Supporting Information

Palladium-Catalyzed Decarbonylative Cross-Coupling of Azinecarboxylates with Arylboronic Acids

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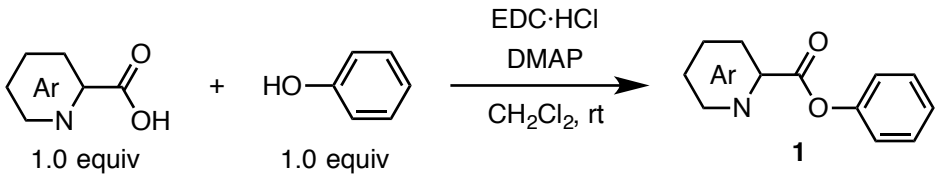
1. General

Unless otherwise noted, all materials including dry solvents were obtained from commercial suppliers and used as received. $Pd(OAc)_2$ and Na_2CO_3 were obtained from Kanto Chemicals. 1,2-Bis(dicyclohexylphosphino)ethane (dcype) was obtained from Kanto Chemical. Phenyl picolinate (**1A**) [1], phenyl pyrazine-2-carboxylate (**1D**)[1], phenyl nicotinate (**1I**)[1], 3,4-bis(dicyclohexylphosphino)thiophene (dcypt)[2] were synthesized according to procedures reported in the literature. Unless otherwise noted, all coupling reactions were performed with dry solvents under an atmosphere of argon in dried glassware using standard vacuum-line techniques. All work-up and purification procedures were carried out with reagent-grade solvents in air.

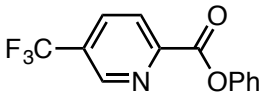
Analytical thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F_{254} precoated plates (0.25 mm). The developed chromatogram was analyzed by UV lamp (254 nm). Flash column chromatography was performed with E. Merck silica gel 60 (230–400 mesh). High-resolution mass spectra (HRMS) were obtained from a JMS-T100TD instrument (DART) and Thermo Scientific Exactive Plus Orbitrap MS (ESI). Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-ECA-400 (^{1}H 400 MHz, ^{13}C 100 MHz) and JEOL JNM-ECA-600 (^{1}H 600 MHz, ^{13}C 150 MHz) spectrometer. Chemical shifts for ^{1}H NMR are expressed in parts per million (ppm) relative to tetramethylsilane (δ 0.00 ppm). Chemical shifts for ^{13}C NMR are expressed in ppm relative to $CDCl_3$ (δ 77.0 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet, br = broad signal), coupling constant (Hz), and integration.

1. Amaike, K.; Muto, K.; Yamaguchi, J.; Itami, K. *J. Am. Chem. Soc*. **2012**, *134,* 13573.
2. Takise, R.; Muto, K.; Yamaguchi, J.; Itami, K. *Angew. Chem., Int. Ed.*, **2014**, *53*, 6791.

2. Preparation of Starting Materials

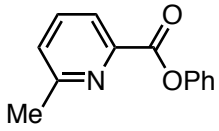


To a round-bottomed flask containing a magnetic stirring bar and carboxylic acid (1.0 equiv) were added phenol (1.0 equiv), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl: 1.2 equiv), *N*,*N*-dimethyl-4-aminopyridine (DMAP: 0.25 equiv) and CH_2Cl_2 (0.50 M). After stirring the mixture for several hours with monitoring reaction progress with TLC, the reaction was quenched with saturated $NaHCO_3$aq and extracted three times with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated *in vacuo*. The residue was purified by flash column chromatography to afford the corresponding phenyl ester **1**.



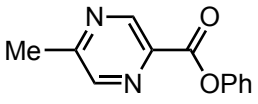
1B

Phenyl 5-(trifluoromethyl)picolinate (1B): Purification by flash column chromatography (hexane/EtOAc = 5:1 to 2:1) afforded **1B** as a white solid (524.0 mg, 3.0 mmol scale, 65% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.10 (s, 1H), 8.41 (d, *J* = 8.4 Hz, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 7.48–7.45 (m, 2H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.29–7.26 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 150.6, 150.5, 146.9 (q, J_{C-F} = 3.8 Hz), 134.6 (q, J_{C-F} = 2.8 Hz), 129.7 (q, J_{C-F} = 34.4 Hz), 129.6, 126.4, 125.4, 122.8 (q, J_{C-F} = 278 Hz), 121.4; HRMS (ESI) *m*/*z* calcd for $C_{13}H_9F_3NO_2^+$ $[M+H]^+$: 268.0580 found 268.0577.



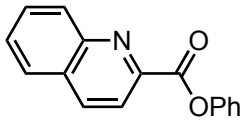
1C

Phenyl 6-methylpicolinate (1C): Purification by flash column chromatography (hexane/EtOAc = 5:1 to 2:1) afforded **1C** as a white solid (662.0 mg, 5.0 mmol scale, 62% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.4 Hz, 1H), 7.79 (t, *J* = 7.2 Hz, 1H), 7.45–7.39 (m, 3H), 7.30–7.22 (m, 3H), 2.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 159.2, 150.9, 146.8, 137.1, 129.3, 127.2, 125.9, 122.9, 121.6, 24.6; HRMS (ESI) *m*/*z* calcd for $C_{13}H_{11}NO_2Na^+$ $[M+Na]^+$: 236.0682 found 236.0680.



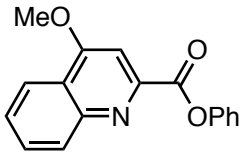
1E

Phenyl 5-methylpyrazine-2-carboxylate (1E): Purification by flash column chromatography (hexane/EtOAc = 5:1 to 1:1) afforded **1E** as a white solid (492 mg, 5 mmol scale, 46% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.34 (s, 1H), 8.67 (s, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.26 (d, *J* = 7.6 Hz, 2H), 2.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 158.3, 150.4, 145.8, 144.4, 140.0, 129.5, 126.3, 121.4, 22.0; HRMS (ESI) *m/z* calcd for $C_{12}H_{10}N_2O_2Na^+$ $[M+Na]^+$: 237.0634 found 237.0632.



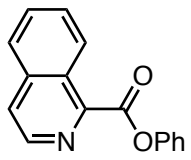
1F

Phenyl quinoline-2-carboxylate (1F): Purification by flash column chromatography (hexane/EtOAc = 10:1 to 3:1) afforded **1F** as a white solid (1.83 g, 10 mmol scale, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.8 Hz, 2H), 8.33 (d, *J* = 8.8 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.84 (ddd, *J* = 8.8, 8.4, 1.6 Hz, 1H), 7.70 (td, *J* = 8.4, 1.6 Hz, 1H), 7.52–7.42 (m, 2H), 7.36–7.28 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 151.0, 147.7, 147.4, 137.4, 130.8, 130.4, 129.5, 128.9, 127.6, 126.1, 121.8, 121.4 (one peak is missing because of overlap); HRMS (ESI) *m/z* calcd for $C_{16}H_{11}NO_2Na^+$ $[M+Na]^+$: 272.0682 found 272.0678.



1G

Phenyl 4-methoxyquinoline-2-carboxylate (1G): Purification by flash column chromatography (hexane/EtOAc = 5:1 to 3:1) afforded **1G** as a white solid (769.8 mg, 5.0 mmol scale, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (t, *J* = 8.4 Hz, 2H), 7.80 (ddd, *J* = 8.4, 6.8, 1.6 Hz, 1H), 7.69 (s, 1H), 7.64 (dd, *J* = 8.4, 7.6 Hz, 1H), 7.49–7.44 (m, 2H), 7.33–7.28 (m, 3H), 4.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 163.4, 151.2, 148.6, 148.5, 130.6, 130.4, 129.5, 127.9, 126.1, 122.3, 121.85, 121.79, 100.5, 56.1; HRMS (ESI) *m/z* calcd for $C_{17}H_{13}NO_3Na^+$ $[M+Na]^+$: 302.0788 found 302.0788.

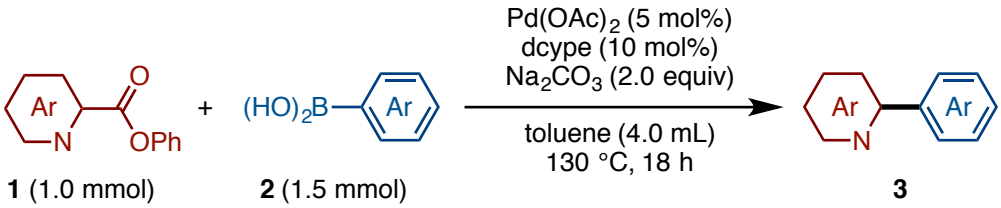


1H

Phenyl isoquinoline-1-carboxylate (1H): Purification by flash column chromatography (hexane/EtOAc = 5:1 to 3:1) afforded **1H** as a white solid (1.63 g, 10 mmol scale, 65% yield). ^{1}H

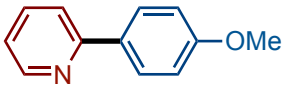
NMR (400 MHz, $CDCl_3$) δ 8.93 (d, J = 9.2 Hz, 1H), 8.75 (d, J = 5.6 Hz, 1H), 7.95–7.90 (m, 2H), 7.80–7.70 (m, 2H), 7.51–7.45 (m, 2H), 7.37–7.30 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 150.8, 147.2, 141.6, 136.9, 130.6, 129.4, 129.0, 127.1, 126.1, 126.0, 124.7, 121.7 (one peak is missing because of overlap); HRMS (ESI) m/z calcd for $C_{16}H_{12}NO_2^+$ $[M+H]^+$: 250.0863 found 250.0862.

3. Pd-Catalyzed Decarbonylative Cross-Coupling



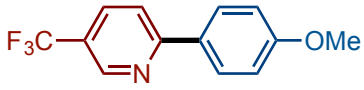
1 (1.0 mmol) **2** (1.5 mmol) **3**

A 50-mL glass Schlenk tube containing a magnetic stirring bar was dried with a heatgun for 3 min *in vacuo* and filled with argon after cooling to room temperature. $Pd(OAc)_2$ (11.2 mg, 0.050 mmol, 5 mol%), 1,2-bis(dicyclohexylphosphino)ethane (dcype: 42.3 mg, 0.10 mmol, 10 mol%), Na_2CO_3 (212.0 mg, 2.0 mmol, 2.0 equiv), **1** (1.0 mmol, 1.0 equiv), and **2** (1.5 mmol, 1.5 equiv) were placed in the Schlenk tube under an argon atmosphere. Then, this tube was added dry degassed toluene (4.0 mL) and equipped reflux condenser under a stream of argon. The reaction mixture was stirred at 130 °C in an oil bath for 18 h. After cooling the reaction mixture to room temperature, the mixture was diluted with EtOAc and pathed through a pad of Celite®. The filtrate was concentrated *in vacuo* and the residue was purified by flash silica-gel column chromatography to afford biaryl **3**.



3Aa
92%

2-(4-Methoxyphenyl)pyridine (3Aa)[3]: Purification by flash silica-gel column chromatography (hexane/ether = 2:1 to 1:1) afforded **3Aa** as a white solid (170.4 mg, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.65 (d, J = 4.8 Hz, 1H), 7.95 (dt, J = 8.4, 2.4 Hz, 2H), 7.78–7.63 (m, 2H), 7.17 (dd, J = 6.4, 4.8 Hz, 1H), 7.00 (dt, J = 8.4, 2.4 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.4, 157.1, 149.5, 136.6, 132.0, 128.1, 121.4, 119.8, 114.1, 55.4; HRMS (DART) m/z calcd for $C_{12}H_{12}NO$ $[M+H]^+$: 186.0919, found 186.0917.

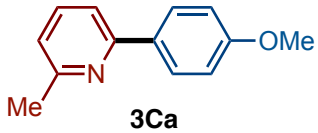


3Ba
68%

2-(4-Methoxyphenyl)-5-(trifluoromethyl)pyridine (3Ba)[4]: 0.75 mmol scale. Purification by flash silica-gel column chromatography (hexane/ether = 9:1) afforded **3Ba** as a white solid (129.2 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.89 (s, 1H), 8.01 (d, J = 8.8 Hz, 2H), 7.93 (d, J = 8.4 Hz, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.02 (d, J = 8.8 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.3, 160.2, 146.5 (q, J_{C-F} = 4.0 Hz), 133.8 (q, J_{C-F} = 4.0 Hz), 130.5, 128.6, 124.0 (q, J_{C-F} = 34.0 Hz), 123.9

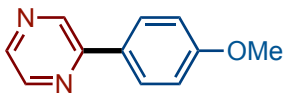
3. Muto, K.; Yamaguchi, J.; Musaev, D. G.; Itami, K. *Nat. Commun.* **2015**, *6*, 7208.
4. Metzger, A.; Melzig, L.; Despotopoulou, C.; Knochel, P. *Org. Lett.* **2009** *11*, 4228–4231.

(q, J_{C-F} = 270.0 Hz), 119.0, 114.3, 55.4; HRMS (DART) *m/z* calcd for $C_{13}H_{11}F_3NO$ $[M+H]^+$: 254.0793, found 254.0801.



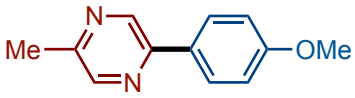
3Ca
35%

2-(4-Methoxyphenyl)-6-methylpyridine (3Ca) [5] : Purification by flash silica-gel column chromatography (hexane/ether = 3:1) afforded **3Ca** as a white solid (69.4 mg, 35% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.8 Hz, 2H), 7.59 (dd, *J* = 8.0, 7.6 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H), 2.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3, 158.2, 156.6, 136.8, 132.4, 128.2, 120.9, 116.8, 114.0, 55.3, 24.7; HRMS (DART) *m/z* calcd for $C_{13}H_{14}NO$ $[M+H]^+$: 200.1075, found 200.1078.



3Da
82%

2-(4-Methoxyphenyl)pyrazine (3Da) [6]**:** Purification by flash silica-gel column chromatography (hexane/ether = 1:1) afforded **3Da** as a pale brown solid (152.7 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.98 (d, *J* = 1.2 Hz, 1H), 8.59 (dd, *J* = 2.4, 1.2 Hz, 1H), 8.44 (d, *J* = 2.4 Hz, 1H), 7.99 (d, *J* = 8.8 Hz, 2H), 7.04 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.2, 152.5, 144.0, 142.1, 141.6, 128.8, 128.3, 114.5, 55.4; HRMS (DART) *m/z* calcd for $C_{11}H_{11}N_2O$ $[M+H]^+$: 187.0871, found 187.0876.



3Ea
86%

2-(4-Methoxyphenyl)-5-methylpyrazine (3Ea): Purification by flash silica-gel column chromatography (hexane/ether = 1:1) afforded **3Ea** as a white solid (172.2 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.85 (d, *J* = 1.2 Hz, 1H), 8.46 (d, *J* = 1.2 Hz, 1H), 7.94 (d, *J* = 8.8 Hz, 2H), 7.02 (d, *J* = 8.8 Hz, 2H), 3.88 (s, 3H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.8, 151.0, 149.6, 143.6, 140.4, 129.1, 128.0, 114.4, 55.4, 21.1; HRMS (DART) *m/z* calcd for $C_{12}H_{13}N_2O$ $[M+H]^+$: 201.1028, found 201.1029.

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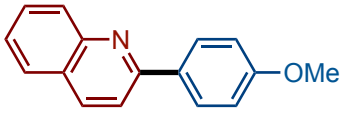
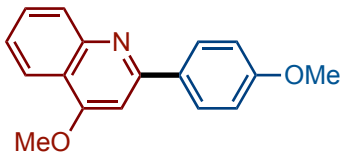
5. Ackermann, L.; Potukuchi, H. K.; Kapdi, A. R.; Schulzke, C. *Chem. Eur. J.* **2010**, *16*, 3300.
6. Hirner, J. J.; Blum, S. A. *Organometallics* **2011**, *30*, 1299.



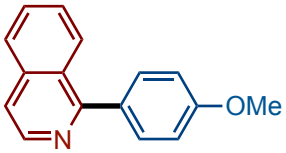
3Fa
37%

2-(4-Methoxyphenyl)quinoline (3Fa)[3]: Purification by flash silica-gel column chromatography (hexane/ether = 4:1 to 3:1) afforded **3Fa** as a white solid (87.4 mg, 37% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, *J* = 8.0 Hz, 1H), 8.16–8.11 (m, 3H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.71 (td, *J* = 8.0, 1.2 Hz, 1H), 7.50 (td, *J* = 8.0, 1.2 Hz, 1H), 7.05 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.8, 156.9, 148.3, 136.6, 132.2, 129.53, 129.49, 128.8, 127.4, 126.9, 125.9, 118.5, 114.2, 55.4; HRMS (DART) *m/z* calcd for $C_{16}H_{14}NO$ $[M+H]^+$: 236.1075, found 236.1076.



3Ga
63%

4-Methoxy-2-(4-methoxyphenyl)quinoline (3Ga)[7]: 0.75 mmol scale. Purification by flash silica-gel column chromatography (hexane/ether = 3:1 to 1:1) gave a mixture of **3Ga** and small amount of **1G**. As further purification, the mixture was diluted with ether and washed with 1M NaOHaq to afford **3Ga** as a yellow solid (126.3 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (dd, *J* = 8.0, 1.2 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 2H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.69 (td, *J* = 8.0, 1.2 Hz, 1H), 7.46 (td, *J* = 8.0, 1.2 Hz, 1H), 7.14 (s, 1H), 7.04 (d, *J* = 8.4 Hz, 2H), 4.12 (s, 3H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.7, 160.7, 158.3, 149.2, 132.9, 129.9, 129.0, 128.8, 125.0, 121.6, 120.2, 114.1, 97.4, 55.6, 55.4; HRMS (DART) *m/z* calcd for $C_{17}H_{16}NO_2$ $[M+H]^+$: 266.1181, found 266.1181.

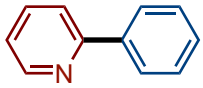


3Ha
53%

1-(4-Methoxyphenyl)isoquinoline (3Ha)[8]: Purification by flash silica-gel column chromatography (hexane/ether = 2:1 to 1:1) afforded **3Ha** as a brown solid (124.7 mg, 53% yield). ^{1}H NMR (400 MHz,

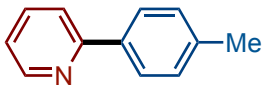
7. Wang, Y.; Peng, C.; Liu, L.; Zhao, J.; Su, L.; Zhu, Q. *Tetrahedron Lett.* **2009**, *50*, 2261.
8. Lee, H. W.; Lam, F. L.; So, C. M.; Lau, C. P.; Chan, A. S. C.; Kwong, F. Y. *Angew. Chem., Int. Ed.* **2009**, *48*, 7436.

$CDCl_3$): δ 8.59 (d, *J* = 6.0 Hz, 1H), 8.15 (d, *J* = 7.6 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.72–7.64 (m, 3H), 7.62 (d, *J* = 6.0 Hz, 1H), 7.57–7.51 (m, 1H), 7.07 (d, *J* = 8.0 Hz, 2H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3, 156.0, 142.2, 136.9, 132.1, 131.2, 129.8, 127.6, 127.0, 126.9, 126.7, 119.5, 113.7, 55.3; HRMS (DART) *m/z* calcd for $C_{16}H_{14}NO$ [M+H]$^+$: 236.1075, found 236.1079.



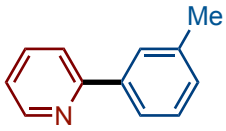
3Ab
85%

2-Phenylpyridine (3Ab)[9]: Purification by flash silica-gel column chromatography (hexane/ether = 3:1) afforded **3Ab** as a pale yellow oil (131.9 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 (d, *J* = 5.2 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 2H), 7.81–7.69 (m, 2H), 7.48 (dd, *J* = 8.0, 7.2 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.26–7.21 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.4, 149.6, 139.4, 136.7, 128.9, 128.7, 126.9, 122.0, 120.5; HRMS (DART) *m/z* calcd for $C_{11}H_{10}N$ [M+H]$^+$: 156.0813, found 156.0817.



3Ac
70%

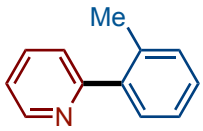
2-(*p*-Tolyl)pyridine (3Aq)[9]: Purification by flash silica-gel column chromatography (hexane/ether = 3:1) afforded **3Ac** as a colorless oil (118.5 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (d, *J* = 4.4 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.82–7.65 (m, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.20 (dd, *J* = 7.6, 4.4 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.4, 149.5, 138.9, 136.61, 136.56, 129.4, 126.7, 121.7, 120.2, 21.2; HRMS (DART) *m/z* calcd for $C_{12}H_{12}N$ [M+H]$^+$: 170.0970, found 170.0978.



3Ad
86%

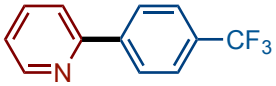
2-(*m*-Tolyl)pyridine (3Ad)[9]: Purification by flash silica-gel column chromatography (hexane/ether = 3:1) afforded **3Ad** as a white solid (145.5 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 (d, *J* = 5.2 Hz, 1H), 7.84 (s, 1H), 7.79–7.69 (m, 3H), 7.37 (dd, *J* = 8.0, 7.8 Hz, 1H), 7.25–7.21 (m, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.6, 149.6, 139.3, 138.4, 136.7, 129.7, 128.6, 127.6, 124.0, 122.0, 120.6, 21.5; HRMS (DART) *m/z* calcd for $C_{12}H_{12}N$ [M+H]$^+$: 170.0970, found 170.0968.

9. Hu, B.; Li, Y.; Dong, W. Xie, X.; Wan, J.; Zhang, Z. *RSC Adv*. **2016**, *6*, 48315.



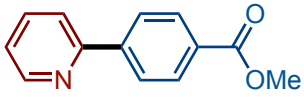
3Ae
44%

2-(*o*-Tolyl)pyridine (3Ae)[9]: Purification by flash silica-gel column chromatography (hexane/ether = 3:1) afforded **3Ae** as a colorless oil (74.7 mg, 44% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 (d, *J* = 4.4 Hz, 1H), 7.75 (td, *J* = 8.0, 2.0 Hz, 1H), 7.43–7.37 (m, 2H), 7.34–7.19 (m, 4H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 149.1, 140.4, 136.1, 135.7, 130.7, 129.6, 128.2, 125.8, 124.1, 121.6, 20.2; HRMS (DART) *m/z* calcd for $C_{12}H_{12}N$ $[M+H]^+$: 170.0970, found 170.0973.



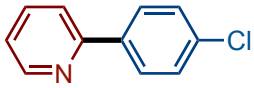
3Af
87%

2-(4-(Trifluoromethyl)phenyl)pyridine (3Af)[9]: Purification by flash silica-gel column chromatography (hexane/ether = 4:1) afforded **3Af** as a white solid (194.2 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (d, *J* = 5.2 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 2H), 7.85–7.75 (m, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.31 (dd, *J* = 7.2, 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.9, 149.9, 142.7, 137.0, 130.8 (q, J_{C-F} = 31.4 Hz), 127.2, 125.7, 124.7 (q, J_{C-F} = 271 Hz), 122.9, 120.8; HRMS (DART) *m/z* calcd for $C_{12}H_9F_3N$ $[M+H]^+$: 224.0687, found 224.0685.



3Ag
81%

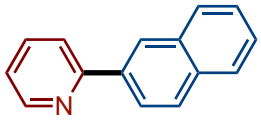
Methyl 4-(pyridin-2-yl)benzoate (3Ag)[10]: Purification by flash silica-gel column chromatography (hexane/ether = 2:1 to 1:1) afforded **3Ag** as a white solid (174.4 mg, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (d, *J* = 4.8 Hz, 1H), 8.15 (d, *J* = 8.0 Hz, 2H), 8.08 (d, *J* = 8.0 Hz, 2H), 7.80 (dd, *J* = 4.8, 1.2 Hz, 2H), 7.29 (dd, *J* = 8.0, 4.8 Hz, 1H), 3.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 156.2, 149.9, 143.5, 136.9, 130.3, 130.0, 126.8, 122.8, 121.0, 52.2; HRMS (DART) *m/z* calcd for $C_{13}H_{12}NO_2$ $[M+H]^+$: 214.0868, found 214.0873.



3Ah
51%

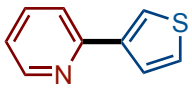
10. Luzung, M. R.; Patel, J. S.; Yin, J. *J. Org. Chem.* **2010**, *75*, 8330.

2-(4-Chlorophenyl)pyridine (3Ah)[9]: Purification by flash silica-gel column chromatography (hexane/ether = 4:1) afforded **3Ah** as a white solid (96.7 mg, 51% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (d, *J* = 5.2 Hz, 1H), 7.94 (d, *J* = 8.8 Hz, 2H), 7.76 (dd, *J* = 8.0, 7.2 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.8 Hz, 2H), 7.23 (dd, *J* = 7.2, 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.2, 149.7, 137.8, 136.8, 135.0, 128.90, 128.86, 128.1, 122.3, 120.3; HRMS (DART) *m/z* calcd for $C_{11}H_9ClN$ $[M+H]^+$: 190.0418, found 190.0417.



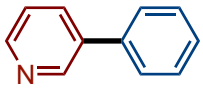
3Ai
88%

2-(Naphthalen-2-yl)pyridine (3Ai)[11]: Purification by flash silica-gel column chromatography (hexane/ether = 3:1) afforded **3Ah** as a white solid (180.6 mg, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (d, *J* = 4.8 Hz, 1H), 8.49 (s, 1H), 8.14 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.98–7.92 (m, 2H), 7.90–7.85 (m, 2H), 7.80 (td, *J* = 8.4, 2.0 Hz, 1H), 7.54–7.48 (m, 2H), 7.29–7.23 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.3, 149.7, 136.8, 136.6, 133.6, 133.5, 128.7, 128.4, 127.6, 126.5, 126.4, 126.3, 124.5, 122.1, 120.8; HRMS (DART) *m/z* calcd for $C_{15}H_{12}N$ $[M+H]^+$: 206.0970, found 206.0960.



3Aj
62%

2-(Thiophen-3-yl)pyridine (3Ai)[10]: Purification by flash silica-gel column chromatography (hexane/ether = 3:1) afforded **3Ai** as a white solid (100.0 mg, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (d, *J* = 4.8 Hz, 1H), 7.90 (d, *J* = 2.8 Hz, 1H), 7.70 (t, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 5.2 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.40 (dd, *J* = 5.2, 2.8 Hz, 1H), 7.17 (dd, *J* = 8.0, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.5, 149.6, 142.1, 136.6, 126.2, 126.1, 123.4, 121.7, 120.2; HRMS (DART) *m/z* calcd for C_9H_8NS $[M+H]^+$: 162.0377, found 162.0382.

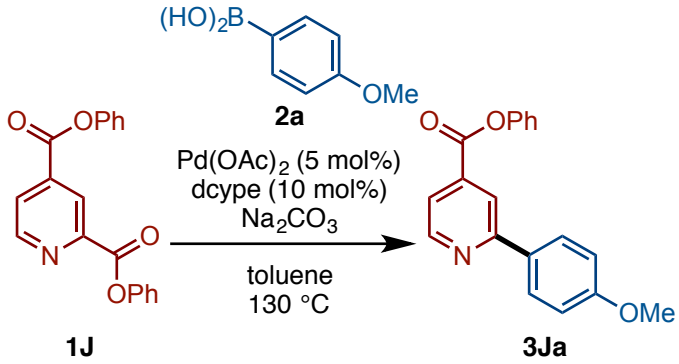


3Ib
55%

3-Phenylpyridine (3Ib)[3]: 0.40 mmol scale. Purification by flash silica-gel column chromatography (hexane/ether = 3:1) afforded **3Ib** as a colorless liquid (with dcype ligand: no reaction; with P(*n*-Bu)$_3$ ligand: 34.0 mg, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.85 (d, *J* = 2.4 Hz, 1H), 8.58 (dd, *J* = 4.8,

11. Kobayashi, O.; Uraguchi, D.; Yamakawa, T. *Org. Lett.* **2009**, *11*, 2679.

2.4 Hz, 1H), 7.87 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.58 (d, *J* = 7.2 Hz, 2H), 7.49 (dd, *J* = 8.4, 7.2 Hz, 2H), 7.40 (t, *J* = 8.4 Hz, 1H), 7.36 (dd, *J* = 8.4, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.3, 148.2, 137.7, 136.6, 134.3, 129.0, 128.0, 127.1, 123.5; HRMS (DART) *m/z* calcd for $C_{11}H_{10}N$ $[M+H]^+$: 156.0808, found 156.0806.

