Supplementary information

Imine-Carbene based ruthenium complexes for Dye-Sensitized Solar Cells: The Effect of Isomeric Mixture on Photovoltaic Performance

Yogesh S. Tingare [1,*], Chaochin Su [1,*], Ming-Tai Shen [2], Sheng-Han Tsai [1], Shih-Yu Ho [1], Subhendu Chakroorty[3] and Wen-Ren Li [2,*]

1. Institute of Organic and Polymeric Materials/Research and Development Center for Smart Textile Technology, National Taipei University of Technology, Taipei 10608, Taiwan, ROC. kieferboy8@hotmail.com (S.-H. T.); stacy760414@hotmail.com (S.-Y. H).
2. Department of Chemistry, National Central University, Chung-Li, Taiwan 32001, ROC. moodplayer@hotmail.com (M.-T S.)
3. School of Sciences, Auro University, Surat, India. Subhendu.chakroborty@aurouniversity.edu.in (S.C)

* Correspondence: yogeshtingare@yahoo.co.in (Y. S. T.); f10913@mail.ntut.edu.tw (C.-C. S.); ch01@ncu.edu.tw (W.-R. L.)

1. Electrochemical measurement.[1]

Cyclic voltammetry (CV) analyses were performed using a CHI 627 C electrochemical analyzer (CH Instruments) and a conventional single-compartment, three-electrode cell. A glassy carbon electrode and a silver wire (Ag/$AgNO_3$ in acetonitrile) were used as the working electrode and the reference electrode, respectively while a Pt wire was utilized as a counter electrode. Dye solutions were prepared at a concentration of 1×10^{-3} M in DMF and a 0.1 M solution of tetrabutylammonium hexafluorophosphate was used as the supporting electrolyte. Ferrocene was utilized as the internal reference for the calibration of the obtained redox potentials. The cyclic voltammograms of **IC101** and **IC102** were recorded at a typical scan rate of 50 mV s^{-1}.

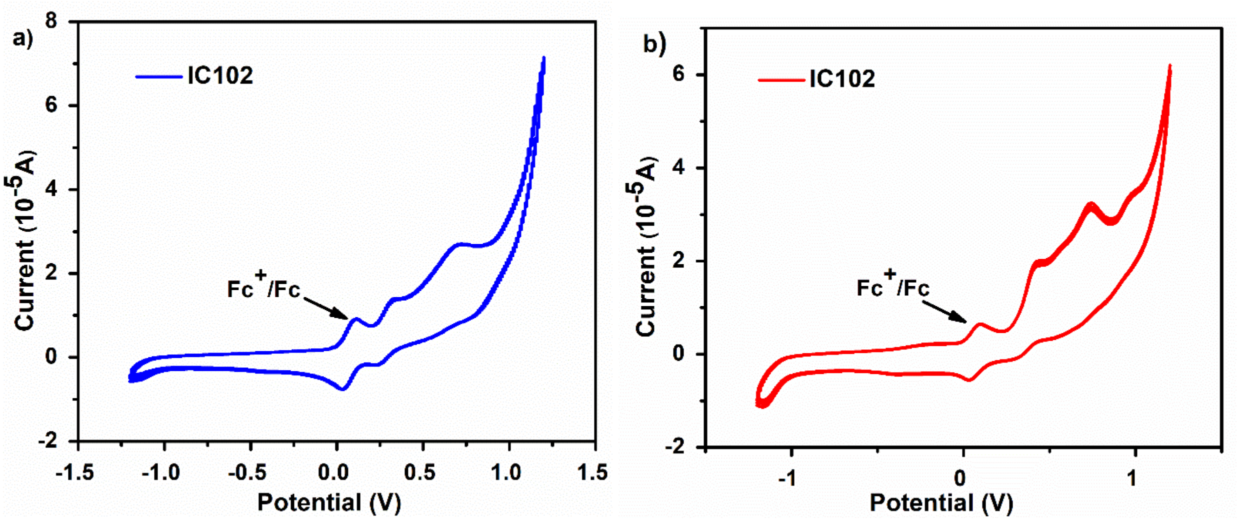


Figure S1: cyclic voltammogram plots for sensitizer **IC101 (a)** and **IC102 (b)**.

2. Theoretical calculation for the location of HOMOs and LUMOs

The location of the frontier orbitals of **IC101** and **IC102** sensitizers were computed using the Gaussian 09W program package and the DFT/B3LYP/LANL2DZ parameters set.

