Electronic Supplementary Information

Rhenium tricarbonyl complexes of AIE active tetraarylethylene ligands: tuning luminescence properties and HSA-specific binding

Moustafa T. Gabr and F. Christopher Pigge

Department of Chemistry, University of Iowa, Iowa City, Iowa 52242, United States

chris-pigge@uiowa.edu

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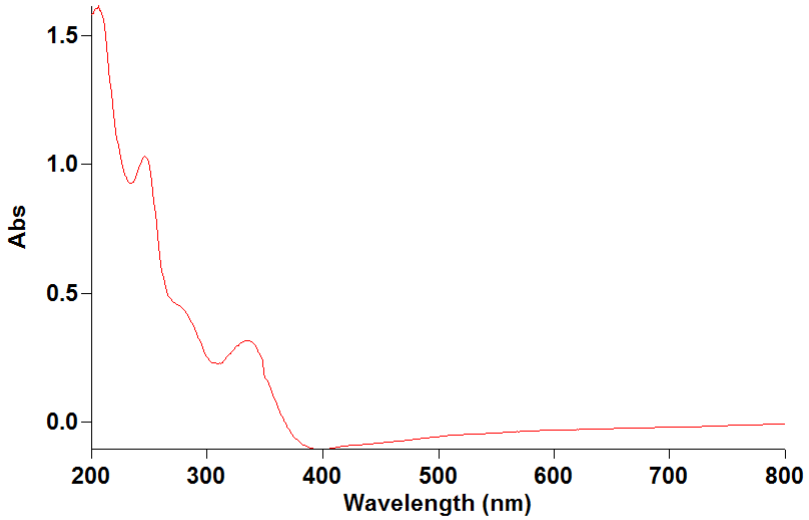


Figure S1. UV-vis absorption spectrum of **2** (CH_3CN, 25 µM).

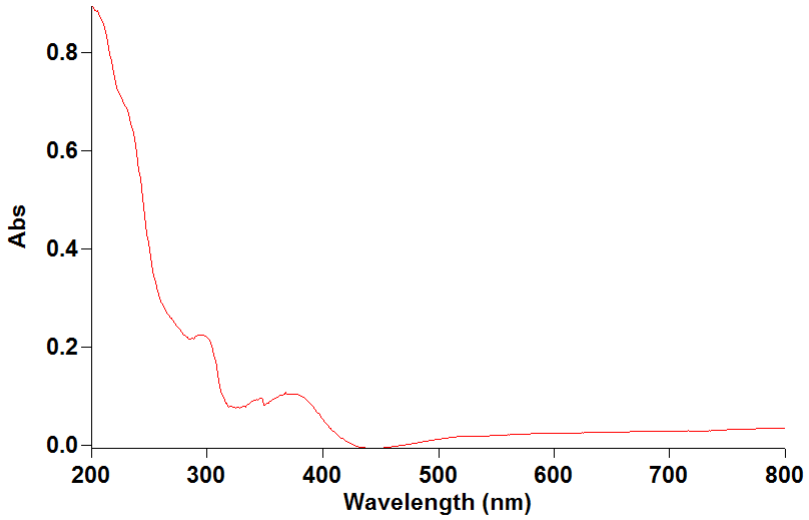


Figure S2. UV-vis absorption spectrum of **3** (CH_3CN, 12.5 µM).

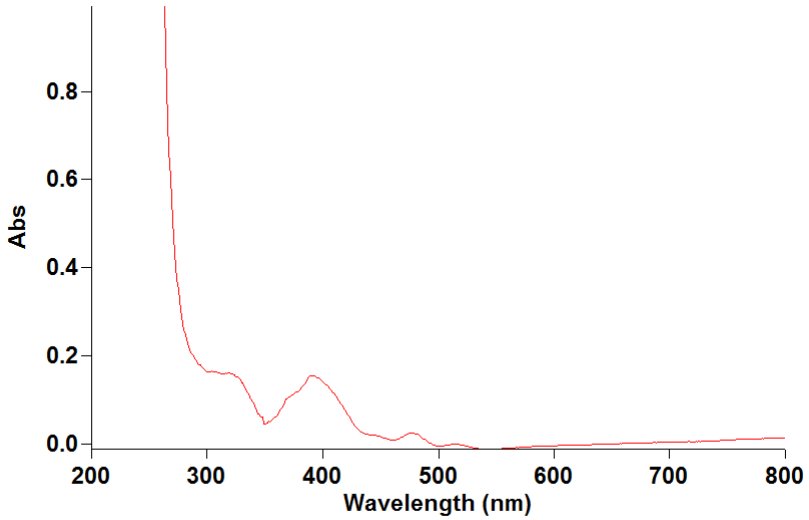


Figure S3. UV-vis absorption spectrum of **4** (CH_3CN, 12.5 μM).

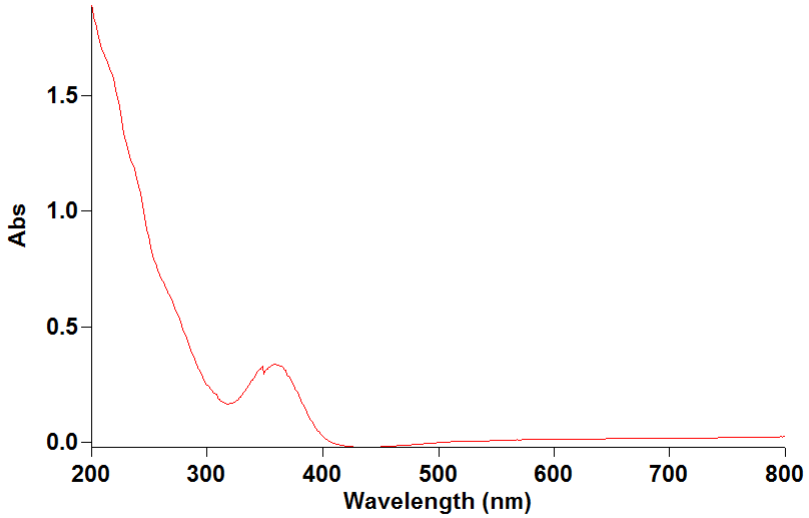


Figure S4. UV-vis absorption spectrum of **5** (CH_3CN, 25 μM).

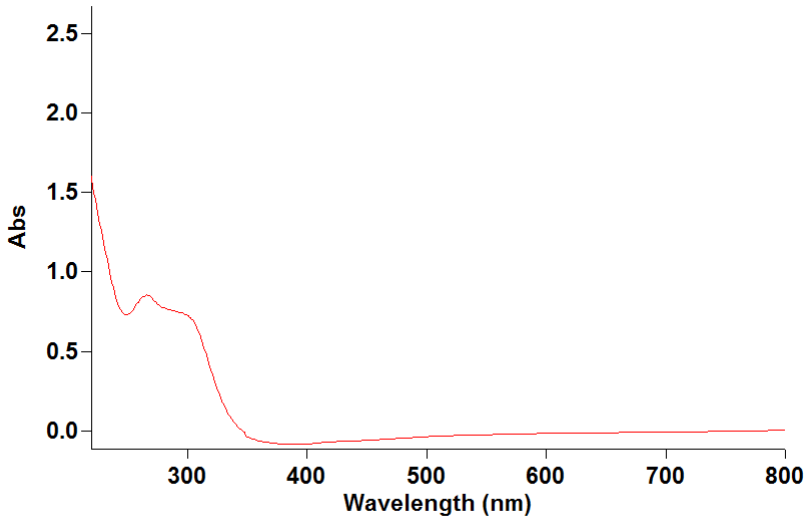


Figure S5. UV-vis absorption spectrum of **6** (CH_3CN, 50 µM).

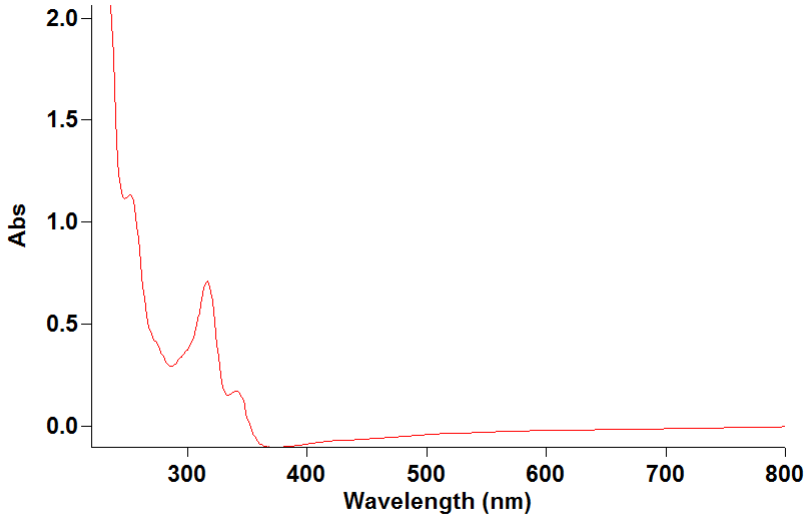


Figure S6. UV-vis absorption spectrum of **7** (CH_3CN, 25 µM).

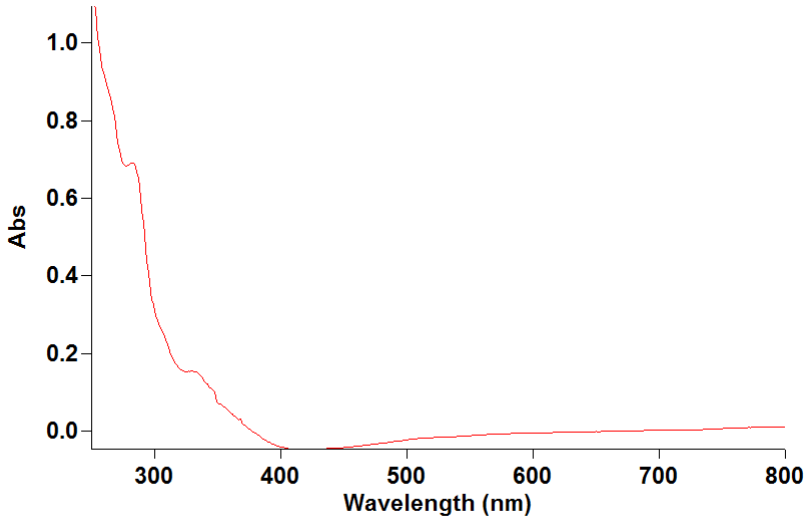


Figure S7. UV-vis absorption spectrum of **8** (CH_3CN, 12.5 µM).

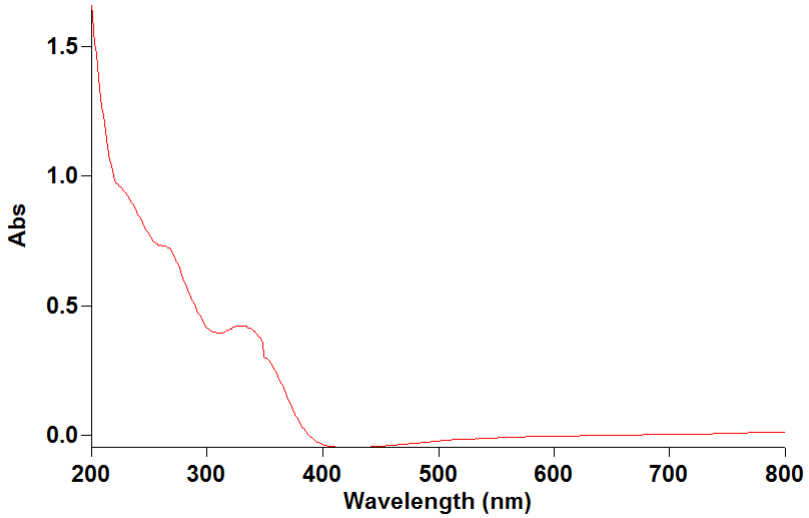


Figure S8. UV-vis absorption spectrum of **9** (CH_3CN, 25 µM).

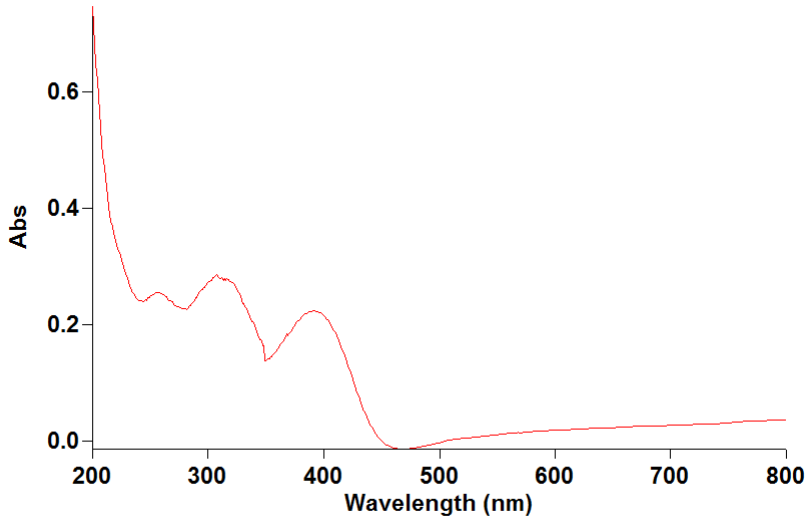


Figure S9. UV-vis absorption spectrum of **10** (CH_3CN, 12.5 µM).

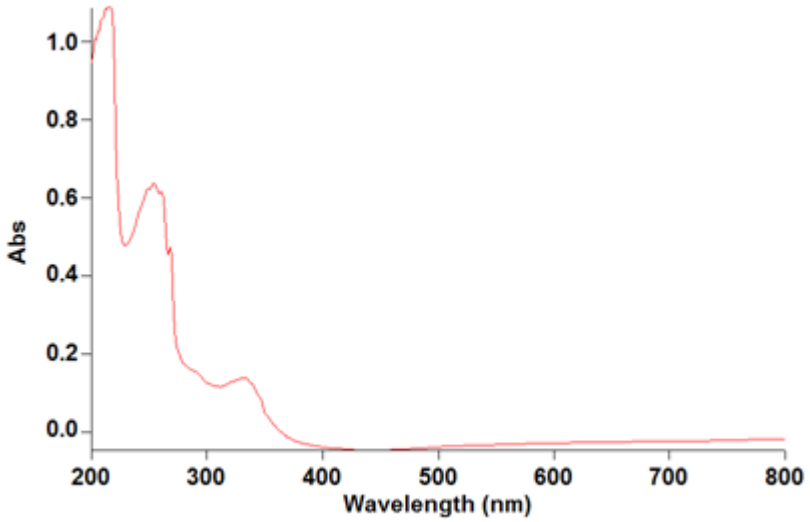


Figure S10. UV-vis absorption spectrum of **11** (CH_3CN, 12.5 µM).

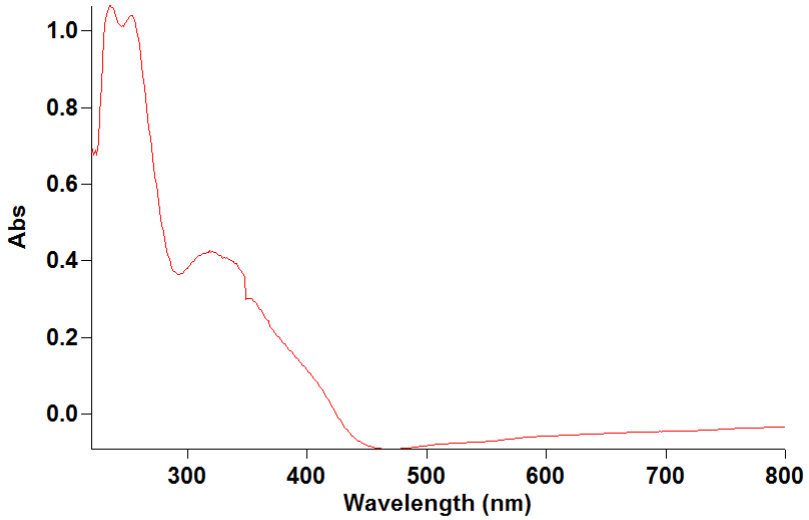


Figure S11. UV-vis absorption spectrum of **12** (CH_3CN, 12.5 µM).

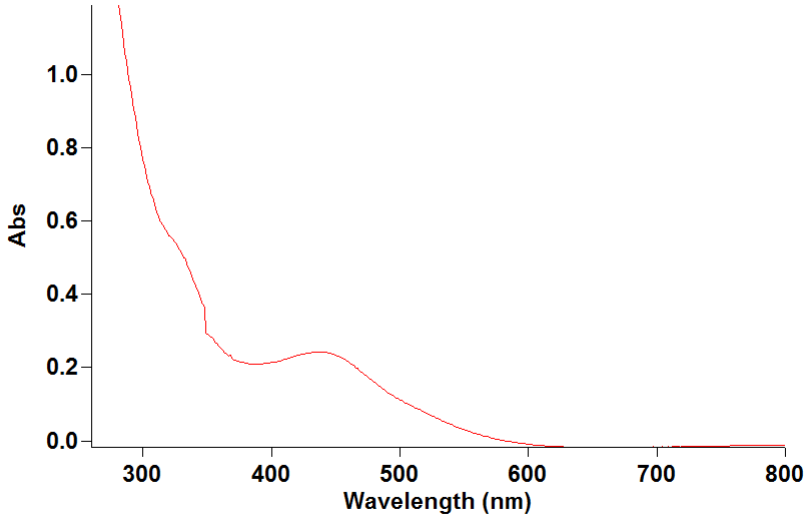


Figure S12. UV-vis absorption spectrum of **13** (CH_3CN, 12.5 µM).

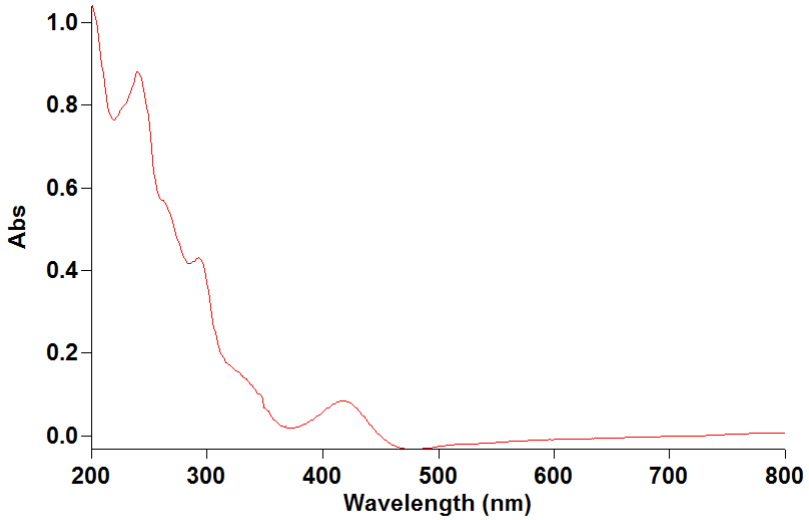


Figure S13. UV-vis absorption spectrum of **14** (CH_3CN, 12.5 µM).

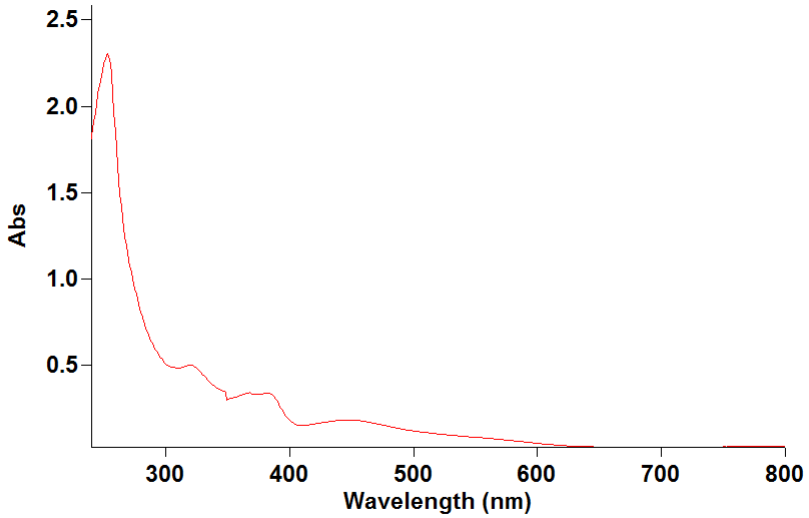


Figure S14. UV-vis absorption spectrum of **15** (CH_3CN, 12.5 µM).

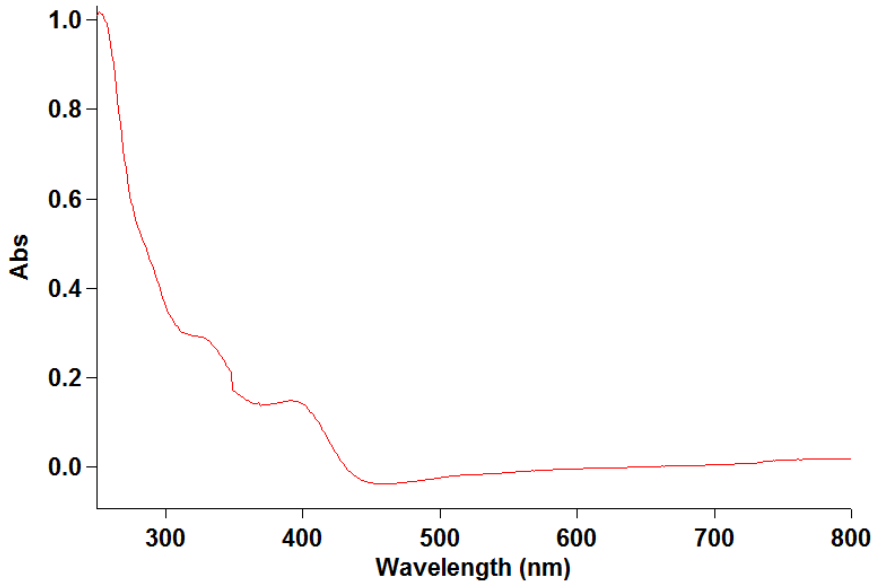


Figure S15. UV-vis absorption spectrum of **16** (CH_3CN, 12.5 μM).

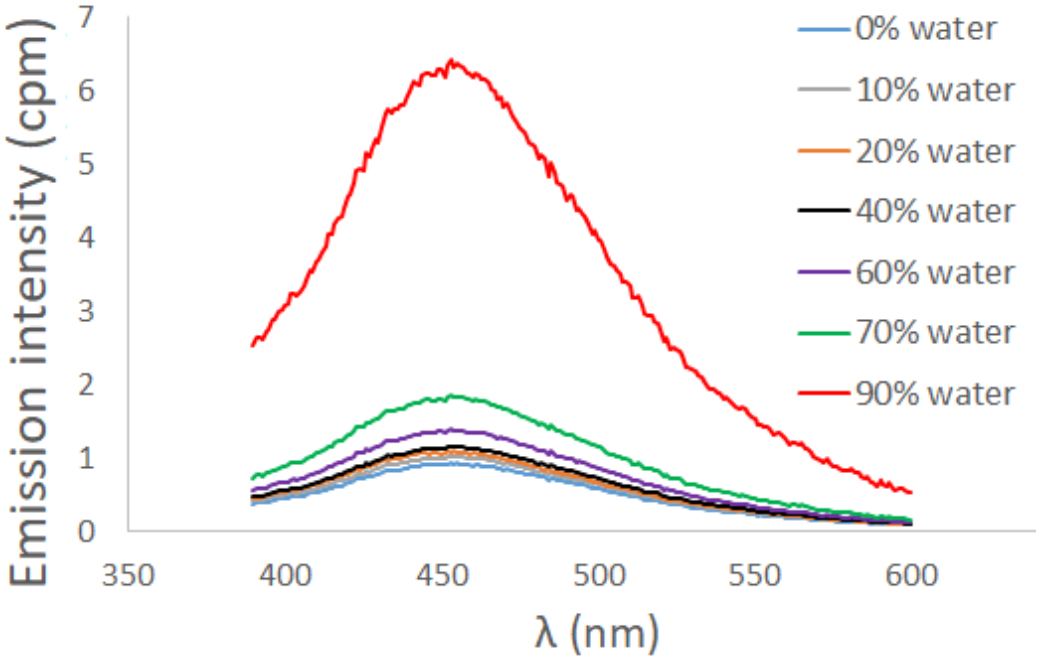


Figure S16. AIE profile of **2** in CH_3CN/H_2O mixtures. λ_{ex} = 318 nm, [**2**] = 10 μM.

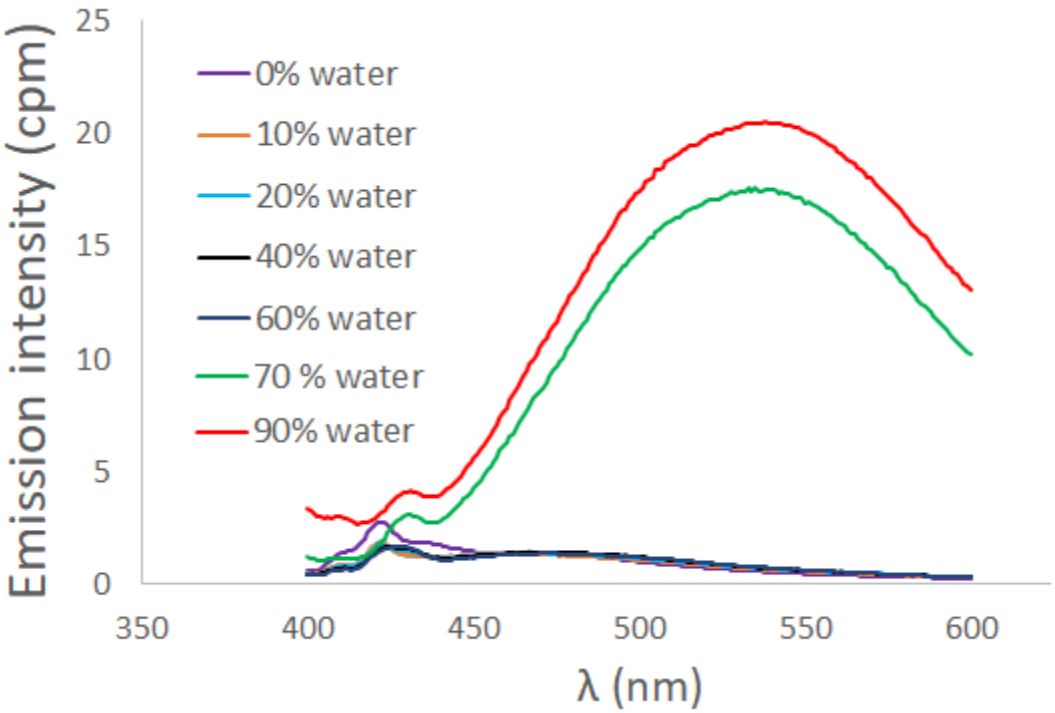


Figure S17. AIE profile of **3** in CH_3CN/H_2O mixtures. λ_{ex} = 367 nm, [**3**] = 10 μM.

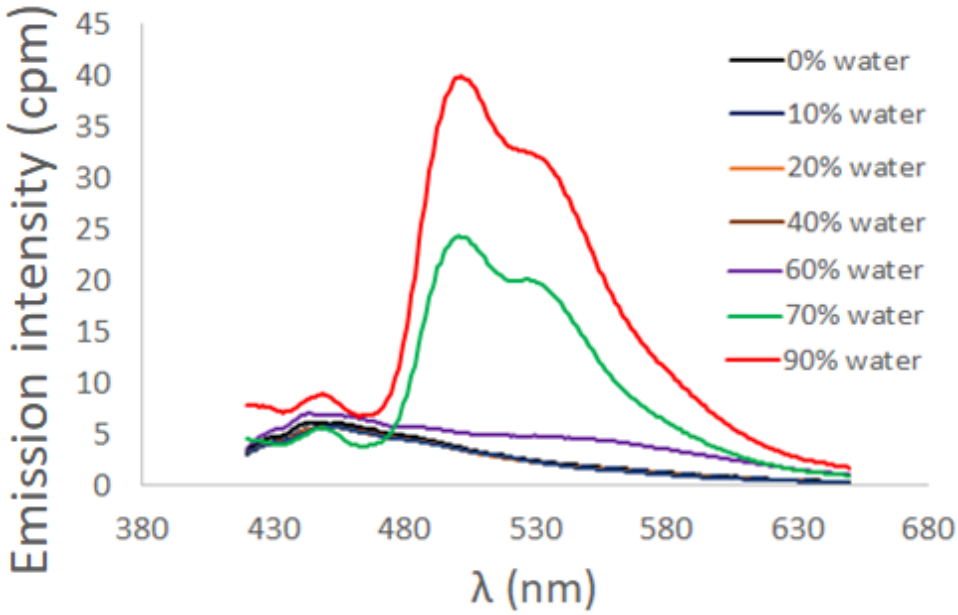


Figure S18. AIE profile of **4** in CH_3CN/H_2O mixtures. λ_{ex} = 393 nm, [**4**] = 10 μM.

