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SUPPORTING INFORMATION

Title: DNA Groove-binding Ability of Luminescent Platinum(II) Complexes based on a Family of Tridentate N^N^C Ligands Bearing Differently substituted Alkyl Tethers
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DNA groove-binding ability of luminescent platinum(II) complexes based on a family of tridentate N^N^C ligands bearing differently substituted alkyl tethers

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Supporting Information

Table of contents

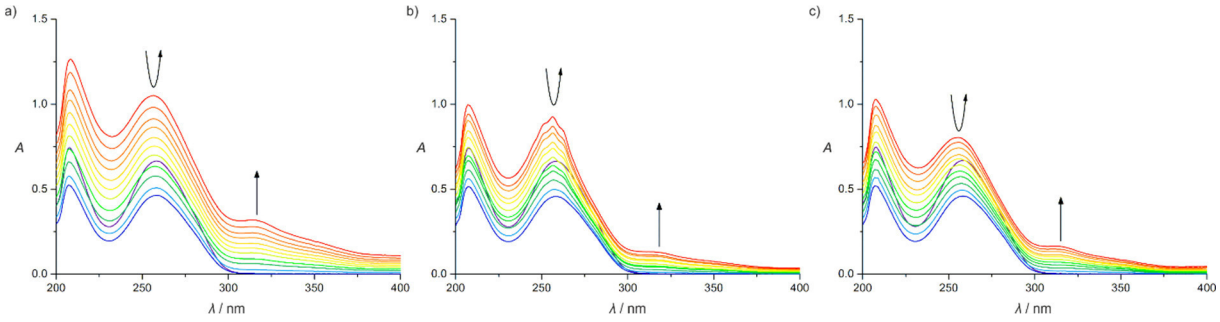


Figure S1. UV/Vis spectra of a solution of ctDNA ($7.6 \cdot 10^{-5}$ M) in Tris-HCl buffer (pH 7.4) at 25 °C upon increasing concentrations of the respective Pt^{II} complex (11 steps with an increase of $3.2 \cdot 10^{-6}$ M per step). Arrows indicate the direction of the changes. Data for a) complex **8**, b) complex **9** and c) complex **10**.

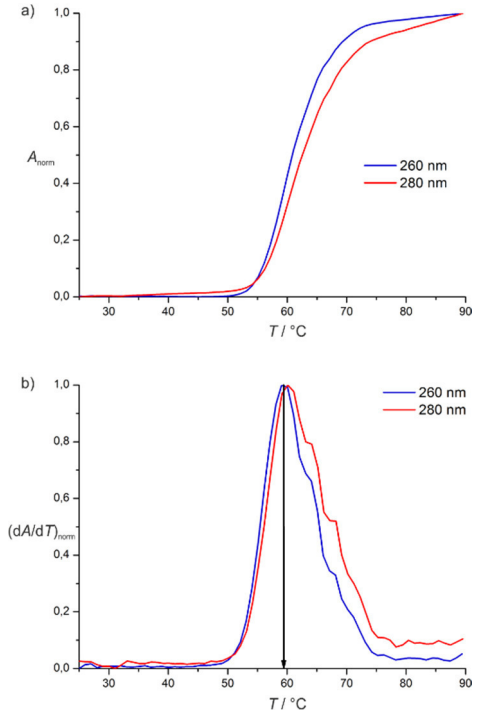


Figure S2. a) Melting curves of ctDNA, determined by temperature-dependent UV spectra at 260 nm and 280 nm, respectively. b) First derivative of the melting curves, used to determine the melting temperature $T_{m,UV}$.

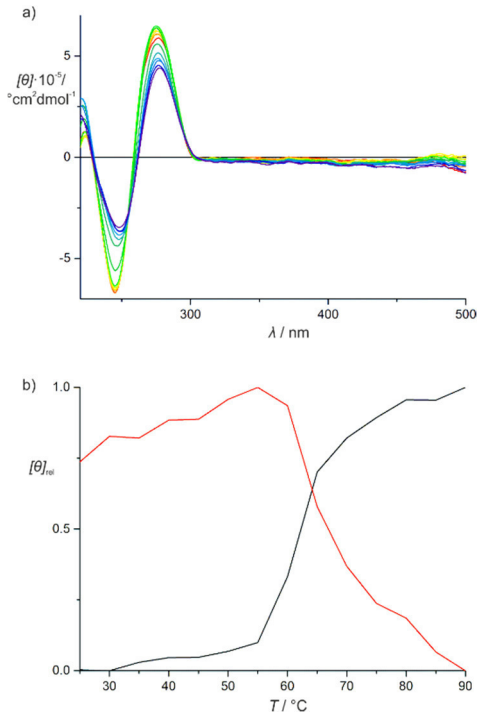


Figure S3. a) Example for temperature-dependent CD spectra (here: ctDNA). b) Temperature-dependent molar ellipticity at selected wavelengths (black: 246 nm, red: 277 nm). A sigmoid fit of these data was used to determine the melting temperature derived via temperature-dependent CD spectroscopy ($T_{m,CD}$).

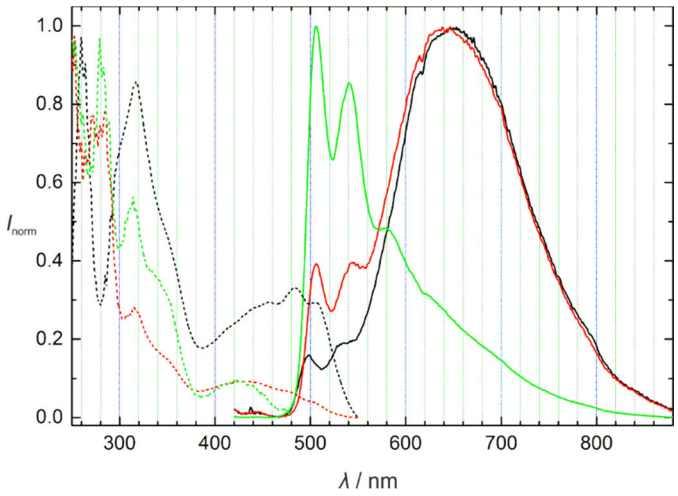


Figure S4. Excitation (dotted line) and emission (solid line) spectra of complex **8** (3.2 μM) in Tris-HCl buffer (pH 7.4) in the absence (black) and presence of ctDNA (red: $7.6 \cdot 10^{-6}$ M; green: $7.6 \cdot 10^{-5}$ M).

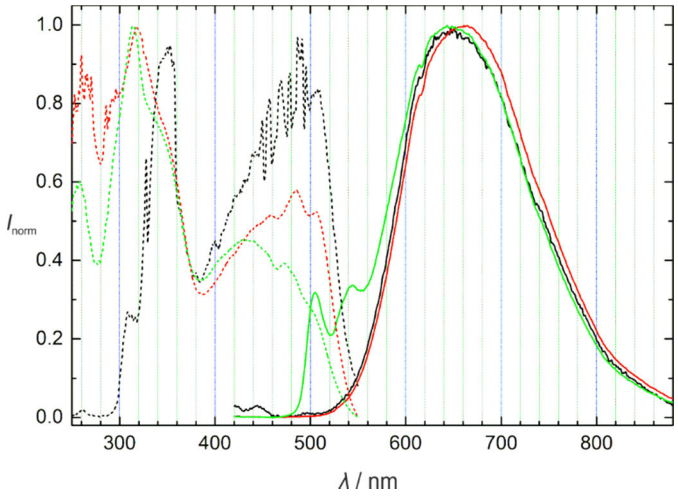


Figure S5. Excitation (dotted line) and emission (solid line) spectra of complex **8** (32 μM) in Tris-HCl buffer (pH 7.4) in the absence (black) and presence of ctDNA (red: $7.6 \cdot 10^{-6}$ M; green: $7.6 \cdot 10^{-5}$ M).

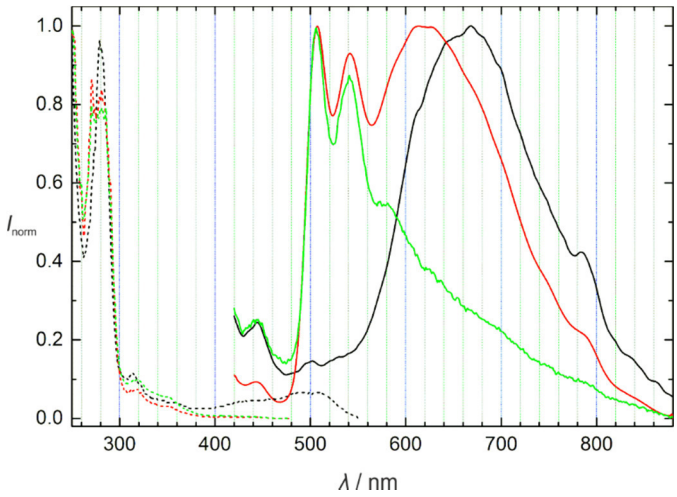


Figure S6. Excitation (dotted line) and emission (solid line) spectra of complex **9** (3.2 μM) in Tris-HCl buffer (pH 7.4) in the absence (black) and presence of ctDNA (red: $7.6 \cdot 10^{-6}$ M; green: $7.6 \cdot 10^{-5}$ M).

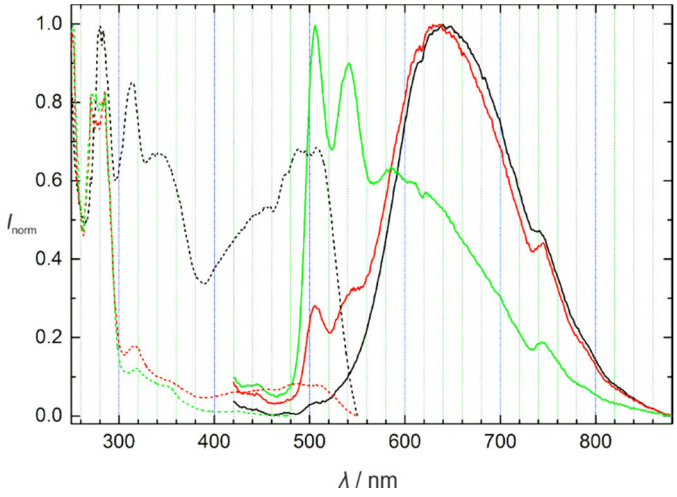


Figure S7. Excitation (dotted line) and emission (solid line) spectra of complex **9** (32 μM) in Tris-HCl buffer (pH 7.4) in the absence (black) and presence of ctDNA (red: $7.6 \cdot 10^{-6}$ M; green: $7.6 \cdot 10^{-5}$ M).

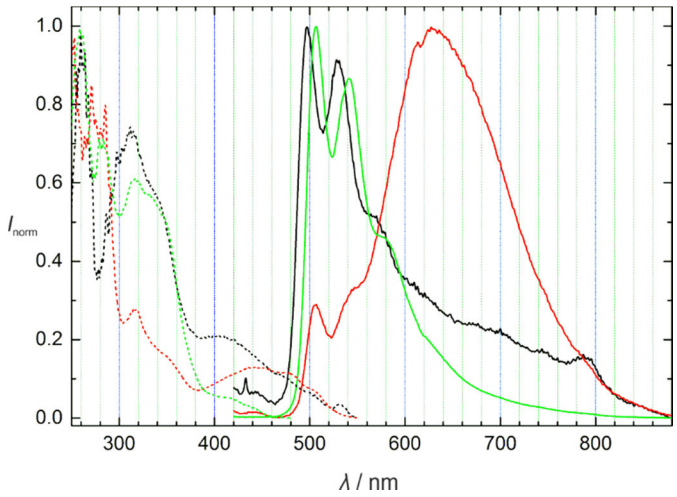


Figure S8. Excitation (dotted line) and emission (solid line) spectra of complex **10** (3.2 μM) in Tris-HCl buffer (pH 7.4) in the absence (black) and presence of ctDNA (red: $7.6 \cdot 10^{-6}$ M; green: $7.6 \cdot 10^{-5}$ M).

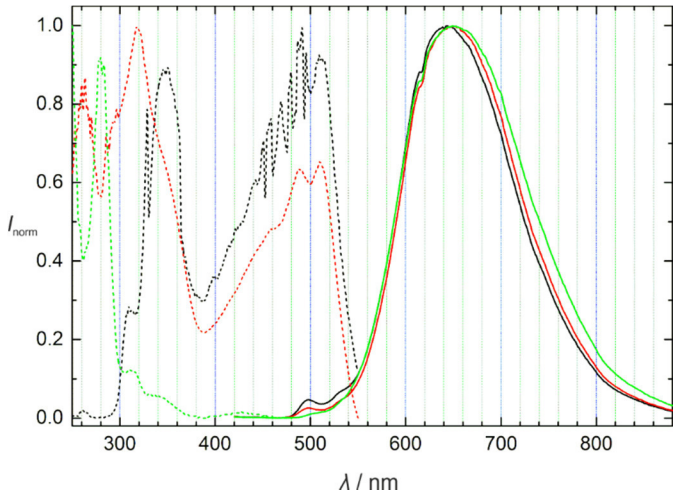


Figure S9. Excitation (dotted line) and emission (solid line) spectra of complex **10** (32 μM) in Tris-HCl buffer (pH 7.4) in the absence (black) and presence of ctDNA (red: $7.6 \cdot 10^{-6}$ M; green: $7.6 \cdot 10^{-5}$ M).