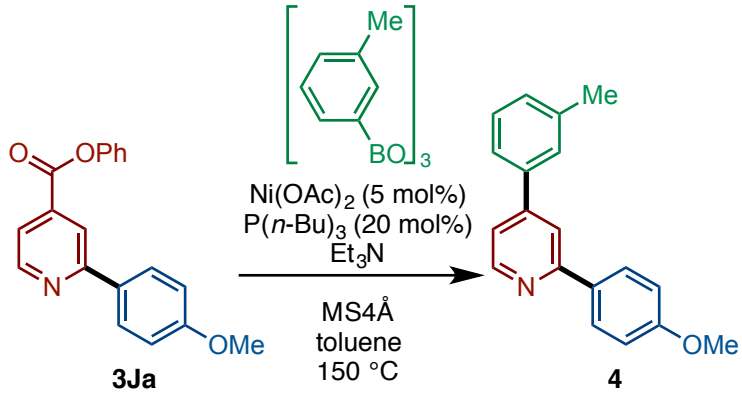


61%

C2-selective

Phenyl 2-(4-methoxyphenyl)isonicotinate (3Ja)

2 mmol scale. A 50-mL glass Schlenk tube containing a magnetic stirring bar was dried with a heatgun for 3 min *in vacuo* and filled with argon after cooling to room temperature. $Pd(OAc)_2$ (22.5 mg, 0.10 mmol, 5 mol%), 1,2-bis(dicyclohexylphosphino)ethane (dcype: 84.5 mg, 0.20 mmol, 10 mol%), Na_2CO_3 (424.0 mg, 2.0 mmol, 2.0 equiv), diphenyl pyridine-2,4-dicarboxylate (**1J**: 638.6 mg, 2.0 mmol, 1.0 equiv), and (4-methoxyphenyl)boronic acid (**2a**: 455.9 mg, 3.0 mmol, 1.5 equiv) were placed in the Schlenk tube under an argon atmosphere. Then, this tube was added dry degassed toluene (8.0 mL) and equipped reflux condenser under a stream of argon. The reaction mixture was stirred at 130 °C in an oil bath for 18 h. After cooling the reaction mixture to room temperature, the mixture was diluted with EtOAc and pathed through a pad of Celite®. The filtrate was concentrated *in vacuo* and the residue was purified by flash silica-gel column chromatography (hexane/ether = 3:1 to 1:1) to afford **3Ja** as a white solid (368.1 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.87 (dd, *J* = 4.8, 1.2 Hz, 1H), 8.38 (d, *J* = 1.2 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 2H), 7.87 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.47 (dd, *J* = 8.0, 7.2 Hz, 2H), 7.33 (d, *J* = 7.2 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.0, 160.9, 158.3, 150.54, 150.45, 137.6, 130.9, 129.6, 128.3, 126.3, 121.4, 120.6, 119.2, 114.2, 55.3; HRMS (DART) *m/z* calcd for $C_{19}H_{16}NO_3$ $[M+H]^+$: 306.1130, found 306.1130.



3Ja **4**

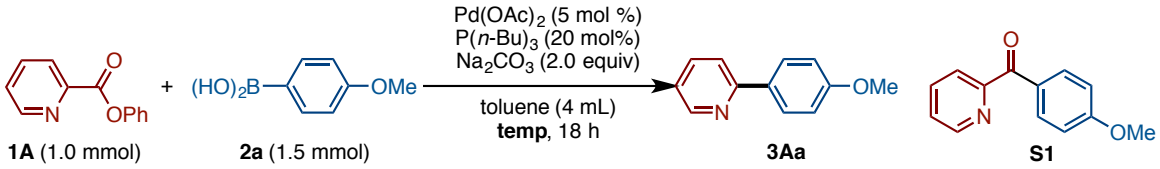
65%

2-(4-Methoxyphenyl)-4-(*m*-tolyl)pyridine (4)

A 100-mL glass J-Young® tube containing a magnetic stirring bar and 250 mg of molecular sieves (4Å) was dried with a heatgun for 10 min *in vacuo* and filled with argon after cooling to room temperature. $Ni(OAc)_2$ (8.8 mg, 0.050 mmol, 5 mol%), phenyl 2-(4-methoxyphenyl)isonicotinate (**3Ja**) (305.3 mg, 1.0 mmol, 1.0 equiv), and *m*-tolyl boroxine (176.9 mg, 0.50 mmol, 0.50 equiv) were placed in the tube under an argon atmosphere. Then, this tube were added P(*n*-Bu)$_3$ (40.5 mg, 0.20 mmol, 20 mol%), Et_3N (151.8 mg, 1.5 mmol, 1.5 equiv), and dry degassed toluene (4.0 mL) and sealed with O-ring tap under a stream of argon. The reaction mixture was stirred at 150 °C in an oil bath for 24 h. After cooling the reaction mixture to room temperature, the mixture was diluted with EtOAc and pathed through a pad of Celite®. The filtrate was concentrated *in vacuo* and the residue was purified by flash silica-gel column chromatography (hexane/ether = 5:2) to afford **4** as a colorless oil (179.0 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (d, *J* = 6.0 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.86 (s, 1H), 7.51–7.47 (m, 2H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 6.0 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 2H), 3.88 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.4, 157.5, 149.8, 149.2, 138.7, 138.6, 132.0, 129.6, 128.9, 128.2, 127.7, 124.1, 119.6, 117.9, 114.0, 55.2, 21.4; HRMS (DART) *m/z* calcd for $C_{19}H_{18}NO$ $[M+H]^+$: 276.1388, found 276.1388.

4. Condition Screening

Effect of temperature

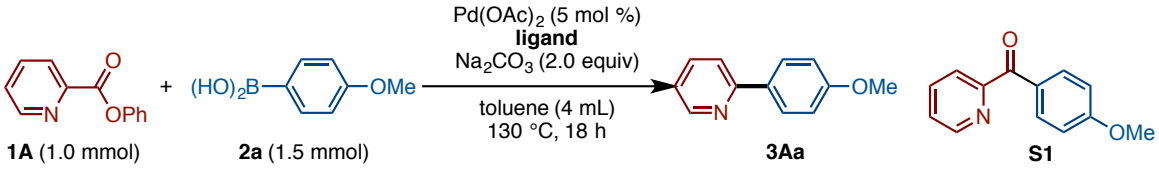


1A (1.0 mmol) **2a** (1.5 mmol) **3Aa** **S1**

entry	temp/°C	NMR yield/% **3Aa**	**S1**
1	150	38	9
2	130	48	7
3	100	8	8
4	80	7	5

NMR yield was detemined by using 1,4-bis(trimethylsilyl)benzene as an internal standard.

Effect of ligand

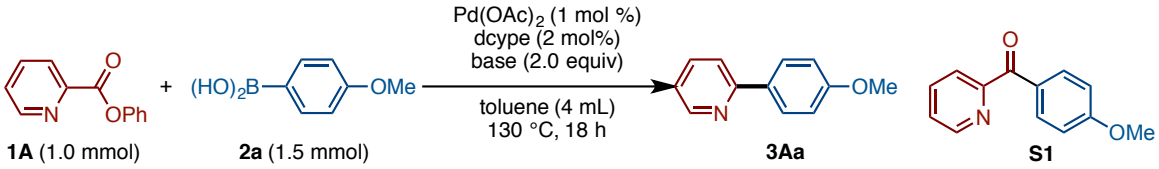


1A (1.0 mmol) **2a** (1.5 mmol) **3Aa** **S1**

entry	ligand/mol%	NMR yield/% **3Aa**	**S1**	entry	ligand/mol%	NMR yield/% **3Aa**	**S1**
1	P(*n*-Bu)$_3$ /20	48	7	11	dcype /10	97	0
2	PPh$_3$ /20	13	0	12	dcypt /20	0	0
3	P(*p*-Anisyl)$_3$ /20	14	0	13	dppe /10	11	0
4	PCy$_3$ /20	7	3	14	dppp /10	20	0
5	SPhos /20	20	3	15	dppb /10	19	0
6	XPhos /20	19	0	16	dppf /20	12	0
7	P(*t*-Bu)$_3$·HBF$_4$ /20	0	0	17	DPEphos	12	0
8	P(*t*-Bu)$_2$Me /20	16	3	18	Xantphos	17	0
9	Amphos /20	4	0	19	IPr·HCl	7	0
10	dcype /20	62	0	20	SIPr·HCl	7	0

NMR yield was detemined by using 1,4-bis(trimethylsilyl)benzene as an internal standard.

Effect of base



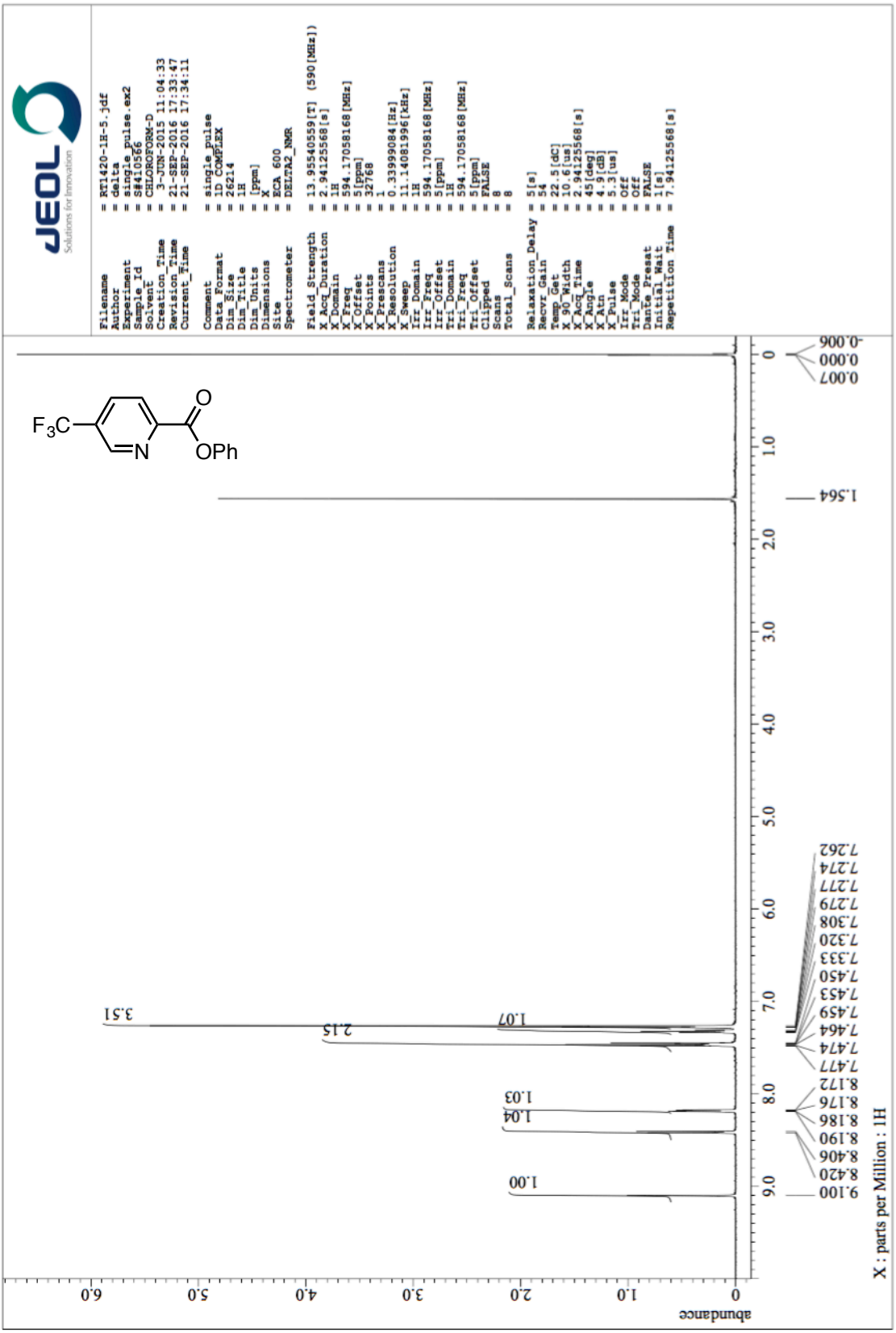
1A (1.0 mmol) **2a** (1.5 mmol) **3Aa** **S1**

entry	base	NMR yield/% **3Aa**	**S1**
1	Na_2CO_3	28	1
2	K_2CO_3	12	0
3	$NaHCO_3$	18	0
4	Li_2CO_3	0	0
5	K_3PO_4	19	0
6	Et_3N	34	0

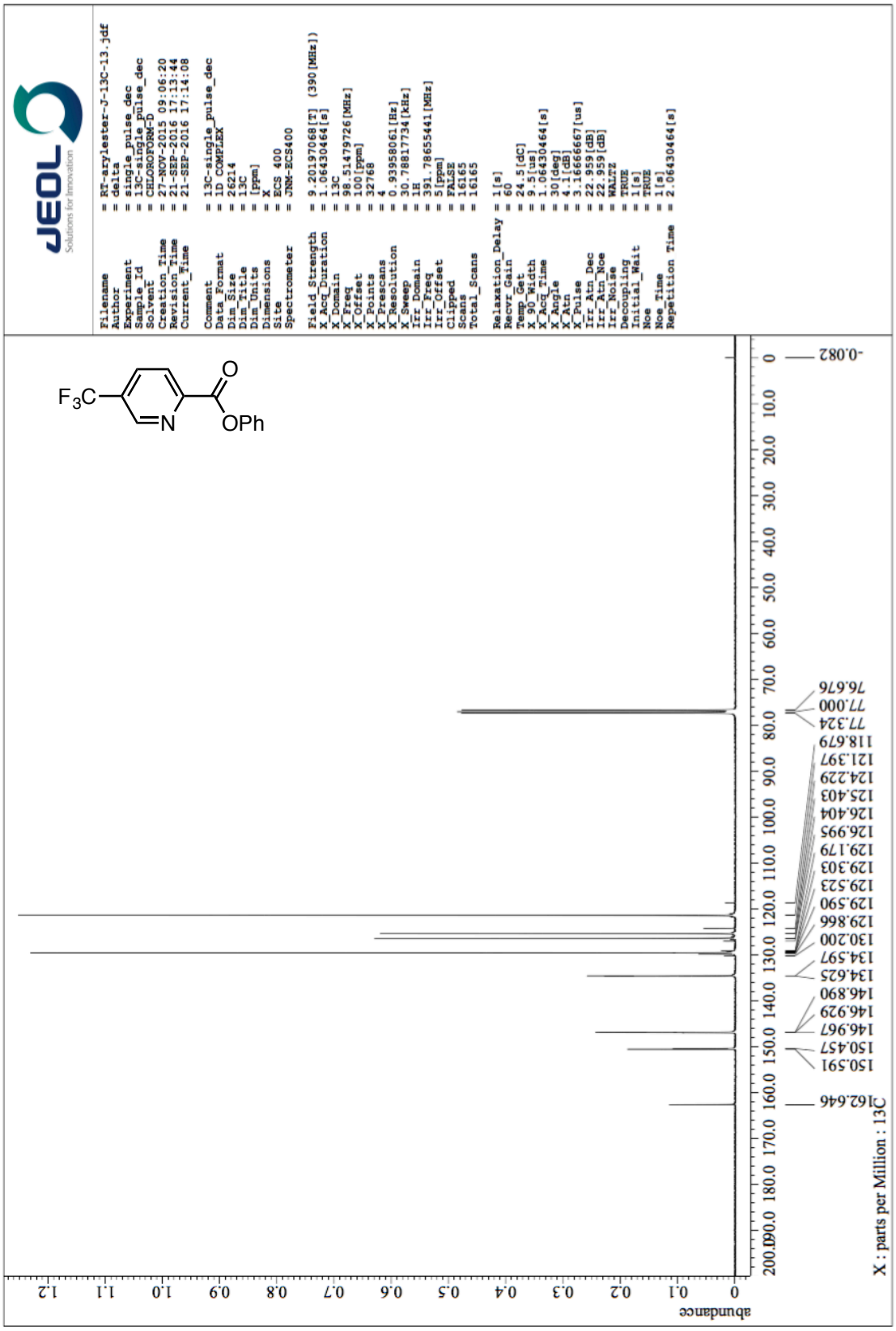
NMR yield was detemined by using 1,4-bis(trimethylsilyl)benzene as an internal standard.

5. ^{1}H NMR and ^{13}C NMR Spectra

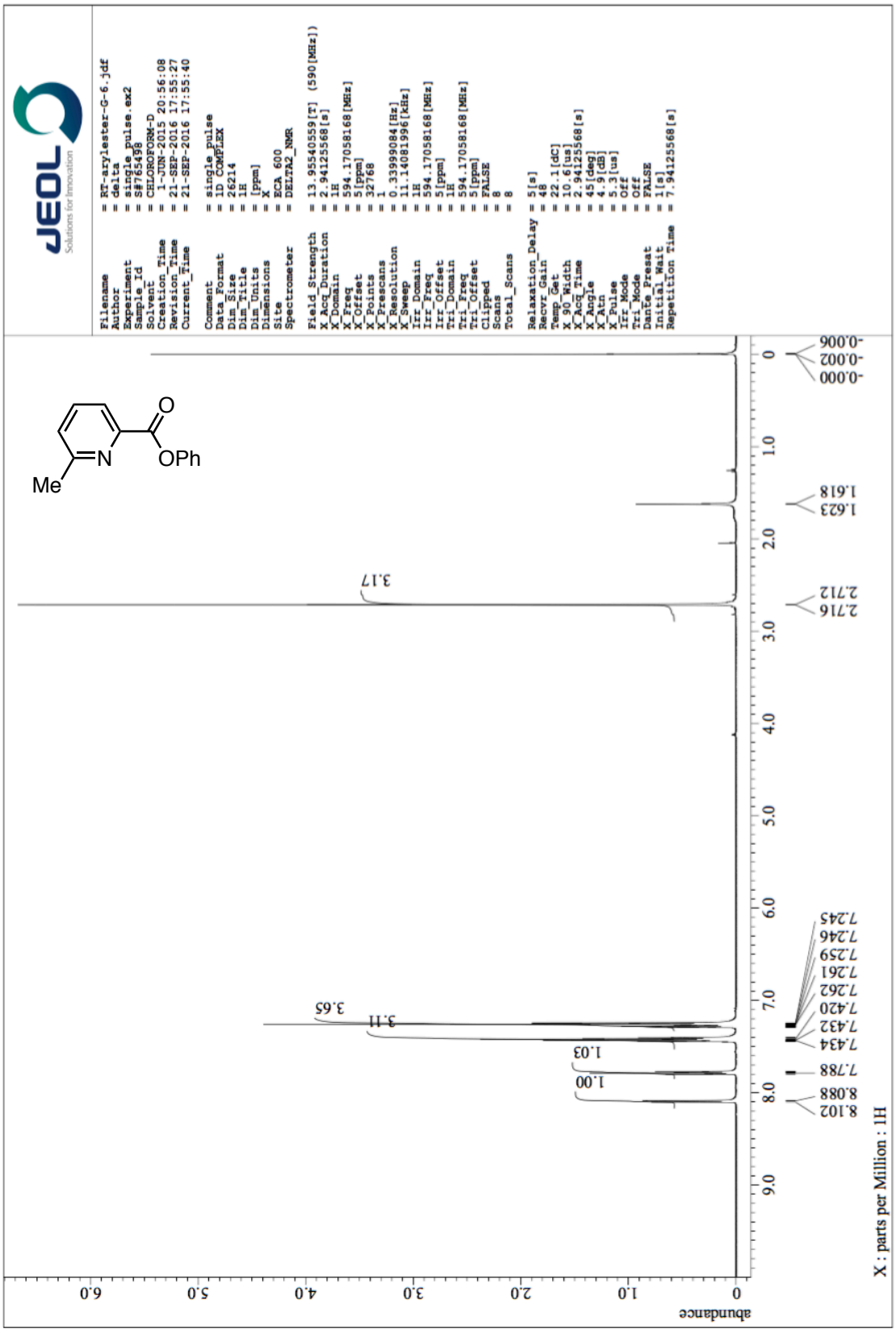
^{1}H NMR of **1B** (600 MHz, $CDCl_3$)



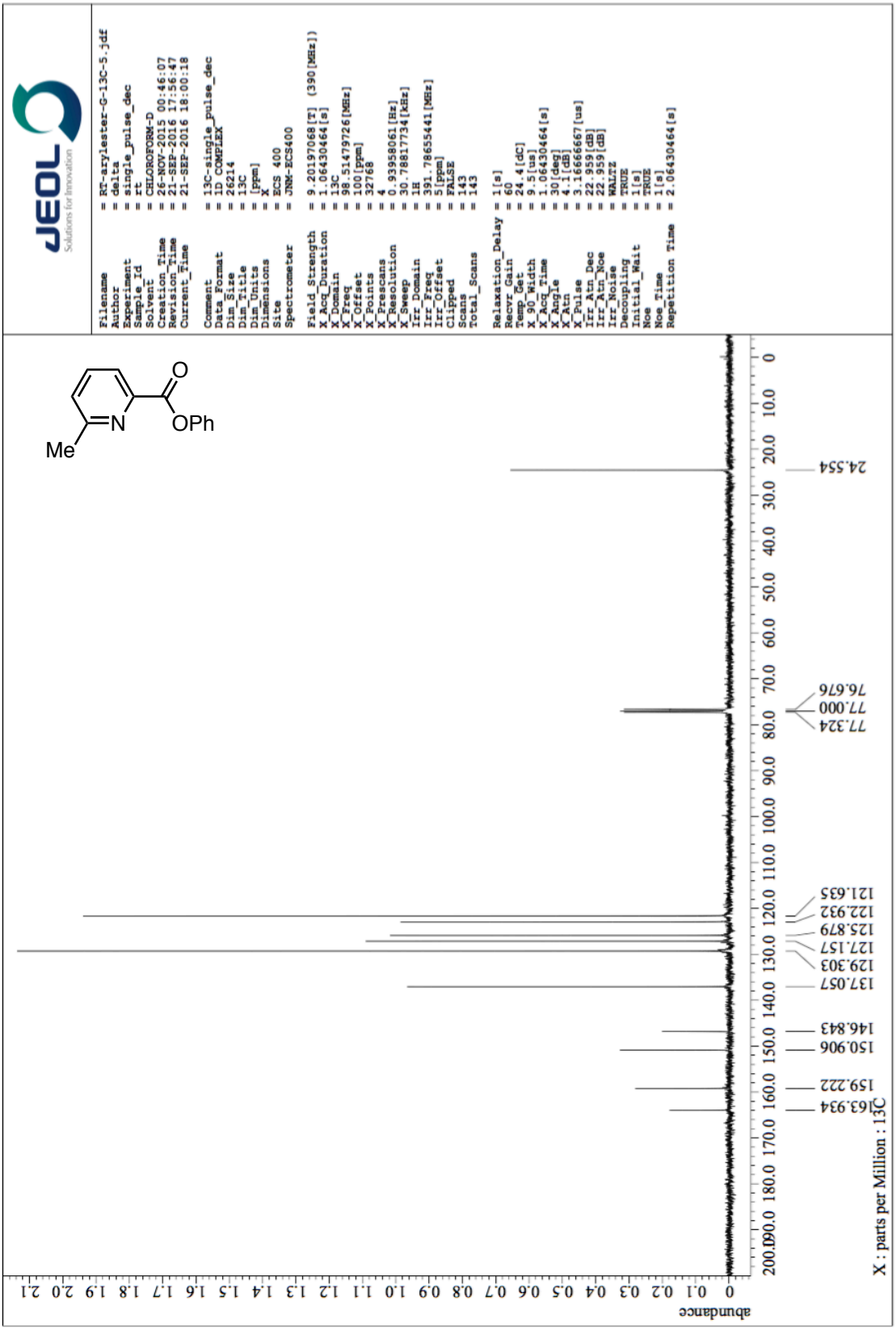
^{13}C NMR of **1B** (400 MHz, $CDCl_3$)



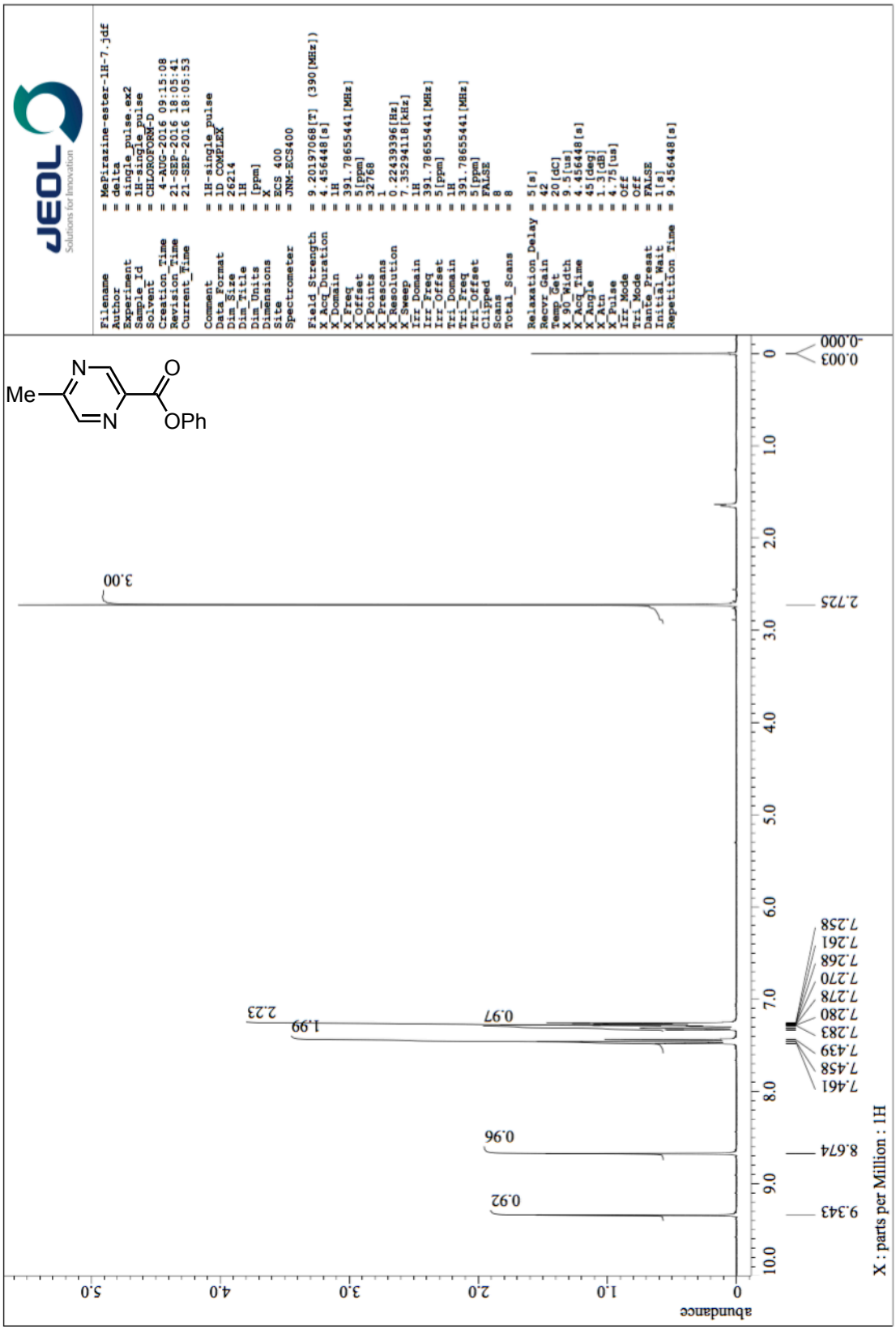
^{1}H NMR of **1C** (600 MHz, $CDCl_3$)



