ELECTRONIC SUPPLEMENTARY INFORMATION

The first structural and spectroscopic characterisation of a ring-opened form of a 2*H*-naphtho[1,2-*b*]pyran: a novel photomerocyanine

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Experimental Section - General

Unless otherwise stated, reagents were used as supplied by major chemical suppliers. ^{1}H (400 MHz and ^{13}C (100 MHz) NMR spectra (Bruker Avance) were recorded in either $CDCl_3$ or d_6-acetone. UV-Irradiation experiments for NMR investigations were performed using typical solution concentrations for NMR spectroscopy with irradiation using a Spectroline 8 Watt TLC inspection lamp at 365 nm with frequent manual agitation. FT-IR spectra were recorded on a Nicolet 380 FT-IR spectrophotometer equipped with a diamond ATR attachment (neat sample). Flash column chromatography was performed on chromatography silica gel (Sigma-Aldrich, 40-63 micron particle size distribution). All compounds were homogeneous by TLC using a range of eluent systems of differing polarity [Merck TLC aluminium sheets either silica gel 60 F254 (cat. No 105554) or neutral aluminium oxide 60 F254 (cat. No 105550)]. High resolution mass spectra were recorded under electrospray ionization using a linear ion trap mass spectrometer [Thermo Scientific LTQ Orbitrap XL Fourier transform mass spectrometer, EPRSC National Mass Spectrometry Service, Swansea]. UV-visible spectra were recorded in spectroscopic grade acetone solutions of the samples (10 mm pathlength quartz cuvette, PTFE capped, concentration ranges *ca*. 3×10^{-4} – 10^{-5} mol dm^{-3}) using an Agilent Technologies Cary 60 spectrophotometer equipped with a temperature controlled (20 ^{o}C) stirred cell. Irradiation of the stirred sample solutions was accomplished with a Spectroline 8 Watt TLC inspection lamp at 365 nm. 1,1-Bis(4-methoxyphenyl)prop-2-yn-1-ol **8a** was prepared according to literature procedures.[S1]

Experimental Section - DFT and TD-DFT modelling

All quantum mechanical simulations have been performed with the Gaussian09 program[S2] using the PBE0 hybrid functional,[S3] and improving the DFT integration grid to *ultrafine* [a pruned (99,590) grid]. First geometry optimizations in acetone have been performed using the PCM (Polarizable Continuum Model) solvent model,[S4] and the 6-31G(d) atomic basis set. In the second step, vibrational calculations were used to establish that the optimized structures corresponded to true minima of the potential energy surface. In the third stage, the first ten lowest-lying singlet excited-states have been determined within the vertical PCM-TD-DFT (Time-Dependent Density Functional Theory) approximation using the 6-31+G(d) atomic basis set and the PBE0 functional. In a fourth stage, the NMR chemical shifts have been obtained by computing shieldings for the investigated molecules and reference (TMS), at the PCM-PBE0/cc-pVTZ level of theory. In addition, we have also determined the optimal geometry and the vibrational frequencies for the first excited-states of **10** and **11**. This allowed to compute vibronic couplings within the FC approximation, with the FC Classes code of Santoro and co-workers,[S5] and hence to determine more

rigorously the relative absorption intensities of the two species. During the FC Classes calculations, the maximal number of integrals was increased to 10^{12}, the other parameters being kept to their default values.

References

S1 C. D. Gabbutt, B. M. Heron, A. C. Instone, D. A. Thomas, S. M. Partington, M. B. Hursthouse, T. Gelbrich, *Eur. J. Org. Chem.*, **2003**, 1220.

S2 Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2009**.

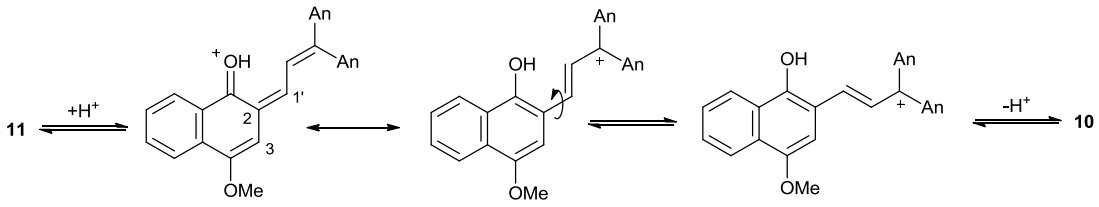
S3 C. Adamo, V. Barone, V. *J. Chem. Phys.* 1999, **110**, 6158.

S4 J. Tomasi, B. Mennucci, R. Cammi, *Chem. Rev.* 2005, **105**, 2999.

S5 See F. J. Avila Ferrer, J. Cerezo, E. Stendardo, R. Improta, F. Santoro, *J. Chem. Theory Comput.* 2013, **9**, 2072 and references therein.

A comment on the acid-mediated isomerization of 11 → 10

Protonation of the carbonyl group in **11** induces polarization in the dienone system. Concomitant reduction in the C1′-C2 bond order facilitates rotational isomerization to the less hindered (*E*)-isomer **10** (Scheme ESI-1)



Scheme ESI-1

Characterisation data for the photochromic response of pyran 9

Table ESI-1

	λ_{max} (nm)[a]	A_o[b]	A_t[c]	Δ_{OD}[d]	K (min^{-1})[e]	$t_{½}$ (min)[f]
9	496	0.033	0.647	0.614	0.0164	42.3

Footnotes: [a] λ_{max} = wavelength of maximum absorption after 2700 s of UV-irradiation in acetone solution at 20 °C; [b] A_o = absorbance before UV-irradiation; [c] A_t = absorbance post UV-irradiation for 2700 s; [d] Δ_{OD} = difference in absorbance (Optical Density) between A_o and A_t; [e] K = fading rate constant at 20 °C; [f] $t_{½}$ = time taken for the absorbance value to fall to half of A_t.

The above data is presented in accord with such characterisation data reported by other authors for the characterisation of the photochromic response of diaryl substituted naphthopytrans.[1]

1. See for example: (a) C. M. Sousa, J. Berthet, S. Delbaere, P. J. Coelho, *J. Org. Chem*., 2013, **78**, 6956; (b) C. M. Sousa, J. Berthet, S. Delbaere, P. J. Coelho, *J. Org. Chem*., 2012, **77**, 3959; (c) K. Guo, Y. Chen, *J. Mater. Chem.*, 2010, **20**, 4193; (d) N. Malic, J. A. Campbell, R. A. Evans, *Macromolecules*, 2008, **41**, 1206; (e) W. Zhao, E. M. Carreira, *Org. Lett*., 2006, **8**, 99; (f) M. Zayat, D. Levy, *J. Mater. Chem*., 2003, **13**, 727.

Experimental method for the preparation of photochromic naphthopyrans

A solution of 4-methoxynaphthol (1.0g, 5.75 mmol) and the requisite 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol (1 mole equiv.), in the presence of pyridinium *p*-toluenesulfonate (PPTS) (75 mg, 0.30 mmol) and trimethyl orthoformate (1.22 g, 11.5 mmol) in 1,2-dichloroethane (50 mL), was heated under reflux for up to 4 h (the reaction time being determined by TLC examination of the reaction mixture). The cooled solvent was removed under vacuum to afford a brown gum that was either purified by flash column chromatography or by crystallisation. The following compounds were obtained in this manner:

6-Methoxy-2,2-bis(4-methoxyphenyl)-2*H*-naphtho[1,2-*b*]pyran 9 from 4-methoxy-1-naphthol and 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol (fraction 1) as a pale pink 'fluffy' solid (894 mg, 36.7 %) after column chromatography using 20 % EtOAc in hexane, mp = 116 – 118 ^{o}C; ν_{max} 3001, 2962, 2836, 1607, 1509, 1458, 1388, 1271, 1248, 1215, 1175, 1161, 1101, 1059, 1031, 989, 971, 828, 662, 555 cm^{-1}; δ_H (d_6-acetone) 3.69 (6H, s, OMe), 3.90 (3H, s, OMe), 6.31 (1H, d, *J* = 9.6 Hz, 3-H), 6.69 (1H, s, 5-H), 6.77 (1H, d, *J* = 9.6 Hz, 4-H), 6.84 (4H, d, *J* = 8.6 Hz, Ar-H), 7.45 (5H, m, Ar-H), 7.54 (1H, m, Ar-H), 8.13 (1H, d, *J* = 8.3 Hz, 7-H), 8.33 (1H, d, *J* = 8.3 Hz, 10-H); δ_C (d_6-acetone) 54.60, 55.17, 82.21, 102.47, 113.32, 115.81, 121.52, 121.94, 123.92, 125.57, 125.60, 126.14, 126.33, 127.92, 128.97, 137.55, 141.31, 149.60, 159.00. (Found M+H$^+$, 425.1747; $C_{28}H_{24}O_4$ requires M+H$^+$, 425.1747). Fraction 2, **(*E*)-2-(3′,3′-bis(4-methoxyphenyl)allylidene)-4-methoxynaphthalen-1(2*H*)-one 10** as deep maroon, lustrous microcrystals (290 mg, 11.9 %), mp = 174 – 176 ^{o}C; ν_{max} 2932, 2834, 1641, 1602, 1589, 1527, 1505, 1373, 1287, 1241, 1176, 1021, 908, 833, 770, 700, 560 cm^{-1}; δ_H (d_6-acetone) 3.84 (3H, s, OMe), 3.90 (3H, s, OMe), 4.02 (3H, s, 4-OMe), 6.82 (1H, s, 3-H), 6.94 (2H, d, *J* = 8.8 Hz, Ar-H), 7.05 (2H, d, *J* = 8.6 Hz, Ar-H), 7.21 (2H, d, *J* = 8.6 Hz, Ar-H), 7.38 (3H, m, Ar-H, 2′-H), 7.48 (1H, m, Ar-H), 7.55 (1H, d, *J* = 12.7 Hz, 1′-H), 7.68 (1H, m, Ar-H), 7.85 (1H, d, *J* = 7.9 Hz, 5-H), 8.10 (1H, d, *J* = 7.7 Hz, 8-H); δ_H ($CDCl_3$) 3.85 (3H, s, OMe), 3.88 (3H, s, OMe), 3.97 (3H, s, 4-OMe), 6.45 (1H, s, 3-H), 6.90 (2H, d, *J* = 8.5 Hz, Ar-H), 6.96 (2H, d, *J* = 8.4 Hz, Ar-H), 7.11 (1H, d, *J* = 12.6 Hz, 2′-H), 7.22 (2H, d, *J* = 8.4 Hz, Ar-H), 7.36 (2H, d, *J* = 8.5 Hz, Ar-H), 7.41 (1H, m, Ar-H), 7.61 (1H, m, Ar-H), 7.66 (1H, d, *J* = 12.6 Hz, 1′-H), 7.85 (1H, d, *J* = 7.9 Hz, 5-H), 8.21 (1H, d, *J* = 7.7 Hz, 8-H); δ_C (d_6-acetone) 54.80, 54.85, 55.14, 97.17, 113.72, 113.81, 120.85, 122.56, 126.91, 128.18, 130.02, 130.04, 131.38, 131.72, 132.30, 133.03, 134.04, 134.60, 134.90, 150.31, 152.36, 160.19, 160.69, 183.01. (Found M+H$^+$, 425.1747; $C_{28}H_{24}O_4$ requires M+H$^+$, 425.1747).

6-Methoxy-2,2-bis(4-methoxyphenyl)-4-(4-methylphenyl)-2*H*-naphtho[1,2-*b*]pyran 12 from 4-methoxy-1-naphthol and 1,1-bis(4-methoxyphenyl)-3-(4-methylphenyl)prop-2-yn-1-ol (fraction 1) as pale fawn fluffy solid, (2.04 g, 69.2 %) after crystallisation twice from hexane and EtOAc, mp = 197 – 199 ^{o}C; ν_{max} 2980, 1607, 1508, 1350, 1249, 1173, 1037, 877, 827, 770, 696 cm^{-1}; δ_H ($CDCl_3$) 2.43 (3H, s, tolyl-Me), 3.76 (6H, s, OMe), 3.77 (3H, s, OMe), 6.13 (1H, s, 3-H), 6.54 (1H, s, 5-H), 6.82 (4H, d, *J* = 8.3 Hz, Ar-H), 7.24 (2H, d, *J* = 7.8 Hz, tolyl-H), 7.42 (2H, d, *J* = 7.8 Hz, tolyl-H), 7.50 (6H, m, Ar-H, 8-H, 9-H), 8.12 (1H, d, *J* = 8.3 Hz, 7-H), 8.37 (1H, d, *J* = 8.3 Hz, 10-H); δ_C ($CDCl_3$) 21.31, 55.21, 55.67, 81.97, 101.72, 113.36, 116.40, 121.89, 122.17, 125.84, 125.89, 126.20, 126.23, 126.62, 128.19, 128.72, 129.12, 135.59, 136.49, 137.56, 137.74, 142.40, 149.08, 158.78. (Found M+H$^+$, 515.2209; $C_{35}H_{30}O_4$ requires M+H$^+$, 515.2217). Column chromatography (25% EtOAc in hexane) of the liquors from the first crystallisation gave fraction 1, further **12** (300 mg, 10.2 %) identical in all aspects to the foregoing material and fraction 2, **1,1-bis(4-methoxyphenyl)-3-(4-methylphenyl)prop-2-enone 13** as deep yellow micro-crystals (180 mg, 8.7 %), mp = 93 – 95 ^{o}C; ν_{max} 2933, 2836, 1654, 1603, 1506, 1461, 1289, 1244, 1172, 1112, 1029, 827, 753, 575, 549 cm^{-1}; δ_H ($CDCl_3$) 2.39 (3H, s, Me), 3.80 (3H, s, OMe), 3.85 (3H, s, OMe), 6.81 (2H, d, *J* = 8.3 Hz, Ar-H), 6.89 (2H, d, *J* = 8.4 Hz, Ar-H), 7.01 (1H, s, 2-H), 7.13 (2H, d, *J* = 8.3 Hz, Ar-H), 7.19 (2H, d, *J* = 7.8 Hz, tolyl-H), 7.34 (2H, d, *J* = 8.4 Hz, Ar-H), 7.84 (2H, d, *J* = 7.8 Hz, tolyl-H); δ_C ($CDCl_3$) 21.67, 55.20, 55.41, 113.44, 113.79, 121.63, 128.84, 129.09, 130.29, 131.43, 131.59, 134.41, 136.23, 143.21, 154.51, 159.79, 160.72, 192.09. (Found [M+H]$^+$ = 359.1636 $C_{24}H_{22}O_3$ requires [M+H]$^+$ = 359.1642).

Preparation of 1,1-bis(4-methoxyphenyl)-3-(4-methylphenyl)prop-2-yn-1-ol 8b

n-BuLi (2.5 M in hexanes, 41.4 mmol, 16.6 mL) was added slowly to a cold (0 ^{o}C) stirred solution of 4-ethynyltoluene (39.4 mmol, 4.58 g) in anhydrous THF (150 mL) under nitrogen. Upon completion of the addition, the cold solution was stirred for 30 min and then 4,4-dimethoxybenzophenone (35.8 mmol, 8.68 g) was added in a single portion and the mixture stirred until none of the benzophenone could be detected by TLC examination of the reaction mixture (~2h). The resulting mixture was poured into water (250 mL) containing brine (30 mL) and the organic layer was separated and the aqueous layer extracted with EtOAc (3 × 50 mL). The organic extracts were combined and washed with water (2 × 100 mL) and dried over anhyd. Na_2SO_4. Removal of the solvent afforded the *1,1-bis(4-methoxyphenyl)-3-(4-methylphenyl)prop-2-yn-1-ol* **8b** (12.1 g, 94 %) as a very viscous pale yellow oil, ν_{max} 3450, 2952, 2835, 1606, 1584, 1505, 1461, 1301, 1243, 1168, 1031, 986, 899, 8115, 742, 587, 526 cm^{-1}; δ_H ($CDCl_3$) 2.38 (3H, s, Me), 3.28 (1H, s, OH (D_2O exchangeable)), 3.80 (6H, s, OMe), 6.90 (4H, m, Ar-H), 7.15 (2H, d, J = 7.88 Hz, tolyl-H), 7.42 (2H, m, tolyl-H), 7.62 (4H, m, Ar-H); δ_C ($CDCl_3$) 21.56, 55.31. 74.18, 86.95, 91.65, 113.56, 119.58, 127.47, 129.13, 131.70, 137.85, 138.74, 158.98. Found $[M\text{-}H_2O+H]^+$ = 341.1532 $C_{24}H_{22}O_3$ requires $[M\text{-}H_2O+H]^+$ = 341.1536. This material was used directly for the preparation of naphthopyran **13**.

Figure S1 ^{1}H NMR spectrum of compound **8b** in commercial $CDCl_3$

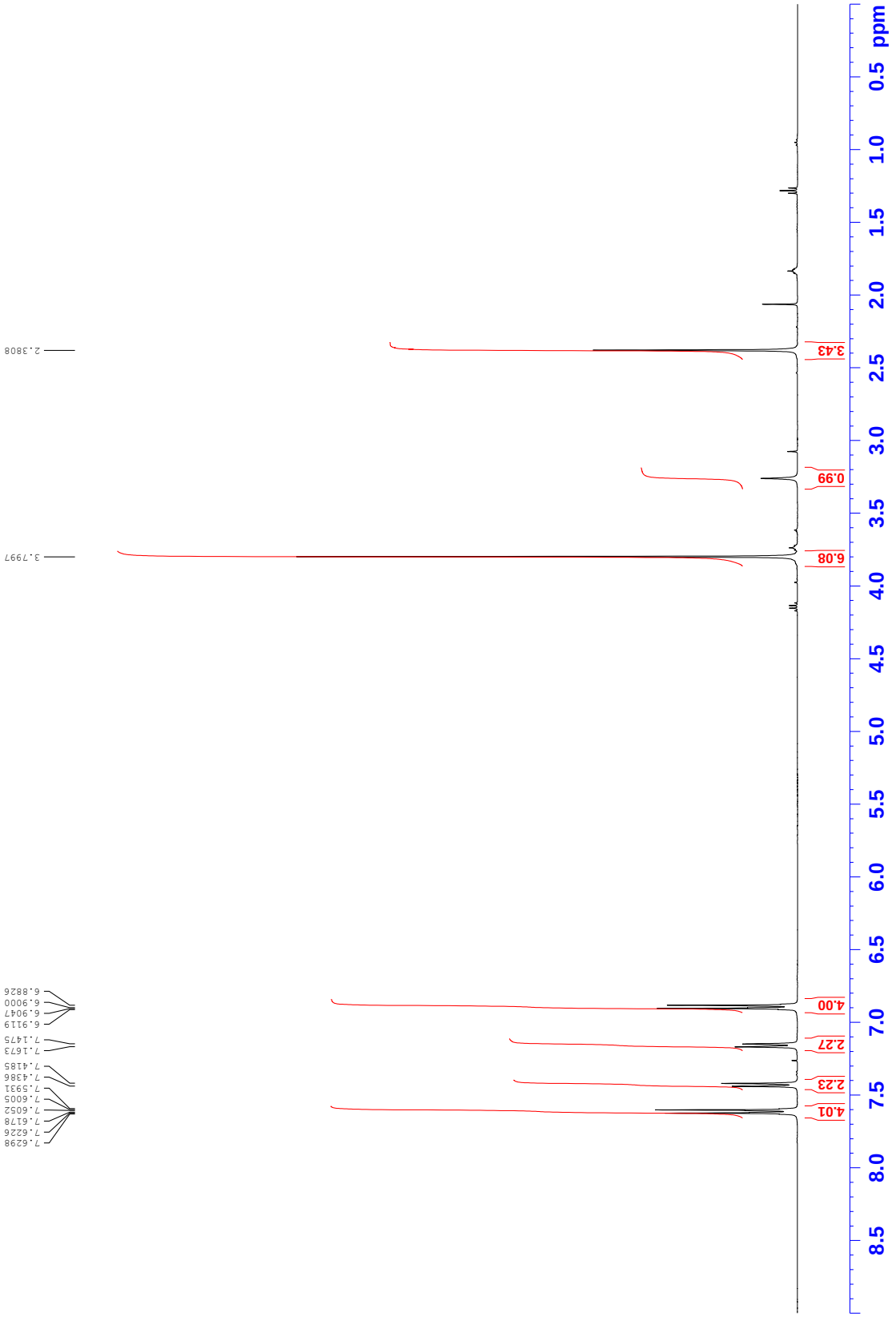
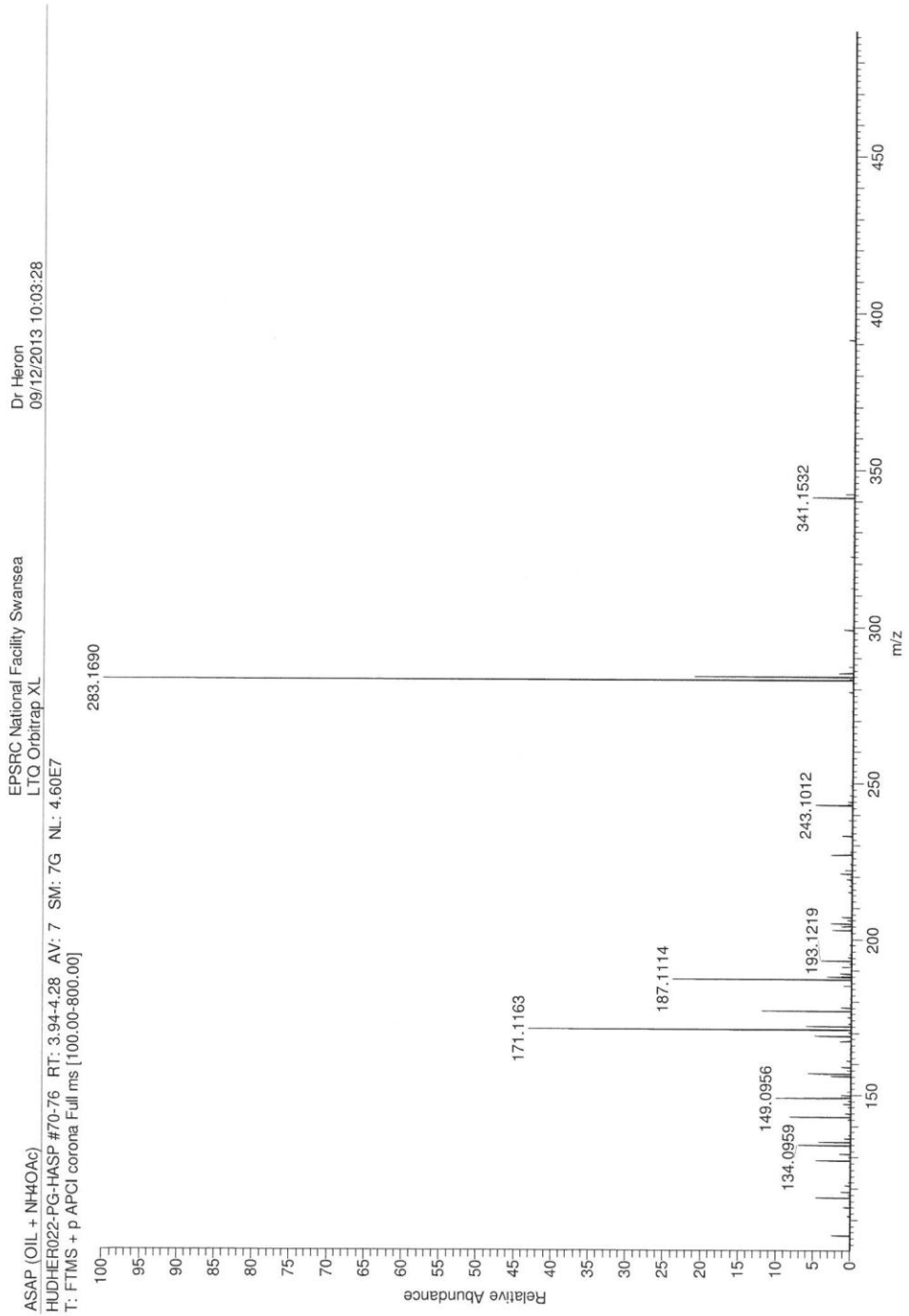
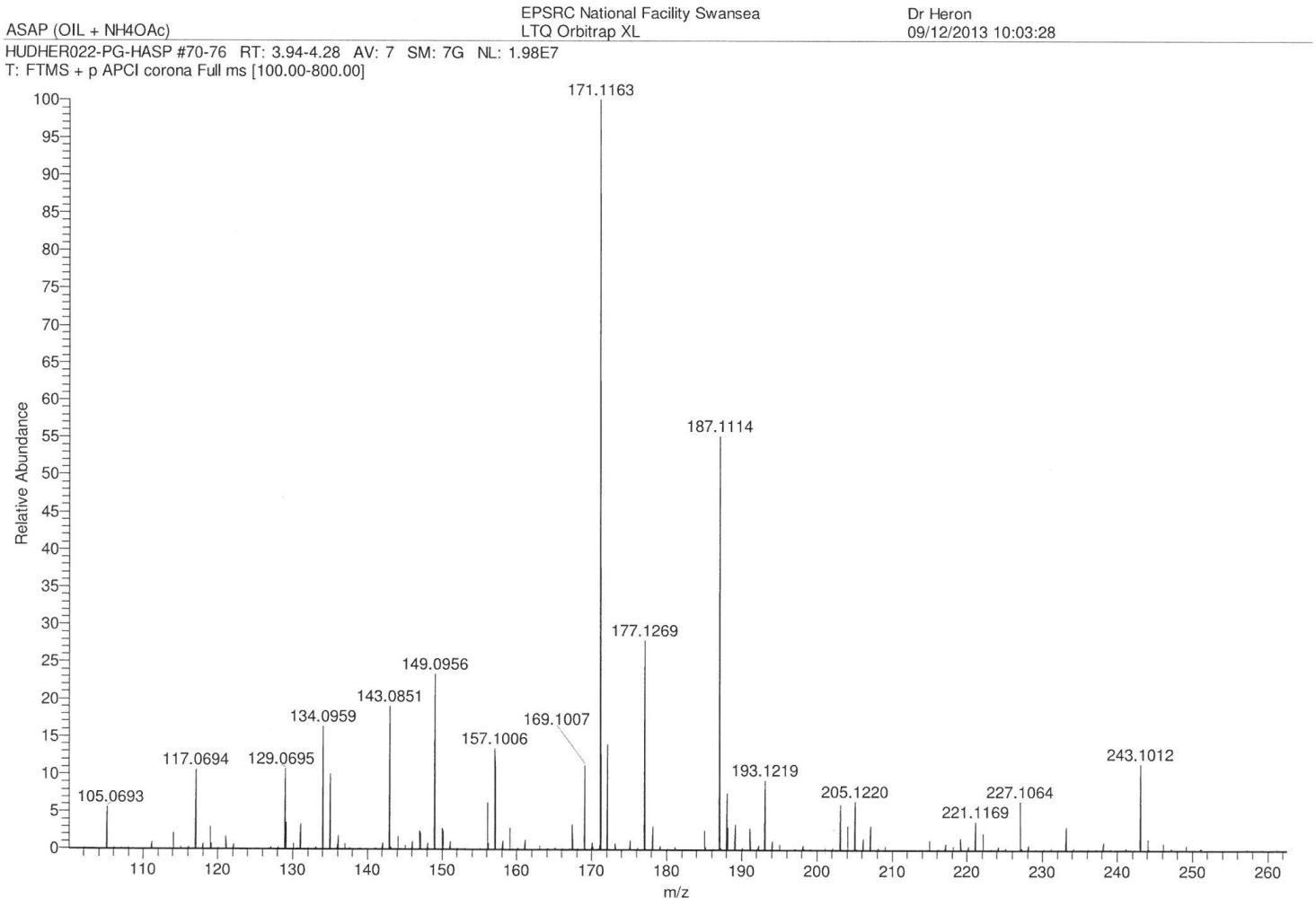


