

*Supplementary Information*

## Direct Photochemical Route to Azoxybenzenes via Nitroarene Homocoupling

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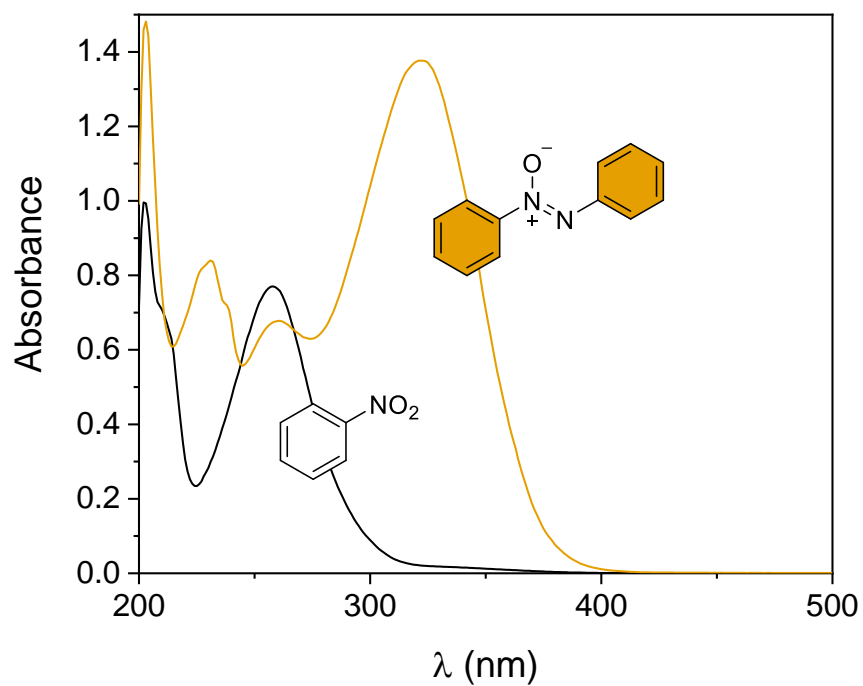
## Materials and Methods

### General Consideration

All reagents were purchased from Sigma-Aldrich and Lancaster. Solvents were purchased from ACP. Reactions were monitored by thin layer chromatography using aluminum backed sheets coated with 200  $\mu\text{m}$  silica (60, F<sub>254</sub>). SiliaFlash® P60, 40-63 mm (230-400 mesh) silica gel from SiliCycle was used for purification of compounds by column chromatography. Mass spectral analysis was performed with a 7890B GC System equipped with a 5977 mass selective detector from Agilent Technologies. NMR spectra were recorded at room temperature with a Bruker Avance II 400 MHz spectrometer using deuterated chloroform (CDCl<sub>3</sub>) as the solvent. All <sup>1</sup>H NMR data are reported as chemical shifts in ppm ( $\delta$ ), integration, coupling constant in Hz, and multiplicity [singlet (*s*), doublet (*d*), triplet (*t*), or multiplet (*m*)]. <sup>13</sup>C NMR data are reported as chemical shifts in ppm ( $\delta$ ). Steady-state absorption spectra were recorded with an Agilent Cary 60 UV-visible spectrometer, using quartz cells with a path length of 1 cm. Illumination at 365 nm was performed using a LEDEngin LZ4-UV00 connected to a heat sink and diaphragm-based active cooling system (Nuventix SynJet). A DC Power Supply provided a current of 700 mA. According to manufacturer specifications these conditions deliver an average radiant flux of 3.3 W.

### General Procedure

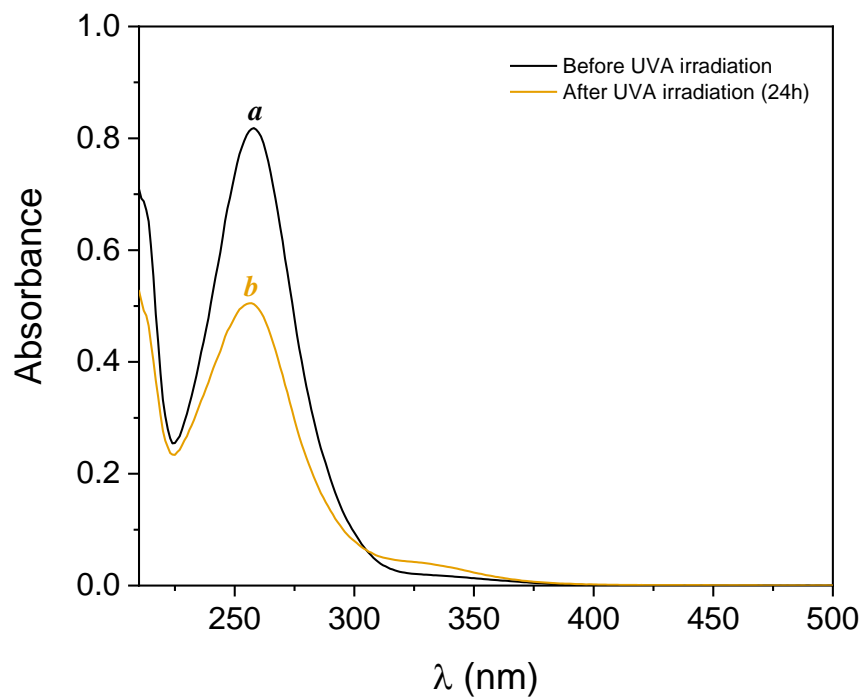
In a clean, oven-dried test tube (8 mL) equipped with a magnetic stir bar, nitrobenzene (110 mg, 0.9 mmol) was dissolved in 6 mL of *i*-PrOH and sealed with a stopper. The reaction was then irradiated at 365 nm while stirring for either 24 or 48 h (noted on pages S10-S14. Note that all reaction entries in Table 1 of the main article were irradiated for 24 h). The solvent was then evaporated by rotary evaporation, and the crude mixture was redissolved in CH<sub>2</sub>Cl<sub>2</sub> and left to evaporate in the dark for an additional 24 h. Products were purified by column chromatography (SiO<sub>2</sub>: hexanes/EtOAc 1:10 (v/v)).



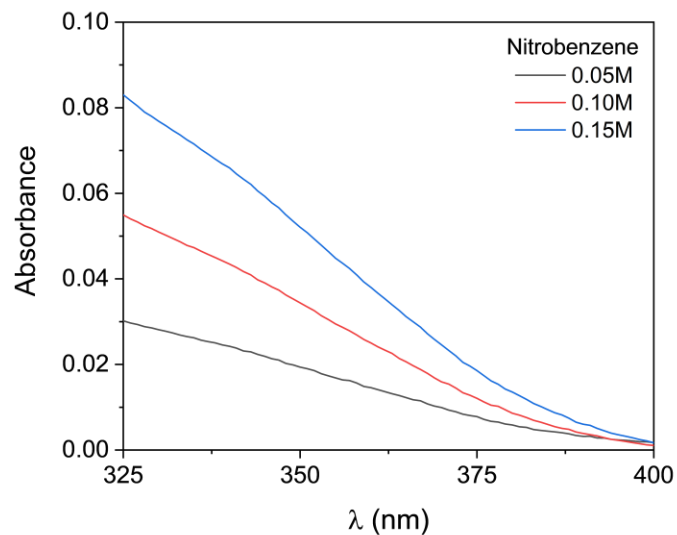
**Fig. S1.** Absorption spectra (80  $\mu$ M, *i*-PrOH, 20°C) of nitrobenzene and azoxybenzene.



**Fig. S2.** Photographs of a solution of nitrobenzene (0.05 M, *i*-PrOH, 20°C) before (*a*) and after (*b*) ultraviolet irradiation for 24 h.

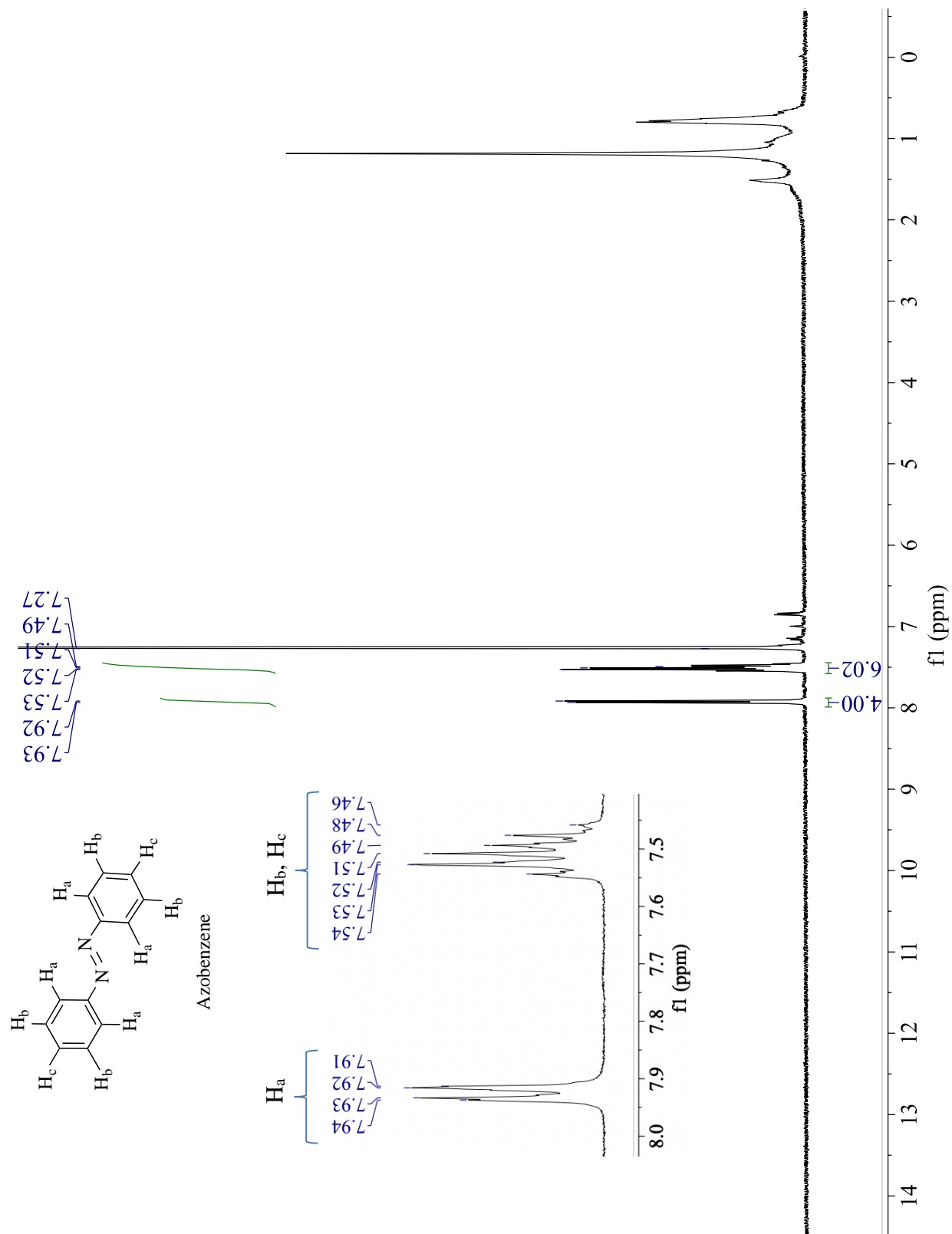


**Fig. S3.** Absorption spectra of a solution of nitrobenzene ( $85 \mu\text{M}$ , *i*-PrOH,  $20^\circ\text{C}$ ) before (**a**) and after (**b**) ultraviolet irradiation for 24 h. Solutions were prepared by diluting 585t the reaction samples depicted in Fig. S2.

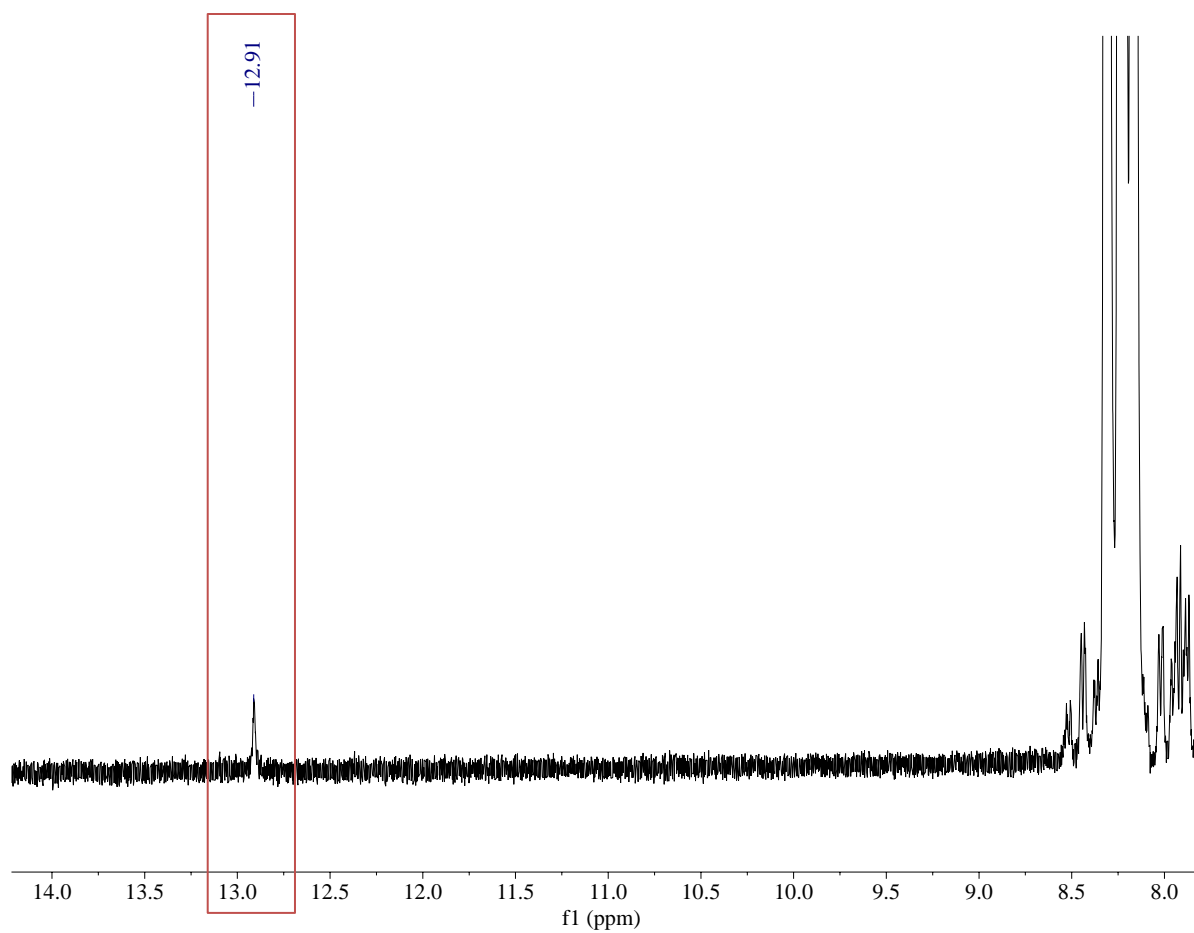


Concentration [M]	Absorbance at 365 nm
0.05	0.0122
0.10	0.0206
0.15	0.0311

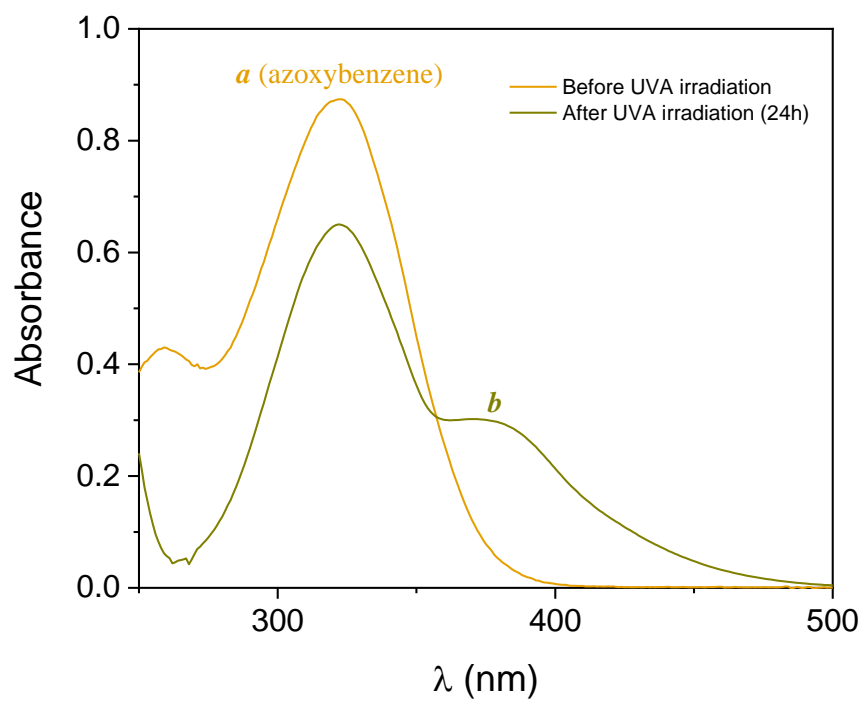
**Fig. S4** Absorption spectra of nitrobenzene solutions at various concentrations. The absorption spectrum for nitrobenzene in IPA was taken at the three indicated concentrations (0.05 M, 0.10 M, and 0.15 M) around 365 nm. The observed variation in absorptivity at 365 nm is nearly linear with respect to concentration. Considering the low extinction coefficient of the starting material at this wavelength, such variations are likely to be responsible for the differences in % conversion observed at varying concentrations of starting material.



**Fig. S5.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $20^\circ\text{C}$ ) of isolated azobenzene produced after UVA irradiation of an aerated solution of azoxybenzene (0.15M) in for 24 h in DMF.

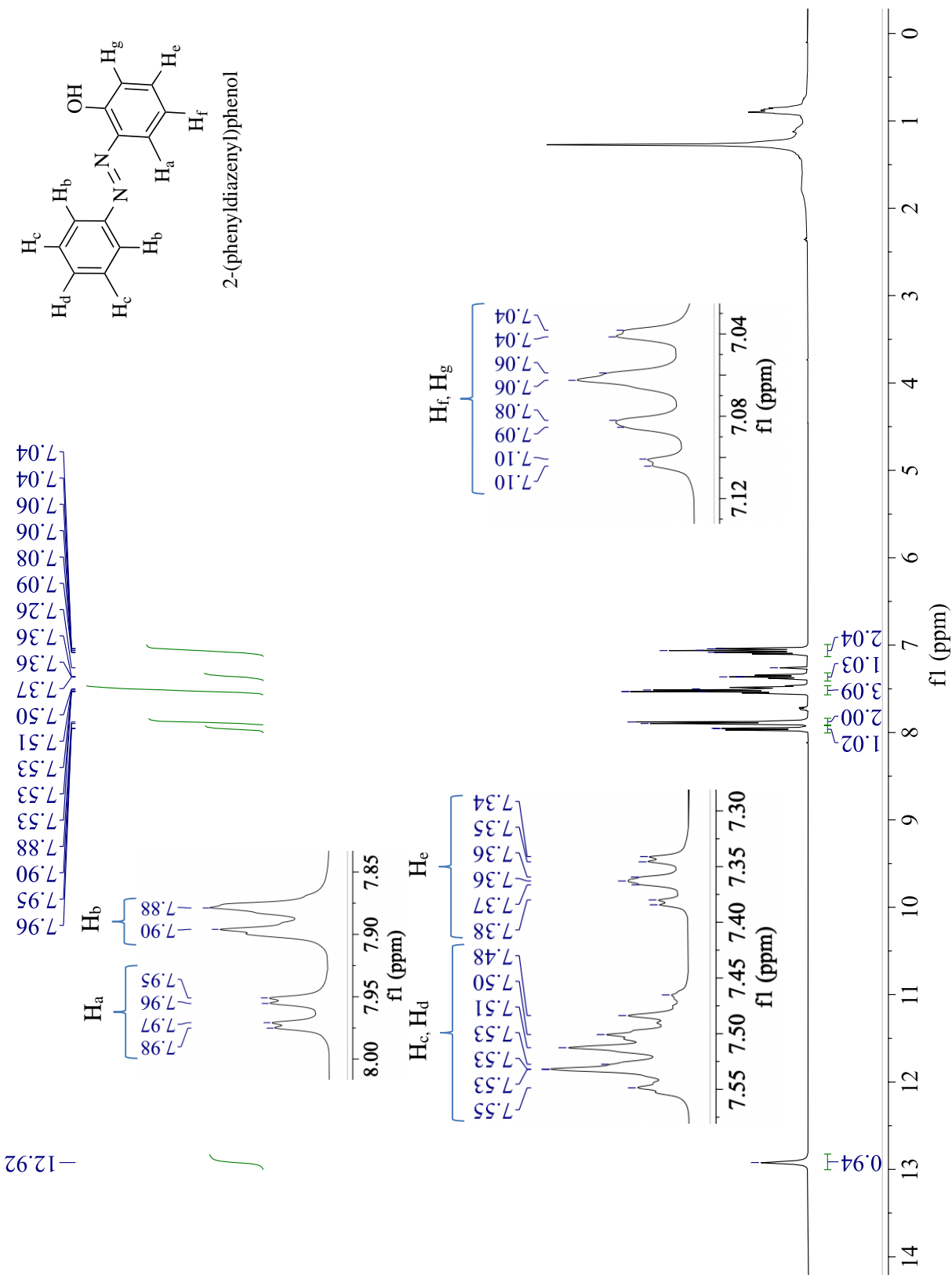


**Fig. S6.** Partial  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) of crude reaction mixture obtained for entry **a** (Table 1, main manuscript). The box highlights the presence of a signal at  $\sim 13$  ppm, which was attributed to 2-hydroxyazobenzene.