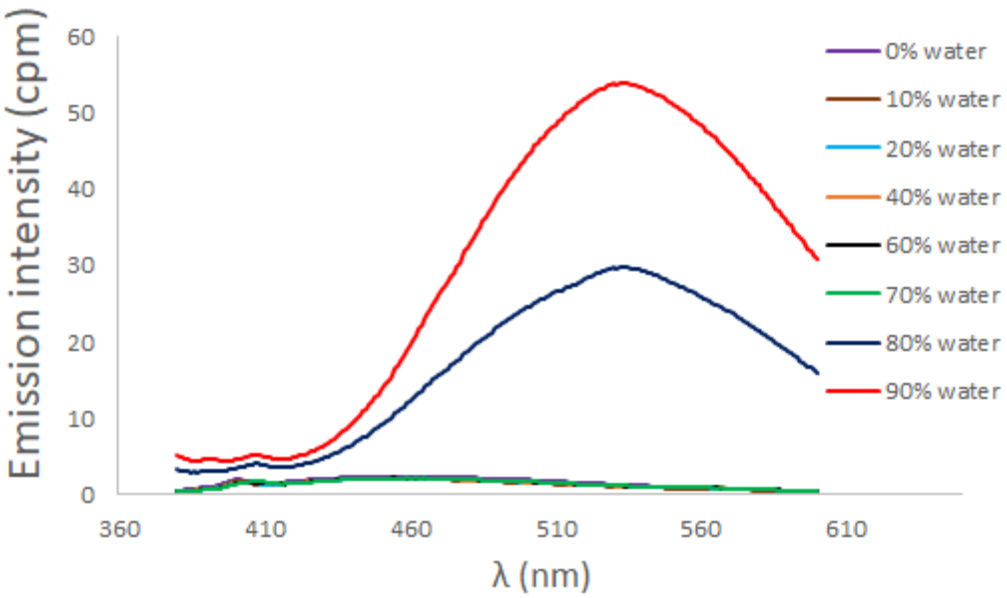


Figure S19. AIE profile of **5** in CH_3CN/H_2O mixtures. λ_{ex} = 354 nm, [**5**] = 10 μM.

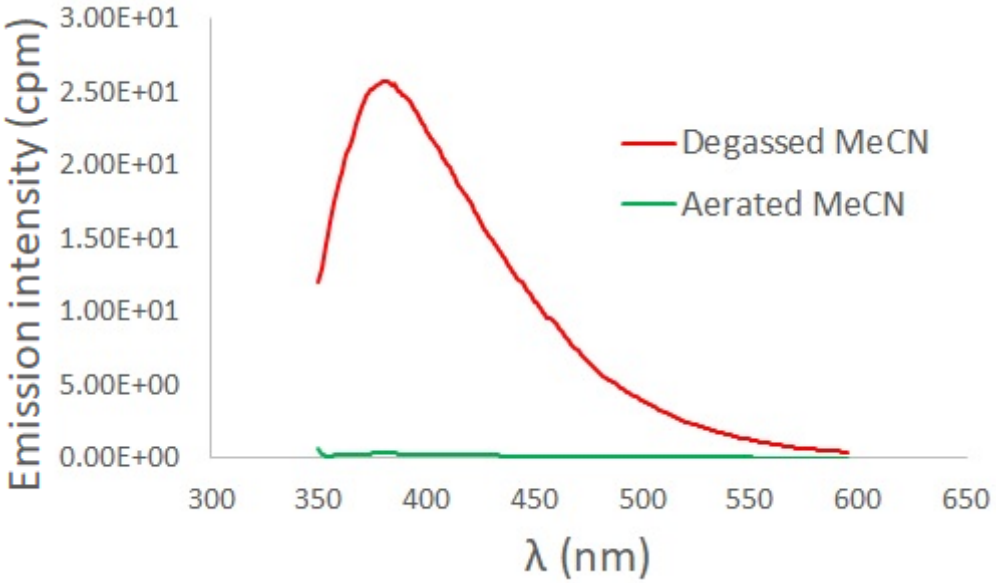


Figure S20. Emission spectra of **6** in degassed and aerated MeCN. λ_{ex} = 326 nm, [**6**] = 10 μM.

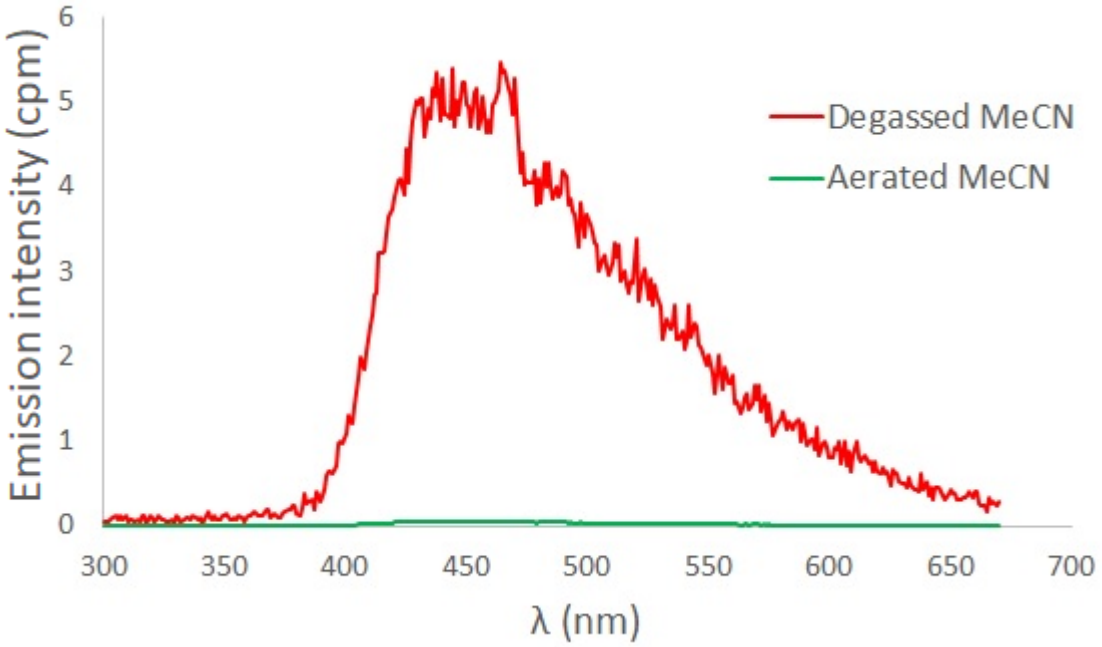


Figure S21. Emission spectra of **7** in degassed and aerated MeCN. λ_{ex} = 340 nm, [**7**] = 10 μM.

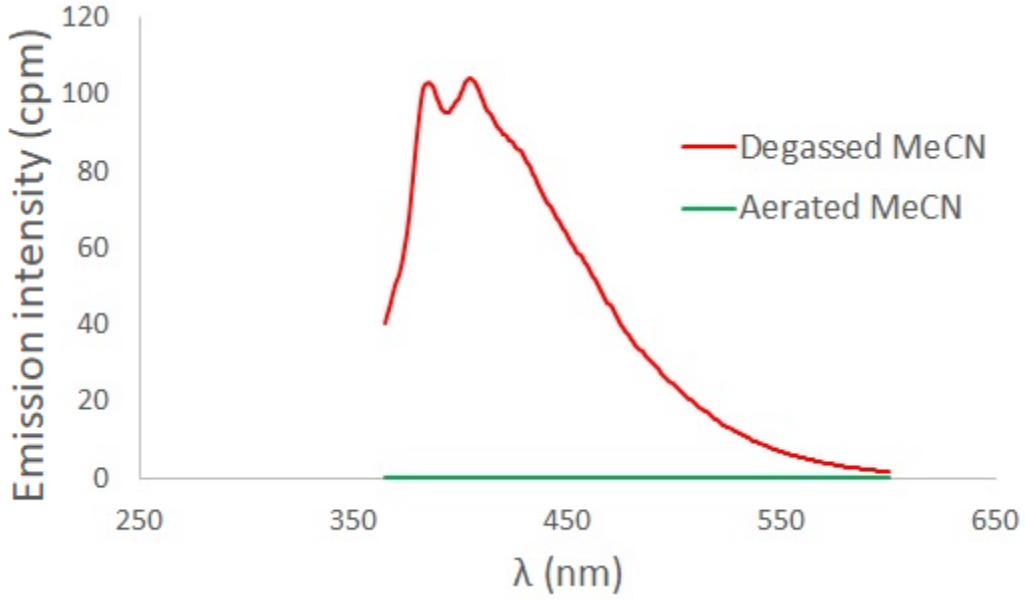


Figure S22. Emission spectra of **8** in degassed and aerated MeCN. λ_{ex} = 337 nm, [**8**] = 10 μM.

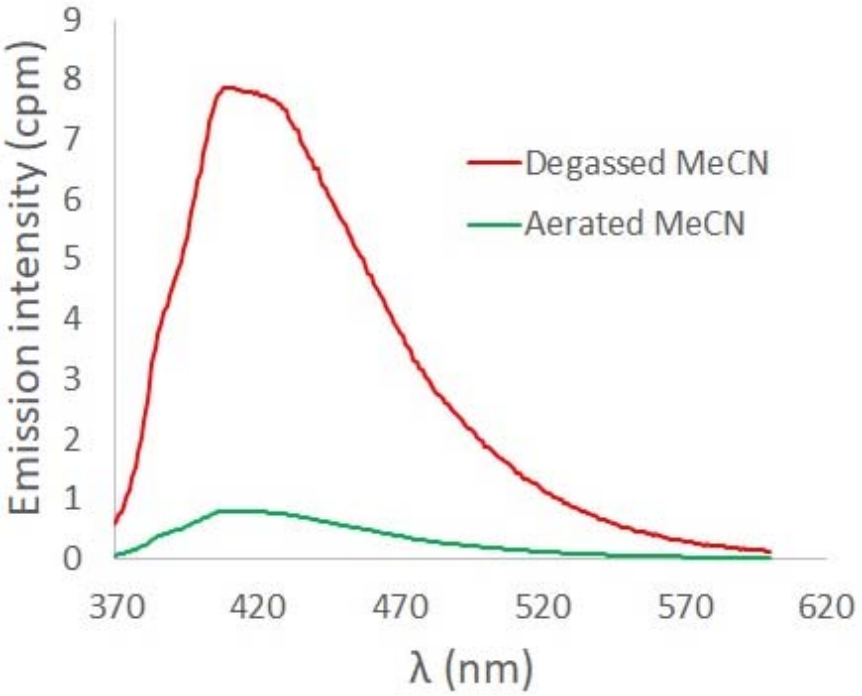


Figure S23. Emission spectra of **9** in degassed and aerated MeCN. λ_{ex} = 341 nm, [**9**] = 10 μM.

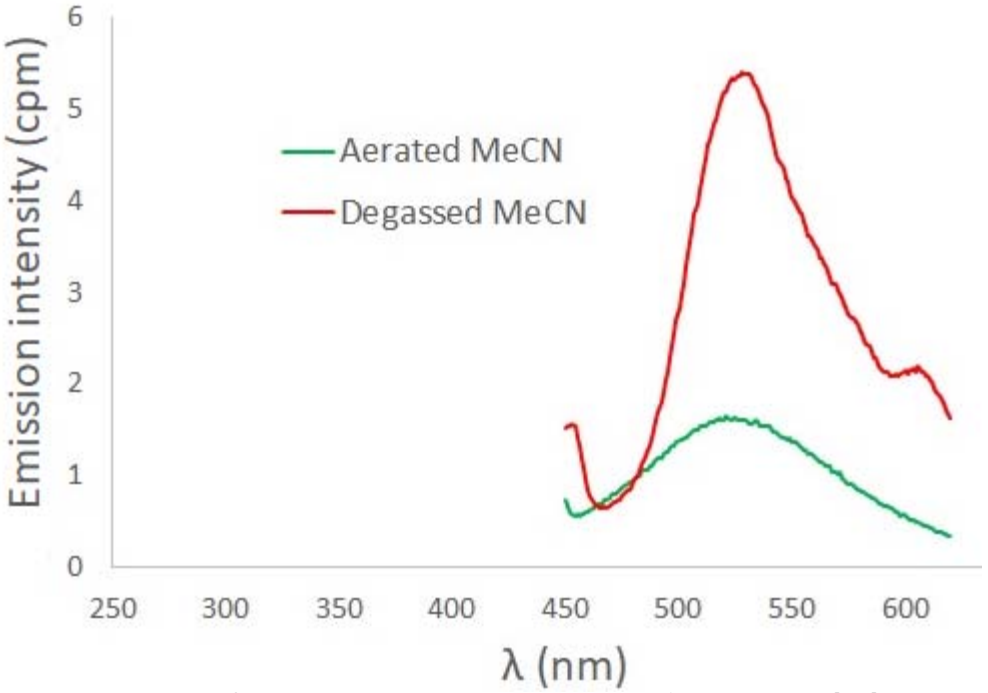


Figure S24. Emission spectra of **10** in degassed and aerated MeCN. λ_{ex} = 394 nm, [**10**] = 10 μM.

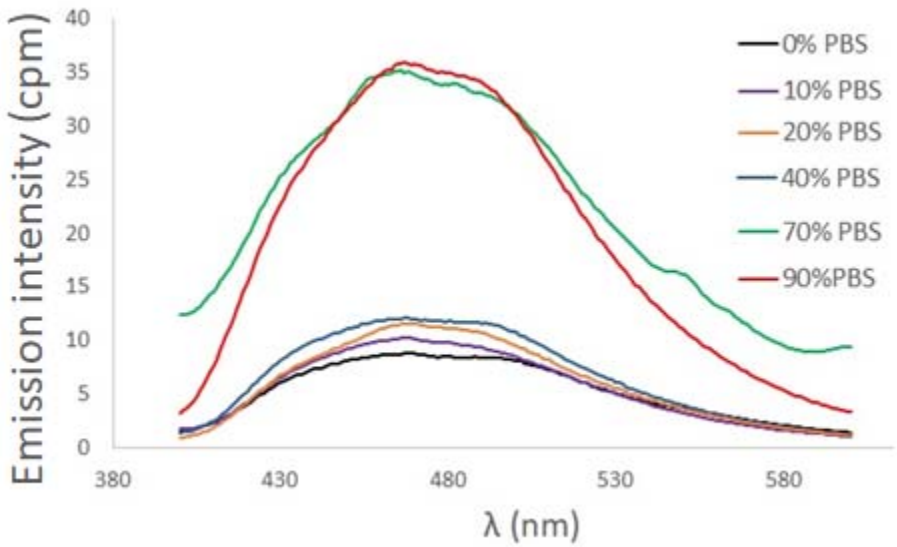


Figure S25. AIE profile of **11** in CH_3CN/PBS (PH=7.4) mixtures. λ_{ex} = 334 nm, [**11**] = 10 μM

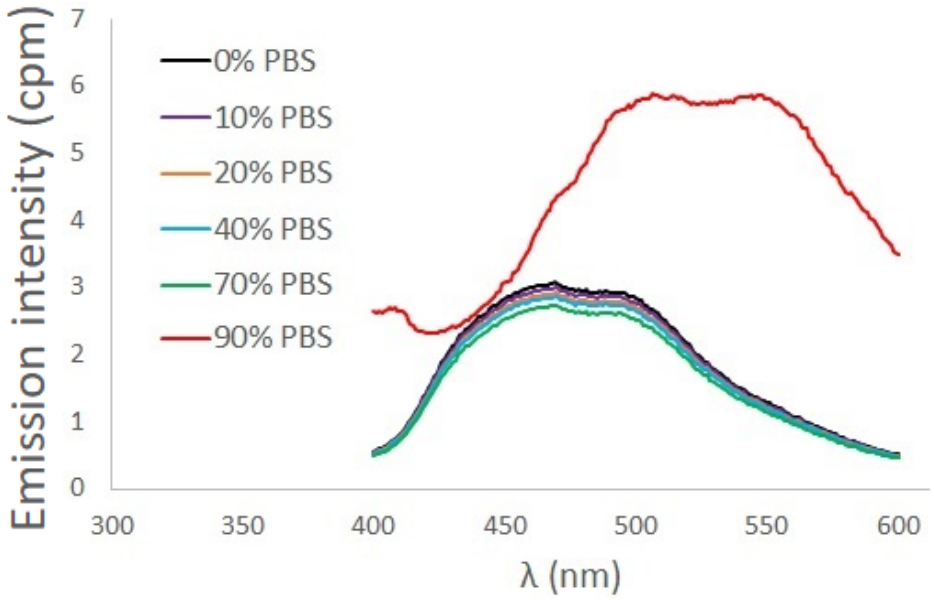


Figure S26. AIE profile of **12** in CH_3CN/PBS (PH= 7.4) mixtures. λ_{ex} = 364 nm, [**12**] = 10 μM.

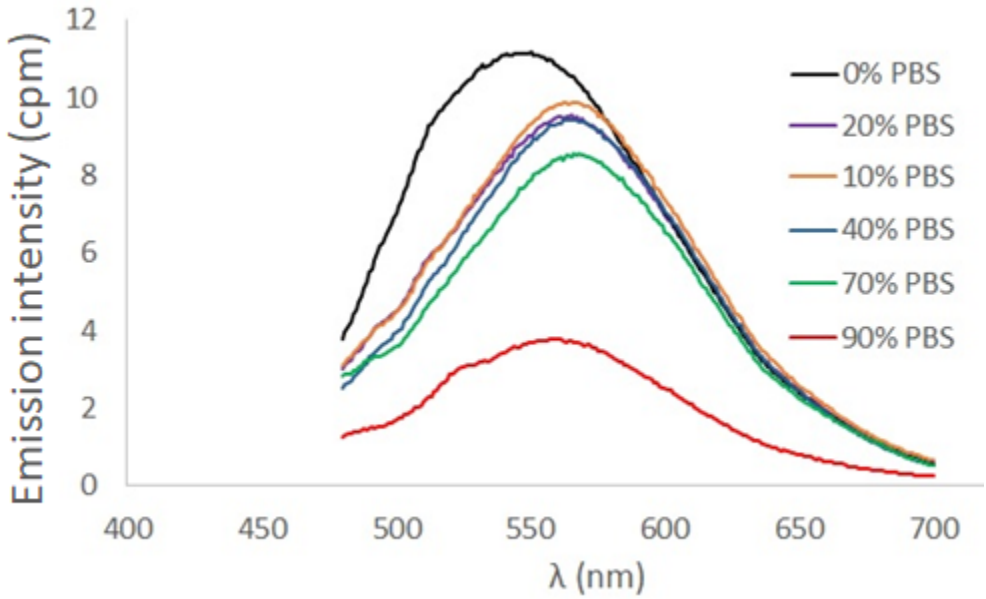


Figure S27. ACQ profile of **13** in CH_3CN/PBS (PH= 7.4) mixtures. λ_{ex} = 447 nm, [**13**] = 10 μM.

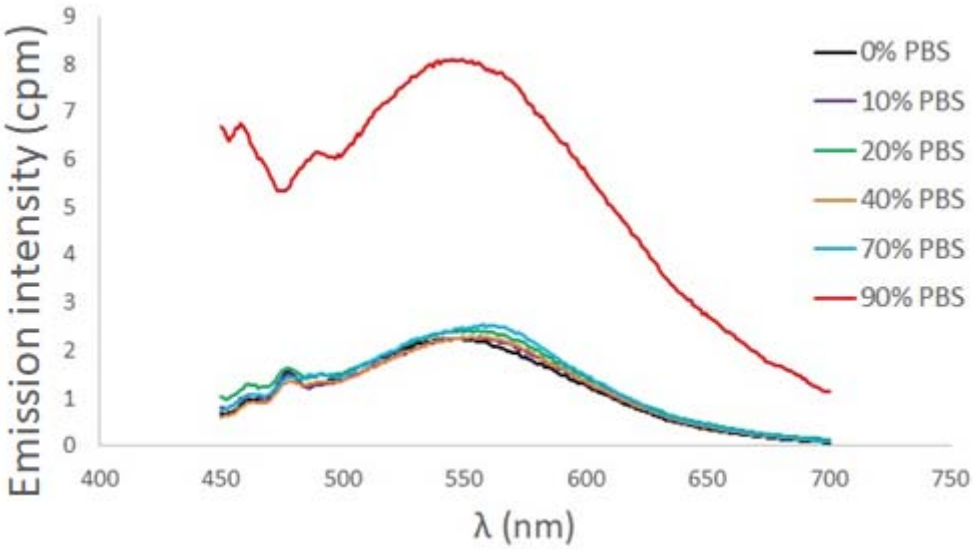


Figure S28. AIE profile of **14** in CH_3CN/PBS mixtures (PH= 7.4). λ_{ex} = 419 nm, [**14**] = 10 μM.

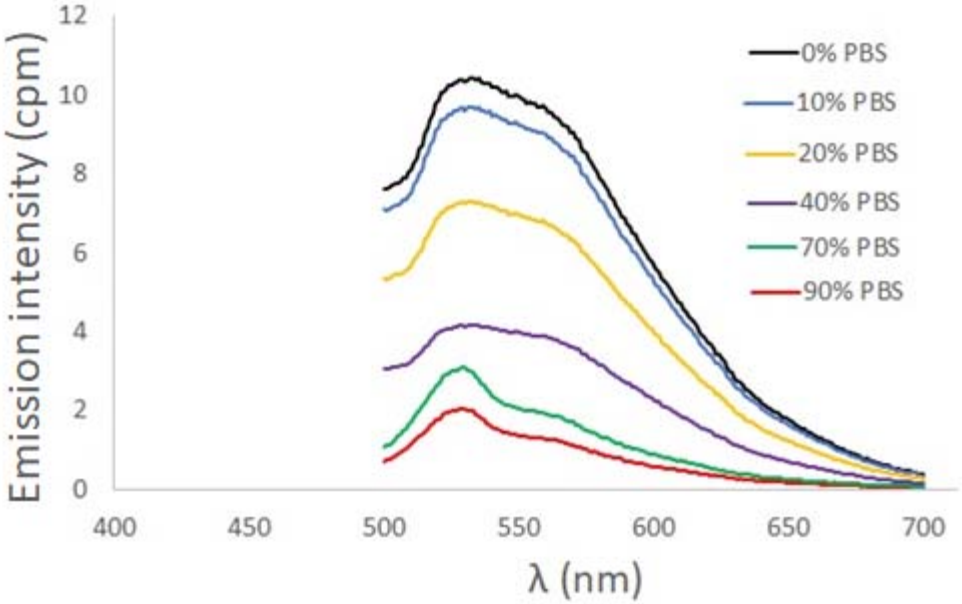


Figure S29. ACQ profile of **15** in CH_3CN/PBS mixtures (PH = 7.4). λ_{ex} = 450 nm, [**15**] = 10 μM.

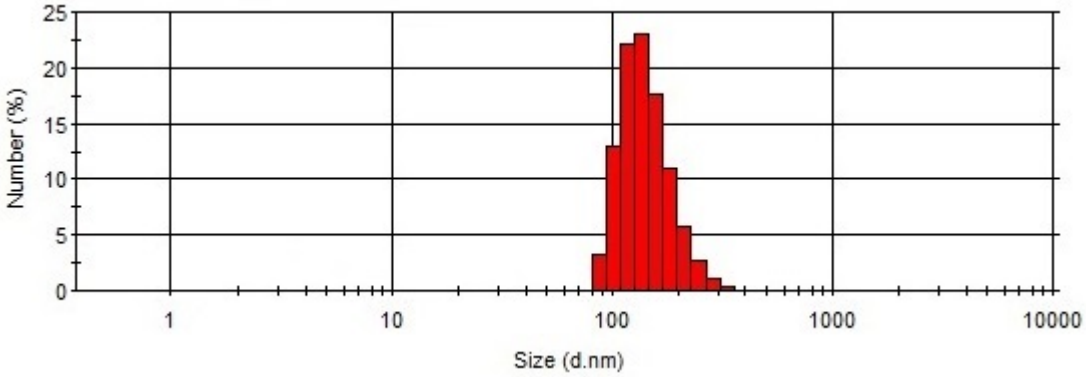


Figure S30. Dynamic light scattering results of **16** (10 μM) in 9:1 PBS:MeCN.

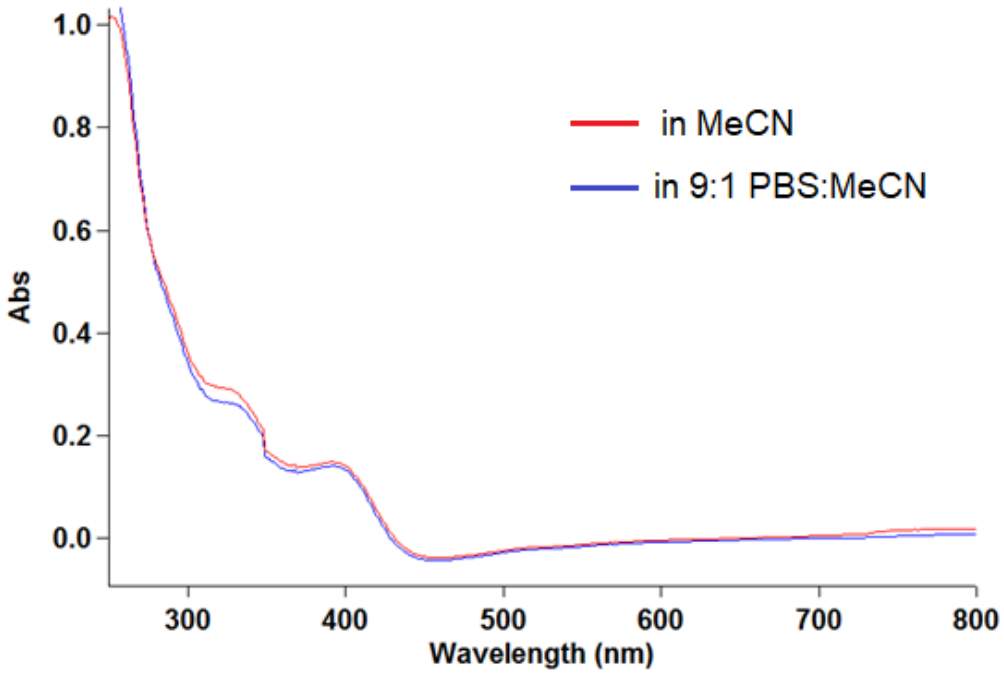


Figure S31. UV-vis absorption spectrum of **16** (12.5 μM) in MeCN and 9:1 PBS:MeCN.

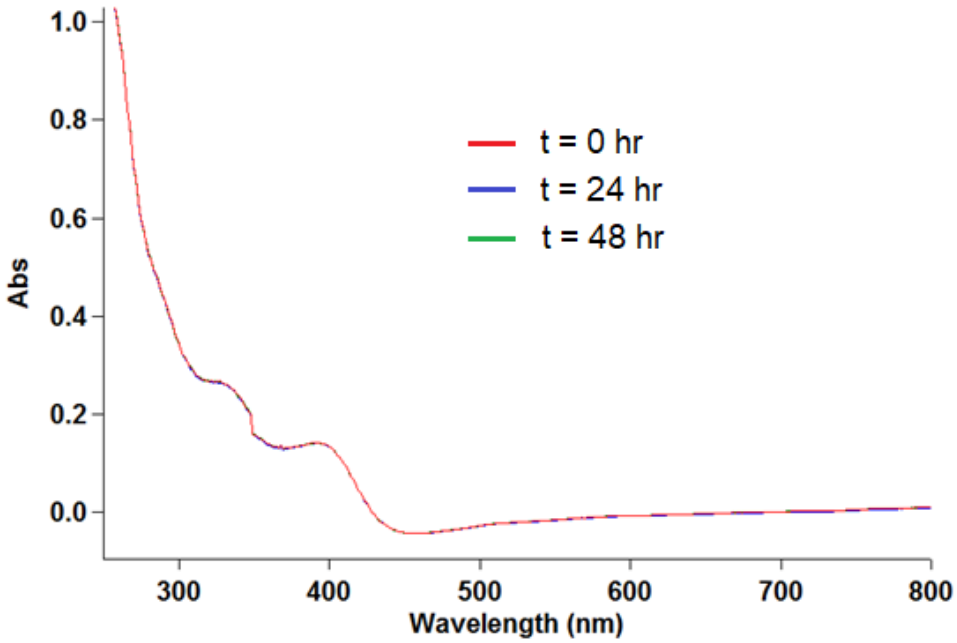


Figure S32. UV-vis absorption spectrum of **16** (12.5 μM, 9:1 PBS:MeCN) over 48 hr period.

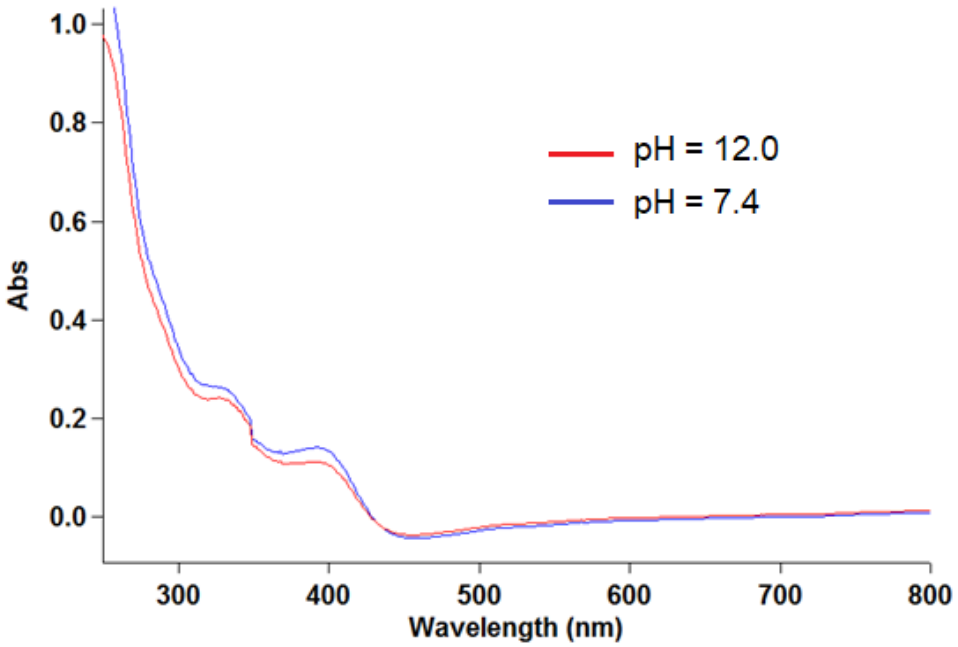


Figure S33. UV-vis absorption spectrum of **16** (12.5 µM, 9:1 PBS:MeCN) at pH = 7.4 and 12.0.