Figure S2 ^{13}C NMR spectrum of compound **8b** in commercial $CDCl_3$

Figure S3 Mass Spectral data for compound **8b**

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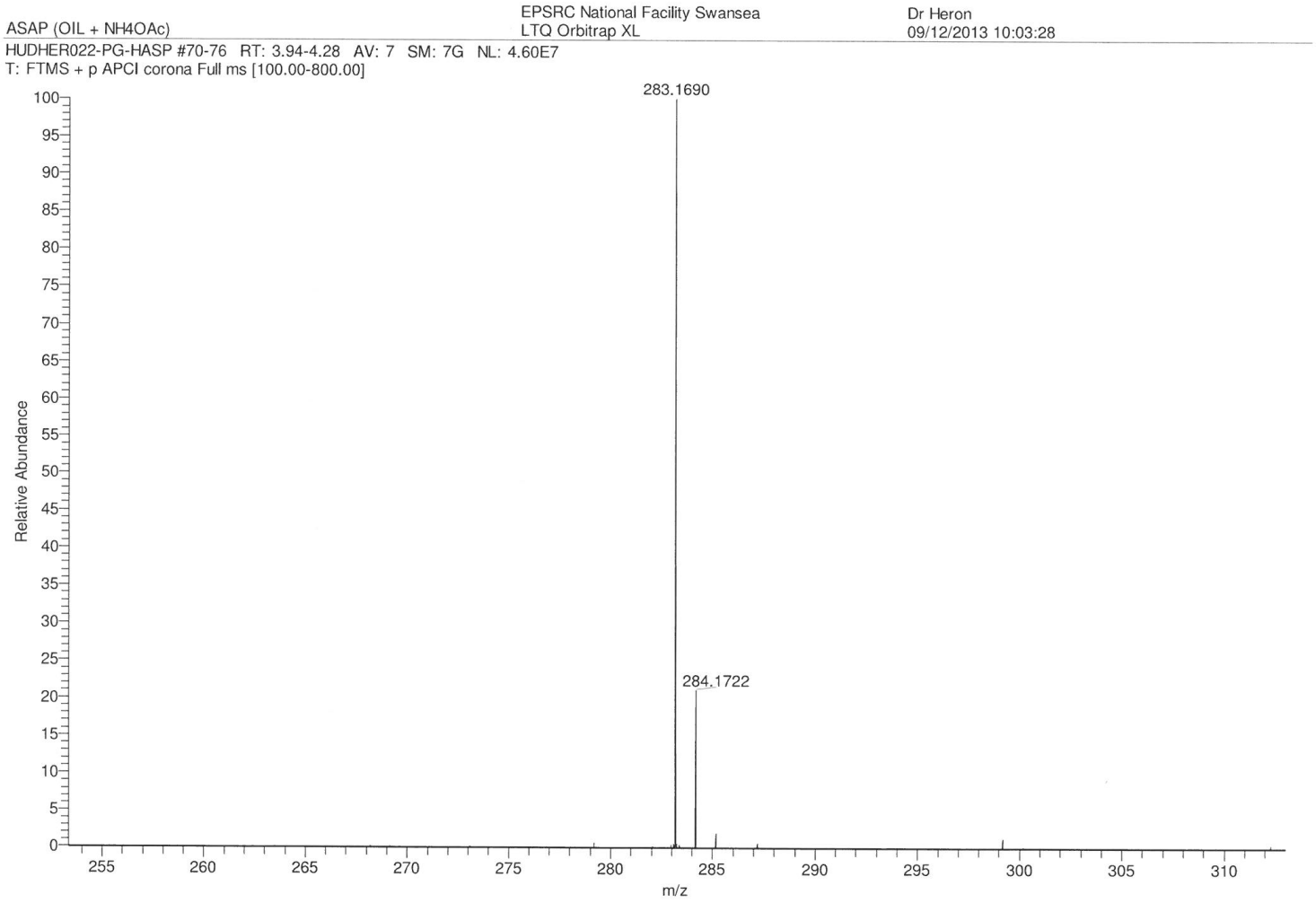
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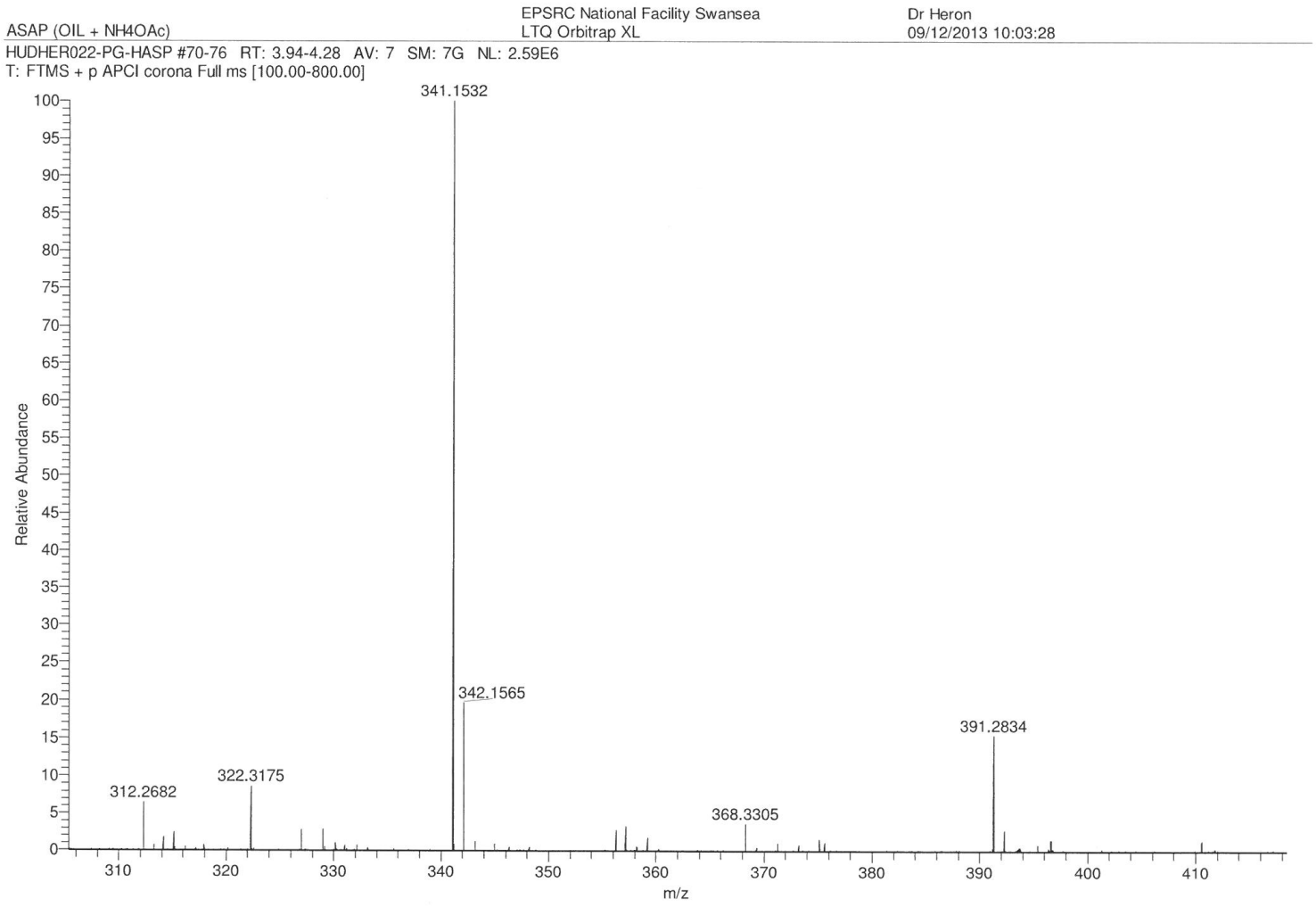
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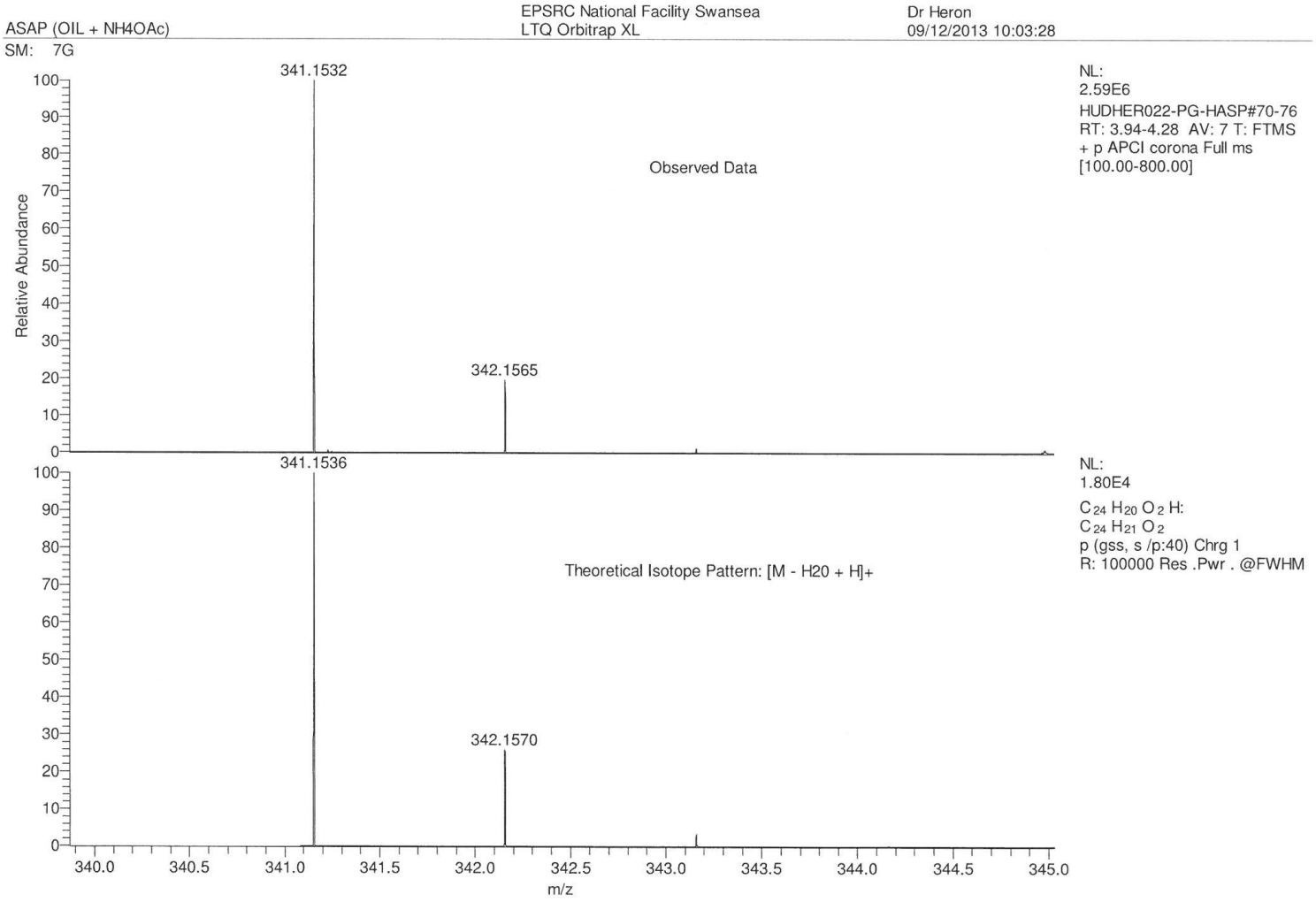
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344.5
345.0

Isotope:	Min. .. Max.		
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16 O	0....10		
12 C	0....60		
1 H	0....70		
23 Na	0....0		
Tolerance Window:	+- 5.00 ppm		
Db/Ring Equiv:	-3.. 100	N-Rule:	Do not use
Fits:	200	Charge:	1

Mass	Theoretical Mass	Delta [ppm]	RDB	Composition
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	341.1528	1.3	2.5	$C_8 H_{21} O_7 N_8$
	341.1541	-2.7	2.0	$C_{10} H_{23} O_8 N_5$
	341.1523	2.7	15.0	$C_{22} H_{19} O_1 N_3$

Figure S4 ^{1}H NMR spectrum of compound **9** in d_6-acetone

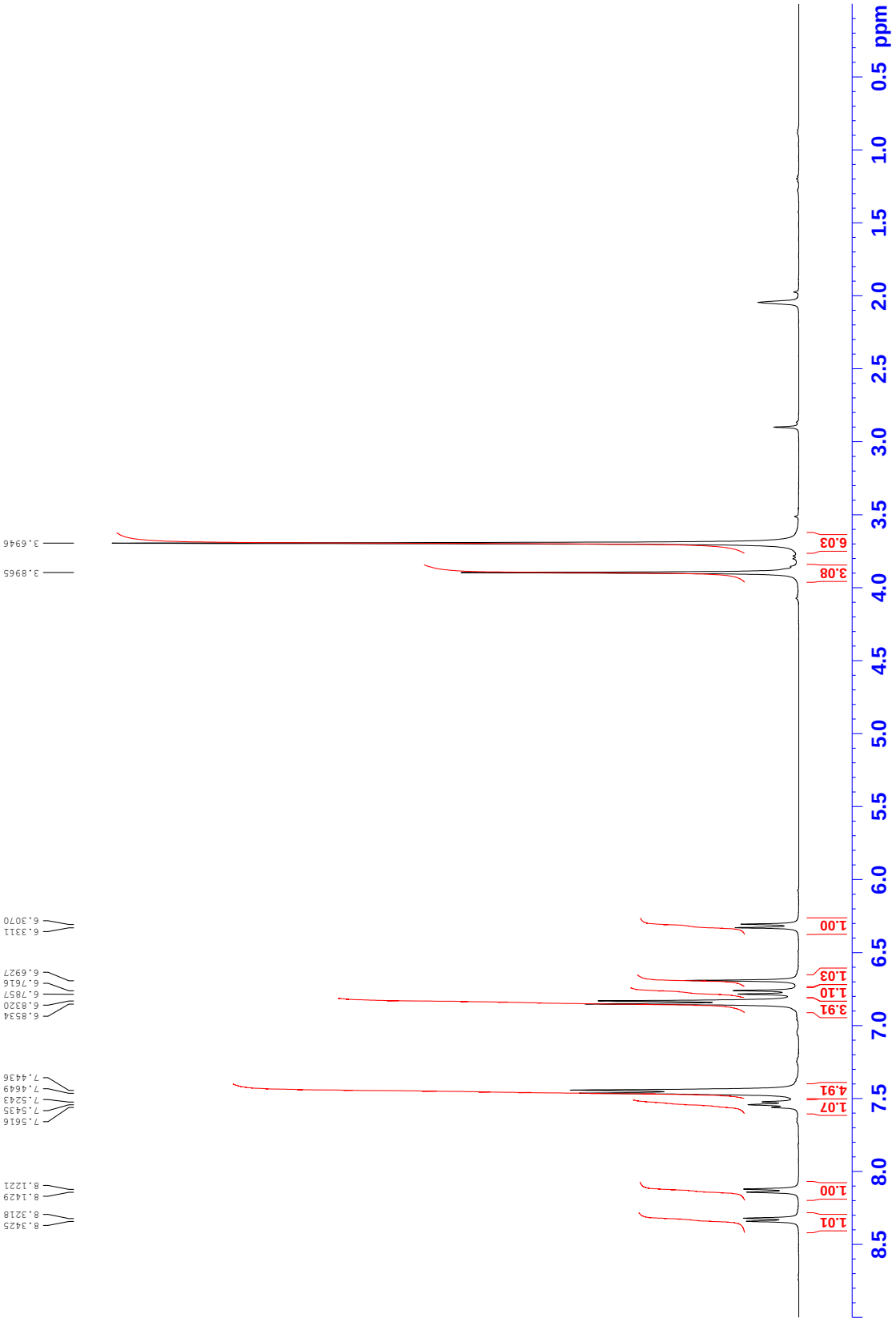


Figure S5 ^{13}C NMR spectrum of compound **9** in d_6-acetone

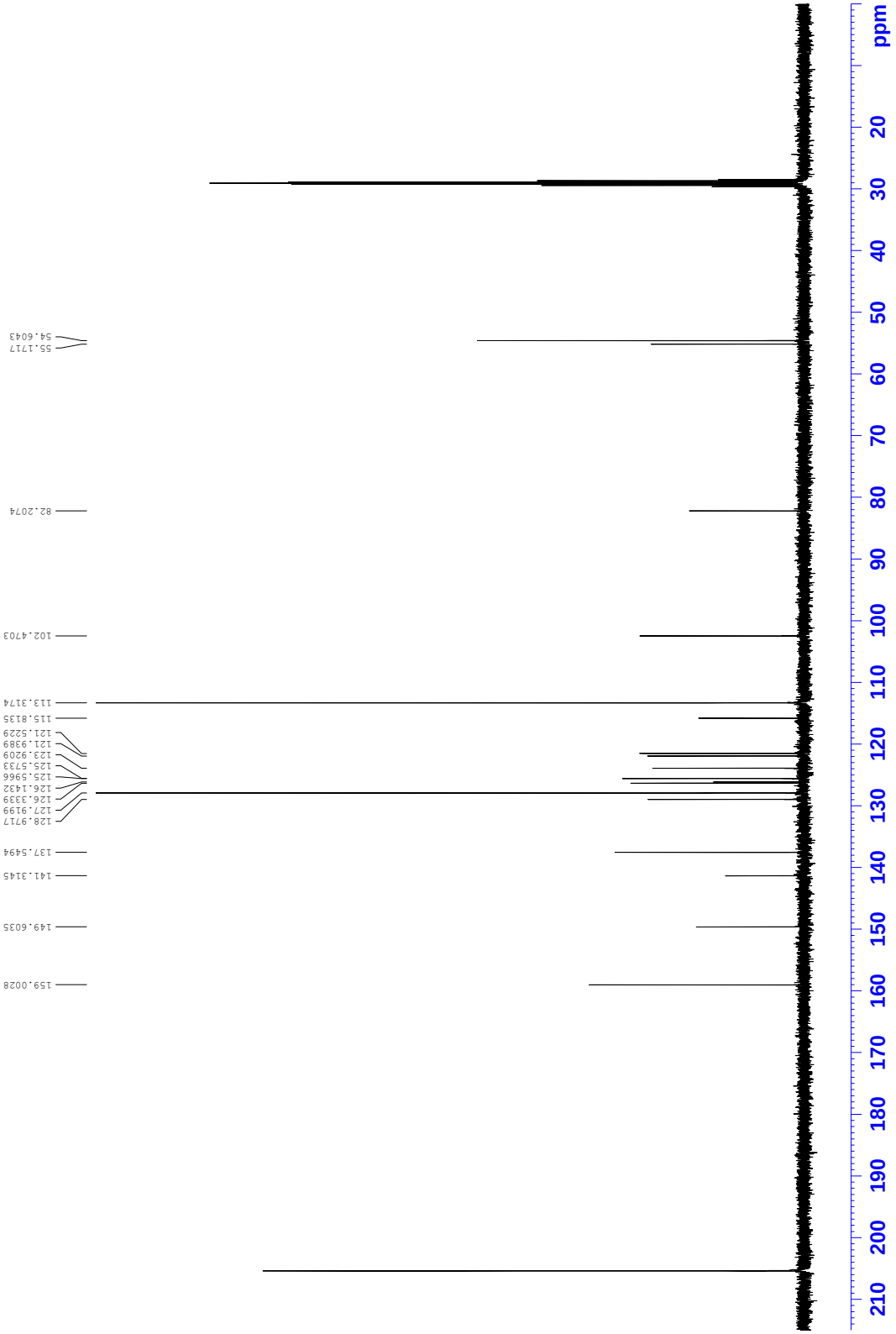


Figure S6 ^{1}H NMR spectrum of compound **9** in d_6-acetone UV irradiated for 30 s

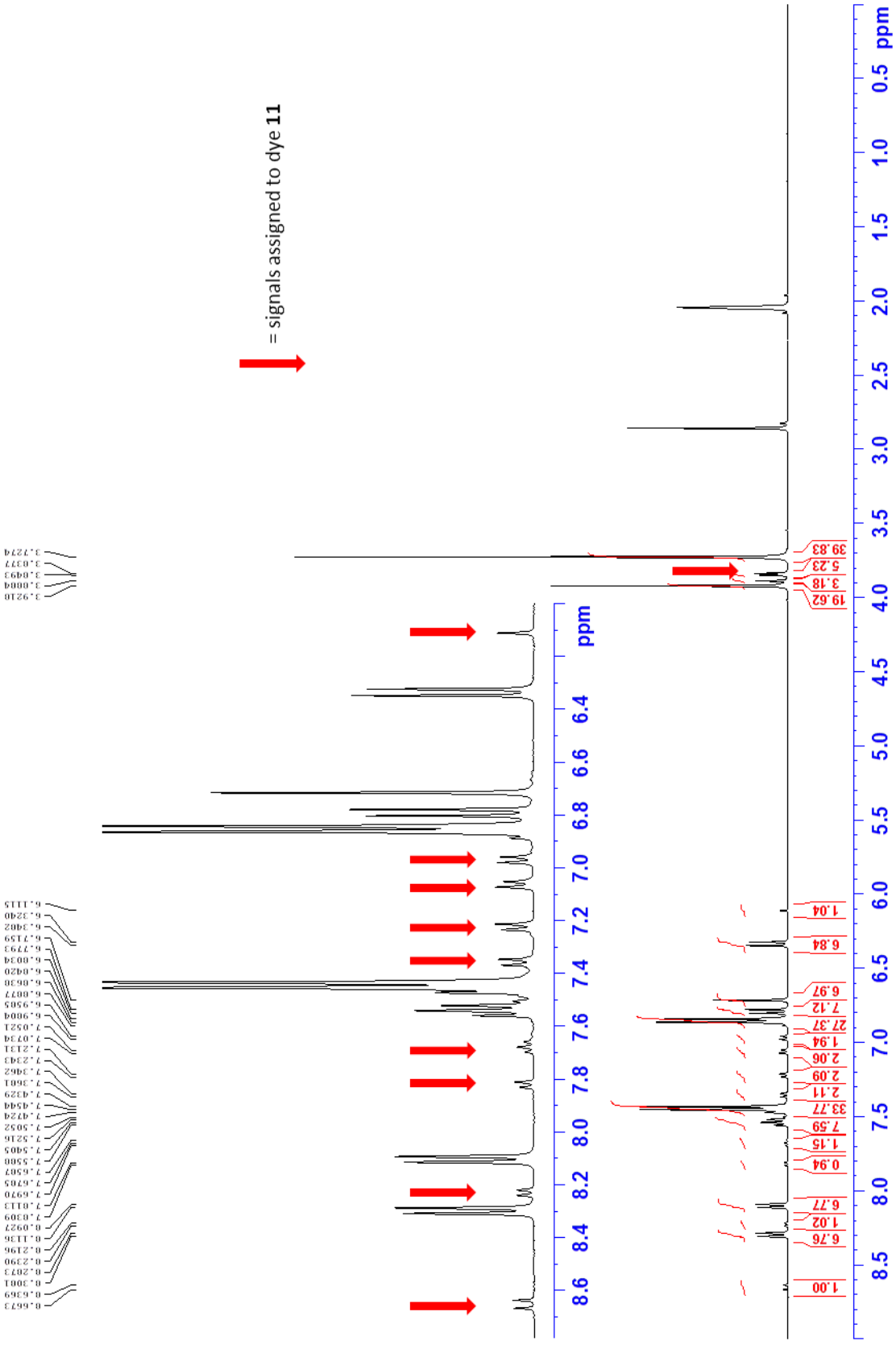


Figure S7 ^{1}H NMR spectrum of compound **9** in d_6-acetone UV irradiated for 40 min