**Fig. S7.** Absorption spectra of a solution of azoxybenzene (45  $\mu$ M, *i*-PrOH, 20°C) before (**a**) and after (**b**) ultraviolet irradiation for 24 h.

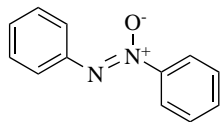




**Fig. S8.** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 20°C) of isolated 2-(phenyldiazenyl)phenol (2-hydroxyazobenzene) produced after UVA irradiation of an aerated solution of azoxybenzene (0.15M) for 24 h.

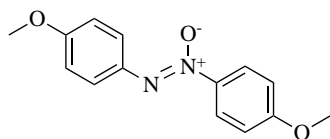
## <sup>1</sup>H NMR, <sup>13</sup>C NMR and GC-MS data obtained for isolated compounds 2a-2e and 2i-2u

### Azoxybenzene (2a)



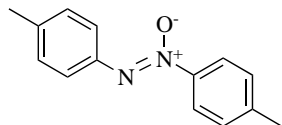
24 h, 82.58 mg, 93%, yellowish solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.31 (2H, d, J = 9.9 Hz), 8.17 (2H, d, J = 10.1 Hz), 7.57-7.55 (5H, m), 7.48-7.39 (1H, m). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 148.3 (C), 143.9 (C), 131.5 (CH × 2), 129.6 (CH × 2), 128.7 (CH × 2), 128.6 (CH × 2), 125.5 (C), 122.3 (C). UV-Vis (CH<sub>3</sub>CN): λ<sub>max</sub> (nm) 319, 256, 228. GC-MS (EI): m/z 198.1 (m/z 77, 91, 169, 182, 198), m/z calculated for C<sub>12</sub>H<sub>10</sub>N<sub>2</sub>O [M]<sup>+</sup>, 198.1. Data corresponds with published characterization data.<sup>1</sup>

### 1,2-Bis (4-methoxyphenyl)diazene oxide (2b)



48 h, 47.54 mg, 66%, yellowish solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.28 (4H, m), 6.98 (4H, m), 3.89 (3H, s), 3.88 (3H, s). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 161.8 (C), 160.2 (C), 141.7 (C), 138.0 (C), 127.9 (CH × 2), 123.7 (CH × 2), 113.7 (CH × 2), 113.6 (CH × 2), 55.7 (CH<sub>3</sub>), 55.5 (CH<sub>3</sub>). UV-Vis (CH<sub>3</sub>CN): λ<sub>max</sub> (nm) 357, 242. GC-MS (EI): m/z 258.1 (m/z 77, 92, 107, 121, 242, 258), m/z calculated for C<sub>14</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub> [M]<sup>+</sup>, 258.1. Data corresponds with published characterization data.<sup>1</sup>

### 1,2-Bis (4-tolylphenyl)diazene oxide (2c)

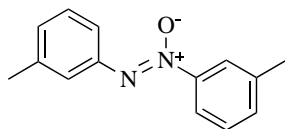


48 h, 73.18 mg, 72%, yellowish solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.18 (2H, d, J = 8.2 Hz), 8.13 (2H, d, J = 8.3 Hz), 7.30-7.28 (4H, m), 2.44 (3H, s), 2.42 (3H, s). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 146.3 (C), 141.9 (C), 141.8 (C), 140.0 (C), 129.3 (CH × 2), 129.3 (CH × 2), 125.7 (CH × 2), 122.1 (CH × 2), 21.6 (CH<sub>3</sub>), 21.3 (CH<sub>3</sub>). UV-Vis (CH<sub>3</sub>CN): λ<sub>max</sub> (nm) 330, 265, 237. GC-MS (EI): m/z 226.1 (m/z 65, 91, 210, 226), m/z calculated for C<sub>14</sub>H<sub>14</sub>N<sub>2</sub>O [M]<sup>+</sup>, 226.1. Data corresponds with published characterization data.<sup>2</sup>

<sup>1</sup> Chen, Y.-F.; Chen, J.; Lin, L.-J.; Chuang, G.J. Synthesis of azoxybenzenes by reductive dimerization of nitrosobenzene. *J Org Chem* **2017**, 82(21), 11626-11630. <https://doi.org/10.1021/acs.joc.7b01887>

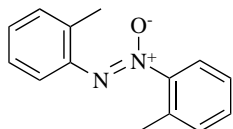
<sup>2</sup> Chen, Z.; Qiu, Y.; Wu, X.; Ni, Y.; Shen, L.; Wu, J.; Jiang, S. Highly selective reduction of nitrobenzenes to azoxybenzenes with a copper catalyst. *Tetrahedron Lett* **2018**, 59(14), 1382-1384. <https://doi.org/10.1016/j.tetlet.2018.02.064>

### 1,2-Bis (3-tolylphenyl)diazene oxide (2d)



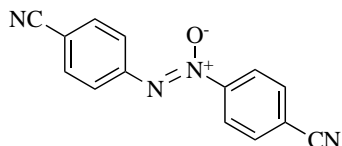
48 h, 70.49 mg, 69%, yellowish solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.12-8.09 (2H, m), 8.00-7.98 (2H, m), 7.36-7.38 (3H, m), 7.26-7.21 (1H, m), 2.44 (3H, s), 2.42 (3H, s).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  148.5 (C), 144.1 (C), 139.0 (C), 138.5 (C), 132.3 (CH), 130.4 (CH), 128.6 (CH), 128.5 (CH), 126.0 (CH), 122.8 (CH), 122.5 (CH), 119.5 (CH), 21.5 ( $\text{CH}_3$ ), 21.4 ( $\text{CH}_3$ ). UV-Vis ( $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  (nm) 329, 269, 237. GC-MS (EI):  $m/z$  226.1 ( $m/z$  65, 91, 198, 226),  $m/z$  calculated for  $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}$   $[\text{M}]^+$ , 226.1. Data corresponds with published characterization data.<sup>2</sup>

### 1,2-Bis (2-tolylphenyl)diazene oxide (2e)



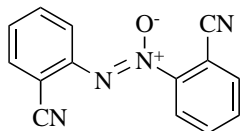
48 h, 38.78 mg, 38%, yellowish solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.03 (1H, d,  $J = 6.6$  Hz), 7.68 (1H, d,  $J = 7.3$  Hz), 7.38-7.24 (6H, m), 2.53 (3H, s), 2.38 (3H, s).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  149.5 (C), 142.8 (C), 134.1 (C), 131.8 (CH), 131.2 (C), 130.8 (CH), 130.0 (CH), 128.6 (CH), 126.6 (CH), 126.0 (CH), 123.6 (CH), 121.5 (CH), 18.5 ( $\text{CH}_3$ ), 18.4 ( $\text{CH}_3$ ). UV-Vis ( $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  (nm) 310, 236. GC-MS (EI):  $m/z$  226.1 ( $m/z$  65, 91, 211, 226),  $m/z$  calculated for  $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}$   $[\text{M}]^+$ , 226.1. Data corresponds with published characterization data.<sup>1</sup>

### 1,2-Bis (4-cyanophenyl)diazene oxide (2i)



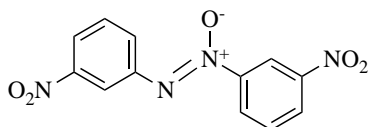
48 h, 76.32 mg, 68%, yellowish solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.46 (2H, d,  $J = 11.5$  Hz), 8.24 (2H, d,  $J = 11.3$  Hz), 7.87 (2H, d,  $J = 12.6$  Hz), 7.80 (2H, d,  $J = 12.5$  Hz).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.3 (C), 146.3 (C), 133.1 (CH  $\times$  2), 132.9 (CH  $\times$  2), 126.1 (CH  $\times$  2), 123.4 (CH  $\times$  2), 118.4 (C), 117.4 (C), 116.2 (C), 113.2 (C). UV-Vis ( $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  (nm) 333, 267. GC-MS (EI):  $m/z$  248.1 ( $m/z$  75, 102, 116, 130, 248),  $m/z$  calculated for  $\text{C}_{14}\text{H}_8\text{N}_4\text{O}$   $[\text{M}]^+$ , 248.1. Data corresponds with published characterization data.<sup>1</sup>

### 1,2-Bis(2-cyanophenyl)diazene oxide (2j)



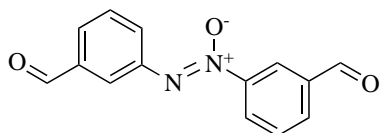
48 h, 17.96 mg, 12%, yellowish solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.87 (1H, d,  $J = 11.1$  Hz), 8.46 (1H, d,  $J = 10.7$  Hz), 7.93 (1H, d,  $J = 10.6$  Hz), 7.84-7.73 (2H, m), 7.53 (1H, t,  $J = 10.9$  Hz).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  153.6 (C), 144.6 (C), 135.3 (CH), 133.6 (CH), 133.5 (CH), 133.3 (CH), 132.1 (CH), 130.2 (CH), 124.9 (CH), 123.3 (CH), 117.0 (C), 116.3 (C), 111.5 (C), 107.6 (C). UV-Vis ( $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  (nm) 327, 217. GC-MS (EI):  $m/z$  248.1 ( $m/z$  75, 102, 130, 146, 248),  $m/z$  calculated for  $\text{C}_{14}\text{H}_8\text{N}_4\text{O}$   $[\text{M}]^+$ , 248.1. Data corresponds with published characterization data.<sup>1</sup>

### 1,2-Bis(3-nitrophenyl)diazene oxide (2k)



48 h, 85.72 mg, 66%, white solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.22 (1H, t,  $J = 2.9$  Hz), 9.12 (1H, t,  $J = 2.9$  Hz), 8.71 (1H, dd,  $J = 7.9, 1.5$  Hz), 8.49 (2H, t,  $J = 9.7$  Hz), 8.32 (1H, dd,  $J = 8.0, 1.5$  Hz), 7.80 (1H, t,  $J = 8.6$  Hz), 7.71 (1H, t,  $J = 8.6$  Hz).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  148.5 (C) 148.3 (C  $\times$  2), 143.9 (C), 131.6 (CH), 130.3 (CH), 129.8 (CH), 128.0 (CH), 126.8 (CH), 124.6 (CH), 120.5 (CH), 118.1 (CH). UV-Vis ( $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  (nm) 318, 261. GC-MS (EI):  $m/z$  288.1 ( $m/z$  76, 92, 122, 150, 207, 288),  $m/z$  calculated for  $\text{C}_{12}\text{H}_8\text{N}_4\text{O}_5$   $[\text{M}]^+$ , 288.1. Data corresponds with published characterization data.<sup>1</sup>

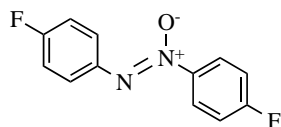
### 1,2-Bis(3-formylphenyl)diazene oxide (2l)



48 h, 63.66 mg, 54%, white solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.16 (1H, s), 10.11 (1H, s), 8.86 (1H, s), 8.76 (1H, s), 8.62 (1H, d,  $J = 9.3$  Hz), 8.41 (1H, d,  $J = 9.1$  Hz), 8.15 (1H, d,  $J = 9.3$  Hz), 7.98 (1H, d,  $J = 9.2$  Hz), 7.70-7.75 (2H, m).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  191.5 (CH) 190.6 (CH), 137.2 (C), 137.0 (C  $\times$  2), 132.4 (C), 131.5 (CH), 130.1 (CH), 129.9 (CH  $\times$  2), 129.6 (CH), 127.8 (CH), 127.2 (CH), 123.6 (CH). UV-Vis ( $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  (nm) 316, 240. GC-MS (EI):  $m/z$  254.1 ( $m/z$  65, 77, 105, 133, 238, 254),  $m/z$  calculated for  $\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_3$   $[\text{M}]^+$ , 254.1. Data corresponds with published characterization data.<sup>3</sup>

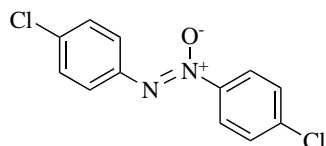
<sup>3</sup> Su, R.; Lu, L.; Zheng, S.; Jin, Y.; An, S. Synthesis and characterization of novel azo-containing or azoxy-containing Schiff bases and their antiproliferative and cytotoxic activities. *Chem Res Chin Univ* **2015**, *31*(1), 60-64.  
<https://doi.org/10.1007/s40242-015-4355-4>

### 1,2-Bis(4-fluorophenyl)diazene oxide (2m)



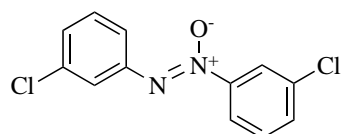
24 h, 29.66 mg, 54%, yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.34-8.31 (2H, m), 8.29-8.24 (2H, m), 7.21-7.16 (4H, m).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  165.8 (C), 163.8 (C), 163.3 (C), 140.3 (C), 128.0 (CH), 128.0 (CH), 124.6 (CH), 124.5 (CH), 115.9 (CH), 115.8 (CH), 115.6 (CH), 115.6 (CH). UV-Vis ( $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  (nm) 325, 235. GC-MS (EI):  $m/z$  234.1 ( $m/z$  75, 95, 109, 123, 205, 234),  $m/z$  calculated for  $\text{C}_{12}\text{H}_8\text{F}_2\text{N}_2\text{O}$   $[\text{M}]^+$ , 234.1. Data corresponds with published characterization data.<sup>2</sup>

### 1,2-Bis(4-chlorophenyl)diazene oxide (2n)



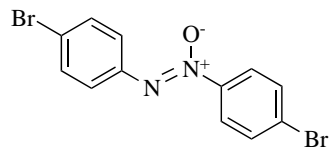
48 h, 76.21 mg, 60%, yellowish solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.25 (2H, d,  $J = 10.3$  Hz), 8.15 (2H, d,  $J = 10.0$  Hz), 7.50-7.44 (4H, m).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  146.5 (C), 142.2 (C), 138.1 (C), 135.2 (C), 129.7 (CH  $\times$  2), 129.0 (CH  $\times$  2), 127.0 (CH  $\times$  2), 123.7 (CH  $\times$  2). UV-Vis ( $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  (nm) 332, 238. GC-MS (EI):  $m/z$  266.0 ( $m/z$  75, 111, 139, 250, 266),  $m/z$  calculated for  $\text{C}_{12}\text{H}_8\text{Cl}_2\text{N}_2\text{O}$   $[\text{M}]^+$ , 266.0. Data corresponds with published characterization data.<sup>1</sup>

### 1,2-Bis(3-chlorophenyl)diazene oxide (2o)



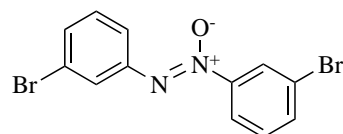
24 h, 45.62 mg, 72%, yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.32 (1H, t,  $J = 3.4$  Hz), 8.26 (1H, t,  $J = 3.5$  Hz), 8.20 (1H, d,  $J = 11.1$  Hz), 8.01 (1H, dt,  $J = 9.9, 2.0$  Hz), 7.59-7.46 (1H, d,  $J = 10.9$  Hz), 7.43-7.39 (3H, m).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  148.8 (C), 144.5 (C), 134.8 (C), 134.4 (C), 132.0 (CH), 129.9 (CH  $\times$  2), 129.7 (CH), 125.4 (CH), 124.0 (CH), 122.8 (CH), 120.6 (CH). UV-Vis ( $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  (nm) 321, 233, 203. GC-MS (EI):  $m/z$  266.0 ( $m/z$  75, 111, 139, 250, 266),  $m/z$  calculated for  $\text{C}_{12}\text{H}_8\text{Cl}_2\text{N}_2\text{O}$   $[\text{M}]^+$ , 266.0. Data corresponds with published characterization data.<sup>1</sup>

### 1,2-Bis(4-bromophenyl)diazene oxide (2p)



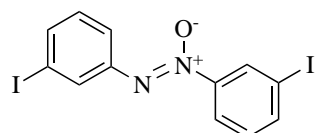
48 h, 75.97 mg, 71%, yellowish solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.17 (2H, d,  $J = 11.9$  Hz), 8.09 (2H, d,  $J = 11.7$  Hz), 7.66-7.60 (4H, m).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  147.0 (C), 142.5 (C), 132.0 (CH  $\times$  2), 131.9 (CH  $\times$  2), 127.1 (CH  $\times$  2), 126.4 (C), 123.9 (CH  $\times$  2), 123.6 (C). UV-Vis ( $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  (nm) 334, 270, 240. GC-MS (EI):  $m/z$  355.9 ( $m/z = 76, 90, 155, 184, 247, 341, 356$ ),  $m/z$  calculated for  $\text{C}_{12}\text{H}_8\text{Br}_2\text{N}_2\text{O}$   $[\text{M}]^+$ , 355.9. Data corresponds with published characterization data.<sup>1</sup>

### 1,2-Bis(3-bromophenyl)diazene oxide (2q)



48 h, 104.61 mg, 61%, yellowish solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.47 (1H, t,  $J = 3.1$  Hz), 8.41 (1H, t,  $J = 3.1$  Hz), 8.23 (1H, d,  $J = 11.3$  Hz), 8.05 (1H, d,  $J = 11.0$  Hz), 7.71 (1H, d,  $J = 11.2$  Hz), 7.53 (1H, d,  $J = 11.0$  Hz), 7.41-7.37 (2H, m).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  148.7 (C), 144.5 (C), 134.8 (CH), 132.6 (CH), 130.0 (CH), 129.9 (CH), 128.2 (CH), 125.5 (CH), 124.3 (CH), 122.3 (C), 122.2 (C), 120.9 (CH). UV-Vis ( $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  (nm) 324, 238, 204. GC-MS (EI):  $m/z$  355.9 ( $m/z = 76, 90, 154, 207, 281, 341, 356$ ),  $m/z$  calculated for  $\text{C}_{12}\text{H}_8\text{Br}_2\text{N}_2\text{O}$   $[\text{M}]^+$ , 355.9. Data corresponds with published characterization data.<sup>1</sup>

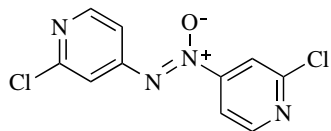
### 1,2-Bis(3-iodophenyl)diazene oxide (2r)



48 h, 99.76 mg, 74%, yellowish solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.65 (1H, t,  $J = 3.0$  Hz), 8.57 (1H, t,  $J = 3.0$  Hz), 8.27 (1H, d,  $J = 10.6$  Hz), 8.10 (1H, d,  $J = 11.1$  Hz), 7.92 (1H, d,  $J = 10.9$  Hz), 7.73 (1H, d,  $J = 10.7$  Hz), 7.28-7.20 (2H, m).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  148.6 (C), 144.8 (C), 134.2 (CH), 131.4 (CH), 130.3 (CH), 130.2 (CH), 124.9 (CH), 121.7 (CH), 122.8 (CH), 120.6 (CH), 93.7 (C), 93.3 (C). UV-Vis ( $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  (nm) 313, 227. GC-MS (EI):  $m/z$  450.0 ( $m/z = 76, 203, 231, 434, 450$ ),  $m/z$  calculated for  $\text{C}_{12}\text{H}_8\text{I}_2\text{N}_2\text{O}$   $[\text{M}]^+$ , 450.0. Data corresponds with published characterization data.<sup>4</sup>

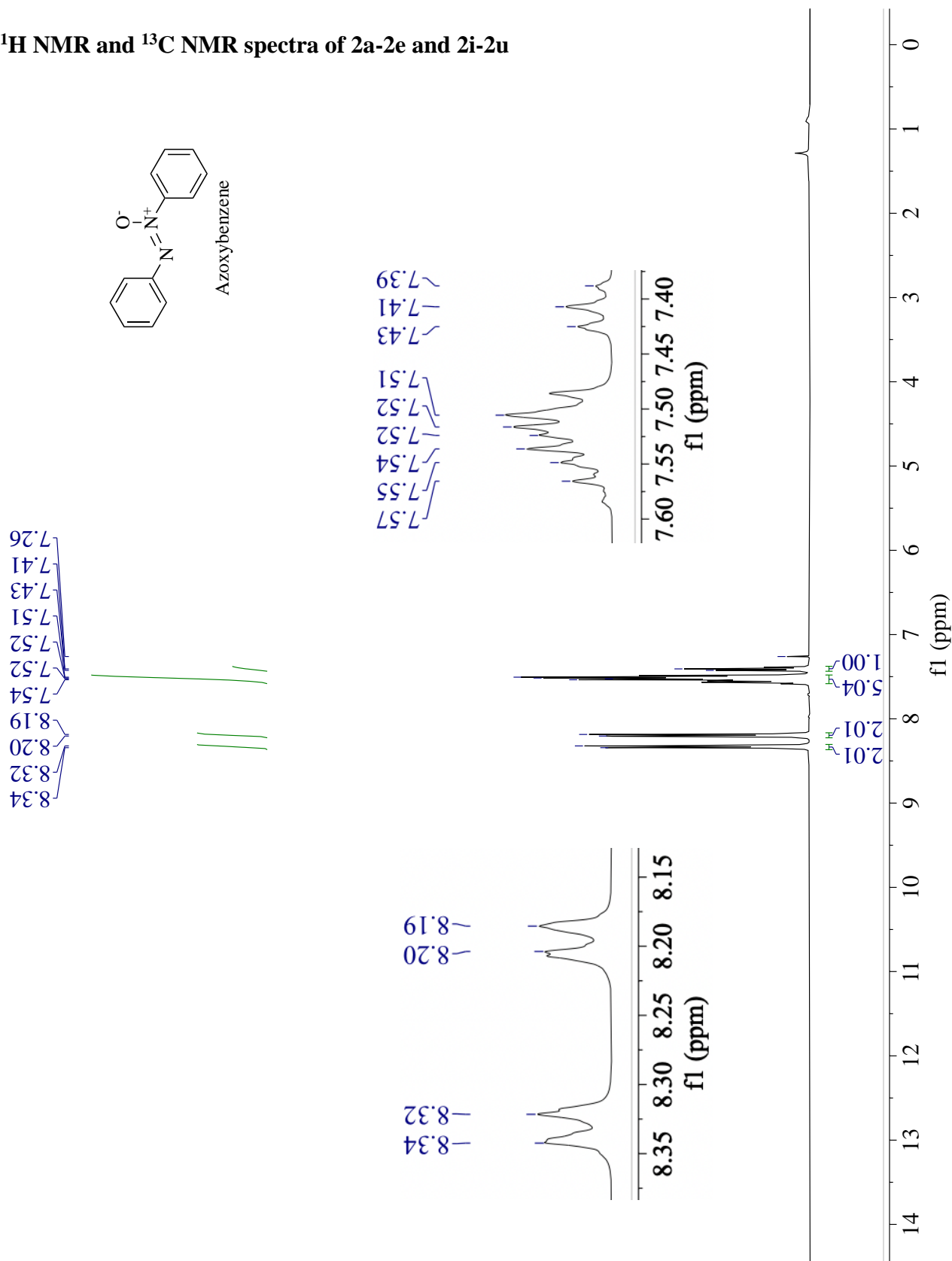
<sup>4</sup> Liu, Y.; Liu, B.; Guo, A.; Dong, Z.; Jin, S.; Lu, Y. Reduction of nitroarenes to azoxybenzenes by potassium borohydride in water. *Molecules* **2011**, *16*(5), 3563–3568. <https://doi.org/10.3390/molecules16053563>

## 1,2-Bis (2-chloropyridine-4-phenyl)diazene oxide (2u)



48 h, 69.16mg, 57%, white solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.67 (1H, d), 8.57 (1H, d), 8.21 (1H, s), 8.10 (1H, dd), 7.99 (1H, s), 7.77 (1H, s).  $^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  155.2 (C), 153.2 (C), 152.8 (C), 151.3 (C), 150.9 (CH), 150.6 (CH), 119.1 (CH), 117.6 (CH), 117.4 (CH), 115.1 (CH). UV-Vis ( $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  (nm) 297, 204. GC-MS (EI):  $m/z$  268.0 ( $m/z$  85, 112, 128, 205, 252, 268),  $m/z$  calculated for  $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}$   $[\text{M}]^+$ , 267.99.