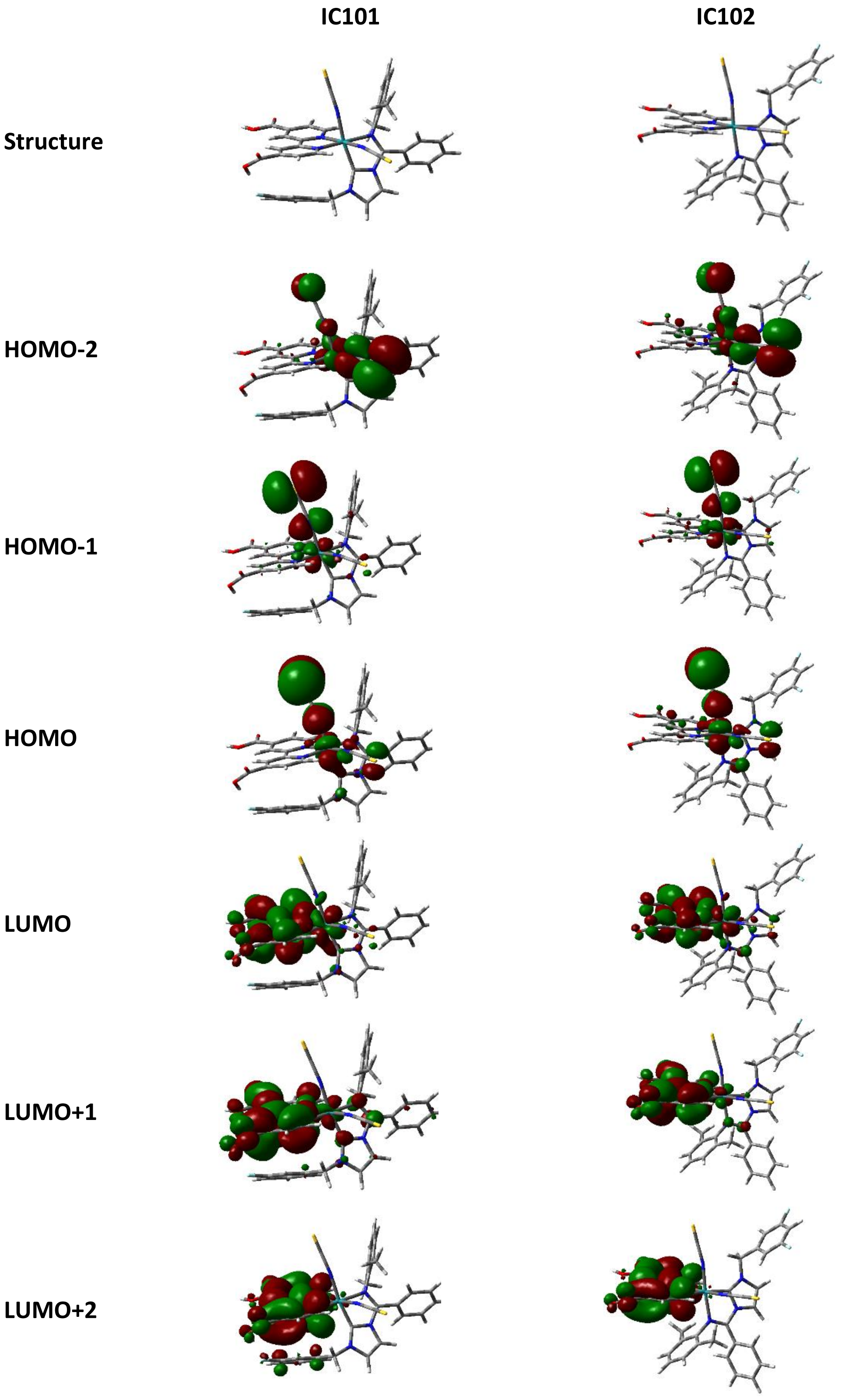


Figure S2: Frontier orbital representations of **IC101** and **IC102** sensitizers.

Preparation of TiO_2 electrodes and DSSC devices. [2]

The preparation of the TiO_2 nanoparticles was carried out by a hydrothermal process as follows. The starting precursor $Ti(OBu)_4$ (22.0 g) was dissolved in 2.0 M CH_3COOH (aq) (108.4 mL) and then stirred vigorously for 5 days. The resulting homogeneous solution was subjected to the hydrothermal treatment in an autoclave at 200 °C for 5 h, and then the obtained TiO_2 colloidal solution was centrifuged twice with ethanol. The residue was dissolved in absolute ethanol (60 mL) and the mixture was stirred vigorously followed by ultra-sonication. The resulting solution was mixed withα-terpineol (38.94 g) and a mixture of ethyl cellulose (10 cps, 2.73 g and 45 cps, 2.10 g) in anhydrous ethanol (43.5 mL) and then sonicated repeatedly. The solvent was evaporated under a reduced pressure of 70 mbar andα-TiO_2 was obtained after grinding. For the preparation of the TiO2 scattering layer, in a round bottom flask, 2.0 g of QF-1125 TiO_2 powder of particle size around 200–300 nm was suspended in 80 mL anhydrous ethanol. After sonication for 2 min, the above solution was combined with α-terpineol (12.98 g) and a solution of ethyl cellulose (10 cps, 0.90 g and 45 cps, 0.70 g) in anhydrous ethanol (14.4 mL). The mixture was then subjected to repeated sonication. Finally, the dispersed solution was concentrated by using an evaporator at 40 °C with 70 mbar. The QF-1125 paste was obtained after grinding by using a three roll mill grinder. The TiO_2 electrode was prepared by spreading the TiO_2 paste onto fluorine-doped SnO_2 conducting glass (FTO, Hartford Glass; sheet resistance: $8\Omega\square^{-1}$; transmittance ⩾ 80%; haze 5%). Subsequently, the TiO_2 electrodes were dried in air and heated at 100 °C for 15 min, followed by annealing at 450 °C for 30 min. The TiO_2 scattering layer was also coated followed by the above procedure using the QF-1125F TiO_2 paste. The average thickness of the TiO_2 film was 15 μm, measured using a Force EZstep profiler. The resulting TiO_2 electrode was scraped to an active area of 0.25 cm^2 (0.5 cm × 0.5 cm), followed by heat treatment at 80 °C. Dye solutions of **N719**, **IC101**, and **IC102** with 3×10^{-4} M concentration in 1 : 1 CH_3CN/*t*-BuOH (v/v) were prepared and then the electrodes were soaked for 36 h. The Pt counter electrodes were prepared by sputter-deposition of 20 nm thick Pt layers onto FTO substrates using a Hitachi E-1045 ion sputter. Prior to assembling of the DSSCs, two holes were drilled on the counter electrodes. The Pt electrodes were then placed over the dye-adsorbed TiO_2 electrodes. The edges of the cells were sealed with a Surlyn 1702 (DuPont; thickness: 125 mm) spacer at 100 °C. To complete the DSSC fabrication, the electrolyte was injected into the intervening space between the TiO_2 and Pt electrodes through the two holes, which were then covered with a microscope slide and sealed with a Surlyn spacer. The electrolyte solution comprised of 0.5 M lithium iodide, 0.05 M iodide, 0.5 M 1,2-dimethyl-3-propylimidazolium iodide, and 0.5 M tert-butylpyridine in acetonitrile was employed as the redox mediator.

DSSC performance measurements. [2]

Photovoltaic parameters were measured by utilizing a Keithley model 2400 source unit equipped with an A-class solar simulator of a 300 W Xenon light source (Oriel, no. 91160) with an AM 1.5 filter (Oriel, no. 81094). The power of the output light at the cell measuring position was calibrated to 100 mW cm^{-2} using a certified reference cell (PVM134, PV Measurement, Inc.). To measure the incident photon-to-current conversion efficiencies (IPCEs), equipment comprised of a 150 W Xenon lamp source (Oriel, no. 66902), a monochromator (Oriel Cornerstone TM 130) and a Keithley model 2400 was employed.

