

Tandem C–H Transformations by a Single Iridium Catalyst: Direct Access to Indoles and Indolines from *o*-Alkyl-*N*-methylanilines

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1. General

All iridium-catalyzed reactions were performed in glovebox under an atmosphere of nitrogen with magnetic stirring. Other reactions were also carried out under an atmosphere of nitrogen with magnetic stirring unless otherwise noted. Materials were weighted by an electric balance, Sartorius CPA225D or Shimadzu AP225WD (readability: 0.01 mg). Column chromatography was performed with SiliaFlash (SILICYCLE, pH 7.0, 40-63 μm , 60 \AA). Gas chromatography (GC) was performed by Shimadzu GC-2010 with Agilent J&W GC Column DB-1 (ϕ 0.32 mm x 15 m). GCMS analyses were performed by Shimadzu GCMS-QP2020 with Agilent J&W GC Column DB-1 (ϕ 0.32 mm x 15 m). ^1H NMR spectra were recorded on a Varian 400-MR (399.89 MHz) spectrometer. ^{13}C NMR spectra were recorded on a Varian 400-MR (100.55 MHz) spectrometer. ^{11}B NMR spectra were recorded on a Varian 400-MR (128.30 MHz) spectrometer. ^1H NMR data were reported as follows: chemical shifts in ppm downfield from tetramethylsilane, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), coupling constant (J), and integration. The chemical shifts of ^{13}C and ^{11}B NMR spectra were reported in ppm downfield from tetramethylsilane (^{13}C) and $\text{BF}_3\cdot\text{OEt}_2$ (^{11}B), respectively. High resolution mass spectra (HRMS) were recorded on a Thermo Scientific Exactive Plus (APCI, ESI) spectrometer.

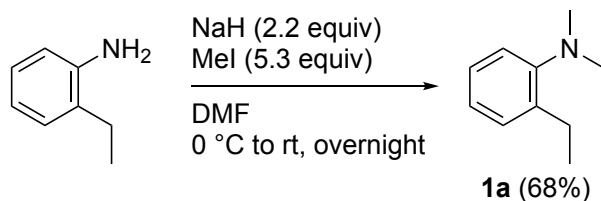
2. Materials

Solvents for Reactions: Mesitylene and 1,4-dioxane were distilled over benzophenone ketyl. Toluene (dehydrated, Super plus, Kanto), tetrahydrofuran (THF, dehydrated, Super plus, Kanto), and diethyl ether (dehydrated, Kanto) were purchased and used without further purification. Methylcyclohexane and hexane were distilled over calcium hydride and degassed. DMF, MeCN, and AcOEt were used as received.

Catalysts and Ligands: $[\text{IrCl}(\text{C}_2\text{H}_4)_2]_2$ was prepared according to the procedure reported previously¹ and stored at $-30\text{ }^\circ\text{C}$ under nitrogen atmosphere. **L1** [(*S*)-SEGPHOS, TCI], **L2** [(*S*)-DM-SEGPHOS, TCI], **L3** [(*S*)-DTBM-SEGPHOS, TCI], **L4** [(*S*)-MeOBIPHEP, Aldrich], **L5** [(*S*)-DTBM-MeOBIPHEP, Aldrich], **L6** [(*S*)-BINAP, Aldrich], and **L7** [(*S*)-DTBM-BINAP, Wako] were used as received from commercial source.

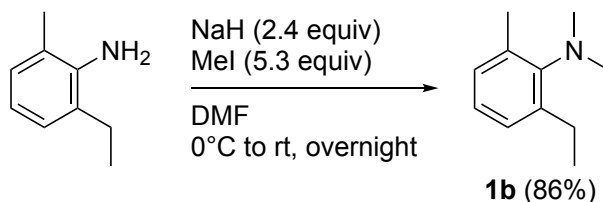
3. Preparation of Substrates 1a–q, 4, 6, 8, 3a, 9, and 11a

2-Ethyl-*N,N*-dimethylaniline (1a)



An oven dried 200 mL three-neck flask, equipped with a magnetic stirring bar, a rubber septum, and a three-way stopcock, was charged with NaH (ca. 60% dispersion in mineral oil, 1.0 g, 25 mmol). The flask was evacuated and backfilled with nitrogen. DMF (20 mL) and 2-ethylaniline (Wako, 1.36 g, 11 mmol) were added to the flask, and the mixture was cooled to 0 °C by ice/water bath. Methyl iodide (8.43 g, 59.5 mmol) was added slowly to the flask. The ice/water bath was removed, and the mixture was stirred overnight at room temperature. Hexane (30 mL), AcOEt (30 mL), and water (60 mL) were added to the flask. The organic phase was collected, washed with water (60 mL x 4) and brine (60 mL), and dried over anhydrous magnesium sulfate. The crude product was purified by column chromatography on silica gel (SiliaFlash; eluent: hexane:Et₂O = 10:1) and Kugelrohr distillation. **1a** (1.13 g, 7.57 mmol, 68% yield) was obtained as a colorless oil. **1a**: ¹H NMR (400 MHz, CDCl₃) δ 7.28 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.22 (td, *J* = 8.0, 1.6 Hz, 1H), 7.14 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.08 (td, *J* = 7.2, 1.6 Hz, 1H), 2.80 (q, *J* = 7.6 Hz, 2H), 2.74 (s, 6H), 1.31 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 152.6, 138.8, 129.0, 126.4, 123.4, 119.2, 45.2, 23.6, 14.9. HRMS (APCI, positive) *m/z* calcd for C₁₀H₁₆N⁺ [M + H]⁺: 150.1277, found: 150.1278.

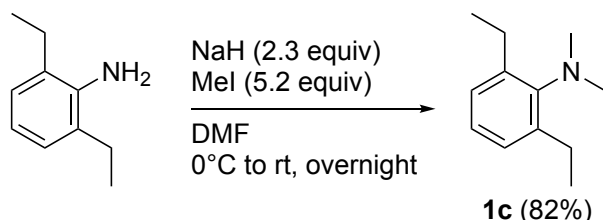
2-Ethyl-*N,N*,6-trimethylaniline (1b)



According to the procedure given for **1a**, **1b** (1.38 g, 8.45 mmol, 86% yield) was prepared as a colorless oil from 2-ethyl-6-methylaniline (TCI, 1.33 g, 9.83 mmol). **1b**: ¹H NMR (400 MHz, CDCl₃) δ 7.01-7.12 (m, 3H), 2.88 (s, 6H), 2.73 (q, *J* = 7.6 Hz, 2H), 2.36 (s, 3H), 1.27 (t, *J* = 7.6

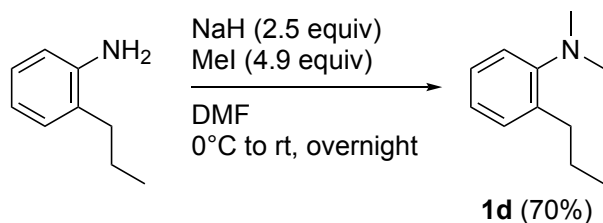
Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 149.3, 143.9, 137.7, 129.0, 127.0, 125.3, 43.1, 25.2, 19.3, 15.7. HRMS (APCI, positive) m/z calcd for $\text{C}_{11}\text{H}_{18}\text{N}^+$ $[\text{M} + \text{H}]^+$: 164.1434, found: 164.1434.

2,6-Diethyl-*N,N*-dimethylaniline (**1c**)



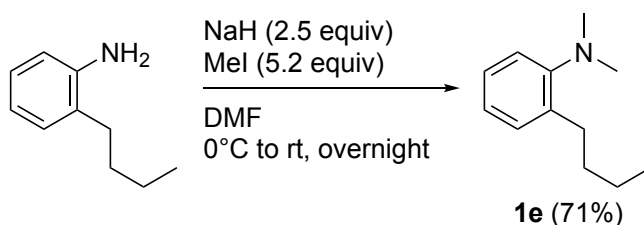
According to the procedure given for **1a**, **1c** (1.50 g, 10.1 mmol, 82% yield) was prepared as a colorless oil from 2,6-diethylaniline (TCI, 1.46 g, 8.24 mmol). **1c**: ^1H NMR (400 MHz, CDCl_3) δ 7.06-7.14 (m, 3H), 2.88 (s, 6H), 2.71 (q, $J = 7.6$ Hz, 4H), 1.27 (t, $J = 7.6$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 148.9, 144.2, 127.1, 125.7, 43.8, 25.1, 15.7. HRMS (APCI, positive) m/z calcd for $\text{C}_{12}\text{H}_{20}\text{N}^+$ $[\text{M} + \text{H}]^+$: 178.1590, found: 178.1590.

N,N-dimethyl-2-propylaniline (**1d**)



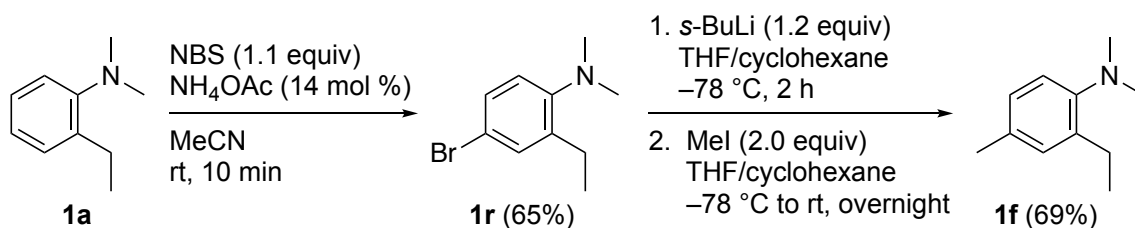
According to the procedure given for **1a**, **1d** (1.36 g, 10.1 mmol, 70% yield) was prepared as a colorless oil from 2-propylaniline (TCI, 1.16 g, 7.11 mmol). **1d**: ^1H NMR (400 MHz, CDCl_3) δ 7.13-7.23 (m, 2H), 7.10 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.02 (td, $J = 7.2, 1.6$ Hz, 1H), 2.69 (s, 6H), 2.65-2.71 (m, 2H), 1.68 (sextet, $J = 7.6$ Hz, 2H), 1.00 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 152.8, 137.6, 129.7, 126.5, 123.4, 119.4, 45.3, 32.9, 23.9, 14.5. HRMS (APCI, positive) m/z calcd for $\text{C}_{11}\text{H}_{18}\text{N}^+$ $[\text{M} + \text{H}]^+$: 164.1434, found: 164.1434.

2-Butyl-*N,N*-dimethylaniline (**1e**)



According to the procedure given for **1a**, **1e** (1.29 g, 7.28 mmol, 71% yield) was prepared as a colorless oil from 2-butylaniline (TCI, 1.52 g, 10.2 mmol). **1e**: ^1H NMR (400 MHz, CDCl_3) δ 7.24 (dd, $J = 7.2, 1.6$ Hz, 1H), 7.16-7.22 (m, 1H), 7.13 [dd (AB pattern), $J = 8.0, 1.6$ Hz, 1H], 7.05 (td, $J = 7.2, 1.6$ Hz, 1H), 2.72 (s, 6H), 2.70-2.77 (m, 2H), 1.63-1.72 (m, 2H), 1.45 (sextet, $J = 7.6$ Hz, 2H), 1.00 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 152.8, 137.7, 129.7, 126.4, 123.4, 119.4, 45.3, 33.0, 30.4, 23.1, 14.2. HRMS (APCI, positive) m/z calcd for $\text{C}_{12}\text{H}_{20}\text{N}^+$ [$\text{M} + \text{H}$] $^+$: 178.1590, found: 178.1590.

2-Ethyl-*N,N*,4-trimethylaniline (**1f**) and 4-Bromo-2-ethyl-*N,N*-dimethylaniline (**1r**)

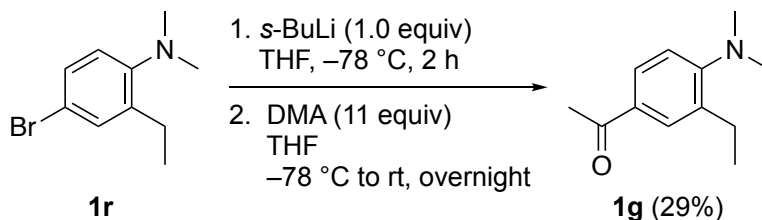


The bromination of **1a** was carried out according to the procedure reported.² A 50 mL flask, equipped with a magnetic stirring bar, was charged with **1a** (0.723 g, 4.84 mmol), ammonium acetate (54 mg, 0.701 mmol) and MeCN (10 mL). *N*-Bromosuccinimide (NBS, nacalai, 0.900 g, 5.06 mmol) was added slowly to the flask under air, and the resulting mixture was stirred for 10 min. The organic materials were extracted with CH_2Cl_2 (30 mL x 3), washed with brine (50 mL x 1), and dried over anhydrous sodium sulfate. The crude product was purified by column chromatography on silica gel (SiliaFlash; eluent: hexane: $\text{Et}_2\text{O} = 20:1$) and Kugelrohr distillation. **1r** (0.721 g, 3.16 mmol, 65% yield) was obtained as a colorless oil. **1r**: ^1H NMR (400 MHz, CDCl_3) δ 7.33 (d, $J = 2.4$ Hz, 1H), 7.26 (dd, $J = 8.4, 2.4$ Hz, 1H), 6.94 (d, $J = 8.4$ Hz, 1H), 2.70 (q, $J = 7.6$ Hz, 2H), 2.66 (s, 6H), 1.25 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 151.7,

141.2, 131.9, 129.3, 121.1, 116.4, 45.1, 23.5, 14.7. HRMS (APCI, positive) m/z calcd for $C_{10}H_{15}BrN^+$ $[M + H]^+$: 228.0382, found: 228.0383.

An oven dried 100 mL two-neck flask, equipped with a magnetic stirring bar, a rubber septum, and a three-way stopcock, was evacuated and backfilled with nitrogen. THF (10 mL) and **1r** (0.589 g, 2.58 mmol) were added to the flask, and the mixture was cooled to $-78\text{ }^\circ\text{C}$ by dry ice/acetone bath. *s*-BuLi (Kanto, 3.0 mL, 1.0 M solution in cyclohexane) was added slowly to the flask, and the resulting mixture was stirred for 2 h at $-78\text{ }^\circ\text{C}$. Methyl iodide (0.729 g, 5.14 mmol) was added slowly to the flask. The dry ice/acetone bath was removed, and the mixture was stirred overnight at room temperature. Water (20 mL) was added to the flask. The organic materials were extracted with Et_2O (15 mL x 3), washed with brine (30 mL x 1), and dried over anhydrous magnesium sulfate. The crude product was purified by column chromatography on silica gel (SiliaFlash; eluent: hexane: Et_2O = 20:1), GPC, and Kugelrohr distillation. **1f** (0.292 g, 1.79 mmol, 69% yield) was obtained as a colorless oil. **1f**: ^1H NMR (400 MHz, CDCl_3) δ 6.99-7.10 (m, 3H), 2.76 (q, J = 7.6 Hz, 2H), 2.70 (s, 6H), 2.34 (s, 3H), 1.29 (t, J = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 150.2, 138.9, 132.9, 129.8, 127.0, 119.3, 45.5, 23.5, 21.0, 15.1. HRMS (APCI, positive) m/z calcd for $C_{11}H_{18}N^+$ $[M + H]^+$: 164.1434, found: 164.1434.

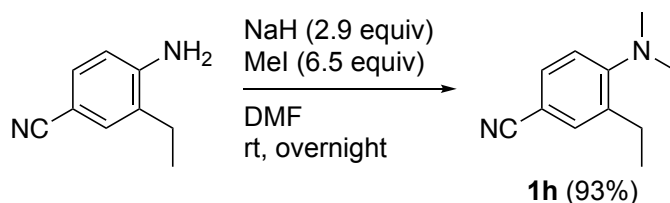
4-Acetyl-2-ethyl-*N,N*-dimethylaniline (**1g**)



An oven dried 100 mL two-neck flask, equipped with a magnetic stirring bar, a rubber septum, and a three-way stopcock, was evacuated and backfilled with nitrogen. THF (8 mL) and **1r** (0.448 g, 1.96 mmol) were added to the flask, and the mixture was cooled to $-78\text{ }^\circ\text{C}$ by dry ice/acetone bath. *s*-BuLi (1.0 M solution in cyclohexane, 2.0 mL, 2.0 mmol) was added slowly to the flask, and the resulting mixture was stirred for 2 h at $-78\text{ }^\circ\text{C}$. *N,N*-Dimethylacetamide (DMA, 2.0 mL, 22 mmol) was added slowly to the flask. The dry ice/acetone bath was removed, and the mixture was stirred overnight at room temperature. Water (20 mL) was added to the flask. The

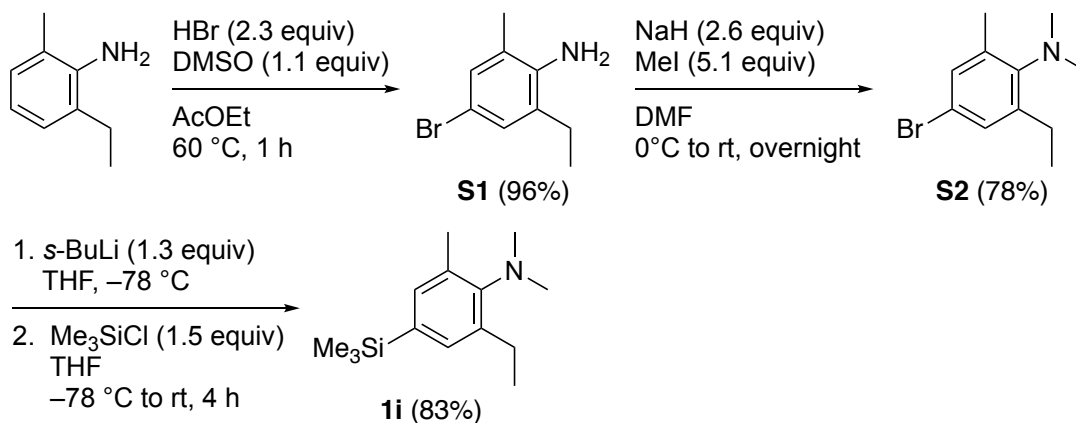
organic materials were extracted with Et₂O (20 mL x 3), washed with brine (50 mL x 1), and dried over anhydrous magnesium sulfate. The crude product was purified by column chromatography on silica gel (SiliaFlash; eluent: hexane:Et₂O = 90:10) and Kugelrohr distillation. **1g** (0.108 g, 0.565 mmol, 29% yield) was obtained as a colorless oil. **1g**: ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J* = 2.0 Hz, 1H), 7.74 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 1H), 2.77 (s, 6H), 2.73 (q, *J* = 7.6 Hz, 2H), 2.55 (s, 3H), 1.29 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 197.6, 157.1, 137.1, 131.3, 129.6, 127.4, 117.9, 44.3, 26.5, 24.2, 14.6. HRMS (APCI, positive) *m/z* calcd for C₁₂H₁₈NO⁺ [M + H]⁺: 192.1383, found: 192.1383.

4-Cyano-2-ethyl-*N,N*-dimethylaniline (**1h**)



According to the procedure given for **1a**, **1h** (0.649 g, 3.72 mmol, 93% yield) was prepared as a colorless oil from 4-cyano-2-ethylaniline (Wako, 0.588 g, 4.02 mmol). **1h**: ¹H NMR (400 MHz, CDCl₃) δ 7.44 (d, *J* = 2.0 Hz, 1H), 7.39 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 2.74 (s, 6H), 2.68 (q, *J* = 7.6 Hz, 2H), 1.24 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 156.5, 138.0, 132.8, 130.5, 119.9, 118.6, 104.8, 44.0, 23.8, 14.1. HRMS (ESI, positive) *m/z* calcd for C₁₁H₁₅N₂⁺ [M + H]⁺: 175.1230, found: 175.1231.

2-Ethyl-*N,N*,6-trimethyl-4-(trimethylsilyl)aniline (**1i**)



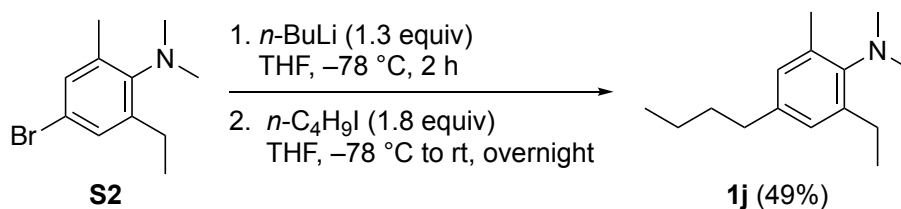
The bromination of 2-ethyl-6-methylaniline was carried out according to the procedure reported.³ A 500 mL three-neck flask, equipped with a magnetic stirring bar, a condenser, a rubber septum, and a three-way stopcock, was charged with EtOAc (80 mL), DMSO (1.65 g, 21.1 mmol), 2-ethyl-6-methylaniline (2.71 g, 20.0 mmol), and hydrogen bromide (48% aqueous solution, 7.68 g, 45.6 mmol). The mixture was stirred for 1 h at 60 °C. After cooling to room temperature, water (100 mL) was added to the flask, and potassium carbonate was added until the aqueous layer was basic. The organic materials were extracted with hexane (100 mL x 3), washed with brine (200 mL x 1), and dried over anhydrous magnesium sulfate. The crude product was purified by Kugelrohr distillation. **S1** (4.12 g, 19.2 mmol, 96% yield) was obtained as a colorless oil. **S1**: ¹H NMR (400 MHz, CDCl₃) δ 7.071 (s, 1H), 7.069 (s, 1H), 3.60 (broad s, 2H, NH₂), 2.49 (q, *J* = 7.6 Hz, 2H), 2.16 (s, 3H), 1.25 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 141.3, 130.4, 129.3, 128.5, 123.9, 109.8, 24.0, 17.5, 12.8. HRMS (APCI, positive) *m/z* calcd for C₉H₁₃BrN⁺ [M + H]⁺: 214.0226, found: 214.0228.

According to the procedure given for **1a**, **S2** (2.82 g, 11.6 mmol, 78% yield) was prepared as a colorless oil from **S1** (3.16 g, 14.8 mmol). **S2**: ¹H NMR (400 MHz, CDCl₃) δ 7.15 [d (AB pattern), *J* = 2.4 Hz, 1H], 7.12 [d (AB pattern), *J* = 2.4 Hz, 1H], 2.79 (s, 6H), 2.63 (q, *J* = 7.6 Hz, 2H), 2.26 (s, 3H), 1.19 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 148.5, 146.0, 139.9, 131.6, 129.8, 118.4, 42.9, 25.0, 19.1, 15.4. HRMS (APCI, positive) *m/z* calcd for C₁₁H₁₇BrN⁺ [M + H]⁺: 242.0539, found: 242.0541.

An oven dried 50 mL two-neck flask, equipped with a magnetic stirring bar, a rubber septum, and a three-way stopcock, was evacuated and backfilled with nitrogen. THF (8 mL) and **S2** (0.454 g, 1.87 mmol) were added to the flask, and the mixture was cooled to -78 °C by dry ice/acetone bath. *s*-BuLi (1.0 M in cyclohexane, 2.4 mL, 2.4 mmol) was added slowly to the flask, and the resulting mixture was stirred for 2 h at -78 °C. Me₃SiCl (0.311 g, 2.86 mmol) was added slowly to the flask. The dry ice/acetone bath was removed, and the mixture was stirred for 4 h at room temperature. Water (20 mL) was added to the flask. The organic materials were extracted with Et₂O (20 mL x 3), washed with brine (50 mL x 1), and dried over anhydrous magnesium sulfate. The crude product was purified by column chromatography on silica gel (SiliaFlash; eluent: hexane only) and Kugelrohr distillation. **1i** (0.367 g, 1.56 mmol, 83% yield) was obtained

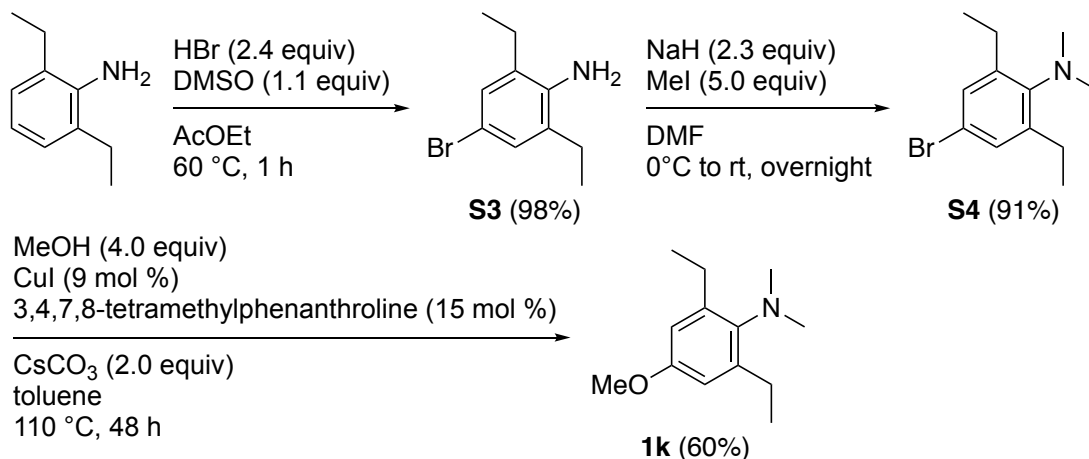
as a colorless oil. **1i**: ^1H NMR (400 MHz, CDCl_3) δ 7.21 (s, 1H), 7.16 (s, 1H), 2.85 (s, 6H), 2.70 (q, $J = 7.6$ Hz, 2H), 2.34 (s, 3H), 1.25 (t, $J = 7.6$ Hz, 3H), 0.28 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 150.1, 142.8, 136.7, 136.6, 134.4, 132.4, 43.1, 25.4, 19.4, 15.9, -0.8 . HRMS (APCI, positive) m/z calcd for $\text{C}_{14}\text{H}_{26}\text{NSi}^+$ [$\text{M} + \text{H}$] $^+$: 236.1829, found: 236.1830.

4-Butyl-2-ethyl-*N,N*,6-trimethylaniline (**1j**)



An oven dried 100 mL two-neck flask, equipped with a magnetic stirring bar, a rubber septum, and a three-way stopcock, was evacuated and backfilled with nitrogen. THF (8 mL) and **S2** (0.440 g, 1.82 mmol) were added to the flask, and the mixture was cooled to -78 $^\circ\text{C}$ by dry ice/acetone bath. *n*-BuLi (1.6 M solution in hexane, 1.5 mL, 2.4 mmol) was added slowly to the flask, and the resulting mixture was stirred for 2 h at -78 $^\circ\text{C}$. Butyl iodide (0.599 g, 3.26 mmol) was added slowly to the flask. The dry ice/acetone bath was removed, and the mixture was stirred overnight at room temperature. Water (20 mL) was added to the flask. The organic materials were extracted with Et_2O (20 mL x 3), washed with brine (50 mL x 1), and dried over anhydrous magnesium sulfate. The crude product was purified by column chromatography on silica gel (SiliaFlash; eluent: hexane: $\text{Et}_2\text{O} = 99:1$), GPC, and Kugelrohr distillation. **1j** (0.196 g, 0.893 mmol, 49% yield) was obtained as a colorless oil. **1j**: ^1H NMR (400 MHz, CDCl_3) δ 6.86 (s, 1H), 6.82 (s, 1H), 2.83 (s, 6H), 2.66 (q, $J = 7.6$ Hz, 2H), 2.50-2.56 (m, 2H), 2.29 (s, 3H), 1.55-1.65 (m, 2H), 1.34-1.46 (m, 2H), 1.22 (t, $J = 7.6$ Hz, 3H), 0.96 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 146.9, 143.5, 139.7, 137.3, 129.0, 127.0, 43.2, 35.3, 33.9, 25.2, 22.8, 19.3, 15.8, 14.2. HRMS (APCI, positive) m/z calcd for $\text{C}_{15}\text{H}_{26}\text{N}^+$ [$\text{M} + \text{H}$] $^+$: 220.2060, found: 220.2061.

2,6-Diethyl-4-methoxy-*N,N*-dimethylaniline (**1k**)



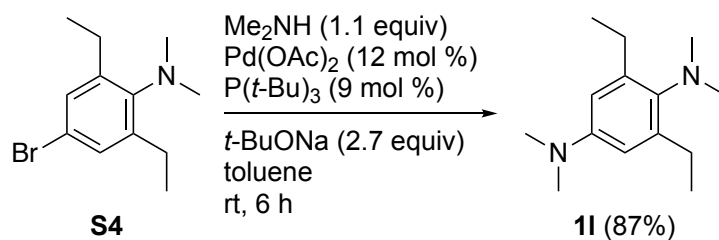
According to the procedure given for **S1**, **S3** (4.39 g, 19.2 mmol, 98% yield) was prepared as a colorless oil from 2,6-diethylaniline (2.92 g, 19.6 mmol). **S3**: ¹H NMR (400 MHz, CDCl₃) δ 7.08 (s, 2H), 3.63 (broad s, 2H, NH₂), 2.50 (q, *J* = 7.6 Hz, 4H), 1.25 (t, *J* = 7.6 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 140.7, 129.7, 128.5, 110.3, 24.1, 12.8. HRMS (APCI, positive) *m/z* calcd for C₁₀H₁₅BrN⁺ [*M* + H]⁺: 228.0382, found: 228.0385.

According to the procedure given for **1a**, **S4** (3.84 g, 15.0 mmol, 91% yield) was prepared as a colorless oil from **S3** (3.74 mg, 16.4 mmol). **S4**: ¹H NMR (400 MHz, CDCl₃) δ 7.16 (s, 2H), 2.80 (s, 6H), 2.63 (q, *J* = 7.6 Hz, 4H), 1.21 (t, *J* = 7.6 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 148.0, 146.4, 129.9, 119.1, 43.6, 24.9, 15.4. HRMS (APCI, positive) *m/z* calcd for C₁₂H₁₉BrN⁺ [*M* + H]⁺: 256.0695, found: 256.0696.

The copper-catalyzed C–O coupling was carried out according to the procedure reported.⁴ A glass tube (outside diameter: 20 mm) having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with CuI (35.4 mg, 0.186 mmol), 3,4,7,8-tetramethyl-1,10-phenanthroline (73.7 mg, 0.312 mmol), and CsCO₃ (1.36 g, 4.17 mmol). The tube was evacuated and backfilled with argon. **S4** (0.528 g, 2.06 mmol), MeOH (13.9 mg, 0.012 mmol), and toluene (1 mL) were added to the tube, and it was sealed by the stopcock. The mixture was stirred at 110 °C by a heating magnetic stirrer with an aluminum heating block (hole size: 21 mm diameter x 33 mm depth). After 48 h, the tube was cooled to room temperature, and water (20 mL) was added to the tube. The organic materials were extracted with AcOEt (20 mL x 3), washed with brine (50 mL x 1), and dried over anhydrous magnesium sulfate. The crude product was purified by column chromatography on silica gel (SiliaFlash; eluent: hexane:AcOEt

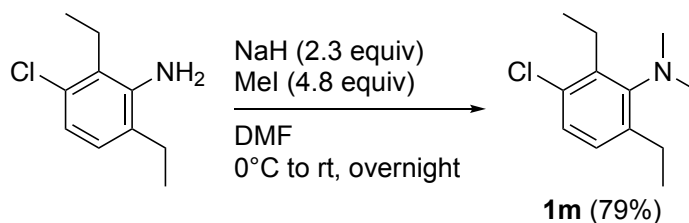
= 100:0 to 0:100) and Kugelrohr distillation. **1k** (0.257 g, 1.24 mmol, 60% yield) was obtained as a colorless oil. **1k**: ^1H NMR (400 MHz, CDCl_3) δ 6.61 (s, 2H), 3.80 (s, 3H), 2.83 (s, 6H), 2.66 (q, $J = 7.6$ Hz, 4H), 1.24 (t, $J = 7.6$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 157.1, 145.6, 142.1, 112.0, 55.3, 44.0, 25.3, 15.6. HRMS (APCI, positive) m/z calcd for $\text{C}_{13}\text{H}_{22}\text{NO}^+$ [$\text{M} + \text{H}$] $^+$: 208.1696, found: 208.1696.

2,6-Diethyl-*N,N,N',N'*-tetramethylbenzene-1,4-diamine (**1l**)



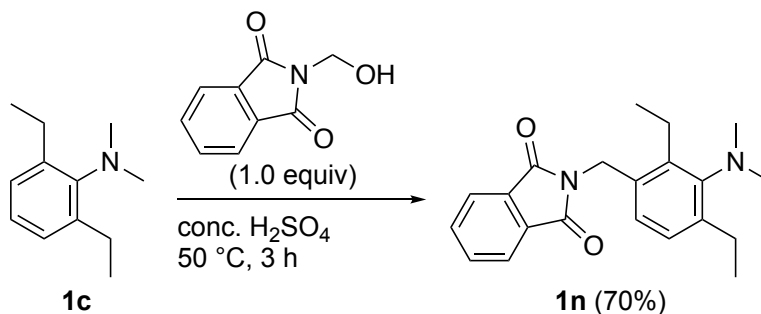
The palladium-catalyzed C–N coupling was carried out according to the procedure reported.⁵ In a glovebox, an oven dried 100 mL two-neck flask, equipped with a magnetic stirring bar, a three-way stop cock, and a rubber septum, was charged with $\text{Pd}(\text{OAc})_2$ (38 mg, 0.169 mmol), $\text{P}(t\text{-Bu})_3$ (26 mg, 0.129 mmol), $t\text{-BuONa}$ (0.37 g, 3.85 mmol), and toluene (2 mL). The stopcock was closed, and the flask was taken out from glovebox. Dimethylamine (0.75 mL, 1.5 mmol) and **S4** (0.362 g, 1.41 mmol) were added, and the mixture was stirred for 6 h at room temperature. Water (20 mL) was added to the flask. The organic materials were extracted with Et_2O (20 mL x 3), washed with brine (50 mL x 1), and dried over anhydrous magnesium sulfate. The crude product was purified by column chromatography on silica gel (SiliaFlash; eluent: hexane: Et_2O = 20:1) and Kugelrohr distillation. **1l** (0.272 g, 1.23 mmol, 87% yield) was obtained as a colorless oil. **1l**: ^1H NMR (400 MHz, CDCl_3) δ 6.47 (s, 2H), 2.94 (s, 6H), 2.83 (s, 6H), 2.65 (q, $J = 7.6$ Hz, 4H), 1.25 (t, $J = 7.6$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 148.6, 144.9, 139.1, 111.7, 44.2, 41.1, 25.6, 16.0. HRMS (APCI, positive) m/z calcd for $\text{C}_{14}\text{H}_{25}\text{N}_2^+$ [$\text{M} + \text{H}$] $^+$: 221.2012, found: 221.2013.

3-Chloro-2,6-diethyl-*N,N*-dimethylaniline (1m)



According to the procedure given for **1a**, **1m** (1.76 g, 8.31 mmol, 79% yield) was prepared as a yellow oil from 3-chloro-2,6-diethylaniline (Aldrich, 1.92 g, 10.5 mmol). **1m**: ^1H NMR (400 MHz, CDCl_3) δ 7.14 (d, $J = 8.4$ Hz, 1H), 6.97 (d, $J = 8.4$ Hz, 1H), 2.85 (s, 6H), 2.82 (q, $J = 7.6$ Hz, 2H), 2.63 (q, $J = 7.6$ Hz, 2H), 1.22 (t, $J = 7.6$ Hz, 3H), 1.21 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 150.5, 143.3, 142.6, 132.1, 127.7, 127.0, 43.9, 24.8, 23.2, 15.5, 14.2. HRMS (APCI, positive) m/z calcd for $\text{C}_{12}\text{H}_{19}\text{ClN}^+ [\text{M} + \text{H}]^+$: 212.1201, found: 212.1202.

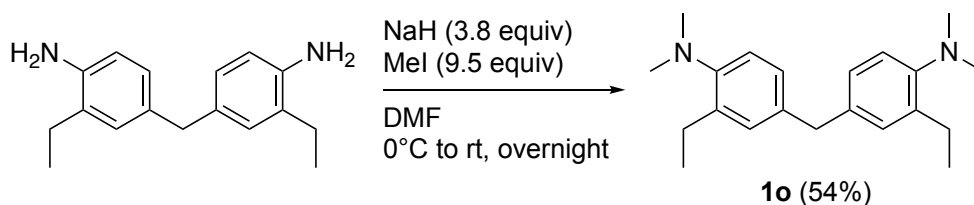
2,6-Diethyl-3-(phthalimidomethyl)-*N,N*-dimethylaniline (1n)



The titled compound was synthesized according to the procedure reported.⁶ An oven dried 200 mL three-neck flask, equipped with a magnetic stirring bar, a rubber septum, and a three-way stopcock, was evacuated and backfilled with nitrogen. **1c** (1.75 g, 9.87 mmol) and conc. H_2SO_4 (10 mL) was added to the flask. *N*-hydroxymethylphthalimide (Kanto, 1.75 g, 9.88 mmol) was added to the flask over 20 min. The mixture was stirred for 3 h at 50 °C. After cooling to room temperature, ice was added to the flask, and potassium carbonate was added until the aqueous layer was basic. The organic materials were extracted with Et_2O (50 mL x 3), washed with brine (50 mL x 1), and dried over anhydrous magnesium sulfate. The crude product was purified by distillation using Kugelrohr. **1n** (2.33 g, 6.93 mmol, 70% yield) was as a white solid. **1n**: ^1H NMR (400 MHz, CDCl_3) δ 7.83-7.89 (m, 2H), 7.69-7.75 (m, 2H), 7.03 [d (AB pattern), $J = 8.0$ Hz, 1H], 6.97 [d (AB pattern), $J = 8.0$ Hz, 1H], 4.89 (s, 2H), 2.92 (q, $J = 7.6$ Hz, 2H), 2.84 (s,

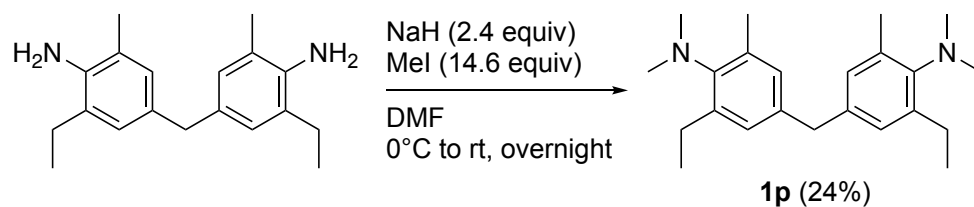
6H), 2.61 (q, $J = 7.6$ Hz, 2H), 1.23 (t, $J = 7.6$ Hz, 3H), 1.19 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 168.4, 149.3, 143.9, 142.9, 134.1, 132.4, 132.3, 127.1, 125.5, 123.4, 44.0, 39.1, 24.7, 21.5, 15.7, 15.4. HRMS (APCI, positive) m/z calcd for $\text{C}_{21}\text{H}_{25}\text{N}_2\text{O}_2^+$ [$\text{M} + \text{H}$] $^+$: 337.1911, found: 337.1912.

4,4'-Methylenebis(2-ethyl-*N,N*-dimethylaniline) (**1o**)



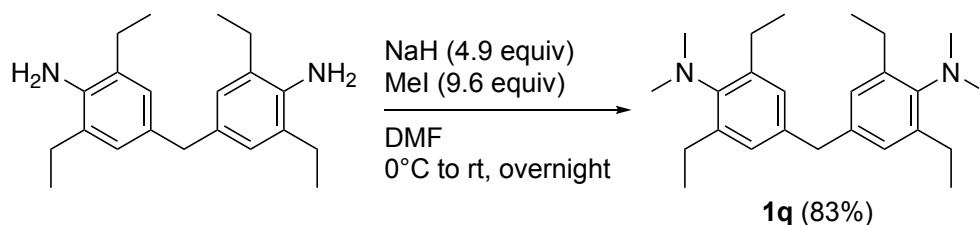
According to the procedure given for **1a**, **1o** (1.84 g, 5.92 mmol, 54% yield) was prepared as a colorless oil from 4,4'-methylenebis(2-ethylaniline) (Combi Blocks, 2.81 g, 11.0 mmol). **1o**: ^1H NMR (400 MHz, CDCl_3) δ 7.24 (d, $J = 2.0$, 2H), 7.17 (d, $J = 8.4$ Hz, 2H), 7.13 (dd, $J = 8.4$, 2.0 Hz, 2H), 4.03 (s, 2H), 2.87 (q, $J = 7.6$ Hz, 4H), 2.81 (s, 12H), 1.40 (t, $J = 7.6$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 150.6, 138.8, 136.4, 129.6, 126.7, 119.3, 45.4, 41.1, 23.6, 15.1. HRMS (APCI, positive) m/z calcd for $\text{C}_{21}\text{H}_{31}\text{N}_2^+$ [$\text{M} + \text{H}$] $^+$: 311.2482, found: 311.2485.

4,4'-Methylenebis(2-ethyl-*N,N*,6-trimethylaniline) (**1p**)



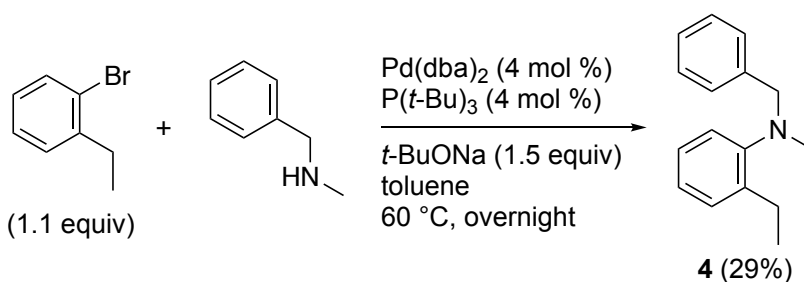
According to the procedure given for **1a**, **1p** (0.843 g, 2.49 mmol, 24% yield) was prepared as a white solid from 4,4'-methylenebis(2-ethyl-6-methylaniline) (TCI, 2.97 g, 10.5 mmol). **1p**: ^1H NMR (400 MHz, CDCl_3) δ 6.94 (d, $J = 2.0$ Hz, 2H), 6.86 (d, $J = 2.0$ Hz, 2H), 3.83 (s, 2H), 2.85 (s, 12H), 2.69 (q, $J = 7.6$ Hz, 4H), 2.31 (s, 6H), 1.24 (t, $J = 7.6$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 147.2, 143.6, 138.1, 137.5, 129.5, 127.5, 43.2, 41.2, 25.3, 19.4, 15.8. HRMS (APCI, positive) m/z calcd for $\text{C}_{23}\text{H}_{35}\text{N}_2^+$ [$\text{M} + \text{H}$] $^+$: 339.2795, found: 339.2799.

4,4'-Methylenebis(2,6-diethyl-*N,N*-dimethylaniline) (**1q**)



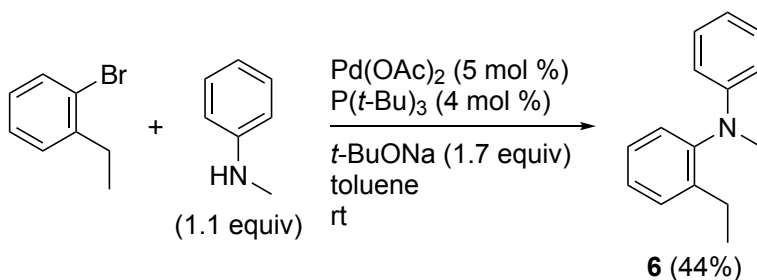
According to the procedure given for **1a**, **1q** (3.14 g, 8.57 mmol, 83% yield) was prepared as a white solid from 4,4'-methylenebis(2,6-diethylaniline) (TCI, 3.20 g, 10.3 mmol). **1q**: ^1H NMR (400 MHz, CDCl_3) δ 6.93 (s, 4H), 3.88 (s, 2H), 2.86 (s, 12H), 2.67 (q, $J = 7.6$ Hz, 8H), 1.24 (t, $J = 7.6$ Hz, 12H). ^{13}C NMR (101 MHz, CDCl_3) δ 146.8, 144.0, 138.3, 127.6, 43.9, 41.4, 25.1, 15.8. HRMS (APCI, positive) m/z calcd for $\text{C}_{25}\text{H}_{39}\text{N}_2^+$ $[\text{M} + \text{H}]^+$: 367.3108, found: 367.3111.

N-Benzyl-2-ethyl-*N*-methylaniline (**4**)



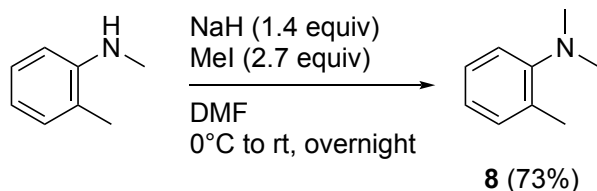
According to the procedure given for **11**, **4** (0.168 g, 0.746 mmol, 29% yield) was prepared as a colorless oil from 1-bromo-2-ethylbenzene (0.502 g, 2.71 mmol) and *N*-methylbenzylamine (0.309 g, 2.55 mmol) using $\text{Pd}(\text{dba})_2$ (4 mol %) instead of $\text{Pd}(\text{OAc})_2$. **4**: ^1H NMR (400 MHz, CDCl_3) δ 7.42-7.47 (m, 2H), 7.35-7.42 (m, 2H), 7.28-7.34 (m, 2H), 7.18-7.27 (m, 2H), 7.09-7.15 (m, 1H), 4.06 (s, 2H), 2.89 (q, $J = 7.6$ Hz, 2H), 2.62 (s, 3H), 1.34 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 152.3, 139.6, 139.4, 129.1, 128.5, 128.4, 127.1, 126.5, 124.0, 121.0, 61.9, 41.9, 23.8, 15.1. HRMS (APCI, positive) m/z calcd for $\text{C}_{16}\text{H}_{20}\text{N}^+$ $[\text{M} + \text{H}]^+$: 226.1590, found: 226.1590.

2-Ethyl-*N*-methyl-*N*-phenylaniline (**6**)



According to the procedure given for **11**, **6** (0.230 g, 1.02 mmol, 44% yield) was prepared as a yellow oil from 1-bromo-2-ethylbenzene (0.428 g, 2.31 mmol) and *N*-methylaniline (0.263 g, 2.45 mmol). **6**: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.36-7.42 (m, 1H), 7.27-7.33 (m, 2H), 7.14-7.25 (m, 3H), 6.75 (t, $J = 7.2$ Hz, 1H), 6.58 (d, $J = 8.0$ Hz, 2H), 3.27 (s, 3H), 2.59 (q, $J = 7.6$ Hz, 2H), 1.21 (t, $J = 7.6$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 149.7, 146.6, 143.0, 129.7, 129.0, 128.7, 127.7, 126.9, 116.8, 112.9, 39.7, 24.2, 14.8. HRMS (APCI, positive) m/z calcd for $\text{C}_{15}\text{H}_{18}\text{N}^+$ [$\text{M} + \text{H}$] $^+$: 212.1434, found: 212.1433.

N,N,2-Trimethylaniline (**8**)

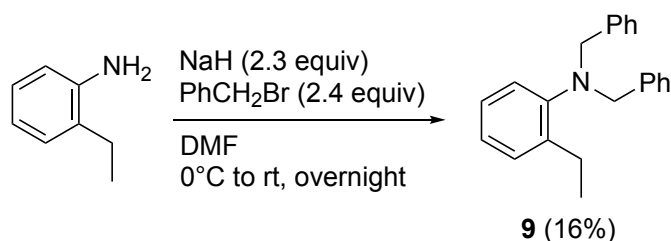


According to the procedure given for **1a**, **8** (1.01 g, 7.47 mmol, 73% yield) was prepared as a colorless oil from *N*,2-dimethylaniline (TCI, 1.24 g, 10.2 mmol). **8**: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.17-7.23 (m, 2H), 7.08 (dd, $J = 8.4, 1.2$ Hz, 1H), 6.99 (td, $J = 7.2, 1.2$ Hz, 1H), 2.74 (s, 6H), 2.38 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 152.8, 132.2, 131.3, 126.5, 122.7, 118.5, 44.3, 18.5. HRMS (APCI, positive) m/z calcd for $\text{C}_9\text{H}_{14}\text{N}^+$ [$\text{M} + \text{H}$] $^+$: 136.1121, found: 136.1120.

N,N-Dimethyl-2-vinylaniline (**3a**)

This compound was prepared from 2-bromo-*N,N*-dimethylaniline by the method reported.⁷

***N,N*-Dibenzyl-2-ethylaniline (9)**



An oven dried 200 mL three-neck flask, equipped with a magnetic stirring bar, a rubber septum, and a three-way stopcock, was charged with NaH (ca. 60% dispersion in mineral oil, 0.9 g, 23 mmol). The flask was evacuated and backfilled with nitrogen. DMF (20 mL) and 2-ethylaniline (Wako, 1.19 g, 9.82 mmol) were added to the flask, and the mixture was cooled to 0 °C by ice/water bath. Benzyl bromide (4.04 g, 23.6 mmol) was added slowly to the flask. The ice/water bath was removed, and the mixture was stirred overnight at room temperature. Hexane (30 mL), AcOEt (30 mL), and water (60 mL) were added to the flask. The organic materials were washed with water (60 mL x 4) and brine (50 mL x 1), and dried over anhydrous magnesium sulfate. The crude product was purified by column chromatography on silica gel (SiliaFlash; eluent: hexane:Et₂O = 97:3) and Kugelrohr distillation. **9** (0.474 g, 1.57 mmol, 16% yield) was obtained as a colorless oil. **9**: ¹H NMR (400 MHz, CDCl₃) δ 7.34-7.47 (m, 11H), 7.17-7.28 (m, 3H), 4.24 (s, 4H), 3.06 (q, *J* = 7.6 Hz, 2H), 1.43 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 149.5, 140.3, 138.6, 129.01, 128.97, 128.2, 127.0, 126.0, 124.3, 123.2, 57.9, 23.5, 14.9. HRMS (APCI, positive) *m/z* calcd for C₂₂H₂₄N⁺ [M + H]⁺: 302.1903, found: 302.1905.

***N*,3-Dimethylindoline (11a)**

This compound was prepared from 3-methylindole by the method reported.⁷

4. Reaction Conditions (Table 1)

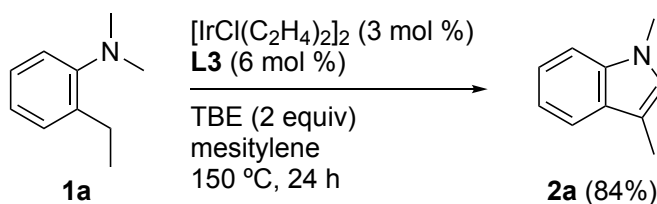
General procedure: In a glovebox, a glass tube (outside diameter: 20 mm, internal volume: 16 mL) having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with [IrCl(C₂H₄)₂]₂ (0.0030 mmol), a ligand (0.0060 mmol), **1a** (0.10 mmol), additive (0–0.30 mmol), and mesitylene (0.2 mL). The tube was sealed by the stopcock and was taken out from the glovebox (Figure S1). The mixture was stirred at 110–150 °C by a heating magnetic stirrer

with an aluminum heating block (hole size: 21 mm diameter x 33 mm depth). After 24 h, the tube was cooled to room temperature. Diphenylmethane (TCI, 16.8 mg, 0.10 mmol, internal standard) was added, and the resulting mixture was analyzed by ^1H NMR to determine the yield of **2a**.



Figure S1. A Glass Tube (internal volume: 16 mL) Containing a Reaction Mixture

The reaction of 1a to afford 1,3-dimethyl-1*H*-indole (2a) (entry 4, Table 1)

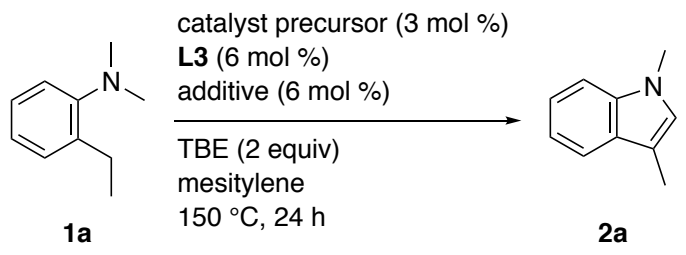


In a glovebox, a glass tube (outside diameter: 20 mm, internal volume: 16 mL) having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with $[\text{IrCl}(\text{C}_2\text{H}_4)_2]_2$ (3.42 mg, 0.00603 mmol), **L3** (13.9 mg, 0.0118 mmol), **1a** (29.9 mg, 0.200 mmol), *tert*-butylethylene (37.6 mg, 0.447 mmol), and mesitylene (0.4 mL). The tube was sealed by the stopcock and was taken out from the glovebox. The mixture was stirred for 24 h at 150 °C by a heating magnetic stirrer with an aluminum heating block (hole size: 21 mm diameter x 33 mm depth). **2a** (24.4 mg, 0.168 mmol, 84%) was obtained as a colorless oil after purification by column chromatography on silica gel (eluent: hexane:Et₂O:Et₃N = 45:1:1). **2a**: ^1H NMR (400 MHz, CDCl₃) δ 7.61 (dt, J = 7.6, 1.2 Hz, 1H), 7.31 [dt (AB pattern), J = 8.0, 1.2 Hz, 1H], 7.22-7.28 (m, 1H), 7.14 (ddd, J = 8.0, 6.8, 1.2 Hz, 1H), 6.85 (d, J = 1.2 Hz, 1H), 3.75 (s, 3H), 2.36 (d, J = 1.2 Hz, 3H). ^{13}C NMR (101 MHz, CDCl₃) δ 137.1, 128.7, 126.6, 121.5, 119.0, 118.6, 110.2, 109.1, 32.6, 9.7. HRMS (APCI, positive) m/z calcd for C₁₀H₁₂N⁺ [M + H]⁺: 146.0964, found: 146.0963.

Additional Results in Screening of Reaction Conditions

The reaction of **1a** proceeded efficiently to afford **2a** in good yields when $[\text{IrCl}(\text{C}_2\text{H}_4)_2]_2$, $[\text{IrCl}(\text{coe})_2]_2$, $[\text{IrCl}(\text{cod})]_2$ were used as catalyst precursors (entries 1–3, Table S1). Addition of AgOTf (6 mol %) inhibited the reaction (entry 4). No reaction took place using $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ as a catalyst precursor (entry 5).

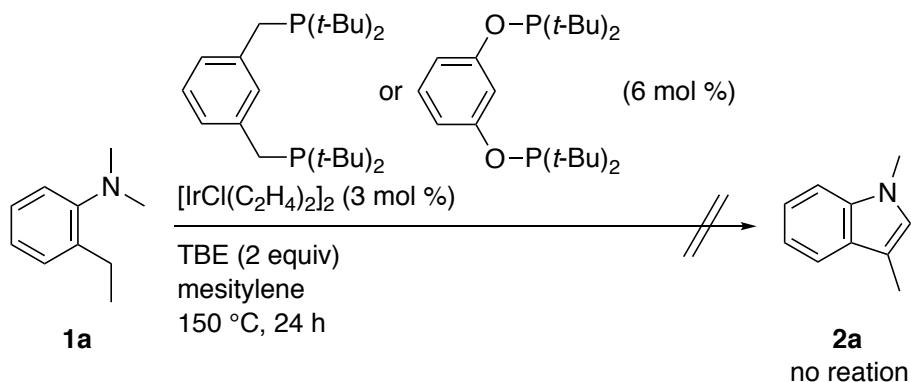
Table S1. Screening of Catalyst Precursors^a



entry	catalyst precursor	additive	% yield of 2a ^b
1	$[\text{IrCl}(\text{C}_2\text{H}_4)_2]_2$	-	93 (84) ^c
2	$[\text{IrCl}(\text{coe})_2]_2$	-	76
3	$[\text{IrCl}(\text{cod})]_2$	-	85
4	$[\text{IrCl}(\text{C}_2\text{H}_4)_2]_2$	AgOTf	0
5	$[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$	-	no reaction

^a **1a** (0.10 mmol), a catalyst precursor (3 mol %), **L3** (6 mol %), additive (0 or 6 mol %), TBE (2 equiv), and mesitylene (0.2 mL) were stirred at 150 °C for 24 h. ^b Determined by ¹H NMR. ^c Isolated yield in the 0.2 mmol scale reaction.

1,3-Bis[(di-*tert*-butylphosphaneyl)methyl]benzene and 1,3-bis[(di-*tert*-butylphosphaneyl)-oxy]benzene, which have been known as ligands to form PCP-pincer iridium complexes, were applied to the reaction of **1a**. No reaction took place.

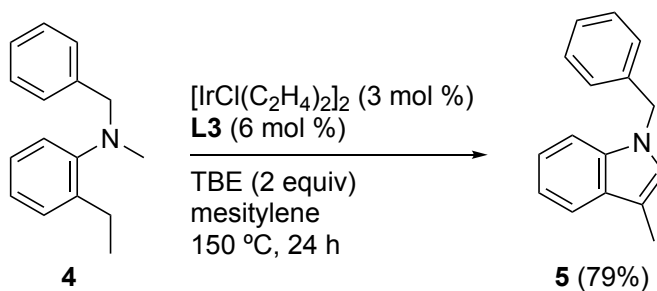


5. Iridium-Catalyzed Dehydrogenation–Intramolecular Dehydrogenative C–H/C–H Coupling of **1** (Scheme 2)

General procedure A: In a glovebox, a glass tube (outside diameter: 20 mm, internal volume: 16 mL) having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with $[\text{IrCl}(\text{C}_2\text{H}_4)_2]_2$ (3.41 mg, 0.00600 mmol), **L3** (14.2 mg, 0.0120 mmol), **1** (0.200 mmol), *tert*-butylethylene (33.7 mg, 0.400 mmol), and mesitylene (0.4 mL). The tube was sealed by the stopcock and was taken out from the glovebox (Figure S1). The mixture was stirred for 24 h at 150 °C by a heating magnetic stirrer with an aluminum heating block (hole size: 21 mm diameter x 33 mm depth). The product **2** was purified by column chromatography on silica gel.

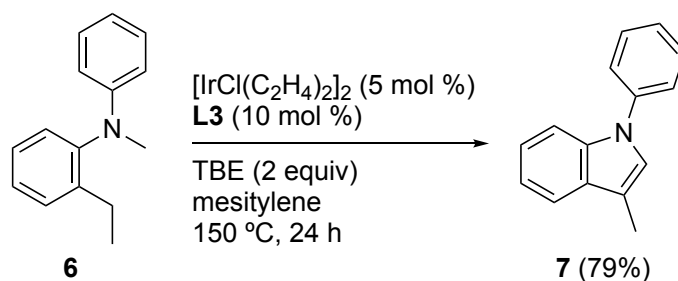
*General procedure B (for the reaction that afford a mixture of alkyl- and alkenyl-substituted indoles):*⁸ In a glovebox, a glass tube (outside diameter: 20 mm, internal volume: 16 mL) having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with $[\text{IrCl}(\text{C}_2\text{H}_4)_2]_2$ (3.41 mg, 0.00600 mmol), **L3** (14.2 mg, 0.0120 mmol), **1** (0.200 mmol), *tert*-butylethylene (33.7 mg, 0.400 mmol), and mesitylene (0.4 mL). The tube was sealed by the stopcock and was taken out from the glovebox (Figure S1). The mixture was stirred at 150 °C by a heating magnetic stirrer with an aluminum heating block (hole size: 21 mm diameter x 33 mm depth). After 24 h, the tube was cooled to room temperature, and it was brought in a glovebox. THF (0.4 mL) was added to the tube. The tube was sealed by the stopcock again and was taken out from the glovebox. The mixture was stirred at 135 °C by a heating magnetic stirrer. After 3 h, the tube was cooled to room temperature, and the volatiles were removed under reduced pressure. The product **2** was purified by column chromatography on silica gel.

The Reaction of **4** to Afford 1-Benzyl-3-methyl-1*H*-indole (**5**) (entry 1)



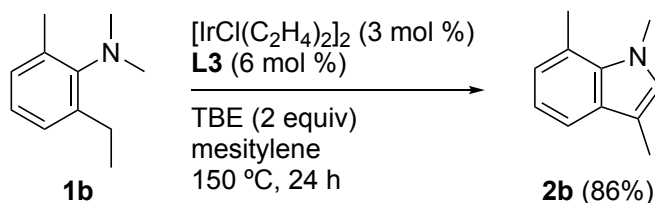
According to the *general procedure A*, the reaction was carried out at 150 °C for 24 h using $[\text{IrCl}(\text{C}_2\text{H}_4)_2]_2$ (3.64 mg, 0.00641 mmol), **L3** (14.1 mg, 0.0120 mmol), **4** (44.6 mg, 0.198 mmol), *tert*-butylethylene (33.6 mg, 0.399 mmol), and mesitylene (0.4 mL). **5** (34.5 mg, 0.156 mmol, 79%) was obtained as a white solid after purification by column chromatography on silica gel (eluent: hexane:Et₂O:Et₃N = 30:1:1). **5**: ¹H NMR (400 MHz, CDCl₃) δ 7.62-7.66 (m, 1H), 7.26-7.36 (m, 4H), 7.13-7.24 (m, 4H), 6.93 (d, *J* = 1.2 Hz, 1H), 5.29 (s, 2H), 2.39 (d, *J* = 1.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 138.0, 136.8, 129.0, 128.8, 127.6, 126.9, 126.0, 121.7, 119.2, 118.9, 111.0, 109.6, 49.9, 9.8. HRMS (APCI, positive) *m/z* calcd for C₁₆H₁₆N⁺ [M + H]⁺: 222.1277, found: 222.1276.

The Reaction of **6** to Afford 1-Phenyl-3-methyl-1*H*-indole (**7**) (entry 2)



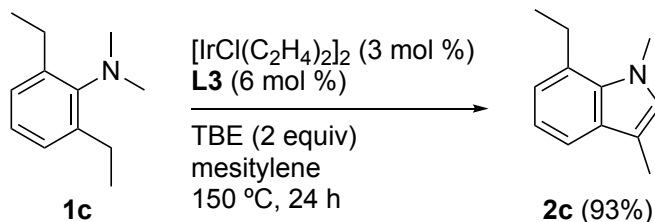
According to the *general procedure A*, the reaction was carried out at 150 °C for 24 h using $[\text{IrCl}(\text{C}_2\text{H}_4)_2]_2$ (5.65 mg, 0.00995 mmol), **L3** (24.2 mg, 0.0205 mmol), **6** (41.5 mg, 0.196 mmol), *tert*-butylethylene (34.0 mg, 0.404 mmol), and mesitylene (0.4 mL). **7** (32.1 mg, 0.155 mmol, 79%) was obtained as a green oil after purification by column chromatography on silica gel (eluent: hexane:Et₂O:Et₃N = 45:1:1). **7**: ¹H NMR (400 MHz, CDCl₃) δ 7.66-7.70 (m 1H), 7.59-7.62 (m, 1H), 7.50-7.56 (m, 4H), 7.32-7.38 (m, 1H), 7.19-7.30 (m, 2H), 7.18 (d, *J* = 1.2 Hz, 1H), 2.44 (d, *J* = 1.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 140.1, 136.1, 129.9, 129.7, 126.0, 125.6, 124.1, 122.5, 119.9, 119.3, 112.9, 110.5, 9.7. HRMS (APCI, positive) *m/z* calcd for C₁₅H₁₄N⁺ [M + H]⁺: 208.1121, found: 208.1121.

The Reaction of **1b** to Afford 1,3,7-Trimethyl-1*H*-indole (**2b**) (entry 3)



According to the *general procedure A*, the reaction was carried out at 150 °C for 24 h using $[\text{IrCl}(\text{C}_2\text{H}_4)_2]_2$ (3.22 mg, 0.00567 mmol), **L3** (14.0 mg, 0.0119 mmol), **1b** (34.0 mg, 0.208 mmol), *tert*-butylethylene (33.9 mg, 0.403 mmol), and mesitylene (0.4 mL). **2b** (28.5 mg, 0.179 mmol, 86% including <2% of a structural isomer) was obtained as a white solid after purification by column chromatography on silica gel (eluent: hexane:Et₂O:Et₃N = 45:1:1). **2b**: ¹H NMR (400 MHz, CDCl₃) δ 7.41-7.46 (m, 1H), 7.02 (t, *J* = 7.2 Hz, 1H), 6.94 [d (AB pattern), *J* = 7.2 Hz, 1H], 6.74 (d, *J* = 1.2 Hz, 1H), 4.02 (s, 3H), 2.79 (s, 3H), 2.33 (d, *J* = 1.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 135.8, 129.8, 128.3, 124.2, 121.2, 118.9, 117.2, 109.9, 36.4, 19.8, 9.6. HRMS (APCI, positive) *m/z* calcd for C₁₁H₁₄N⁺ [M + H]⁺: 160.1121, found: 160.1119.

The Reaction of **1c** to Afford 7-Ethyl-1,3-dimethyl-1*H*-indole (**2c**) (entry 4)



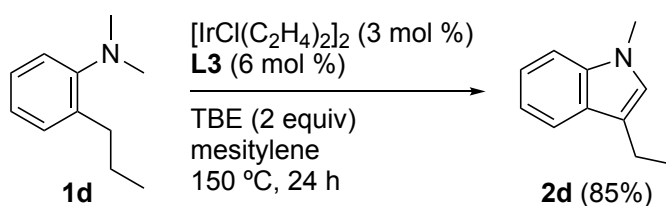
According to the *general procedure A*, the reaction was carried out at 150 °C for 24 h using $[\text{IrCl}(\text{C}_2\text{H}_4)_2]_2$ (3.72 mg, 0.00655 mmol), **L3** (14.6 mg, 0.0124 mmol), **1c** (36.1 mg, 0.204 mmol), *tert*-butylethylene (35.3 mg, 0.419 mmol), and mesitylene (0.4 mL). **2c** (32.7 mg, 0.189 mmol, 93%) was obtained as a white solid after purification by column chromatography on silica gel (eluent: hexane:Et₂O:Et₃N = 45:1:1). **2c**: ¹H NMR (400 MHz, CDCl₃) δ 7.45 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.08 (t, *J* = 8.0 Hz, 1H), 7.00-7.04 (m, 1H), 6.75 (d, *J* = 1.2 Hz, 1H), 4.00 (s, 3H), 3.14 (q, *J* = 7.6 Hz, 2H), 2.34 (d, *J* = 1.2 Hz, 3H), 1.39 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 135.0, 130.3, 128.6, 127.8, 122.5, 119.1, 117.1, 110.1, 36.4, 25.6, 16.9, 9.6. HRMS (APCI, positive) *m/z* calcd for C₁₂H₁₆N⁺ [M + H]⁺: 174.1277, found: 174.1276.

1 mmol scale reaction

In a glovebox, a glass tube (internal volume: 36 mL) having PTFE stopcock (J. Young),

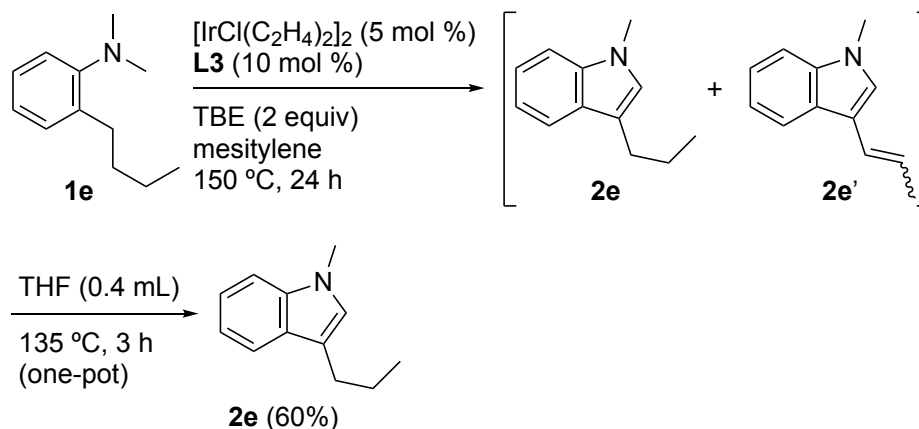
equipped with a magnetic stirring bar, was charged with $[\text{IrCl}(\text{C}_2\text{H}_4)_2]_2$ (17.2 mg, 0.0303 mmol), **L3** (71.4 mg, 0.0605 mmol), **1c** (177 mg, 0.998 mmol), *tert*-butylethylene (172 mg, 2.04 mmol), and mesitylene (2 mL). The tube was sealed by the stopcock and was taken out from the glovebox. The mixture was stirred at 150 °C by an oil bath. After 24 h, the tube was cooled to room temperature, and the volatiles were removed under reduced pressure. **2c** (145 mg, 0.837 mmol, 84%) was obtained as a colorless oil after purification by column chromatography on silica gel (eluent: hexane:Et₂O:Et₃N = 45:1:1).

The Reaction of **1d** to Afford 3-Ethyl-1-methyl-1*H*-indole (**2d**) (entry 5)



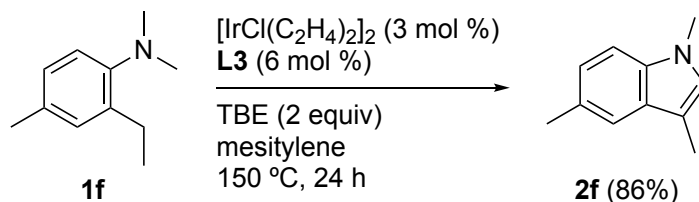
According to the *general procedure A*, the reaction was carried out at 150 °C for 24 h using $[\text{IrCl}(\text{C}_2\text{H}_4)_2]_2$ (3.83 mg, 0.00675 mmol), **L3** (14.8 mg, 0.0126 mmol), **1d** (33.7 mg, 0.206 mmol), *tert*-butylethylene (33.7 mg, 0.400 mmol), and mesitylene (0.4 mL). **2d** (27.9 mg, 0.175 mmol, 85%) was obtained as a colorless oil after purification by column chromatography on silica gel (eluent: hexane:Et₂O:Et₃N = 47:1:1). **2d**: ¹H NMR (400 MHz, CDCl₃) δ 7.65 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.32 [dt (AB pattern), *J* = 8.0, 1.2 Hz, 1H], 7.23-7.29 (m, 1H), 7.14 (ddd, *J* = 7.6, 6.8, 1.2 Hz, 1H), 6.86 (s, 1H), 3.77 (s, 3H), 2.83 (q, *J* = 7.6 Hz, 2H), 1.37 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 137.2, 127.9, 125.5, 121.6, 119.2, 118.6, 117.4, 109.2, 32.6, 18.4, 14.9. HRMS (APCI, positive) *m/z* calcd for C₁₁H₁₄N⁺ [M + H]⁺: 160.1121, found: 160.1119.

The Reaction of **1e** to Afford 1-Methyl-3-propyl-1*H*-indole (**2e**) (entry 6)



According to the *general procedure B*, the reaction was carried out at 150 °C for 24 h using $[\text{IrCl}(\text{C}_2\text{H}_4)_2]_2$ (5.33 mg, 0.00939 mmol), **L3** (23.0 mg, 0.0195 mmol), **1e** (30.5 mg, 0.172 mmol), *tert*-butylethylene (31.3 mg, 0.372 mmol), and mesitylene (0.4 mL). The reaction mixture was then treated with THF (0.4 mL) for 3 h at 135 °C. **2e** (18.0 mg, 0.104 mmol, 60%) was obtained as a colorless oil after purification by column chromatography on silica gel (eluent: hexane:Et₂O:Et₃N = 40:1:1). **2e**: ¹H NMR (400 MHz, CDCl₃) δ 7.62 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.30 [dt (AB pattern), *J* = 8.0, 1.2 Hz, 1H], 7.23 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.11 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 6.84 (s, 1H), 3.75 (s, 3H), 2.74 (t, *J* = 7.6 Hz, 2H), 1.74 (sextet, *J* = 7.6 Hz, 2H), 1.02 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 137.1, 128.1, 126.2, 121.5, 119.2, 118.5, 115.6, 109.2, 32.7, 27.4, 23.7, 14.3. HRMS (APCI, positive) *m/z* calcd for C₁₂H₁₆N⁺ [M + H]⁺: 174.1277, found: 174.1277.

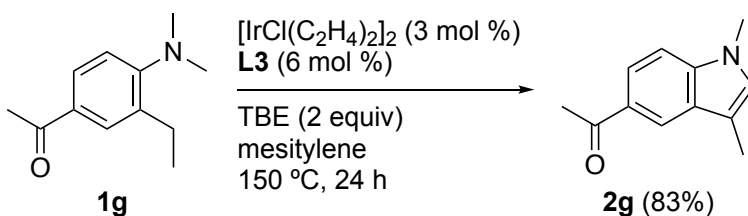
The Reaction of **1f** to Afford 1,3,5-Trimethyl-1*H*-indole (**2f**) (entry 7)



According to the *general procedure A*, the reaction was carried out at 150 °C for 24 h using $[\text{IrCl}(\text{C}_2\text{H}_4)_2]_2$ (3.11 mg, 0.00548 mmol), **L3** (13.4 mg, 0.0114 mmol), **1f** (30.5 mg, 0.187 mmol), *tert*-butylethylene (31.3 mg, 0.372 mmol), and mesitylene (0.4 mL). **2f** (25.7 mg, 0.161 mmol, 86%) was obtained as a colorless oil after purification by column chromatography on silica gel

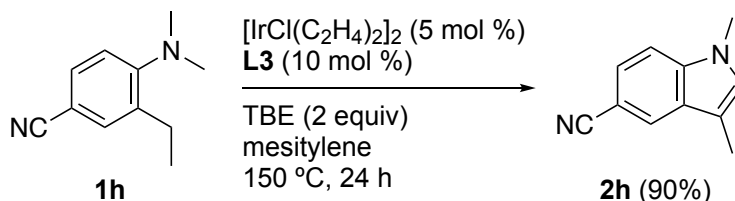
(eluent: hexane:Et₂O:Et₃N = 45:1:1). **2f**: ¹H NMR (400 MHz, CDCl₃) δ 7.36-7.40 (m, 1H), 7.19 [d (AB pattern), *J* = 8.4 Hz, 1H], 7.07 [dd (AB pattern), *J* = 8.4, 1.6 Hz, 1H], 6.80 (d, *J* = 1.2 Hz, 1H), 3.72 (s, 3H), 2.51 (s, 3H), 2.33 (d, *J* = 1.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 135.6, 129.0, 127.8, 126.8, 123.1, 118.7, 109.6, 108.8, 32.6, 21.6, 9.7. HRMS (APCI, positive) *m/z* calcd for C₁₁H₁₄N⁺ [M + H]⁺: 160.1121, found: 160.1119.

The Reaction of **1g** to Afford 5-Acetyl-1,3-dimethyl-1*H*-indole (**2g**) (entry 8)



According to the *general procedure A*, the reaction was carried out at 150 °C for 24 h using [IrCl(C₂H₄)₂]₂ (3.39 mg, 0.00597 mmol), **L3** (14.2 mg, 0.0120 mmol), **1g** (37.6 mg, 0.197 mmol), *tert*-butylethylene (33.6 mg, 0.399 mmol), and mesitylene (0.4 mL). **2g** (30.6 mg, 0.163 mmol, 83%) was obtained as a white solid after purification by column chromatography on silica gel (eluent: hexane:AcOEt = 3:1). **2g**: ¹H NMR (400 MHz, CDCl₃) δ 8.24 (s, 1H), 7.88 (d, *J* = 8.8 Hz, 1H), 7.26 (d, *J* = 8.8 Hz, 1H), 6.87 (s, 1H), 3.74 (s, 3H), 2.68 (s, 3H), 2.36 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 198.5, 139.5, 128.8, 128.3, 128.1, 122.0, 121.3, 112.5, 108.9, 32.8, 26.7, 9.6. HRMS (APCI, positive) *m/z* calcd for C₁₂H₁₄NO⁺ [M + H]⁺: 188.1070, found: 188.1068.

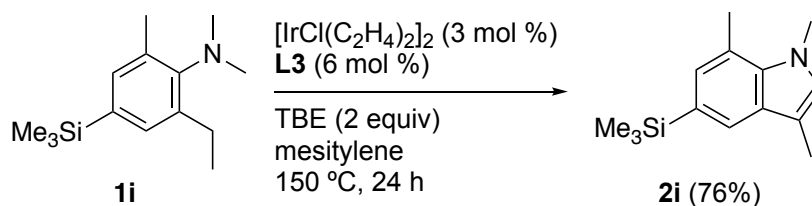
The Reaction of **1h** to Afford 5-Cyano-1,3-dimethyl-1*H*-indole (**2h**) (entry 9)



According to the *general procedure A*, the reaction was carried out at 150 °C for 24 h using [IrCl(C₂H₄)₂]₂ (5.85 mg, 0.0103 mmol), **L3** (23.7 mg, 0.0201 mmol), **1h** (34.9 mg, 0.200 mmol), *tert*-butylethylene (34.2 mg, 0.406 mmol), and mesitylene (0.4 mL). **2r** (30.4 mg, 0.179 mmol, 90%) was obtained as a white solid after purification by column chromatography on silica gel

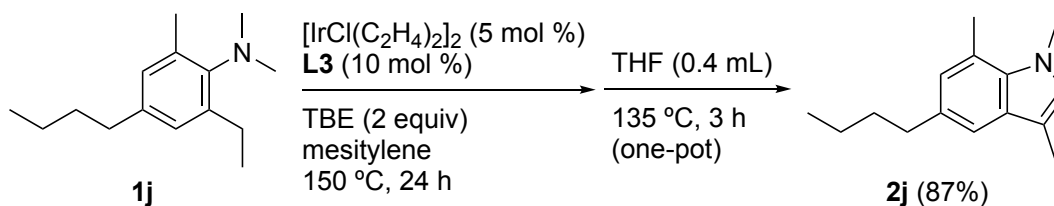
(eluent: hexane:AcOEt = 2:1). **2h**: ^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, $J = 1.6$ Hz, 1H), 7.41 [dd (AB pattern), $J = 8.8, 1.6$ Hz, 1H], 7.29 [d (AB pattern), $J = 8.8$ Hz, 1H], 6.93 (d, $J = 1.2$ Hz, 1H), 3.76 (s, 3H), 2.31 (d, $J = 1.2$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 138.5, 128.8, 128.5, 124.7, 124.4, 121.2, 111.5, 109.9, 101.5, 32.8, 9.4. HRMS (ESI, positive) m/z calcd for $\text{C}_{11}\text{H}_{11}\text{N}_2^+$ $[\text{M} + \text{H}]^+$: 171.0917, found: 171.0918.

The Reaction of **1i** to Afford 1,3,7-Trimethyl-5-(trimethylsilyl)-1*H*-indole (**2i**) (entry 10)



According to the *general procedure A*, the reaction was carried out at 150 °C for 24 h using $[\text{IrCl}(\text{C}_2\text{H}_4)_2]_2$ (3.40 mg, 0.00599 mmol), **L3** (14.2 mg, 0.0120 mmol), **1i** (47.1 mg, 0.200 mmol), *tert*-butylethylene (32.8 mg, 0.390 mmol), and mesitylene (0.4 mL). **2i** (34.9 mg, 0.151 mmol, 76% including <2% of a structural isomer) was obtained as a white solid after purification by column chromatography on silica gel (eluent: hexane: Et_2O : Et_3N = 45:1:1). **2i**: ^1H NMR (400 MHz, CDCl_3) δ 7.60 (s, 1H), 7.07 (s, 1H), 6.72 (d, $J = 1.2$ Hz, 1H), 4.01 (s, 3H), 2.80 (s, 3H), 2.35 (d, $J = 1.2$ Hz, 3H), 0.36 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 136.5, 129.7, 129.0, 128.8, 128.3, 122.7, 120.6, 110.0, 36.4, 19.9, 9.6, -0.5. HRMS (APCI, positive) m/z calcd for $\text{C}_{14}\text{H}_{22}\text{NSi}^+$ $[\text{M} + \text{H}]^+$: 232.1516, found: 232.1516.

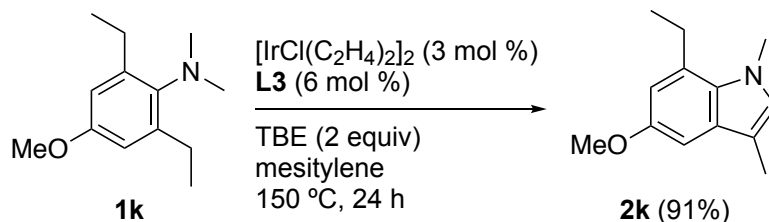
The Reaction of **1j** to Afford 5-*n*-Butyl-1,3,7-trimethyl-1*H*-indole (**2j**) (entry 11)



According to the *general procedure B*, the reaction was carried out at 150 °C for 24 h using $[\text{IrCl}(\text{C}_2\text{H}_4)_2]_2$ (5.46 mg, 0.00962 mmol), **L3** (24.0 mg, 0.0204 mmol), **1j** (39.9 mg, 0.182 mmol), *tert*-butylethylene (32.6 mg, 0.387 mmol), and mesitylene (0.4 mL). The resulting reaction mixture was then treated with THF (0.4 mL) for 3 h at 135 °C. **2j** (34.3 mg, 0.159 mmol, 87%

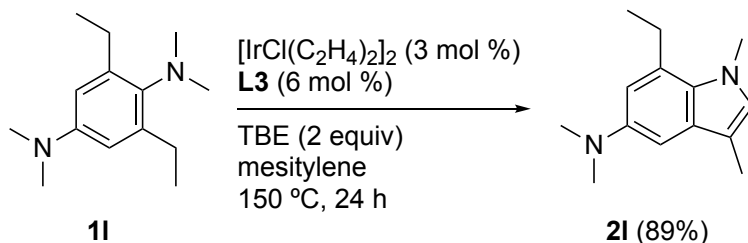
including <5% of a structural isomer) was obtained as a colorless oil after purification by column chromatography on silica gel (eluent: hexane:Et₂O:Et₃N = 40:1:1). **2j**: ¹H NMR (400 MHz, CDCl₃) δ 7.20 (s, 1H), 6.78 (s, 1H), 6.70 (d, *J* = 1.2 Hz, 1H), 3.98 (s, 3H), 2.75 (s, 3H), 2.70 (t, *J* = 7.6 Hz, 2H), 2.30 (d, *J* = 1.2 Hz, 3H), 1.64-1.73 (m, 2H), 1.36-1.49 (m, 2H), 0.99 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 134.4, 133.5, 130.0, 128.4, 125.4, 120.8, 116.1, 109.5, 36.4, 35.7, 34.7, 22.7, 19.8, 14.2, 9.6. HRMS (APCI, positive) *m/z* calcd for C₁₅H₂₂N⁺ [M + H]⁺: 216.1747, found: 216.1747.

The Reaction of **1k** to Afford 7-Ethyl-5-methoxy-1,3-dimethyl-1*H*-indole (**2k**) (entry 12)



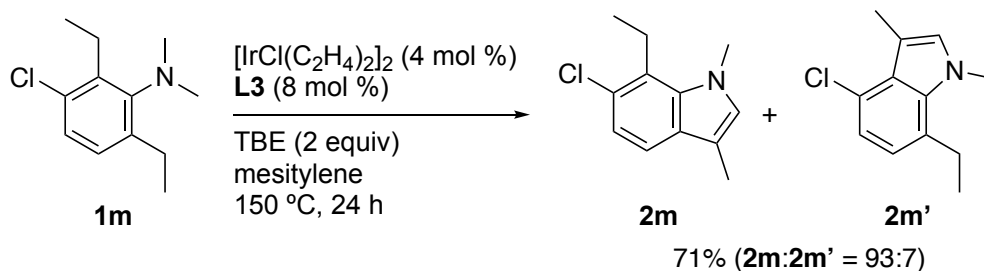
According to the *general procedure A*, the reaction was carried out at 150 °C for 24 h using [IrCl(C₂H₄)₂]₂ (3.85 mg, 0.00678 mmol), **L3** (15.3 mg, 0.0130 mmol), **1k** (42.4 mg, 0.205 mmol), *tert*-butylethylene (37.0 mg, 0.440 mmol), and mesitylene (0.4 mL). **2k** (37.8 mg, 0.186 mmol, 91%) was obtained as a white solid after purification by column chromatography on silica gel (eluent: hexane:Et₂O:Et₃N = 20:1:1). **2k**: ¹H NMR (400 MHz, CDCl₃) δ 6.86 (d, *J* = 2.4 Hz, 1H), 6.72 (s, 1H), 6.70 (d, *J* = 2.4 Hz, 1H), 3.94 (s, 3H), 3.90 (s, 3H), 3.08 (q, *J* = 7.6 Hz, 2H), 2.30 (s, 3H), 1.37 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 153.7, 130.5 (two non-equivalent peaks overlapped), 129.2, 129.1, 112.7, 109.6, 98.2, 55.8, 36.4, 25.5, 16.4, 9.7. ¹³C NMR (101 MHz, C₆D₆) δ 154.6, 131.4, 130.9, 129.0, 128.9, 113.4, 109.6, 98.6, 55.3, 35.7, 25.6, 16.5, 9.9. HRMS (APCI, positive) *m/z* calcd for C₁₃H₁₈NO⁺ [M + H]⁺: 204.1383, found: 204.1382.

The Reaction of 11 to Afford 7-Ethyl-5-(dimethylamino)-1,3-dimethyl-1H-indole (21) (entry 13)



According to the *general procedure A*, the reaction was carried out at 150 °C for 24 h using $[\text{IrCl}(\text{C}_2\text{H}_4)_2]_2$ (3.33 mg, 0.00587 mmol), **L3** (14.0 mg, 0.0119 mmol), **11** (44.1 mg, 0.200 mmol), *tert*-butylethylene (34.4 mg, 0.409 mmol), and mesitylene (0.4 mL). **21** (38.2 mg, 0.177 mmol, 89%) was obtained as a yellow oil after purification by column chromatography on silica gel (eluent: hexane:Et₂O:Et₃N = 20:1:1). **21**: ¹H NMR (400 MHz, CDCl₃) δ 6.80 (d, *J* = 2.4 Hz, 1H), 6.74 (d, *J* = 2.4 Hz, 1H), 6.69 (d, *J* = 0.8 Hz, 1H), 3.93 (s, 3H), 3.08 (q, *J* = 7.6 Hz, 2H), 2.96 (s, 6H), 2.29 (d, *J* = 0.8 Hz, 3H), 1.38 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 145.6, 130.7, 129.8, 128.9, 128.4, 114.1, 109.3, 101.5, 43.2, 36.3, 25.9, 16.8, 9.7. HRMS (APCI, positive) *m/z* calcd for C₁₄H₂₁N₂⁺ [*M* + H]⁺: 217.1699, found: 217.1698.

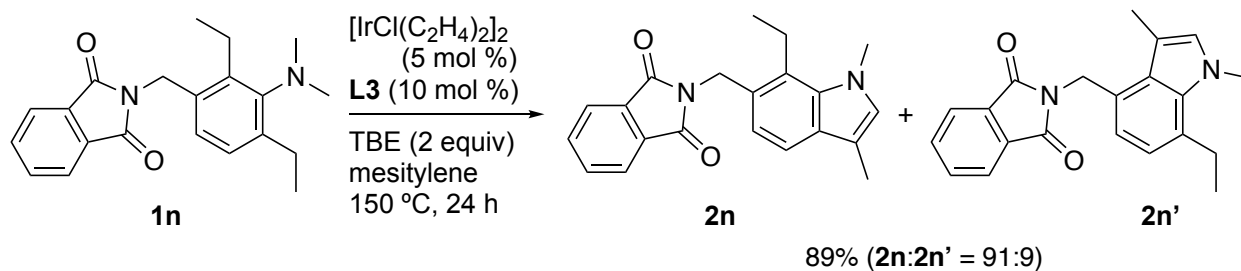
The Reaction of 1m to Afford 6-Chloro-7-ethyl-1,3-dimethyl-1H-indole (2m) (entry 14)



According to the *general procedure A*, the reaction was carried out at 150 °C for 24 h using $[\text{IrCl}(\text{C}_2\text{H}_4)_2]_2$ (4.31 mg, 0.00759 mmol), **L3** (18.8 mg, 0.0159 mmol), **1m** (41.3 mg, 0.195 mmol), *tert*-butylethylene (31.9 mg, 0.379 mmol), and mesitylene (0.4 mL). **2m** (28.9 mg, 0.139 mmol, 71%, containing 7% of an isomer **2m'**) was obtained as a yellow oil after purification by column chromatography on silica gel (eluent: hexane:CH₂Cl₂:Et₃N = 45:3:2). **2m**: ¹H NMR (400 MHz, CDCl₃) δ 7.30 [d (AB pattern), *J* = 8.4 Hz, 1H], 7.11 [d (AB pattern), *J* = 8.4 Hz, 1H], 6.72 (d, *J* = 1.2 Hz, 1H), 3.97 (s, 3H), 3.23 (q, *J* = 7.2 Hz, 2H), 2.27 (d, *J* = 1.2 Hz, 3H), 1.32 (t, *J* = 7.2 Hz,

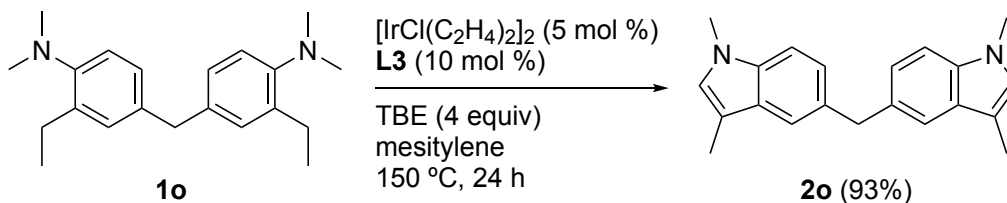
3H). ^{13}C NMR (101 MHz, CDCl_3) δ 135.4, 129.5, 129.2, 128.2, 125.2, 120.8, 117.5, 110.1, 36.7, 21.8, 15.6, 9.4. HRMS (APCI, positive) m/z calcd for $\text{C}_{12}\text{H}_{15}\text{ClN}^+$ $[\text{M} + \text{H}]^+$: 208.0888, found: 208.0887. A mixture of **2m** and **2m'** was used for HRMS measurement. **2m'**: ^1H NMR (400 MHz, CDCl_3) δ 6.95 [d (AB pattern), $J = 8.0$ Hz, 1H], 6.83 [d (AB pattern), $J = 8.0$ Hz, 1H], 6.71 (d, $J = 1.2$ Hz, 1H), 3.94 (s, 3H), 3.05 (q, $J = 7.6$ Hz, 2H), 2.53 (d, $J = 1.2$ Hz, 3H), 1.32 (t, $J = 7.6$ Hz, 3H).

The Reaction of 1m to Afford 7-Ethyl-6-(phthalimidomethyl)-1,3-dimethyl-1H-indole (2n)
(entry 15)



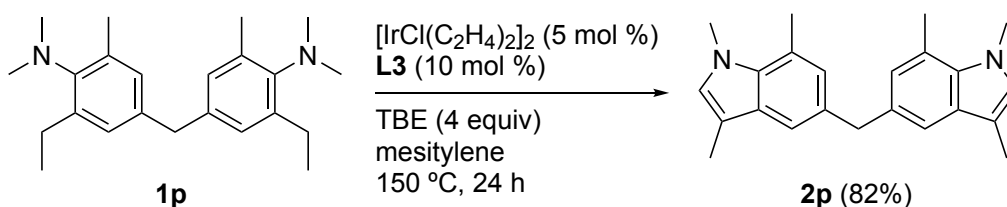
According to the *general procedure A*, the reaction was carried out at 150 °C for 24 h using $[\text{IrCl}(\text{C}_2\text{H}_4)_2]_2$ (5.63 mg, 0.00992 mmol), **L3** (23.7 mg, 0.0201 mmol), **1n** (67.0 mg, 0.199 mmol), *tert*-butylethylene (34.2 mg, 0.406 mmol), and mesitylene (0.4 mL). **2n** (59.0 mg, 0.177 mmol, 89%, containing 9% of an isomer **2n'**) was obtained as a yellow solid after purification by column chromatography on silica gel (eluent: hexane:AcOEt = 3:1). **2n**: ^1H NMR (400 MHz, CDCl_3) δ 7.81-7.87 (m, 2H), 7.66-7.72 (m, 2H), 7.34 [d (AB pattern), $J = 8.4$ Hz, 1H], 7.17 [d (AB pattern), $J = 8.4$ Hz, 1H], 6.71 (d, $J = 1.2$ Hz, 1H), 5.05 (s, 2H), 3.99 (s, 3H), 3.40 (q, $J = 7.6$ Hz, 2H), 2.25 (d, $J = 1.2$ Hz, 3H), 1.36 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 168.5, 135.0, 134.0, 132.3, 130.1, 129.8, 127.4, 126.5, 123.3, 120.9, 116.9, 109.7, 39.0, 36.8, 20.2, 17.1, 9.4. HRMS (APCI, positive) m/z calcd for $\text{C}_{21}\text{H}_{21}\text{N}_2\text{O}_2^+$ $[\text{M} + \text{H}]^+$: 333.1598, found: 333.1601. A mixture of **2n** and **2n'** was used for HRMS measurement. **2n'**: ^1H NMR (400 MHz, CDCl_3) δ 7.87-7.91 (m, 2H), 7.71-7.75 (m, 2H), 6.82 [d (AB pattern), $J = 7.6$ Hz, 1H], 6.73 (d, $J = 1.2$ Hz, 1H), 6.68 [d (AB pattern), $J = 7.6$ Hz, 1H], 5.43 (s, 2H), 3.94 (s, 3H), 3.04 (q, $J = 7.6$ Hz, 2H), 2.65 (d, $J = 1.2$ Hz, 3H), 1.30 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 168.5, 135.8, 134.0, 132.3, 130.2, 127.2, 127.1, 127.0, 123.4, 122.5, 116.6, 109.9, 38.9, 36.6, 25.4, 16.7, 13.7.

