Fifth-Order Nonlinear Optical Properties of through space charge transfer Pyridinium Salt

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General considerations

Column chromatography was performed using reversed phase C18-silica gel columns (RP18 25-40 μm) and direct phase silica gel columns.

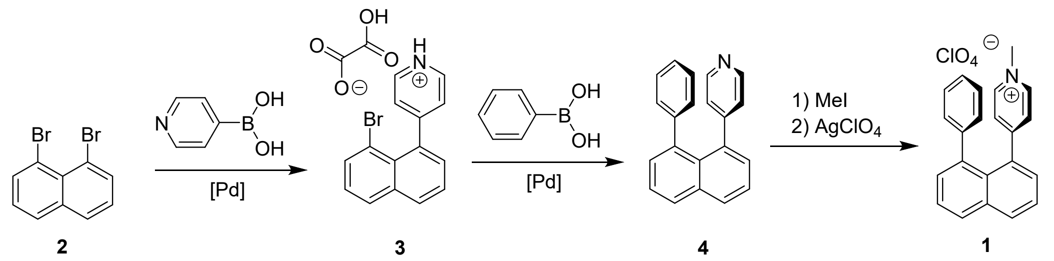
Nuclear magnetic resonance spectra were recorded on NMR spectrometers at the following frequencies: ^{1}H, 400 MHz, 300 MHz; ^{13}C{^{1}H}, 101 MHz. Chemical shifts are reported in parts per million (ppm) relative to TMS or with the residual solvent peak as an internal reference. High-resolution mass spectra (HRMS (ESI-TOF)) were recorded on a mass spectrometer with a time-of-flight (TOF) mass analyzer using the ESI technique. Melting points are uncorrected.

Unless otherwise noted, all chemicals were used as received from commercial sources.

The absorption data was collected with Edinburgh Instruments *FS5* Spectrofluorometer; NLO properties were characterized by Z-scan method using ORPHEUS-HP + PHAROS PH2 femtosecond laser with a repetition rate of 5 kHz to 500 kHz and pulse width of 150 fs was used as laser source.

Emitter Synthesis

Synthesis of **1**:



Synthesis of **3**. 1,8-Dibromonaphthalene (**2**, 2.0 g, 7.0 mmol, 1.0 equiv), pyridine-4-boronic acid hydrate (0.84 g, 7.0 mmol, 1.0 equiv), Pd(dppf)Cl$_2$ × CH$_2$Cl$_2$ (0.29 g, 0.35 mmol, 0.05 equiv), K$_2$CO$_3$ (2.9 g, 21.0 mmol, 3.0 equiv) were weighed into a 100 mL round bottom flask. Acetonitrile (30 mL) and water (10 mL) were added and the resulting brown emulsion was refluxed for 2h. The reaction mixture was cooled, diluted with CH$_2$Cl$_2$ (50 mL) and sat. aq. K$_2$CO$_3$ (50 mL) solution. Layers were separated and the aqueous layer was extracted with CH$_2$Cl$_2$ (3 x 50 mL). Combined organic layers were dried over Na$_2$SO$_4$, filtered and concentrated *in vacuo.* Purification of the residue by silica gel column chromatography using gradient elution from 10:1 to 3:1 Hexanes:EtOAc afforded a pale yellow amorphous material. The latter was dissolved in Et$_2$O (20 mL) and a solution of oxalic acid (0.64 g, 7.0 mmol, 1.0 equiv) in 20 mL Et$_2$O was added leading to formation of a colorless precipitate. The resulting suspension was filtered, washed with Et$_2$O and dried under vacuum to afford **3** as colorless needles (1.7 g, 65%); mp (MeCN/Et$_2$O) 198–200 °C (colorless needles).

