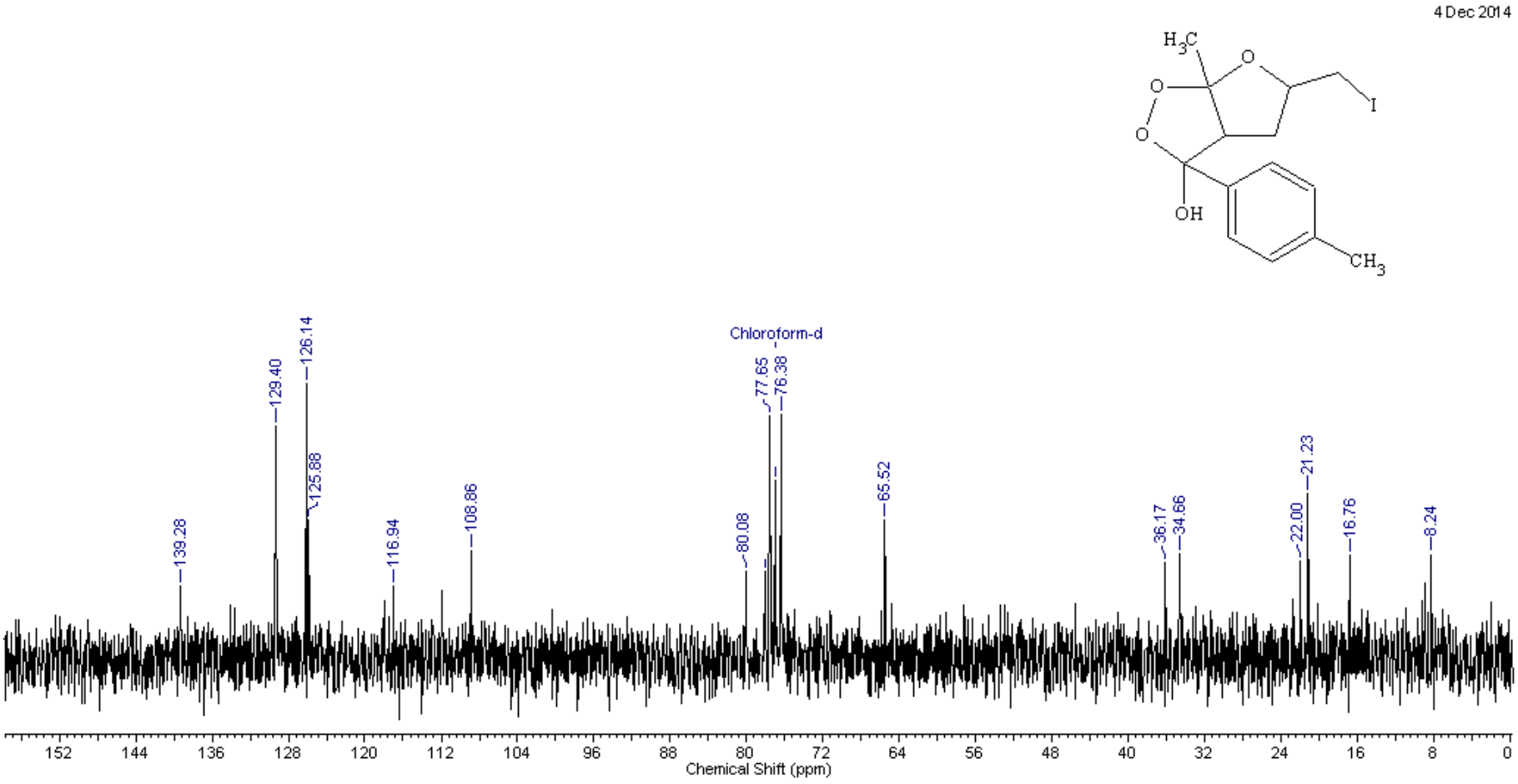


Bruker Compass DataAnalysis 4.0 printed: 20.11.2014 17:20:40 Page 1 of 1

^{1}H NMR of 5-iodomethyl-6a-methyl-3-(4-methylphenyl)tetrahydro-3*H*-furo[2,3-*c*][1,2]dioxol-3-ol, 2b+2'b



^{13}C NMR of 5-iodomethyl-6a-methyl-3-(4-methylphenyl)tetrahydro-3*H*-furo[2,3-*c*][1,2]dioxol-3-ol, 2b+2'b



HRMS-ESI of 5-iodomethyl-6a-methyl-3-(4-methylphenyl)tetrahydro-3*H*-furo[2,3-*c*][1,2]dioxol-3-ol, 2b+2'b

Display Report

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Comment	CH3CN 100 %, dil 200		