The Reaction of **1n** to Afford Bis(1,3-dimethyl-1*H*-indol-5-yl)methane (**2o**) (entry 16)



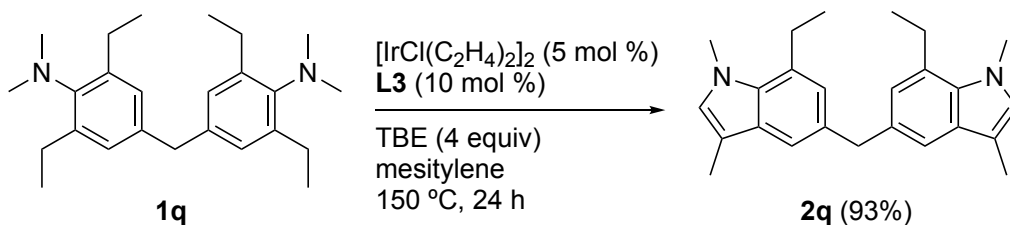
According to the *general procedure A*, the reaction was carried out at 150 °C for 24 h using $[\text{IrCl}(\text{C}_2\text{H}_4)_2]_2$ (5.37 mg, 0.00946 mmol), **L3** (22.6 mg, 0.0192 mmol), **1o** (58.1 mg, 0.187 mmol), *tert*-butylethylene (67.7 mg, 0.804 mmol), and mesitylene (0.4 mL). **2o** (52.3 mg, 0.173 mmol, 93%) was obtained as a white solid after purification by column chromatography on silica gel (eluent: hexane: CH_2Cl_2 : Et_3N = 10:1:1). **2o**: ^1H NMR (400 MHz, CDCl_3) δ 7.52 (d, J = 1.2 Hz, 2H), 7.24 [d (AB pattern), J = 8.4 Hz, 2H], 7.17 [dd (AB pattern), J = 8.4, 1.2 Hz, 2H], 6.83 (d, J = 1.2 Hz, 2H), 4.31 (s, 2H), 3.74 (s, 6H), 2.37 (d, J = 1.2 Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 135.8, 132.7, 128.8, 126.7, 123.2, 118.9, 109.9, 109.0, 42.4, 32.6, 9.7. HRMS (APCI, positive) m/z calcd for $\text{C}_{21}\text{H}_{23}\text{N}_2^+$ [$\text{M} + \text{H}$] $^+$: 303.1856, found: 303.1860.

The Reaction of **1o** to Afford Bis(1,3,7-trimethyl-1*H*-indol-5-yl)methane (**2p**) (entry 17)



According to the *general procedure A*, the reaction was carried out at 150 °C for 24 h using $[\text{IrCl}(\text{C}_2\text{H}_4)_2]_2$ (5.61 mg, 0.00988 mmol), **L3** (23.9 mg, 0.0203 mmol), **1p** (66.5 mg, 0.196 mmol), *tert*-butylethylene (67.9 mg, 0.807 mmol), and mesitylene (0.4 mL). **2p** (53.2 mg, 0.161 mmol, 82% including <10% of a structural isomer) was obtained as a white crystal after purification by column chromatography on silica gel (eluent: hexane: CH_2Cl_2 : Et_3N = 10:1:1). **2p**: ^1H NMR (400 MHz, CDCl_3) δ 7.25 (s, 2H), 6.78 (s, 2H), 6.67 (d, J = 1.2 Hz, 2H), 4.09 (s, 2H), 3.96 (s, 6H), 2.68 (s, 6H), 2.26 (d, J = 1.2 Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 134.5, 133.0, 129.9, 128.3, 125.9, 121.0, 116.9, 109.7, 42.0, 36.4, 19.8, 9.7. HRMS (APCI, positive) m/z calcd for $\text{C}_{23}\text{H}_{27}\text{N}_2^+$ [$\text{M} + \text{H}$] $^+$: 331.2169, found: 331.2173.

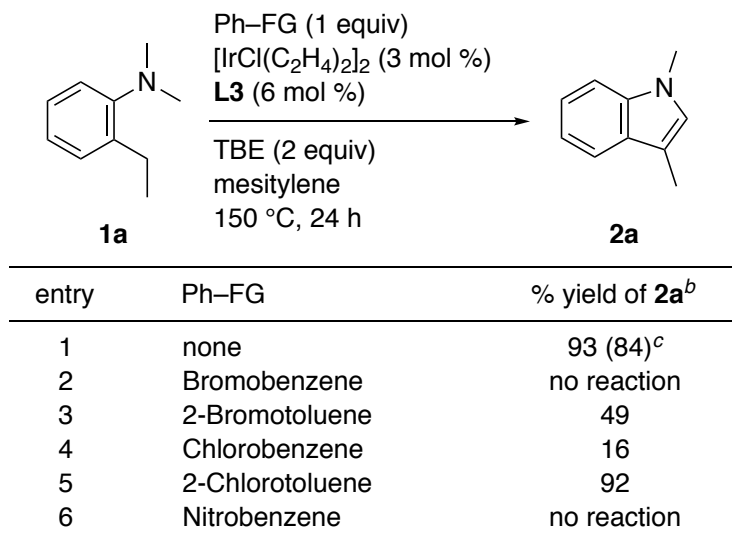
The Reaction of **1q** to Afford Bis(1,3,7-trimethyl-1*H*-indol-5-yl)methane (**2q**) (entry 18)



According to the *general procedure A*, the reaction was carried out at 150 °C for 24 h using $[\text{IrCl}(\text{C}_2\text{H}_4)_2]_2$ (5.68 mg, 0.0100 mmol), **L3** (24.0 mg, 0.0204 mmol), **1q** (72.6 mg, 0.198 mmol), *tert*-butylethylene (67.8 mg, 0.806 mmol), and mesitylene (0.4 mL). **2q** (66.0 mg, 0.184 mmol, 93%) was obtained as a white solid after purification by column chromatography on silica gel (eluent: hexane: CH_2Cl_2 : Et_3N = 10:1:1). **2q**: ^1H NMR (400 MHz, CDCl_3) δ 7.27 (d, J = 1.6 Hz, 2H), 6.89 (d, J = 1.6 Hz, 2H), 6.70 (d, J = 0.8 Hz, 2H), 4.17 (s, 2H), 3.94 (s, 6H), 3.04 (q, J = 7.6 Hz, 4H), 2.27 (d, J = 0.8 Hz, 6H), 1.32 (t, J = 7.6 Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 133.6, 132.9, 130.4, 128.5, 127.6, 124.4, 116.9, 109.9, 42.0, 36.3, 25.6, 17.1, 9.7. HRMS (APCI, positive) m/z calcd for $\text{C}_{25}\text{H}_{31}\text{N}_2^+$ [$\text{M} + \text{H}$] $^+$: 359.2482, found: 359.2486.

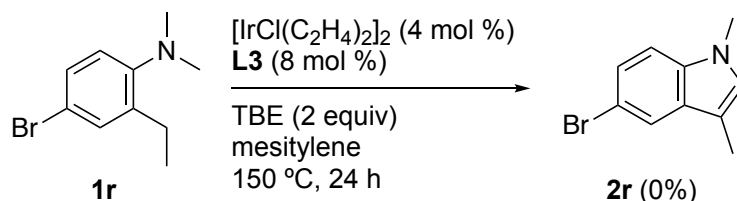
Preliminary Investigations for Functional Group Compatibility

To check functional group compatibility, we carried out the reaction of **1a** in the presence of functionalized benzenes (1 equiv) (Table S2). No reaction took place with bromobenzene (entry 2) probably due to the loss of catalytic activity by oxidative addition of the C–Br bond into Ir(I). Similar deactivation of the catalyst was also observed in the reaction with 2-bromotoluene and chlorobenzene (entries 3 and 4), whereas 2-chlorotoluene did not interfere the reaction (entry 5). These results indicate that sterically shielded halogen is less likely to affect the catalyst. The reaction with nitrobenzene did not proceed probably due to strong coordination of the nitro group to the iridium center prevent the coordination of **1a** (entry 6).

Table S2. The Reaction of **1a** in the presence of a Functionalized Benzenes^a

^a **1a** (0.10 mmol), $[\text{IrCl}(\text{C}_2\text{H}_4)_2]_2$ (3 mol %), **L3** (6 mol %), TBE (2 equiv), and mesitylene (0.2 mL) were stirred at 150 °C for 24 h. ^b Determined by ¹H NMR. ^c Isolated yield in the 0.2 mmol scale reaction.

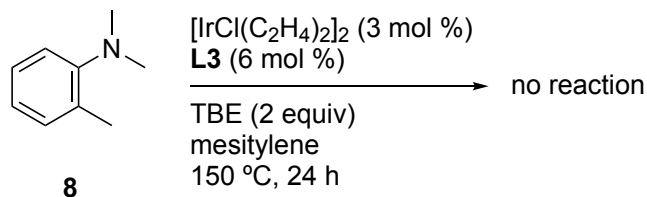
The Reaction of **1r**



According to the *general procedure A*, the reaction was carried out at 150 °C for 24 h using $[\text{IrCl}(\text{C}_2\text{H}_4)_2]_2$ (2.41 mg, 0.00425 mmol), **L3** (8.92 mg, 0.0756 mmol), **1r** (26.9 mg, 0.118 mmol), *tert*-butylethylene (18.8 mg, 0.223 mmol), and mesitylene (0.2 mL). No reaction took place.

6. Reactions of Other Anilines and an Indoline (Figure 1)

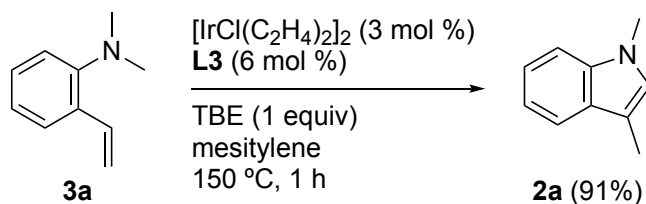
The Reaction of **8** (entry 1)



According to the *general procedure A* described in section 5, the reaction was carried out at 150 °C for 24 h using $[\text{IrCl}(\text{C}_2\text{H}_4)_2]_2$ (1.60 mg, 0.00282 mmol), **L3** (7.38 mg, 0.00626 mmol), **8**

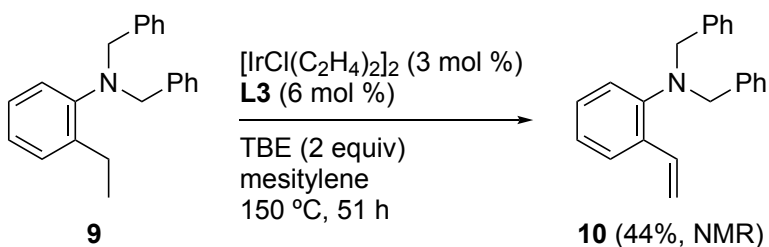
(14.7 mg, 0.109 mmol), *tert*-butylethylene (18.2 mg, 0.216 mmol), and mesitylene (0.2 mL). No reaction took place.

The Reaction of **3a** to Afford **2a** (entry 2)



According to the *general procedure A* described in section 5, the reaction was carried out at 150 °C for 1 h using $[\text{IrCl}(\text{C}_2\text{H}_4)_2]_2$ (4.20 mg, 0.00740 mmol), **L3** (17.1 mg, 0.0145 mmol), **3a** (37.7 mg, 0.256 mmol), *tert*-butylethylene (21.2 mg, 0.252 mmol), and mesitylene (0.4 mL). **2a** (33.8 mg, 91%) was obtained as a colorless oil after purification by column chromatography on silica gel (eluent: hexane:Et₂O:Et₃N = 45:1:1).

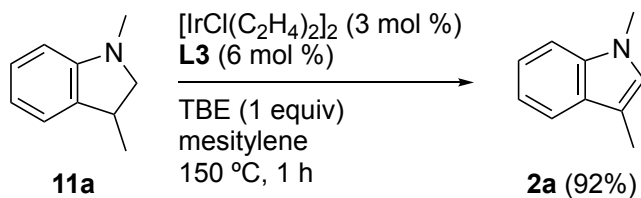
The Reaction of **9** to Afford 2-Ethenyl-*N,N*-dibenzylaniline (**10**) (entry 3)



According to the *general procedure A* described in section 5, the reaction was carried out at 150 °C for 51 h using $[\text{IrCl}(\text{C}_2\text{H}_4)_2]_2$ (1.70 mg, 0.00300 mmol), **L3** (7.02 mg, 0.00600 mmol), **9** (26.5 mg, 0.0879 mmol), *tert*-butylethylene (19.9 mg, 0.236 mmol), and mesitylene (0.2 mL). ¹H NMR analysis of the resulting solution (internal standard: diphenylmethane) indicated that no cyclization took place, although formation of the transfer dehydrogenation product **10** (44%) was observed. **10** was isolated as a colorless oil after purification by HPLC [column: LiChlosorb CN (ϕ 25 mm x 250 mm, 7 μm); eluent: hexane only] and Kugelrohr distillation. **10**: ¹H NMR (400 MHz, CDCl₃) δ 7.54 (dd, J = 8.0, 1.6 Hz, 1H), 7.39 (dd, J = 17.6, 10.8 Hz, 1H), 7.20-7.32 (m, 10H), 7.12 (td, J = 7.6, 1.6 Hz, 1H), 7.00-7.06 (m, 1H), 6.86 (dd, J = 8.0, 0.8 Hz, 1H), 5.74 (dd, J = 17.6, 1.6 Hz, 1H), 5.32 (dd, J = 10.8, 1.6 Hz, 1H), 4.13 (s, 4H). ¹³C NMR (101 MHz, CDCl₃) δ

149.1, 138.2, 134.7, 133.2, 128.8, 128.3, 128.1, 127.1, 126.9, 123.2, 122.1, 113.9, 56.7. HRMS (APCI, positive) m/z calcd for $C_{22}H_{22}N^+$ $[M + H]^+$: 300.1747, found: 300.1751.

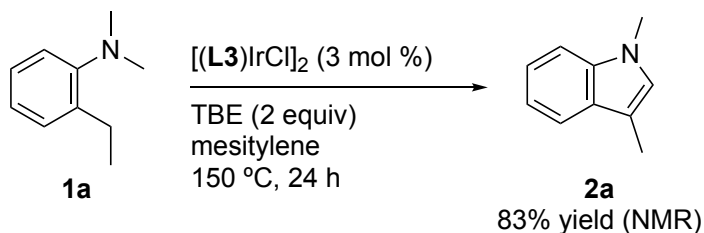
The Reaction of **11a** to Afford **2a** (entry 4)



According to the *general procedure A* described in section 5, the reaction was carried out at 150 °C for 1 h using $[\text{IrCl}(\text{C}_2\text{H}_4)_2]_2$ (3.74 mg, 0.00659 mmol), **L3** (14.6 mg, 0.0124 mmol), **11a** (29.1 mg, 0.198 mmol), *tert*-butylethylene (17.5 mg, 0.208 mmol), and mesitylene (0.4 mL). **2a** (26.5 mg, 0.182 mmol, 92%) was obtained as a colorless oil after purification by column chromatography on silica gel (eluent: hexane:Et₂O:Et₃N = 45:1:1).

An Additional Result involving Reaction Mechanism (ref. 20 in the text)

The reaction of **1a** was examined using an isolated $[(\text{L3})\text{IrCl}]_2$ complex^{8c} as a catalyst. The reaction afforded **2a** in 83% yield, which is almost comparable to the result obtained by $[\text{IrCl}(\text{C}_2\text{H}_4)_2]_2$ with **L3**.

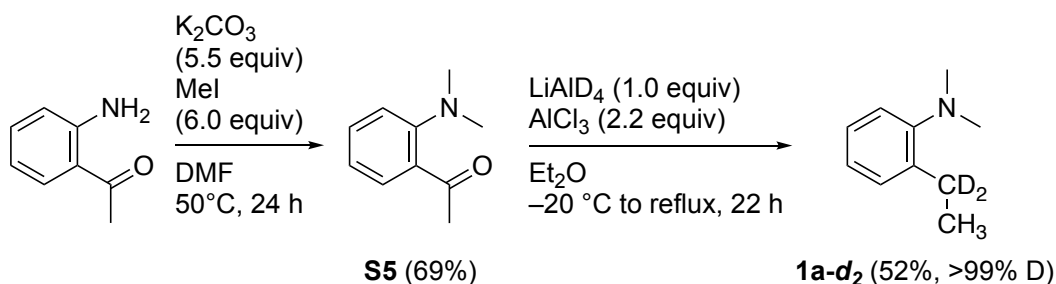


cf. $[\text{IrCl}(\text{C}_2\text{H}_4)_2]_2$ (3 mol %)/**L3** (6 mol %) afforded **2a** in 93% yield (NMR).

7. Reaction of D-Labeled Substrates (Figure 2)

7-1. Preparation of D-Labeled Substrates

2-(Ethyl-1,1-*d*₂)-*N,N*-dimethylaniline (**1a-d**₂)

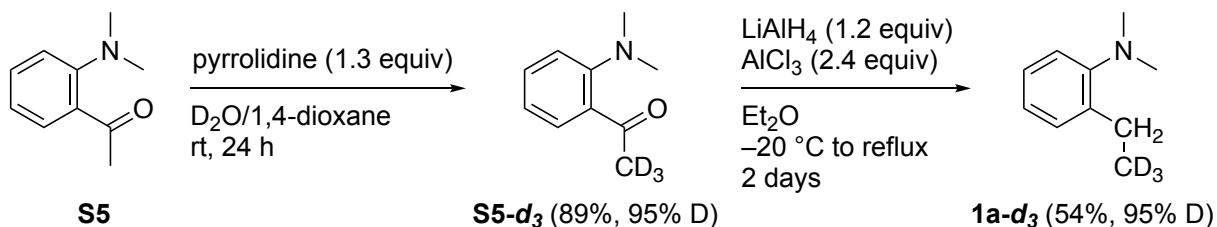


An oven dried 500 mL three-neck flask, equipped with a magnetic stirring bar, a rubber septum, and a three-way stopcock, was charged with potassium carbonate (11.5 g, 83.2 mmol). The flask was evacuated and backfilled with nitrogen. DMF (30 mL), 2-acetylaniline (TCI, 2.05 g, 15.2 mmol), and methyl iodide (13.7 g, 96.5 mmol) were added to the flask. The mixture was stirred for 24 h at 50 °C. Hexane (40 mL), AcOEt (40 mL), and water (50 mL) were added to the flask. The organic materials were collected, washed with water (50 mL x 4) and brine (50 mL x 2), and dried over anhydrous magnesium sulfate. The crude product was purified by column chromatography on silica gel (SiliaFlash; eluent: hexane:Et₂O = 90:10) and Kugelrohr distillation. **S5** (1.71 g, 10.5 mmol, 69% yield) was obtained as a yellow liquid. **S5**: ¹H NMR (400 MHz, CDCl₃) δ 7.41 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.34 (ddd, *J* = 8.4, 7.6, 1.6 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.91 (td, *J* = 7.6, 0.8 Hz, 1H), 2.78 (s, 6H), 2.58 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 203.7, 151.9, 132.6, 131.9, 129.5, 120.2, 117.1, 44.4, 28.6. HRMS (APCI, positive) *m/z* calcd for C₁₀H₁₄NO⁺ [M + H]⁺: 164.1070, found: 164.1068.

The conversion of **S5** into **1a-d**₂ was carried out according to the procedure reported.⁹ An oven dried 50 mL two-neck flask, equipped with a magnetic stirring bar, a condenser with a three-way stopcock, and a rubber septum, was charged with lithium aluminum deuteride (86.0 mg, 2.05 mmol). The flask was evacuated and backfilled with nitrogen. Et₂O (5 mL) was added to the flask, and it was cooled to -20 °C by dry ice/acetone bath. Aluminum chloride (TCI, 597 mg, 4.48 mmol) was added to the flask and the mixture was stirred for 20 min at -20 °C. A Et₂O (1 mL) solution of **S5** (322 mg, 1.97 mmol) was added slowly to the flask. The cooling bath was removed, and the mixture was stirred for 22 h under reflux. The mixture was cooled to 0 °C by

ice/water bath, and ethyl acetate (10 mL) and H₂SO₄ (20% aqueous solution, 8 mL) were added slowly to the flask. The cooling bath was removed, and sodium hydroxide (5N aqueous solution) and sodium carbonate was added until the aqueous layer was basic. The organic materials were extracted with Et₂O (10 mL x 3), washed with brine (50 mL x 2), and dried over anhydrous magnesium sulfate. The crude product was purified by column chromatography on silica gel (eluent: hexane:Et₂O = 97:3) and Kugelrohr distillation. **1a-d₂** (155 mg, 1.02 mmol, 52% yield, >99% D) was obtained as a colorless oil. **1a-d₂**: ¹H NMR (400 MHz, CDCl₃) δ 7.25 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.19 (ddd, *J* = 8.0, 7.2, 1.6 Hz, 1H), 7.11 [dd (AB pattern), *J* = 8.0, 1.6 Hz, 1H], 7.05 (td, *J* = 7.2, 1.6 Hz, 1H), 2.71 (s, 6H), 1.27 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 152.6, 138.8, 129.1, 126.4, 123.4, 119.2, 45.3, 22.9 (quintet, *J* = 19 Hz, CD₂), 14.8. HRMS (APCI, positive) *m/z* calcd for C₁₀H₁₄D₂N⁺ [M + H]⁺: 152.1403, found: 152.1402.

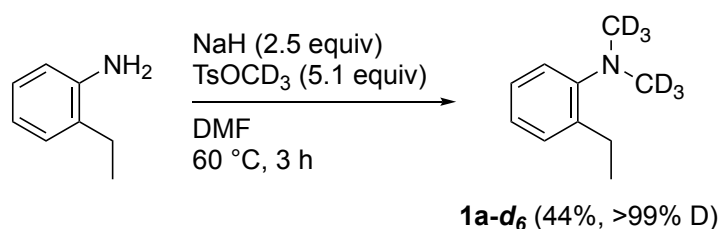
2-(Ethyl-2,2,2-d₃)-*N,N*-dimethylaniline (**1a-d₃**)



The conversion of **S5** into **S5-d₃** was carried out according to the procedure reported.¹⁰ An oven dried 100 mL two-neck flask, equipped with a magnetic stirring bar, a rubber septum, and a three-way stopcock, was evacuated and backfilled with nitrogen. 1,4-Dioxane (4.5 mL), deuterium oxide (Wako, 4.5 mL), pyrrolidine (0.3 mL, 3.7 mmol), and **S5** (480 mg, 2.94 mmol) were added to the flask. The mixture was stirred for 24 h at room temperature. The organic materials were extracted with Et₂O (20 mL x 3), washed with brine (30 mL x 2), and dried over anhydrous magnesium sulfate. The crude product was purified by Kugelrohr distillation. **S5-d₃** (435 mg, 2.62 mmol, 89% yield, 95% D) was obtained as a yellow liquid. **S5-d₃**: ¹H NMR (400 MHz, CDCl₃) δ 7.43 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.35 (ddd, *J* = 8.4, 7.6, 1.6 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 6.92 (td, *J* = 7.6, 0.8 Hz, 1H), 2.79 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 203.9, 152.0, 132.6, 132.0, 129.7, 120.3, 117.2, 44.5, 28.0 (septet, *J* = 20 Hz, CD₃). HRMS (APCI, positive) *m/z* calcd for C₁₀H₁₁D₃NO⁺ [M + H]⁺: 167.1258, found: 167.1257.

An oven dried 50 mL two-neck flask, equipped with a magnetic stirring bar, a condenser with a three-way stopcock, and a rubber septum, was charged with lithium aluminum hydride (87.0 mg, 2.29 mmol). The flask was evacuated and backfilled with nitrogen. Et₂O (5 mL) was added to the flask, and it was cooled to -20 °C by dry ice/acetone bath. Aluminum chloride (TCI, 640 mg, 4.80 mmol) was added to the flask and the mixture was stirred for 20 min at -20 °C. **S5-d₃** (325 mg, 1.96 mmol) was added slowly to the flask. The cooling bath was removed, and the mixture was stirred for 2 days under reflux. The mixture was cooled to 0 °C by ice/water bath, and ethyl acetate (10 mL) and H₂SO₄ (20% aqueous solution, 8 mL) were added slowly to the flask. The cooling bath was removed, and potassium carbonate was added until the aqueous layer was basic. The organic materials were extracted with Et₂O (20 mL x 3), washed with brine (50 mL x 2), and dried over anhydrous magnesium sulfate. The crude product was purified by column chromatography on silica gel (eluent: hexane:Et₂O = 97:3) and Kugelrohr distillation. **1a-d₃** (160 mg, 1.05 mmol, 54% yield, 95% D) was obtained as a colorless oil. **1a-d₃**: ¹H NMR (400 MHz, CDCl₃) δ 7.24-7.29 (m, 1H), 7.17-7.23 (m, 1H), 7.13 [dd (AB pattern), *J* = 8.0, 1.6 Hz, 1H], 7.07 (td, *J* = 7.2, 1.2 Hz, 1H), 2.77 (s, 2H), 2.73 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 152.6, 138.8, 129.0, 126.4, 123.4, 119.2, 45.3, 23.3, 13.6-14.8 (m, CD₃). HRMS (APCI, positive) *m/z* calcd for C₁₀H₁₃D₃N⁺ [M + H]⁺: 153.1466, found: 153.1465.

2-Ethyl-*N,N*-bis(methyl-*d*₃)aniline (**1a-d₆**)

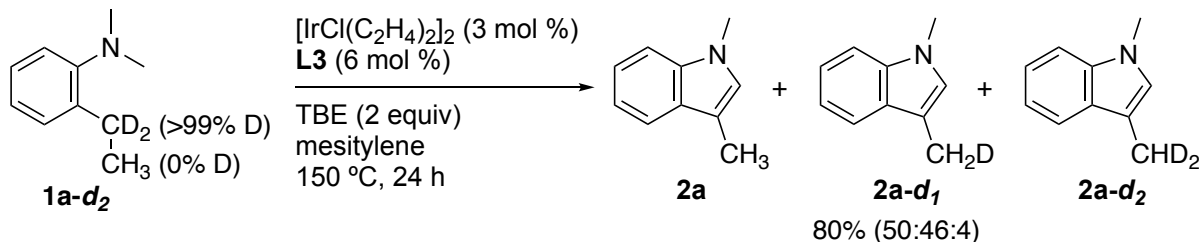


An oven dried 50 mL two-neck flask, equipped with a magnetic stirring bar, a rubber septum, and a condenser, was charged with NaH (ca. 60% dispersion in mineral oil, 0.3 g, 7.5 mmol). The flask was evacuated and backfilled with nitrogen. DMF (9 mL), 2-ethylaniline (Wako, 0.364 g, 3.00 mmol), and TsOCD₃ (2.91 g, 15.4 mmol)¹¹ were added to the flask. The mixture was stirred for 3 h at 60 °C. After cooling to room temperature, hexane (10 mL), AcOEt (10 mL), and water (20 mL) were added to the flask. The organic materials were washed with water (20 mL x 4) and

brine (20 mL x 1), and dried over anhydrous magnesium sulfate. The crude product was purified by column chromatography on silica gel (SiliaFlash; eluent: hexane:Et₂O = 97:3) and Kugelrohr distillation. **1a-d₆** (0.203 g, 1.31 mmol, 44% yield) was obtained as a colorless oil. **1a-d₆**: ¹H NMR (400 MHz, CDCl₃) δ 7.25 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.15-7.21 (m, 1H), 7.10 [dd (AB pattern), *J* = 7.6, 1.2 Hz, 1H], 7.05 (td, *J* = 7.6, 1.2 Hz, 1H), 2.76 (q, *J* = 7.6 Hz, 2H), 1.28 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 152.6, 138.8, 129.0, 126.4, 123.4, 119.1, 44.3 (septet, *J* = 20 Hz, CD₃), 23.6, 14.9. HRMS (APCI) *m/z* calcd for C₁₀H₁₀D₆N⁺ [M + H]⁺: 156.1654, found: 156.1652.

7-2. Reaction of D-Labeled Substrates (Figure 2)

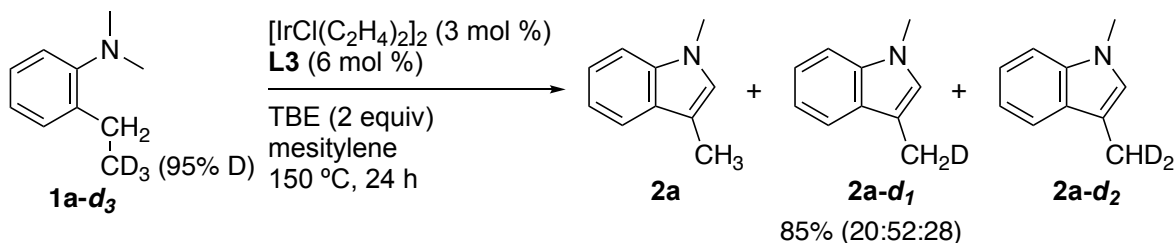
The Reaction of **1a-d₂** (entry 1)



According to the *general procedure A* described in section 5, the reaction was carried out at 150 °C for 24 h using [IrCl(C₂H₄)₂]₂ (3.41 mg, 0.00601 mmol), **L3** (14.0 mg, 0.0119 mmol), **1a-d₂** (31.1 mg, 0.206 mmol), *tert*-butylethylene (34.2 mg, 0.406 mmol), and mesitylene (0.4 mL). A mixture of **2a** and **2a-d₁** (24.0 mg, 0.164 mmol, 80%) was obtained as a white solid after purification by column chromatography on silica gel (eluent: hexane:Et₂O:Et₃N = 45:1:1). **2a** and **2a-d₁** were detected by HRMS analysis of the mixture. Although **2a-d₂** did not detected by HRMS analysis, ¹H NMR analysis indicated formation of it. The ratio of **2a**, **2a-d₁**, and **2a-d₂** was determined as 50:46:4 by ²H-decoupled ¹H NMR measurement. This ratio did not change after 48 h under the reaction conditions. Followings are the peaks observed in NMR analyses of a mixture of **2a**, **2a-d₁**, and **2a-d₂**: ¹H NMR (400 MHz, CDCl₃) δ 7.61 (d, *J* = 8.0 Hz, 1H), 7.31 [d (AB pattern), *J* = 8.0 Hz, 1H], 7.26 (t, *J* = 8.0 Hz, 1H), 7.15 (t, *J* = 8.0 Hz, 1H), 6.85 (s, 1H), 3.76 (s, 3H), 2.34-2.39 (m, 2.45H). ¹³C NMR (101 MHz, CDCl₃) δ 137.1, 128.8, 126.6, 121.5, 119.0, 118.6, 110.2, 109.1, 32.6, 9.7 (CH₃), 9.4 (t, *J* = 20 Hz, CH₂D). **2a**: HRMS (APCI, positive) *m/z*

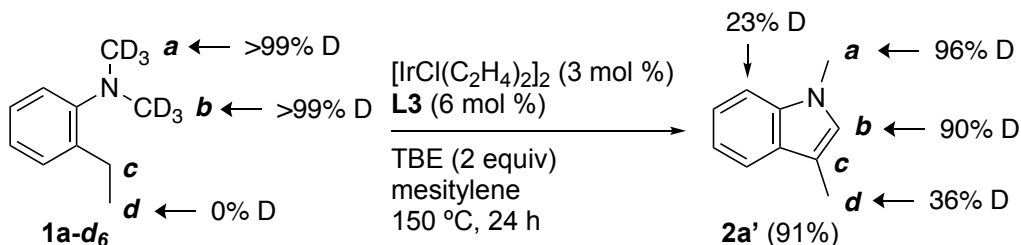
calcd for $C_{10}H_{12}N^+$ $[M + H]^+$: 146.0964, found: 146.0963. **2a-d₁**: HRMS (APCI, positive) m/z calcd for $C_{10}H_{11}DN^+$ $[M + H]^+$: 147.1027, found: 147.1022.

The Reaction of **1a-d₃** (entry 2)



According to the *general procedure A* described in section 5, the reaction was carried out at 150 °C for 24 h using $[IrCl(C_2H_4)_2]_2$ (4.01 mg, 0.00707 mmol), **L3** (15.3 mg, 0.0130 mmol), **1a-d₃** (28.7 mg, 0.188 mmol), *tert*-butylethylene (32.8 mg, 0.390 mmol), and mesitylene (0.4 mL). A mixture of **2a**, **2a-d₁**, and **2a-d₂** (24.4 mg, 0.160 mmol, 85%) was obtained as a white solid after purification by column chromatography on silica gel (eluent: hexane:Et₂O:Et₃N = 45:1:1). **2a**, **2a-d₁**, and **2a-d₂** were detected by HRMS analysis of the mixture. The ratio of **2a**, **2a-d₁**, and **2a-d₂** was determined as 20:52:28 by ²H-decoupled ¹H NMR measurement. This ratio did not change after 48 h under the reaction conditions. Followings are the peaks observed in NMR analyses of a mixture of **2a**, **2a-d₁**, and **2a-d₂**: ¹H NMR (400 MHz, CDCl₃) δ 7.61 (d, $J = 7.6$ Hz, 1H), 7.31 [d (AB pattern), $J = 7.6$ Hz, 1H], 7.26 (t, $J = 7.6$ Hz, 1H), 7.14 (t, $J = 7.6$ Hz, 1H), 6.85 (s, 1H), 3.75 (s, 3H), 2.31-2.39 (m, 1.91H). ¹³C NMR (101 MHz, CDCl₃) δ 137.1, 128.8, 126.6, 121.5, 119.1, 118.6, 110.2, 109.1, 32.6, 9.7 (CH₃), 9.4 (t, $J = 20$ Hz, CH₂D), 9.2 (quintet, $J = 20$ Hz, CHD₂). **2a**: HRMS (APCI, positive) m/z calcd for $C_{10}H_{12}N^+$ $[M + H]^+$: 146.0964, found: 146.0966. **2a-d₁**: HRMS (APCI, positive) m/z calcd for $C_{10}H_{11}DN^+$ $[M + H]^+$: 147.1027, found: 147.1027. **2a-d₂**: HRMS (APCI, positive) m/z calcd for $C_{10}H_{10}D_2N^+$ $[M + H]^+$: 148.1090, found: 148.1088.

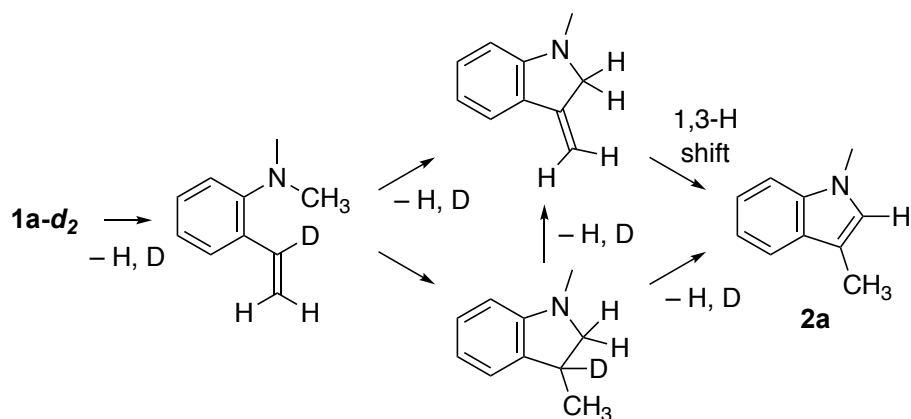
The Reaction of **1a-d₆** (ref. 22 in the text)



According to the *general procedure A* described in section 5, the reaction was carried out at 150 °C for 24 h using [IrCl(C₂H₄)₂]₂ (4.48 mg, 0.00789 mmol), **L3** (15.1 mg, 0.0128 mmol), **1a-d₆** (28.7 mg, 0.185 mmol), *tert*-butylethylene (34.9 mg, 0.415 mmol), and mesitylene (0.4 mL). **2a'** (25.5 mg, 0.169 mmol, 91%) was obtained as a white solid after purification by column chromatography on silica gel (eluent: hexane:Et₂O:Et₃N = 45:1:1). ¹H NMR analysis of **2a'** indicated that 36% of H on C^d was replaced by D. The exact mass for C₁₀H₆D₅N (**d₅**) and C₁₀H₅D₆N (**d₆**) were detected by HRMS analysis of **2a'**. **2a'**: ¹H NMR (400 MHz, CDCl₃) δ 7.62 (dt, *J* = 8.0, 1.2 Hz, 1.00H), 7.32 [dt (AB pattern), *J* = 8.4, 1.2 Hz, 0.77H], 7.24-7.29 (m, 1.00H), 7.13-7.18 (m, 1.00H), 6.85 (s, 0.10H), 3.71-3.76 (m, 0.11H), 2.32-2.38 (m, 1.91H). ¹³C NMR (101 MHz, CDCl₃) δ 137.1, 128.8, 126.6, 121.5, 121.4, 119.0, 118.6, 110.2, 110.0, 109.1, 31.2-32.2 (m), 30.5, 8.89-9.8 (m). HRMS (APCI, positive) *m/z* calcd for C₁₀H₇D₅N⁺ [M + H]⁺: 151.1278, found: 151.1277; *m/z* calcd for C₁₀H₆D₆N⁺ [M + H]⁺: 152.1341, found: 152.1338.

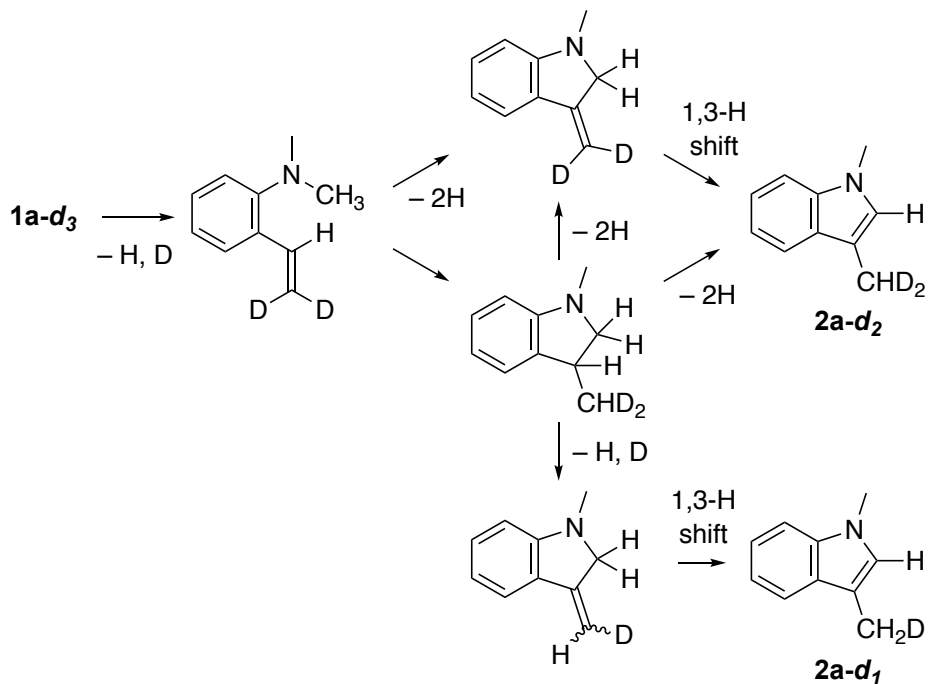
7-3. Discussion for the H/D Scrambling

Assuming that H/D scrambling through elimination–addition of H–Ir–D does not occur, the reaction pathways for the conversion of **1a-d₂** are proposed as shown in Scheme S1. Based on the pathways, **2a** is only an expected product. The experimental result that **2a-d₁** was formed with **2a** reasonably explained by existence of fast equilibrium between **A** and **B** and slow ligand exchange of **B** with *tert*-butylethylene to give **C** and **3** (Scheme 4).



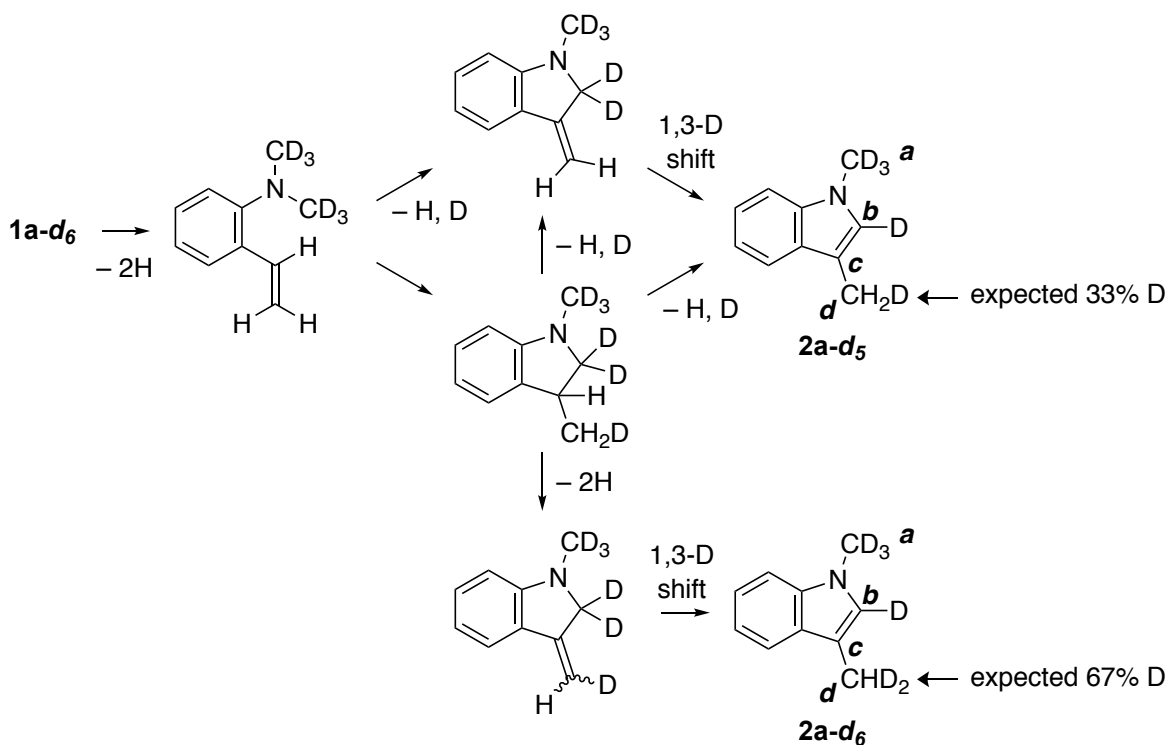
Scheme S1. Possible Reaction Pathways of **1a-d₂** Assuming no H/D Scrambling through Elimination–Addition of H–Ir–D

Under the same assumption, the reaction pathways for the conversion of **1a-d₃** are proposed as shown in Scheme S2. Based on the pathways, **2a-d₁** and **2a-d₂** are expected products. The experimental result that **2a** was formed with **2a-d₁** and **2a-d₂** also reasonably explained by existence of fast equilibrium between **A** and **B** and slow ligand exchange of **B** with *tert*-butylethylene to give **C** and **3** (Scheme 4).



Scheme S2 Possible Reaction Pathways of **1a-d₃** Assuming no H/D Scrambling through Elimination–Addition of H–Ir–D

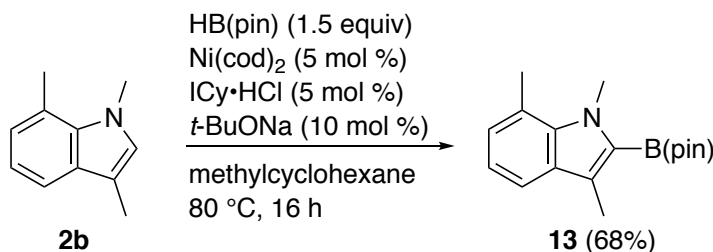
Under the same assumption, the reaction pathways for the conversion of **1a-d₆** are proposed as shown in Scheme S3. Based on the pathways, the percentage of D at the C^d of the product is expected to be 33–67%. The experimental result (36% D) is within this range.



Scheme S3 Possible Reaction Pathways of **1a-d₆** Assuming no H/D Scrambling through Elimination–Addition of H–Ir–D

8. Application for the Isomer-Selective Synthesis of Borylindoles (Scheme 4-i)

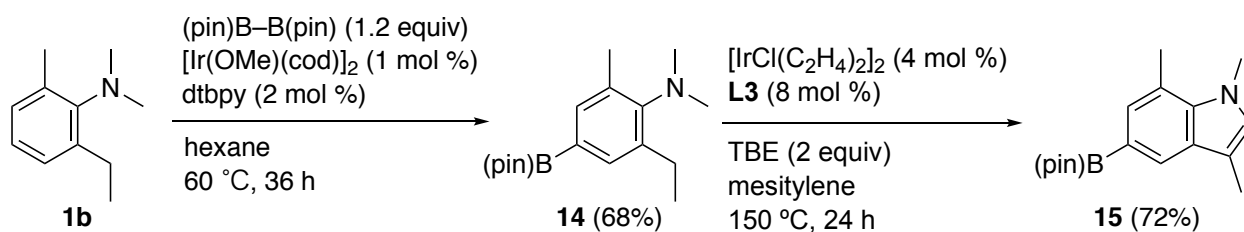
8-1. Synthesis of 1,3,7-Trimethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (**13**)



The nickel-catalyzed C–H borylation was carried out according to the procedure reported.¹² In a glovebox, a glass tube (outside diameter: 20 mm) having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with Ni(cod)₂ (1.28 mg, 0.00465 mmol), ICy·HCl (1.28 mg, 0.00476 mmol), *t*-BuONa (0.97 mg, 0.0101 mmol), HB(pin) (17.5 mg, 0.137 mmol), **2b**

(14.9 mg, 0.0936 mmol), and methylcyclohexane (0.125 mL). The tube was sealed by the stopcock and was taken out from the glovebox. The mixture was stirred at 80 °C by a heating magnetic stirrer with an aluminum heating block (hole size: 21 mm diameter x 33 mm depth). After 16 h, the tube was cooled to room temperature, and the volatiles were removed under reduced pressure. **13** (18.2 mg, 0.0638 mmol, 68%) was obtained as a white solid after purification by column chromatography on silica gel (eluent: hexane:Et₂O = 20:1). **13**: ¹H NMR (400 MHz, CDCl₃) δ 7.41-7.47 (m, 1H), 6.91-6.97 (m, 2H), 4.22 (s, 3H), 2.79 (s, 3H), 2.53 (s, 3H), 1.38 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 139.1, 129.6, 126.3, 125.1, 121.5, 118.8, 118.0, 83.3, 35.6, 25.0, 20.8, 10.4. The boron-bound carbon was not detected due to quadrupolar relaxation. ¹¹B NMR (101 MHz, CDCl₃) δ 28.6. HRMS (APCI, positive) *m/z* calcd for C₁₇H₂₅BNO₂⁺ [M + H]⁺: 286.1973, found: 286.1978.

8-2. Synthesis of 1,3,7-Trimethyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (**15**)



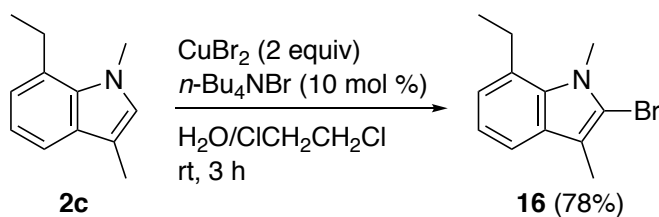
The iridium-catalyzed C–H borylation was carried out according to the procedure reported.¹³ In a glovebox, a glass tube (outside diameter: 20 mm) having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with [Ir(OMe)(cod)]₂ (26.1 mg, 0.0394 mmol), 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtbpy, 22.4 mg, 0.0835 mmol), bis(pinacolato)diboron (1.20 g, 4.73 mmol), hexane (6 mL), and **1b** (0.634 g, 3.88 mmol). The tube was sealed by the stopcock and was taken out from the glovebox. The mixture was stirred at 60 °C by a heating magnetic stirrer with an aluminum heating block (hole size: 21 mm diameter x 33 mm depth). After 36 h, the tube was cooled to room temperature, and the volatiles were removed under reduced pressure. **14** (0.762 g, 2.63 mmol, 68%) was obtained as a white solid after purification by column chromatography on silica gel (eluent: hexane:Et₂O = 20:1) and Kugelrohr distillation. **14**: ¹H NMR (400 MHz, CDCl₃) δ 7.59 (s, 1H), 7.55 (s, 1H), 2.90 (s, 6H), 2.75 (q, *J* = 7.6 Hz,

2H), 2.38 (s, 3H), 1.40 (s, 12H), 1.30 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 152.5, 142.8, 136.7, 135.8, 134.0, 125.3 (broad, C–B), 83.6, 42.9, 25.3, 24.9, 19.2, 15.8. ^{11}B NMR (128 MHz, CDCl_3) δ 30.4. HRMS (APCI, positive) m/z calcd for $\text{C}_{17}\text{H}_{29}\text{BNO}_2^+$ [$\text{M} + \text{H}$] $^+$: 290.2286, found: 290.2288.

According to the *general procedure A* described in section 5, the reaction was carried out at 150 °C for 24 h using $[\text{IrCl}(\text{C}_2\text{H}_4)_2]_2$ (4.63 mg, 0.00816 mmol), **L3** (17.7 mg, 0.0150 mmol), **14** (57.9 mg, 0.200 mmol), *tert*-butylethylene (32.3 mg, 0.384 mmol), and mesitylene (0.4 mL). **15** (40.8 mg, 0.143 mmol, 72% including <2% of a structural isomer) was obtained as a white solid after purification by column chromatography on silica gel (eluent: toluene: $\text{Et}_3\text{N} = 30:1$). **15**: ^1H NMR (400 MHz, CDCl_3) δ 7.92 (s, 1H), 7.35 (s, 1H), 6.69 (d, $J = 1.2$ Hz, 1H), 3.98 (s, 3H), 2.75 (s, 3H), 2.30 (d, $J = 1.2$ Hz, 3H), 1.38 (s, 12H). ^{13}C NMR (101 MHz, CDCl_3) δ 137.8, 130.0, 129.5, 128.2, 125.1, 120.2, 110.8, 83.3, 36.3, 24.9, 19.5, 9.6. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, CDCl_3) δ 30.7. HRMS (APCI, positive) m/z calcd for $\text{C}_{17}\text{H}_{25}\text{BNO}_2^+$ [$\text{M} + \text{H}$] $^+$: 286.1973, found: 286.1977.

9. Application for the Isomer-Selective Synthesis of Bromoindoles (Scheme 4-ii)

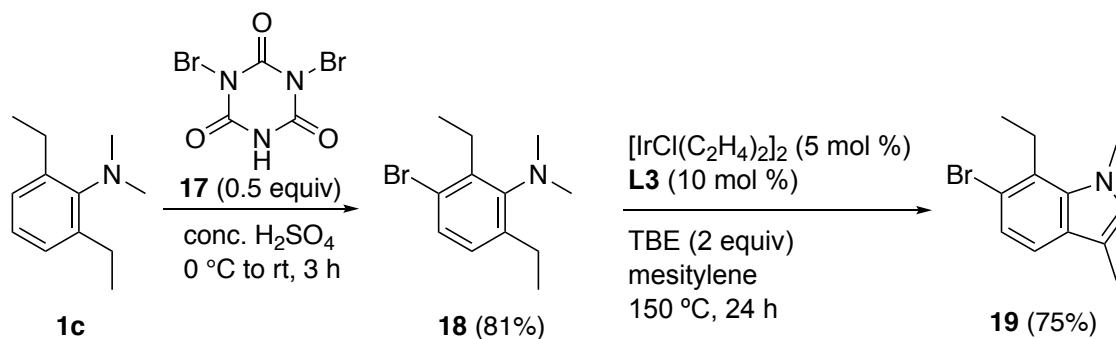
9-1. Synthesis of 2-Bromo-7-ethyl-1,3-dimethyl-1*H*-indole (**16**)



The bromination using CuBr_2 and $n\text{-Bu}_4\text{NBr}$ was carried out according to the procedure reported.¹⁴ In a glovebox, a glass tube (outside diameter: 20 mm) having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with CuBr_2 (97.4 mg, 0.436 mmol), tetrabutylammonium bromide (7.56 mg, 0.0235 mmol), **2c** (36.3 mg, 0.210 mmol), and 1,2-dichloroethane (2 mL). The tube was sealed by the stopcock and was taken out from the glovebox. Water (0.080 mL) was added to the tube under the nitrogen stream, and the tube was sealed by the stopcock again. The mixture was stirred for 3 h at room temperature. **16** (41.3 mg, 0.164 mmol, 78%) was obtained as a white solid after purification by column chromatography on

silica gel (eluent: hexane:Et₂O = 80:1). **16**: ¹H NMR (400 MHz, CDCl₃) δ 7.38 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.98-7.02 (m, 1H), 4.00 (s, 3H), 3.12 (q, *J* = 7.6 Hz, 2H), 2.31 (s, 3H), 1.37 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 135.3, 129.0, 127.4, 123.2, 119.8, 116.4, 114.8, 111.0, 34.6, 26.1, 16.7, 10.4. HRMS (APCI, positive) *m/z* calcd for C₁₂H₁₅BrN⁺ [M + H]⁺: 252.0382, found: 252.0384.

9-2. Synthesis of 6-Bromo-7-ethyl-1,3-dimethyl-1*H*-indole (**19**)



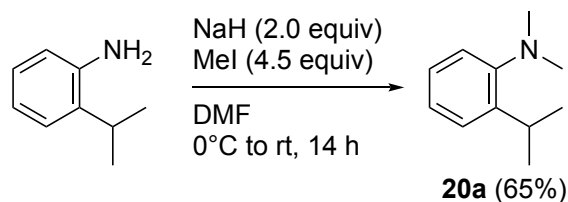
The bromination using dibromoisocyanuric acid (**17**) was carried out according to the procedure reported.¹⁵ A 100 mL three-neck flask, equipped with a magnetic stirring bar, a dropping funnel, a rubber septum, and a three-way stopcock, was evacuated and backfilled with nitrogen. **1c** (0.340 g, 1.92 mmol) and conc. H₂SO₄ (2 mL) were added to the flask, and the mixture was cooled to 0 °C by ice/water bath. A suspension of **17** (0.296 g, 1.03 mmol) in conc. H₂SO₄ (4 mL) was added slowly to the flask through the dropping funnel. The cooling bath was removed, and the mixture was stirred for 3 h at room temperature. Ice was added to the flask, and then potassium carbonate were added until the aqueous layer was basic. The organic materials were extracted with Et₂O (60 mL x 3), washed with brine (100 mL x 1), and dried over anhydrous magnesium sulfate. The crude product was purified by column chromatography on silica gel (eluent: hexane) and Kugelrohr distillation. **18** (0.396 g, 1.55 mmol, 81%) was obtained as a colorless oil. **18**: ¹H NMR (400 MHz, CDCl₃) δ 7.33 (d, *J* = 8.0 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 2.84 (s, 6H), 2.83 (q, *J* = 7.6 Hz, 2H), 2.61 (q, *J* = 7.6 Hz, 2H), 1.21 (t, *J* = 7.6 Hz, 3H), 1.20 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 150.5, 144.2, 144.1, 130.5, 128.2, 122.4, 44.0, 25.8, 24.8, 15.5, 14.4. HRMS (APCI, positive) *m/z* calcd for C₁₂H₁₈BrN⁺ [M + H]⁺: 256.0695, found: 256.0697.

According to the *general procedure A* described in section 5, the reaction was carried out at 150 °C for 24 h using $[\text{IrCl}(\text{C}_2\text{H}_4)_2]_2$ (5.49 mg, 0.00967 mmol), **L3** (23.8 mg, 0.0202 mmol), **18** (51.9 mg, 0.203 mmol), *tert*-butylethylene (35.0 mg, 0.416 mmol), and mesitylene (0.4 mL). **19** (38.7 mg, 0.153 mmol, 75%) was obtained as a colorless oil after purification by column chromatography on silica gel (eluent: hexane: CH_2Cl_2 : Et_3N = 45:3:2). **19**: ^1H NMR (400 MHz, CDCl_3) δ 7.28 [d (AB pattern), J = 8.4 Hz, 1H], 7.23 [d (AB pattern), J = 8.4 Hz, 1H], 6.71 (d, J = 0.8 Hz, 1H), 3.96 (s, 3H), 3.25 (q, J = 7.6 Hz, 2H), 2.29 (d, J = 0.8 Hz, 3H), 1.32 (t, J = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 135.4, 129.7, 129.5, 126.8, 123.9, 119.0, 118.0, 110.1, 36.8, 24.7, 15.6, 9.4. HRMS (APCI, positive) m/z calcd for $\text{C}_{12}\text{H}_{15}\text{BrN}^+$ $[\text{M} + \text{H}]^+$: 252.0382, found: 252.0385.

10. Asymmetric Conversion of **20** Affording Enantioenriched Indolines **21** (Table 2)

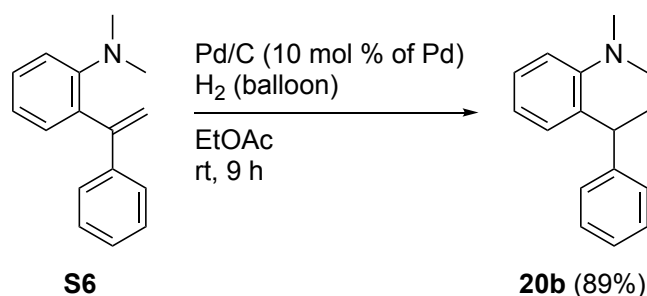
10-1. Preparation of **20a–e**

2-Isopropyl-*N,N*-dimethylaniline (**20a**)



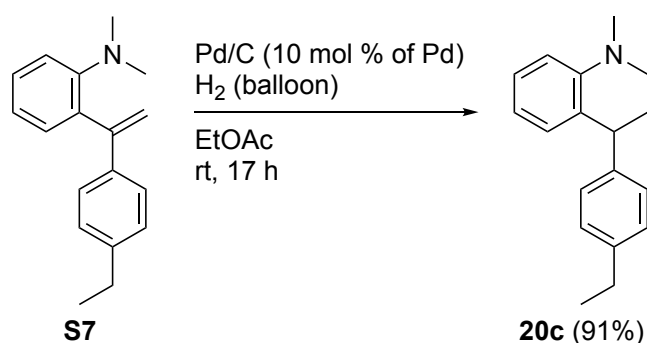
According to the procedure given for **1a**, **20a** (1.19 g, 7.29 mmol, 65% yield) was prepared as a colorless oil from 2-isopropylaniline (TCI, 1.53 g, 11.3 mmol). **20a**: ^1H NMR (400 MHz, CDCl_3) δ 7.29 (dd, J = 7.6, 1.6 Hz, 1H), 7.07-7.20 (m, 3H), 3.58 (septet, J = 6.8 Hz, 1H), 2.71 (s, 6H), 1.25 (d, J = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 151.9, 144.3, 126.6, 126.3, 124.1, 119.7, 46.0, 26.8, 24.3. HRMS (APCI, positive) m/z calcd for $\text{C}_{11}\text{H}_{18}\text{N}^+$ $[\text{M} + \text{H}]^+$: 164.1434, found: 164.1432.

N,N-Dimethyl-2-(1-phenylethyl)aniline (**20b**)



A 100 mL two-neck flask, equipped with a magnetic stirring bar, a rubber septum, and a three-way stopcock, was charged with Pd/C (Aldrich, 5 wt% Pd, 3.30 g, 0.75 mmol of Pd). The flask was evacuated and backfilled with nitrogen. H₂ balloon was attached, and the flask was evacuated and backfilled with H₂. EtOAc (45 mL) and **S6**⁷ (1.67 g, 7.48 mmol) were added to the flask, and the mixture was stirred for 9 h at room temperature. Insoluble materials were removed by filtration through a pad of celite. **20b** (1.57 g, 6.97 mmol, 89%) was obtained as a colorless oil after purification by Kugelrohr distillation (110 °C, 0.3 Torr). **20b**⁷: ¹H NMR (400 MHz, CDCl₃) δ 7.11-7.28 (m, 8H), 7.03-7.08 (m, 1H), 4.86 (q, *J* = 7.2 Hz, 1H), 2.62 (s, 6H), 1.59 (d, *J* = 7.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 152.4, 147.0, 142.1, 128.4, 128.1, 127.6, 126.7, 125.5, 124.1, 120.4, 45.8, 37.4, 22.3.

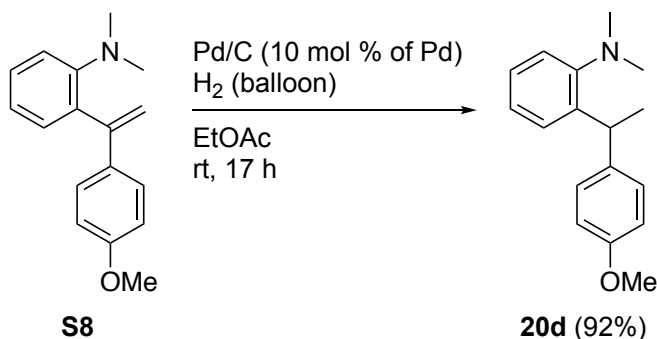
N,N-Dimethyl-2-[1-(4-ethylphenyl)ethyl]aniline (**20c**)



According to the procedure given for **20b**, **20c** (0.920 g, 3.63 mmol, 91% yield) was prepared as a colorless oil from **S7**⁷ (1.00 g, 3.98 mmol). **20c**: ¹H NMR (400 MHz, CDCl₃) δ 7.13-7.24 (m, 5H), 7.02-7.12 (m, 3H), 4.84 (q, *J* = 7.2 Hz, 1H), 2.64 (s, 6H), 2.61 (q, *J* = 7.6 Hz, 2H), 1.59 (d, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 152.5, 144.3, 142.5, 141.5,

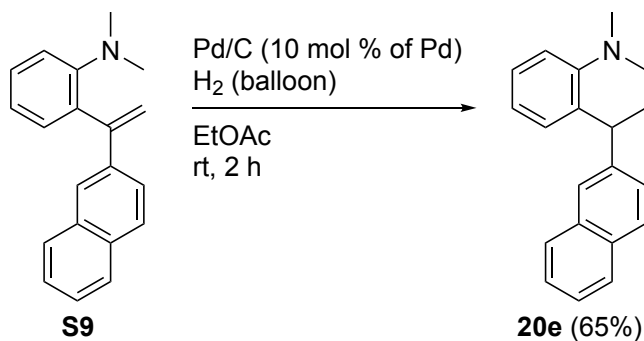
128.6, 127.73, 127.66, 126.7, 124.2, 120.5, 46.0, 37.1, 28.5, 22.6, 15.7. HRMS (ESI) m/z calcd for $C_{18}H_{24}N^+$ $[M + H]^+$: 254.1903, found: 254.1905.

N,N-Dimethyl-2-[1-(4-methoxyphenyl)ethyl]aniline (**20d**)



According to the procedure given for **20b**, **20d** (1.17 g, 4.58 mmol, 92% yield) was prepared as a colorless oil from **S8**⁷ (1.26 g, 4.97 mmol). **20d**: ¹H NMR (400 MHz, CDCl₃) δ 7.15-7.22 (m, 5H), 7.03-7.10 (m, 1H), 6.79-6.84 (m, 2H), 4.82 (q, $J = 7.2$ Hz, 1H), 3.78 (s, 3H), 2.64 (s, 6H), 1.57 (d, $J = 7.2$ Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 157.6, 152.5, 142.5, 139.3, 128.6, 128.5, 126.7, 124.2, 120.5, 113.6, 55.3, 46.0, 36.7, 22.7. HRMS (ESI) m/z calcd for $C_{17}H_{22}NO^+$ $[M + H]^+$: 256.1696, found: 256.1697.

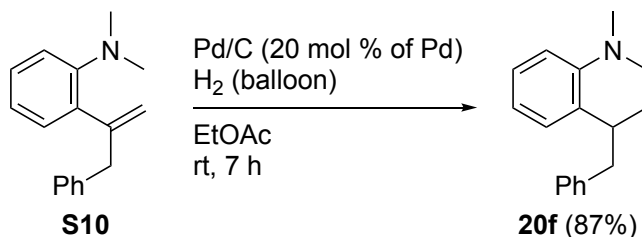
N,N-Dimethyl-2-[1-(2-naphthyl)ethyl]aniline (**20e**)



According to the procedure given for **20b**, **20e** (0.417 g, 1.11 mmol, 65% yield) was prepared as a colorless oil from **S9**⁷ (0.465 g, 1.70 mmol). **20e**: ¹H NMR (400 MHz, CDCl₃) δ 7.78-7.84 (m, 2H), 7.72-7.77 (m, 2H), 7.37-7.50 (m, 3H), 7.21-7.28 (m, 3H), 7.06-7.13 (m, 1H), 5.06 (q, $J = 7.2$ Hz, 1H), 2.69 (s, 6H), 1.73 (d, $J = 7.2$ Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 152.6, 144.7,

142.0, 133.6, 132.0, 128.8, 127.9, 127.8, 127.6, 127.5, 126.9, 125.9, 125.3, 125.0, 124.3, 120.6, 46.0, 37.7, 22.3. HRMS (ESI) m/z calcd for $C_{20}H_{22}N^+$ $[M + H]^+$: 276.1747, found: 276.1750.

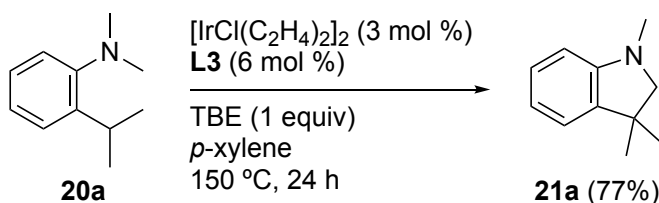
N,N-Dimethyl-2-(1-phenylpropan-2-yl)aniline (**20f**)



According to the procedure given for **20b**, **20f** (1.98 g, 8.27 mmol, 87% yield) was prepared as a colorless oil from **S10**⁷ (2.25 g, 9.48 mmol). **20f**: ¹H NMR (400 MHz, CDCl₃) δ 7.30-7.48 (m, 1H), 7.20-7.62 (m, 2H), 6.98-7.20 (m, 6H), 3.69-3.80 (m, 1H), 2.92 [dd (AB pattern), $J = 13.6, 6.4$ Hz, 1H], 2.72 [dd (AB pattern), $J = 13.6, 8.8$ Hz, 1H], 2.60 (s, 6H), 1.19 (d, $J = 6.8$ Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 152.5, 142.9, 141.5, 129.3, 128.1, 126.9, 126.5, 125.8, 124.1, 120.2, 45.9, 45.0, 34.0, 21.2. HRMS (ESI) m/z calcd for $C_{17}H_{22}N^+$ $[M + H]^+$: 240.1747, found: 240.1747.

10-2. Reaction of **20a**–**e** (Table 2)

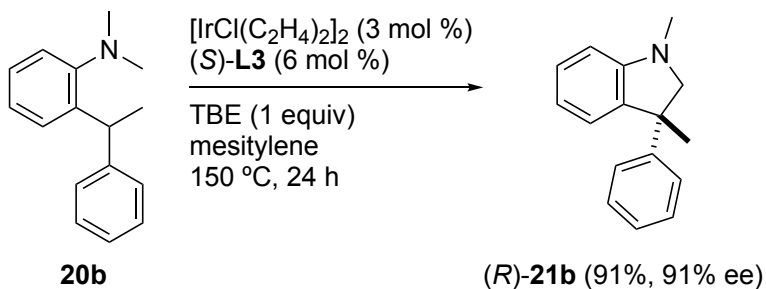
The Reaction of **20a** to Afford 1,3,3-Trimethylindoline (**21a**) (entry 1)



According to the *general procedure A* described in section 5, the reaction was carried out at 150 °C for 24 h using $[\text{IrCl}(\text{C}_2\text{H}_4)_2]_2$ (3.55 mg, 0.00625 mmol), **L3** (14.2 mg, 0.0120 mmol), **20a** (34.0 mg, 0.208 mmol), *tert*-butylethylene (17.6 mg, 0.209 mmol), and *p*-xylene (0.4 mL). Since mesitylene was difficult to separate from **21a**, *p*-xylene was used as a solvent. **21a** (26.0 mg, 0.161 mmol, 77%) was obtained as a colorless oil after purification by column chromatography on silica gel (eluent: hexane:Et₂O:Et₃N = 45:1:1). **21a**: ¹H NMR (400 MHz, CDCl₃) δ 7.12 (t, $J = 7.6$ Hz, 1H), 7.03 (d, $J = 7.2$ Hz, 1H), 6.73 (t, $J = 7.6$ Hz, 1H), 6.51 (d, $J = 7.6$ Hz, 1H), 3.09 (s,

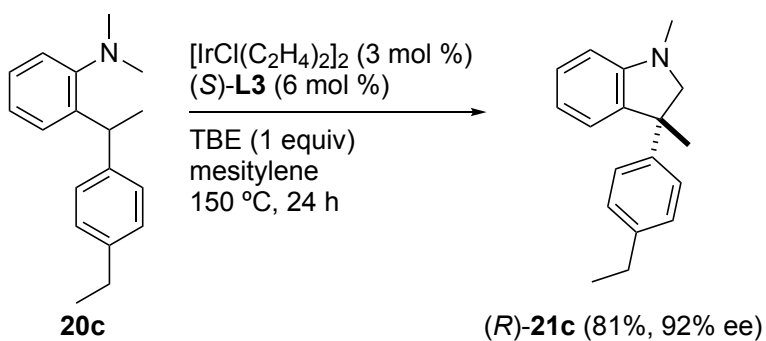
2H), 2.77 (s, 3H), 1.32 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 152.1, 139.4, 127.6, 121.7, 118.0, 107.5, 70.4, 40.4, 36.2, 27.5. HRMS (APCI, positive) m/z calcd for $\text{C}_{11}\text{H}_{16}\text{N}^+$ $[\text{M} + \text{H}]^+$: 162.1277, found: 162.1276.

The Reaction of **20b** to Afford 1,3-Dimethyl-3-phenylindoline (**21b**) (entry 2)



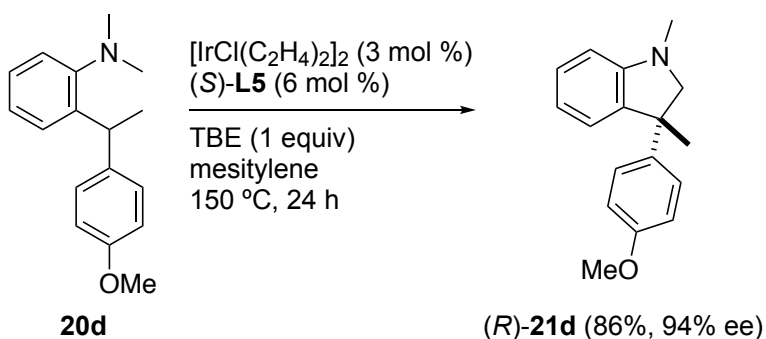
According to the *general procedure A* described in section 5, the reaction was carried out at 150 °C for 24 h using $[\text{IrCl}(\text{C}_2\text{H}_4)_2]_2$ (3.51 mg, 0.00618 mmol), $(S)\text{-L3}$ (15.1 mg, 0.0128 mmol), **20c** (46.1 mg, 0.205 mmol), *tert*-butylethylene (18.7 mg, 0.222 mmol), and mesitylene (0.4 mL). **21c** (41.8 mg, 0.187 mmol, 91%) was obtained as a colorless oil after purification by column chromatography on silica gel (eluent: hexane: Et_2O = 10:1). Enantiomeric excess of **21c** was determined to be 91% by SFC analysis [column: Daicel Chiralcel OD-H (4.6 mm x 250 mm); eluent: CO_2 :2-PrOH = 100:2; flow rate: 3.06 mL/min; detection wavelength: 220 nm; T_R = 6.7 (major), 7.5 (minor) min]. The absolute configuration of the major enantiomer was assigned as *R* on the basis of the previous study.⁷ $(R)\text{-21b}$ ⁷: ^1H NMR (400 MHz, CDCl_3) δ 7.25-7.34 (m, 4H), 7.16-7.24 (m, 1H), 7.15 (dd, J = 7.6, 1.6 Hz, 1H), 6.96 (dd, J = 7.2, 1.6 Hz, 1H), 6.74 (td, J = 7.6, 0.8 Hz, 1H), 6.58 (d, J = 8.0 Hz, 1H), 3.53 (d, J = 8.8 Hz, 1H), 3.31 (d, J = 8.8 Hz, 1H), 2.78 (s, 3H), 1.71 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 152.7, 147.7, 137.8, 128.3, 128.0, 126.7, 126.3, 123.9, 118.3, 107.8, 72.3, 48.4, 36.1, 26.4. $[\alpha]_D^{26} +31.2$ (c 0.52, CHCl_3 , 91% ee).

The Reaction of **20c** to Afford 3-(4-Ethylphenyl)-1,3-dimethylindoline (**21c**) (entry 3)



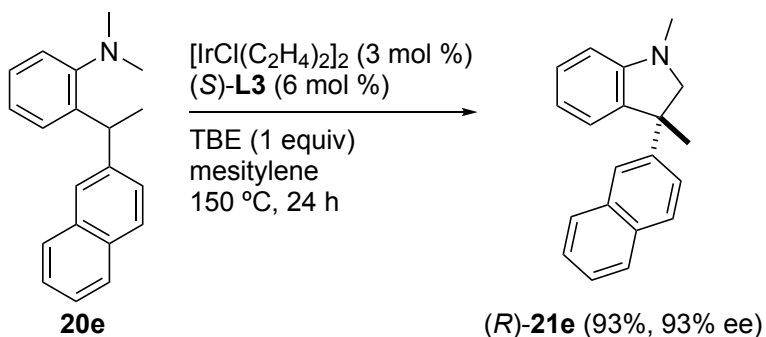
According to the *general procedure A* described in section 5, the reaction was carried out at 150 °C for 24 h using $[\text{IrCl}(\text{C}_2\text{H}_4)_2]_2$ (3.74 mg, 0.00659 mmol), **(S)-L3** (14.4 mg, 0.0122 mmol), **20c** (52.7 mg, 0.208 mmol), *tert*-butylethylene (20.8 mg, 0.247 mmol), and mesitylene (0.4 mL). **21c** (42.6 mg, 0.169 mmol, 81%) was obtained as a colorless oil after purification by column chromatography on silica gel (eluent: hexane:Et₂O = 10:1). Enantiomeric excess of **21c** was determined to be 92% by SFC analysis [column: Daicel Chiralcel OD-H (4.6 mm x 250 mm); eluent: CO₂:2-PrOH = 100:3; flow rate: 3.09 mL/min; detection wavelength: 220 nm; T_R = 5.5 (major), 6.3 (minor) min]. The absolute configuration of the major enantiomer was assigned as *R* on the basis of the previous study.⁷ **(R)-21c**⁷: ¹H NMR (400 MHz, CDCl₃) δ 7.22-7.26 (m, 2H), 7.16 (td, *J* = 7.6, 1.2 Hz, 1H), 7.10-7.14 (m, 2H), 6.98 (dd, *J* = 7.2, 0.8 Hz, 1H), 6.75 (td, *J* = 7.2, 0.8 Hz, 1H), 6.58 (d, *J* = 8.0 Hz, 1H), 3.52 (d, *J* = 8.8 Hz, 1H), 3.30 (d, *J* = 8.8 Hz, 1H), 2.78 (s, 3H), 2.62 (q, *J* = 7.6 Hz, 2H), 1.71 (s, 3H), 1.22 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 152.7, 144.9, 142.1, 137.9, 127.9, 127.8, 126.7, 123.8, 118.2, 107.8, 72.3, 48.1, 36.2, 28.4, 26.5, 15.6. $[\alpha]_{\text{D}}^{28} +27.7$ (c 0.49, CHCl₃, 92% ee).

The Reaction of **20d** to Afford 3-(4-Methoxyphenyl)-1,3-dimethylindoline (**21d**) (entry 4)



According to the *general procedure A* described in section 5, the reaction was carried out at 150 °C for 24 h using $[\text{IrCl}(\text{C}_2\text{H}_4)_2]_2$ (3.66 mg, 0.00645 mmol), (*S*)-**L5** (15.1 mg, 0.0131 mmol), **20d** (53.5 mg, 0.210 mmol), *tert*-butylethylene (19.4 mg, 0.231 mmol), and mesitylene (0.4 mL). **21d** (45.7 mg, 0.180 mmol, 86%) was obtained as a colorless oil after purification by column chromatography on silica gel (eluent: hexane:Et₂O = 5:1). Enantiomeric excess of **21d** was determined to be 94% by SFC analysis [column: Daicel Chiralcel OD-H (4.6 mm x 250 mm); eluent: CO₂:2-PrOH = 100:5; flow rate: 3.15 mL/min; detection wavelength: 220 nm; T_R = 6.1 (major), 11.1 (minor) min]. The absolute configuration of the major enantiomer was assigned as *R* on the basis of the previous study.⁷ The reaction using (*S*)-**L3** afforded also *R* isomer as the major enantiomer (68% yield, 89% ee). (*R*)-**21d**⁷: ¹H NMR (400 MHz, CDCl₃) δ 7.21-7.25 (m, 2H), 7.15 (td, *J* = 7.6, 1.2 Hz, 1H), 6.93-6.97 (m, 1H), 6.80-6.84 (m, 2H), 6.73 (td, *J* = 7.6, 0.8 Hz, 1H), 6.57 (d, *J* = 8.0 Hz, 1H), 3.78 (s, 3H), 3.48 (d, *J* = 8.8 Hz, 1H), 3.28 (d, *J* = 8.8 Hz, 1H), 2.77 (s, 3H), 1.69 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 158.0, 152.6, 139.8, 138.0, 127.9, 127.8, 123.7, 118.2, 113.6, 107.8, 72.4, 55.3, 47.8, 36.2, 26.5. $[\alpha]_D^{26} +25.2$ (c 0.51, CHCl₃, 94% ee).

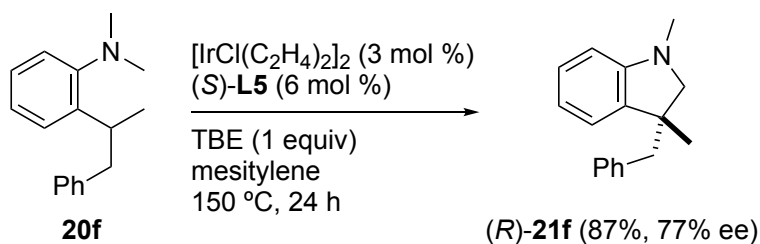
The Reaction of **20e** to Afford 1,3-Dimethyl-3-(naphthalen-2-yl)indoline (**21e**) (entry 5)



According to the *general procedure A* described in section 5, the reaction was carried out at 150 °C for 24 h using $[\text{IrCl}(\text{C}_2\text{H}_4)_2]_2$ (3.46 mg, 0.00610 mmol), (*S*)-**L3** (14.6 mg, 0.0124 mmol), **20e** (55.6 mg, 0.202 mmol), *tert*-butylethylene (18.1 mg, 0.215 mmol), and mesitylene (0.4 mL). **21e** (51.3 mg, 0.188 mmol, 93%) was obtained as a colorless oil after purification by column chromatography on silica gel (eluent: hexane:Et₂O = 10:1). Enantiomeric excess of **21e** was determined to be 93% by SFC analysis [column: Daicel Chiralcel OD-H (4.6 mm x 250 mm);

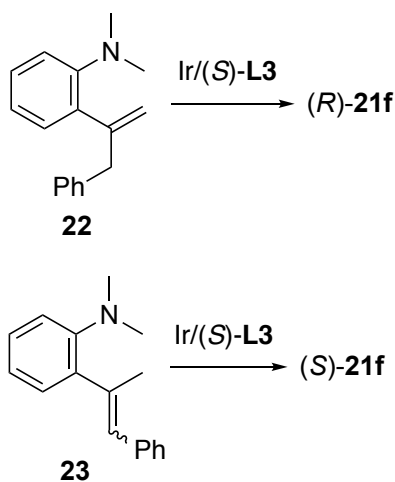
eluent: CO₂:2-PrOH = 100:5; flow rate: 3.15 mL/min; detection wavelength: 220 nm; T_R = 8.8 (major), 10.6 (minor) min]. The absolute configuration of the major enantiomer was assigned as *R* on the basis of the previous study.⁷ (*R*)-**21e**⁷: ¹H NMR (400 MHz, CDCl₃) δ 7.72-7.80 (m, 4H), 7.48 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.40-7.46 (m, 2H), 7.19 (t, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 7.2 Hz, 1H), 6.75 (t, *J* = 7.2 Hz, 1H), 6.61 (d, *J* = 7.6 Hz, 1H), 3.63 (d, *J* = 8.8 Hz, 1H), 3.38 (d, *J* = 8.8 Hz, 1H), 2.81 (s, 3H), 1.82 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 152.7, 144.9, 137.7, 133.2, 132.2, 128.2, 128.1, 128.0, 127.5, 126.0, 125.9, 125.7, 124.7, 123.9, 118.3, 107.9, 72.0, 48.6, 36.1, 26.4. [α]_D²⁷ -30.2 (c 0.49, CHCl₃, 93% ee).

The Reaction of **20f** to Afford 3-Benzyl-1,3-dimethylindoline (**21f**) (entry 6)



According to the *general procedure A* described in section 5, the reaction was carried out at 150 °C for 24 h using [IrCl(C₂H₄)₂]₂ (3.53 mg, 0.00622 mmol), (*S*)-**L5** (14.8 mg, 0.0129 mmol), **20f** (49.2 mg, 0.206 mmol), *tert*-butylethylene (19.1 mg, 0.227 mmol), and mesitylene (0.4 mL). **21f** (42.6 mg, 0.180 mmol, 87%) was obtained as a colorless oil after purification by column chromatography on silica gel (eluent: hexane:Et₂O = 10:1). Enantiomeric excess of **21f** was determined to be 77% by SFC analysis [column: Daicel Chiralcel OJ-H (4.6 mm x 250 mm); eluent: CO₂:2-PrOH = 100:3; flow rate: 3.09 mL/min; detection wavelength: 220 nm; T_R = 3.5 (minor), 4.8 (major) min]. The absolute configuration of the major enantiomer was assigned as *R* on the basis of the previous study.⁷ The reaction using (*S*)-**L3** afforded also *R* isomer as the major enantiomer (74% yield, 74% ee). (*R*)-**21f**⁷: ¹H NMR (400 MHz, CDCl₃) δ 7.19-7.29 (m, 3H), 7.12 (td, *J* = 8.0, 1.2 Hz, 1H), 7.05-7.09 (m, 2H), 6.82 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.68 (td, *J* = 7.6, 0.8 Hz, 1H), 6.51 (d, *J* = 7.6 Hz, 1H), 3.34 (d, *J* = 8.8 Hz, 1H), 2.89 [d (AB pattern), *J* = 13.2 Hz, 1H], 2.842 (d, *J* = 8.8 Hz, 1H), 2.841 [d (AB pattern), *J* = 13.2 Hz, 1H], 2.75 (s, 3H), 1.28 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 152.4, 138.6, 137.8, 130.7, 127.9, 127.8, 126.3, 122.8, 117.7, 107.5, 68.1, 45.9, 44.7, 36.1, 24.3. [α]_D²⁵ -70.8 (c 0.52, CHCl₃, 77% ee).

We previously revealed in the Ir/(*S*)-**L3**-catalyzed intramolecular C(sp³)-H addition reaction, *N,N*-dimethyl-2-(3-phenylprop-1-en-2-yl)aniline (**22**) afforded (*R*)-**21f**, whereas (*S*)-**21f** was formed from *N,N*-dimethyl-2-(1-phenylprop-1-en-2-yl)aniline (**23**) (Scheme S4).⁷ In the reaction of **20f** with Ir/(*S*)-**L3** and Ir/(*S*)-**L5**, (*R*)-**21f** was formed as a major enantiomer (74 and 77% ees, respectively). The absolute configuration of the product **21f** suggests that the C-H addition took place through terminal alkene **22** generated by dehydrogenation rather than the stilbene-type internal alkene **23**.



Scheme S4. Previous Findings in Enantioselective Cyclization of **22** and **23**

11. References

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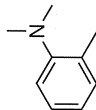
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12. ¹H and ¹³C NMR Spectra of New Compounds and Key Compounds

¹H and ¹³C NMR spectra of **1a–e**, **1r**, **1f–h**, **S1**, **S2**, **1i–j**, **S3**, **S4**, **1k–q**, **4**, **6**, **8**, **9**, **2a**, **5**, **7**, **2b–q**, **10**, **S5**, **1a-d₂**, **S5-d₃**, **1a-d₃**, **1a-d₆**, **2a'**, **13–16**, **18**, **19**, **20a**, **20c–f**, and **21a** are given in following pages. ¹H and ¹³C NMR spectra for the reaction of **1a-d₂** and **1a-d₃** are also provided.