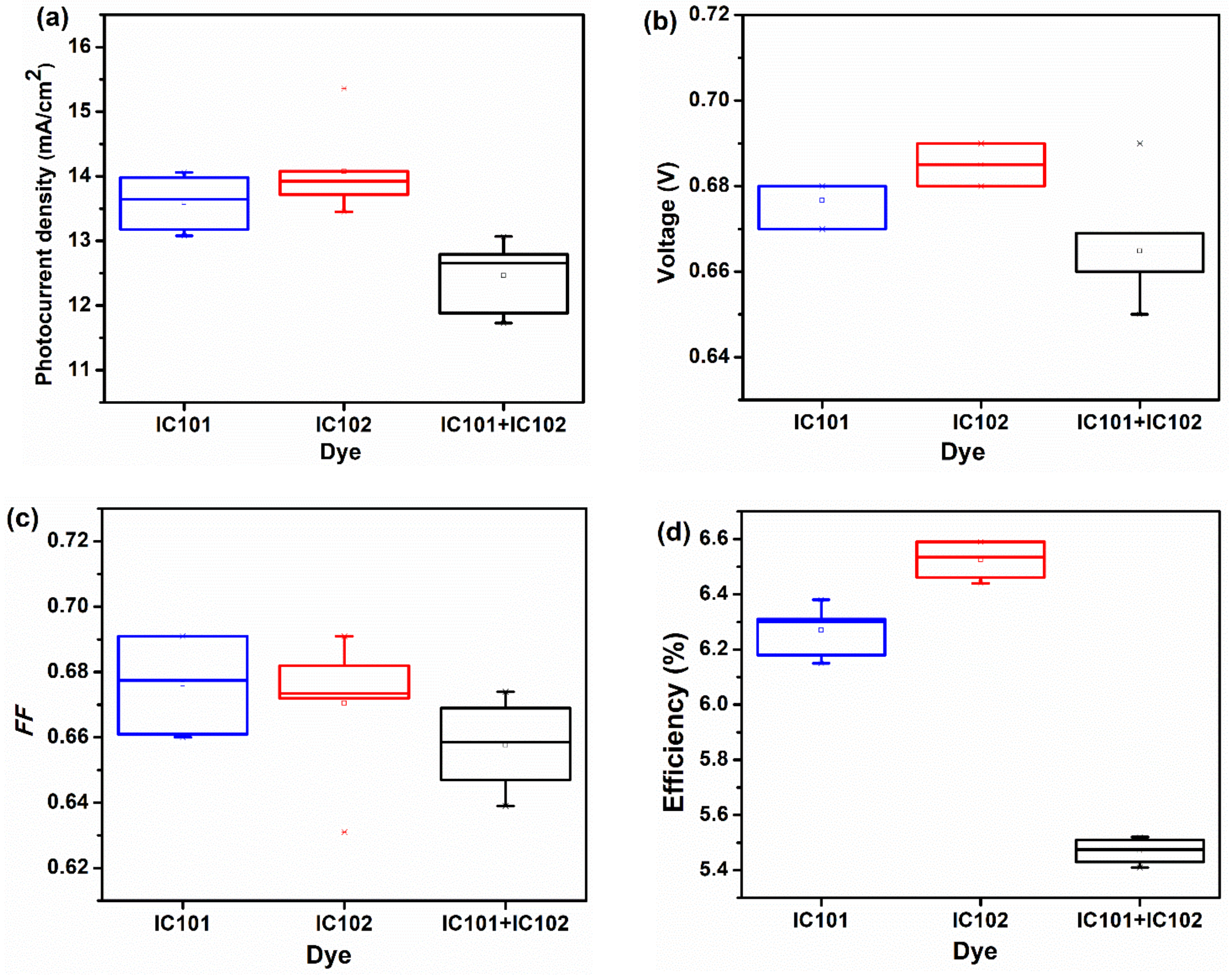


Figure S3: (a) J_{sc}, (b) V_{oc}, (c) FF, (d) efficiency (η) of 6 devices of **IC101**, **IC102**, **IC101+IC102** sensitizers.

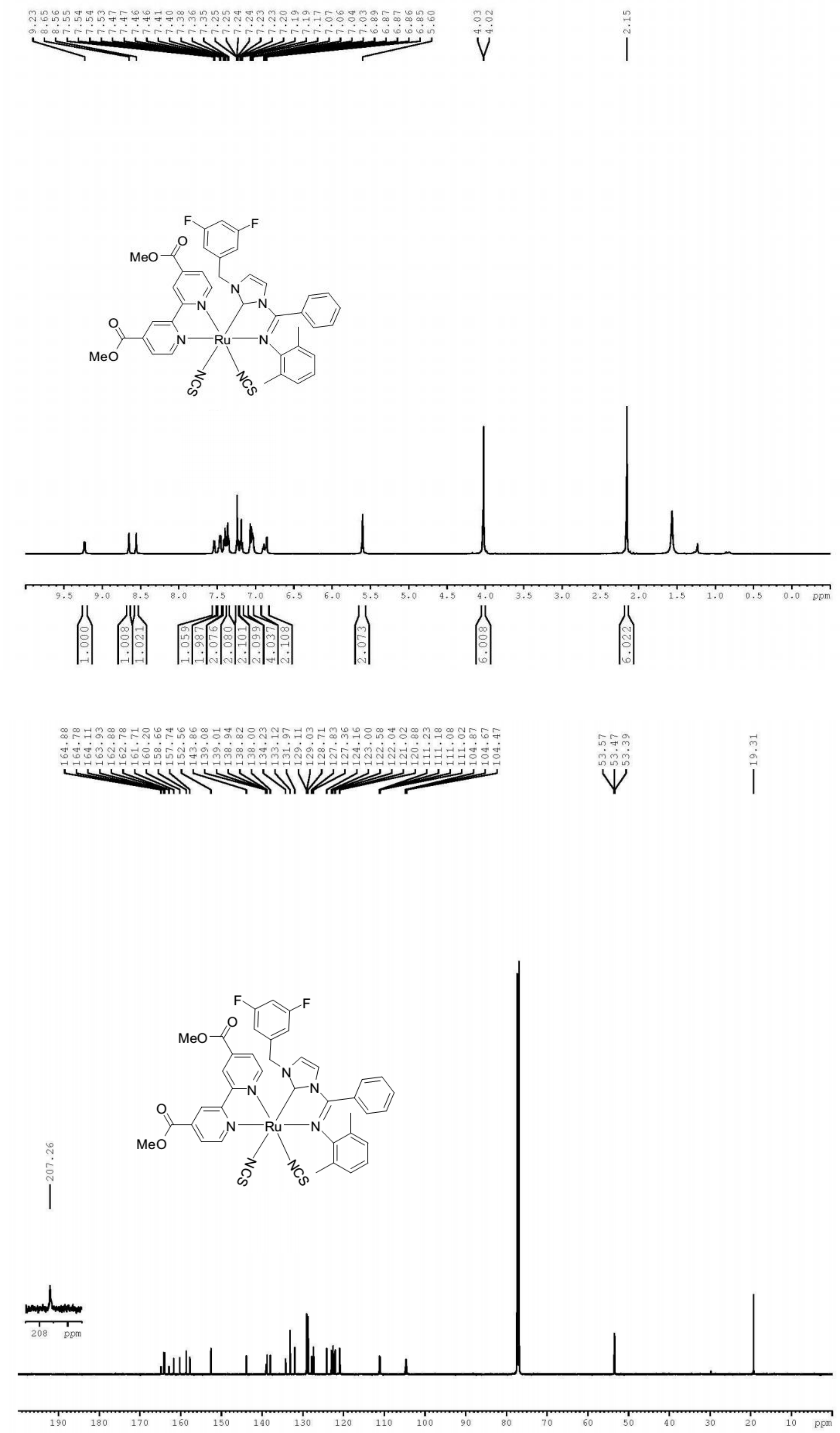
Table S1: Photovoltaic parameters of devices incorporating with different ratios of **IC101+IC102** sensitizers.