Table S1. Emission lifetimes of compound **8** (3.2 μM) with and without ctDNA (as derived from data depicted in Figure S4).[a]

Detection	Additive		
	None	$7.6 \cdot 10^{-6}$ M ctDNA	$7.6 \cdot 10^{-5}$ M ctDNA
500 nm	τ_{av} = 0.94 μs fractional amplitudes: τ_1 (1.24 μs): 41.0% τ_2 (0.73 μs): 59.0%	τ_{av} = 10.8 μs fractional amplitudes: τ_1 (5.29 μs): 14.9% τ_2 (0.64 μs): 31.5% τ_3 (18.26 μs): 53.6%	τ_{av} = 16.6 μs fractional amplitudes: τ_1 (18.8 μs): 83.0% τ_2 (5.96 μs): 17.0% τ_{av} = 18.1 μs (deaerated) fractional amplitudes: τ_1 (21.5 μs): 79.6% τ_2 (4.54 μs): 20.4%
650 nm	τ_{av} = 0.68 μs fractional amplitudes: τ_1 (0.634 μs): 45.7% τ_2 (0.231 μs): 27.2% τ_3 (1.20 μs): 27.1%	τ_{av} = 0.82 μs fractional amplitudes: τ_1 (0.91 μs): 61.8% τ_2 (0.30 μs): 27.9% τ_3 (1.7036 μs): 10.3%	τ_{av} = 1.4 μs fractional amplitudes: τ_1 (15.7 μs): 1.8% τ_2 (1.73 μs): 38.0% τ_3 (0.76 μs): 60.2%

[a] τ_{av} = amplitude-weighted average lifetimes

Table S2. Emission lifetimes of compound **8** (32 μM) with and without ctDNA (as derived from data depicted in Figure S5).[a]

Detection	Additive		
	None	$7.6 \cdot 10^{-6}$ M ctDNA	$7.6 \cdot 10^{-5}$ M ctDNA
500 nm	not determined	not determined	τ_{av} = 14.4 μs fractional amplitudes: τ_1 (17.4 μs): 78.2% τ_2 (3.26 μs): 21.8% τ_{av} = 14.1 μs (deaerated) fractional amplitudes: τ_1 (7.9 μs): 19.6% τ_2 (1.37 μs): 22.4% τ_3 (21.1 μs): 58.0%
650 nm	τ_{av} = 0.58 μs fractional amplitudes: τ_1 (0.54 μs): 51.8% τ_2 (0.19 μs): 24.2% τ_3 (1.08 μs): 24.0%	τ_{av} = 0.62 μs fractional amplitudes: τ_1 (0.51 μs): 43.9% τ_2 (0.19 μs): 20.4% τ_3 (0.99 μs): 35.7%	τ_{av} = 0.87 μs fractional amplitudes: τ_1 (6.6 μs): 0.2% τ_2 (1.17 μs): 50.0% τ_3 (0.54 μs): 49.8%

[a] τ_{av} = amplitude-weighted average lifetimes

Table S3. Emission lifetimes of compound **9** (3.2 μM) with and without ctDNA (as derived from data depicted in Figure S6).[a]

Detection	Additive		
	None	$7.6 \cdot 10^{-6}$ M ctDNA	$7.6 \cdot 10^{-5}$ M ctDNA
500 nm	not determined	τ_{av} = 10.2 μs fractional amplitudes: τ_1 (17.8 μs): 51.0% τ_2 (4.90 μs): 18.6% τ_3 (0.652 μs): 30.4%	τ_{av} = 14.5 μs fractional amplitudes: τ_1 (17.2 μs): 80.6% τ_2 (2.95 μs): 19.4% τ_{av} = 14.2 μs (deaerated) fractional amplitudes: τ_1 (21.3 μs): 89.4% τ_2 (3.74 μs): 10.6%
650 nm	τ_{av} = 0.35 μs fractional amplitudes: τ_1 (1.14 μs): 9.4% τ_2 (0.40 μs): 40.7% τ_3 (0.145 μs): 49.9%	τ_{av} = 0.82 μs fractional amplitudes: τ_1 (2.71 μs): 5.1% τ_2 (1.05 μs): 51.4% τ_3 (0.33 μs): 43.5%	τ_{av} = 1.0 μs fractional amplitudes: τ_1 (14.4 μs): 2.3% τ_2 (1.52 μs): 28.6% τ_3 (0.350 μs): 69.1%

[a] τ_{av} = amplitude-weighted average lifetimes

Table S4. Emission lifetimes of compound **9** (32 μM) with and without ctDNA (as derived from data depicted in Figure S7).[a]

Detection	Additive		
	None	$7.6 \cdot 10^{-6}$ M ctDNA	$7.6 \cdot 10^{-5}$ M ctDNA
500 nm	not determined	τ_{av} = 2.0 μs fractional amplitudes: τ_1 (13.2 μs): 12.5% τ_2 (0.242 μs): 71.2% τ_3 (1.20 μs): 16.3%	τ_{av} = 9.9 μs fractional amplitudes: τ_1 (4.44 μs): 16.0% τ_2 (0.413 μs): 25.2% τ_3 (15.5 μs): 58.8% τ_{av} = 10.2 μs (deaerated) fractional amplitudes: τ_1 (21.0 μs): 89.5% τ_2 (0.70 μs): 2.5% τ_3 (4.14 μs): 8.0%
650 nm	τ_{av} = 0.21 μs fractional amplitudes: τ_1 (0.861 μs): 6.9% τ_2 (0.264 μs): 37.7% τ_3 (0.083 μs): 55.4%	τ_{av} = 0.25 μs fractional amplitudes: τ_1 (1.02 μs): 8.1% τ_2 (0.324 μs): 35.3% τ_3 (0.091 μs): 56.6%	τ_{av} = 0.38 μs fractional amplitudes: τ_1 (0.110 μs): 44.4% τ_2 (1.146 μs): 12.4% τ_3 (0.381 μs): 42.9% τ_4 (6.69 μs): 0.3%

[a] τ_{av} = amplitude-weighted average lifetimes

Table S5. Emission lifetimes of compound **10** (3.2 μM) with and without ctDNA (as derived from data depicted in Figure S8).[a]

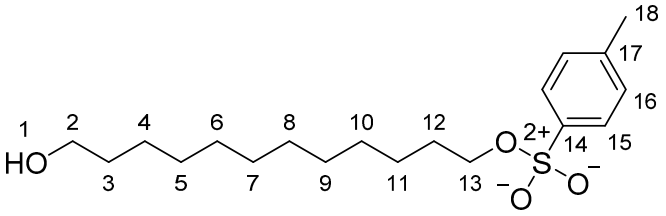
Detection	Additive		
	None	$7.6 \cdot 10^{-6}$ M ctDNA	$7.6 \cdot 10^{-5}$ M ctDNA
500 nm	τ_{av} = 0.90 μs fractional amplitudes: τ_1 (3.84 μs): 1.8% τ_2 (0.98 μs): 61.0% τ_3 (0.64 μs): 37.2% τ_{av} = 1.64 μs (deaerated) fractional amplitudes: τ_1 (1.11 μs): 81.3% τ_2 (3.97 μs): 18.8%	τ_{av} = 6.8 μs fractional amplitudes: τ_1 (4.70 μs): 21.4% τ_2 (1.00 μs): 45.9% τ_3 (16.3 μs): 32.7%	τ_{av} = 16.1 μs fractional amplitudes: τ_1 (18.5 μs): 81.8% τ_2 (5.6 μs): 18.2% τ_{av} = 17.2 μs (deaerated) fractional amplitudes: τ_1 (11.4 μs): 23.8% τ_2 (22.0 μs): 64.8% τ_3 (2.47 μs): 11.4%
650 nm	τ_{av} = 0.55 μs fractional amplitudes: τ_1 (1.70 μs): 10.7% τ_2 (0.645 μs): 44.3% τ_3 (0.179 μs): 45.0%	τ_{av} = 1.14 μs fractional amplitudes: τ_1 (1.46 μs): 52.8% τ_2 (0.78 μs): 47.2%	τ_{av} = 1.02 μs fractional amplitudes: τ_1 (1.21 μs): 72.5% τ_2 (0.53 μs): 27.5%

[a] τ_{av} = amplitude-weighted average lifetimes

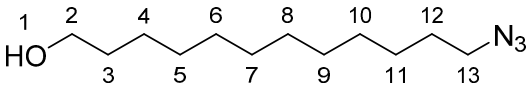
Table S6. Emission lifetimes of compound **10** (32 μM) with and without ctDNA (as derived from data depicted in Figure S9).[a]

Detection	Additive		
	None	$7.6 \cdot 10^{-6}$ M ctDNA	$7.6 \cdot 10^{-5}$ M ctDNA
500 nm	τ_{av} = 0.86 μs fractional amplitudes: τ_1 (1.24 μs): 24.2% τ_2 (0.74 μs): 75.8%	not determined	not determined
650 nm	τ_{av} = 1.02 μs fractional amplitudes: τ_1 (1.17 μs): 66.6% τ_2 (0.74 μs): 33.4%	τ_{av} = 0.78 μs fractional amplitudes: τ_1 (1.03 μs): 57.3% τ_2 (0.51 μs): 34.3% τ_3 (0.122 μs): 8.4%	τ_{av} = 1.02 μs fractional amplitudes: τ_1 (1.21 μs): 72.5% τ_2 (0.53 μs): 27.5%

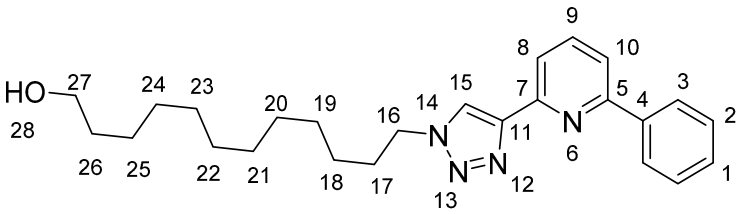
[a] τ_{av} = amplitude-weighted average lifetimes



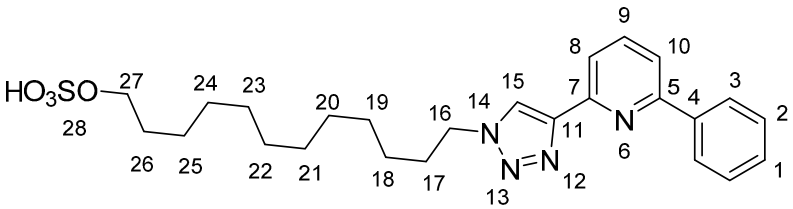
Scheme S1. Structural representation of compound **1** for NMR characterization.



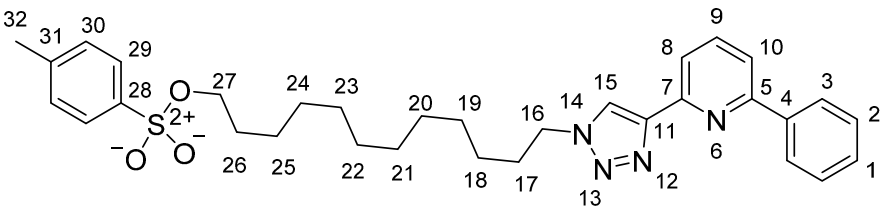
Scheme S2. Structural representation of compound **2** for NMR characterization.



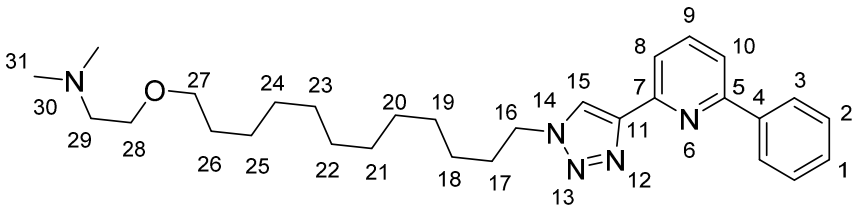
Scheme S3. Structural representation of compound **3** for NMR characterization.



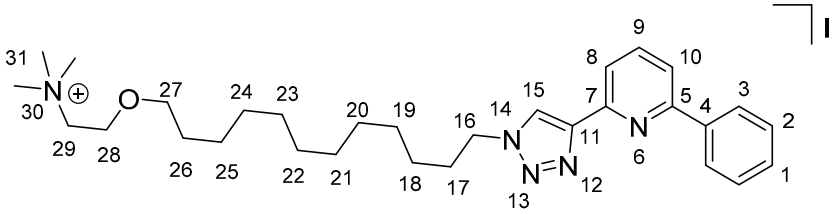
Scheme S4. Structural representation of compound **4** for NMR characterization.



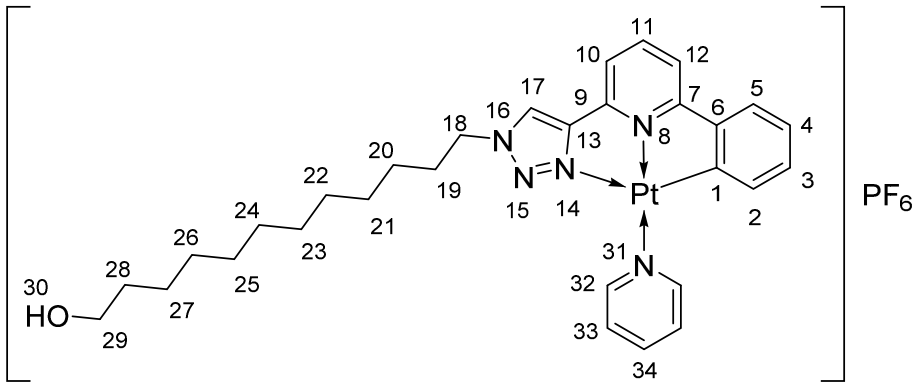
Scheme S5. Structural representation of compound **5** for NMR characterization.



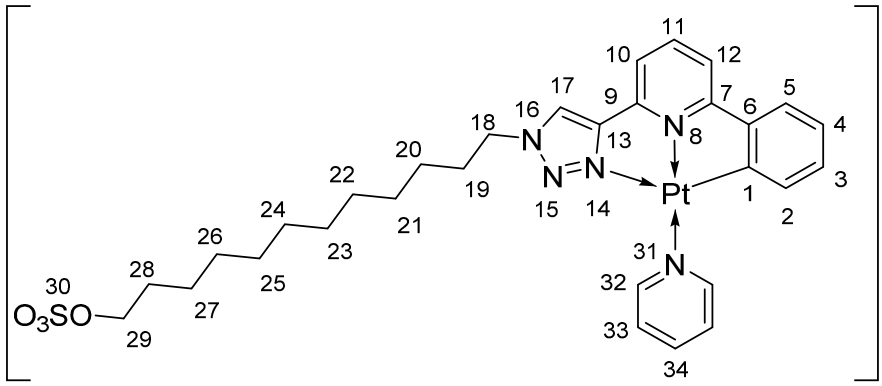
Scheme S6. Structural representation of compound **6** for NMR characterization.



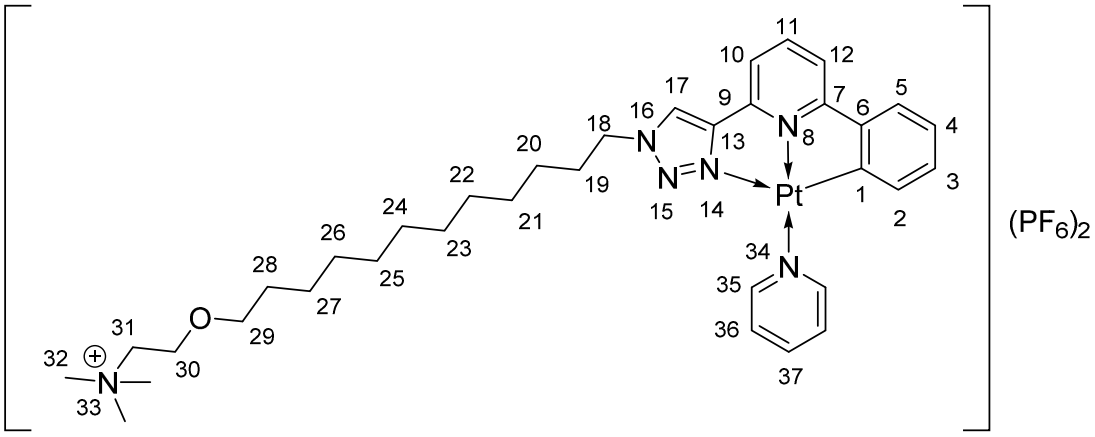
Scheme S7. Structural representation of compound **7** for NMR characterization.