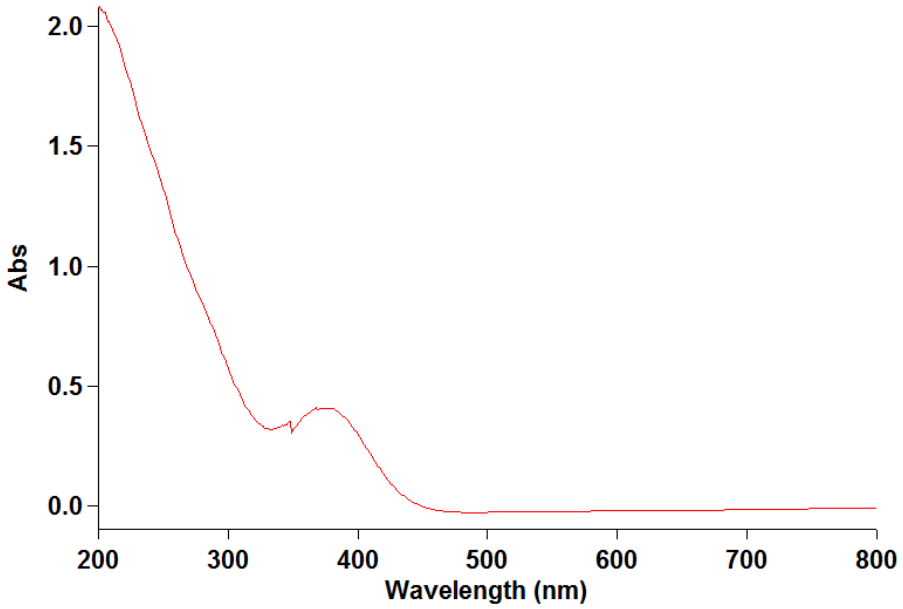


Figure S34. UV-vis absorption spectrum of **17** (MeCN, 25 µM).

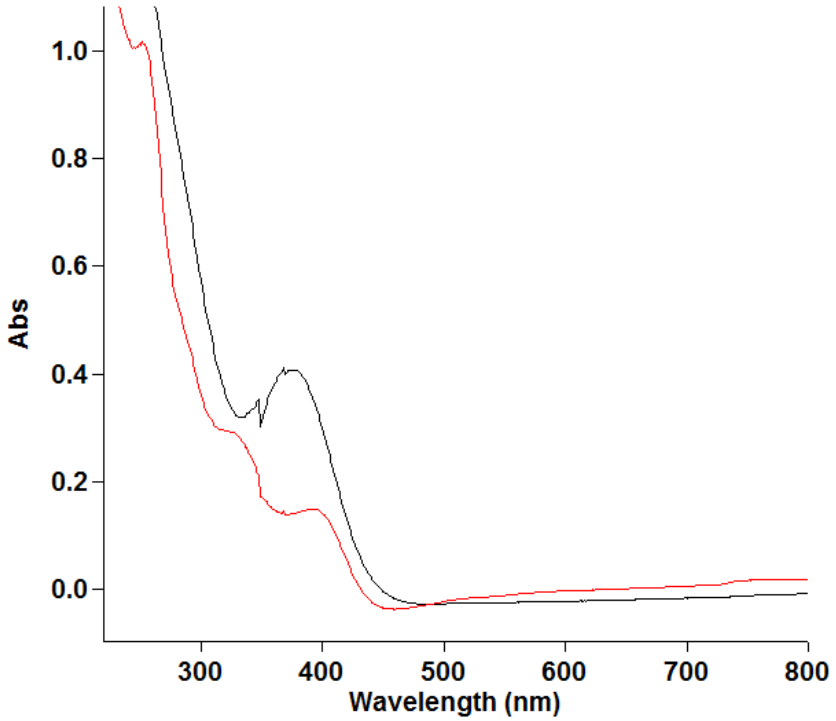


Figure S35. Overlay of UV-vis absorption spectra of **16** (MeCN, 12.5 µM) in red and **17** (MeCN, 25 µM) in black.

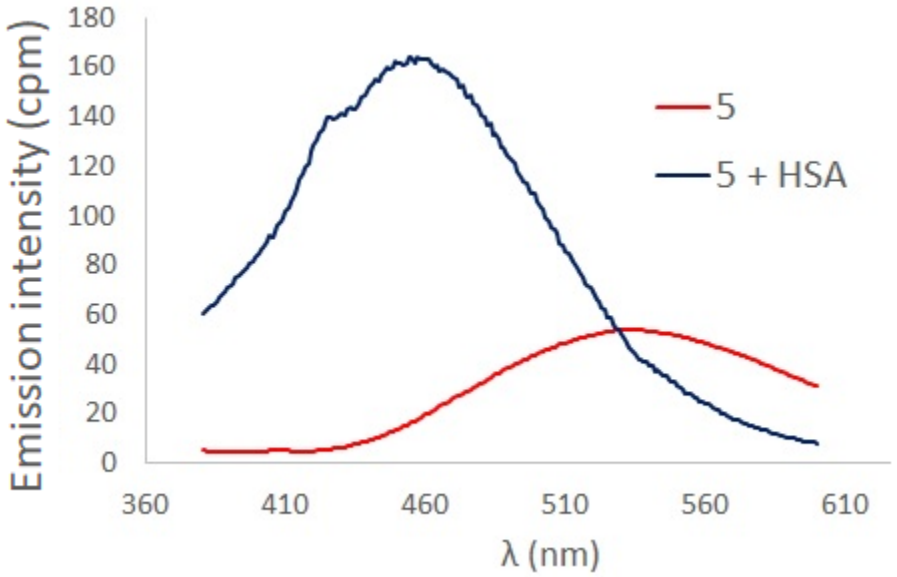


Figure S36. Emission response of **5** in presence and absence of 20 µM HSA in 9:1 PBS:MeCN (PH= 7.4). λ_{ex} = 354 nm, [**5**] = 10 µM.

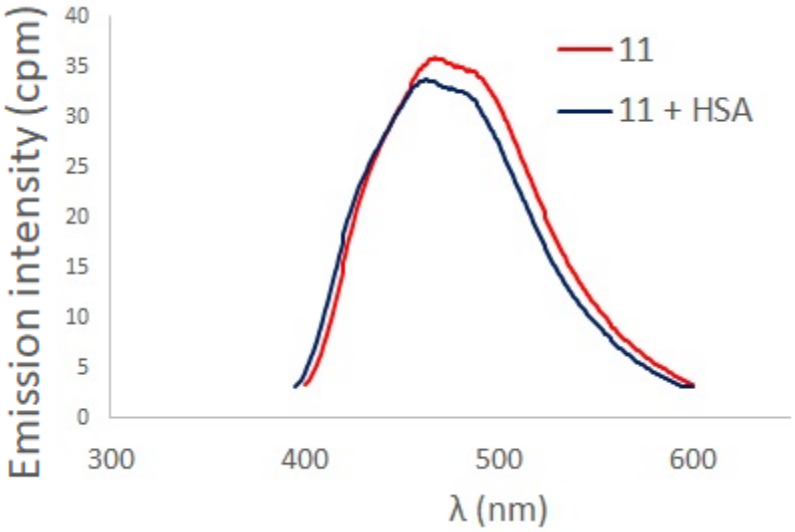


Figure S37. Emission response of **11** in presence and absence of 20 μM HSA in 9:1 PBS:MeCN (PH=7.4). λ_{ex} = 334 nm, [**11**] = 10 μM.

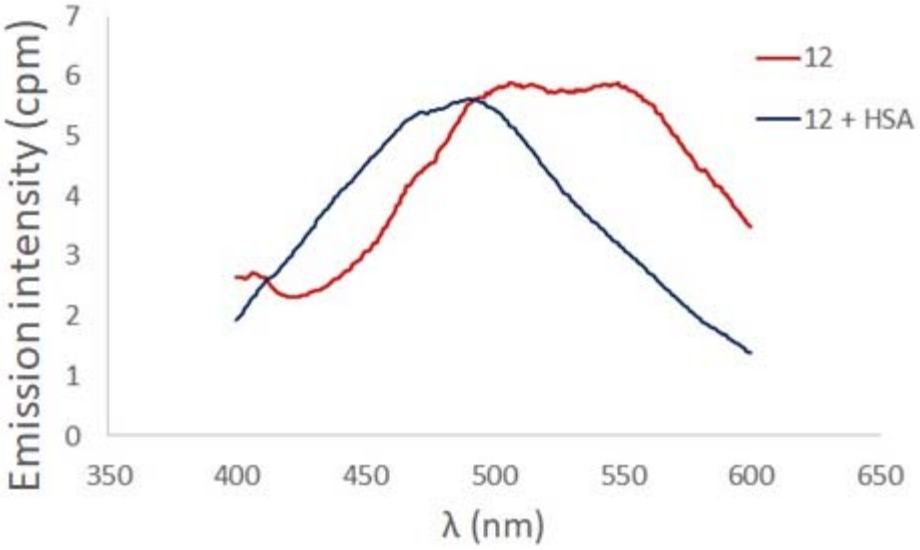


Figure S38. Emission response of **12** in presence and absence of 20 μM HSA in 9:1 PBS:MeCN (PH=7.4). λ_{ex} = 364 nm, [**12**] = 10 μM.

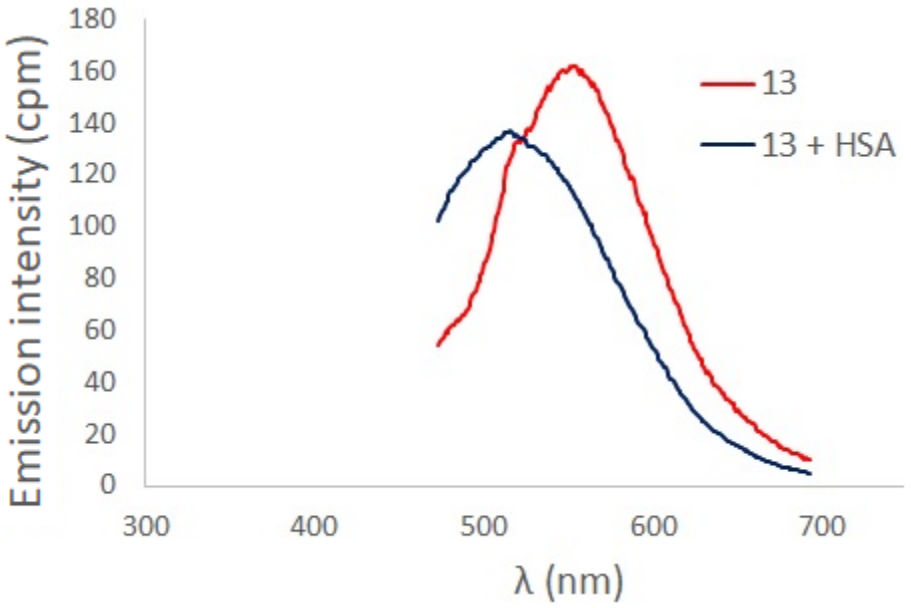


Figure S39. Emission response of **13** in presence and absence of 20 μM HSA in 9:1 PBS:MeCN (PH=7.4). λ_{ex} = 447 nm, [**13**] = 10 μM.

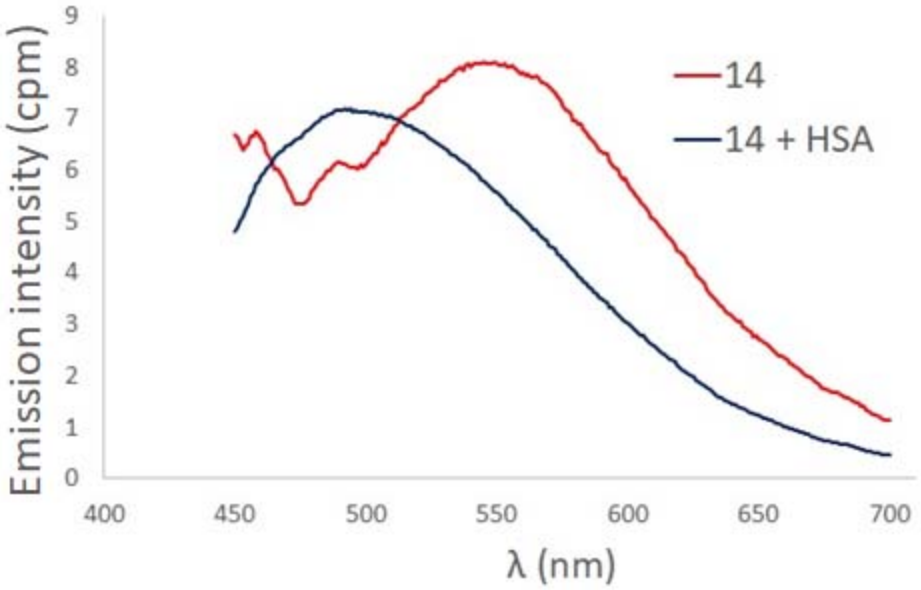


Figure S40. Emission response of **14** in presence and absence of 20 μM HSA in 9:1 PBS:MeCN (PH=7.4). λ_{ex} = 419 nm, [**14**] = 10 μM.

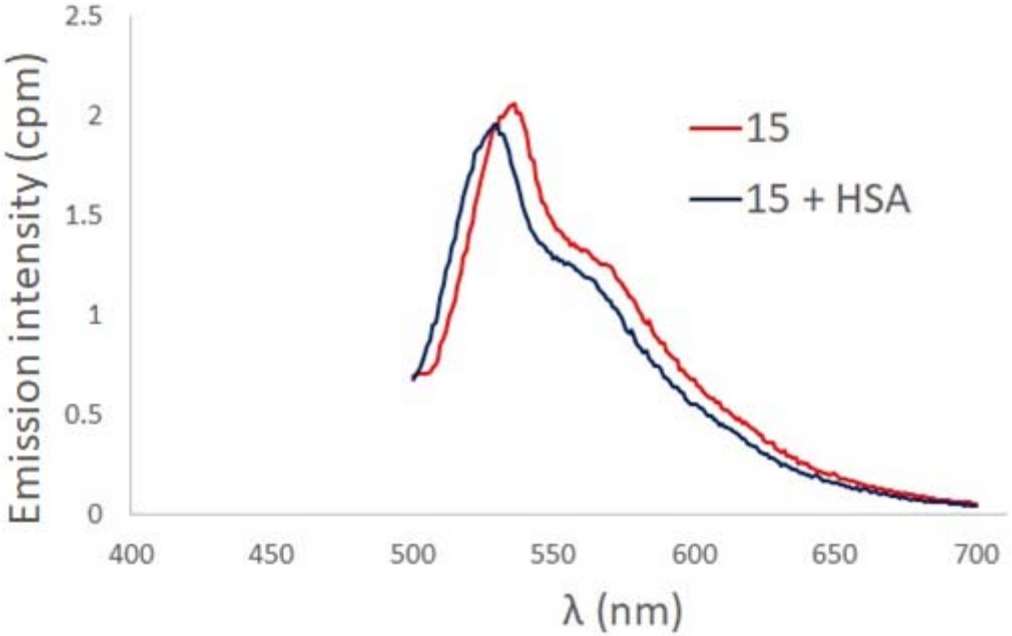


Figure S41. Emission response of **15** in presence and absence of 20 μM HSA in 9:1 PBS:MeCN (PH=7.4). λ_{ex} = 450 nm, [**15**] = 10 μM.

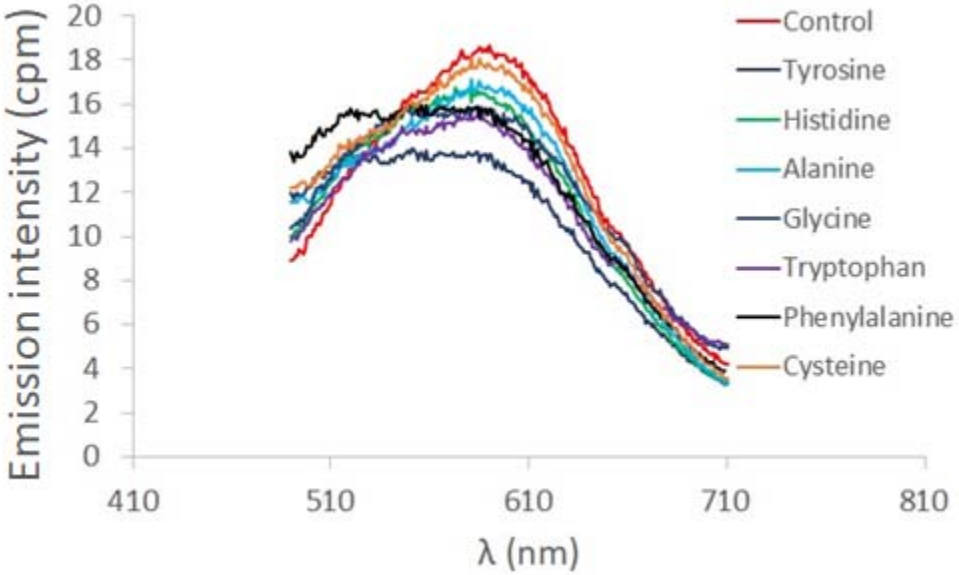


Figure S42. Emission response of **16** in presence and absence of different amino acids in 9:1 PBS:MeCN (PH=7.4). λ_{ex} = 396 nm, [**16**] = 10 μM.

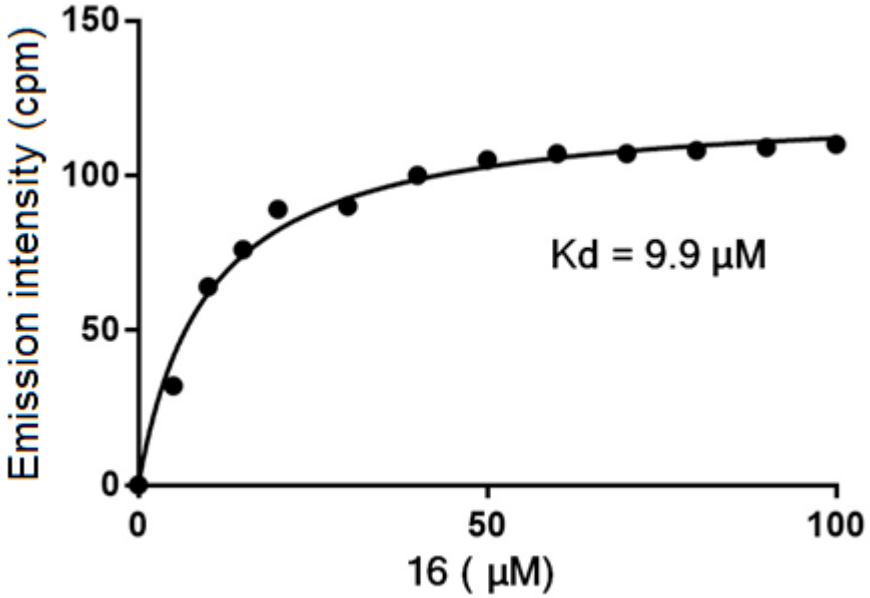


Figure S43. Saturation binding assay generated by GraphPad Prism using various concentrations of **16** (0-100 μM) towards HSA (20 μM).

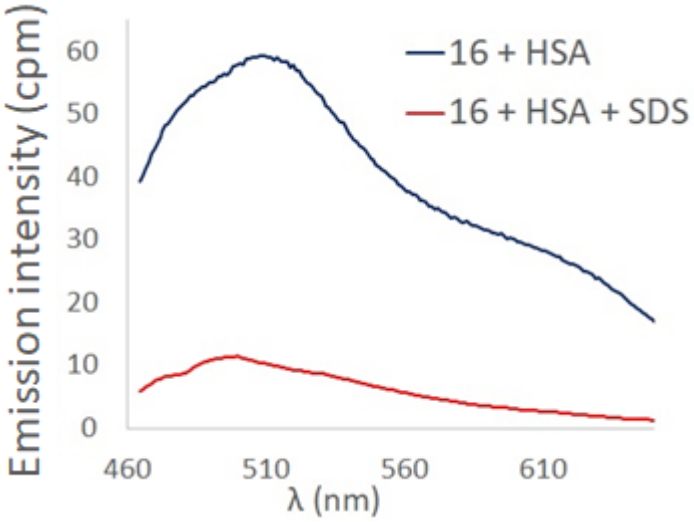


Figure S44. Emission response of **16**.HSA complex in presence and absence of SDS (20 μM) in 9:1 PBS:MeCN (PH= 7.4). λ_{ex} = 396 nm, [**16**] = 10 μM, [HSA] = 20 μM.

Table S1. Photophysical properties of **6-16**.

Compound No.	*λ_{ex} in MeCN (nm)*	*λ_{em} in MeCN (nm)*	*λ_{em} in MeCN: PBS (1:9) (nm)*	*Stokes shift (MeCN)*	*Φ* (%) in aerated MeCN[a]	*Φ* (%) in degassed MeCN[a]	*Φ* (%) in *MeCN: PBS (1:9)*[a]
6	326	385	nd[b]	59	nd	3.2	nd
7	340	444	nd	104	nd	2.1	nd
8	337	410	nd	73	nd	3.7	nd
9	341	420	423	79	0.7	4.1	1.1
10	394	526	529	132	1.4	6.3	1.4
11	334	474	476	140	3.1	8.1	11.5
12	364	469	518	105	5.1	9.4	10.1
13	447	547	563	100	6.2	12.1	1.6
14	419	543	549	124	6.8	17.4	19.8
15	450	527	521	77	8.4	14.5	1.4
16	396	505	595	109	3.8	10.3	10.7

[a] Quantum yields calculated using tris(2,2'-bipyridyl)ruthenium(II) chloride in aerated water (Φ = 2.8 %)[1] as a reference.

[b]nd: not determined.

Table 2. Crystallographic data for **12**.

Formula	$C_{31}H_{18}ClN_2O_3ReS_2,C_7H_8$
FW	844.38
Crystal System	Triclinic
Space group	P -1
a/Å	8.7755(9)
b/Å	13.4717(14)
c/Å	15.1412(15)
α/°	78.884(5)
β/°	77.789(5)
γ/°	72.824(5)
V/Å^3	1655.11(16)
Z	2
D_{calc}	1.694
μ (mm^{-1})	3.919
T/K	190.15
No. of reflections	30896
No. of unique reflections	9988
No. of reflections with I > 2σ(I)	7097
R_1 [I > 2σ(I)]	0.0185
wR_2	0.0408
CCDC No.	1571905

This complex crystallized with a full molecule in the asymmetric unit along with one full disordered toluene solvate molecule. One thiophene ring is disordered by a two-fold rotation about the C5-C11 bond. The C5-C11 and C5-C11' bonds were restrained to be the same. The anisotropic displacement parameters (adp's) of the disordered pair were restrained by the rigid bond and similarity restraints. The toluene molecule was disordered over an inversion center with two positions that are coplanar and in a 180° angle relative to each other. Toluene solvate was refined by using geometry restraints with two positions for each atom.

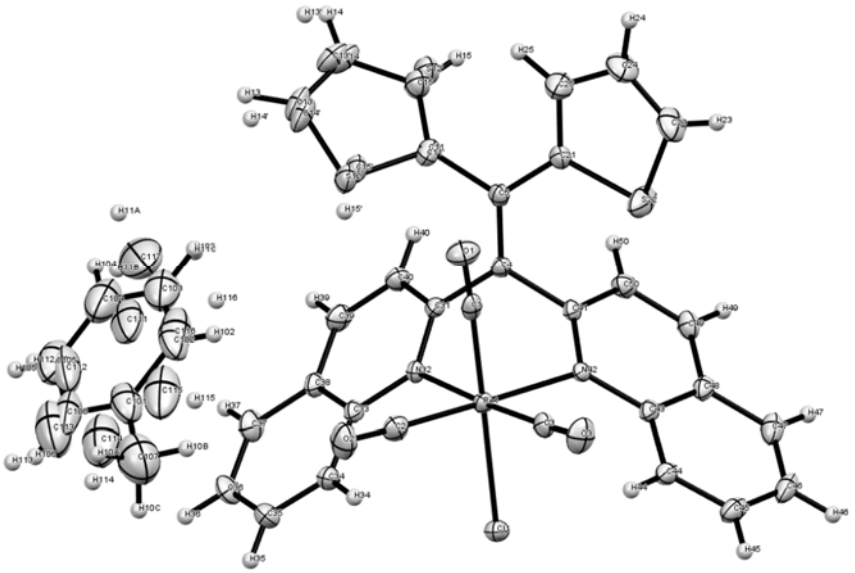
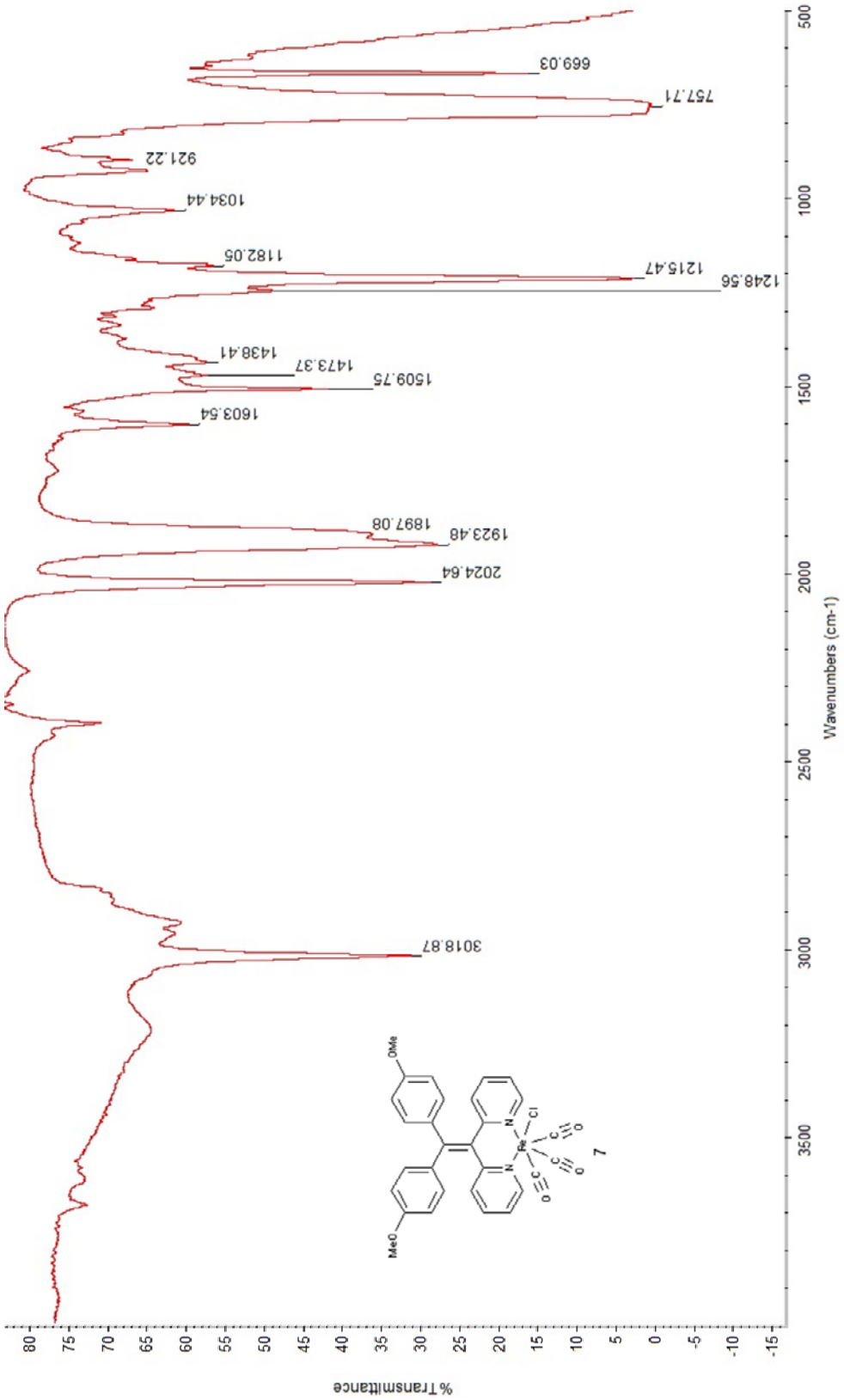
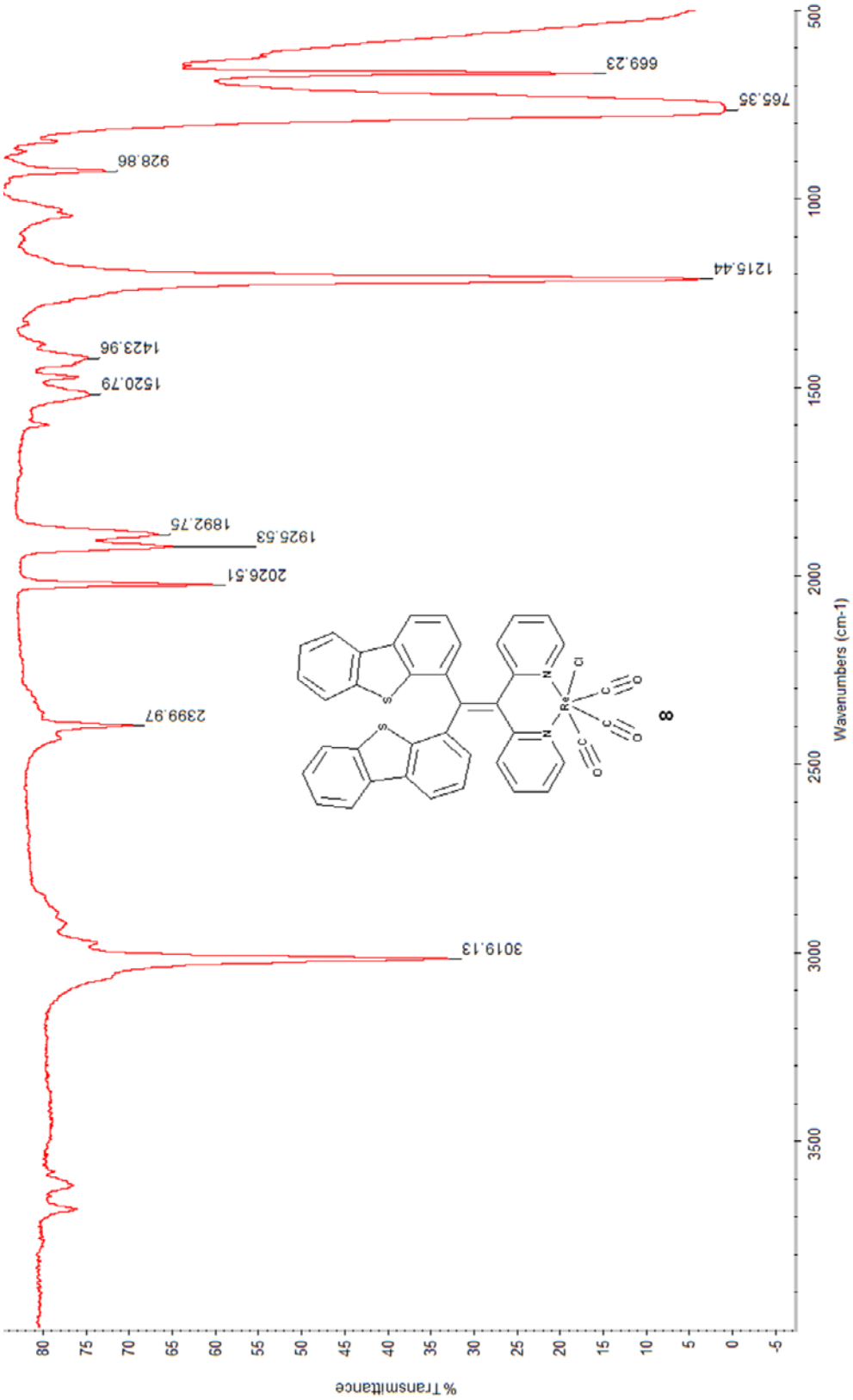