Acquisition Parameter

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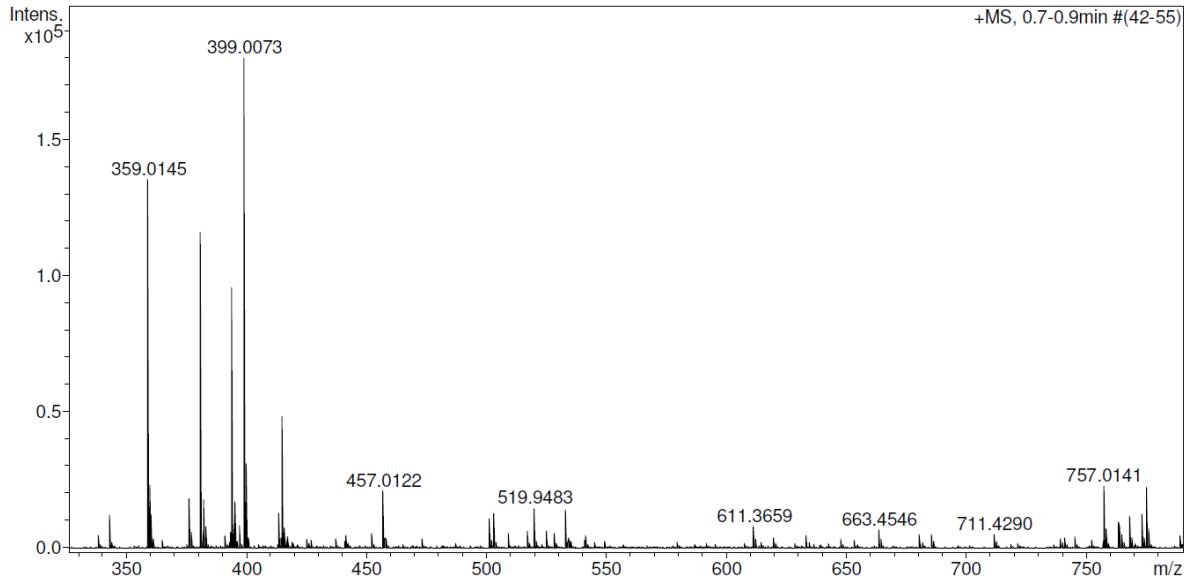
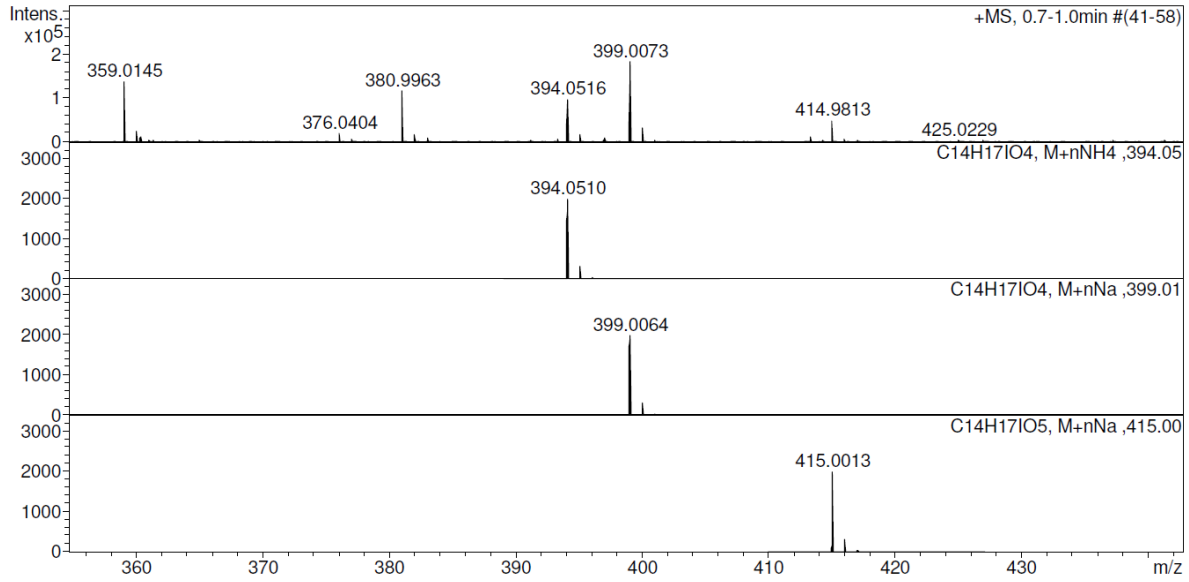
Scan End	3000 m/z	Set Collision Cell RF	1200.0 Vpp	Set Divert Valve	Waste





Crystallographic data of **2b**

Table S1. Crystal data for **2b**.