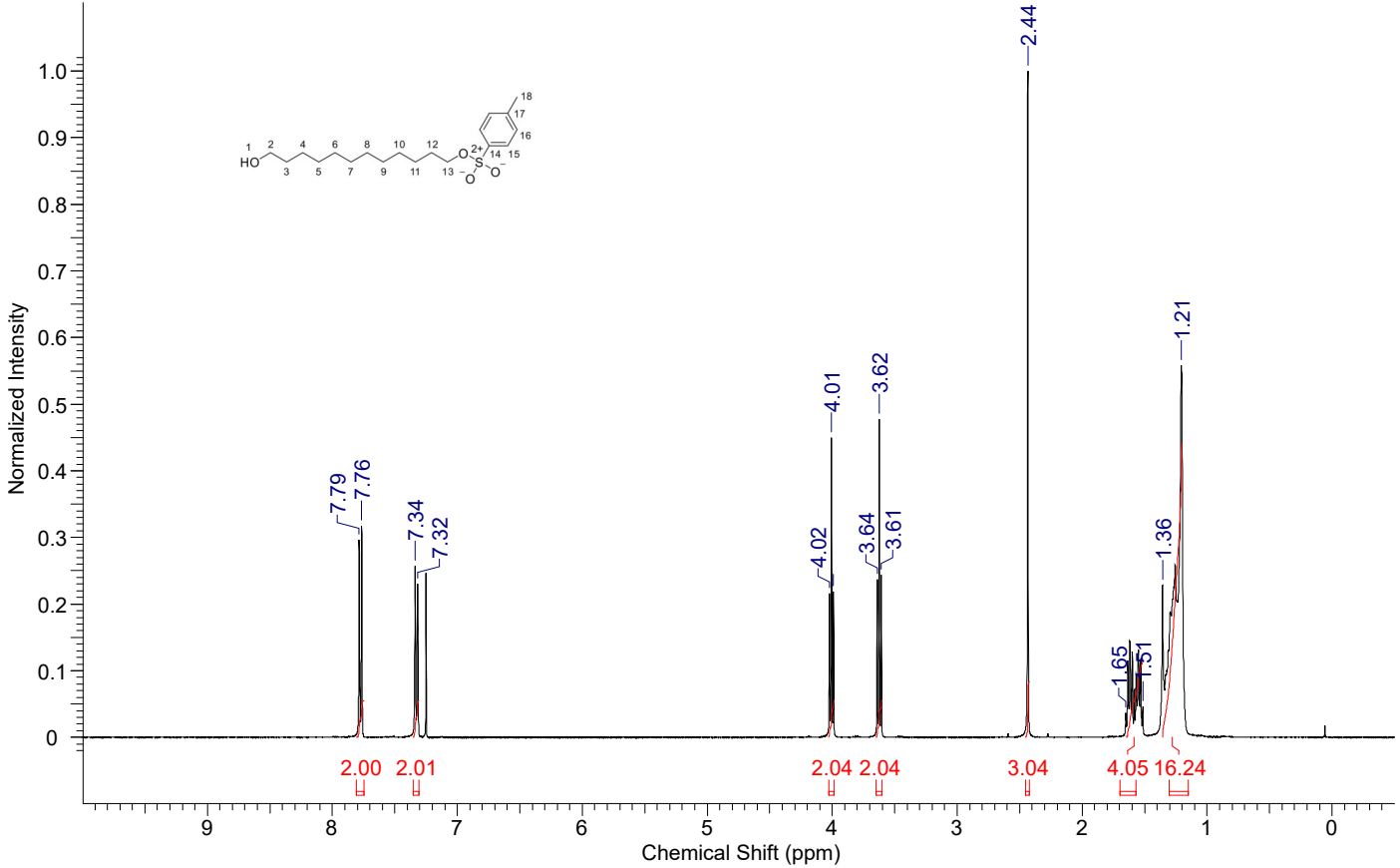
Scheme S8. Structural representation of compound **8** for NMR characterization.



Scheme S9. Structural representation of compound **9** for NMR characterization.