Dye	Ration	J_{SC} (mA/cm^2)	V_{OC} (V)	*FF*	η (%)
IC101+IC102	**1:0**	14.06	0.680	0.661	6.31
	0:1	15.36	0.680	0.631	6.59
	1:2	13.08	0.670	0.691	6.06
	1:1	13.07	0.660	0.639	5.51
	2:1	11.92	0.670	0.679	5.42

Reference:

1. a) Cardona, C. M.; Li, W.; Kaifer, A. E.; Stockdale, D.; Bazan, G. C. *Adv. Mater.* **2011**, *23*, 2367. b) Hua, Y.; Xu, B.; Liu, P.; Chen, H.; Tian, H.; Cheng, M.; Kloo, L.; Sun, L. *Chem. Sci.* **2016**, *7*, 2633. C) Lim, K.; Kang, M.-S.; Myung, Y.; Seo, J.-H.; Banerjee, P.; Marks, T. J.; Ko, J. *J. Mater. Chem. A* **2016**, *4*, 1186.
2. Y. S. Tingare, S. B. Akula, M.-T. Shen, C. Su, S.-Y. Ho, S.-H. Tsai, Y.-F. Lin and W.-R. Li, *Dalton Trans.*, 2018, **47**, 8356-8363

Figure S4: H^{1}NMR , C^{13}NMR and Mass spectra.



