Alaska Department of Transportation & Public Facilities

Research & Technology Transfer

Specialized Testing of Asphalt Cements from Various ADOT&PF Paving Projects

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13. ABSTRACT (Maximum 200 words)

The Alaska Department of Transportation and Public Facilities (ADOT&PF) sampled five different asphalt cements for specialized testing at Queen's University in Kingston, Ontario. This report documents and discusses the findings. The tested asphalts were: PG 58-34, PG 52-40D, PG 52-40N, PG 58-28, and PG 64-28. Testing results showed that grade losses according to Ontario's LS-308 Extended Bending Beam Rheometer (EBBR) ranged from 3.4°C to 6.3°C. Losses according to Ontario's LS-228 Modified Pressure Aging Vessel (PAV) ranged from 0°C to 7.3°C. Grade losses of 3°C and higher are significant in terms of their ability to reduce pavement life cycles. Double-edge-notched tension (DENT) tests according to Ontario's LS-299 DENT protocol were done on PAV residues. The critical crack tip opening displacement (CTOD) was determined and, at 15°C, it varied from a low of 19 mm for the PG 58-28 to a high of 175 mm for the PG 58-34. The PG 58- 40D showed a CTOD of 139 mm, contrasting with the low polymer PG 52-40N at only 36 mm, a nearly four-fold difference. All the results obtained from this specialized testing effort suggest that these materials will provide significant differences in performance. This report provides recommendations on how to obtain better value for money by implementing a few simple changes to the ADOT&PF asphalt cement specifications.

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METRIC (SI*) CONVERSION FACTORS

APPROXIMATE CONVERSIONS TO SI UNITS

Symbol	When You Know	Multiply By	To Find	Symbol
		LENGTH		
in	inches	25.4		mm
ft	feet	0.3048		m
yd	yards	0.914		m
mi	Miles (statute)	1.61		km
		AREA		
in^2	square inches	645.2	millimeters squared	cm^2
ft^2	square feet	0.0929	meters squared	m^2
yd^2	square yards	0.836	meters squared	m^2
mi^2	square miles	2.59	kilometers squared	km^2
ac	acres	0.4046	hectares	ha
		MASS (weight)		
oz	Ounces (avdp)	28.35	grams	g
lb	Pounds (avdp)	0.454	kilograms	kg
T	Short tons (2000 lb)	0.907	megagrams	mg
		VOLUME		
fl oz	fluid ounces (US)	29.57	milliliters	mL
gal	Gallons (liq)	3.785	liters	liters
ft^3	cubic feet	0.0283	meters cubed	m^3
yd^3	cubic yards	0.765	meters cubed	m^3

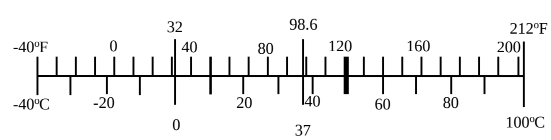
Note: Volumes greater than 1000 L shall be shown in m^3

Symbol	When You Know	Multiply By	To Find	Symbol
		TEMPERATURE (exact)		
ºF	Fahrenheit temperature	5/9 (ºF-32)	Celsius temperature	ºC
		ILLUMINATION		
fc	Foot-candles	10.76	lux	lx
fl	foot-lamberts	3.426	candela/m^2	cd/cm^2
		FORCE and PRESSURE or STRESS		
lbf	pound-force	4.45	newtons	N
psi	pound-force per square inch	6.89	kilopascals	kPa

These factors conform to the requirement of FHWA Order 5190.1A *SI is the symbol for the International System of Measurements

APPROXIMATE CONVERSIONS FROM SI UNITS

Symbol	When You Know	Multiply By	To Find	Symbol
		LENGTH		
mm	millimeters	0.039	inches	in
m	meters	3.28	feet	ft
m	meters	1.09	yards	yd
km	kilometers	0.621	Miles (statute)	mi
		AREA		
mm^2	millimeters squared	0.0016	square inches	in^2 m^2
	meters squared	10.764	square feet	ft^2 km^2
	kilometers squared	0.39	square miles	mi^2 ha
	hectares (10,000 m^2)	2.471	acres	ac
		MASS (weight)		
g	grams	0.0353	Ounces (avdp)	oz
kg	kilograms	2.205	Pounds (avdp)	lb mg
	megagrams (1000 kg)	1.103	short tons	T
		VOLUME		
mL	milliliters	0.034	fluid ounces (US)	fl oz
liters	liters	0.264	Gallons (liq)	gal
m^3	meters cubed	35.315	cubic feet	ft^3
m^3	meters cubed	1.308	cubic yards	yd^3
		TEMPERATURE (exact)		
ºC	Celsius temperature	9/5 ºC+32	Fahrenheit temperature	ºF
		ILLUMINATION		
lx	lux	0.0929	foot-candles	fc
cd/cm^2	candela/m^2	0.2919	foot-lamberts	fl
		FORCE and PRESSURE or STRESS		
N	newtons	0.225	pound-force	lbf
kPa	kilopascals	0.145	pound-force per square inch	psi



EXECUTIVE SUMMARY

During the 2013-2014 construction seasons, the Alaska Department of Transportation and Public Facilities (ADOT&PF) sampled five different asphalt cements from the following paving projects:

Binder Can Label	Supplier	Project / Region
PG 58-34	A	Anchorage Airport #53598 / Central
PG 52-40 D	B	Deadhorse Airport #14-236 / Northern
PG 52-40 N	C	Nome Airport #61413 / Northern
PG 58-28	C	HYD Salmon River Rd #68602 / Southcoast
PG 64-28	C	JNU Yandukin Dr #68045 / Southcoast

Samples of the five asphalts were sent to Queen's University in Kingston, Ontario for specialized performance testing. This report documents and discusses the findings of the investigation.

Infrared (IR) spectroscopic analysis showed a reasonable but variable amount of Styrene-Butadiene (SB) type polymer modifier, typically used to prepare better quality asphalt grades. The two PG 52-40 binders showed styrene indices that differed by nearly a factor of two, suggesting that one of the two suppliers likely used a hybrid technology to reach the 92°C (52+40) grade span.

Phosphorous-31 nuclear magnetic resonance (NMR) spectroscopy confirmed that all binders were free of polyphosphoric acid (PPA), which is often used as a low-cost replacement for SB-type polymers to reach modified grades. Carbon-13 NMR and X-ray fluorescence (XRF) analysis further showed no signs of recycled engine oil bottoms (REOB), another common substitute, in any of the samples. Hence, it is possible/likely that the PG 52-40N binder with the significantly lower SB content was modified with additional wax, air-blown residue, and/or pitch, or that it was prepared through the blending of two incompatible base asphalts.

The IR spectra showed no major carbonyl peaks in any of the samples, ruling out the presence of other deleterious additives (e.g., vegetable oils, tall oils, etc.).

X-ray fluorescence analysis showed major zinc peaks in the PG 52-40D and PG 58-28 binders, which likely originate from the deliberate addition of zinc oxide as a hydrogen sulfide scavenger.

Four of the five samples graded within a degree or two from their designated AASHTO M320 grades while the fifth (PG 58-28) graded to meet all the requirements for a PG 64-28. Hence, it is likely that a PG 64-28 grade is shipped in a single vessel and stored in a single tank but sold under both PG 58-28 and PG 64-28 designations.

Grade losses according to Ontario's LS-308 Extended Bending Beam Rheometer (EBBR), which addresses the physical hardening phenomenon, ranged from 3.4°C to 6.3°C. A grade loss of 6°C, over a 72 hours period of cold conditioning, typically reduces the confidence that in a given winter the road is not damaged from the intended 98% reliability to around 50%. Grade losses of 3°C and higher are thus significant in terms of their ability to reduce pavement life cycles by considerable amounts.

Grade losses according to Ontario's LS-228 Modified Pressure Aging Vessel (PAV), which assesses a binder's durability in terms of oxidative hardening, ranged from 0°C to 7.3°C. Again, large differences will most likely result in significant performance variability in terms of thermal and fatigue cracking distress.

Double-edge-notched tension (DENT) tests according to Ontario's LS-299 DENT protocol were done on PAV residues. The critical crack tip opening displacement (CTOD), which reflects strain tolerance in the ductile state under severe constraint, was determined at temperatures of 5°C, 10°C and 15°C. At 15°C, the CTOD varied from a low of 19 mm for the PG 58-28 to a high of 175 mm for the PG 58-34. The PG 58- 40D showed a CTOD of 139 mm, contrasting with the low SB PG 52-40N at only 36 mm, a nearly four-fold difference. It is therefore likely that the PG 52-40N is significantly more susceptible to fatigue cracking distress than the PG 52-40D.

All the results obtained from this specialized testing effort suggest that these materials will provide significant differences in performance over the coming years. This report provides recommendations on how to obtain better value for money by implementing a few simple changes to the ADOT&PF asphalt cement specifications.

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1.0 OBJECTIVES AND SCOPE

The Superpave™ asphalt cement specification is known to provide less than adequate control of thermal and fatigue cracking, with binders of identical grades often showing from best-case to worst-case performance [Hesp et al., *Proc. CTAA*, 2009]. While the basic foundation of Superpave appears to be sound, the main deficiency in its implementation across North America has been that it largely relies on rheological properties in the linear viscoelastic (LVE) regime, it lacks a measure of strain tolerance in ductile failure, and it lacks measures of durability for both oxidative and physical aging/hardening [Hesp et al., *Proc. CTAA*, 2009].

The Superpave grade consists of high (XX), intermediate (II) and low (YY) limiting temperatures, as determined by dynamic shear rheometer (DSR) and bending beam rheometer (BBR) testing at low strains and different temperatures. Materials are tested after minimal conditioning at various temperatures to obtain pass and fail properties. Continuous grades are subsequently determined by interpolation to the acceptance criterion for the particular grading test. Modified binders are those with grade spans (XX+YY) that are typically above 86°C [Varadaraj et al., *Can. Pat. 2512192*, 2006; Kodrat et al., *JTRB*, 2007]. Such materials can be obtained through a wide range of approaches: polymers (SB, SBS, RET, SBR), acids (PPA, H_2SO_4, H_3PO_4, sulfonic), bases (NaOH), waxes (Fischer-Tropsch, oxidized PE, naphthenic wax), air-blown residues, recycled engine oil bottoms (REOB), vegetable oils, and a range of others, as well as combinations of the aforementioned, can be used to increase Superpave grade spans of marginal base asphalts. The problem that arises is that not all base asphalts and modifiers are of equal cost and benefit. Suppliers and contractors are often motivated by using the most economical solutions to reach a given grade. Hence, binders sold in North America can show widely variable performance largely due to the abovementioned inadequacies of test protocols.

Materials sampled from five ADOT&PF paving projects were tested at Queen's University in order to measure their performance-based properties provided under improved Ontario specification test protocols. Binders came from three different suppliers. Testing included chemical analysis utilizing IR, NMR and XRF and further assessment of durability and strain tolerance in extended BBR (Ontario method LS-308), DENT (Ontario method LS-299) and modified PAV (Ontario method LS-228). This report documents and discusses the findings of the investigation.

2.0 Investigative Approach

2.1 Rolling Thin Film Oven (RTFO) and Pressure Aging Vessel (PAV) Treatment

Tank asphalt cement samples provided were aged according to standard RTFO (AASHTO T 240) and PAV (AASHTO R 28) protocols to produce aged residue for further testing in the dynamic shear rheometer (DSR) according to AASHTO method T 315, bending beam rheometer (BBR) according to AASHTO method T 313 and MTO method LS-308, and double-edge-notched tension (DENT) tester according to MTO method LS-299.

After all tests were completed, PAV residues were aged for a further 20 h according to Ontario method LS-228 and subsequently tested in the BBR at pass and fail temperatures and in the DSR at both intermediate and high temperatures. Limiting temperatures for BBR and DSR tests were determined according to standard protocols by interpolation.

A flow chart of the standard Superpave tests conducted is provided in Figure 1.

Figure 1 – Schematic for Superpave Testing for Performance Grade XX-II-YY.

2.2 Infrared Spectroscopy (IR)

Infrared spectroscopy is based on the absorbance of incident radiation in the infrared by specific chemical bonds increasing their vibrational energy.

The method provides a semi-quantitative measure for the presence of styrene-butadiene (SBS) polymer through absorbance peaks from the butadiene functionality at wavenumbers between 983 cm^{-1} and 955 cm^{-1}, and the styrene functionality between 710 cm^{-1} and 690 cm^{-1}.

In addition to the detection of SB-type polymer modifiers in the asphalt, IR can also provide a measure of the degree of oxidation from the carbonyl peak at wavenumbers between 1760 cm^{-1} and 1655 cm^{-1}.

Figure 2 provides an image of the Perkin-Elmer IR spectrometer used for this investigation.

FIGURE 2 – Perkin Elmer Spectrum 400 Infrared Spectrometer used for the detection of butadiene, styrene and carbonyl in ADOT&PF binders. Courtesy: Perkin Elmer Company.

2.3 X-Ray Fluorescence (XRF)

X-ray fluorescence analysis is a technique that provides a quantitative measure for the presence of a wide range of metals and other elements such as sulfur (S), phosphorous (P), bromine (Br) and silicon (Si), which are sometimes found in modified asphalt binders.

The material to be analyzed is irradiated with high energy X-rays of 40 keV, which generate holes within the inner shells of most heavy atoms. The holes formed are subsequently filled by outer shell electrons falling into the inner shell holes. This fall is accompanied by the emission of fluorescent X-rays of element specific energies that are less than 40 keV. The XRF analyzer detects the emitted X-rays and the software provides a number of counts versus energy. From specific peaks in the spectrum it is then possible to obtain qualitative and sometimes quantitative information regarding the presence of a large number of elements provided a reference material with known concentrations of these elements is available for comparison. Figure 3 provides a schematic of the XRF analysis and Figure 4 provides an actual image of the hand-held XRF analyzer.

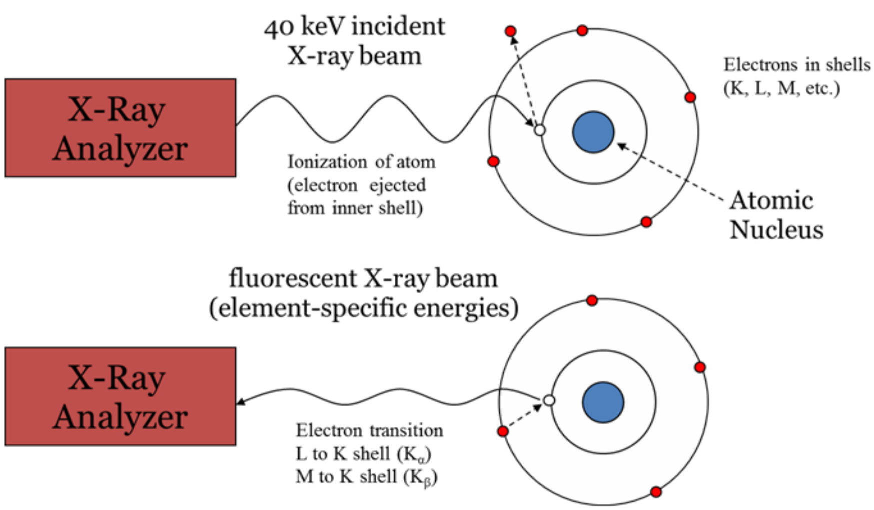

FIGURE 3 – Schematic of the X-ray analysis procedure.

FIGURE 4 – Handheld Bruker XRF analyzer used for the detection of zinc (Zn), copper (Cu), chromium (Cr), lead (Pb), molybdenum (Mo), bromine (Br), and other elements of interest. Courtesy: Bruker Corporation.

2.4 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Nuclear magnetic resonance (NMR) spectroscopy was used to detect phosphorous, polyisobutylene (from REOB), SB-type modifiers, and other as yet unknown additives. The NMR spectrometer applies a very high magnetic field to the samples that are irradiated with known frequency radio waves. Nuclei with an uneven number of particles (H-1, C-13, Si-29, P-31, others) possess a net magnetic moment that aligns to a limited degree with the external field. There are two semi-stable orientations of the individual spins; one aligned and another opposed to the external field. Transitions between the two states occur when the sample inside the magnet is irradiated at frequencies that are specific to the local magnetic field strength, which is influenced by electron clouds around atoms in the direct vicinity.

Figure 5 provides a photograph of the Bruker UltraShield™ 600 MHz NMR spectrometer used for the analysis of ADOT&PF asphalt cements.

FIGURE 5 – Bruker UltraShield 600 MHz NMR spectrometer used for the collection of phosphorous-31, proton, and carbon-13 spectra on ADOT&PF asphalt cements.

2.5 AASHTO M320 Grade Verification and MSCR Testing

The AASHTO M320 Superpave grades for the recovered binders were determined according to standard procedures embodied in AASHTO R 29-08 *Grading or Verifying the Performance Grade (PG) of an Asphalt Binder.*

The limit on $G^*/\sin\delta$ to determine the high temperature grade for the PAV-aged binders was set at 2.2 kPa, equal to that specified for an RTFO residue.

Multiple stress creep recovery testing was conducted according to standard protocols outlined in AASHTO standard test method T350-14.