^{1}H NMR (400 MHz, CD$_3$OD, ppm) δ 8.77–8.70 (m, 2H), 8.12 (dd, *J*=8.2, 1.2 Hz, 1H), 8.07 (dd, *J*=8.2, 1.2 Hz, 1H), 7.89 (dd, *J*=7.5, 1.2 Hz, 1H), 7.84–7.79 (m, 2H), 7.68–7.61 (m, 1H), 7.52 (dd, *J*=7.2, 1.2 Hz, 1H), 7.49–7.43 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, CD$_3$OD, ppm) δ 164.5, 159.4, 144.8, 144.7, 137.8, 137.0, 135.5, 132.8, 132.4, 130.6, 129.8, 128.6, 128.3, 126.7, 119.8.

IR (KBr, cm^{-1}) 2559 (O–H), 1711 (C=O).

HR-MS (*m/z*) Calc. Mass for $C_{15}H_{11}BrN^+$: 284.0069; Found: 284.0086.

Synthesis of **4**. 4-(8-Bromonaphthalen-1-yl)pyridin-1-ium oxalate (**3**, 1.72 g, 4.6 mmol, 1.0 equiv), 4-phenylboronic acid (0.66 g, 5.5 mmol, 1.2 equiv), Pd(dppf)Cl$_2$ × CH$_2$Cl$_2$ (0.19 g, 0.2 mmol, 0.05 equiv), K$_2$CO$_3$ (1.90 g, 13.7 mmol, 3.0 equiv) were weighed into a 100 mL round bottom flask. MeCN (24 mL) and water (6 mL) were added to the flask and the resulting brown emulsion was refluxed. After 2h the reaction mixture was cooled and directly adsorbed on silica gel. Purification by silica gel column chromatography using gradient elution from 6:1 to 3:1 hexane:EtOAc afforded **4** as colorless plates (0.79 g, 62%). Analytical TLC on silica gel, 1:3 EtOAc/Hexanes, R_f=0.39, mp (hexane/EtOAc) 194–195 °C (colorless plates).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.17–8.12 (m, 2H), 8.01 (dd, *J*=8.2, 1.3 Hz, 1H), 7.98 (dd, *J*=8.2, 1.3 Hz, 1H), 7.63–7.54 (m, 2H), 7.46 (dd, *J*=7.0, 1.4 Hz, 1H), 7.37 (dd, *J*=7.0, 1.4 Hz, 1H), 7.06–6.94 (m, 5H), 6.89–6.85 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, ppm) δ 151.1, 148.6, 142.8, 140.1, 137.8, 135.5, 131.2, 131.1, 130.1, 129.9, 129.0, 128.8, 127.7, 126.8, 125.7, 125.2, 124.8.

IR (KBr, cm^{-1}) 1592 (C=C).

HR-MS (*m/z*) Calc. Mass for $C_{21}H_{16}N^+$: 282.1283; Found: 282.1300.

Synthesis of **1**. 4-(8-Phenylnaphthalen-1-yl)pyridine (**4**, 0.79 g 2.8 mmol, 1.0 equiv) was dissolved in MeCN (30 mL) followed by addition of MeI (1.2 g, 8.4 mmol, 3.0 equiv), the vial sealed with septum and heated in a 70 °C oil bath for 2h. After cooling Et_2O was added to form precipitate, which was filtered, washed with Et_2O and redissolved in MeCN (25 mL). To the MeCN solution of the iodide salt a solution of $AgClO_4$ (0.75 g, 3.6 mmol, 1.3 equiv) in MeCN (5 mL) was added. The resulting suspension was stirred at room temperature for 30 minutes, filtered through a pad of celite, and the pad was washed with MeCN. The filtrate was partially evaporated to roughly 5 mL volume, then diluted with *i*-PrOH (40 mL), evaporated again to approximately 5 mL volume and diluted with *i*-PrOH (40 mL) again, then sonified, and left to stand at –15 °C for 2h. The formed suspension was filtered and washed with *i*-PrOH to afford **1** as colorless plates (0.90 g, 81%); mp (*i*-PrOH/MeCN) 201–203°C (colorless plates).