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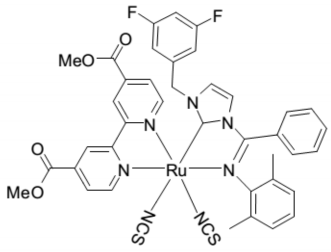
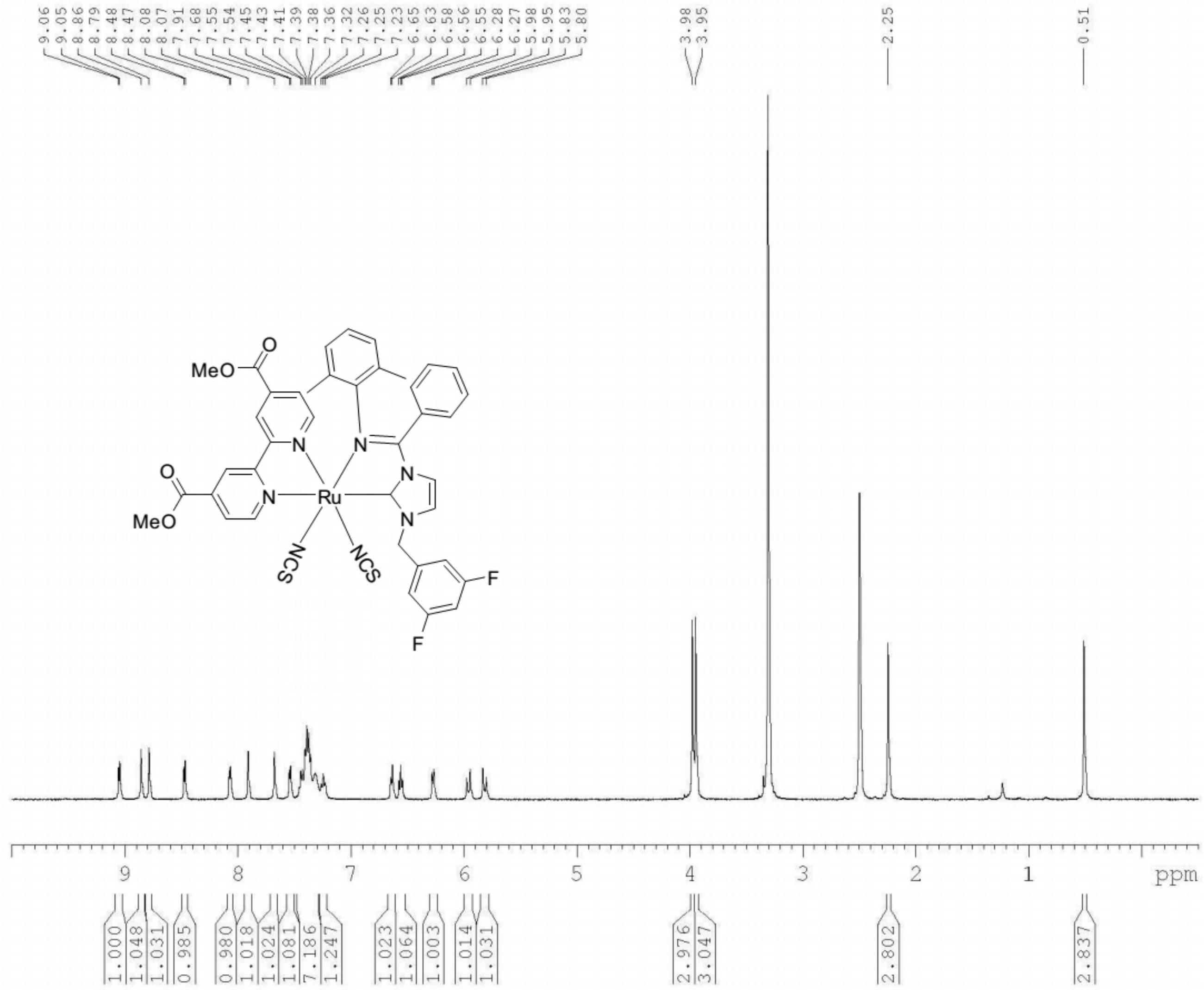
T: FTMS + p ESI Full ms [150.00-2000.00]
m/z= 891.94-892.29
Isotope  Min   Max
O-16       0     5
C-12       0    42
H-1        0    35
N-14       0     8
Ru-102     0     1
S-32       0     2
F-19       0     2
Charge 1
Mass tolerance 1000.00 ppm
Nitrogen rule not used
RDB equiv -1.00-100.00
max results 1
   m/z    Intensity Relative Theo. Mass  Delta      Composition
                                         (ppm)
 892.1132   72947.9   100.00   892.1120    1.40 C41 H34 O4 N7 F2 Ru S2
```

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7.39
7.38
7.36
7.32
7.26
7.25
7.23
6.65
6.63
6.58
6.56
6.55
6.28
6.27
5.98
5.95
5.83
5.80