	rd91
empirical formula	$C_{14}H_{17}IO_4$
M_r	376.17
crystal size, mm^3	0.40 x 0.31 x 0.10
crystal form, color	block, colorless
crystal system	Monoclinic
space group	$P2_1/c$
unit cell dimensions:	
a, Å	10.890(5)
b, Å	12.115(5)
c, Å	11.686(4)
β, º	93.47(3)
volume, $Å^3$	1538.9(11)
Z	4
D_x, g cm^{-1}	1.624
m, mm^{-1}	16.423
no. reflections	2827/2682
collected/independent	[*R(int)* = 0.0403]
no. parameters	1677
GOF	1.045
final *R* indices [*I>2s(I)*]	*R* = 0.0779, *wR* = 0.2192

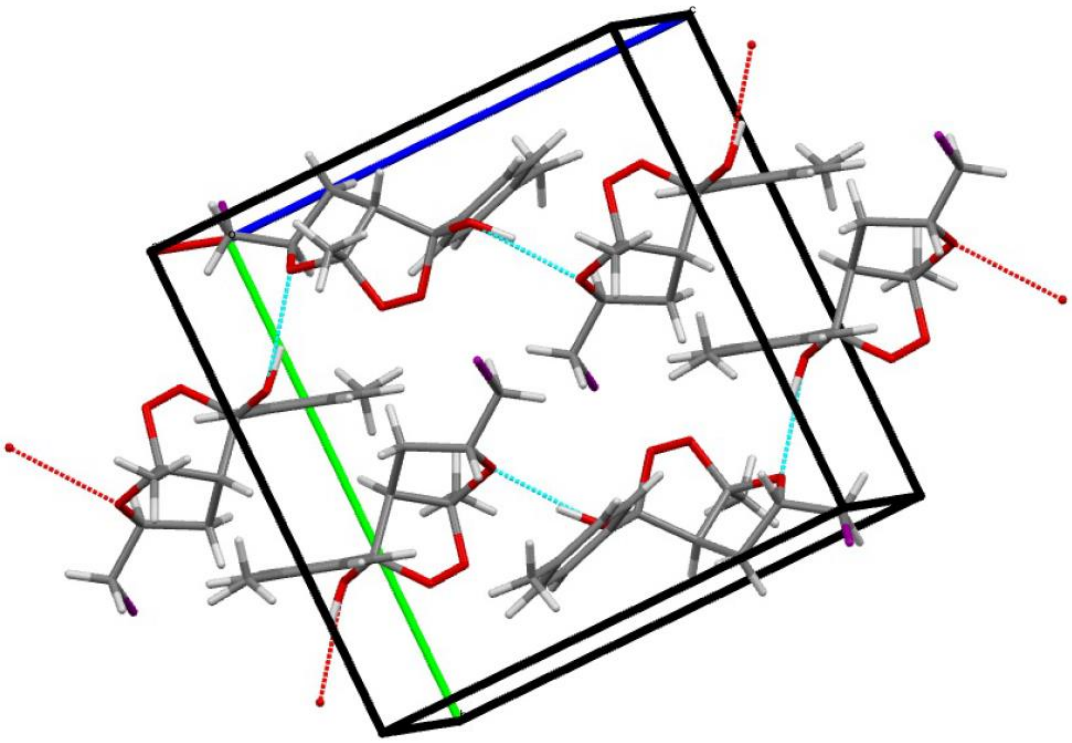
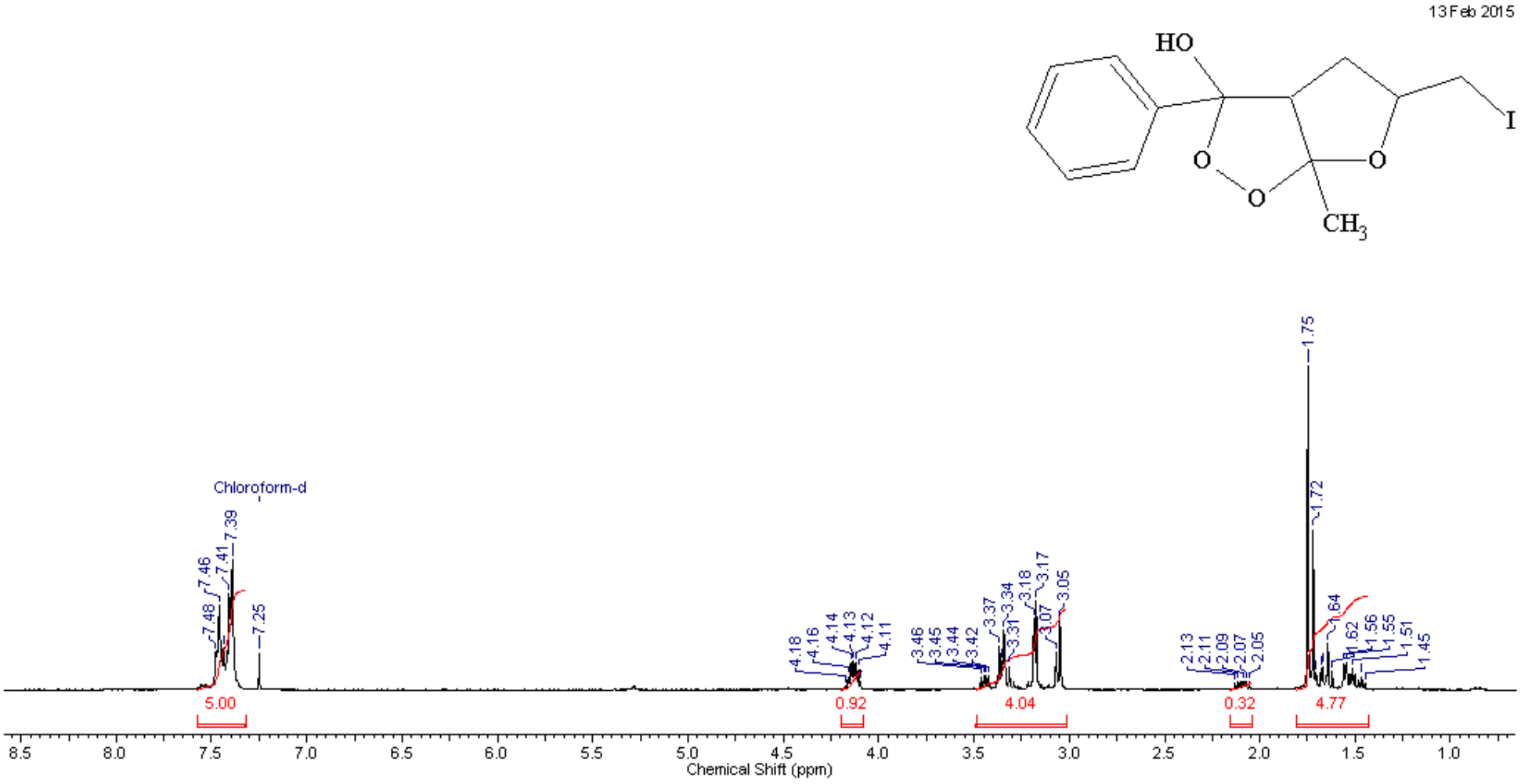
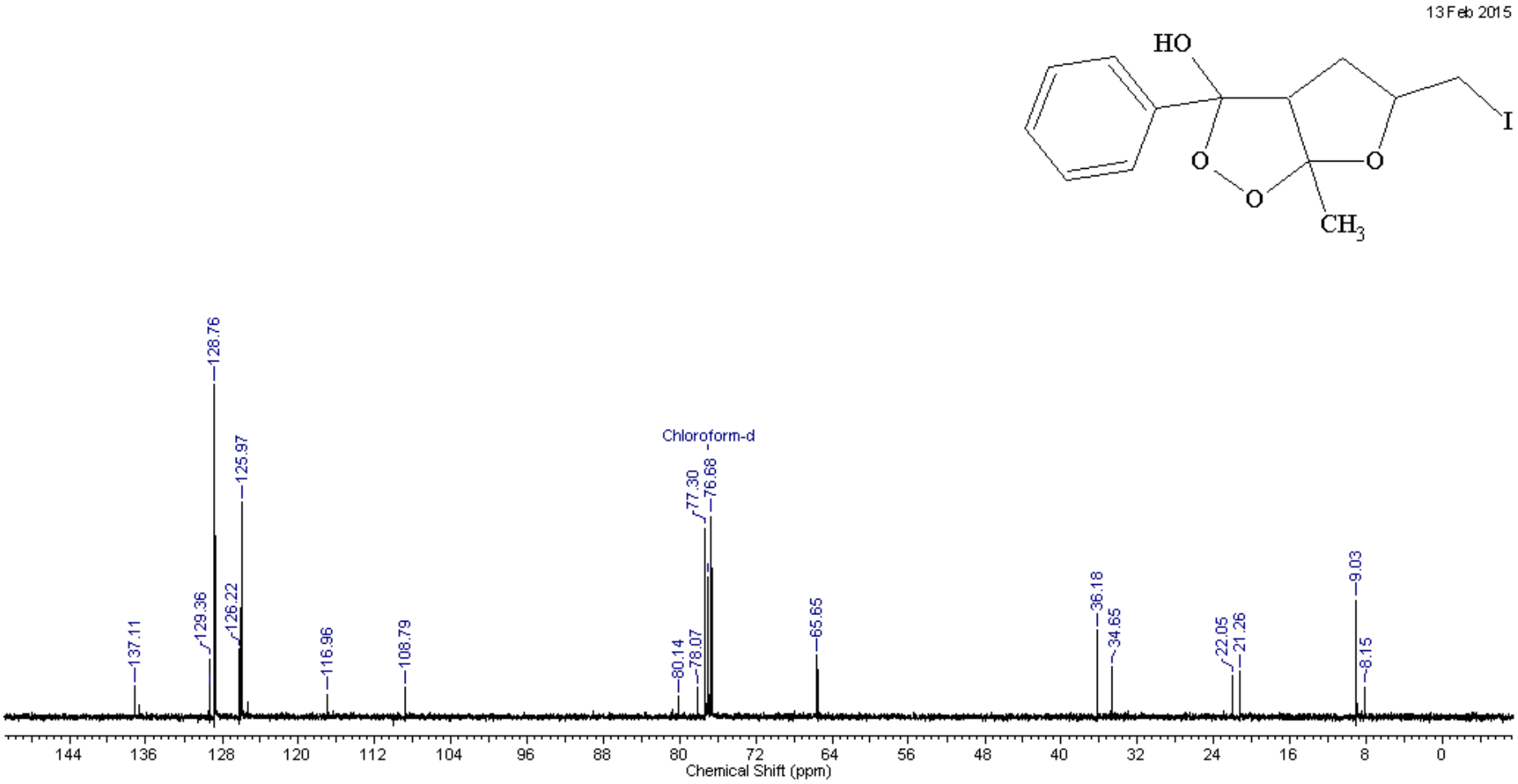