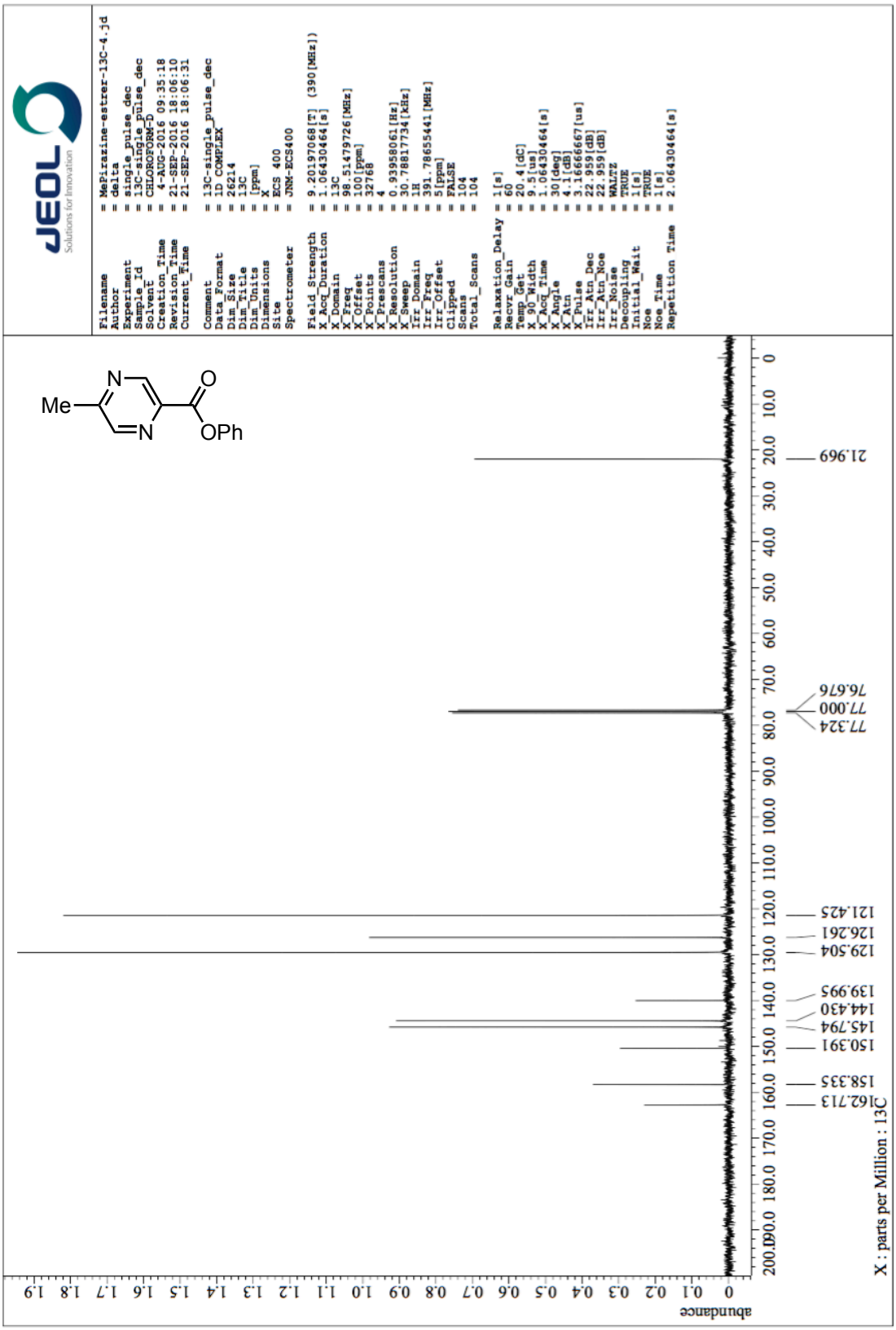
^{13}C NMR of **1C** (100 MHz, $CDCl_3$)



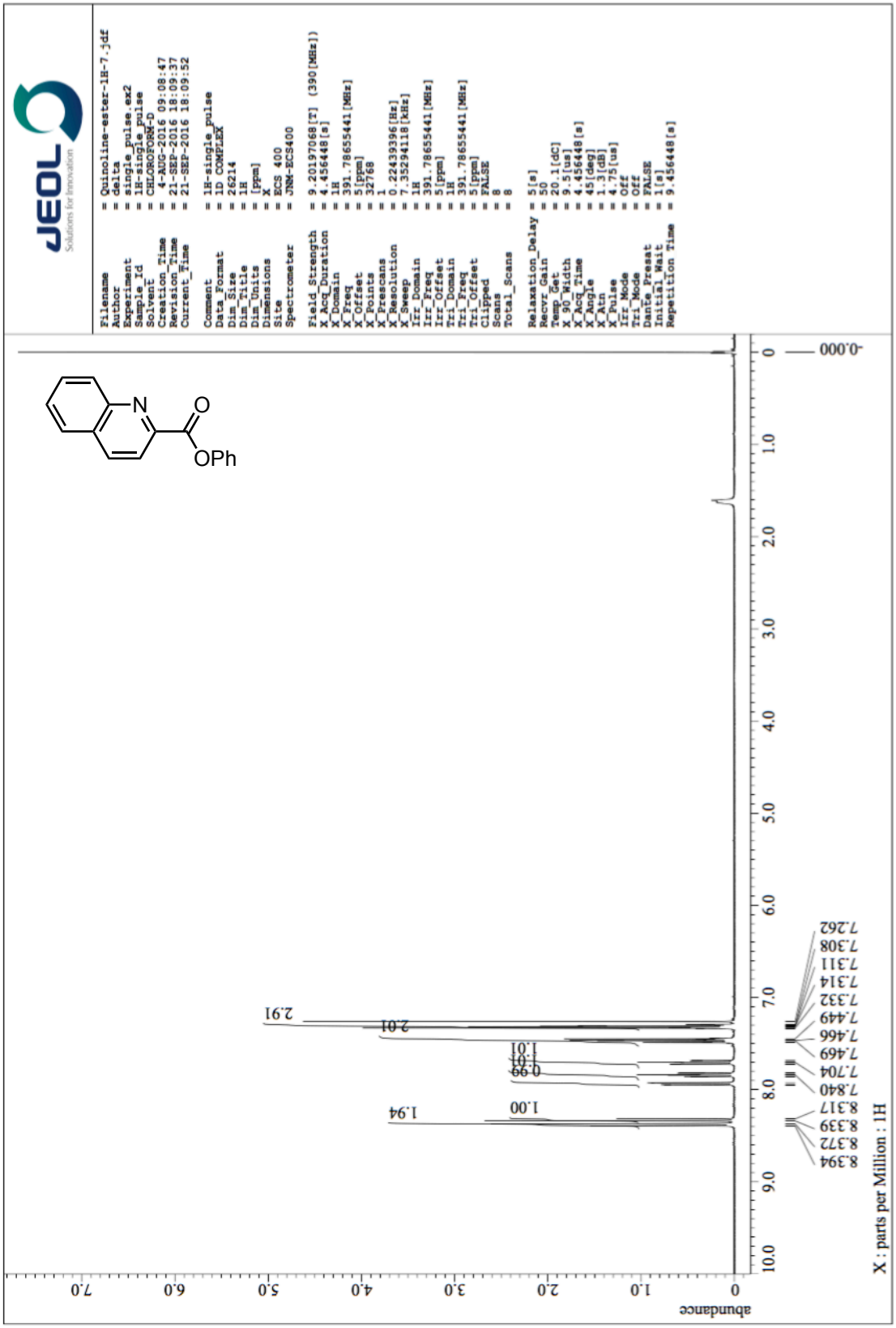
^{1}H NMR of **1E** (400 MHz, $CDCl_3$)



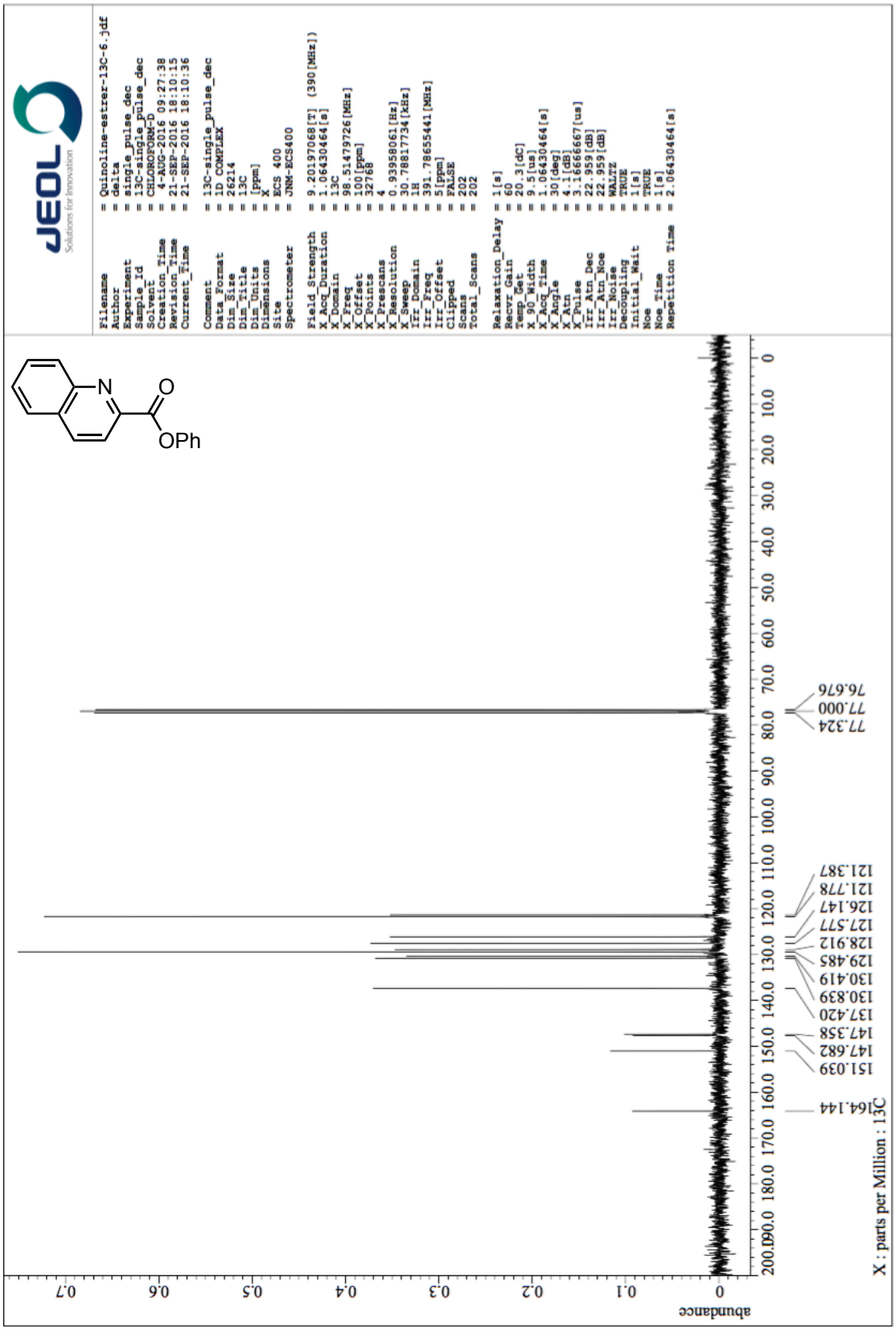
^{13}C NMR of **1E** (100 MHz, $CDCl_3$)



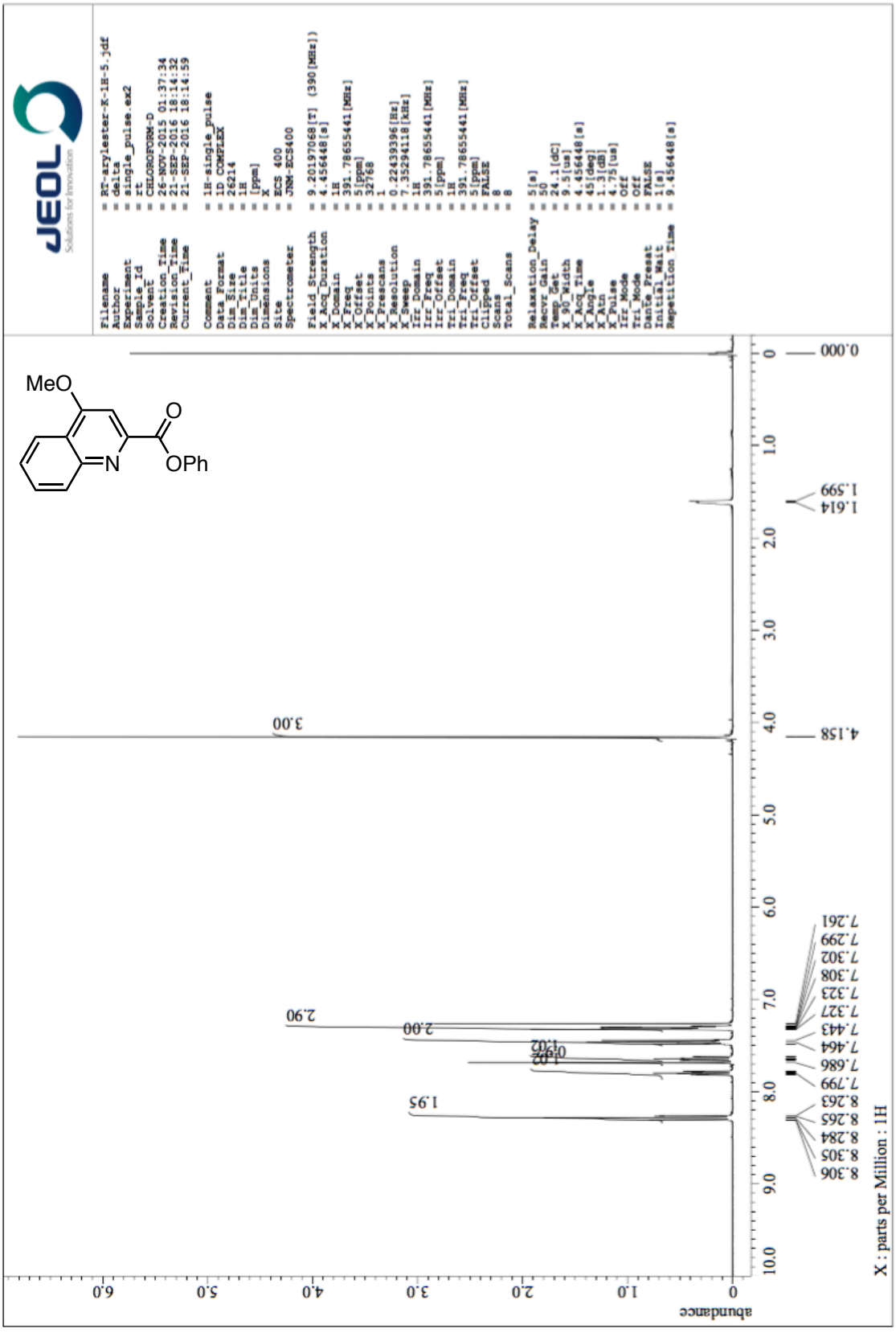
^{1}H NMR of **1F** (400 MHz, $CDCl_3$)



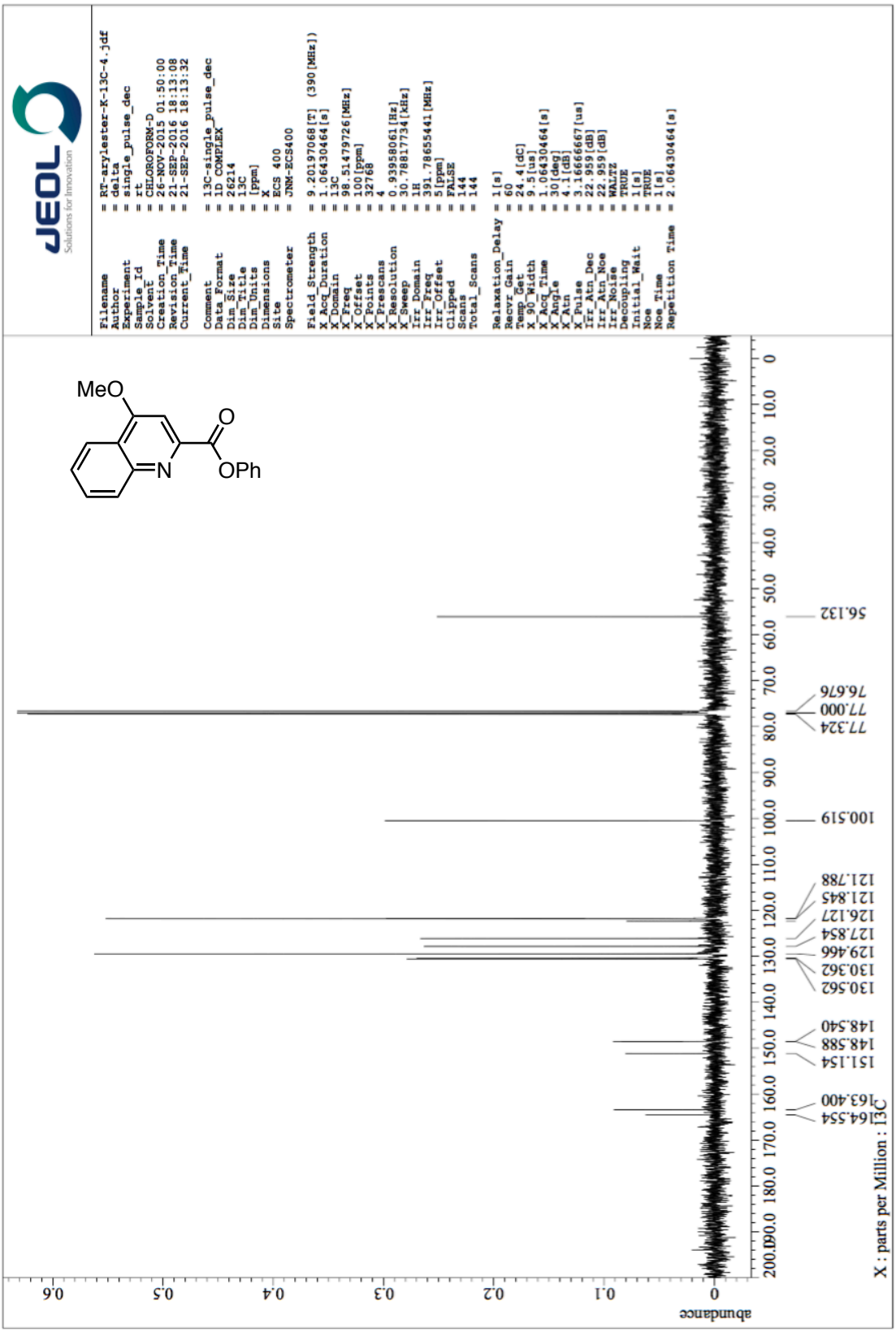
^{13}C NMR of **1F** (100 MHz, $CDCl_3$)



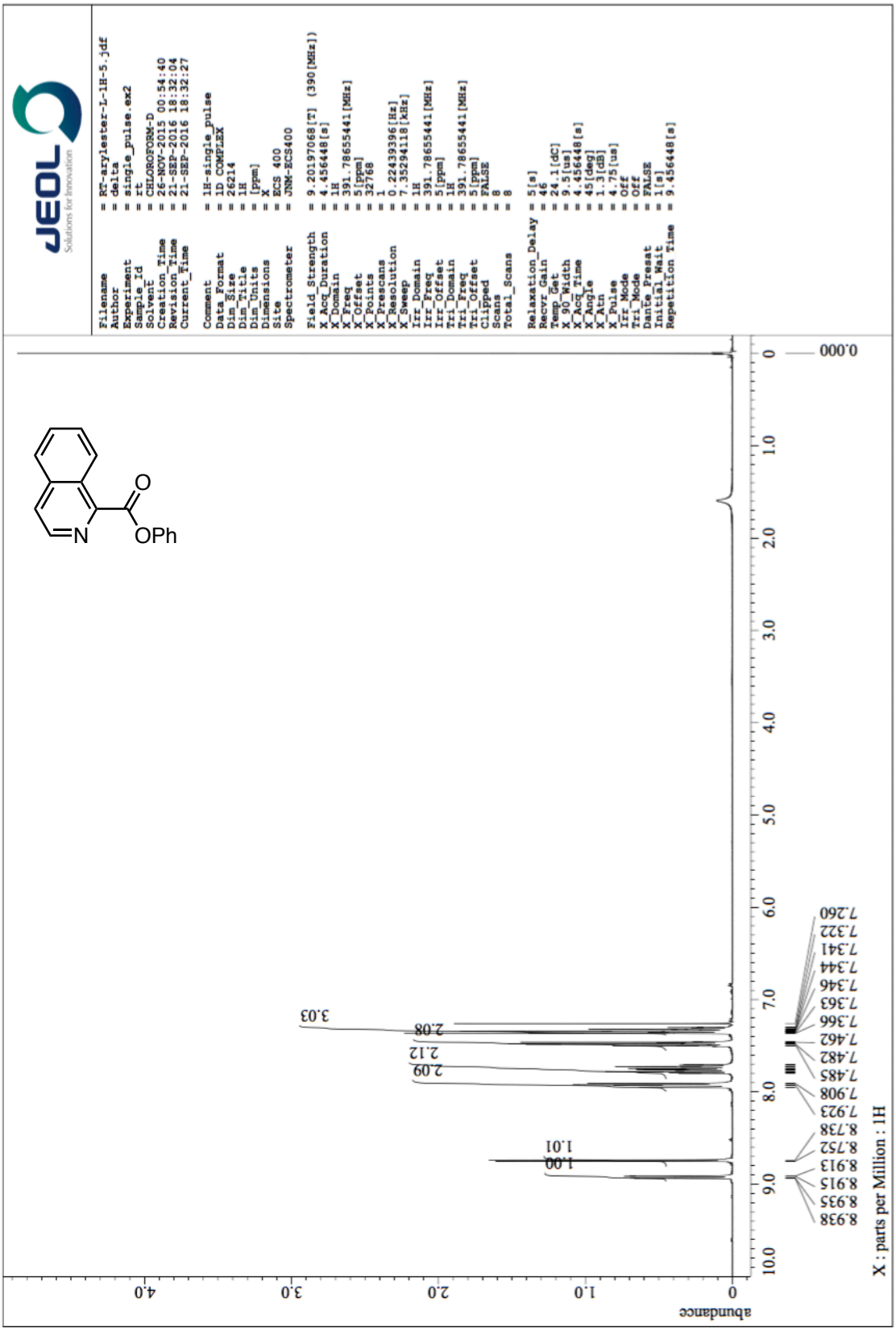
^{1}H NMR of **1G** (400 MHz, $CDCl_3$)



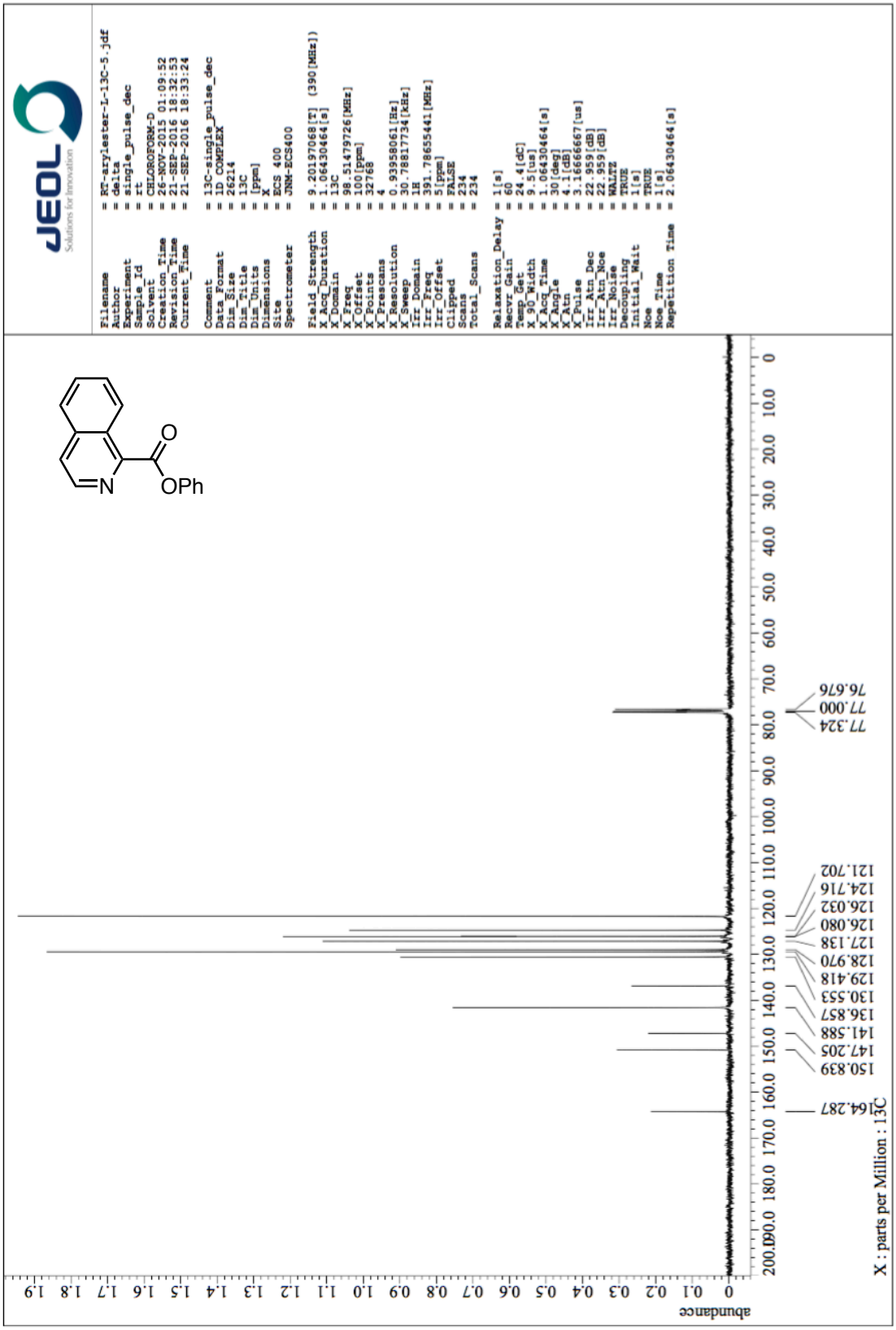
^{13}C NMR of **1G** (100 MHz, $CDCl_3$)



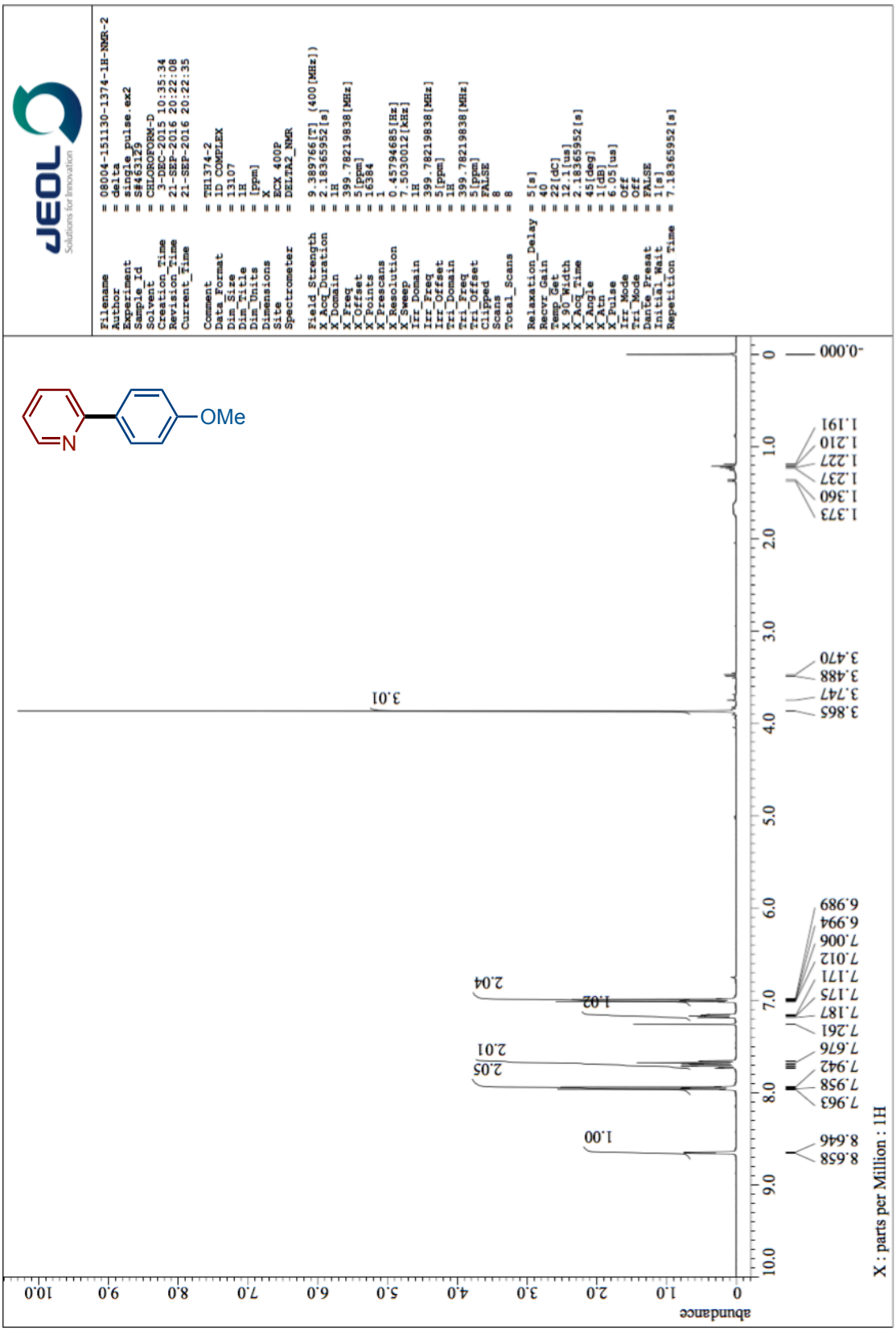
^{1}H NMR of **1H** (400 MHz, $CDCl_3$)