3.98
3.95
2.25
0.51
MeO
O
N
Ru
SCN
NCS
F
9
8
7
6
5
4
3
2
1
ppm
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1.031
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0.980
1.018
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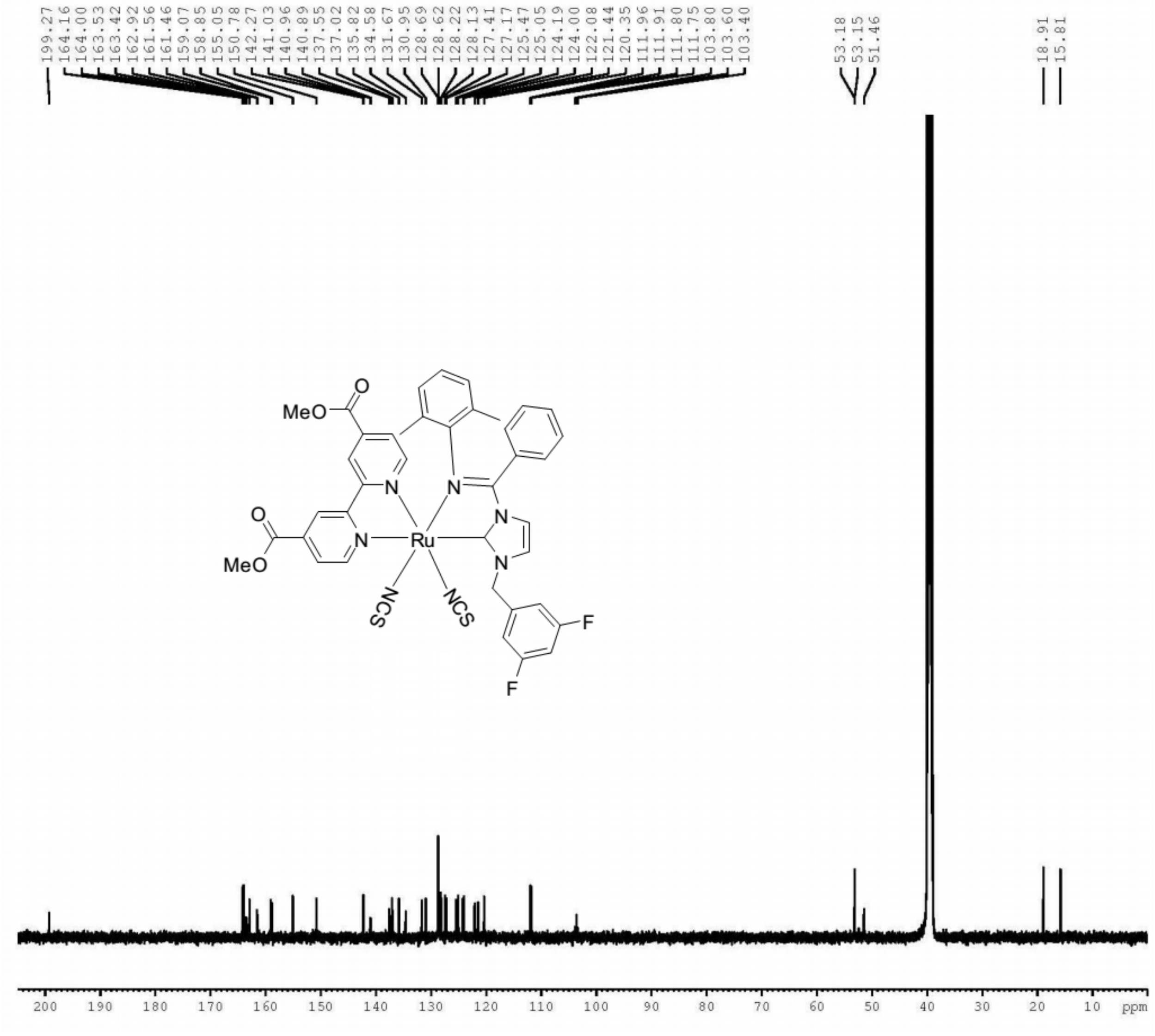
2.837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141.03
140.96
140.89
137.55
137.02
135.82
134.58
131.67
130.95
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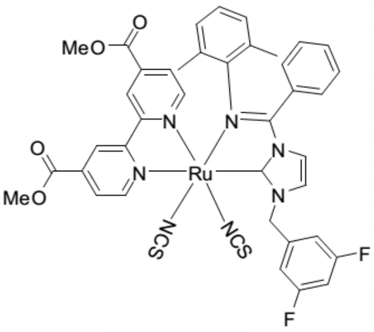
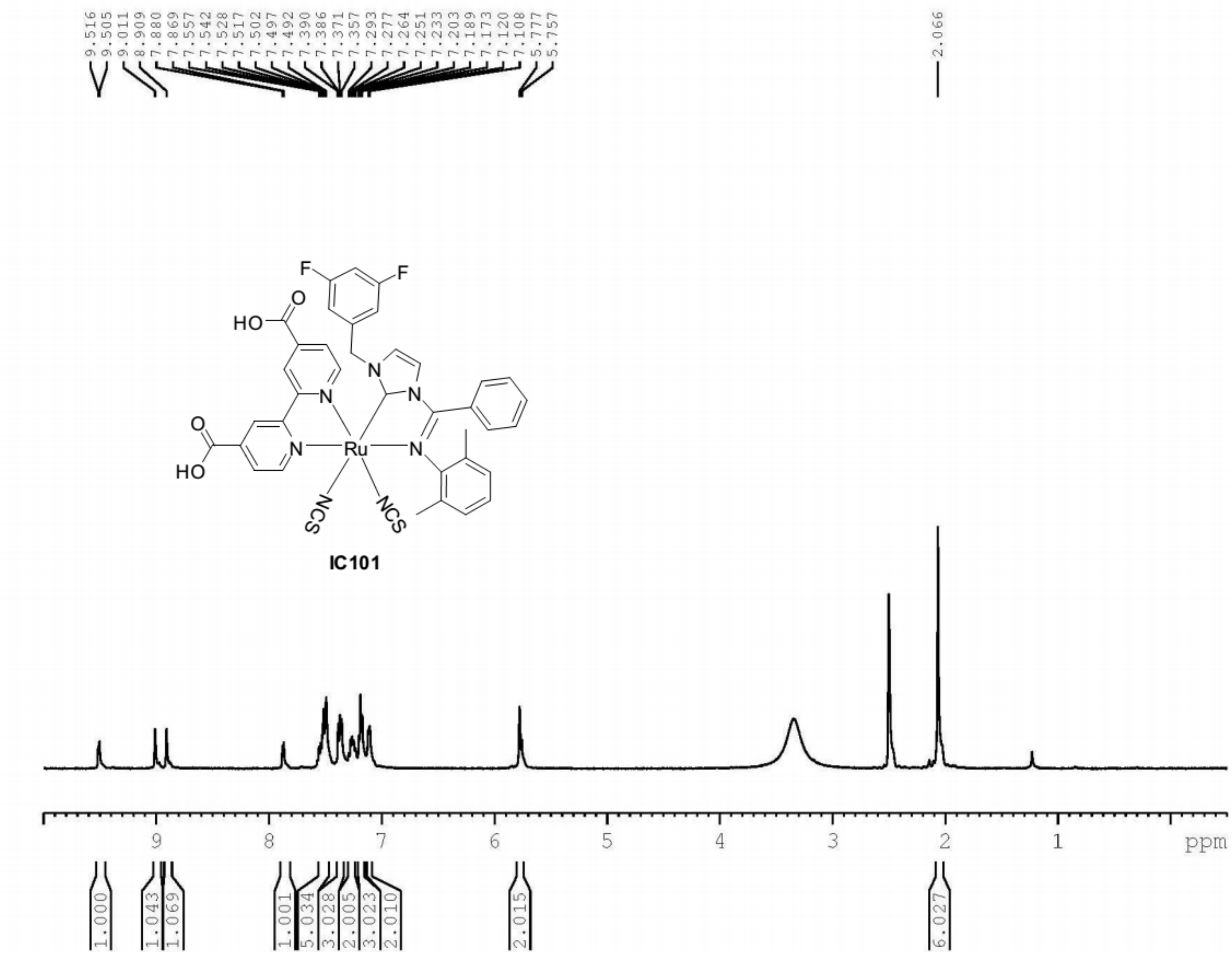
128.62
128.22
128.13
127.41
127.17
125.47
125.05
124.19
124.00
122.08
121.44
120.35
111.96
111.91
111.80
111.75
103.80
103.60
103.40
53.18
53.15
51.46
18.91
15.81
MeO
O
N
Ru
SCN
NCS
F
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