STANDARD PROTON PARAMETERS

Sample Name:
KY295
Data Collected on:
Agilent-NMR-vmms400
Archive directory:
Sample directory:
FidFile: KY295
Pulse Sequence: PROTON (szpul)
Solvent: cdcl3
Data collected on: Mar 13 2018
Operator: vmml
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6410.3 Hz
16 repetitions
OBSERVE HL, 399.8641866 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min 20 sec



1a

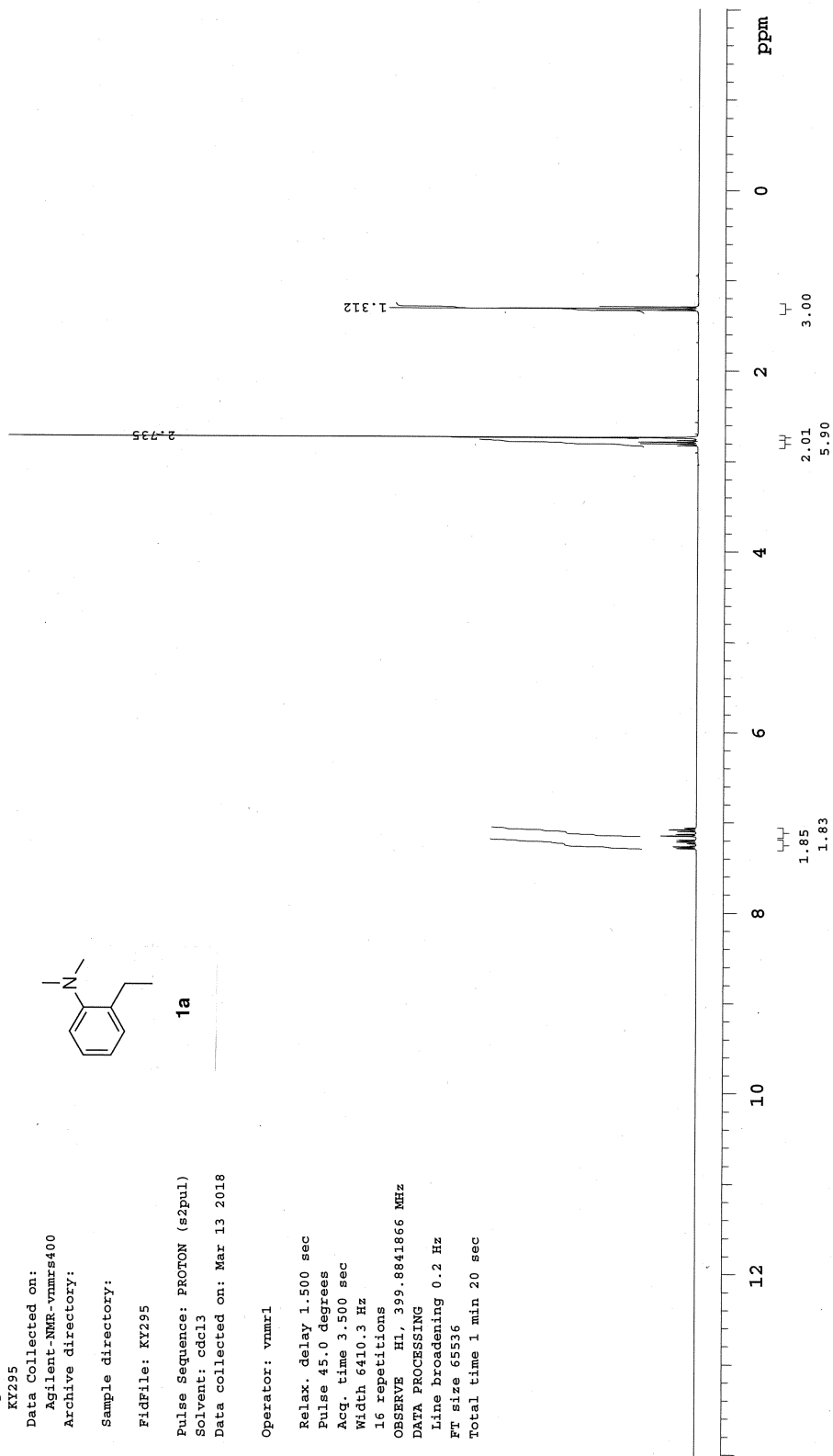


Figure S2. ^1H NMR Spectrum of **1a** (400 MHz, CDCl_3)

STANDARD CARBON PARAMETERS

Sample Name:

Data Collected on:
Agilent-NMR-vmr400

Archive directory:

Sample directory:

File: KY786_13C

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Jul 5 2019

Temp. 25.0 C / 298.1 K

Operator: vmr1

Relax. delay 0.715 sec

Pulse 45.0 degrees

Acq. time 1.285 sec

Width 25510.2 Hz

512 repetitions

OBSERVE C13, 100.5509498 MHz

DECOUPLE H1, 399.8861860 MHz

Power 41 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 17 min

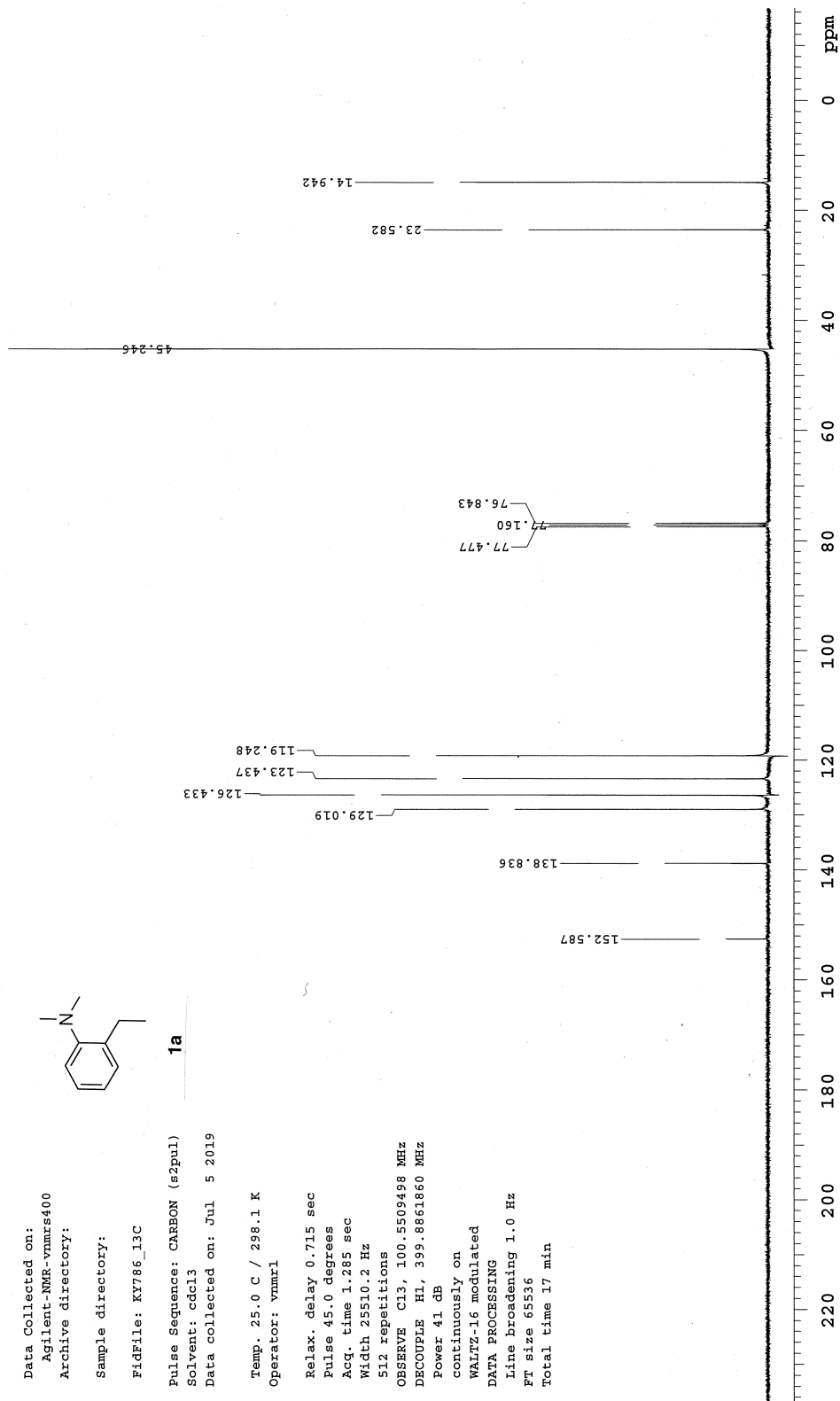


Figure S3. ¹³C NMR Spectrum of 1a (101 MHz, CDCl₃)

STANDARD PROTON PARAMETERS

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Archive directory:
Sample directory:
FidFile: KY311
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr 6 2018
Operator: vmnr1
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6410.3 Hz
16 repetitions
OBSERVE HL, 399.8841859 MHz
DATA PROCESSING
Line broadening 0.2 Hz
Ft size 65536
Total time 1 min 20 sec

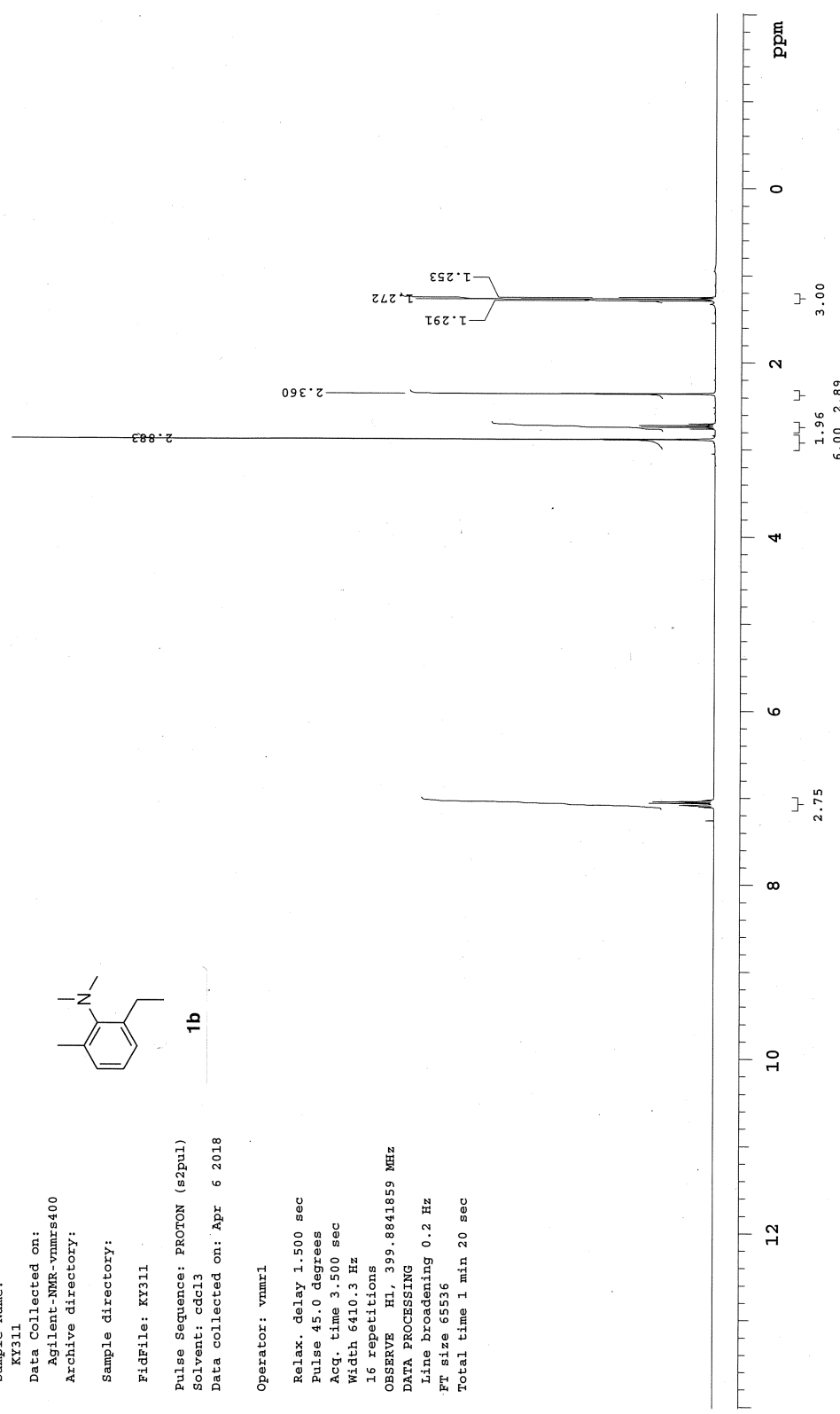
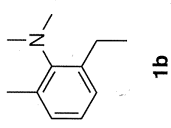


Figure S4. ¹H NMR Spectrum of **1b** (400 MHz, CDCl₃)

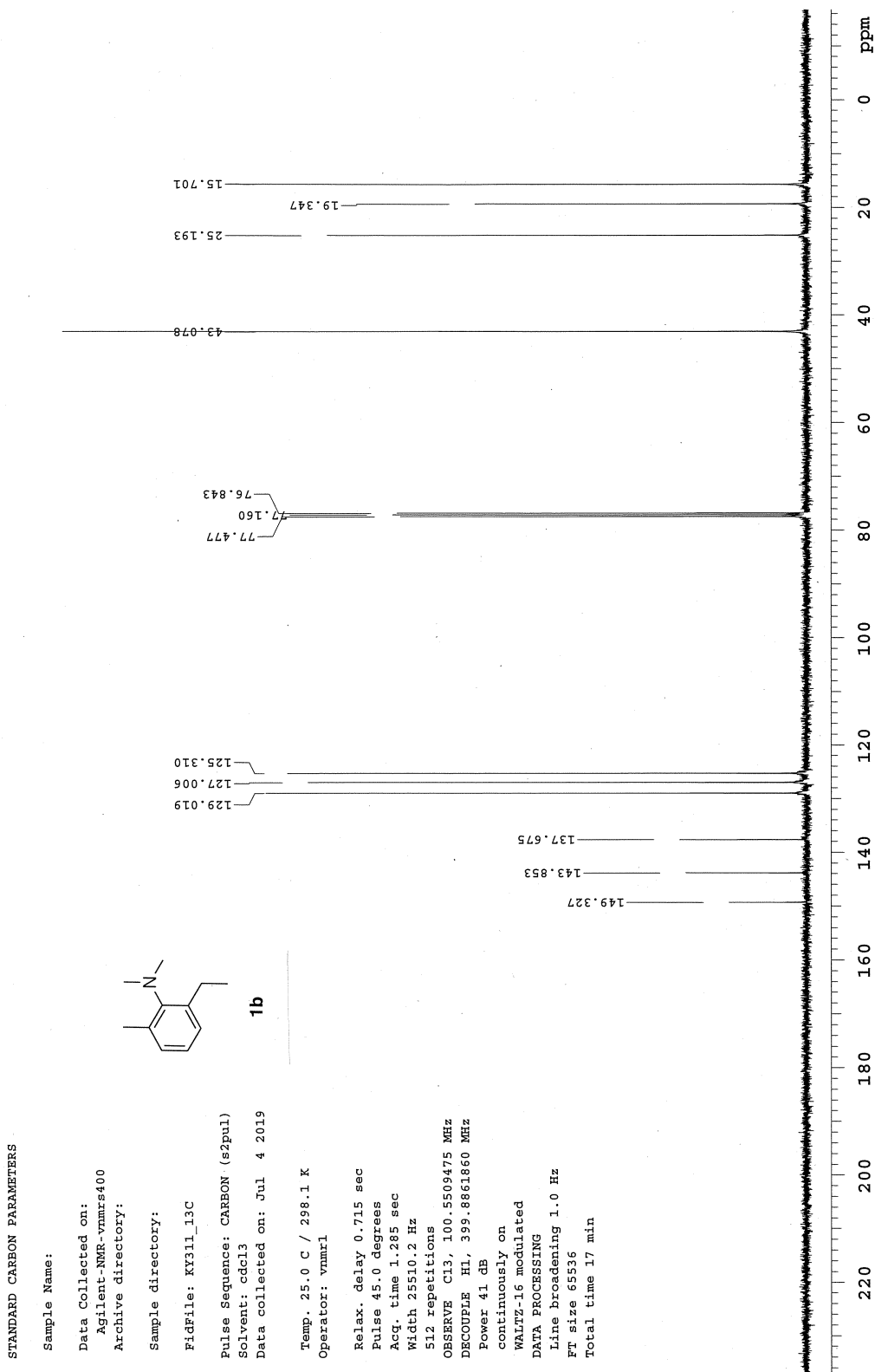
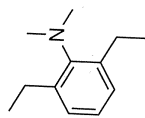


Figure S5. ^{13}C NMR Spectrum of **1b** (101 MHz, CDCl_3)

STANDARD PROTON PARAMETERS

Sample Name:
KY306
Data Collected on:
Agilent-NMR-vmrns400
Archive directory:
Sample directory:
File: KY306
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr 5 2018
Operator: vmr1
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6410.3 Hz
16 repetitions
OBSERVE H1, 399.8841859 MHz
DATA PROCESSING
Line broadening 0.2 Hz
Ft size 65536
Total time 1 min 20 sec



1c

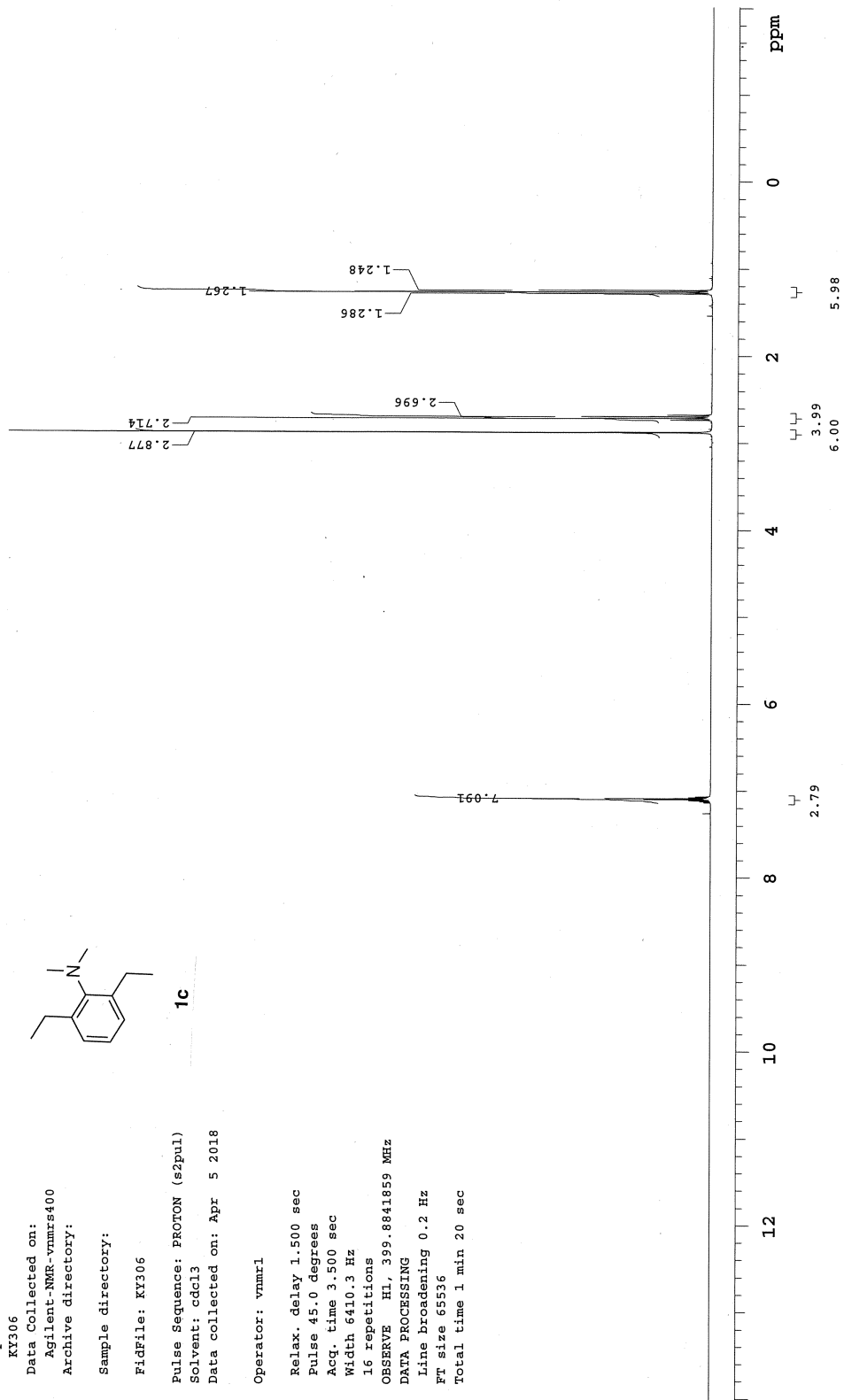


Figure S6. ¹H NMR Spectrum of 1c (400 MHz, CDCl₃)

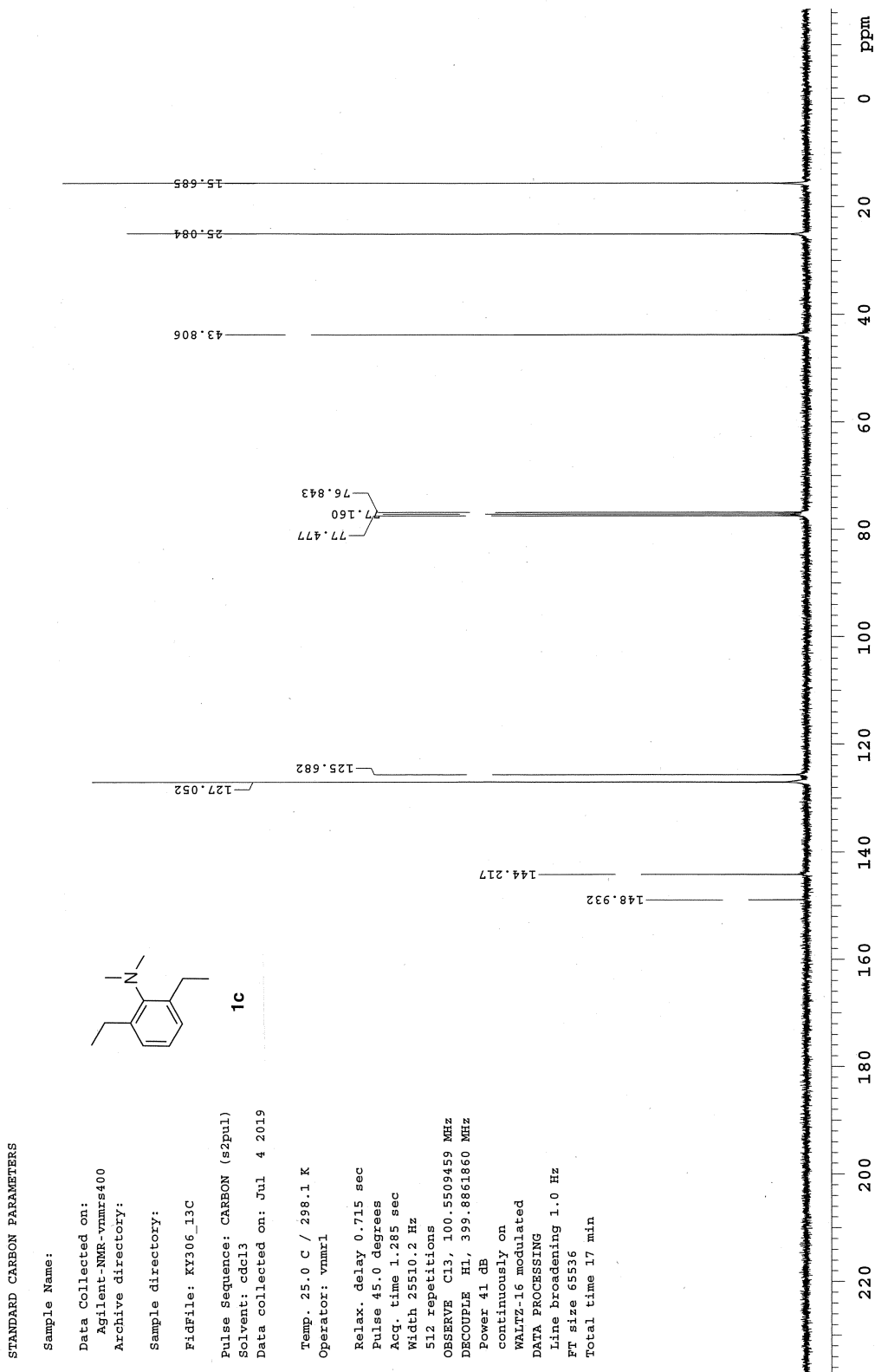
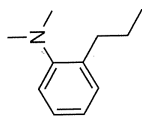


Figure S7. ^{13}C NMR Spectrum of **1c** (101 MHz, CDCl_3)

STANDARD PROTON PARAMETERS

Sample Name:
Data Collected on:
Agilent-NMR-vmnrs400
Archive directory:
Sample directory:
FidFile: KY459
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Sep 6 2018
Operator: vmnrl
Relax. delay 15.000 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6410.3 Hz
16 repetitions
OBSERVE HL, 399.8841865 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 4 min 56 sec



1d

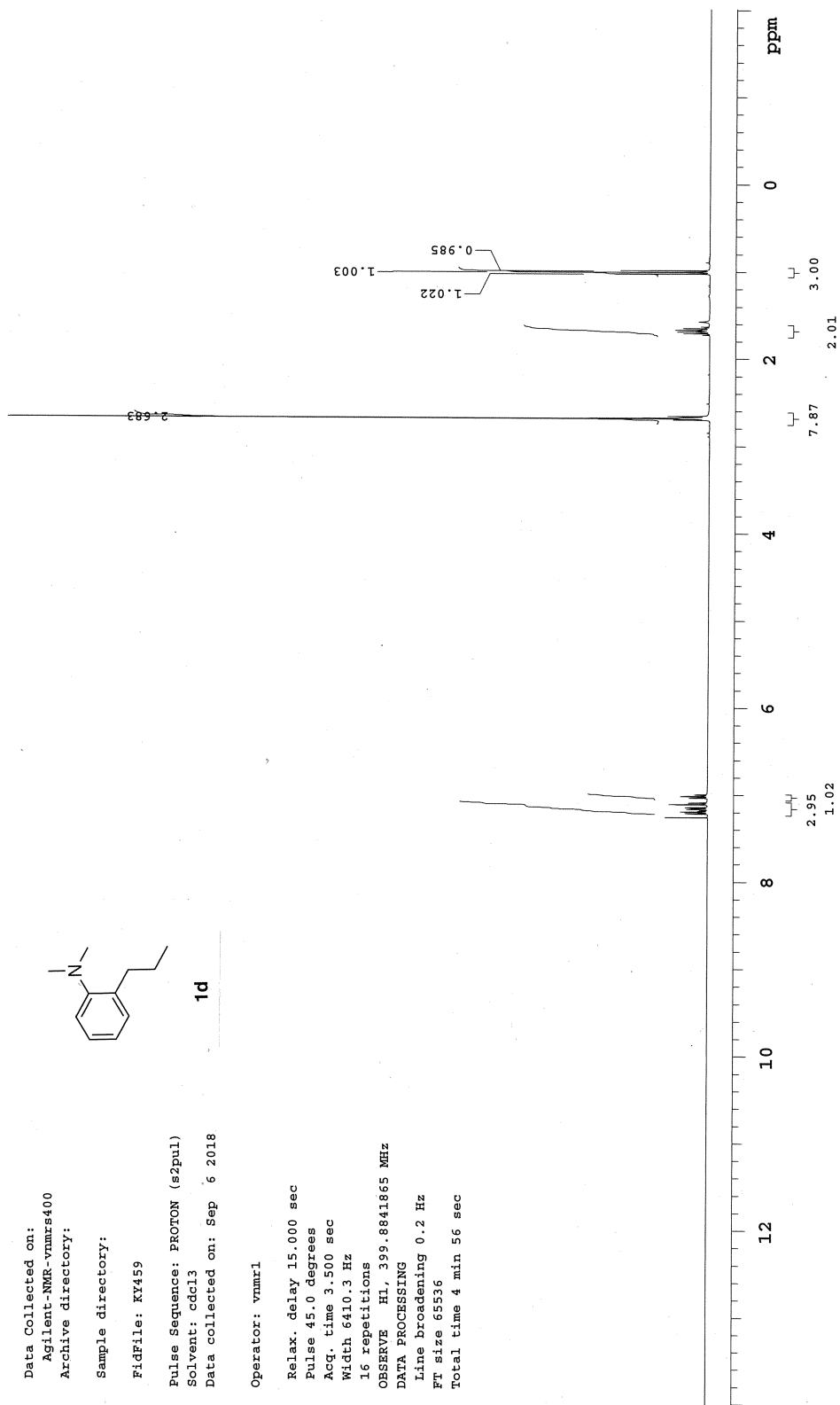


Figure S8. ¹H NMR Spectrum of 1d (400 MHz, CDCl₃)

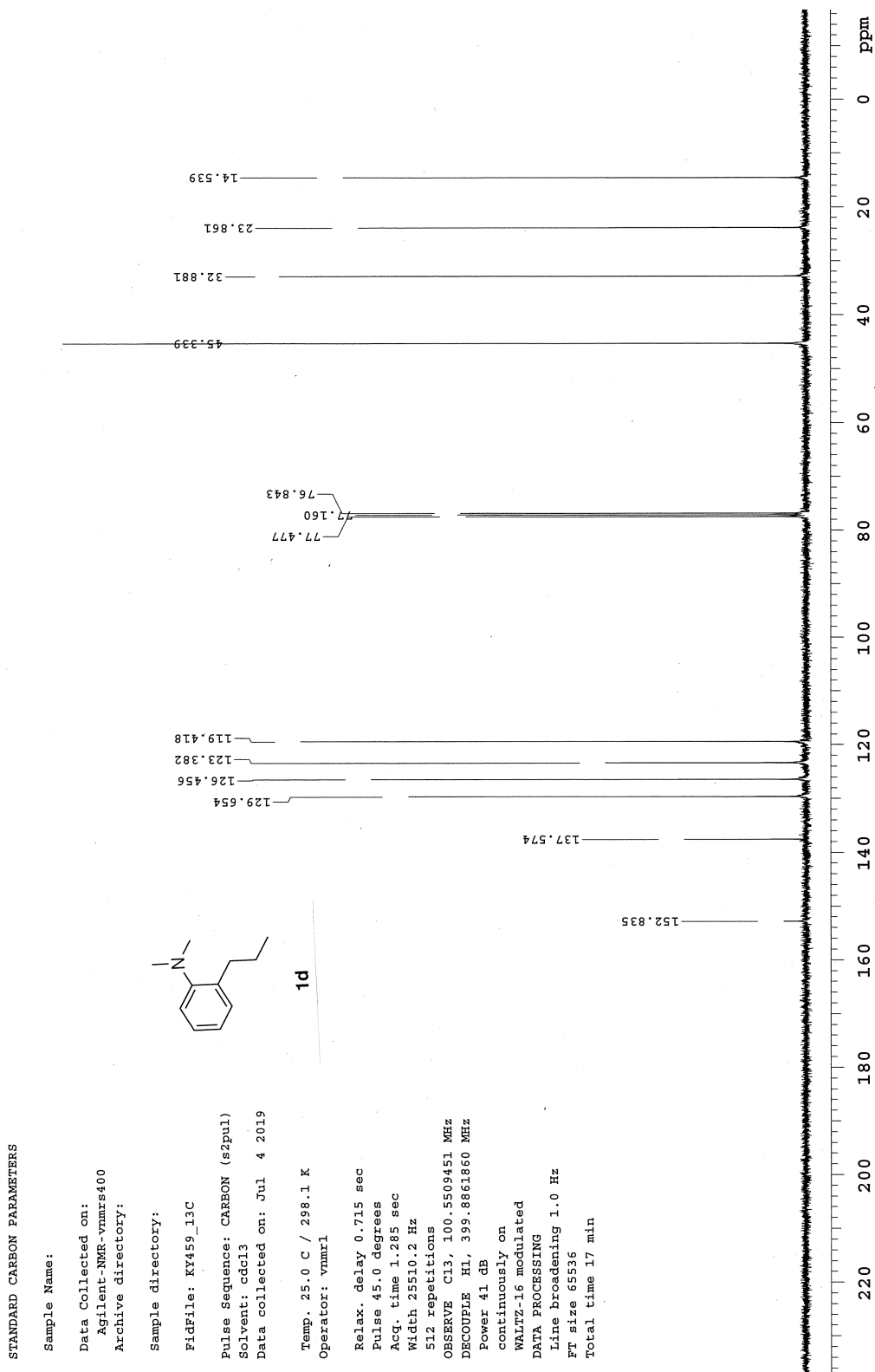


Figure S9. ^{13}C NMR Spectrum of **1d** (101 MHz, CDCl_3)

STANDARD PROTON PARAMETERS

Sample Name:

Data Collected on:

Agilent-NMR-vnmrs400

Archive directory:

Sample directory:

File: KY623

Pulse Sequence: PROTON (s2pul)

Solvent: cdcl3

Data collected on: Feb 22 2019

Temp. 25.0 C / 298.1 K

Operator: vnmr1

Relax. delay 15.000 sec

Pulse 45.0 degrees

Acq. time 3.500 sec

Width 6410.3 Hz

16 repetitions

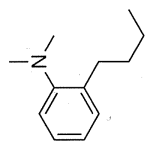
OBSERVE H1. 399.8841859 MHZ

DATA PROCESSING

Line broadening 0.2 Hz

FT size 65536

Total time 4 min 56 sec



1e

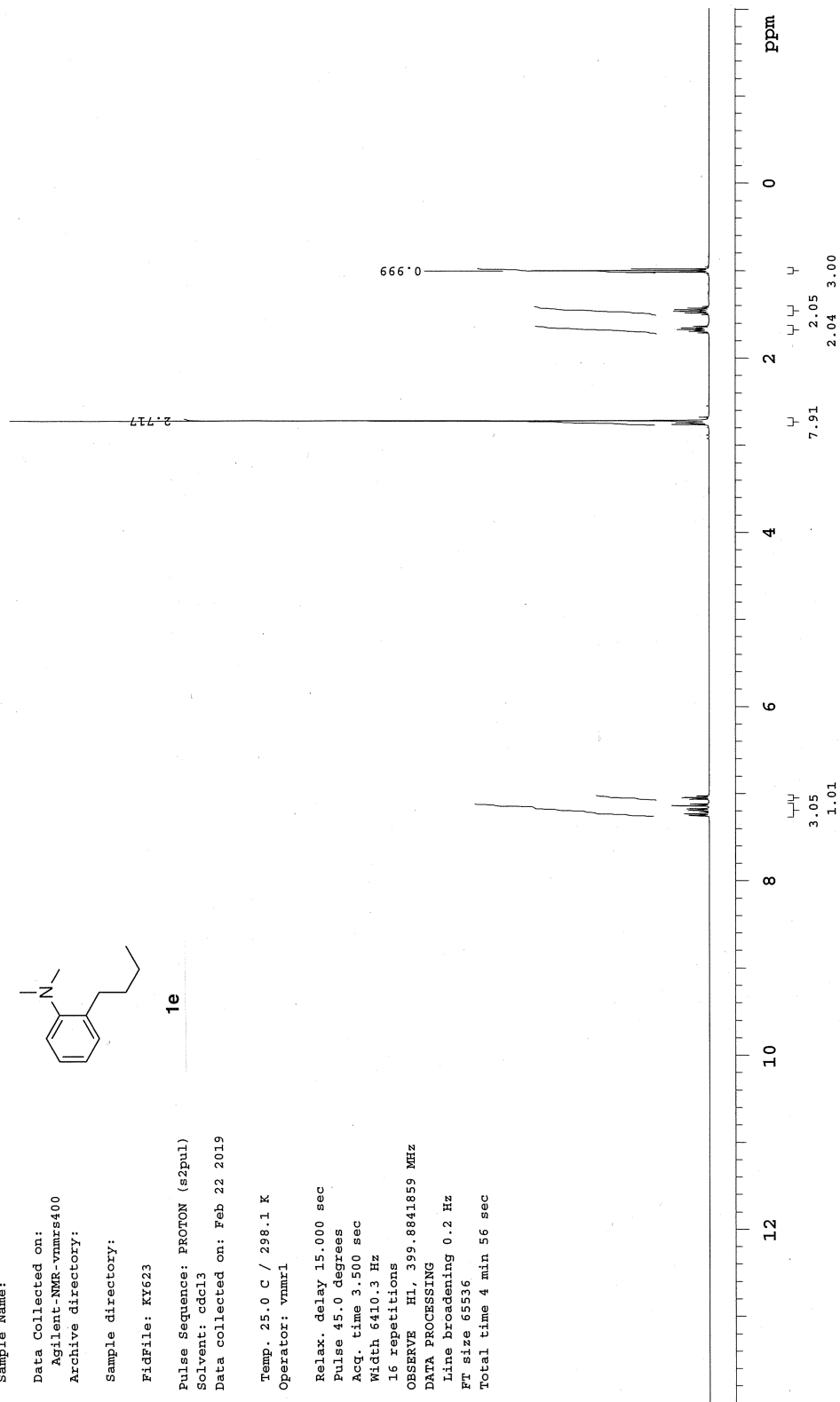


Figure S10. ¹H NMR Spectrum of **1e** (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:

Data Collected on:

Agilent-NMR-vmr400

Archive directory:

Sample directory:

File: KY623_13C

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Jul 4 2019

Temp. 25.0 C / 298.1 K

Operator: vmr1

Relax. delay 0.715 sec

Pulse 45.0 degrees

Acq. time 1.285 sec

Width 25510.2 Hz

512 repetitions

OBSERVE C13, 100.5509457 MHz

DECOUPLE H1, 399.8861860 MHz

Power 41 dB

continuously on

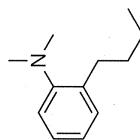
WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 17 min



1e

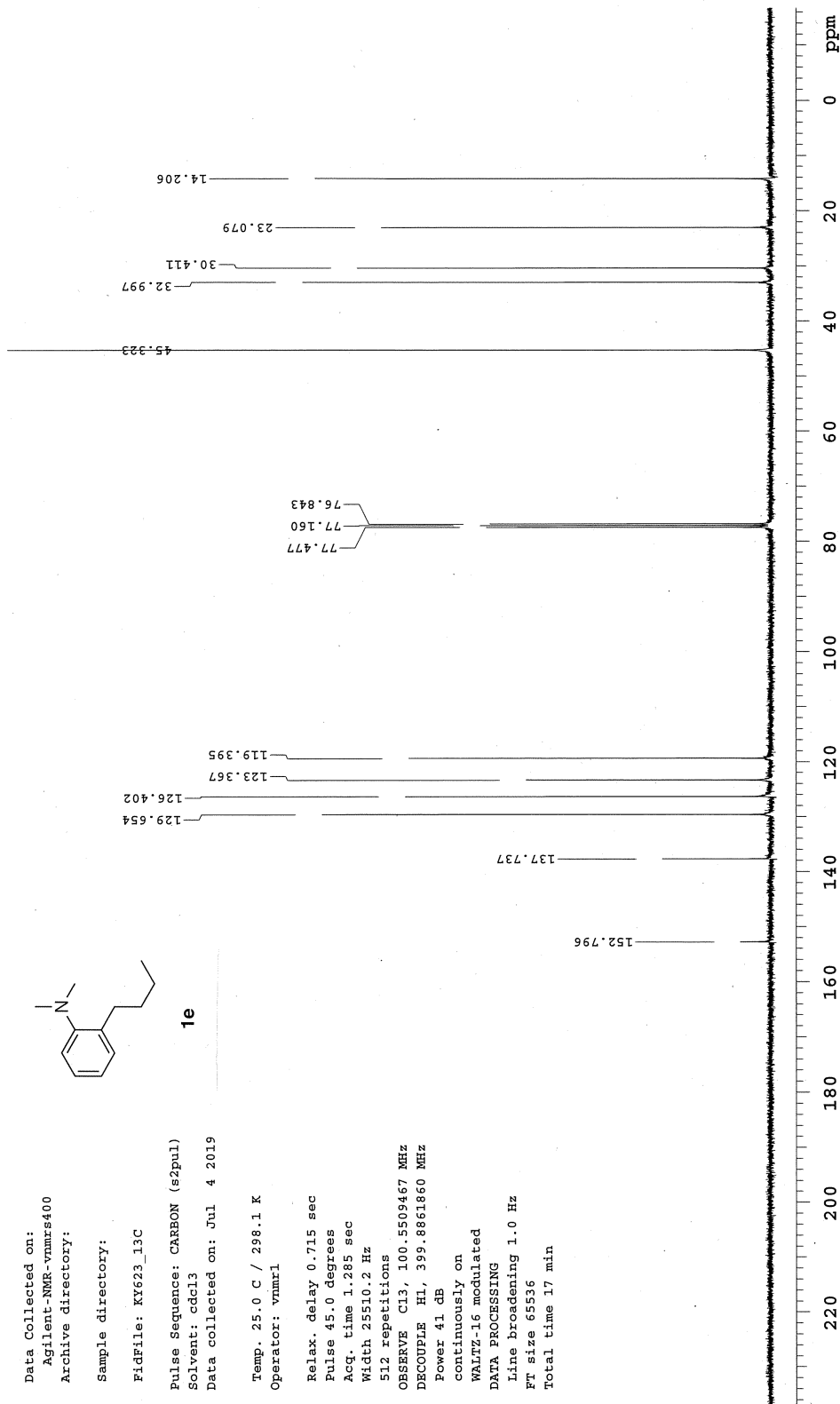


Figure S11. ¹³C NMR Spectrum of 1e (101 MHz, CDCl₃)

STANDARD PROTON PARAMETERS

Sample Name:
 KY506
 Data Collected on:
 Agilent-NMR-vmr400
 Archive directory:
 Sample directory:
 FidFile: KY506
 Pulse Sequence: PROTON (s2pul)
 Solvent: cdcl3
 Data collected on: Nov 6 2018
 Temp. 25.0 C / 298.1 K
 Operator: vmr1
 Relax. delay 15.000 sec
 Pulse 45.0 degrees
 Acq. time 3.500 sec
 Width 6410.3 Hz
 16 repetitions
 OBSERVE H1, 399.8841861 MHZ
 DATA PROCESSING
 Line broadening 0.2 Hz
 FT size 65536
 Total time 4 min 56 sec

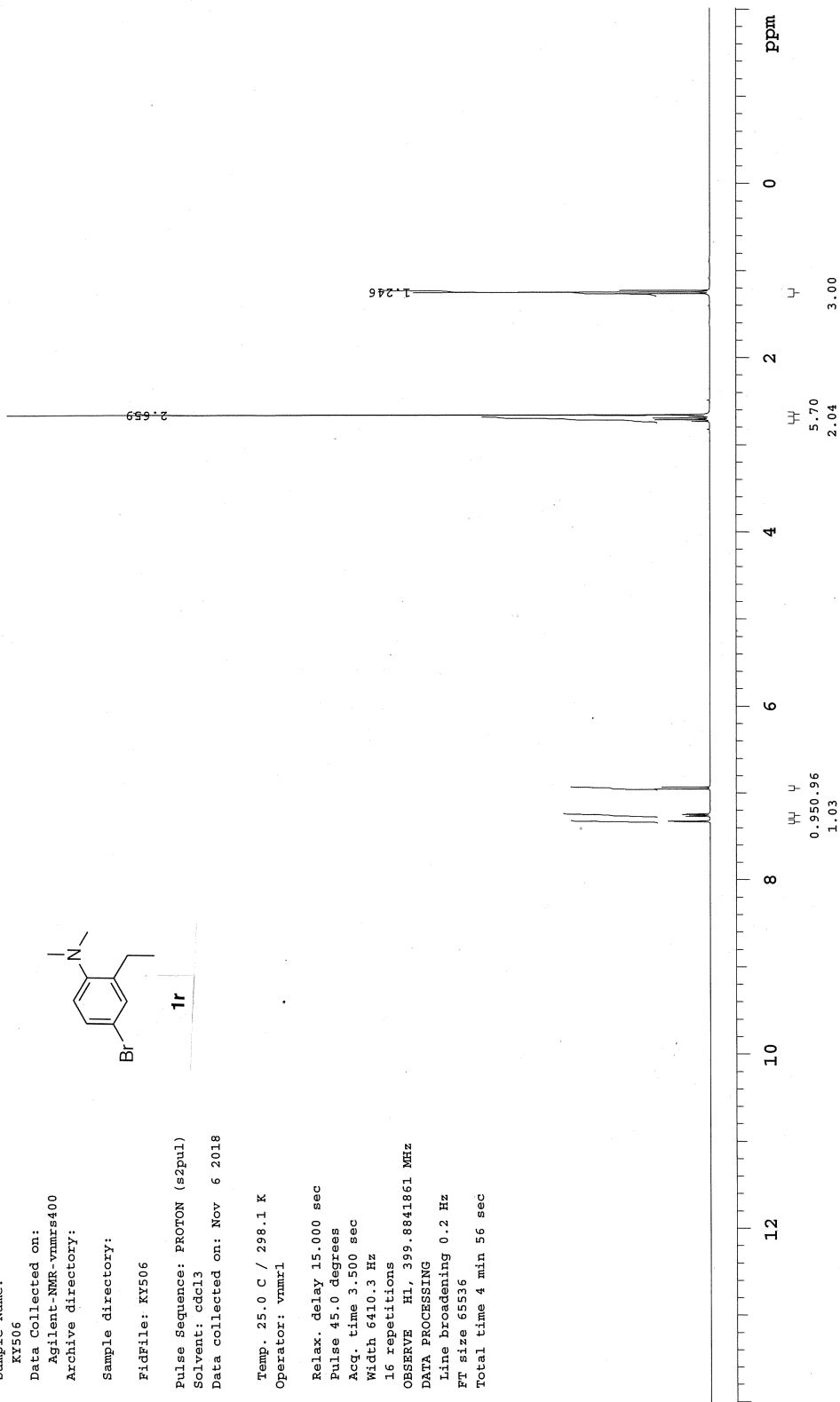
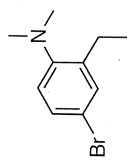


Figure S12. ¹H NMR Spectrum of **1r** (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:

Data Collected on:
Agilent-NMR-vmrs400
Archive directory:

Sample directory:

FIDfile: KY506_13C

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Nov 6 2018

Temp. 25.0 C / 298.1 K
Operator: vmr1

Relax. delay 0.715 sec
Pulse 45.0 degrees
Acq. time 1.285 sec
Width 25510.2 Hz
512 repetitions

OBSERVE C13, 100.5509451 MHz
DECOUPLE H1, 399.8861860 MHz
Power 41 dB
continuously on

WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz

FT size 65536
Total time 17 min

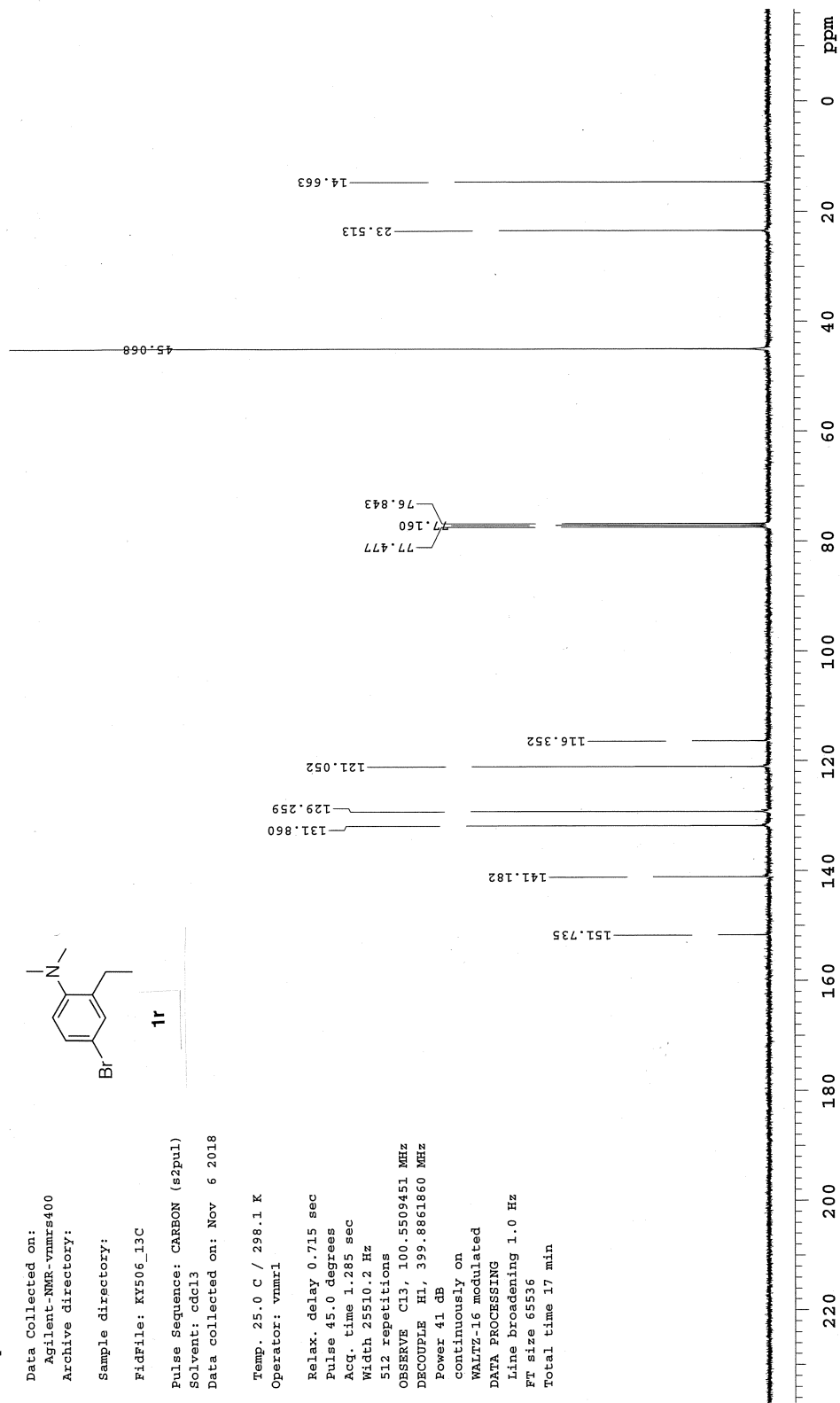
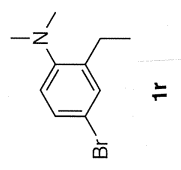


Figure S13. ¹³C NMR Spectrum of **1r** (101 MHz, CDCl₃)

STANDARD PROTON PARAMETERS

Sample Name:

KY577

Data Collected on:

Agilent-NMR-vmms400

Archive directory:

Sample directory:

Fidfile: KY577

Pulse Sequence: PROTON (s2pul)

Solvent: cdcl3

Data collected on: Jan 31 2019

Operator: vnmr1

Relax. delay 15.000 sec

Pulse 45.0 degrees

Acq. time 3.500 sec

Width 6410.3 Hz

16 repetitions

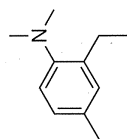
OBSERVE H1, 399.8841833 MHz

DATA PROCESSING

Line broadening 0.2 Hz

FT size 65536

Total time 4 min 56 sec



1f

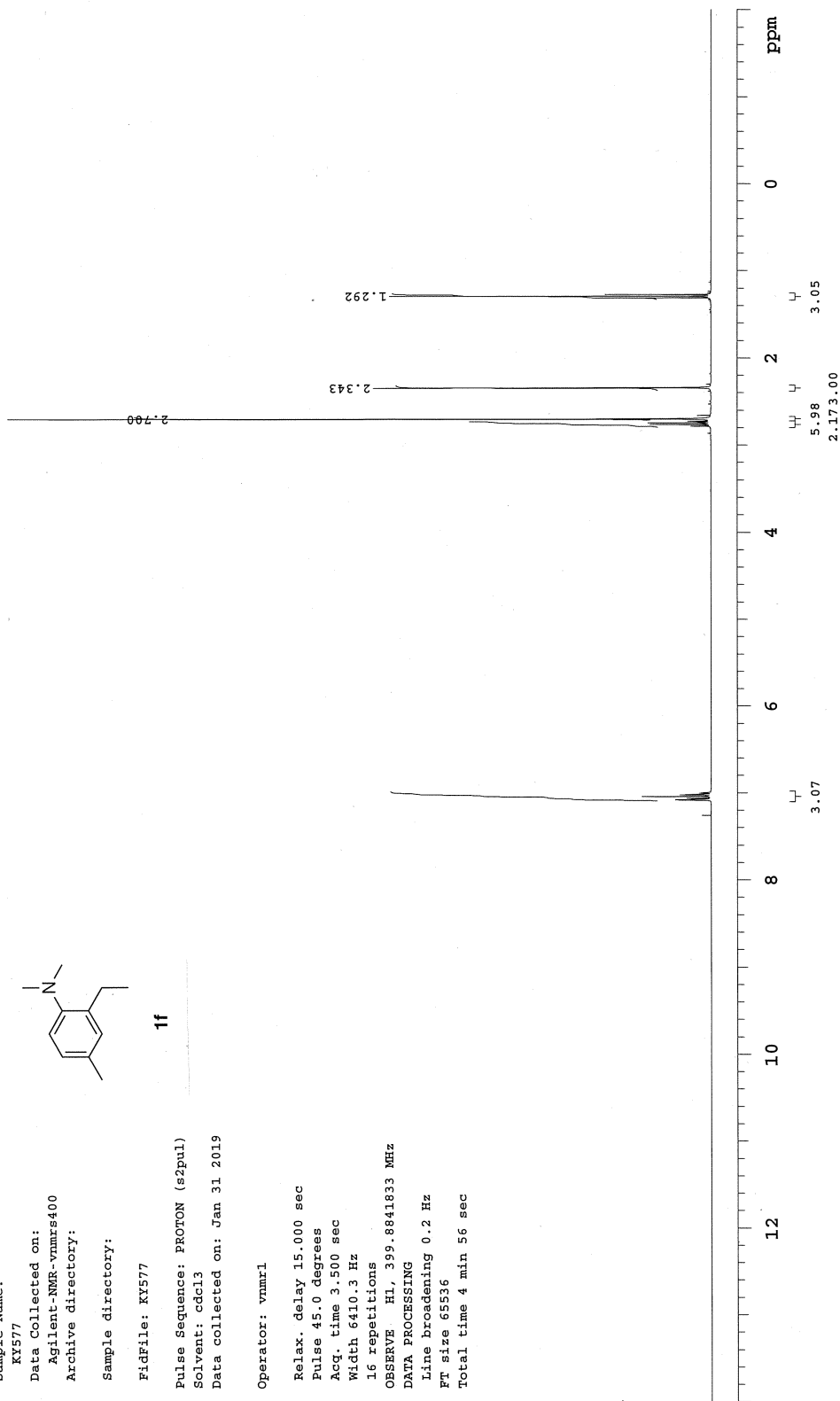


Figure S14. ^1H NMR Spectrum of **1f** (400 MHz, CDCl_3)

STANDARD CARBON PARAMETERS

Sample Name:

Data Collected on:
Agilent-NMR-vmrzs400
Archive directory:

Sample directory:

File: KY577_l3C

Pulse Sequence: CARON (s2pul)

Solvent: cdcl3
Data collected on: Jul 6 2019

Temp. 25.0 C / 298.1 K
Operator: vmr1

Relax. delay 0.715 sec

Pulse 45.0 degrees

Acq. time 1.285 sec

Width 25510.2 Hz

512 repetitions

OBSERVE C13, 100.5509459 MHz

DECOUPLE H1, 399.8861860 MHz

Power 41 dB

continuously on

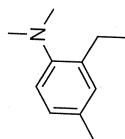
WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 17 min



1f

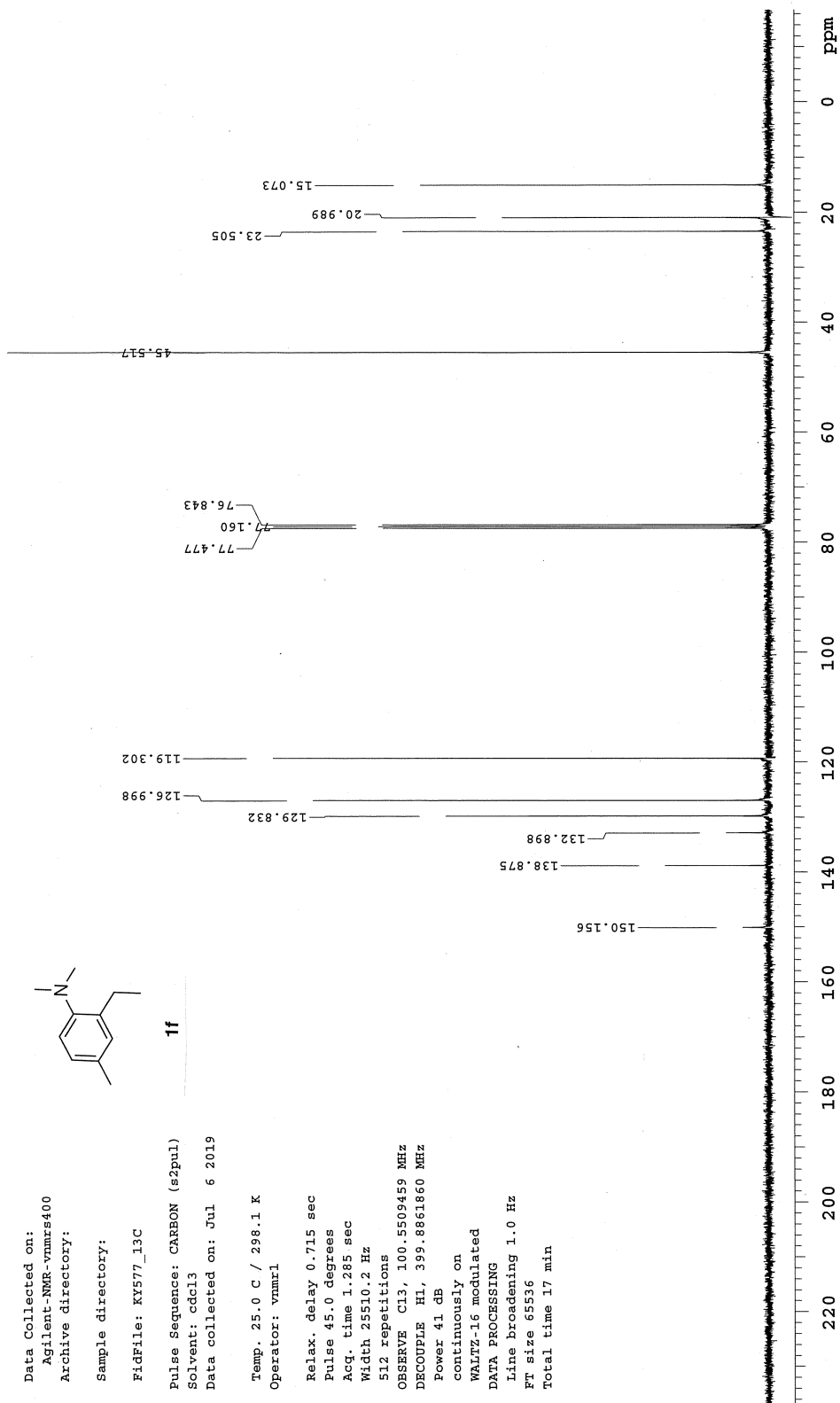


Figure S15. ^{13}C NMR Spectrum of **1f** (101 MHz, CDCl_3)

STANDARD PROTON PARAMETERS

Sample Name:

Data Collected on:
Agilent-NMR-vnmrs400
Archive directory:

Sample directory:

Fidfile: KY745

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: May 21 2019

Operator: vnmr1

Relax. delay 15.000 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6410.3 Hz
16 repetitions
OBSERVE H1, 399.8841800 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 4 min 56 sec

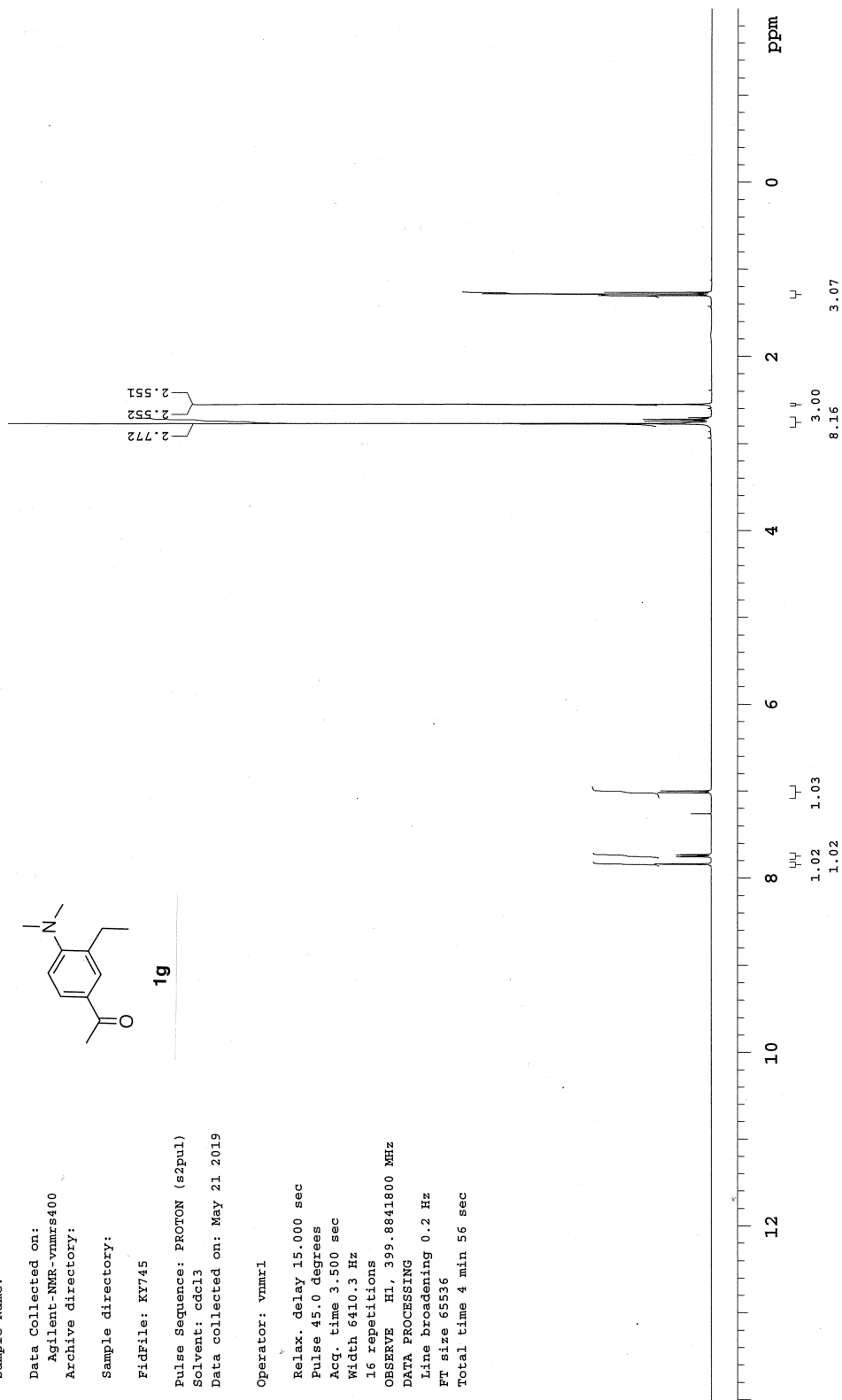
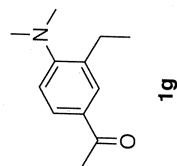


Figure S16. ¹H NMR Spectrum of **1g** (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:
 Data Collected on:
 Agilent-NMR-vmnr400
 Archive directory:
 Sample directory:
 FIDFile: KY745_13C
 Pulse Sequence: CARBON (s2pul)
 Solvent: cdcl3
 Data collected on: May 21 2019
 Operator: vmnr1
 Relax. delay 0.715 sec
 Pulse 45.0 degrees
 Acq. time 1.285 sec
 Width 25510.2 Hz
 512 repetitions
 OBSERVE C13, 100.5509451 MHZ
 DECOUPLE H1, 399.8661860 MHZ
 Power 41 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 17 min

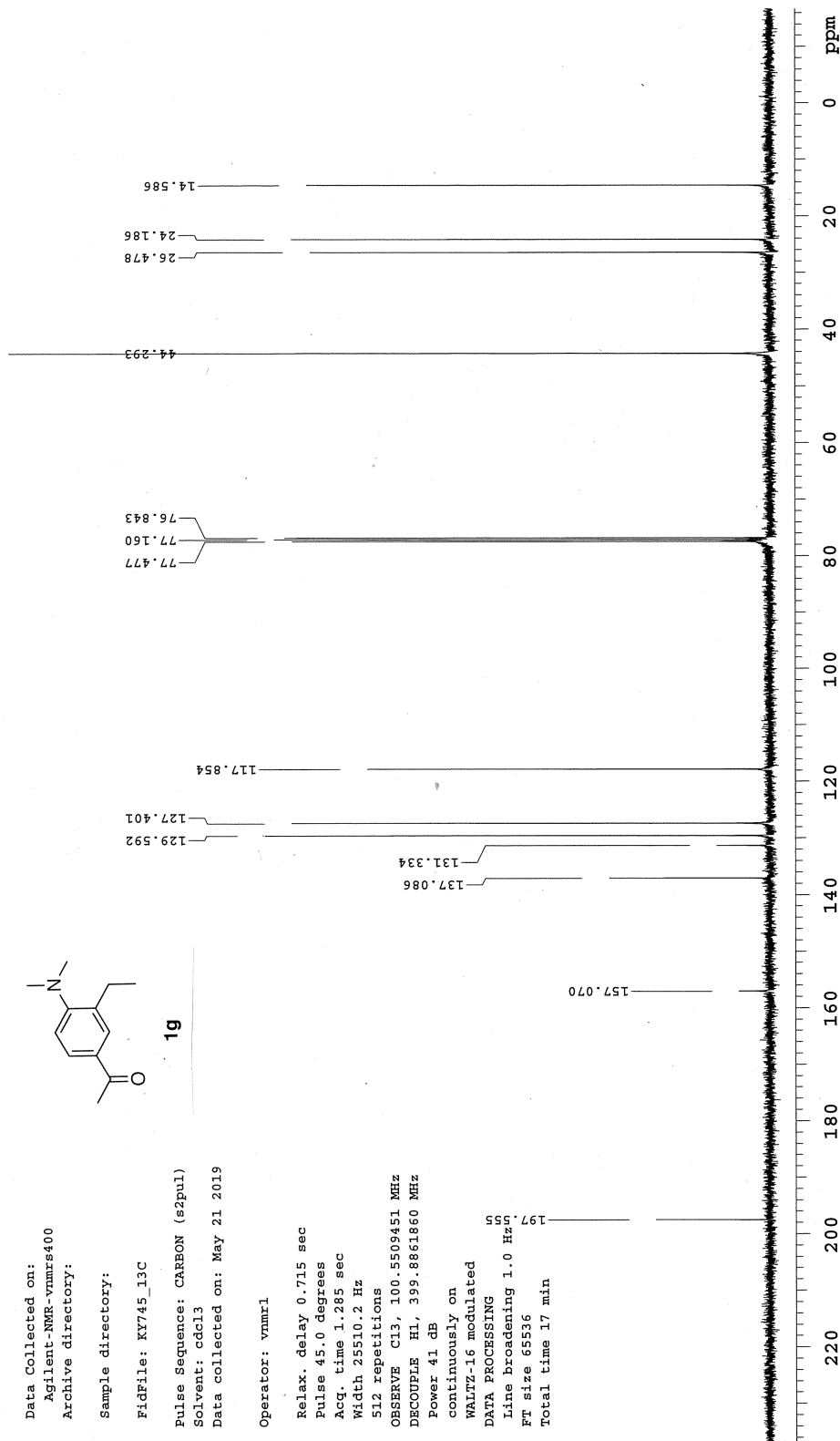
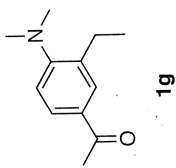


Figure S17. ¹³C NMR Spectrum of **1g** (101 MHz, CDCl₃)

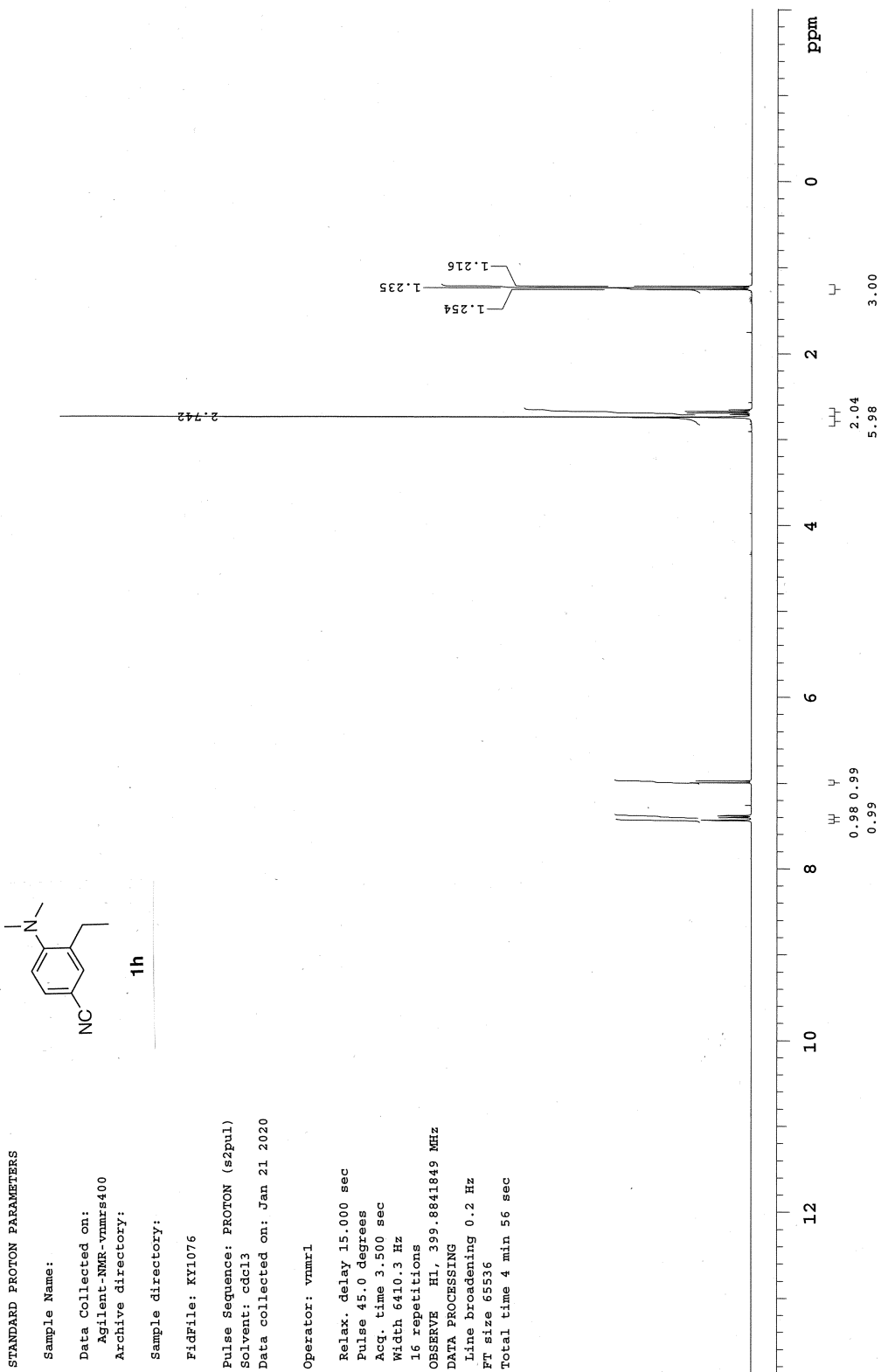


Figure S18. ¹H NMR Spectrum of **1h** (400 MHz, CDCl₃)

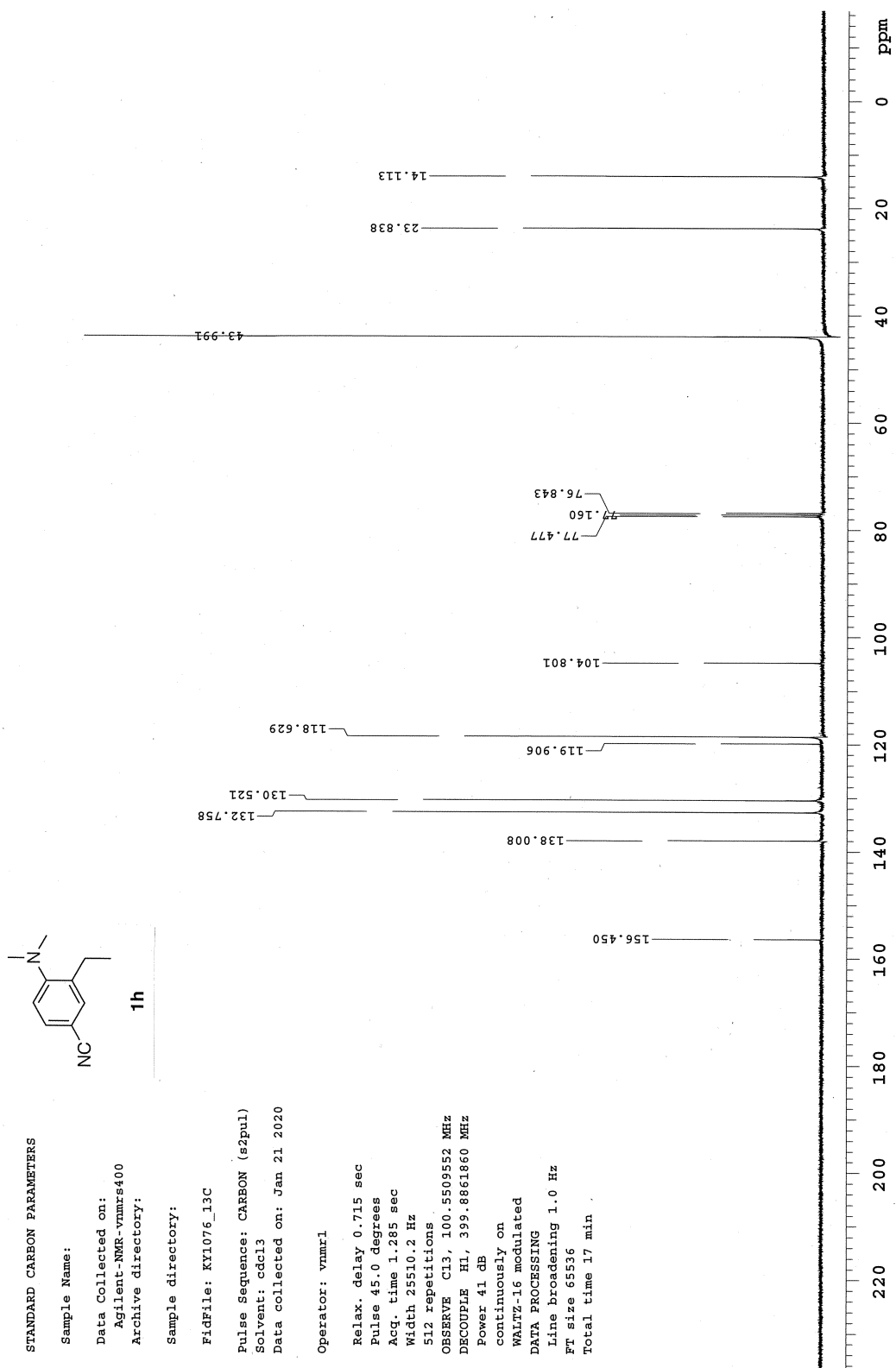


Figure S19. ¹³C NMR Spectrum of **1h** (101 MHz, CDCl₃)

STANDARD PROTON PARAMETERS

Sample Name:

Data Collected on:
Agilent-NMR-vmr400
Archive directory:

Sample directory:

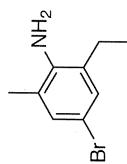
Fidfile: KY532

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Nov 17 2018

Temp. 25.0 C / 298.1 K
Operator: vmr1

Relax. delay 15.000 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6410.3 Hz
16 repetitions

OBSERVE HL, 399.8841861 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 4 min 56 sec



S1

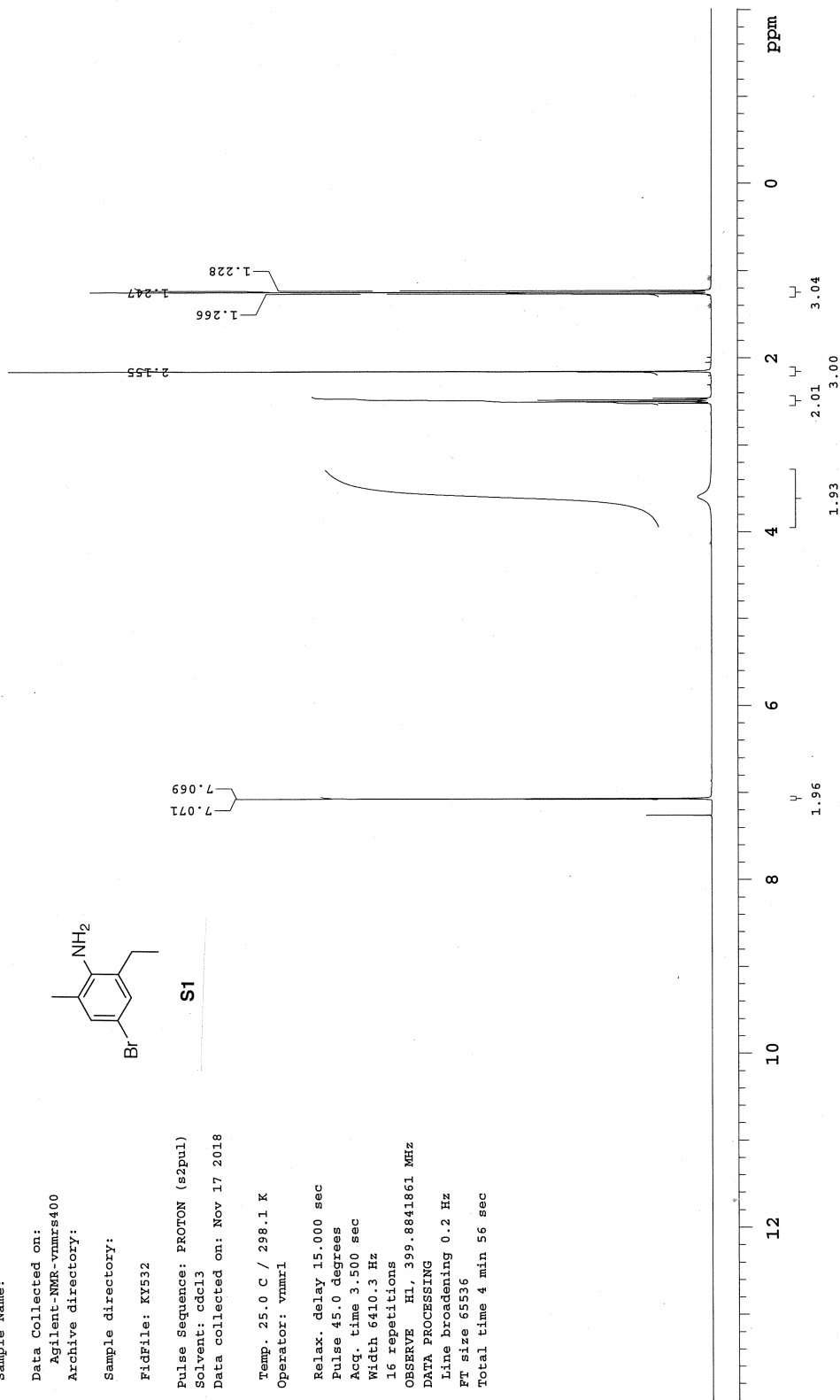


Figure S20. ¹H NMR Spectrum of S1 (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:
 Data Collected on:
 Agilent-NMR-vmrns400
 Archive directory:
 Sample directory:
 FIDfile: KY792_13C
 Pulse Sequence: CARBON (s2pul)
 Solvent: cdcl3
 Data collected on: Jul 11 2019
 Temp. 25.0 C / 298.1 K
 Operator: vmr1
 Relax. delay 0.715 sec
 Pulse 45.0 degrees
 Acq. time 1.285 sec
 Width 25510.2 Hz
 512 repetitions
 OBSERVE C13, 100.5509654 MHz
 DECOUPLE H1, 399.8861860 MHz
 Power 41 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 17 min

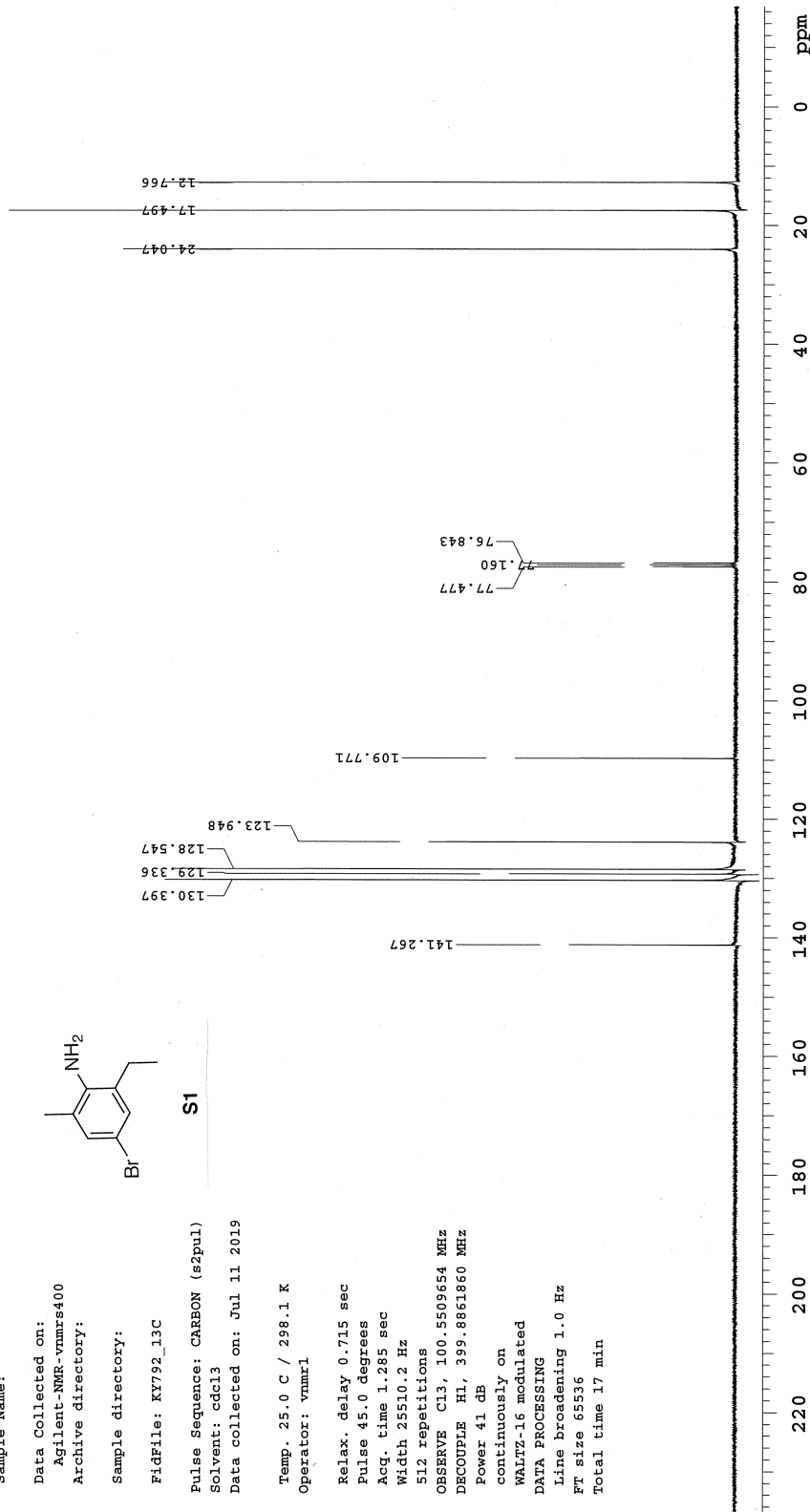
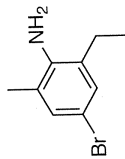


Figure S21. ¹³C NMR Spectrum of S1 (101 MHz, CDCl₃)

STANDARD PROTON PARAMETERS

Sample Name:

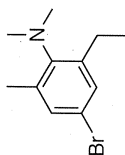
Data Collected on:
Agilent-NMR-vnmrs400
Archive directory:

Sample directory:

F1dfile: KY538

Pulse Sequence: PROTON (s2pul)
Solvent: cdc13
Data collected on: Nov 24 2018

S2



Temp. 25.0 C / 298.1 K
Operator: vnmr1

Relax. delay 15.000 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6410.3 Hz
16 repetitions

OBSERVE H1, 399.8841861 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 4 min 56 sec

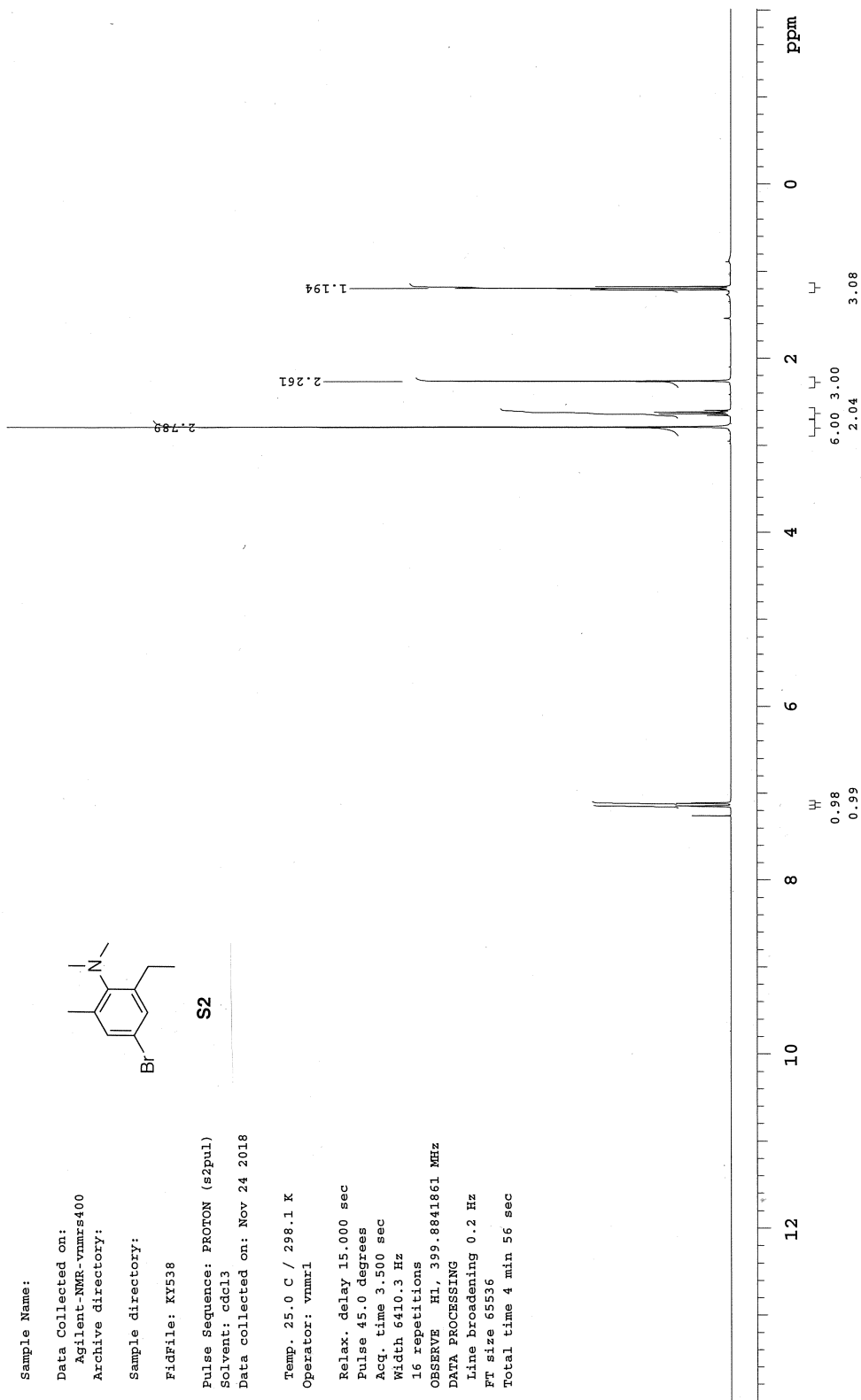


Figure S22. ¹H NMR Spectrum of S2 (400 MHz, CDCl₃)

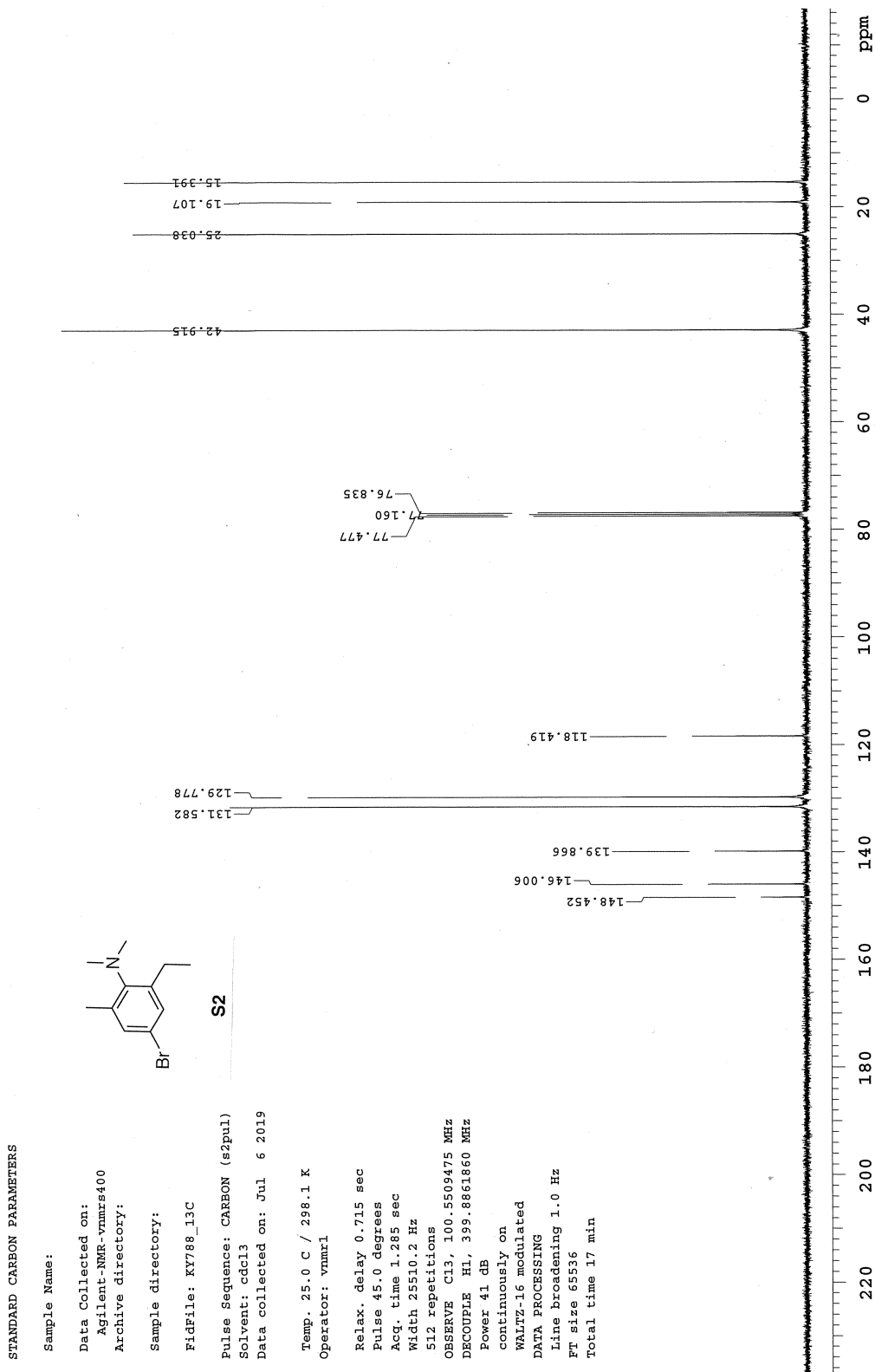


Figure S23. ^{13}C NMR Spectrum of S2 (101 MHz, CDCl_3)

STANDARD PROTON PARAMETERS

Sample Name:
 KY557_GPC
 Data Collected on:
 Agilent-NMR-vnmrs400
 Archive directory:
 Sample directory:
 FIDFile: KY557_GPC
 Pulse Sequence: PROTON (s2pul)
 Solvent: cdcl3
 Data collected on: Jan 29 2019
 Operator: vnmr1
 Relax. delay 15.000 sec
 Pulse 45.0 degrees
 Acq. time 3.500 sec
 Width 6410.3 Hz
 16 repetitions
 OBSERVE H1, 399.8841833 MHz
 DATA PROCESSING
 Line broadening 0.2 Hz
 FT size 65536
 Total time 4 min 56 sec

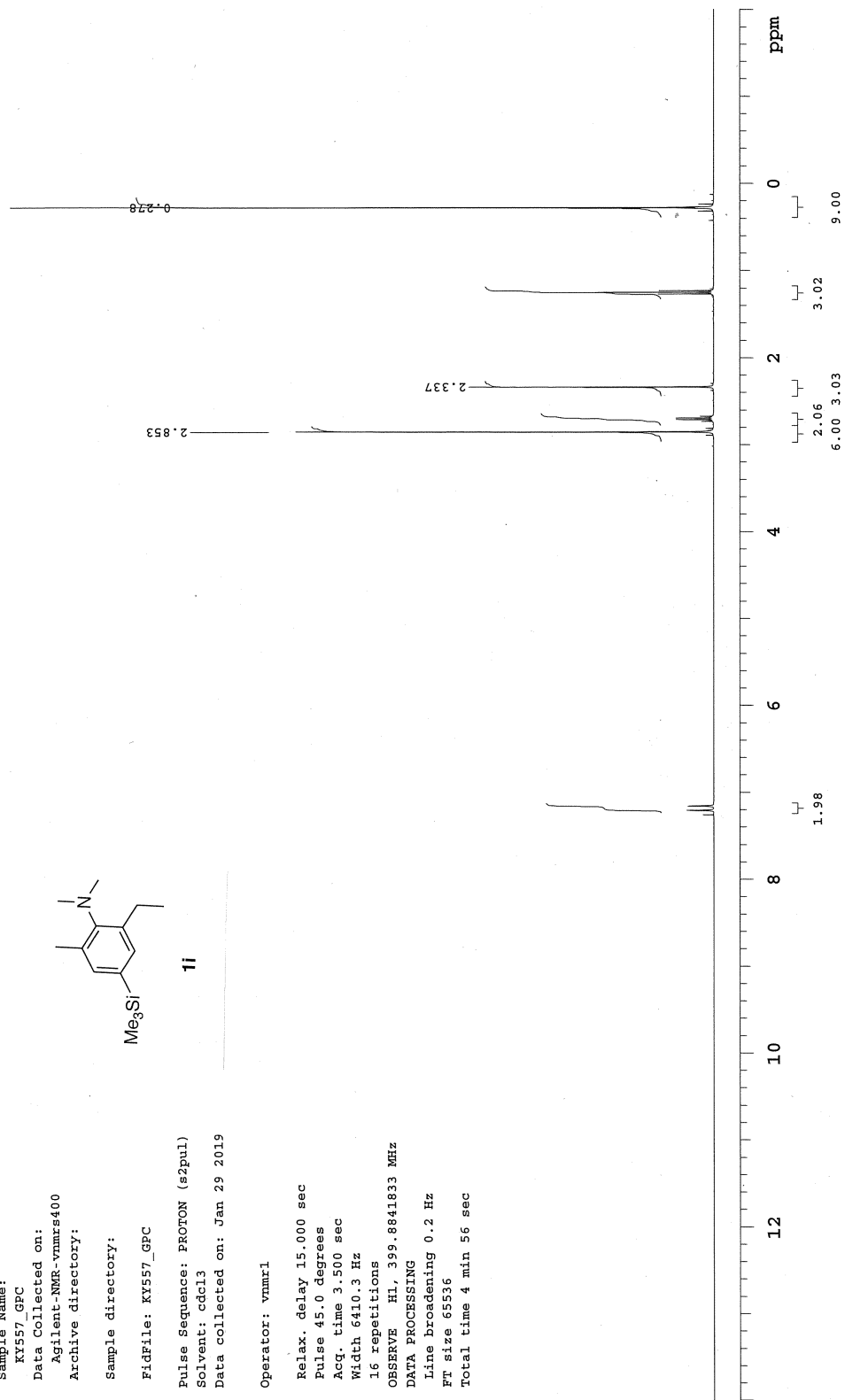
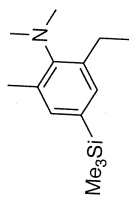


Figure S24. ¹H NMR Spectrum of **1i** (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:

Data Collected on:

Agilent-NMR-vmrns400

Archive directory:

Sample directory:

File: KY557_GPC_13C

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Jan 30 2019

Operator: vmr1

Relax. delay 0.715 sec

Pulse 45.0 degrees

Acq. time 1.285 sec

Width 25510.2 Hz

512 repetitions

OBSERVE C13, 100.5509436 MHz

DECOUPLE H1, 399.8861860 MHz

Power 41 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 17 min

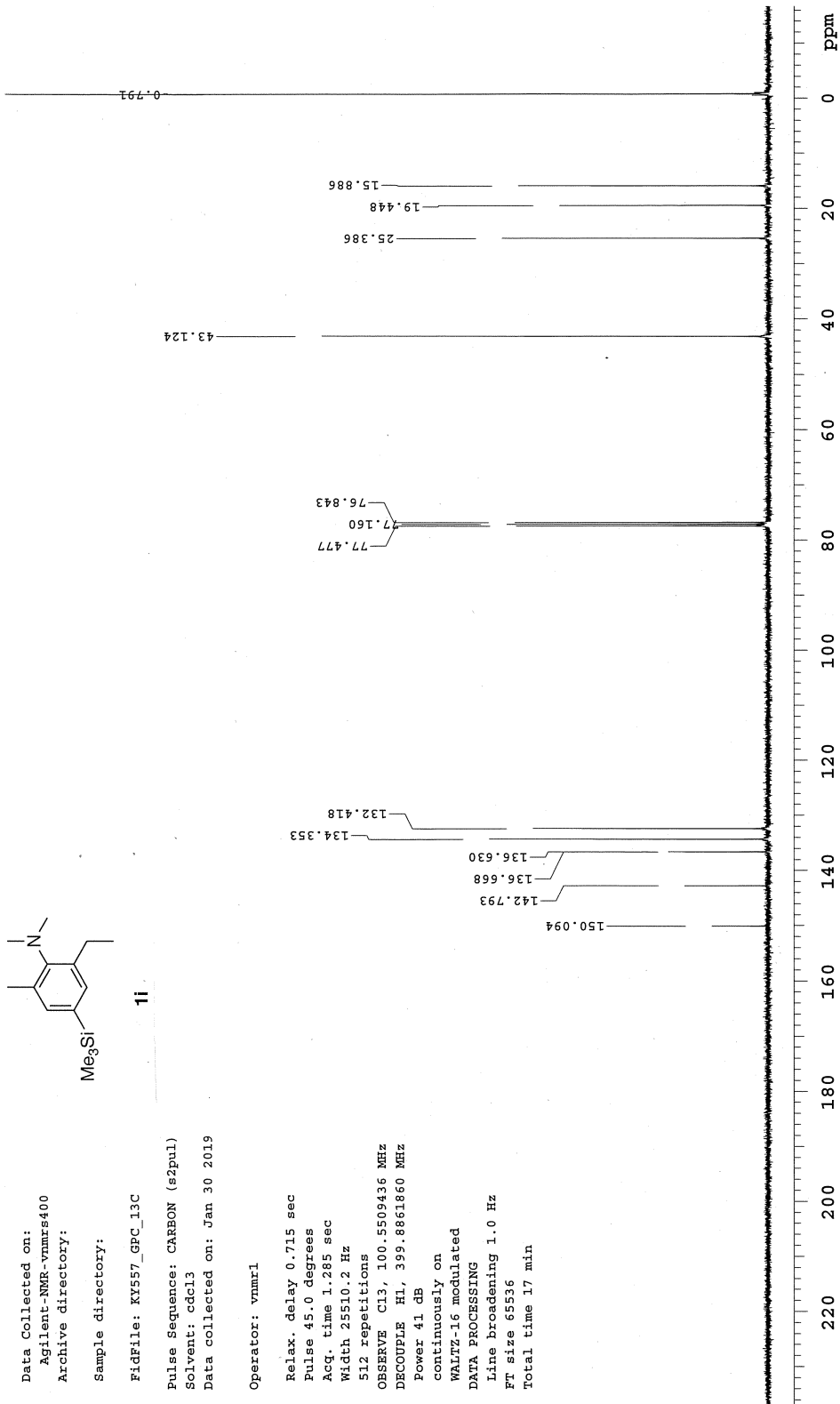


Figure S25. ¹³C NMR Spectrum of **1i** (101 MHz, CDCl₃)

