## SUPPLEMENTARY INFORMATION

## MATERIALS AND METHODS

### Synthesis of ligands 3, 5, 6 and 8

**3**: 420.4 mg (2.0 mmol) 1,10-phenanthroline-5,6-dione was dissolved in 20 ml glacial acetic acid, added 5.78 g (75.0 mmol) and refluxed. To this refluxing solution 276.3 mg (2.0 mmol) 2,3-dihydroxybenzaldehyde in 15 ml warm glacial acetic acid was added and refluxed for two hours. Then the resulting yellow coloured solution was cooled to 0°C and neutralised with aqueous ammonia solution (pH=7). The yellow precipitate was filtered, washed with water, methanol and dried in vacuum. Yield: 550 mg (82%). $^1$H NMR (400 MHz, DMSO-d6): δ= 6.87-6.92 (m, 2H), 7.60-7.62 (d, 1H, *J* = 7.64Hz), 7.79-7.82 (q, 2H, *J* = 4.60 Hz), 8.85-8.87 (d, 2H, *J* = 8.40 Hz), 9.01-9.02 (d, 2H, *J* = 3.80 Hz). ESI-MS: *m/z* 328.3510 [M$^+$] (calcd M$^+$ = 328.0960). Anal. Calcd for $C_{19}H_{12}N_4O_2$: C, 69.51; H, 3.68; N, 17.06. Found: C, 69.65; H, 3.61; N, 17.10.

**5**: The procedure was similar to that for 3, except that 4-methoxy benzaldehyde (272.3 mg, 2.0 mmol) was used in place of 2,3-dihydroxybenzaldehyde. Yield: 581 mg (89%); $^1$H NMR (25°C, 400 MHz, DMSO-d6): δ= 3.86 (s, 3H), 7.16-7.18 (d, 2H, *J* = 8.40 Hz), 7.81-7.84 (m, 2H), 8.24-8.26 (d, 2H, *J* = 8.40 Hz), 8.91-8.94 (dd, 2H, *J* = 8.40 Hz, 1.56 Hz), 9.02-9.03 (dd, 2H, *J* = 6.08 Hz, 1.52 Hz). ESI-MS: *m/z* 327.3351 [M$^+$ H] (calcd M$^+$ = 326.1168). Anal. Calcd for $C_{20}H_{14}N_4O$: C, 73.61; H, 4.32; N, 17.17. Found: C, 73.68; H, 4.25; N, 17.11.

**6**: The procedure was similar to that for 3, except that 2-methoxy benzaldehyde (272.3 mg, 2.0 mmol) was used in place of 2,3-dihydroxybenzaldehyde. Yield: 542 mg (83%); $^1$H NMR (25°C, 400 MHz, DMSO-d6): δ= 4.01 (s, 3H), 7.14-7.17 (t, 1H, *J* = 7.24 Hz), 7.25-7.27 (d, 1H, *J* = 8.40 Hz), 7.48-7.52 (t, 1H, *J* = 8.02 Hz), 7.80-7.82 (m, 2H), 8.21-8.23 (d, 1H, *J* = 7.64 Hz), 9.00-9.01 (m, 2H), 9.05-9.07 (d, 2H, *J* = 7.64 Hz). ESI-MS: *m/z* 327.3439 [M$^+$ H] (calcd M$^+$ = 326.1168). Anal. Calcd for $C_{20}H_{14}N_4O$: C, 73.61; H, 4.32; N, 17.17. Found: C, 73.71; H, 4.27; N, 17.12.

**8**: The procedure was similar to that for 3, except that 2-hydroxy-3-methoxybenzaldehyde (304.3 mg, 2.0 mmol) was used in place of 2,3-dihydroxybenzaldehyde. Yield: 571 mg (84%); $^1$H NMR (25°C, 400 MHz, DMSO-d6): δ= 1.87 (s, 3H), 6.88-6.92 (t, 1H, *J* = 8.02 Hz), 6.97-6.99 (d, 1H, *J* = 6.88 Hz), 7.76-7.79 (q, 2H, *J* = 3.05 Hz), 7.82-7.84 (dd, 1H, *J* = 7.64 Hz, 1.52 Hz), 8.33 (s, 1H), 8.85-8.87 (dd, 2H, *J* = 8.40 Hz, 1.52 Hz), 8.95-

8.97 (dd, 2H, *J* = 4.60 Hz, 1.52 Hz). ESI-MS: *m/z* 343.1687 [$M^+$ H] (calcd $M^+$ = 342.1117). Anal. Calcd for $C_{20}H_{14}N_4O_2$: C, 70.17; H, 4.12; N, 16.37. Found: C, 70.27; H, 4.08; N, 16.35.

**Synthesis of iridium(III) complexes C1, C3 - C10 and rhenium(I) complex C11**

**C1**: 107.2 mg (0.1 mmol) $[Ir(ppy)_2Cl]_2$ and 62.5 mg (0.2 mmol) ligand 1 were refluxed in (1:1:1) methanol : dichloromethane : acetonitrile for 3h. The resulting orange-yellow coloured solution was purified using thin layer chromatography using (1:19) methanol : dichloromethane as eluent. Yield: 113.2 mg (67%). $^1H$ NMR (25°C, 400 MHz, $CDCl_3$): δ=6.28-6.30 (d, 2H, *J* = 5.80 Hz), 6.94-6.97 (t, 2H, *J* = 6.30 Hz), 6.98-7.02 (t, 4H, *J* = 6.44 Hz), 7.04-7.07 (t, 2H, *J* = 6.06 Hz), 7.49 (s, 2H), 7.86-7.89 (t, 2H, *J* = 5.80 Hz), 7.94-7.96 (d, 2H, *J* = 5.80 Hz), 8.06-8.07 (m, 2H), 8.12-8.14 (m, 2H), 8.20-8.22 (d, 2H, *J* = 6.80 Hz), 8.25-8.27 (d, 2H, *J* = 6.56 Hz), 9.15-9.17 (d, 1H, *J* = 6.04 Hz), 9.33-9.35 (d, 1H, *J* = 6.80 Hz), 10.11 (b, 1H), 14.37 (b, 1H). ESI-MS: *m/z* 812.9058 [$M^+ - Cl$] (calcd $M^+ - Cl$ = 813.1954). Anal. Calcd for $C_{41}H_{28}ClIrN_6O$: C, 58.05; H, 3.33; N, 9.91. Found: C, 58.15; H, 3.27; N, 9.98. IR ($cm^{-1}$): 758, 1477, 1608.

**C3**: The procedure was similar to that for **C1**, except 3 (65.7 mg, 0.2 mmol) was used in place of 1. Yield: 98.2 mg (57%); $^1H$ NMR (25°C, 400 MHz, $CDCl_3$): δ=6.39-6.41 (d, 2H, *J* = 6.88 Hz), 6.87 (s, 2H), 6.93-6.97 (t, 3H, *J* = 7.26 Hz), 7.04-7.08 (t, 3H, *J* = 7.24 Hz), 7.46-7.47 (d, 2H, *J* = 4.56 Hz), 7.64-7.72 (m, 8H), 7.90-7.92 (d, 3H, *J* = 7.64 Hz), 8.09-8.11 (d, 2H, *J* = 4.60 Hz). ESI-MS: *m/z* 828.9341 [$M^+ - Cl$] (calcd $M^+ - Cl$ = 829.1903). Anal. Calcd for $C_{41}H_{28}ClIrN_6O_2$: C, 56.97; H, 3.27; N, 9.72. Found: C, 57.02; H, 3.21; N, 9.79. IR ($cm^{-1}$): 759, 1384, 1580.

**C5**: The procedure was similar to that for **C1**, except 1e (65.3 mg, 2.0 mmol) was used in place of 1. Yield: 108.4 mg (63%); $^1H$ NMR (25°C, 400 MHz, $CDCl_3$): δ= 3.83 (s, 3H), 6.40-6.42 (d, 2H, *J* = 6.88Hz), 6.85-6.90 (m, 2H), 6.95-6.99 (m, 4H), 7.07-7.10 (t, 2H, *J* = 7.62 Hz), 7.37 (s, 2H), 7.68-7.75 (m, 8H), 7.92-7.94 (d, 2H, *J* = 8.40 Hz), 8.12-8.13 (m, 2H), 8.35-8.38 (d, 2H, *J* = 8.40 Hz), 14.60 (b, 1H). ESI-MS: *m/z* 827.0107 [$M^+ - Cl$] (calcd $M^+ - Cl$ = 827.2110). Anal. Calcd for $C_{42}H_{30}ClIrN_6O$: C, 58.49; H, 3.51; N, 9.74. Found: C, 58.59; H, 3.48; N, 9.78. IR ($cm^{-1}$): 758, 1268, 1477, 1605.

**C6**: The procedure was similar to that for **C1**, except 1f (65.3 mg, 0.2 mmol) was used in place of 1. Yield: 122.5 mg (71%); $^1H$ NMR (25°C, 400 MHz, $CDCl_3$): δ= 4.18 (s, 3H), 6.40-6.42 (d, 2H, *J* = 6.88 Hz), 6.80-6.84 (t, 2H, *J* = 6.48 Hz), 6.95-6.98 (t, 2H, *J* = 7.26 Hz), 7.06-7.10 (m, 4H), 7.33-7.34 ( d, 2H, *J* = 5.32 Hz), 7.40-7.44 (t, 1H, *J* = 8.02 Hz), 7.67-7.77 (m, 8H), 7.91-7.93 (d, 2H, *J* = 8.40 Hz), 8.10-8.11 (d, 2H, *J* = 4.56 Hz), 8.29-8.31 (d, 1H, *J* =

7.64 Hz). ESI-MS: *m/z* 827.0247 [$M^+ - Cl$] (calcd $M^+ - Cl$ = 827.2110). Anal. Calcd for $C_{42}H_{30}ClIrN_6O$: C, 58.49; H, 3.51; N, 9.74. Found: C, 58.60; H, 3.41; N, 9.78. IR (cm$^{-1}$): 761, 1474, 1603.

**C7**: The procedure was similar to that for **C1**, except 7 (84.9 mg, 0.2 mmol) was used in place of 1. Yield: 106.5 mg (55%); $^1$H NMR (25°C, 400 MHz, $CDCl_3$): δ=1.42 (s, 9H), 1.52 (s, 9H), 6.39-6.41 (d, 2H, *J* = 7.64 Hz), 6.89-6.97 (m, 5H), 7.06-7.10 (t, 2H, *J* = 7.64 Hz), 7.50-7.54 (m, 2H), 7.66 (s, 1H), 7.79-7.82 (t, 2H, *J* = 7.64 Hz), 7.86-7.88 (d, 2H, *J* = 7.64 Hz), 8.01-8.04 (t, 2H, *J* = 5.74 Hz), 8.13-8.15 (d, 2H, *J* = 8.40 Hz), 8.17 (s, 1H), 8.40-8.33 (t, 2H, *J* = 6.12 Hz), 9.17-9.19 (d, 1H, *J* = 8.40 Hz), 9.23-9.25 (d, 1H, *J* = 7.64 Hz). ESI-MS: *m/z* 926.0308 [$M^+ + H - Cl$] (calcd $M^+ - Cl$ = 925.3206). Anal. Calcd for $c_{50}H_{48}ClIrN_6O$: C, 61.49; H, 4.95; N, 8.61. Found: C, 61.61; H, 4.90; N, 8.68. IR (cm$^{-1}$): 761, 1073, 1458, 1617,

**C8**: The procedure was similar to that for **C1**, except 8 (68.5 mg, 0.2 mmol) was used in place of 1. Yield: 116.4 mg (66%); $^1$H NMR (25°C, 400 MHz, $CDCl_3$): δ=3.92 (s, 3H), 6.41-6.42 (d, 2H, *J* = 6.88 Hz), 6.84-6.89 (m, 4H), 6.95-6.99 (m, 2H), 7.05-7.09 (m, 2H), 7.15-7.17 (m, 1H), 7.26-7.26 (m, 1H), 7.39-7.42 (t, 2H, *J* = 6.48 Hz), 7.66-7.73 (m, 6H), 7.90-7.92 (d, 2H, *J* =8.40 Hz), 8.09-8.11 (d, 2H, *J* = 5.32 Hz), 9.22 (b, 2H). ESI-MS: *m/z* 843.0223 [$M^+ - Cl$] (calcd $M^+ - Cl$ = 843.2059). Anal. Calcd for $C_{42}H_{30}ClIrN_6O_2$: C, 57.43; H, 3.44; N, 9.57. Found: C, 57.45; H, 3.39; N, 9.62. IR (cm$^{-1}$): 803, 1030, 1085, 1261.

