Supporting Information

Iron-Catalyzed Directed C(sp^2)–H and C(sp^3)–H Functionalization with Trimethylaluminum

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1. General

All the reactions dealing with air- or moisture-sensitive compounds were carried out in a dry reaction vessel under a positive pressure of nitrogen. Air- and moisture-sensitive liquids and solutions were transferred *via* syringe or teflon cannula. Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25-mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light (UV). Organic solutions were concentrated by rotary evaporation at *ca*. 15 Torr (evacuated with a diaphragm pump). Flash column chromatography was performed as described by Still et al. (*J. Org. Chem*. **1978**, *43*, 2923–2924), employing Kanto Silica gel 60 (spherical, neutral, 140–325 mesh). Gas-liquid chromatographic (GLC) analysis was performed on a Shimadzu 2025 machine equipped with glass capillary column HR-1 (0.25-mm i.d. × 25 m). Gel permeation column chromatography was performed on a Japan Analytical Industry LC-908 (eluent: toluene) with JAIGEL 1H and 2H polystyrene columns.

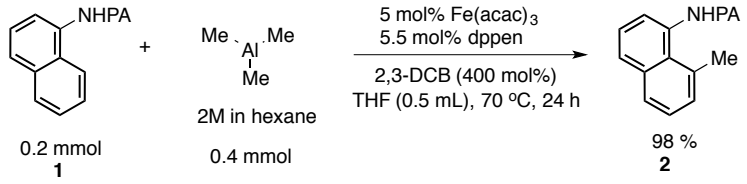
Proton nuclear magnetic resonance (^{1}H NMR) and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded with JEOL ECA-500 NMR or JEOL ECX-400 spectrometers. Chemical data for protons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced internally to tetramethylsilane. Carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded at 125 MHz or 100 MHz. Chemical data for carbons are reported in parts per million (ppm, δ scale) and are referenced to the carbon resonance of the solvent ($CDCl_3$: δ = 77.0). The data is presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiplet resonances, br = broad), coupling constant in Hertz (Hz), and integration. Mass spectra (GS MS) are taken at SHIMADZU Parvum 2 gas chromatograph mass spectrometer. Mass spectra were acquired by Bruker microTOF II (APCI) Spectrometer. High-resolution mass spectra were obtained with a calibration standard of polyethylene glycol (MW 600). Melting points of solid materials were measured on a Mel-Temp capillary melting-point apparatus and were uncorrected.

Commercial reagents were purchased from Tokyo Kasei Co., Aldrich Inc., and other commercial suppliers and were used after appropriate purification. Anhydrous ether solvents (stabilizer-free) were purchased from WAKO Pure Chemical and purified by a solvent purification system (GlassContour) equipped with columns of activated alumina and supported copper catalyst (Q-5) prior to use (*Organometallics* **1996**, *15*, 1518-1520). The content of water in the solvents or the substrates were confirmed to be less than 20 ppm by Karl-Fischer moisture titrator. Trimethylaluminium (Sure/Seal®) and bis(trimethylaluminum)-1,4-diazabicyclo-[2.2.2.]octane adduct (DABCO•2AlMe$_3$) were purchased from Aldrich Inc.. Fe(acac)$_3$ (99.9+%) was purchased from Aldrich Inc. and used as received. (*Z*)-1,2-bis (diphenylphosphino)ethene (dppEn) was purchased from Aldrich Inc. and used as received. (*Z*)-(1-phenylethene-1,2-diyl)bis(diphenylphosphane) (Ph-dppEn) was prepared according to literature method (*J. Am. Chem. Soc.* **2007**, *129*, 4099–4104). 2,3-Dichlorobutane (2,3-DCB) was purchased from TCI, dried over molecular sieves and stored under argon.

Caution: we observed that contamination of the reaction mixture by atmospheric moisture reduces the yield. We sometimes observed complete suppression of the reaction when using incompletely anhydrous solvents, and we ascribe this to the poisoning of the iron catalyst by hydroxide species. For best results, all the experiments described herein must be performed under rigorously anhydrous and air free conditions using a freshly purchased or prepared trimethylaluminium solution.

2. Investigation of the Key Reaction Parameters

General Procedure for the optimization study

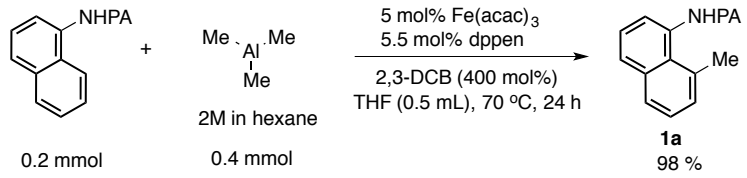


Under a nitrogen atmosphere, a 0.25 M solution (molar ratio of Fe/Ligand = 1:1.1) of $Fe(acac)_3$ (5.0 mol%) and (*Z*)-1,2-bis (diphenylphosphino)ethene (dppEn) (5.5 mol%) in THF (40 μL) was injected into an anhydrous tetrahydrofuran (THF, 0.5 mL) solution of *N*-(naphthalen-1-yl)picolinamide (**1**) (50 mg, 0.20 mmol). Sequentially, a solution of trimethylaluminum (2.0 equiv, 2.0 M in hexane, 0.2 mL) was slowly added. After stirring for 10 min to finish generating methane at room temperature, 2,3-dichlorobutane (2,3-DCB) (4.0 equiv, 93 μL) was added via a microsyringe, and the mixture was heated at 70 ^{o}C for 24 h. After cooling to r.t., the mixture was diluted with diethyl ether, and methanol (100 μL) was slowly added via a microsyringe to quench the aluminium reagent. Tridecane (0.1 mmol, 25 mL) was added as an internal standard. Aqueous potassium sodium tartrate was then added. The organic layer was extracted with diethyl ether and passed over a Florisil column. The mixture was analyzed by GC using tridecane as an internal standard, or analyzed by ^{1}H-NMR using 1,1,2,2-tetrachloroethane as internal standard.

Investigation of the key parameters

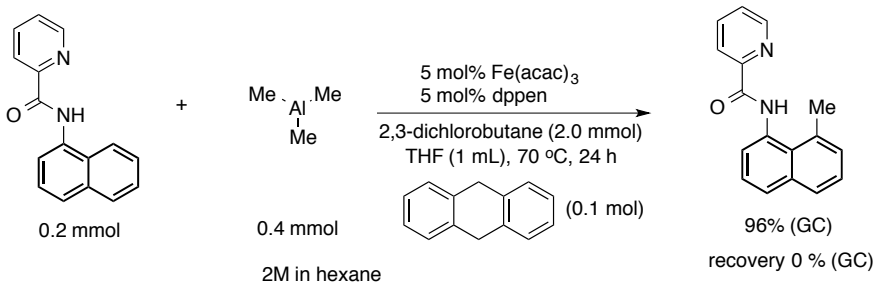
The reactions were performed according to the General Procedure (SI Table 1). After aqueous work up, the crude mixture was analyzed by gas chromatography in the presence of tridecane as an internal standard.

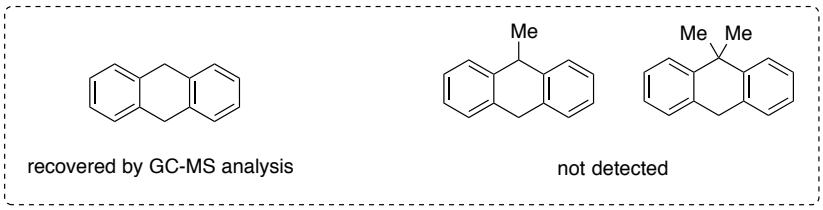
SI Table 1



Entry	Variation from the optimal condition	yield of **1a (GC)**
1	no $Fe(acac)_3$	0% (96% recovery)
2	no dppen	24%
3	0.6 mmol Me_2AlCl instead of $AlMe_3$	8 %
4	5 mol% $Fe(acac)_2$ instead of $Fe(acac)_3$	80% (15% recovery)
5	2 mol% $Fe(OTf)_3$/dppen instead of 5 mol% $Fe(acac)_3$/dppen	98%
6	r.t. instead of 70 °C	33%
7	no 2,3-dichlorobutane	26%
8	adding 0.1 mmol of 9,10-dihydroanthracene	96%

Radical trap experiment (SI Table 1, Entry 8):

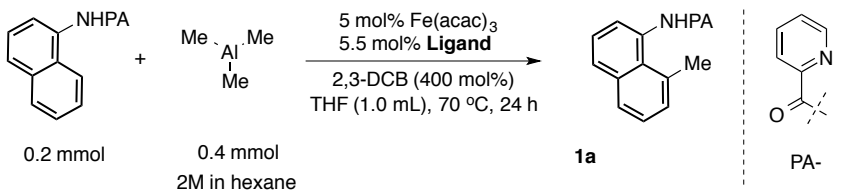




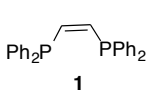
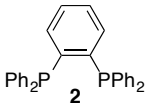
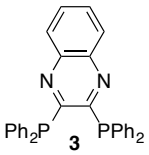
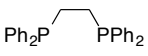
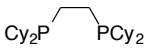
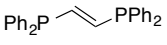
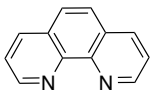
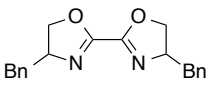
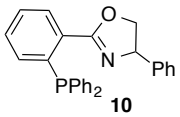
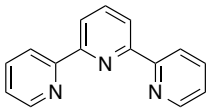
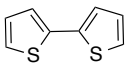
Investigation of the ligand effect

The reactions were performed according to the General Procedure using different ligands (SI Table 2). After aqueous work up, the crude mixture was analyzed by ^{1}H-NMR in the presence of 1,1,2,2-tetrachloroethane as an internal standard.

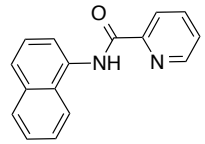
SI Table 2



0.2 mmol | 0.4 mmol, 2M in hexane | **1a** | PA-

 **1** 98%	 **2** 94%	 **3** 95%	 **4** 83%
 **5** 24%	 **6** 10%	 **7** 33%	 **8** 47%
 **9** 45%	 **10** 26%	 **11** <5%	 **12** 16%

3. Preparation and Characterization of Carboxamides



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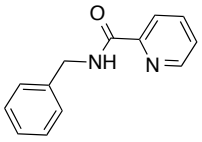

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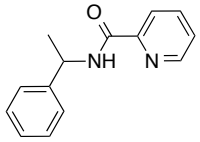

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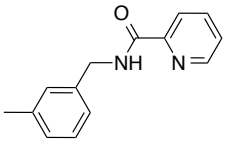

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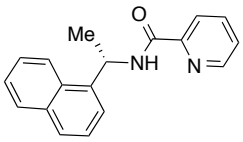

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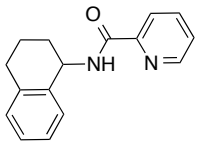

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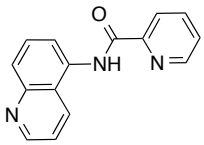

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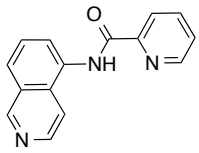

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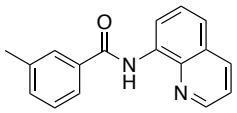

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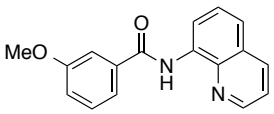

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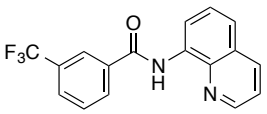

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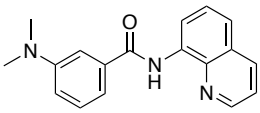

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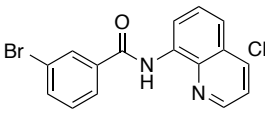

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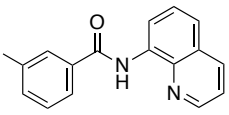

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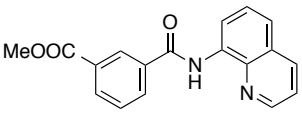

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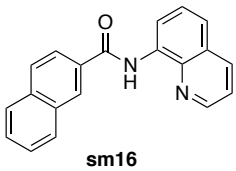

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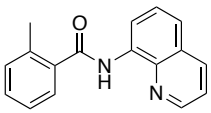

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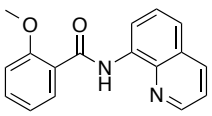

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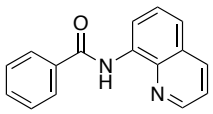

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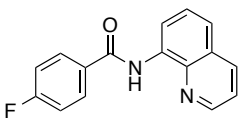

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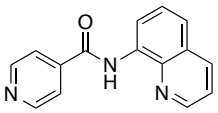

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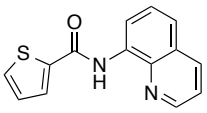

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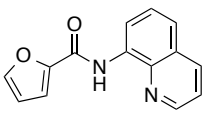

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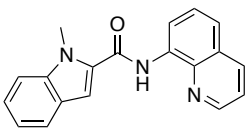

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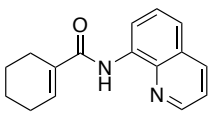

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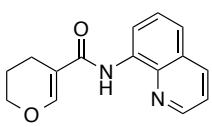


sm26

General procedure:

Preparation of picolinamides (compounds sm1-sm8)

To a suspension of picolinoyl chloride hydrochloride (6.0 mmol) in dry THF (10 mL) was added amine (5.0 mmol) and Et_3N (20 mmol) at 0 ^oC. The reaction mixture was subsequently stirred over night at room temperature. After addition of water (20 mL) the mixture was extracted with dichloromethane (20 mL x 3), the extracts were combined and dried over $MgSO_4$. After filtration and evaporation of volatiles, the obtained crude amide product was purified by silica gel chromatography (hexane: ethyl acetate = 3:1-1:1).

Preparation of 8-aminoquinolinyl amides (compounds sm9-sm26)

*Preparation of 8-aminoquinoline amides from the acid halide (compounds **sm9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20**)*

In a 100-mL flask, 8-aminoquinoline (10 mmol) and NEt_3 (11 mmol) were dissolved in dichloromethane (20 mL), followed by slow dropwise addition of an acid chloride (12 mmol). The resulting mixture was stirred at r.t. for 6 h. The mixture was transferred to a separating funnel and washed with water (15 mL), sat. $NaHCO_3$ (15 mL) and brine (15 mL). The organic layer was dried over $MgSO_4$. After filtration and evaporation of volatiles, the obtained crude amide product was purified by silica gel chromatography (hexane: ethyl acetate = 10:1). (Reference: *J. Am. Chem. Soc.* **2005**, *127*, 13155.)

*Synthesis of amides from the carboxylic acid (compounds **sm21, 22, 23, 24, 25**)*

In a 100-mL flask was placed a carboxylic acid (11 mmol). $SOCl_2$ (10 mL) was slowly added to the solution. The reaction mixture was refluxed for 3 h at 85 °C, then the excess $SOCl_2$ was removed under vacuo to give the crude acid chloride. The crude acid chloride was diluted with dry CH_2Cl_2 (20 mL). A solution of 8-aminoquinoline (10 mmol) and NEt_3 (11 mmol) in dichloromethane (20 mL) was added dropwise to the acid chloride solution at 0 °C. The resulting mixture was allowed warm to r.t., and then stirred overnight. The mixture was quenched with saturated $NaHCO_3$ solution and extracted with CH_2Cl_2 three times. These extracts were combined and dried over $MgSO_4$. After evaporation under vacuo, the crude amide product was purified by silica gel chromatography (hexane: ethyl acetate = 10:1). (Reference: *J. Am. Chem. Soc.* **2009**,

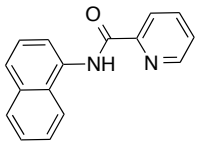
131, 6898).

*Compound **sm26** was prepared according to literature procedure.* (Reference: *J. Am. Chem. Soc.* **2014**, *136*, 13126)

Characterization of Carboxamide Substrates

Spectral data for the following compounds showed good agreement with the literature data:

N-(naphthalen-1-yl)picolinamide **(sm1)** Reference: *J. Org. Chem.*, **2013**, *78*, 9689



This amide was obtained as a white solid. Melting point: 131–132 °C (CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.77 (br, 1H), 8.71 (d, *J* = 4.2 Hz, 1H), 8.42-8.35 (m, 2H), 8.10 (d, *J* = 8.3 Hz, 1H), 7.96 – 7.88 (m, 2H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.60 – 7.53 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2, 150.0, 148.1, 137.7, 134.0, 132.3, 128.8, 126.5, 126.3, 126.2, 126.0, 125.9, 125.0, 122.5, 120.4, 118.5.

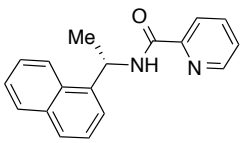
GC MS (EI) *m*/*z* (relative intensity): 248 (M^+, 100), 207 (14), 144 (15), 115 (32), 79 (75).

N-benzylpicolinamide **(sm2)** Reference: *Org. Lett.*, **2009**, *11*, 5726

N-(1-phenylethyl)picolinamide **(sm3)** Reference: *J. Org. Chem.,* **2013**, *78*, 9689

N-(3-methylbenzyl)picolinamide **(sm4)** Reference: *Org. Lett.*, **2012**, *14*, 2948

(*S*)-*N*-(1-(naphthalen-1-yl)ethyl)picolinamide **(sm5)**



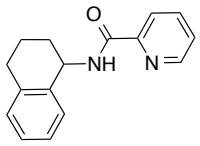
This amide was obtained as a yellow oil. The enantiopurity was >99% ee.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 8.37 (br, 1H), 8.22 (t, *J* = 8.0 Hz, 2H), 7.87 – 7.79 (m, 3H), 7.62 (d, *J* = 6.5 Hz, 1H), 7.55-7.46 (m, 3H), 7.38 (t, *J* = 6.4 Hz, 1H), 6.14 (t, *J* = 6.4 Hz, 1H), 1.79 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2, 149.8, 148.0, 138.4, 137.3, 133.9, 131.1, 128.7, 128.2, 126.5, 126.1, 125.7, 125.3, 123.4, 122.6, 122.3, 44.6, 21.2.

GC MS (EI) *m*/*z* (relative intensity): 276 (M^+, 16), 261 (8), 170 (100), 153 (17).

N-(1,2,3,4-tetrahydronaphthalen-1-yl)picolinamide **(sm6)**



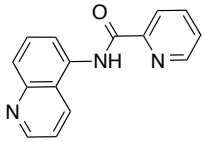
This amide was obtained as a white solid. Melting point: 137–138 °C (CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 4.0 Hz, 1H), 8.33 (d, *J* = 7.6 Hz, 1H), 8.26 (d, *J* = 8.0 Hz, 1H), 7.85 (t, *J* = 7.2 Hz, 1H), 7.41 (t, *J* = 5.2 Hz, 1H), 7.33 (d, *J* = 7.2 Hz, 1H), 7.22 – 7.12 (m, 3H), 5.39 (t, *J* = 6.8 Hz, 1H), 2.90 – 2.78 (m, 2H), 2.23 – 2.08 (m, 1H), 2.01 – 1.74 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 149.9, 148.0, 137.5, 137.3, 136.6, 129.1, 128.8, 127.2, 126.2, 126.1, 122.3, 47.4, 30.2, 29.2, 20.1.

GC MS (EI) *m*/*z* (relative intensity): 252 (M^+, 1), 146 (100), 130 (29).

N-(quinolin-5-yl)picolinamide **(sm7)**



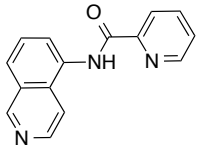
This amide was obtained as a yellow solid. Melting point: 146–147 °C (CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.68 (br, 1H), 8.95 (s, 1H), 8.68 (s, 1H), 8.43 – 8.23 (m, 3H), 7.99 – 7.85 (m, 2H), 7.75 (m, 1H), 7.56 – 7.36 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 150.3, 149.5, 148.6, 148.1, 137.8, 132.3, 129.5, 129.3, 126.7, 126.5, 122.5, 121.7, 120.9, 119.3.

GC MS (EI) *m*/*z* (relative intensity): 249 (M^+, 89), 207 (31), 171 (34).

N-(isoquinolin-5-yl)picolinamide **(sm8)**



This amide was obtained as a brown solid. Melting point: 144–145 °C (CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.78 (br, 1H), 9.30 (s, 1H), 8.73 – 8.64 (m, 3H), 8.36 (d, *J* = 7.8 Hz, 1H), 7.97 (td, *J* = 7.7, 1.6 Hz, 1H), 7.82-7.88 (m, 2H), 7.69 (t, *J* = 7.9 Hz,

1H), 7.56 (t, *J* = 6.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 153.2, 149.6, 148.2, 143.4, 137.9, 131.8, 129.0, 128.7, 127.6, 126.8, 124.1, 122.6, 121.9, 113.6.

GC MS (EI) *m*/*z* (relative intensity): 249 (M^+, 93), 171 (34), 106 (28).

3-methyl-*N*-(quinolin-8-yl)benzamide **(sm9)** Reference: *Org. Lett.* **2009**, *11*, 5726

3-methoxy-*N*-(quinolin-8-yl)benzamide **(sm10)** Reference: *J. Am. Chem. Soc.* **2012**, *134*, 18237

N-(quinolin-8-yl)-3-(trifluoromethyl)benzamide **(sm11)** Reference: *J. Am. Chem. Soc.* **2012**, *134*, 18237

3-(dimethylamino)-*N*-(quinolin-8-yl)benzamide **(sm12)** Reference: *Chem. Sci*. **2013**, *4*, 2201

3-bromo-*N*-(quinolin-8-yl)benzamide **(sm13)** Reference: *Chem. Sci*. **2013**, *4*, 2201

3-chloro-*N*-(quinolin-8-yl)benzamide **(sm14)** Reference: *Chem. Sci*. **2013**, *4*, 2201

methyl 3-(quinolin-8-ylcarbamoyl)benzoate **(sm15)** Reference: *J. Am. Chem. Soc.* **2014**, *136* 14349

N-(quinolin-8-yl)-2-naphthamide **(sm16)** Reference: *Org. Lett.* **2012**, *14*, 354

2-methyl-*N*-(quinolin-8-yl)benzamide **(sm17)** Reference: *J. Am. Chem. Soc.* **2012**, *134*, 18237

2-methoxy-*N*-(quinolin-8-yl)benzamide **(sm18)** Reference: *J. Am. Chem. Soc.* **2014**, *136* 14349.

N-(quinolin-8-yl)benzamide (**sm19**) Reference: *Org. Lett.* **2009**, *11*, 5726

4-fluoro-*N*-(quinolin-8-yl)benzamide **(sm20)** Reference: *J. Am. Chem. Soc.*, **2013**, *135*, 17755

N-(quinolin-8-yl)isonicotinamide **(sm21)** Reference: *Chem. Eur. J.*, **2014**, *20*, 9902

N-(quinolin-8-yl)thiophene-2-carboxamide **(sm22)** Reference: *Org. Lett.* **2012**, *14*, 354

N-(quinolin-8-yl)furan-2-carboxamide **(sm23)** Reference: *Org. Lett.*, **2014,** *16*, 4684

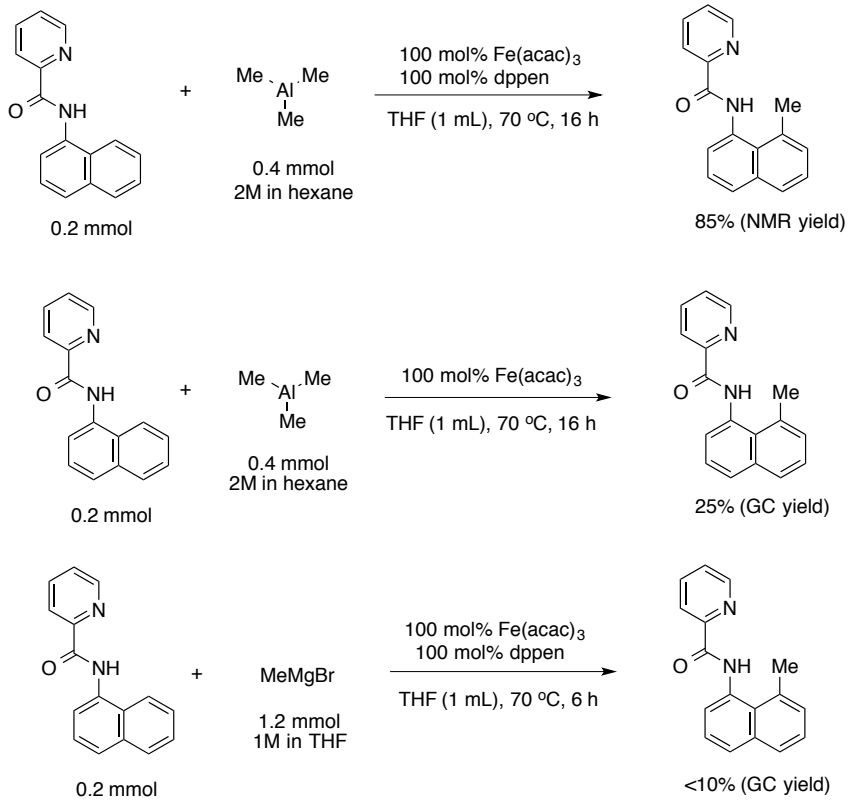
1-methyl-*N*-(quinolin-8-yl)-1*H*-indole-2-carboxamide **(sm24)** Reference: *J. Am. Chem. Soc.*, **2013**, *135*, 17755

N-(quinolin-8-yl)cyclohex-1-ene-1-carboxamide **(sm25)** Reference: *J. Am. Chem. Soc.* **2013**, *135*, 5308

N-(quinolin-8-yl)-3,4-dihydro-2*H*-pyran-5-carboxamide **(sm26)** Reference: *J. Am. Chem. Soc.* **2014**, *136*, 13126

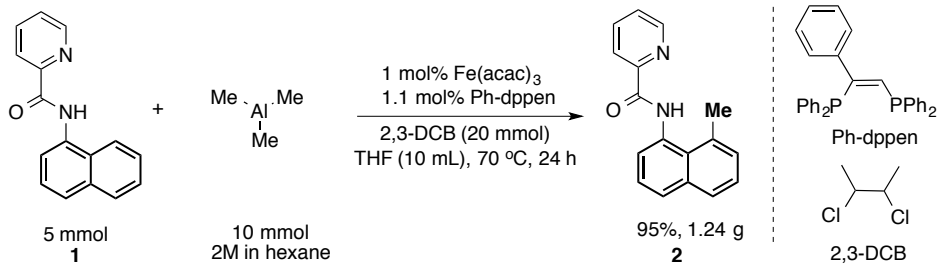
4. Experiments using Stoichiometric Amount of Iron(III) Without Oxidant

Under a nitrogen atmosphere, $Fe(acac)_3$ (100 mol%), (*Z*)-1,2-bis (diphenylphosphino)ethene (dppen) (100 mol%), and *N*-(naphthalen-1-yl)picolinamide (**1**) (50 mg, 0.20 mmol) were placed in an oven dried Schlenck tube. The tube was evacuated and filled with nitrogen for three times. THF (1.0 mL) was injected to dissolve the mixture. Sequentially, a solution of trimethylaluminum (2.0 equiv, 2.0 M in hexane, 0.2 mL) was slowly added at room temperature. After stirring at room temperature for 10 min, the mixture was heated at 70 ^{o}C for 16 h. After cooling to r.t., the mixture was diluted with diethyl ether and methanol (100 μL) was slowly added via a microsyringe to quench the aluminium reagent. Tridecane (0.1 mmol, 25 μL) was added as an internal standard. Aqueous potassium sodium tartrate was then added. The organic layer was extracted with diethyl ether and passed over a Florisil column. The mixture was analyzed by GC using tridecane as an internal standard, or analyzed by ^{1}H-NMR using 1,1,2,2-tetrachloroethane as an internal standard.



5. Iron-Catalyzed Methylation of C-H Bonds with Trimethylaluminum

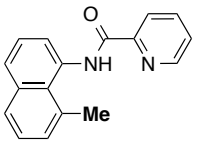
Directed C–H methylation of *N*-(naphthalen-1-yl)picolinamide on gram scale



Under a nitrogen atmosphere, a 0.25 M solution of $Fe(acac)_3$ (1.0 mol%, 0.05 mmol) and (*Z*)-(1-phenylethene-1,2-diyl)bis(diphenylphosphane) (Ph-dppEn) (1.1 mol%, 0.055 mmol) in THF (200 μL) was injected into an anhydrous tetrahydrofuran (THF, 10 mL) solution of *N*-(naphthalen-1-yl)picolinamide (**1**) (1.24 g, 5.0 mmol). Sequentially, a solution of trimethylaluminium solution (2.0 equiv, 2.0 M in hexane, 5.0 mL) was slowly added. After stirring for 30 min at room temperature to finish generating methane, 2,3-dichlorobutane (2,3-DCB) (4.0 equiv, 2.33 mL) was added via a gastight syringe, and the mixture was heated at 70 °C for 24 h. After cooling to r.t., the mixture was diluted with diethyl ether and methanol (2.0 mL) was slowly added via a microsyringe to quench the aluminium reagent. Saturated aqueous solution of Rochelle's salt was added (10 mL), and the organic layer was extracted with diethyl ether (30 mL x 3). The combined organic layers were washed with brine, passed through a pad of Florisil, dried over $MgSO_4$, and concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica gel (hexane:ethyl acetate = 15:1) to afford *N*-(8-methylnaphthalen-1-yl)picolinamide as a yellow solid (1.24 g, 95% yield).

Compound Data:

N*-(8-Methylnaphthalen-1-yl)picolinamide (2):** obtained in 97% yield as a yellow solid. Melting point: 93–94 °C (CH_2Cl_2). The compound data was in agreement with the literature (Ref. *J. Org. Chem.* **2014, 79,* 6720). However, the literature reported a much higher melting point (184–185 °C).

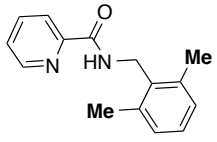


^{1}H NMR (400 MHz, $CDCl_3$) δ 10.61 (br, 1H), 8.66 (d, *J* = 4.8 Hz, 1H), 8.36 (d, *J* = 8.0 Hz, 1H), 8.07 (d, *J* = 7.6 Hz, 1H), 7.92 (td, *J* = 7.2, 1.6 Hz, 1H), 7.72 (t, *J* = 6.8 Hz, 2H), 7.51-7.47 (m, 2H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 6.8 Hz, 1H), 2.98 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 150.0, 148.1, 137.6, 135.8, 133.1, 132.5, 130.0, 128.0, 127.7, 127.3, 126.4, 125.4, 125.3, 123.4, 122.6, 25.0.
GC MS (EI) *m*/*z* (relative intensity): 262 (M^+, 29), 244 (100), 234 (28), 218 (16).
HRMS (APCI) Calcd for $C_{17}H_{15}N_2O$+ [M+H]+ 263.1179, found, 263.1177.

General procedure for Iron-Catalyzed Methylation of C-H Bonds with Trimethylaluminum:

Under a nitrogen atmosphere, a 0.10 M solution of $Fe(acac)_3$ and (*Z*)-1,2-bis (diphenylphosphino)ethene (dppen) in THF (molar ratio of Fe/Ligand = 1:1.1, refer to Table 2 for the exact amount) was injected into an anhydrous tetrahydrofuran (THF, 0.5-1.0 mL, see below for exact amount) solution of amide (0.5 mmol). Sequentially, a solution of trimethylaluminium (2.0 equiv, 2.0 M in hexane, 0.5 mL) was slowly added. After stirring for 10 min to finish generating methane at room temperature, 2,3-dichlorobutane (2,3-DCB) (4.0 equiv, 230 μL) was added via a microsyringe, and the mixture was heated at 70 ^{o}C for 24 h. After cooling to r.t., the mixture was diluted with diethyl ether and methanol (200 μL) was slowly added via a microsyringe to quench the aluminium reagent. Saturated aqueous solution of Rochelle's salt was added (1.0 mL), and the organic layer was extracted with diethyl ether (5 mL x 3). The combined organic layers were passed through a pad of Florisil and concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica gel to afford the desired methylation product.

N-(2,6-Dimethylbenzyl)picolinamide **(5):** the reaction was performed using 3.0 mol% $Fe(acac)_3$, 3.3 mol% dppen, 3.0 equiv. $AlMe_3$, 0.5 mL THF, **5** was obtained in 78% yield as a white solid. Melting point: 133–135 °C (CH_2Cl_2). The compound data was in agreement with the literature. (Ref. *J. Am. Chem. Soc.* **2012***, 134,* 7)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 4.2 Hz, 1H), 8.23 (d, *J* = 7.8 Hz, 1H), 7.92

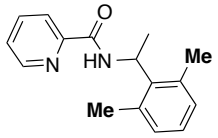
(br, 1H), 7.85 (td, *J* = 7.6, 2.0 Hz, 1H), 7.42 – 7.37 (m, 1H), 7.14 (d, *J* = 6.5 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 2H), 4.68 (d, *J* = 5.2 Hz, 2H), 2.42 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1, 149.7, 148.0, 137.6, 137.3, 133.8, 128.4, 127.8, 126.1, 122.1, 38.1, 19.8.

GC MS (EI) *m*/*z* (relative intensity): 240 (M^+, 10), 196 (4), 134 (100), 118 (88).

HRMS (APCI) Calcd for $C_{15}H_{17}N_2O$+ [M+H]+ 241.1335, found, 241.1335.

N-(1-(2,6-Dimethylphenyl)ethyl)picolinamide **(6):** the reaction was performed using 3.0 mol% $Fe(acac)_3$, 3.3 mol% dppen, 3.0 equiv. $AlMe_3$, 0.5 mL THF, **6** was obtained in 79% yield as a yellow solid. Melting point: 66–67 °C (CH_2Cl_2).



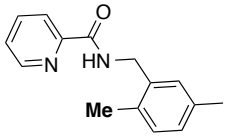
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 6.8 Hz, 1H), 8.55 (d, *J* = 4.0 Hz, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.82 (td, *J* = 8.0, 2.0, 1H), 7.42 – 7.37 (m, 1H), 7.06 – 6.97 (m, 3H), 5.74 (p, *J* = 8.0 Hz, 1H), 2.55 (s, 6H), 1.64 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2, 149.9, 148.0, 139.1, 137.3, 135.5, 129.5, 126.8, 126.0, 122.1, 45.6, 21.0, 19.6.

GC MS (EI) *m*/*z* (relative intensity): 254 (M^+, 5), 239 (20), 207 (9), 148 (34), 132 (100).

HRMS (APCI) Calcd for $C_{16}H_{19}N_2O^+$ [M+H]+ 255.1492, found, 255.1497.

N-(2,5-Dimethylbenzyl)picolinamide **(7):** the reaction was performed using 2.0 mol% $Fe(acac)_3$, 2.2 mol% dppen, 2.0 equiv. $AlMe_3$, 0.5 mL THF, **7** was obtained in 96% yield as a yellow oil.

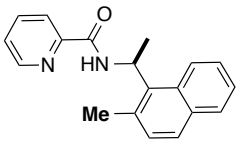


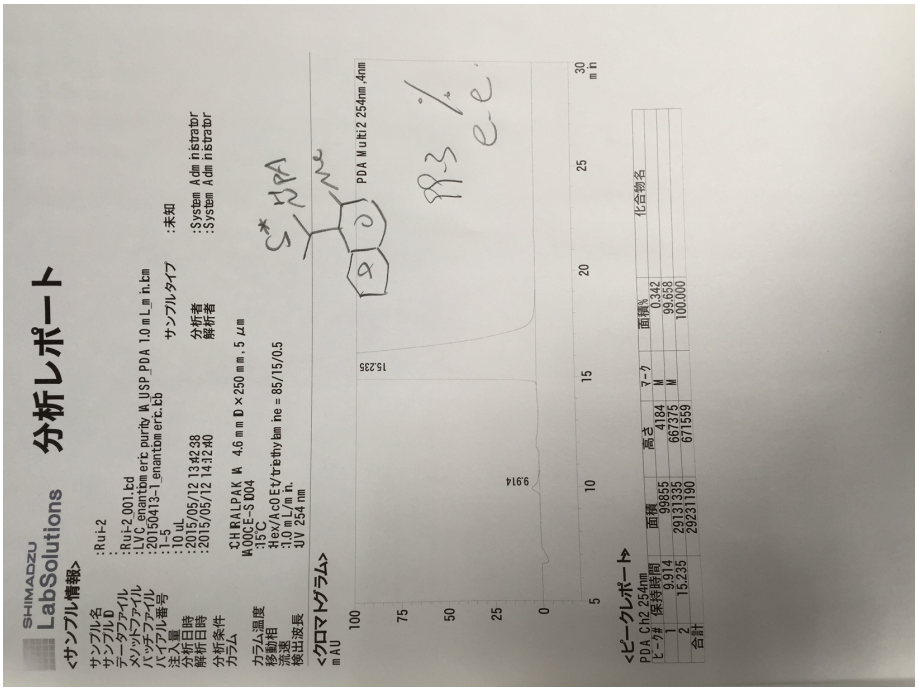
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 4.0 Hz, 1H), 8.23 (m, 2H), 7.85 (td, *J* = 7.7, 1.7 Hz, 1H), 7.42 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 7.13 (s, 1H), 7.08 (d, *J* = 7.2 Hz, 1H), 7.02 (d, *J* = 7.2 Hz, 1H), 4.63 (d, *J* = 5.8 Hz, 2H), 2.33 (s, 3H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 149.7, 148.0, 137.3, 135.6, 135.5, 133.3, 130.4, 129.4, 128.3, 126.1, 122.3, 41.6, 20.9, 18.6.

GC MS (EI) *m*/*z* (relative intensity): 240 (M^+, 12), 134 (100), 118 (49), 107 (21).

(*S*)-*N*-(1-(2-Methylnaphthalen-1-yl)ethyl)picolinamide **(8):** the reaction was performed using 3.0 mol% $Fe(acac)_3$, 3.3 mol% dppen, 2.0 equiv. $AlMe_3$, 0.5 mL THF, **8** was obtained in 97% yield as a yellow oil. Enantiomeric purity was determined by HPLC analysis (CHIRALPAK IA column, Hexane/EtOAc/Et_3N=85/15/0.5, flow rate 1.0 mL/min, retention time 10.1 min (minor) and 19.5 min (major)), >99% ee.





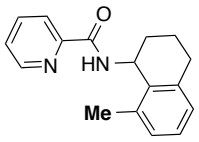
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (d, *J* = 6.0 Hz, 1H), 8.51 (d, *J* = 4.8 Hz, 1H), 8.34 (d, *J* = 8.8 Hz, 1H), 8.15 (d, *J* = 7.6 Hz, 1H), 7.87 – 7.75 (m, 2H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.38 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 6.12 (t, *J* = 7.2 Hz, 1H), 2.72 (s, 3H), 1.87 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 149.9, 148.0, 137.3, 135.2, 133.4, 130.9, 129.8, 129.3, 127.8, 126.1, 126.0, 124.5, 123.9, 122.1, 45.7, 21.3, 20.7. (one carbon signal is overlapped)

GC MS (EI) *m*/*z* (relative intensity): 290 (M^+, 24), 275 (20), 257 (7), 184 (100), 168 (51), 153 (46).

HRMS (APCI) Calcd for $C_{19}H_{19}N_2O^+$ [M+H]+ 291.1492, found, 291.1491.

N-(8-Methyl-1,2,3,4-tetrahydronaphthalen-1-yl)picolinamide **(9):** the reaction was performed using 3.0 mol% $Fe(acac)_3$, 3.3 mol% dppen, 2.0 equiv. $AlMe_3$, 0.5 mL THF, **9** was obtained in 88% yield as a white solid. Melting point: 141–142 °C (CH_2Cl_2).



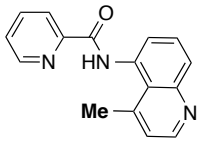
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 4.2 Hz, 1H), 8.25 (d, *J* = 7.8 Hz, 1H), 8.15 (d, *J* = 7.4 Hz, 1H), 7.85 (t, *J* = 7.1 Hz, 1H), 7.40 (dd, *J* = 6.8, 5.1 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.07 – 7.00 (m, 2H), 5.37 (d, *J* = 8.1 Hz, 1H), 2.81-2.93 (m, 2H), 2.26 (s, 4H), 1.84 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9, 150.0, 148.0, 138.3, 138.0, 137.3, 133.7, 128.2, 127.4, 127.2, 126.1, 122.2, 44.4, 29.8, 29.6, 18.7, 18.1.

GC MS (EI) *m*/*z* (relative intensity): 266 (M^+, 1), 160 (50), 144 (100), 129 (68).

HRMS (APCI) Calcd for $C_{17}H_{19}N_2O^+$ [M+H]+ 267.1492, found, 267.1499.

N-(4-Methylquinolin-5-yl)picolinamide **(10):** the reaction was performed using 5.0 mol% $Fe(acac)_3$, 5.5 mol% dppen, 2.0 equiv. $AlMe_3$, 0.5 mL THF, **10** was obtained in 64% yield as a yellow solid. Melting point: 122–123 °C (CH_2Cl_2).



X-ray crystallographic analysis

Single-crystal X-ray diffraction measurements were performed on a RIGAKU R-AXIS RAPID II diffractometer equipped with an imaging plate detector, using CuK_α(graphite monochromated, λ = 1.5419 Å) radiation. The positional and thermal parameters were refined by the full-matrix least-squares method using SHELXL97 program.[1] The Yadokari-XG software was used for refinement of the structure.[2]

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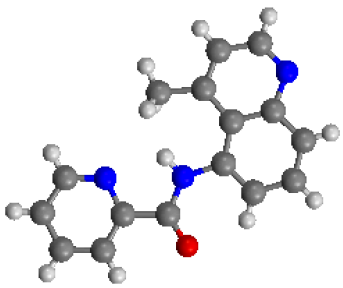
[1] Sheldrick, G. M. *Acta Crystallogr., A, Found. Crystallogr.* **2008**, *64*, 112–122.

[2] Yadokari-XG, Software for Crystal Structure Analyses, K. Wakita (2001); Release of Software (Yadokari-XG 2009) for Crystal Structure Analyses, C. Kabuto, S. Akine, T. Nemoto, and E. Kwon, J. Cryst. Soc. Jpn., **2009**, *51*, 218-224.

