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SUPPLEMENTARY INFORMATION

Visible-Light Photocatalytic Metal-Free Multicomponent Ugi-like Chemistry

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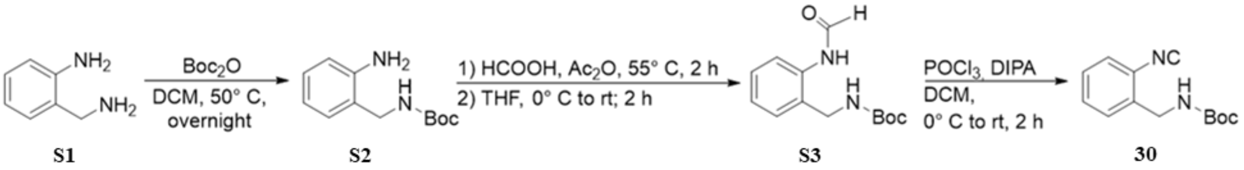
Contents:

Synthetic procedure for the synthesis of isocyanide *30*



In a 50 mL round bottom flask equipped with a magnetic stir bar, 2-aminobenzylamine ***S1*** (500.0 mg, 4.1 mmol) was dissolved in dichloromethane (16.4 mL, 0.25 M) and di-*tert*-butyl dicarbonate (893.2 mg, 1 equiv.) was added to the solution. The resulting mixture was stirred at 50° C overnight, until the completion of the reaction, as monitored by TLC. Then the solvent was removed under vacuum and the crude mixture was purified by silica gel chromatography (*n*-hexane/ethyl acetate 97:3) to afford *tert*-butyl (2-aminobenzyl)carbamate ***S2*** as a white solid (829.5 mg, 91% yield).

In a 50 mL two-necked round bottom flask, a mixture of formic acid (362.0 µL, 9.6 mmol, 2.7 equiv.) and acetic anhydride (771.2 µL, 8.2 mmol, 2.3 equiv.,) was stirred at 55°C for 2 h. After the reaction was cooled at room temperature, the crude mixture was added dropwise to a solution of ***S2*** (790.0 mg, 3.5 mmol, 1 equiv.) in THF (5.8 mL, 0.6 M), at 0° C. The resulting mixture was stirred at room temperature for additional 2 h, until the completion of the reaction, as monitored by TLC. Then the reaction was cooled to 0° C and a saturated aqueous solution of $NaHCO_3$ was added slowly under vigorous stirring, until neutral pH was reached. EtOAc was added, and the two phases were separated; the aqueous layer was further extracted with EtOAc (x2), then the combined organic extracts were washed with brine, dried over sodium sulfate, and concentrated under reduced pressure to give ***S3*** in a quantitative yield. The crude material was used in the next step without further purification.

In a 100 ml round bottom flask equipped whit a magnetic stir bar, *tert*-butyl (2-formamidobenzyl)carbamate ***S3*** (876.1 mg, 3.5 mmol) was dissolved in dichloromethane (50 mL, 0.07 M), and diisopropylamine (3.0 mL, 21 mmol, 6 equiv.) was added to the solution. After cooling to 0°C, phosphorus oxychloride (687 µL, 7.3 mmol, 2.1 equiv.) was added dropwise to the reaction mixture, which was stirred at room temperature for 2 h. After the completion of the reaction, as monitored by TLC, the mixture was cooled to 0° C and a saturated aqueous solution of $NaHCO_3$ was added slowly under vigorous stirring, until pH ~ 9. Then CH_2Cl_2 was added, and the two phases were separated; the organic layer was further washed with a saturated aqueous solution of $NaHCO_3$ (x2), brine (x1), dried over sodium sulfate, and concentrated under vacuum. The crude mixture was purified by silica gel chromatography (*n*-hexane/ethyl acetate 95:5) to afford *tert*-butyl (2-isocyanobenzyl)carbamate ***30*** as a yellow solid (510.5 mg, 63% yield).

N-(N-methyl-N-phenylglycyl)-N-(tosylmethyl)benzamide (**5**).[1] The crude material (reaction time: 20 h) was purified by column chromatography (*n*-hexane/ethyl acetate 93:7) to give the product as a yellow amorphous solid (19.6 mg, 56% yield). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.76 (d, J = 8.2 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.54 (d, J = 7.3 Hz, 2H), 7.42 (t, J = 7.8 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.17 – 7.15 (m, 2H), 6.77 (t, J = 7.3 Hz, 1H), 6.46 (d, J = 8.2 Hz, 2H), 5.09 (s, 2H), 4.13 (s, 2H), 2.72 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 173.1, 171.7, 148.4, 145.6, 134.4, 133.3, 132.6, 129.9, 129.2, 129.2, 129.0, 129.0, 118.3, 112.8, 65.1, 57.5, 40.01, 21.8; HRMS (ESI) *m/z:* calcd $[M + H]^+$ for $C_{24}H_{25}N_2O_4S^+$ 437.1530; found $[M + H]^+$ 437.1532.

Methyl 2-(5-((methyl(phenyl)amino)methyl)-1H-tetrazol-1-yl)acetate (**15**).[2] The crude material was purified by column chromatography (*n*-hexane/ethyl acetate 88:12) to give the product as a pale-yellow solid (77.7 mg, 99% yield). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.26 – 7.24 (m, 2H), 6.87 (t, J = 7.3 Hz, 1H), 6.79 (d, J = 8.1 Hz, 2H), 5.10 (s, 2H), 4.78 (s, 2H), 3.66 (s, 3H), 2.88 (s, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 165.9, 153.6, 148.8, 129.6, 120.0, 114.6, 53.0, 48.5, 48.0, 40.1; HRMS (ESI) *m/z:* calcd $[M + H]^+$ for $C_{12}H_{16}N_5O_2^+$ 262.1299; found $[M + H]^+$ 262.1305; m.p. 96-97°C.

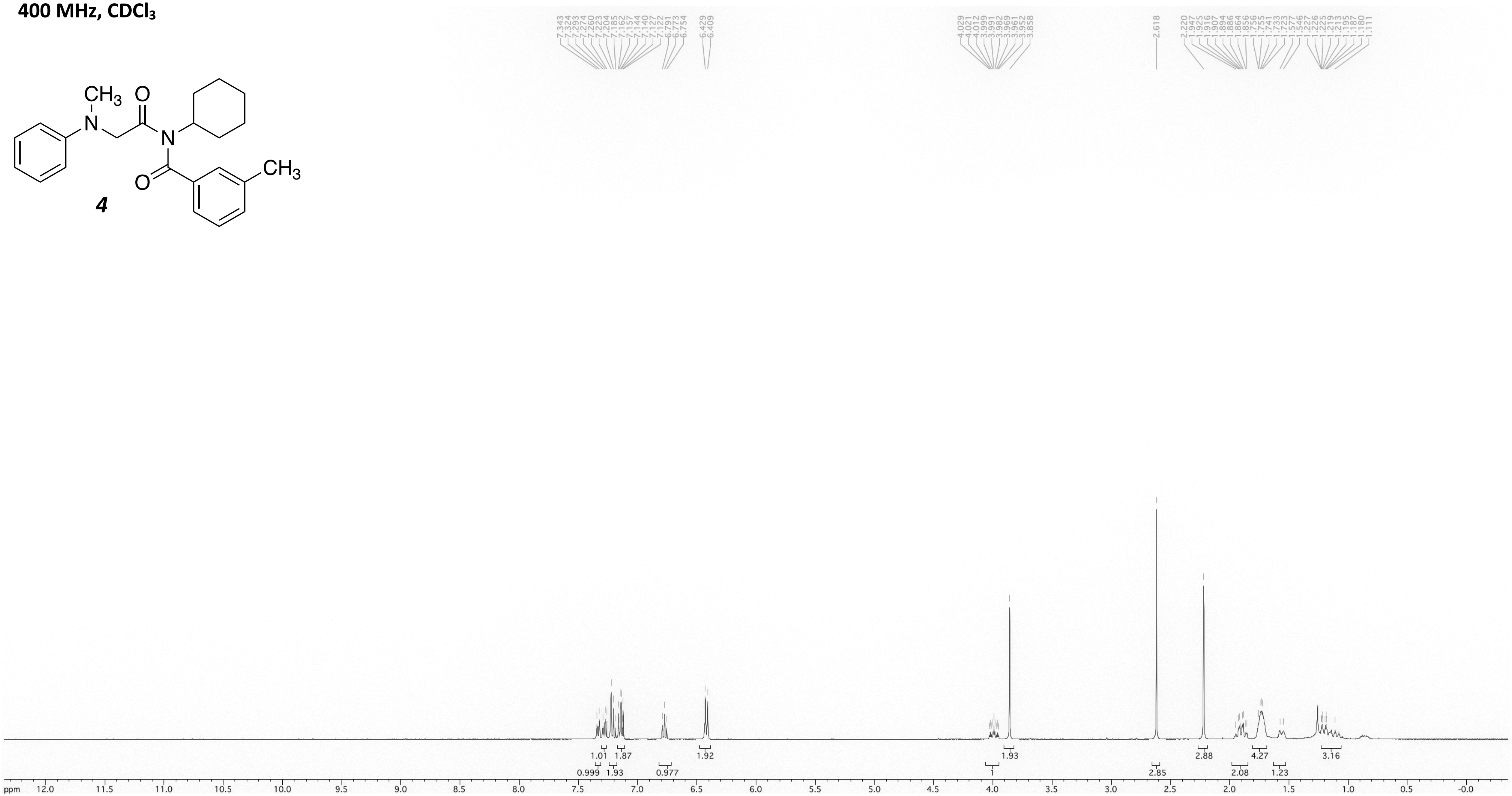
References

1) X. Ye, C. Xie, Y. Pan, L. Han and T. Xie, *Org. Lett.* 2010, **12**, 4240-4243.

2) D. Li and J. Lei, *Tetrahedron Lett.* 2020, **61** (38), 152345.

^{1}H NMR
400 MHz, $CDCl_3$

4



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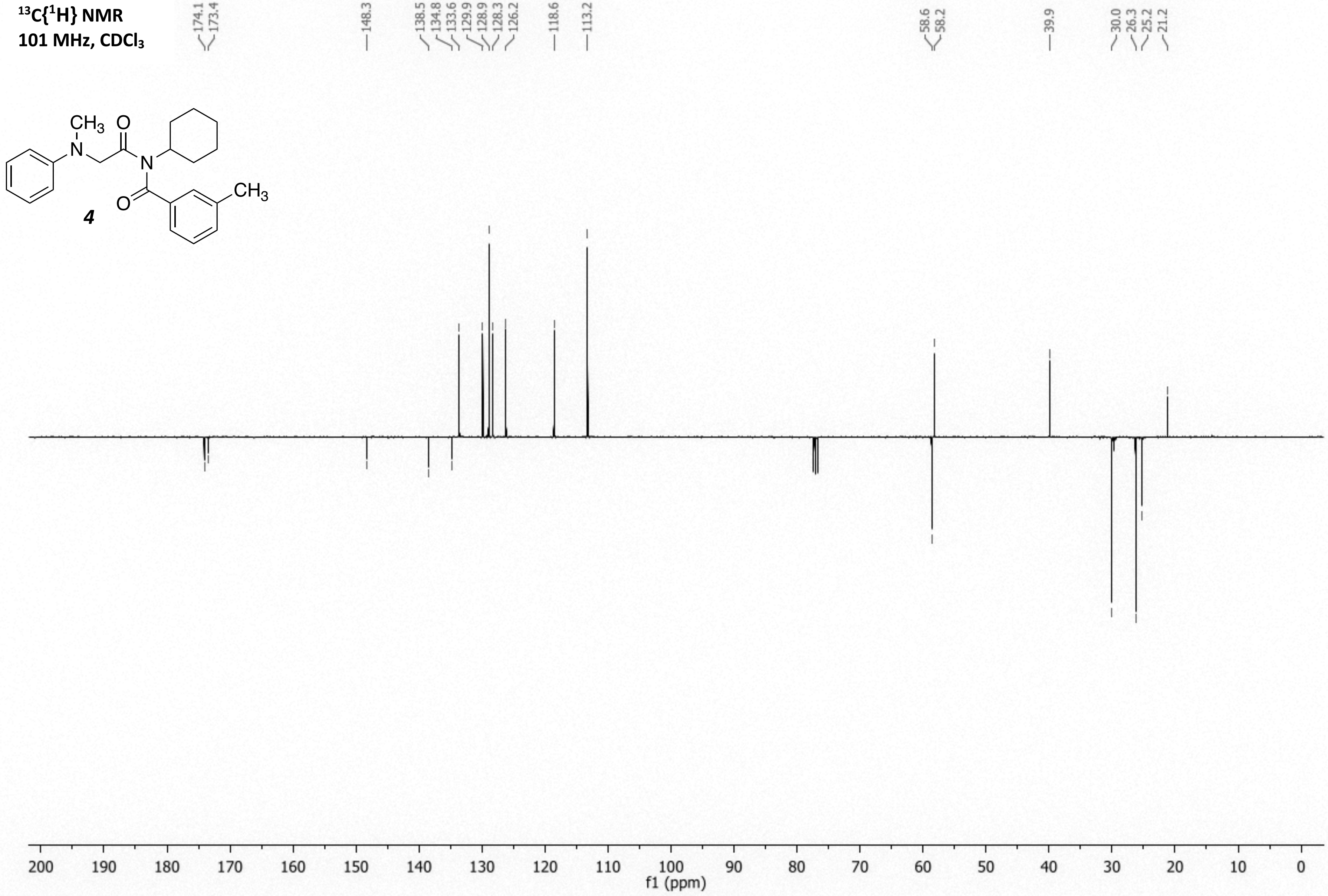

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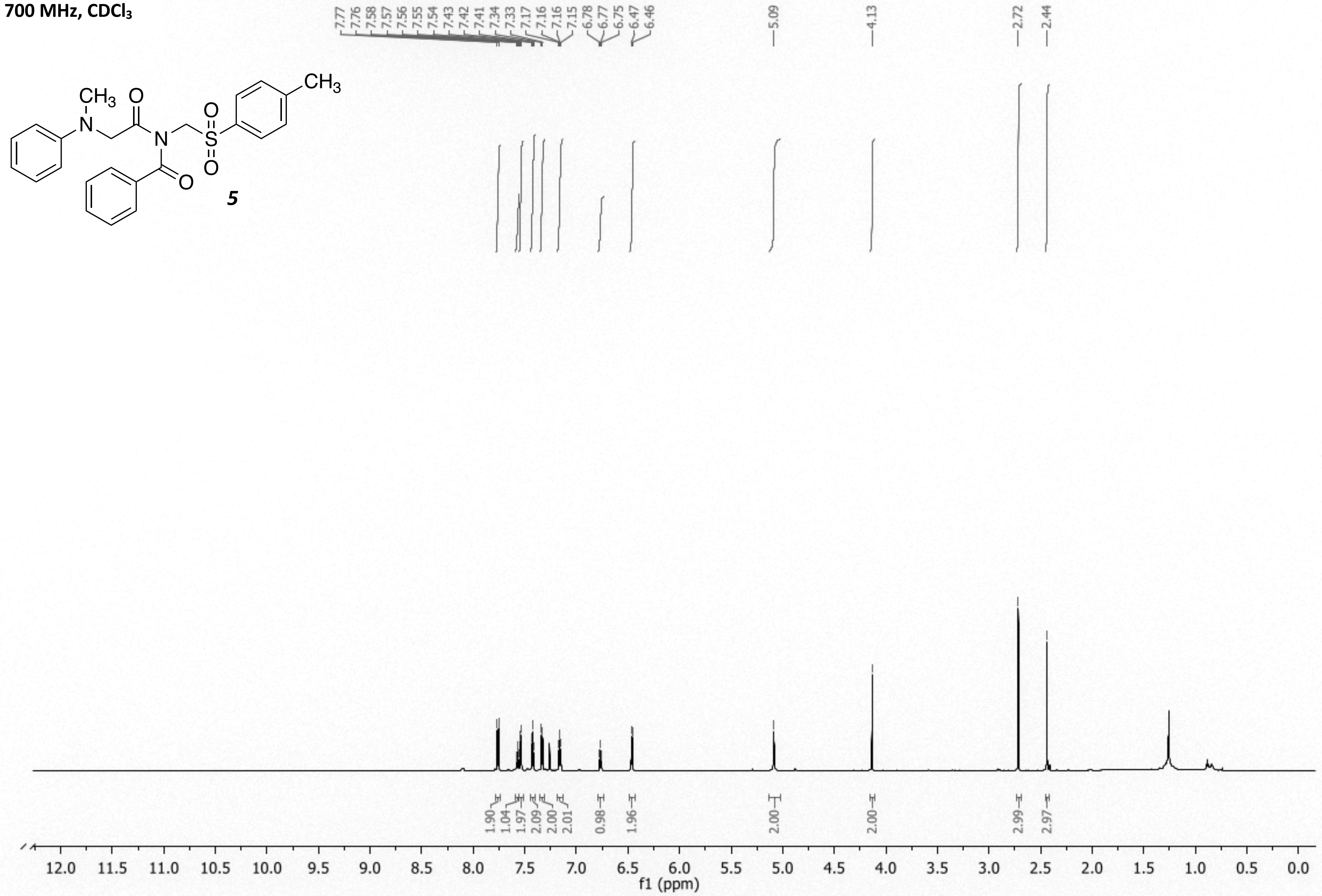
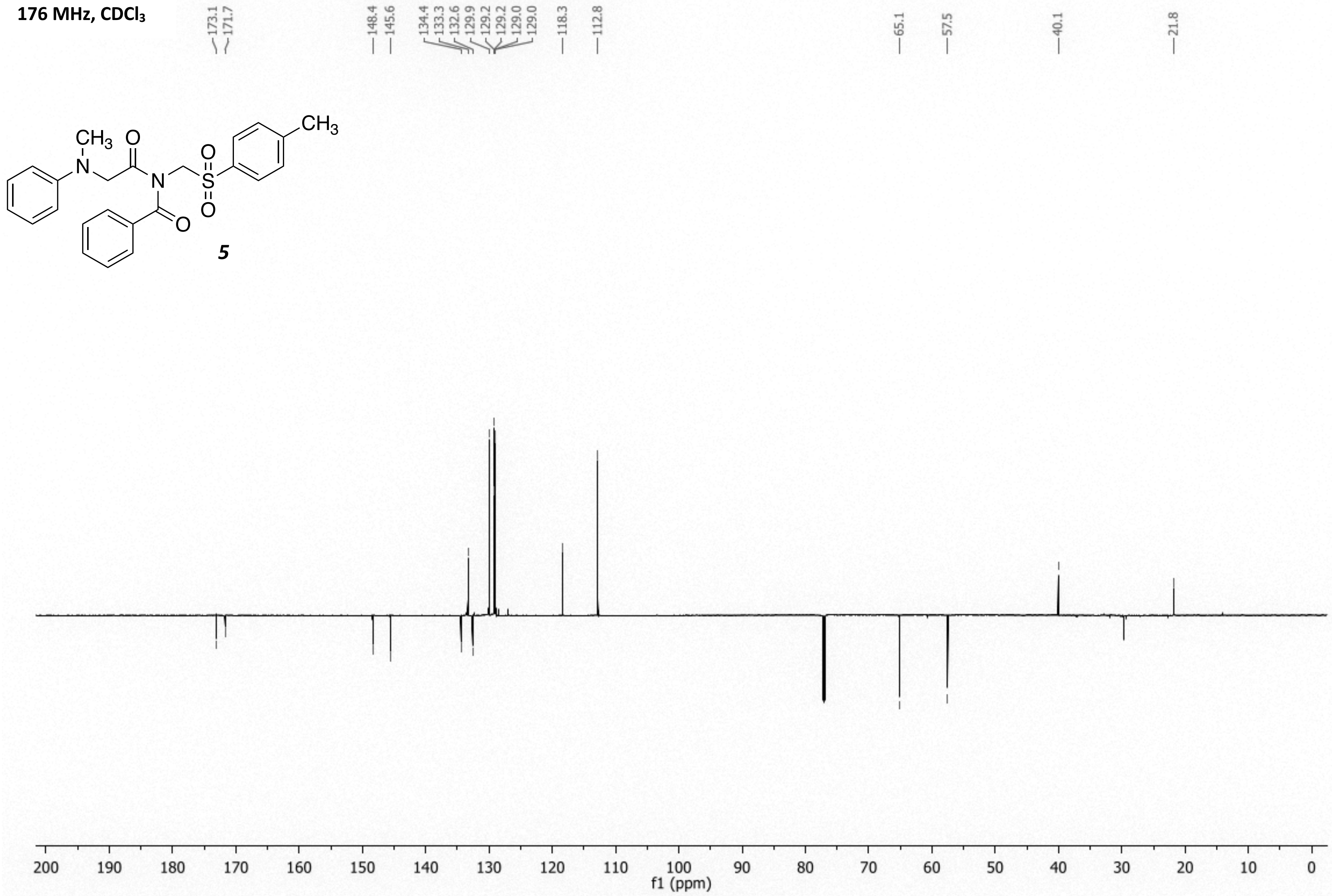
^{1}H NMR
700 MHz, $CDCl_3$



$^{13}C\{^1H\}$ NMR
176 MHz, $CDCl_3$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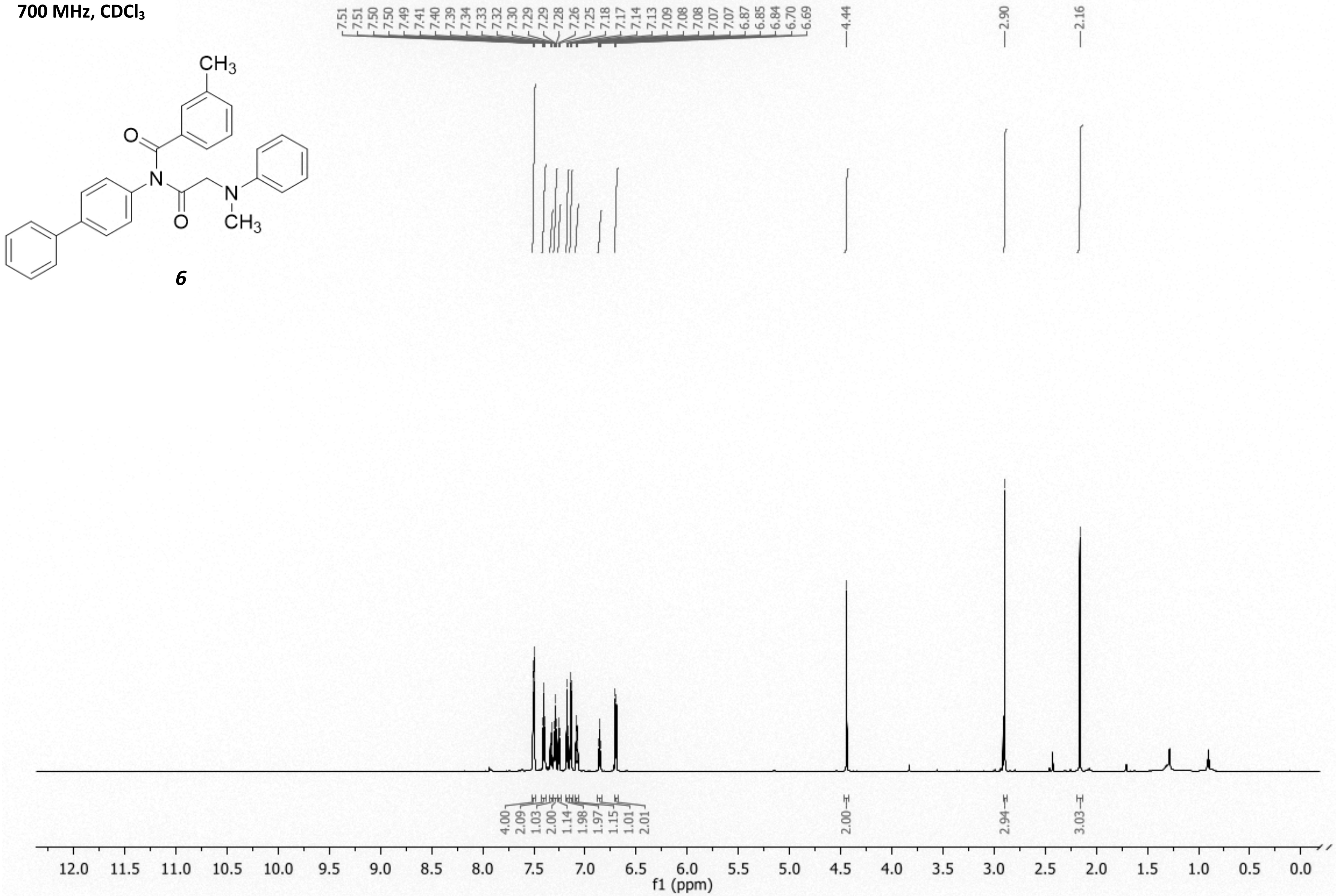
700 MHz, $CDCl_3$