```
112-IC101-2-ester-H#1-20 RT: 0.01-0.28 AV: 20
T: FTMS - p ESI Full ms [150.00-2000.00]
m/z= 889.75-890.68
Isotope  Min   Max
N-14       0     7
O-16       0     4
C-12       0    41
H-1        0    35
F-19       0     2
S-32       0     2
Ru-102     0     1
Charge 1
Mass tolerance 10.00 ppm
Nitrogen rule not used
RDB equiv -1.00-100.00
max results 1
   m/z    |Intensity|Relative|Theo. Mass| Delta  |   Composition
          |         |        |          | (ppm)  |
 890.0962 | 22525.4 | 100.00 | 890.0963 |  -0.11 |C41 H32 O4 N7 F2 Ru S2
```

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7.264
7.251
7.233
7.203
7.189
7.173
7.120
7.108
5.777
5.757
2.066
F
F
HO
O
O
HO
N
N
N
N
Ru
N
NCS
NCS
IC101
9
8
7
6
5
4
3
2
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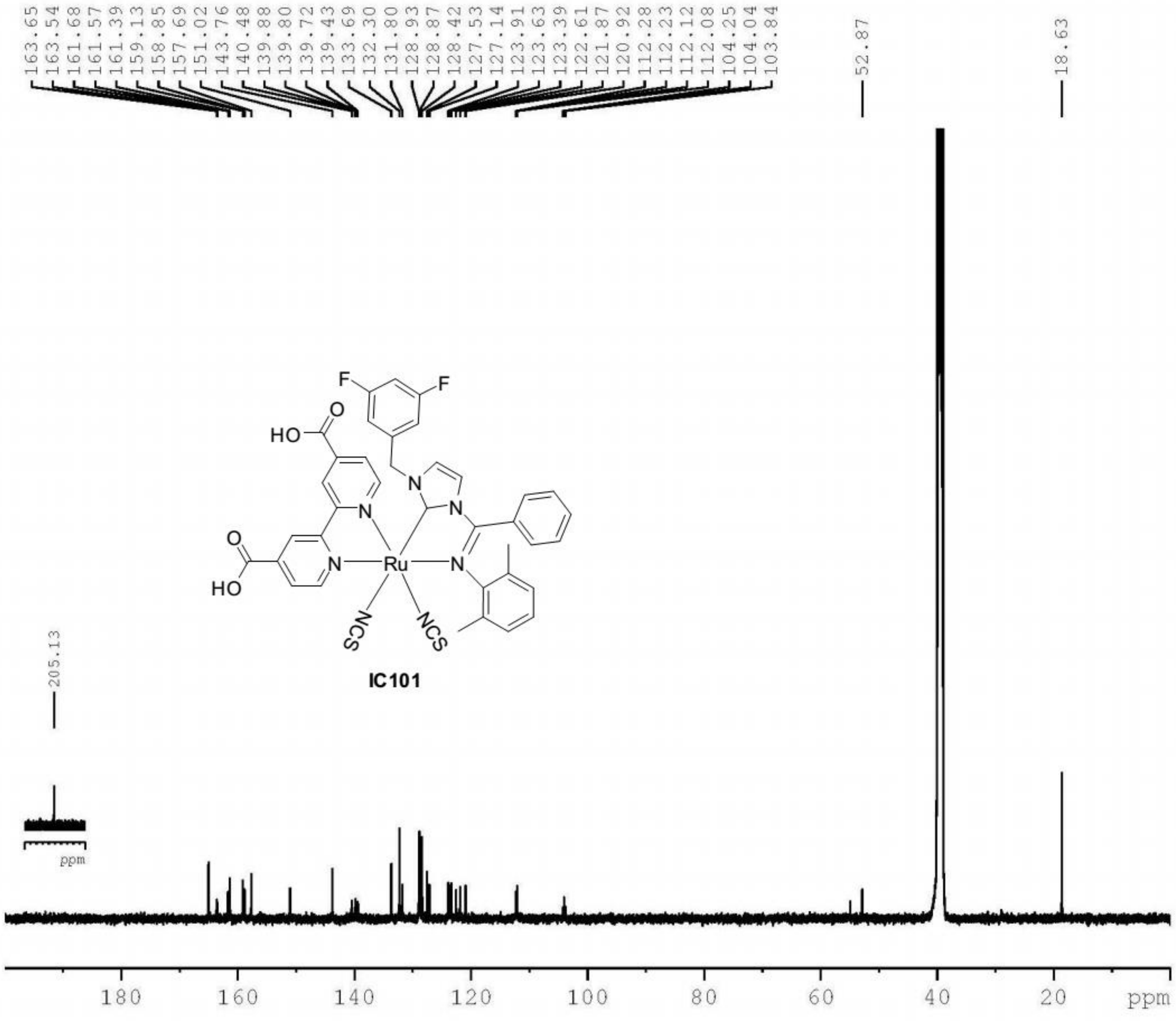
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139.43
133.69
132.30
131.80
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128.42
127.53
127.14
123.91
123.63
123.39
122.61
121.87
120.92
112.28
112.23
112.12
112.08
104.25
104.04
103.84
52.87
18.63
F
F
HO
O
O
HO
N
N
N
N
Ru
N
NCS
NCS
IC101
205.13
ppm
180
160
140
120
100
80
60
40
20
ppm