2.6 Extended Bending Beam Rheometer Testing

The PAV-aged binders were tested according to standard procedures embodied in MTO LS-308 *Determination of Performance Grade of Physically Aged Asphalt Cement Using Extended Bending Beam Rheometer (BBR) Method* (MTO 2009). The extended BBR test determines the tendency of binder to physically harden during cold conditioning and T + 10 and T + 20, where T denotes the pavement design temperature (-28°C, -34°C and -40°C for these materials).

2.7 Double-Edge-Notched Tension Testing

The PAV-aged binders were tested according to standard procedures embodied in MTO LS-299 *Determination of Asphalt Cement's Resistance to Ductile Failure Using Double-Edge-Notched Tension Test (DENT)*. The DENT test determines the failure strain of a tiny fiber (fibril) of asphalt cement at 15°C at a rate of 50 mm/min. Samples were conditioned for three hours prior to testing. After testing at 15°C in duplicate the residues were reheated and poured once more for single measurements at both 10°C and 5°C.

Figure 6 provides a photograph of the force-ductility instrument and the specimens with three different notch depths just prior to testing in a water bath.

(a)  (b) 

FIGURE 6 – (a) PetroLab force-ductility machine as used for the double-edge-notched tension (DENT) test according to Ontario method LS-299 and (b) close-up of specimens just prior to testing (water left out of bath for image clarity).

3.0 RESULTS AND DISCUSSIONS

3.1 INFRARED SPECTROSCOPY

Infrared spectra were obtained for all tank samples. These spectra were collected to check for the presence of styrene and butadiene (SBS triblock, SB diblock or SBR random copolymer), to monitor the consistency of the polymer loading, and to check for the presence of oxidation products.

The binders were all found to contain minor quantities of styrene and butadiene and only the PG 58-34 contained a small carbonyl signal. Figure 7 provides the area of interest in the IR spectrum of the PG 58-34 binder.

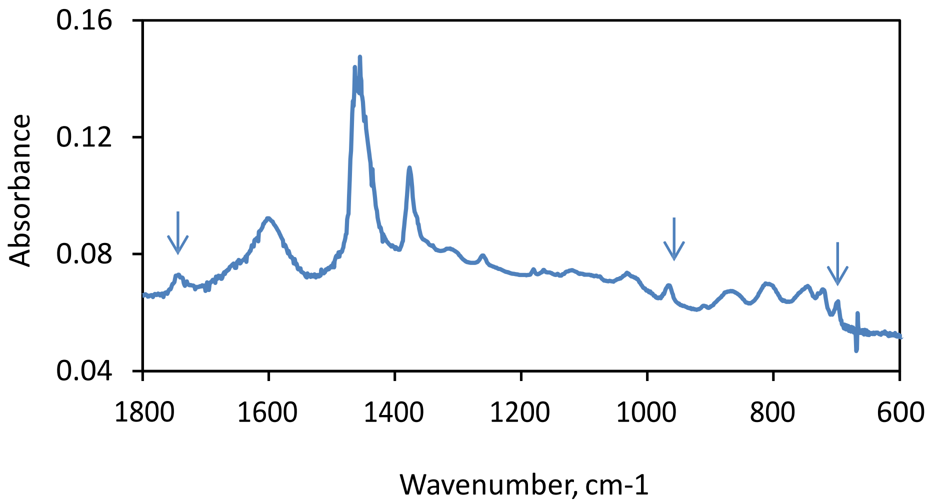

Figure 7 – Infrared spectrum for an asphalt binder with small carbonyl (1760-1655 cm^{-1}), butadiene (983-955 cm^{-1}) and styrene (710-690 cm^{-1}) peaks.

Table 1 provides a listing of all the IR results obtained for these samples. The peak indices were calculated by dividing individual peak areas by the area of a large internal standard methylene (CH_2) peak between 3,121 cm^{-1} and 2,746 cm^{-1}.

TABLE 1 – IR FINDINGS FOR ADOT&PF ASPHALT CEMENTS

Sample	Supplier	Carbonyl Index	Styrene Index	Butadiene Index
PG 58-34	A	0.0053	0.0024	0.0032
PG 52-40D	B	0.0014	0.0021	0.0034
PG 52-40N	C	0.0000	**0.0012**	**0.0020**
PG 58-28	C	0.0015	0.0011	0.0018
PG 64-28	C	0.0000	0.0016	0.0026

The carbonyl, styrene and butadiene indices for these tank samples are reasonable and suggest there were no issues with contamination or absence of polymer. Styrene indices for municipal contracts in Ontario range from 0.0013 to 0.0017.

It is noteworthy that the PG 52-40N contains only 57% of the SB-type polymer compared to the PG 52-40D of the same grade span (0.0012/0.0021). It is further interesting to note that the PG 58-28, which is normally an unmodified grade in most of North America, contains a considerable amount of SB-type polymer.

3.2 X-Ray Fluorescence

All binders were tested with XRF. There was no detectable amount of molybdenum suggesting that REOB is absent from the five binders. XRF test results for the five binders investigated in this project are provided in Table 2. The strong zinc signals in two of the binders may have originated, in part, from zinc oxide that is sometimes added as a hydrogen sulfide scavenger.

TABLE 2 – XRF FINDINGS FOR ADOT&PF ASPHALT CEMENTS

Sample	Supplier	Zinc Counts	Molybdenum Counts	Sulfur Counts
PG 58-34	A	140	0	3200
PG 52-40D	B	**44000**	0	3245
PG 52-40N	C	60	0	6000
PG 58-28	C	**5400**	0	5000
PG 64-28	C	0	0	6362

3.3 Nuclear Magnetic Resonance Testing

All samples were tested in NMR for the detection of potential additives. No remarkable findings can be reported. The proton (H-1), HSQC (C-13 versus H-1), DOSY (diffusion coefficient versus H-1), and P-31 spectra are provided in the appendices to this report.

3.4 AASHTO M320 Grade Verification and MSCR Testing

The AASHTO M320 grades for the binders were determined according to standard AASHTO R 29 procedures. The high temperature grade represents the temperature where the $G^*/\sin\delta$ property of the RTFO binder reaches 2.2 kPa and the low temperature is the warmest of the two temperatures where the creep stiffness, S(60 s), reaches 300 MPa, or the creep rate, m(60 s), reaches 0.300. Table 3 provides a summary of the experimental findings.

TABLE 3 – AASHTO M320 GRADES FOR ADOT&PF ASPHALT CEMENTS

Sample	Supplier	XX-II-YY	Grade Span	$G^*/\sin\delta$ = 2.2 kPa (PAV)
PG 58-34	A	59-10-35	94	65
PG 52-40D	B	57-5-40	97	65
PG 52-40N	C	51-5-41	92	**67**
PG 58-28	C	66-16-32	98	75
PG 64-28	C	66-14-33	99	78

The PG 52-40N binder misses the high temperature grade requirement by 1°C. However, in practice, these grade measurements have a minor degree of random error so this likely constitutes a pass.

The high temperature grades all significantly increase upon PAV aging compared to their RTFO samples. This change reflects how susceptible the materials are to further oxidation. The increase in high temperature grade for the PG 52-40N is a worrisome 16°C (67-51) while for the superior PG 58-34 it is a lesser 6°C (65-59).

Multiple stress creep recovery (MSCR) testing was conducted to measure the resistance to rutting. The MSCR test provides an improved measure of resistance to repeated wheel loading. All the samples in this study were tested under repeated shear loadings of 20 cycles at 100 Pa followed by 10 cycles at 3,200 Pa at a temperature of 52°C. Table 4 provides the findings for these samples.

TABLE 4 – MULITPLE STRESS CREEP RECOVERY DATA FOR ADOT&PF BINDERS

Sample	Supplier	100 Pa		3,200 Pa		Difference, %	
		ER, %	J_{nr}, kPa	ER, %	J_{nr}, kPa	ER	J_{nr}
PG 58-34	A	92	0.10	78	0.30	15	**203**
PG 52-40D	B	94	0.09	81	0.32	15	**256**
PG 52-40N	C	86	0.34	49	1.65	43	**378**
PG 58-28	C	48	0.33	36	0.43	26	31
PG 64-28	C	68	0.21	57	0.29	16	40

ER = elastic recovery, J_{nr} = non-recoverable creep compliance.

The results show that the first three binders in the table are rather shear sensitive with increases in the non-recoverable creep compliance (Jnr) of well over 200%. However, rutting resistance is largely determined by the aggregate properties and the mix design. Hence, these MSCR results are less of a concern than the findings related to cracking susceptibilities, which are largely determined by the asphalt cement properties.

3.5 Extended Bending Beam Rheometer Testing (LS-308)

The extended BBR test was conducted by storing the PAV-aged binders at 10°C and 20°C above their lower grade temperatures (YY+10 and YY+20), followed by testing for pass and fail properties after 1, 24 and 72 hours of conditioning. All stiffness and m-values used to calculate the limiting grades are averages of three separate measurements. Hence, a single LS-308 grade and grade loss determination involves 36 measurements of 72 data points over a three day period. Table 5 provides a summary of the findings while the complete data sets are provided in the appendices to this report.

TABLE 5 – LS-308 GRADES AND GRADE LOSSES FOR ADOT&PF BINDERS

Sample	Supplier	XX-II-YY	LS-308 EBBR Grade, °C	LS-308 Grade Loss, °C
PG 58-34	A	59-10-35	-31	4.1
PG 52-40D	B	57-5-40	**-35**	**5.4**
PG 52-40N	C	51-5-41	-38	3.4
PG 58-28	C	66-16-32	**-26**	**5.9**
PG 64-28	C	66-14-33	**-26**	**6.3**

The results are important in several respects. First, the grade losses are all moderate to high. Best performance in this test has been found to be binders from Laguna, Venezuela, which typically lose close to nothing when conditioned for extended periods of time at cold temperatures [Hesp et al., 2007]. Laguna asphalt cement is widely used in Sweden and that is one of the reasons for why the roads in that country look much better than in North America. The best quality western Canadian crude oils found in the Cold Lake, Bow River, and Lloydminster regions produce binders that lose approximately 2 to 4°C during three days of cold conditioning. Average commercial binders sold in Ontario lose just less than 6°C, while worst quality binders extracted from prematurely cracked pavements lose 10°C or more when tested according to the LS-308 protocol.

The grades after 72 h of cold conditioning fail to meet the contract requirements of -28°C, -34°C and -40°C by anywhere from 2 to 5°C. While this does not appear to be significant, it should be realized that the PAV protocol is also deficient and therefore the deficits in low temperature properties are likely significantly worse. Therefore, these pavements are under-designed for thermal cracking distress.

3.6 Double-Edge-Notched Tension Testing (LS-299)

The DENT test was conducted on PAV residues and the findings are summarized in Table 6. The PG 52-40N with the lower SB polymer content suffers from low essential work and CTOD. These are dramatically lower at both 10°C and 15°C compared to the PG 52-40D material. The plastic work of failure term, βw_p, is also very low (and close to zero) reflecting its inability to transmit and distribute vehicle loads. Hence, the binder is expected to perform worst in terms of fatigue cracking.

Other binders are rather average (PG 58-28 and PG 64-28) or somewhat above average (PG 58-34 and PG 52-40).

TABLE 6 – LS-299 DENT PROPERTIES FOR ADOT&PF BINDERS

Sample	**Supplier**	**XX-II-YY**	5°C		
			w_e, kJ.m^{-2}	βw_p, MJ.m^{-3}	CTOD, mm
PG 58-34	A	59-10-35	22	3.9	15
PG 52-40D	B	57-5-40	25	2.1	30
PG 52-40N	C	51-5-41	**26**	**0.2**	**29**
PG 58-28	C	66-16-32	**14**	**2.7**	**6.5**
PG 64-28	C	66-14-33	**6.9**	**3.6**	**2.4**

Sample	**Supplier**	**XX-II-YY**	10°C		
			w_e, kJ.m^{-2}	βw_p, MJ.m^{-3}	CTOD, mm
PG 58-34	A	59-10-35	29	2.9	47
PG 52-40D	B	57-5-40	18	2.1	50
PG 52-40N	C	51-5-41	**13**	**0.4**	**32**
PG 58-28	C	66-16-32	24	2.1	12
PG 64-28	C	66-14-33	24	2.1	14

Sample	**Supplier**	**XX-II-YY**	15°C		
			w_e, kJ.m^{-2}	βw_p, MJ.m^{-3}	CTOD, mm
PG 58-34	A	59-10-35	33	0.9	175
PG 52-40D	B	57-5-40	19	0.9	139
PG 52-40N	C	51-5-41	**7**	**0.2**	**36**
PG 58-28	C	66-16-32	16	2.5	19
PG 64-28	C	66-14-33	20	1.4	24

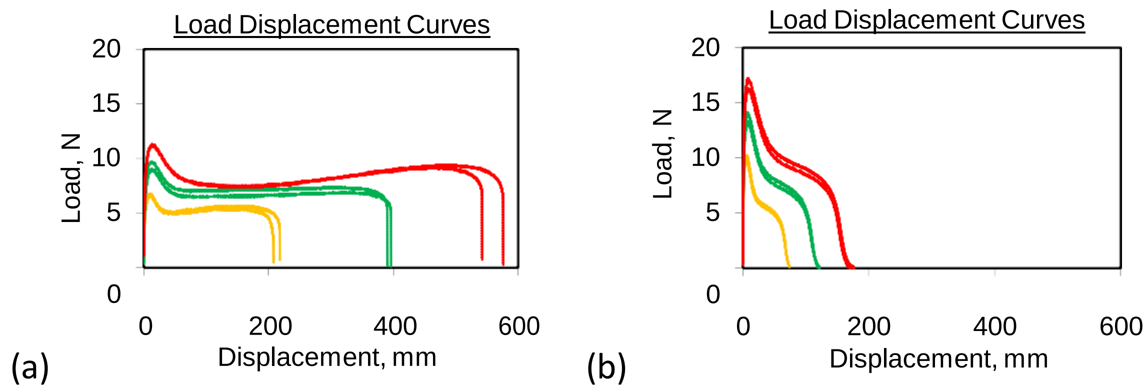

Figure 8 – Duplicate force-displacement curves for (a) PG 52-40D and (b) PG 52-40N at a temperature of 15°C and loading rate of 50 mm/min.

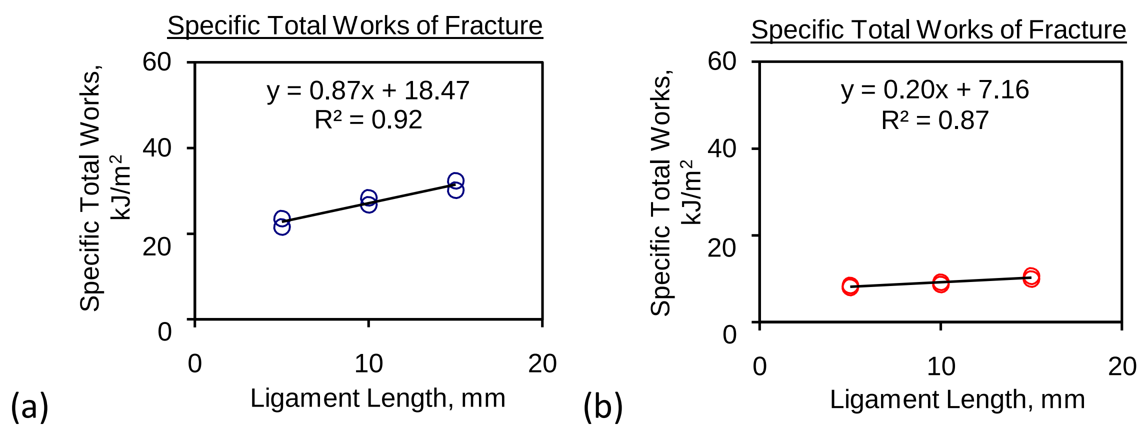

Figure 9 – Essential work of failure analysis for (a) PG 52-40D and (b) PG 52-40N at a temperature of 15°C and loading rate of 50 mm/min (duplicates for each).

Figures 8 and 9 provide the force-displacement data and the essential works of failure analyses, respectively. It is obvious from these graphs that while the Superpave grades are the same, the PG 52-40D binder can stretch a lot more before failing compared to the PG 52-40N. Higher ductility means the subgrade will be able to respond with a reactive, compressive force before the binder fibrils fail. Figure 9 also shows that the PG 58-40D has a significantly higher plastic work of failure (0.87 versus 0.2) which indicates that it is better able to distribute the load away from the stress concentration under tires and around cracks.

3.7 Modified Pressure Aging Vessel Treatment (LS-228)

The binders recovered from the above testing were aged for an additional 20 h according to Ontario's LS-228 Modified Pressure Aging Vessel protocol. The residues so obtained were tested in both the DSR and BBR to assess their durability. Changes from the original Superpave high (XX), intermediate (II) and lower limits (YY) can be used to provide measures of durability. Best performing binders from Laguna, Venezuela, and western Canadian sources change very little while poorer quality materials can lose (YY, II) or gain (XX) several grades. The findings of the investigation are provided in Table 7 with additional raw data in the appendix.