^{1}H NMR (400 MHz, $(CD_3)_2SO$, ppm) δ 8.41–8.37 (m 2H), 8.26 (dd, *J*=8.3, 1.2 Hz, 1H), 8.16 (dd, *J*=8.3, 1.2 Hz, 1H), 7.76–7.70 (m, 2H), 7.61–7.53 (m, 4H), 7.18–7.12 (m, 1H), 7.08–7.03 (m, 2H), 7.02–6.97 (m, 2H), 4.12 (s, 3H).

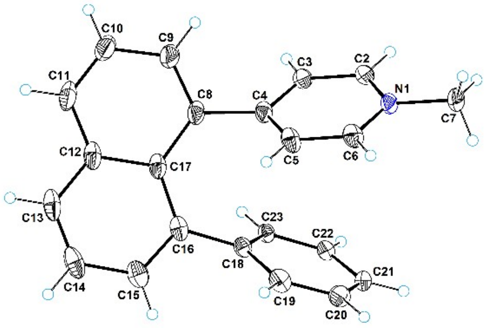
^{13}C{^{1}H} NMR (101 MHz, $(CD_3)_2SO$, ppm) δ 158.9, 143.3, 142.3, 138.8, 135.2, 134.1, 132.2, 132.1, 131.6, 130.6, 129.5, 128.6, 128.2, 128.0, 127.0, 126.9, 125.9, 47.1.

IR (KBr, cm^{-1}) 1640 (C=C);

HR-MS (*m/z*) Calc. Mass for $C_{22}H_{18}N^+$: 296.1439; Found: 296.1436.

Elem. Anal. Calcd for $C_{22}H_{18}ClNO_4$: C, 66.75; H, 4.58; N, 3.54. Found: C, 66.69; H, 4.56; N, 3.50.

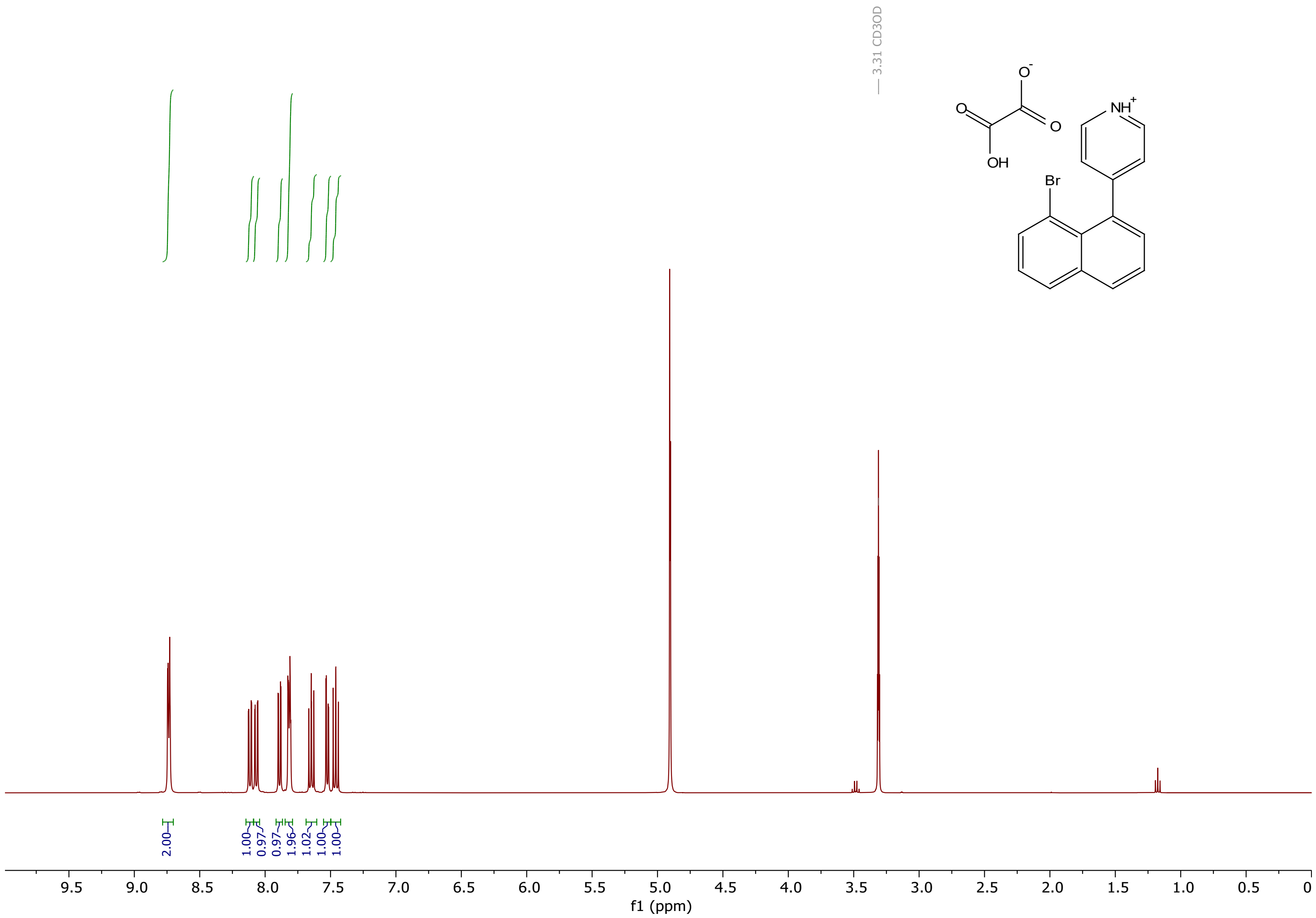
X-Ray Structure, crystal data and structure refinements for 1



