

Supporting Information

Synthesis of Bis(oxazoline) Ligands Possessing C-5 *gem*-disubstitution and Their Application in Asymmetric Friedel-Crafts Alkylations

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Centre for Synthesis and Chemical Biology, School of Chemistry and Chemical Biology, University College Dublin, Belfield, Dublin 4, Ireland.

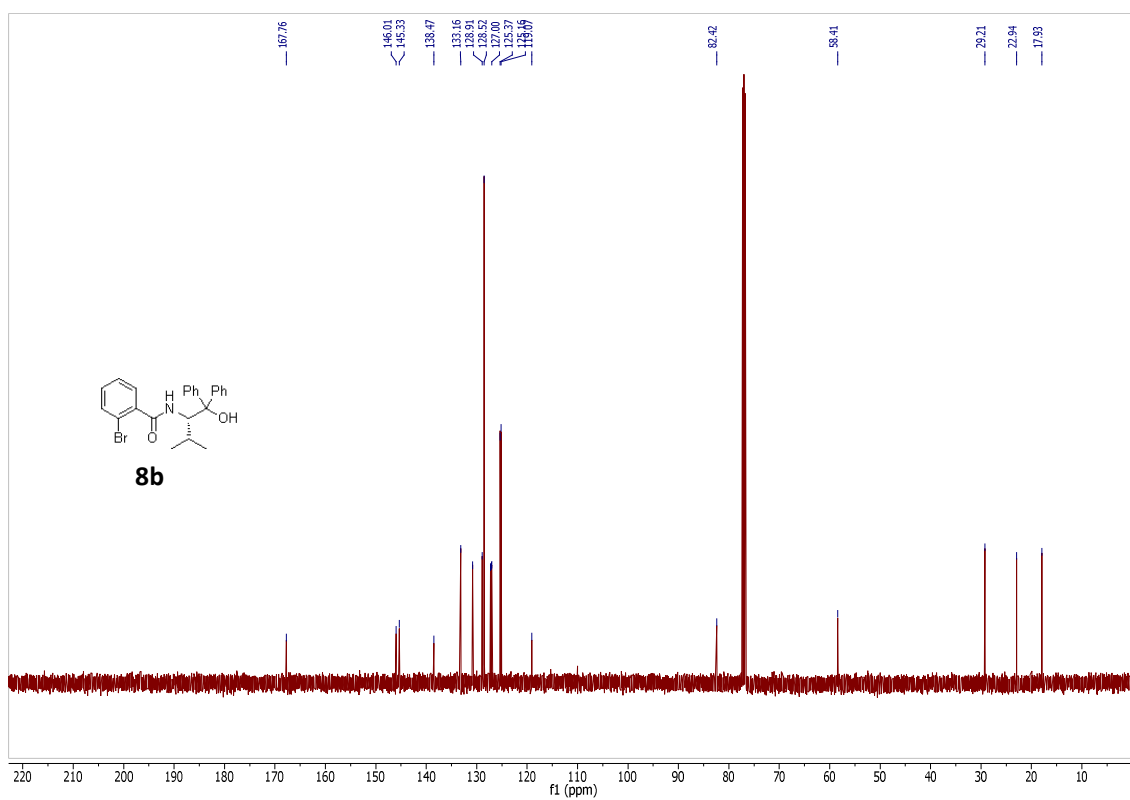
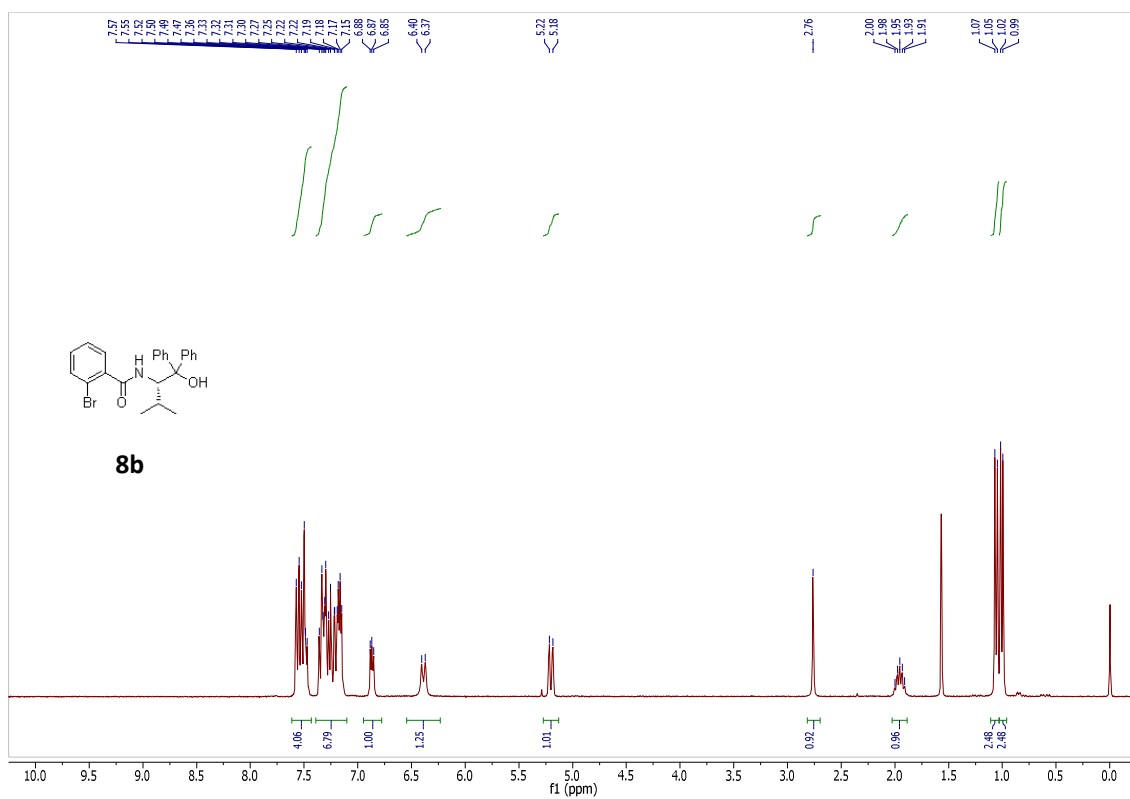
E-mail: p.guiry@ucd.ie

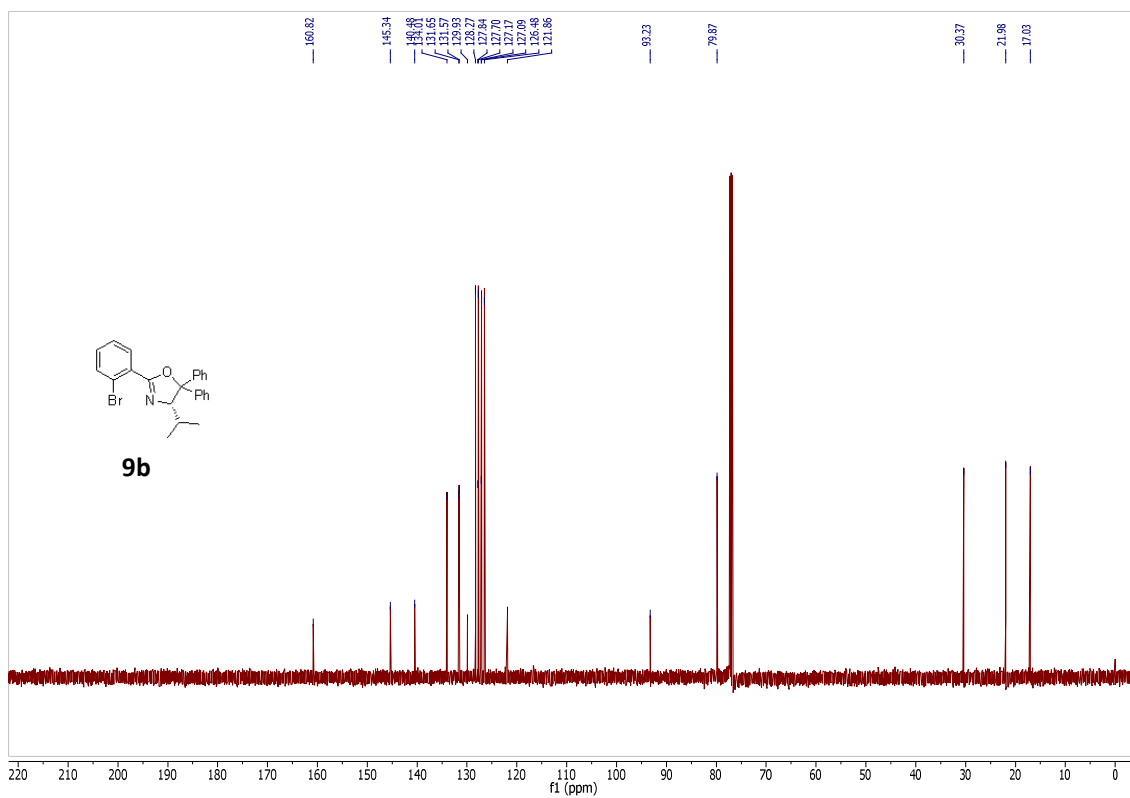
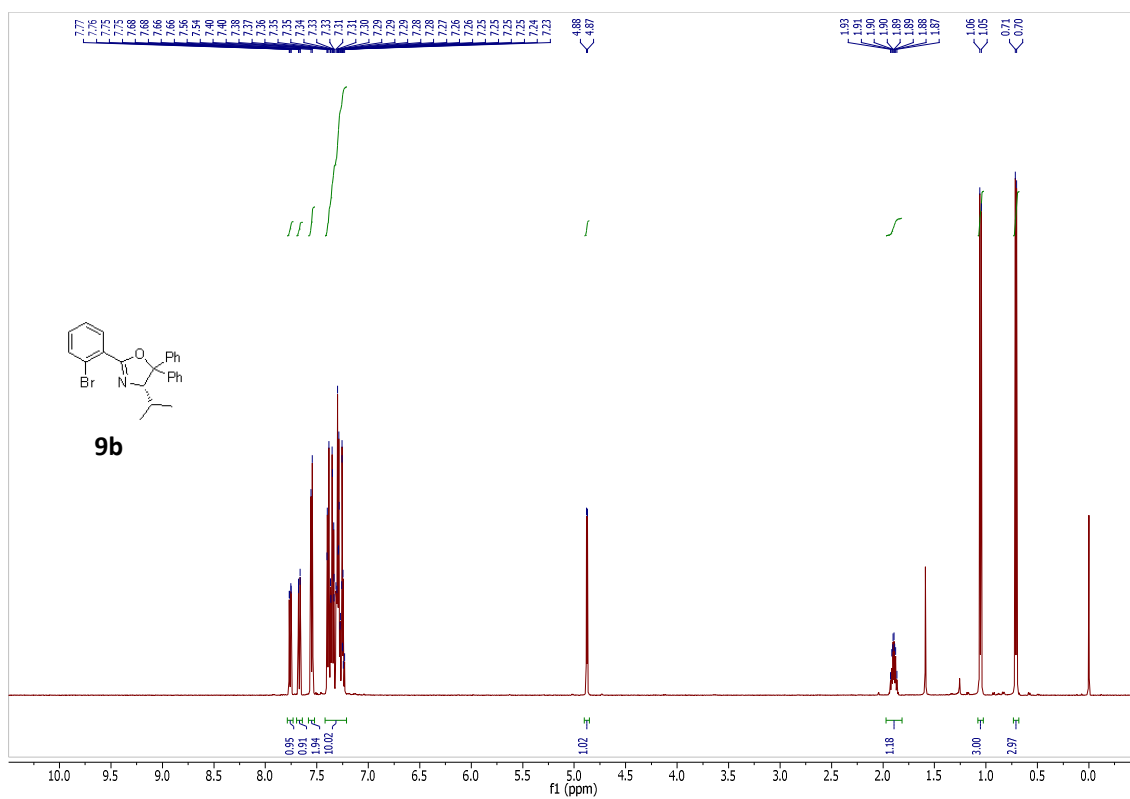
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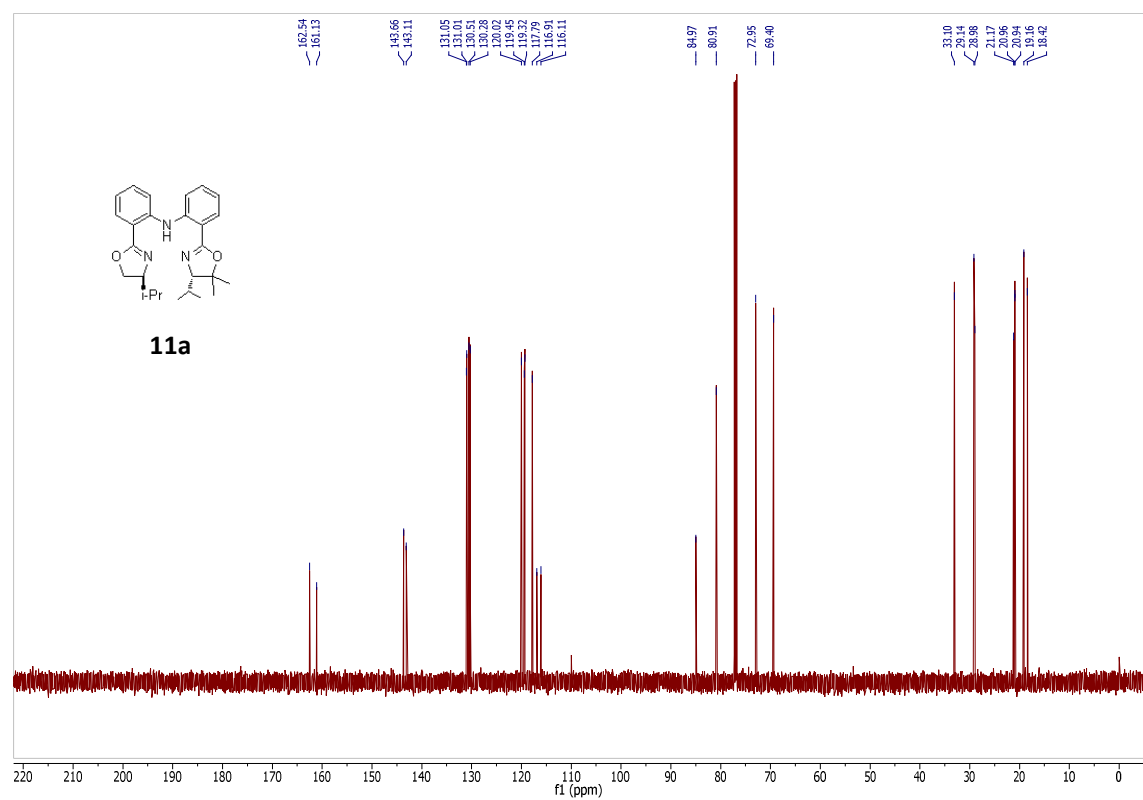
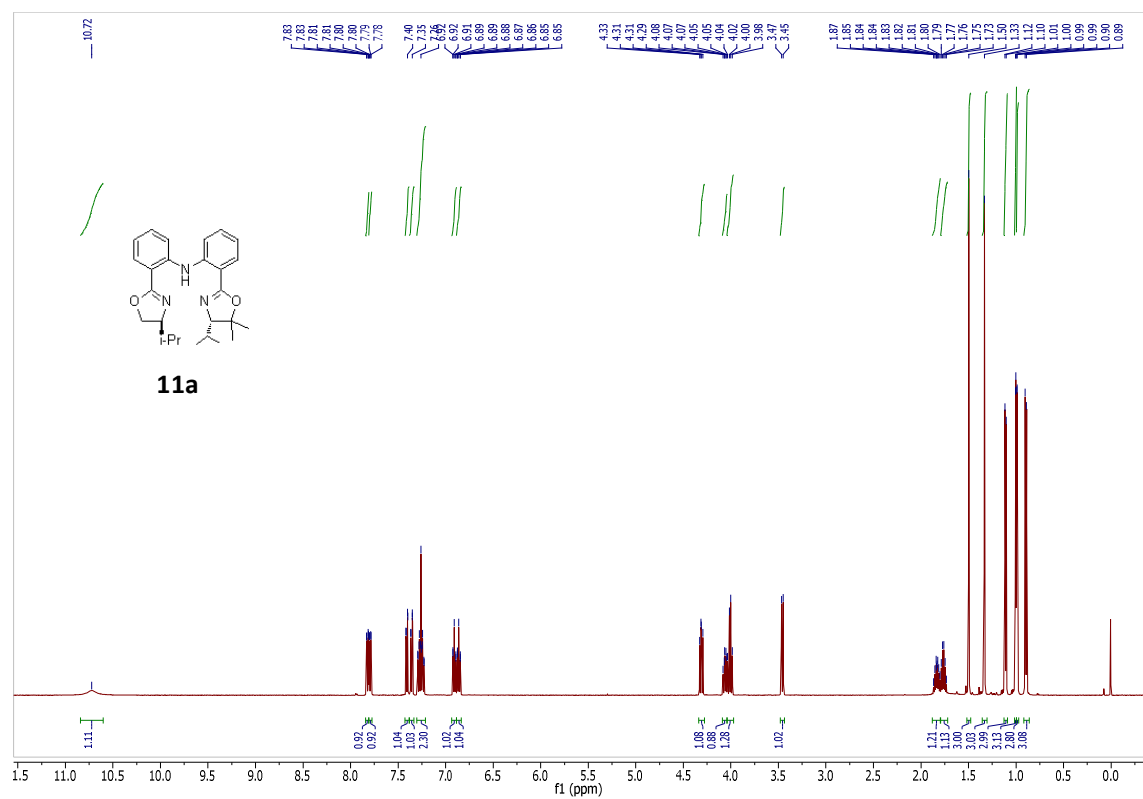
¹H and ¹³C NMR spectra of ligands and intermediates **S2 – S11**