TABLE 7 – LS-228 MODIFIED PAV PROPERTIES FOR ALASKA DOT BINDERS

Sample	Supplier	PAV20			PAV40			CHANGE		
		XX	II	YY	XX	II	YY	XX	II	YY
PG 58-34	A	59	10	35	70	14	35	11	4	0
PG 52-40D	B	57	5	40	67	7	39	10	2	1
PG 52-40N	C	51	5	41	**75**	6	42	**24**	1	-1
PG 58-28	C	66	16	32	**83**	18	**26**	**17**	2	**6**
PG 64-28	C	66	14	33	**86**	16	**26**	**20**	2	**7**

Numbers are rounded to the nearest 1°C.

It is clear that all binders harden at the high end and that supplier C binders harden excessively by up to 4 grades (24°C). This likely reflects their much higher susceptibility to thermal cracking and, depending on the pavement designs, climates and traffic levels, these materials may suffer from a reduced life cycle because of this liability.

In order to put these differences in perspective, Figure 10 shows two images and crack maps of adjacent pavement test sections of 500 m in length on Highway 655 in northeastern Ontario (crack maps are for 50 m length each). The pavement design, age, climate, subgrade, and construction are all identical and the only difference is the asphalt cement quality. The poor performer was extracted after 5 years of service and showed a lower limiting temperature (YY) that was 7.6°C warmer than the satisfactory performer [Hesp et al., 2009].

Figure 10 – Representative images and crack maps for two 5 year old pavement trial sections constructed with identical PG 64-34 Superpave grade asphalt cements and identical designs on Highway 655 in northeastern Ontario.

4.0 Conclusions and Recommendations

Given the results and discussions provided in this report, the following summary, conclusions and recommendations are given:

- The five tested ADOT&PF binders were largely free of known deleterious additives (PPA, REOB, vegetable oils, tall oils, etc) and contained reasonable amounts of SB- type polymer modifiers.
- A significant difference between the polymer content for the two PG 52-40 binders indicates that the PG 52-40N could have been produced with unknown or difficult to detect additives (waxes, sulfuric acid, others) or process technologies (blending of incompatible asphalts/crudes).
- A DENT CTOD acceptance criterion, and/or a minimum polymer content specification together with IR acceptance tests, would go some way to level the playing field.
- ADOT&PF should consider purchasing IR and XRF instruments to continuously monitor for the presence/absence of beneficial SB polymer and detrimental/nefarious REOB, air-blown residues, vegetable oils, etc.
- ADOT&PF binders showed moderate to high tendencies for physical hardening during cold conditioning with grade losses ranging from 3.4°C to 6.3°C according to Ontario's extended BBR protocol LS-308. Setting a limit of 6°C on the maximum 72 grade loss in the extended BBR will likely assure that future projects/contracts stay within reasonable bounds.
- The lower limiting temperatures as specified in the contracts, -28°C, -34°C and -40°C, were missed by anywhere from 2 to 5°C. Hence, by using the PG 58-34 in the current PG 58-28 climatic zone, significant cost savings in terms of reduced rehabilitation and reconstruction costs could be realized (provided rutting and stripping problems are also controlled).
- Adding slightly more SB polymer to the PG 58-34 would also likely produce a better performing PG 64-28. However, it is recommended that ADOT&PF monitor the SB content and make sure that asphalt binders do not contain lower cost additives such as REOB, PPA, waste oils, etc..
- The five tested ADOT&PF binders were rather sensitive to additional

oxidative hardening in the pressure aging vessel. Changes in low temperature grades (YY) upon doubling the conditioning time in the PAV ranged from -1°C to +7°C while changes in the high temperature grade (XX) ranged from +10°C to +24°C. The latter increases are absolutely enormous and suggest that base asphalt quality and durability is far from ideal. Further work in this area should investigate if there is room for improvement.

- Currently the LS-299 DENT and LS-308 EBBR methods are implemented on numerous paving contracts around Ontario (Provincial and Municipal). The Ontario Ministry of Transportation is working with asphalt suppliers and has implemented LS-299 on nearly all contracts and LS-308 on selected contracts. LS-228 Modified PAV discussions have yet to start. Municipal users (such as the cities of Kingston and Timmins as well as Regional Municipalities of York, Peel, Durham, Waterloo and Niagara) have implemented both LS-299 and LS-308 and instituted a ban on all known and unknown detrimental additives. In order to use a modifier/additive/diluent, the asphalt binder supplier has to obtain preapproval from the user agency.

5.0 References

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Ontario Ministry of Transportation. LS-299 – Method of Test for Asphalt Cement's Resistance to Fatigue Fracture Using Double-Edge-Notched Tension Test (DENT). Revision 23 to MTO Laboratory Testing Manual, 2007.

Ontario Ministry of Transportation. LS-308 – Method of Test for Determination of Performance Grade of Physically Aged Asphalt Cement Using Extended Bending Beam Rheometer (BBR) Method. Revision 29 to MTO Laboratory Testing Manual, February 2015.

APPENDICES

Additional raw data for DSR and BBR tests.
LS-299 and LS-308 raw data for all ADOT&PF binders tested.
NMR spectra for all ADOT&PF binders tested.

APPENDIX – RAW BBR AND DSR DATA

INFO ON CAN	SUPERPAVE LIMITING TEMPERATURES, °C					SUPERPAVE GRADE	SUPERPAVE GRADE SPAN
	DSR_0	DSR_{RTFO}	DSR_{PAV}	$BBR_{S(60s)}$	$BBR_{m(60s)}$	XX-II-YY	
PG 58-34	66	59	10	-25	-26	59-10-35	94
PG 52-40D	59	57	5	-32	-30	57-5-40	97
PG 52-40N	58	**51**	5	-31	-33	51-5-41	92
PG 58-28	66	66	16	-22	-23	66-16-32	98
PG 64-28	67	66	14	-23	-23	66-14-33	99

INFO ON CAN	DSR ON PAV RESIDUES			LS-308 EBBR RESULTS, °C		LS-228 MODIFIED PAV (40 HR), °C	
	DSR_{PAV20} $G^*/\sin\delta$ = 2.2 kPa	DSR_{PAV40} $G^*\sin\delta$ = 5.0 MPa	DSR_{PAV40} $G^*/\sin\delta$ = 2.2 kPa	72 h Grade	72 h Loss	$BBR_{S(60\,s)}$	$BBR_{m(60\,s)}$
PG 58-34	65	14	**70**	**-31**	4.1	-26	-25
PG 52-40D	65	7	**67**	**-35**	**5.4**	-31	-29
PG 52-40N	**67**	6	**75**	-38	3.4	-32	-36
PG 58-28	**75**	18	**83**	**-26**	**5.9**	-22	**-15.9**
PG 64-28	**78**	16	**86**	**-26**	**6.3**	-23	**-15.7**

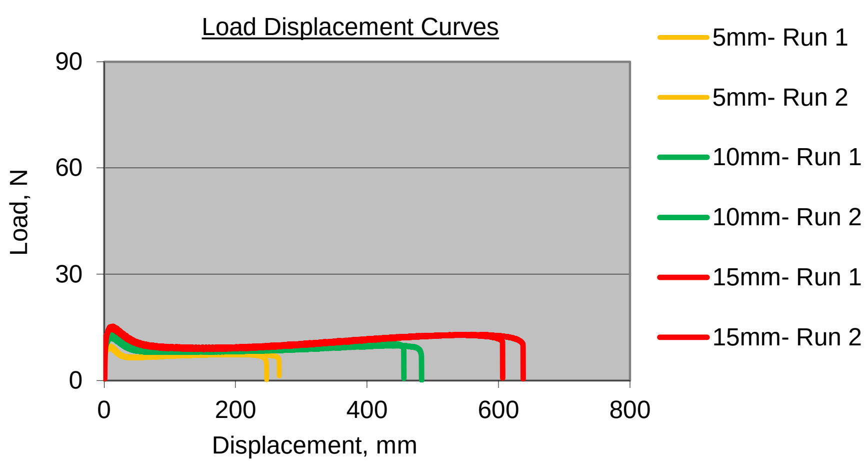
Summary of Double-Edge-Notched Tension Test Results
MTO Standard Test Method LS-299

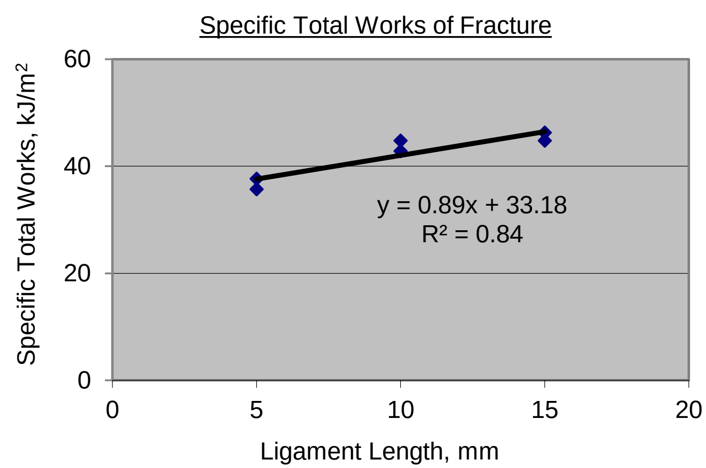
SPEED: 50 mm/min
TEMPERATURE: 15 ± 0.3 °C

SUPPLIER: A
LAB ID: AL-1
TEST DATE: FEB 8 2015
AASHTO M320 GRADE: PG 58-34

l, ligament length, mm	5		10		15	
W_t, total works of fracture, J	1.88	1.79	4.28	4.48	6.95	6.72
w_t, specific total works of fracture, kJ/m^2	37.7	35.7	42.8	44.8	46.3	44.8
w_e, specific essential work of fracture, kJ/m^2	33.2					
βw_p, specific plastic work of fracture, MJ/m^3	0.89					
δ_t, approximate CTOD average, mm	**174.6**					

Maximum Loads (5 mm)		
Trial 1	9.2	N
Trial 2	9.8	N
Average	9.5	N





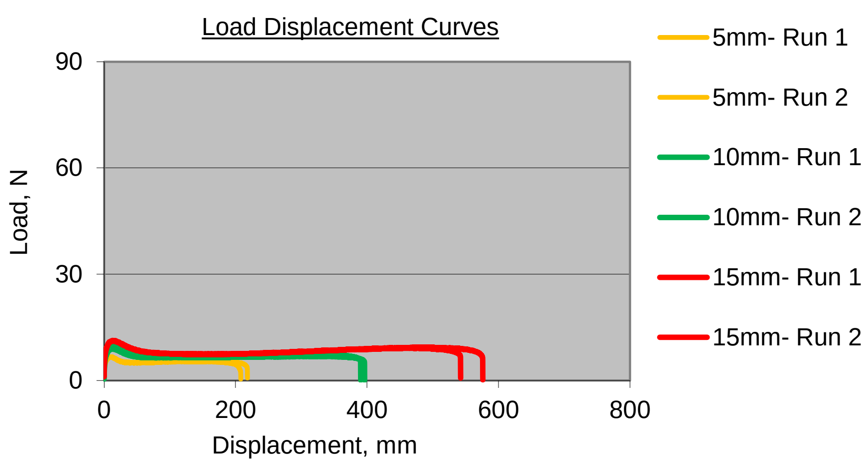
Summary of Double-Edge-Notched Tension Test Results
MTO Standard Test Method LS-299

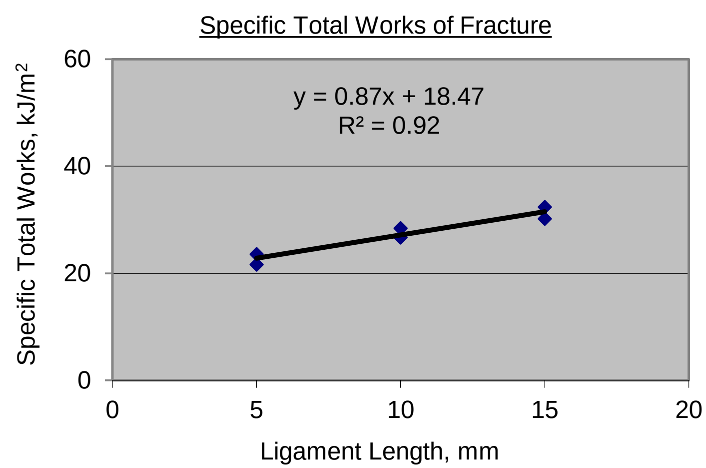
SUPPLIER: B
SPEED: 50 mm/min
LAB ID: AL-2
TEMPERATURE: 15 ± 0.3 °C
TEST DATE: FEB 8 2015
AASHTO M320 GRADE: PG 52-40D

l, ligament length, mm	5		10		15	
W_t, total works of fracture, J	1.08	1.18	2.67	2.84	4.86	4.53
w_t, specific total works of fracture, kJ/m^2	21.6	23.6	26.7	28.4	32.4	30.2
w_e, specific essential work of fracture, kJ/m^2	18.5					
βw_p, specific plastic work of fracture, MJ/m^3	0.87					
δ_t, approximate CTOD average, mm	**138.9**					

Maximum Loads (5 mm)

Trial 1	6.6	N
Trial 2	6.7	N
Average	6.7	N





Summary of Double-Edge-Notched Tension Test Results
MTO Standard Test Method LS-299

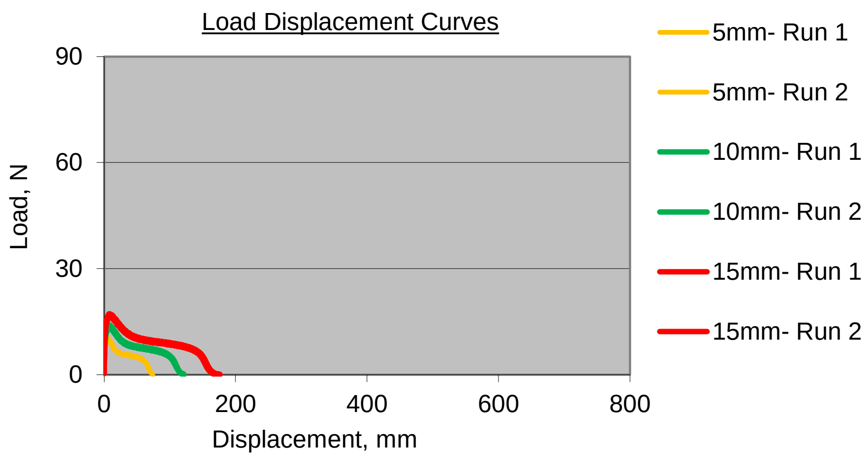
SPEED:	50	mm/min	
TEMPERATURE:	15	± 0.3 °C	

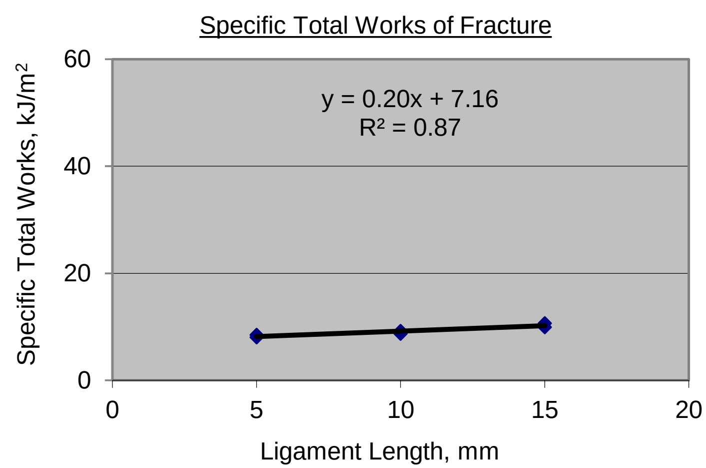
SUPPLIER: C
LAB ID: AL-3 PAV20
TEST DATE: FEB 8 2015
AASHTO M320 GRADE: PG 52-40N

l, ligament length, mm	5		10		15	
W_t, total works of fracture, J	0.40	0.42	0.87	0.92	1.50	1.60
w_t, specific total works of fracture, kJ/m^2	8.1	8.5	8.7	9.2	10.0	10.6
w_e, specific essential work of fracture, kJ/m^2	**7.2**					
βw_p, specific plastic work of fracture, MJ/m^3	**0.20**					
δ_t, approximate CTOD average, mm	**35.6**					

Maximum Loads (5 mm)

Trial 1	9.9	N
Trial 2	10.2	N
Average	10.1	N





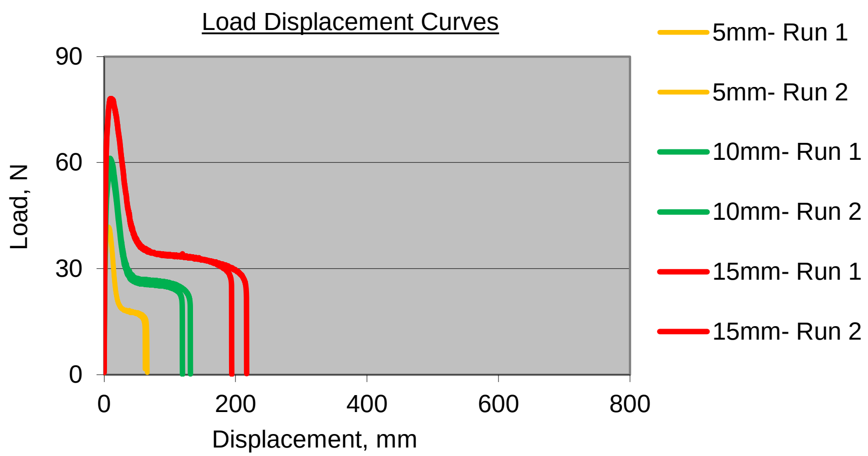
Summary of Double-Edge-Notched Tension Test Results
MTO Standard Test Method LS-299

