

A Straightforward and Versatile Protocol for the Direct Conversion of Benzylic Azides to Ketones and Aldehydes

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C O N T E N T

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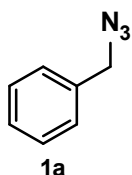
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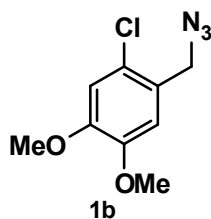
2.2. Products (carbonyl compounds) 52

1. CHARACTERIZATION DATA OF ALL COMPOUNDS

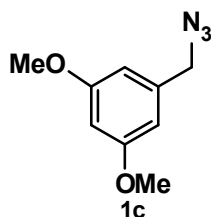
1.1. STARTING MATERIALS (AZIDO COMPOUNDS)

**Benzyl azide**¹

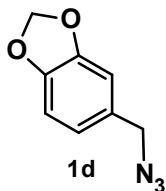
Colorless liquid

¹H NMR: (300 MHz, CDCl₃) δ = 7.48–7.29 (m, 5 Ar-H), 4.35 (s, 2 H) ppm.¹³C NMR: (75 MHz, CDCl₃) δ = 135.39 (C), 128.84 (2 CH), 128.30 (2 CH), 128.21 (C), 54.82 (CH₂-N₃) ppm.**1-(azidomethyl)-2-chloro-4,5-dimethoxybenzene**²

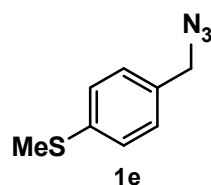
Yellow oil

¹H NMR: (300 MHz, CDCl₃) δ = 6.88 (d, *J* = 1.8 Hz, 1 ArH), 6.73 (d, *J* = 2.1 Hz, 1 Ar-H), 4.22 (s, 2 H), 3.84 (s, 3 H), 3.83 (s, 3 H) ppm.¹³C NMR: (75 MHz, CDCl₃) δ = 153.97 (C), 145.27 (C), 131.87 (C), 128.36 (C), 121.34 (CH), 110.57 (CH), 60.59 (OCH₃), 56.06 (OCH₃), 54.10 (CH₂-N₃) ppm.**3,5-dimethoxybenzyl azide**³

Yellow oil

¹H NMR: (300 MHz, CDCl₃) δ = 6.47 (d, *J* = 2.3 Hz, 2 Ar-H), 6.44 (t, *J* = 2.3 Hz, 1 Ar-H), 4.27 (s, 2 H), 3.80 (s, 6 H) ppm.¹³C NMR: (75 MHz, CDCl₃) δ = 161.14 (2 C), 137.63 (C), 106.03 (2 CH), 100.18 (CH), 55.35 (2 OMe), 54.86 (CH₂-N₃) ppm.**5-(azidomethyl)benzo[d][1,3]dioxole**⁴

Yellow oil

¹H NMR: (300 MHz, CDCl₃) δ = 6.86–6.74 (m, 3 Ar-H), 5.97 (s, 2 H), 4.22 (s, 2 H) ppm.¹³C NMR: (75 MHz, CDCl₃) δ = 148.07 (C), 147.70 (C), 129.06 (C), 121.94 (CH), 108.75 (CH), 108.37 (CH), 101.27 (CH₂), 54.72 (CH₂-N₃) ppm.**4-(methylthio)benzyl azide**⁵

Yellow oil

¹H NMR: (300 MHz, CDCl₃) δ = 7.28 (d, *J* = 2.2 Hz, 2 Ar-H), 7.25 (d, *J* = 2.6 Hz, 2 Ar-H), 4.29 (s, 2 H), 2.49 (s, 3 H) ppm.¹³C NMR: (75 MHz, CDCl₃) δ = 138.93 (C), 132.06 (C), 128.76 (2 CH), 126.79 (2 CH), 54.42 (CH₂-N₃), 15.72 (SMe) ppm.

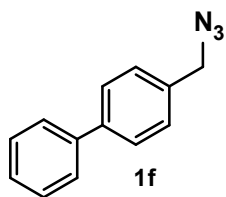
¹ (a) S. Giovani, R. Singh, R. Fasan, *Chem. Sci.* **2016**, 7, 234-239. (b) H. P. Zhang, Y. Z. Dai, L. M. Tao, *J. Chem. Res.* **2011**, 35, 720-722. (c) M. Maddani, K. R. Prabhu, *Tetrahedron Lett.* **2008**, 49, 4526–4530. (d) S. Pramanik, P. Ghorai, *Org. Lett.* **2014**, 16, 2104–2107

² D. González-Calderón, A. Fuentes-Benites, E. Díaz-Torres, C. A. González-González, C. González-Romero, *Eur. J. Org. Chem.* **2016**, 668–672.

³ Vivian Wing Wah Yam, Kobe Man Chung Tang, Maggie Mei Yee Chan, Keith Man Chung Wong, Patent US20130228758 A1, Sep 5, **2013**.

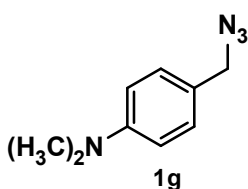
⁴ S. S. Kulkarni, X. Hu, R. Manetsch, *Chem. Commun.* **2013**, 49, 1193–1195.

⁵ S. S. Kulkarni, X. Hu, R. Manetsch, *Chem. Commun.* **2013**, 49, 1193–1195.

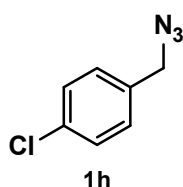
**4-Phenylbenzyl azide**⁶

White solid

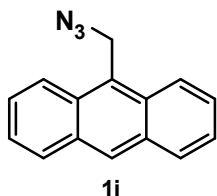
m.p. 36–38 °C

¹H NMR: (300 MHz, CDCl₃) δ = 7.67–7.55 (m, 4 Ar-H), 7.52–7.31 (m, 5 Ar-H), 4.39 (s, 2 H) ppm.¹³C NMR: (75 MHz, CDCl₃) δ = 141.28 (C), 140.52 (C), 134.34 (C), 128.81 (2 CH), 128.65 (2 CH), 127.56 (C), 127.50 (2 CH), 127.10 (2 CH), 54.55 (CH₂-N₃) ppm.**4-(Dimethylamino)benzyl azide**⁷

Yellow oil

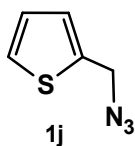
¹H NMR: (300 MHz, CDCl₃) δ = 7.21–7.15 (m, 2 Ar-H), 6.74–6.67 (m, 2 Ar-H), 4.21 (s, 2 H), 2.95 (s, 6 H) ppm.¹³C NMR: (75 MHz, CDCl₃) δ = 150.53 (C), 129.58 (2 CH), 122.70 (2 CH), 112.42 (C), 54.73 (CH₂-N₃), 40.43 (2 Me) ppm.**4-chlorobenzyl azide**⁸

Colorless oil

¹H NMR: (300 MHz, CDCl₃) δ = 7.38–7.31 (m, 2 H), 7.27–7.20 (m, 2 H), 4.30 (s, 2 H) ppm.¹³C NMR: (75 MHz, CDCl₃) δ = 134.21 (C), 133.89 (C), 129.50 (2 CH), 129.02 (2 CH), 54.03 (CH₂-N₃) ppm.**9-(azidomethyl)anthracene**⁹

White solid

m.p. 78–80 °C

¹H NMR: (300 MHz, CDCl₃) δ = 8.52 (s, 1 Ar-H), 8.30 (d, *J* = 8.8 Hz, 2 Ar-H), 8.06 (d, *J* = 8.4 Hz, 2 Ar-H), 7.67–7.45 (m, 4 Ar-H), 5.34 (s, 2 H) ppm.¹³C NMR: (75 MHz, CDCl₃) δ = 131.40 (2 C), 130.74 (2 C), 129.31 (2 CH), 129.00 (CH), 126.85 (C), 125.80 (2 CH), 125.21 (2 CH), 123.53 (2 CH), 46.39 (CH₂-N₃) ppm.**2-(azidomethyl)thiophene**¹⁰

Yellow oil

¹H NMR: (300 MHz, CDCl₃) δ = 7.33 (dd, *J* = 5.0, 1.2 Hz, 1 Ar-H), 7.11–6.98 (m, 2 Ar-H), 4.50 (s, 2 H) ppm.¹³C NMR: (75 MHz, CDCl₃) δ = 137.26 (C), 127.38 (CH), 127.14 (CH), 126.45 (CH), 49.10 (CH₂-N₃) ppm.

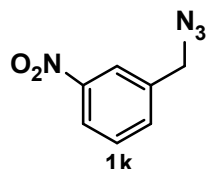
⁶ (a) S. S. Kulkarni, X. Hu, R. Manetsch, *Chem. Commun.* **2013**, 49, 1193–1195. (b) H. P. Zhang, Y. Z. Dai, L. M. Tao, *J. Chem. Res.* **2011**, 35, 720–722. (c) S. Pramanik, P. Ghorai, *Org. Lett.* **2014**, 16, 2104–2107.

⁷ (a) H. P. Zhang, Y. Z. Dai, L. M. Tao, *J. Chem. Res.* **2011**, 35, 720–722. (b) S. S. Kulkarni, X. Hu, R. Manetsch, *Chem. Commun.* **2013**, 49, 1193–1195.

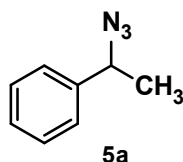
⁸ (a) S. S. Kulkarni, X. Hu, R. Manetsch, *Chem. Commun.* **2013**, 49, 1193–1195. (b) M. Maddani, K. R. Prabhu, *Tetrahedron Lett.* **2008**, 49, 4526–4530. (c) S. Pramanik, P. Ghorai, *Org. Lett.* **2014**, 16, 2104–2107.

⁹ M. Maddani, K. R. Prabhu, *Tetrahedron Lett.* **2008**, 49, 4526–4530.

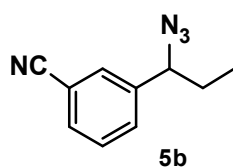
¹⁰ (a) S. Giovani, R. Singh, R. Fasan, *Chem. Sci.* **2016**, 7, 234–239. (b) H. P. Zhang, Y. Z. Dai, L. M. Tao, *J. Chem. Res.* **2011**, 35, 720–722. (c) S. Pramanik, P. Ghorai, *Org. Lett.* **2014**, 16, 2104–2107.

**3-nitrobenzyl azide¹¹**

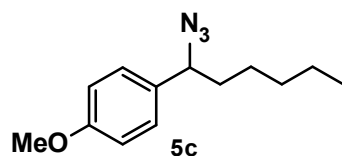
Yellow oil

¹H NMR: (300 MHz, CDCl₃) δ = 8.22–8.12 (m, 2 Ar-H), 7.69–7.63 (m, 1 Ar-H), 7.60–7.52 (m, 1 Ar-H), 4.49 (s, 2 H) ppm.¹³C NMR: (75 MHz, CDCl₃) δ = 148.47 (C), 137.74 (C), 133.96 (CH), 129.92 (CH), 123.17 (CH), 122.81 (CH), 53.72 (CH₂-N₃) ppm.**(1-azidoethyl)benzene¹²**

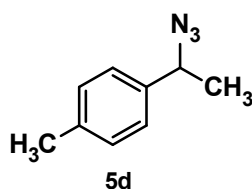
Slightly yellow oil

¹H NMR: (300 MHz, CDCl₃) δ = 7.38–7.28 (m, 5 Ar-H), 4.59 (q, *J* = 6.8 Hz, 2 H), 1.51 (d, *J* = 6.8 Hz, 6H).¹³C NMR: (75 MHz, CDCl₃) δ = 140.90 (C), 128.79 (2 CH), 128.15 (CH), 126.40 (2 CH), 61.12 (CH-N₃), 21.59 (Me) ppm.**3-(1-azidopropyl)benzonitrile**

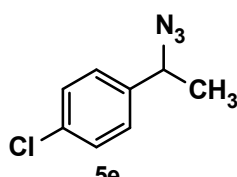
Yellow oil

¹H NMR: (300 MHz, CDCl₃) δ = 7.65–7.41 (m, 4 Ar-H), 4.41 (t, *J* = 7.0 Hz, 1 H), 1.96–1.68 (m, 2 H), 0.92 (td, *J* = 7.4, 1.2 Hz, 3 H) ppm.¹³C NMR: (75 MHz, CDCl₃) δ = 141.51 (C), 131.73 (CH), 131.30 (CH), 130.47 (CH), 129.64 (CH), 118.50 (C≡N), 112.94 (C), 66.74 (CH-N₃), 29.45 (CH₂), 10.39 (CH₃) ppm.HRMS (ESI): calcd. for C₁₀H₁₀N₄ [M+H]⁺: 187.3564; found: 187.3537.**1-(1-azidohexyl)-4-methoxybenzene¹³**

Yellow oil

¹H NMR: (300 MHz, CDCl₃) δ = 7.27–7.16 (m, 2 Ar-H), 6.97–6.83 (m, 2 Ar-H), 4.34 (t, *J* = 7.3 Hz, 1 H), 3.79 (s, 3 H), 1.91–1.63 (m, 2 H), 1.46–1.18 (m, 6 H), 0.98–0.75 (m, 3H) ppm.¹³C NMR: (75 MHz, CDCl₃) δ = 159.36 (C), 131.87 (C), 128.04 (2 CH), 113.99 (2 CH), 65.92 (CH-N₃), 55.13 (OMe), 35.95 (CH₂), 31.37 (CH₂), 25.92 (CH₂), 22.42 (CH₂), 13.89 (Me) ppm.**1-(1-azidoethyl)-4-methylbenzene¹⁴**

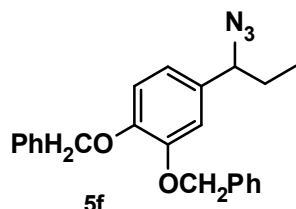
Yellow oil

¹H NMR: (300 MHz, CDCl₃) δ = 7.30–7.08 (m, 4 Ar-H), 4.57 (q, *J* = 6.8 Hz, 1 H), 2.35 (s, 3 H), 1.51 (d, *J* = 6.9 Hz, 3 H) ppm.¹³C NMR: (75 MHz, CDCl₃) δ = 137.88 (C), 137.86 (C), 129.42 (2 CH), 126.33 (2 CH), 60.94 (CH-N₃), 21.51 (Me), 21.10 (Ar-Me) ppm.**1-(1-azidoethyl)-4-chlorobenzene¹⁵**

Yellow oil

¹H NMR: (300 MHz, CDCl₃) δ = 7.36–7.29 (m, 2 Ar-H), 7.28–7.21 (m, 2 Ar-H), 4.57 (q, *J* = 6.8 Hz, 1 H), 1.48 (d, *J* = 6.8 Hz, 3 H) ppm.¹³C NMR: (75 MHz, CDCl₃) δ = 139.46 (C), 133.87 (C-Cl), 128.94 (2¹¹ M. Maddani, K. R. Prabhu, *Tetrahedron Lett.* **2008**, *49*, 4526–4530. (c) S. Pramanik, P. Ghorai, *Org. Lett.* **2014**, *16*, 2104–2107.¹² (a) K. Alagiri, K. R. Prabhu, *Tetrahedron* **2011**, *67*, 8544–8551. (b) M. Maddani, K. R. Prabhu, *Tetrahedron Lett.* **2008**, *49*, 4526–4530.¹³ J. Tummatorn et al. *Synthesis* **2015**, *47*, 323–329¹⁴ K. Alagiri, K. R. Prabhu, *Tetrahedron* **2011**, *67*, 8544–8551.¹⁵ J. Tummatorn et al. *Synthesis* **2015**, *47*, 323–329

CH), 127.76 (2 CH), 60.38 (CH-N₃), 21.55 (Me) ppm.



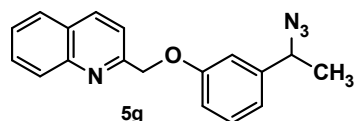
(4-(1-azidopropyl)-1,2-phenylene)bis(oxy)bis(methylene)dibenzene

Yellow oil

¹H NMR: (300 MHz, CDCl₃) δ = 7.47–7.19 (m, 10 Ar-H), 6.91–6.71 (m, 3 Ar-H), 5.12 (s, 2 H), 5.09 (s, 2 H), 4.18 (t, *J* = 7.2 Hz, 1 H), 1.87–1.55 (m, 2 H), 0.83 (t, *J* = 7.4 Hz, 3 H) ppm.

¹³C NMR: (75 MHz, CDCl₃) δ = 148.97 (2 C), 137.17 (C), 137.08 (C), 132.80 (C), 128.43 (2 CH), 128.41 (2 CH), 127.79 (CH), 127.76 (CH), 127.41 (2 CH), 127.23 (2 CH), 120.26 (CH), 114.73 (CH), 113.97 (CH), 71.44 (Ph-CH₂), 71.19 (Ph-CH₂), 67.49 (CH-N₃), 29.12 (CH₂), 10.68 (Me) ppm.

HRMS (ESI): calcd. for C₂₃H₂₃N₃O₂ [M+H]⁺: 374.2159; found: 374.2136



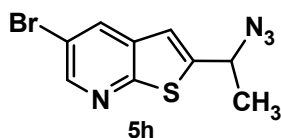
2-((3-(1-azidoethyl)phenoxy)methyl)quinoline

Yellow oil

¹H NMR: (300 MHz, CDCl₃) δ = 8.15–7.98 (m, 2 Ar-H), 7.73–7.50 (m, 3 Ar-H), 7.47–7.35 (m, 1 Ar-H), 7.15–7.06 (m, 2 Ar-H), 7.04–7.00 (m, 1 Ar-H), 6.95–6.88 (m, 1 Ar-H), 5.33 (s, 2 H), 4.45 (q, *J* = 6.8 Hz, 1 H), 1.39 (d, *J* = 6.8 Hz, 3 H) ppm.

¹³C NMR: (75 MHz, CDCl₃) δ = 158.68 (C), 157.50 (C), 147.32 (C), 142.58 (C), 137.07 (CH), 129.87 (CH), 129.79 (CH), 129.38 (CH), 127.69 (CH), 127.51 (C), 126.51 (CH), 125.62 (CH), 119.13 (CH), 115.64 (CH), 113.18 (CH), 71.06 (CH₂), 60.75 (CH-N₃), 21.37 (Me) ppm.