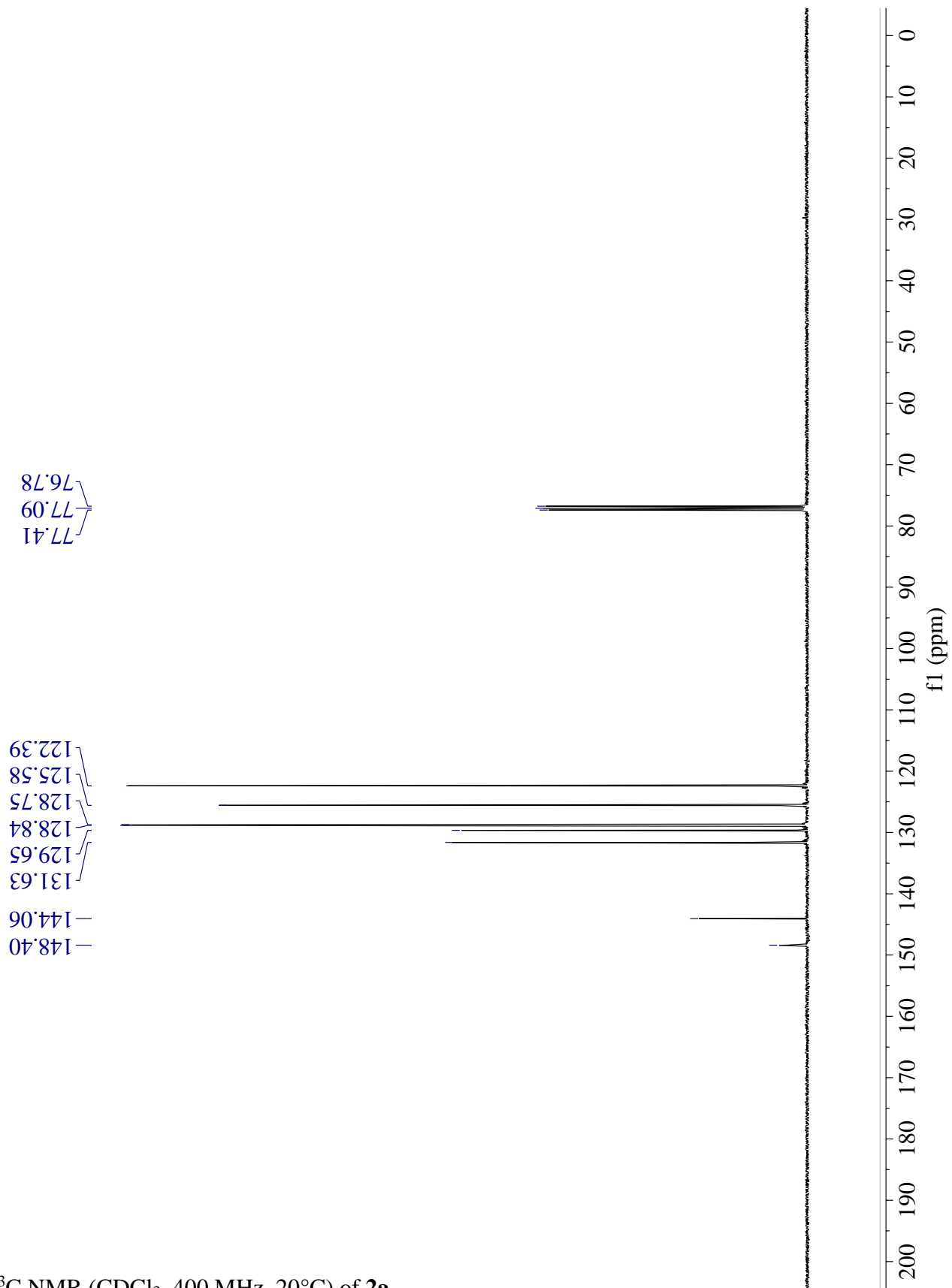
$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of 2a-2e and 2i-2u



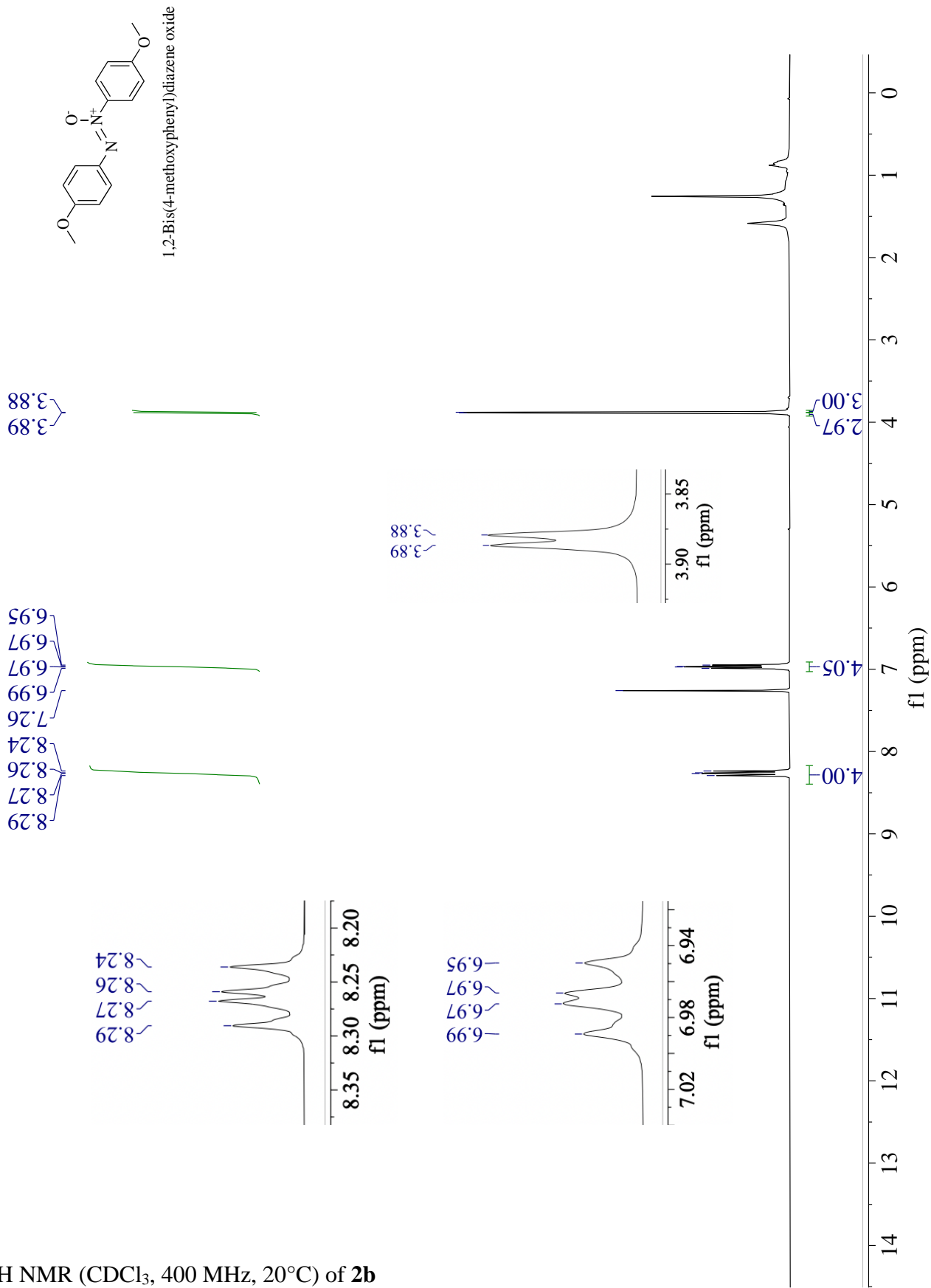
$^1\text{H}$  NMR (CDCl<sub>3</sub>, 400 MHz, 20°C) of **2a**



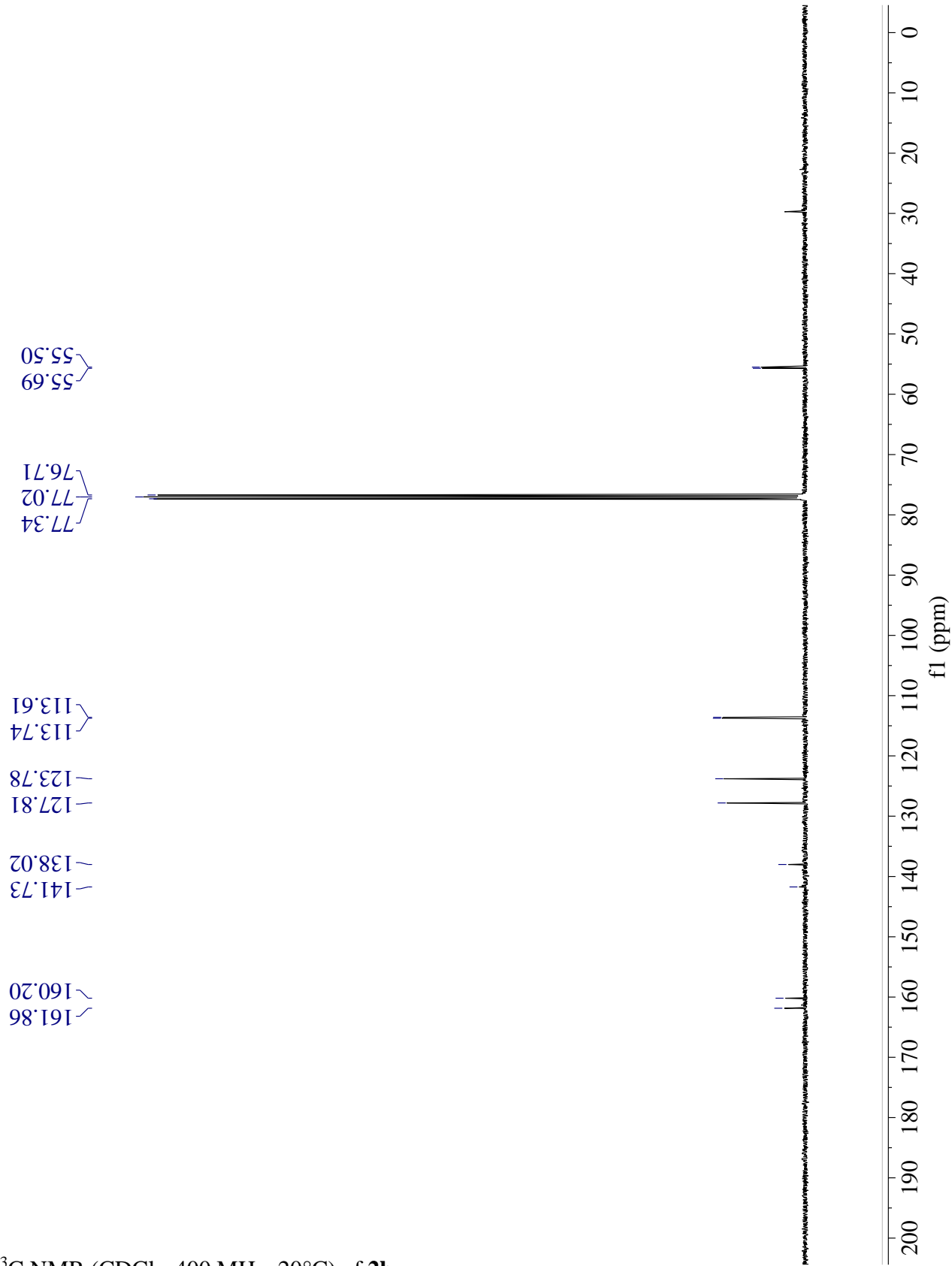
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 400 MHz,  $20^\circ\text{C}$ ) of **2a**



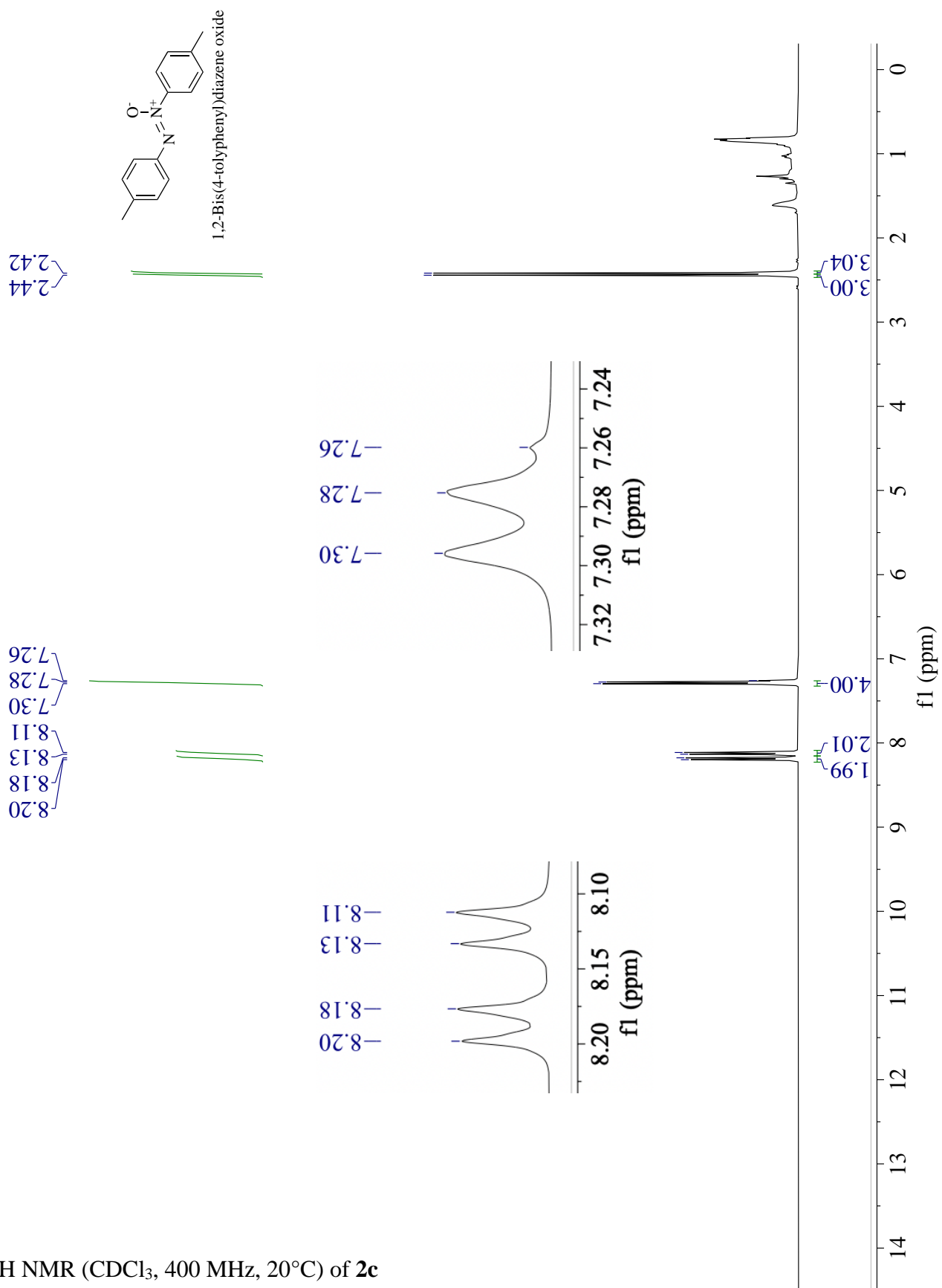
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz,  $20^\circ\text{C}$ ) of **2b**



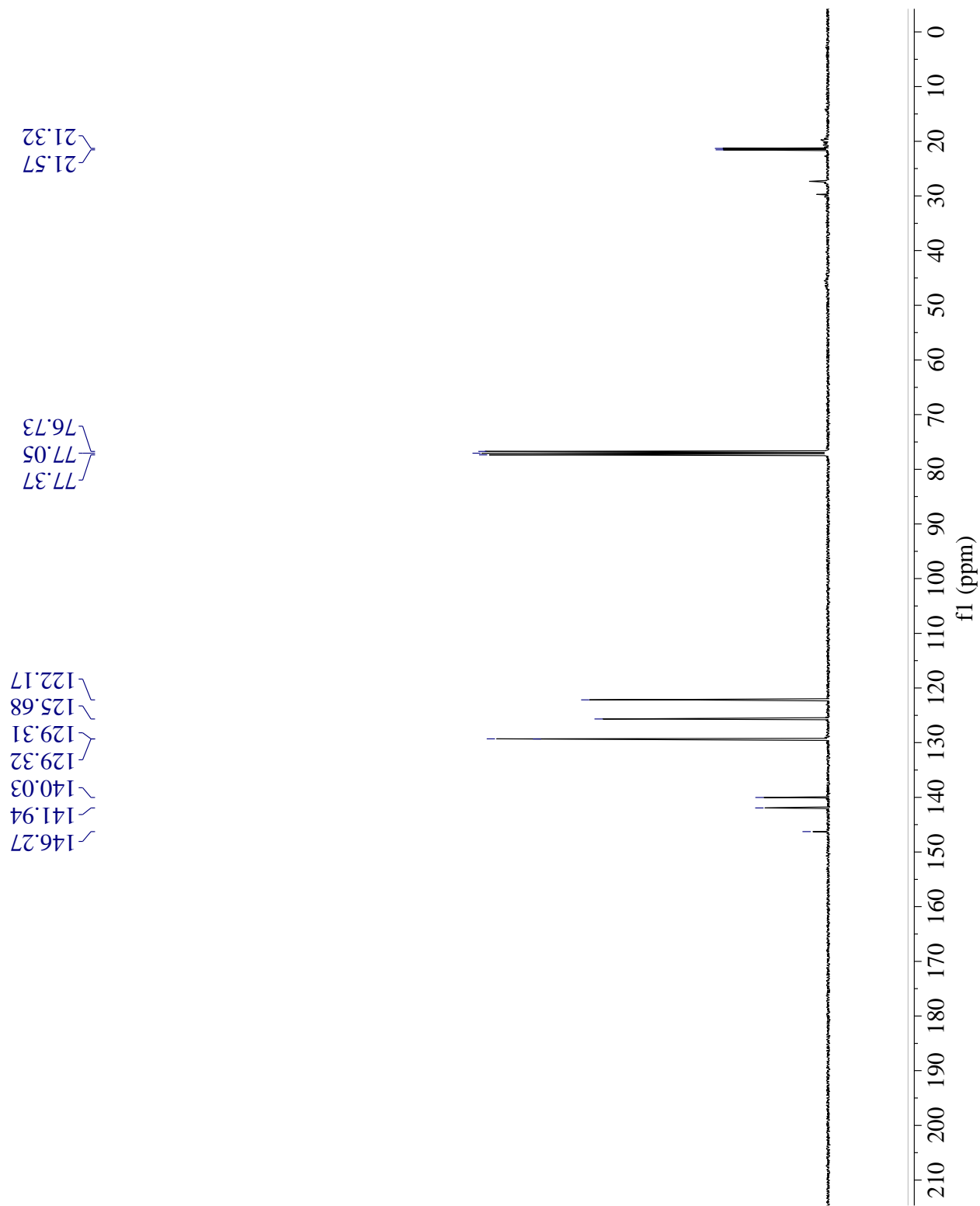
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 400 MHz,  $20^\circ\text{C}$ ) of **2b**