STANDARD PROTON PARAMETERS

Sample Name:

Data Collected on:

Agilent-NMR-vmr400

Archive directory:

Sample directory:

File: KY713

Pulse Sequence: PROTON (s2pul)

Solvent: cdcl3

Data collected on: May 13 2019

Operator: vmr1

Relax. delay 15.000 sec

Pulse 45.0 degrees

Acq. time 3.500 sec

Width 6410.3 Hz

16 repetitions

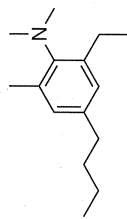
OBSERVE H1, 399.8841857 MHz

DATA PROCESSING

Line broadening 0.2 Hz

FT size 65536

Total time 4 min 56 sec



1j

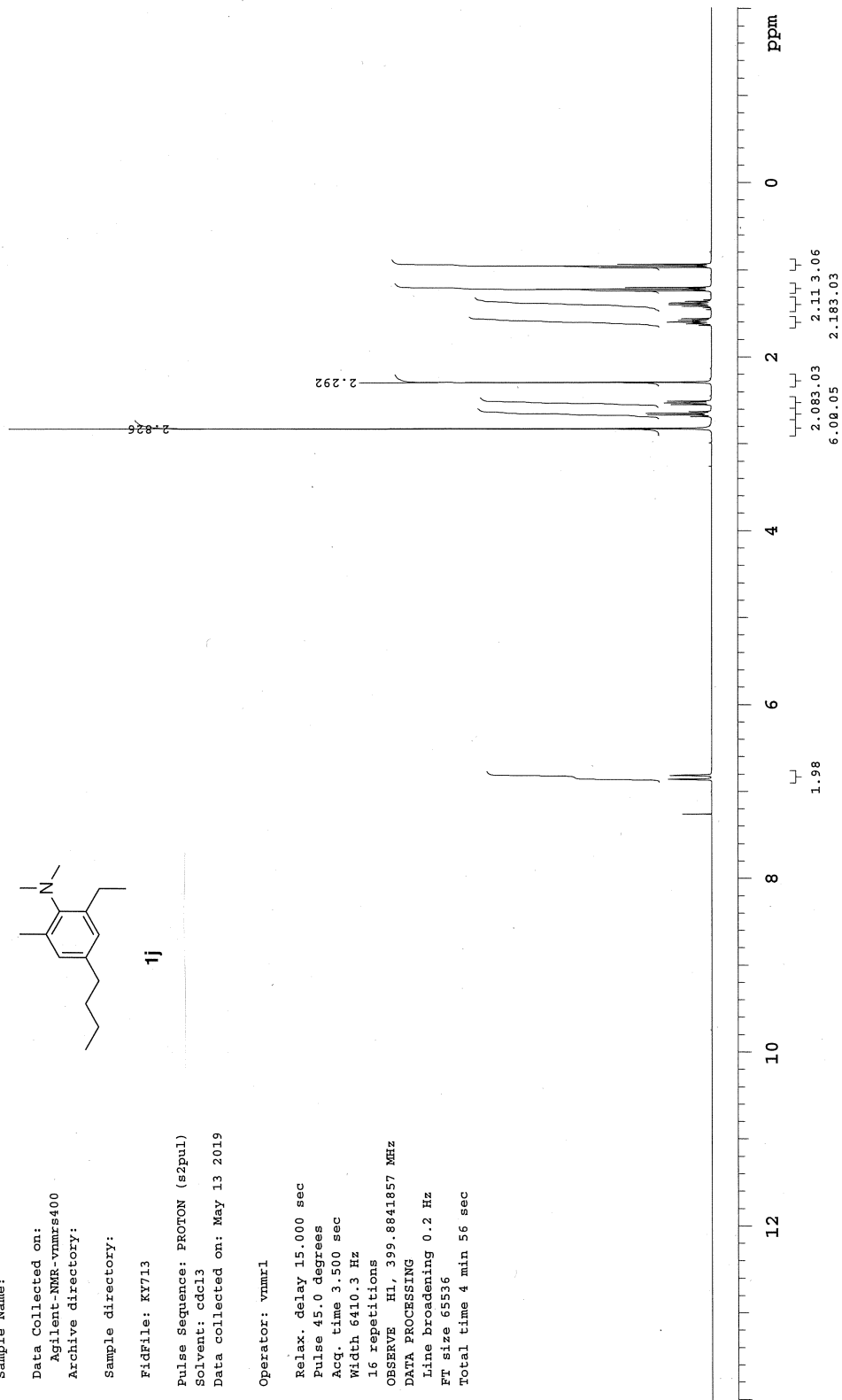


Figure S26. ¹H NMR Spectrum of 1j (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:

Data Collected on:

Agilent-NMR-vmr-s400

Archive directory:

Sample directory:

File: KY713_13C

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: May 13 2019

Operator: vmr1

Relax. delay 0.715 sec

Pulse 45.0 degrees

Acq. time 1.285 sec

Width 25510.2 Hz

512 repetitions

OBSERVE C13, 100.5509451 MHz

DECOUPLE H1, 399.8861860 MHz

Power 41 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 17 min

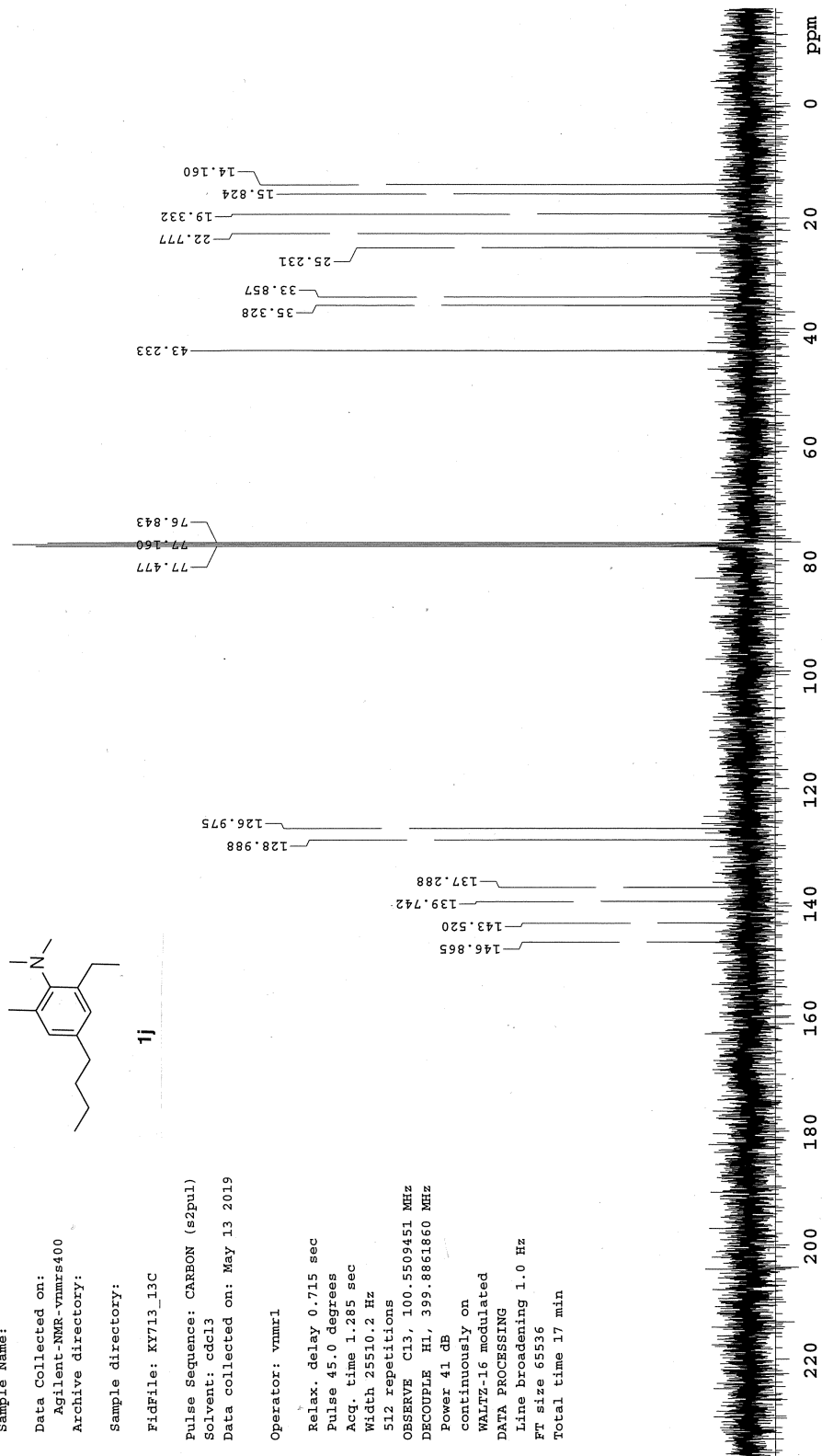


Figure S27. ¹³C NMR Spectrum of 1j (101 MHz, CDCl₃)

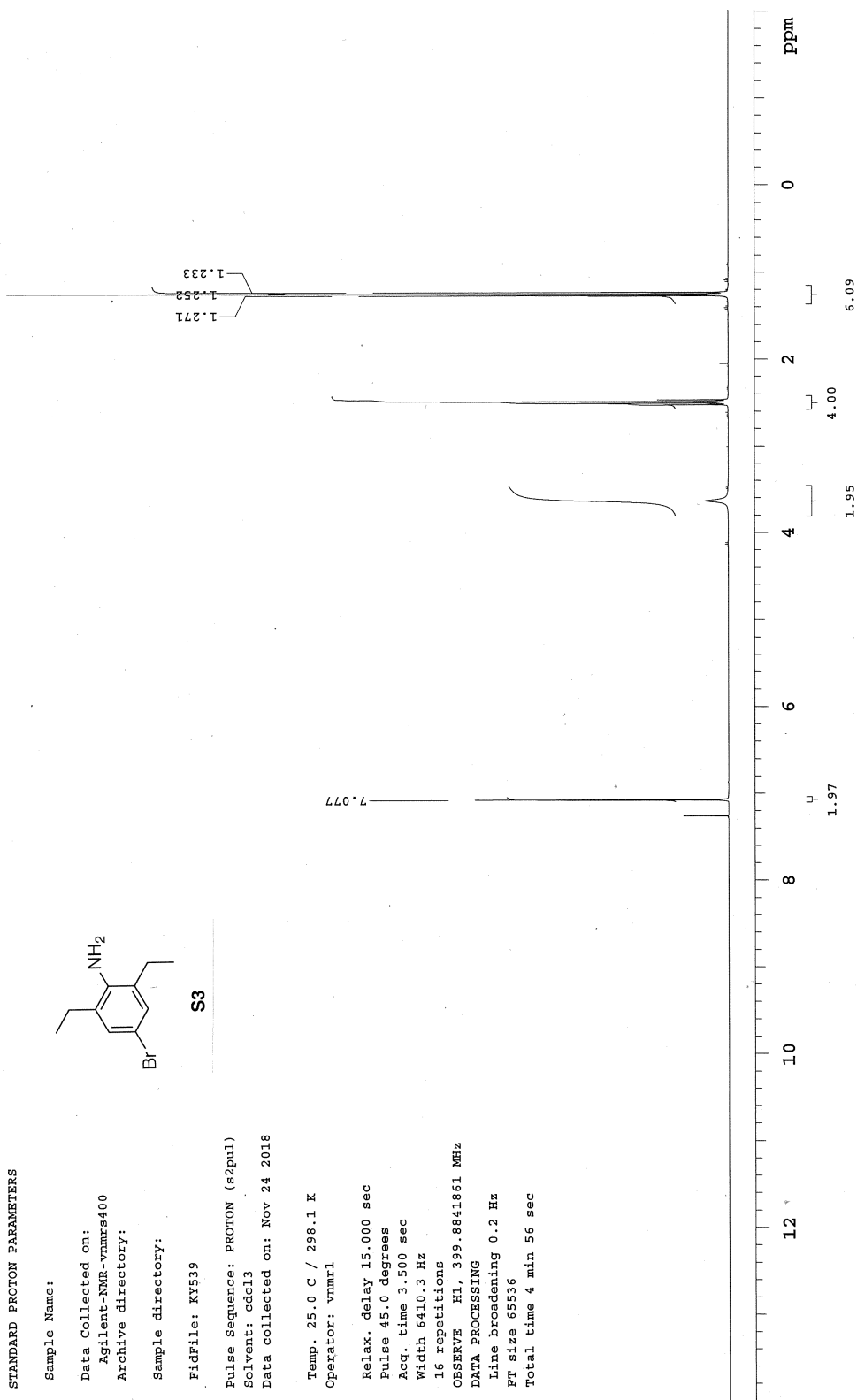


Figure S28. ¹H NMR Spectrum of S3 (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:

Data Collected on:
Agilent-NMR-vmr400
Archive directory:

Sample directory:

File: KY787_13C

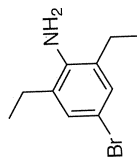
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jul 5 2019

Temp. 25.0 C / 298.1 K
Operator: vmr1

Relax. delay 0.715 sec
Pulse 45.0 degrees
Acq. time 1.285 sec
Width 25510.2 Hz

512 repetitions
OBSERVE C13, 100.5509607 MHz
DECOUPLE H1, 399.8861860 MHz

Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 17 min



S3

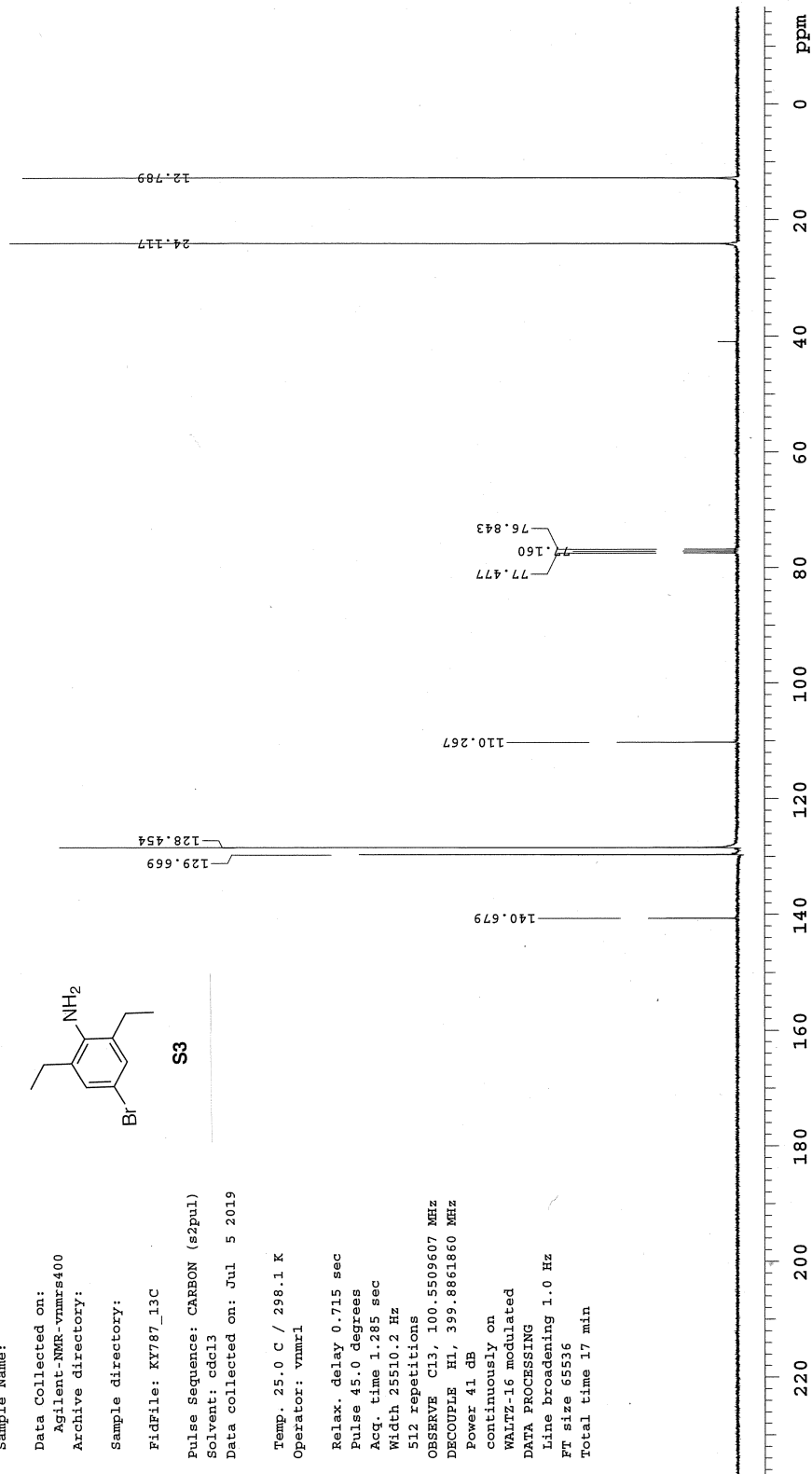


Figure S29. ¹³C NMR Spectrum of S3 (101 MHz, CDCl₃)

STANDARD PROTON PARAMETERS

Sample Name:
KY540
Data Collected on:
Agilent-NMR-vmrs400
Archive directory:
Sample directory:
File: KY540
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Nov 28 2018

Temp. 25.0 C / 298.1 K
Operator: vmr1

Relax. delay 15.000 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6410.3 Hz
16 repetitions
OBSERVE H1, 399.8841861 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 4 min 56 sec

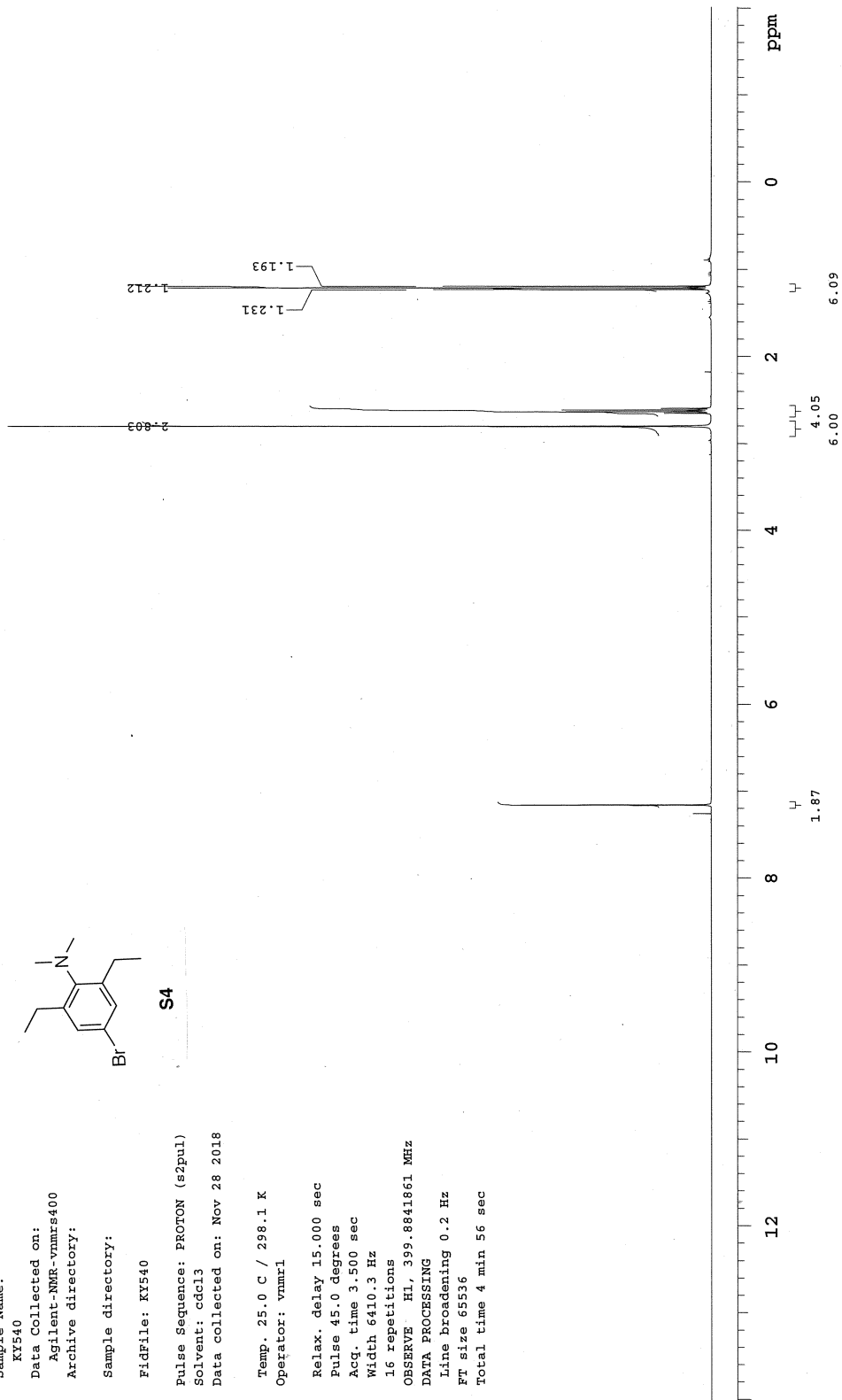
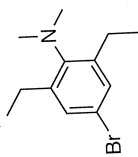


Figure S30. ¹H NMR Spectrum of S4 (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:
 Data Collected on:
 Agilent-NMR-vmrns400
 Archive directory:
 Sample directory:
 FIDFile: KY789_13C
 Pulse Sequence: CARBON (s2pul)
 Solvent: cdcl3
 Data collected on: Jul 6 2019
 Temp. 25.0 C / 298.1 K
 Operator: vmrnl
 Relax. delay 0.715 sec
 Pulse 45.0 degrees
 Acq. time 1.285 sec
 Width 25510.2 Hz
 1024 repetitions
 OBSERVE C13, 100.5509459 MHz
 DECOUPLE H1, 399.8861860 MHz
 Power 41 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 34 min

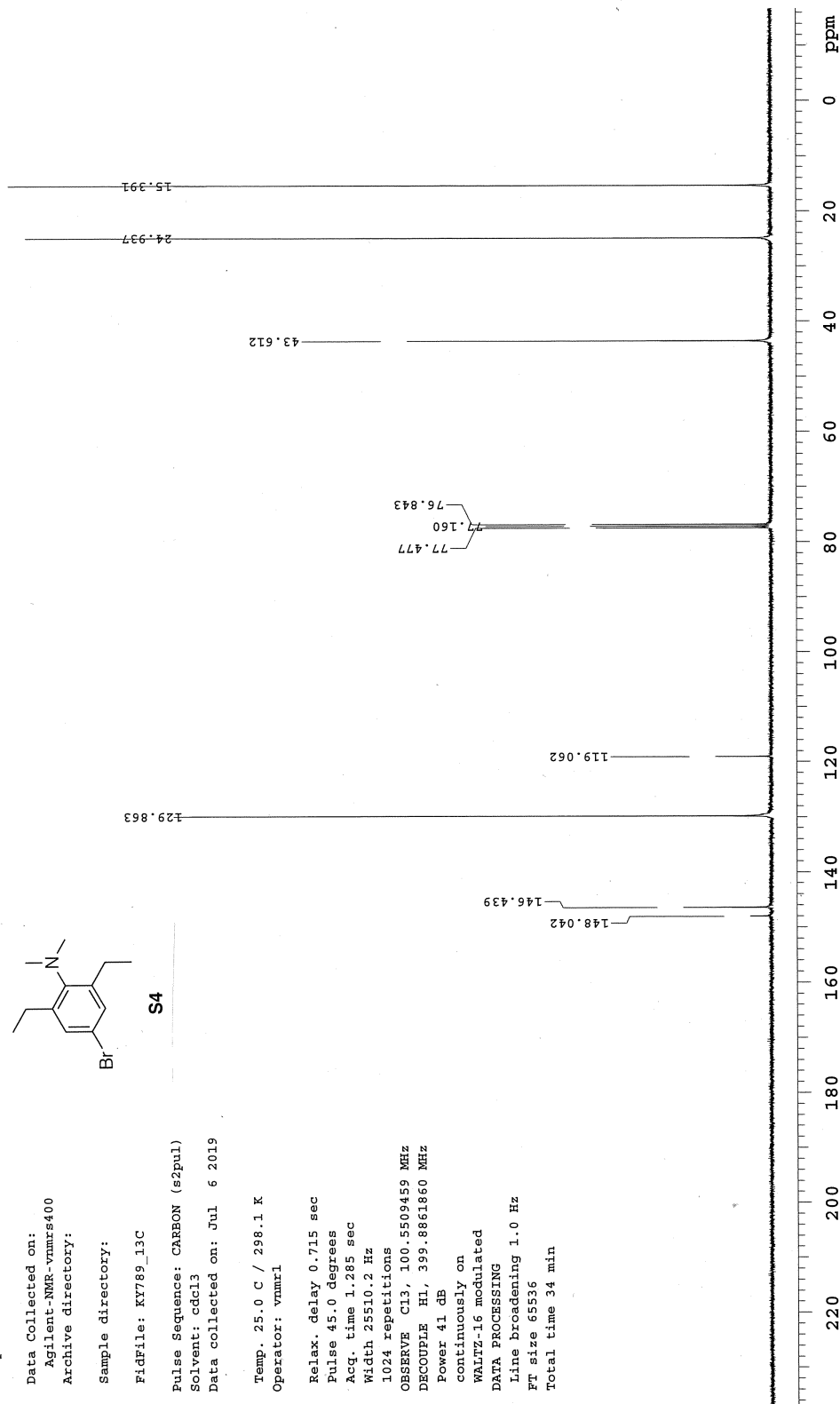
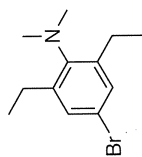


Figure S31. ¹³C NMR Spectrum of S4 (101 MHz, CDCl₃)

STANDARD PROTON PARAMETERS

Sample Name:

Data Collected on:

Agilent-NMR-vmms400

Archive directory:

Sample directory:

FidFile: KY709

Pulse Sequence: PROTON (s2pul)

Solvent: cdcl3

Data collected on: May 14 2019

Operator: vmml

Relax. delay 15.000 sec

Pulse 45.0 degrees

Acq. time 3.500 sec

Width 6410.3 Hz

16 repetitions

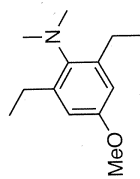
OBSERVE H1, 399.8841857 MHz

DATA PROCESSING

Line broadening 0.2 Hz

FT size 65536

Total time 4 min 56 sec



1k

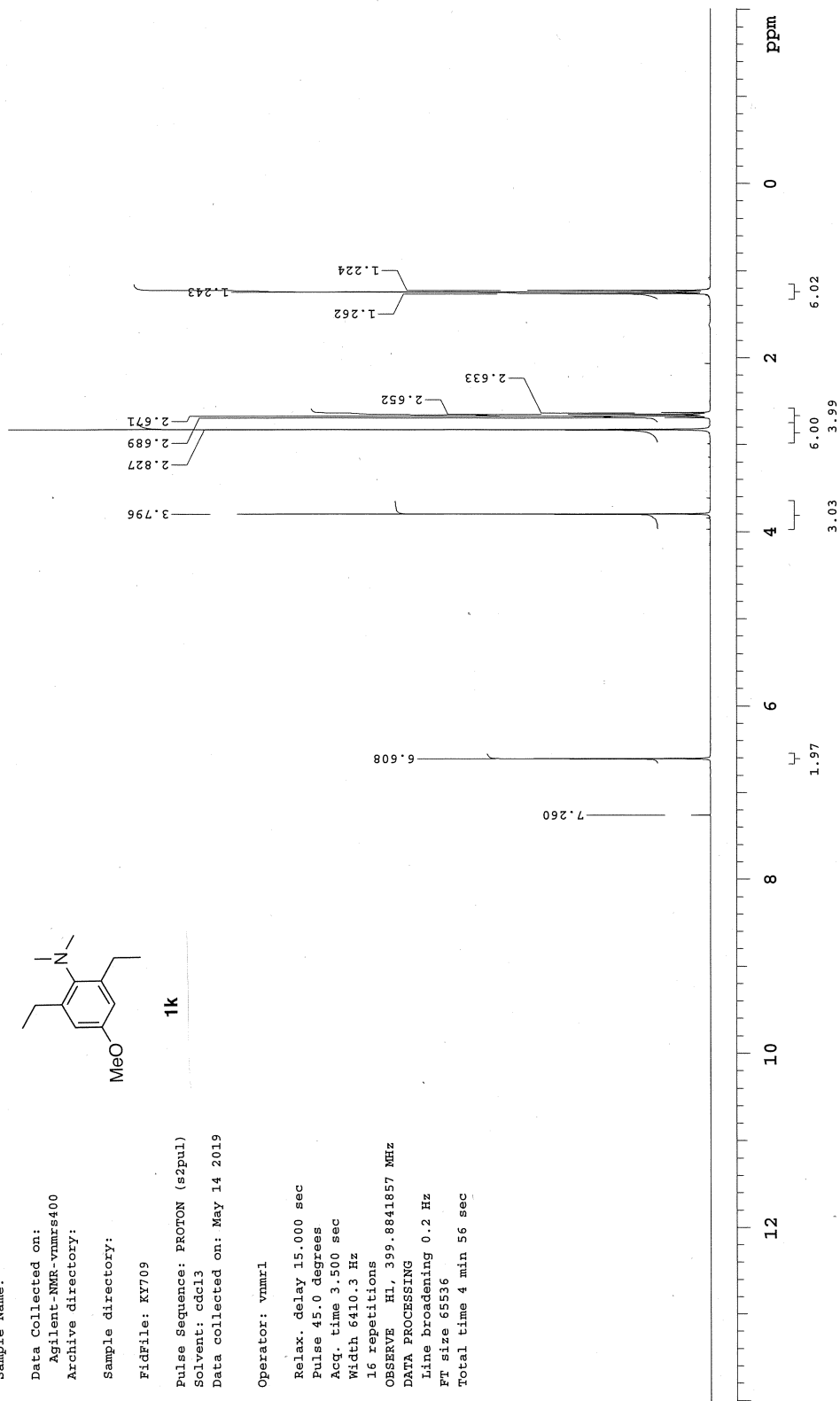


Figure S32. ¹H NMR Spectrum of 1k (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:
 Data Collected on: Agilent-NMR-vmrns400
 Archive directory:
 Sample directory:
 FidFile: KY709_13C
 Pulse Sequence: CARBON (s2pul)
 Solvent: cdcl3
 Data collected on: May 14 2019
 Operator: vmr1
 Relax. delay 0.715 sec
 Pulse 45.0 degrees
 Acq. time 1.285 sec
 Width 25510.2 Hz
 512 repetitions
 OBSERVE C13, 100.5509459 MHZ
 DECOUPLE H1, 399.8861860 MHZ
 Power 41 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 17 min

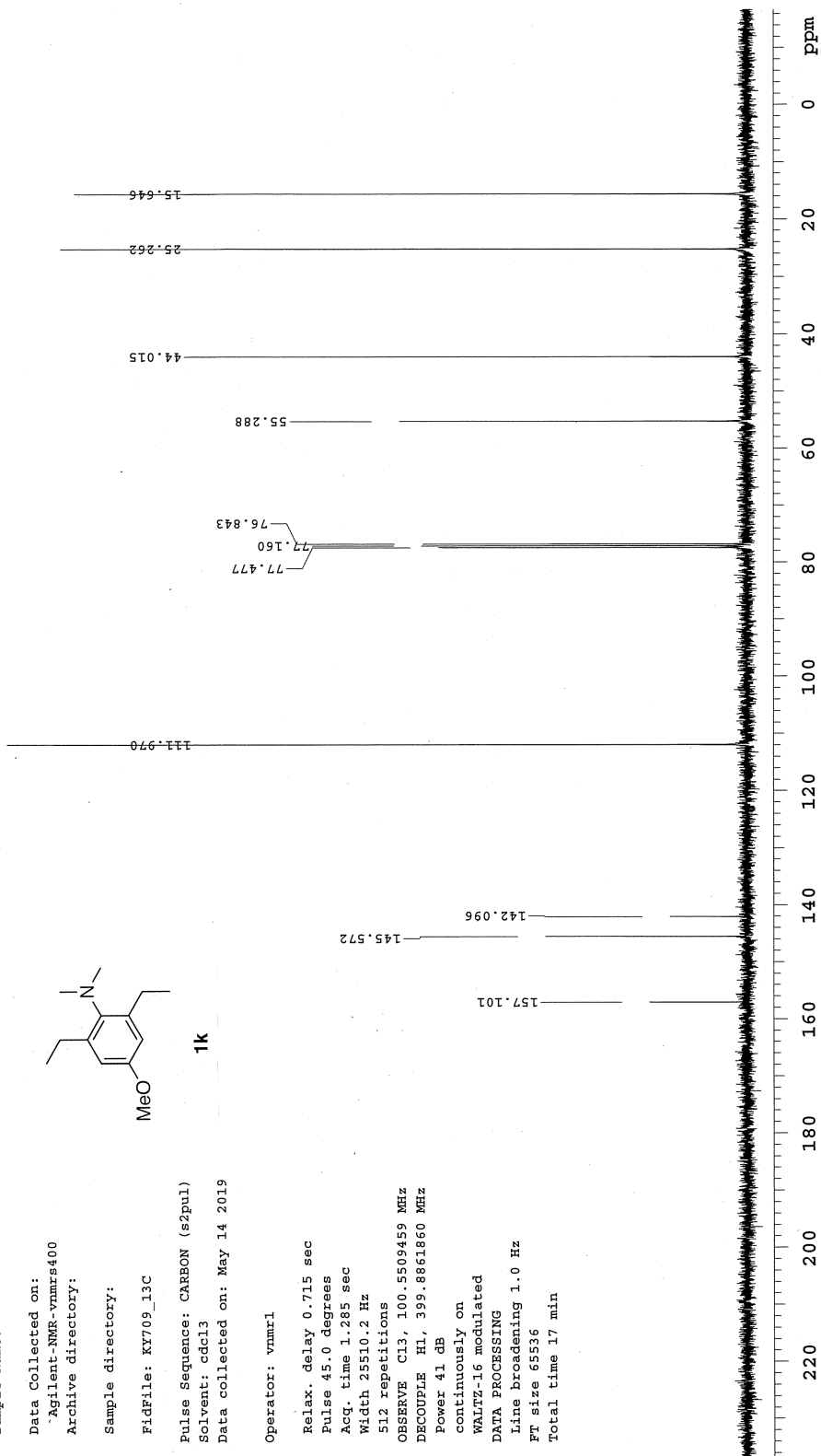
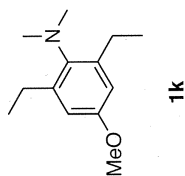


Figure S33. ¹³C NMR Spectrum of 1k (101 MHz, CDCl₃)

STANDARD PROTON PARAMETERS

Sample Name:
 KY735
 Data Collected on:
 Agilent-NMR-vnmrs400
 Archive directory:
 Sample directory:
 FidFile: KY735
 Pulse Sequence: PROTON (s2pul)
 Solvent: cdcl3
 Data collected on: May 19 2019
 Operator: vnmr1
 Relax. delay 15.000 sec
 Pulse 45.0 degrees
 Acq. time 3.500 sec
 Width 6410.3 Hz
 16 repetitions
 OBSERVE H1, 399.8841857 MHz
 DATA PROCESSING
 Line broadening 0.2 Hz
 FT size 65536
 Total time 4 min 56 sec

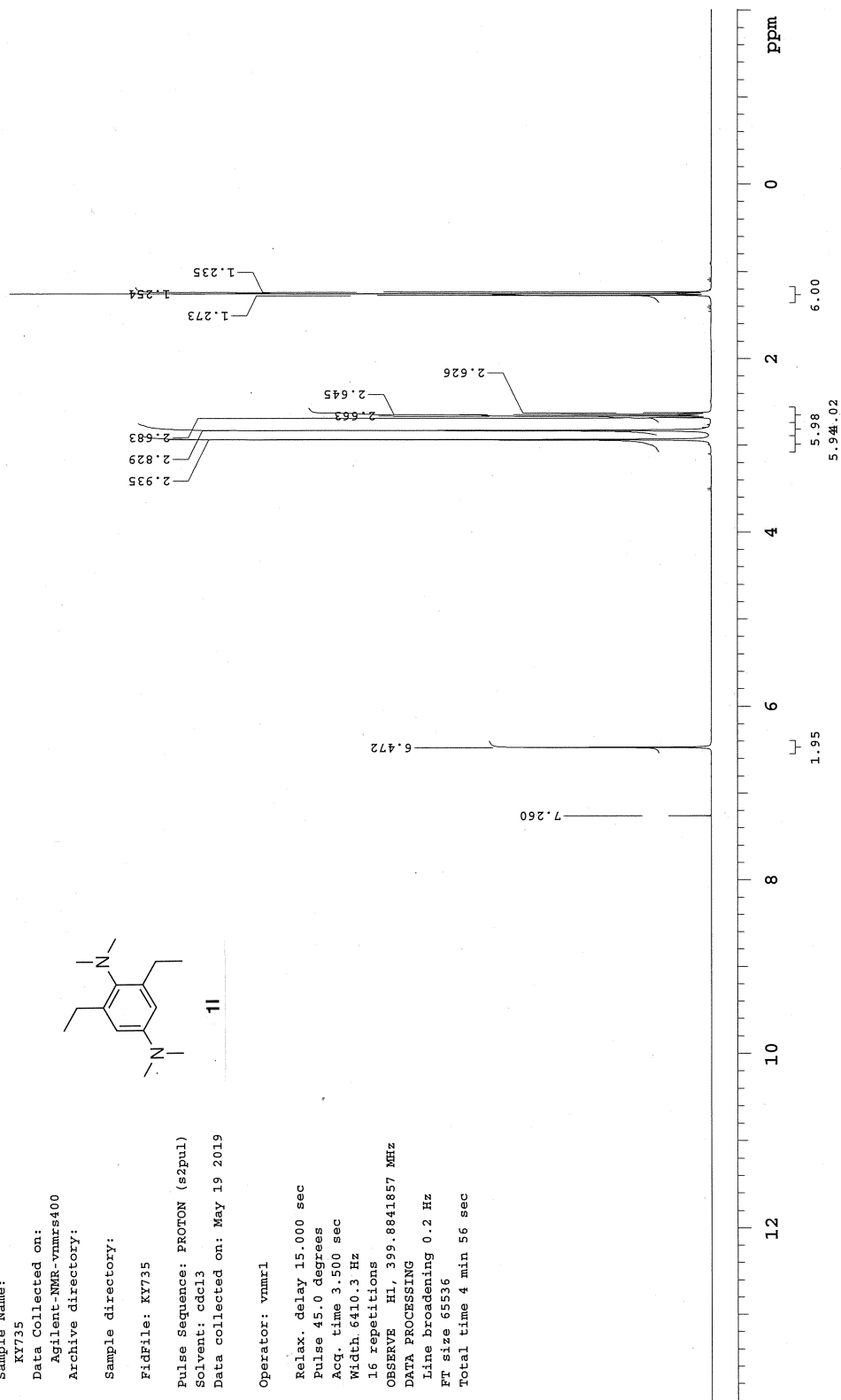
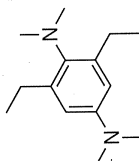


Figure S34. ¹H NMR Spectrum of **11** (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:
 Data Collected on:
 Agilent-NMR-vnmrs400
 Archive directory:
 Sample directory:
 FIDFile: KY735_13C
 Pulse Sequence: CARBON (s2pul)
 Solvent: cdcl3
 Data collected on: May 19 2019
 Operator: vnmr1
 Relax. delay 0.715 sec
 Pulse 45.0 degrees
 Acq. time 1.285 sec
 Width 25510.2 Hz
 512 repetitions
 OBSERVE C13, 100.5509459 MHz
 DECOUPLE H1, 399.8861860 MHz
 Power 41 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 17 min

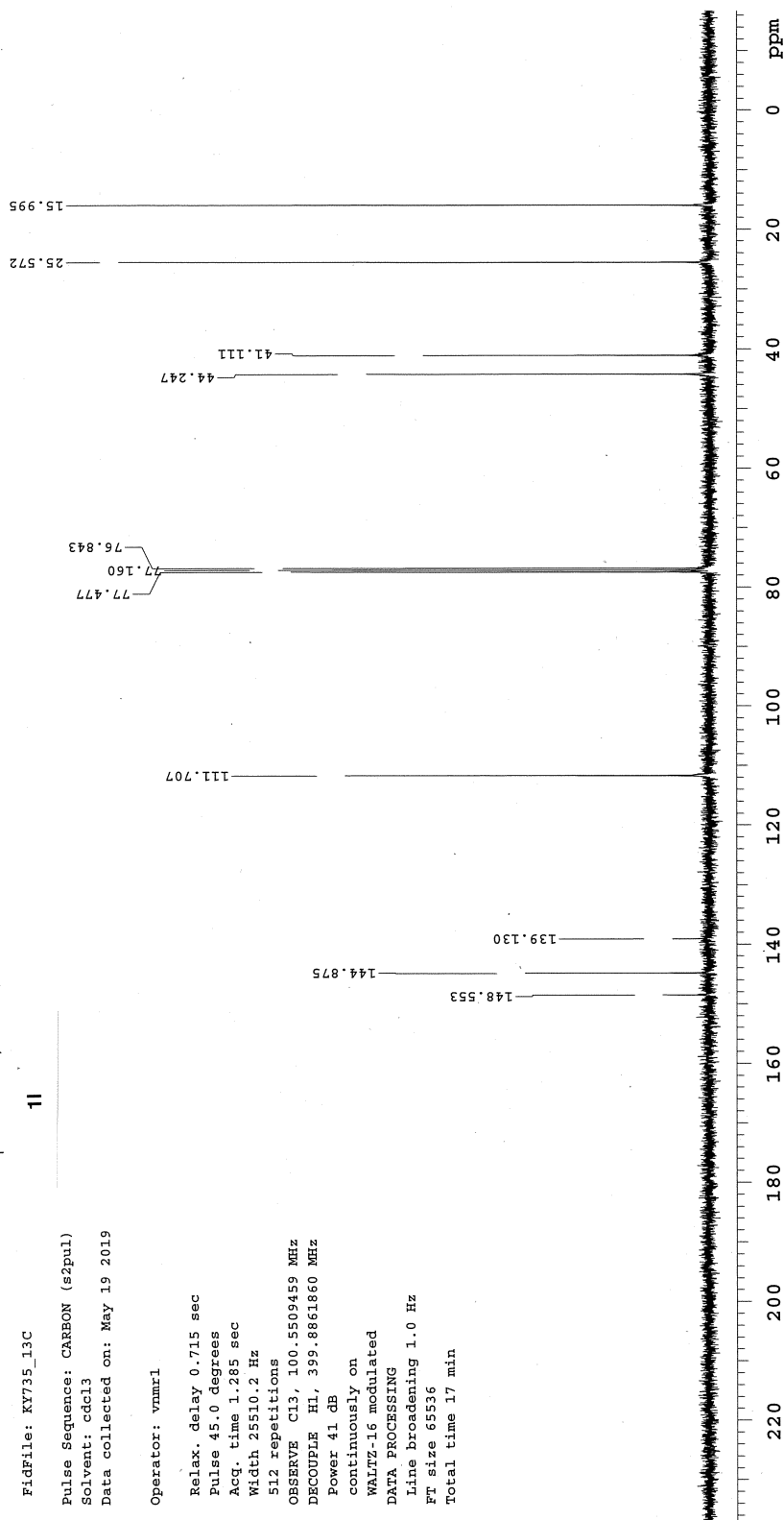
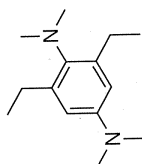
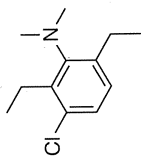


Figure S35. ¹³C NMR Spectrum of **11** (101 MHz, CDCl₃)

STANDARD PROTON PARAMETERS

Sample Name:
 Data Collected on:
 Agilent-NMR-vmrns400
 Archive directory:
 Sample directory:
 Fidfile: KY565
 Pulse Sequence: PROTON (s2pul)
 Solvent: cdcl3
 Data collected on: Jul 3 2019
 Temp. 25.0 C / 298.1 K
 Operator: vmrnl
 Relax. delay 15.000 sec
 Pulse 45.0 degrees
 Acq. time 3.500 sec
 Width 6410.3 Hz
 16 repetitions
 OBSERVE H1, 399.8841863 MHZ
 DATA PROCESSING
 Line broadening 0.2 Hz
 FT size 65536
 Total time 4 min 56 sec



1m

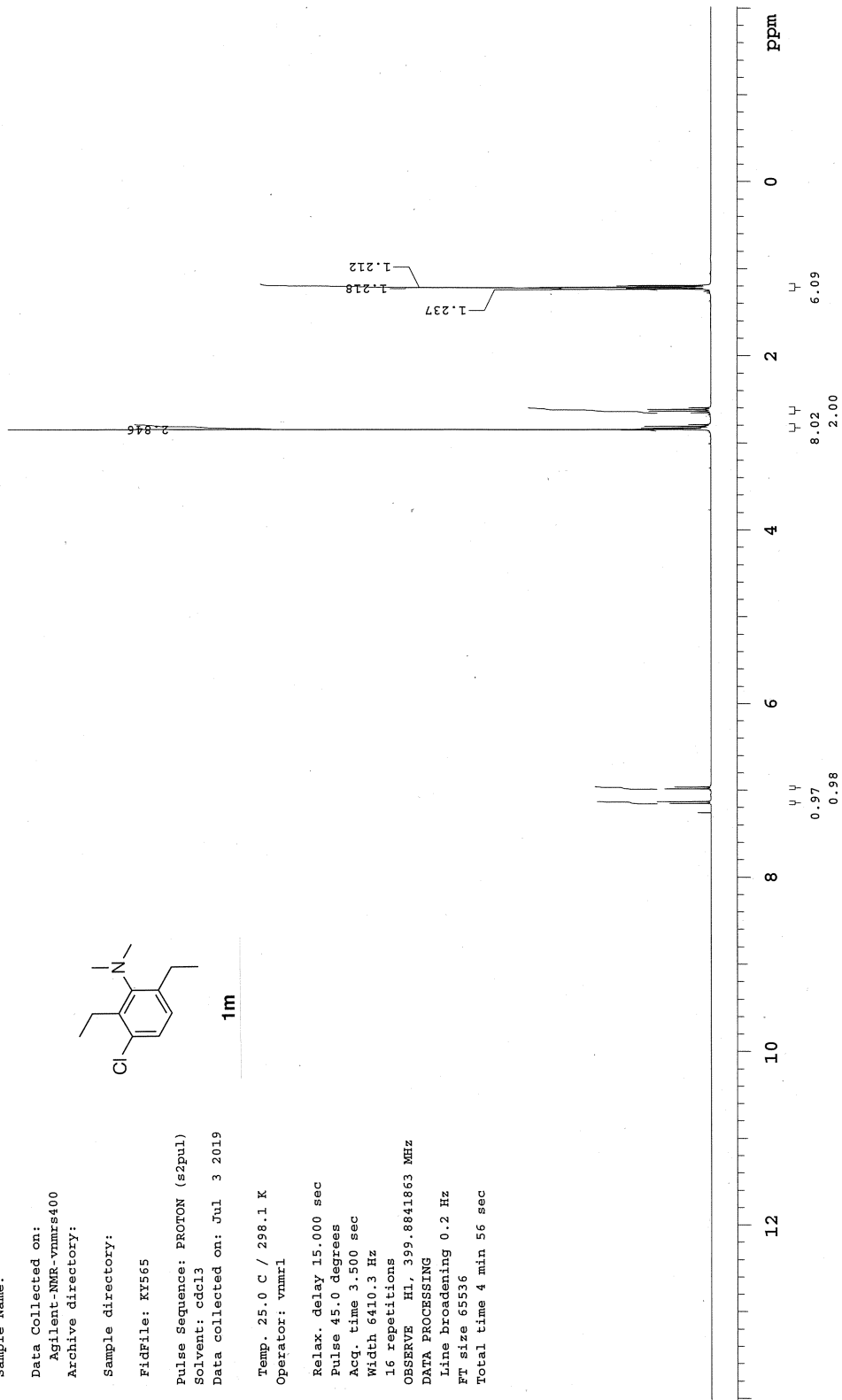
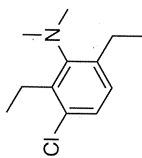


Figure S36. ¹H NMR Spectrum of 1m (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:
 Data Collected on:
 Agilent-NMR-vmr400
 Archive directory:
 Sample directory:
 File: KY565_13C
 Pulse Sequence: CARBON (s2pul)
 Solvent: cdcl3
 Data collected on: Jul 3 2019
 Temp. 25.0 C / 298.1 K
 Operator: vmr1
 Relax. delay 0.715 sec
 Pulse 45.0 degrees
 Acq. time 1.285 sec
 Width 25510.2 Hz
 512 repetitions
 OBSERVE C13, 100.5509436 MHz
 DECOUPLE H1, 399.8661860 MHz
 Power 41 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 17 min



1m

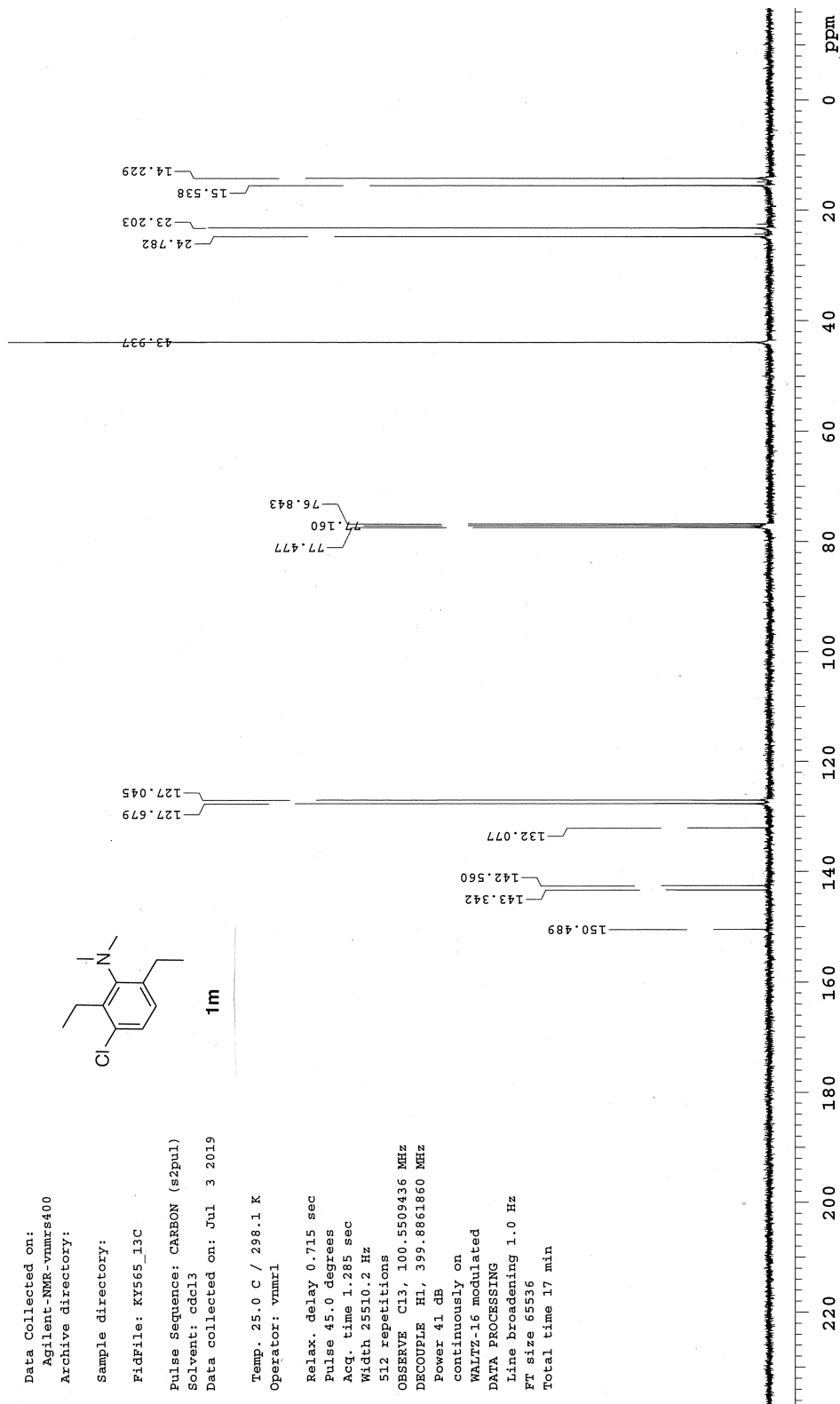
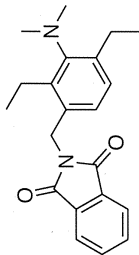


Figure S37. ¹³C NMR Spectrum of 1m (101 MHz, CDCl₃)

STANDARD PROTON PARAMETERS

Sample Name:
 Data Collected on:
 Agilent-NMR-vmms400
 Archive directory:
 Sample directory:
 FidFile: KY756
 Pulse Sequence: PROTON (s2pul)
 Solvent: cdc13
 Data collected on: Jun 11 2019
 Temp. 25.0 C / 298.1 K
 Operator: vmr1
 Relax. delay 15.000 sec
 Pulse 45.0 degrees
 Acq. time 3.500 sec
 Width 6410.3 Hz
 16 repetitions
 OBSERVE H1, 399.8841866 MHz
 DATA PROCESSING
 Line broadening 0.2 Hz
 FT size 65536
 Total time 4 min 56 sec



1n

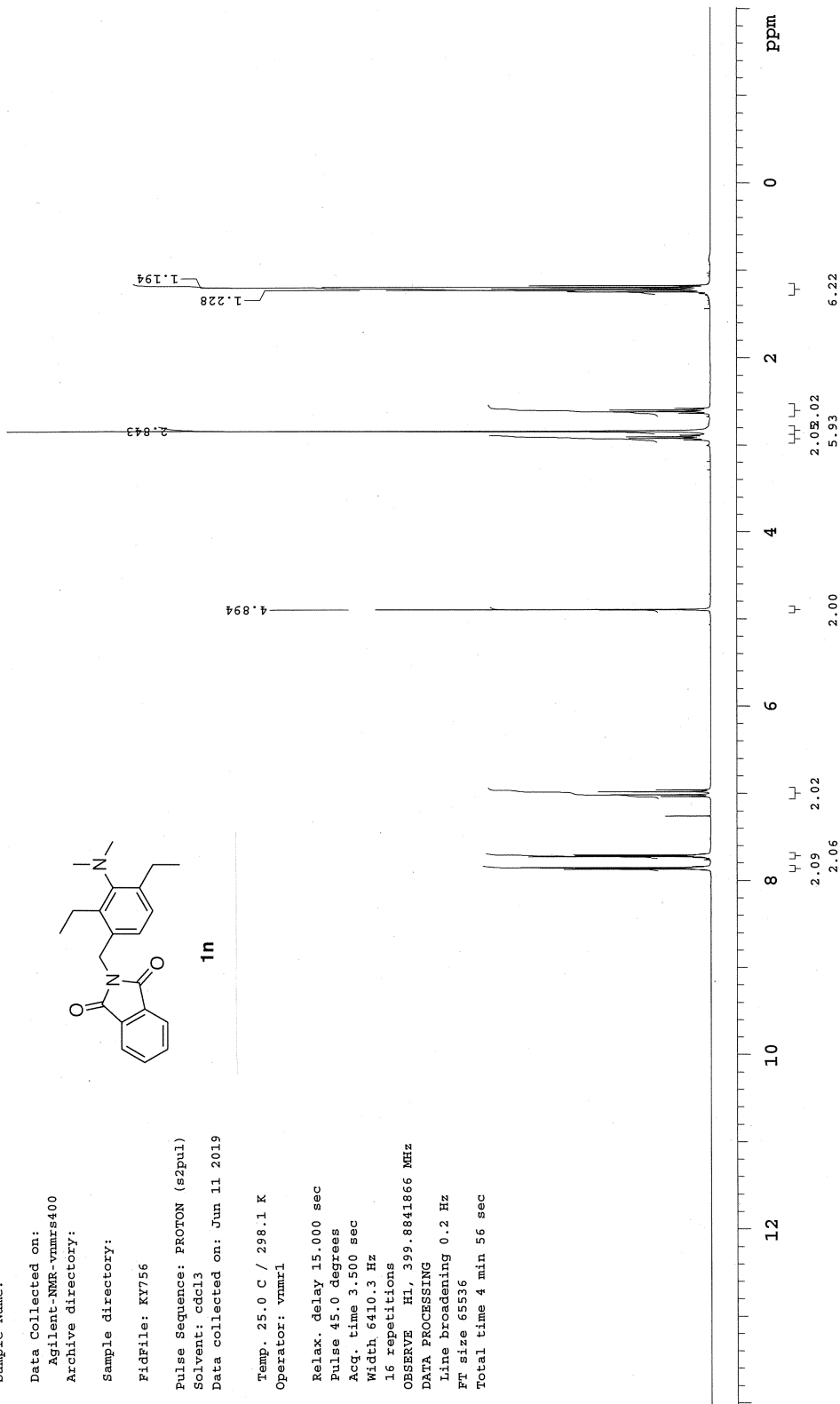


Figure S38. ¹H NMR Spectrum of **1n** (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:

Data Collected on:

Agilent-NMR-vnmrs400

Archive directory:

Sample directory:

File: KY756_13C

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Jun 11 2019

Temp. 25.0 C / 298.1 K

Operator: vnmr1

Relax. delay 0.715 sec

Pulse 45.0 degrees

Acq. time 1.285 sec

Width 25510.2 Hz

512 repetitions

OBSERVE C13, 100.5509475 MHZ

DECOUPLE H1, 399.8661860 MHZ

Power 41 dB

continuously on

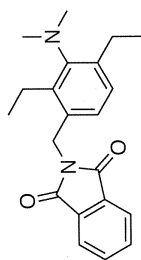
WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 17 min



1n

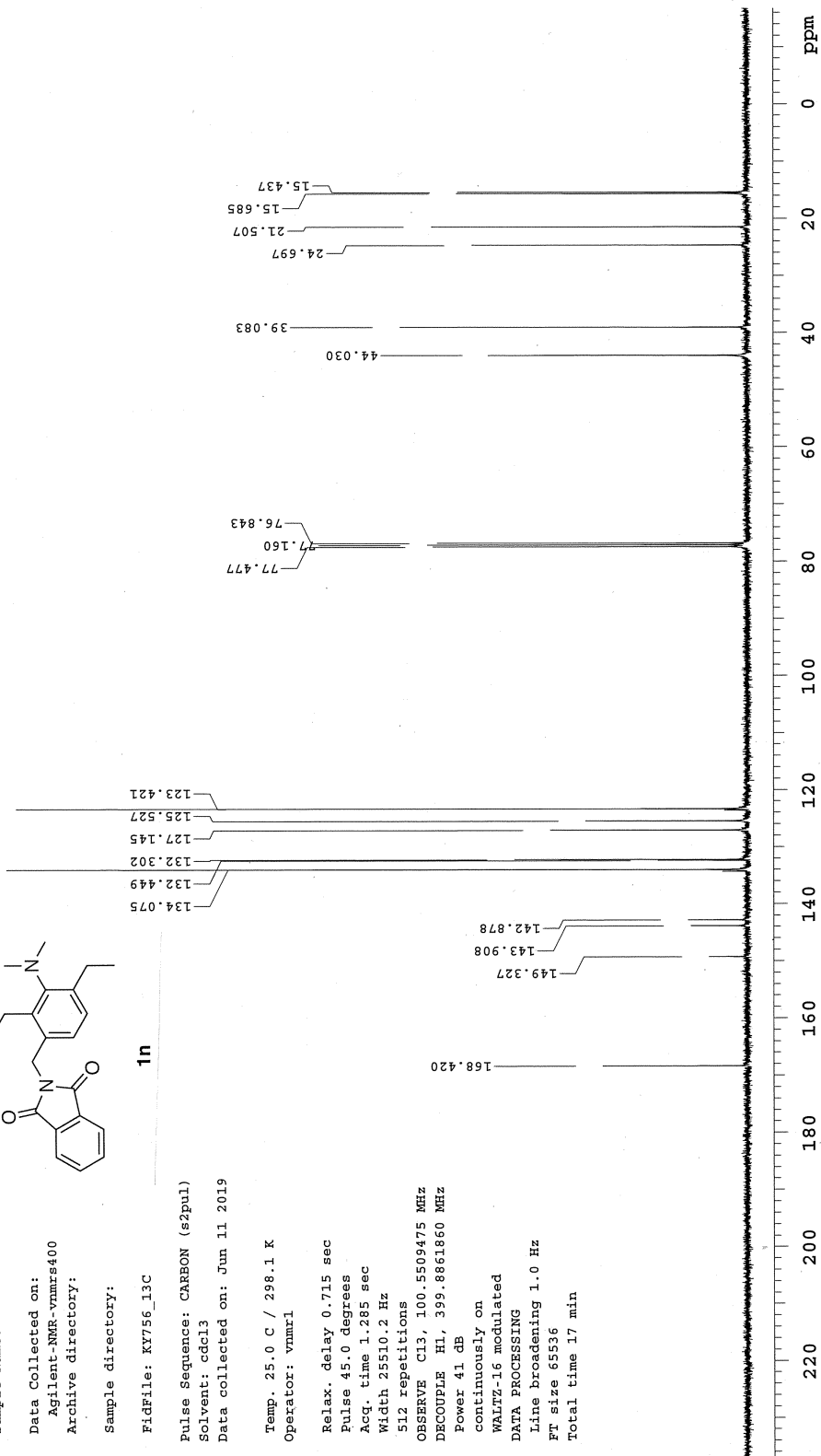


Figure S39. ¹³C NMR Spectrum of 1n (101 MHz, CDCl₃)

STANDARD PROTON PARAMETERS

Sample Name:

Data Collected on:

Agilent-NMR-vnmrs400

Archive directory:

Sample directory:

FIDfile: KY604

Pulse Sequence: PROTON (s2pul)

Solvent: cdcl3

Data collected on: Feb 13 2019

Operator: vnmr1

Relax. delay 15.000 sec

Pulse 45.0 degrees

Acq. time 3.500 sec

Width 6410.3 Hz

16 repetitions

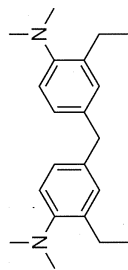
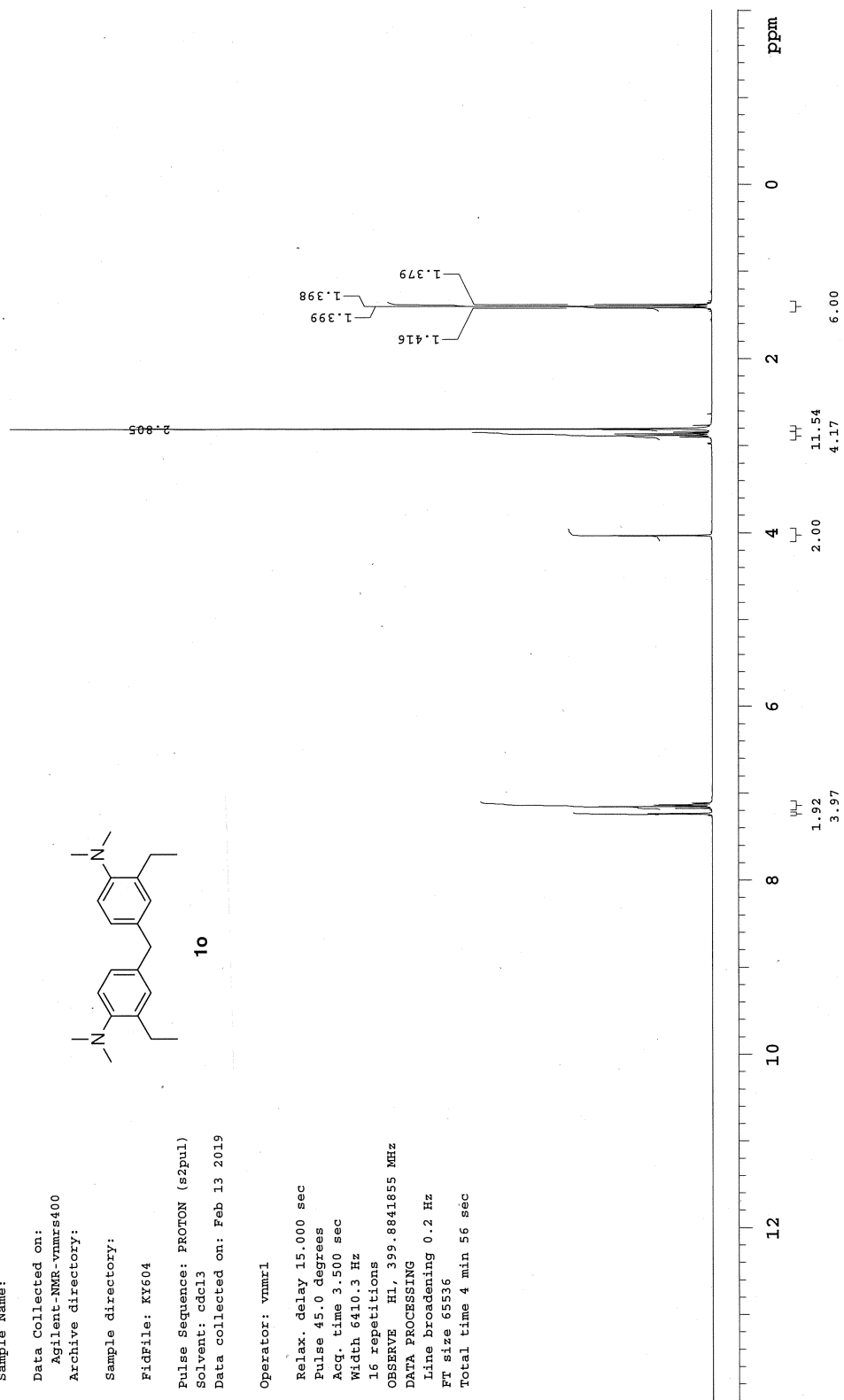
OBSERVE H1, 399.8841855 MHz

DATA PROCESSING

Line broadening 0.2 Hz

FT size 65536

Total time 4 min 56 sec

**1o**Figure S40. ¹H NMR Spectrum of **1o** (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:

Data Collected on:
Agilent-NMR-vmr400
Archive directory:

Sample directory:

File: KY604_13C

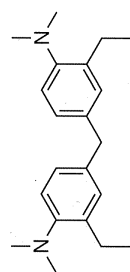
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jul 6 2019

Temp. 25.0 C / 298.1 K
Operator: vmr1

Relax. delay 0.715 sec
Pulse 45.0 degrees
Acq. time 1.285 sec
Width 25510.2 Hz

512 repetitions
OBSERVE C13, 100.5509490 MHz
DECOUPLE H1, 399.8861860 MHz

Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 17 min



1o

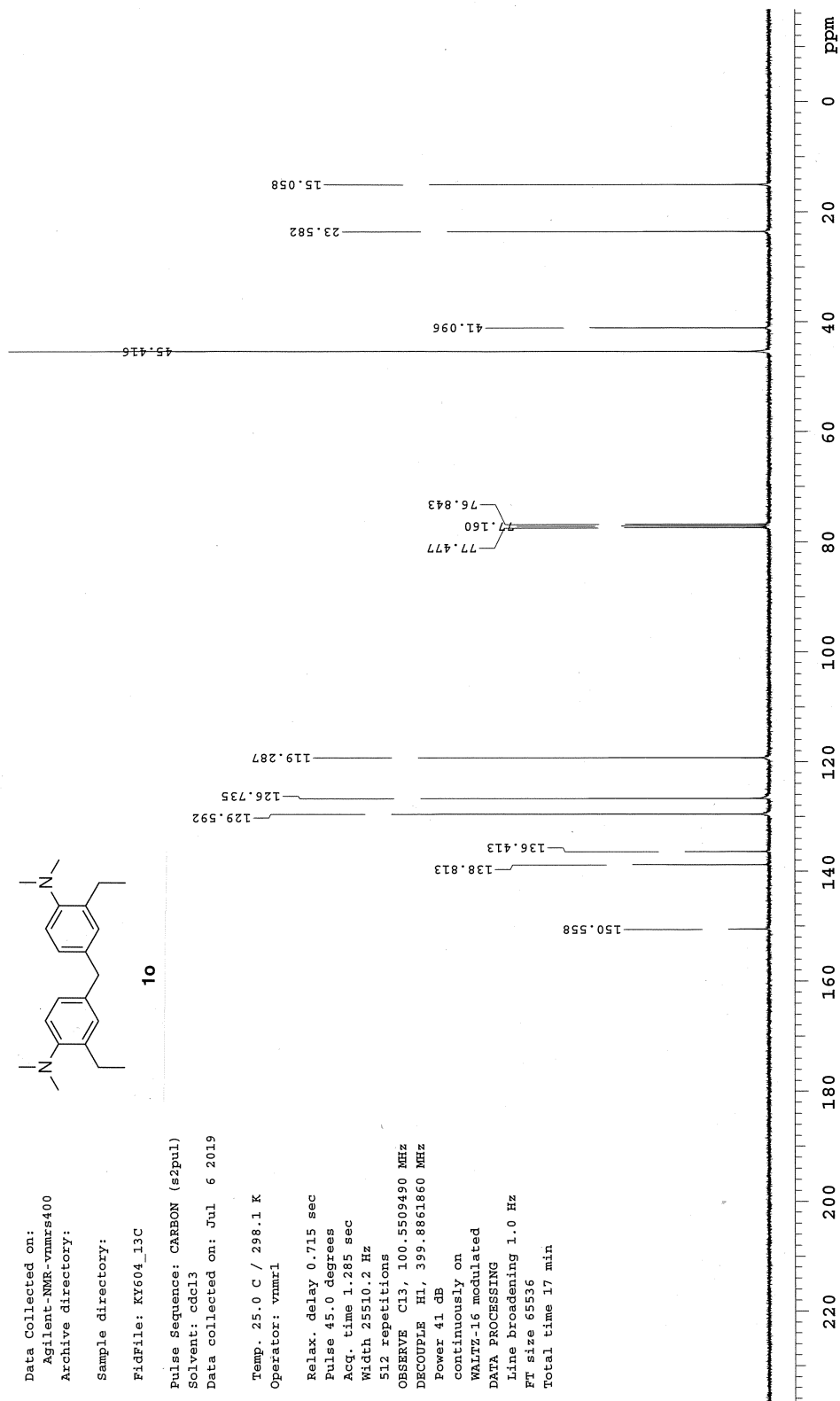


Figure S41. ^{13}C NMR Spectrum of **1o** (101 MHz, CDCl_3)

STANDARD PROTON PARAMETERS

Sample Name:

Data Collected on:
Agilent-NMR-vnmrs400
Archive directory:

Sample directory:

File: KY464

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Sep 13 2018

1p

Operator: vnmr1

Relax. delay 15.000 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6410.3 Hz
16 repetitions
OBSERVE H1, 399.8841861 MHz
DATA PROCESSING
Line broadening 0.2 Hz
Ft size 65536
Total time 4 min 56 sec

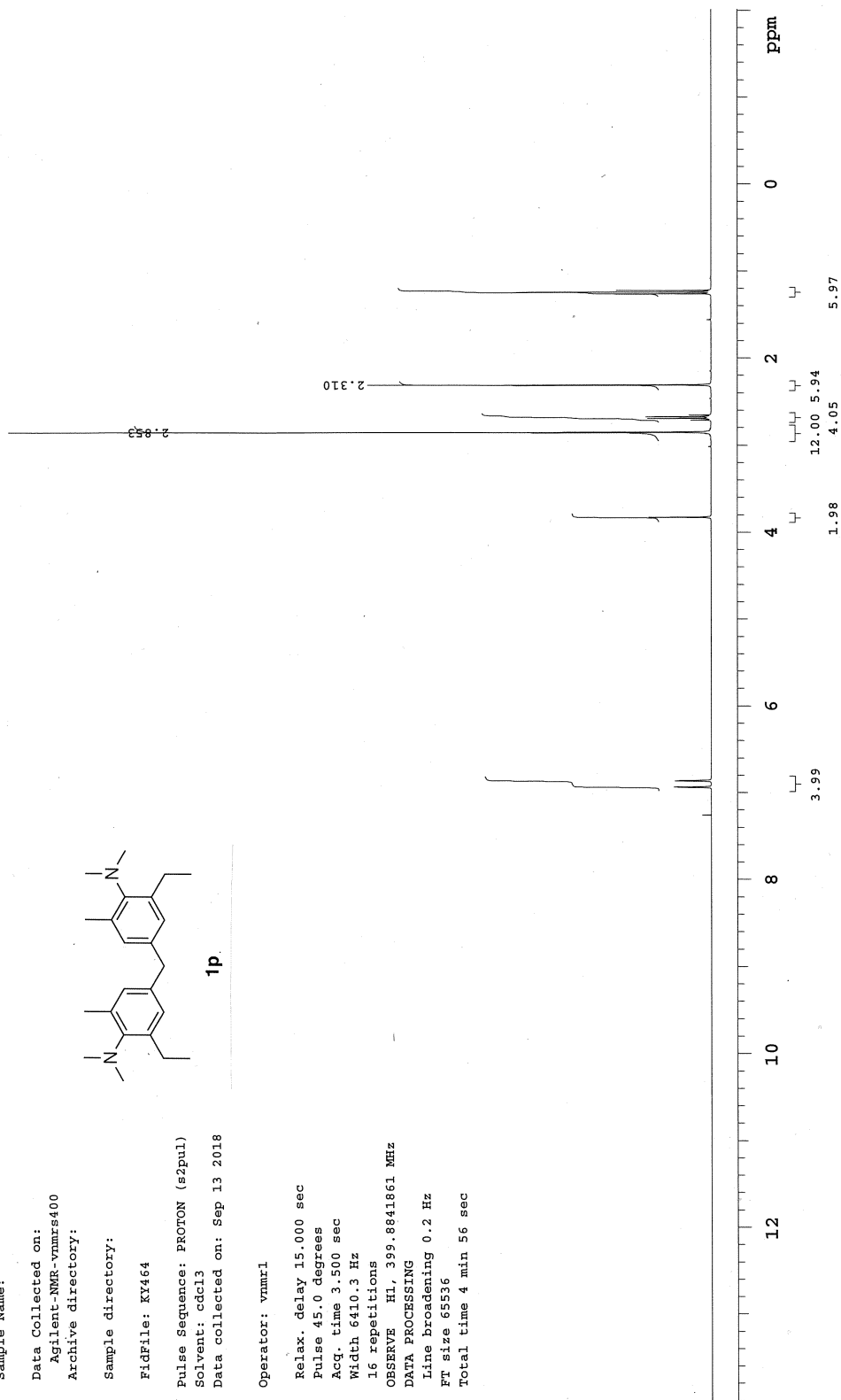


Figure S42. ¹H NMR Spectrum of 1p (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:

Data Collected on:
Agilent-NMR-vmms400
Archive directory:

Sample directory:

FIDfile: XY464C13

Pulse Sequence: CARBON (s2pul)

Solvent: cdc13
Data collected on: Sep 13 2018

Operator: vnmr1

Relax. delay 0.715 sec
Pulse 45.0 degrees
Acq. time 1.285 sec
Width 25510.2 Hz
512 repetitions
OBSERVE C13, 100.5509490 MHz
DECOUPLE H1, 399.8861860 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 17 min

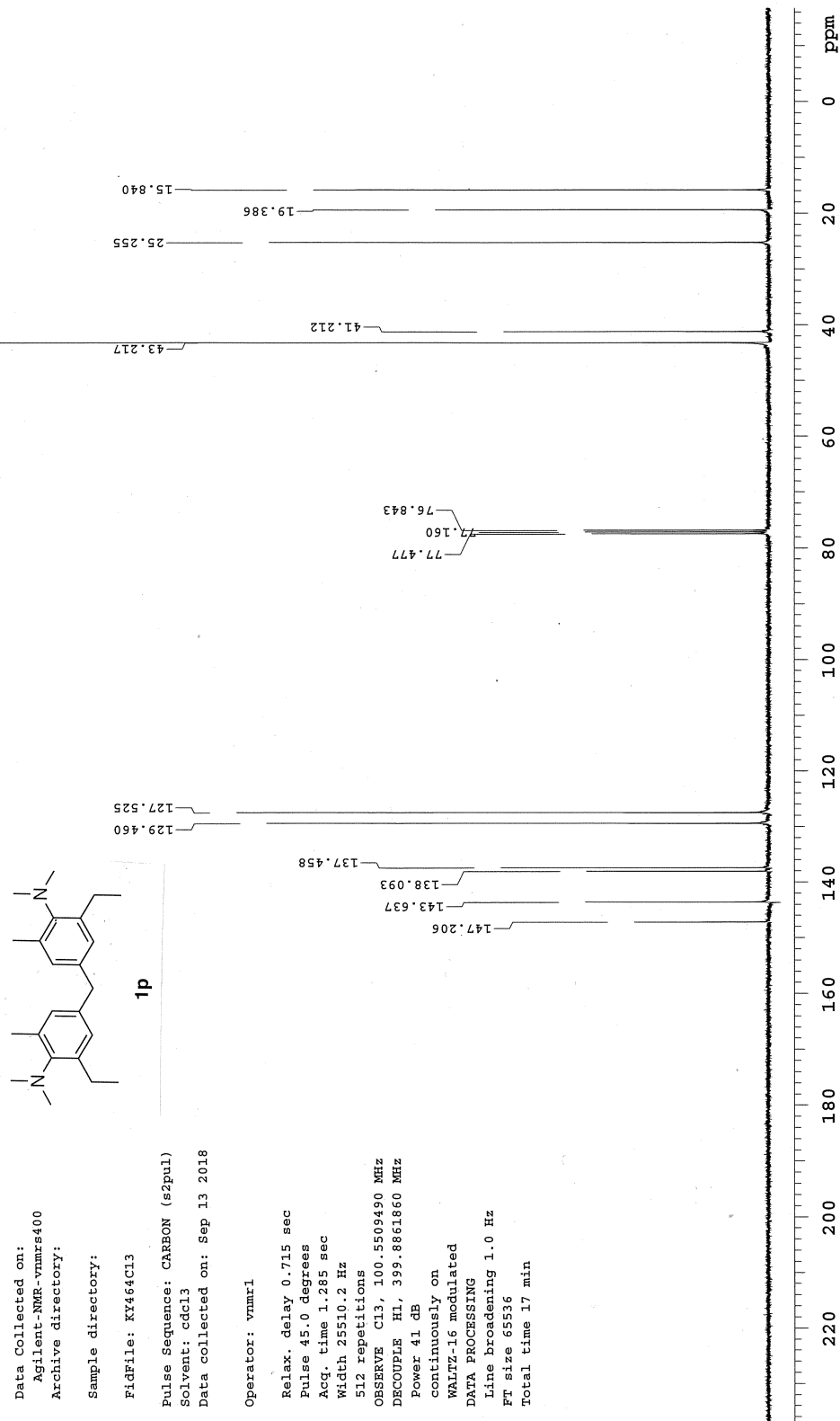


Figure S43. ¹³C NMR Spectrum of **1p** (101 MHz, CDCl₃)

STANDARD PROTON PARAMETERS

Sample Name:

Data Collected on:

Agilent-NMR-vmrs400

Archive directory:

Sample directory:

FidFile: KY385_2

Pulse Sequence: PROTON (s2pul)

Solvent: cdcl3

Data collected on: Oct 2 2018

Temp. 25.0 C / 298.1 K

Operator: vmr1

Relax. delay 15.000 sec

Pulse 45.0 degrees

Acq. time 3.500 sec

Width 6410.3 Hz

16 repetitions

OBSERVE H1, 399.8841861 MHZ

DATA PROCESSING

Line broadening 0.2 Hz

FT size 65536

Total time 4 min 56 sec

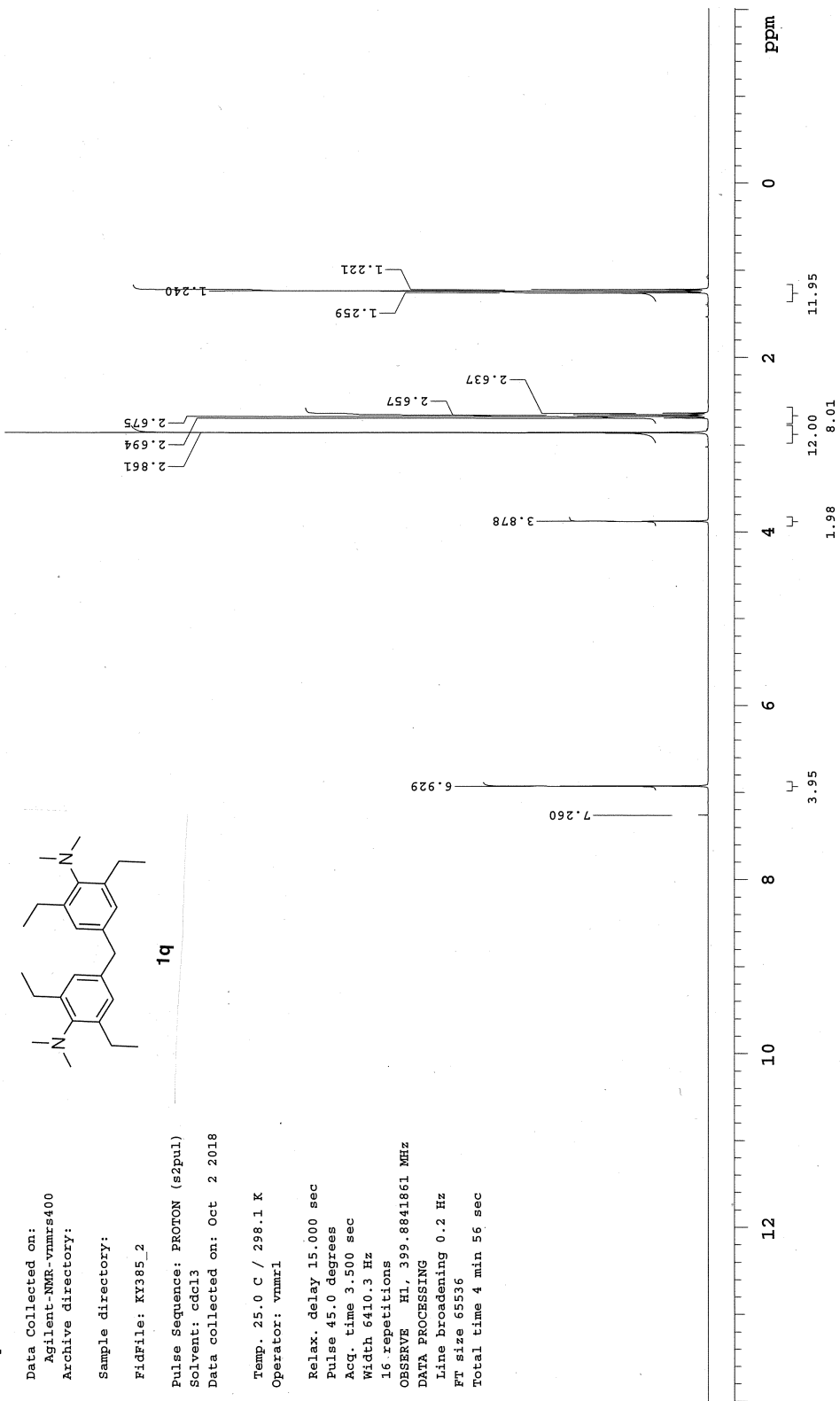


Figure S44. ¹H NMR Spectrum of **1q** (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:

Data Collected on:

Agilent-NMR-vnmrs400

Archive directory:

Sample directory:

File: KY385_13C

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Oct 2 2018

Temp. 25.0 C / 298.1 K

Operator: vnmr1

Relax. delay 0.715 sec

Pulse 45.0 degrees

Acq. time 1.285 sec

Width 25510.2 Hz

512 repetitions

OBSERVE C13, 100.5509467 MHZ

DECOUPLE H1, 399.8661860 MHZ

Power 41 dB

continuously on

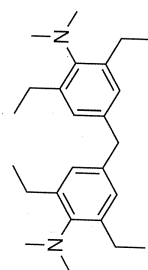
WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 17 min



1q

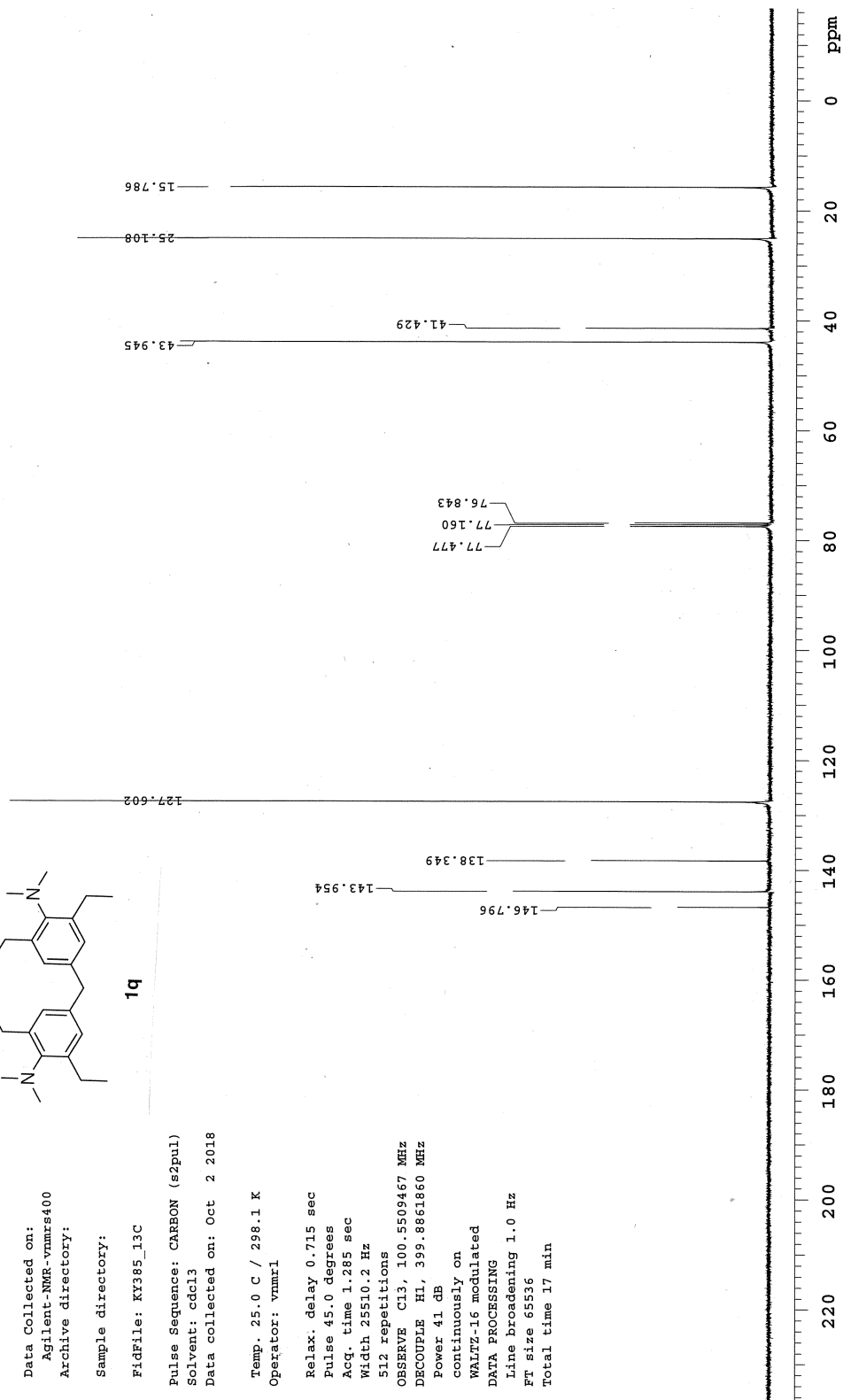


Figure S45. ¹³C NMR Spectrum of 1q (101 MHz, CDCl₃)

STANDARD PROTON PARAMETERS

Sample Name:
 Data Collected on:
 Agilent-NMR-vmms400
 Archive directory:
 Sample directory:
 Fidfile: KY645
 Pulse Sequence: PROTON (szpul)
 Solvent: cdcl3
 Data collected on: Mar 4 2019
 Temp. 25.0 C / 298.1 K
 Operator: vmr1
 Relax. delay 15.000 sec
 Pulse 45.0 degrees
 Acq. time 3.500 sec
 Width 6410.3 Hz
 16 repetitions
 OBSERVE H1, 399.8841859 MHz
 DATA PROCESSING
 Line broadening 0.2 Hz
 FT size 65536
 Total time 4 min 56 sec

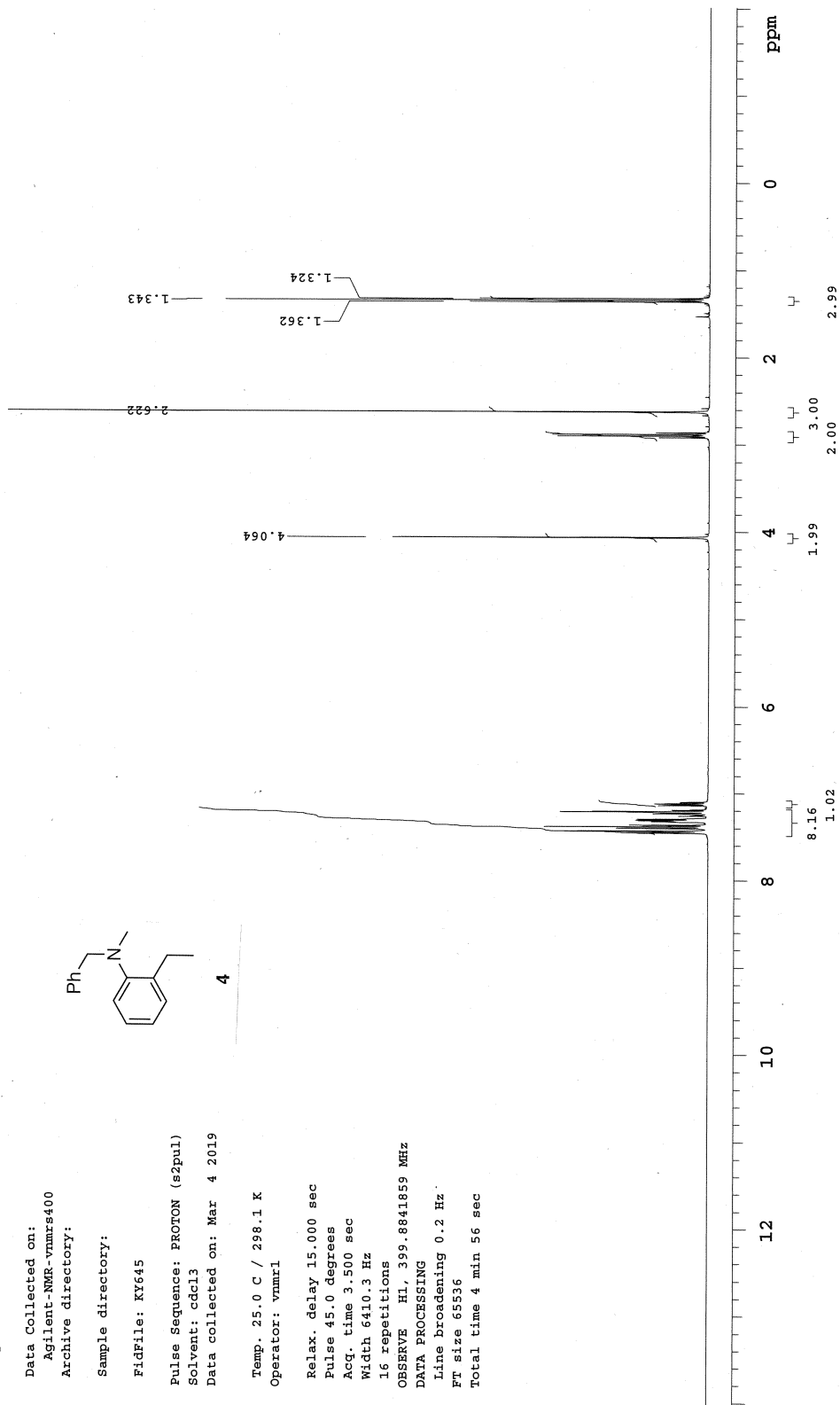
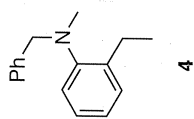


Figure S46. ¹H NMR Spectrum of **4** (400 MHz, CDCl₃)