Figure S1 Packing of **2b**

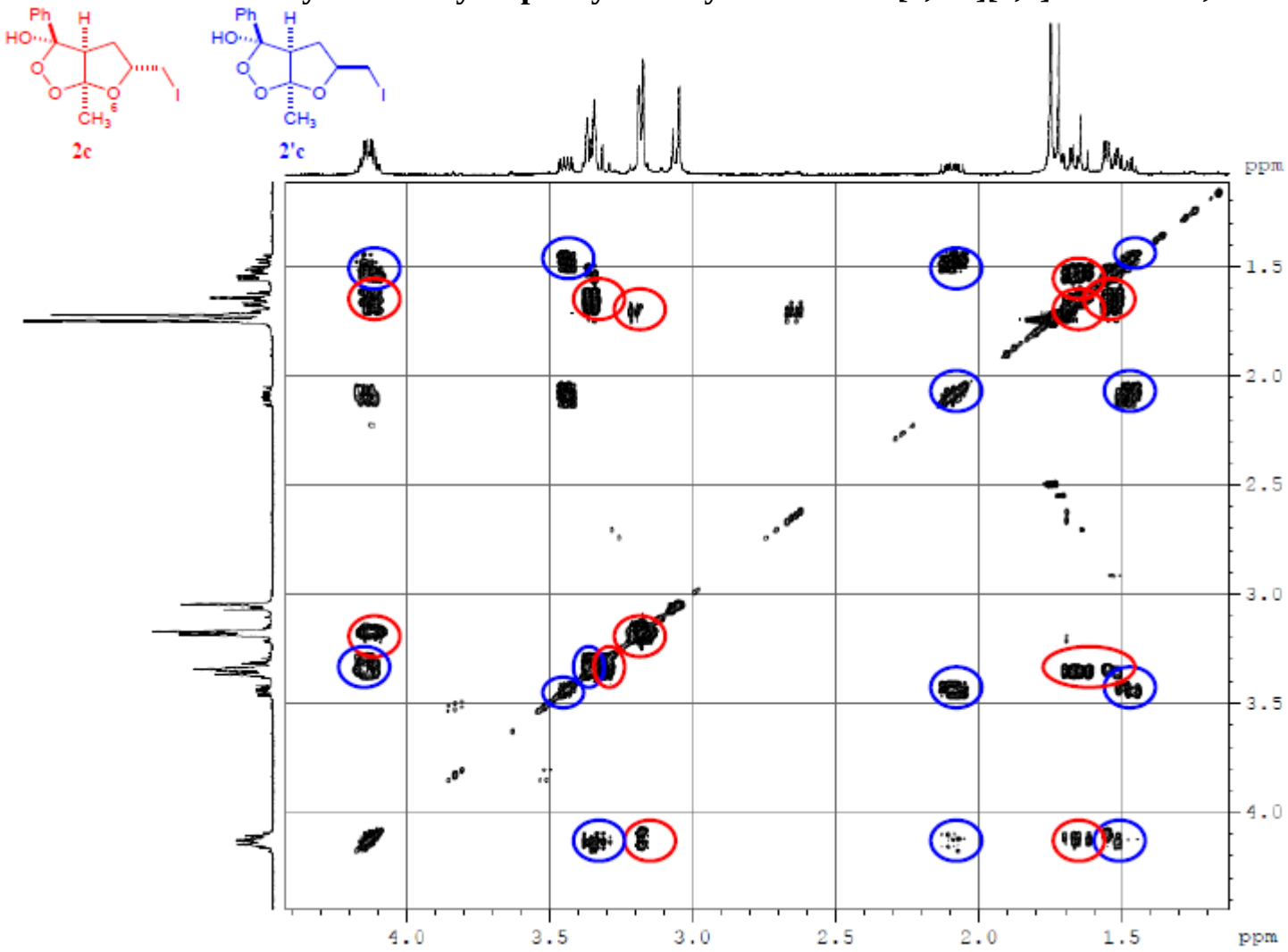
^{1}H NMR of 5-iodomethyl-6a-methyl-3-phenyltetrahydro-3*H*-furo[2,3-*c*][1,2]dioxol-3-ol, 2c+2'c



