Electronic Supplementary Material (ESI) for RSC Advances.

ESI

A styryl-containing aza-BODIPY as near-infrared dye

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1 General

The melting points were measured using a SGW® X-4 melting point apparatus. ^{1}H NMR spectra were recorded on a Bruker AVANCE III 500 MHz spectrometer. ^{1}H NMR chemical shifts (δ) are given in ppm downfield from Me_4Si, determined by chloroform (δ = 7.26 ppm). ^{13}C NMR spectra were recorded on a Bruker AVANCE III 125 MHz spectrometer. ^{13}C NMR chemical shifts (δ) are reported in ppm with the internal $CDCl_3$ at δ 77.0 ppm as standard. ESI was measured by LCQ Deca XP.

Tetrahydrofuran (THF) was freshly distilled from Na/benzophenone, *n*-hexane was distilled over Na, and other solvents were distilled over CaH_2. Merck silica gel 60 was used for the column chromatography.

Fluorescence spectra were recorded on F-4600 spectrophotometer. UV/Vis spectra were recorded on UV-2550 spectrophotometer at room temperature. The refractive index of the medium was measured by 2 W Abbe's refractometer at 20 °C.

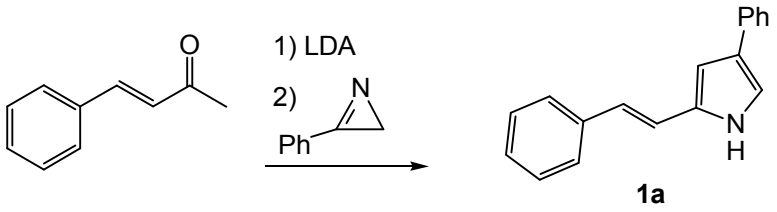
The fluorescence quantum yields (Φ_f) of the BODIPY systems were calculated using the following relationship (equation 1):

$$\Phi_f = \Phi_{ref} F_{sampl} A_{ref} n^2_{sampl} / F_{ref} A_{sampl} n^2_{ref} \quad (1)$$

Here, F denotes the integral of the corrected fluorescence spectrum, A is the absorbance at the excitation wavelength, ref and sampl denote parameters from the reference and unknown experimental samples, respectively. The reference systems used was boronazadipyrromethene compound aza-BODIPY (Φ_f = 0.36 in chloroform).[1]

The MO calculations were performed at the DFT level, and the frontier molecular orbitals of BODIPYs **2a** and **4** at the B3LYP/6-31G(d) level with Gaussian 03.[2]

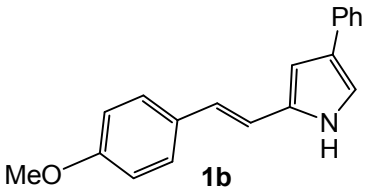
2. Synthesis



1a

(E)-4-phenyl-2-styryl-1H-pyrrole 1a

Under N_2, LDA (1.0 mmol) in THF (3 mL) was added to (E)-4-phenylbut-3-en-2-one[3] (146 mg, 1.0 mmol) in THF (8 mL) at −78 °C. Then, 3-phenyl-2*H*-azirine (175 mg, 1.5 mmol) in THF (5 mL) was added and the resulting mixture was stirred for 1 h at the same temperature. The reaction was allowed to warm up to room temperature slowly. It was quenched with water, neutralized with dilute HCl to a pH about 7. The mixture was extracted with CH_2Cl_2 (2 × 50 mL), and the organic layer was washed with brine (2 × 50 mL) and dried over anhydrous $MgSO_4$. After removal of the solvents by evaporation, the resulting crude mixture was separated by column chromatography (*n*-hexane : CH_2Cl_2 = 1 : 2) to afford **1a** as green solids (110 mg, 45%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.36 (br s, 1H), 7.54 (d, J = 7.5 Hz, 2H), 7.44 (d, J = 7.5 Hz, 2H), 7.36 (t, J = 7.5 Hz, 2H), 7.34 (t, J = 7.5 Hz, 2H), 7.17-7.24 (m, 2H), 7.02-7.11 (m, 1H), 6.98 (d, J = 16.5 Hz, 1H), 6.73 (d, J = 16.5 Hz, 1H), 6.64-6.67 (m, 1H).

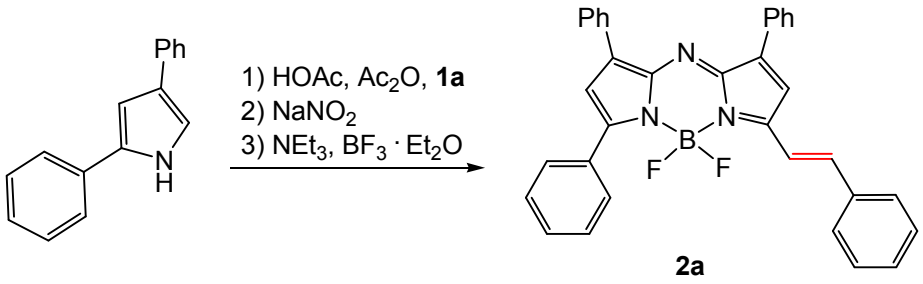


1b

(E)-2-(4-methoxystyryl)-4-phenyl-1H-pyrrole 1b

(E)-4-(4-methoxyphenyl)but-3-en-2-one[3] (176 mg, 1.0 mmol) were used as the starting material, and **1b** was obtained as green solids (137 mg, 50%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.33 (br s, 1H), 7.53 (d, J = 7.5 Hz, 2H), 7.37 (t, J = 7.5 Hz, 2H), 7.35 (t, J = 7.5 Hz, 2H), 7.19 (t, J = 7.5 Hz, 1H), 7.07-7.08 (m, 1H), 6.88 (d, J =

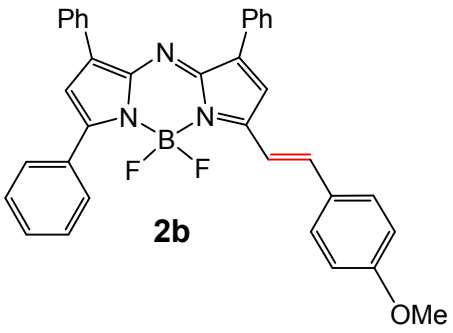
7.5 Hz, 2H), 6.84 (d, J = 16.5 Hz, 1H), 6.78 (d, J = 16.5 Hz, 1H), 6.61-6.62 (m, 1H), 3.82 (s, 3H).



2a

Styryl-containing aza-BODIPY dye 2a

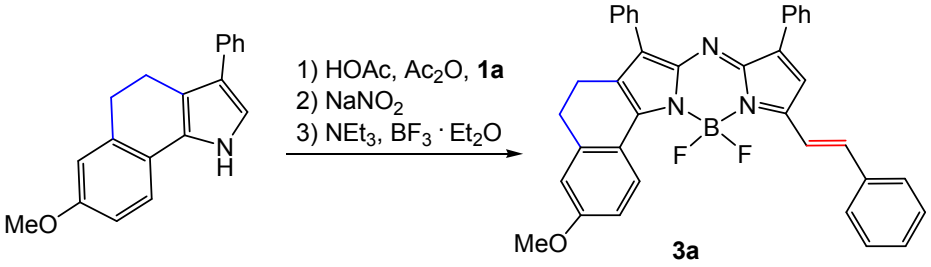
Sodium nitrite (6.9 mg, 0.1 mmol) was added to a suspension of 2,4-diphenyl-1H-pyrrole[1] (21.9 mg, 0.1 mmol) in acetic acid (1 mL) at 0 °C, and was stirred for 10 min. The color changed from colorless to brown, then green, and finally brown was observed. The second pyrrole moiety **1a** (24.5 mg, 0.1 mmol) was added, followed by addition of acetic anhydride (0.4 mL). The mixture turned blue immediately. After 0.5 h stirring, the mixture was heated at 80 °C for 0.5 h. Crushed ice was added to the mixture, the resulted blue dye was filtered, washed with water. The blue dye was dissolved in CH_2Cl_2, filtered through a pad of alumina (activity III). Solvent was removed under reduced pressure, and the residue was dissolved in dry 1,2-dichloroethane. Triethylamine (0.28 mL, 2.0 mmol) was added, followed by dropwise addition of $BF_3{\cdot}Et_2O$ (0.50 mL, 4.0 mmol) with stirring at room temperature. The mixture was stirred for 0.5 h, then heated in 80 °C for 0.5 h. The reaction was quenched with crushed ice, extracted with CH_2Cl_2, and purified by chromatography on silica gel followed by recrystallization from CH_2Cl_2/*n*-hexane to afford **2a** (15.7 mg, 30%) as coppery solids. M.p.: 91.0–91.8 ºC (decomp.). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.05-8.11 (m, 4H), 7.30 (s, 1H), 7.31-7.67 (m, 18H), 7.02 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 141.4, 135.8, 132.7, 132.0, 131.9, 130.5, 130.4, 129.5, 129.4, 129.3, 129.2, 129.1, 129.0, 128.6, 128.5, 128.4, 128.3, 118.9, 115.5, 48.3, 47.0, 29.6, 18.8, 8.6. MS (ESI(+)): m/z = 523.2 $[M]^+$, found 522.9.