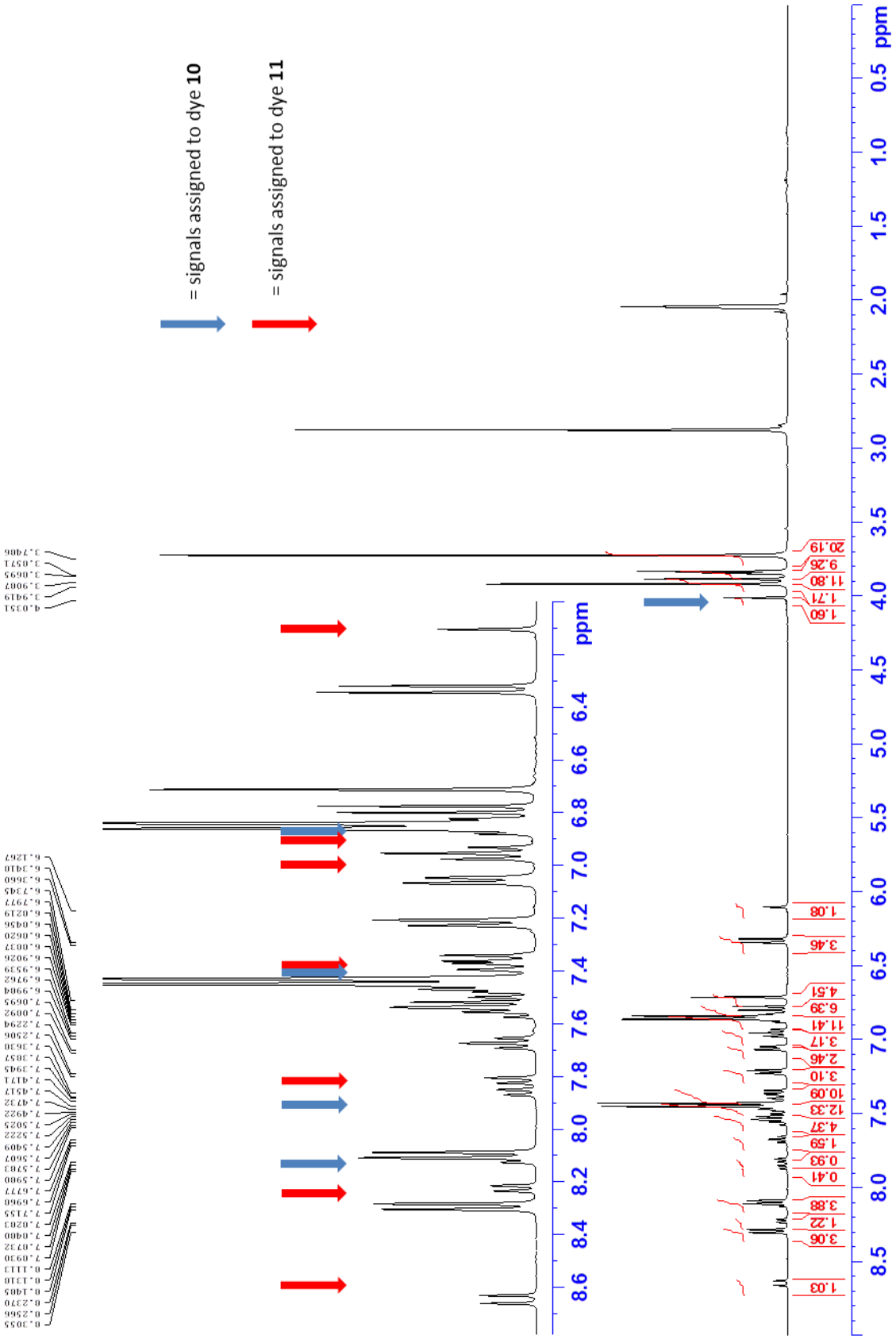


Figure S8 ^{1}H NMR spectrum of compound **9** in commercial $CDCl_3$

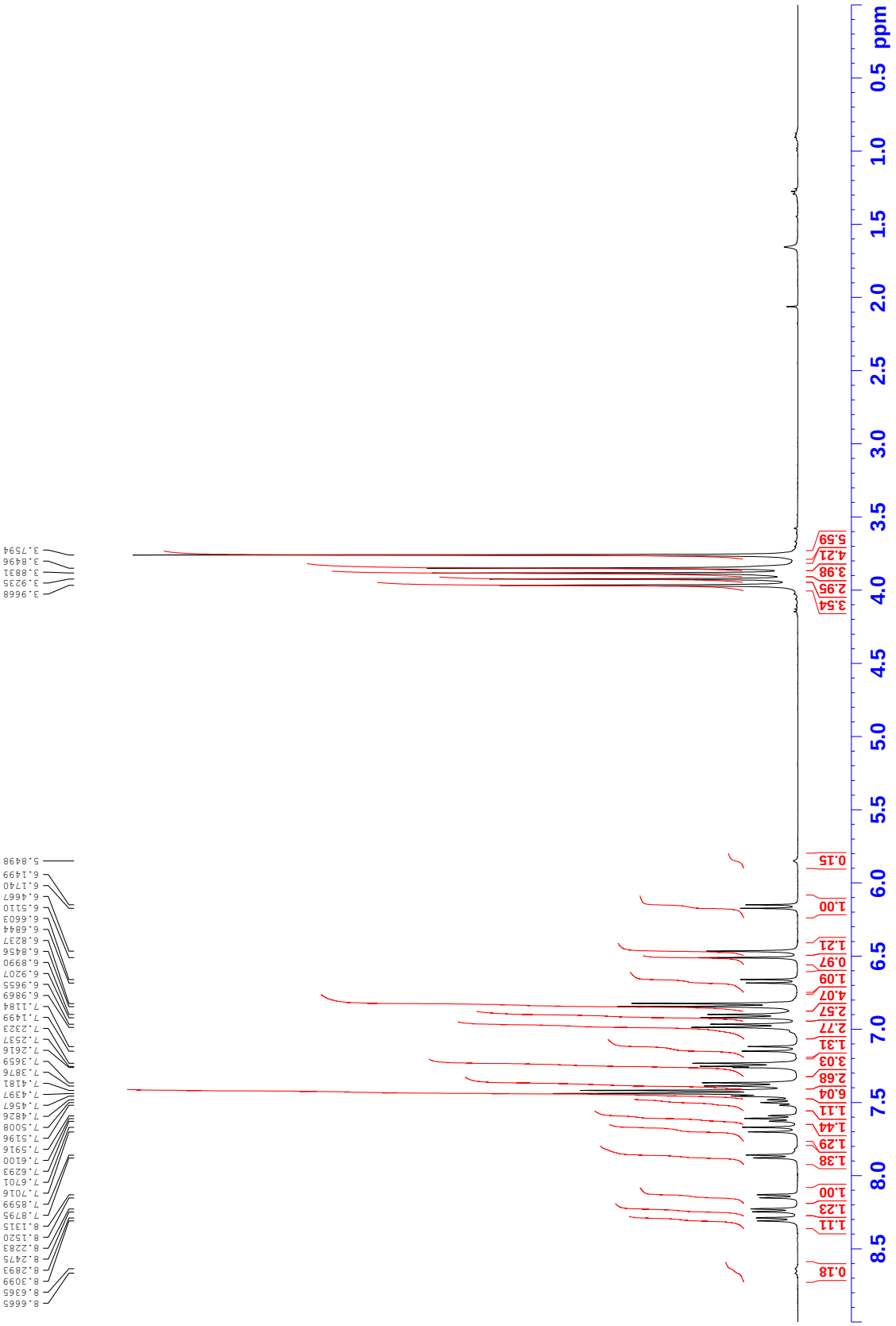


Figure S9 ^{13}C NMR spectrum of compound **9** in commercial $CDCl_3$

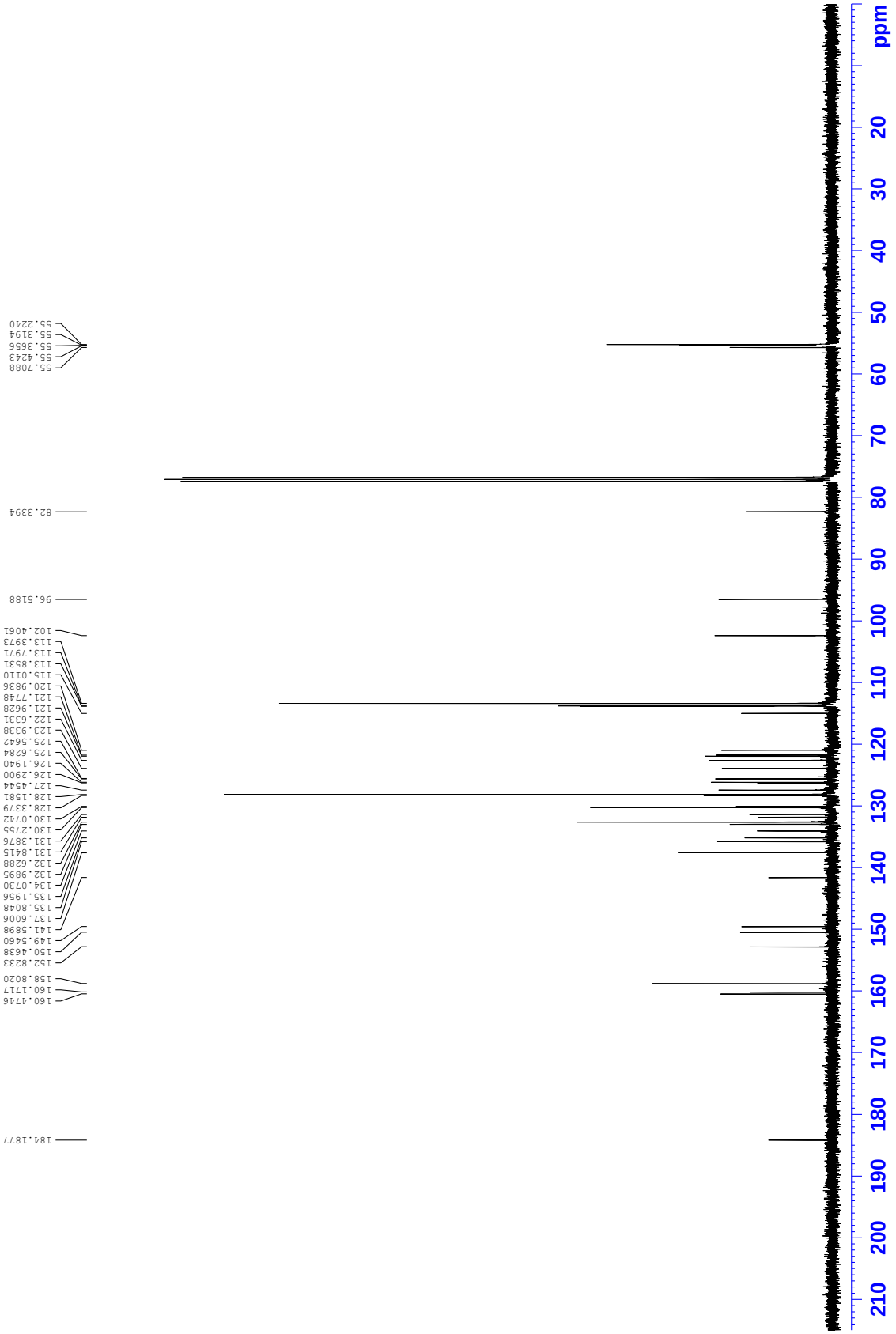


Figure S10 ^{1}H NMR spectrum of compound **9** in aq. K_2CO_3 washed $CDCl_3$

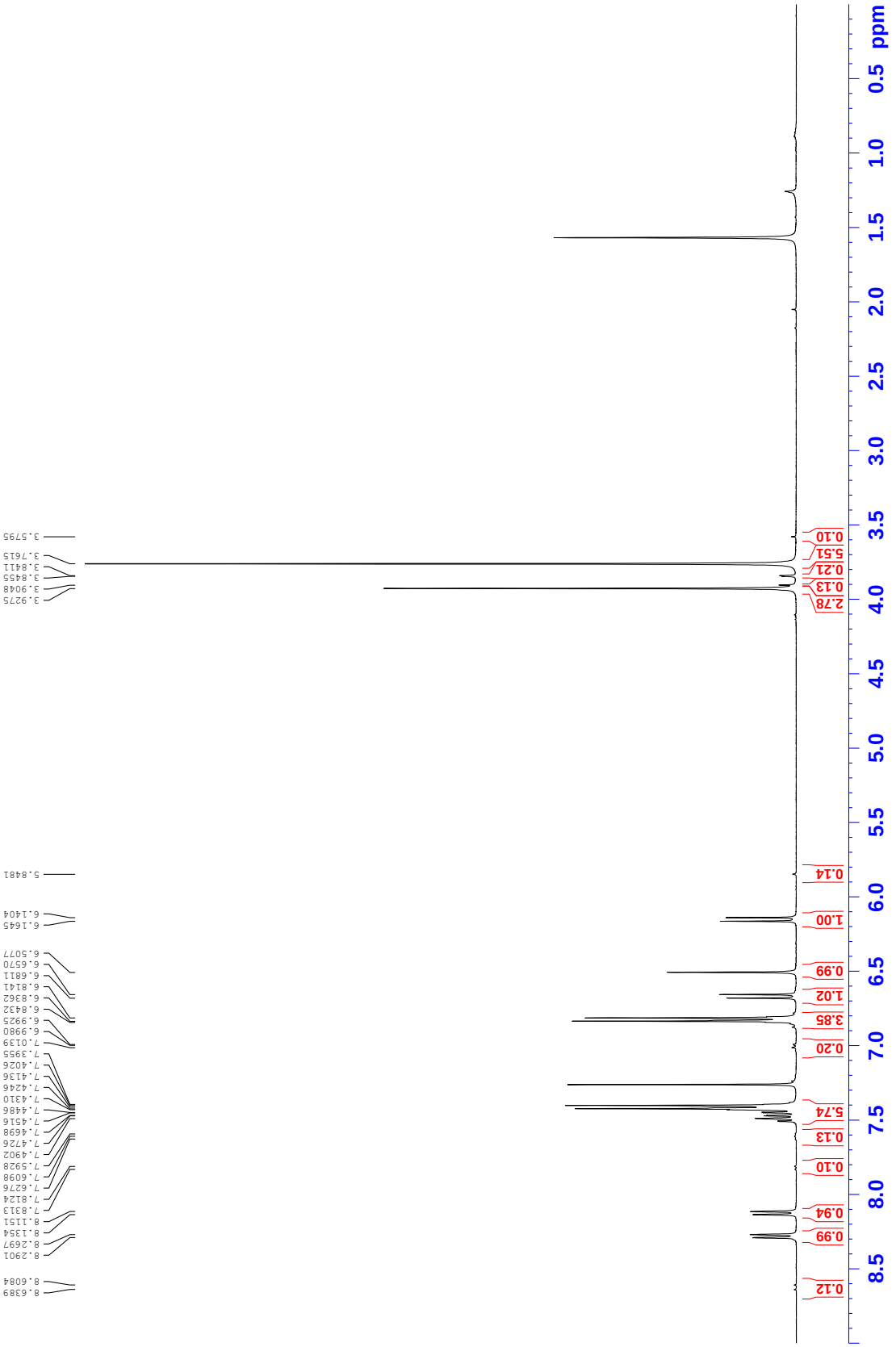


Figure S11 ^{13}C NMR spectrum of compound **9** in aq. K_2CO_3 washed $CDCl_3$

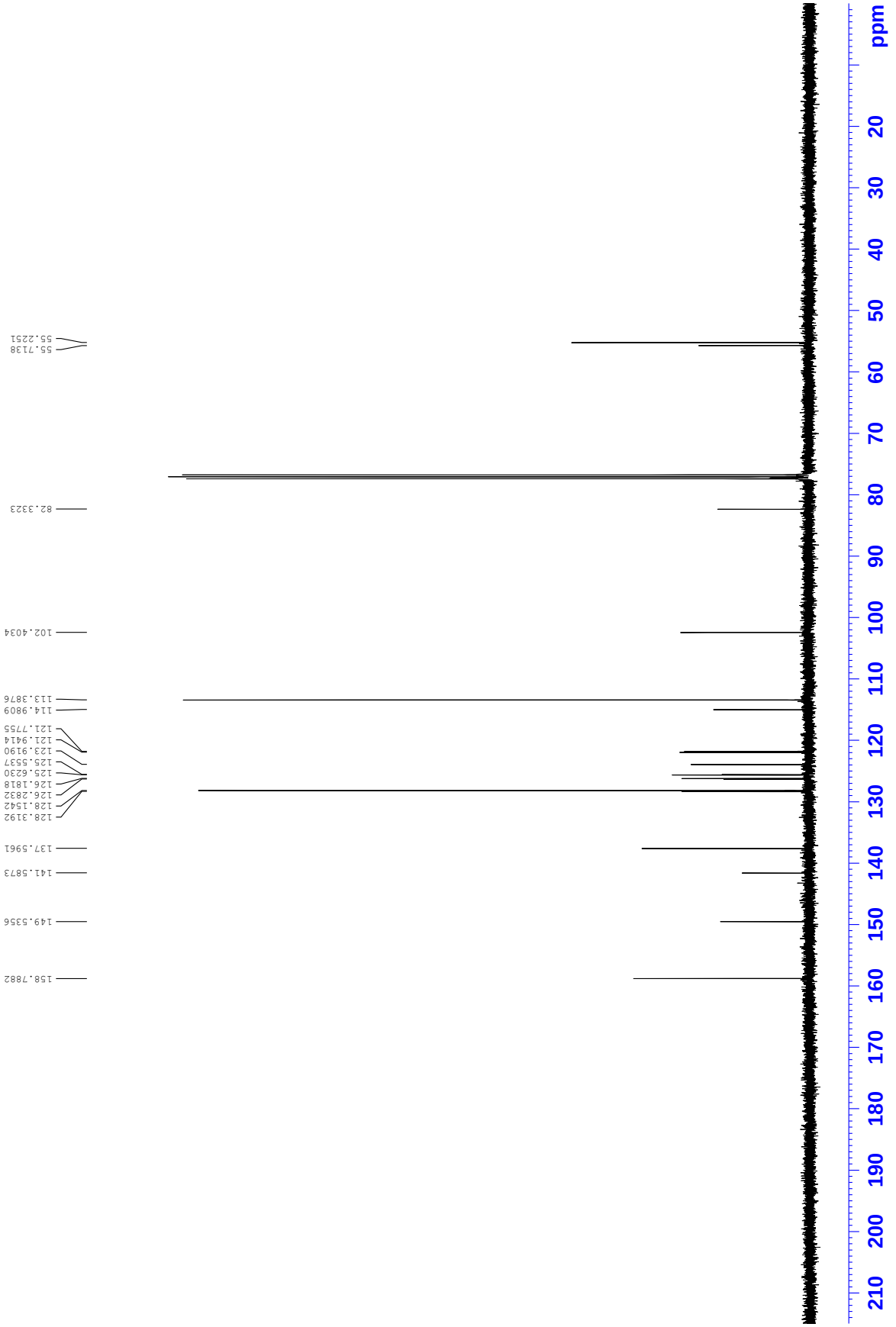
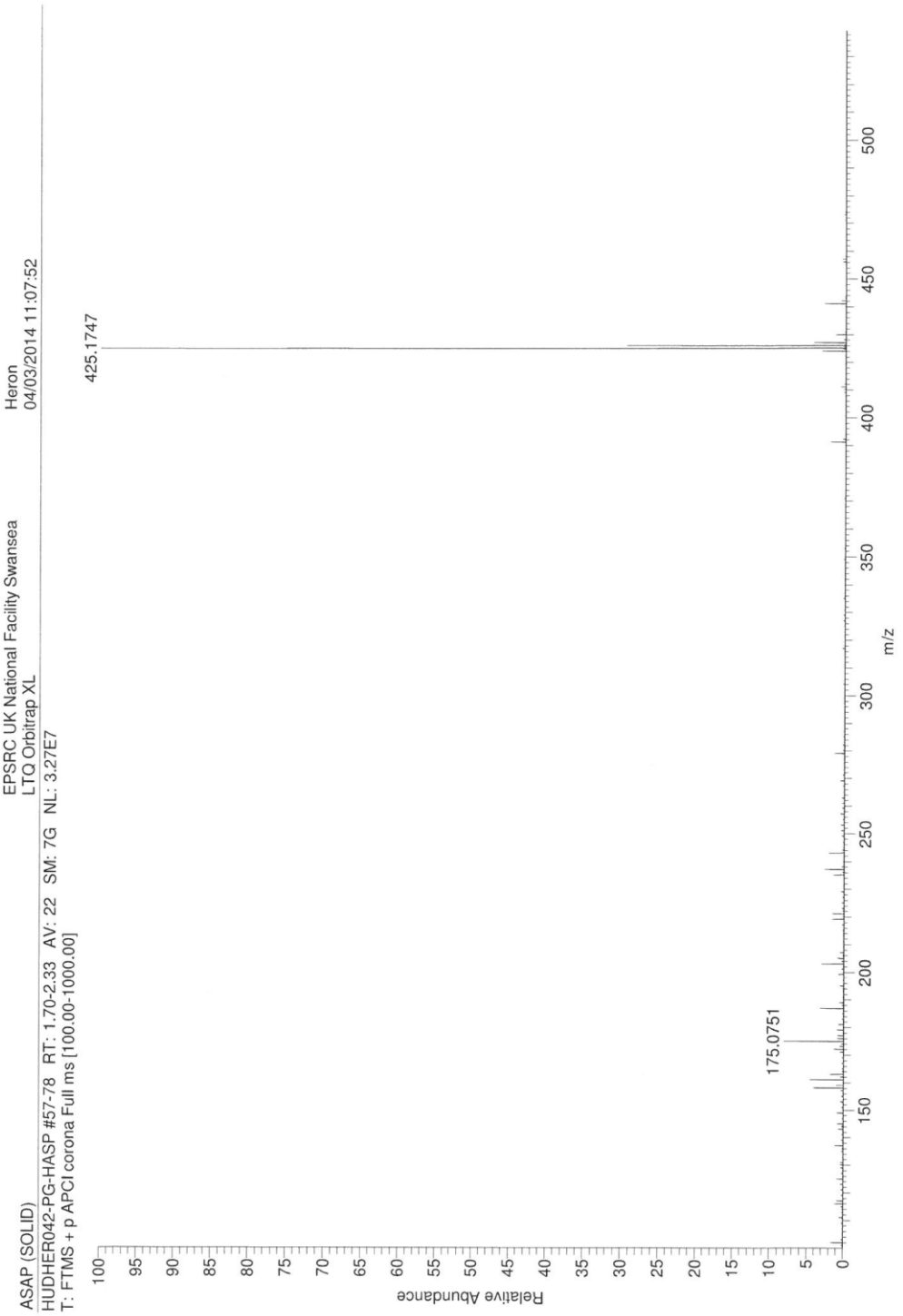
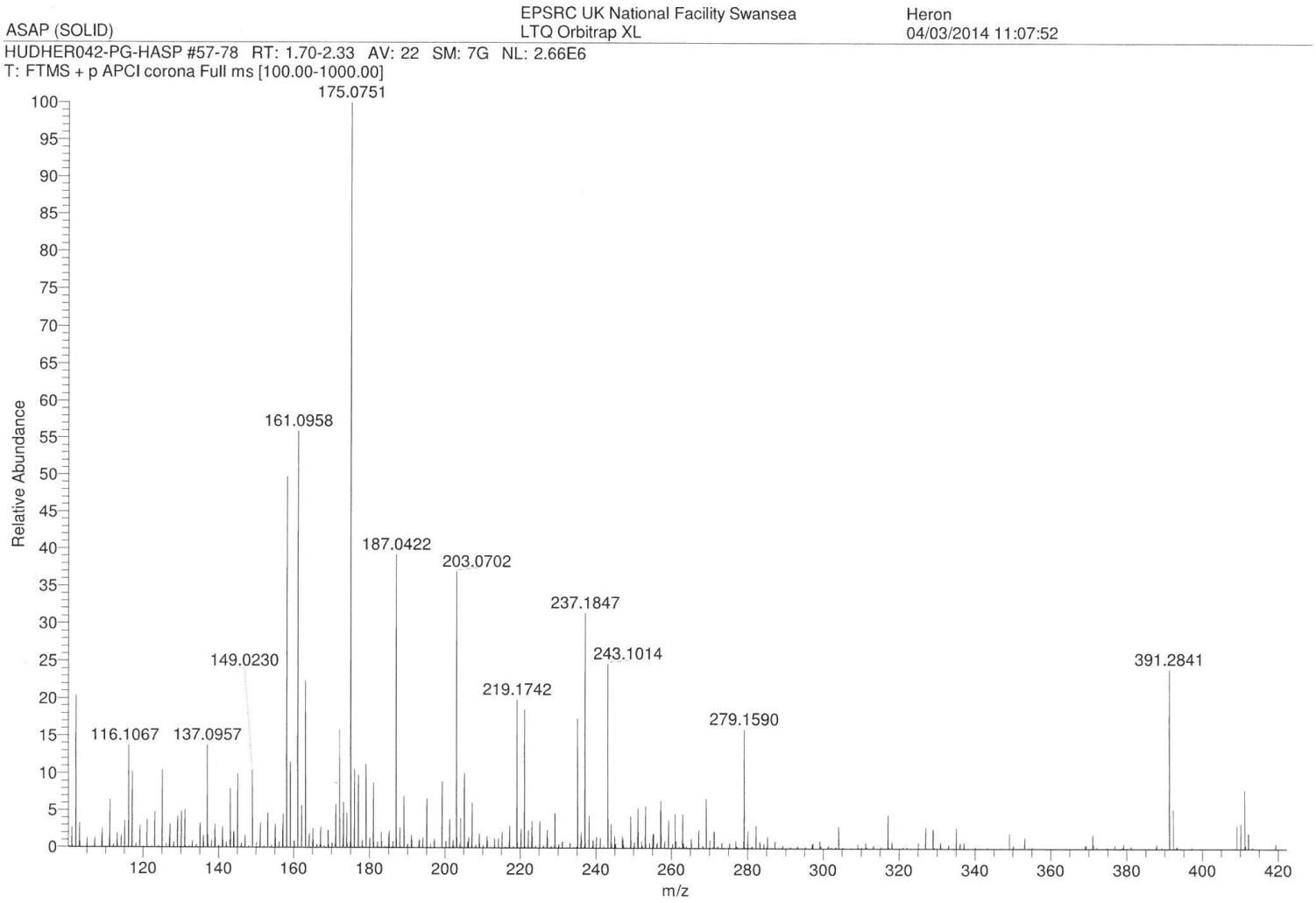