Crystal data for X (CCDC 1063984) [3]

Empirical Formula	$C_{16}H_{13}N_3O$
Formula Weight	263.29
Measurement Temperature	123(2) K
Crystal System	monoclinic
Space Group	$P2_1/n$
Lattice Parameters	$a = 8.7323(3)$ Å
	$b = 26.7612(7)$ Å
	$c = 10.8183(3)$ Å
	$\alpha = 90°$
	$\beta = 97.865(2)°$
	$\gamma = 90°$
Volume	2504.3(1) Å^3
Z value	8
Density (calculated)	1.397 g/cm^3
Number of Reflections Measured	25247
Number of Unique Reflections	4557
R_{merge}	0.1155
Number of Observed Reflections ($I > 2\sigma(I)$)	1360
Goodness of Fit Indicator	0.759
Final R_1 Indices [$I > 2\sigma(I)$] (R_{obs}, wR_{obs})	0.0684, 0.1428
R indices [all data] (R_{all}, wR_{all})	0.1730, 0.1955
Largest diff peak and hole	0.320/–0.292 e·Å^{-3}

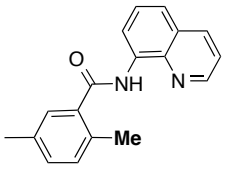


^{1}H NMR (400 MHz, $CDCl_3$) δ 10.54 (br, 1H), 8.72 (d, J = 4.3 Hz, 1H), 8.65 (d, J = 4.2 Hz, 1H), 8.34 (d, J = 7.8 Hz, 1H), 8.09 (d, J = 7.5 Hz, 1H), 8.01 (dd, J = 8.4, 1.0 Hz, 1H), 7.94 (td, J = 7.7, 1.7 Hz, 1H), 7.71 (t, J = 8.0 Hz, 1H), 7.52 (ddd, J = 7.6, 4.8, 1.1

[3] CCDC 1063984 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

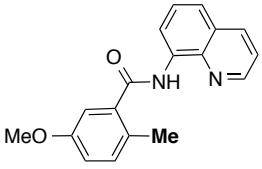
Hz, 1H), 7.16 (d, J = 4.0 Hz, 1H), 2.96 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5, 149.8, 149.7, 149.7, 148.2, 142.9, 137.8, 133.0, 128.7, 128.6, 126.6, 124.5, 124.0, 123.7, 122.7, 24.3.
GC MS (EI) *m*/*z* (relative intensity): 263 (M^+, 28), 245 (84), 235 (44), 219 (23).
HRMS (APCI) Calcd for $C_{16}H_{14}N_3O^+$ [M+H]+ 264.1131, found, 264.1134.

2,5-Dimethyl-*N*-(quinolin-8-yl)benzamide **(12):** the reaction was performed using 1.0 mol% $Fe(acac)_3$, 1.1 mol% dppen, 2.0 equiv. $AlMe_3$, 0.5 mL THF, **12** was obtained in 94% yield as a white solid. Melting point: 81–82 °C (CH_2Cl_2). The compound data is in agreement with the literature. (Ref. *Adv. Synth. Catal.,* DOI: 10.1002/adsc.201500276)



^{1}H NMR (400 MHz, $CDCl_3$) δ 10.18 (br, 1H), 8.94 (d, J = 7.4 Hz, 1H), 8.78 (dd, J = 4.2, 1.6 Hz, 1H), 8.17 (dd, J = 8.3, 1.6 Hz, 1H), 7.63 – 7.52 (m, 2H), 7.49 – 7.43 (m, 2H), 7.20 (s, 2H), 2.55 (s, 3H), 2.40 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 148.2, 138.6, 136.5, 136.3, 135.6, 134.7, 133.3, 131.2, 131.0, 128.0, 127.8, 127.4, 121.7, 121.6, 116.5, 20.9, 19.7.
GC MS (EI) *m*/*z* (relative intensity): 276 (M^+, 28), 259 (50), 244 (8), 232 (21), 207 (20), 133 (100).

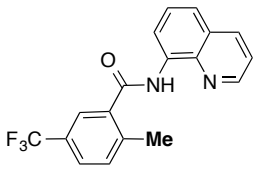
5-Methoxy-2-methyl-*N*-(quinolin-8-yl)benzamide **(13):** the reaction was performed using 1.0 mol% $Fe(acac)_3$, 1.1 mol% dppen, 2.0 equiv. $AlMe_3$, 0.5 mL THF, **13** was obtained in 87% yield as a white solid. Melting point: 92–93 °C (CH_2Cl_2).



^{1}H NMR (400 MHz, $CDCl_3$) δ 10.20 (br, 1H), 8.93 (d, J = 7.4 Hz, 1H), 8.77 (d, J = 4.4 Hz, 1H), 8.17 (dd, J = 8.3, 1.5 Hz, 1H), 7.54-7.61 (m, 2H), 7.45 (dd, J = 8.3, 4.1 Hz, 1H), 7.20-7.22 (m, 2H), 6.95 (dd, J = 8.4, 2.7 Hz, 1H), 3.84 (s, 3H), 2.52 (s, 3H).

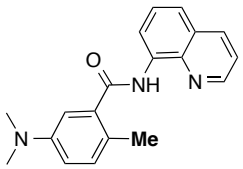
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 157.6, 148.3, 138.5, 137.4, 136.3, 134.6, 132.3, 128.1, 127.9, 127.4, 121.8, 121.6, 116.5, 116.0, 112.7, 55.5, 19.2.
GC MS (EI) *m*/*z* (relative intensity): 292 (M^+, 47), 275 (64), 248 (30), 207 (36), 149 (100), 121 (63).

2-Methyl-*N*-(quinolin-8-yl)-5-(trifluoromethyl)benzamide **(14):** the reaction was performed using 1.0 mol% $Fe(acac)_3$, 1.1 mol% dppen, 2.0 equiv. $AlMe_3$, 0.5 mL THF, **14** was obtained in 95% yield as a white solid. Melting point: 105–106 °C (CH_2Cl_2).



^{1}H NMR (400 MHz, $CDCl_3$) δ 10.21 (br, 1H), 8.91 (d, *J* = 6.3 Hz, 1H), 8.79 (d, *J* = 3.0 Hz, 1H), 8.19 (d, *J* = 7.9 Hz, 1H), 7.92 (s, 1H), 7.67 – 7.56 (m, 3H), 7.49 – 7.41 (m, 2H), 2.65 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 148.4, 140.6, 138.5, 137.2, 136.4, 134.2, 131.8, 128.5 (d, *J* = 32.9 Hz), 128.0, 127.3, 126.8 (q, *J* = 3.7 Hz), 124.2 (q, *J* = 3.8 Hz), 123.9 (d, *J* = 272.1 Hz), 122.2, 121.8, 116.7, 20.2.
GC MS (EI) *m*/*z* (relative intensity): 330 (M^+, 52), 313 (100), 286 (47), 187 (80), 159 (60), 144 (82).

5-(Dimethylamino)-2-methyl-*N*-(quinolin-8-yl)benzamide **(15):** the reaction was performed using 1.0 mol% $Fe(acac)_3$, 1.1 mol% dppen, 2.0 equiv. $AlMe_3$, 0.5 mL THF, 1**5** was obtained in 98% yield as a yellow solid. Melting point: 89–90 °C (CH_2Cl_2).

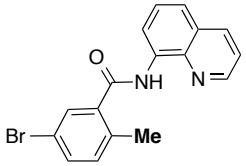


^{1}H NMR (400 MHz, $CDCl_3$) δ 10.21 (br, 1H), 8.95 (d, *J* = 7.5 Hz, 1H), 8.76 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.17 (m, *J* = 8.4 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.44 (ddd, *J* = 8.3, 4.2, 1.3 Hz, 1H), 7.16 (d, *J* = 8.5 Hz, 1H), 7.04 (d, *J* = 2.4 Hz, 1H), 6.80 (d, *J* = 8.4, 2.4 Hz, 1H), 2.97 (s, 6H), 2.49 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 148.9, 148.2, 138.6, 137.2, 136.3, 134.8, 131.9,

127.9, 127.4, 123.6, 121.6, 116.4, 114.7, 111.7, 40.8, 19.0. (one carbon signal is overlapped)

GC MS (EI) *m*/*z* (relative intensity): 305 (M^+, 97), 288 (19), 207 (16), 162 (40), 133 (100).

5-Bromo-2-methyl-*N*-(quinolin-8-yl)benzamide **(16):** the reaction was performed using 2.0 mol% $Fe(acac)_3$, 2.2 mol% dppen, 2.0 equiv. $AlMe_3$, 0.5 mL THF, **16** was obtained in 71% yield as a white solid. Melting point: 129–130 °C (CH_2Cl_2).

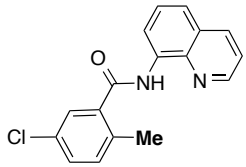


^{1}H NMR (400 MHz, $CDCl_3$) δ 10.16 (br, 1H), 8.90 (d, *J* = 7.5 Hz, 1H), 8.80 (dd, *J* = 8.8, 1.6, 1H), 8.19 (dd, *J* = 8.4, 1.6, 1H), 7.79 (d, *J* = 2.1 Hz, 1H), 7.60 – 7.44 (m, 4H), 7.18 (d, *J* = 8.4 Hz, 1H), 2.53 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 148.4, 138.5, 138.4, 136.4, 135.4, 134.3, 133.2, 132.9, 130.0, 127.9, 127.3, 122.1, 121.8, 119.4, 116.6, 19.7.

GC MS (EI) *m*/*z* (relative intensity): 342 (M^+, 40), 340 (M^+, 35), 325 (78), 323 (79), 298 (52), 296 (48), 199 (65), 197 (68), 171 (56), 169 (44).

5-Chloro-2-methyl-*N*-(quinolin-8-yl)benzamide **(17):** the reaction was performed using 1.0 mol% $Fe(acac)_3$, 1.1 mol% dppen, 2.0 equiv. $AlMe_3$, 0.5 mL THF, **17** was obtained in 96% yield as a white solid. Melting point: 124–125 °C (CH_2Cl_2).

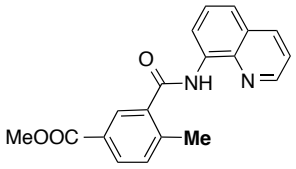


^{1}H NMR (400 MHz, $CDCl_3$) δ 10.17 (br, 1H), 8.91 (d, *J* = 6.7 Hz, 1H), 8.80 (d, *J* = 4.0 Hz, 1H), 8.19 (d, *J* = 8.2 Hz, 1H), 7.68 – 7.53 (m, 3H), 7.48 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.37 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.25 (d, *J* = 8.6 Hz, 1H), 2.55 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 148.4, 138.5, 138.0, 136.4, 135.0, 134.3, 132.7, 131.6, 130.2, 127.0, 128.34, 127.2, 122.1, 121.8, 116.6, 19.6.

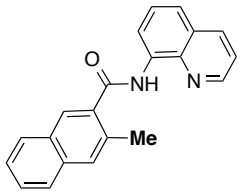
GC MS (EI) *m*/*z* (relative intensity): 296 (M^+, 55), 279 (100), 252 (54), 153 (98), 144 (53).

Methyl 4-methyl-3-(quinolin-8-ylcarbamoyl)benzoate **(18):** the reaction was performed using 1.0 mol% $Fe(acac)_3$, 1.1 mol% dppen, 2.0 equiv. $AlMe_3$, 0.5 mL THF, **18** was obtained in 77% yield as a white solid. Melting point: 159–160 °C (CH_2Cl_2).



^{1}H NMR (400 MHz, $CDCl_3$) δ 10.21 (br, 1H), 8.94 (d, *J* = 6.7 Hz, 1H), 8.78 (dd, *J* = 4.1, 1.4 Hz, 1H), 8.34 (d, *J* = 1.3 Hz, 1H), 8.19 (d, *J* = 8.2 Hz, 1H), 8.06 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.64 – 7.53 (m, 2H), 7.47 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 3.93 (s, 3H), 2.64 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 166.4, 148.4, 142.2, 138.5, 136.8, 136.4, 134.4, 131.5, 131.2, 128.3, 128.0, 127.9, 127.3, 122.1, 121.7, 116.6, 52.2, 20.4.
GC MS (EI) *m*/*z* (relative intensity): 320 (M^+, 47), 303 (90), 289 (10), 276 (45), 177 (100), 149 (30).

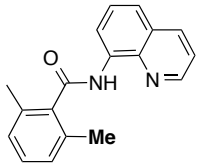
3-Methyl-*N*-(quinolin-8-yl)-2-naphthamide **(19):** the reaction was performed using 1.0 mol% $Fe(acac)_3$, 1.1 mol% dppen, 2.0 equiv. $AlMe_3$, 0.5 mL THF, **19** was obtained in 96% yield as a white solid. Melting point: 149–150 °C (CH_2Cl_2).



^{1}H NMR (400 MHz, $CDCl_3$) δ 10.35 (br, 1H), 8.99 (d, *J* = 7.5 Hz, 1H), 8.77 (d, *J* = 4.4 Hz, 1H), 8.19 – 8.17 (m, 2H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.74 (s, 1H), 7.65 – 7.42 (m, 5H), 2.74 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 148.3, 138.5, 136.4, 135.4, 134.7, 134.2, 133.4, 131.2, 129.4, 128.2, 128.0, 127.41, 127.40, 127.1, 127.0, 125.9, 121.8, 121.7, 116.5, 20.5.

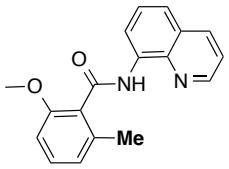
GC MS (EI) *m*/*z* (relative intensity): 312 (M^+, 42), 295 (44), 268 (34), 169 (100), 155 (40), 141 (66).

2,6-Dimethyl-*N*-(quinolin-8-yl)benzamide **(20):** the reaction was performed using 1.0 mol% $Fe(acac)_3$, 1.1 mol% dppen, 2.0 equiv. $AlMe_3$, 0.5 mL THF, **20** was obtained in 95% yield as a white solid. Melting point: 131–132 °C (CH_2Cl_2). The compound data was in agreement with the literature. (Ref. *J. Am. Chem. Soc.* **2015**, *137*, 531)



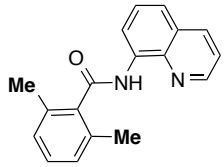
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.94 (br, 1H), 9.00 (dd, *J* = 7.4, 1.4 Hz, 1H), 8.74 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.18 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.60 (m, 2H), 7.45 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.25 (t, *J* = 8.0 Hz, 1H), 7.14 – 7.09 (d, 2H), 2.44 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 148.3, 138.5, 138.0, 136.3, 134.5, 134.4, 129.0, 128.0, 127.7, 127.4, 121.9, 121.7, 116.7, 19.4.
GC MS (EI) *m*/*z* (relative intensity): 276 (M^+, 21), 259 (36), 245 (30), 218 (12), 133 (100), 119 (68).

2-Methoxy-6-methyl-*N*-(quinolin-8-yl)benzamide **(21):** the reaction was performed using 1.0 mol% $Fe(acac)_3$, 1.1 mol% dppen, 2.0 equiv. $AlMe_3$, 0.5 mL THF, **21** was obtained in 59% yield as a white solid. Melting point: 124–125 °C (CH_2Cl_2).



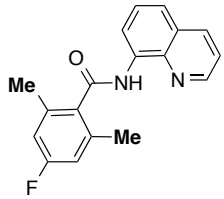
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.11 (br, 1H), 9.02 (d, *J* = 7.2 Hz, 1H), 8.75 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.16 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.62 – 7.52 (m, 2H), 7.43 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.29 (t, *J* = 8.0 Hz, 1H), 6.86 (dd, *J* = 17.6, 8.0 Hz, 2H), 3.84 (s, 3H), 2.45 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 156.4, 148.1, 138.5, 137.4, 136.3, 134.7, 130.1, 128.0, 127.4, 126.9, 122.8, 121.6, 121.5, 116.7, 108.5, 55.8, 19.5.
GC MS (EI) *m*/*z* (relative intensity): 292 (M^+, 24), 275 (9), 149 (100), 91 (27).

2,6-Dimethyl-*N*-(quinolin-8-yl)benzamide **(22):** the reaction was performed using 3.0 mol% $Fe(acac)_3$, 3.3 mol% dppen, 3.0 equiv. $AlMe_3$, 0.5 mL THF, **22** was obtained in 91% yield as a white solid.



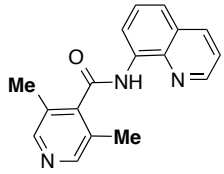
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (br, 1H), 8.91 (dd, *J* = 7.4, 1.6 Hz, 1H), 8.65 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.10 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.56 – 7.46 (m, 2H), 7.36 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 7.6 Hz, 2H), 2.35 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 148.2, 138.4, 138.0, 136.3, 134.5, 134.3, 128.9, 127.9, 127.6, 127.3, 121.9, 121.6, 116.7, 19.4.
GC MS (EI) *m*/*z* (relative intensity): 276 (M^+, 25), 259 (42), 133 (100), 105 (45).

4-Fluoro-2,6-dimethyl-*N*-(quinolin-8-yl)benzamide **(23):** the reaction was performed using 3.0 mol% $Fe(acac)_3$, 3.3 mol% dppen, 3.0 equiv. $AlMe_3$, 0.5 mL THF, **23** was obtained in 90% yield as a white solid. Melting point: 123–125 °C (CH_2Cl_2). The compound data was in agreement with the literature. (Ref. *J. Chem. Res.* **2013**, *37*, 606)



^{1}H NMR (400 MHz, $CDCl_3$) δ 9.94 (br, 1H), 8.99 (dd, *J* = 7.2, 1.3 Hz, 1H), 8.78 (dd, *J* = 4.1, 1.5 Hz, 1H), 8.21 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.63 – 7.59 (m, 2H), 7.48 (dd, *J* = 8.2, 4.2 Hz, 1H), 6.84 (d, *J* = 9.4 Hz, 2H), 2.45 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7 (d, *J* = 277.2 Hz), 163.7, 148.4, 138.4, 137.4, 137.3, 136.4, 134.2 (d, *J* = 3.4 Hz), 128.0, 127.4, 122.1, 121.7, 116.7, 114.4 (d, *J* = 21.4 Hz), 19.6 (d, *J* = 1.6 Hz).
GC MS (EI) *m*/*z* (relative intensity): 294 (M^+, 26), 277 (48), 151 (100), 123 (26).

3,5-Dimethyl-*N*-(quinolin-8-yl)isonicotinamide **(24):** the reaction was performed using 2.0 mol% $Fe(acac)_3$, 2.2 mol% dppen, 3.0 equiv. $AlMe_3$, 0.5 mL THF, **24** was obtained in 48% yield as a yellow solid. Melting point: 96–98 °C (CH_2Cl_2).



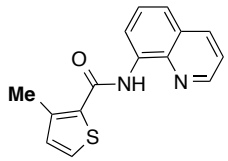
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (br, 1H), 8.94 (dd, *J* = 6.0, 3.2 Hz, 1H), 8.76 (d, *J* = 3.2 Hz, 1H), 8.41 (s, 2H), 8.21 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.63 – 7.61 (m, 2H), 7.48 (dd, *J* = 8.2, 4.2 Hz, 1H), 2.42 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 148.9, 148.5, 144.3, 138.4, 136.4, 133.7, 128.7, 128.0, 127.3, 122.5, 121.8, 117.0, 16.2.

GC MS (EI) *m*/*z* (relative intensity): 277 (M^+, 60), 260 (57), 232 (13), 171 (21), 144 (100), 106 (81).

HRMS (APCI) Calcd for $C_{17}H_{16}N_3O^+$ [M+H]+ 278.1288, found, 278.1294.

3-Methyl-*N*-(quinolin-8-yl)thiophene-2-carboxamide **(25):** the reaction was performed using 1.0 mol% $Fe(acac)_3$, 1.1 mol% dppen, 2.0 equiv. $AlMe_3$, 0.5 mL THF, **25** was obtained in 99% yield as a white solid. Melting point: 108–109 °C (CH_2Cl_2).



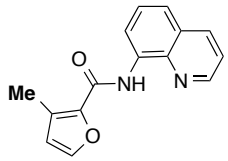
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.47 (br, 1H), 8.88 – 8.80 (m, 2H), 8.17 (d, *J* = 8.2 Hz, 1H), 7.59-7.51 (m, 2H), 7.46 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.40 (d, *J* = 5.0 Hz, 1H), 6.98 (d, *J* = 5.2 Hz, 1H), 2.74 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.2, 148.3, 141.0, 138.6, 136.3, 134.6, 132.8, 132.3, 127.9, 127.7, 127.4, 121.6, 121.5, 116.4, 16.1.

GC MS (EI) *m*/*z* (relative intensity): 268 (M^+, 43), 251 (25), 224 (10), 144 (24), 125 (100).

HRMS (APCI) Calcd for $C_{15}H_{13}N_2OS^+$ [M+H]+ 269.0743, found, 269.0743.

3-Methyl-*N*-(quinolin-8-yl)furan-2-carboxamide **(4):** the reaction was performed using 1.0 mol% $Fe(acac)_3$, 1.1 mol% dppen, 2.0 equiv. $AlMe_3$, 0.5 mL THF, **4** was obtained in 99% yield as a white solid. Melting point: 122–123 °C (CH_2Cl_2).



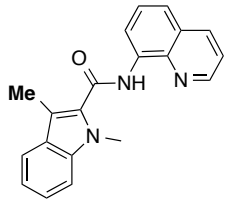
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.73 (br, 1H), 8.90 – 8.85 (m, 2H), 8.16 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.58 – 7.44 (m, 4H), 6.42 (s, 1H), 2.52 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 148.3, 142.8, 142.5, 138.6, 136.3, 134.4, 128.8, 128.0, 127.3, 121.6, 121.4, 116.2, 115.7, 11.4.

GC MS (EI) *m*/*z* (relative intensity): 252 (M^+, 71), 235 (15), 223 (64), 207 (32), 144 (39), 109 (100).

HRMS (APCI) Calcd for $C_{15}H_{13}N_2O_2^+$ [M+H]+ 253.0972, found, 253.0974.

1,3-Dimethyl-*N*-(quinolin-8-yl)-1*H*-indole-2-carboxamide **(26):** the reaction was performed using 1.0 mol% $Fe(acac)_3$, 1.1 mol% dppen, 2.0 equiv. $AlMe_3$, 0.5 mL THF, **26** was obtained in 87% yield as a white solid. Melting point: 159–160 °C (CH_2Cl_2).



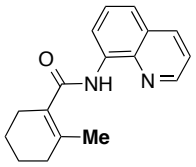
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.51 (br, 1H), 8.94 (d, *J* = 7.4, 1H), 8.82 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.20 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.64 – 7.56 (m, 2H), 7.48 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.41 – 7.35 (m, 2H), 7.19 (t, *J* = 7.8 Hz, 1H), 4.04 (s, 3H), 2.77 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.2, 148.4, 138.7, 138.3, 136.3, 134.6, 130.6, 128.0, 127.4, 127.3, 124.4, 121.72, 121.70, 120.2, 119.7, 116.3, 113.6, 109.9, 31.6, 10.5.

GC MS (EI) *m*/*z* (relative intensity): 315 (M^+, 65), 271 (8), 172 (100), 143 (89).

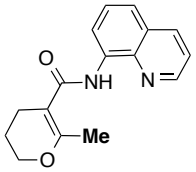
HRMS (APCI) Calcd for $C_{20}H_{18}N_3O^+$ [M+H]+ 316.1444, found, 316.1447.

2-Methyl-*N*-(quinolin-8-yl)cyclohex-1-ene-1-carboxamide **(27):** the reaction was performed using 1.0 mol% $Fe(acac)_3$, 1.1 mol% dppen, 2.0 equiv. $AlMe_3$, 0.5 mL THF, **27** was obtained in 81% yield as a yellow oil.



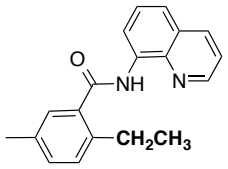
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (br, 1H), 8.86 (d, *J* = 7.8 Hz, 1H), 8.81 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 7.58 – 7.49 (m, 2H), 7.45 (dd, *J* = 8.0, 4.0 Hz, 1H), 2.44 (br, 2H), 2.12 (br, 2H), 1.95 (s, 3H), 1.72 – 1.69 (m, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 148.1, 138.6, 136.8, 136.3, 134.6, 129.7, 128.0, 127.4, 121.5, 121.3, 116.4, 31.9, 26.9, 22.4, 22.3, 21.3.
GC MS (EI) *m*/*z* (relative intensity): 266 (M^+, 20), 249 (5), 144 (100), 123 (46), 95 (52).

6-Methyl-*N*-(quinolin-8-yl)-3,4-dihydro-2*H*-pyran-5-carboxamide **(28):** the reaction was performed using 1.0 mol% $Fe(acac)_3$, 1.1 mol% dppen, 2.0 equiv. $AlMe_3$, 0.5 mL THF, **28** was obtained in 96% yield as a white solid. Melting point: 110–111 °C (CH_2Cl_2).



^{1}H NMR (400 MHz, $CDCl_3$) δ 10.03 (br, 1H), 8.85 – 8.78 (m, 2H), 8.15 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.54 (t, *J* = 7.9 Hz, 1H), 7.50 – 7.42 (m, 2H), 4.09 (t, *J* = 5.0 Hz, 2H), 2.57 (t, *J* = 5.2 Hz, 2H), 2.30 (s, 3H), 2.03 – 1.96 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 160.4, 148.0, 138.7, 136.3, 135.0, 128.0, 127.5, 121.5, 120.8, 116.0, 105.0, 66.1, 22.0, 21.8, 19.9.
GC MS (EI) *m*/*z* (relative intensity): 268 (M^+, 17), 251 (10), 144 (15), 125 (100).

2-Ethyl-5-methyl-*N*-(quinolin-8-yl)benzamide **(Scheme 2):** obtained in 82% yield as a yellow oil.



^{1}H NMR (400 MHz, $CDCl_3$) δ 10.15 (br, 1H), 8.95 (d, *J* = 7.4 Hz, 1H), 8.77 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.18 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.63 – 7.53 (m, 2H), 7.47 – 7.44 (m, 2H), 7.25 (s, 2H), 2.90 (q, *J* = 7.6 Hz, 2H), 2.40 (s, 3H), 1.28 (t, *J* = 7.6 Hz, 3H).

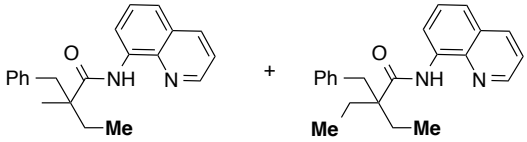
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 148.2, 139.6, 138.5, 136.4, 136.3, 135.6, 134.77, 131.06, 129.6, 128.0, 127.7, 127.4, 121.7, 121.6, 116.5, 26.1, 20.9, 16.1.

GC MS (EI) *m*/*z* (relative intensity): 290 (M^+, 56), 273 (16), 246 (16), 207 (31), 146 (100).

2-Benzyl-2-methyl-*N*-(quinolin-8-yl)butanamide and

2-benzyl-2-ethyl-*N*-(quinolin-8-yl)butanamide **(Scheme 3):** obtained in 84% yield and 11% yield as a yellow oil.

2-Benzyl-2-methyl-*N*-(quinolin-8-yl)butanamide



^{1}H NMR (400 MHz, $CDCl_3$) δ 10.16 (br, 1H), 8.87 (dd, *J* = 7.5, 1.3 Hz, 1H), 8.75 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.15 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.59 – 7.49 (m, 2H), 7.43 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.24 – 7.15 (m, 5H), 3.28 (d, *J* = 13.3 Hz, 1H), 2.84 (d, *J* = 13.3 Hz, 1H), 2.07 (dq, *J* = 14.7, 7.4 Hz, 1H), 1.60 (dq, *J* = 14.2, 7.4 Hz, 1H), 1.36 (s, 3H), 1.00 (t, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.2, 148.1, 138.7, 137.8, 136.2, 134.4, 130.2, 127.9, 127.8, 127.4, 126.2, 121.5, 121.3, 116.2, 48.9, 45.9, 32.8, 20.1, 9.1.

GC MS (EI) *m*/*z* (relative intensity): 318 (M^+, 28), 289 (15), 227 (15), 171 (100), 144 (57), 91 (46). (Ref. *J. Am. Chem. Soc.* **2014**, *136*, 898.)

2-Benzyl-2-ethyl-*N*-(quinolin-8-yl)butanamide: The compound data was in agreement with the literature (Ref. *Angew. Chem. Int. Ed.* **2014**, *53*, 3706)

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.16 (br, 1H), 8.87-8.85 (m, 1H), 8.75 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.15 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.59 – 7.49 (m, 2H), 7.43 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.20 – 7.09 (m, 5H), 3.08 (s, 2H), 1.89 (dq, *J* = 14.6 Hz, 7.5, 2H), 1.72 (dq, *J* =

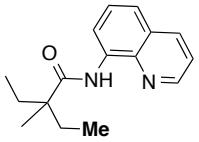
14.7, 7.4 Hz, 2H), 1.03 (t, J = 7.4 Hz, 6H).

GC MS (EI) m/z (relative intensity): 332 (M^+, 21), 303 (21), 241 (24), 171 (100), 144 (73), 91 (85).

2-Ethyl-2-methyl-*N*-(quinolin-8-yl)butanamide **(29)**

The reaction was performed using 10 mol% $Fe(acac)_3$, 11 mol% Ph-dppen, 2.0 equiv. $AlMe_3$ (2.0 M toluene solution), 400 mol% DCIB in 0.5 mL THF. The product was isolated by GPC (eluent = chloroform) and was obtained as a yellow oil. The compound data was in agreement with the literature. (Ref. *J. Am. Chem. Soc.*, **2014**, *136*, 1789)

Dimethyled product was detected by GC-MS in <5% yield.



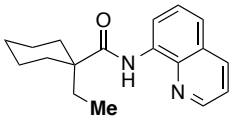
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.23 (br, 1H), 8.84-8.82 (m, 2H), 8.15 (dd, J = 8.3, 1.6 Hz, 1H), 7.55 – 7.43 (m, 3H), 1.95 – 1.84 (m, 2H), 1.69 – 1.60 (m, 2H), 1.36 (s, 3H), 0.94 (t, J = 7.4 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.0, 148.2, 138.7, 136.2, 134.6, 127.9, 127.4, 121.5, 121.1, 116.1, 47.9, 32.5, 20.1, 9.0.

GC MS (EI) m/z (relative intensity): 256 (M^+, 12), 171 (100), 144 (51), 116 (19).

1-Ethyl-*N*-(quinolin-8-yl)cyclohexane-1-carboxamide **(30)**

The reaction was performed using 10 mol% $Fe(acac)_3$, 11 mol% Ph-dppen, 2.0 equiv. $AlMe_3$ (2.0 M toluene solution), 400 mol% DCIB in 0.5 mL THF. The product was isolated by GPC (eluent = toluene) and was obtained as a yellow oil. The compound data was in agreement with the literature. (Ref. *Angew. Chem. Int. Ed.* **2014**, *53*, 3706; the literature data misses one carbon signal)



^{1}H NMR (400 MHz, $CDCl_3$) δ 10.27 (br, 1H), 8.86-8.80 (m, 2H), 8.13 (dd, J = 8.3, 1.6 Hz, 1H), 7.55 – 7.41 (m, 3H), 2.26 – 2.20 (m, 2H), 1.74 – 1.45 (m, 9H), 1.38– 1.36 (m, 1H), 0.90 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.3, 148.2, 138.7, 136.2, 134.6, 127.9, 127.4, 121.4,

121.0, 116.0, 48.2, 34.0, 33.5, 26.1, 23.0, 8.5.

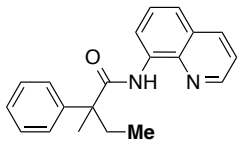
GC MS (EI) *m*/*z* (relative intensity): 282 (M^+, 14), 171 (100), 144 (80), 116 (24).

2-Methyl-2-phenyl-*N*-(quinolin-8-yl)butanamide **(31)**

The reaction was performed using 10 mol% $Fe(acac)_3$, 11 mol% Ph-dppen, 2.0 equiv. $AlMe_3$ (2.0 M toluene solution), 400 mol% DCIB in 0.5 mL THF. The product was isolated by GPC (toluene) and was obtained as a yellow solid. Melting point: 77–78 °C (CH_2Cl_2). The compound data was in agreement with the literature. (Ref. *J. Am. Chem. Soc.*, **2014**, *136*, 1789).

Dimethyled product was detected by GC-MS in <5% yield.

The methylation of the phenyl group was not detected.

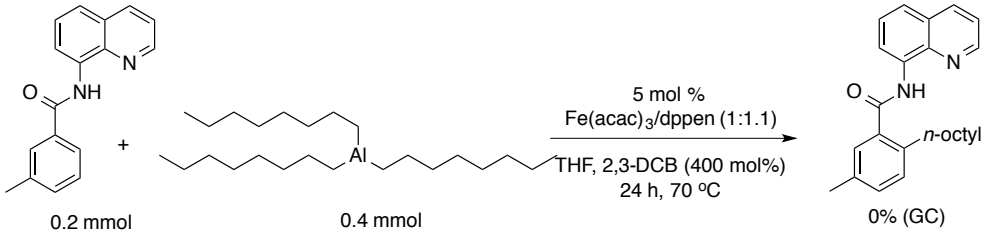


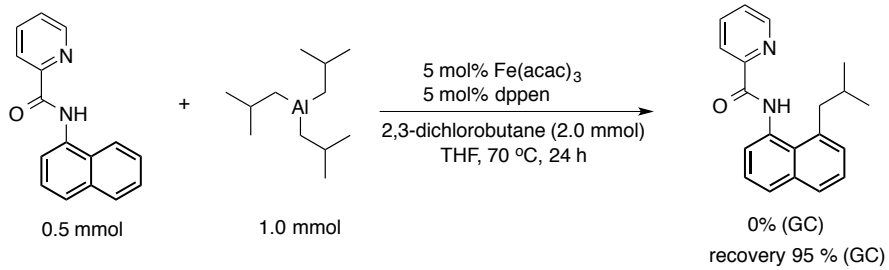
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (br, 1H), 8.77 (d, *J* = 7.6 Hz, 1H), 8.60 (d, *J* = 3.2, 1H), 8.07 (d, *J* = 8.3 1H), 7.52 – 7.49 (m, 3H), 7.46-7.33 (m, 4H), 7.31 – 7.26 (m, 1H), 2.31 – 2.17 (m, 2H), 1.76 (s, 3H), 0.91 (t, *J* = 7.3 Hz, 3H).

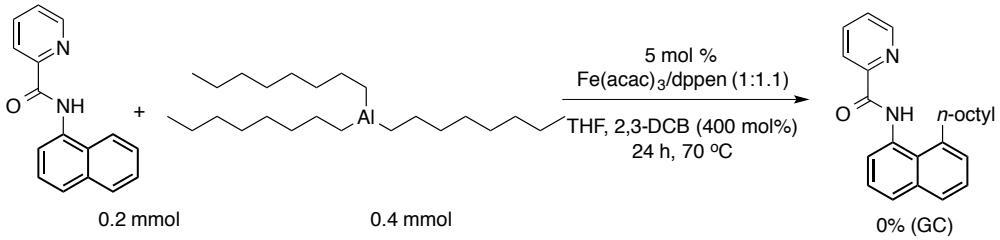
^{13}C NMR (101 MHz, $CDCl_3$) δ 175.4, 148.1, 143.8, 138.6, 136.0, 134.6, 128.7, 127.9, 127.3, 126.8, 121.4, 121.1, 115.9, 52.2, 31.6, 22.9, 9.0.

GC MS (EI) *m*/*z* (relative intensity): 304 (M^+, 8), 171 (100), 144 (13), 116 (17), 91 (51).

Unsuccessful substrates:





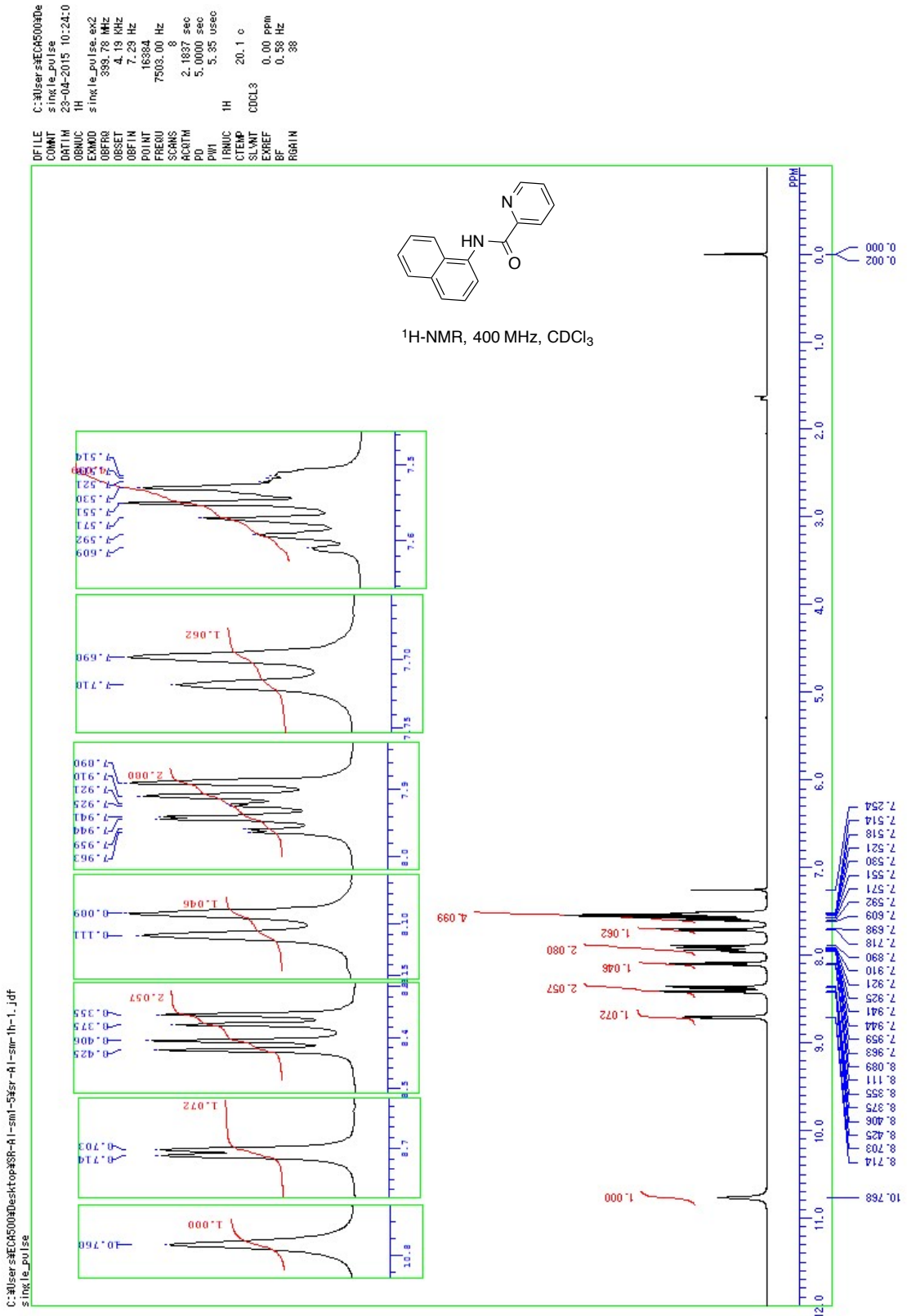


6. Iron-Catalyzed Methylation of C-H Bonds with bis(trimethylaluminum) -1,4-diazabicyclo-[2.2.2.]octane adduct

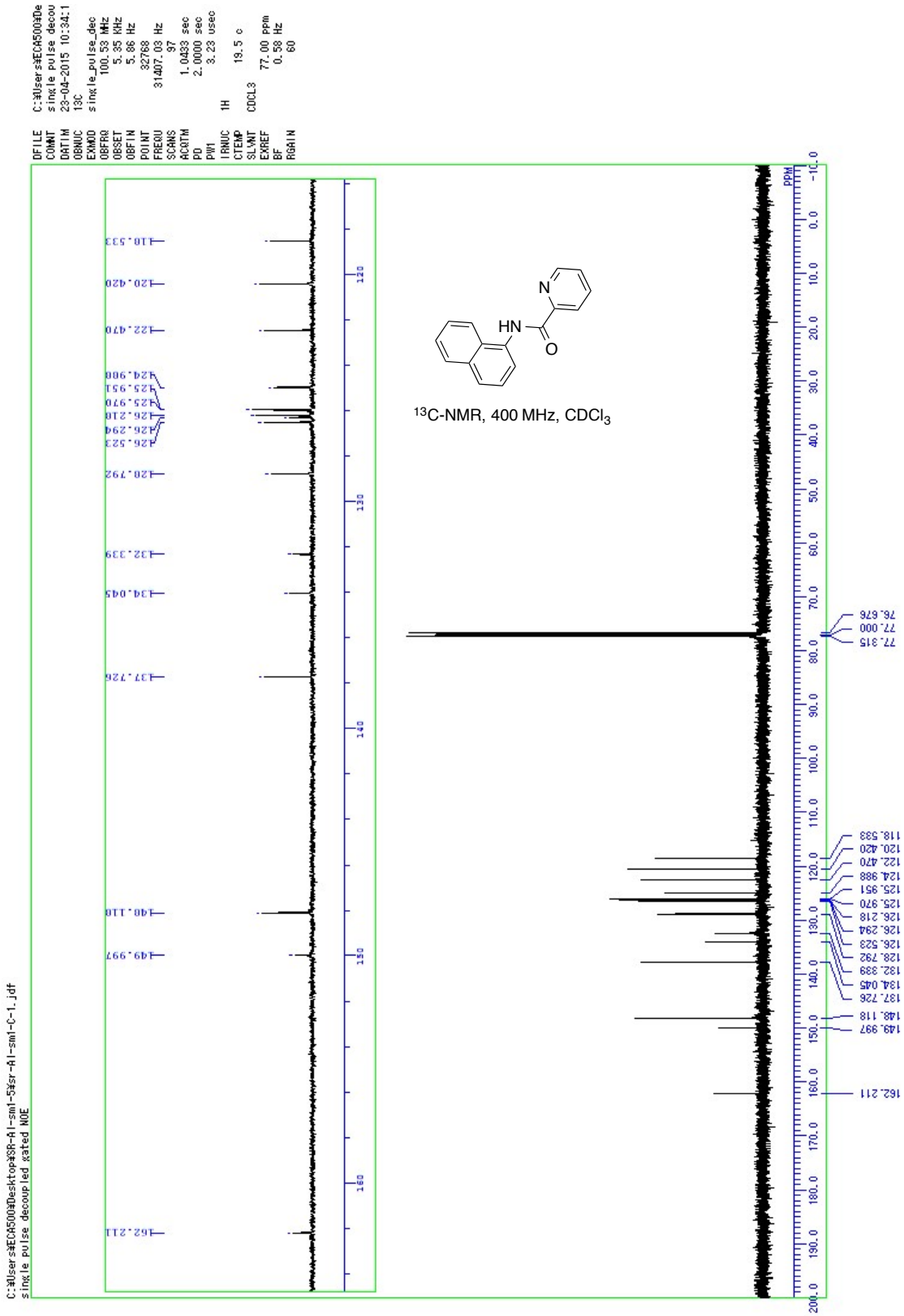
Under a nitrogen atmosphere, $Fe(acac)_3$ (5.0 mol%), (*Z*)-1,2-bis (diphenylphosphino)ethene (dppen) (5.5 mol%), *N*-(naphthalen-1-yl)picolinamide (**1**) (124 mg, 0.50 mmol) and bis(trimethylaluminum)-1,4-diazabicyclo-[2.2.2.]octane adduct (128 mg, 0.50 mmol) were placed in an oven dried Schlenck tube. The tube was evacuated and filled with nitrogen for three times. THF (1.0 mL) was added to dissolve the solids. After stirring for 10 min at room temperature, 2,3-dichlorobutane (2,3-DCB) (4.0 equiv, 230 μL) was added via a microsyringe, and the mixture was heated at 70 ^{o}C for 24 h. After cooling to r.t., the mixture was diluted with diethyl ether, and methanol (200 μL) was slowly added via a microsyringe to quench the aluminium reagent. Saturated aqueous solution of Rochelle's salt was added (1.0 mL), and the organic layer was extracted with diethyl ether (5.0 mL x 3). The combined organic layers were passed through a pad of Florisil and concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica gel to afford the methylated product.