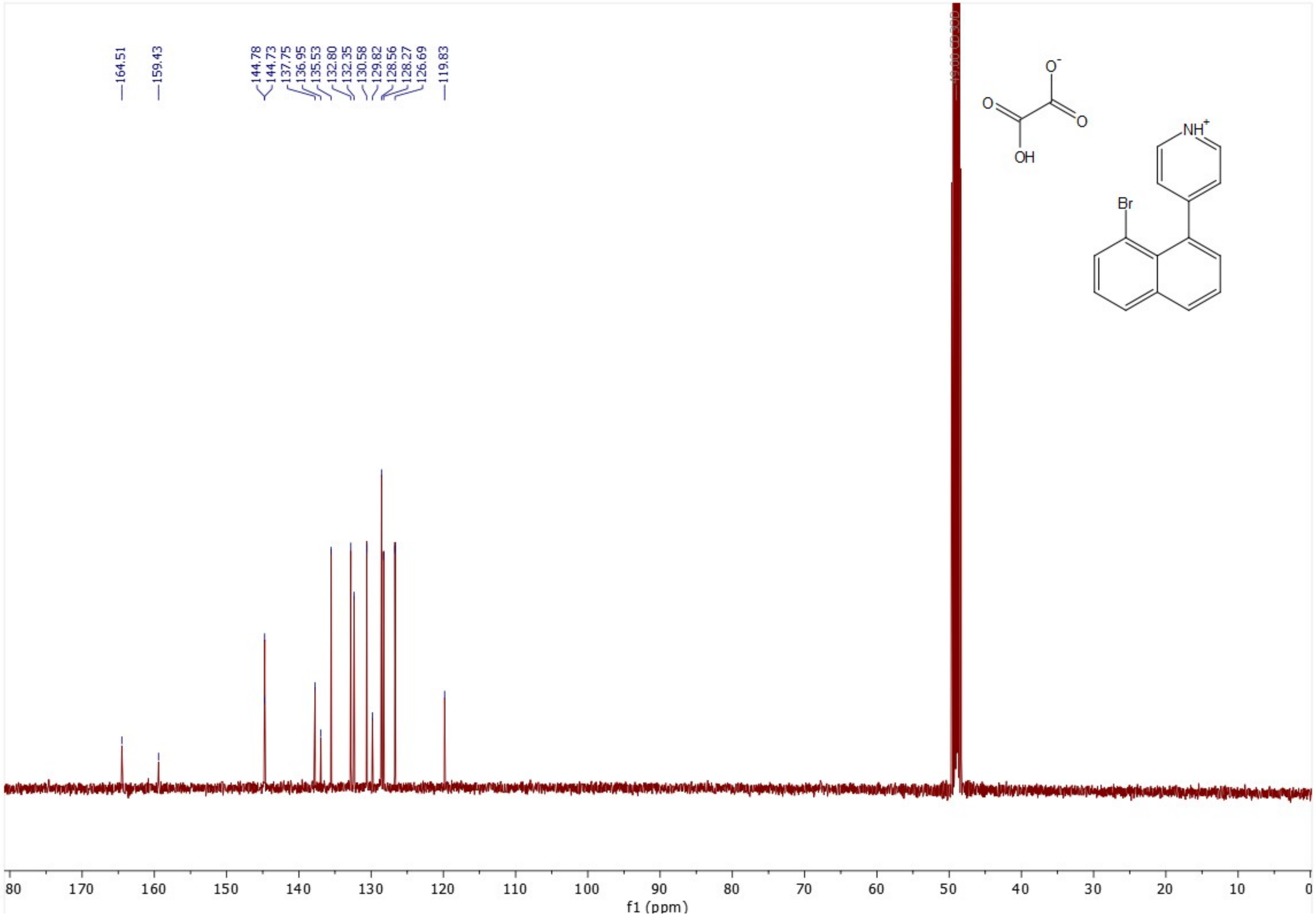
Identification code	LSK-74
Empirical formula	$C_{22}H_{18}ClNO_4$
Formula weight	395.84
Temperature/K	150.0(1)
Crystal system	monoclinic
Space group	*C*2/*c*
a/Å	18.08322(13)
b/Å	8.31078(6)
c/Å	25.0348(2)
α/°	90
β/°	102.7311(8)
γ/°	90
Volume/Å^3	3669.88(5)
Z	8
ρ_{calc}g/cm^3	1.4328
μ/mm^{-1}	2.097
F(000)	1648
Crystal size/mm^3	0.18 × 0.08 × 0.01
Radiation	Cu Kα (λ = 1.54184 Å)
2Θ max. for data collection/°	160
Index ranges	$-21 \leq h \leq 23$, $-9 \leq k \leq 10$, $-29 \leq l \leq 31$
Reflections collected	19552
Independent reflections	3978 [R_{int} = 0.0240, R_{sigma} = 0.0200]
Data/restraints/parameters	3978/0/263
Goodness-of-fit on F^2	1.290
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0861, wR_2 = 0.2319
Largest diff. peak/hole / e Å^{-3}	1.51/-1.94