HRMS (ESI): calcd. for C₁₈H₁₆N₄O [M+H]⁺: 305.4267; found: 305.4248



2-(1-azidoethyl)-5-bromothieno[2,3-*b*]pyridine

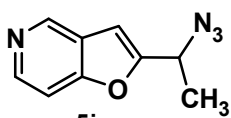
White solid

m.p. 65–67 °C

¹H NMR: (300 MHz, CDCl₃) δ = 8.50 (d, *J* = 2.1 Hz, 1 Ar-H), 8.03 (d, *J* = 2.2 Hz, 1 Ar-H), 7.03 (d, *J* = 1.1 Hz, 1 Ar-H), 4.84 (q, *J* = 6.8 Hz, 1 H), 1.63 (d, *J* = 6.8 Hz, 3 H) ppm.

¹³C NMR: (75 MHz, CDCl₃) δ = 159.33 (C), 147.71 (C), 147.39 (CH), 133.96 (C), 132.99 (CH), 117.72 (CH), 116.77 (C), 57.08 (CH-N₃), 21.37 (Me) ppm.

HRMS (ESI): calcd. for C₉H₇BrN₄S [M+H]⁺: 284.6538; found: 284.6517.



2-(1-azidoethyl)furo[3,2-*c*]pyridine¹⁶

Brown oil

¹H NMR: (300 MHz, CDCl₃) δ = 8.90 (s, 1 Ar-H), 8.50 (d, *J* = 5.8 Hz, 1 Ar-H), 7.43 (d, *J* = 5.8 Hz, 1 Ar-H), 6.74 (s, 1 Ar-H), 4.72 (q, *J* = 6.9

Hz, 1 H), 1.67 (d, $J=6.9$ Hz, 3 H) ppm.

^{13}C NMR: (75 MHz, CDCl_3) $\delta = 158.31$ (C), 147.24 (CH), 144.73 (CH), 141.02 (C), 125.68 (C), 107.14 (CH), 103.54 (CH), 54.71 (C–N₃), 13.92 (Me) ppm.



(1-azido-2-methylpropyl)benzene

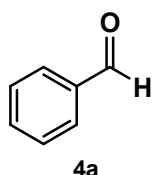
Colorless oil

^1H NMR: (300 MHz, CDCl_3) $\delta = 7.42$ – 7.18 (m, 5 Ar-H), 4.12 (d, $J=8.0$ Hz, 1 H), 1.97 (tt, $J=14.7, 7.5$ Hz, 1 H), 1.01 (d, $J=6.6$ Hz, 3 H), 0.79 (d, $J=6.7$ Hz, 3 H) ppm.

^{13}C NMR: (75 MHz, CDCl_3) $\delta = 138.94$ (C), 128.53 (2 CH), 128.01 (C), 127.43 (2 CH), 73.20 (C–N₃), 34.02 (C), 19.49 (Me), 19.19 (Me) ppm.

HRMS (ESI): calcd. for $\text{C}_{10}\text{H}_{13}\text{N}_3$ $[\text{M}+\text{H}]^+$: 176.7584; found: 176.7564.

1.2. PRODUCTS (CARBONYL COMPOUNDS)

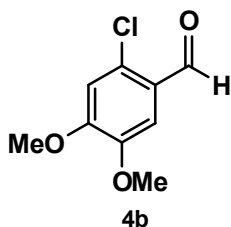


Benzaldehyde¹⁷

yellowish liquid

^1H NMR: (300 MHz, CDCl_3) $\delta = 10.00$ (s, 1 H), 7.93–7.83 (m, 2 Ar-H), 7.66–7.41 (m, 3 Ar-H) ppm.

^{13}C NMR: (75 MHz, CDCl_3) $\delta = 192.45$ (C=O), 136.38 (C), 134.47 (CH), 129.73 (2 CH), 128.99 (2 CH), ppm.



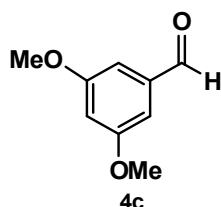
2-Chloroveratraldehyde¹⁸

White solid

m.p. 70–73 °C

^1H NMR: (300 MHz, CDCl_3) $\delta = 9.85$ (s, 1 H), 7.51 (d, $J=1.9$ Hz, 1 Ar-H), 7.36 (d, $J=1.8$ Hz, 1 Ar-H), 3.97 (s, 3 H), 3.94 (s, 3 H) ppm.

^{13}C NMR: (75 MHz, CDCl_3) $\delta = 190.06$ (C=O), 154.33 (C), 150.76 (C), 132.41 (C), 128.88 (C), 125.85 (CH), 109.37 (CH), 60.98 (OMe), 56.28 (OMe) ppm.



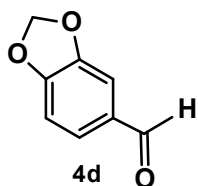
3,5-dimethoxybenzaldehyde¹⁹

Slightly yellow crystals

46–49 °C

^1H NMR: (300 MHz, CDCl_3) $\delta = 9.91$ (s, 1 H), 7.02 (d, $J=2.4$ Hz, 2 Ar-H), 6.71 (t, $J=2.3$ Hz, 1 Ar-H), 3.85 (s, 6 H) ppm.

^{13}C NMR: (75 MHz, CDCl_3) $\delta = 191.99$ (C=O), 161.20 (2 C), 138.34 (C), 107.16 (CH), 107.09 (2 CH), 55.63 (2 OMe) ppm.

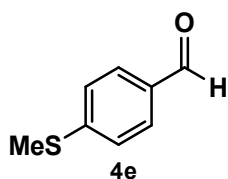
**Piperonal**²⁰

White solid

m.p. 34-38 °C

¹H NMR: (300 MHz, CDCl₃) δ = 9.82 (s, 1 H), 7.42 (dd, *J* = 7.9, 1.6 Hz, 1 Ar-H), 7.34 (d, *J* = 1.6 Hz, 1 Ar-H), 6.94 (d, *J* = 8.0 Hz, 1 Ar-H), 6.08 (s, 2 H) ppm.

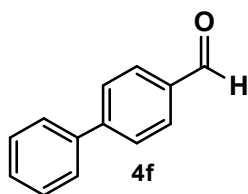
¹³C NMR: (75 MHz, CDCl₃) δ = 190.26 (C=O), 153.10 (C), 148.71 (C), 131.90 (C), 128.63 (CH), 108.35 (CH), 106.94 (CH), 102.09 (CH₂) ppm.

**4-(methylthio)benzaldehyde**²¹

yellowish liquid

¹H NMR: (300 MHz, CDCl₃) δ = 9.90 (s, 1 H), 7.75 (dd, *J* = 8.5, 2.2 Hz, 2 Ar-H), 7.30 (dd, *J* = 8.5, 2.2 Hz, 2 Ar-H), 2.51 (s, 3 H) ppm.

¹³C NMR: (75 MHz, CDCl₃) δ = 191.18 (C=O), 147.89 (C), 132.86 (C), 129.93 (2 CH), 125.10 (2 CH), 14.60 (Me) ppm

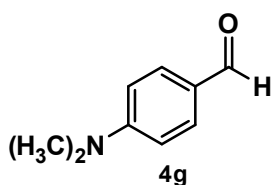
**4-Phenylbenzaldehyde**²²

Slightly yellow crystals

m.p. 58-60 °C

¹H NMR: (300 MHz, CDCl₃) δ = 10.04 (s, 1 H), 7.97–7.90 (m, 2 Ar-H), 7.78–7.69 (m, 2 Ar-H), 7.66–7.58 (m, 2 Ar-H), 7.52–7.36 (m, 3 Ar-H) ppm.

¹³C NMR: (75 MHz, CDCl₃) δ = 191.89 (C=O), 147.13 (C), 139.66 (C), 135.16 (C), 130.24 (2 CH), 128.99 (2 CH), 128.45 (CH), 127.64 (2 CH), 127.33 (2 CH) ppm.

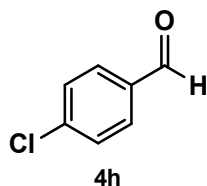
**4-(Dimethylamino)benzaldehyde**²³

Yellow Solid

m.p. 72-74 °C

¹H NMR: (300 MHz, CDCl₃) δ = 9.73 (s, 1 H), 7.77–7.68 (m, 2 Ar-H), 6.73–6.64 (m, 2 Ar-H), 3.07 (s, 6 H) ppm.

¹³C NMR: (75 MHz, CDCl₃) δ = 190.24 (C=O), 154.32 (C), 131.93 (2 CH), 125.10 (C), 110.97 (2 CH), 40.03 (2 CH₃) ppm.

**4-Chlorobenzaldehyde**²⁴

Beige crystals

m.p. 46-49 °C

¹H NMR: (300 MHz, CDCl₃) δ = 9.98 (s, 1 H), 7.88–7.78 (m, 2 Ar-H), 7.56–7.47 (m, 2 Ar-H).

¹³C NMR: (75 MHz, CDCl₃) δ = 190.84 (C=O), 140.88 (C), 134.67 (C), 130.88 (2 CH), 129.41 (2 CH) ppm.

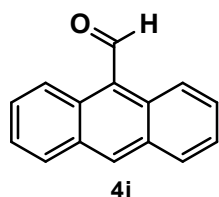
²⁰ S. S. Kulkarni, X. Hu, R. Manetsch, *Chem. Commun.* **2013**, 49, 1193–1195.

²¹ S. S. Kulkarni, X. Hu, R. Manetsch, *Chem. Commun.* **2013**, 49, 1193–1195.

²² (a) S. S. Kulkarni, X. Hu, R. Manetsch, *Chem. Commun.* **2013**, 49, 1193–1195. (b) H. P. Zhang, Y. Z. Dai, L. M. Tao, *J. Chem. Res.* **2011**, 35, 720-722.

²³ (a) S. S. Kulkarni, X. Hu, R. Manetsch, *Chem. Commun.* **2013**, 49, 1193–1195. (b) H. P. Zhang, Y. Z. Dai, L. M. Tao, *J. Chem. Res.* **2011**, 35, 720-722.

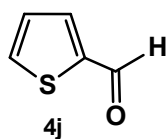
²⁴ (a) S. S. Kulkarni, X. Hu, R. Manetsch, *Chem. Commun.* **2013**, 49, 1193–1195. (b) M. Maddani, K. R. Prabhu, *Tetrahedron Lett.* **2008**, 49, 4526–4530.

**9-Anthracenecarboxaldehyde**²⁵

Yellow Solid
m.p. 102-104 °C

¹H NMR: (300 MHz, CDCl₃) δ = 11.43 (s, 1 H), 8.90 (d, *J* = 9.0 Hz, 2 Ar-H), 8.56 (s, 1 Ar-H), 7.96 (d, *J* = 8.4 Hz, 2 Ar-H), 7.71–7.56 (m, 2 Ar-H), 7.56–7.42 (m, 2 Ar-H) ppm.

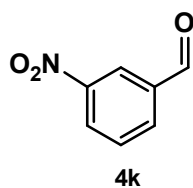
¹³C NMR: (75 MHz, CDCl₃) δ = 192.86 (C=O), 135.11 (CH), 132.01 (2 C), 130.94 (2 C), 129.19 (2 CH), 129.01 (2 CH), 125.58 (2 CH), 124.55 (C), 123.44 (2 CH) ppm.

**2-Thiophenecarboxaldehyde**²⁶

colorless liquid

¹H NMR: (300 MHz, CDCl₃) δ = 9.94 (s, 1 H), 7.81–7.73 (m, 2 Ar-H), 7.24–7.18 (m, 1 Ar-H).

¹³C NMR: (75 MHz, CDCl₃) δ = 182.97 (C=O), 144.08 (C), 136.26 (CH), 135.11 (CH), 128.30 (CH) ppm.

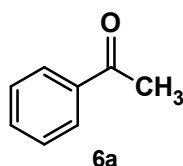
**3-nitrobenzaldehyde**²⁷

Slightly yellow solid

m.p. 55–58 °C

¹H NMR: (300 MHz, CDCl₃) δ = 10.11 (s, 1 H), 8.69 (t, *J* = 1.9 Hz, 1 Ar-H), 8.47 (ddd, *J* = 8.2, 2.3, 1.1 Hz, 1 Ar-H), 8.23 (dt, *J* = 7.7, 1.4 Hz, 1 Ar-H), 7.77 (t, *J* = 7.9 Hz, 1 Ar-H) ppm.

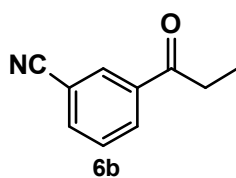
¹³C NMR: (75 MHz, CDCl₃) δ = 189.80 (C=O), 148.78 (C), 137.41 (C), 134.72 (CH), 130.43 (CH), 128.59 (CH), 124.42 (CH) ppm.

**Acetophenone**²⁸

colorless liquid

¹H NMR: (300 MHz, CDCl₃) δ = 7.96–7.89 (m, 2 Ar-H), 7.56–7.48 (m, 1 Ar-H), 7.47–7.37 (m, 2 Ar-H), 2.56 (s, 3 H) ppm.

¹³C NMR: (75 MHz, CDCl₃) δ = 198.05 (C=O), 137.11 (C), 133.07 (CH), 128.55 (2 CH), 128.28 (2 CH), 26.56 (CH₃) ppm.

**3-propionylbenzonitrile**²⁹

slightly pink solid

¹H NMR: (300 MHz, CDCl₃) δ = 8.19 (t, *J* = 1.7 Hz, 1 Ar-H), 8.15 (dt, *J* = 7.9, 1.6 Hz, 1 Ar-H), 7.79 (dt, *J* = 7.7, 1.4 Hz, 1 Ar-H), 7.58 (t, *J* = 7.8 Hz, 1 Ar-H), 2.99 (q, *J* = 7.2 Hz, 2 H), 1.20 (t, *J* = 7.2 Hz, 3 H) ppm.

¹³C NMR: (75 MHz, CDCl₃) δ = 198.59 (C=O), 137.59 (C), 135.80 (CH), 131.95 (CH), 131.69 (CH), 129.69 (CH), 118.02 (C≡N), 113.09 (C), 31.98 (CH₂), 7.93 (CH₃) ppm.

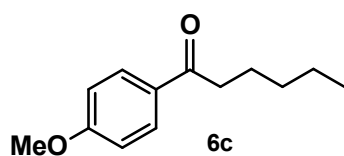
²⁵ M. Maddani, K. R. Prabhu, *Tetrahedron Lett.* **2008**, *49*, 4526–4530.

²⁶ (a) S. Giovani, R. Singh, R. Fasan, *Chem. Sci.* **2016**, *7*, 234–239. (b) H. P. Zhang, Y. Z. Dai, L. M. Tao, *J. Chem. Res.* **2011**, *35*, 720–722.

²⁷ M. Maddani, K. R. Prabhu, *Tetrahedron Lett.* **2008**, *49*, 4526–4530.

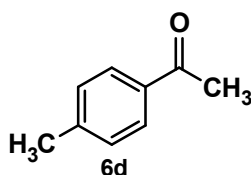
²⁸ (a) K. Alagiri, K. R. Prabhu, *Tetrahedron* **2011**, *67*, 8544–8551. (b) M. Maddani, K. R. Prabhu, *Tetrahedron Lett.* **2008**, *49*, 4526–4530.

²⁹ S. Thaisrivongs, K. D. Watenpaugh, W. J. Howe, P. K. Tomich, L. A. Dolak, K. T. Chong, C. S. C. Tomich, A. G. Tomasselli, S. R. Turner, *J. Med. Chem.* **1995**, *38*, 3624–3637.