8. NMR Spectra

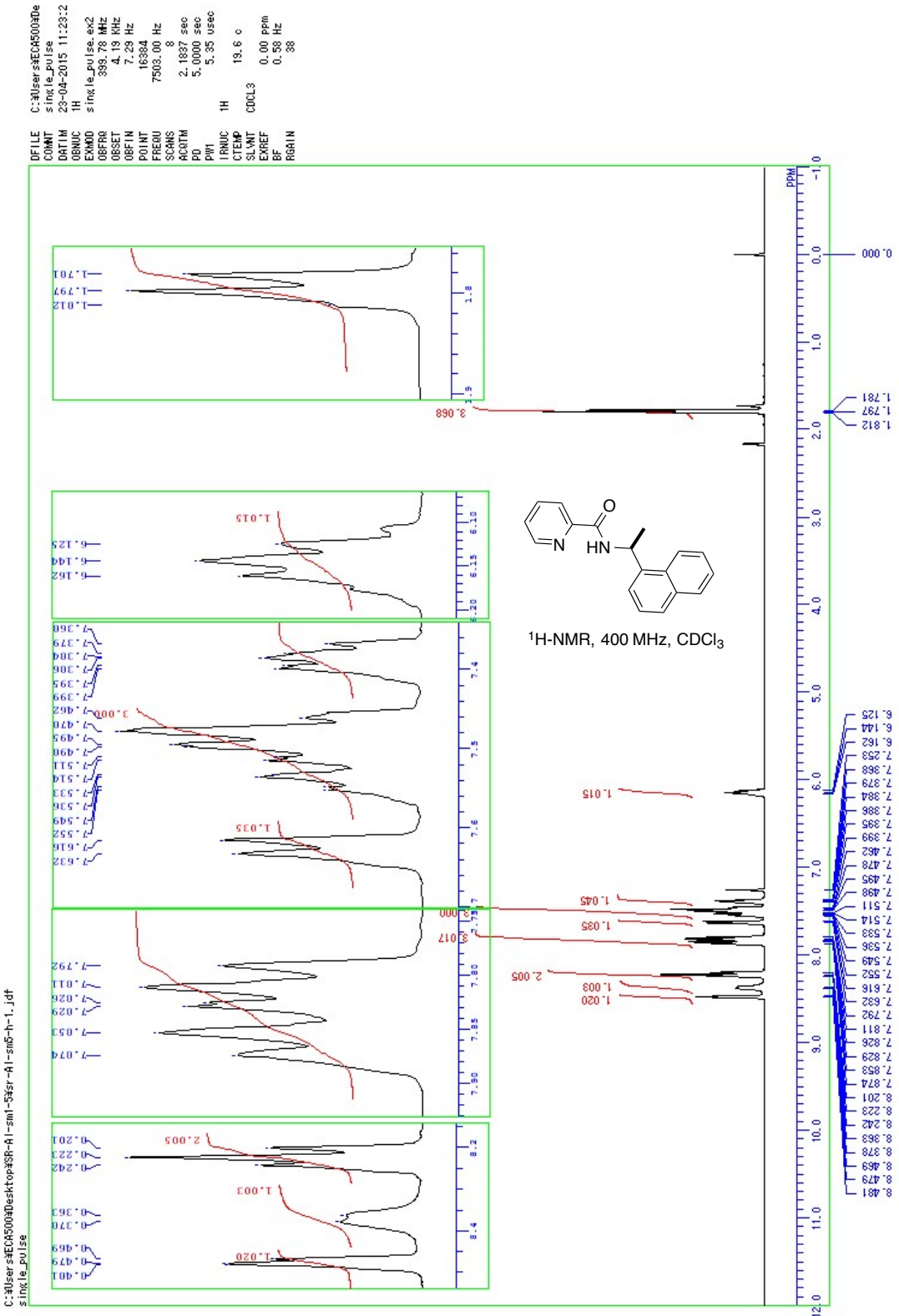
^{1}H NMR spectrum of ***N*-(naphthalen-1-yl)picolinamide (sm1)**



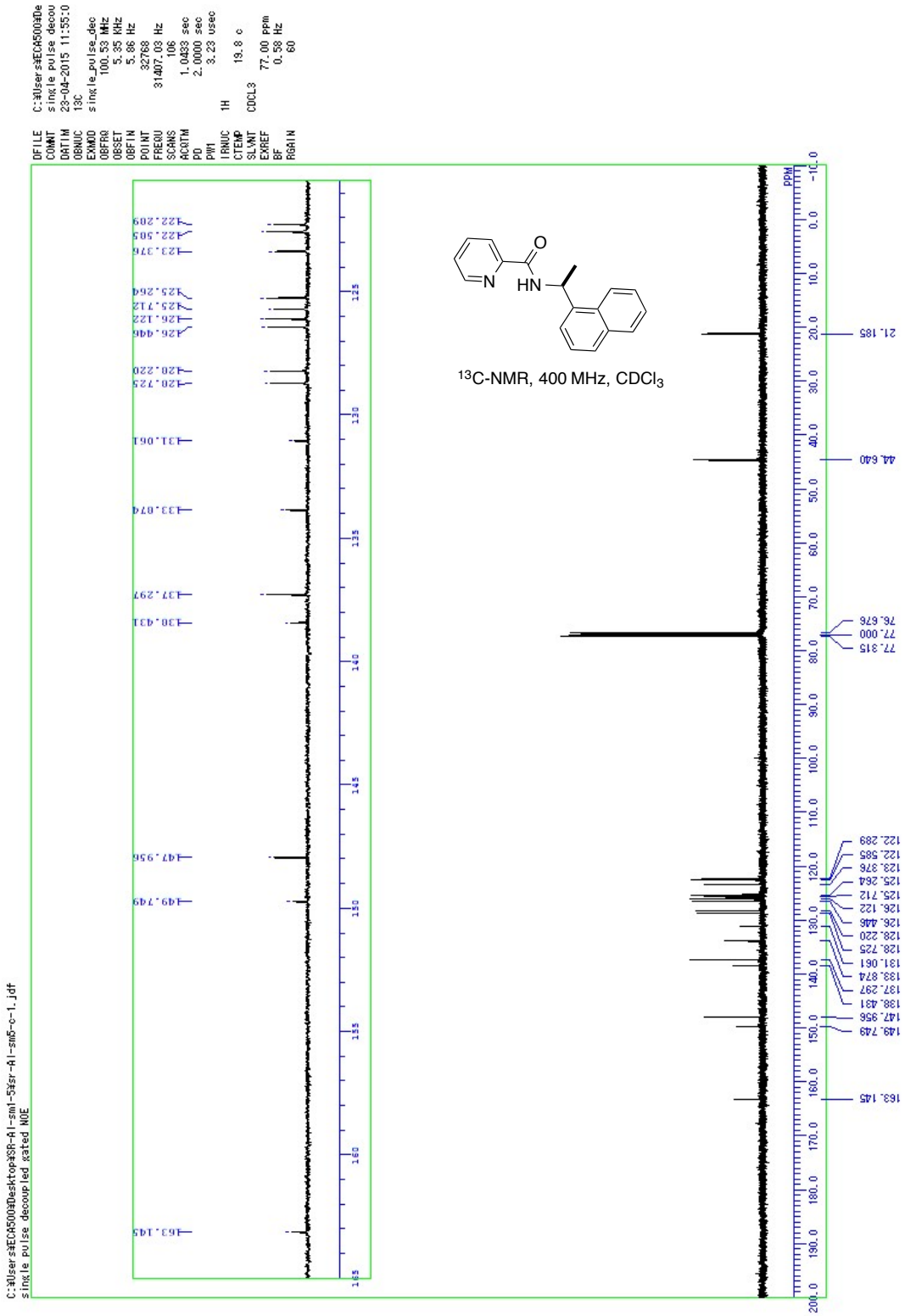
^{13}C NMR spectrum of spectrum of ***N*-(naphthalen-1-yl)picolinamide (sm1)**



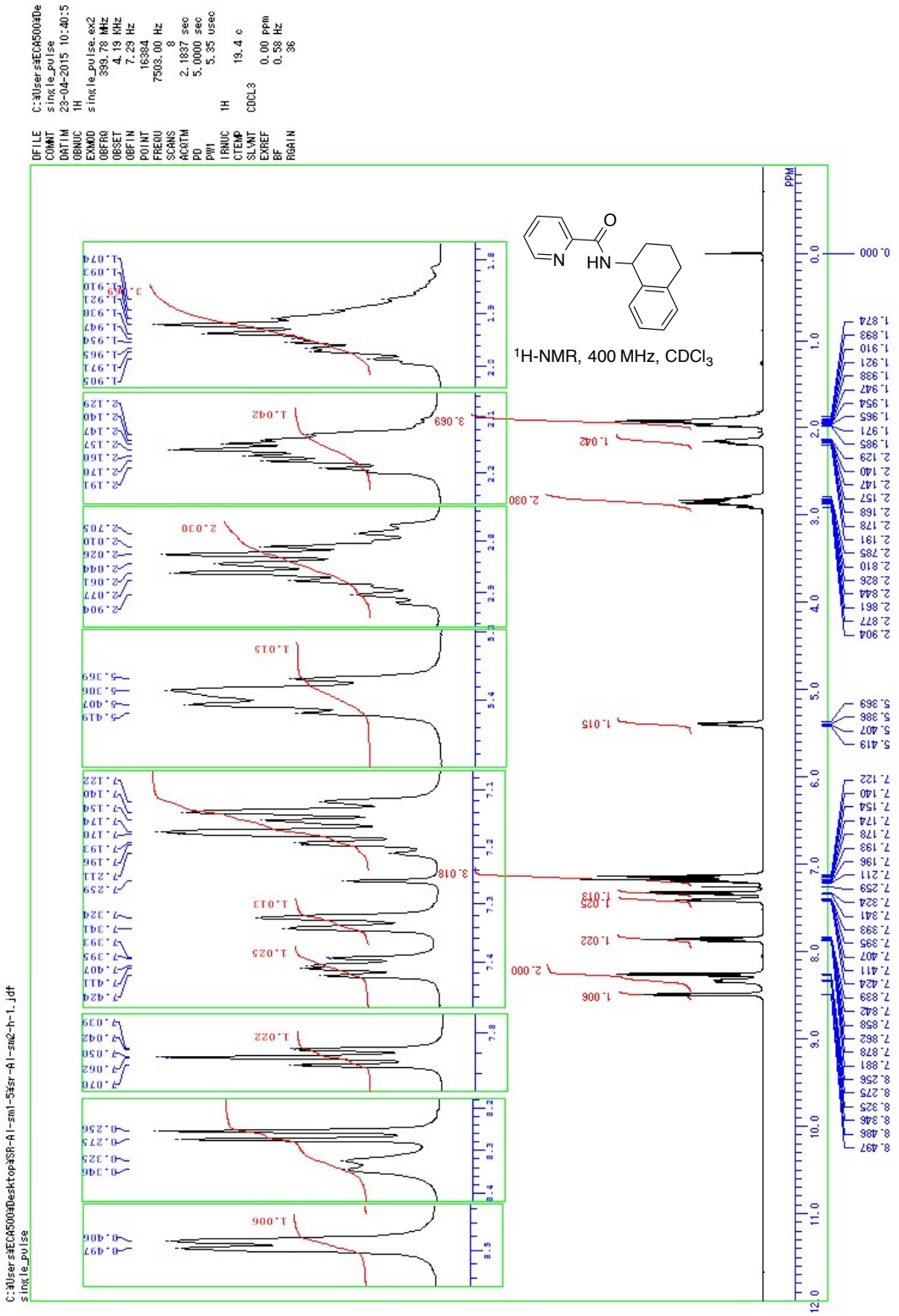
^{1}H NMR spectrum of **(*S*)-*N*-(1-(naphthalen-1-yl)ethyl)picolinamide (sm5)**



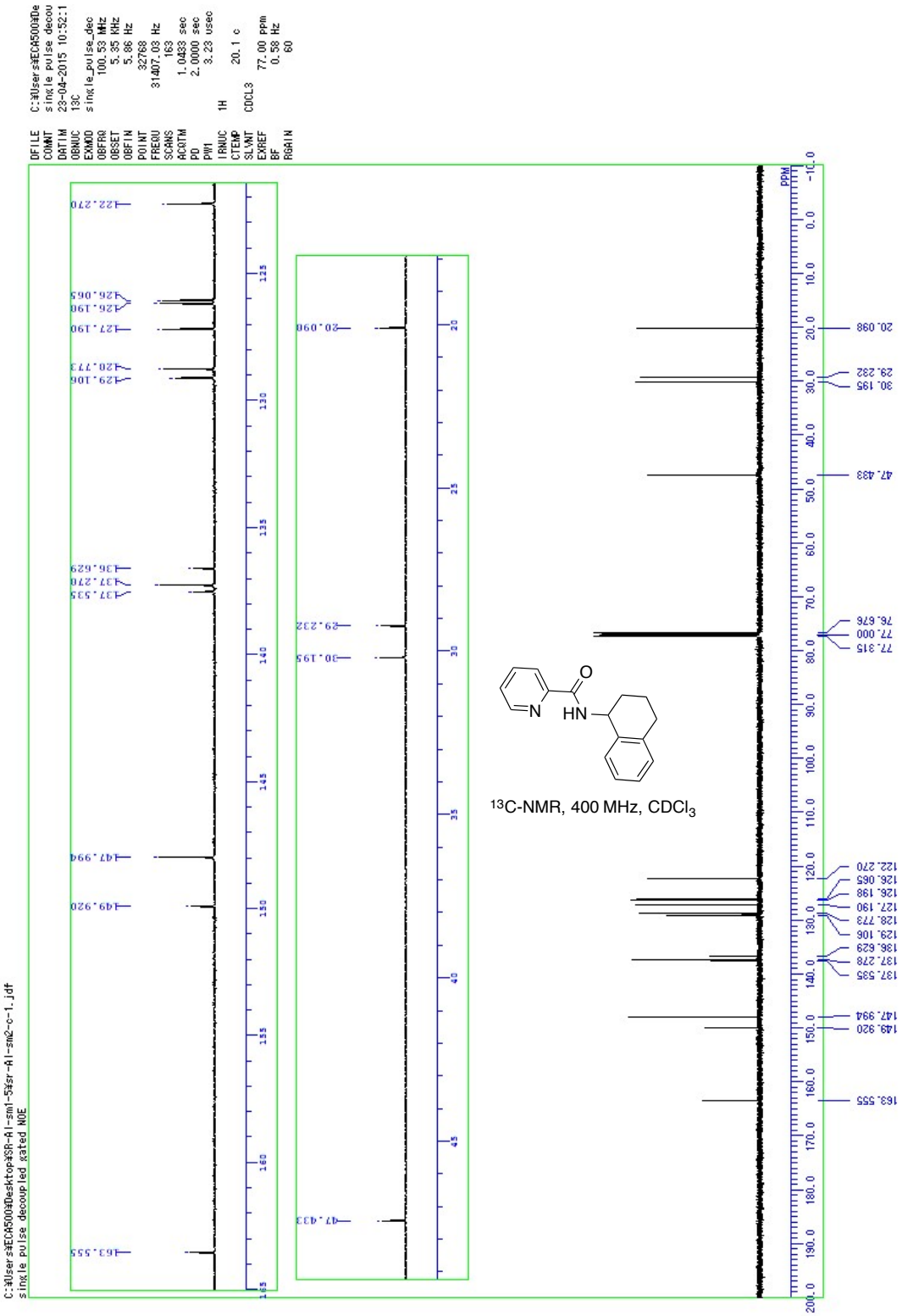
^{13}C NMR spectrum of **(*S*)-*N*-(1-(naphthalen-1-yl)ethyl)picolinamide (sm5)**



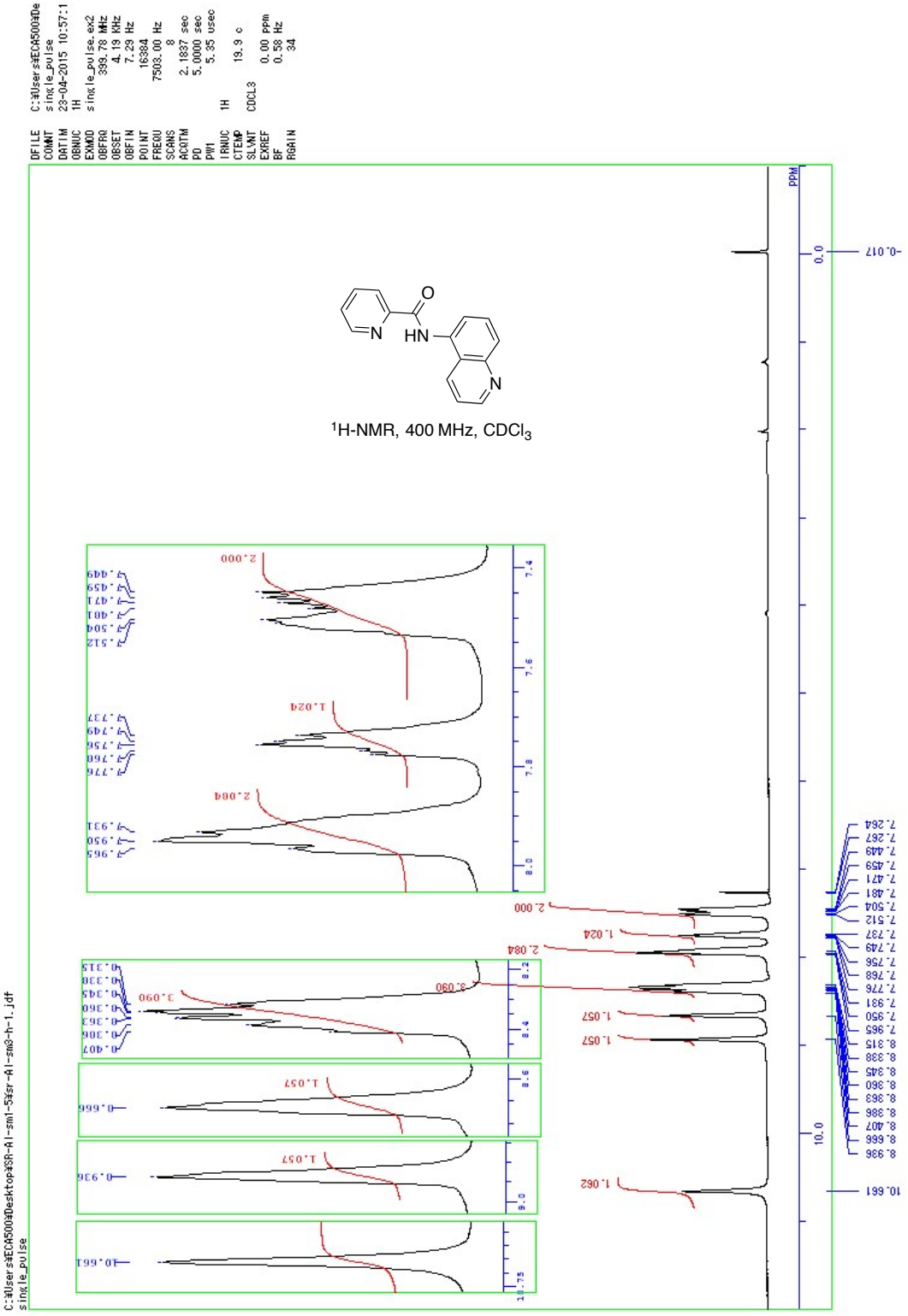
^{1}H NMR spectrum of ***N*-(1,2,3,4-tetrahydronaphthalen-1-yl)picolinamide (sm6)**



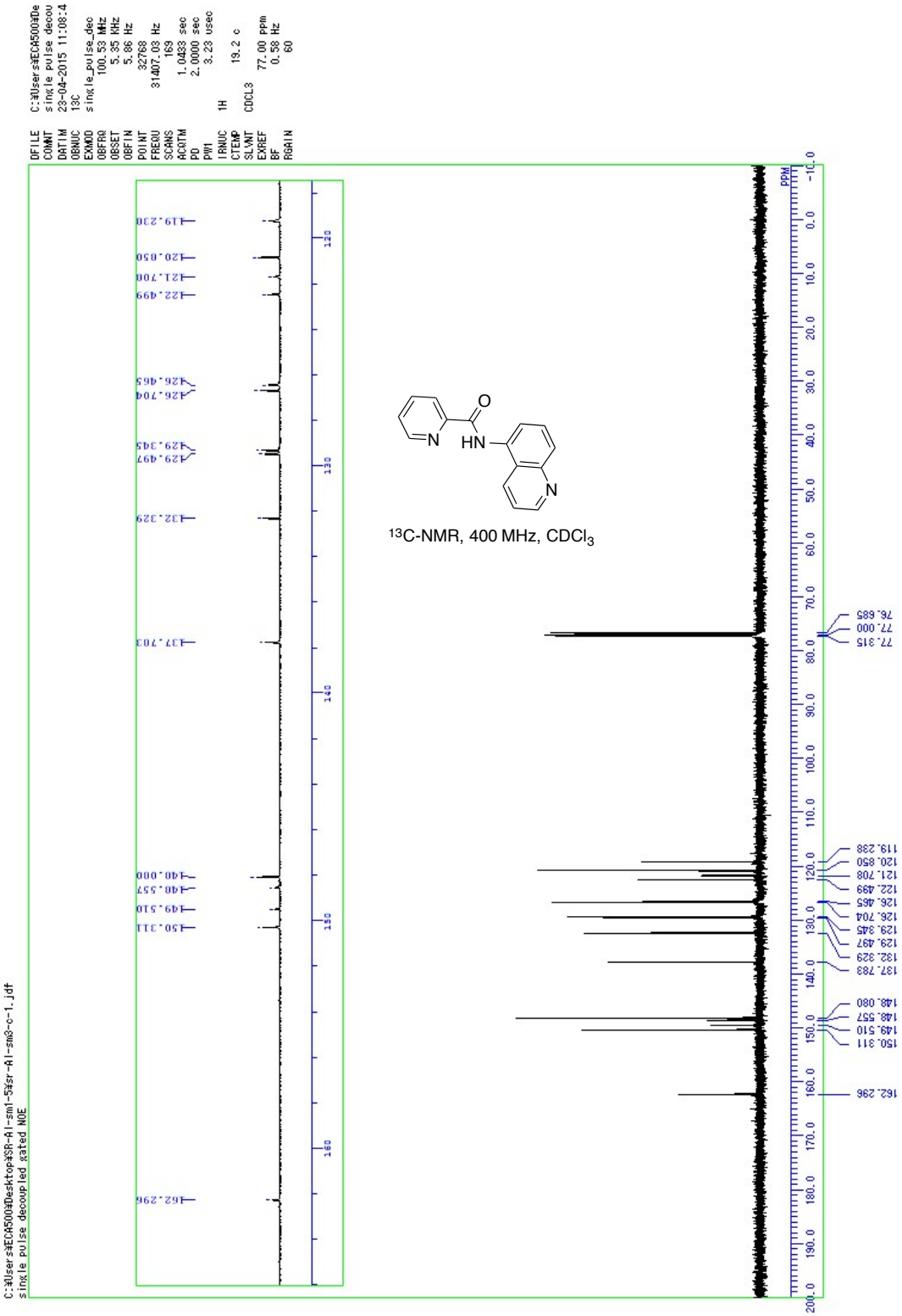
^{13}C NMR spectrum of ***N*-(1,2,3,4-tetrahydronaphthalen-1-yl)picolinamide (sm6)**



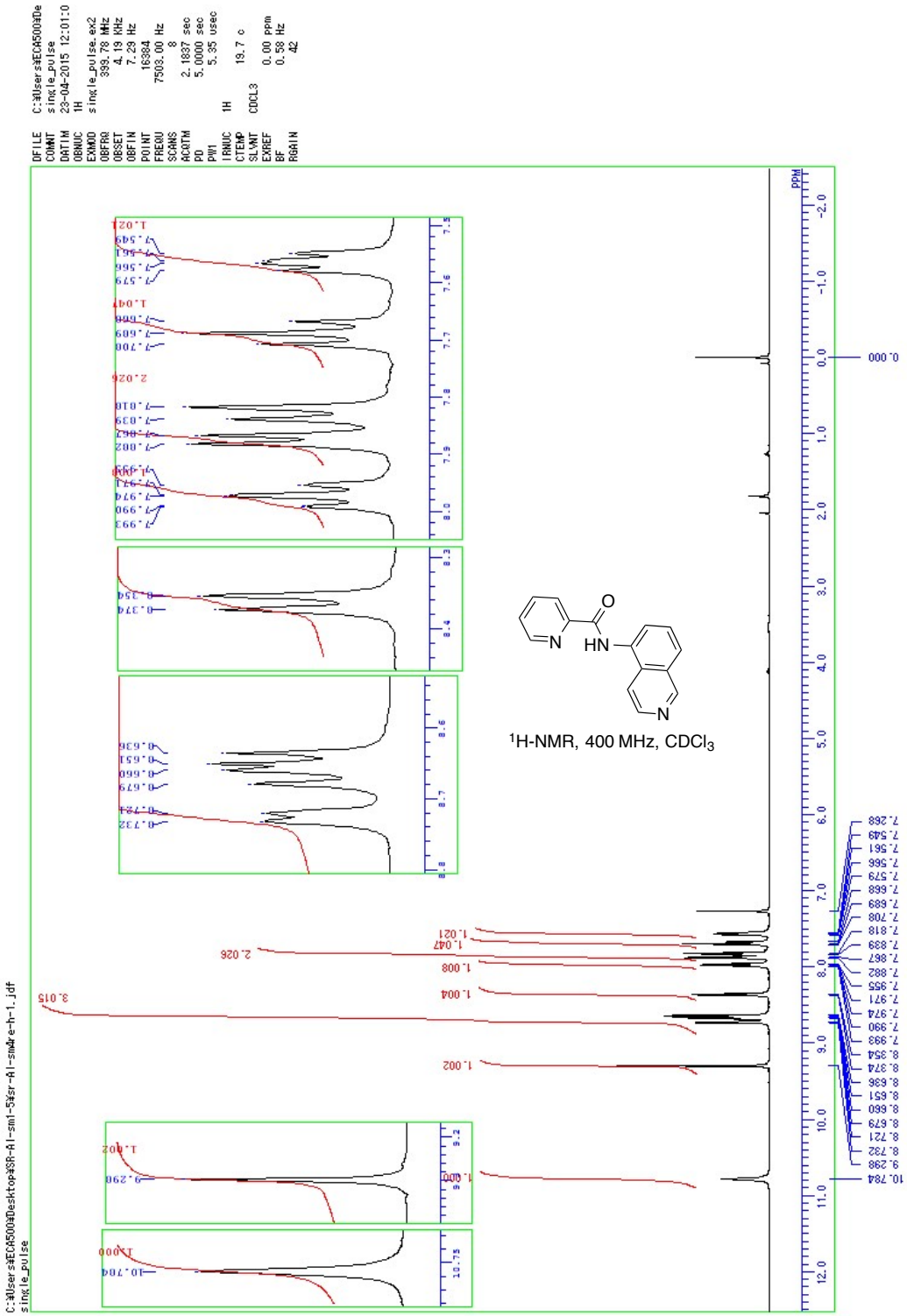
^{1}H NMR spectrum of ***N*-(quinolin-5-yl)picolinamide (sm7)**



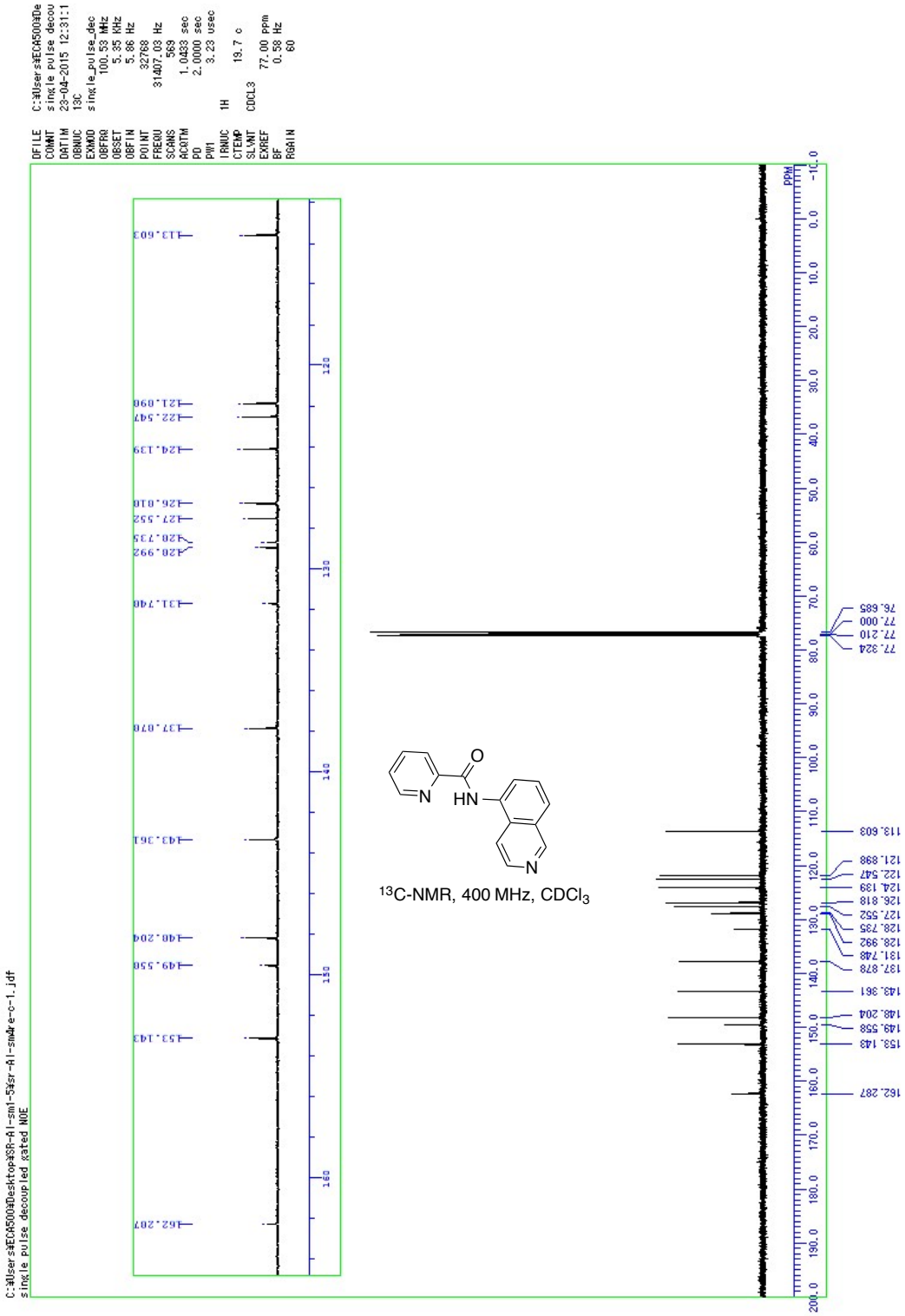
^{13}C NMR spectrum of ***N*-(quinolin-5-yl)picolinamide (sm7)**



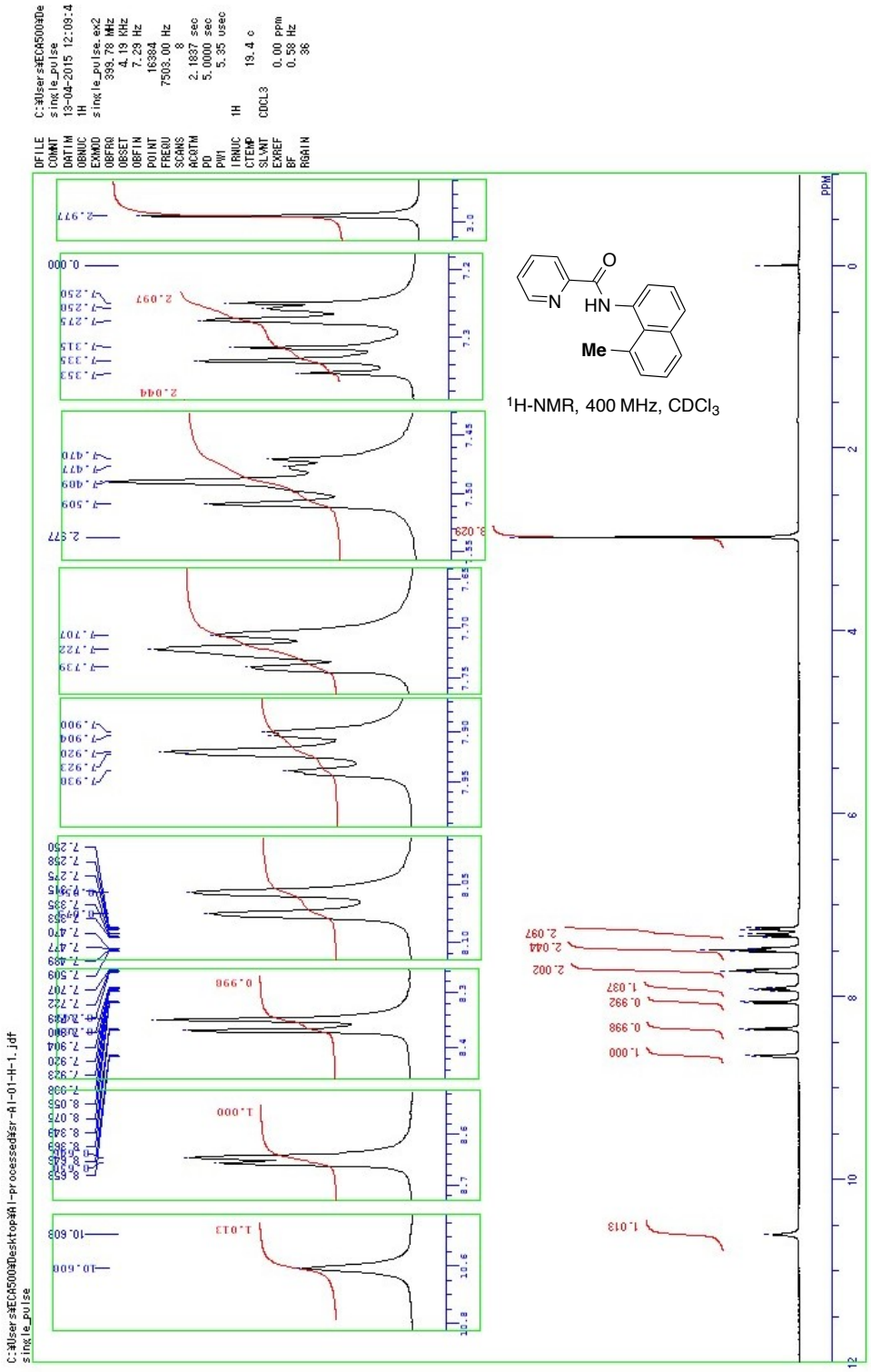
^{1}H NMR spectrum of ***N*-(isoquinolin-5-yl)picolinamide (sm8)**



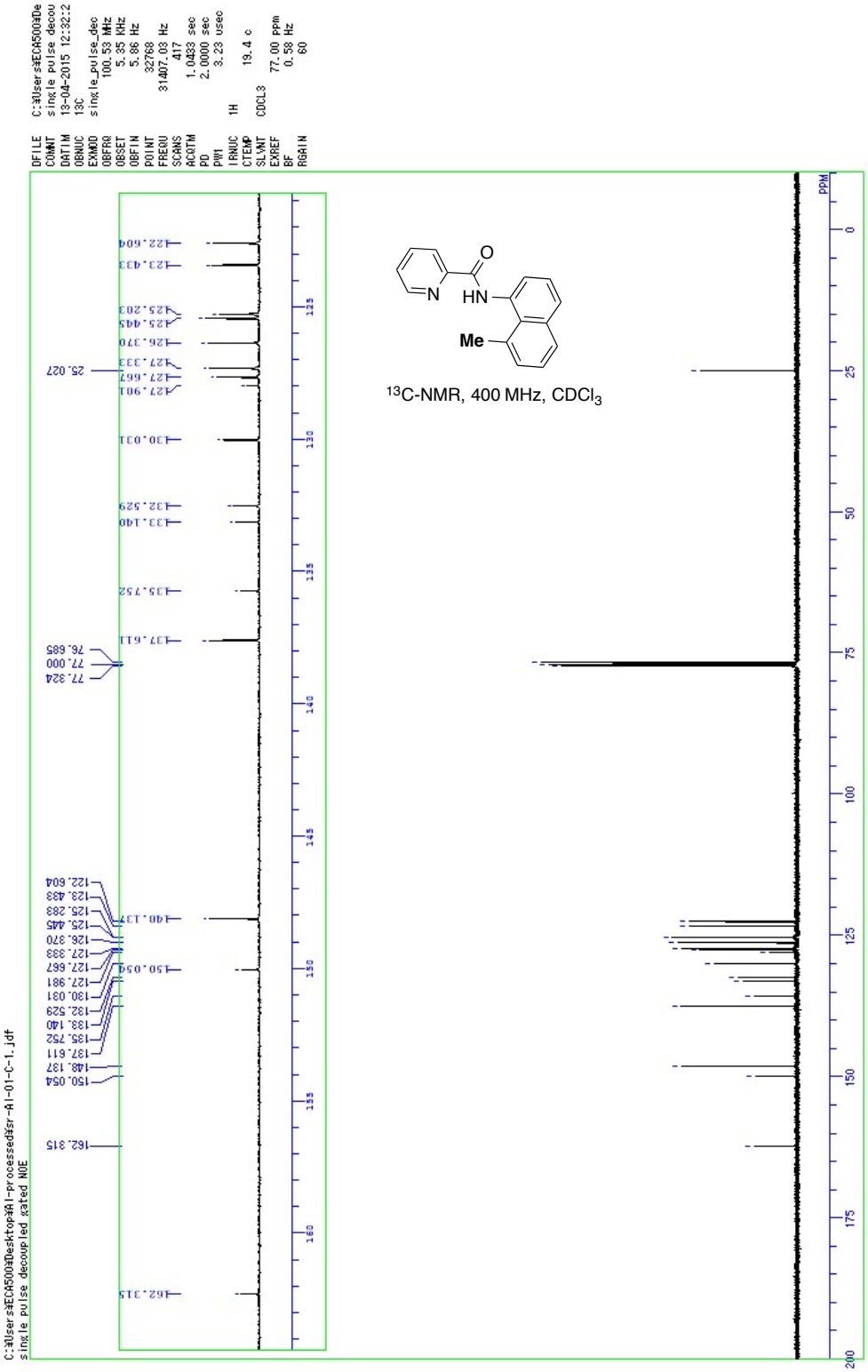
^{13}C NMR spectrum of ***N*-(isoquinolin-5-yl)picolinamide (sm8)**



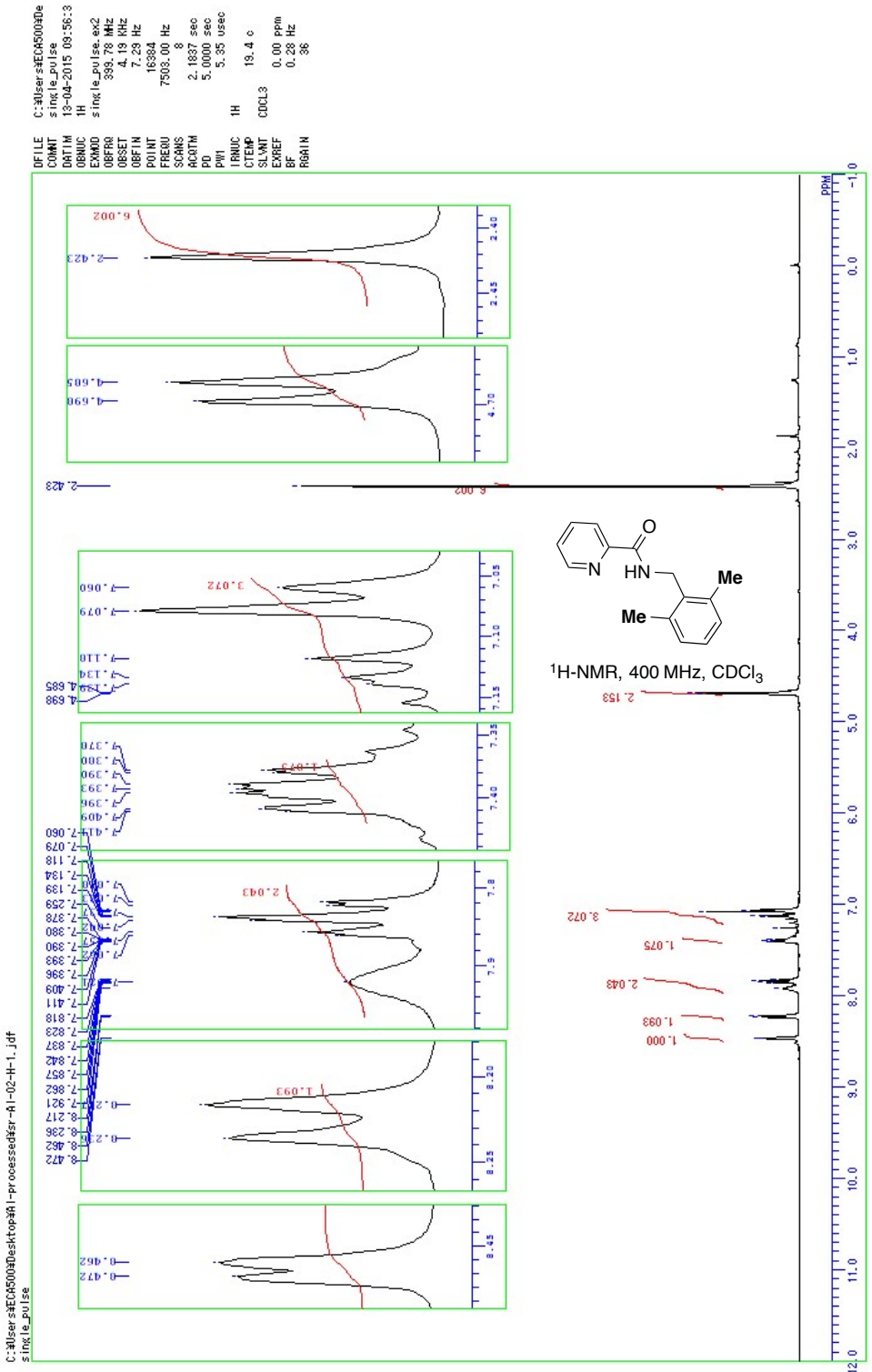
^{1}H NMR spectrum of ***N*-(8-methylnaphthalen-1-yl)picolinamide (2)**