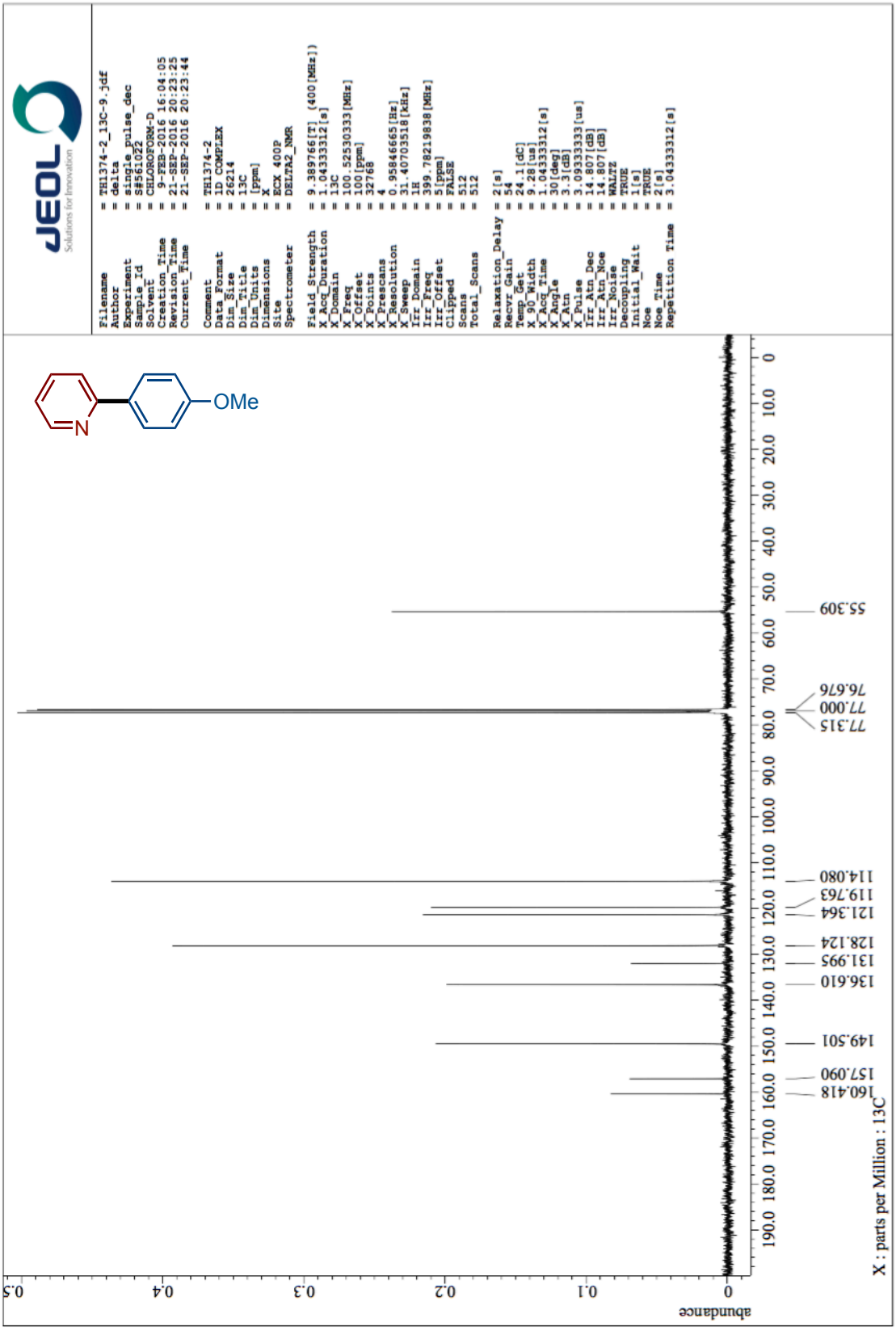
^{13}C NMR of **1H** (100 MHz, $CDCl_3$)



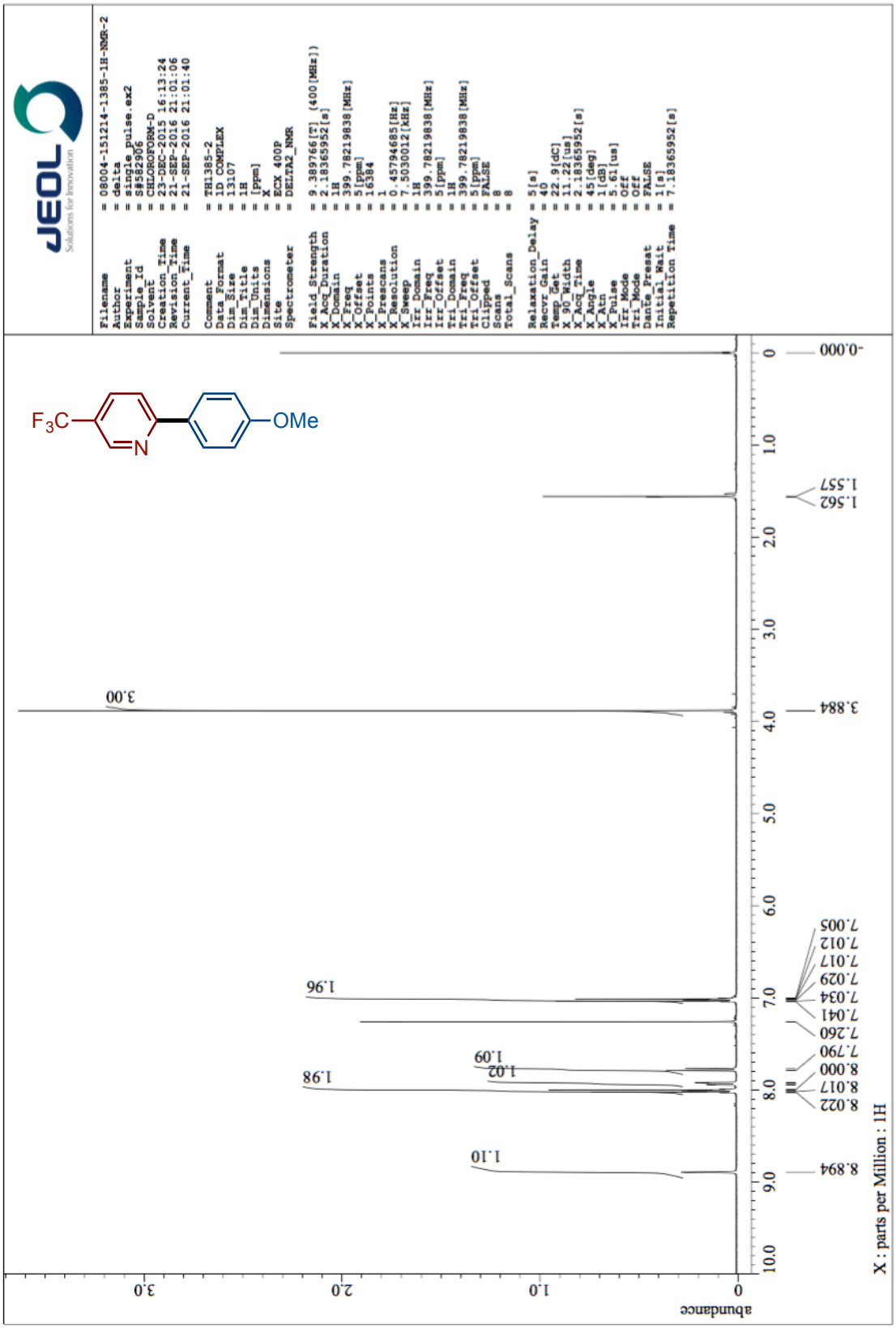
^{1}H NMR of **3Aa** (400 MHz, $CDCl_3$)



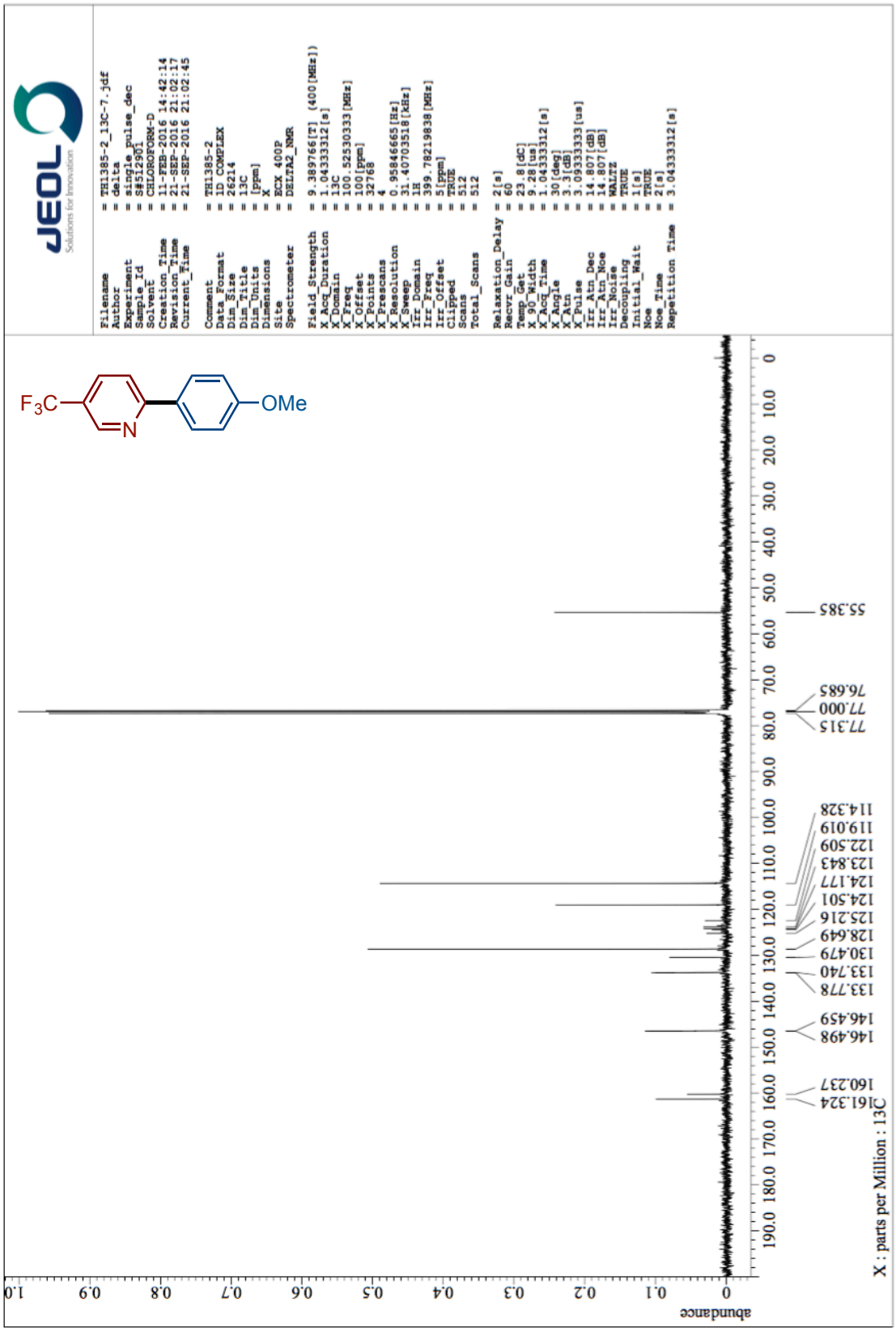
^{13}C NMR of **3Aa** (100 MHz, $CDCl_3$)



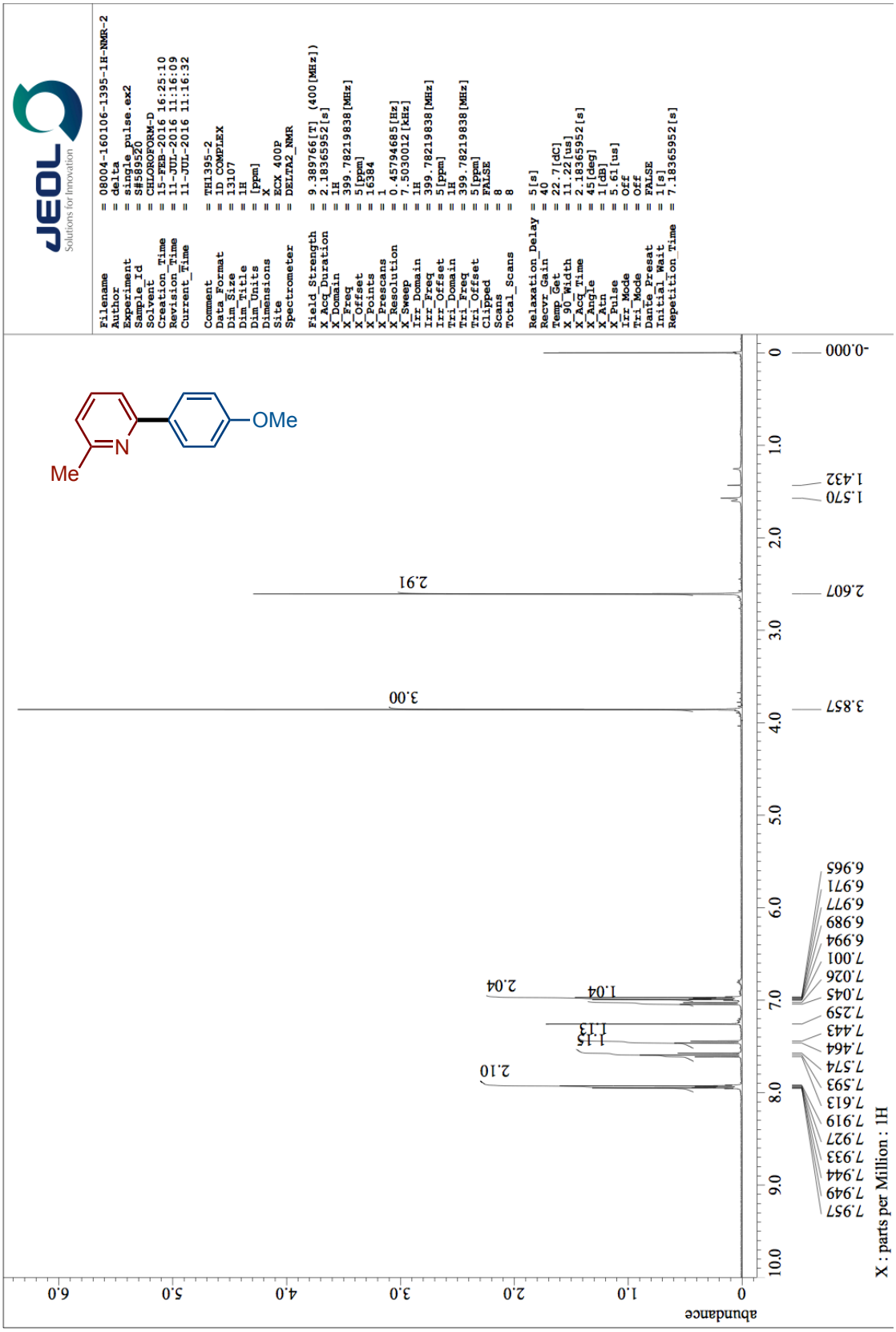
^{1}H NMR **3Ba** (400 MHz, $CDCl_3$)



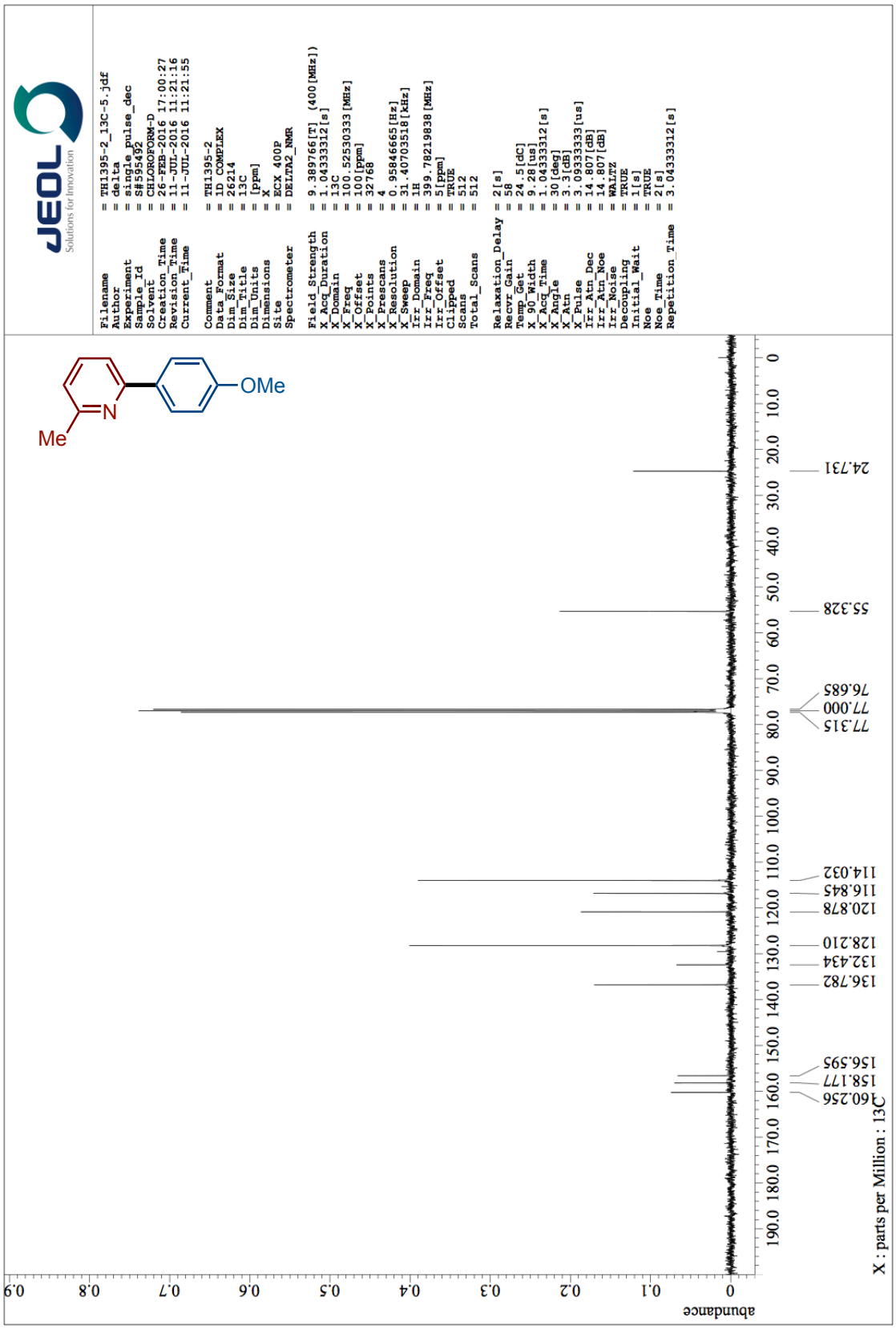
^{13}C NMR **3Ba** (100 MHz, $CDCl_3$)



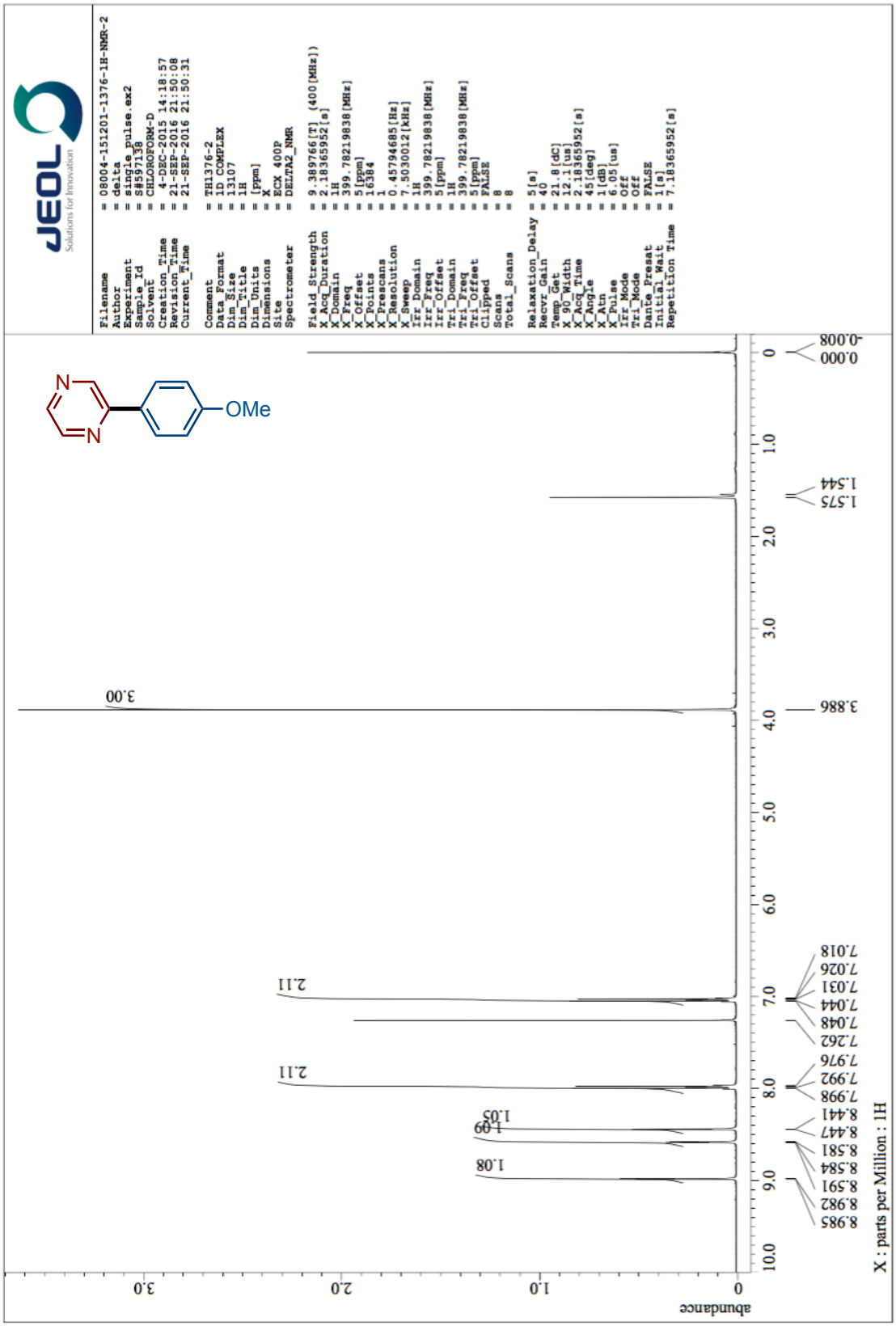
^{1}H NMR **3Ca** (400 MHz, $CDCl_3$)



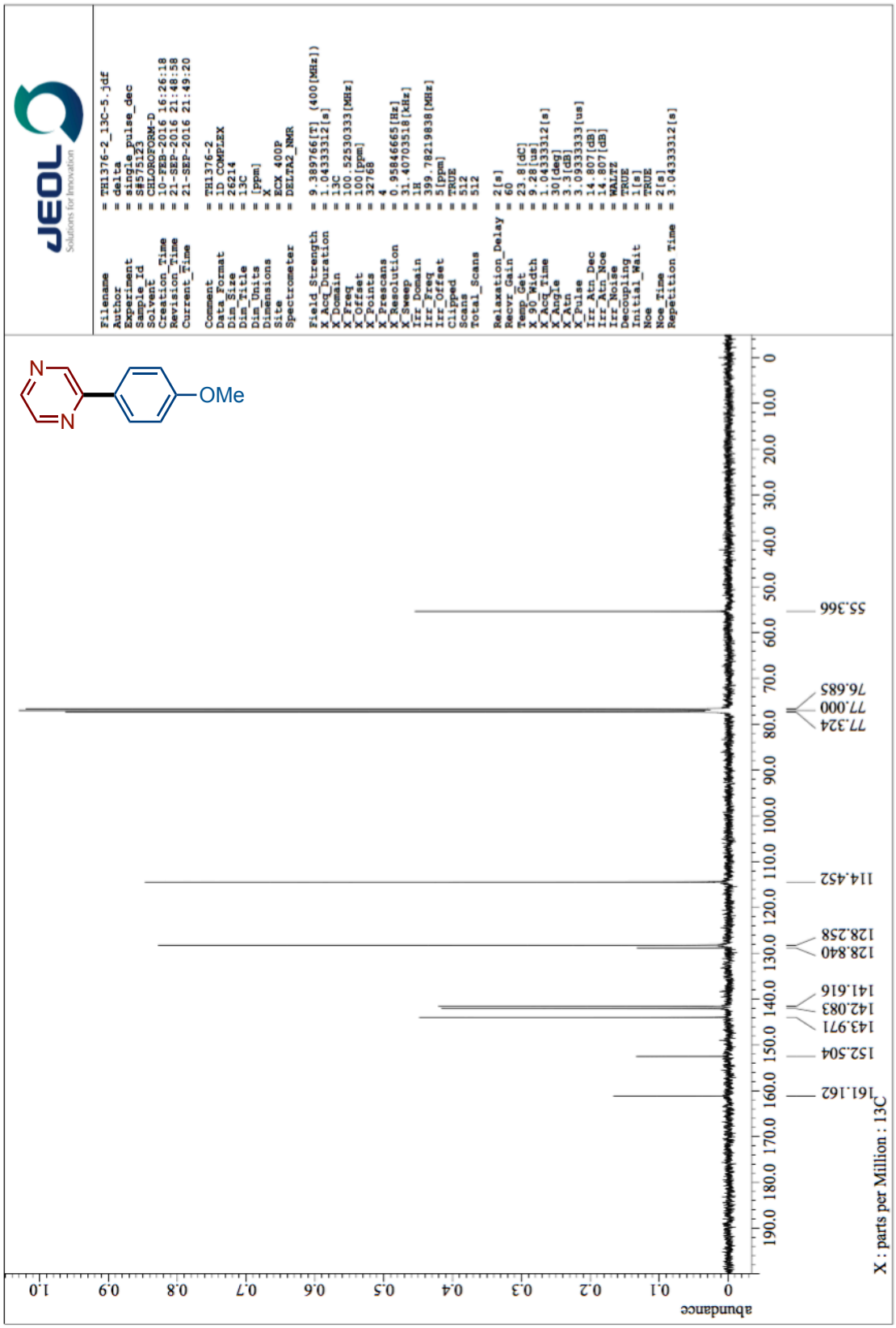
^{13}C NMR **3Ca** (100 MHz, $CDCl_3$)



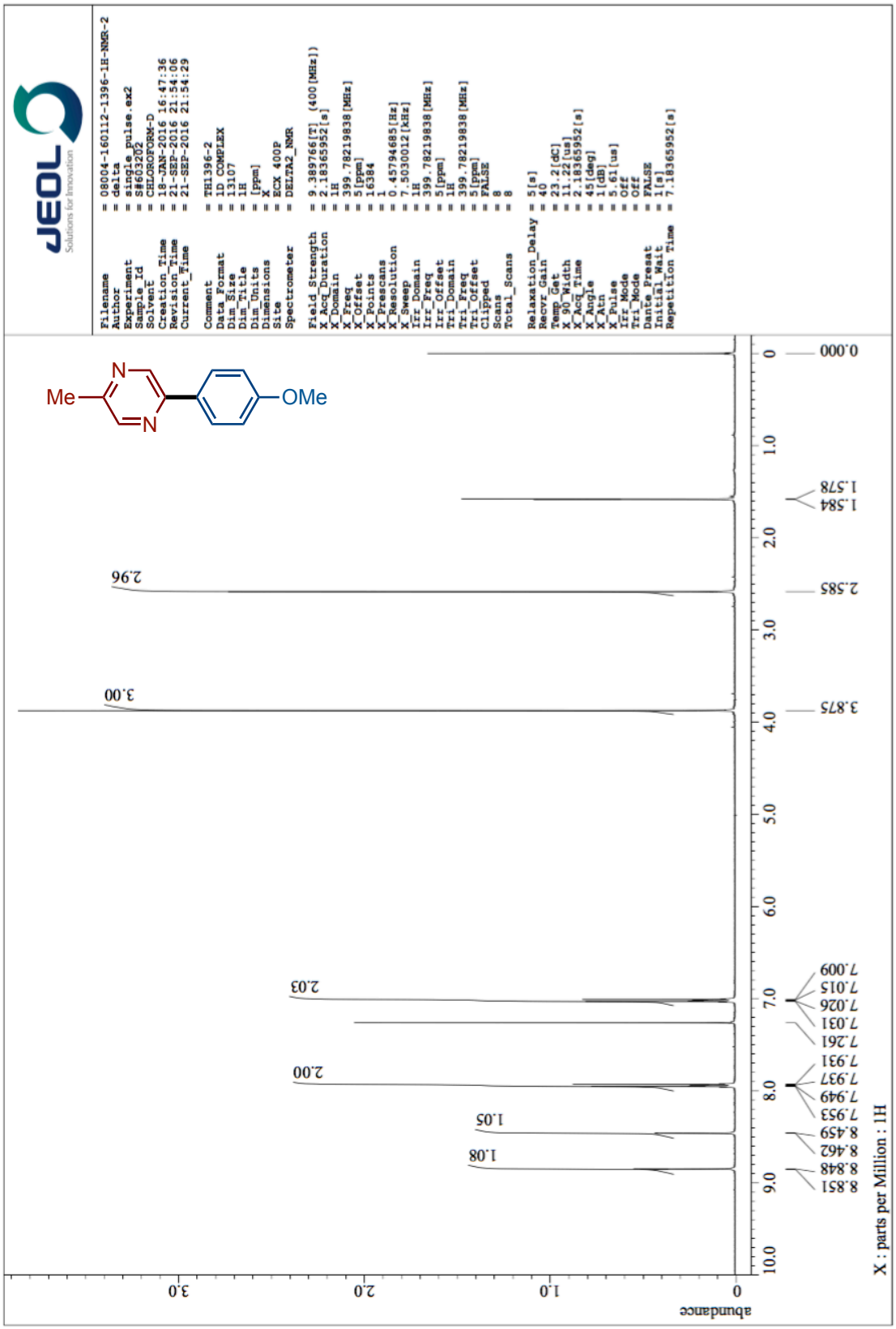
^{1}H NMR **3Da** (400 MHz, $CDCl_3$)



