Supporting Information

Near-IR Light-induced Photorelease of nitric oxide (NO) on Ruthenium Nitrosyl Complexes: Formation, reactivity aspects, and biological effects

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Figure captions:

Fig. S1. ^{1}H NMR spectra of [**1**](PF_6) in $(CD_3)_2SO$ at room temperature.

Fig. S2. ^{1}H NMR spectra of [**2**]$(PF_6)_2$ in $(CD_3)_2SO$ at room temperature.

Fig. S3. ^{1}H NMR spectra of [**3**](PF_6) in $(CD_3)_2SO$ at room temperature.

Fig. S4. ^{1}H NMR spectra of [**4**]$(PF_6)_3$ in $(CD_3)_2SO$ at room temperature.

Fig. S5. ESI-MS(+) spectra of (a) [**1**](PF_6) (b) [**2**]$(PF_6)_2$ (c) [**3**](PF_6) and (d) [**4**]$(PF_6)_3$ in acetonitrile.

Fig. S6. Cyclic voltammograms of [**1**](PF_6), [**2**]$(PF_6)_2$ and [**3**](PF_6) in CH_3CN/0.1M TBAP versus SCE, scan rate 100 mVs^{-1}.

Fig. S7. FTIR spectra of [**1**](PF_6) (Solid).

Fig. S8. FTIR spectra of [**2**]$(PF_6)_2$ (Solid).

Fig. S9. FTIR spectra of [**3**](PF_6) (Solid).

Fig. S10. FTIR spectra of [**4**]$(PF_6)_3$ (Solid).

Fig. S11. FTIR spectra of [**4**]$(PF_6)_2$ (Solid).

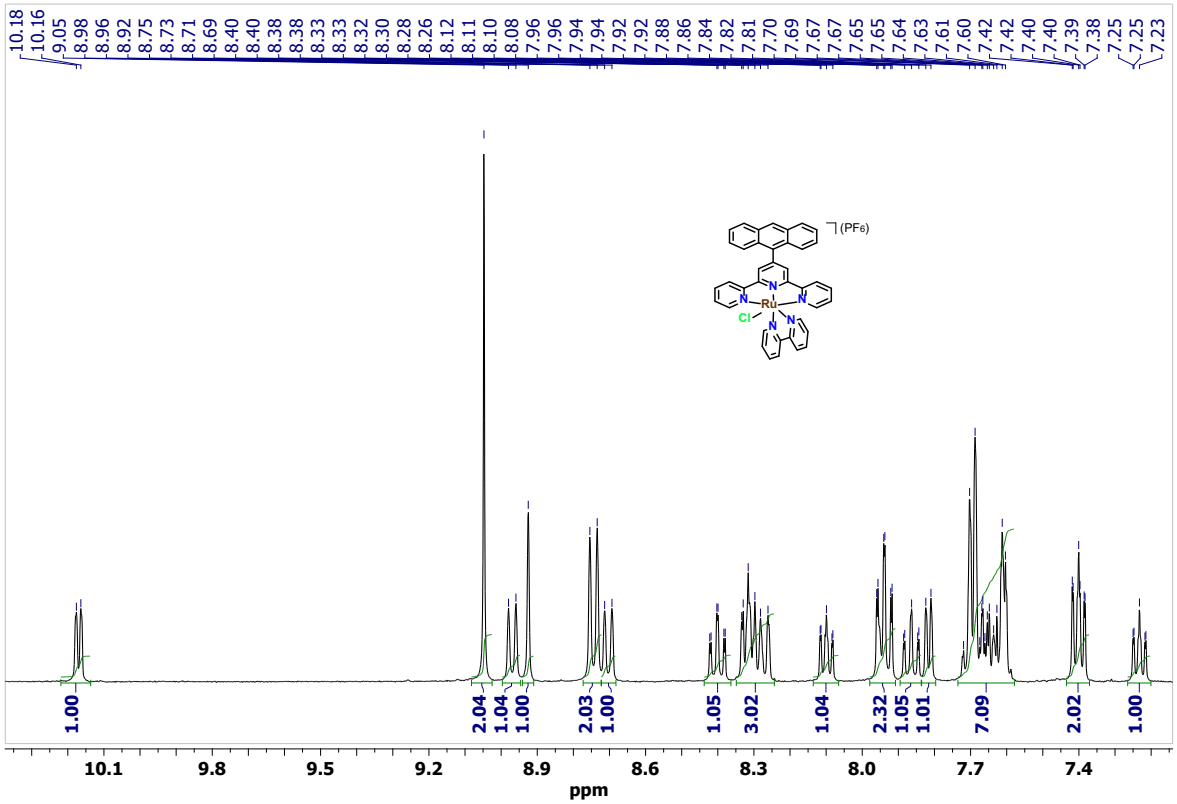
Fig. S12. Bright-field images of VCaP cells treated with various compounds. (A) VCaP cells following addition of 3 μM [**1**](PF_6), (B) 3 μM [**1**](PF_6) treated VCaP cells before photo-irradiation, (C) 3 μM [**1**](PF_6) treated VCaP cells following photo-irradiation for 15 min, (D) VCaP cells following addition of 3 μM [**2**]$(PF_6)_2$, (E) 3 μM [**2**]$(PF_6)_2$ treated VCaP cells before photo-irradiation, (F) 3 μM [**2**]$(PF_6)_2$ treated VCaP cells following photo-irradiation for 15 min, (G) VCaP cells following addition of 3 μM [**3**](PF_6), (H) 3 μM [**3**](PF_6) treated VCaP cells before photo-irradiation, (I) 3 μM [**3**](PF_6) treated VCaP cells following photo-irradiation for 15 min, (J) VCaP cells following addition of 3 μM [**4**]$(PF_6)_2$, (K) 3 μM [**4**]$(PF_6)_2$ treated VCaP cells before photo-irradiation, (L) 3 μM [**4**]$(PF_6)_2$ treated VCaP cells following photo-irradiation for 5 min, (M) 3 μM [**4**]$(PF_6)_2$ treated VCaP cells following photo-irradiation for 10 min, (N) 3 μM [**4**]$(PF_6)_2$ treated VCaP cells following photo-irradiation for 15 min.