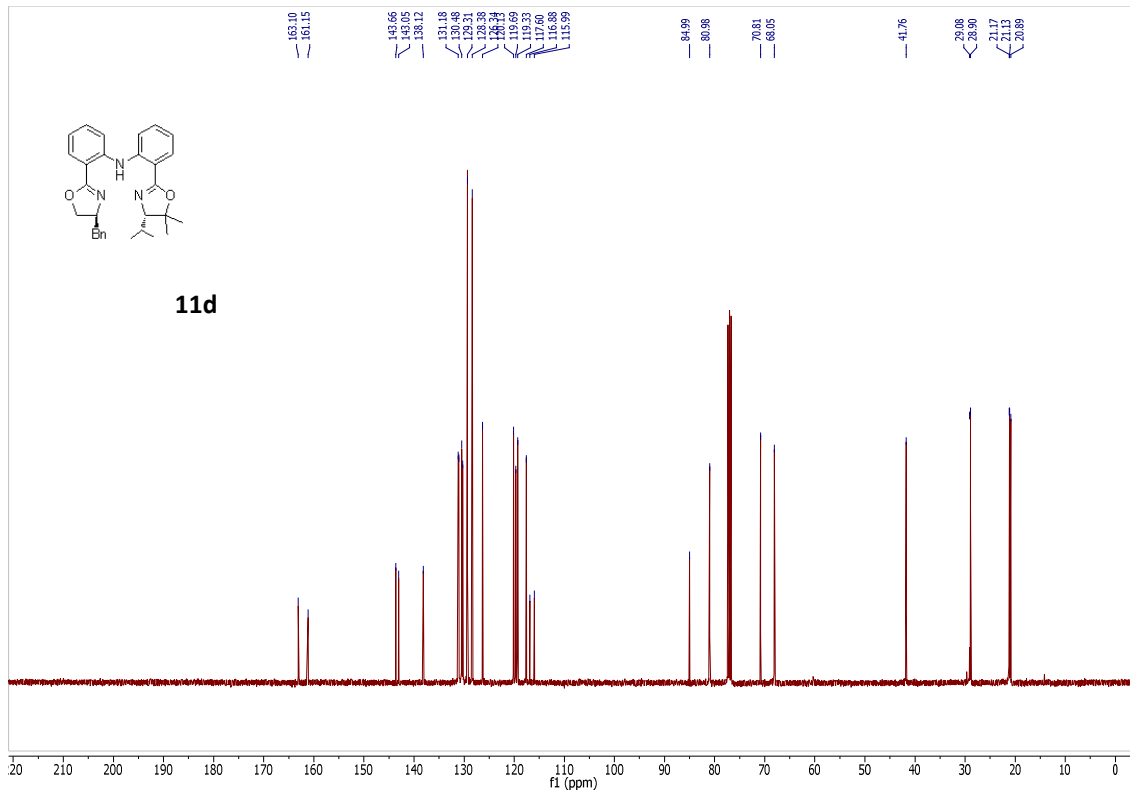
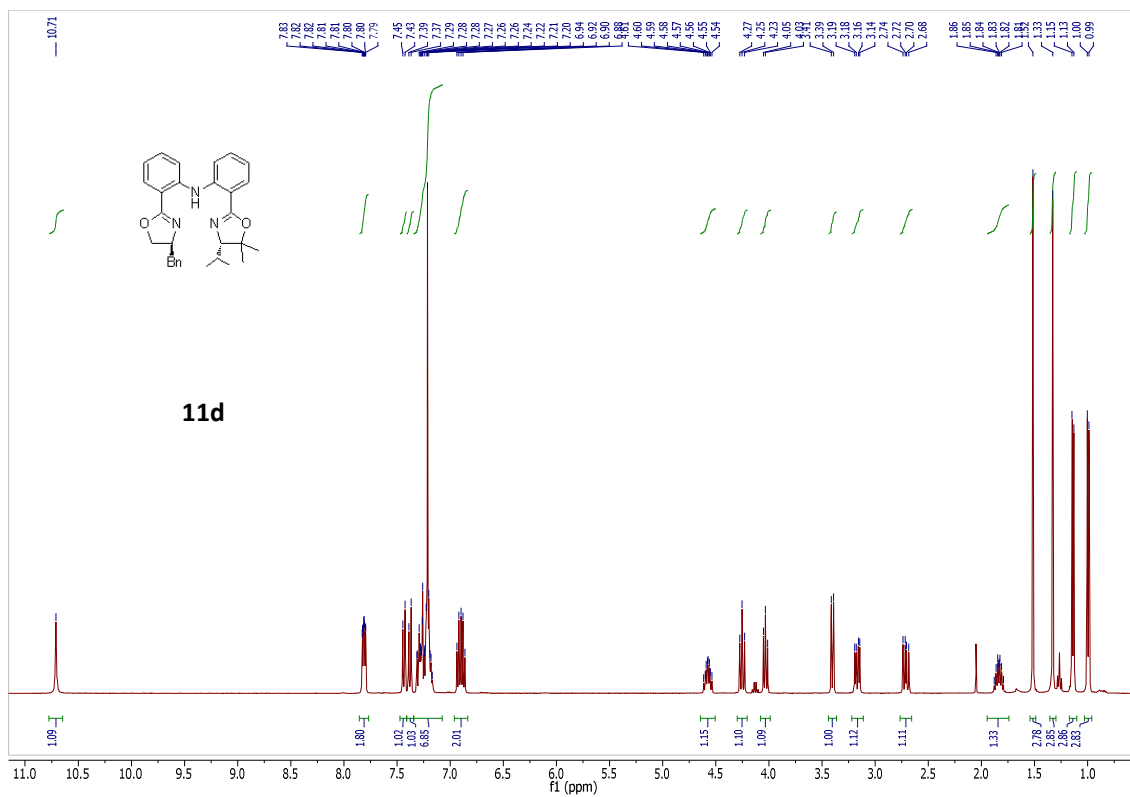
¹H and ¹³C NMR spectra and HPLC analysis of catalysis **S12 – S27**

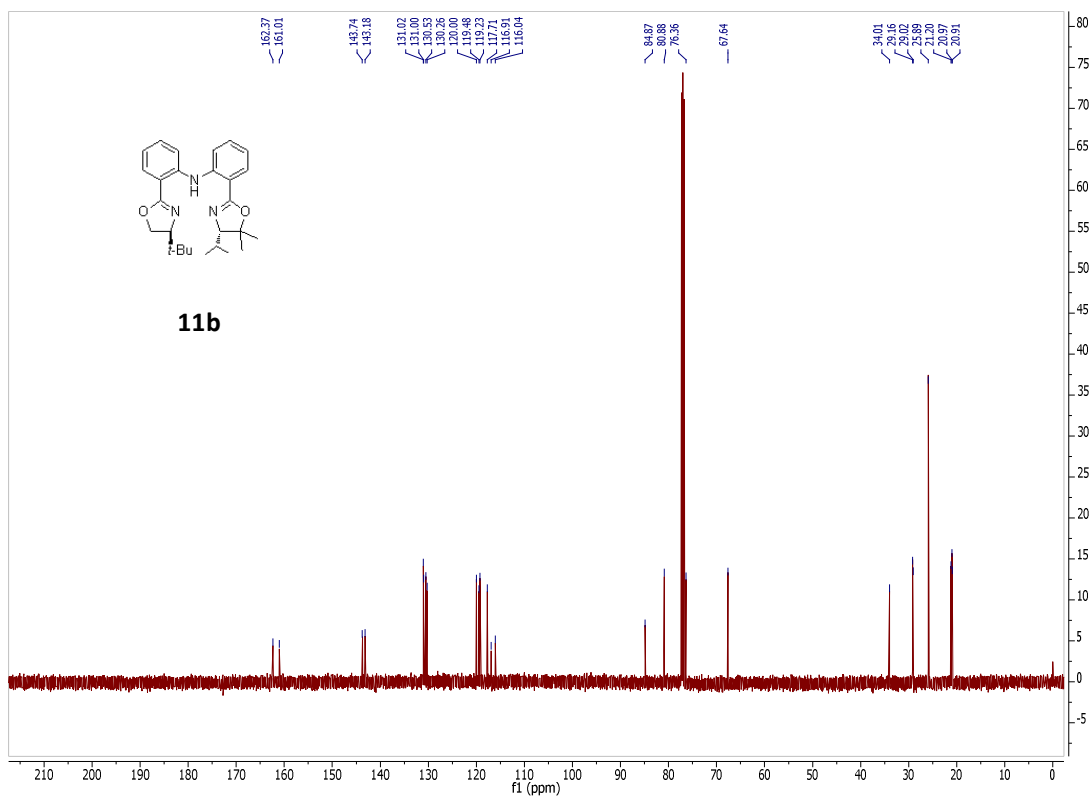
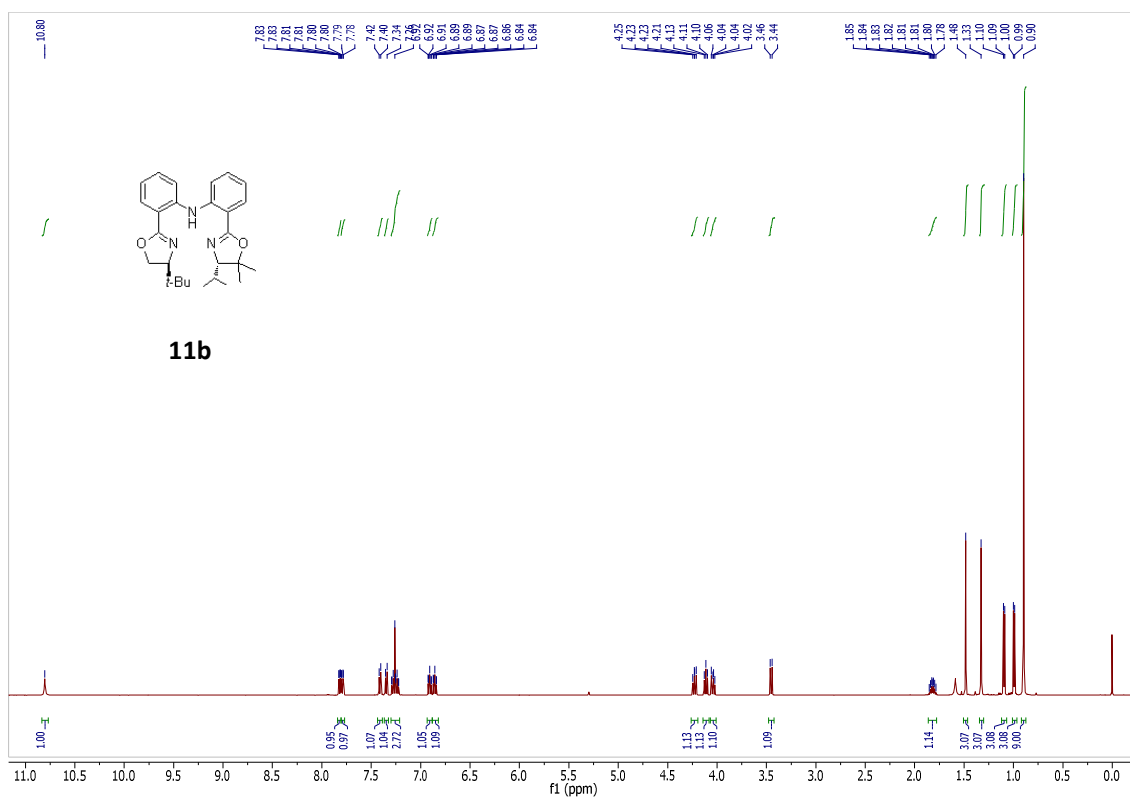
X-ray crystallographic structures and information **S28 – S39**

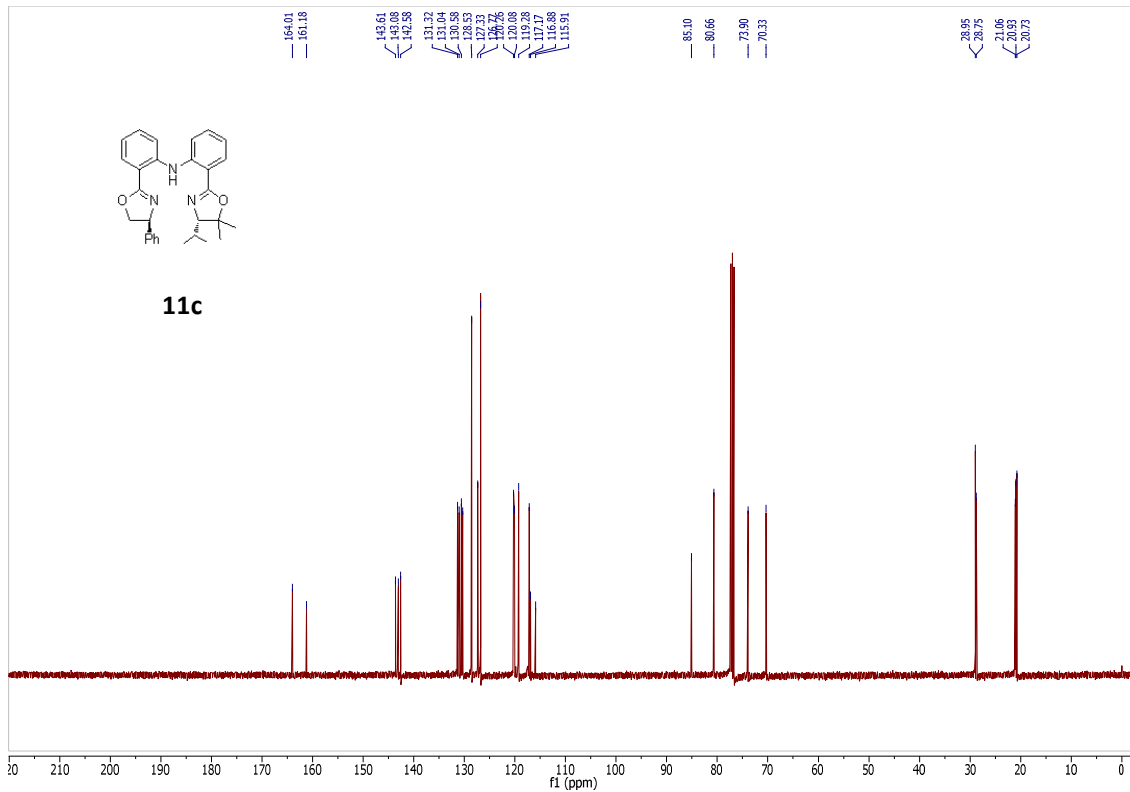
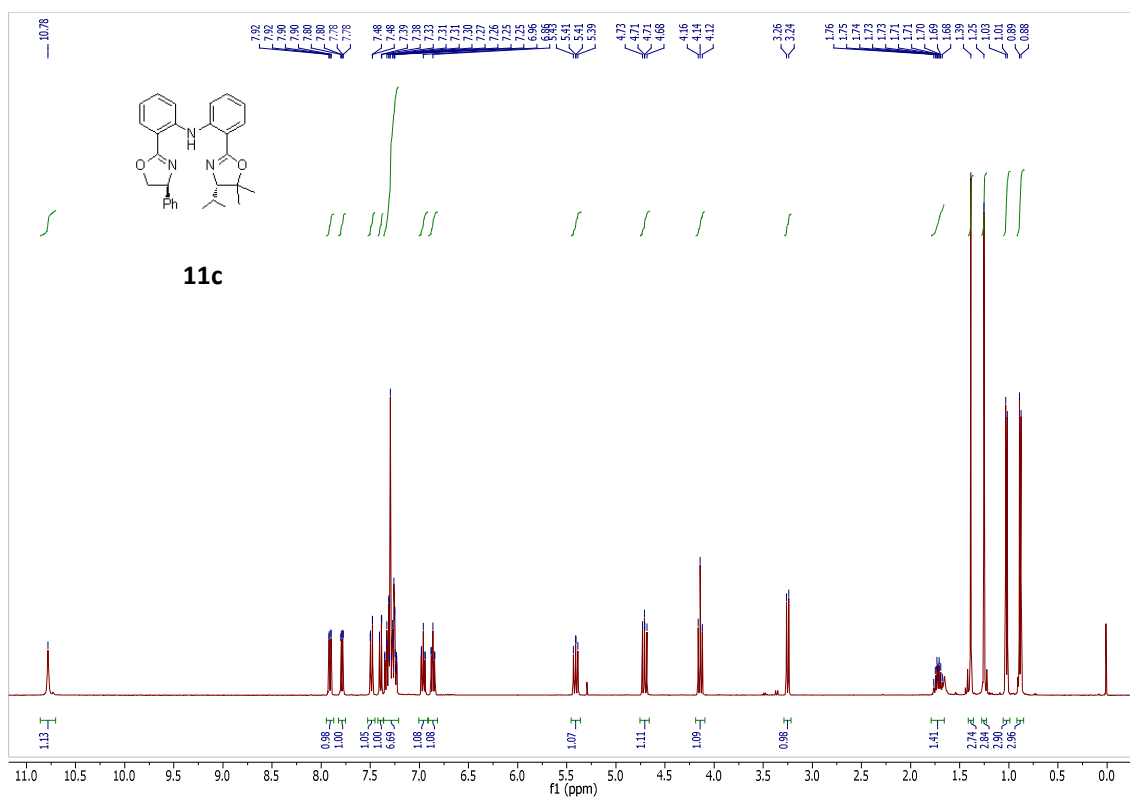