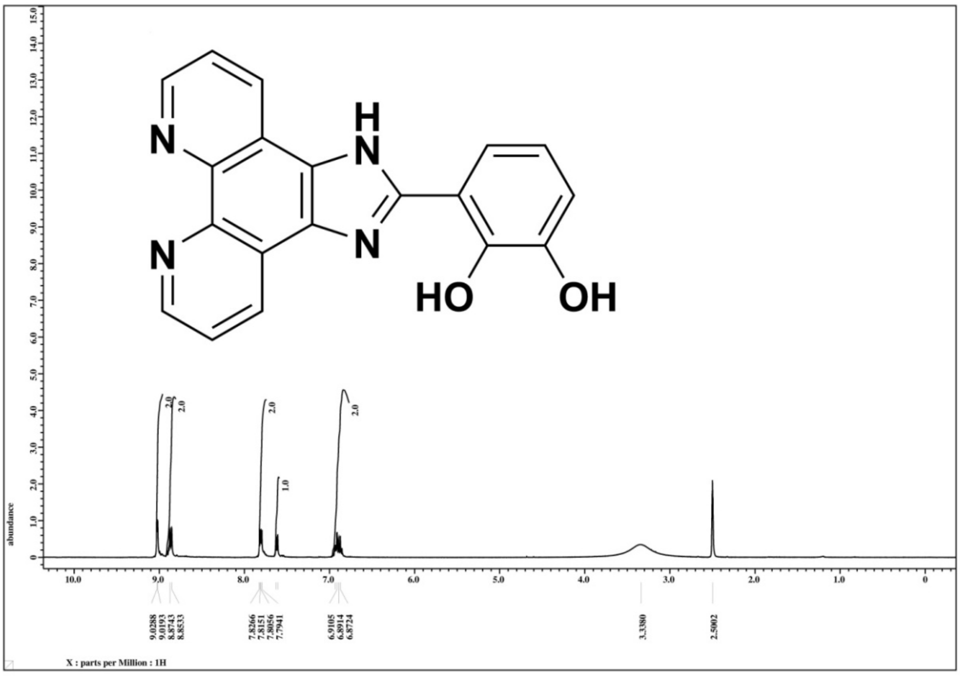
**C9**: The procedure was similar to that for **C1**, except 2a (83.6 mg, 0.2 mmol) was used in place of 1. Yield: 105.7 mg (53%); $^1$H NMR (25°C, 400 MHz, $CDCl_3$): δ= 4.03 (s, 3H), 6.56-6.60 (dt, 2H, *J* = 7.64 Hz, 1.52 Hz), 6.75-6.77 (d, 1H, J = 9.16 Hz), 6.86-6.89 (dd, 2H, *J* = 8.40 Hz, 1.56 Hz), 7.13-7.15 (d, 3H, J = 8.40 Hz), 7.22-7.23 (m, 4H), 7.32-7.35 (q, 2H, J = 4.60 Hz), 7.39-7.42 (dd, 2H, J = 8.40 Hz, 1.52 Hz), 7.52-7.55 (d, 5H, J = 8.40 Hz), 7.71-7.73 (d, 1H, J = 9.16 Hz), 7.76-7.80 (q, 2H, J = 3.80 Hz), 8.98-9.00 (d, 2H, J = 8.40 Hz), 9.06-9.07 (dd, 2H, J = 4.56 Hz, 1.52 Hz), 9.20-9.21 (d, 2H, J = 4.60 Hz), 13.39 (b, 1H). ESI-MS: *m/z* 920.5782 [$M^+ + H - Cl$] (calcd $M^+ - Cl$ = 919.2372). Anal. Calcd for $C_{48}H_{34}ClIrN_6O_2$: C, 60.40; H, 3.59; N, 8.80. Found: C, 60.51; H, 3.62; N, 8.70. IR (cm$^{-1}$): 758, 1251, 1491, 1599.

**C10**: The procedure was similar to that for **C1**, except $[Ir(dhq)_2Cl]_2$ (116.8 mg, 0.2 mmol) was used instead of $[Ir(ppy)_2Cl]_2$ and ligand 2 62.5 mg (0.2 mmol) was used instead of 1. Yield: 112.9 mg (63%); $^1$H NMR (25°C, 400 MHz, $CDCl_3$): δ=6.42-6.44 (d, 2H, *J* = 7.64 Hz), 6.77-6.81 (t, 1H, *J* = 7.64 Hz), 6.95-6.97 (d, 1H, *J* = 8.40 Hz), 7.04-7.07 (t, 1H, *J* = 7.64 Hz), 7.11-7.13 (d, 1H, *J* = 8.40 Hz), 7.15-7.19 (t, 2H, *J* = 7.64 Hz), 7.27-7.28 (m, 1H), 7.40-7.43 (m, 2H), 7.45-7.77 (d, 2H, *J* = 8.40 Hz), 7.62 (s, 1H), 7.63-7.65 (m, 2H), 7.68-7.70 (q, 1H, *J* = 3.80 Hz), 8.00-8.01 (d, 2H, *J* = 5.36 Hz), 8.06-8.08 (m, 1H), 8.14-8.16 (d, 2H, *J* = 6.20 Hz), 8.55-8.60 (m, 1H), 8.62-8.64 (dd, 1H, *J* = 7.64 Hz, 1.56 Hz), 9.16-9.20 (m, 2H), 11.05 (b, 1H). ESI-MS: *m/z* 861.4888 [$M^+ - Cl$] (calcd $M^+ - Cl$ = 861.1954). Anal. Calcd for $C_{45}H_{28}ClIrN_6O$: C, 60.29; H, 3.15; N, 9.38. Found: C, 60.25; H, 3.10; N, 9.48. IR ($cm^{-1}$): 752, 835, 1254, 1406, 1607.

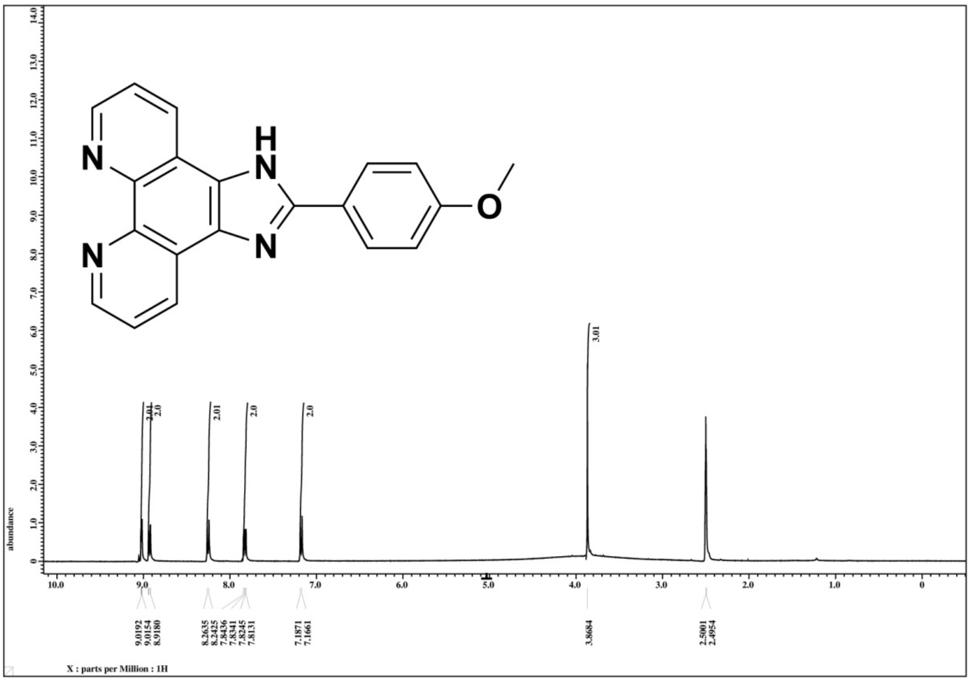
**C11**: 72.34 mg (0.2 mmol) $Re(CO)_5Cl$ and ligand 2 62.5 mg (0.2 mmol) was refluxed in toluene for 24h, the resulting yellow precipitate was filtered, washed with toluene and dried in vacuum. Yield: 106.4 mg (86%); $^1H$ NMR (25°C, 400 MHz, $CDCl_3$): δ=7.04-7.06 (d, 2H, *J* = 8.52 Hz), 7.38-7.42 (t, 1H, *J* = 7.62 Hz), 8.11-8.36 (m, 3H), 9.27-9.29 (d, 2H, *J* = 7.96 Hz), 9.37-9.39 (d, 2H, *J* = 4.24 Hz), 12.14 (b, 1H), 14.21 (b, 1H). ESI-MS: *m/z* 622.9115 [$M^+ + 2H$] (calcd $M^+$ = 621.0339). Anal. Calcd for $C_{22}H_{15}ClN_4O_4Re$: C, 42.55; H, 2.43; N, 9.02. Found: C, 42.65; H, 2.38; N, 9.05. IR ($cm^{-1}$): 757, 1255, 1409, 1608, 1901, 2026.

**Figure S1**: $^1$H nmr spectra of ligands 3, 5, 6 and 8

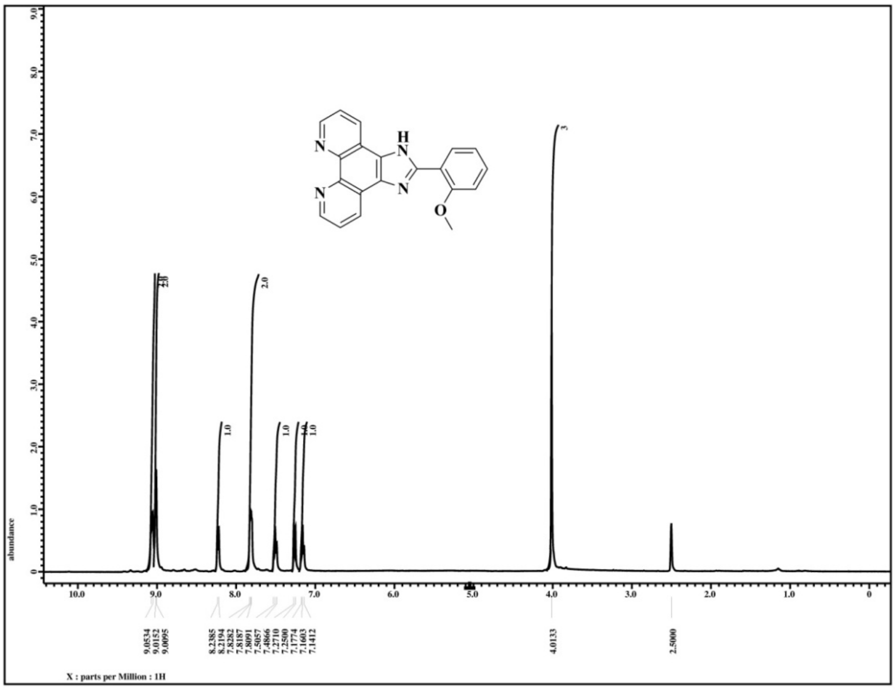
$^1$H NMR spectra of **3** in DMSO-d6 (400MHz)



$^1$H NMR spectra of **5** in DMSO-d6 (400MHz)



$^{1}$H NMR spectra of **6** in DMSO-d6 (400MHz)



$^{1}$H NMR spectra of **8** in DMSO-d6 (400MHz)

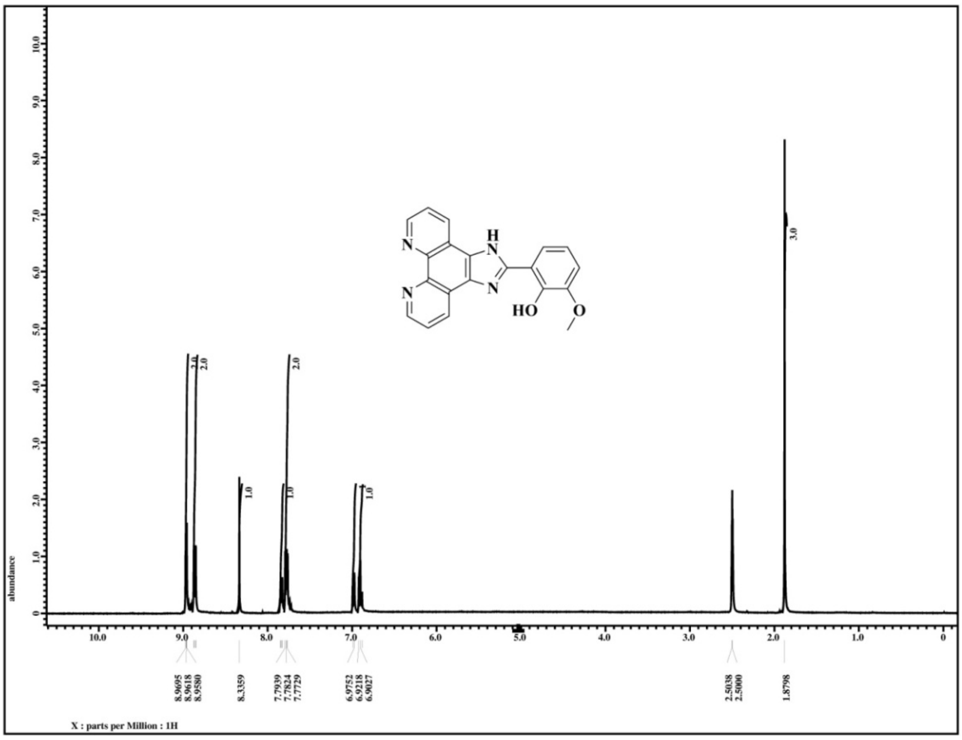
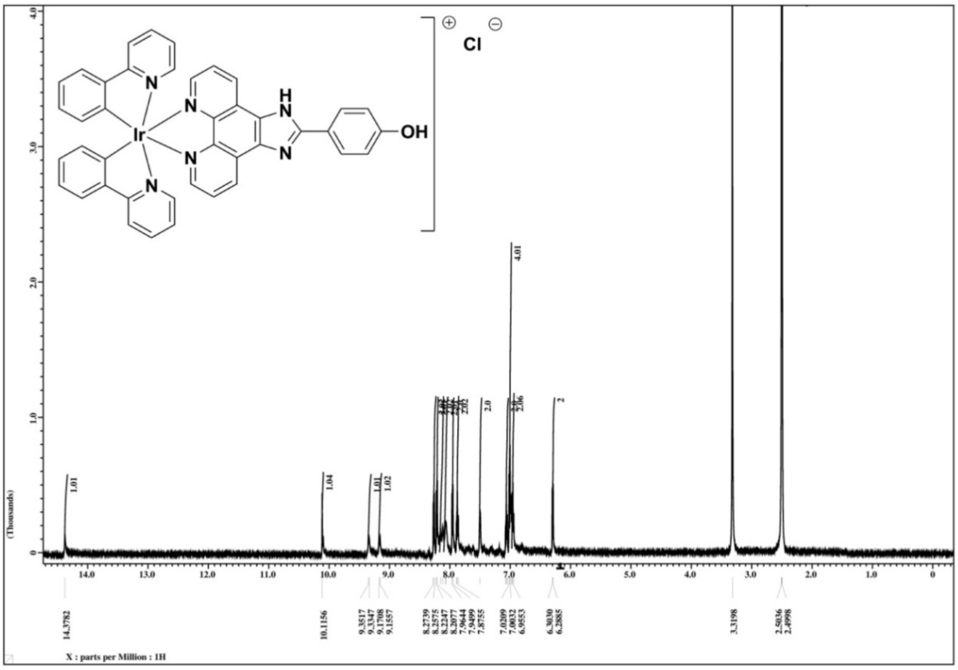
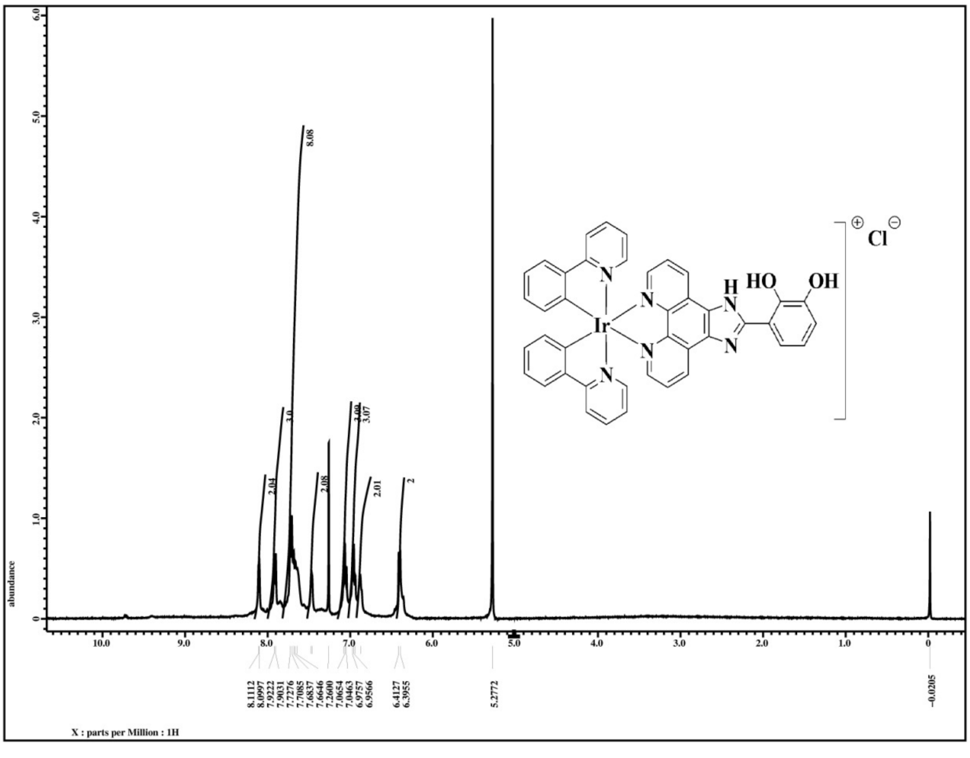