Table S1. ^{1}H NMR spectral data in $(CD_3)_2SO$

Complexes	δ, ppm (*J*, Hz)	
	Aromatic Protons	Aliphatic Protons
[**1**](PF_6)	10.17 (4.96) (d, 1H), 9.04 (s, 2H), 8.96 (8.16) (d, 1H), 8.92 (s, 1H), 8.74 (8.12) (d, 2H), 8.70 (8.08) (d, 1H), 8.40 (7.84, 7.8) (t, 1H), 8.30 (m, 3H), 8.09 (6.92, 6.16) (t, 1H), 7.94 (7.84, 7.76) (t, 2H), 7.86 (8.84, 6.76) (t, 1H), 7.81 (5.72) (d, 1H), 7.66 (m, 7H), 7.40 (7.12, 7.04) (t, 2H), 7.23 (7.08, 7.12) (t, 1H)	-
[**2**]$(PF_6)_2$	9.74 (5.24) (d, 1H), 9.18 (s, 2H), 9.02 (8.24) (d, 1H), 8.95 (s, 1H), 8.83 (8.04) (d, 2H), 8.78 (8.2) (d, 1H), 8.48 (7.88, 7.8) (t, 1H), 8.33 (m, 2H), 8.22 (820) (d, 1H), 8.06 (m, 4H), 7.80 (m, 4H), 7.67 (m, 3H), 7.59 (7.56, 7.88) (t, 1H), 7.50 (7.32, 7.08) (t, 2H), 7.38 (7.16, 7.24) (t, 1H)	2.44 (s, 3H)
[**3**](PF_6)	9.83 (4.92) (d, 1H), 9.07 (s, 2H), 8.97 (8.20) (d, 1H), 8.94 (s, 1H), 8.76 (m, 3H), 8.41 (7.88, 7.76) (t, 1H), 8.32 (6.8, 7.48) (t, 2H), 8.23 (8.32) (d, 1H), 8.10 (7.12, 6.04) (t, 1H), 8.00 (m, 3H), 7.90 (5.16) (d, 1H), 7.76 (4.92) (d, 2H), 7.66 (m, 5H), 7.44 (7.08, 6.08) (t, 2H), 7.36 (6.04, 6.08) (t, 1H)	
[**4**]$(PF_6)_3$	9.84 (5.2) (d, 1H), 9.15 (s, 2H), 8.97 (8.20) (d, 1H), 8.77 (8.04, 7.8) (t, 2H), 8.71–8.68 (m, 2H), 8.60 (7.96) (d, 2H), 8.48–8.40 (m, 2H), 8.34–8.31 (m, 1H), 8.14–8.09 (m, 2H), 8.04 (8.96, 7.96) (t, 3H), 7.99–7.91 (m, 4H), 7.78 (4.68) (d, 2H), 7.47 (7.12, 6.08) (t, 2H), 7.36–7.31 (m, 1H)	

Table S2. Vibrational frequencies of PF_6^- of corresponding complexes.

Complexes	$\nu(PF_6^-)$	
	Stretching (cm^{-1})	Bending (cm^{-1})
[**1**](PF_6)	828	548
[**2**]$(PF_6)_2$	830	552
[**3**](PF_6)	833	549
[**4**]$(PF_6)_3$	835	554
[**4**]$(PF_6)_2$	835	552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8.73
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8.69
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8.38
8.38
8.33
8.33
8.32
8.30
8.28
8.26
8.12
8.11
8.10
8.08
7.96
7.96
7.94
7.94
7.92
7.92
7.88
7.86
7.84
7.82
7.81
7.70
7.69
7.67
7.67
7.65
7.65
7.64
7.63
7.61
7.60
7.42
7.42
7.40
7.40
7.39
7.38
7.25
7.25
7.23
(PF6)
N
N
N
Ru
Cl
N
N
1.00
2.04
1.04
1.00
2.03
1.00
1.05
3.02
1.04
2.32
1.05
1.01
7.09
2.02
1.00
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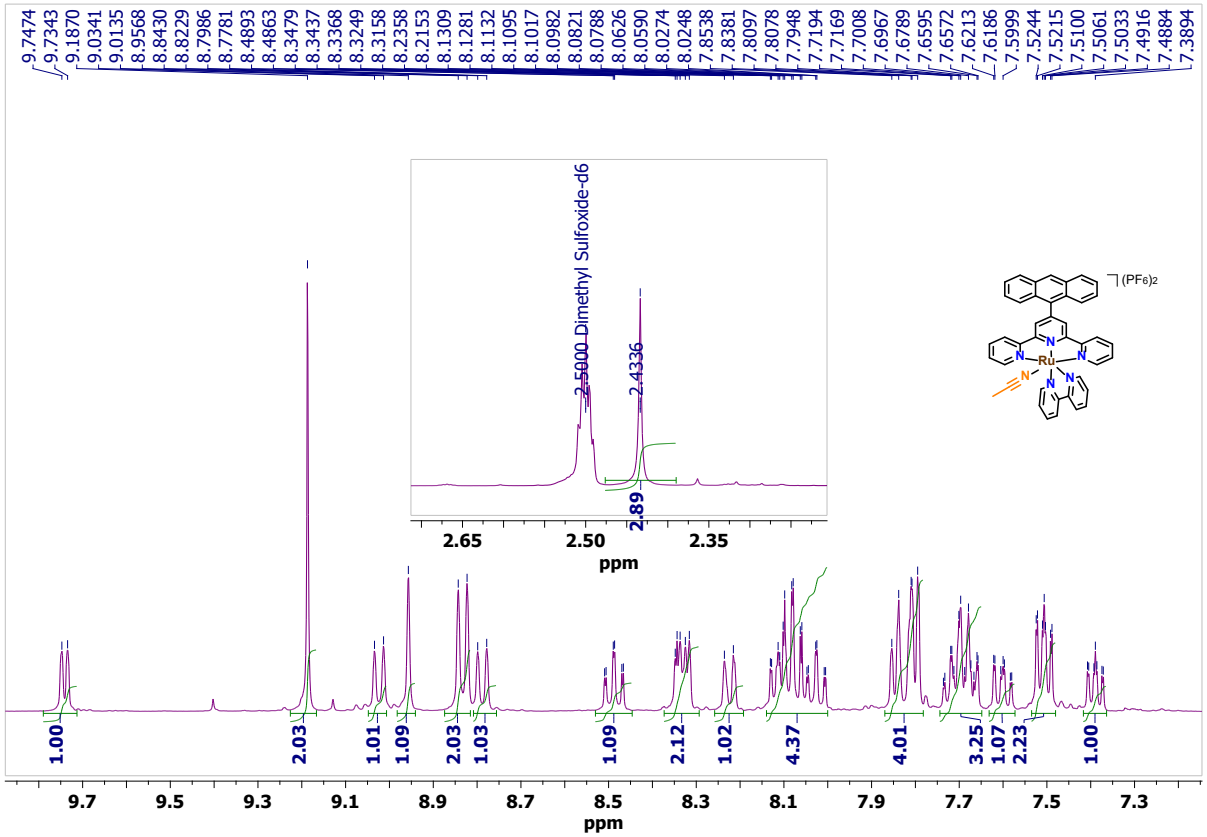
7.7
7.4
ppm