Scheme S10. Structural representation of compound **10** for NMR characterization.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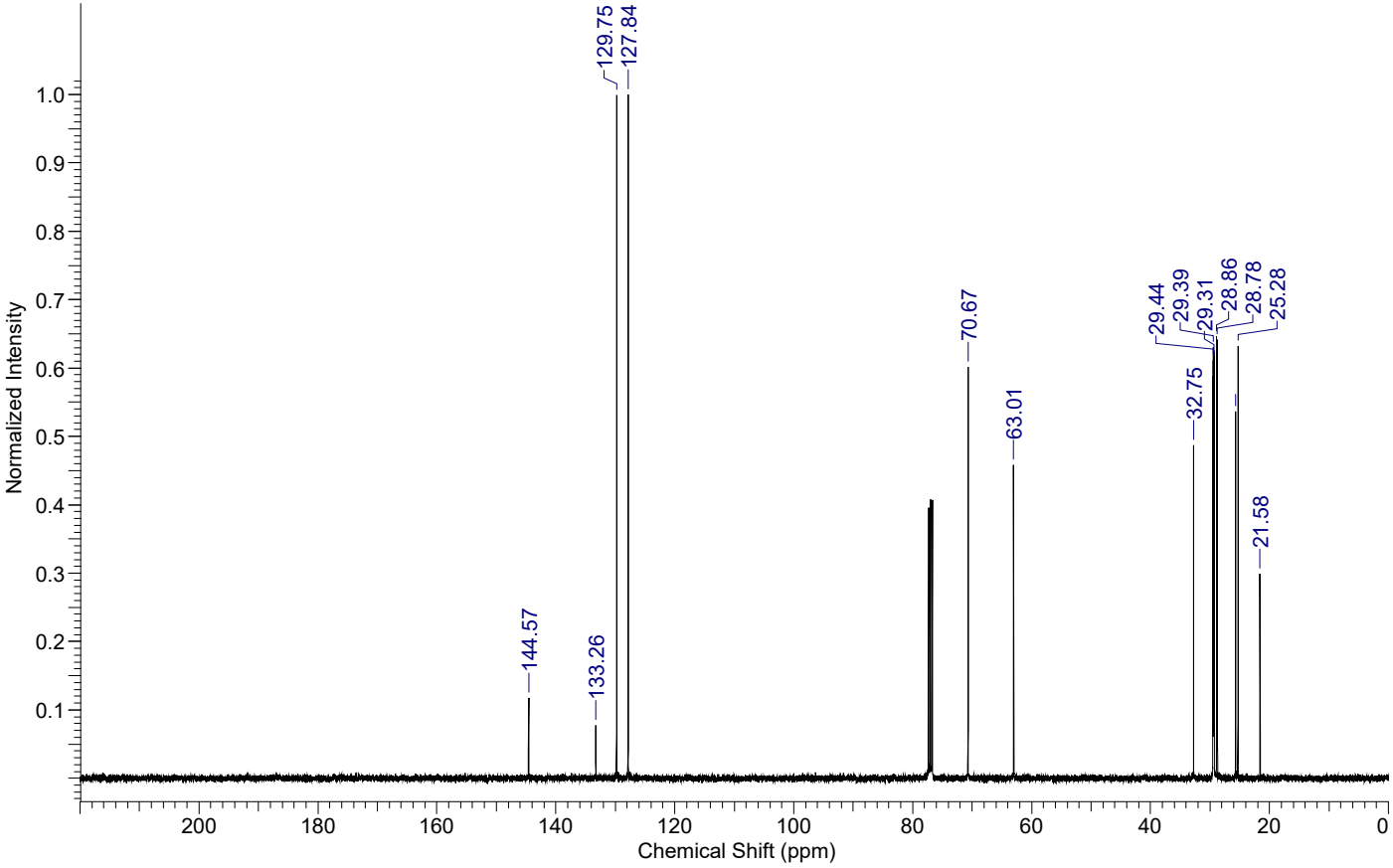
16.24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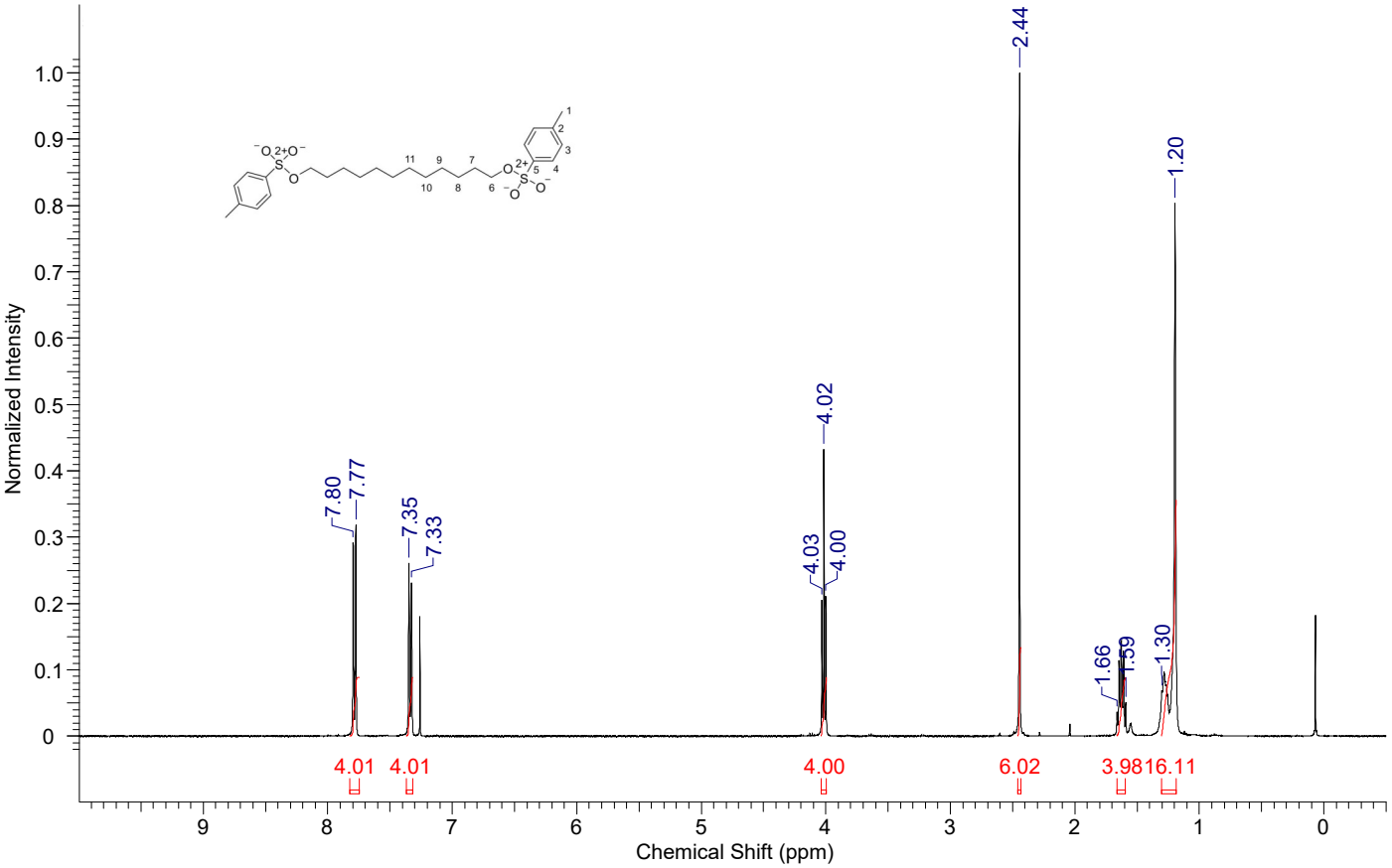
Normalized Intensity
Chemical Shift (ppm)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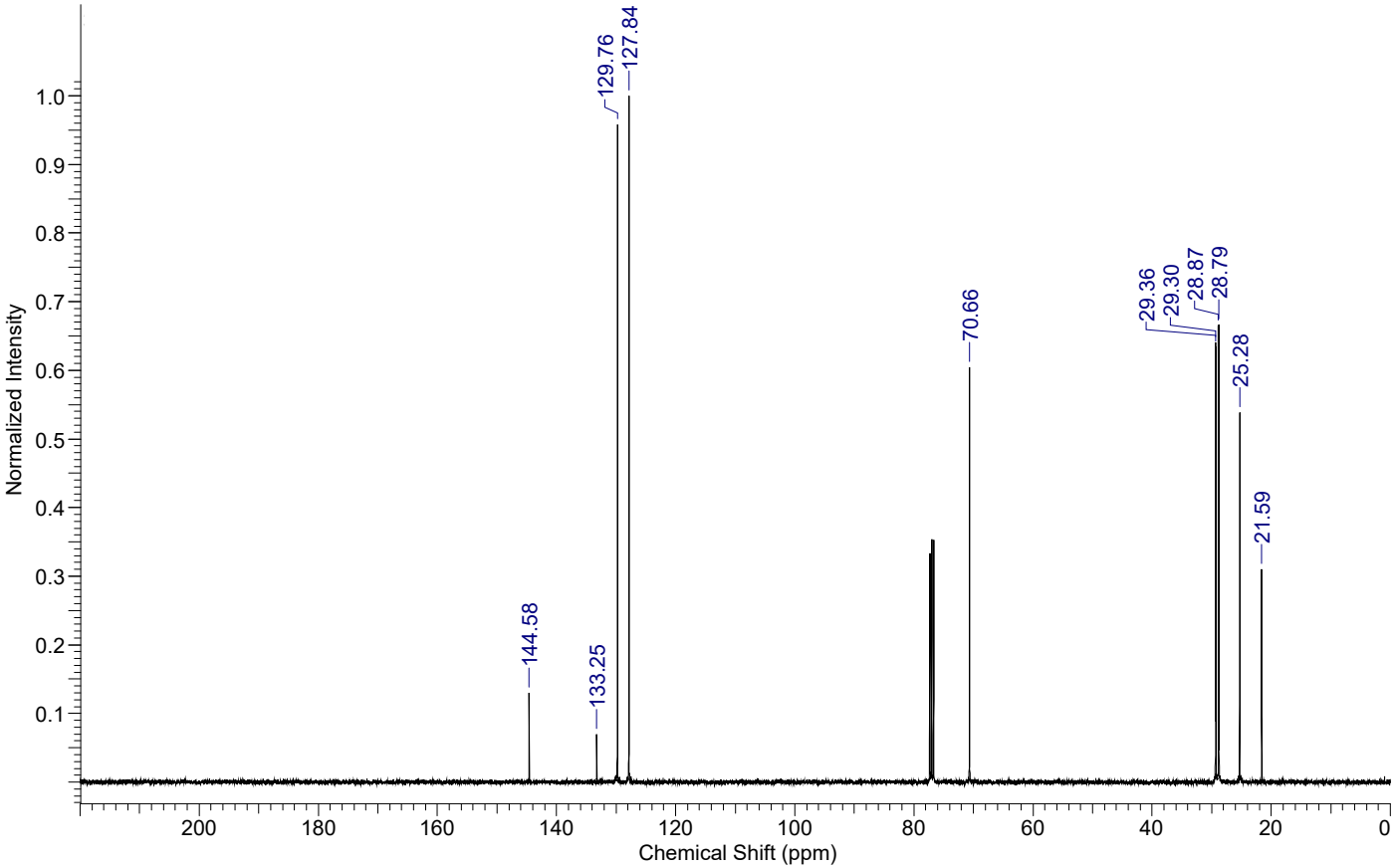
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129.76
127.84
70.66
29.36
29.30
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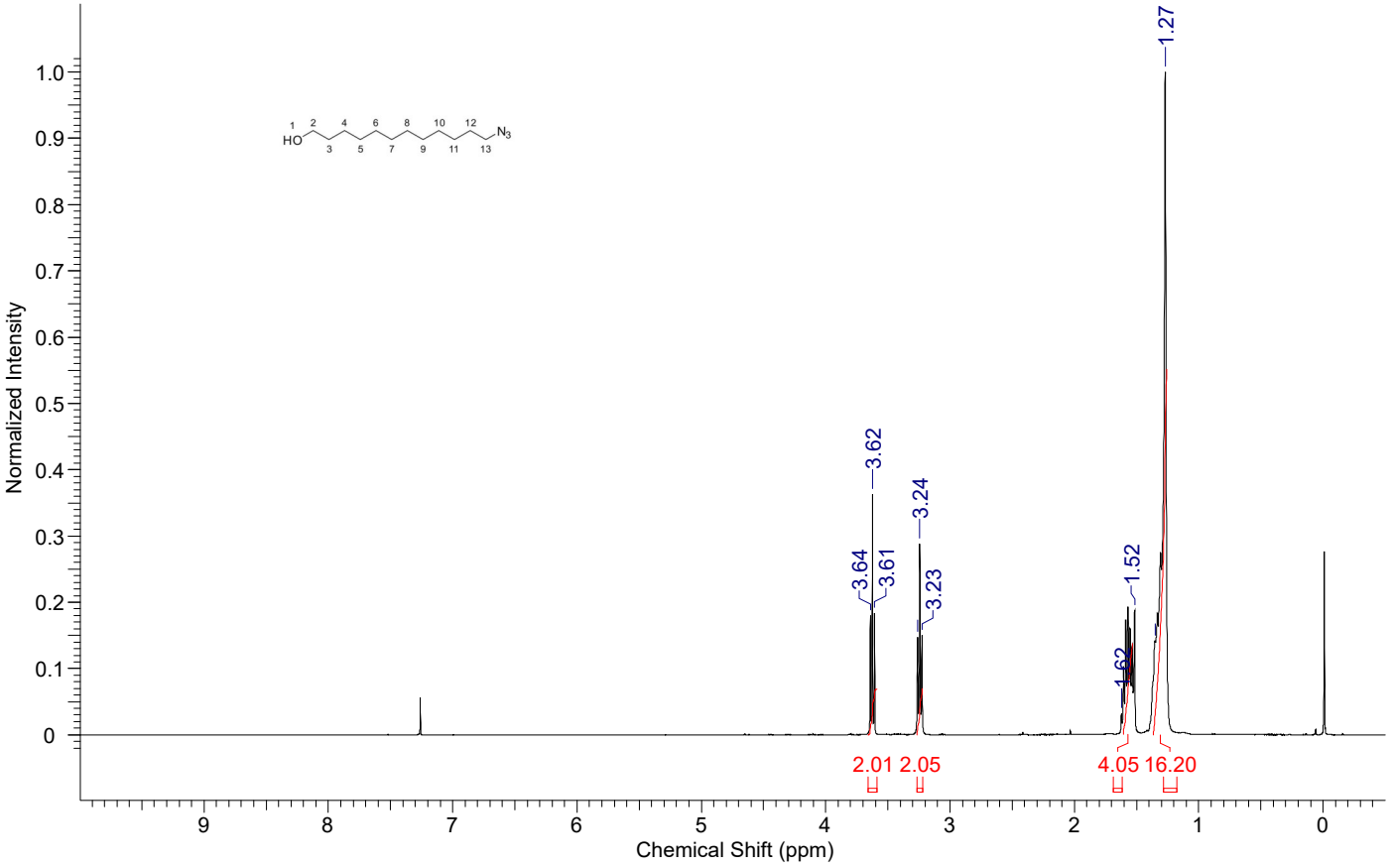
Chemical Shift (ppm)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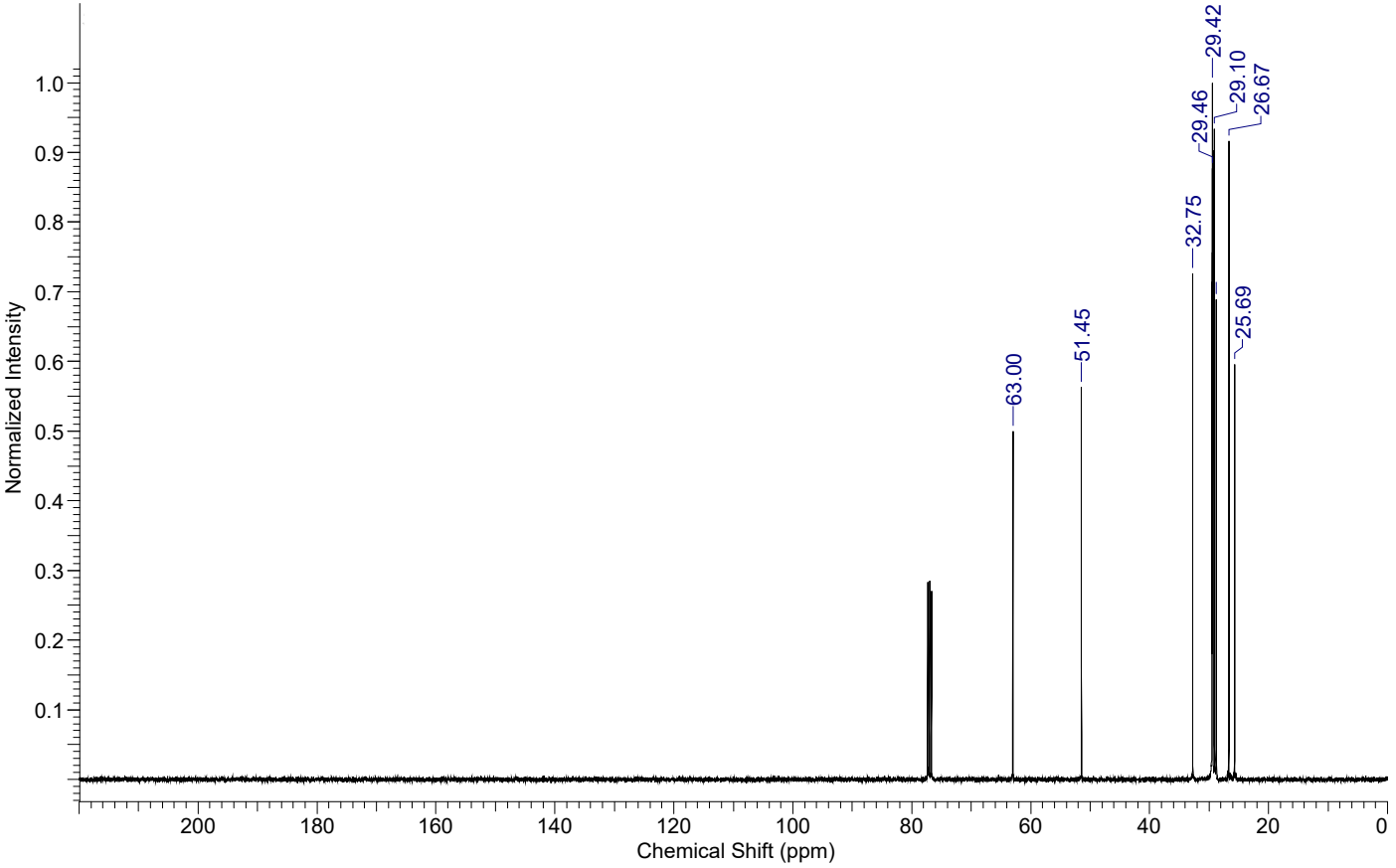
4.05
16.20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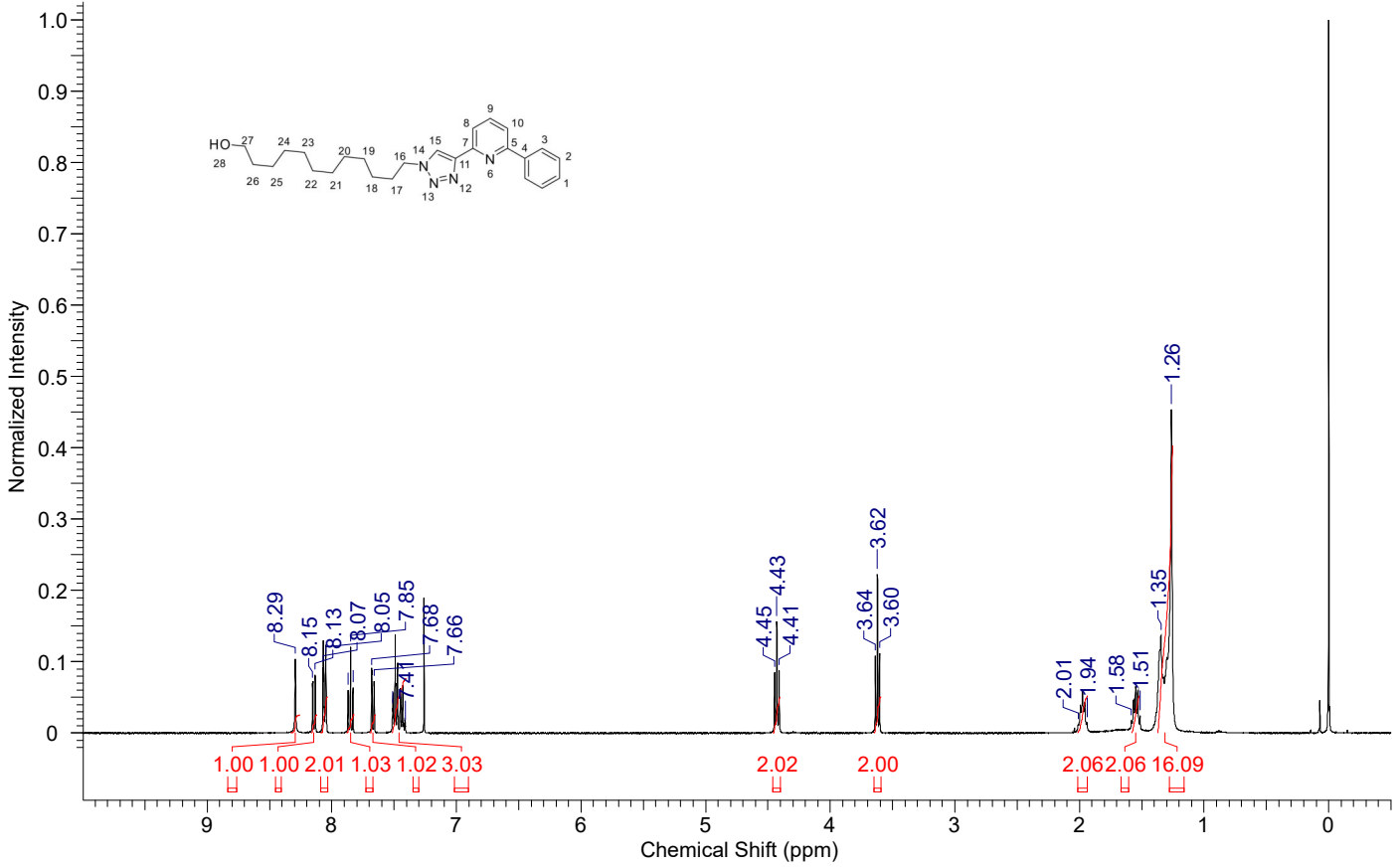
Chemical Shift (ppm)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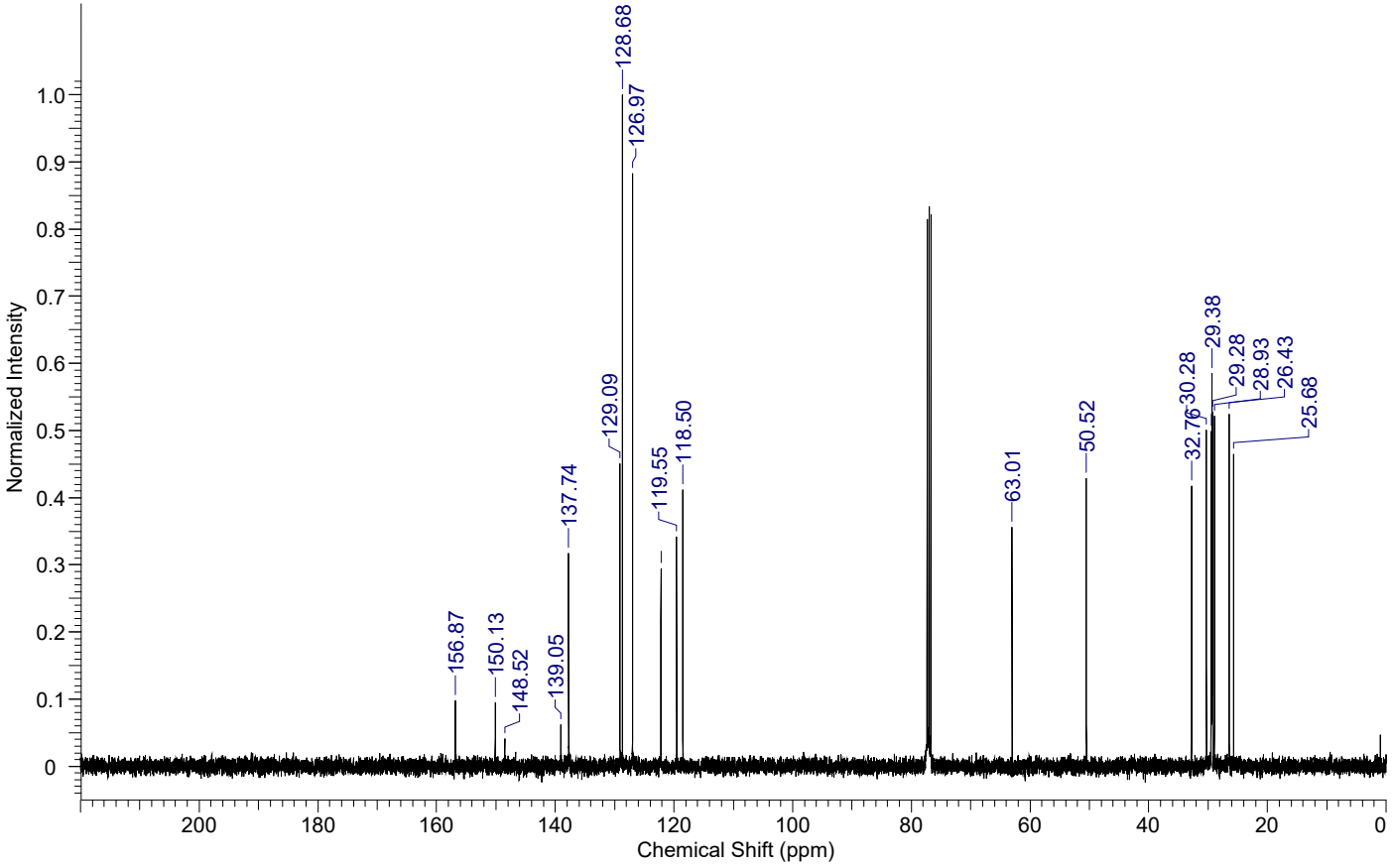
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0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)
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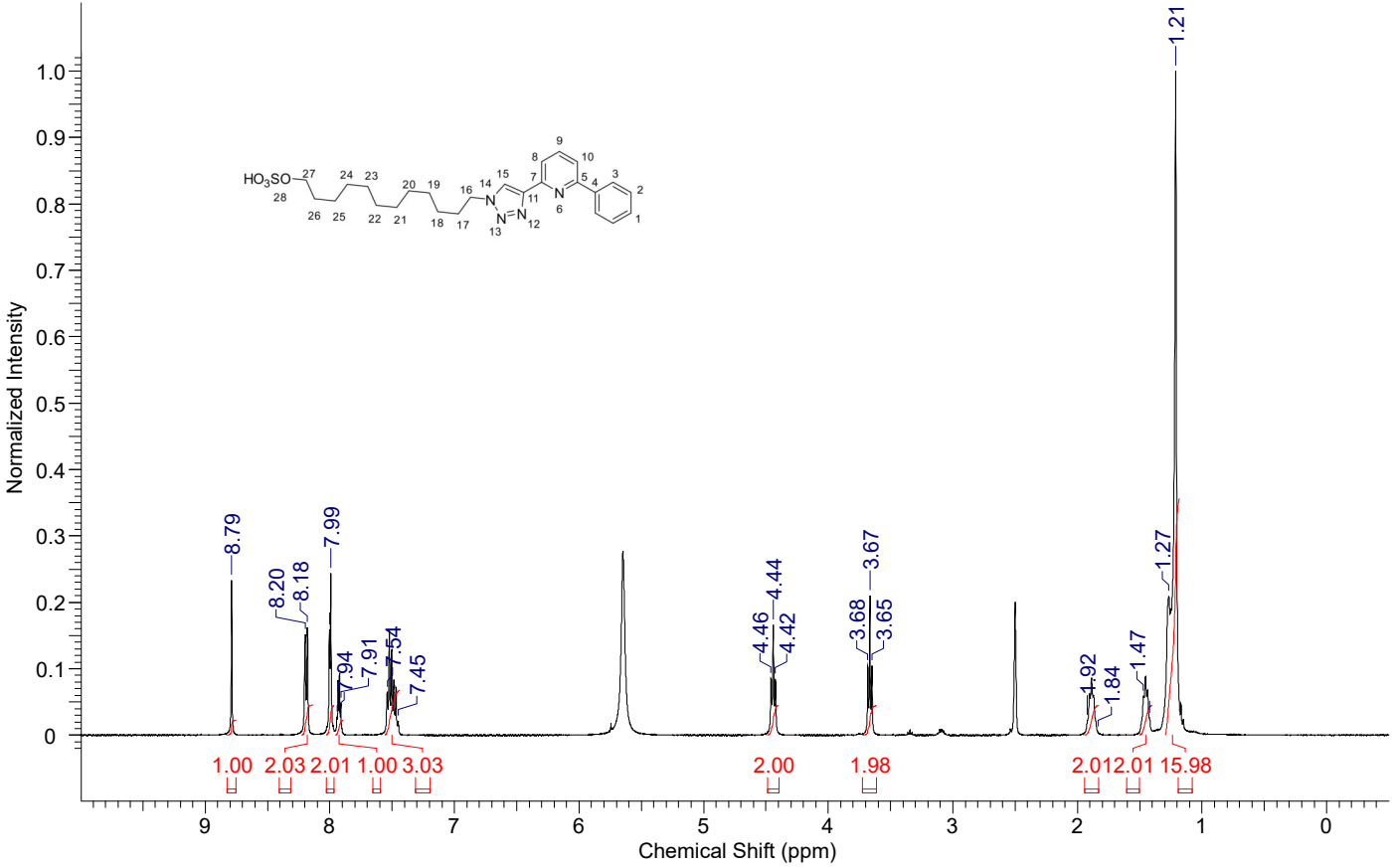
150.13
148.52
139.05
137.74
129.09
128.68
126.97
119.55
118.50
63.01
50.52
32.76
30.28
29.38
29.28
28.93
26.43
25.68