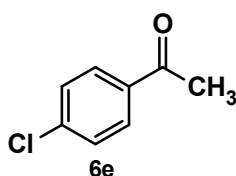
**1-(4-methoxyphenyl)hexan-1-one**³⁰

Colorless crystals

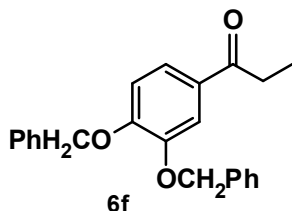
m.p. 30-33 °C

¹H NMR: (300 MHz, CDCl₃) δ = 7.95–7.87 (m, 2 Ar-H), 6.93–6.85 (m, 2 Ar-H), 3.82 (s, 3 H), 2.86 (t, *J* = 7.4 Hz, 2 H), 1.69 (p, *J* = 7.3 Hz, 2 H), 1.34 (dd, *J* = 7.3, 3.6 Hz, 4 H), 0.93–0.82 (m, 3 H) ppm.¹³C NMR: (75 MHz, CDCl₃) δ = 199.06 (C=O), 163.27 (C), 130.23 (2 CH), 130.16 (C), 113.61 (2 CH), 55.35 (OCH₃), 38.19 (CH₂), 31.58 (CH₂), 24.28 (CH₂), 22.52 (CH₂), 13.92 (CH₃) ppm.**4'-Methylacetophenone**³¹

colorless liquid

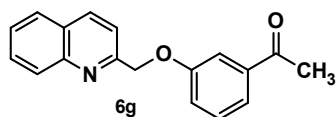
¹H NMR: (300 MHz, CDCl₃) δ = 7.86 (d, *J* = 8.2 Hz, 2 Ar-H), 7.25 (d, *J* = 7.9 Hz, 2 Ar-H), 2.56 (s, 3 H), 2.41 (s, 3 H) ppm.¹³C NMR: (75 MHz, CDCl₃) δ = 197.61 (C=O), 143.78 (C), 134.71 (C), 129.21 (2 CH), 128.41 (2 CH), 26.42 (CH₃), 21.55 (CH₃) ppm.**4'-Chloroacetophenone**³²

colorless liquid

¹H NMR: (300 MHz, CDCl₃) δ = 7.97–7.77 (m, 2 Ar-H), 7.45–7.31 (m, 2 Ar-H), 2.55 (s, 3 H) ppm.¹³C NMR: (75 MHz, CDCl₃) δ = 196.54 (C=O), 139.36 (C), 135.41 (C), 129.70 (2 CH), 128.78 (2 CH), 26.44 (CH₃) ppm.**1-(3,4-bis(benzyloxy)phenyl)propan-1-one**³³

slightly pink solid

m.p. 52-55 °C

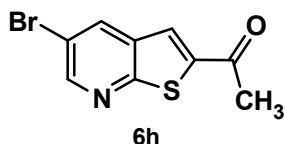
¹H NMR: (300 MHz, CDCl₃) δ = 7.61 (d, *J* = 2.1 Hz, 1 Ar-H), 7.57–7.25 (m, 11 Ar-H), 6.91 (d, *J* = 8.4 Hz, 1 Ar-H), 5.19 (s, 2 H), 5.18 (s, 2 H), 2.87 (q, *J* = 7.3 Hz, 2 H), 1.17 (t, *J* = 7.3 Hz, 3 H) ppm.¹³C NMR: (75 MHz, CDCl₃) δ = 199.34 (C=O), 152.93 (C), 148.54 (C), 136.83 (C), 136.50 (C), 130.42 (C), 128.56 (2 CH), 128.50 (2 CH), 127.97 (CH), 127.90 (CH), 127.37 (2 CH), 127.07 (2 CH), 122.81 (CH), 113.73 (CH), 112.94 (CH), 71.12 (CH₂), 70.76 (CH₂), 31.28 (CH₂), 8.47 (CH₃) ppm.**1-(3-(quinolin-2-ylmethoxy)phenyl)ethanone**³⁴

slightly brown crystals

m.p. 64-67 °C

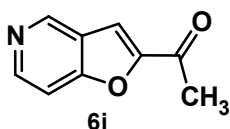
¹H NMR: (300 MHz, CDCl₃) δ = 8.20 (d, *J* = 8.5 Hz, 1 Ar-H), 8.09 (d, *J* = 8.4 Hz, 1 Ar-H), 7.83 (d, *J* = 8.1 Hz, 1 Ar-H), 7.74 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1 Ar-H), 7.70–7.63 (m, 2 Ar-H), 7.60–7.51 (m, 2 Ar-H), 7.37 (t, *J* = 7.9 Hz, 1 Ar-H), 7.23 (ddd, *J* = 8.2, 2.7, 1.0 Hz, 1 Ar-H), 5.43 (s, 2 H), 2.58 (s, 3 H) ppm.¹³C NMR: (75 MHz, CDCl₃) δ = 197.72 (C=O), 158.65 (C), 157.24 (C), 147.61 (C), 138.62 (C), 137.08 (CH), 129.86 (CH), 129.74 (CH), 129.03 (CH), 127.70 (CH), 127.61 (C), 126.63 (CH), 121.38 (CH), 119.83 (CH), 119.15 (CH), 114.28 (CH), 71.51 (CH₂), 26.73 (CH₃) ppm.³⁰ M. M. Dell'Anna, P. Mastrorilli, C. F. Nobile, G. Marchese, M. R. Taurino, *J. Molecular Cat. A: Chemical*, **2000**, 61, 239–243³¹ K. Alagiri, K. R. Prabhu, *Tetrahedron* **2011**, 67, 8544–8551.³² W. A. Herrmann, C. P. Reisinger, M. Spiegler, *J. Organometallic Chem.* **1998**, 557, 93–96³³ A. Guzman, J. M. Muchowski, N. T. Naal, *J. Org. Chem.*, **1981**, 46, 1224–1227.³⁴ J. H. Musser, Aminoguanidine derivatives, US 4889935 A (1989)

ppm.

**1-(5-bromothieno[2,3-b]pyridin-2-yl)ethanone³⁵**

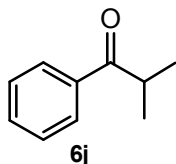
orange solid

m.p. 152-156 °C

¹H NMR: (300 MHz, CDCl₃) δ = 8.72 (d, *J* = 2.2 Hz, 1 Ar-H), 8.30 (d, *J* = 2.2 Hz, 1 Ar-H), 7.80 (s, 1 Ar-H), 2.67 (s, 3 H) ppm.¹³C NMR: (75 MHz, CDCl₃) δ = 191.72 (C=O), 161.34 (C), 150.52 (CH), 145.51 (C), 135.26 (CH), 134.08 (C), 125.55 (CH), 117.15 (C), 26.67 (CH₃) ppm.**1-(furo[3,2-c]pyridin-2-yl)ethanone³⁶**

Brown solid

m.p. 120-123 °C

¹H NMR: (300 MHz, CDCl₃) δ = 9.09 (s, 1 Ar-H), 8.65 (d, *J* = 5.8 Hz, 1 Ar-H), 7.57 (d, *J* = 1.0 Hz, 1 Ar-H), 7.54 (dt, *J* = 5.8, 1.1 Hz, 1 Ar-H), 2.65 (s, 3 H) ppm.¹³C NMR: (75 MHz, CDCl₃) δ = 188.19 (C=O), 159.62 (C), 153.11 (C), 147.43 (CH), 146.81 (CH), 124.48 (C), 110.72 (CH), 107.93 (CH), 26.69 (CH₃) ppm.**Isobutyrophenone³⁷**

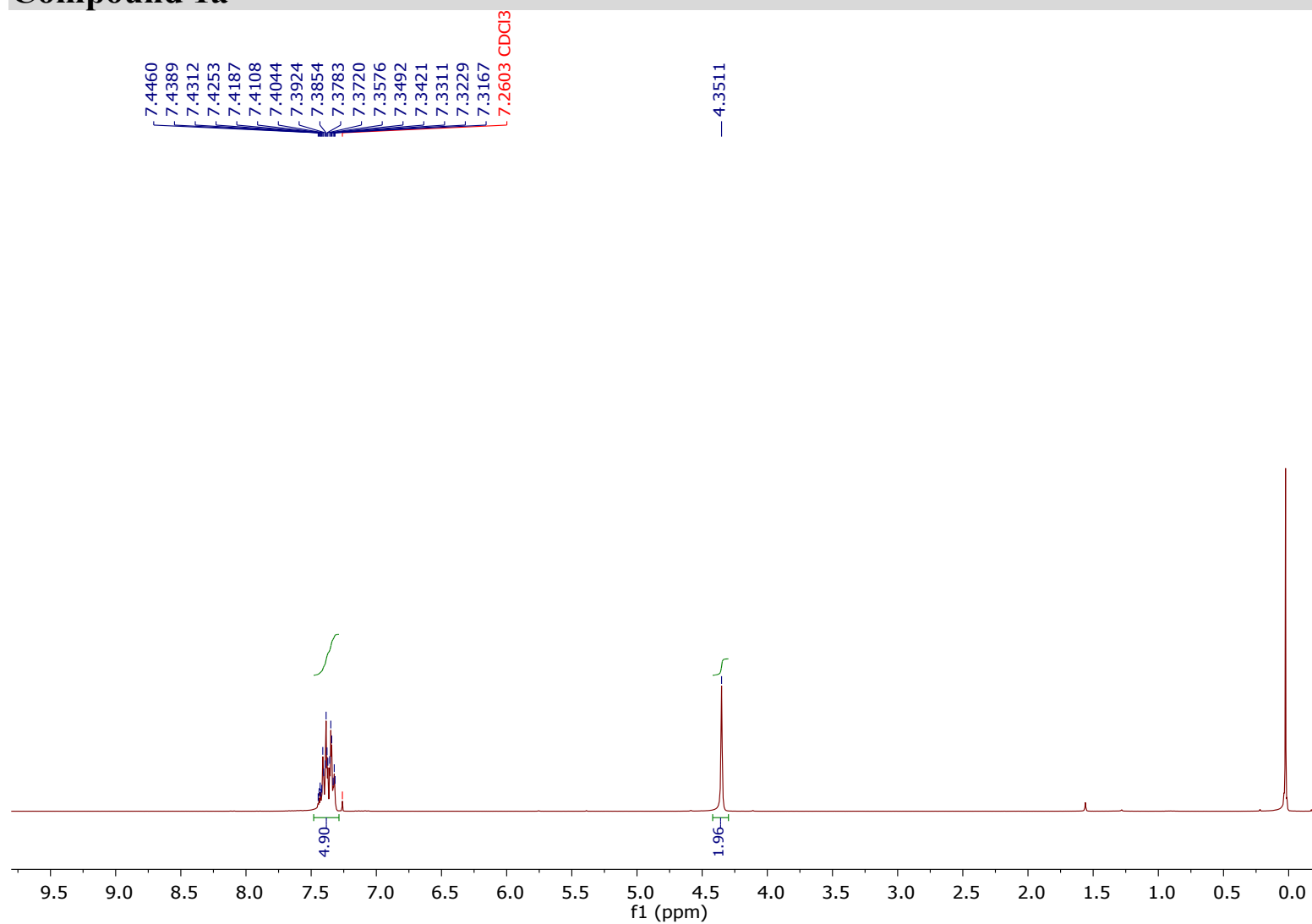
Colorless oil

¹H NMR: (300 MHz, CDCl₃) δ = 7.94 (dd, *J* = 7.0, 1.5 Hz, 2 Ar-H), 7.52 (td, *J* = 7.2, 1.5 Hz, 1 Ar-H), 7.43 (td, *J* = 7.3, 1.4 Hz, 2 Ar-H), 3.54 (dq, *J* = 13.6, 6.8, 1.3 Hz, 1 H), 1.21 (d, *J* = 1.4 Hz, 3 H), 1.18 (d, *J* = 1.5 Hz, 3 H) ppm.¹³C NMR: (75 MHz, CDCl₃) δ = 204.40 (C=O), 136.21 (C), 132.77 (C), 128.59 (2 CH), 128.29 (2 CH), 35.33 (CH), 19.14 (2 Me) ppm.³⁵ Z. An, L. Chen, S. Chen, J. M. Defauw, S. D. Holmstrom, P. Hu, C. Tang, W. Hunter White, W. Wu, Y. Zhang, Dihydroisoxazole compounds, parasiticidal uses and formulations thereof, WO2012155352 A1 (2012).³⁶ A. Thurkauf, D. Chen, A. Phadke, S. Li, M. Deshpande, Azabenzofuran substituted thioureas; inhibitors of viral replication, US 7439374 B2 (2008)³⁷ V. N. Telvekar, K. A. Sasanea, *Synthetic Commun.* 2012, 42, 1325-1329.

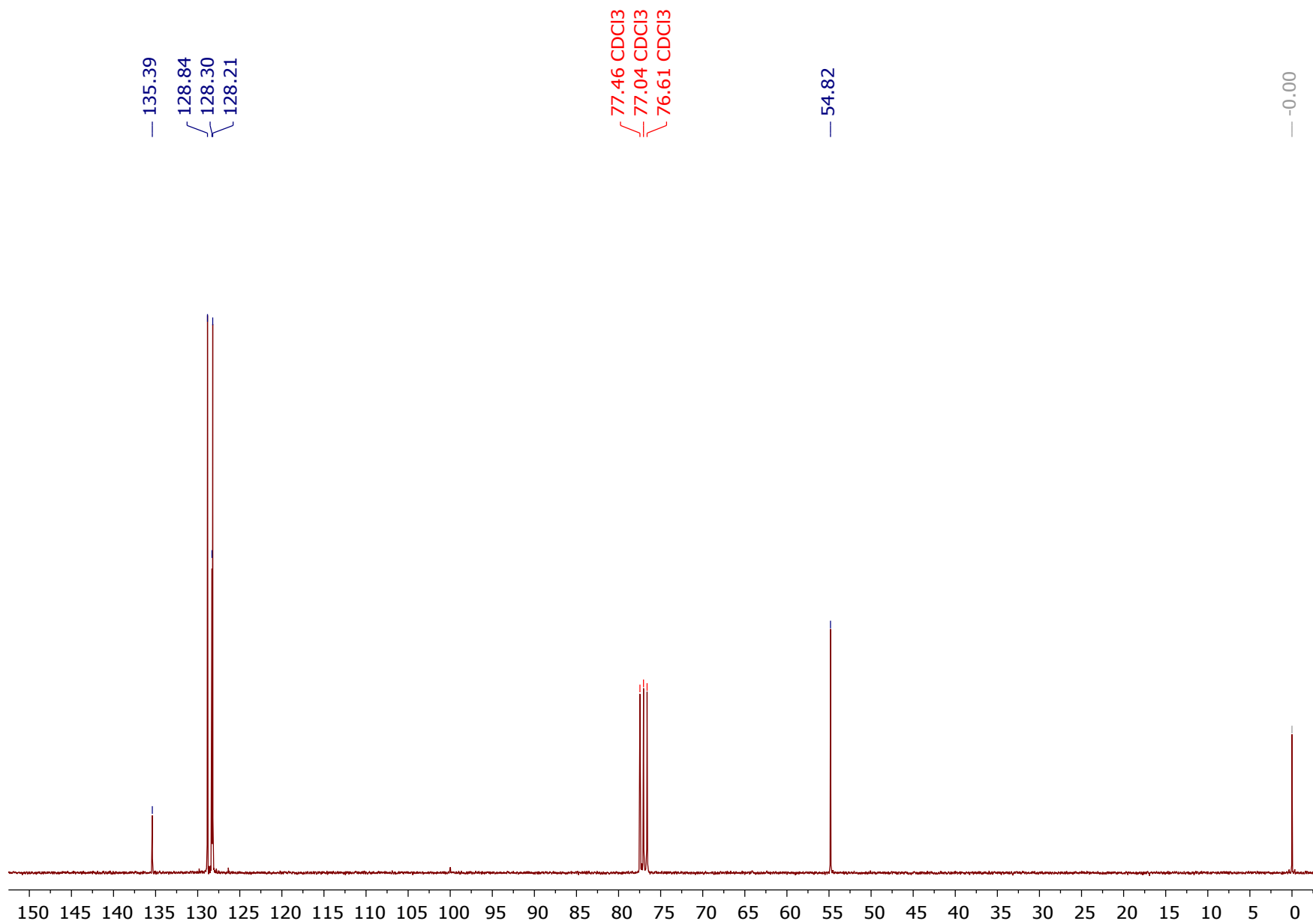
2. COPIES OF ^1H -NMR, AND ^{13}C -NMR OF ALL COMPOUNDS

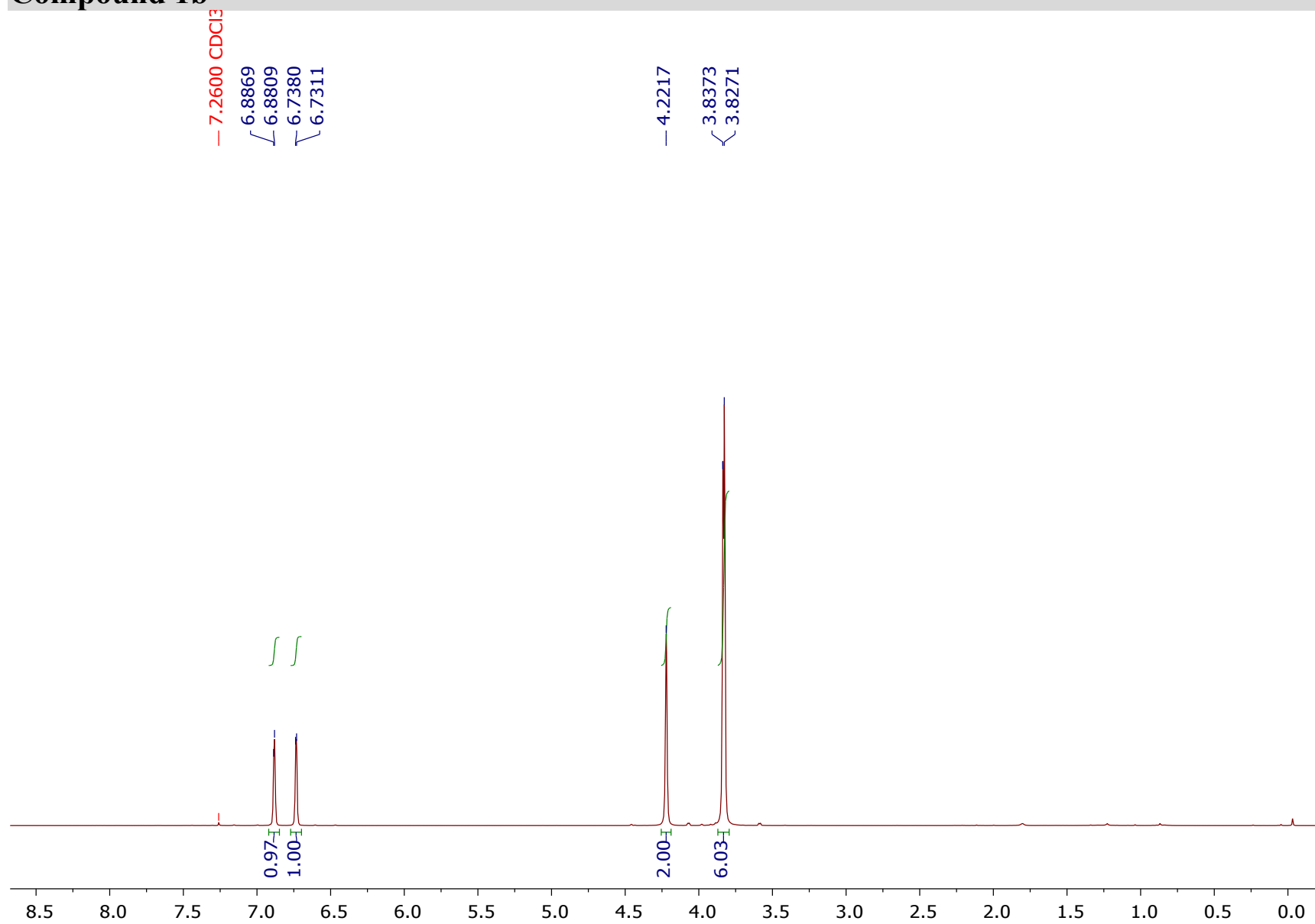
2.1. STARTING MATERIALS (AZIDO COMPOUNDS)