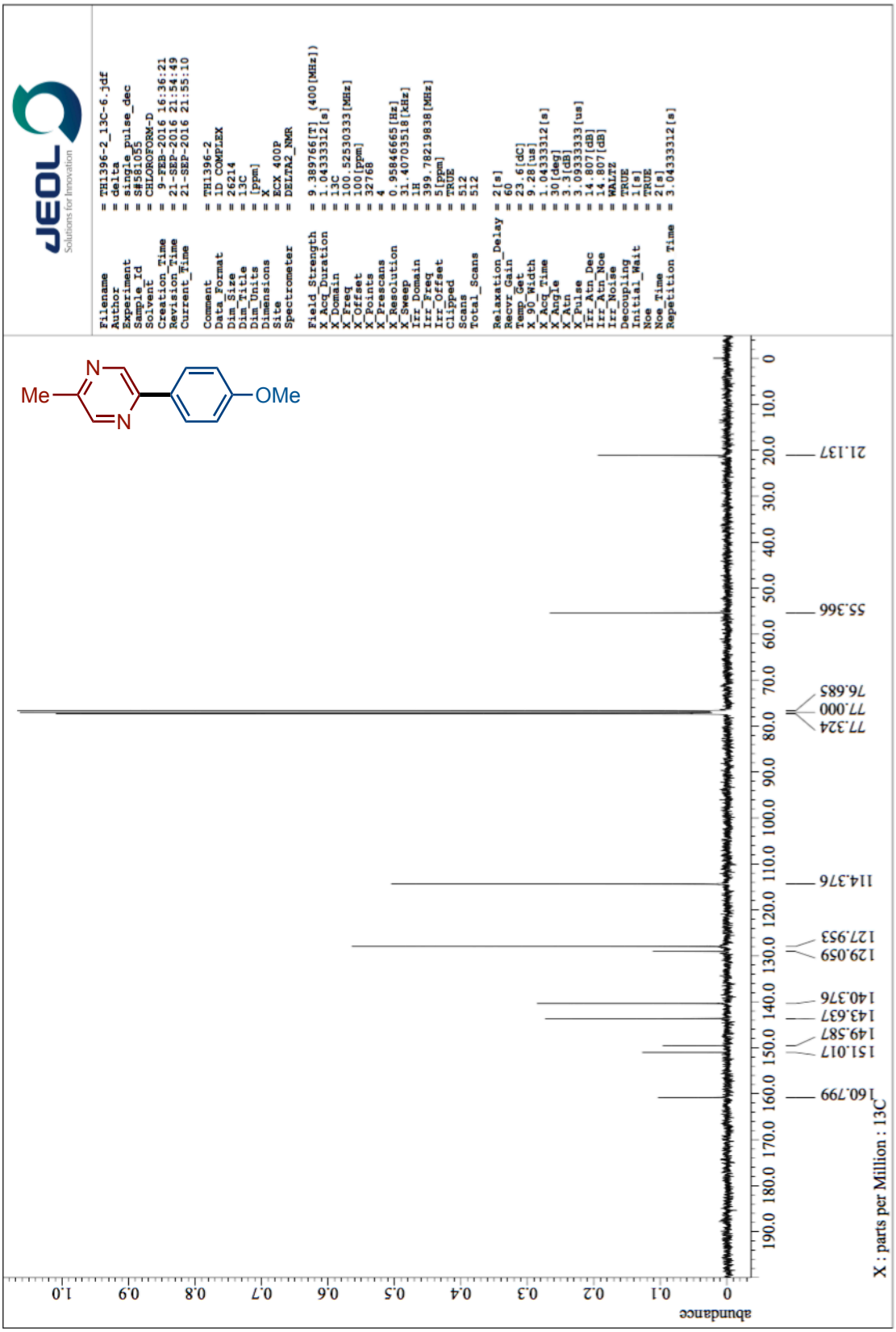
^{13}C NMR **3Da** (100 MHz, $CDCl_3$)



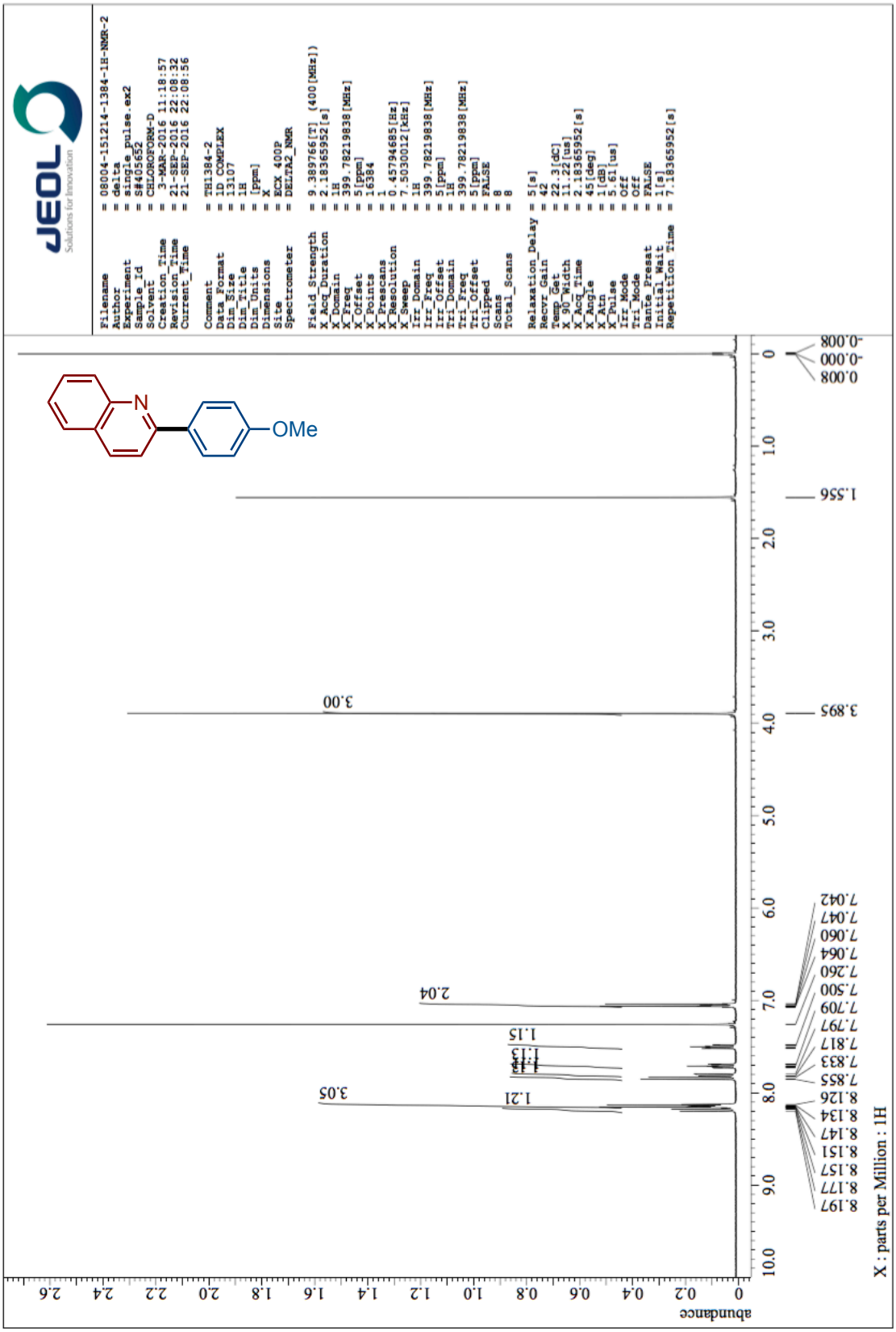
^{1}H NMR **3Ea** (400 MHz, $CDCl_3$)



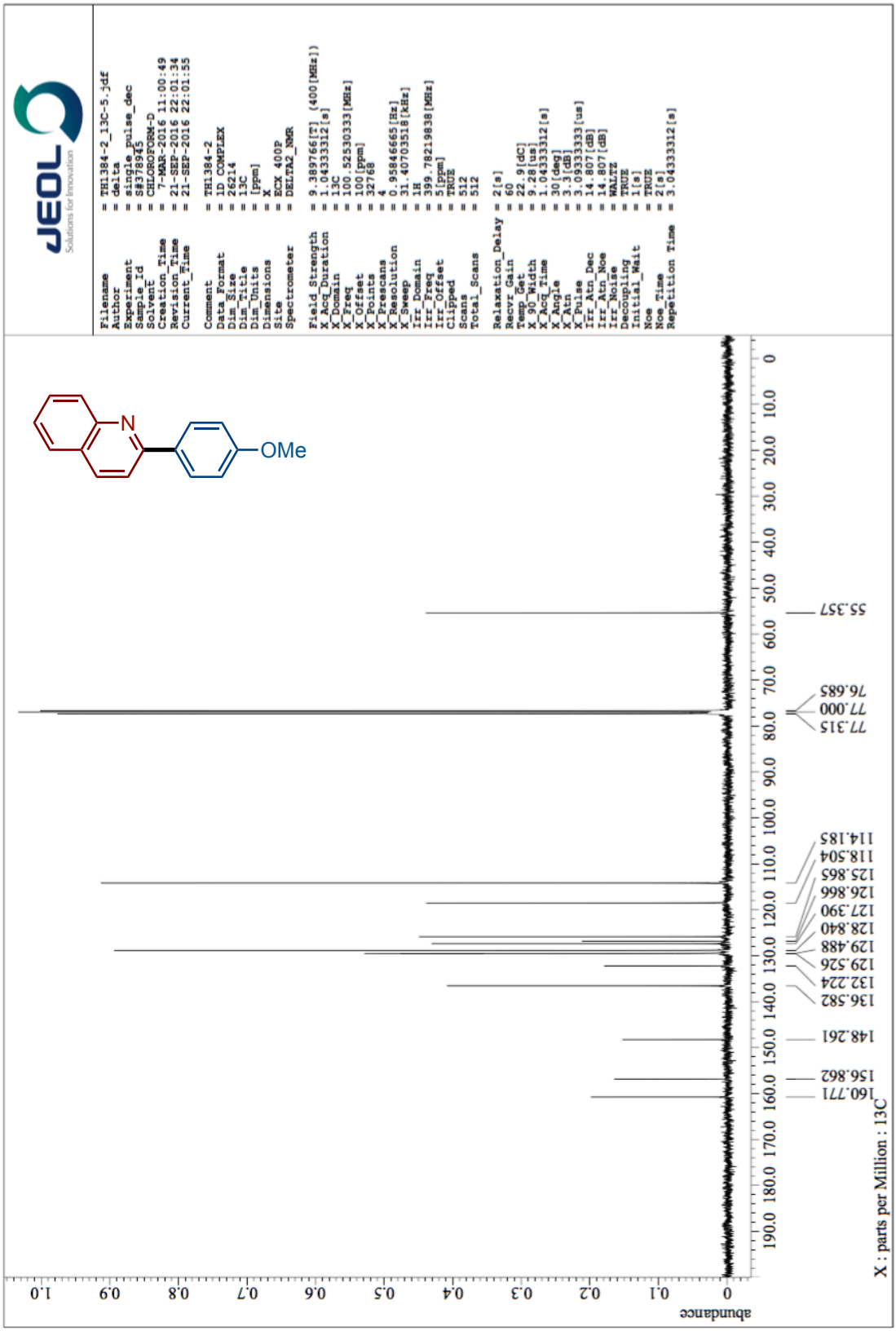
^{13}C NMR **3Ea** (100 MHz, $CDCl_3$)



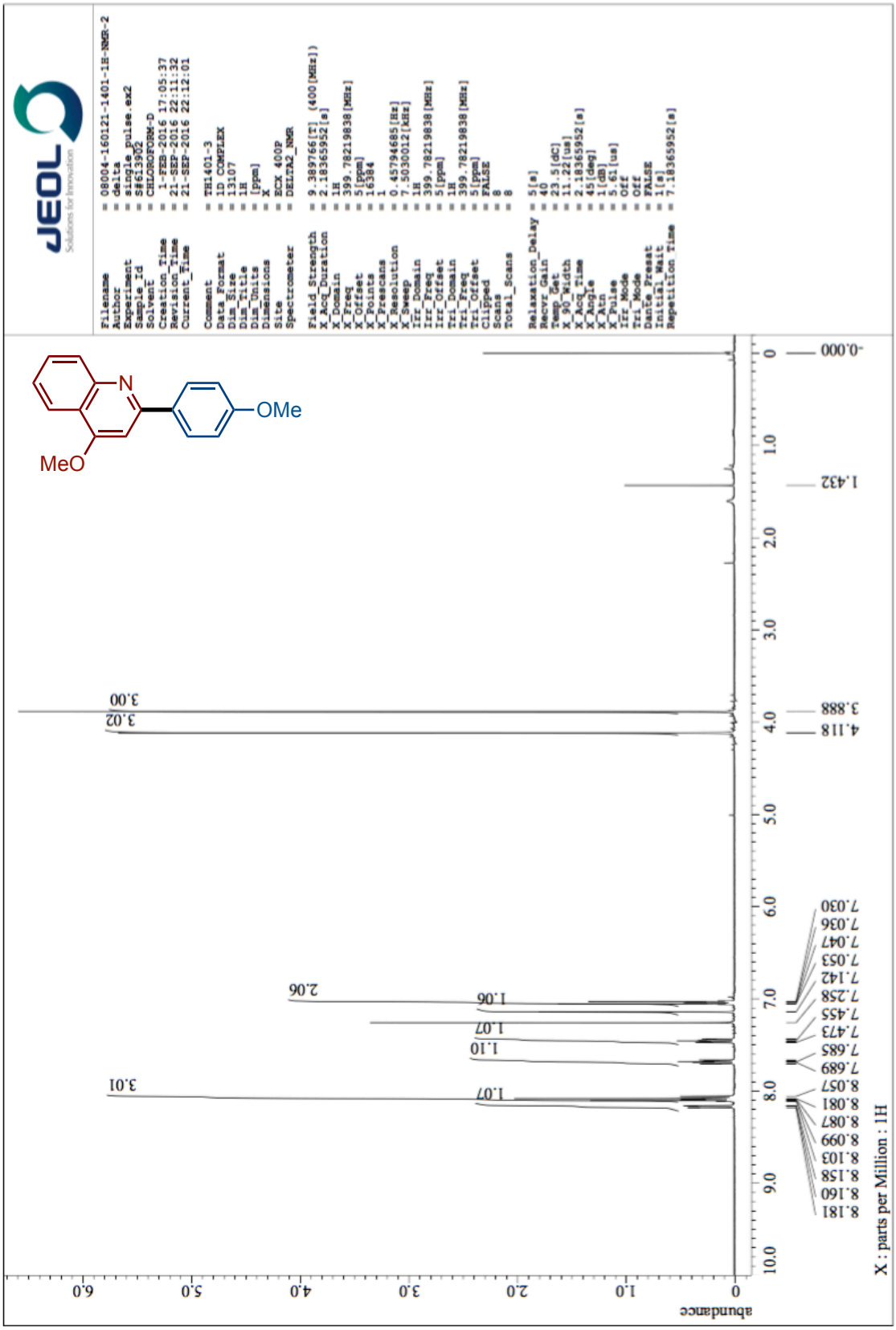
^{1}H NMR **3Fa** (400 MHz, $CDCl_3$)



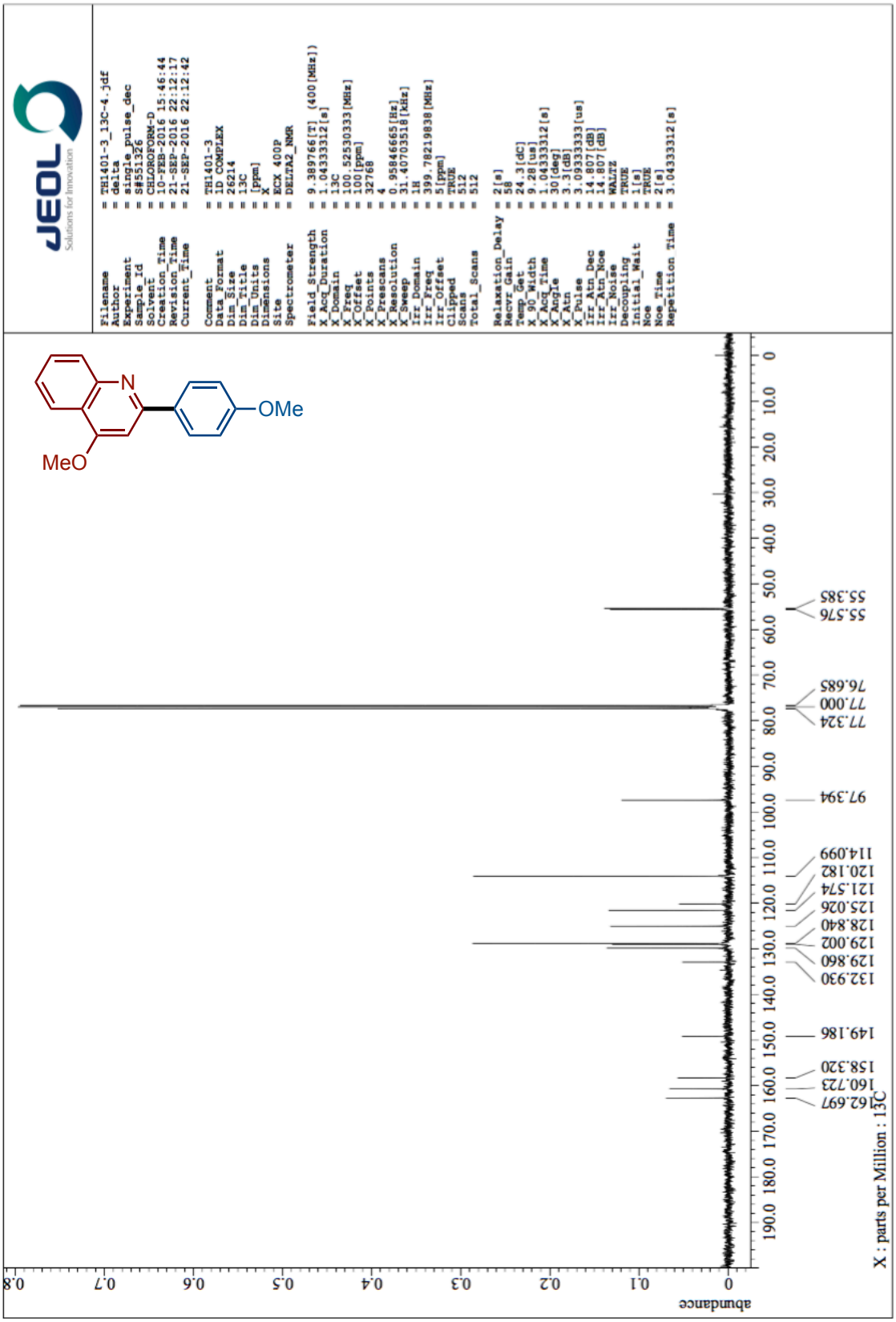
^{13}C NMR **3Fa** (100 MHz, $CDCl_3$)



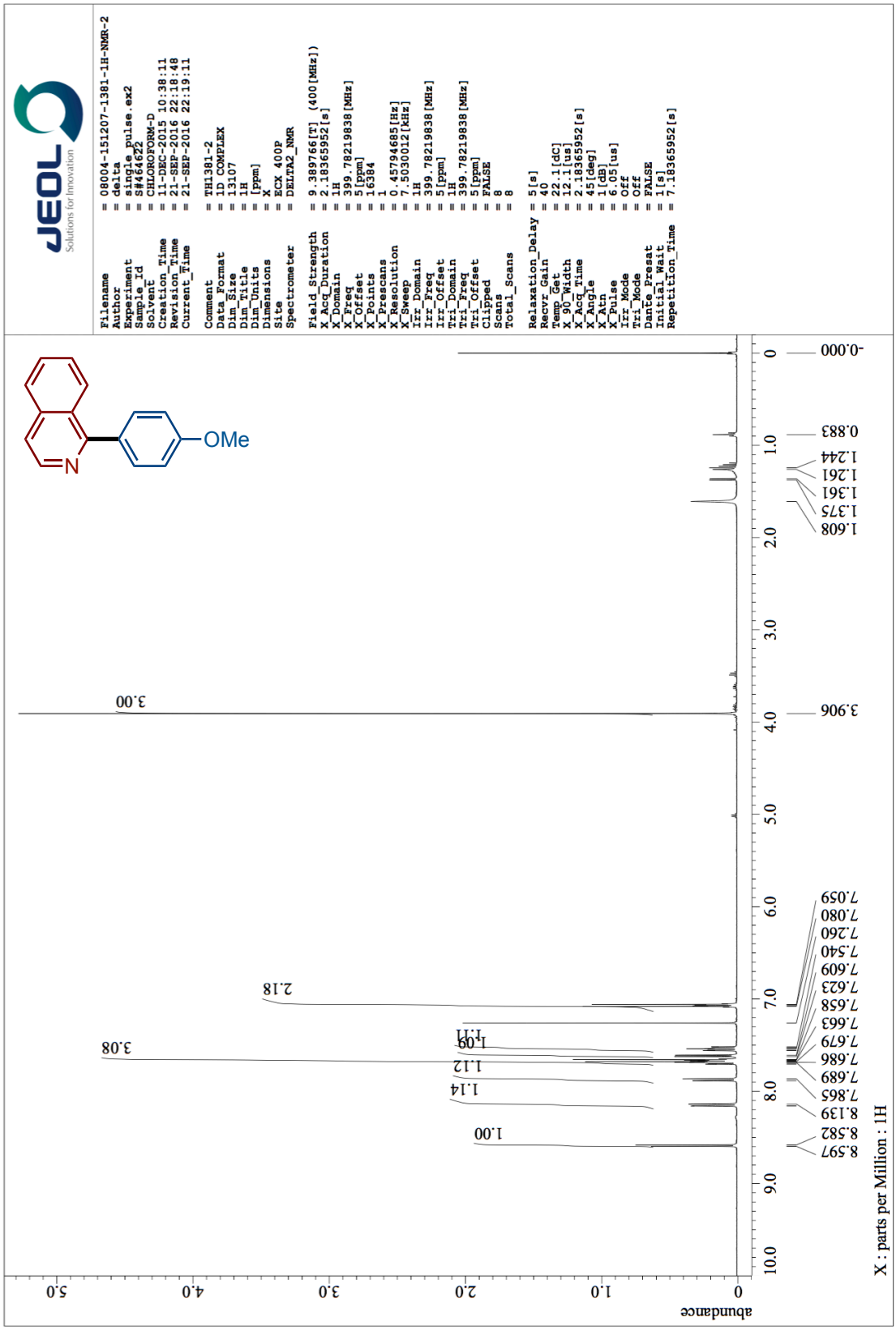
^{1}H NMR **3Ga** (400 MHz, $CDCl_3$)



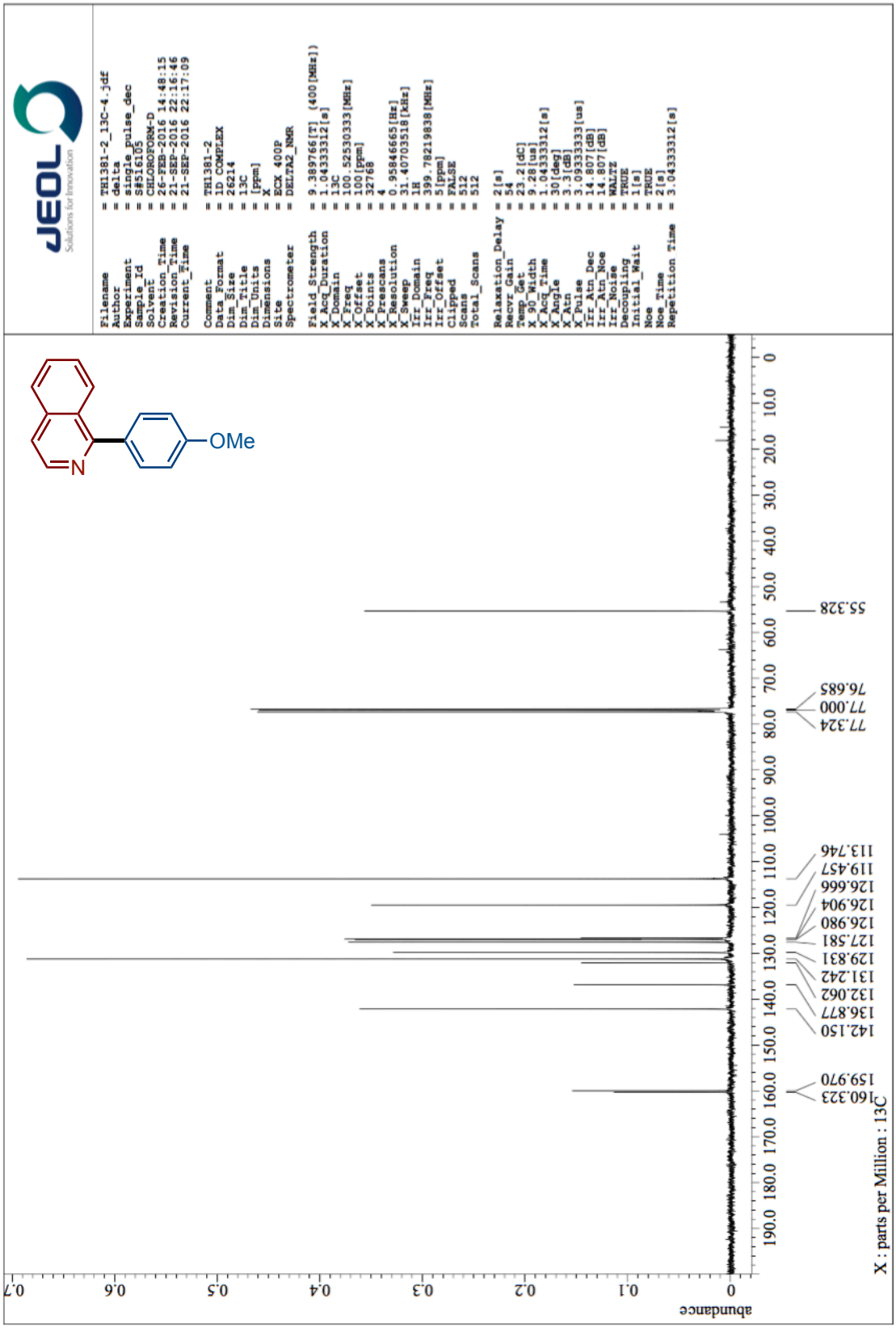
^{13}C NMR **3Ga** (100 MHz, $CDCl_3$)