Fig. S1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8.4863
8.3479
8.3437
8.3368
8.3249
8.3158
8.2358
8.2153
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8.1281
8.1132
8.1095
8.1017
8.0982
8.0821
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2.65
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1.09
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1.03
1.09
2.12
1.02
4.37
4.01
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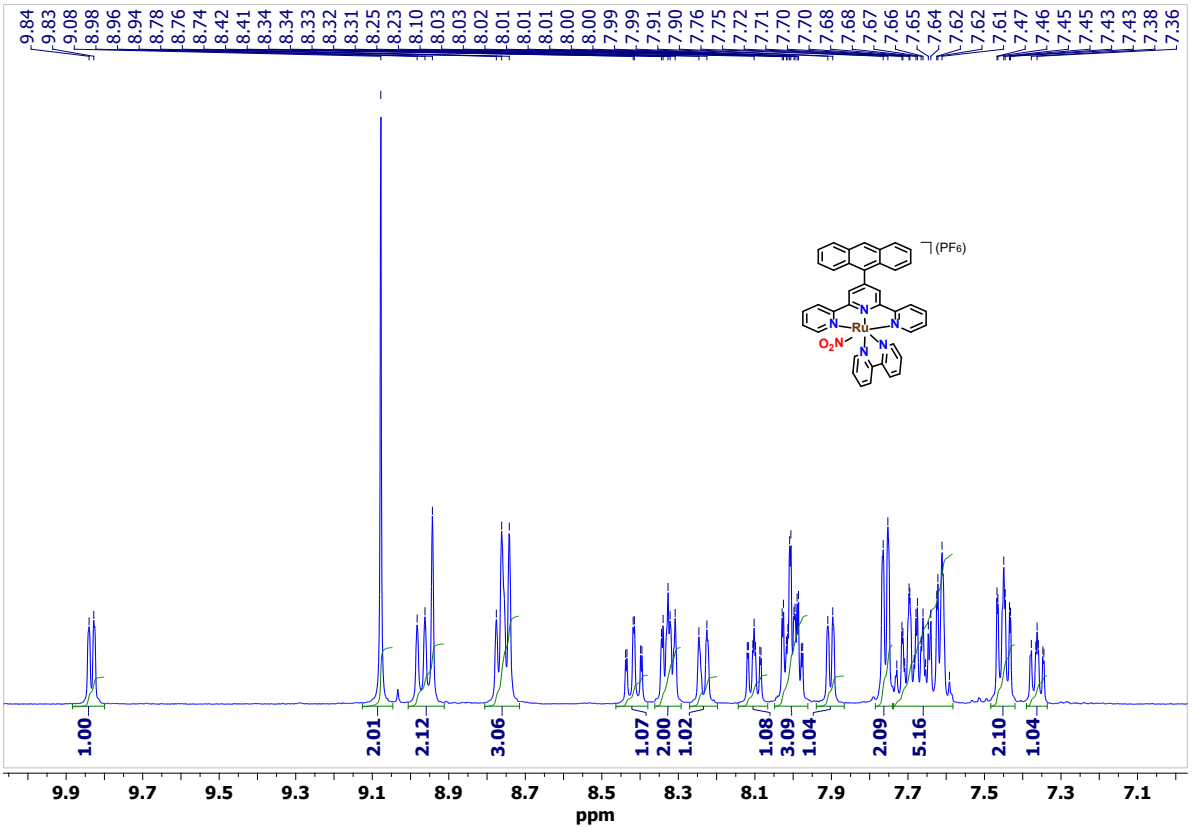
Fig. S2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8.01
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7.90
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7.61
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1.07
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1.02
1.08
3.09
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2.10
1.04
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9.5
9.3
9.1
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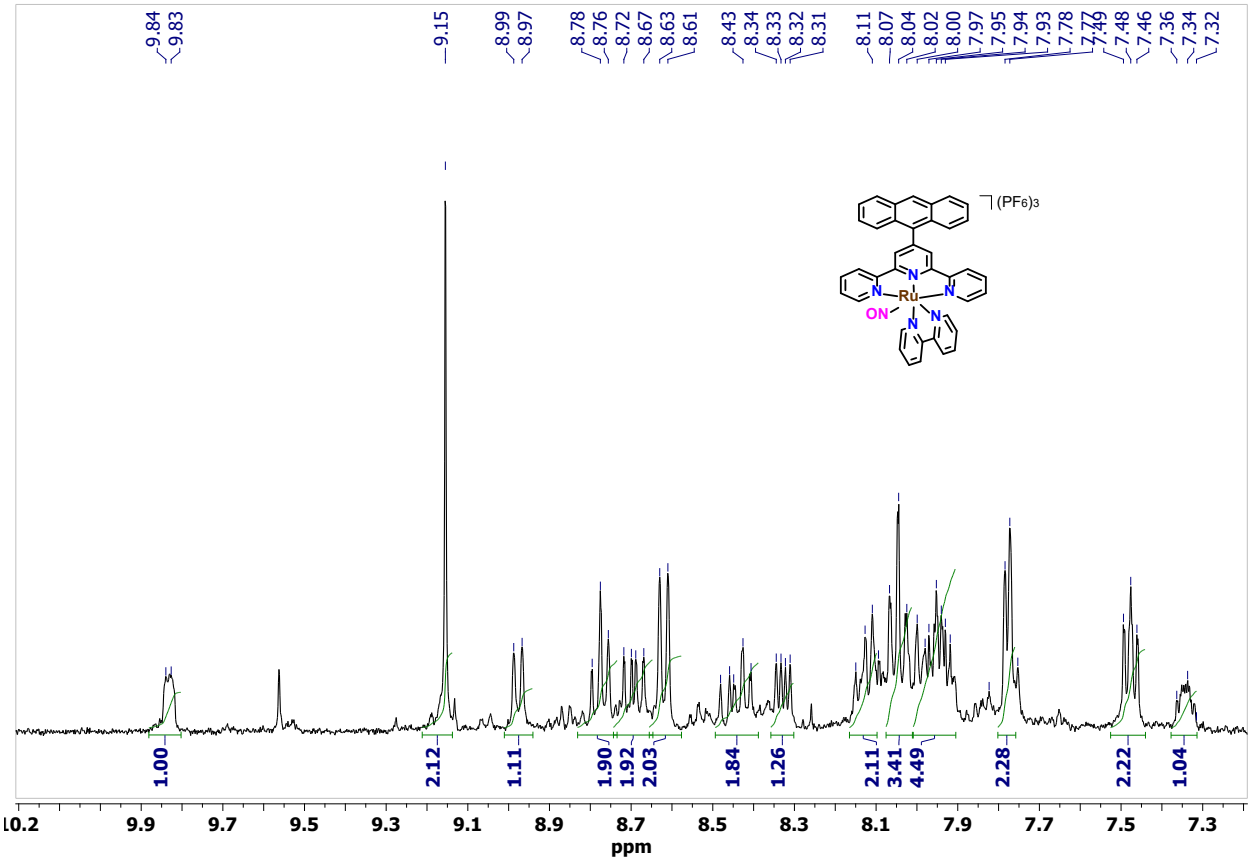
7.1
ppm

