

Supporting Information

Electrochemical Synthesis of 1,1'-Binaphthalene-2,2'-diamines via Transition-metal-free Oxidative Homocoupling

Duona Fan, Md. Imrul Khalid, Ganesh Tatya Kamble, Hiroaki Sasai, and Shinobu Takizawa*

SANKEN, Osaka University, Mihogaoka, Ibaraki-shi, Osaka 567-0047, Japan.

E-mail: taki@sanken.osaka-u.ac.jp

Table of Contents

1.	General information	S2
2.	Optimization of the reaction conditions	S3
3.	Experimental procedures	S3
	3.1. Synthesis of substrates 1c , 1e , and 1f	S3
	3.2. Synthesis of substrates 1d , 1g-1i , and 1l	S5
	3.3. Synthesis of substrates 1j-1k	S7
	3.4 Synthesis of substrates 1o	S9
	3.5. General procedure for electrochemical homo-coupling of 2-naphthylamines	S9
	3.6. Synthesis of BINAM	S13
	3.7 Heterocoupling of 1b and 1e	S14
	3.8 Scale up reaction of 1a	S14
4.	References	S15
5.	CV chart	S16
6.	NMR spectra	S17

1. General information

^1H - and ^{13}C -NMR spectra were recorded at 25 °C using a JEOL JMN ECS400 FT NMR instrument (^1H -NMR 400 MHz; ^{13}C -NMR 100 MHz). The ^1H -NMR spectra are reported as follows: chemical shift in ppm downfield of tetramethylsilane and referenced to a residual solvent peak (CHCl_3) at 7.26 ppm, integration, multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constants (Hz). The ^{13}C -NMR spectra are reported in ppm relative to the central line of the triplet for CDCl_3 at 77.16 ppm. ESI-MS spectra were obtained using a JMS-T100LC instrument (JEOL). FT-IR spectra were recorded using a JASCO FT-IR system (FT/IR4100). Thin-layer chromatography (TLC) analysis of the reaction mixture was performed on Merck silica gel 60 F254 TLC plates and visualized under UV light. Column chromatography on SiO_2 was performed using Kanto Silica Gel 60 (63–210 μm). Substrate **1a** is commercially available purchased from Tokyo Chemical Industries (TCI). Other commercially available organic and inorganic compounds were directly used without further purification. All electrochemical oxidative coupling reactions were carried out by using ElectraSyn 2.0 (IKA®) setup (**Figure 1**). With advantages of standard electrodes and accessories, ElectraSyn device avoids deviation and allows better reproducibility.

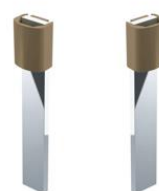
a) ElectraSyn 2.0 (IKA®) setup



b) Vials and electrode



5 mL standard vial



Platinum standard electrode

Figure S1. IKA device ElectraSyn 2.0 standard setup

2. Optimization of the reaction conditions

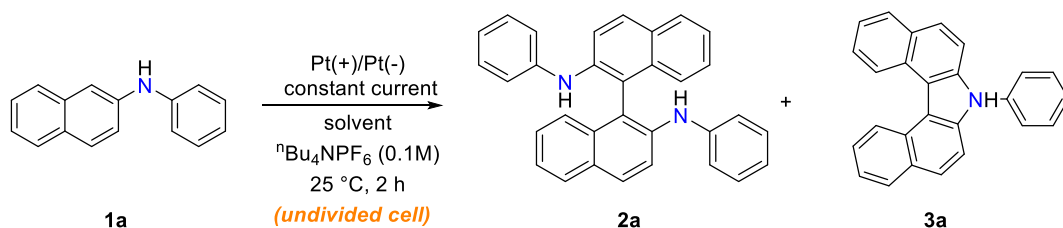


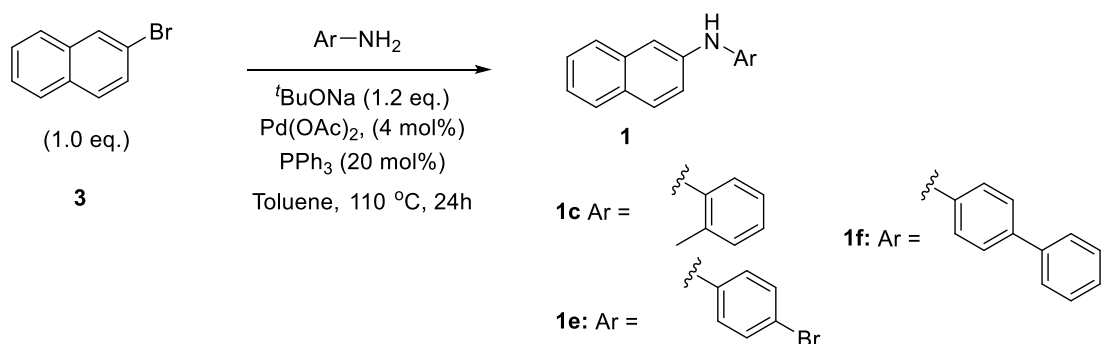
Table S1. Screening solvent of constant current for optimizing reaction conditions.

Entry	Solvent	Constant current (mA)	% Yield ^a (% Current efficiency)	
			2a	3a
1	MeOH	4	10 (7)	5
2	MeCN	4	No reaction	
3	Toluene	4	No Reaction	
4	HFIP/EtOH 1:1(v/v)	4	30 (20)	6
5	HFIP	4	98 (66)	-
6	EtOH	4	6 (4)	5
7	HFIP	1	35 (24)	-
8	HFIP	2	60 (40)	-
9	HFIP	3	82 (55)	-
10	HFIP	5	65 (44)	-
11	HFIP	6	49 (22)	-
12	HFIP	8	Complex mixture	

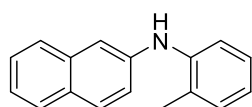
^a NMR yield using 1,3,5- trimethoxybenzene as internal standard.

3. Experimental procedures

3.1. Synthesis of substrates 1c, 1e, and 1f



N-2-Tolyl-2-naphthylamine (1c)



N-2-Tolyl-2-naphthylamine (1c) was prepared followed by literature procedure [1]. 2-bromonaphthalene (2.0 g, 10.0 mmol), 2-toluidine (1.0 mL, 12.0 mmol), PPh₃ (0.4 g, 2.0 mmol), and Pd(OAc)₂ (0.09 g, 0.04 mmol), and sodium *tert*-butoxide (1.0 g, 10.0 mmol) were added to dry toluene solution (70.0 mL) under N₂ atmosphere. The mixture was stirred for 24 h at 110 °C

until reaction completed. Then the reaction mixture was quenched by water, and was extracted with ethyl acetate (3 times), dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica-gel (hexane/ethyl acetate = 20/1) to give the product **1c** as brown liquid in 95% yield.

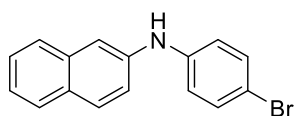
¹H-, ¹³C-NMR, HRMS are in accordance with the reported literature [2].

¹H-NMR (400 MHz, CDCl₃): δ 7.69 (dd, *J* = 8.5, 3.4 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.37-7.33 (m, 1H), 7.31-7.20 (m, 3H), 7.17-7.12 (m, 3H), 7.00-6.94 (m, 1H), 5.48 (s, 1H), 2.25 (s, 3H).

¹³C-NMR (100 MHz, CDCl₃): δ 142.0, 141.2, 134.9, 131.2, 129.3, 129.2, 129.1, 127.8, 127.0, 126.6, 126.6, 123.4, 122.7, 120.0, 119.8, 111.2, 18.1.

HRMS (APCI): calcd for C₁₇H₁₅N: *m/z* [M + H]⁺ 234.1278, found 234.1277.

N-4-Bromophenyl-2-naphthylamine (**1e**)



N-4-Bromophenyl 2-naphthylamine (**1e**) was prepared followed by literature procedure [1]. 2-bromonaphthalene (2.0 g, 10.0 mmol), 4-bromoaniline (2.1 g, 12.0 mmol), PPh₃ (0.4 g, 2.0 mmol), and Pd(OAc)₂ (0.09 g, 0.04 mmol), and sodium tert-butoxide (1.0 g, 10.0 mmol) were added to dry toluene solution (70.0 mL) under N₂ atmosphere. The mixture was stirred for

24 h at 110 °C until reaction completed. The reaction mixture was quenched by water, and the product was extracted with ethyl acetate (3 times), dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 20/1) to give the product **1e** as pale white solid in 95% yield.

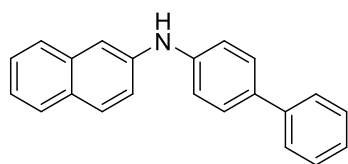
¹H-, ¹³C-NMR, HRMS are in accordance with the reported literature [3].

¹H-NMR (400 MHz, CDCl₃): δ 7.77-7.75 (m, 2H), 7.66 (d, *J* = 8.5 Hz, 1H), 7.45-7.38 (m, 4H), 7.33 (td, *J* = 7.4, 1.2 Hz, 1H), 7.21 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.03 (dt, *J* = 9.6, 2.5 Hz, 2H), 5.90 (s, 1H).

¹³C-NMR (100 MHz, CDCl₃): δ 142.3, 140.2, 134.6, 132.4, 129.5, 129.4, 127.8, 126.7, 126.6, 124.0, 120.2, 119.6, 113.2, 112.5.

HRMS (ESI): calcd for C₁₆H₁₃BrN: *m/z* [M + H]⁺ 298.0226, found 298.0222.

N-([1,1'-Biphenyl]-4-yl)-2-naphthylamine (**1f**)



N-([1,1'-Biphenyl]-4-yl)-2-naphthylamine (**1f**) was prepared according to literature procedure [4] and could afford in quantitative yield as pale yellow solid. A suspension of 2-bromonaphthalene (941 mg, 4.54 mmol), [1,1'-biphenyl]-4-amine (1.0 g, 5.91 mmol), Pd(OAc)₂ (30.6 mg, 3.0 mol%), *rac*-BINAP (126.1 mg, 4.5 mol%) and Cs₂CO₃ (2.2 g, 1.5 eq.) in 25 mL dry toluene was refluxed under N₂ atmosphere for 12 h. After

cooling, the reaction mixture was then filtered through a short pad of silica gel and the organic solvent was evaporated under reduced pressure. The crude product was then purified by silica column chromatography (hexane/dichloromethane = 3/2) to afford the desired product **1f** as colorless solid in 82% yield.

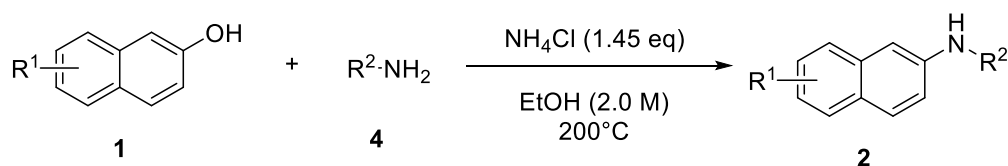
¹H-, ¹³C-NMR, HRMS are in accordance with the reported patent [5].

¹H-NMR (400 MHz, CDCl₃): δ 7.78-7.75 (m, 2H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.61-7.54 (m, 4H), 7.50 (d, *J* = 2.3 Hz, 1H), 7.45-7.40 (m, 3H), 7.34-7.30 (m, 2H), 7.28 (d, *J* = 2.3 Hz, 1H), 7.25-7.22 (m, 2H), 5.96 (s, 1H)

¹³C-NMR (100 MHz, CDCl₃): δ 142.4, 140.9, 140.6, 134.7, 134.2, 129.3, 128.9, 128.2, 127.8, 126.8, 126.7, 126.6, 126.6, 123.7, 120.2, 118.3, 112.1.

HRMS (APCI) calcd for C₂₂H₁₈N: *m/z* [M+H]⁺ 296.1434, found 296.1429.

3.2. Synthesis of substrate 1d, 1g-1k, and 1p



1d: R¹ = H, R² = 3,4- OMe- Ph

1g: R¹ = H, R² = Me

1h: R¹ = H, R² = Et

1i: R¹ = H, R² = *i*Pr

1j: R¹ = H, R² = *t*Bu

1k: R¹ = 7-OMe, R² = Ph

2d: R¹ = H, R² = 3,4- OMe- Ph

2g: R¹ = H, R² = Me

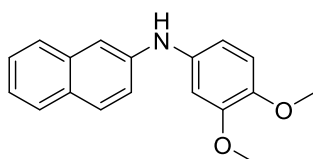
2h: R¹ = H, R² = Et

2i: R¹ = H, R² = *i*Pr

2j: R¹ = H, R² = *t*Bu

2k: R¹ = 7-OMe, R² = Ph

N-(3,4-Dimethoxyphenyl)-2-naphthylamine (**1d**)



N-(3,4-Dimethoxyphenyl)-2-naphthylamine (**1d**) was prepared according to the literature procedure [1]. In a dry 100 mL steel bomb, 2-naphthol (1.0 g, 6.9 mmol), NH₄Cl (535 mg, 10.0 mmol), and 3,4-dimethoxyaniline (2.1 g, 13.8 mmol) were added, then dissolved in 3.5 mL EtOH, the resulting mixture was heated up to 200 °C and stirred for 16 h. The reaction mixture was quenched with 6N NaOH after reaction completed. Then the mixture

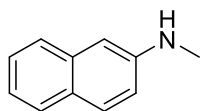
was extracted with ethyl acetate, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by silica column chromatography (hexane/ethyl acetate = 6/1) to afford the product **1d** in 39% yield as pale red liquid.

¹H-NMR (400 MHz, DMSO-D₆): δ 8.10 (s, 1H), 7.67 (t, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.31-7.26 (m, 2H), 7.17-7.14 (m, 2H), 6.88 (d, *J* = 8.2 Hz, 1H), 6.77 (d, *J* = 2.3 Hz, 1H), 6.72 (dd, *J* = 8.6, 2.3 Hz, 1H), 3.70 (s, 3H), 3.69 (s, 3H).

¹³C-NMR (100 MHz, CDCl₃): δ 149.8, 145.1, 142.7, 136.2, 134.9, 129.3, 128.7, 127.7, 126.5, 126.4, 123.1, 119.2, 112.7, 112.3, 109.5, 105.8, 56.4, 56.0.

HRMS (APCI) calcd for C₁₈H₁₇NO₂: *m/z* [M+H]⁺ 280.1332, found 280.1328.

N-methylnaphthalen-2-amine (**1g**)

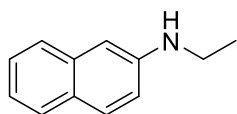


Compound **1g** was prepared according to the literature procedure [1]. In a dry 100 mL steel bomb, added 2-naphthol (500 mg, 3.47 mmol), ammonium chloride (408.5 mg, 7.6 mmol), methylamine (40% in methanol, 3.) and ethanol (2.0M, 1.8 mL). The reaction mixture was heated up to 200 °C, for 12 h.

The reaction was quenched by 6N NaOH after completion. Then filter the residue and extracted with EtOAc, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by silica column chromatography (*n*-Hexane/EtOAc = 20/1) to afford the desired product *N*-methylnaphthalen-2-amine (**1g**) in 80% yield as yellow oil. Analytic data is in accordance with the reported literature [1].

¹H NMR (400 MHz, CHLOROFORM-D) δ 7.72-7.57 (m, 3H), 7.42-7.36 (m, 1H), 7.21 (td, *J* = 7.4, 1.2 Hz, 1H), 6.89 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.81 (d, *J* = 2.3 Hz, 1H), 3.88 (s, 1H), 2.95 (s, 3H).

N-Ethyl-2-naphthylamine (**1h**)



N-Ethyl-2-naphthylamine (**1h**) was prepared according to the literature procedure [1]. In a dry 100 mL steel bomb, added 2-naphthol (500 mg, 3.47 mmol), ammonium chloride (408.5 mg, 7.6 mmol), ethylamine (2.0 M in methanol, 11.2 mL) and ethanol (2.0M, 1.8 mL). The reaction mixture was heated up to 200 °C, for 16 h. The reaction was quenched by 6N NaOH after the completion. Then

filter the residue and extracted with ethyl acetate, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by silica column chromatography (hexane/ethyl acetate = 20/1) to afford the product **1h** in 80% yield as brown oil.

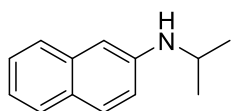
¹H-, ¹³C-NMR, HRMS are in accordance with the reported literature [5].

¹H-NMR (400 MHz, CDCl₃): δ 7.67 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.38-7.34 (m, 1H), 7.21-7.17 (m, 1H), 6.86 (m, 1H), 6.80 (d, *J* = 1.8 Hz, 1H), 3.26 (q, *J* = 7.2 Hz, 2H), 1.32 (t, *J* = 7.2 Hz, 3H).

¹³C-NMR (100 MHz, CDCl₃): δ 146.2, 135.4, 129.0, 127.8, 127.6, 126.4, 126.0, 122.0, 118.1, 104.4, 38.6, 14.9.

HRMS (APCI): calcd for C₁₂H₁₃N: *m/z* [M + H]⁺ 172.1121, found 172.1118.

N-Isopropyl-2-naphthylamine (**1i**)



N-Isopropyl-2-naphthylamine (**1i**) was prepared according to the literature procedure [1]. In a dry 100 mL steel bomb, 2-naphthol (1.0 g, 6.9 mmol), NH₄Cl (505 mg, 10 mmol), and isopropyl amine (17.8 mL) were dissolved in EtOH (2.0 M, 3.5 mL), the resulting mixture was heated up to 200 °C, for 16 h. The reaction mixture was evaporated under reduced pressure to remove excess isopropyl

amine, then wash with 6N NaOH, and extracted with ethyl acetate, dried over Na₂SO₄, and concentrated the organic layer under reduced pressure. The residue was purified by silica column chromatography (hexane/ethyl acetate = 10/1) to afford the product **1i** in 90% yield as light brown liquid.

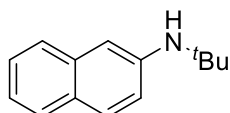
¹H-, ¹³C-NMR, HRMS are in accordance with the reported literature [1].

¹H-NMR (400 MHz, CDCl₃): δ 7.77 (d, *J* = 8.1 Hz, 1H), 7.73-7.71 (m, 2H), 7.47 (dd, *J* = 8.1, 7.8 Hz, 1H), 7.30 (dd, *J* = 8.1, 7.8 Hz, 1H), 6.93-6.90 (m, 2H), 3.85 (sept, *J* = 6.3 Hz, 1H), 3.70 (brs, 1H), 1.36 (d, *J* = 6.3 Hz, 6H)

¹³C-NMR (100 MHz, CDCl₃): δ 144.9, 135.3, 129.1, 127.7, 127.5, 126.4, 126.0, 122.0, 118.5, 105.4, 44.6, 22.9

HRMS (APCI): calcd for C₁₃H₁₆N: *m/z* [M + H]⁺ 186.1277, found 186.1276.

N-(tert-butyl)naphthalen-2-amine (**1j**)



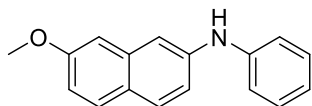
N-(tert-butyl)naphthalen-2-amine (**1j**) was prepared followed by literature procedure [1]. 2-bromonaphthalene (2.0 g, 10.0 mmol), *tert*-butylamine (1.3 mL, 12.0 mmol), PPh₃ (0.4 g, 2.0 mmol), and Pd(OAc)₂ (0.09 g, 0.04 mmol), and sodium *tert*-butoxide (1.0 g, 10.0 mmol) were added to dry toluene solution (70.0 mL) under N₂ atmosphere. The mixture was stirred for 24 h at

110 °C until reaction completed. Then the reaction mixture was quenched by water and was extracted with ethyl acetate (3 times), dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica-gel (hexane/ethyl acetate = 20/1) to give the product **1j** as brown liquid in 75% yield.

¹H NMR (400 MHz, CHLOROFORM-D) δ 7.66 (d, *J* = 8.2 Hz, 1H), 7.61 (d, *J* = 8.7 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 1.8 Hz, 1H), 6.90 (dd, *J* = 8.7, 2.3 Hz, 1H), 1.42 (s, 9H).

N-Phenyl-7-methoxy-2-naphthylamine (**1k**)

N-Phenyl-7-methoxy-2-naphthylamine (**1k**) was prepared followed by literature procedure [1]. In a dry 100 mL steel bomb, 7-methoxynaphthalen-2-ol (174 mg, 1.0 mmol), NH₄Cl (77.8 mg, 1.45 mmol), and aniline (2.8 mL, 31.5 mmol) were added, then dissolved in 2 mL EtOH, the resulting mixture was heated up to 200 °C and stirred for 16 h. The reaction mixture was quenched with 6N NaOH after reaction completed. Then the mixture was extracted with ethyl acetate, dried over Na₂SO₄,



and concentrated under reduced pressure. The residue was purified by silica column chromatography (*n*-hexane/ethyl acetate = 10/1) to afford the product **1k** in 60% yield as pale white solid.

^1H -, ^{13}C -NMR, HRMS are in accordance with the reported literature [6]

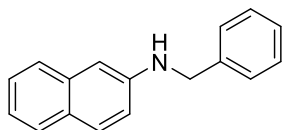
^1H -NMR (400 MHz, CDCl_3): δ 7.63 (dd, J = 12.8, 9.2 Hz, 2H), 7.34-7.28 (m, 3H), 7.17-7.15 (m, 2H), 7.06 (dd, J = 8.7, 2.3 Hz, 1H), 6.99-6.94 (m, 3H), 5.85 (s, 1H), 3.88 (s, 3H).

^{13}C -NMR (100 MHz, CDCl_3): δ 158.3, 142.9, 141.6, 136.0, 129.5, 129.2, 129.1, 124.6, 121.5, 118.6, 117.6, 116.2, 110.7, 104.8, 55.3.

HRMS (APCI) calcd for $\text{C}_{17}\text{H}_{16}\text{NO}$: m/z $[\text{M}+\text{H}]^+$ 250.1227, found 250.1226.

IR (KBr): 3393, 2995, 2969, 1631, 1505, 1463, 1308, 1219, 1028, 843, 748 cm^{-1}

N-Benzyl-2-naphthylamine (**1p**)



N-Benzyl-2-naphthylamine (**1p**) was prepared followed by literature procedure [1]. In a dry 100 mL steel bomb, 2-naphthol (2.88 g, 20.0 mmol), NH_4Cl (2.4 g, 22.0 mmol), and benzylamine (40 mL) were dissolved in EtOH (2.0 M, 5.0 mL), the resulting mixture was heated up to 200 $^\circ\text{C}$, for 16 h. The reaction mixture was quenched with 6N NaOH after the

reaction completed. Then the mixture was extracted with ethyl acetate, dried over Na_2SO_4 , and concentrated under reduced pressure. The residue was purified by silica column chromatography (hexane/ethyl acetate = 10/1) to afford the product **1p** in 30% yield as pale yellow solid.

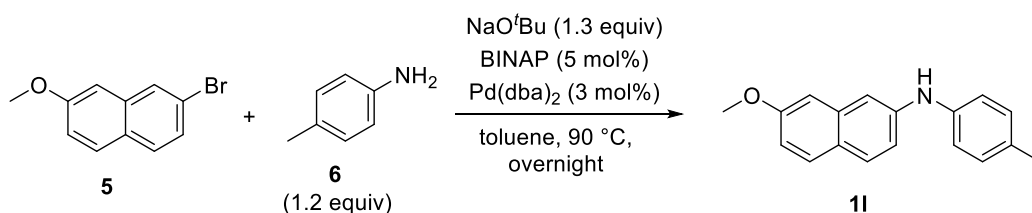
^1H -, ^{13}C -NMR, HRMS are in accordance with the reported literature [7].

^1H -NMR (400 MHz, CDCl_3): δ 7.68-7.58 (m, 3H), 7.42 (d, J = 7.4 Hz, 2H), 7.38-7.28 (m, 4H), 7.20 (td, J = 7.4, 1.2 Hz, 1H), 6.93 (dd, J = 8.7, 2.5 Hz, 1H), 6.84 (d, J = 2.5 Hz, 1H), 4.45 (s, 2H), 4.20 (s, 1H).

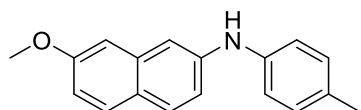
^{13}C -NMR (100 MHz, CDCl_3): δ 145.6, 139.1, 135.2, 129.1, 128.8, 128.8, 127.8, 127.7, 127.5, 126.4, 126.1, 122.2, 118.0, 105.0, 48.6.

HRMS (APCI) calcd for $\text{C}_{17}\text{H}_{16}\text{N}$: m/z $[\text{M}+\text{H}]^+$ 234.1277, found 234.1276.

3.3. Synthesis of substrates 1l-n



N-4-Tolyl-7-methoxy-2-naphthylamine (**1l**)



A toluene solution (30 mL) of 2-bromo-7-methoxynaphthalene (**5**) (30 mmol), 4-toluidine (**6**) (3.8 g, 36 mmol), $\text{Pd}(\text{dba})_2$ (3 mol%), *rac*-BINAP (5 mol%), and NaO^tBu (4.5 g, 40 mmol) was stirred at 90 $^\circ\text{C}$ under N_2 atmosphere. After stirring for 12 h, the reaction mixture was filtered. Then the filtrate was directly purified on silica gel (*n*-

hexane/ethyl acetate = 10/1) to give **1l** (70% yield) as a white solid.

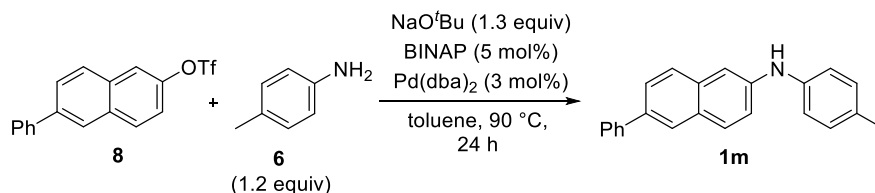
^1H -NMR (400 MHz, CDCl_3): δ 7.60-7.65 (m, 2H), 7.26 (d, J = 2.3 Hz, 1H), 7.14 (d, J = 8.5 Hz, 2H), 7.10 (d, J = 8.5 Hz,

2H), 7.02 (dd, $J = 8.5, 2.3$ Hz, 1H), 6.93-6.96 (m, 2H), 5.75 (s, 1H), 3.89 (s, 3H), 2.34 (s, 3H).

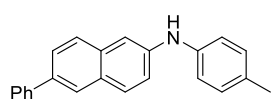
^{13}C -NMR (100 MHz, CDCl_3): δ 158.4, 142.5, 140.2, 136.1, 131.6, 130.1, 129.3, 129.1, 124.4, 119.7, 117.2, 115.9, 109.5, 104.8, 55.4, 20.9.

HRMS (APCI): calcd for $\text{C}_{18}\text{H}_{18}\text{NO}$: m/z 264.1383 $[\text{M} + \text{H}]^+$, found 264.1378.

IR (KBr): 3387, 3027, 2998, 2922, 2861, 1631, 1514, 1214, 1030, 817 cm^{-1} .



6-Phenyl-*N*-(*p*-tolyl)naphthalen-2-amine (**1m**)



A coupling of **1m** was performed following the same procedures used as that of **1l**.

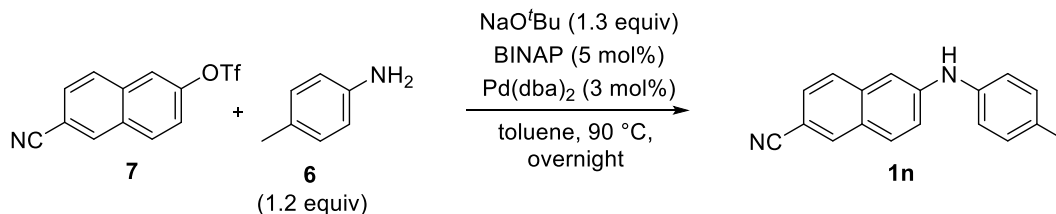
1m (51% yield): a white solid.

^1H NMR (400 MHz, CDCl_3): δ 7.93 (s, 1H), 7.78 (d, $J = 9.2$ Hz, 1H), 7.67-7.71 (m, 4H), 7.47 (ddd, $J = 7.8, 7.3, 1.4$ Hz, 2H), 7.38 (d, $J = 2.3$ Hz, 1H), 7.35 (tt, $J = 7.3, 1.5$ Hz, 1H), 7.20 (dd, $J = 8.7, 2.3$ Hz, 1H), 7.10-7.16 (m, 4H), 5.82 (s, 1H), 2.34 (s, 3H).

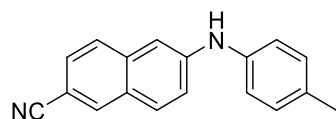
^{13}C NMR (100 MHz, CDCl_3): δ 142.02, 141.43, 140.10, 135.98, 134.07, 131.63, 130.11, 129.60, 129.17, 128.93, 127.26, 127.07, 126.99, 126.20, 125.70, 120.06, 119.61, 110.02, 20.90.

HRMS (APCI): calcd for $\text{C}_{23}\text{H}_{20}\text{N}$: m/z 310.1590 $[\text{M} + \text{H}]^+$, found 310.1586.

IR (KBr): 3421, 3060, 3021, 2922, 2857, 1605, 1523, 1445, 1307, 816 cm^{-1} .



N-4-Tolyl-6-cyano-2-naphthylamine (**1n**)



N-4-Tolyl-6-cyano-2-naphthylamine (**1n**) was prepared with the same procedures as that of **1l**.

1n (72% yield): a yellow solid.

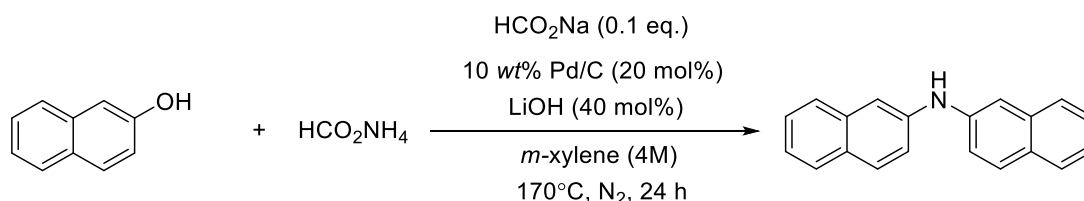
^1H -NMR (600 MHz, CDCl_3): δ 8.05 (s, 1H), 7.73 (d, $J = 9.0$ Hz, 1H), 7.60 (d, $J = 8.4$ Hz, 1H), 7.47 (dd, $J = 8.4, 1.7$ Hz, 1H), 7.28 (d, $J = 9.0$ Hz, 1H), 7.18-7.22 (m, 3H), 7.13-7.16 (m, 2H), 5.99 (s, 1H), 2.37 (s, 3H).

^{13}C -NMR (150 MHz, CDCl_3): δ 145.3, 138.3, 136.7, 133.9, 133.4, 130.3, 130.0, 127.2, 127.22, 127.16, 121.4, 120.3, 120.1, 107.8, 105.5, 21.0.

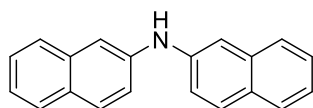
HRMS (APCI): calcd for $\text{C}_{18}\text{H}_{15}\text{N}_2$: m/z $[\text{M} + \text{H}]^+$ 259.1230, found 259.1230.

IR (KBr): 3357, 3060, 3026, 2914, 2857, 2217, 1533, 1407, 1314, 816 cm^{-1} .

3.4. Synthesis of substrates **1o**



2,2'-Dinaphthylamine (**1o**)



2,2'-Dinaphthylamine (**1o**) was prepared followed by literature procedure [8]. To a 10.0 mL flame-dried Schlenk flask, the naphthol (2.0 mmol, 10 equiv), ammonium formate (2.0 mmol, 1equiv), lithium hydroxide (0.08 mmol, 0.4 equiv), and activated 10 wt% Pd/C (0.20 mmol, 20 mol%) were added. Under N₂ protection, the anhydrous m-xylene (0.5 mL) was

added. The reaction mixture was heated with stirring to 160°C. After 24 h, the reaction mixture was diluted with EtOAc (10 mL) and filtered through silica gel and the organic solvent was removed by evaporation under reduced pressure. 2N aqueous NaOH solution to quench the reaction. The aqueous layer was extracted with EtOAc and the combined organic phase was washed with brine and dried over sodium sulfate. The solvent was removed under reduced pressure and the residue was purified by column chromatography (eluent:hexane/ethyl acetate, 5:1 v/v). The product was obtained in 40% yield as yellow solid and analytic data are in accordance with the reported paper [8].

¹H NMR (400 MHz, DMSO-D₆) δ 9.71 (s, 1H), 7.71 (dd, J = 8.2, 5.0 Hz, 4H), 7.62 (d, J = 7.8 Hz, 2H), 7.35-7.31 (m, 2H), 7.22-7.18 (m, 2H), 7.04 (td, J = 8.9, 2.4 Hz, 4H).

¹³C-NMR (100 MHz, DMSO-D₆): δ 155.8, 135.1, 129.8, 128.3, 128.1, 126.6, 126.5, 123.2, 119.1, 109.2.

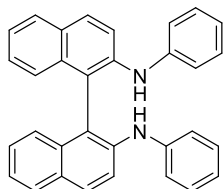
HRMS (APCI): calcd for C₂₀H₁₅N: m/z [M + H]⁺ 270.1277, found 270.1274.

3.5 General procedure for the preparation of homocoupling of 2-naphthylamine

ElectraSyn 2.0 and platinum were utilized as the reaction device and electrode, respectively. A suspension of 2-naphthylamines **1** (0.1 mmol) and ⁿBu₄NPF₆ (0.1 M, 193.7 mg, 0.5 mmol) in HFIP (5 mL) was added to an undivided vessel and stirred under a constant current of 4 mA at 25 °C. After stirring for 2 h, the electrolyte was removed using short silica gel column chromatography (*n*-hexane/ethyl acetate = 1/1). The fraction was dried, and the crude product was purified by silica-gel column chromatography (*n*-hexane/ethyl acetate = 20/1) to afford the pure homocoupling product **2**.

N,N'-di-p-tolyl-[1,1'-binaphthalene]-2,2'-diamine (**2a**)

2a (98% yield): a white solid.



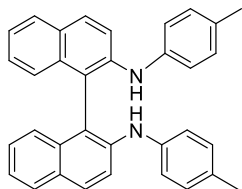
¹H-NMR (400 MHz, CDCl₃): δ 7.94 (dd, J = 14.0, 8.5 Hz, 4H), 7.76 (d, J = 9.2 Hz, 2H), 7.37-7.41 (m, 2H), 7.30-7.34 (m, 2H), 7.23-7.28 (m, 6H), 7.02 (q, J = 8.1 Hz, 6H), 5.68 (s, 2H).

¹³C-NMR (100 MHz, CDCl₃): δ 142.6, 140.5, 134.1, 129.6, 129.5, 129.4, 128.3, 127.2, 124.6, 123.6, 122.3, 120.1, 118.0, 116.5.

HRMS (APCI): calcd for C₃₂H₂₅N: m/z [M + H]⁺ 437.2012, found 437.2007.

IR (KBr): 3381, 1619, 1496, 1473, 1415, 1338, 1292, 812 cm⁻¹

N,N'-di-p-tolyl-[1,1'-binaphthalene]-2,2'-diamine (**2b**)



2b (92% yield): a white solid.

¹H-NMR (400 MHz, CDCl₃): δ 7.83 (t, *J* = 9.4 Hz, 4H), 7.60 (d, *J* = 9.2 Hz, 2H), 7.30-7.27 (m, 2H), 7.25-7.21 (m, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 7.01 (d, *J* = 8.2 Hz, 4H), 6.89 (dd, *J* = 11.0, 2.3 Hz, 4H), 5.53 (s, 2H), 2.27 (s, 6H).

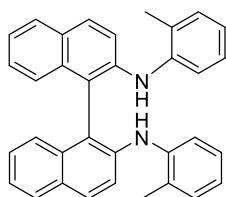
¹³C-NMR (100 MHz, CDCl₃): δ 141.3, 134.2, 134.0, 132.3, 129.9, 129.5, 129.3, 128.3, 127.1,

124.5, 123.3, 121.2, 117.5, 115.5, 20.9.

HRMS (APCI): calcd for C₃₄H₂₉NO₂: *m/z* [M + H]⁺ 465.2325, found 465.2314.

IR (KBr): 3381, 2915, 2849, 1616, 1509, 1412, 1342, 1293, 858, 815 cm⁻¹

*N*², *N*^{2'}-di-*o*-tolyl-[1,1'-binaphthalene]-2,2'-diamine (**2c**)



2c (83% yield): a white solid.

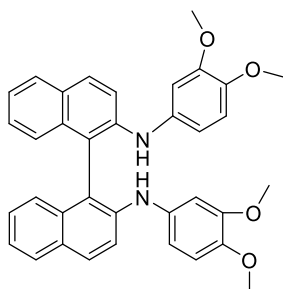
¹H-NMR (400 MHz, CDCl₃): δ 7.82-7.85 (m, 4H), 7.43 (d, *J* = 2.1 Hz, 1H), 7.41 (d, *J* = 2.1 Hz, 1H), 7.25-7.31 (m, 6H), 7.20-7.22 (m, 2H), 7.11 (t, *J* = 6.6 Hz, 4H), 6.94 (t, *J* = 7.6 Hz, 2H), 5.41 (s, 2H), 1.89 (s, 6H).

¹³C-NMR (100 MHz, CDCl₃): δ 141.4, 140.4, 134.0, 131.0, 129.5, 129.0, 128.4, 127.2, 126.8, 124.3, 123.4, 123.2, 121.6, 117.0, 115.0, 17.8.

HRMS (APCI): calcd for C₃₄H₂₉N: *m/z* 465.2325 [M + H]⁺, found 465.2311.

IR (KBr): 3386, 2913, 2317, 1613, 1494, 1412, 1341, 1293, 814, 742 cm⁻¹

*N*², *N*^{2'}-bis(3,4-dimethoxyphenyl)-[1,1'-binaphthalene]-2,2'-diamine (**2d**)



2d (89% yield): a red liquid.

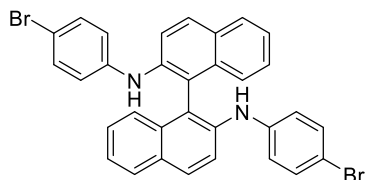
¹H-NMR (400 MHz, CDCl₃): δ 7.72 (d, *J* = 8.6 Hz, 4H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.36-7.40 (m, 2H), 7.27-7.29 (m, 2H), 7.14 (dd, *J* = 8.6, 2.6 Hz, 2H), 6.86 (d, *J* = 8.2 Hz, 2H), 6.80 (d, *J* = 2.6 Hz, 2H), 6.77 (dd, *J* = 8.6, 2.6 Hz, 2H), 5.69 (s, 2H), 3.90 (s, 6H), 3.85 (s, 6H).

¹³C-NMR (100 MHz, CDCl₃): δ 149.8, 145.1, 142.8, 136.2, 134.9, 129.3, 128.78, 127.76, 126.6, 126.4, 123.2, 119.2, 112.8, 112.3, 109.5, 105.8, 56.4, 56.0.

HRMS (APCI): calcd for C₃₆H₃₃N₂O₄: *m/z* 557.2435 [M + H]⁺, found 557.2438.

IR (KBr): 3365, 2933, 2833, 1601, 1511, 1465, 1228, 1024, 838, 811 cm⁻¹

*N*², *N*^{2'}-bis(4-bromophenyl)-[1,1'-binaphthalene]-2,2'-diamine (**2e**)



2e (76% yield): a white solid.

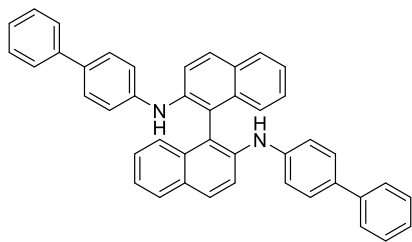
¹H-NMR (400 MHz, CDCl₃): δ 7.90 (d, *J* = 9.2 Hz, 2H), 7.86 (d, *J* = 7.8 Hz, 2H), 7.60 (d, *J* = 9.2 Hz, 2H), 7.32-7.36 (m, 2H), 7.23-7.25 (m, 6H), 7.11 (d, *J* = 8.7 Hz, 2H), 6.77 (d, *J* = 2.1 Hz, 2H), 6.75 (d, *J* = 2.1 Hz, 2H), 5.44 (s, 2H).

¹³C-NMR (100 MHz, CDCl₃): δ 141.9, 139.7, 134.0, 132.3, 129.9, 129.8, 128.5, 127.4, 124.6, 124.1, 121.0, 118.4, 117.5, 114.2.

HRMS (APCI) calcd for C₃₂H₂₃Br₂N₂: *m/z* 595.0203 [M+H]⁺, found 595.0203.

IR (KBr): 3411, 3380, 2924, 2858, 1616, 1494, 1340, 1258, 817, 748 cm⁻¹

*N*², *N*^{2'}-di([1,1'-biphenyl]-4-yl)-[1,1'-binaphthalene]-2,2'-diamine (**2f**)



2f (66% yield): a white solid.

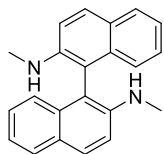
¹H-NMR (400 MHz, CDCl₃) δ 7.92 (d, *J* = 9.0 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 9.0 Hz, 2H), 7.47-7.49 (m, 4H), 7.32-7.40 (m, 10H), 7.27-7.25 (m, 4H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.98-7.00 (m, 4H), 5.63 (s, 2H).

¹³C-NMR (100 MHz, CDCl₃) δ 142.1, 140.8, 140.1, 134.9, 134.1, 129.7, 129.6, 128.8, 128.4, 127.9, 127.2, 126.8, 126.7, 124.6, 123.8, 119.7, 118.5, 117.1.

