Supporting information

for

New palladium(II) complexes with 3-(2-pyridyl)-5-alkyl-1,2,4-triazole ligands as recyclable C–C coupling catalysts

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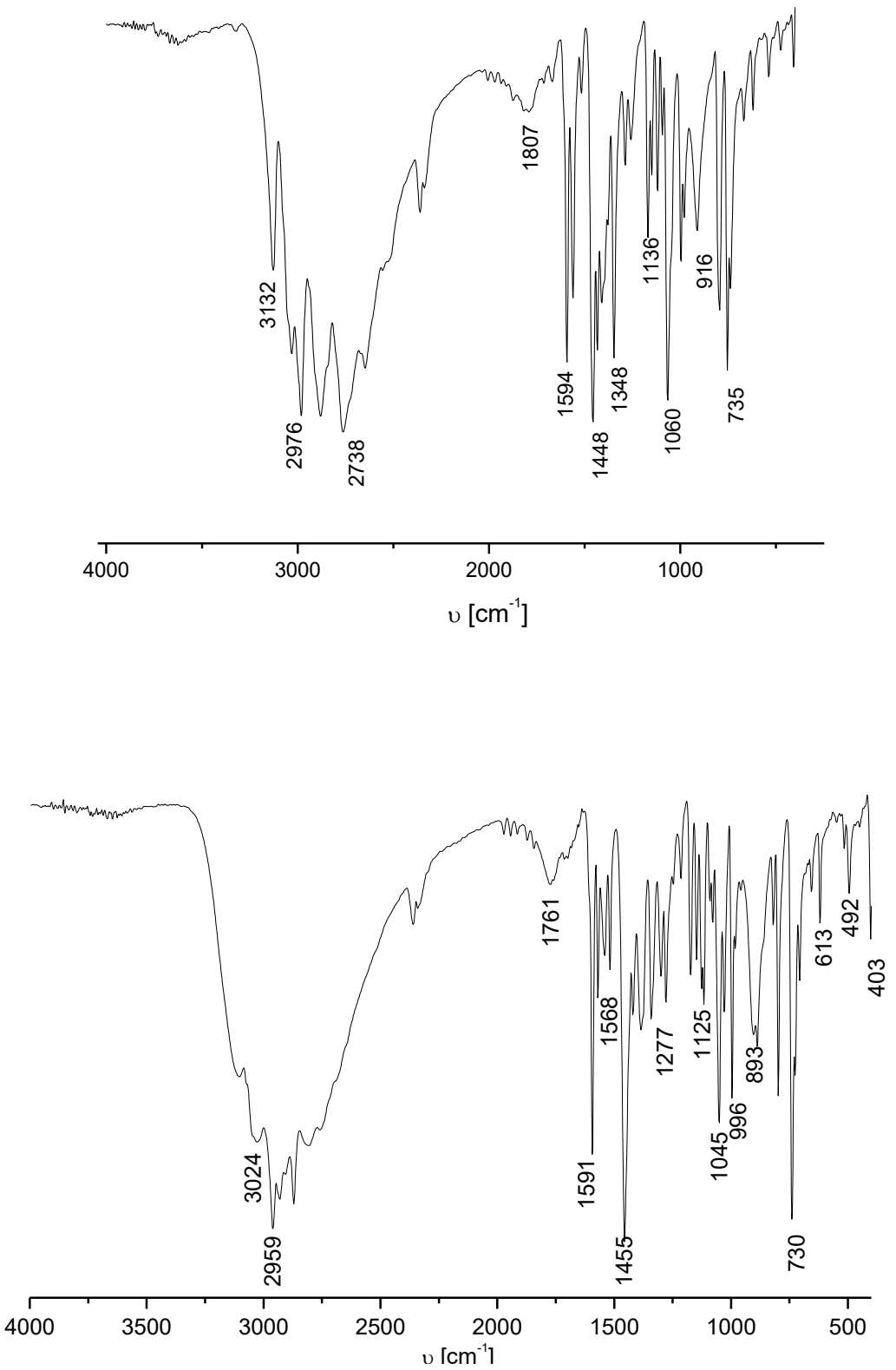
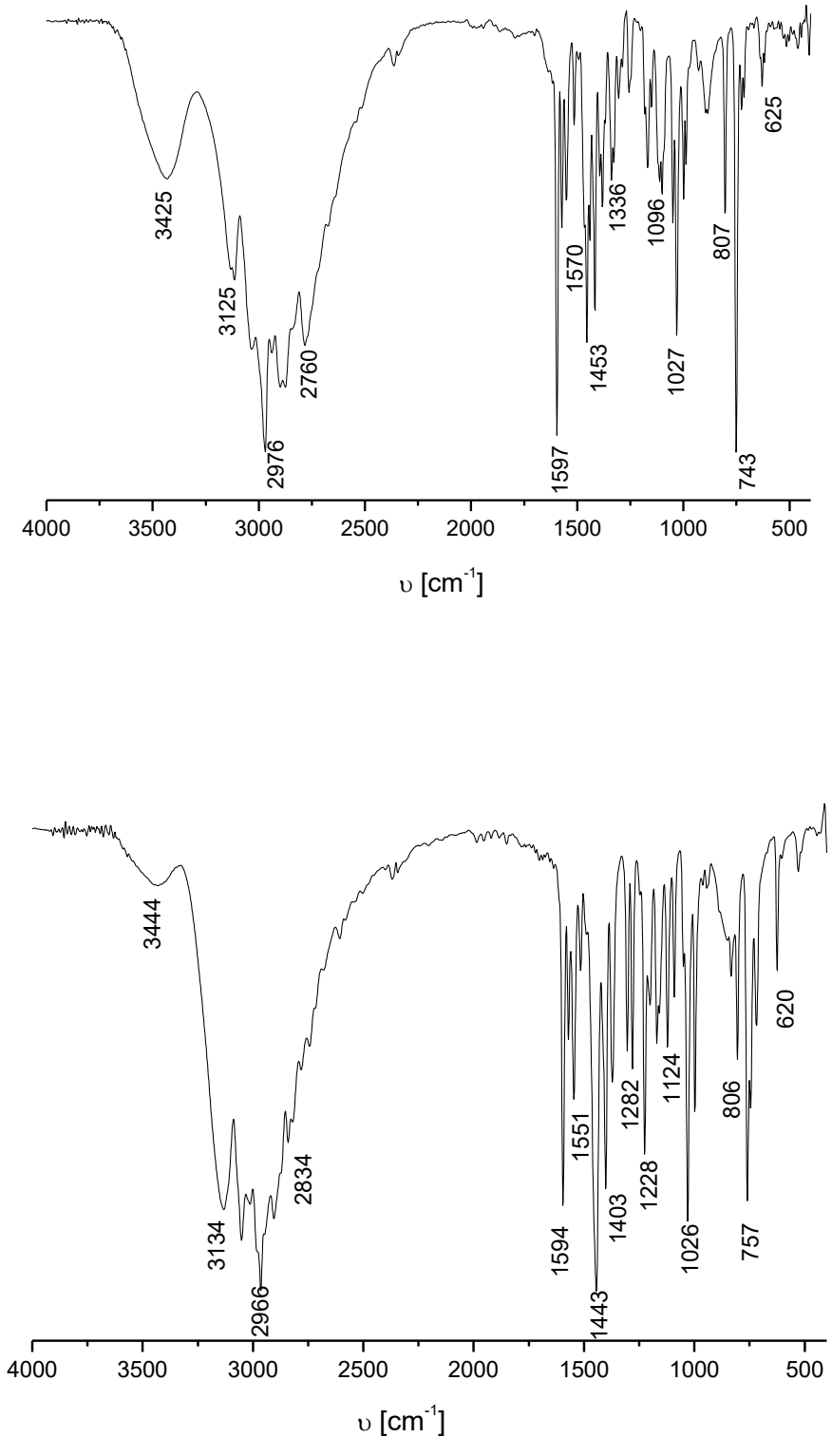


Figure S1. IR for **3a** (top) and **3b** (bottom)



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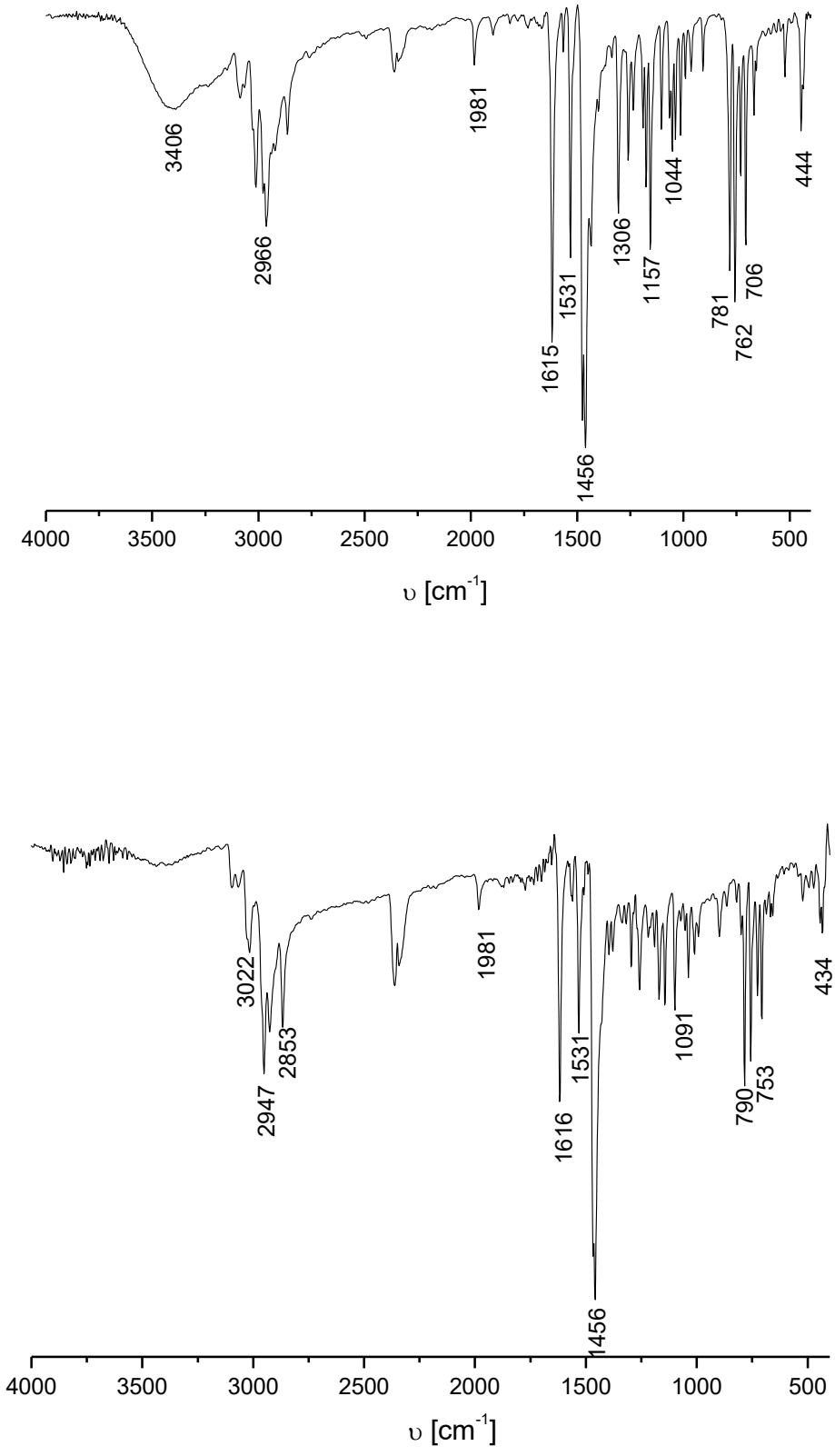