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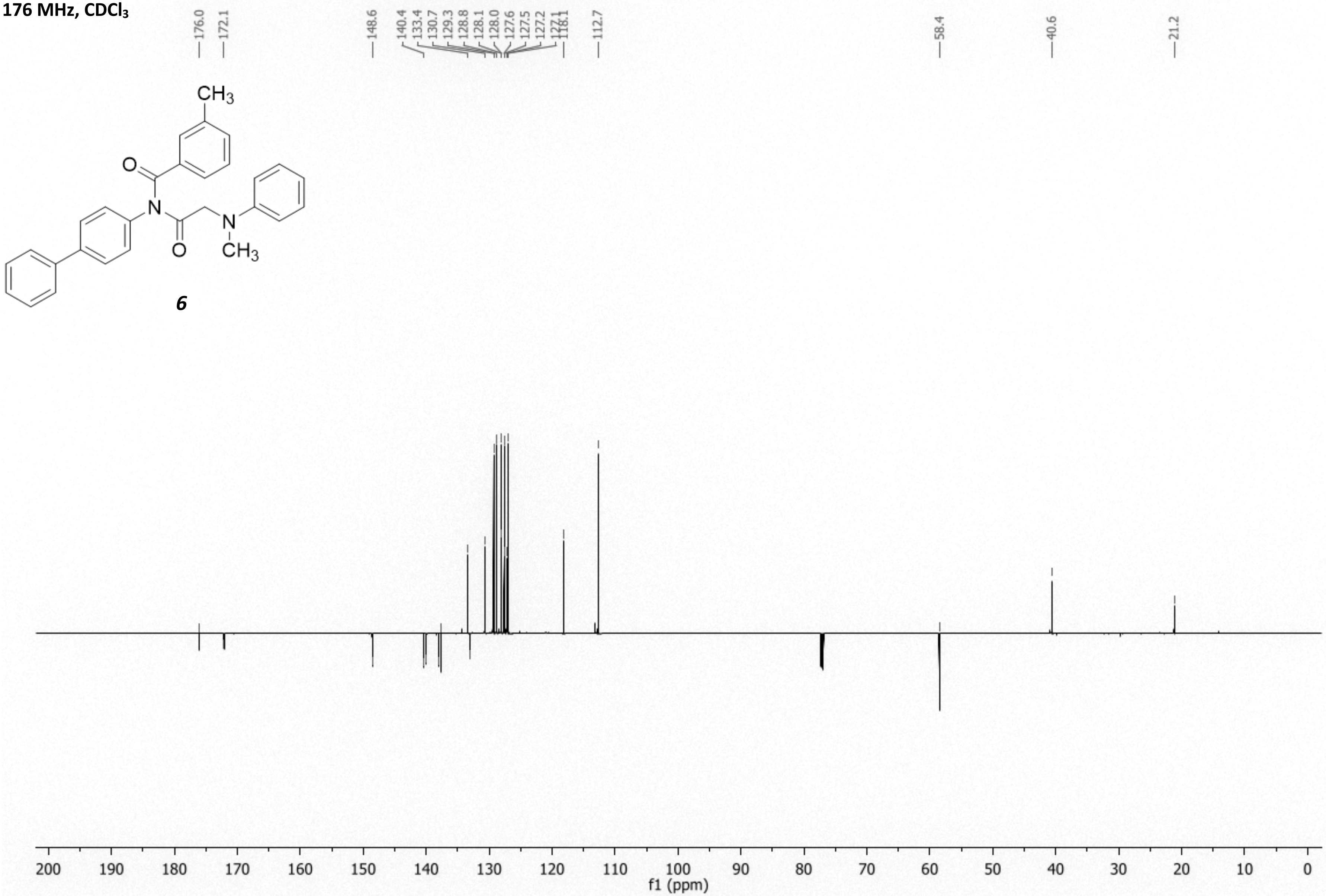

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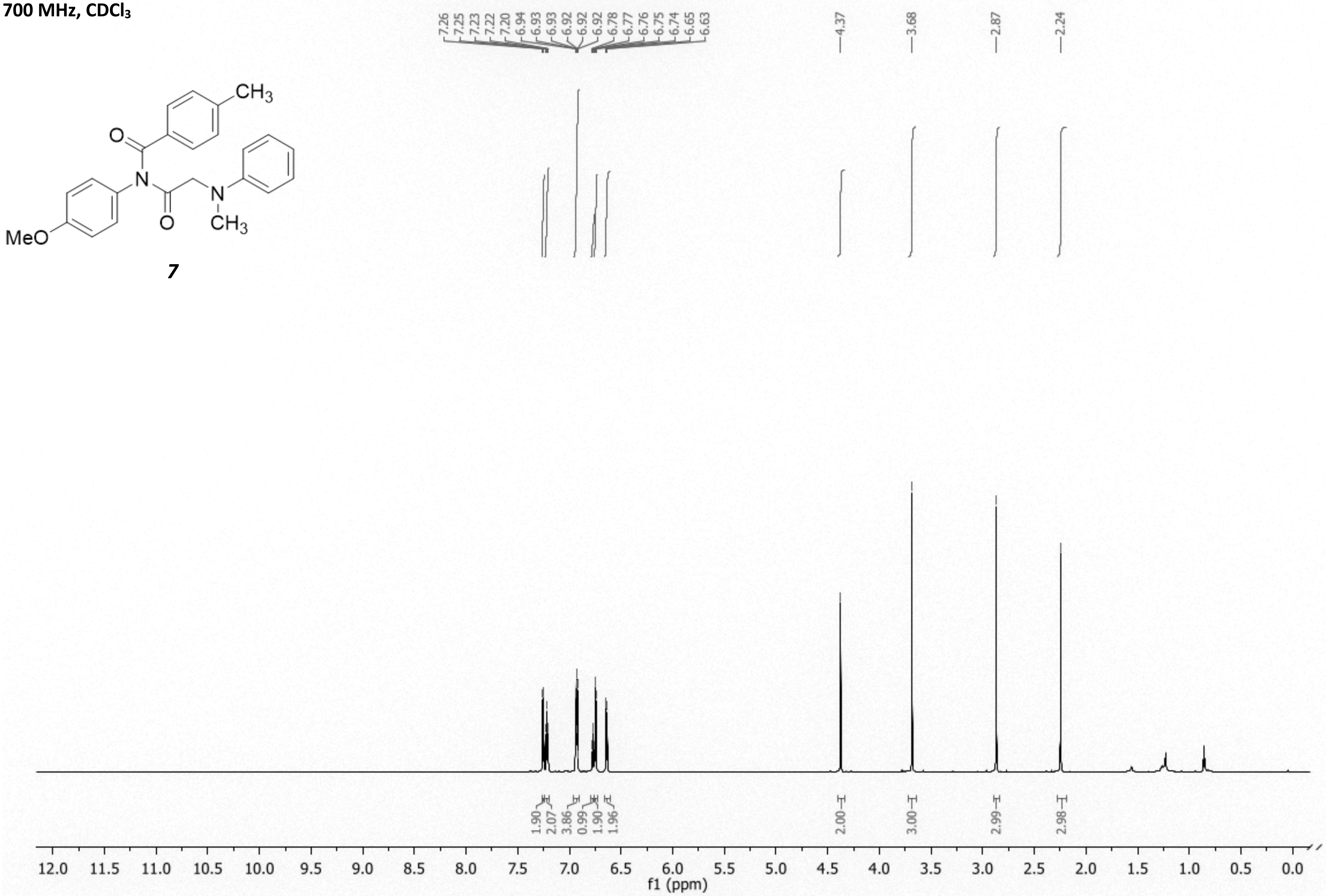

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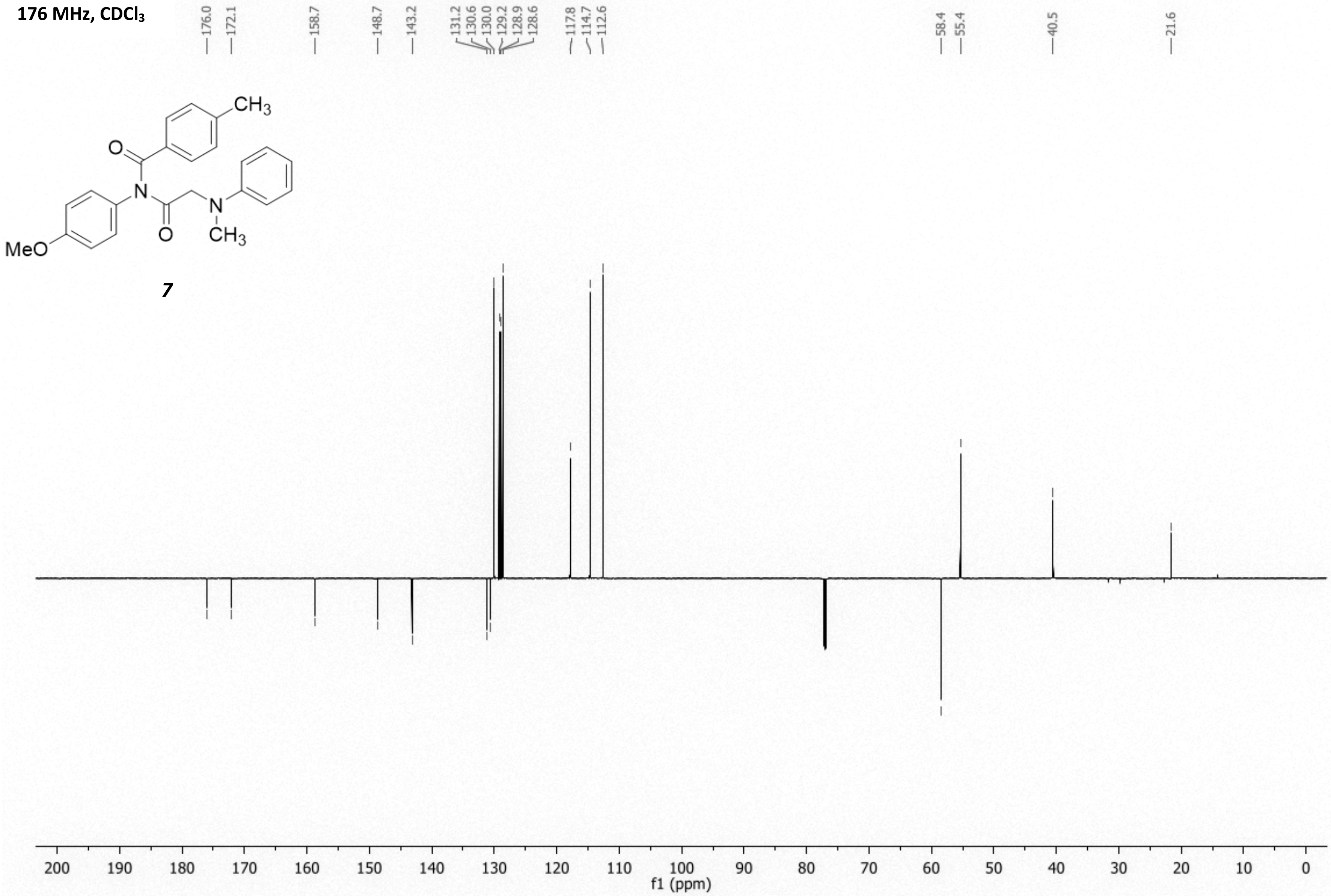

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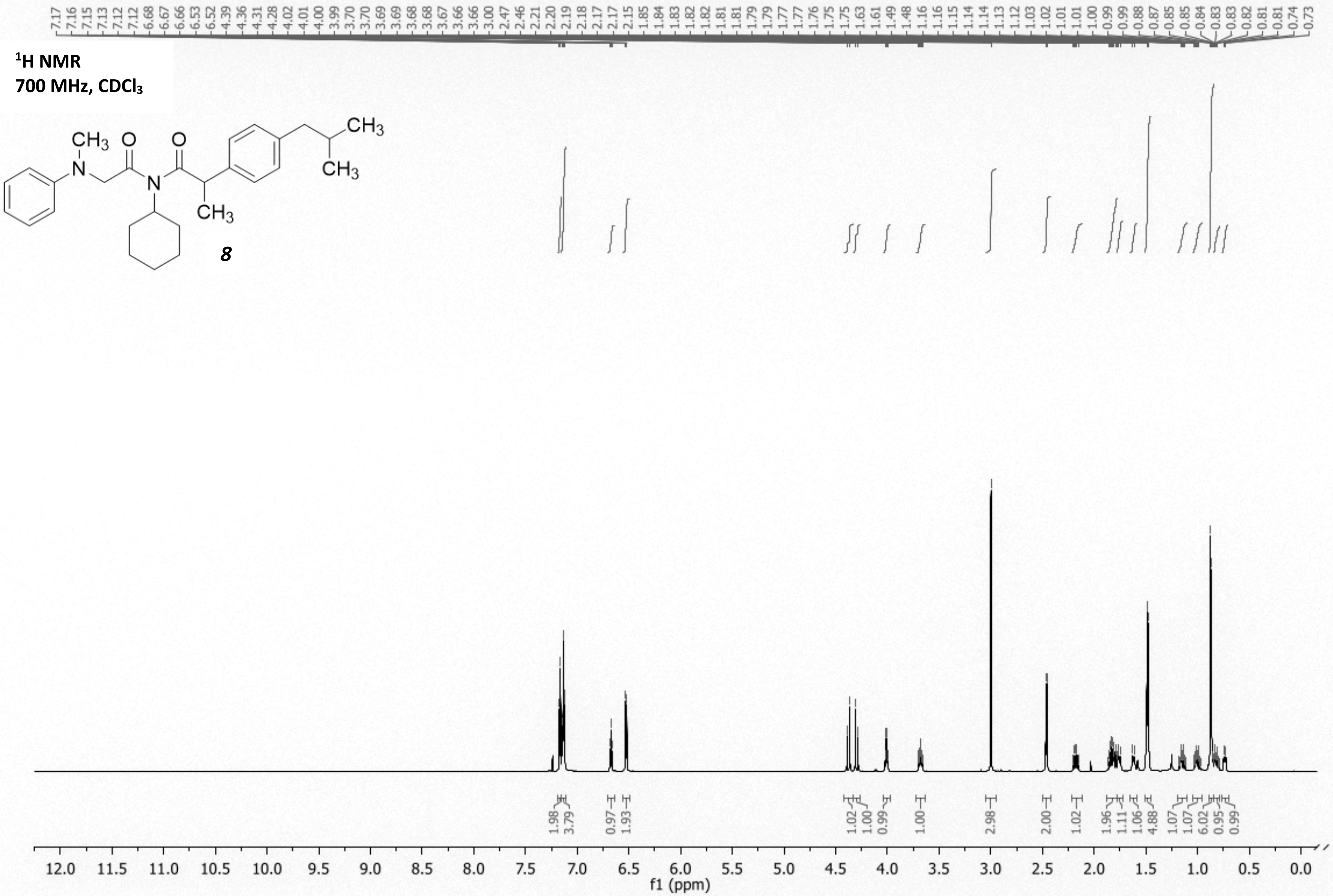

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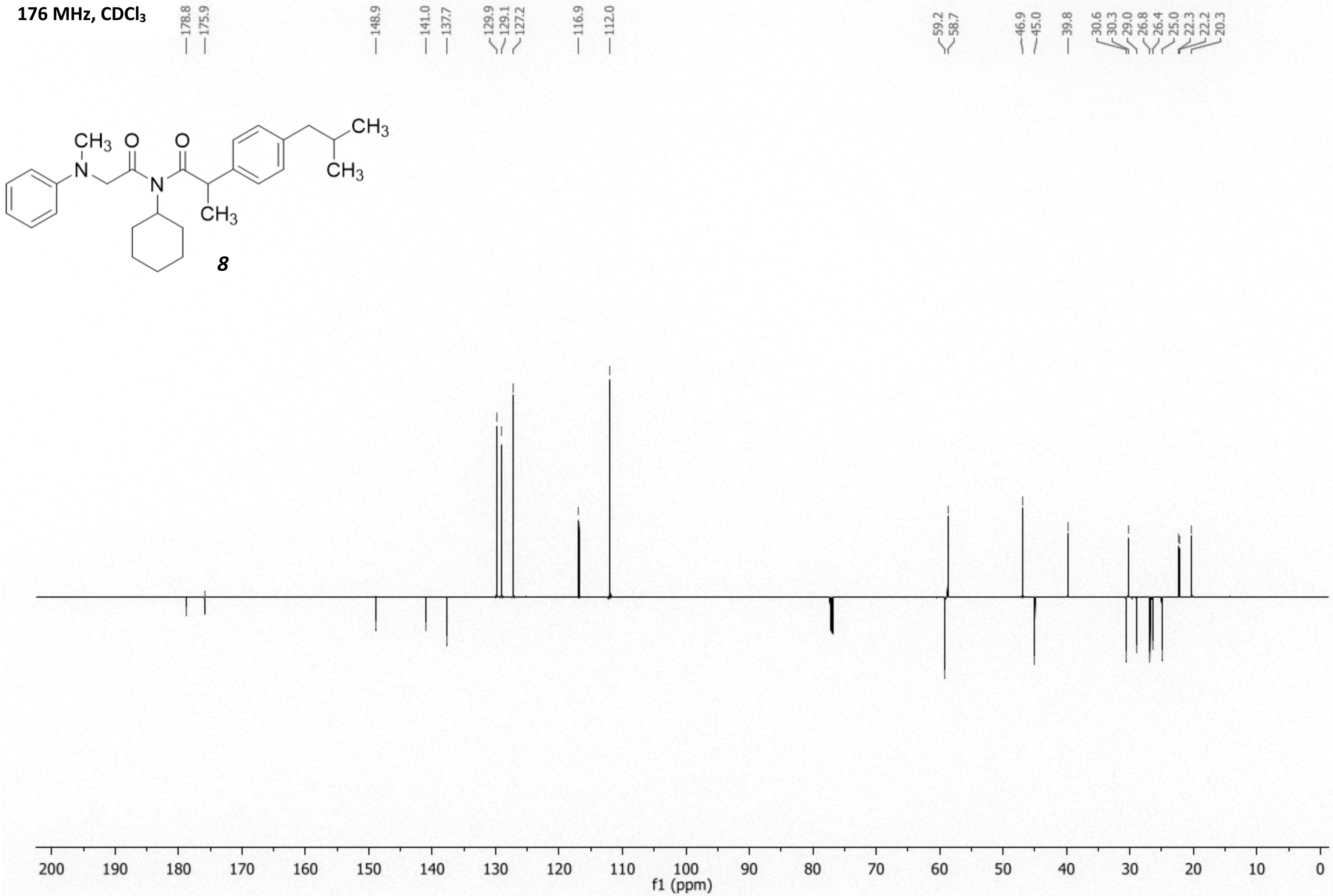

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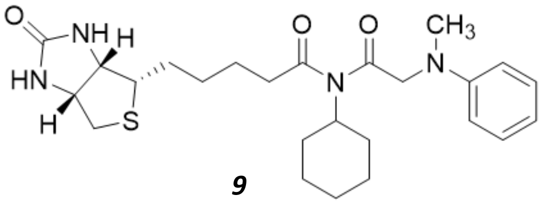

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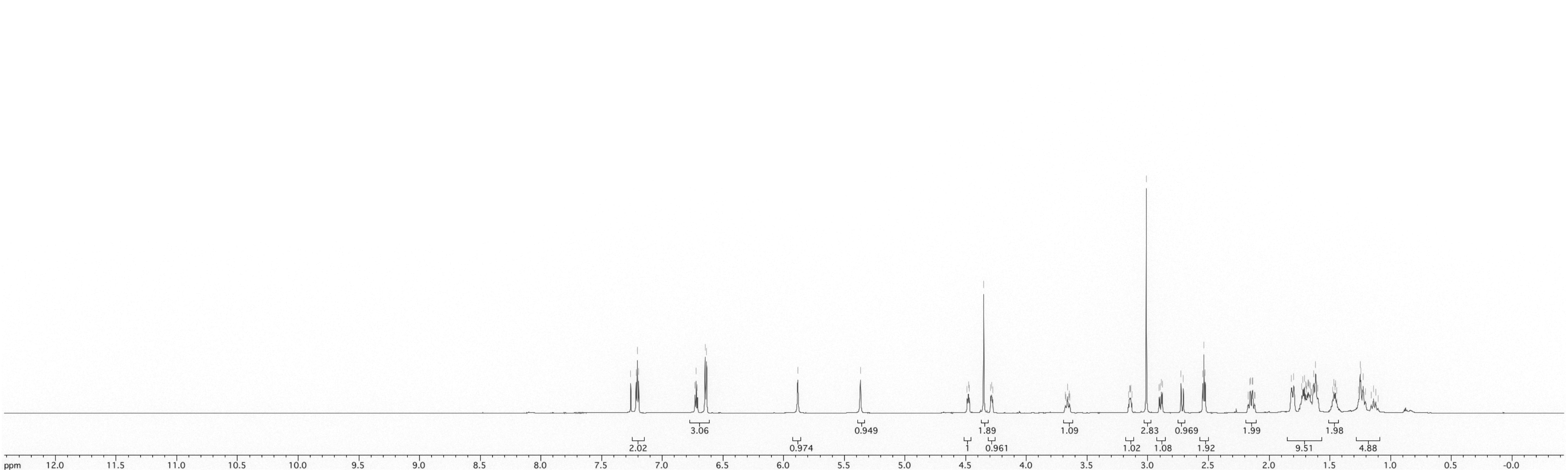

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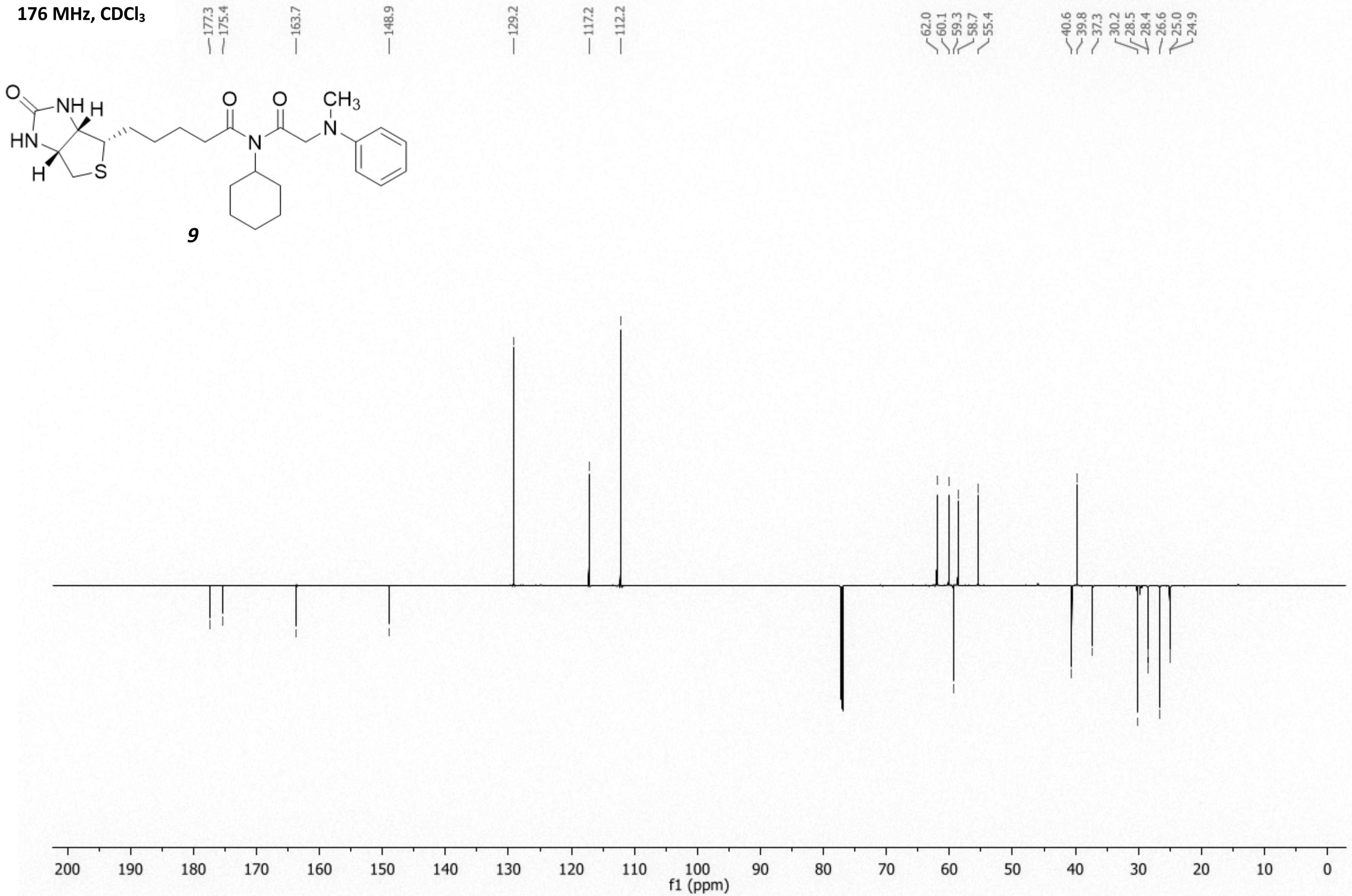

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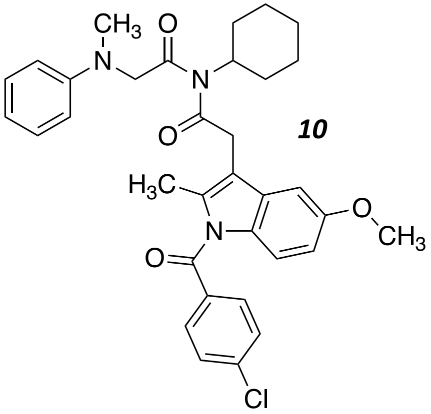