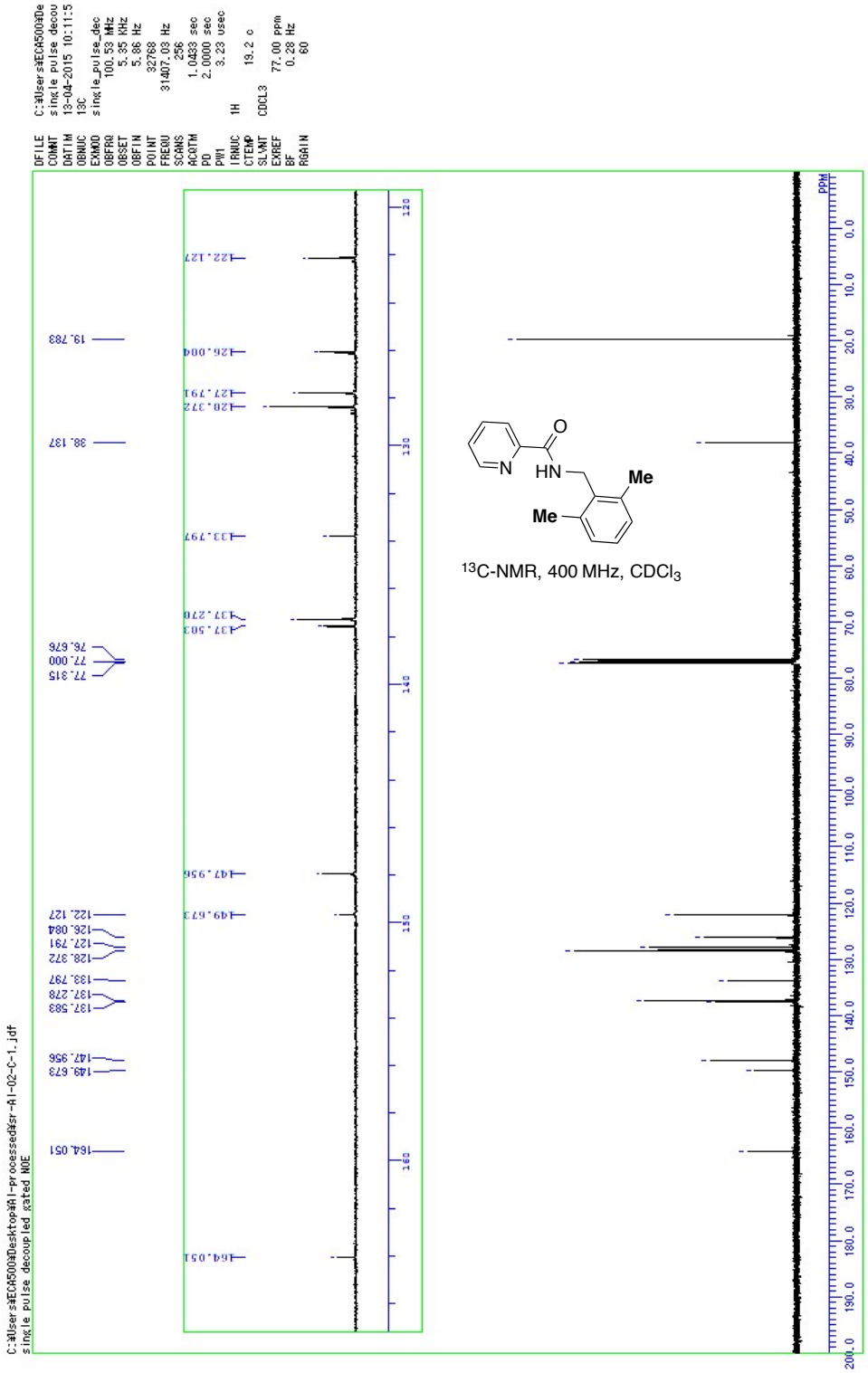
^{13}C NMR spectrum of ***N*-(8-methylnaphthalen-1-yl)picolinamide (2)**



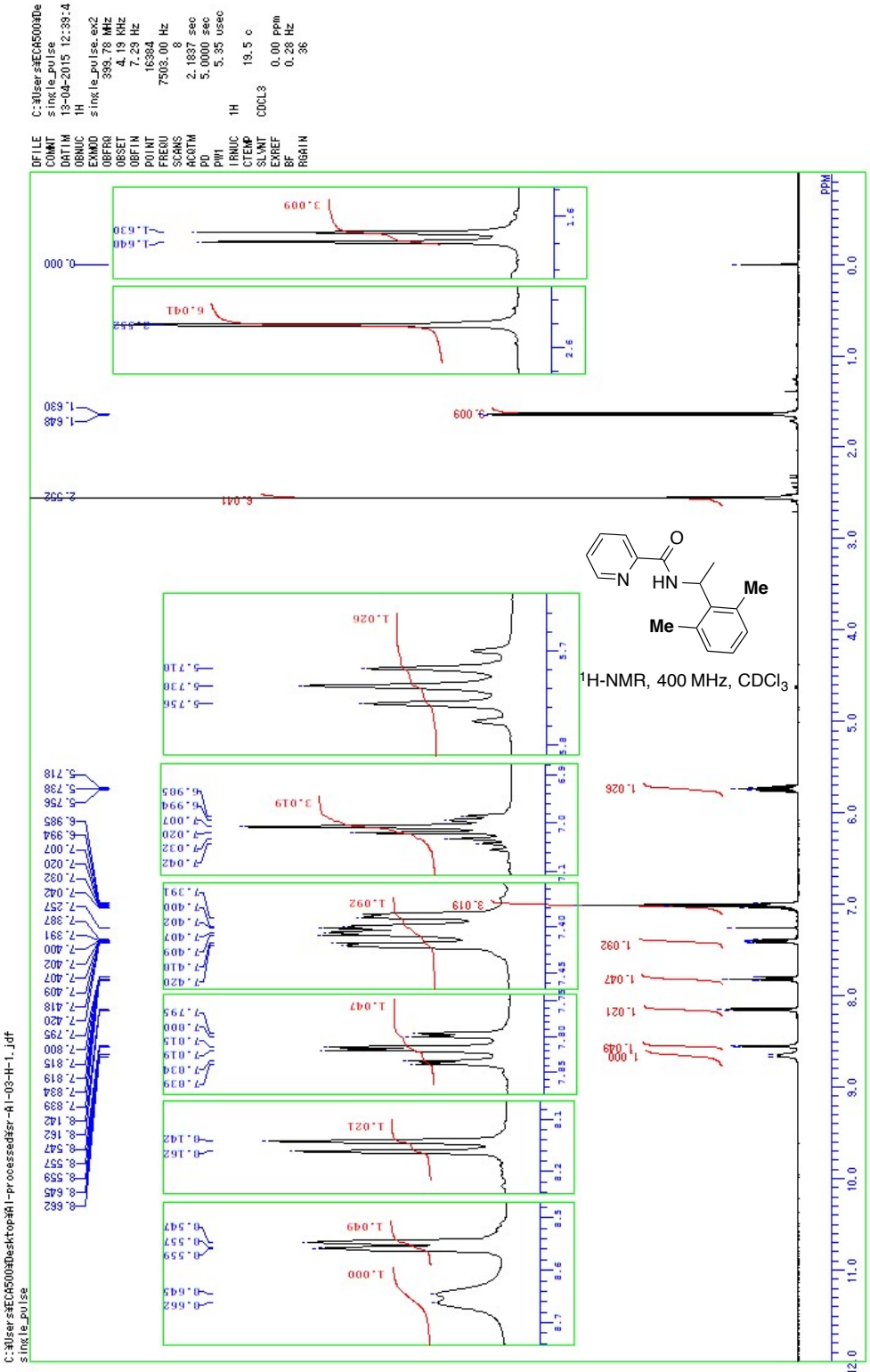
[1]H NMR spectrum of ***N*-(2,6-dimethylbenzyl)picolinamide (5)**



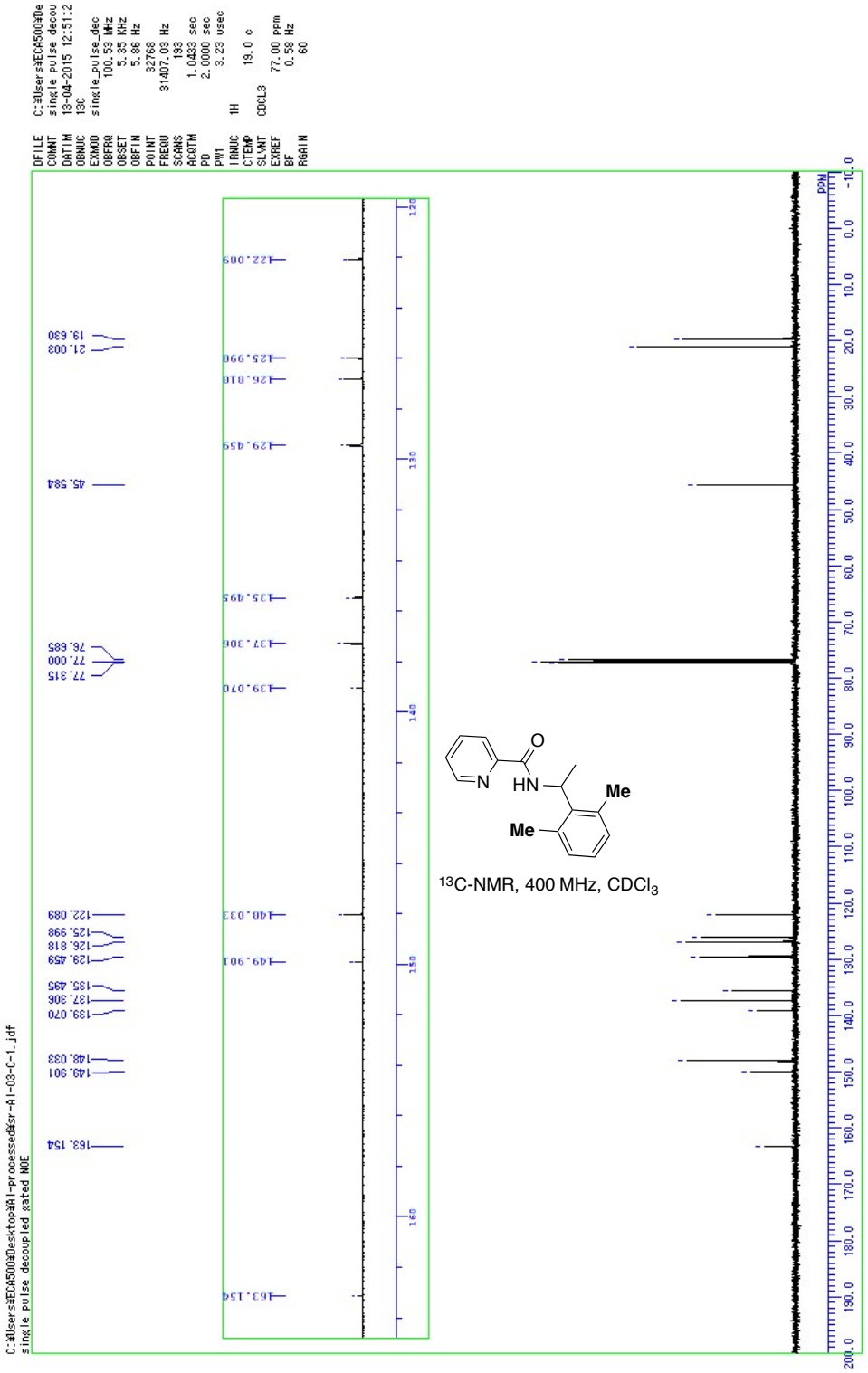
^{13}C NMR spectrum of ***N*-(2,6-dimethylbenzyl)picolinamide (5)**



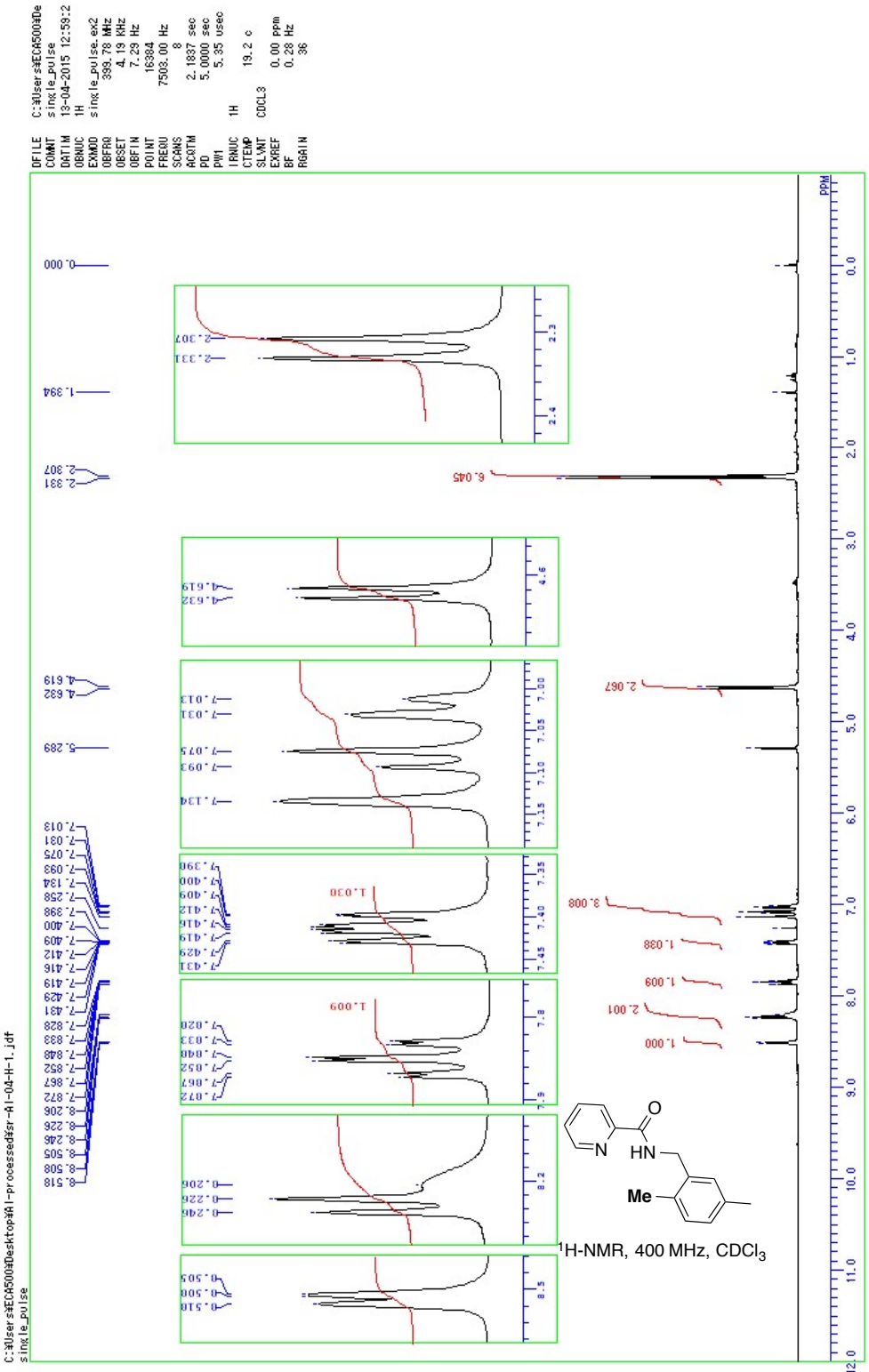
^{1}H NMR spectrum of ***N*-(1-(2,6-dimethylphenyl)ethyl)picolinamide (6)**



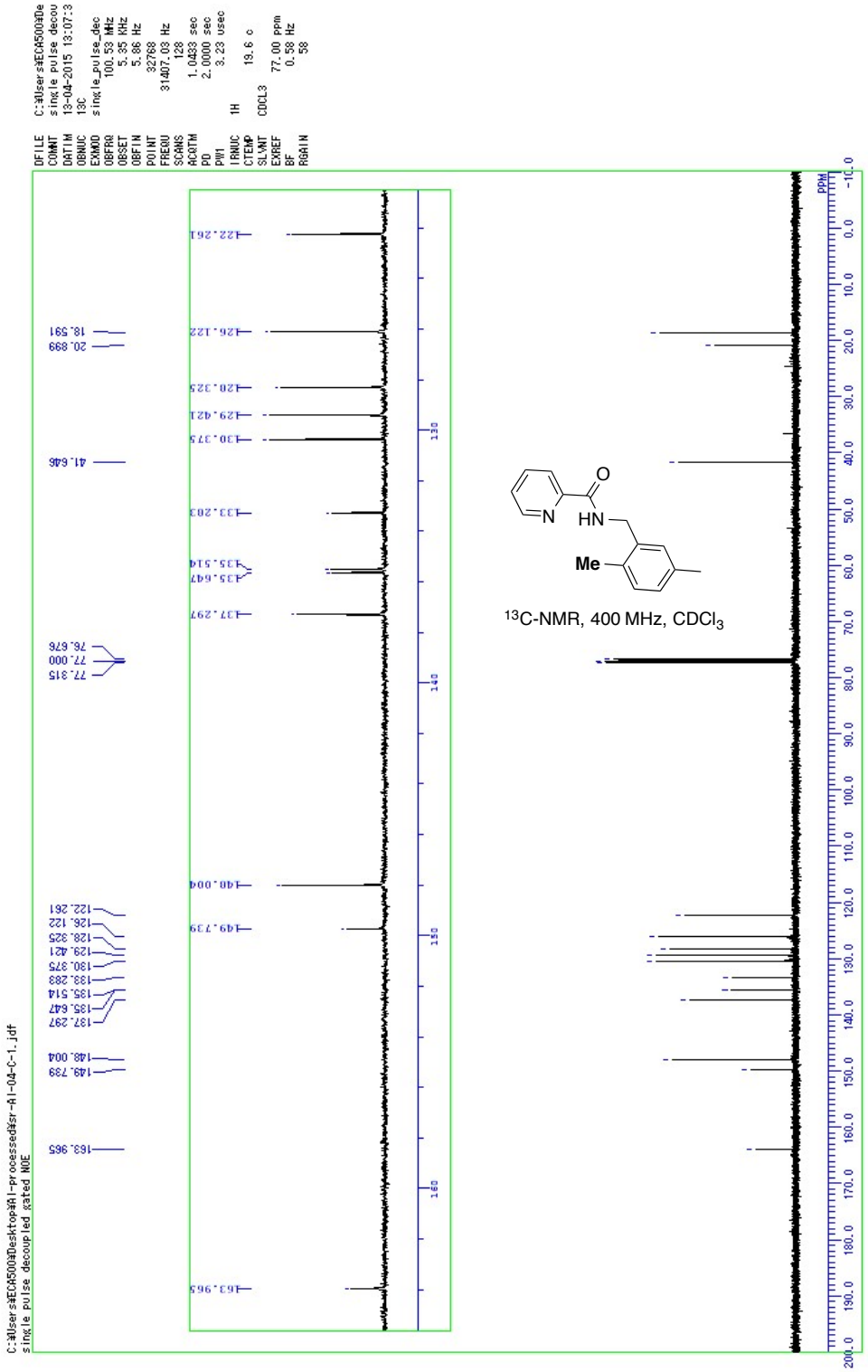
^{13}C NMR spectrum of ***N*-(1-(2,6-dimethylphenyl)ethyl)picolinamide (6)**



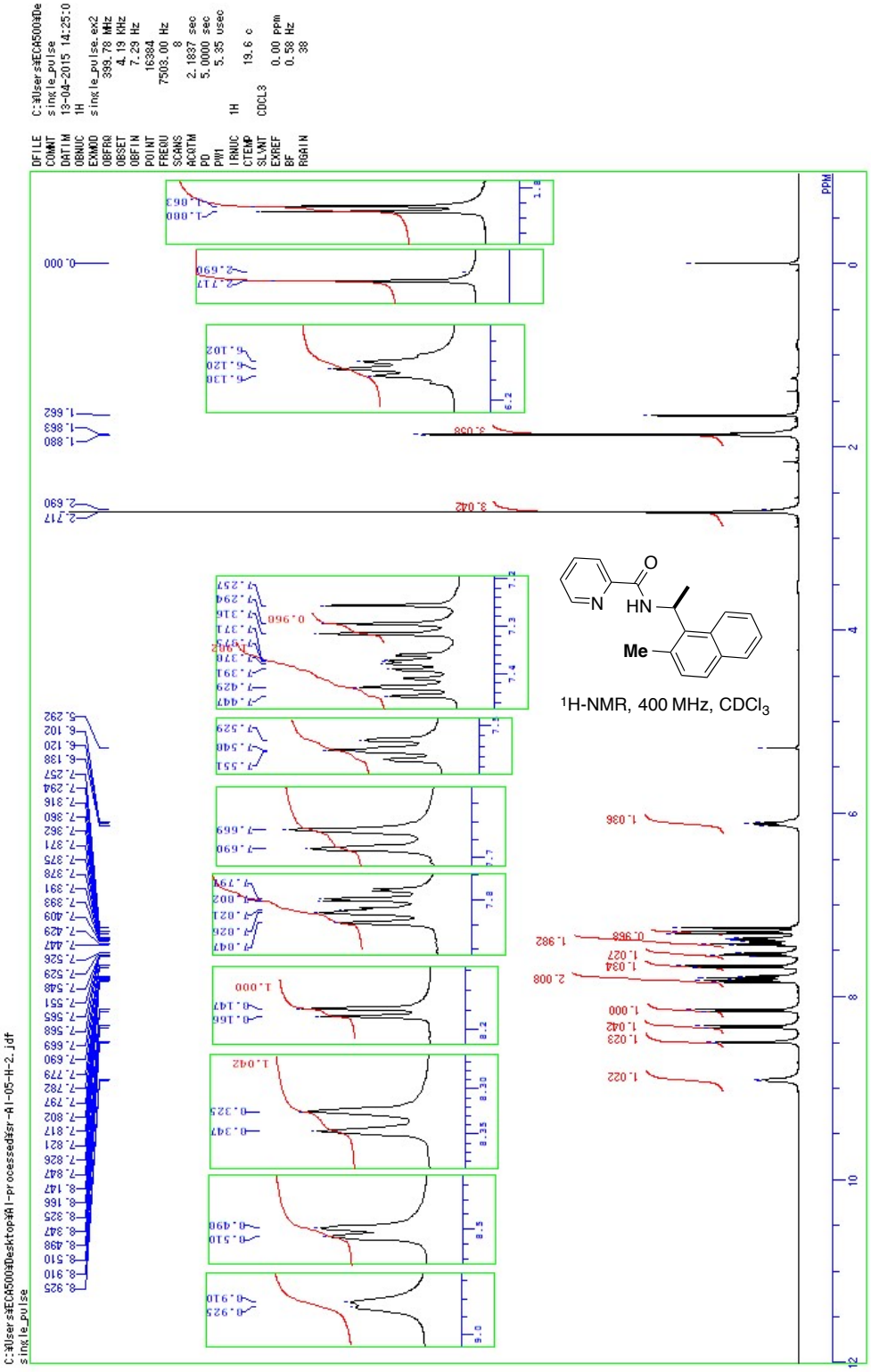
^{1}H NMR spectrum of ***N*-(2,5-dimethylbenzyl)picolinamide (7)**



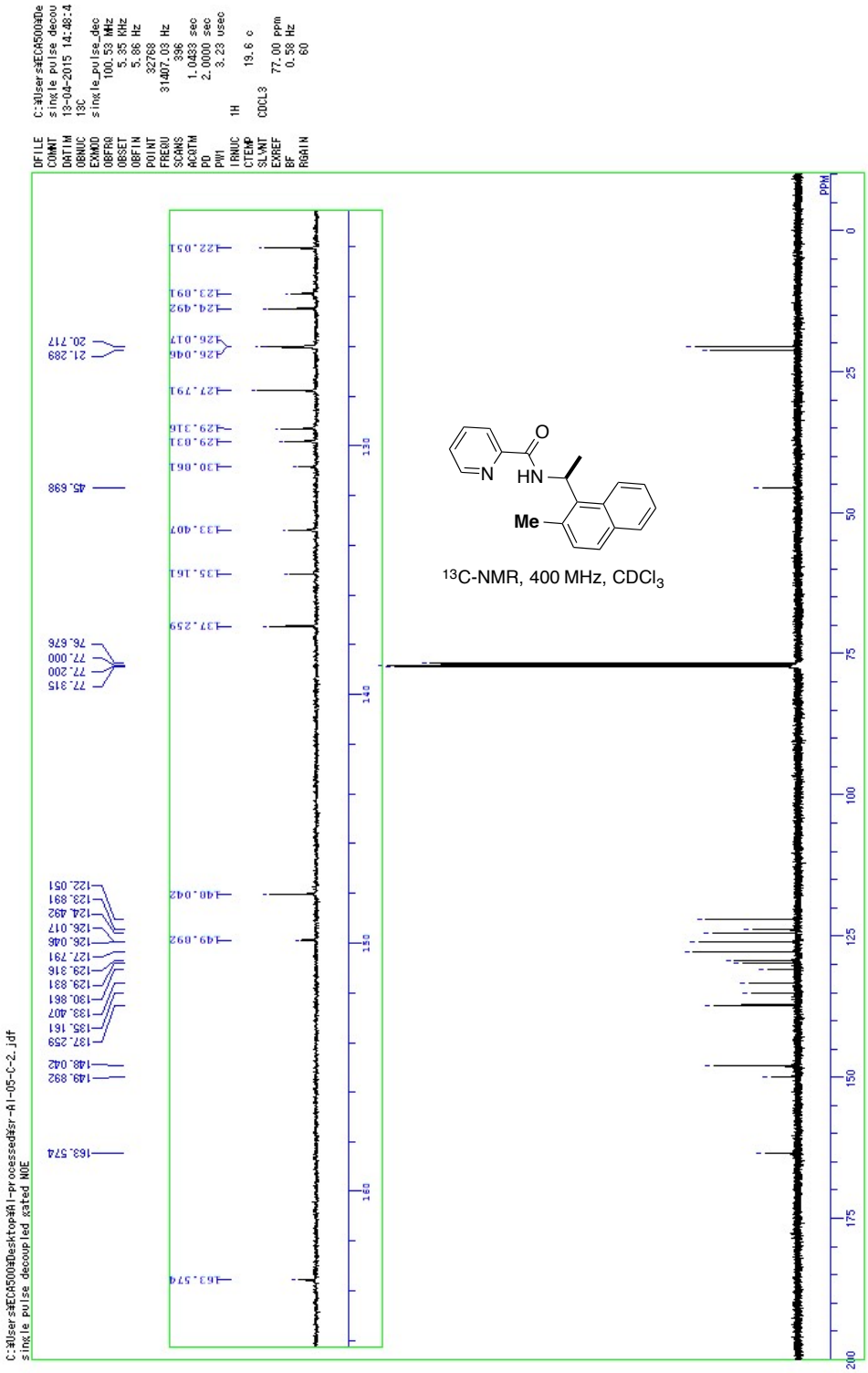
^{13}C NMR spectrum of ***N*-(2,5-dimethylbenzyl)picolinamide (7)**



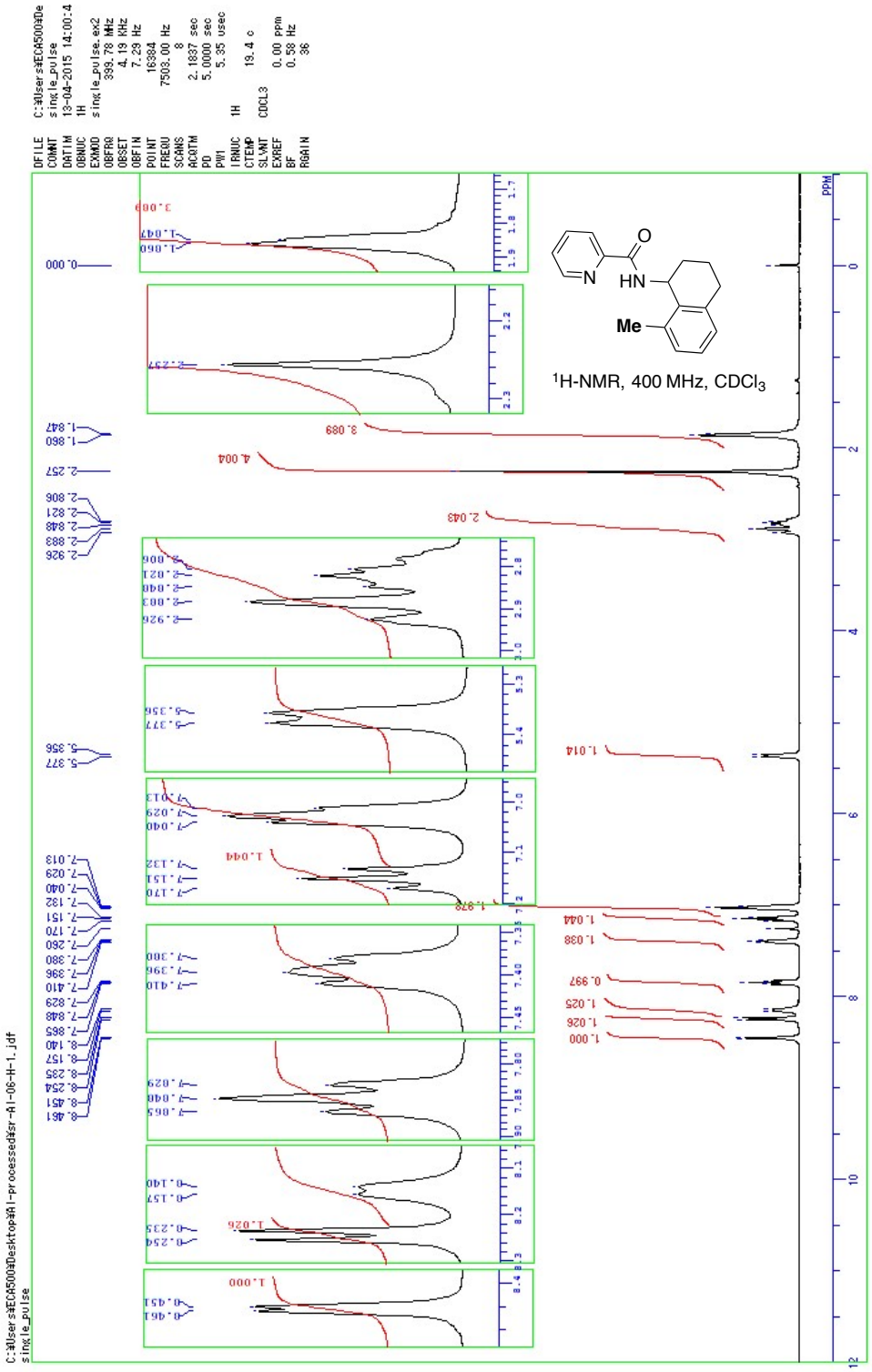
^{1}H NMR spectrum of **(*S*)-*N*-(1-(2-methylnaphthalen-1-yl)ethyl)picolinamide (8)**



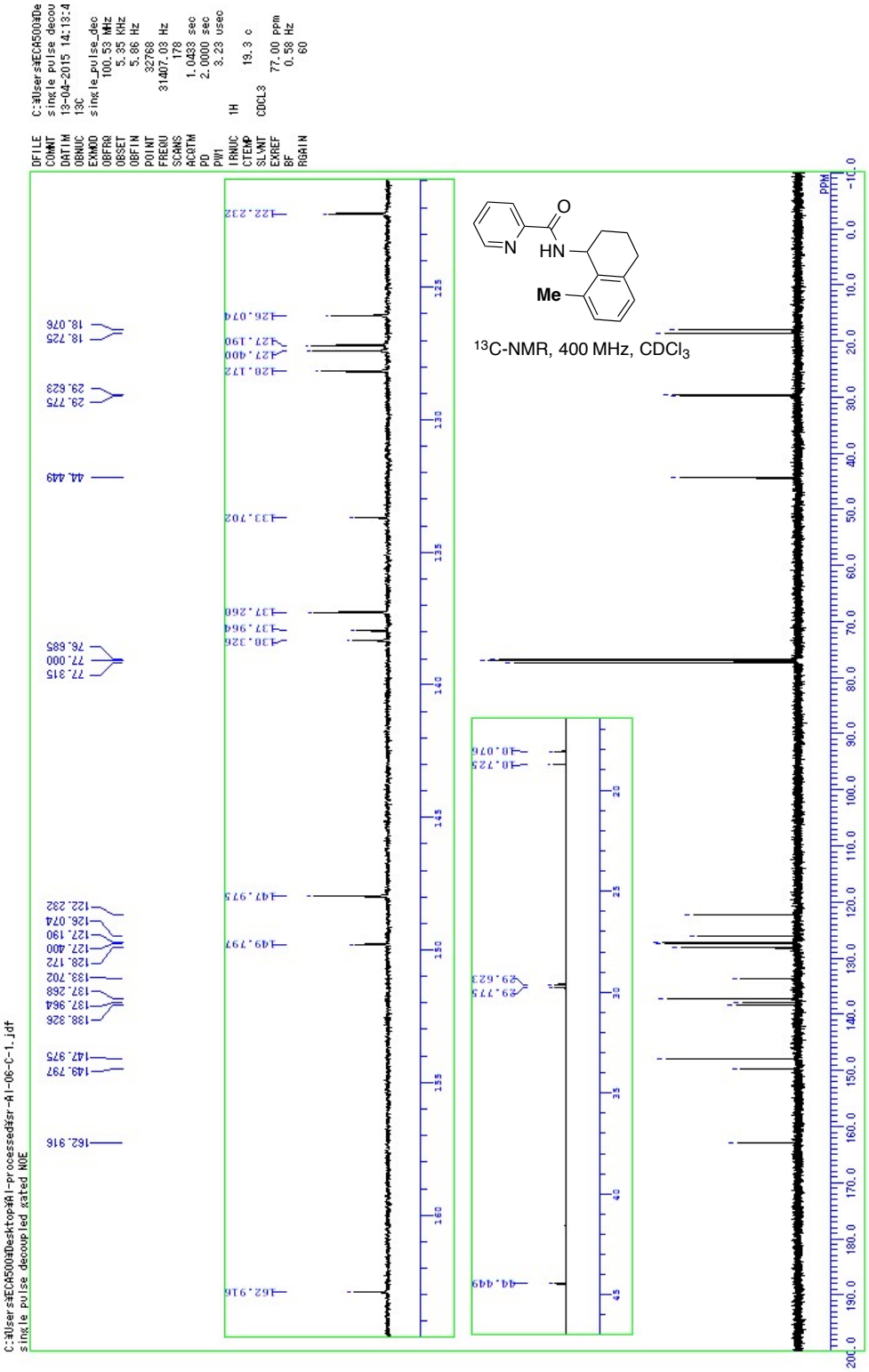
^{13}C NMR spectrum of **(*S*)-*N*-(1-(2-methylnaphthalen-1-yl)ethyl)picolinamide (8)**



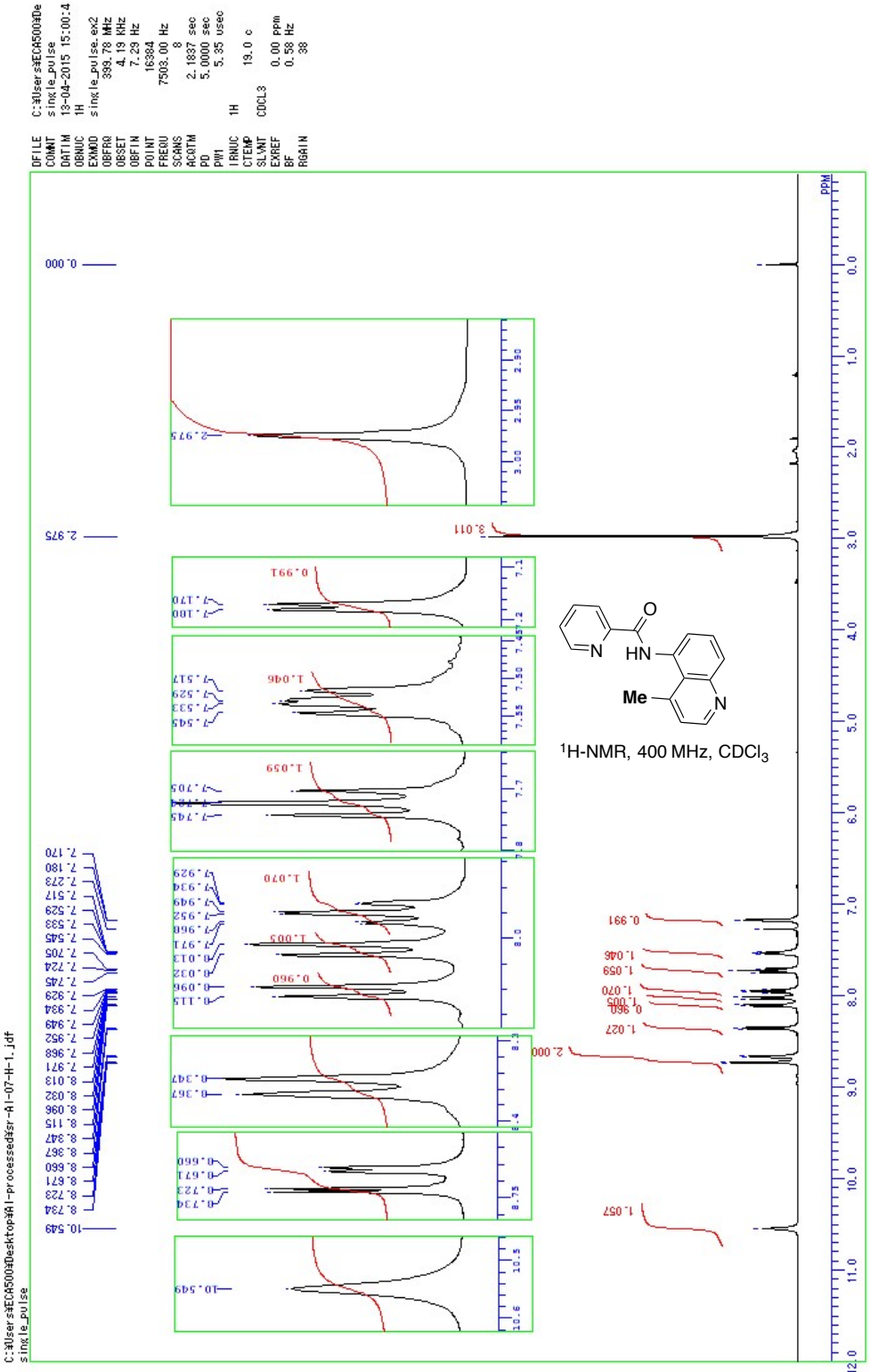
^{1}H NMR spectrum of ***N*-(8-methyl-1,2,3,4-tetrahydronaphthalen-1-yl)picolinamide (9)**



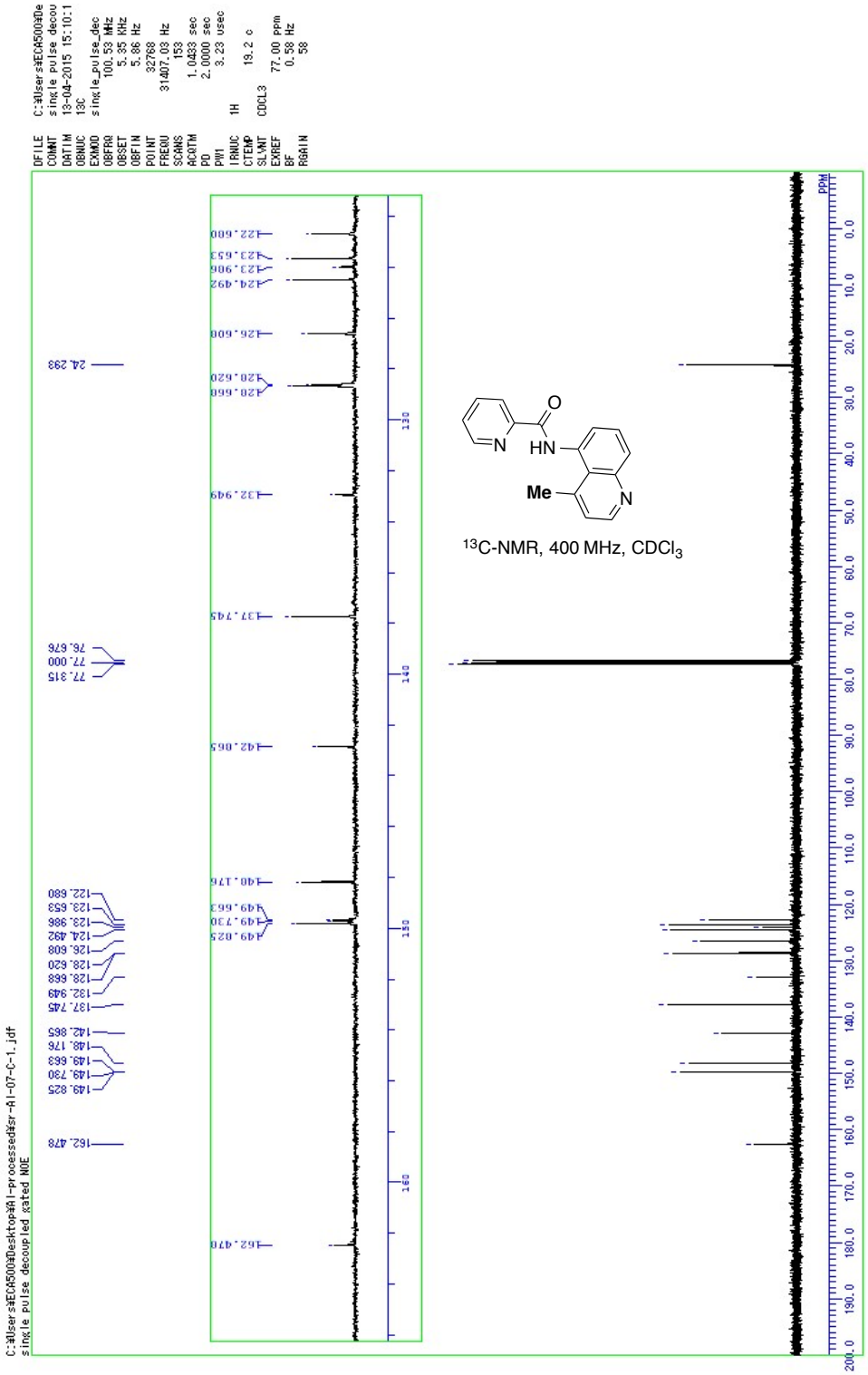
^{13}C NMR spectrum of ***N*-(8-methyl-1,2,3,4-tetrahydronaphthalen-1-yl)picolinamide (9)**