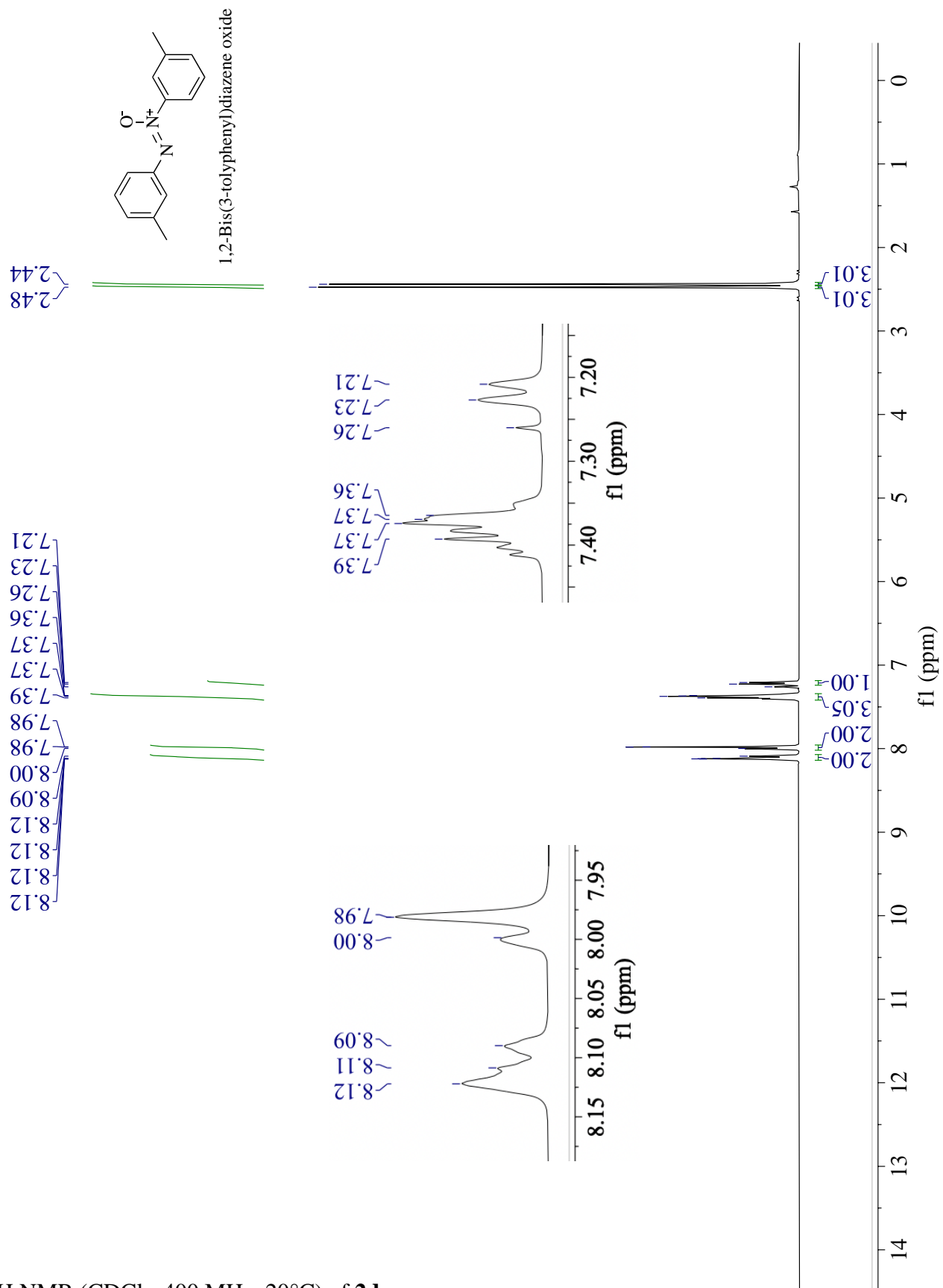
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz,  $20^\circ\text{C}$ ) of **2c**



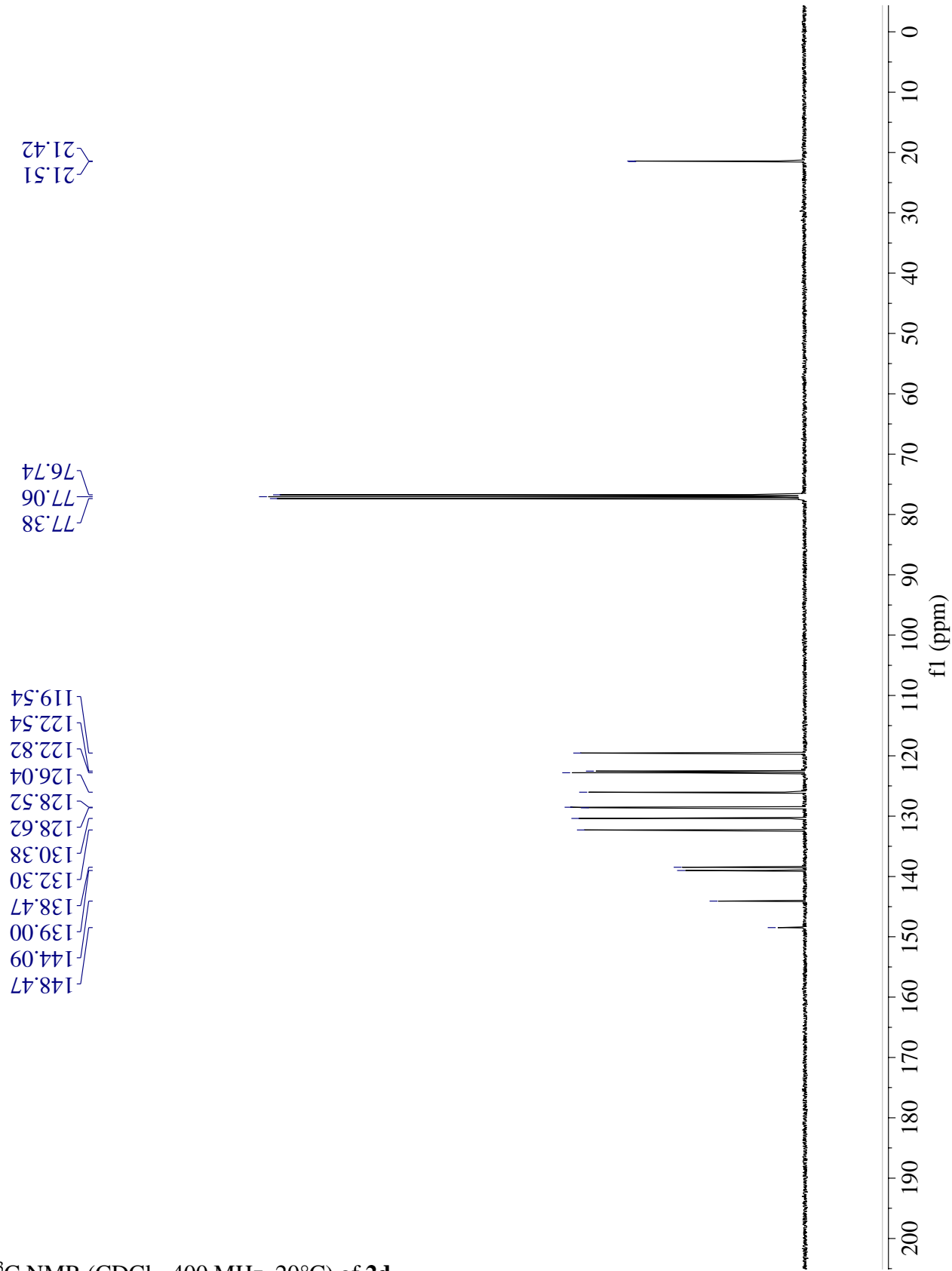
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 400 MHz,  $20^\circ\text{C}$ ) of **2c**



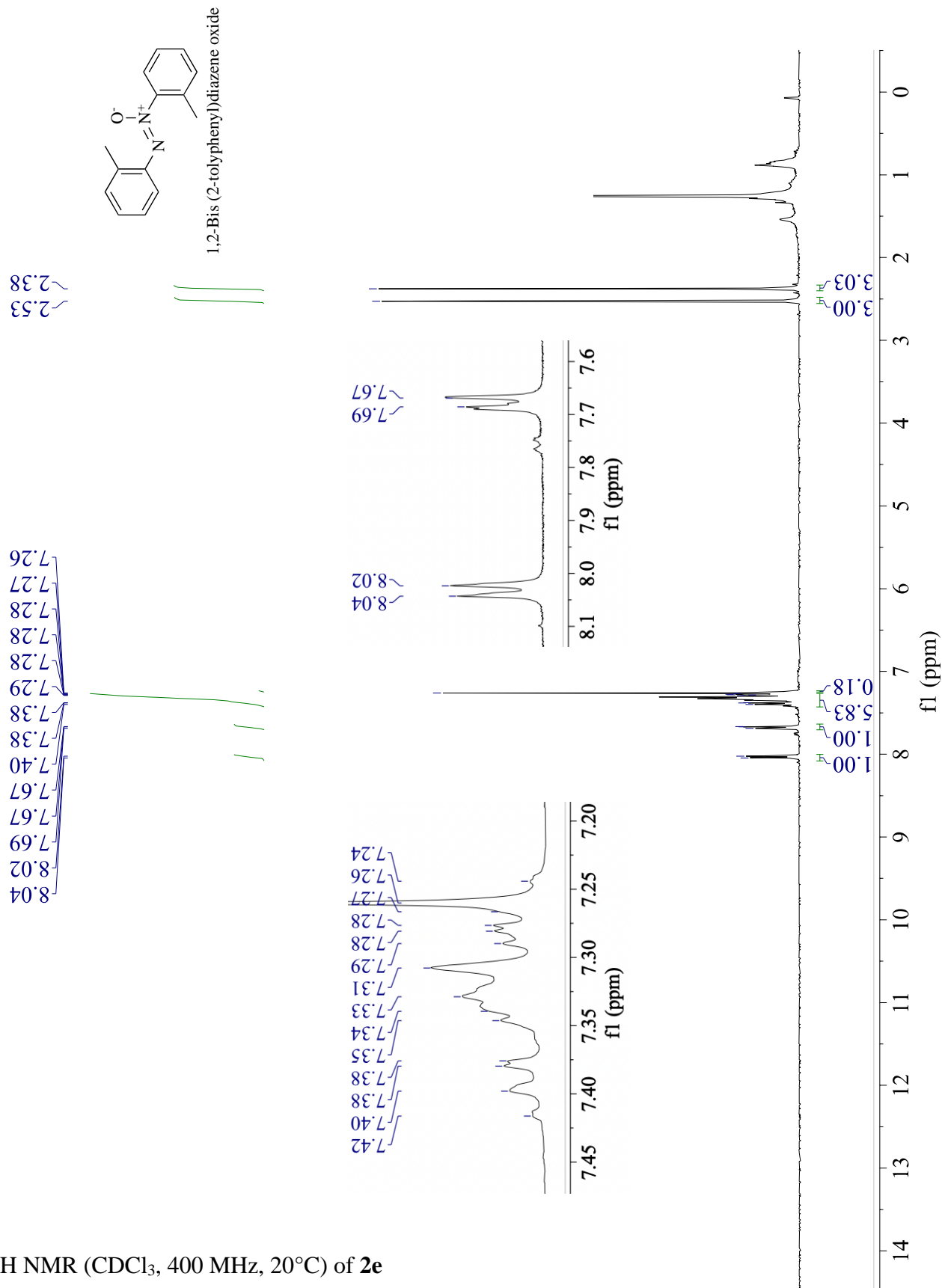
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 20°C) of **2d**



<sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz, 20°C) of **2d**

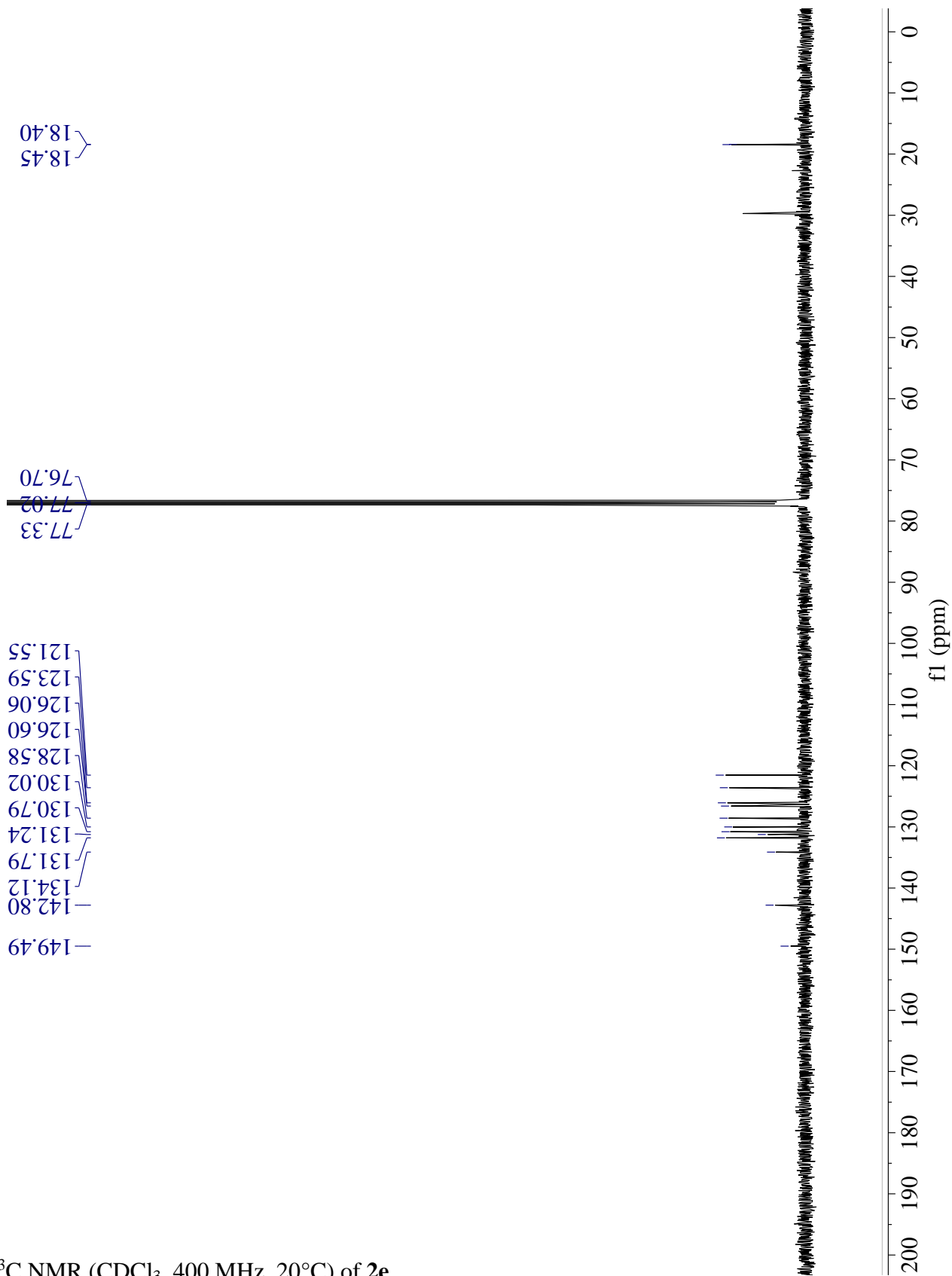


$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz,  $20^\circ\text{C}$ ) of **2e**

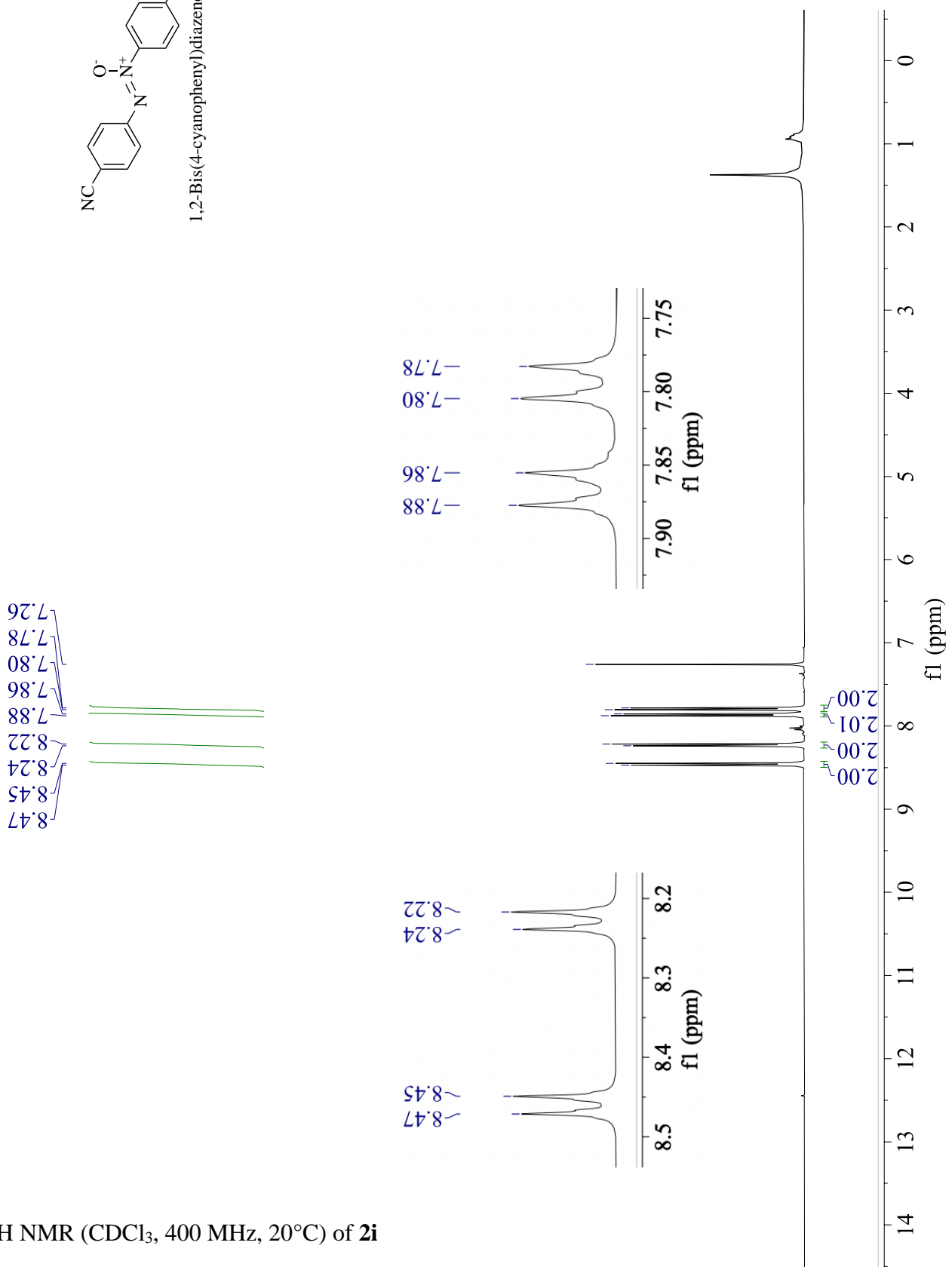




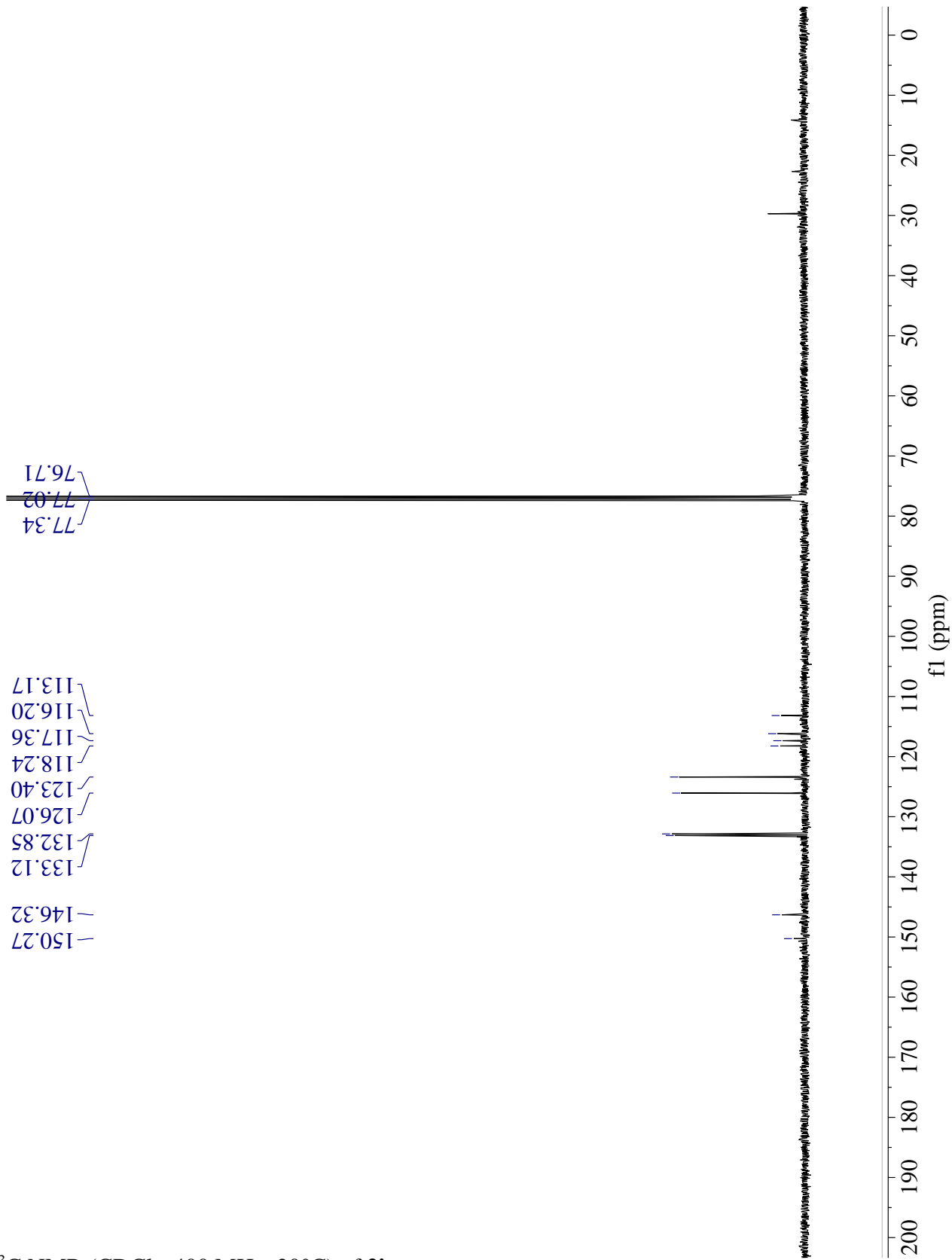
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz, 20°C) of **2e**