Normalized Intensity
Chemical Shift (ppm)
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8.20
8.18
7.99
7.94
7.91
7.54
7.45
4.46
4.44
4.42
3.68
3.67
3.65
1.92
1.84
1.47
1.27
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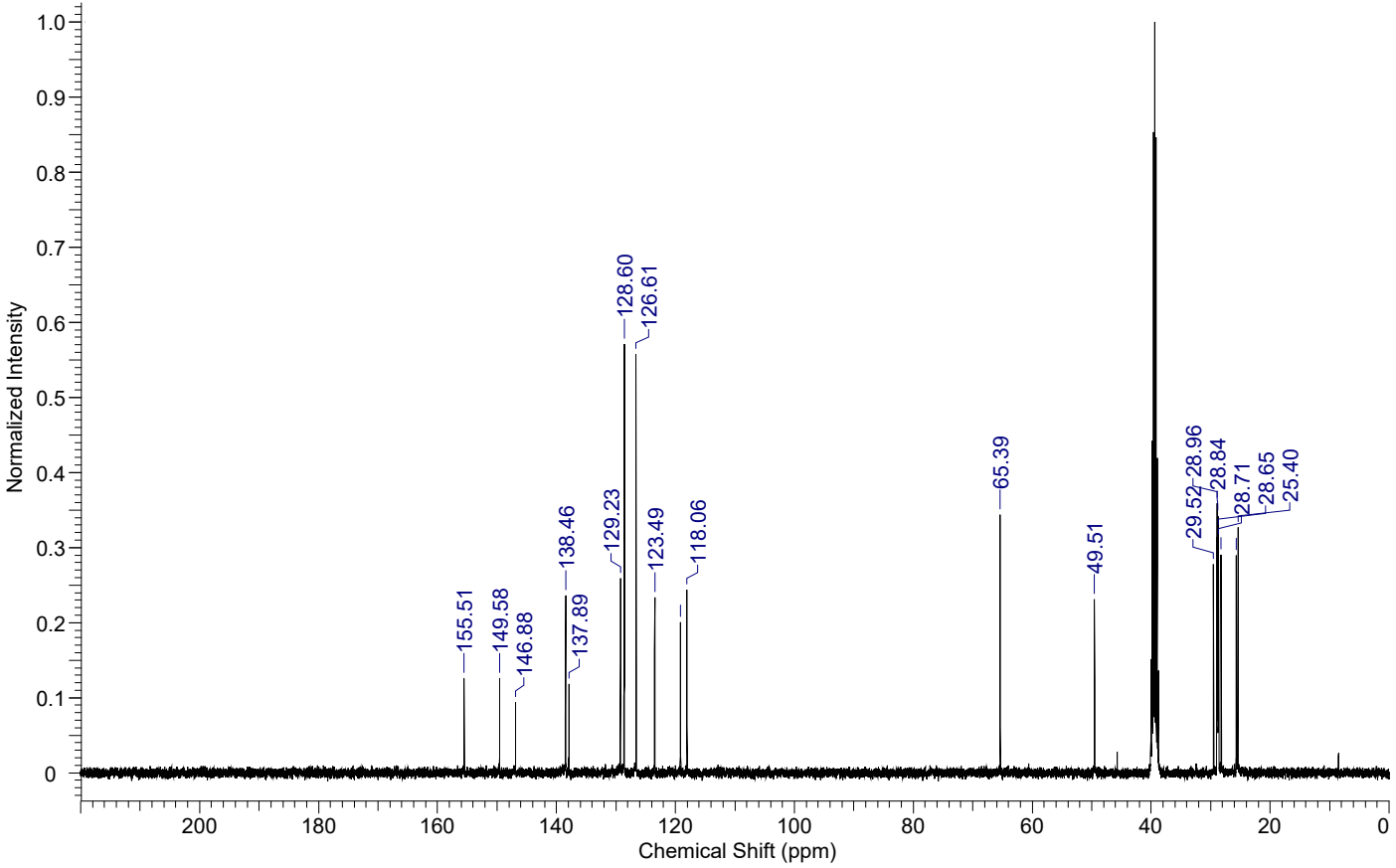
1.00
2.03
2.01
1.00
3.03
2.00
1.98
2.01
2.01
15.98


Normalized Intensity
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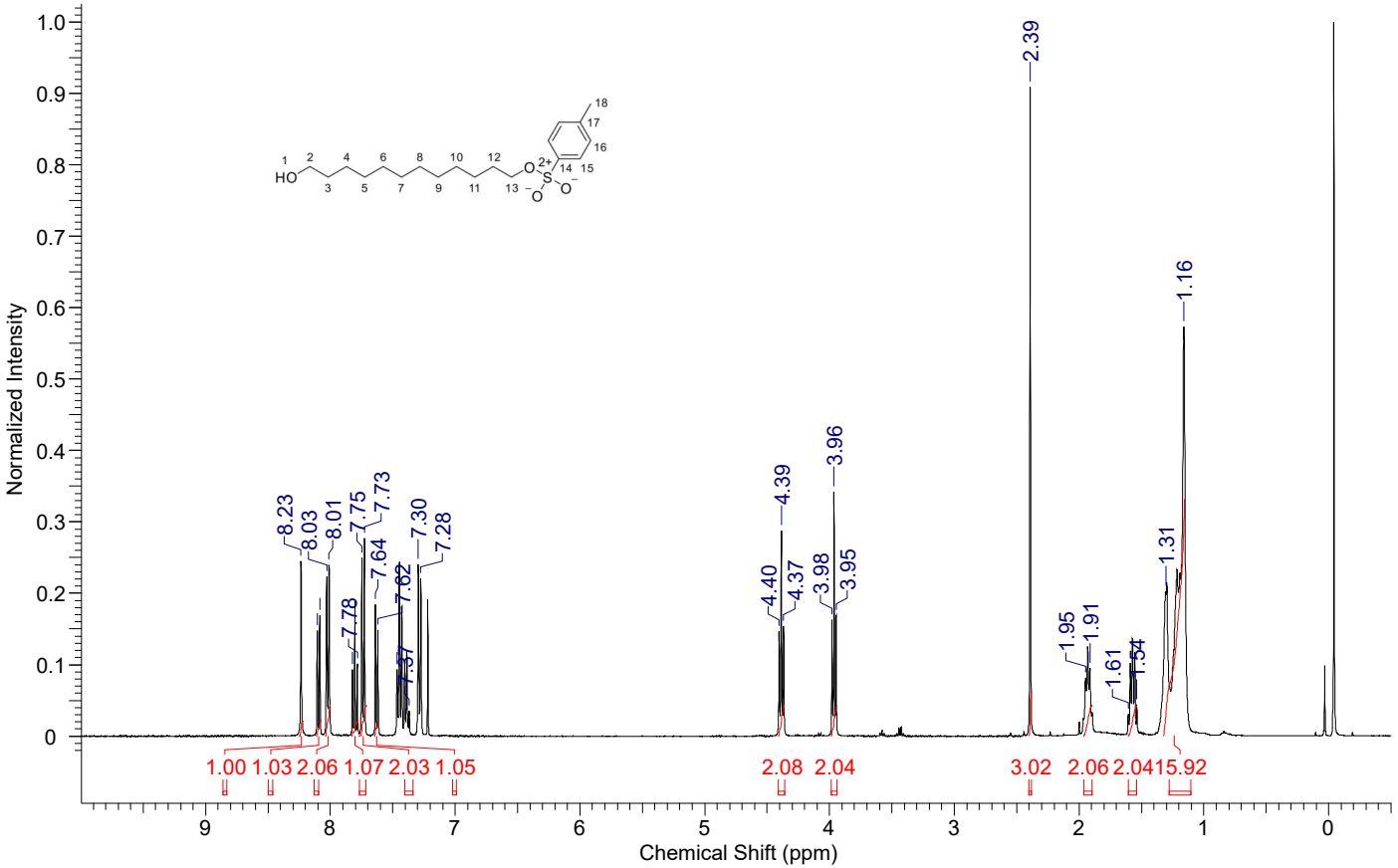
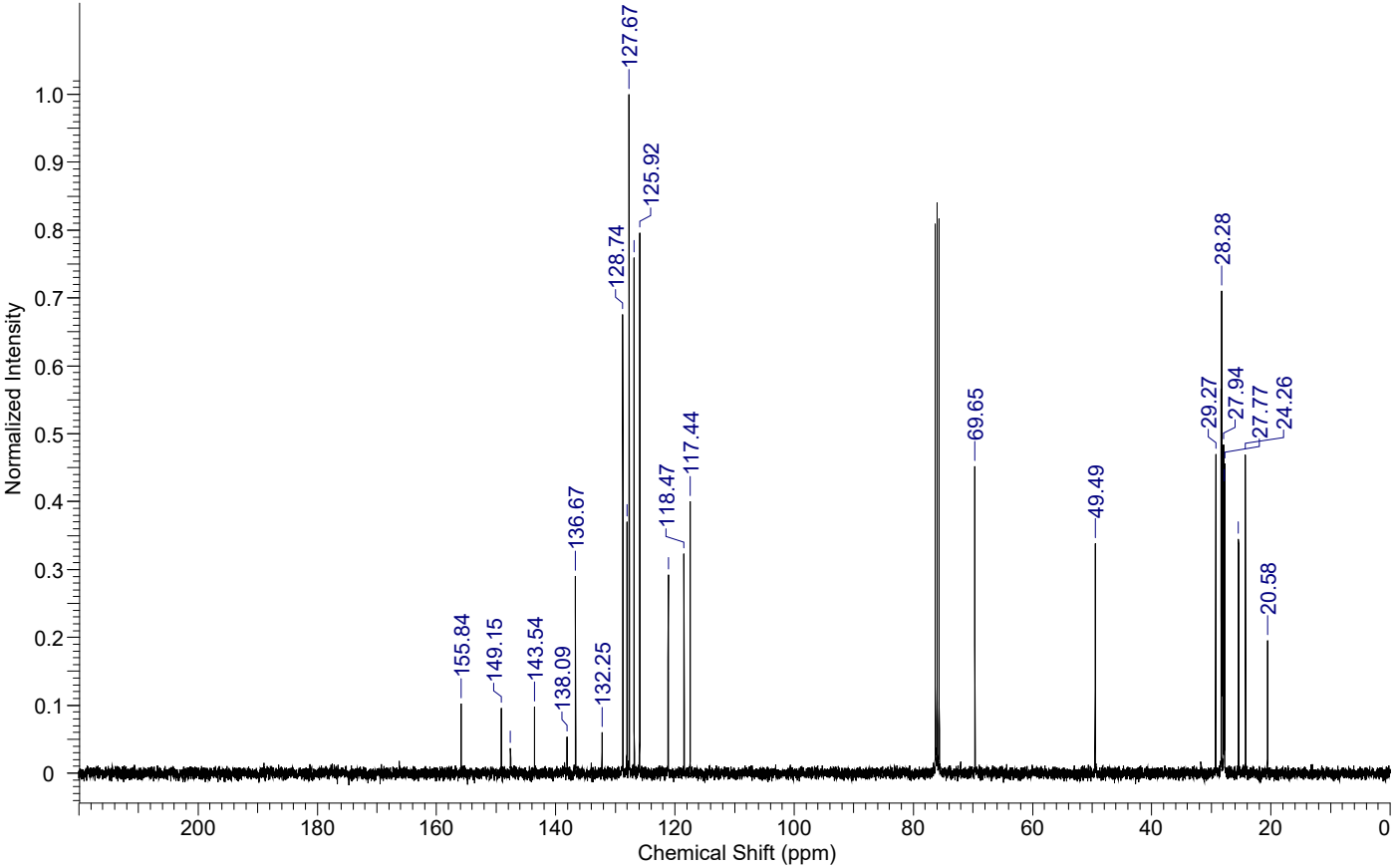
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
155.51
149.58
146.88
138.46
137.89
129.23
128.60
126.61
123.49
118.06
65.39
49.51
29.52
28.96
28.84
28.71
28.65
25.40
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