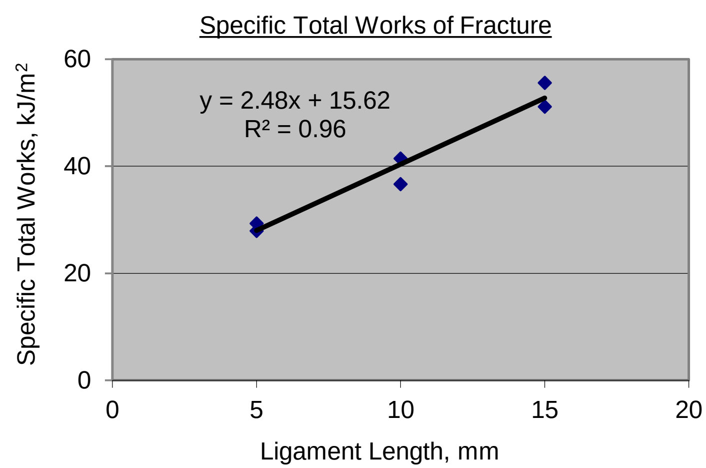
SUPPLIER: C
SPEED: 50 mm/min
LAB ID: AL-4
TEMPERATURE: 15 ± 0.3 ^oC
TEST DATE: FEB 10 2015
AASHTO M320 GRADE: PG 58-28

l, ligament length, mm	5		10		15	
W_t, total works of fracture, J	1.40	1.47	3.67	4.15	7.68	8.34
w_t, specific total works of fracture, kJ/m^2	28.0	29.3	36.7	41.5	51.2	55.6
w_e, specific essential work of fracture, kJ/m^2	15.6					
βw_p, specific plastic work of fracture, MJ/m^3	2.48					
δ_t, approximate CTOD average, mm	**18.7**					

Maximum Loads (5 mm)

Trial 1	41.6	N
Trial 2	41.8	N
Average	41.7	N





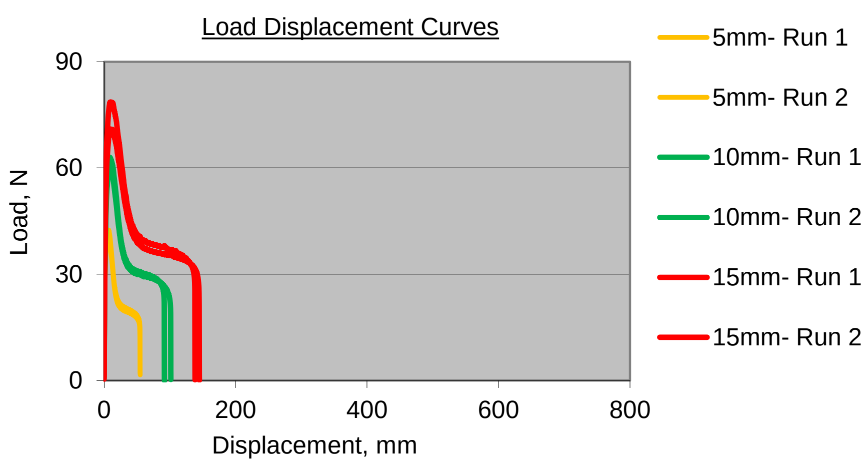
Summary of Double-Edge-Notched Tension Test Results
MTO Standard Test Method LS-299

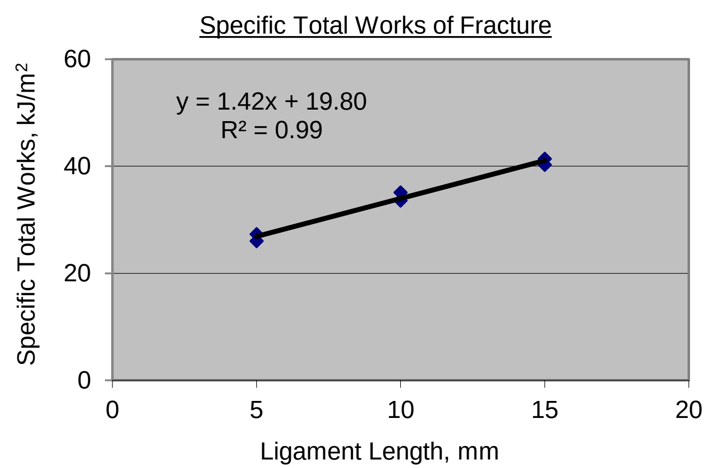
SUPPLIER: C
SPEED: 50 mm/min   LAB ID: AL-5
TEMPERATURE: 15 ± 0.3 °C   TEST DATE: FEB 10 2015
AASHTO M320 GRADE: PG 64-28

l, ligament length, mm	5		10		15	
W_t, total works of fracture, J	1.30	1.37	3.36	3.51	6.21	6.05
w_t, specific total works of fracture, kJ/m^2	26.1	27.3	33.6	35.1	41.4	40.3
w_e, specific essential work of fracture, kJ/m^2	19.8					
βw_p, specific plastic work of fracture, MJ/m^3	1.42					
δ_t, approximate CTOD average, mm	**23.9**					

Maximum Loads (5 mm)

Trial 1	40.4	N
Trial 2	42.5	N
Average	41.5	N





Summary of Extended Bending Beam Rheometer Test Results
MTO Standard Test Method LS-308

LAB ID: AL-1
TEST DATES: FEB 20-23 2015
AASHTO M320 GRADE: PG 58-34
SUPPLIER: A

Conditioning Temperature	Conditioning Period	Average m-values		Average Creep Stiffnesses		T_m	T_S	Limiting Temperature at m=0.300 T_m -10(°C)	Limiting Temperature at S=300 T_S -10(°C)	Limiting Grade T_L (°C)	Grade Loss (°C)
		T_{HT} -18	T_{LT} -24	T_{HT} -18	T_{LT} -24						
T +20°C	1 hour	0.392	0.323	95.3	246.7	-26.0	-25.2	-36.0	-35.2	-35.2	-0.1
	24 hours	0.350	0.289	128.3	292.0	-22.9	-24.2	-32.9	-34.2	-32.9	2.3
-14°C	72 hours	0.343	0.296	137.3	302.7	-23.5	-23.9	-33.5	-33.9	-33.5	1.7
T +10°C	1 hour	0.424	0.331	88.8	246.0	-26.0	-25.2	-36.0	-35.2	-35.2	0.0
	24 hours	0.363	0.265	138.7	339.7	-21.9	-23.2	-31.9	-33.2	-31.9	3.3
-24°C	72 hours	0.344	0.259	141.7	375.0	-21.1	-22.6	-31.1	-32.6	-31.1	4.1

(orange)	10, 11, 12
(yellow)	4, 5, 6
(blue)	7, 8, 9
(green)	1, 2, 3

PG XX-YY:

T + 20 = -14
T + 10 = -24

Note: The conditioning temperatures were kept constant at -14C and -24C. All stiffnesses and m-values are averages of three measurements.

Queen's University

Summary of Extended Bending Beam Rheometer Test Results
MTO Standard Test Method LS-308

LAB ID: AL-2
TEST DATES: FEB 15-18 2015
AASHTO M320 GRADE: PG 52-40D
SUPPLIER: B

Conditioning Temperature	Conditioning Period	Average m-values T_{HT} -24	Average m-values T_{LT} -30	Average Creep Stiffnesses T_{HT} -24	Average Creep Stiffnesses T_{LT} -30	T_m	T_S	Limiting Temperature at m=0.300 T_m -10(°C)	Limiting Temperature at S=300 T_S -10(°C)	Limiting Grade T_L (°C)	Grade Loss (°C)
T +20°C	1 hour	0.359	0.312	104.2	257.7	-31.5	-31.0	-41.5	-41.0	-41.0	-0.6
	24 hours	0.318	0.265	136.7	300.0	-26.0	-30.0	-36.0	-40.0	-36.0	4.4
-20°C	72 hours	0.308	0.258	146.0	311.0	-25.0	-29.7	-35.0	-39.7	**-35.0**	5.4
T +10°C	1 hour	0.386	0.305	104.7	231.3	-30.4	-32.0	-40.4	-42.0	**-40.4**	0.0
	24 hours	0.336	0.251	129.3	317.0	-26.5	-29.6	-36.5	-39.6	-36.5	3.9
-30°C	72 hours	0.316	0.242	152.7	342.0	-25.3	-29.0	-35.3	-39.0	-35.3	5.1

(orange)	10, 11, 12
(yellow)	4, 5, 6
(blue)	7, 8, 9
(green)	1, 2, 3

PG XX-YY:

T + 20 = -20
T + 10 = -30

Note: The conditioning temperatures were kept constant at -20C and -30C. All stiffnesses and m-values are averages of three measurements.

Summary of Extended Bending Beam Rheometer Test Results
MTO Standard Test Method LS-308

LAB ID: AL-3
TEST DATES: FEB 15-18 2015
AASHTO M320 GRADE: PG 52-40N
SUPPLIER: C

Conditioning Temperature	Conditioning Period	Average m-values T_{HT} -24	Average m-values T_{LT} -30	Average Creep Stiffnesses T_{HT} -24	Average Creep Stiffnesses T_{LT} -30	T_m	T_S	Limiting Temperature at m=0.300 T_m -10(°C)	Limiting Temperature at S=300 T_S -10(°C)	Limiting Grade T_L (°C)	Grade Loss (°C)
T +20°C -20°C	1 hour	0.357	0.317	104.3	271.3	-32.6	-30.6	-42.6	-40.6	-40.6	0.3
	24 hours	0.338	0.294	130.3	292.7	-29.1	-30.2	-39.1	-40.2	-39.1	1.8
	72 hours	0.329	0.294	138.3	312.3	-29.0	-29.7	-39.0	-39.7	-39.0	2.0
T +10°C -30°C	1 hour	0.390	0.329	102.9	259.3	-32.8	-30.9	-42.8	-40.9	-40.9	0.0
	24 hours	0.355	0.281	133.7	333.7	-28.4	-29.3	-38.4	-39.3	-38.4	2.5
	72 hours	0.344	0.270	146.7	343.7	-27.6	-29.0	-37.6	-39.0	-37.6	3.4

Orange	10, 11, 12
Yellow	4, 5, 6
Blue	7, 8, 9
Green	1, 2, 3

PG XX-YY: T + 20 = -20
T + 10 = -30

Note: The conditioning temperatures were kept constant at -20C and -30C..

Summary of Extended Bending Beam Rheometer Test Results
MTO Standard Test Method LS-308

LAB ID: AL-4
TEST DATES: FEB 17-20 2015
AASHTO M320 GRADE: PG 58-28
SUPPLIER: C

Conditioning Temperature	Conditioning Period	Average m-values		Average Creep Stiffnesses		T_m	T_S	Limiting Temperature at m=0.300	Limiting Temperature at S=300	Limiting Grade	Grade Loss
		T_{HT} -12	T_{LT} -18	T_{HT} -12	T_{LT} -18			T_m -10(°C)	T_S -10(°C)	T_L (°C)	(°C)
T +20°C	1 hour	0.385	0.328	81.9	178.3	-21.0	-22.0	-31.0	-32.0	-31.0	0.8
	24 hours	0.345	0.290	103.2	212.3	-16.9	-20.9	-26.9	-30.9	-26.9	4.9
-8°C	72 hours	0.339	0.298	107.7	205.7	-17.8	-21.5	-27.8	-31.5	-27.8	4.0
T +10°C	1 hour	0.383	0.338	84.3	184.0	-23.1	-21.8	-33.1	-31.8	**-31.8**	0.0
	24 hours	0.354	0.287	103.1	250.0	-16.8	-19.2	-26.8	-29.2	-26.8	4.9
-18°C	72 hours	0.334	0.280	115.3	264.0	-15.8	-18.9	-25.8	-28.9	-25.8	**5.9**

Orange	10, 11, 12
Yellow	4, 5, 6
Blue	7, 8, 9
Green	1, 2, 3

PG XX-YY:

T + 20 =	-8
T + 10 =	-18

Note: The conditioning temperatures were kept constant at -8C and -18C. All stiffnesses and m-values are averages of three replicate measurements.

Queen's University

Summary of Extended Bending Beam Rheometer Test Results
MTO Standard Test Method LS-308

LAB ID: AL-5
TEST DATES: FEB 17-20 2015
AASHTO M320 GRADE: PG 64-28
SUPPLIER: C

Conditioning Temperature	Conditioning Period	Average m-values T_{HT} -12	Average m-values T_{LT} -18	Average Creep Stiffnesses T_{HT} -12	Average Creep Stiffnesses T_{LT} -18	T_m	T_S	Limiting Temperature at m=0.300 T_m -10(°C)	Limiting Temperature at S=300 T_S -10(°C)	Limiting Grade T_L (°C)	Grade Loss (°C)
T +20°C -8°C	1 hour	0.377	0.331	73.9	154.0	-22.0	-23.5	-32.0	-33.5	-32.0	0.7
	24 hours	0.349	0.307	87.3	173.7	-19.0	-22.8	-29.0	-32.8	-29.0	3.7
	72 hours	0.338	0.303	91.2	185.3	-18.6	-22.1	-28.6	-32.1	-28.6	4.1
T +10°C -18°C	1 hour	0.401	0.344	68.1	156.7	-22.7	-22.7	-32.7	-32.7	-32.7	0.0
	24 hours	0.348	0.295	96.3	202.3	-17.5	-21.2	-27.5	-31.2	-27.5	5.2
	72 hours	0.346	0.282	94.6	215.3	-16.3	-20.4	-26.3	-30.4	-26.3	6.3

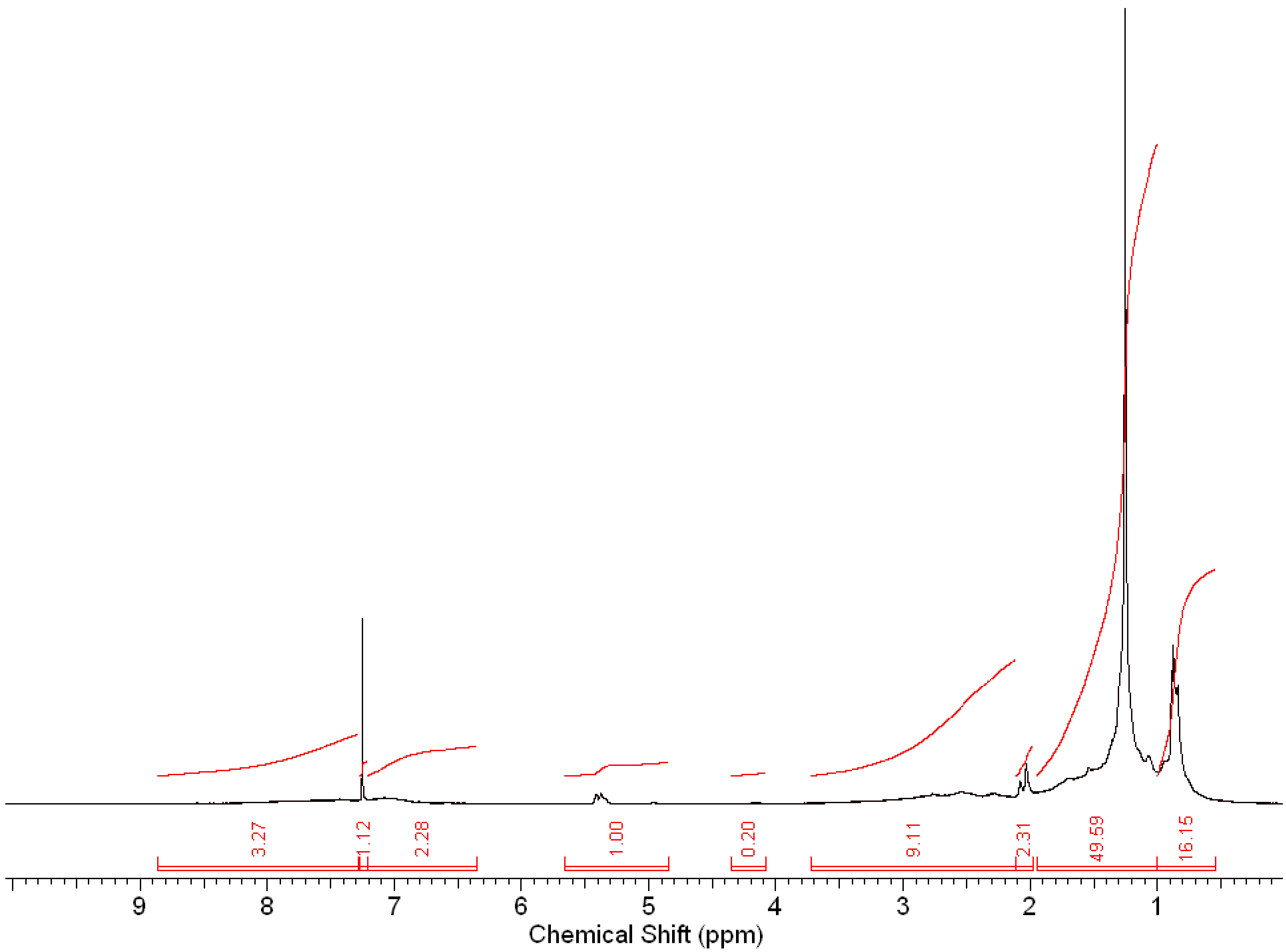
Orange	10, 11, 12
Yellow	4, 5, 6
Blue	7, 8, 9
Green	1, 2, 3