2b

Styryl-containing aza-BODIPY dye 2b

Pyrrole **1b** (27.6 mg, 0.1 mmol) were used as the starting material, and BODIPY **2b** was obtained as coppery solids (18.3 mg, 34 %). M.p.: 240.1–241.0 ºC (decomp.). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.09 (d, J = 7.0 Hz, 4H), 8.09 (d, J = 8.5 Hz, 2H), 7.63 (d, J = 9.0 Hz, 2H), 7.39-7.57 (m, 11H), 7.30 (s, 1H), 6.99 (s, 1H), 6.94 (d, J = 8.5 Hz, 2H), 3.87 (s, 3H). MS (ESI(+)): m/z = 553.2 $[M]^+$, found 553.8.

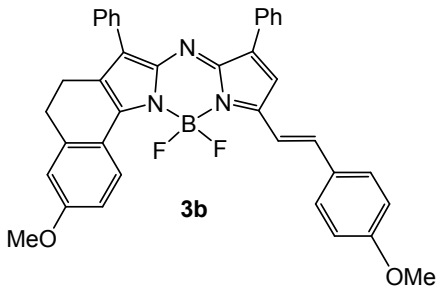


3a

Styryl-containing aza-BODIPY dye 3a

Sodium nitrite (6.9 mg, 0.1 mmol) was added to a suspension of 7-methoxy-3-phenyl-4,5-dihydro-1H-benzo[g]indole[4] (27.5 mg, 0.1 mmol) in acetic acid (1 mL) at 0 °C, and was stirred for 10 min. The color changed from colorless to brown, then green, and finally brown was observed. The second pyrrole moiety **1a** (24.5 mg, 0.1 mmol) was added, followed by addition of acetic anhydride (0.4 mL). The mixture turned blue immediately. After 0.5 h stirring, the mixture was heated at 80 °C for 0.5 h. Crushed ice was added to the mixture, the resulted blue dye was filtered, washed with water. The blue dye was dissolved in CH_2Cl_2, filtered through a pad of alumina (activity III). Solvent was removed under reduced pressure, and the residue was dissolved in dry 1,2-dichloroethane. Triethylamine (0.28 mL, 2.0 mmol) was added, followed by dropwise addition of $BF_3{\cdot}Et_2O$ (0.50 mL, 4.0 mmol) with stirring at room

temperature. The mixture was stirred for 0.5 h, then heated in 80 °C oil bath for 0.5 h. The reaction was quenched with crushed ice, extracted with CH_2Cl_2, and purified by chromatography on silica gel followed by recrystallization from CH_2Cl_2/*n*-hexane to afford **3a** (22.0 mg, 38%) as coppery solids. M.p.: 290.2–290.9 ºC (decomp.). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.80 (d, J = 9.0 Hz, 1H), 8.08 (d, J = 7.5 Hz, 2H), 7.66-7.74 (m, 5H), 7.35-7.49 (m, 10H), 7.22 (s, 1H), 7.07 (d, J = 7.5 Hz, 1H), 6.87 (s, 1H), 3.93 (s, 3H), 2.97 (s, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 162.7, 151.3, 147.2, 144.9, 144.4, 140.2, 138.2, 137.5, 136.4, 132.7, 131.9, 130.4, 129.3, 128.8, 128.7, 128.6, 128.5, 128.4, 128.1, 127.7, 120.0, 119.2, 114.6, 113.2, 55.5, 30.5, 21.7. MS (ESI(+)): m/z = 579.2 $[M]^+$, found 579.0. HRMS-MALDI (m/z): $[M+H]^+$ calcd for $C_{37}H_{29}BF_2N_3O$: 580.2372; found 580.2366.