Compound 1a

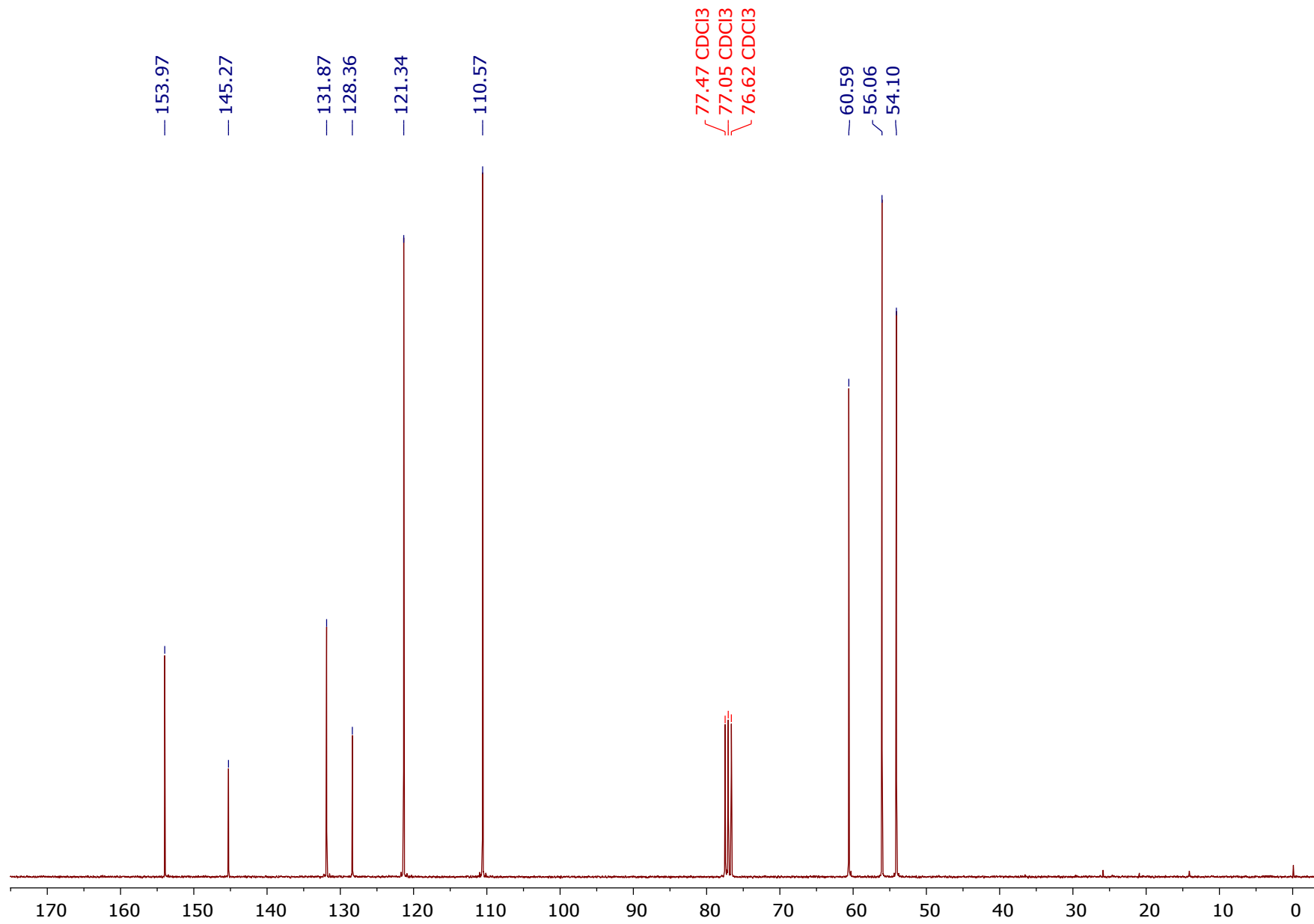


[12]

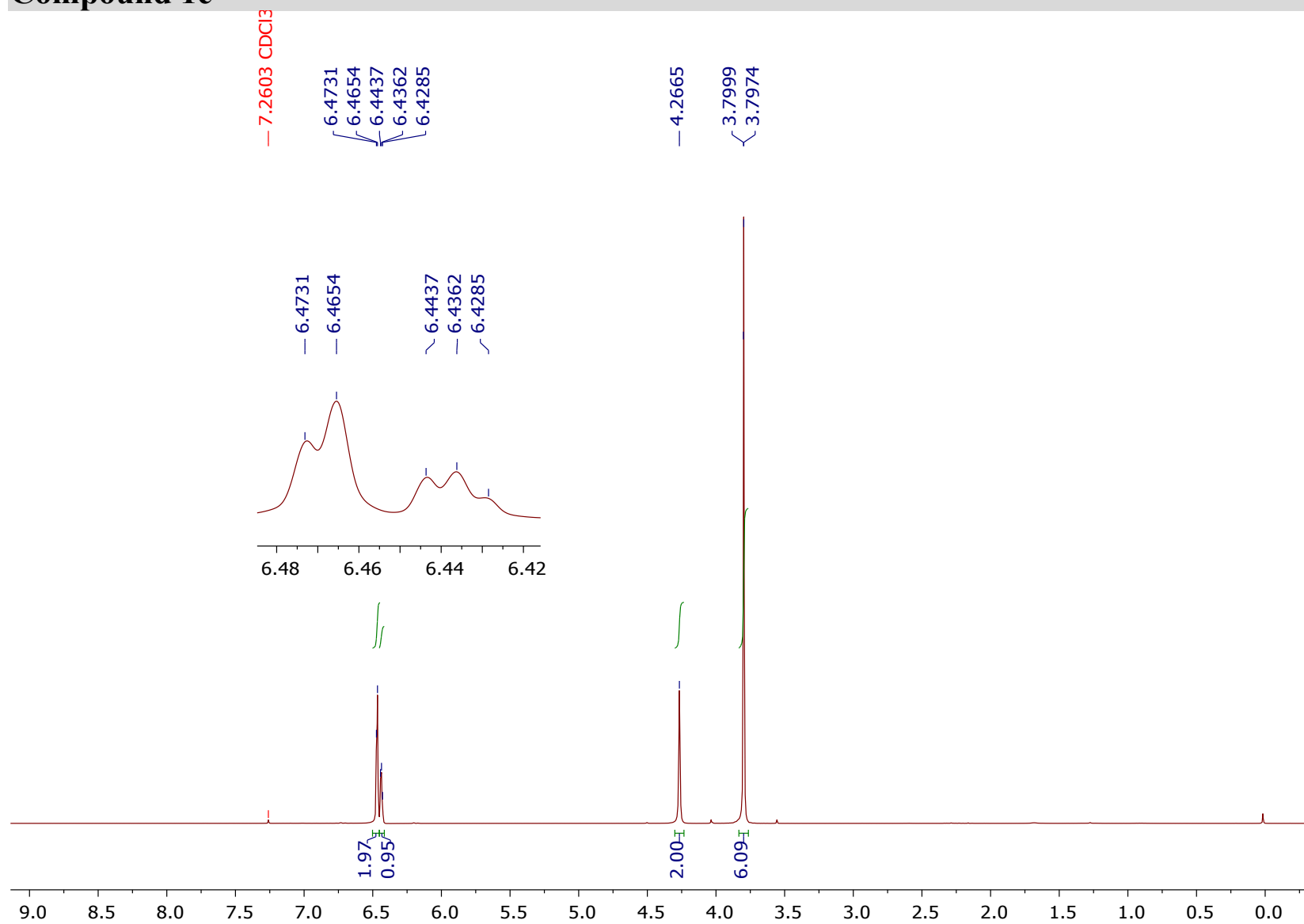


Compound 1b

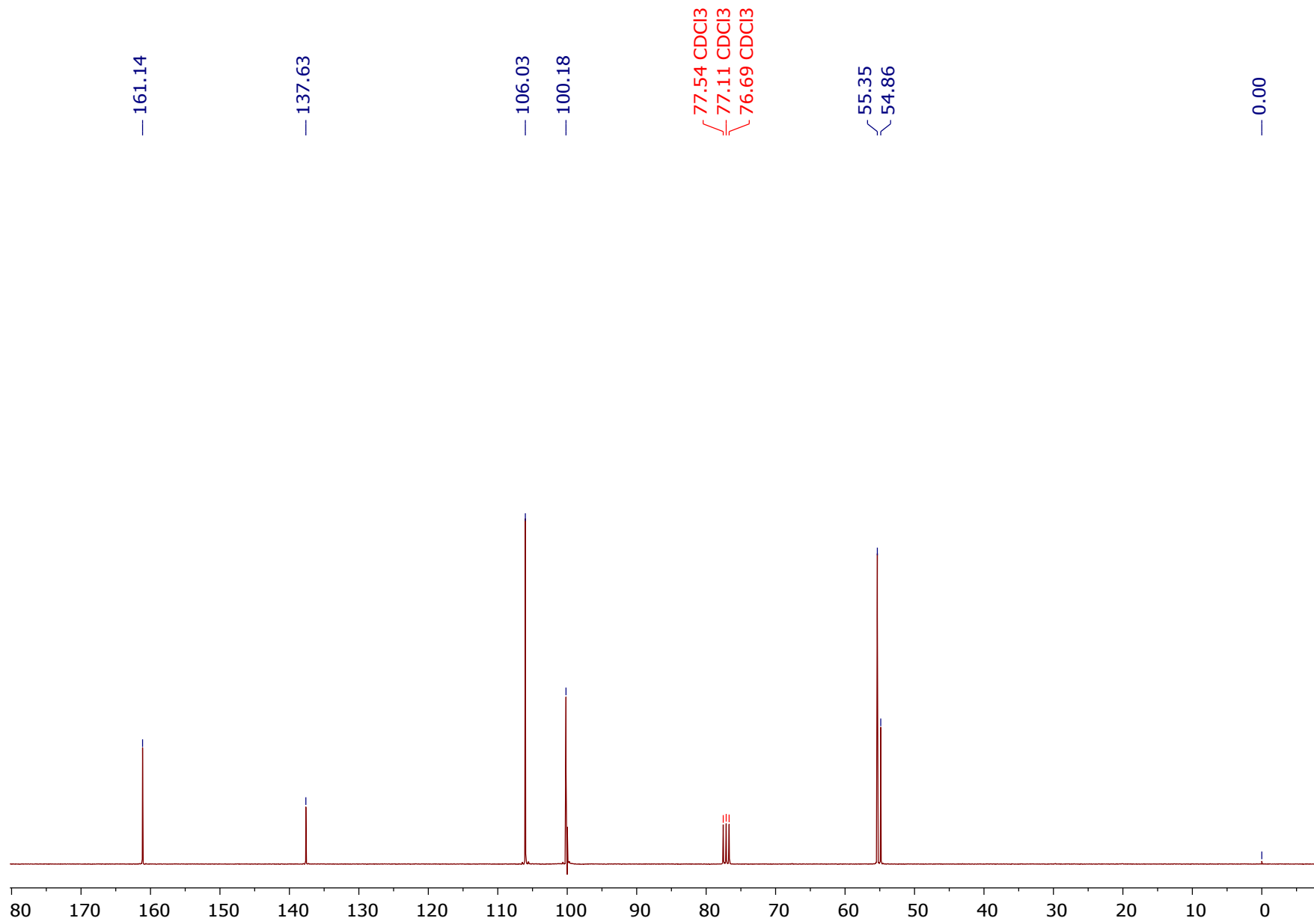
[14]