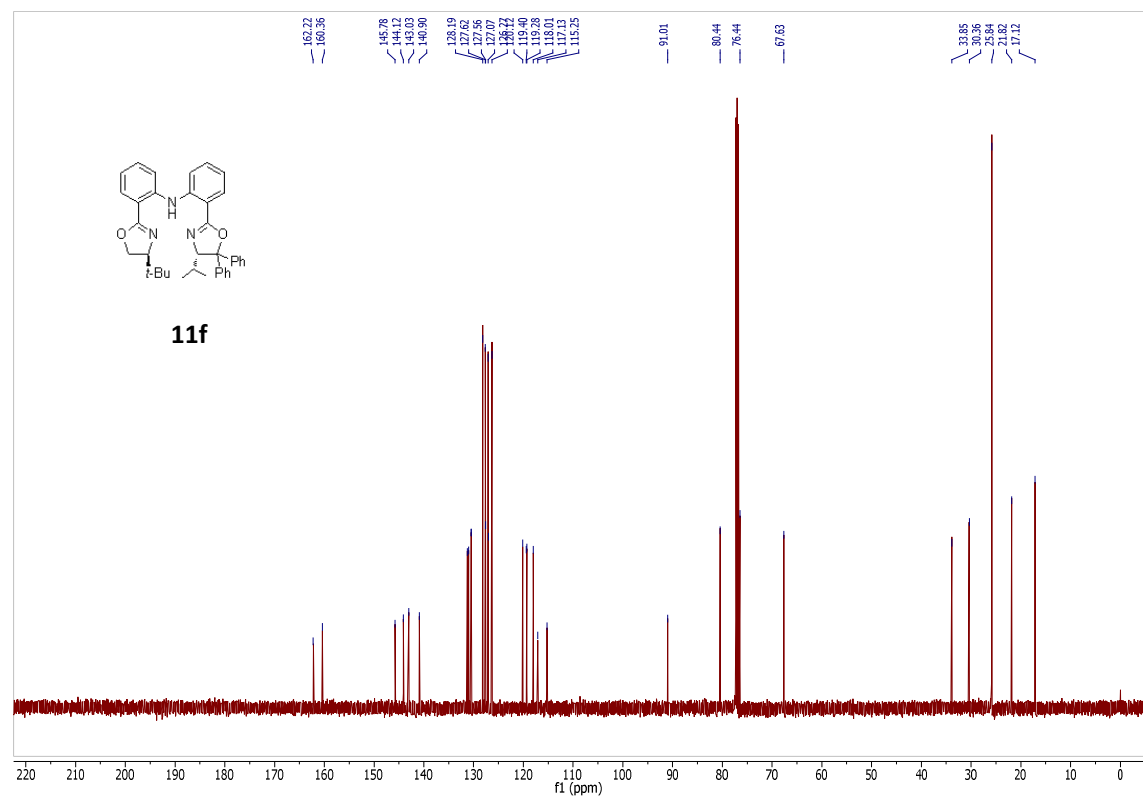
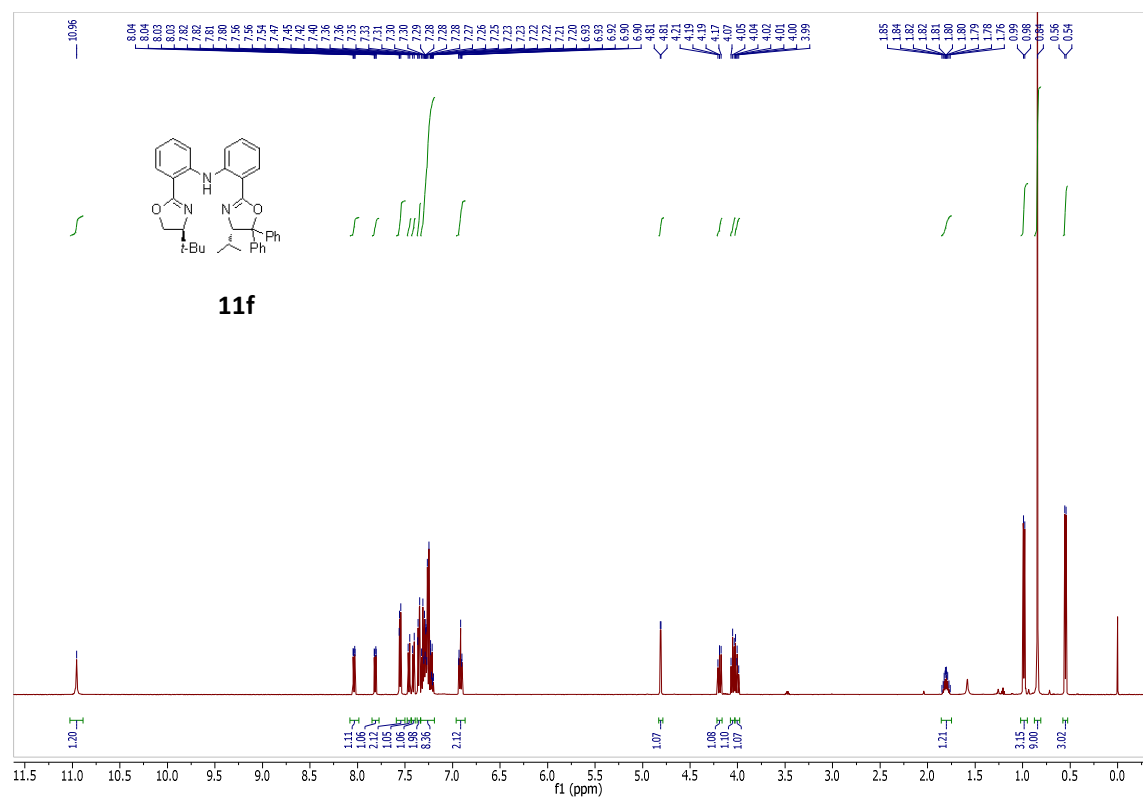


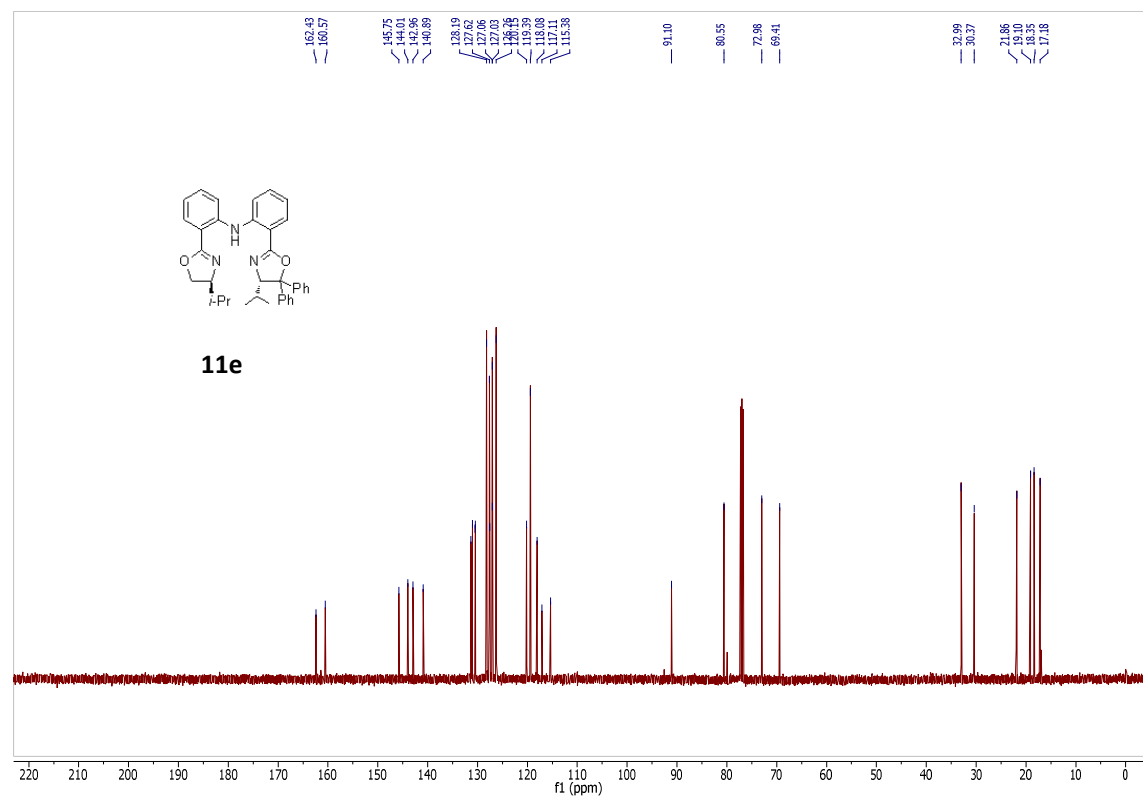
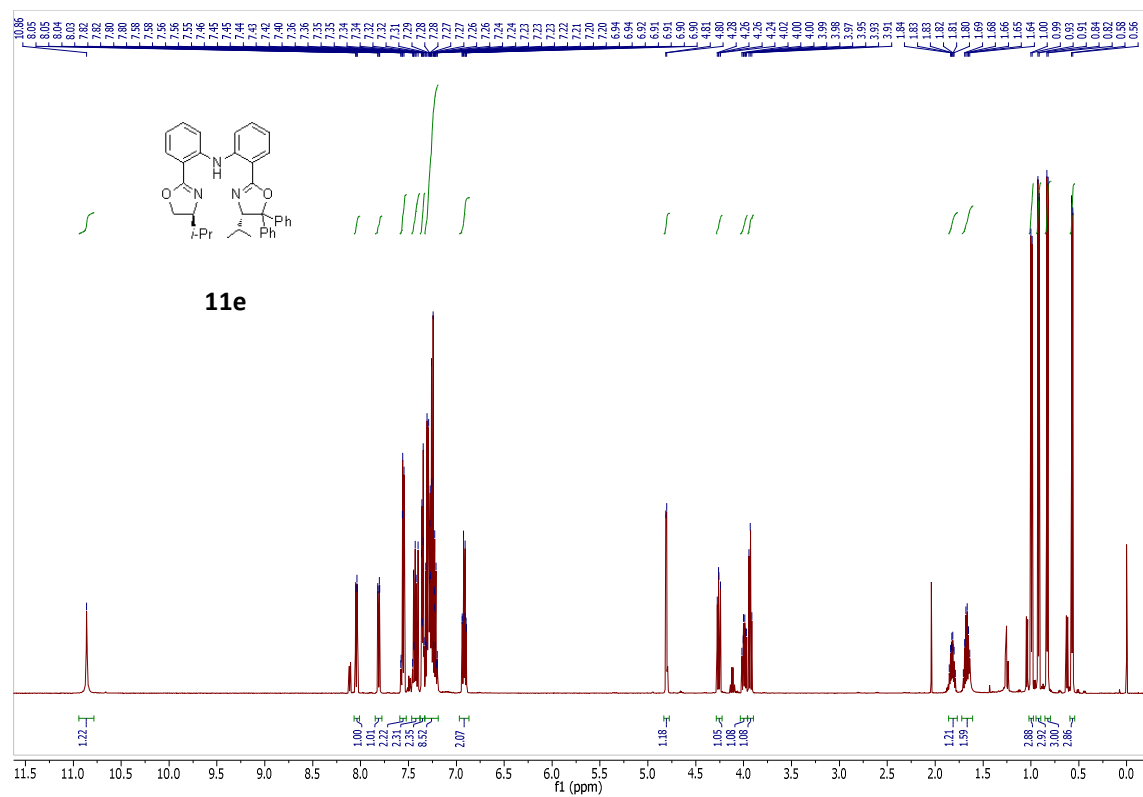


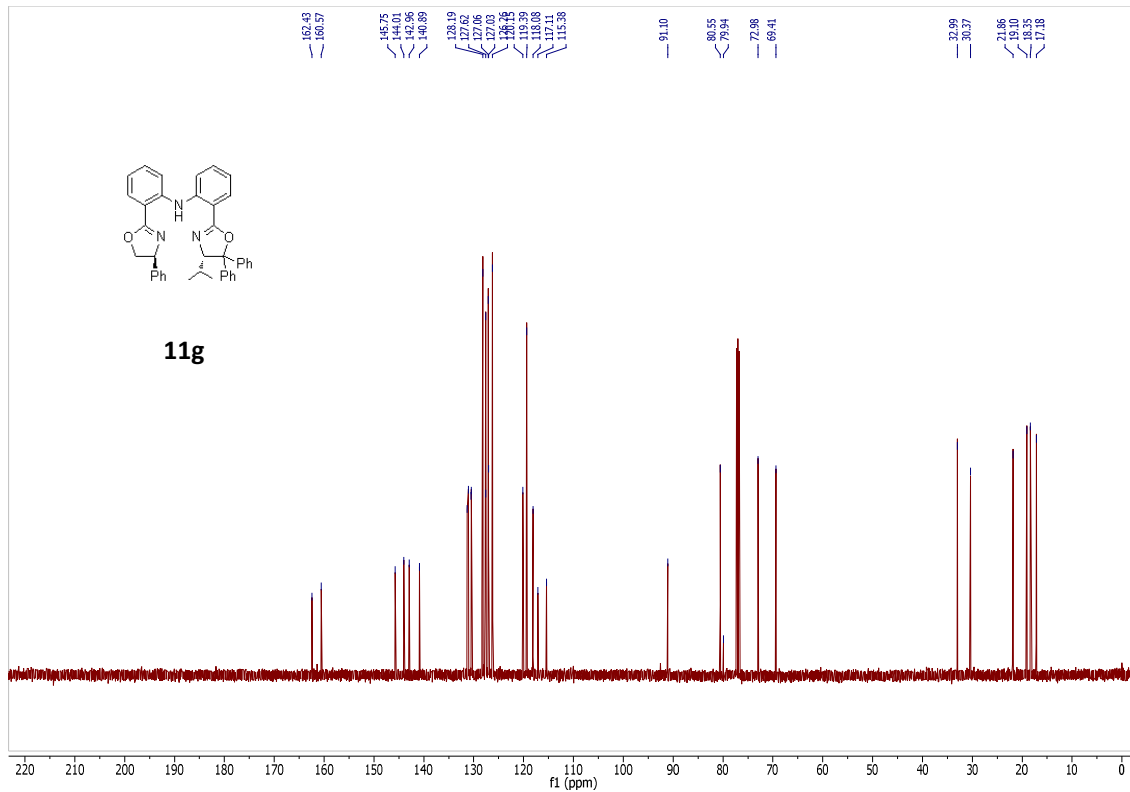
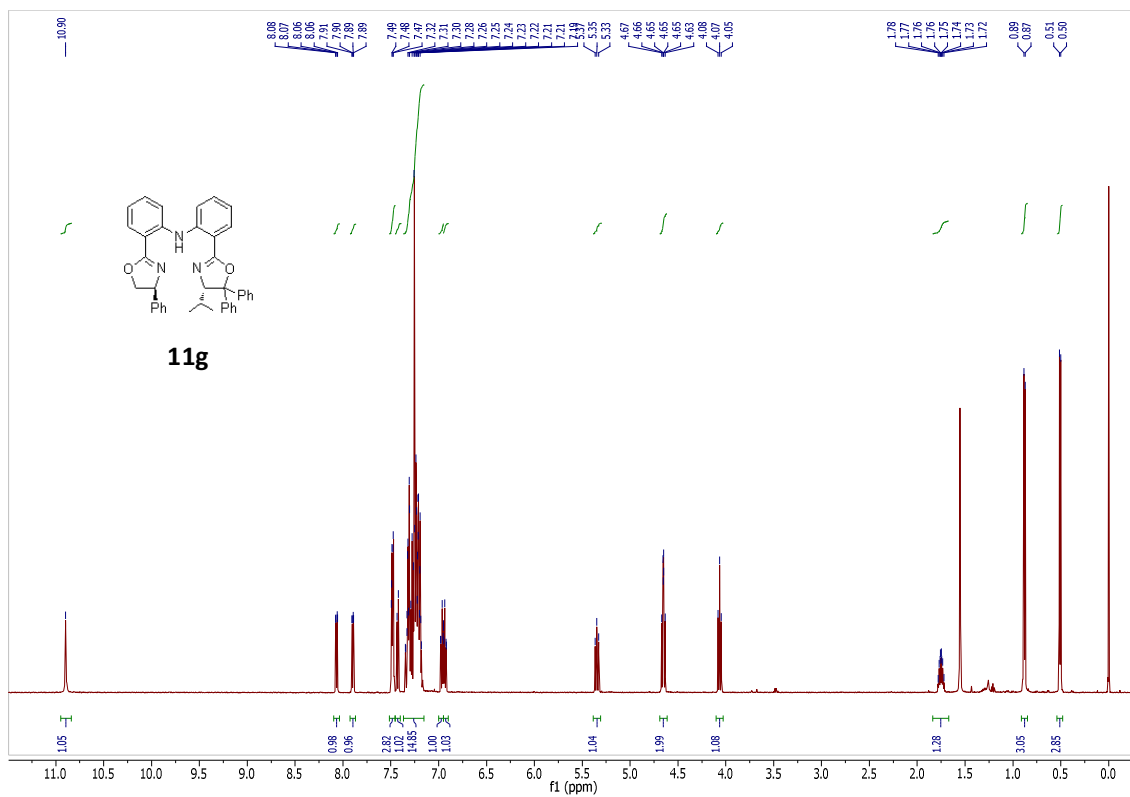