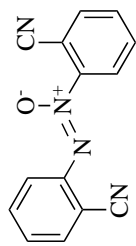


$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz,  $20^\circ\text{C}$ ) of **2i**

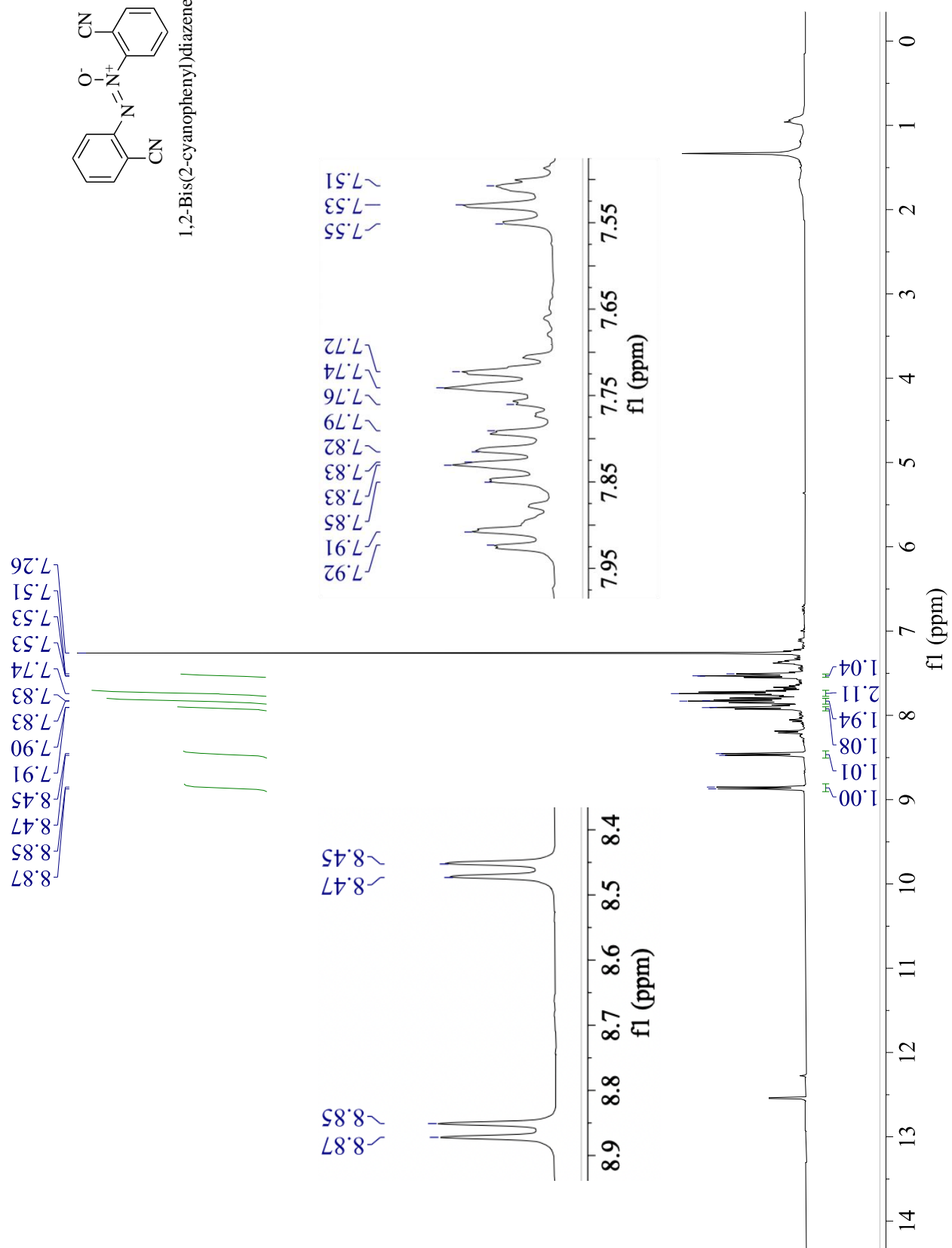


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 20°C) of **2i**



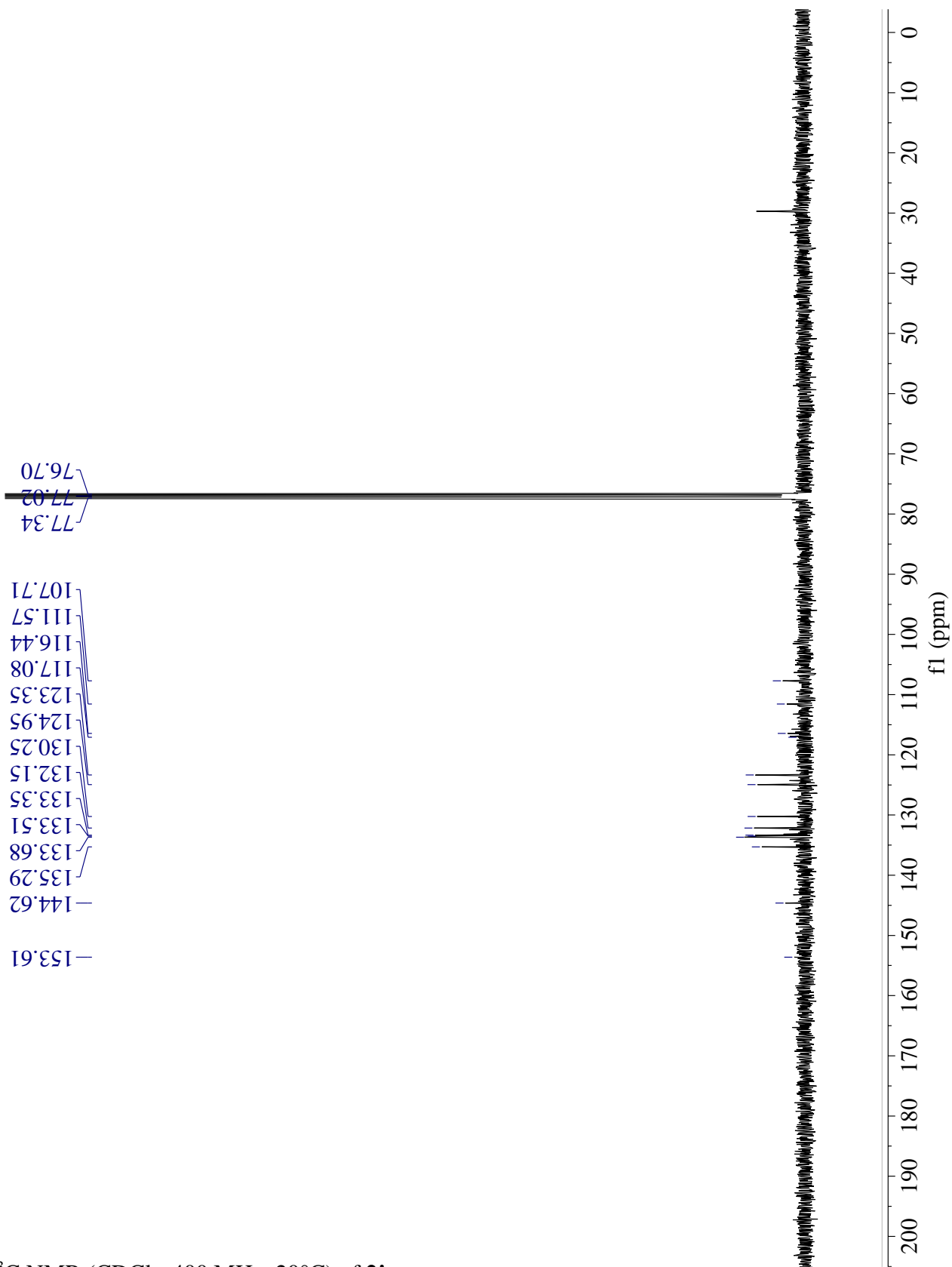


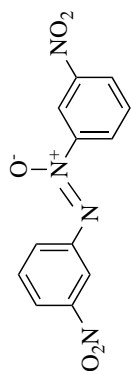
1,2-Bis(2-cyanophenyl)diazene oxide



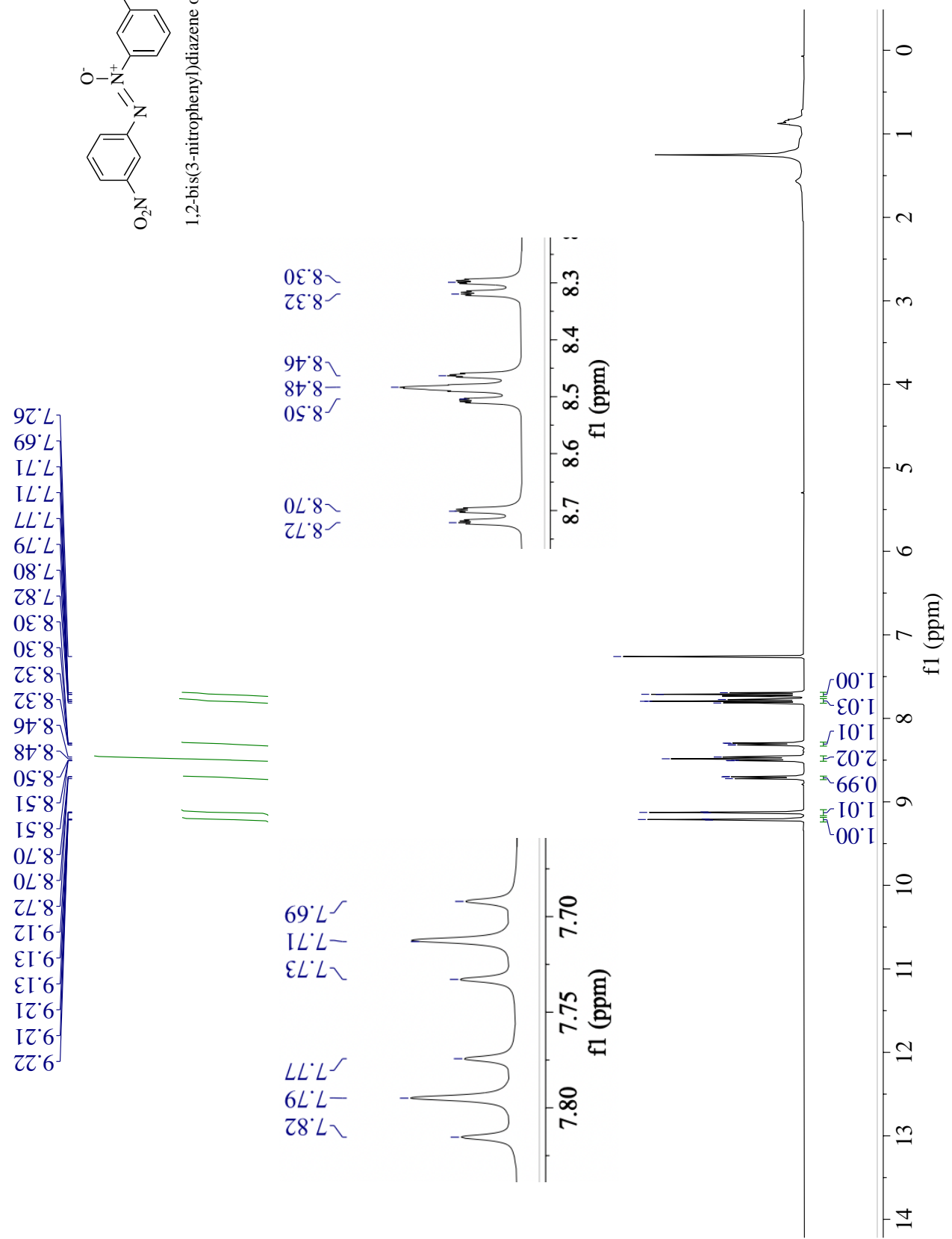
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz,  $20^\circ\text{C}$ ) of **2j**

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 20°C) of **2j**



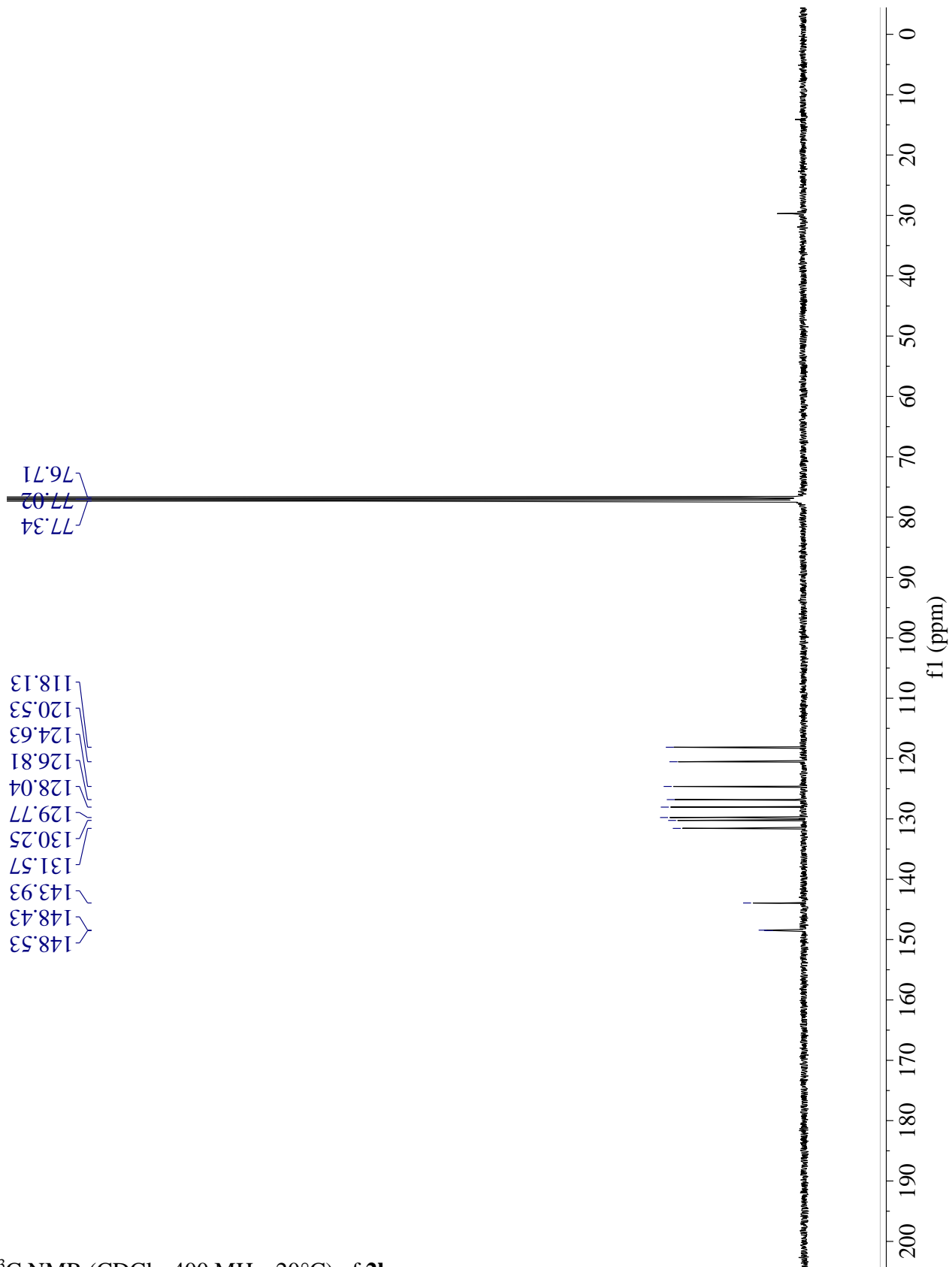


1,2-bis(3-nitrophenyl)diazene oxide

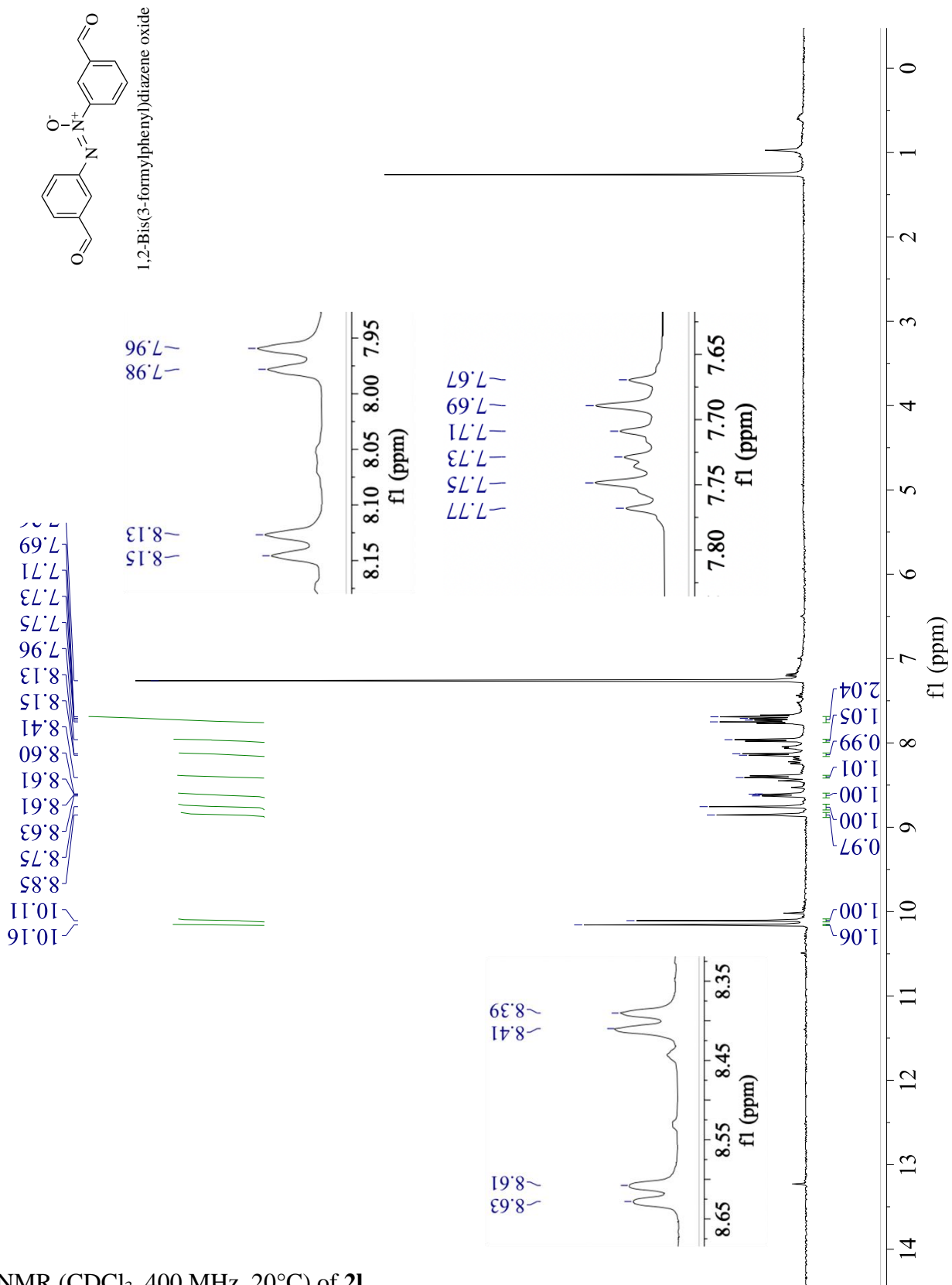


<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 20°C) of **2k**

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 400 MHz,  $20^\circ\text{C}$ ) of **2k**