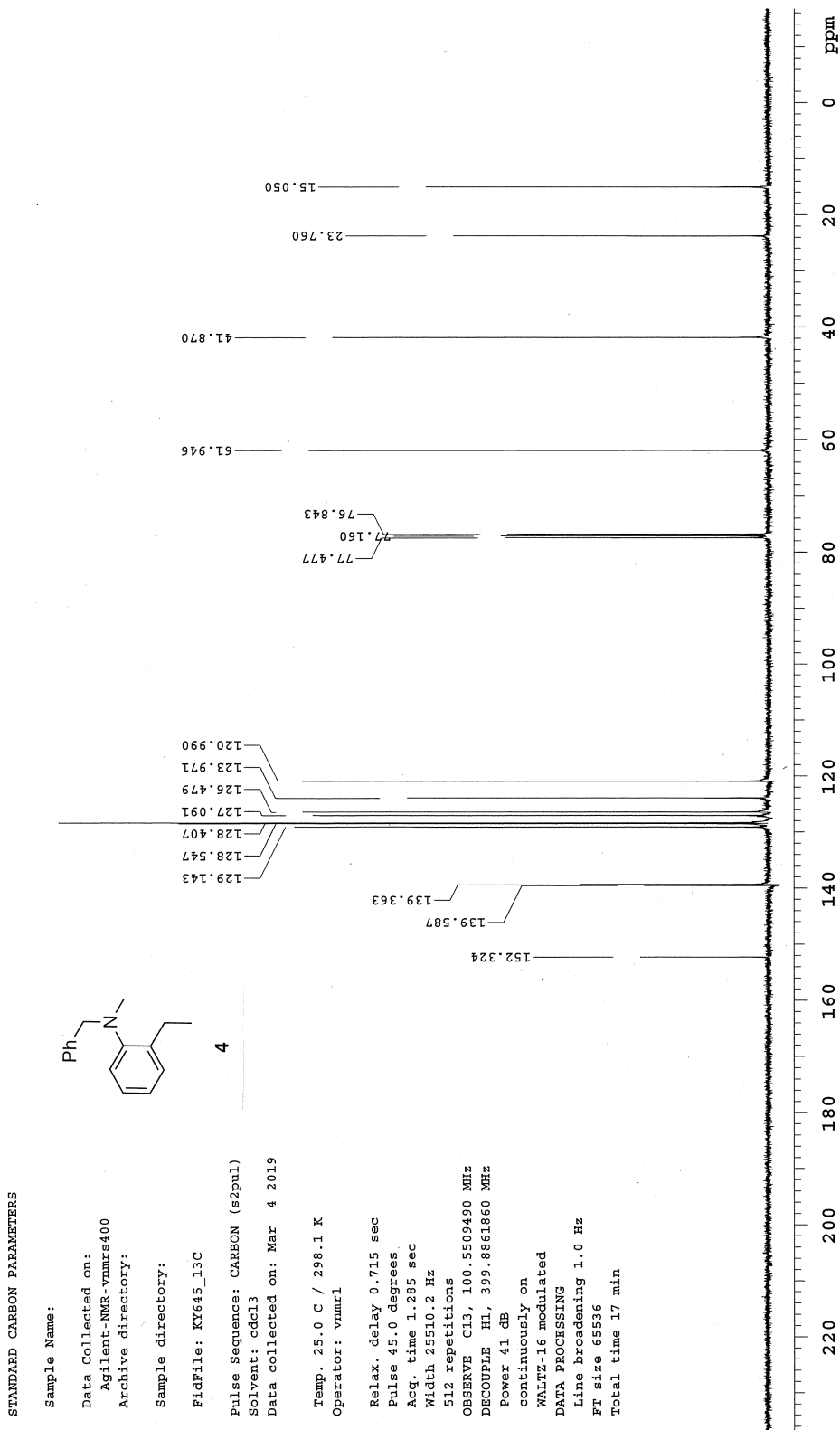


Figure S47. ^{13}C NMR Spectrum of 4 (101 MHz, CDCl_3)

STANDARD PROTON PARAMETERS

Sample Name:
 KY641
 Data Collected on:
 Agilent-NMR-vnmrs400
 Archive directory:
 Sample directory:
 FidFile: KY641
 Pulse Sequence: PROTON (s2pul)
 Solvent: cdcl3
 Data collected on: Mar 2 2019
 Temp. 25.0 C / 298.1 K
 Operator: vnmr1
 Relax. delay 15.000 sec
 Pulse 45.0 degrees
 Acq. time 3.500 sec
 Width 6410.3 Hz
 16 repetitions
 OBSERVE H1, 399.8841859 MHz
 DATA PROCESSING
 Line broadening 0.2 Hz
 FT size 65536
 Total time 4 min 56 sec

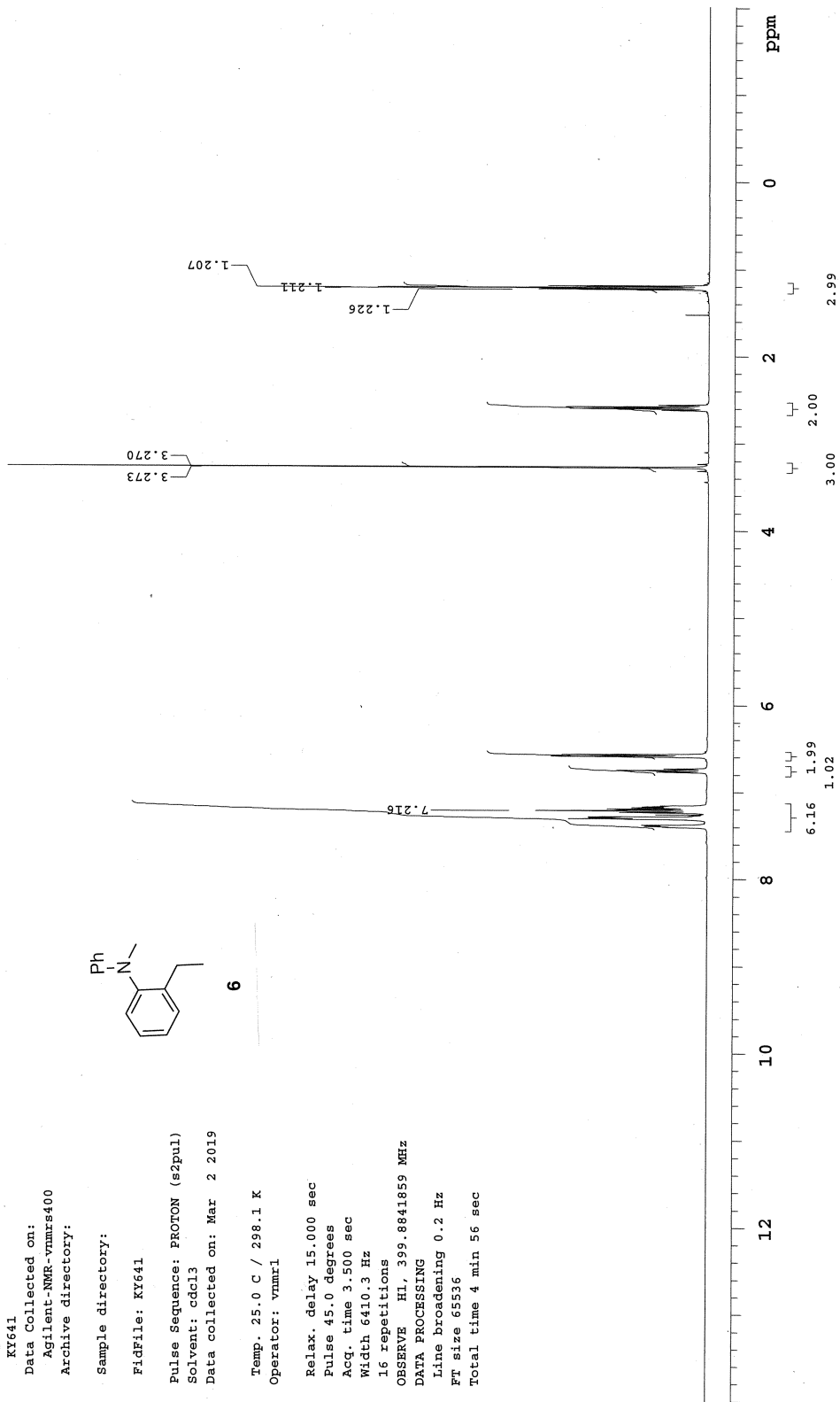
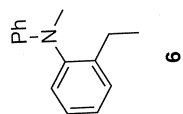


Figure S48. ¹H NMR Spectrum of 6 (400 MHz, CDCl₃)

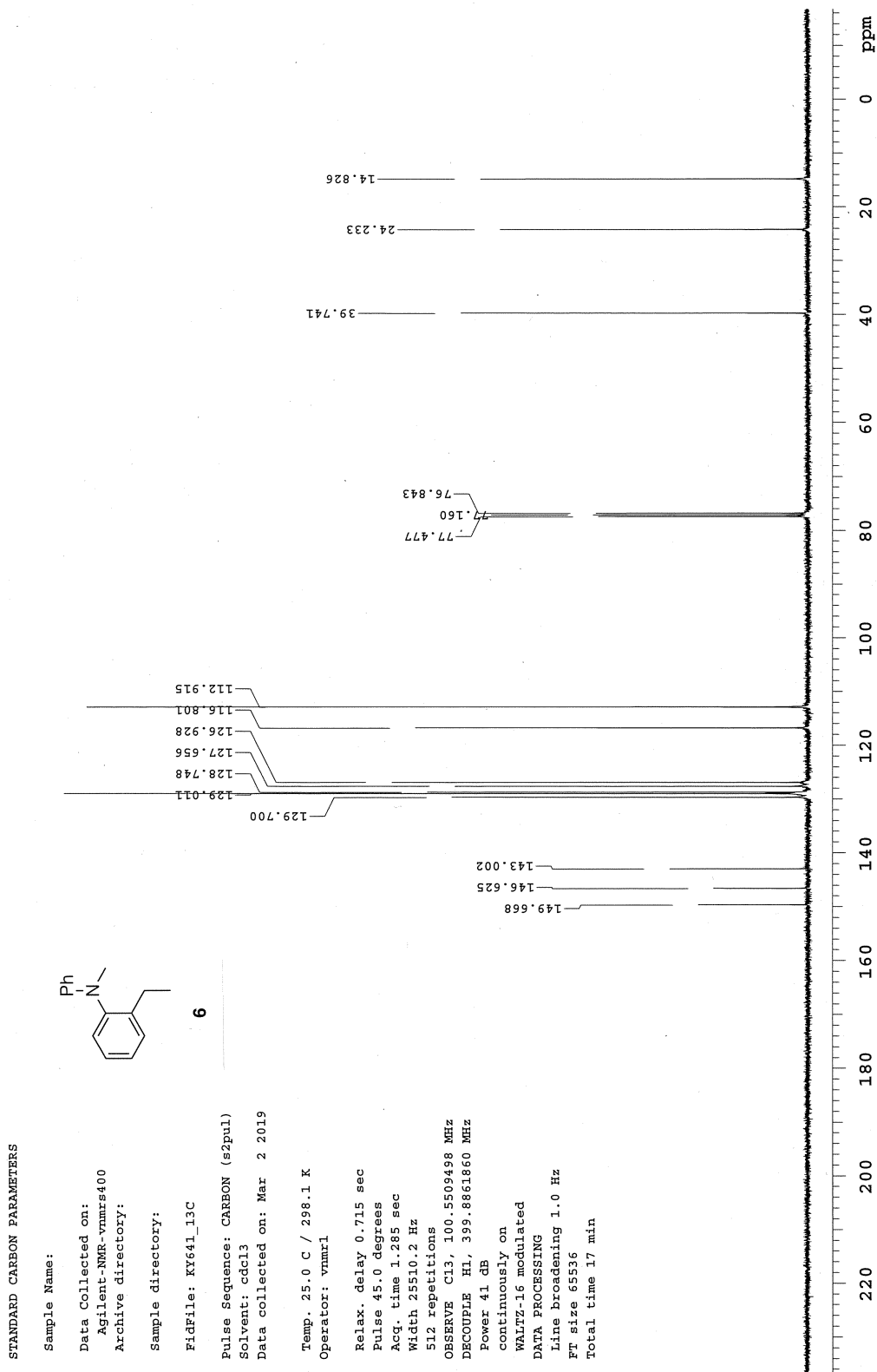
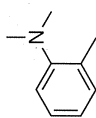


Figure S49. ^{13}C NMR Spectrum of 6 (101 MHz, CDCl_3)

STANDARD PROTON PARAMETERS

Sample Name: KY317
 Data Collected on: Agilent-NMR-vmnr400
 Archive directory:
 Sample directory:
 Fidfile: KY317
 Pulse Sequence: PROTON (szpul)
 Solvent: cdcl3
 Data collected on: Apr 19 2018
 Temp. 25.0 C / 298.1 K
 Operator: vmnr1
 Relax. delay 1.500 sec
 Pulse 45.0 degrees
 Acq. time 3.500 sec
 Width 6410.3 Hz
 16 repetitions
 OBSERVE H1, 399.8841866 MHz
 DATA PROCESSING
 Line broadening 0.2 Hz
 FT size 65536
 Total time 1 min 20 sec



8

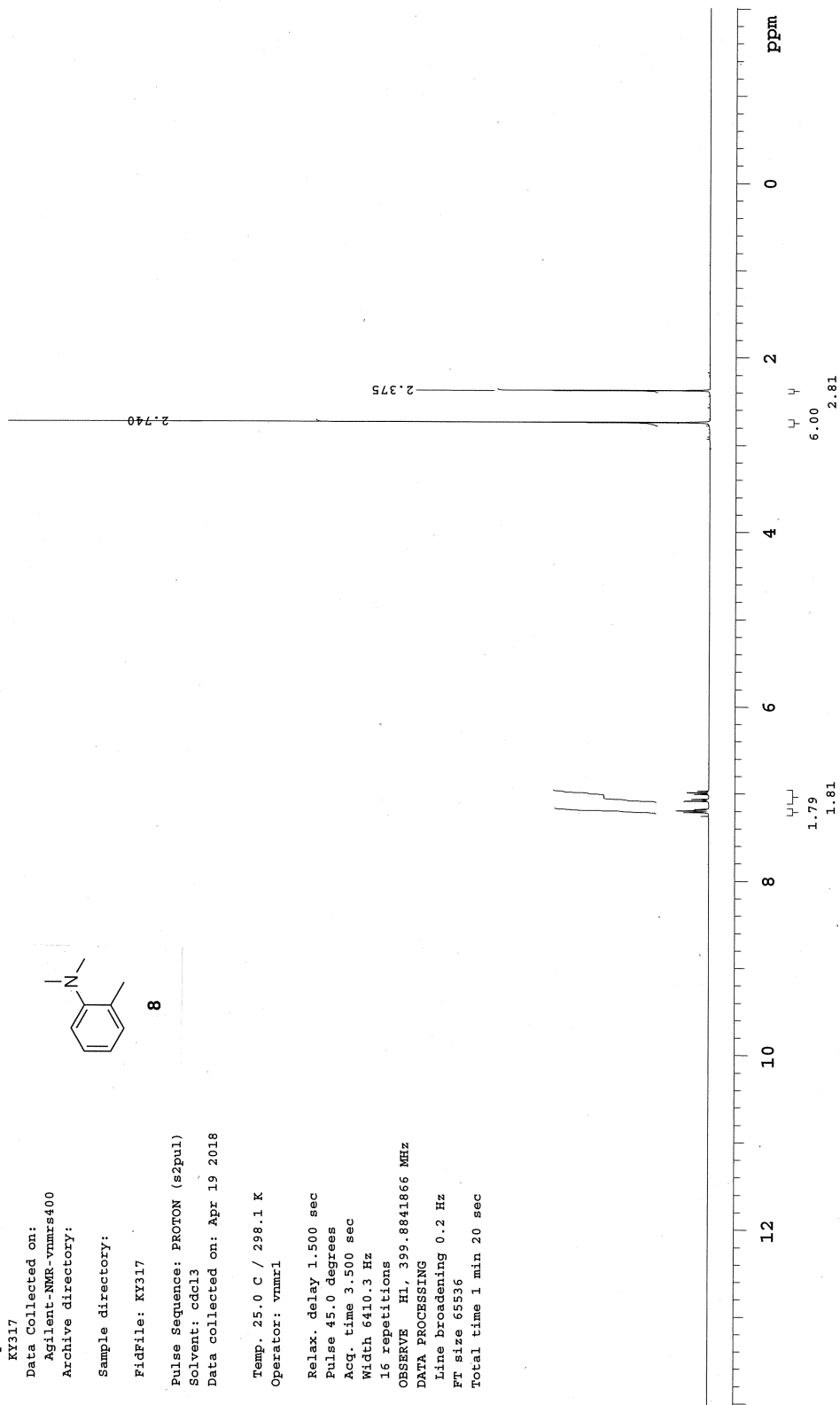


Figure S50. ¹H NMR Spectrum of **8** (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:

Data Collected on:
Agilent-NMR-vmrns400
Archive directory:

Sample directory:

File: KY317_13C

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3
Data collected on: Jul 6 2019

Temp. 25.0 C / 298.1 K
Operator: vmr1

Relax. delay 0.715 sec

Pulse 45.0 degrees

Acq. time 1.285 sec

Width 25510.2 Hz

512 repetitions

OBSERVE C13, 100.5509506 MHz

DECOUPLE H1, 399.8861860 MHz

Power 41 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 17 min

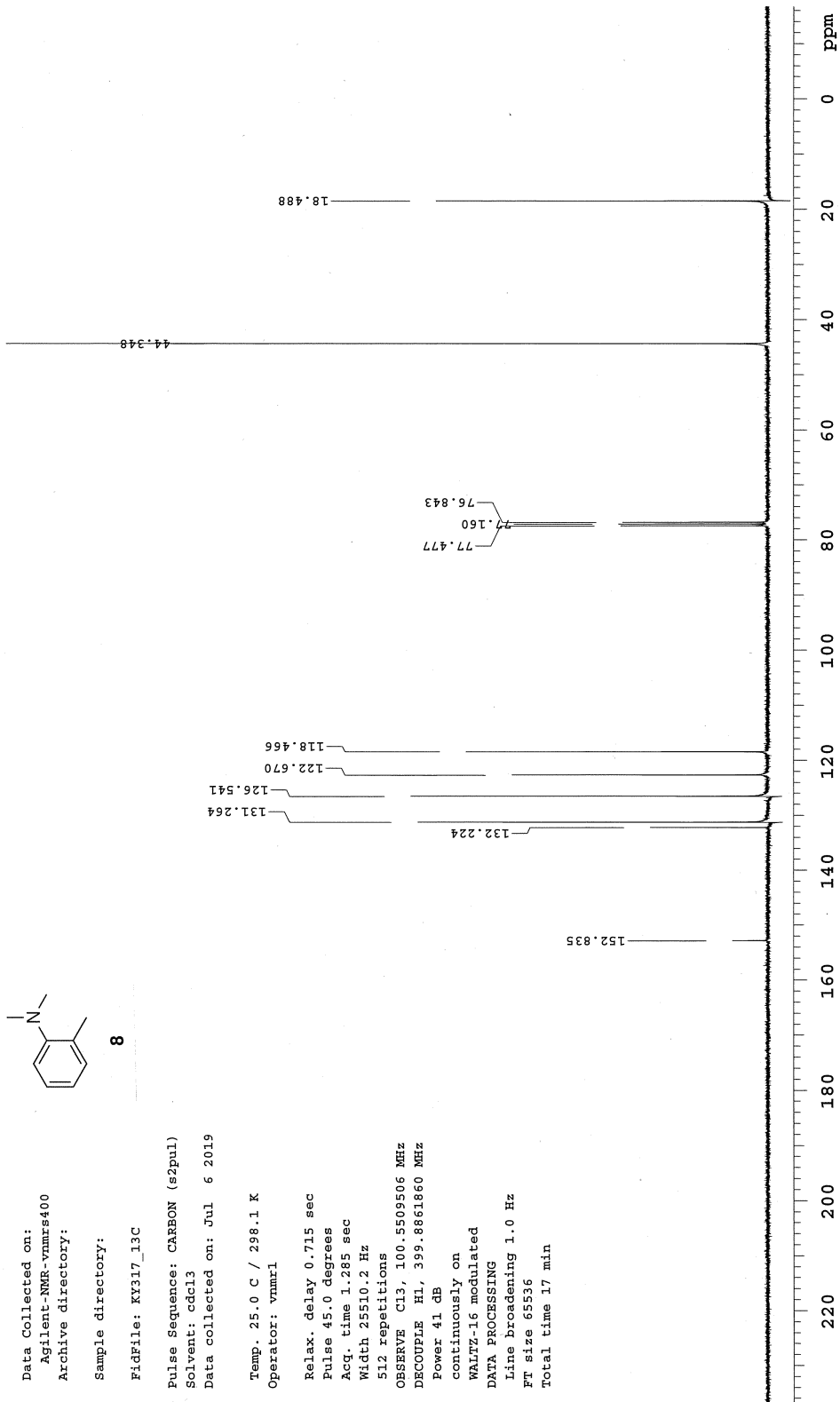


Figure S51. ¹³C NMR Spectrum of **8** (101 MHz, CDCl₃)

STANDARD PROTON PARAMETERS

Sample Name:
 Data Collected on:
 Agilent-NMR-vmms400
 Archive directory:
 Sample directory:
 Fidfile: KY680
 Pulse Sequence: PROTON (s2pul)
 Solvent: cdcl3
 Data collected on: Apr 11 2019
 Temp. 25.0 C / 298.1 K
 Operator: vmml
 Relax. delay 15.000 sec
 Pulse 45.0 degrees
 Acq. time 3.500 sec
 Width 6410.3 Hz
 16 repetitions
 OBSERVE H1, 399.8841866 MHz
 DATA PROCESSING
 Line broadening 0.2 Hz
 FT size 65536
 Total time 4 min 56 sec

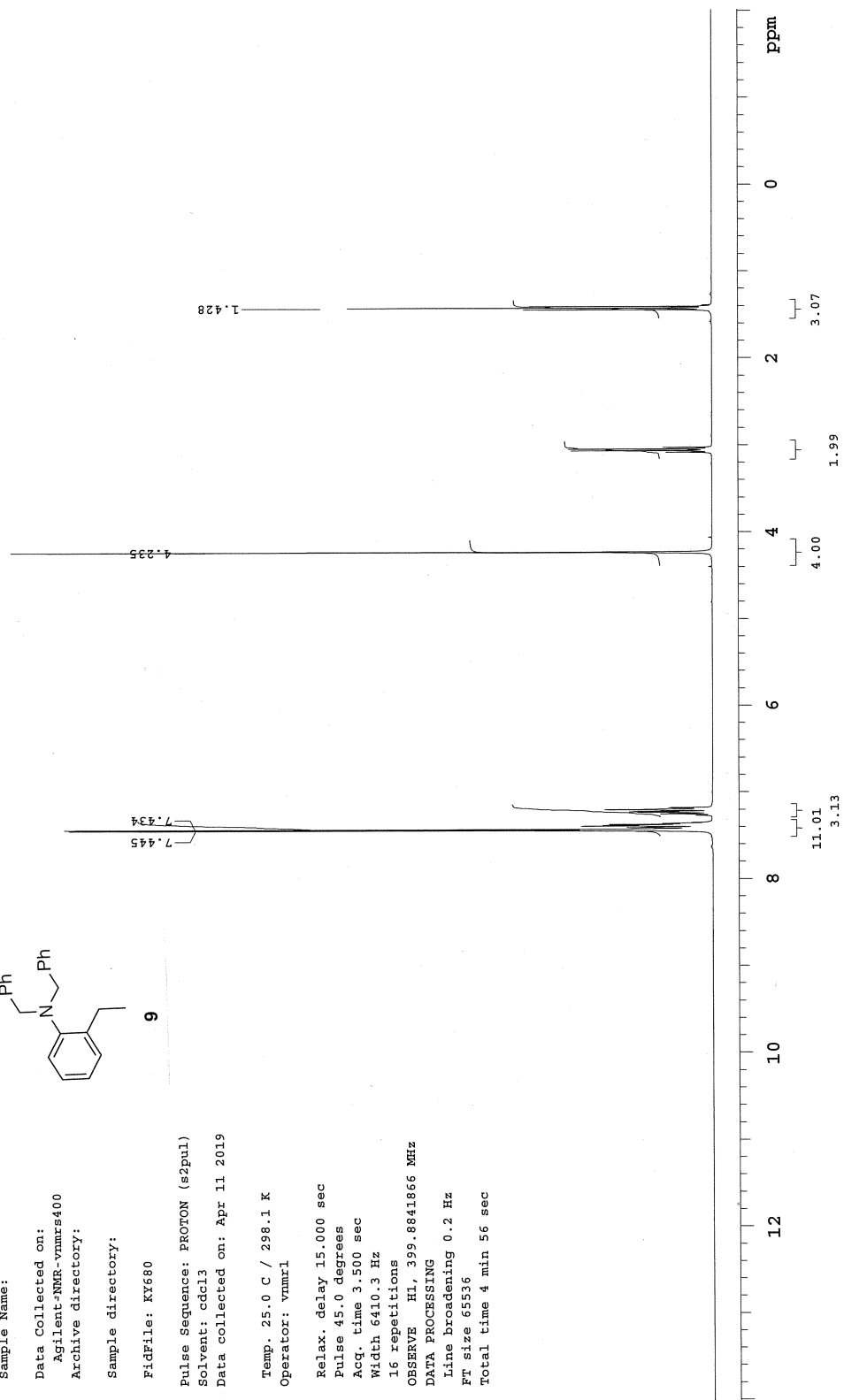
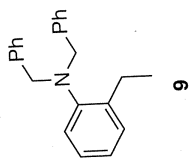


Figure S52. ¹H NMR Spectrum of **9** (400 MHz, CDCl₃)

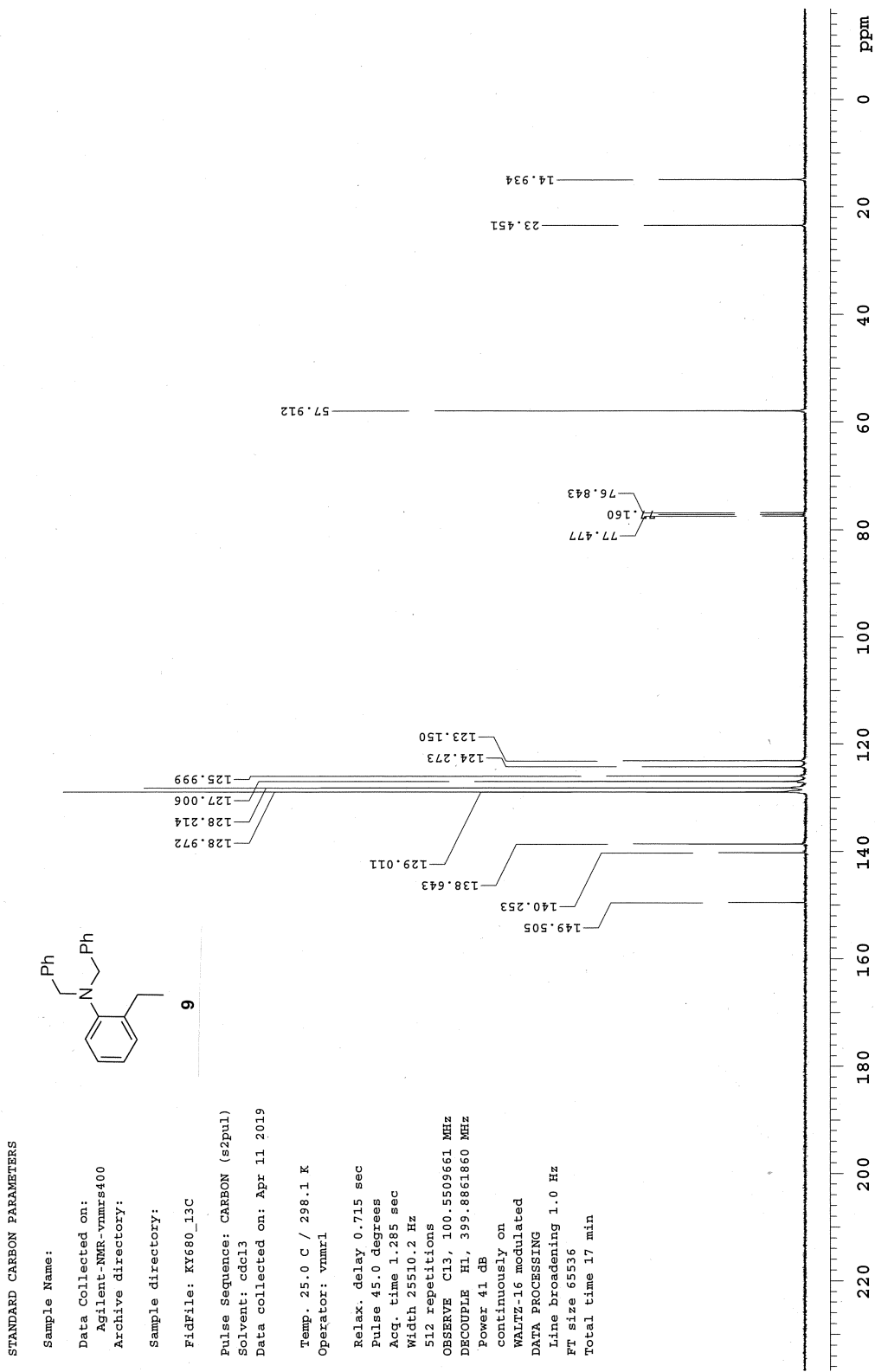
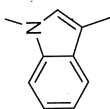


Figure S53. ^{13}C NMR Spectrum of 9 (101 MHz, CDCl_3)

STANDARD PROTON PARAMETERS

Sample Name:
 KV491
 Data Collected on:
 Agilent-NMR-vmms400
 Archive directory:
 Sample directory:
 FidFile: KV491
 Pulse Sequence: PROTON (s2pul)
 Solvent: cdcl3
 Data collected on: Oct 18 2018
 Operator: vmnr1
 Relax. delay 15.000 sec
 Pulse 45.0 degrees
 Acq. time 3.500 sec
 Width 6410.3 Hz
 16 repetitions
 OBSERVE HL, 399.8841861 MHz
 DATA PROCESSING
 Line broadening 0.2 Hz
 FT size 65536
 Total time 4 min 56 sec



2a

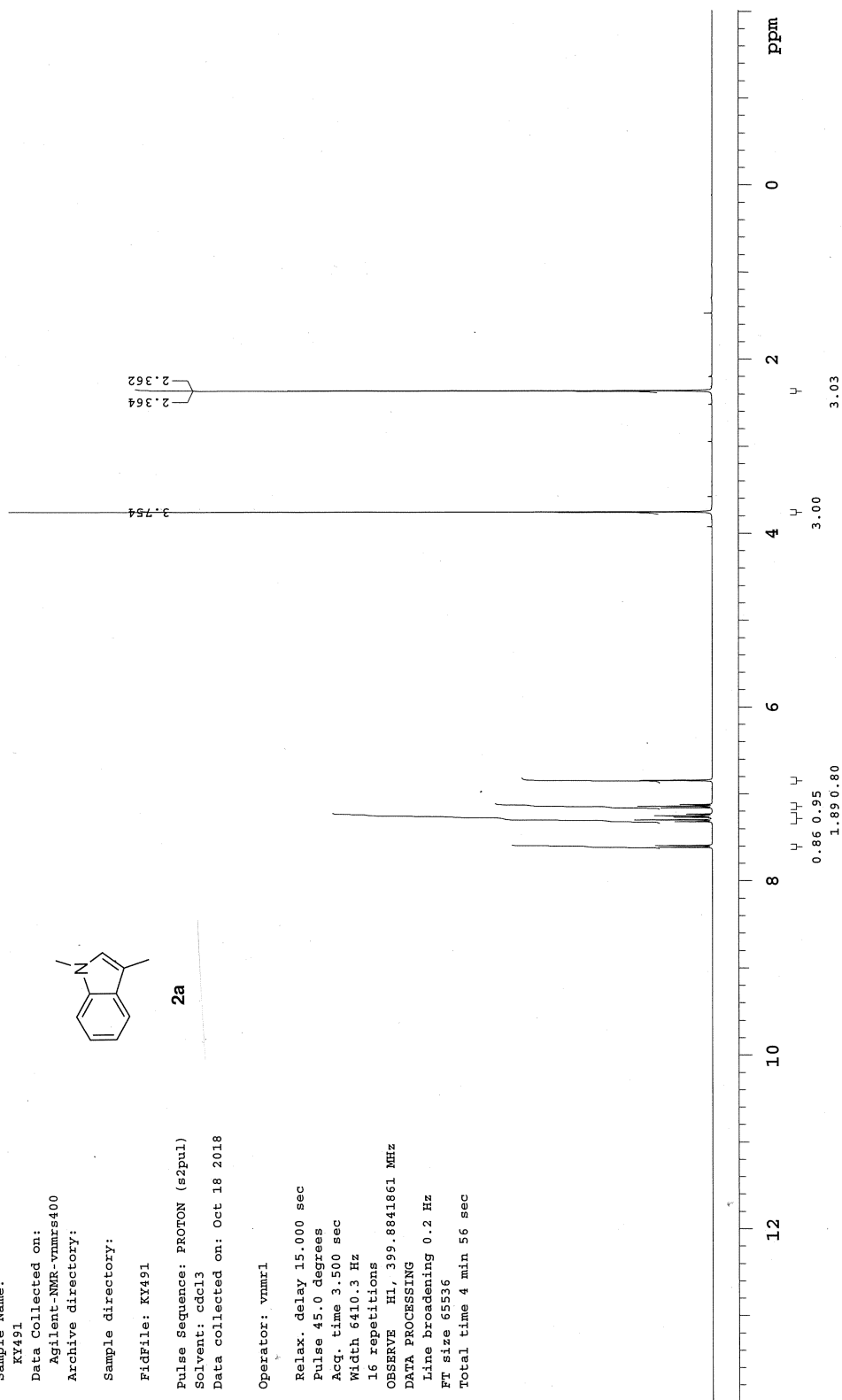
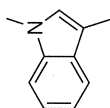


Figure S54. ¹H NMR Spectrum of **2a** (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:
 Data Collected on:
 Agilent-NMR-vmr400
 Archive directory:
 Sample directory:
 FidFile: KY758_13C
 Pulse Sequence: CARBON (s2pul)
 Solvent: cdcl3
 Data collected on: Jun 13 2019

Operator: vmr1
 Relax. delay 0.715 sec
 Pulse 45.0 degrees
 Acq. time 1.285 sec
 Width 25510.2 Hz
 512 repetitions
 OBSERVE C13, 100.5509498 MHz
 DECOUPLE H1, 399.8861860 MHz
 Power 41 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 17 min



2a

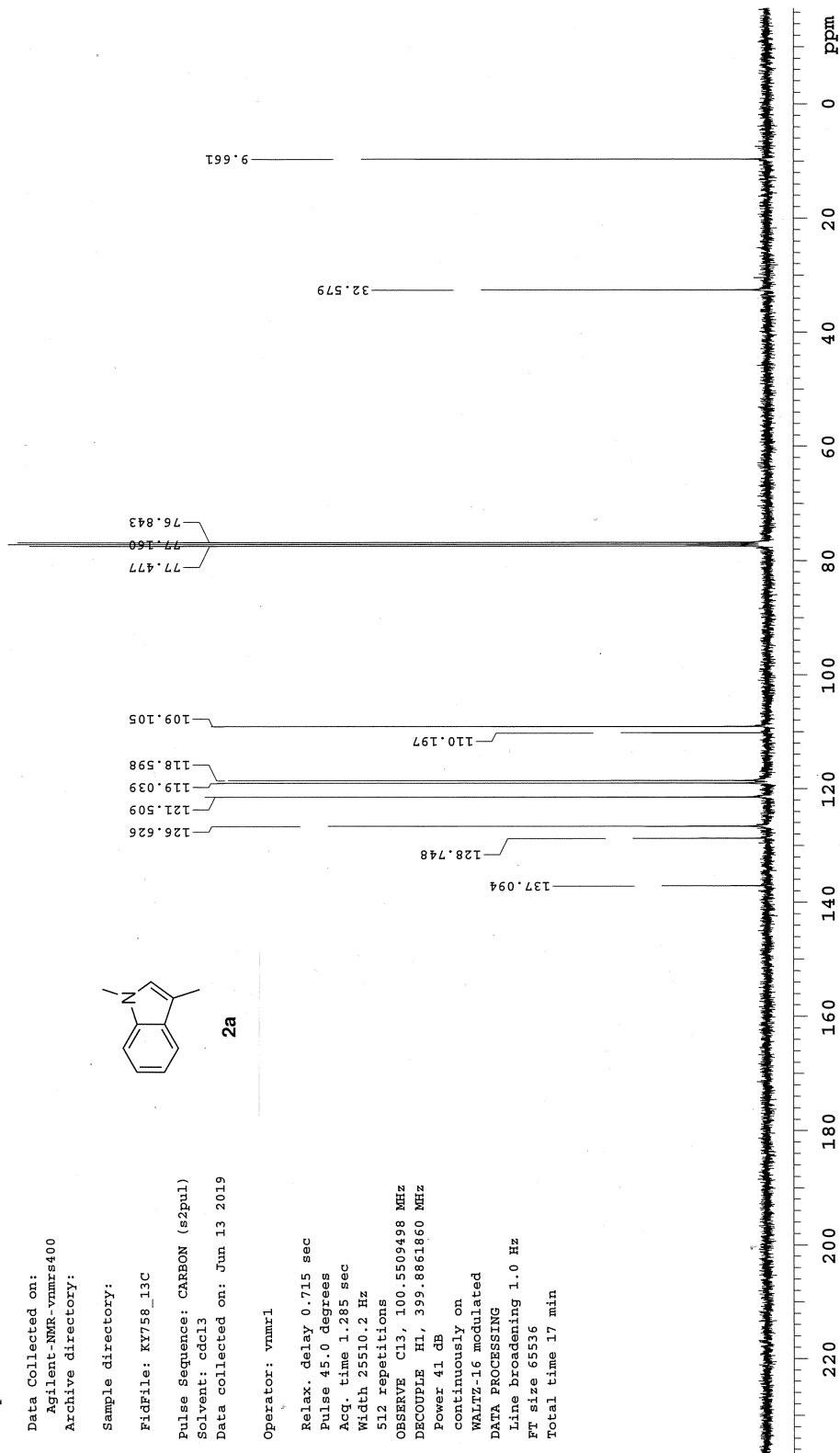


Figure S55. ¹³C NMR Spectrum of 2a (101 MHz, CDCl₃)

STANDARD PROTON PARAMETERS

Sample Name:

Data Collected on:

Agilent-NMR-vmr400

Archive directory:

Sample directory:

File: KY657

Pulse Sequence: PROTON (s2pul)

Solvent: cdcl3

Data collected on: Mar 8 2019

Temp. 25.0 C / 298.1 K

Operator: vmr1

Relax. delay 15.000 sec

Pulse 45.0 degrees

Acq. time 3.500 sec

Width 6410.3 Hz

16 repetitions

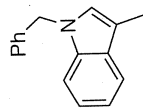
OBSERVE H1, 399.8841859 MHz

DATA PROCESSING

Line broadening 0.2 Hz

Ft size 65536

Total time 4 min 56 sec



5

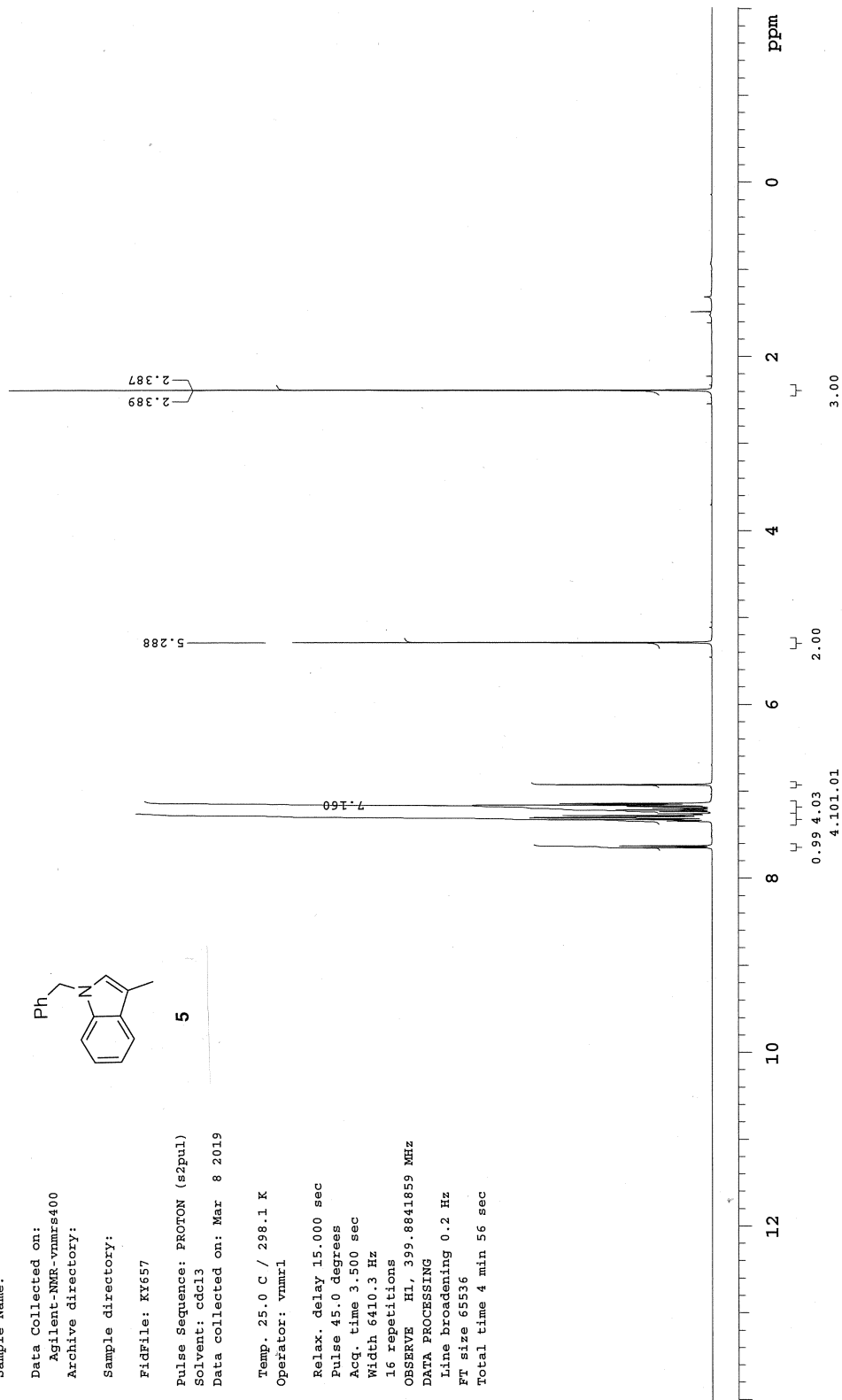


Figure S56. ¹H NMR Spectrum of **5** (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:

Data Collected on:

Agilent-NMR-vmrs400

Archive directory:

Sample directory:

File: KY657_13C

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Mar 8 2019

Temp. 25.0 C / 298.1 K

Operator: vmr1

Relax. delay 0.715 sec

Pulse 45.0 degrees

Acq. time 1.285 sec

Width 25510.2 Hz

512 repetitions

OBSERVE C13, 100.5509490 MHz

DECOUPLE H1, 399.8861860 MHz

Power 41 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 17 min

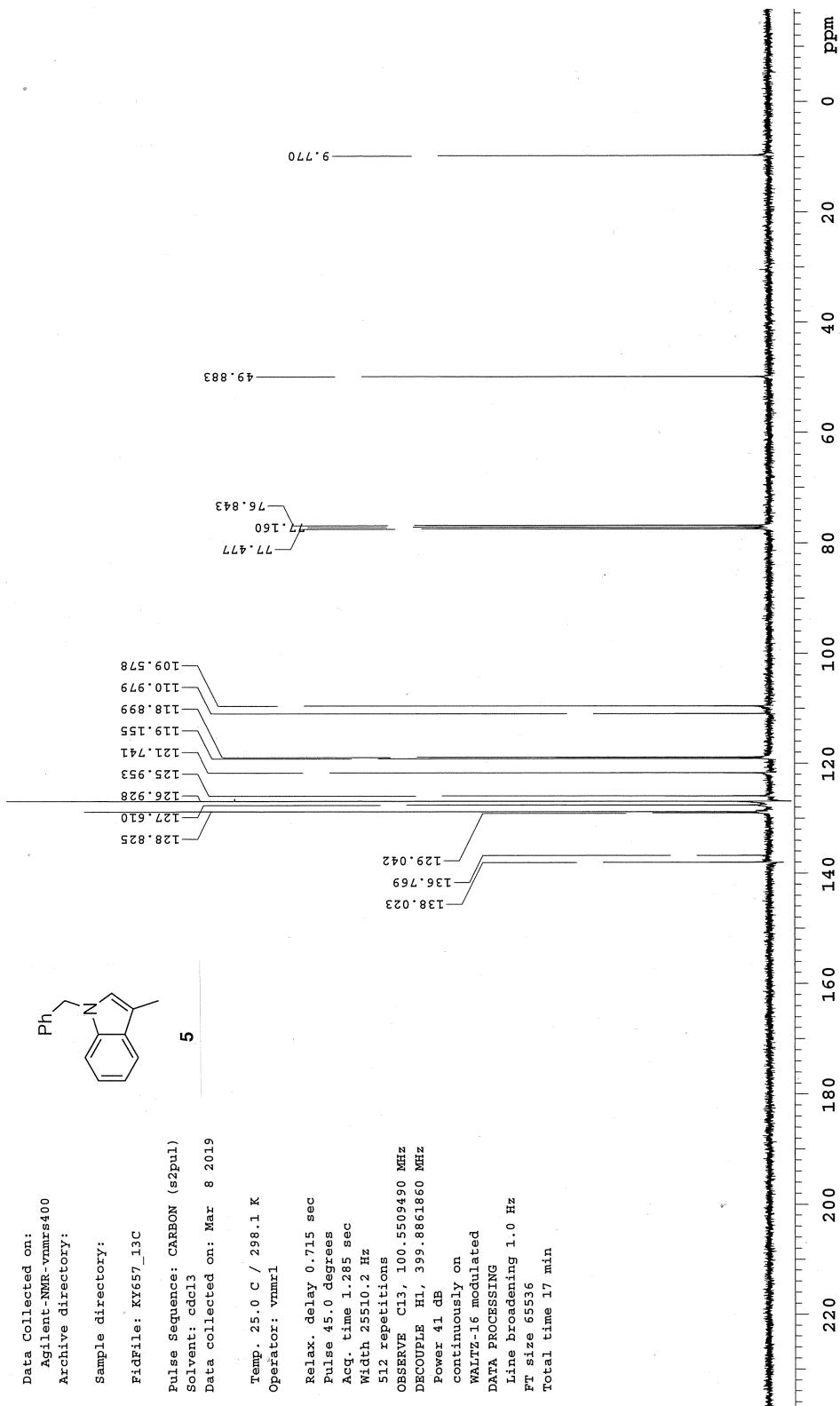


Figure S57. ¹³C NMR Spectrum of 5 (101 MHz, CDCl₃)

STANDARD PROTON PARAMETERS

Sample Name:
Data Collected on:
Agilent-NMR-vmms400
Archive directory:
Sample directory:
FidFile: KY691
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr 17 2019
Operator: vmmr1
Relax. delay 15.000 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6410.3 Hz
16 repetitions
OBSERVE H1, 399.8841871 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 4 min 56 sec

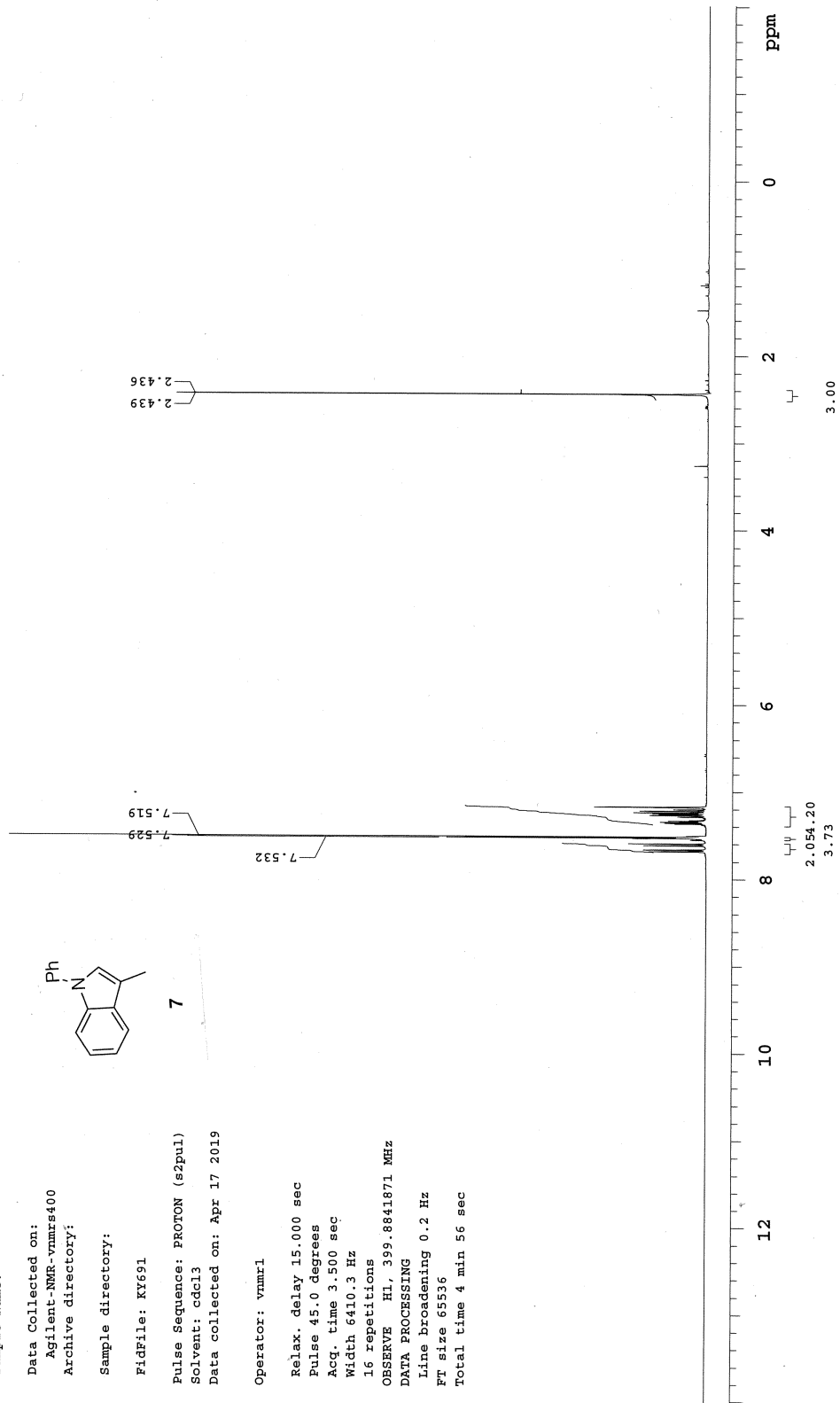
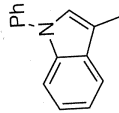


Figure S58. ¹H NMR Spectrum of 7 (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:
 Data Collected on:
 Agilent-NMR-vmrs400
 Archive directory:
 Sample directory:
 FIDfile: KY691_13C
 Pulse Sequence: CARBON (s2pul)
 Solvent: cdcl3
 Data collected on: Apr 17 2019
 Operator: vmr1
 Relax. delay 0.715 sec
 Pulse 45.0 degrees
 Acq. time 1.285 sec
 Width 25510.2 Hz
 512 repetitions
 OBSERVE C13, 100.5509490 MHz
 DECOUPLE H1, 399.8861860 MHz
 Power 41 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 17 min

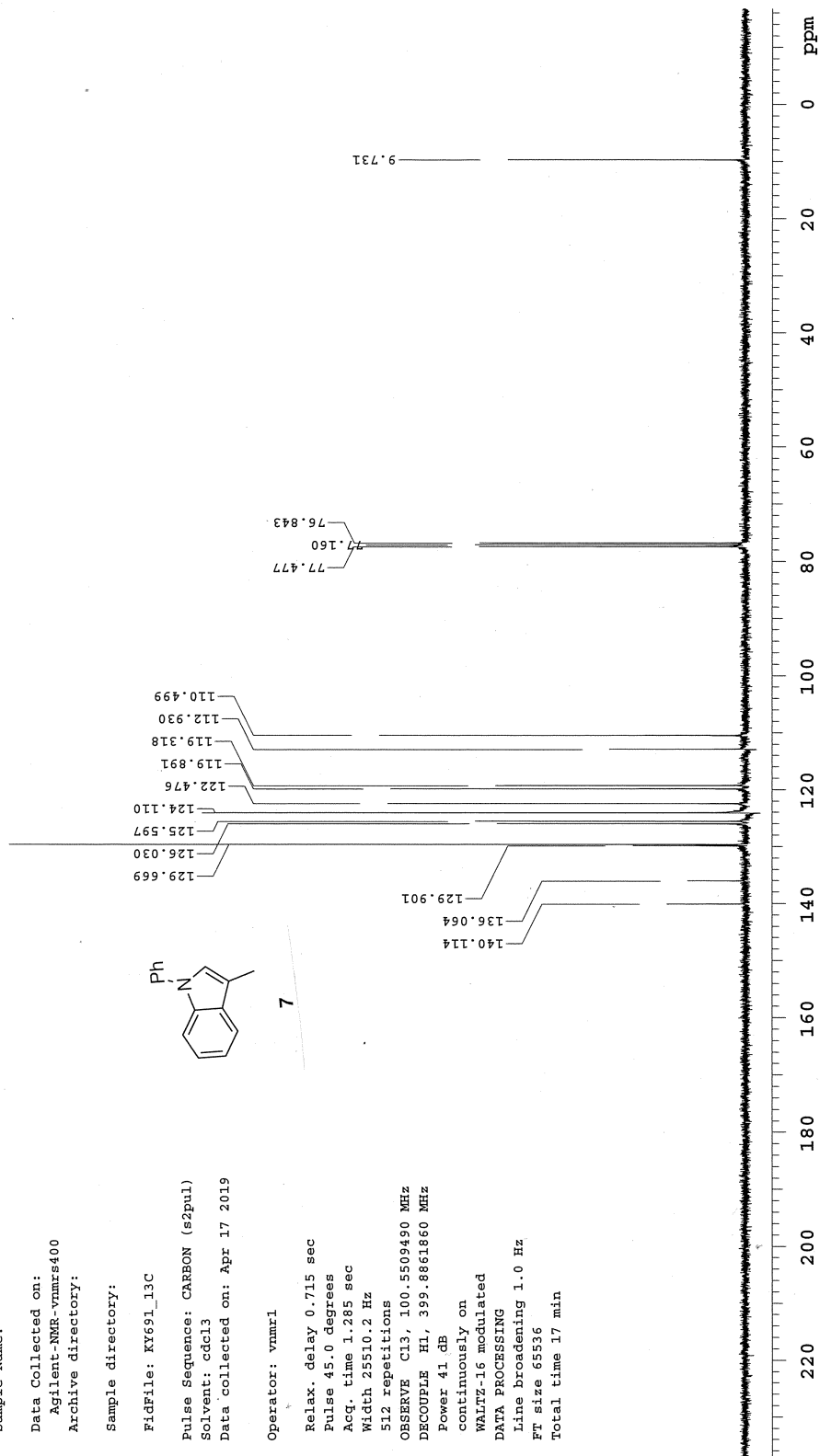
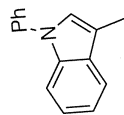
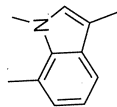


Figure S59. ¹³C NMR Spectrum of 7 (101 MHz, CDCl₃)

STANDARD PROTON PARAMETERS

Sample Name:
 KY527
 Data Collected on:
 Agilent-NMR-vmnrs400
 Archive directory:
 Sample directory:
 File: KY527
 Pulse Sequence: PROTON (s2pul)
 Solvent: cdcl3
 Data collected on: Nov 18 2018
 Temp. 25.0 C / 298.1 K
 Operator: vnmr1
 Relax. delay 15.000 sec
 Pulse 45.0 degrees
 Acq. time 3.500 sec
 Width 6410.3 Hz
 16 repetitions
 OBSERVE HL, 399.8641861 MHz
 DATA PROCESSING
 Line broadening 0.2 Hz
 FT size 65536
 Total time 4 min 56 sec



2b

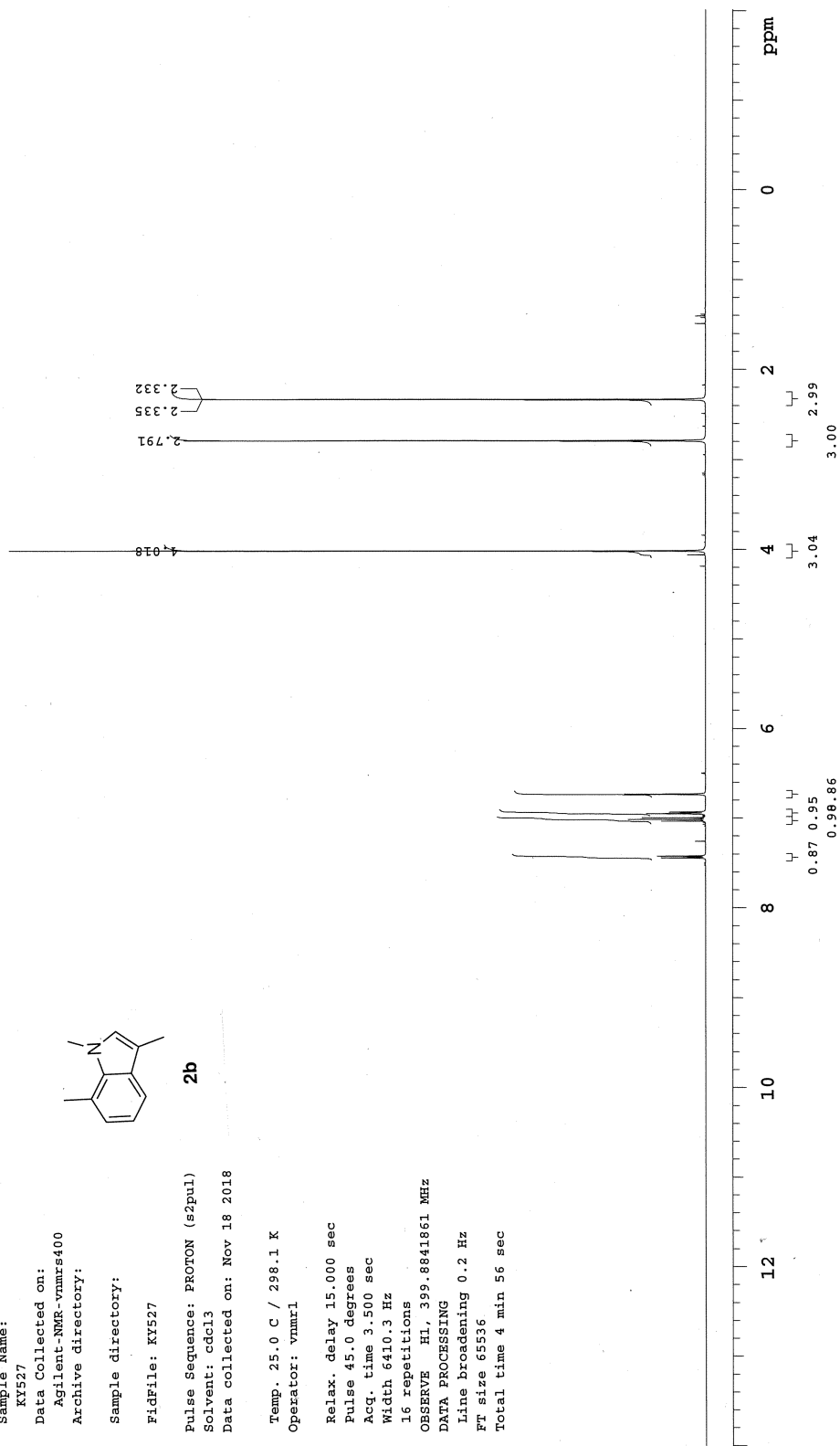


Figure S60. ¹H NMR Spectrum of **2b** (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:

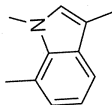
Data Collected on:
Agilent-NMR-vmms400
Archive directory:

Sample directory:

FIDfile: KY527_13C

Pulse Sequence: CARBON (s2pul)
Solvent: cdc13
Data collected on: Nov 18 2018

2b



Temp. 25.0 C / 298.1 K
Operator: vmml

Relax. delay 0.715 sec
Pulse 45.0 degrees
Acq. time 1.285 sec
Width 25510.2 Hz
512 repetitions

OBSERVE C13, 100.5509482 MHz
DECOUPLE H1, 399.8861860 MHz

Power 41 dB
continuously on

WALTZ-16 modulated
DATA PROCESSING

Line broadening 1.0 Hz
FT size 65536
Total time 17 min

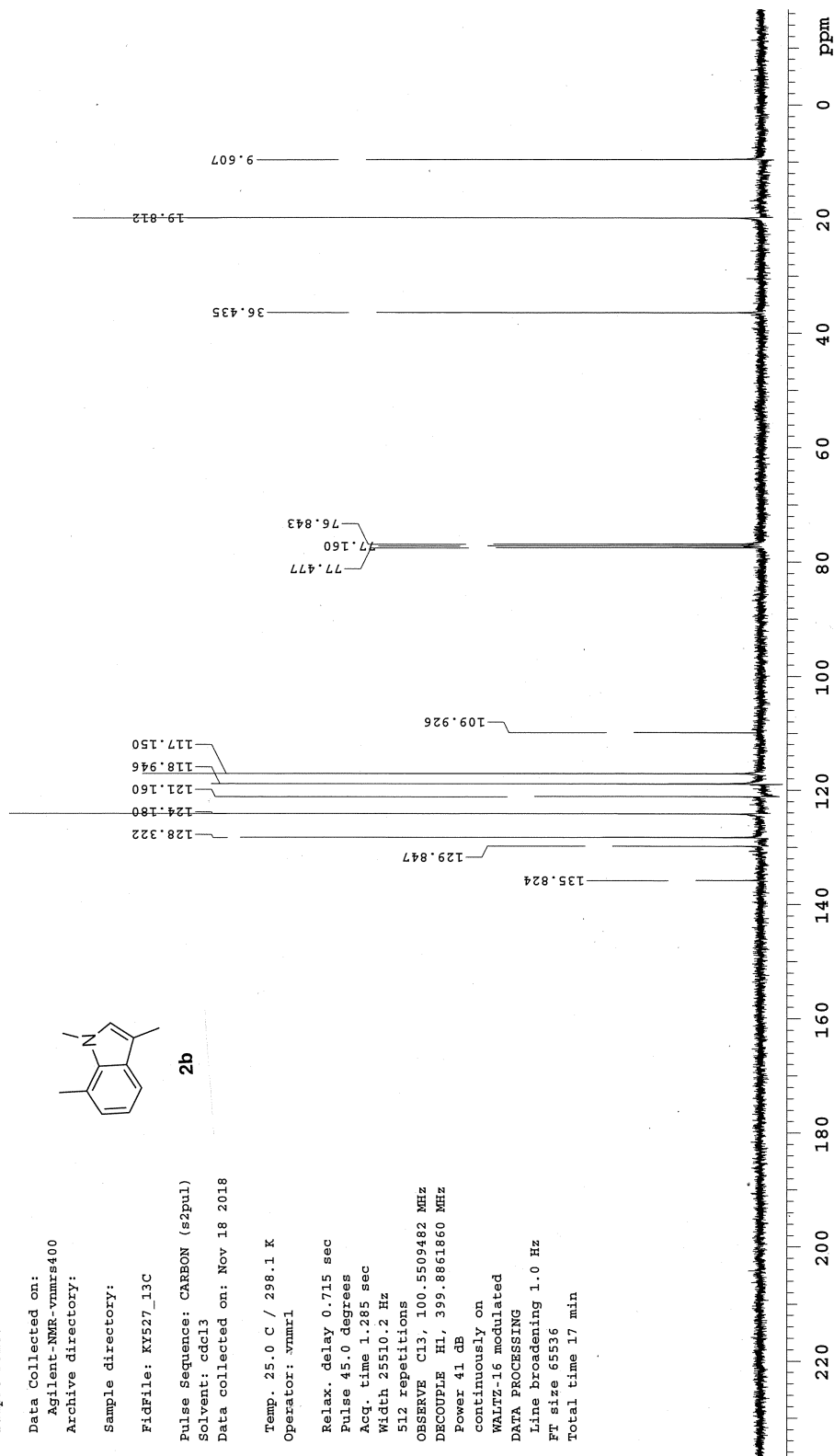


Figure S61. ¹³C NMR Spectrum of **2b** (101 MHz, CDCl₃)

STANDARD PROTON PARAMETERS

Sample Name:

Data Collected on:
Agilent-NMR-vmrns400
Archive directory:

Sample directory:

File: KY522

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Nov 14 2018

Temp. 25.0 C / 298.1 K
Operator: vmrnl

Relax. delay 15.000 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6410.3 Hz
16 repetitions

OBSERVE HL, 399.8841859 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 4 min 56 sec

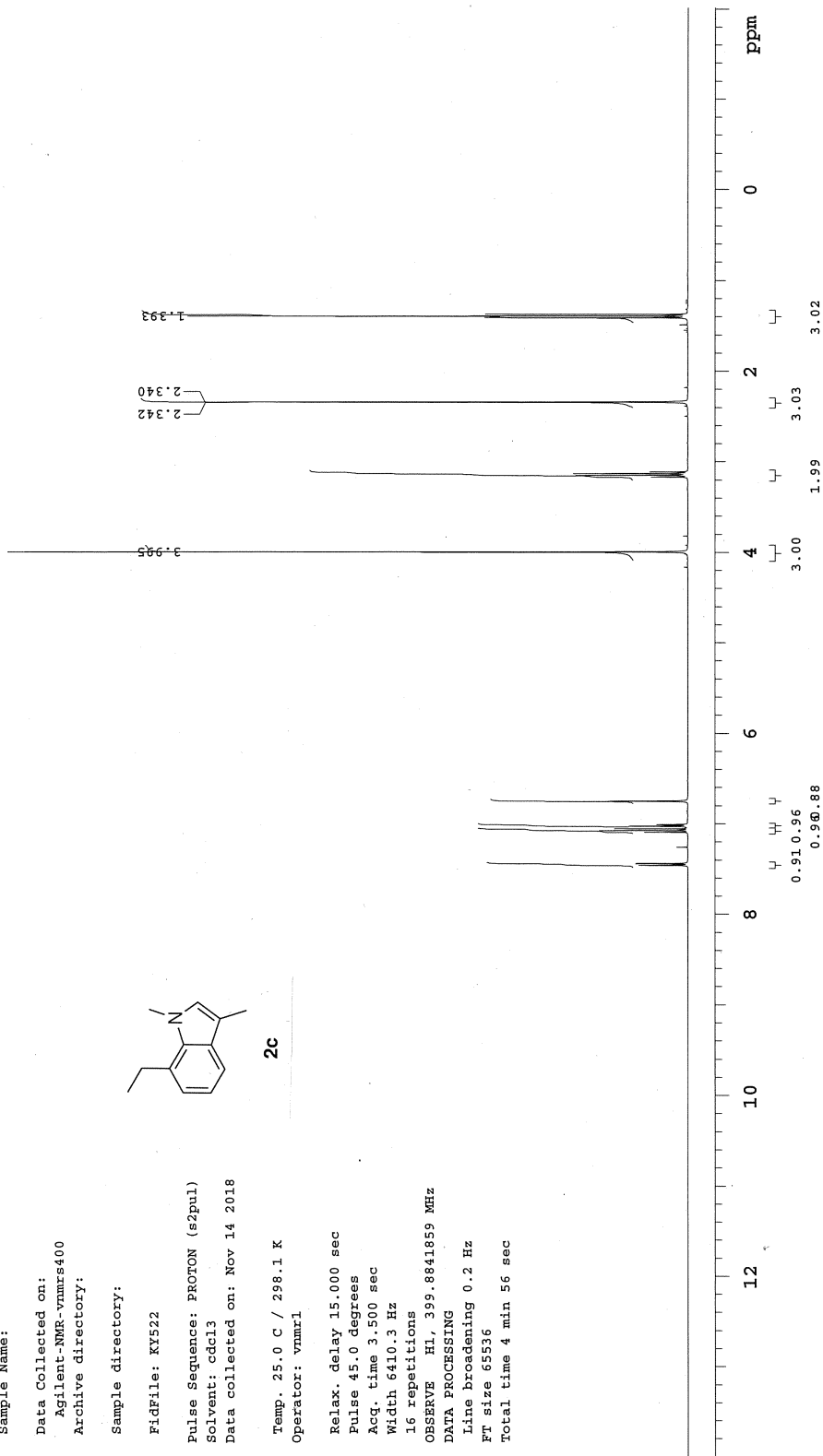
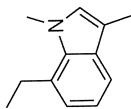


Figure S62. ¹H NMR Spectrum of **2c** (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:
 Data Collected on:
 Agilent-NMR-vmr400
 Archive directory:
 Sample directory:
 FIDFile: KY522_13C
 Pulse Sequence: CARBON (s2Pul)
 Solvent: cdcl3
 Data collected on: Nov 14 2018
 Temp. 25.0 C / 298.1 K
 Operator: vmr1
 Relax. delay 0.715 sec
 Pulse 45.0 degrees
 Acq. time 1.285 sec
 Width 25510.2 Hz
 512 repetitions
 OBSERVE C13, 100.5509475 MHZ
 DECOUPLE H1, 399.8861860 MHZ
 Power 41 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 17 min



2c

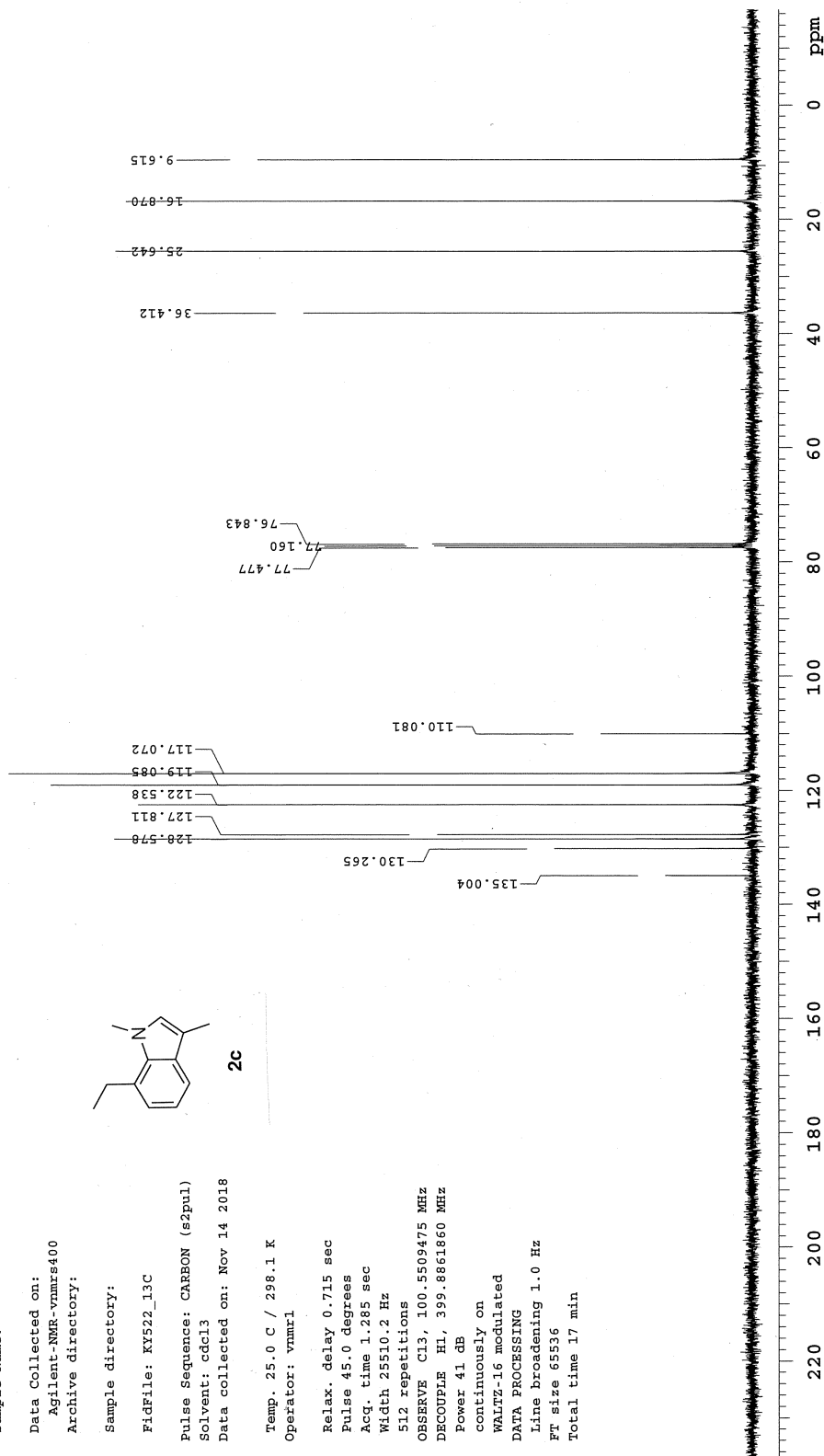


Figure S63. ¹³C NMR Spectrum of 2c (101 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:

Data Collected on:
Agilent-NMR-vmrs400
Archive directory:

Sample directory:

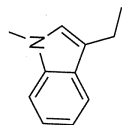
FidFile: KY531_13C

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Nov 22 2018

Temp. 25.0 C / 298.1 K
Operator: vnmr1

Relax. delay 0.715 sec
Pulse 45.0 degrees
Acq. time 1.285 sec
Width 25510.2 Hz
512 repetitions
OBSERVE C13, 100.5509467 MHz
DECOUPLE H1, 399.8861860 MHz

Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 17 min



2d

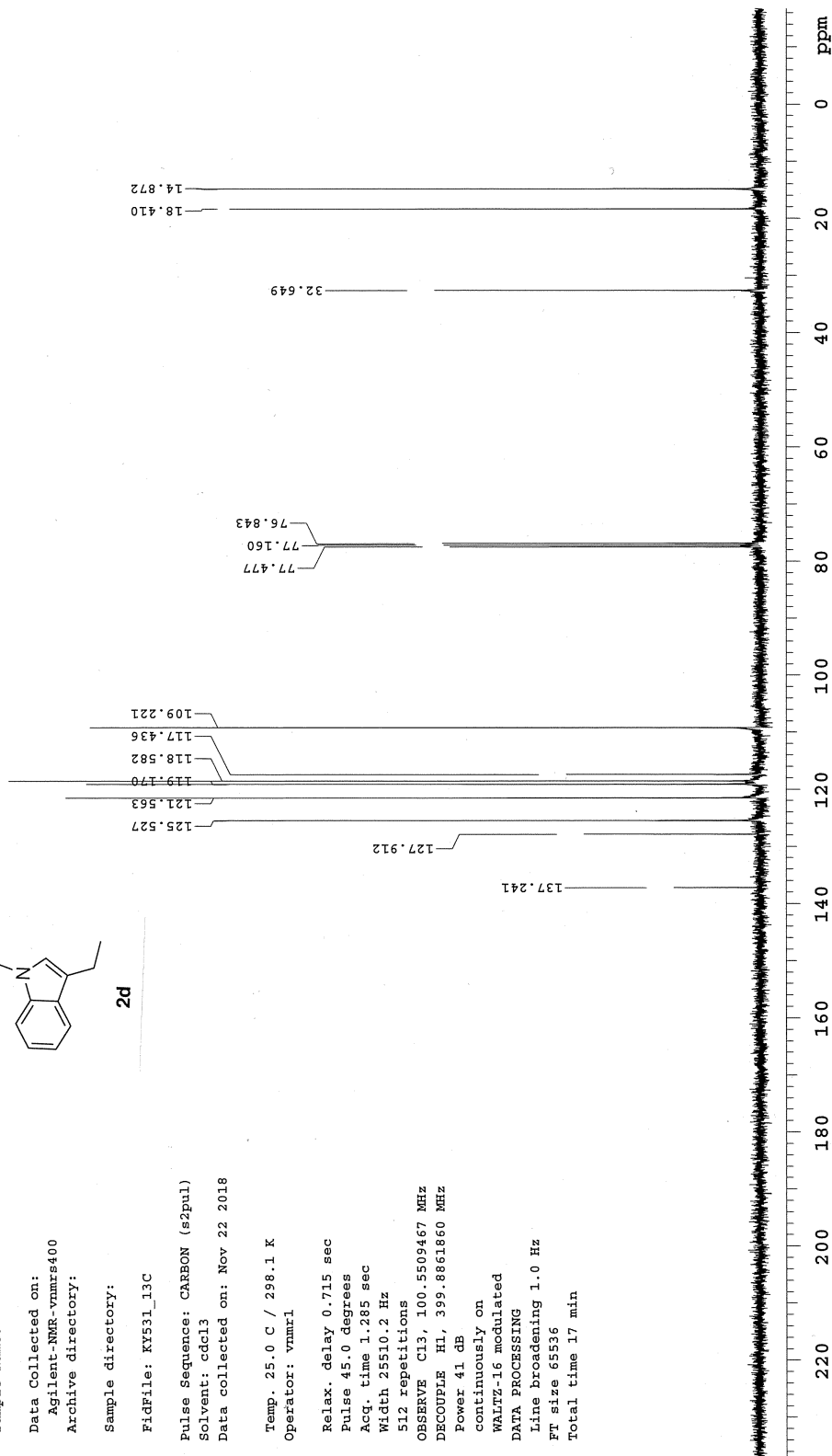
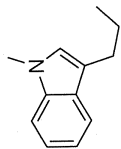


Figure S65. ¹³C NMR Spectrum of 2d (101 MHz, CDCl₃)

STANDARD PROTON PARAMETERS

Sample Name:
 Data Collected on:
 Agilent-NMR-vmrns400
 Archive directory:
 Sample directory:
 FidFile: KY731
 Pulse Sequence: PROTON (szpul)
 Solvent: cdcl3
 Data collected on: May 19 2019
 Operator: vmrml
 Relax. delay 15.000 sec
 Pulse 45.0 degrees
 Acq. time 3.500 sec
 Width 6410.3 Hz
 16 repetitions
 OBSERVE H1, 399.8841859 MHz
 DATA PROCESSING
 Line broadening 0.2 Hz
 FT size 65536
 Total time 4 min 56 sec



2e

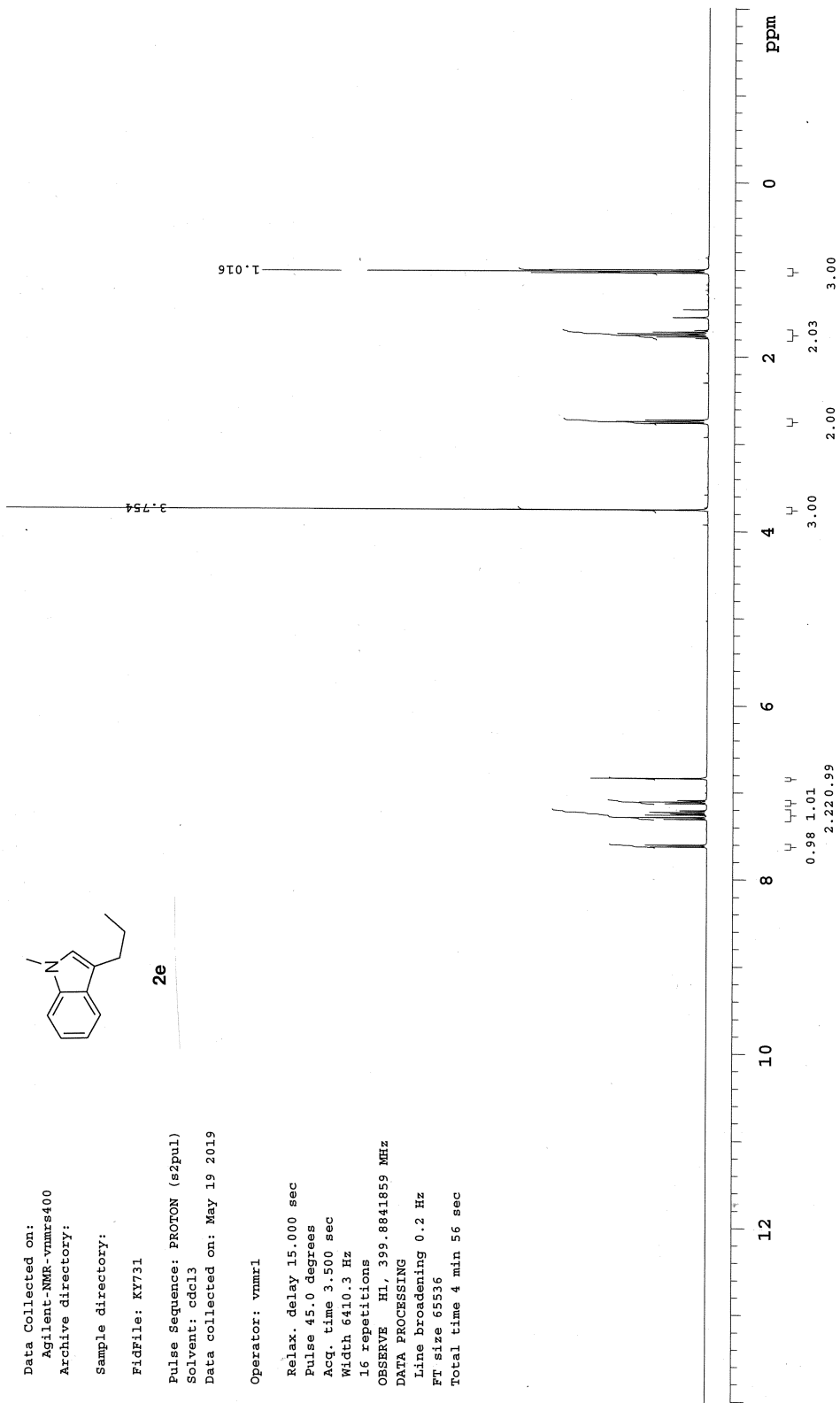
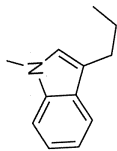


Figure S66. ¹H NMR Spectrum of **2e** (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:
 Data Collected on:
 Agilent-NMR-vmrs400
 Archive directory:
 Sample directory:
 FIDFile: KY731_13C
 Pulse Sequence: CARBON (s2Pul)
 Solvent: cdcl3
 Data collected on: May 19 2019
 Operator: vmr1
 Relax. delay 0.715 sec
 Pulse 45.0 degrees
 Acq. time 1.285 sec
 Width 25510.2 Hz
 4096 repetitions
 OBSERVE C13, 100.5509459 MHZ
 DECOUPLE H1, 399.8861860 MHZ
 Power 41 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 2 hr, 16 min



2e

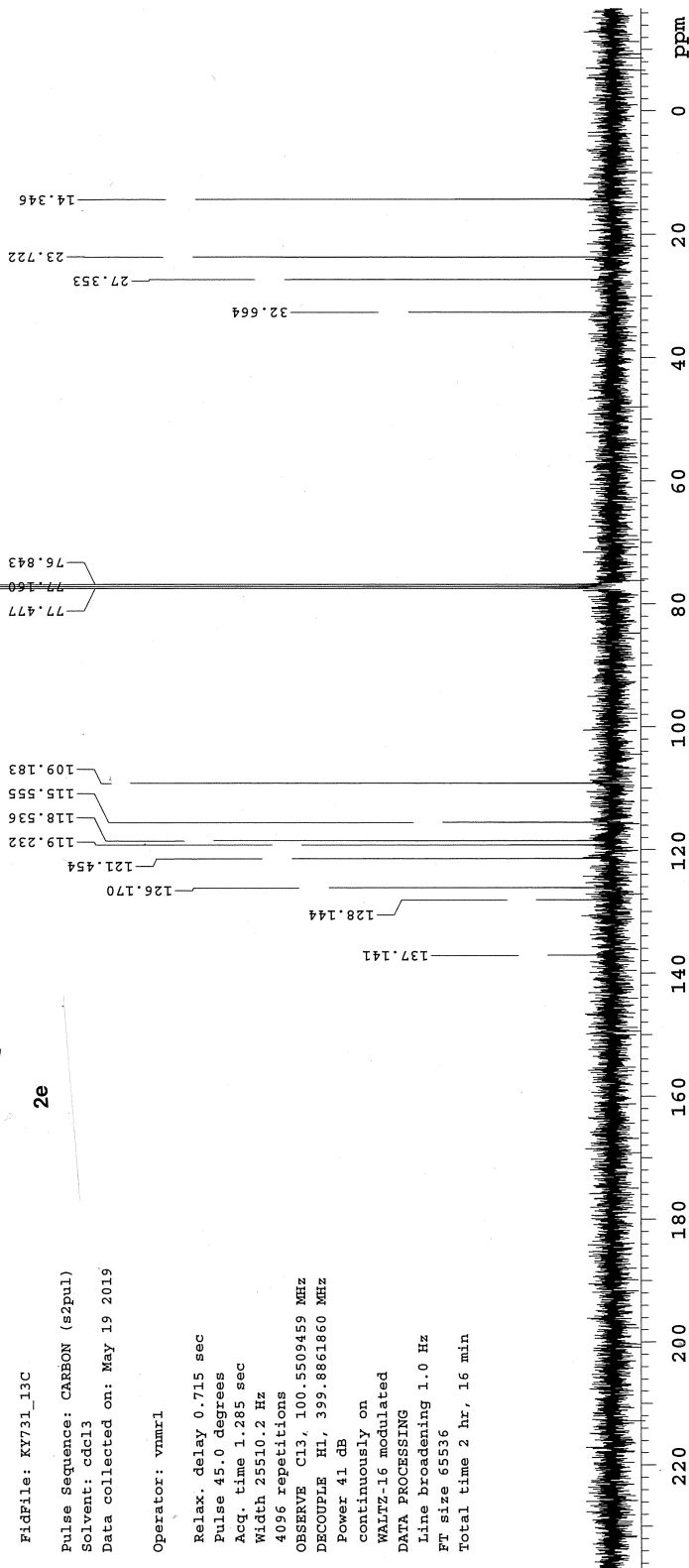


Figure S67. ^{13}C NMR Spectrum of 2e (101 MHz, CDCl_3)

STANDARD PROTON PARAMETERS

Sample Name:

Data Collected on:

Agilent-NMR-vmrns400

Archive directory:

Sample directory:

FidFile: KY621

Pulse Sequence: PROTON (s2pul)

Solvent: cdcl3

Data collected on: Feb 21 2019

Temp. 25.0 C / 296.1 K

Operator: vmr1

Relax. delay 15.000 sec

Pulse 45.0 degrees

Acq. time 3.500 sec

Width 6410.3 Hz

16 repetitions

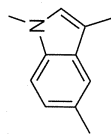
OBSERVE HL, 399.8841859 MHz

DATA PROCESSING

Line broadening 0.2 Hz

FT size 65536

Total time 4 min 56 sec



2f

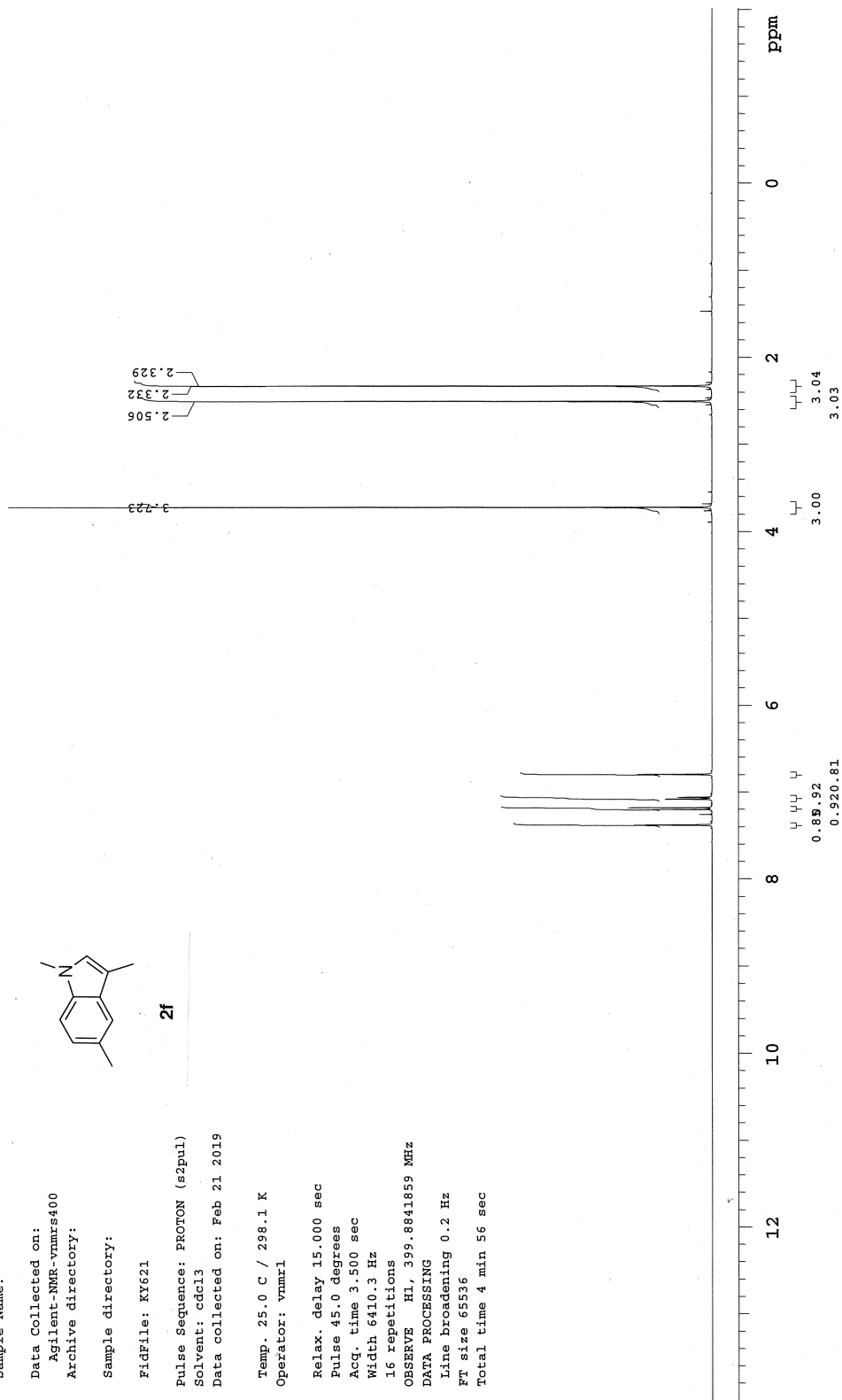


Figure S68. ¹H NMR Spectrum of **2f** (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:

Data Collected on:
Agilent-NMR-vmrns400

Archive directory:

Sample directory:

File: KY621_13C

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Feb 21 2019

Temp. 25.0 C / 298.1 K

Operator: vmr1

Relax. delay 0.715 sec

Pulse 45.0 degrees

Acq. time 1.285 sec

Width 25510.2 Hz

512 repetitions

OBSERVE C13, 100.5509451 MHZ

DECOUPLE H1, 399.8861860 MHZ

Power 41 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 17 min

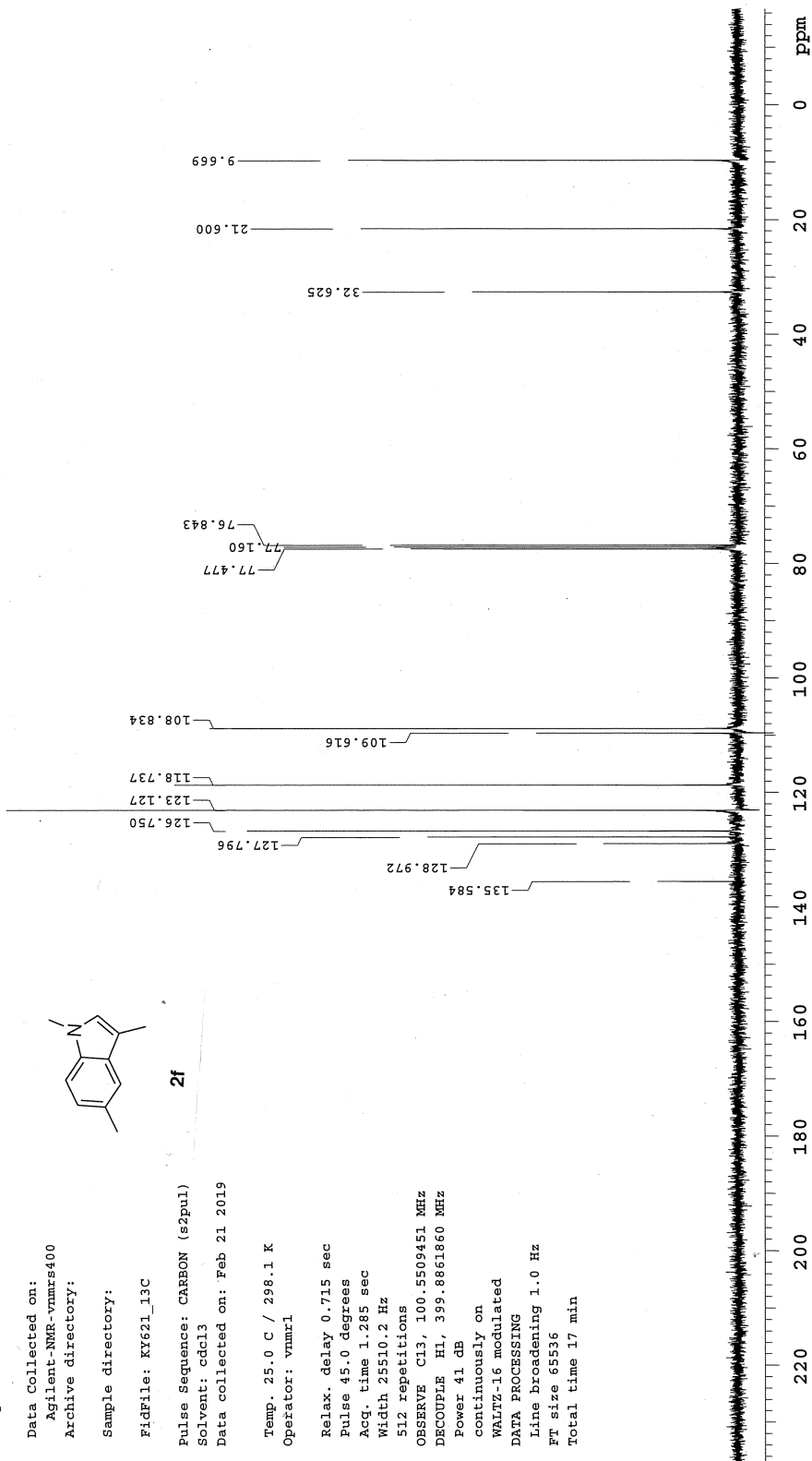


Figure S69. ¹³C NMR Spectrum of 2f (101 MHz, CDCl₃)