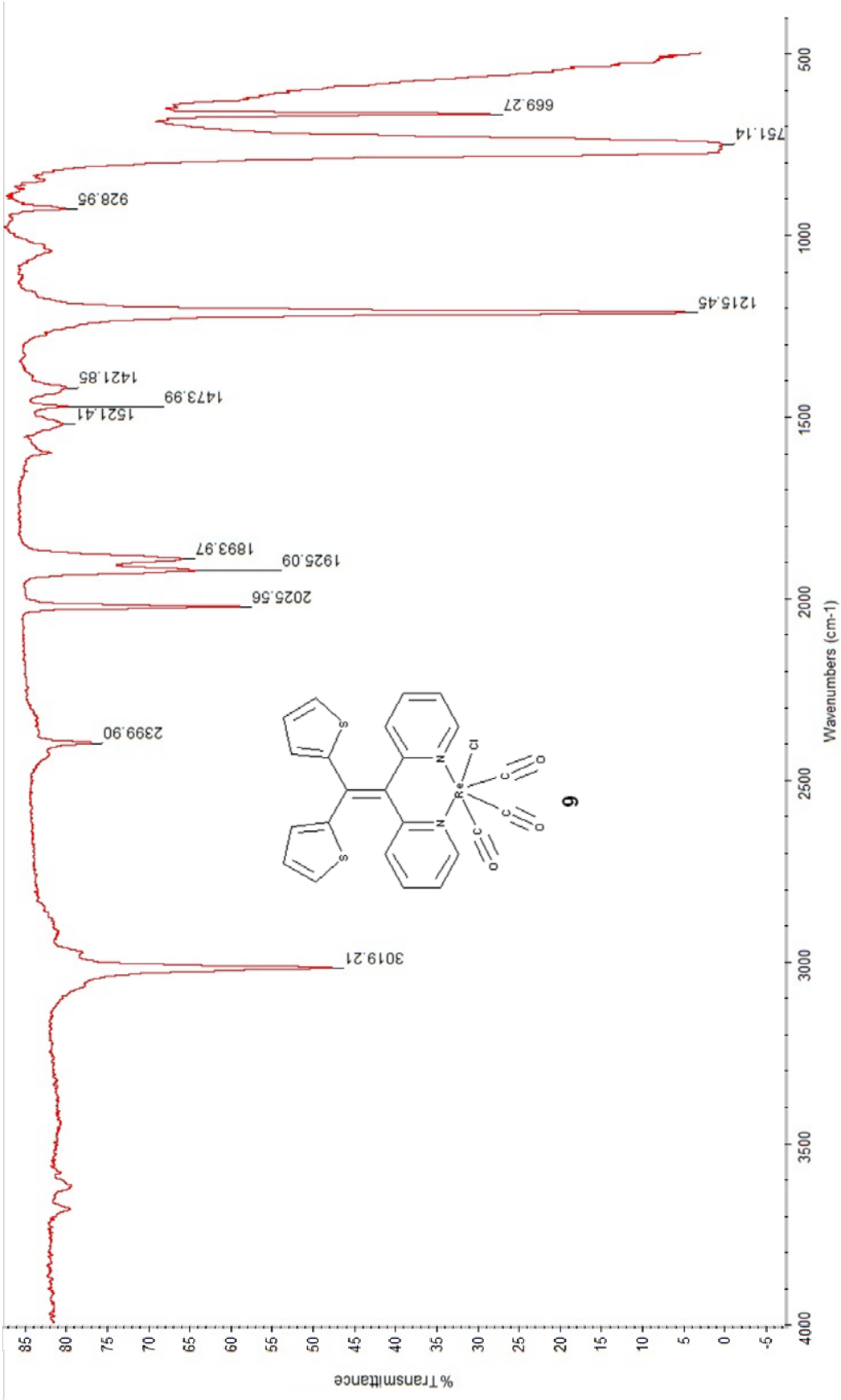
Figure S45. ORTEP plot of **12**·toluene.

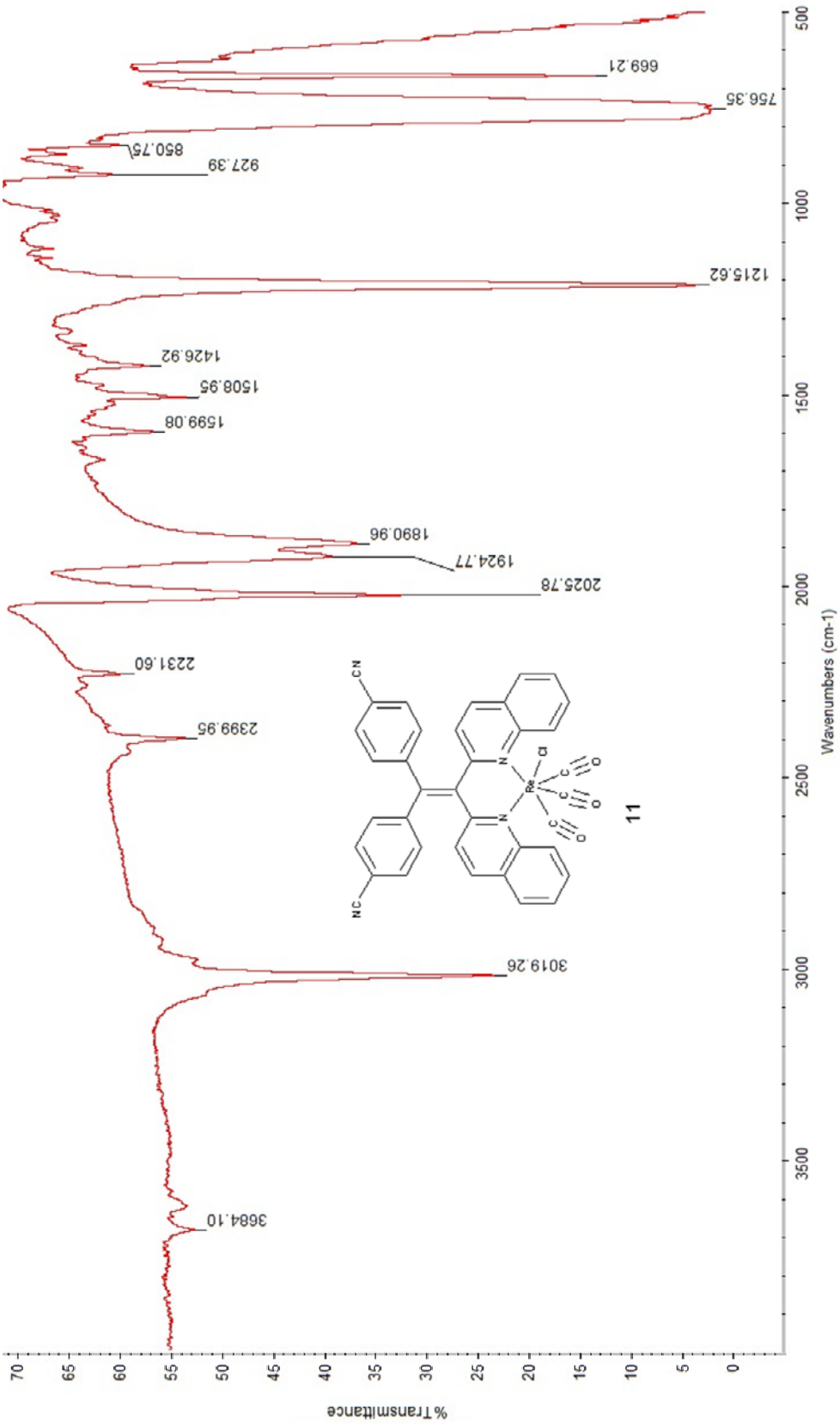
References:

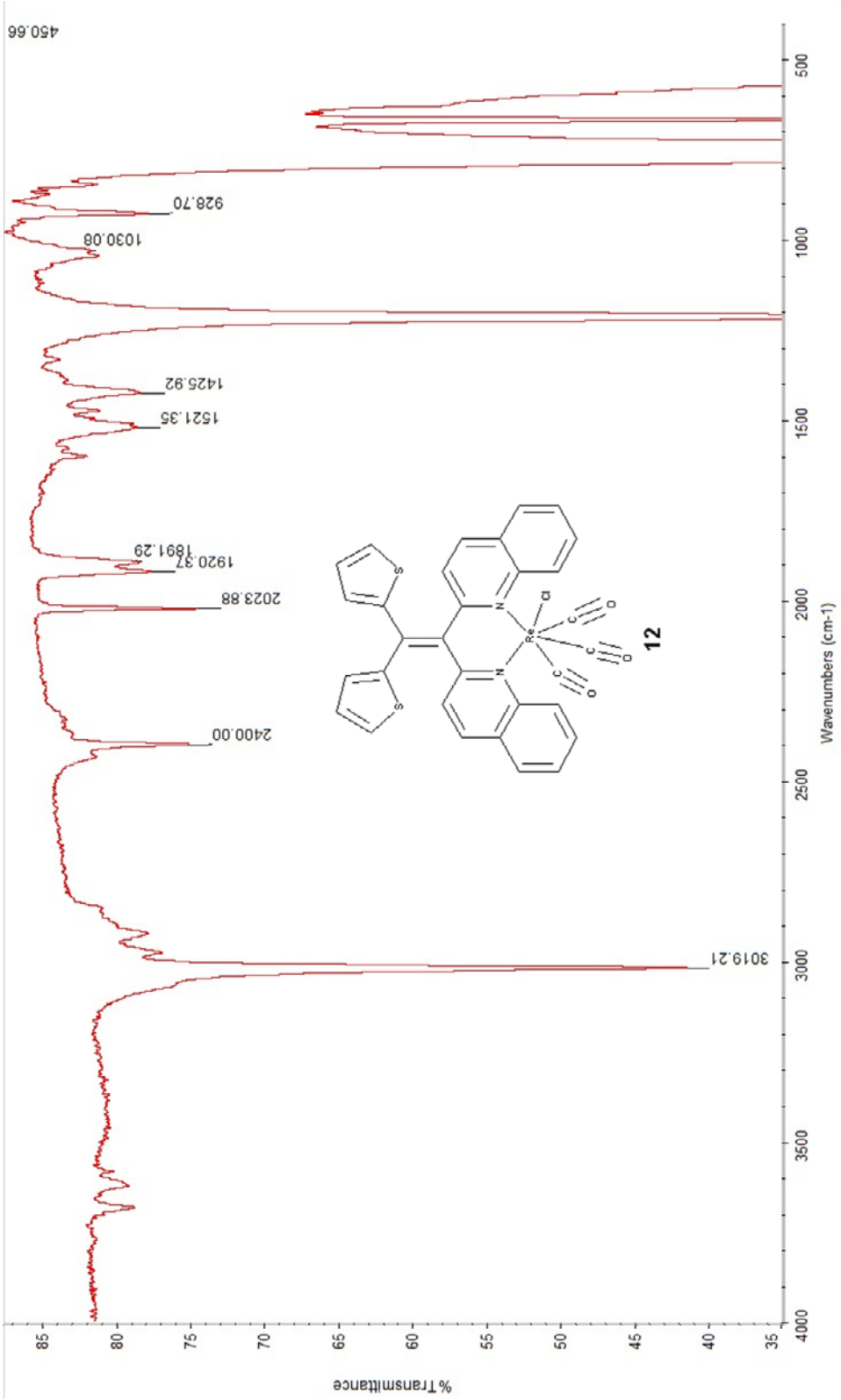
1. K. Nakamaru, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 2697-2705.

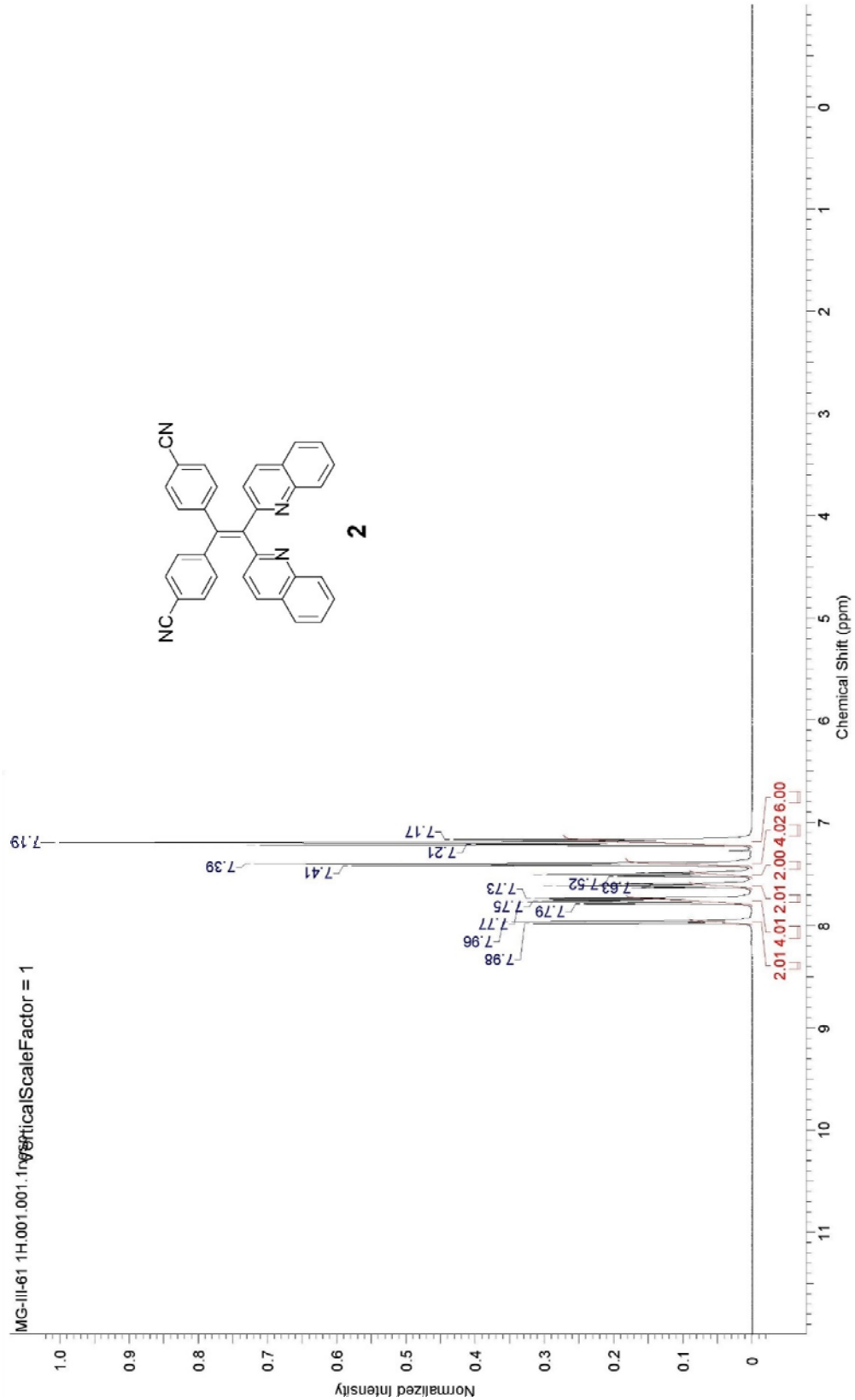

% Transmittance
Wavenumbers (cm-1)
3018.87
2024.64
1923.48
1897.08
1603.54
1509.75
1473.37
1438.41
1248.56
1215.47
1182.05
1034.44
921.22
757.71
669.03
MeO
OMe
7

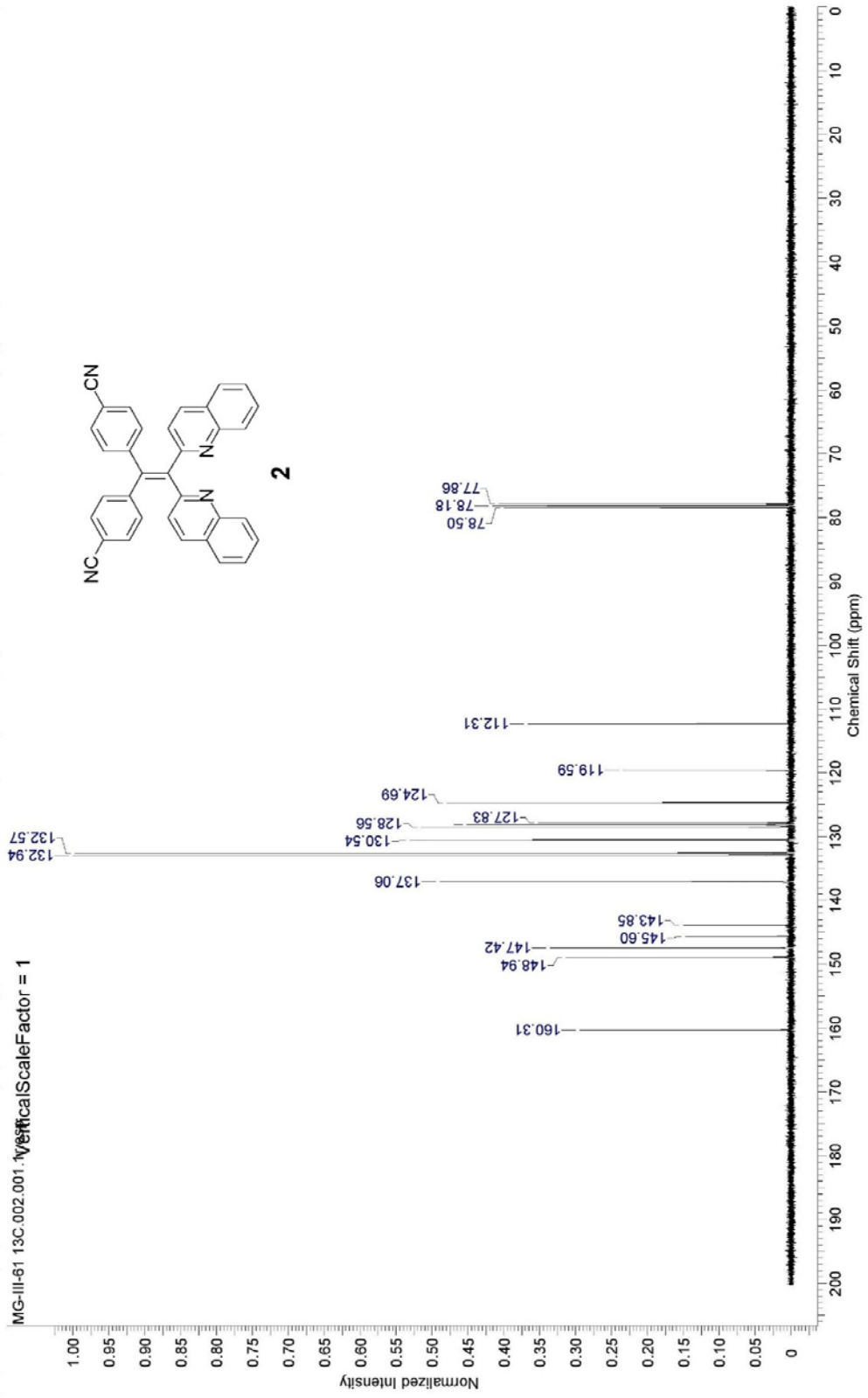

8
3019.13
2399.97
2026.51
1925.53
1892.75
1520.79
1423.96
1215.44
928.86
765.35
669.23
Wavenumbers (cm-1)
% Transmittance

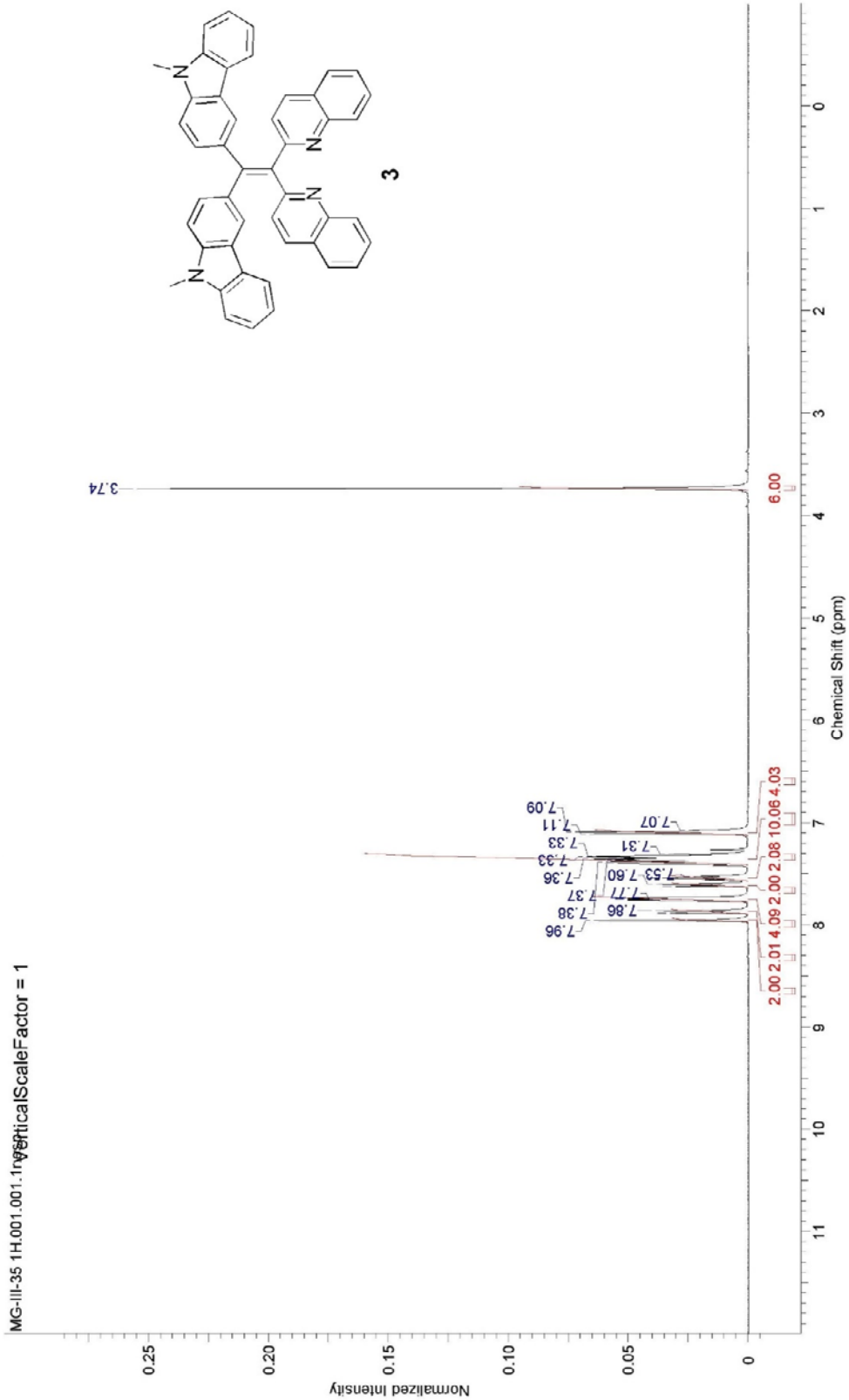

% Transmittance
Wavenumbers (cm-1)
3019.21
2399.90
2025.56
1925.09
1893.97
1521.41
1473.99
1421.85
1215.45
928.95
751.14
669.27
9

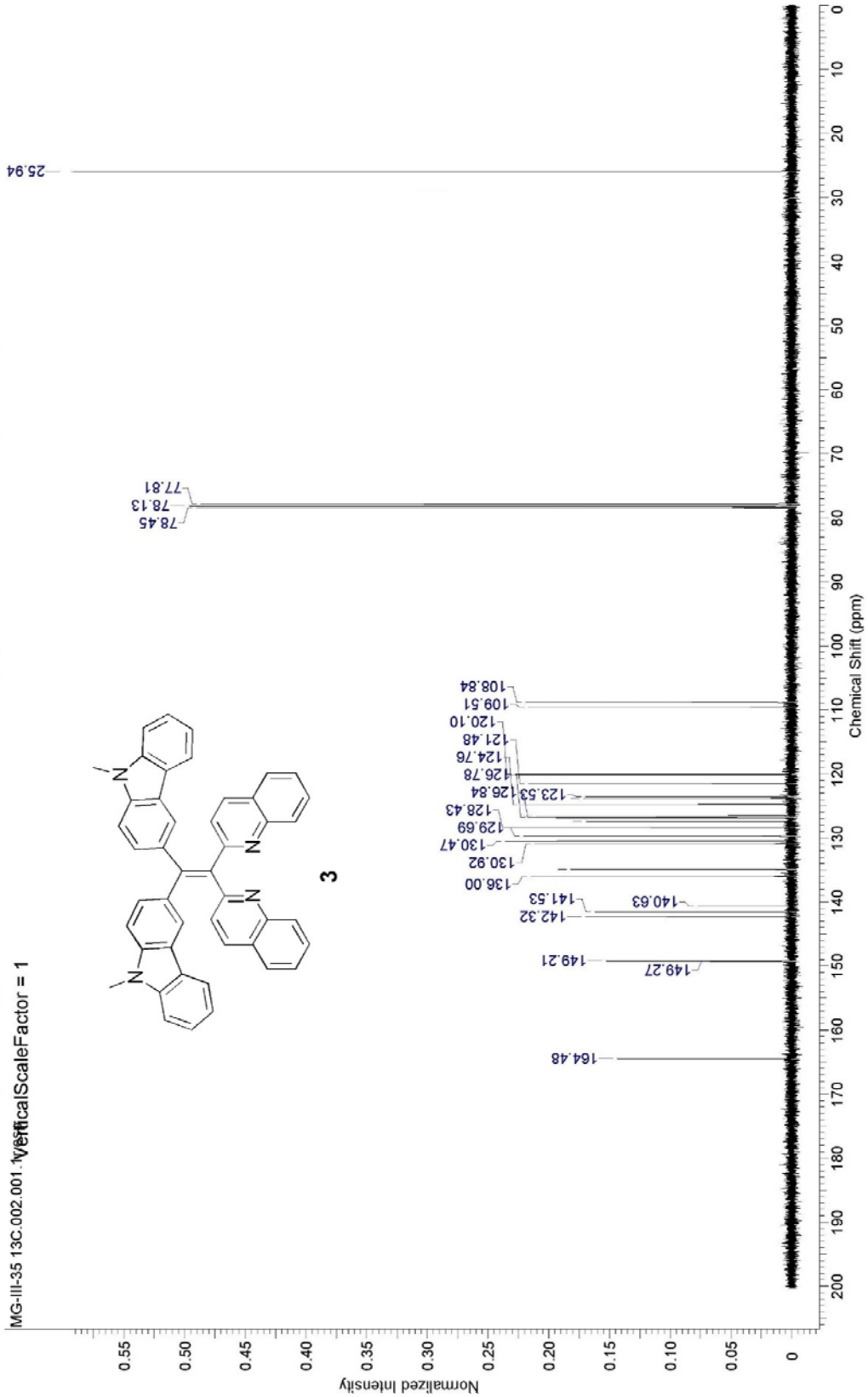

% Transmittance
Wavenumbers (cm-1)
3684.10
3019.26
2399.95
2231.60
2025.78
1924.77
1890.96
1599.08
1508.95
1426.92
1215.62
927.39
850.75
756.35
669.21
11