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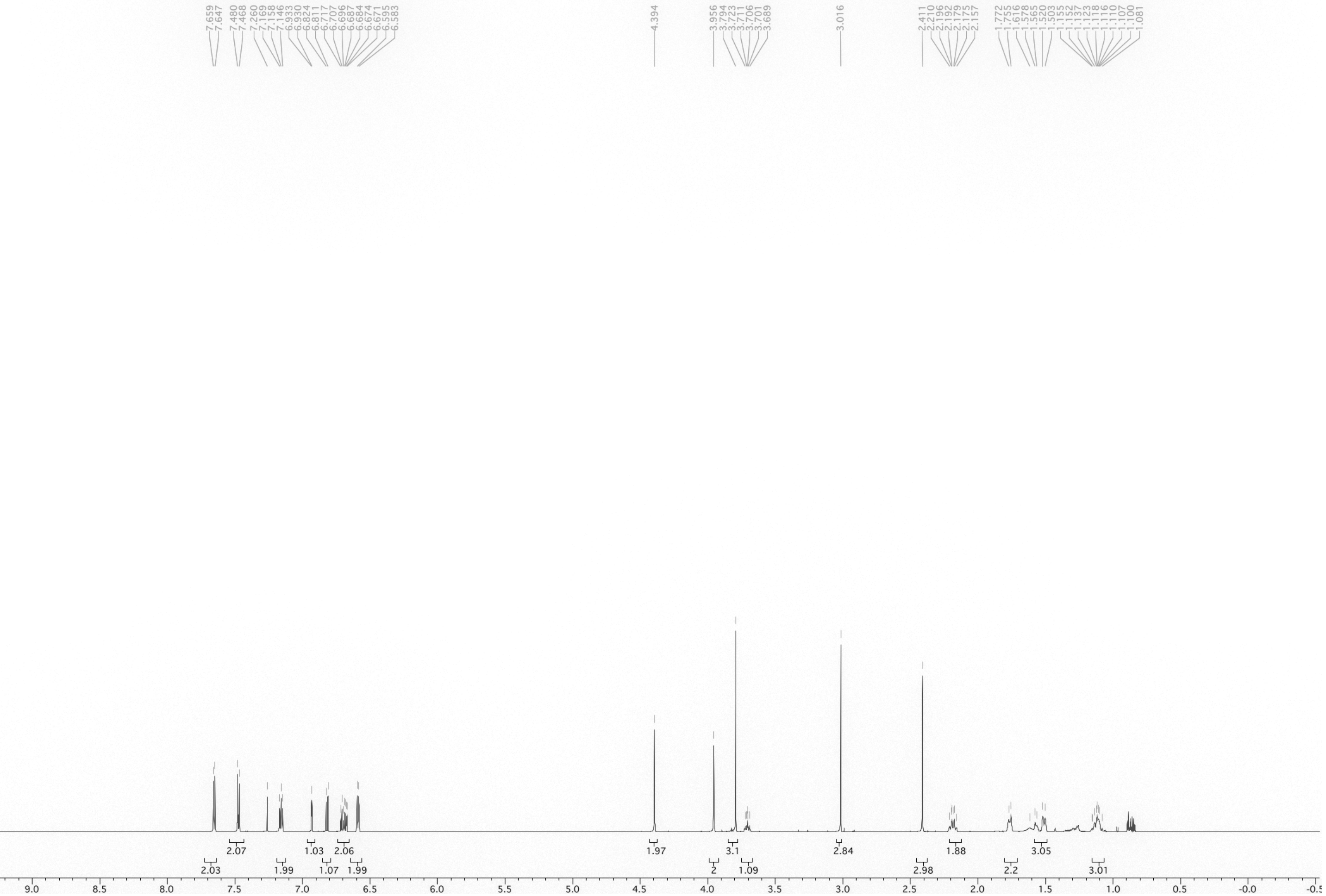

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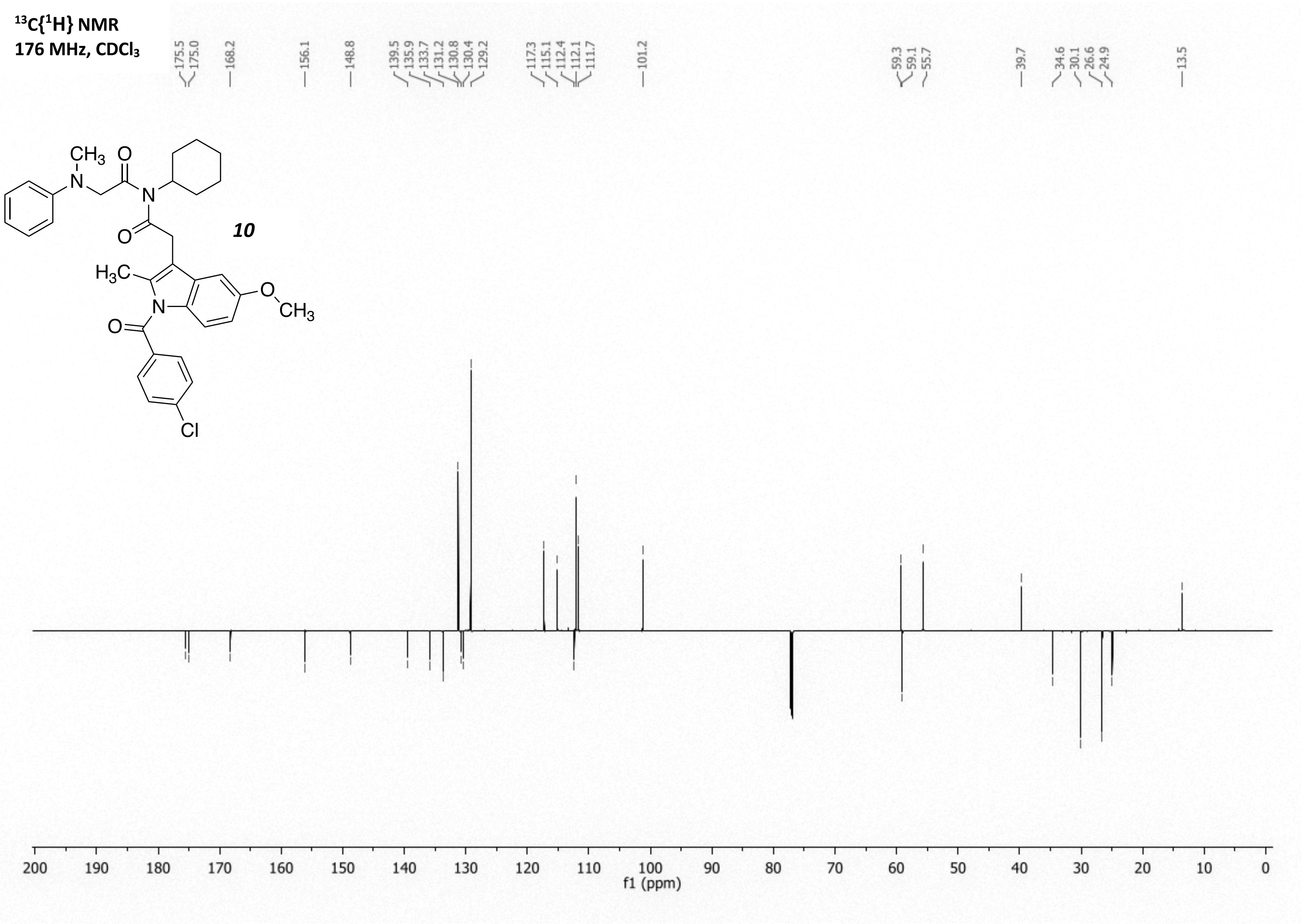

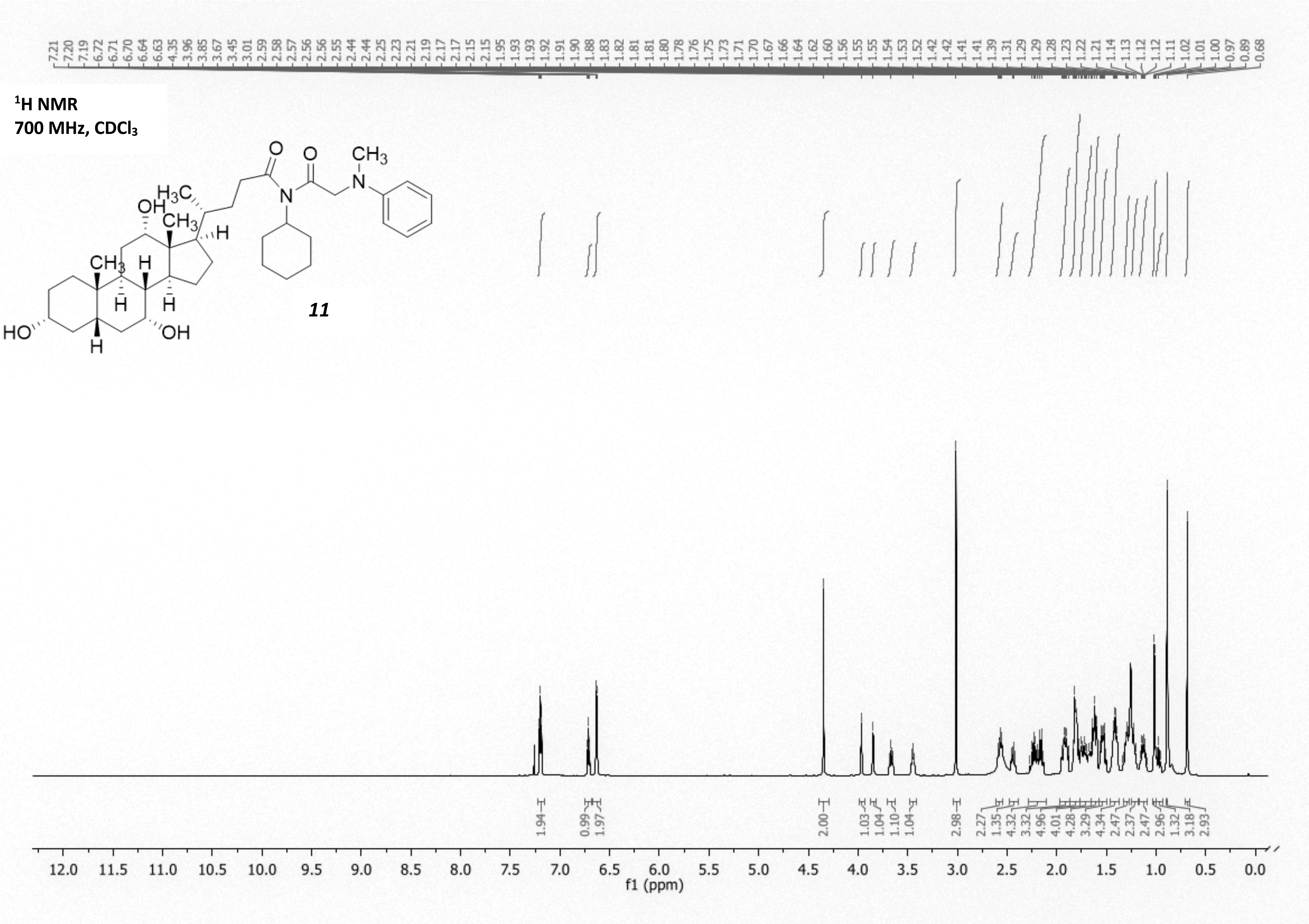

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700 MHz, $CDCl_3$

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$^{13}C\{^{1}H\}$ NMR
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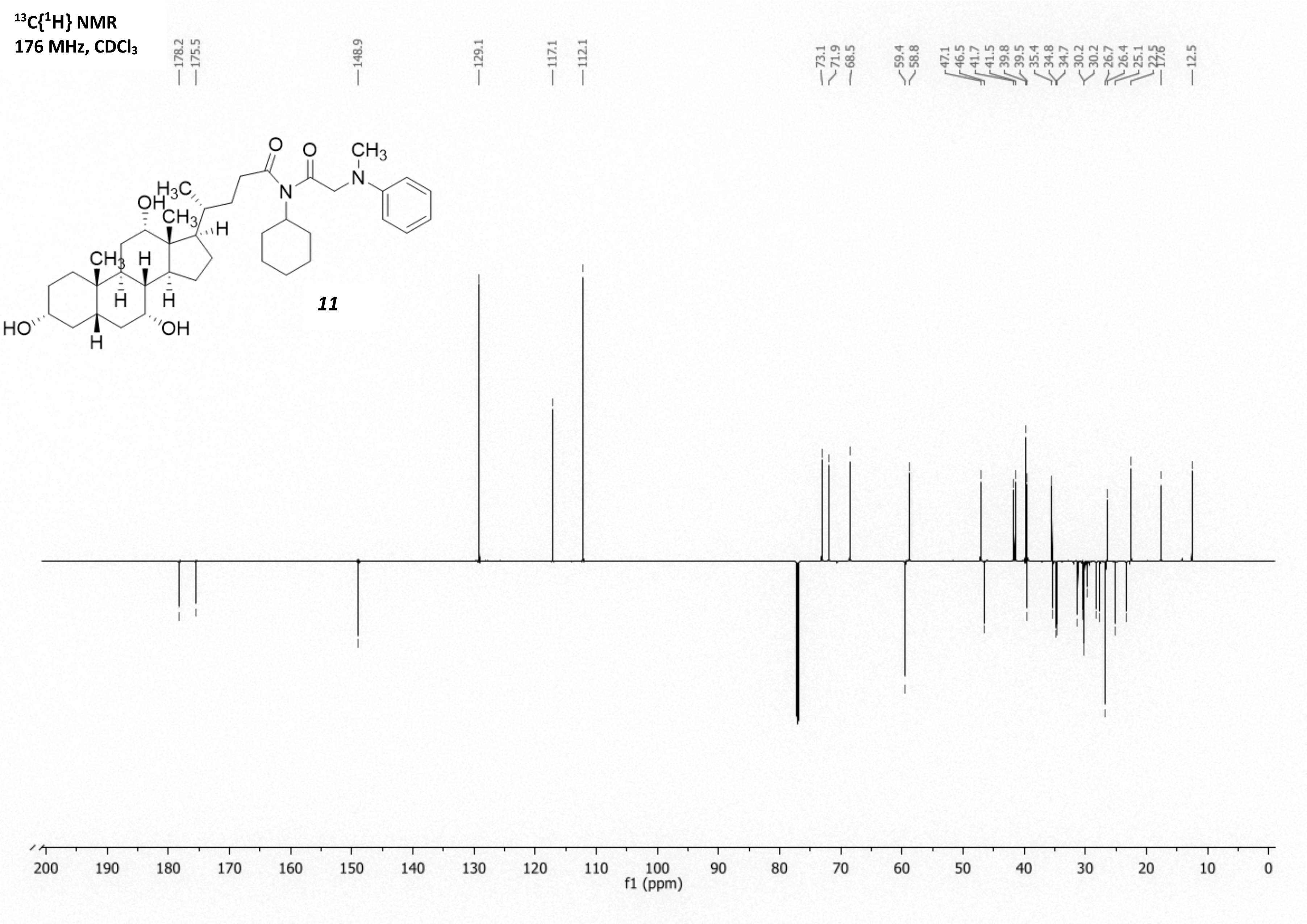

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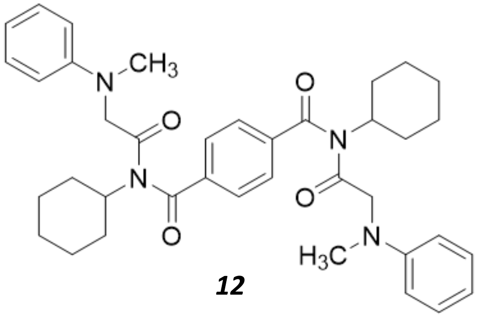

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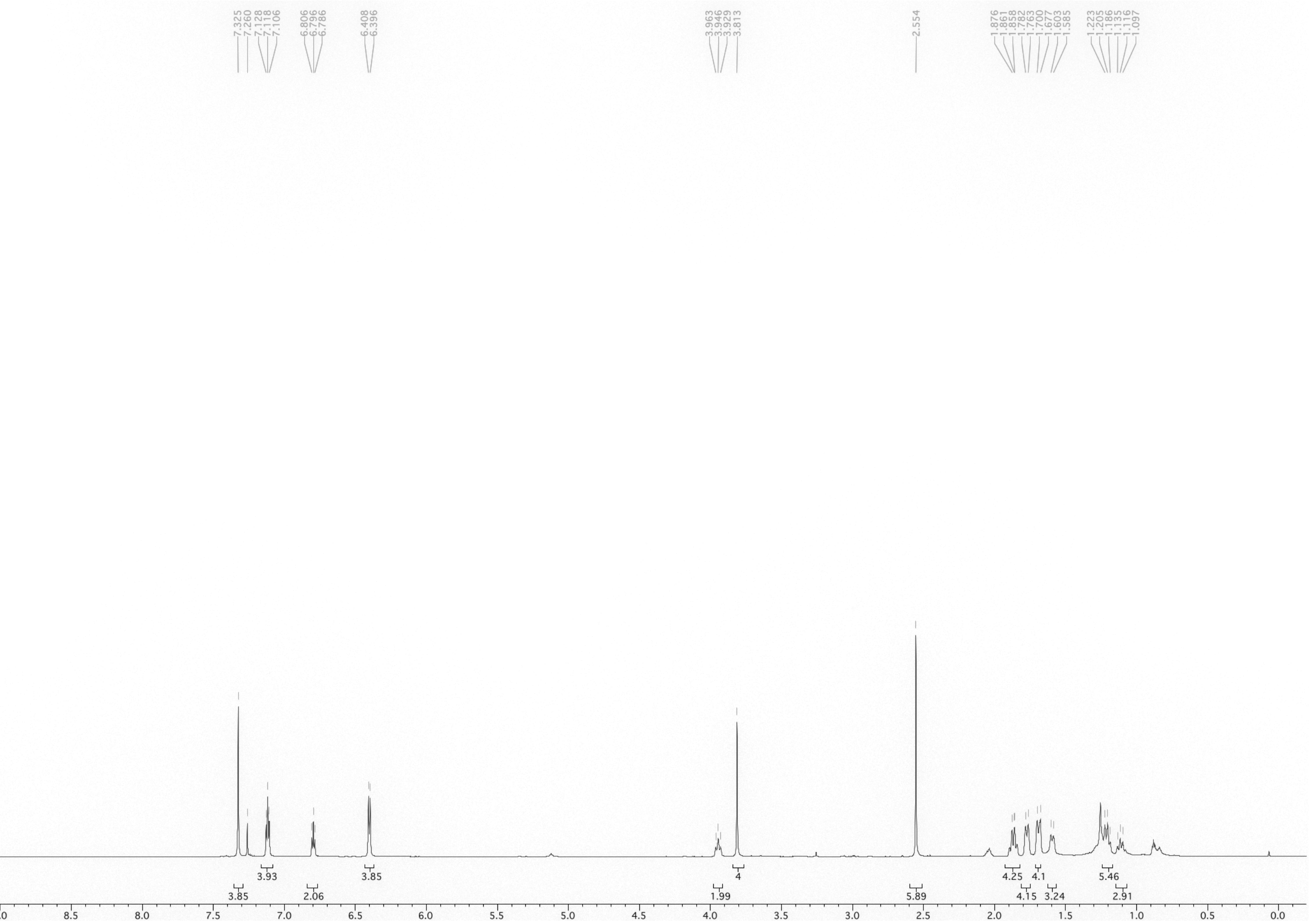

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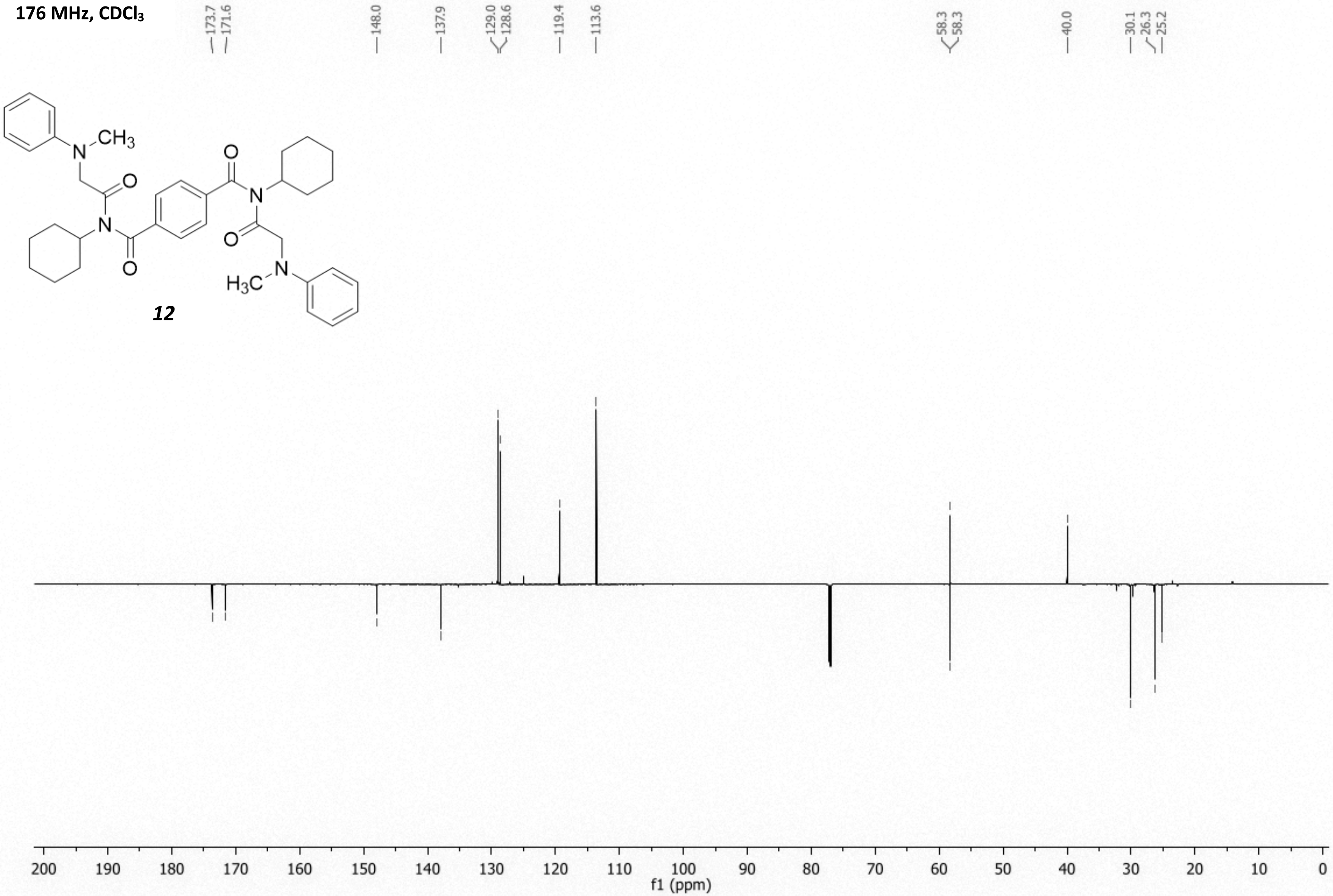

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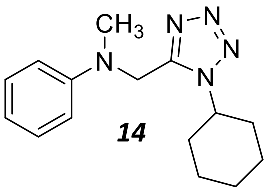

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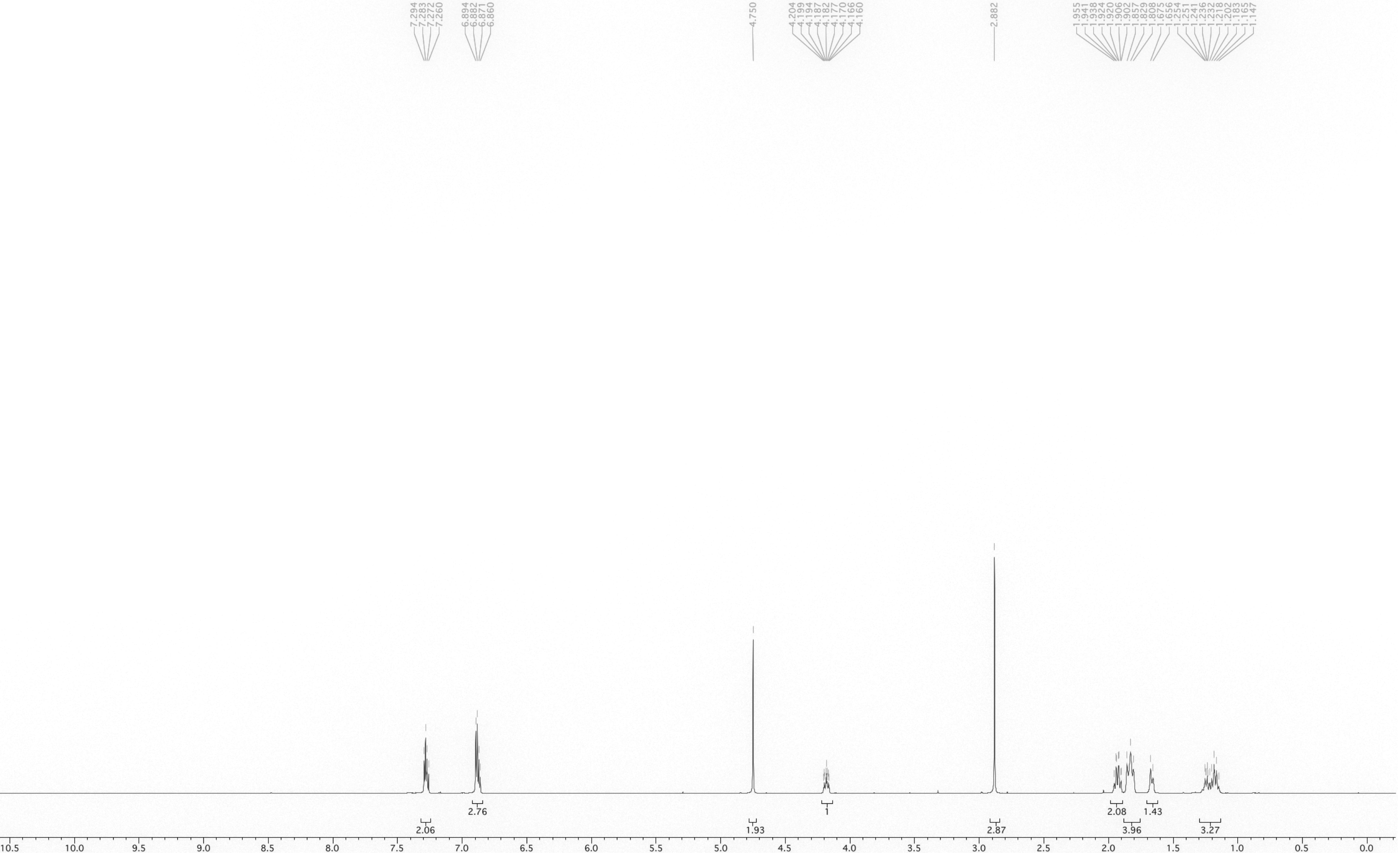