**Figure S2**: $^1$H NMR spectra of iridium(III) complexes C1, C3 - C10 and rhenium(I) complex C11

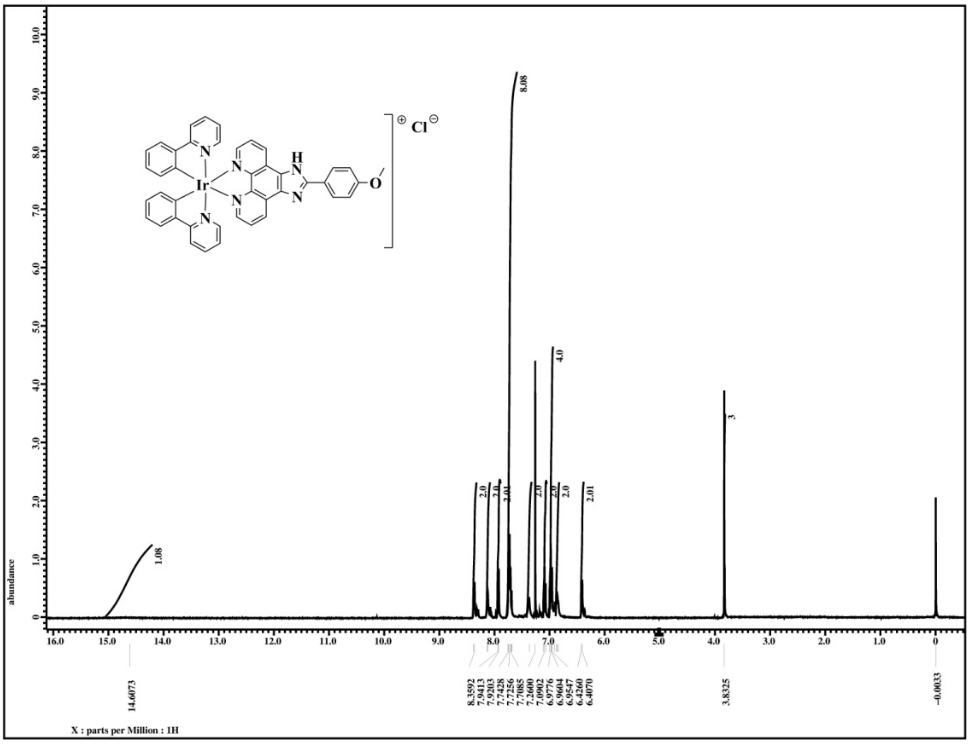
$^1$H NMR spectra of C**1** in $CDCl_3$ (400MHz)



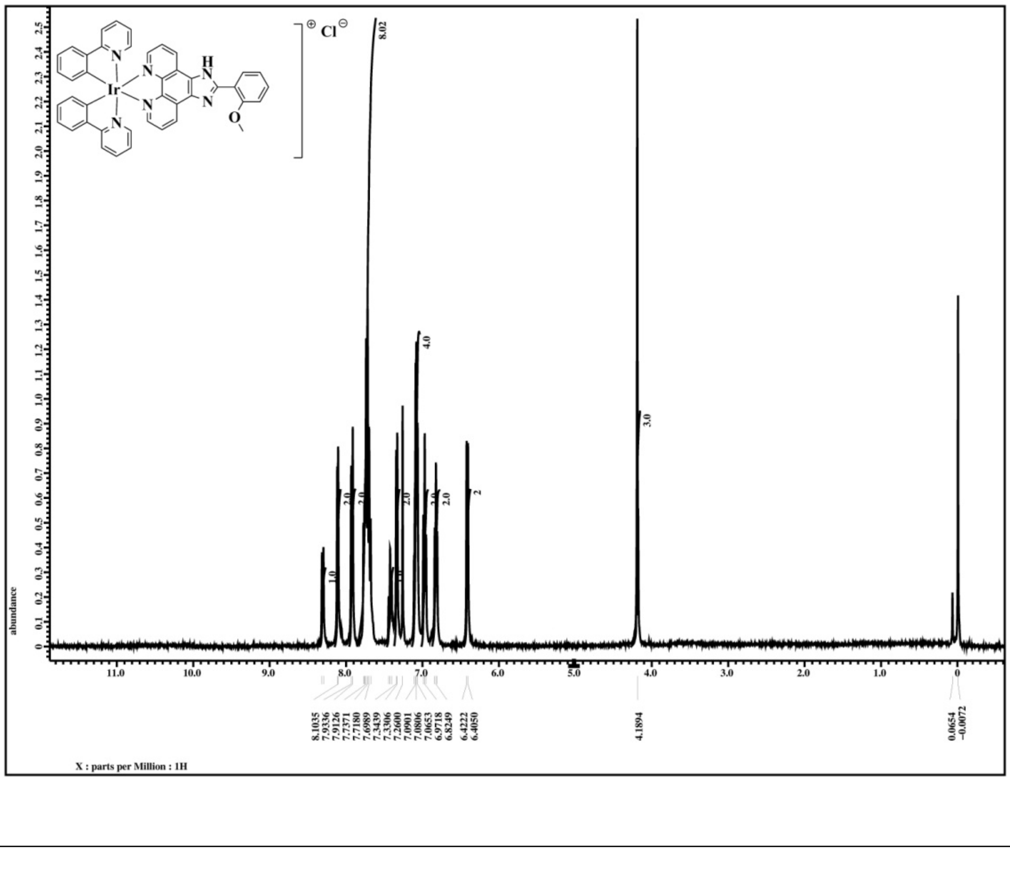
$^1$H NMR spectra of C**3** in $CDCl_3$ (400MHz)



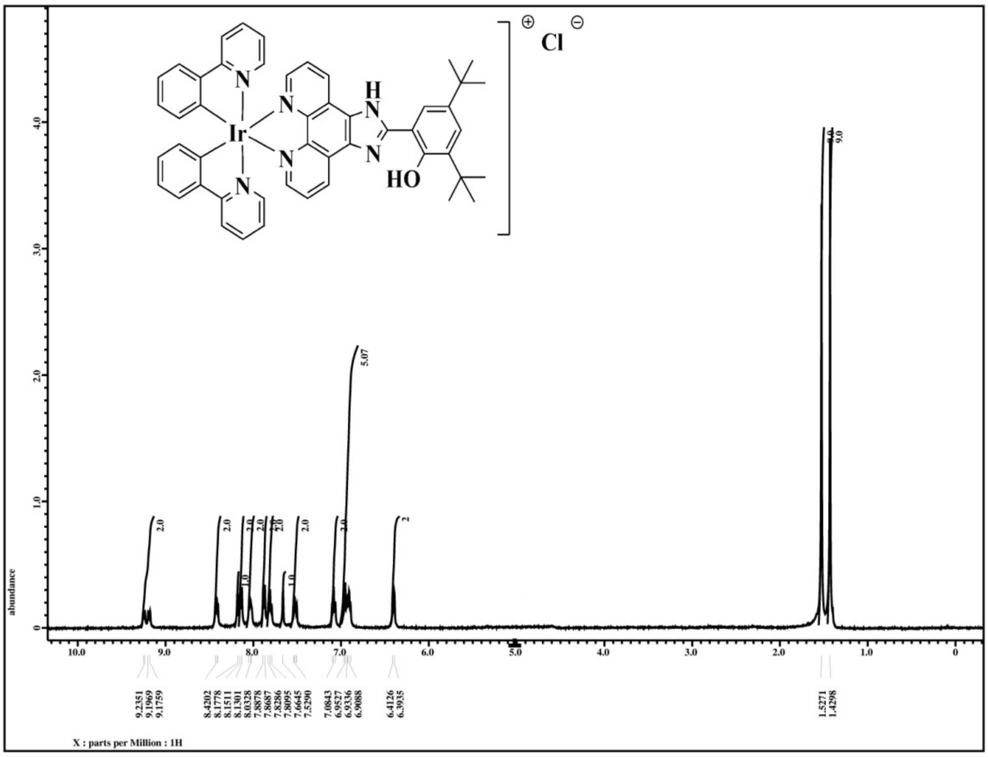
$^1$H NMR spectra of C**5** in $CDCl_3$ (400MHz)



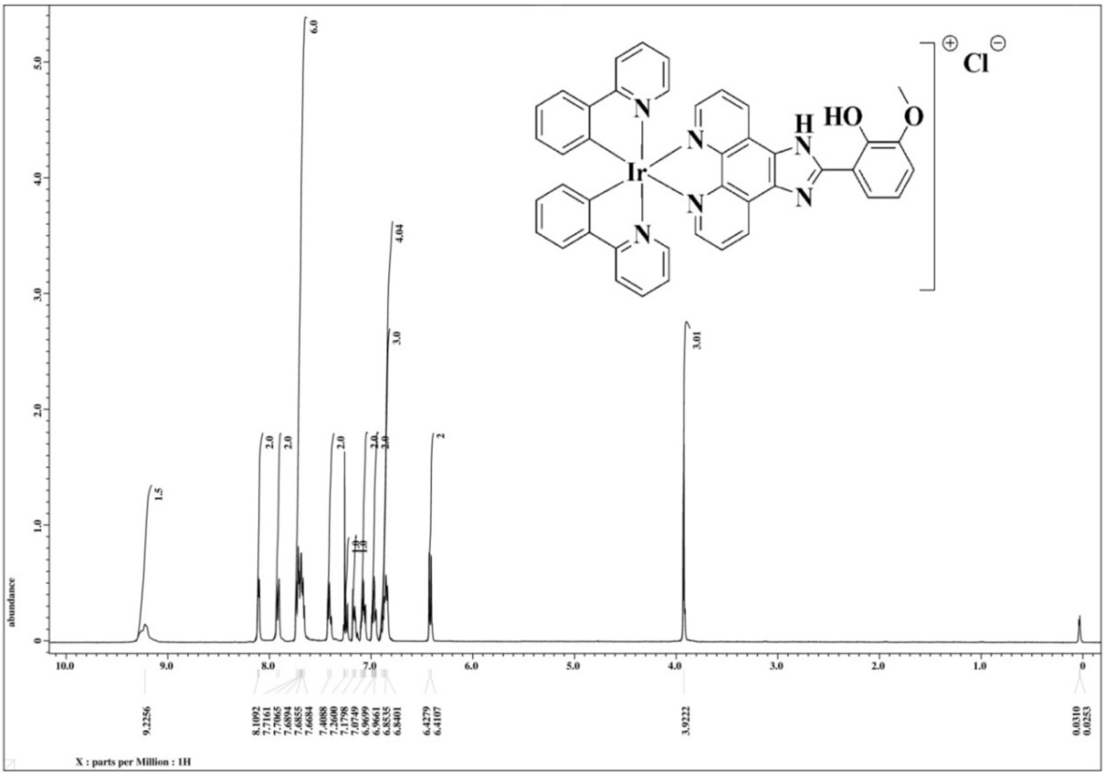
$^1$H NMR spectra of **C6** in $CDCl_3$ (400MHz)