Fig. S3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8.32
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7.48
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7.36
7.34
7.32
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1.26
2.11
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4.49
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9.3
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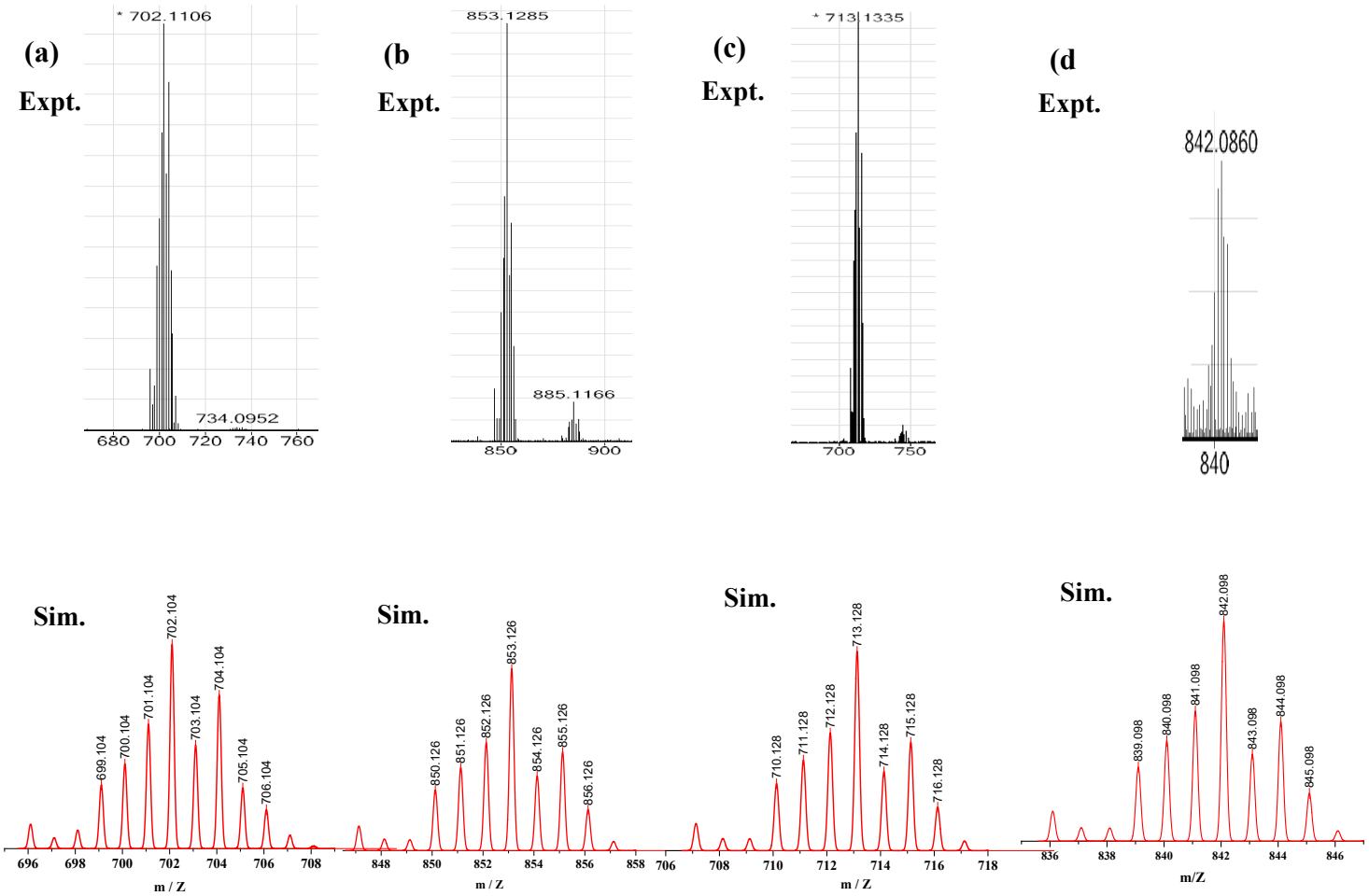
7.5
7.3
ppm