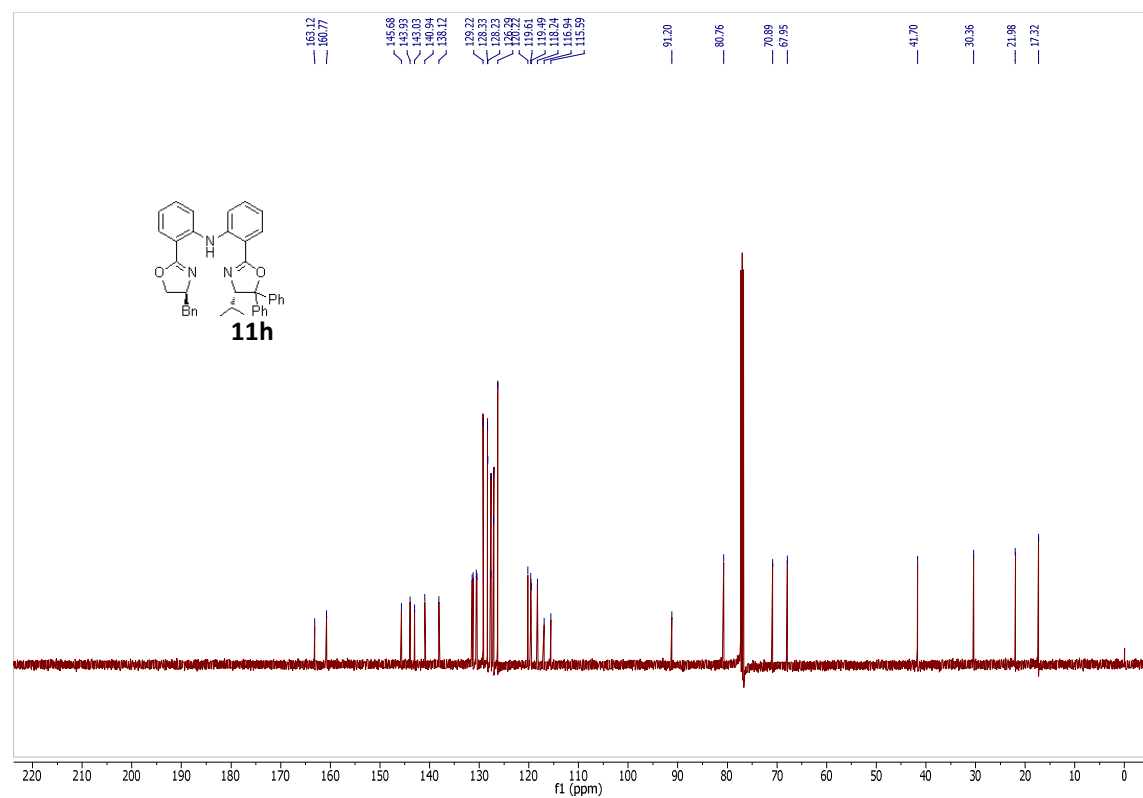
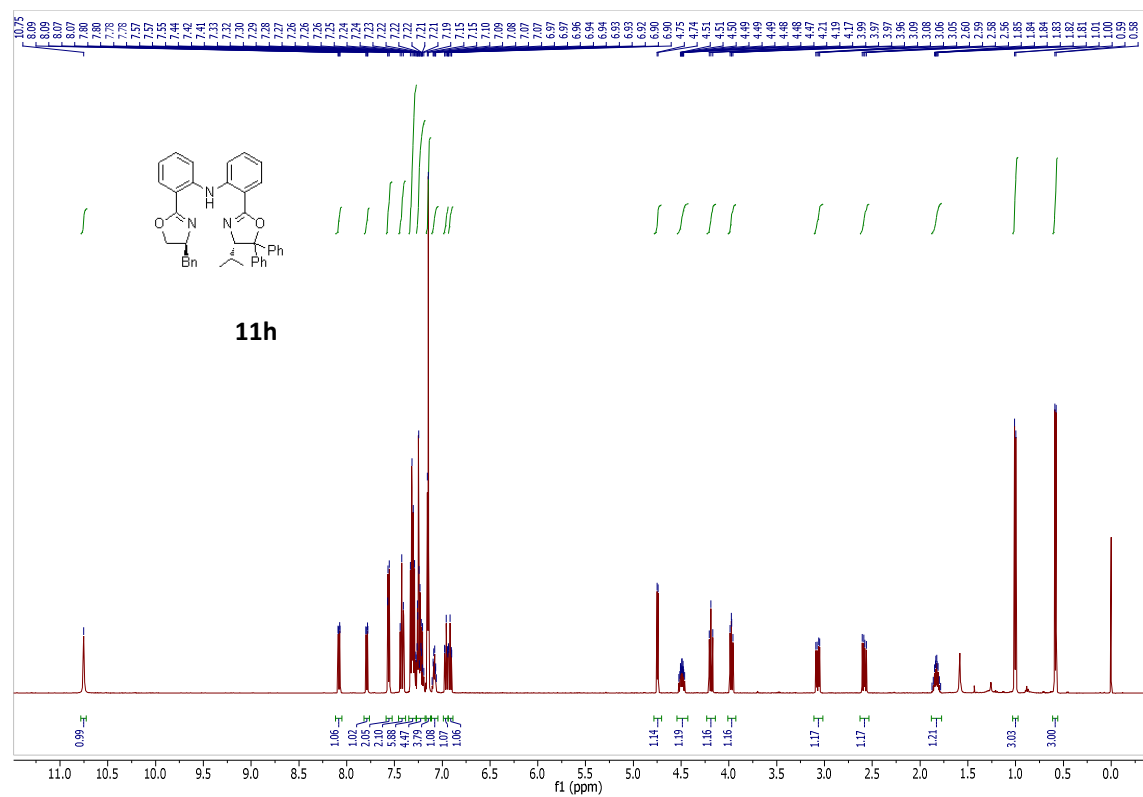






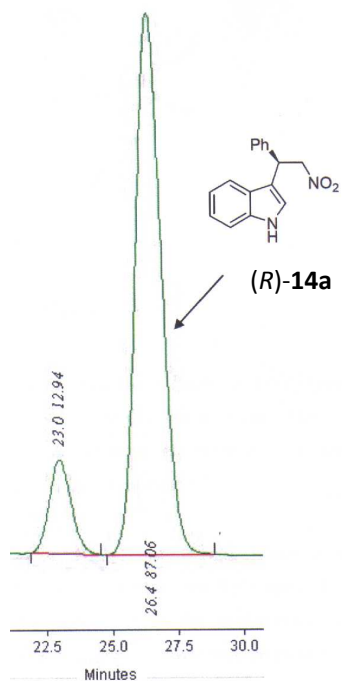




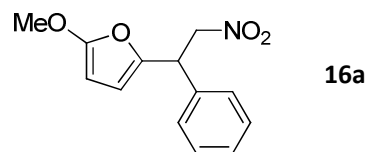


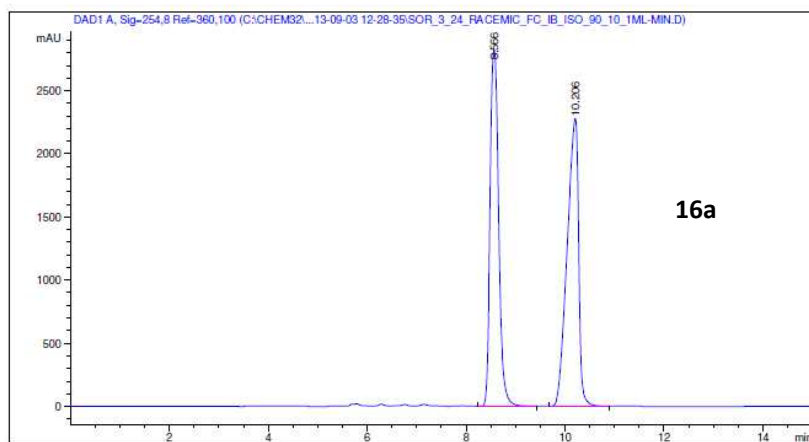
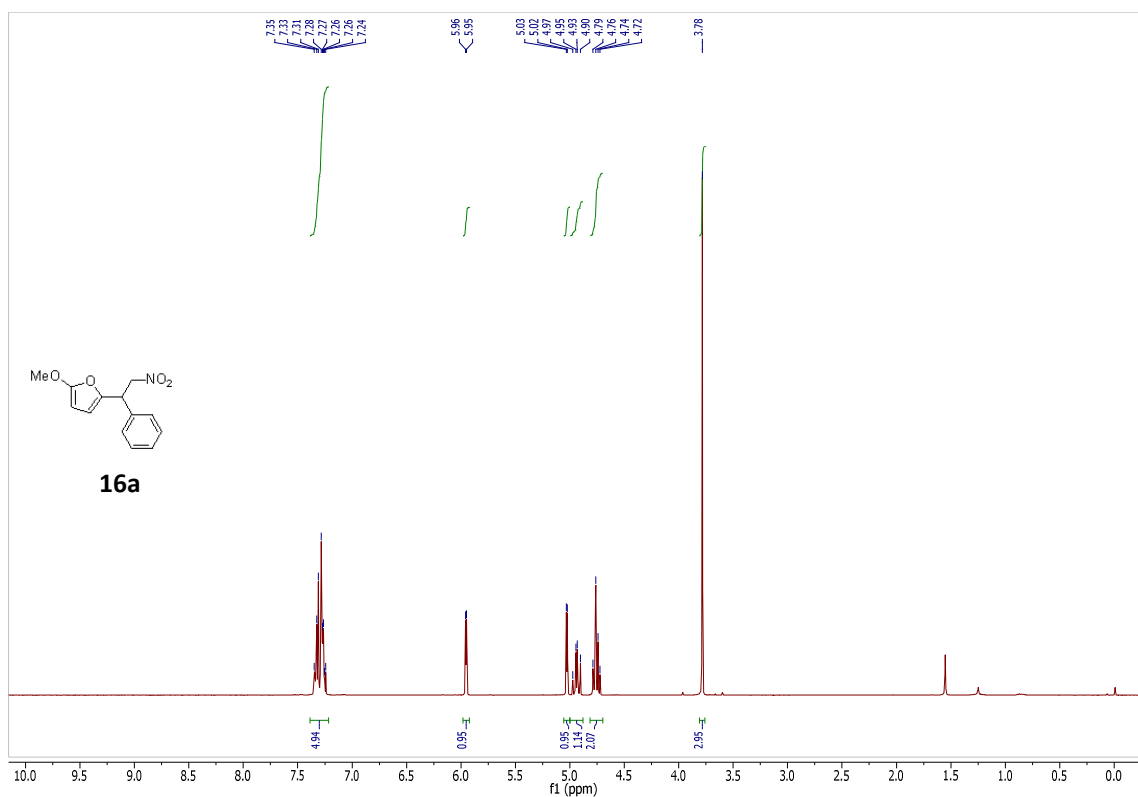
Chromatographic trace for 14a

HPLC: Chiralcel® IB, (heptane:ethanol, 70:30, 0.9 mL/min). Retention times: $t_{\text{minor}} = 23.0$ min, $t_{\text{major}} = 26.5$ min).



NMR spectra and chromatographic traces for 16





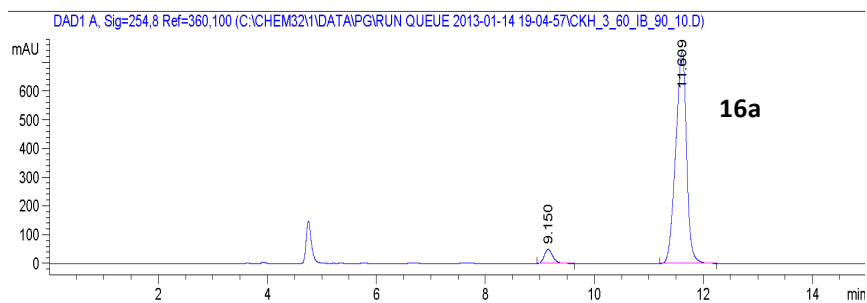
Area Percent Report

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Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig-254,8 Ref-360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.566	VB	0.1876	3.38232e4	2826.45264	48.0505
2	10.206	BB	0.2630	3.65678e4	2280.84277	51.9495

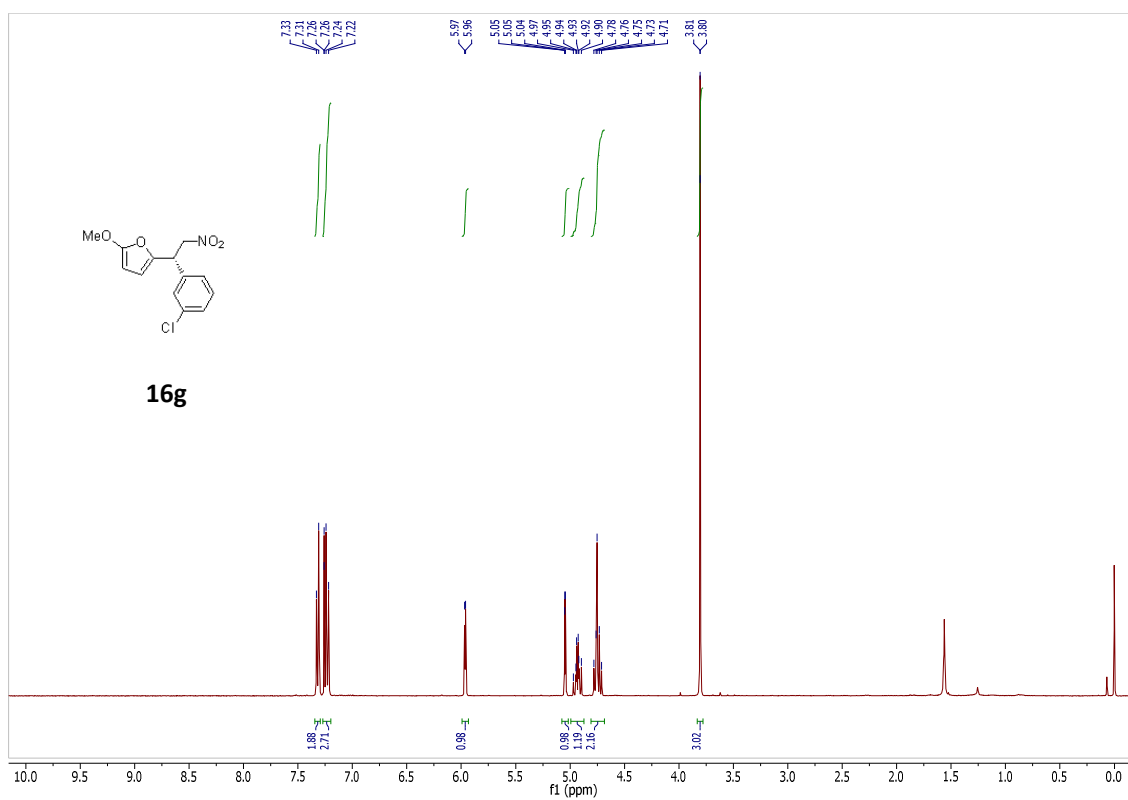
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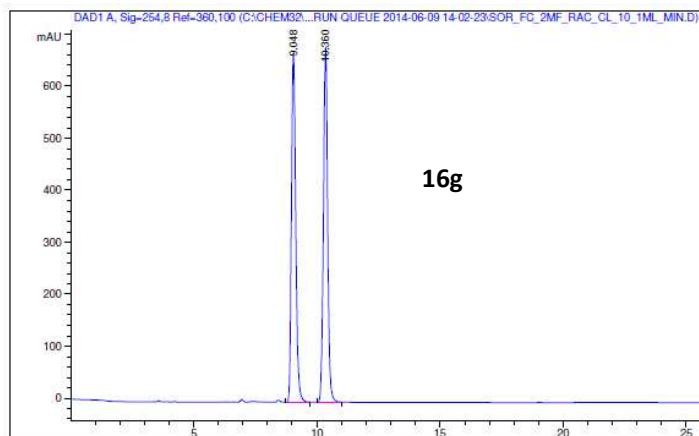


Signal 1: DAD1 A, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.150	BB	0.1680	557.07367	49.98060	5.1595
2	11.609	BB	0.2128	1.02399e4	743.15887	94.8405

Totals : 1.07970e4 793.13948





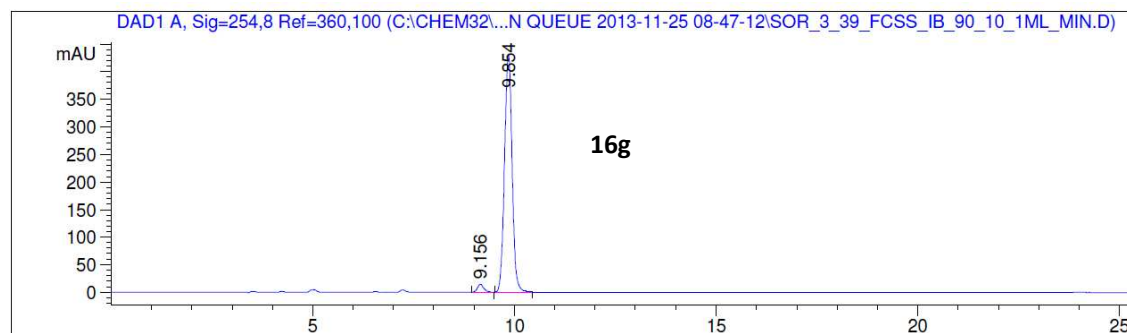
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Use Multiplier & Dilution Factor with ISTDs

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1	9.048	VB	0.1863	8071.39209	671.13824	49.8099
2	10.360	BB	0.1832	8132.99268	681.72882	50.1901