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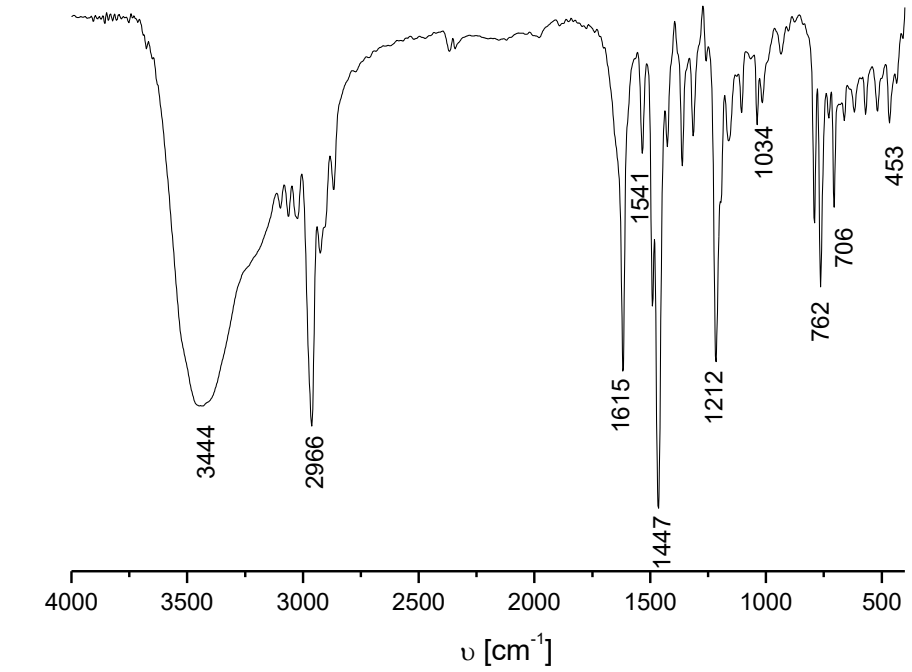

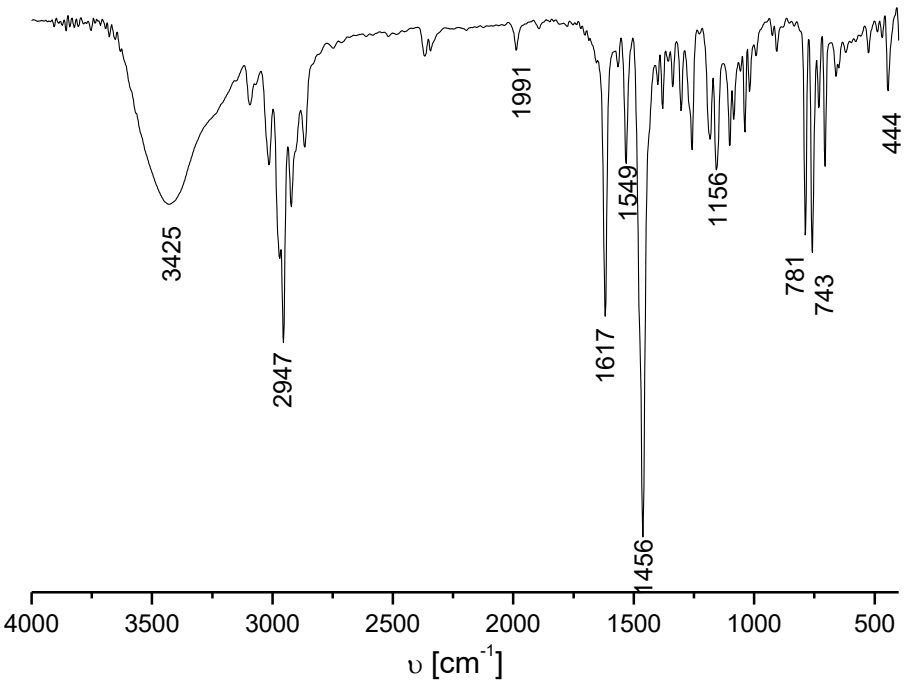

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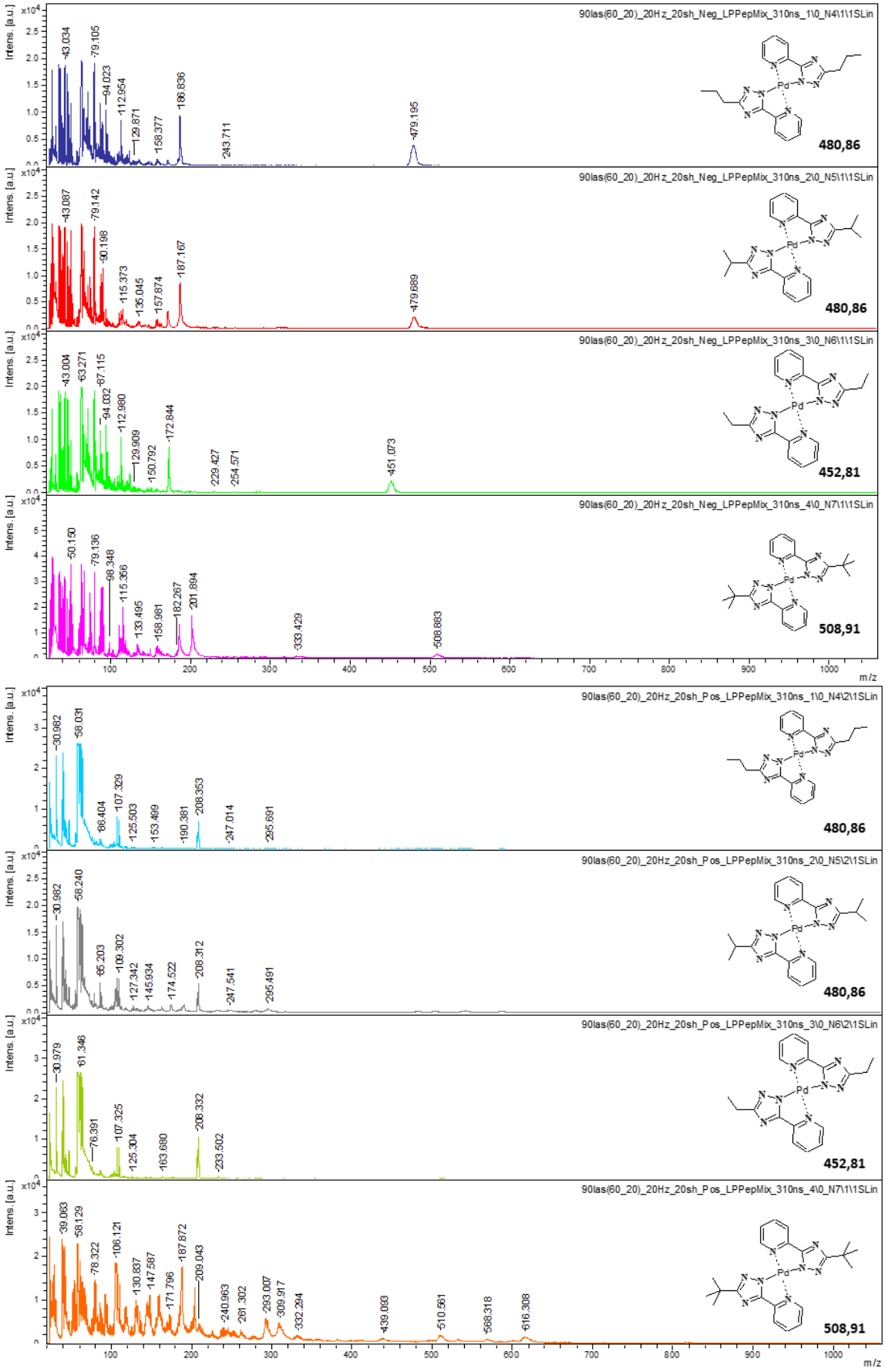

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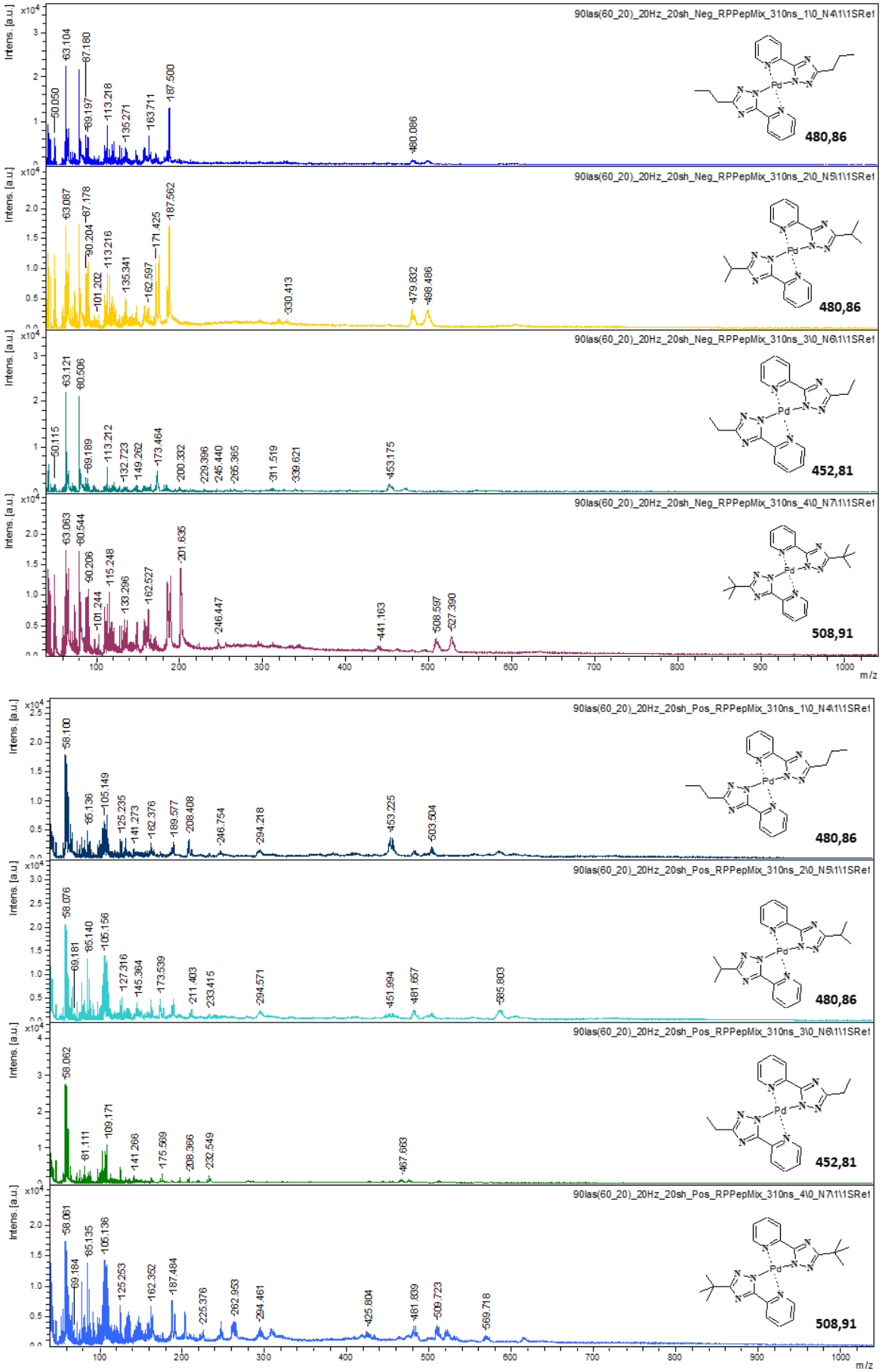