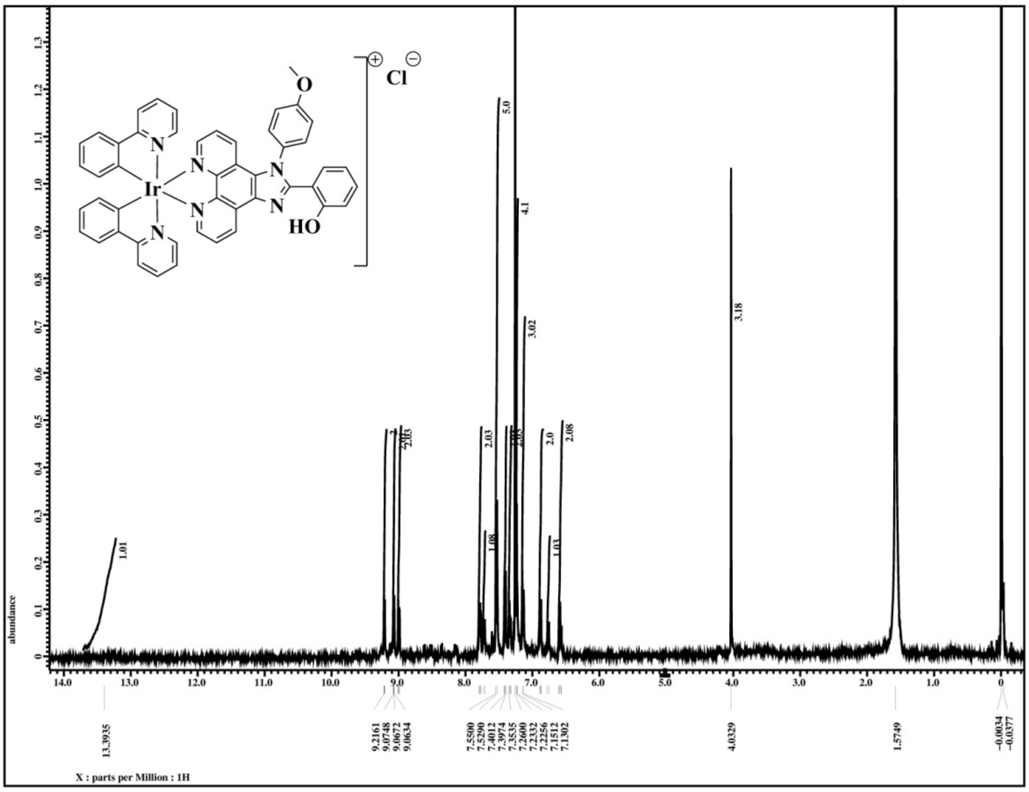
$^1$H NMR spectra of C**7** in CDCl$_3$ (400MHz)



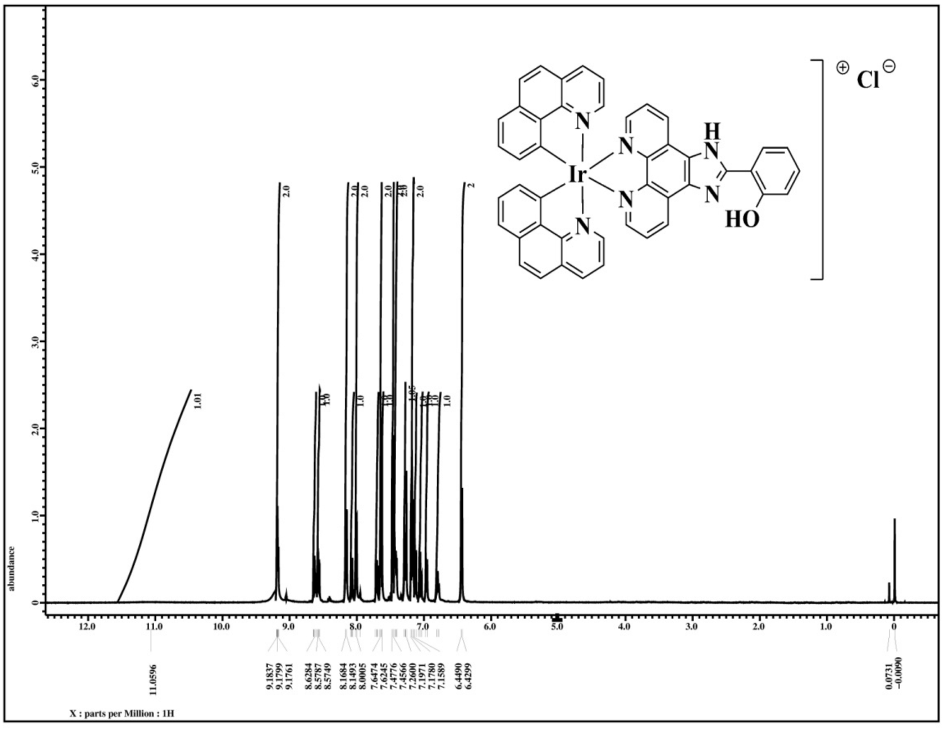
$^1$H NMR spectra of C**8** in CDCl$_3$ (400MHz)



$^1$H NMR spectra of C**9** in $CDCl_3$ (400MHz)



$^1$H NMR spectra of C**10** in $CDCl_3$ (400MHz)



$^1$H NMR spectra of C**11** in $CDCl_3$ (400MHz)

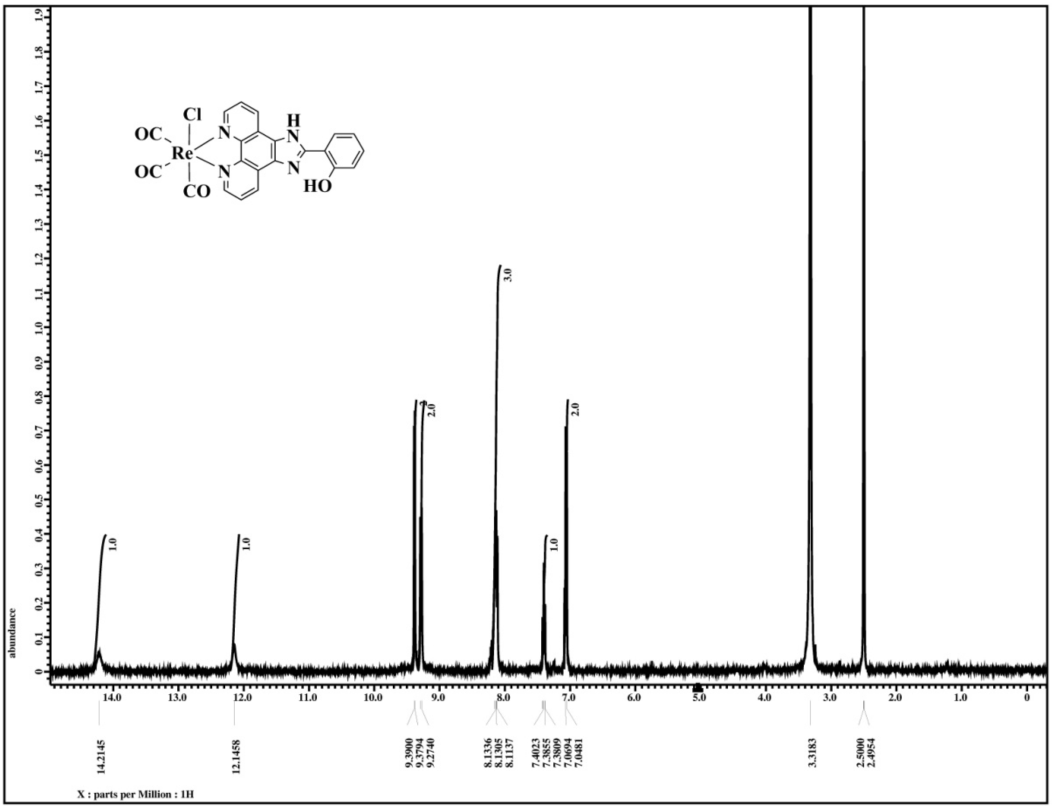
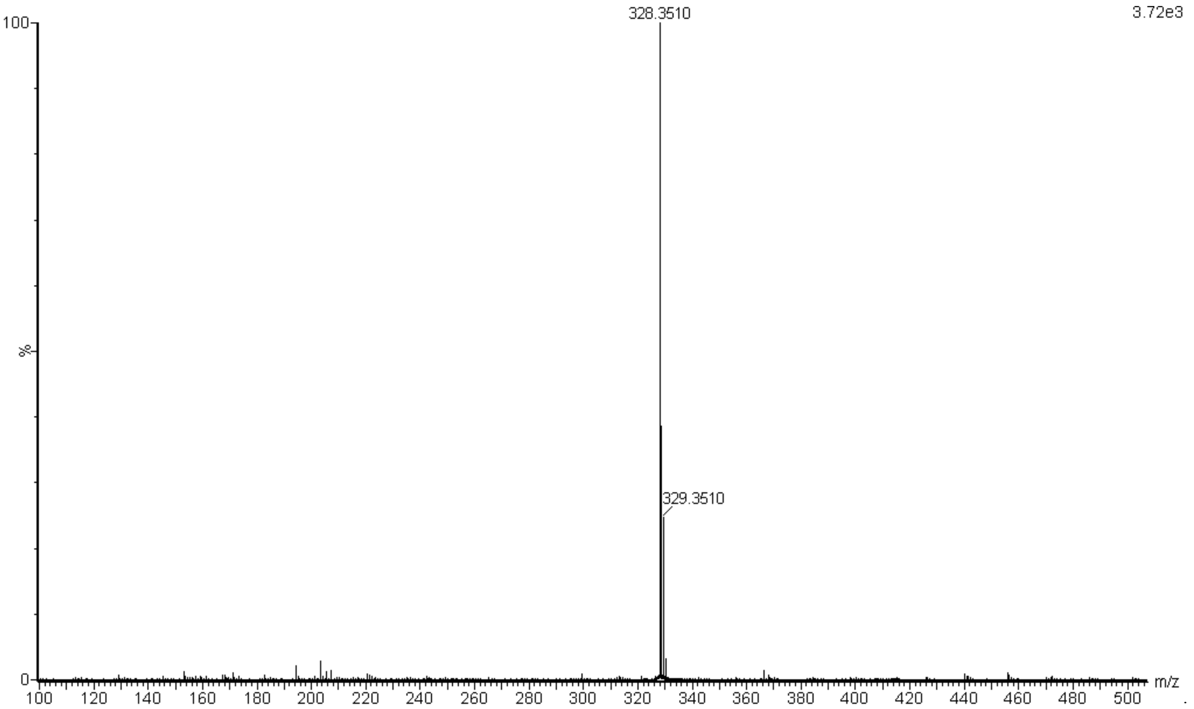
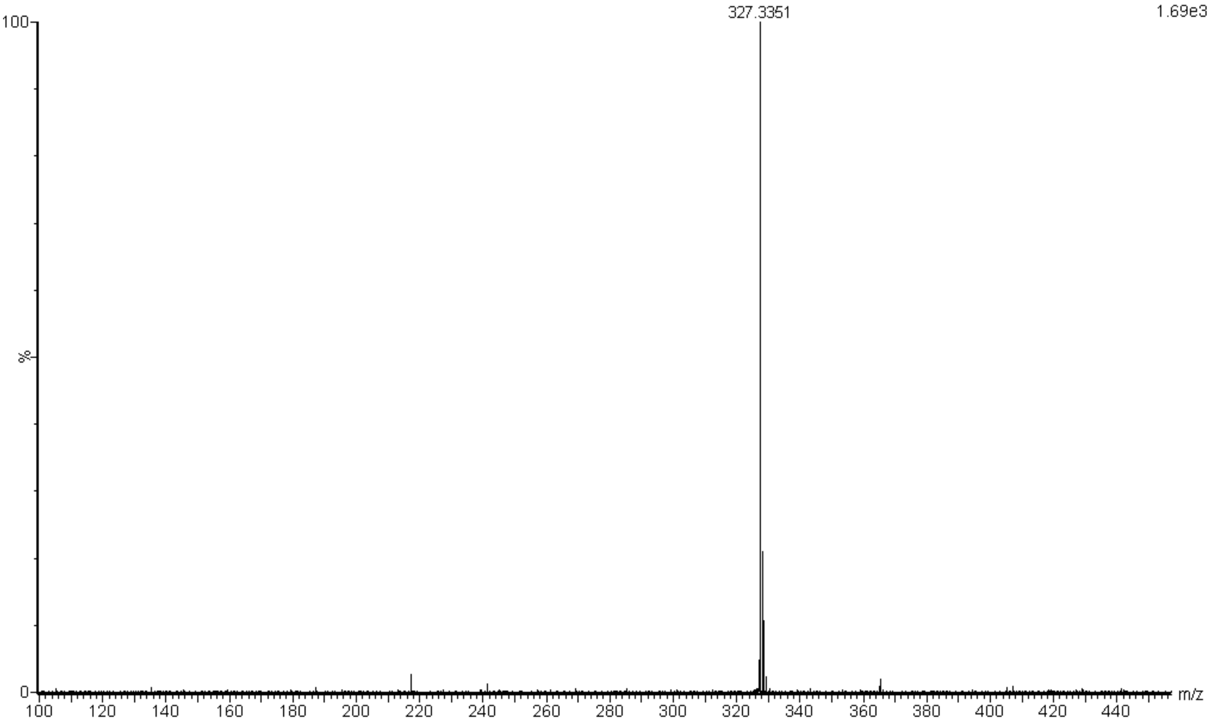