HRMS (APCI): calcd for C₄₄H₃₃N₂: *m/z* 589.2638 [M + H]⁺, found 589.2631.

IR (KBr): 3394, 1596, 1510, 1488, 1302, 907, 822, 760 cm⁻¹

***N*²,*N*^{2'}-dimethyl-[1,1'-binaphthalene]-2,2'-diamine(**2g**)**



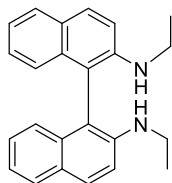
2g (30% yield): a pale yellow solid.

Analytic data is in accordance with the reported literature [9].

¹H-NMR (400 MHz, CDCl₃): δ 9.22 (d, *J* = 8.2 Hz, 2H), 8.05 (dd, *J* = 8.0, 1.1 Hz, 2H), 7.94-7.92 (m, 2H), 7.75-7.66 (m, 4H), 7.53-7.50 (m, 2H), 4.12 (s, 2H), 1.57 (s, 6H).

¹³C-NMR (100 MHz, CDCl₃): δ 137.8, 129.8, 129.3, 126.7, 125.5, 125.2, 123.3, 117.3, 110.8, 29.7.

***N*²,*N*^{2'}-diethyl-[1,1'-binaphthalene]-2,2'-diamine (**2h**)**



2h (87% yield): a yellow liquid.

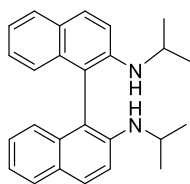
¹H-NMR (400 MHz, CDCl₃): δ 7.89 (d, *J* = 9.2 Hz, 2H), 7.78-7.80 (m, 2H), 7.13-7.28 (m, 6H), 6.95-6.97 (m, 2H), 3.62 (s, 2H), 3.23 (d, *J* = 6.8 Hz, 4H), 1.03 (t, *J* = 6.8 Hz, 6H).

¹³C-NMR (100 MHz, CDCl₃): δ 144.7, 134.0, 129.7, 128.2, 127.8, 126.8, 124.0, 122.0, 114.3, 112.3, 38.7, 15.4.

HRMS (APCI): calcd for C₂₄H₂₅N: *m/z* 341.2012 [M + H]⁺, found 341.2003.

IR (KBr): 3387, 2967, 2866, 1613, 1510, 1426, 1306, 1279, 813, 745 cm⁻¹

***N*²,*N*^{2'}-diisopropyl-[1,1'-binaphthalene]-2,2'-diamine (**2i**)**



2i (87% yield): a white solid.

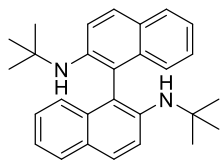
¹H-NMR (400 MHz, CDCl₃): δ 7.85 (d, *J* = 9.2 Hz, 2H), 7.74-7.76 (m, 2H), 7.23-7.26 (m, 2H), 7.09-7.18 (m, 4H), 6.90 (d, *J* = 8.2 Hz, 2H), 3.77 (s, 2H), 3.39 (s, 2H), 1.04 (d, *J* = 6.2 Hz, 6H), 0.96 (d, *J* = 6.2 Hz, 6H).

¹³C-NMR (100 MHz, CDCl₃): δ 144.2, 134.2, 129.6, 128.0, 127.7, 126.6, 124.1, 121.9, 115.1, 112.5, 44.6, 23.4.

HRMS (APCI): calcd for C₂₆H₂₉N₂: *m/z* 369.2325 [M + H]⁺, found 369.2325.

IR (KBr): 3393, 2972, 2924, 2866, 1617, 1508, 1491, 1299, 1176, 809, 745 cm⁻¹

***N*²,*N*^{2'}-di-tert-butyl-[1,1'-binaphthalene]-2,2'-diamine (**2j**)**



2j (72% yield): a white solid.

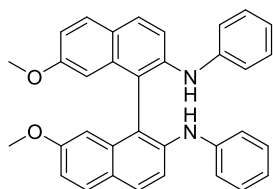
¹H-NMR (400 MHz, CDCl₃): δ 7.82 (q, *J* = 4.6 Hz, 2H), 7.76 (t, *J* = 6.4 Hz, 2H), 7.49 (dd, *J* = 8.7, 5.5 Hz, 2H), 7.10-7.20 (m, 4H), 6.92 (t, *J* = 6.6 Hz, 2H), 3.63 (s, 2H), 1.20 (d, *J* = 5.5 Hz, 18H)

¹³C-NMR (100 MHz, CDCl₃): δ 144.44, 134.09, 128.76, 127.95, 127.76, 126.49, 124.47, 122.11, 117.74, 114.84, 51.44, 30.76

HRMS (APCI): calcd for C₂₈H₃₂N₂: *m/z* [M + H]⁺ 397.2639, found 397.2639.

IR (KBr): 3393, 2967, 2919, 2866, 1621, 1491, 1336, 815 cm⁻¹.

7,7'-dimethoxy-*N*²,*N*^{2'}-diphenyl-[1,1'-binaphthalene]-2,2'-diamine (**2k**)



2k (95% yield): a white solid.

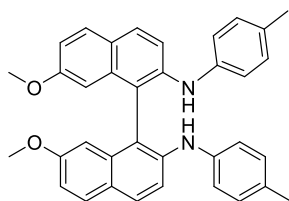
¹H-NMR (400 MHz, CDCl₃): δ 7.79 (d, *J* = 9.0 Hz, 2H), 7.73 (d, *J* = 9.0 Hz, 2H), 7.54 (d, *J* = 9.0 Hz, 2H), 7.17-7.21 (m, 4H), 6.91-6.99 (m, 8H), 6.52 (d, *J* = 2.3 Hz, 2H), 5.60 (s, 2H), 3.55 (s, 6H).

¹³C-NMR (100 MHz, CDCl₃): δ 158.8, 142.7, 141.0, 135.2, 129.9, 129.4, 129.3, 124.0, 122.2, 120.0, 115.7, 115.5, 115.4, 103.4, 55.2.

HRMS (APCI): calcd for C₃₄H₂₉N₂O₂: *m/z* [M + H]⁺ 497.2224, found 497.2212.

IR (KBr): 3360, 2924, 2849, 2370, 1620, 1509, 1458, 1275, 1028, 830, 750 cm⁻¹

7,7'-dimethoxy-*N*²,*N*^{2'}-di-*p*-tolyl-[1,1'-binaphthalene]-2,2'-diamine (**2l**)



2l (87% yield): a white solid.

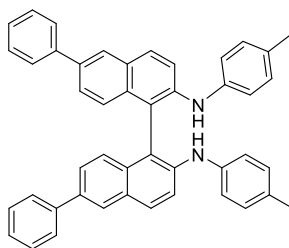
¹H-NMR (400 MHz, CDCl₃): δ 7.75 (d, *J* = 9.0 Hz, 2H), 7.71 (d, *J* = 9.0 Hz, 2H), 7.46 (d, *J* = 9.0 Hz, 2H), 7.02 (d, *J* = 7.8 Hz, 4H), 6.90-6.95 (m, 6H), 6.51 (d, *J* = 2.3 Hz, 2H), 5.53 (s, 2H), 3.55 (s, 6H), 2.27 (s, 6H).

¹³C-NMR (100 MHz, CDCl₃): δ 158.8, 141.8, 140.0, 135.2, 132.2, 129.9, 129.9, 129.2, 124.7, 121.1, 115.3, 114.9, 114.5, 103.2, 55.2, 20.9.

HRMS (APCI): calcd for C₃₆H₃₃N₂O₂: *m/z* [M + H]⁺ 525.2537, found 525.2543.

IR (KBr): 3388, 3360, 2957, 2922, 2361, 2350, 1622, 1510, 1336, 1217, 1031, 882, 844, 824 cm⁻¹

6,6'-diphenyl-*N*²,*N*^{2'}-di-*p*-tolyl-[1,1'-binaphthalene]-2,2'-diamine (**2m**)



2m (65% yield): a red solid.

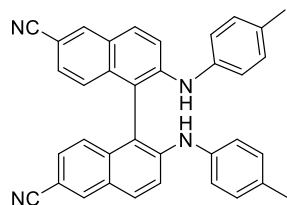
¹H-NMR (400 MHz, CDCl₃): δ 8.04 (d, *J* = 1.8 Hz, 2H), 7.92 (d, *J* = 9.2 Hz, 2H), 7.63-7.68 (m, 6H), 7.51-7.54 (m, 2H), 7.45 (t, *J* = 7.8 Hz, 4H), 7.33 (t, *J* = 7.3 Hz, 2H), 7.27 (s, 1H), 7.25 (s, 1H), 7.03 (d, *J* = 8.2 Hz, 4H), 6.93 (d, *J* = 8.2 Hz, 4H), 5.60 (s, 2H), 2.28 (s, 6H)

¹³C-NMR (100 MHz, CDCl₃): δ 141.49, 139.80, 135.96, 133.35, 132.45, 129.95, 129.49, 128.93, 127.25, 127.11, 126.79, 126.30, 124.99, 121.34, 117.83, 20.90

HRMS (APCI): calcd for C₄₆H₃₆N₂: *m/z* [M + H]⁺ 617.2951, found 617.2947.

IR (KBr): 3404, 2961, 2852, 1598, 1512, 1491, 1266, 809 cm⁻¹.

2,2'-bis(p-tolylamino)-[1,1'-binaphthalene]-6,6'-dicarbonitrile (**2n**)



2n (87% yield): a yellow solid.

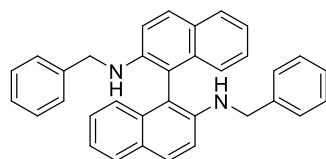
¹H-NMR (400 MHz, CDCl₃): δ 8.05 (s, 2H), 7.73 (d, *J* = 8.7 Hz, 2H), 7.60 (d, *J* = 8.7 Hz, 2H), 7.47 (dd, *J* = 8.7, 2.0 Hz, 2H), 7.18-7.22 (m, 6H), 7.14 (dd, *J* = 6.2, 2.0 Hz, 4H), 5.98 (s, 2H), 2.37 (s, 6H).

¹³C-NMR (100 MHz, CDCl₃): δ 145.3, 138.4, 136.7, 133.9, 133.4, 130.3, 130.0, 127.2, 127.2, 127.2, 121.4, 120.3, 120.1, 107.8, 105.5, 21.0.

HRMS (APCI): calcd for C₃₆H₂₇N₄: *m/z* [M + H]⁺ 515.2230, found 515.2230.

IR (KBr): 3357, 2919, 2855, 2318, 2214, 1606, 1591, 1509, 1313, 903, 814 cm⁻¹

*N*², *N*^{2'}-dibenzyl-[1,1'-binaphthalene]-2,2'-diamine (**2p**)



2p (85% yield): a white solid.

¹H-NMR (400 MHz, CDCl₃): δ 7.86 (d, *J* = 9.2 Hz, 2H), 7.80-7.83 (m, 2H), 7.31-7.26 (m, 6H), 7.25-7.20 (m, 10H), 7.10 (dt, *J* = 7.3, 3.1 Hz, 2H), 4.46 (d, *J* = 5.5 Hz, 4H), 4.37 (d, *J* = 5.5 Hz, 2H).

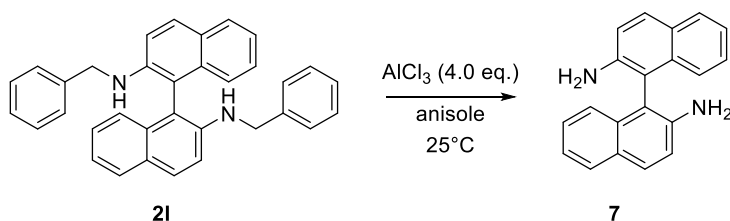
¹³C-NMR (100 MHz, CDCl₃): δ 144.3, 140.0, 134.0, 129.8, 128.6, 128.3, 127.9, 127.0,

126.90, 126.86, 124.0, 122.2, 114.3, 112.1, 47.7.

HRMS (APCI): calcd for C₃₄H₂₉N₂: *m/z* [M + H]⁺ 465.2325, found 456.2321.

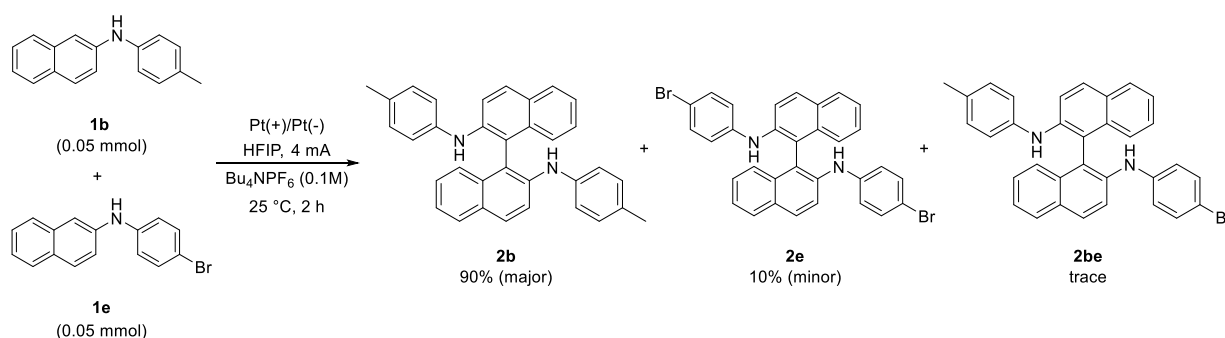
IR (KBr): 3417, 3059, 2924, 2854, 1616, 1508, 1426, 1298, 907, 809 cm⁻¹

3.6. Synthesis of BINAM



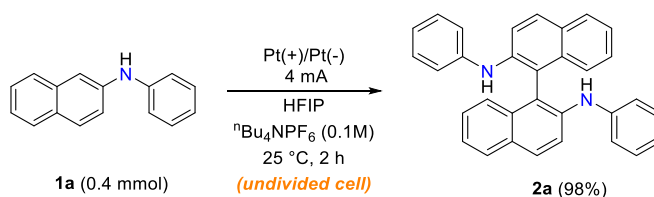
The synthesis of compound **7** was followed by the reported procedure [10]. A solution of **2l** (0.01 mmol) in anisole (0.1 mL) was added to a suspension of 4 equiv. AlCl₃ in anisole (0.1 mL). The mixture was stirred under 25 °C for 48 h. The reaction was quenched by water and extracted with ethyl acetate. The organic layer was dried over MgSO₄ and concentrated under reduced pressure. The residue was purified by silica column chromatography (hexane/ethyl acetate = 3/1) to afford the **7** in 32% yield. The ¹H-NMR data of **7** are in accordance with the reported literature [11].

3.7 Electrochemical heterocoupling of substrate 1b and 1e



ElectraSyn 2.0 with platinum electrode were utilized for the electrochemical hetero-coupling of **1b** and **1e**. A mixture of **1b** (14.9 mg, 0.05 mmol), **1e** (11.7 mg, 0.05 mmol) and $n\text{Bu}_4\text{NPF}_6$ (0.1 M, 193.7 mg, 0.5 mmol) in HFIP (5 mL) was added to an undivided vessel and stirred under a constant current of 4 mA at 25 °C. After stirring for 2 h, the electrolyte was removed by short silica gel column chromatography (*n*-hexane/ethyl acetate = 1/1). The fraction was dried, and the residue was analyzed by using ^1H -NMR with 1,3,5-trimethoxybenzene as a standard. The determination of the each ration of products by using the NMR and HPLC analysis was difficult because of overlapping of each peak, finally, the crude product was purified by silica-gel column chromatography (*n*-hexane/ethyl acetate = 20/1) to afford **2b** in 90%, **2e** in 10%, trace amount of **2be**, along with recovery of **1b** and **1e**.

3.8 Scale up reaction of **1a**



ElectraSyn 2.0 and platinum were utilized as the reaction device and electrode, respectively. A mixture of 2-naphthylamines **1** (87.7 mg, 0.4 mmol) and $n\text{Bu}_4\text{NPF}_6$ (0.1 M, 774.8 mg, 2.0 mmol) in HFIP (20 mL) was added to an undivided vessel and stirred under a constant current of 4 mA at 25 °C. After stirring for 2 h, the electrolyte was removed using short silica gel column chromatography (*n*-hexane/ethyl acetate = 1/1). The fraction was dried, and the crude product was purified by silica-gel column chromatography (*n*-hexane/ethyl acetate = 20/1) to afford the pure homocoupling product **2** with 98% yield.

4. References

1. Cortright, S.B.; Huffman, J.C.; Yoder, R.A.; Coalter, J.N.; Johnston, J.N. IAN Amines: Chiral C₂-Symmetric Zirconium(IV) Complexes from Readily Modified Axially Chiral C₁-Symmetric β -Diketimines. *Organometallics* **2004**, *23*, 2238-2250, doi:10.1021/om049897p.
2. Jiang, J.; Zhu, H.; Shen, Y.; Tu, T. Acenaphthoimidazolium chloride-enabled nickel-catalyzed amination of bulky aryl tosylates. *Organic Chemistry Frontiers* **2014**, *1*, 1172-1175, doi:10.1039/c4qo00233d.
3. Wang, Z.; Li, C.; Huang, H.; Deng, G.J. Elemental Sulfur-Promoted Aerobic Dehydrogenative Aromatization of Cyclohexanones with Amines. *The Journal of Organic Chemistry* **2020**, *85*, 9415-9423, doi:10.1021/acs.joc.0c01122.
4. Shiozuka, A.; Sekine, K.; Toki, T.; Kawashima, K.; Mori, T.; Kuninobu, Y. Photoinduced Divergent Deaminative Borylation and Hydrodeamination of Primary Aromatic Amines. *Organic Letters* **2022**, *24*, 4281-4285, doi:10.1021/acs.orglett.2c01663.
5. Fang, H.; Wang, G.; Oestreich, M. Mild reductive rearrangement of oximes and oxime ethers to secondary amines with hydrosilanes catalyzed by B(C₆F₅)₃. *Organic Chemistry Frontier* **2021**, *8*, 3280-3285, doi:10.1039/D1QO00251A.
6. Sajiki, H.; Ikawa, T.; Hirota, K. Reductive and Catalytic Monoalkylation of Primary Amines Using Nitriles as an Alkylating Reagent. *Organic Letters* **2004**, *6*, 4977-4980, doi:10.1021/ol047871o.
7. Li, G.; Liu, Y.; Du, H. B(C₆F₅)₃-catalyzed metal-free hydrogenation of naphthylamines. *Organic & Biomolecular Chemistry* **2015**, *13*, 2875-2878, doi:10.1039/c5ob00009b.
8. Dominguez-Huerta, A.; Perepichka, I.; Li, C.J. Direct Synthesis of Diphenylamines from Phenols and Ammonium Formate Catalyzed by Palladium. *ChemSystems* **2019**, *12*, 2999-3002, doi:10.1002/cssc.201900928.
9. Shi, M.; Wang, C.-J. Axially dissymmetric binaphthylidimine chiral Salen-type ligands for catalytic asymmetric addition of diethylzinc to aldehyde. *Tetrahedron: Asymmetry* **2002**, *13*, 2161-2166, doi:https://doi.org/10.1016/S0957-4166(02)00571-2.
10. Watanabe, T.; Kobayashi, A.; Nishiura, M.; Takahashi, H.; Usui, T.; Kamiyama, I.; Mochizuki, N.; Noritake, K.; Yokoyama, Y.; Murakami, Y. Synthetic Studies on Indoles and Related Compounds. XXVI. The Debenzylation of Protected Indole Nitrogen with Aluminum Chloride. (2). *Chemical & Pharmaceutical Bulletin* **1991**, *39*, 1152-1156, doi:10.1248/cpb.39.1152.
11. Li, B.; Zhang, S.; Chen, W. An efficient and practical synthesis of BINAM derivatives by diastereoselective [3,3]-rearrangement. *Tetrahedron: Asymmetry* **2014**, *25*, 1002-1007, doi:10.1016/j.tetasy.2014.06.006.

5. CV chart

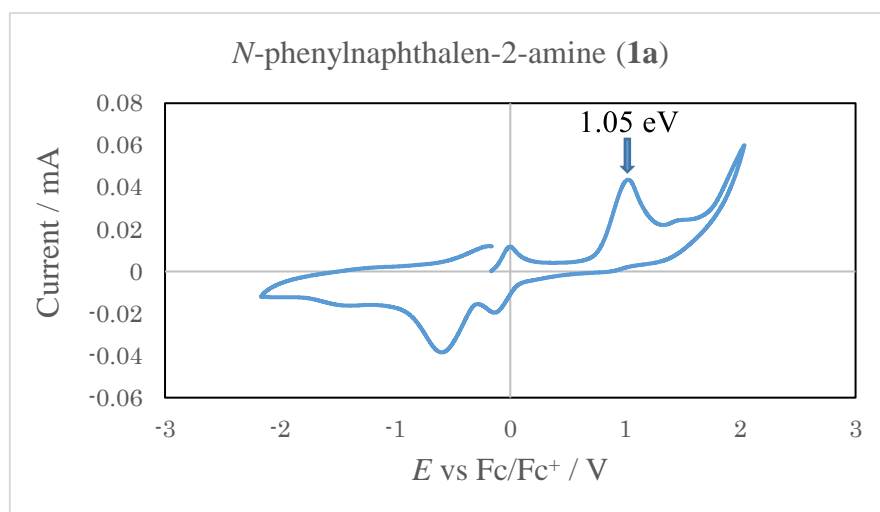
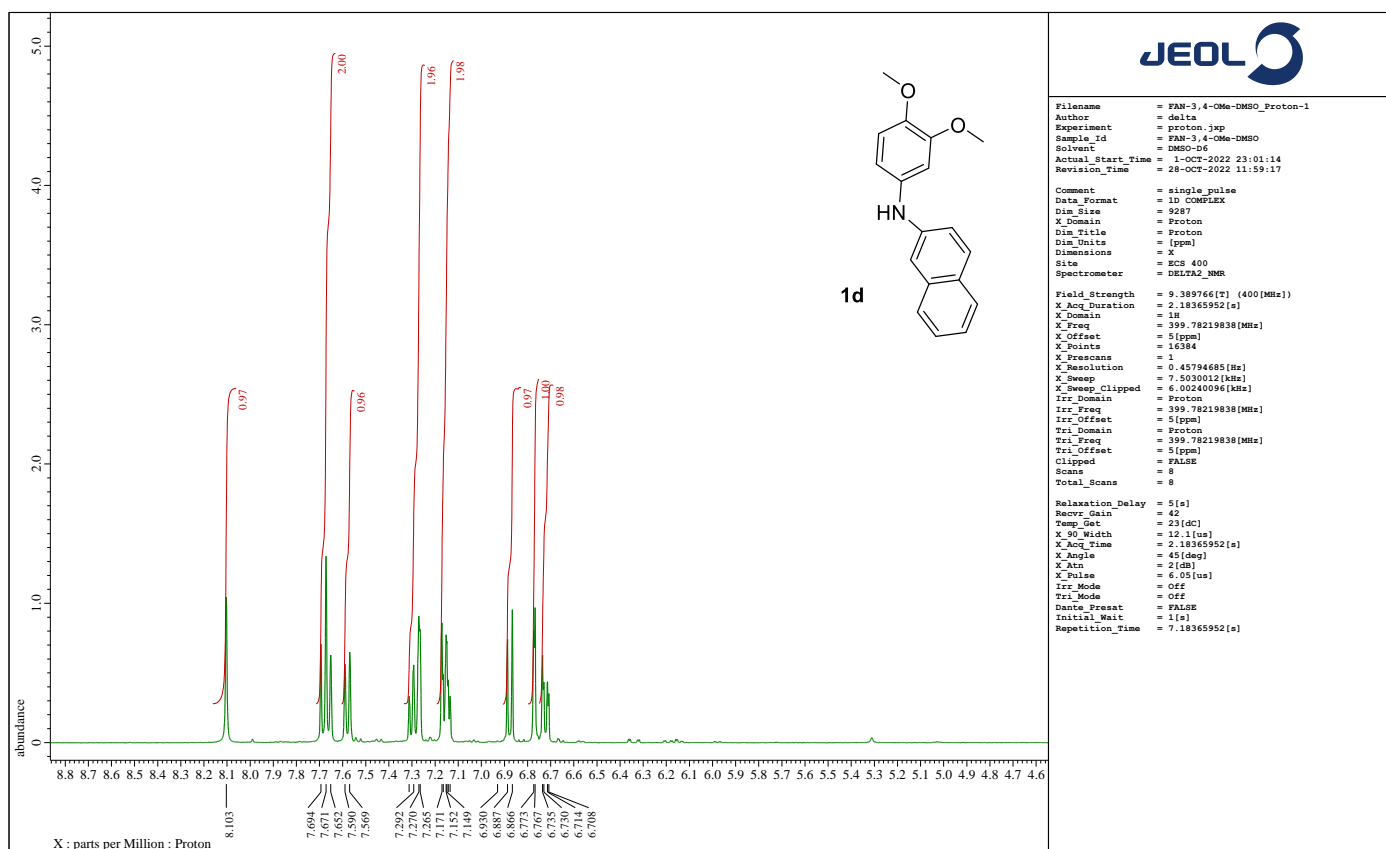
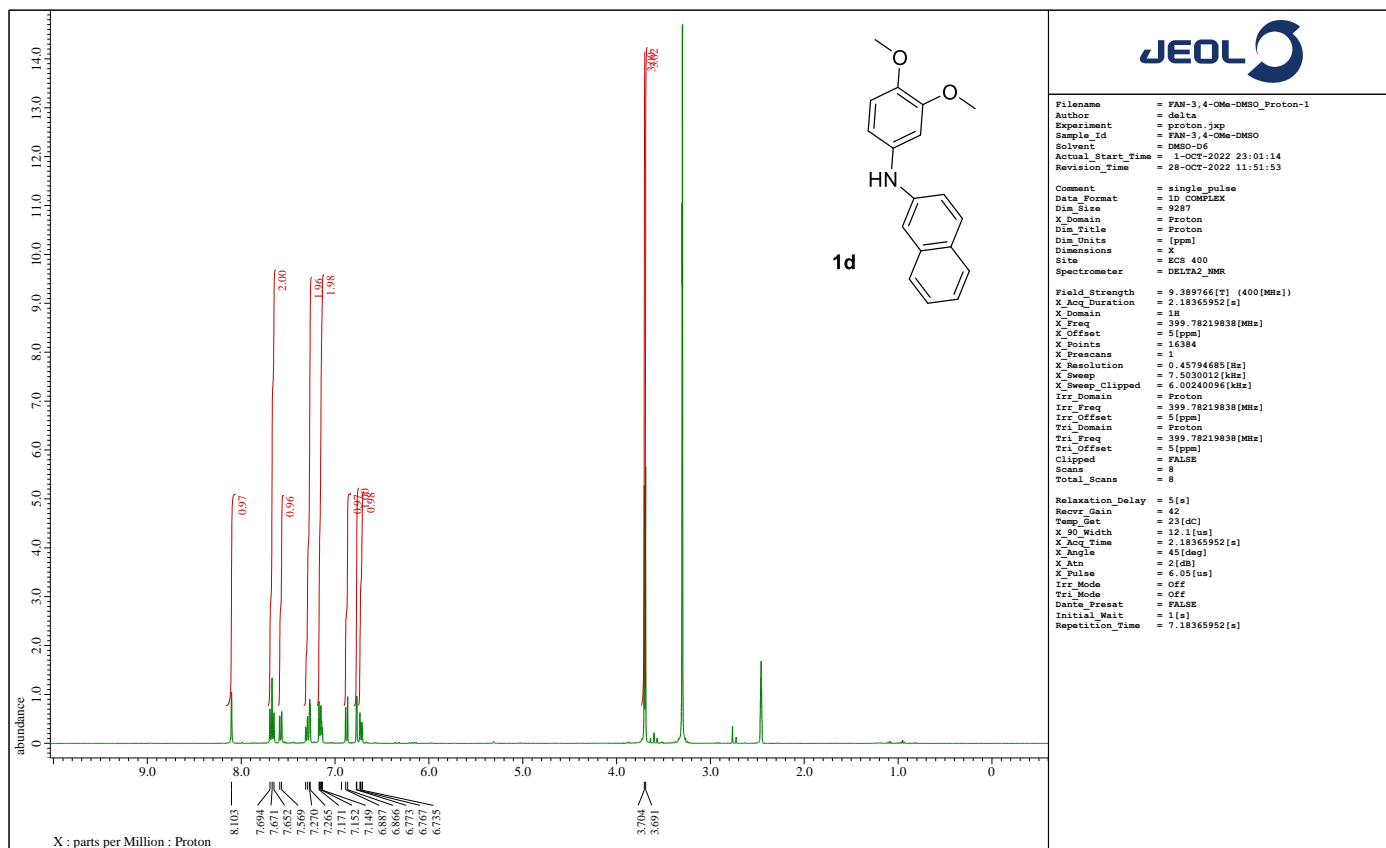
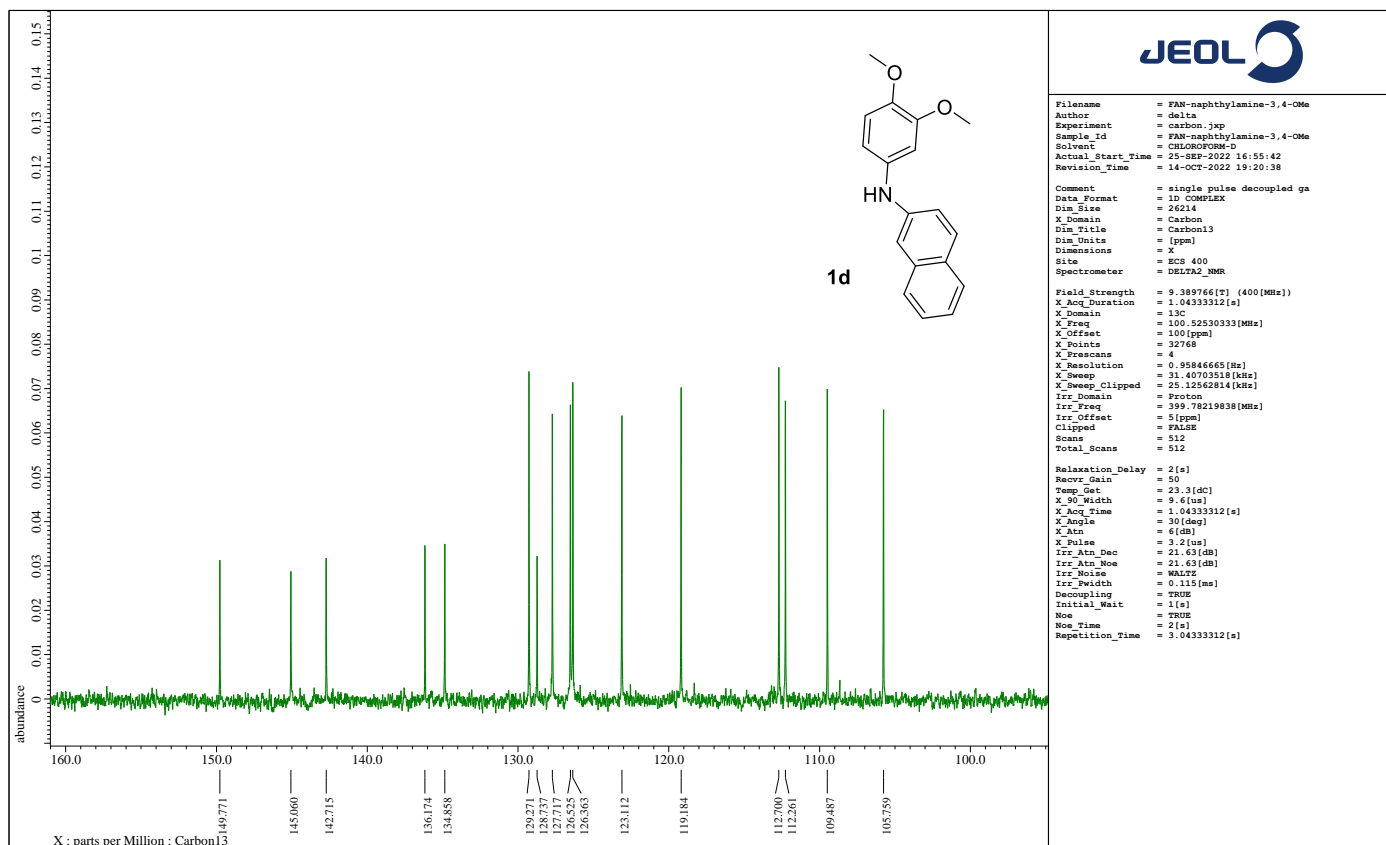
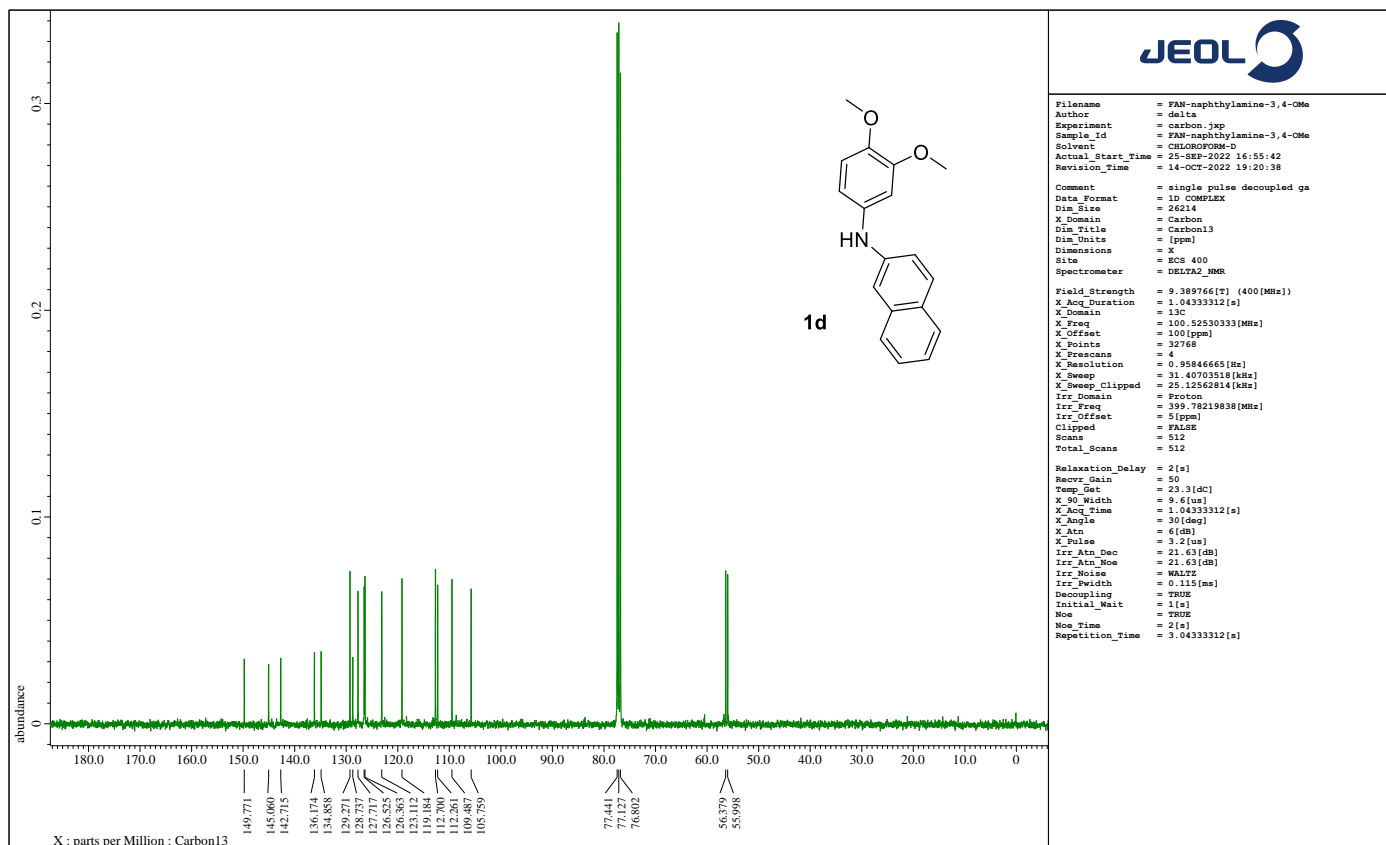


Figure S2. CV experiments (MeCN) as a solvent with Bu₄NPF₆ (0.1 M) as electrolyte.