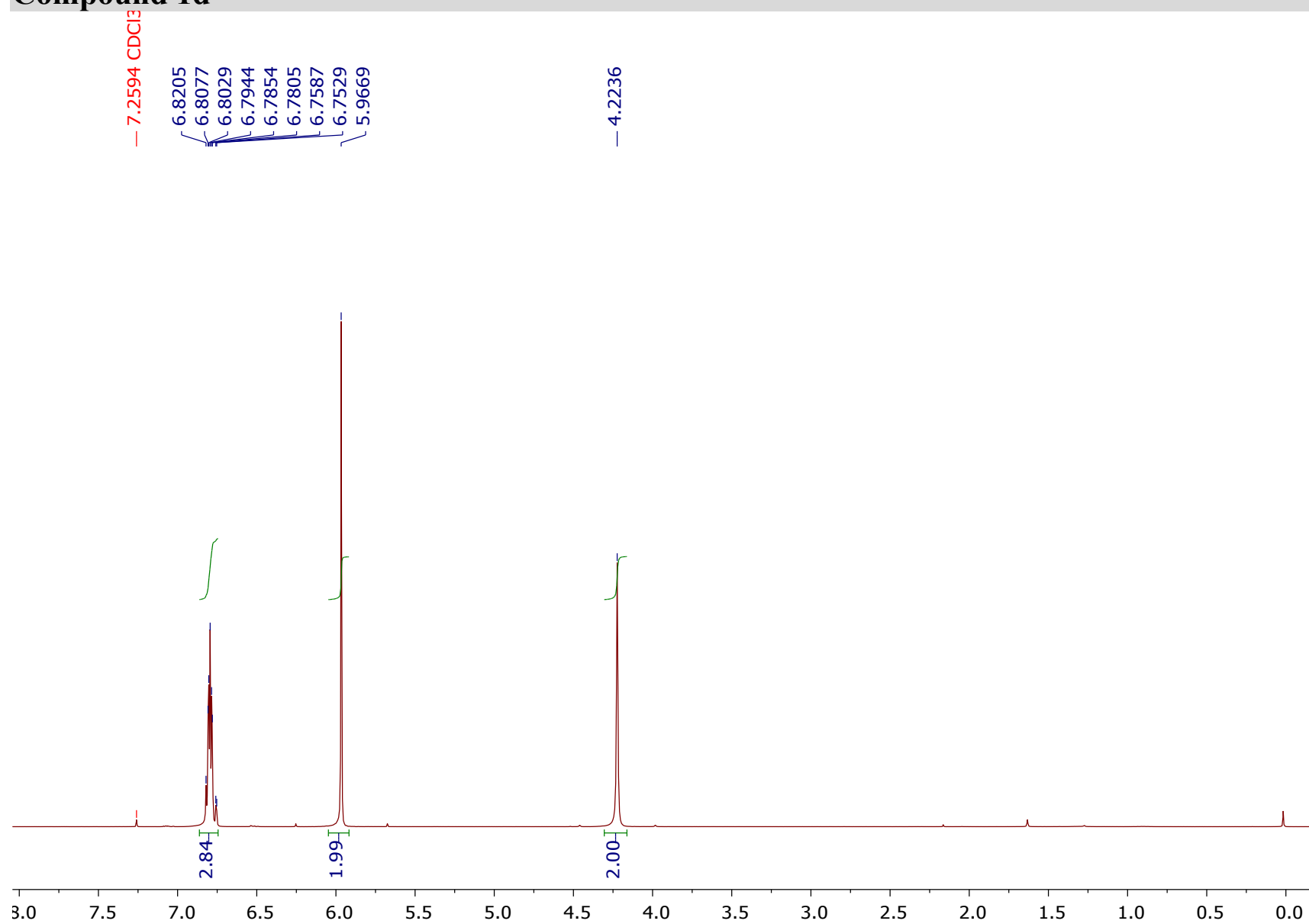


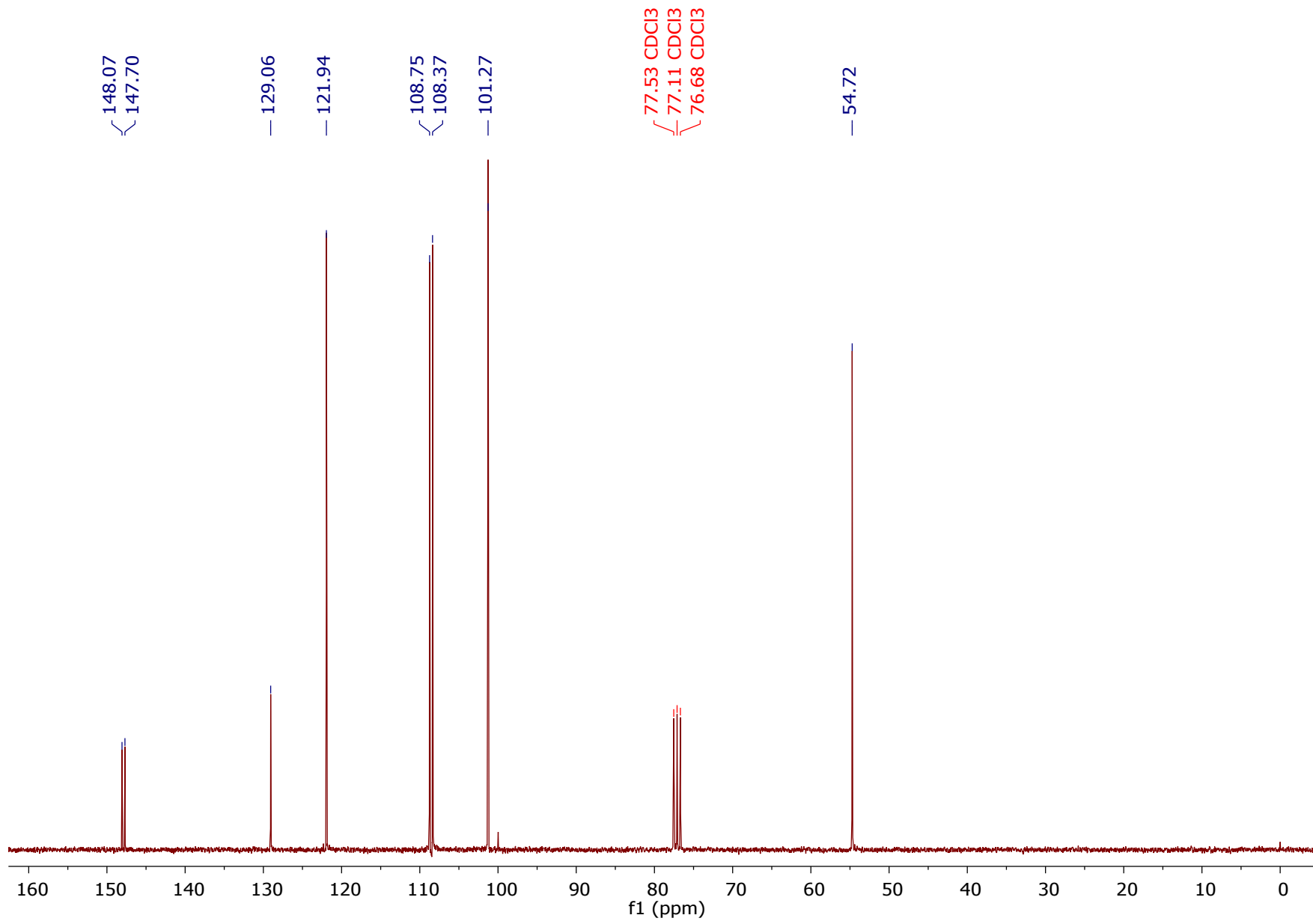
Compound 1c



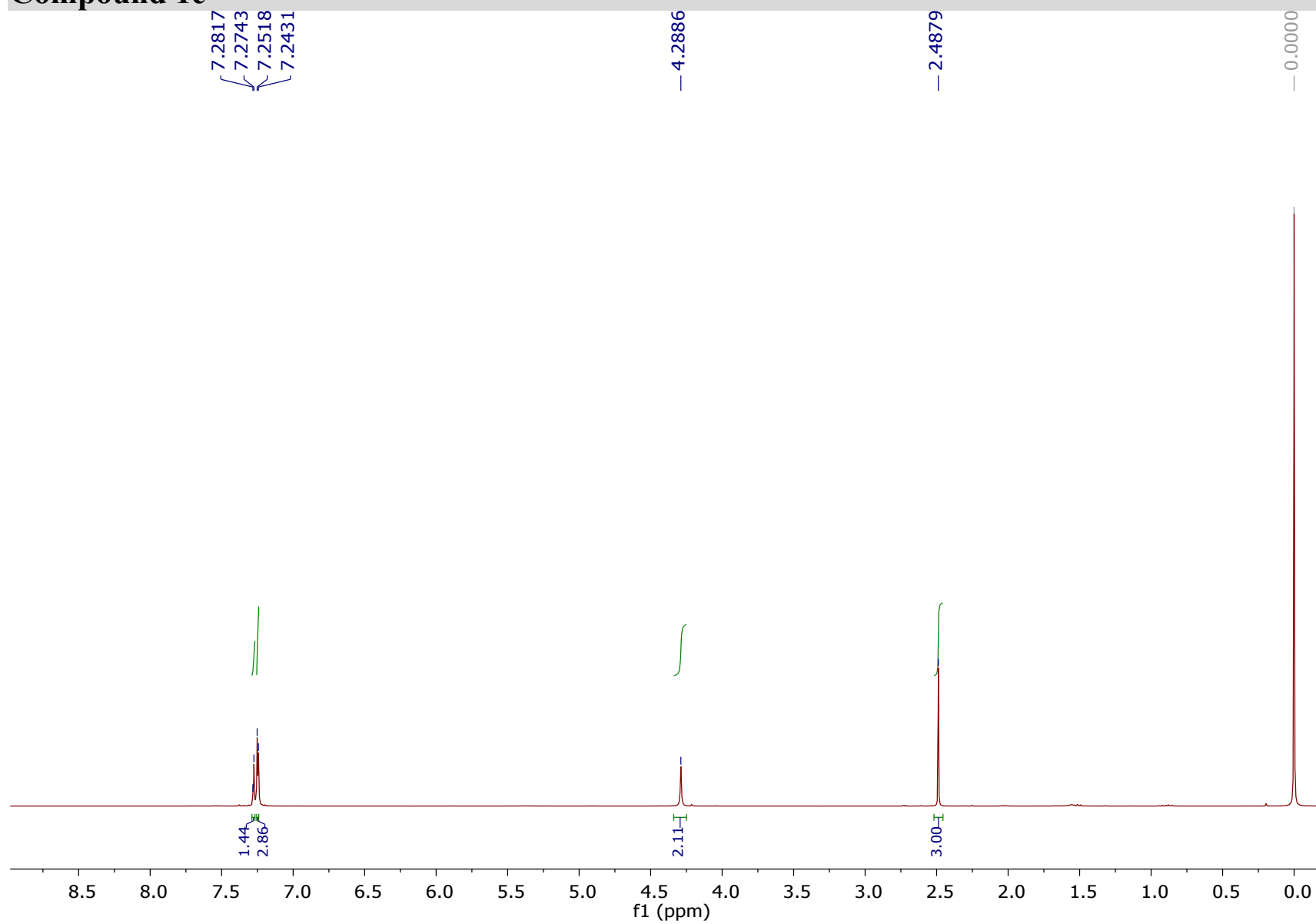
[16]



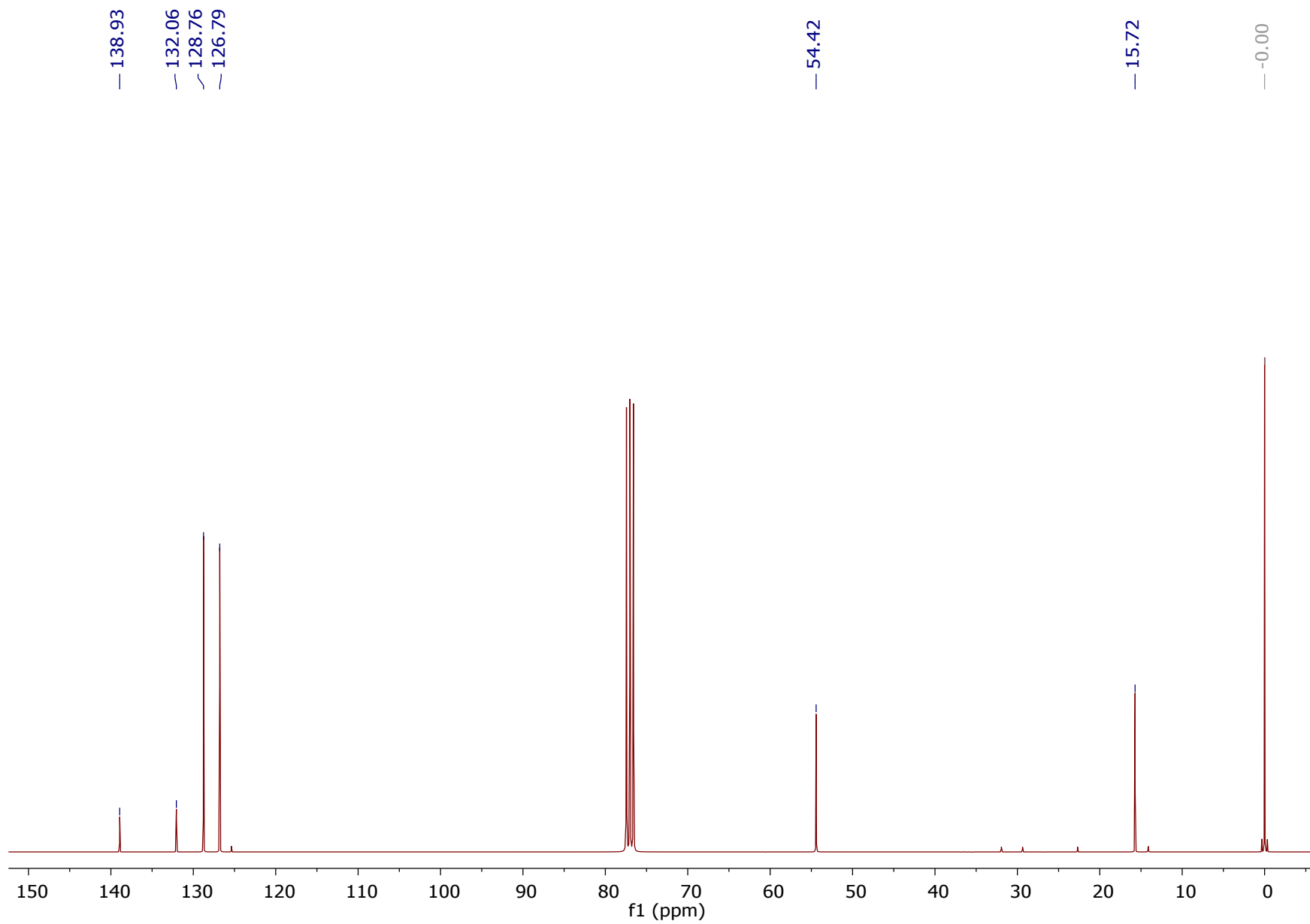
Compound 1d



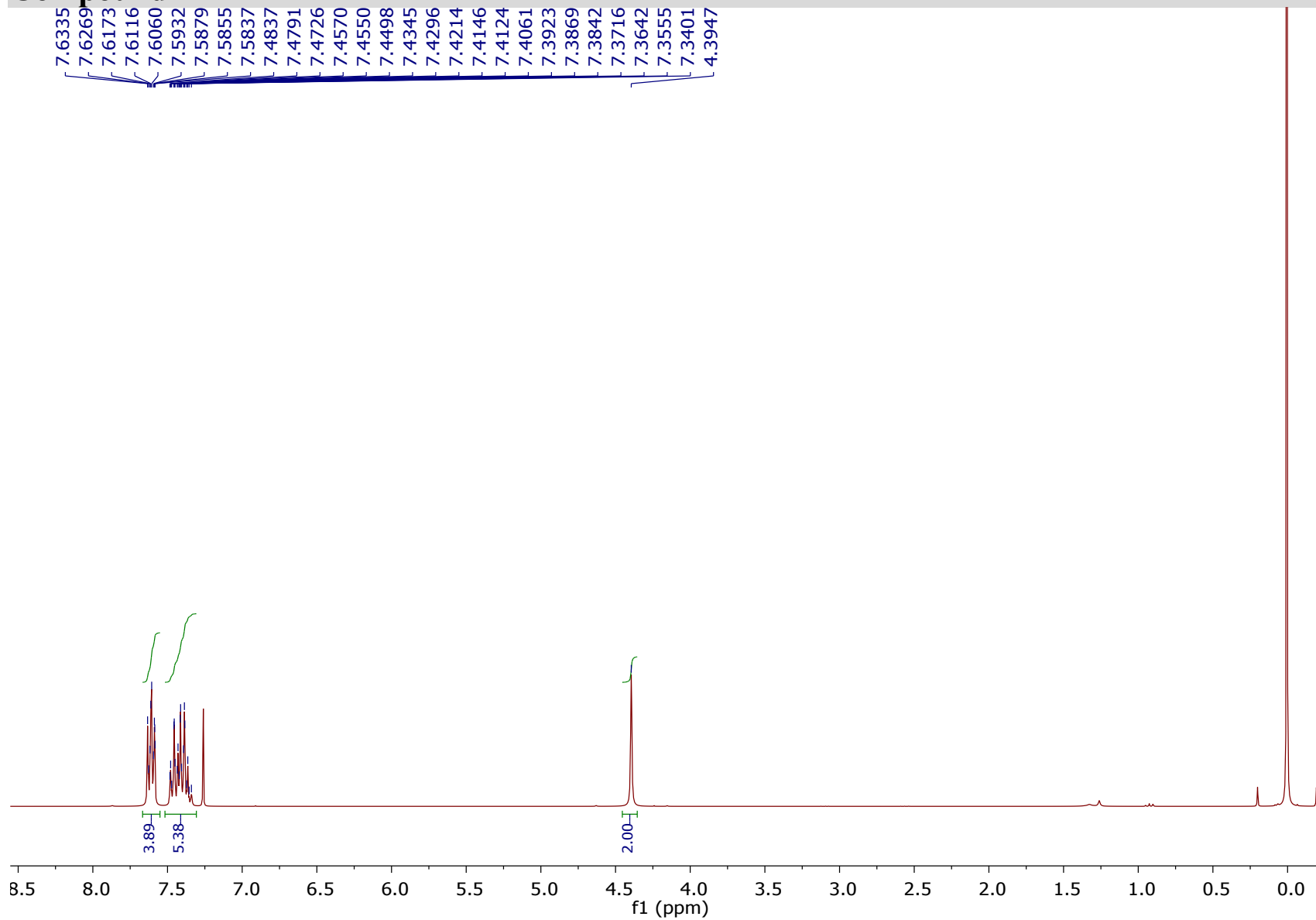
Compound 1e



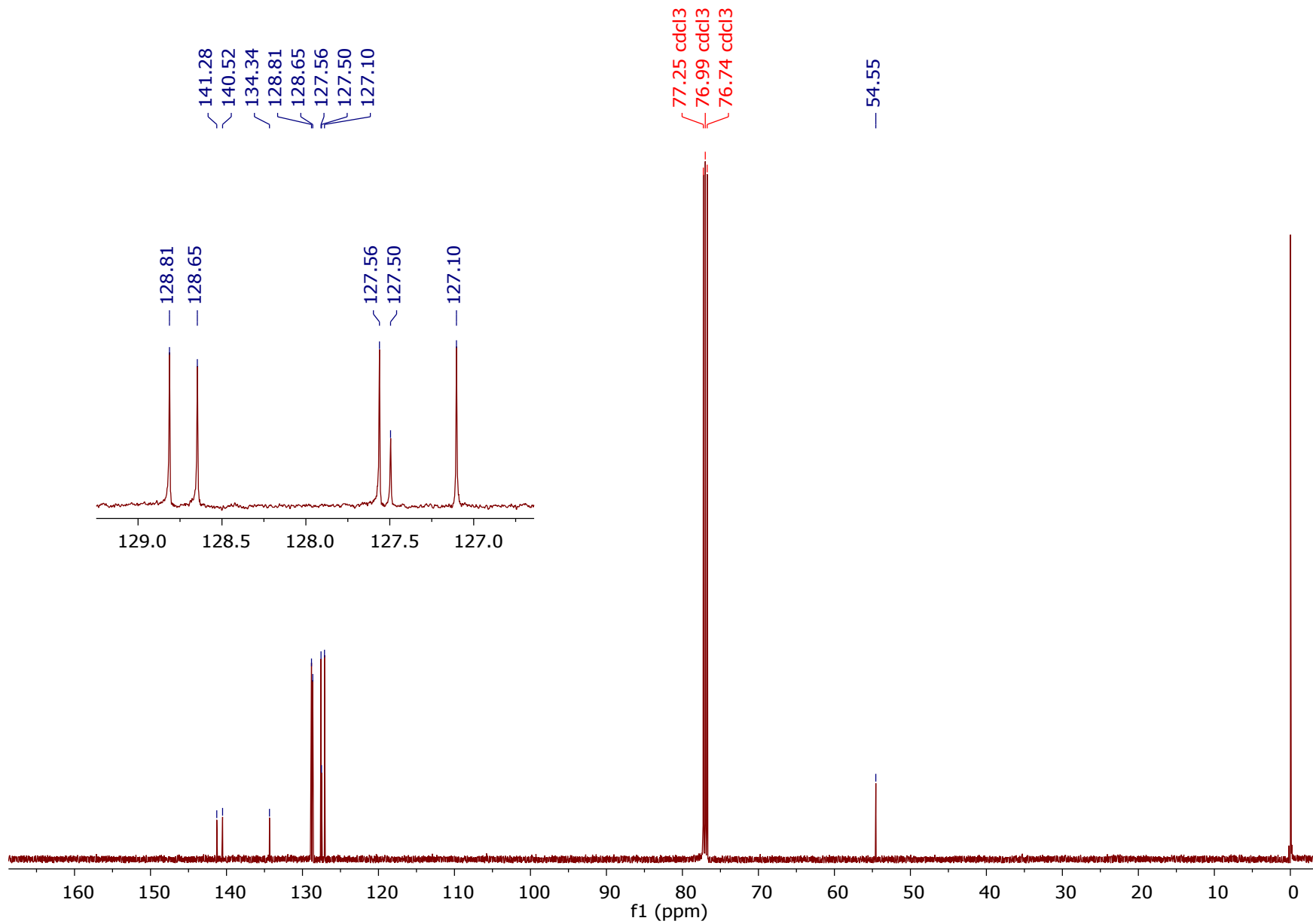
[20]