STANDARD PROTON PARAMETERS

Sample Name:

Data Collected on:
Agilent-NMR-vmr400
Archive directory:

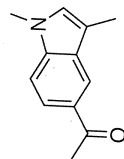
Sample directory:

File: KY761

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jun 14 2019

Operator: vmr1

Relax. delay 15.000 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6410.3 Hz
16 repetitions
OBSERVE HL, 399.8641876 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 4 min 56 sec



2g

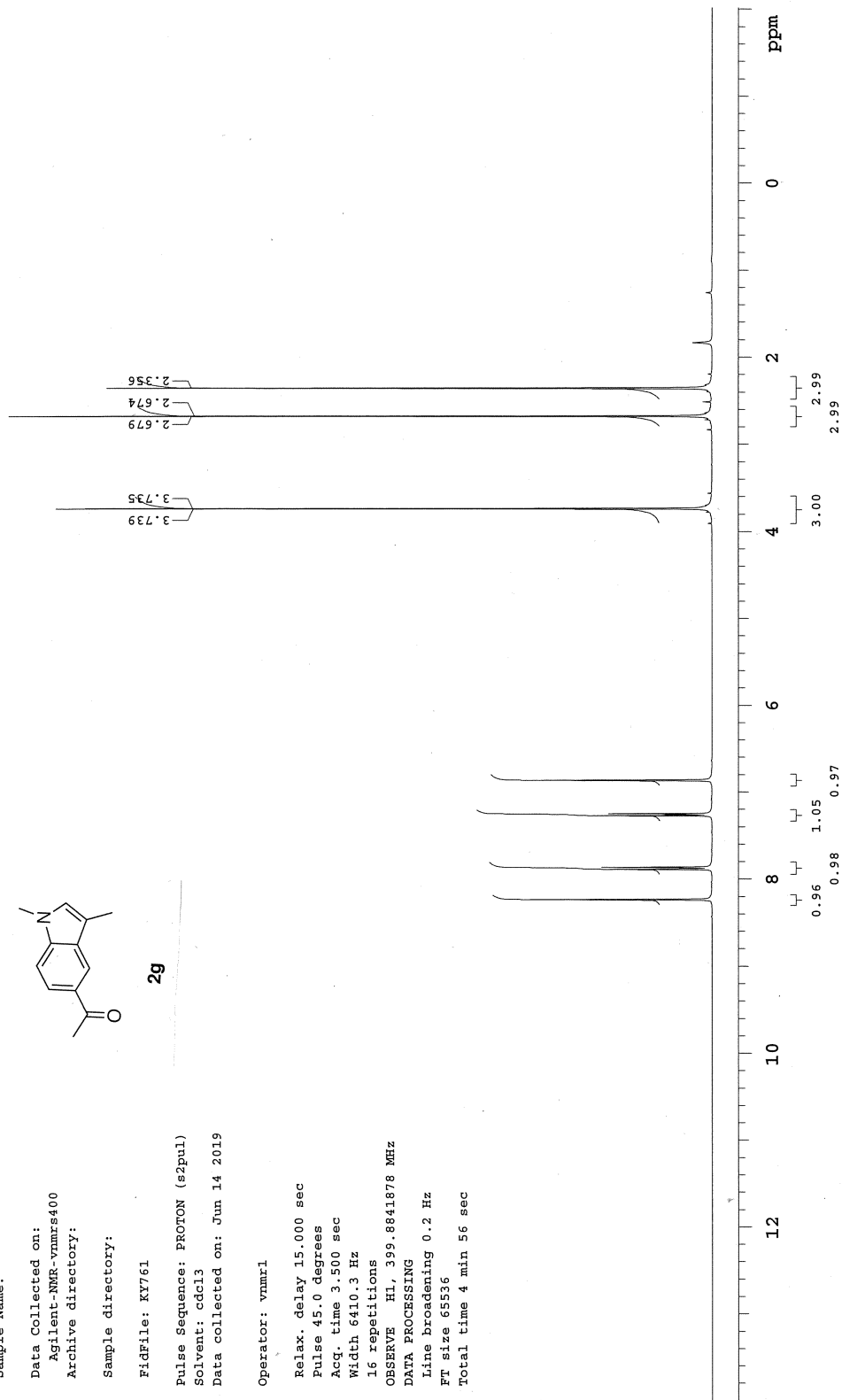


Figure S70. ¹H NMR Spectrum of **2g** (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:

Data Collected on:

Agilent-NMR-vmr400

Archive directory:

Sample directory:

File: KY761_13C

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Jun 14 2019

Operator: vmr1

Relax. delay 0.715 sec

Pulse 45.0 degrees

Acq. time 1.285 sec

Width 25510.2 Hz

512 repetitions

OBSERVE C13, 100.5509496 MHz

DECOUPLE H1, 399.8861860 MHz

Power 41 dB

continuously on

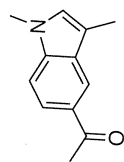
WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 17 min



2g

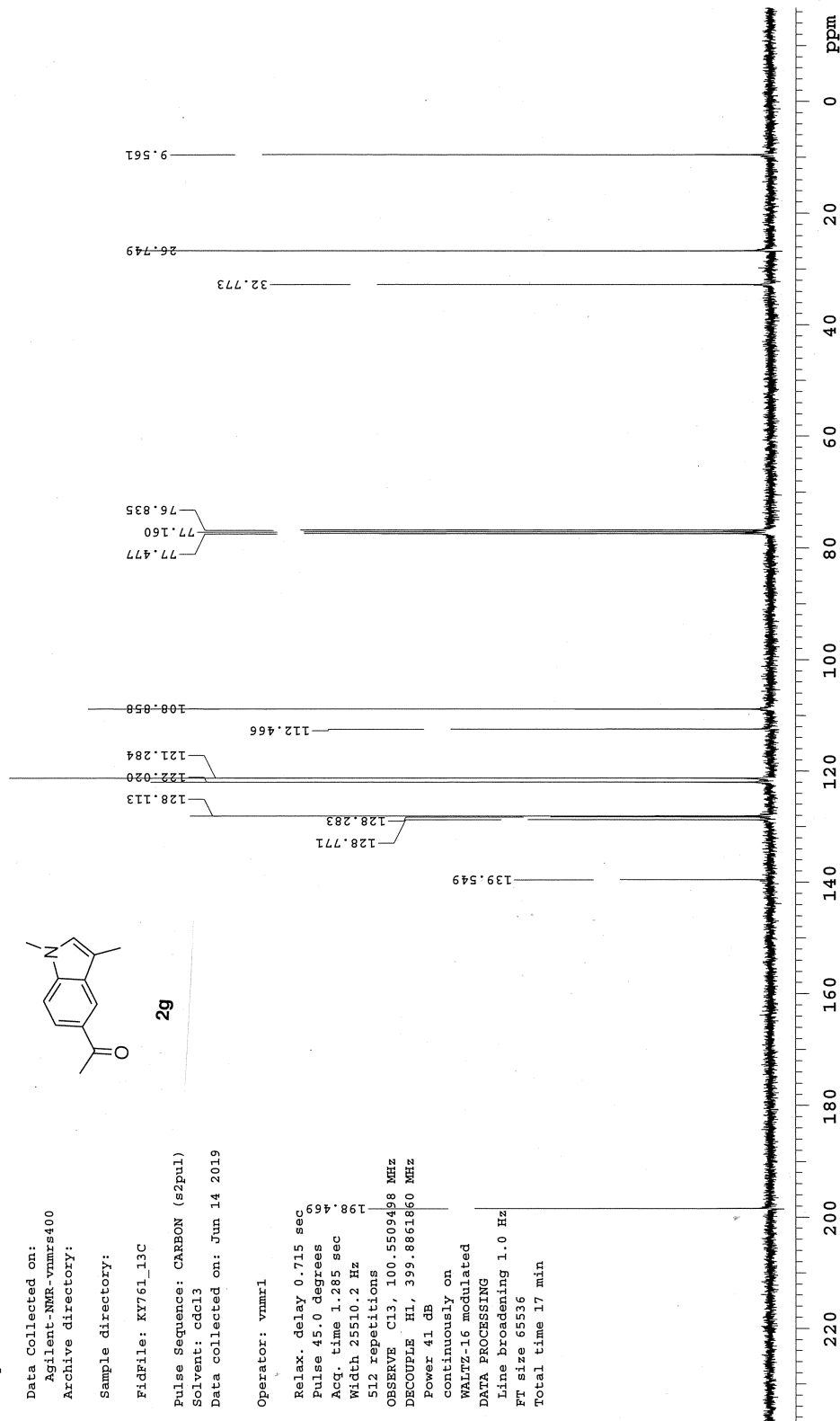


Figure S71. ¹³C NMR Spectrum of 2g (101 MHz, CDCl₃)

STANDARD PROTON PARAMETERS

Sample Name:
 Data Collected on:
 Agilent-NMR-vmms400
 Archive directory:
 Sample directory:
 FidFile: KY1085
 Pulse Sequence: PROTON (s2pul)
 Solvent: cdcl3
 Data collected on: Jan 23 2020
 Operator: vmr1
 Relax. delay 15.000 sec
 Pulse 45.0 degrees
 Acq. time 3.500 sec
 Width 6410.3 Hz
 16 repetitions
 OBSERVE HL, 399.8841847 MHz
 DATA PROCESSING
 Line broadening 0.2 Hz
 FT size 65536
 Total time 4 min 56 sec

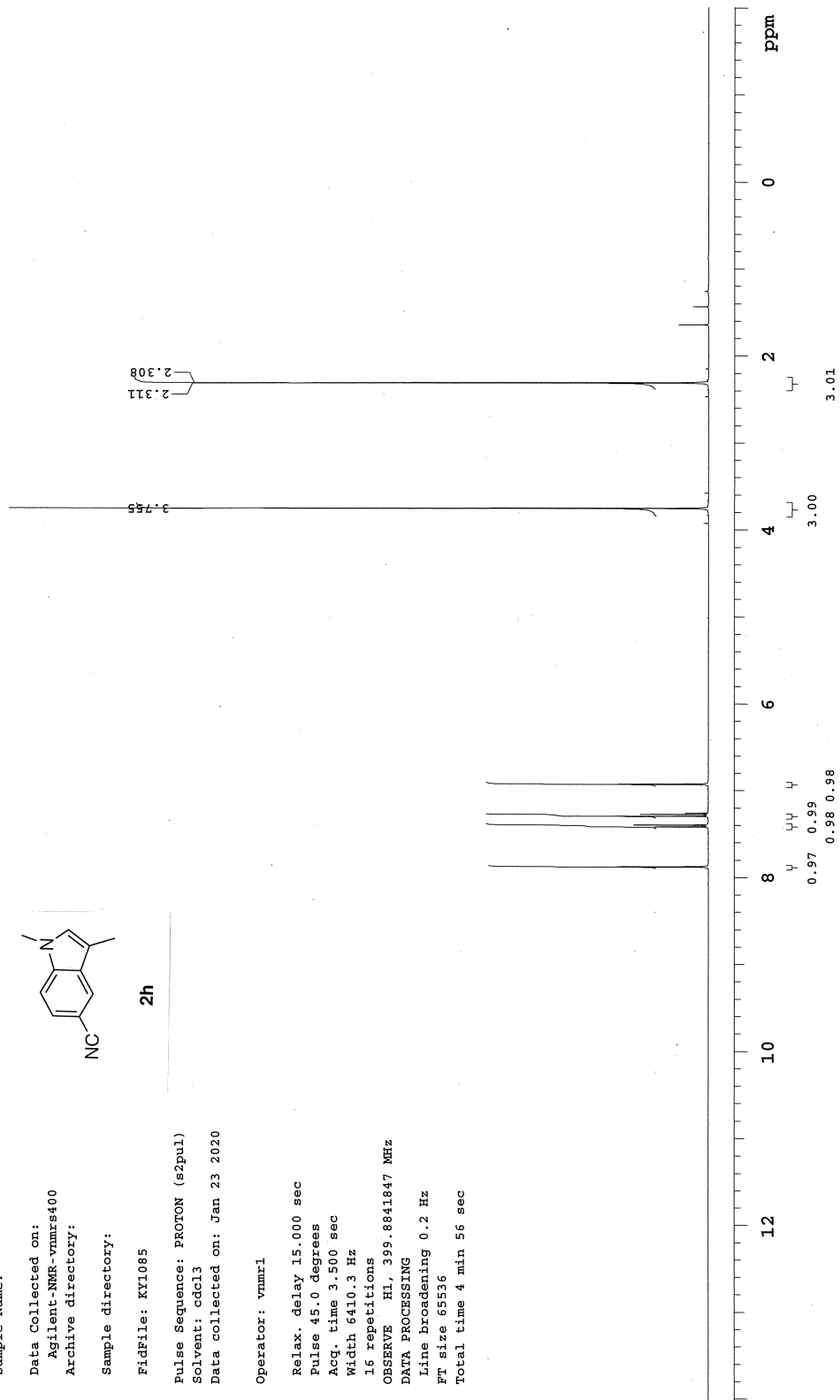
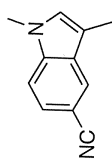


Figure S72. ¹H NMR Spectrum of **2h** (400 MHz, CDCl₃)

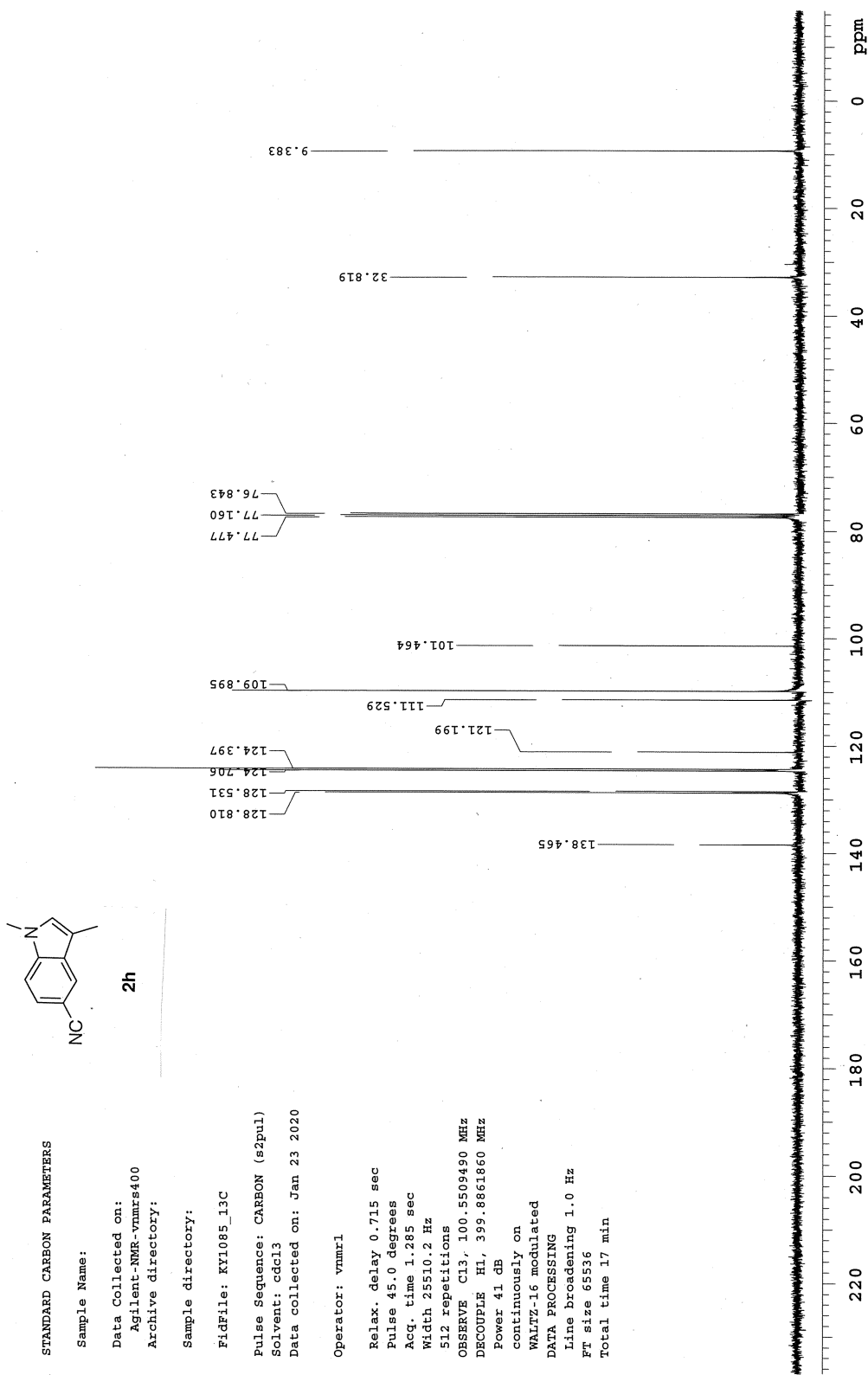


Figure S73. ^{13}C NMR Spectrum of 2h (101 MHz, CDCl_3)

STANDARD PROTON PARAMETERS

Sample Name:

Data Collected on:

Agilent-NMR-vmr400

Archive directory:

Sample directory:

FidFile: KY630

Pulse Sequence: PROTON (s2pul)

Solvent: cdcl3

Data collected on: Feb 26 2019

Temp. 25.0 C / 298.1 K

Operator: vmxr1

Relax. delay 15.000 sec

Pulse 45.0 degrees

Acq. time 3.500 sec

Width 6410.3 Hz

16 repetitions

OBSERVE H1, 399.8841859 MHz

DATA PROCESSING

Line broadening 0.2 Hz

FT size 65536

Total time 4 min 56 sec

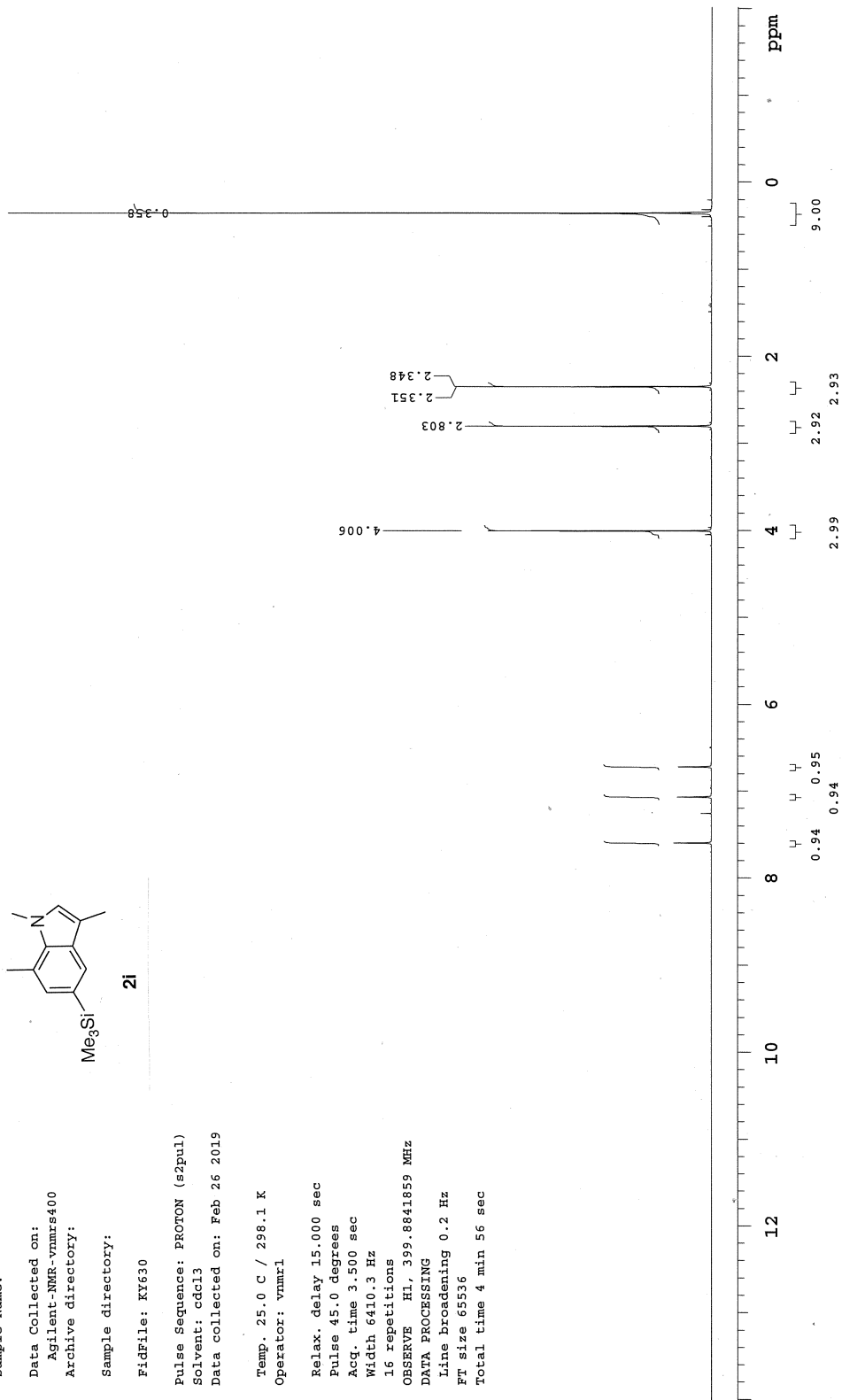


Figure S74. ¹H NMR Spectrum of **2i** (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:

Data Collected on:
Agilent-NMR-vmr400
Archive directory:

Sample directory:

File: KY567_C13

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Dec 20 2018

Operator: vmr1

Relax. delay 0.715 sec
Pulse 45.0 degrees
Acq. time 1.285 sec
Width 25510.2 Hz
512 repetitions
OBSERVE C13, 100.5509482 MHz
DECOUPLE H1, 399.8861860 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
Ft size 65536
Total time 17 min

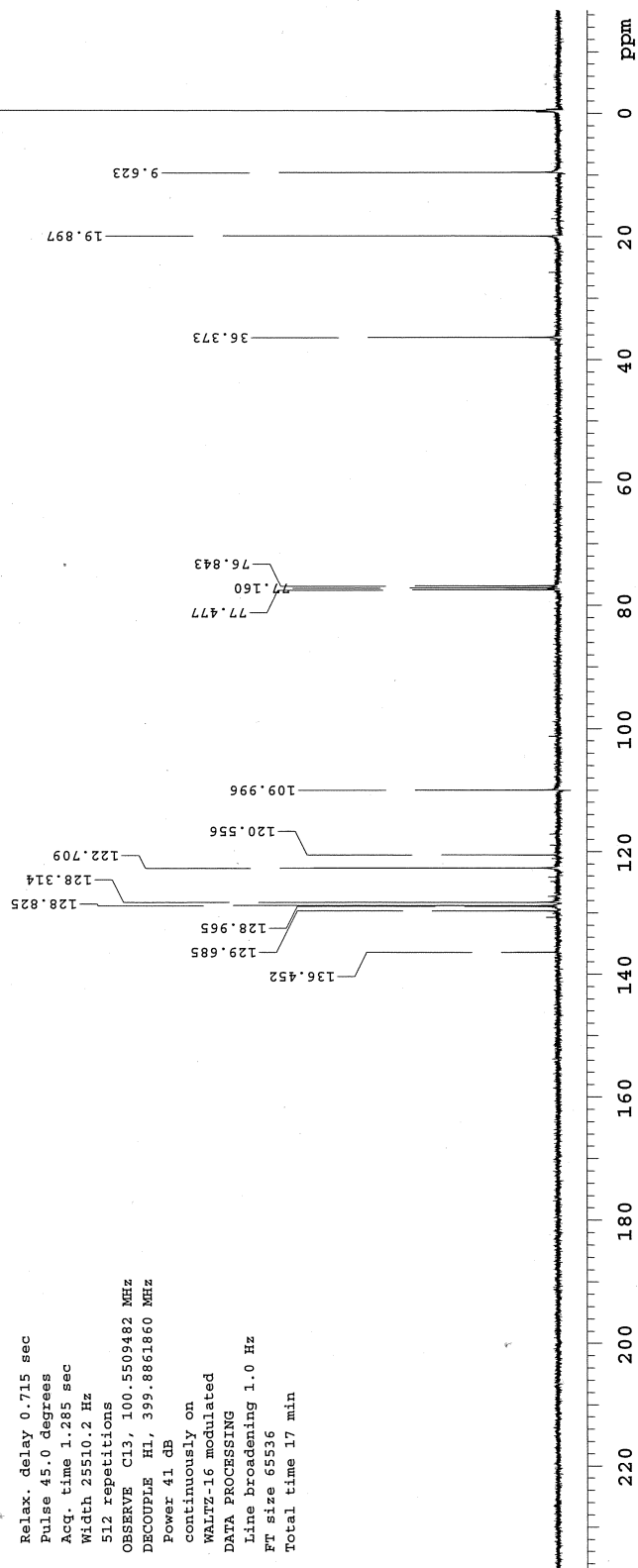
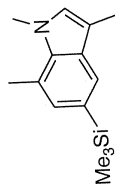


Figure S75. ¹³C NMR Spectrum of **2i** (101 MHz, CDCl₃)

STANDARD PROTON PARAMETERS

Sample Name:

Data Collected on:

Agilent-NMR-vmrns400

Archive directory:

Sample directory:

File: KY722

Pulse Sequence: PROTON (s2pul)

Solvent: cdcl3

Data collected on: May 17 2019

Operator: vmr1

Relax. delay 15.000 sec

Pulse 45.0 degrees

Acq. time 3.500 sec

Width 6410.3 Hz

16 repetitions

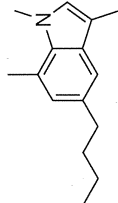
OBSERVE HL, 399.8641857 MHz

DATA PROCESSING

Line broadening 0.2 Hz

FT size 65936

Total time 4 min 56 sec



2j

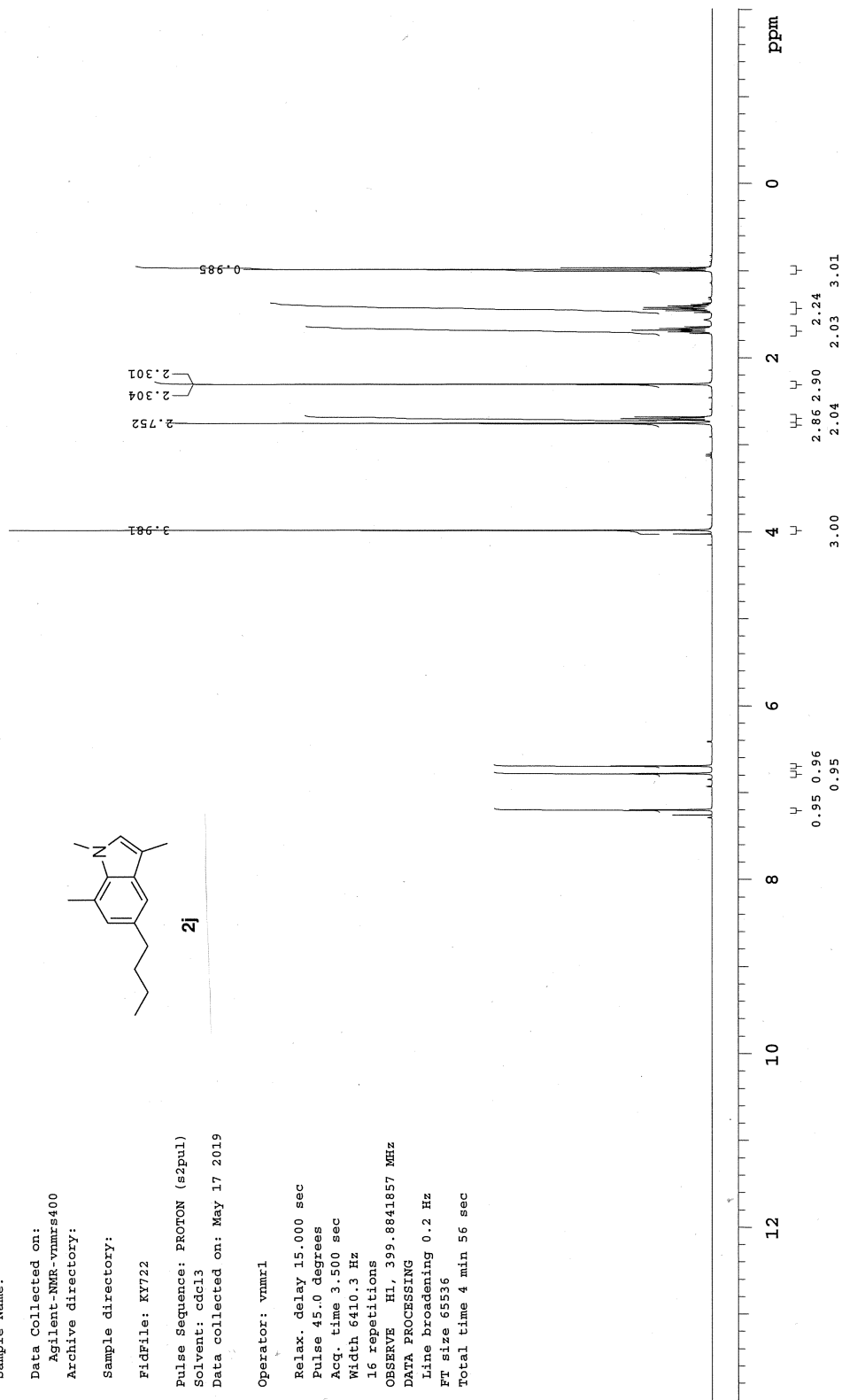


Figure S76. ¹H NMR Spectrum of **2j** (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:

Data Collected on:

Agilent-NMR-vmrns400

Archive directory:

Sample directory:

File: KY722_13C

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: May 17 2019

Operator: vmr1

Relax. delay 0.715 sec

Pulse 45.0 degrees

Acq. time 1.285 sec

Width 25510.2 Hz

512 repetitions

OBSERVE C13, 100.5509482 MHz

DECOUPLE H1, 399.8861860 MHz

Power 41 dB

continuously on

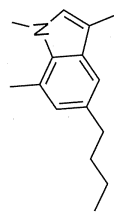
WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 17 min



2j

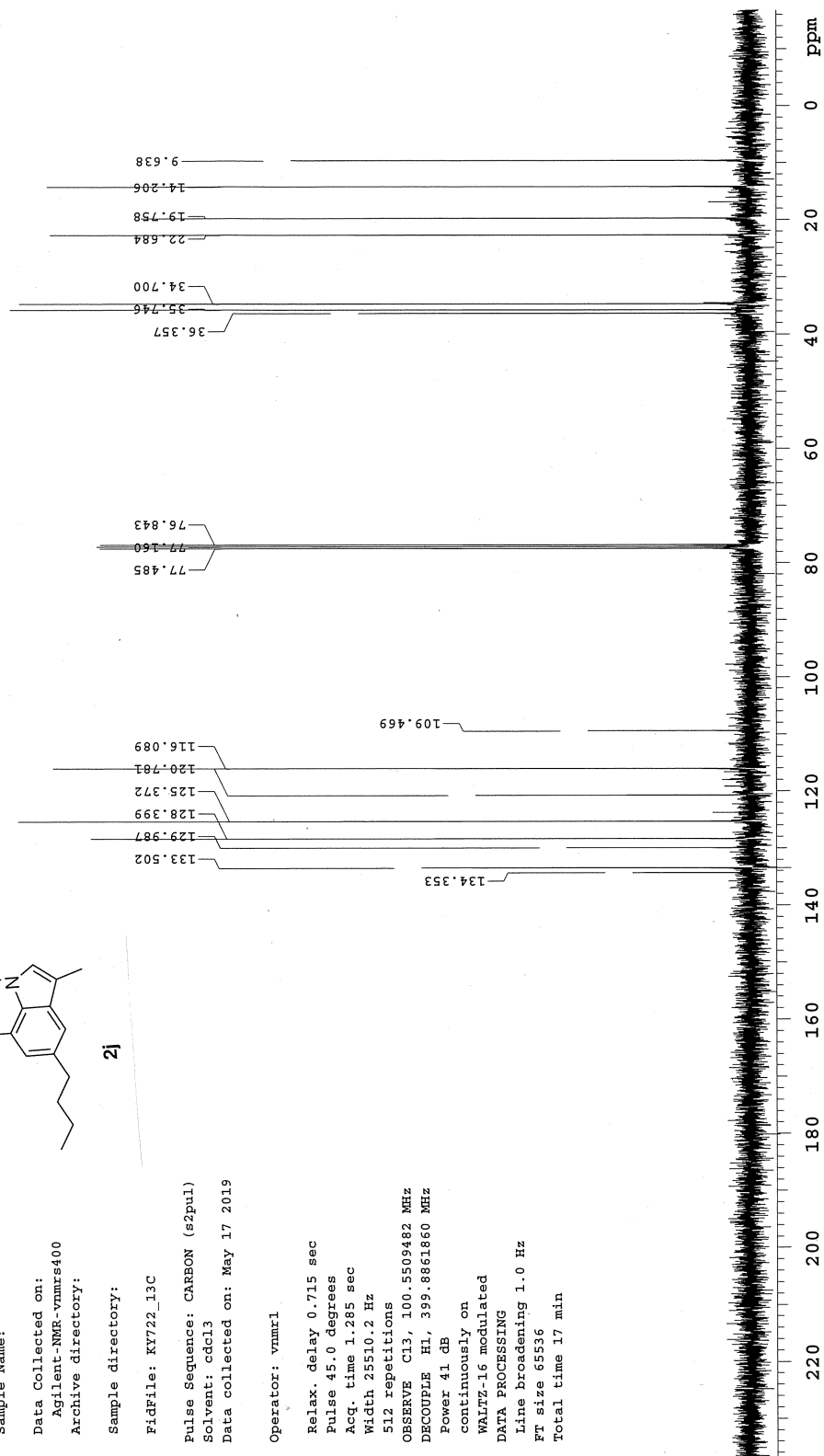


Figure S77. ^{13}C NMR Spectrum of 2j (101 MHz, CDCl_3)

STANDARD PROTON PARAMETERS

Sample Name:

Data Collected on:
Agilent-NMR-vmr400
Archive directory:

Sample directory:

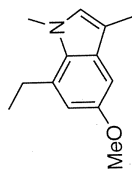
FidFile: KY784

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jul 5 2019

Temp. 25.0 C / 298.1 K
Operator: vmxr1

Relax. delay 15.000 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6410.3 Hz
16 repetitions

OBSERVE HL, 399.8841861 MHz
DATA PROCESSING
Line broadening 0.2 Hz
Ft size 65536
Total time 4 min 56 sec



2k

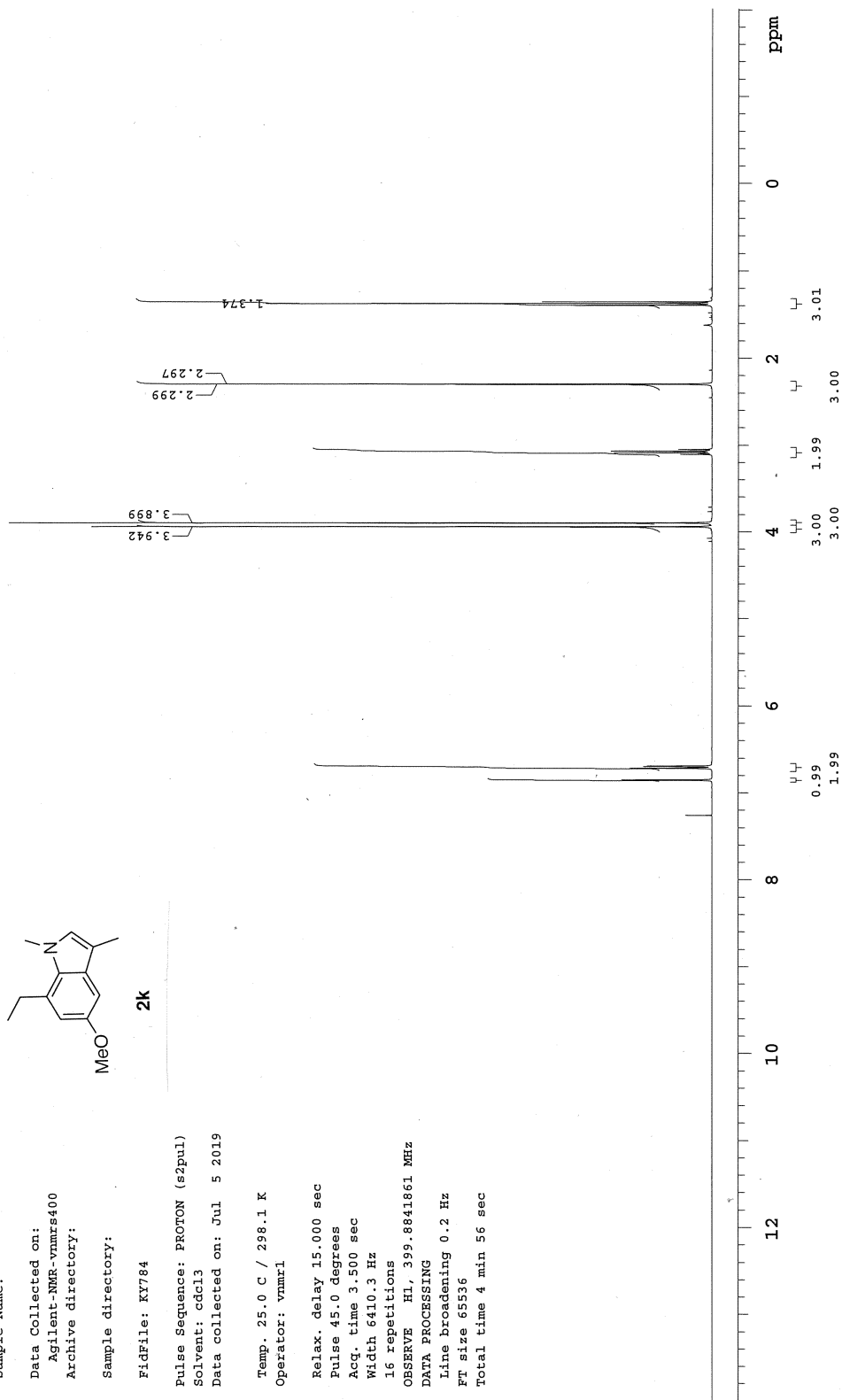


Figure S78. ¹H NMR Spectrum of **2k** (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:

Data Collected on:
Agilent-NMR-vmrs400
Archive directory:

Sample directory:

FidFile: KY784_13C

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jul 5 2019

Temp. 25.0 C / 298.1 K
Operator: vnmr1

Relax. delay 0.715 sec
Pulse 45.0 degrees
Acq. time 1.285 sec
Width 25510.2 Hz
512 repetitions
OBSERVE C13, 100.5509498 MHz
DECOUPLE H1, 399.8861860 MHz

Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
Ft size 65536
Total time 17 min

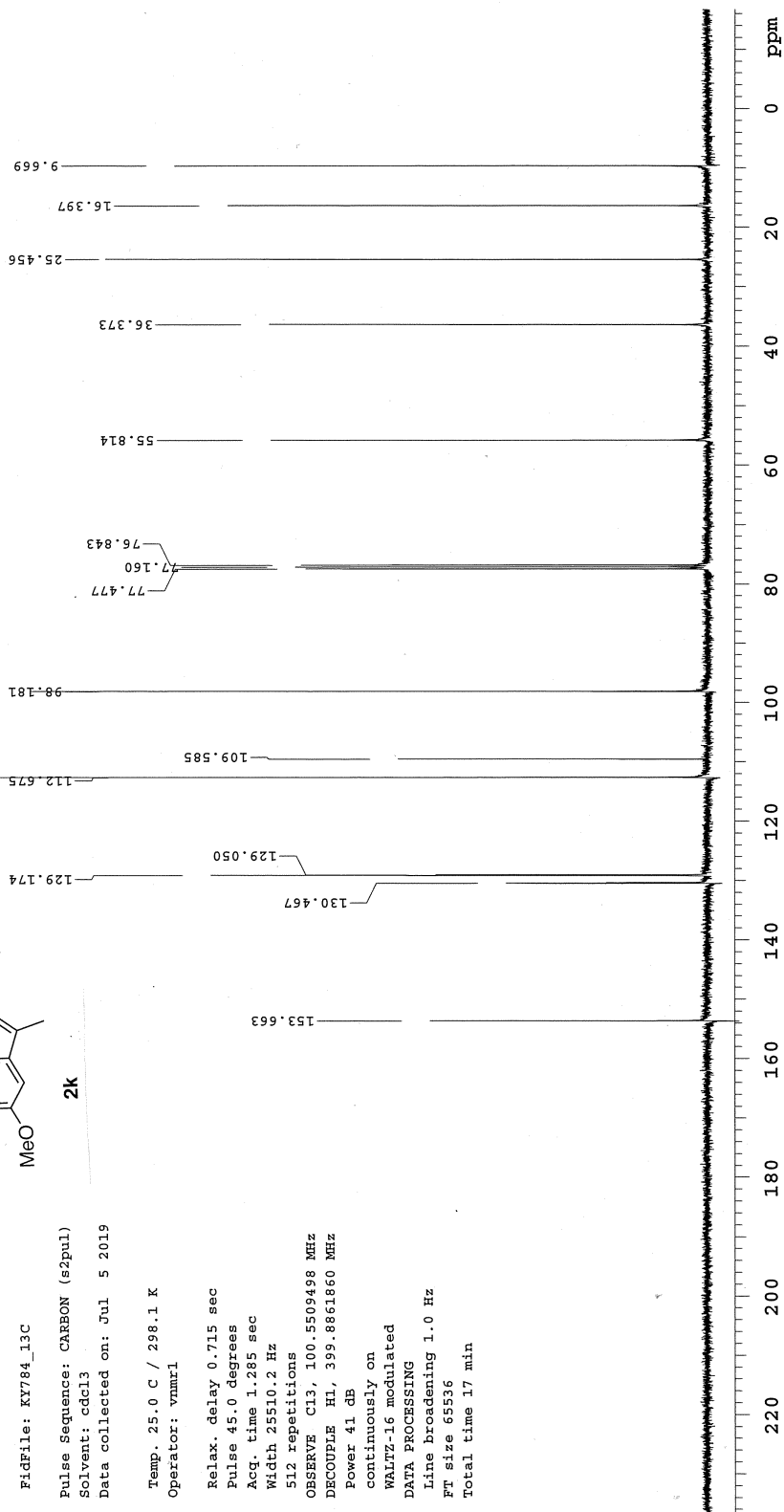
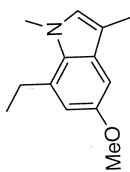


Figure S79. ^{13}C NMR Spectrum of **2k** (101 MHz, CDCl_3)

STANDARD CARBON PARAMETERS

Sample Name:
 Data Collected on:
 Agilent-NMR-vmnr400
 Archive directory:
 Sample directory:
 Fidfile: KY784_C6D6_13C
 Pulse Sequence: CARBON (szpul)
 Solvent: c6d6
 Data collected on: Sep 21 2019
 Temp. 25.0 C / 298.1 K
 Operator: vmnr1
 Relax. delay 0.715 sec
 Pulse 45.0 degrees
 Acq. time 1.285 sec
 Width 25510.2 Hz
 512 repetitions
 OBSERVE C13, 100.5509275 MHZ
 DECOUPLE H1, 399.8862220 MHZ
 Power 41 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 17 min

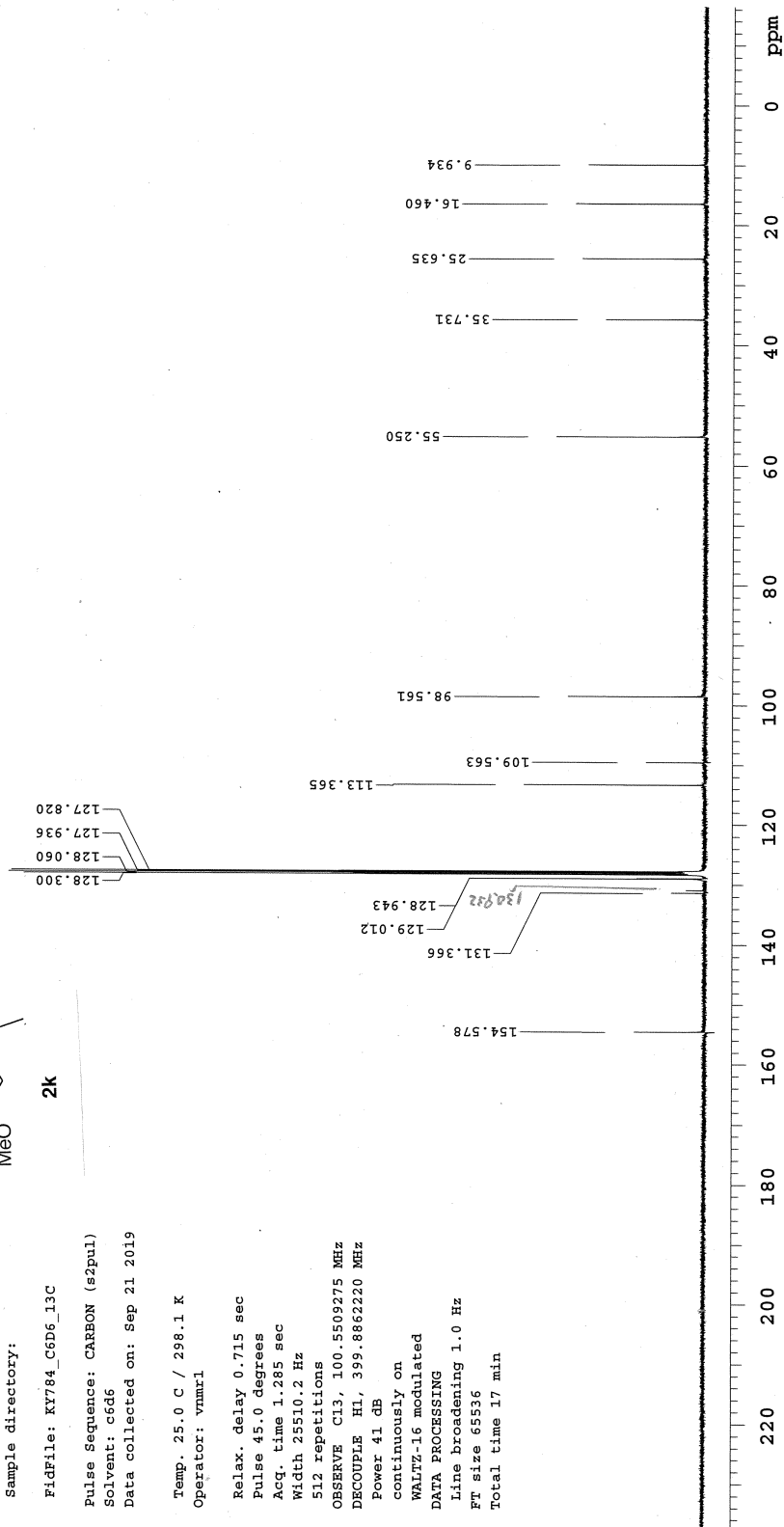
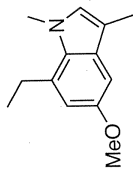


Figure S80. ¹³C NMR Spectrum of 2k (101 MHz, C₆D₆)

STANDARD PROTON PARAMETERS

Sample Name:

Data Collected on:
Agilent-NMR-vmr400
Archive directory:

Sample directory:

FidFile: KY747

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: May 24 2019

Operator: vmr1

Relax. delay 15.000 sec

Pulse 45.0 degrees

Acq. time 3.500 sec

Width 6410.3 Hz

16 repetitions

OBSERVE H1, 399.8641802 MHz

DATA PROCESSING

Line broadening 0.2 Hz

FT size 65536

Total time 4 min 56 sec

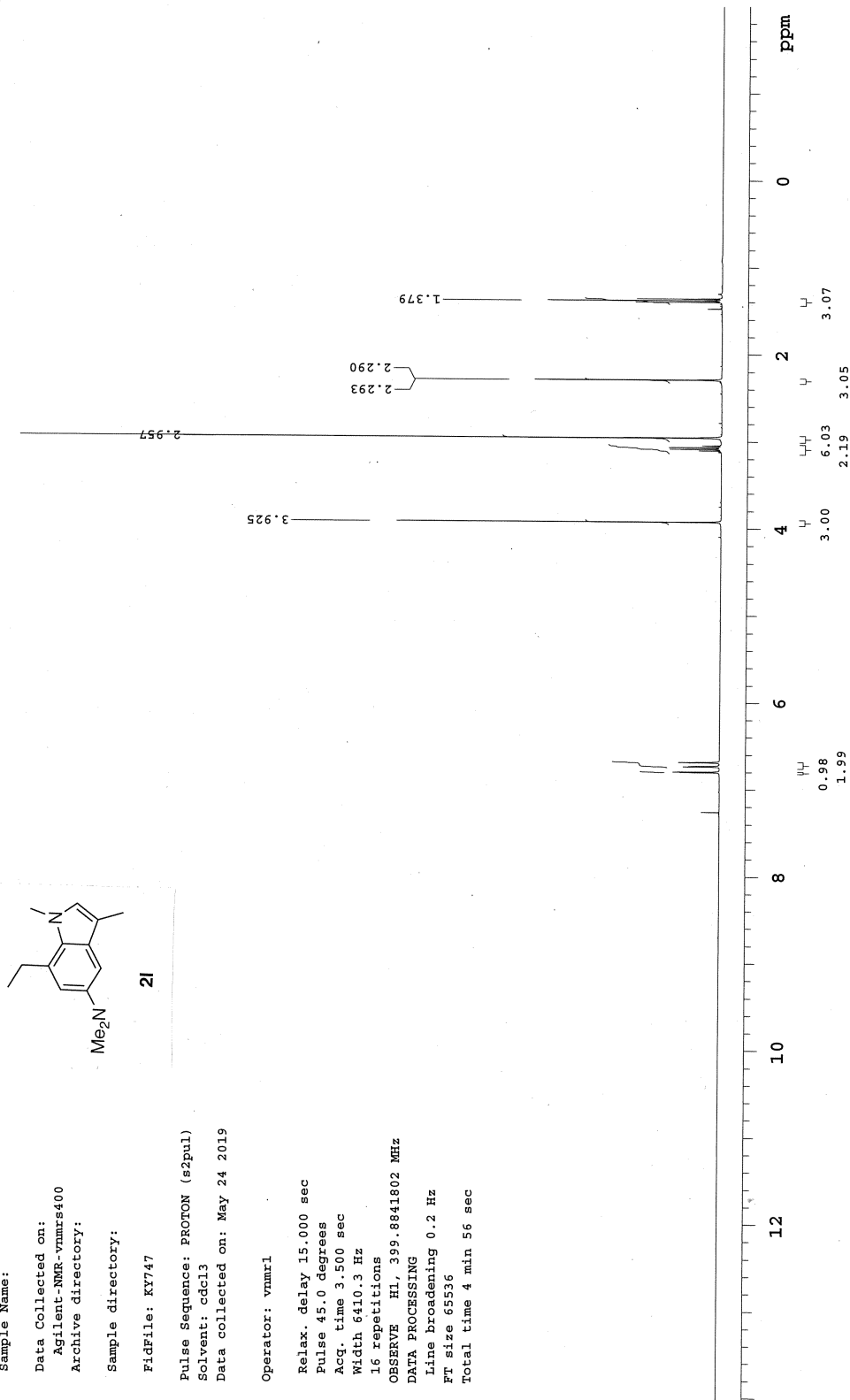


Figure S81. ¹H NMR Spectrum of **2I** (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:
Data Collected on:
Agilent-NMR-vmrs400
Archive directory:
Sample directory:
FidFile: KY747_13C
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: May 24 2019
Operator: vnmr1
Relax. delay 0.715 sec
Pulse 45.0 degrees
Acq. time 1.285 sec
Width 25510.2 Hz
512 repetitions
OBSERVE C13, 100.5509490 MHz
DECOUPLE H1, 399.8861860 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 17 min

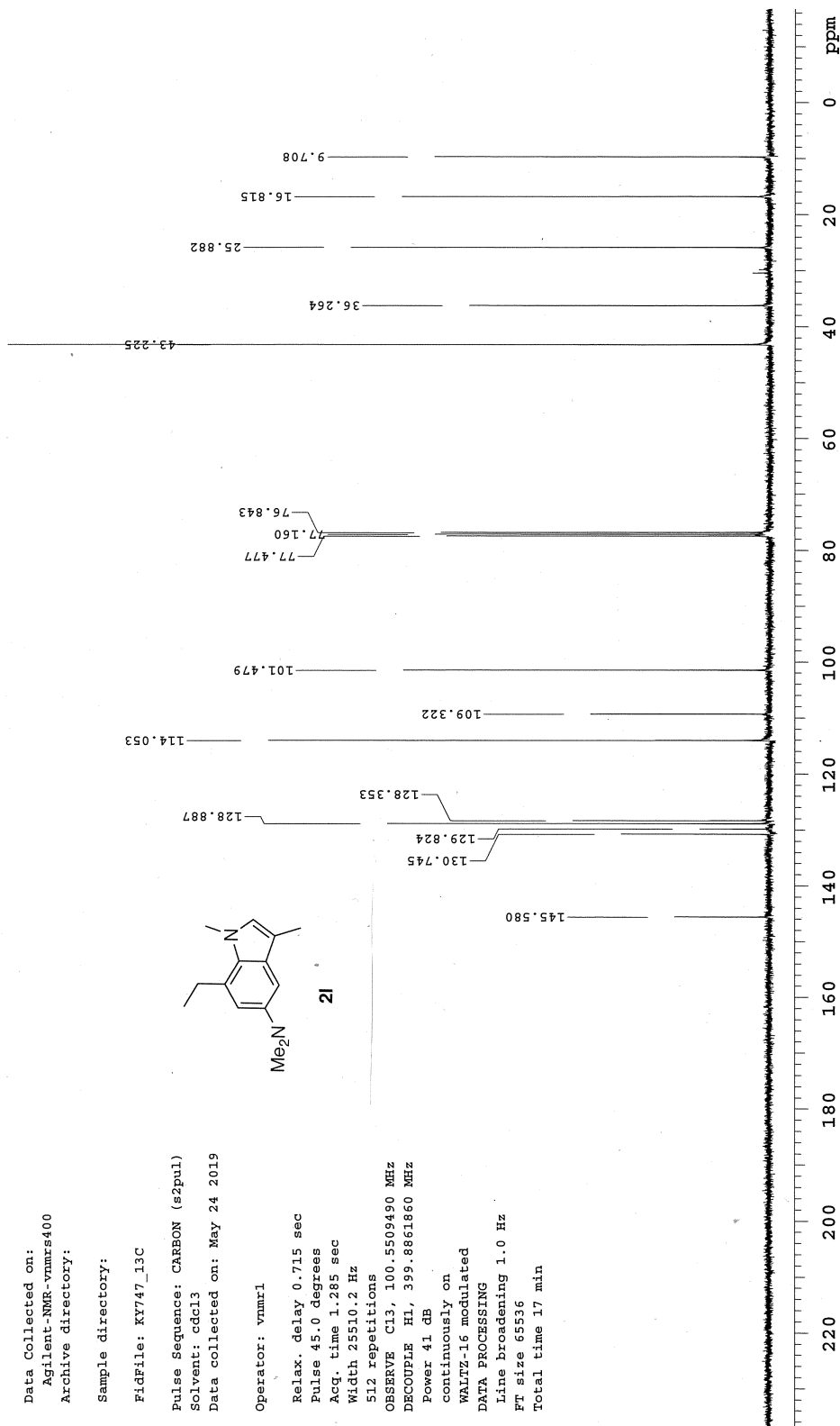
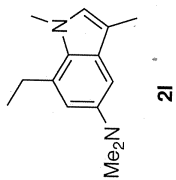


Figure S82. ^{13}C NMR Spectrum of 21 (101 MHz, CDCl_3)

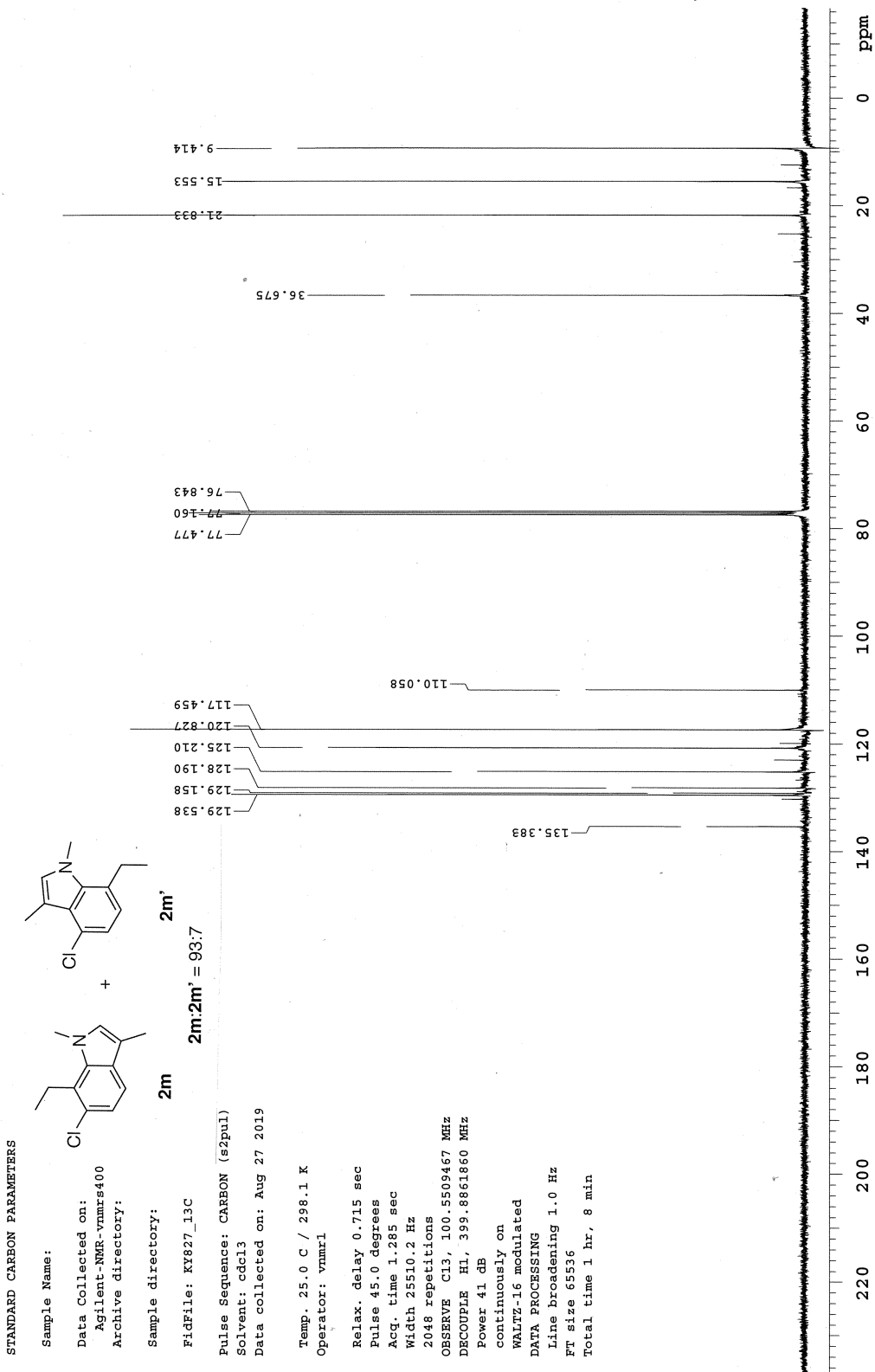


Figure S84. ^{13}C NMR Spectrum of 2m (101 MHz, CDCl_3)

STANDARD CARBON PARAMETERS

Sample Name:

Data Collected on:
Agilent-NMR-vmr5400
Archive directory:

Sample directory:

FidFile: KY762_13C2

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jun 15 2019

Operator: vmx1

Relax. delay 0.715 sec
Pulse 45.0 degrees
Acq. time 1.285 sec
Width 25510.2 Hz
8192 repetitions
OBSERVE C13, 100.5509529 MHz
DECOUPLE H1, 399.8861860 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 4 hr, 33 min

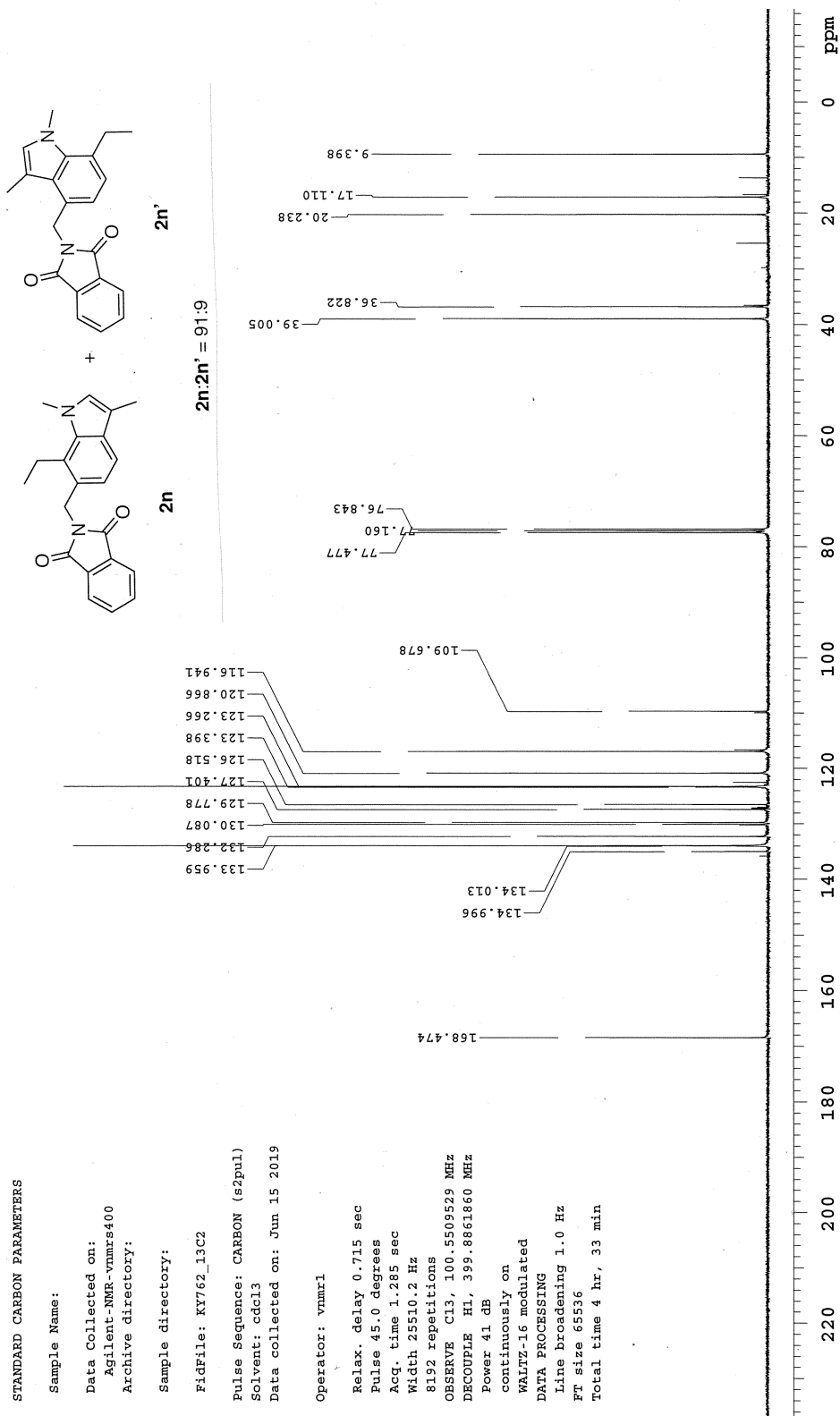


Figure S86. ¹³C NMR Spectrum of **2n** (101 MHz, CDCl₃)

STANDARD PROTON PARAMETERS

Sample Name:

Data Collected on:
Agilent-NMR-vmrns400
Archive directory:

Sample directory:

FidFile: KY717_2

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: May 16 2019

Operator: vmr1

Relax. delay 15.000 sec

Pulse 45.0 degrees

Acq. time 3.500 sec

Width 6410.3 Hz

16 repetitions

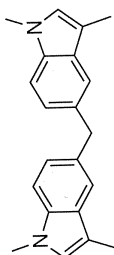
OBSERVE HL, 399.8641855 MHz

DATA PROCESSING

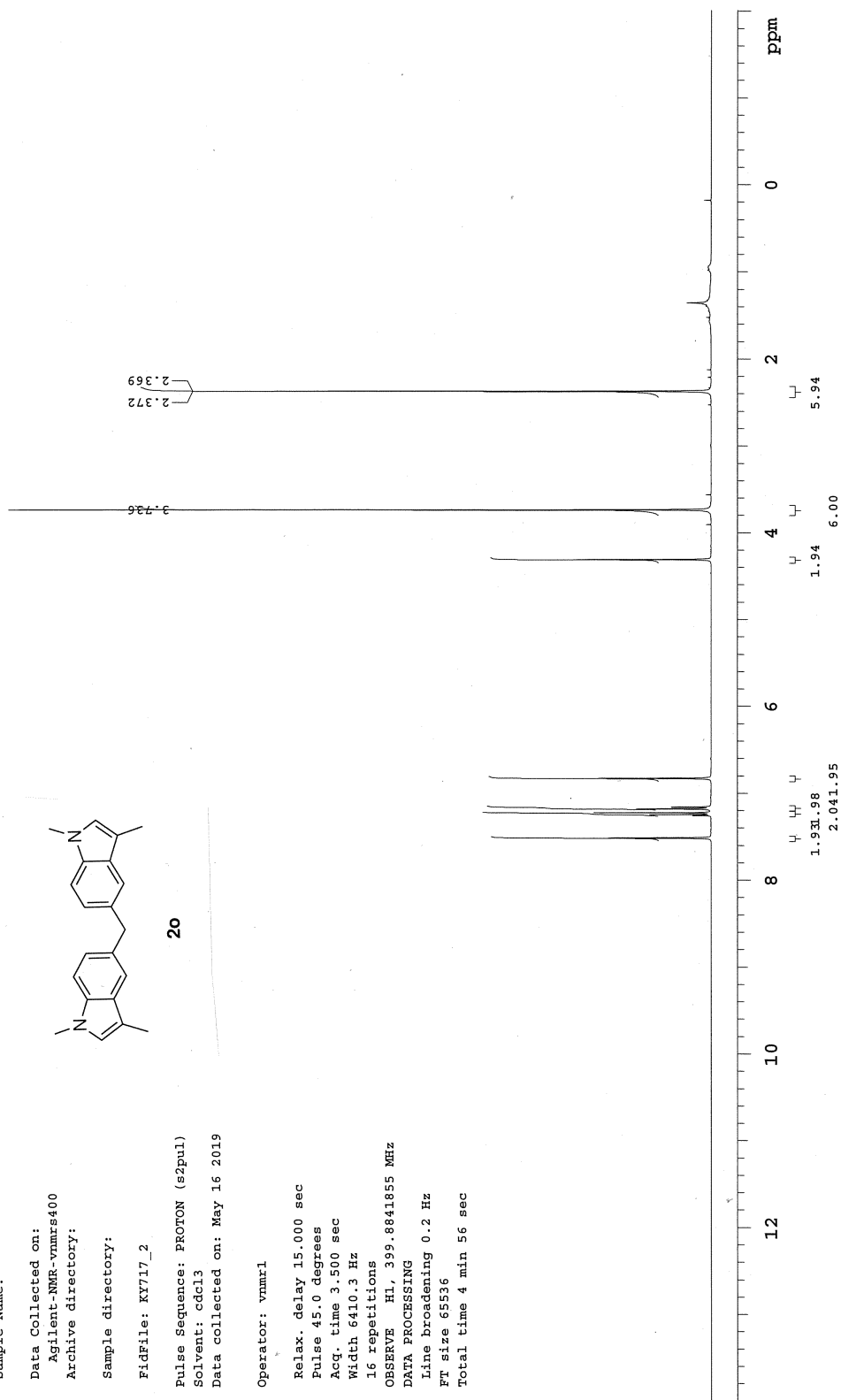
Line broadening 0.2 Hz

FT size 65536

Total time 4 min 56 sec



2o

Figure S87. ¹H NMR Spectrum of 2o (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:

Data Collected on:
Agilent-NMR-vmr400
Archive directory:

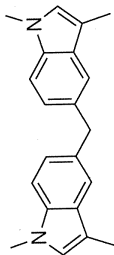
Sample directory:

File: KY717_2_13C

Pulse Sequence: CARBON (s2Pul)
Solvent: cdcl3
Data collected on: May 16 2019

Operator: vmr1

Relax. delay 0.715 sec
Pulse 45.0 degrees
Acq. time 1.285 sec
Width 25510.2 Hz
512 repetitions
OBSERVE C13, 100.5509545 MHz
DECOUPLE H1, 399.8861860 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 17 min



20

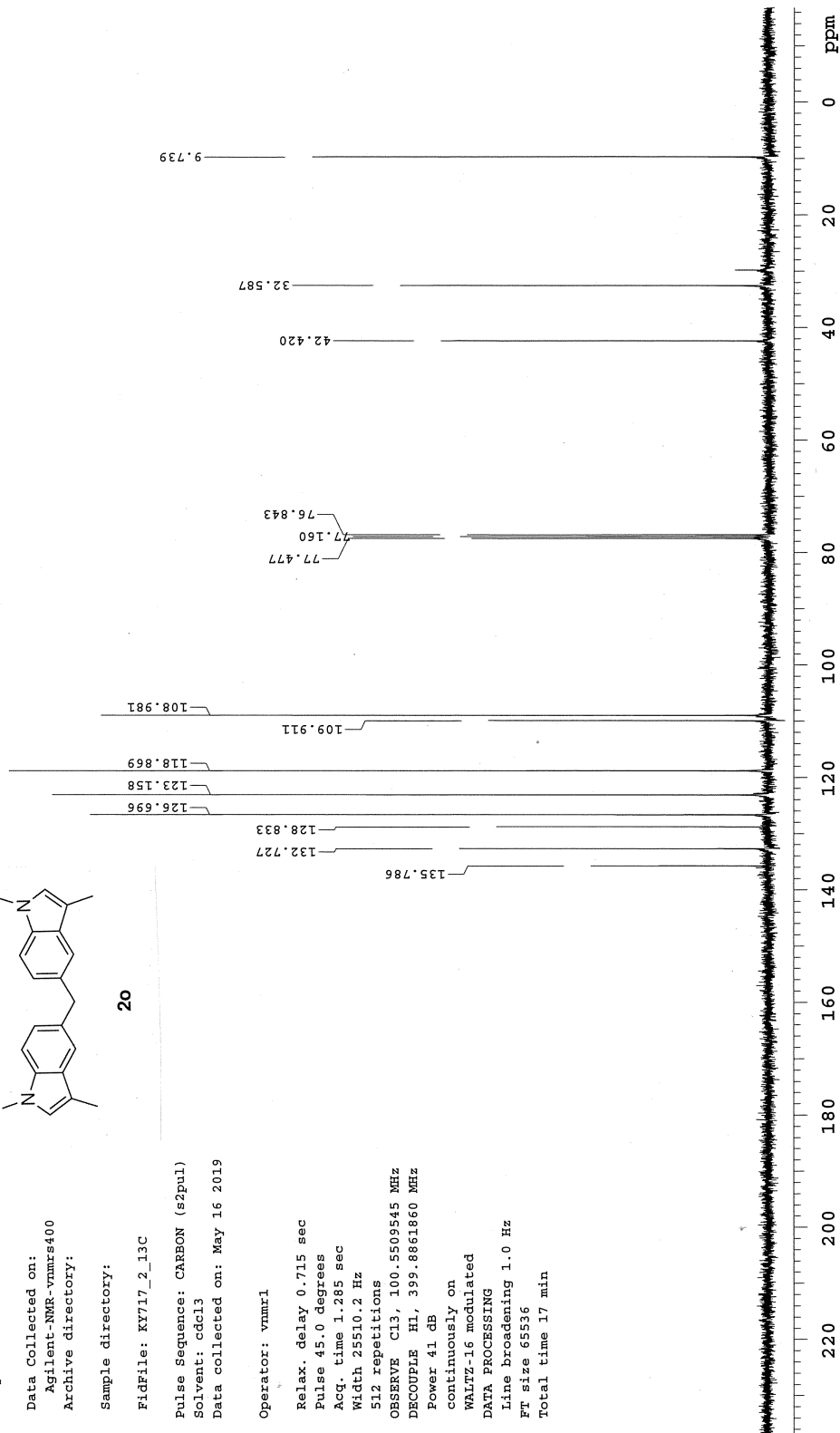


Figure S88. ^{13}C NMR Spectrum of **20** (101 MHz, CDCl_3)

STANDARD PROTON PARAMETERS

Sample Name:

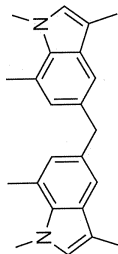
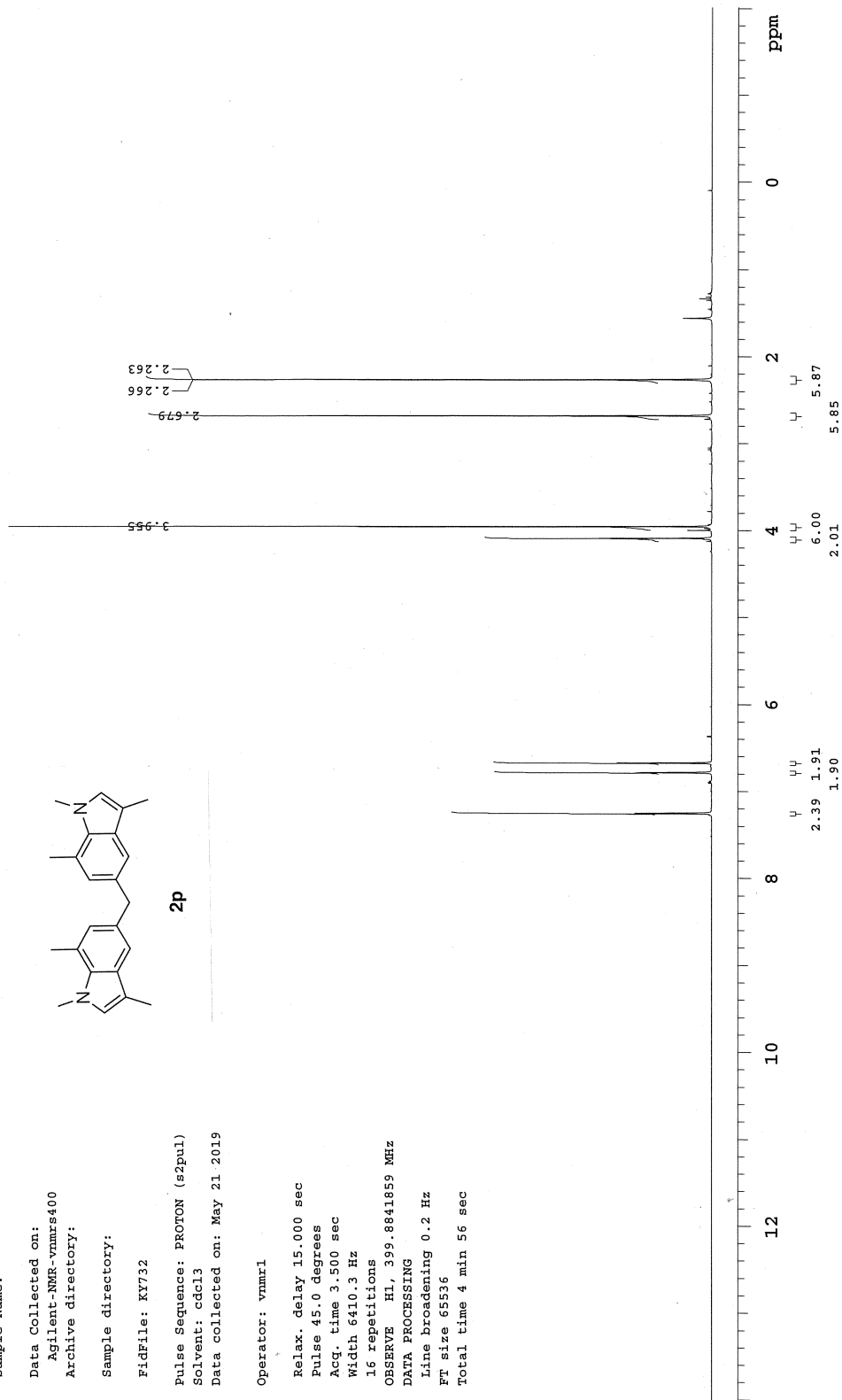
Data Collected on:
Agilent-NMR-vmrzs400
Archive directory:

Sample directory:

FidFile: KY732

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: May 21 2019

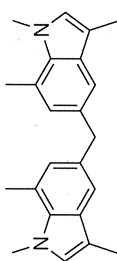
Operator: vmr1

Relax. delay 15.000 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6410.3 Hz
16 repetitions
OBSERVE HL, 399.8841859 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 4 min 56 sec**2p**Figure S89. ¹H NMR Spectrum of **2p** (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:
 Data Collected on:
 Agilent-NMR-vmr400
 Archive directory:
 Sample directory:
 File: KY732_13C
 Pulse Sequence: CARBON (s2pul)
 Solvent: cdcl3
 Data collected on: May 21 2019

Operator: vmr1
 Relax. delay 0.715 sec
 Pulse 45.0 degrees
 Acq. time 1.285 sec
 Width 25510.2 Hz
 512 repetitions
 OBSERVE C13, 100.5509459 MHz
 DECOUPLE H1, 399.8861860 MHz
 Power 41 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 17 min



2p

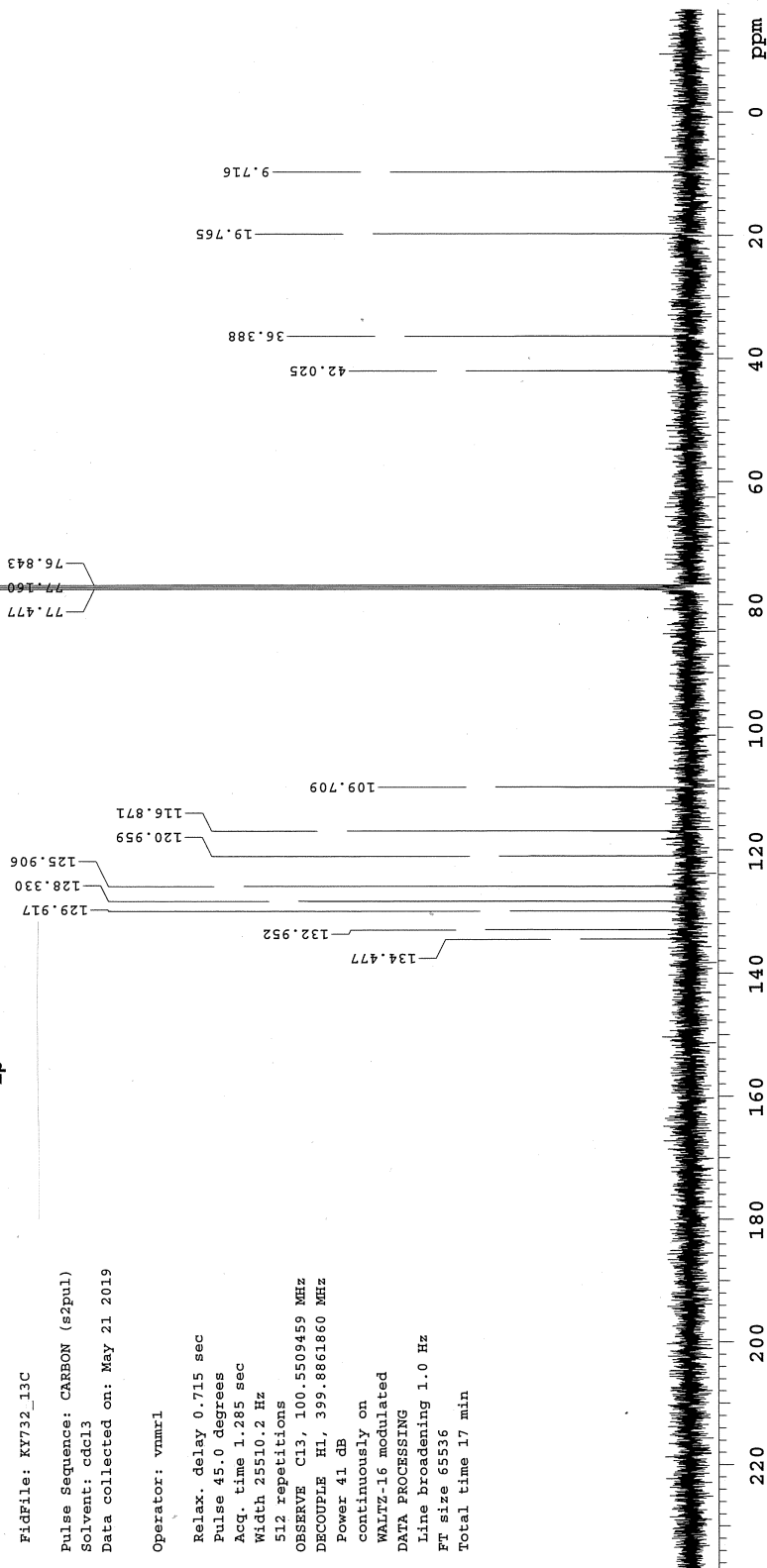


Figure S90. ¹³C NMR Spectrum of 2p (101 MHz, CDCl₃)

STANDARD PROTON PARAMETERS

Sample Name:

Data Collected on:
Agilent-NMR-vmr400
Archive directory:

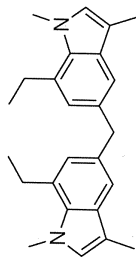
Sample directory:

File: KY733

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: May 22 2019

Operator: vmr1

Relax. delay 15.000 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6410.3 Hz
16 repetitions
OBSERVE HL, 399.8841802 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 4 min 56 sec



2q

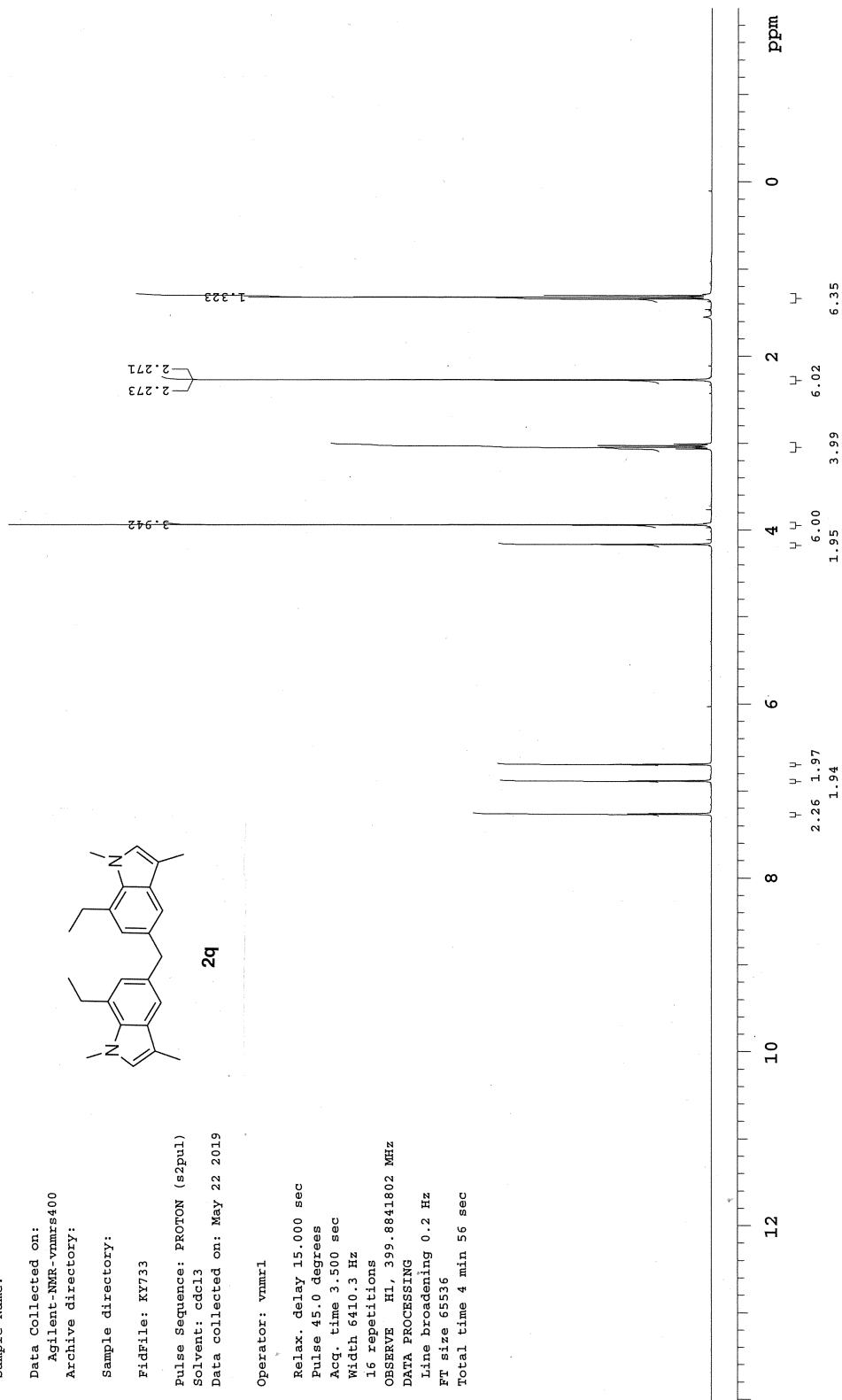
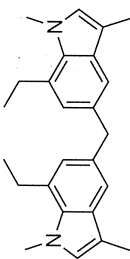


Figure S91. ¹H NMR Spectrum of **2q** (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS



2q

Sample Name:
 Data Collected on:
 Agilent-NMR-vmrns400
 Archive directory:
 Sample directory:
 FidFile: KY733_13C
 Pulse Sequence: CARBON (s2Pul)
 Solvent: cdcl3
 Data collected on: May 22 2019

Operator: vmr1
 Relax. delay 0.715 sec
 Pulse 45.0 degrees
 Acq. time 1.285 sec
 Width 25510.2 Hz
 512 repetitions
 OBSERVE C13, 100.5509459 MHz
 DECOUPLE H1, 399.8861860 MHz
 Power 41 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 17 min

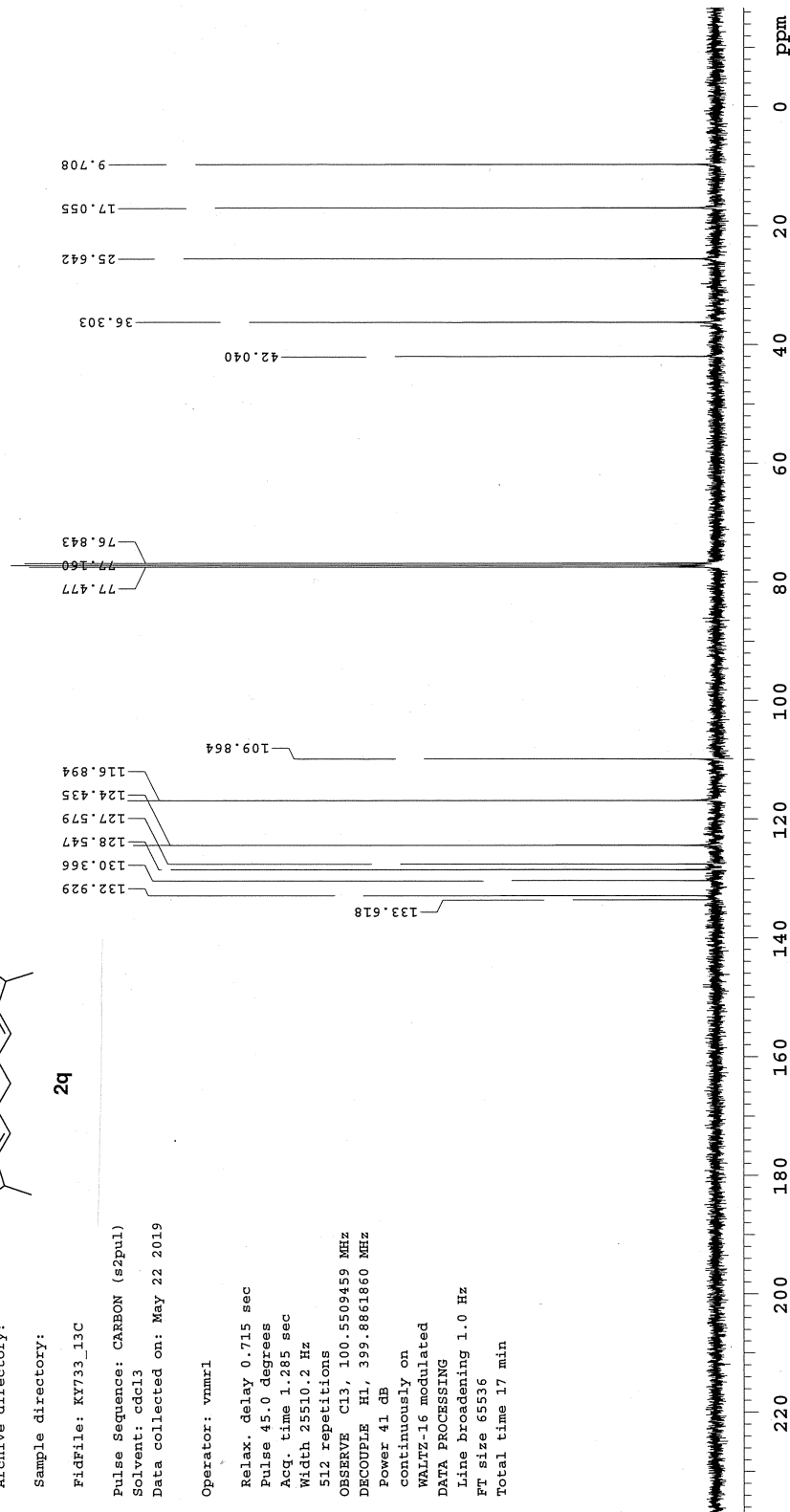


Figure S92. ¹³C NMR Spectrum of 2q (101 MHz, CDCl₃)

STANDARD PROTON PARAMETERS

Sample Name:
 Data Collected on:
 Agilent-NMR-vmrns400
 Archive directory:
 Sample directory:
 Fidfile: KY767_2
 Pulse Sequence: PROTON (s2pul)
 Solvent: cdcl3
 Data collected on: Jun 27 2019
 Operator: vmrml
 Relax. delay 15.000 sec
 Pulse 45.0 degrees
 Acq. time 3.500 sec
 Width 6410.3 Hz
 16 repetitions
 OBSERVE HL, 399.8841863 MHz
 DATA PROCESSING
 Line broadening 0.2 Hz
 FT size 65536
 Total time 4 min 56 sec