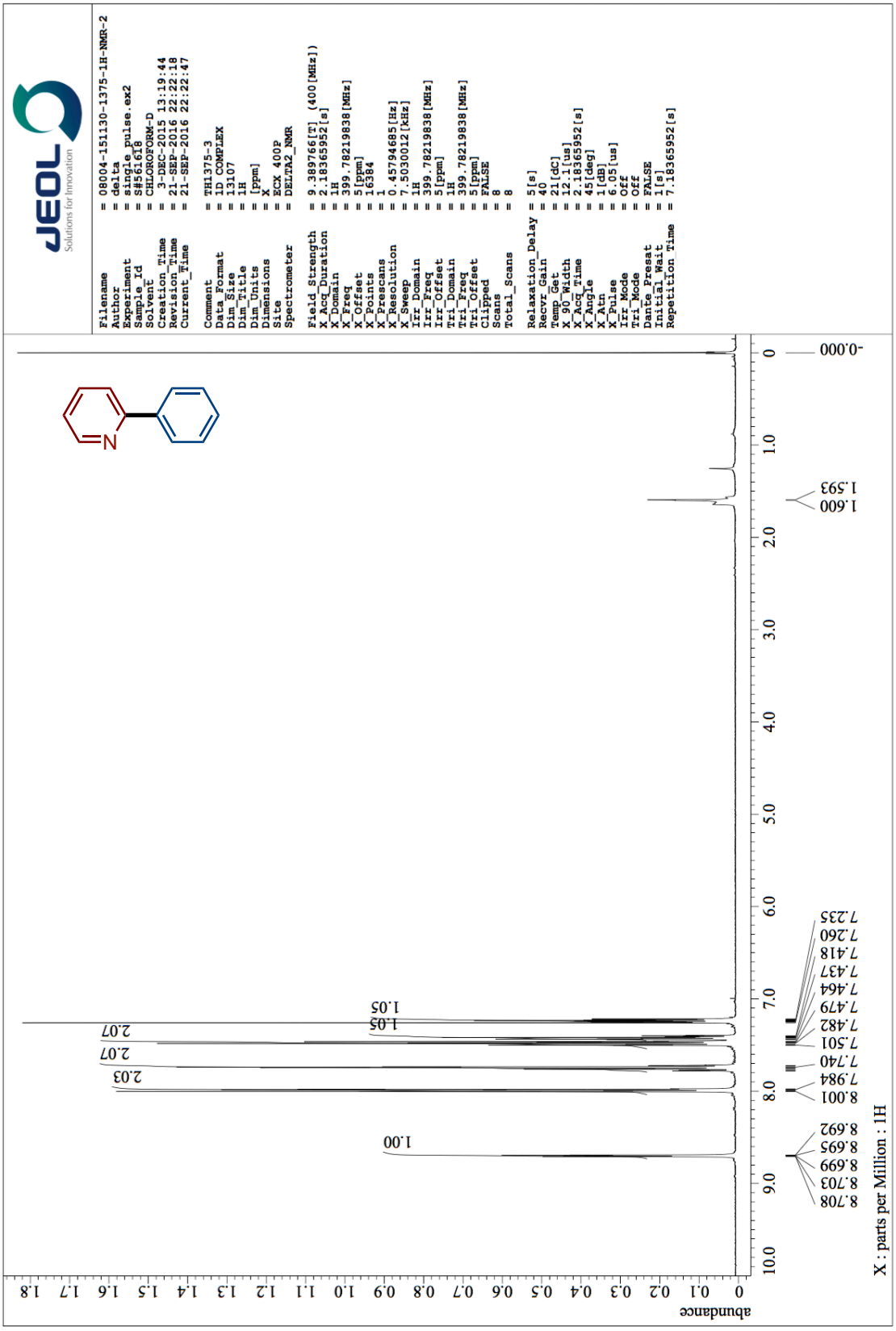
^{1}H NMR **3Ha** (400 MHz, $CDCl_3$)



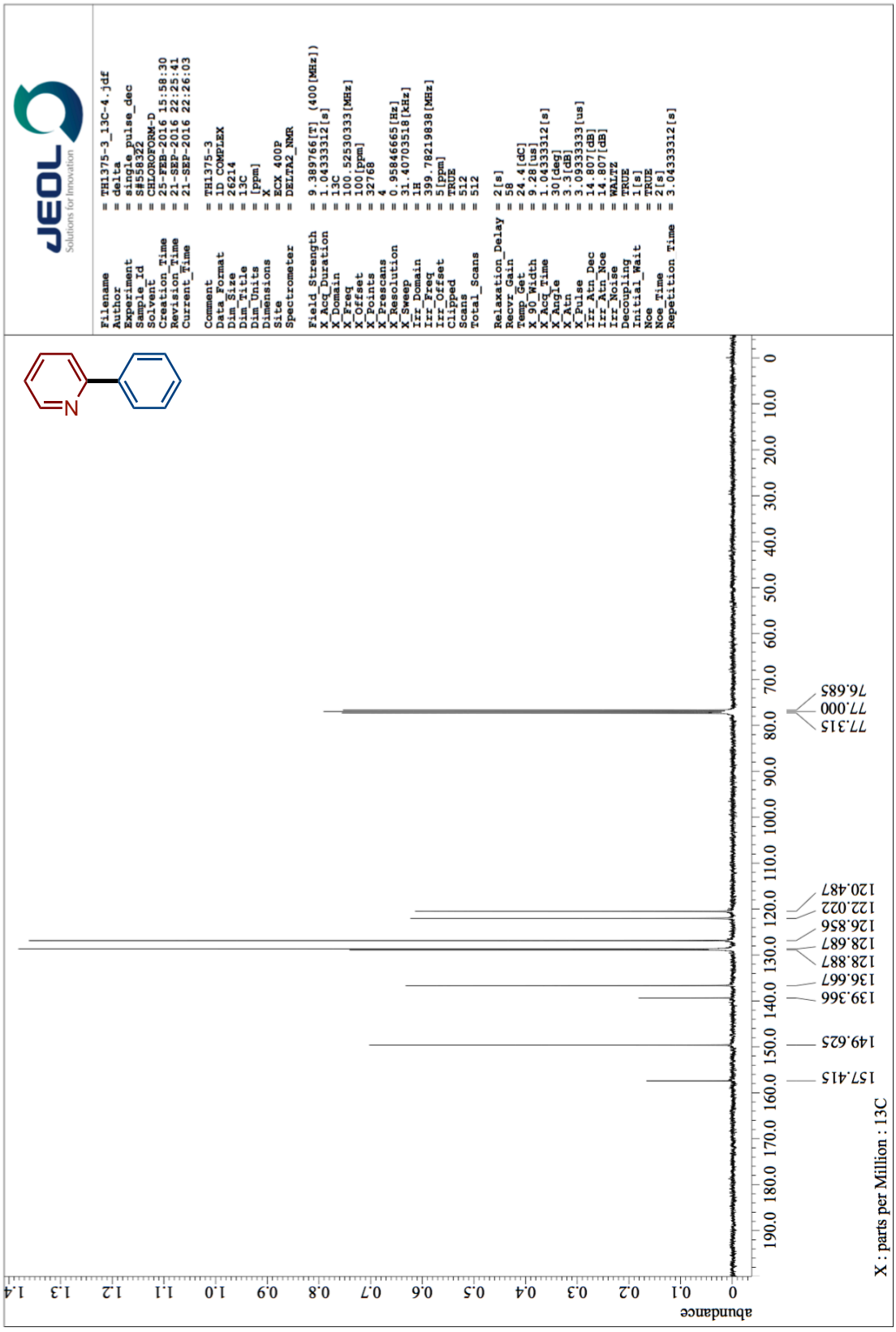
^{13}C NMR **3Ha** (100 MHz, $CDCl_3$)



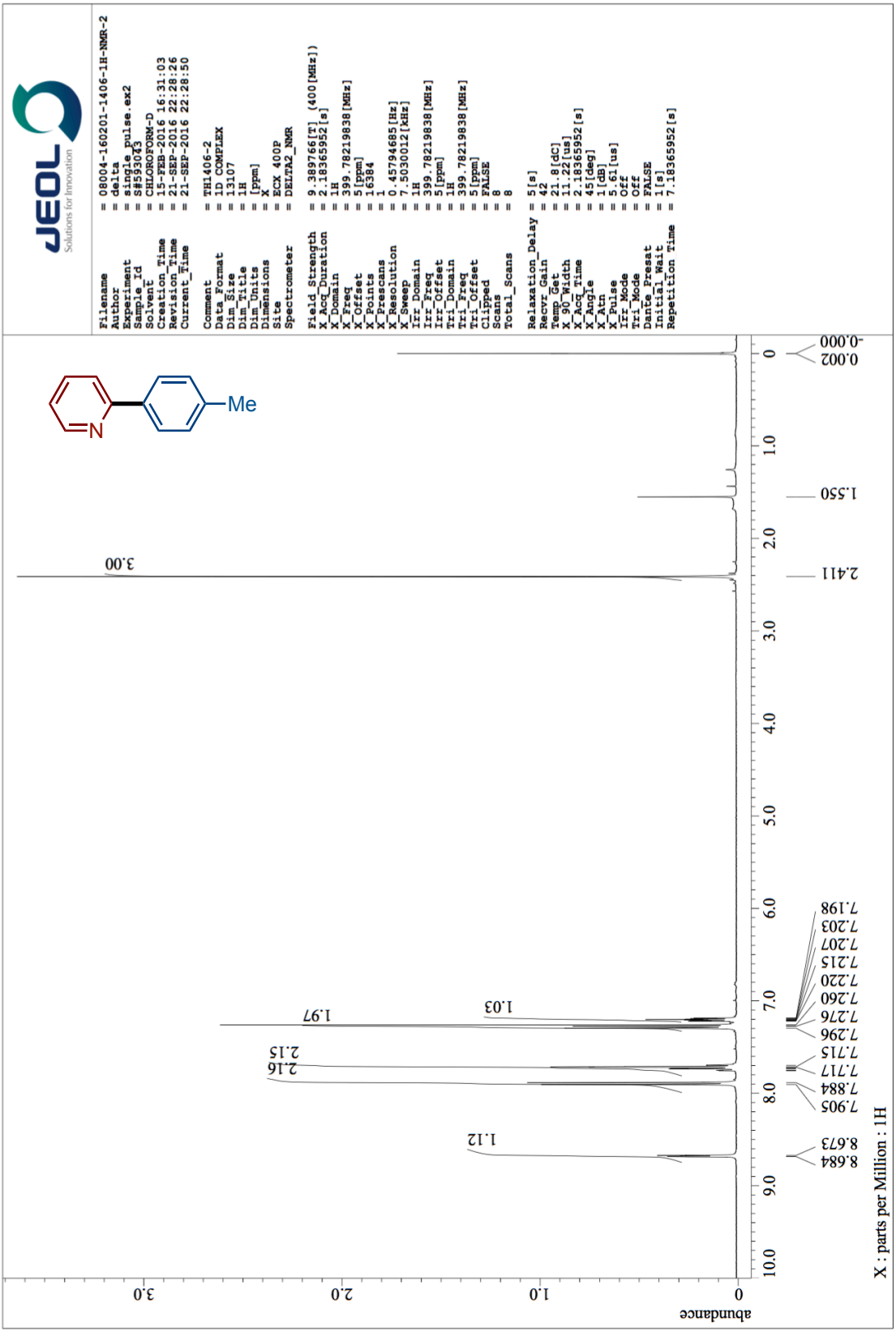
^{1}H NMR **3Ab** (400 MHz, $CDCl_3$)



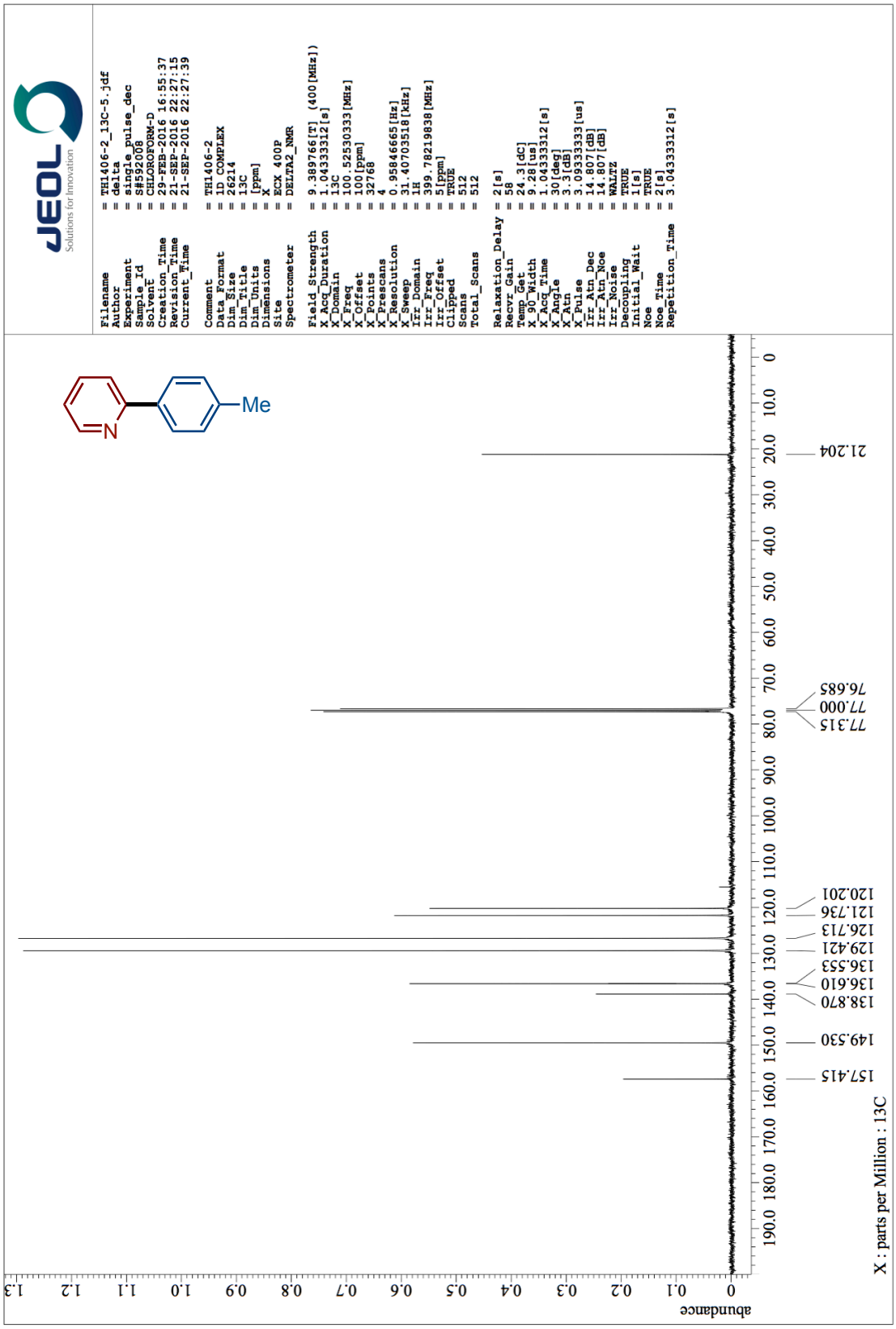
^{13}C NMR **3Ab** (100 MHz, $CDCl_3$)



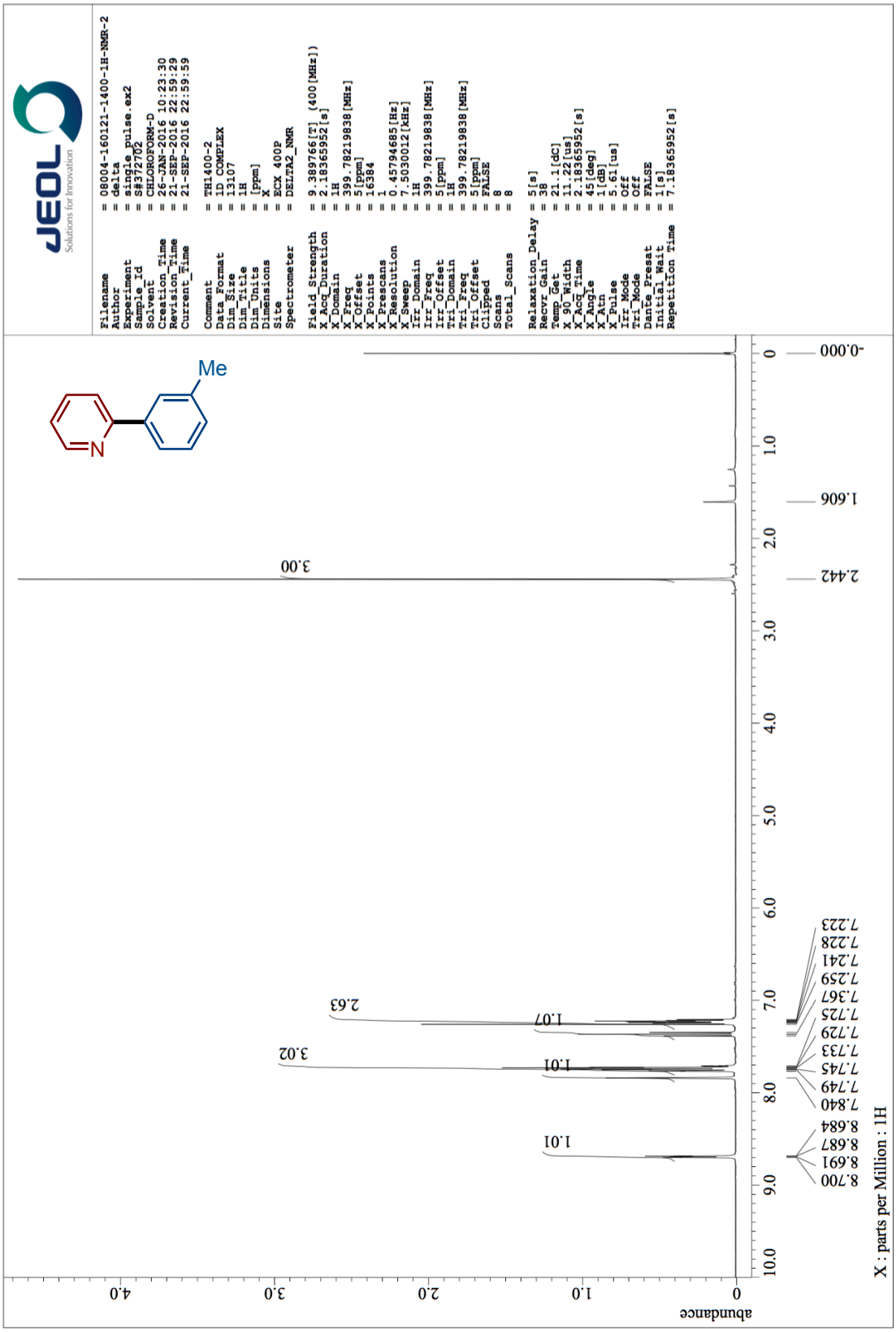
^{1}H NMR **3Ac** (400 MHz, $CDCl_3$)



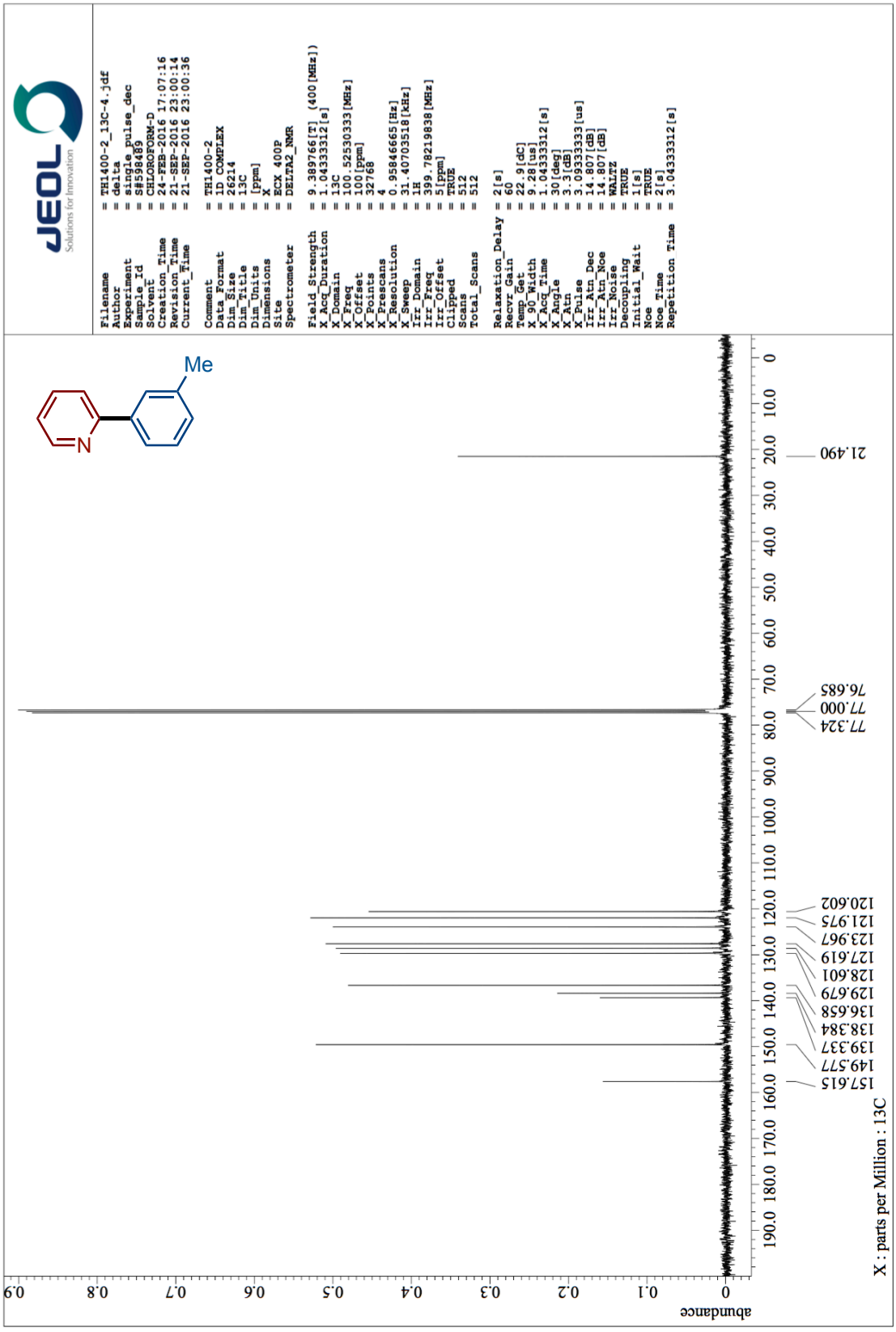
^{13}C NMR **3Ac** (100 MHz, $CDCl_3$)



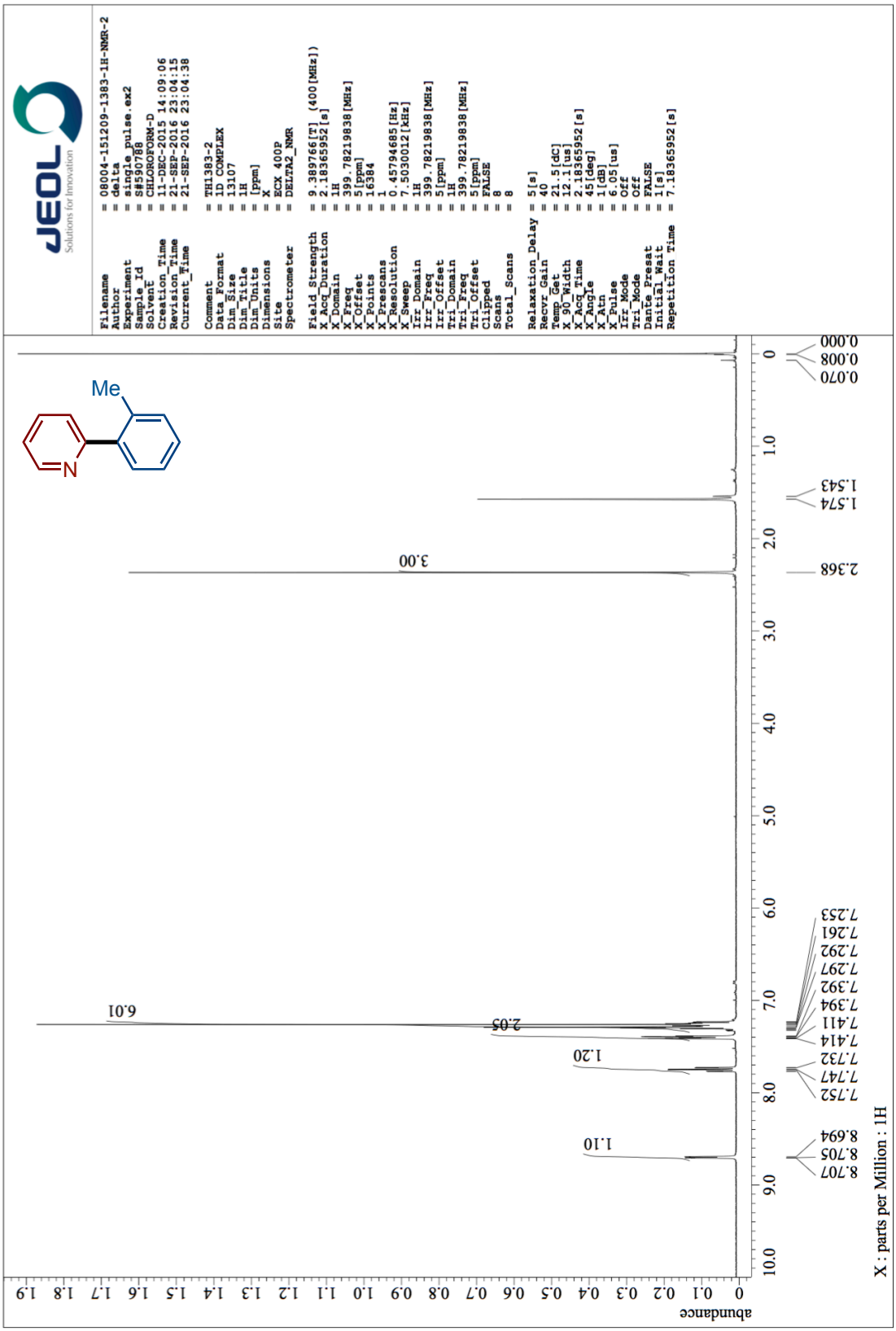
^{1}H NMR **3Ad** (400 MHz, $CDCl_3$)



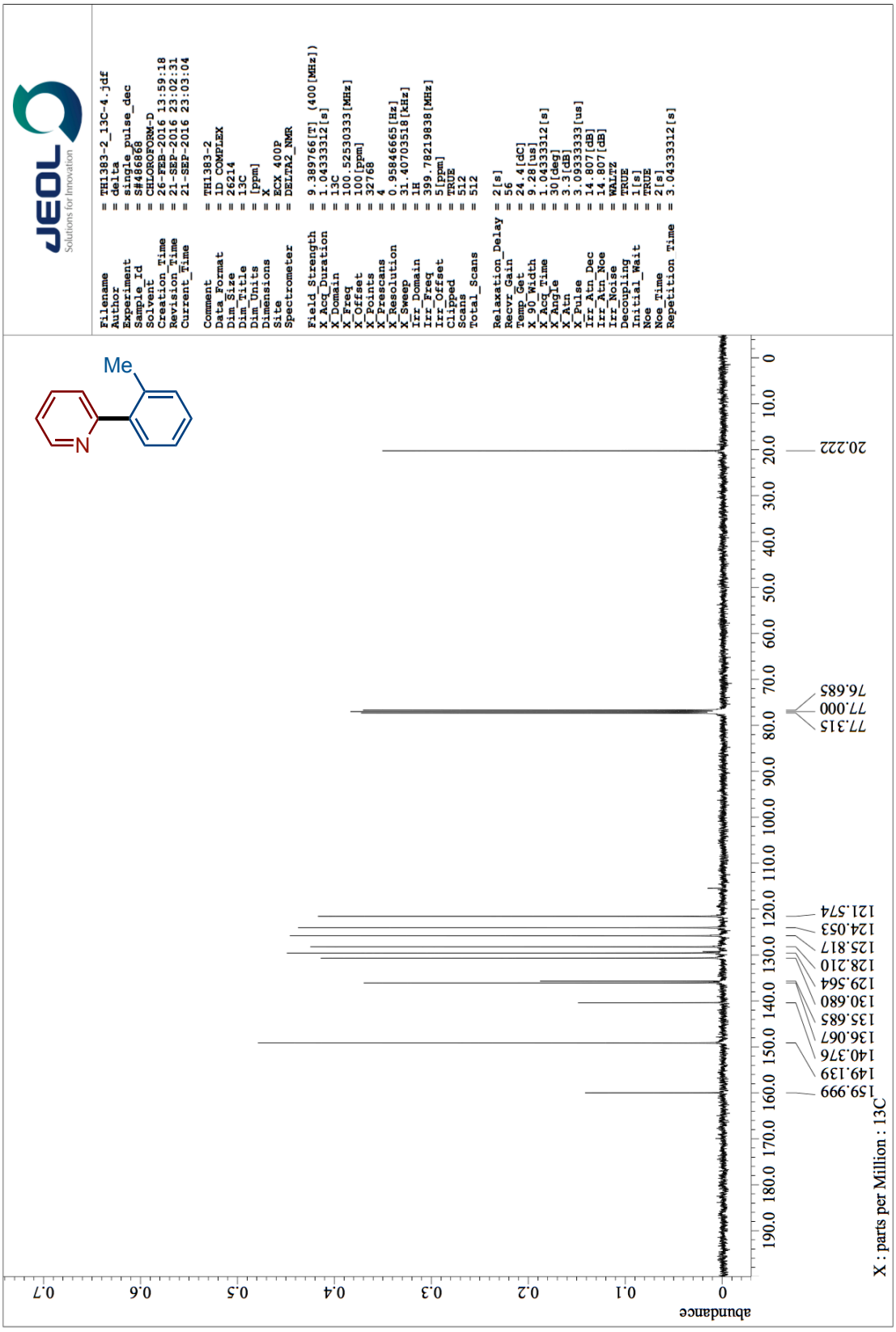
^{13}C NMR **3Ad** (100 MHz, $CDCl_3$)