Figure S12 Mass Spectral data for compound **9**

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EPSRC UK National Facility Swansea
LTQ Orbitrap XL
Heron
04/03/2014 11:07:52
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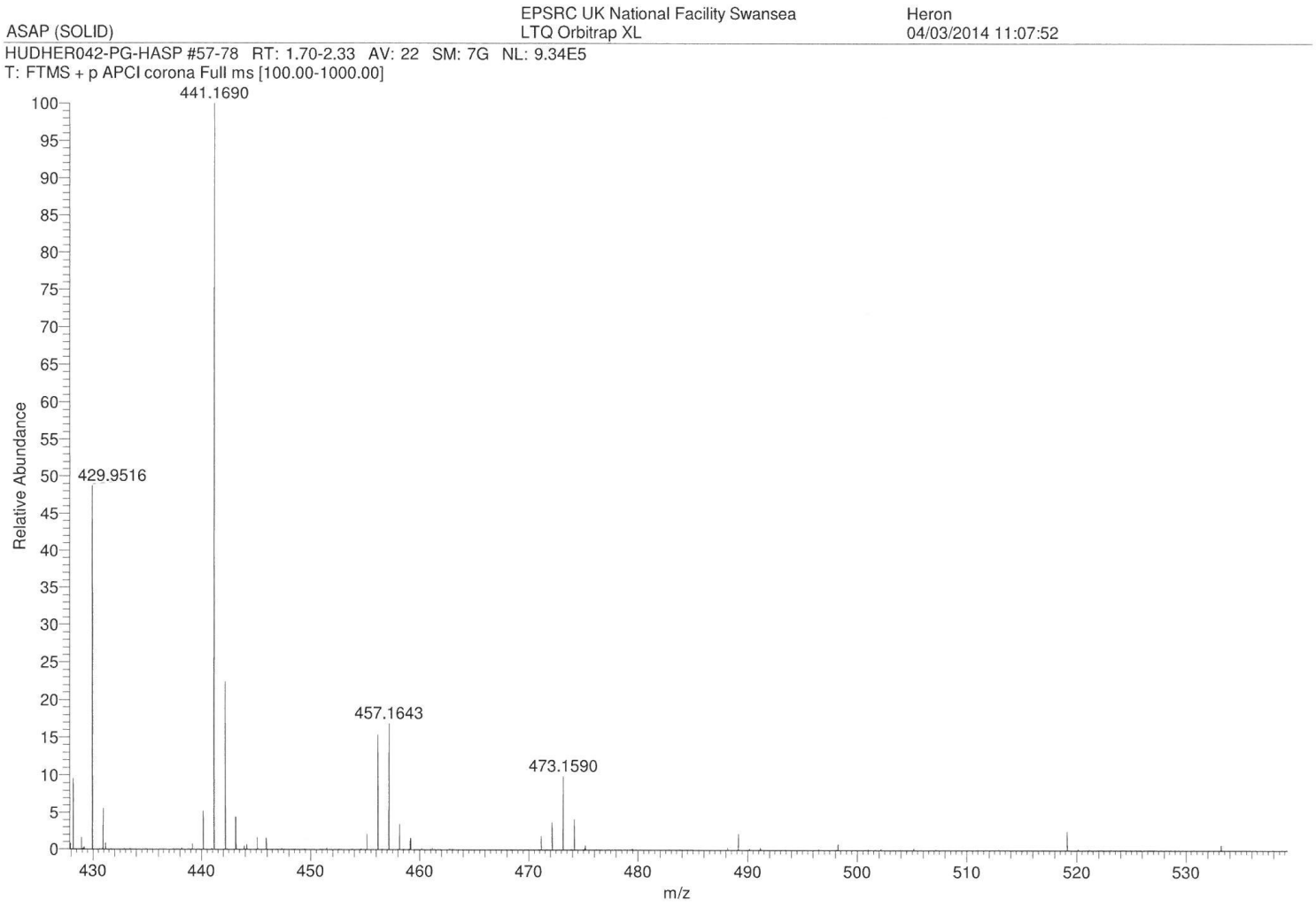
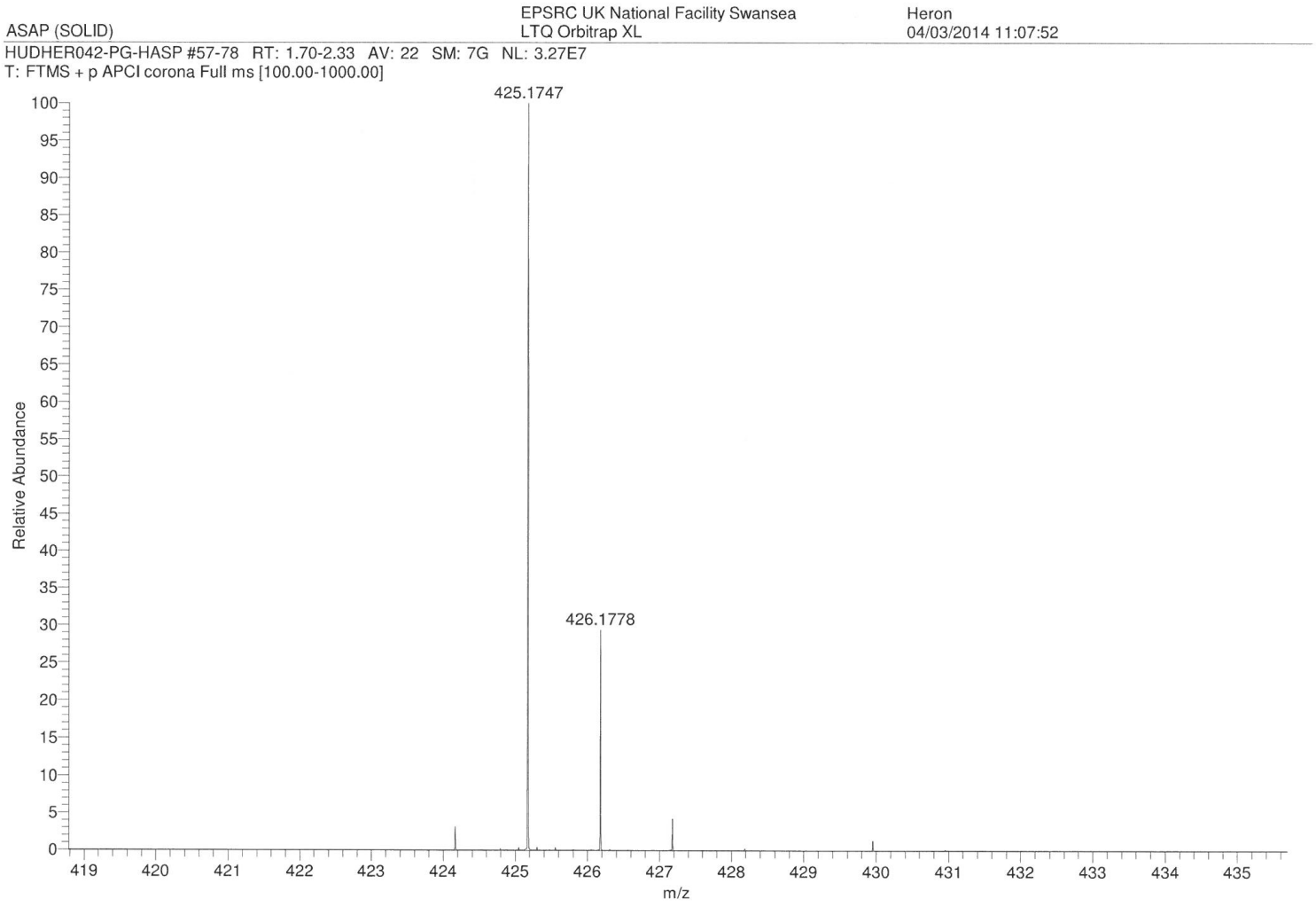
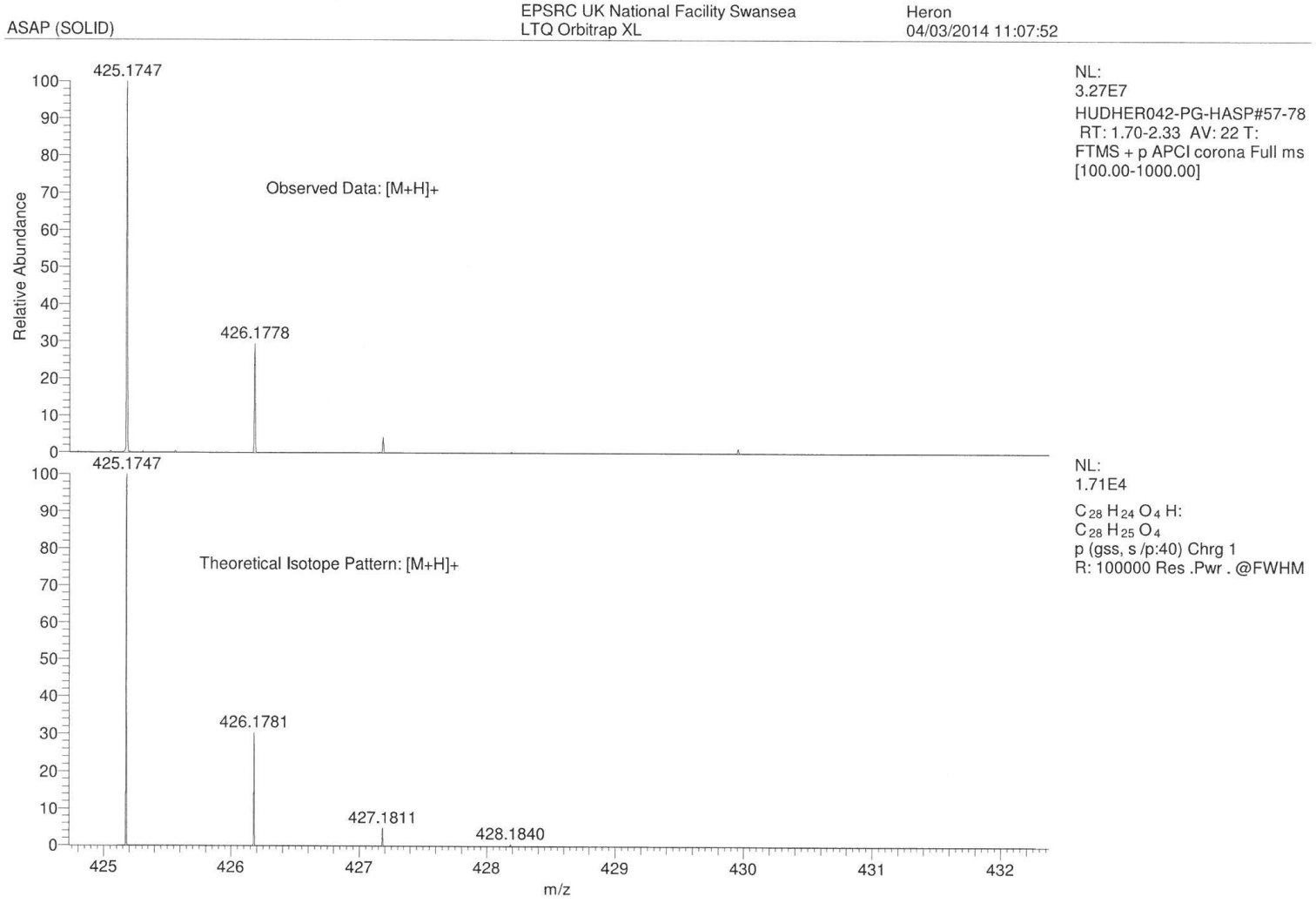
T: FTMS + p APCI corona Full ms [100.00-1000.00]
Relative Abundance
m/z
175.0751
161.0958
187.0422
203.0702
237.1847
243.1014
391.2841
149.0230
219.1742
279.1590
116.1067
137.0957


ASAP (SOLID)
EPSRC UK National Facility Swansea
LTQ Orbitrap XL
Heron
04/03/2014 11:07:52
HUDHER042-PG-HASP #57-78 RT: 1.70-2.33 AV: 22 SM: 7G NL: 9.34E5
T: FTMS + p APCI corona Full ms [100.00-1000.00]
441.1690
429.9516
457.1643
473.1590
Relative Abundance
m/z


ASAP (SOLID)
EPSRC UK National Facility Swansea
LTQ Orbitrap XL
Heron
04/03/2014 11:07:52
HUDHER042-PG-HASP #57-78 RT: 1.70-2.33 AV: 22 SM: 7G NL: 3.27E7
T: FTMS + p APCI corona Full ms [100.00-1000.00]
425.1747
426.1778
Relative Abundance
m/z


ASAP (SOLID)
EPSRC UK National Facility Swansea
LTQ Orbitrap XL
Heron
04/03/2014 11:07:52
425.1747
Observed Data: [M+H]+
426.1778
NL:
3.27E7
HUDHER042-PG-HASP#57-78
RT: 1.70-2.33 AV: 22 T:
FTMS + p APCI corona Full ms
[100.00-1000.00]
Relative Abundance
425.1747
Theoretical Isotope Pattern: [M+H]+
426.1781
427.1811
428.1840
NL:
1.71E4
C28 H24 O4 H:
C28 H25 O4
p (gss, s /p:40) Chrg 1
R: 100000 Res .Pwr . @FWHM
m/z

Isotope:	Min. .. Max.		
14 N	0....15		
16 O	0....15		
12 C	0....60		
1 H	0....70		
23 Na	0....0		
Tolerance Window:	+- 5.00 ppm		
Db/Ring Equiv:	-3.. 100	N-Rule:	Do not use
Fits:	100	Charge:	1

Mass	Theoretical Mass	Delta [ppm]	RDB	Composition
425.1747	425.1747	-0.1	16.5	$C_{28}H_{25}O_4$
	425.1752	-1.3	9.5	$C_{13}H_{21}O_5N_{12}$
	425.1752	-1.3	4.0	$C_{14}H_{27}O_{10}N_5$
	425.1739	1.9	-1.0	$C_{13}H_{31}O_{14}N_1$
	425.1739	1.9	4.5	$C_{12}H_{25}O_9N_8$
	425.1739	1.9	10.0	$C_{11}H_{19}O_4N_{15}$
	425.1734	3.1	17.0	$C_{26}H_{23}O_3N_3$
	425.1761	-3.2	21.5	$C_{29}H_{21}N_4$
	425.1766	-4.4	9.0	$C_{15}H_{23}O_6N_9$
	425.1766	-4.4	3.5	$C_{16}H_{29}O_{11}N_2$

Figure S13 ^{1}H NMR spectrum of compound **10** in d_6-acetone

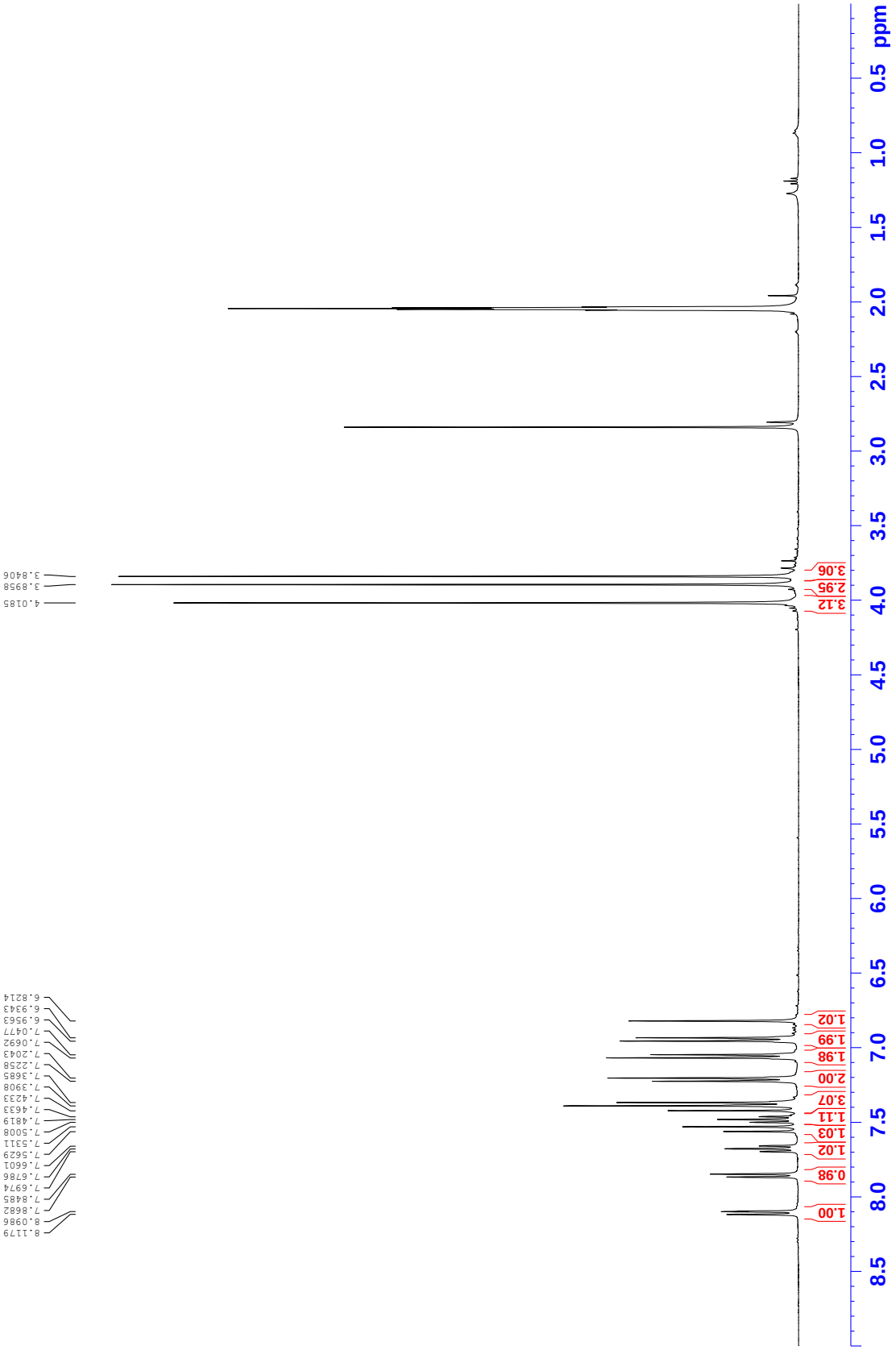


Figure S14 ^{13}C NMR spectrum of compound **10** in d_6-acetone

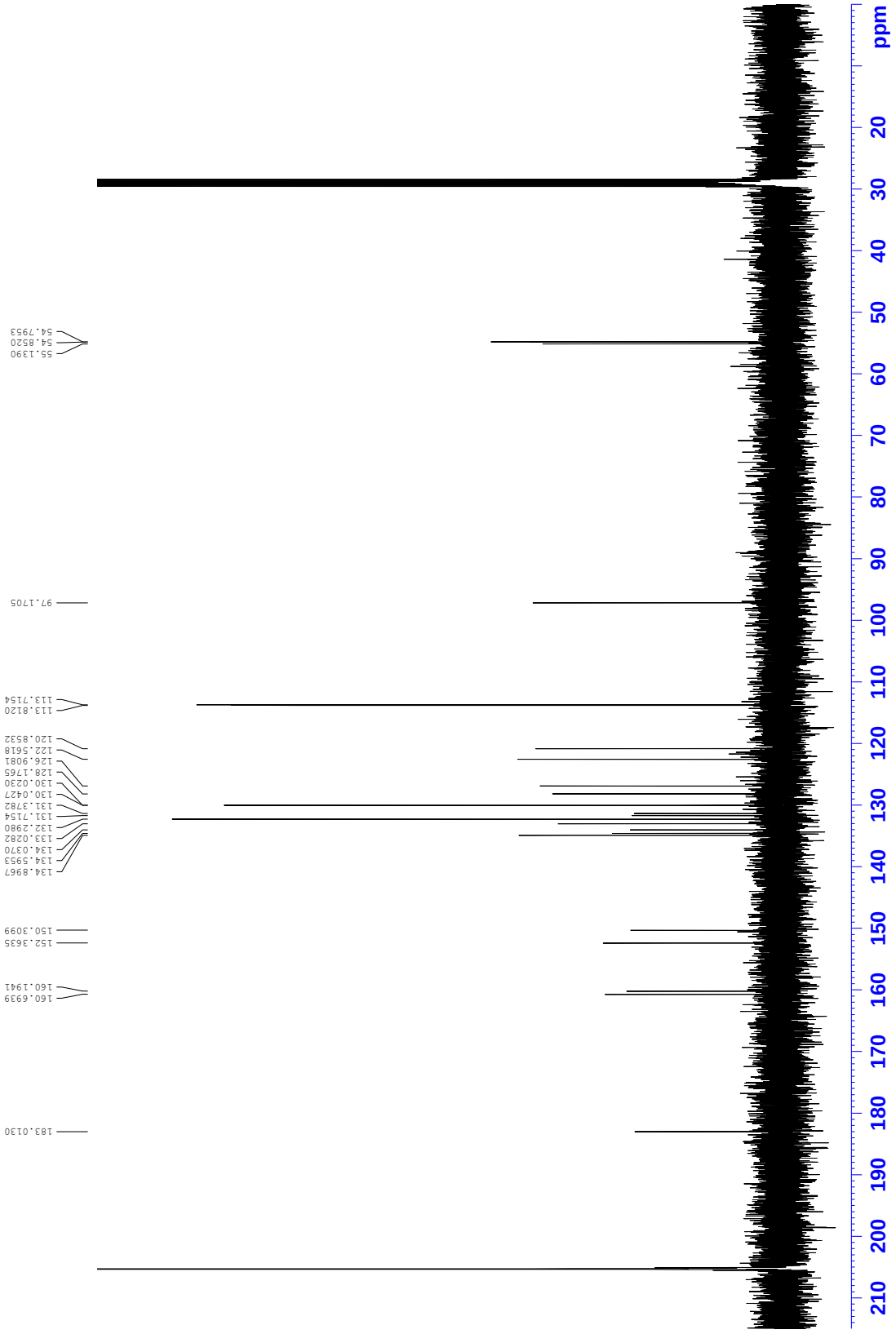
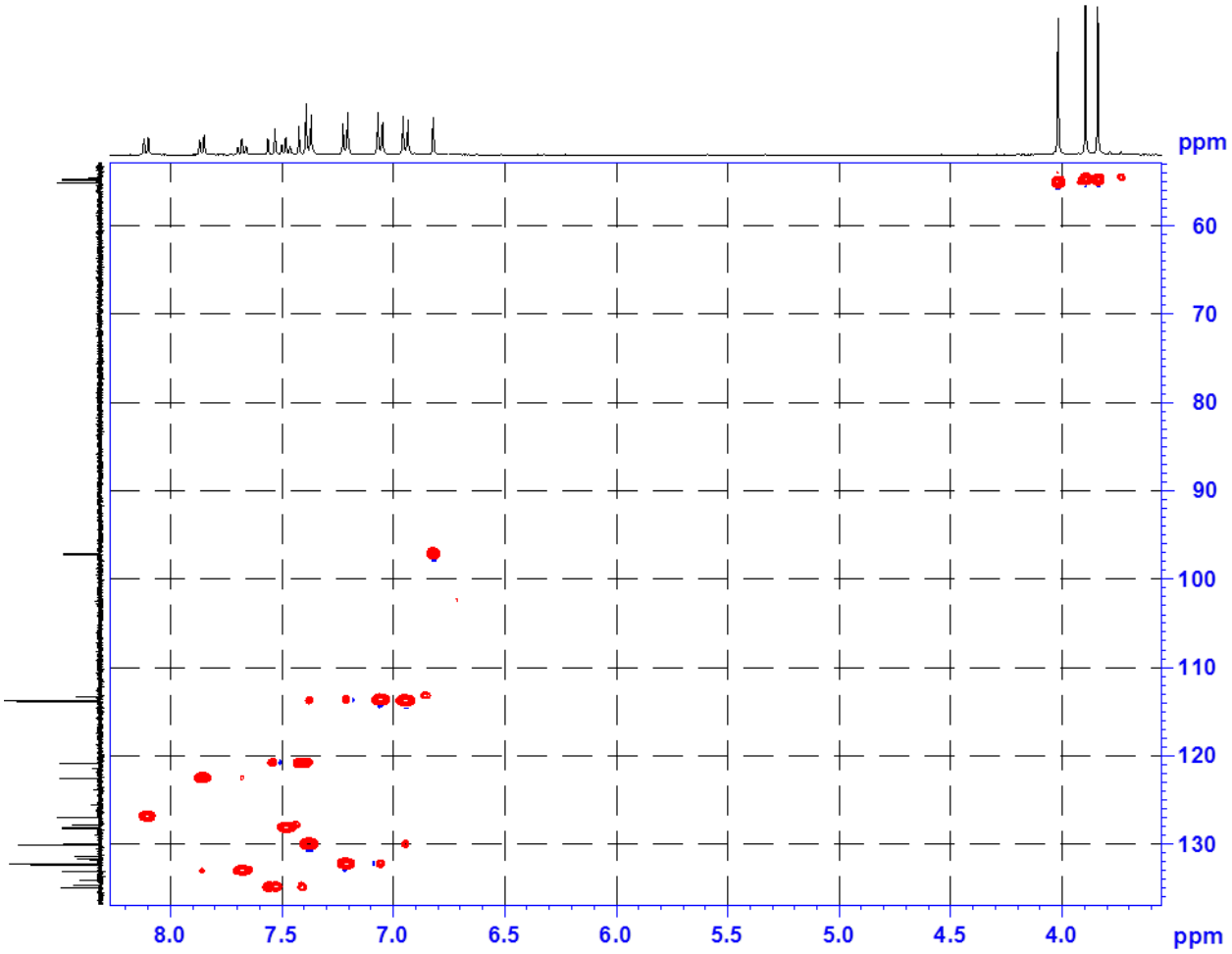
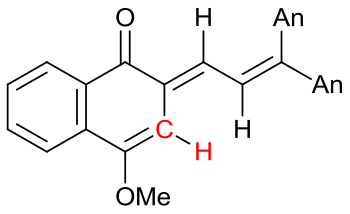


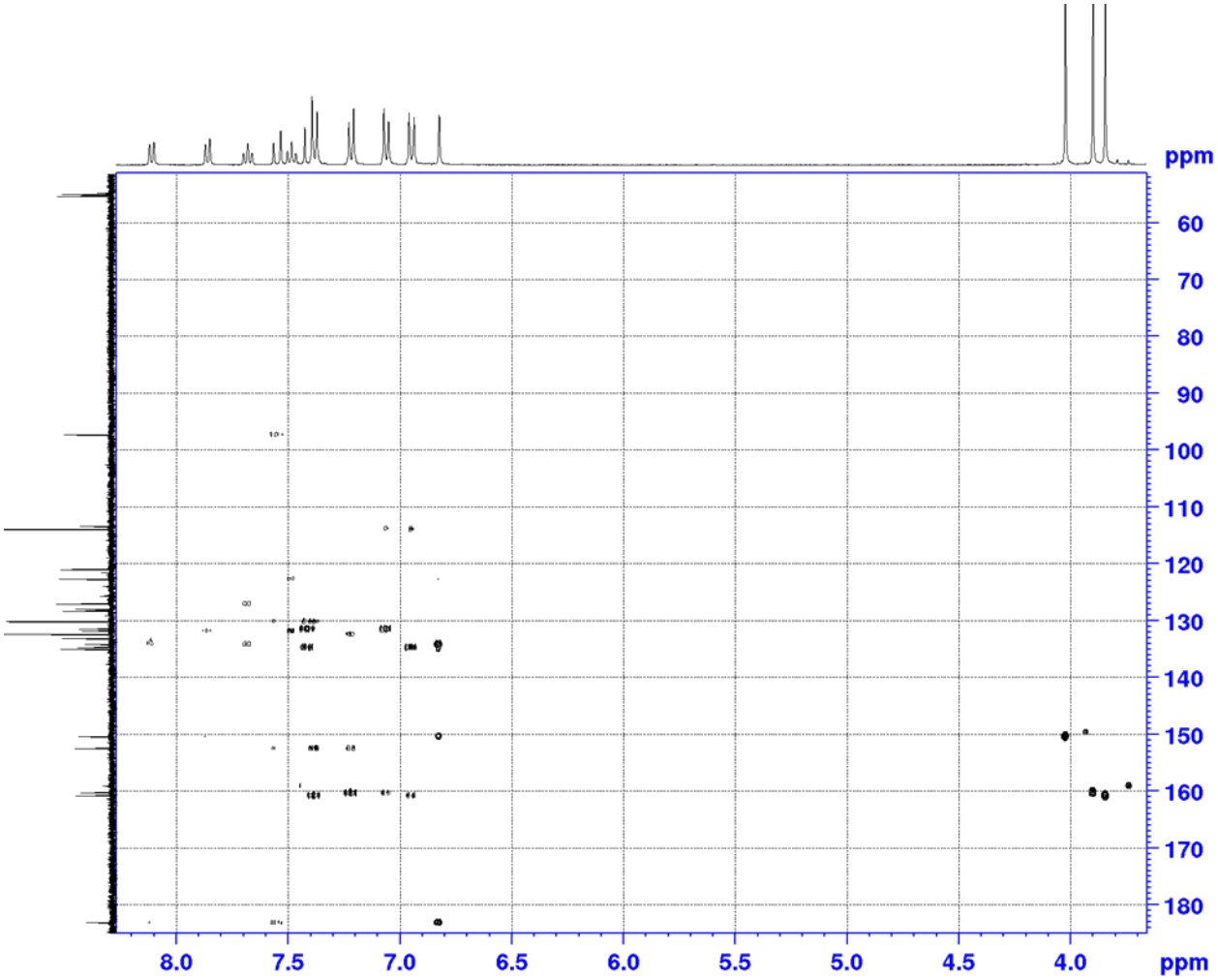
Figure S15 HSQC spectrum of compound **10** in d_6-acetone