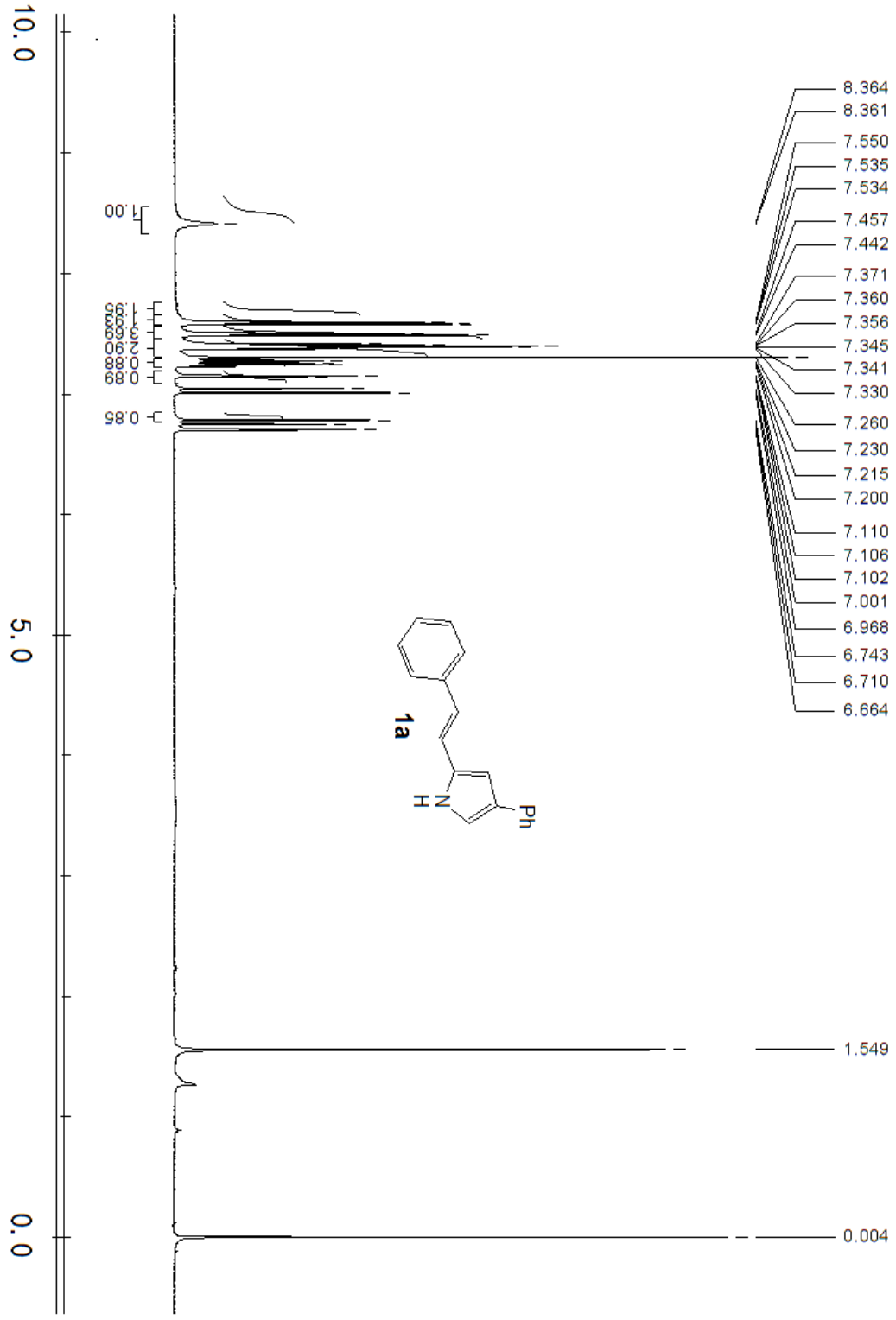


3b

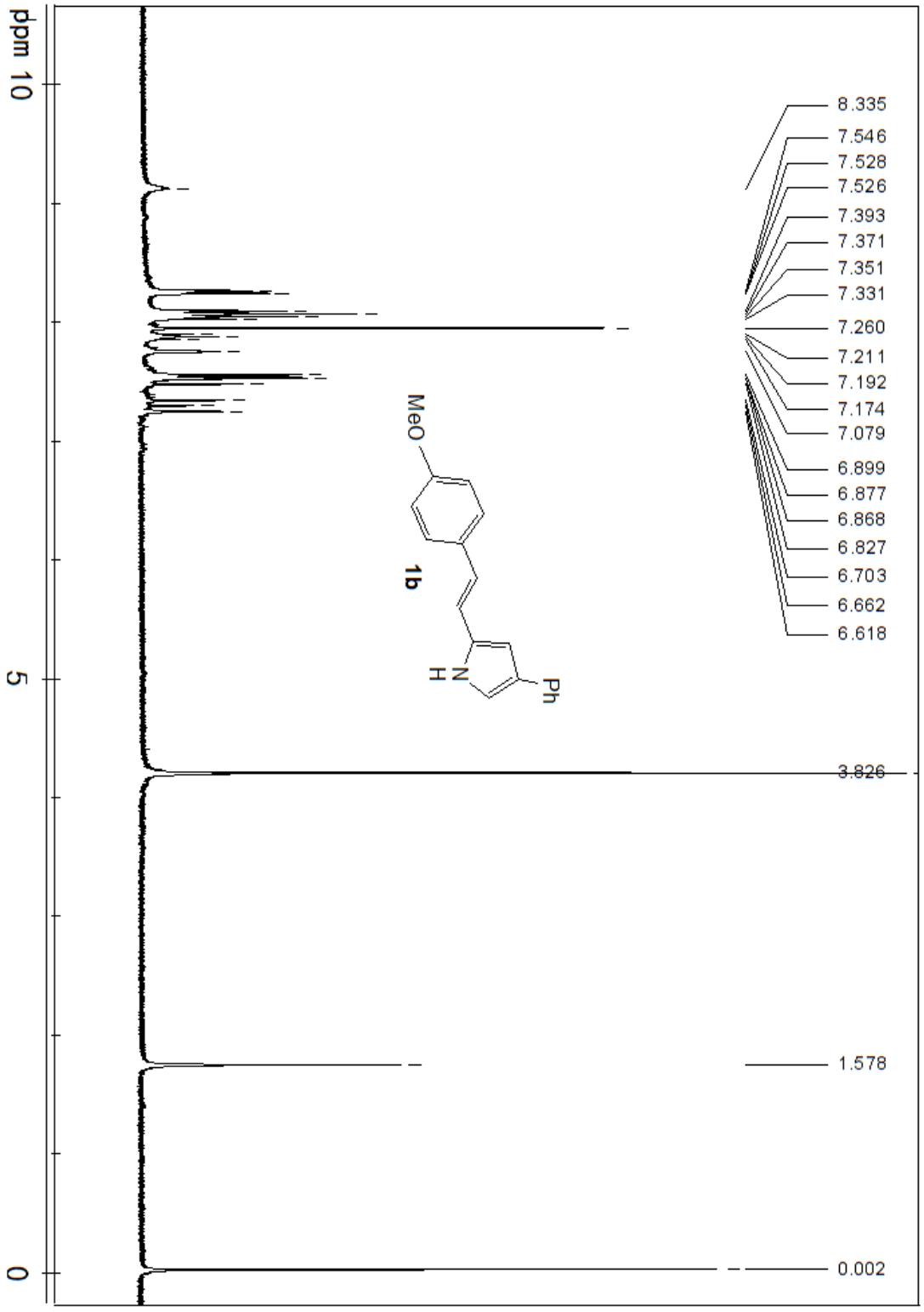
Styryl-containing aza-BODIPY dye 3b

Pyrrole **1b** (27.6 mg, 0.1 mmol) were used as the starting material, and BODIPY **3b** was obtained as coppery solids (24.9 mg, 41 %). M.p.: 253.0–253.7 ºC (decomp.). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.77 (d, J = 9.0 Hz, 1H), 8.08 (d, J = 7.5 Hz, 2H), 7.72 (d, J = 7.5 Hz, 2H), 7.62 (d, J = 8.5 Hz, 2H), 7.51-7.58 (m, 2H), 7.49 (t, J = 7.5 Hz, 2H), 7.34-7.45 (m, 4H), 7.21 (s, 1H), 7.05 (dd, J = 9.0, 2.5 Hz, 1H), 6.95 (d, J = 8.5 Hz, 2H), 6.86 (d, J = 2.5 Hz, 1H), 3.92 (s, 3H), 3.86 (s, 3H), 2.95 (s, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 162.3, 161.0, 153.3, 152.5, 146.7, 144.7, 144.4, 138.0, 137.6, 132.6, 132.1, 131.4, 130.4, 129.6, 129.3, 128.7, 128.6, 128.4, 128.2, 128.0, 120.3, 117.1, 114.4, 113.5, 113.1, 55.5, 55.4, 30.5, 21.7. MS (ESI(+)): m/z = 609.2 $[M]^+$, found 609.4. HRMS-MALDI (m/z): $[M+H]^+$ calcd for $C_{38}H_{31}BF_2N_3O_2$: 610.2478; found 610.2457.