^{1}H and ^{13}C NMR data

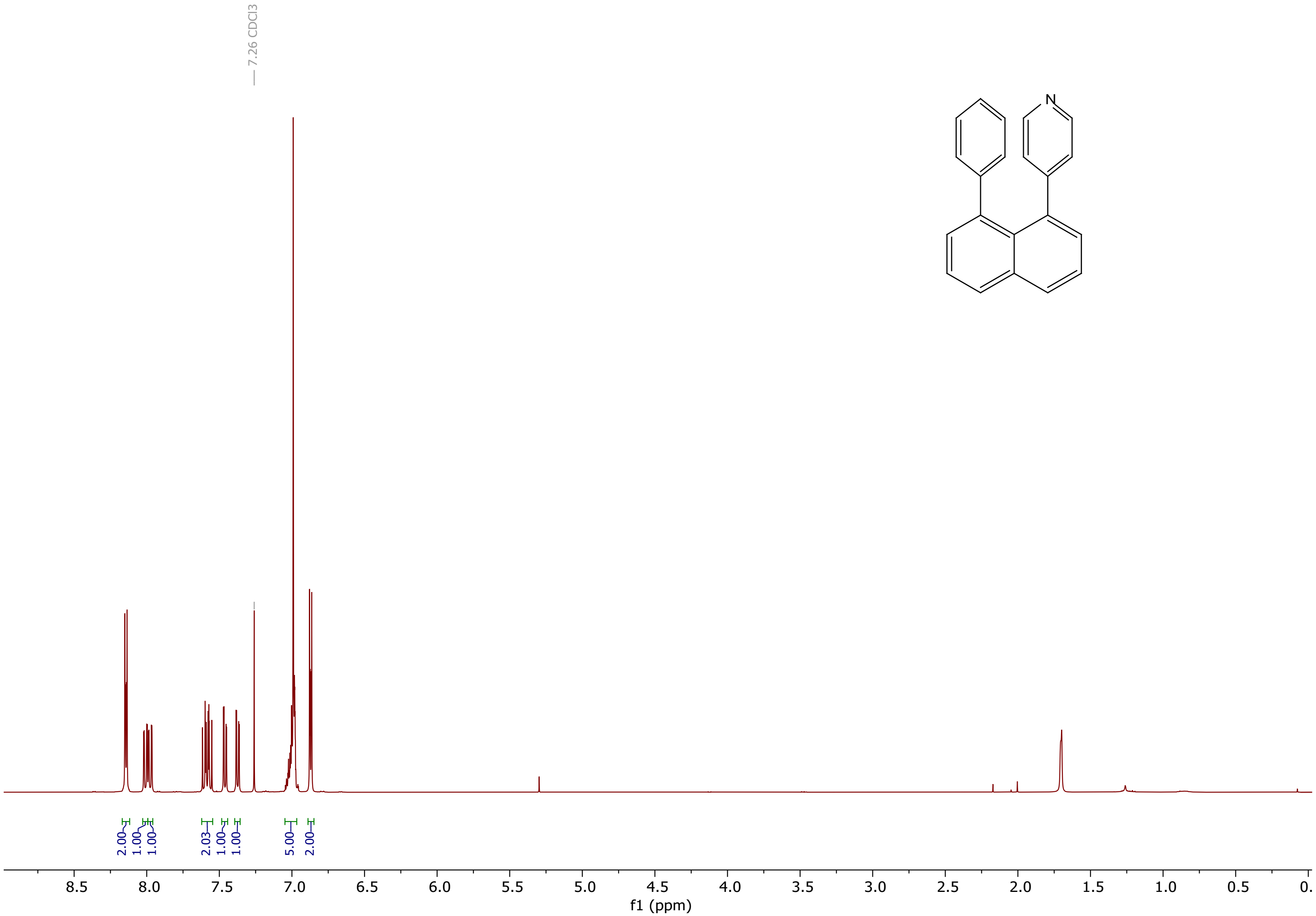
^{1}H NMR (400 MHz, CD_3OD, ppm) spectrum of 4-(8-bromonaphthalen-1-yl)pyridin-1-ium carboxyformate (**3**)