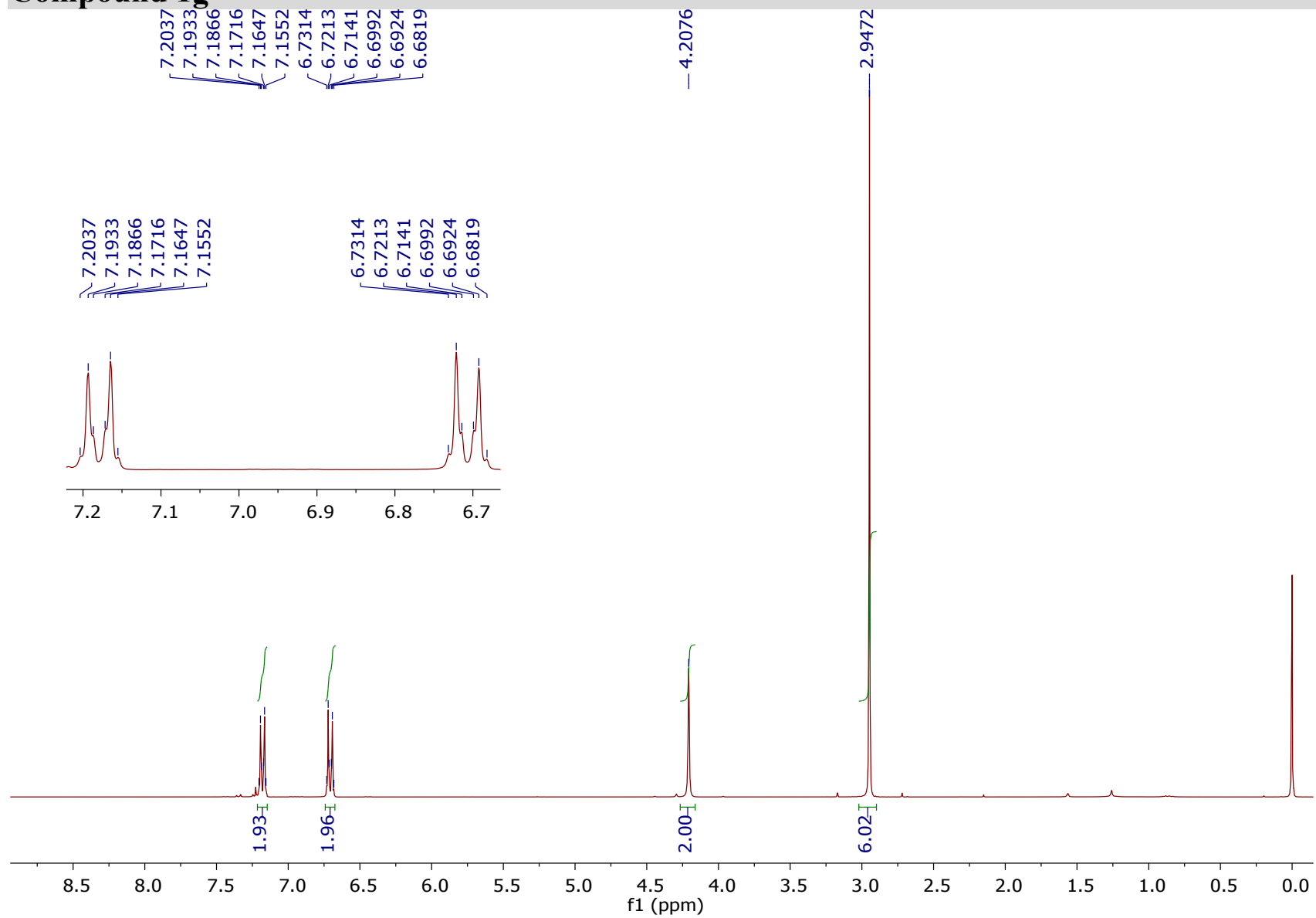
Compound 1f



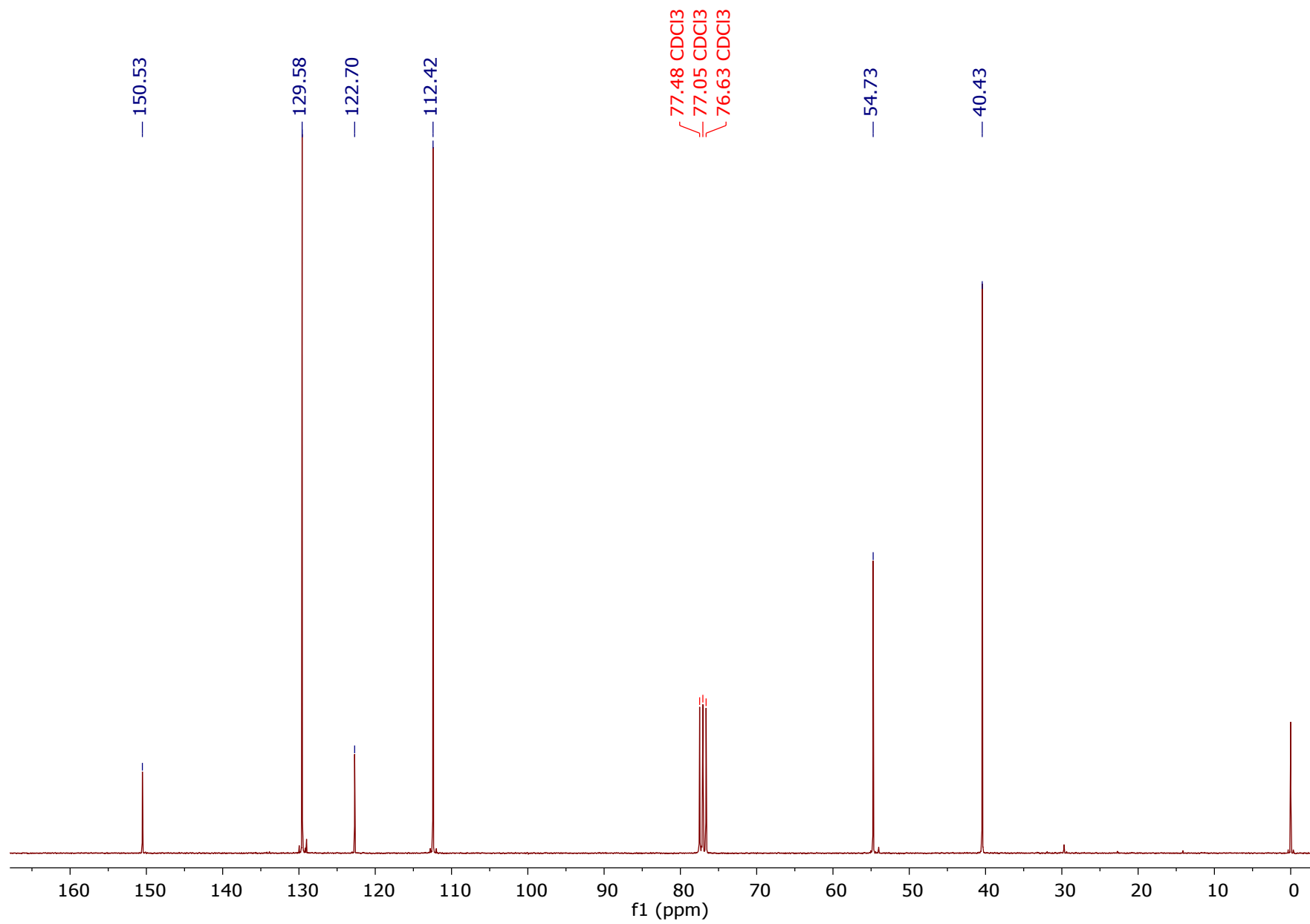
[22]



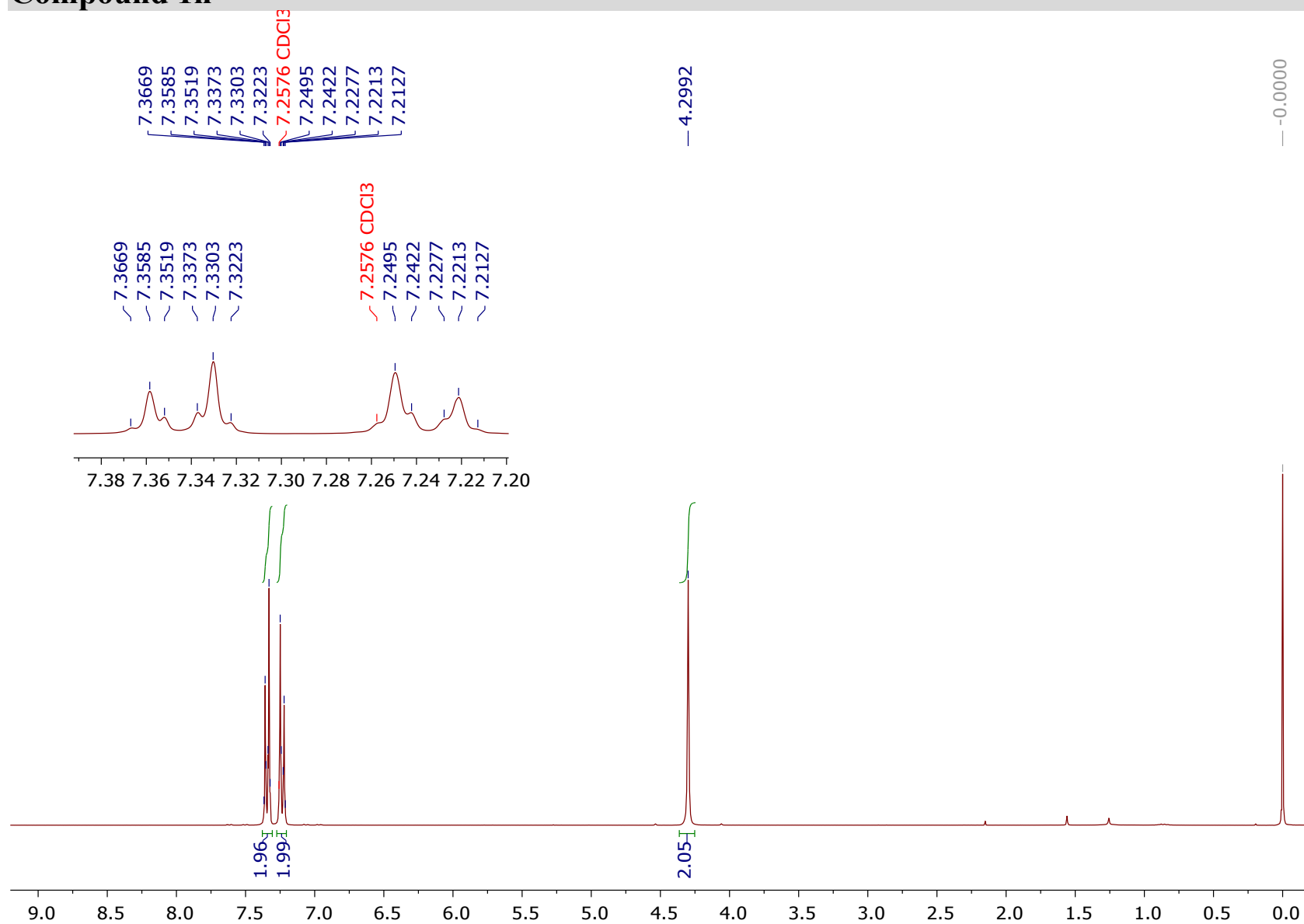
Compound 1g



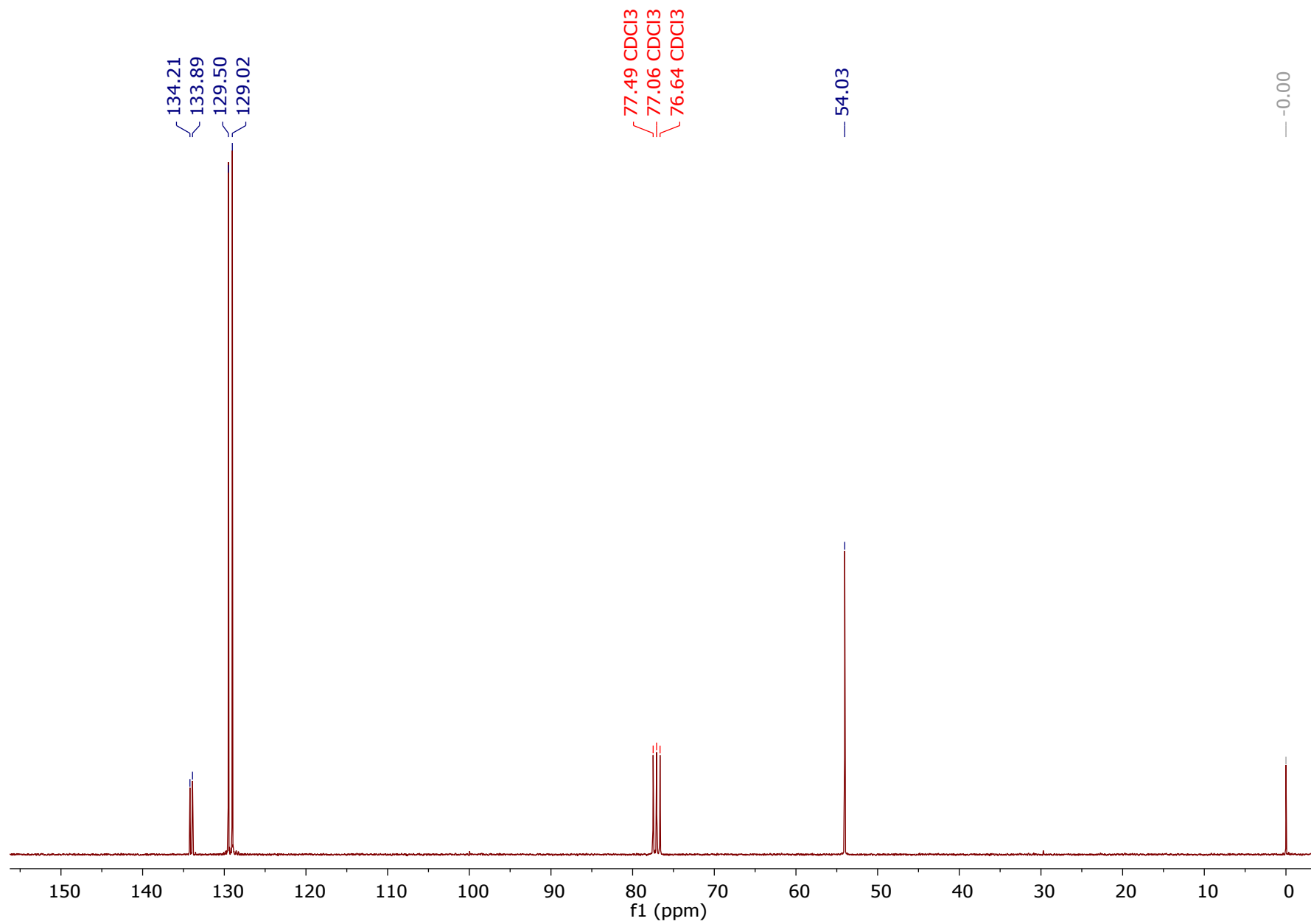
[24]



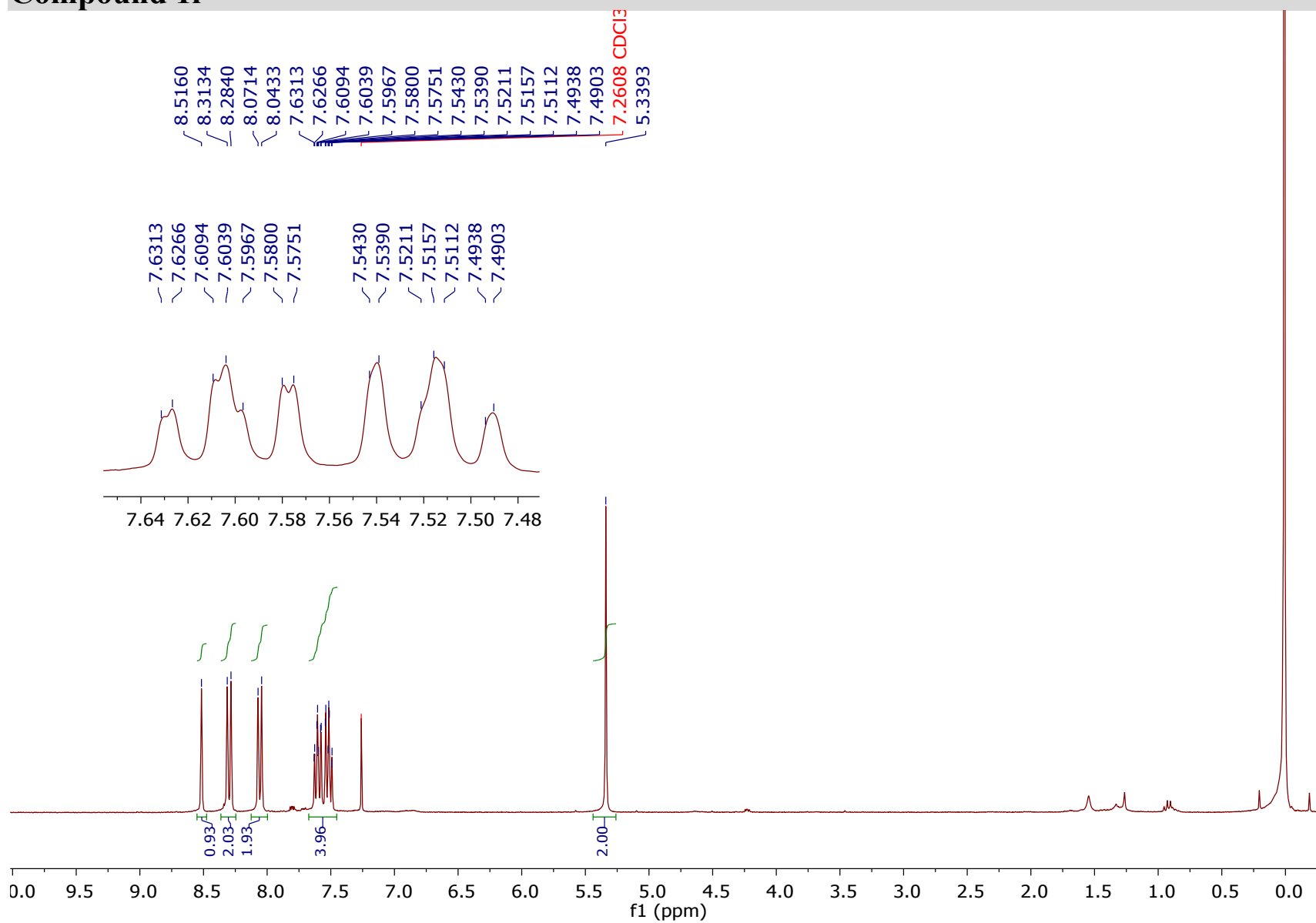
Compound 1h

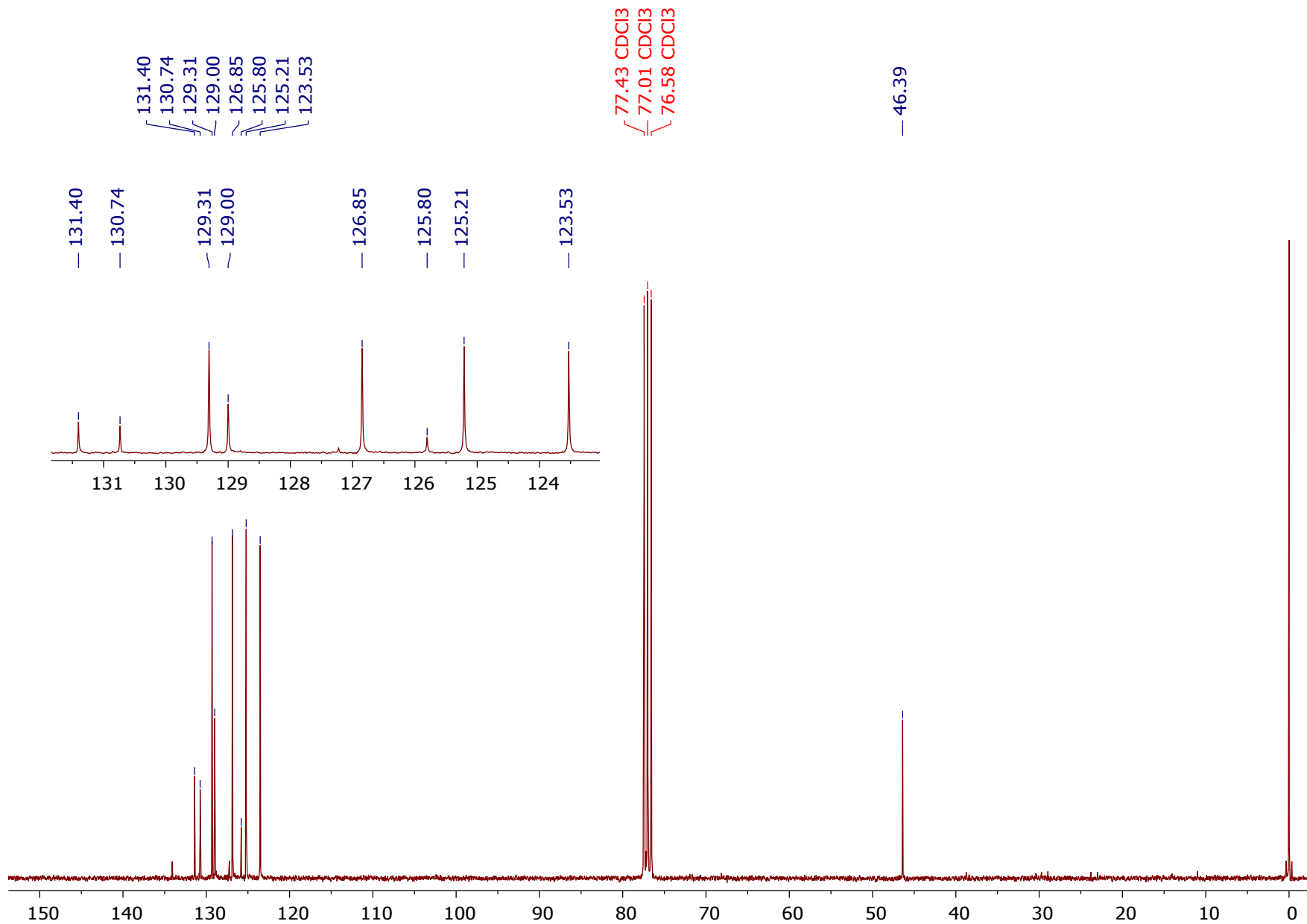


[26]