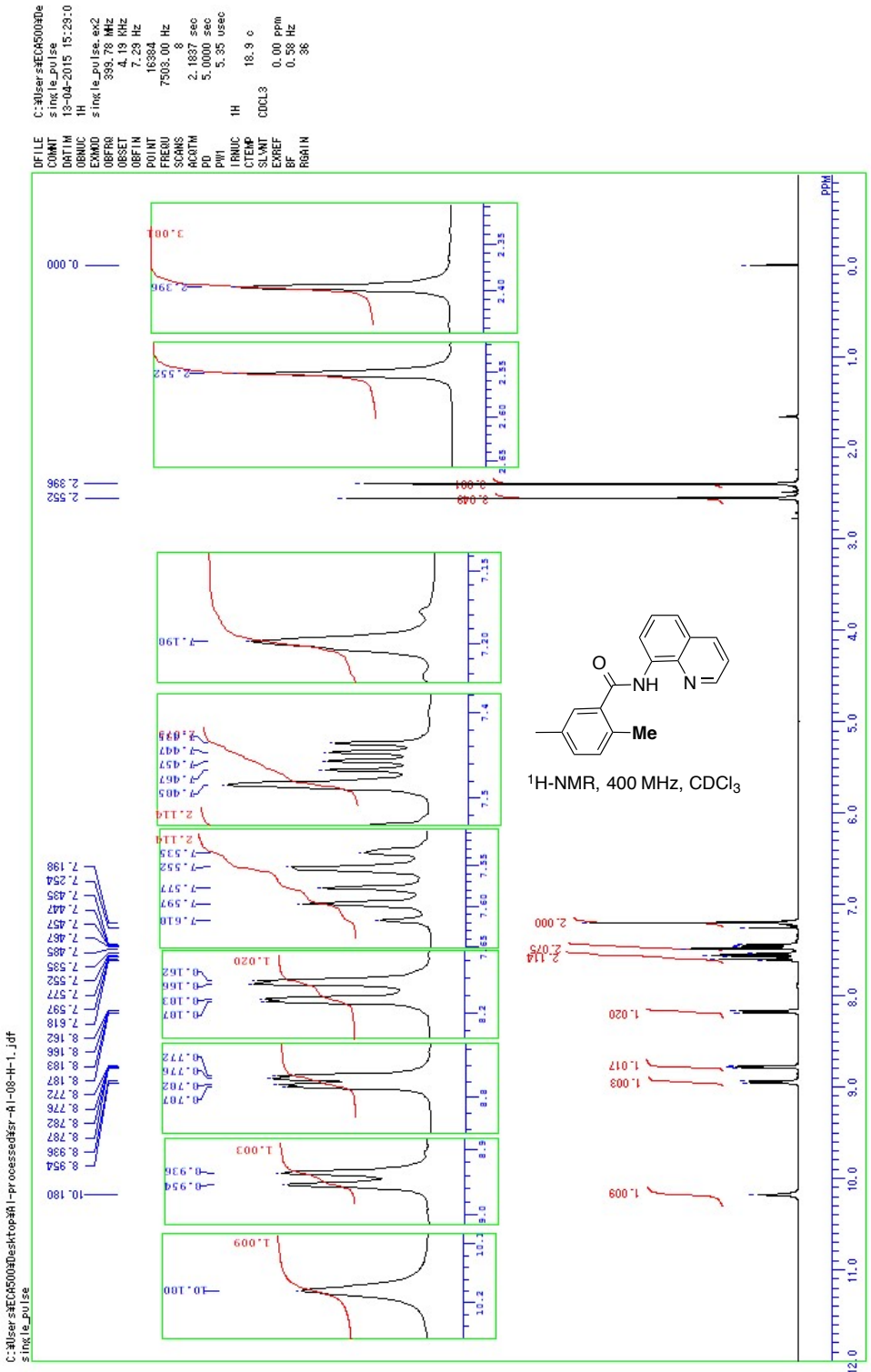
^{1}H NMR spectrum of ***N*-(4-methylquinolin-5-yl)picolinamide (10)**



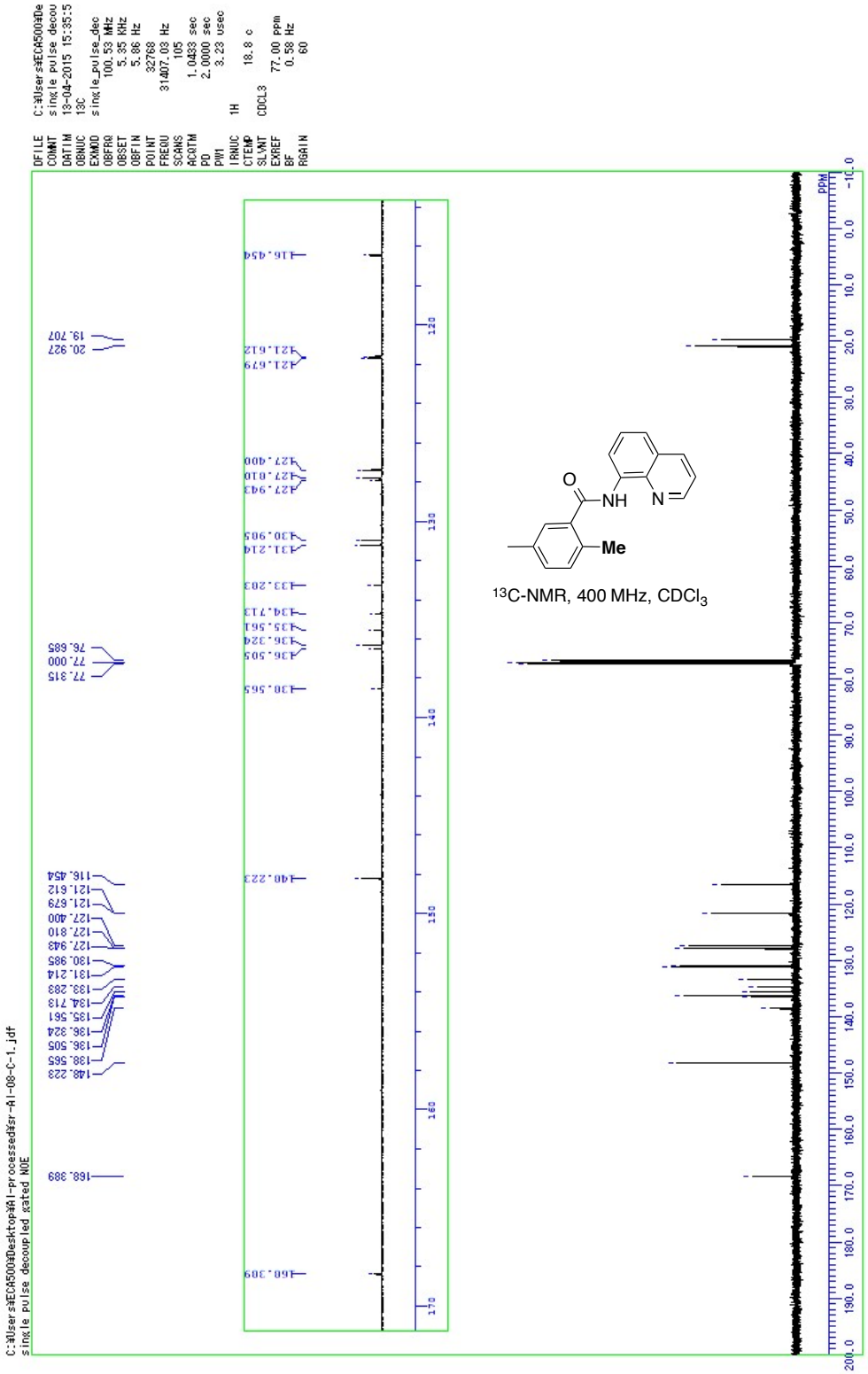
^{13}C NMR spectrum of ***N*-(4-methylquinolin-5-yl)picolinamide (10)**



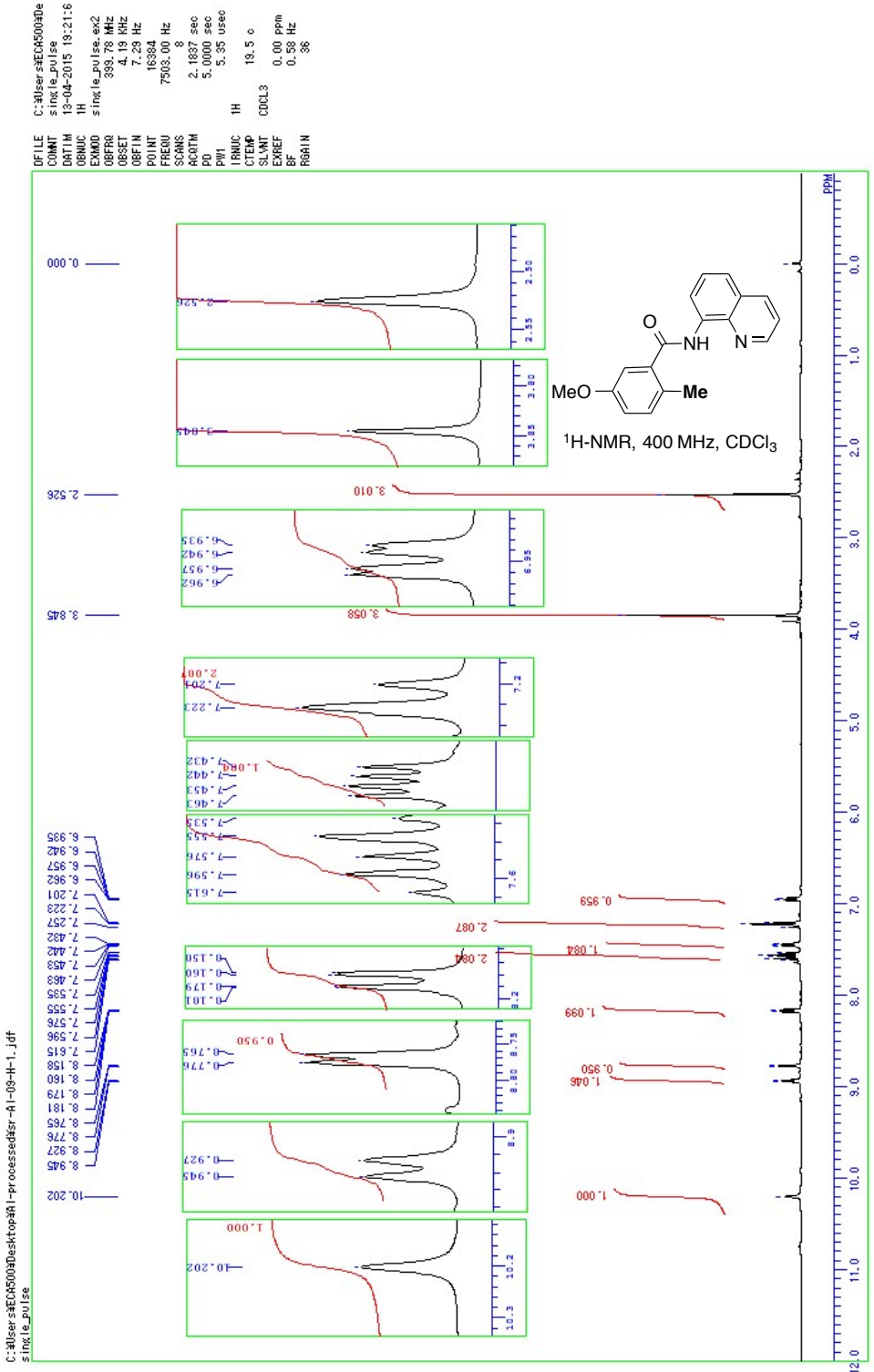
^{1}H NMR spectrum of **2,5-dimethyl-*N*-(quinolin-8-yl)benzamide (12)**



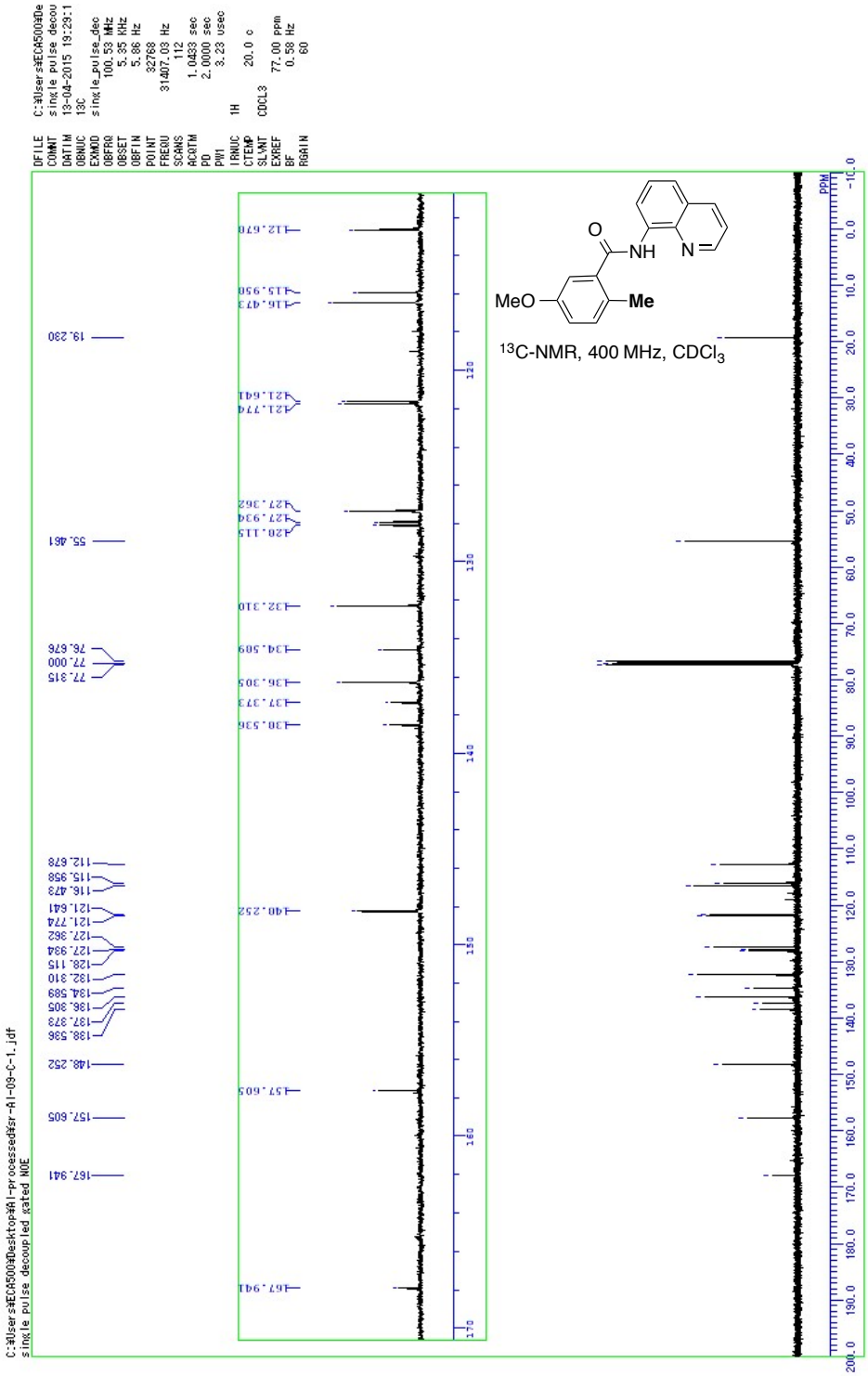
^{13}C NMR spectrum of **2,5-dimethyl-*N*-(quinolin-8-yl)benzamide (12)**



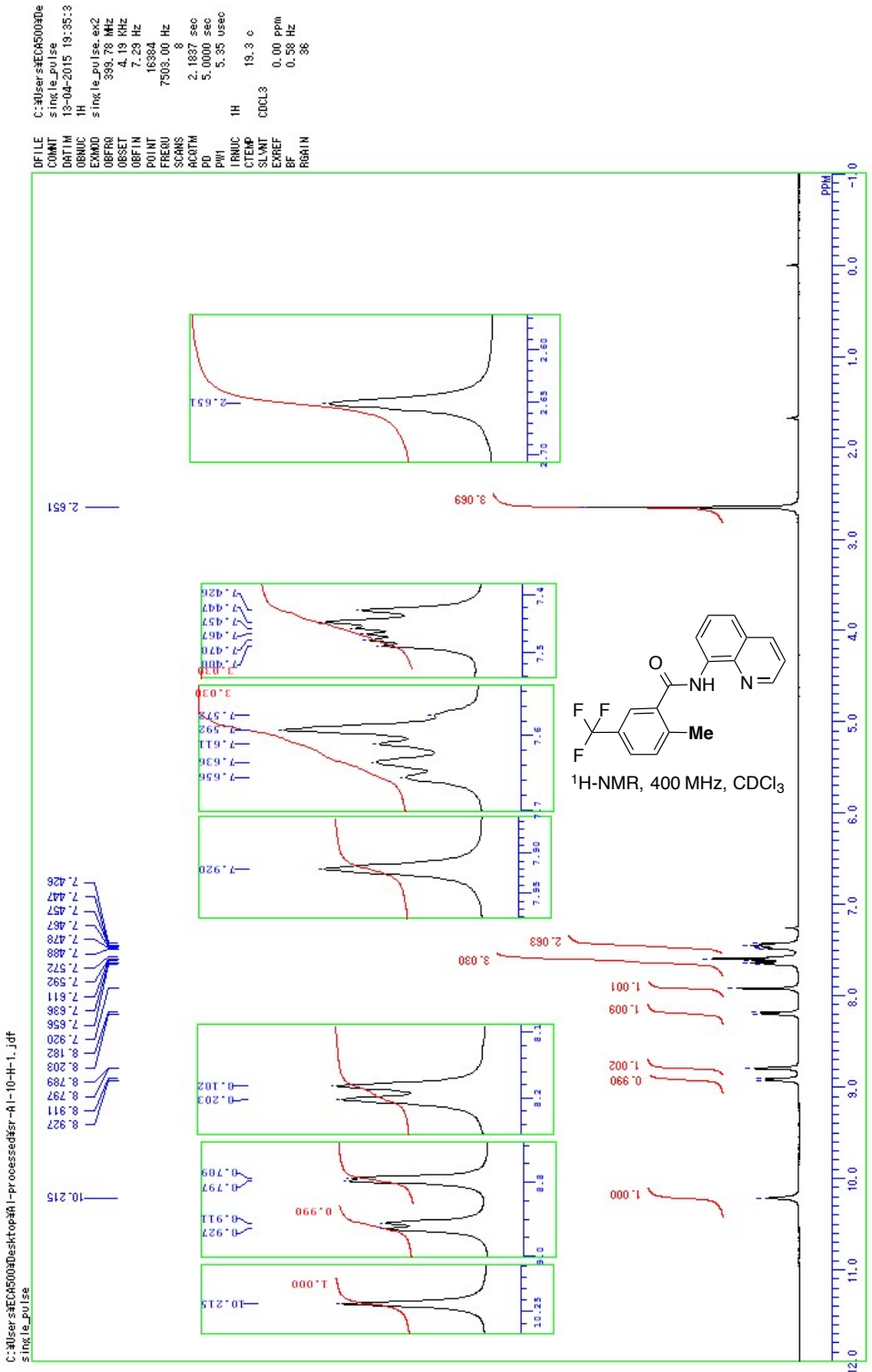
^{1}H NMR spectrum of **5-methoxy-2-methyl-*N*-(quinolin-8-yl)benzamide (13)**



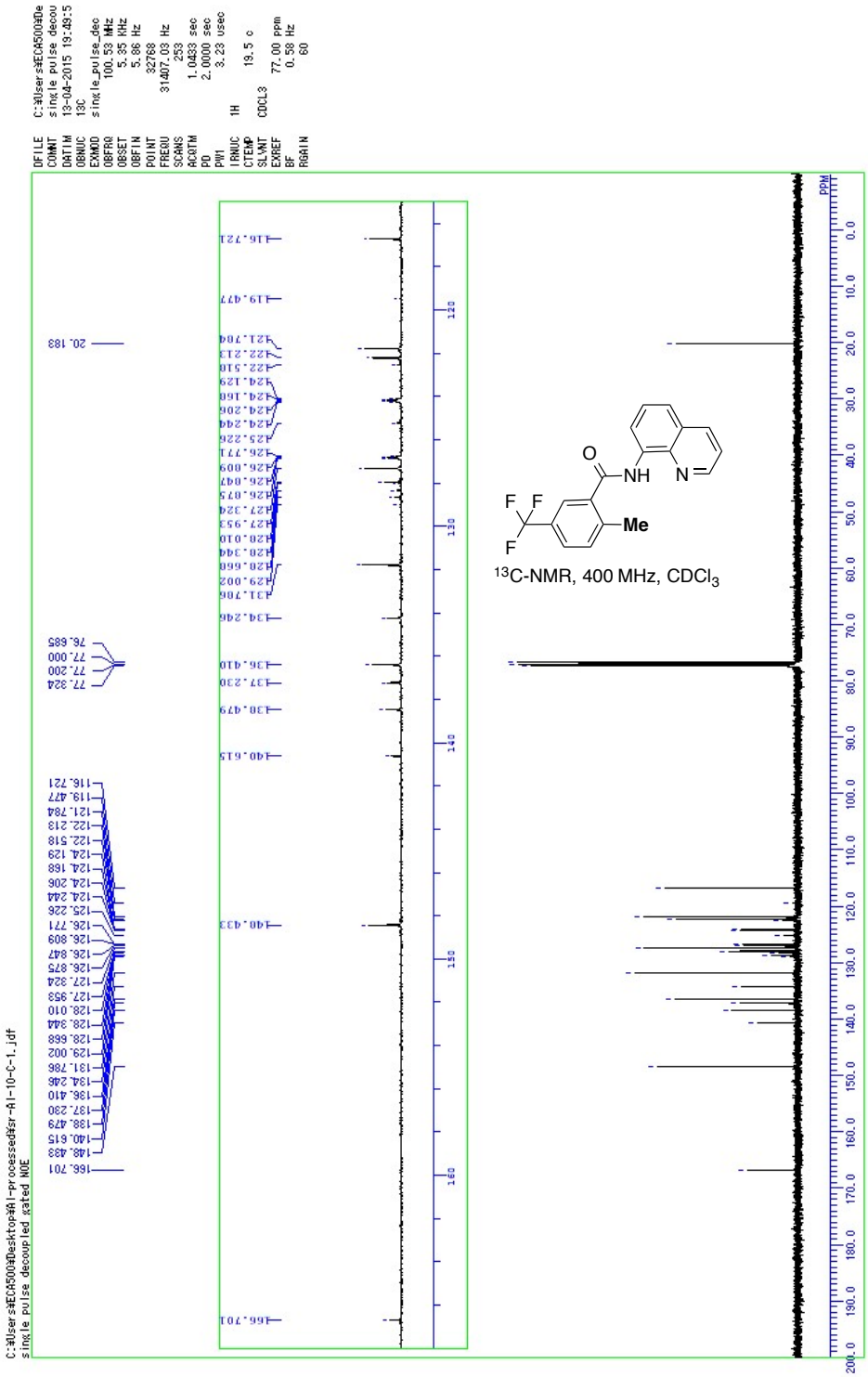
^{13}C NMR spectrum of **5-methoxy-2-methyl-*N*-(quinolin-8-yl)benzamide (13)**



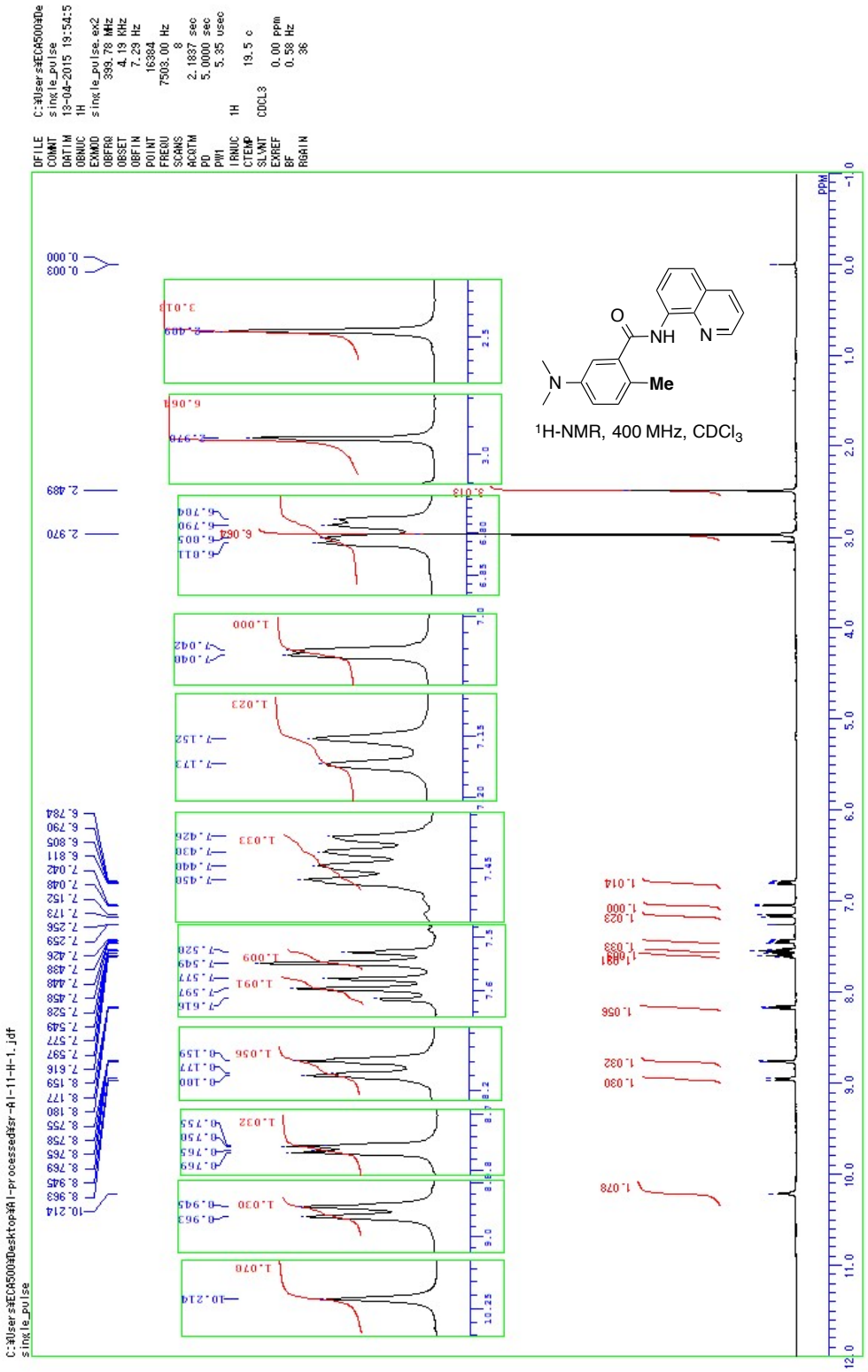
^{1}H NMR spectrum of **2-methyl-*N*-(quinolin-8-yl)-5-(trifluoromethyl)benzamide (14)**



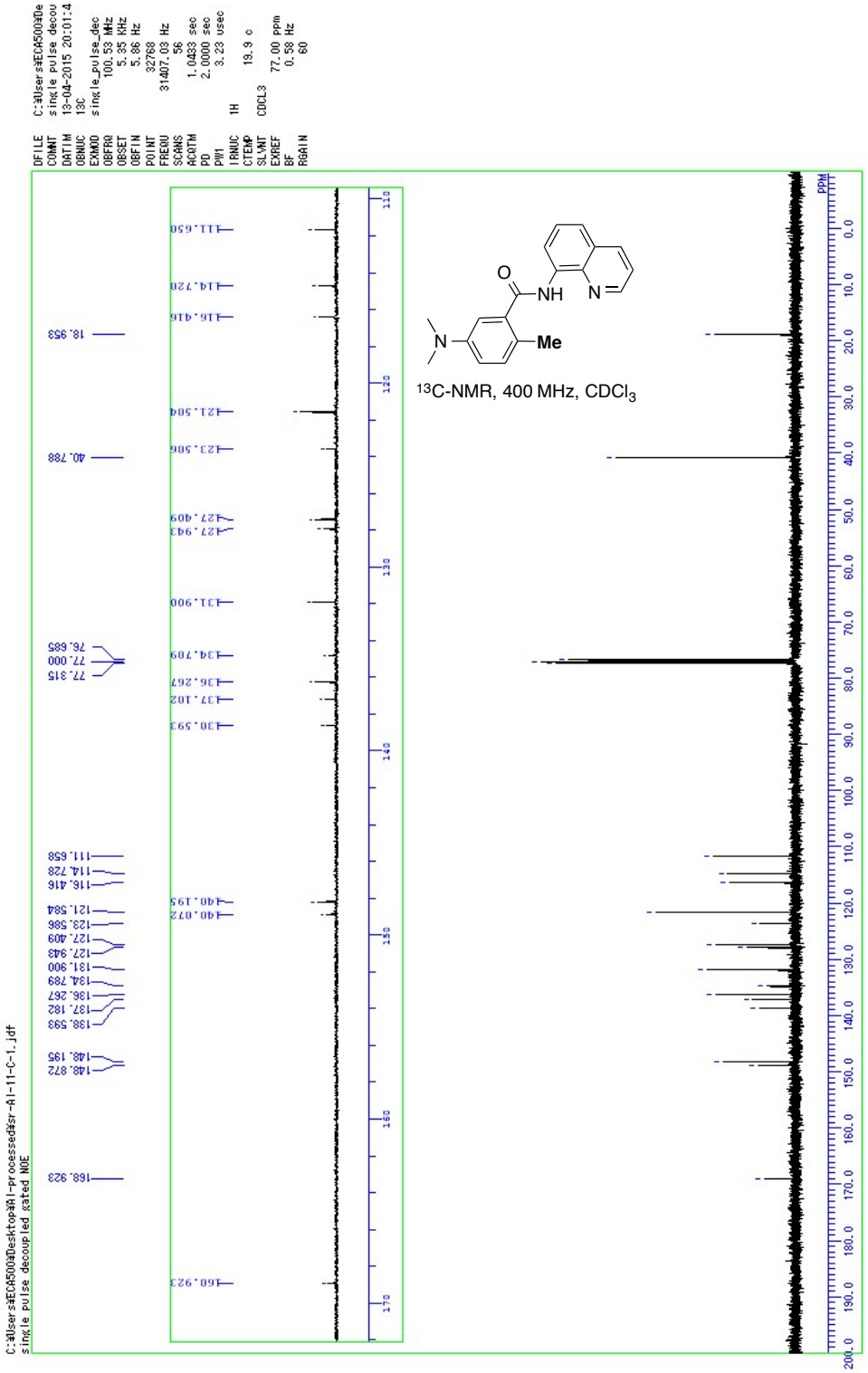
^{13}C NMR spectrum of **2-methyl-*N*-(quinolin-8-yl)-5-(trifluoromethyl)benzamide (14)**



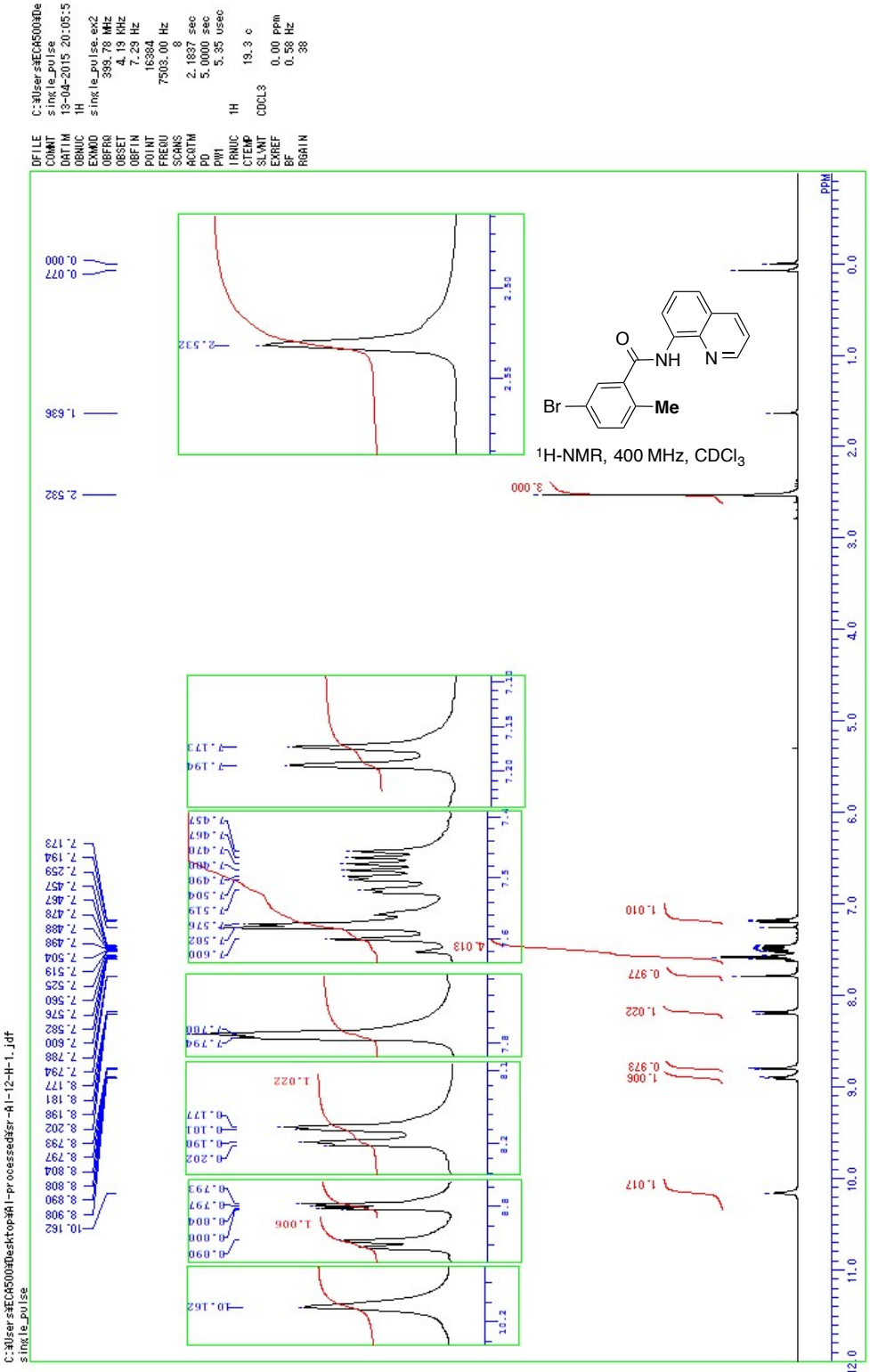
^{1}H NMR spectrum of **5-(dimethylamino)-2-methyl-*N*-(quinolin-8-yl)benzamide (15)**



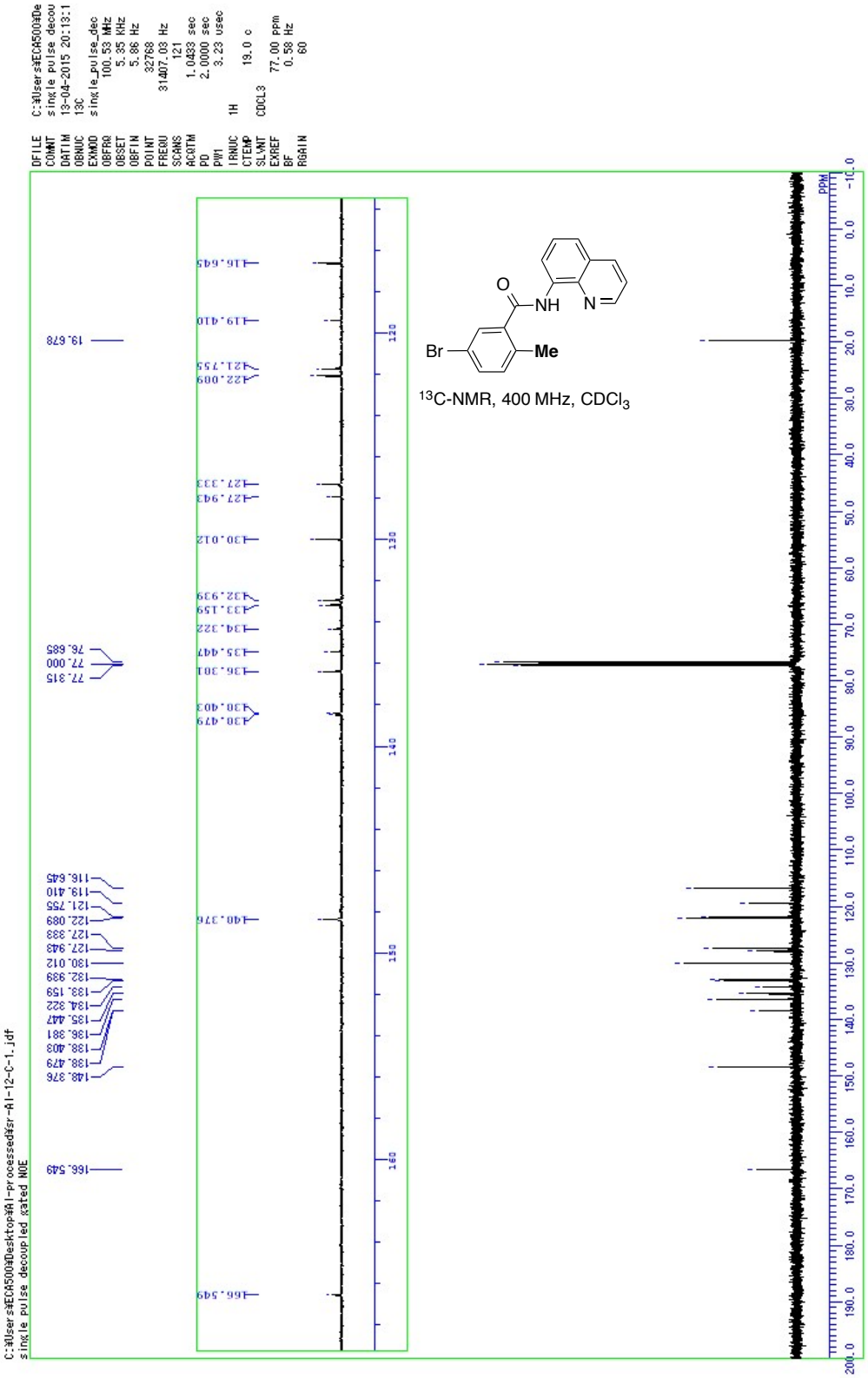
^{13}C NMR spectrum of **5-(dimethylamino)-2-methyl-*N*-(quinolin-8-yl)benzamide (15)**



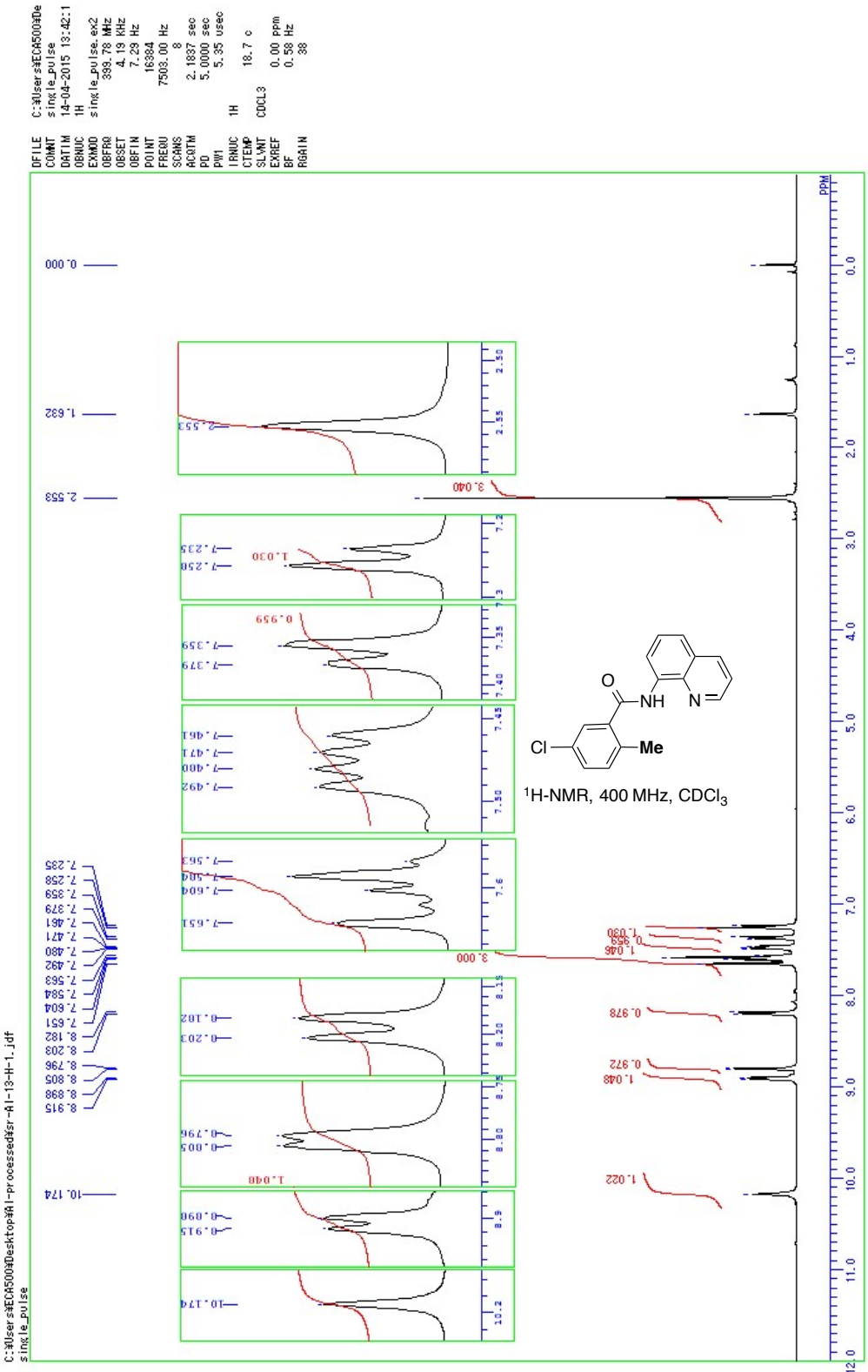
^{1}H NMR spectrum of **5-bromo-2-methyl-*N*-(quinolin-8-yl)benzamide (16)**



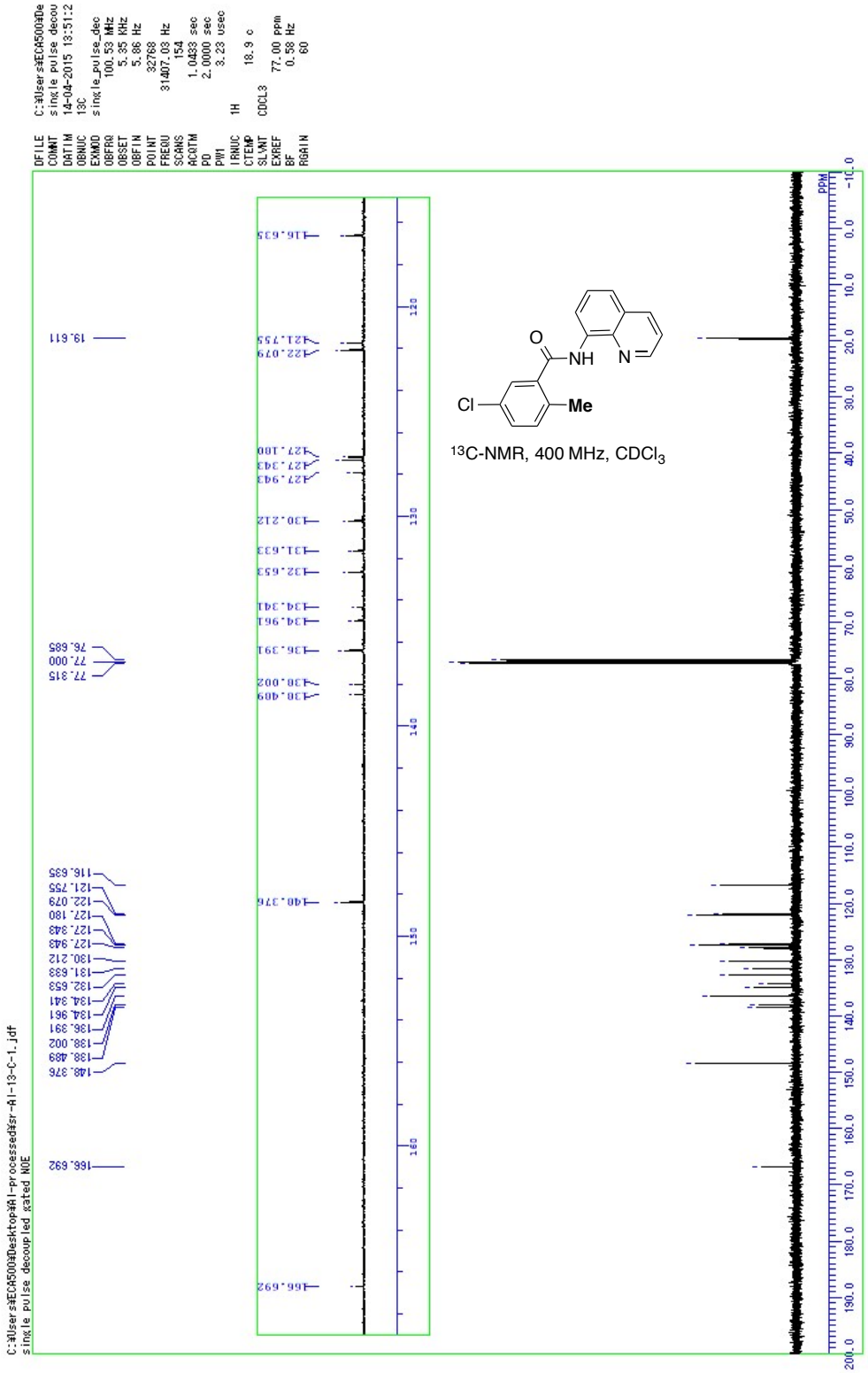
^{13}C NMR spectrum of **5-bromo-2-methyl-*N*-(quinolin-8-yl)benzamide (16)**