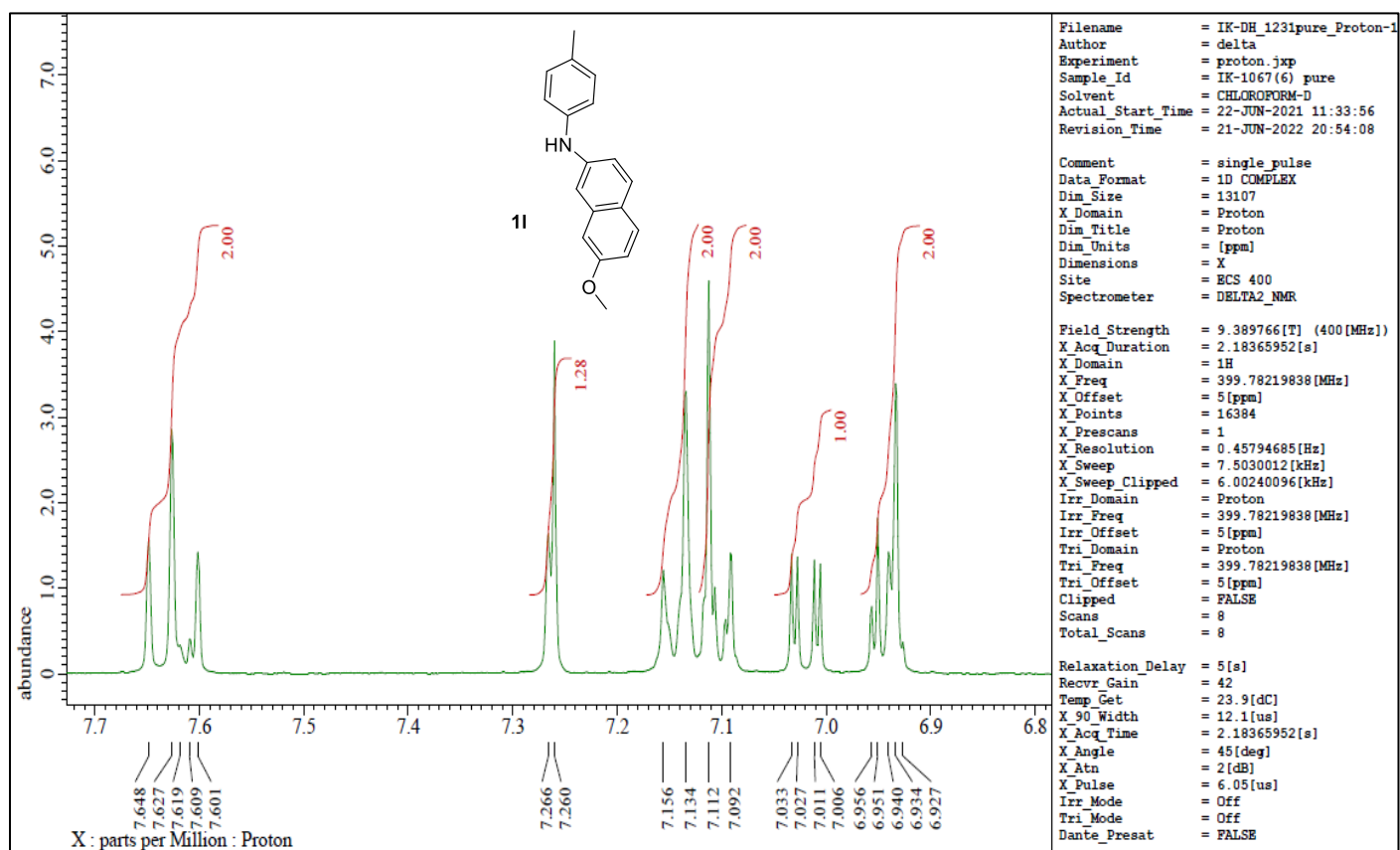
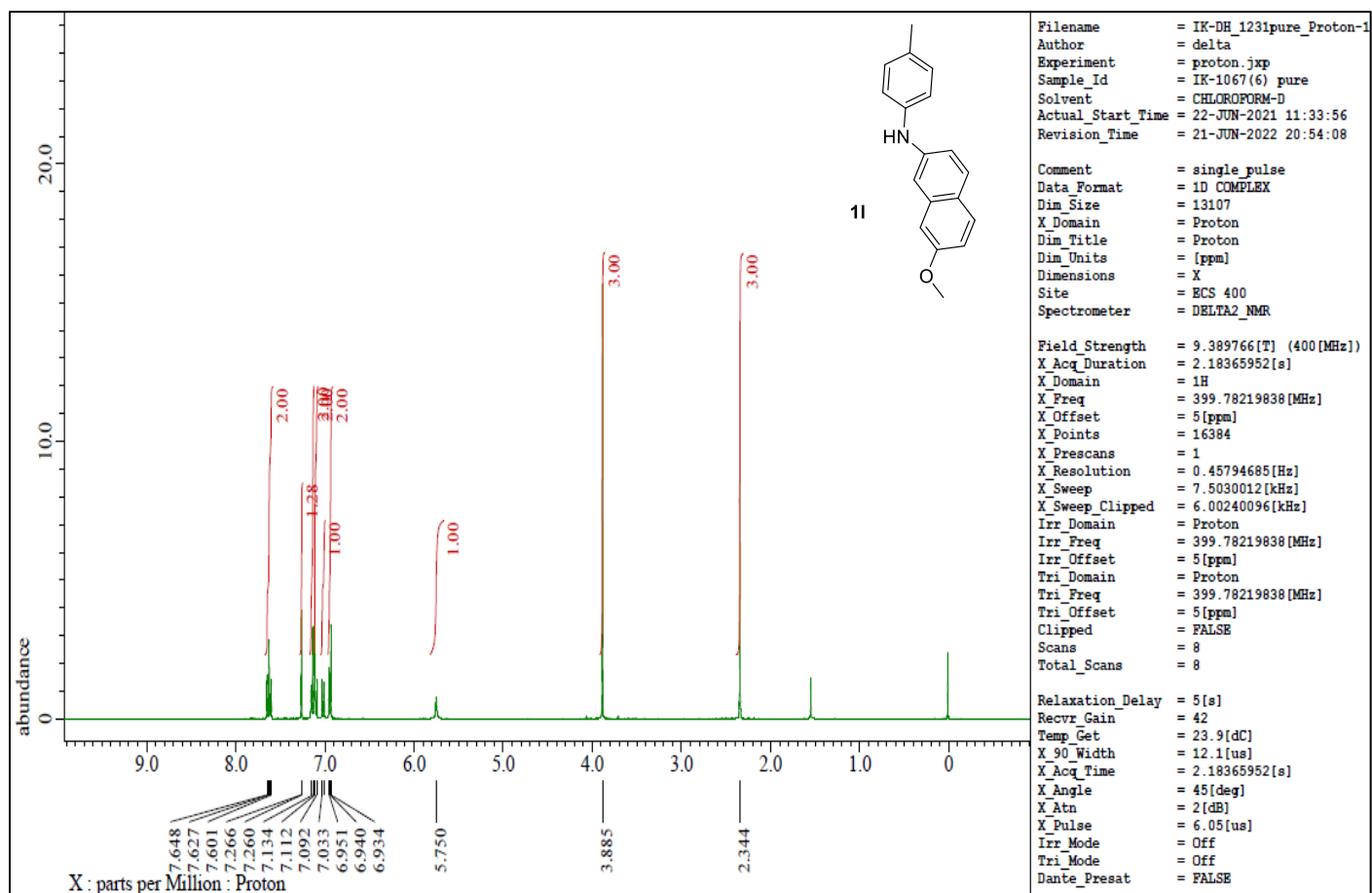
6. NMR Spectra



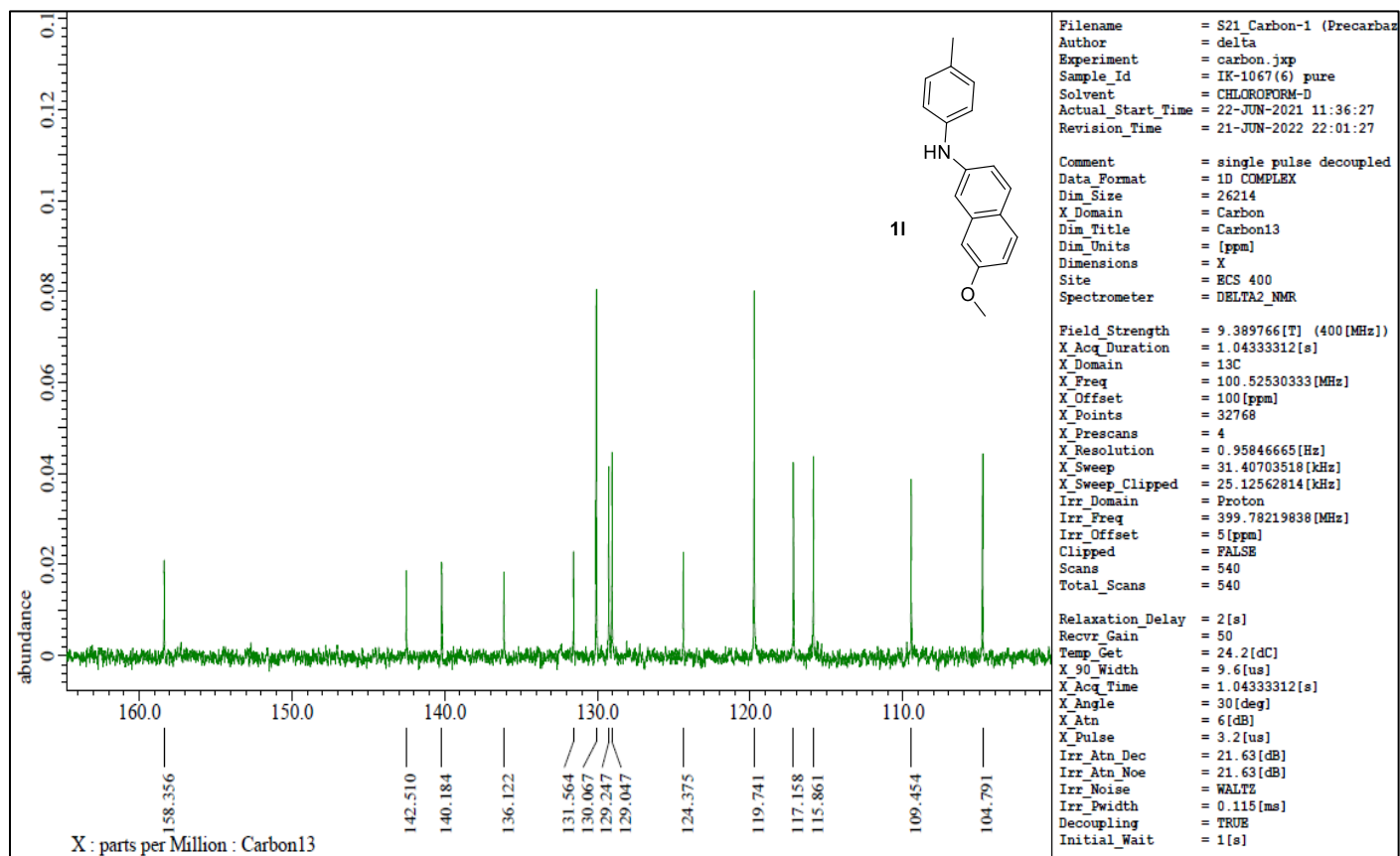
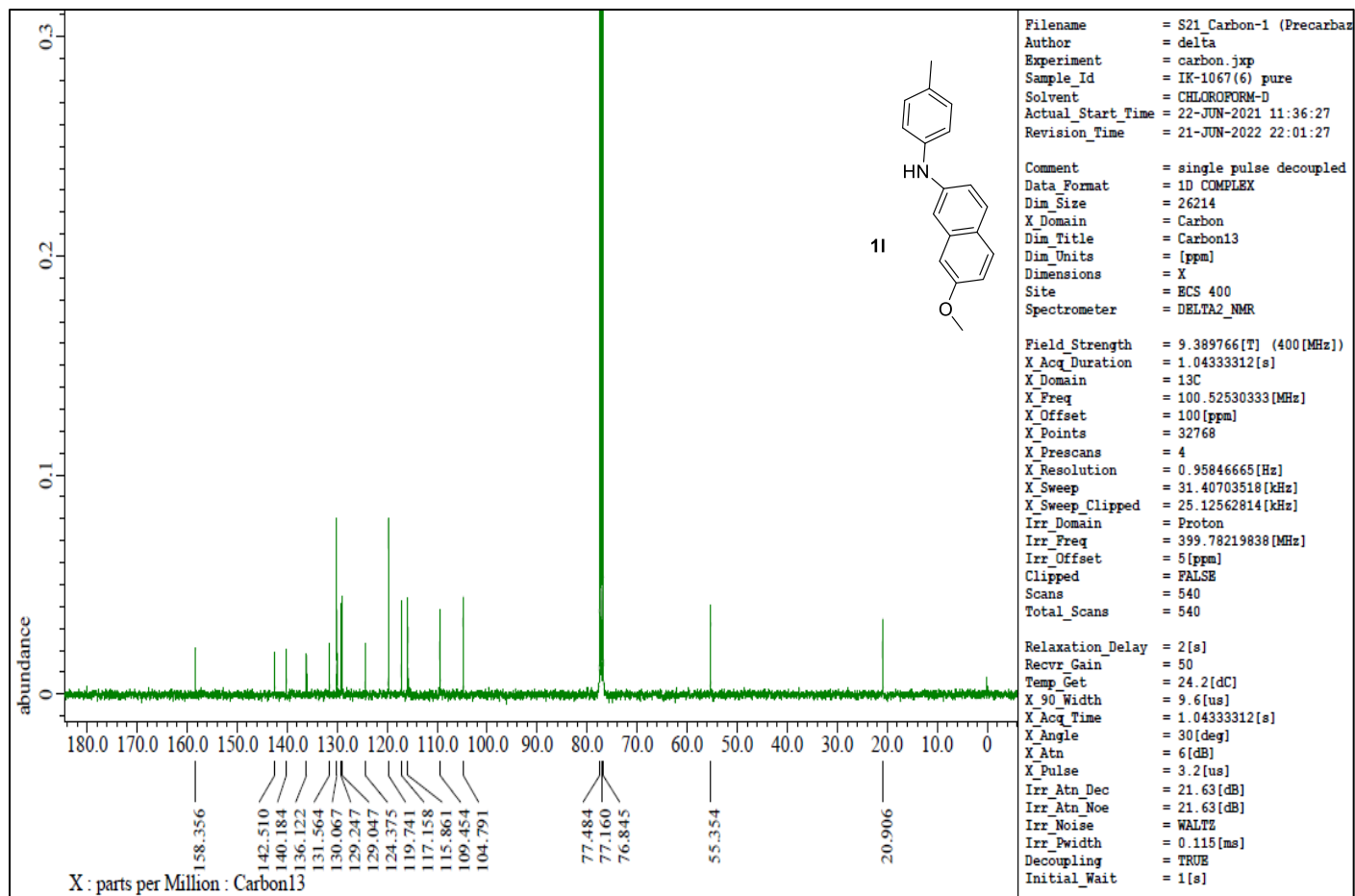
Compound **1d** (^1H NMR, 400 MHz, DMSO).



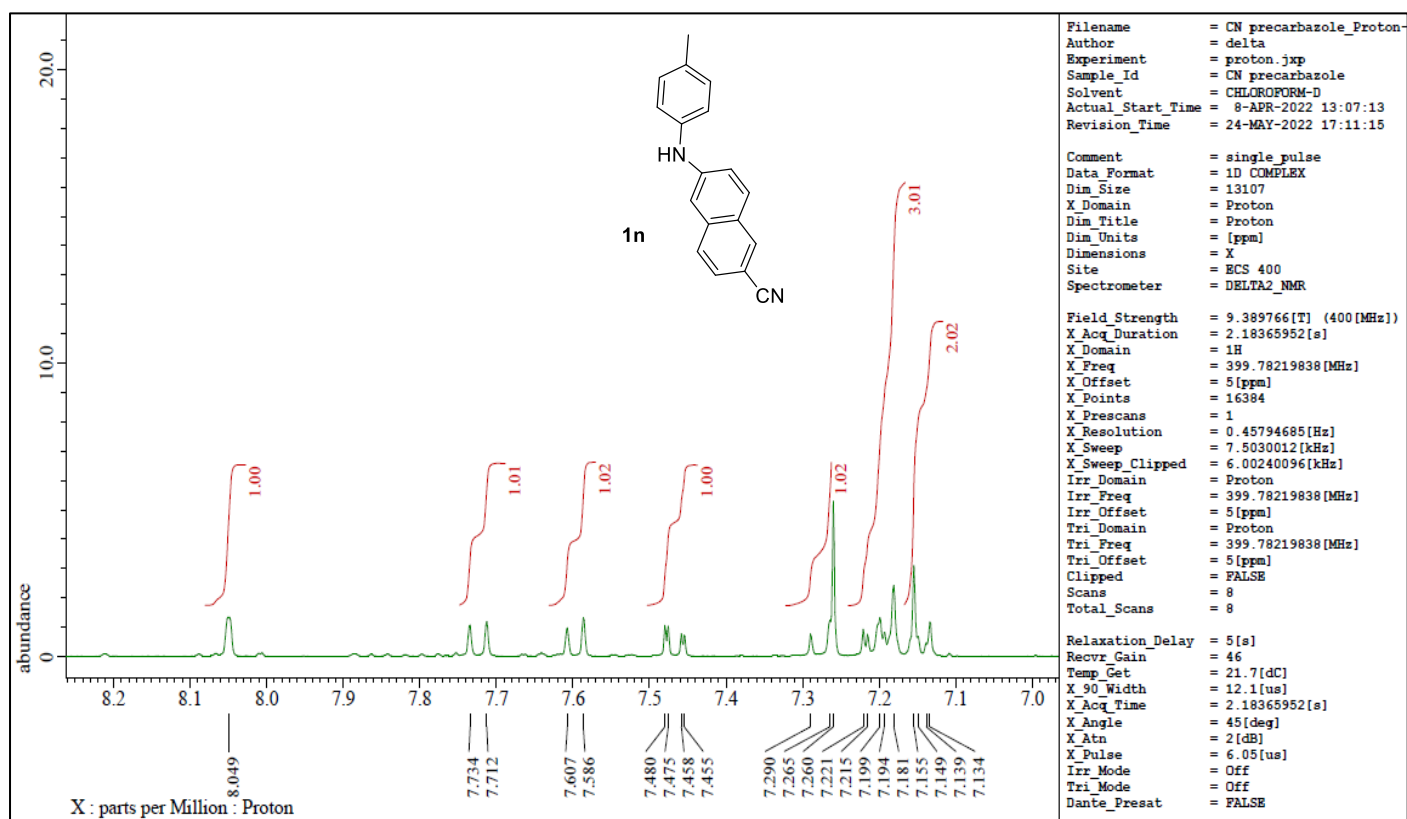
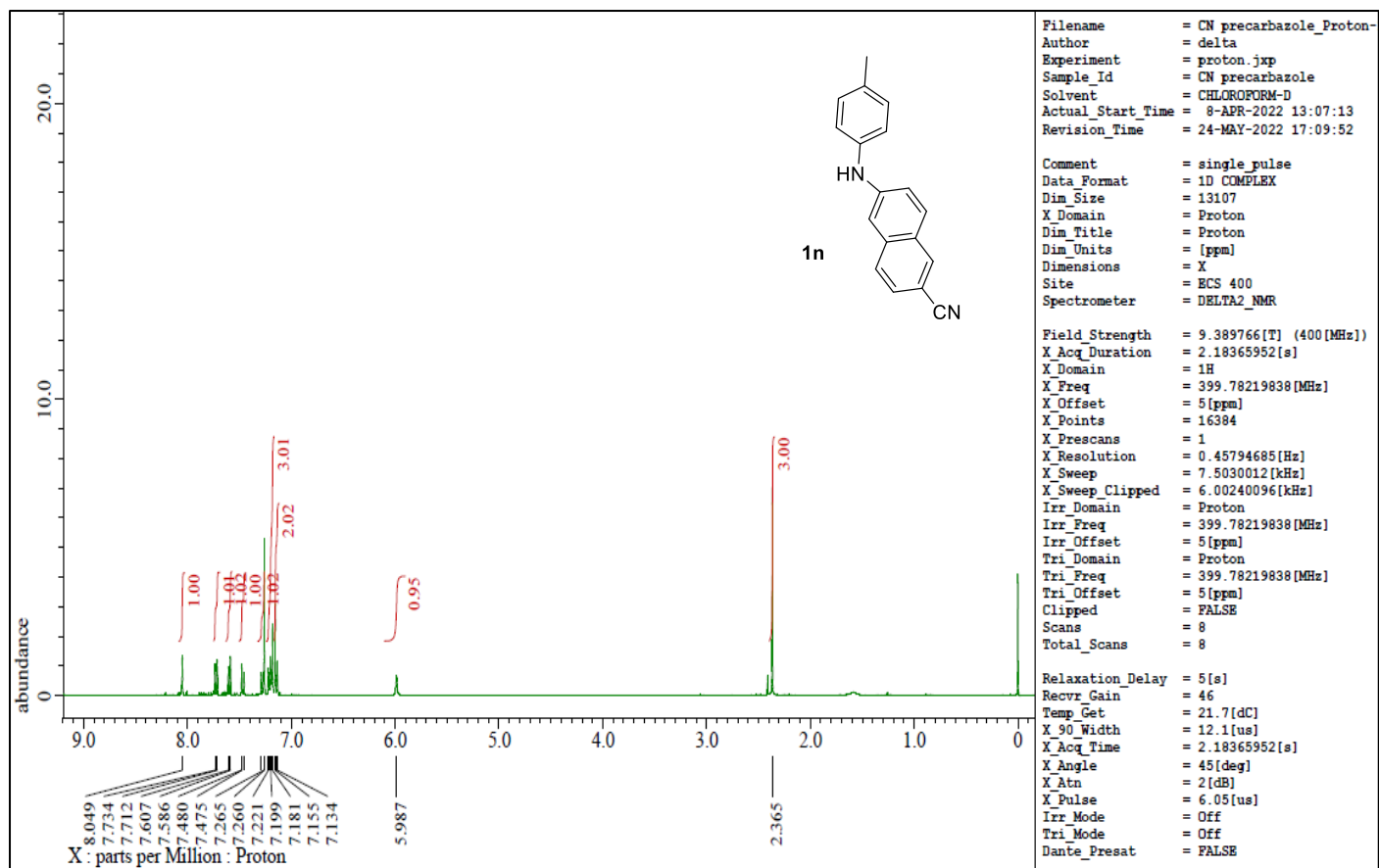
Compound **1d** (¹³C NMR, 100 MHz, CDCl₃).



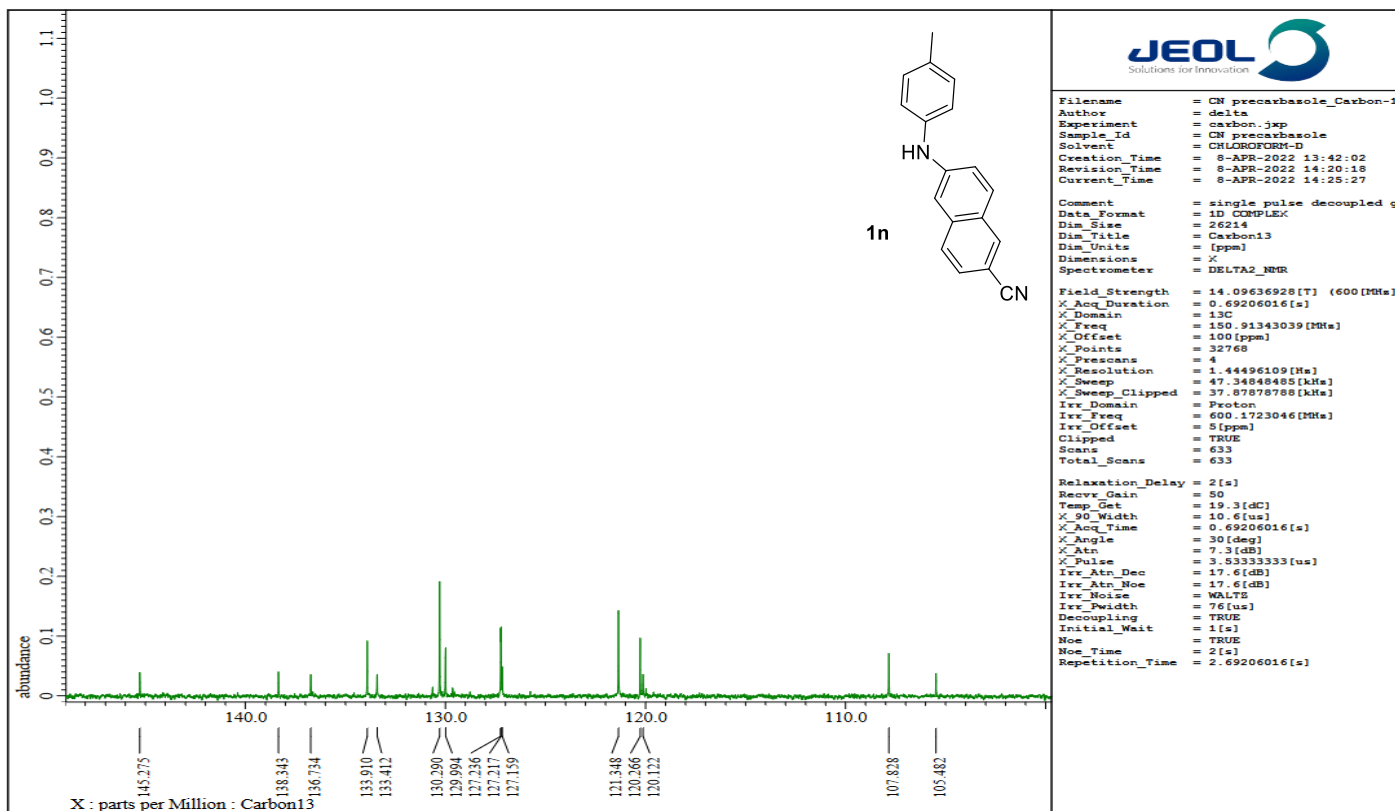
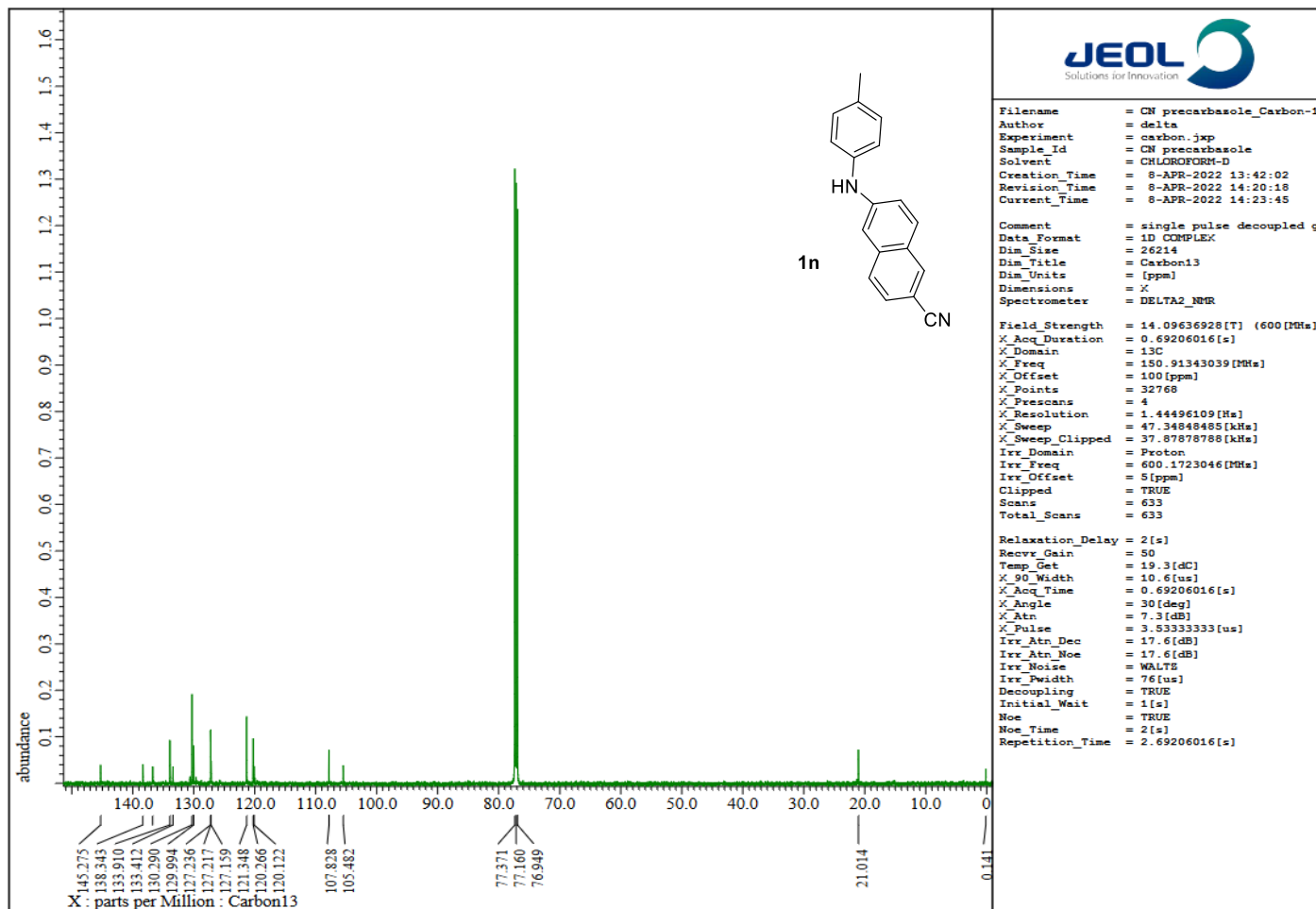
Compound **11** (^1H NMR, 400 MHz, CDCl_3).



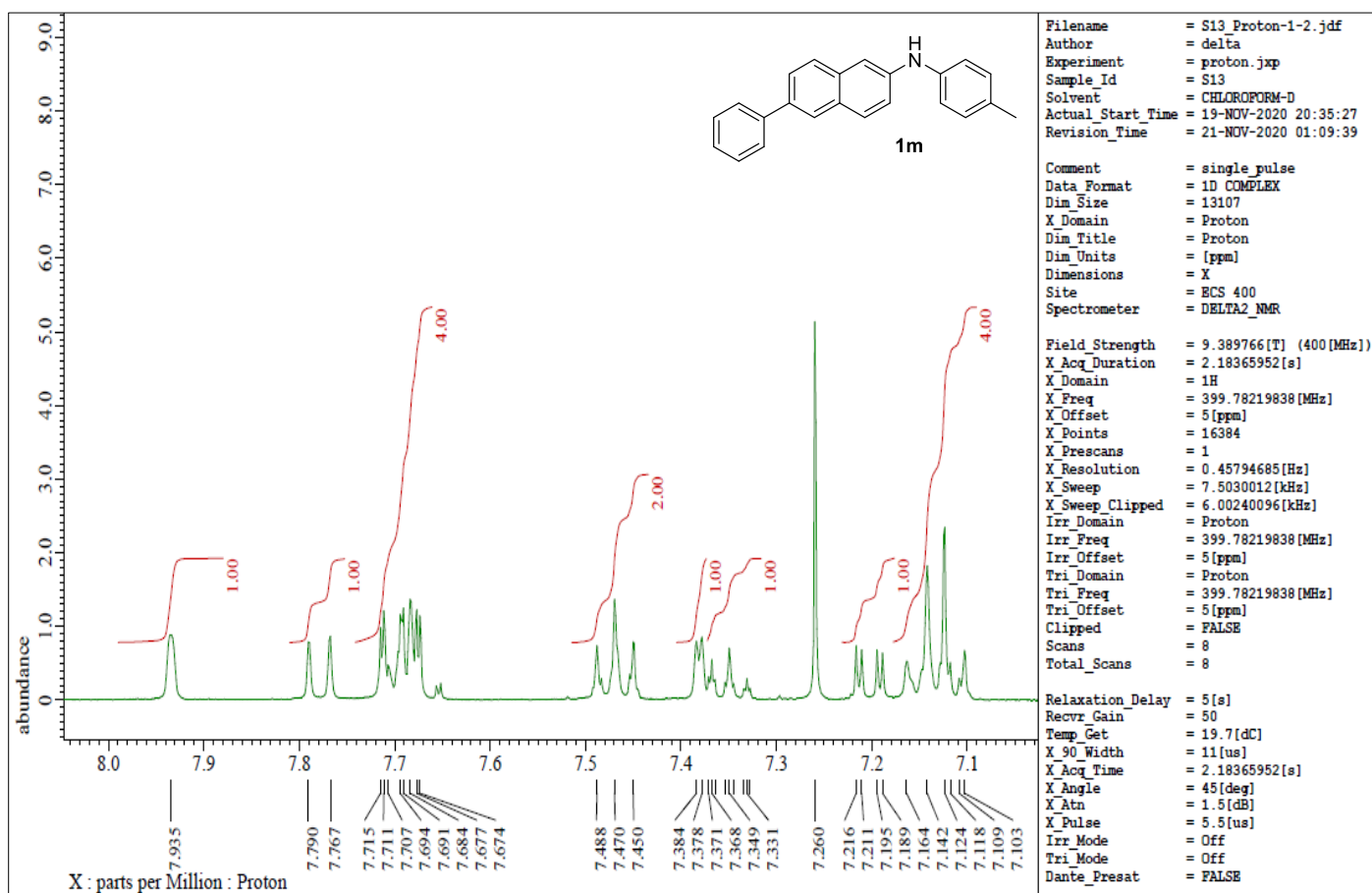
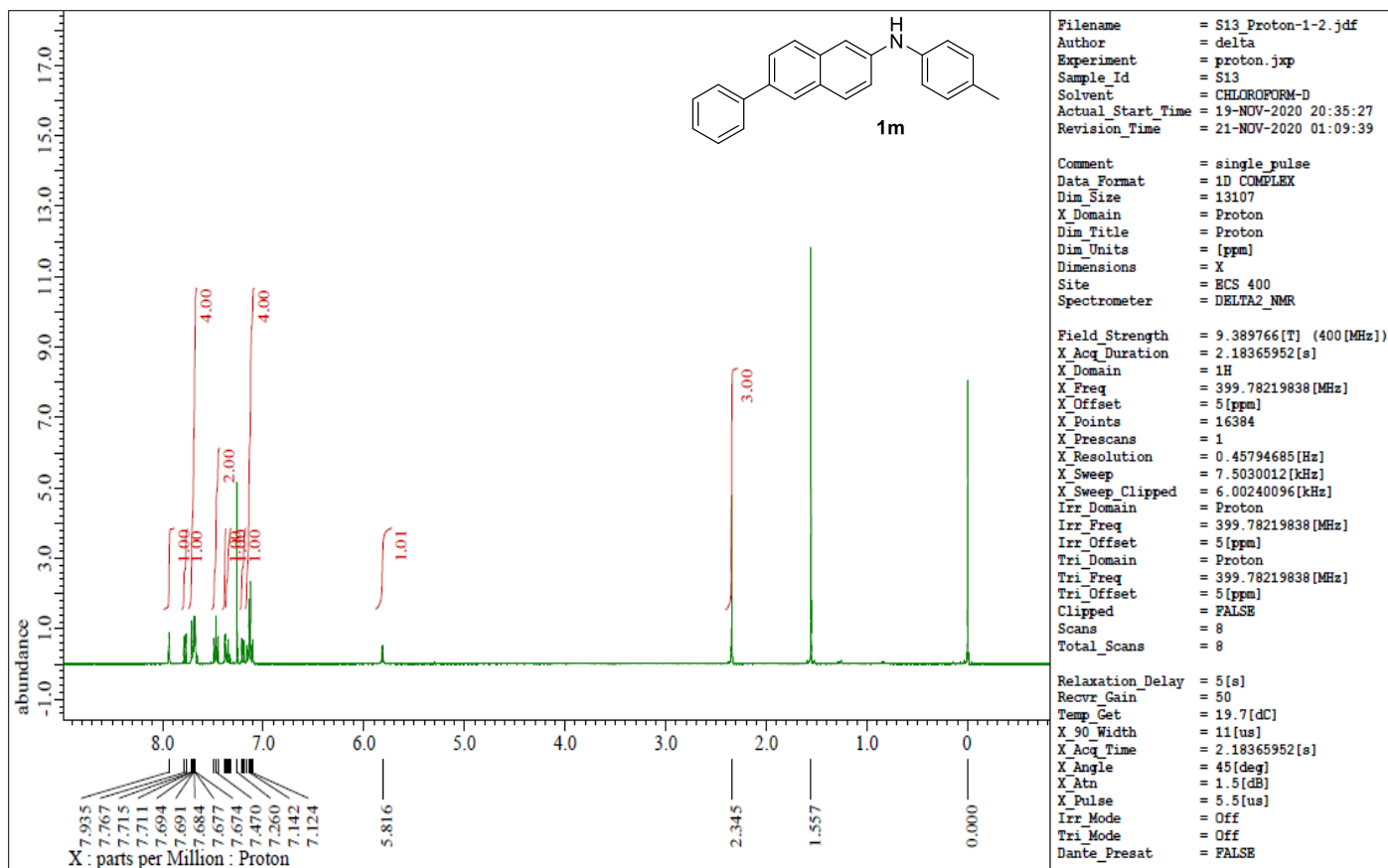
Compound **11** (¹³C NMR, 100 MHz, CDCl₃).



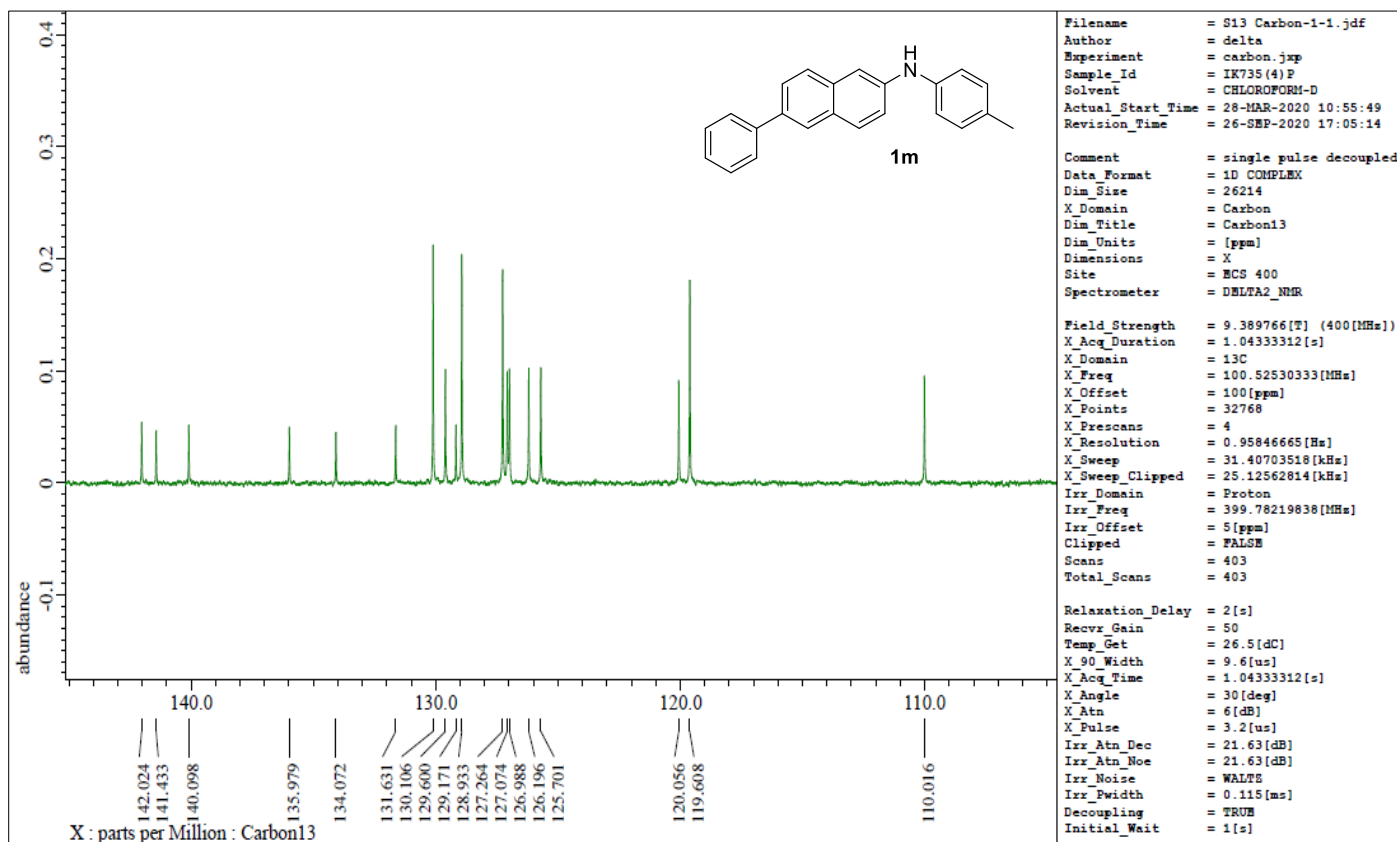
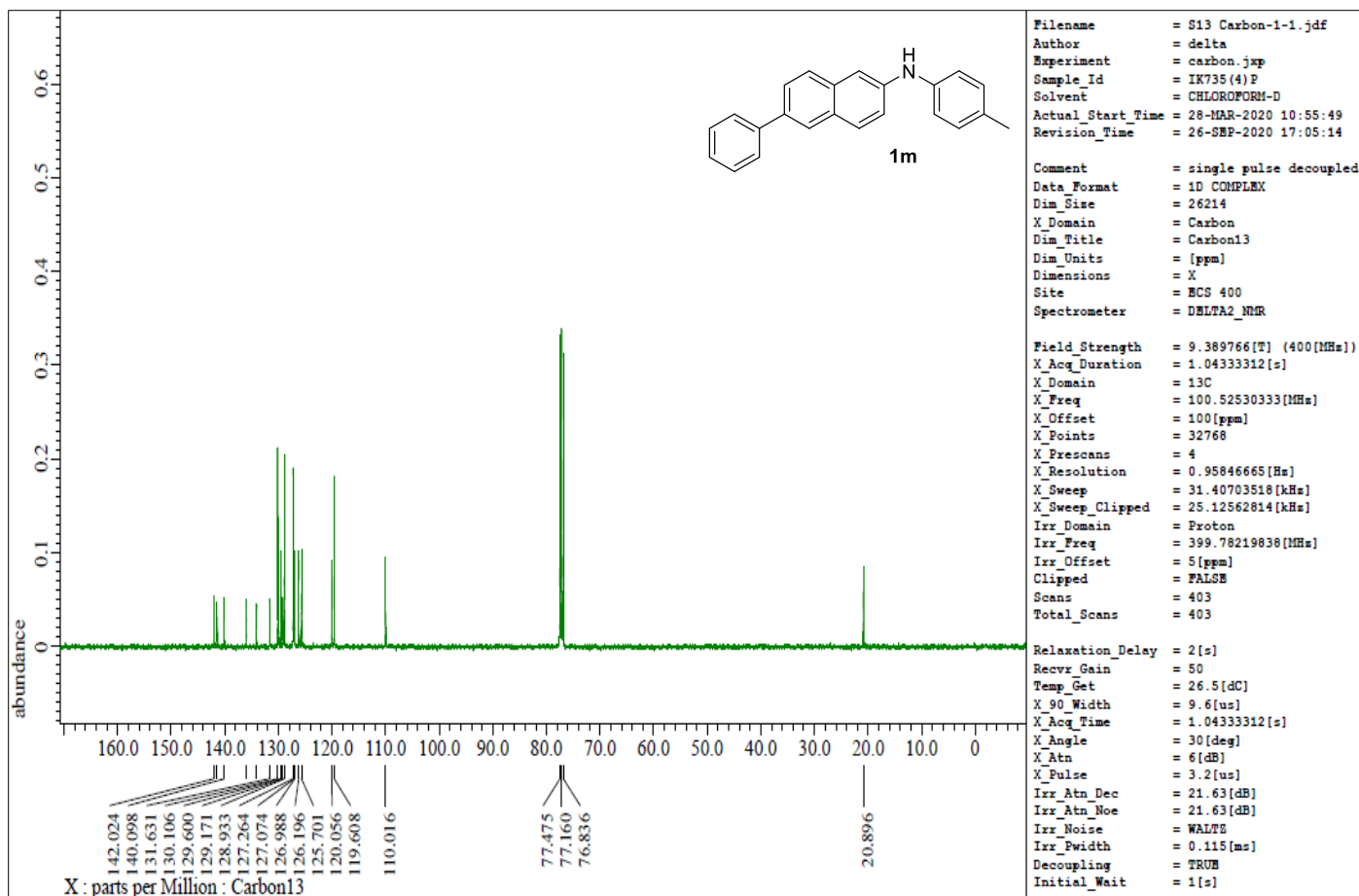
Compound **1n** (¹H NMR, 400 MHz, CDCl₃).