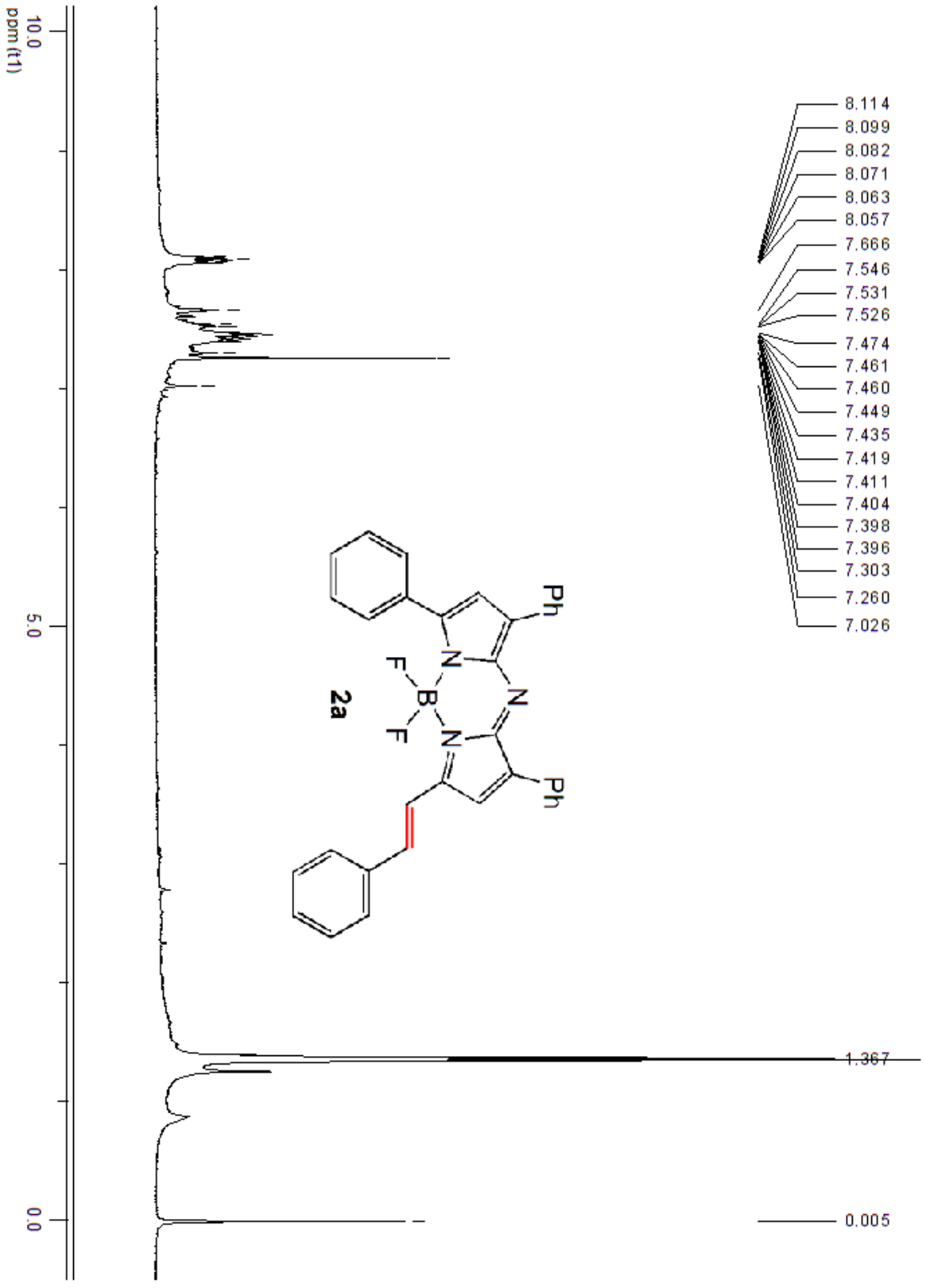
3 Spectroscopic data



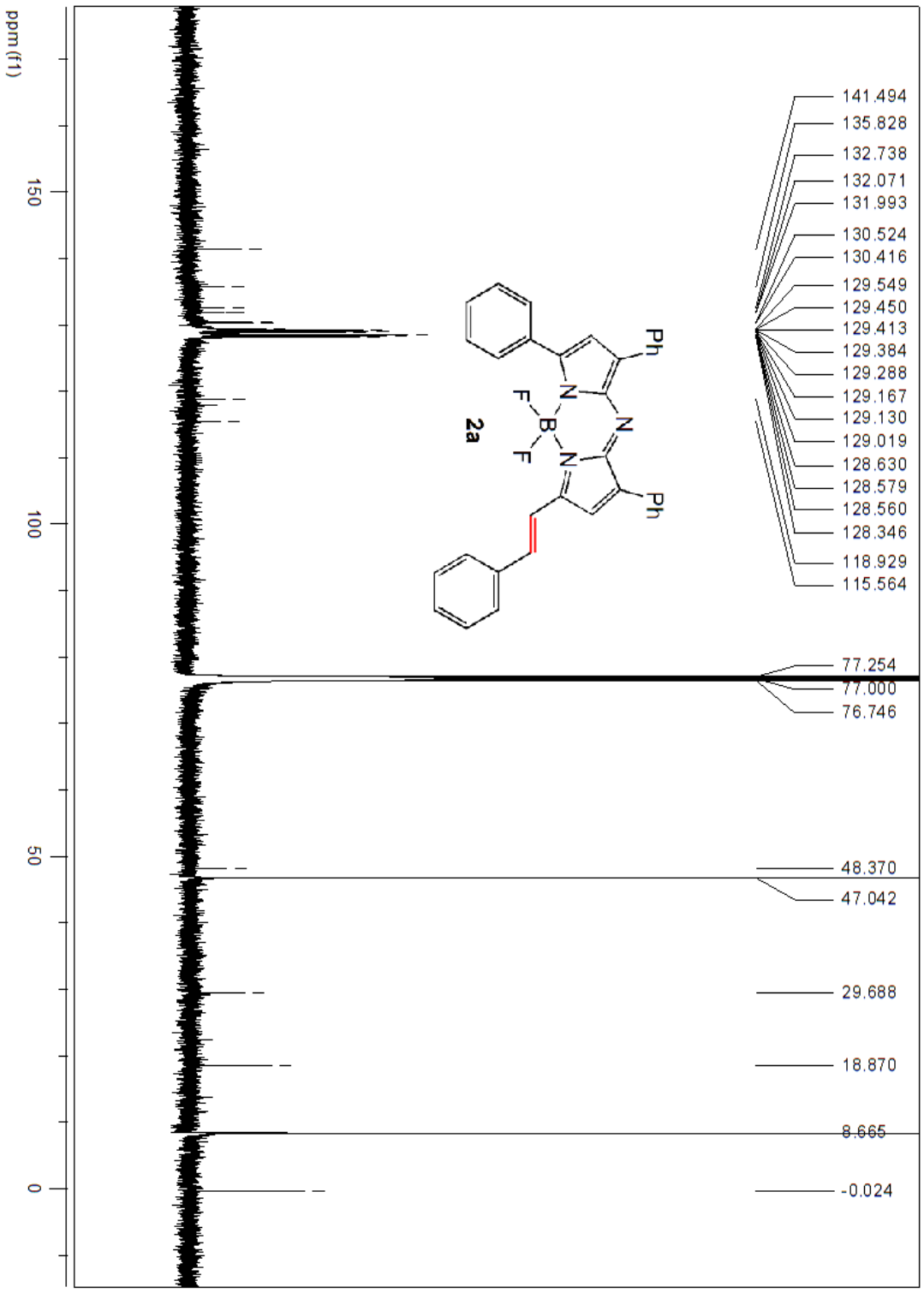
^{1}H NMR (500 MHz, $CDCl_3$) of dye **1a**



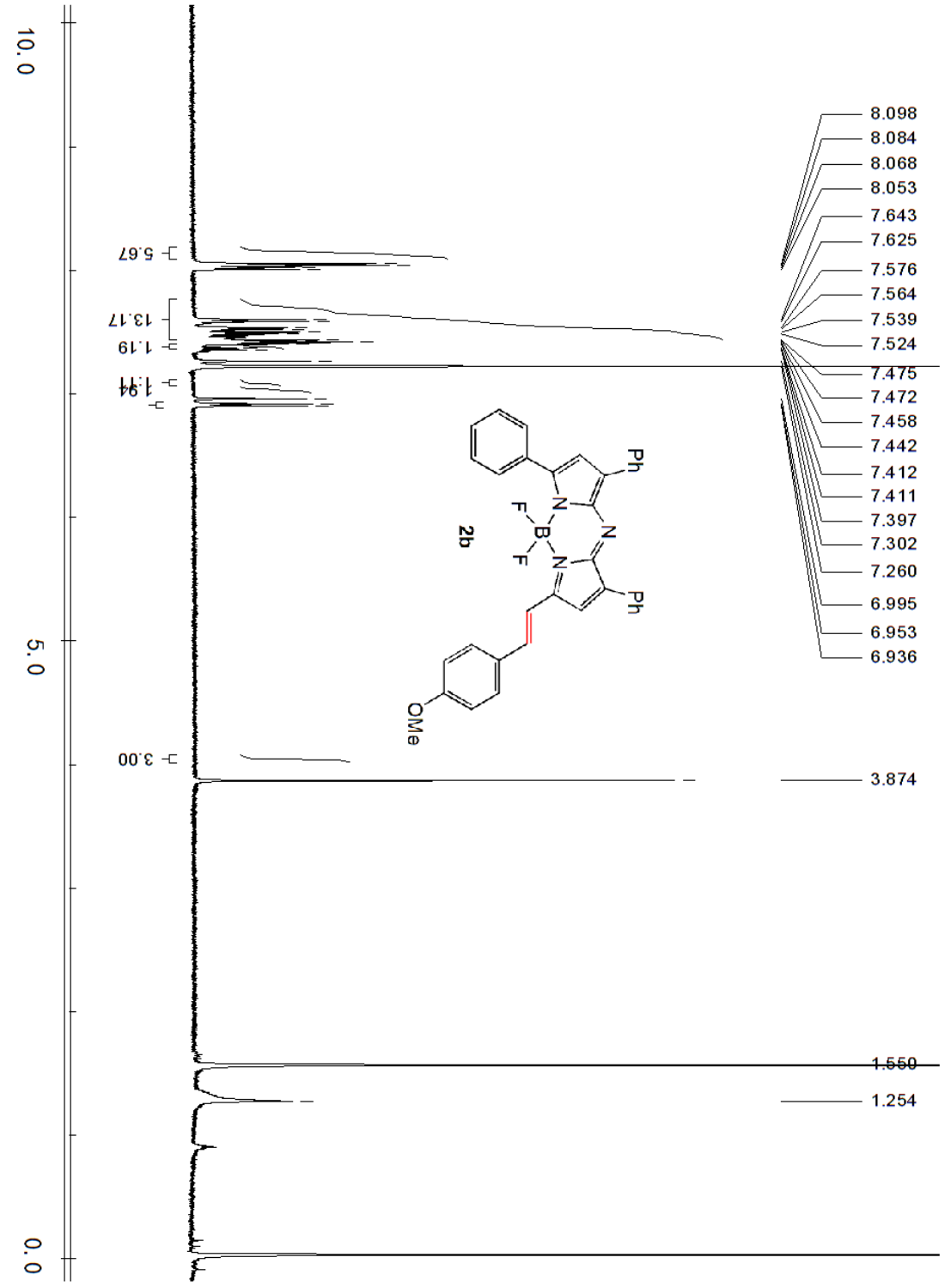
^{1}H NMR (500 MHz, $CDCl_3$) of dye **1b**



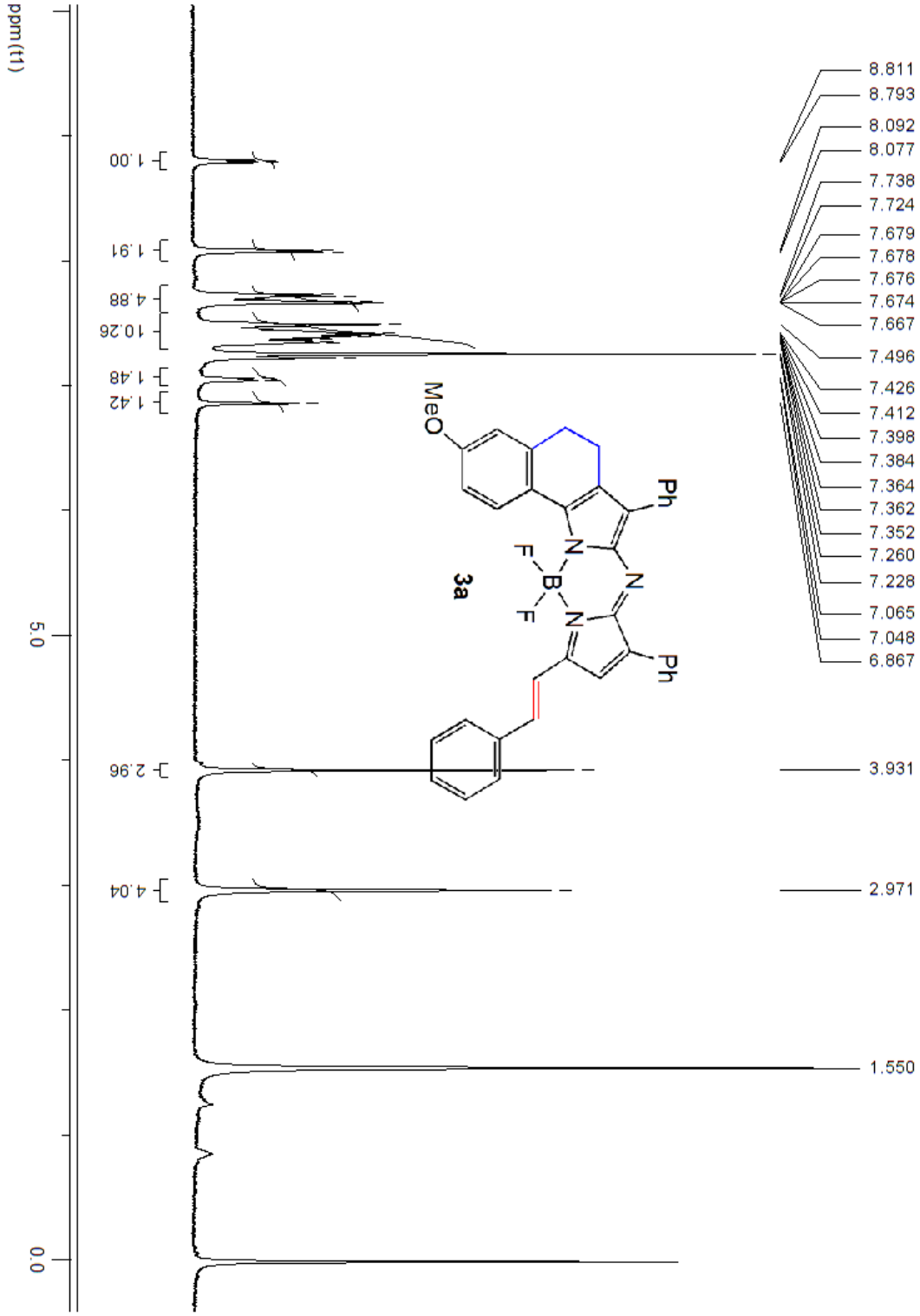
^{1}H NMR (500 MHz, $CDCl_3$) of dye **2a**