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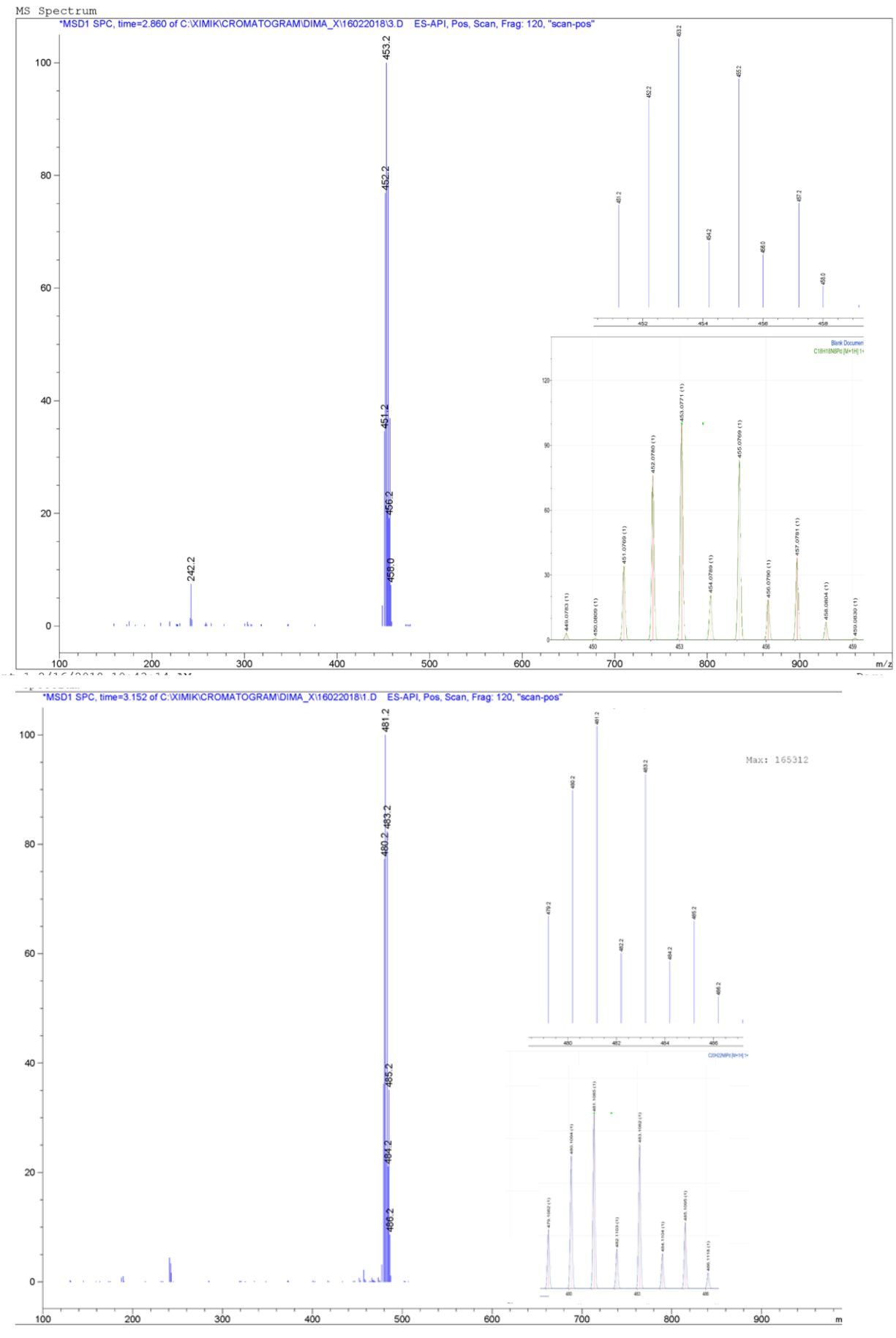

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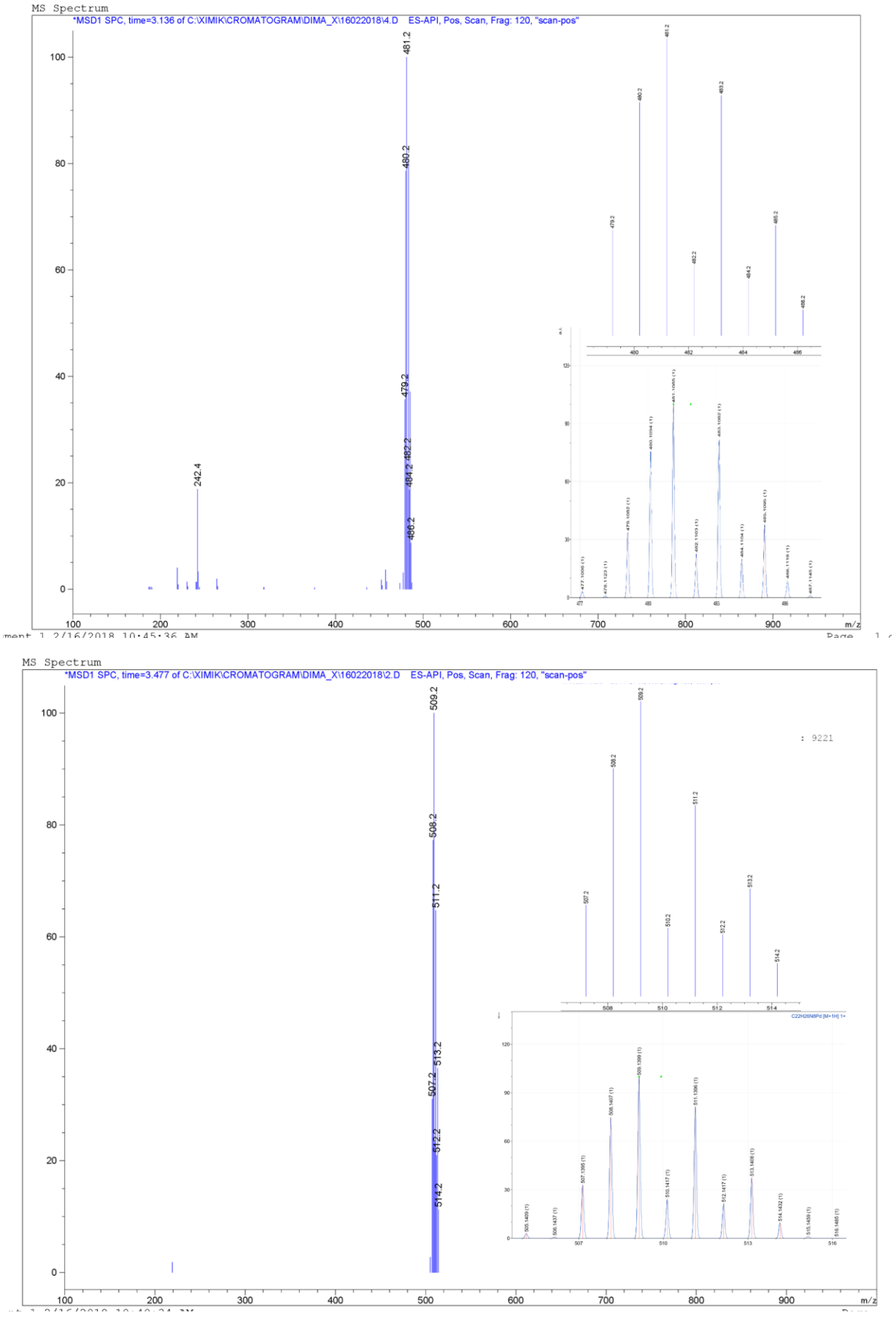

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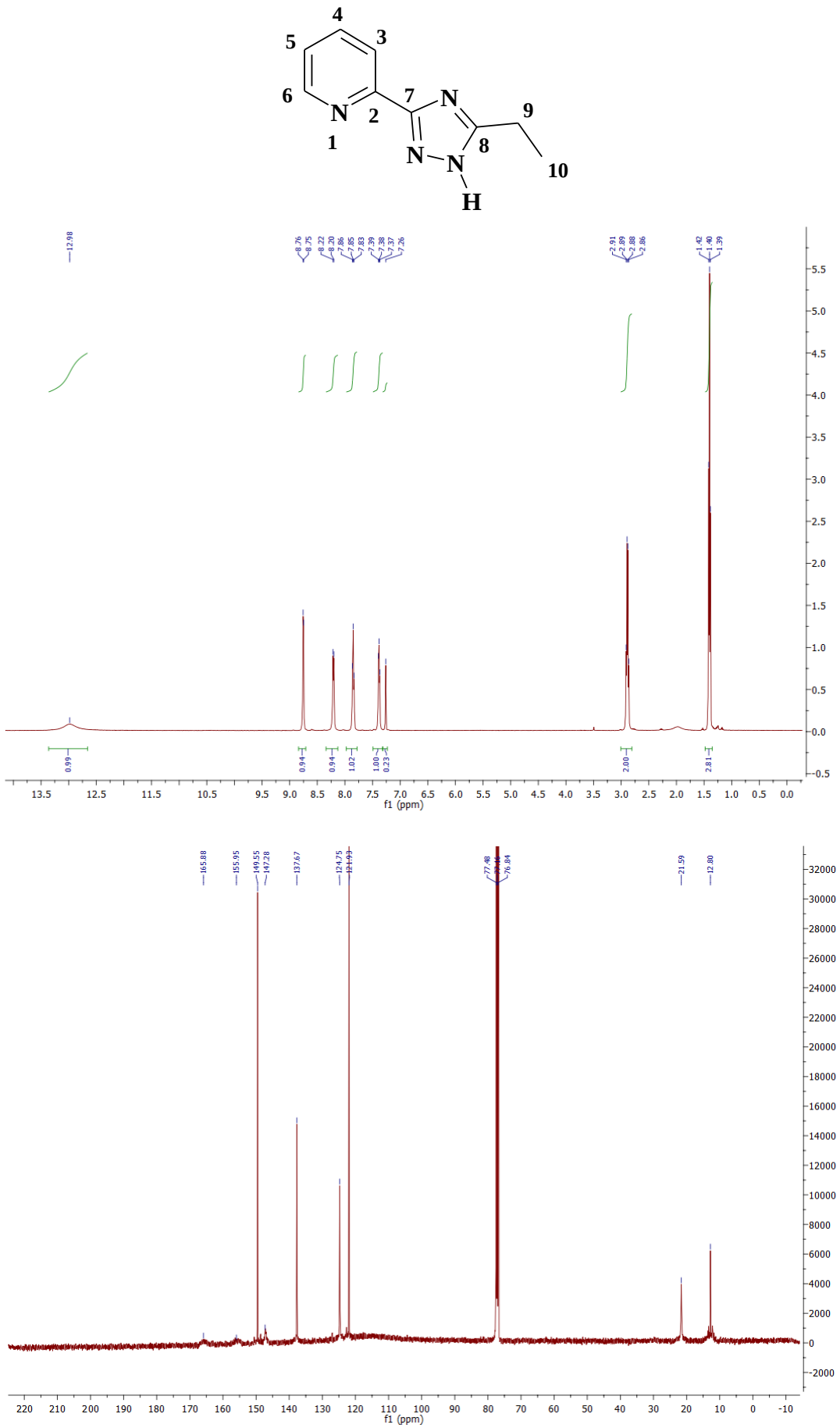

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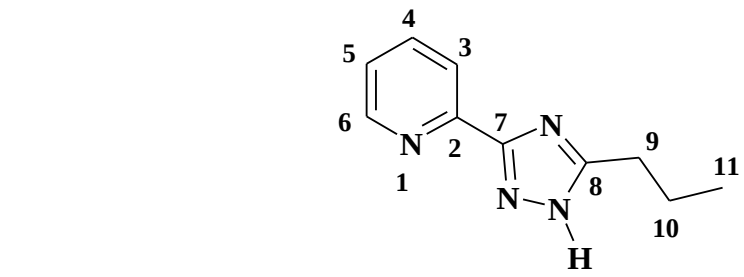