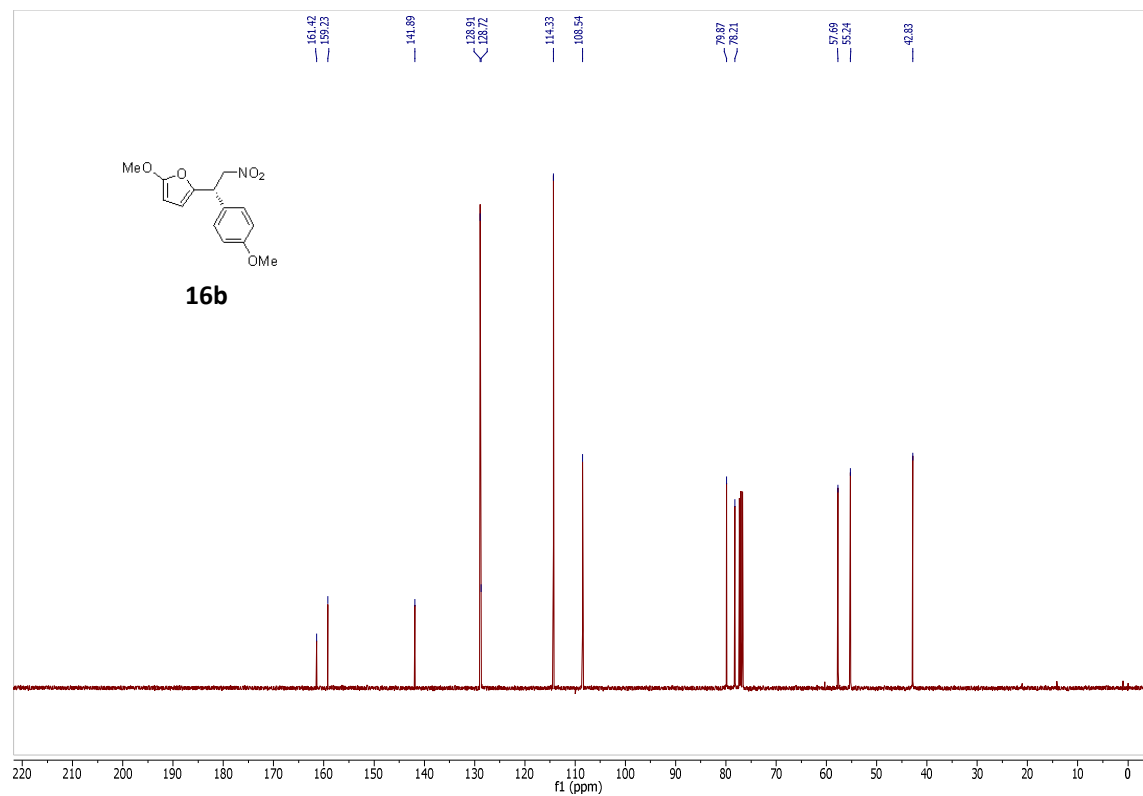
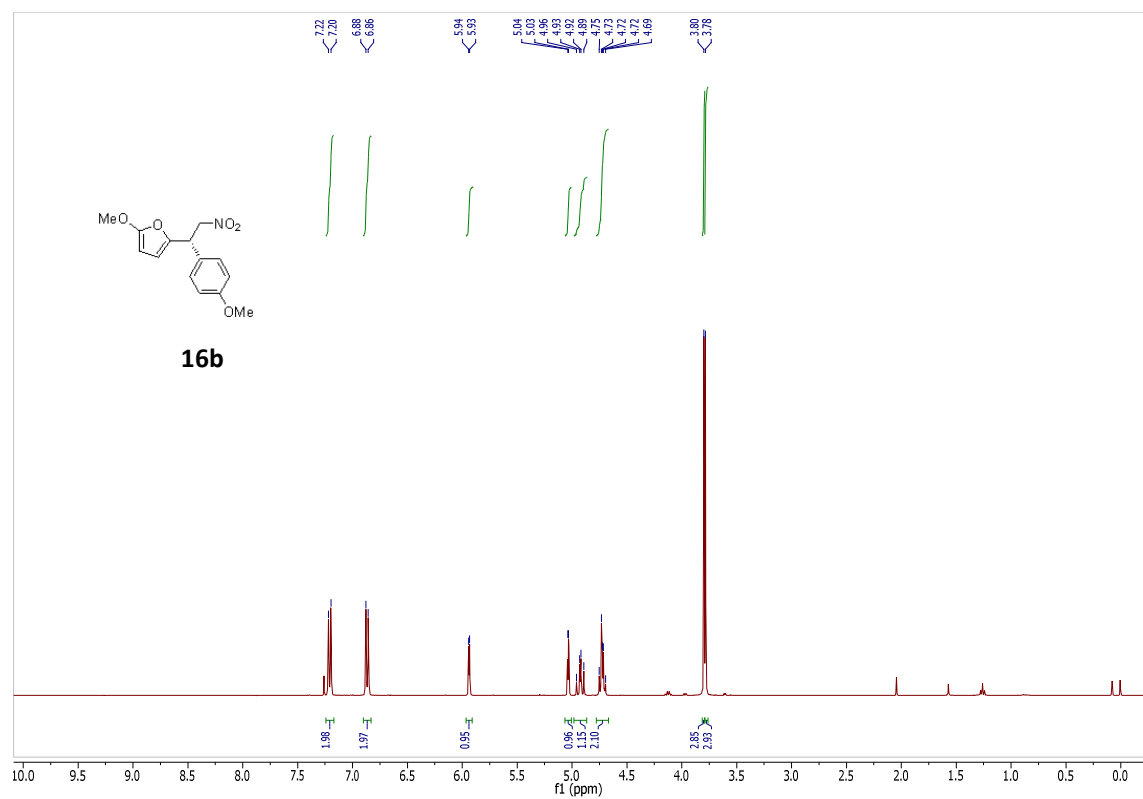
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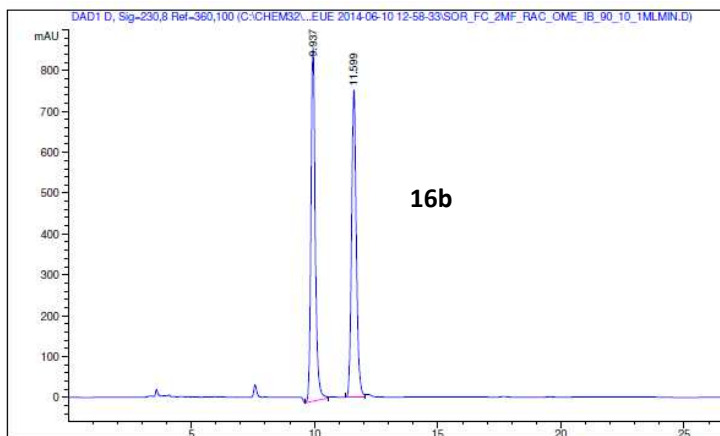


Signal 1: DAD1 A, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.156	BB	0.1696	157.59575	14.18279	2.7328
2	9.854	BB	0.1997	5609.28076	431.35233	97.2672

Totals : 5766.87651 445.53511





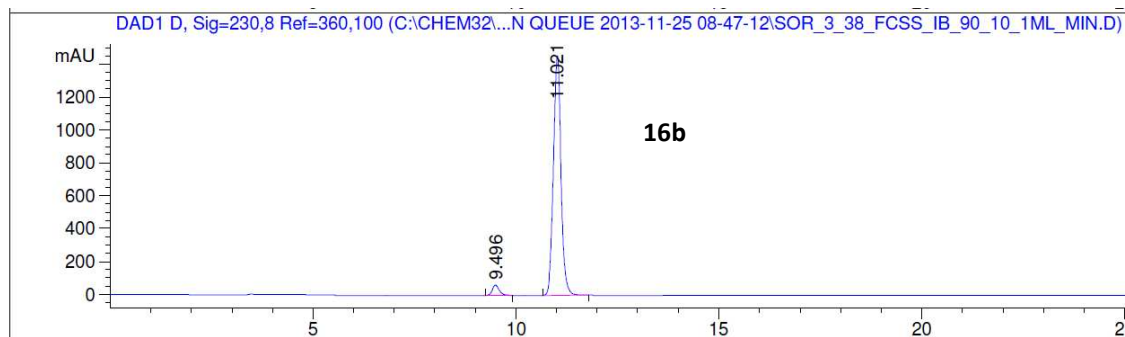
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Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 D, Sig=230,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.937	BB	0.1838	1.05288e4	866.11761	50.9630
2	11.599	BV	0.2072	1.01309e4	751.99884	49.0370

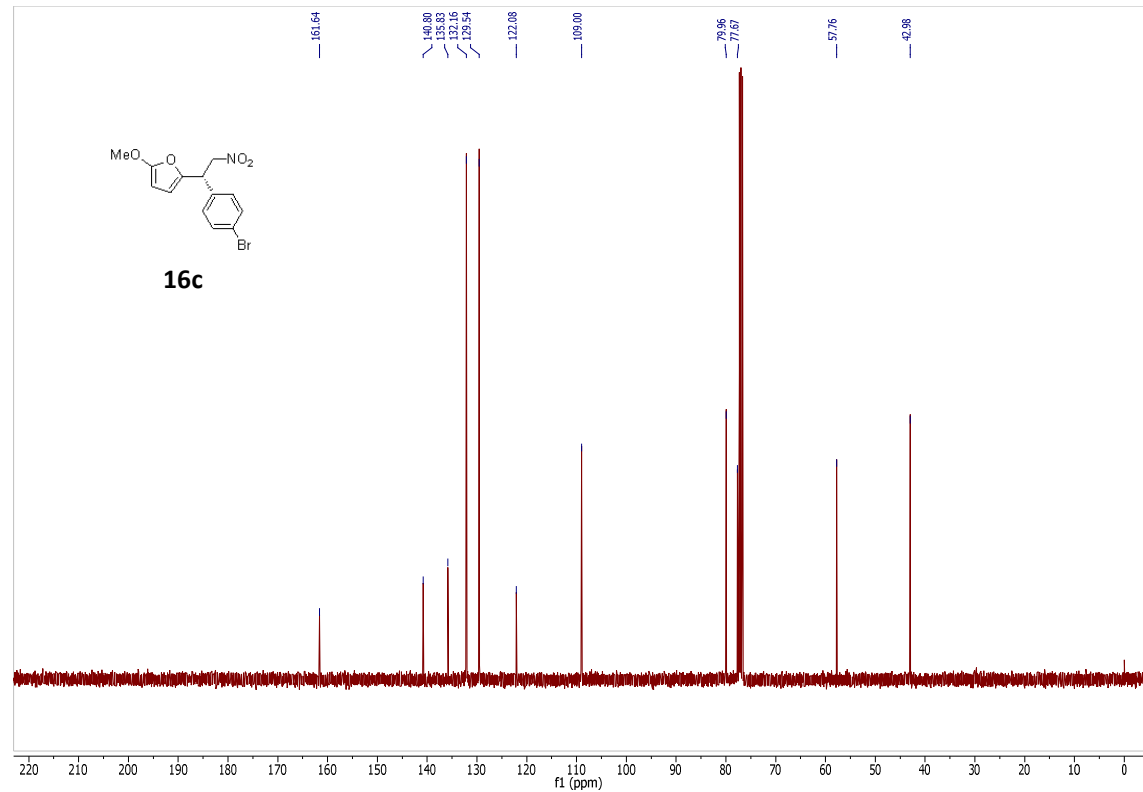
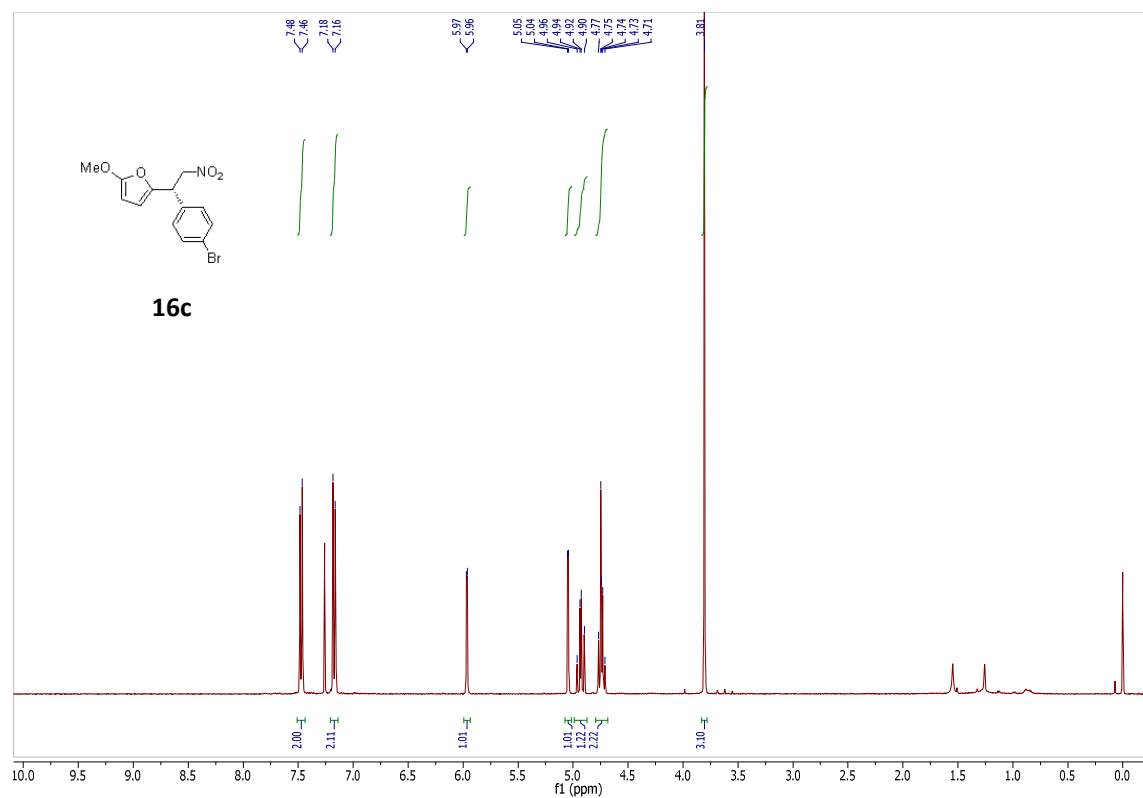
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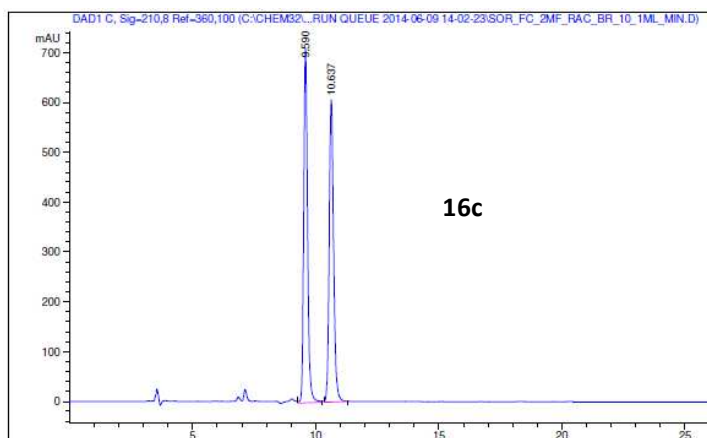


Signal 3: DAD1 D, Sig=230,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.496	BB	0.1810	764.39233	64.16113	3.8654
2	11.021	BB	0.2001	1.90107e4	1457.72217	96.1346

Totals : 1.97751e4 1521.88330





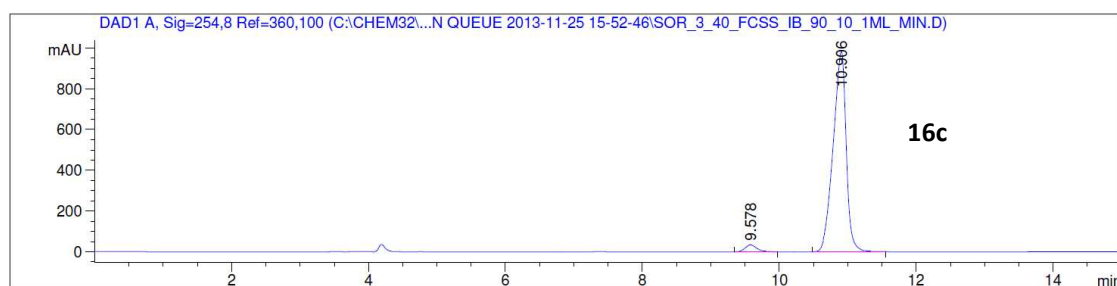
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Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.590	VB	0.1633	7632.33691	710.70807	50.2960
2	10.637	BB	0.1890	7542.51660	606.81372	49.7040