**Figure S3**: ESI-MS of Ligands 3,5,6 and 8

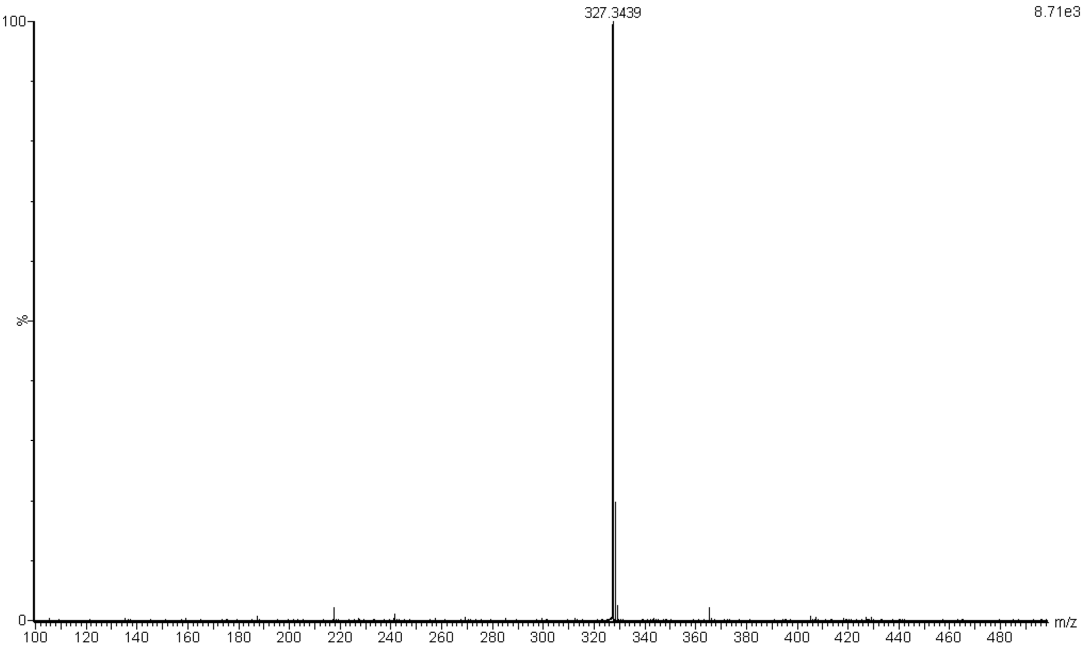
ESI-MS spectra of **3**



ESI-MS spectra of **5**



ESI-MS spectra of **6**



ESI-MS spectra of **8**

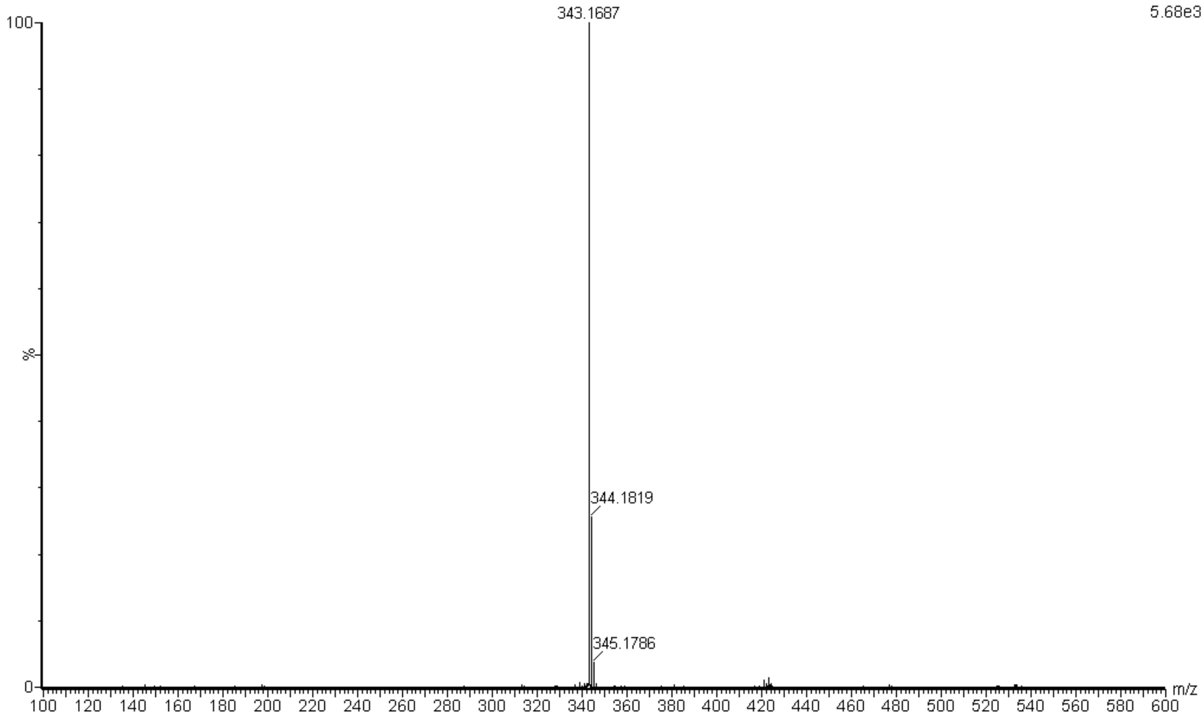
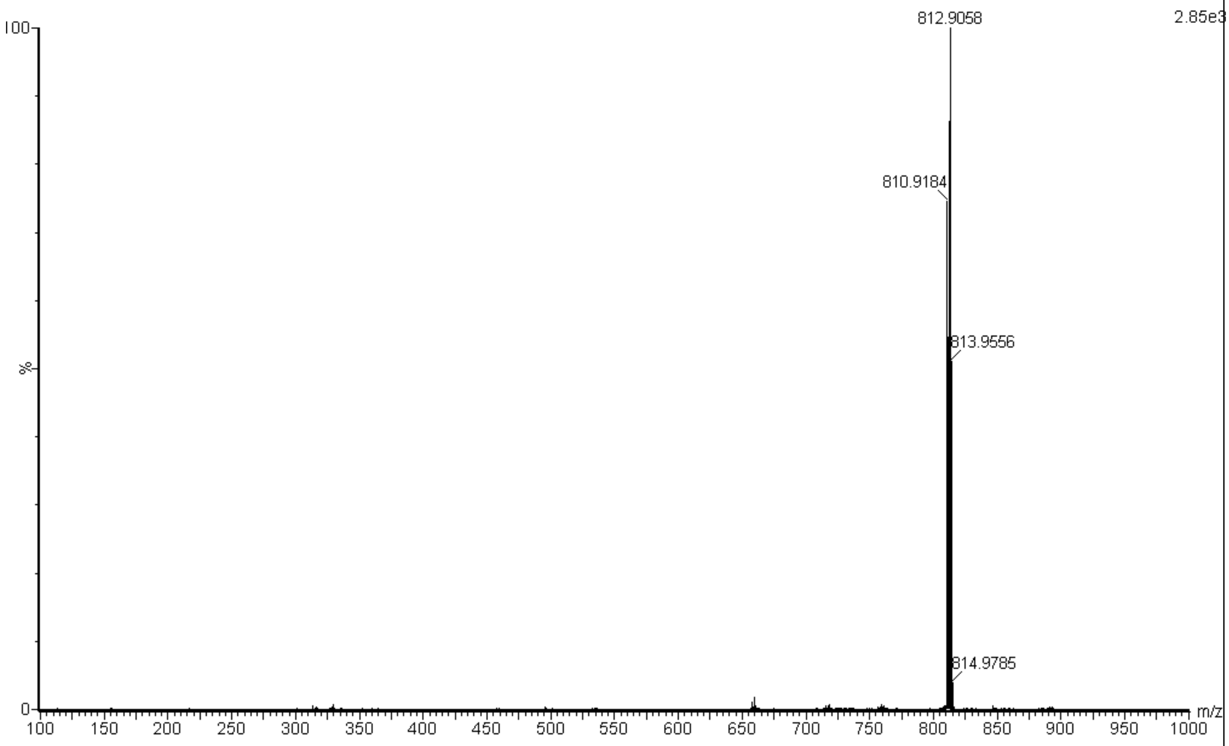
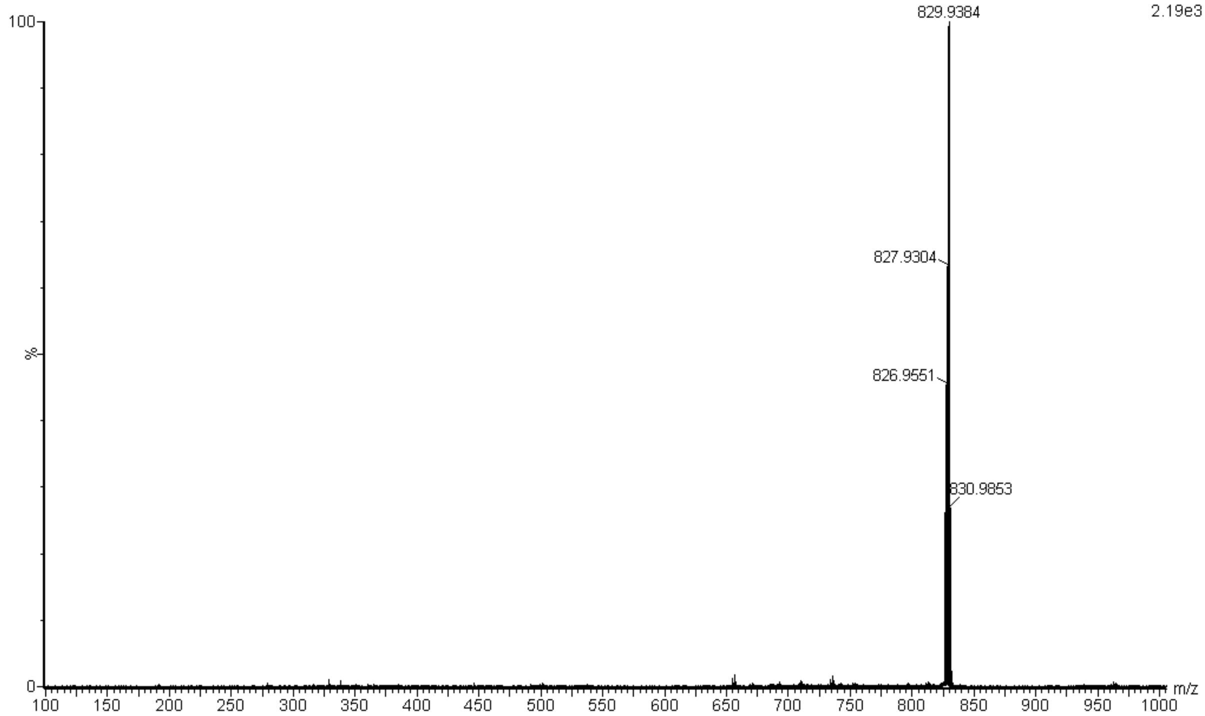