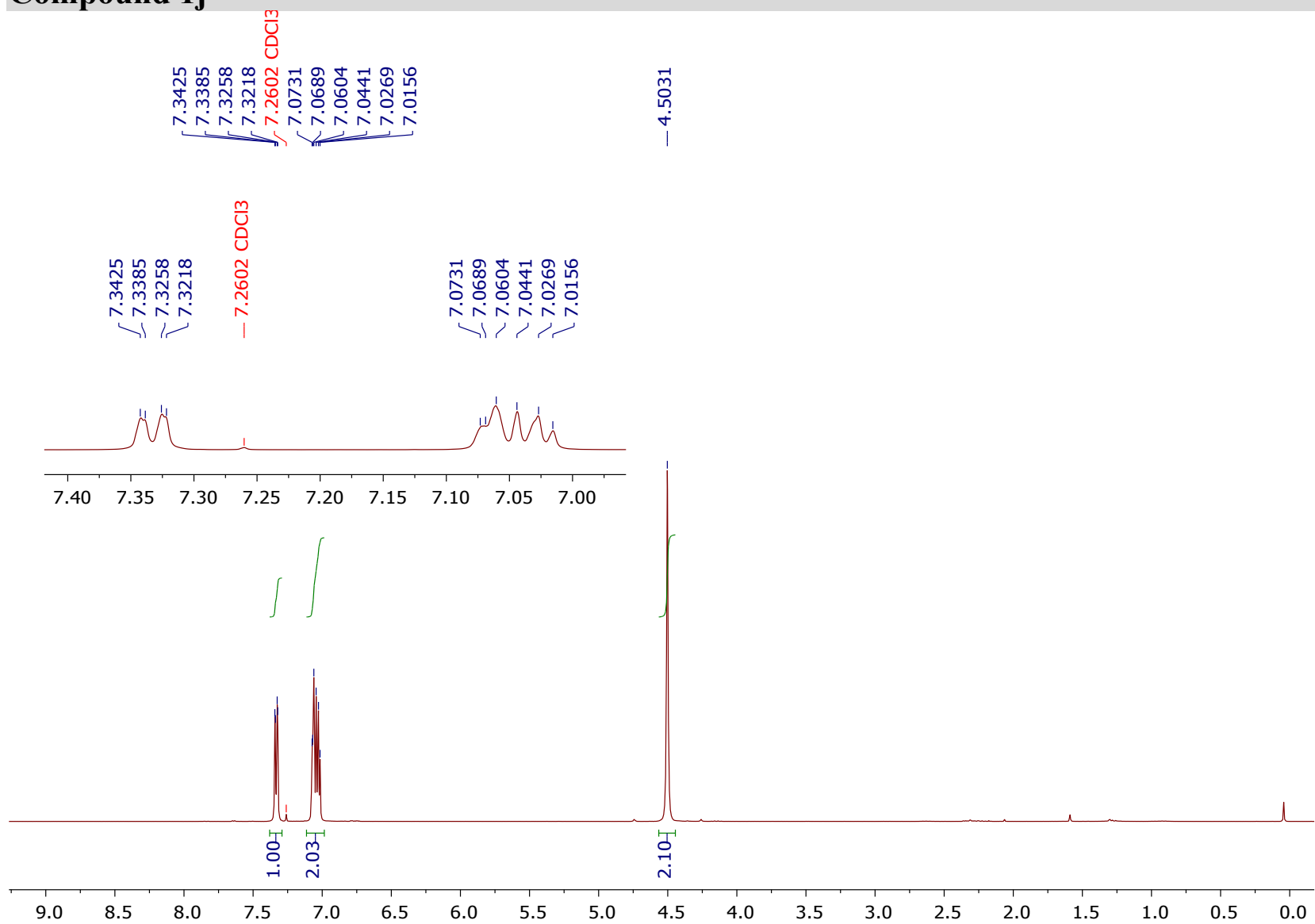


Compound 1i

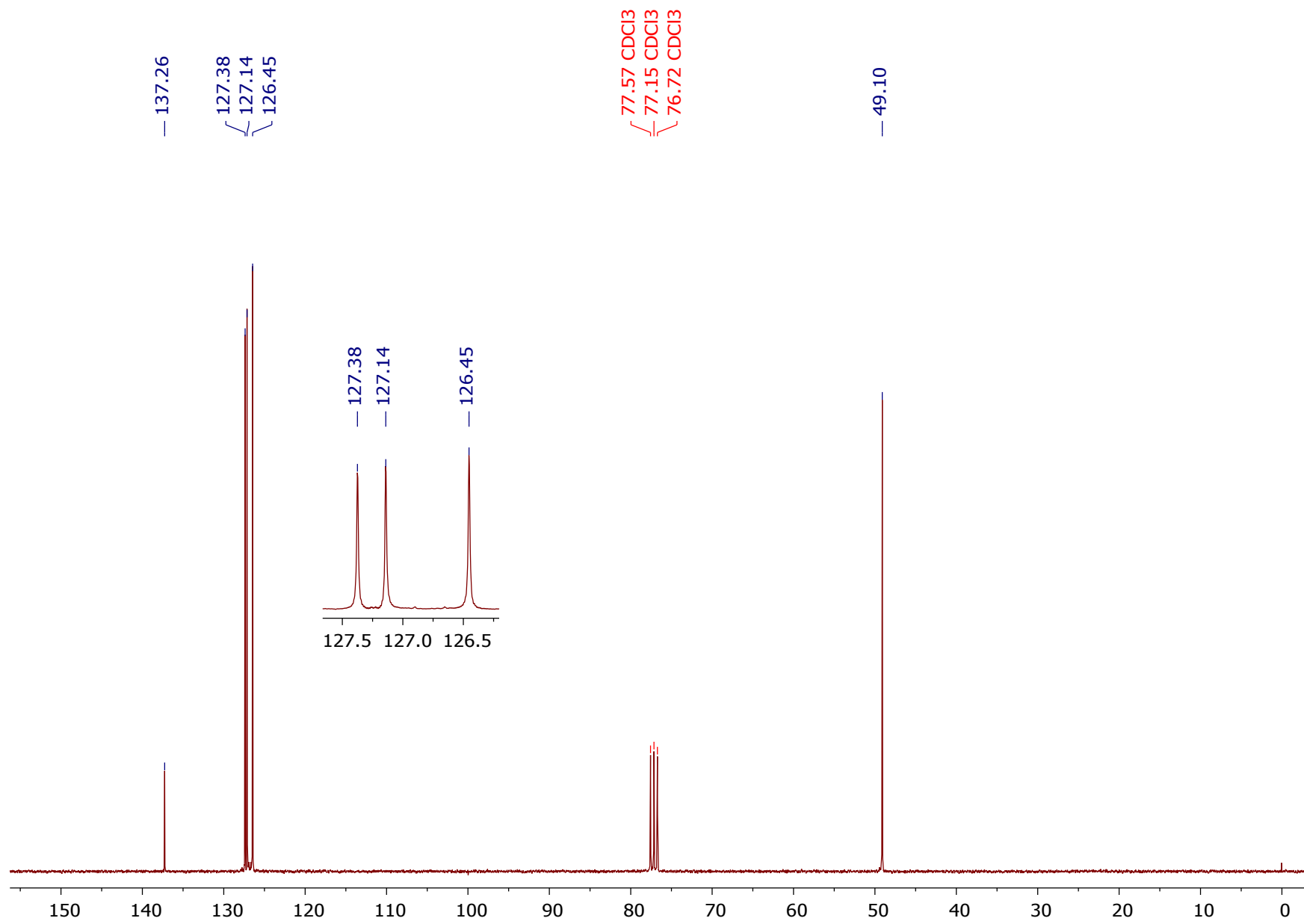


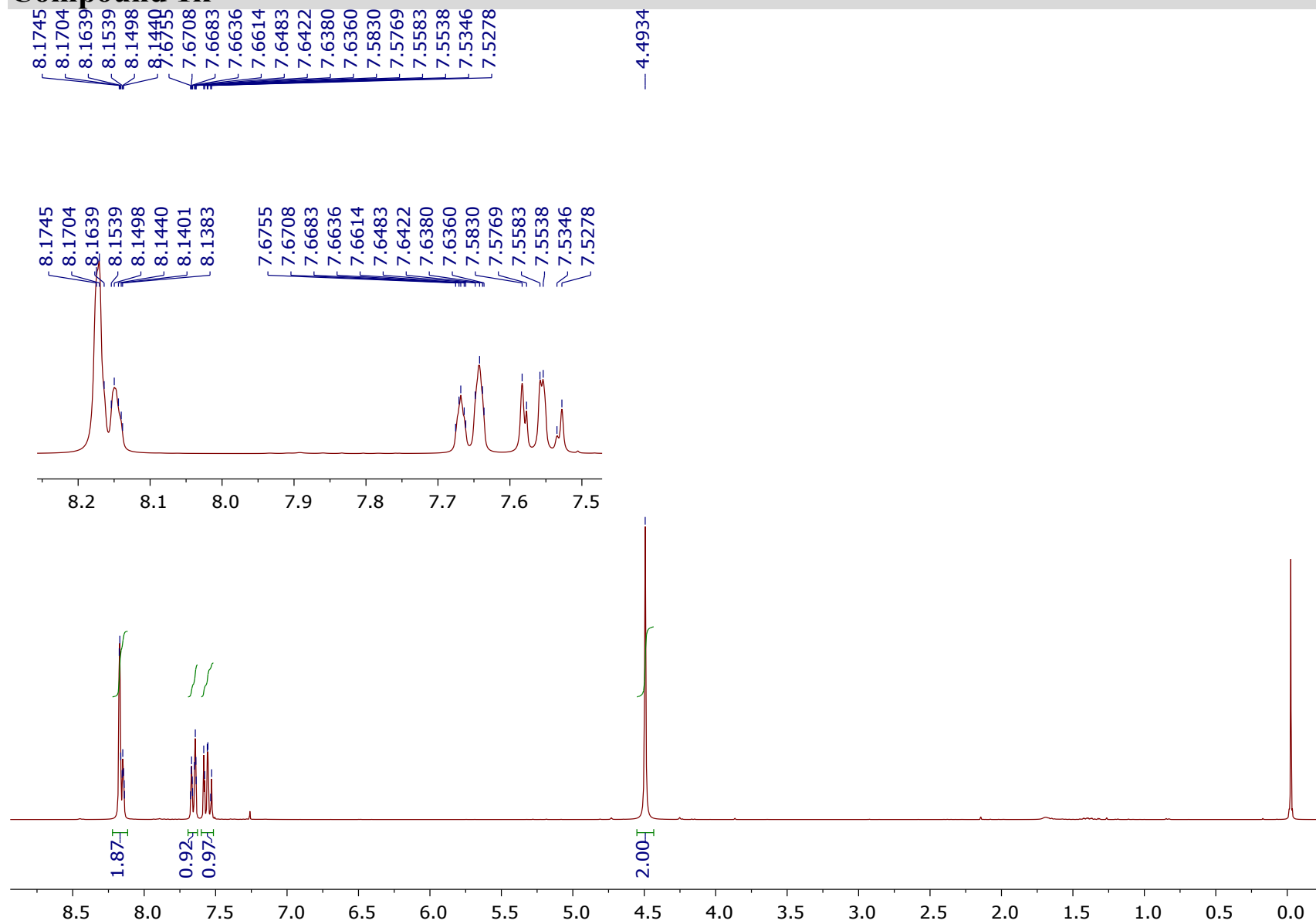


Compound 1j

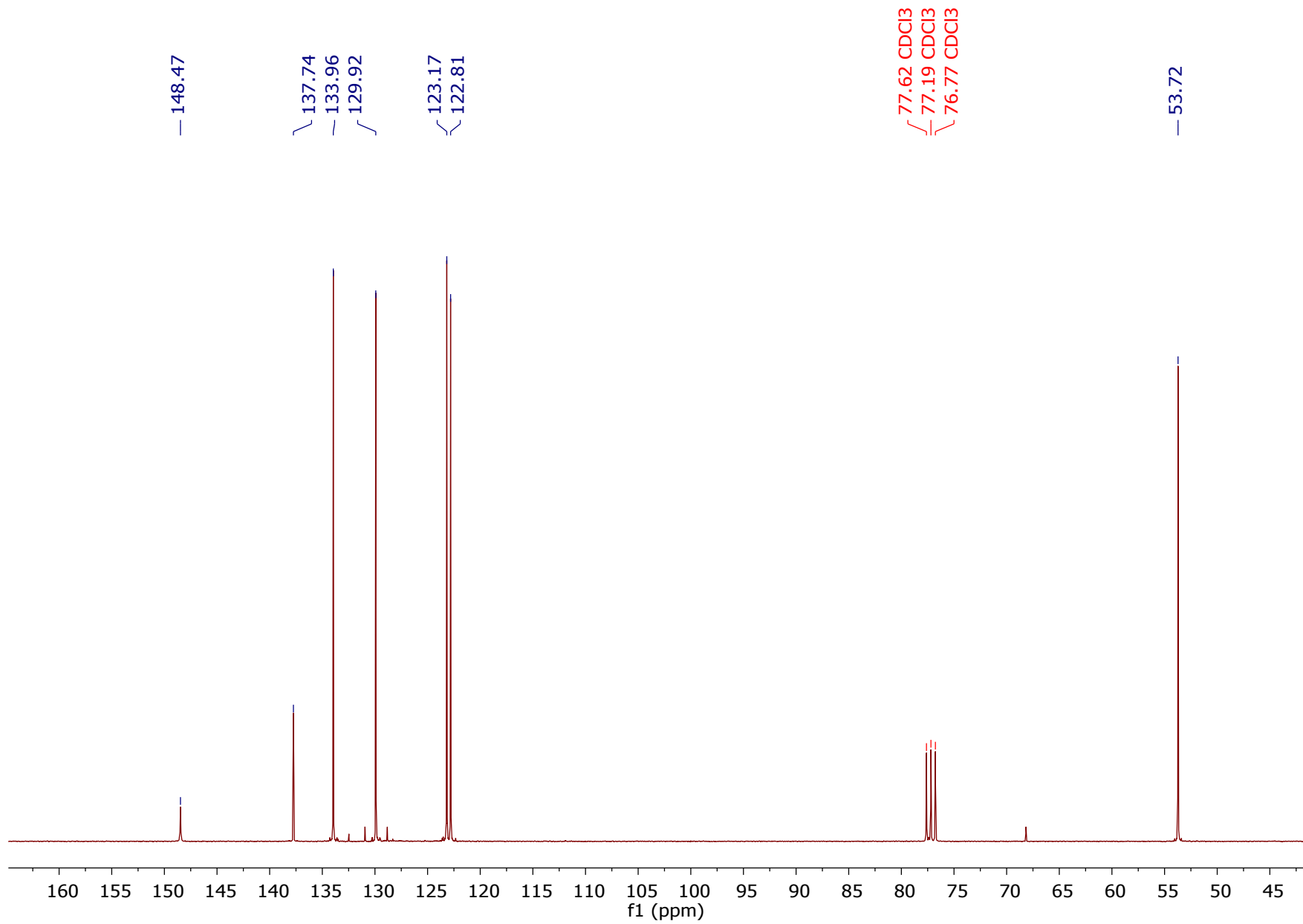


[30]