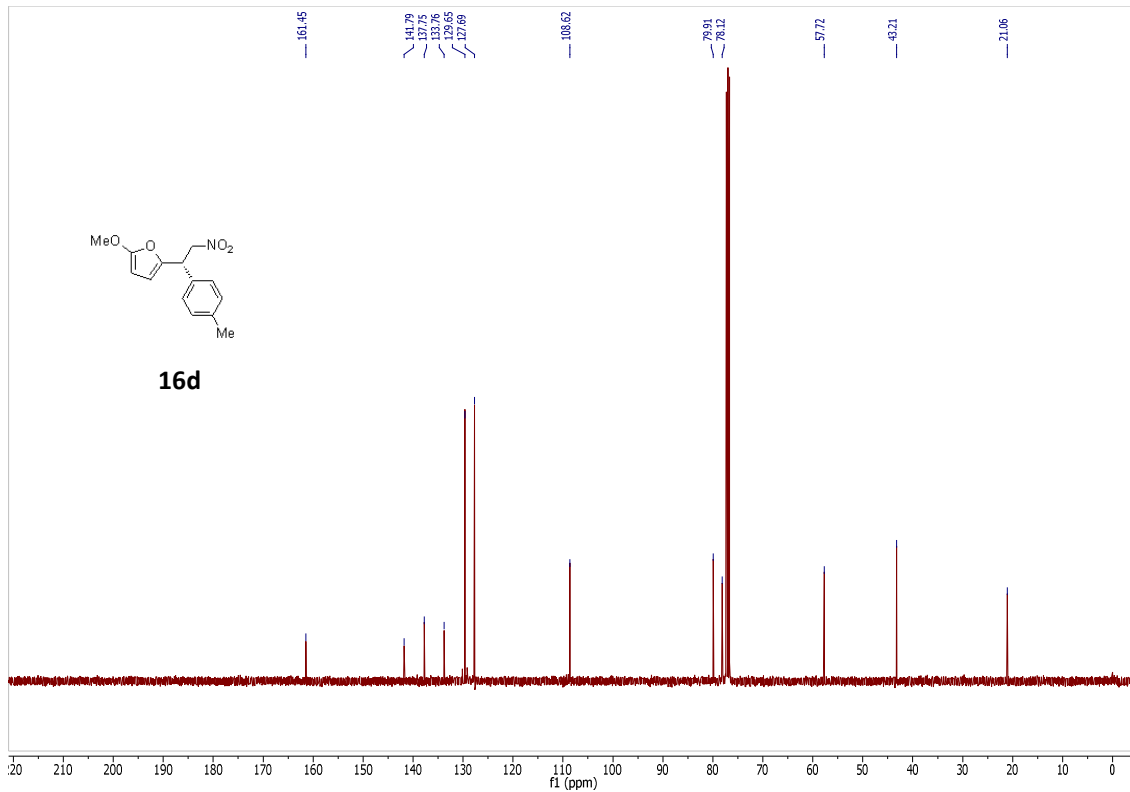
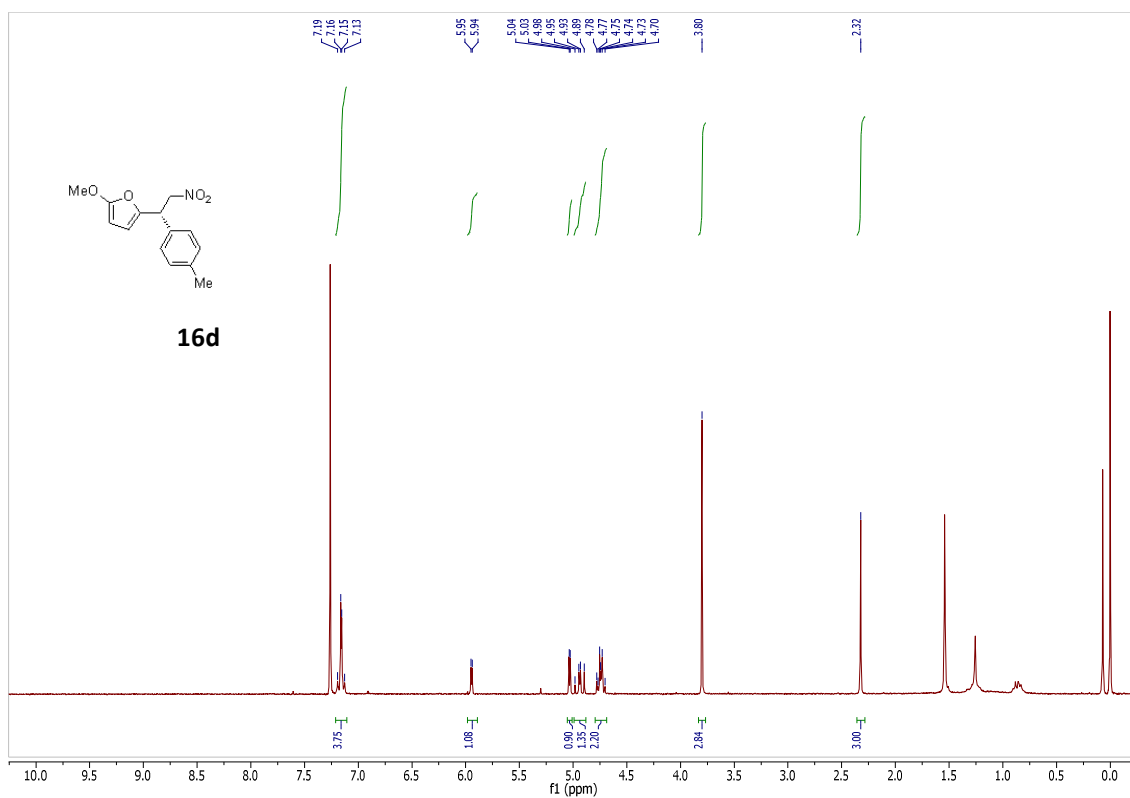
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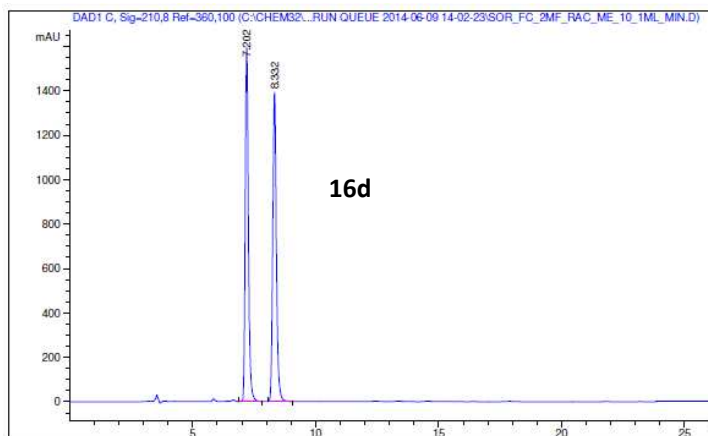


Signal 1: DAD1 A, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.578	BB	0.1879	424.08554	34.38583	3.1242
2	10.906	BB	0.2011	1.31502e4	989.43732	96.8758

Totals : 1.35743e4 1023.82315





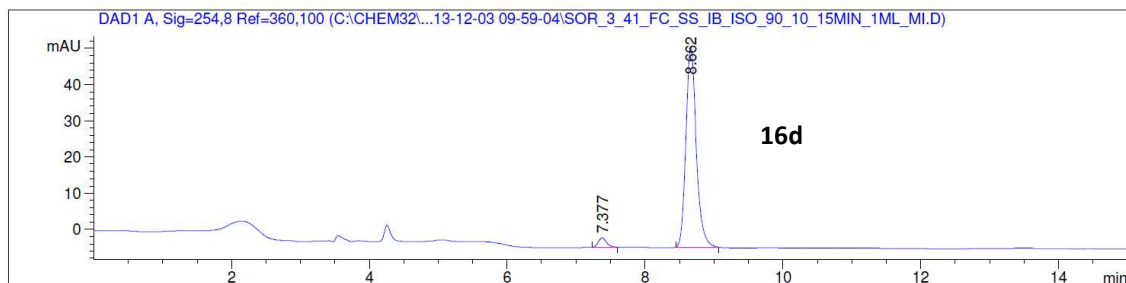
Area Percent Report

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Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.202	VB	0.1339	1.42093e4	1595.17261	49.8958
2	8.332	BB	0.1555	1.42686e4	1393.53381	50.1042

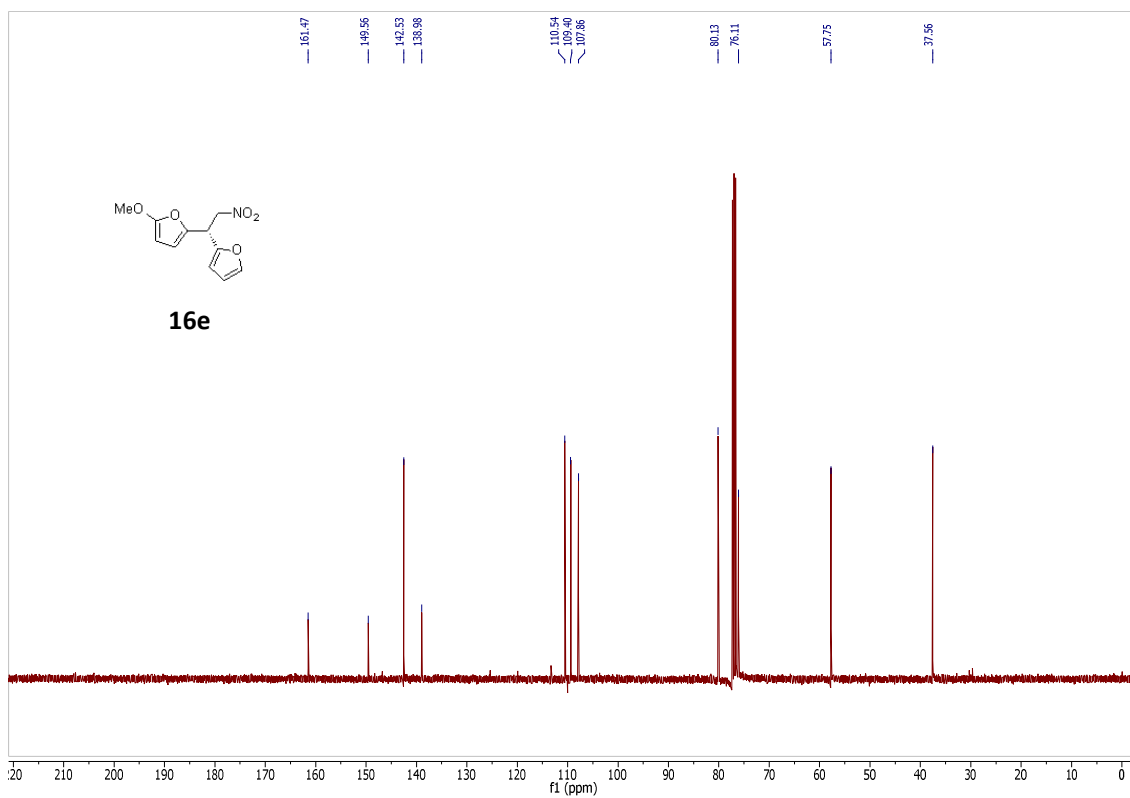
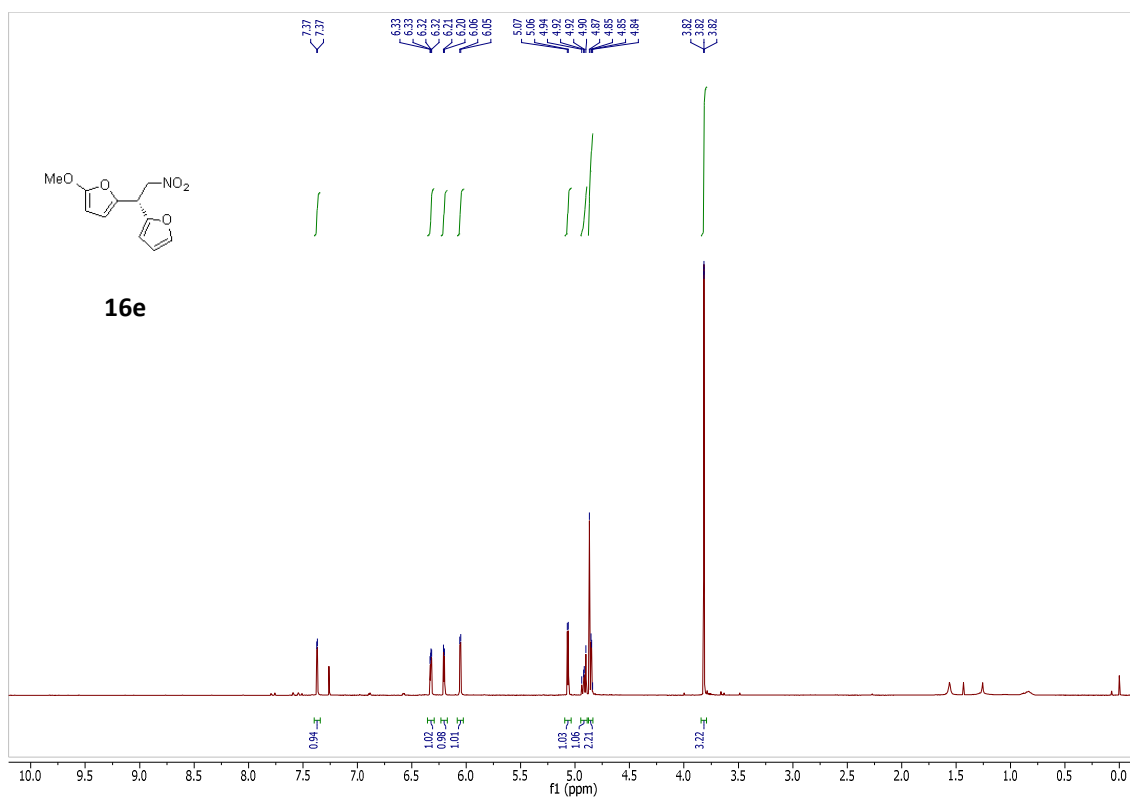
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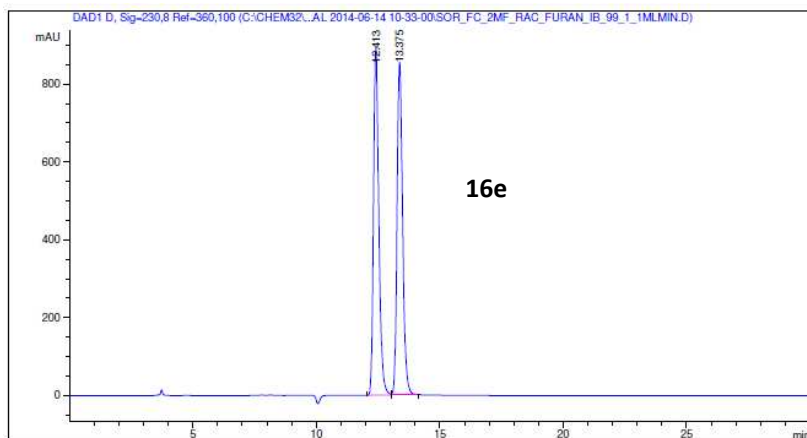


Signal 1: DAD1 A, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.377	BB	0.1274	22.21622	2.66108	3.6743
2	8.662	BB	0.1601	582.41650	55.63231	96.3257

Totals : 604.63273 58.29340





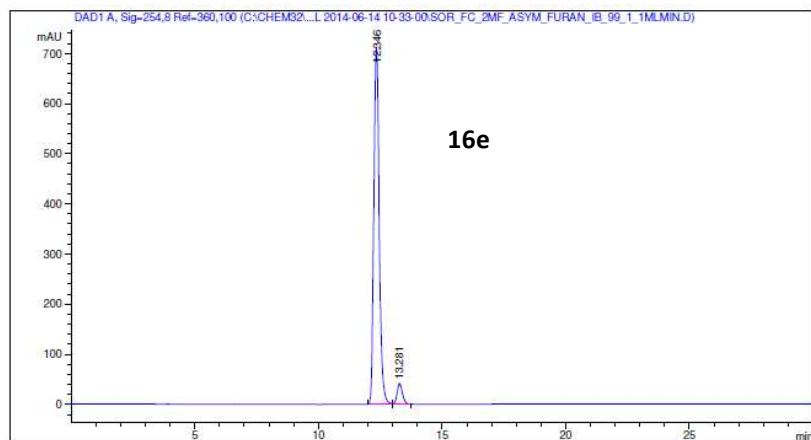
Area Percent Report

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Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 D, Sig=230,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.413	BV	0.2310	1.34030e4	893.29462	50.1648
2	13.375	VB	0.2376	1.33149e4	855.61719	49.8352

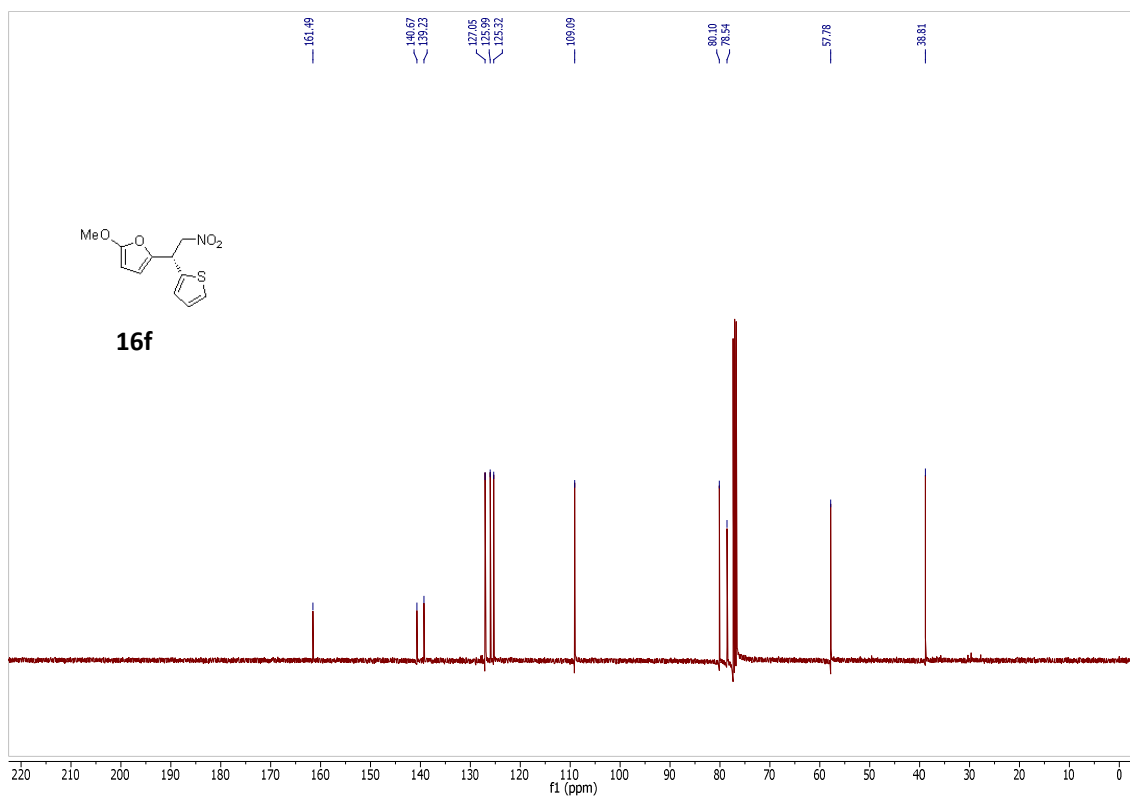
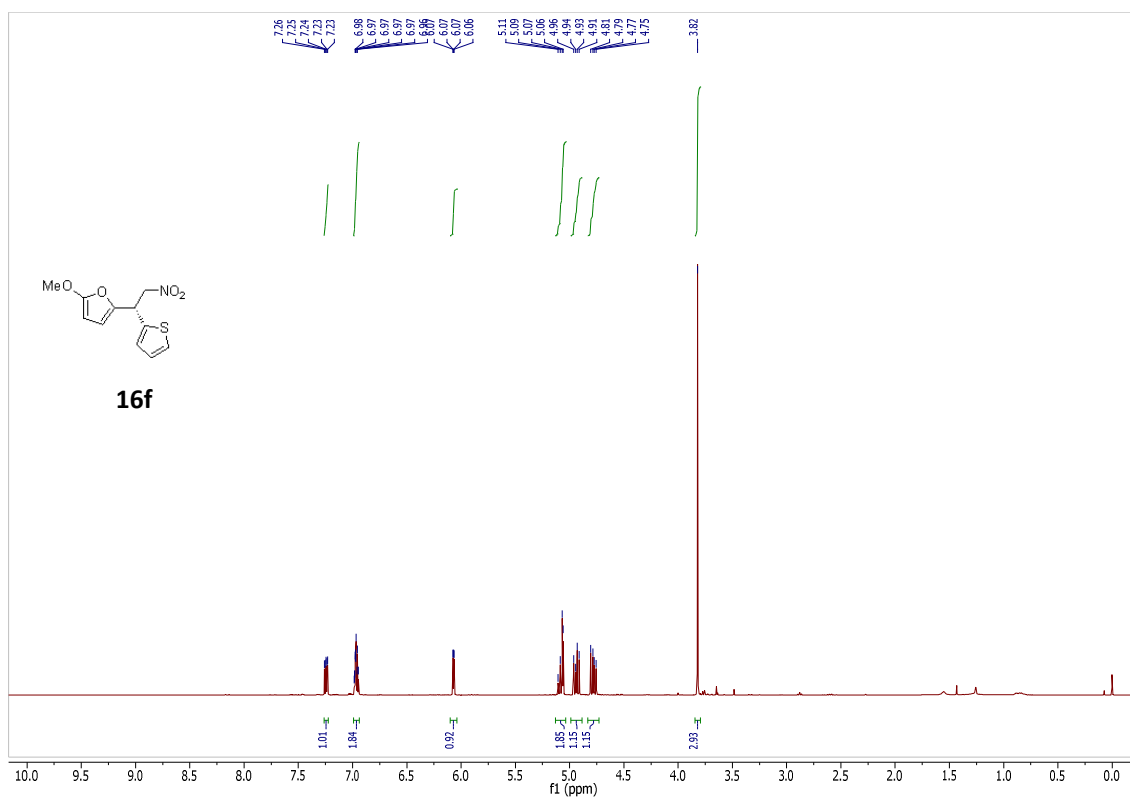
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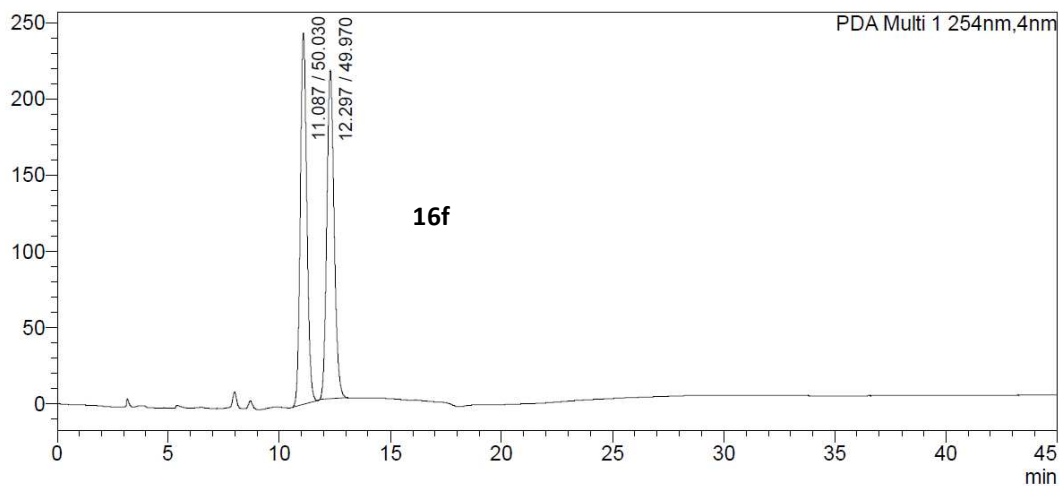
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Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.346	BV	0.2322	1.07449e4	711.63568	94.4605
2	13.281	VB	0.2307	630.12036	41.59678	5.5395