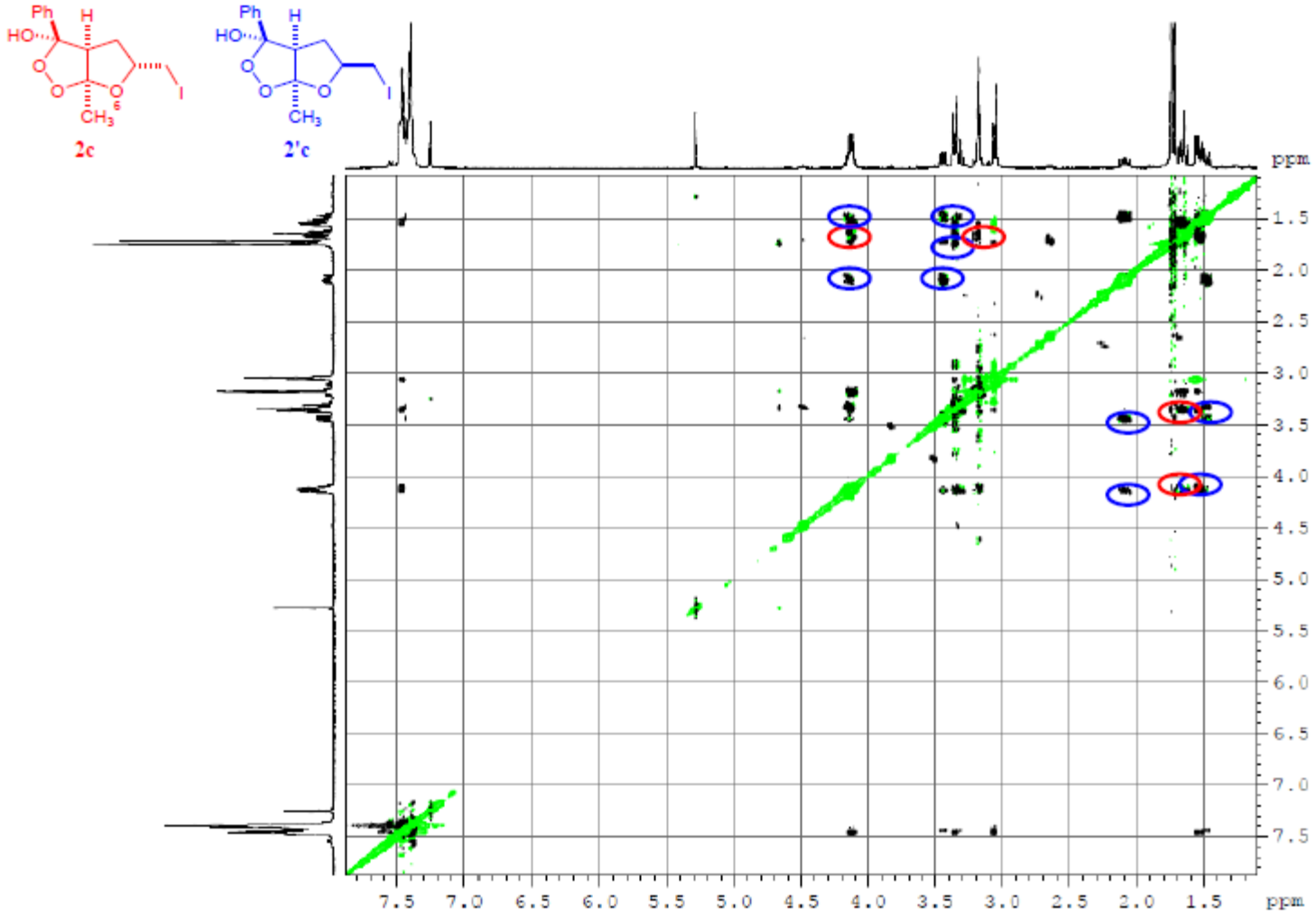
^{13}C NMR of 5-iodomethyl-6a-methyl-3-phenyltetrahydro-3*H*-furo[2,3-*c*][1,2]dioxol-3-ol, 2c+2'c