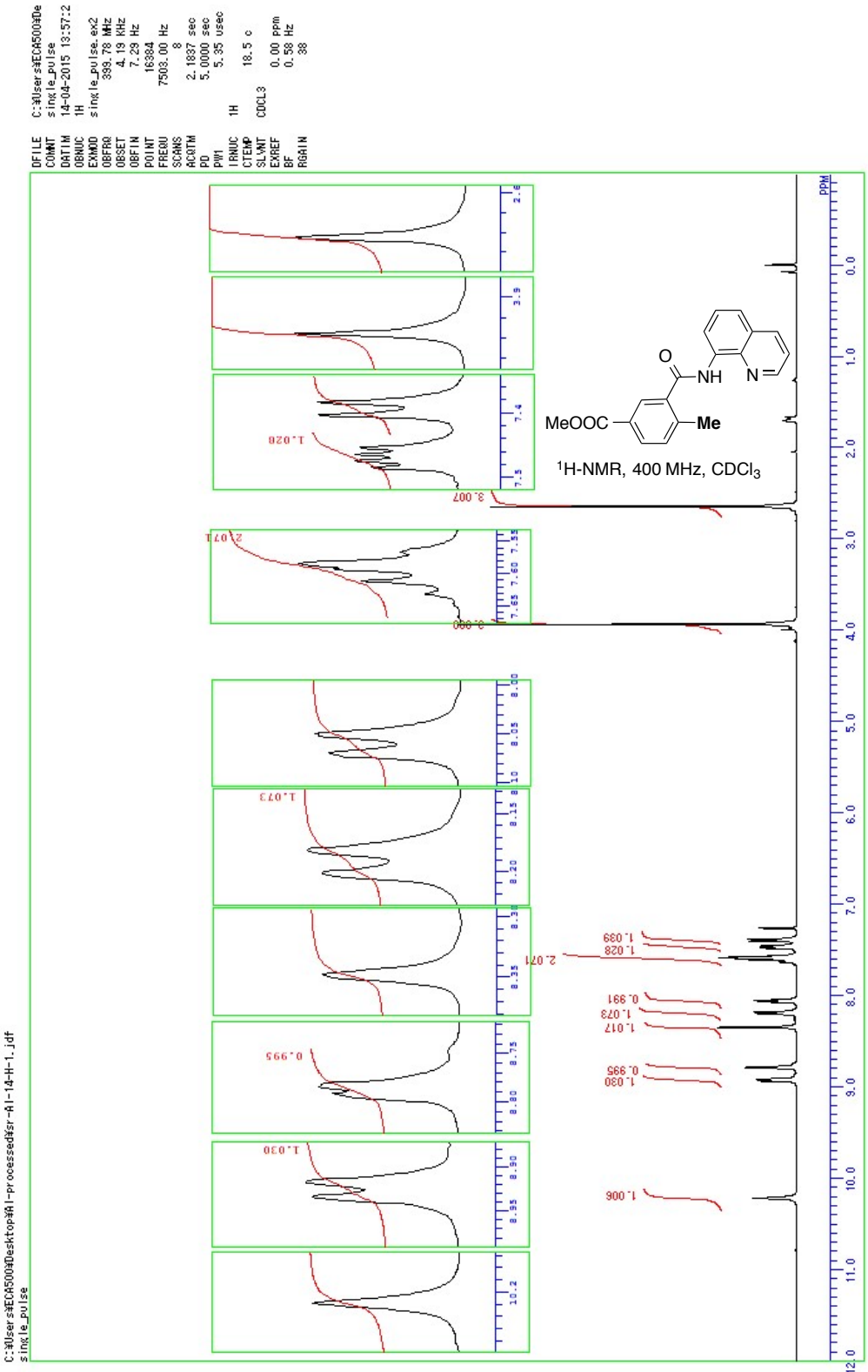
^{1}H NMR spectrum of **5-chloro-2-methyl-*N*-(quinolin-8-yl)benzamide (17)**



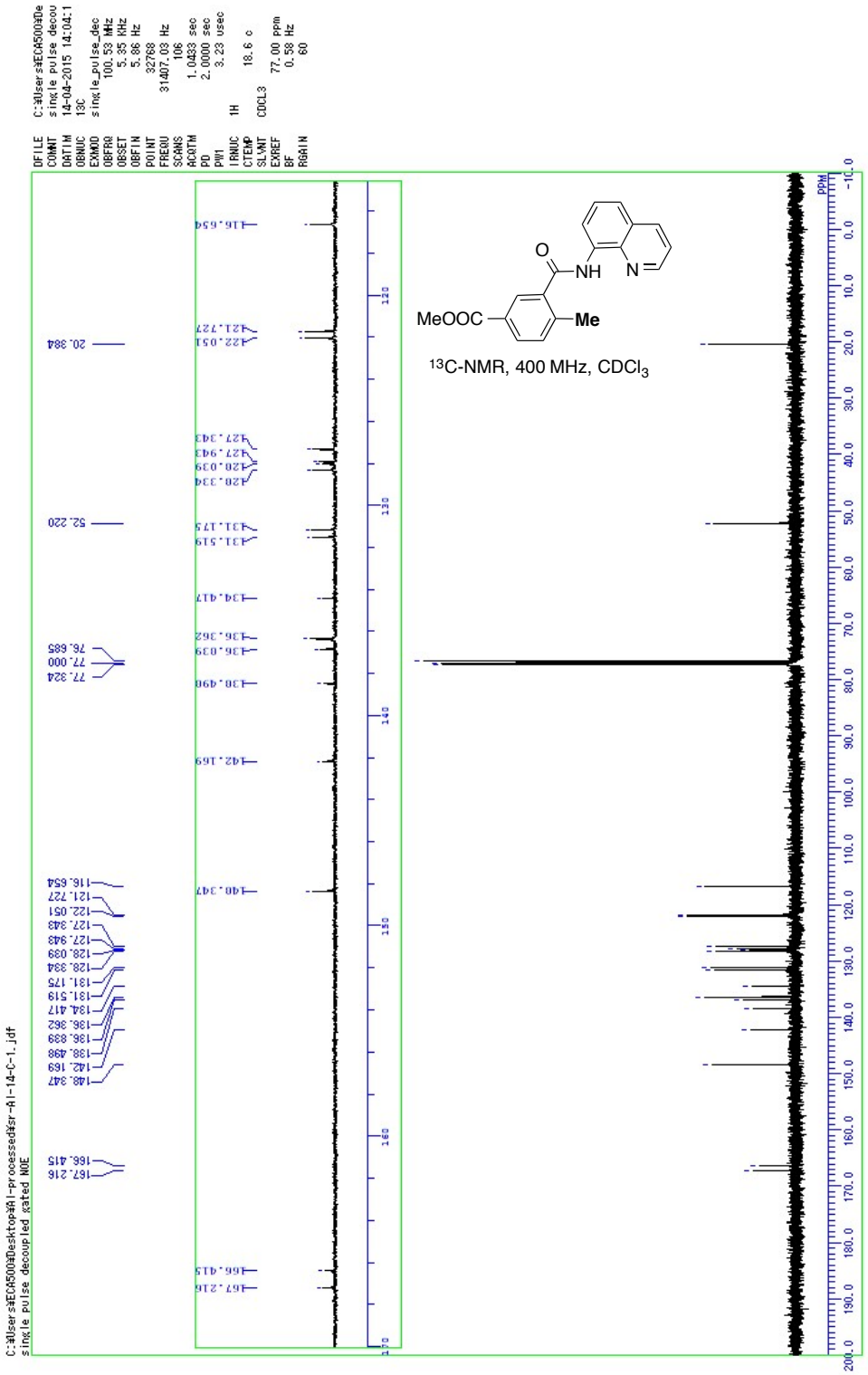
^{13}C NMR spectrum of **5-chloro-2-methyl-*N*-(quinolin-8-yl)benzamide (17)**



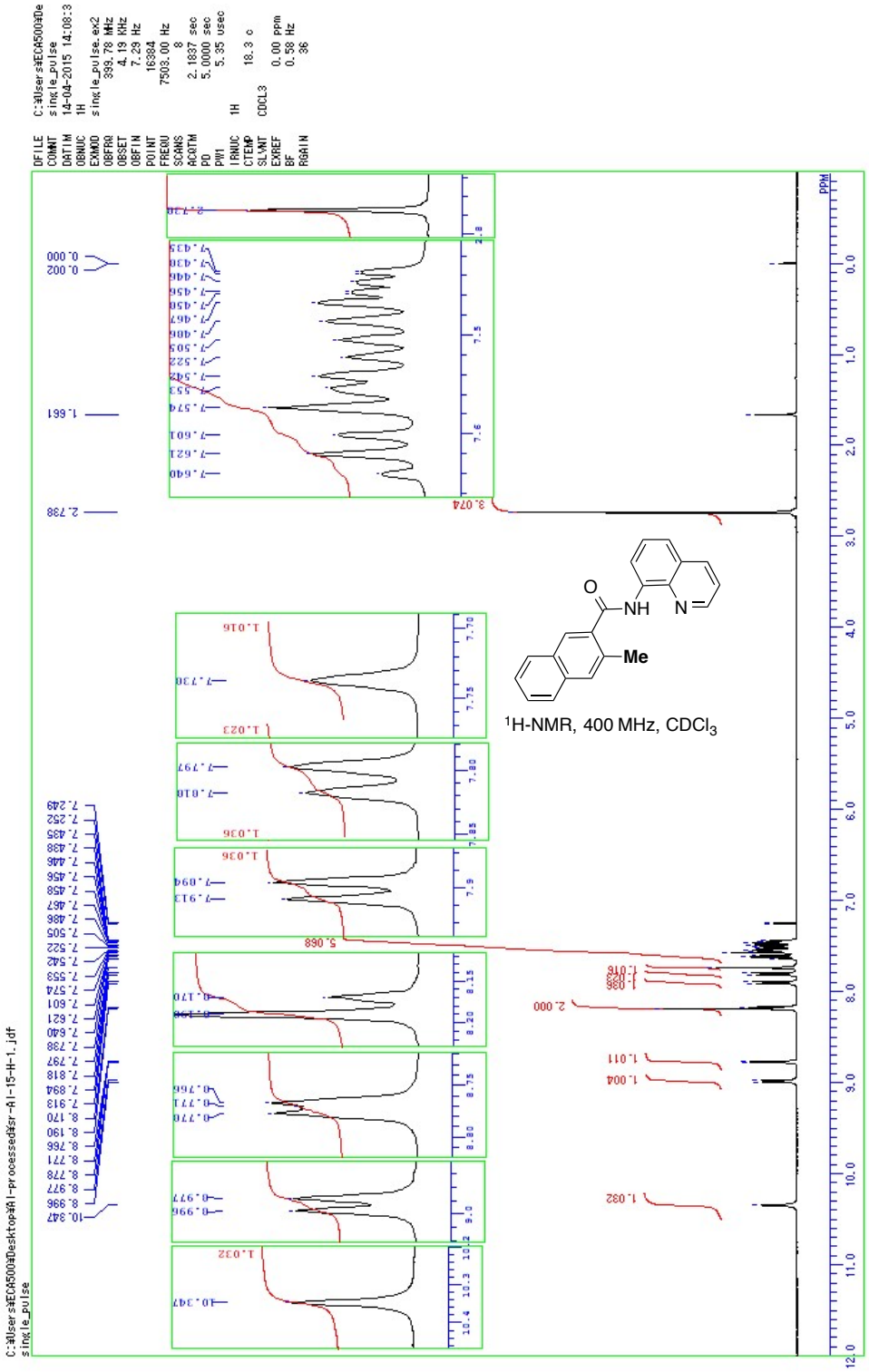
^{1}H NMR spectrum of **methyl 4-methyl-3-(quinolin-8-ylcarbamoyl)benzoate (18)**



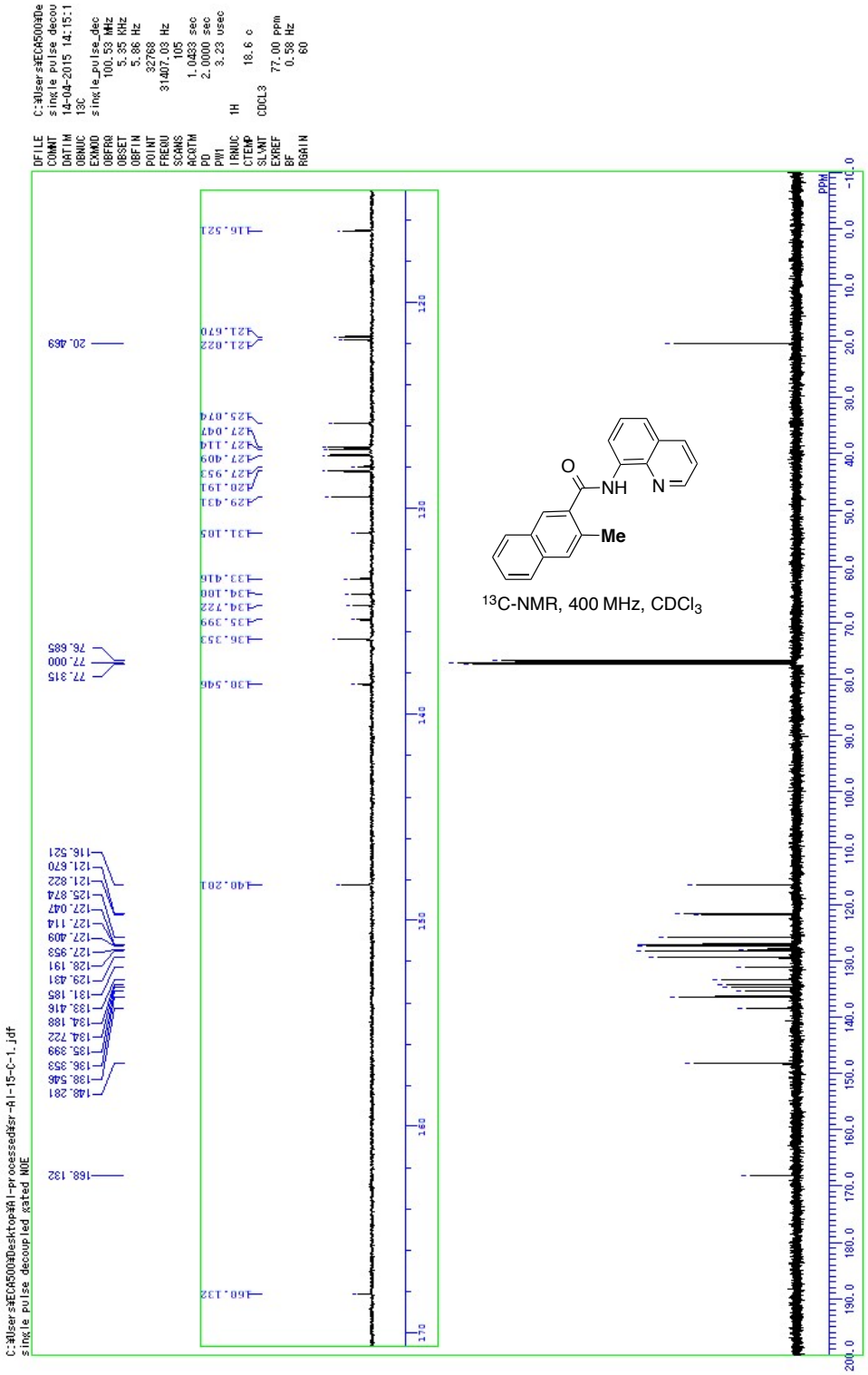
^{13}C NMR spectrum of **methyl 4-methyl-3-(quinolin-8-ylcarbamoyl)benzoate (18)**



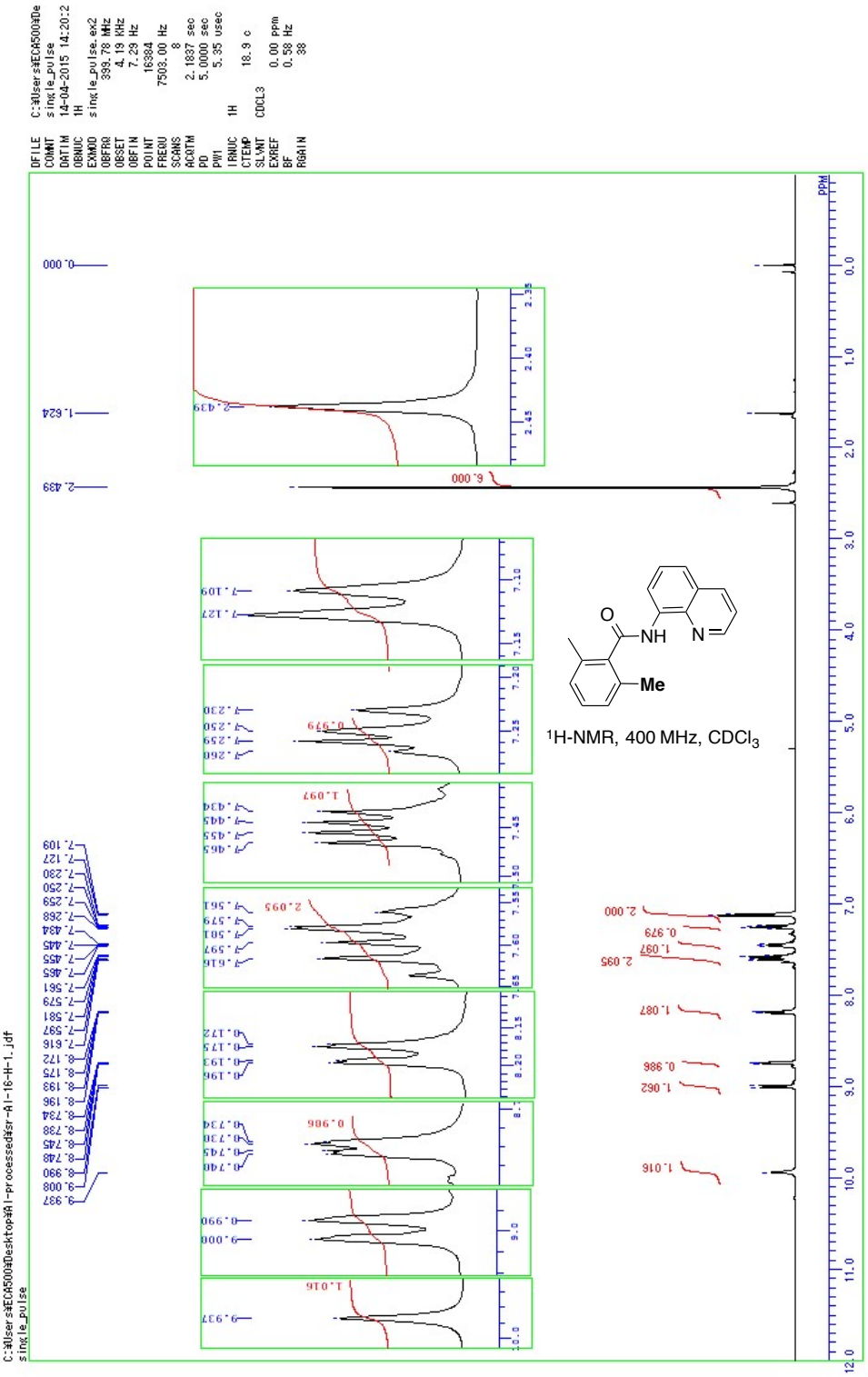
^{1}H NMR spectrum of **3-methyl-*N*-(quinolin-8-yl)-2-naphthamide (19)**



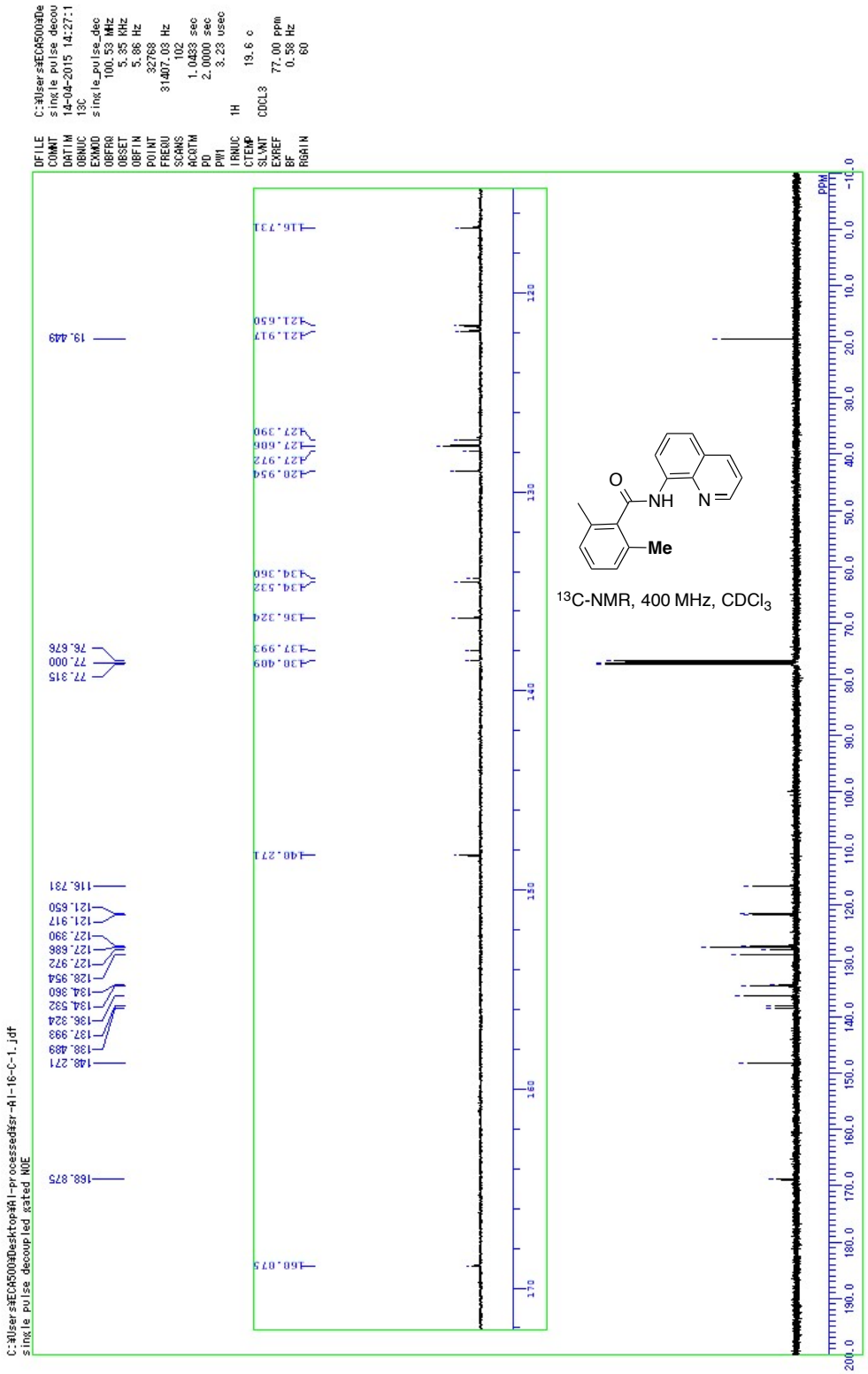
^{13}C NMR spectrum of **3-methyl-*N*-(quinolin-8-yl)-2-naphthamide (19)**



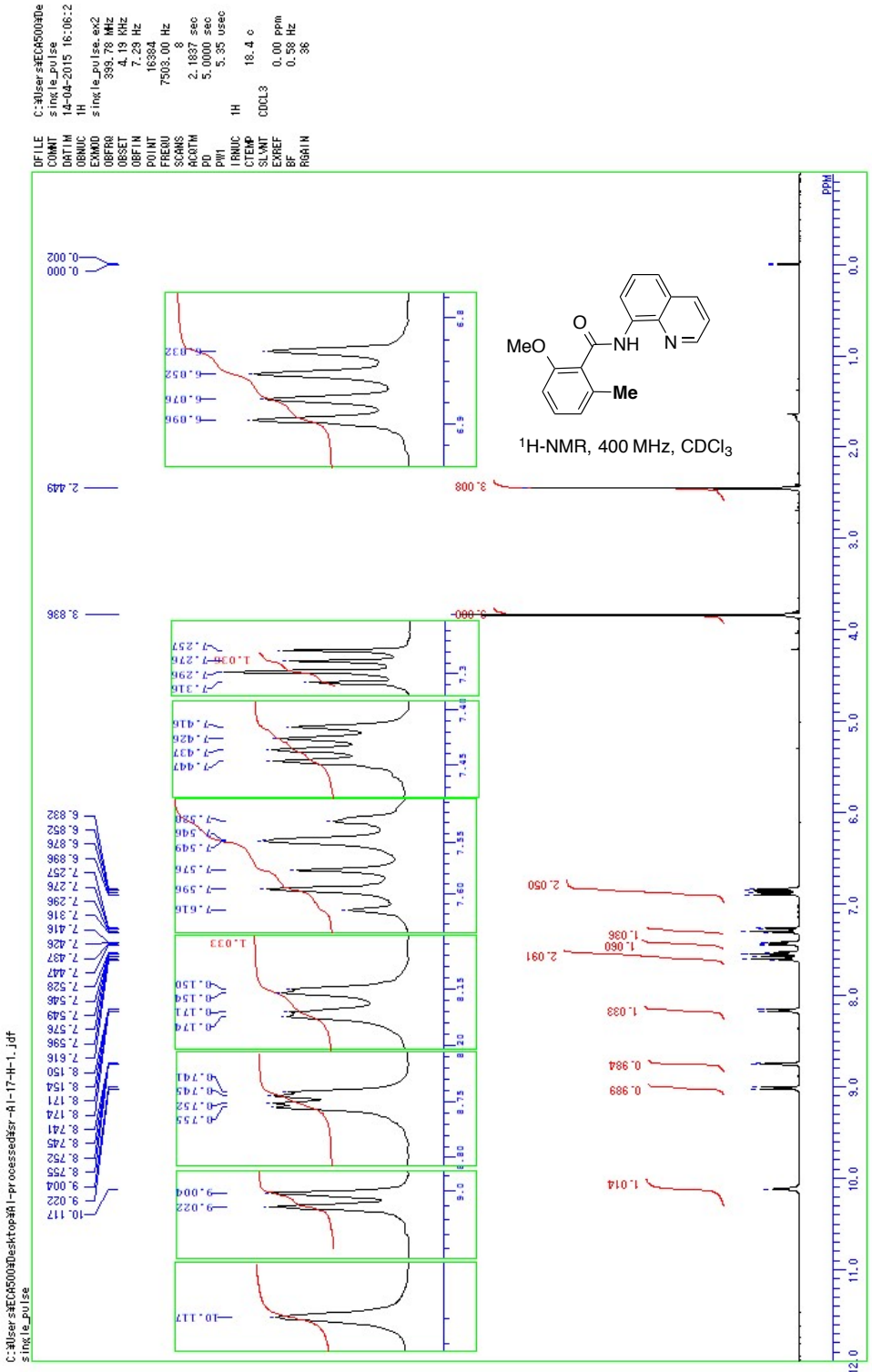
^{1}H NMR spectrum of **2,6-dimethyl-*N*-(quinolin-8-yl)benzamide (20)**



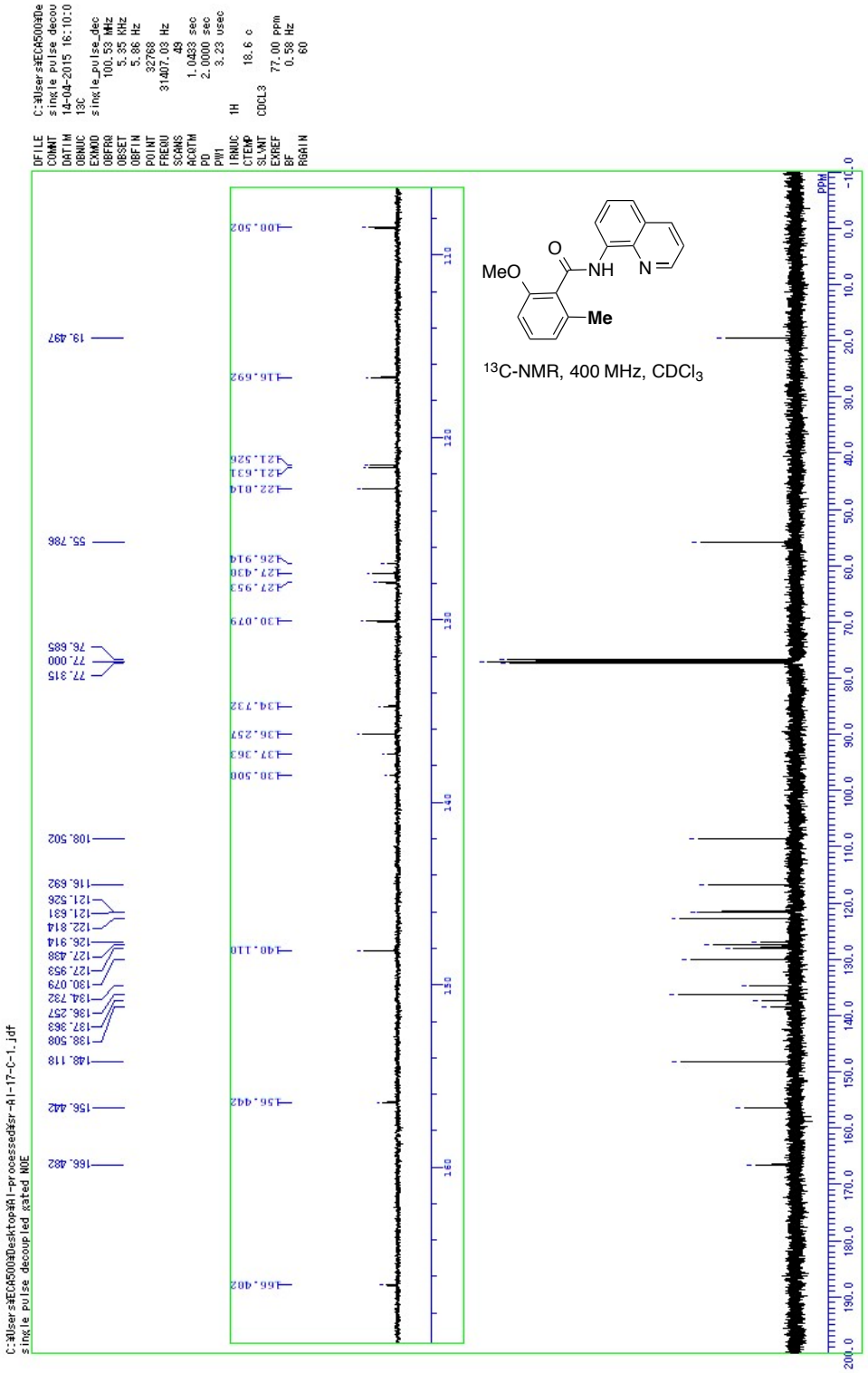
^{13}C NMR spectrum of **2,6-dimethyl-*N*-(quinolin-8-yl)benzamide (20)**



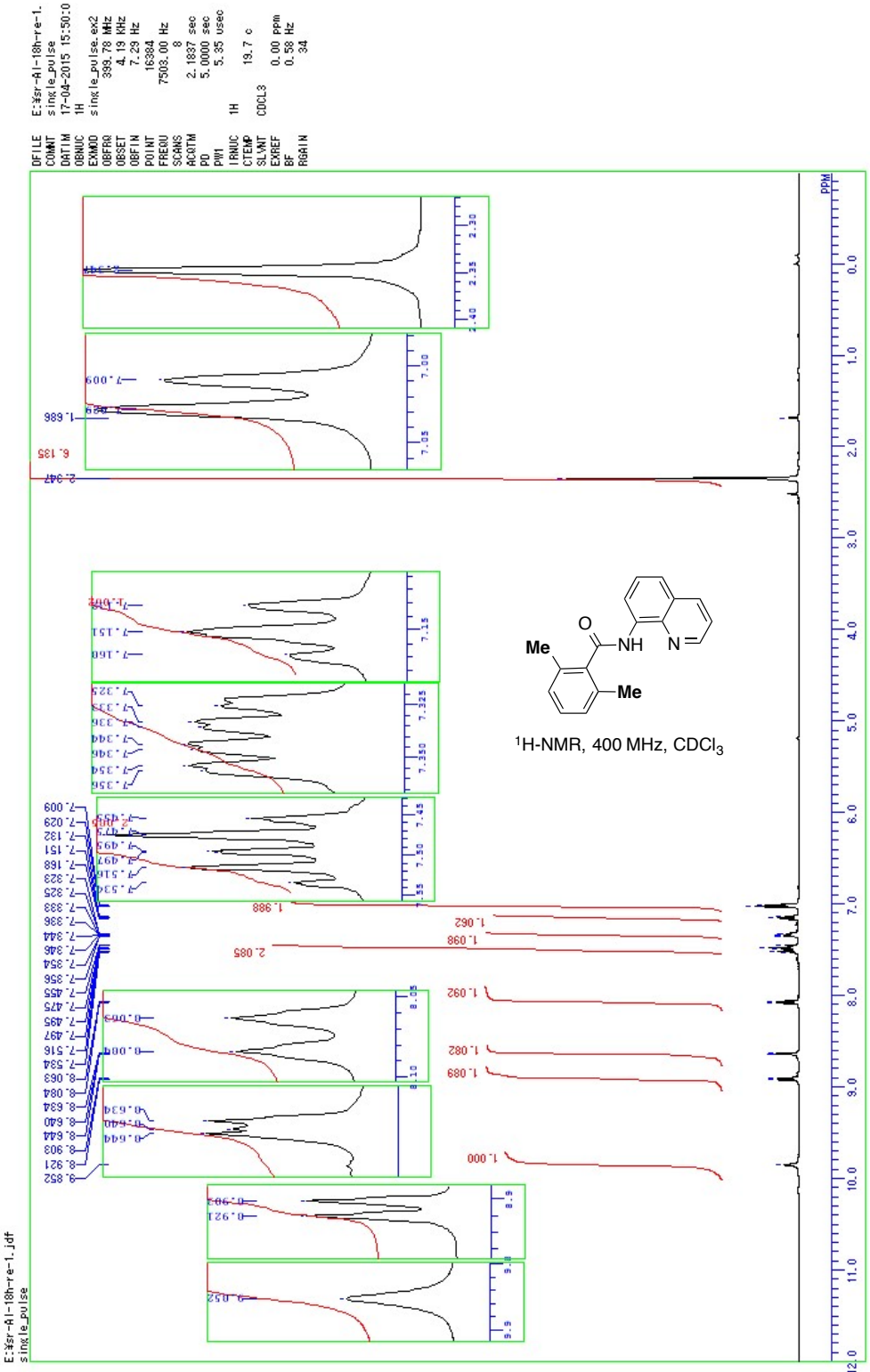
^{1}H NMR spectrum of **2-methoxy-6-methyl-*N*-(quinolin-8-yl)benzamide (21)**



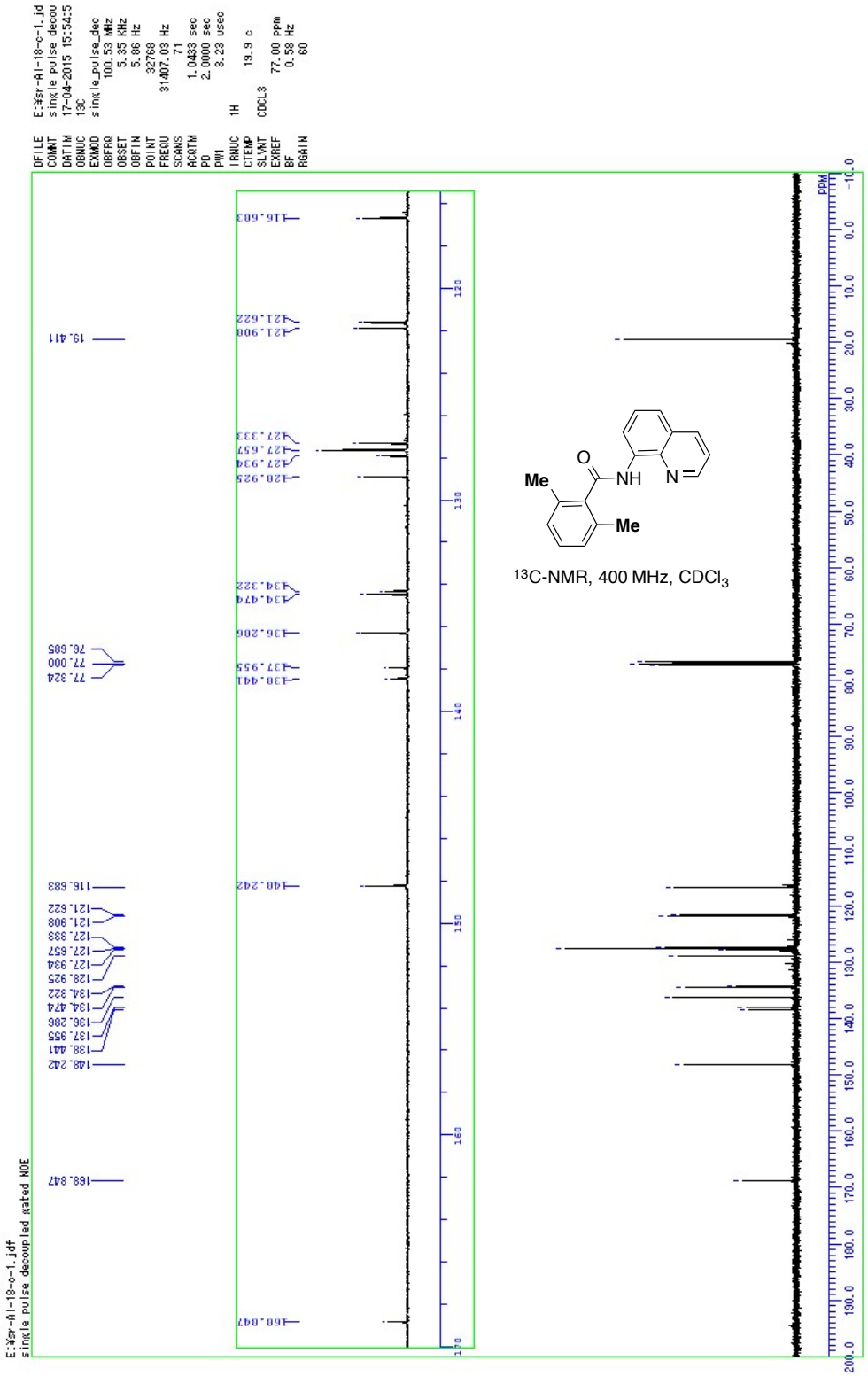
^{13}C NMR spectrum of **2-methoxy-6-methyl-*N*-(quinolin-8-yl)benzamide (21)**



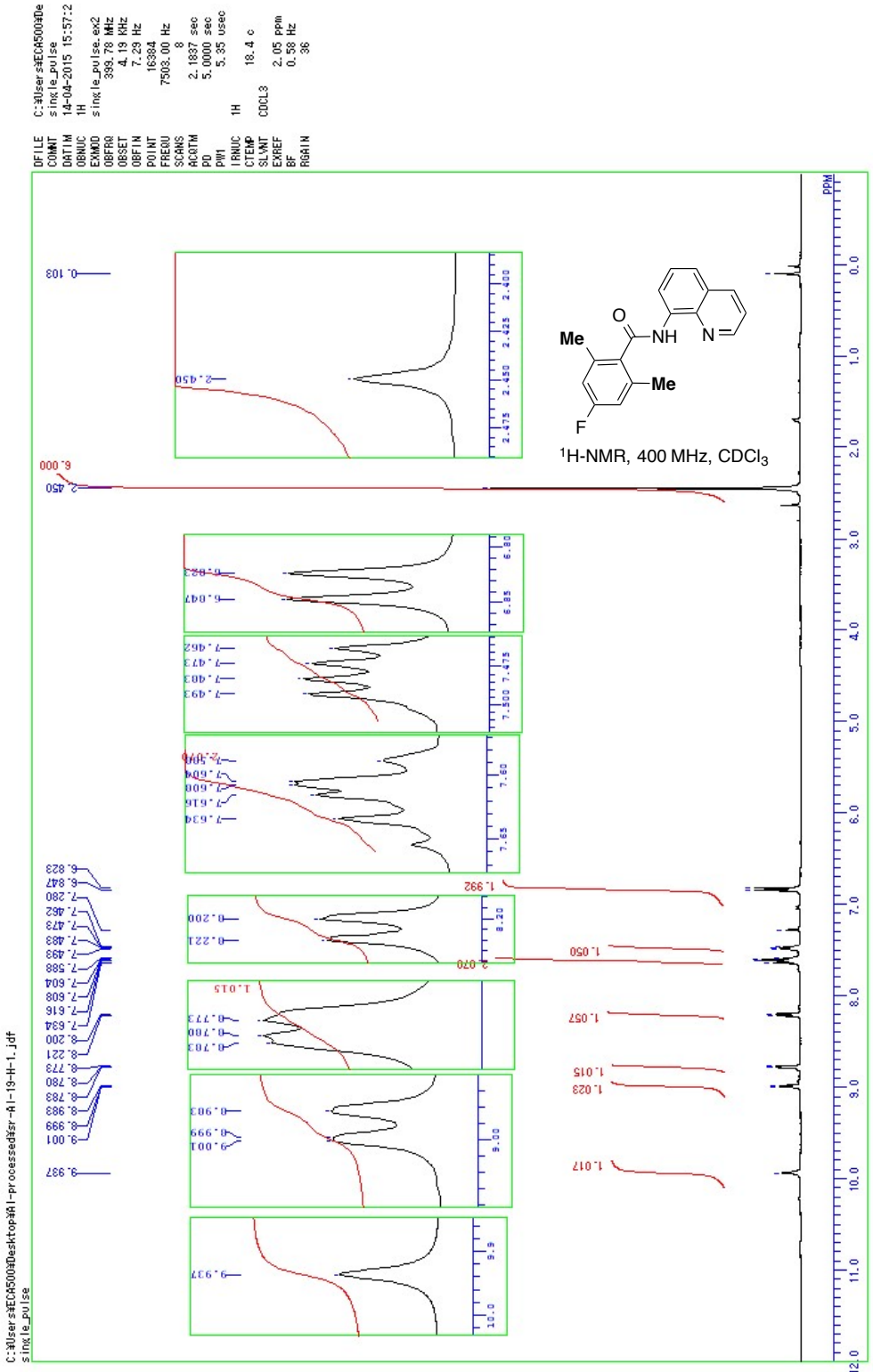
^{1}H NMR spectrum of **2,6-dimethyl-*N*-(quinolin-8-yl)benzamide (22)**