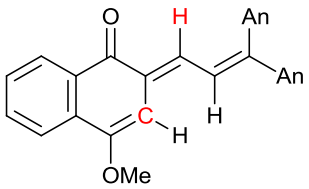




One bond correlation between H at δ 6.82 and C at δ 97.17

Figure S16 HMBC spectrum of compound **10** in d_6-acetone





Three bond correlation between H at δ 7.55 and C at δ 97.17

Figure S17 COSY spectrum of compound **10** in d_6-acetone (aromatic region)

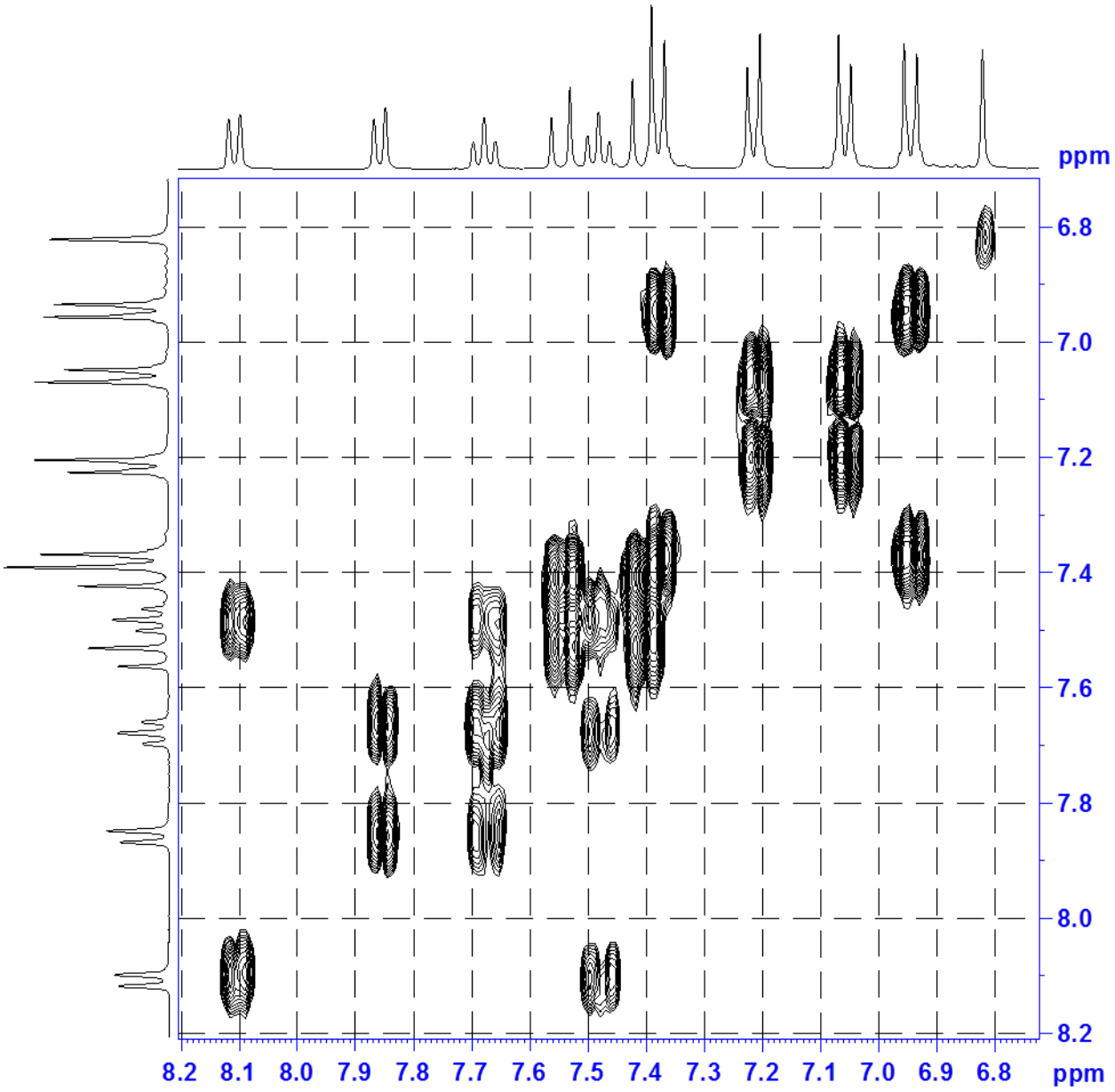
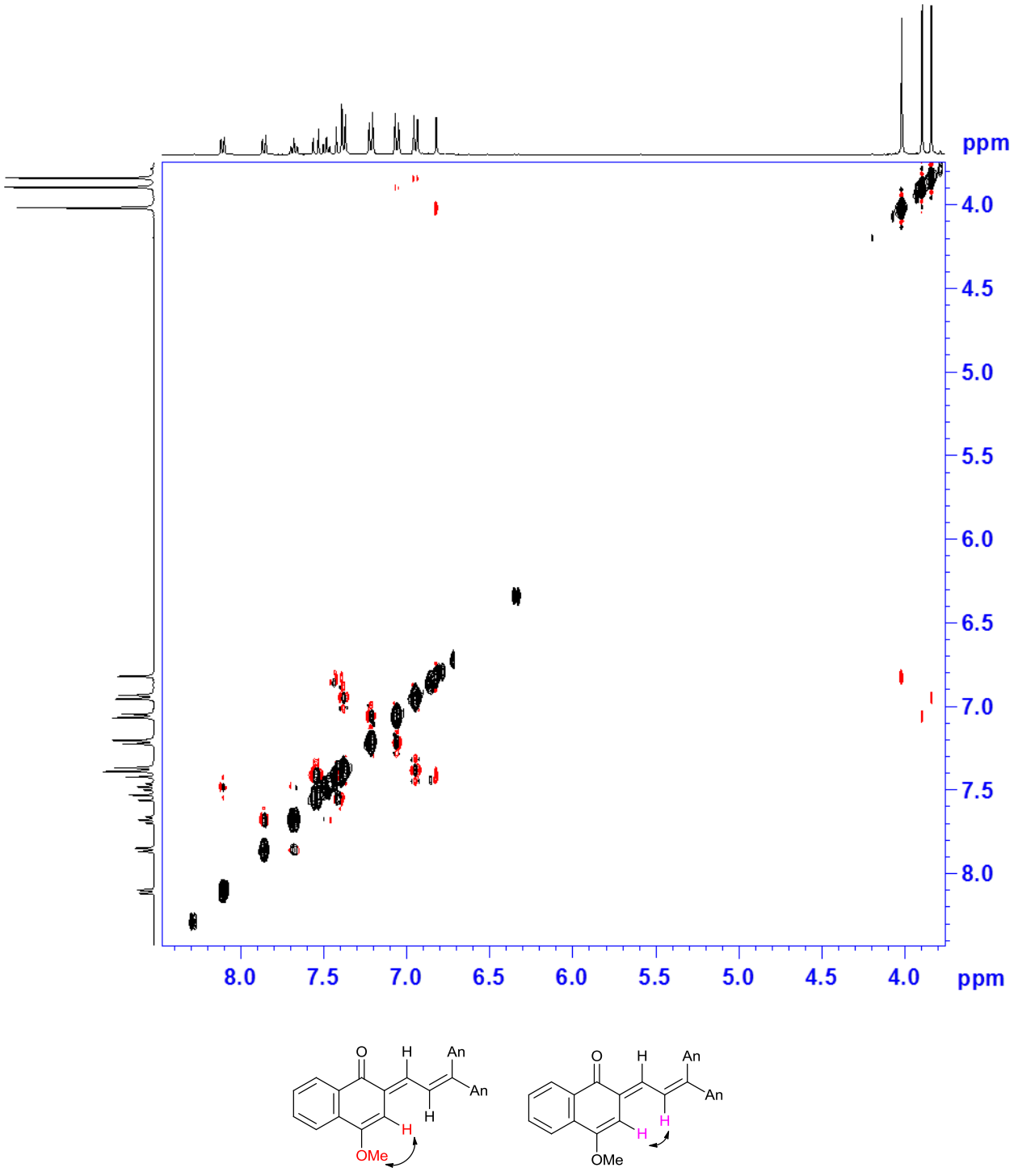


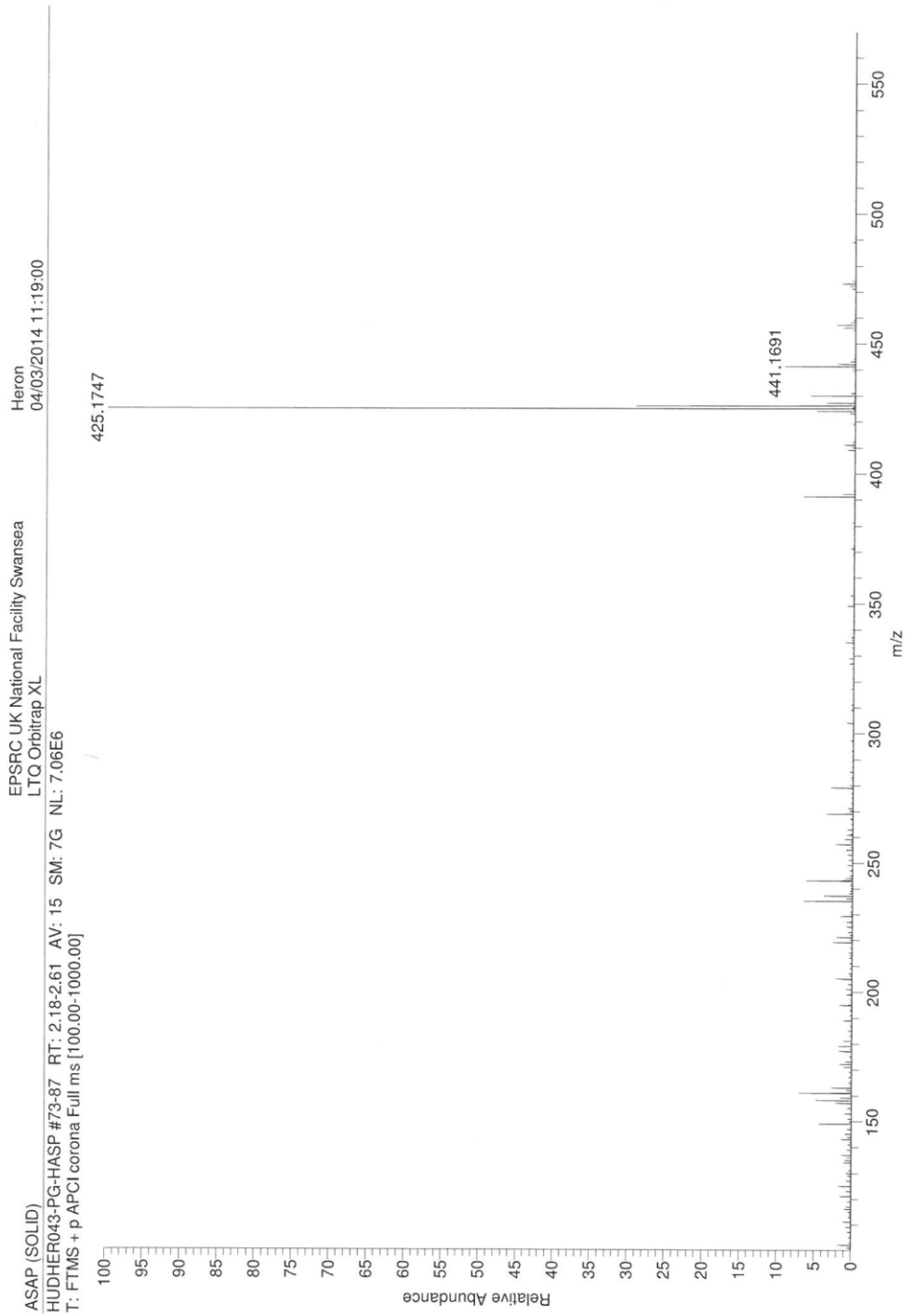
Figure S18 NOE spectrum of compound **10** in d_6-acetone

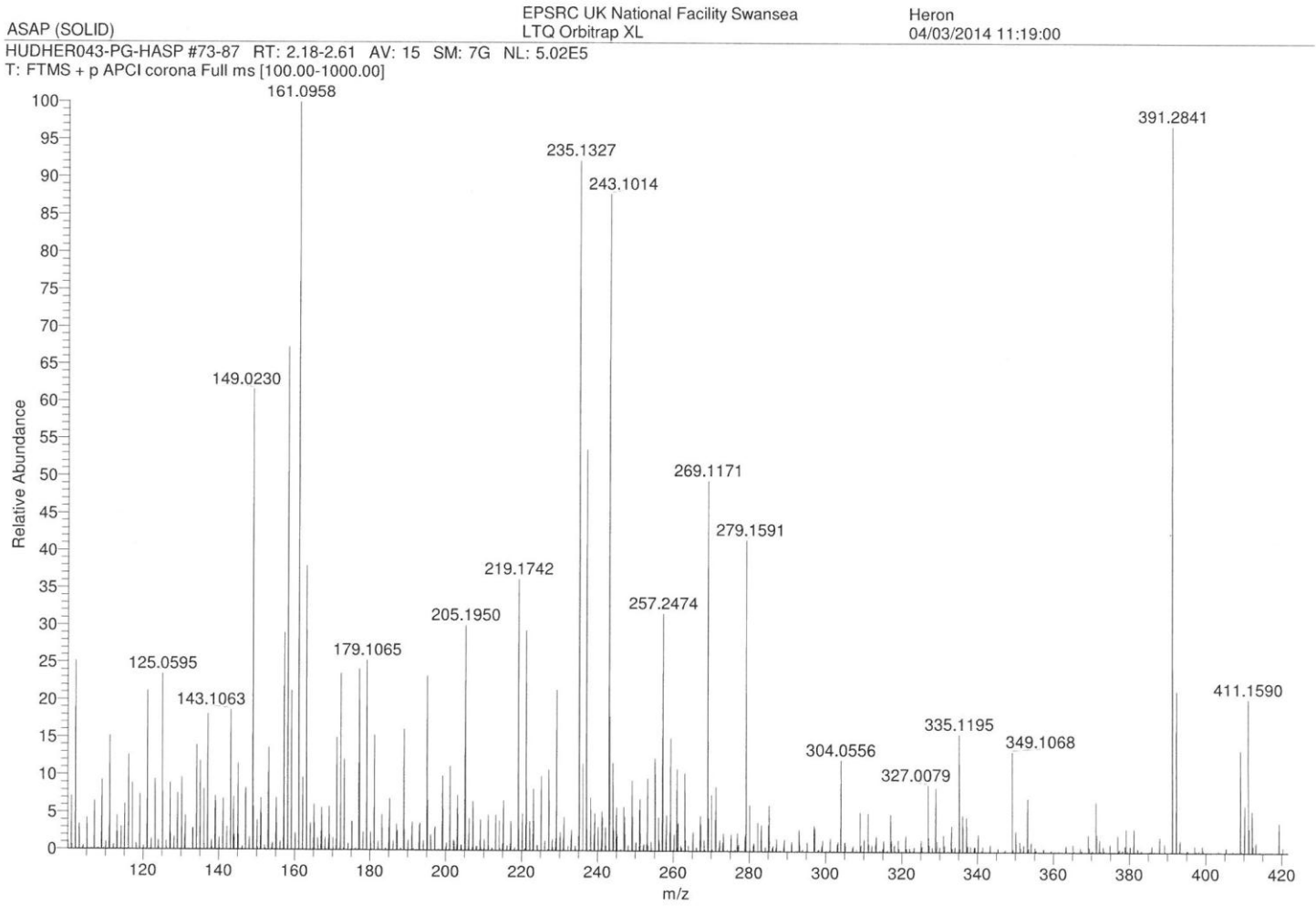


Weak correlation between H at δ 6.82 and OMe at δ 4.02

Weak correlation between H at δ 6.82 and H at δ 7.44

Figure S19 Mass Spectral data for compound **10**

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EPSRC UK National Facility Swansea
LTQ Orbitrap XL
Heron
04/03/2014 11:19:00
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T: FTMS + p APCI corona Full ms [100.00-1000.00]
Relative Abundance
m/z
161.0958
391.2841
235.1327
243.1014
149.0230
269.1171
279.1591
219.1742
257.2474
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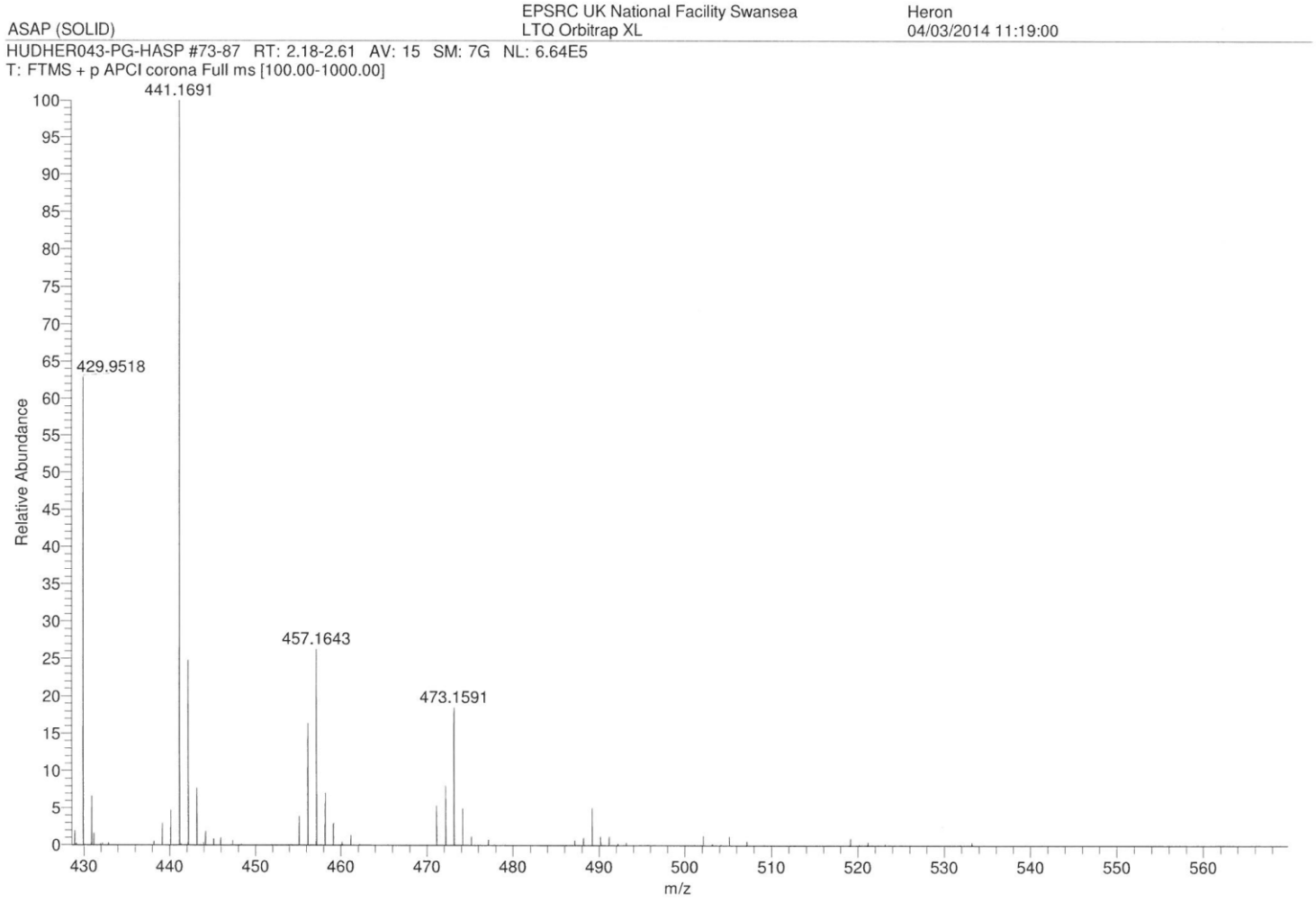
179.1065
125.0595
143.1063
411.1590
335.1195
349.1068
304.0556
327.0079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EPSRC UK National Facility Swansea
LTQ Orbitrap XL
Heron
04/03/2014 11:19:00
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T: FTMS + p APCI corona Full ms [100.00-1000.00]
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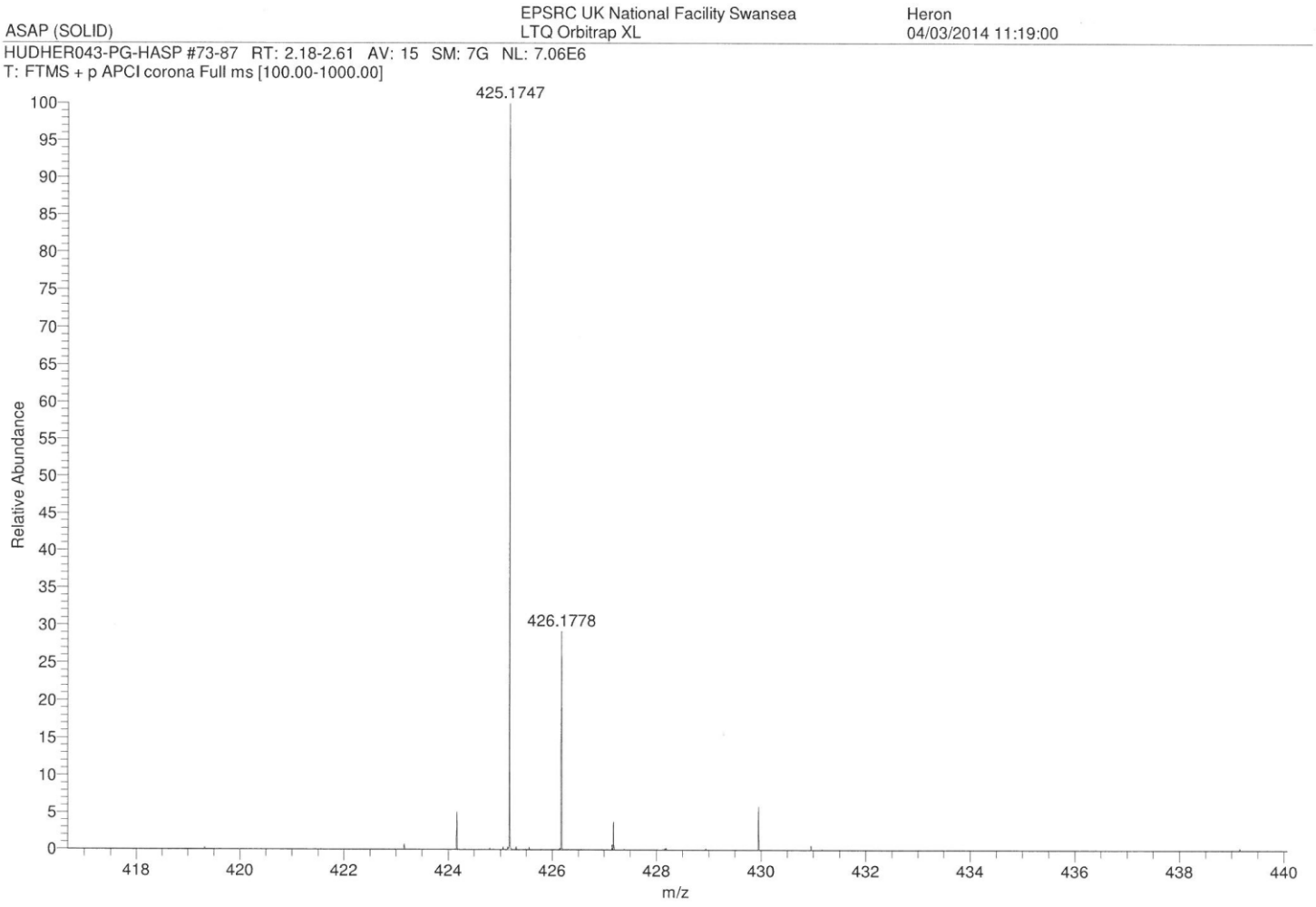
429.9518
457.1643
473.1591
Relative Abundance
m/z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EPSRC UK National Facility Swansea
LTQ Orbitrap XL
Heron
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T: FTMS + p APCI corona Full ms [100.00-1000.00]
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426.1778
Relative Abundance
m/z
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95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
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10
5
0
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420
422
424
426
428
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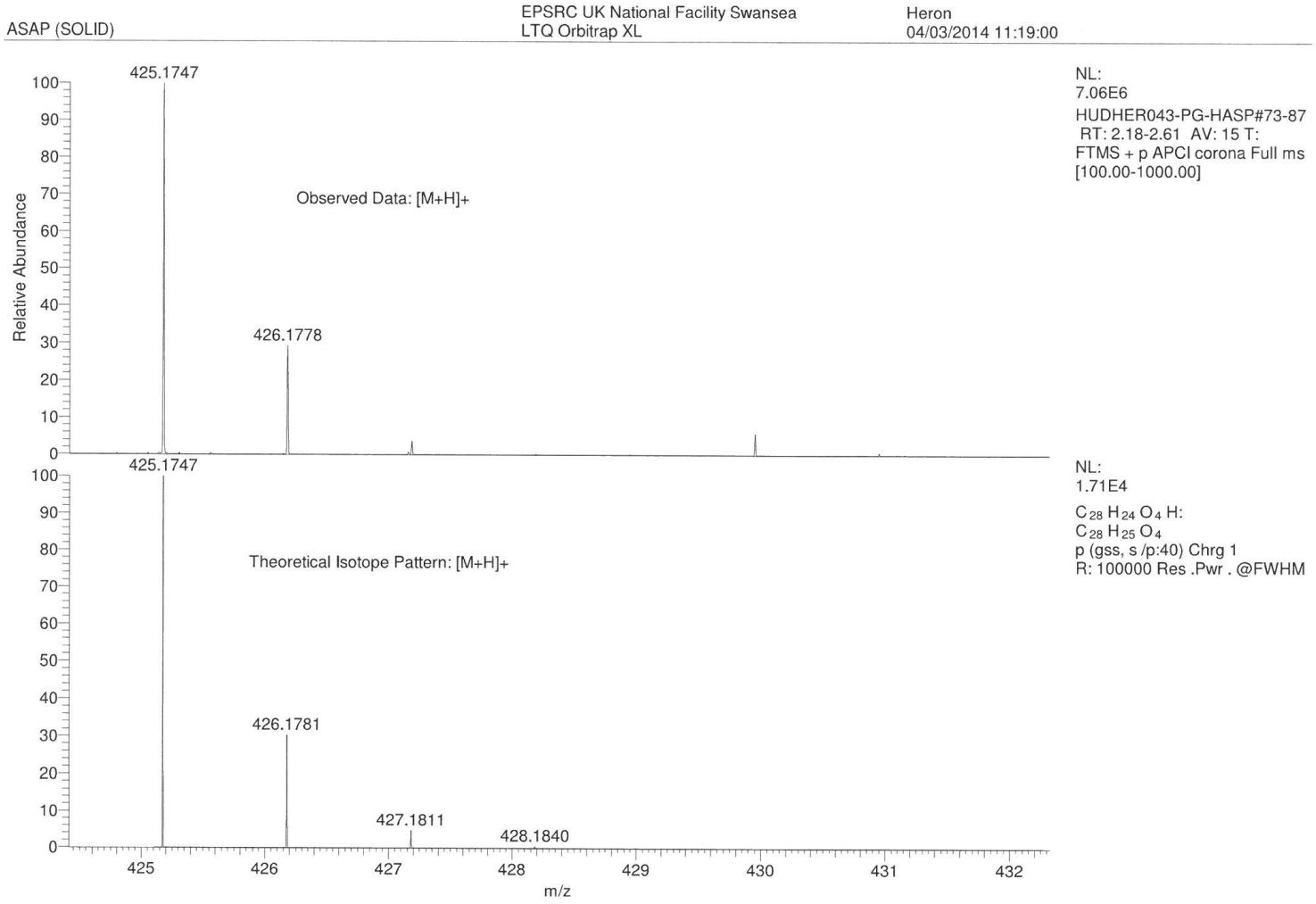
432
434
436
438
440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EPSRC UK National Facility Swansea
LTQ Orbitrap XL
Heron
04/03/2014 11:19:00
425.1747
Observed Data: [M+H]+
426.1778
NL:
7.06E6
HUDHER043-PG-HASP#73-87
RT: 2.18-2.61 AV: 15 T:
FTMS + p APCI corona Full ms
[100.00-1000.00]
Relative Abundance
425.1747
Theoretical Isotope Pattern: [M+H]+
426.1781
427.1811
428.1840
NL:
1.71E4
C28 H24 O4 H:
C28 H25 O4
p (gss, s /p:40) Chrg 1
R: 100000 Res .Pwr . @FWHM
m/z