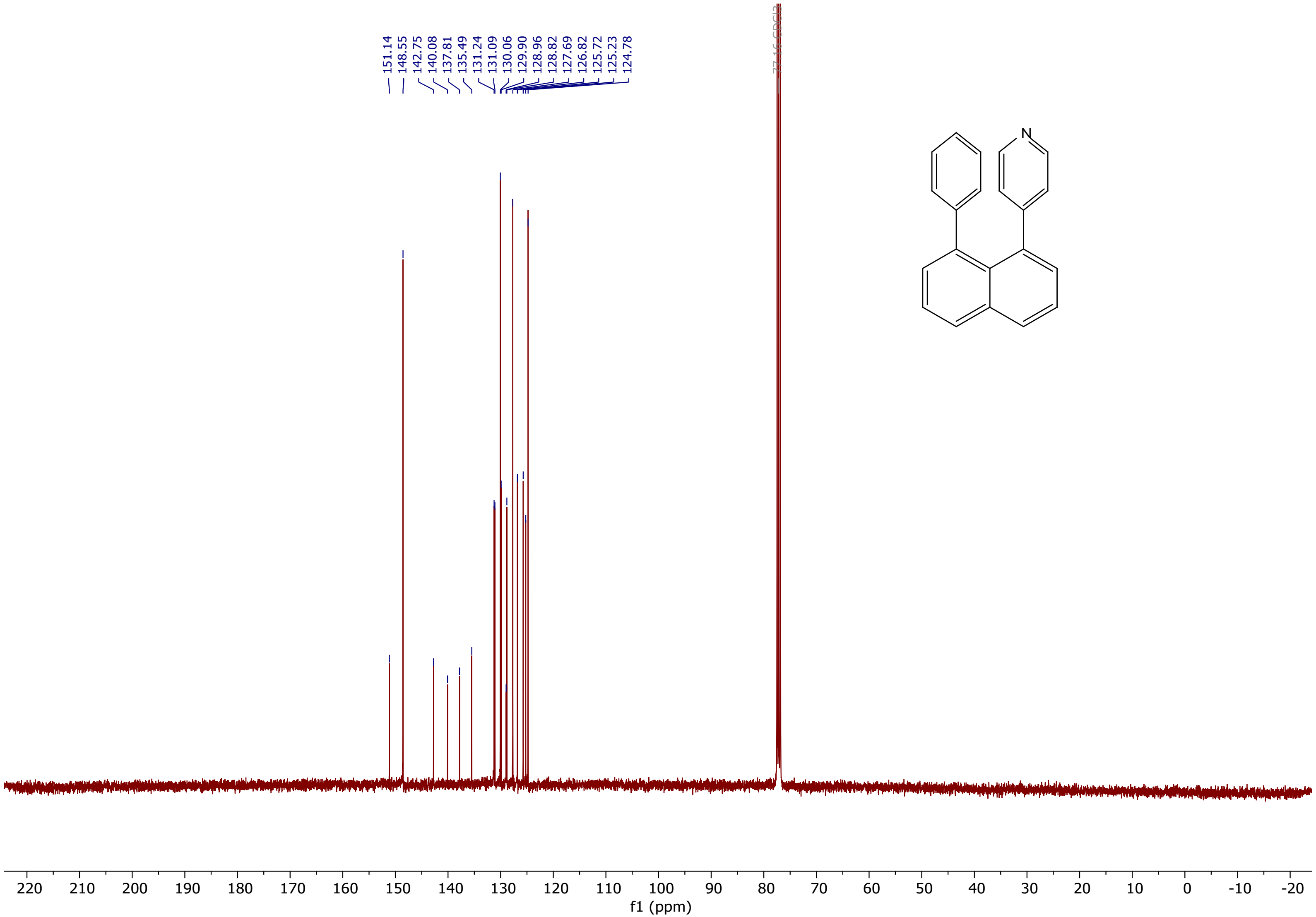
^{13}**C{^{1}H} NMR** (101 MHz, CD_3OD, ppm) spectrum of 4-(8-bromonaphthalen-1-yl)pyridin-1-ium carboxyformate (**3**)