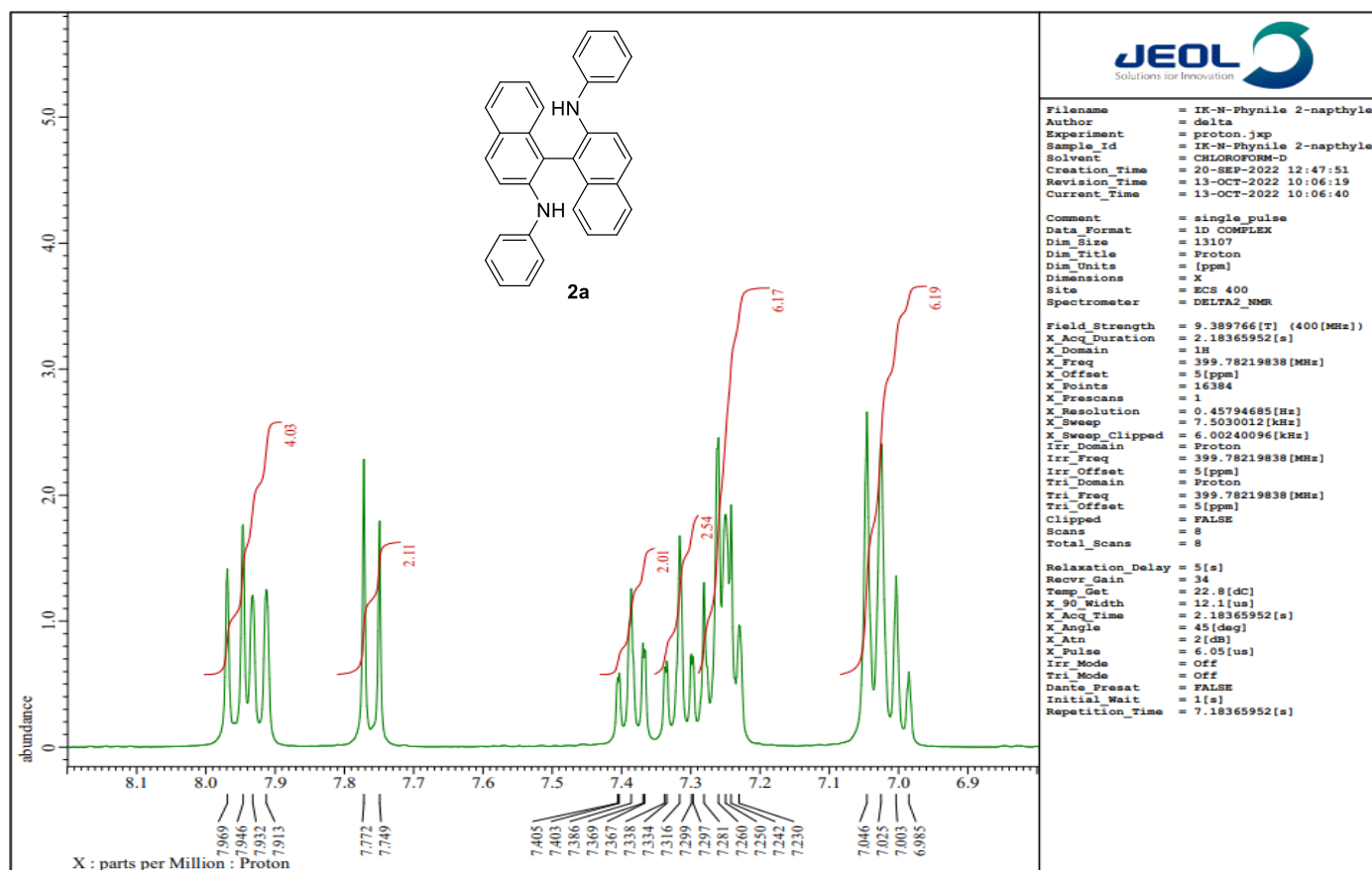
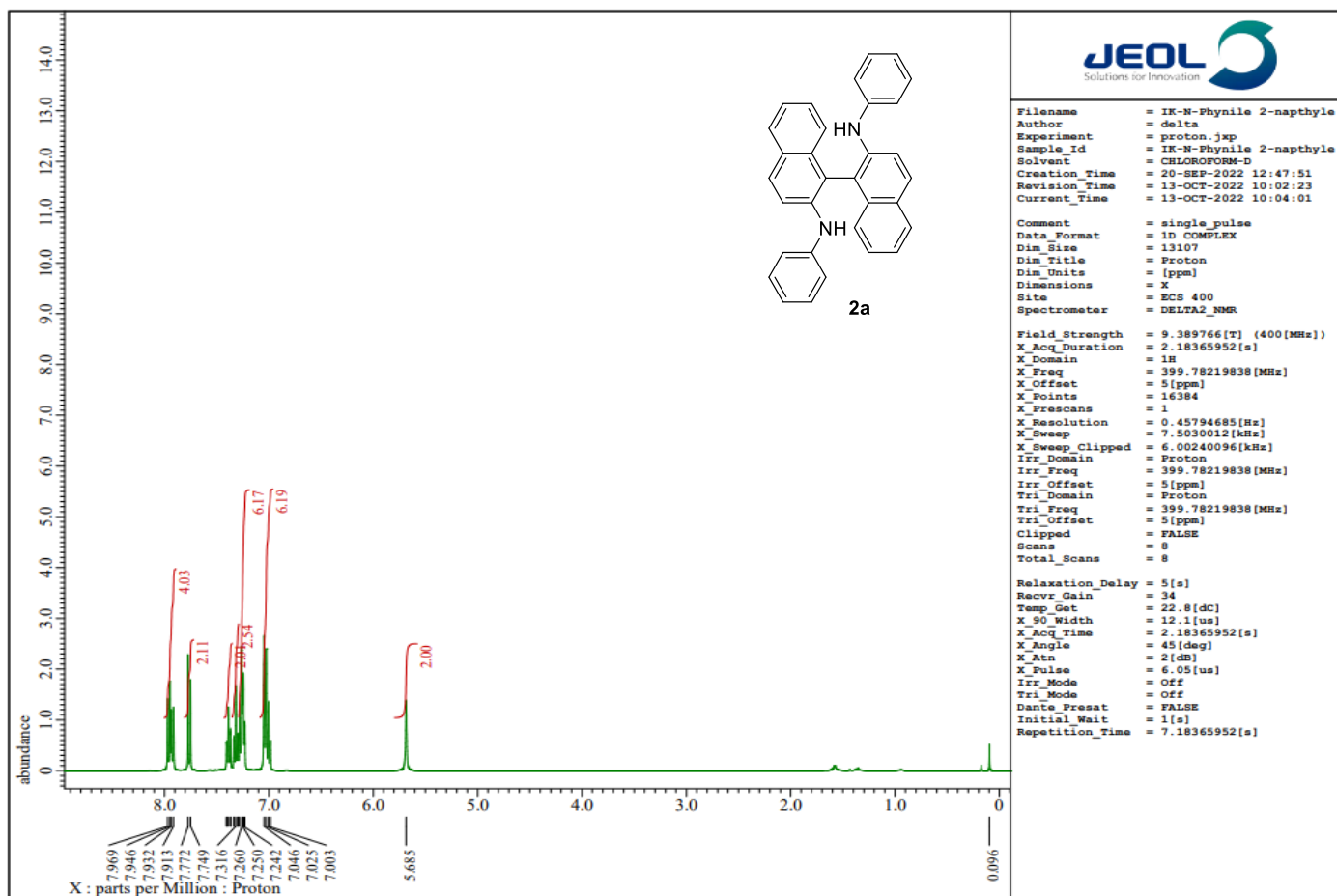
Compound **1n** (^{13}C NMR, 100 MHz, CDCl_3).



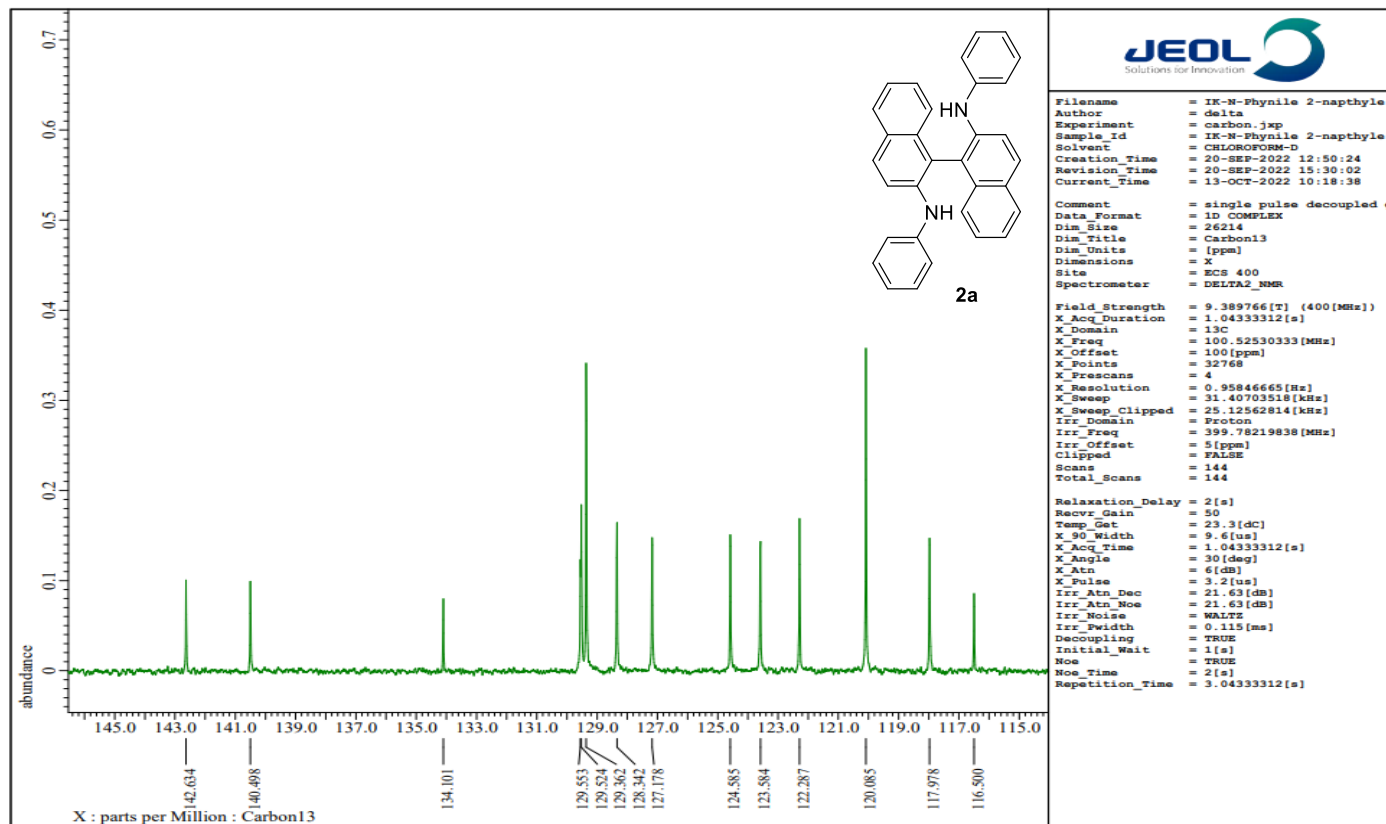
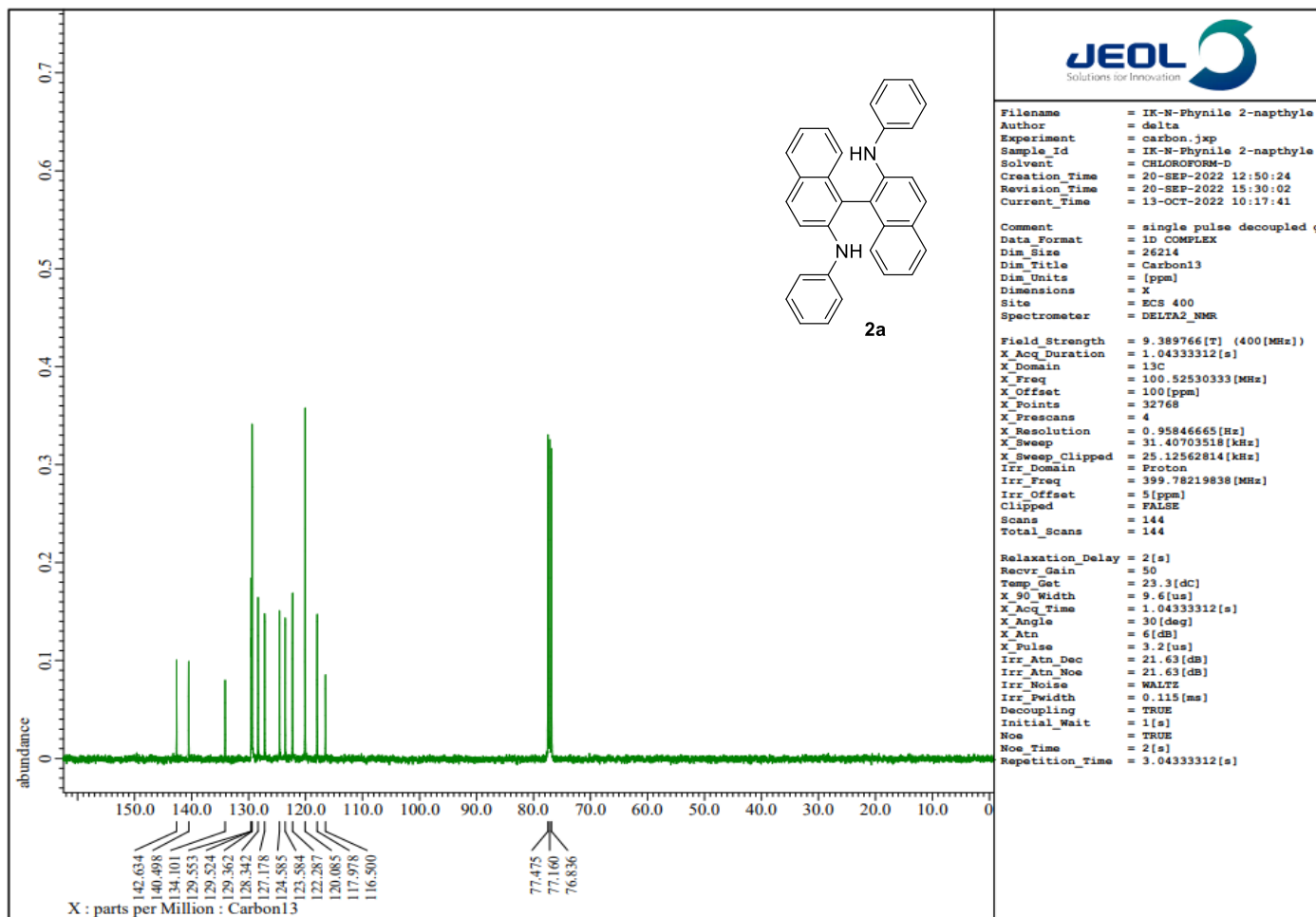
Compound **1m** (^1H NMR, 400 MHz, CDCl_3).



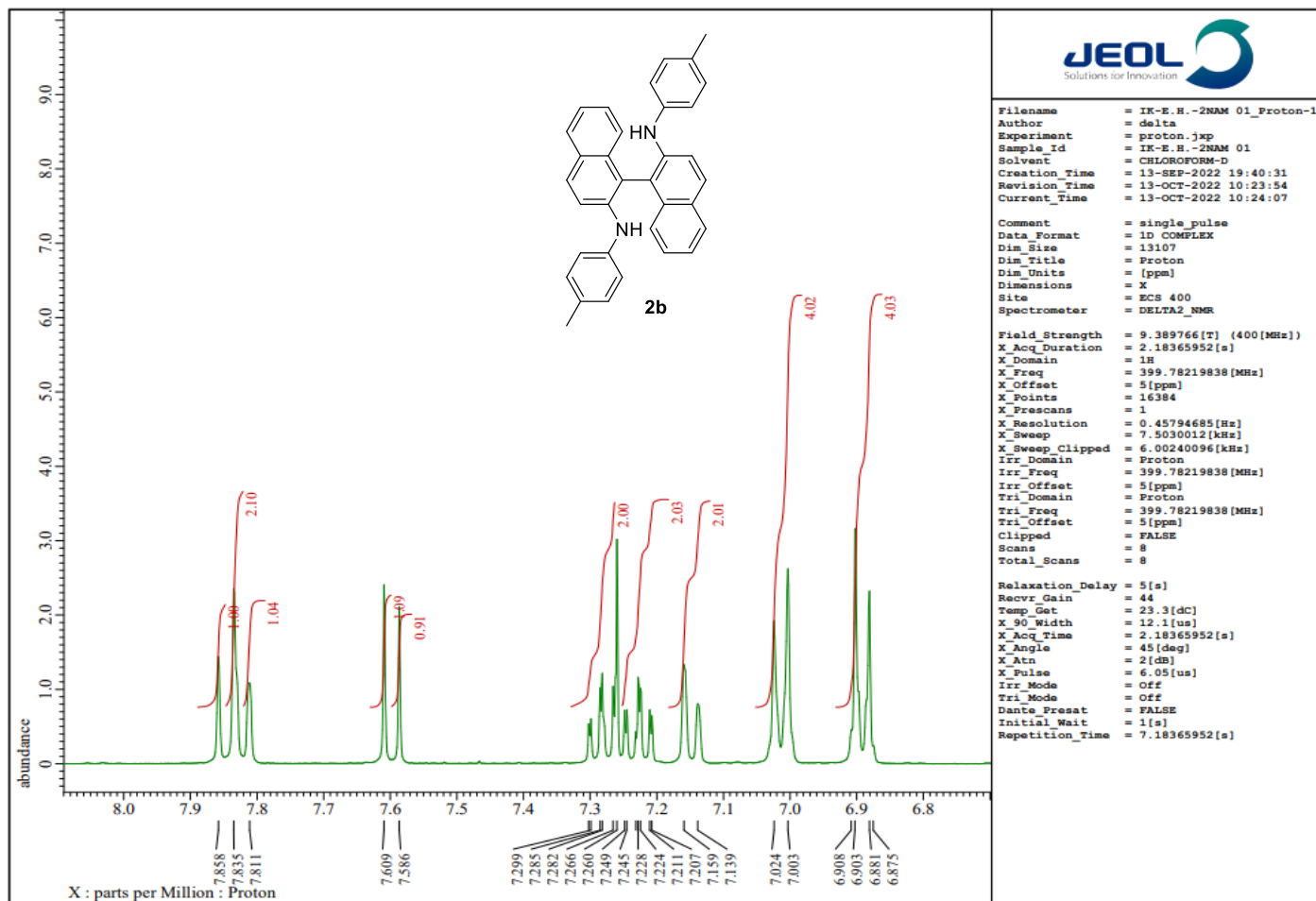
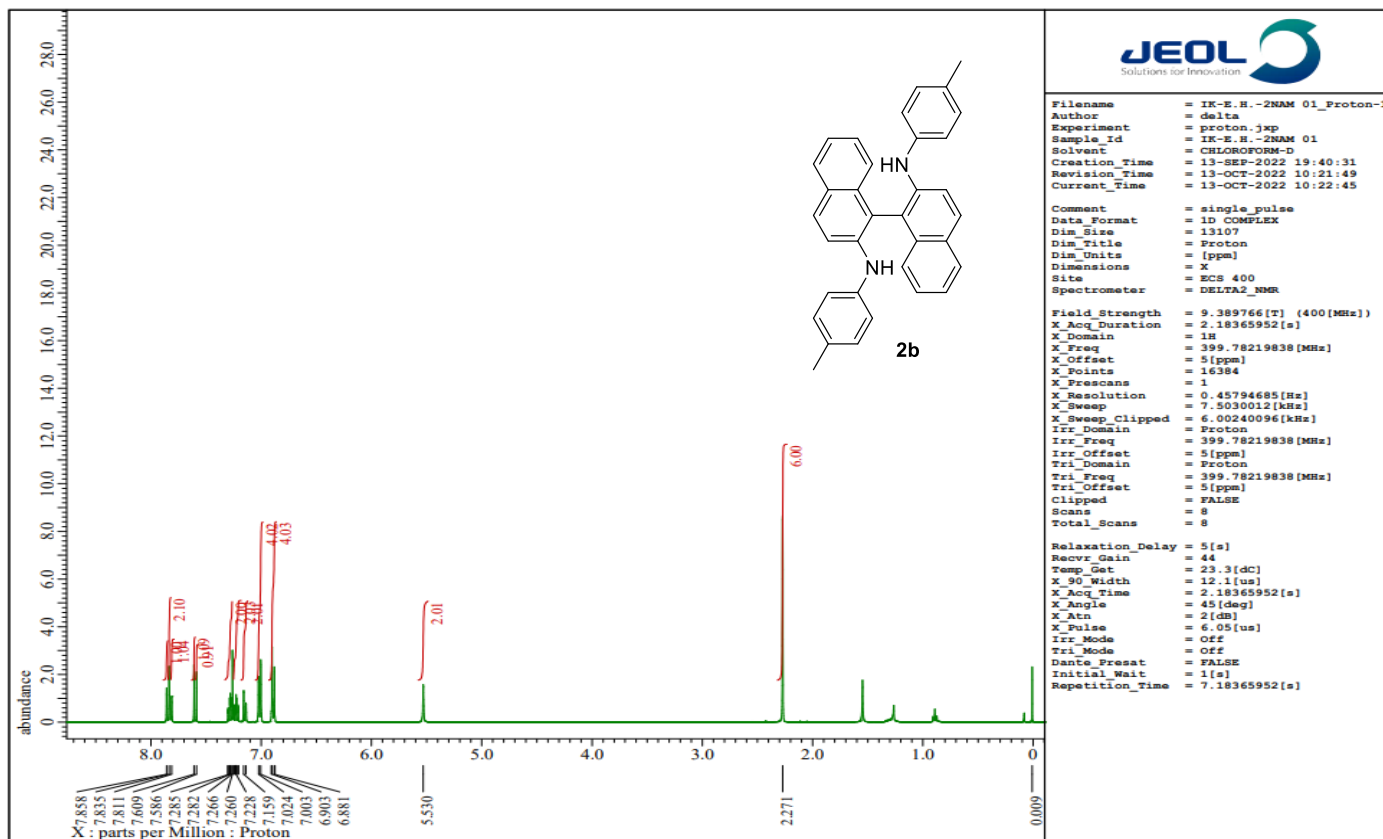
Compound **1m** (^{13}C NMR, 100 MHz, CDCl_3).



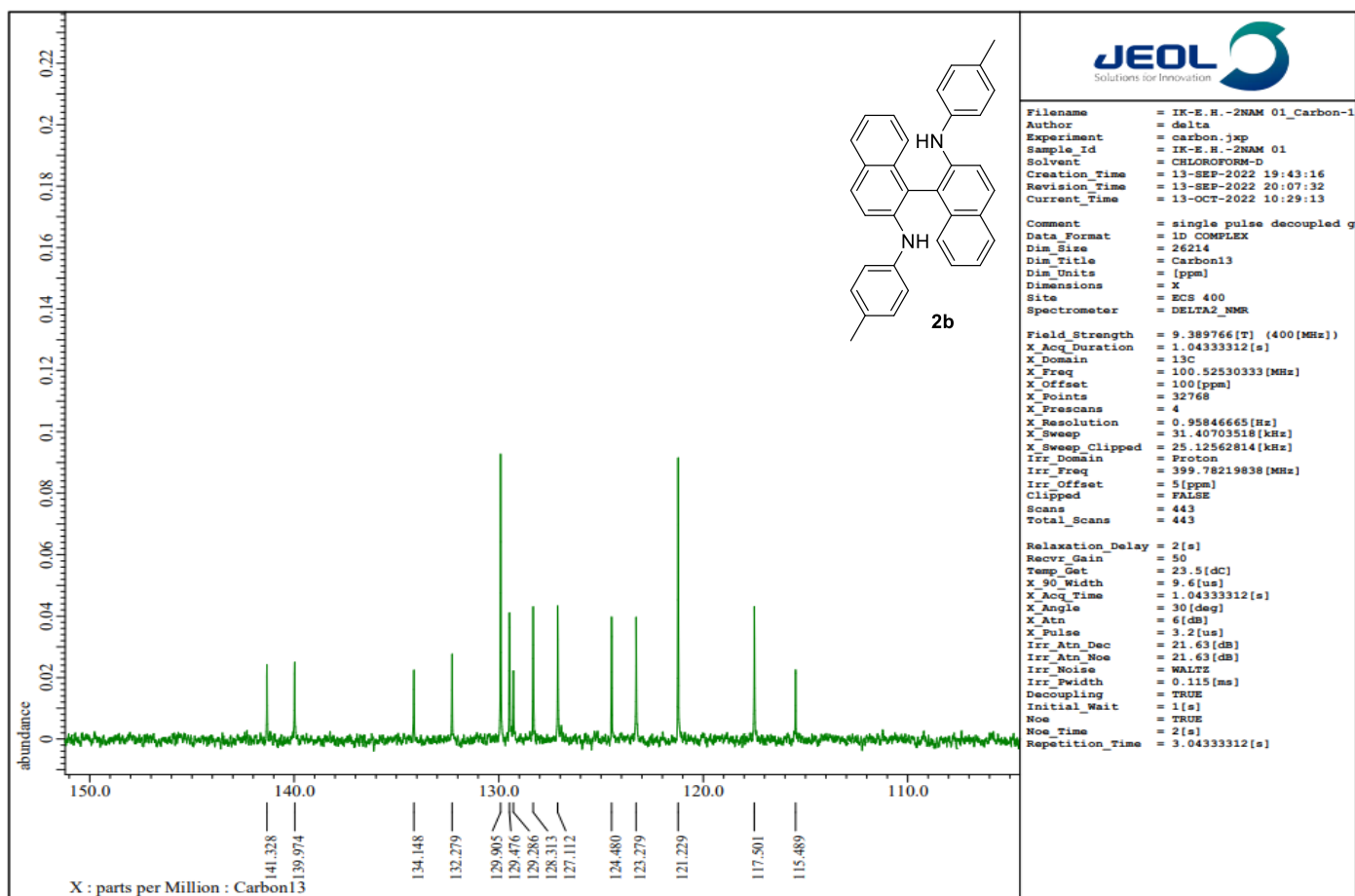
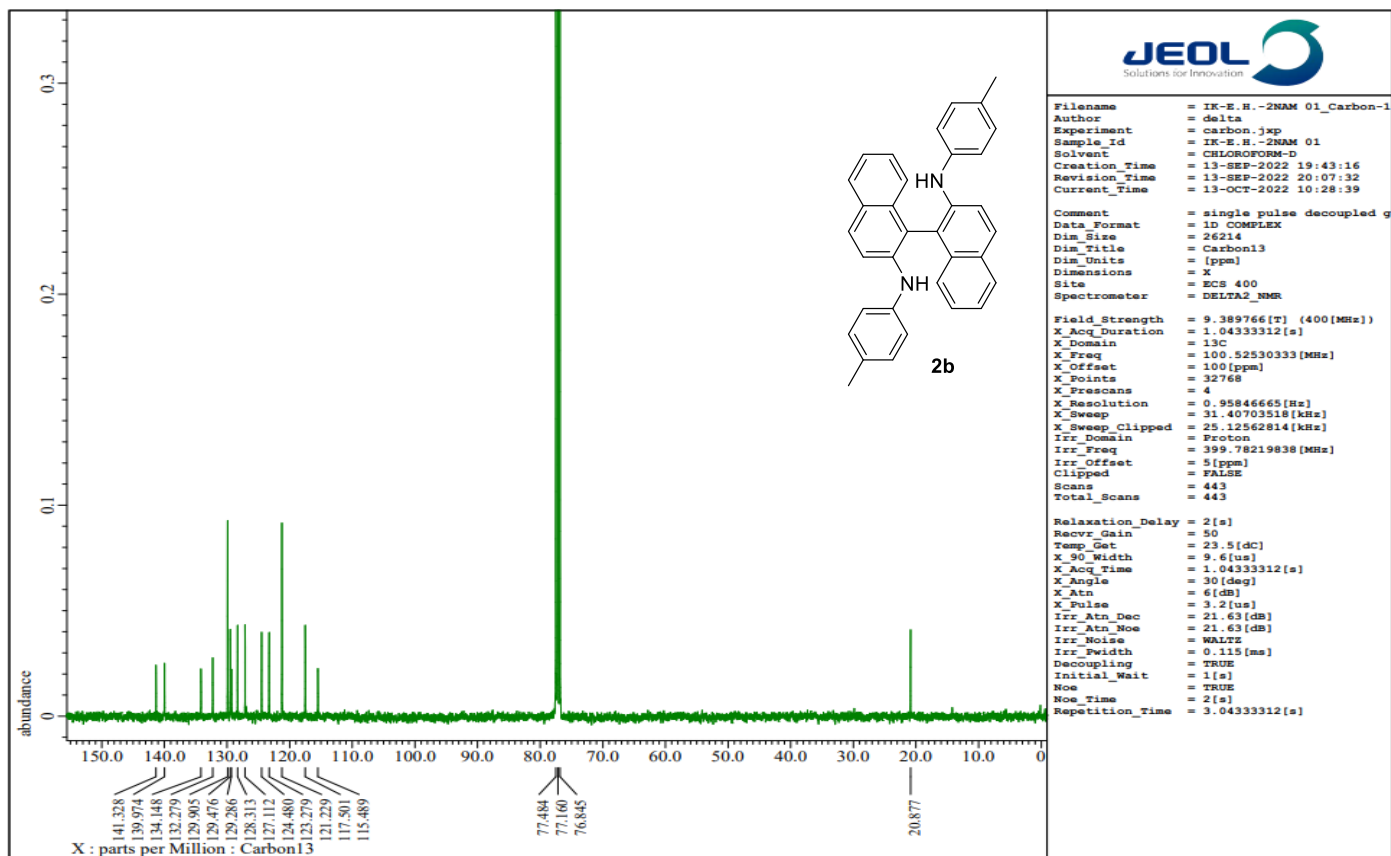
Compound **2a** (¹H NMR, 400 MHz, CDCl₃).



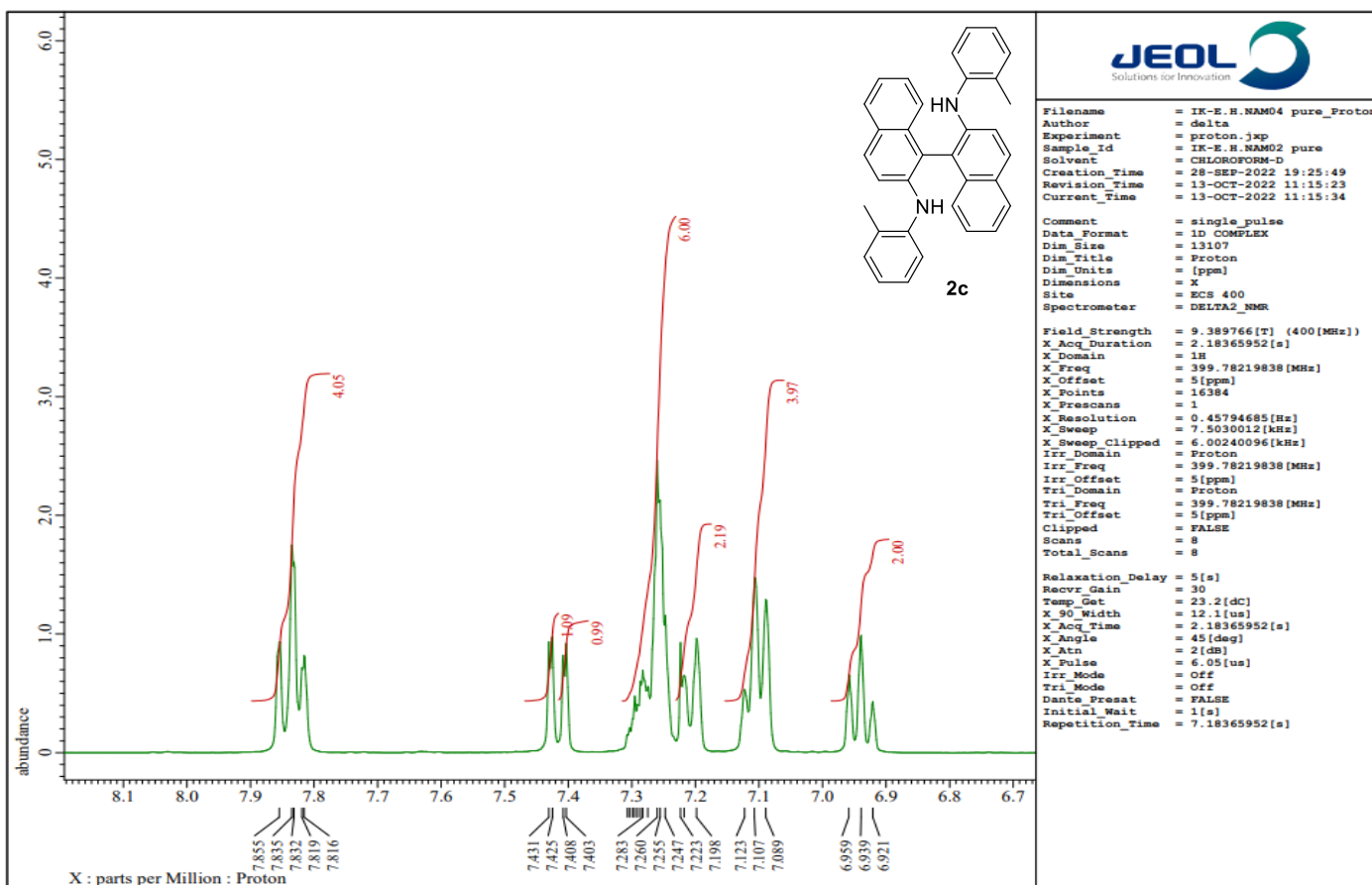
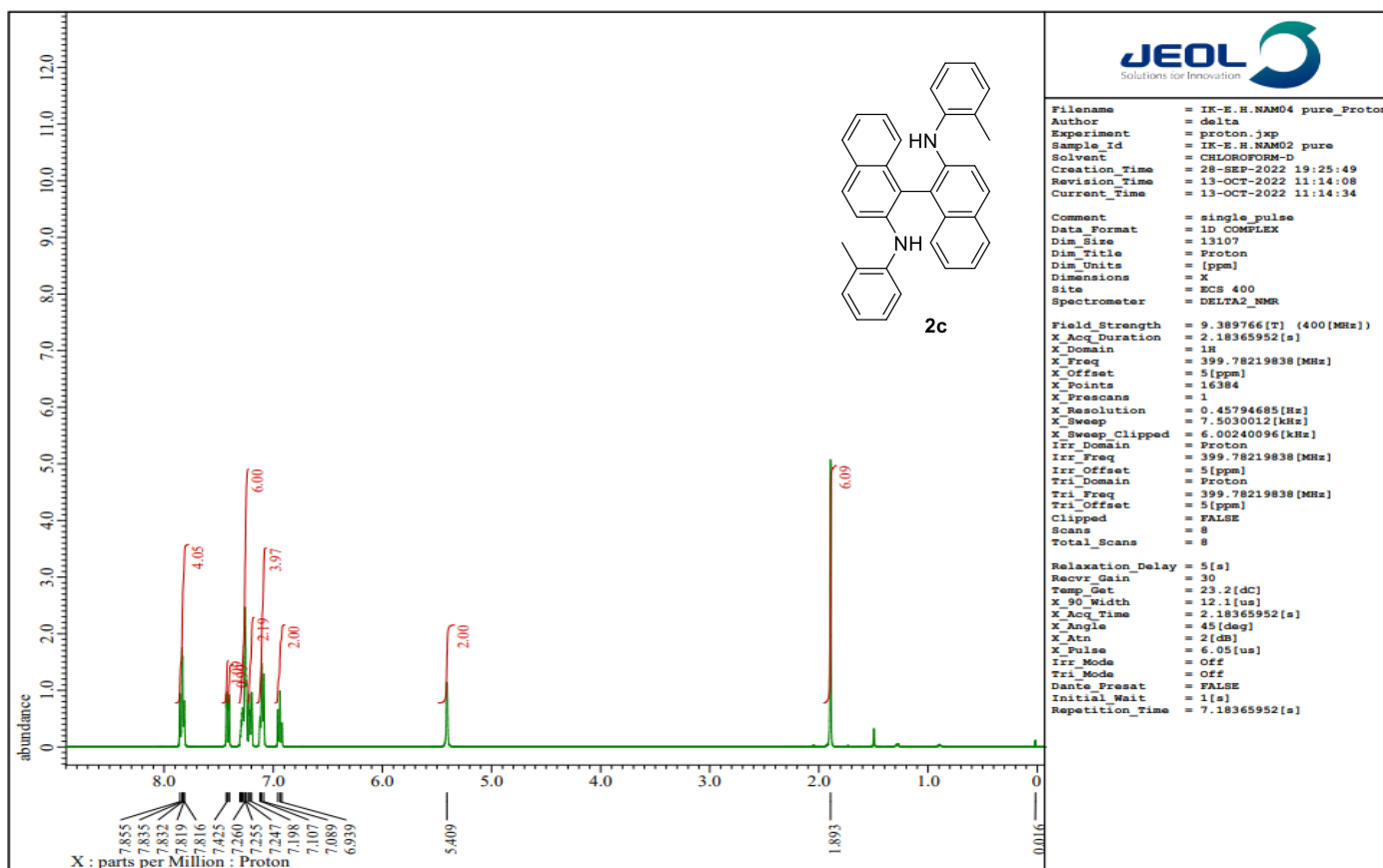
Compound **2a** (^{13}C NMR, 100 MHz, CDCl_3).



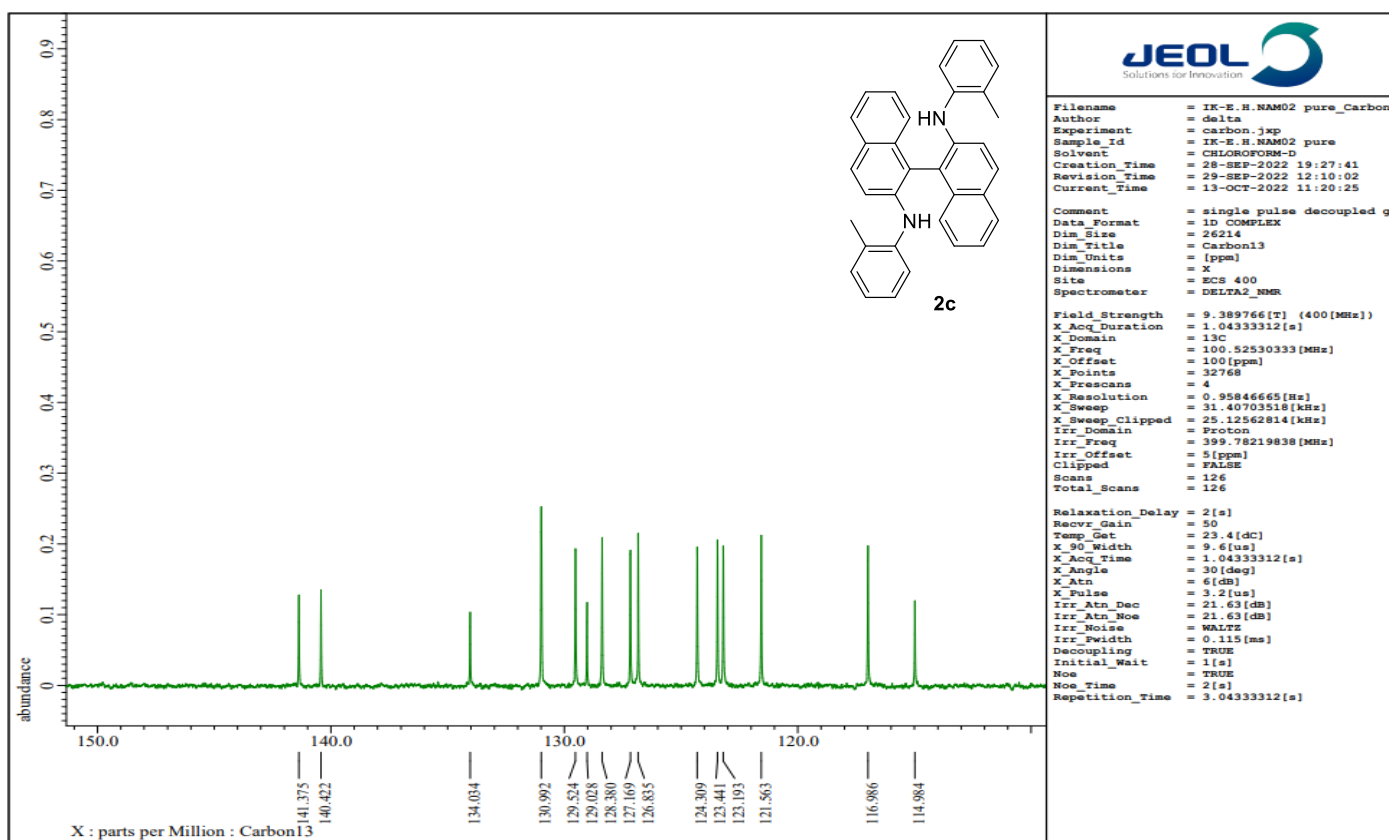
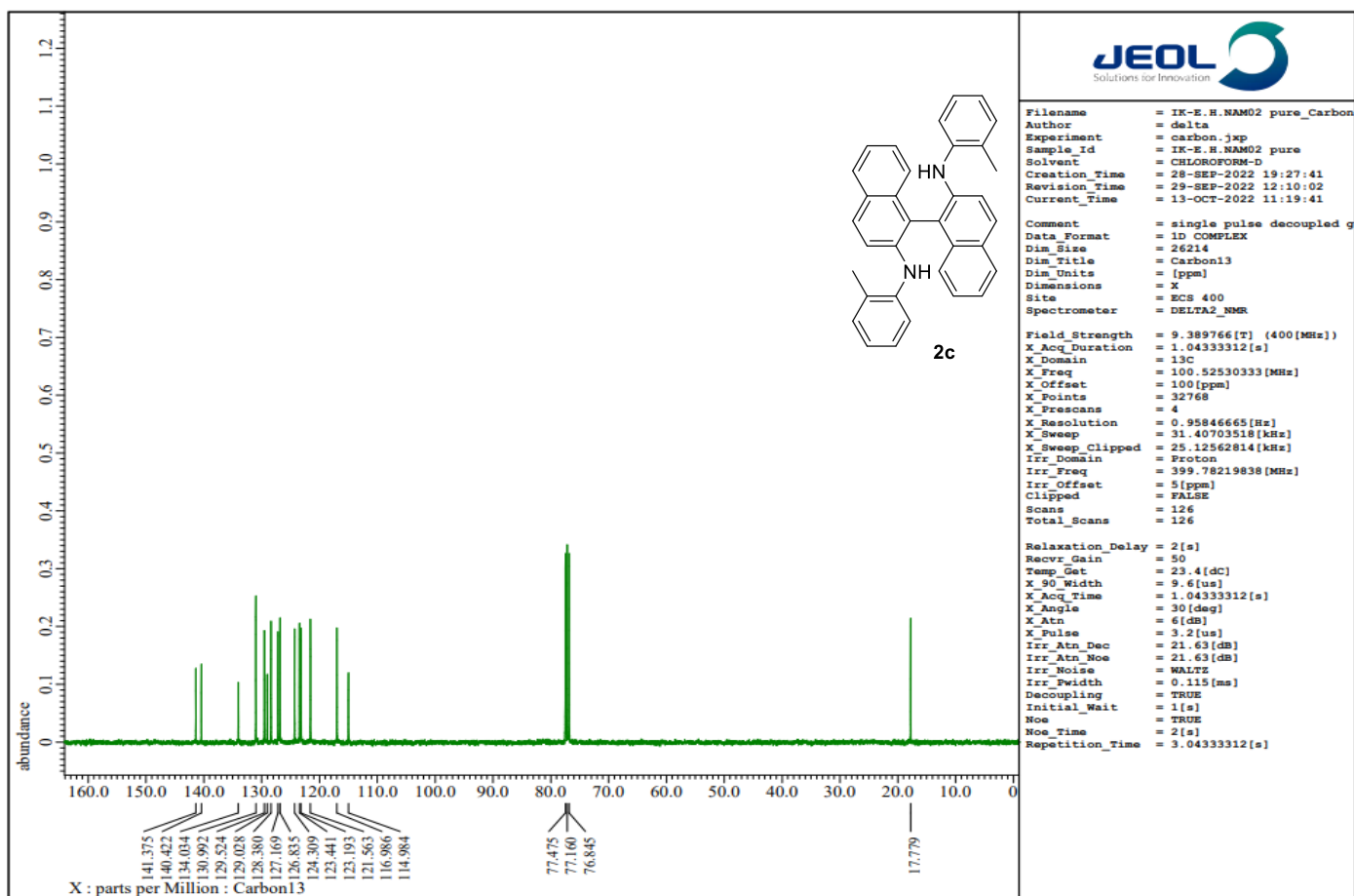
Compound **2b** (¹H NMR, 400 MHz, CDCl₃).