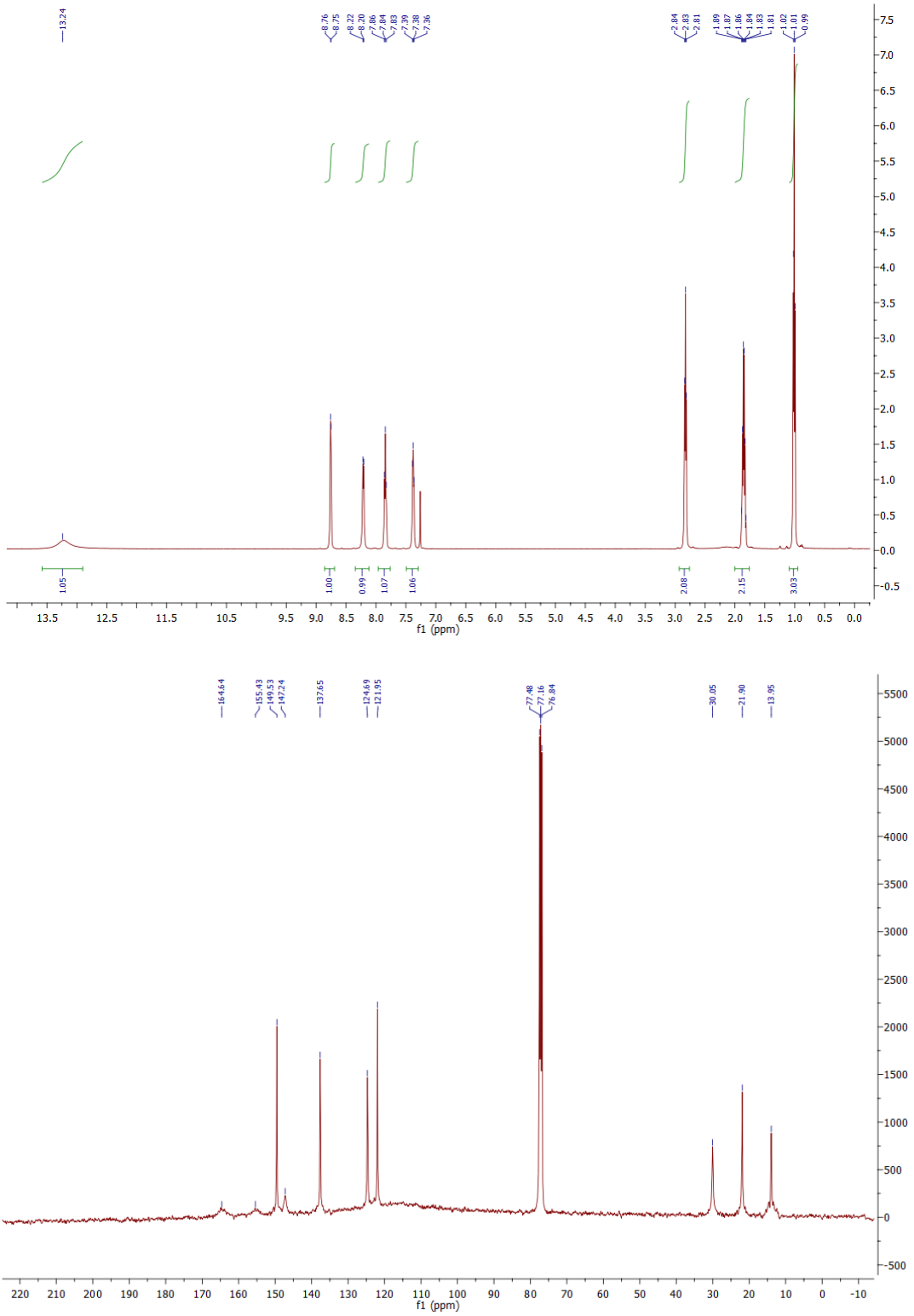

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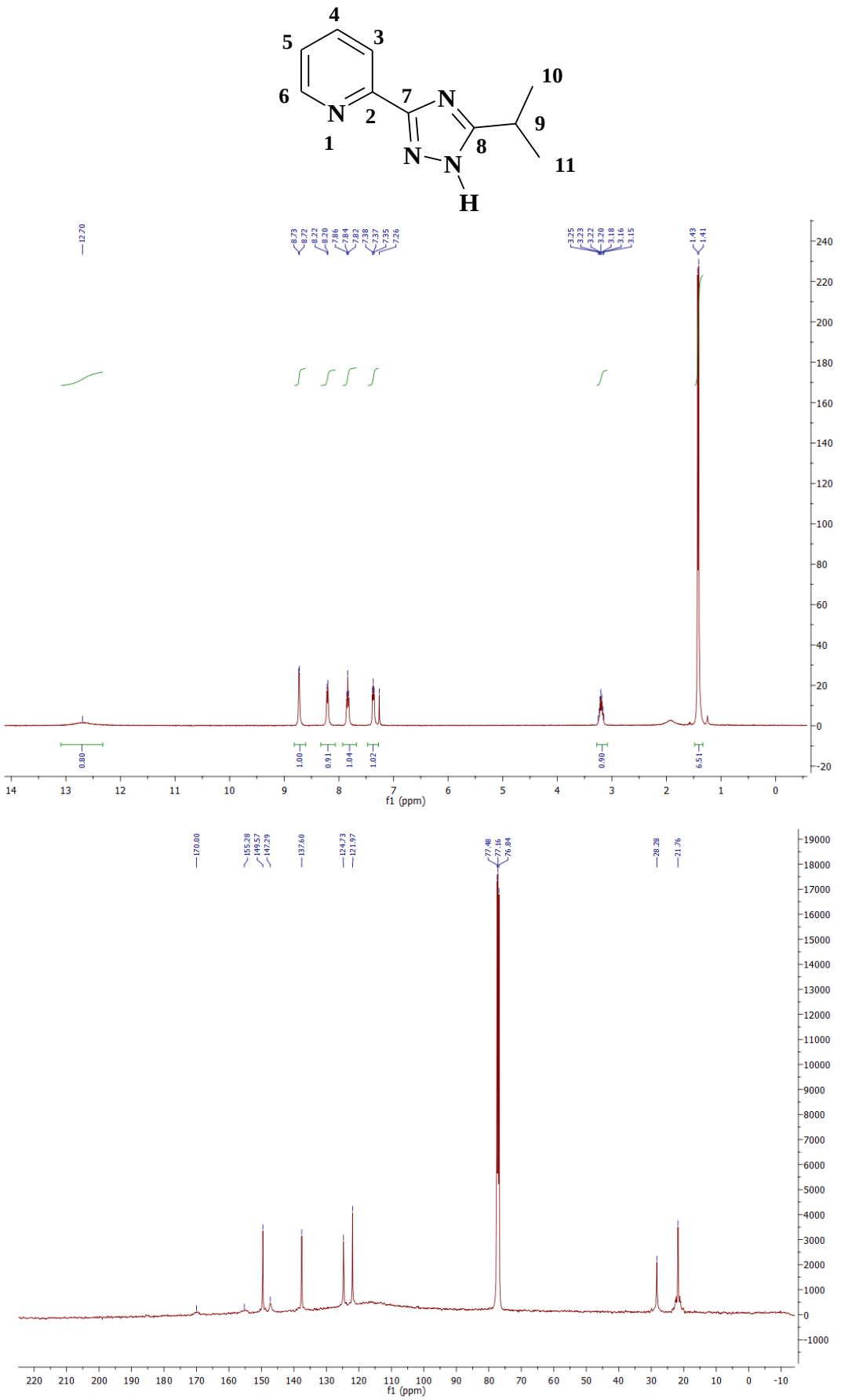

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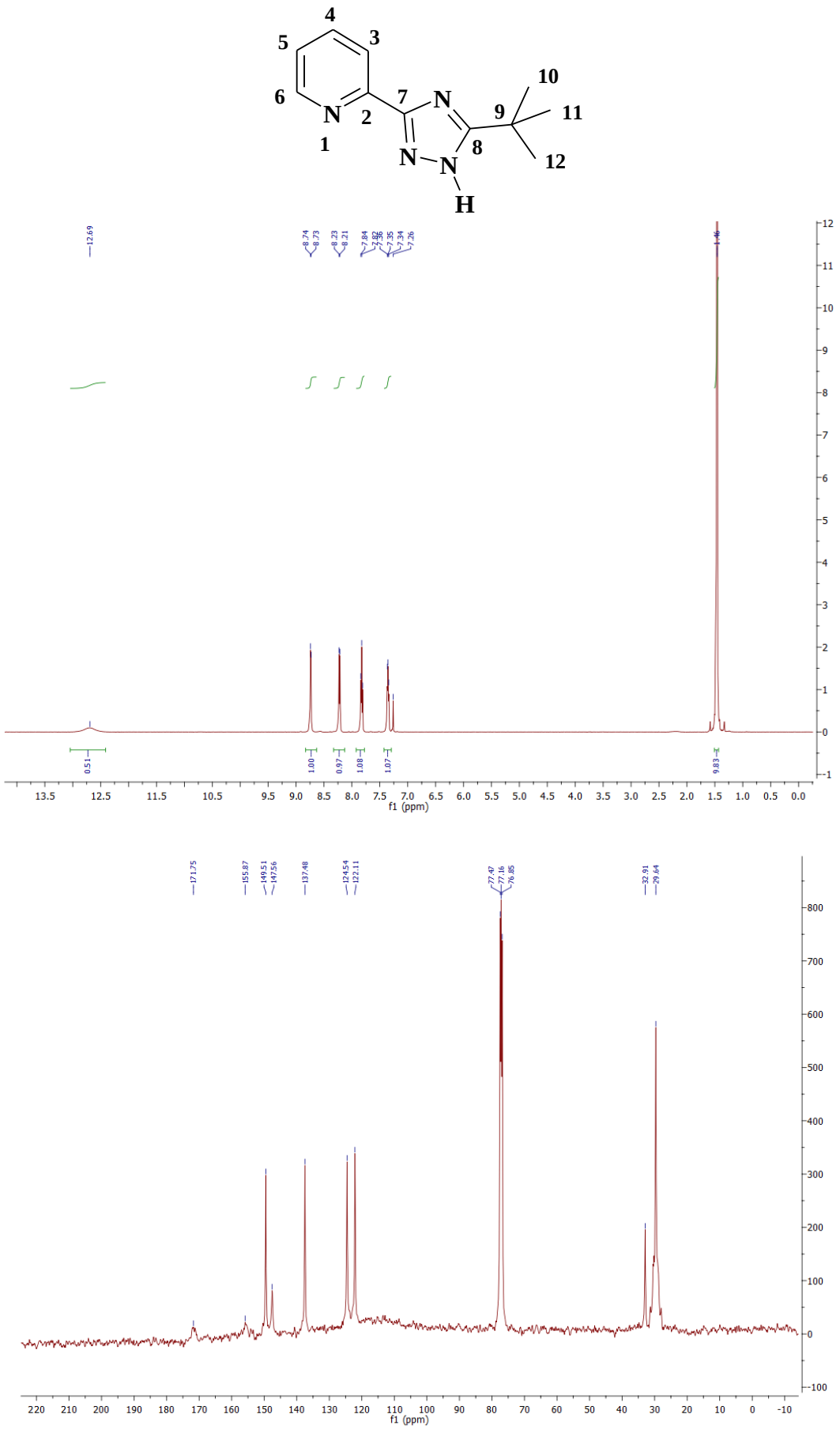