Fig. S4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680 700 720 740 760
(b
Expt.
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850 900
(c)
Expt.
* 713.1335
700 750
(d
Expt.
842.0860
840
Sim.
699.104
700.104
701.104
702.104
703.104
704.104
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706.104
696 698 700 702 704 706 708
m / Z
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848 850 852 854 856 858
m / Z
Sim.
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m / Z
Sim.
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m/Z

Fig. S5

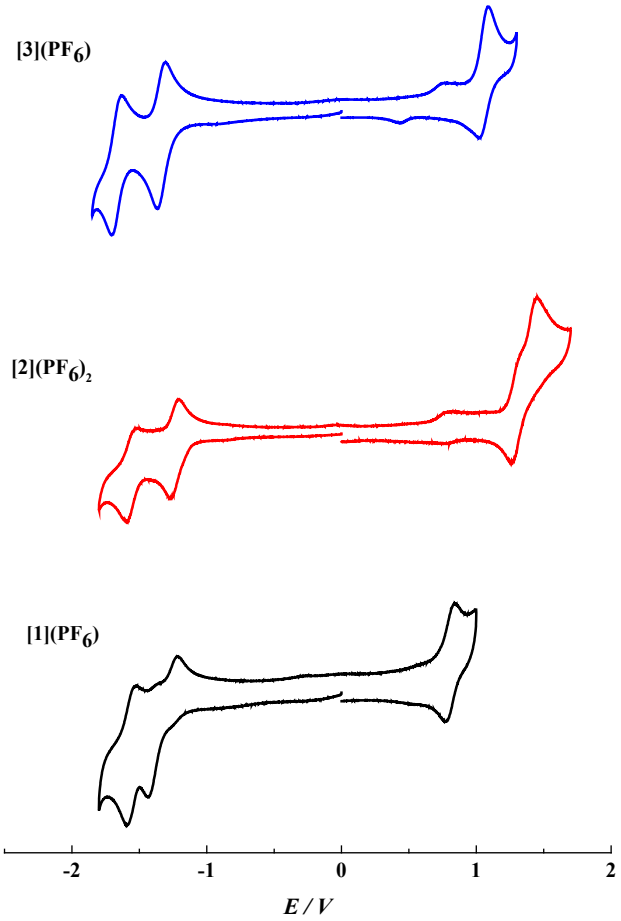
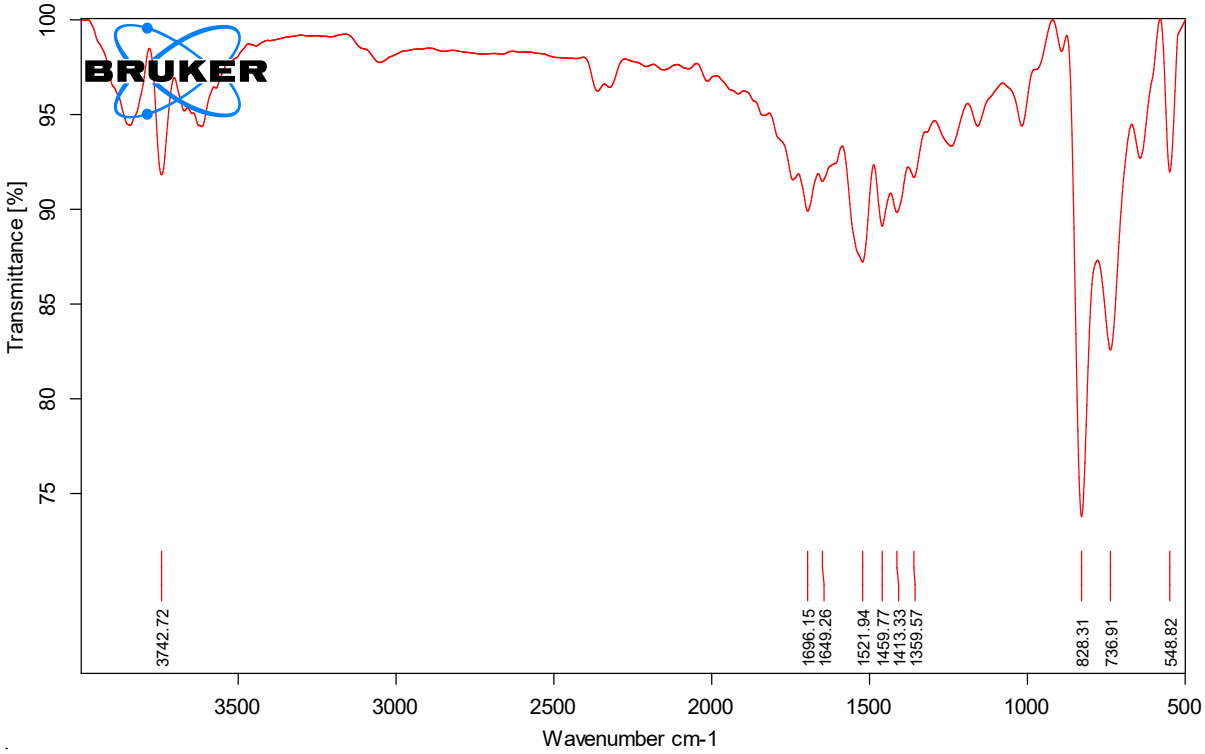