**Figure S4:** ESI-MS spectra of iridium(III) complexes C1, C3 - C10 and rhenium(I) complex C11

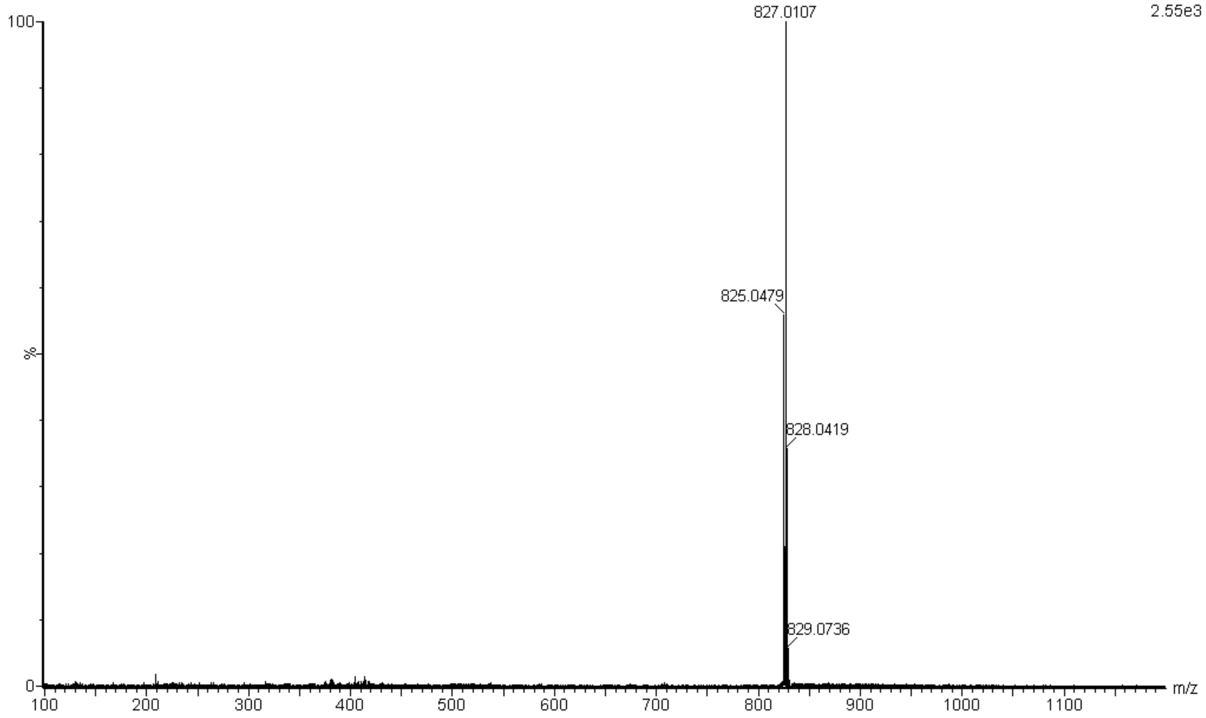
ESI-MS spectra of C**1**



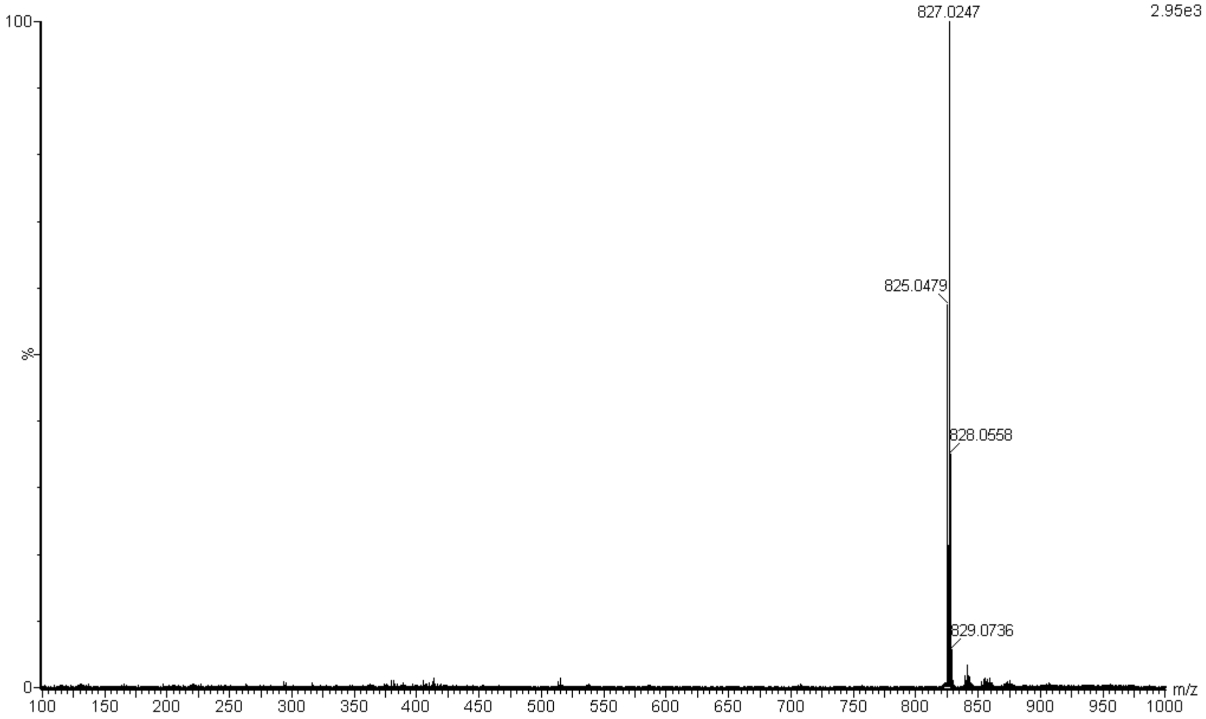
ESI-MS spectra of C**3**



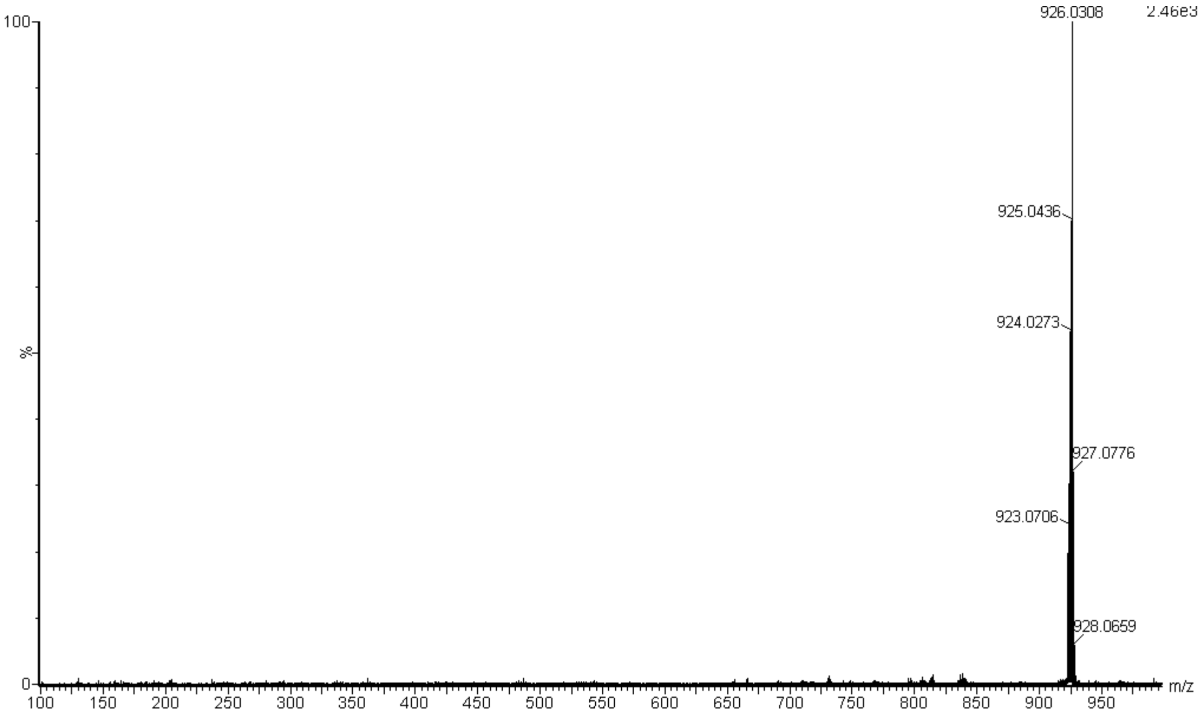
ESI-MS spectra of C**5**



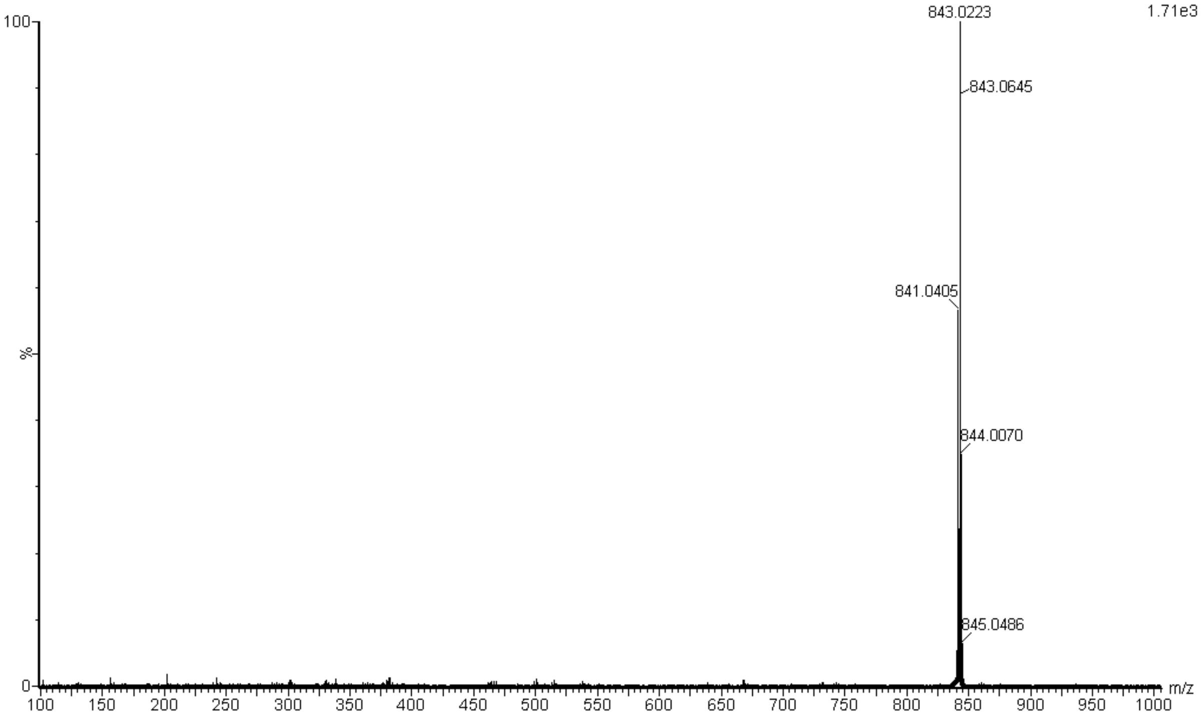
ESI-MS spectra of C**6**



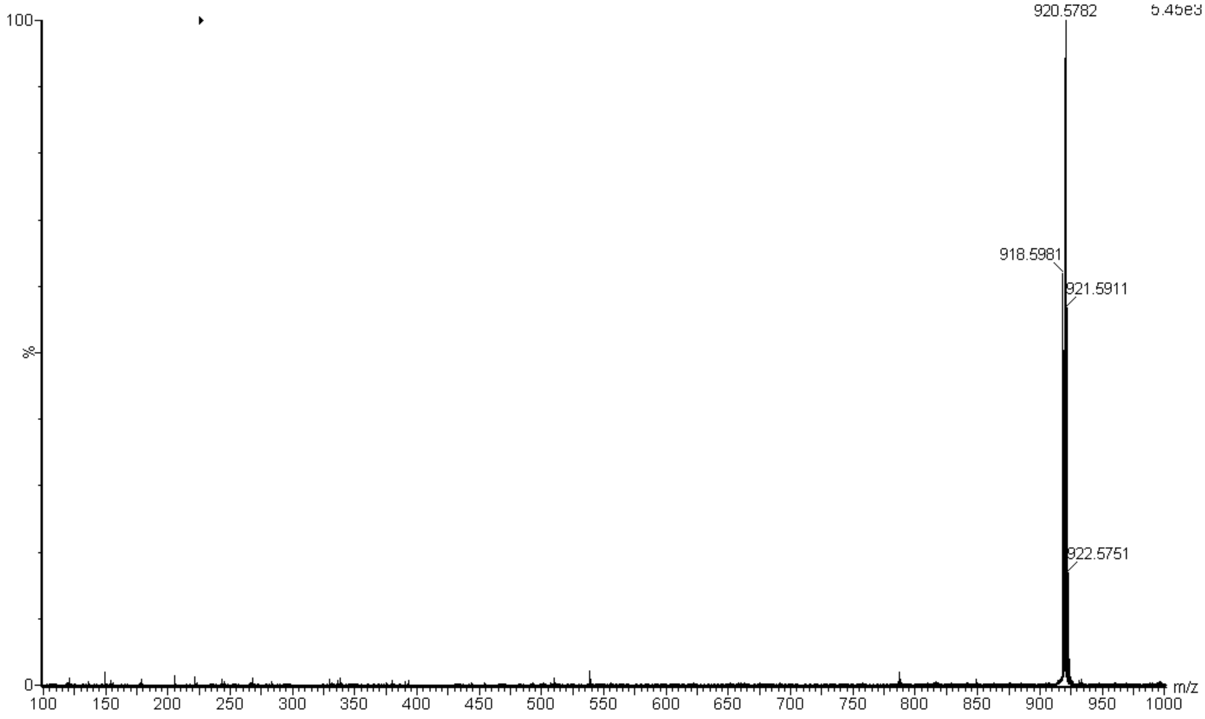
ESI-MS spectra of C**7**



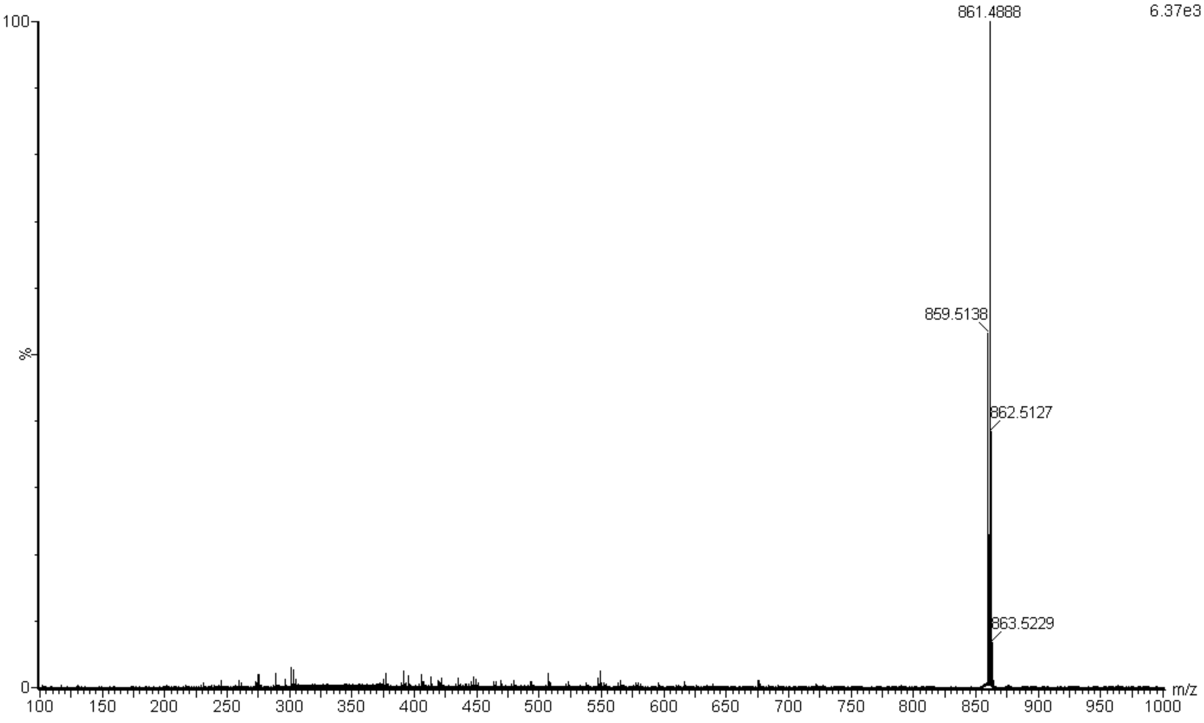
ESI-MS spectra of C**8**



ESI-MS spectra of C**9**



ESI-MS spectra of C**10**



ESI-MS spectra of C**11**