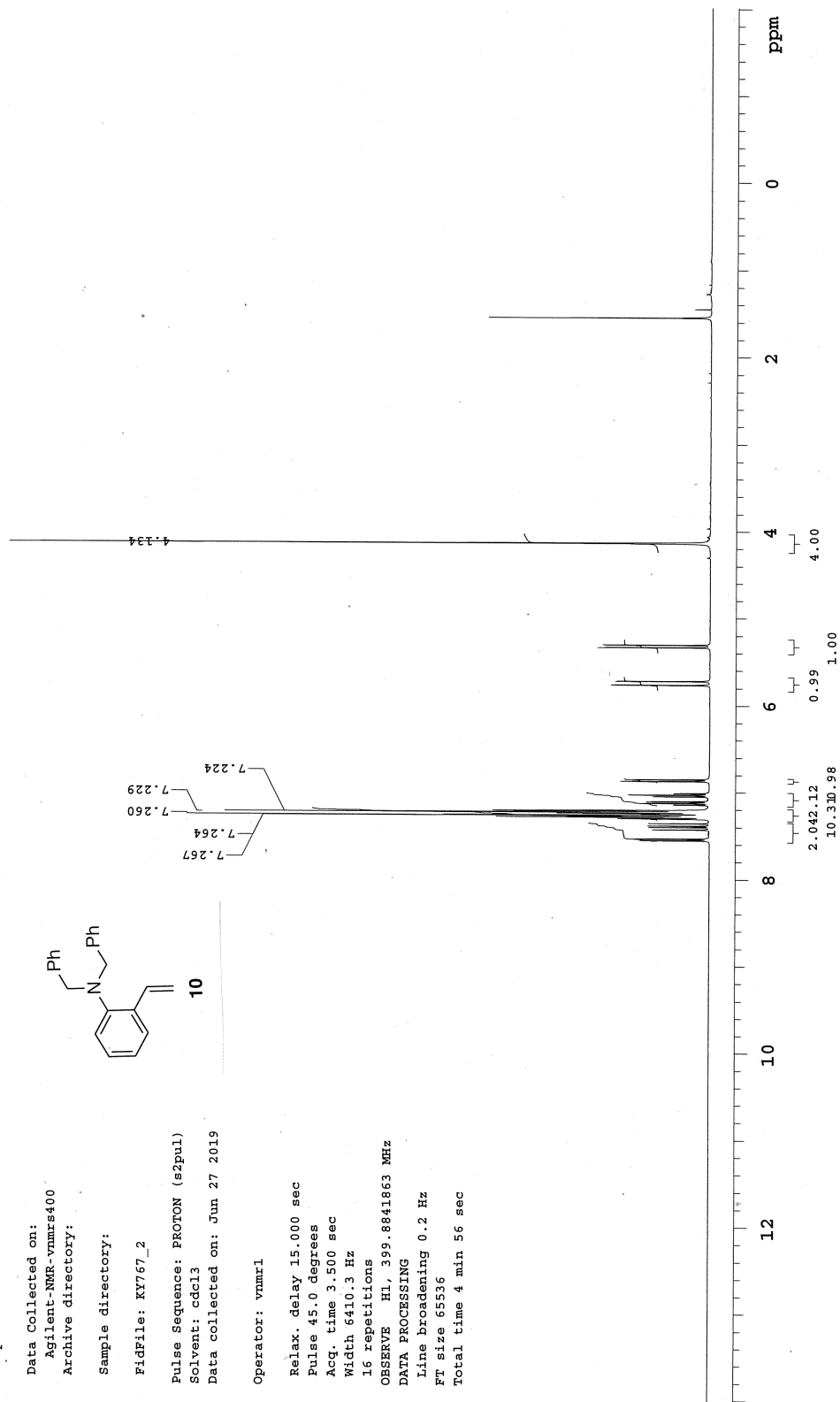
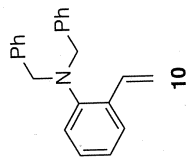


Figure S93. ¹H NMR Spectrum of **10** (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:
 Data Collected on:
 Agilent-NMR-vmr400
 Archive directory:
 Sample directory:
 File: KY767_2_13C
 Pulse Sequence: CARBON (s2pul)
 Solvent: cdcl3
 Data collected on: Jun 28 2019
 Temp. 25.0 C / 296.1 K
 Operator: vmr1
 Relax. delay 0.715 sec
 Pulse 45.0 degrees
 Acq. time 1.285 sec
 Width 25510.2 Hz
 512 repetitions
 OBSERVE C13, 100.5509443 MHZ
 DECOUPLE H1, 399.8861860 MHZ
 Power 41 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 17 min

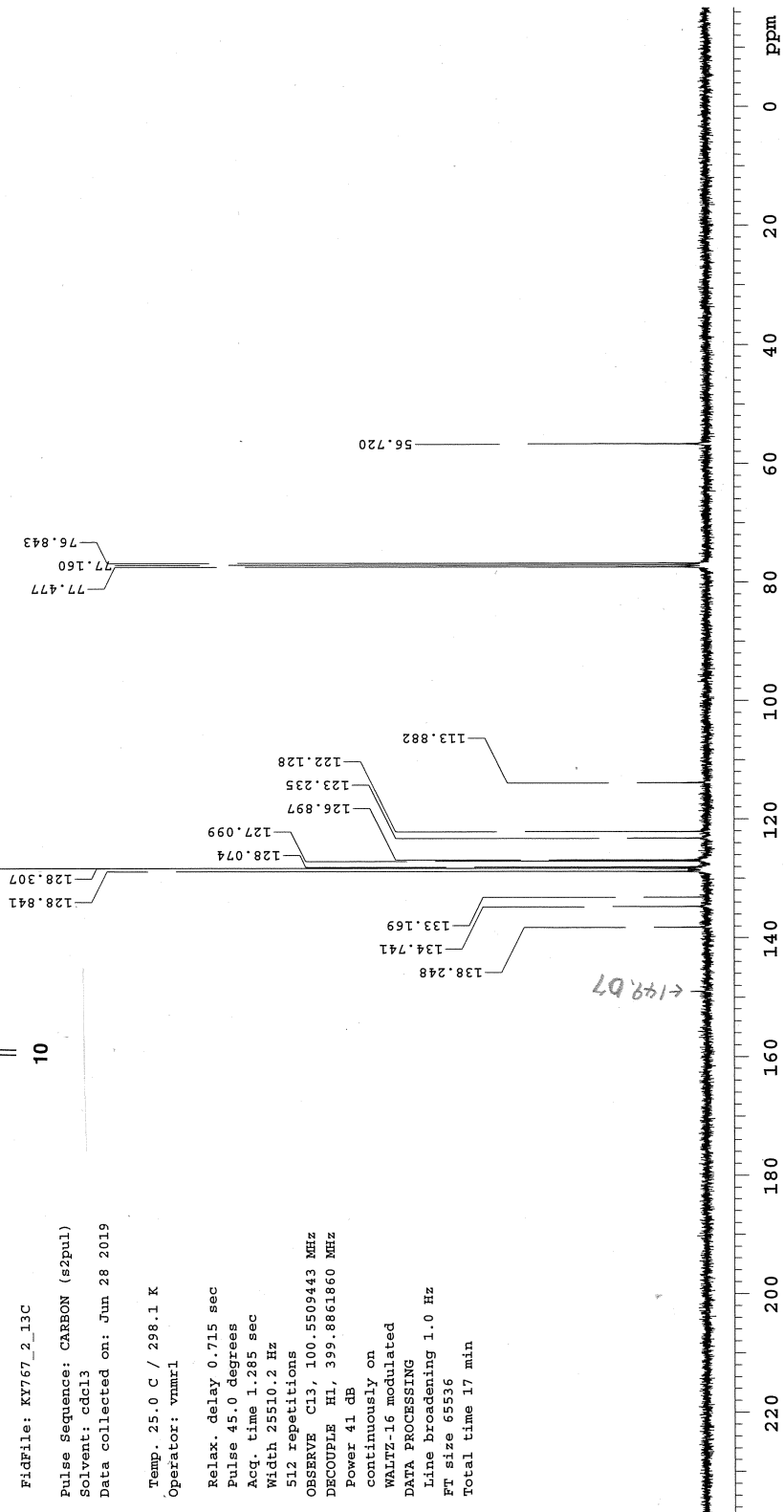
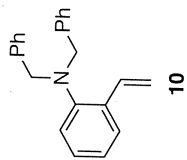


Figure S94. ¹³C NMR Spectrum of **10** (101 MHz, CDCl₃)

STANDARD PROTON PARAMETERS

Sample Name:
Data Collected on:
Agilent-NMR-vmr400
Archive directory:
Sample directory:
FidFile: KY766
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jun 19 2019
Operator: vmr1
Relax. delay 15.000 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6410.3 Hz
16 repetitions
OBSERVE HL, 399.8841865 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 4 min 56 sec

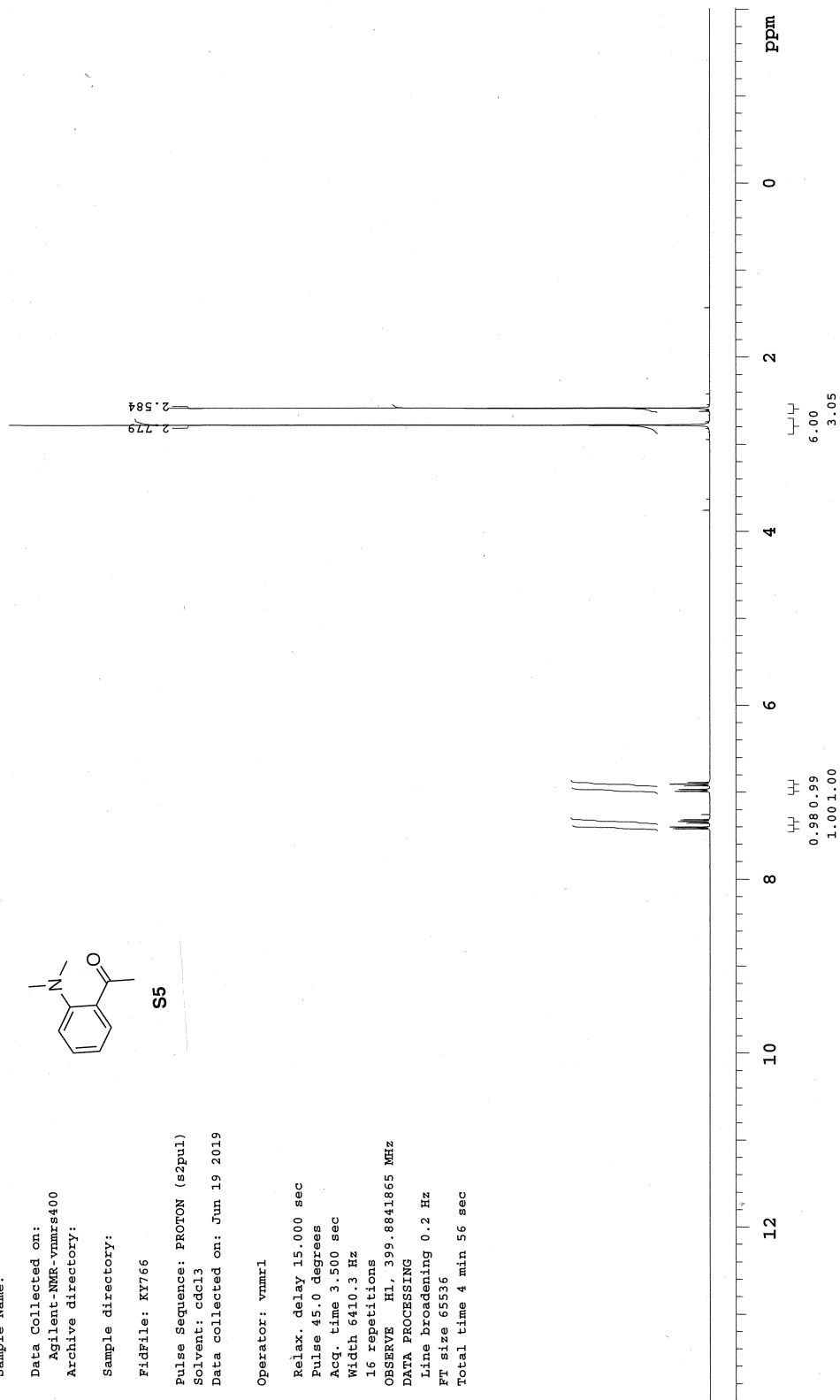
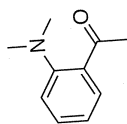
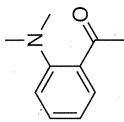


Figure S95. ¹H NMR Spectrum of S5 (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:
 Data Collected on:
 Agilent-NMR-vmnrs400
 Archive directory:
 Sample directory:
 FIDFile: KY755_13C
 Pulse Sequence: CARBON (s2pul)
 Solvent: cdcl3
 Data collected on: Jun 11 2019



S5

Temp. 25.0 C / 298.1 K
 Operator: vnmr1
 Relax. delay 0.715 sec
 Pulse 45.0 degrees
 Acq. time 1.285 sec
 Width 25510.2 Hz
 512 repetitions
 OBSERVE C13, 100.5509568 MHZ
 DECOUPLE H1, 399.8861860 MHZ
 Power 41 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 17 min

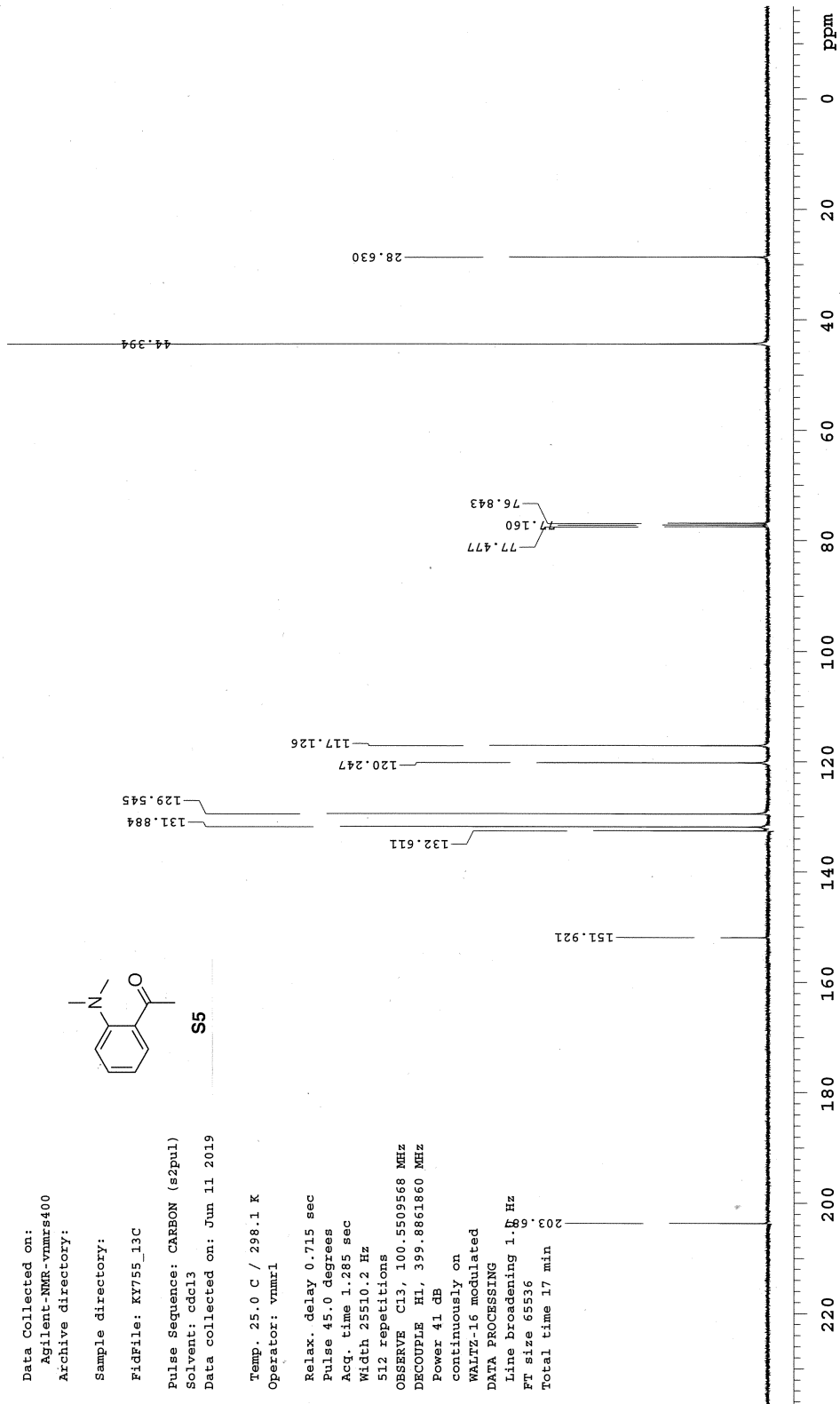
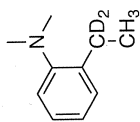


Figure S96. ¹³C NMR Spectrum of S5 (101 MHz, CDCl₃)

STANDARD PROTON PARAMETERS

Sample Name:
 Data Collected on:
 Agilent-NMR-vmnrs400
 Archive directory:
 Sample directory:
 Fidfile: KY791
 Pulse Sequence: PROTON (szpul)
 Solvent: cdcl3
 Data collected on: Jul 9 2019
 Temp. 25.0 C / 298.1 K
 Operator: vmnr1
 Relax. delay 15.000 sec
 Pulse 45.0 degrees
 Acq. time 3.500 sec
 Width 6410.3 Hz
 16 repetitions
 OBSERVE H1, 399.8841866 MHZ
 DATA PROCESSING
 Line broadening 0.2 Hz
 FT size 65536
 Total time 4 min 56 sec



1a-d₂

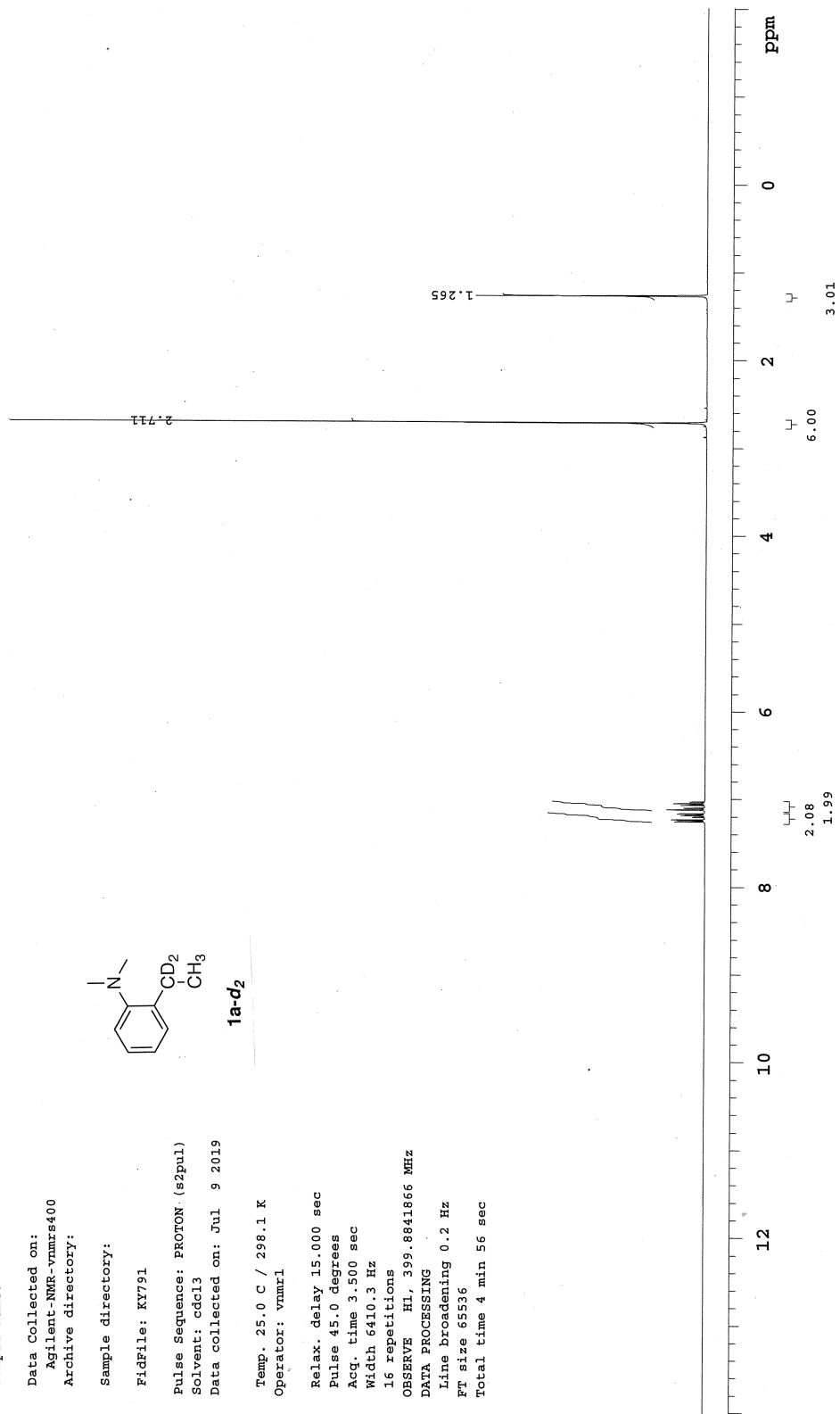
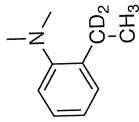


Figure S97. ¹H NMR Spectrum of 1a-d₂ (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:
 Data Collected on:
 Agilent-NMR-vmrs400
 Archive directory:
 Sample directory:
 FidFile: KY791_13C
 Pulse Sequence: CARBON (s2pul)
 Solvent: cdcl3
 Data collected on: Jul 10 2019



1a-d₂

Temp. 25.0 C / 298.1 K
 Operator: vmr1
 Relax. delay 0.715 sec
 Pulse 45.0 degrees
 Acq. time 1.285 sec
 Width 25510.2 Hz
 2048 repetitions
 OBSERVE C13, 100.5509459 MHz
 DECOUPLE H1, 399.8861860 MHz
 Power 41 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 1 hr, 8 min

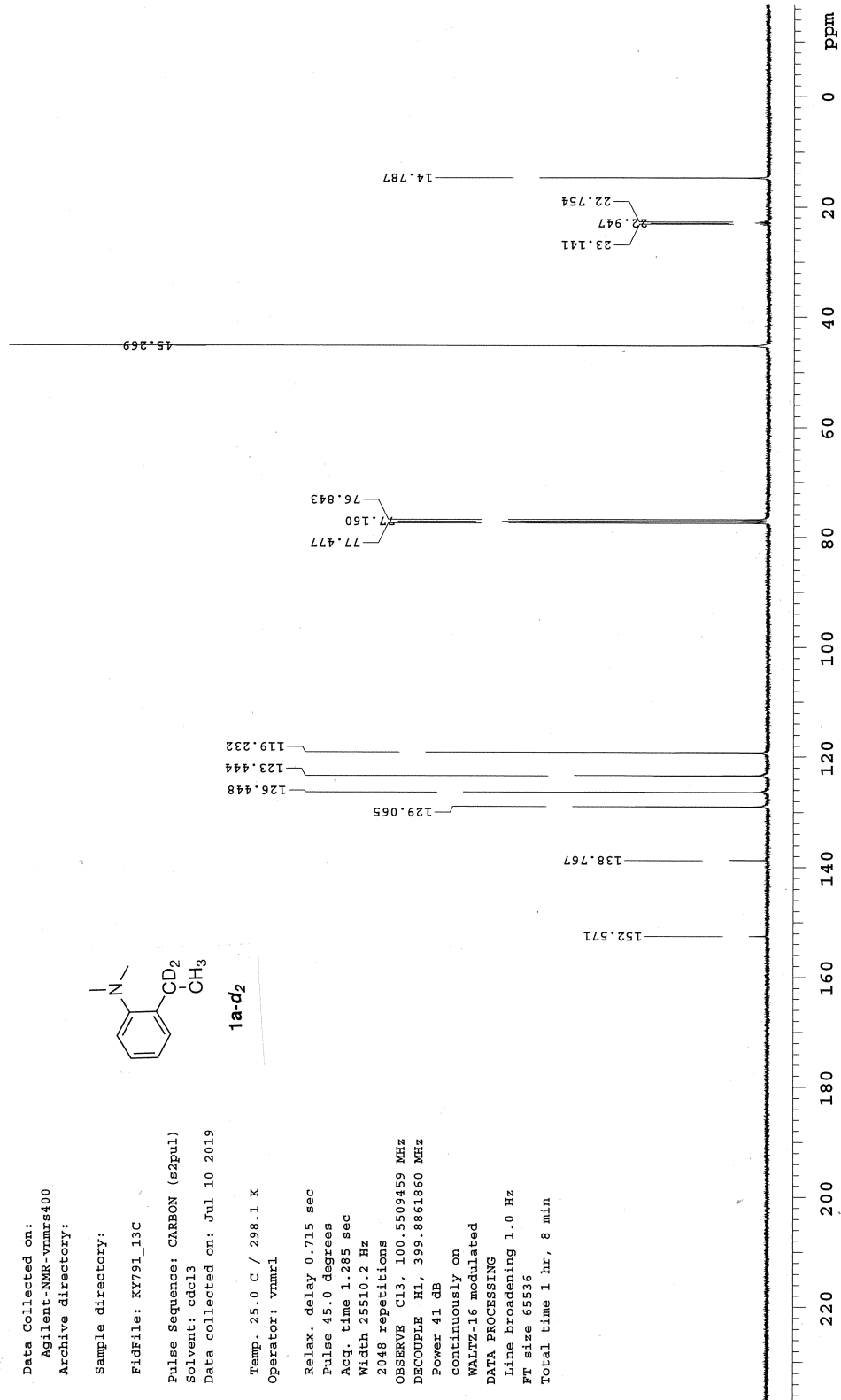


Figure S98. ¹³C NMR Spectrum of 1a-d₂ (101 MHz, CDCl₃)

STANDARD PROTON PARAMETERS

Sample Name:
Data Collected on:
Agilent-NMR-vmr400
Archive directory:
Sample directory:
FidFile: KY759
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jun 13 2019
Operator: vmr1
Relax. delay 15.000 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6410.3 Hz
16 repetitions
OBSERVE HL, 399.8841865 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 4 min 56 sec

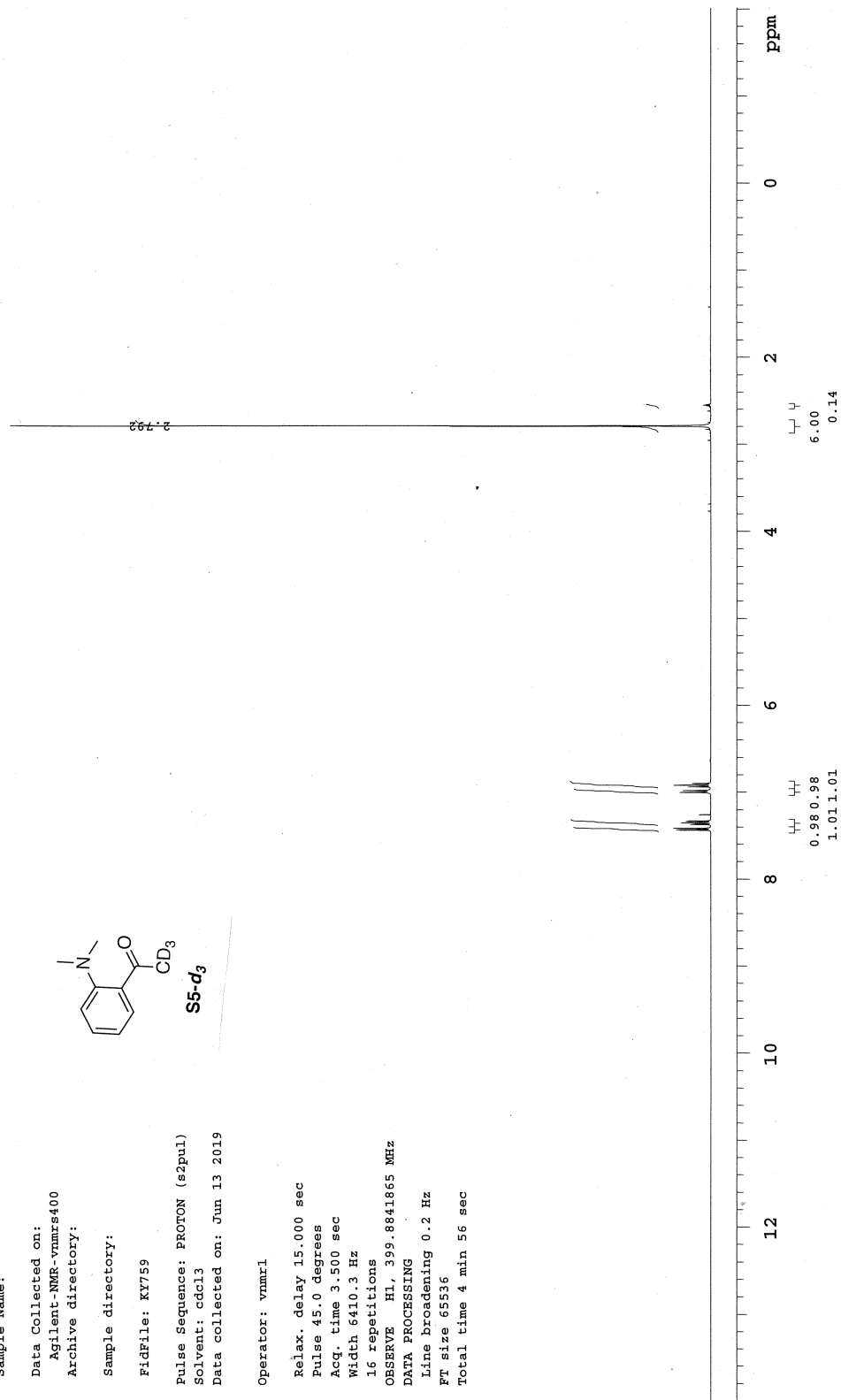
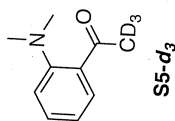


Figure S99. ¹H NMR Spectrum of S5-d₃ (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:

Data Collected on:
Agilent-NMR-vmrns400
Archive directory:

Sample directory:

FIDFile: KY759_13C

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jun 13 2019

Operator: vmr1

Relax. delay 0.715 sec

Pulse 45.0 degrees

Acq. time 1.285 sec

Width 25510.2 Hz

512 repetitions

OBSERVE C13, 100.5509498 MHz

DECOUPLE H1, 399.8861860 MHz

Power 41 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 17 min

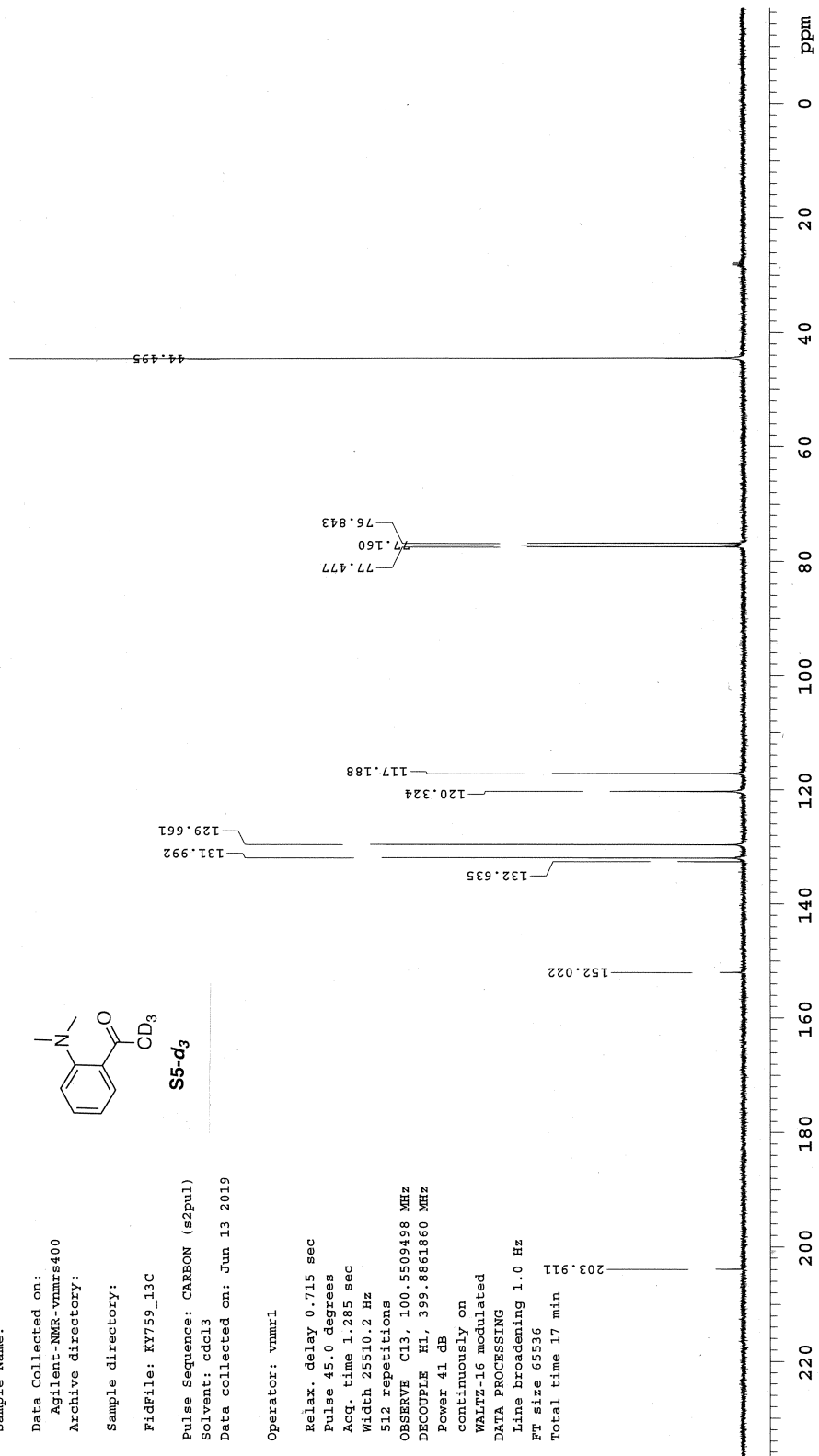


Figure S100. ¹³C NMR Spectrum of S5-d₃ (101 MHz, CDCl₃)

STANDARD PROTON PARAMETERS

Sample Name:

Data Collected on:

Agilent-NMR-vmnrs400

Archive directory:

Sample directory:

Fidfile: KY820

Pulse Sequence: PROTON (s2pul)

Solvent: cdcl3

Data collected on: Aug 2 2019

Temp. 25.0 C / 298.1 K

Operator: vmnr1

Relax. delay 15.000 sec

Pulse 45.0 degrees

Acq. time 3.500 sec

Width 6410.3 Hz

16 repetitions

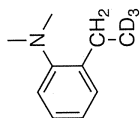
OBSERVE HL, 399.8841859 MHz

DATA PROCESSING

Line broadening 0.2 Hz

FT size 65536

Total time 4 min 56 sec



1a-d₃

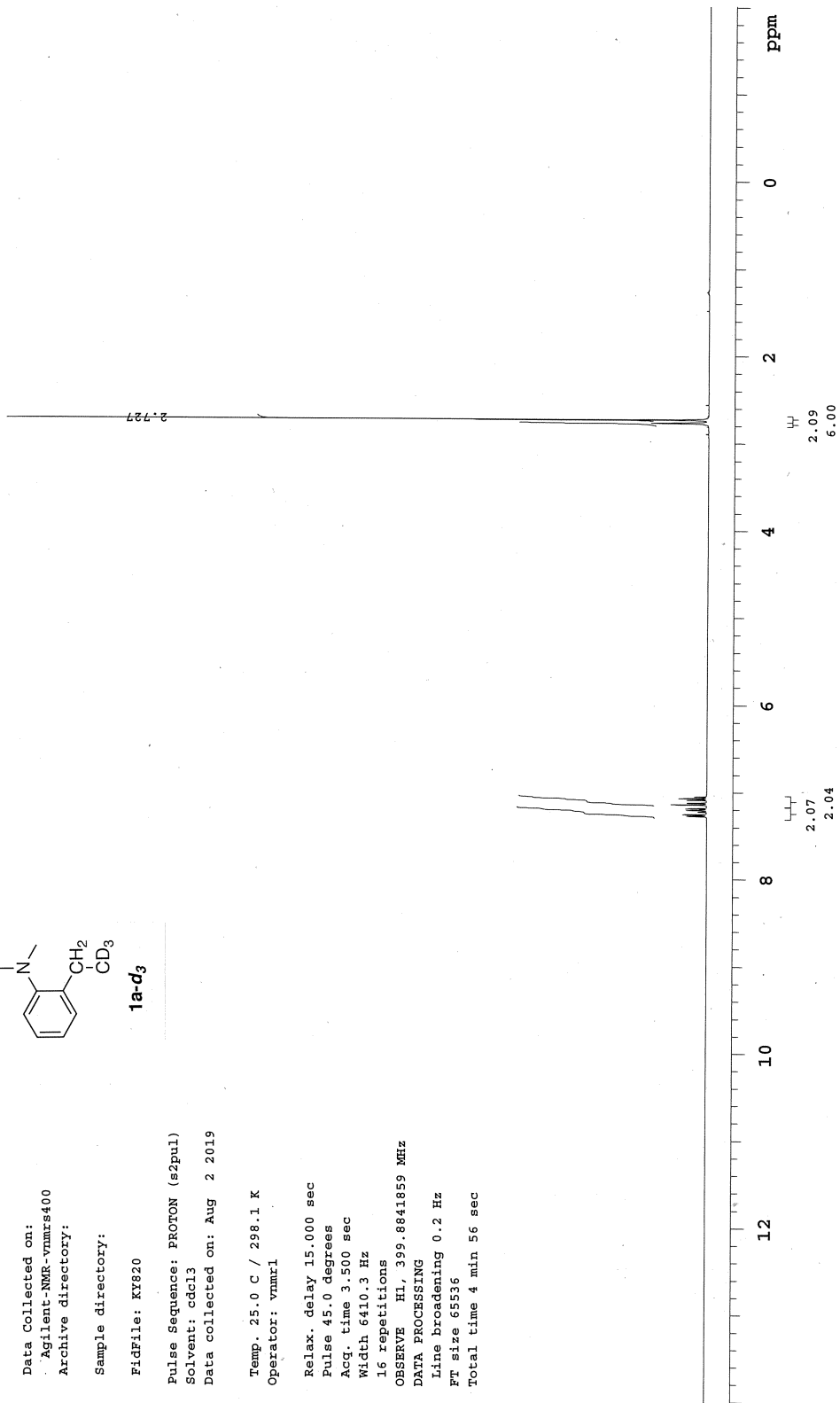


Figure S101. ¹H NMR Spectrum of 1a-d₃ (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:
 Data Collected on:
 Agilent-NMR-vmrs400
 Archive directory:
 Sample directory:
 FIDFile: KY771_13C_2
 Pulse Sequence: CARBON (s2pul)
 Solvent: cdcl3
 Data collected on: Jun 26 2019
 Operator: vmr1
 Relax. delay 0.715 sec
 Pulse 45.0 degrees
 Acq. time 1.285 sec
 Width 25510.2 Hz
 4096 repetitions
 OBSERVE C13, 100.5509459 MHz
 DECOUPLE H1, 399.8861860 MHz
 Power 41 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 2 hr, 16 min

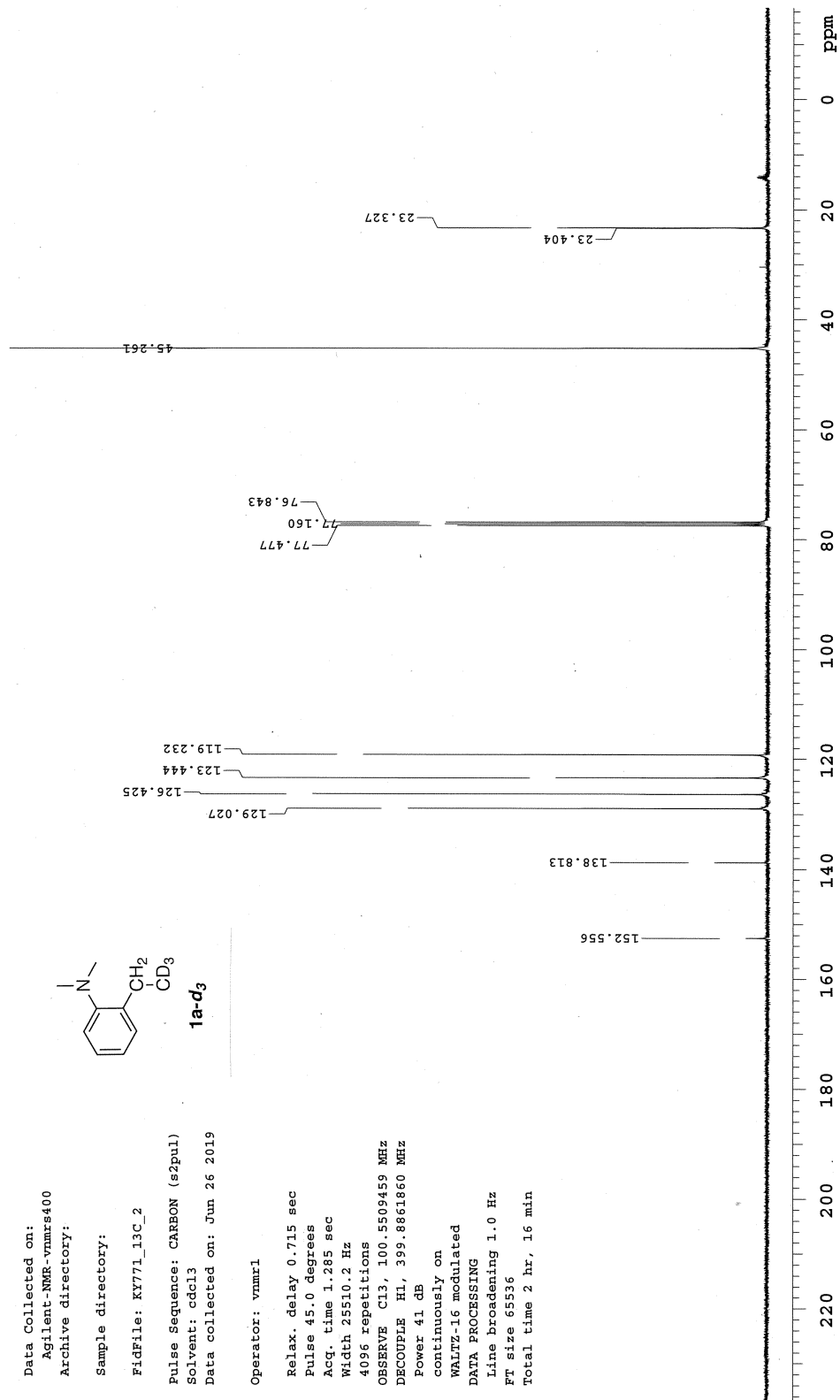
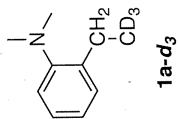


Figure S102. ¹³C NMR Spectrum of **1a-d₃** (101 MHz, CDCl₃)

STANDARD PROTON PARAMETERS

Sample Name:
 Data Collected on:
 Agilent-NMR-vmnrs400
 Archive directory:
 Sample directory:
 Fidfile: KY810
 Pulse Sequence: PROTON (szpul)
 Solvent: cdcl3
 Data collected on: Jul 25 2019
 Temp. 25.0 C / 298.1 K
 Operator: vnmr1
 Relax. delay 15.000 sec
 Pulse 45.0 degrees
 Acq. time 3.500 sec
 Width 6410.3 Hz
 16 repetitions
 OBSERVE H1, 399.8841863 MHz
 DATA PROCESSING
 Line broadening 0.2 Hz
 Ft size 65536
 Total time 4 min 56 sec

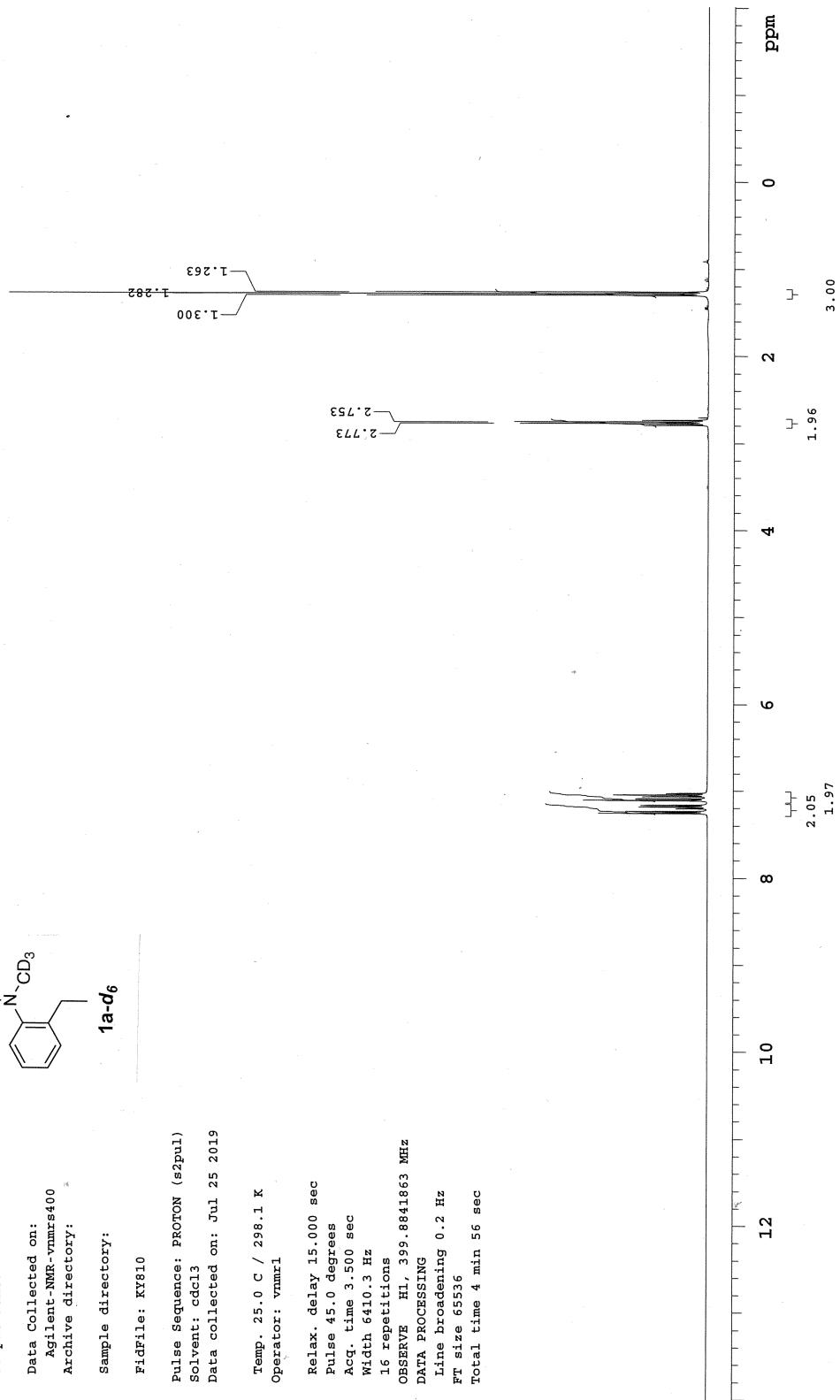
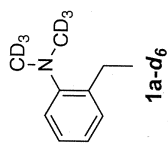
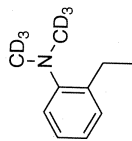


Figure S103. ¹H NMR Spectrum of **1a-d₆** (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:
 Data Collected on:
 Agilent-NMR-vmrs400
 Archive directory:
 Sample directory:
 Fidfile: KY810_13C
 Pulse Sequence: CARBON (s2pul)
 Solvent: cdcl3
 Data collected on: Jul 25 2019

Temp. 25.0 C / 298.1 K
 Operator: vnmr1
 Relax. delay 0.715 sec
 Pulse 45.0 degrees
 Acq. time 1.285 sec
 Width 25510.2 Hz
 4096 repetitions
 OBSERVE C13, 100.5509459 MHz
 DECOUPLE H1, 399.8861860 MHz
 Power 41 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 2 hr, 16 min



1a-d₆

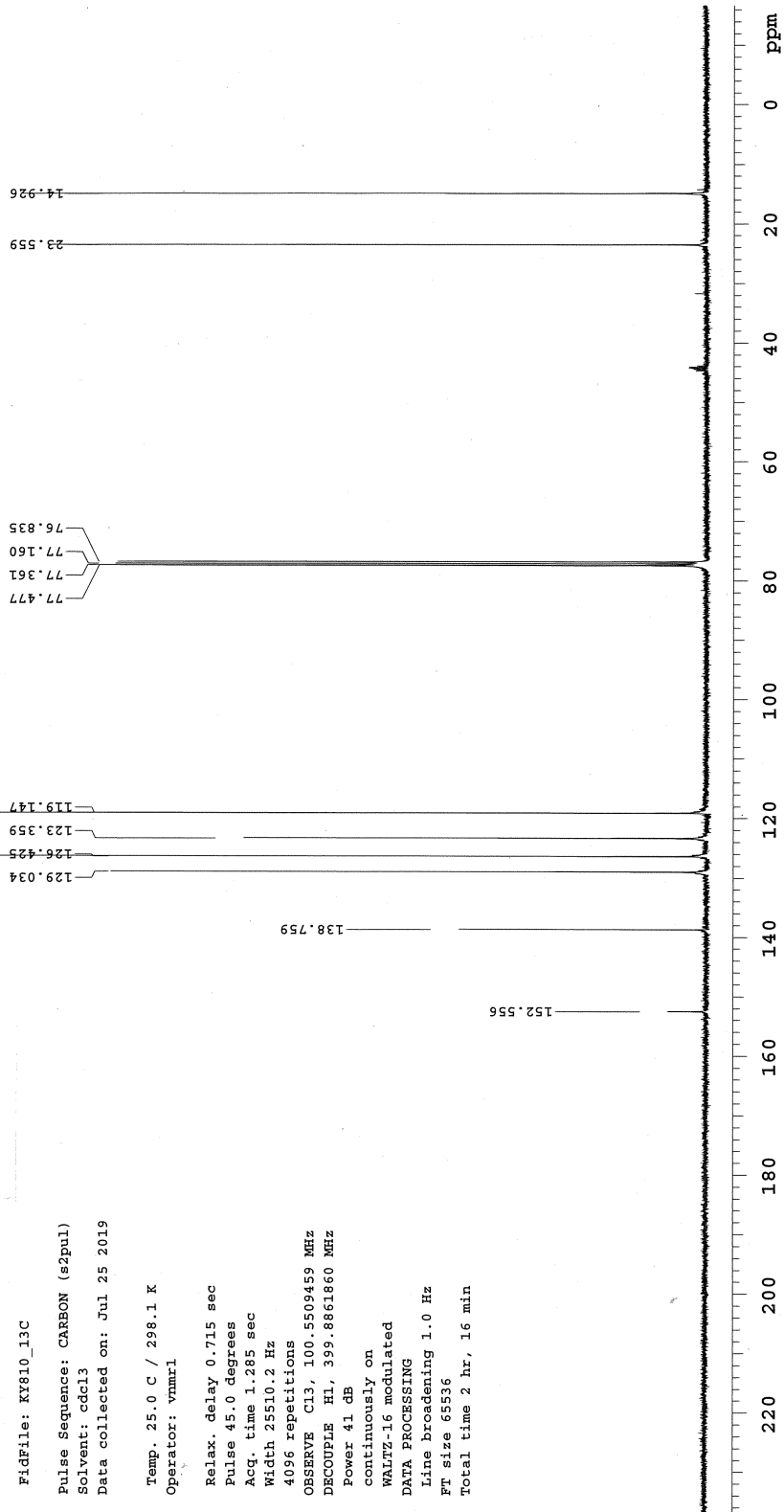


Figure S104. ¹³C NMR Spectrum of 1a-d₆ (101 MHz, CDCl₃)

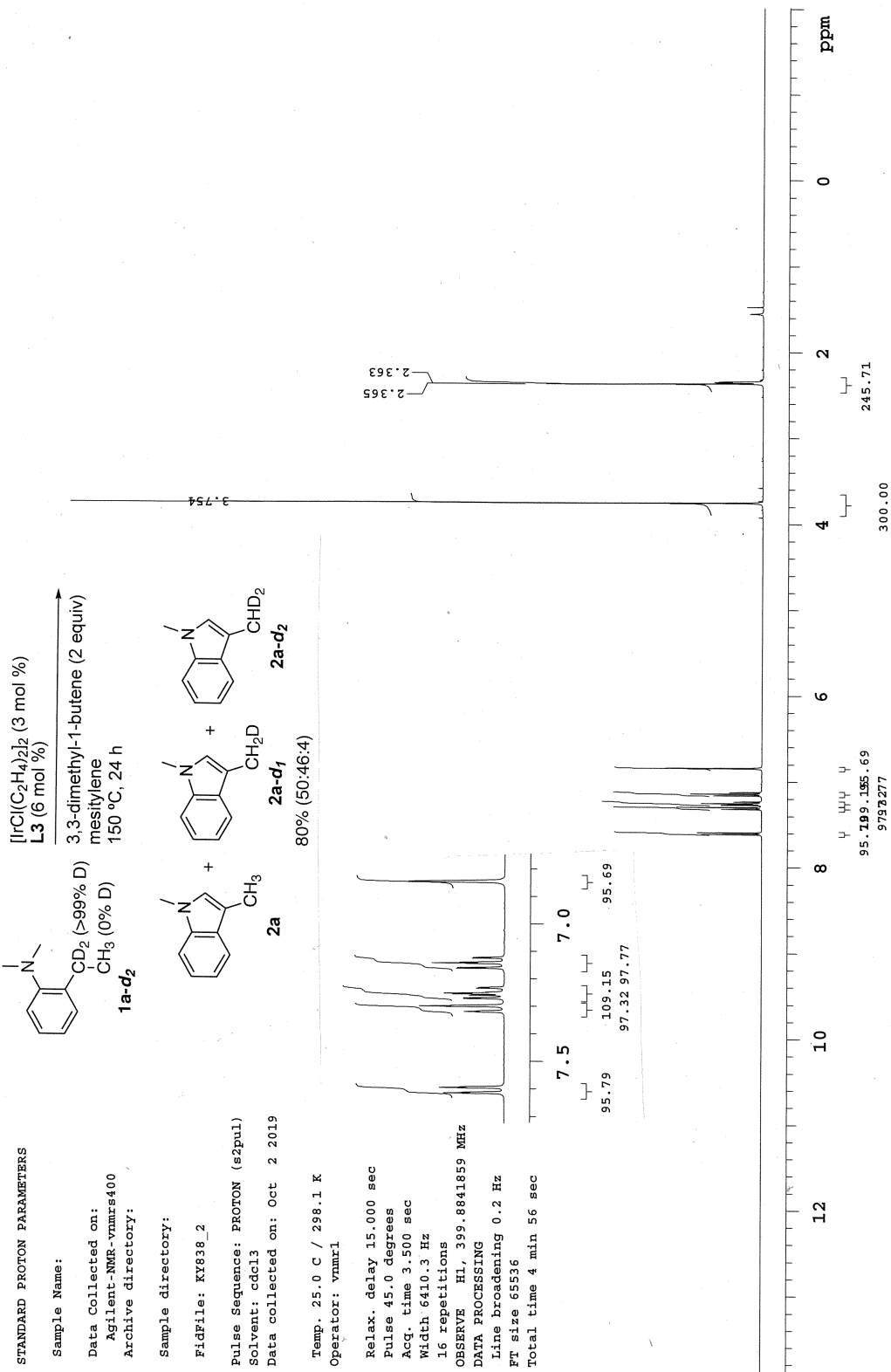


Figure S105. ^1H NMR Spectrum for the Reaction of **1a-d₂** (400 MHz, CDCl_3)

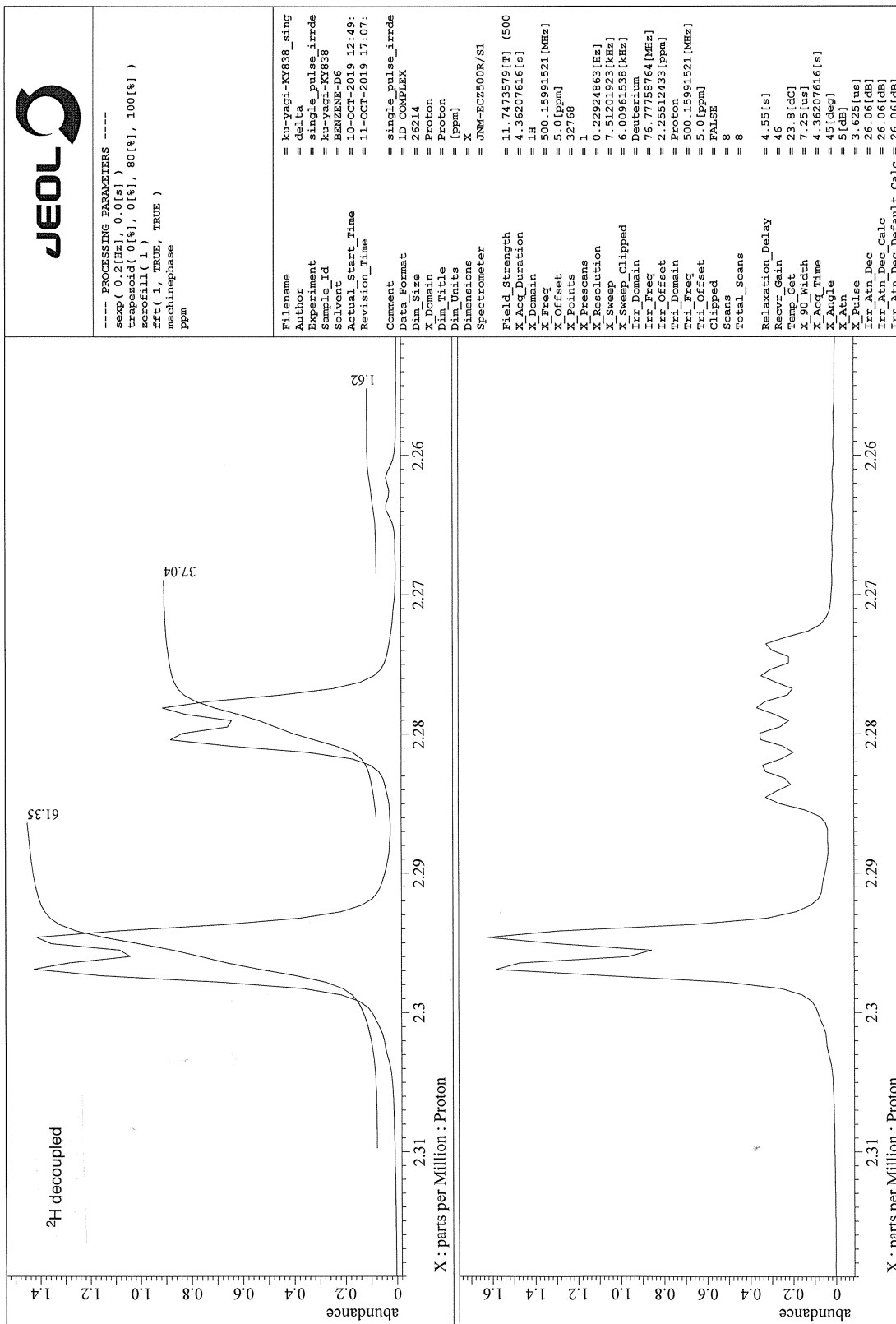


Figure S106. ¹H NMR Spectrum for the Reaction of **1a-d₂**, Expansion (500 MHz, C₆D₆)

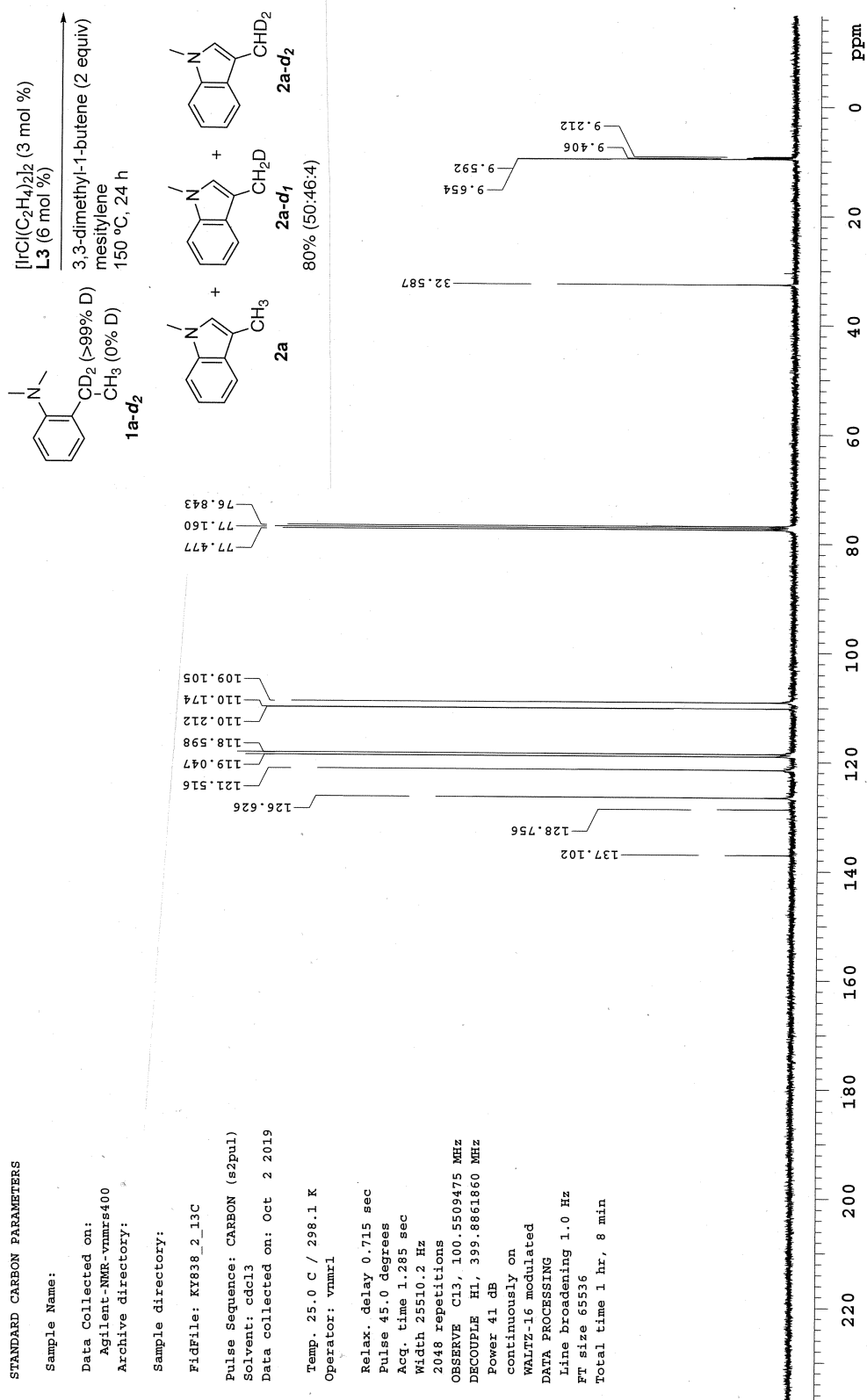


Figure S107. ¹³C NMR Spectrum for the Reaction of **1a-d₂** (101 MHz, CDCl₃)

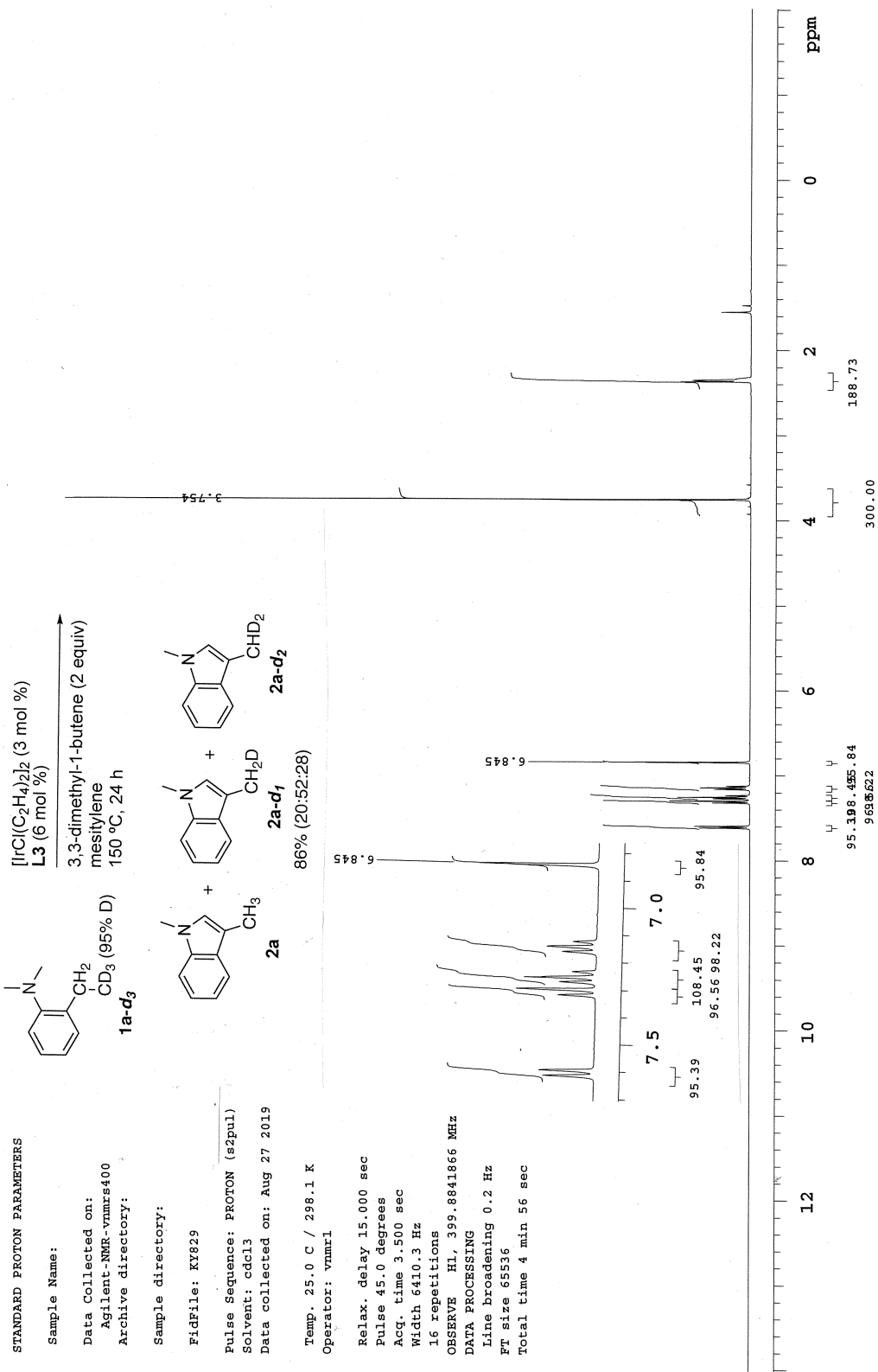


Figure S108. ^1H NMR Spectrum for the Reaction of **1a-d₃** (400 MHz, CDCl_3)

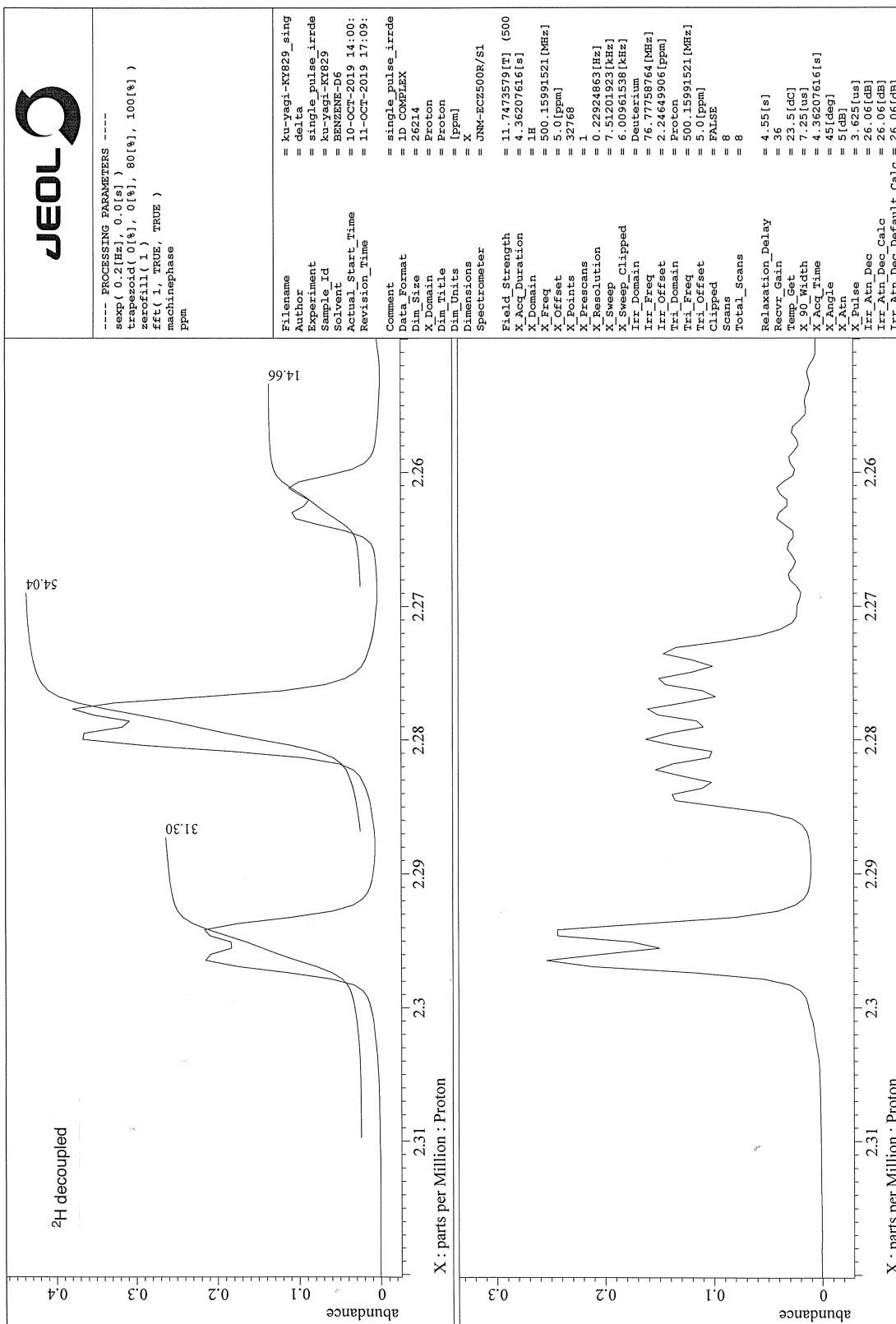


Figure S109. ^1H NMR Spectrum for the Reaction of **1a-d₃**, Expansion (500 MHz, C_6D_6)

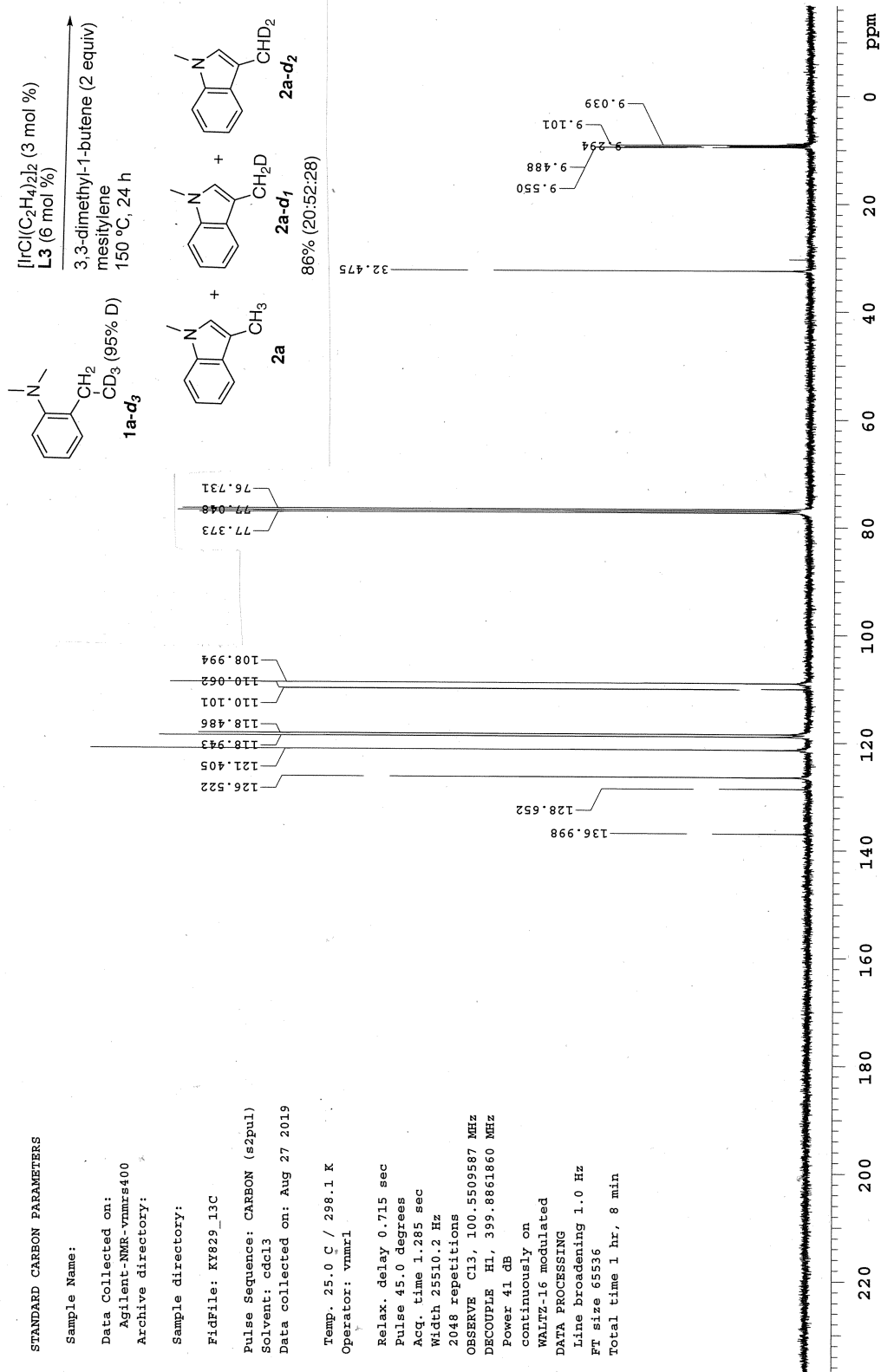


Figure S110. ^{13}C NMR Spectrum for the Reaction of **1a-d₃** (101 MHz, CDCl_3)

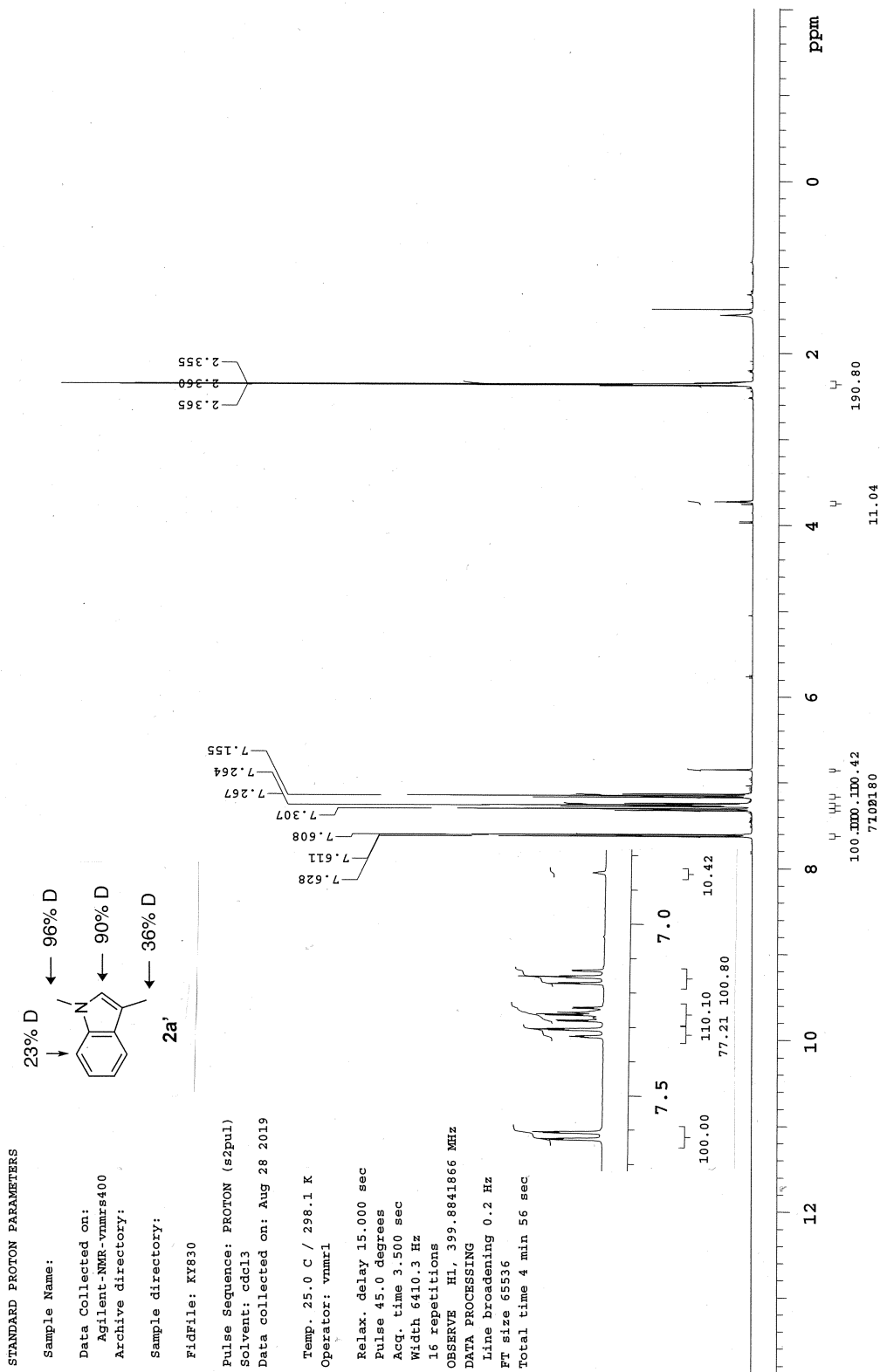


Figure S111. ^1H NMR Spectrum of **2a'** (400 MHz, CDCl_3)

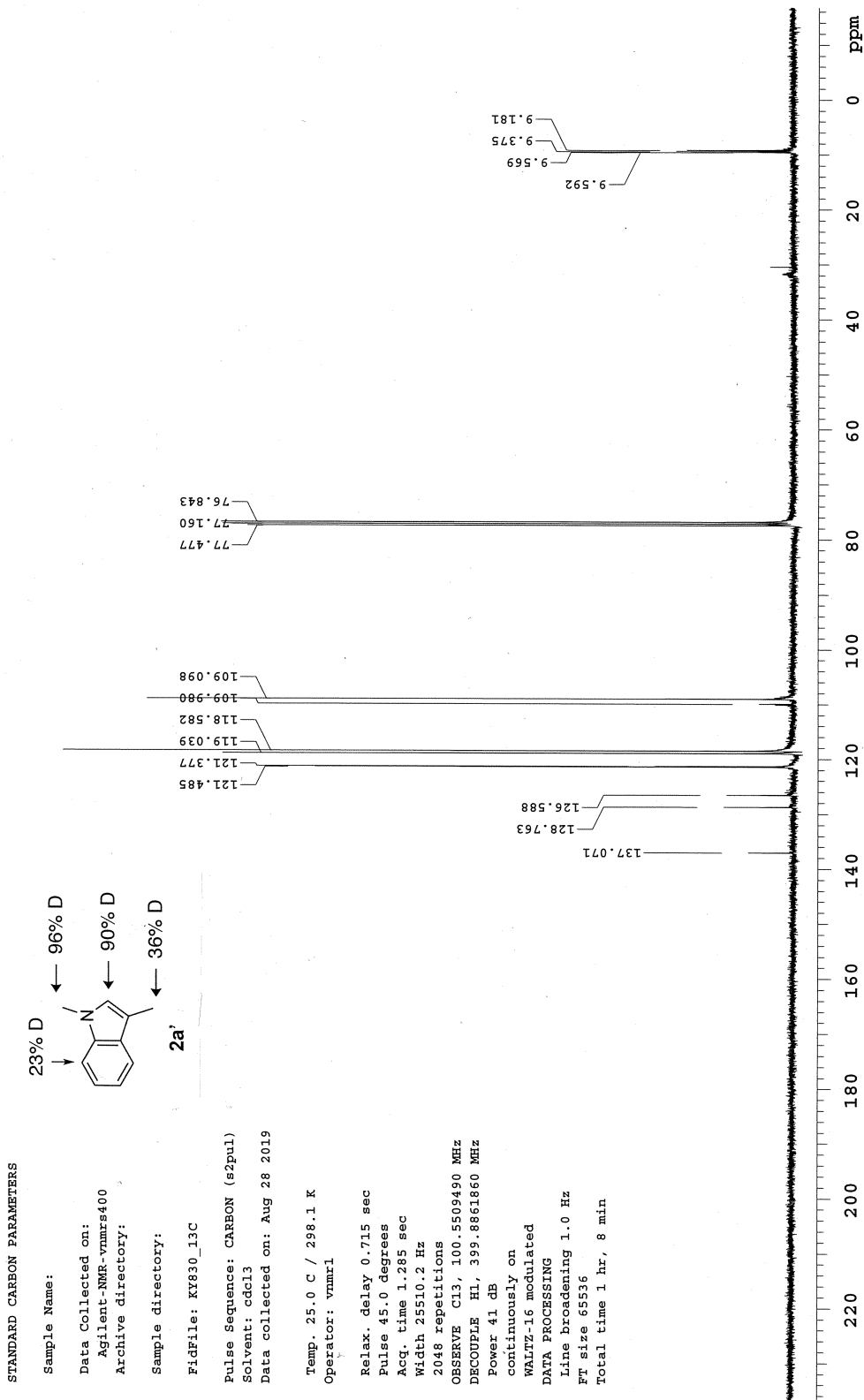


Figure S112. ^{13}C NMR Spectrum of **2a'** (101 MHz, CDCl_3)

STANDARD PROTON PARAMETERS

Sample Name:

Data Collected on:
Agilent-NMR-vmr400
Archive directory:

Sample directory:

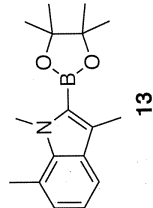
File: KY683

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr 14 2019

Temp. 25.0 C / 298.1 K
Operator: vmr1

Relax. delay 15.000 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6410.3 Hz

16 repetitions
OBSERVE H1, 399.8841861 MHz
DATA PROCESSING
Line broadening 0.2 Hz
Ft size 65536
Total time 4 min 56 sec



13

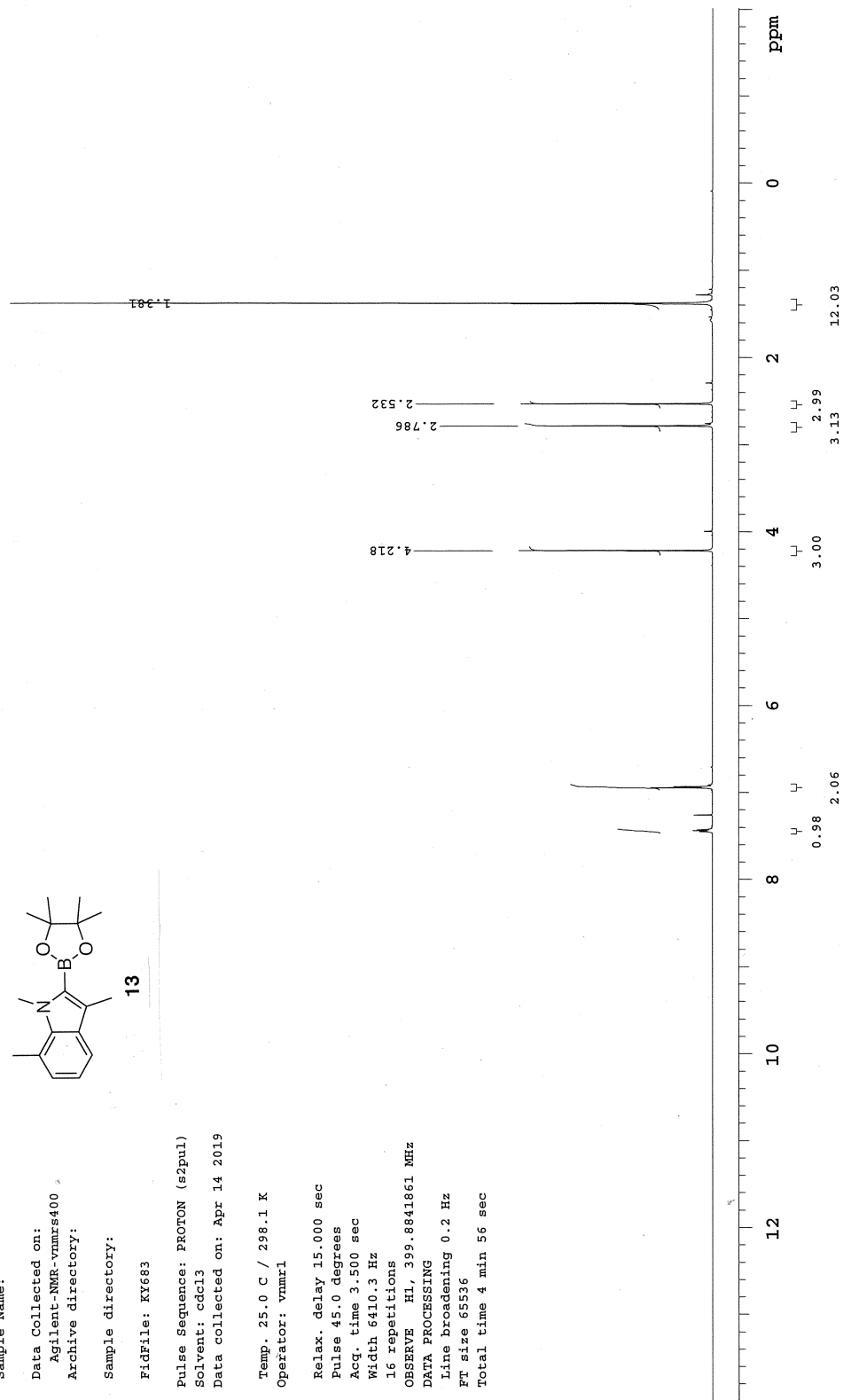


Figure S113. ¹H NMR Spectrum of 13 (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:

Data Collected on:

Agilent-NMR-vmrns400 2

Archive directory:

Sample directory:

File: KY683_13C

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Apr 14 2019

Temp. 25.0 C / 298.1 K

Operator: vmr1

Relax. delay 0.715 sec

Pulse 45.0 degrees

Acq. time 1.285 sec

Width 25510.2 Hz

512 repetitions

OBSERVE C13, 100.5509443 MHZ

DECOUPLE H1, 399.8861860 MHZ

Power 41 dB

continuously on

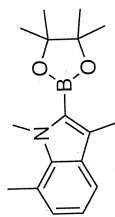
WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 17 min



13

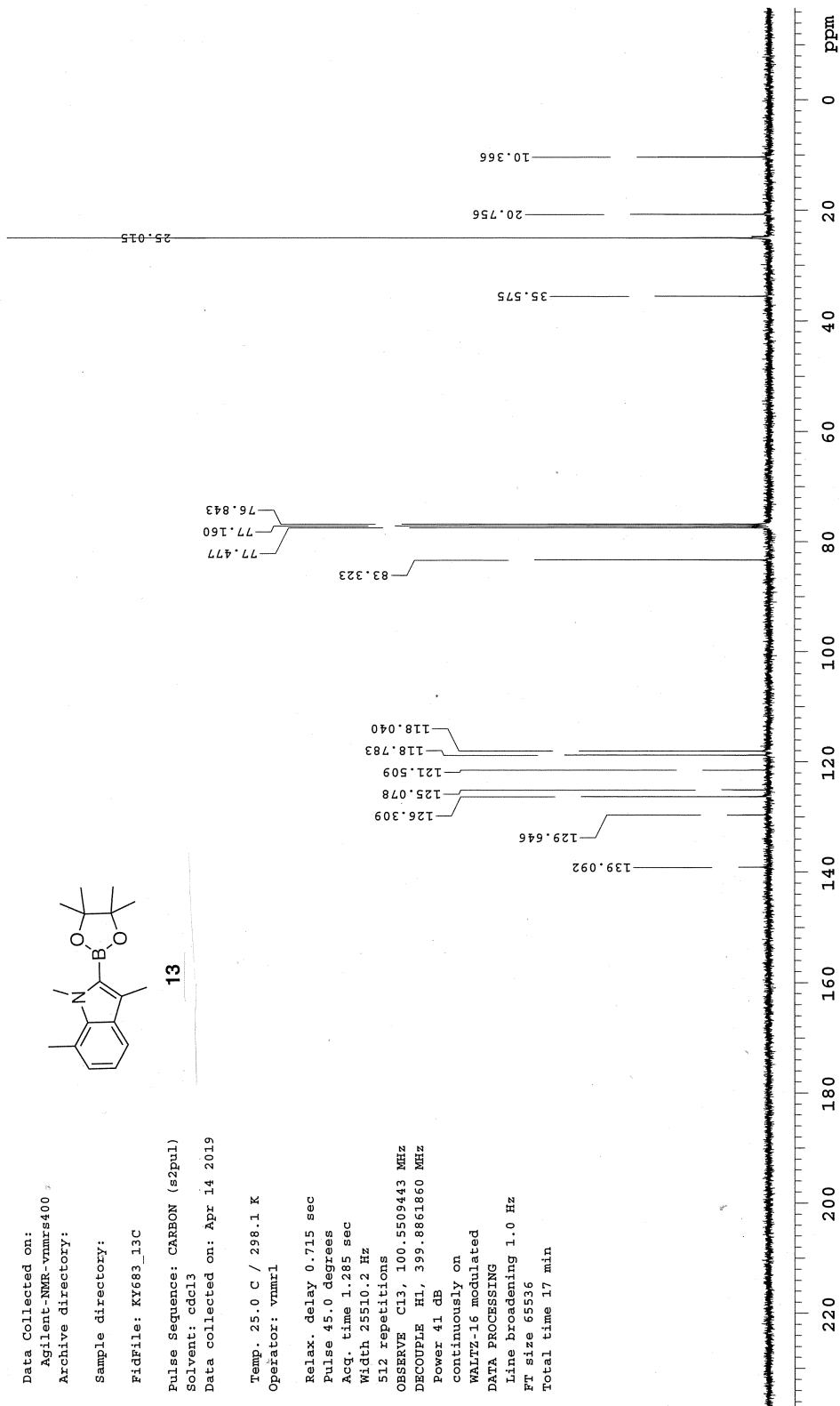
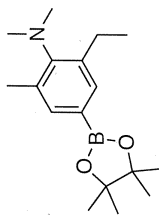


Figure S114. ¹³C NMR Spectrum of 13 (101 MHz, CDCl₃)

STANDARD PROTON PARAMETERS

Sample Name:
 Data Collected on: Agilent-NMR-vmrs400
 Archive directory:
 Sample directory:
 FidFile: KY622
 Pulse Sequence: PROTON (s2pul)
 Solvent: cdcl3
 Data collected on: Feb 24 2019
 Temp. 25.0 C / 298.1 K
 Operator: vnmr1
 Relax. delay 15.000 sec
 Pulse 45.0 degrees
 Acq. time 3.500 sec
 Width 6410.3 Hz
 16 repetitions
 OBSERVE H1, 399.8841855 MHz
 DATA PROCESSING
 Line broadening 0.2 Hz
 FT size 65536
 Total time 4 min 56 sec