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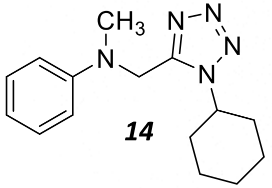

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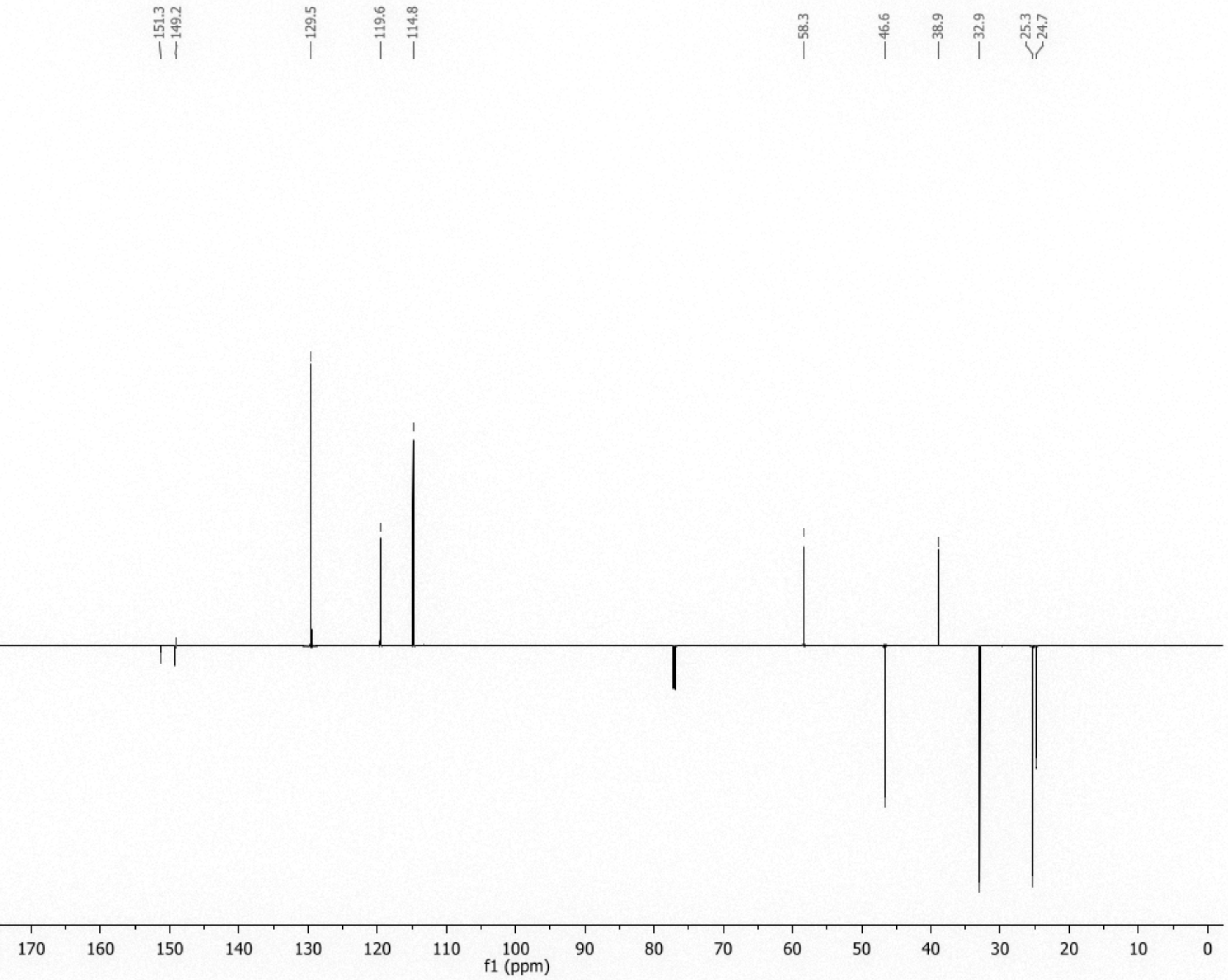

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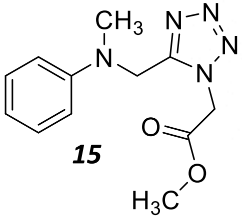

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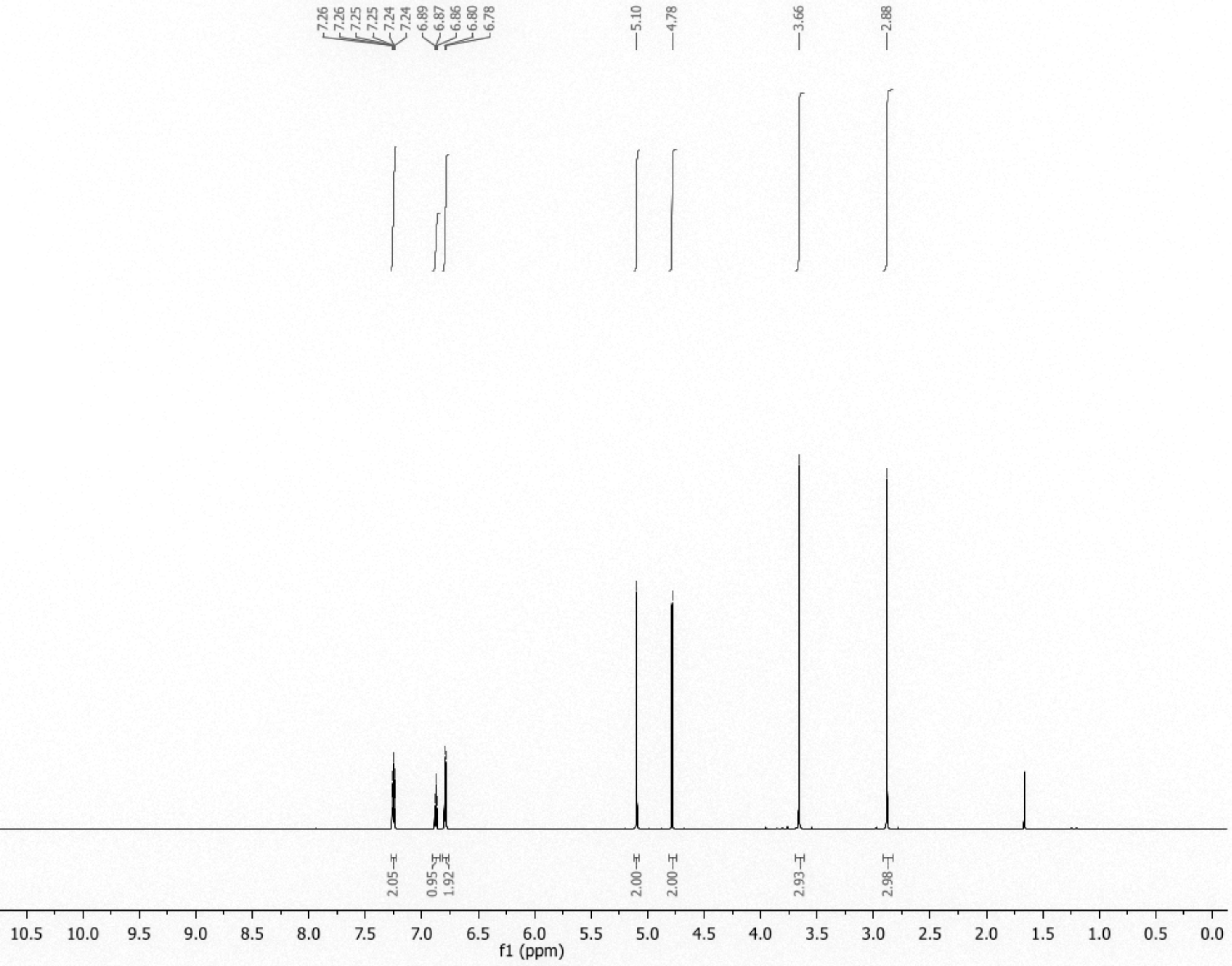

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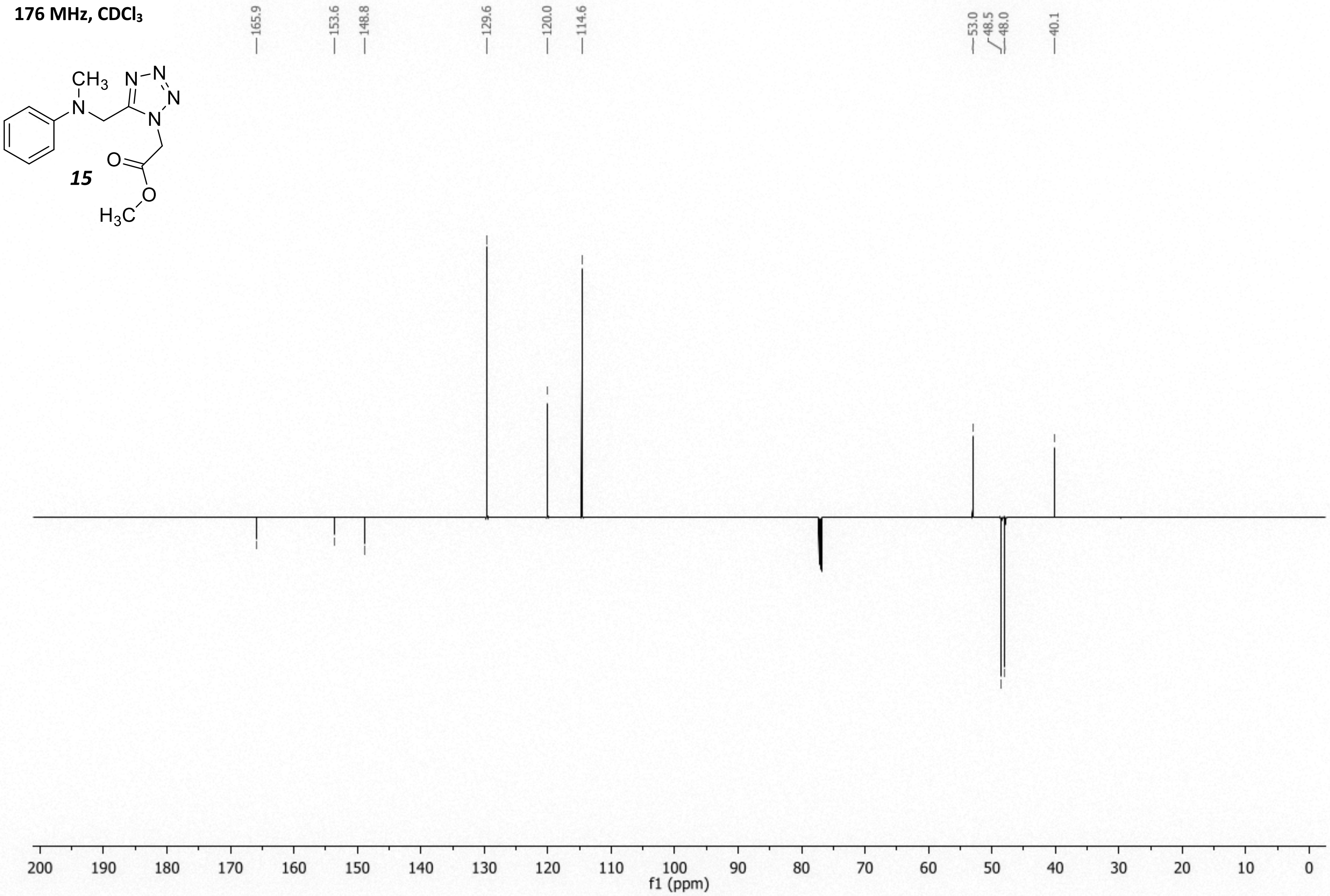

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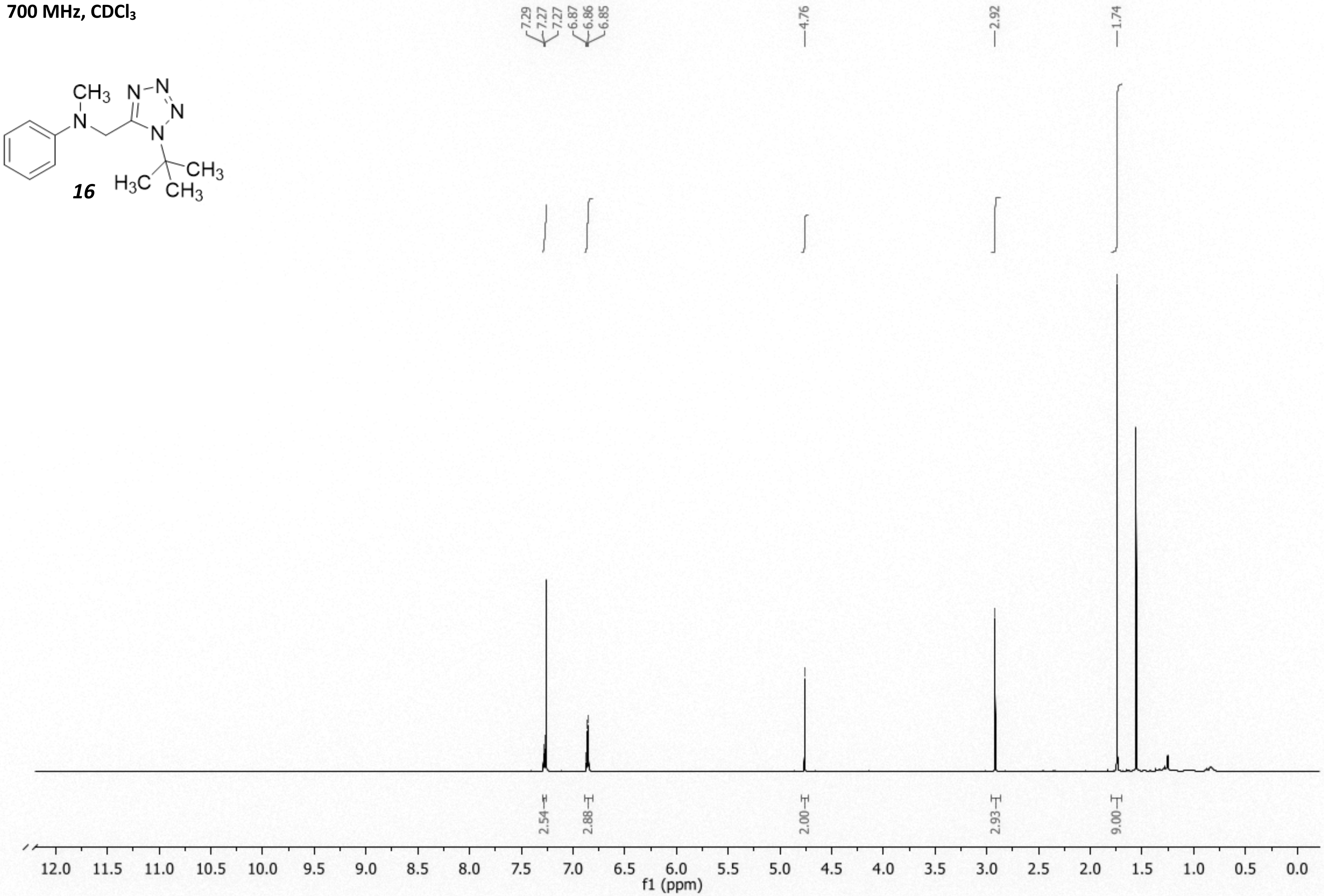

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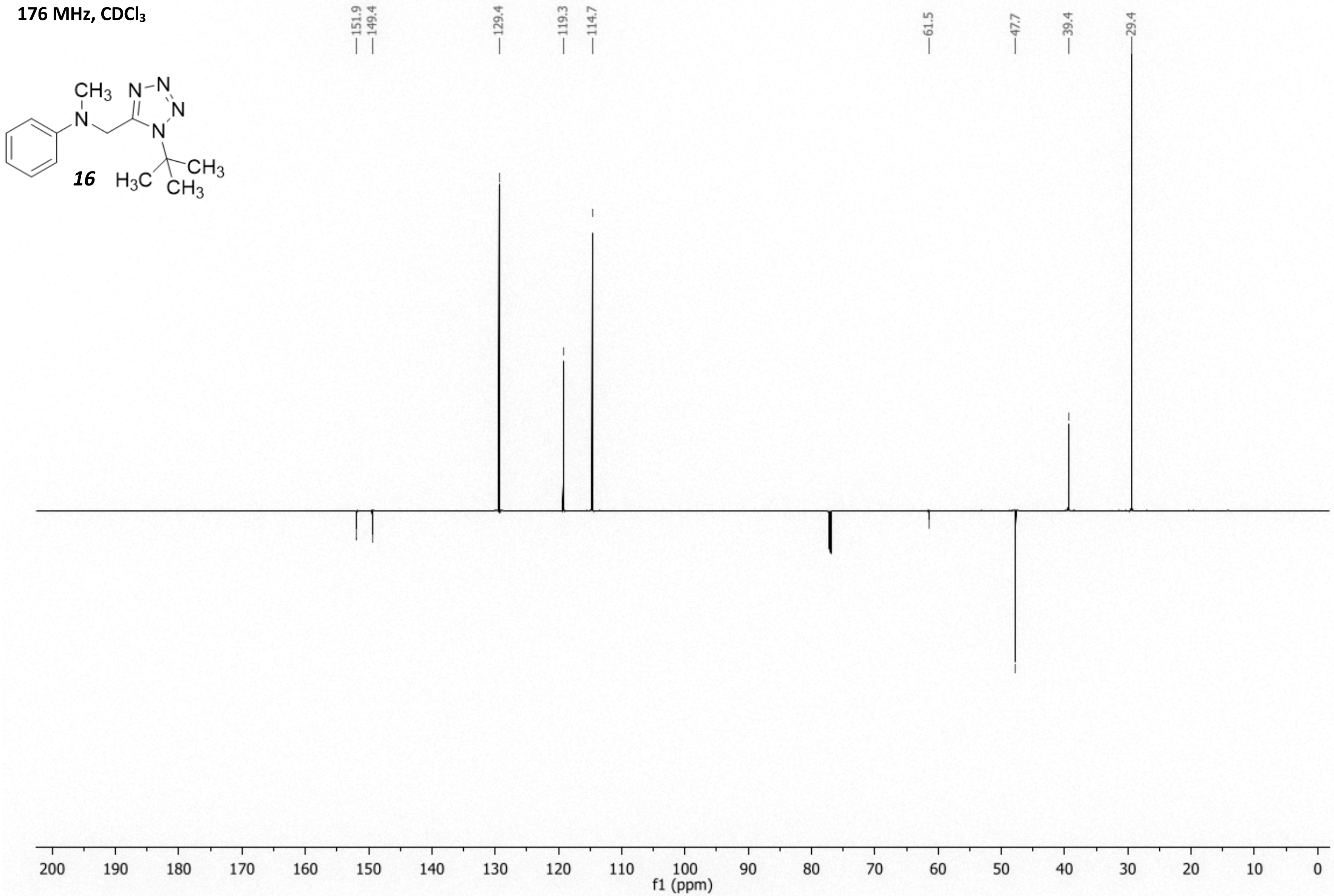

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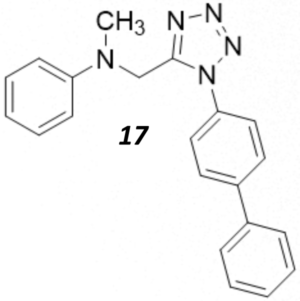

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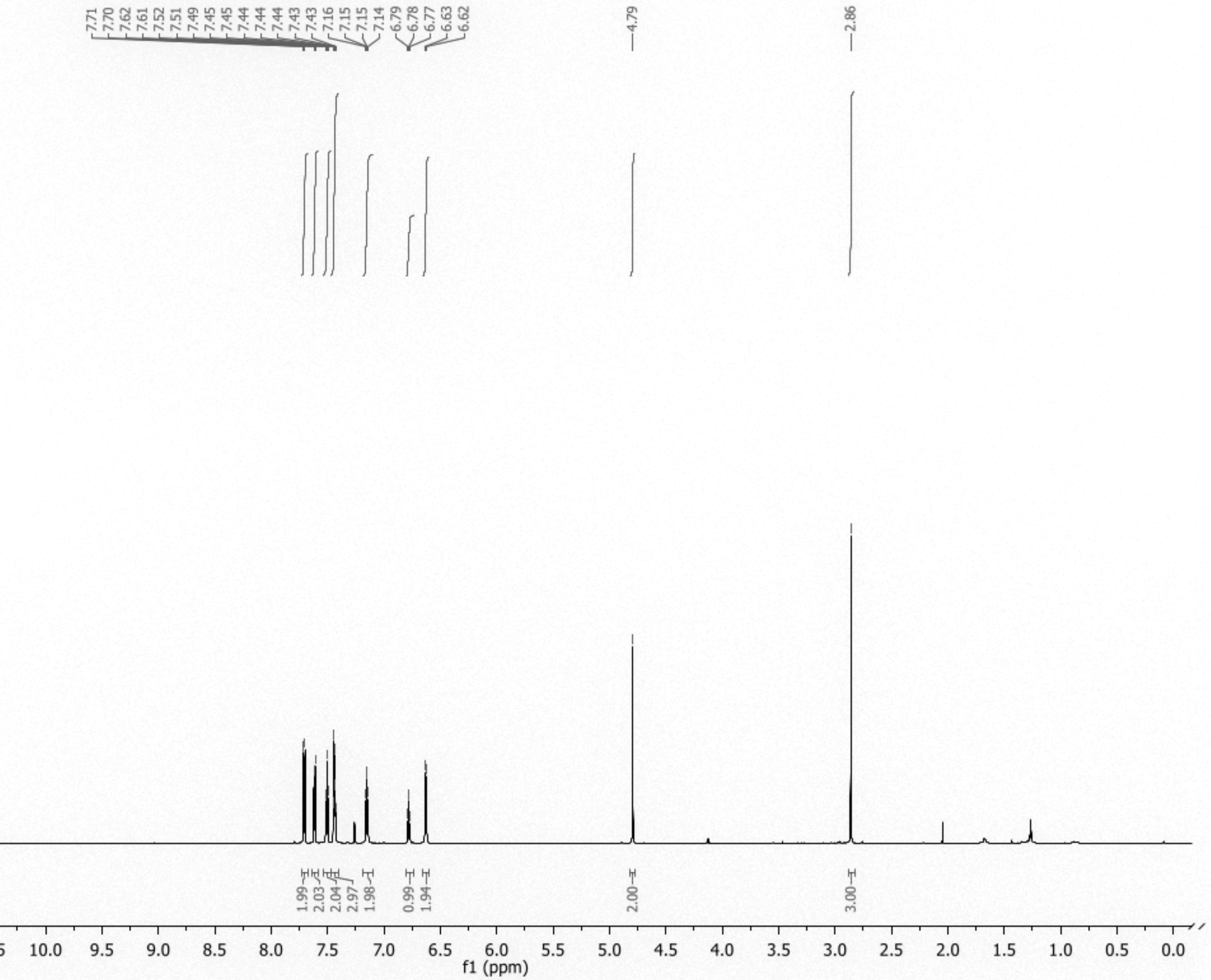

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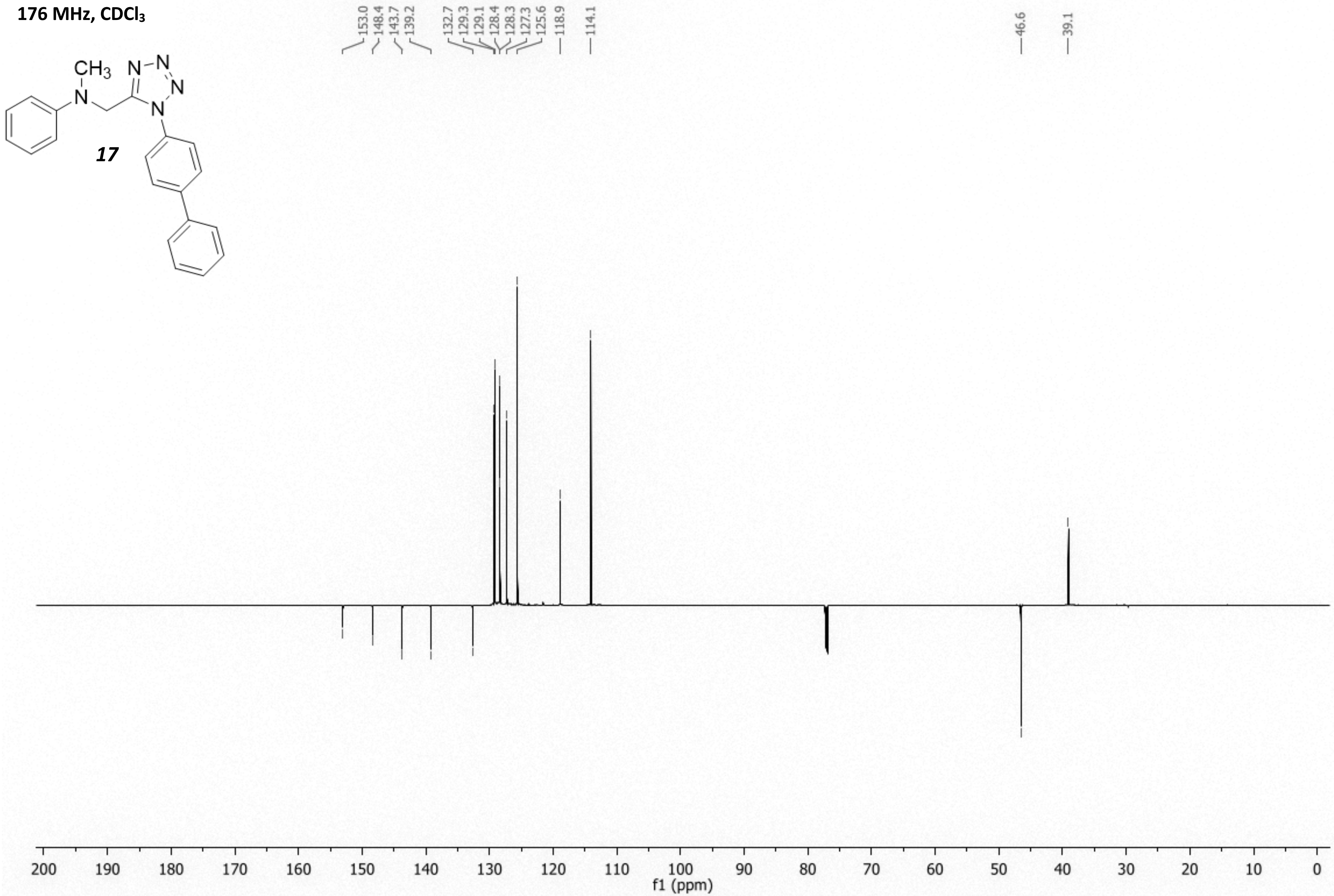