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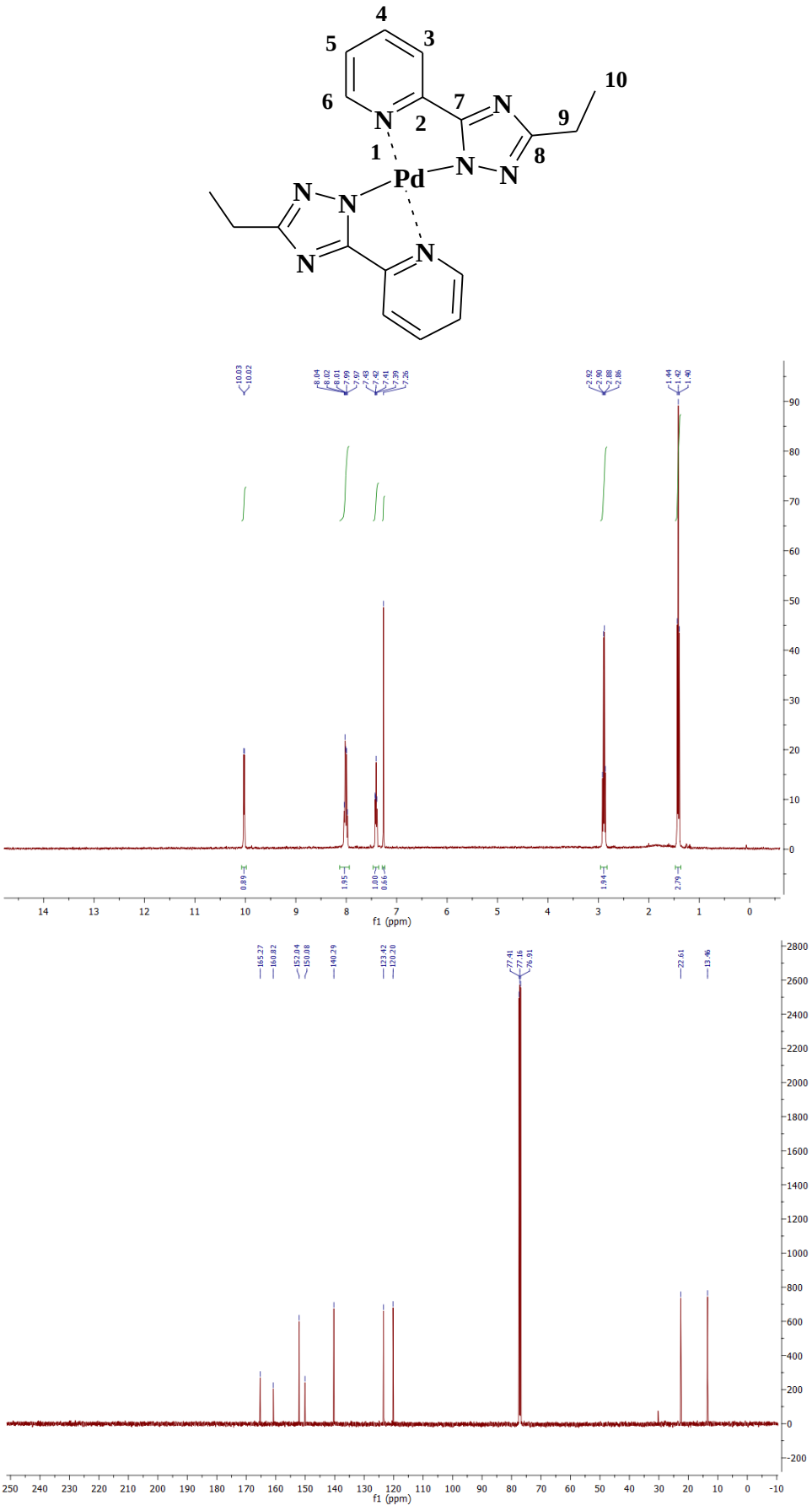

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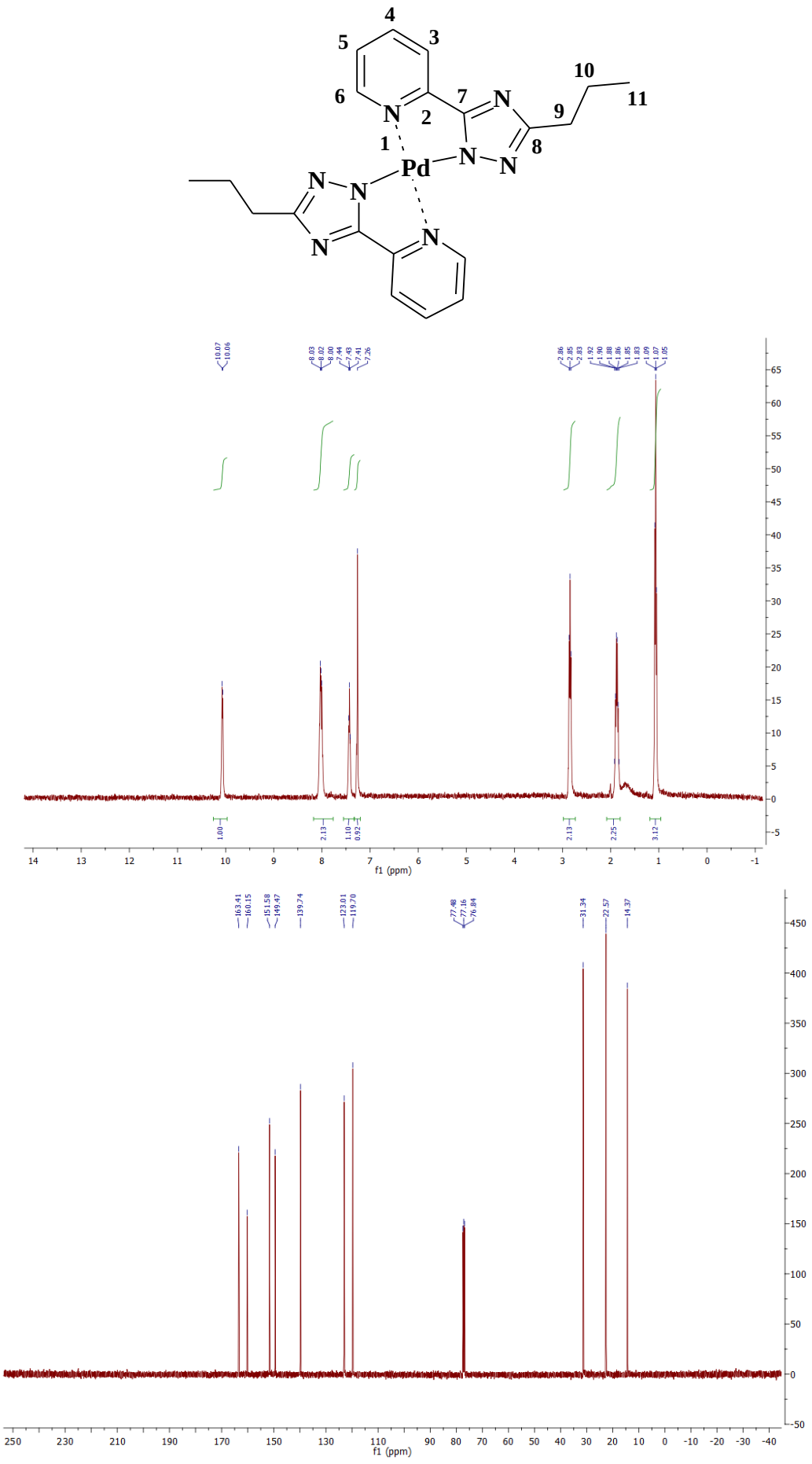

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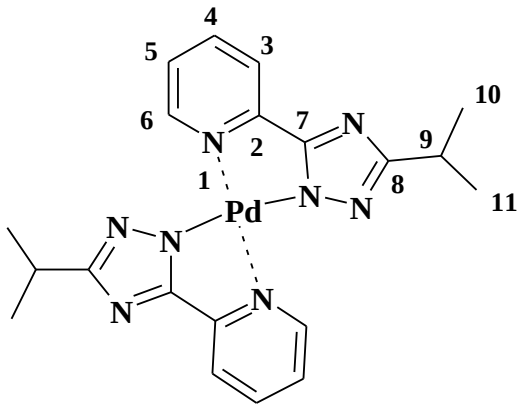