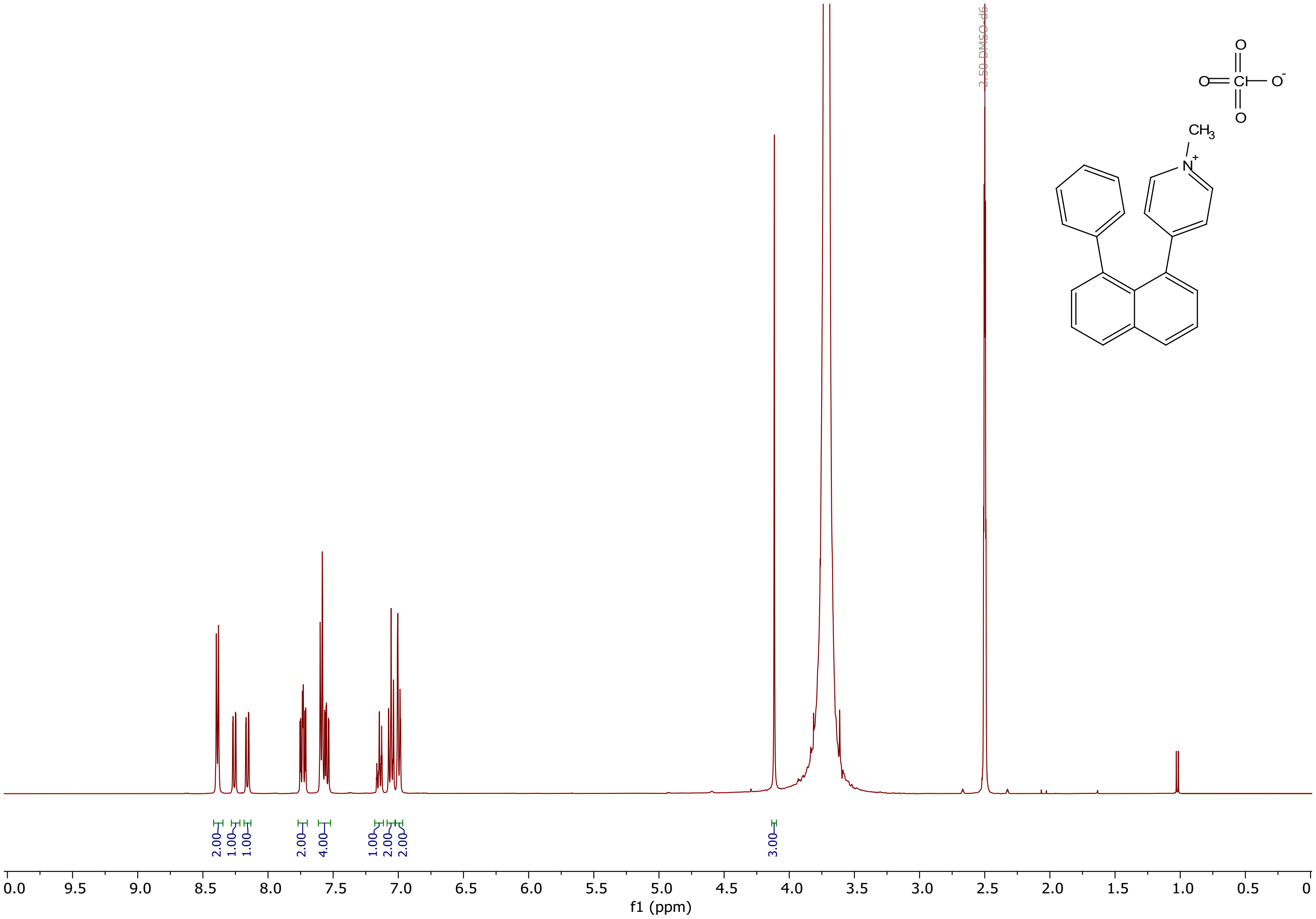
^{1}H NMR (400 MHz, $CDCl_3$, ppm) spectrum of 4-(8-phenylnaphthalen-1-yl)pyridine (**4**)



^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, ppm) spectrum of 4-(8-phenylnaphthalen-1-yl)pyridine (**4**)



^{1}H NMR (400 MHz, $(CD_3)_2SO$, ppm) spectrum of 1-methyl-4-(8-phenylnaphthalen-1-yl)pyridin-1-ium perchlorate (**1**)



$^{13}C\{^{1}H\}$ NMR (101 MHz, $(CD_3)_2SO$, ppm) spectrum of 1-methyl-4-(8-phenylnaphthalen-1-yl)pyridin-1-ium perchlorate (**1**)