Isotope:	Min. .. Max.		
14 N	0....15		
16 O	0....15		
12 C	0....60		
1 H	0....70		
23 Na	0....0		
Tolerance Window:	+- 5.00 ppm		
Db/Ring Equiv:	-3.. 100	N-Rule:	Do not use
Fits:	100	Charge:	1

Mass	Theoretical Mass	Delta [ppm]	RDB	Composition
425.1747	425.1747	-0.1	16.5	$C_{28} H_{25} O_4$
	425.1752	-1.3	9.5	$C_{13} H_{21} O_5 N_{12}$
	425.1752	-1.3	4.0	$C_{14} H_{27} O_{10} N_5$
	425.1739	1.9	-1.0	$C_{13} H_{31} O_{14} N_1$
	425.1739	1.9	4.5	$C_{12} H_{25} O_9 N_2$
	425.1739	1.9	10.0	$C_{11} H_{19} O_4 N_{15}$
	425.1734	3.1	17.0	$C_{26} H_{23} O_3 N_3$
	425.1761	-3.2	21.5	$C_{29} H_{21} N_4$
	425.1766	-4.4	9.0	$C_{15} H_{23} O_6 N_9$
	425.1766	-4.4	3.5	$C_{16} H_{29} O_{11} N_2$

Figure S20 ^{1}H NMR spectrum of compound **9** in d_6-acetone + CF_3CO_2H after 2 h

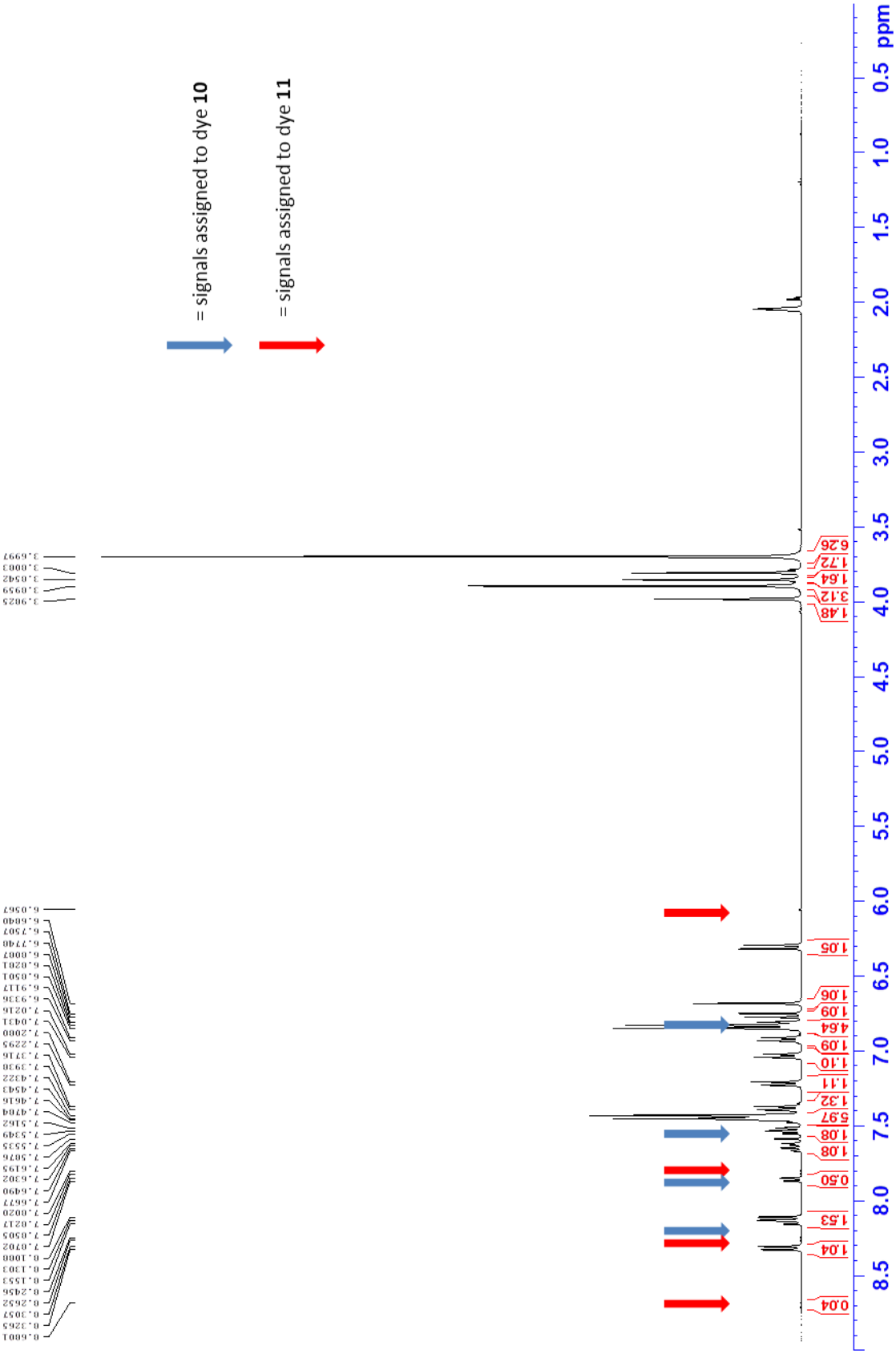


Figure S21 ^{1}H NMR spectrum of compound **10** in d_6-acetone + CF_3CO_2H after 2 h

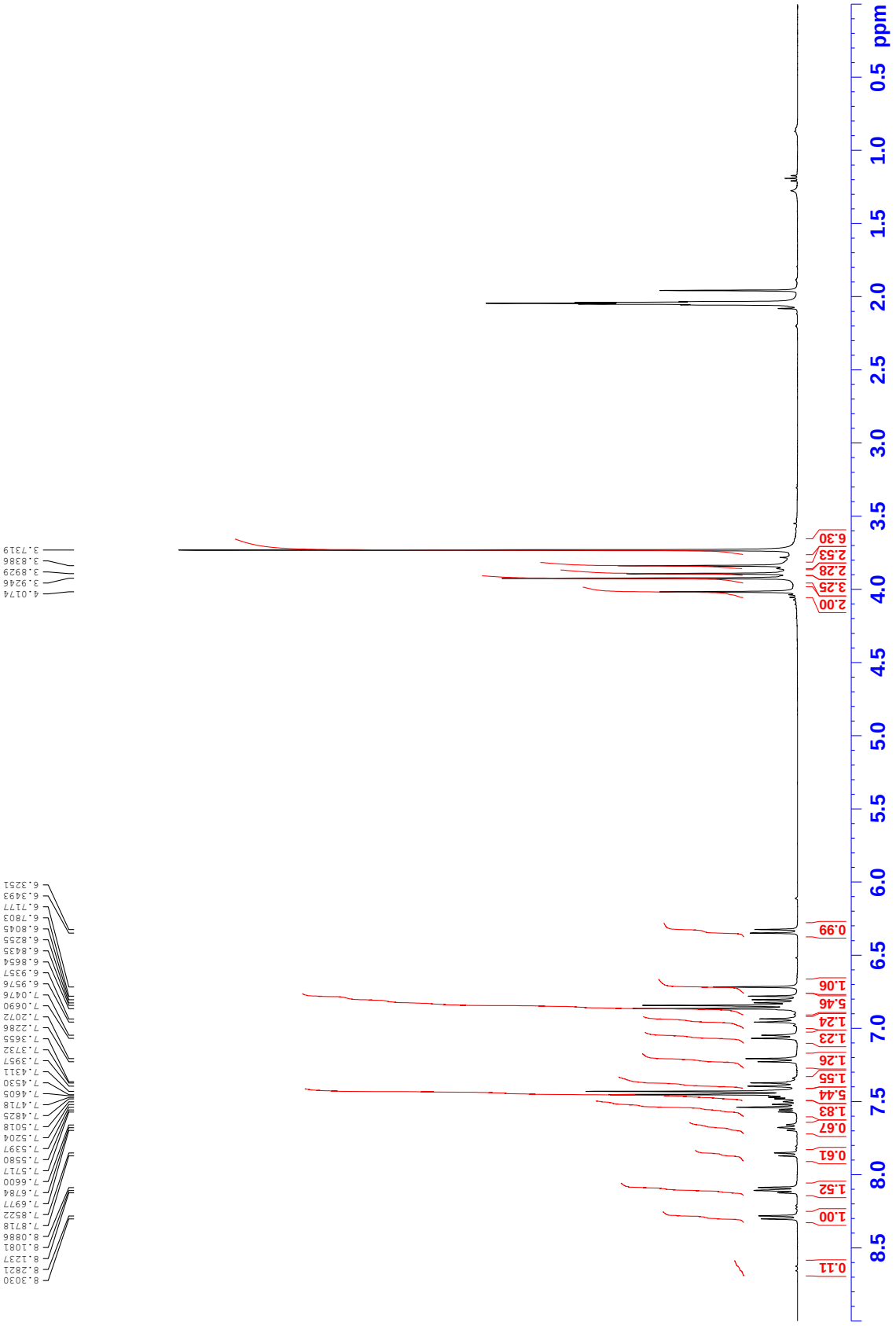


Figure S22 ^{1}H NMR spectrum of compound **12** in commercial $CDCl_3$

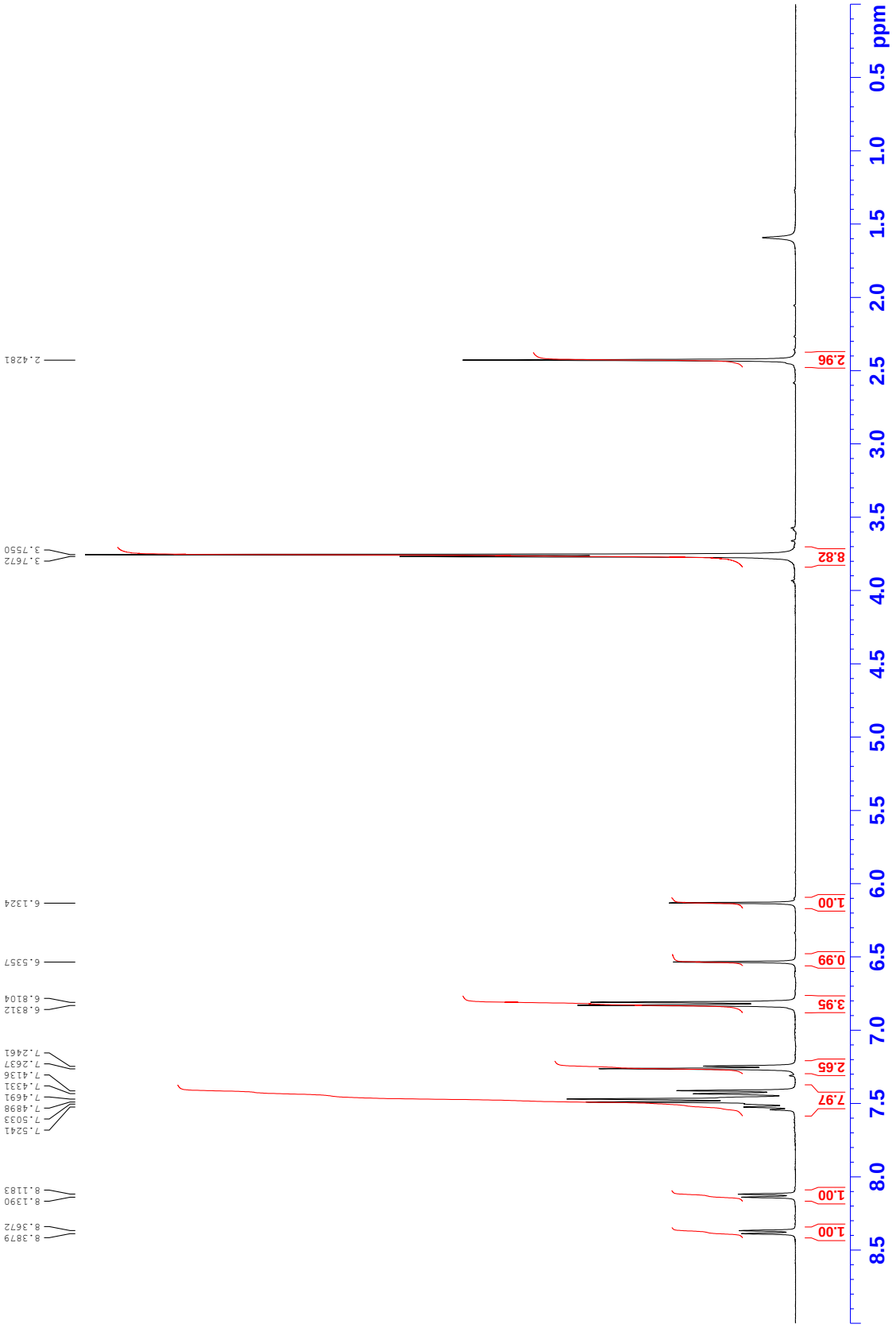


Figure S23 ^{13}C NMR spectrum of compound **12** in commercial $CDCl_3$

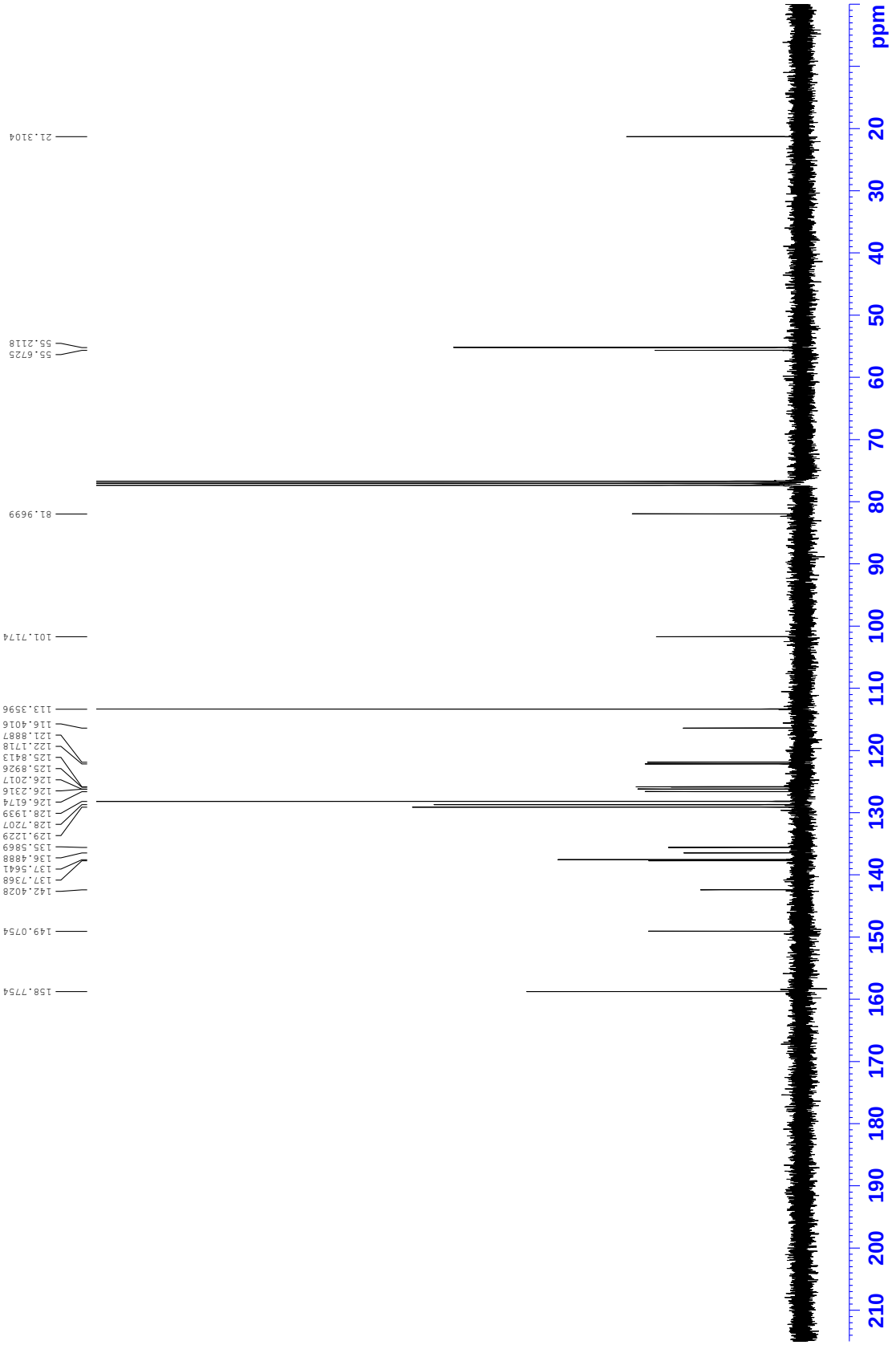
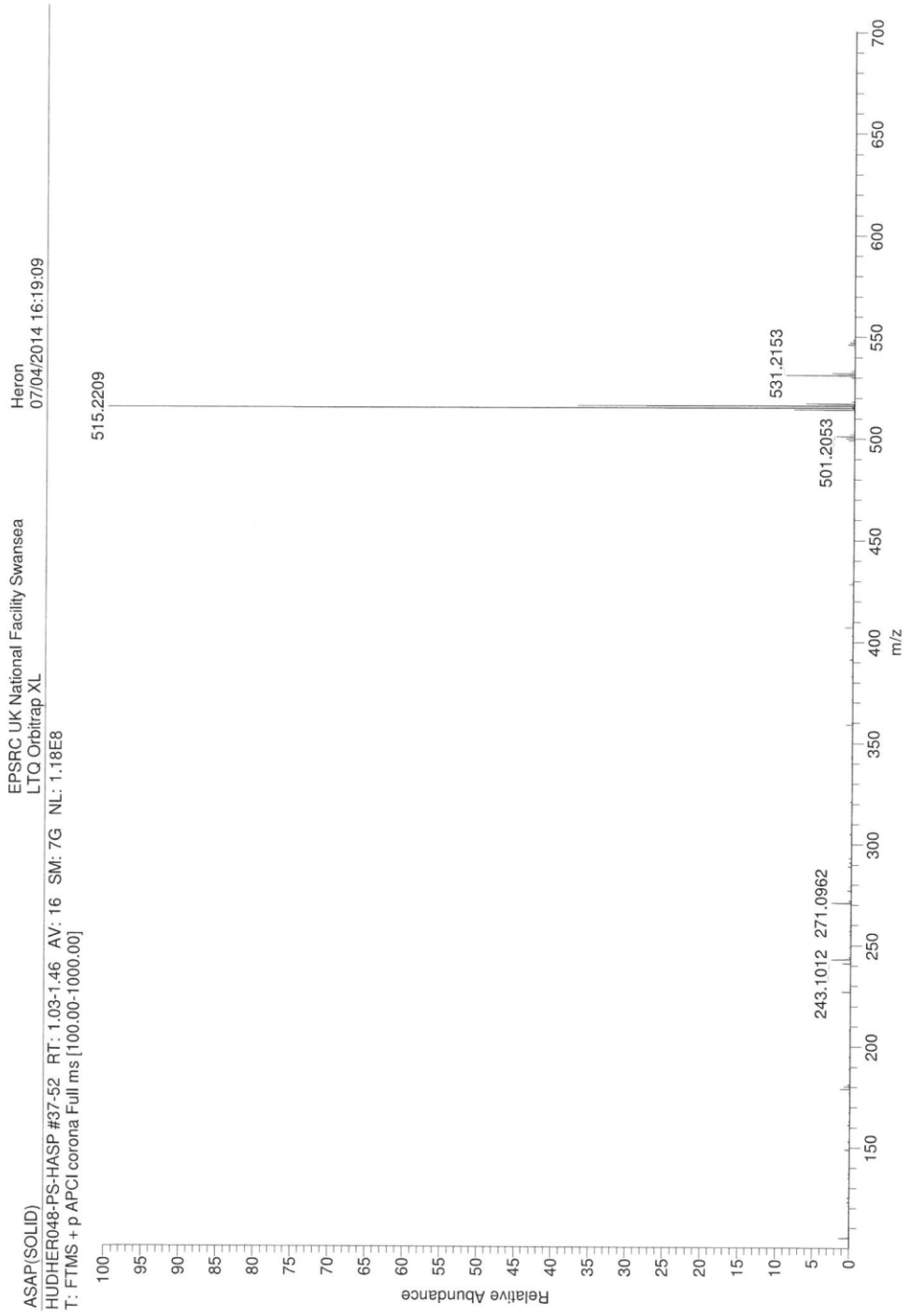
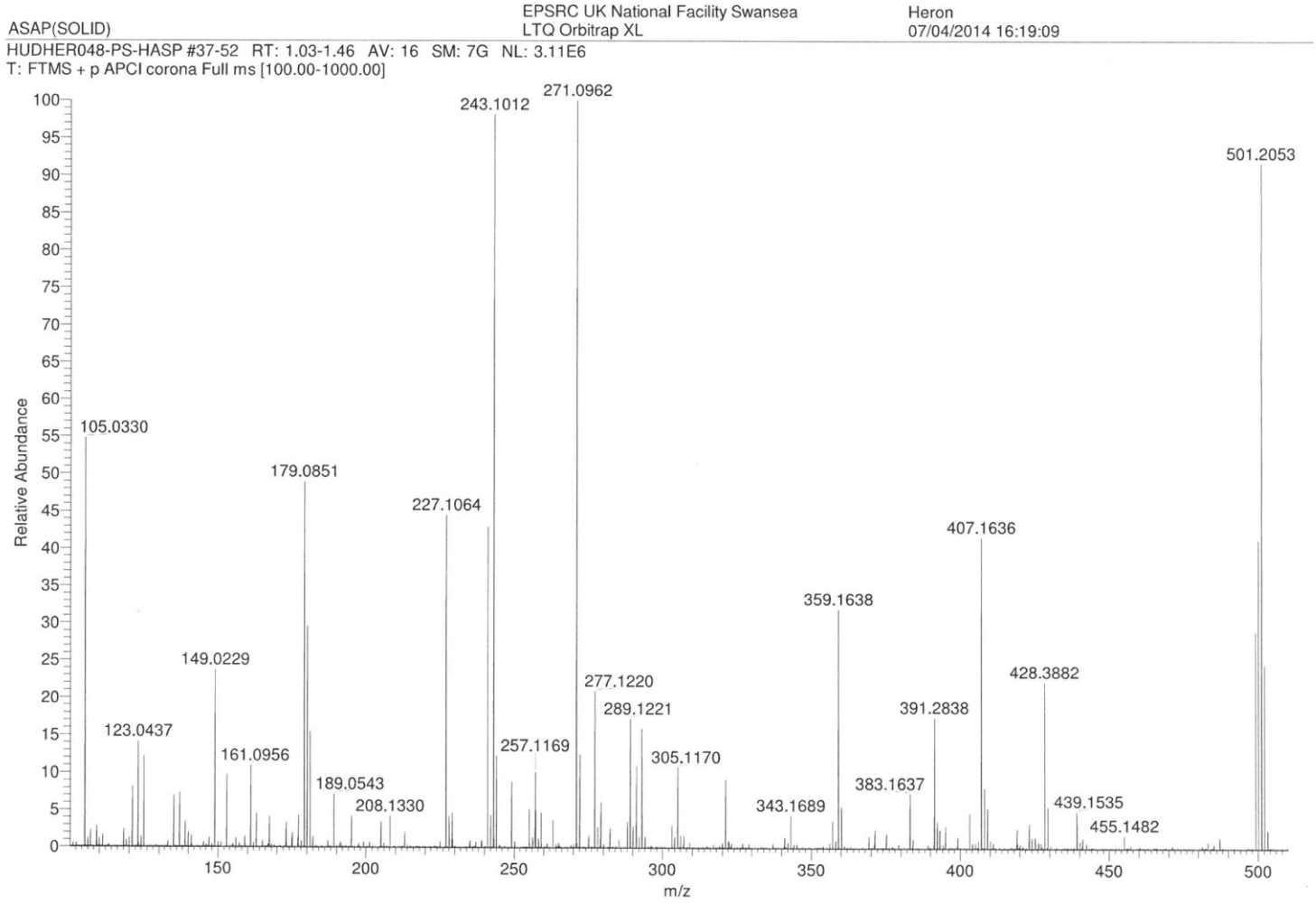