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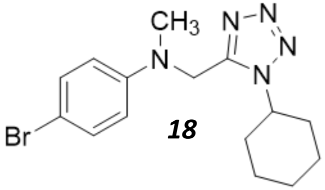

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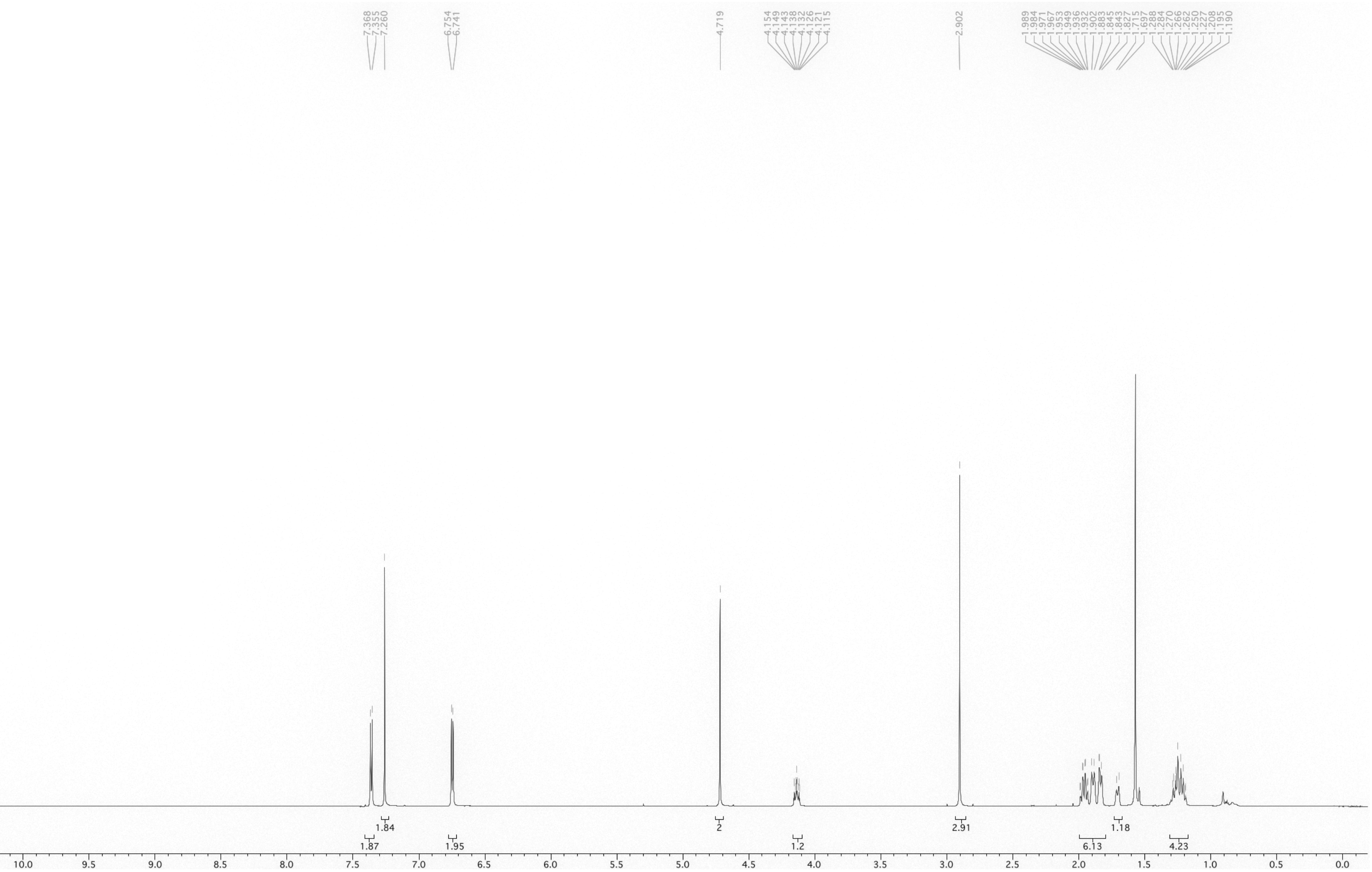

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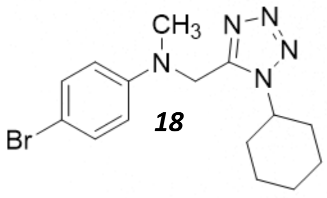

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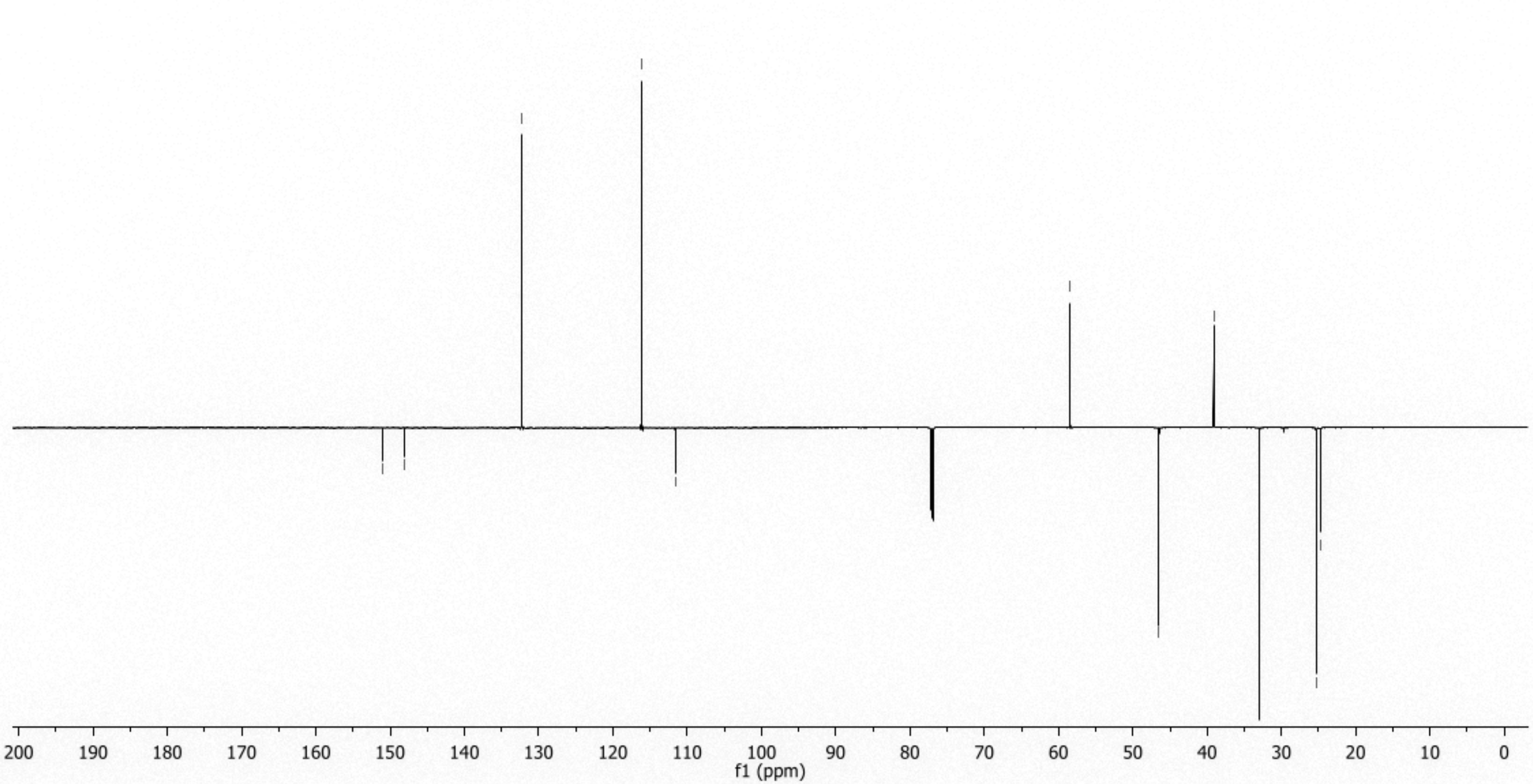

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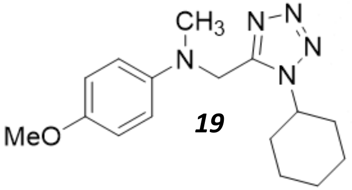

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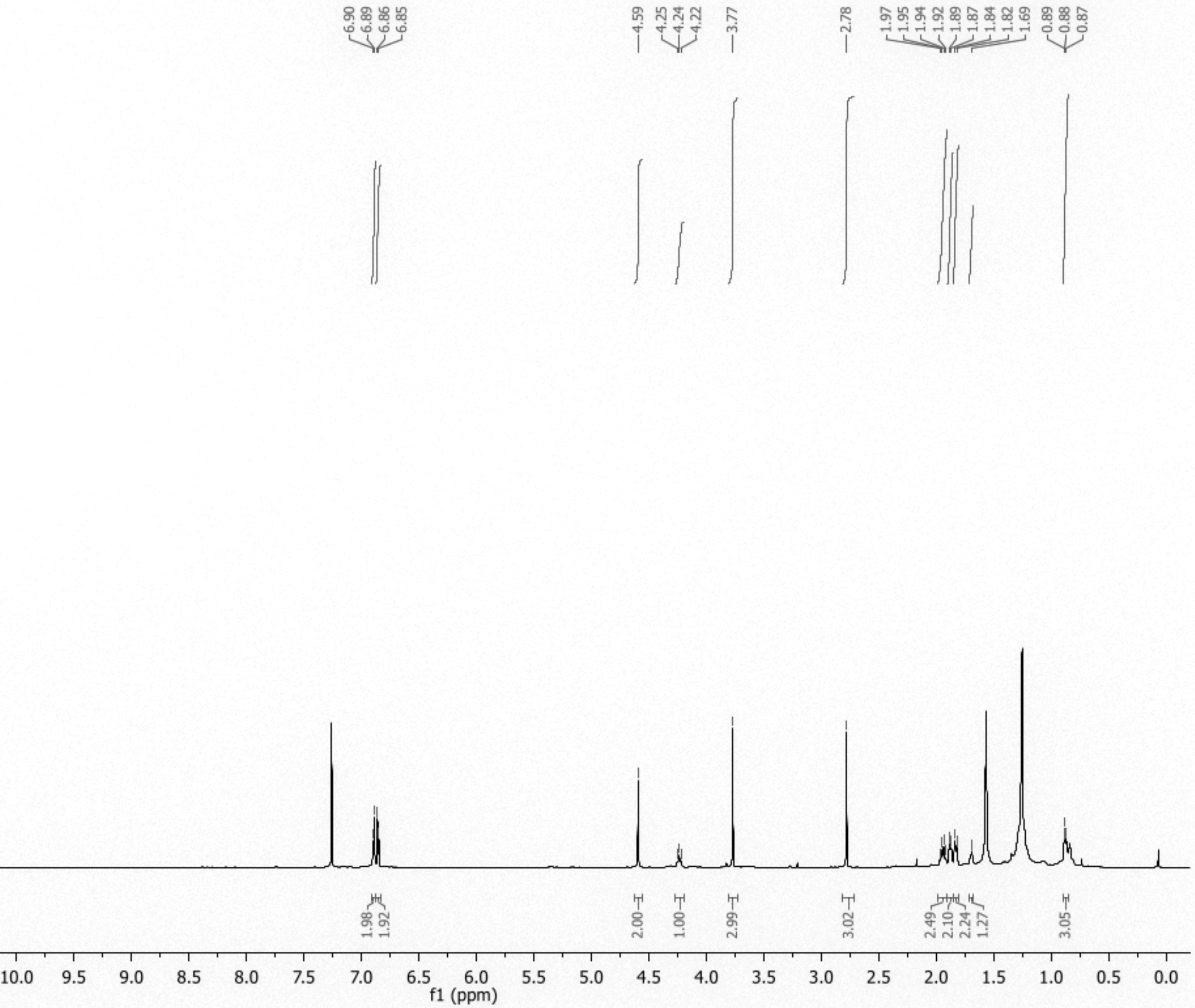

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176 MHz, $\mathrm{CDCl_3}$

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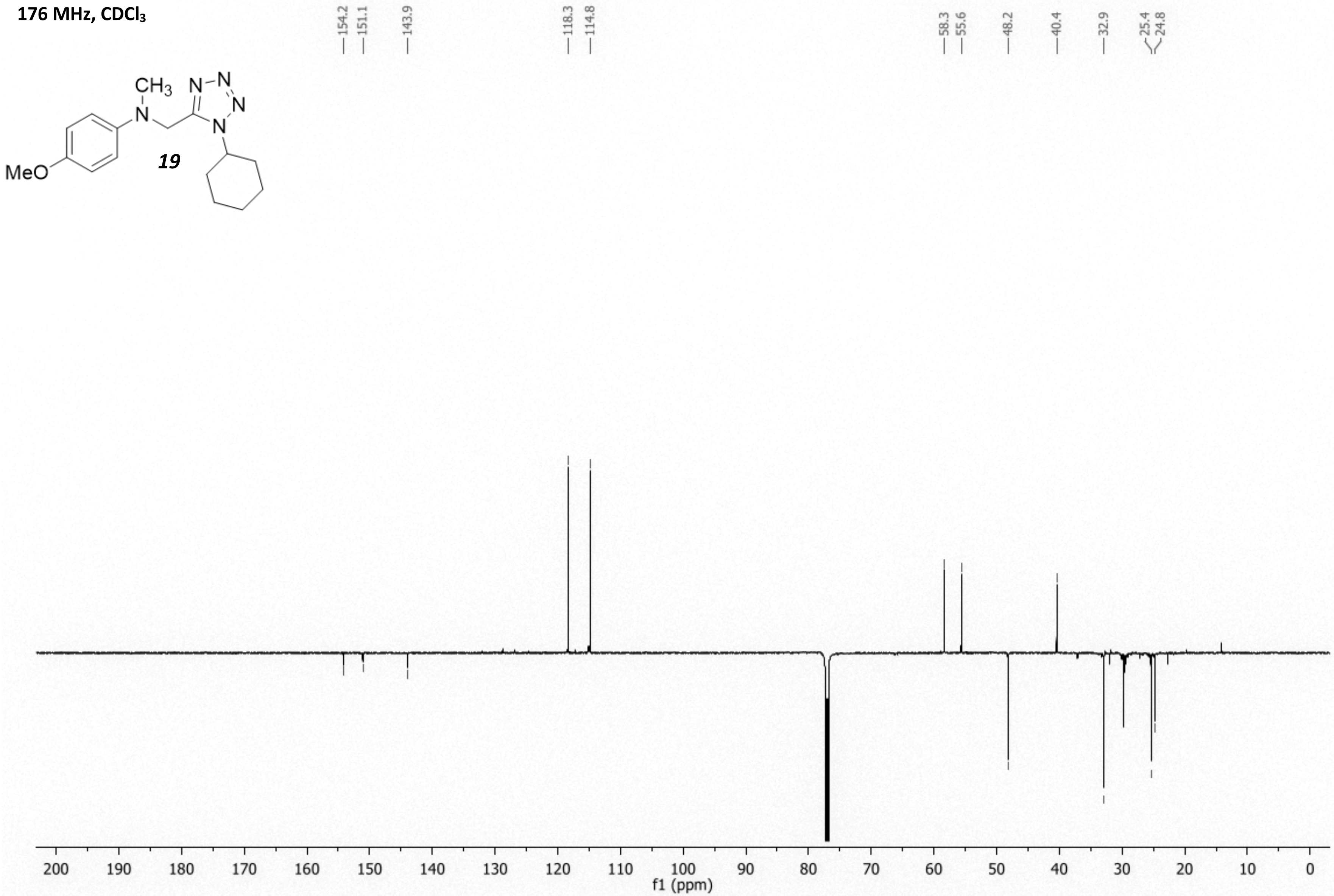

^{1}H NMR

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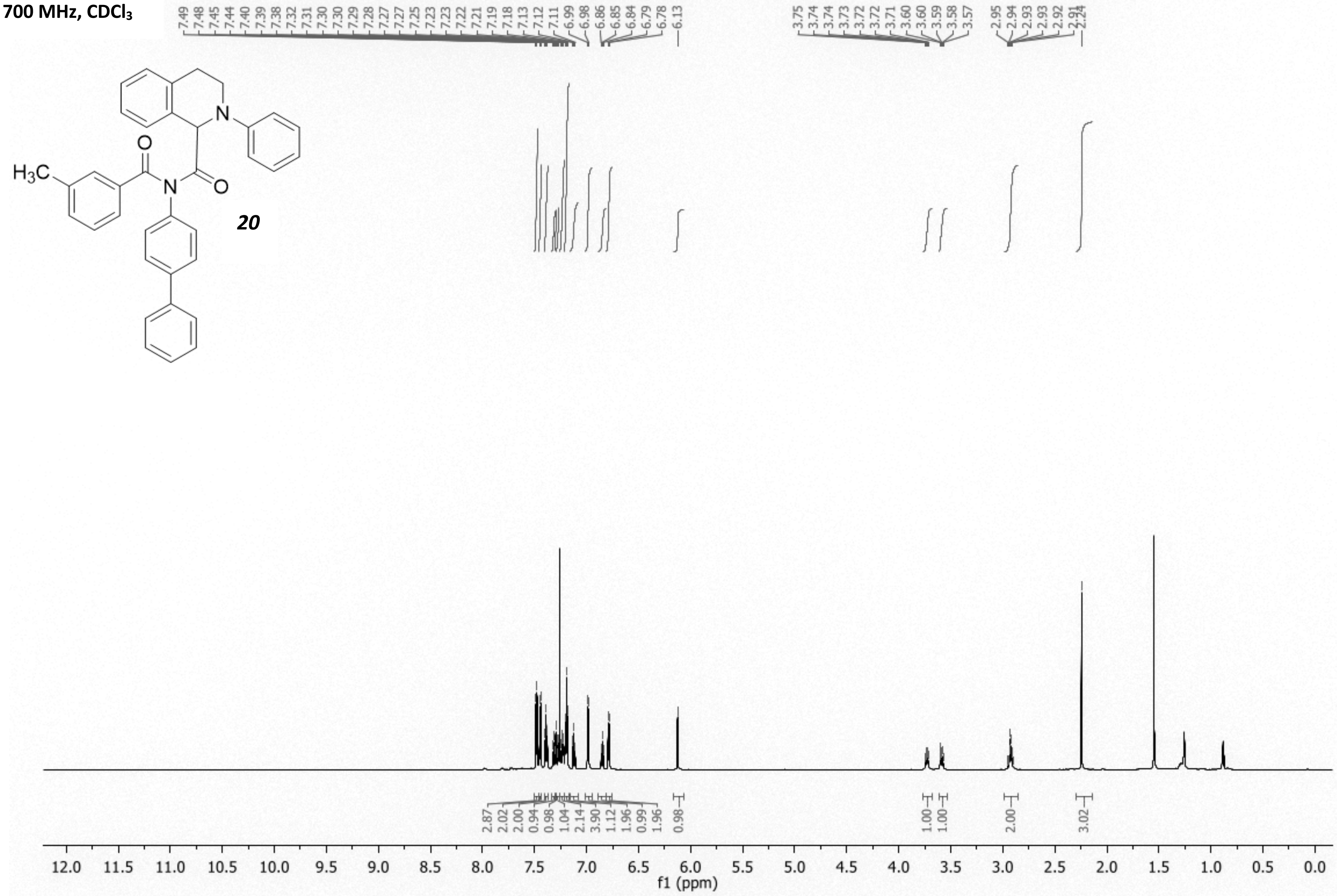

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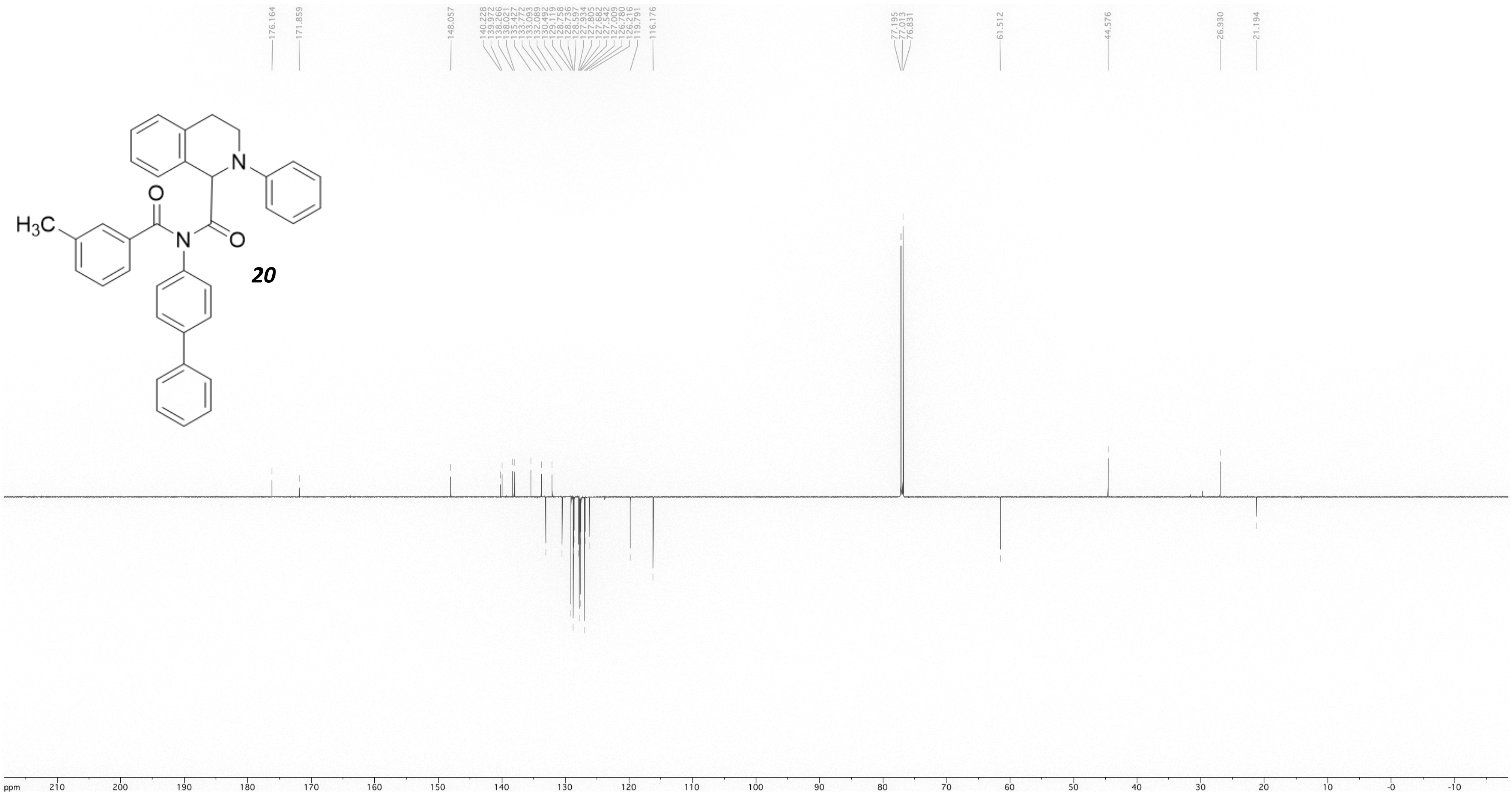

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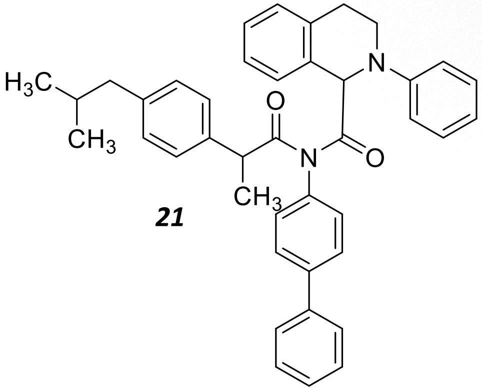