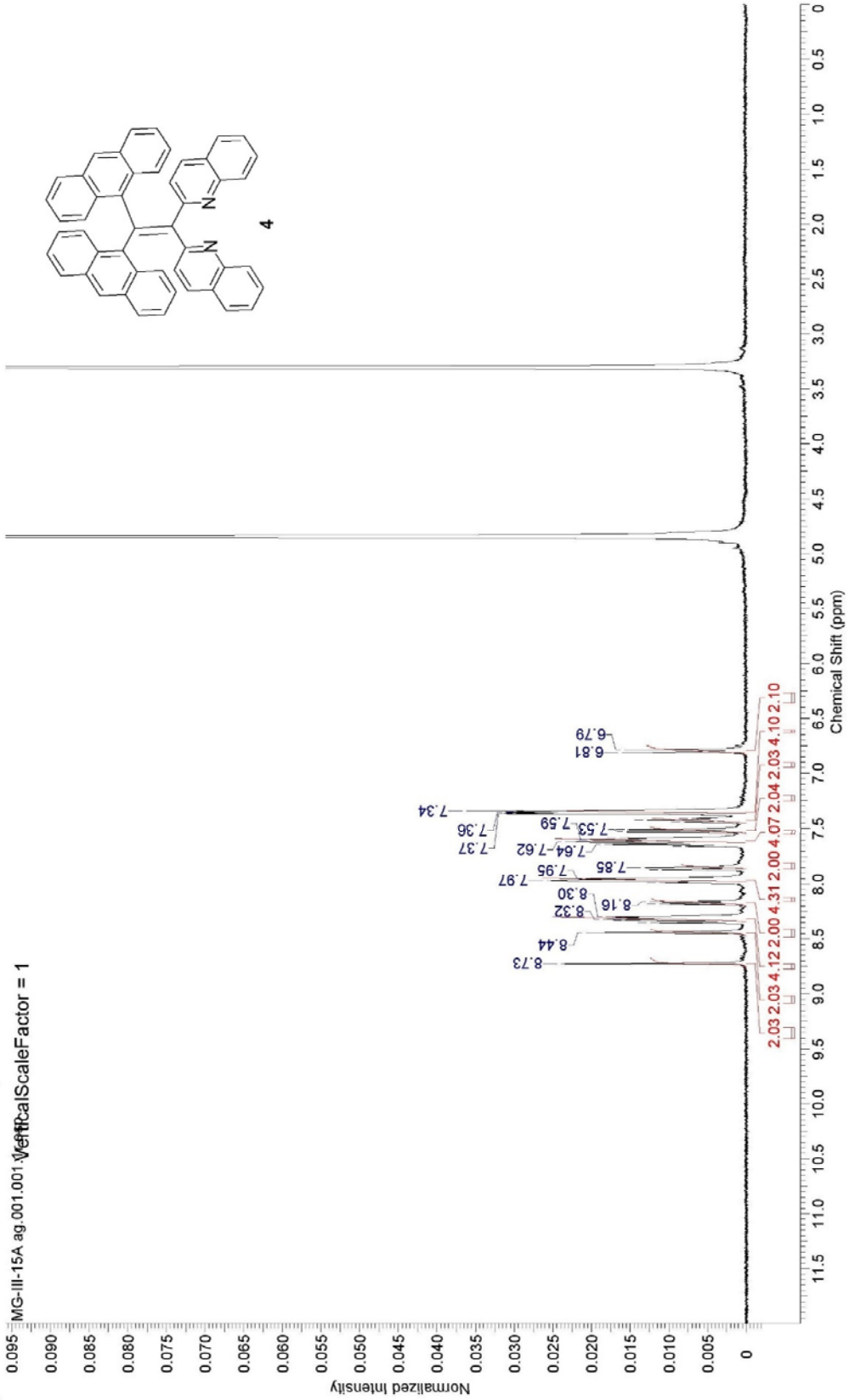

% Transmittance
Wavenumbers (cm-1)
3019.21
2400.00
2023.88
1920.37
1891.29
1521.35
1425.92
1030.08
928.70
450.66
12

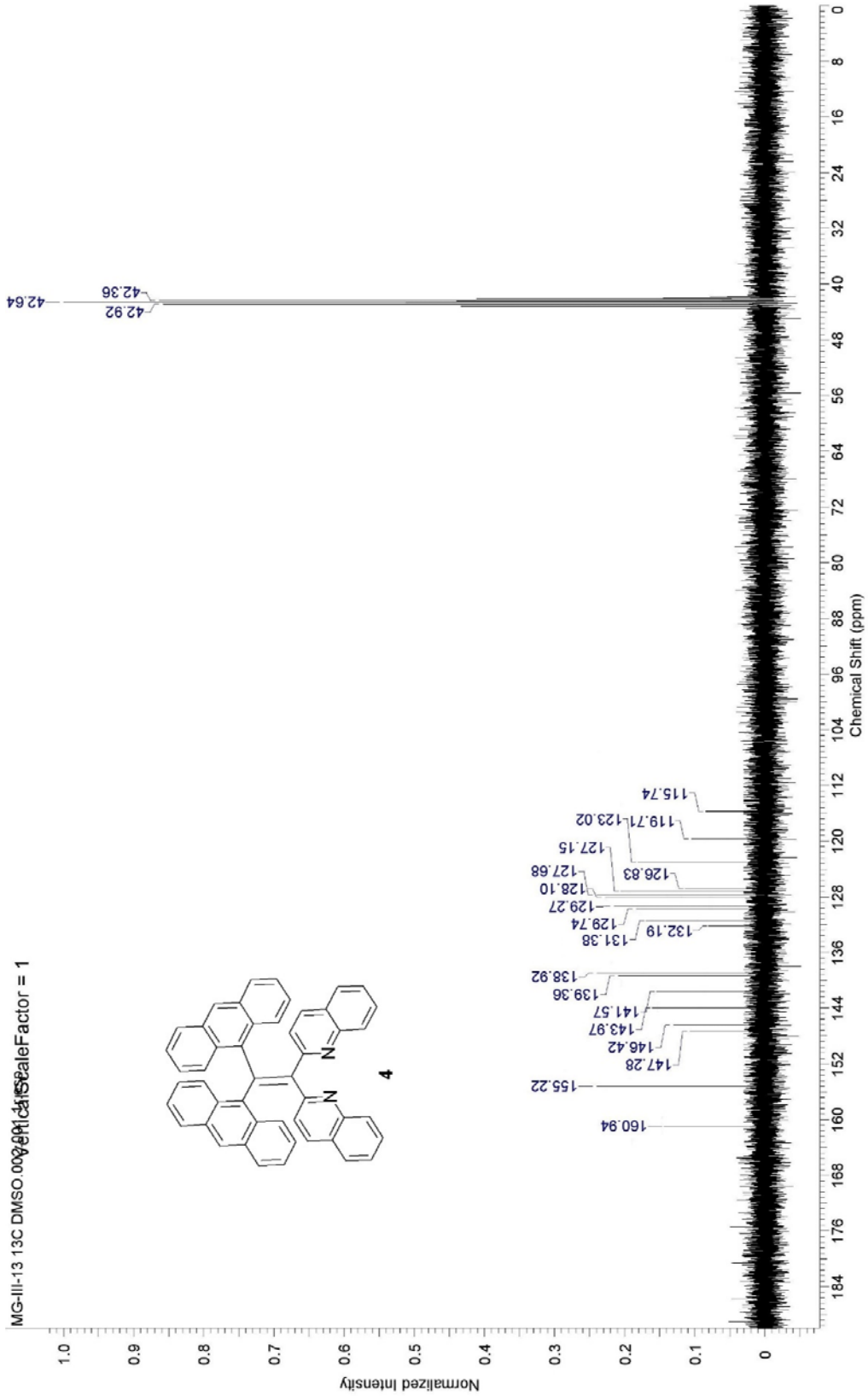

MG-III-61 1H.001.001.1r verticalScaleFactor = 1
7.19
7.39
7.41
7.21
7.17
7.98
7.96
7.77
7.79
7.75
7.73
7.63 7.52
2.01 4.01 2.01 2.00 4.02 6.00
Normalized Intensity
Chemical Shift (ppm)
NC
CN
N
N
2

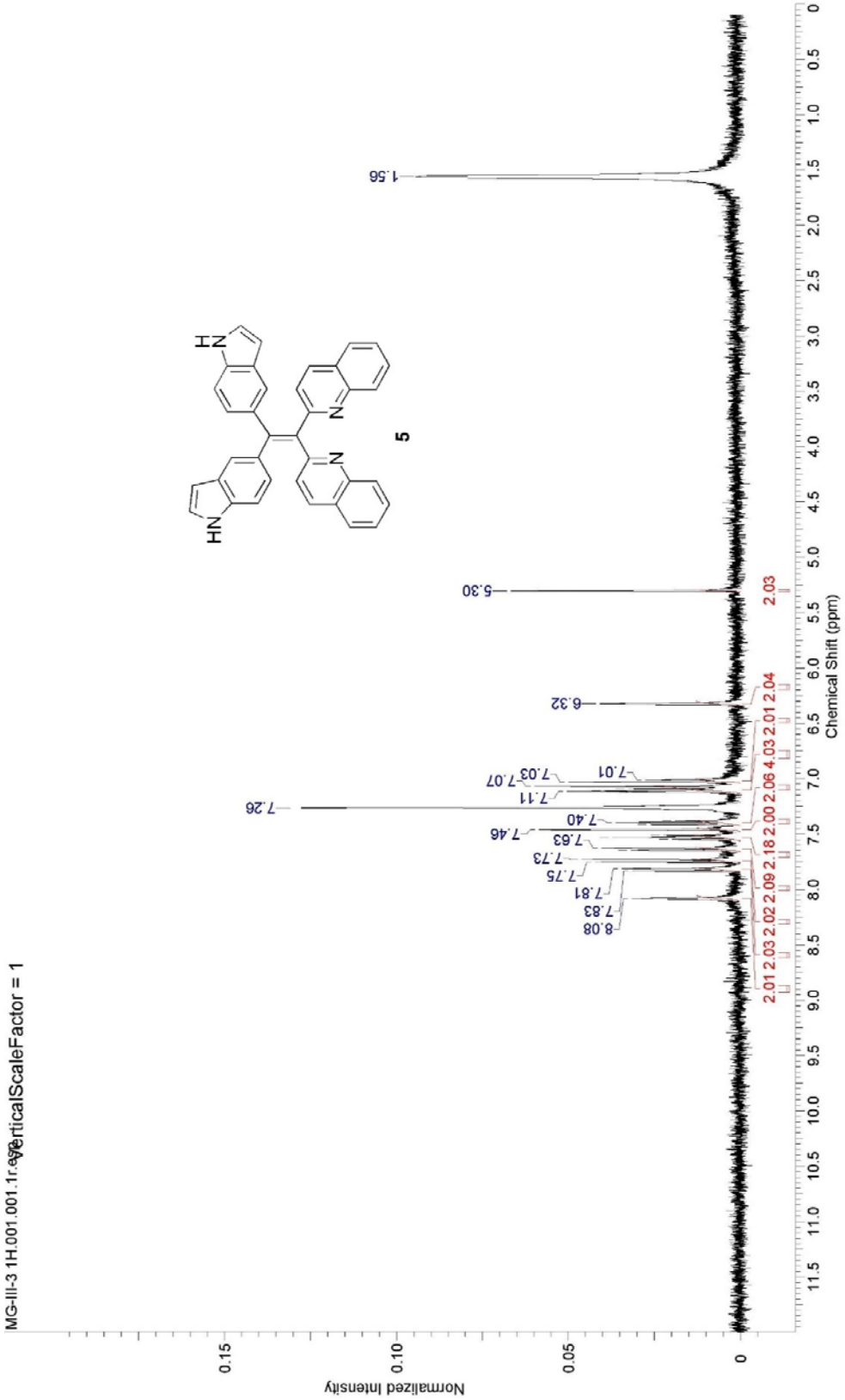

MG-III-61 13C.002.001.1.esm
VerticalScaleFactor = 1
NC
CN
N
N
2
78.50
78.18
77.86
112.31
119.59
124.69
127.83
128.56
130.54
132.94
132.57
137.06
143.85
145.60
147.42
148.94
160.31
Chemical Shift (ppm)
Normalized Intensity

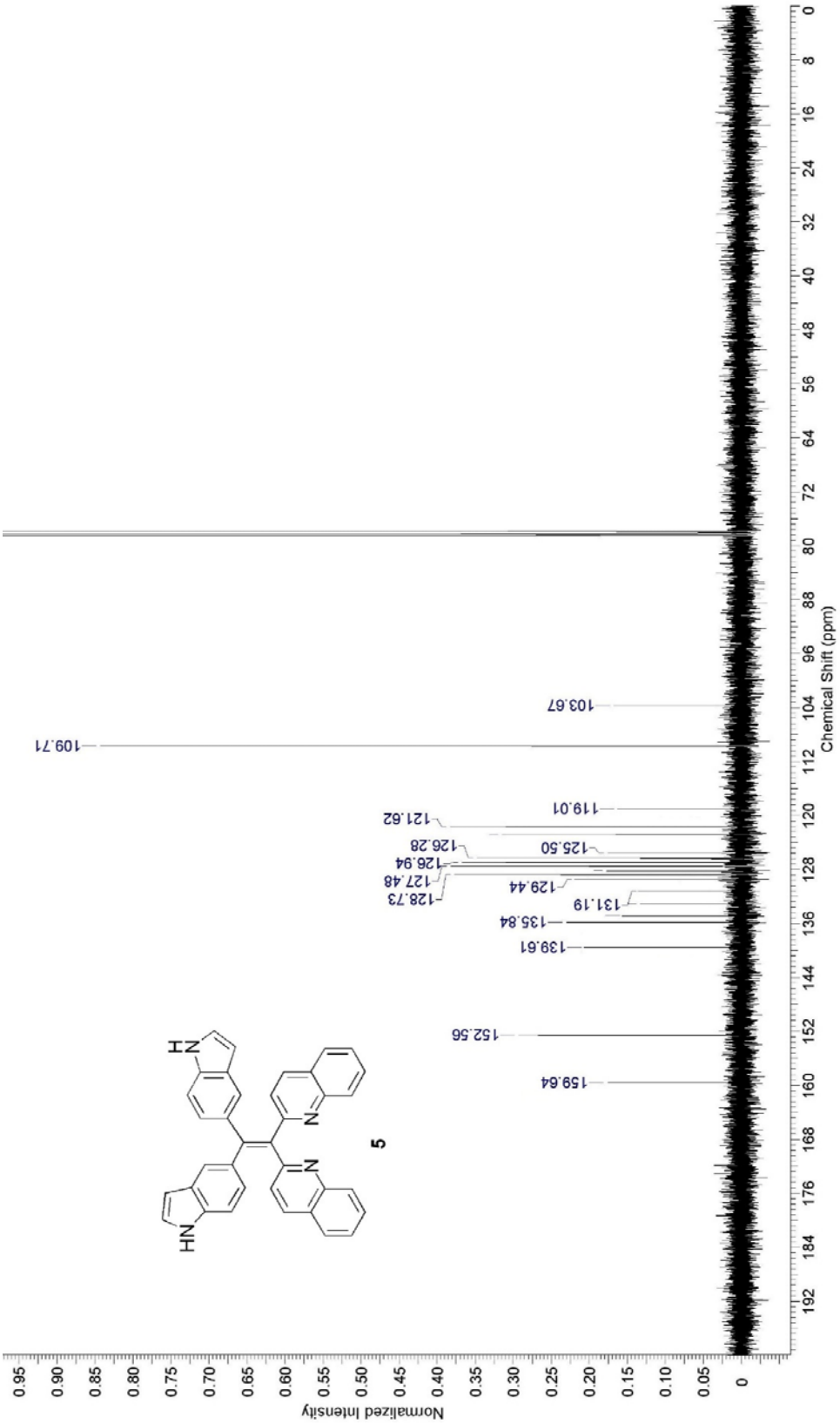

MG-III-35 1H.001.001.1rg VerticalScaleFactor = 1
Normalized Intensity
Chemical Shift (ppm)
3
3.74
6.00
2.00 2.01 4.09 2.00 2.08 10.06 4.03
7.96
7.86
7.38
7.77
7.37
7.53 7.60
7.36
7.33
7.33
7.31
7.07
7.11
7.09

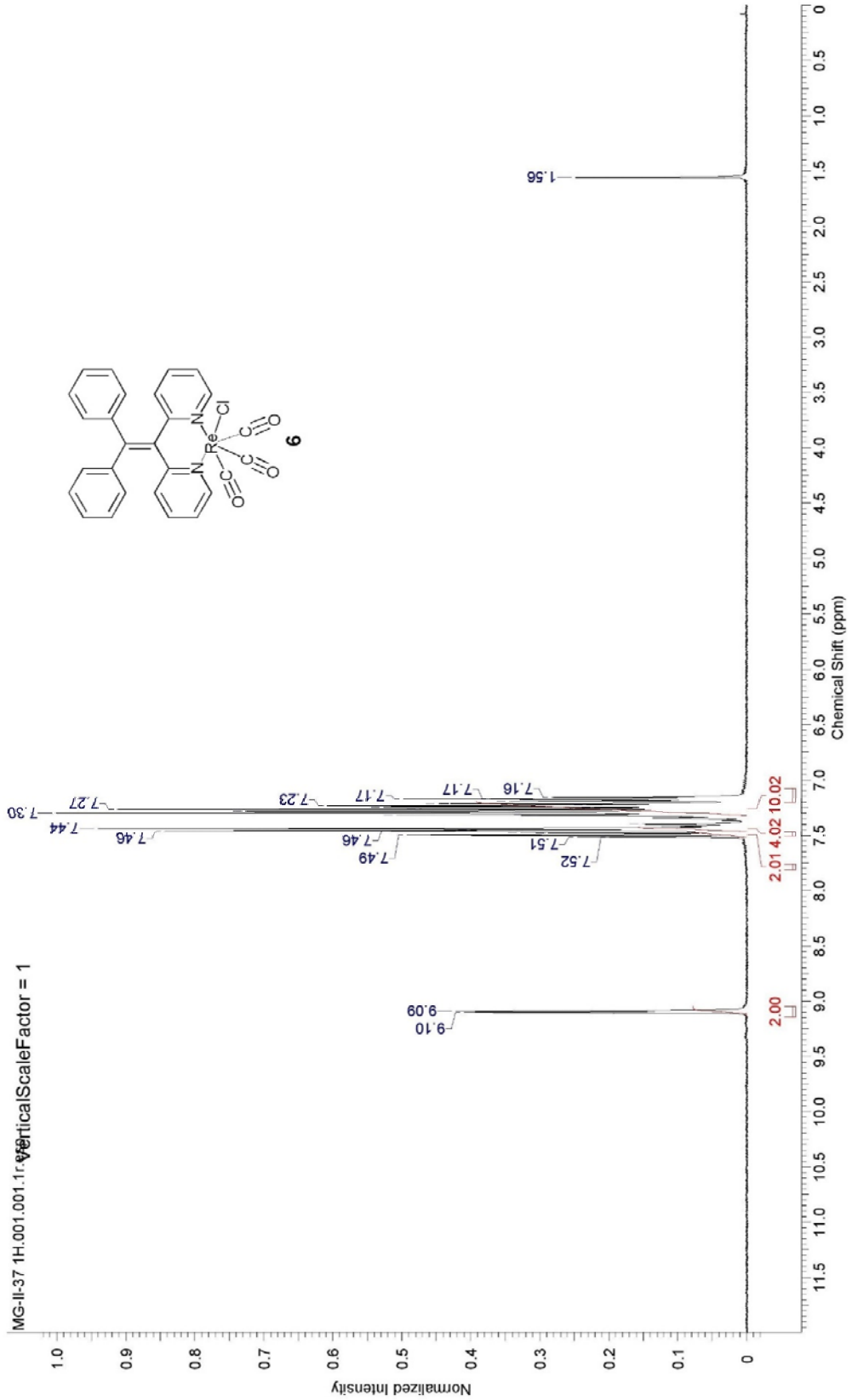

MG-III-35 13C.002.001.1.ver
VerticalScaleFactor = 1
3
N
N
N
N
Normalized Intensity
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
Chemical Shift (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
25.94
78.45
78.13
77.81
108.84
109.51
120.10
121.48
124.76
126.78
126.84
123.53
128.43
129.69
130.47
130.92
136.00
140.63
141.53
142.32
149.21
149.27
164.48

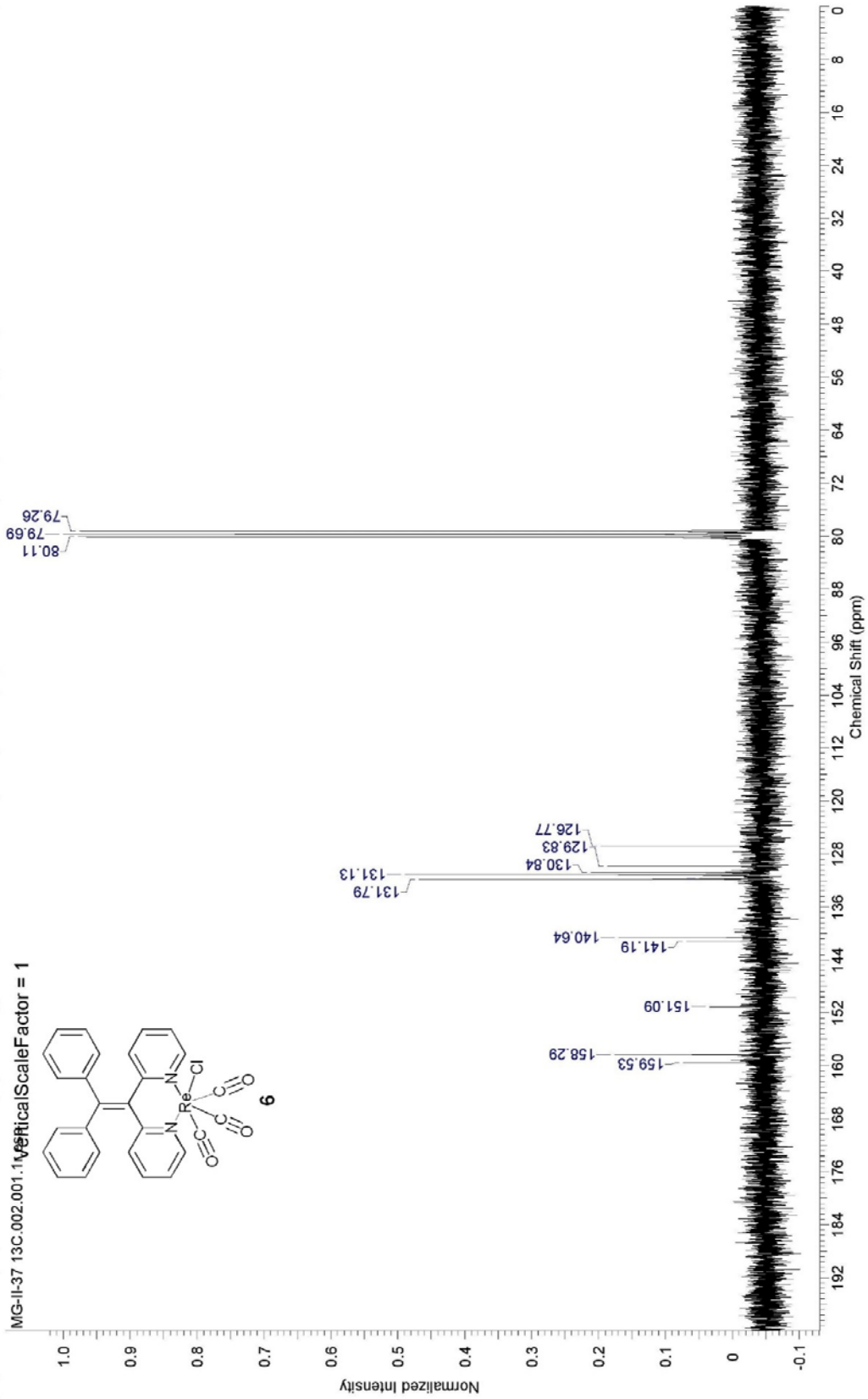

MG-III-15A ag.001.001.1r
Vertical Scale Factor = 1
Normalized Intensity
Chemical Shift (ppm)
8.73
8.44
8.32
8.30
8.16
7.97
7.95
7.85
7.64
7.62
7.59
7.53
7.37
7.36
7.34
6.81
6.79
2.03 2.03 4.12 2.00 4.31 2.00 4.07 2.04 2.03 4.10 2.10
N
N
4

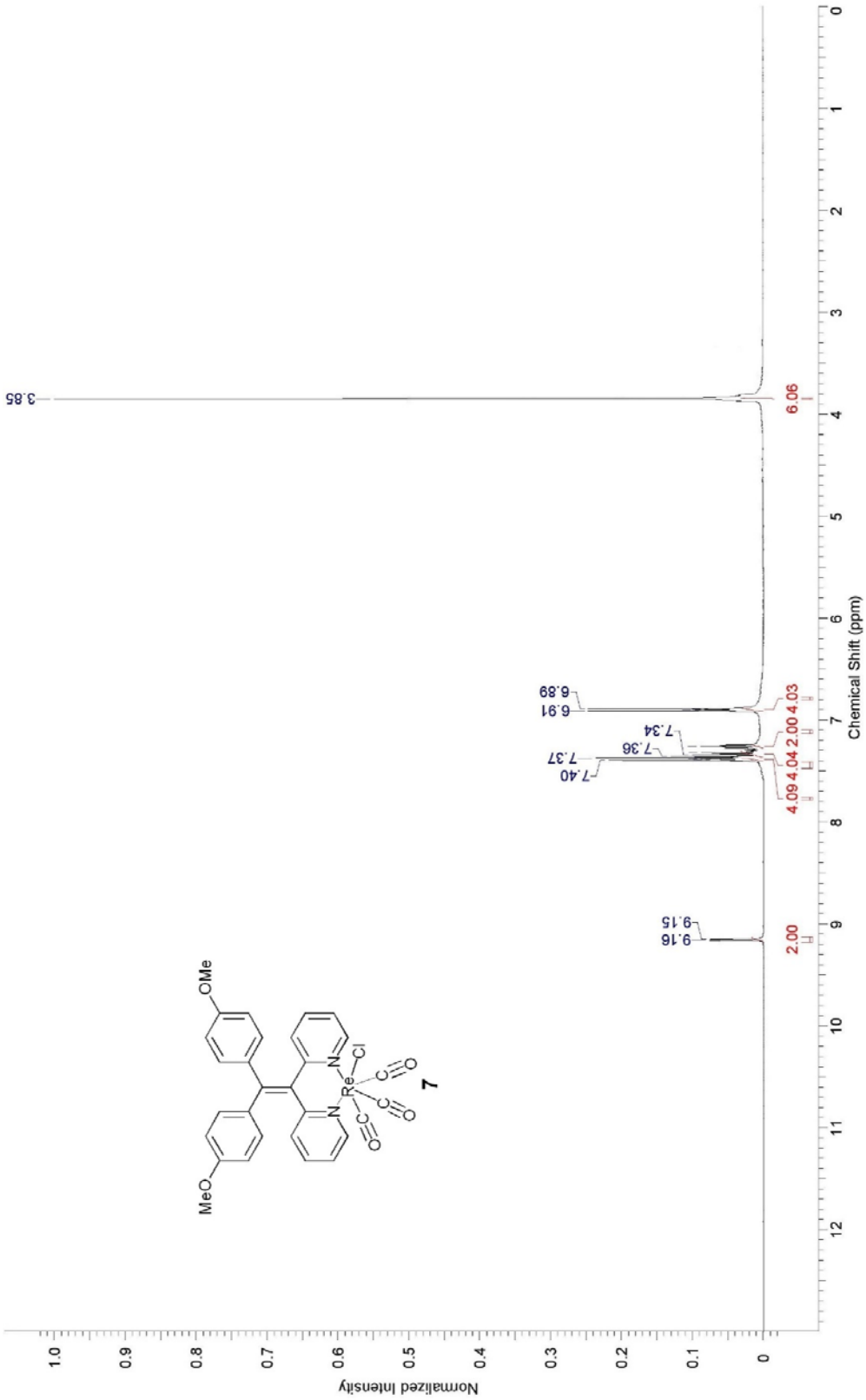

MG-III-13 13C DMSO.002.001.dx
Vertical Scale Factor = 1
4
N
N
42.64
42.36
42.92
160.94
155.22
147.28
146.42
143.97
141.57
139.36
138.92
132.19
131.38
129.74
129.27
128.10
127.68
126.83
127.15
119.71
123.02
115.74
Normalized Intensity
Chemical Shift (ppm)