PG XX-YY: T + 20 = -8
T + 10 = -18

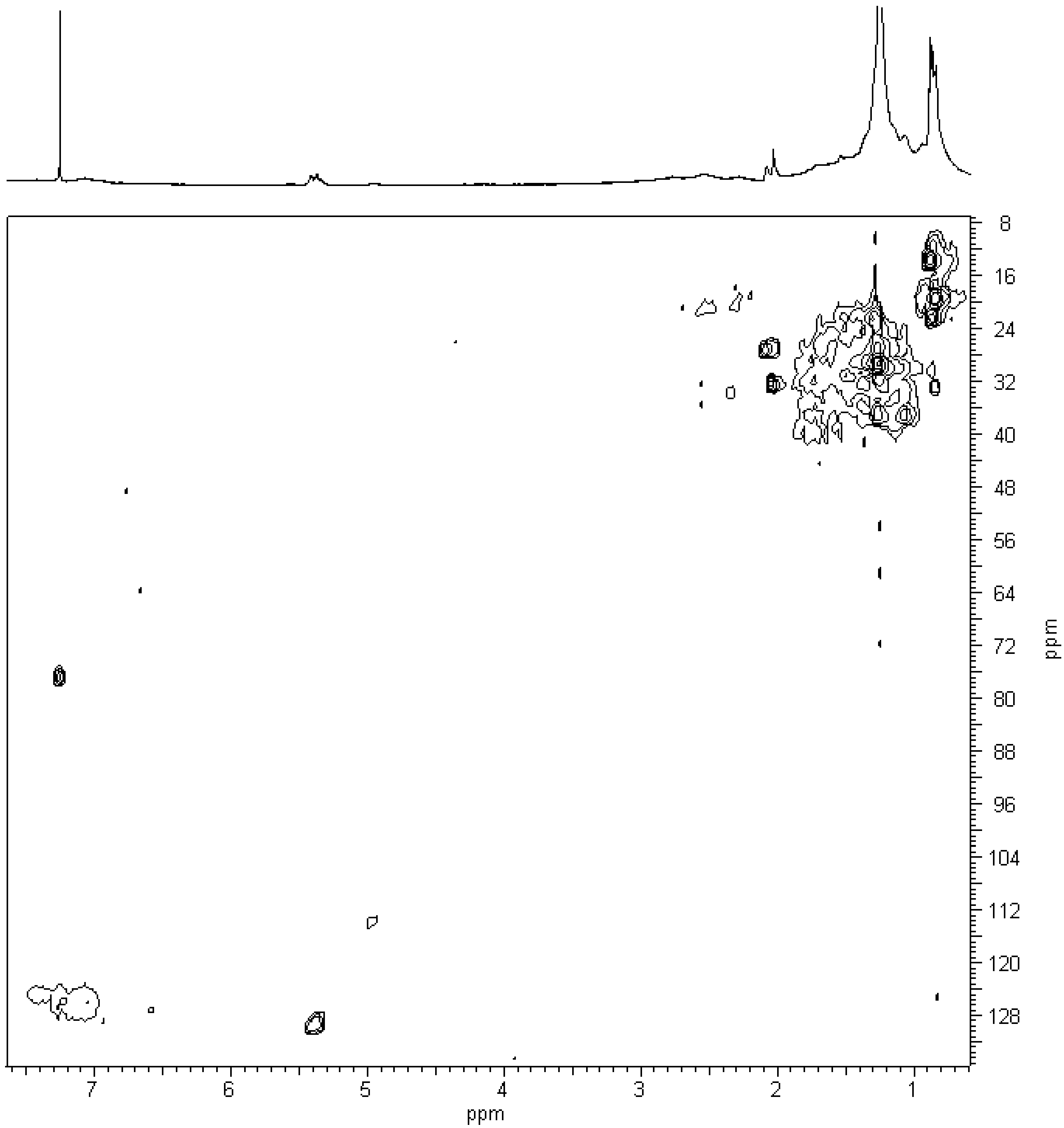
Note: The conditioning temperatures were kept constant at -8C and -18C. All stiffnesses and m-values are averages of three replicate measurements.

AL-1 in CDCl3

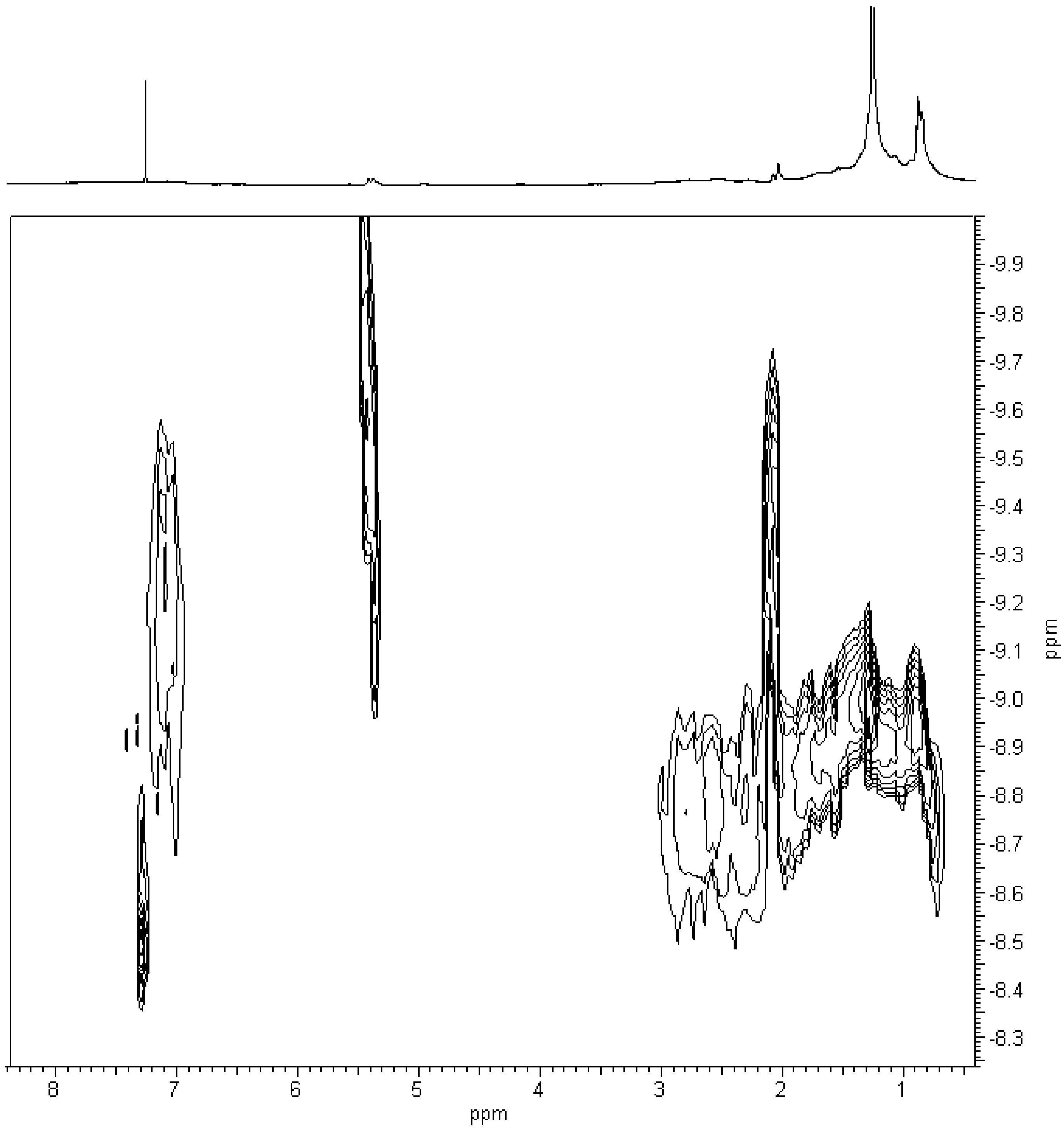
H-NMR



HSQC

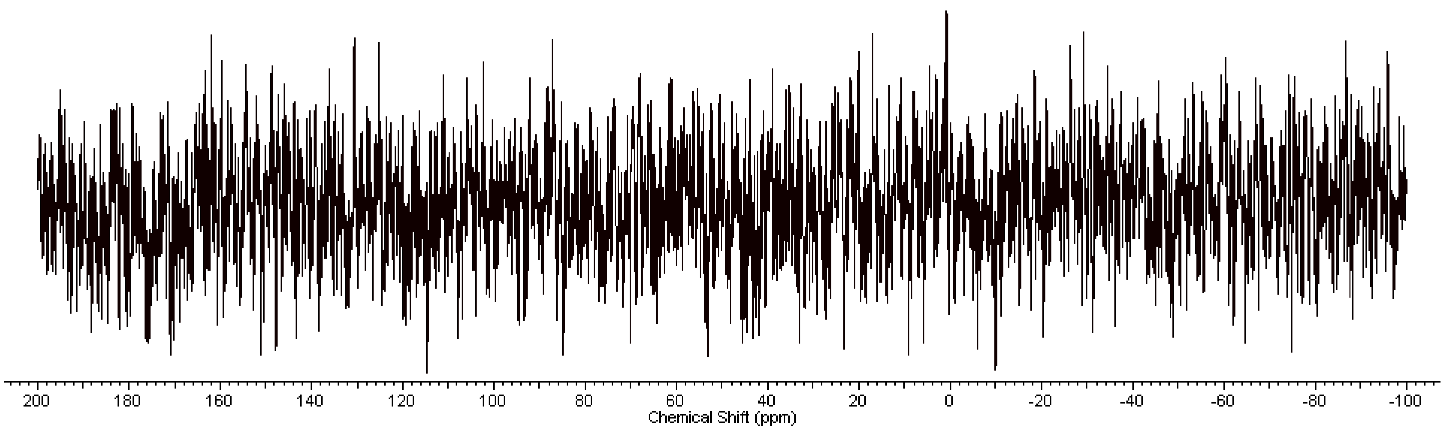


One-shot DOSY



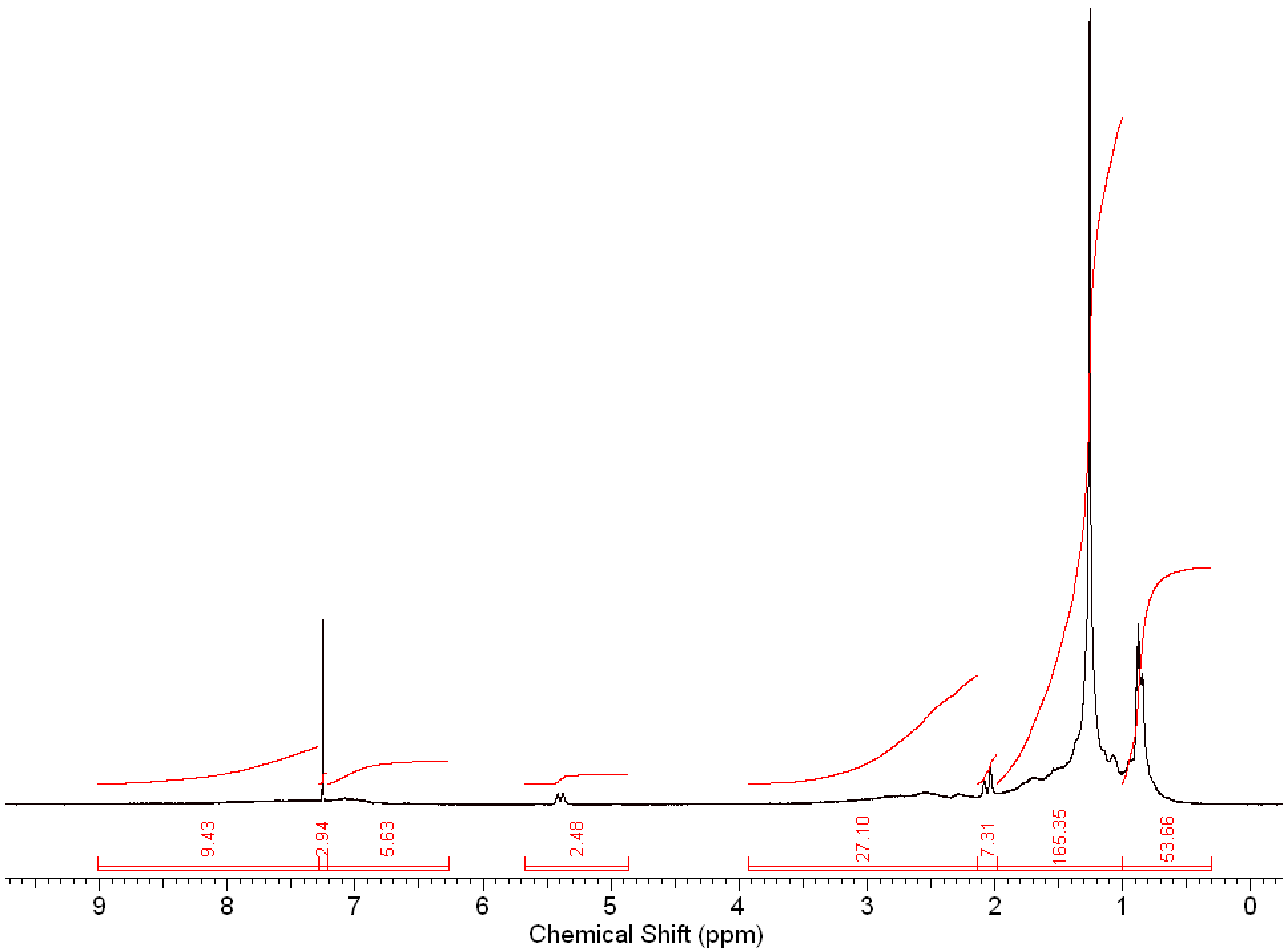
P31 NMR

Acquisition Time (sec)	0.5407	***Comment***	AL-1-P31 in CDCl3 17-Feb-2015 P31 NMR {H}			***Date***	17 Feb 2015 12:12:32
Date Stamp	17 Feb 2015 12:12:32			***File Name***	\\130.15.98.10\data\hesp\nmr\AL-1-P31\1\PDATA\1\1r		
Frequency (MHz)	202.05	***Nucleus***	31P	***Number of Transients***	256	***Origin***	spect
Original Points Count	32768	***Owner***	root	***Points Count***	32768	***Pulse Sequence***	zgdc30
Receiver Gain	16384.00	***SW(cyclical) (Hz)***	60606.06	***Solvent***	CHLOROFORM-d		
Spectrum Offset (Hz)	10100.9102	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	60604.21	***Temperature (degree C)***	25.200