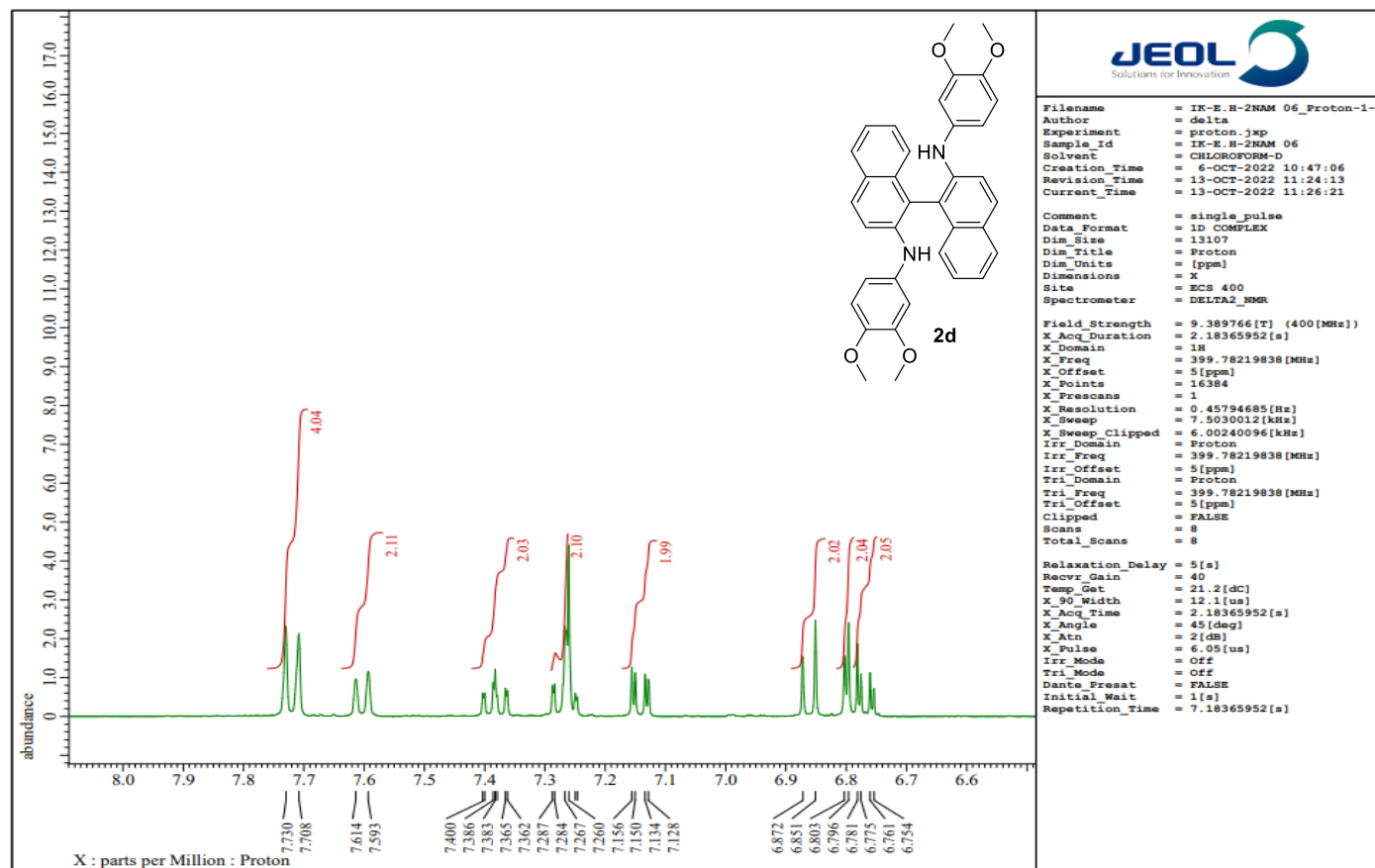
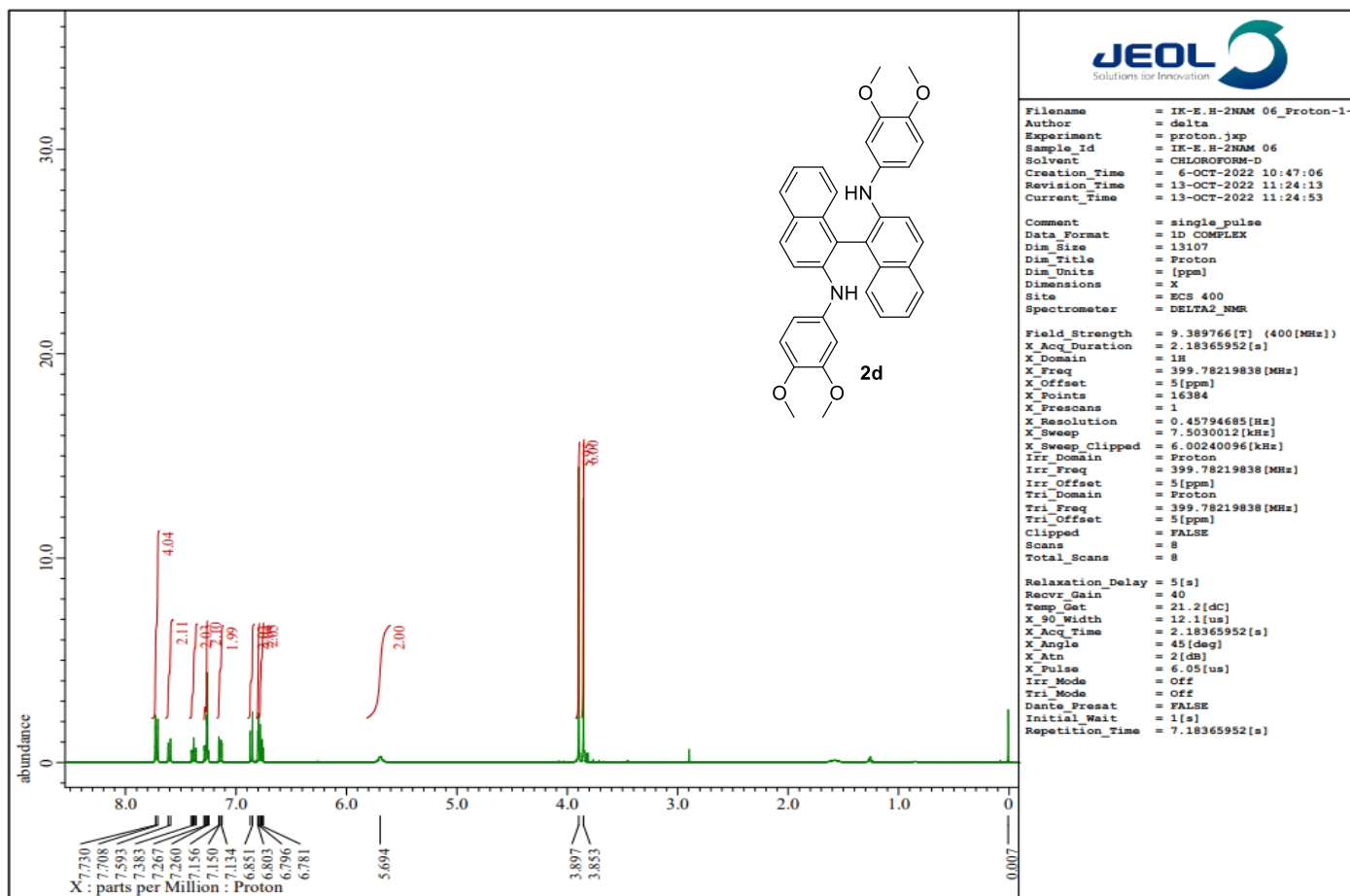
Compound **2b** (^{13}C NMR, 100 MHz, CDCl_3).



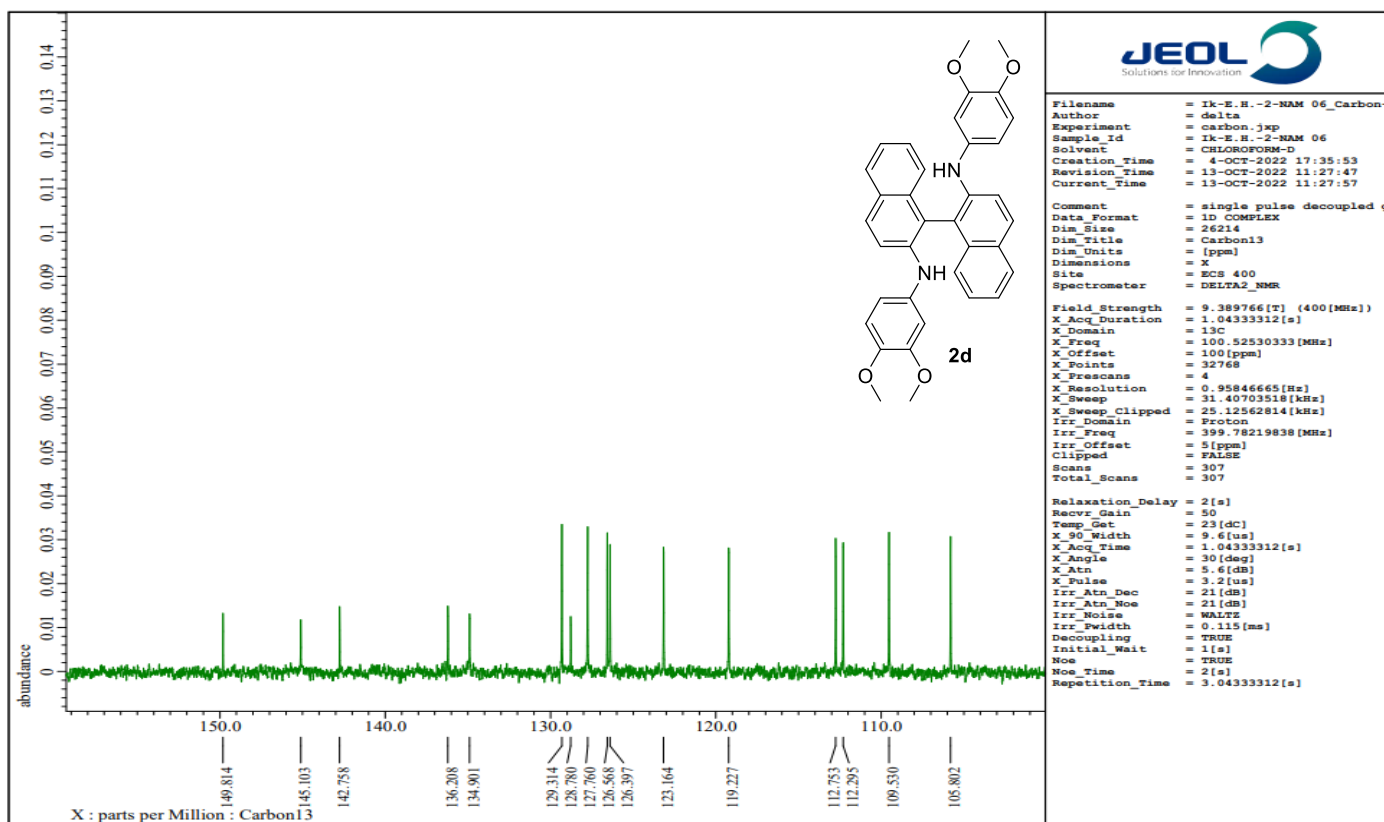
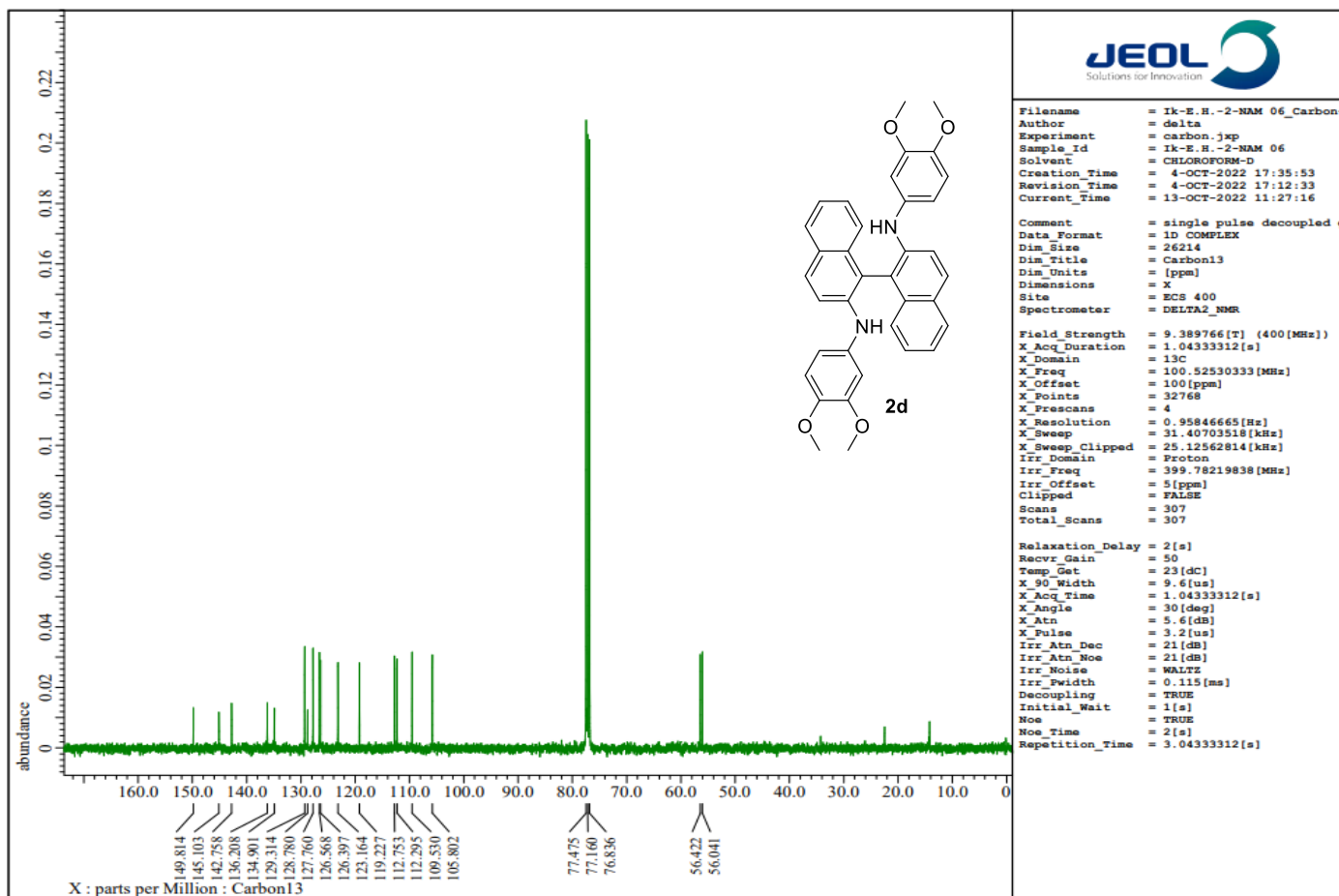
Compound **2c** (^1H NMR, 400 MHz, CDCl_3).



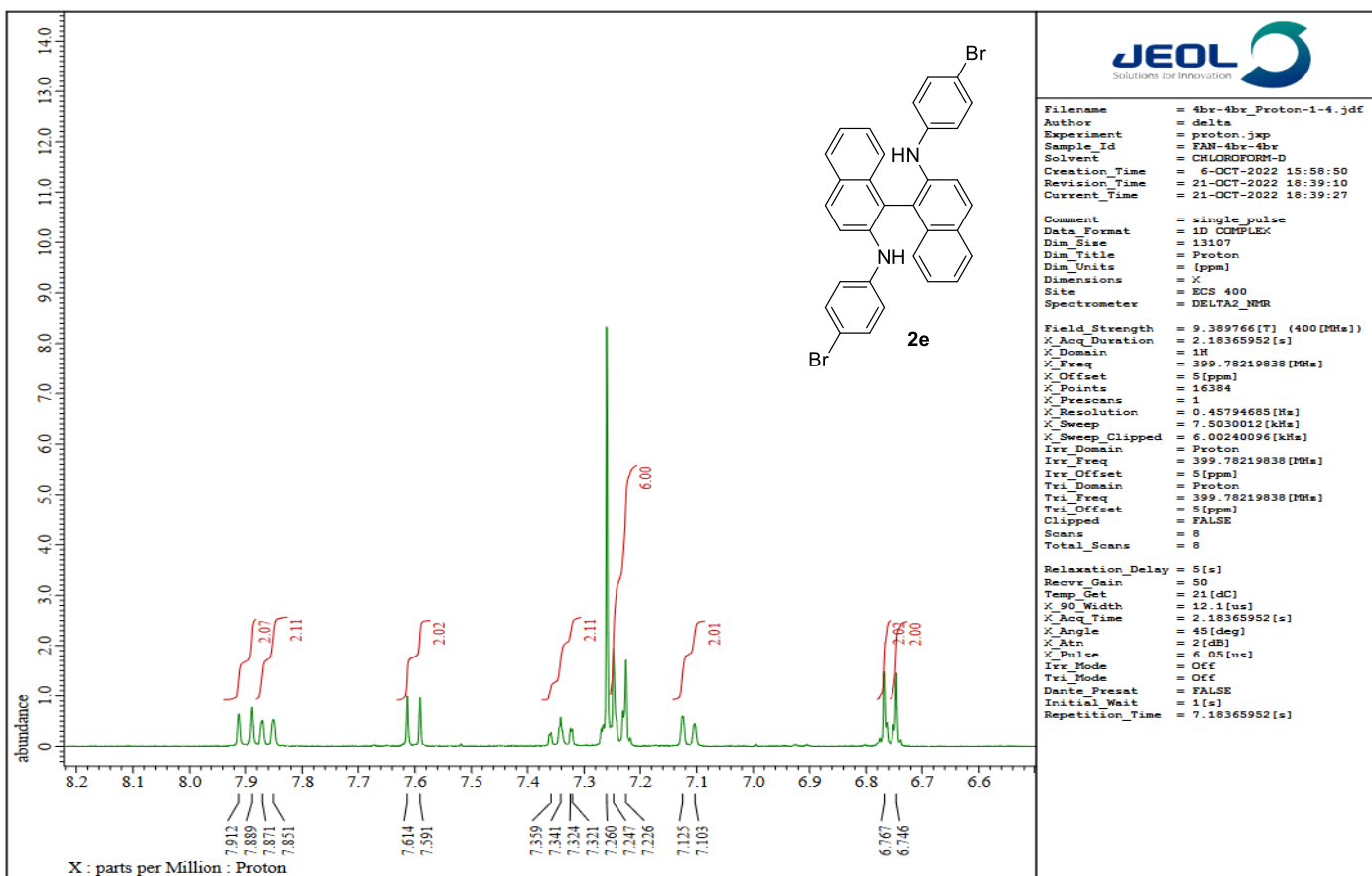
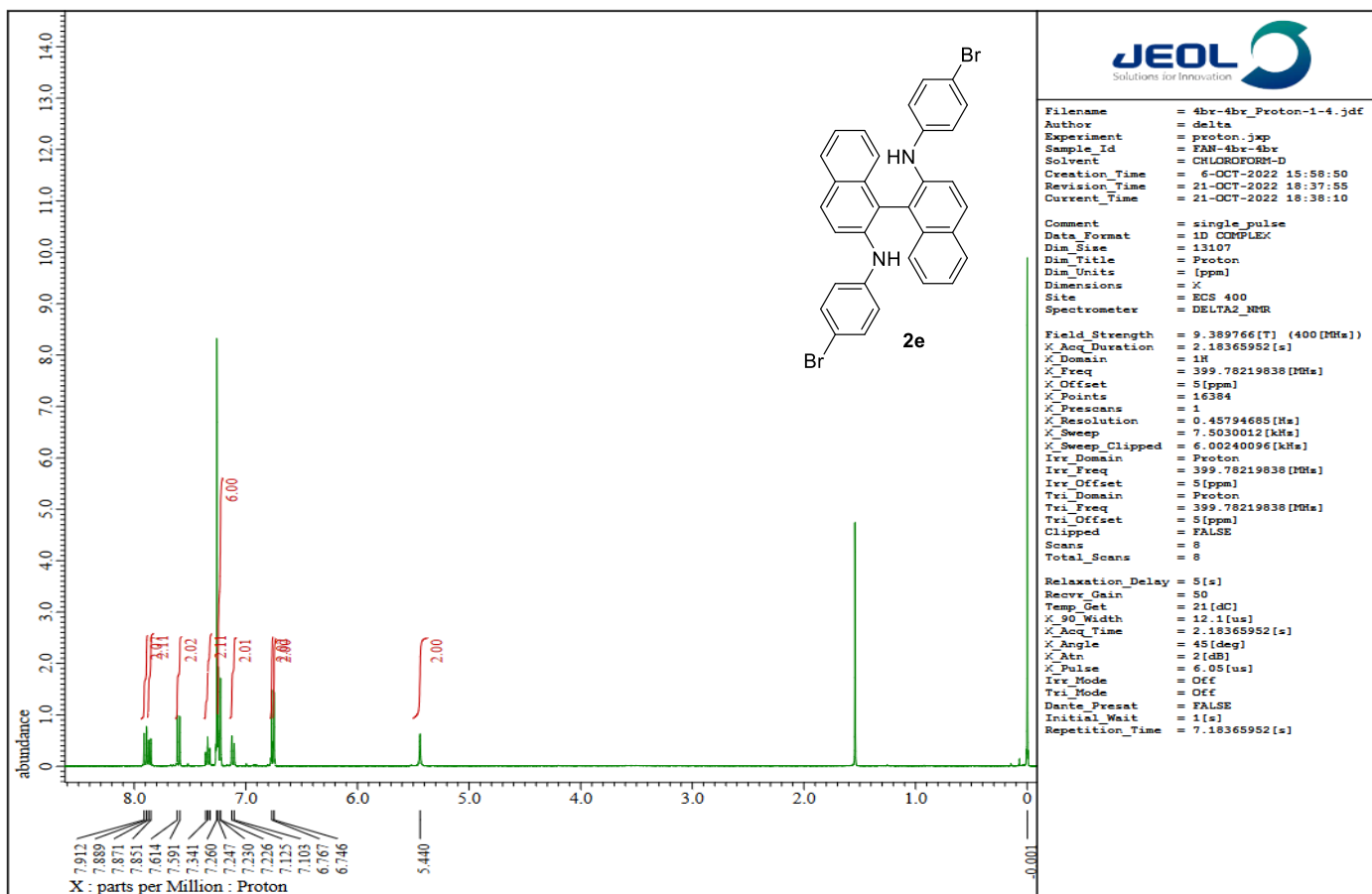
Compound **2c** (^{13}C NMR, 100 MHz, CDCl_3).



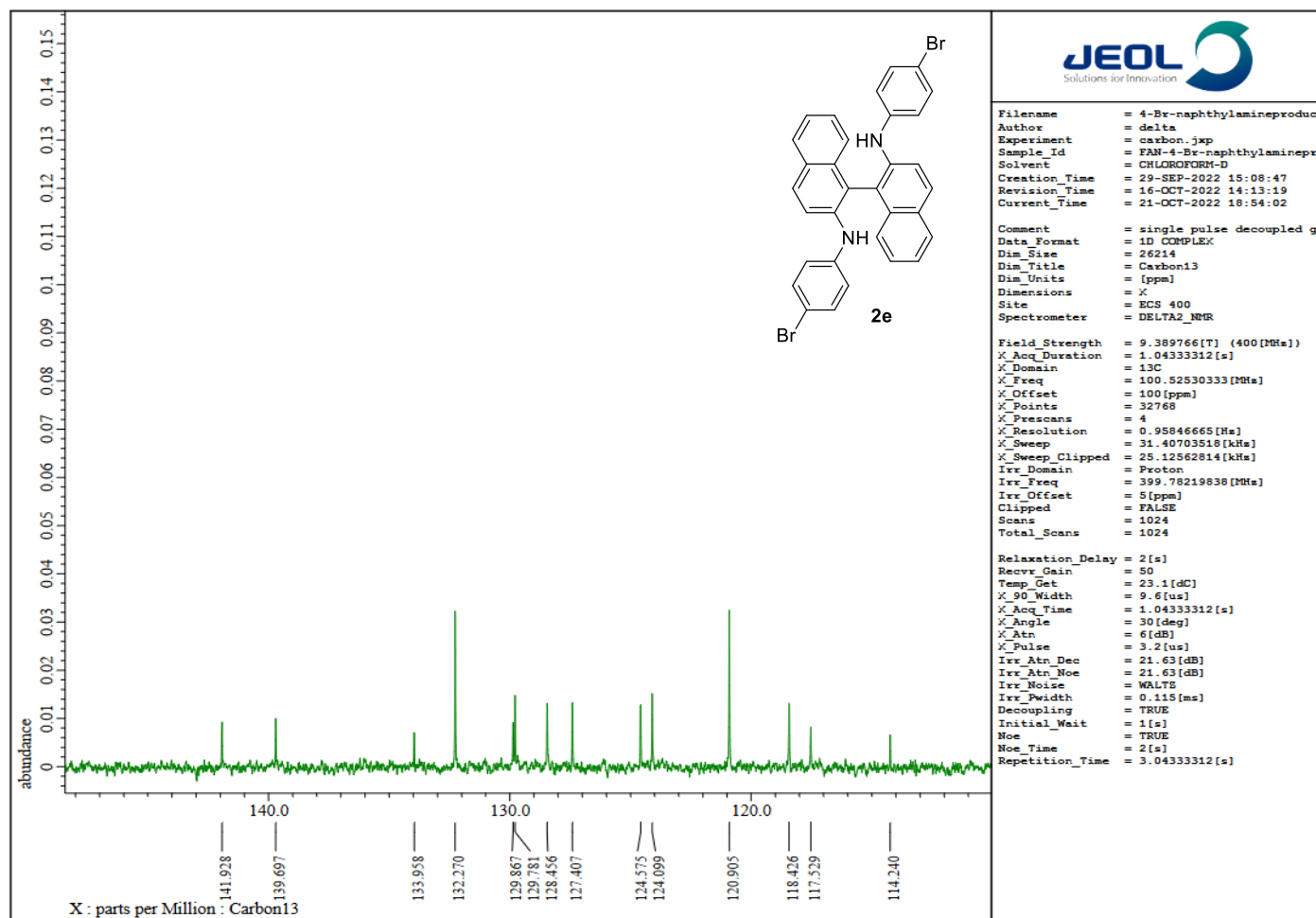
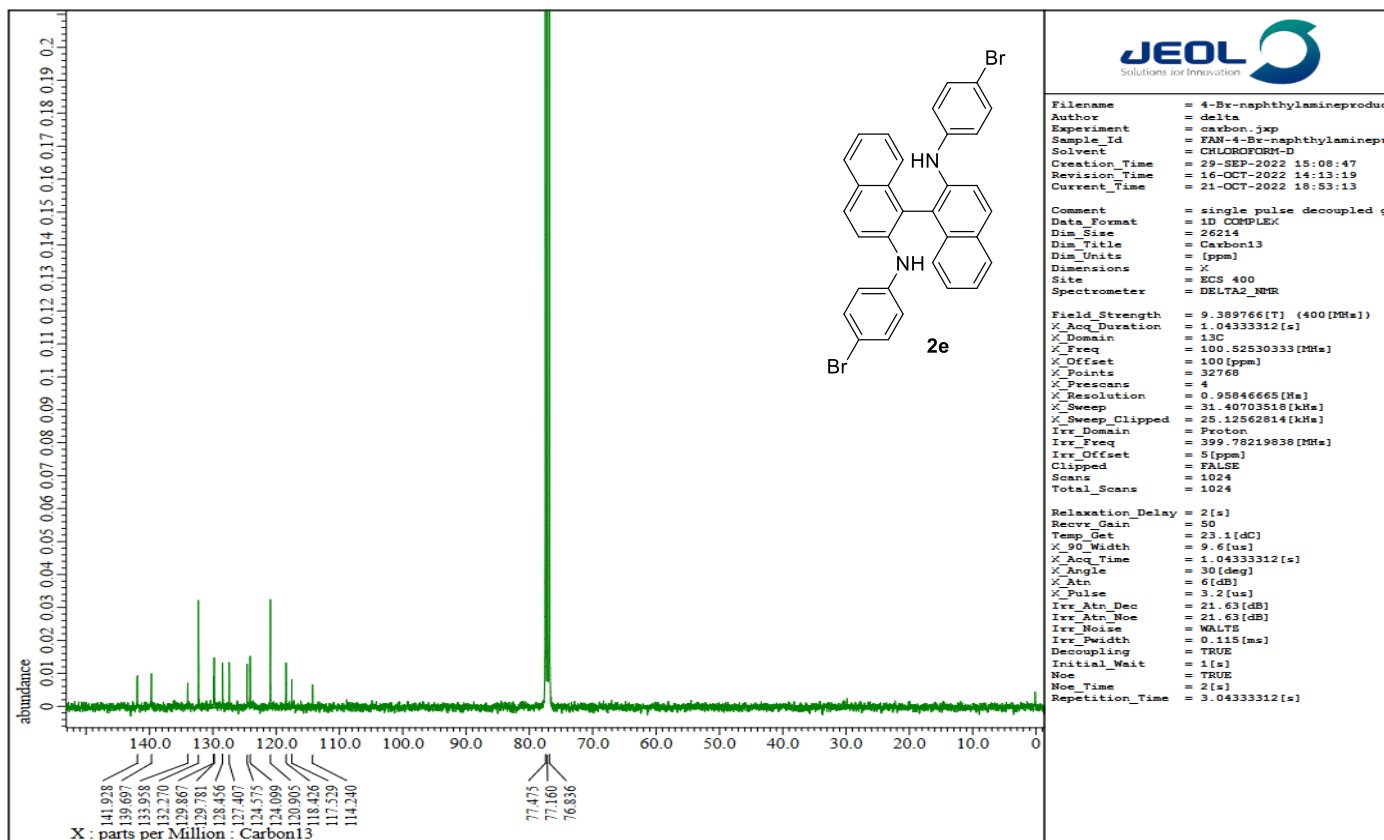
Compound **2d** (¹H NMR, 400 MHz, CDCl₃).



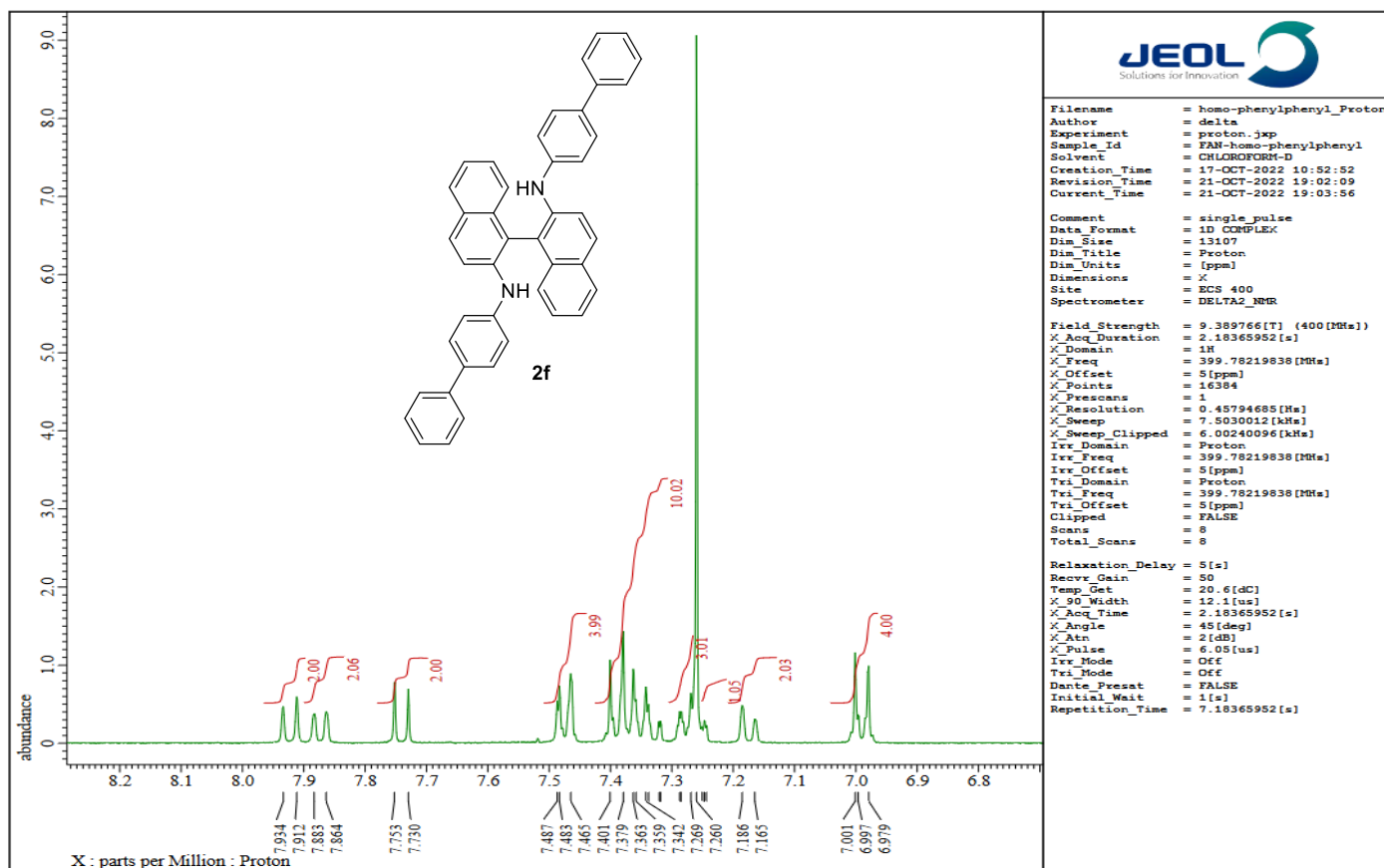
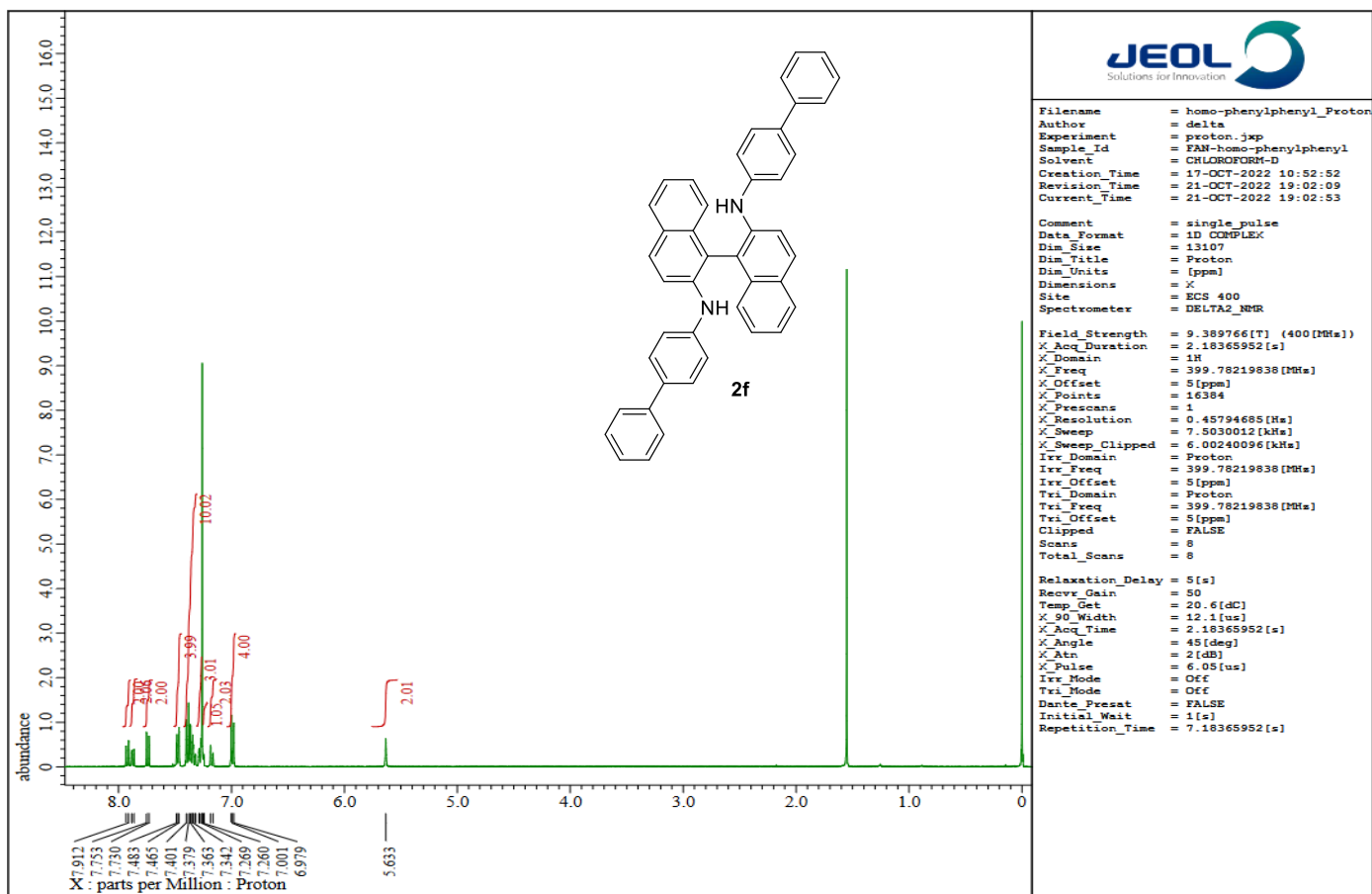
Compound **2d** (^{13}C NMR, 100 MHz, CDCl_3).