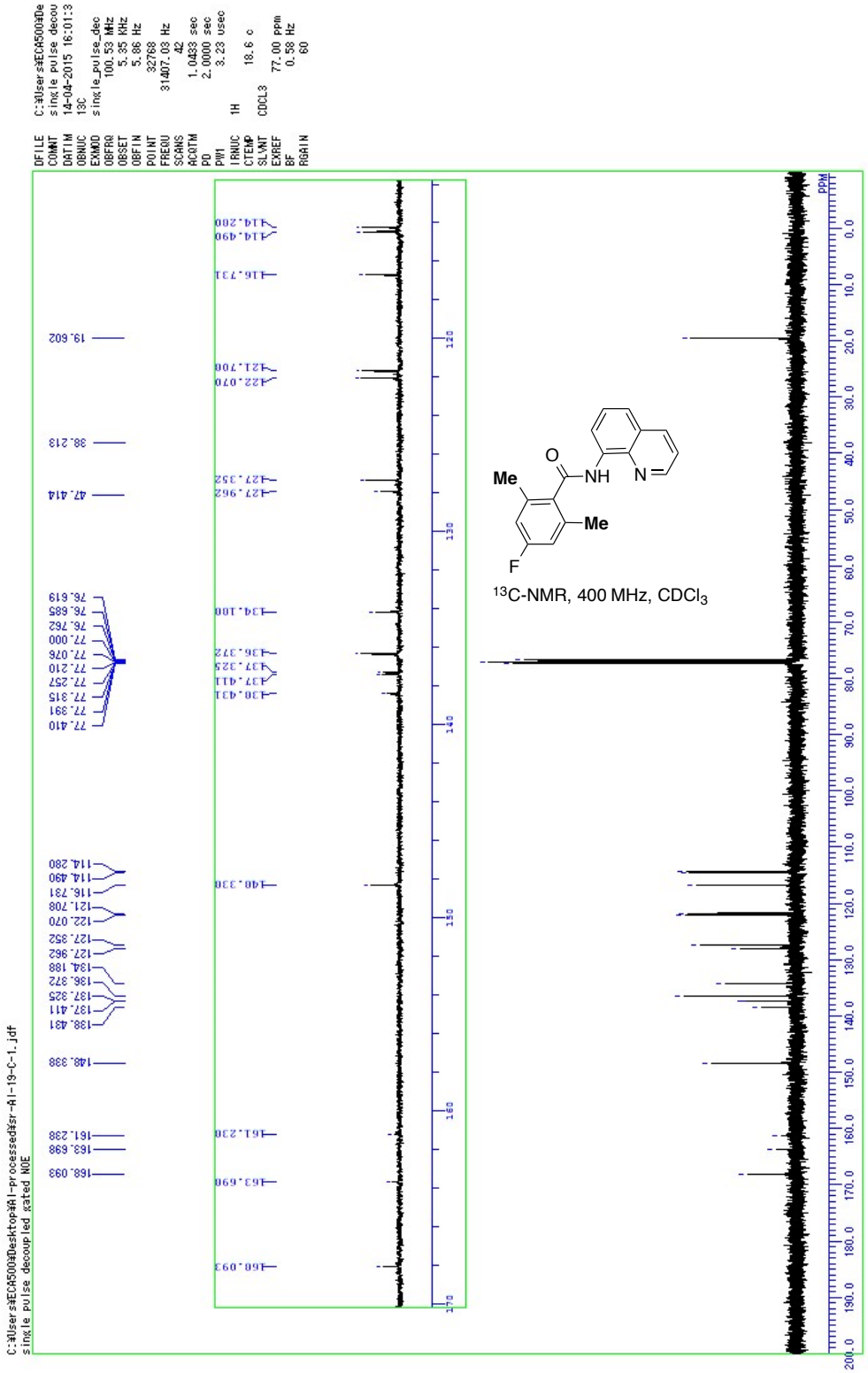
^{13}C NMR spectrum of **2,6-dimethyl-*N*-(quinolin-8-yl)benzamide (22)**



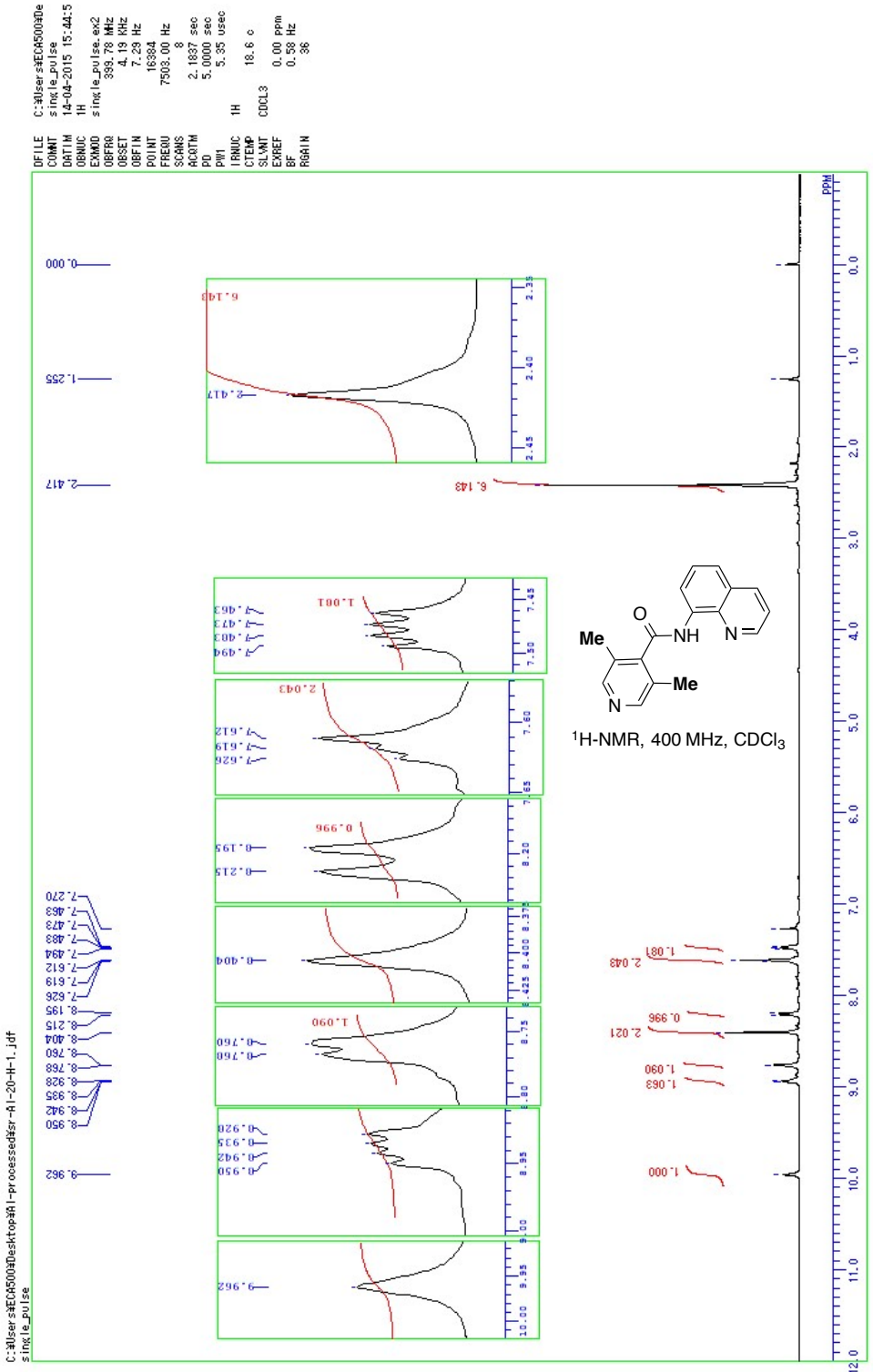
^{1}H NMR spectrum of **4-fluoro-2,6-dimethyl-*N*-(quinolin-8-yl)benzamide (23)**



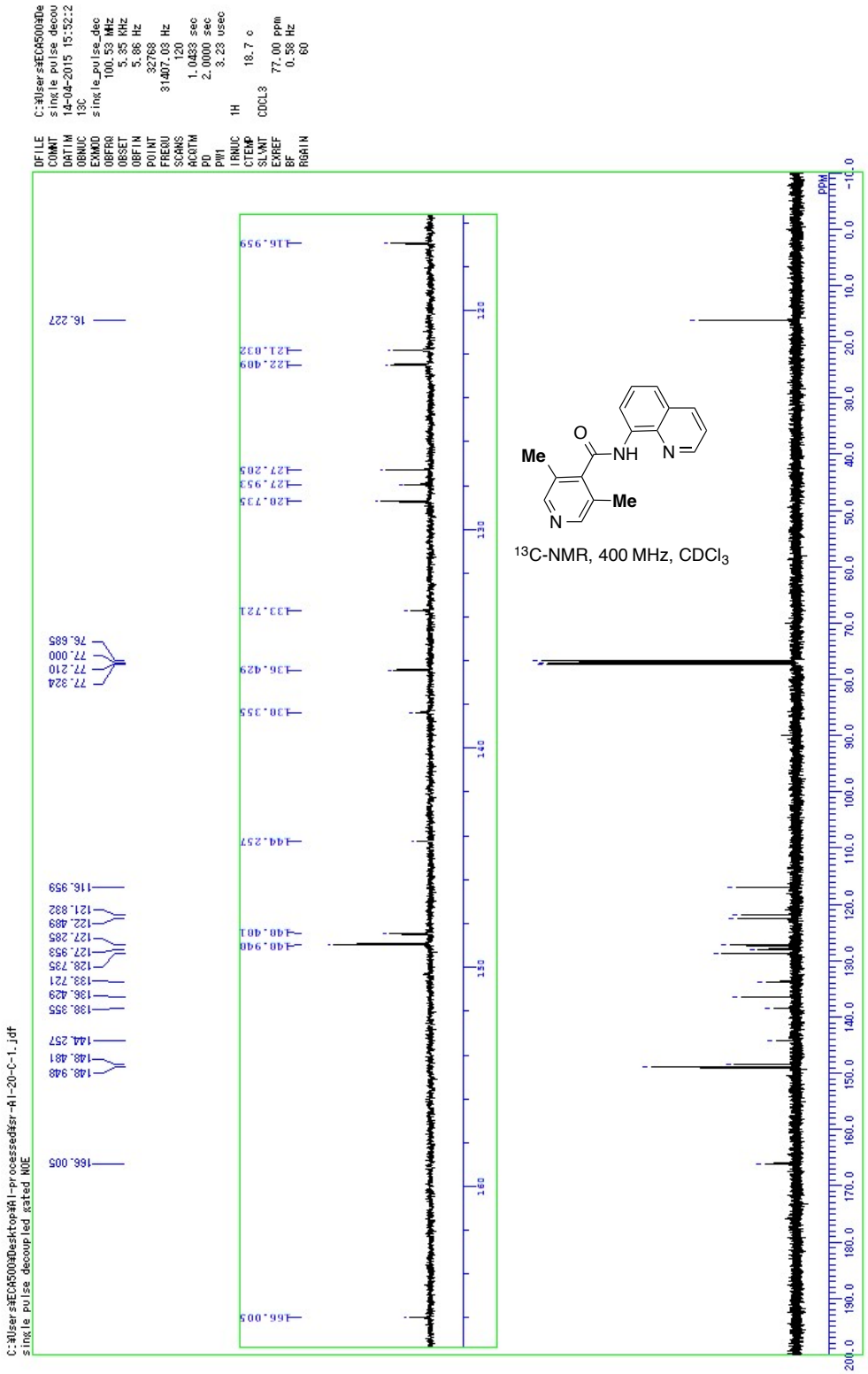
^{13}C NMR spectrum of **4-fluoro-2,6-dimethyl-*N*-(quinolin-8-yl)benzamide (23)**



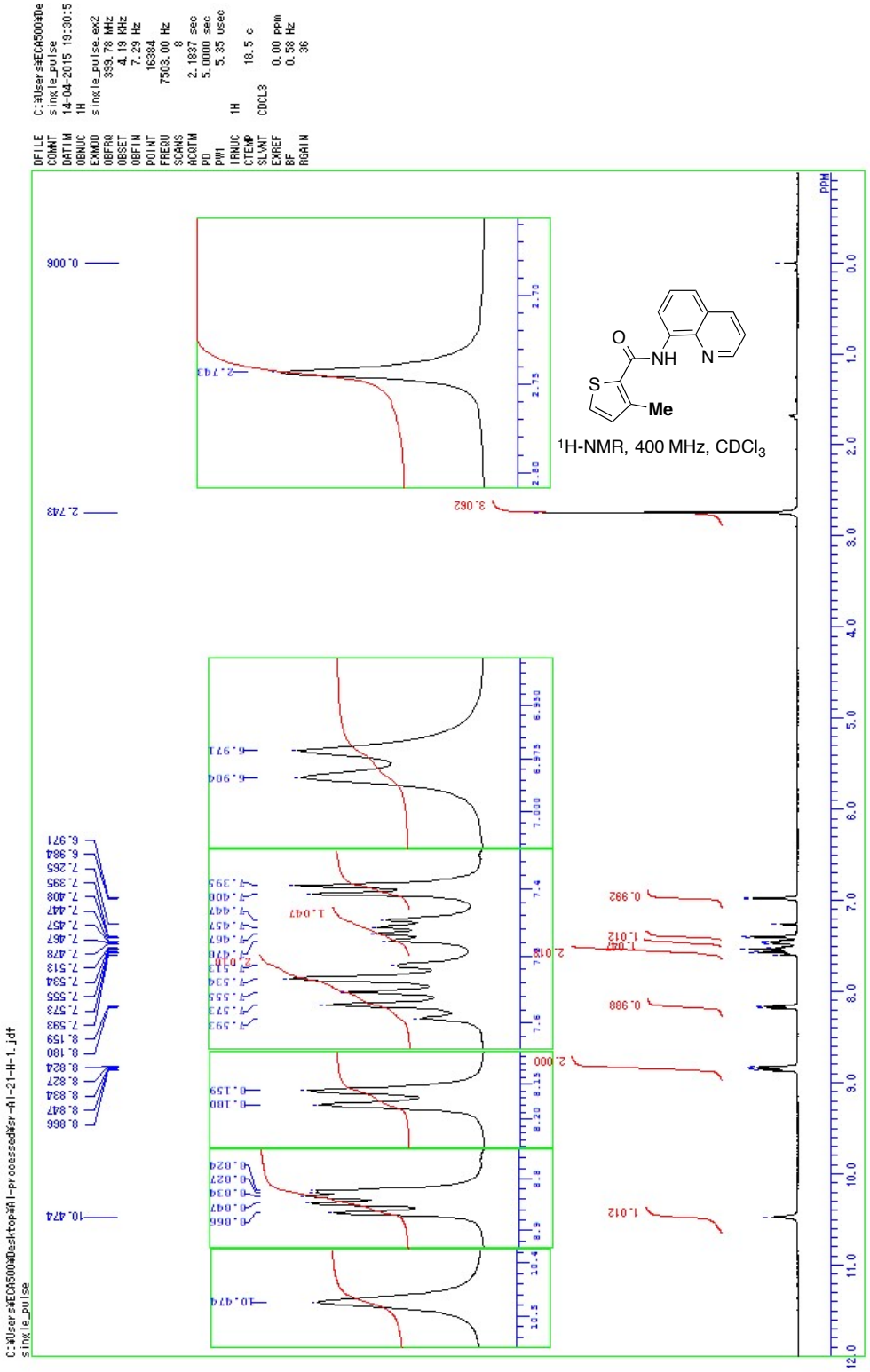
^{1}H NMR spectrum of **3,5-dimethyl-*N*-(quinolin-8-yl)isonicotinamide (24)**



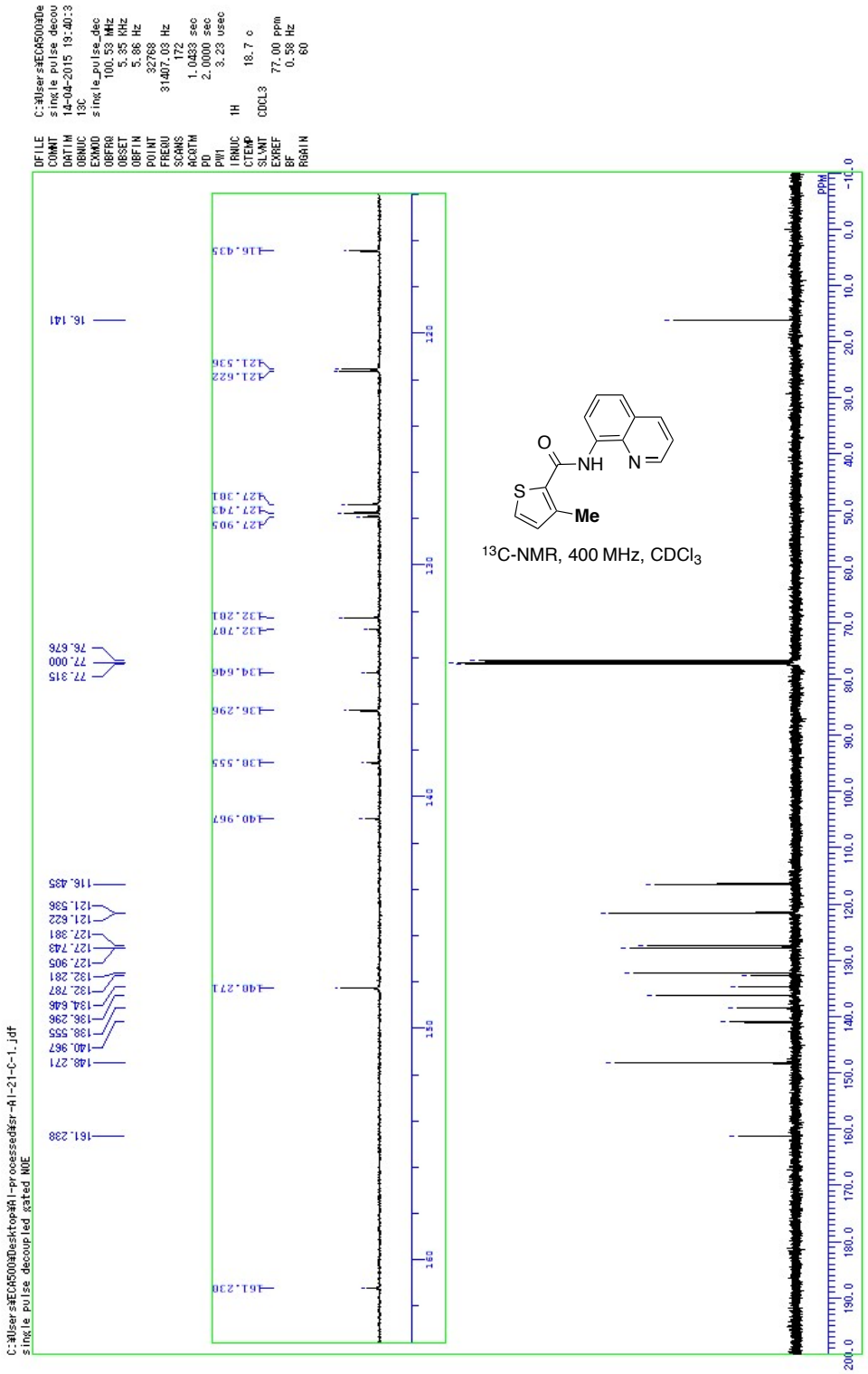
^{13}C NMR spectrum of **3,5-dimethyl-*N*-(quinolin-8-yl)isonicotinamide (24)**



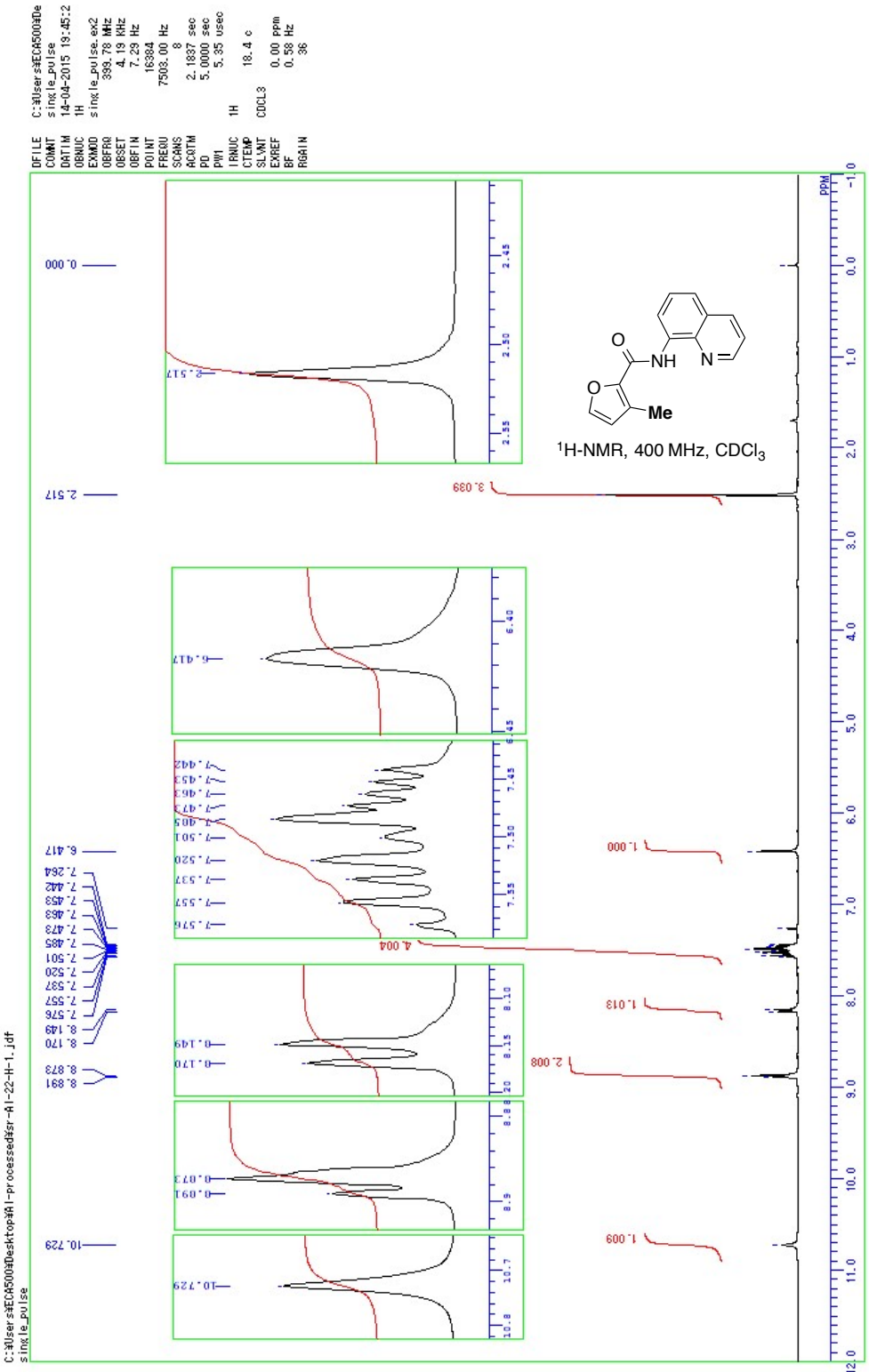
^{1}H NMR spectrum of **3-methyl-*N*-(quinolin-8-yl)thiophene-2-carboxamide (25)**



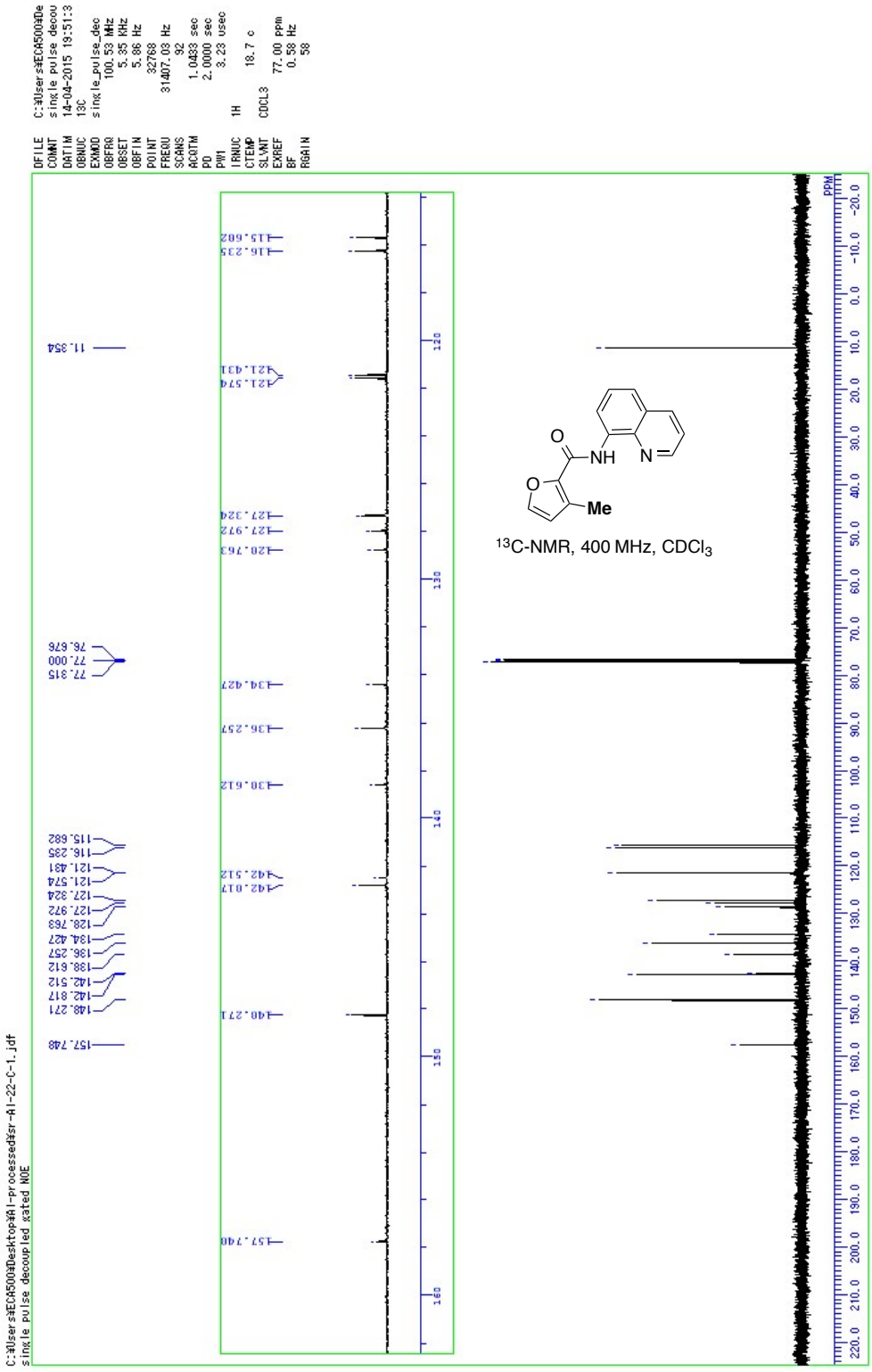
^{13}C NMR spectrum of **3-methyl-*N*-(quinolin-8-yl)thiophene-2-carboxamide (25)**



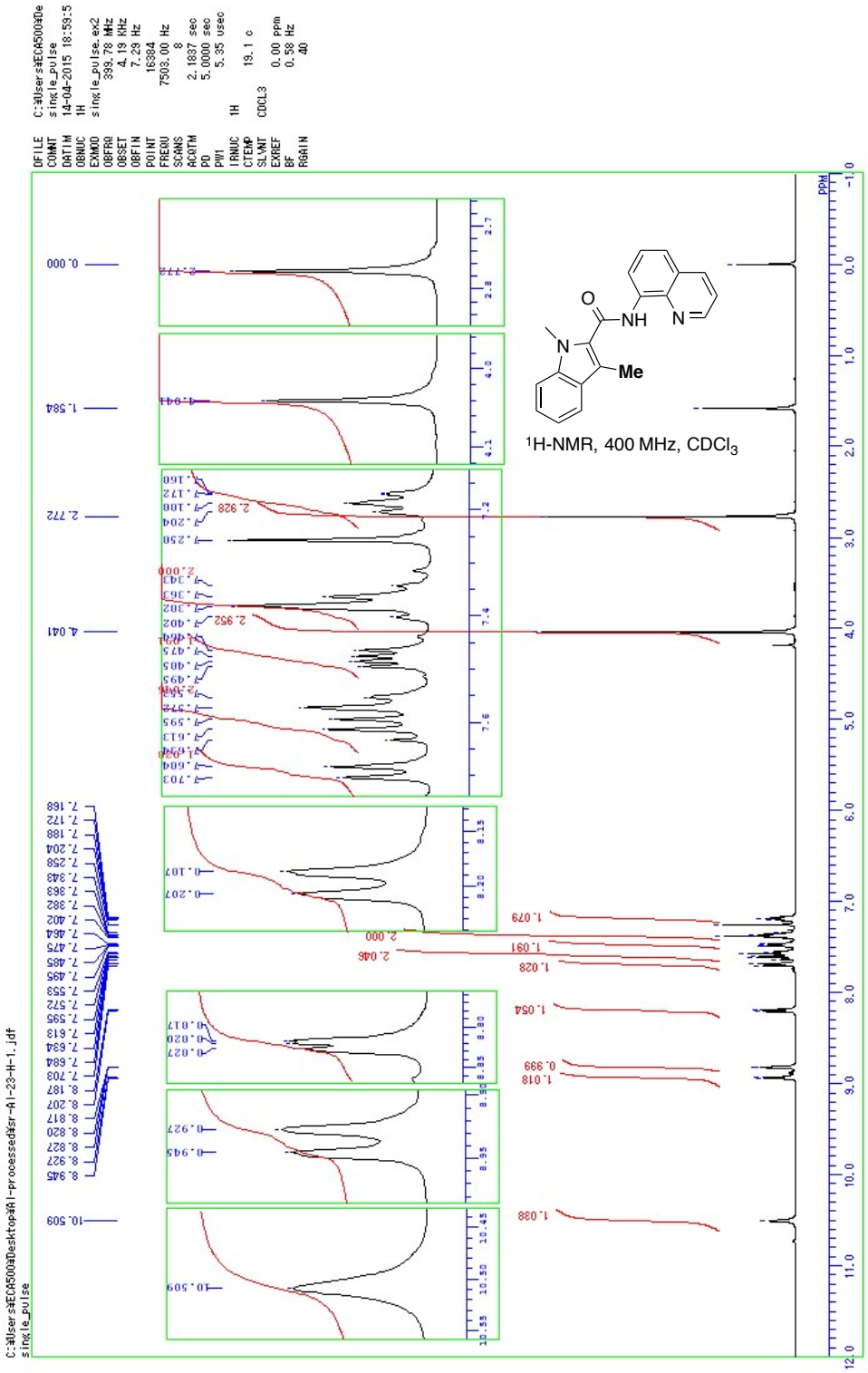
^{1}H NMR spectrum of **3-methyl-*N*-(quinolin-8-yl)furan-2-carboxamide (4)**



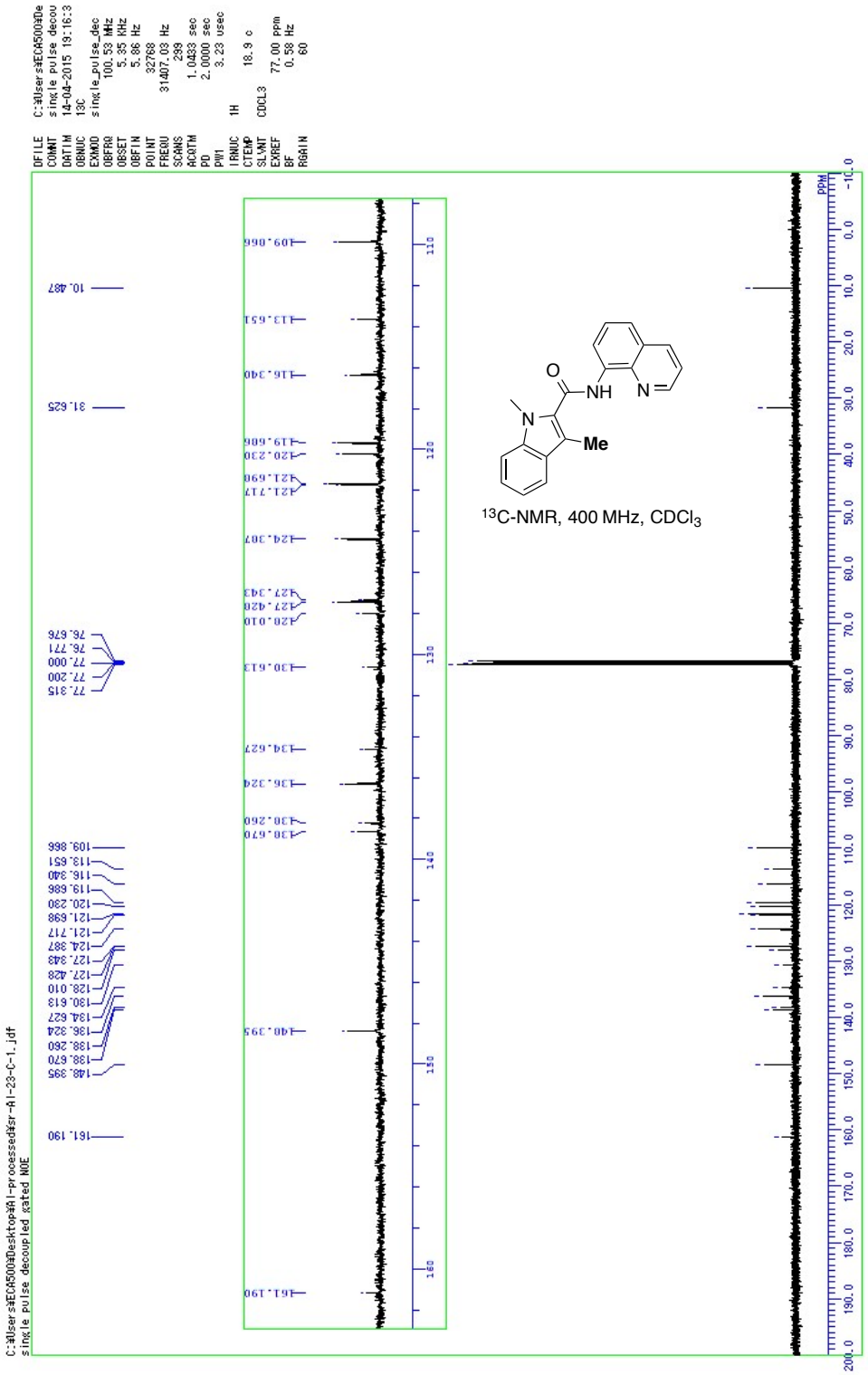
^{13}C NMR spectrum of **3-methyl-*N*-(quinolin-8-yl)furan-2-carboxamide (4)**



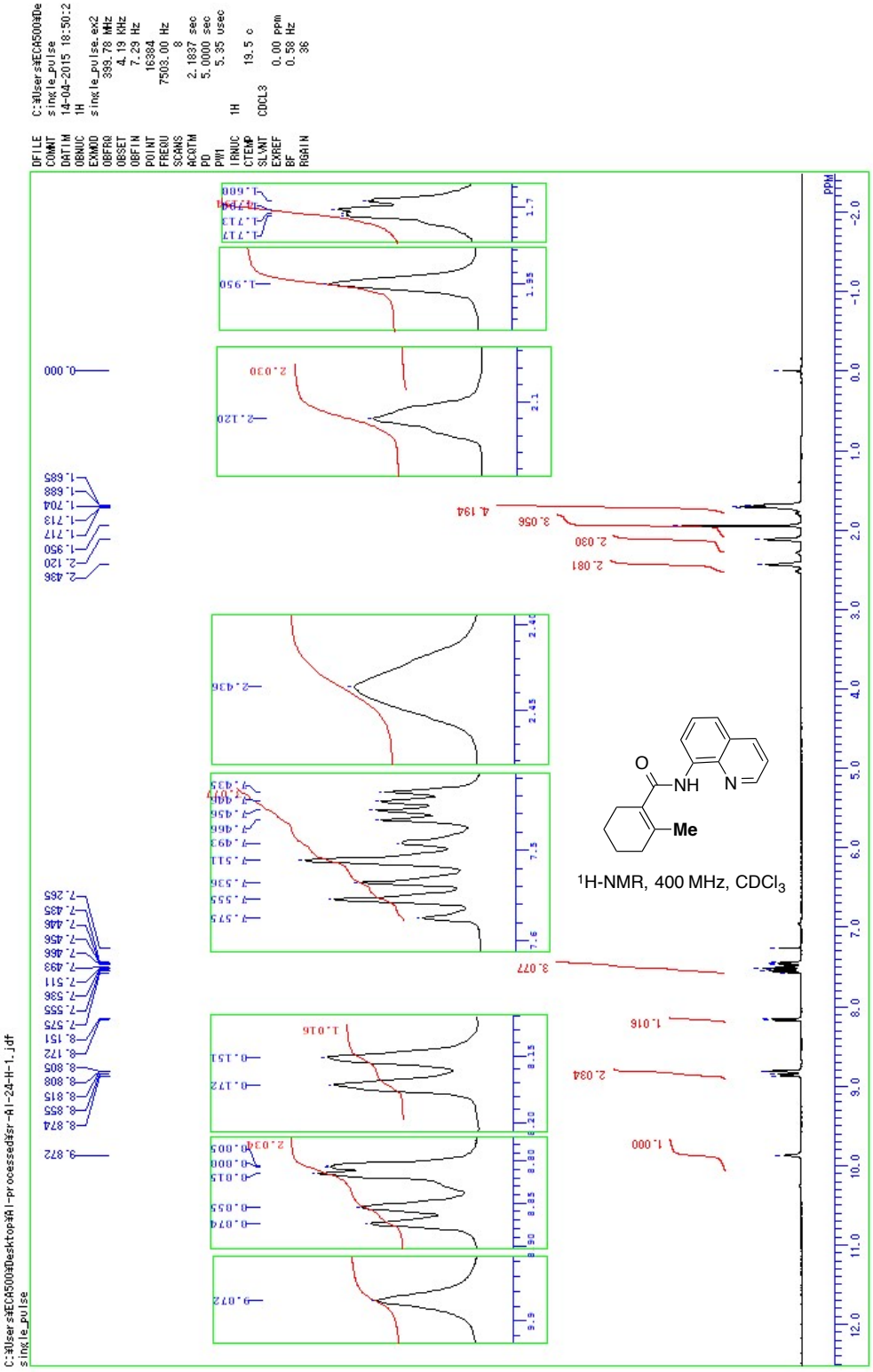
^{1}H NMR spectrum of **1,3-dimethyl-*N*-(quinolin-8-yl)-1*H*-indole-2-carboxamide (26)**



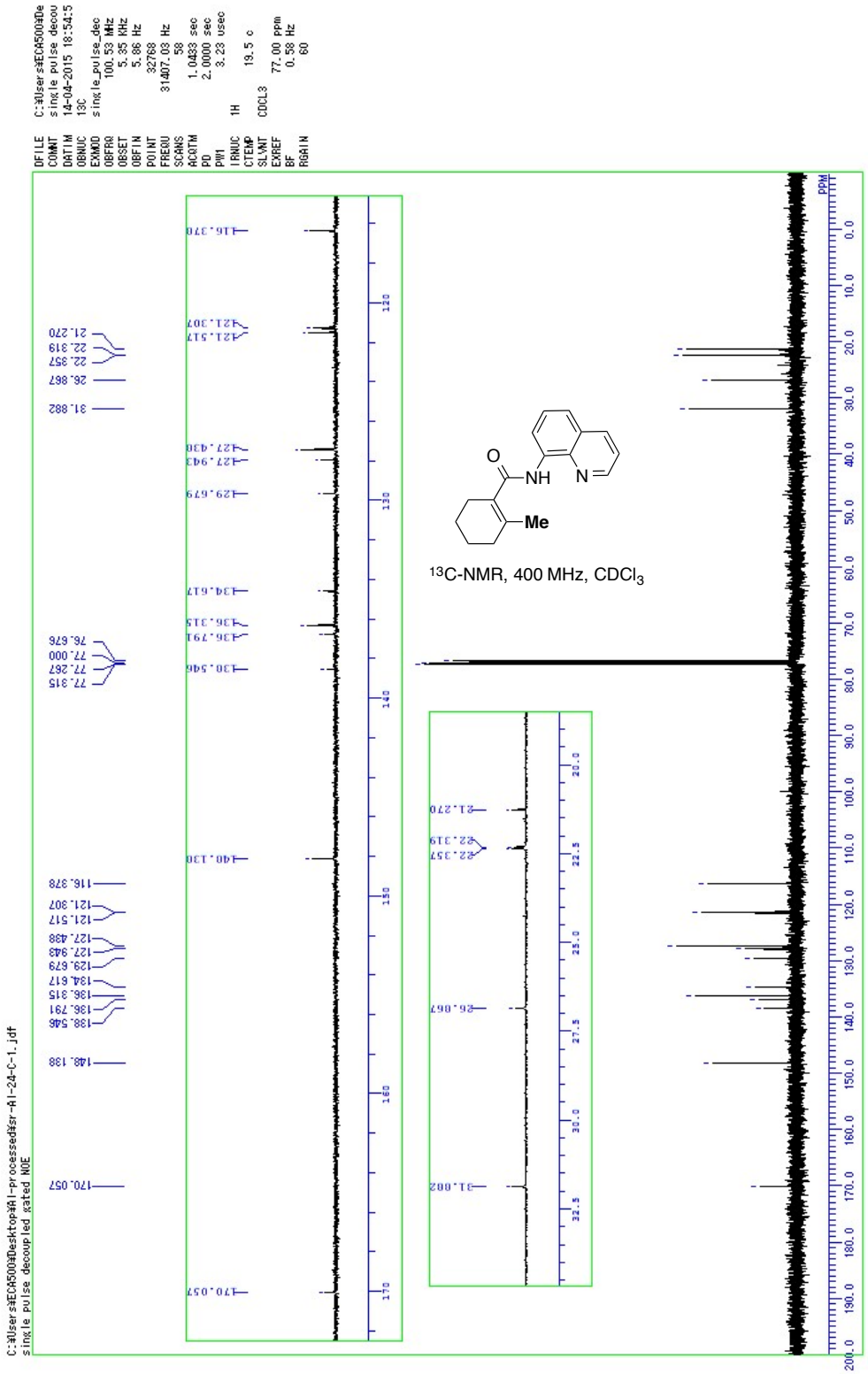
^{13}C NMR spectrum of **1,3-dimethyl-*N*-(quinolin-8-yl)-1*H*-indole-2-carboxamide (26)**