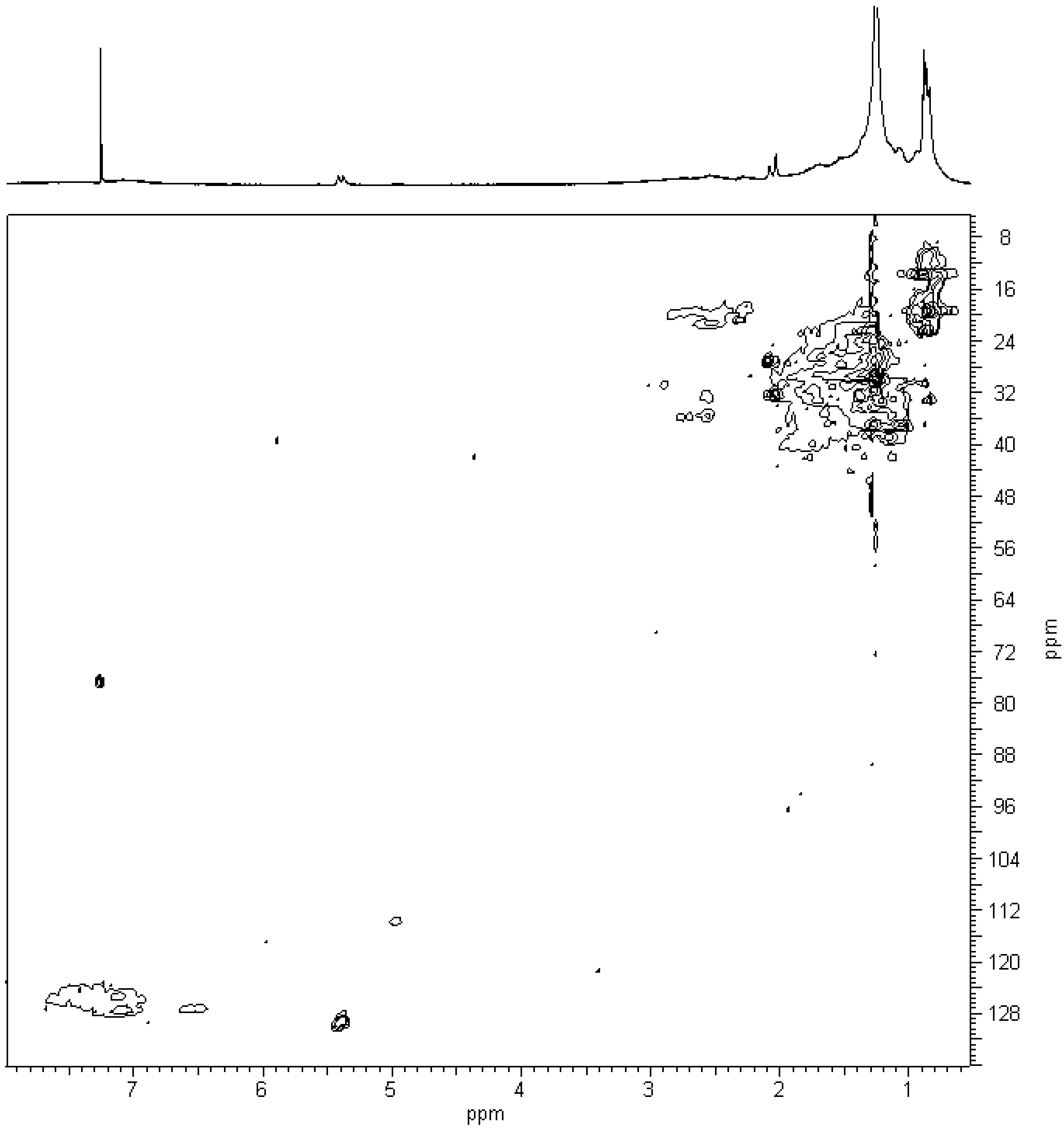


AL-2 in CDCl3

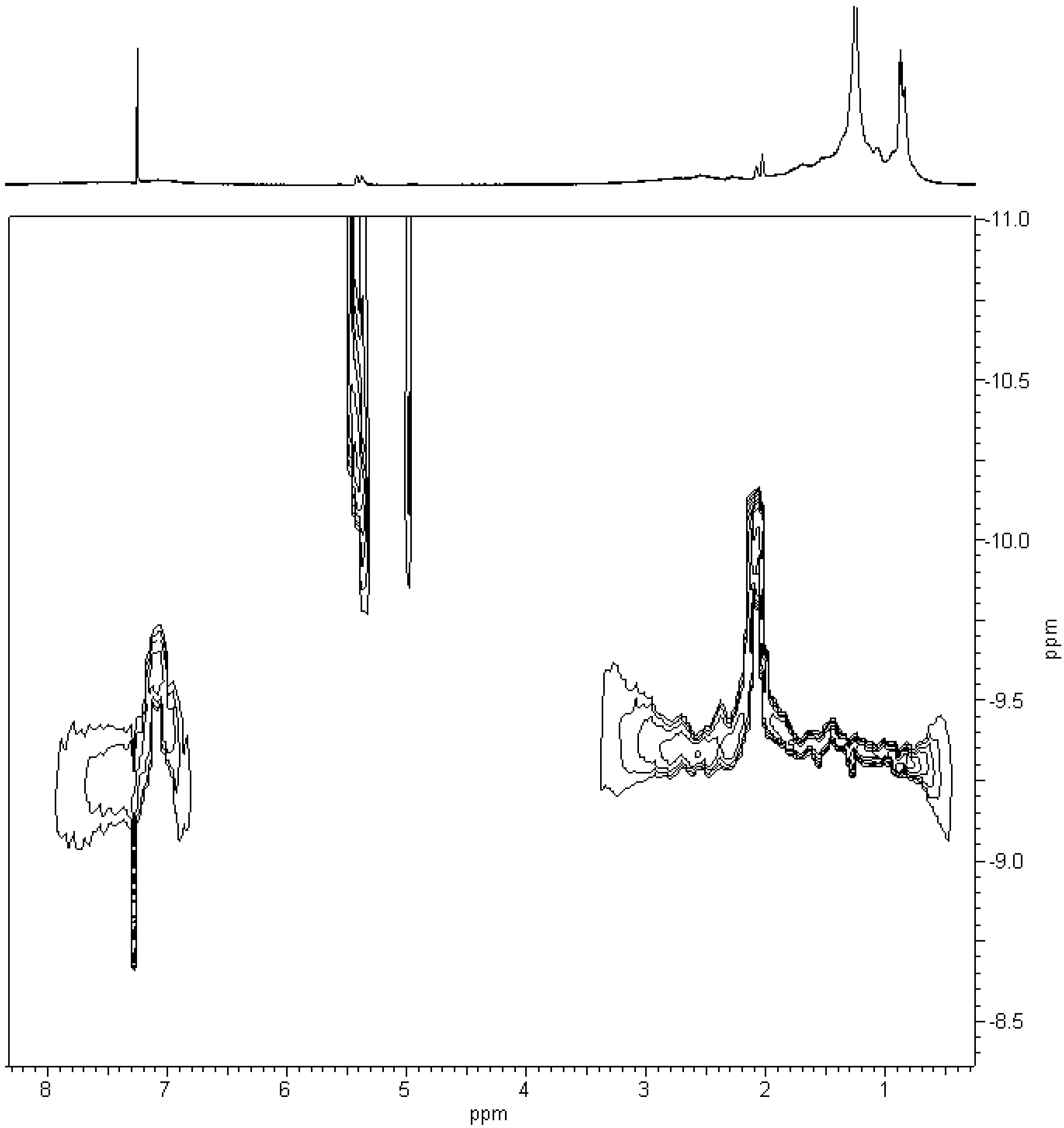
H-NMR



HSQC

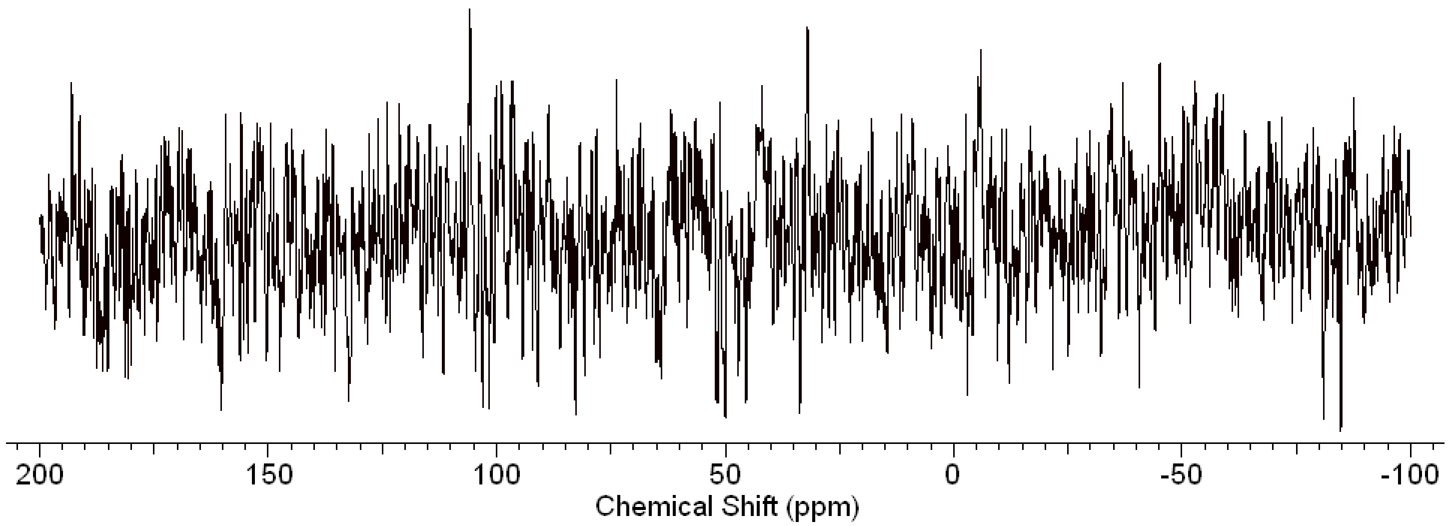


One-shot DOSY



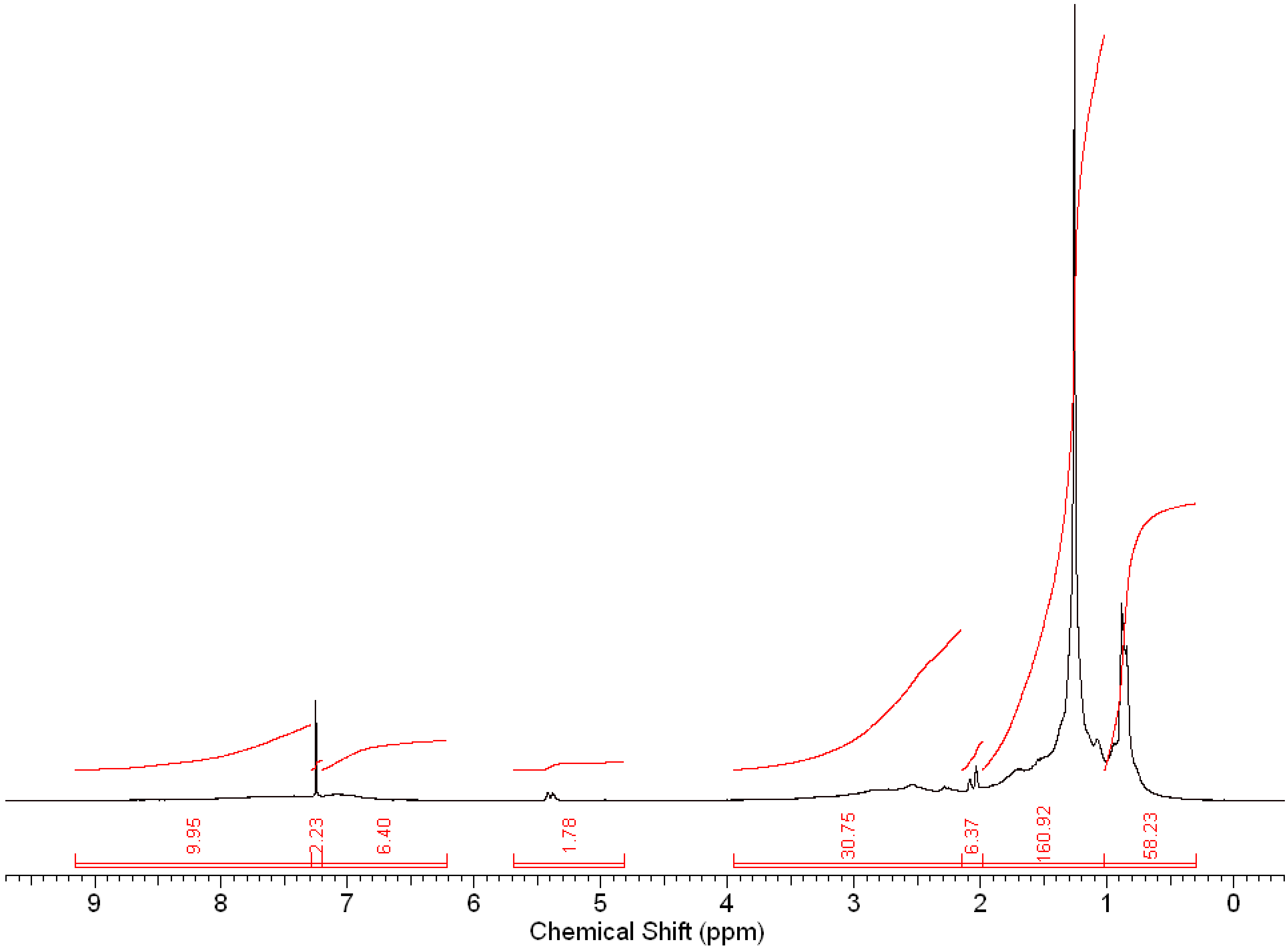
P31 NMR

Acquisition Time (sec)	0.5407	**Comment**	AL-2-P31 in CDCl3 17-Feb-2015 P31 NMR {H}			**Date**	17 Feb 2015 12:25:20
Date Stamp	17 Feb 2015 12:25:20			**File Name**	\\130.15.98.10\data\hesp\nmr\AL-2-P31\1\PDATA\1\1r		
Frequency (MHz)	202.05	**Nucleus**	31P	**Number of Transients**	256	**Origin**	spect
Original Points Count	32768	**Owner**	root	**Points Count**	32768	**Pulse Sequence**	zgdc30
Receiver Gain	16384.00	**SW(cyclical) (Hz)**	60606.06	**Solvent**	CHLOROFORM-d		
Spectrum Offset (Hz)	10100.9102	**Spectrum Type**	STANDARD	**Sweep Width (Hz)**	60604.21	**Temperature (degree C)**	25.300