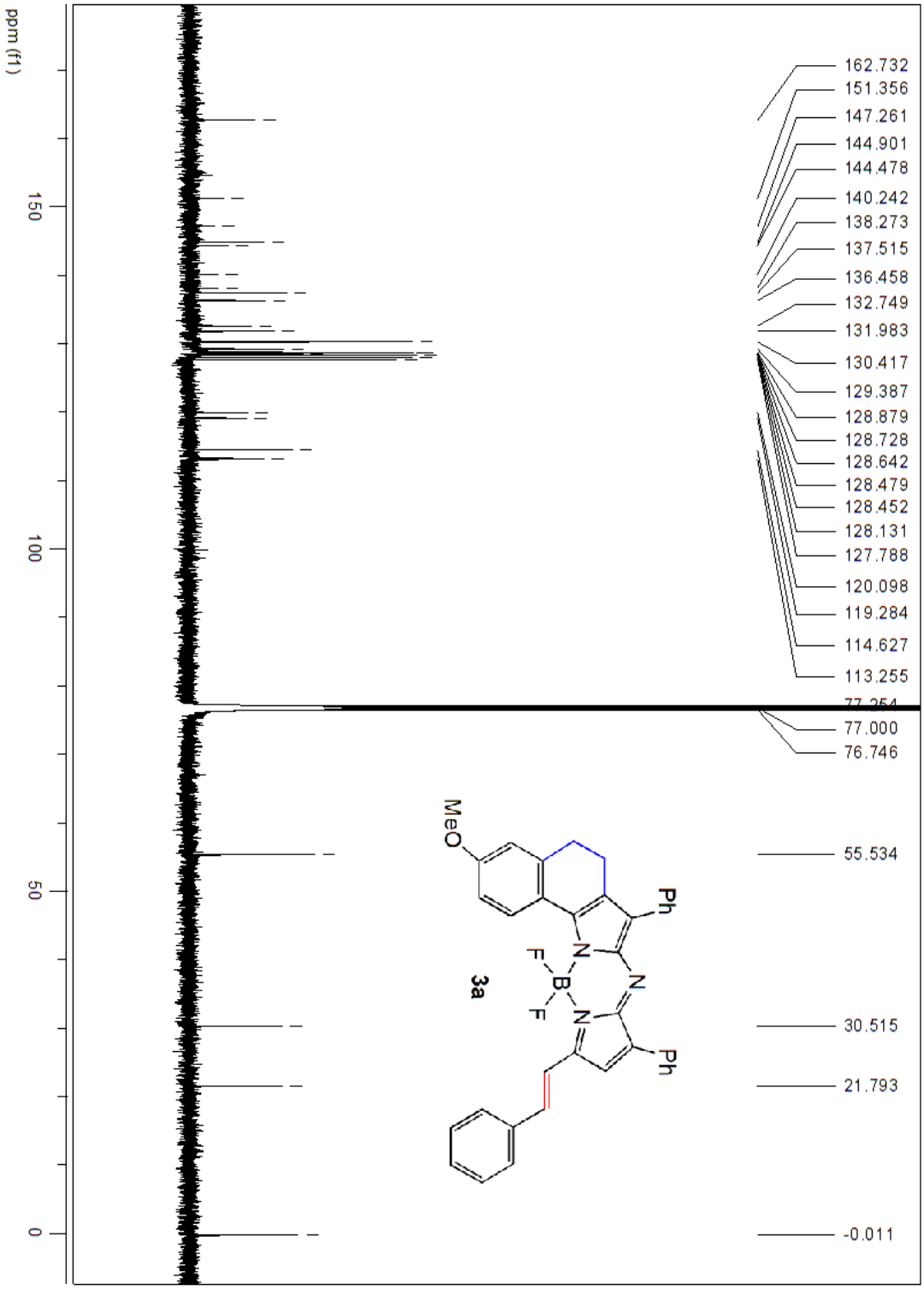
^{13}C NMR (125 MHz, $CDCl_3$) of dye **2a**



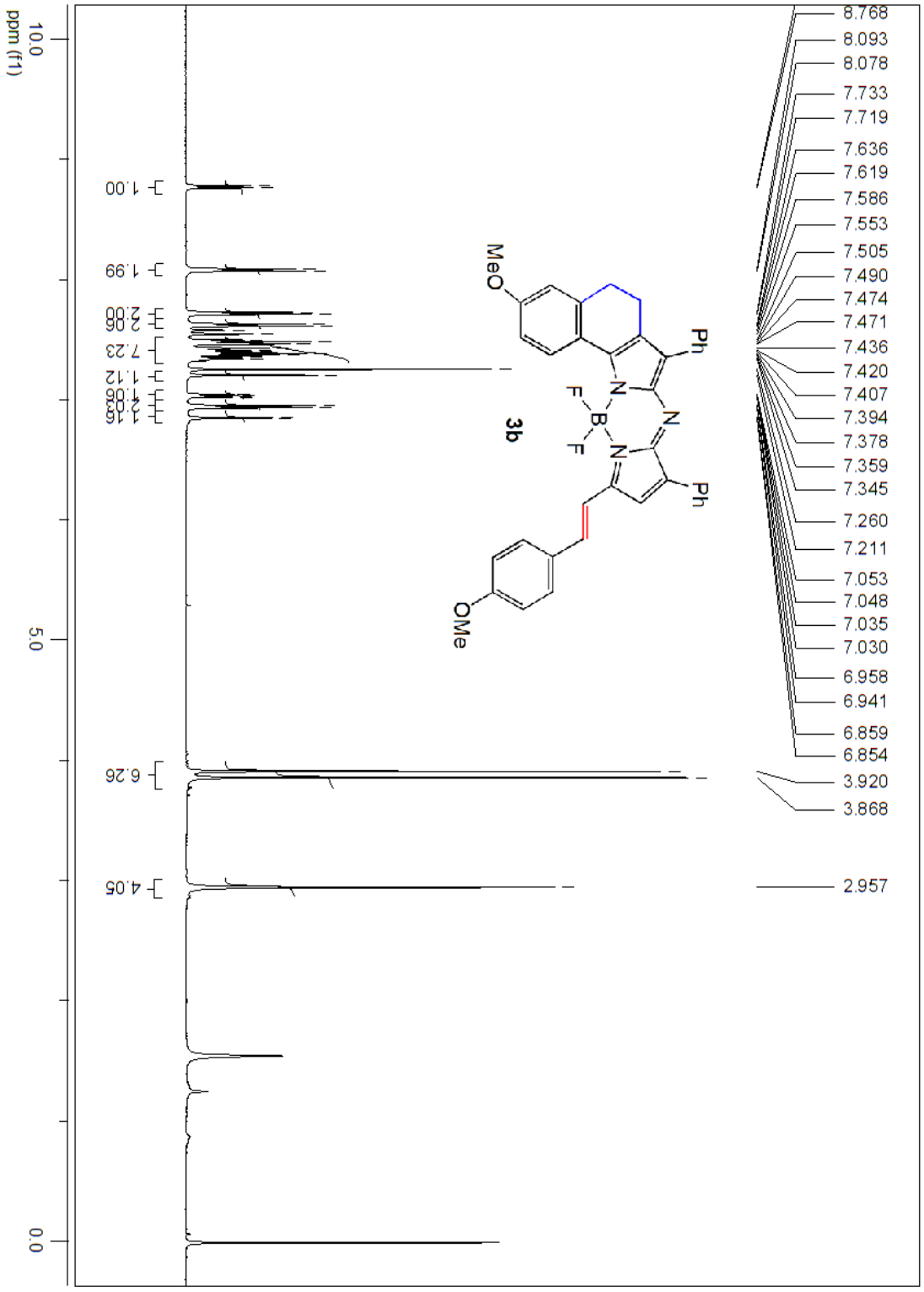
^{1}H NMR (500 MHz, $CDCl_3$) of dye **2b**