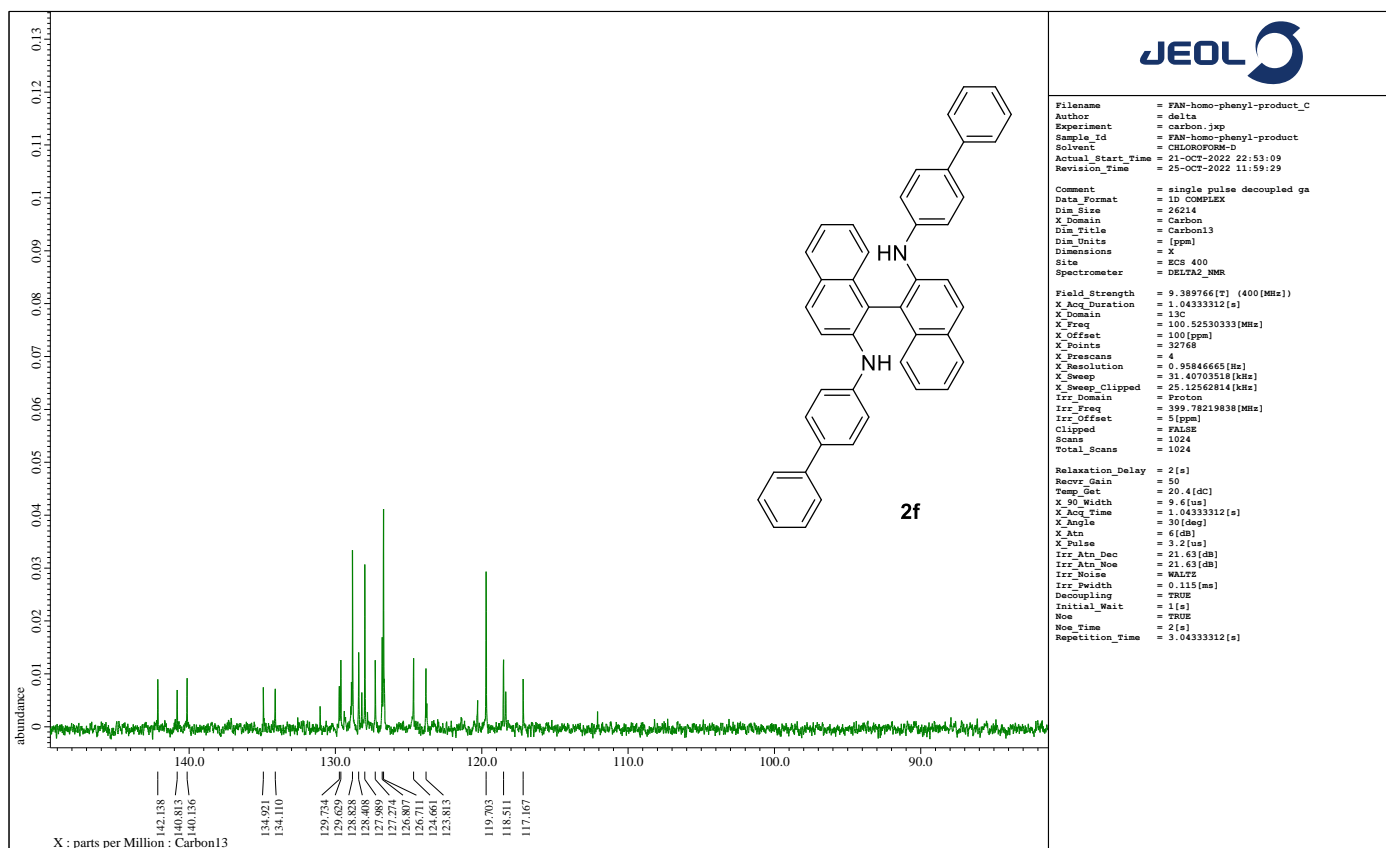
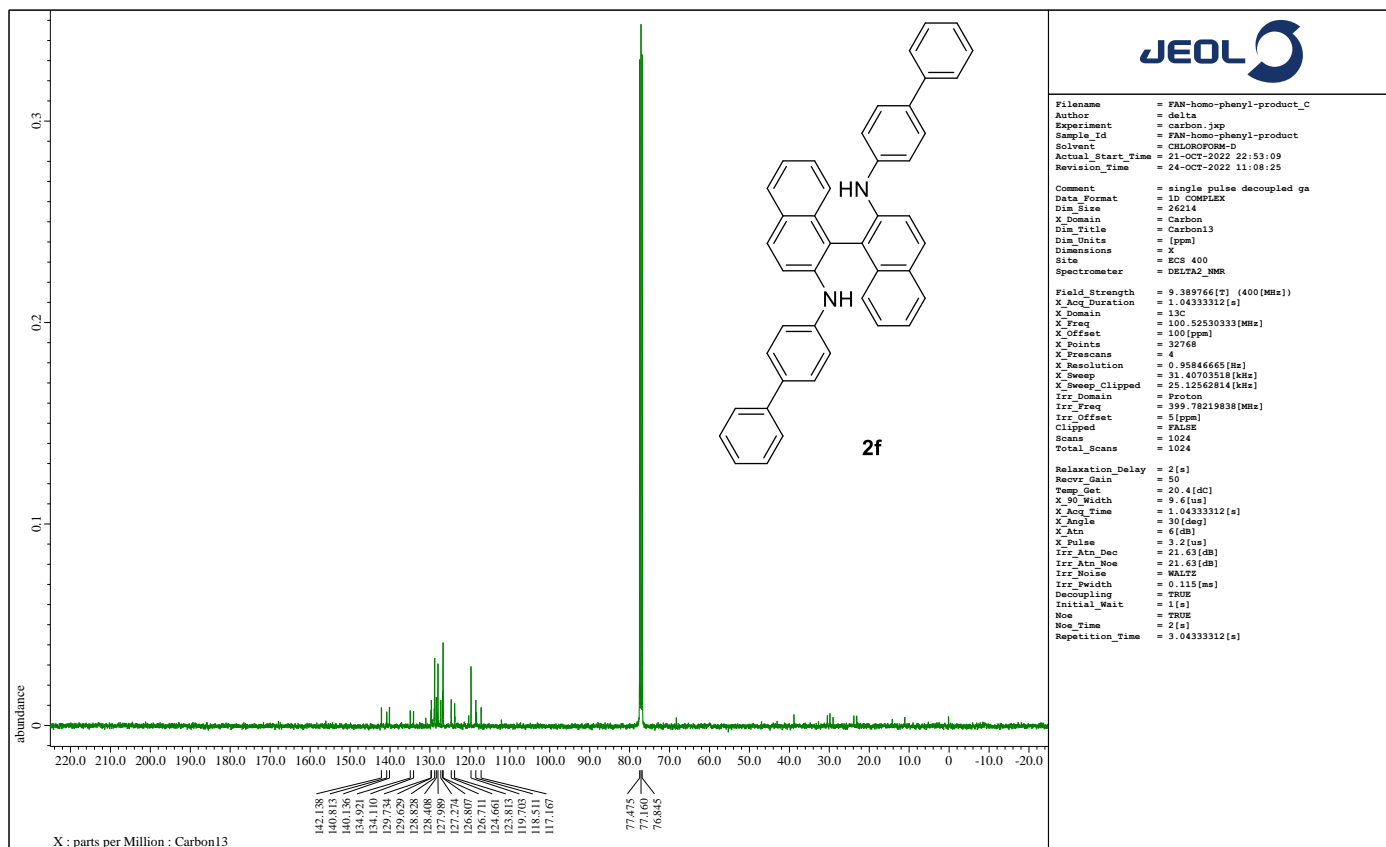
Compound **2e** (^1H NMR, 400 MHz, CDCl_3).



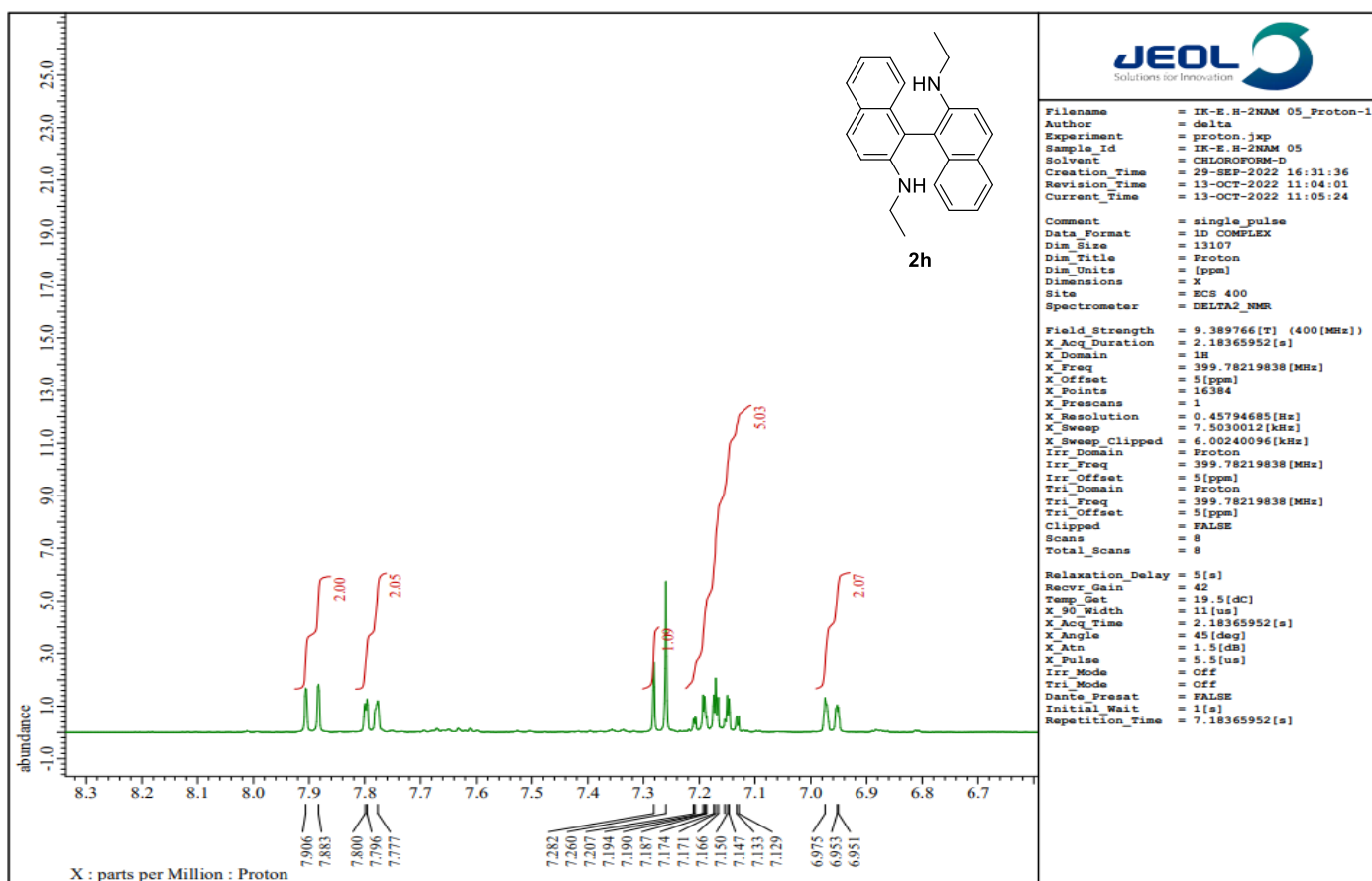
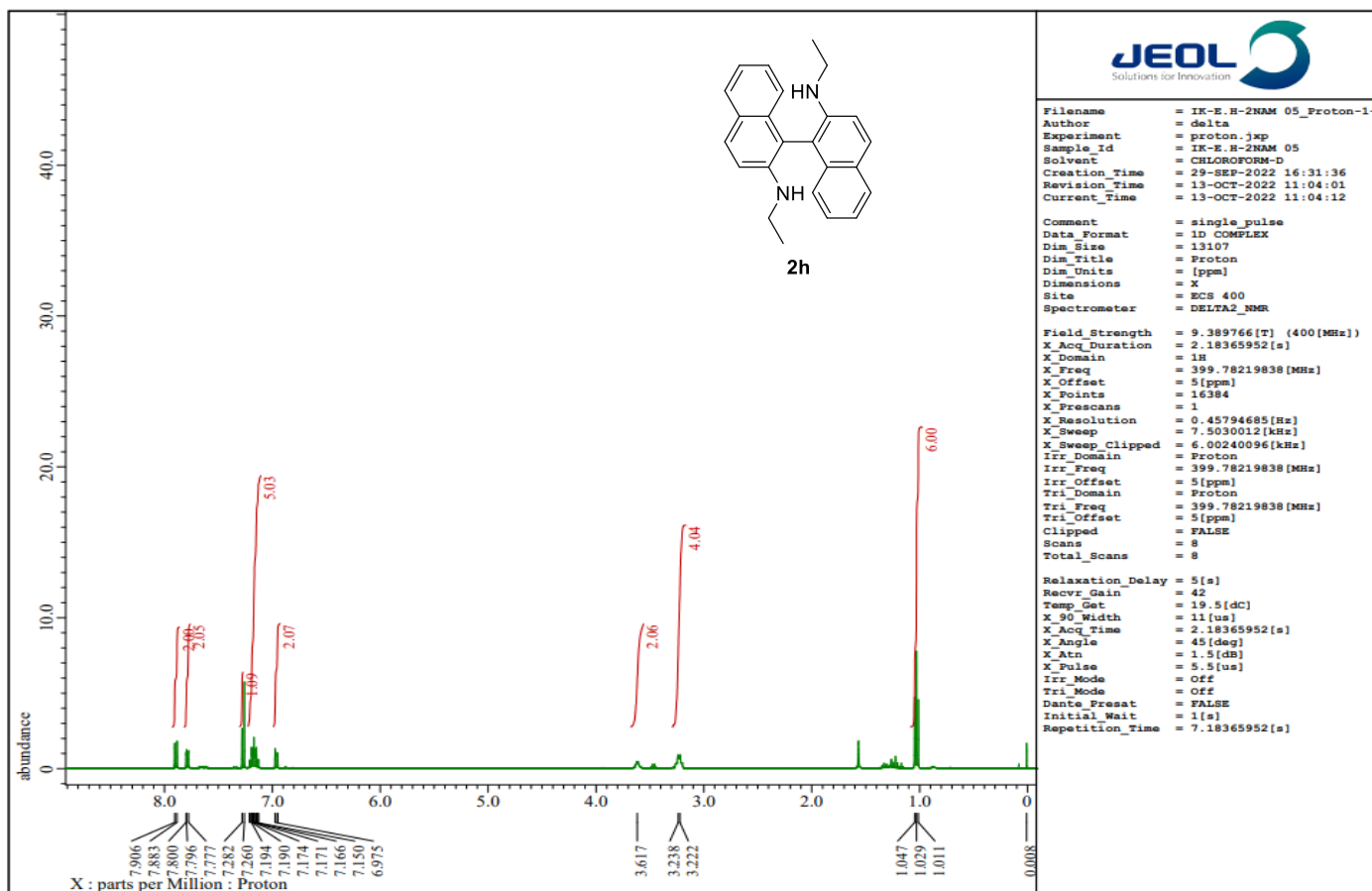
Compound **2e** (¹³C NMR, 100 MHz, CDCl₃).



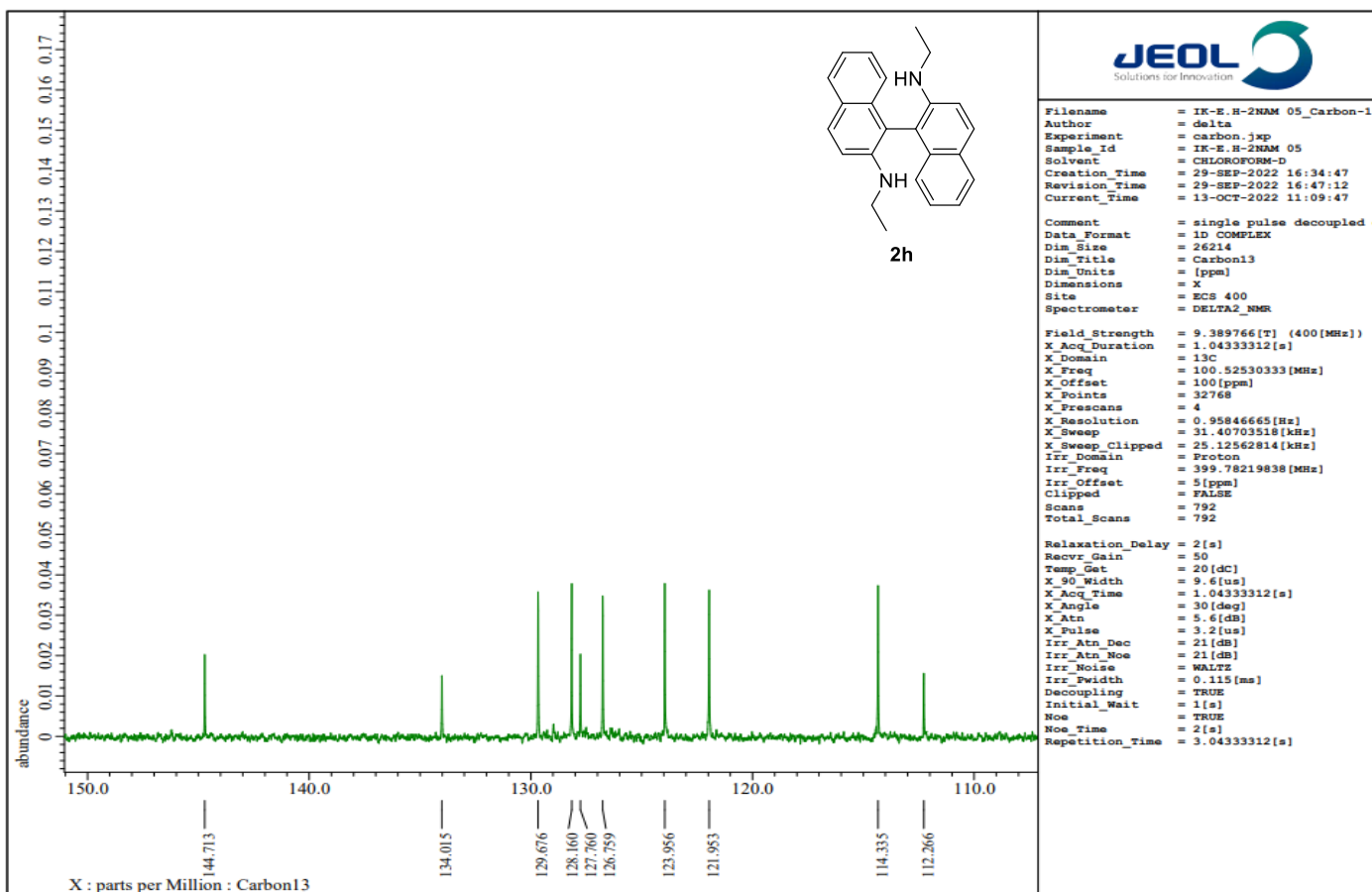
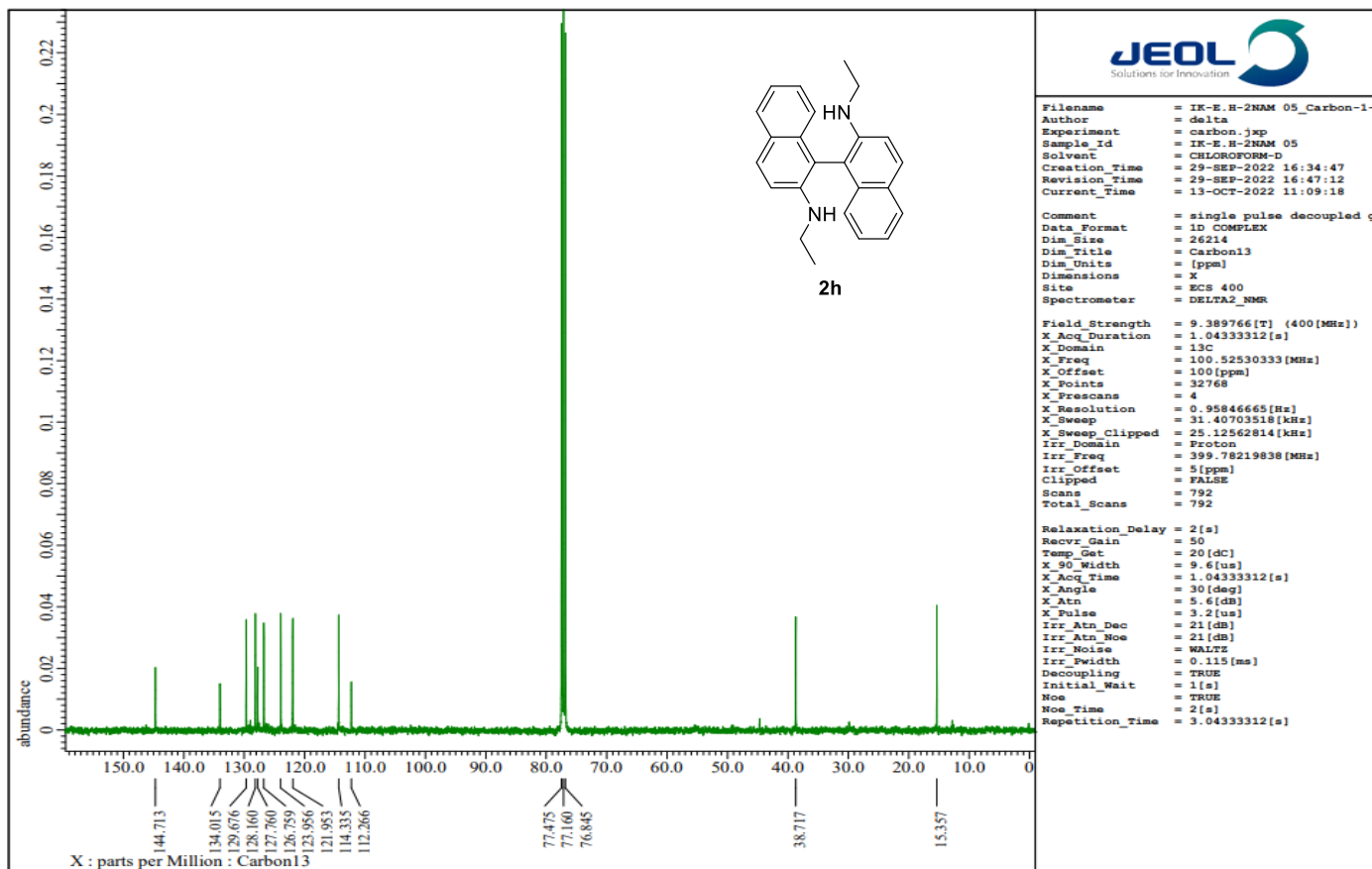
Compound **2f** (¹H NMR, 400 MHz, CDCl₃).



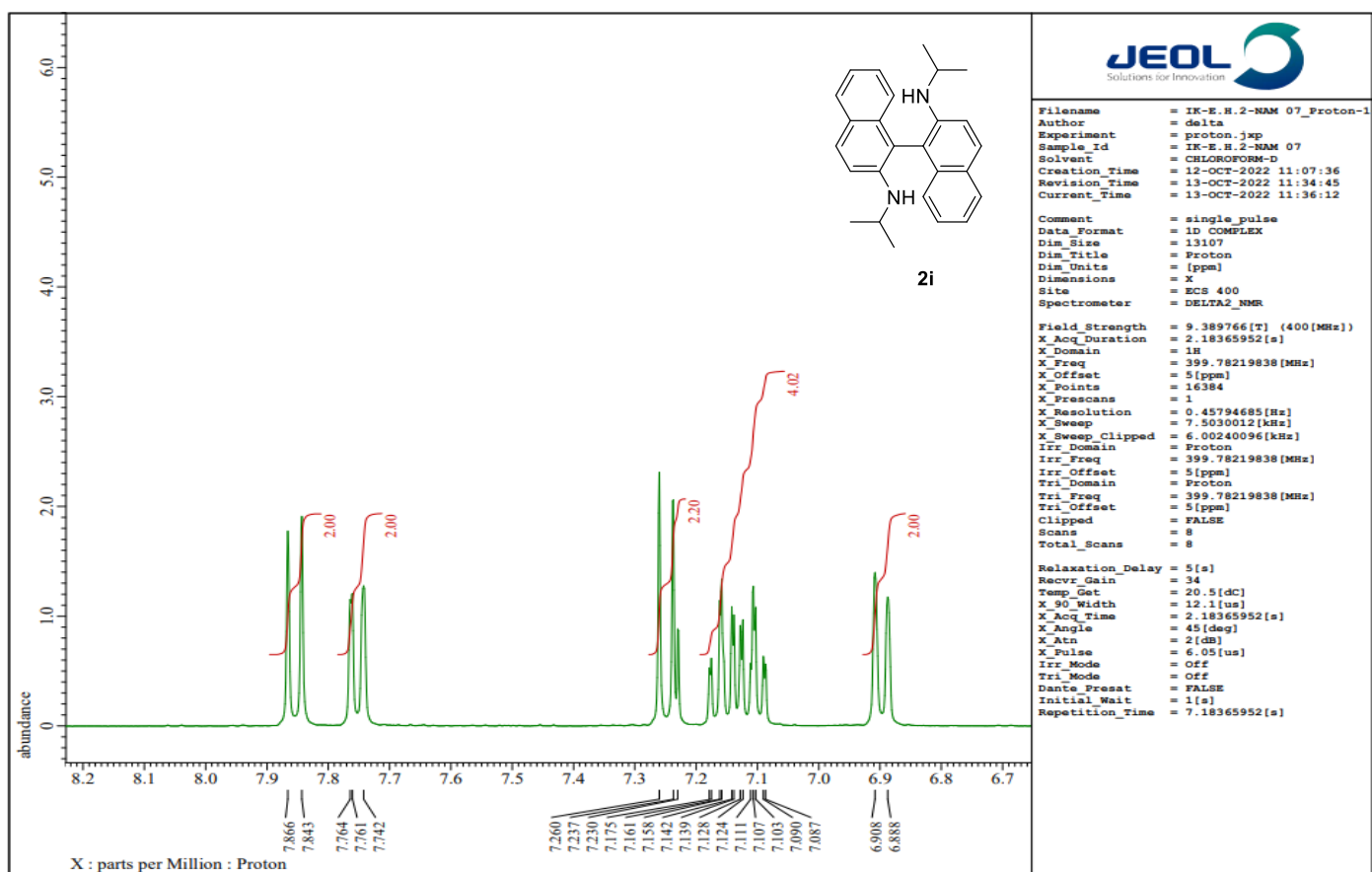
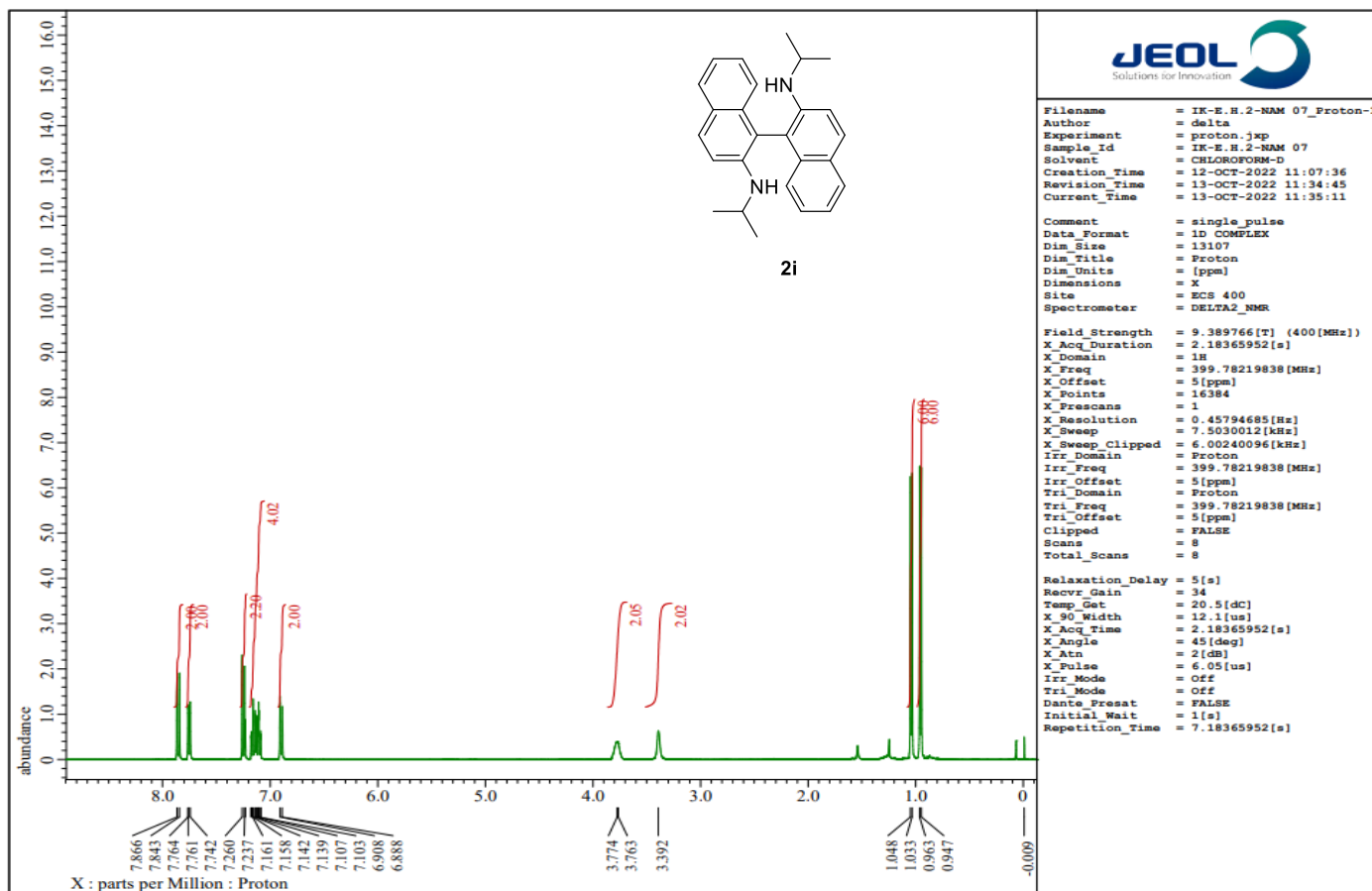
Compound **2f** (^{13}C NMR, 100 MHz, CDCl_3).



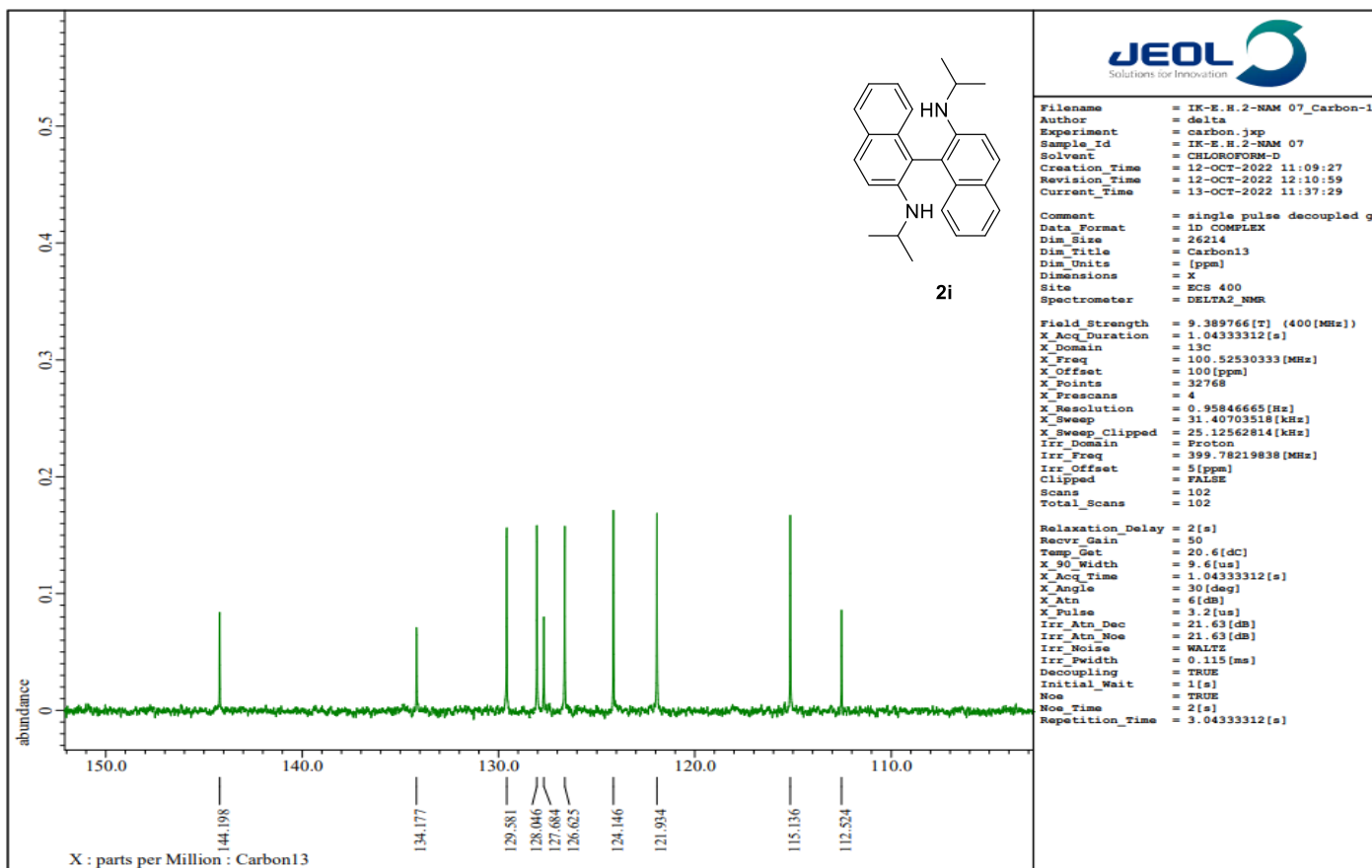
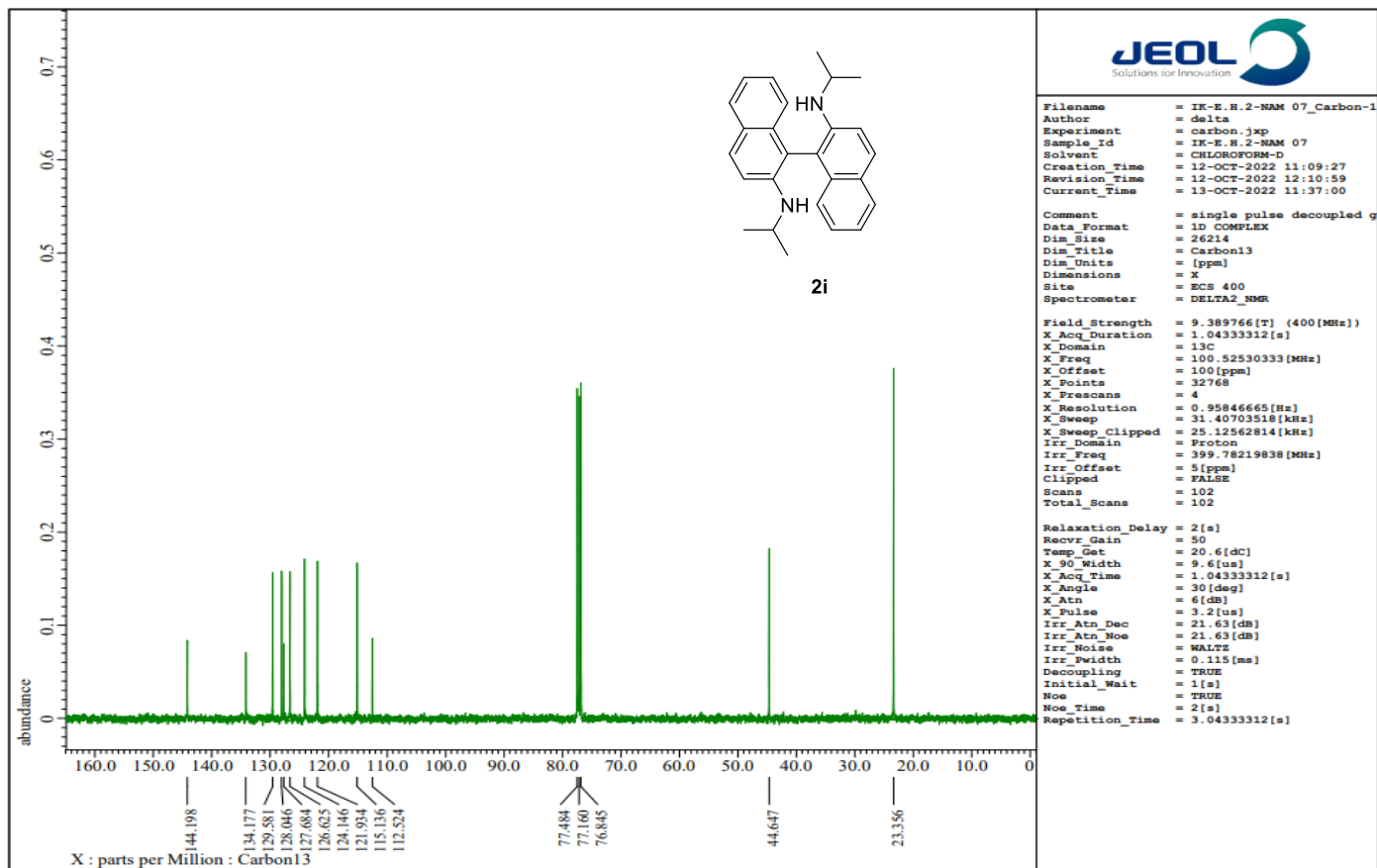
Compound **2h** (^1H NMR, 400 MHz, CDCl_3).



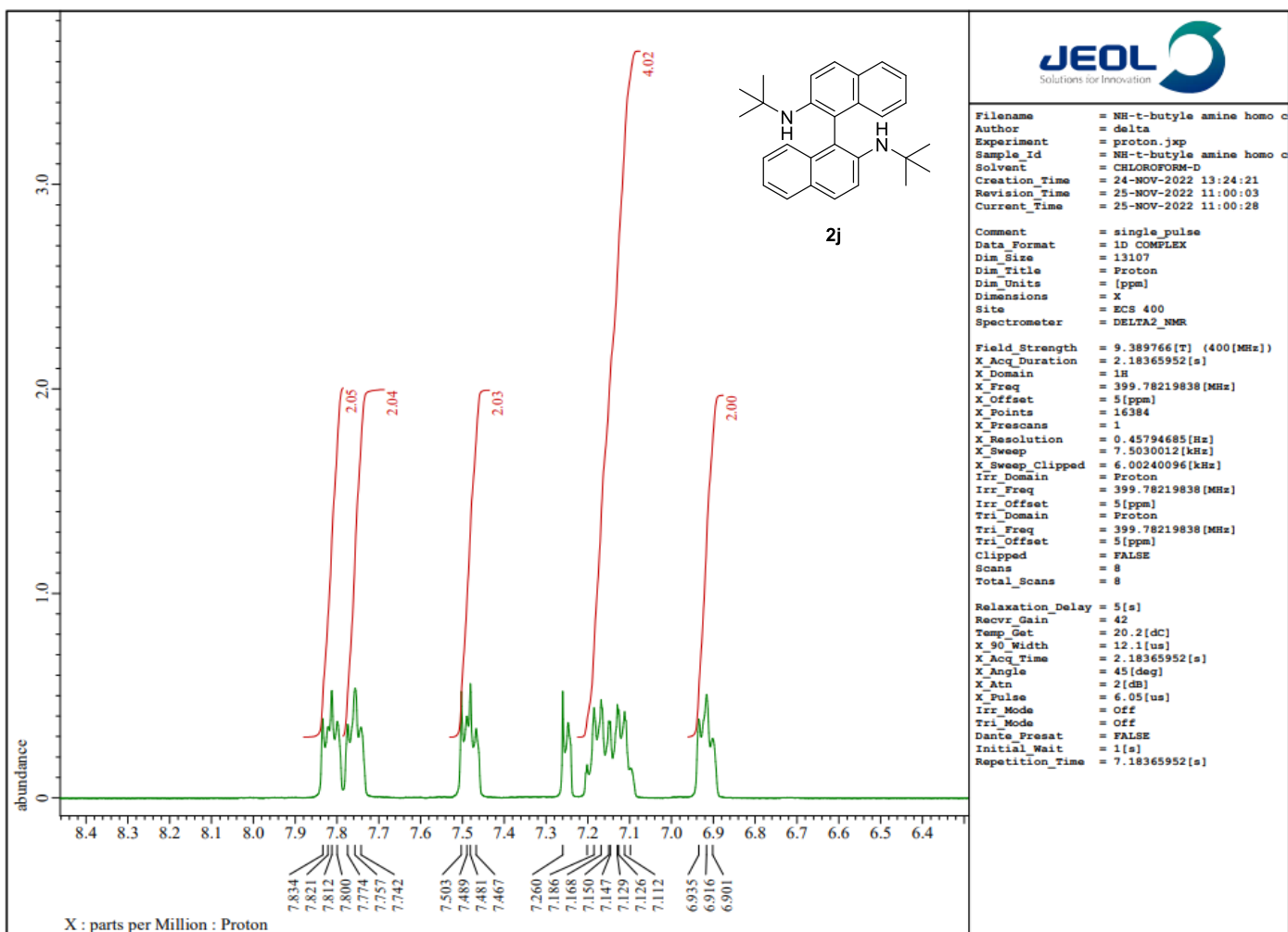
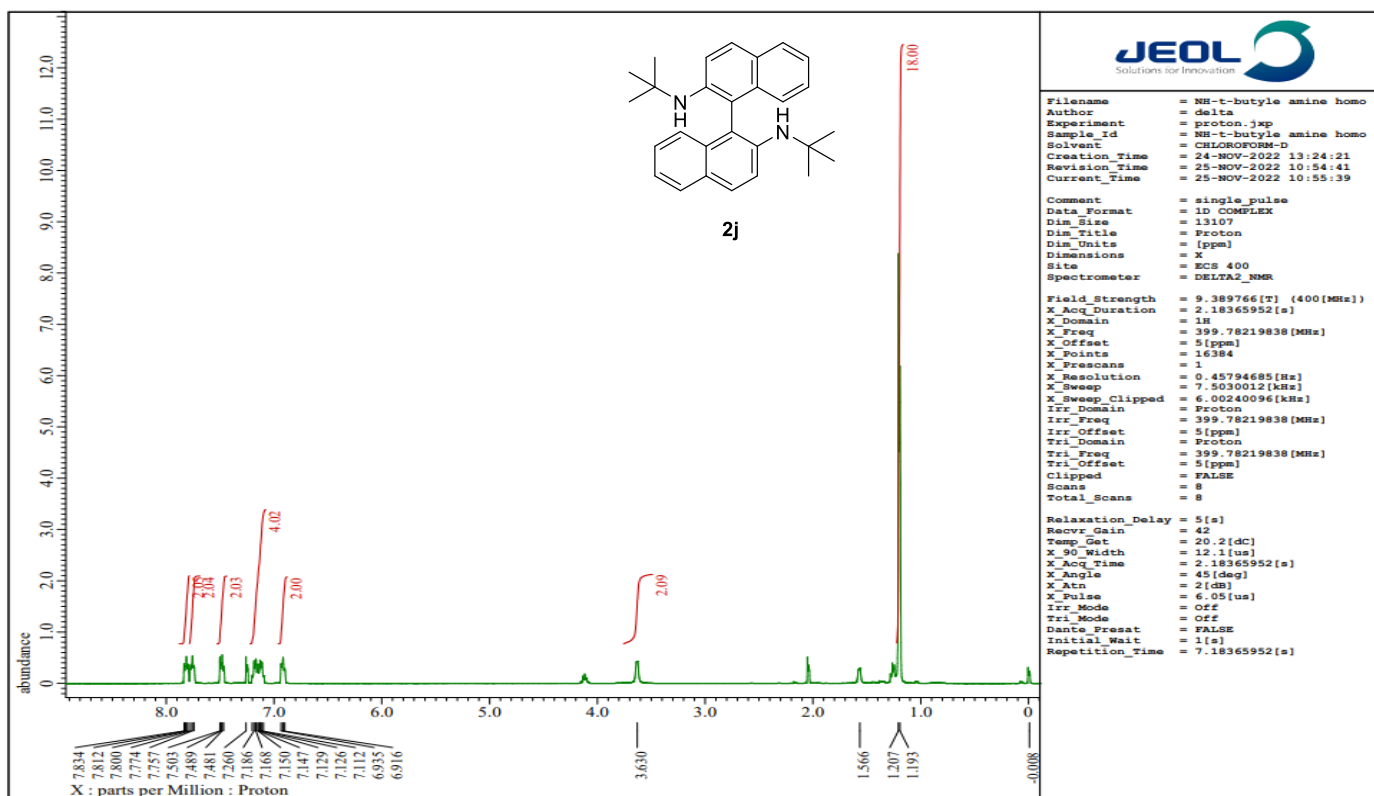
Compound **2h** (^{13}C NMR, 100 MHz, CDCl_3).