Normalized Intensity
Chemical Shift (ppm)
8.23
8.03
8.01
7.78
7.75
7.73
7.64
7.62
7.57
7.30
7.28
4.40
4.39
4.37
3.98
3.96
3.95
2.39
1.95
1.91
1.61
1.54
1.31
1.16
1.00 1.03 2.06 1.07 2.03 1.05
2.08 2.04
3.02 2.06 2.04 15.92


Normalized Intensity
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0.9
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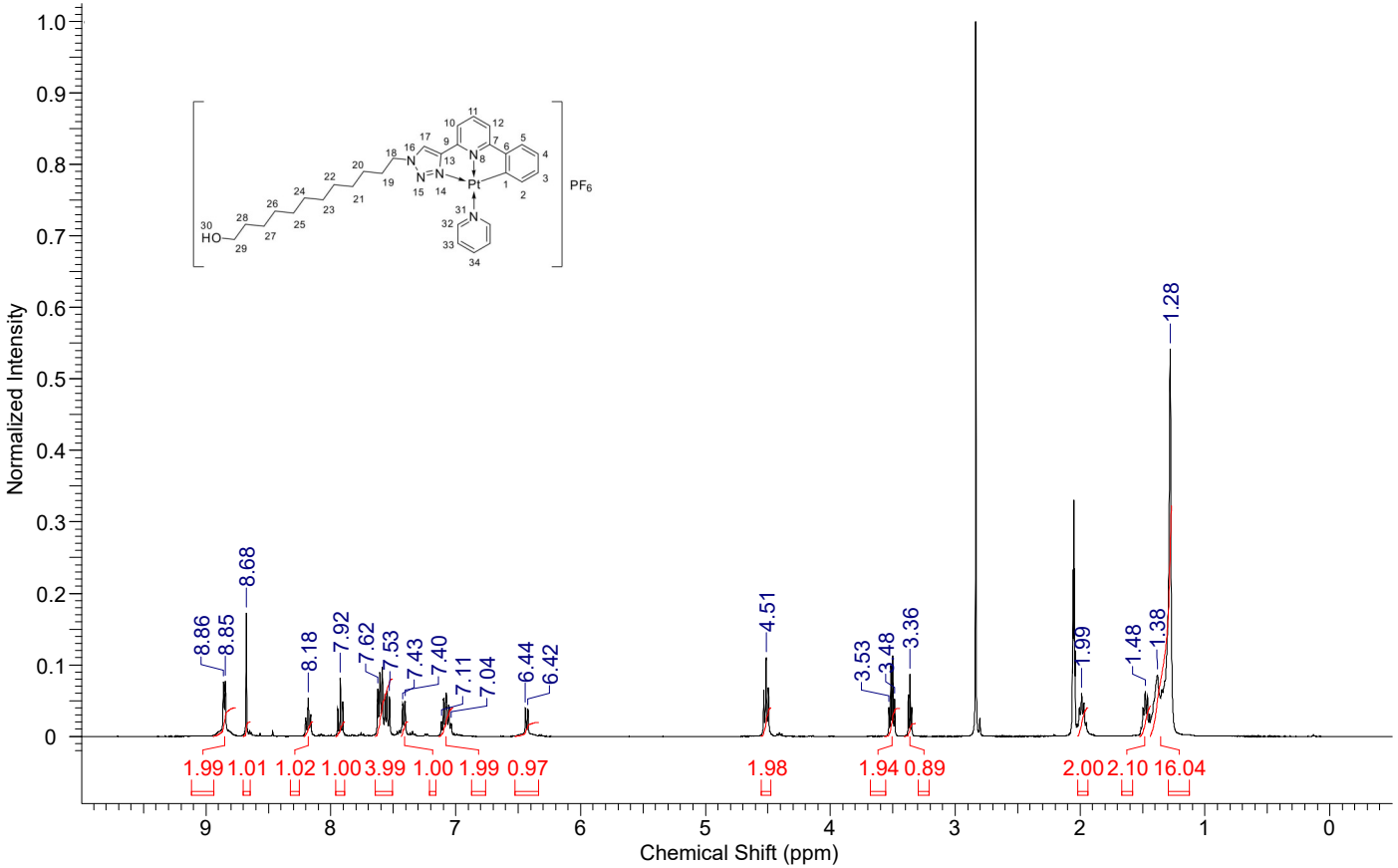
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)
155.84
149.15
143.54
138.09
136.67
132.25
128.74
127.67
125.92
118.47
117.44
69.65
49.49
29.27
28.28
27.94
27.77
24.26
20.58


Normalized Intensity
Chemical Shift (ppm)
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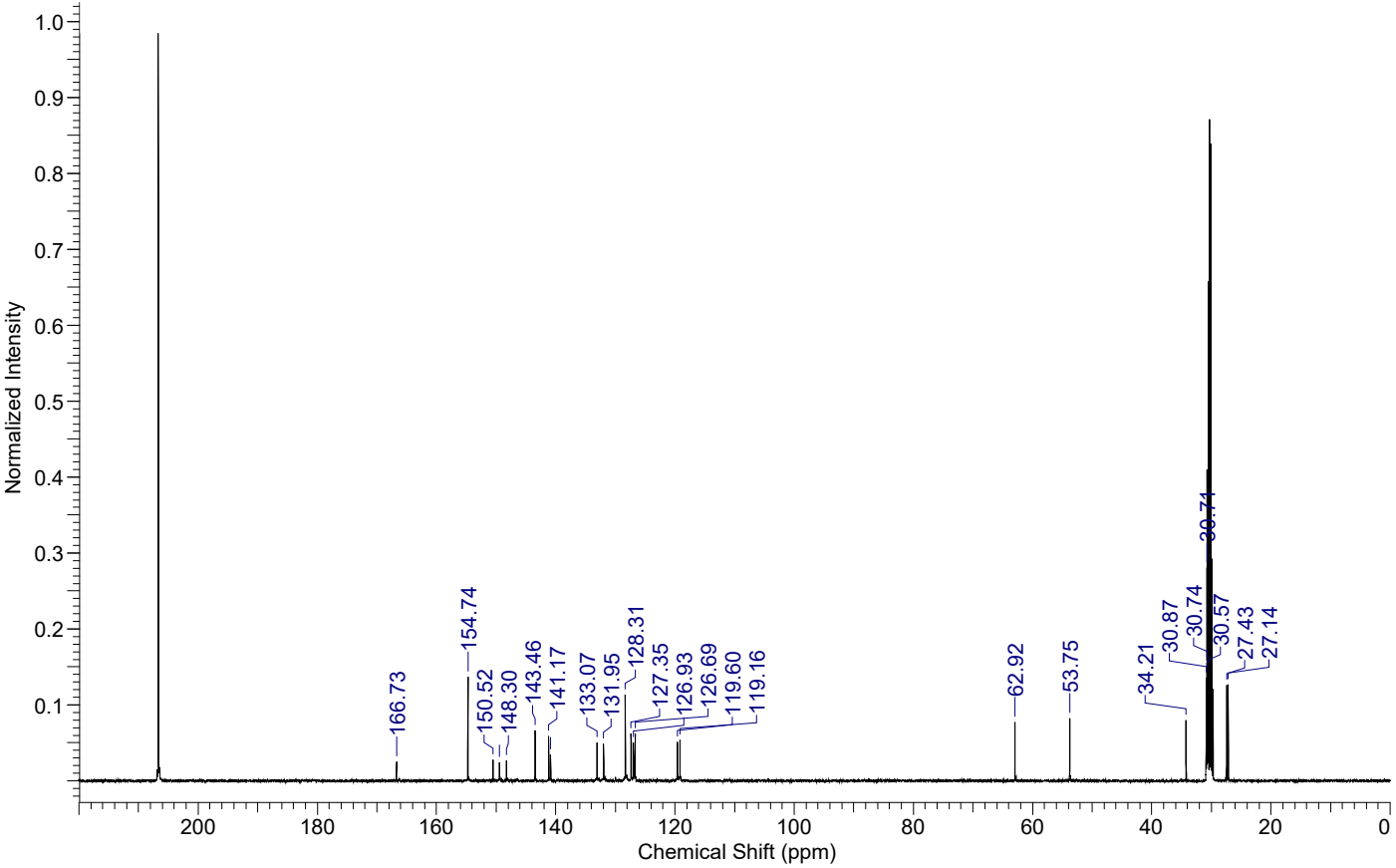
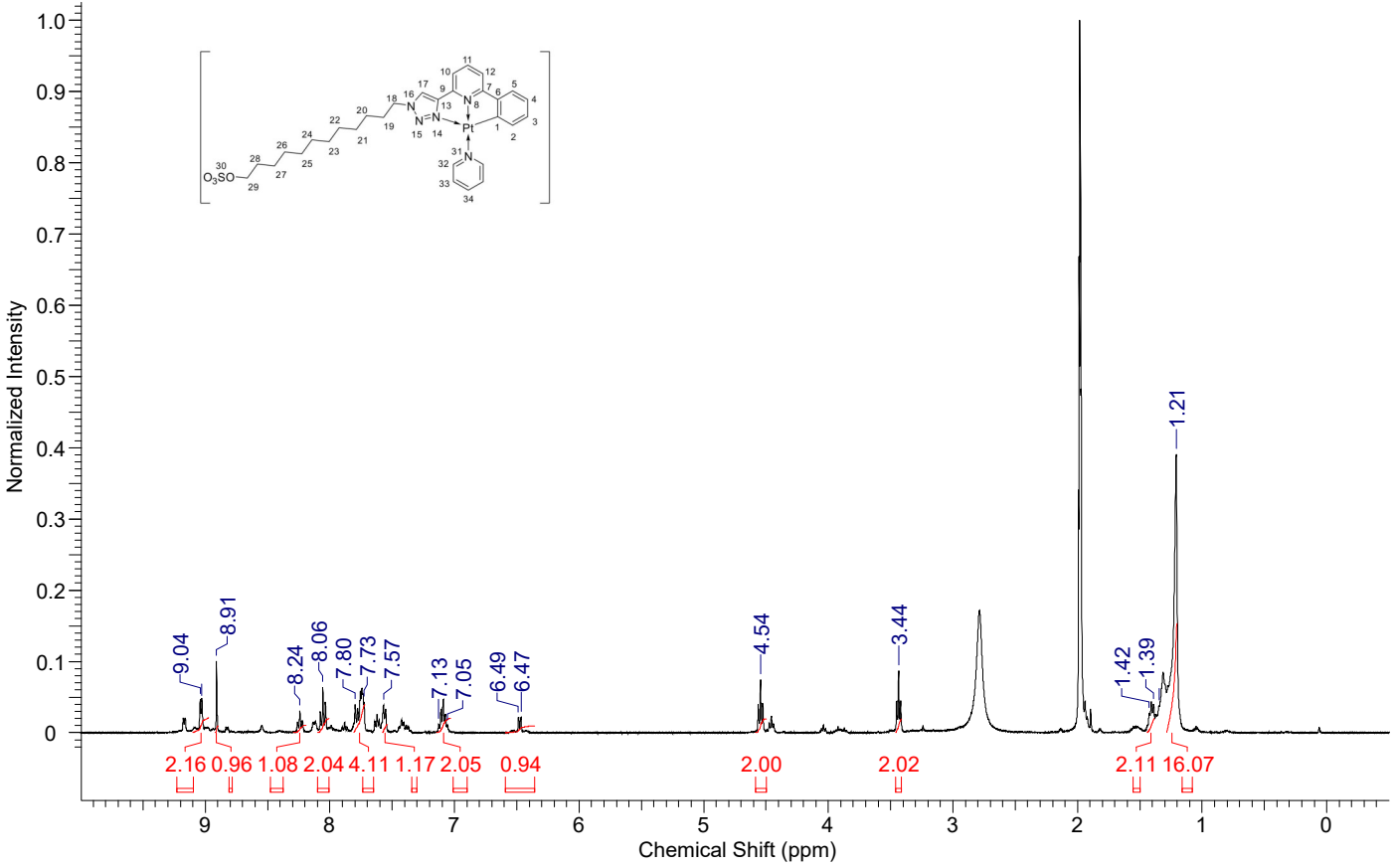
8.85
8.68
8.18
7.92
7.62
7.53
7.43
7.40
7.11
7.04
6.44
6.42
4.51
3.53
3.48
3.36
1.99
1.48
1.38
1.28
1.99 1.01 1.02 1.00 3.99 1.00 1.99 0.97
1.98
1.94 0.89
2.00 2.10 16.04
PF6


Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
166.73
154.74
150.52
148.30
143.46
141.17
133.07
131.95
128.31
127.35
126.93
126.69
119.60
119.16
62.92
53.75
34.21
30.87
30.74
30.71
30.57
27.43
27.14
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


Normalized Intensity
Chemical Shift (ppm)
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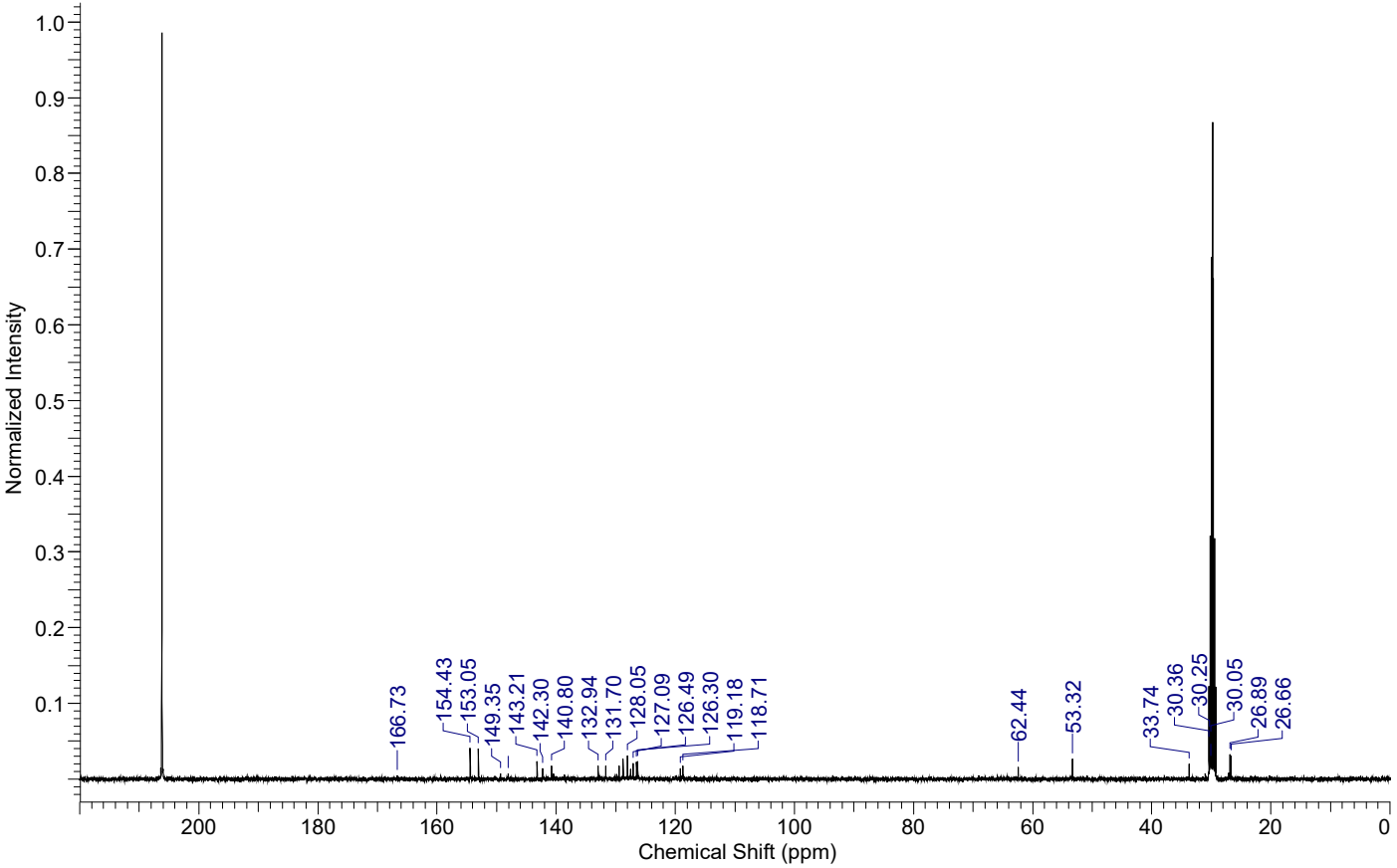
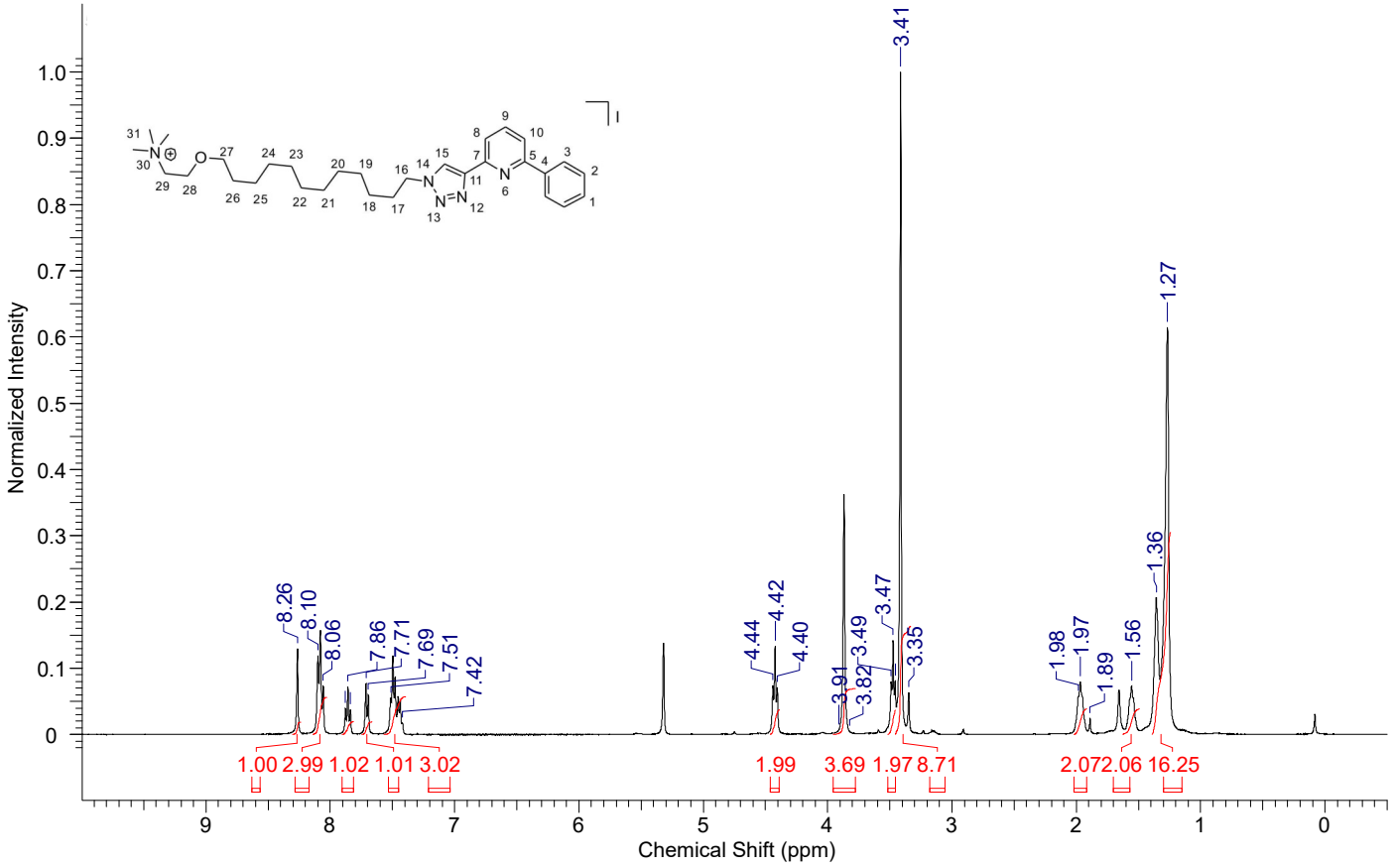
8.91
8.24
8.06
7.80
7.73
7.57
7.13
7.05
6.49
6.47
4.54
3.44
1.42
1.39
1.21
2.16 0.96 1.08 2.04 4.11 1.17 2.05 0.94
2.00
2.02
2.11 16.07


Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
166.73
154.43
153.05
149.35
143.21
142.30
140.80
132.94
131.70
128.05
127.09
126.49
126.30
119.18
118.71
62.44
53.32
33.74
30.36
30.25
30.05
26.89
26.66
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