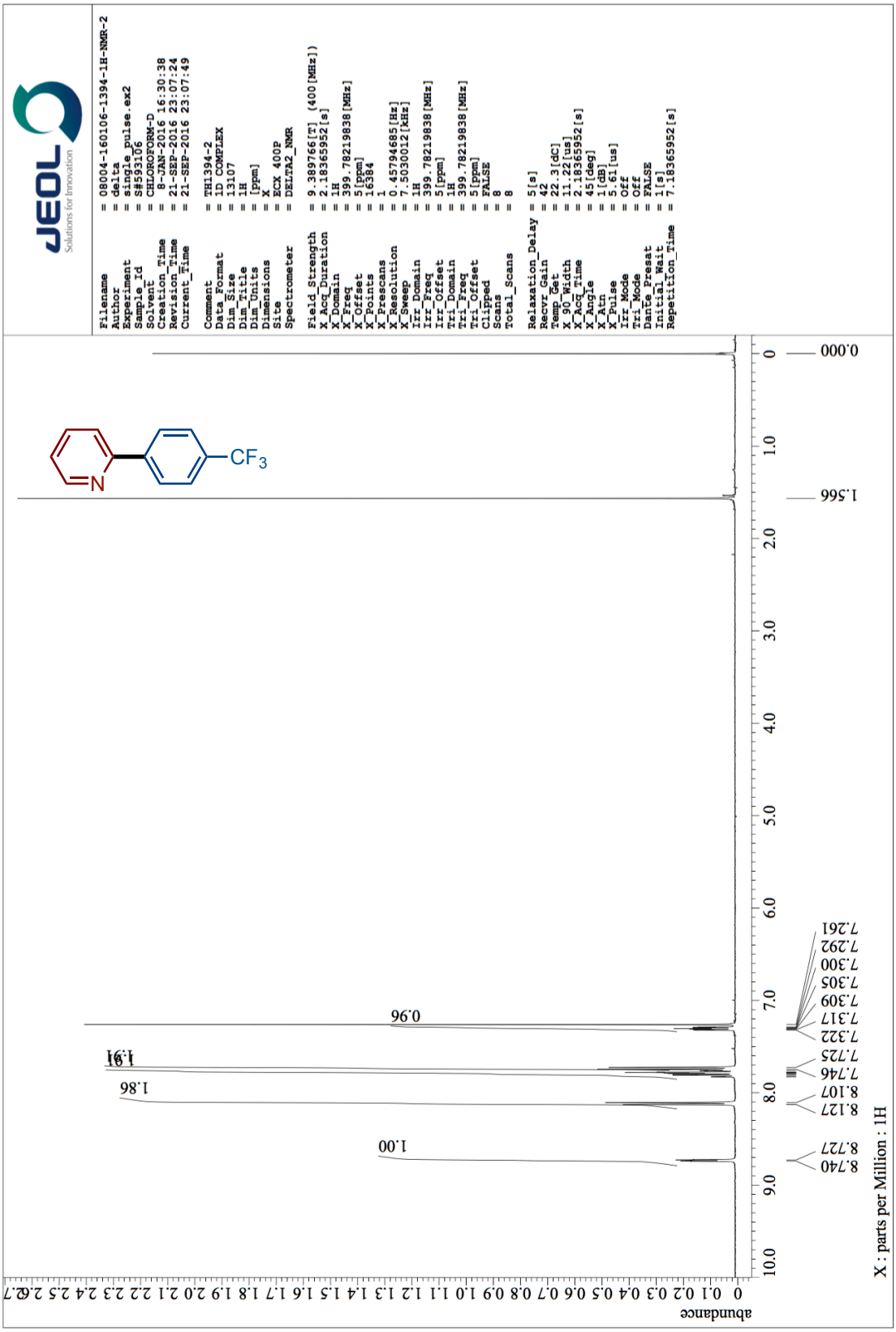
^{1}H NMR **3Ae** (400 MHz, $CDCl_3$)



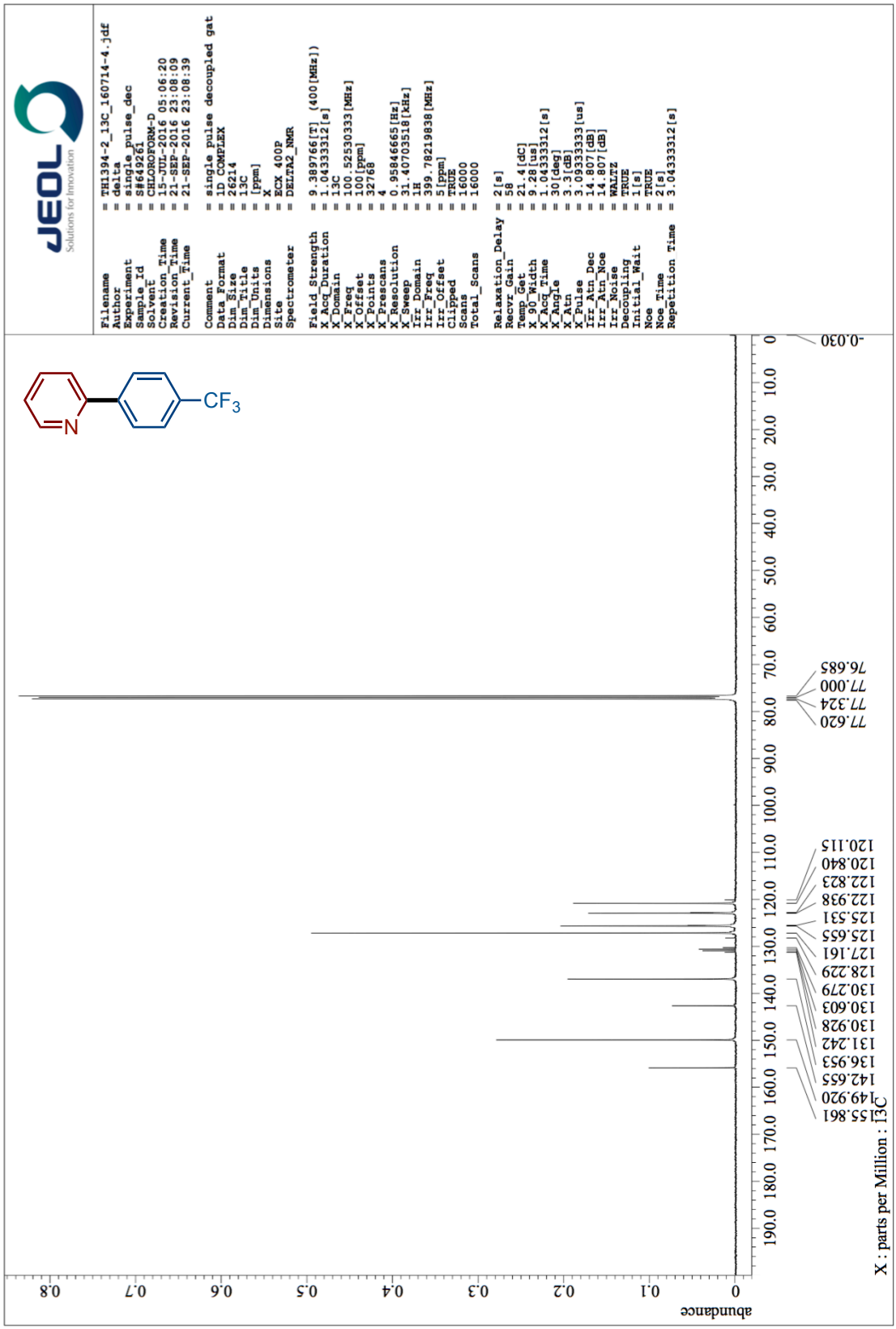
^{13}C NMR **3Ae** (100 MHz, $CDCl_3$)



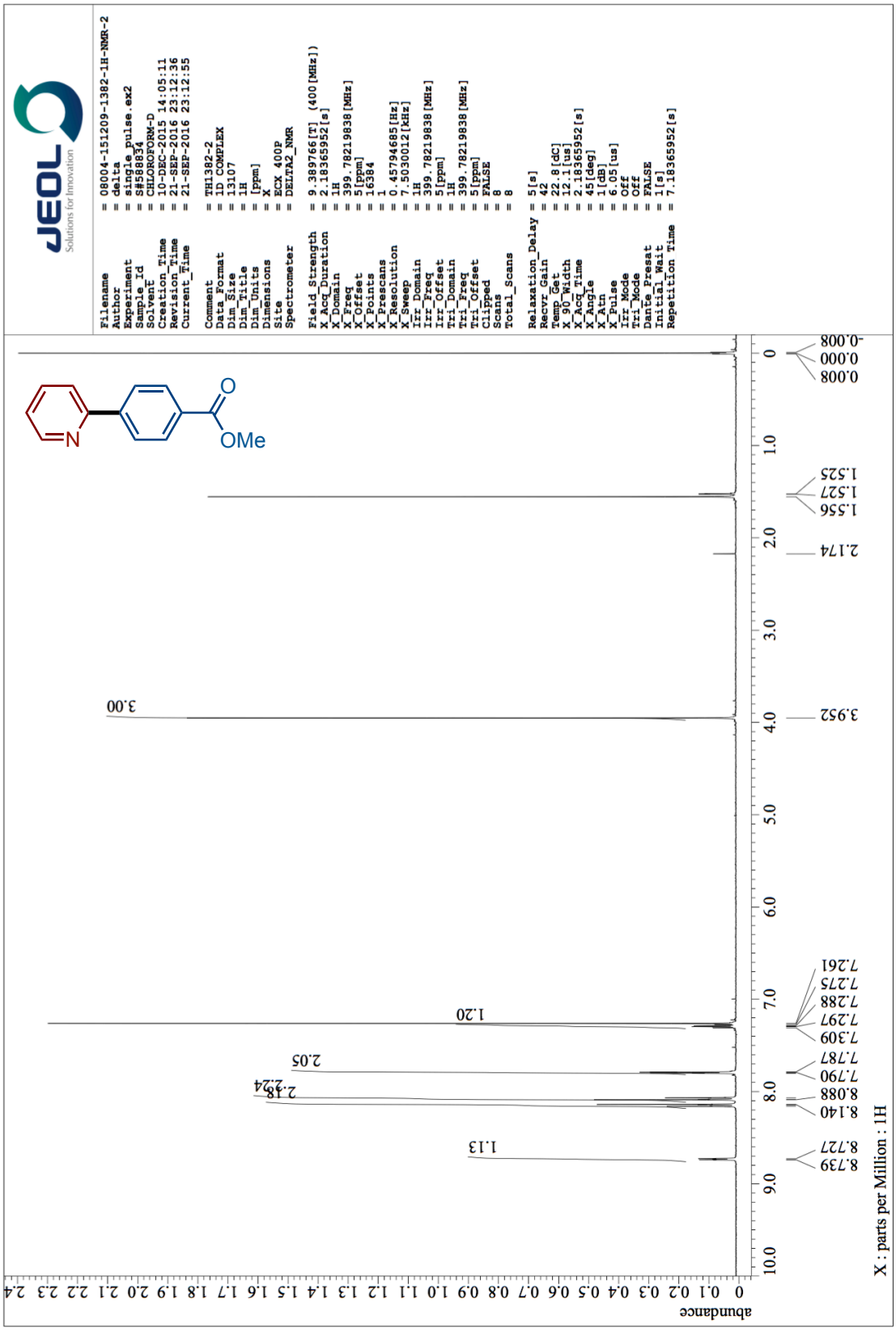
^{1}H NMR **3Af** (400 MHz, $CDCl_3$)



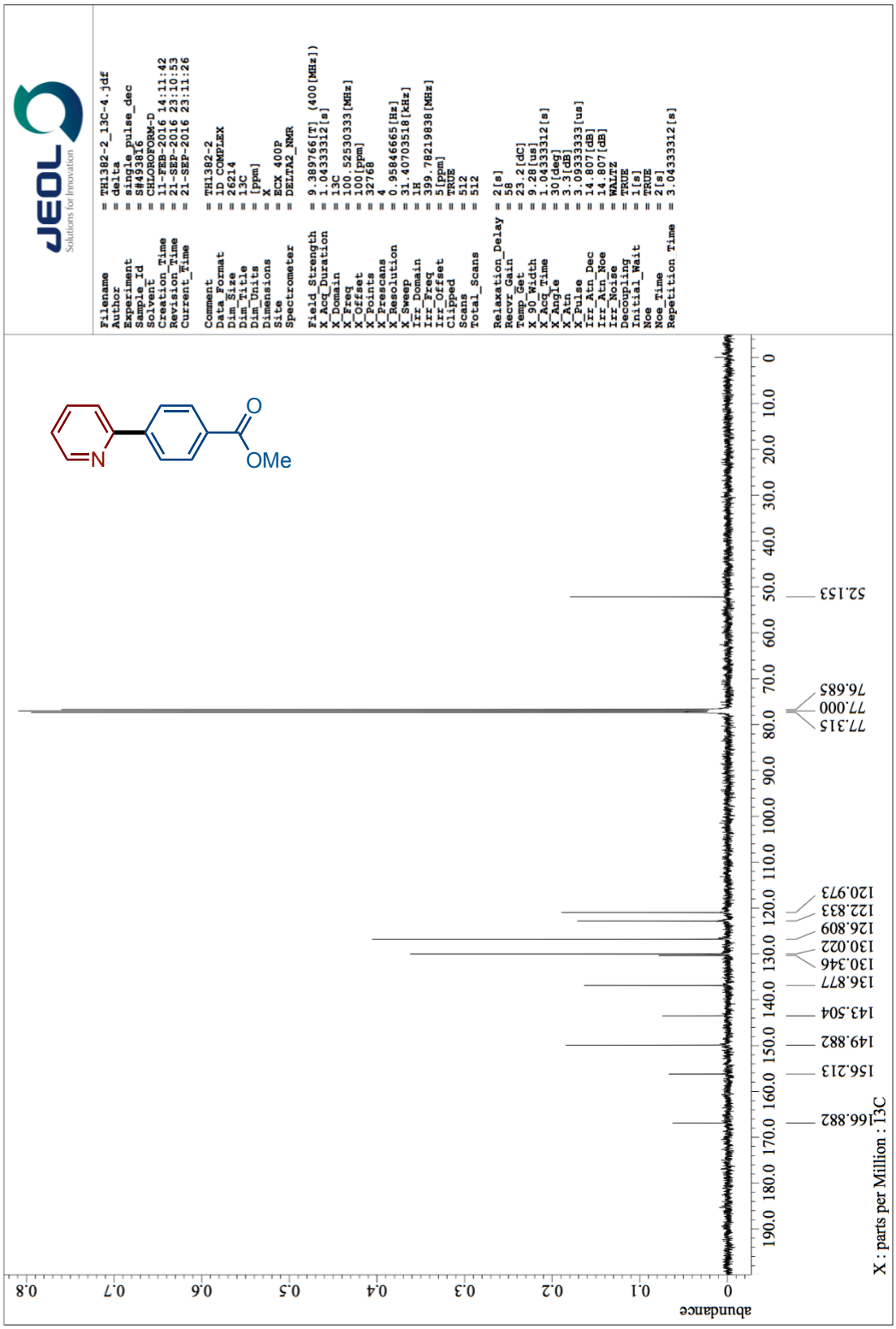
^{13}C NMR **3Af** (100 MHz, $CDCl_3$)



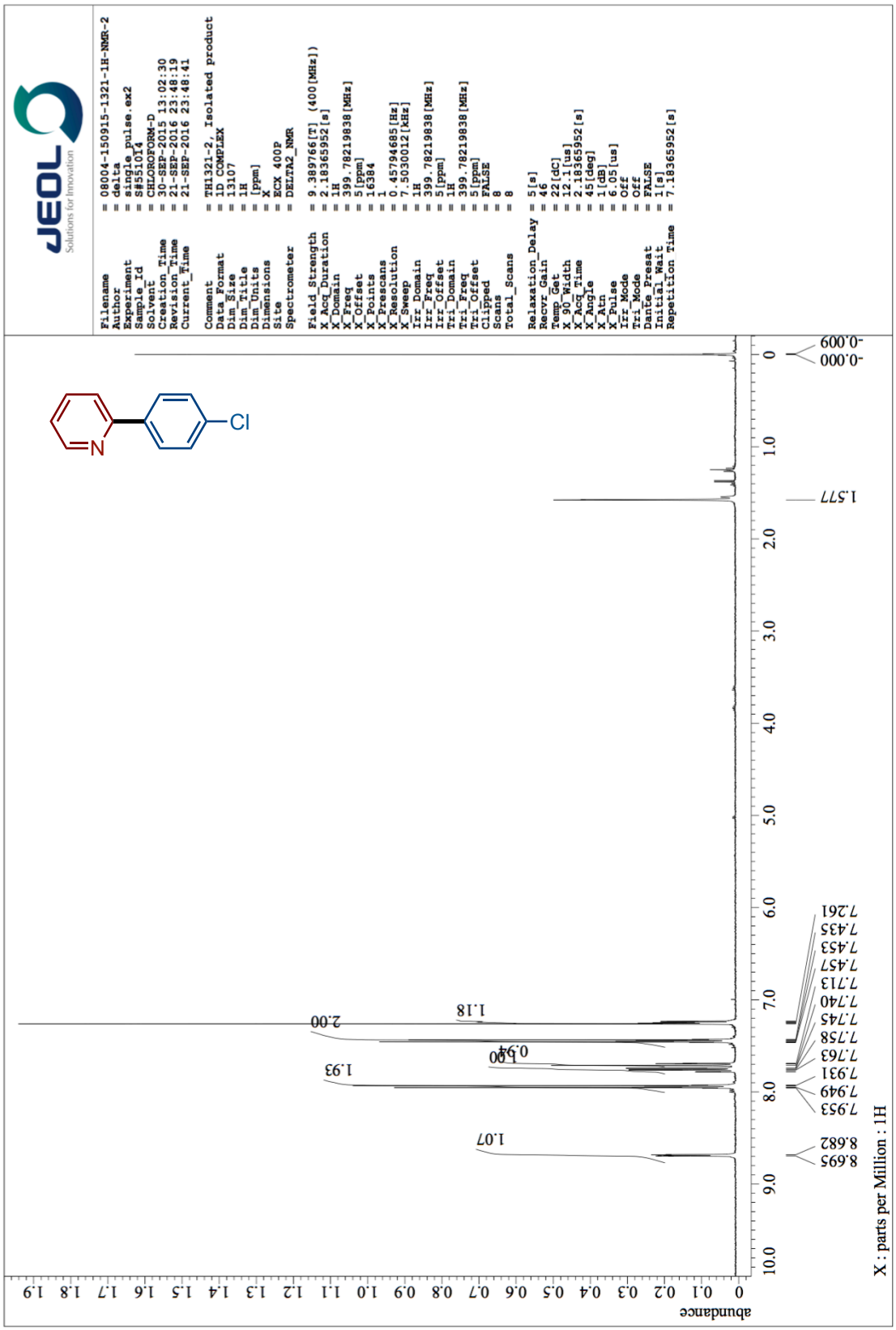
^{1}H NMR **3Ag** (400 MHz, $CDCl_3$)



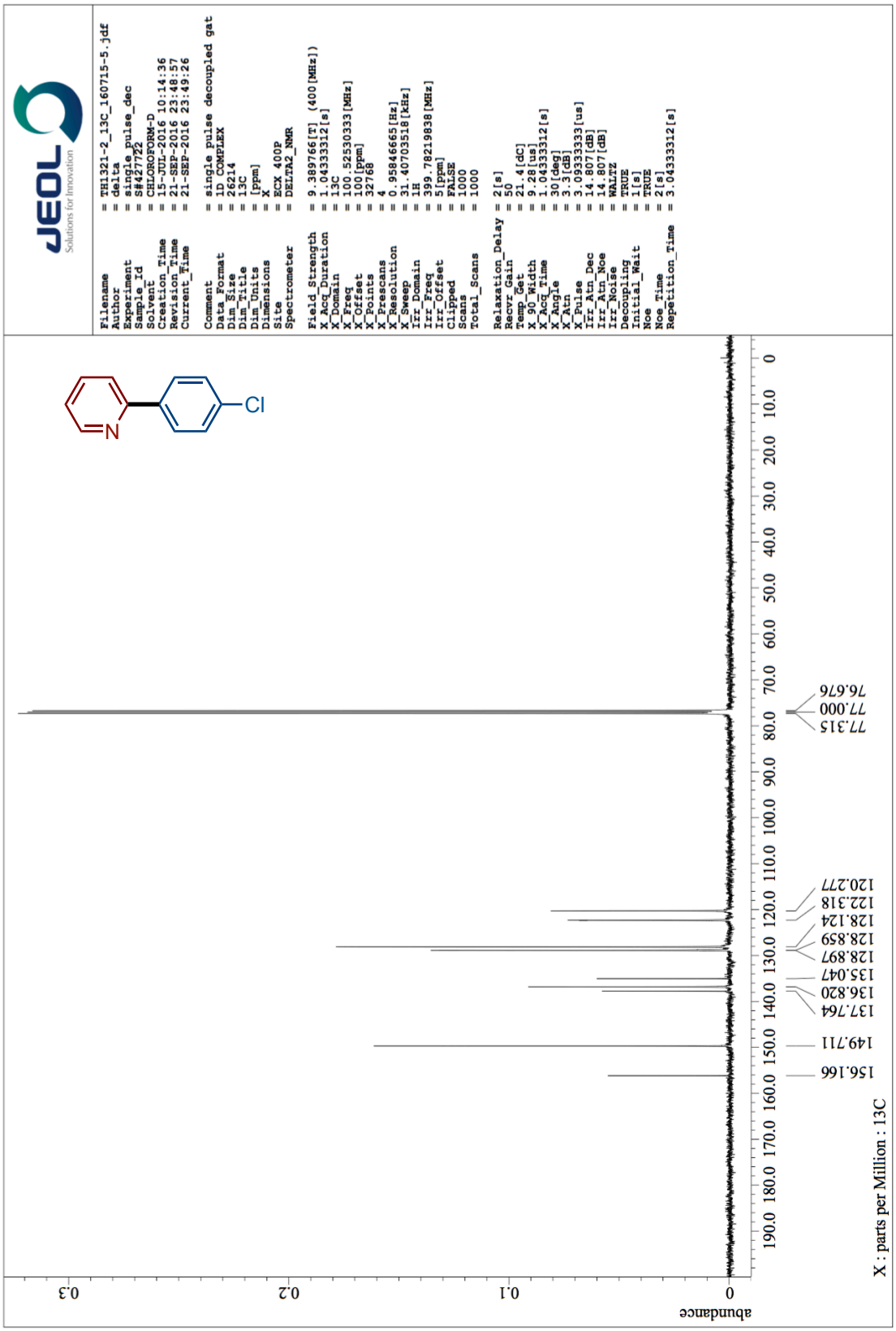
^{13}C NMR **3Ag** (100 MHz, $CDCl_3$)



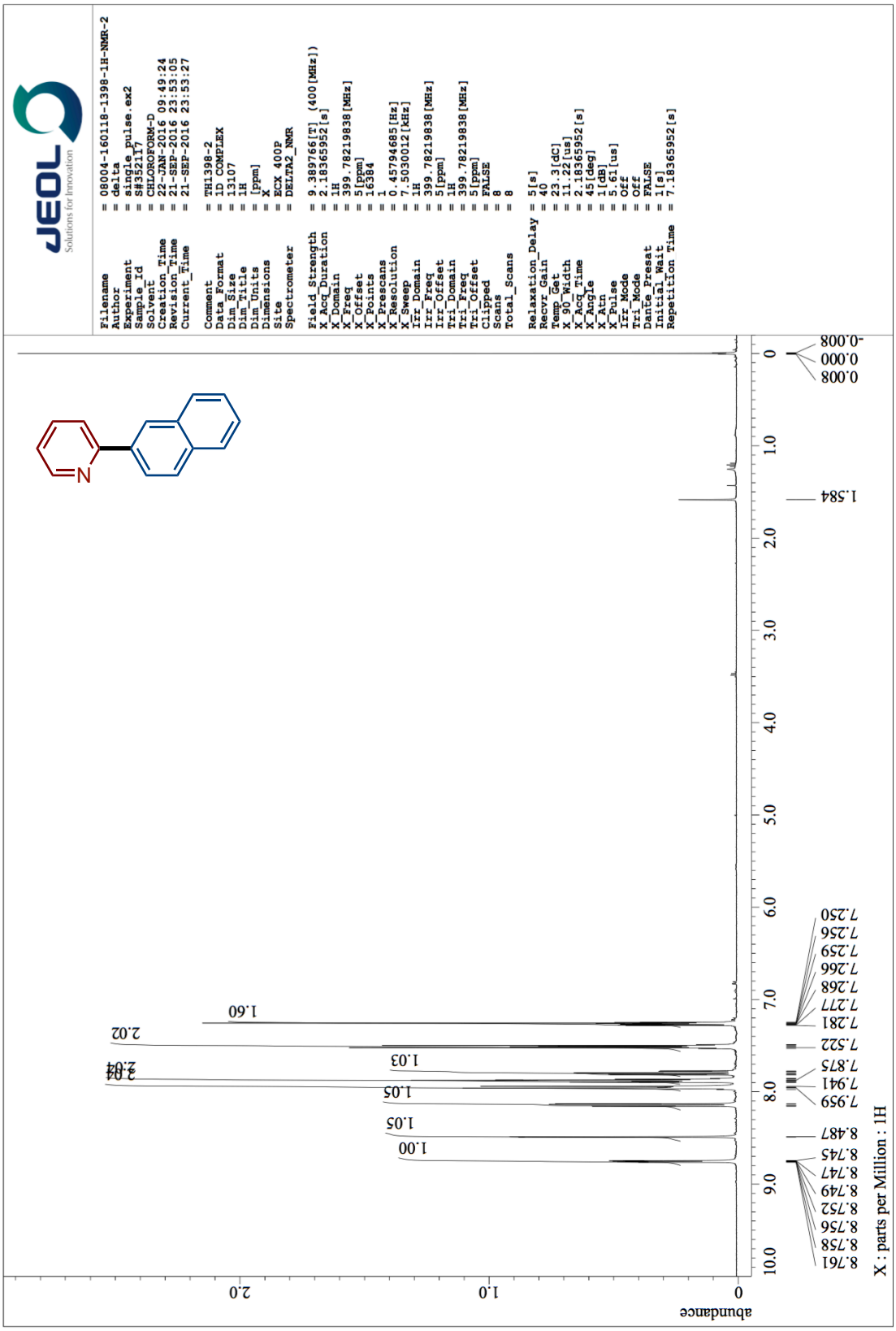
^{1}H NMR **3Ah** (400 MHz, $CDCl_3$)