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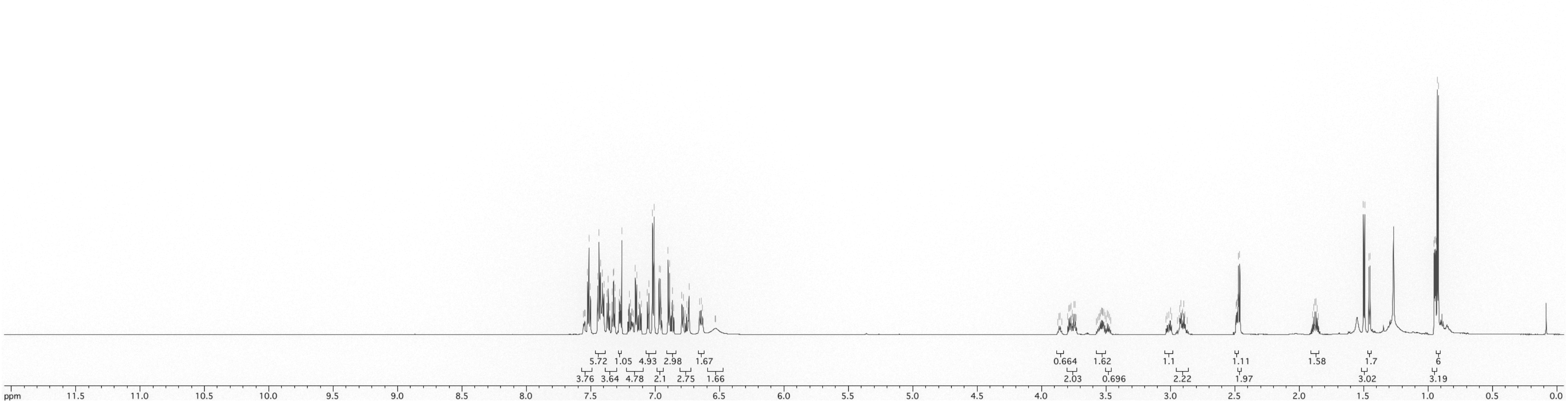

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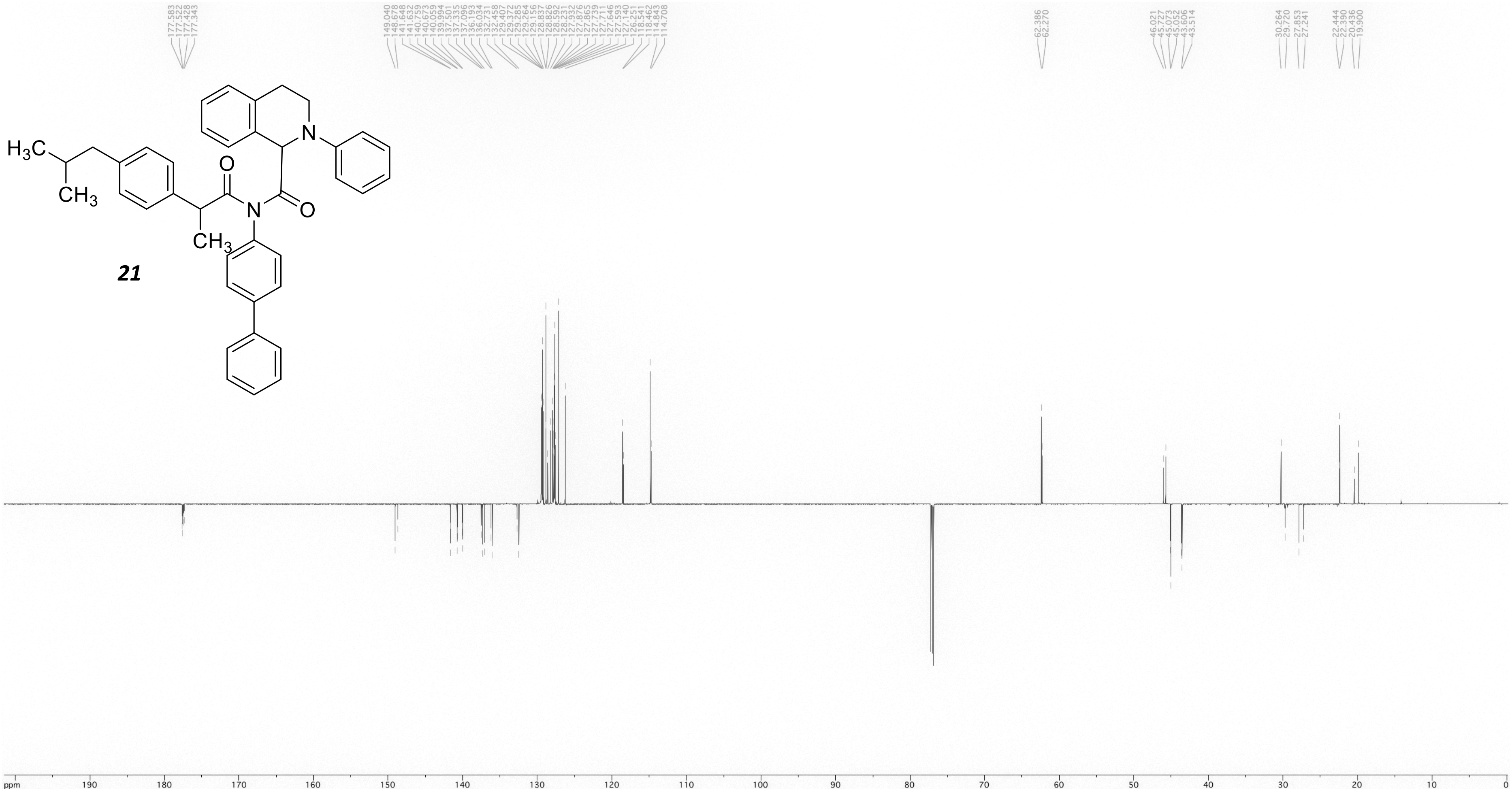
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700 MHz, CDCl$_3$

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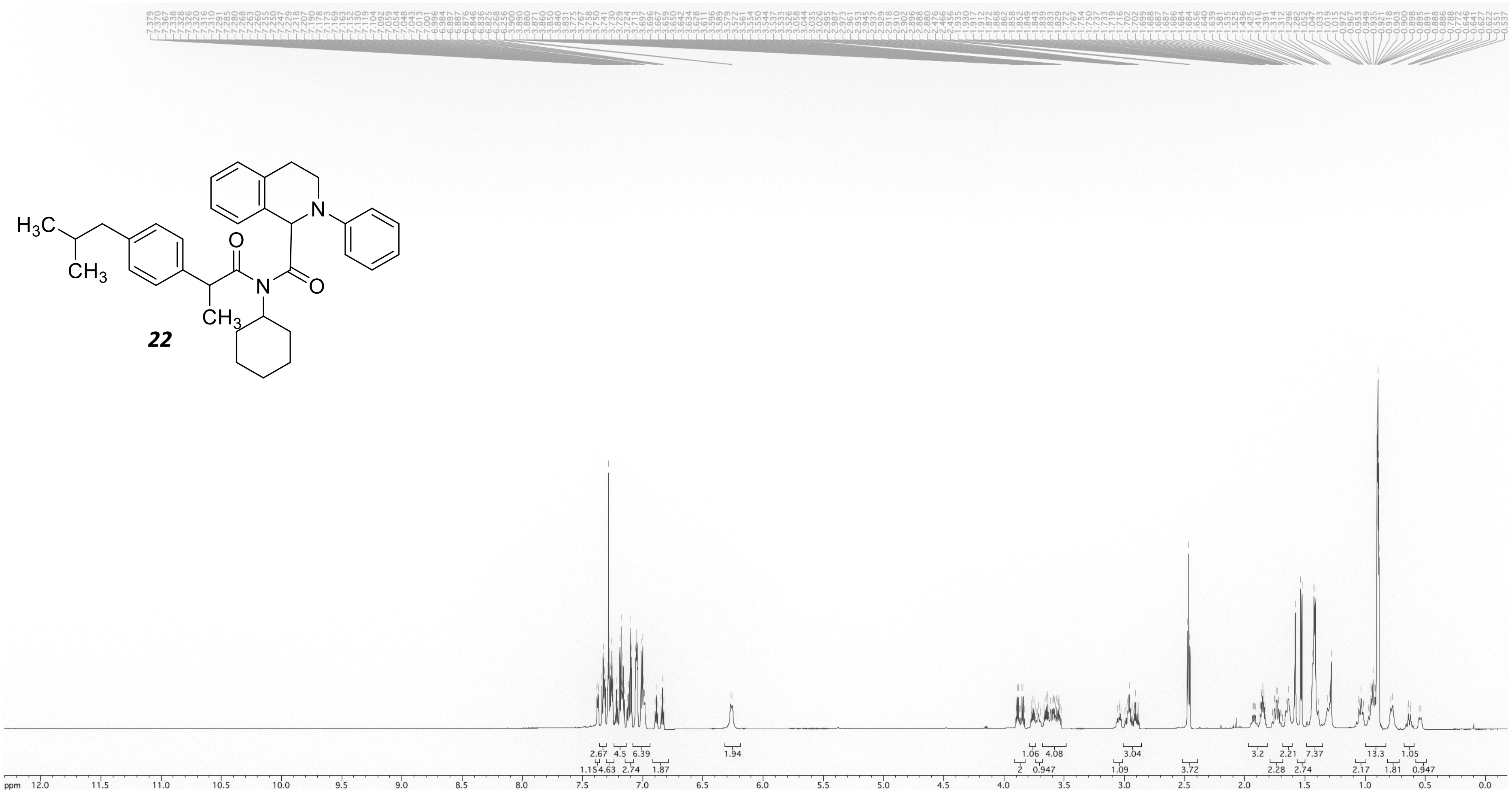

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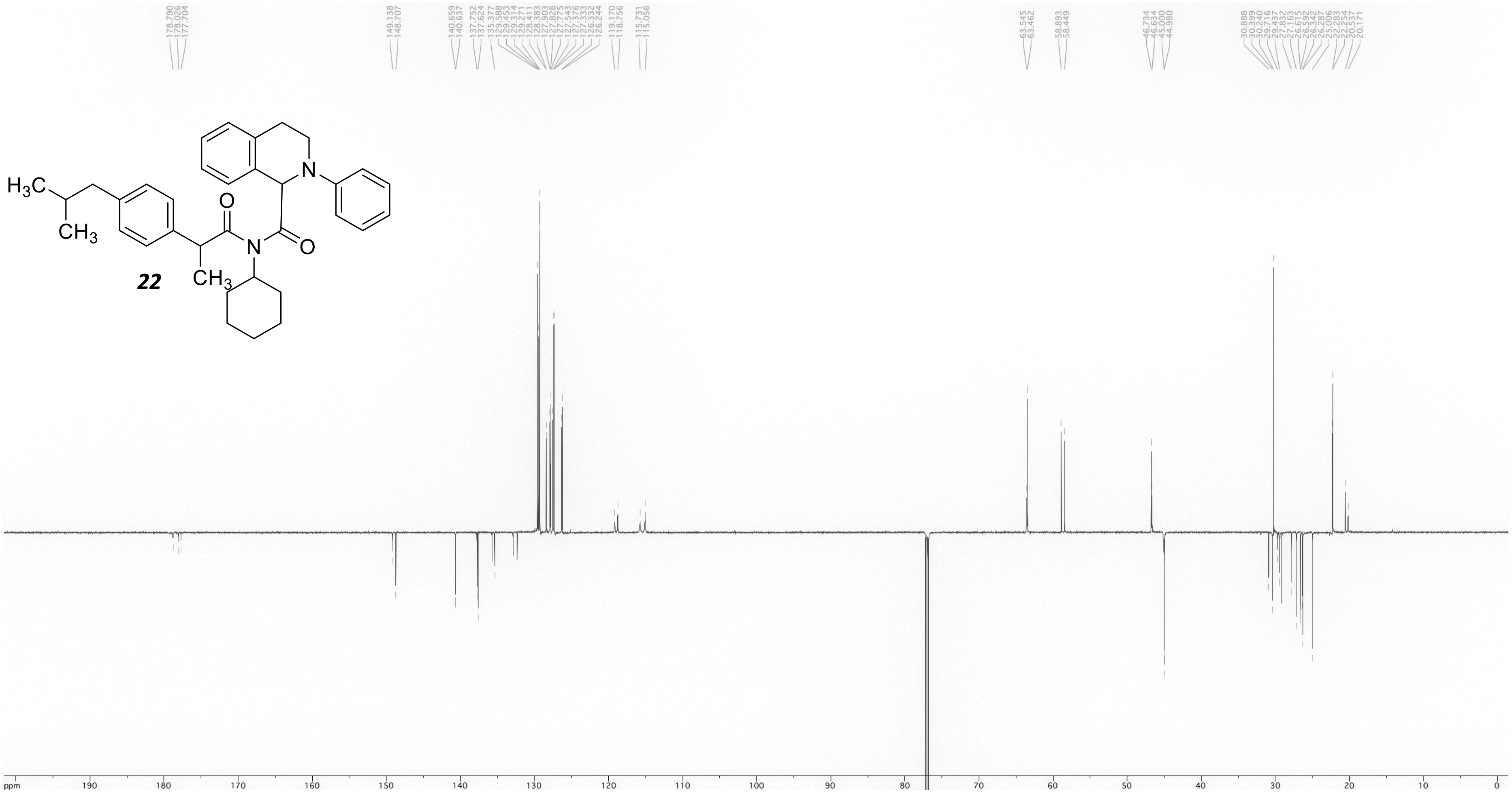

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700 MHz, $CDCl_3$

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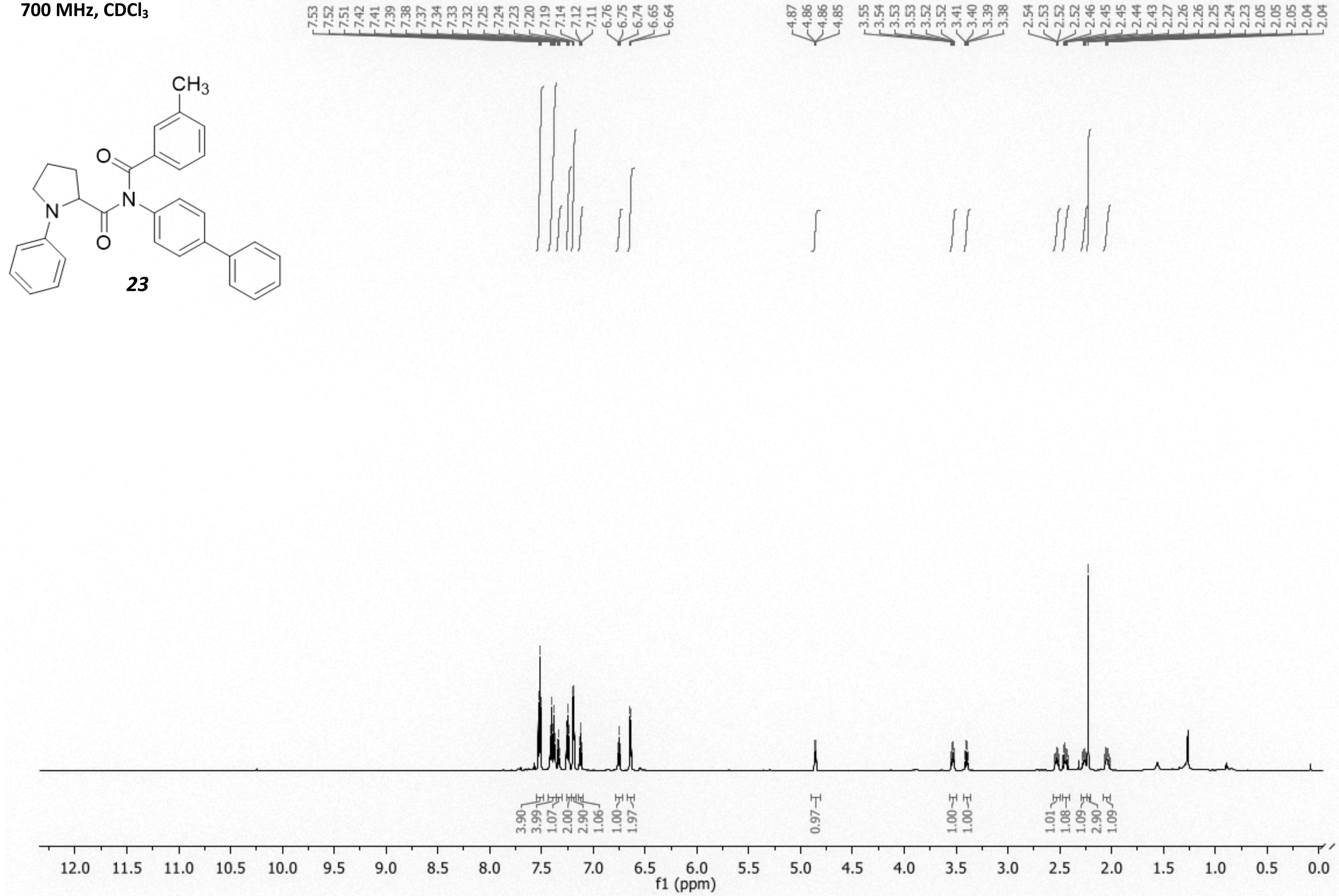

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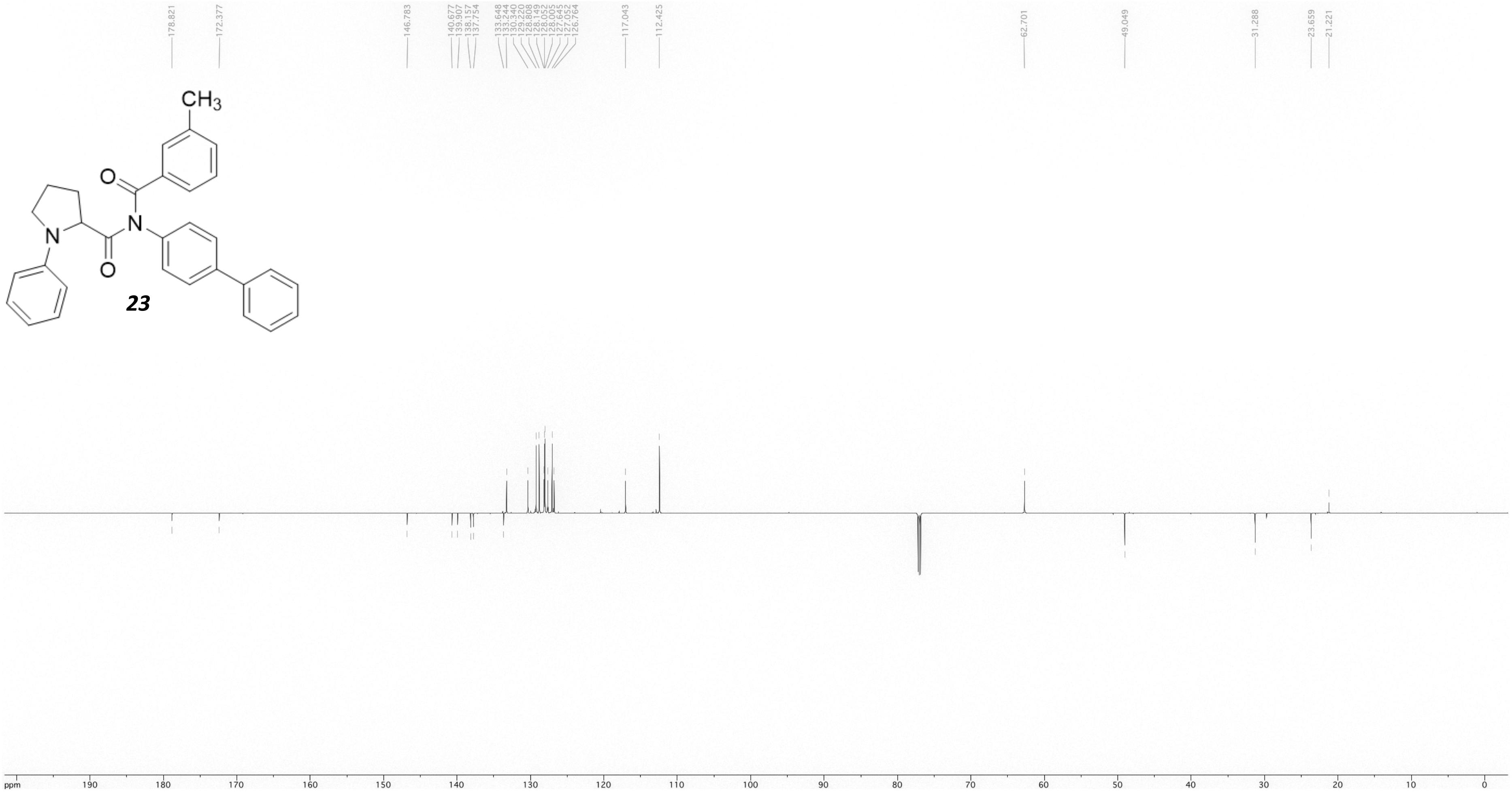

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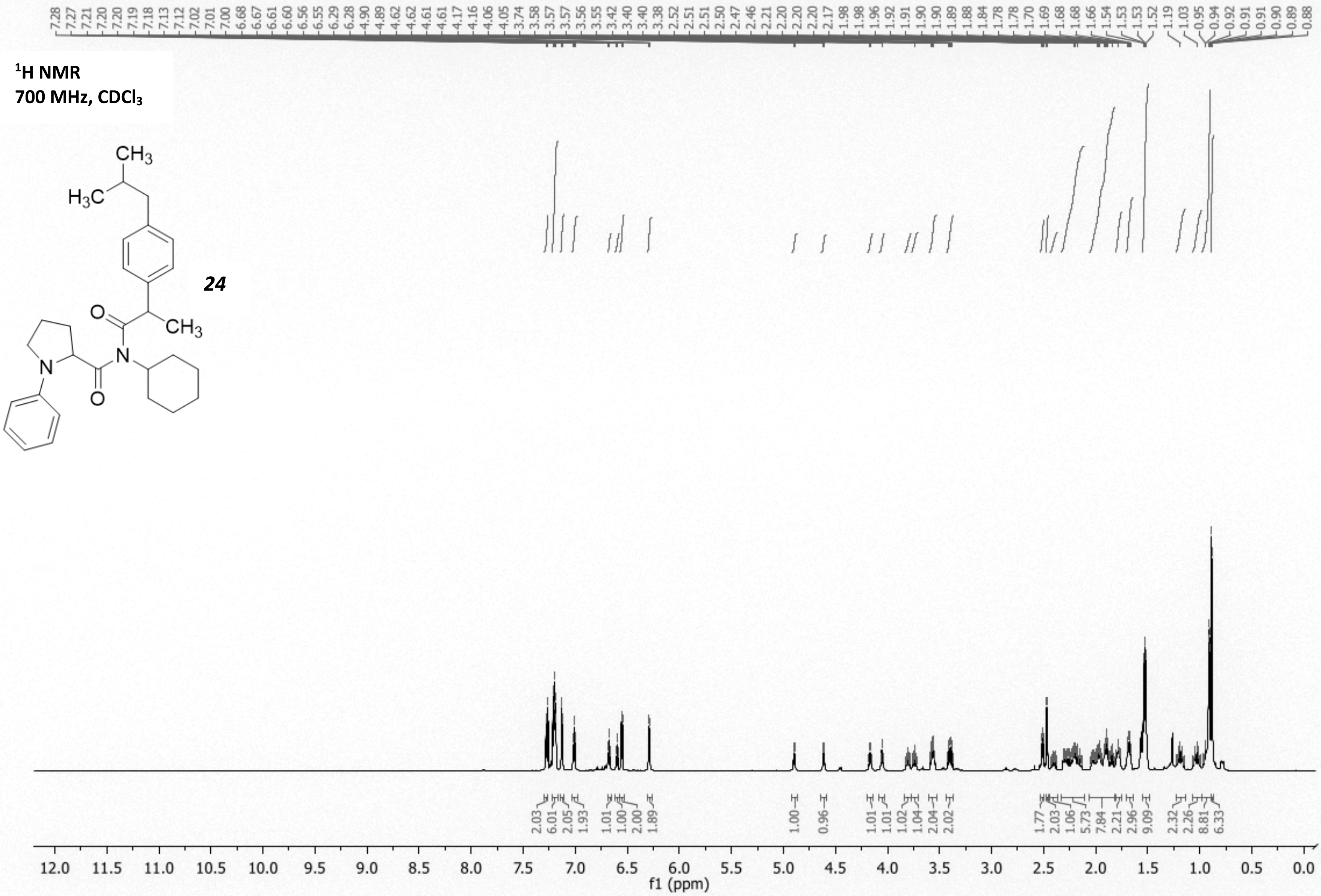