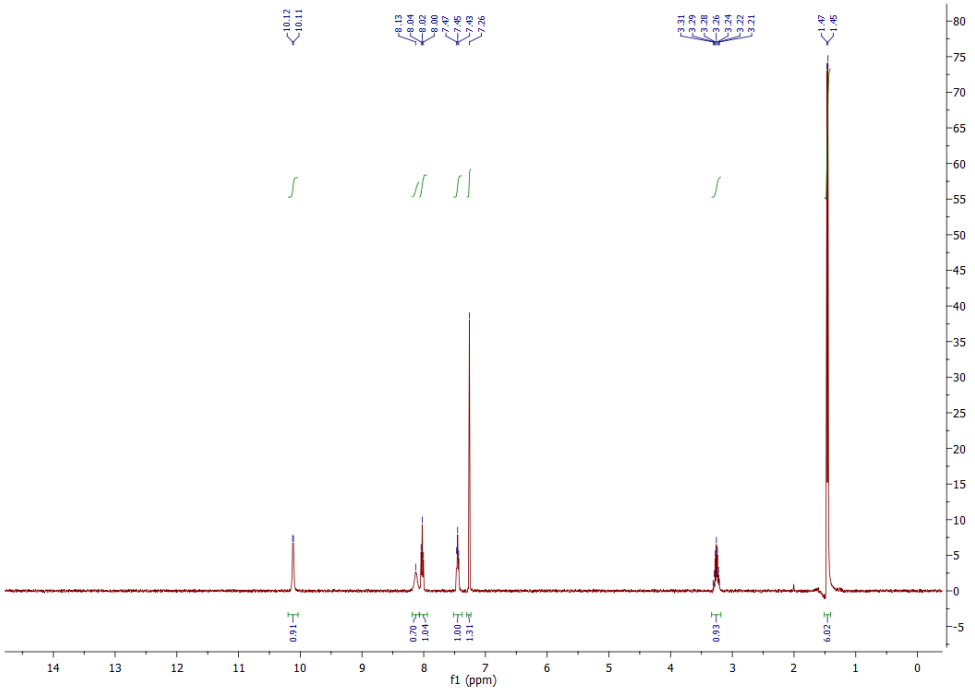

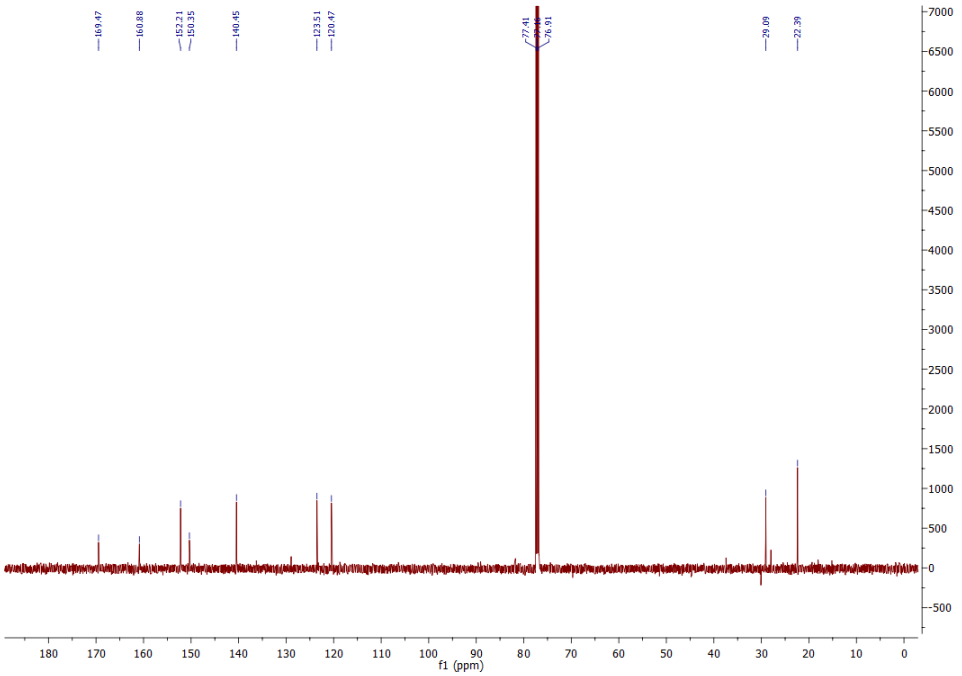

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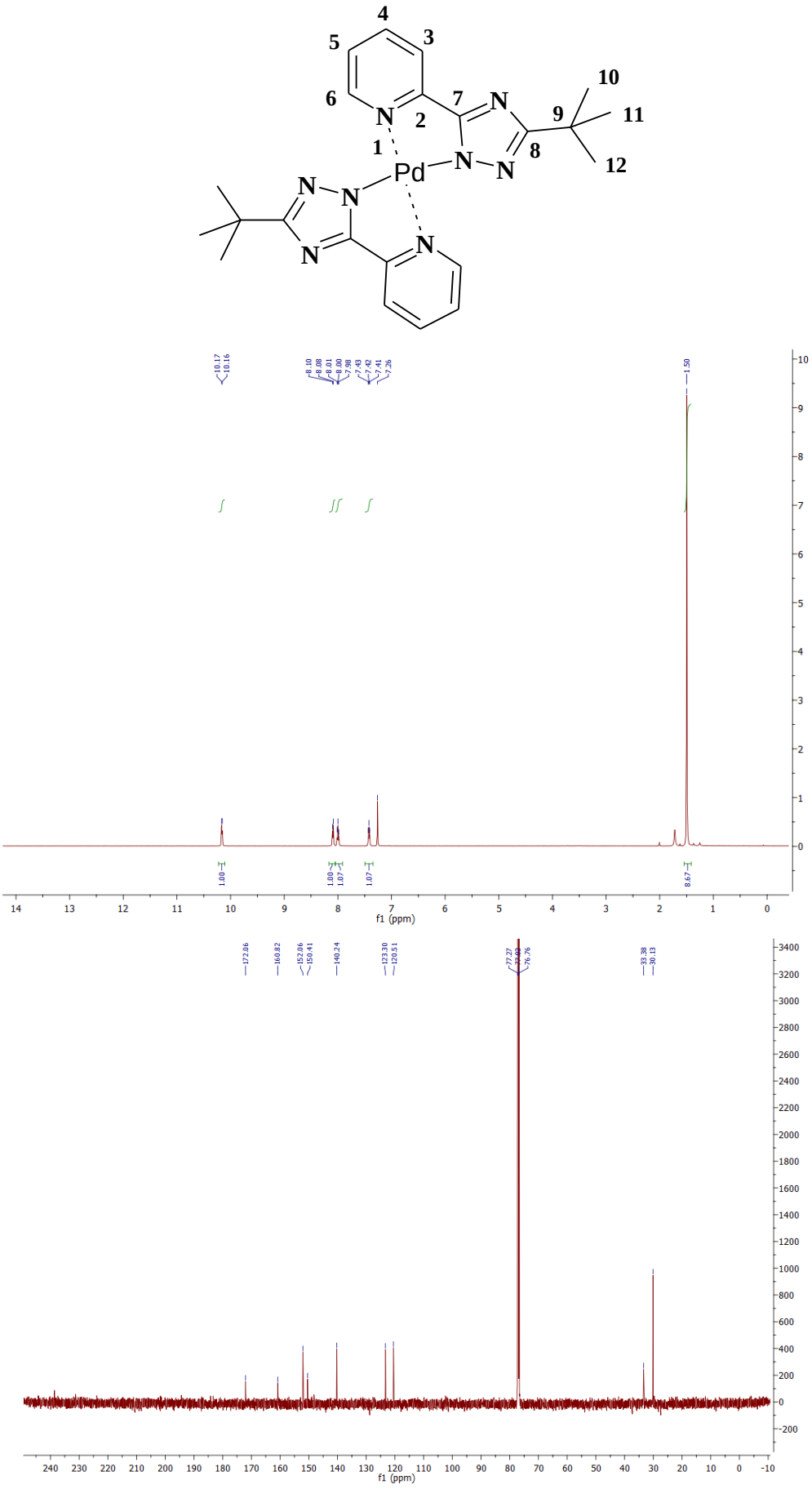

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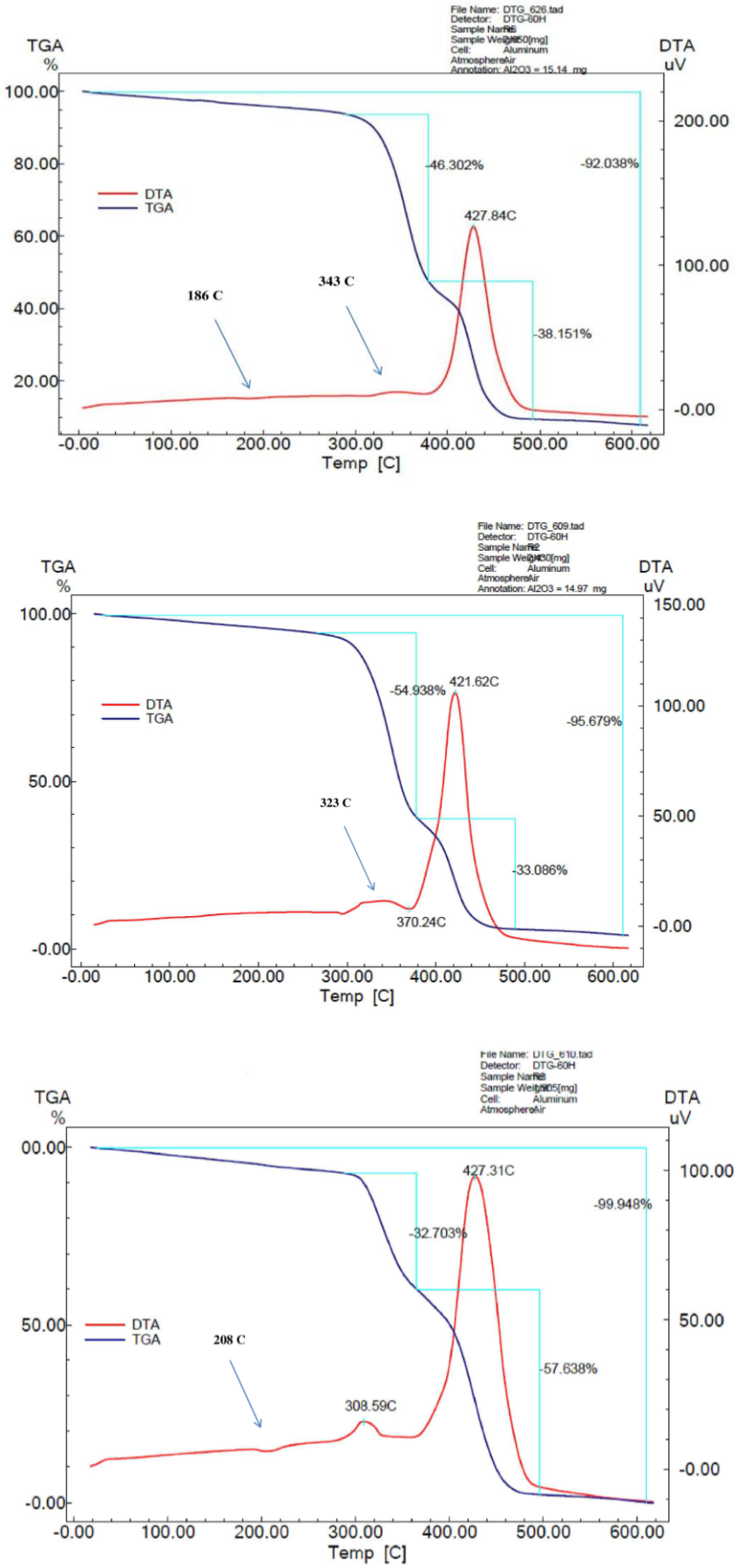

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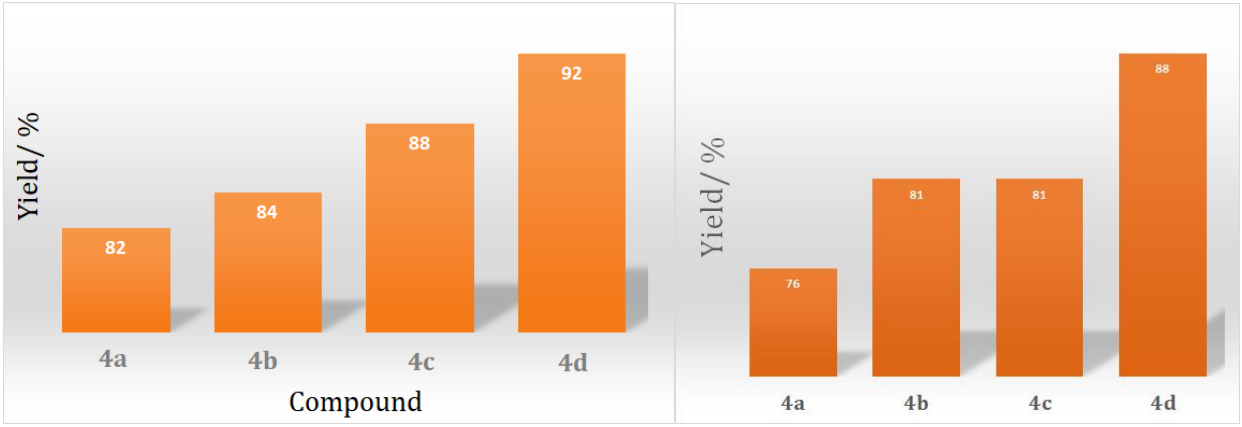


Figure S18. Yields for the Henry reaction between benzaldehyde and nitroethane catalysed by **4a-d** in water (25 °C – left and 75 °C- right).