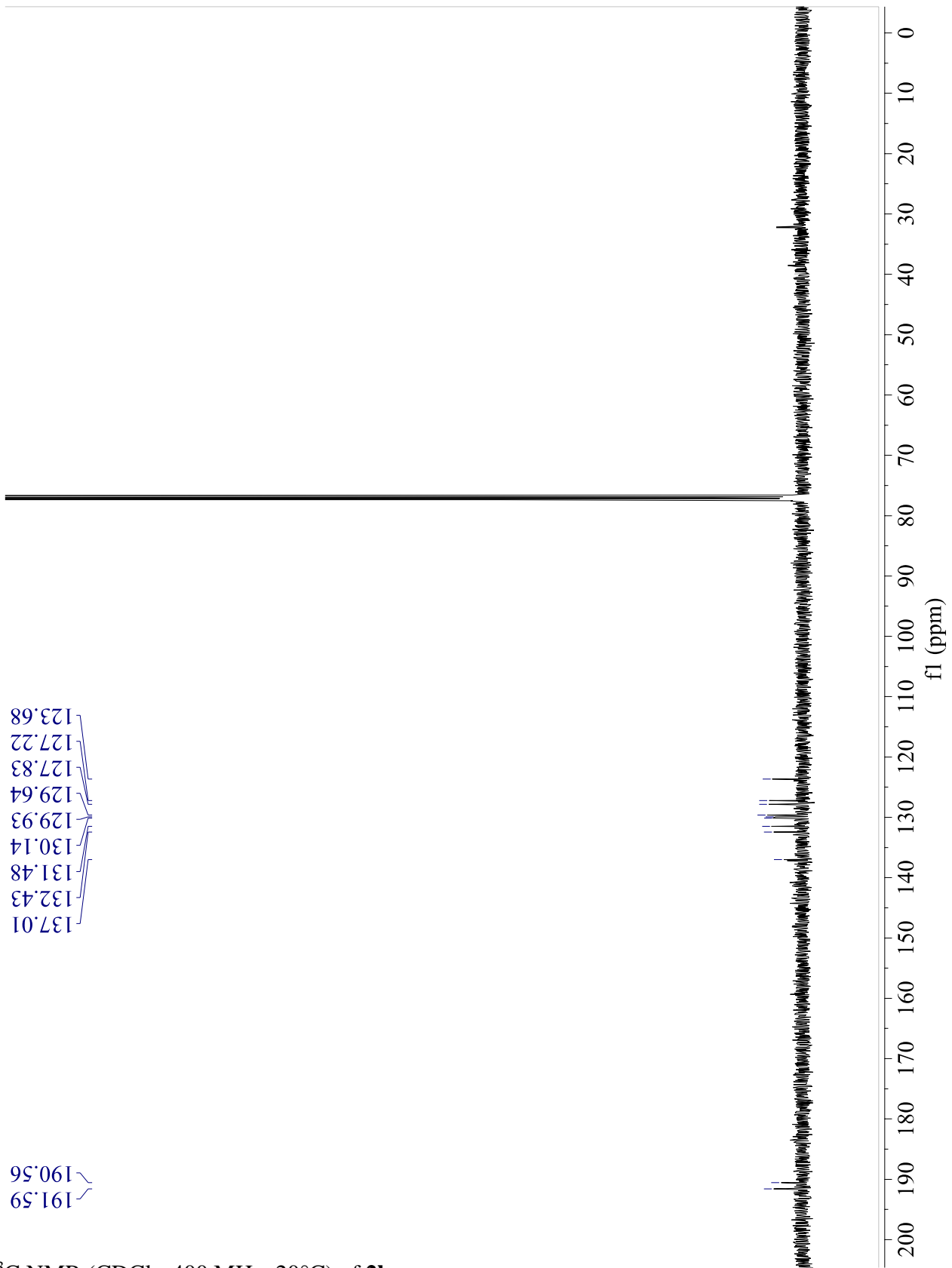


<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 20°C) of **2l**

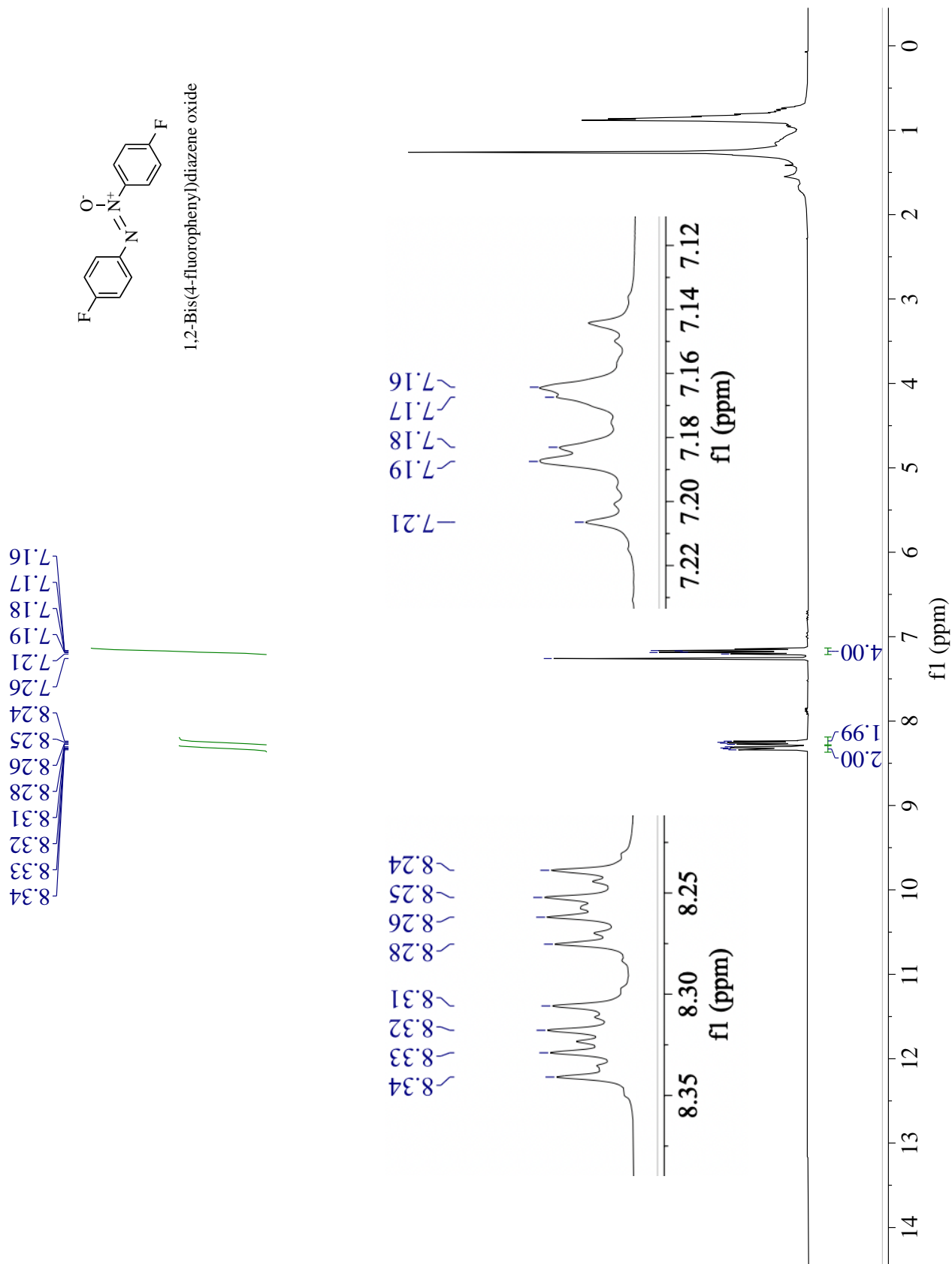




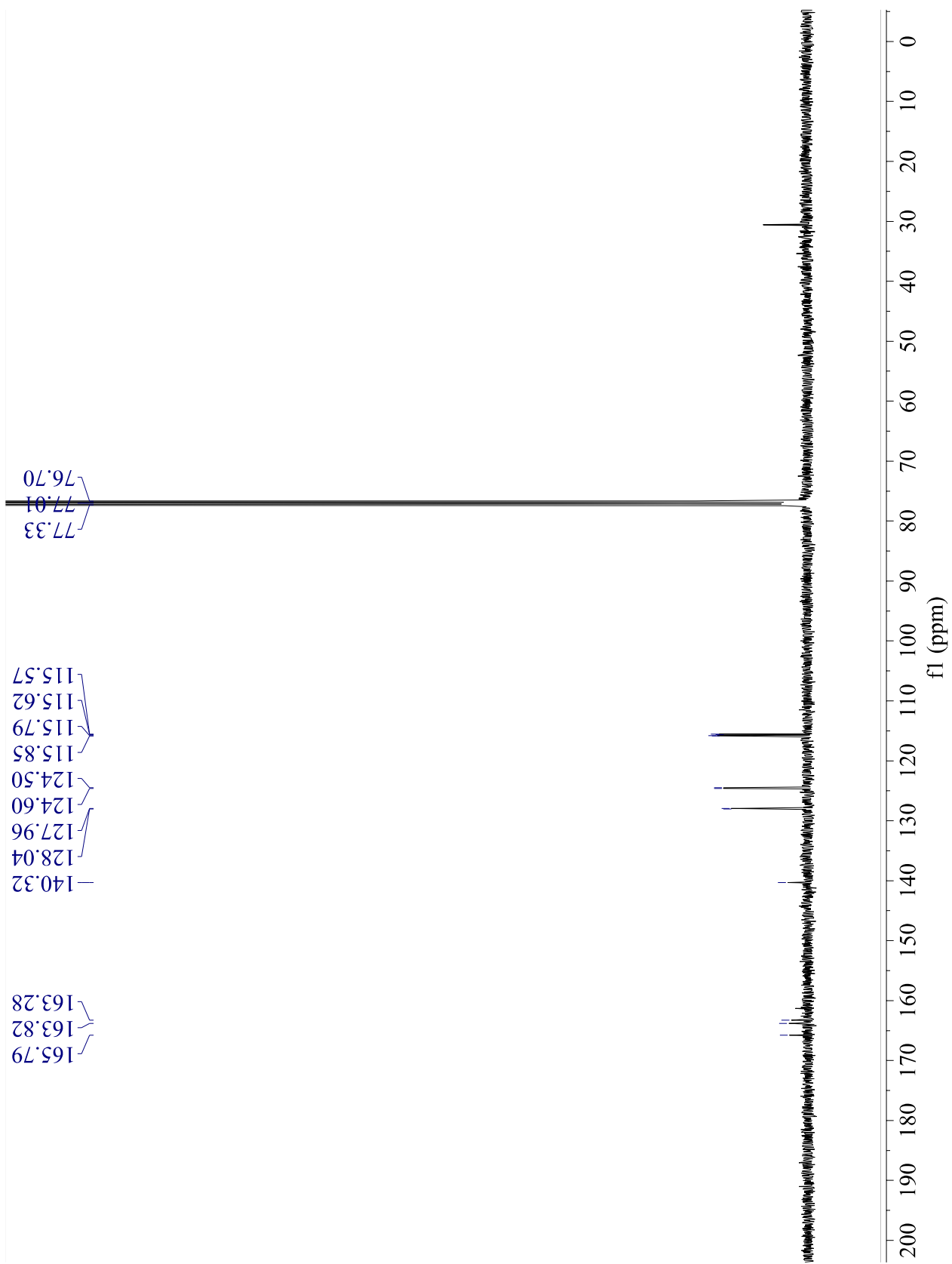
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz, 20°C) of **21**



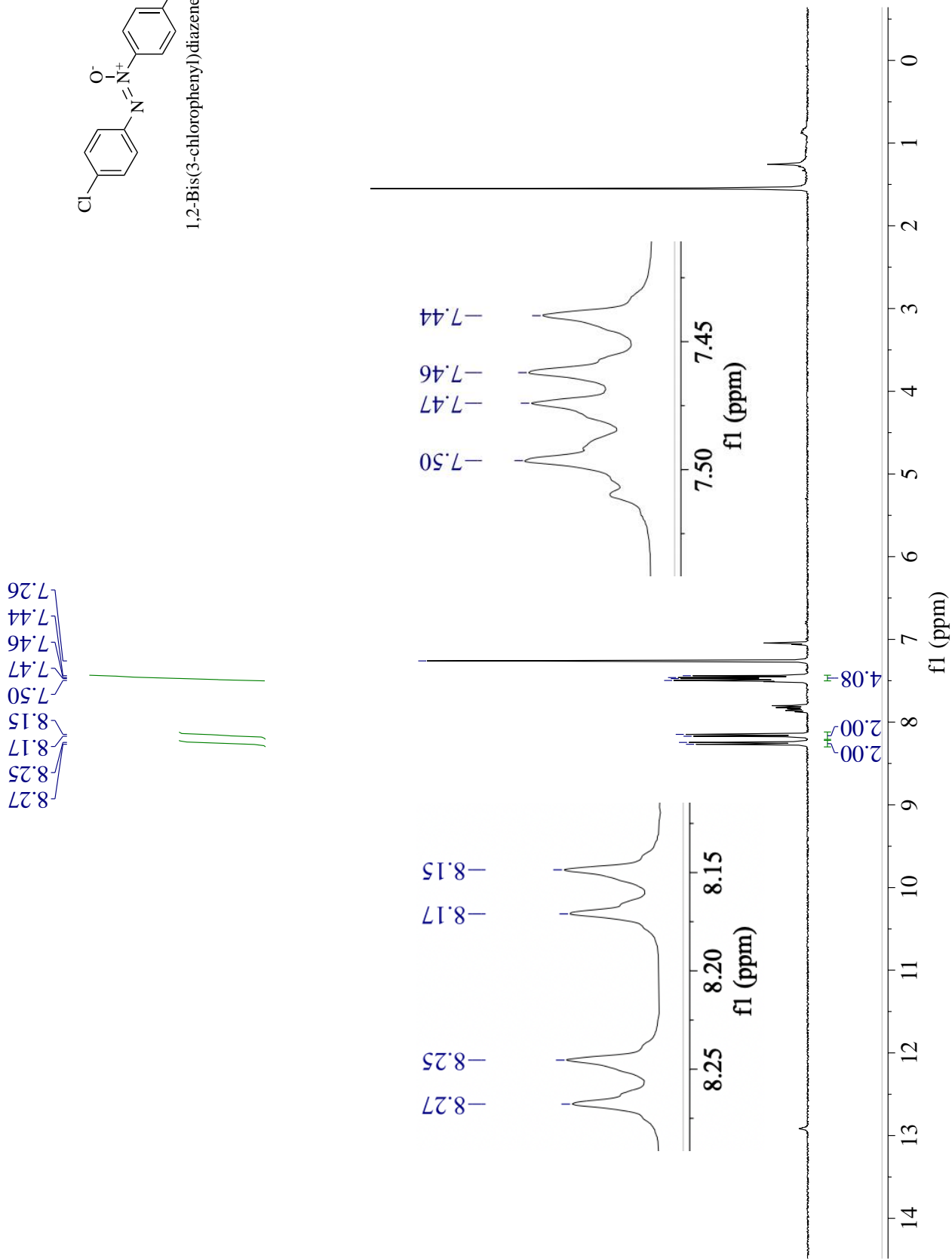
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz,  $20^\circ\text{C}$ ) of **2m**



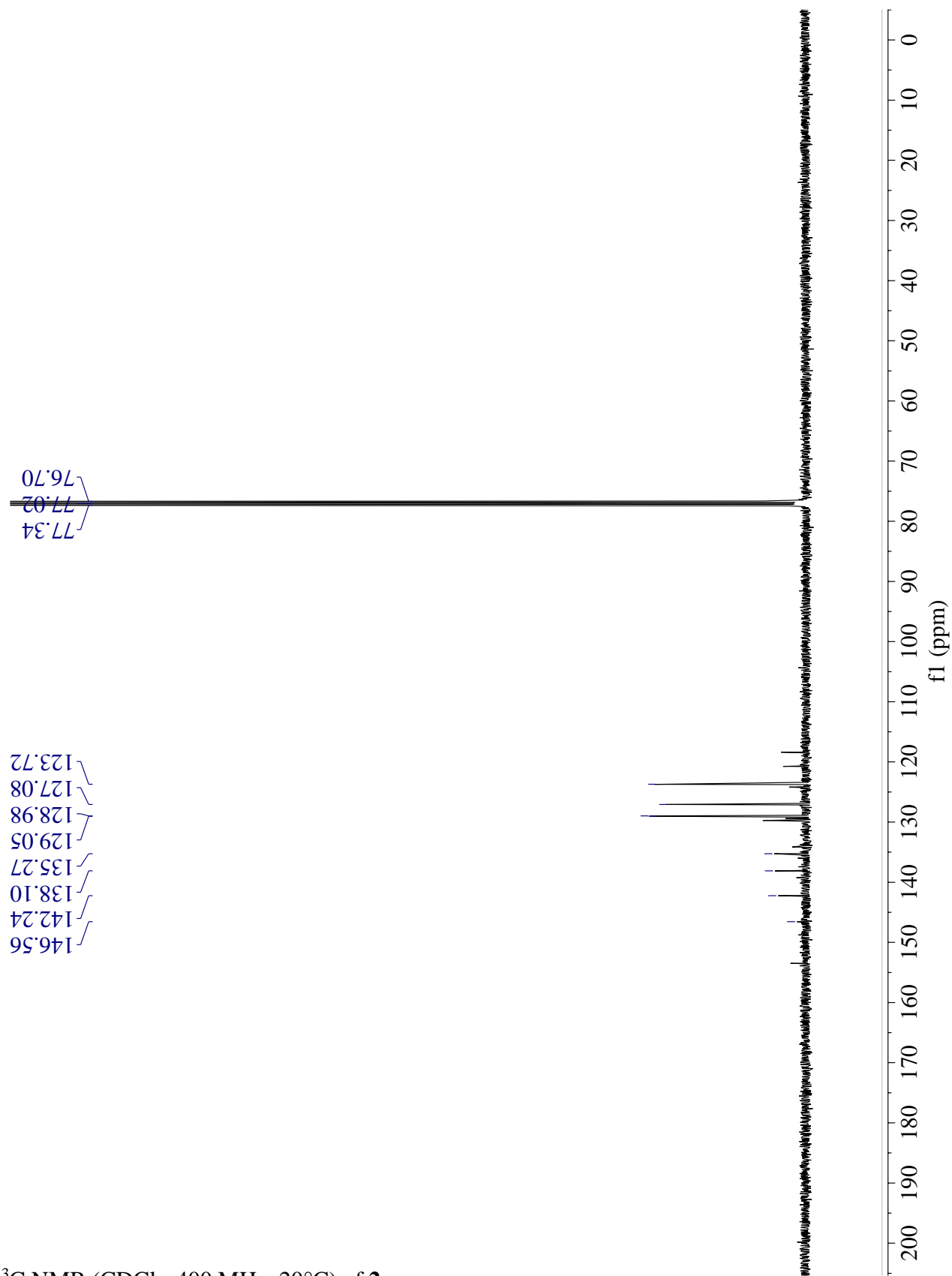
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 400 MHz,  $20^\circ\text{C}$ ) of **2m**



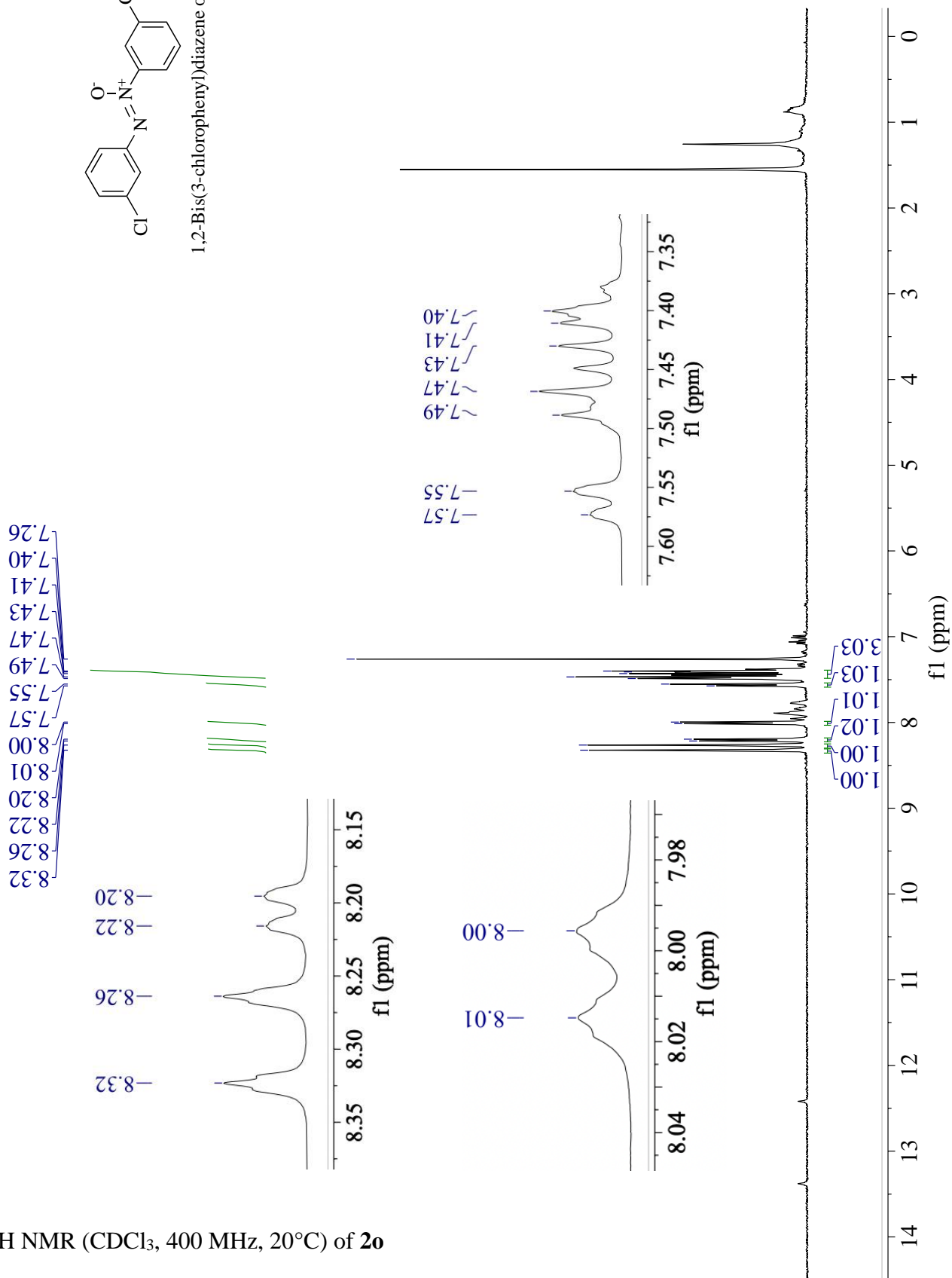
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz,  $20^\circ\text{C}$ ) of **2n**