Totals : 1.13750e4 753.23246



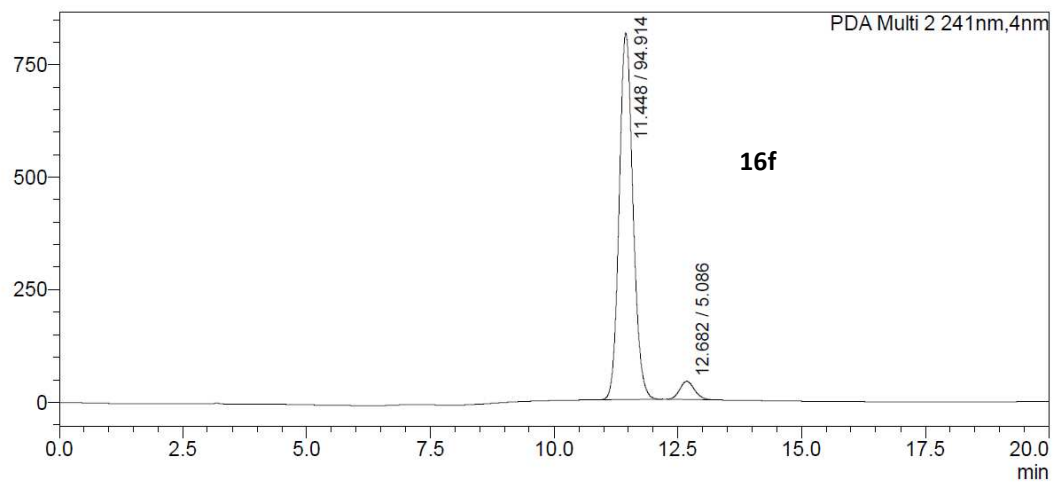
mAU



PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Name	Area%
1	11.087	4955078	243310		50.030
2	12.297	4949204	215426		49.970
Total		9904282	458737		100.000

mAU



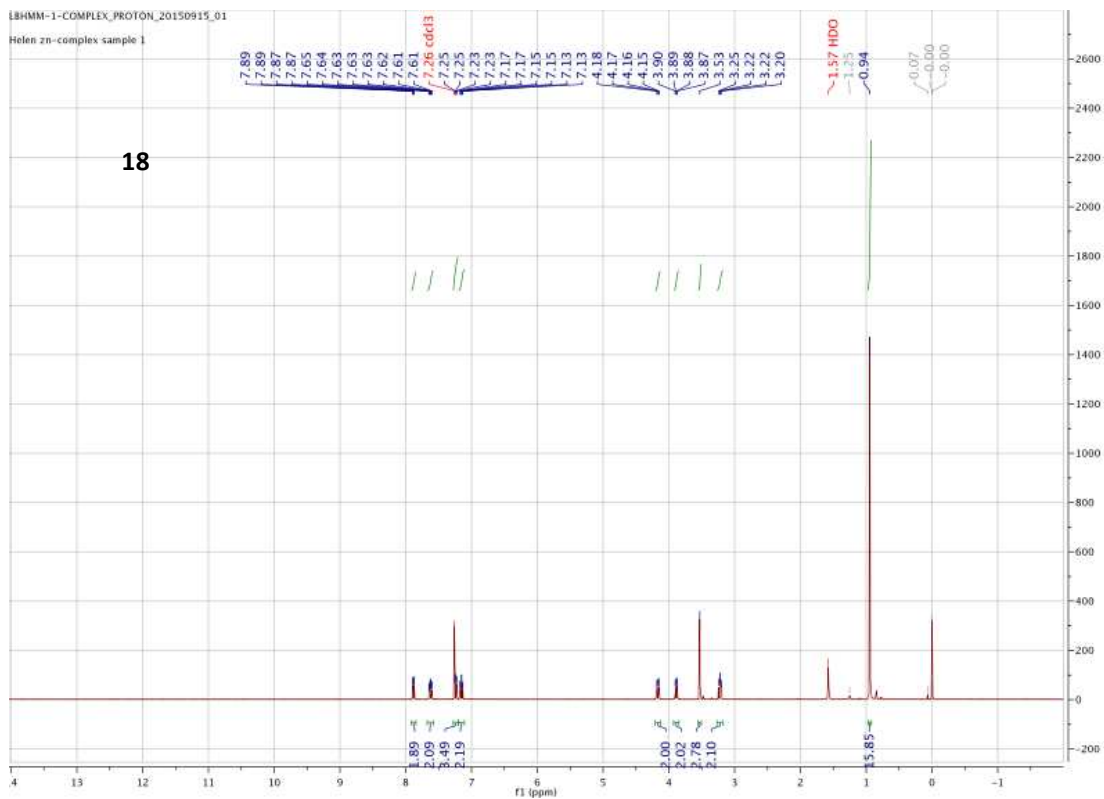
PDA Ch2 241nm

Peak#	Ret. Time	Area	Height	Name	Area%
1	11.448	15818036	813854		94.914
2	12.682	847553	40450		5.086
Total		16665589	854304		100.000

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Helen zn-complex sample 1

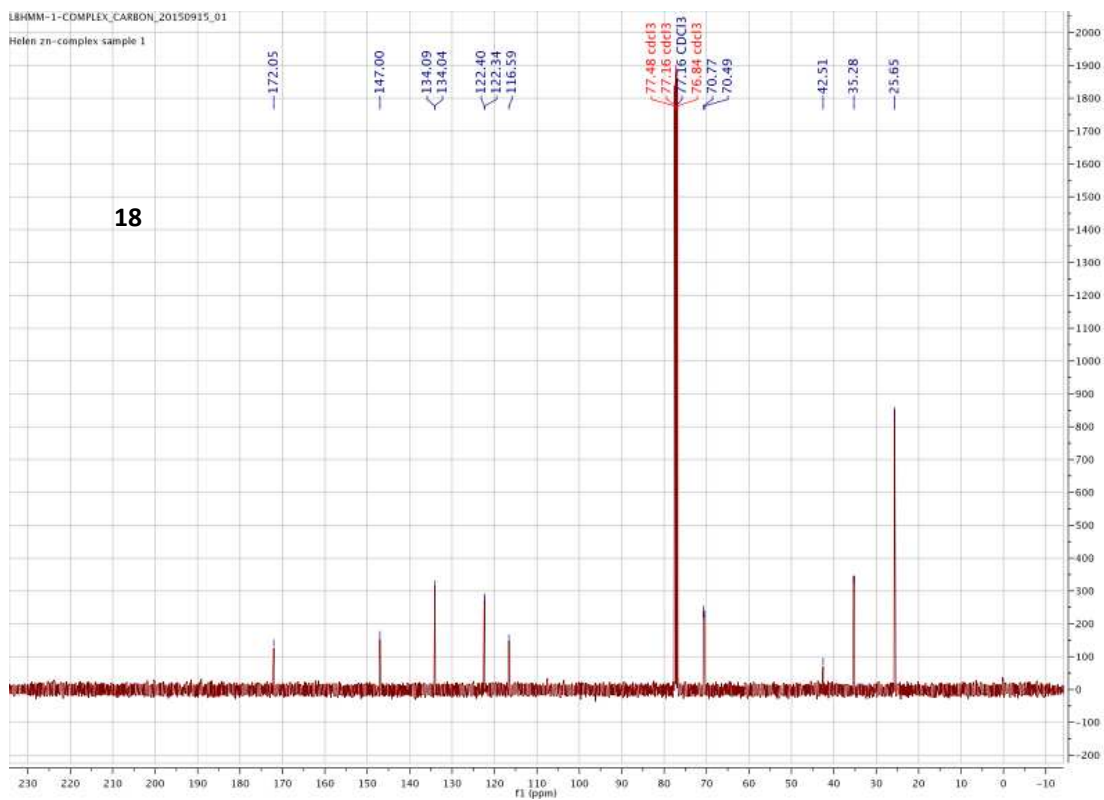
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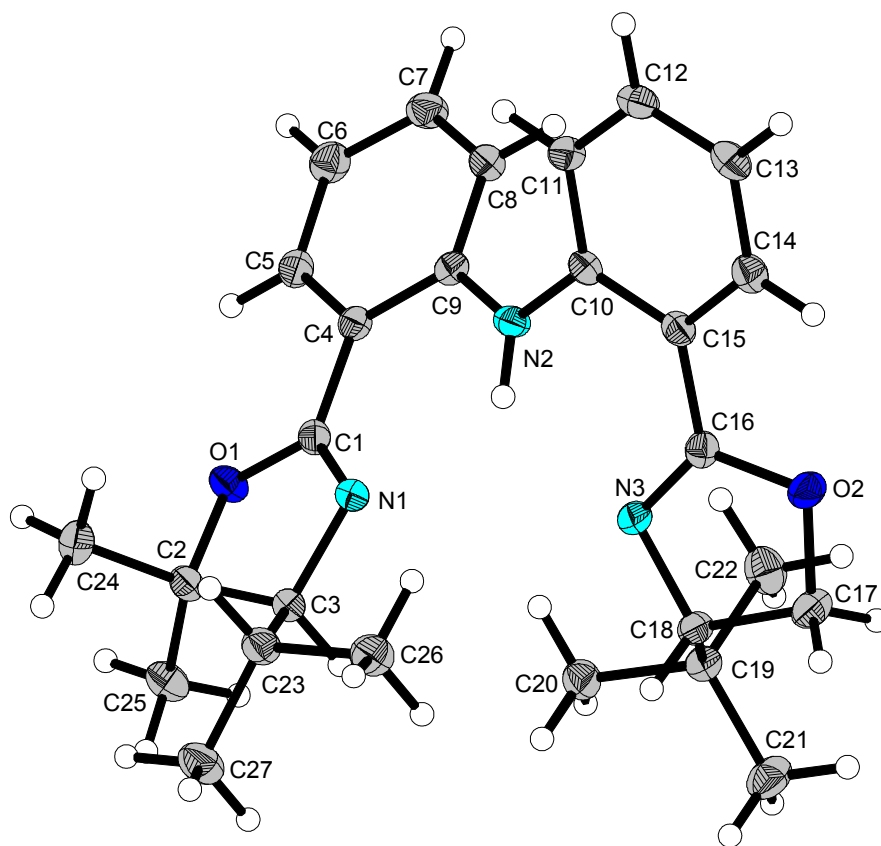
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Helen zn-complex sample 1

18



X-ray crystal structure of **11b**



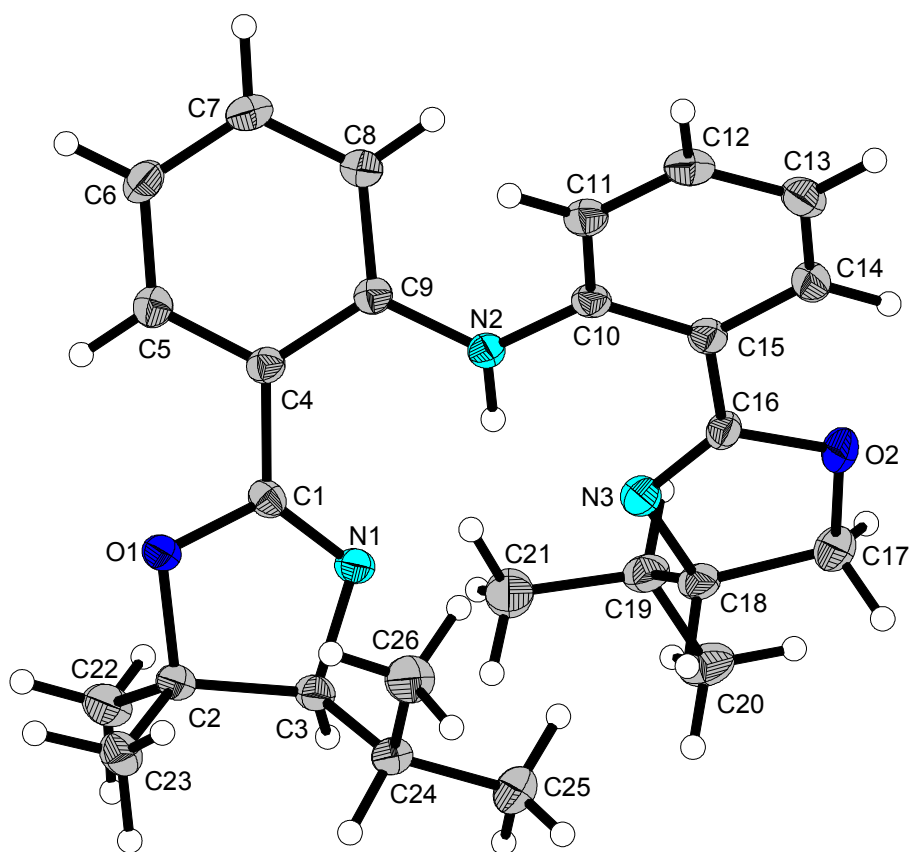
11b, molecule; thermal ellipsoids are drawn on the 50% probability level

Table 1. Crystal data and structure refinement for **11b**.

Identification code	gui78
Empirical formula	C ₂₇ H ₃₅ N ₃ O ₂
Formula weight	433.58
Temperature	100(2) K
Wavelength	1.54184 Å
Crystal system	Orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁ (#19)
Unit cell dimensions	a = 9.54492(6) Å α = 90°.
	b = 12.68954(7) Å β = 90°.