Normalized Intensity
Chemical Shift (ppm)
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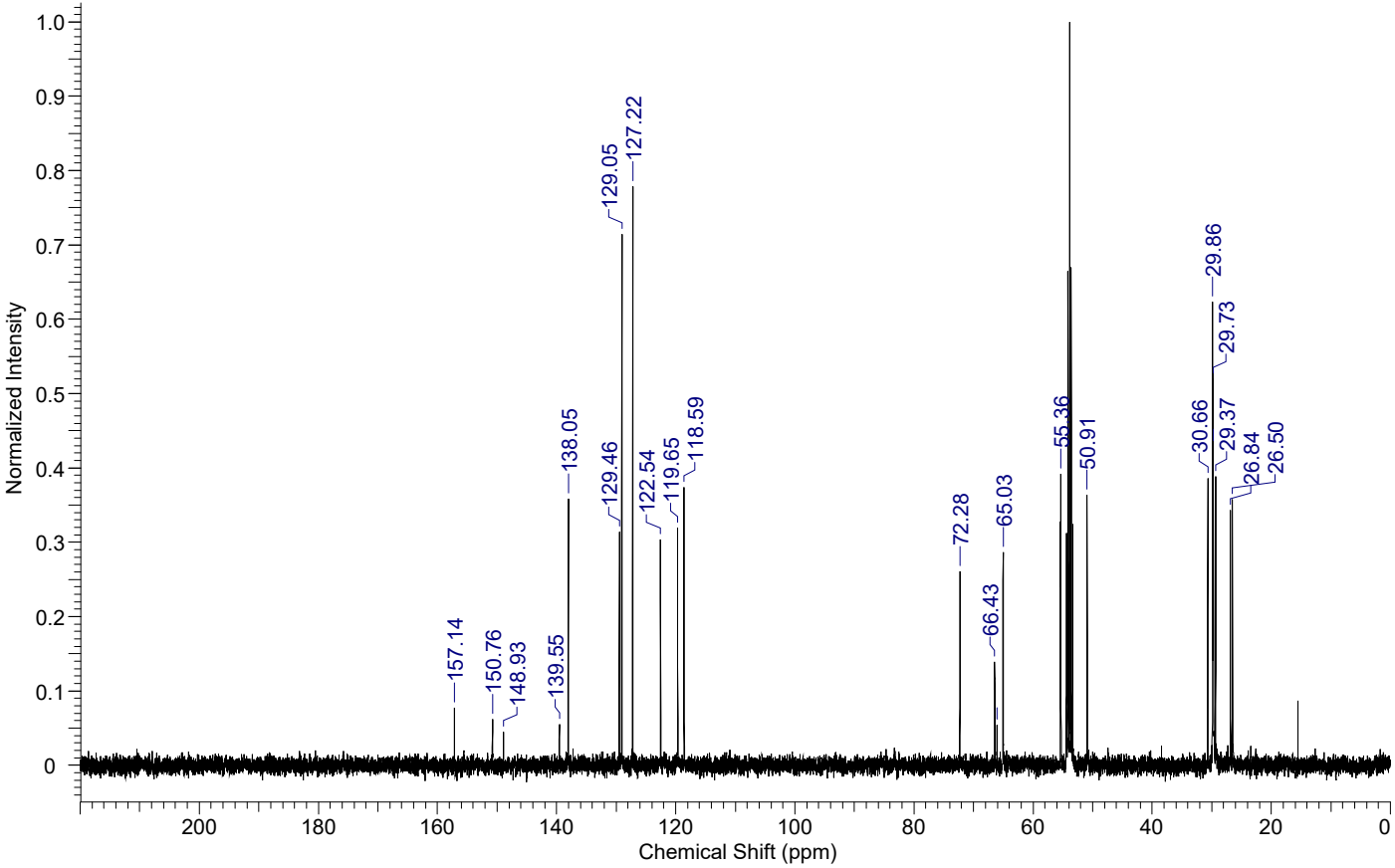
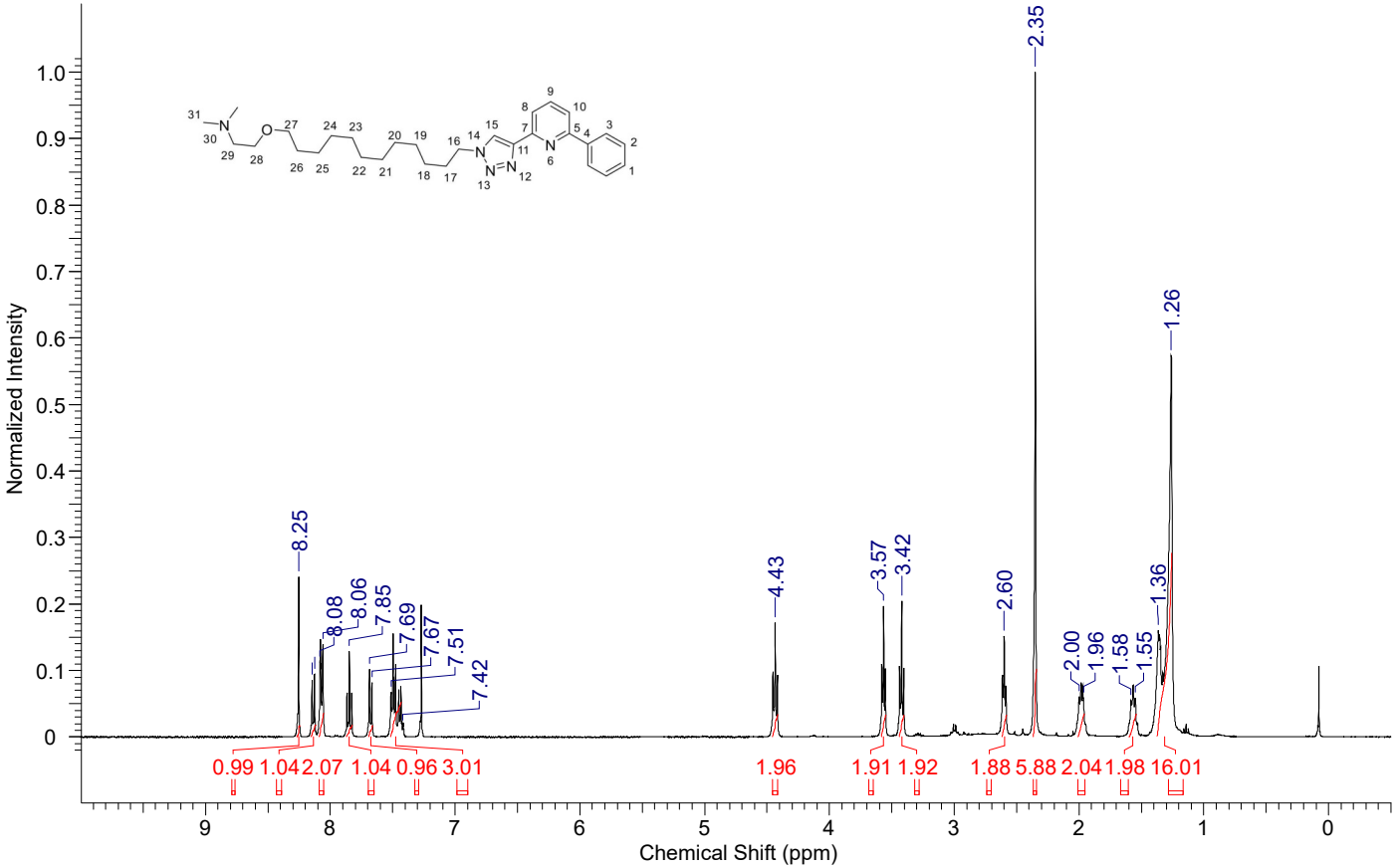
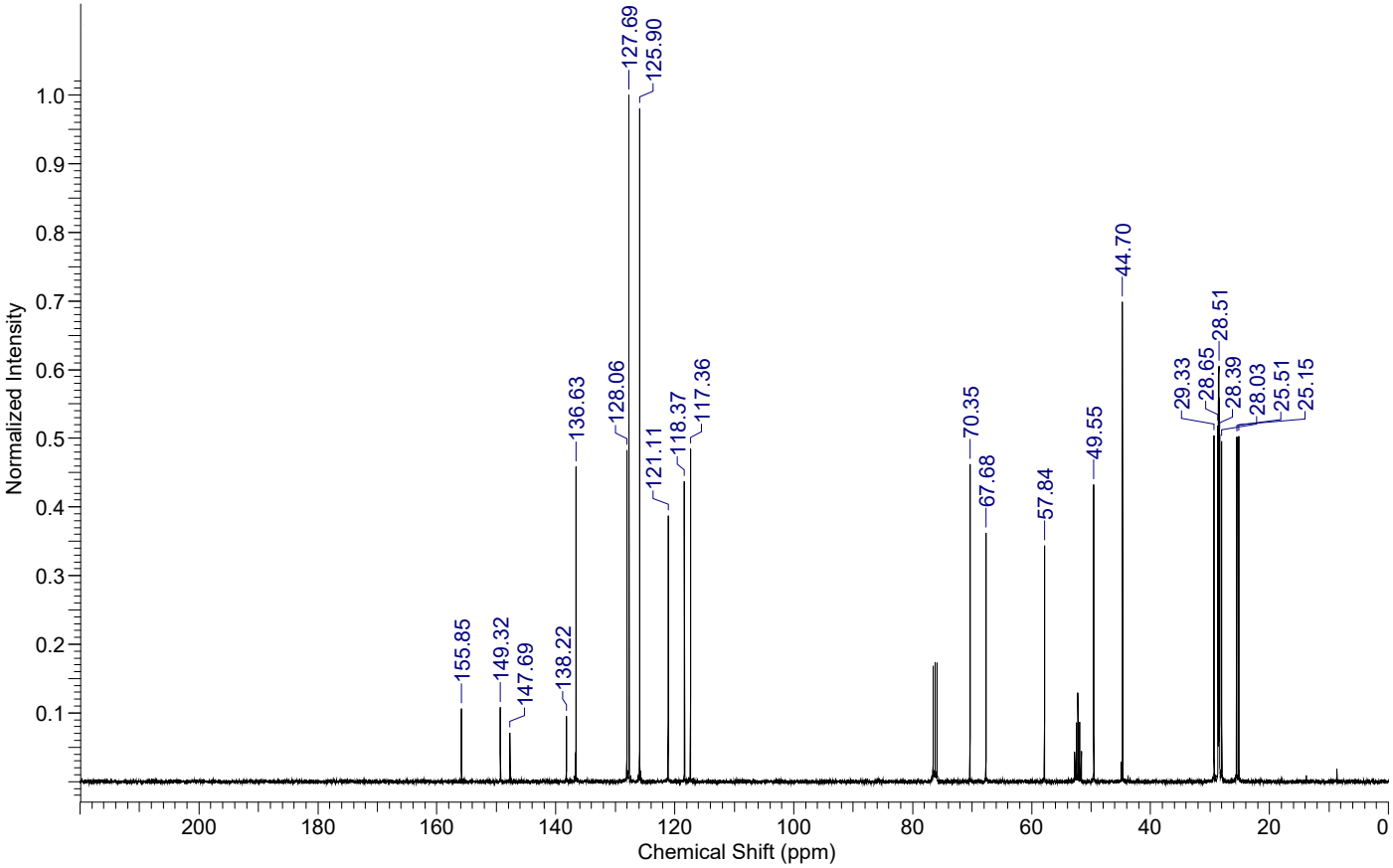
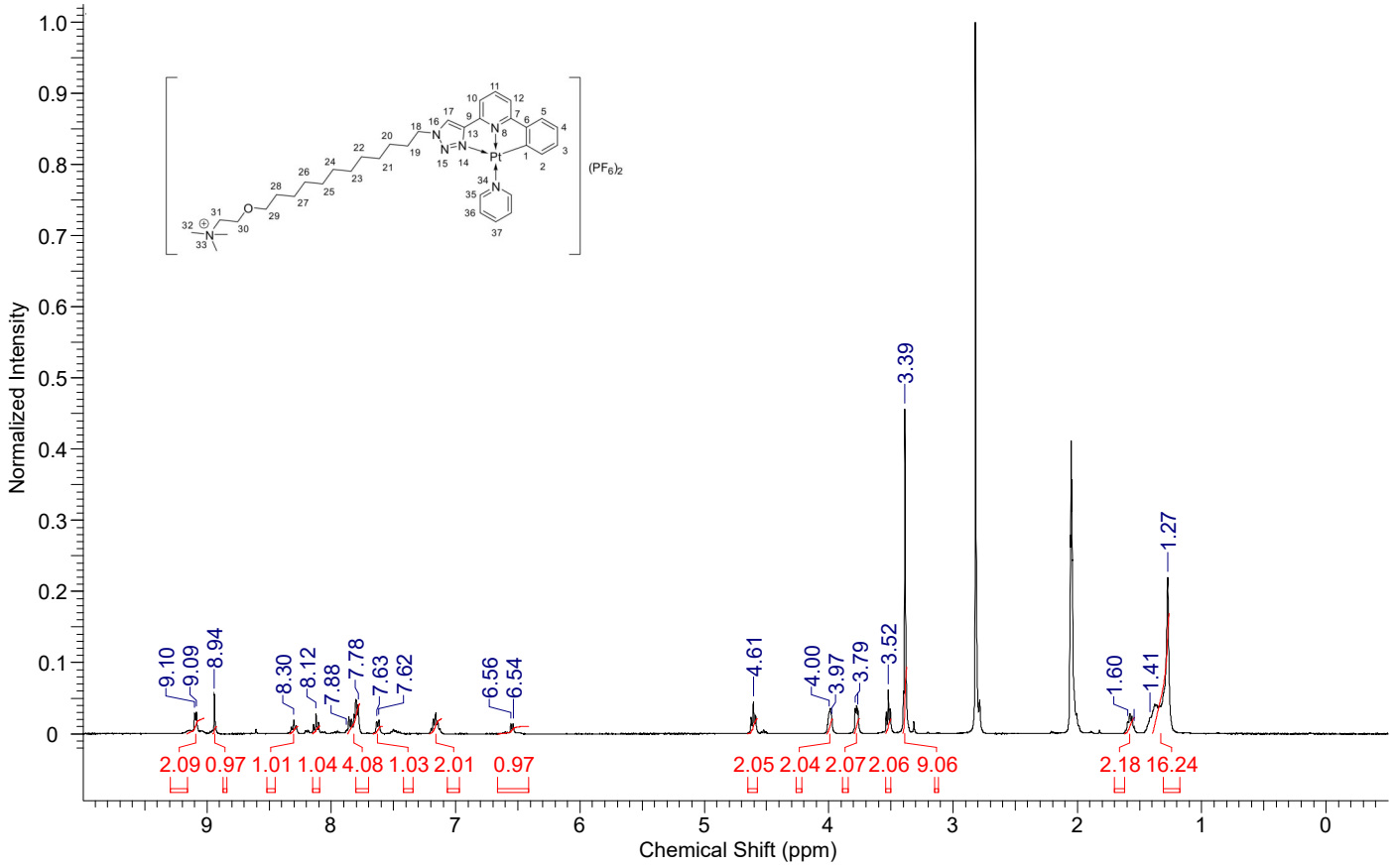
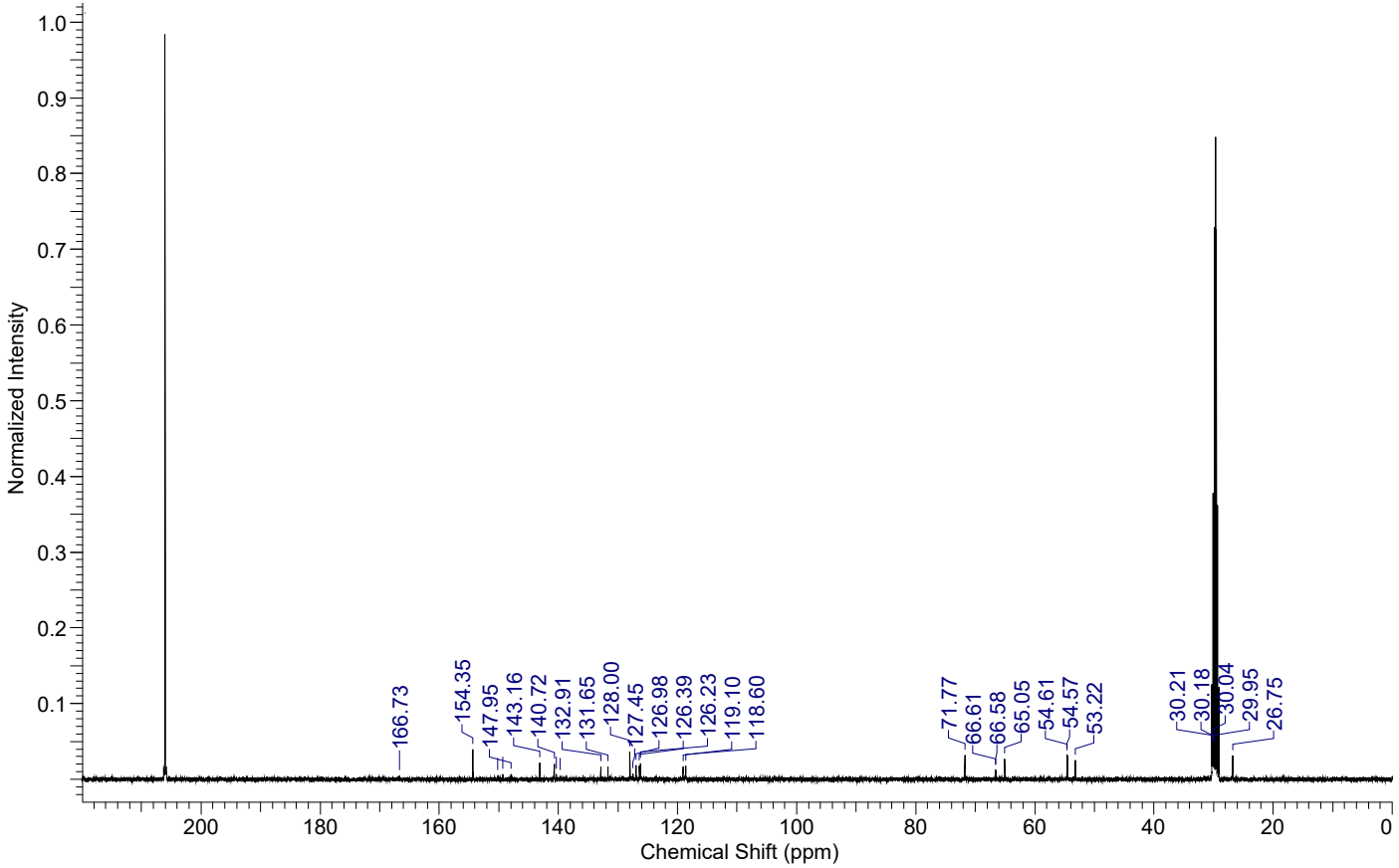
8.10
8.06
7.86
7.71
7.69
7.51
7.42
4.44
4.42
4.40
3.91
3.82
3.49
3.47
3.41
3.35
1.98
1.97
1.89
1.56
1.36
1.27
1.00 2.99 1.02 1.01 3.02
1.99 3.69 1.97 8.71
2.07 2.06 16.25


Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
157.14
150.76
148.93
139.55
138.05
129.46
129.05
127.22
122.54
119.65
118.59
72.28
66.43
65.03
55.36
50.91
30.66
29.86
29.73
29.37
26.84
26.50
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


Normalized Intensity
Chemical Shift (ppm)
8.25
8.08
8.06
7.85
7.69
7.67
7.51
7.42
4.43
3.57
3.42
2.60
2.35
2.00
1.96
1.58
1.55
1.36
1.26
0.99 1.04 2.07 1.04 0.96 3.01
1.96
1.91 1.92
1.88 5.88 2.04 1.98 16.01


Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
155.85
149.32
147.69
138.22
136.63
128.06
127.69
125.90
121.11
118.37
117.36
70.35
67.68
57.84
49.55
44.70
29.33
28.65
28.51
28.39
28.03
25.51
25.15
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


Normalized Intensity
Chemical Shift (ppm)
9.10
9.09
8.94
8.30
8.12
7.88
7.78
7.63
7.62
6.56
6.54
4.61
4.00
3.97
3.79
3.52
3.39
1.60
1.41
1.27
2.09 0.97 1.01 1.04 4.08 1.03 2.01 0.97
2.05 2.04 2.07 2.06 9.06
2.18 16.24
(PF6)2


Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
166.73
154.35
147.95
143.16
140.72
132.91
131.65
128.00
127.45
126.98
126.39
126.23
119.10
118.60
71.77
66.61
66.58
65.05
54.61
54.57
53.22
30.21
30.18
30.04
29.95
26.75
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)