Fig. S6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85
80
75
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1413.33
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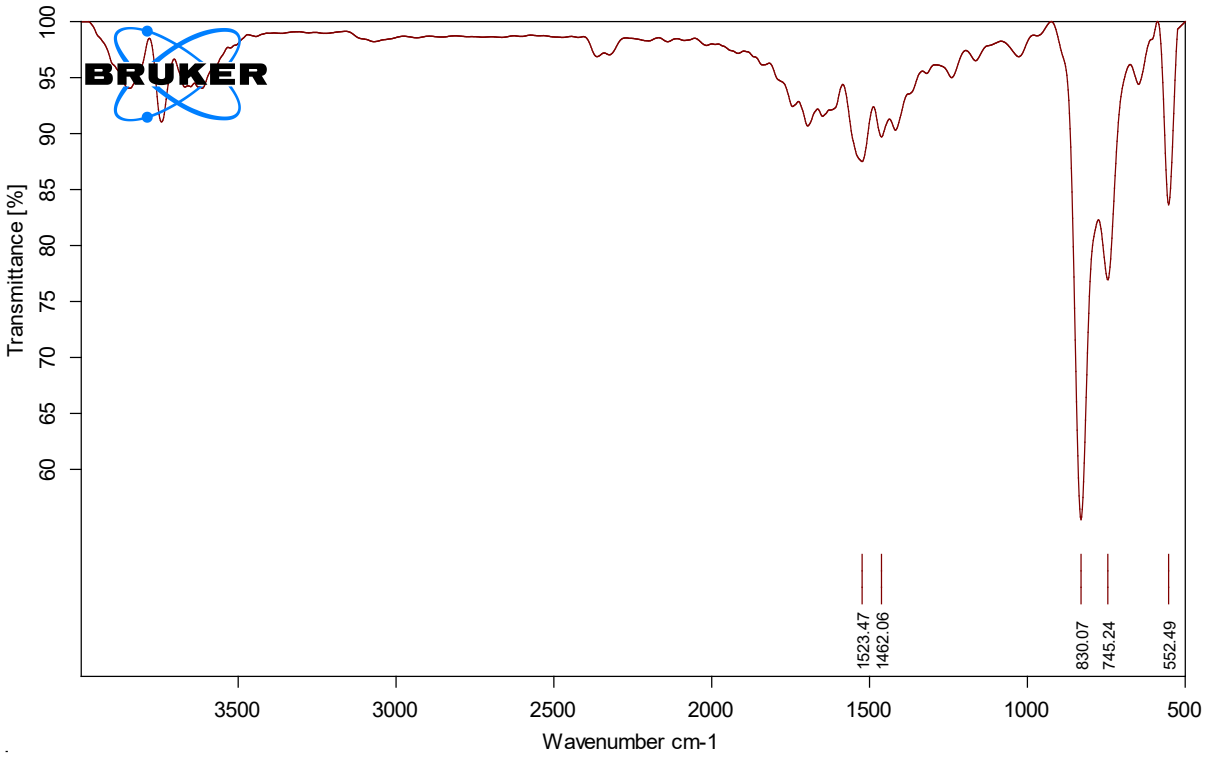
2000
1500
1000
500
Wavenumber cm-1

Fig. S7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1000
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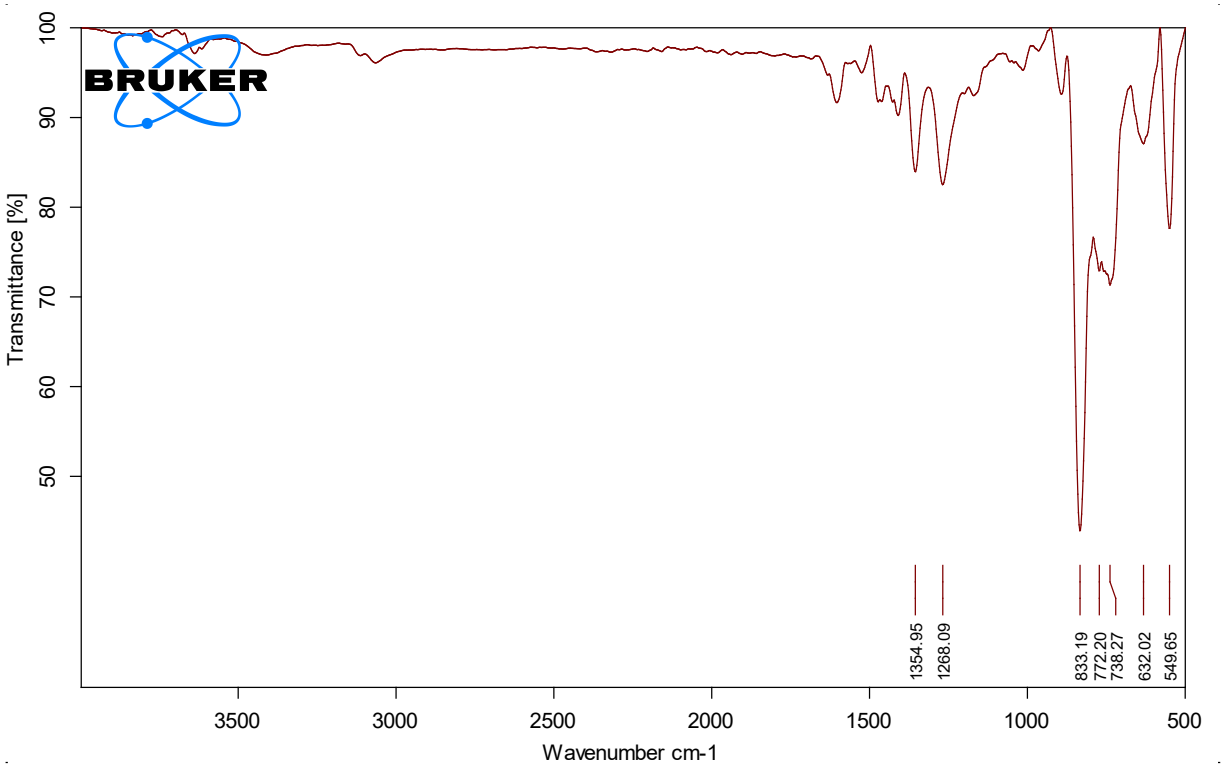
Wavenumber cm-1