	$c = 19.9983(1) \text{ \AA}$ $\gamma = 90^\circ$.
Volume	$2422.21(2) \text{ \AA}^3$
Z	4
Density (calculated)	1.189 Mg/m^3
Absorption coefficient	0.591 mm^{-1}
F(000)	936
Crystal size	$0.3189 \times 0.2074 \times 0.1535 \text{ mm}^3$
Theta range for data collection	4.13 to 76.84° .
Index ranges	$-9 \leq h \leq 11$, $-15 \leq k \leq 15$, $-25 \leq l \leq 25$
Reflections collected	25062
Independent reflections	5041 [R(int) = 0.0328]
Completeness to theta = 76.84°	99.3 %
Absorption correction	Analytical
Max. and min. transmission	0.947 and 0.900
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5041 / 0 / 297
Goodness-of-fit on F^2	1.037
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0266$, $wR2 = 0.0678$
R indices (all data)	$R1 = 0.0277$, $wR2 = 0.0686$
Absolute structure parameter	$-0.09(14)$
Extinction coefficient	$0.00248(17)$
Largest diff. peak and hole	0.221 and $-0.146 \text{ e.\AA}^{-3}$

X-ray crystal structure of 11a



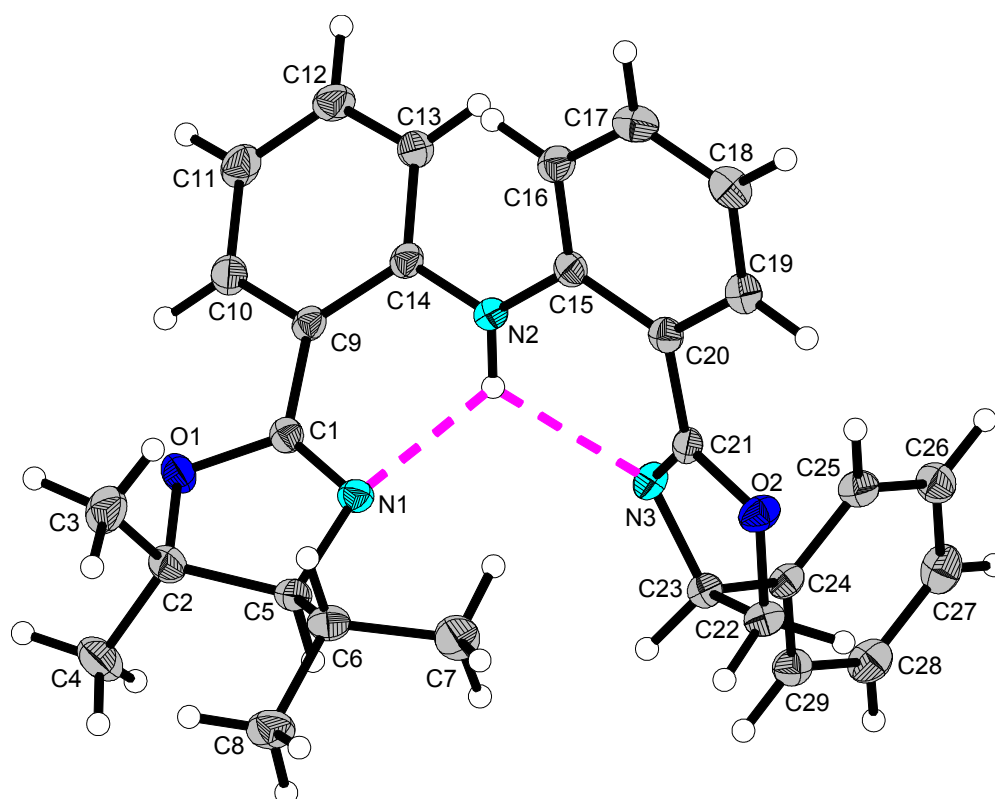
11a, molecule; thermal ellipsoids are drawn on the 50% probability level

Table 1. Crystal data and structure refinement for **11a**

Identification code	gui79
Empirical formula	C ₂₆ H ₃₃ N ₃ O ₂
Formula weight	419.55
Temperature	100(2) K
Wavelength	1.54184 Å
Crystal system	Trigonal
Space group	P3 ₁ 21 (#152)
Unit cell dimensions	a = 9.51079(4) Å α = 90°.

	$b = 9.51079(4) \text{ \AA}$ $\beta = 90^\circ$.
	$c = 44.3094(2) \text{ \AA}$ $\gamma = 120^\circ$.
Volume	$3471.04(3) \text{ \AA}^3$
Z	6
Density (calculated)	1.204 Mg/m^3
Absorption coefficient	0.603 mm^{-1}
F(000)	1356
Crystal size	$0.2822 \times 0.1983 \times 0.1369 \text{ mm}^3$
Theta range for data collection	2.99 to 76.92° .
Index ranges	$-11 \leq h \leq 11$, $-11 \leq k \leq 11$, $-55 \leq l \leq 55$
Reflections collected	77335
Independent reflections	4857 [$R(\text{int}) = 0.0374$]
Completeness to $\theta = 76.92^\circ$	99.7 %
Absorption correction	Analytical
Max. and min. transmission	0.940 and 0.892
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4855 / 0 / 291
Goodness-of-fit on F^2	1.040
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0253$, $wR2 = 0.0670$
R indices (all data)	$R1 = 0.0257$, $wR2 = 0.0675$
Absolute structure parameter	$0.03(13)$
Extinction coefficient	$0.00086(10)$
Largest diff. peak and hole	0.197 and $-0.126 \text{ e.\AA}^{-3}$

X-ray crystal structure of 11c



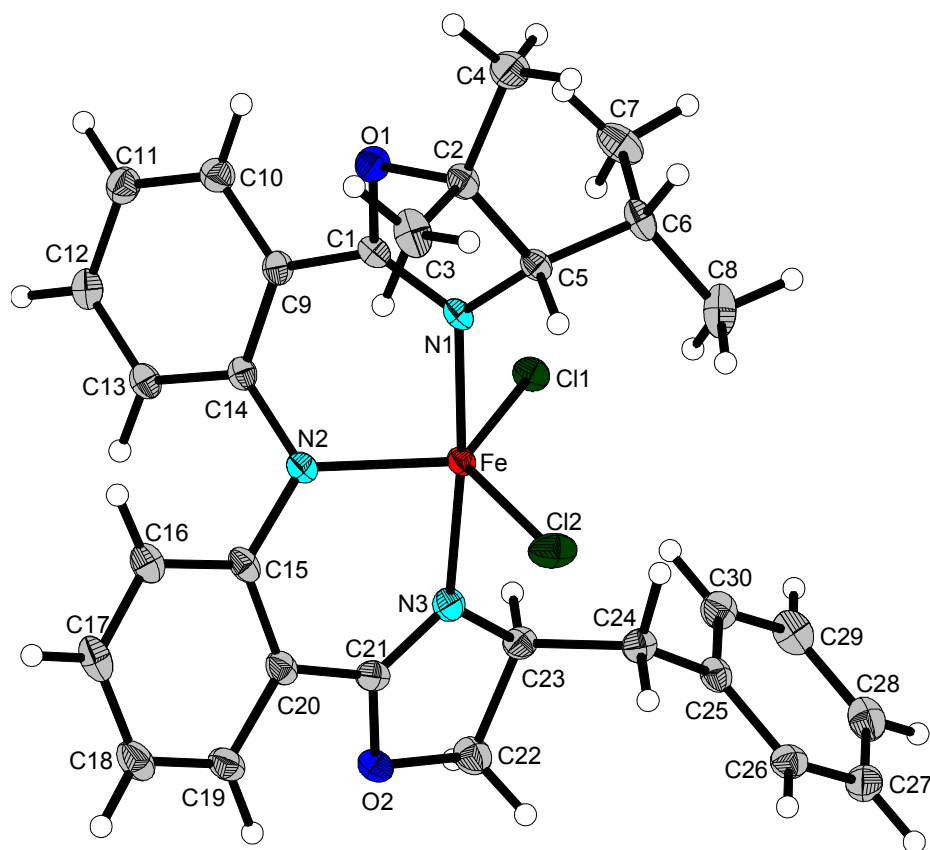
11c, molecule; thermal ellipsoids are drawn on the 50% probability level

Table 1. Crystal data and structure refinement for **11c**

Identification code	gui84
Empirical formula	C ₂₉ H ₃₁ N ₃ O ₂
Formula weight	453.57
Temperature	100(2) K
Wavelength	1.54184 Å
Crystal system	Triclinic
Space group	P1 (#1)
Unit cell dimensions	a = 9.86627(6) Å α = 112.4411(8)°.

	$b = 10.19647(8) \text{ \AA}$	$\beta = 90.0964(6)^\circ$.
	$c = 13.1369(1) \text{ \AA}$	$\gamma = 91.9641(6)^\circ$.
Volume	1220.632(17) $\text{\AA}^3$	
Z	2	
Density (calculated)	1.234 Mg/m^3	
Absorption coefficient	0.615 mm^{-1}	
F(000)	484	
Crystal size	0.2454 x 0.1524 x 0.1376 mm^3	
Theta range for data collection	3.64 to 76.73 $^\circ$.	
Index ranges	$-11 \leq h \leq 12$, $-12 \leq k \leq 12$, $-16 \leq l \leq 16$	
Reflections collected	48983	
Independent reflections	9742 [R(int) = 0.0269]	
Completeness to theta = 76.73 $^\circ$	99.4 %	
Absorption correction	Analytical	
Max. and min. transmission	0.928 and 0.879	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9742 / 3 / 630	
Goodness-of-fit on F^2	1.023	
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0257, wR2 = 0.0638	
R indices (all data)	R1 = 0.0267, wR2 = 0.0647	
Absolute structure parameter	0.02(9)	
Extinction coefficient	0.0059(2)	
Largest diff. peak and hole	0.182 and $-0.131 \text{ e.\AA}^{-3}$	

X-ray crystal structure of **11d**[FeCl₂] complex



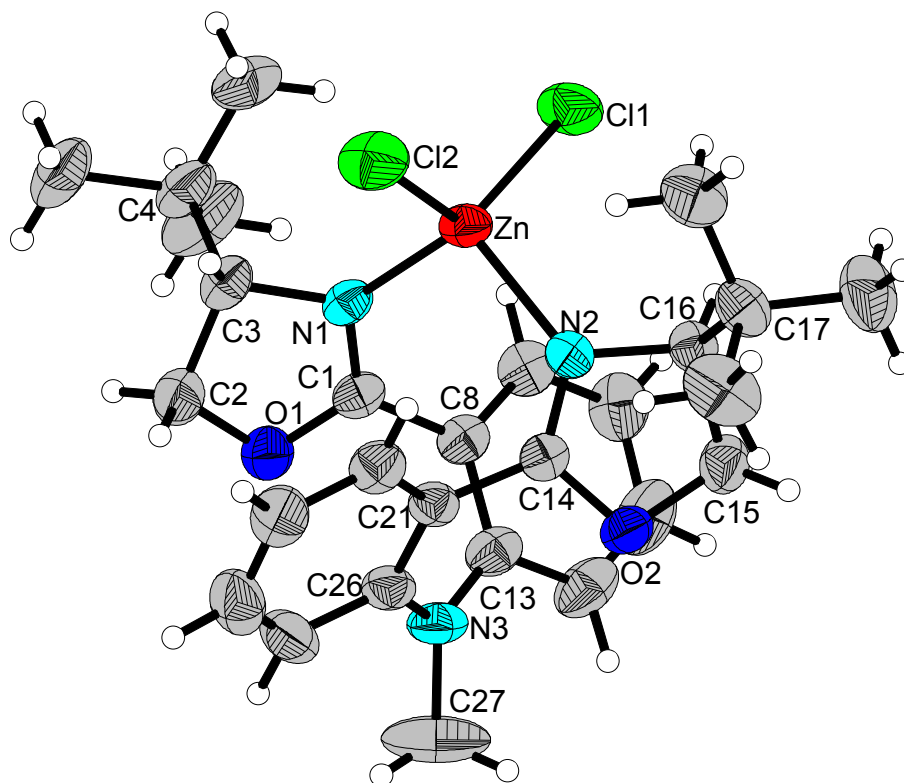
11d[FeCl₂], molecule; thermal ellipsoids are drawn on the 50% probability level

Table 1. Crystal data and structure refinement for **11d**[FeCl₂]

Identification code	gui86
Empirical formula	C ₃₀ H ₃₂ N ₃ O ₂ Cl ₂ Fe
Formula weight	593.34
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 ₁ (#4)
Unit cell dimensions	a = 8.4077(1) Å α = 90°.

	$b = 17.5482(3) \text{ \AA}$ $\beta = 94.439(2)^\circ$.
	$c = 9.4560(2) \text{ \AA}$ $\gamma = 90^\circ$.
Volume	$1390.95(4) \text{ \AA}^3$
Z	2
Density (calculated)	1.417 Mg/m^3
Absorption coefficient	0.767 mm^{-1}
F(000)	618
Crystal size	$0.3129 \times 0.2120 \times 0.1540 \text{ mm}^3$
Theta range for data collection	3.12 to 31.22° .
Index ranges	$-12 \leq h \leq 11$, $-24 \leq k \leq 25$, $-13 \leq l \leq 13$
Reflections collected	26571
Independent reflections	7971 [R(int) = 0.0300]
Completeness to $\theta = 29.00^\circ$	99.6 %
Absorption correction	Analytical
Max. and min. transmission	0.920 and 0.869
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7971 / 1 / 347
Goodness-of-fit on F^2	1.036
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0271$, $wR2 = 0.0559$
R indices (all data)	$R1 = 0.0298$, $wR2 = 0.0575$
Absolute structure parameter	$-0.017(7)$
Largest diff. peak and hole	0.267 and $-0.255 \text{ e.\AA}^{-3}$

X-ray crystal structure of **18**



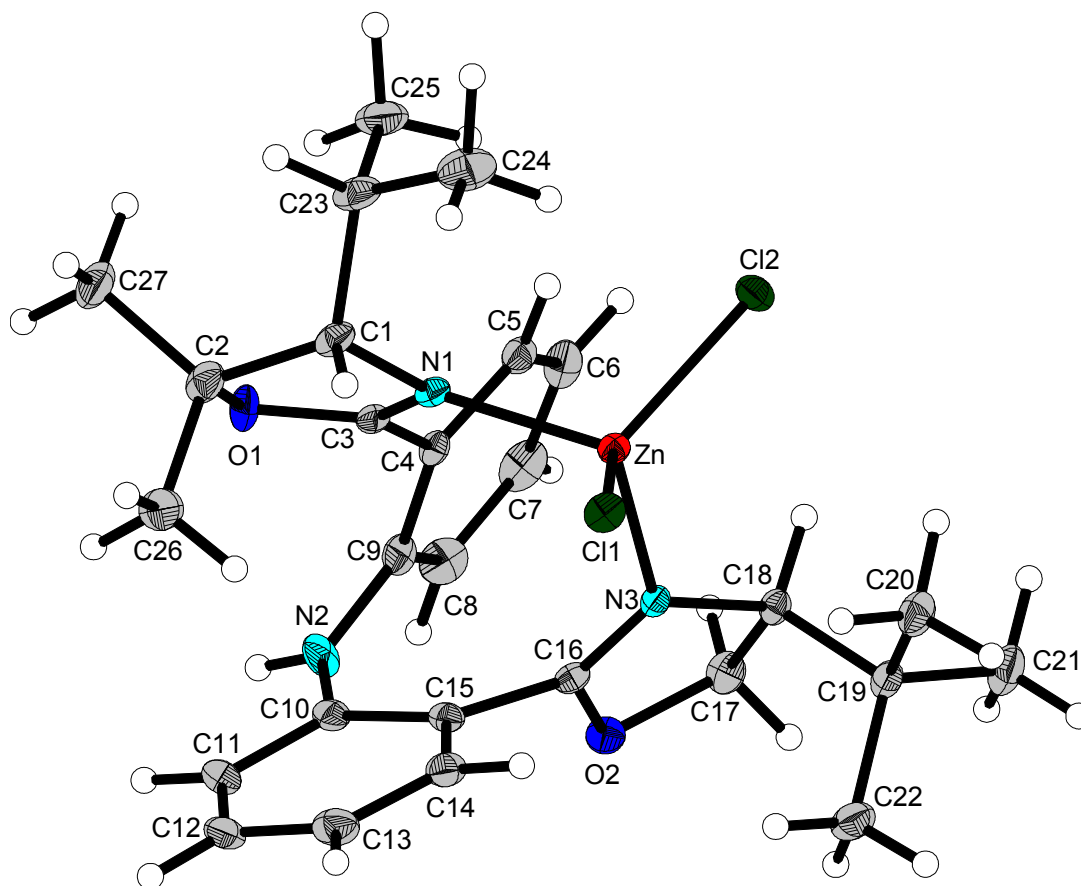
18, molecule (thermal ellipsoids are drawn on the 50% probability level)

Table 1. Crystal data and structure refinement for **18**.

Identification code	gui01
Empirical formula	C ₂₈ H ₃₇ N ₃ O ₂ Cl ₄ Zn
Molecular formula	C ₂₇ H ₃₅ N ₃ O ₂ Cl ₂ Zn x CH ₂ Cl ₂
Formula weight	654.78
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 ₁ (#4)

Unit cell dimensions	a = 9.9185(8) Å	$\alpha = 90^\circ$.
	b = 10.6832(9) Å	$\beta = 94.3360(10)^\circ$.
	c = 14.5573(12) Å	$\gamma = 90^\circ$.
Volume	1538.1(2) Å ³	
Z	2	
Density (calculated)	1.414 Mg/m ³	
Absorption coefficient	1.176 mm ⁻¹	
F(000)	680	
Crystal size	0.80 x 0.60 x 0.50 mm ³	
Theta range for data collection	2.37 to 29.35°.	
Index ranges	-13 ≤ h ≤ 13, -14 ≤ k ≤ 14, -19 ≤ l ≤ 19	
Reflections collected	13999	
Independent reflections	7493 [R(int) = 0.0171]	
Completeness to theta = 29.35°	93.7 %	
Absorption correction	Numerical	
Max. and min. transmission	0.5910 and 0.4531	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	7493 / 1 / 360	
Goodness-of-fit on F ²	1.044	
Final R indices [I > 2sigma(I)]	R1 = 0.0366, wR2 = 0.0945	
R indices (all data)	R1 = 0.0390, wR2 = 0.0962	
Absolute structure parameter	-0.001(8)	
Largest diff. peak and hole	0.751 and -0.281 e.Å ⁻³	

X-ray crystal structure of **19**



19, molecule; thermal ellipsoids are drawn on the 50% probability level

Table 1. Crystal data and structure refinement for **19**.

Identification code	gui111
Empirical formula	C ₂₇ H ₃₅ N ₃ O ₂ Cl ₂ Zn
Formula weight	569.85
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁ (#19)

Unit cell dimensions	a = 9.3141(2) Å $\alpha = 90^\circ$. b = 11.2722(2) Å $\beta = 90^\circ$. c = 26.2759(4) Å $\gamma = 90^\circ$.
Volume	2758.72(9) Å ³
Z	4
Density (calculated)	1.372 Mg/m ³
Absorption coefficient	1.112 mm ⁻¹
F(000)	1192
Crystal size	0.2815 x 0.2457 x 0.1779 mm ³
Theta range for data collection	2.84 to 29.59°.
Index ranges	-11 ≤ h ≤ 12, -15 ≤ k ≤ 14, -35 ≤ l ≤ 36
Reflections collected	30100
Independent reflections	6912 [R(int) = 0.0336]
Completeness to theta = 27.50°	99.3 %
Absorption correction	Analytical
Max. and min. transmission	0.864 and 0.792
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6912 / 0 / 327
Goodness-of-fit on F ²	1.040
Final R indices [I > 2σ(I)]	R1 = 0.0247, wR2 = 0.0490
R indices (all data)	R1 = 0.0275, wR2 = 0.0502
Absolute structure parameter	-0.010(6)
Largest diff. peak and hole	0.254 and -0.323 e.Å ⁻³