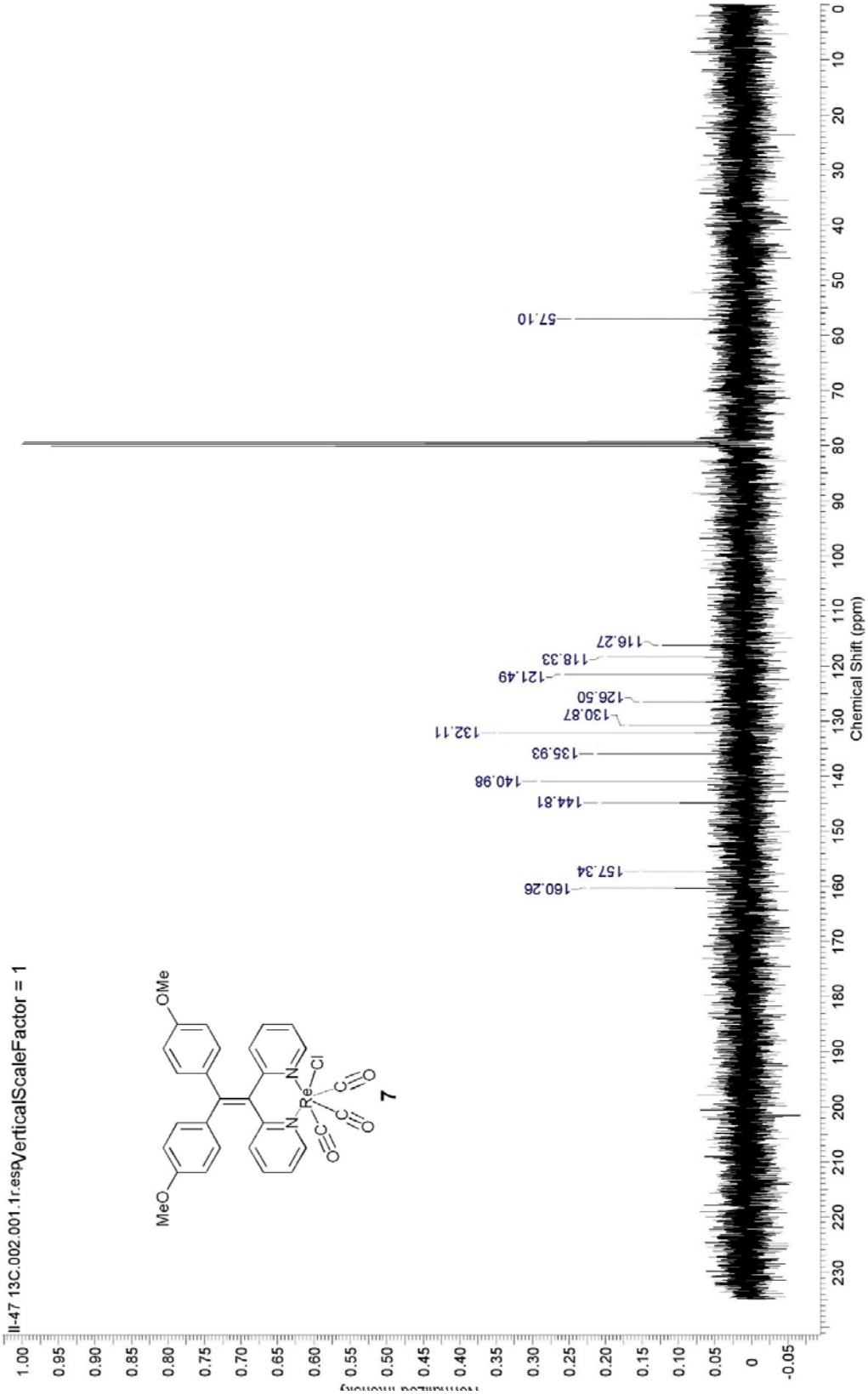

MG-III-3 1H.001.001.1r.esp VerticalScaleFactor = 1
Normalized Intensity
Chemical Shift (ppm)
5
1.56
5.30
6.32
7.26
7.01
7.03
7.07
7.11
7.40
7.46
7.63
7.73
7.75
7.81
7.83
8.08
2.01 2.03 2.02 2.09 2.18 2.00 2.06 4.03 2.01 2.04
2.03

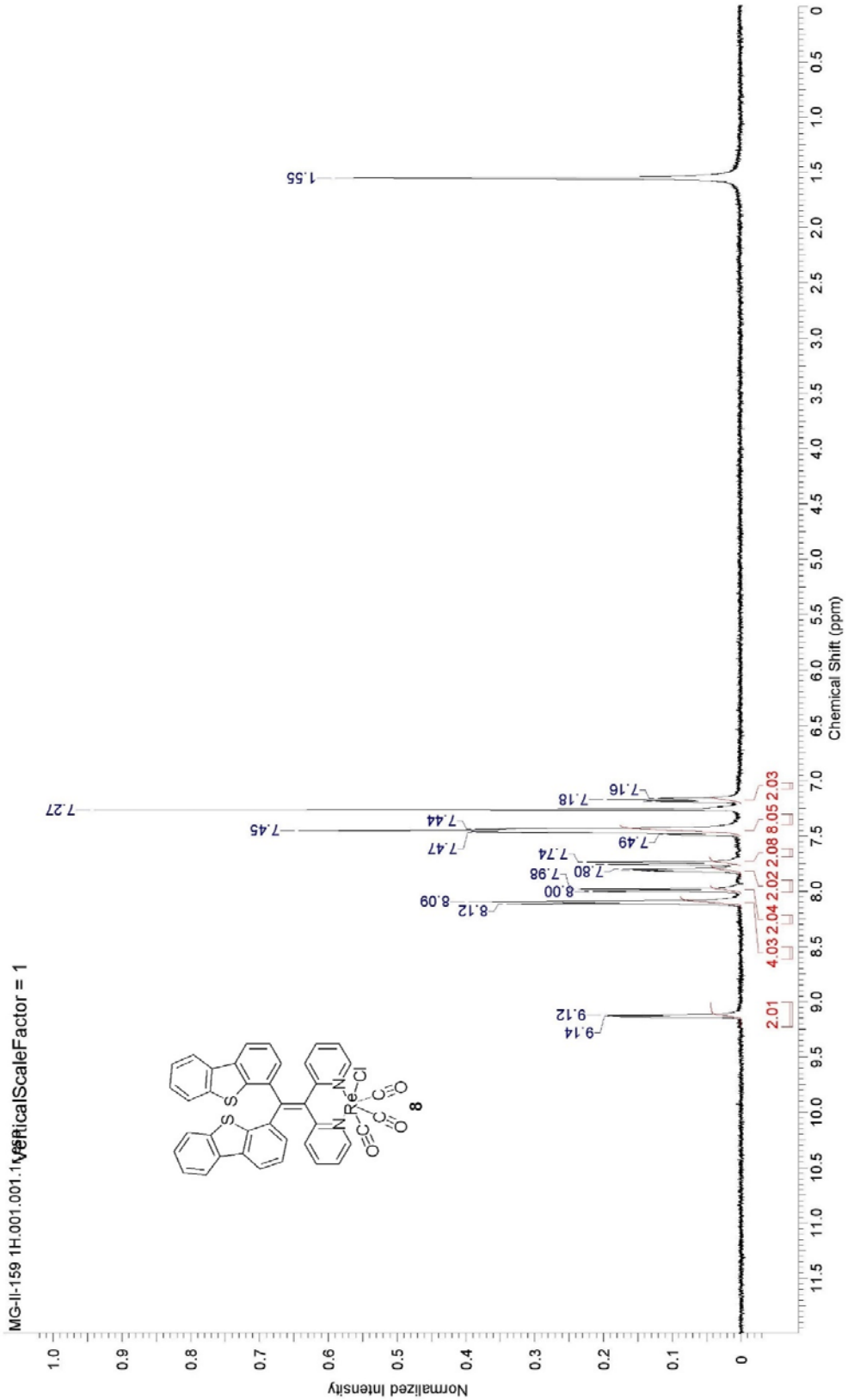

Normalized Intensity
Chemical Shift (ppm)
109.71
103.67
119.01
121.62
125.50
126.28
126.94
127.48
128.73
129.44
131.19
135.84
139.61
152.56
159.64
5

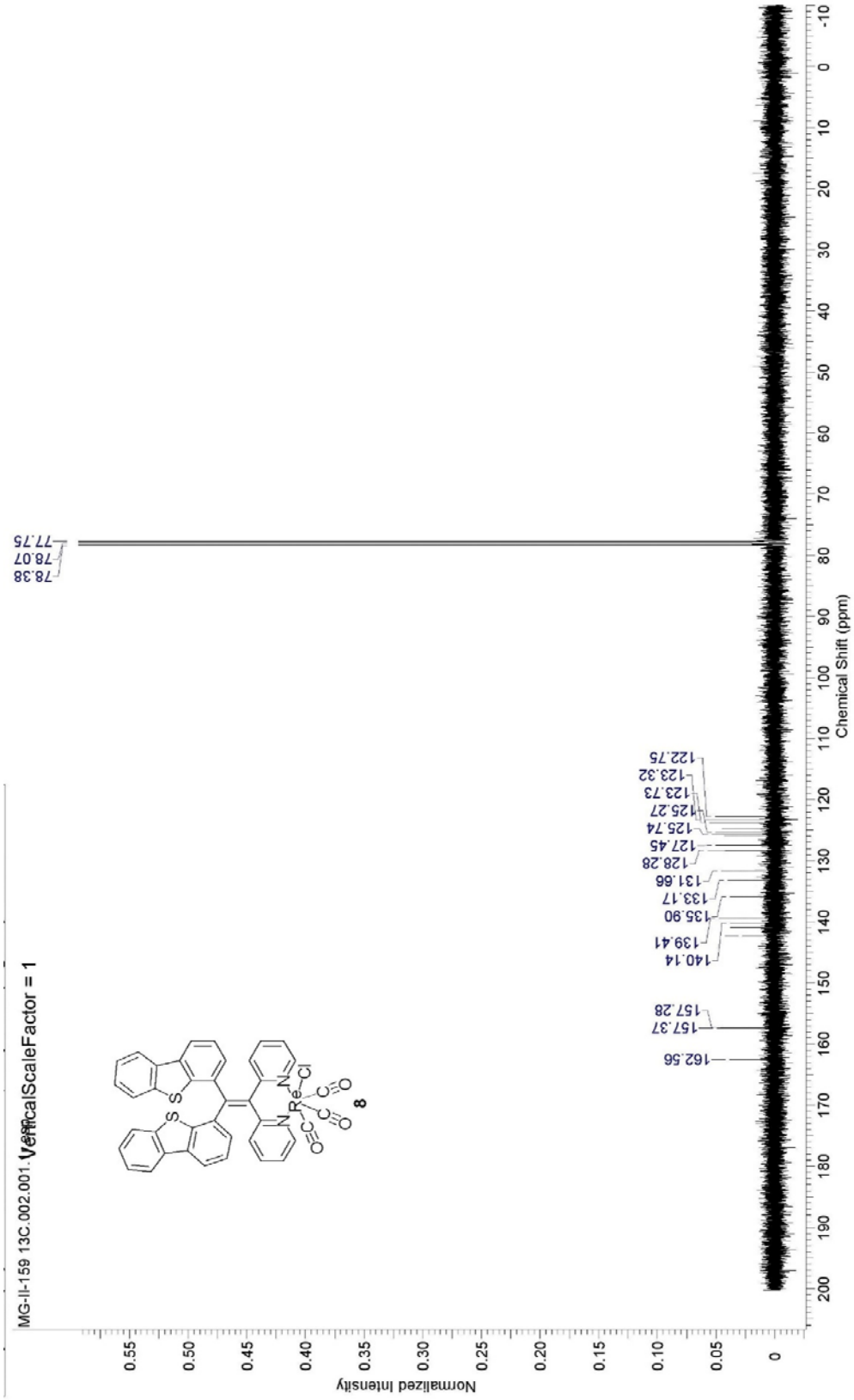

MG-II-37 1H.001.001.1r.esp VerticalScaleFactor = 1
Normalized Intensity
Chemical Shift (ppm)
9.10
9.09
7.52
7.51
7.49
7.46
7.46
7.44
7.30
7.27
7.23
7.17
7.16
1.56
2.00
2.01
4.02
10.02
Re
Cl
N
N
C
O
9

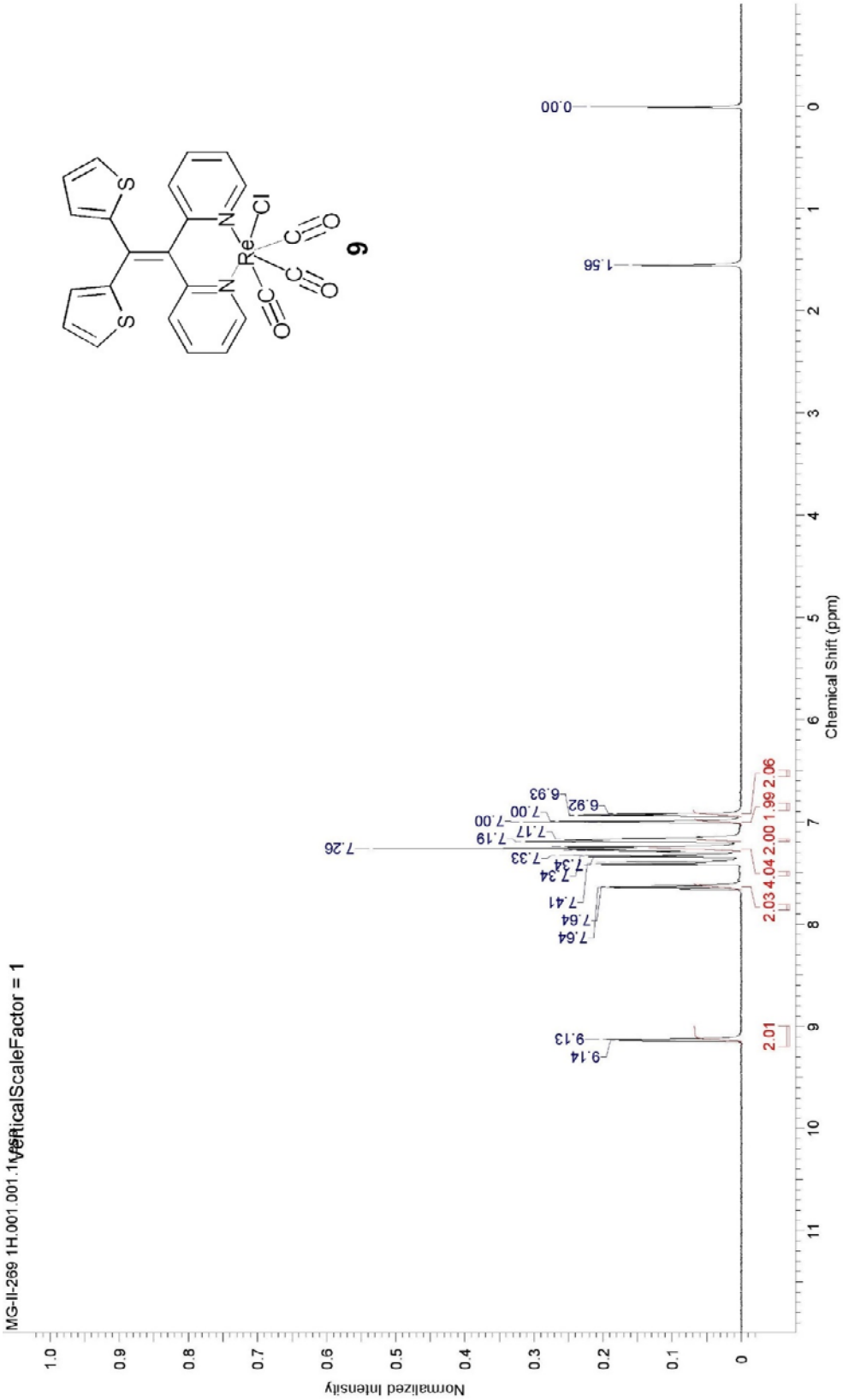

MG-II-37 13C.002.001.1.fid
VerticalScaleFactor = 1
9
Re
Cl
N
N
C
O
Normalized Intensity
Chemical Shift (ppm)
80.11
79.69
79.26
131.79
131.13
130.84
129.83
126.77
141.19
140.64
151.09
159.53
158.29

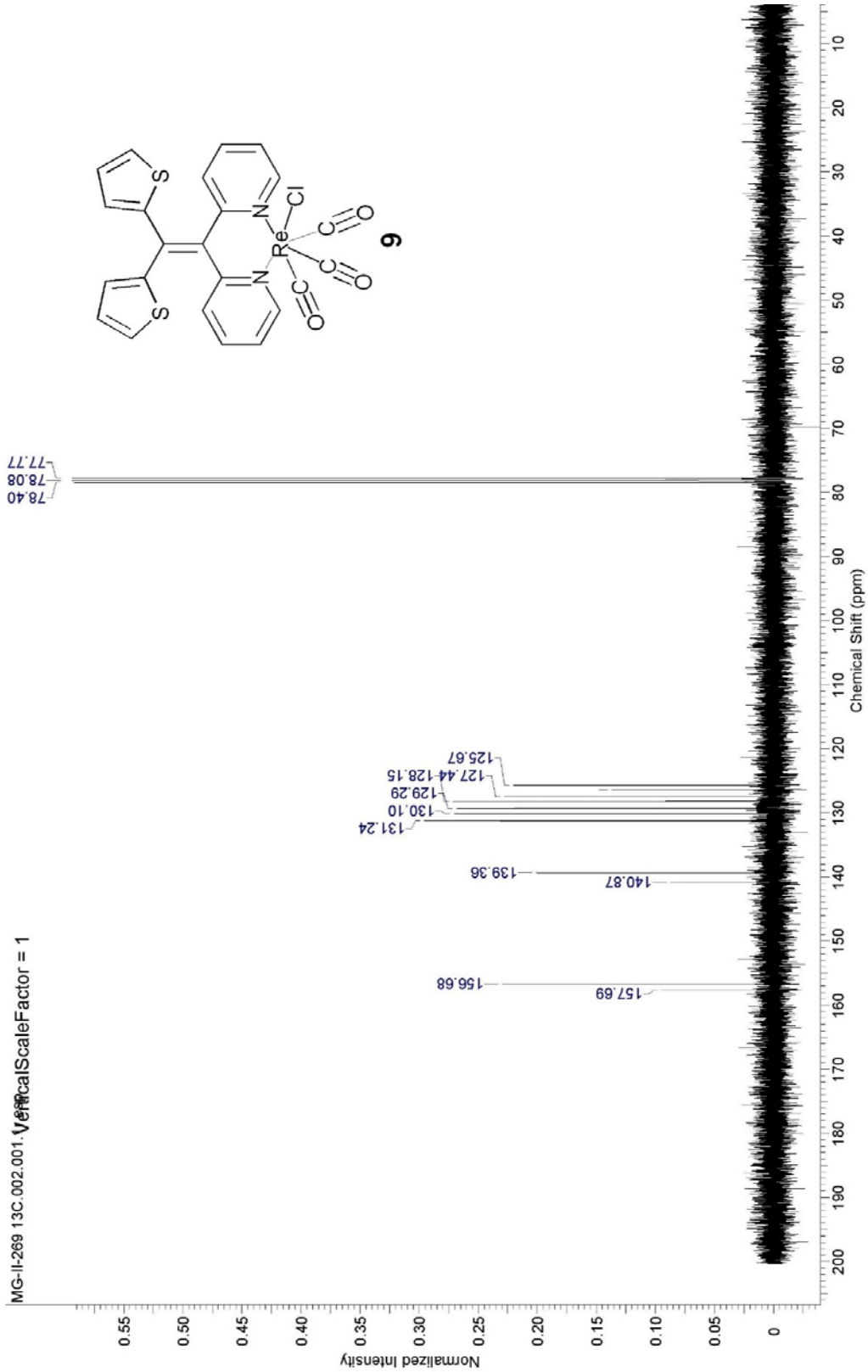

Normalized Intensity
Chemical Shift (ppm)
3.85
6.06
6.91
6.89
7.40
7.37
7.36
7.34
4.09
4.04
2.00
4.03
9.16
9.15
2.00
MeO
OMe
Re
Cl
N
N
C
O
7

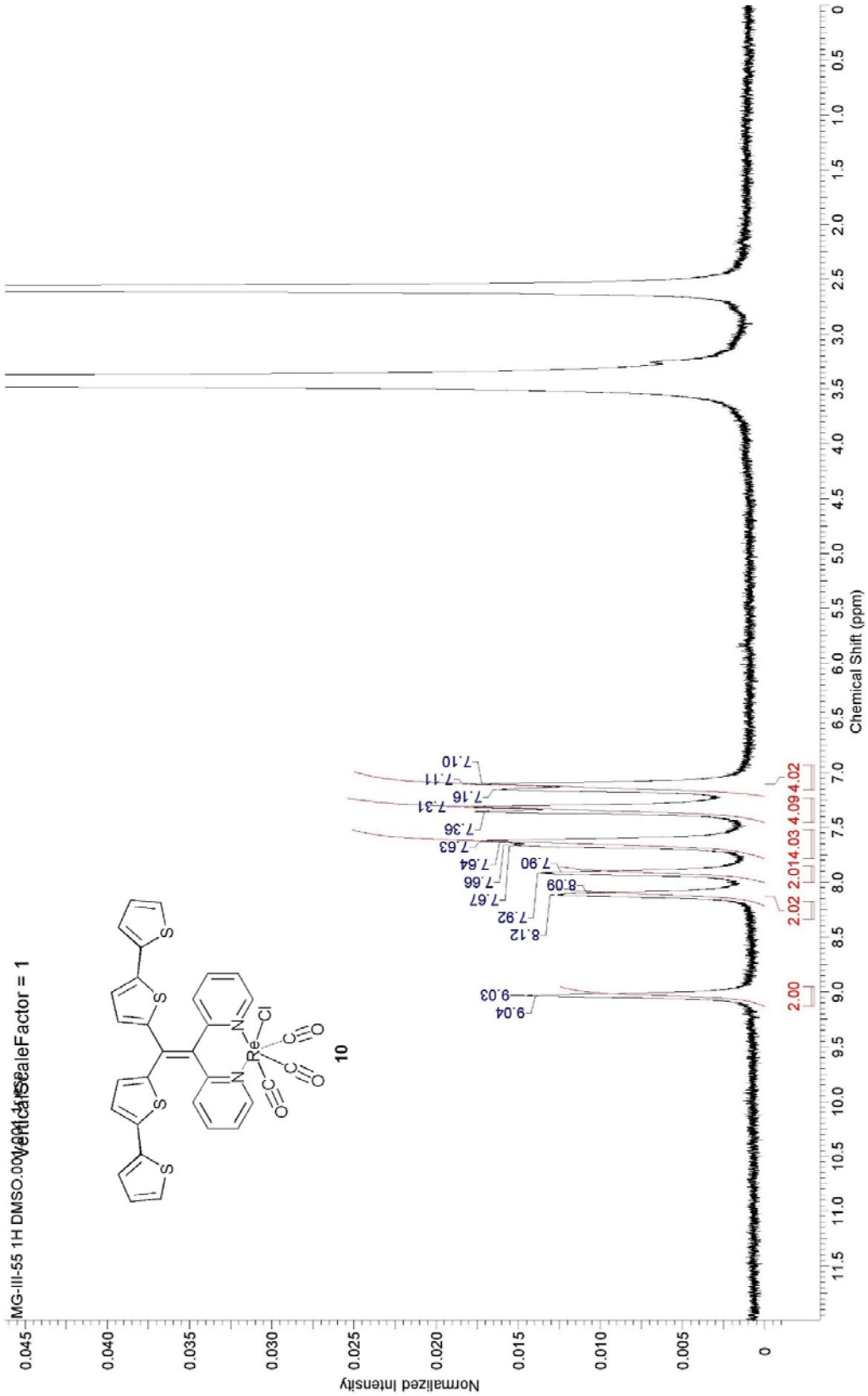

II-47 13C.002.001.1r.esp VerticalScaleFactor = 1
MeO
OMe
N
N
Re
Cl
C
O
7
57.10
116.27
118.33
121.49
126.50
130.87
132.11
135.93
140.98
144.81
157.34
160.26
Chemical Shift (ppm)
Normalized Intensity

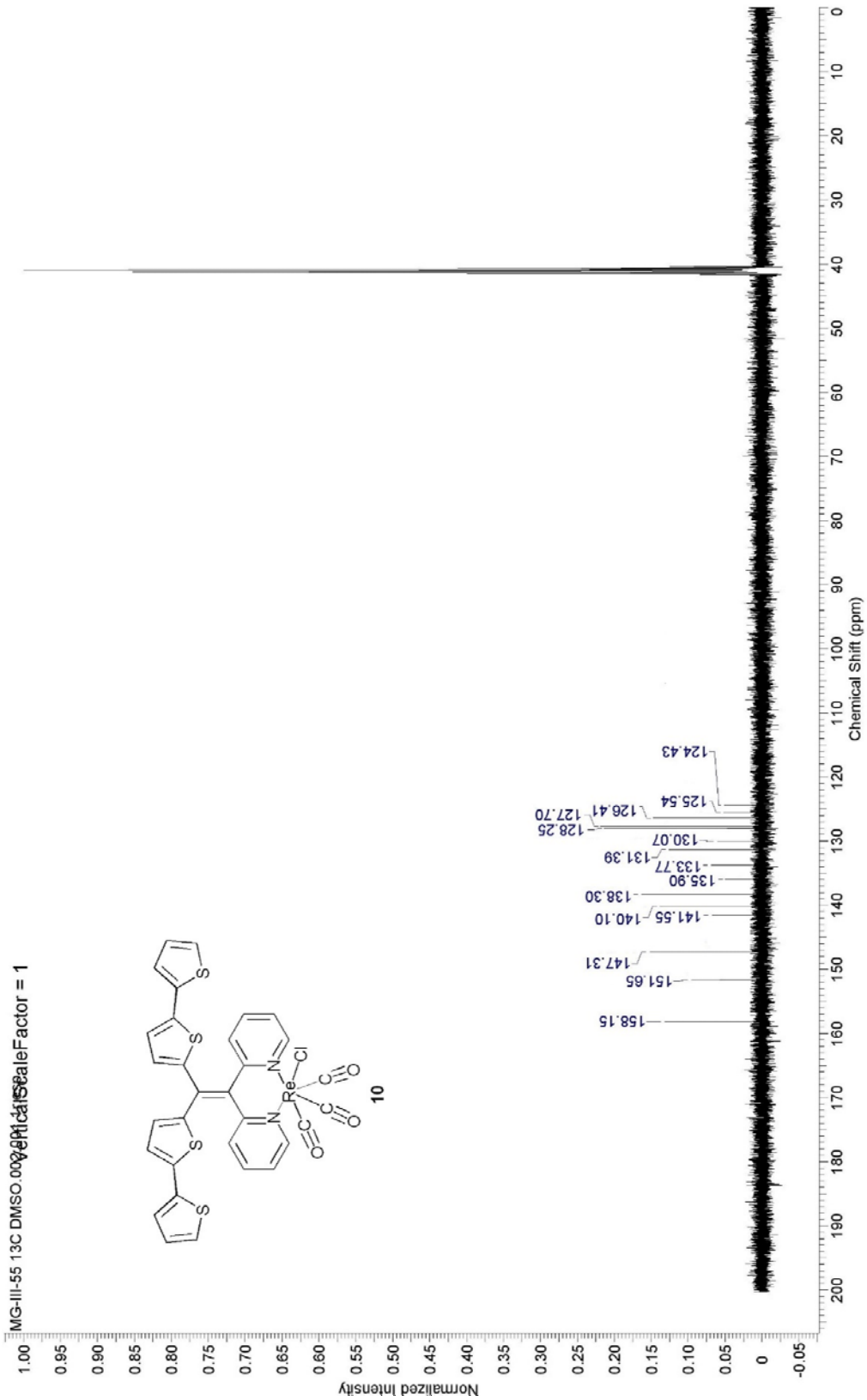

MG-II-159 1H.001.001.1.1.esp
VerticalScaleFactor = 1
Normalized Intensity
Chemical Shift (ppm)
1.55
7.27
7.45
7.44
7.47
7.49
7.74
7.80
7.98
8.00
8.09
8.12
9.12
9.14
7.16
7.18
2.01
4.03
2.04
2.02
2.08
8.05
2.03
8