14

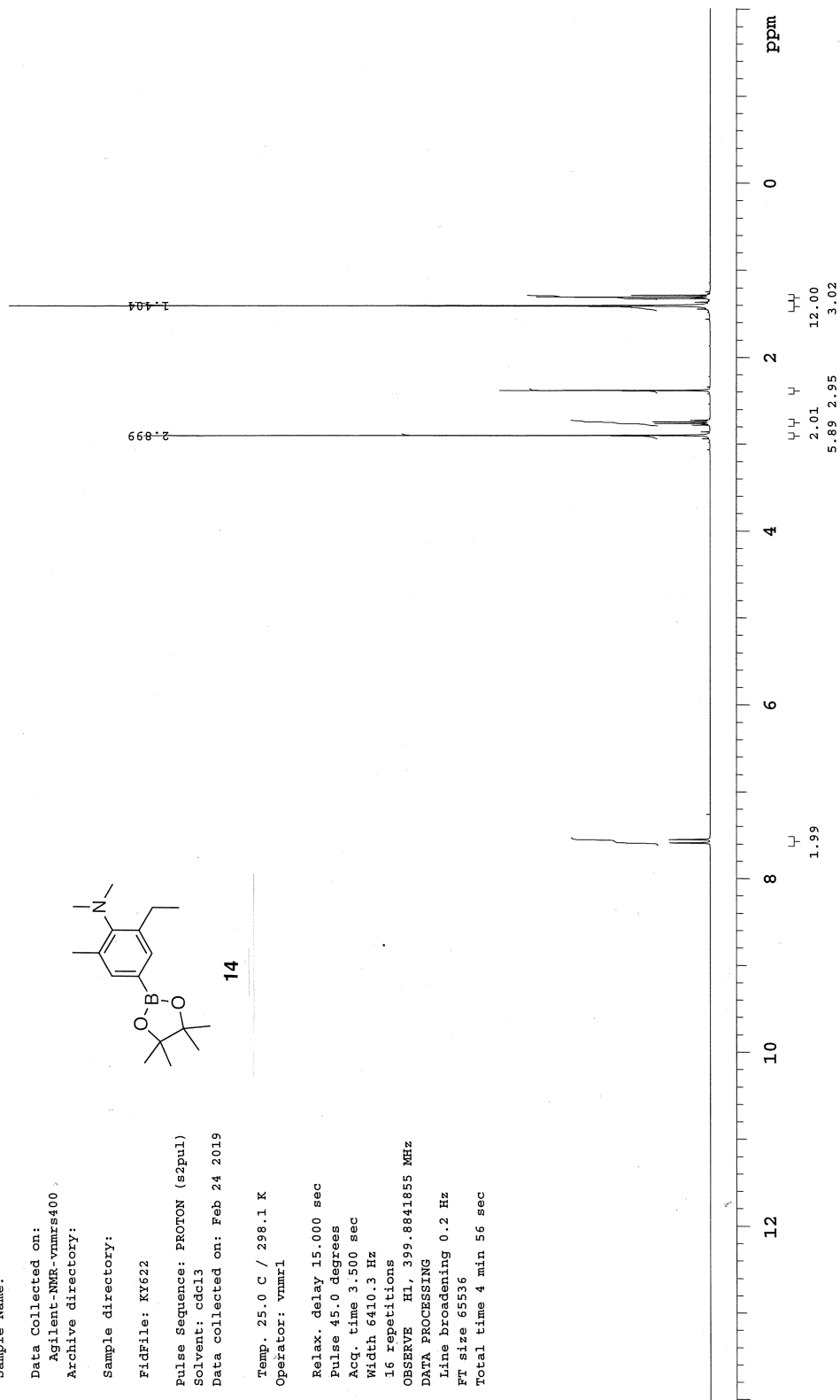


Figure S115. ¹H NMR Spectrum of 14 (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:

Data Collected on:

Agilent-NMR-vmr400

Archive directory:

Sample directory:

Fidfile: KY622_13C

14

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Feb 24 2019

Temp. 25.0 C / 298.1 K

Operator: vmr1

Relax. delay 0.715 sec

Pulse 45.0 degrees

Acq. time 1.285 sec

Width 25510.2 Hz

512 repetitions

OBSERVE C13, 100.5509568 MHz

DECOUPLE H1, 399.8861860 MHz

Power 41 dB

continuously on

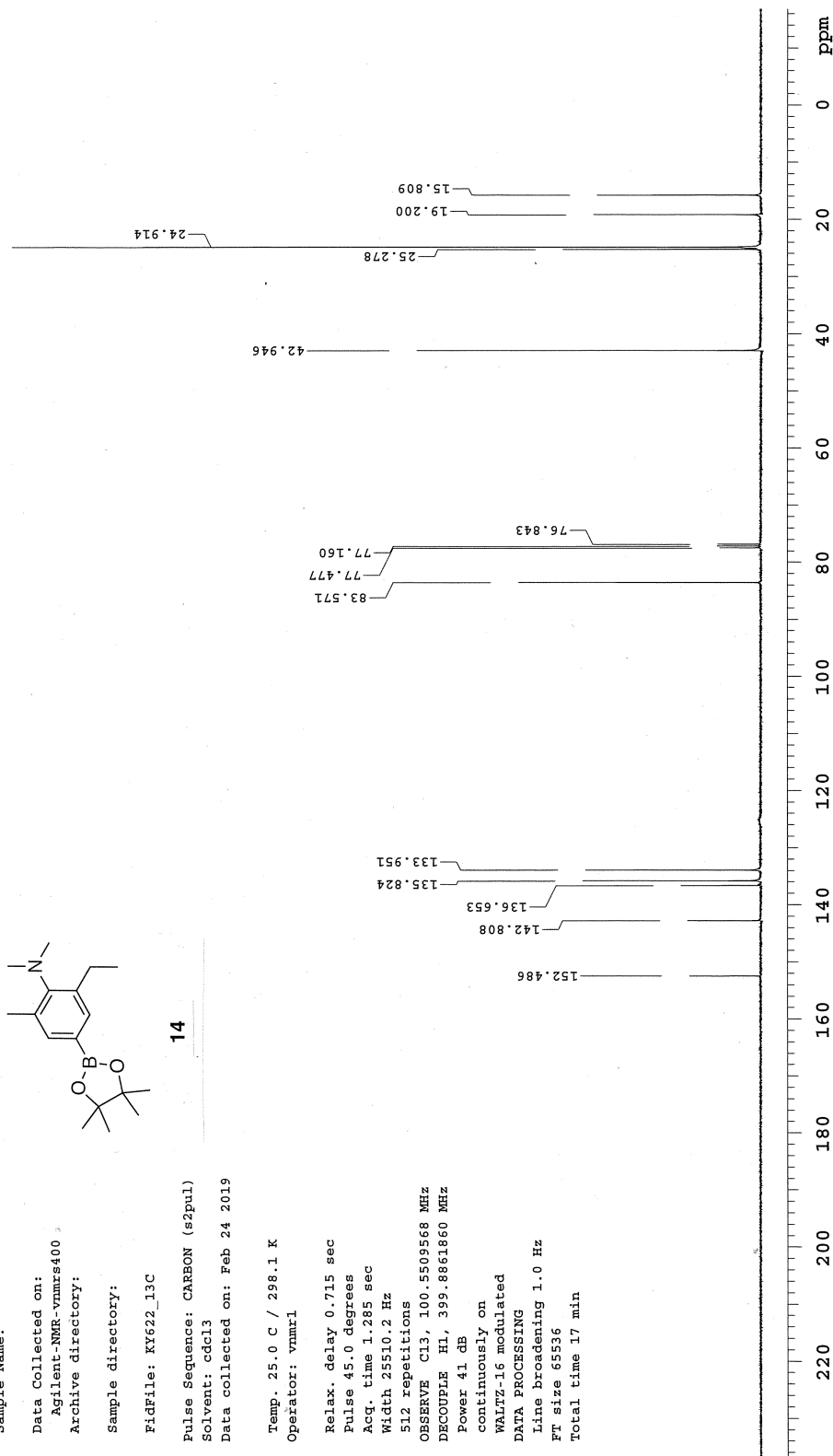
WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 17 min

Figure S116. ^{13}C NMR Spectrum of 14 (101 MHz, CDCl_3)

STANDARD PROTON PARAMETERS

Sample Name:

Data Collected on:

Agilent-NMR-vnmrs400

Archive directory:

Sample directory:

FidFile: K1651_2

Pulse Sequence: PROTON (s2pul)

Solvent: cdcl3

Data collected on: Jul 9 2019

Temp. 25.0 C / 298.1 K

Operator: vnmr1

Relax. delay 15.000 sec

Pulse 45.0 degrees

Acq. time 3.500 sec

Width 6410.3 Hz

16 repetitions

OBSERVE H1, 399.8841863 MHZ

DATA PROCESSING

Line broadening 0.2 Hz

FT size 65536

Total time 4 min 56 sec

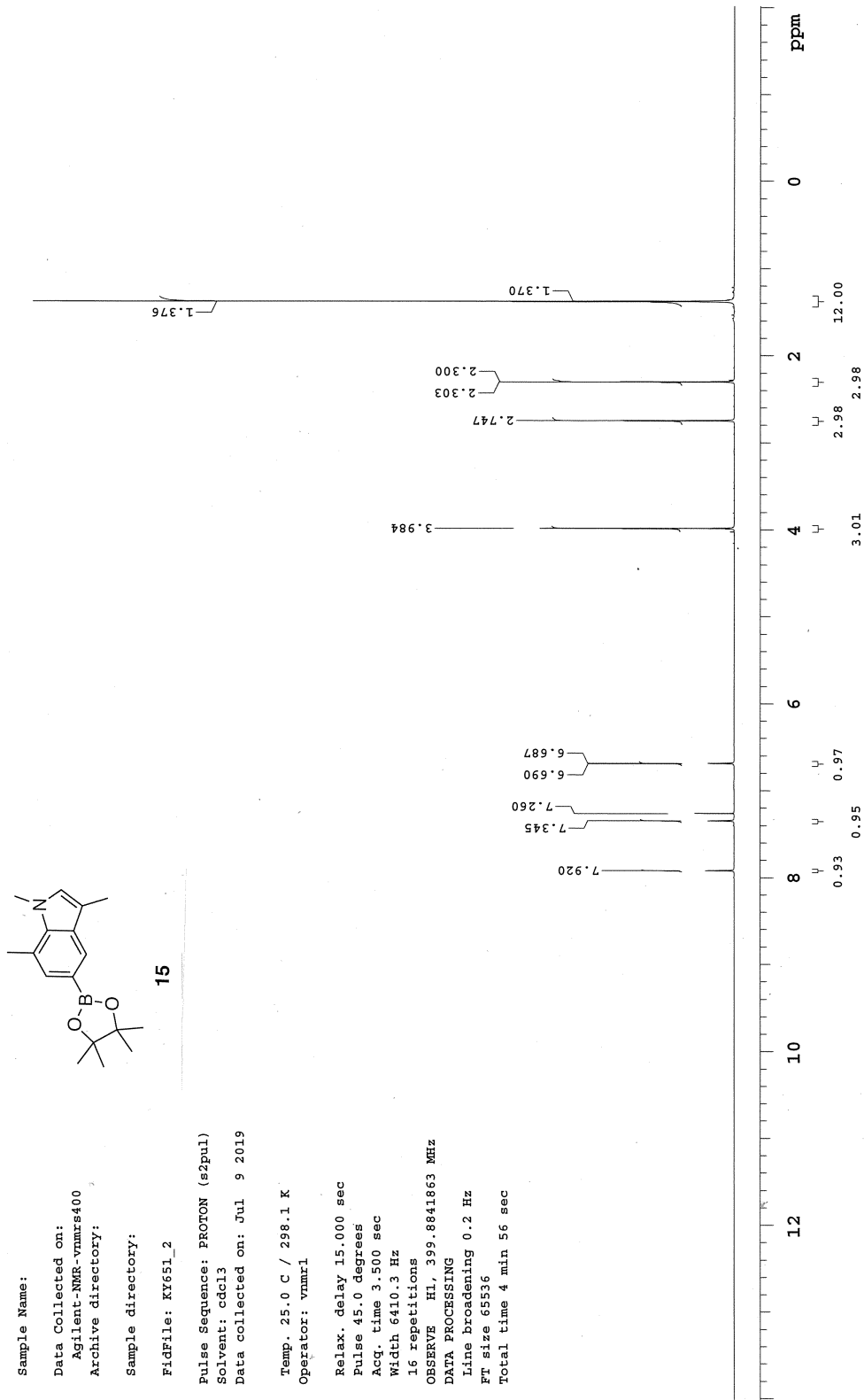


Figure S117. ¹H NMR Spectrum of 15 (400 MHz, CDCl₃)

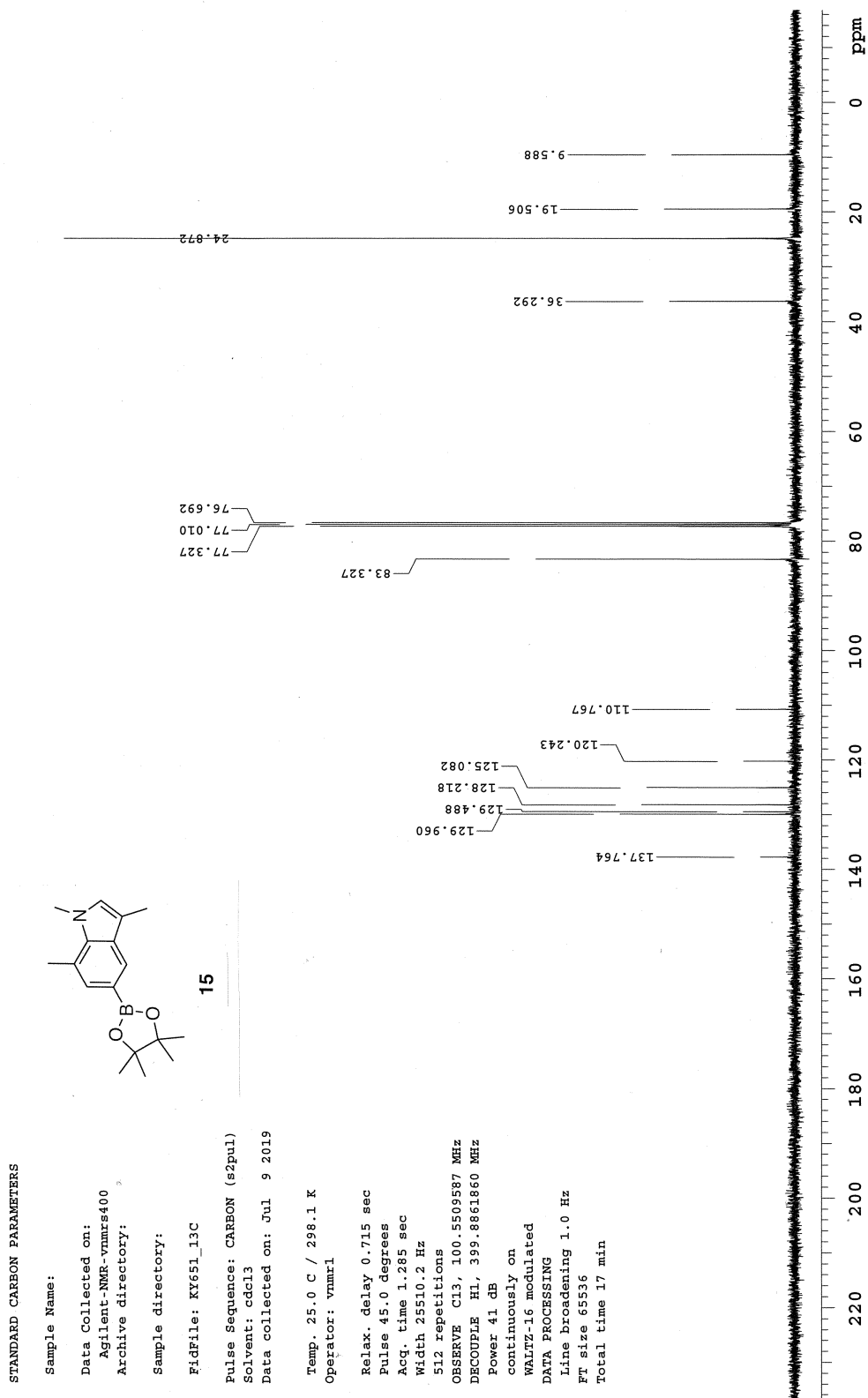
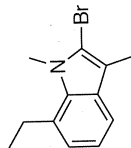


Figure S118. ¹³C NMR Spectrum of 15 (101 MHz, CDCl₃)

STANDARD PROTON PARAMETERS

Sample Name:
 Data Collected on:
 Agilent-NMR-vmnrs400
 Archive directory:
 Sample directory:
 FidFile: KY772
 Pulse Sequence: PROTON (s2pul)
 Solvent: cdcl3
 Data collected on: Jun 24 2019
 Operator: vmnr1
 Relax. delay 15.000 sec
 Pulse 45.0 degrees
 Acq. time 3.500 sec
 Width 6410.3 Hz
 16 repetitions
 OBSERVE HL, 399.8841867 MHz
 DATA PROCESSING
 Line broadening 0.2 Hz
 FT size 65536
 Total time 4 min 56 sec



16

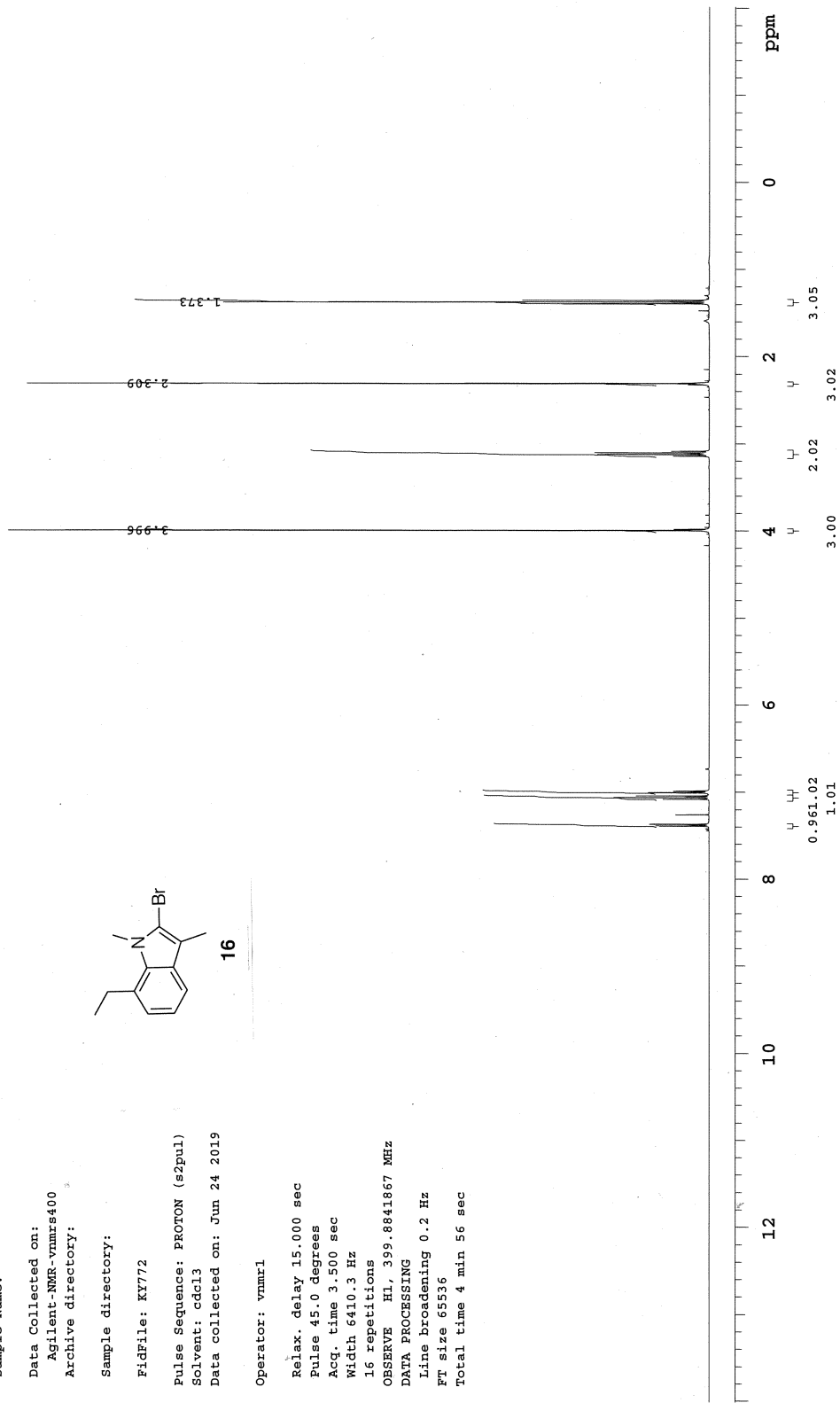
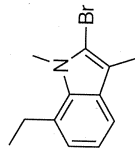


Figure S119. ¹H NMR Spectrum of 16 (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:
 Data Collected on:
 Agilent-NMR-vmrns400
 Archive directory:
 Sample directory:
 FidFile: KY772_13C
 Pulse Sequence: CARBON (szpul)
 Solvent: cdcl3
 Data collected on: Jun 24 2019
 Operator: vmr1
 Relax. delay 0.715 sec
 Pulse 45.0 degrees
 Acq. time 1.285 sec
 Width 25510.2 Hz
 512 repetitions
 OBSERVE C13, 100.5509482 MHz
 DECOUPLE H1, 399.8861860 MHz
 Power 41 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 17 min



16

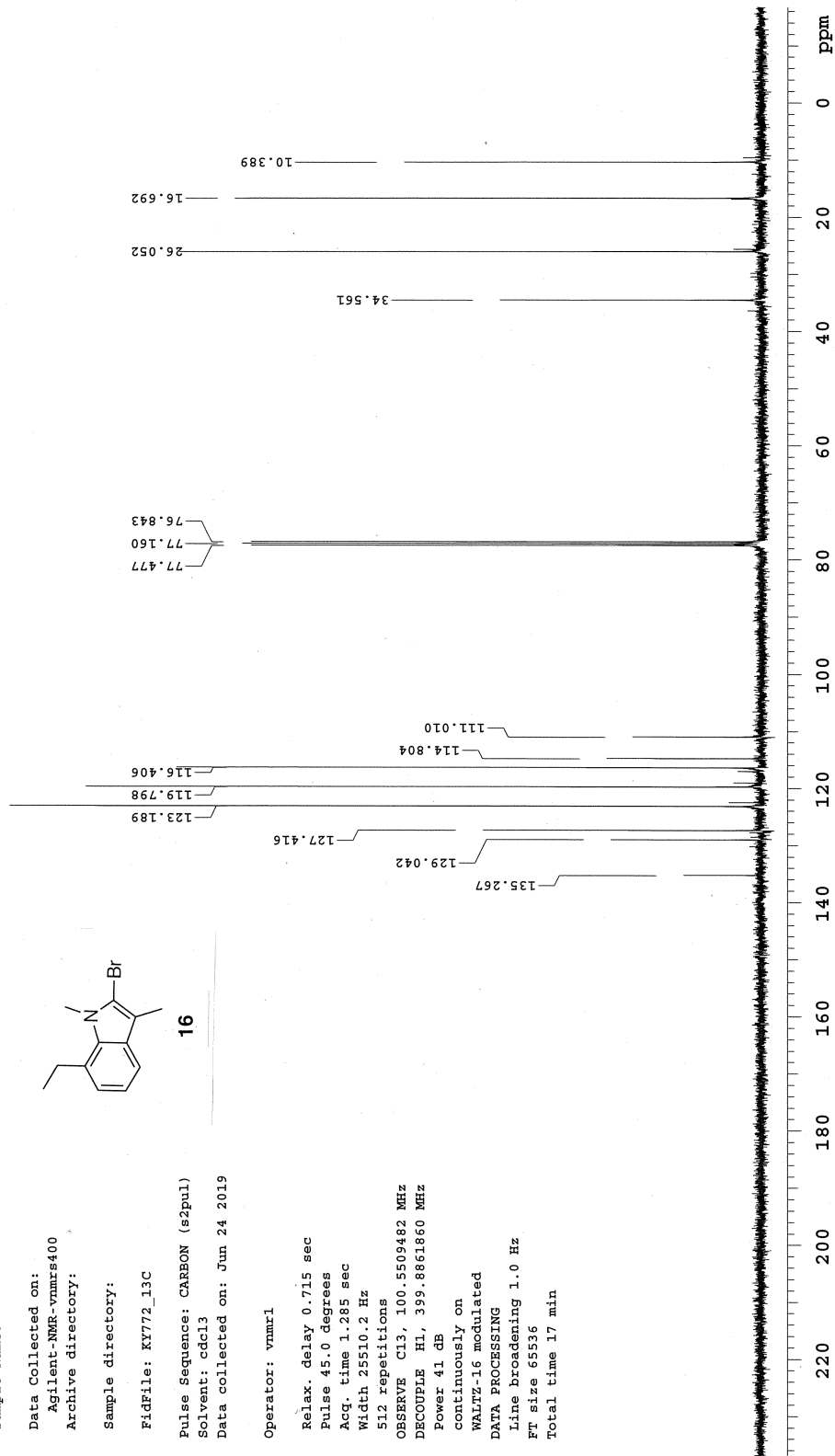


Figure S120. ¹³C NMR Spectrum of 16 (101 MHz, CDCl₃)

STANDARD PROTON PARAMETERS

Sample Name:

Data Collected on:
Agilent-NMR-vmnrs400
Archive directory:

Sample directory:

File: KY705

Pulse Sequence: PROTON (s2pul)

Solvent: cdcl3
Data collected on: May 11 2019

Operator: vnmr1

Relax. delay 15.000 sec

Pulse 45.0 degrees

Acq. time 3.500 sec

Width 6410.3 Hz

16 repetitions

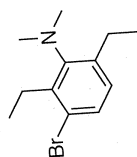
OBSERVE H1, 399.8841859 MHz

DATA PROCESSING

Line broadening 0.2 Hz

FT size 65536

Total time 4 min 56 sec



18

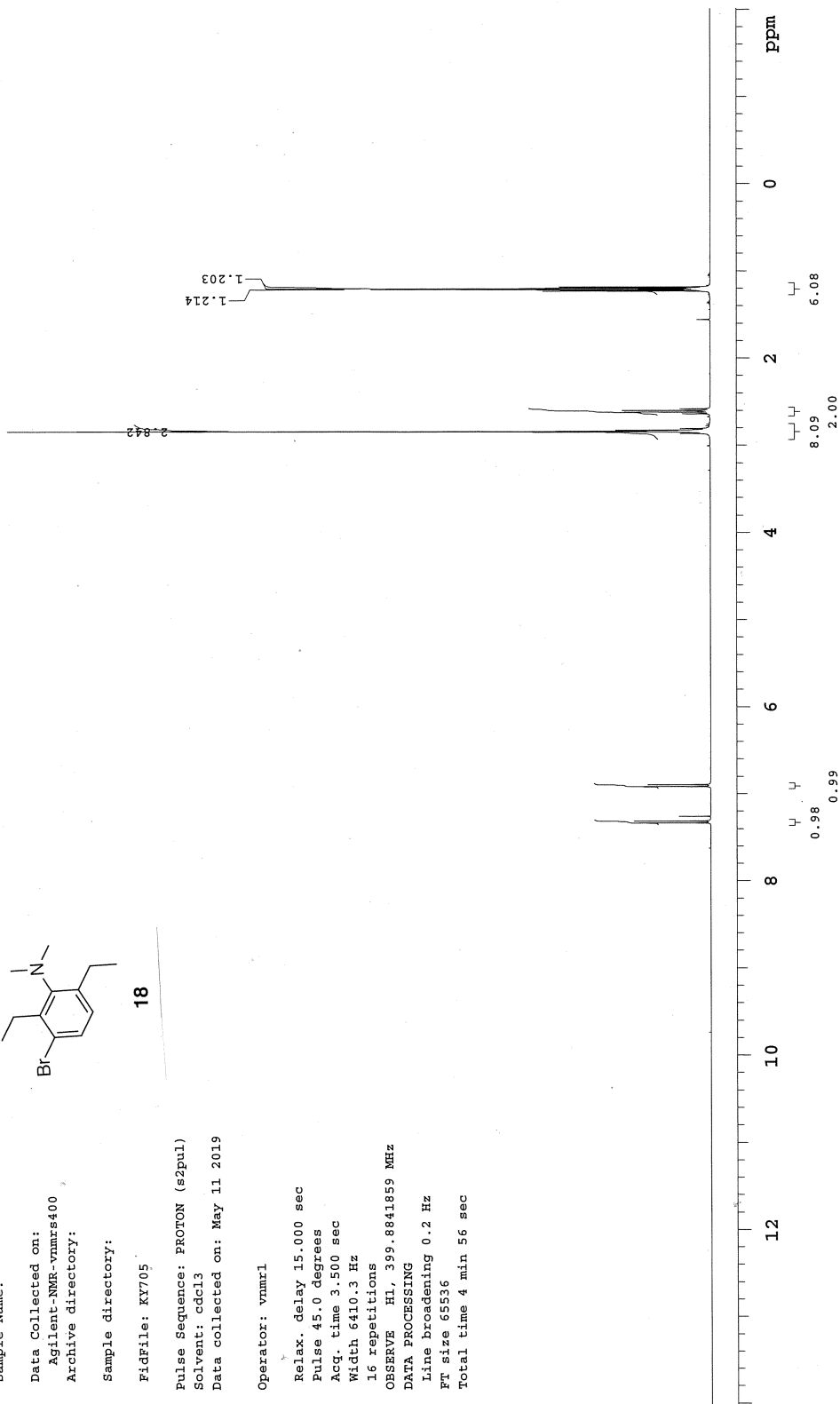


Figure S121. ¹H NMR Spectrum of 18 (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:

Data Collected on:

Agilent-NMR-vmrs400

Archive directory:

Sample directory:

File: KY705_13C_3

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Jul 6 2019

Temp. 25.0 C / 298.1 K

Operator: vnmr1

Relax. delay 0.715 sec

Pulse 45.0 degrees

Acq. time 1.285 sec

Width 25510.2 Hz

1024 repetitions

OBSERVE C13, 100.5509467 MHz

DECOUPLE H1, 399.8861860 MHz

Power 41 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 34 min

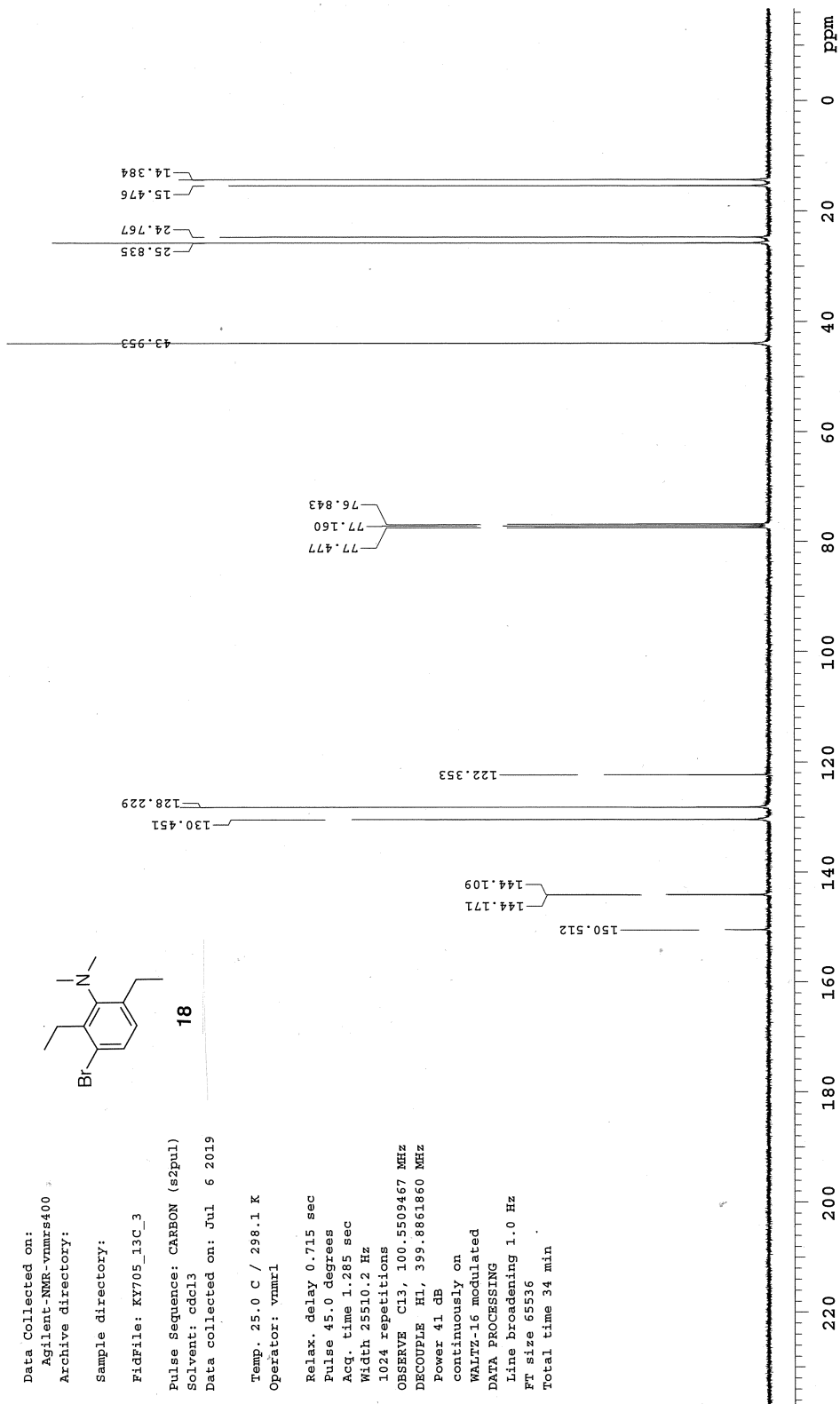
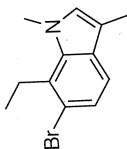


Figure S122. ¹³C NMR Spectrum of 18 (101 MHz, CDCl₃)

STANDARD PROTON PARAMETERS

Sample Name:
 Data Collected on:
 Agilent-NMR-vmms400
 Archive directory:
 Sample directory:
 File: KY695
 Pulse Sequence: PROTON (s2pul)
 Solvent: cdcl3
 Data collected on: Apr 19 2019



Operator: vmr1
 Relax. delay 15.000 sec
 Pulse 45.0 degrees
 Acq. time 3.500 sec
 Width 6410.3 Hz
 16 repetitions
 OBSERVE HL, 399.8841873 MHz
 DATA PROCESSING
 Line broadening 0.2 Hz
 FT size 65536
 Total time 4 min 56 sec

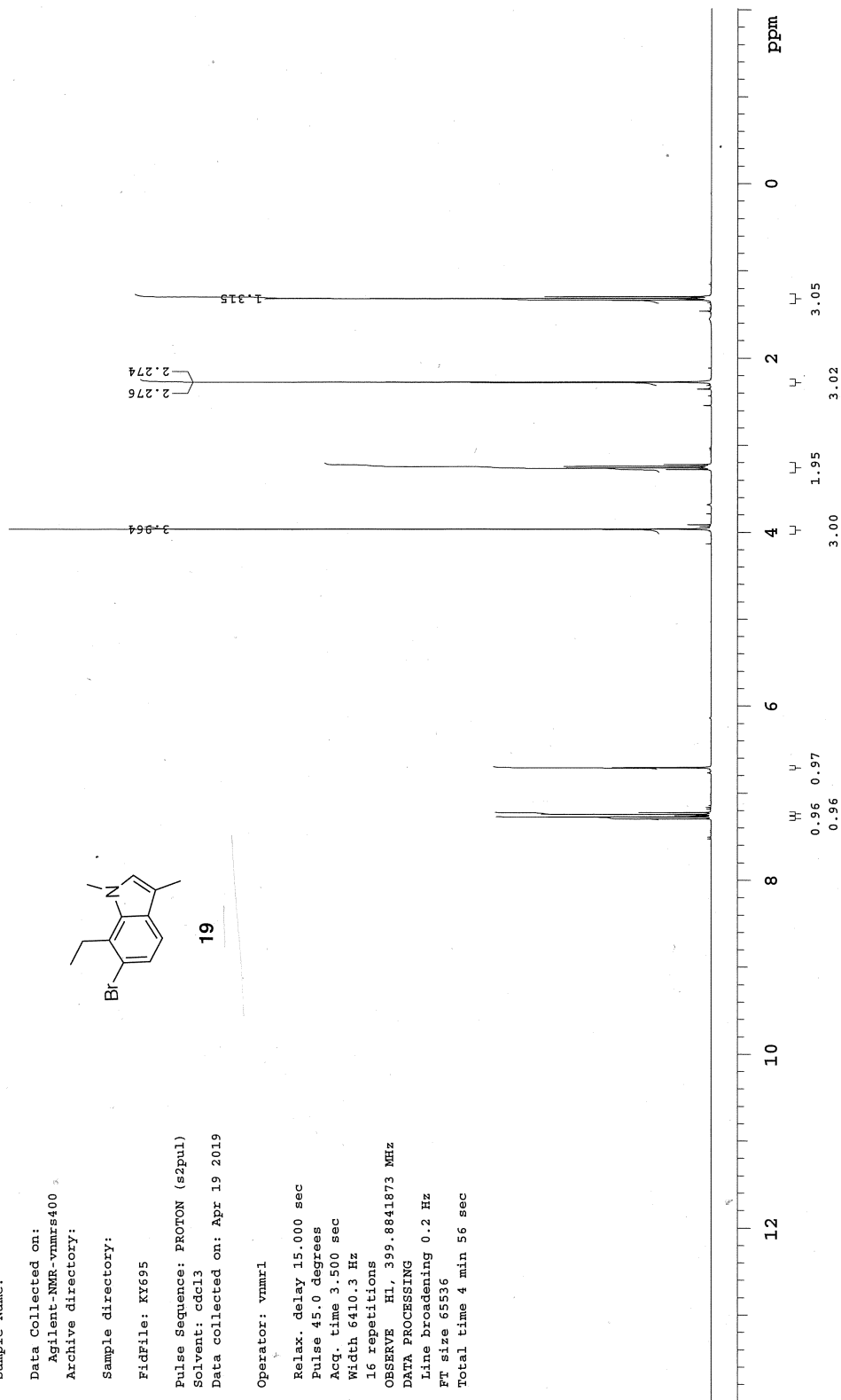


Figure S123. ¹H NMR Spectrum of **19** (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:
 Data Collected on: Agilent-NMR-vmrns400
 Archive directory:
 Sample directory:
 File: KY695_13C
 Pulse Sequence: CARBON (s2pul)
 Solvent: cdcl3
 Data collected on: Apr 19 2019

Operator: vmr1
 Relax. delay 0.715 sec
 Pulse 45.0 degrees
 Acq. time 1.285 sec
 Width 25510.2 Hz
 512 repetitions
 OBSERVE C13, 100.5509475 MHz
 DECOUPLE H1, 399.8861860 MHz
 Power 41 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 17 min

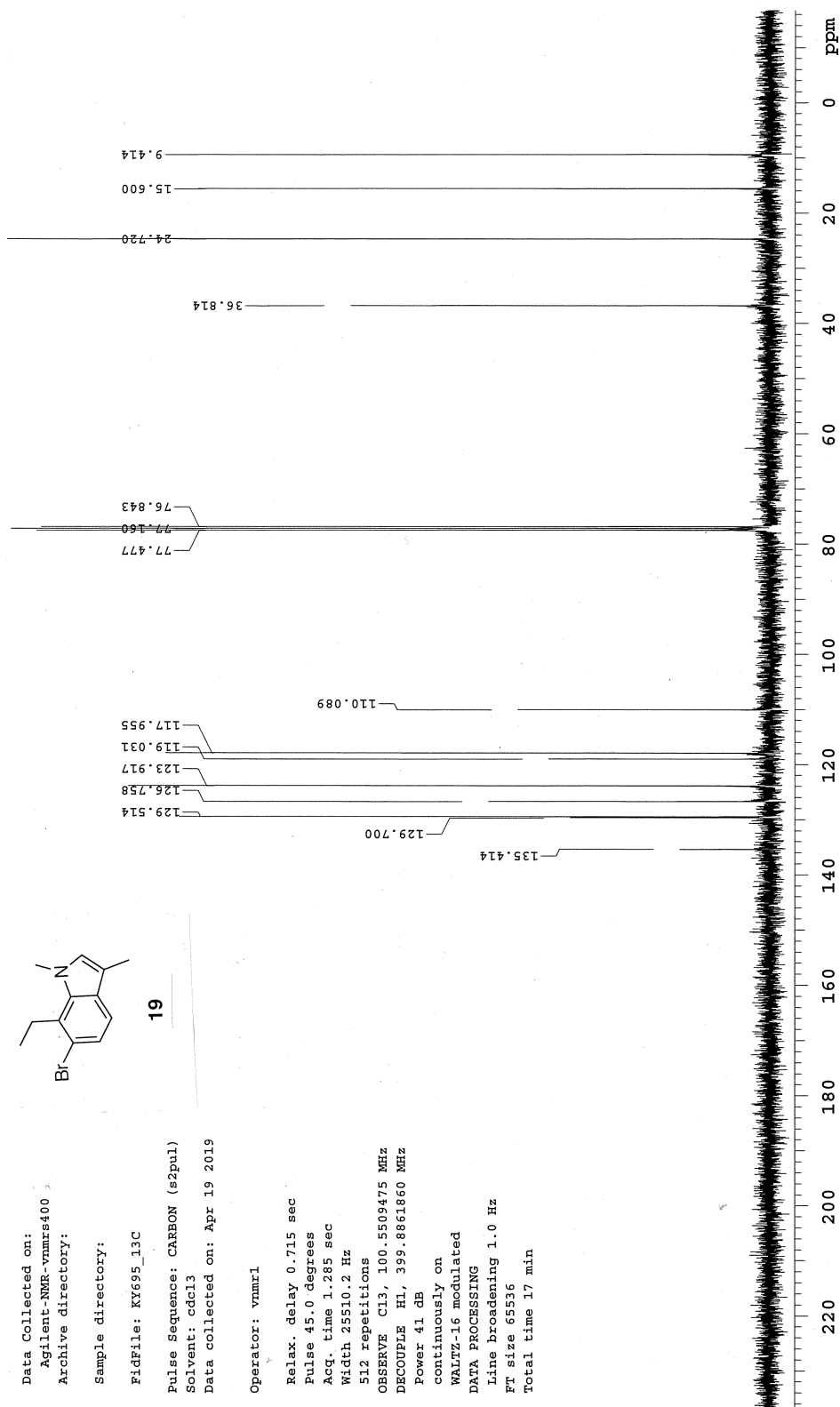
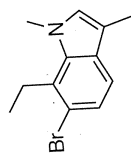


Figure S124. ¹³C NMR Spectrum of 19 (101 MHz, CDCl₃)

STANDARD PROTON PARAMETERS

Sample Name:

Data Collected on:

Agilent-NMR-vmms400

Archive directory:

Sample directory:

FidFile: KY294

Pulse Sequence: PROTON (s2pul)

Solvent: cdcl3

Data collected on: Mar 9 2018

Operator: vmml

Relax. delay 1.500 sec

Pulse 45.0 degrees

Acq. time 3.500 sec

Width 6410.3 Hz

16 repetitions

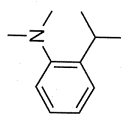
OBSERVE HL, 399.8841859 MHz

DATA PROCESSING

Line broadening 0.2 Hz

FT size 65536

Total time 1 min 20 sec



20a

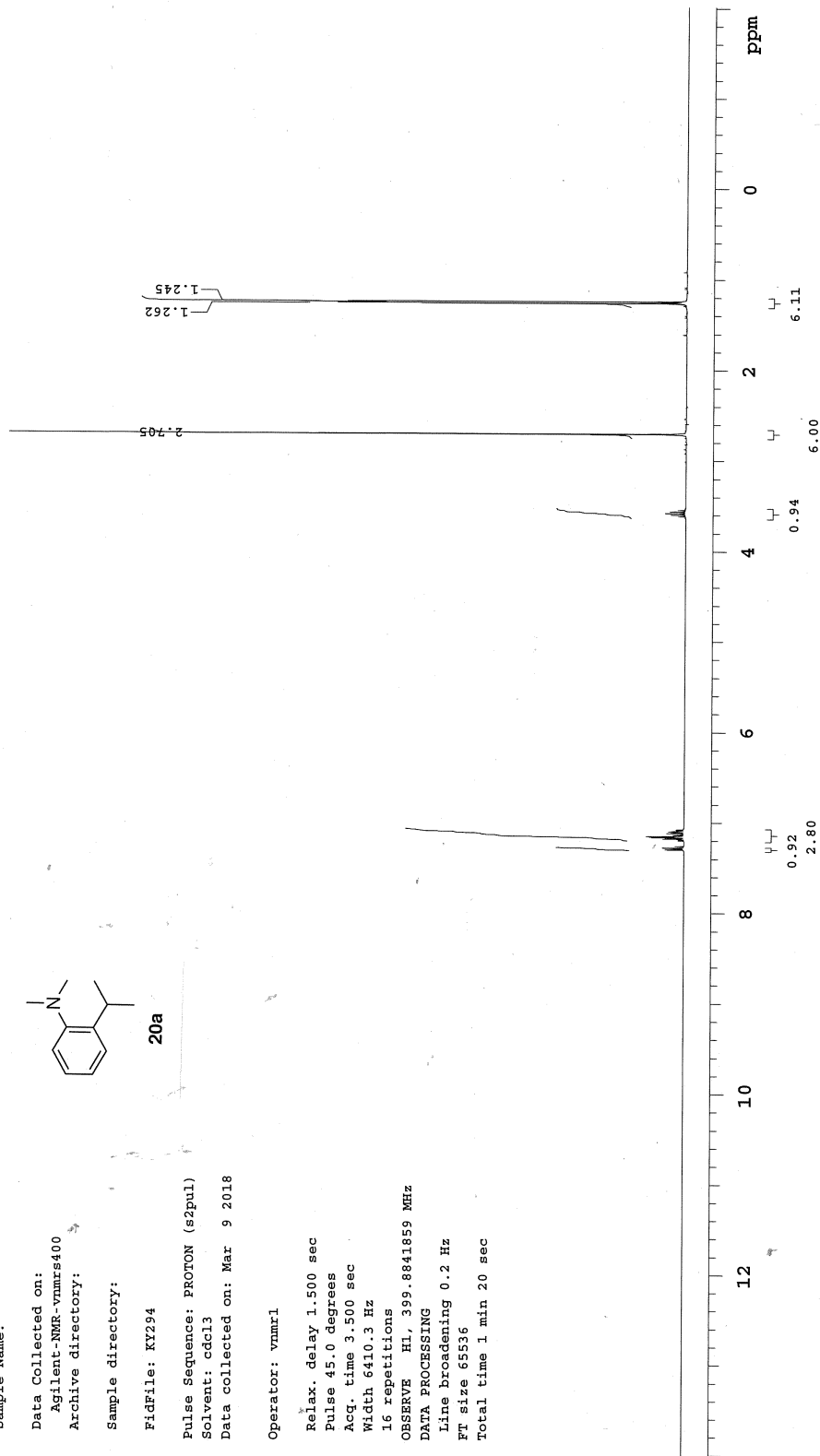
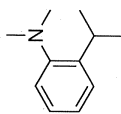


Figure S125. ¹H NMR Spectrum of 20a (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:
 Data Collected on:
 Agilent-NMR-vmms400
 Archive directory:
 Sample directory:
 FIDFile: KY782_13C
 Pulse Sequence: CARBON (s2pul)
 Solvent: cdcl3
 Data collected on: Jul 3 2019



20a

Temp. 25.0 C / 298.1 K
 Operator: vmml
 Relax. delay 0.715 sec
 Pulse 45.0 degrees
 Acq. time 1.285 sec
 Width 25510.2 Hz
 512 repetitions
 OBSERVE C13, 100.5509467 MHZ
 DECOUPLE H1, 399.8661860 MHZ
 Power 41 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 17 min

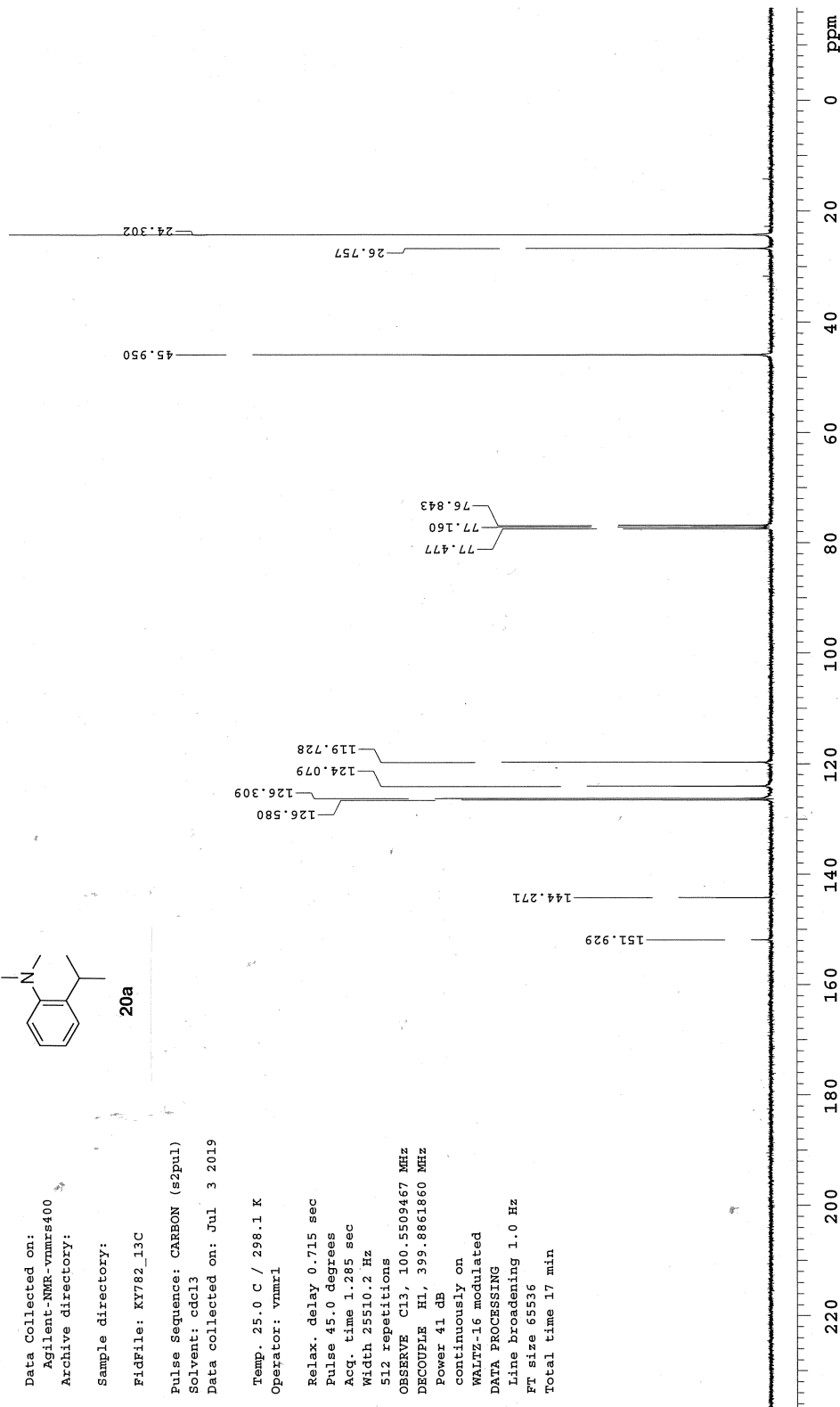


Figure S126. ¹³C NMR Spectrum of 20a (101 MHz, CDCl₃)

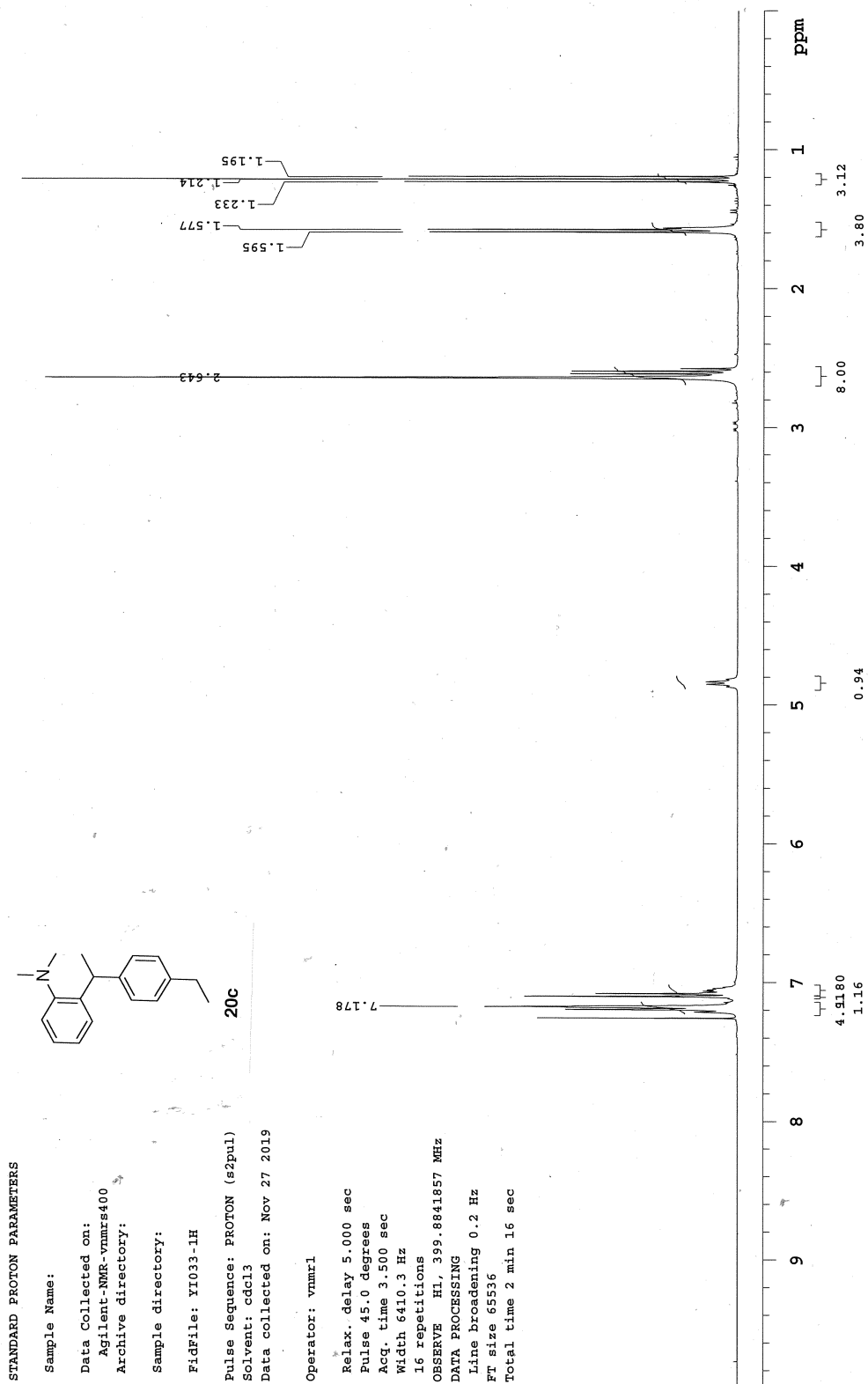


Figure S127. ^1H NMR Spectrum of **20c** (400 MHz, CDCl_3)

STANDARD CARBON PARAMETERS

Sample Name:
 Data Collected on:
 Agilent-NMR-vmars400
 Archive directory:
 Sample directory:
 FidFile: Y1033-13C-2
 Pulse Sequence: CARBON (szpul)
 Solvent: cdcl3
 Data collected on: Nov 28 2019

Operator: vmmr1

Relax. delay 0.715 sec
 Pulse 45.0 degrees
 Acq. time 1.285 sec
 Width 25510.2 Hz
 512 repetitions
 OBSERVE C13, 100.5509451 MHz
 DECOUPLE H1, 399.8861860 MHz
 Power 41 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 17 min

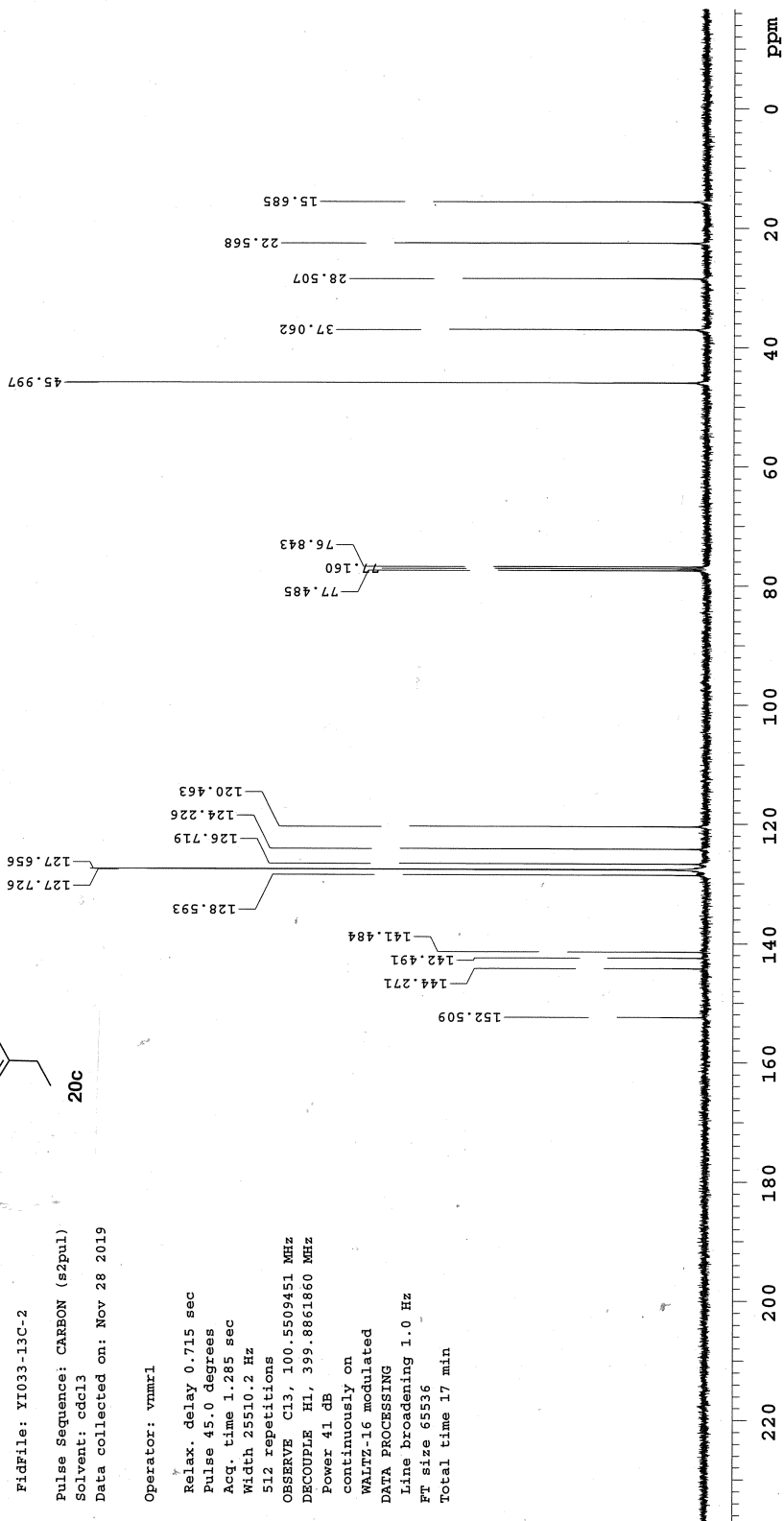
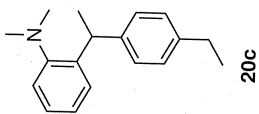


Figure S128. ¹³C NMR Spectrum of 20c (101 MHz, CDCl₃)

STANDARD PROTON PARAMETERS

Sample Name:
 Data Collected on:
 Agilent-NMR-vmnr400
 Archive directory:
 Sample directory:
 F1dFile: KS1119-LH
 Pulse Sequence: PROTON (szpul)
 Solvent: cdcl3
 Data collected on: Nov 9 2019
 Operator: vmnr1
 Relax. delay 5.000 sec
 Pulse 45.0 degrees
 Acq. time 3.500 sec
 Width 6410.3 Hz
 16 repetitions
 OBSERVE H1, 399.8841859 MHz
 DATA PROCESSING
 Line broadening 0.2 Hz
 FT size 65536
 Total time 2 min 16 sec

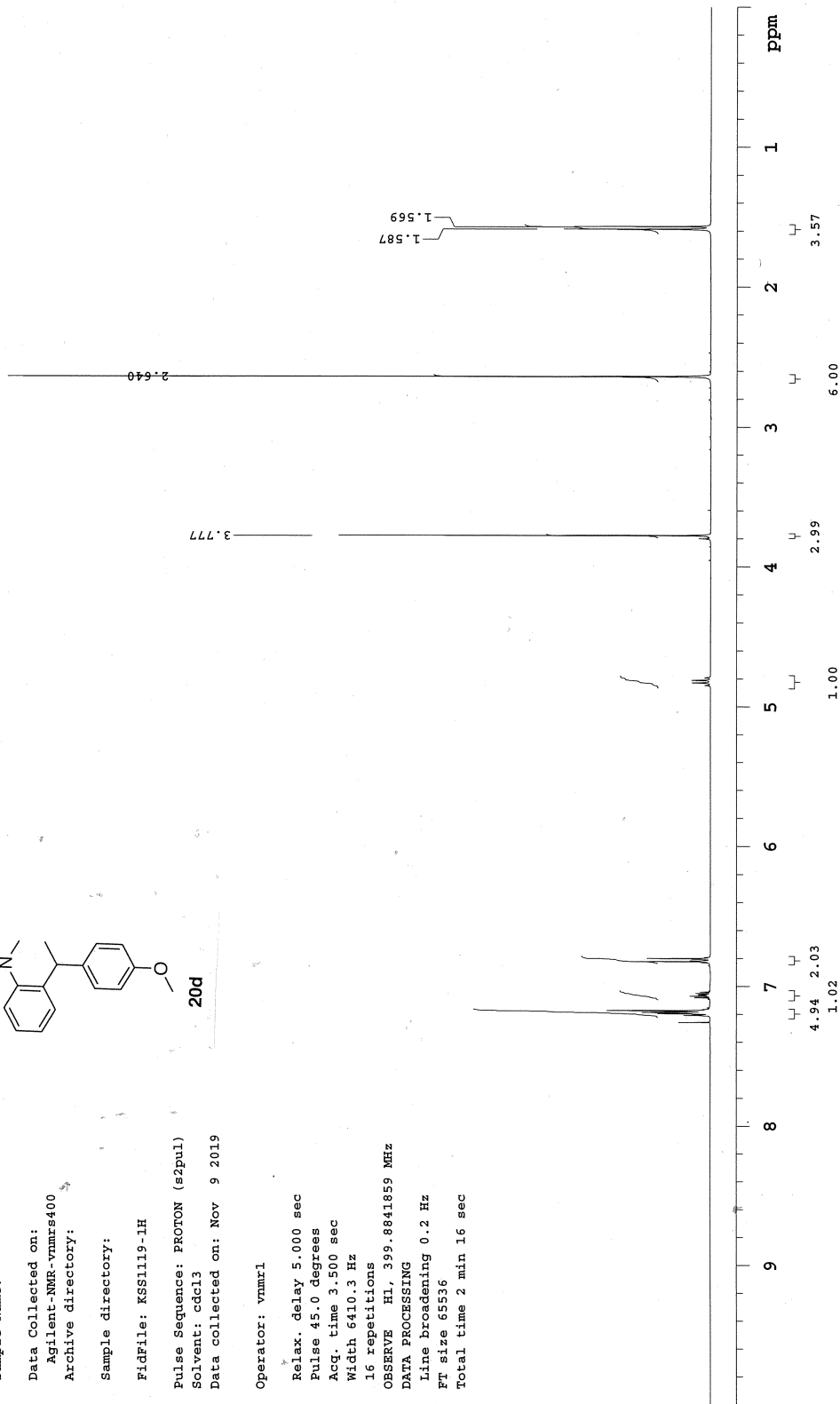
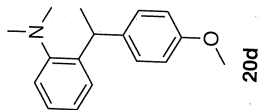


Figure S129. ¹H NMR Spectrum of **20d** (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:
 Data Collected on:
 Agilent-NMR-vmms400
 Archive directory:
 Sample directory:
 FidFile: KSI1119-13C
 Pulse Sequence: CARBON (s2pul)
 Solvent: cdcl3
 Data collected on: Nov 9 2019

Operator: vmml
 Relax. delay 0.715 sec
 Pulse 45.0 degrees
 Acq. time 1.285 sec
 Width 25510.2 Hz
 256 repetitions
 OBSERVE C13, 100.5509451 MHz
 DECOUPLE H1, 399.8861860 MHz
 Power 41 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 17 min

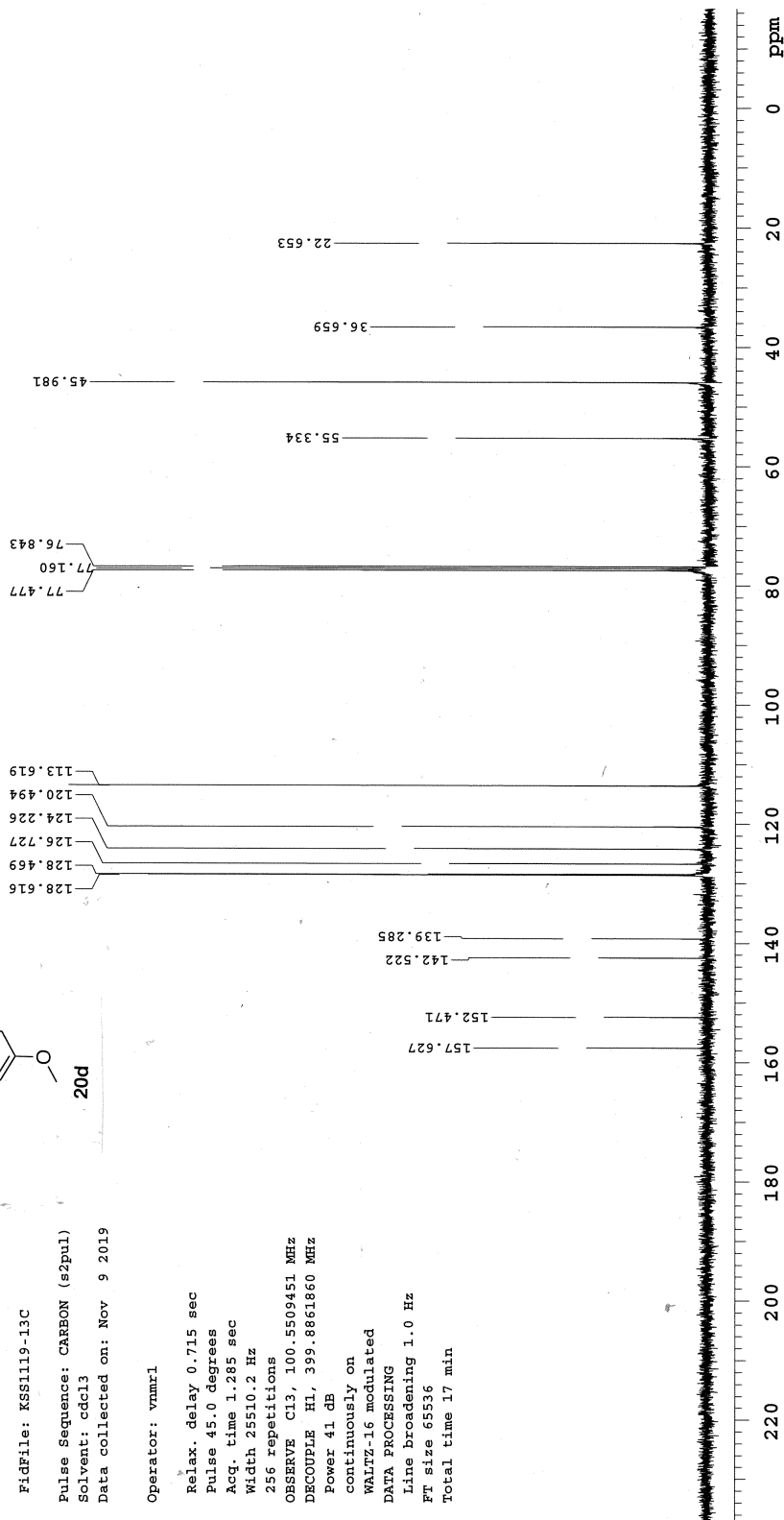
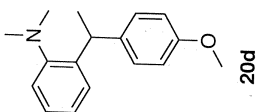


Figure S130. ¹³C NMR Spectrum of 20d (101 MHz, CDCl₃)

STANDARD PROTON PARAMETERS

Sample Name:
Data Collected on:
Agilent-NMR-vmr400
Archive directory:
Sample directory:
FidFile: KS1120-1H
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Nov 9 2019

Operator: vmr1
Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6410.3 Hz
16 repetitions
OBSERVE HL, 399.8841857 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 2 min 16 sec

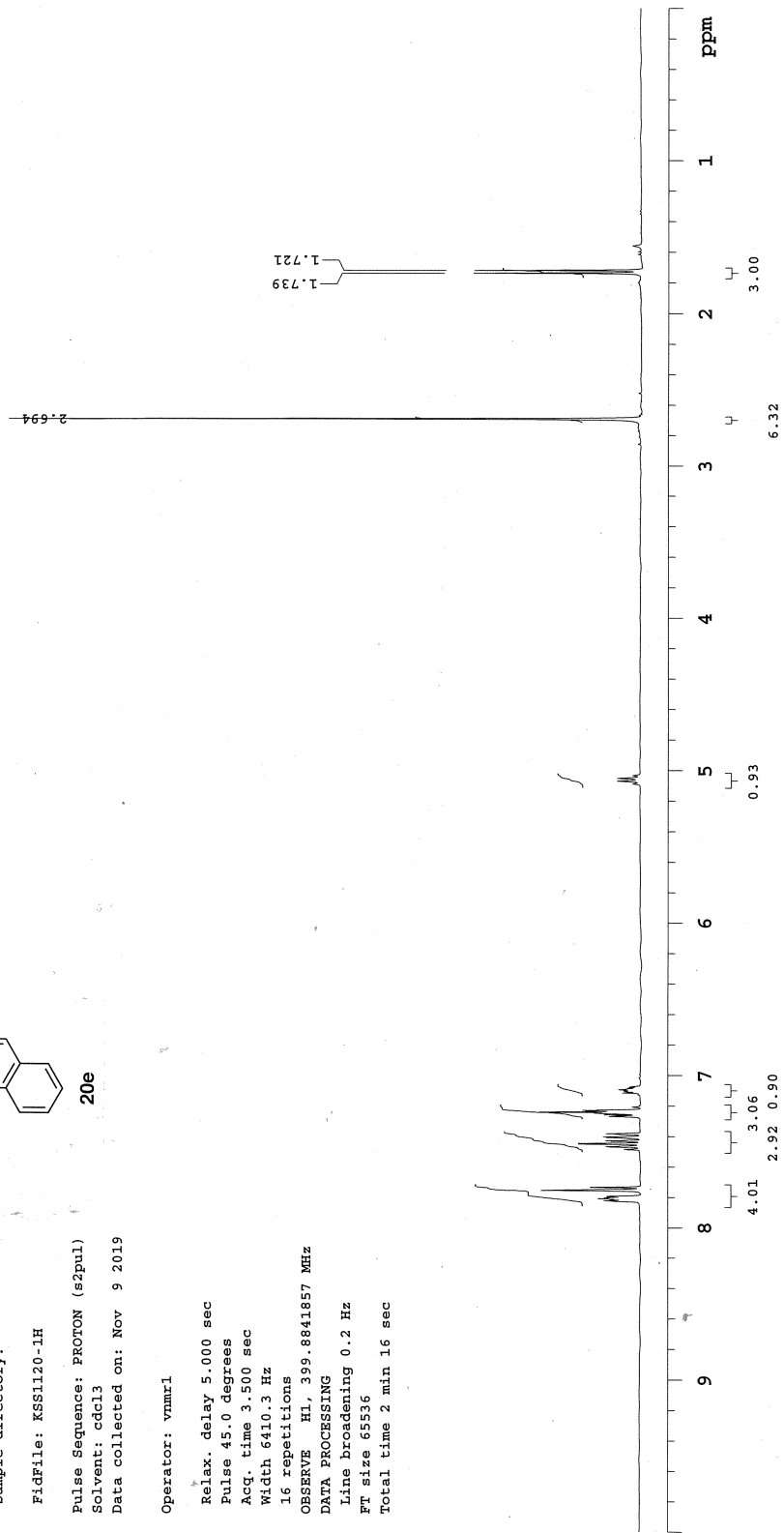
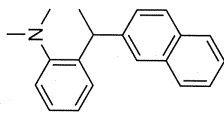


Figure S131. ¹H NMR Spectrum of **20e** (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:
 Data Collected on:
 Agilent-NMR-vmms400
 Archive directory:
 Sample directory:
 FidFile: KSS1120-13C
 Pulse Sequence: CARBON (szpul)
 Solvent: cdcl3
 Data collected on: Nov 9 2019

Operator: vmml
 Relax. delay 0.715 sec
 Pulse 45.0 degrees
 Acq. time 1.285 sec
 Width 25510.2 Hz
 256 repetitions
 OBSERVE C13, 100.5509475 MHz
 DECOUPLE H1, 399.8861860 MHz
 Power 41 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 17 min

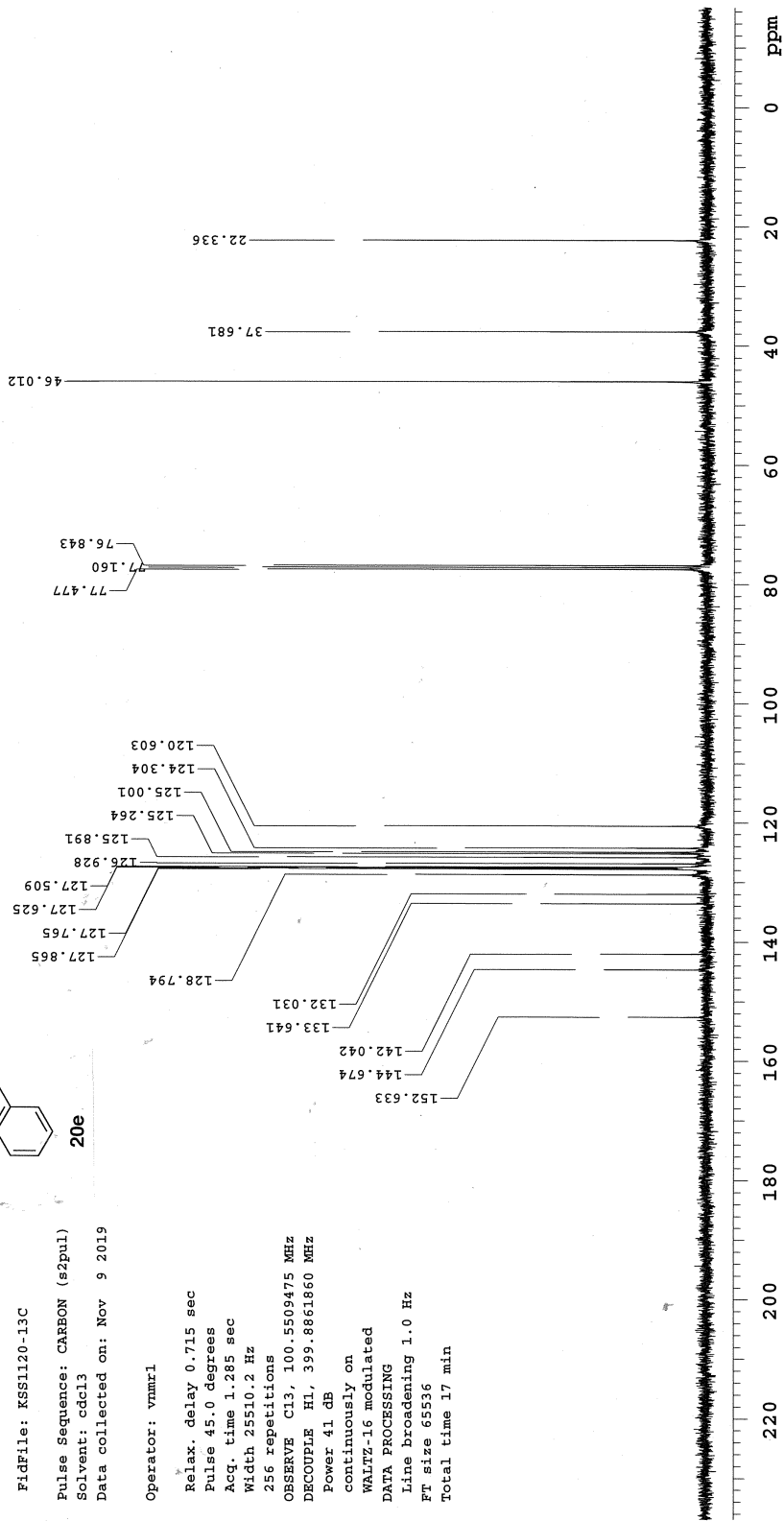
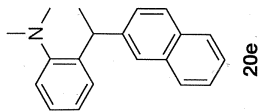
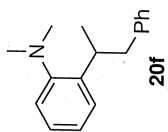


Figure S132. ¹³C NMR Spectrum of 20e (101 MHz, CDCl₃)



STANDARD PROTON PARAMETERS

Sample Name:
 Data Collected on:
 Agilent-NMR-vmrs400
 Archive directory:
 Sample directory:
 FidFile: KSS1204-1H
 Pulse Sequence: PROTON (s2pul)
 Solvent: cdcl3
 Data collected on: Jan 18 2020
 Operator: vmr1
 Relax. delay 5.000 sec
 Pulse 45.0 degrees
 Acq. time 3.500 sec
 Width 6410.3 Hz
 16 repetitions
 OBSERVE HL, 399.8841849 MHz
 DATA PROCESSING
 Line broadening 0.2 Hz
 FT size 65536
 Total time 2 min 16 sec

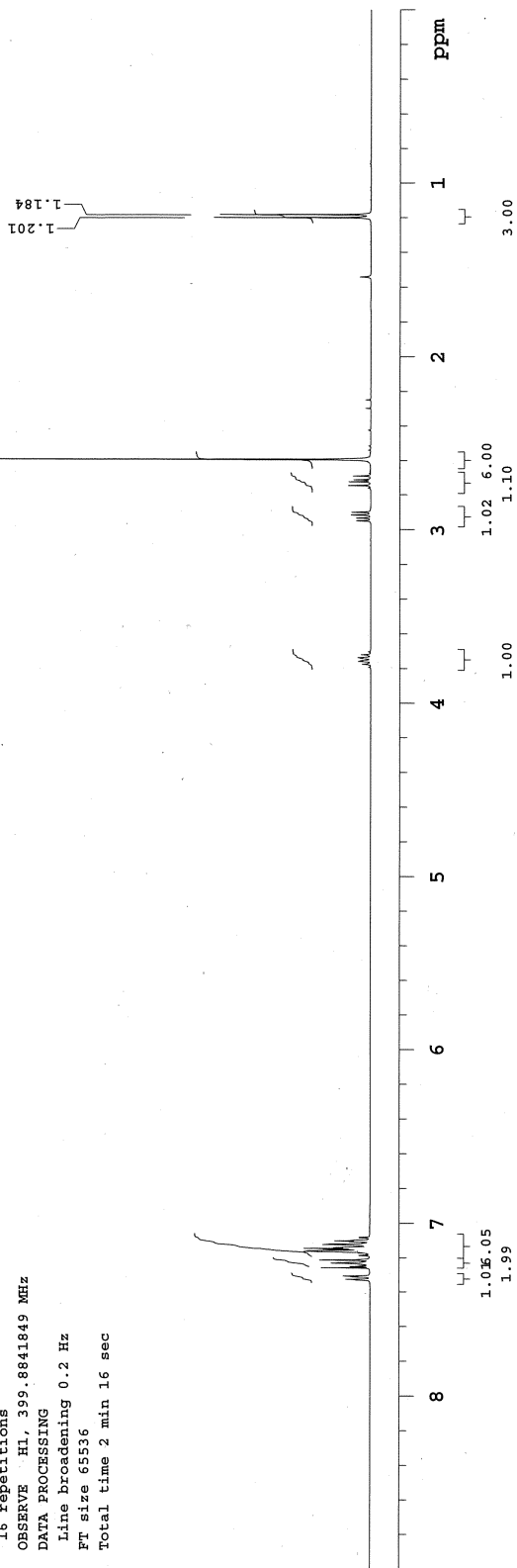


Figure S133. ¹H NMR Spectrum of **20f** (400 MHz, CDCl₃)

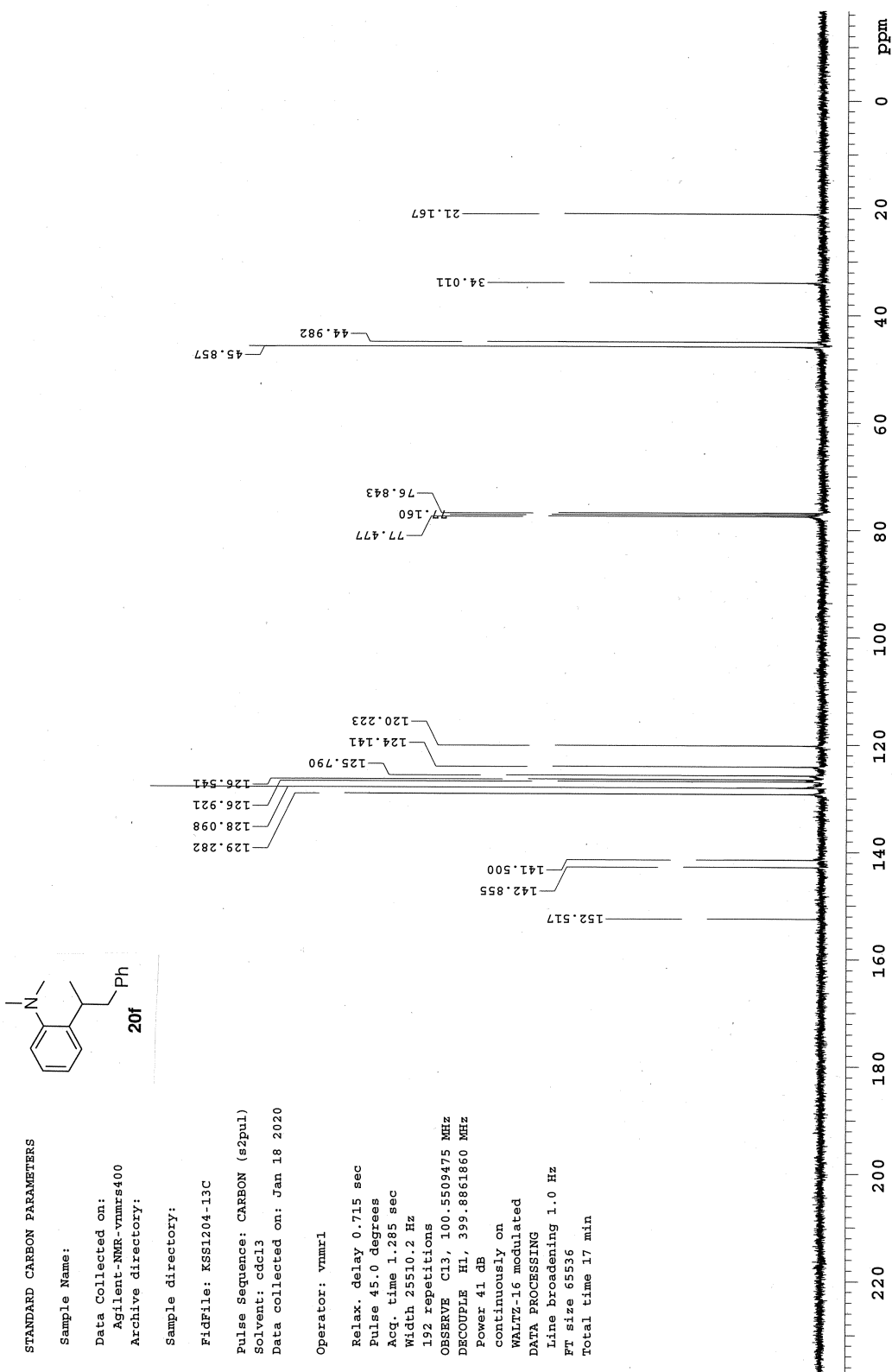
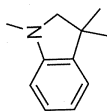


Figure S134. ^{13}C NMR Spectrum of **20f** (101 MHz, CDCl_3)

STANDARD PROTON PARAMETERS

Sample Name:
 Data Collected on: Agilent-NMR-vmms400
 Archive directory:
 Sample directory:
 File: KY715
 Pulse Sequence: PROTON (s2pul)
 Solvent: cdcl3
 Data collected on: May 14 2019
 Operator: vmr1
 Relax. delay 15.000 sec
 Pulse 45.0 degrees
 Acq. time 3.500 sec
 Width 6410.3 Hz
 16 repetitions
 OBSERVE HL, 399.8641859 MHz
 DATA PROCESSING
 Line broadening 0.2 Hz
 FT size 65536
 Total time 4 min 56 sec



21a

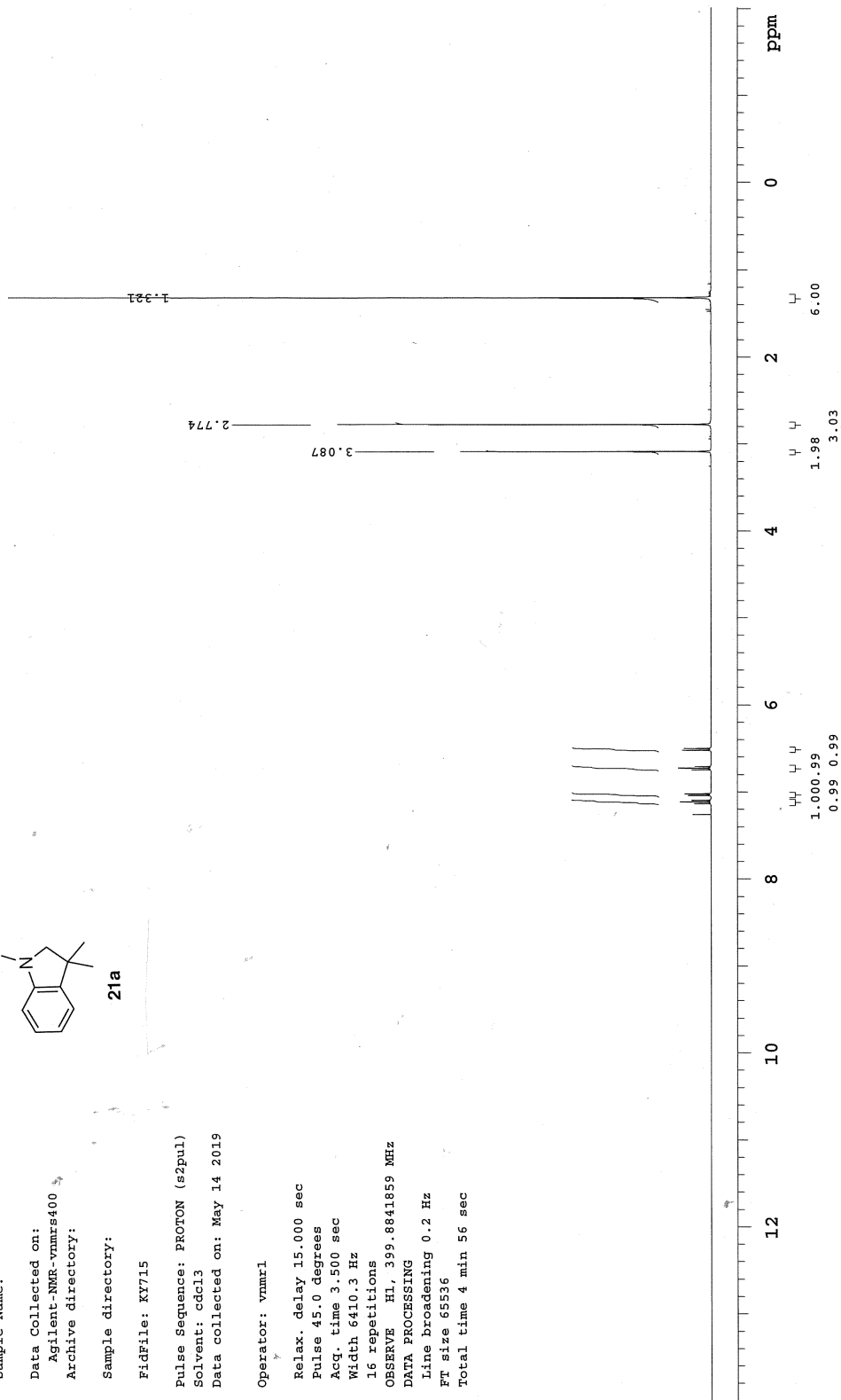


Figure S135. ¹H NMR Spectrum of 21a (400 MHz, CDCl₃)

STANDARD CARBON PARAMETERS

Sample Name:

Data Collected on:

Agilent-NMR-vmr400

Archive directory:

Sample directory:

FigFile: KY715_13C

Pulse Sequence: CARBON (s2Pul)

Solvent: cdcl3

Data collected on: May 15 2019

Operator: vmr1

Relax. delay 0.715 sec

Pulse 45.0 degrees

Acq. time 1.285 sec

Width 25510.2 Hz

4096 repetitions

OBSERVE C13, 100.5509459 MHz

DECOUPLE H1, 399.8861860 MHz

Power 41 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 2 hr, 16 min

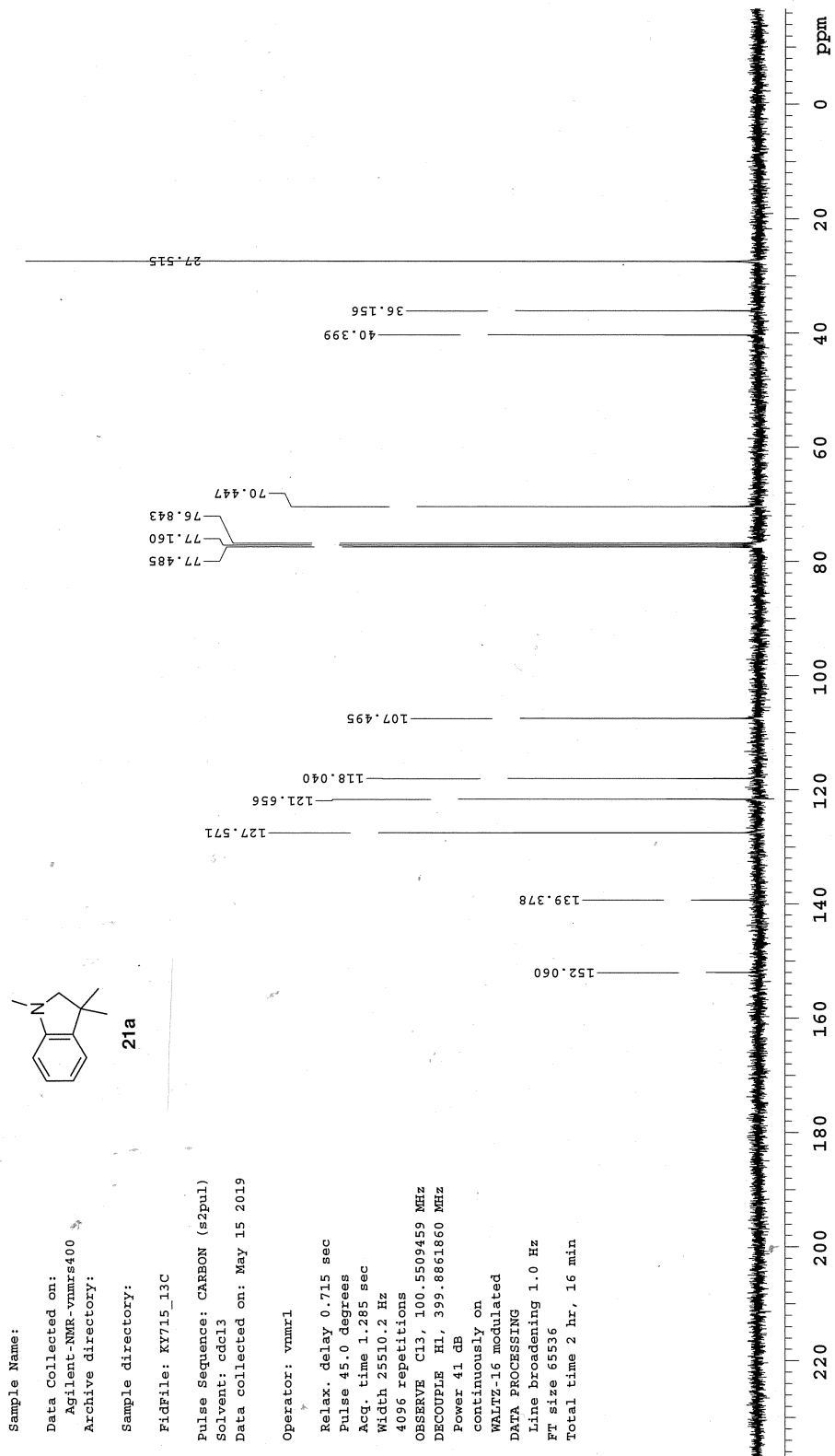


Figure S136. ¹³C NMR Spectrum of 21a (101 MHz, CDCl₃)