Figure S24 Mass Spectral data for compound **12**

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EPSRC UK National Facility Swansea
LTQ Orbitrap XL
Heron
07/04/2014 16:19:09
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T: FTMS + p APCI corona Full ms [100.00-1000.00]
Relative Abundance
m/z
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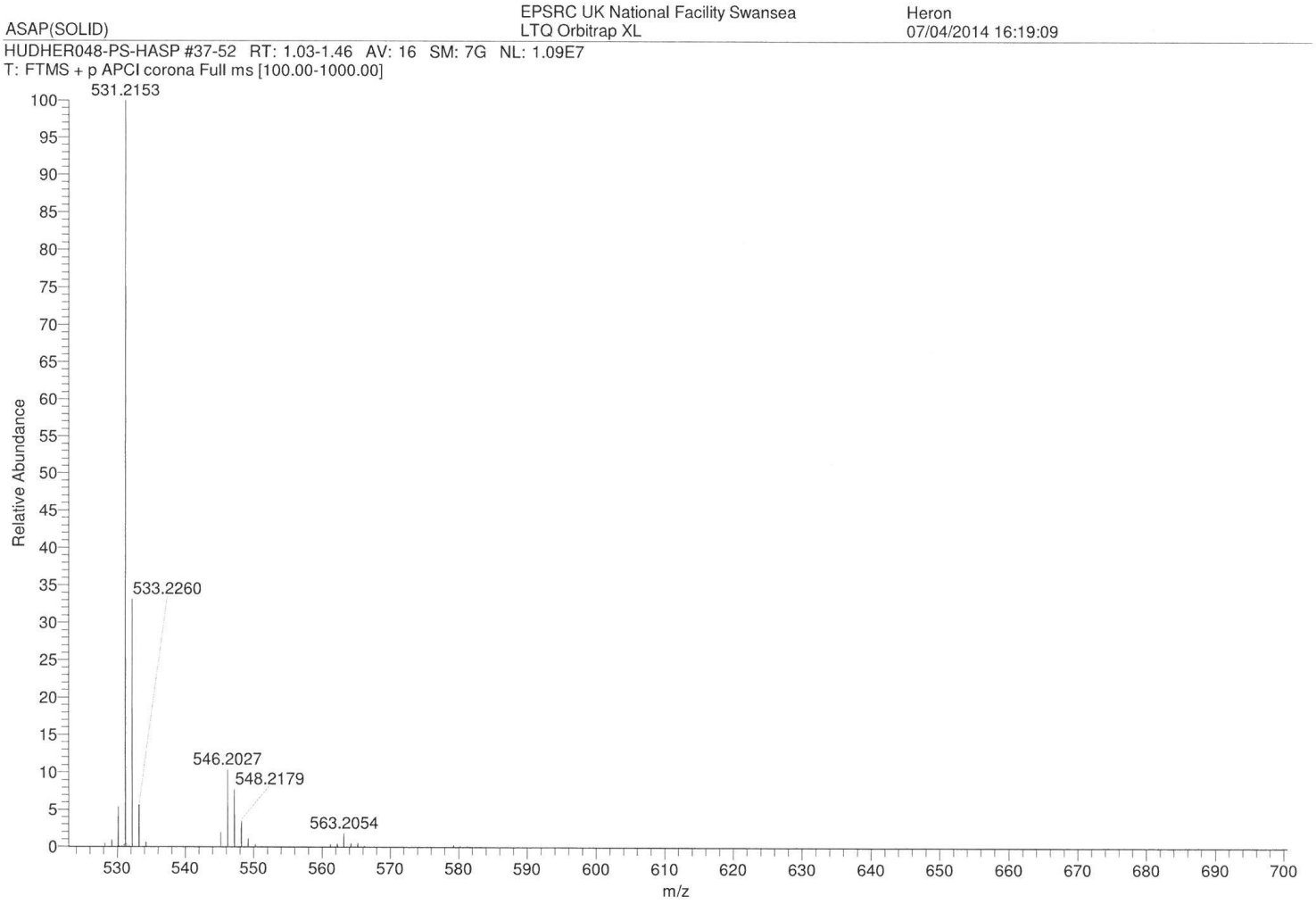
149.0229
161.0956
179.0851
189.0543
208.1330
227.1064
243.1012
257.1169
271.0962
277.1220
289.1221
305.1170
343.1689
359.1638
383.1637
391.2838
407.1636
428.3882
439.1535
455.1482
501.2053


ASAP(SOLID)
EPSRC UK National Facility Swansea
LTQ Orbitrap XL
Heron
07/04/2014 16:19:09
HUDHER048-PS-HASP #37-52 RT: 1.03-1.46 AV: 16 SM: 7G NL: 1.09E7
T: FTMS + p APCI corona Full ms [100.00-1000.00]
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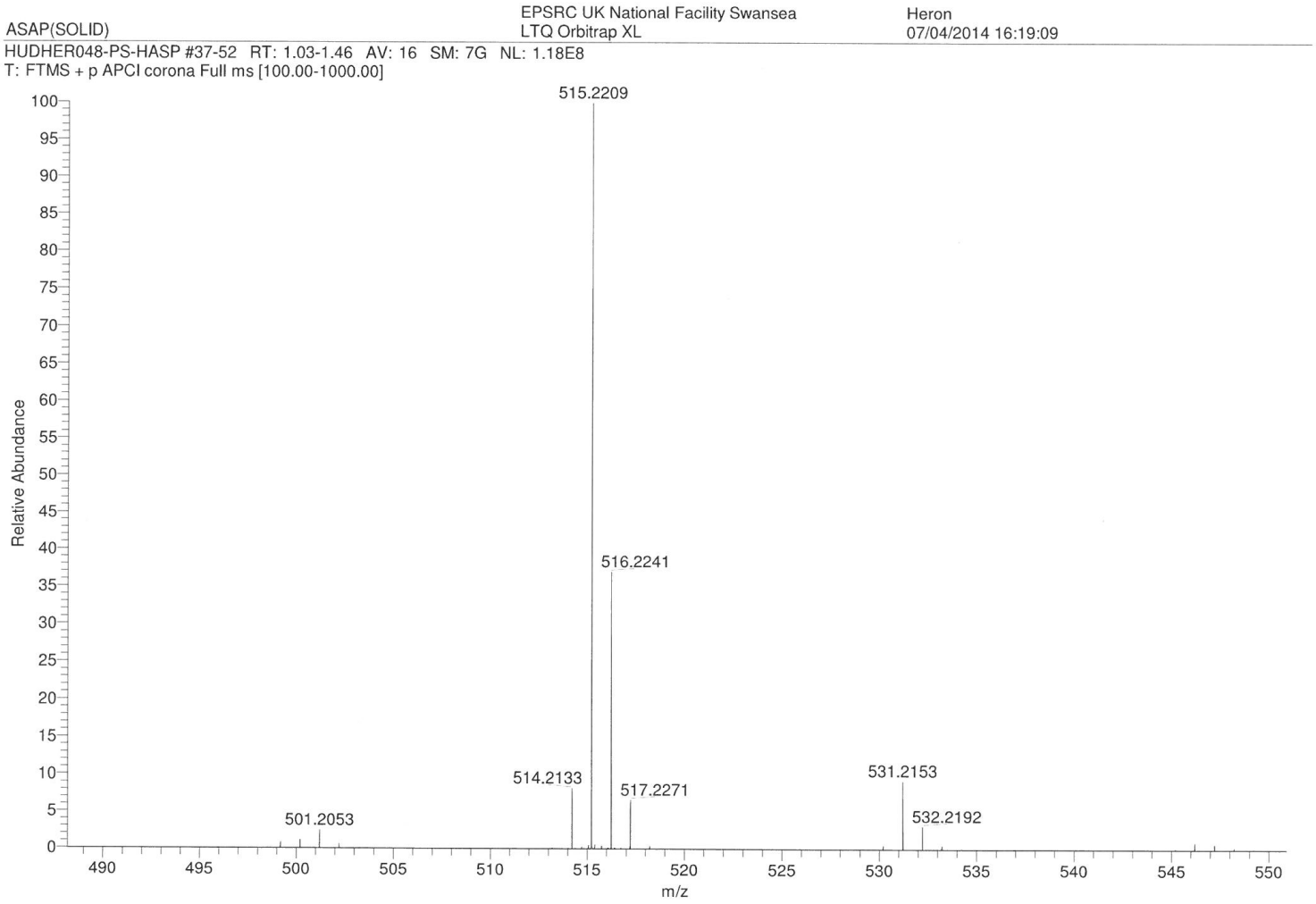
533.2260
546.2027
548.2179
563.2054
Relative Abundance
m/z


ASAP(SOLID)
EPSRC UK National Facility Swansea
LTQ Orbitrap XL
Heron
07/04/2014 16:19:09
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T: FTMS + p APCI corona Full ms [100.00-1000.00]
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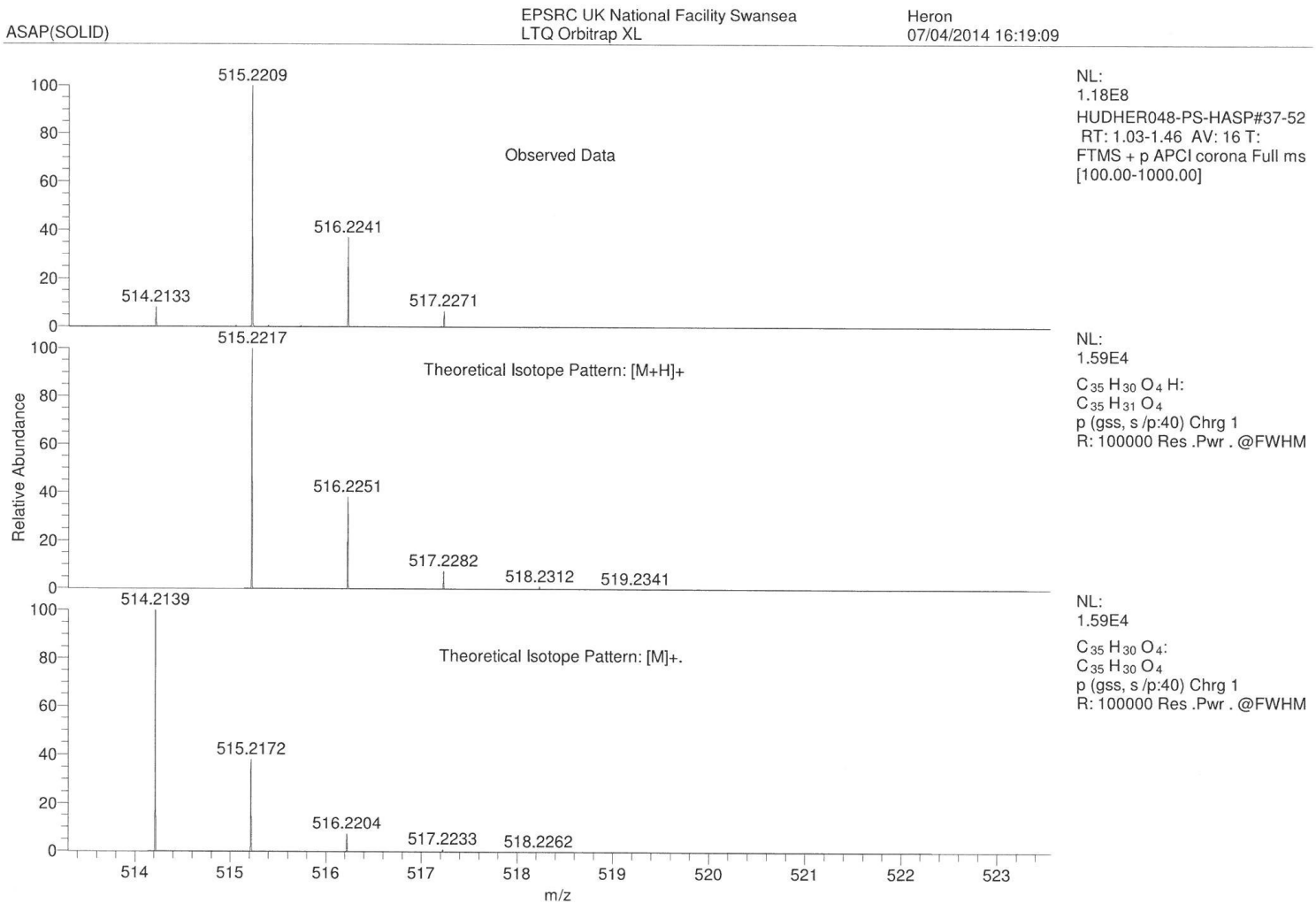
514.2133
517.2271
501.2053
531.2153
532.2192
Relative Abundance
m/z


ASAP(SOLID)
EPSRC UK National Facility Swansea
LTQ Orbitrap XL
Heron
07/04/2014 16:19:09
Observed Data
515.2209
516.2241
514.2133
517.2271
NL:
1.18E8
HUDHER048-PS-HASP#37-52
RT: 1.03-1.46 AV: 16 T:
FTMS + p APCI corona Full ms
[100.00-1000.00]
Theoretical Isotope Pattern: [M+H]+
515.2217
516.2251
517.2282
518.2312
519.2341
NL:
1.59E4
C35 H30 O4 H:
C35 H31 O4
p (gss, s /p:40) Chrg 1
R: 100000 Res .Pwr . @FWHM
Theoretical Isotope Pattern: [M]+.
514.2139
515.2172
516.2204
517.2233
518.2262
NL:
1.59E4
C35 H30 O4:
C35 H30 O4
p (gss, s /p:40) Chrg 1
R: 100000 Res .Pwr . @FWHM
Relative Abundance
m/z
0
20
40
60
80
100
514
515
516
517
518
519
520
521
522
523

Isotope:	Min. .. Max.		
14 N	0....14		
16 O	0....16		
12 C	0....90		
1 H	0....100		
23 Na	0....0		
Tolerance Window:	+- 5.00 ppm		
Db/Ring Equiv:	-3.. 100	N-Rule:	Do not use
Fits:	100	Charge:	1

Mass	Theoretical Mass	Delta [ppm]	RDB	Composition
515.2209	515.2209	0.1	3.0	$C_{20}H_{27}O_{14}N_{1}$
	515.2209	0.1	8.5	$C_{19}H_{31}O_{9}N_{8}$
	515.2203	1.1	21.0	$C_{33}H_{29}O_{3}N_{2}$
	515.2217	-1.5	20.5	$C_{35}H_{31}O_{4}$
	515.2222	-2.5	13.5	$C_{20}H_{27}O_{5}N_{12}$
	515.2222	-2.5	8.0	$C_{21}H_{33}O_{10}N_{5}$
	515.2195	2.7	3.5	$C_{18}H_{35}O_{13}N_{4}$
	515.2195	2.7	9.0	$C_{17}H_{29}O_{8}N_{11}$
	515.2190	3.7	21.5	$C_{31}H_{27}O_{2}N_{6}$
	515.2230	-4.1	25.5	$C_{36}H_{27}N_{4}$

Figure S25 ^{1}H NMR spectrum of compound **13** in commercial $CDCl_3$

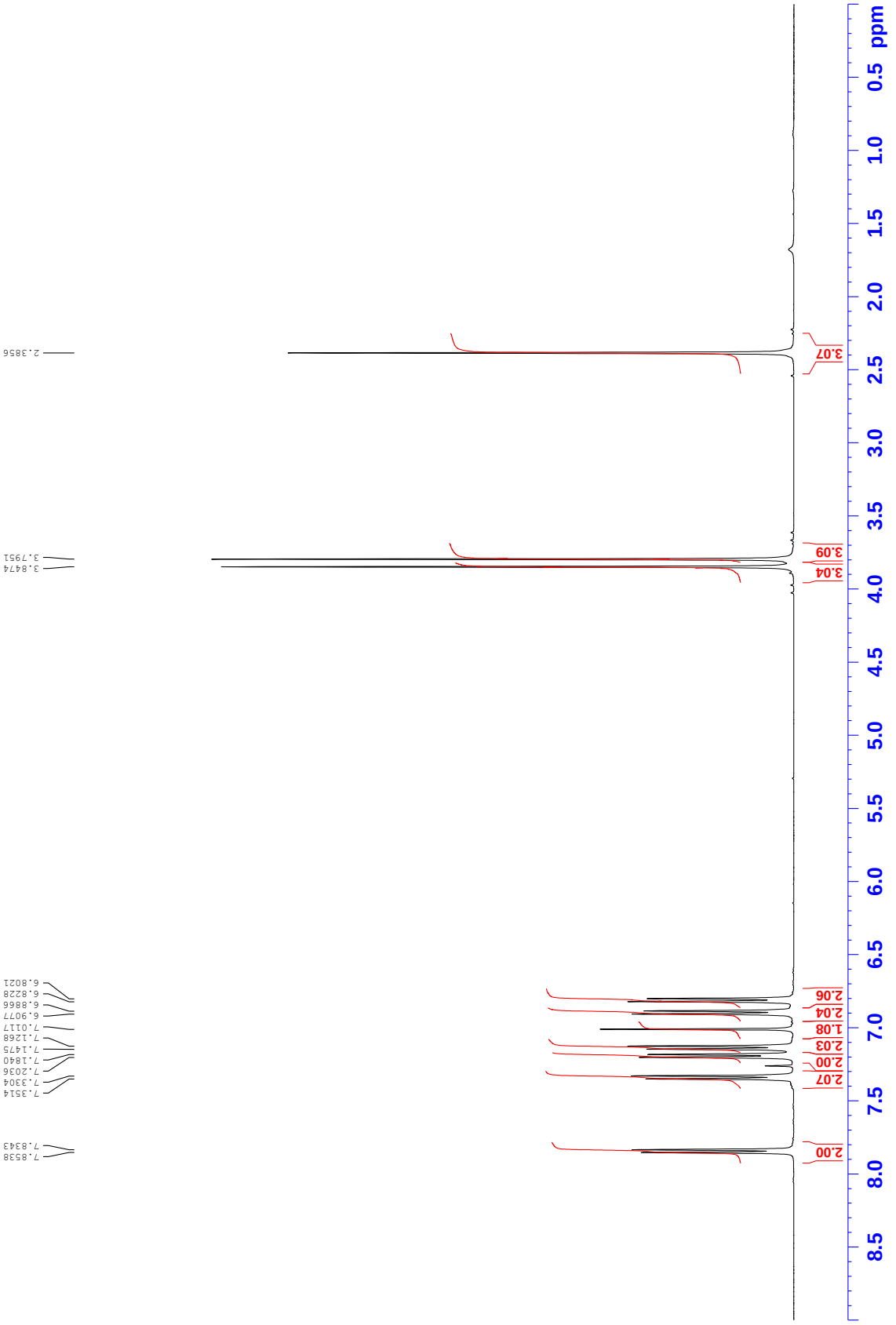


Figure S26 ^{13}C NMR spectrum of compound **13** in commercial $CDCl_3$

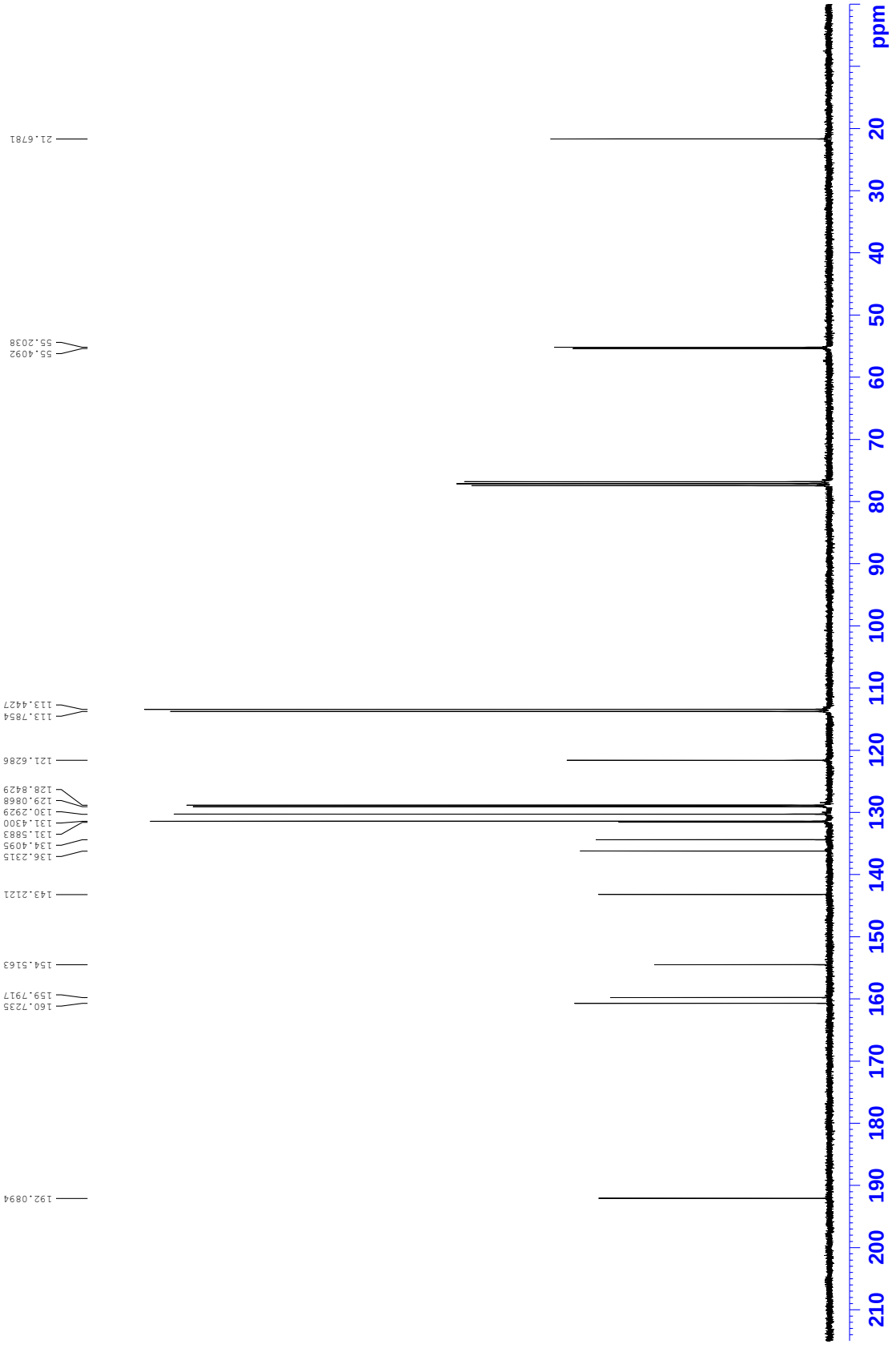
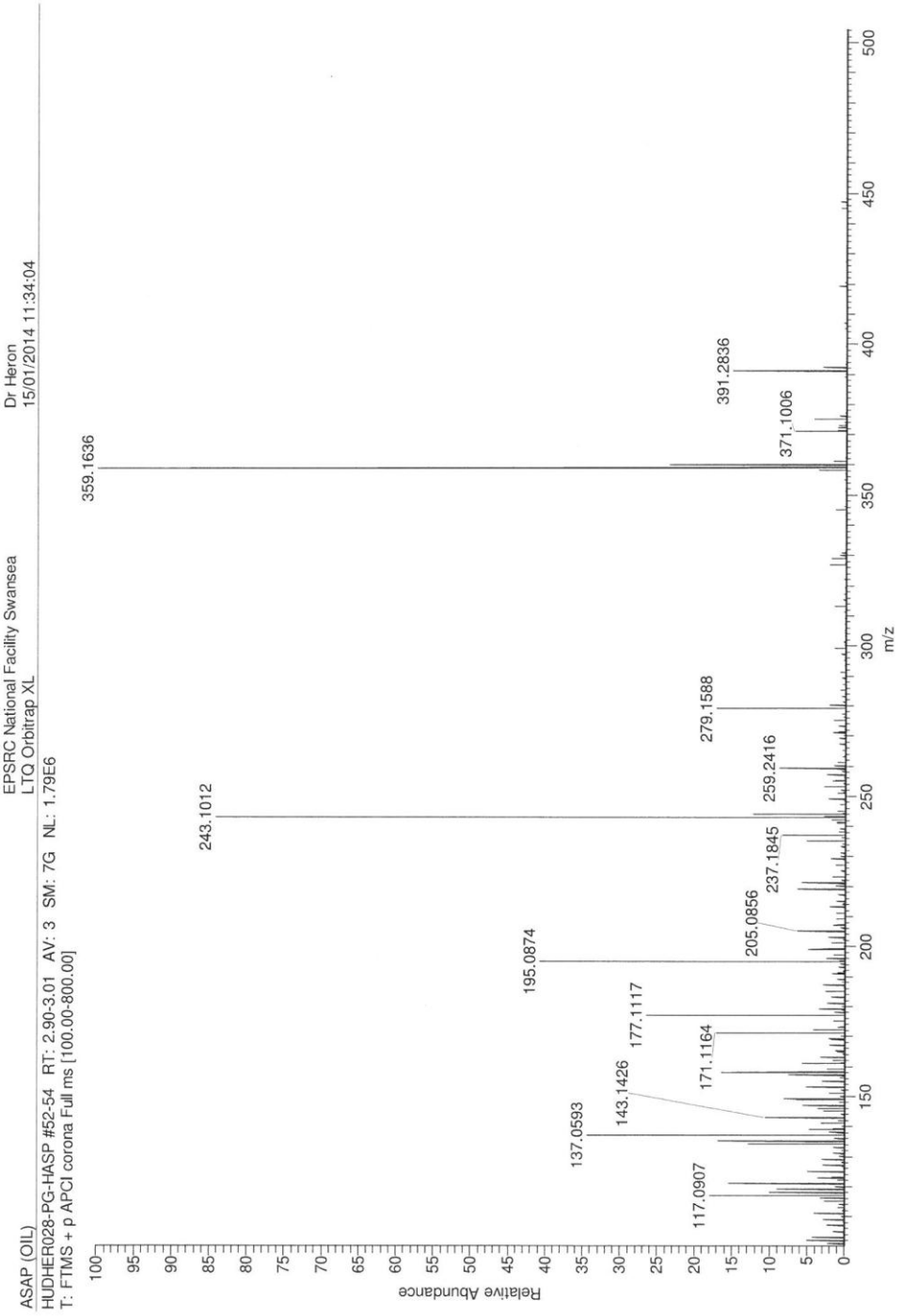
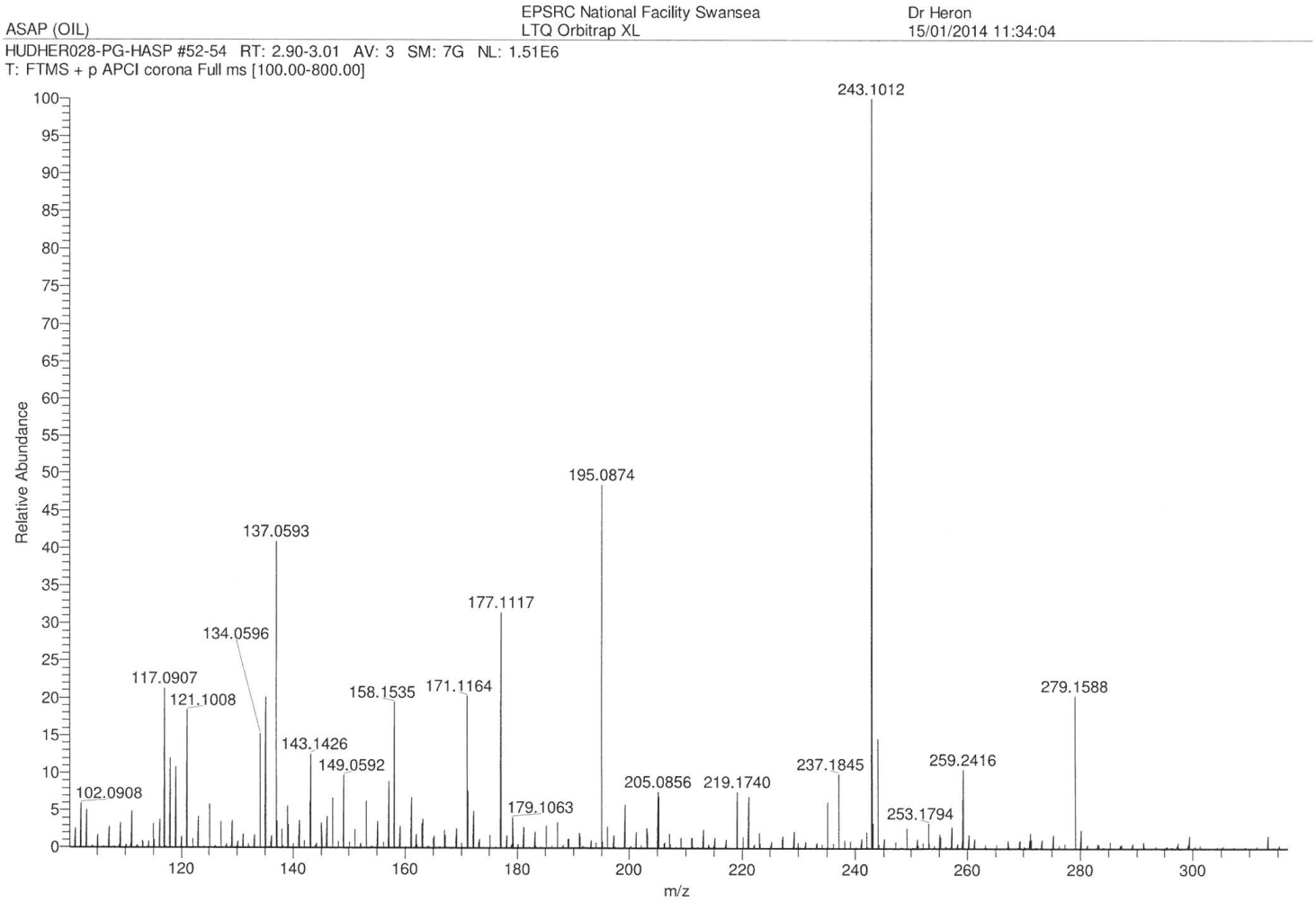