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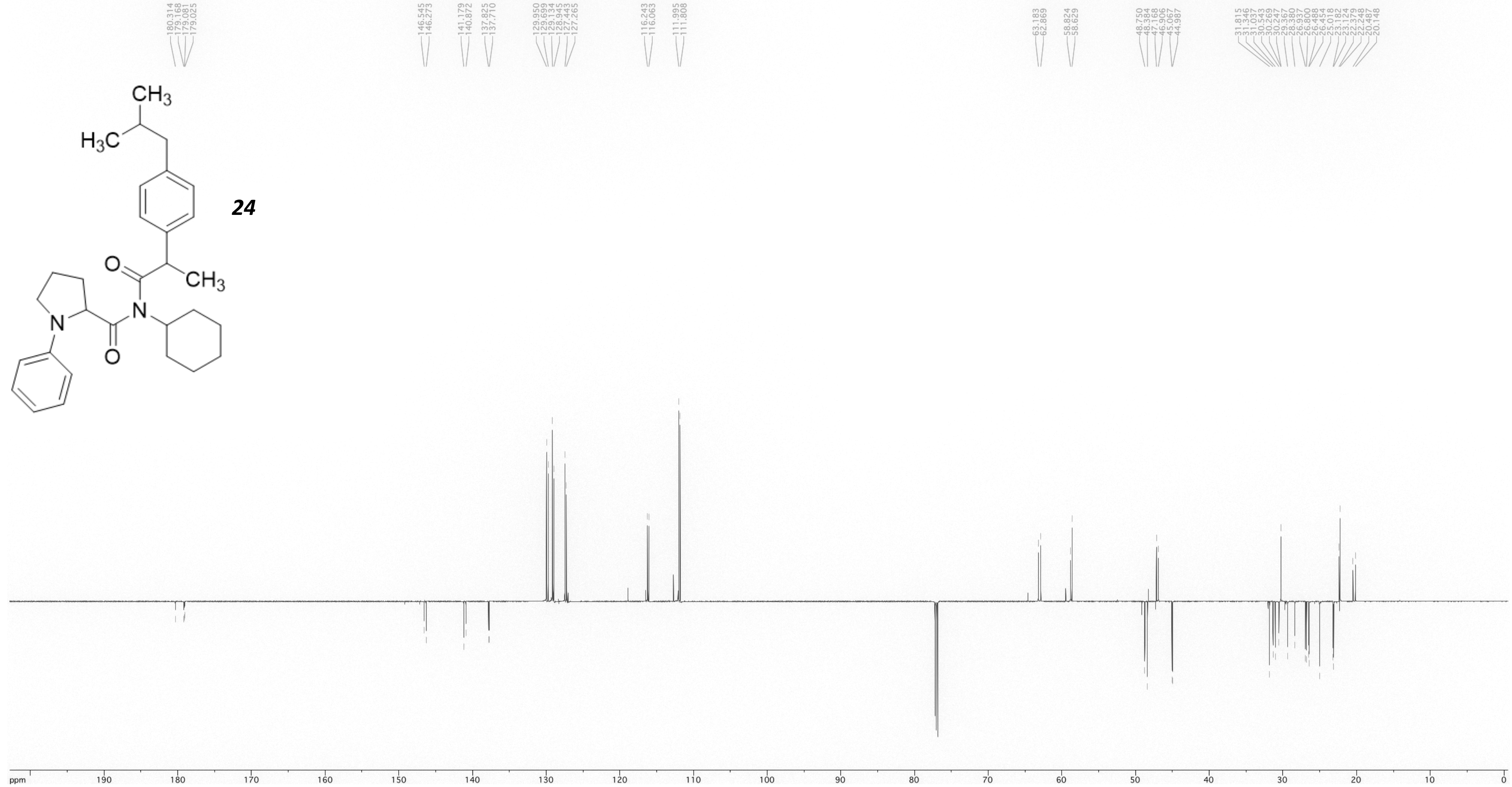

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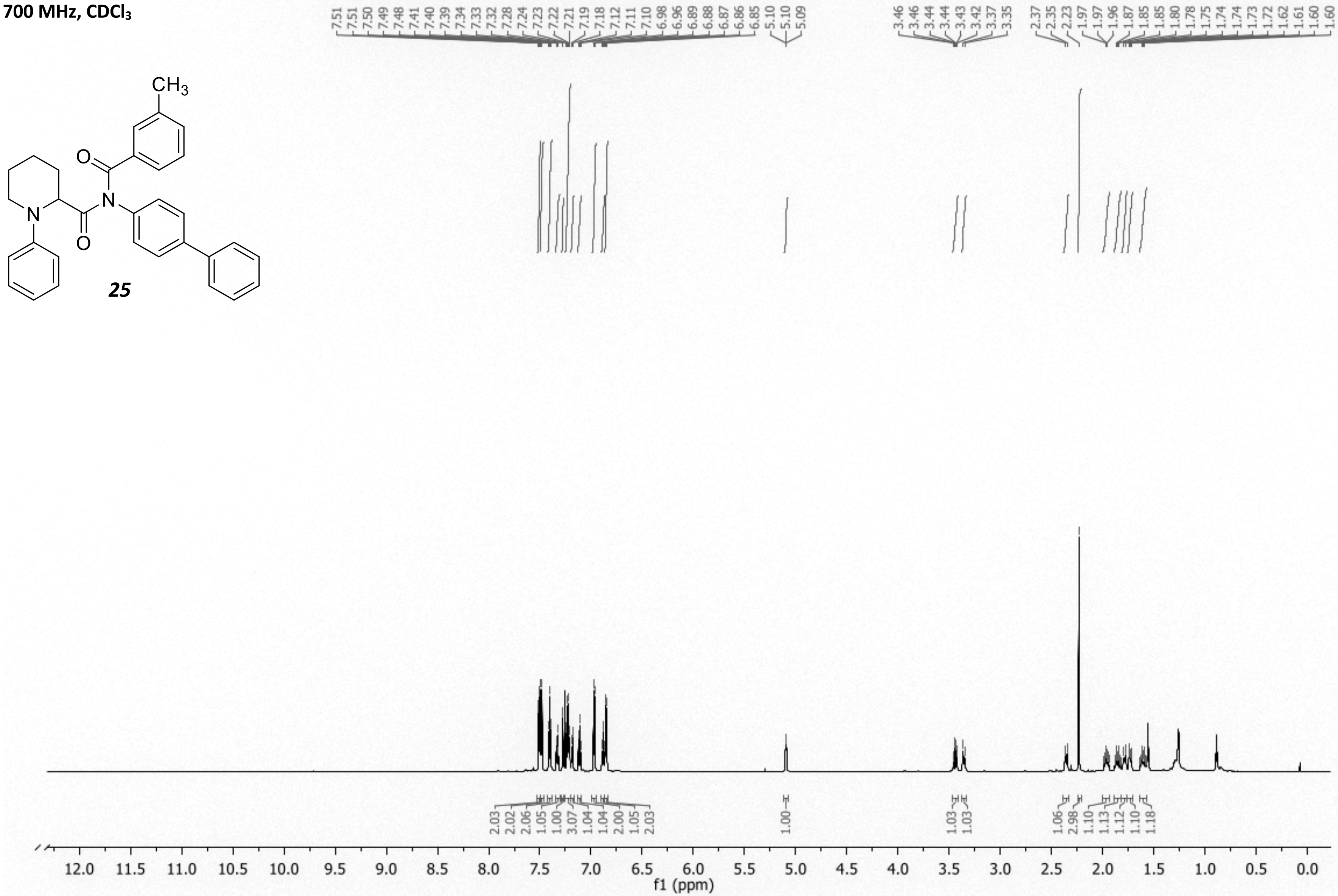
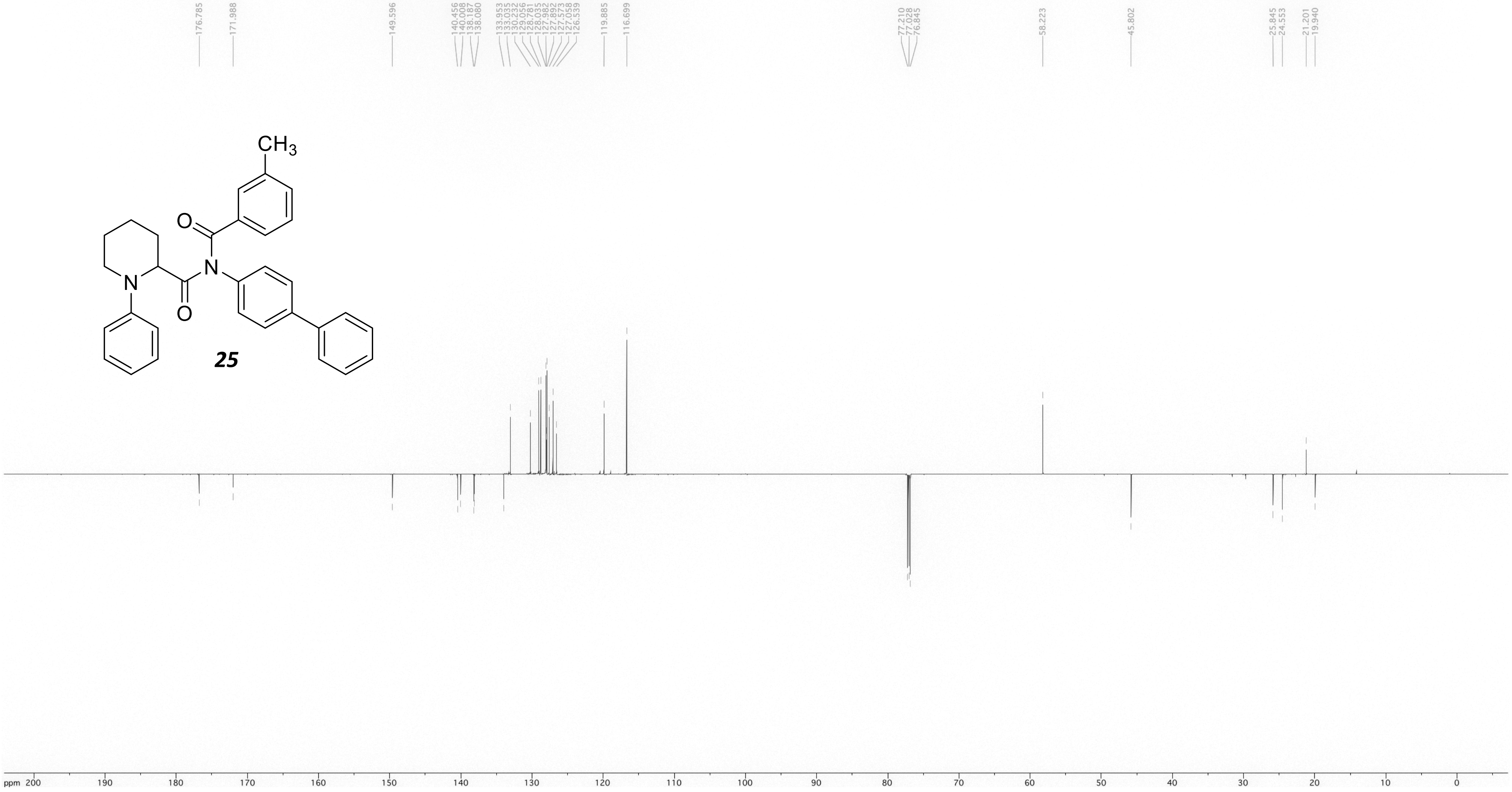
^{1}H NMR
700 MHz, $CDCl_3$



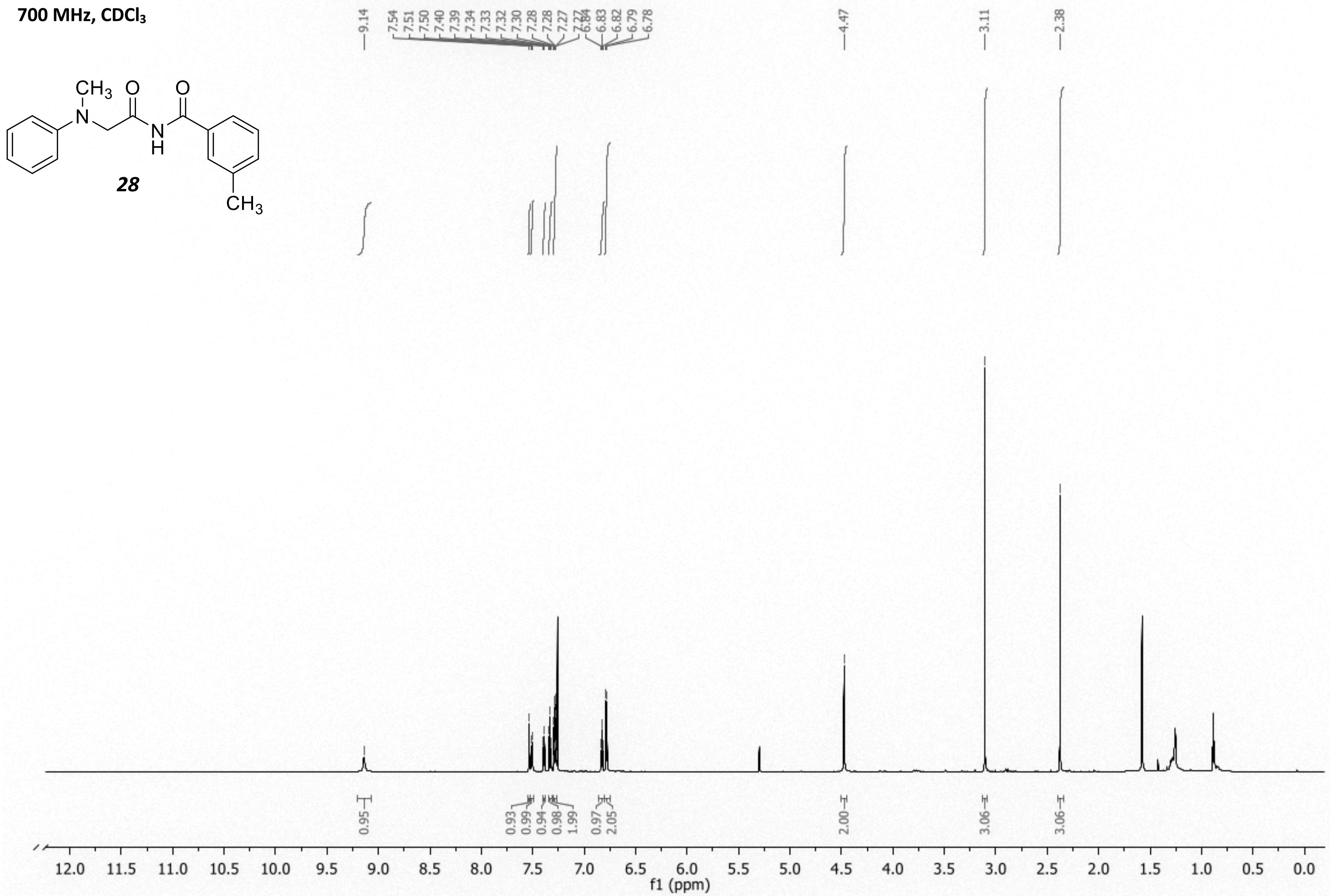
25

$^{13}C\{^1H\}$ NMR
176 MHz, $CDCl_3$



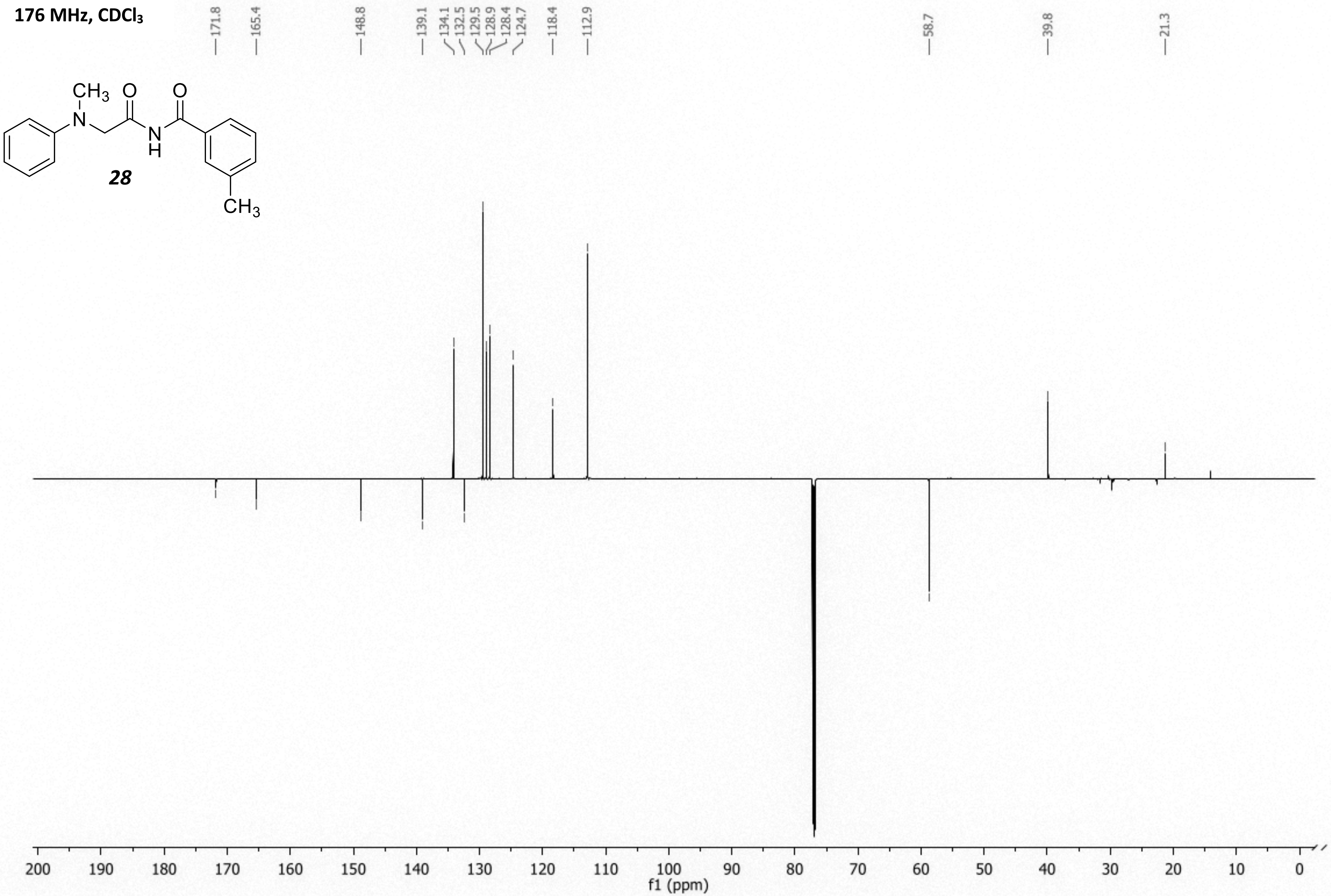
25

^{1}H NMR
700 MHz, CDCl$_3$



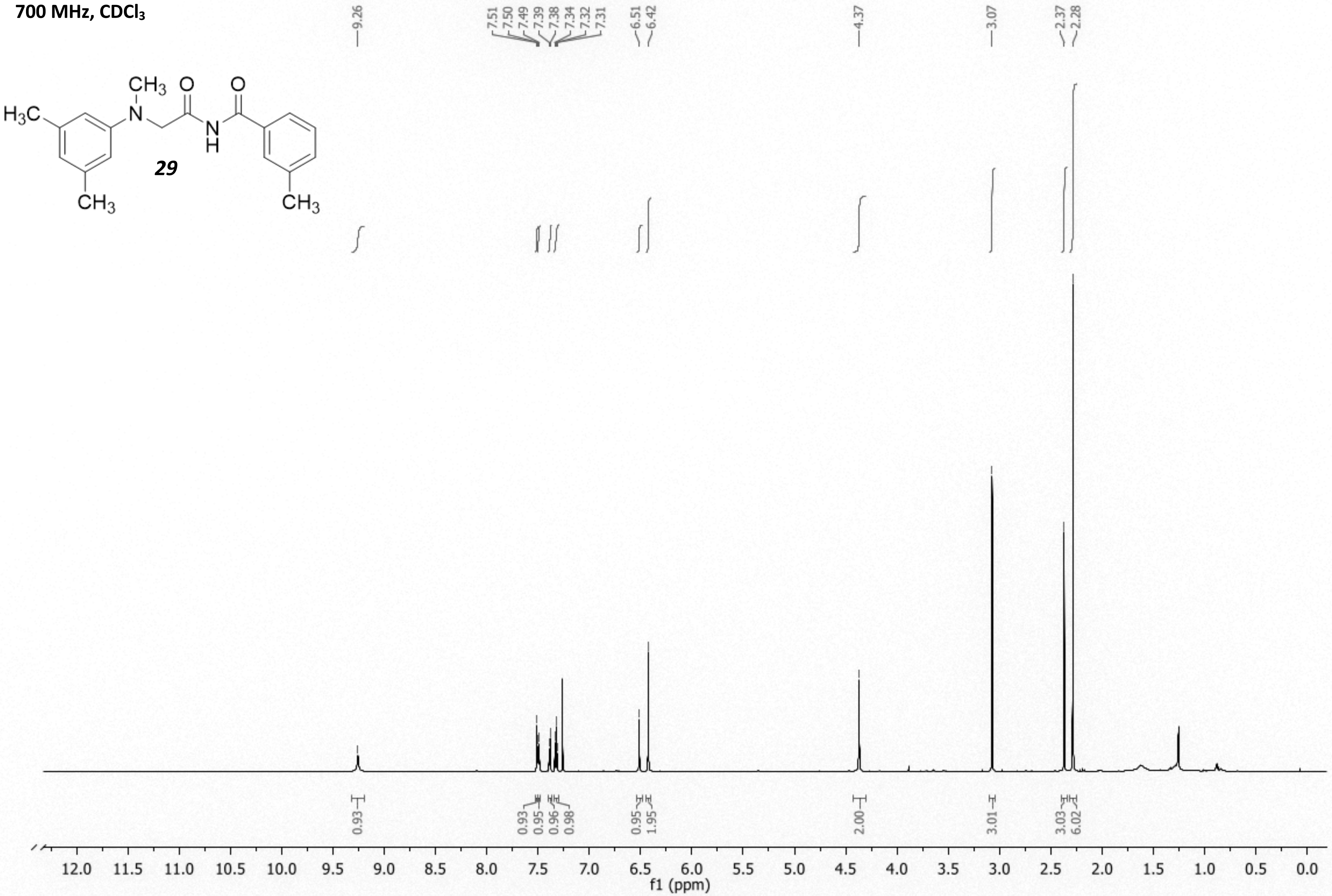
28

$^{13}C\{^1H\}$ NMR
176 MHz, $CDCl_3$

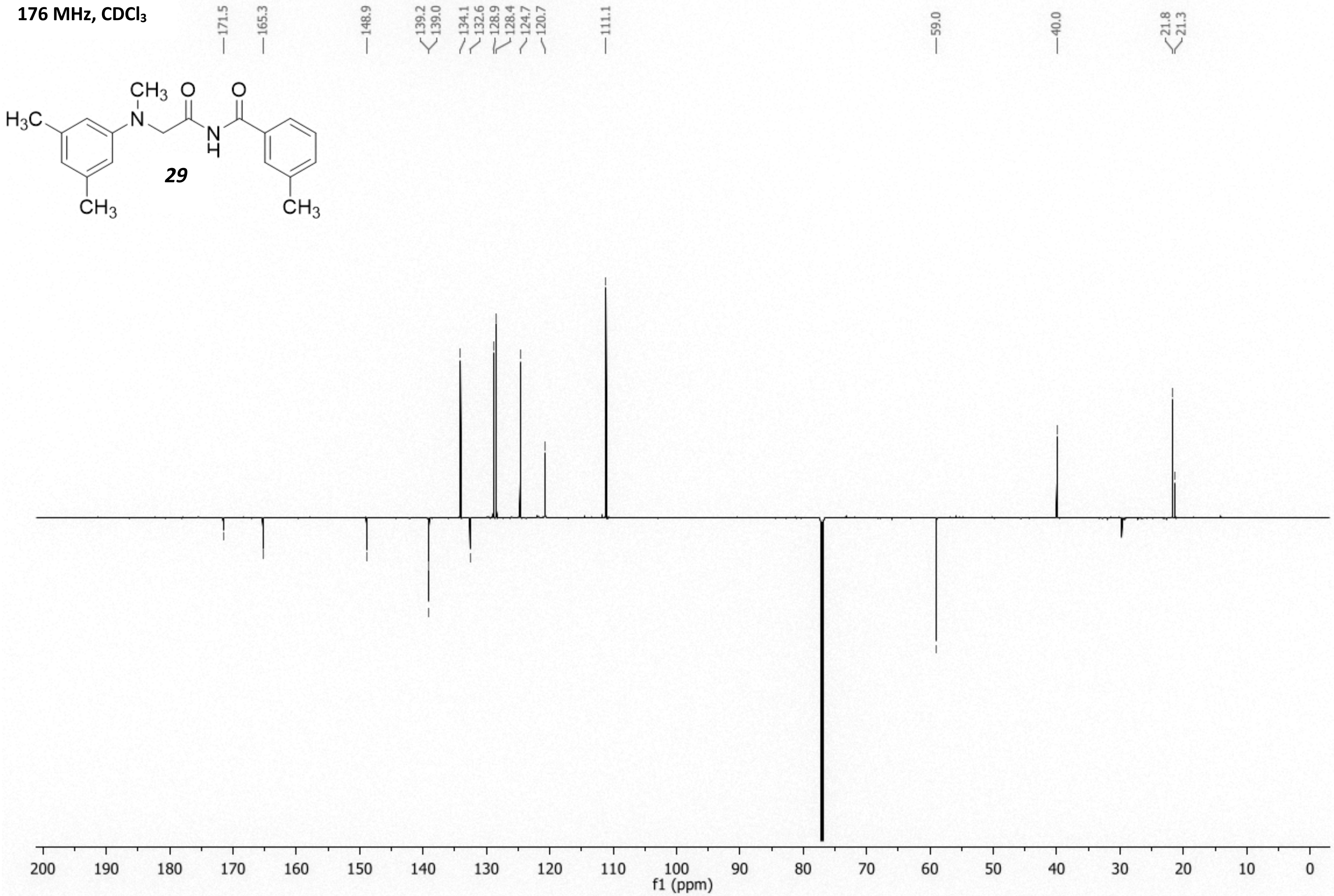


28

^{1}H NMR
700 MHz, CDCl$_3$



$^{13}C\{^1H\}$ NMR
176 MHz, $CDCl_3$



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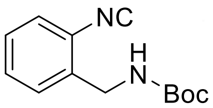
^{1}H NMR
700 MHz, $CDCl_3$