Fig. S8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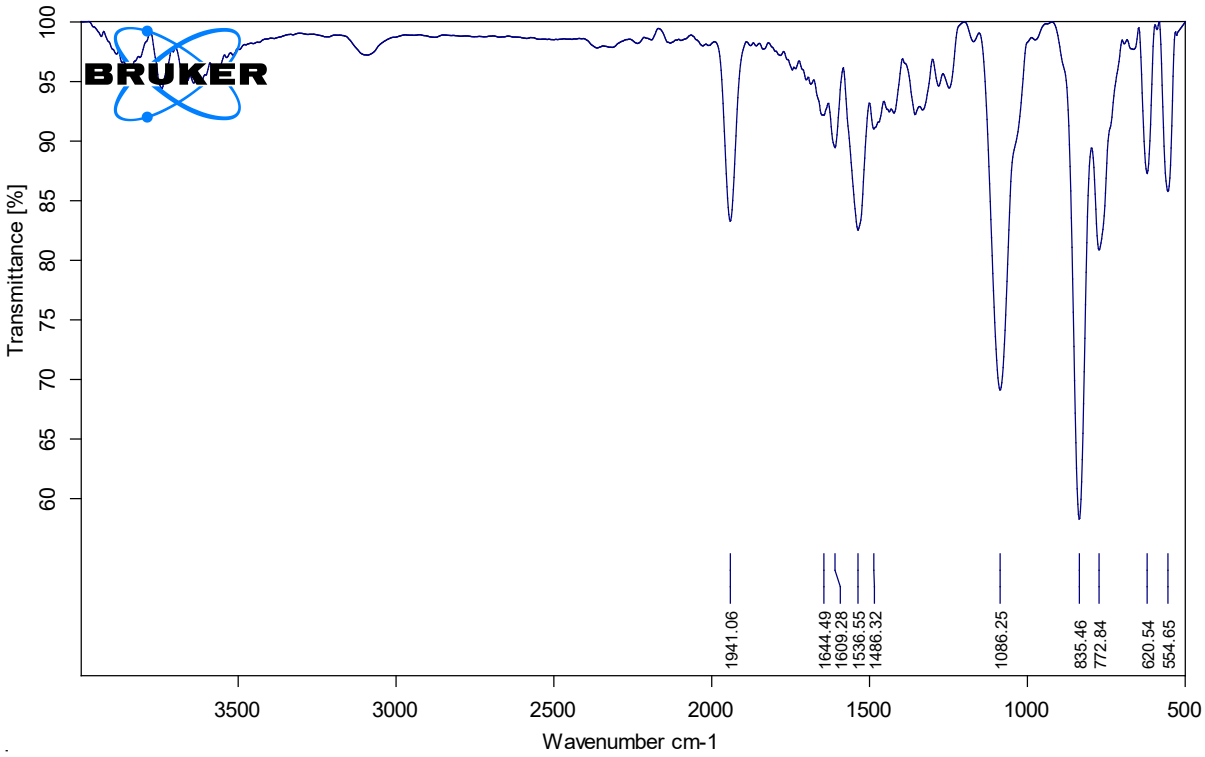
2000
1500
1000
500
Wavenumber cm-1