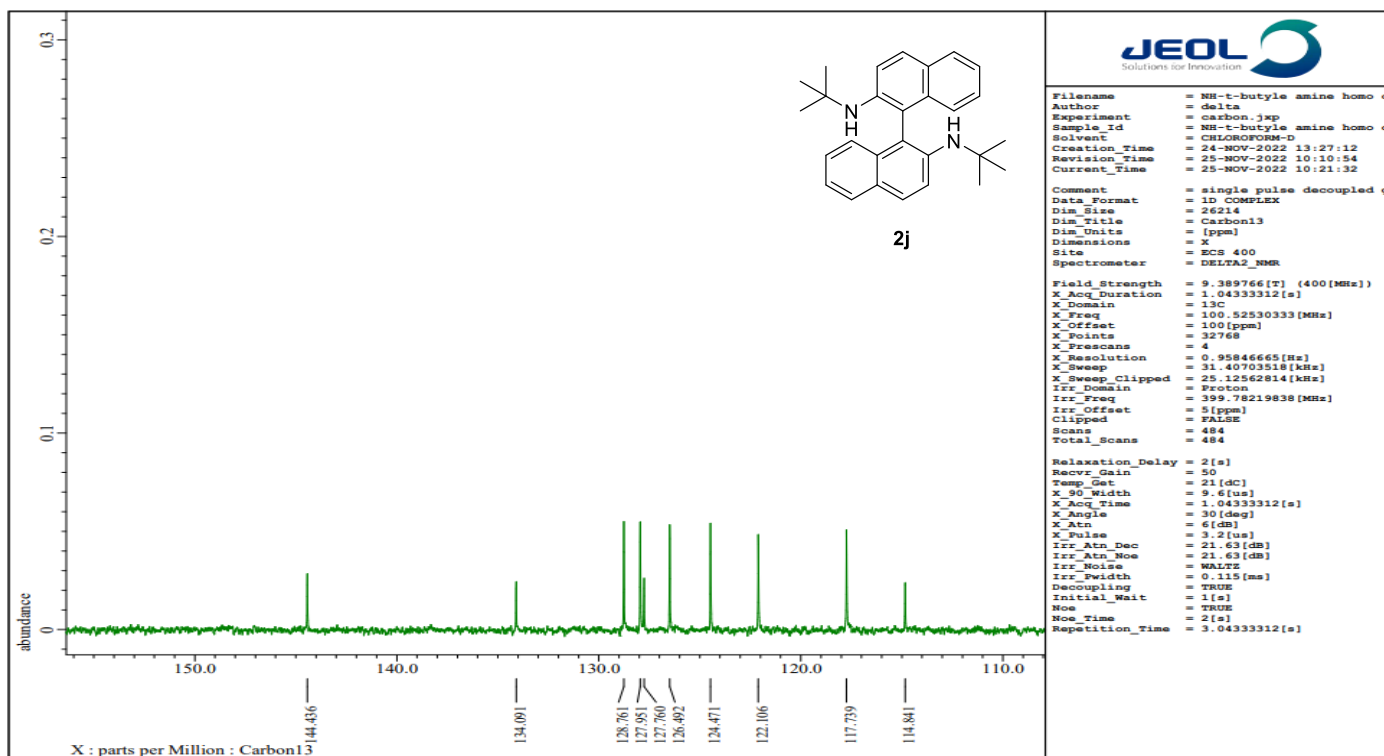
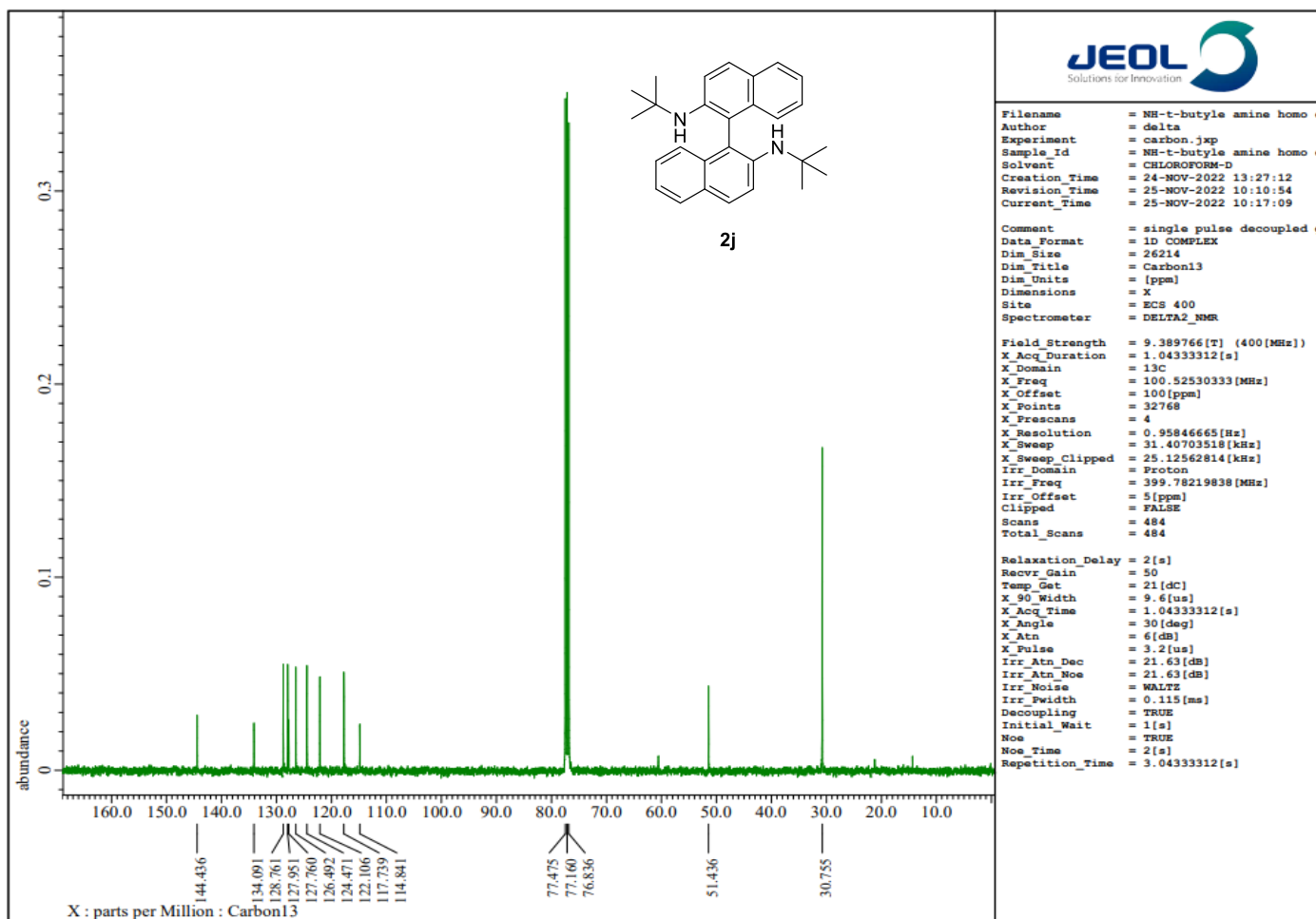
Compound **2i** (¹H NMR, 400 MHz, CDCl₃).



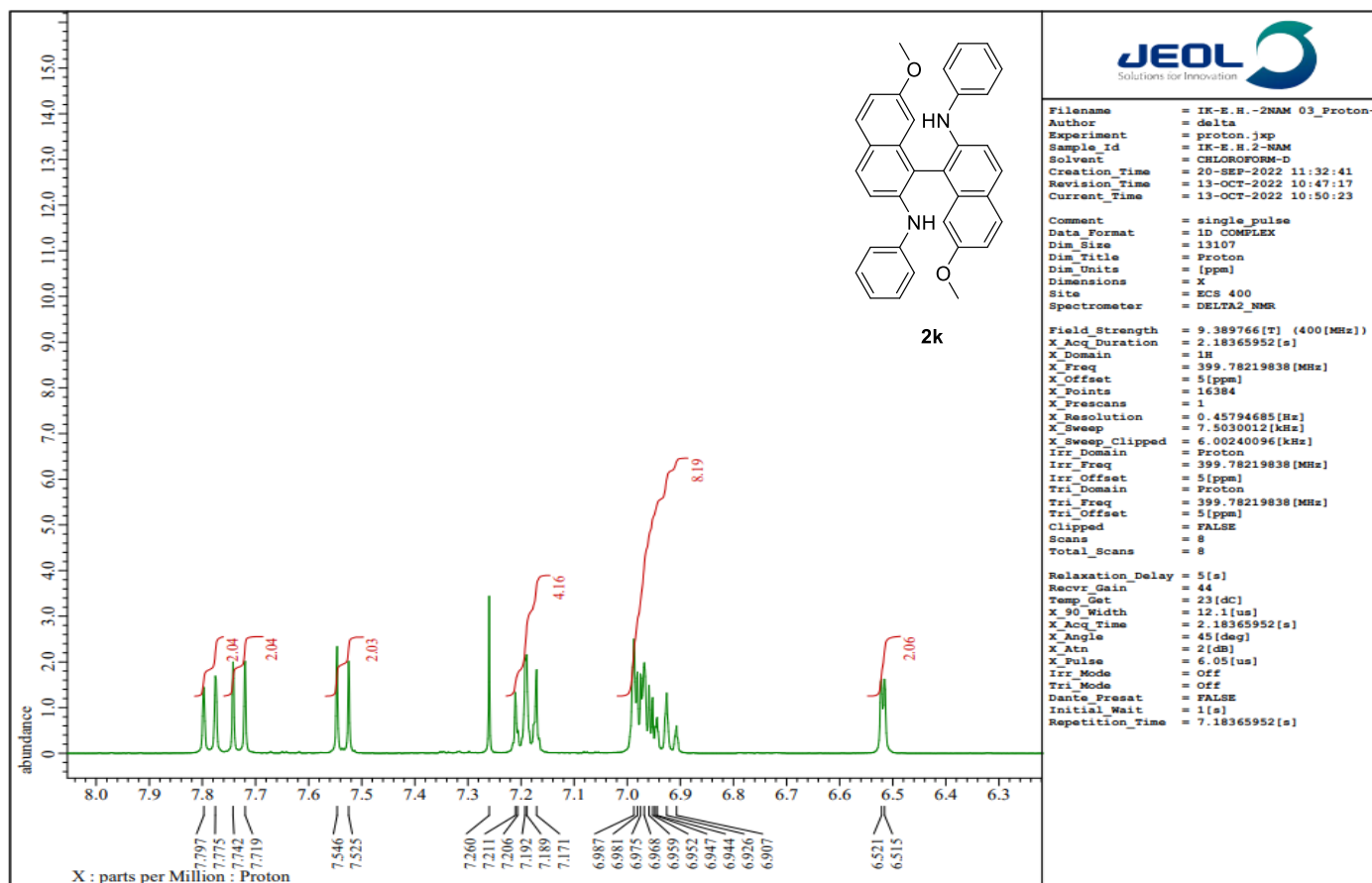
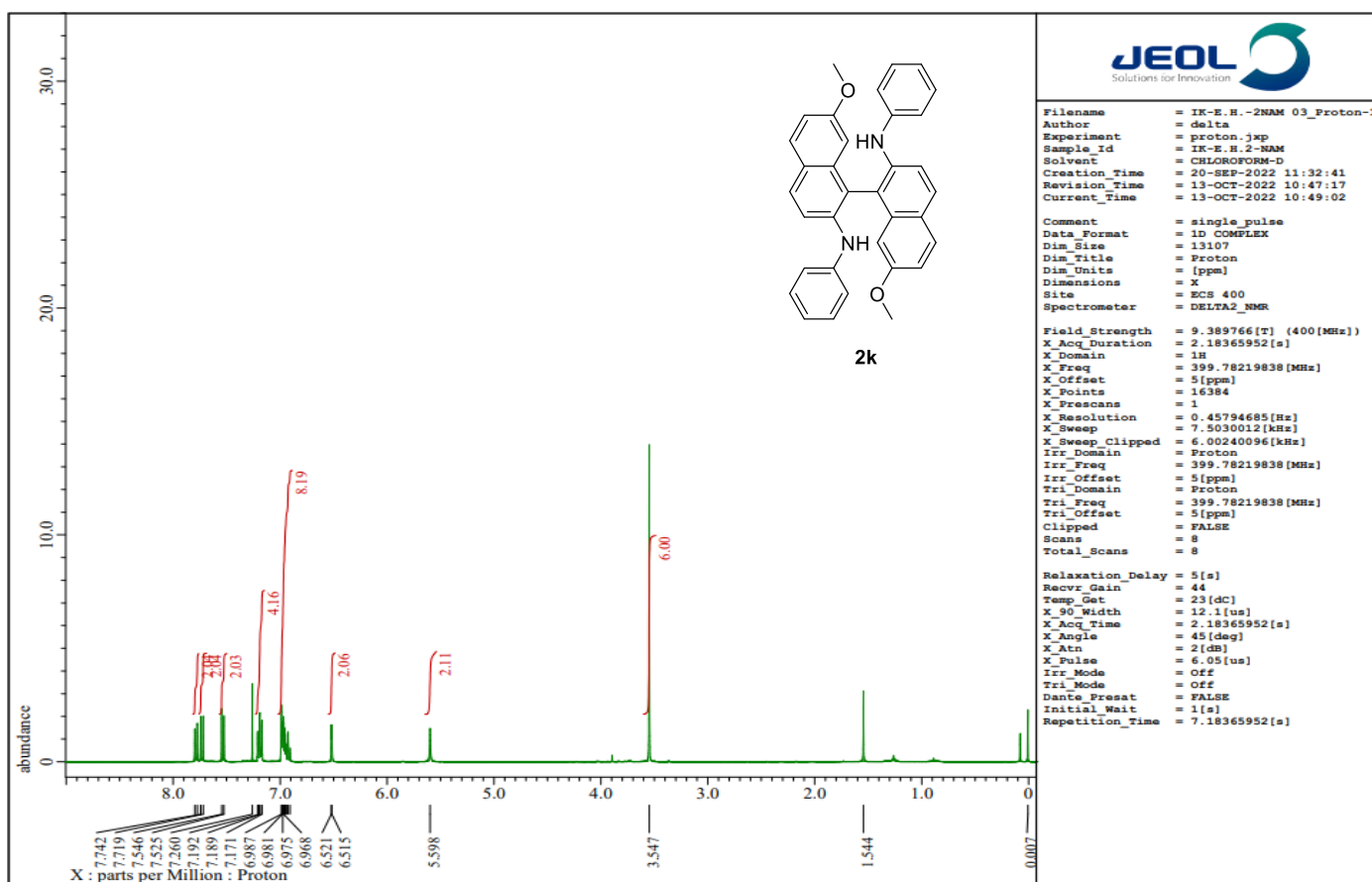
Compound **2i** (¹³C NMR, 100 MHz, CDCl₃).



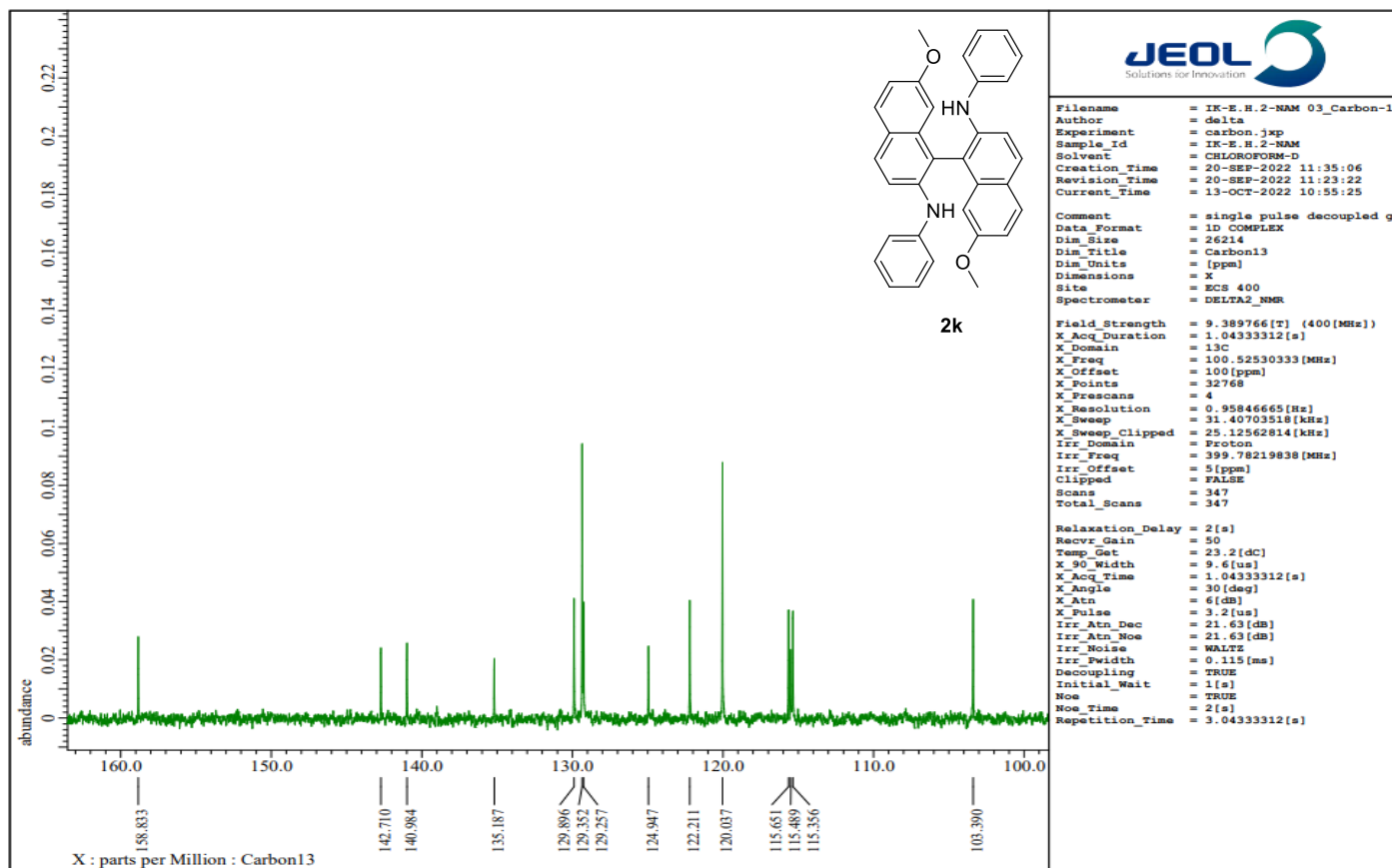
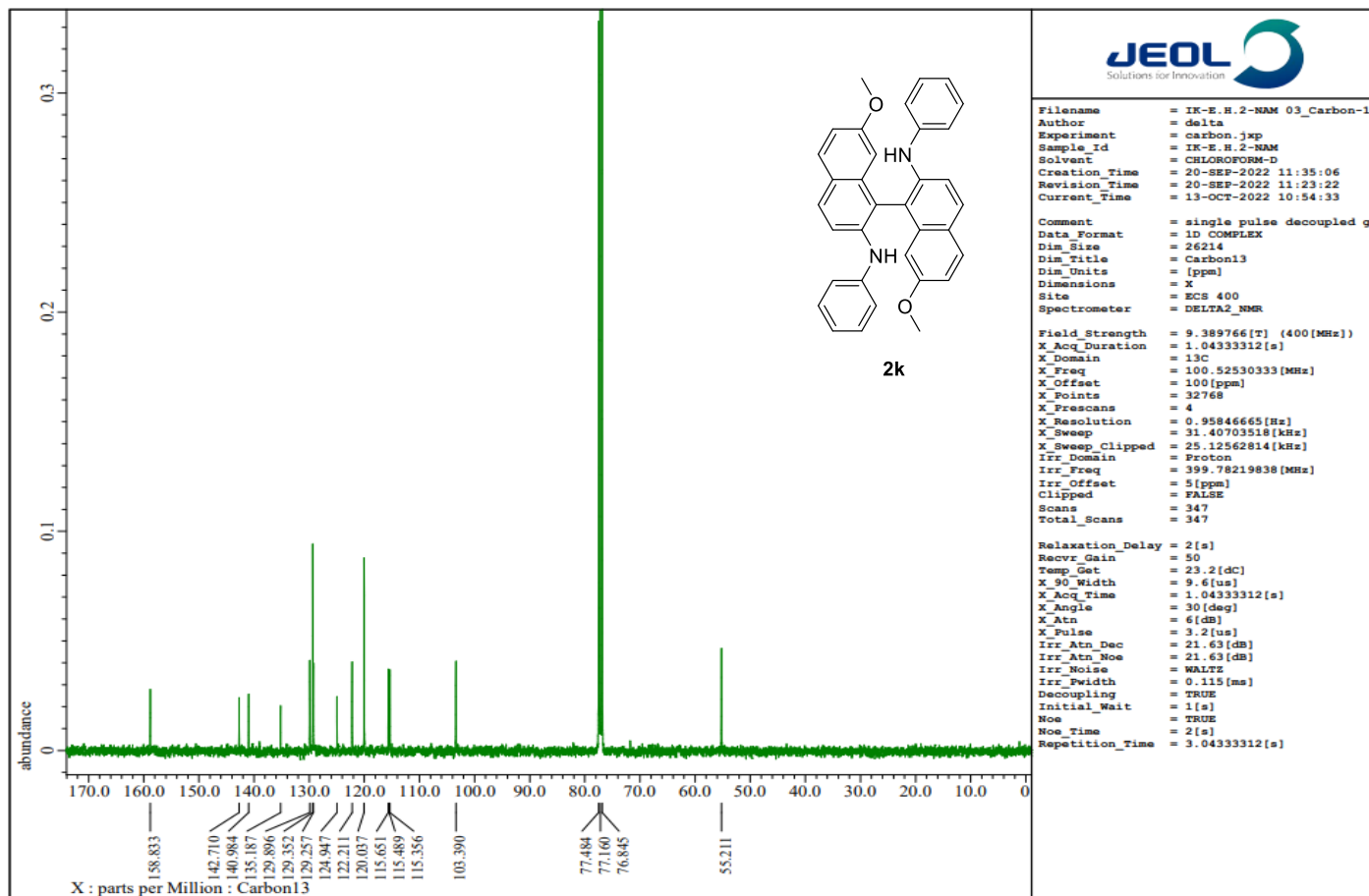
Compound **2j** (^1H NMR, 400 MHz, CDCl_3).



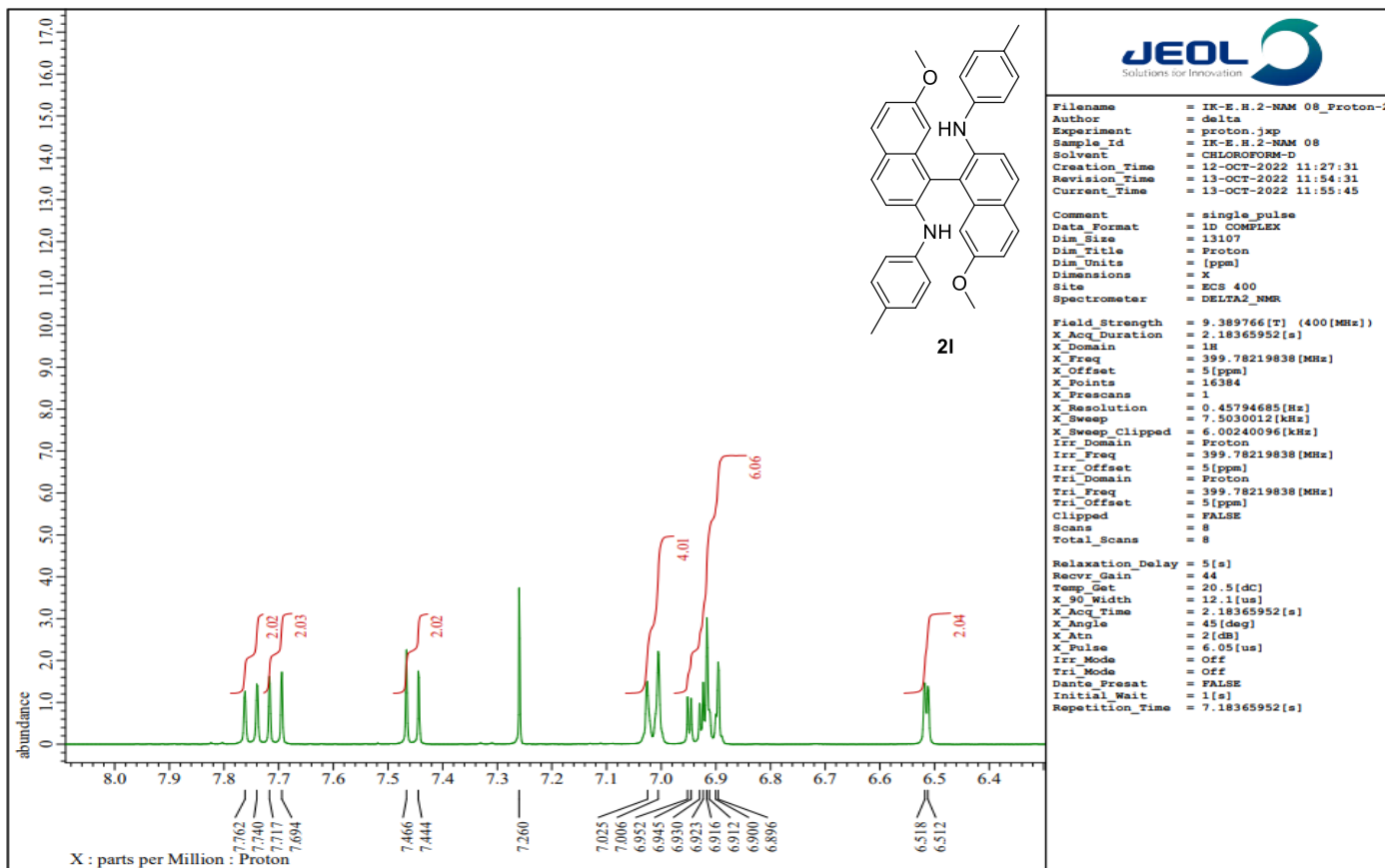
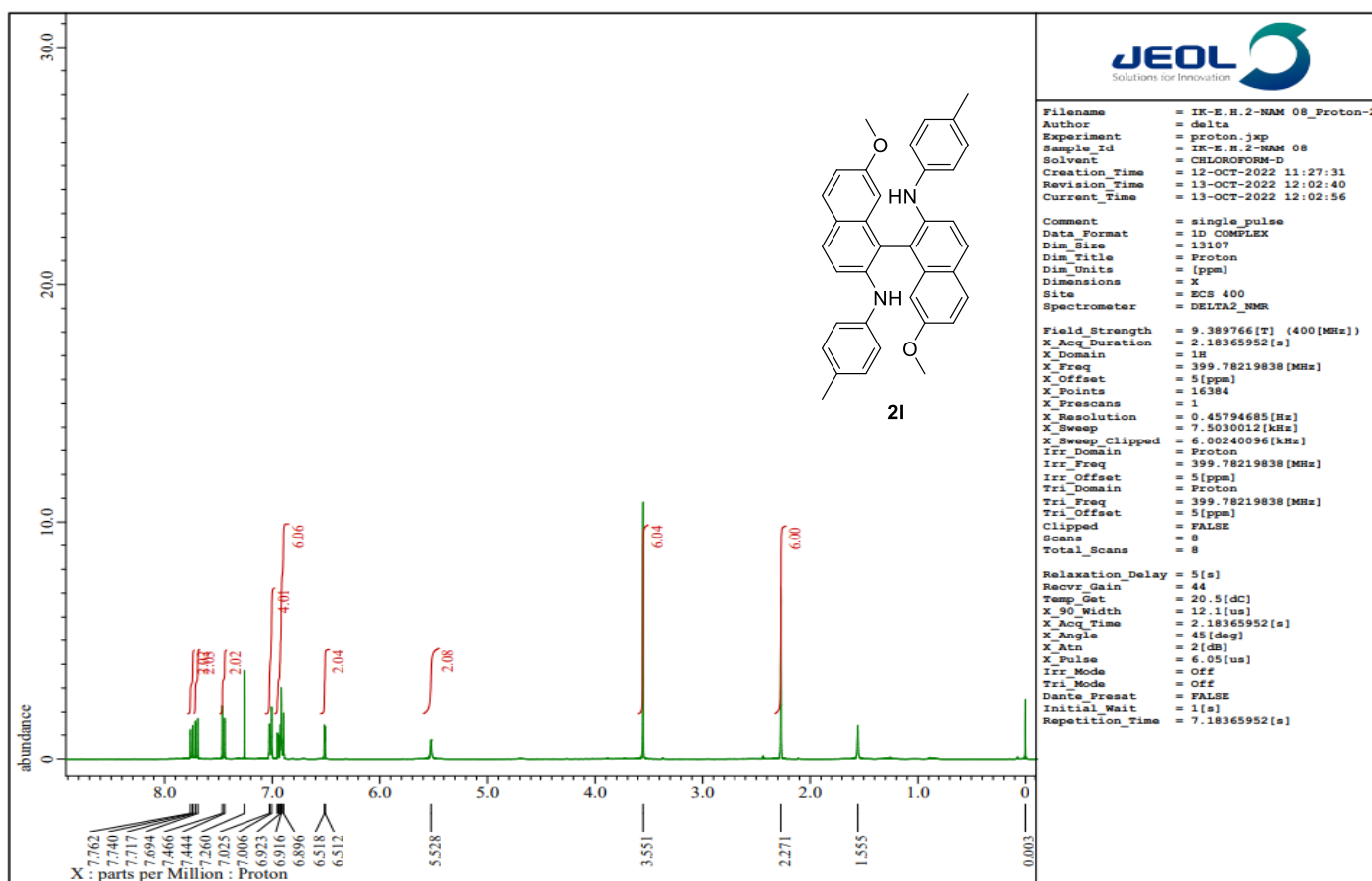
Compound **2j** (^{13}C NMR, 100 MHz, CDCl_3).



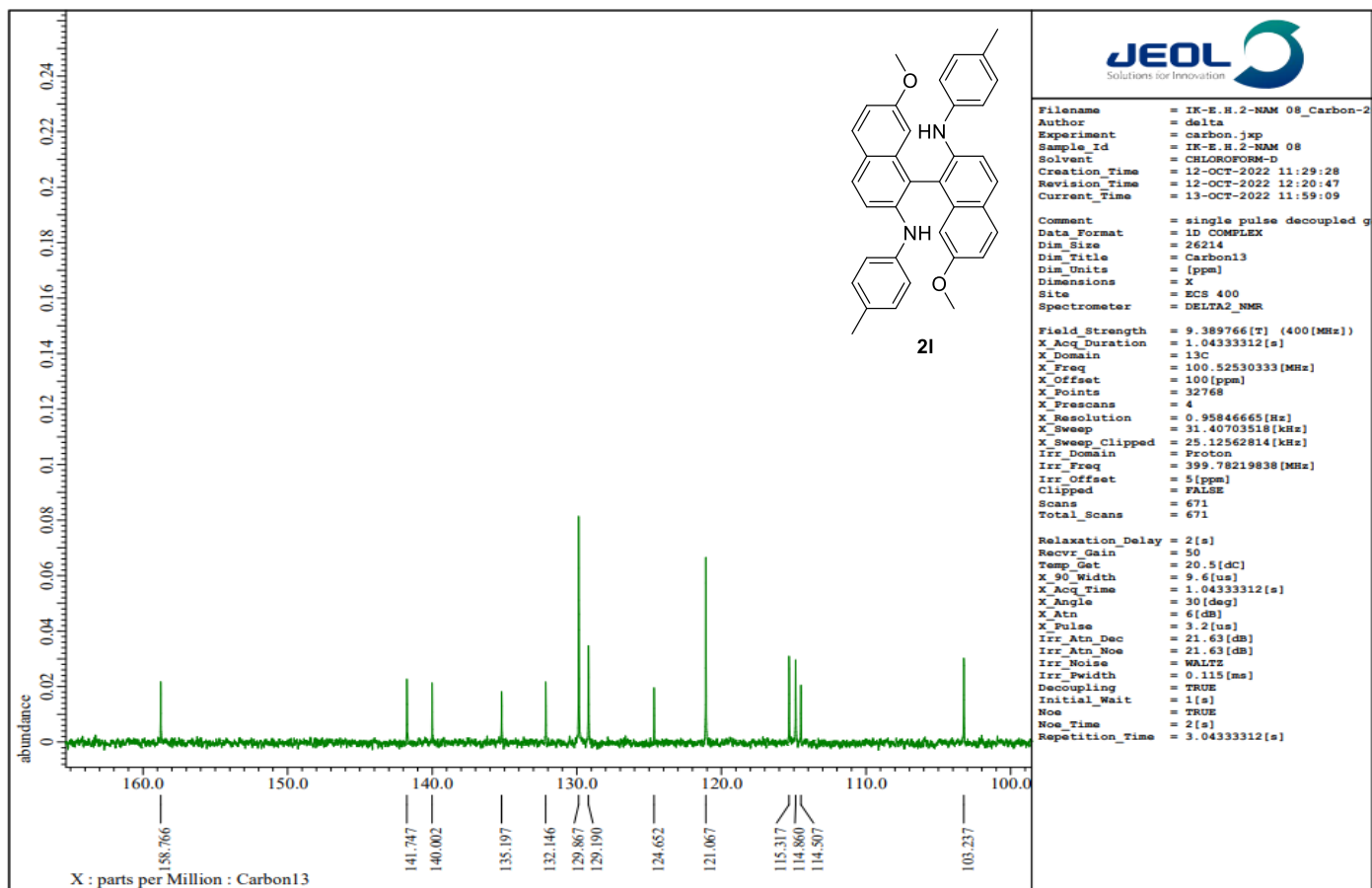
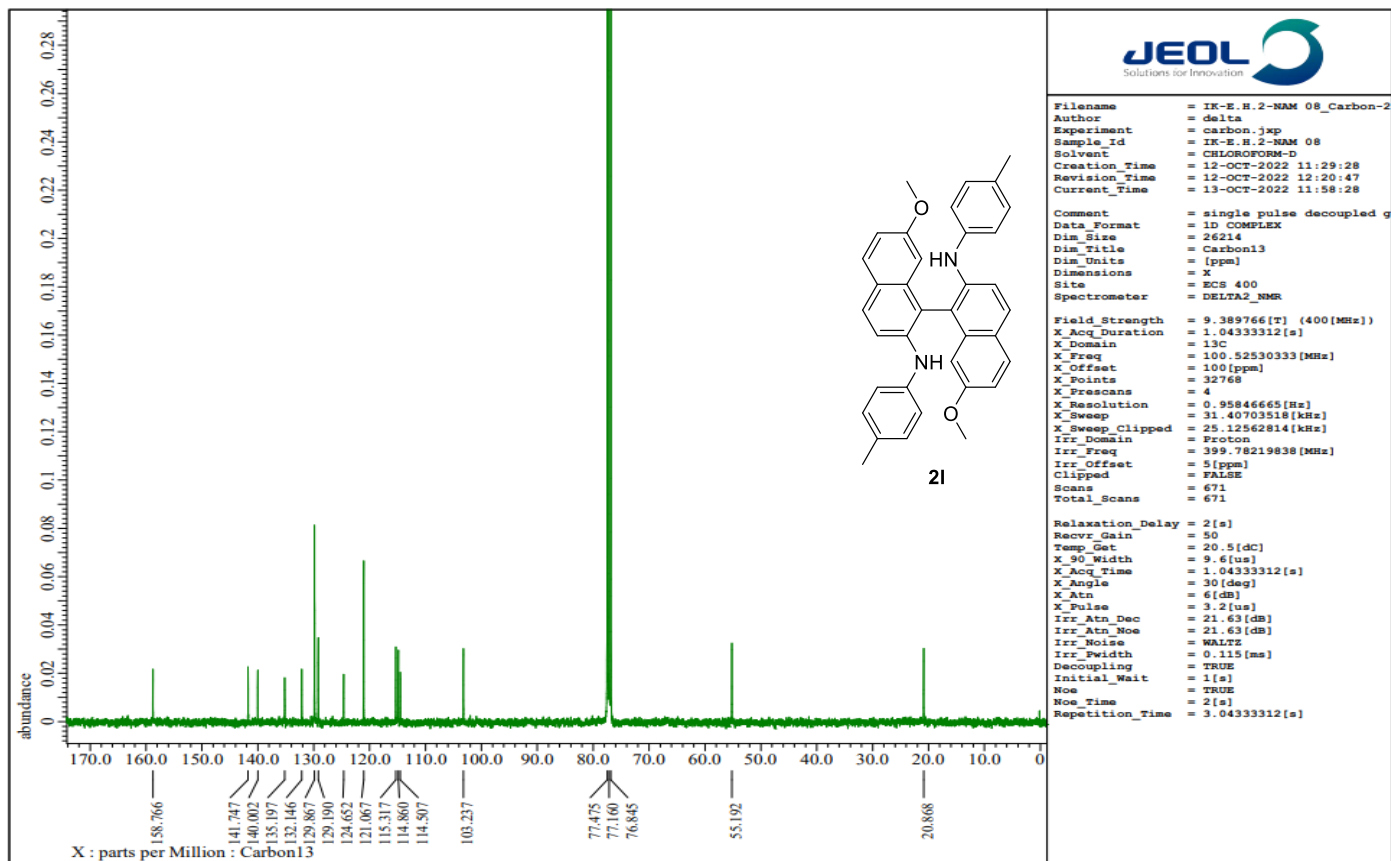
Compound **2k** (^1H NMR, 400 MHz, CDCl_3).