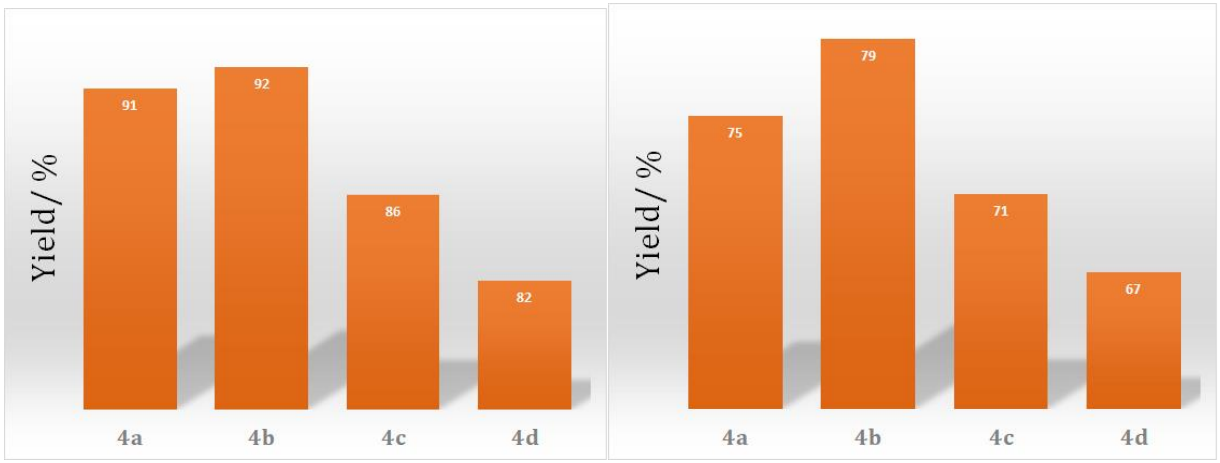
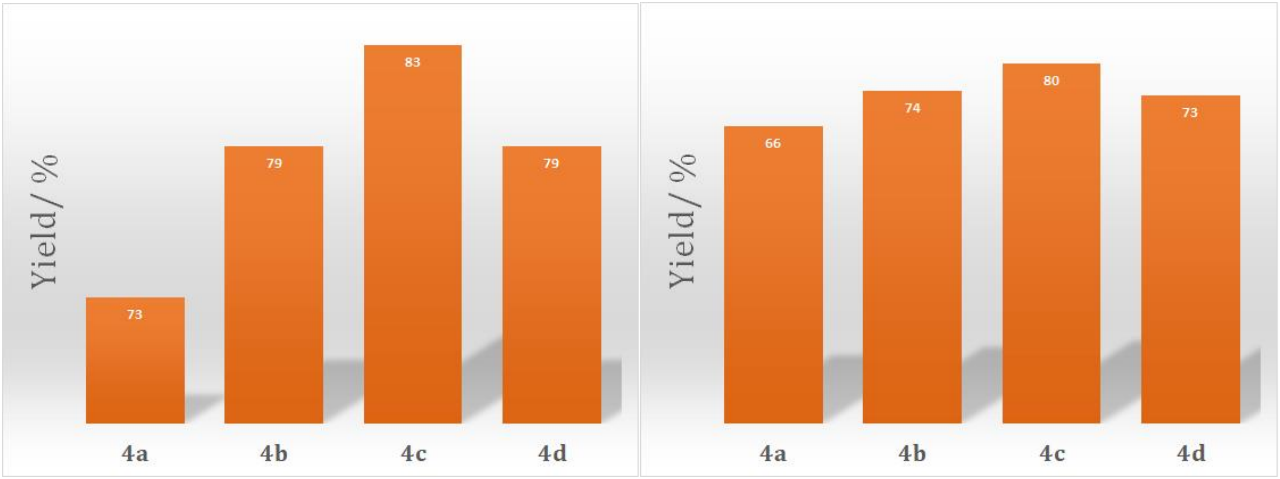


Figure S19. Yields for the Henry reaction between benzaldehyde and nitroethane catalysed by **4a-d** in EtOH (25 °C – left and 75 °C- right).



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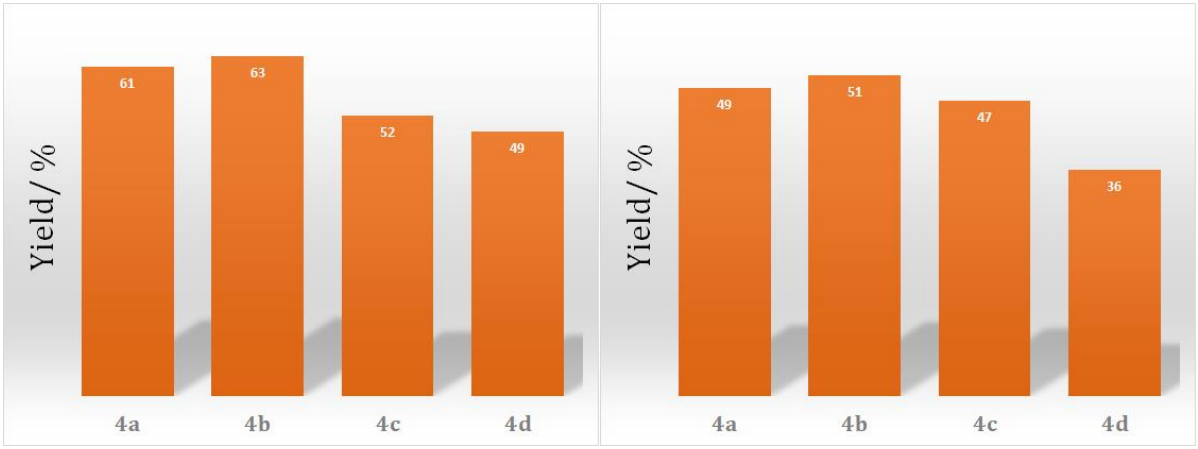

Figure S21. Yield for the MW-assisted Suzuki-Miyaura reaction between 4-methoxybromobenzene and phenyl boronic acid catalysed by **4a-d** in water (K_2CO_3 –left and Cs_2CO_3- right).

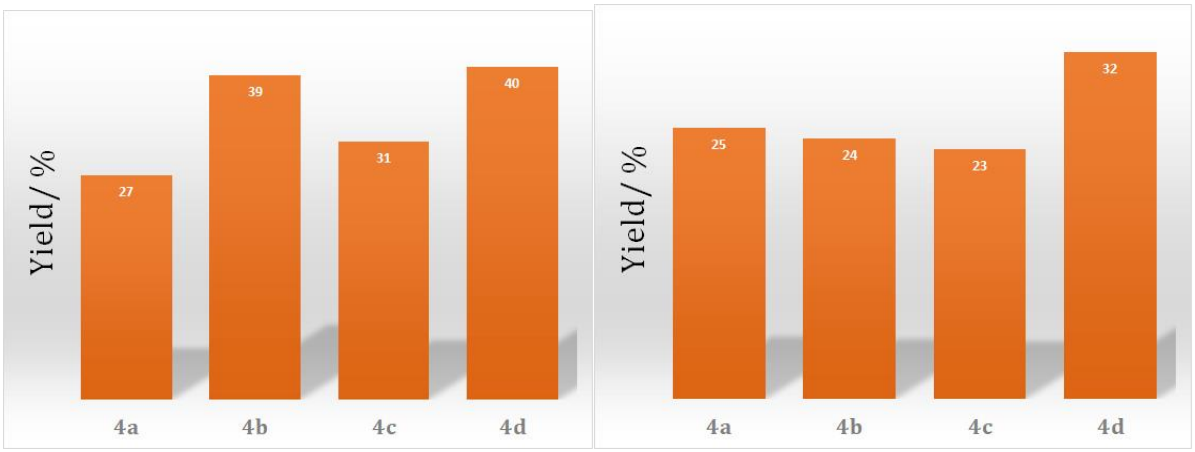

Figure S22. Yield for the MW-assisted Suzuki-Miyaura reaction between 4-methoxybromobenzene and phenyl boronic acid catalysed by **4a-d** in $CHCl_3$ (K_2CO_3 –left and Cs_2CO_3- right).

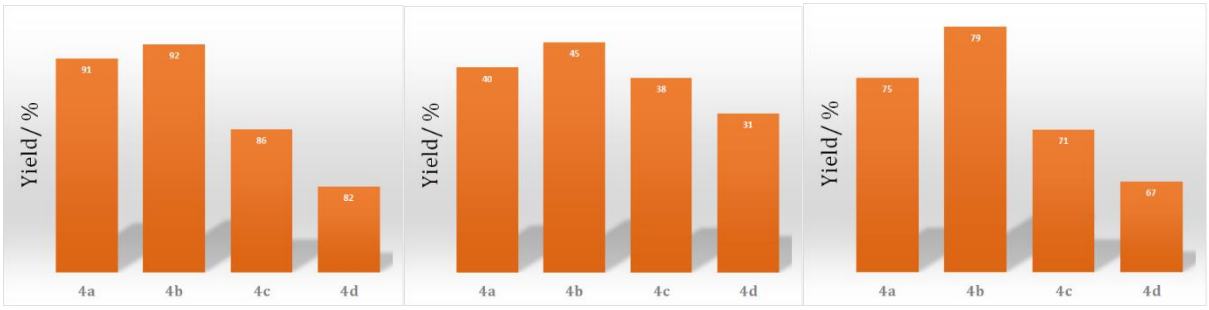

Figure S23. Yield for the MW-assisted Suzuki-Miyaura reaction between 4-methoxybromobenzene and phenyl boronic acid catalysed by **4a-d** in EtOH (K_2CO_3 –left, in centre - K_2CO_3 under conventional heating instead of MW irradiation. and Cs_2CO_3- right).

Table-S1.-Bond-lengths-[Å]-and-angles-[°]-for-**4a**.

Pd1-N1[1]	2.036(4)	N1[1]-Pd1-N1	180.0
Pd1-N1	2.037(4)	N2[1]-Pd1-N1[1]	79.73(18)
Pd1-N2	1.995(4)	N2-Pd1-N1	79.73(18)
Pd1-N2[1]	1.995(4)	N2[1]-Pd1-N1	100.27(18)
N1-C1	1.333(6)	N2-Pd1-N1[1]	100.27(18)
N1-C5	1.374(6)	N2-Pd1-N2[1]	180.0
N2-N3	1.348(5)	C1-N1-Pd1	125.8(3)
N2-C6	1.340(6)	C1-N1-C5	118.8(5)
N3-C7	1.342(6)	C5-N1-Pd1	115.4(4)
N4-C6	1.330(6)	N3-N2-Pd1	136.4(3)
N4-C7	1.367(6)	C6-N2-Pd1	115.7(4)
C1-C2	1.381(7)	C6-N2-N3	107.9(4)
C2-C3	1.362(7)	C7-N3-N2	104.1(4)
C3-C4	1.370(7)	C6-N4-C7	101.4(4)
C4-C5	1.375(7)	N1-C1-C2	121.6(5)
C5-C6	1.455(7)	C3-C2-C1	119.2(6)
C7-C8	1.481(7)	C2-C3-C4	120.6(5)
C8-C9	1.511(8)	C3-C4-C5	118.5(5)
		N1-C5-C4	121.4(5)
		N1-C5-C6	112.4(5)
		C4-C5-C6	126.2(5)
		N2-C6-C5	116.8(5)
		N4-C6-N2	112.8(5)
		N4-C6-C5	130.4(5)
		N3-C7-N4	113.8(5)
		N3-C7-C8	122.0(5)
		N4-C7-C8	124.0(5)
		C7-C8-C9	112.8(5)

1-x,1-y, 1-z

Table-S2.-Bond-lengths-[Å]-and-angles-[°]-for-**4b**.

Pd1-N1[1]	2.0387(19)	N1[1]-Pd1-N1	180.0
Pd1-N1	2.0387(19)	N2[1]-Pd1-N1	100.68(8)
Pd1-N2	1.995(2)	N2-Pd1-N1[1]	100.68(8)
Pd1-N2[1]	1.995(2)	N2-Pd1-N1	79.32(8)
N1-C1	1.347(3)	N2[1-]Pd1-N1[1]	79.31(8)
N1-C5	1.352(3)	N2-Pd1-N2[1]	180.0
N2-N3	1.366(3)	C1-N1-Pd1	125.25(17)
N2-C6	1.332(3)	C1-N1-C5	119.3(2)
N3-C7	1.338(3)	C5-N1-Pd1	115.45(15)
N4-C6	1.327(3)	N3-N2-Pd1	136.30(16)
N4-C7	1.359(3)	C6-N2-Pd1	116.04(16)
C1-C2	1.370(4)	C6-N2-N3	107.66(19)
C2-C3	1.375(4)	C7-N3-N2	103.5(2)
C3-C4	1.379(4)	C6-N4-C7	101.7(2)
C4-C5	1.375(3)	N1-C1-C2	121.1(2)
C5-C6	1.458(3)	C1-C2-C3	120.0(2)

C7-C8	1.490(3)	C2-C3-C4	118.9(2)
C8-C9	1.523(4)	C5-C4-C3	119.3(2)
C9-C10	1.510(4)	N1-C5-C4	121.4(2)
		N1-C5-C6	113.1(2)
		C4-C5-C6	125.5(2)
		N2-C6-C5	116.1(2)
		N4-C6-N2	112.9(2)
		N4-C6-C5	130.9(2)
		N3-C7-N4	114.3(2)
		N3-C7-C8	121.9(2)
		N4-C7-C8	123.8(2)
		C7-C8-C9	113.7(2)
		C10-C9-C8	112.9(2)

[1]1-x,-y,-z

Table-S3.-Bond-lengths-[Å]-and-angles-[°]-for-**4c**.