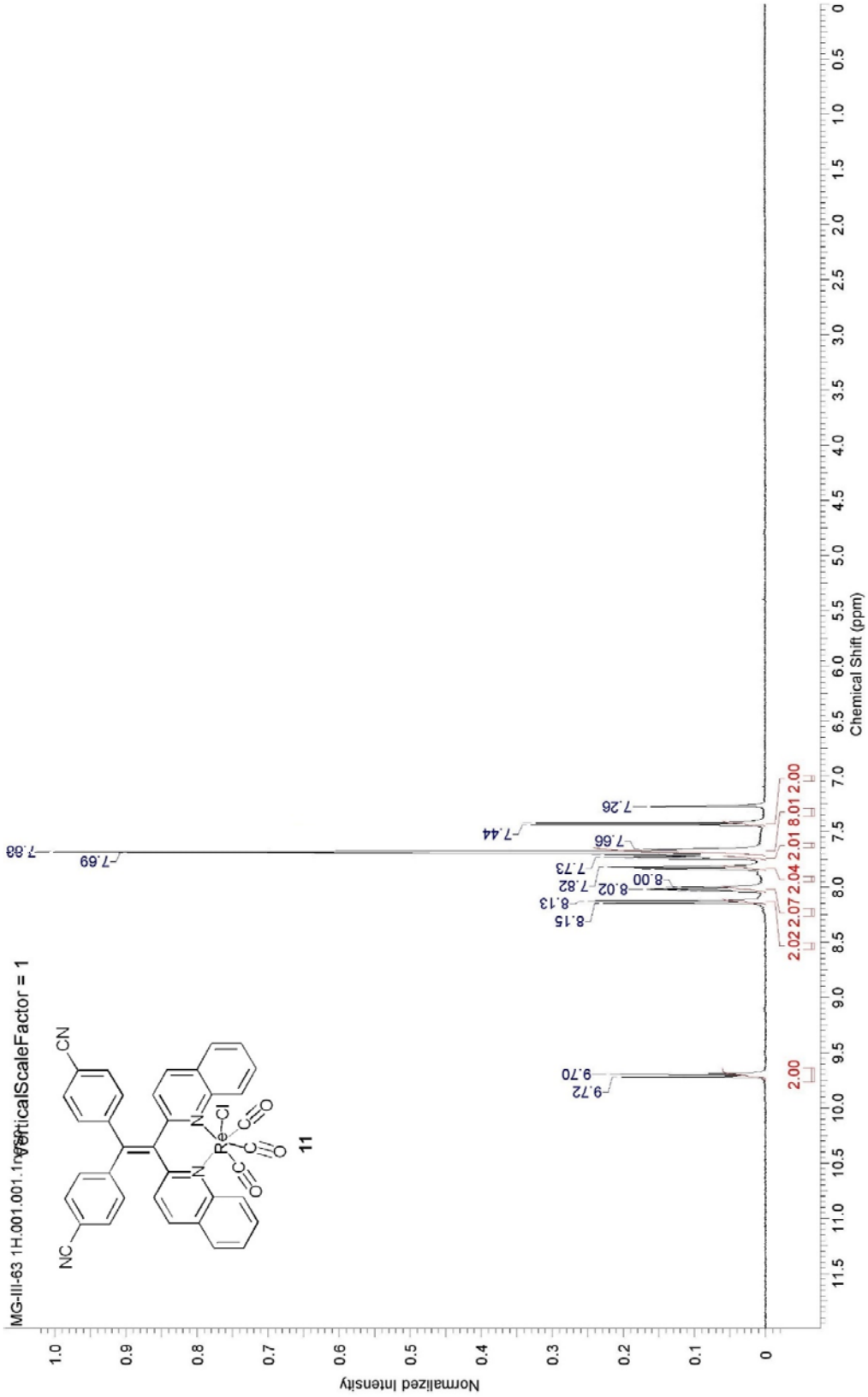

MG-II-159 13C.002.001
VerticalScaleFactor = 1
8
Normalized Intensity
Chemical Shift (ppm)
78.38
78.07
77.75
162.56
157.37
157.28
140.14
139.41
135.90
133.17
131.66
128.28
127.45
125.74
125.27
123.73
123.32
122.75

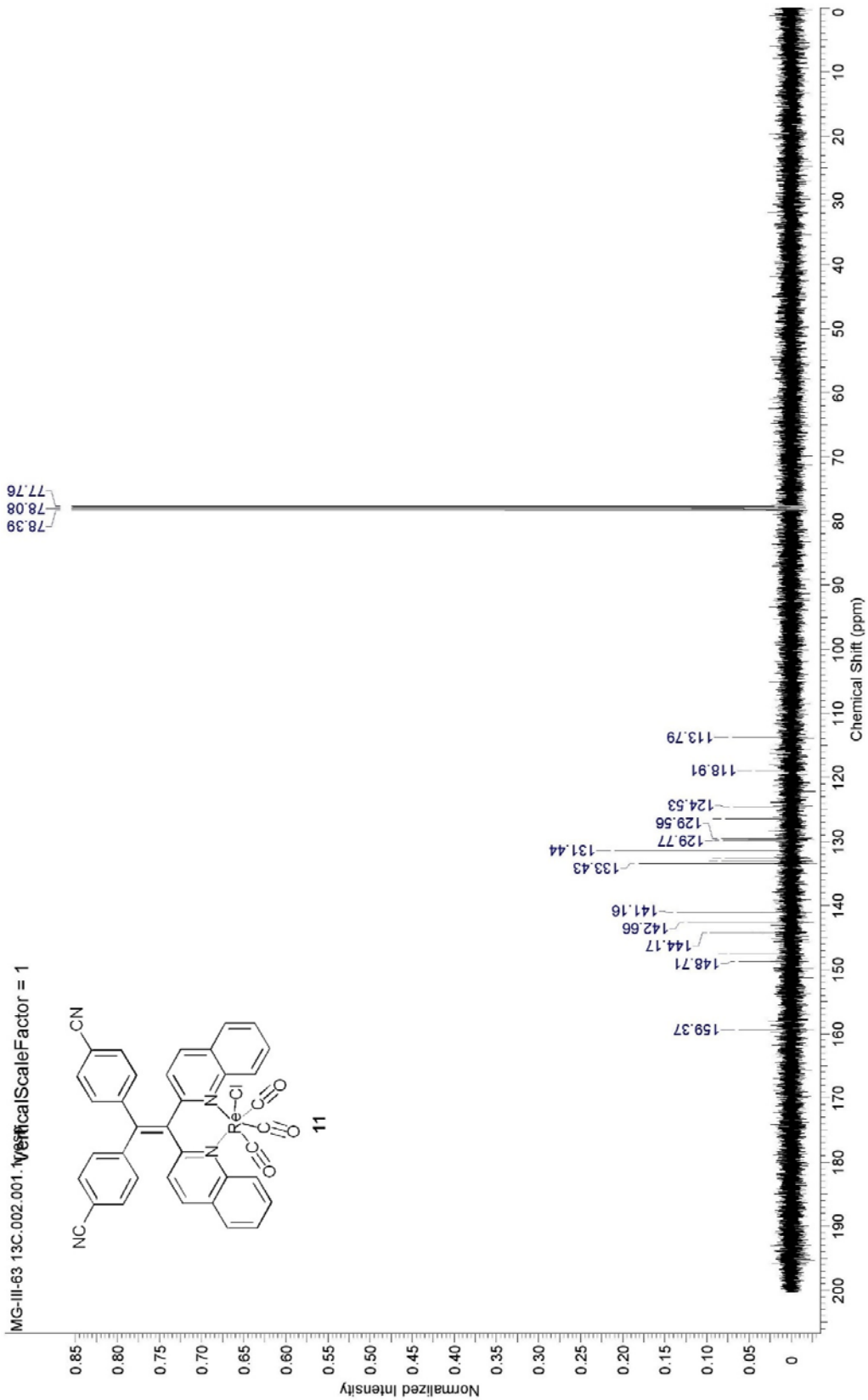

MG-II-269 1H.001.001.1.fid
VerticalScaleFactor = 1
Normalized Intensity
Chemical Shift (ppm)
9.14
9.13
7.64
7.64
7.41
7.34
7.34
7.33
7.26
7.19
7.17
7.00
6.92
6.93
1.56
0.00
2.01
2.03
4.04
2.00
1.99
2.06
Re
Cl
N
N
S
S
C
O
6

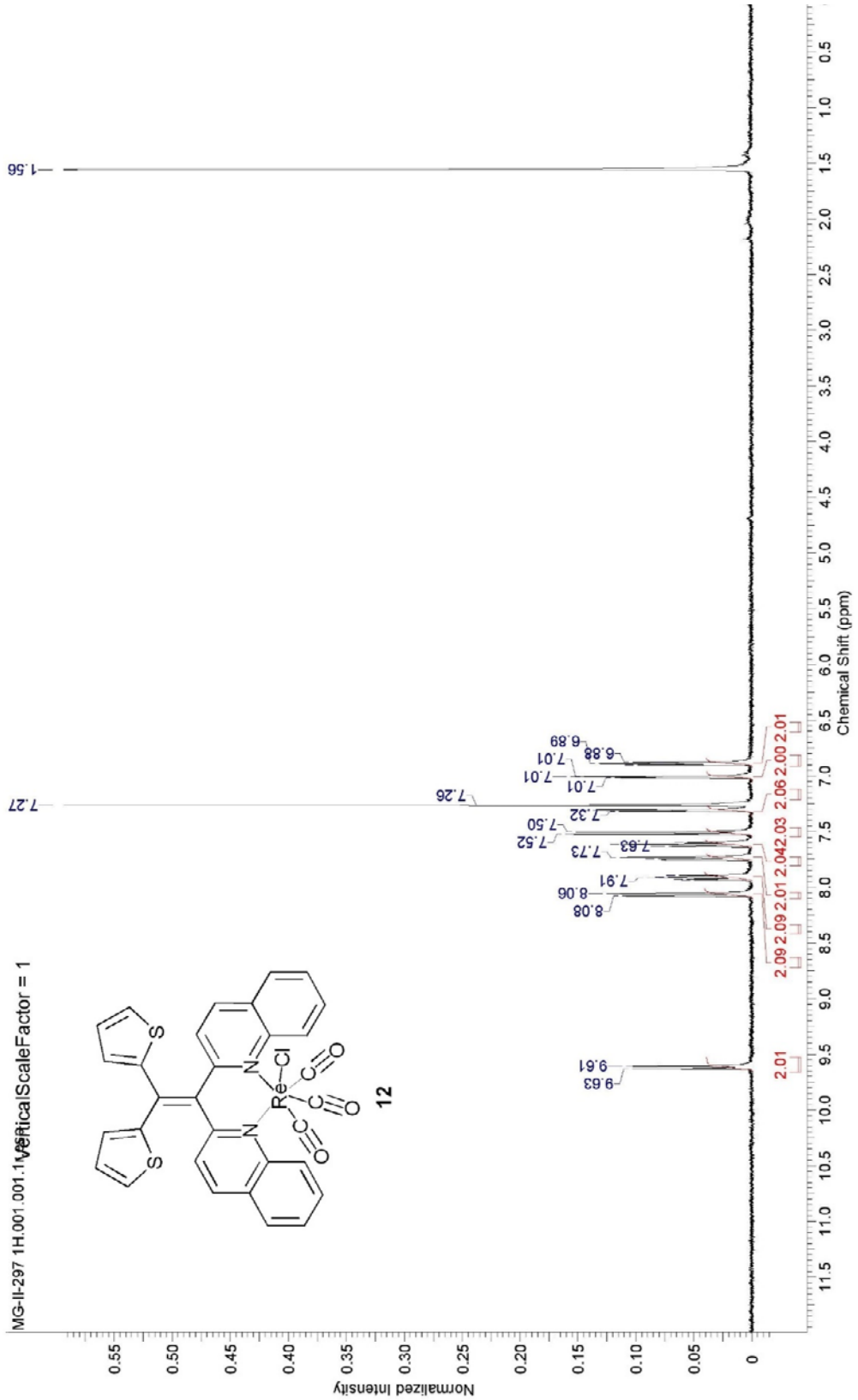

MG-II-269 13C.002.001.
VerticalScaleFactor = 1
Normalized Intensity
Chemical Shift (ppm)
78.40
78.08
77.77
131.24
130.10
129.29
127.44
128.15
125.67
139.36
140.87
156.68
157.69
9
Re
Cl
N
N
S
S
C
O

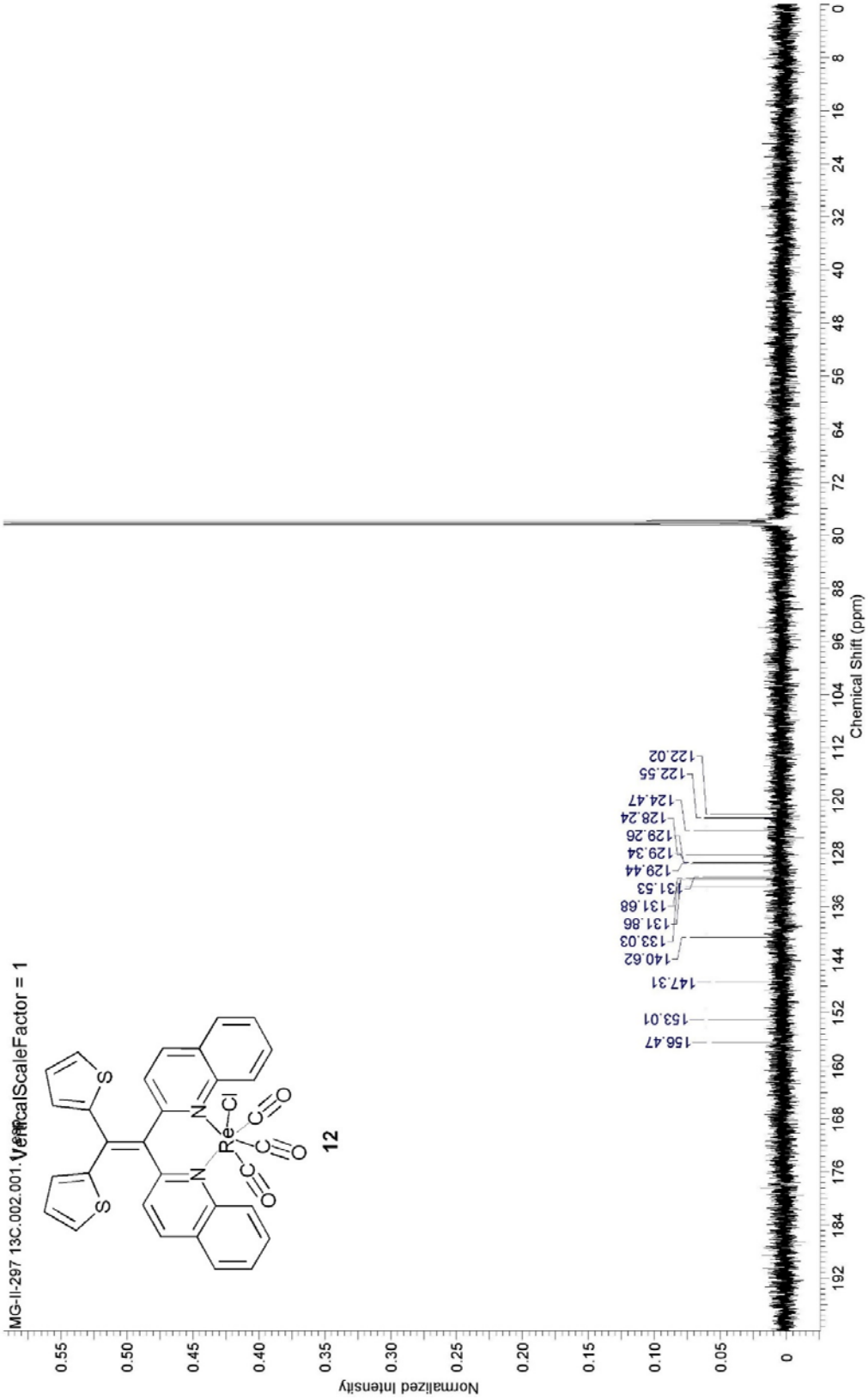

MG-III-55 1H DMSO.001.001.1r.esa
Vertical Scale Factor = 1
10
Normalized Intensity
Chemical Shift (ppm)
9.04
9.03
8.12
7.92
8.09
7.67
7.66
7.90
7.64
7.63
7.36
7.31
7.16
7.11
7.10
2.00
2.02
2.01
4.03
4.09
4.02

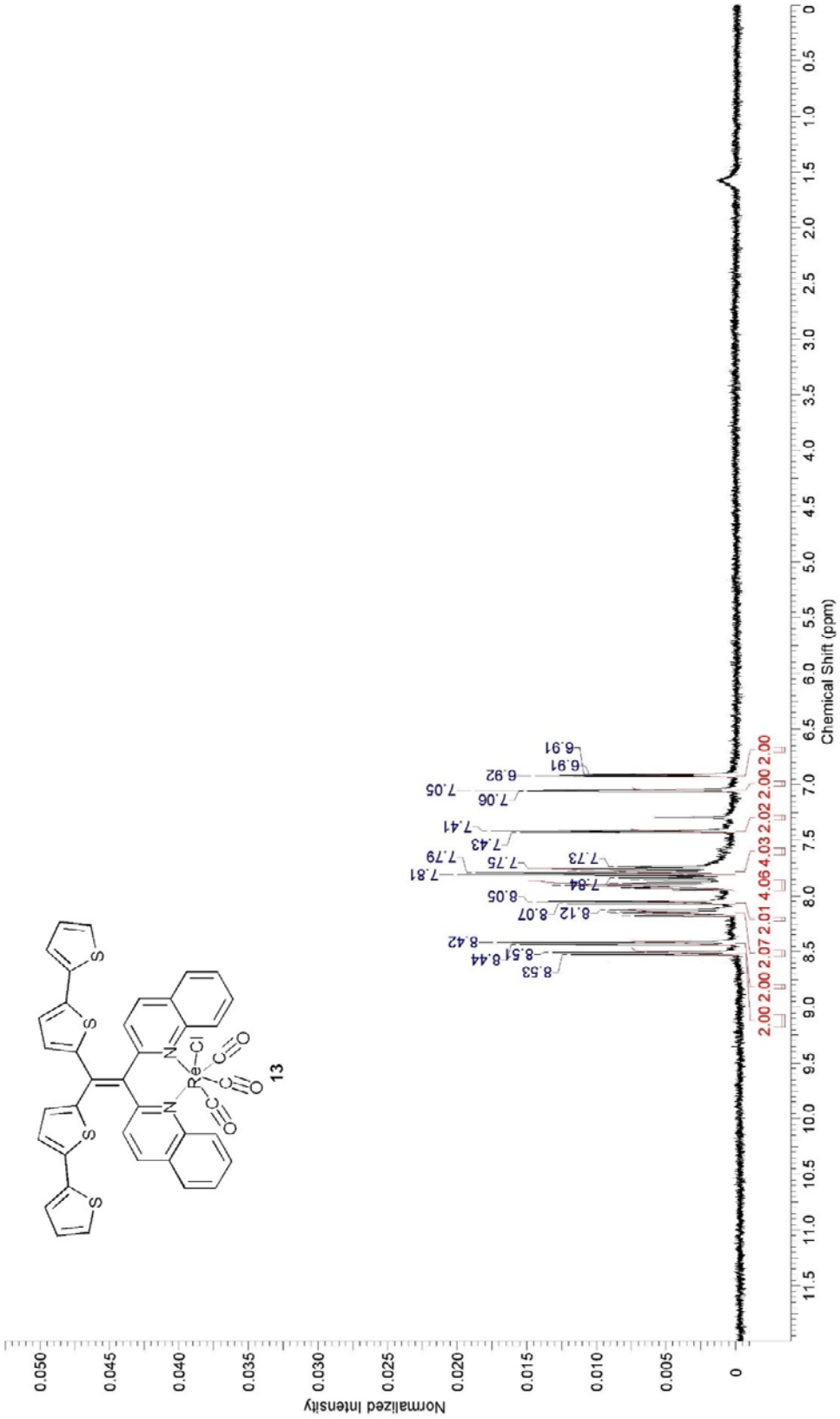

MG-III-55 13C DMSO.002.001.csv
VerticalScaleFactor = 1
10
Normalized Intensity
Chemical Shift (ppm)
158.15
151.65
147.31
141.55
140.10
138.30
135.90
133.77
131.39
130.07
128.25
127.70
126.41
125.54
124.43

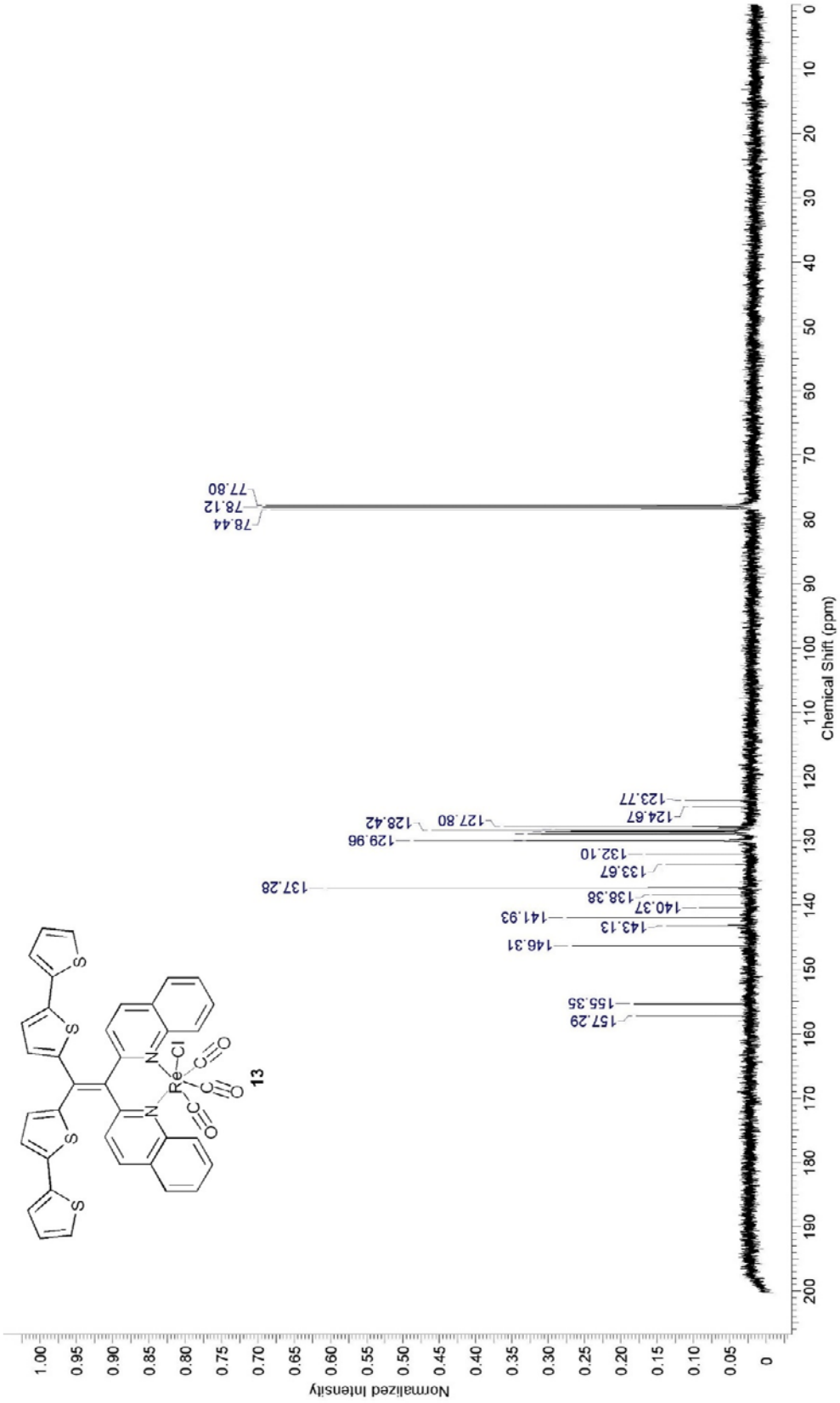

MG-III-63 1H.001.001.1r
VerticalScaleFactor = 1
CN
NC
N
N
Re
Cl
C
O
C
O
C
O
11
9.72
9.70
8.15
8.13
8.02
8.00
7.82
7.73
7.69
7.68
7.66
7.44
7.26
2.00
2.02
2.07
2.04
2.01
8.01
2.00
Normalized Intensity
Chemical Shift (ppm)

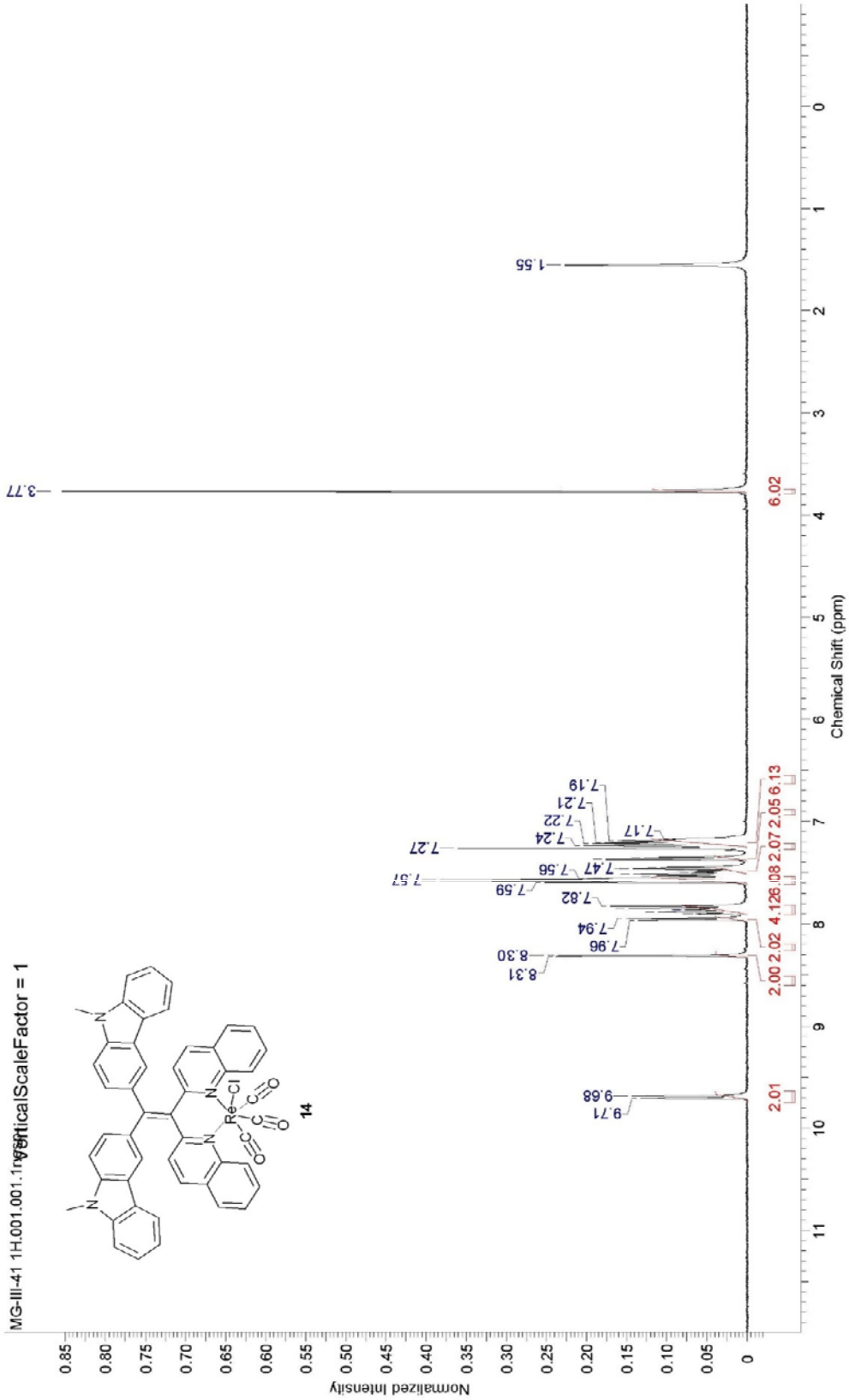

MG-III-63 13C.002.001.1.ver
VerticalScaleFactor = 1
11
Normalized Intensity
Chemical Shift (ppm)
78.39
78.08
77.76
113.79
118.91
124.53
129.56
129.77
131.44
133.43
141.16
142.66
144.17
148.71
159.37