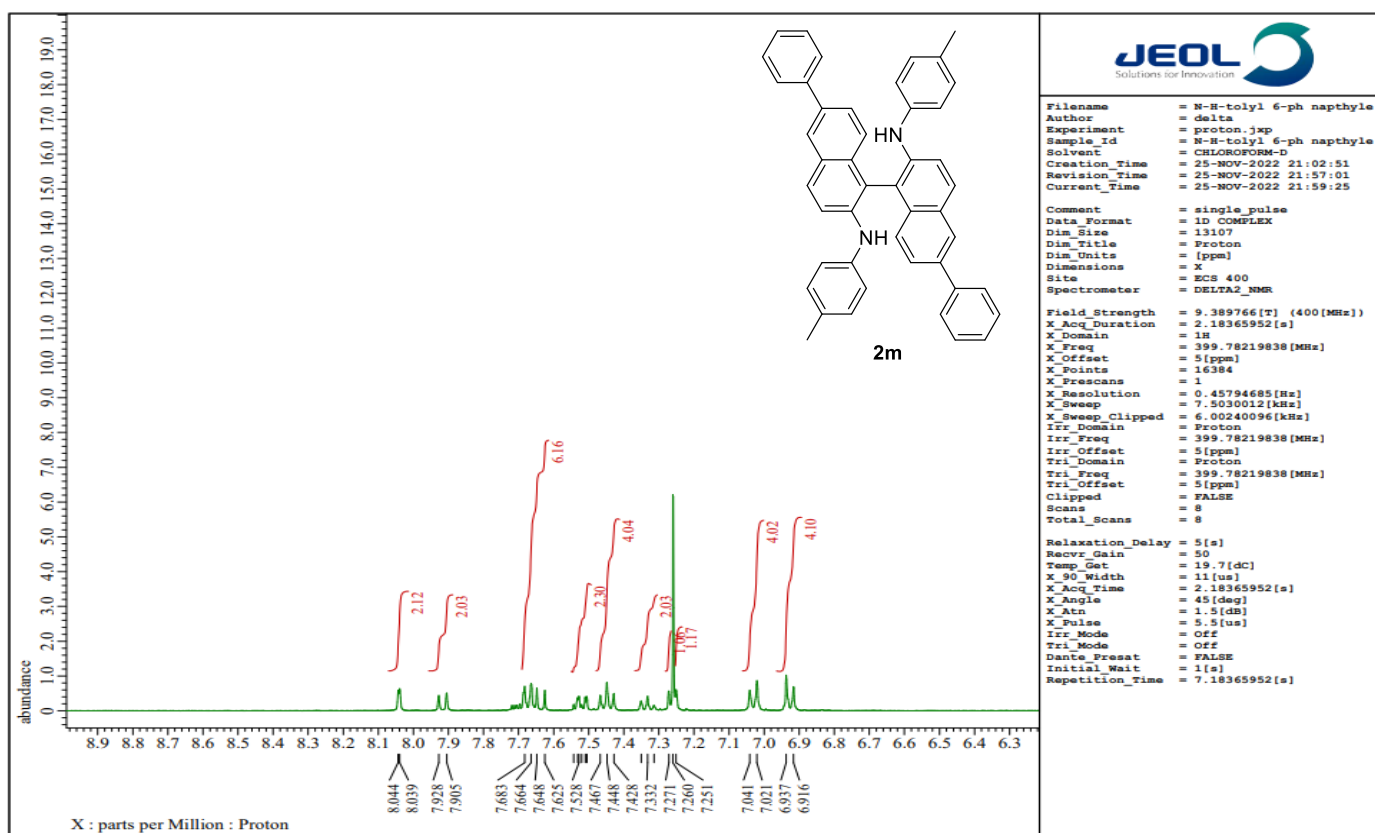
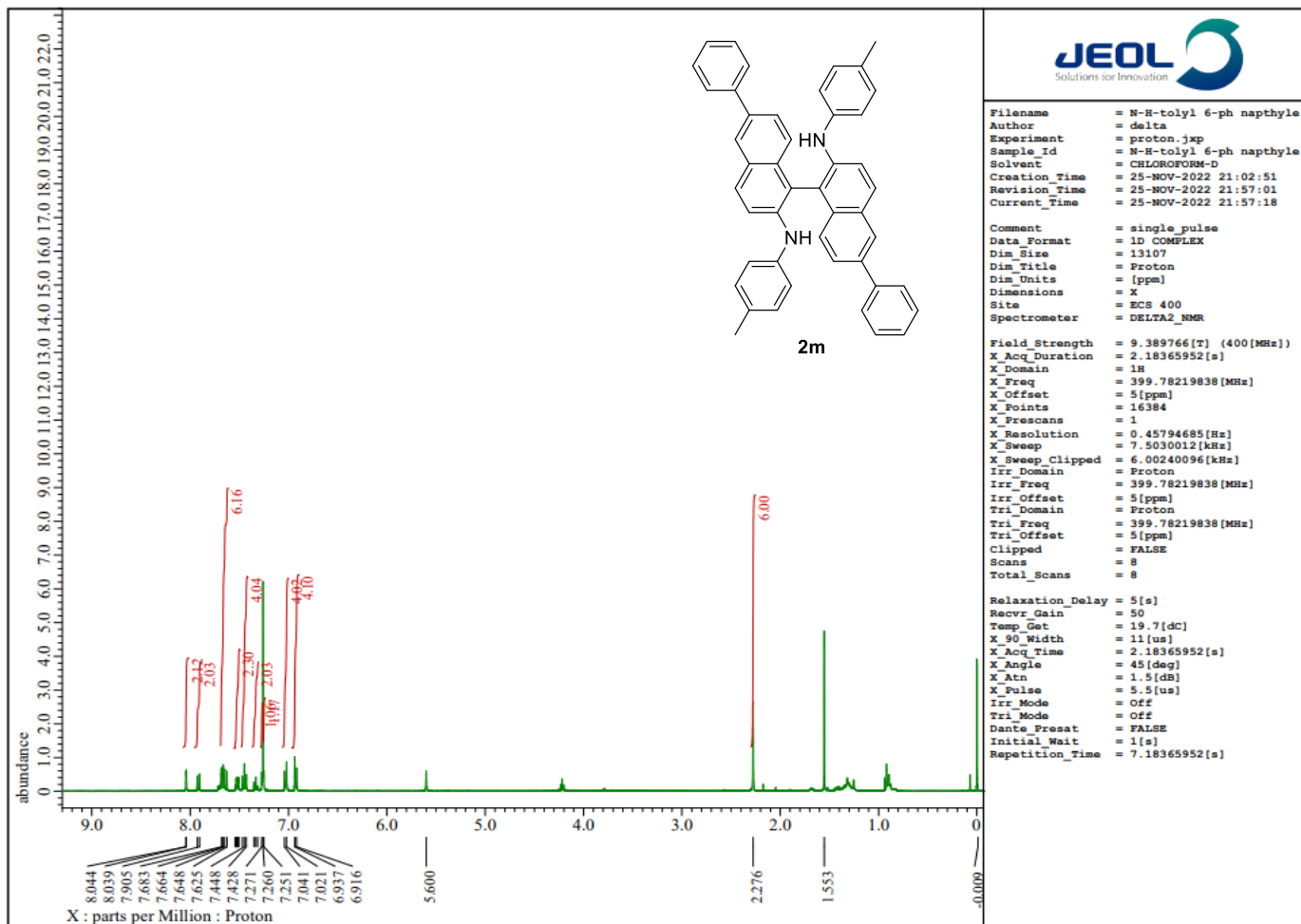
Compound **2k** (^{13}C NMR, 100 MHz, CDCl_3).



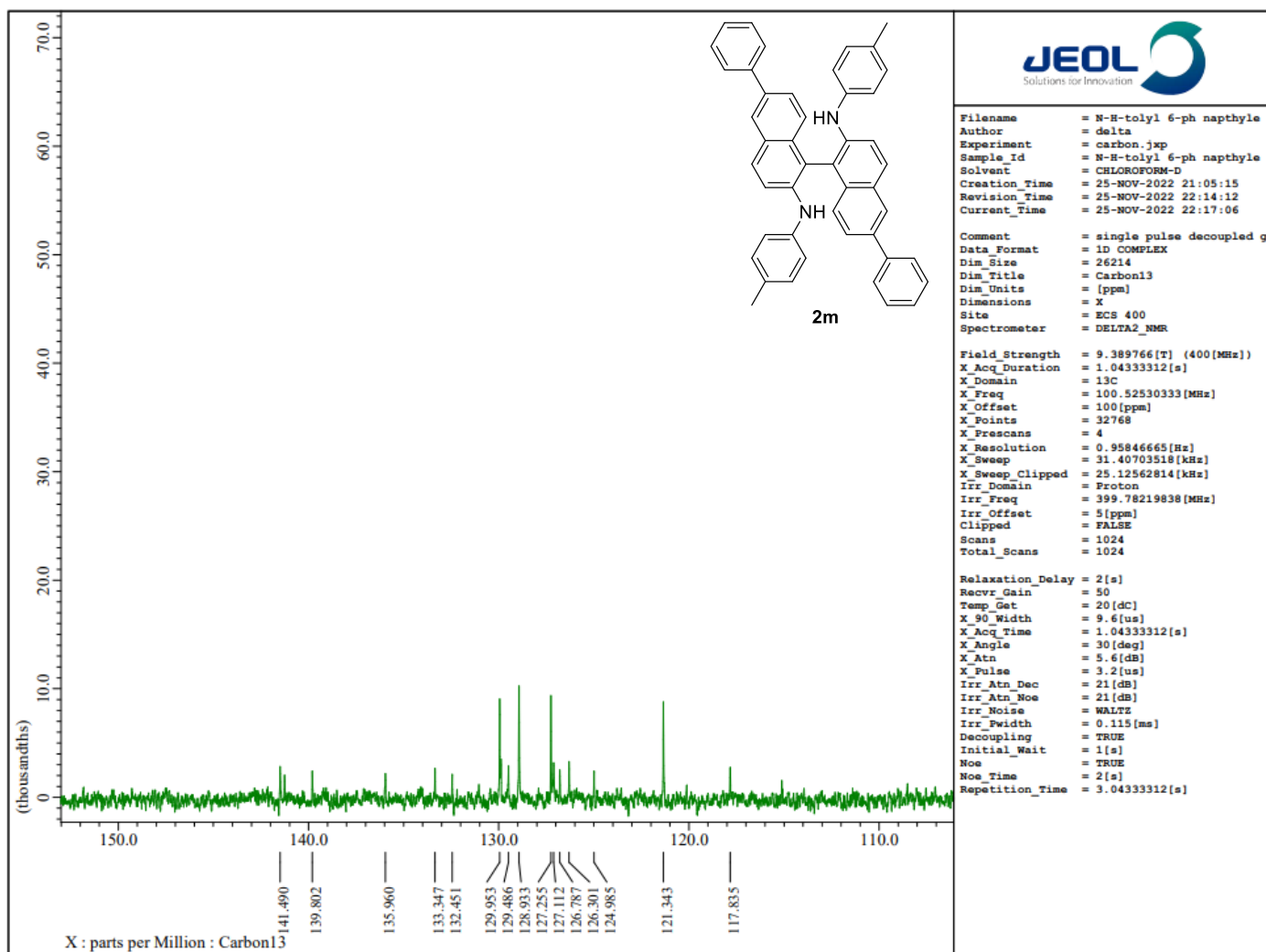
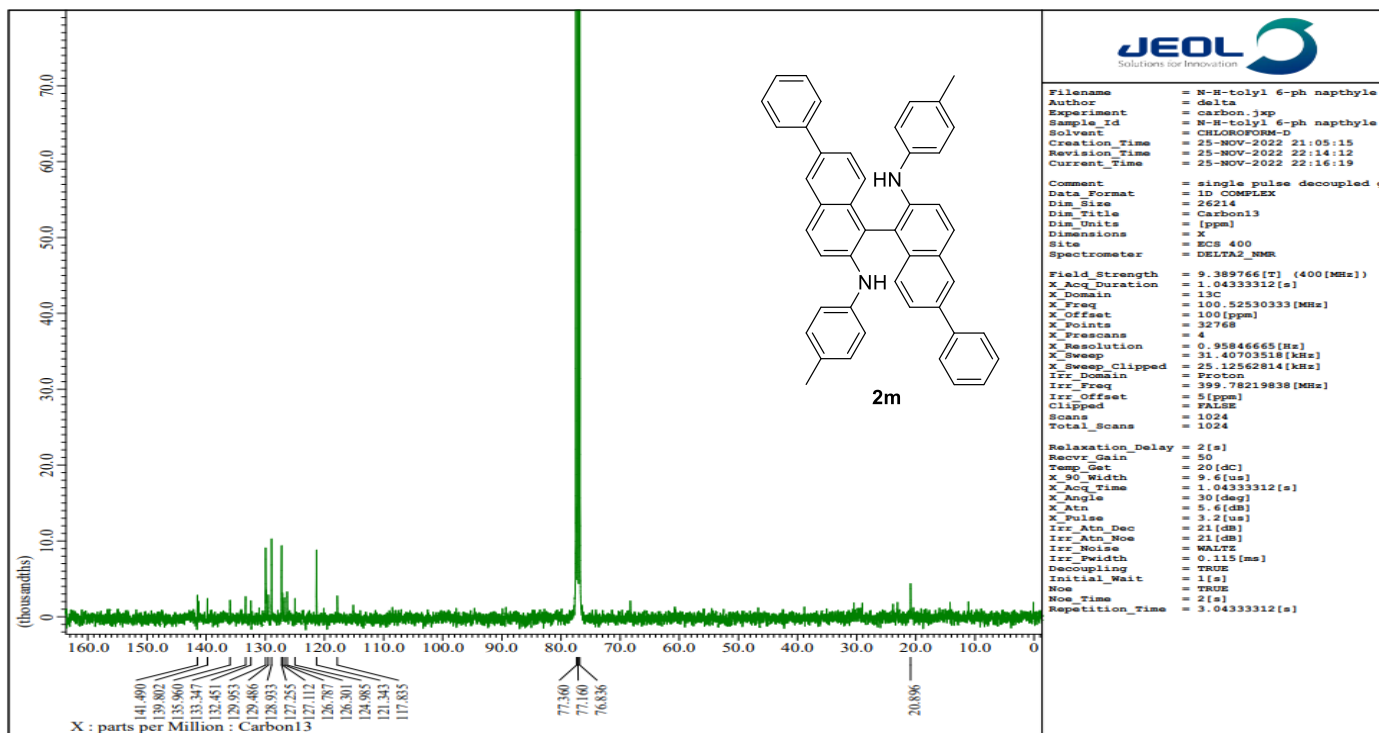
Compound **21** (¹H NMR, 400 MHz, CDCl₃).



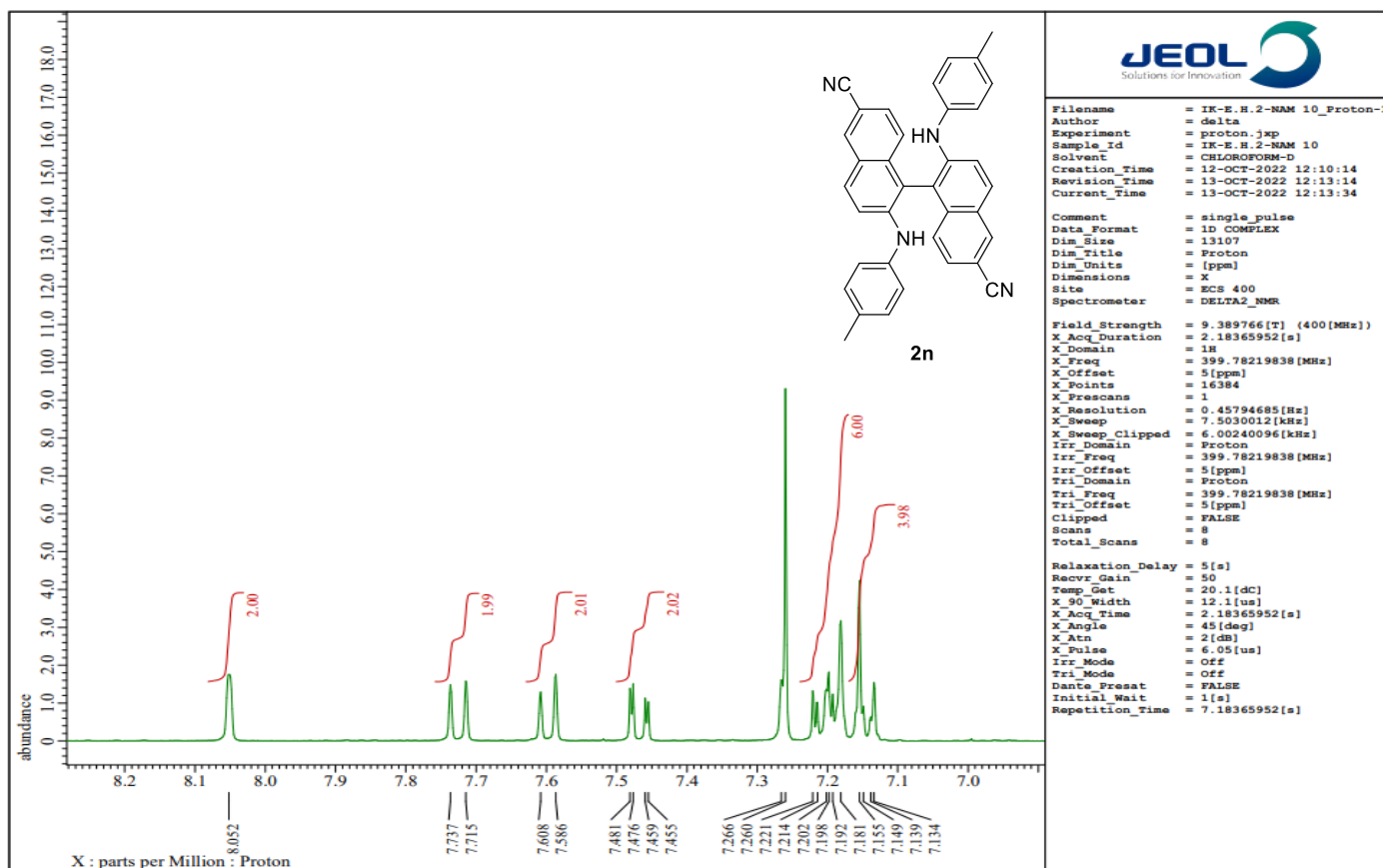
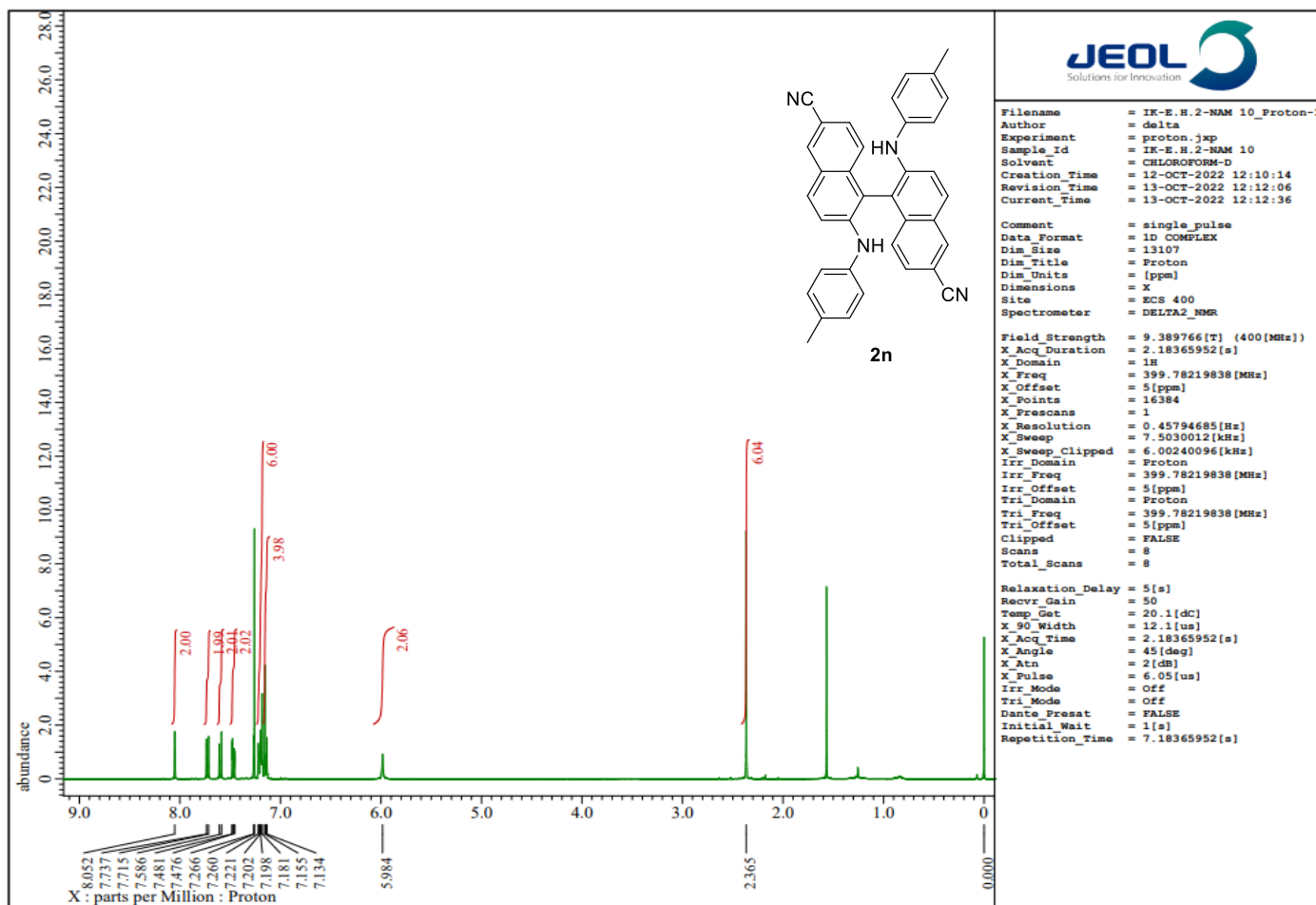
Compound **2I** (¹³C NMR, 100 MHz, CDCl₃).



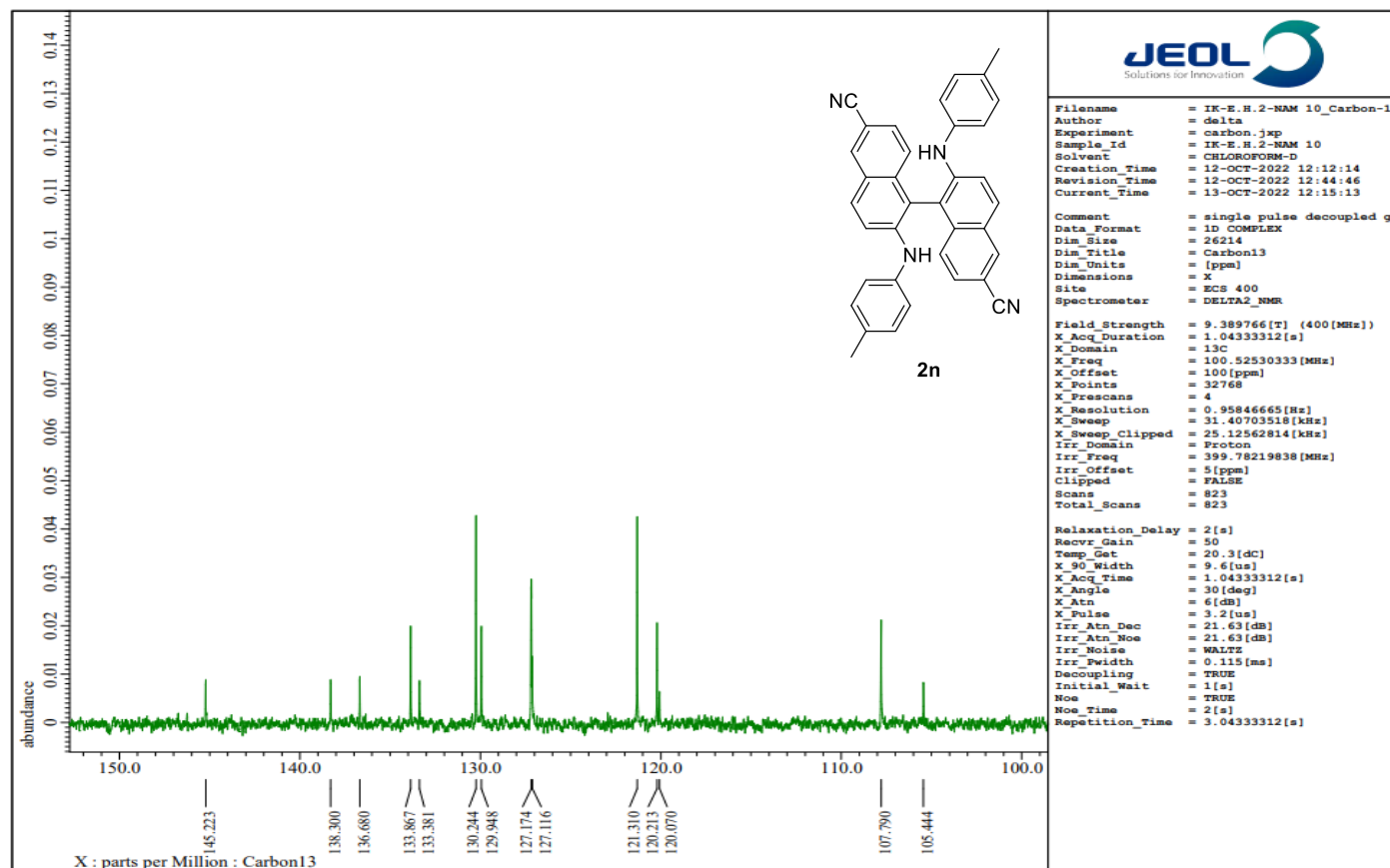
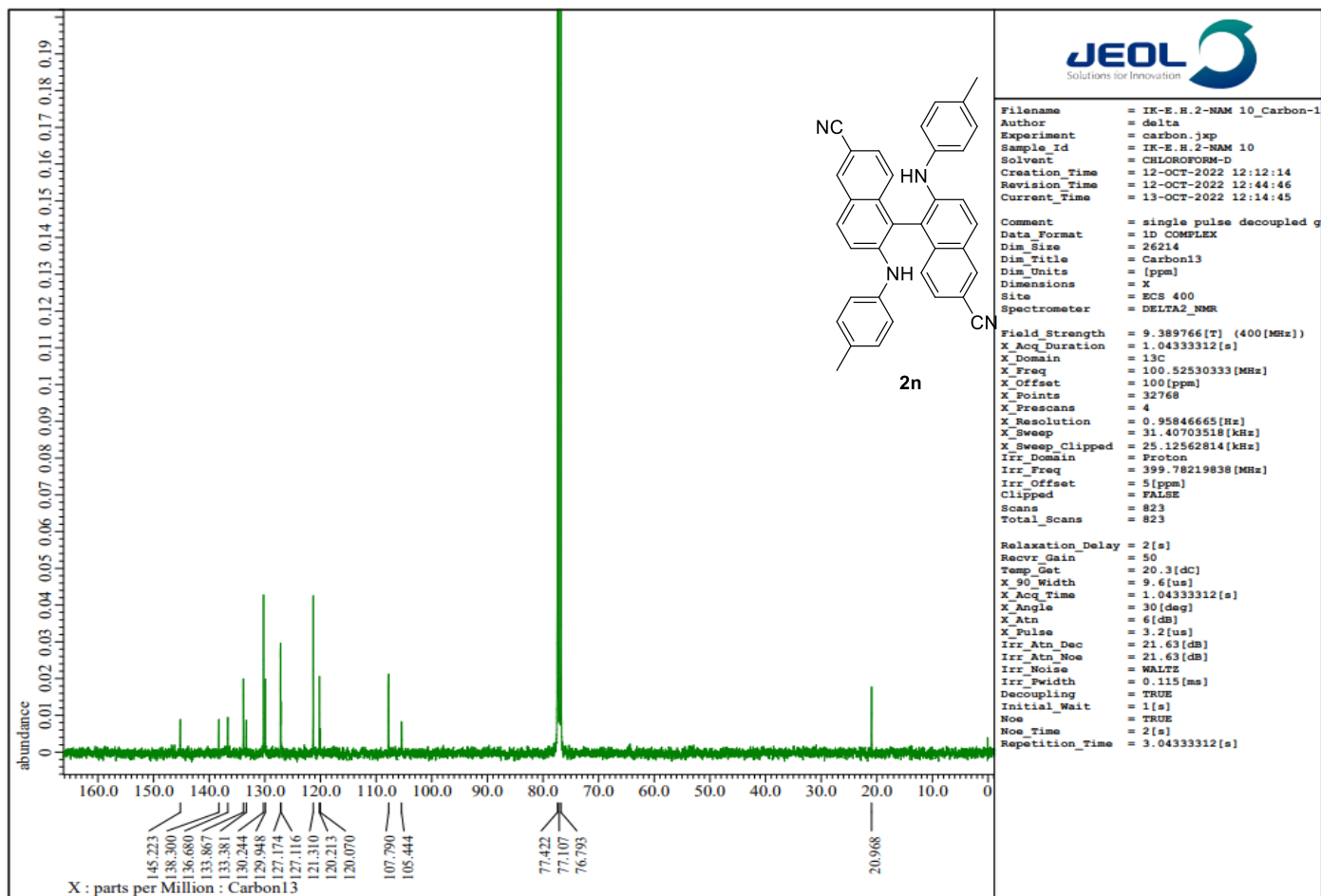
Compound **2m** (¹H NMR, 400 MHz, CDCl₃).



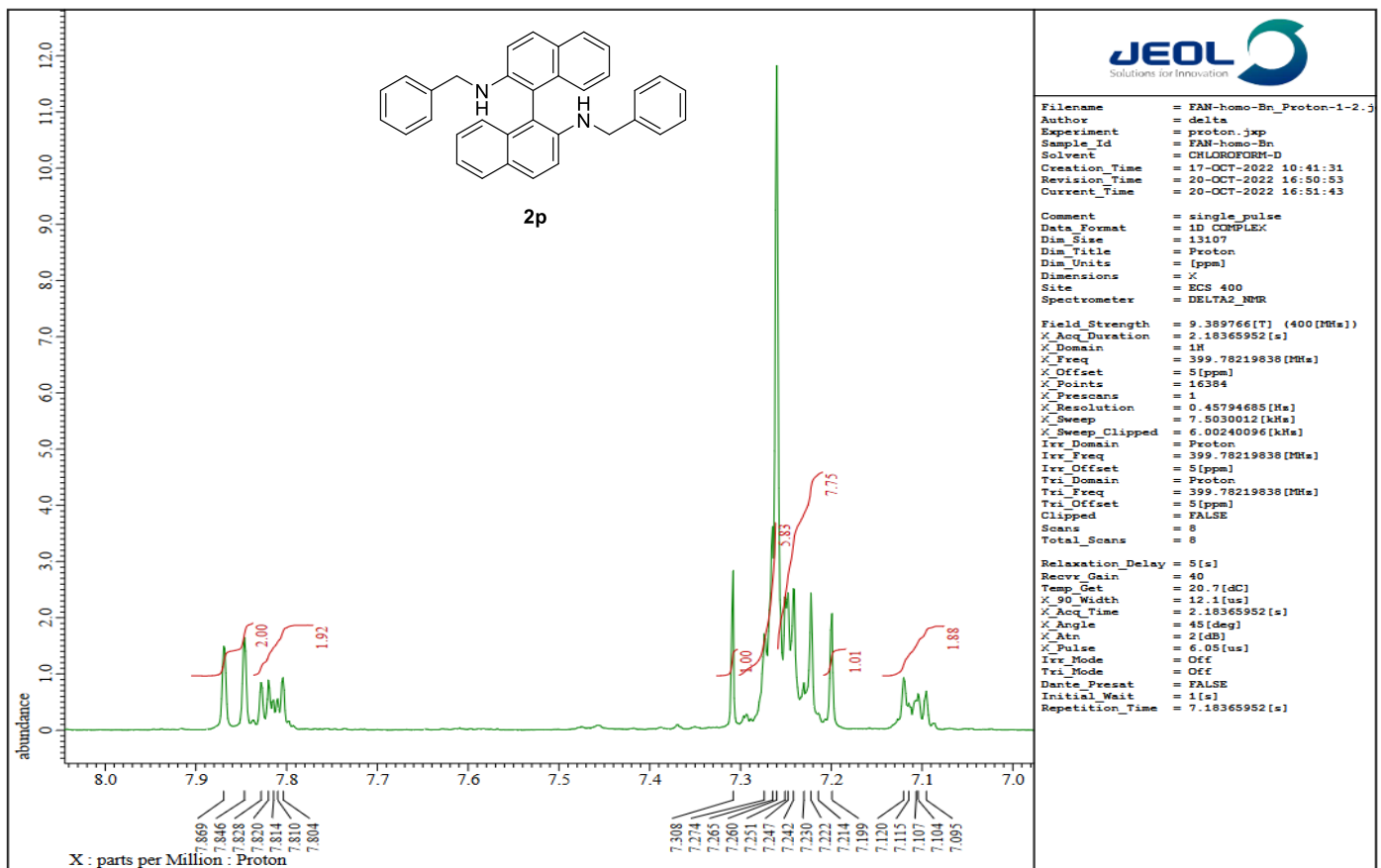
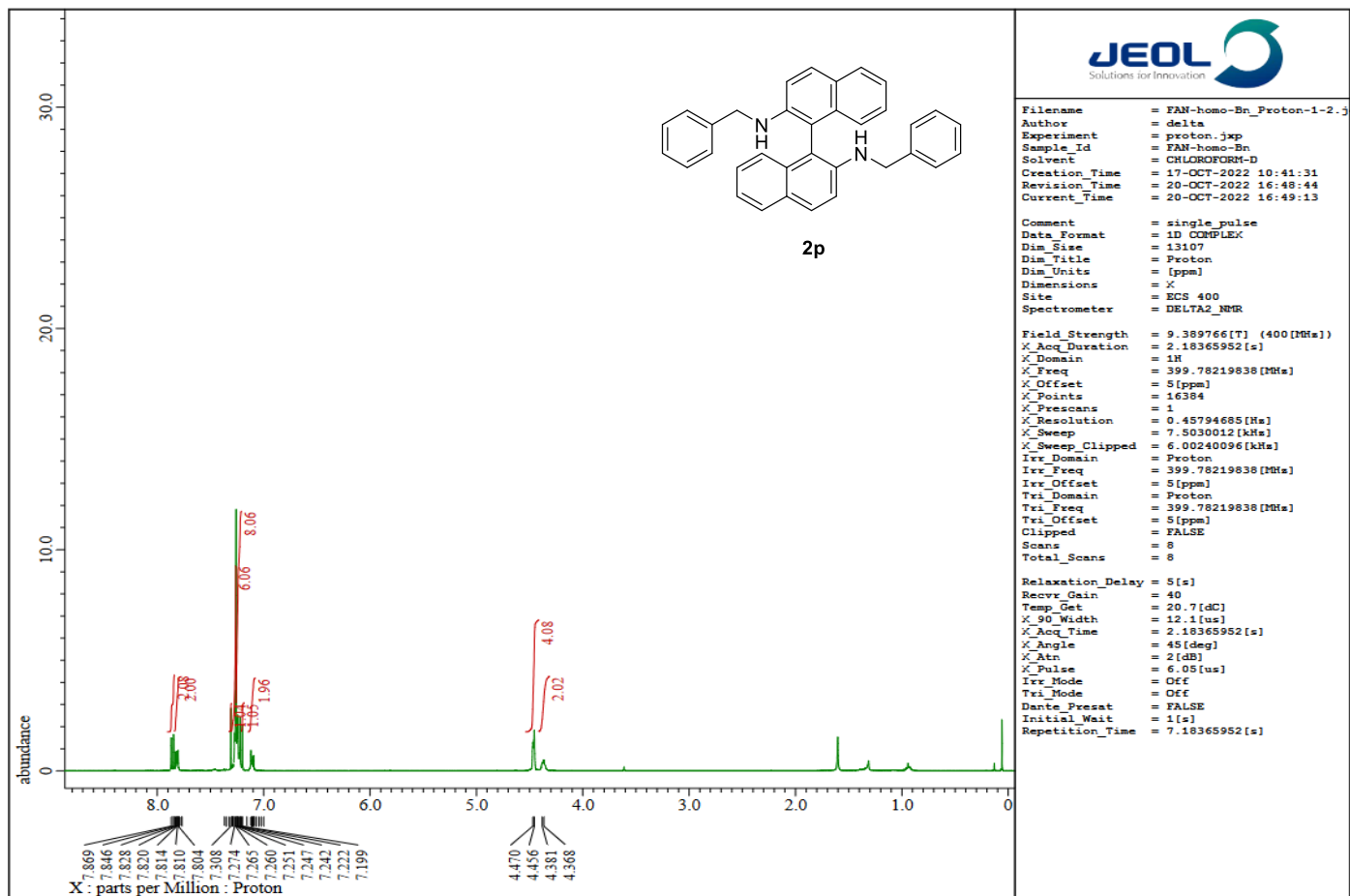
Compound **2m** (¹³C NMR, 100 MHz, CDCl₃).



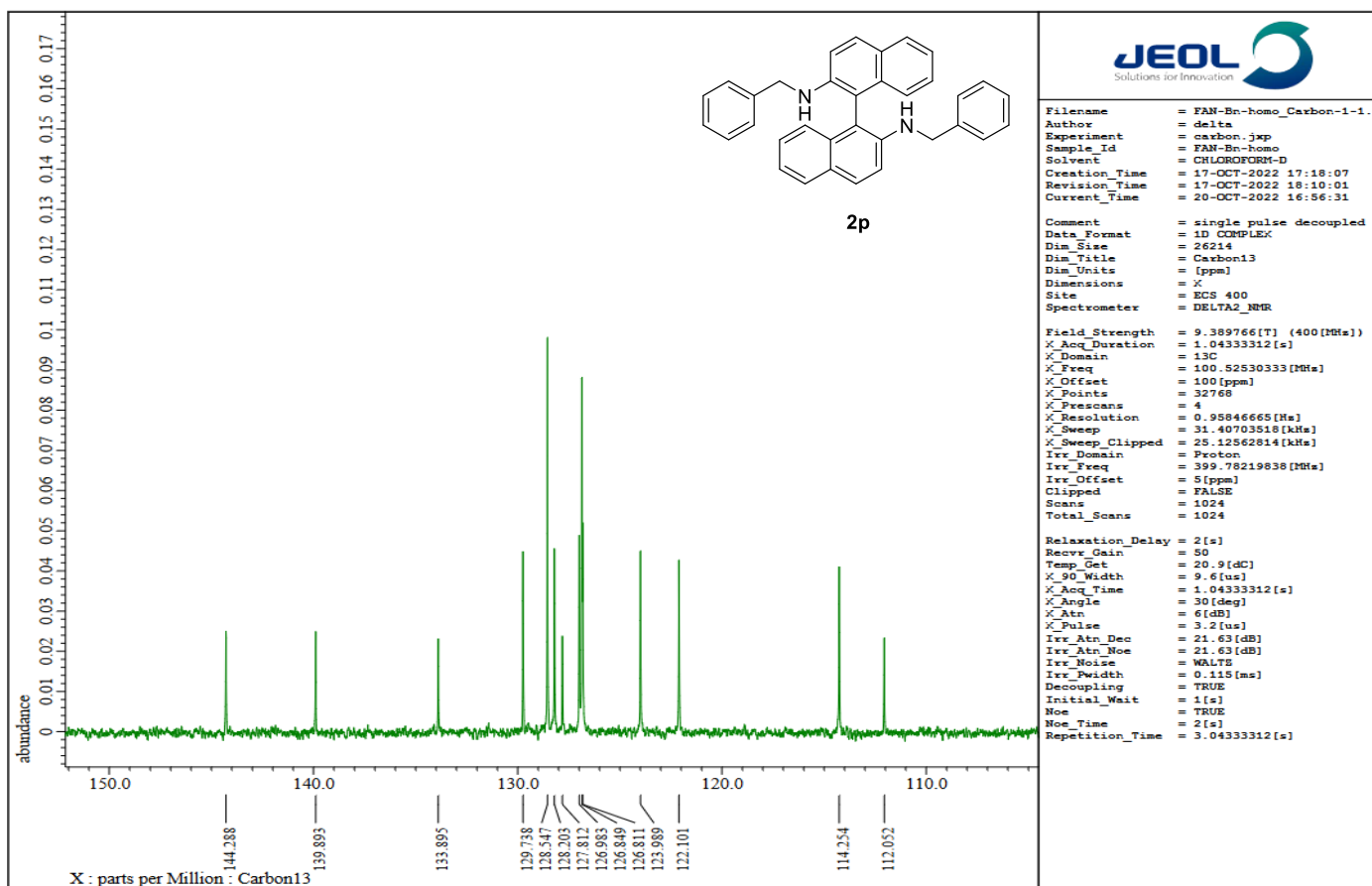
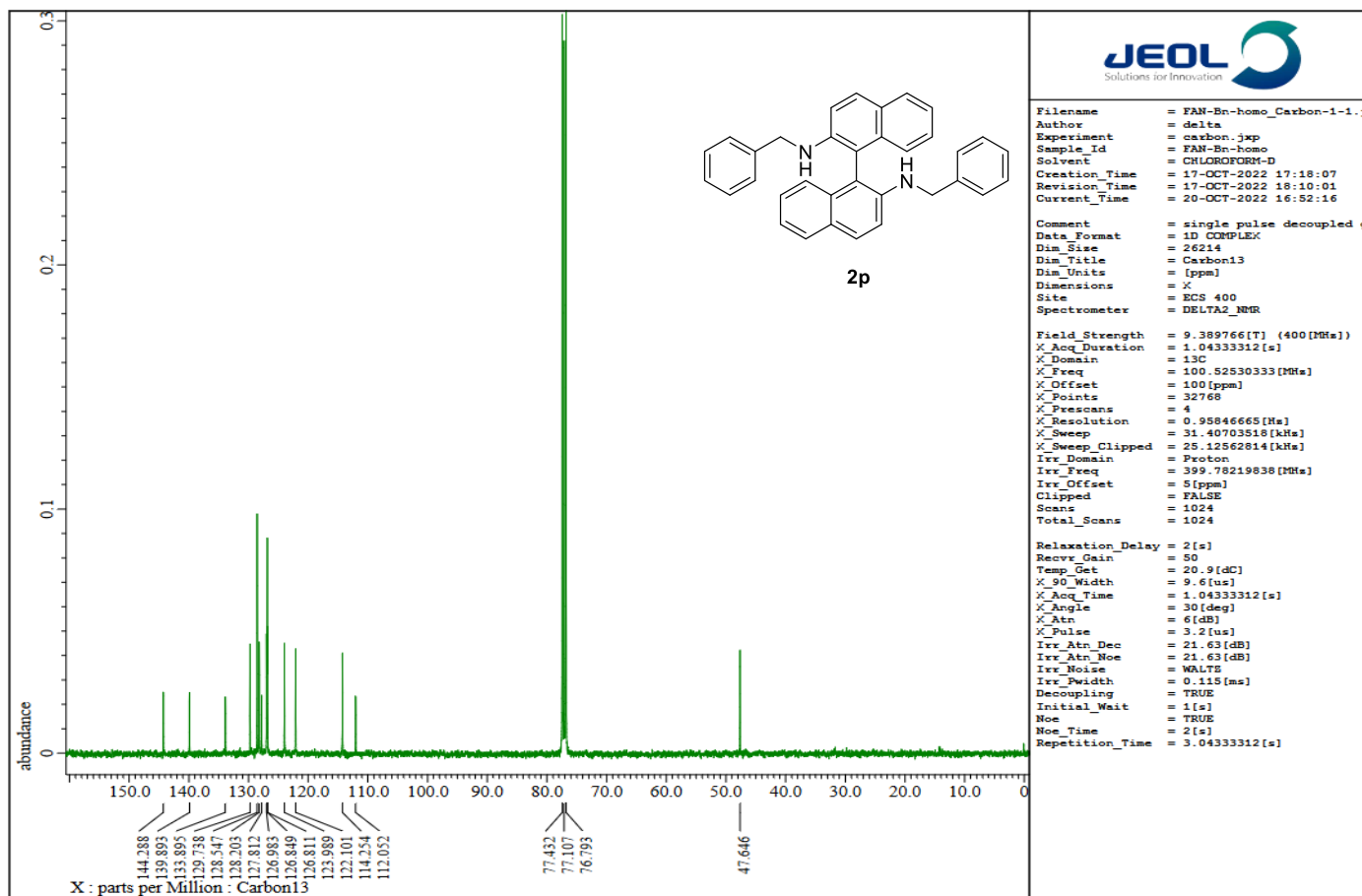
Compound **2n** (¹H NMR, 400 MHz, CDCl₃).



Compound **2n** (¹³C NMR, 100 MHz, CDCl₃).



Compound **2p** (^1H NMR, 400 MHz, CDCl_3).



Compound **2p** (^{13}C NMR, 100 MHz, CDCl_3).