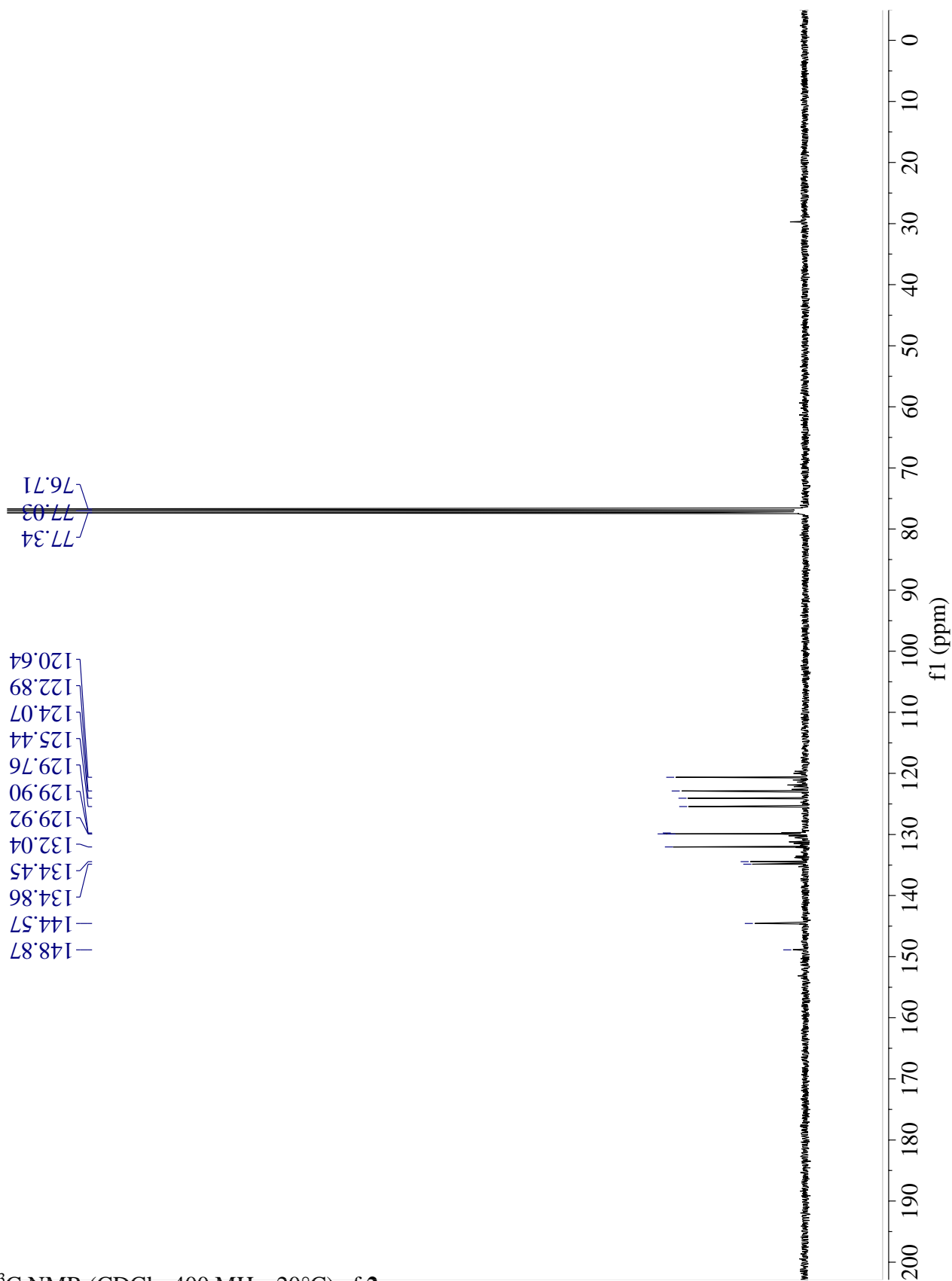
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 400 MHz,  $20^\circ\text{C}$ ) of **2n**

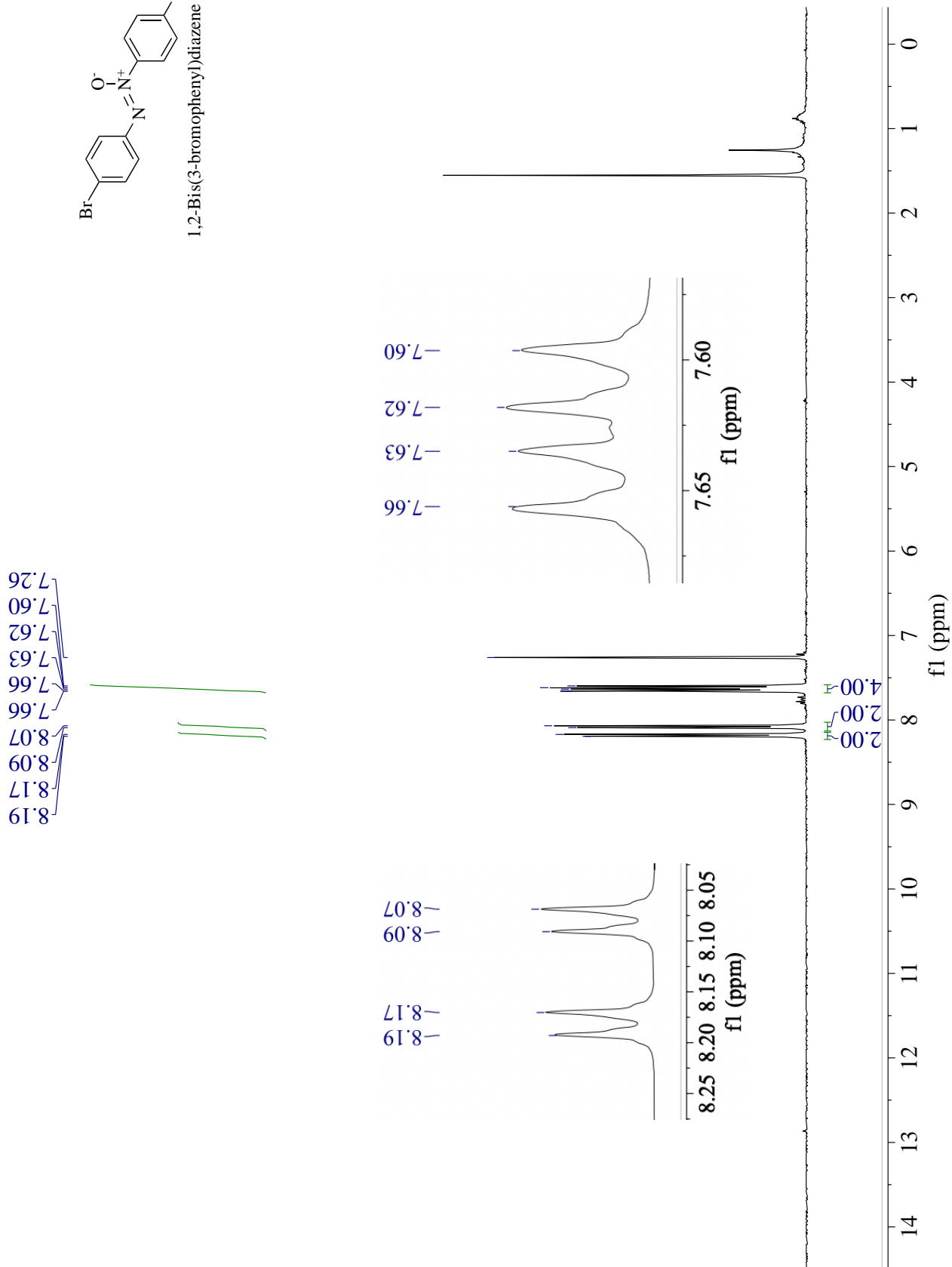
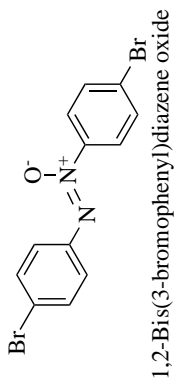


$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 20°C) of **2o**



<sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz, 20°C) of **2o**

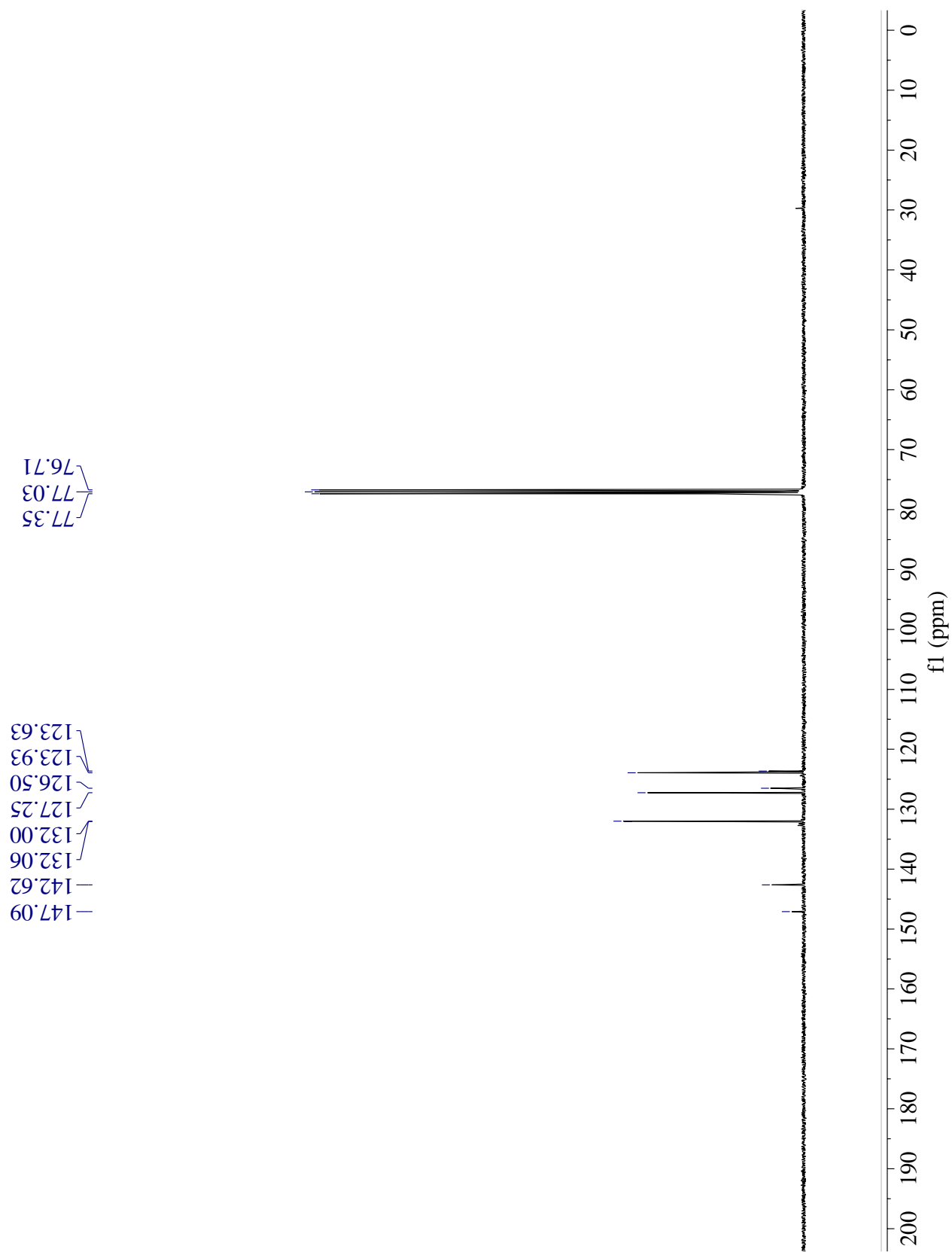




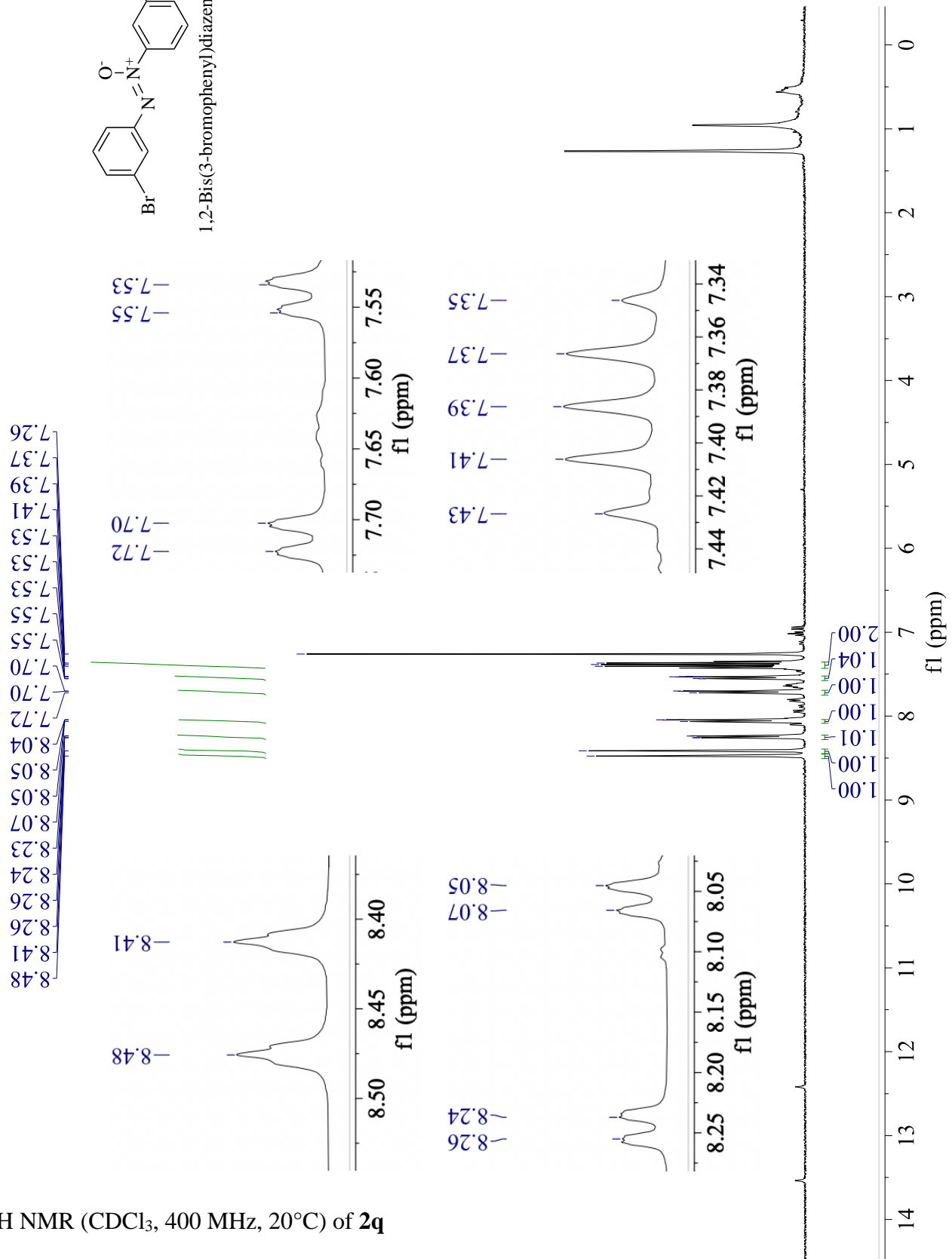
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz,  $20^\circ\text{C}$ ) of **2p**



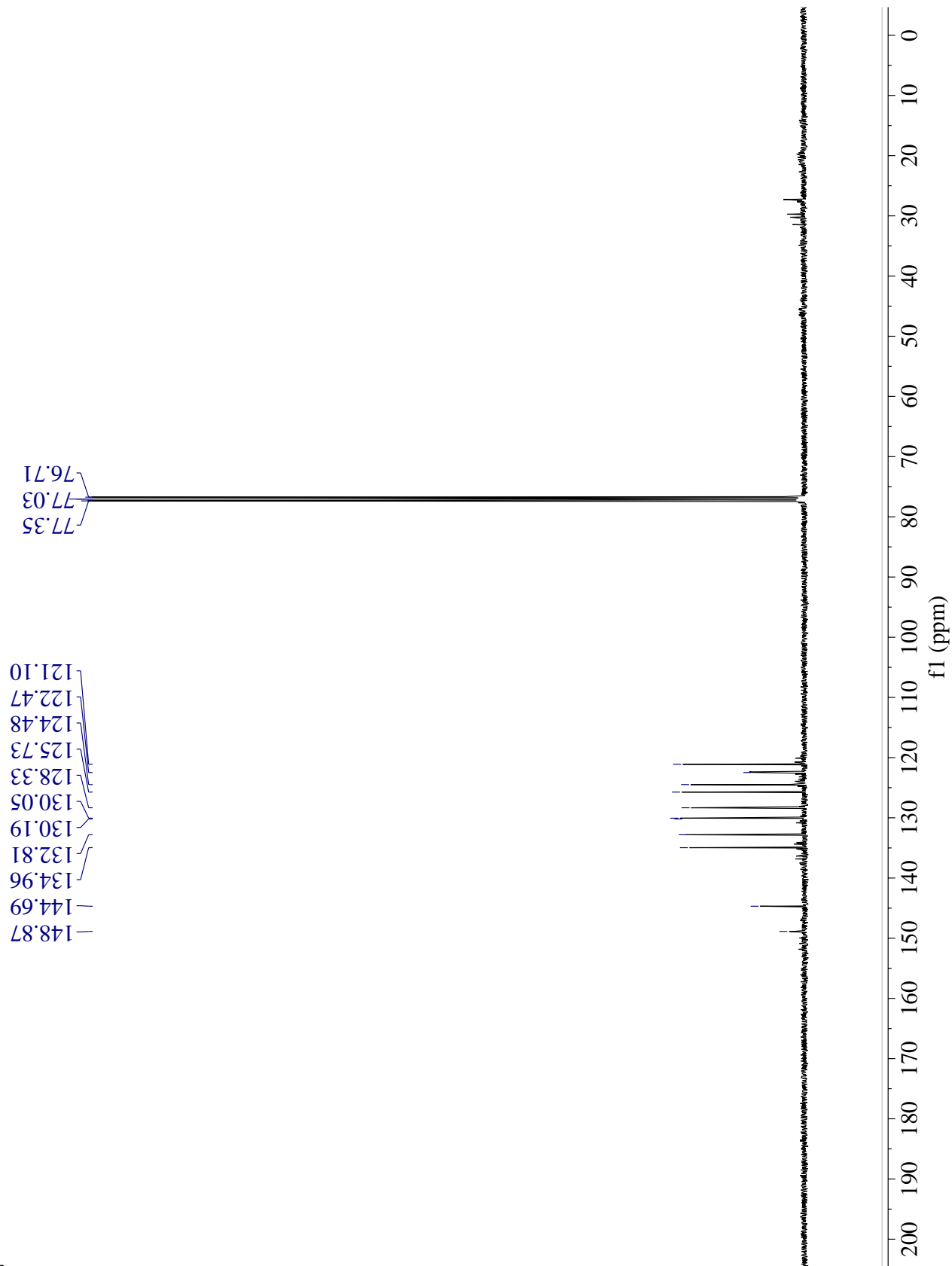
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 400 MHz,  $20^\circ\text{C}$ ) of **2p**



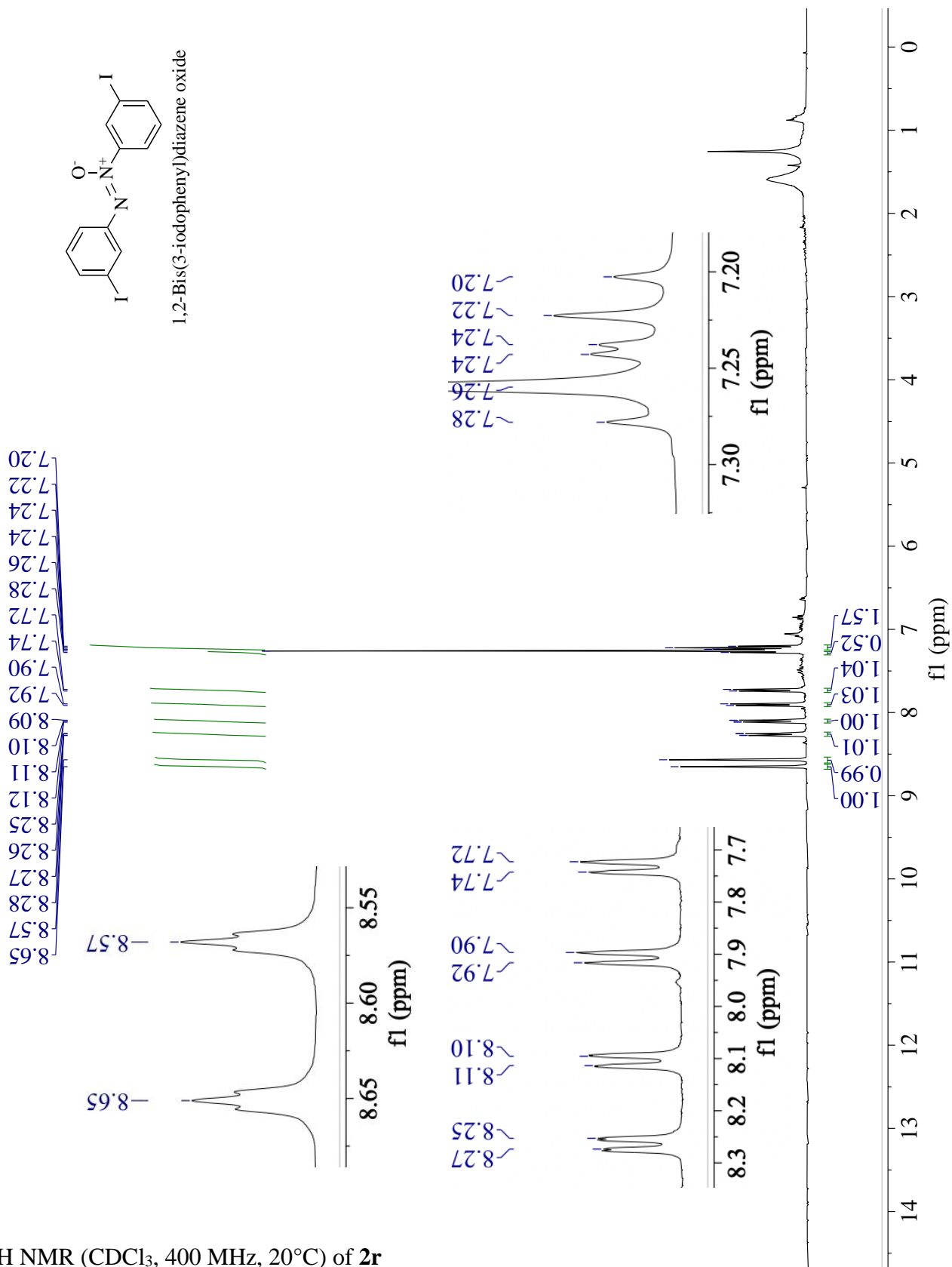
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz,  $20^\circ\text{C}$ ) of **2q**