Pd1-N1[1]	2.021(6)	N1[1]-Pd1-N1	180.0
Pd1-N1	2.021(6)	N2-Pd1-N1	79.0(3)
Pd1-N2[1]	1.963(6)	N2[1]-Pd1-N1[1]	79.0(3)
Pd1-N2	1.963(6)	N2-Pd1-N1[1]	101.0(3)
N1-C1	1.329(10)	N2[1]-Pd1-N1	101.0(3)
N1-C5	1.338(10)	N2[1]-Pd1-N2	180.0(3)
N2-N3	1.356(9)	C1-N1-Pd1	124.7(6)
N2-C6	1.339(11)	C1-N1-C5	119.8(7)
N3-C7	1.314(10)	C5-N1-Pd1	115.4(5)
N4-C6	1.315(10)	N3-N2-Pd1	136.3(6)
N4-C7	1.352(10)	C6-N2-Pd1	117.0(6)
C1-C2	1.363(11)	C6-N2-N3	106.6(7)
C2-C3	1.360(12)	C7-N3-N2	103.8(6)
C3-C4	1.384(11)	C6-N4-C7	100.7(7)
C4-C5	1.378(11)	N1-C1-C2	121.5(8)
C5-C6	1.434(12)	C3-C2-C1	119.8(9)
C7-C8	1.492(11)	C2-C3-C4	119.2(8)
C8-C9	1.498(12)	C5-C4-C3	118.5(8)
C8-C10	1.525(12)	N1-C5-C4	121.2(8)
		N1-C5-C6	113.9(7)
		C4-C5-C6	124.8(8)
		N2-C6-C5	114.6(8)
		N4-C6-N2	113.5(8)
		N4-C6-C5	131.9(8)
		N3-C7-N4	115.3(7)
		N3-C7-C8	122.1(7)
		N4-C7-C8	122.5(8)
		C7-C8-C9	112.2(7)
		C7-C8-C10	109.3(7)
		C9-C8-C10	110.7(7)

[1]1-x,2-y,1-z

Table-S4.-Bond-lengths-[Å]-and-angles-[°]-for-**4d**.

Pd1A-N1A	2.026(6)	N1A-Pd1A-N5A	179.7(3)
Pd1A-N2A	2.022(7)	N2A-Pd1A-N1A	79.3(3)
Pd1A-N5A	2.029(6)	N2A-Pd1A-N5A	100.4(3)
Pd1A-N6A	2.003(6)	N6A-Pd1A-N1A	101.0(3)
N1A-C1A	1.346(9)	N6A-Pd1A-N2A	179.7(3)
N1A-C5A	1.324(10)	N6A-Pd1A-N5A	79.3(3)
N2A-N3A	1.359(8)	C1A-N1A-Pd1A	125.9(5)
N2A-C6A	1.335(9)	C5A-N1A-Pd1A	117.6(6)
N3A-C7A	1.348(10)	C5A-N1A-C1A	116.5(7)
N4A-C6A	1.336(10)	N3A-N2A-Pd1A	136.5(5)
N4A-C7A	1.356(10)	C6A-N2A-Pd1A	114.6(6)
N5A-C11A	1.339(10)	C6A-N2A-N3A	108.9(7)
N5A-C15A	1.348(10)	C7A-N3A-N2A	102.5(7)
N6A-N7A	1.371(9)	C6A-N4A-C7A	101.5(7)
N6A-C16A	1.338(9)	C11A-N5A-Pd1A	125.7(6)
N7A-C17A	1.337(10)	C11A-N5A-C15A	118.1(7)
N8A-C16A	1.334(10)	C15A-N5A-Pd1A	116.2(5)
N8A-C17A	1.356(10)	N7A-N6A-Pd1A	136.4(5)
C1A-C2A	1.398(10)	C16A-N6A-Pd1A	116.4(6)
C2A-C3A	1.380(11)	C16A-N6A-N7A	107.2(6)
C3A-C4A	1.380(11)	C17A-N7A-N6A	103.4(7)
C4A-C5A	1.366(10)	C16A-N8A-C17A	101.1(7)
C5A-C6A	1.491(11)	N1A-C1A-C2A	122.7(8)
C7A-C8A	1.517(11)	C3A-C2A-C1A	118.9(8)
C8A-C9A	1.525(11)	C4A-C3A-C2A	118.0(8)
C8A-C10A	1.517(7)	C5A-C4A-C3A	119.2(8)
C8A-C10A^{1}	1.517(7)	N1A-C5A-C4A	124.7(8)
C11A-C12A	1.372(10)	N1A-C5A-C6A	111.9(7)
C12A-C13A	1.365(11)	C4A-C5A-C6A	123.4(8)
C13A-C14A	1.355(11)	N2A-C6A-N4A	112.1(7)
C14A-C15A	1.388(10)	N2A-C6A-C5A	116.6(8)
C15A-C16A	1.479(11)	N4A-C6A-C5A	131.3(8)
C17A-C18A	1.518(11)	N3A-C7A-N4A	114.9(8)
C18A-C19A^{1}	1.522(8)	N3A-C7A-C8A	123.6(8)
C18A-C19A	1.522(8)	N4A-C7A-C8A	121.5(8)
C18A-C20A	1.535(11)	C7A-C8A-C9A	110.8(8)
Pd1B-N1B^{2}	2.031(7)	C10A-C8A-C7A	108.9(5)
Pd1B-N1B	2.031(7)	C10A^{1}-C8A-C7A	108.9(5)
Pd1B-N2B^{2}	1.990(7)	C10A^{1}-C8A-C9A	108.1(5)
Pd1B-N2B	1.990(7)	C10A-C8A-C9A	108.1(5)
N1B-C1B	1.376(10)	C10A^{1}-C8A-C10A	112.2(9)
N1B-C5B	1.349(10)	N5A-C11A-C12A	122.1(8)
N2B-N3B	1.381(9)	C13A-C12A-C11A	120.3(9)
N2B-C6B	1.339(10)	C14A-C13A-C12A	117.7(8)
N3B-C7B	1.343(10)	C13A-C14A-C15A	121.0(8)
N4B-C6B	1.350(10)	N5A-C15A-C14A	120.8(8)
N4B-C7B	1.365(11)	N5A-C15A-C16A	113.1(7)

C1B-C2B	1.374(11)	C14A-C15A-C16A	126.1(8)
C2B-C3B	1.376(11)	N6A-C16A-C15A	115.0(7)
C3B-C4B	1.417(12)	N8A-C16A-N6A	113.2(7)
C4B-C5B	1.348(11)	N8A-C16A-C15A	131.8(8)
C5B-C6B	1.452(12)	N7A-C17A-N8A	115.0(8)
C7B-C8B	1.539(11)	N7A-C17A-C18A	122.2(8)
C8B-C9B^{3}	1.506(8)	N8A-C17A-C18A	122.8(8)
C8B-C9B	1.506(8)	C17A-C18A-C19A^{1}	109.1(5)
C8B-C10B	1.527(11)	C17A-C18A-C19A	109.1(5)
Cl1-C1	1.709(10)	C17A-C18A-C20A	109.9(8)
Cl2-C1	1.753(7)	C19A^{1}-C18A-C19A	111.4(9)
		C19A-C18A-C20A	108.6(5)
		C19A^{1}-C18A-C20A	108.6(5)
		N1B-Pd1B-N1B^{2}	180.0
		N2B-Pd1B-N1B^{2}	101.4(3)
		N2B^{2}-Pd1B-N1B	101.4(3)
		N2B^{2}-Pd1B-N1B^{2}	78.6(3)
		N2B-Pd1B-N1B	78.6(3)
		N2B-Pd1B-N2B^{2}	180.0
		C1B-N1B-Pd1B	125.2(6)
		C5B-N1B-Pd1B	117.5(6)
		C5B-N1B-C1B	117.3(8)
		N3B-N2B-Pd1B	135.9(6)
		C6B-N2B-Pd1B	115.8(6)
		C6B-N2B-N3B	108.3(7)
		C7B-N3B-N2B	103.4(7)
		C6B-N4B-C7B	102.2(7)
		C2B-C1B-N1B	121.2(9)
		C1B-C2B-C3B	120.5(10)
		C2B-C3B-C4B	118.3(9)
		C5B-C4B-C3B	118.2(9)
		N1B-C5B-C4B	124.5(9)
		N1B-C5B-C6B	111.0(8)
		C4B-C5B-C6B	124.4(8)
		N2B-C6B-N4B	111.8(8)
		N2B-C6B-C5B	117.1(8)
		N4B-C6B-C5B	131.1(8)
		N3B-C7B-N4B	114.3(8)
		N3B-C7B-C8B	121.3(9)
		N4B-C7B-C8B	124.4(8)
		C9B^{3}-C8B-C7B	108.1(5)
		C9B-C8B-C7B	108.1(5)
		C9B-C8B-C9B^{3}	114.2(10)
		C9B-C8B-C10B	108.3(5)
		C9B^{3}-C8B-C10B	108.3(5)
		C10B-C8B-C7B	109.9(8)
		Cl1-C1-Cl2^{1}	111.1(4)
		Cl1-C1-Cl2	111.1(4)
		Cl2-C1-Cl2^{1}	109.0(7)

[1]+x,1-y,+z;[2]-x,1-y,-z; [3]+x, -y,+z;

Table S5. Crystallographic data, details of data collection and structure refinement parameters for **4a - 4d**.

Identification code	**4a**	**4b**	**4c**	**4d**
Empirical formula	$C_{18}H_{18}N_8Pd$	$C_{20}H_{22}N_8Pd$	$C_{20}H_{22}N_8Pd$	$C_{68}H_{84}Cl_6N_{24}O_2Pd_3$
Formula weight	452.80	480.85	480.85	1801.49
Temperature/K	293	200	293	293
Space group	*P*-1	*P*-1	$P2_1/c$	*C*2/*m*
a/Å	4.5732(7)	5.4343(3)	4.4346(9)	30.046(8)
b/Å	9.8193(12)	8.4913(3)	10.181(4)	6.8662(12)
c/Å	10.5527(13)	10.9739(5)	21.341(7)	23.785(6)
α/°	71.200(11)	88.134(3)	90	90
β/°	86.444(11)	80.550(4)	92.15(2)	126.80(4)
γ/°	76.934(12)	76.336(4)	90	90
Volume/Å^3	436.95(11)	485.36(4)	962.9(5)	3929(2)
Z	1	1	2	2
ρ_{calc}g/cm^3	1.721	1.645	1.659	1.523
μ/mm^{-1}	1.084	0.981	0.989	0.943
Crystal size/mm^3	0.10 × 0.05 × 0.02	0.20 × 0.20 × 0.15	0.30 × 0.10 × 0.10	0.2 × 0.15 × 0.15
$\theta_{min,}$ θ_{max}(°)	4.078 to 50.05	3.762 to 50.048	4.434 to 58.998	3.386 to 50.054
Reflections collected	2905	3495	2623	7696
Independent reflections	1543[R_{int} = 0.0519]	1724 [R_{int} = 0.0314]	1722 [R_{int} = 0.0314]	3784 [R_{int} = 0.0722]
Data/restraints/parameters	1543/0/125	1724/0/134	2623/0/136	3784/0/299
GOF[a]	1.081	1.004	1.010	0.928
R_1[b]($I>2\sigma(I)$)	0.0615	0.0250,	0.0702	0.0601
wR_2[c](all data)	0.0865	0.0579	0.1615	0.1030
Largest diff. peak/hole / e Å^{-3}	0.77/-0.58	0.60/-0.42	2.27/-1.27	1.23/-0.60

[a] GOF = $\{\Sigma[w(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined; [b]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [c]$wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.