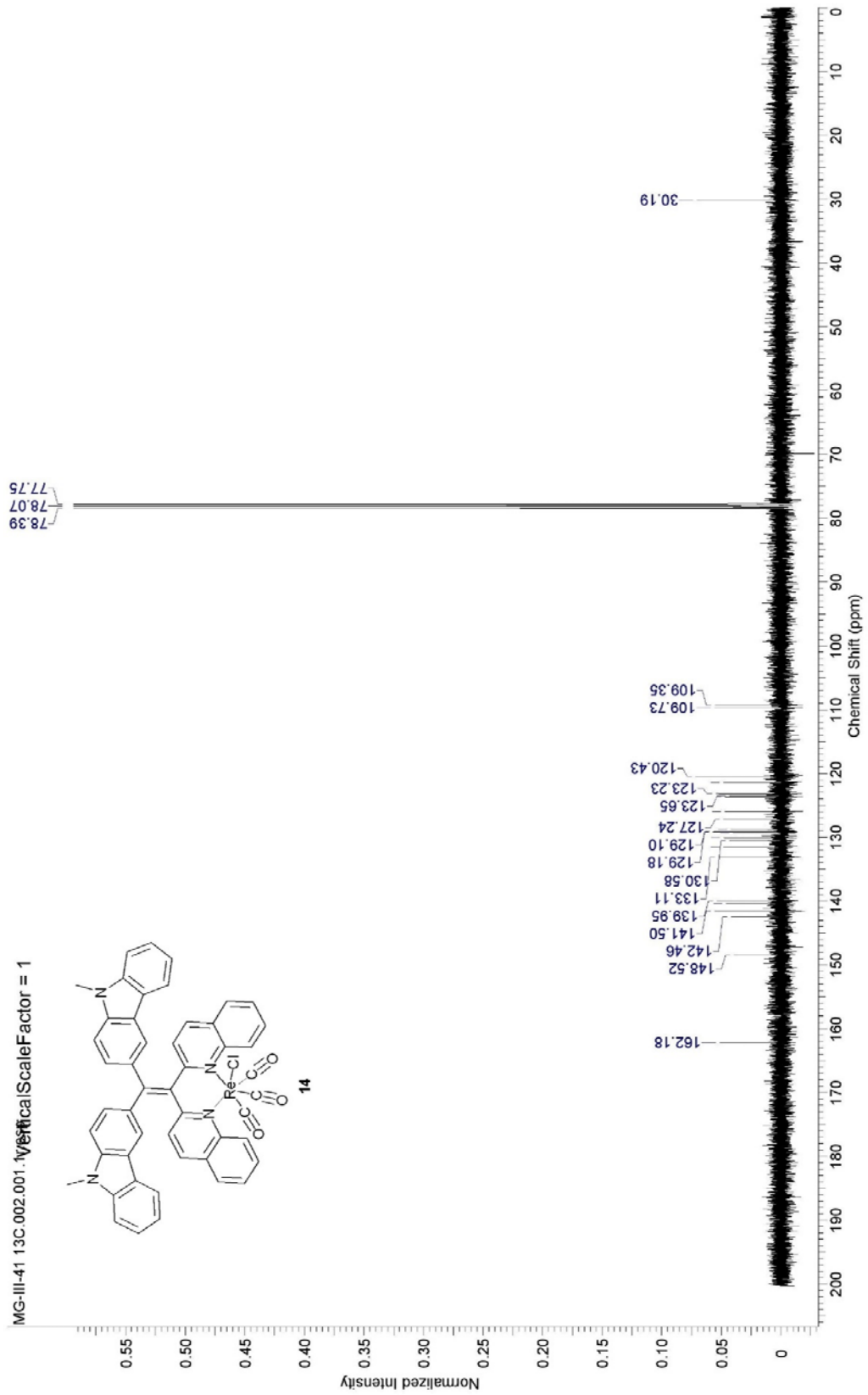

MG-II-297 1H.001.001.1.esr
VerticalScaleFactor = 1
12
Chemical Shift (ppm)
Normalized Intensity
9.63
9.61
8.08
8.06
7.91
7.73
7.63
7.52
7.50
7.32
7.26
7.27
7.01
7.01
6.88
6.89
1.56
2.09
2.09
2.01
2.04
2.03
2.06
2.00
2.01
2.01

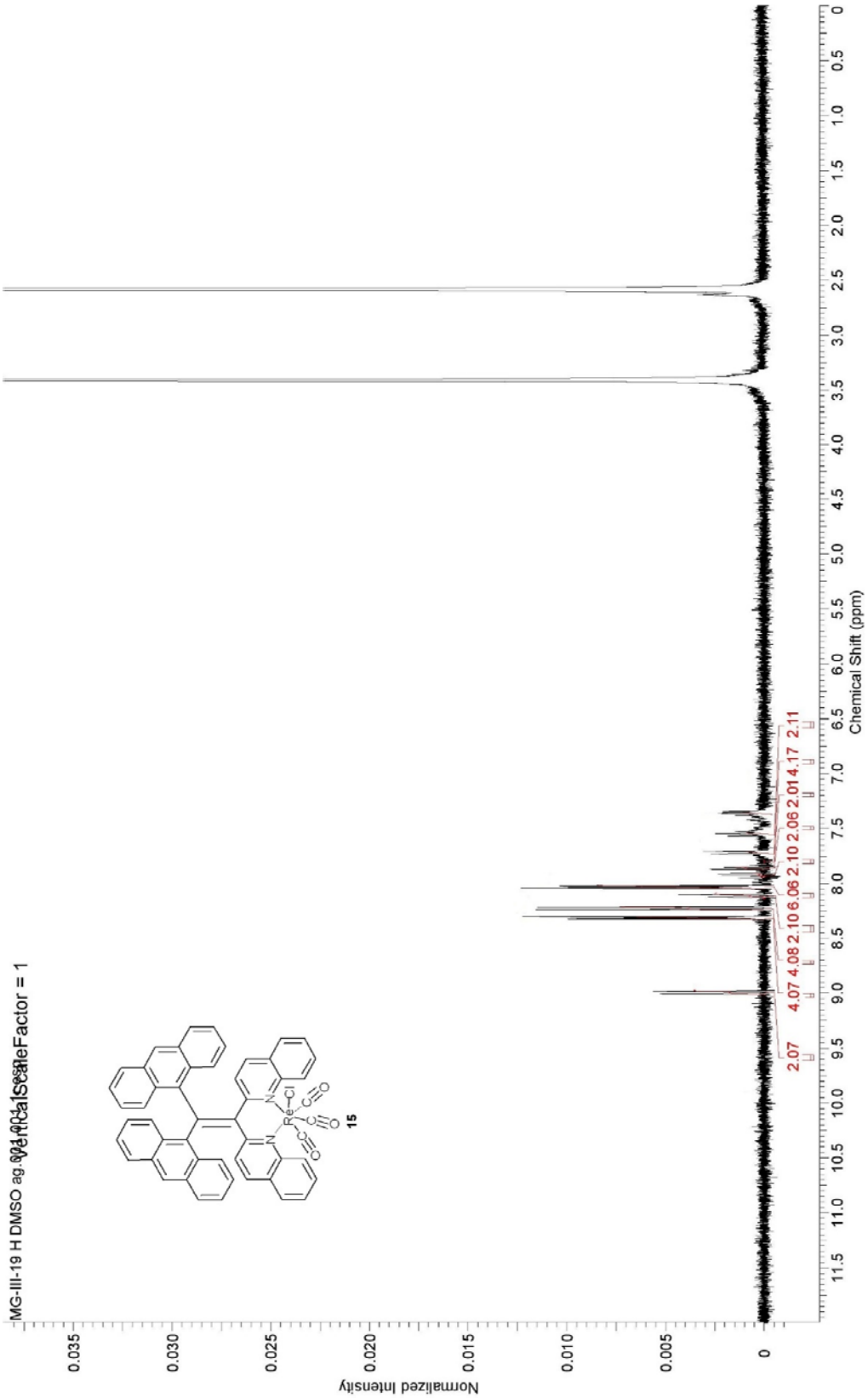

MG-II-297 13C.002.001.
VerticalScaleFactor = 1
12
Normalized Intensity
Chemical Shift (ppm)
156.47
153.01
147.31
140.62
133.03
131.86
131.68
131.53
129.44
129.34
129.26
128.24
124.47
122.55
122.02

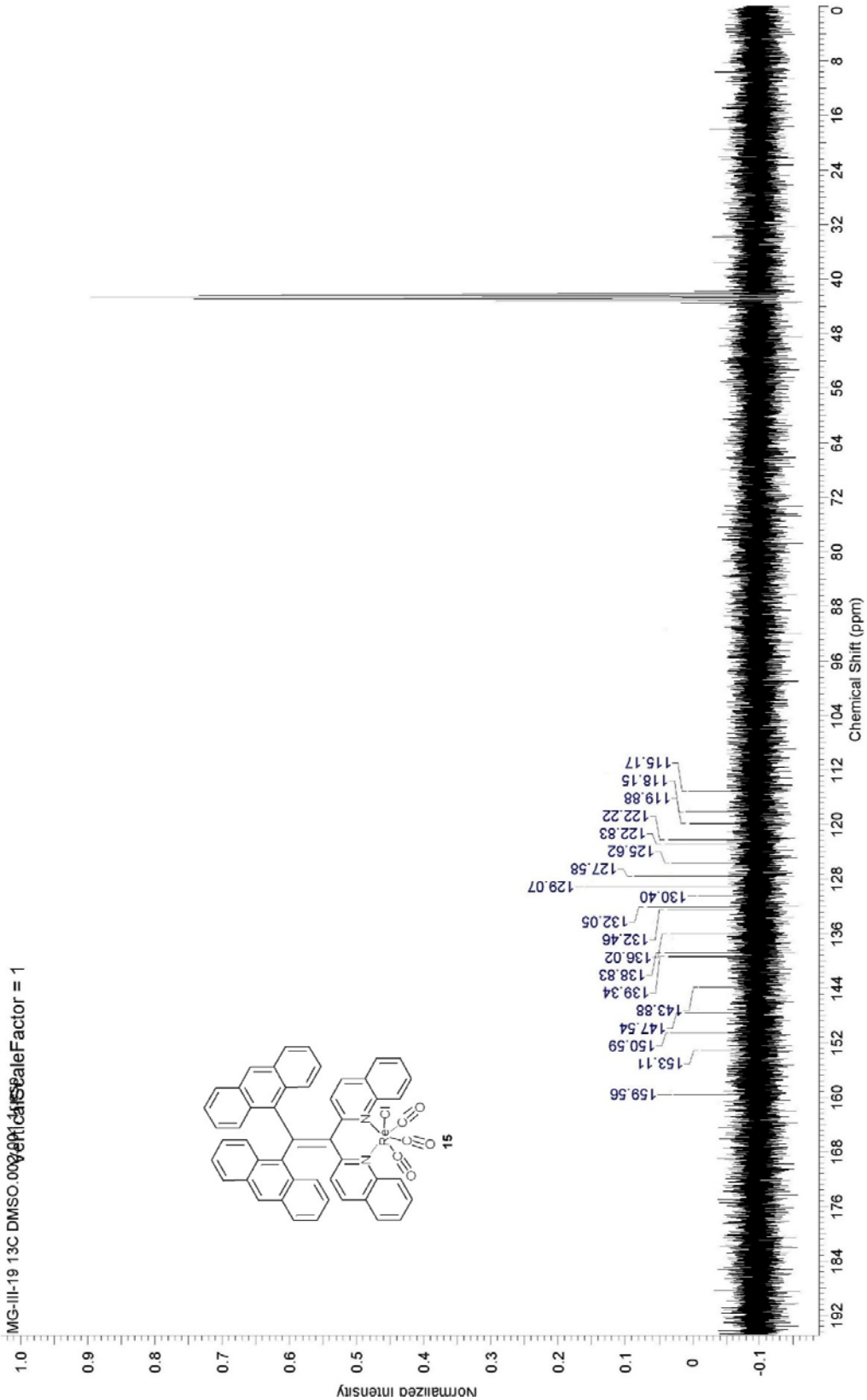

13
Chemical Shift (ppm)
Normalized Intensity
8.53
8.51
8.44
8.42
8.12
8.07
8.05
7.84
7.81
7.79
7.75
7.73
7.43
7.41
7.06
7.05
6.92
6.91
6.91
2.00 2.00 2.07 2.01 4.06 4.03 2.02 2.00 2.00

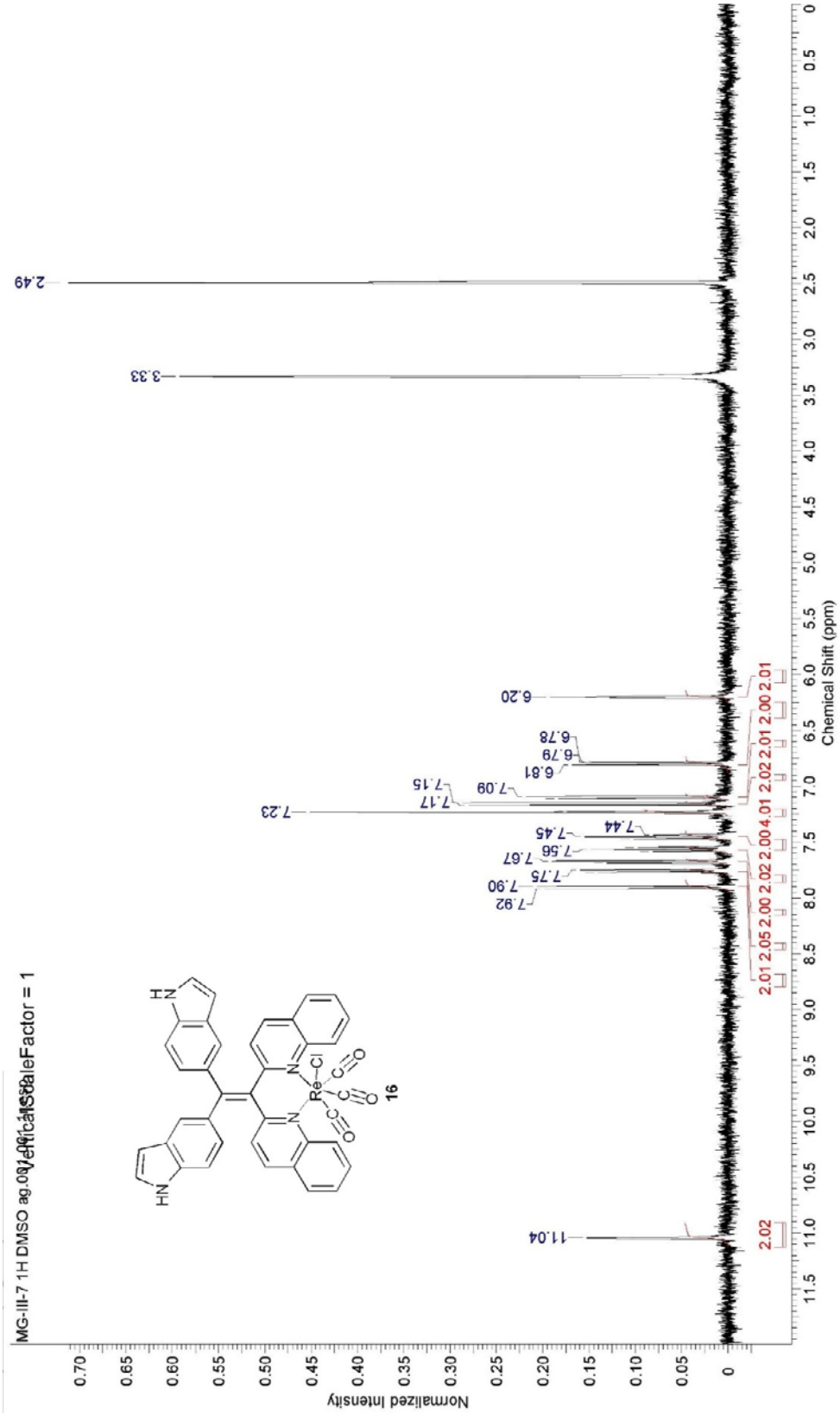

13
Chemical Shift (ppm)
Normalized Intensity
157.29
155.35
146.31
143.13
141.93
140.37
138.38
137.28
133.67
132.10
129.96
127.80
128.42
124.67
123.77
78.44
78.12
77.80

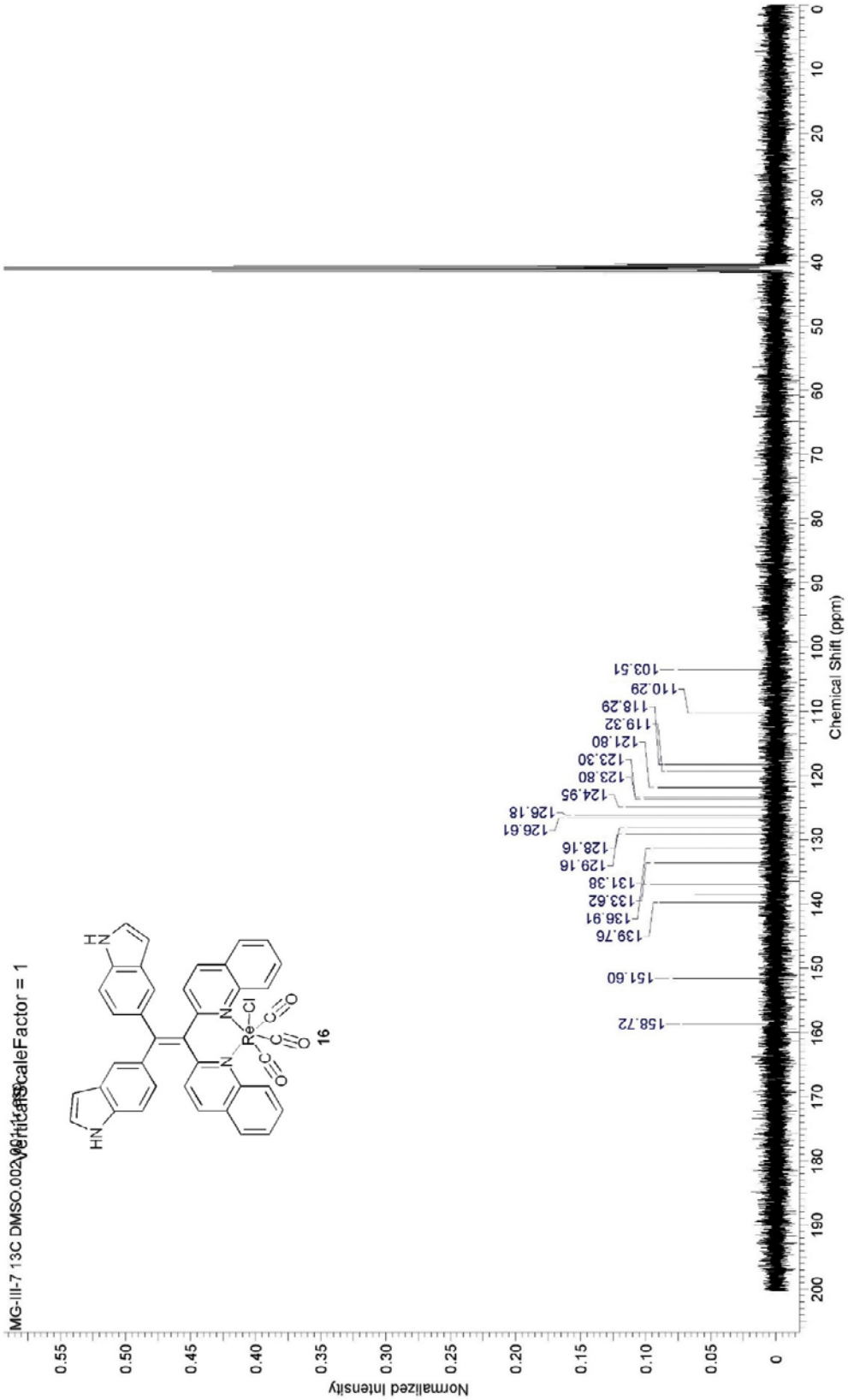

MG-III-41 1H.001.001.1r.fid VerticalScaleFactor = 1
14
Re
Cl
N
C
O
Chemical Shift (ppm)
Normalized Intensity
9.71
9.68
8.31
8.30
7.96
7.94
7.82
7.59
7.57
7.56
7.47
7.27
7.24
7.22
7.21
7.19
7.17
3.77
1.55
2.01
2.00
2.02
4.12
6.08
2.07
2.05
6.13
6.02

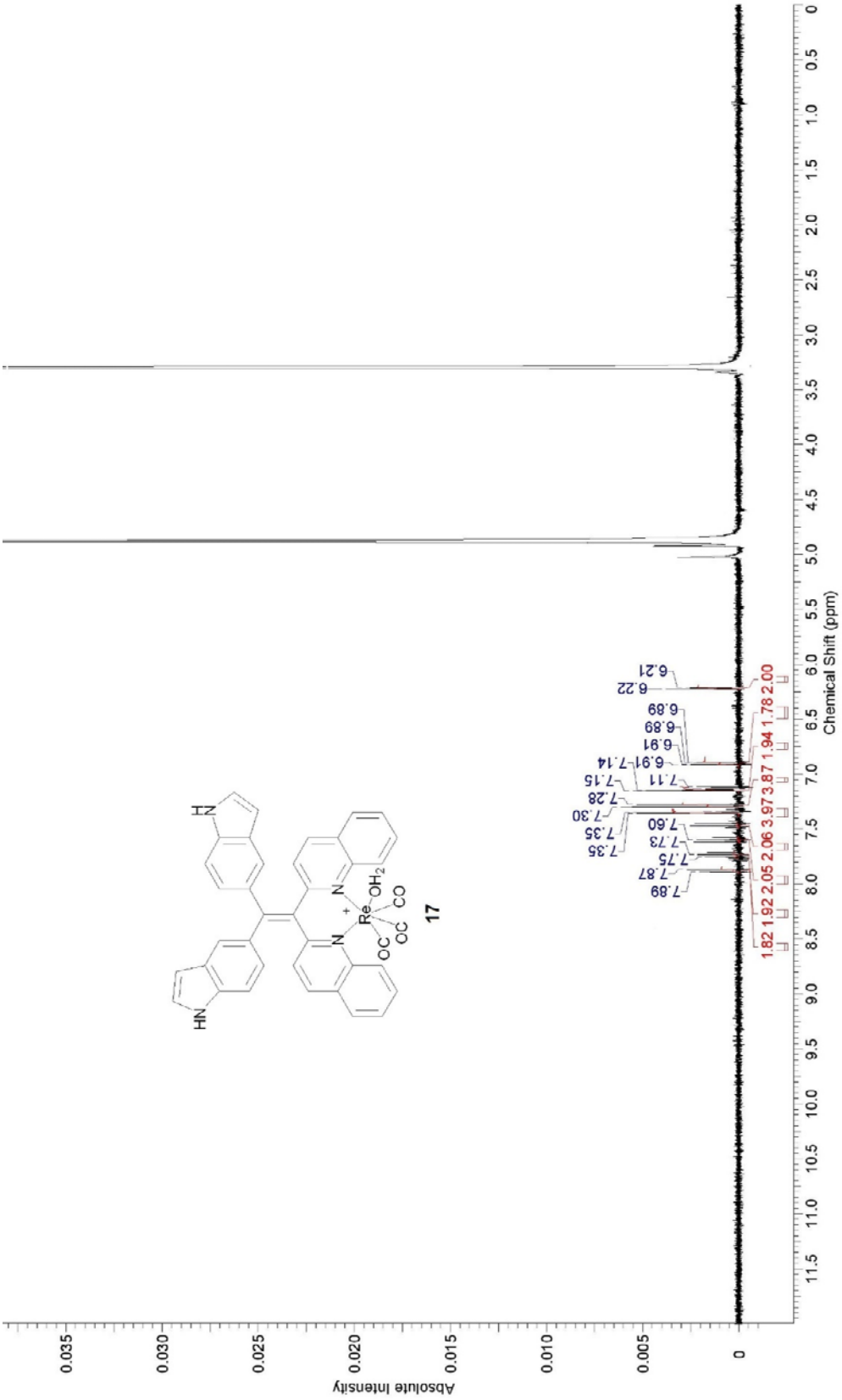

MG-III-41 13C.002.001.1.ver
VerticalScaleFactor = 1
14
Re
Cl
N
Chemical Shift (ppm)
Normalized Intensity
78.39
78.07
77.75
30.19
109.73
109.35
120.43
123.23
123.65
127.24
129.10
129.18
130.58
133.11
139.95
141.50
142.46
148.52
162.18

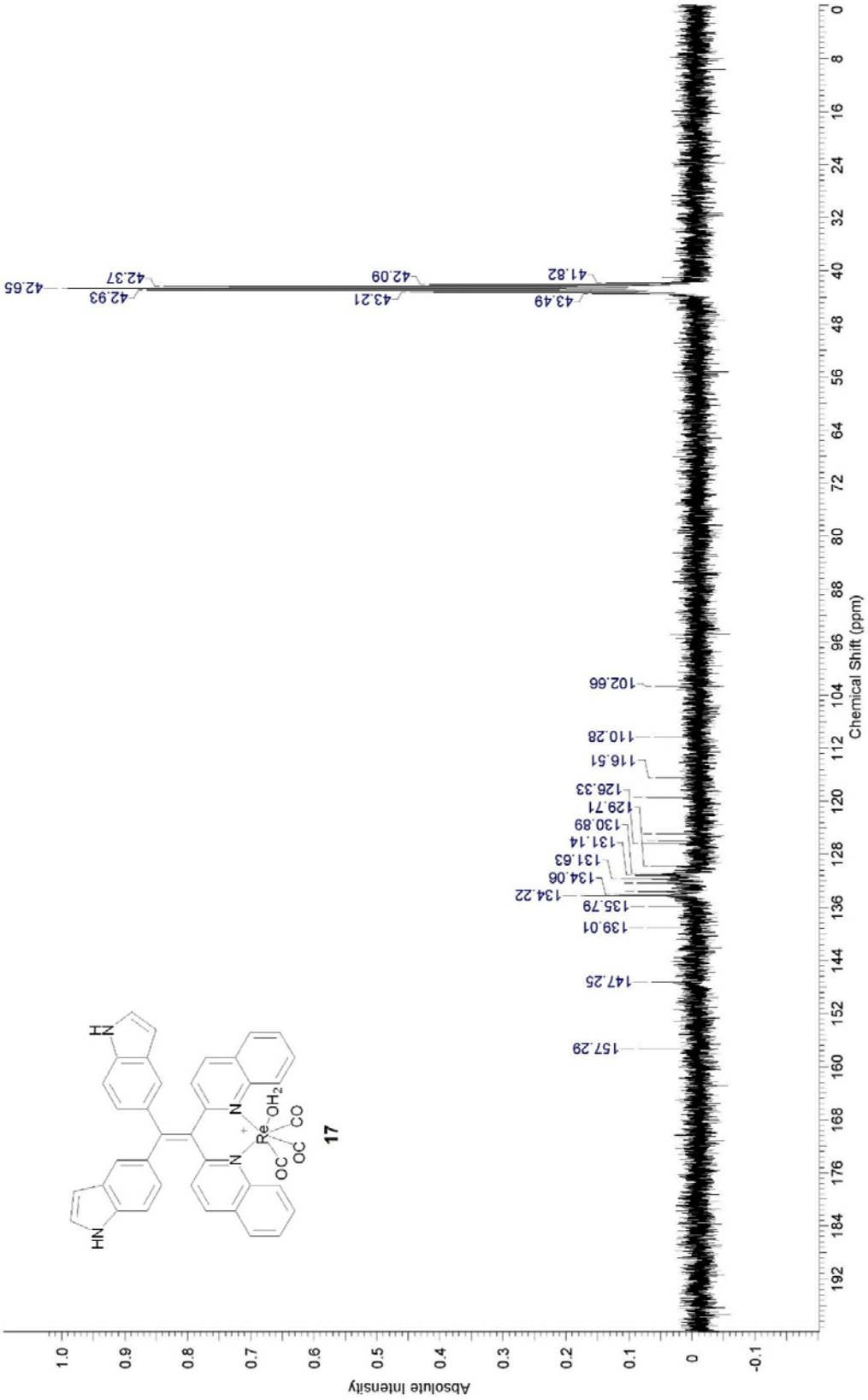

MG-III-19 H DMSO ag 001.001.1r
Vertical Scale Factor = 1
15
Normalized Intensity
Chemical Shift (ppm)
2.07 4.07 4.08 2.10 6.06 2.10 2.06 2.01 4.17 2.11


MG-III-19 13C DMSO 002 01 1d ESCaleFactor = 1
Normalized Intensity
Chemical Shift (ppm)
159.56
153.11
150.59
147.54
143.88
139.34
138.83
136.02
132.46
132.05
130.40
129.07
127.58
125.62
122.83
122.22
119.88
118.15
115.17
15


MG-III-7 1H DMSO ag.001 Vertical Scale Factor = 1
Normalized Intensity
Chemical Shift (ppm)
11.04
7.92
7.90
7.75
7.67
7.66
7.45
7.44
7.23
7.17
7.15
7.09
6.81
6.79
6.78
6.20
3.33
2.49
2.02
2.01 2.05 2.00 2.02 2.00 4.01 2.02 2.01 2.00 2.01
16


MG-III-7 13C DMSO.002.fid
VertScaleFactor = 1
16
Normalized Intensity
Chemical Shift (ppm)
158.72
151.60
139.76
136.91
133.62
131.38
129.16
128.16
126.61
126.18
124.95
123.80
123.30
121.80
119.32
118.29
110.29
103.51


17
Chemical Shift (ppm)
Absolute Intensity
7.89
7.87
7.75
7.73
7.60
7.35
7.35
7.30
7.28
7.15
7.14
7.11
6.91
6.91
6.89
6.89
6.22
6.21
1.82 1.92 2.05 2.06 3.97 3.87 1.94 1.78 2.00


Absolute Intensity
Chemical Shift (ppm)
17
157.29
147.25
139.01
135.79
134.22
134.06
131.63
131.14
130.89
129.71
126.33
116.51
110.28
102.66
43.49
43.21
41.82
42.93
42.09
42.37
42.65