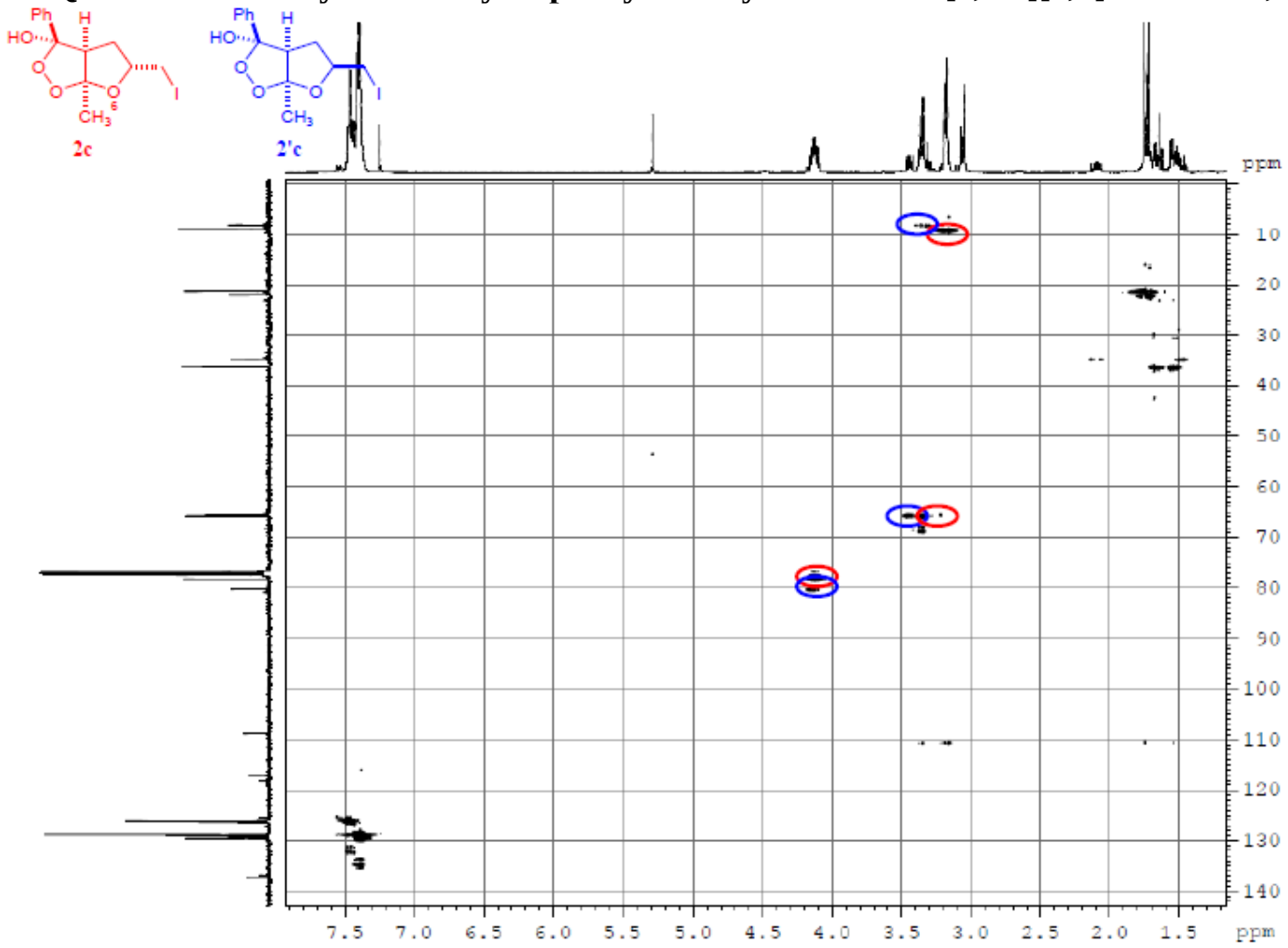
COSY of 5-iodomethyl-6a-methyl-3-phenyltetrahydro-3*H*-furo[2,3-*c*][1,2]dioxol-3-ol, 2c+2'c