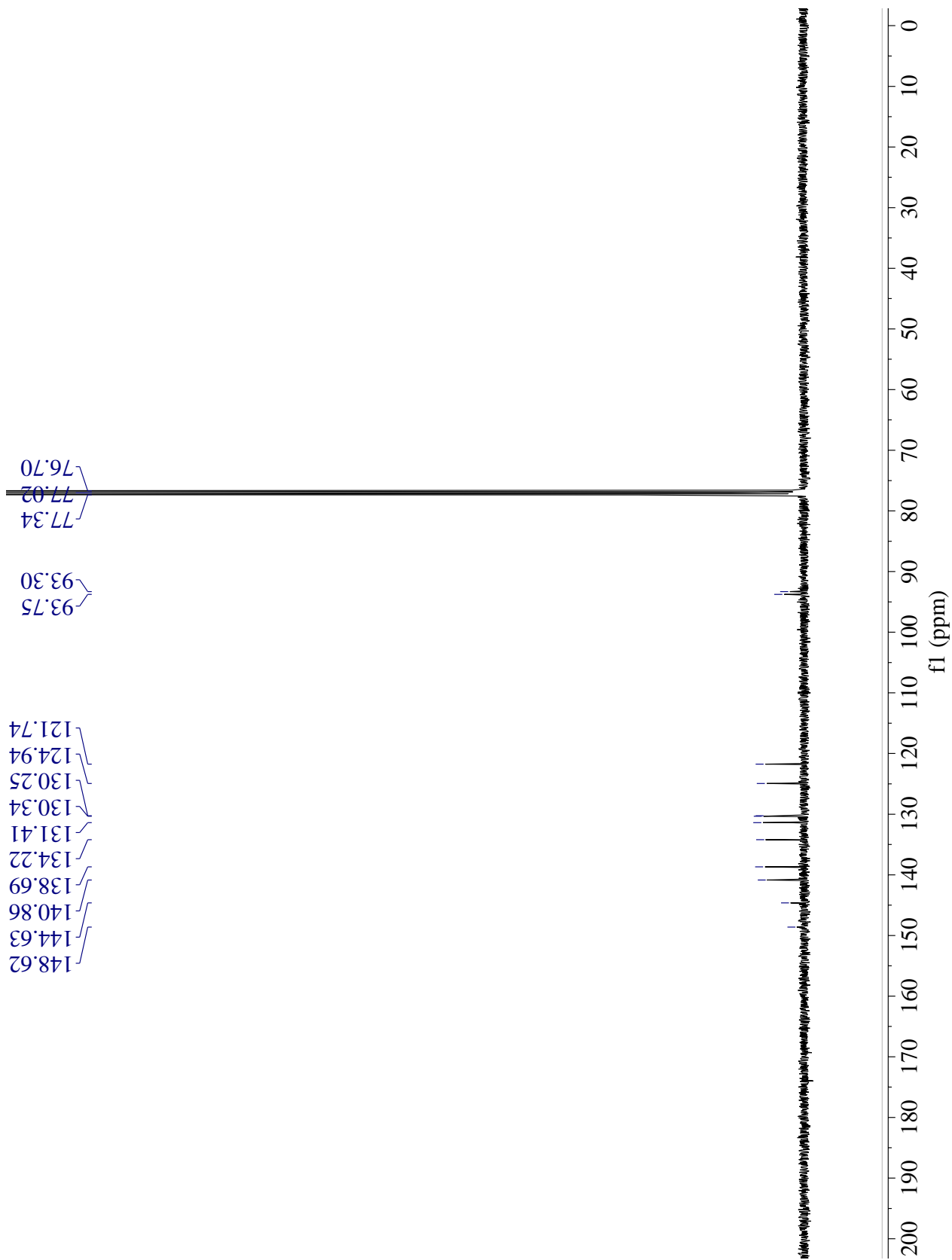
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 400 MHz,  $20^\circ\text{C}$ ) of **2q**

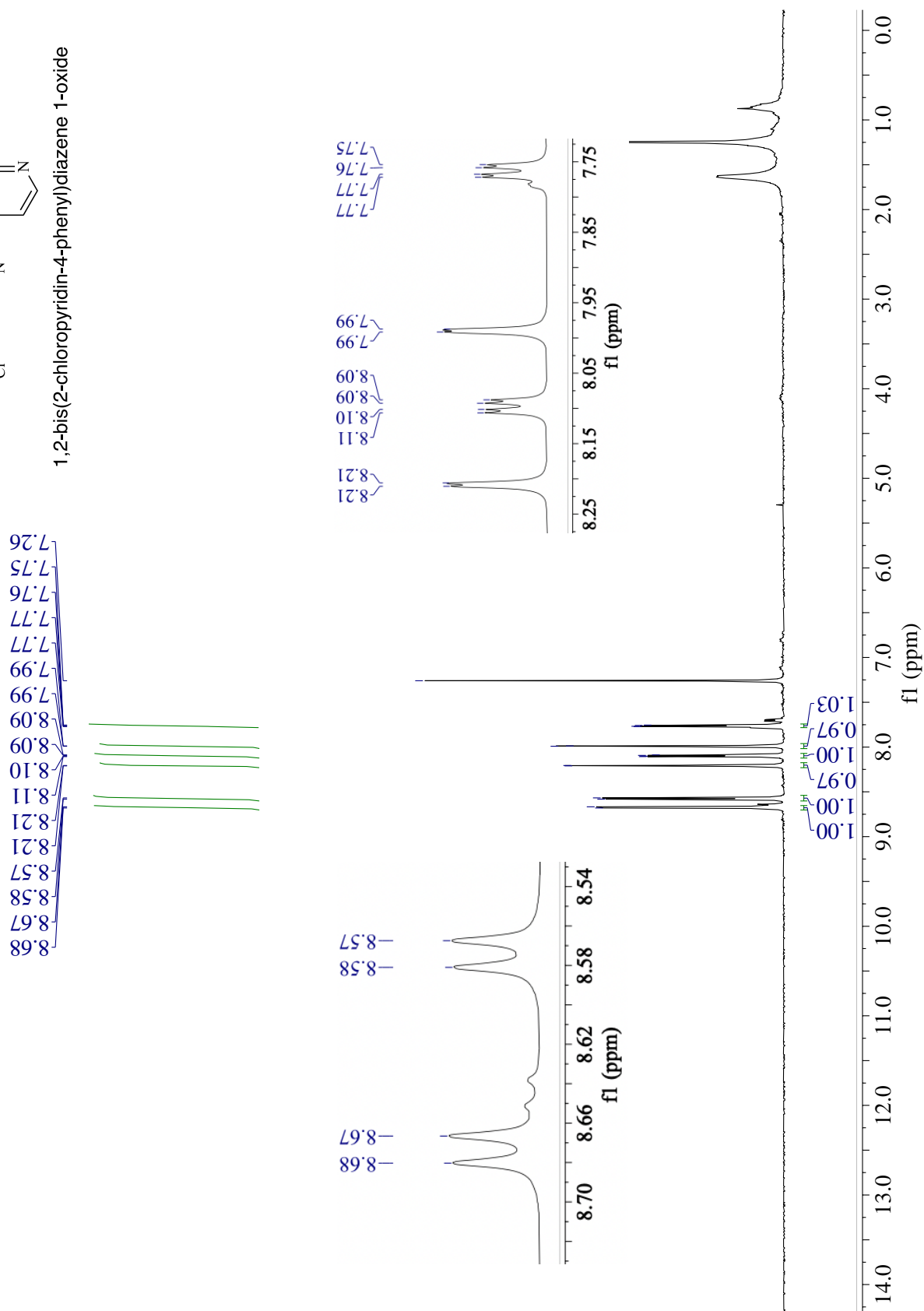
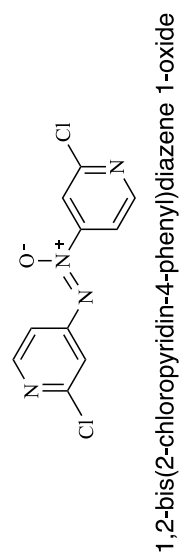


$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz,  $20^\circ\text{C}$ ) of **2r**



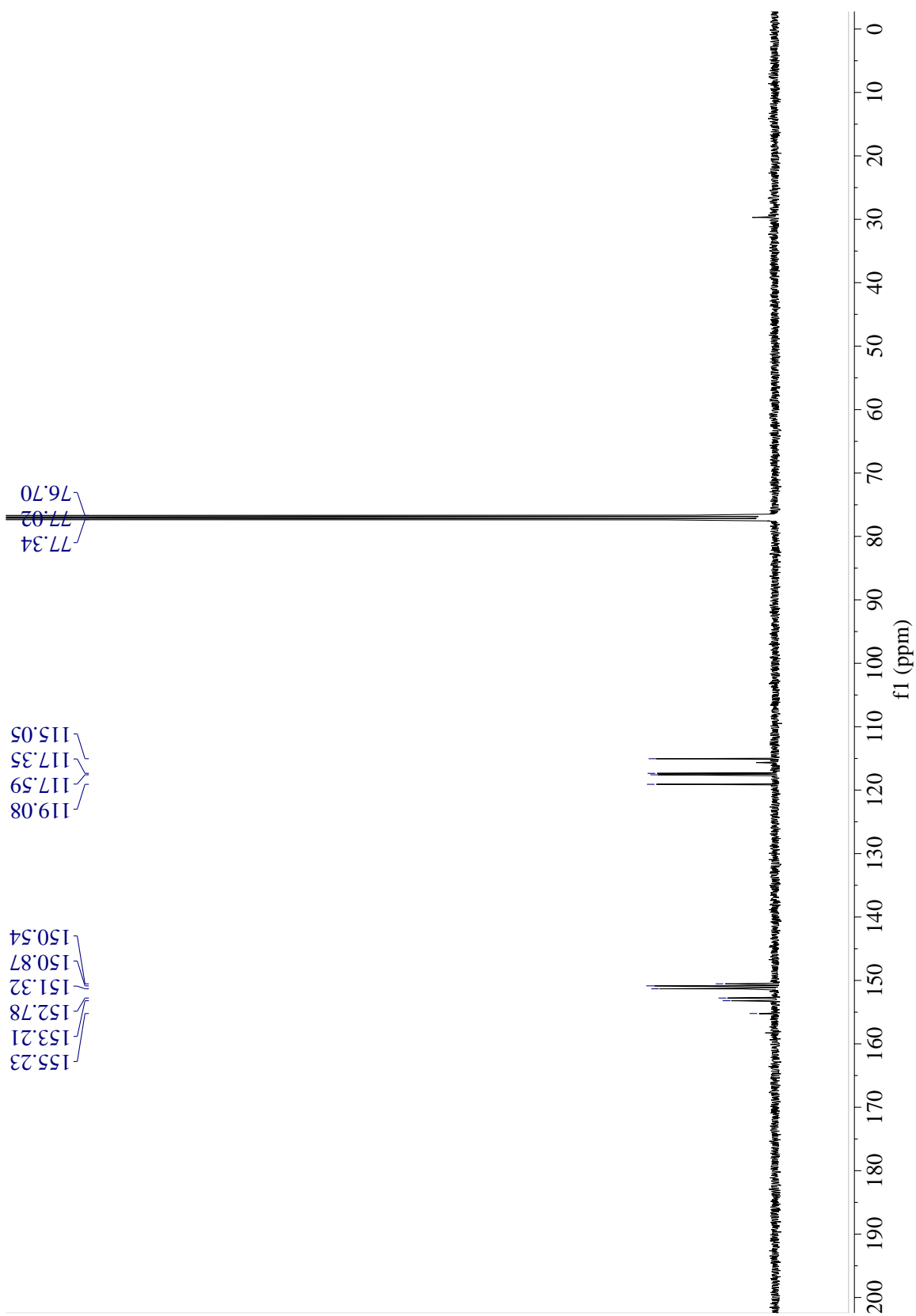
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz, 20°C) of **2r**

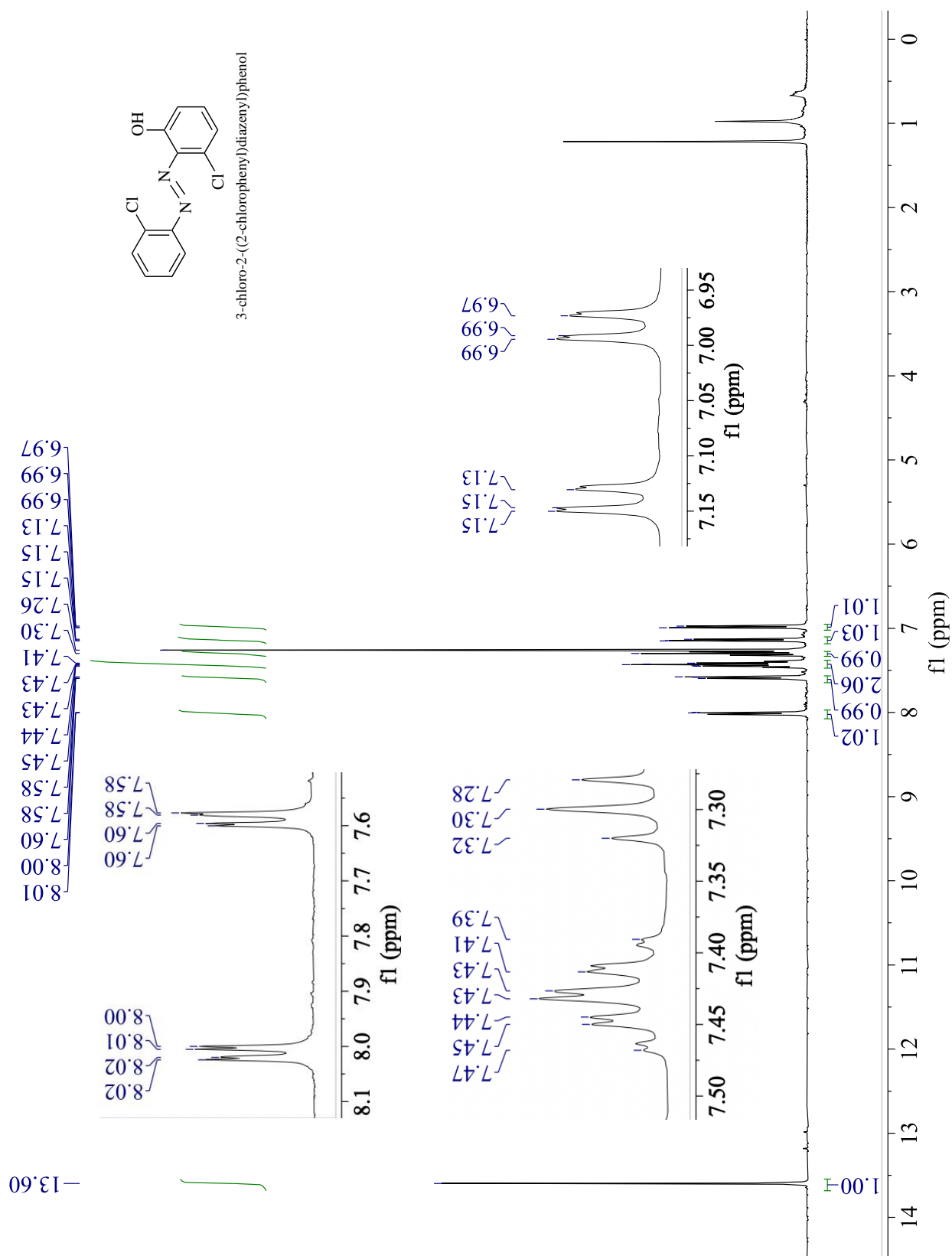




$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz,  $20^\circ\text{C}$ ) of **2u**

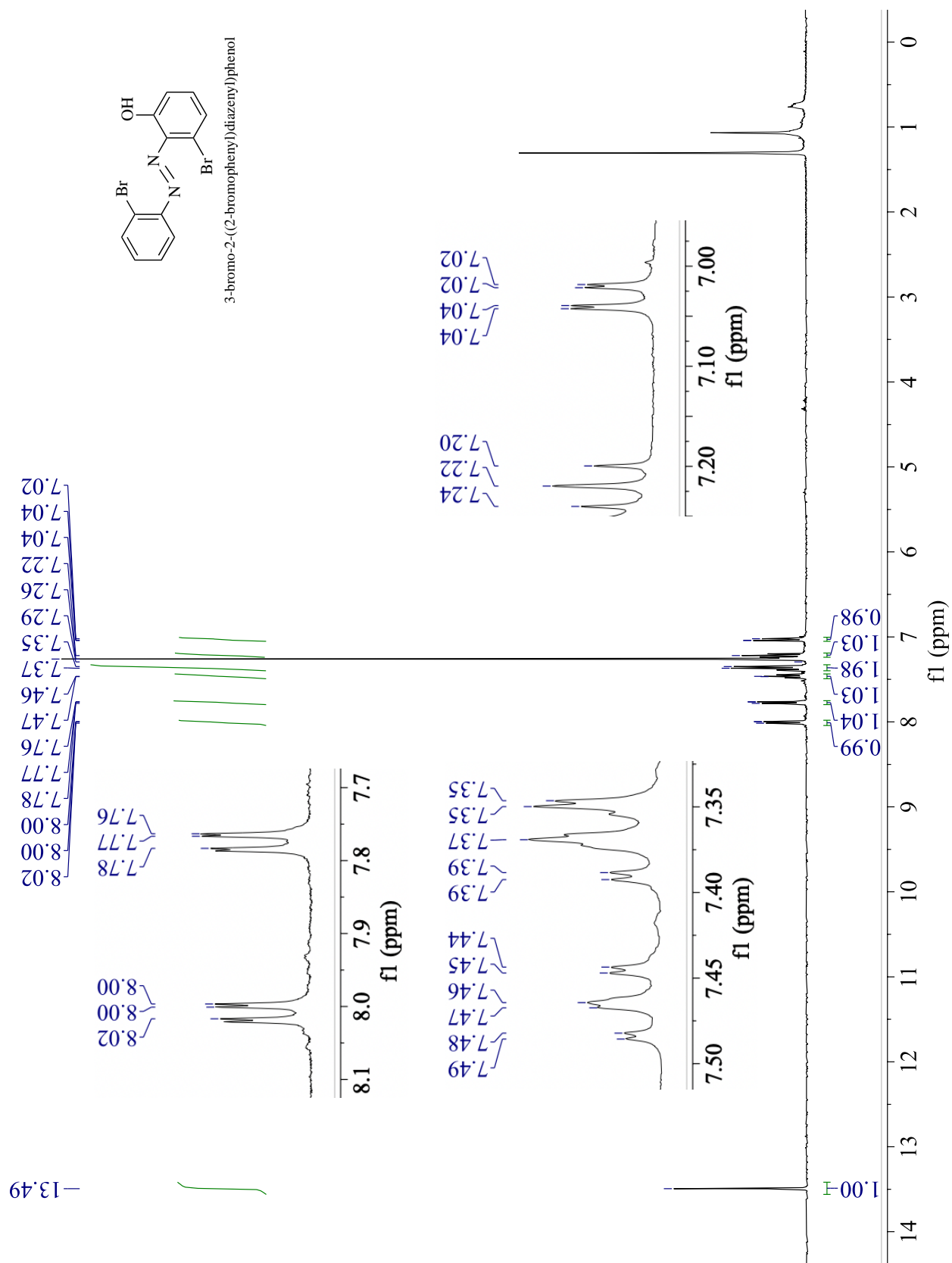
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 400 MHz,  $20^\circ\text{C}$ ) of **2u**





**Fig. S9** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 20°C) of isolated 3-chloro-2-((2-chlorophenyl)diazanyl)phenol (**3v**) produced after UVA irradiation of an aerated solution of 1-chloro-2-nitrobenzene (0.15M) in for 48h in *i*-PrOH.





**Fig. S10.** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 20°C) of isolated 3-bromo-2-((2-bromophenyl)diazinyl)phenol (**3w**) produced after UVA irradiation of an aerated solution of 1-bromo-2-nitrobenzene (0.15M) in for 48h in *i*-PrOH.