^{1}H NMR spectrum of **2-methyl-*N*-(quinolin-8-yl)cyclohex-1-ene-1-carboxamide (27)**

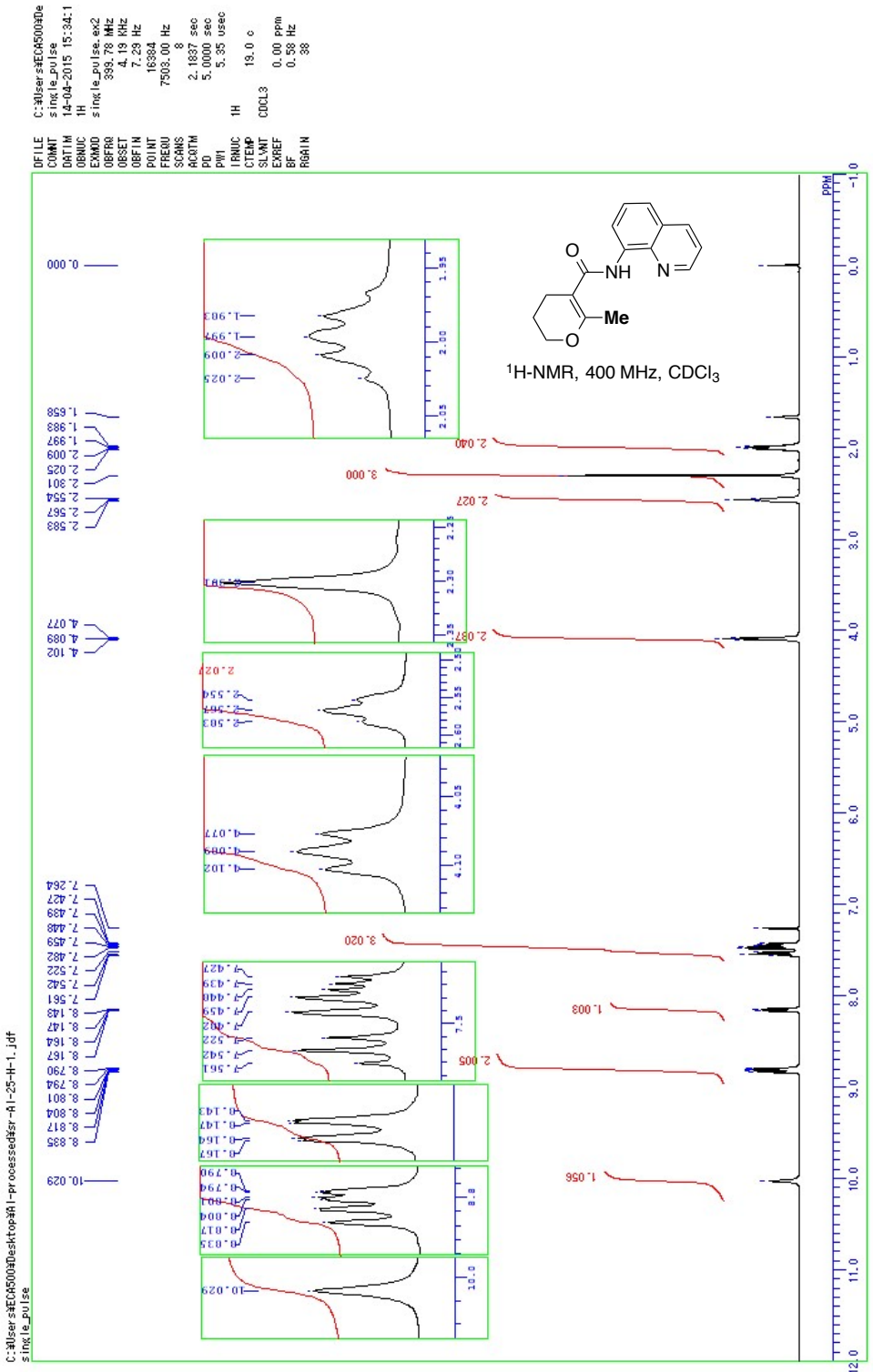


^{13}C NMR spectrum of **2-methyl-*N*-(quinolin-8-yl)cyclohex-1-ene-1-carboxamide (27)**



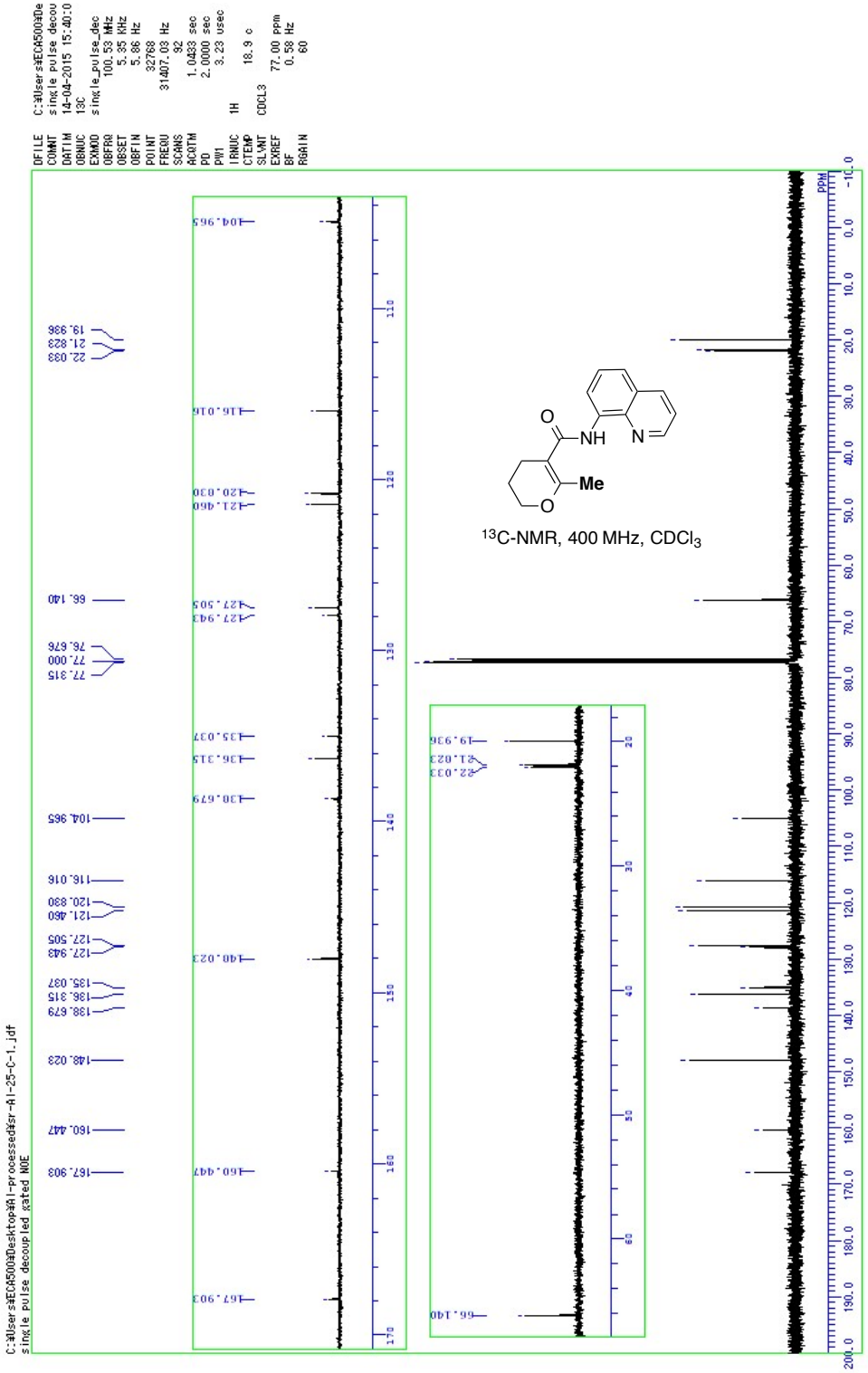
^{1}H NMR spectrum of

6-methyl-*N*-(quinolin-8-yl)-3,4-dihydro-2*H*-pyran-5-carboxamide (28)

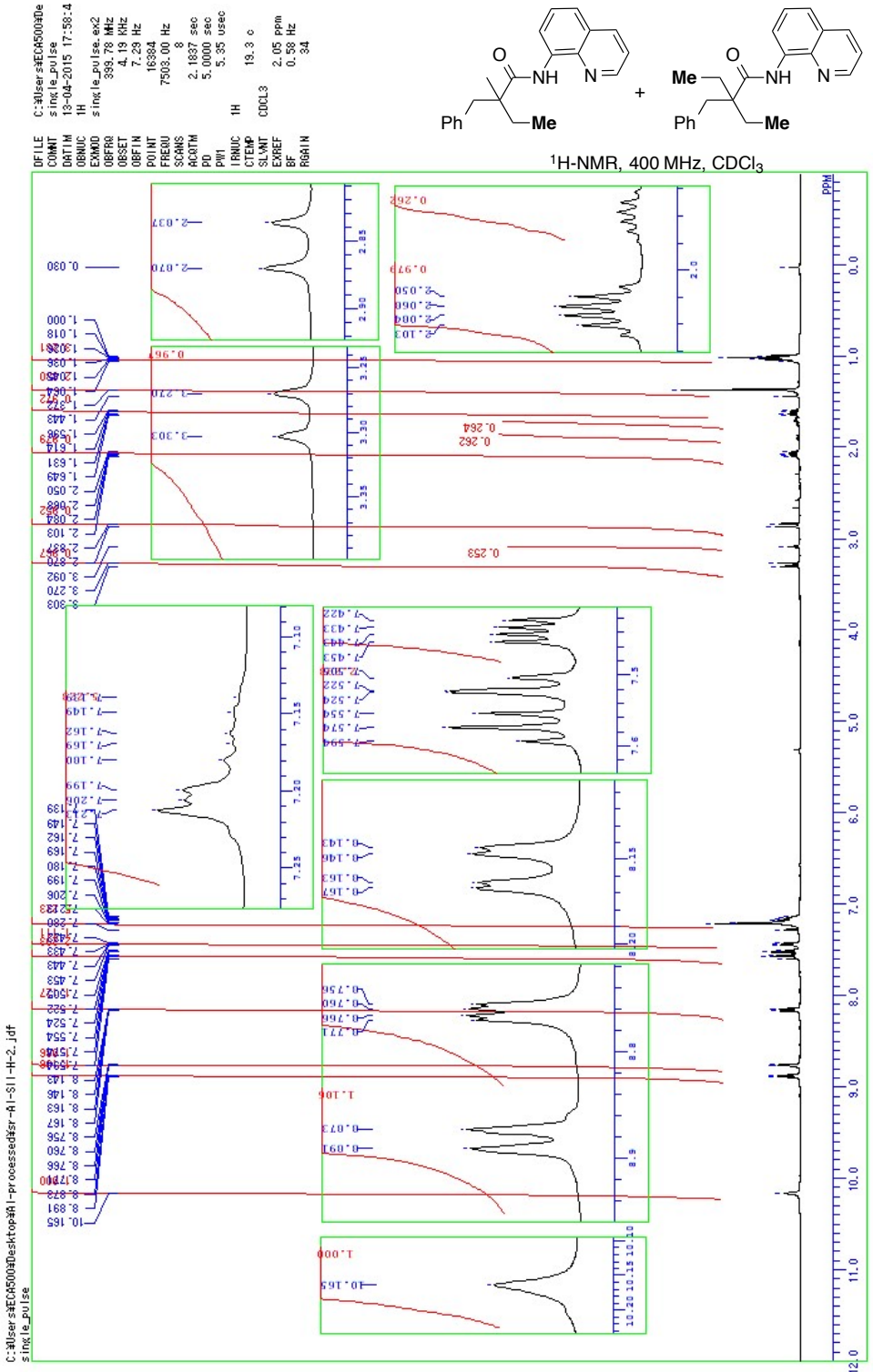


^{13}C NMR spectrum of

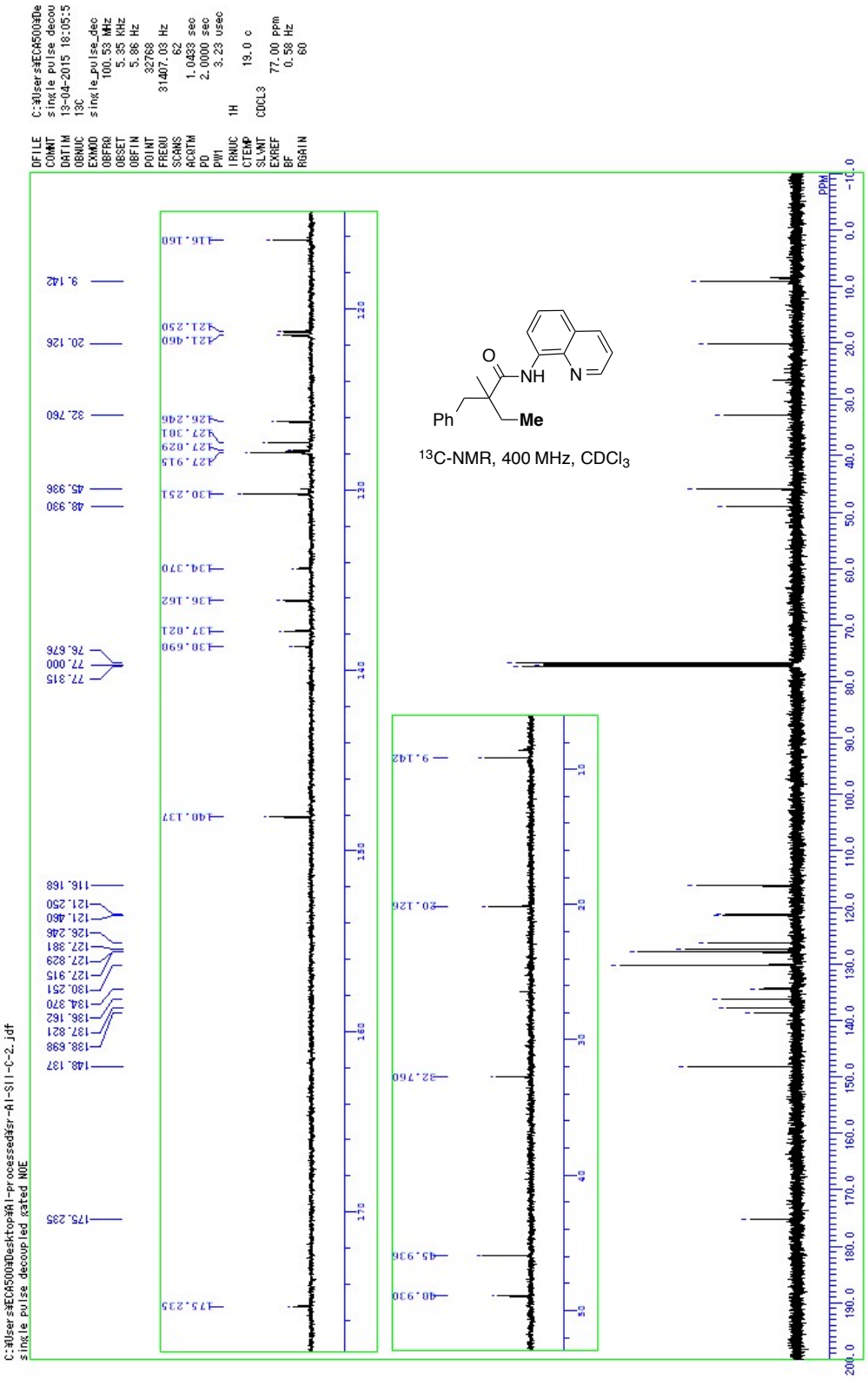
6-methyl-*N*-(quinolin-8-yl)-3,4-dihydro-2*H*-pyran-5-carboxamide (28)



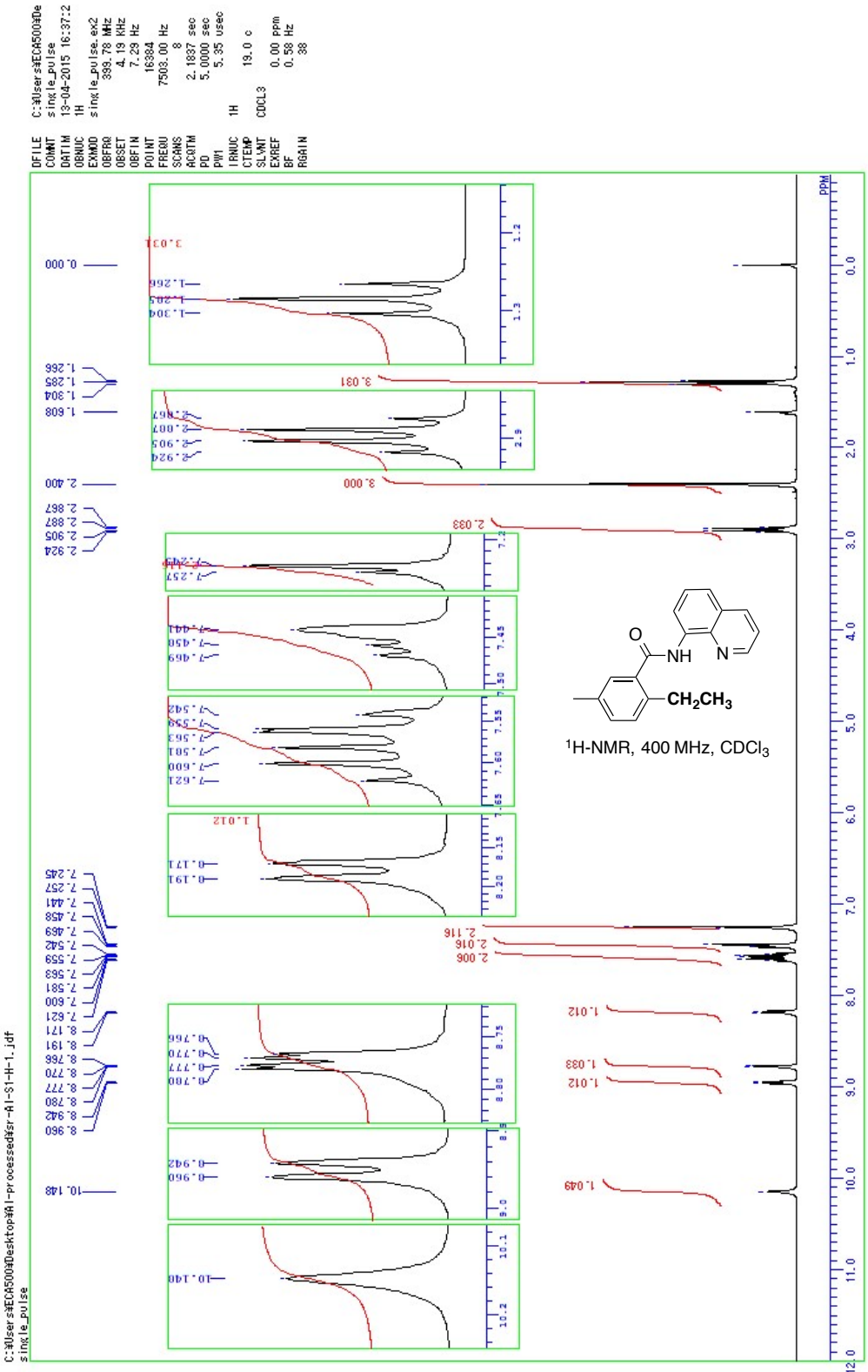
^{1}H NMR spectrum of **2-benzyl-2-methyl-*N*-(quinolin-8-yl)butanamide** and **2-benzyl-2-ethyl-*N*-(quinolin-8-yl)butanamide**



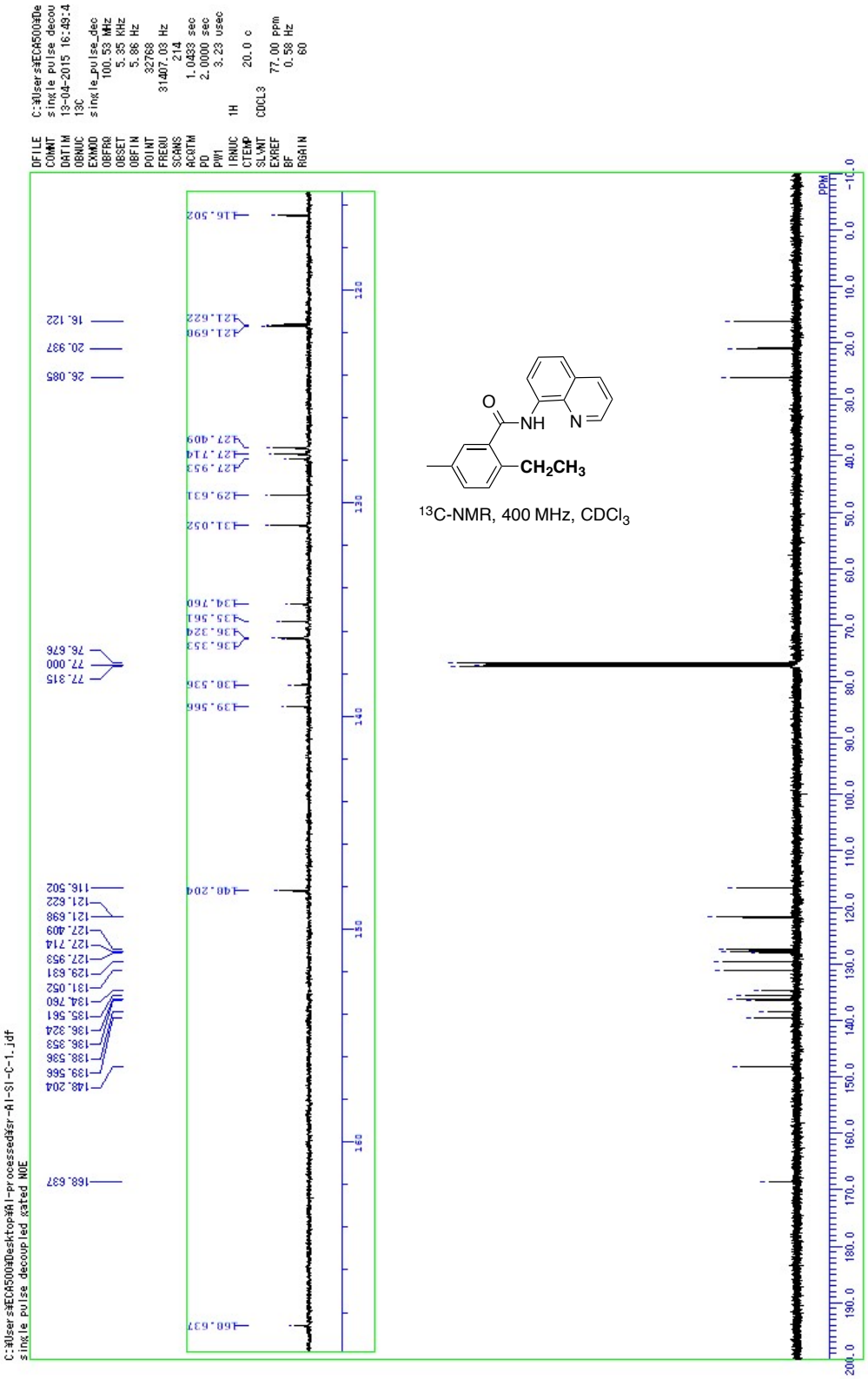
^{13}C NMR spectrum of **2-benzyl-2-methyl-*N*-(quinolin-8-yl)butanamide**



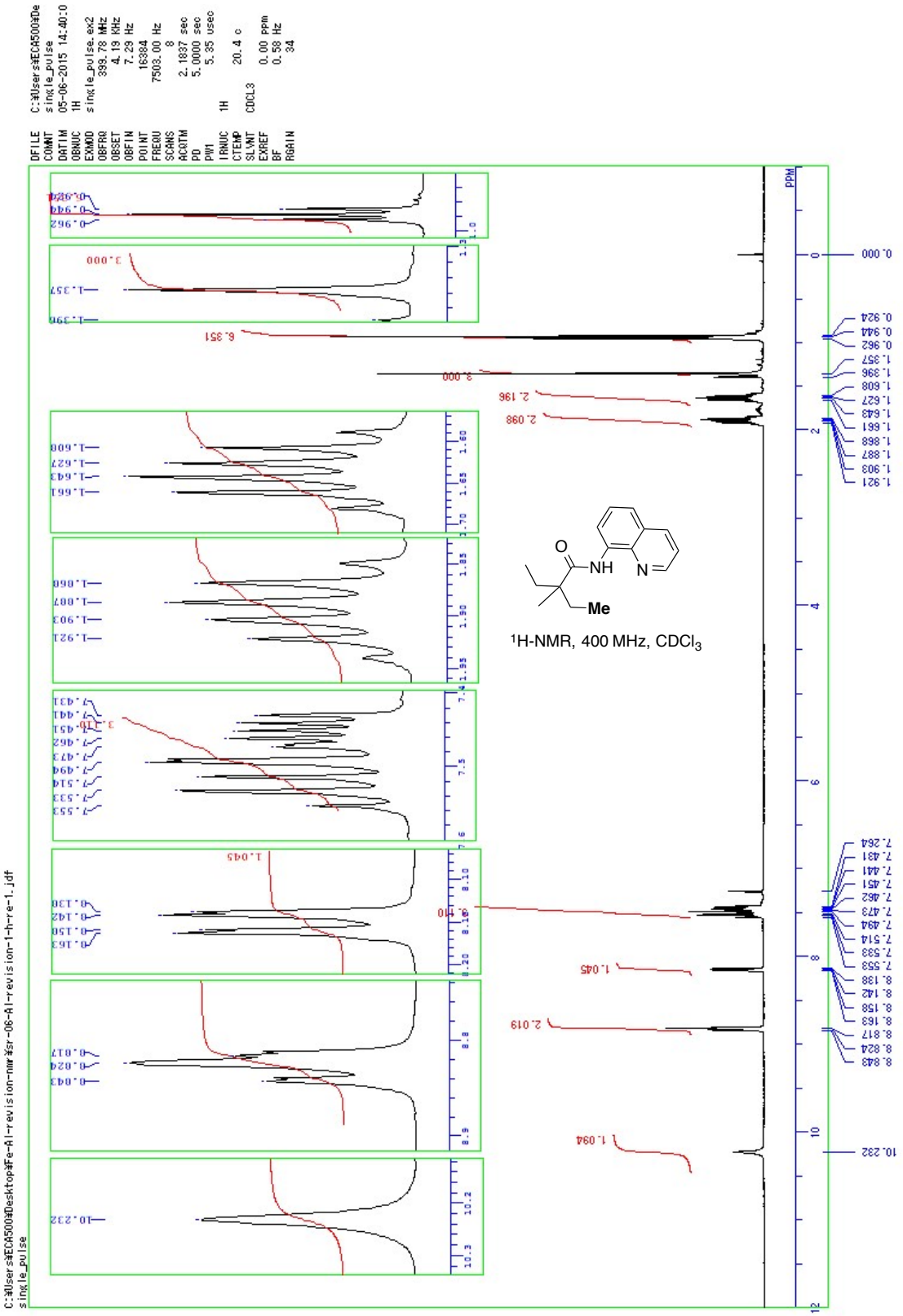
^{1}HNMR spectrum of **2-ethyl-5-methyl-*N*-(quinolin-8-yl)benzamide**



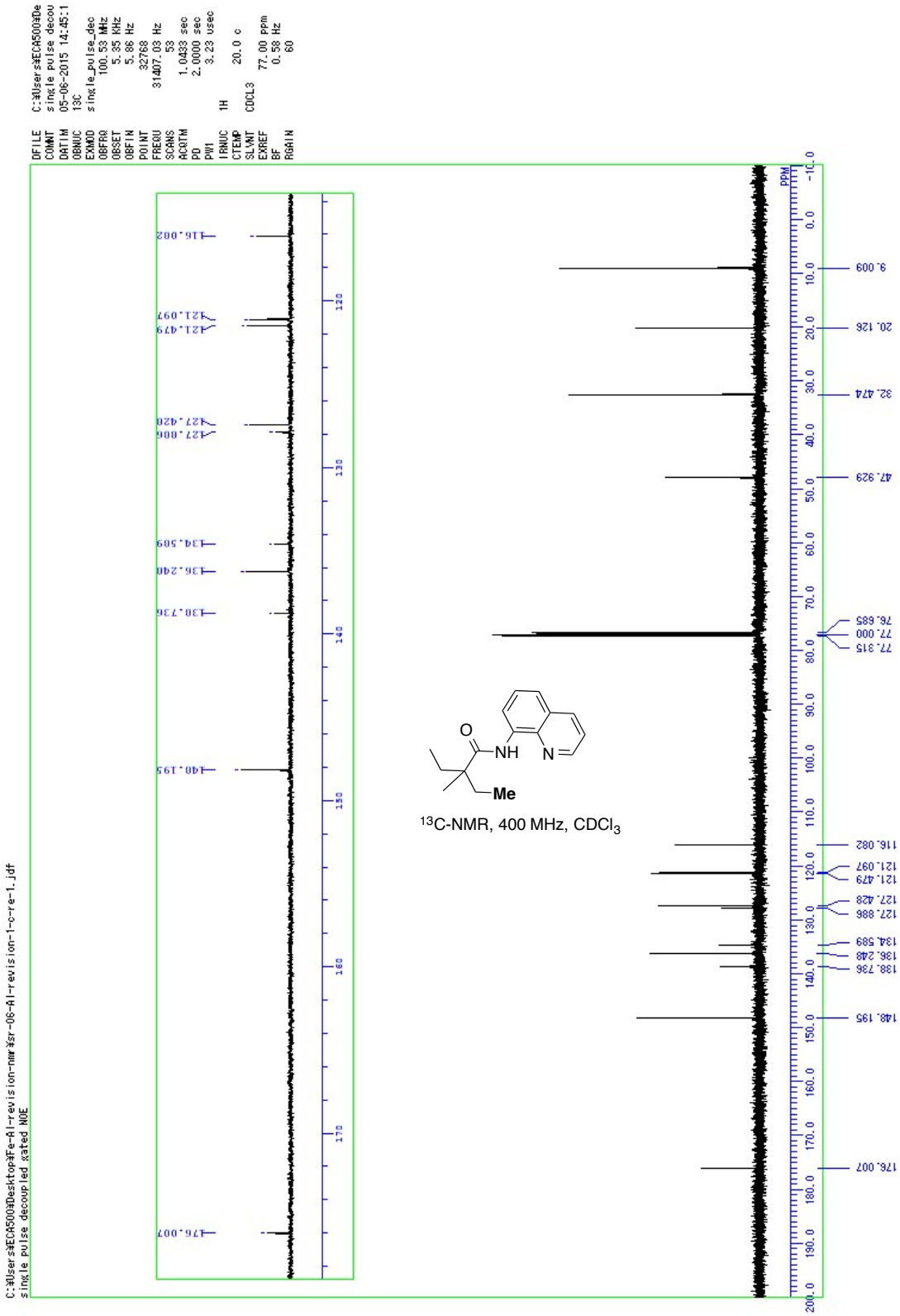
^{13}C NMR spectrum of **2-ethyl-5-methyl-*N*-(quinolin-8-yl)benzamide**



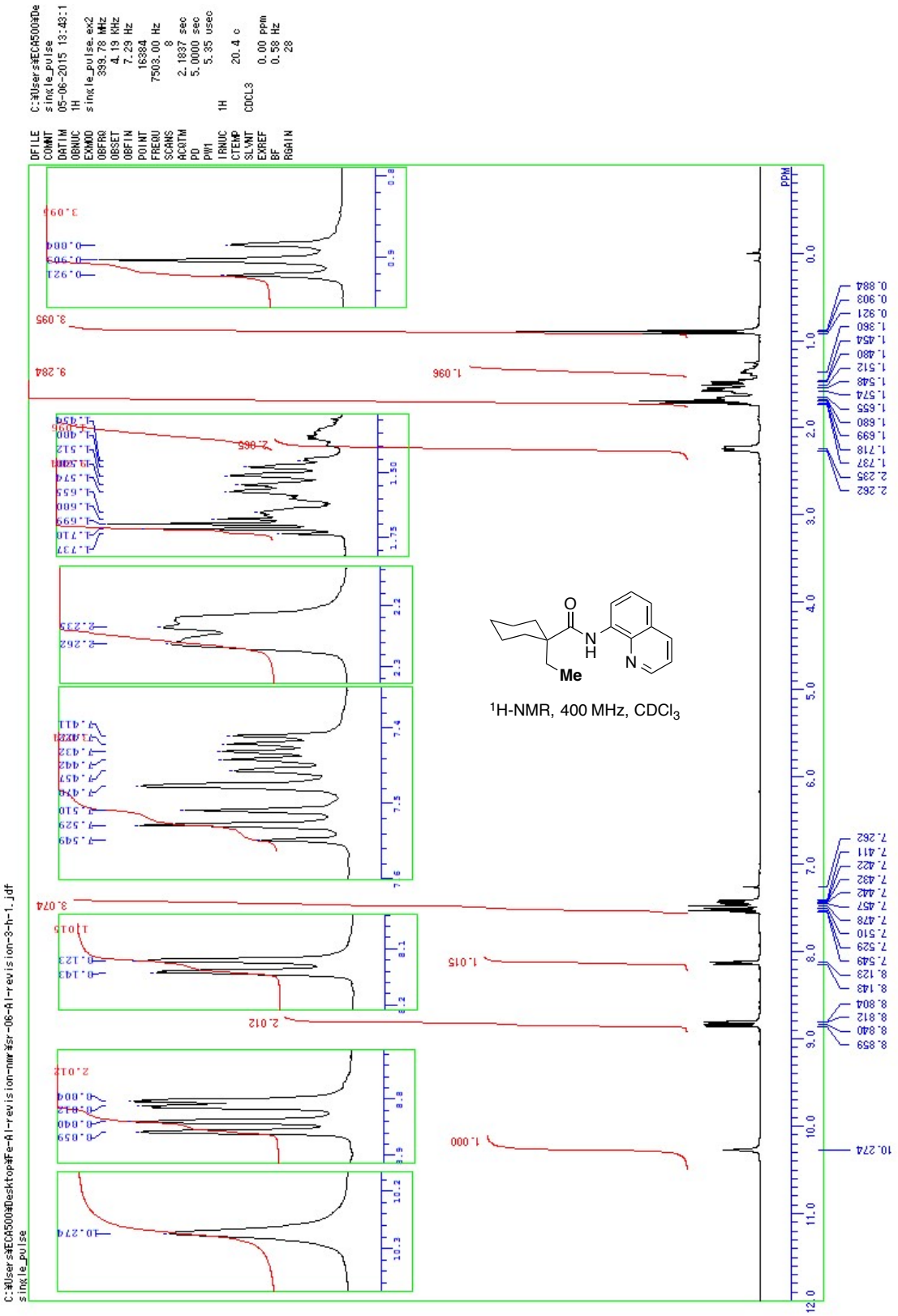
[1]HNMR spectrum of **2-ethyl-2-methyl-*N*-(quinolin-8-yl)butanamide (29)**



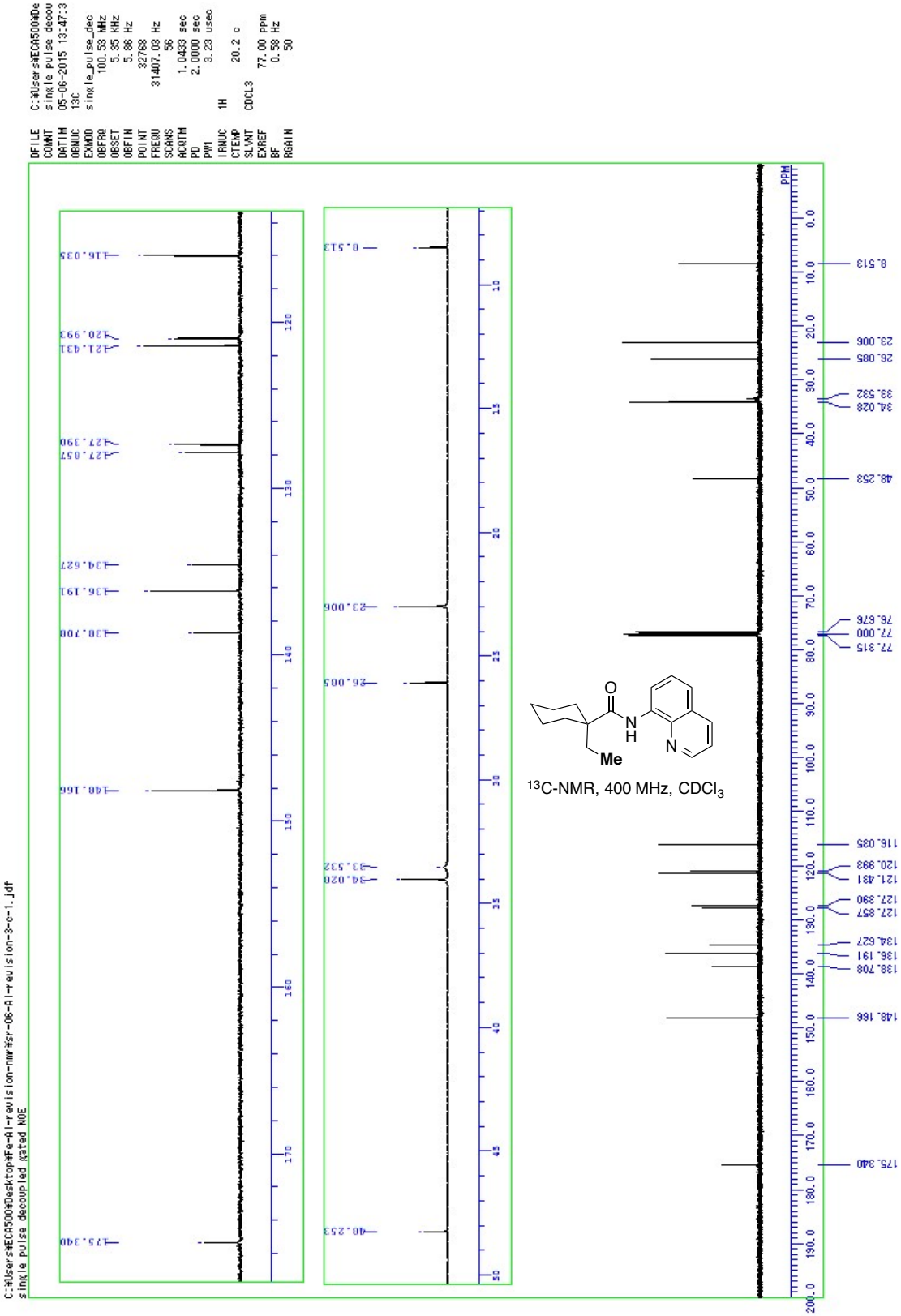
^{13}C NMR spectrum of **2-ethyl-2-methyl-*N*-(quinolin-8-yl)butanamide (29)**



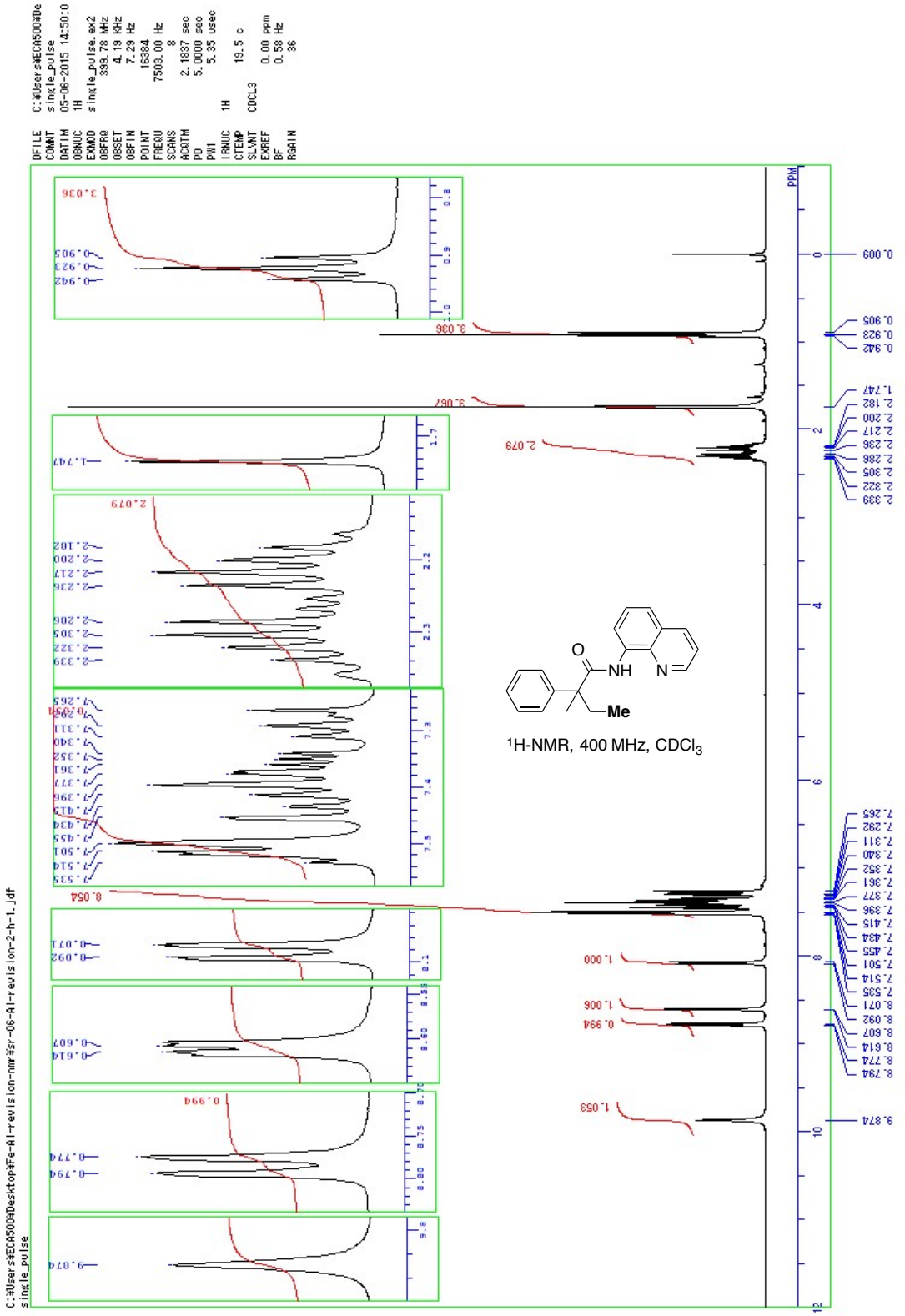
[1]HNMR spectrum of **1-ethyl-*N*-(quinolin-8-yl)cyclohexane-1-carboxamide (30)**



^{13}C NMR spectrum of **1-ethyl-*N*-(quinolin-8-yl)cyclohexane-1-carboxamide (30)**



^{1}HNMR spectrum of **2-methyl-2-phenyl-*N*-(quinolin-8-yl)butanamide (31)**



^{13}C NMR spectrum of **2-methyl-2-phenyl-*N*-(quinolin-8-yl)butanamide (31)**