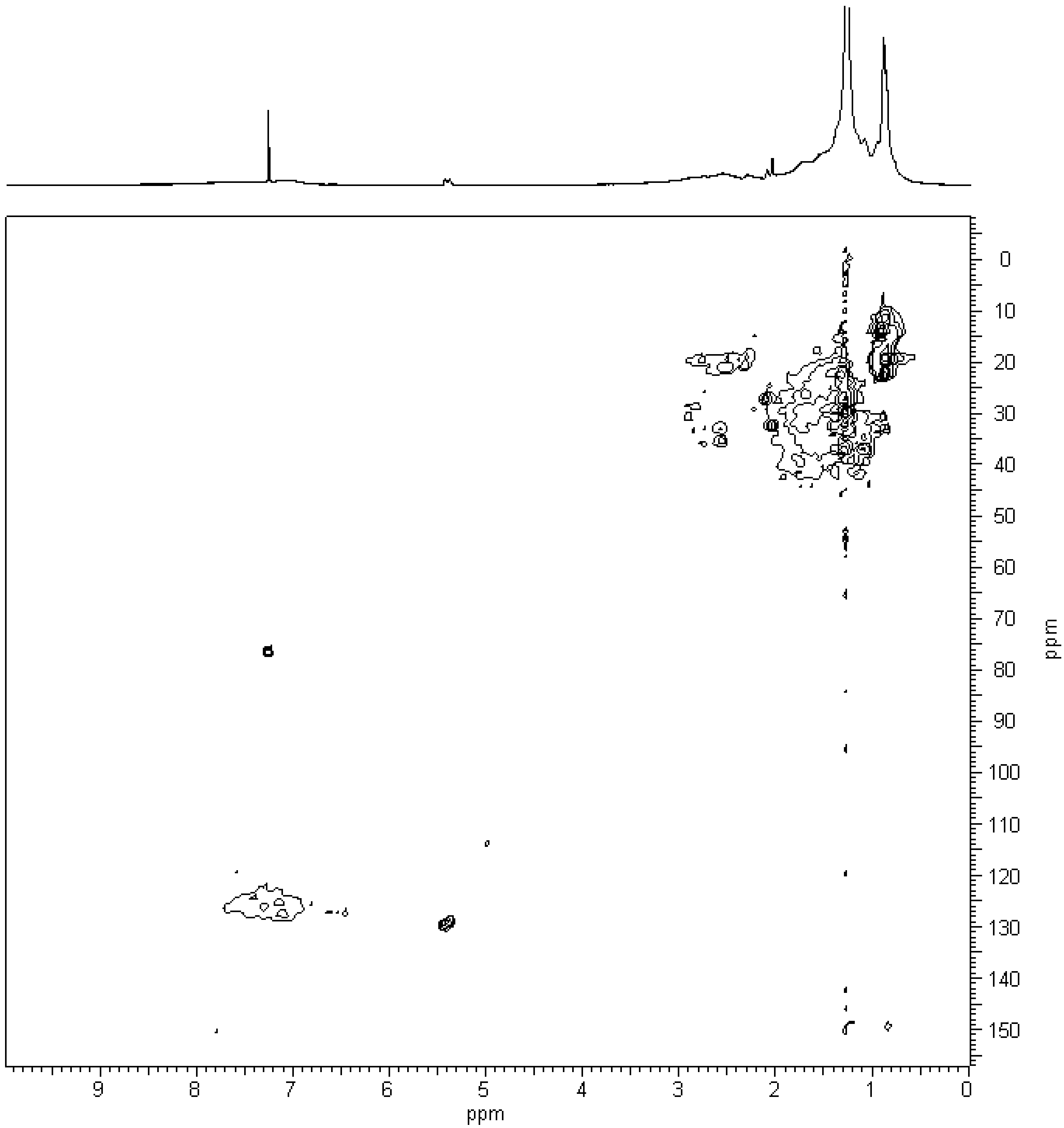


AL-3 in CDCl3

H-NMR



HSQC



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60
70
80
90
100
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120
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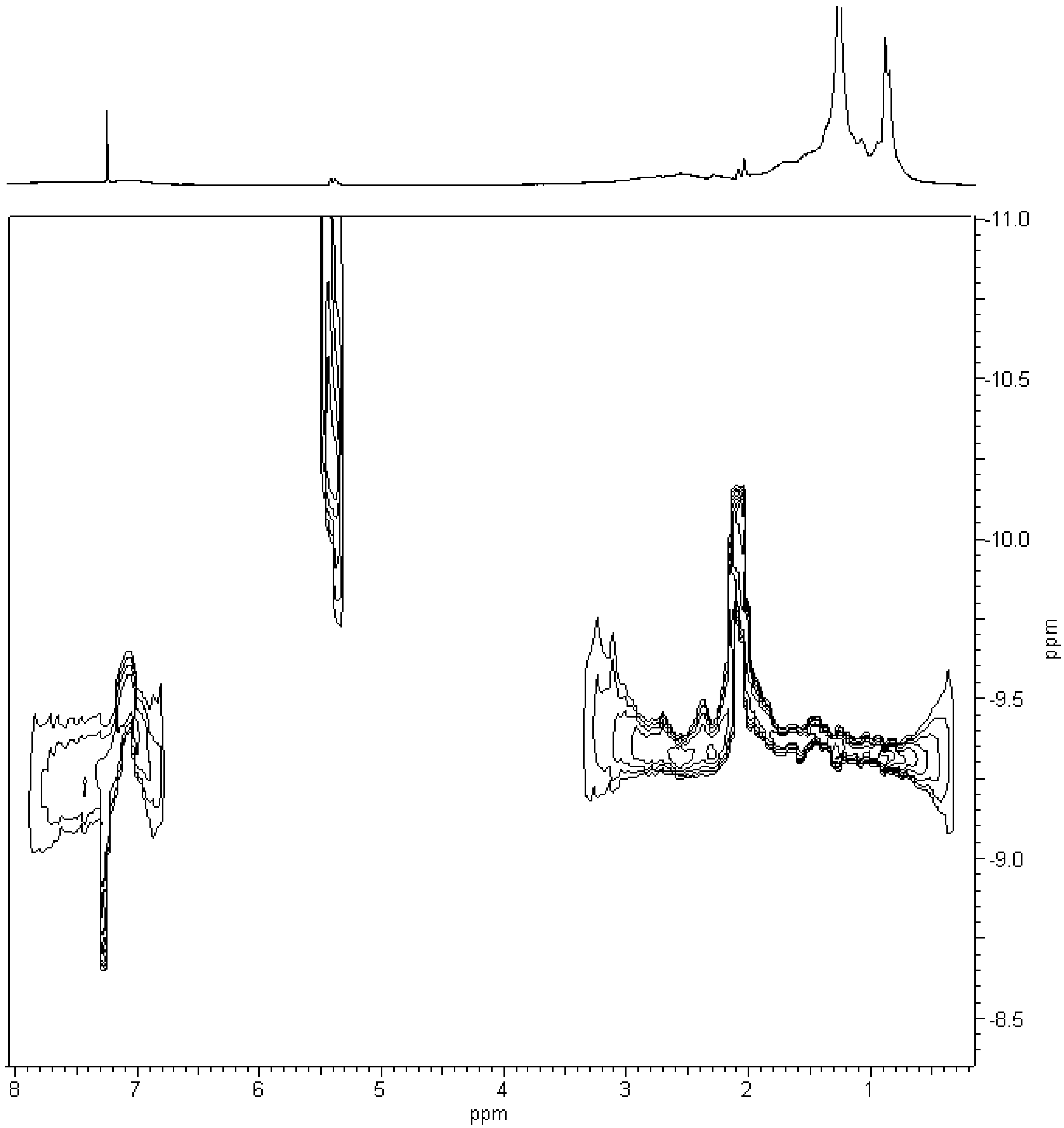
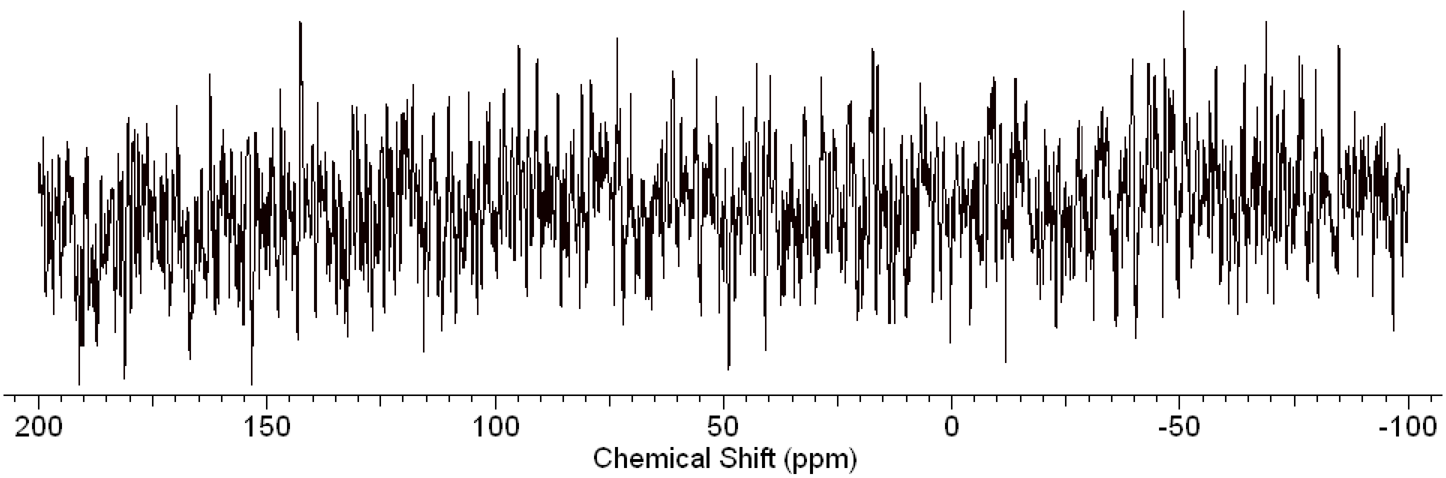
140
150
ppm
9
8
7
6
5
4
3
2
1
0
ppm

One-shot DOSY



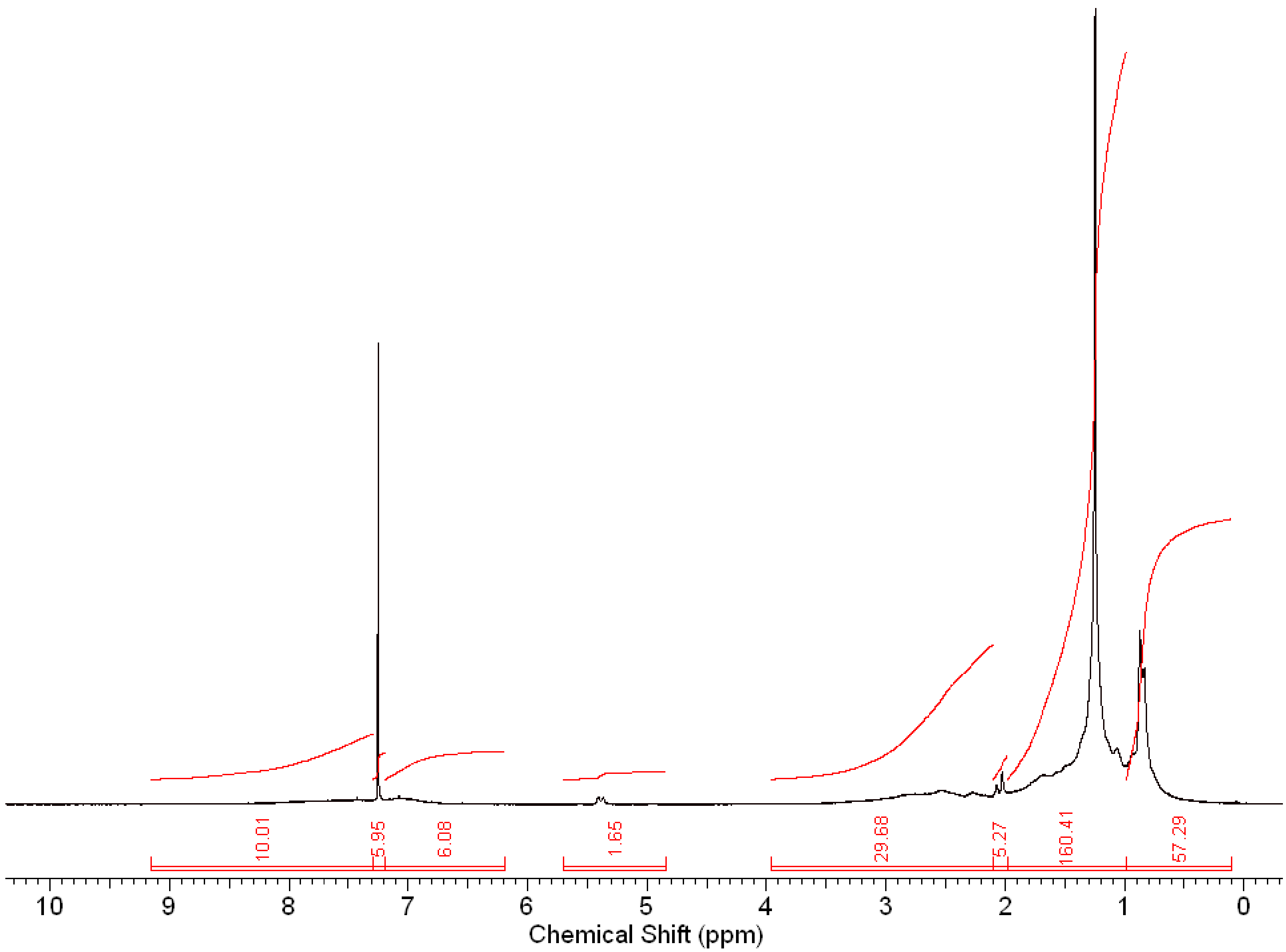
P31

Acquisition Time (sec)	0.5407	**Comment**	AL-3-P31 in CDCl3 17-Feb-2015 P31 NMR {H}			**Date**	17 Feb 2015 12:38:08
Date Stamp	17 Feb 2015 12:38:08			**File Name**	\\130.15.98.10\data\hesp\nmr\AL-3-P31\1\PDATA\1\1r		
Frequency (MHz)	202.05	**Nucleus**	31P	**Number of Transients**	256	**Origin**	spect
Original Points Count	32768	**Owner**	root	**Points Count**	32768	**Pulse Sequence**	zgdc30
Receiver Gain	16384.00	**SW(cyclical) (Hz)**	60606.06	**Solvent**	CHLOROFORM-d		
Spectrum Offset (Hz)	10100.9102	**Spectrum Type**	STANDARD	**Sweep Width (Hz)**	60604.21	**Temperature (degree C)**	25.200