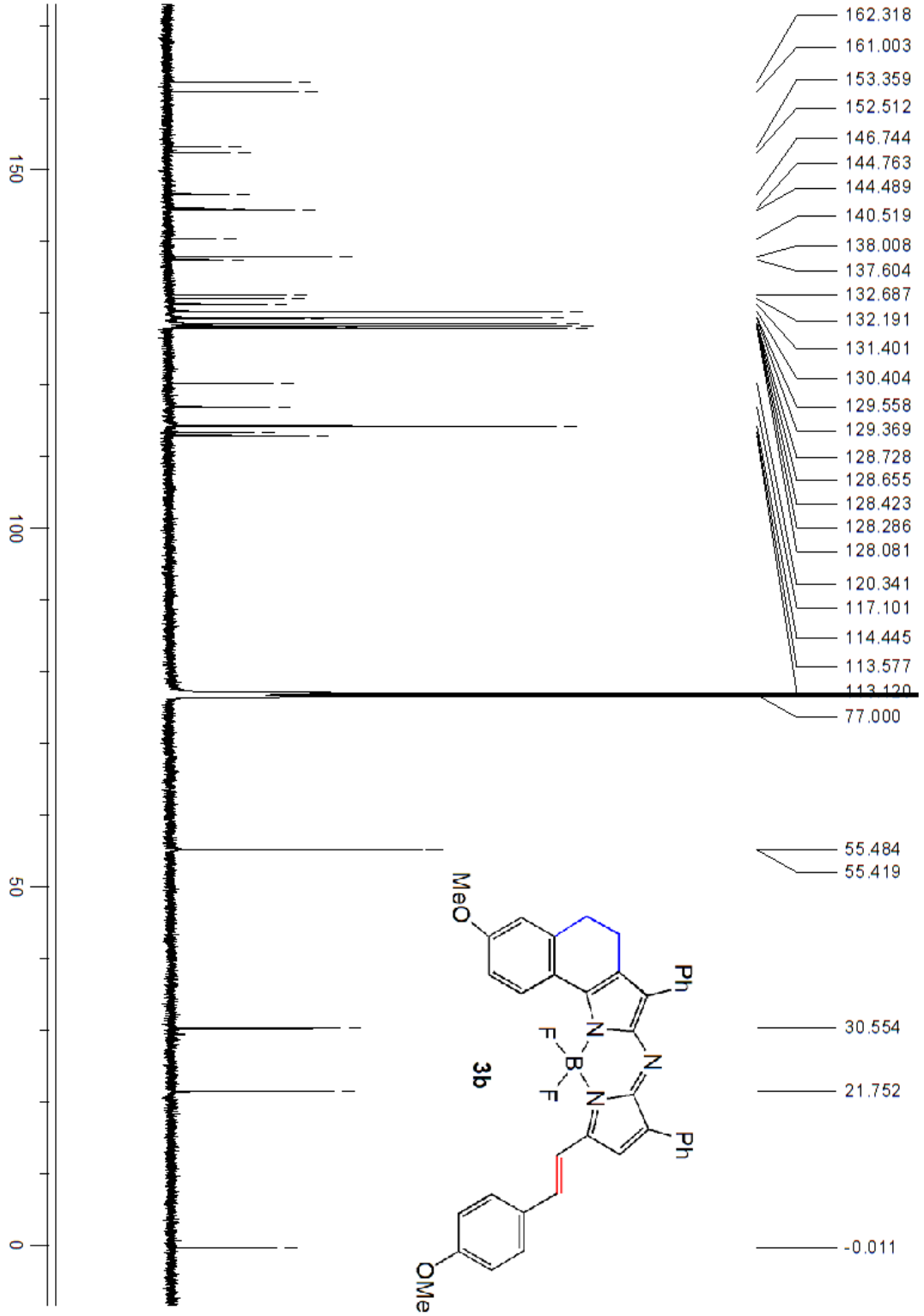
^{1}H NMR (500 MHz, $CDCl_3$) of dye **3a**