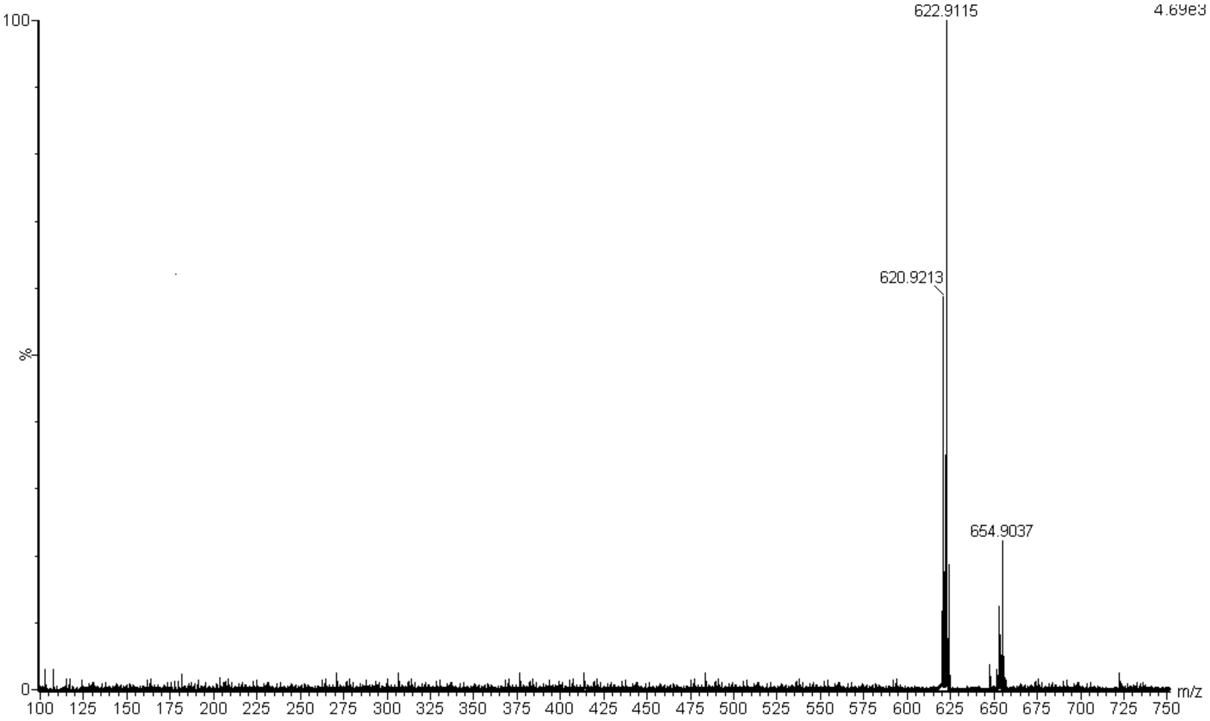
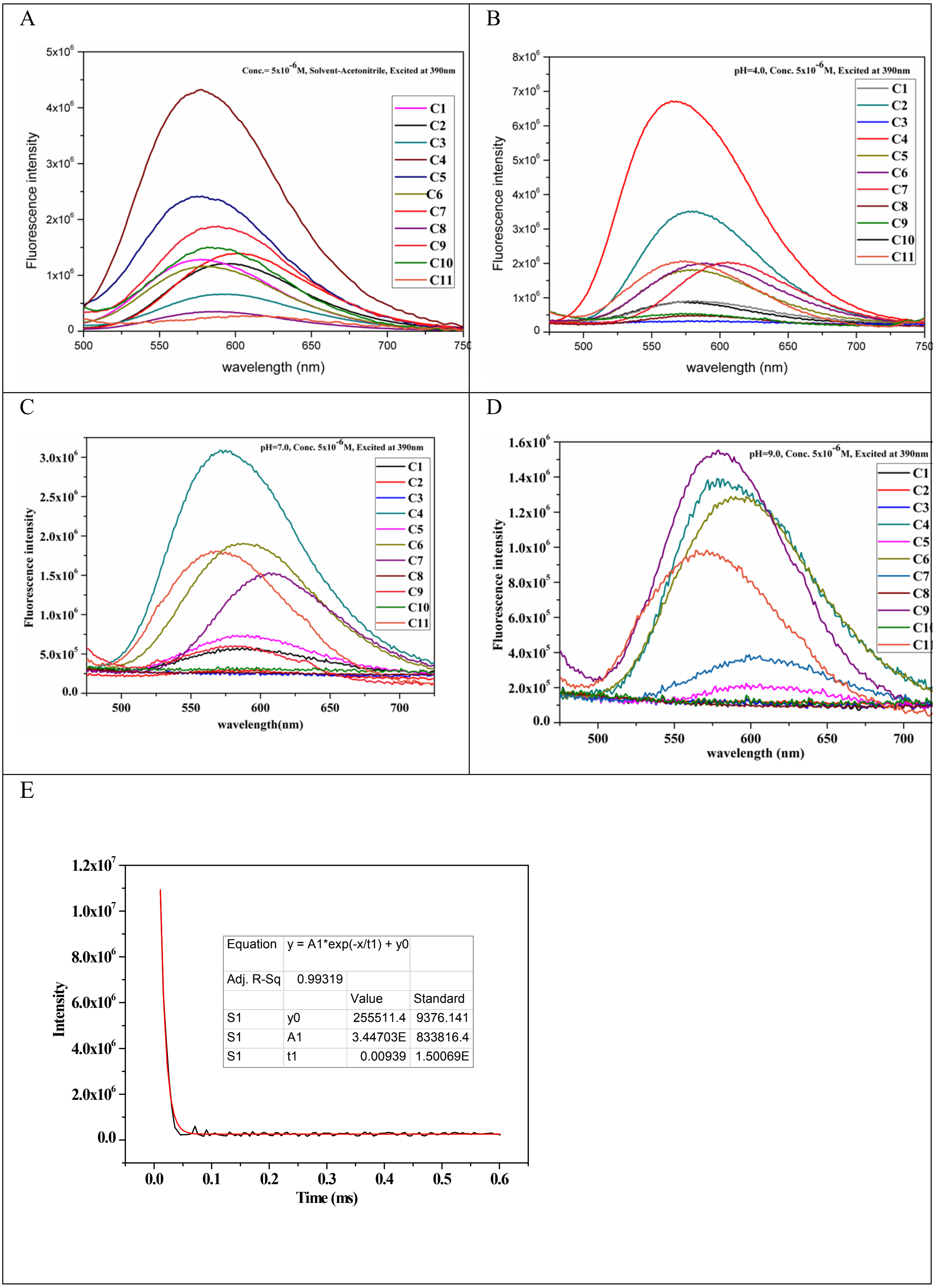


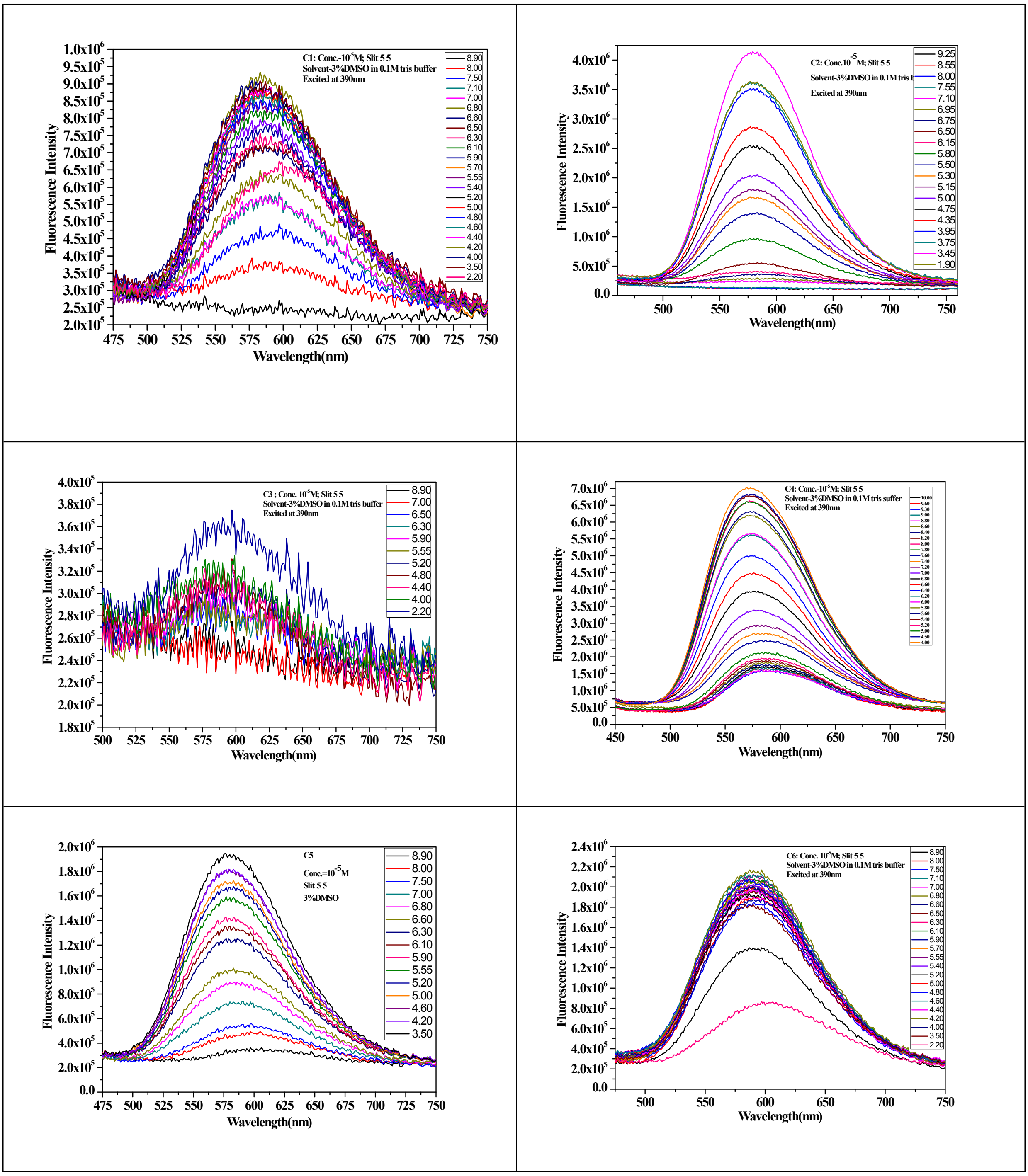
**Figure S5**:

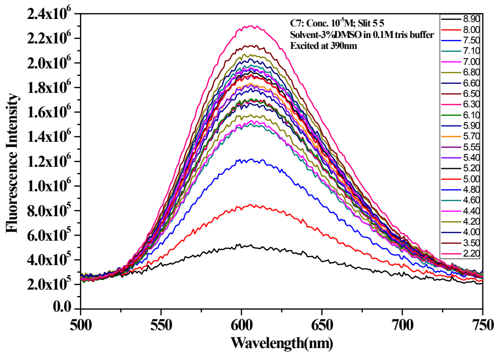
Fluorescence spectra of complexes A. **C1-C11** in acetonitrile solvent, B. at pH 4, C. at pH 7, and D. pH 9, E. Exponential decay curve of **C2**

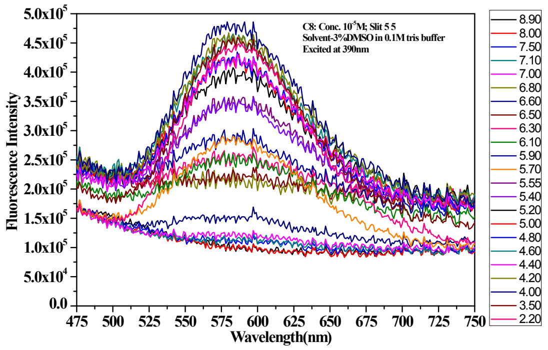


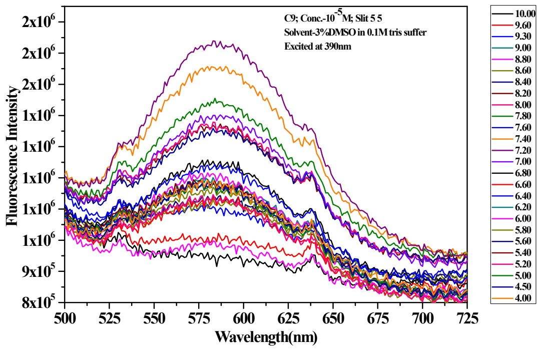
| Equation | y = A1*exp(-x/t1) + y0 | | |
|---|---|---|---|
| Adj. R-Sq | 0.99319 | | |
| | | Value | Standard |
| S1 | y0 | 255511.4 | 9376.141 |
| S1 | A1 | 3.44703E | 833816.4 |
| S1 | t1 | 0.00939 | 1.50069E |