Fig. S9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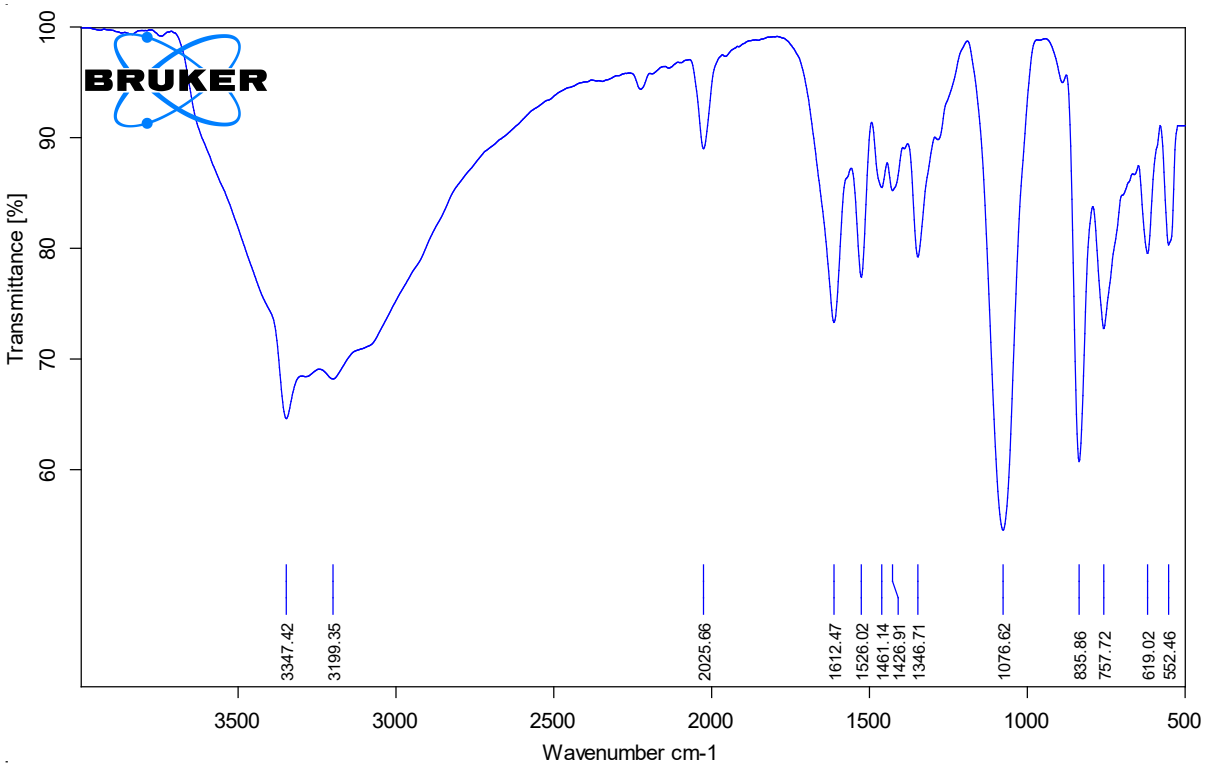
Wavenumber cm-1

Fig. S10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1426.91
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1500
1000
500
Wavenumber cm-1

Fig. S11

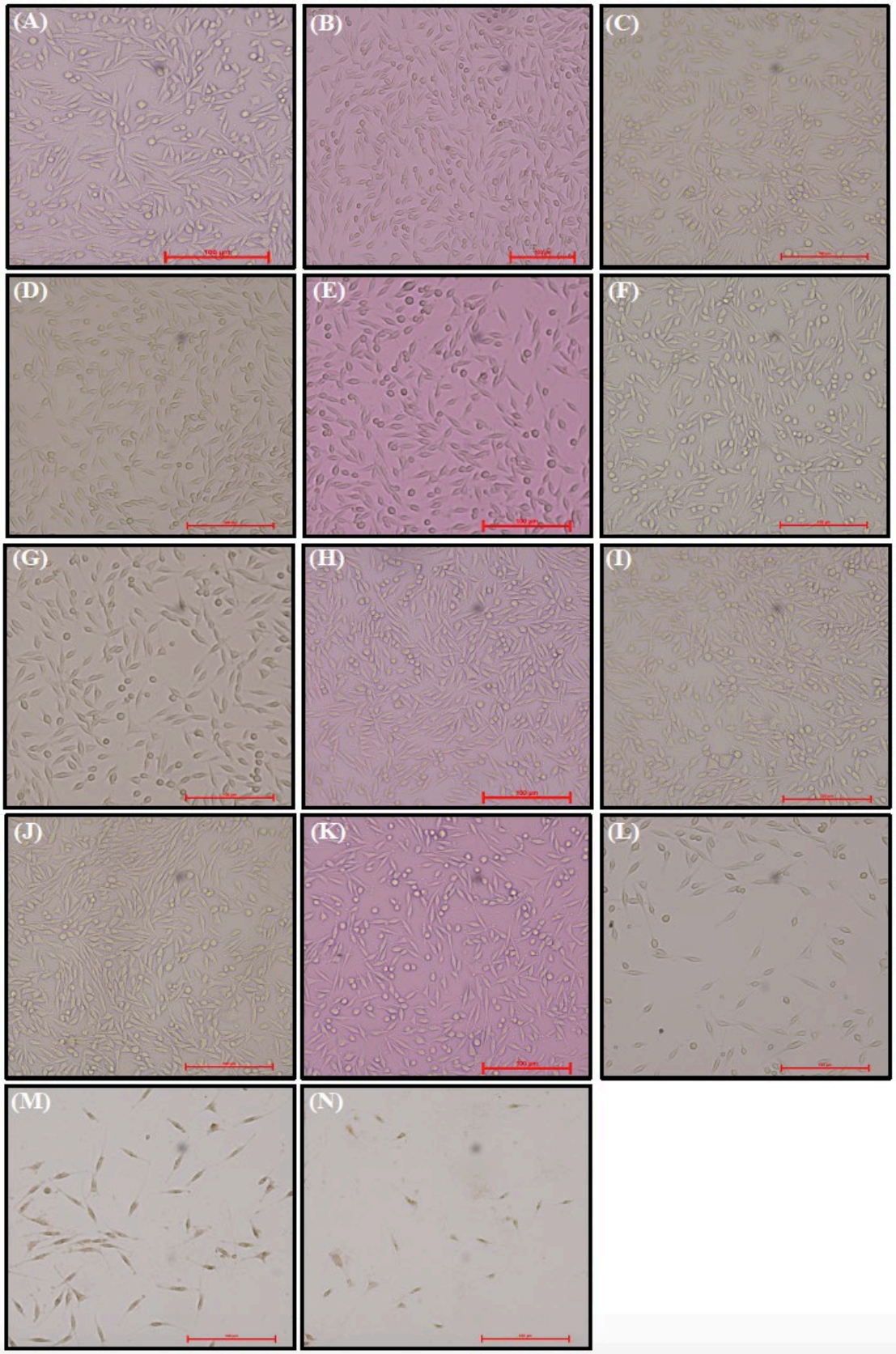

Fig. S12