^{13}C NMR (125 MHz, $CDCl_3$) of dye **3a**

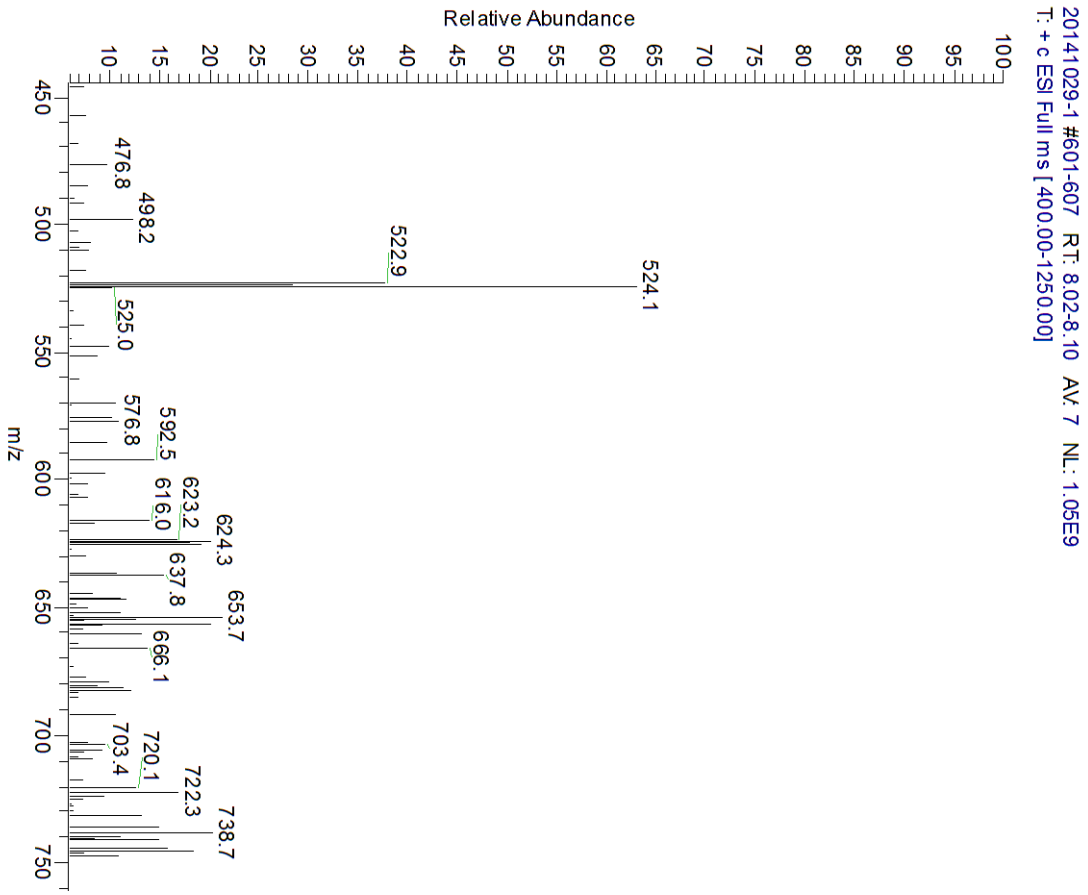


^{1}H NMR (500 MHz, $CDCl_3$) of dye **3b**

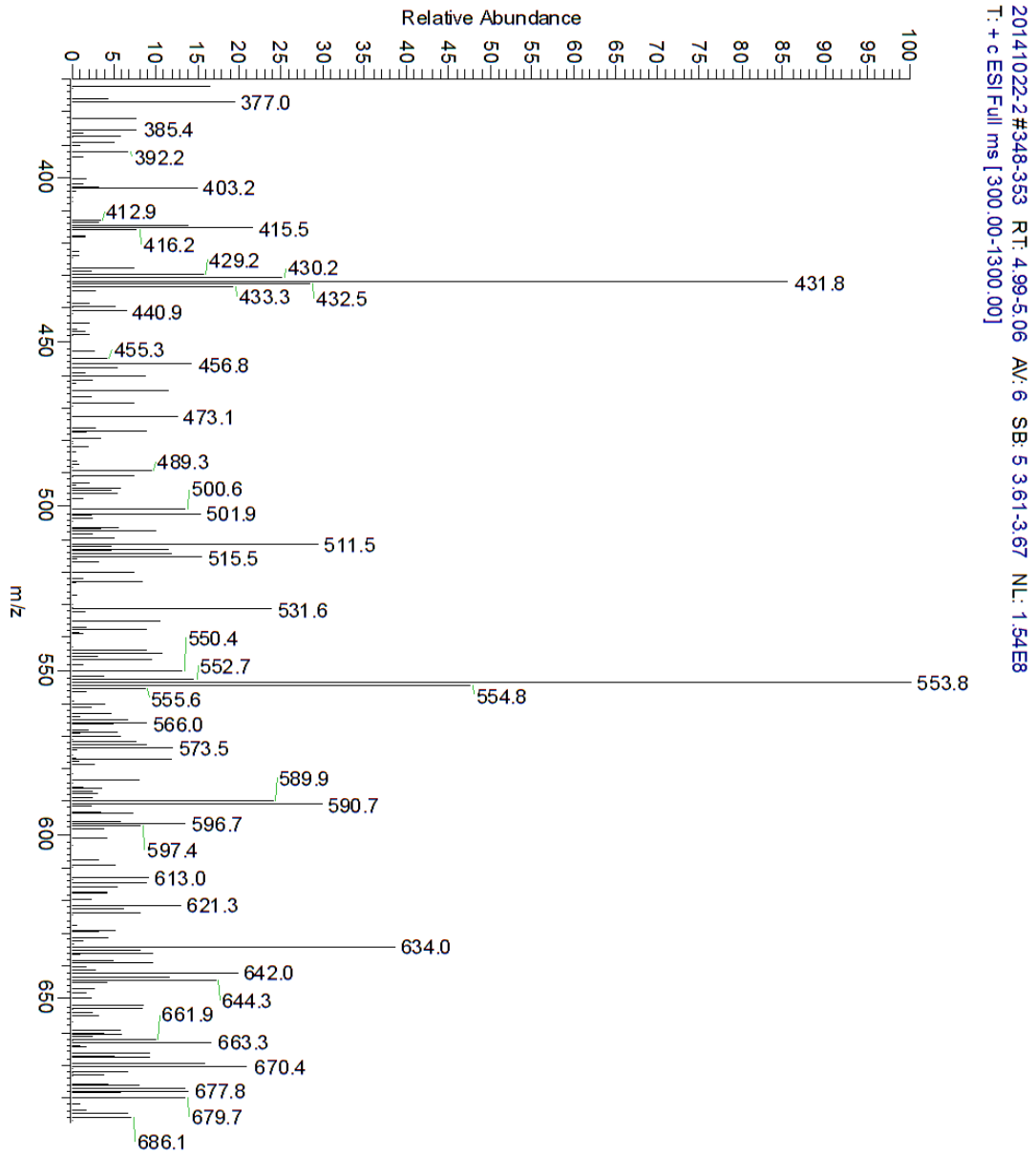


^{13}C NMR (125 MHz, $CDCl_3$) of dye **3b**

4. Ms



MS (ESI) of **2a**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m/z
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385.4
392.2
403.2
412.9
415.5
416.2
429.2
430.2
431.8
433.3
432.5
440.9
455.3
456.8
473.1
489.3
500.6
501.9
511.5
515.5
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552.7
553.8
555.6
554.8
566.0
573.5
589.9
590.7
596.7
597.4
613.0
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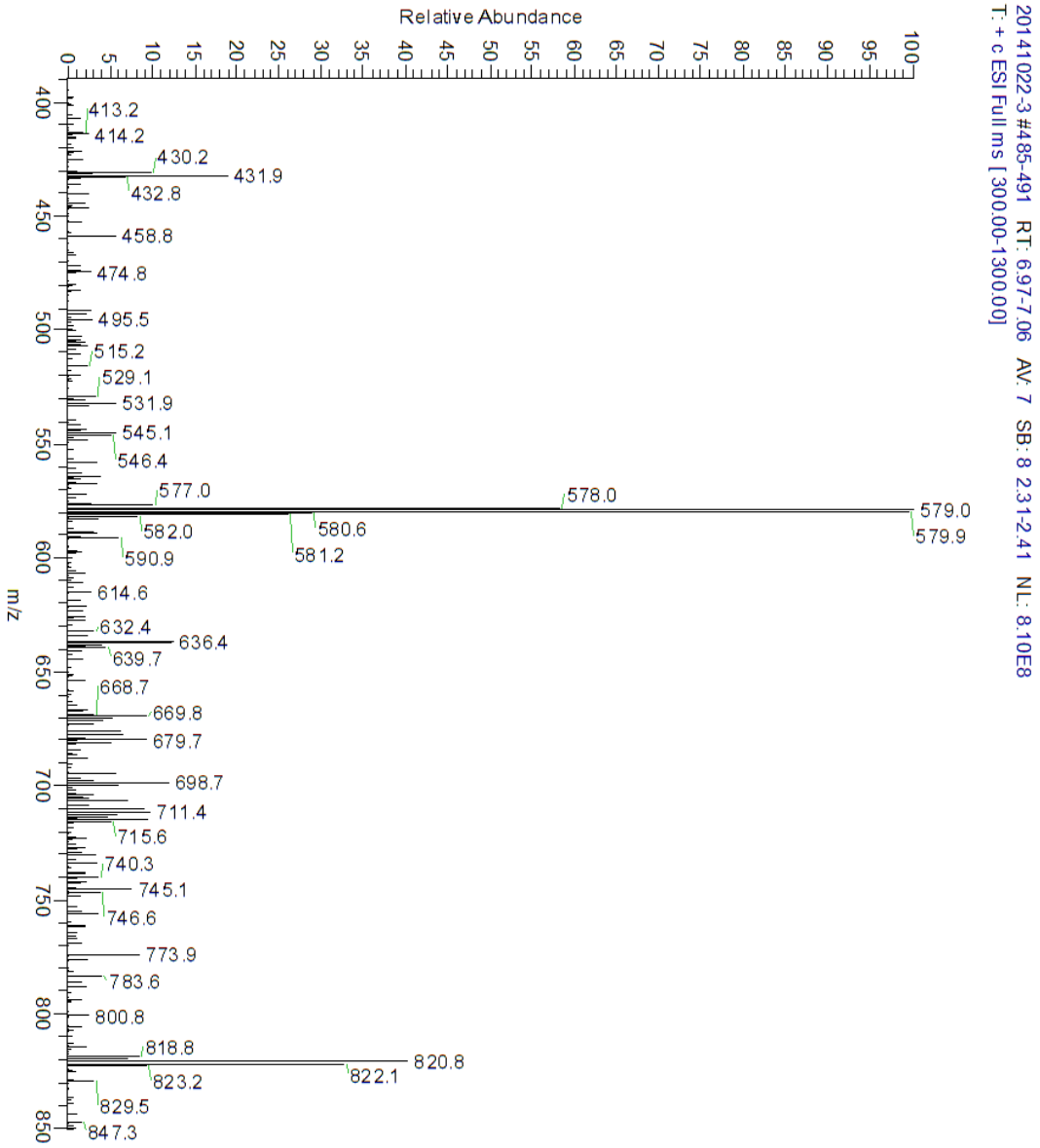
663.3
670.4
677.8
679.7
686.1