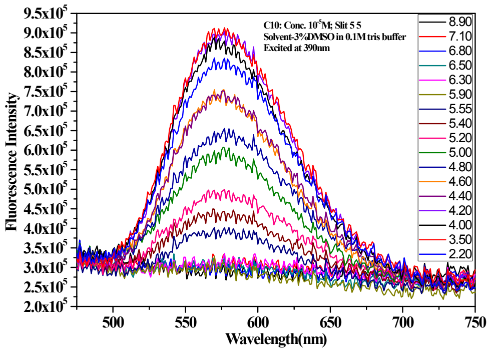
**Figure S6**: pH dependent Fluorescence spectrum of complexes **C1 - C11**




C7: Conc. 10$^{-5}$M; Slit 5 5
Solvent-3%DMSO in 0.1M tris buffer
Excited at 390nm
Fluorescence Intensity
Wavelength(nm)
2.4x10$^6$
2.2x10$^6$
2.0x10$^6$
1.8x10$^6$
1.6x10$^6$
1.4x10$^6$
1.2x10$^6$
1.0x10$^6$
8.0x10$^5$
6.0x10$^5$
4.0x10$^5$
2.0x10$^5$
0.0
500
550
600
650
700
750
8.90
8.00
7.50
7.10
7.00
6.80
6.60
6.50
6.30
6.10
5.90
5.70
5.55
5.40
5.20
5.00
4.80
4.60
4.40
4.20
4.00
3.50
2.20


C8: Conc. 10$^{-5}$M; Slit 5 5
Solvent-3%DMSO in 0.1M tris buffer
Excited at 390nm
Fluorescence Intensity
Wavelength(nm)
5.0x10$^5$
4.5x10$^5$
4.0x10$^5$
3.5x10$^5$
3.0x10$^5$
2.5x10$^5$
2.0x10$^5$
1.5x10$^5$
1.0x10$^5$
5.0x10$^4$
0.0
475
500
525
550
575
600
625
650
675
700
725
750
8.90
8.00
7.50
7.10
7.00
6.80
6.60
6.50
6.30
6.10
5.90
5.70
5.55
5.40
5.20
5.00
4.80
4.60
4.40
4.20
4.00
3.50
2.20


C9; Conc.-10$^{-5}$M; Slit 5 5
Solvent-3%DMSO in 0.1M tris suffer
Excited at 390nm
Fluorescence Intensity
Wavelength(nm)
2x10$^6$
2x10$^6$
2x10$^6$
1x10$^6$
1x10$^6$
1x10$^6$
1x10$^6$
1x10$^6$
9x10$^5$
8x10$^5$
500
525
550
575
600
625
650
675
700
725
10.00
9.60
9.30
9.00
8.80
8.60
8.40
8.20
8.00
7.80
7.60
7.40
7.20
7.00
6.80
6.60
6.40
6.20
6.00
5.80
5.60
5.40
5.20
5.00
4.50
4.00


C10: Conc. 10$^{-5}$M; Slit 5 5
Solvent-3%DMSO in 0.1M tris buffer
Excited at 390nm
Fluorescence Intensity
Wavelength(nm)
9.5x10$^5$
9.0x10$^5$
8.5x10$^5$
8.0x10$^5$
7.5x10$^5$
7.0x10$^5$
6.5x10$^5$
6.0x10$^5$
5.5x10$^5$
5.0x10$^5$
4.5x10$^5$
4.0x10$^5$
3.5x10$^5$
3.0x10$^5$
2.5x10$^5$
2.0x10$^5$
500
550
600
650
700
750
8.90
7.10
6.80
6.50
6.30
5.90
5.55
5.40
5.20
5.00
4.80
4.60
4.40
4.20
4.00
3.50
2.20

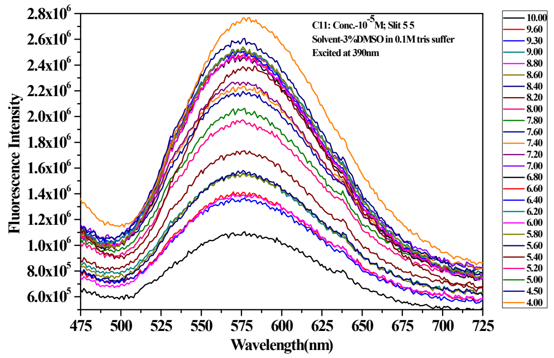

C11: Conc.-10$^{-5}$M; Slit 5 5
Solvent-3%DMSO in 0.1M tris suffer
Excited at 390nm
Fluorescence Intensity
Wavelength(nm)
2.8x10$^6$
2.6x10$^6$
2.4x10$^6$
2.2x10$^6$
2.0x10$^6$
1.8x10$^6$
1.6x10$^6$
1.4x10$^6$
1.2x10$^6$
1.0x10$^6$
8.0x10$^5$
6.0x10$^5$
475
500
525
550
575
600
625
650
675
700
725
10.00
9.60
9.30
9.00
8.80
8.60
8.40
8.20
8.00
7.80
7.60
7.40
7.20
7.00
6.80
6.60
6.40
6.20
6.00
5.80
5.60
5.40
5.20
5.00
4.50
4.00

Figure S7: DIC and confocal fluorescence images of live MCF7 cells not treated with **C2** but exposed to photoirradiation at 405 nm for 30 min. The cells were treated with DCFDA and fluorescence images were obtained at 529 nm after excitation at 495 nm. The central tile represents the field which was exposed to the laser whereas the surrounding tiles represent the fields not exposed.

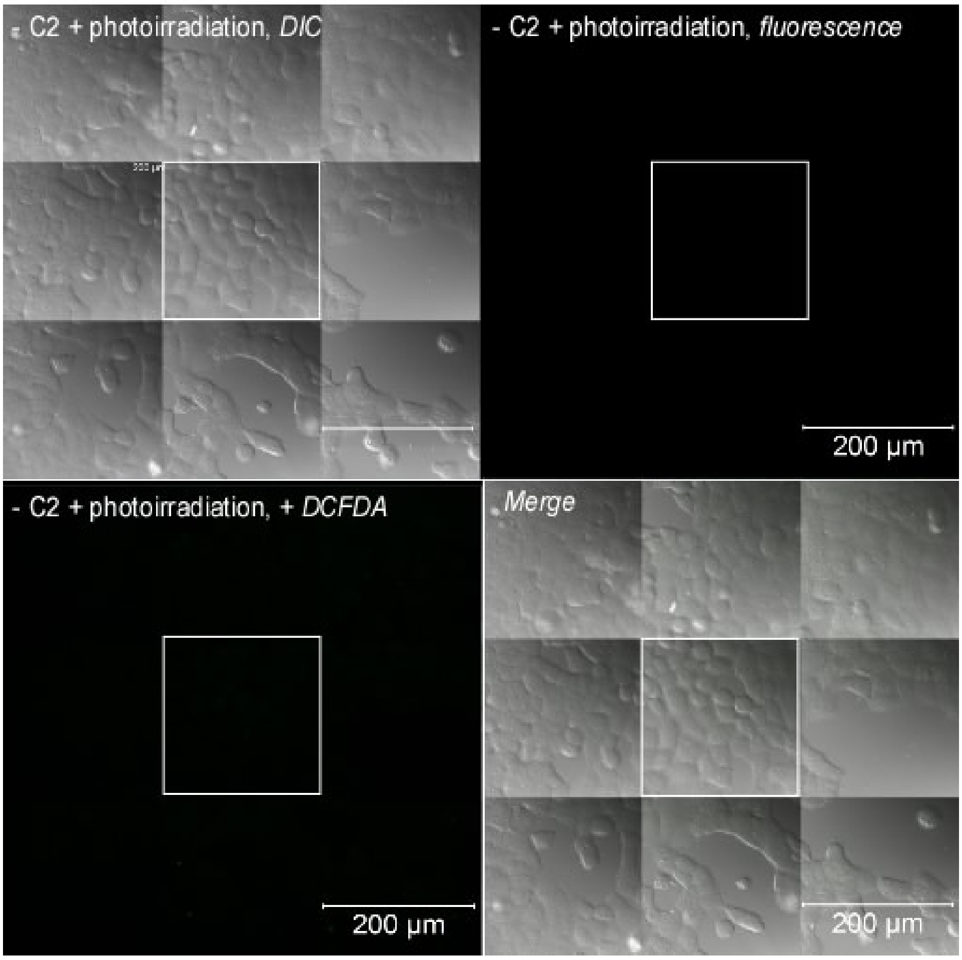


**TABLE S1: Photophysical, electrochemical, lipophilicity data of complexes C1 - C11**

| Complex | Electronic spectral data[a] ($\varepsilon \times 10^{-4}$ LMol$^{-1}$cm$^{-1}$) | Emission spectrum[a] | $\tau$(μs)[b] | Adj. R-square | $\phi$(%) |
|---|---|---|---|---|---|
| C1 | 416(0.57), 330(2.81), 281(6.62), 273(6.49) | 576 | 11.25 | 0.99077 | 16.40 |
| C2 | 470(0.27), 402(0.76), 349(3.42), 334(3.85), 285(5.55), 274(5.82) | 593 | 9.39 | 0.99319 | 12.91 |
| C3 | 478(0.23), 389(1.13), 344(2.98), 332(3.26), 290(5.76), 279(6.09) | 592 | 9.21 | 0.99116 | 14.57 |
| C4 | 469(0.10), 406(0.60), 383(0.69), 295(4.09), 276(5.75) | 575 | 14.47 | 0.99027 | 41.21 |
| C5 | 411(0.40), 352(1.16), 285(3.78) | 575 | 10.62 | 0.99738 | 16.31 |
| C6 | 470(0.08), 410(0.71), 339(2.77), 322(3.77), 295(5.09), 273(6.97) | 577 | 10.34 | 0.99343 | 23.73 |
| C7 | 469(0.06), 399(0.61), 348(1.66), 271(5.59) | 601 | 11.66 | 0.99312 | 18.99 |
| C8 | 470(0.16), 398(0.42), 335(2.13), 292(3.44) | 587 | 8.60 | 0.9931 | 6.74 |
| C9 | 470(0.24), 397(0.62), 338(1.34), 295(2.13), 270(3.01) | 587 | 11.98 | 0.99263 | 13.33 |
| C10 | 410(0.60), 349(4.88), 333(5.81), 273(7.19) | 584 | 15.52 | 0.98793 | 18.69 |
| C11 | 436(0.20), 418(0.32), 345(0.97), 327(1.27), 303(1.30), 278 (2.24) | 612 | 5.46 | 0.98373 | 22.90 |

[a] $\lambda_{max}$(nm), Dichloromethane solution. [b] Solvent dry deaerated dichloromethane;

**Table S2:** pH dependent phosphorescence lifetime of complex **C2**

| pH | Lifetime($\tau$, μs) | Adj. R Sq. |
|---|---|---|
| 4.0 | 12.74 | 0.98334 |
| 4.5 | 11.80 | 0.98986 |
| 5.0 | 10.68 | 0.99479 |
| 5.5 | 9.76 | 0.99748 |
| 6.0 | 9.10 | 0.99864 |

| | | |
|---|---|---|
| 6.5 | 8.61 | 0.99002 |
| 7.0 | 8.52 | 0.99484 |
| 7.5 | 8.44 | 0.98937 |
| 8.0 | 8.00 | 0.9934 |
| 8.5 | 2.76 | 0.99512 |
| 9.0 | 2.60 | 0.99679 |
| 9.5 | 2.58 | 0.9929 |
| 10.0 | 2.53 | 0.99551 |

**Table S3**: Bond distances (Å) and bond angles (°) of **C2**

| Bond distances (Å) | Bond angles (°) | Bond angles (°) |
|---|---|---|
| Ir1 −N1 2.065(3) | N1−Ir1−N2 170.48(16) | N2−Ir1−C22 80.27(11) |
| Ir1 −N2 2.053(3) | N1−Ir1−N3 89.2(3) | N3−Ir1−N4 78.6(4) |
| Ir1 −N3 2.151(11) | N1−Ir1−N4 96.9(3) | N3−Ir1−C11 98.7(3) |
| Ir1 −N4 2.109(11) | N1−Ir1−C11 80.06(10) | N3−Ir1−C22 171.2(3) |
| Ir1 −C11 2.073(3) | N1−Ir1−C22 96.19(12) | N4−Ir1−C11 176.0(3) |
| Ir1 −C22 2.061(3) | N2−Ir1−N3 95.5(3) | N4−Ir1−C22 93.8(3) |
| | N2−Ir1−N4 92.1(3) | C11−Ir1−C22 89.09(11) |
| | N2−Ir1−C11 90.99(12) | |

**Table S4**: Cyclic voltammetric data of complexes **C1** – **C11**

| Complex | Cyclic voltammetric data (V)[a] |
|---|---|
| **C1** | 0.71, 1.41, 1.88, -0.96, -1.47, 1.53[b](120)[c] |
| **C2** | 0.72, 1.42, 1.88, -0.95, -1.47, 1.53[b] (120)[c] |
| **C3** | 0.43, 0.99, 1.39, -0.78, -1.33, -1.56[b](110)[c] |
| **C4** | 0.62, 1.17, 1.47, -0.94, -1.52[b](80)[c] |
| **C5** | 1.24, 1.34, -1.04, -1.64 |

| | |
|---|---|
| **C6** | 1.24, 1.56, 1.88, -0.78, -1.54 |
| **C7** | 1.08, 1.38, -0.72, -1.20 |
| **C8** | 0.56, 1.40, 1.80, -1.07, -1.55[b] (80)[c] |
| **C9** | 0.73, 1.39, -0.97, -1.40 |
| **C10** | 0.72, 1.26, -1.00, -1.52 |
| **C11** | 1.45, -1.00, -1.30[b](80)[c], -1.52 |

[a]Dichloromethane/acetonitrile (1:9), TBAP supporting electrolyte; [b]$E_{1/2}$ = 0.5 ($E_{pa}$ +$E_{pc}$), where $E_{pa}$ and $E_{pc}$ are anodic and cathodic peak potentials respectively, scan rate 50 mV s-1. [c]ΔEp = Epa – Epc in mV.