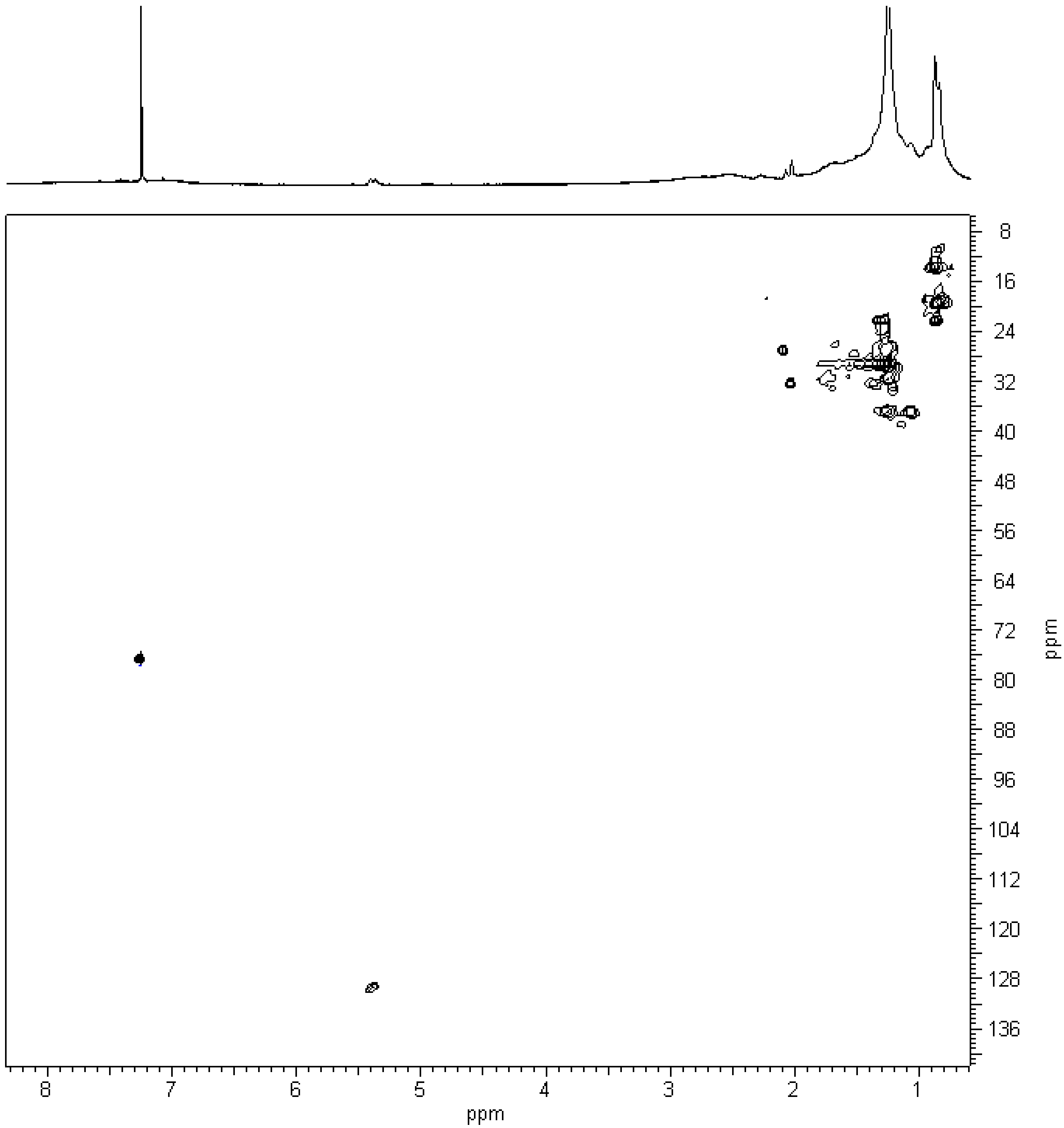


AL-4 in CDCl3

H-NMR



HSQC



8
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ppm
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4
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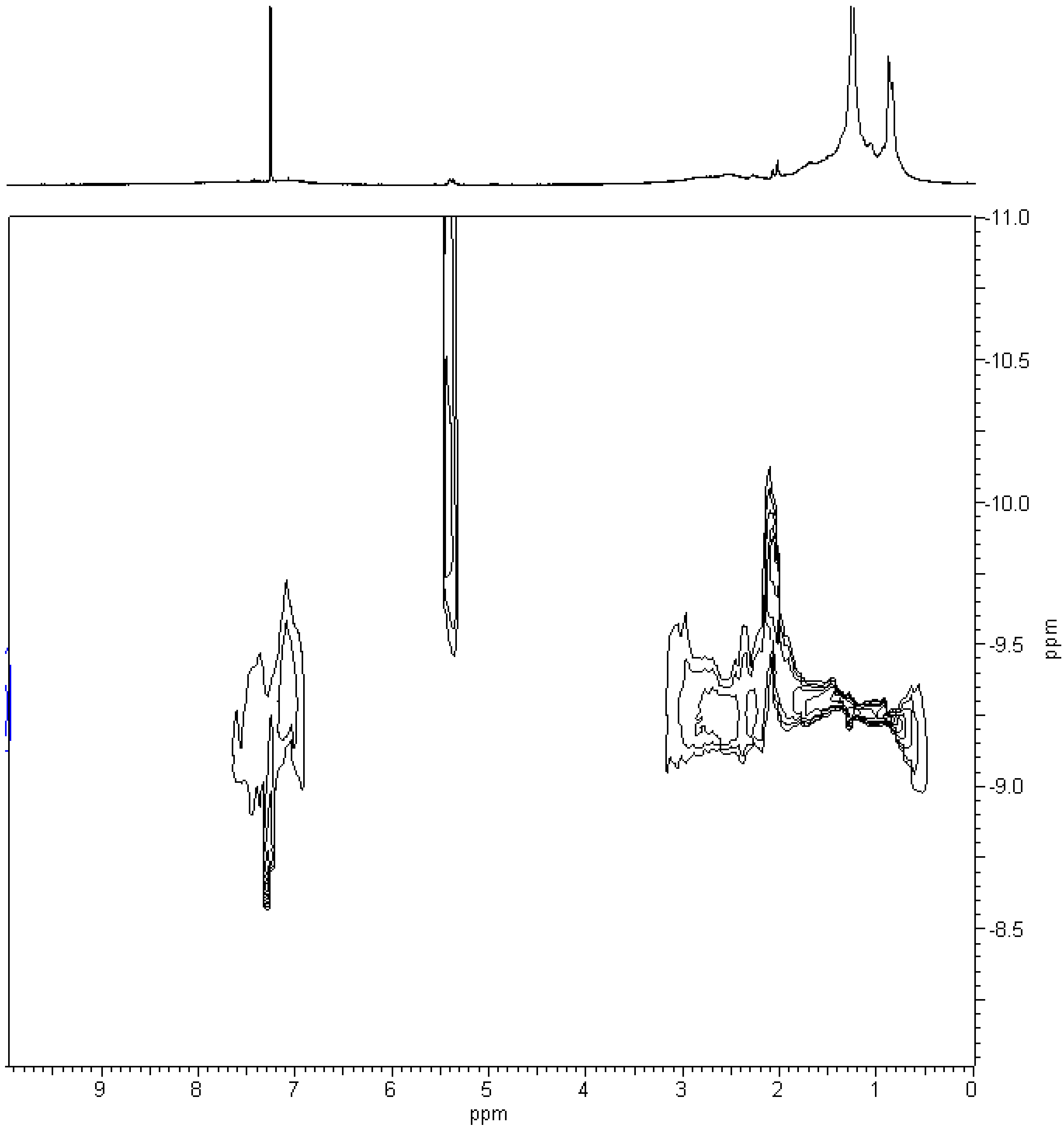
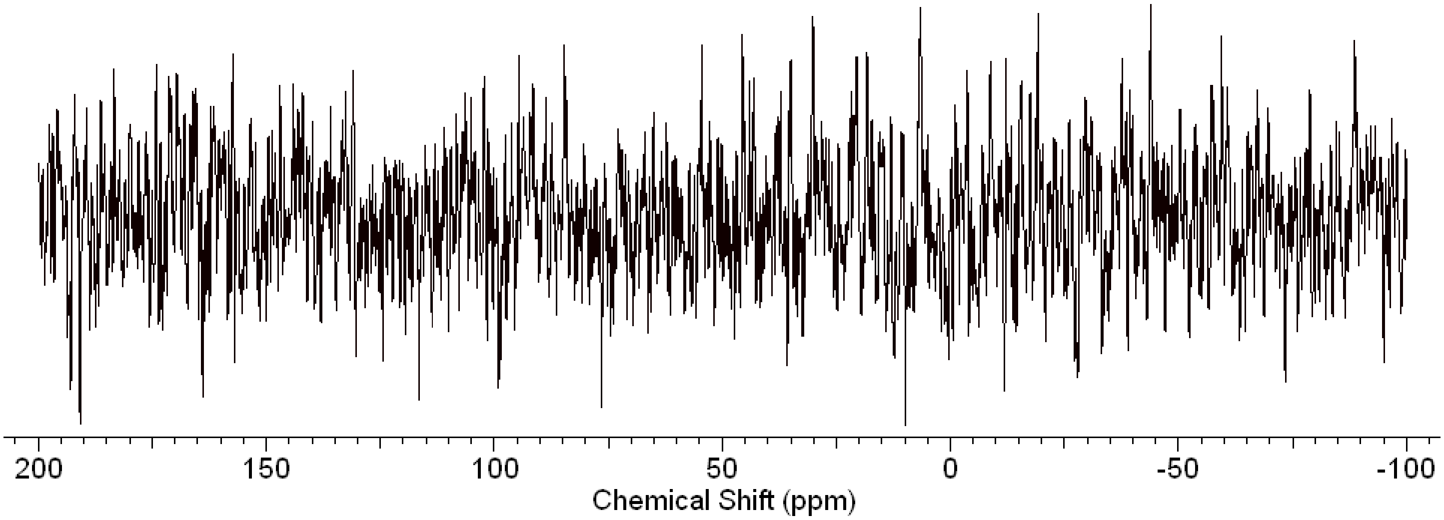
1
ppm

One-shot DOSY



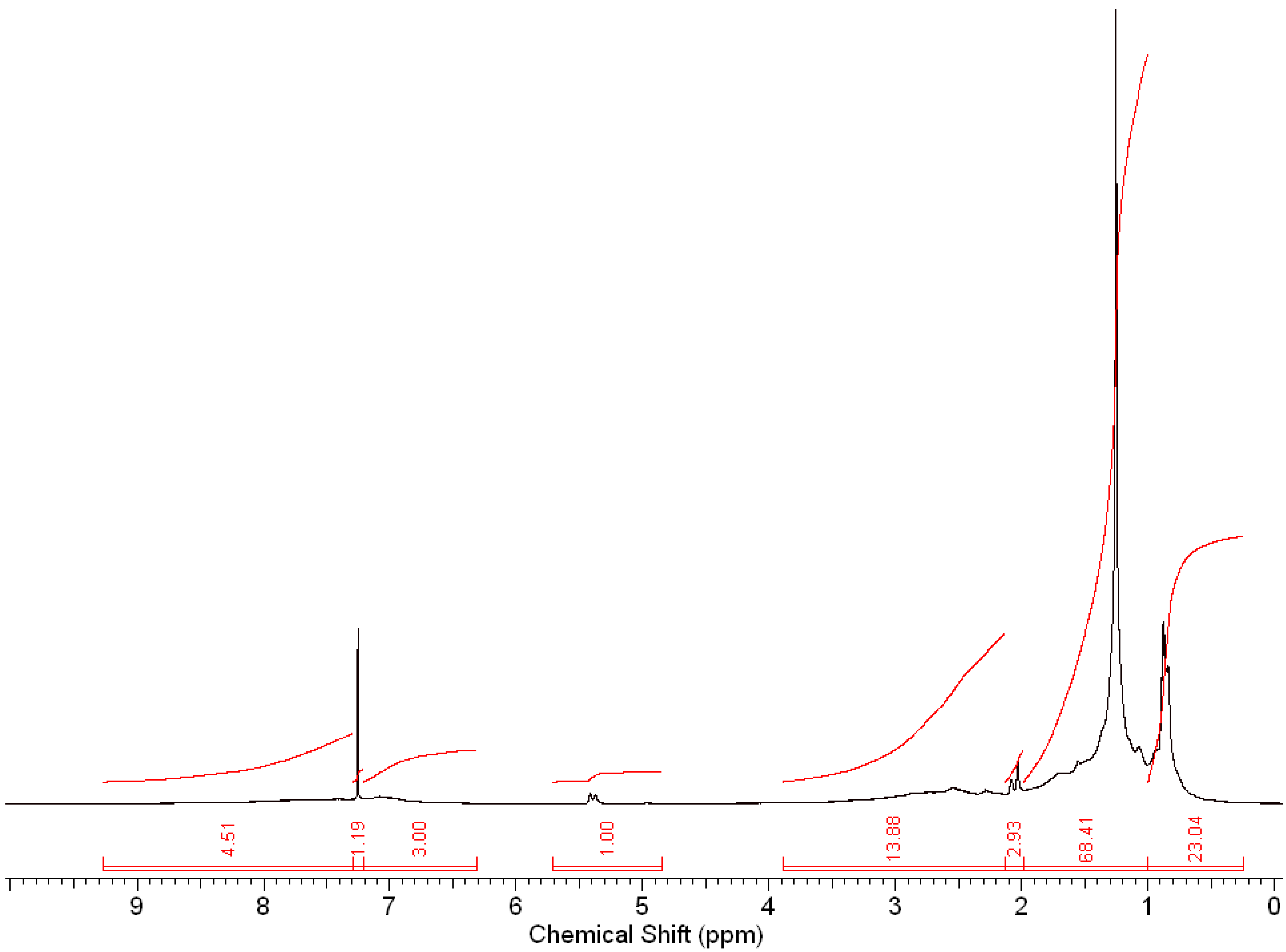
P31-NMR

Acquisition Time (sec)	0.5407	**Comment**	AL-4-P31 in CDCl3 17-Feb-2015 P31 NMR {H}			**Date**	17 Feb 2015 12:53:04
Date Stamp	17 Feb 2015 12:53:04			**File Name**	\\130.15.98.10\data\hesp\nmr\AL-4-P31\1\PDATA\1\1r		
Frequency (MHz)	202.05	**Nucleus**	31P	**Number of Transients**	256	**Origin**	spect
Original Points Count	32768	**Owner**	root	**Points Count**	32768	**Pulse Sequence**	zgdc30
Receiver Gain	16384.00	**SW(cyclical) (Hz)**	60606.06	**Solvent**	CHLOROFORM-d		
Spectrum Offset (Hz)	10100.9102	**Spectrum Type**	STANDARD	**Sweep Width (Hz)**	60604.21	**Temperature (degree C)**	25.600

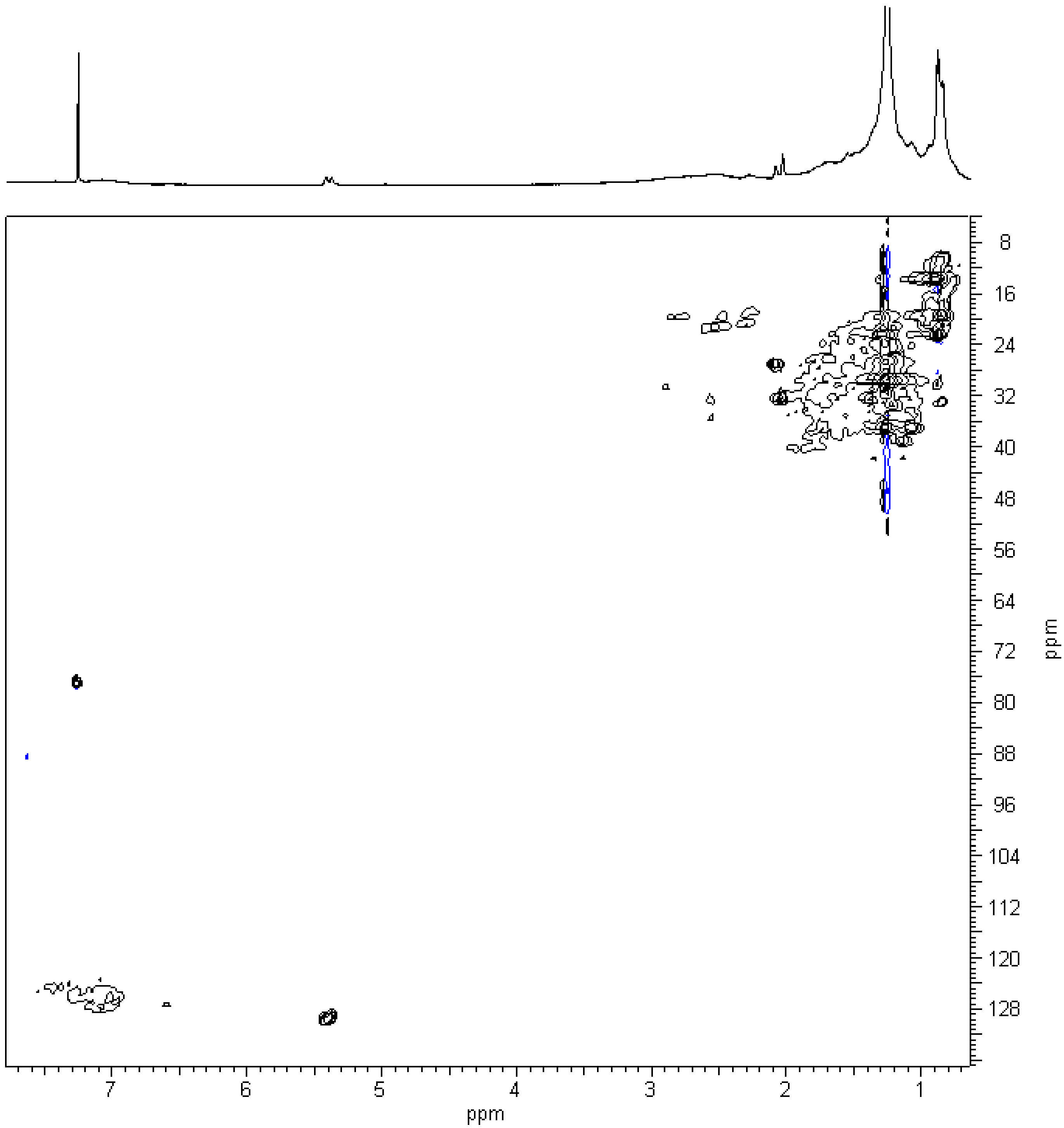


AL-5 in CDCl3

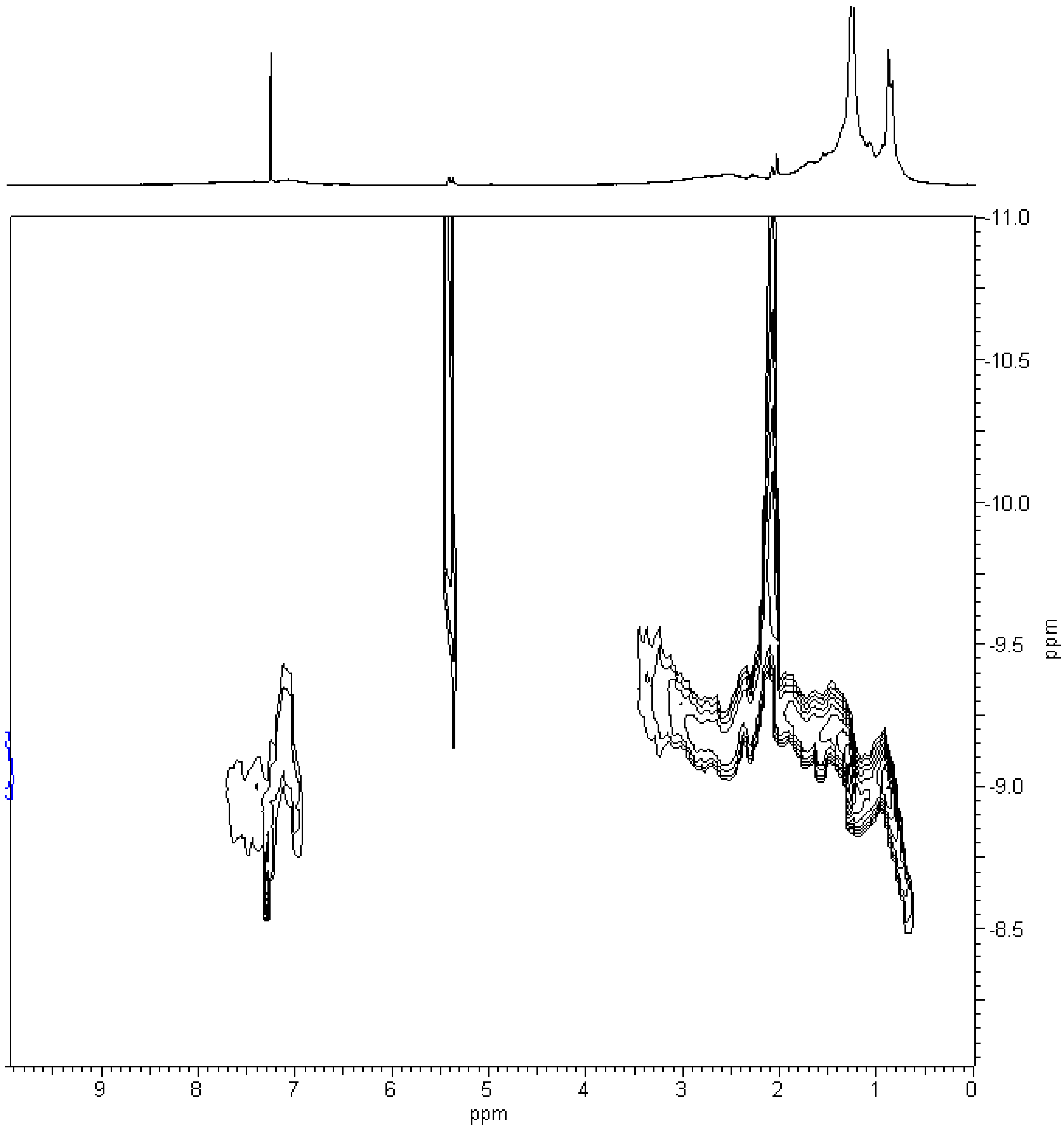
H-NMR



HSQC



One-shot DOSY



P31-NMR

Acquisition Time (sec)	0.5407	*Comment*	AL-5-P31 in CDCl3 18-Feb-2015 P31 NMR {H}			*Date*	18 Feb 2015 10:21:36
Date Stamp	18 Feb 2015 10:21:36			*File Name*	\\130.15.98.10\data\hesp\nmr\AL-5-P31\1\PDATA\1\1r		
Frequency (MHz)	202.05	*Nucleus*	31P	*Number of Transients*	1024	*Origin*	spect
Original Points Count	32768	*Owner*	root	*Points Count*	32768	*Pulse Sequence*	zgdc30
Receiver Gain	16384.00	*SW(cyclical) (Hz)*	60606.06	*Solvent*	CHLOROFORM-d		
Spectrum Offset (Hz)	10100.9102	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	60604.21	*Temperature (degree C)*	26.000