MS (ESI) of **2b**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m/z
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414.2
430.2
431.9
432.8
458.8
474.8
495.5
515.2
529.1
531.9
545.1
546.4
577.0
578.0
579.0
579.9
582.0
580.6
581.2
590.9
614.6
632.4
636.4
639.7
668.7
669.8
679.7
698.7
711.4
715.6
740.3
745.1
746.6
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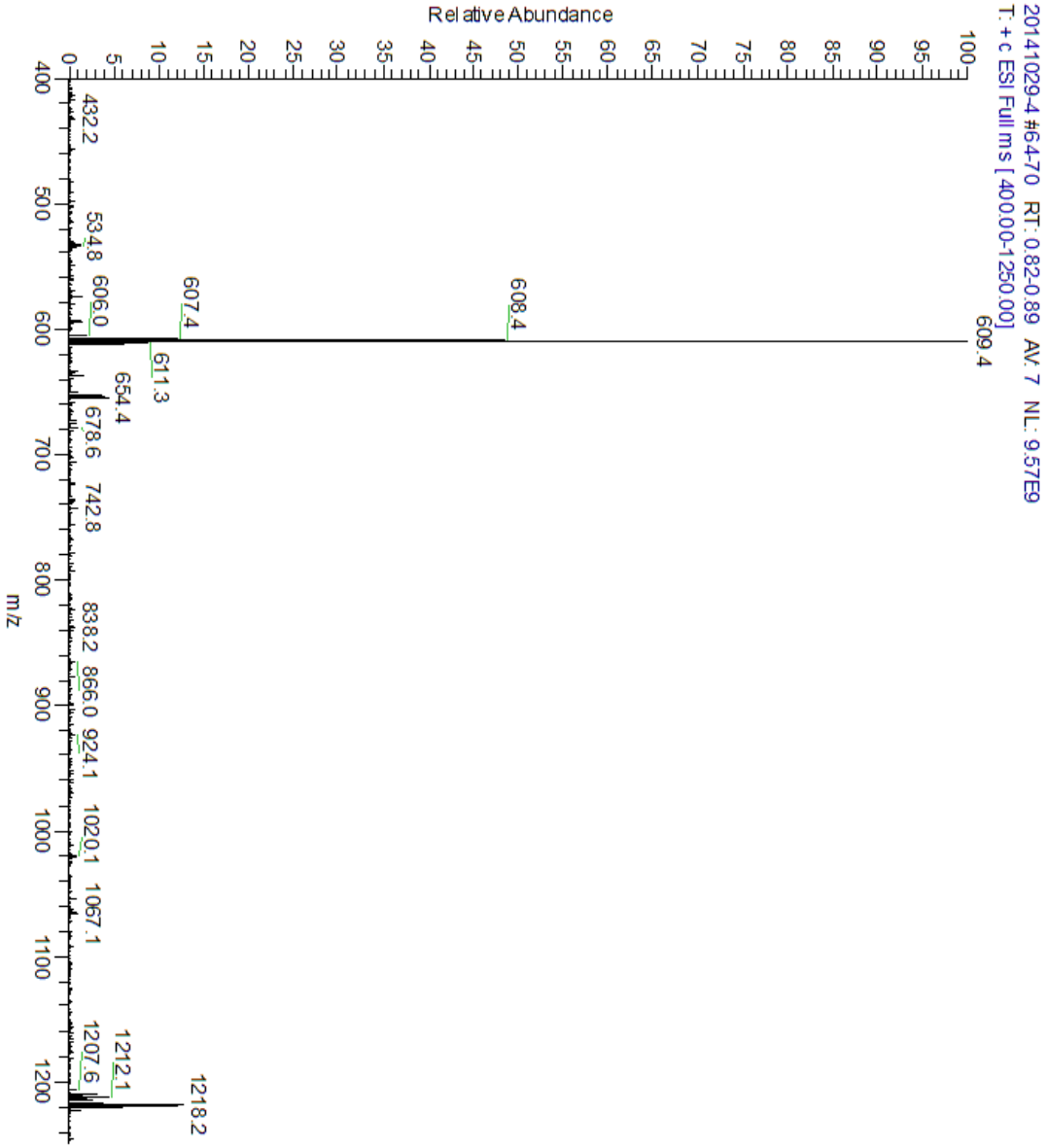
MS (ESI) of **3a**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Relative Abundance
m/z
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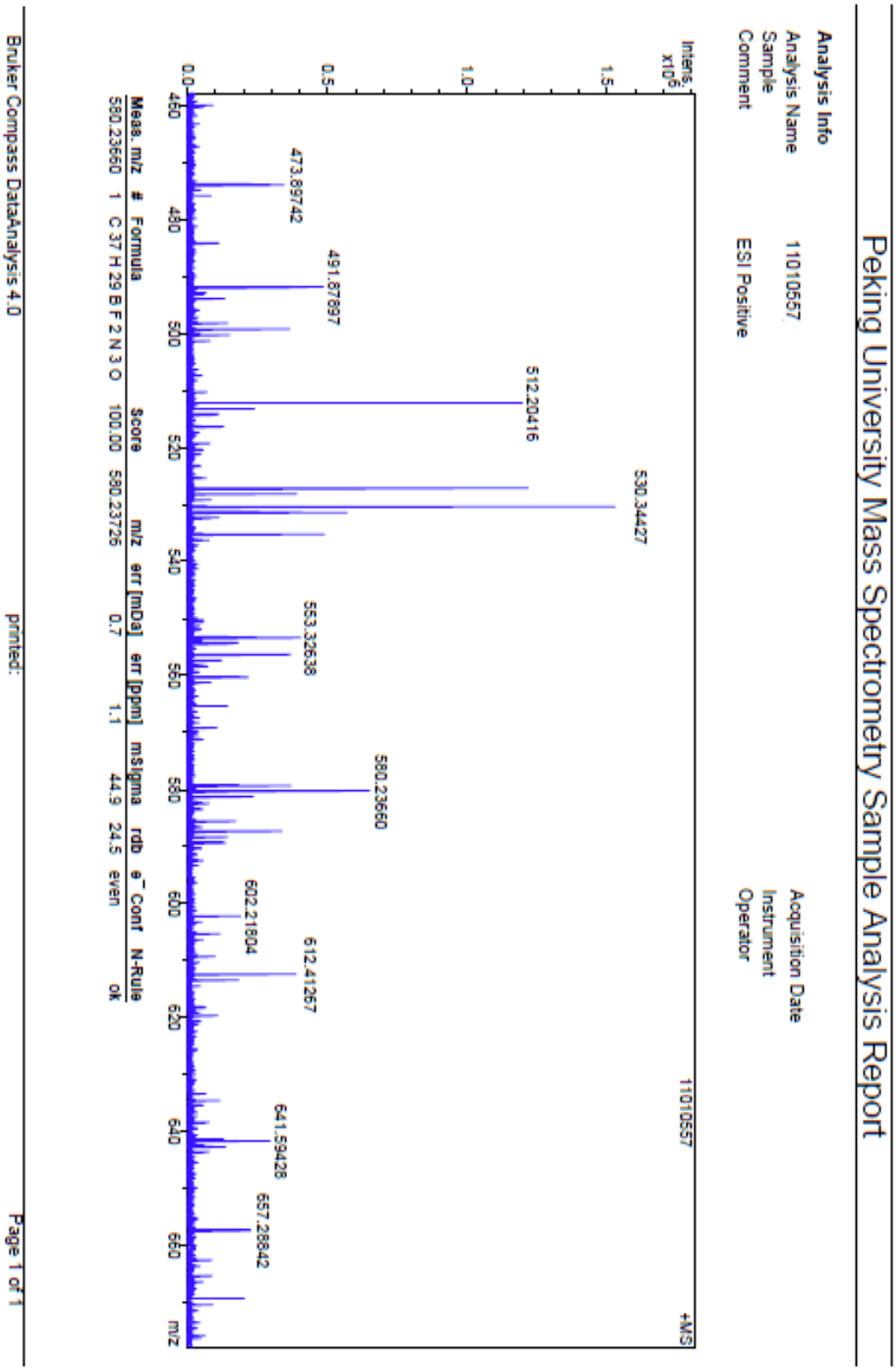
607.4
608.4
609.4
611.3
654.4
678.6
742.8
838.2
866.0
924.1
1020.1
1067.1
1207.6
1212.1
1218.2

MS (ESI) of **3b**

5. HRMS



HRMS of **3a**

Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

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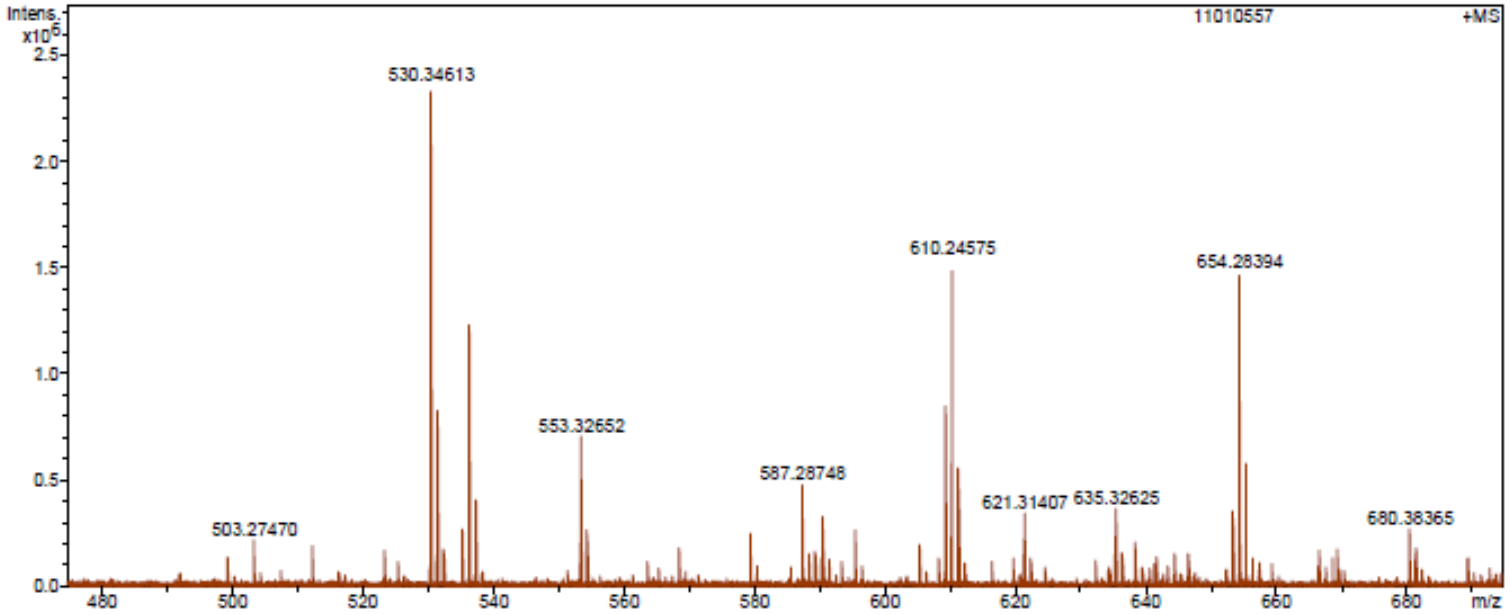
Sample		Instrument	
Comment	ESI Positive	Operator	



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
610.24575	1	C 36 H 32 B F 2 N 3 Na O 2	100.00	610.24540	-0.3	-0.6	146.4	21.5	even	ok
	2	C 38 H 31 B F 2 N 3 O 2	31.56	610.24784	2.1	3.4	147.8	24.5	even	ok

HRMS of **3b**

6. References

1 A. Gorman, J. Killoran, C. O'Shea, T. Kenna, W. M. Gallagher and D. F. O'Shea, *J. Am. Chem. Soc.*, 2004, **126**, 10619.

2 Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A.; Gaussian, Inc.: Pittsburgh, PA, 2003.

3 H. KnoÈlker, B. Ahrens, P. Gonser, M. Heininger and P. G. Jones, *Tetrahedron*, 2000, **56**, 2259.

4 X.-D. Jiang, J. Zhang, X. Shao and W. Zhao, *Org. Biomol. Chem*., 2012, **10**, 1966.