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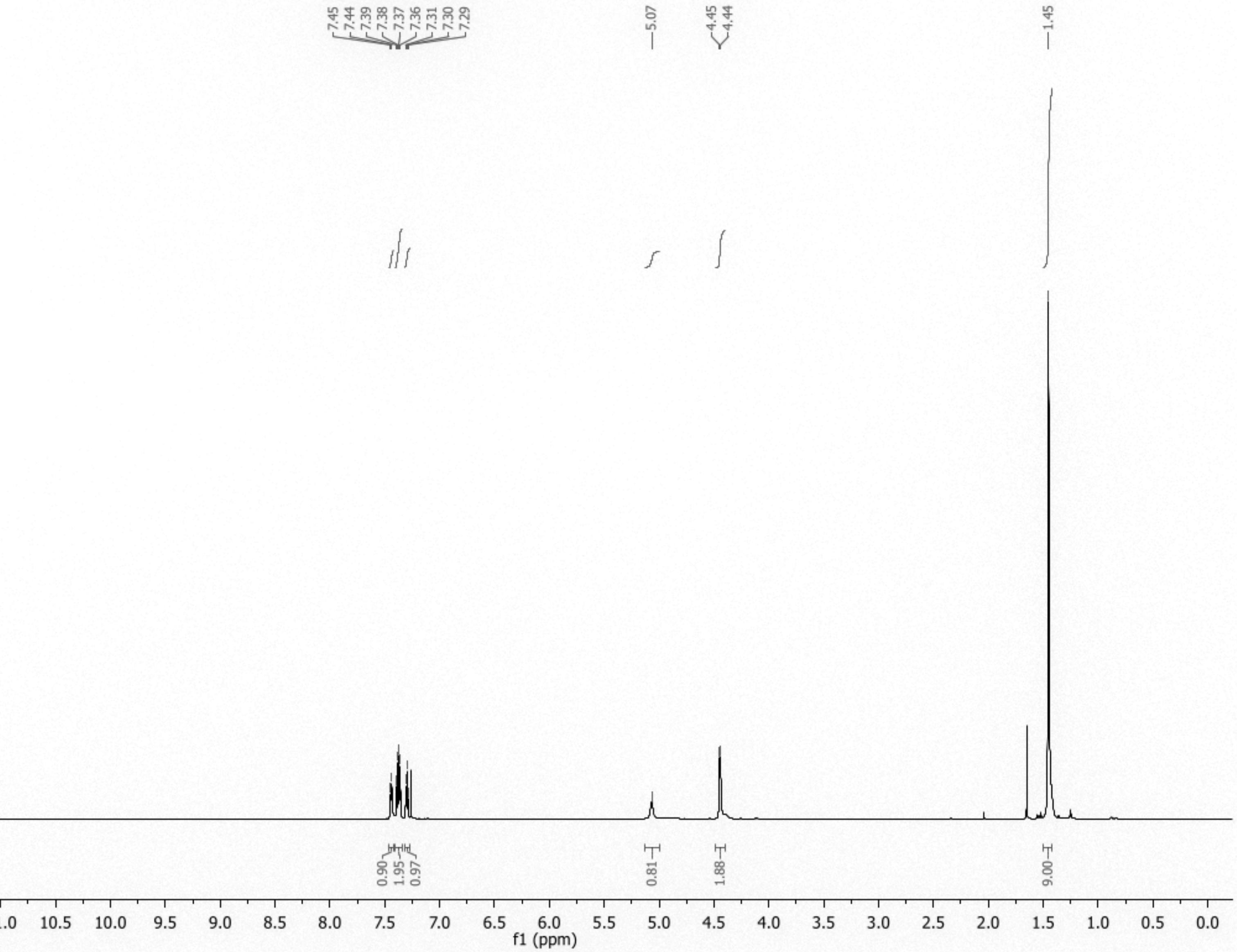
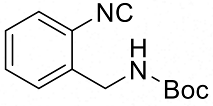


$^{13}C\{^{1}H\}$ NMR
176 MHz, $CDCl_3$



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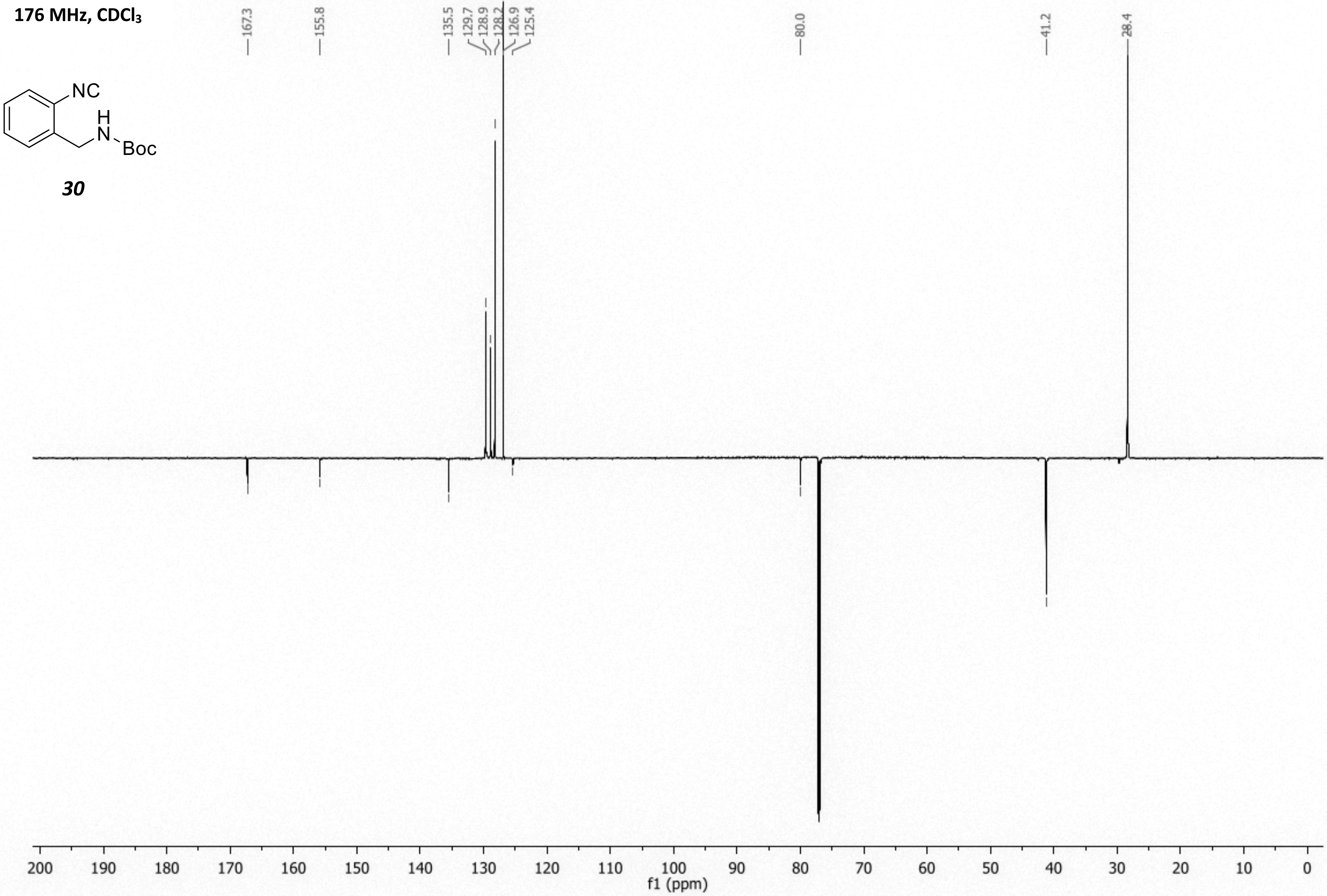
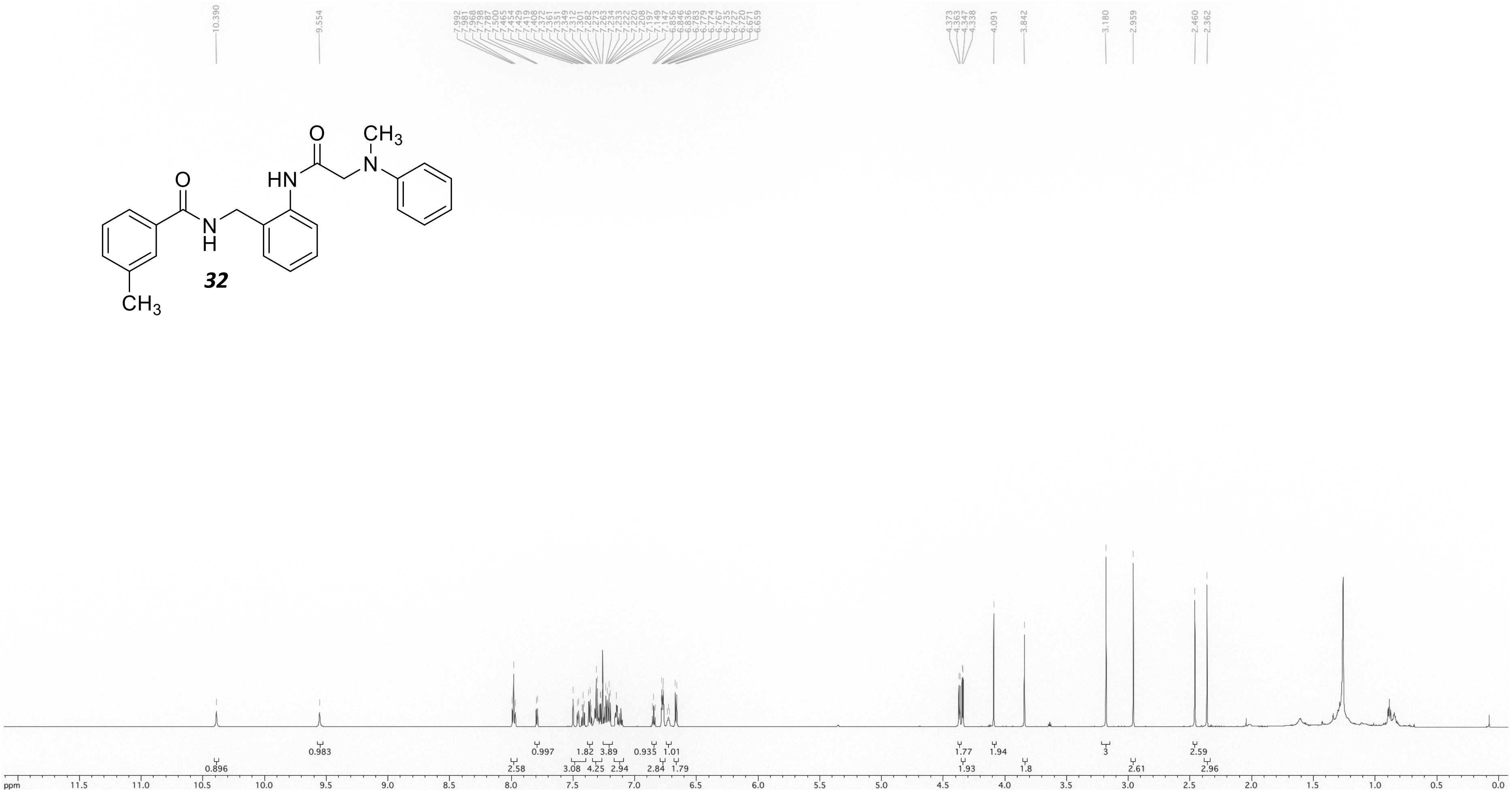


^{1}H NMR
700 MHz, $CDCl_3$



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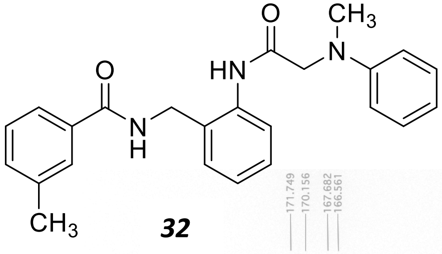
$^{13}C\{^1H\}$ NMR
176 MHz, $CDCl_3$



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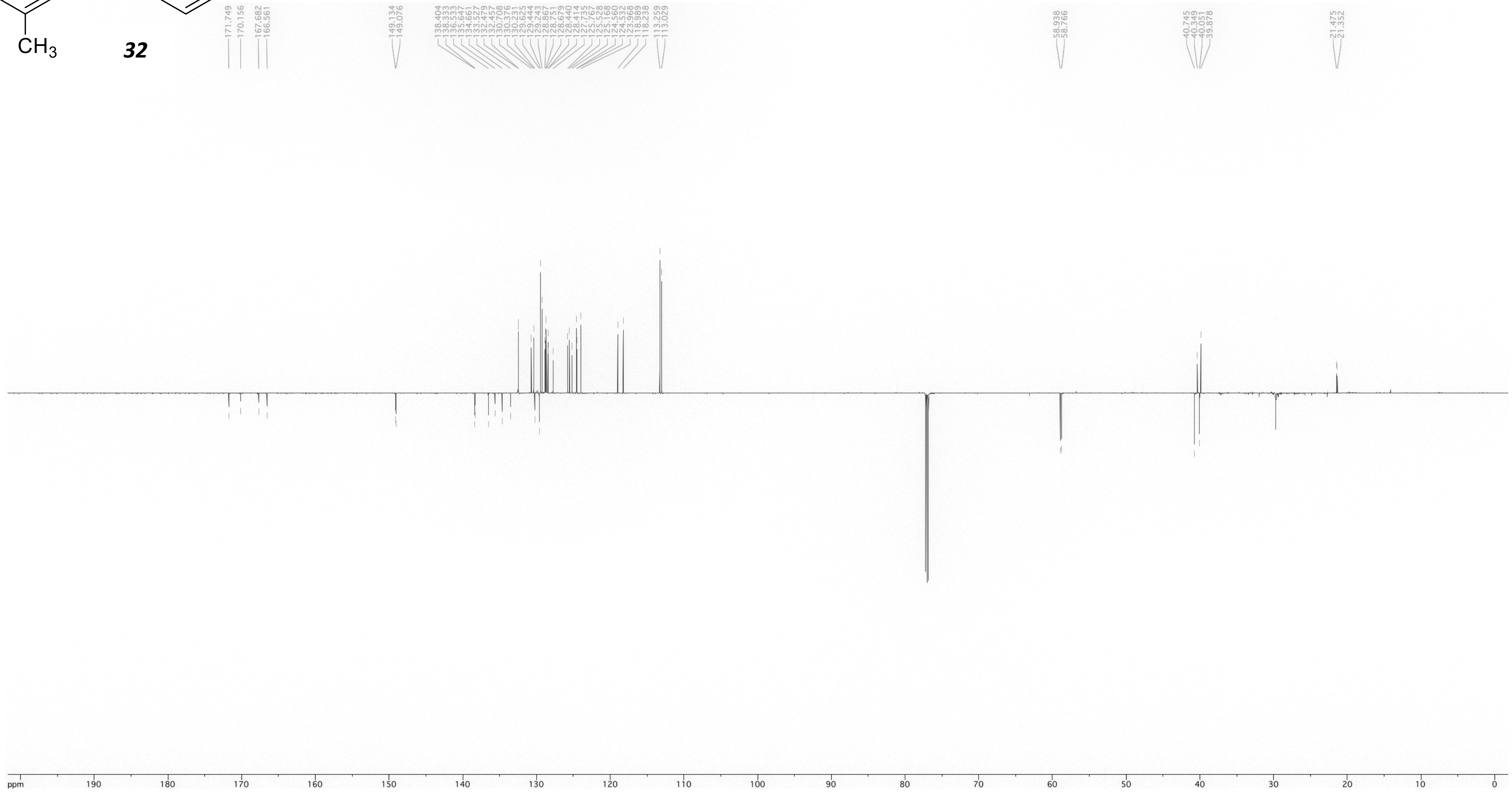
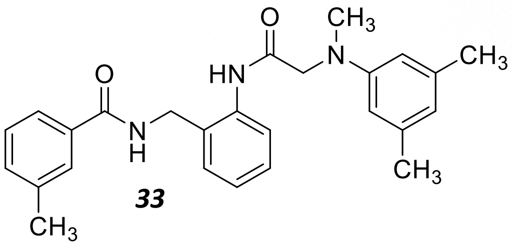


^{1}H NMR
700 MHz, $CDCl_3$



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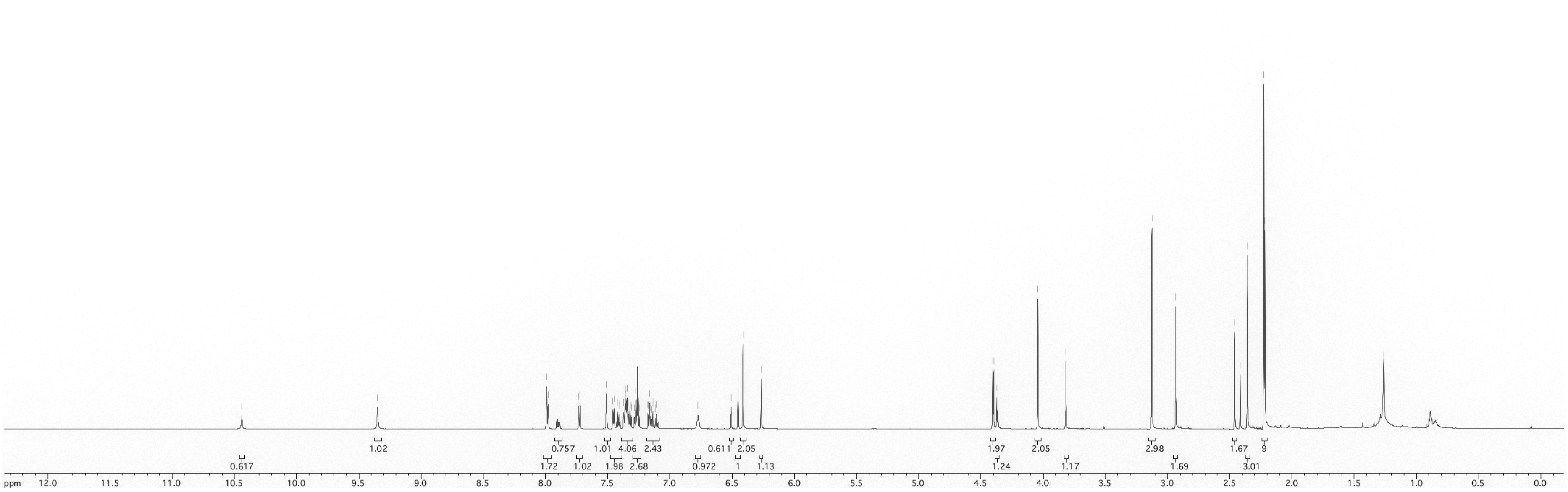
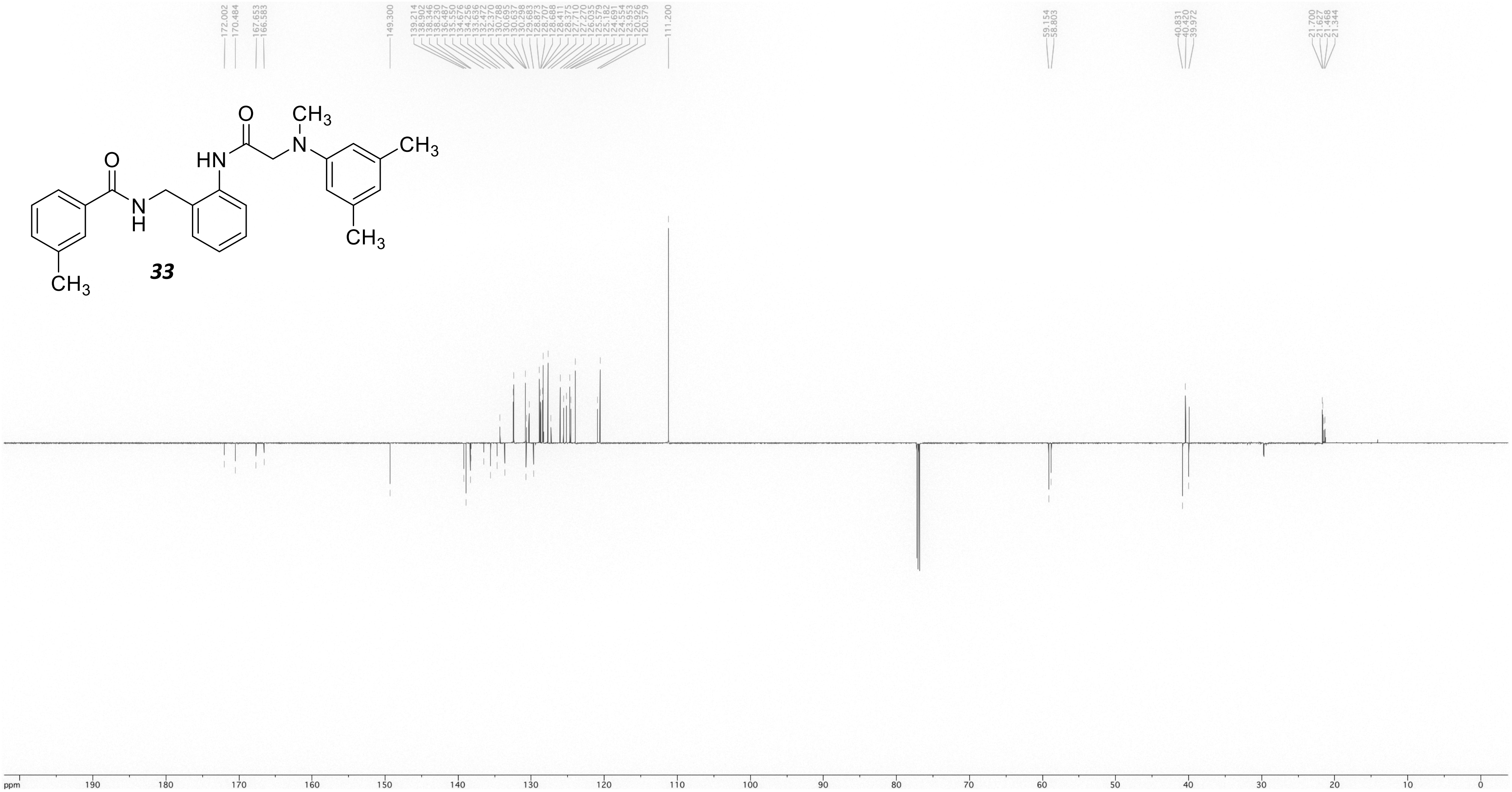
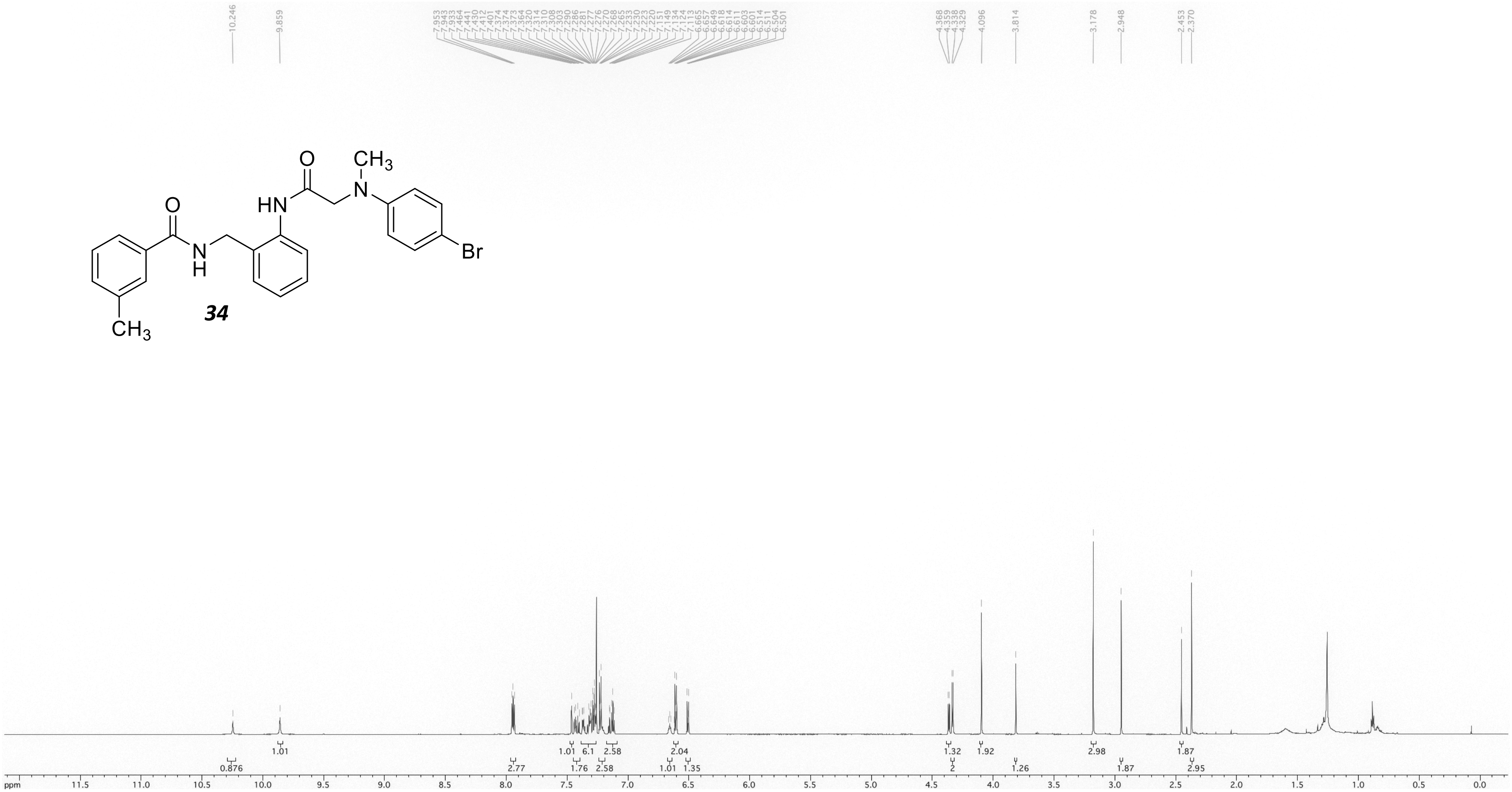


$^{13}C\{^{1}H\}$ NMR
176 MHz, $CDCl_3$



^{1}H NMR
700 MHz, CDCl$_3$

34



$^{13}C\{^1H\}$ NMR
176 MHz, $CDCl_3$