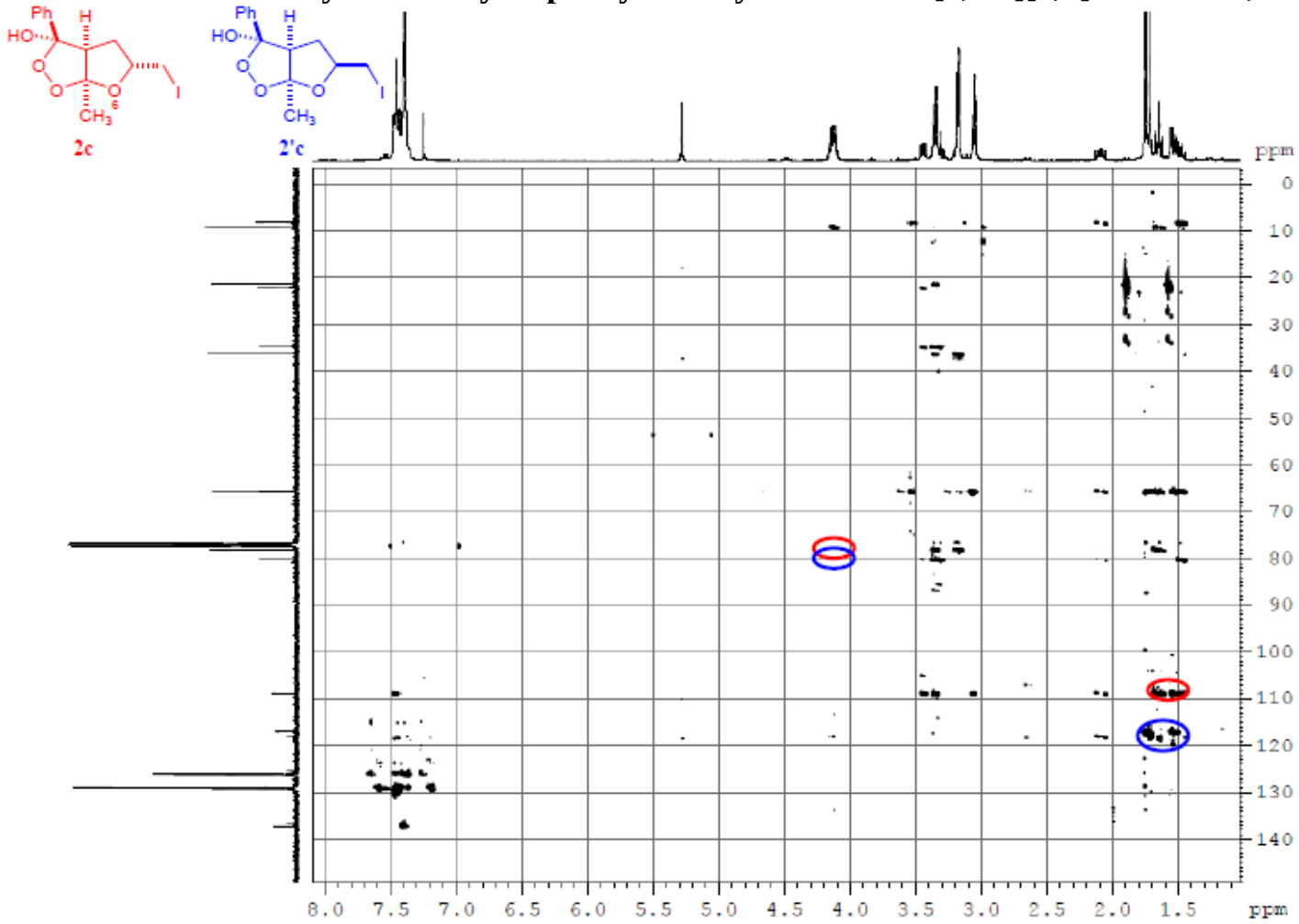
NOESY of 5-iodomethyl-6a-methyl-3-phenyltetrahydro-3*H*-furo[2,3-*c*][1,2]dioxol-3-ol, 2c+2'c



HSQC of 5-iodomethyl-6a-methyl-3-phenyltetrahydro-3*H*-furo[2,3-*c*][1,2]dioxol-3-ol, 2c+2'c



HMBC of 5-iodomethyl-6a-methyl-3-phenyltetrahydro-3*H*-furo[2,3-*c*][1,2]dioxol-3-ol, 2c+2'c



HRMS-ESI of 5-iodomethyl-6a-methyl-3-phenyltetrahydro-3*H*-furo[2,3-*c*][1,2]dioxol-3-ol, 2c+2'c

Display Report

Analysis Info

Analysis Name	D:\Data\Ivanova\RD-107.d	Acquisition Date	19.12.2014 18:02:22
Method	tune_wide.m	Operator	BDAL@DE
Sample Name	/TERN RD-107	Instrument	maXis 43
Comment	CH3CN 100%,dil 200		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	1200.0 Vpp	Set Divert Valve	Waste