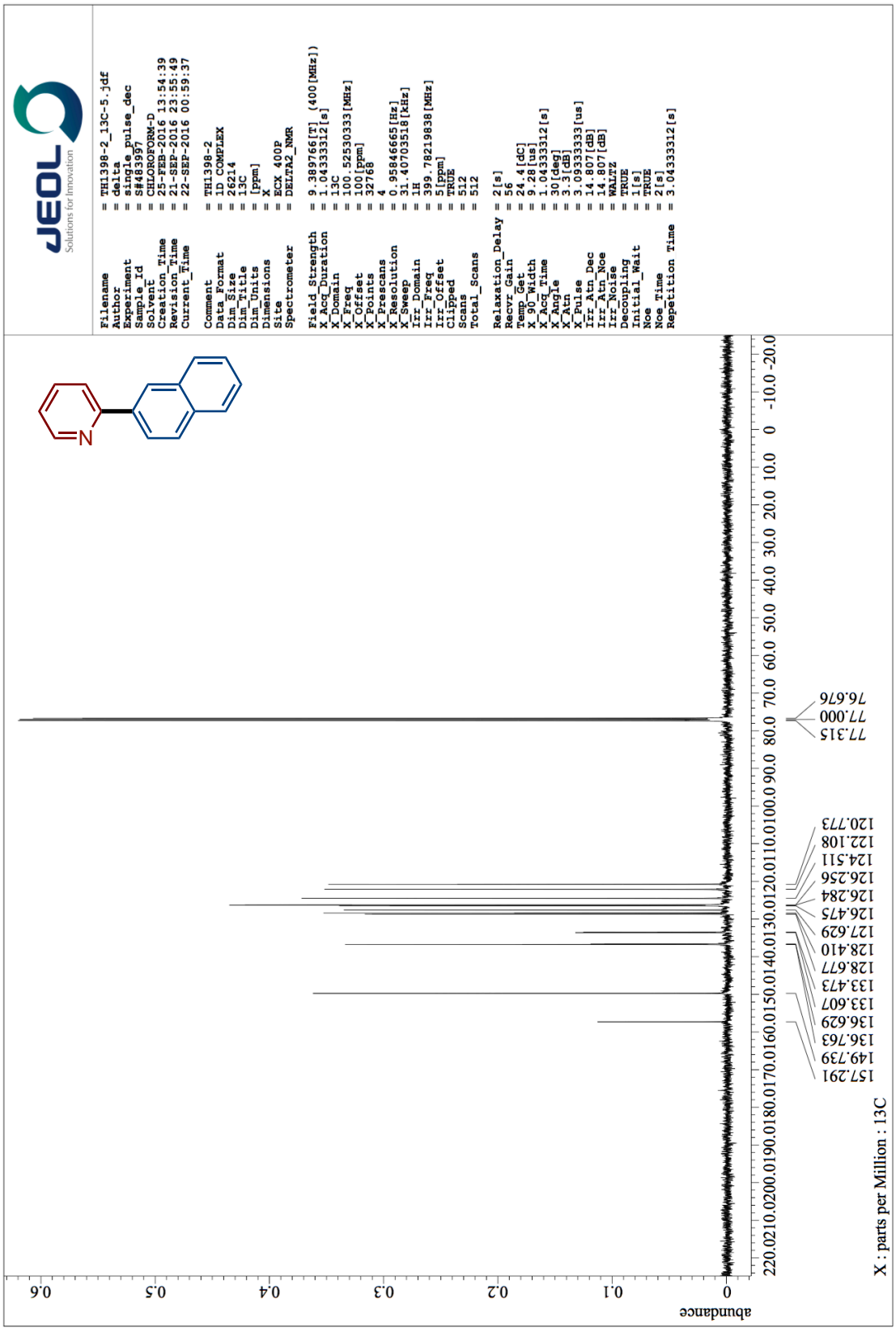
^{13}C NMR **3Ah** (100 MHz, $CDCl_3$)



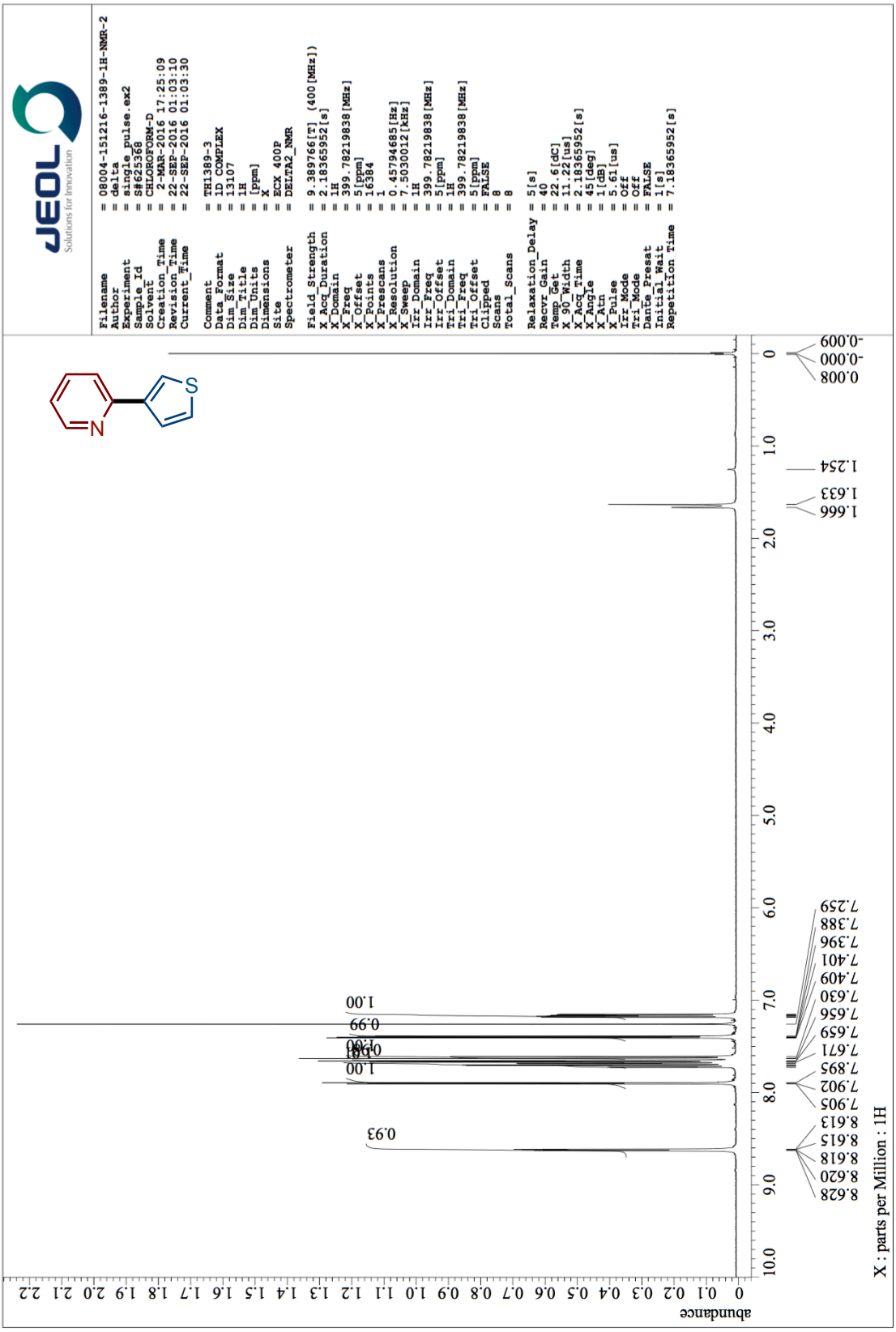
^{1}H NMR **3Ai** (400 MHz, $CDCl_3$)



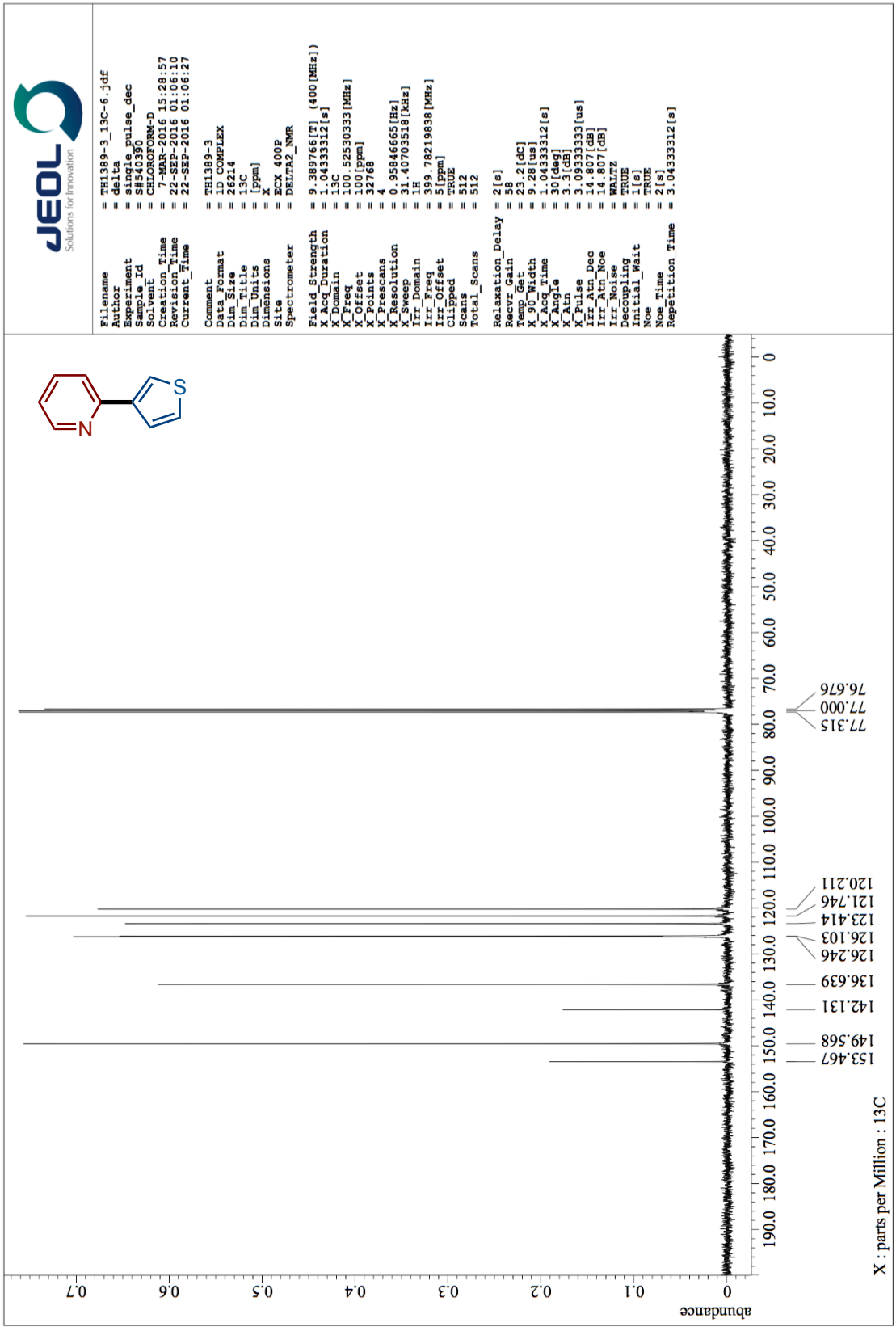
^{13}C NMR **3Ai** (100 MHz, $CDCl_3$)



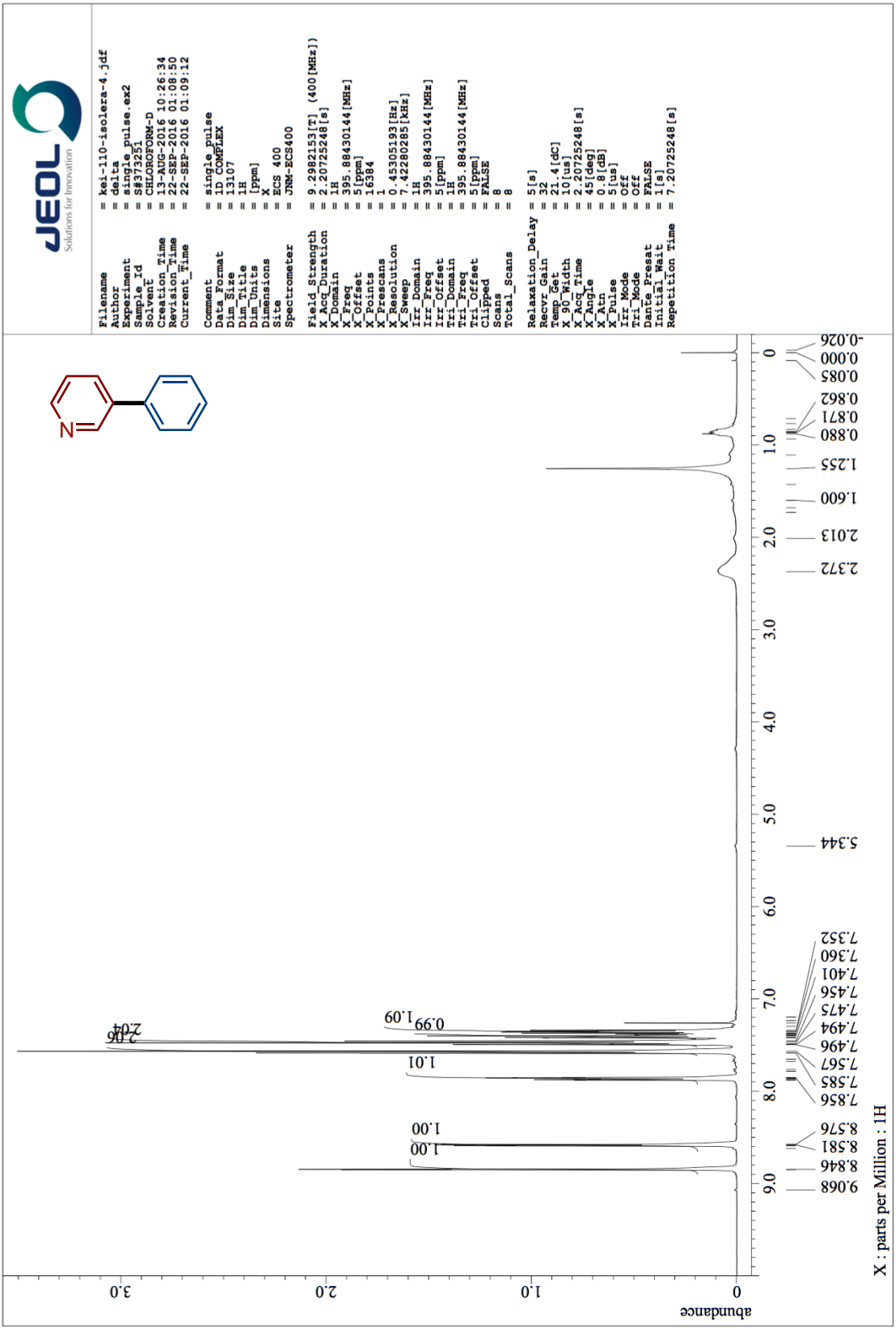
^{1}H NMR **3Aj** (400 MHz, $CDCl_3$)



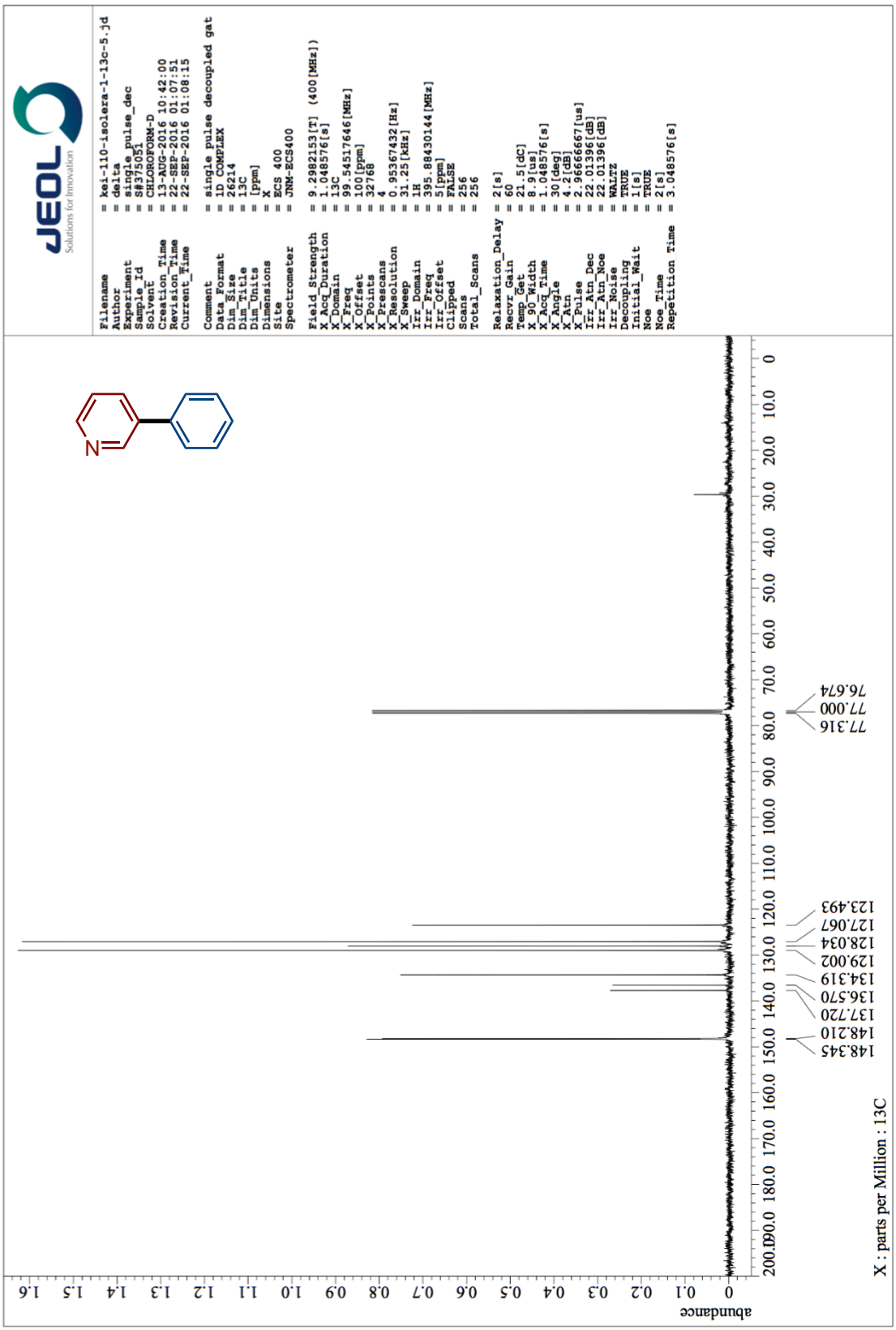
^{13}C NMR **3Aj** (100 MHz, $CDCl_3$)



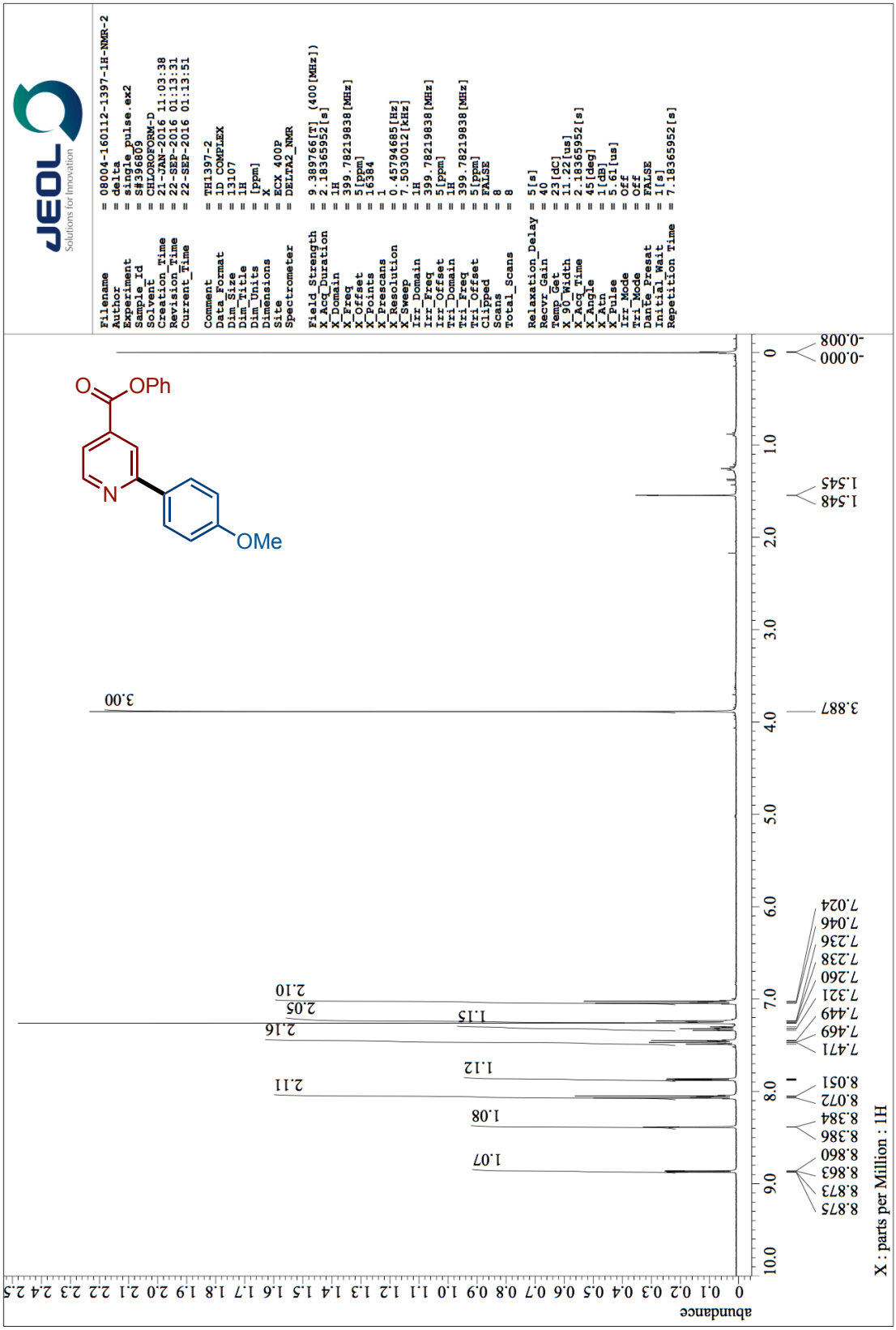
^{1}H NMR **3Ib** (400 MHz, $CDCl_3$)



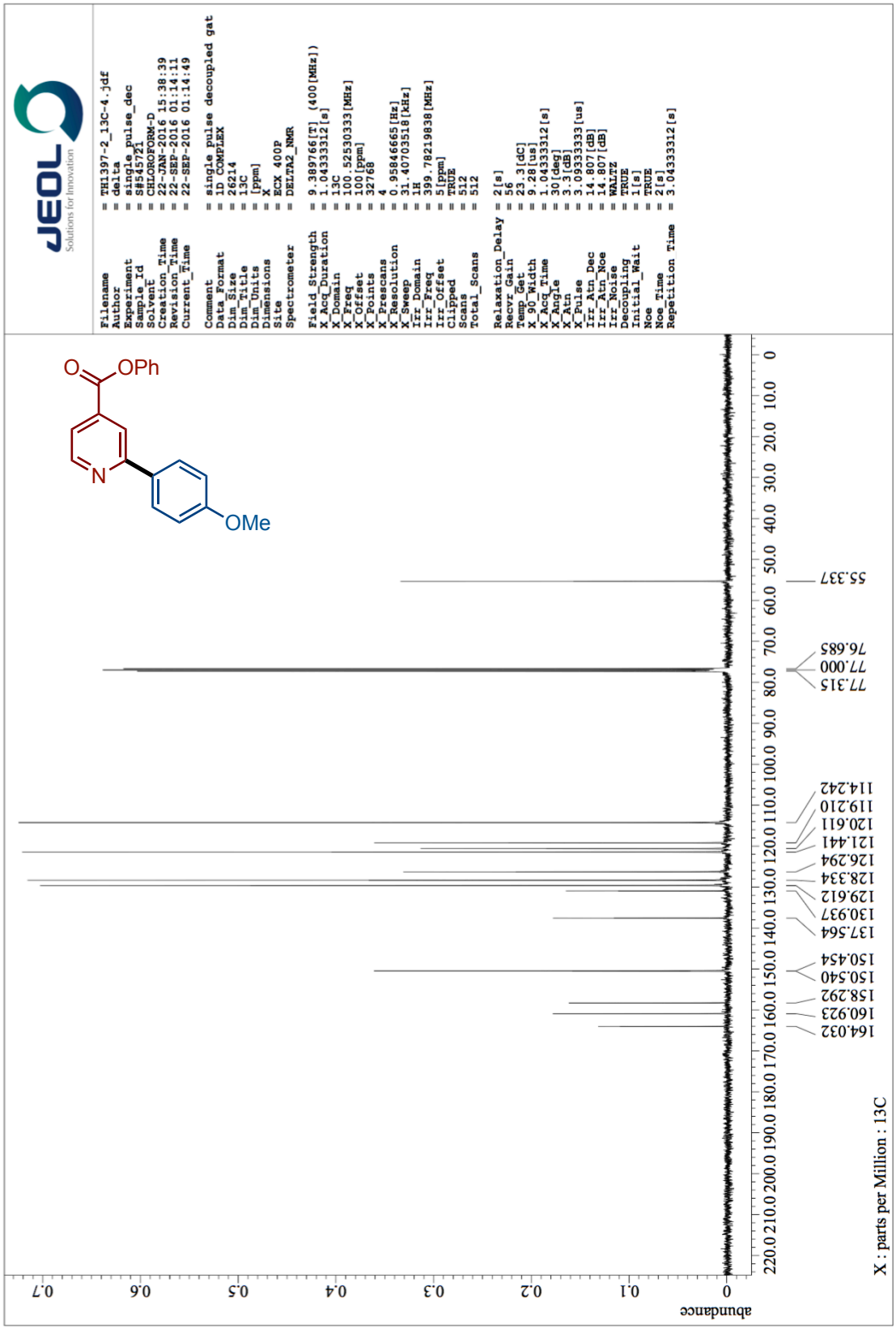
^{13}C NMR **3Ib** (100 MHz, $CDCl_3$)



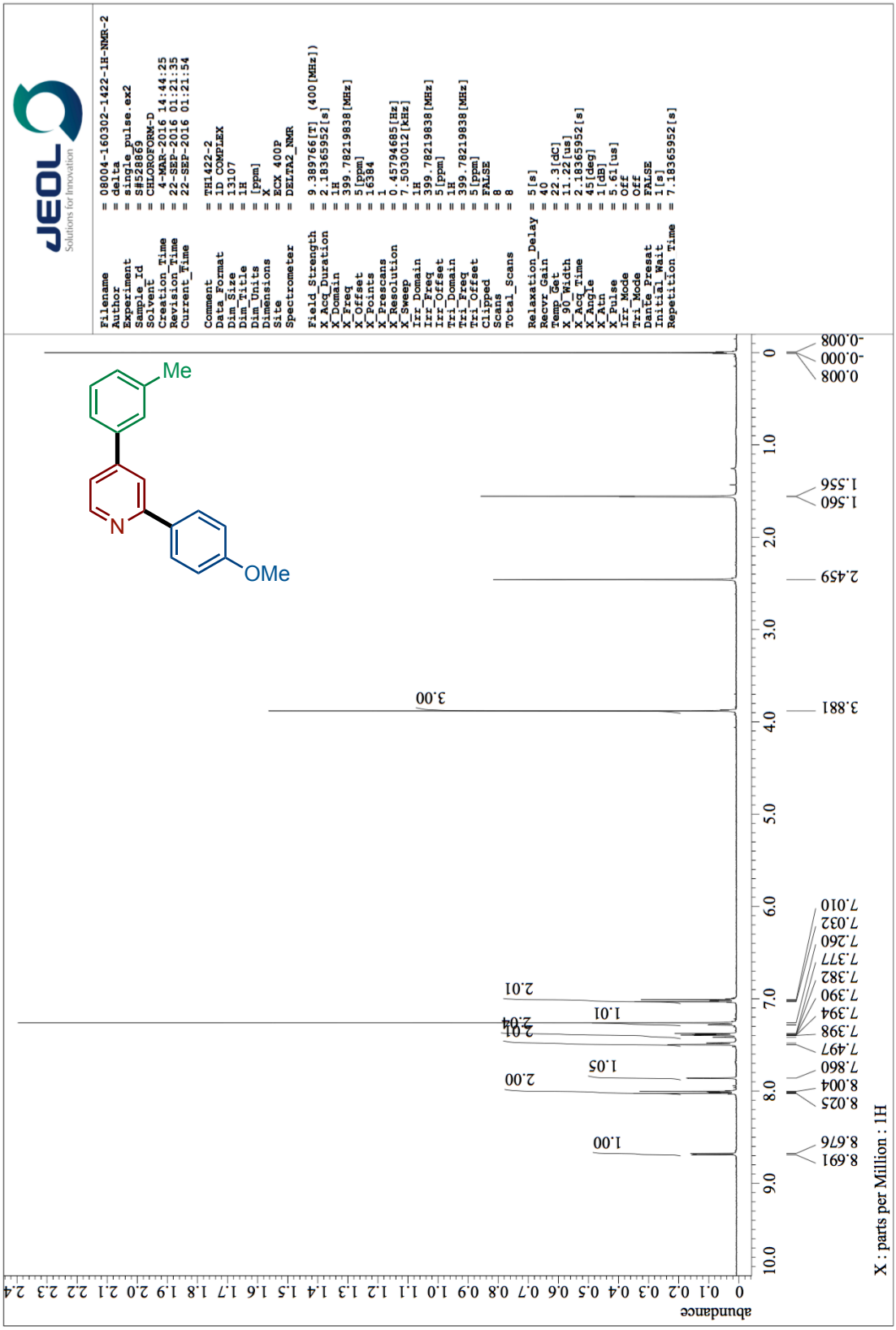
^{1}H NMR **3Ja** (400 MHz, $CDCl_3$)



^{13}C NMR **3Ja** (100 MHz, $CDCl_3$)



^{1}H NMR **4** (400 MHz, $CDCl_3$)



^{13}C NMR **4** (100 MHz, $CDCl_3$)