Figure S27 Mass Spectral data for compound **13**

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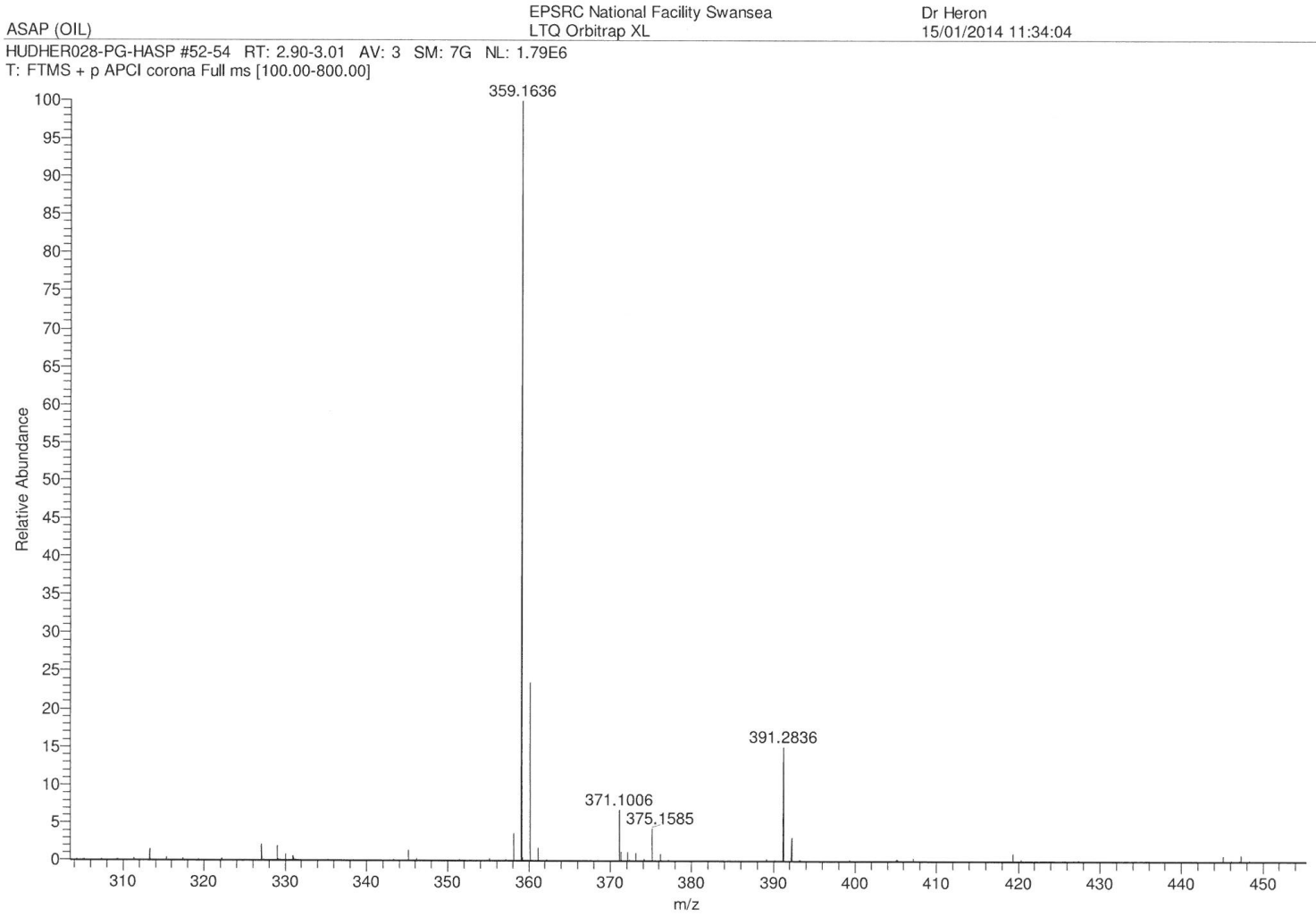
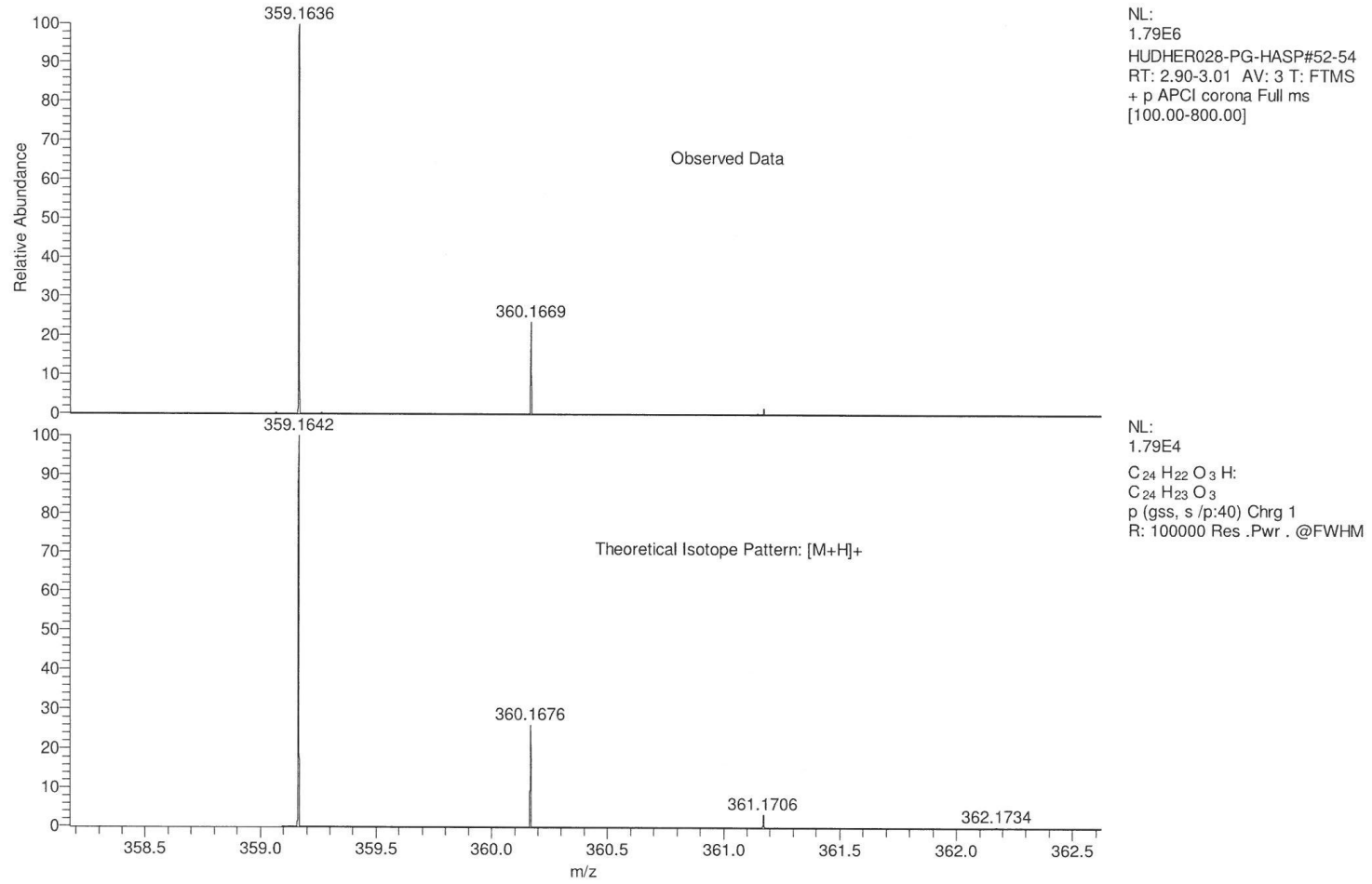
EPSRC National Facility Swansea
LTQ Orbitrap XL
Dr Heron
15/01/2014 11:34:04
HUDHER028-PG-HASP #52-54 RT: 2.90-3.01 AV: 3 SM: 7G NL: 1.51E6
T: FTMS + p APCI corona Full ms [100.00-800.00]
Relative Abundance
m/z
243.1012
195.0874
137.0593
177.1117
134.0596
117.0907
121.1008
158.1535
171.1164
279.1588
143.1426
149.0592
237.1845
259.2416
205.0856
219.1740
102.0908
179.1063
253.1794


ASAP (OIL)
EPSRC National Facility Swansea
LTQ Orbitrap XL
Dr Heron
15/01/2014 11:34:04
HUDHER028-PG-HASP #52-54 RT: 2.90-3.01 AV: 3 SM: 7G NL: 1.79E6
T: FTMS + p APCI corona Full ms [100.00-800.00]
359.1636
391.2836
371.1006
375.1585
Relative Abundance
m/z


ASAP (OIL)
EPSRC National Facility Swansea
LTQ Orbitrap XL
Dr Heron
15/01/2014 11:34:04
359.1636
NL:
1.79E6
HUDHER028-PG-HASP#52-54
RT: 2.90-3.01 AV: 3 T: FTMS
+ p APCI corona Full ms
[100.00-800.00]
Observed Data
360.1669
Relative Abundance
359.1642
NL:
1.79E4
C24 H22 O3 H:
C24 H23 O3
p (gss, s /p:40) Chrg 1
R: 100000 Res .Pwr . @FWHM
Theoretical Isotope Pattern: [M+H]+
360.1676
361.1706
362.1734
m/z

Isotope:	Min. .. Max.		
14 N	0....12		
16 O	0....13		
12 C	0....60		
1 H	0....70		
23 Na	0....0		
Tolerance Window:	+- 5.00 ppm		
Db/Ring Equiv:	-3.. 100	N-Rule:	Do not use
Fits:	100	Charge:	1

Mass	Theoretical Mass	Delta [ppm]	RDB	Composition
359.1636	359.1633	0.7	1.5	$C_8 H_{23} O_8 N_8$
	359.1642	-1.6	13.5	$C_{24} H_{23} O_5$
	359.1628	2.1	14.0	$C_{22} H_{21} O_2 N_3$
	359.1647	-3.0	6.5	$C_9 H_{19} O_4 N_{12}$
	359.1647	-3.0	1.0	$C_{10} H_{25} O_8 N_5$
	359.1620	4.5	2.0	$C_6 H_{21} O_7 N_{11}$

Cartesian coordinates (Å) for molecule **10** (ground-state) obtained by DFT [PCM-PBE0/6-31G(d)]

E= -1380.71673921 au

6	2.499386	-1.472469	0.290691
6	3.802944	-1.845077	0.366646
6	4.877383	-0.912922	0.048774
6	4.556871	0.403601	-0.342565
6	3.150105	0.853277	-0.441342
6	2.108103	-0.144894	-0.110712
1	6.473126	-2.305126	0.427107
1	1.720409	-2.181125	0.546744
6	6.224689	-1.293335	0.125791
6	5.581331	1.305535	-0.646540
6	6.911015	0.920003	-0.567693
6	7.228848	-0.385044	-0.179834
1	5.301704	2.311430	-0.944587
1	7.700801	1.626792	-0.805631
1	8.268709	-0.693947	-0.115979
8	2.879521	2.007326	-0.785977
6	0.802046	0.281515	-0.206156
6	-0.368556	-0.500609	-0.013669
1	0.678935	1.323699	-0.491365
1	-0.243829	-1.573428	0.114475
6	-1.658583	-0.025613	-0.021970
6	-1.968911	1.415413	-0.002719
6	-1.301548	2.301078	0.853361
6	-2.965183	1.948582	-0.843139
6	-1.589045	3.662526	0.869907
1	-0.559034	1.913623	1.545178
6	-3.252295	3.300503	-0.848160
1	-3.505302	1.287782	-1.515426
6	-2.565374	4.172329	0.009537
1	-1.057143	4.308666	1.559169
1	-4.008719	3.710433	-1.510761
6	-2.784113	-0.973745	-0.032199
6	-3.995988	-0.673703	0.620298
6	-2.689107	-2.217373	-0.674198
6	-5.042559	-1.576404	0.647171
1	-4.104601	0.277833	1.132413
6	-3.734952	-3.132560	-0.662612
1	-1.786729	-2.466782	-1.225481
6	-4.922911	-2.817164	0.005710
1	-5.968494	-1.344775	1.165098
1	-3.621161	-4.075154	-1.186316
8	4.244608	-3.068483	0.734845
8	-5.999708	-3.627913	0.080865
8	-2.922347	5.472630	-0.062380
6	-2.252764	6.393497	0.779911
1	-2.681086	7.370825	0.555099
1	-2.417830	6.159392	1.838259
1	-1.176071	6.412029	0.574271
6	-5.924755	-4.894954	-0.547659
1	-5.118273	-5.503910	-0.122606
1	-6.882769	-5.380085	-0.358010
1	-5.775709	-4.795667	-1.629275
6	3.277431	-4.045619	1.064849
1	2.673453	-3.730000	1.924126
1	3.834588	-4.947008	1.322101
1	2.617384	-4.252220	0.213699

Cartesian coordinates (Å) for molecule **10** (excited-state) obtained by DFT [PCM-PBE0/6-31G(d)]

E(TD)= -1380.64376071 au

6	2.519738	-1.355567	0.376330
6	3.857321	-1.743957	0.451403
6	4.901210	-0.847818	0.054644
6	4.544074	0.447391	-0.413878
6	3.146012	0.881422	-0.498942
6	2.128566	-0.088205	-0.084487
1	6.527009	-2.200337	0.478827
1	1.754620	-2.057185	0.690735
6	6.261892	-1.211323	0.119131
6	5.562368	1.329663	-0.802260
6	6.894797	0.958260	-0.735088
6	7.245395	-0.320976	-0.270477
1	5.269348	2.313015	-1.157956
1	7.670317	1.655072	-1.041505
1	8.290590	-0.612615	-0.217209
8	2.838804	2.020395	-0.907401
6	0.765524	0.331279	-0.178112
6	-0.357740	-0.431624	0.074394
1	0.647540	1.357867	-0.515463
1	-0.217097	-1.485658	0.308920
6	-1.707708	0.004319	0.023768
6	-2.053823	1.419427	0.044258
6	-1.341648	2.350439	0.827332
6	-3.128788	1.923796	-0.726810
6	-1.667869	3.698548	0.849648
1	-0.534141	1.998510	1.462102
6	-3.455144	3.264287	-0.724199
1	-3.689263	1.244409	-1.362432
6	-2.728773	4.169712	0.065754
1	-1.101657	4.370704	1.484947
1	-4.266723	3.644121	-1.337828
6	-2.759020	-0.993652	-0.037331
6	-4.054832	-0.747032	0.484495
6	-2.533529	-2.276436	-0.586060
6	-5.041204	-1.709462	0.462146
1	-4.267086	0.212377	0.946319
6	-3.518909	-3.251236	-0.617831
1	-1.571657	-2.502053	-1.037069
6	-4.787654	-2.975809	-0.090997
1	-6.022803	-1.513905	0.883810
1	-3.298233	-4.213691	-1.066375
8	4.262691	-2.944529	0.888769
8	-5.815447	-3.846745	-0.067574
8	-3.124873	5.456370	0.003922
6	-2.414703	6.412958	0.771363
1	-2.888127	7.373025	0.564052
1	-2.486605	6.195619	1.843374
1	-1.359845	6.455048	0.476567
6	-5.607774	-5.142855	-0.601590
1	-4.813718	-5.672201	-0.062285
1	-6.551047	-5.674049	-0.471738
1	-5.358769	-5.098193	-1.668161
6	3.295631	-3.897585	1.301061
1	2.712863	-3.524968	2.150559
1	3.860919	-4.778688	1.604132
1	2.623697	-4.157930	0.475935

Cartesian coordinates (Å) for molecule **11** (ground-state) obtained by DFT [PCM-PBE0/6-31G(d)]

E= -1380.71488583 au

6	-3.100579	0.963911	0.443573
6	-4.435672	0.721966	0.419442
6	-4.950115	-0.585084	0.042326
6	-4.042687	-1.606014	-0.310504
6	-2.578117	-1.378723	-0.312536
6	-2.118041	-0.038246	0.101743
1	-7.023864	-0.069393	0.290793
1	-2.724582	1.940432	0.732494
6	-6.326622	-0.855043	0.020569
6	-4.529030	-2.866539	-0.675054
6	-5.890834	-3.124506	-0.691546
6	-6.789686	-2.111518	-0.341949
1	-3.807189	-3.631852	-0.943133
1	-6.258148	-4.106857	-0.974554
1	-7.858639	-2.306735	-0.353629
8	-1.812088	-2.288102	-0.651807
6	-0.781247	0.305418	0.182565
6	0.358395	-0.517724	-0.018683
1	-0.582566	1.335106	0.479941
1	0.173181	-1.575010	-0.167856
6	1.660951	-0.072430	0.003244
6	2.007835	1.360630	-0.014773
6	1.382491	2.256486	-0.891825
6	2.994956	1.875965	0.847438
6	1.702323	3.610937	-0.909428
1	0.648632	1.881075	-1.599513
6	3.313147	3.220943	0.852001
1	3.502607	1.207004	1.536786
6	2.668854	4.103101	-0.028091
1	1.203941	4.264832	-1.616264
1	4.062159	3.617419	1.531017
6	2.760696	-1.048262	0.022545
6	4.000783	-0.764865	-0.583580
6	2.613130	-2.305953	0.627783
6	5.024609	-1.693406	-0.599600
1	4.150181	0.194813	-1.069411
6	3.634965	-3.247108	0.626341
1	1.685605	-2.546555	1.139418
6	4.852542	-2.946039	0.005729
1	5.972314	-1.473618	-1.082104
1	3.479476	-4.200049	1.119749
8	-5.401333	1.618348	0.729888
8	5.910074	-3.782520	-0.055032
8	3.054584	5.395148	0.045306
6	2.431556	6.325230	-0.822100
1	2.877869	7.293503	-0.593186
1	2.619446	6.078184	-1.873658
1	1.350379	6.372335	-0.646341
6	5.781052	-5.063644	0.535268
1	4.973819	-5.638873	0.066996
1	6.732043	-5.569000	0.363977
1	5.598203	-4.989322	1.613665
6	-4.991474	2.915802	1.112195
1	-4.371187	2.885178	2.016314
1	-5.905762	3.474215	1.316138
1	-4.432903	3.408464	0.306956

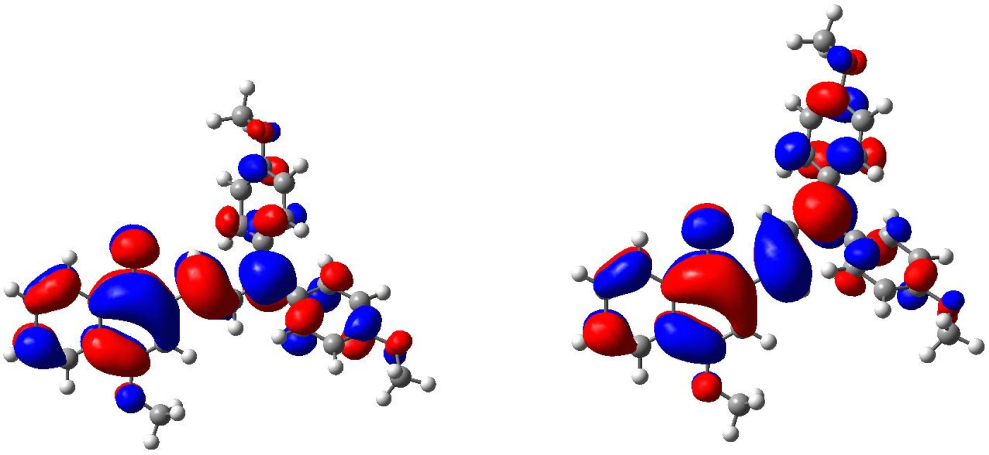
Cartesian coordinates (Å) for molecule **11** (excited-state) obtained by DFT [PCM-PBE0/6-31G(d)]

E(TD)= -1380.64377307au

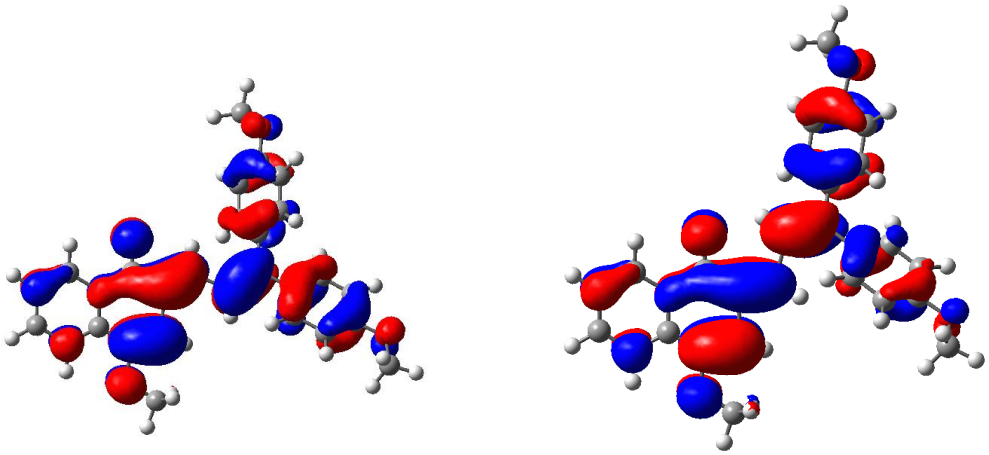
6	-3.067820	1.000552	0.408841
6	-4.445955	0.791145	0.377769
6	-4.970650	-0.494356	0.036335
6	-4.054434	-1.541015	-0.260904
6	-2.597945	-1.347055	-0.223316
6	-2.127372	-0.005988	0.120347
1	-7.047608	0.057131	0.220388
1	-2.687993	1.986202	0.661295
6	-6.357119	-0.747904	-0.009959
6	-4.563413	-2.805189	-0.592988
6	-5.927465	-3.039789	-0.637093
6	-6.829884	-2.003447	-0.342681
1	-3.849837	-3.592988	-0.814786
1	-6.301445	-4.025765	-0.899696
1	-7.900043	-2.187739	-0.375953
8	-1.824317	-2.297201	-0.474083
6	-0.742824	0.359247	0.184059
6	0.349237	-0.437239	-0.100788
1	-0.556020	1.380407	0.515743
1	0.130840	-1.467162	-0.363354
6	1.711911	-0.038018	-0.046536
6	2.097792	1.368049	-0.044300
6	1.423247	2.324407	-0.829627
6	3.169455	1.838058	0.752072
6	1.782969	3.664865	-0.832064
1	0.620073	1.997720	-1.483466
6	3.528216	3.170434	0.769980
1	3.701257	1.138715	1.390781
6	2.840226	4.101449	-0.024349
1	1.246090	4.356991	-1.471471
1	4.337301	3.523730	1.402531
6	2.731514	-1.067182	-0.003149
6	4.050703	-0.839257	-0.473703
6	2.449536	-2.367347	0.476884
6	5.006727	-1.832006	-0.463322
1	4.307110	0.131517	-0.886598
6	3.403731	-3.372139	0.495717
1	1.463779	-2.584812	0.877048
6	4.697743	-3.112875	0.024217
1	6.006880	-1.649081	-0.845261
1	3.138226	-4.347571	0.888490
8	-5.354896	1.737694	0.653320
8	5.699459	-4.013492	-0.005708
8	3.267788	5.377595	0.058016
6	2.600331	6.357666	-0.717444
1	3.094761	7.303395	-0.493725
1	2.688782	6.145532	-1.789319
1	1.540811	6.426845	-0.444852
6	5.435414	-5.325395	0.460685
1	4.645295	-5.805011	-0.128533
1	6.366627	-5.879089	0.337849
1	5.151028	-5.321319	1.519325
6	-4.915234	3.040586	1.003331
1	-4.308470	3.019263	1.915192
1	-5.821191	3.619922	1.180432
1	-4.342350	3.494875	0.187501

Frontier molecular orbitals obtained for **10** and **11**

LUMO



HOMO



10 **11**

Vibrationally resolved spectrum (stick+convoluted) computed for **10** and **11**

We note that the spectra are more structured than experimentally, but this is only related to the choice of a rather narrow broadening Gaussian, allowing to see that the vibrational couplings are indeed similar for the two dyes, but that the absolute intensities (ε) are not.