```
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T: FTMS + p ESI Full ms [150.00-2000.00]
m/z= 857.58-870.47
Isotope  Min   Max
C-12       0    39
H-1        0    30
F-19       0     2
N-14       0     7
O-16       0     4
Ru-102     0     1
S-32       0     2
Charge 1
Mass tolerance 10.00 ppm
Nitrogen rule not used
RDB equiv -1.00-100.00
max results 1
    m/z    |Intensity|Relative|Theo. Mass |  Delta  |    Composition
           |         |        |           |  (ppm)  |
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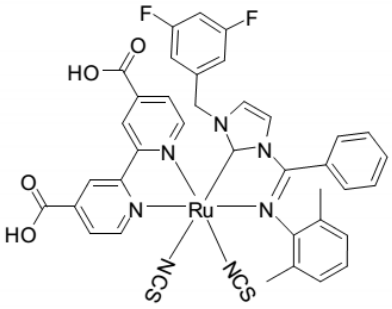
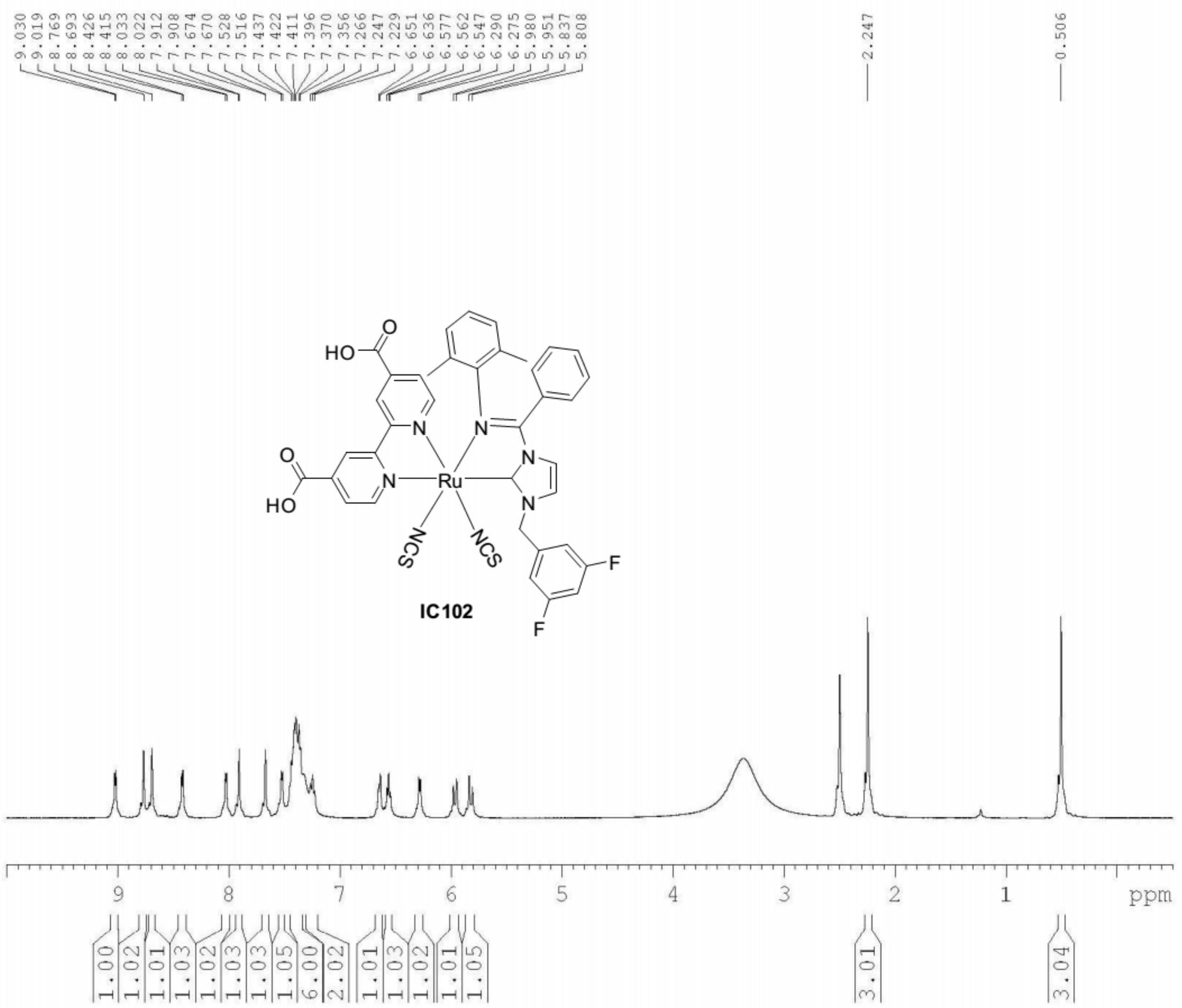
```



IC101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8
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6
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4
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1.02
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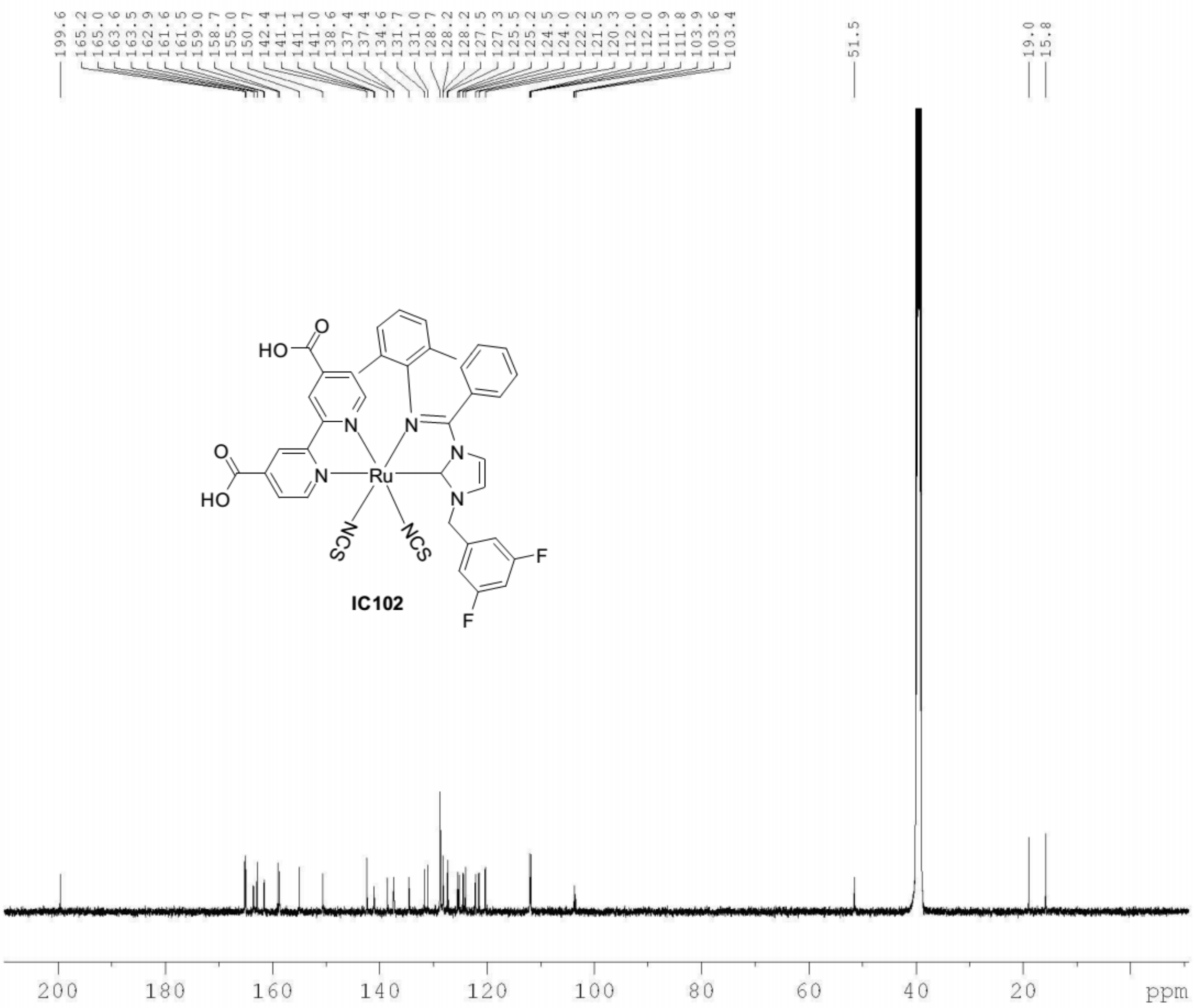
3.04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141.1
141.0
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137.4
137.4
134.6
131.7
131.0
128.7
128.2
128.2
127.5
127.3
125.5
125.2
124.5
124.0
122.2
121.5
120.3
112.0
111.9
111.8
103.9
103.6
103.4
51.5
19.0
15.8
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N
Ru
NCS
F
IC102
200
180
160
140
120
100
80
60
40
20
ppm

```
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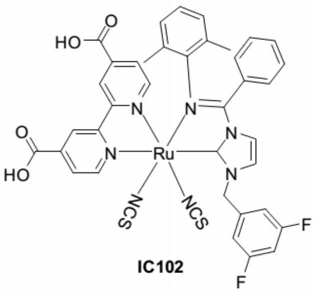
m/z= 848.21-887.87
Isotope  Min   Max
C-12       0    39
H-1        0    42
O-16       0     4
N-14       0     7
S-32       0     2
F-19       0     2
Ru-102     0     1
Charge 1
Mass tolerance 1000.00 ppm
Nitrogen rule not used
RDB equiv -1.00-100.00
max results 1
    m/z    |Intensity|Relative|Theo. Mass|  Delta   |    Composition
           |         |        |          |  (ppm)   |
  862.0660 | 332934.9|  100.00|  862.0650|      1.10|C39 H28 O4 N7 F2 Ru S2
```



IC102