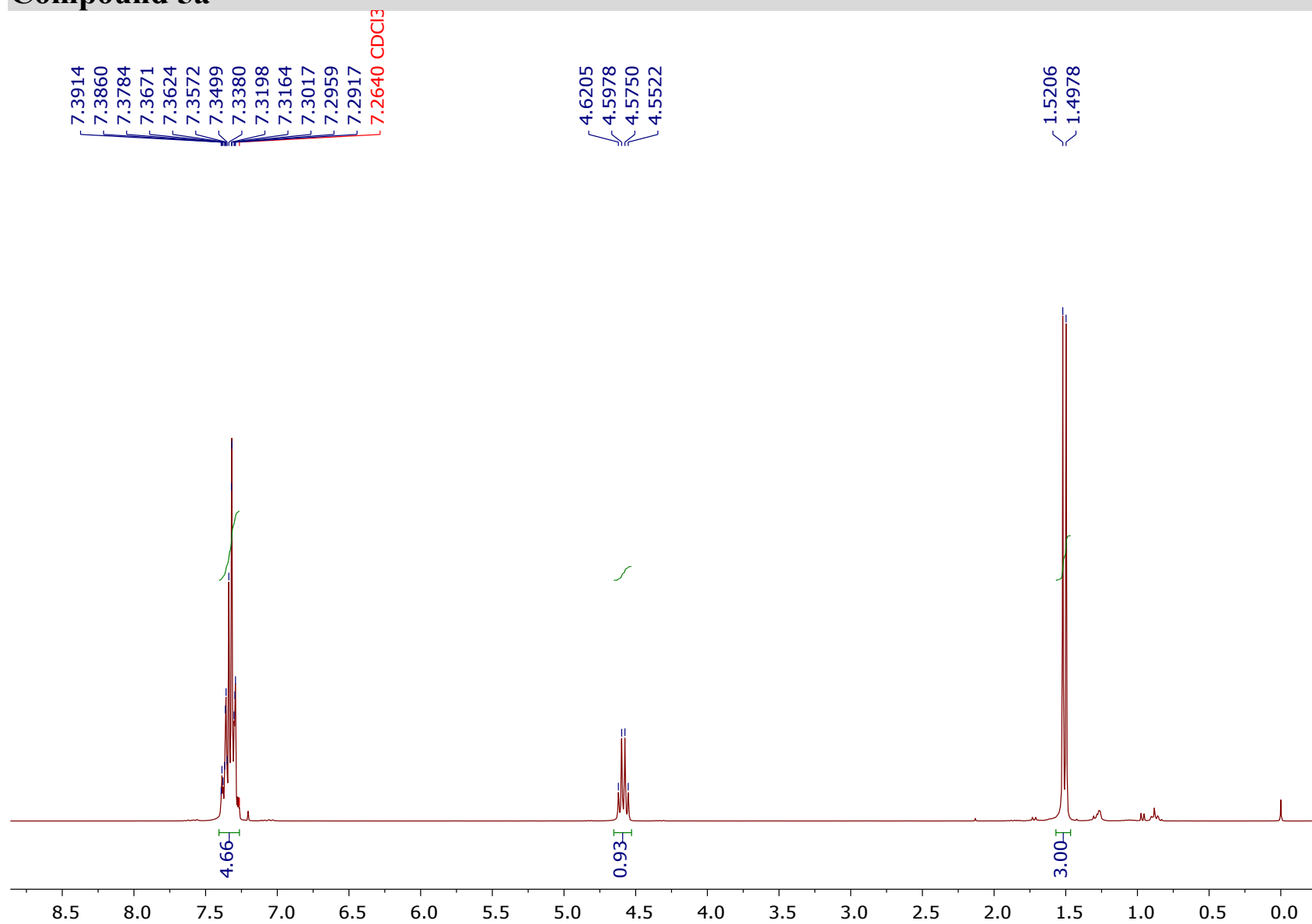


Compound 1k

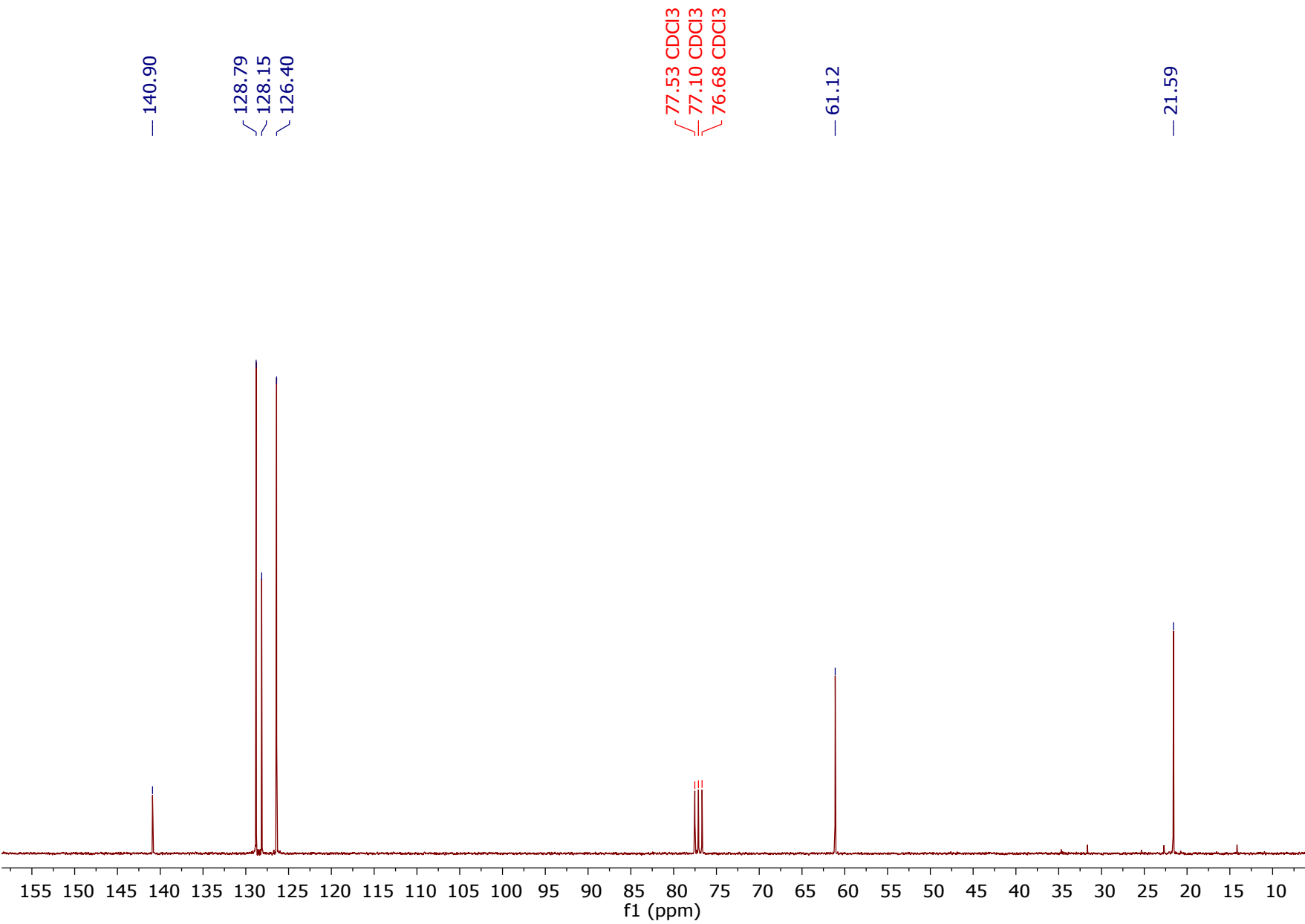
[32]



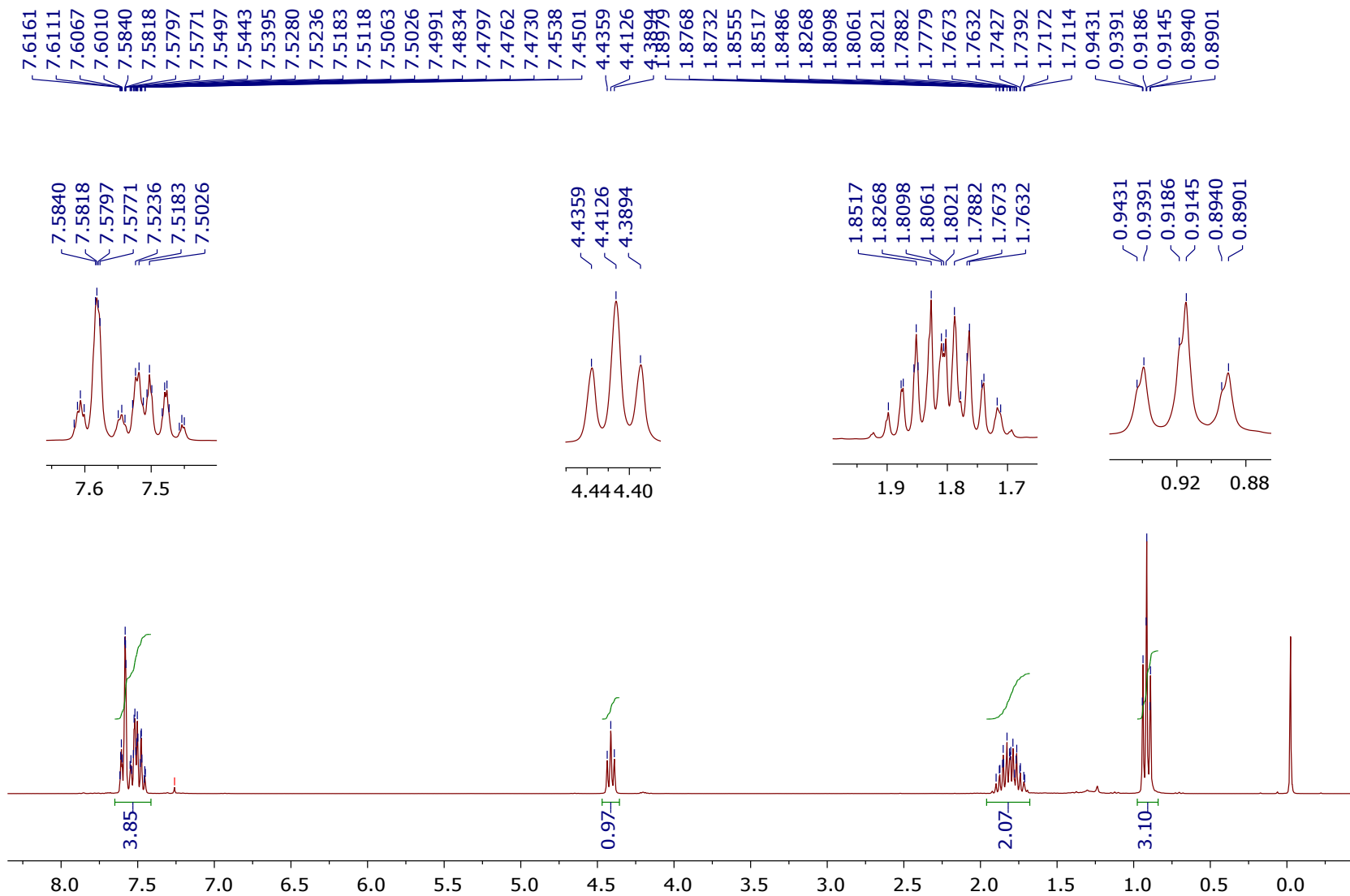
Compound 5a



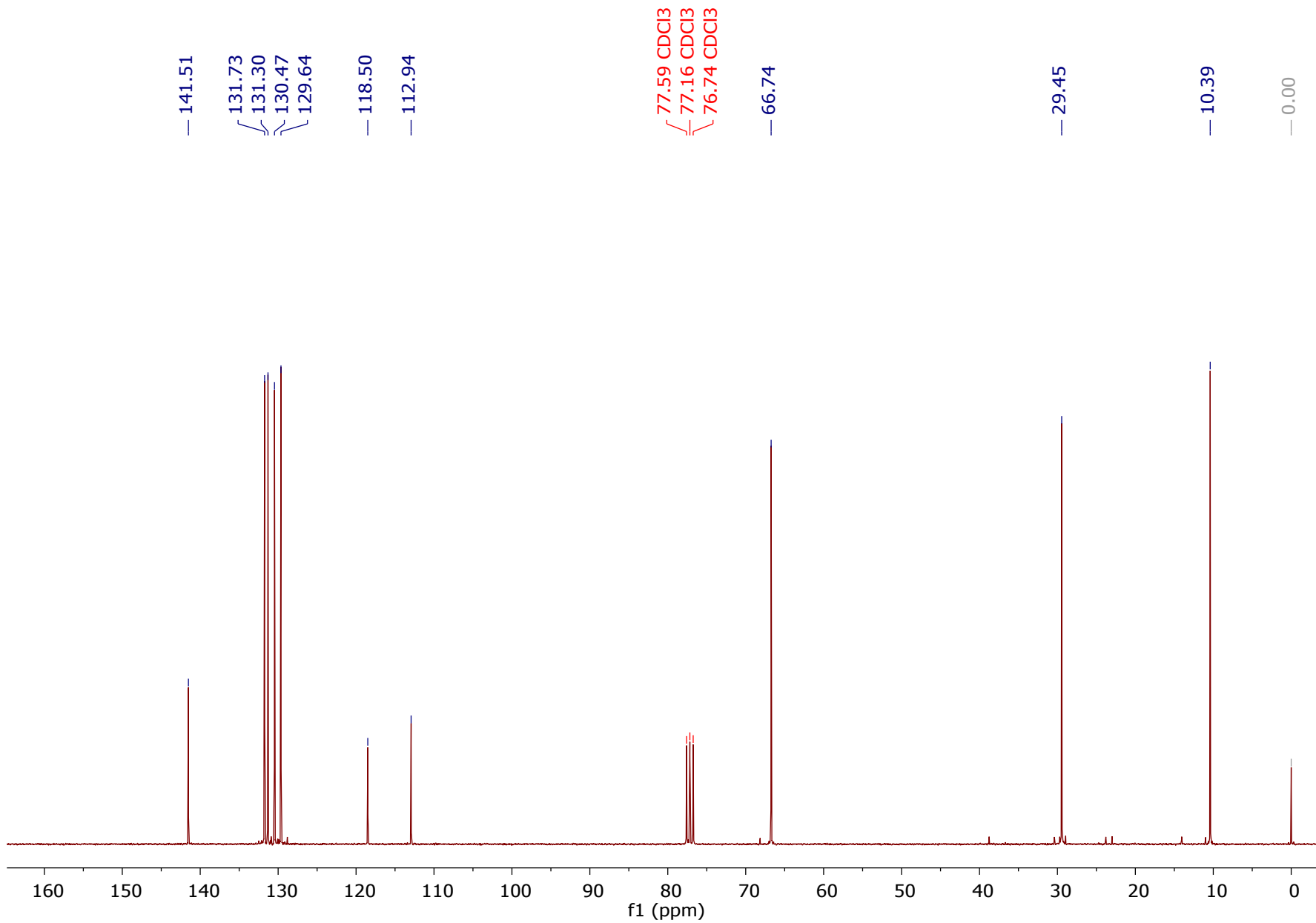
[34]



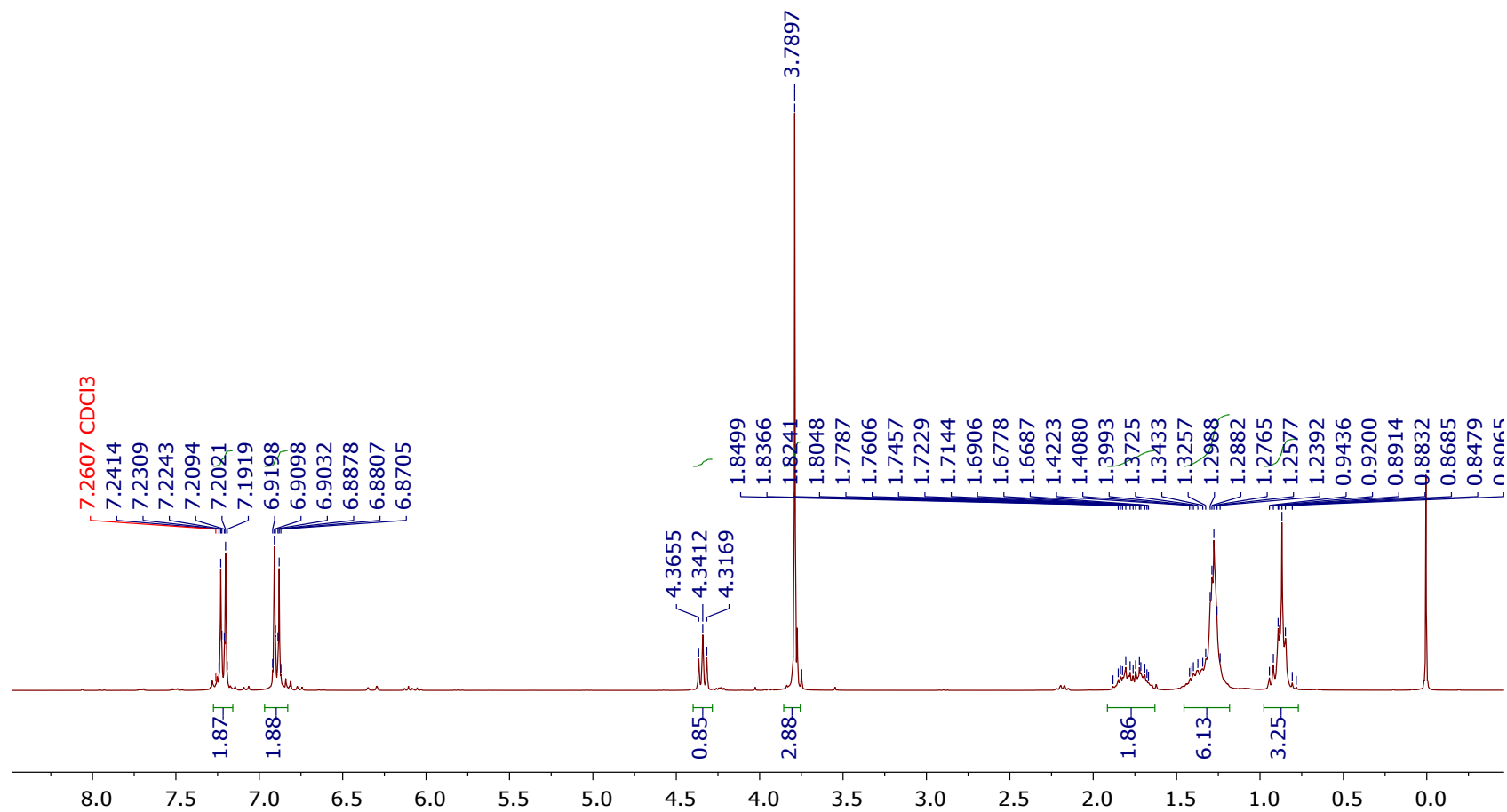
Compound 5b



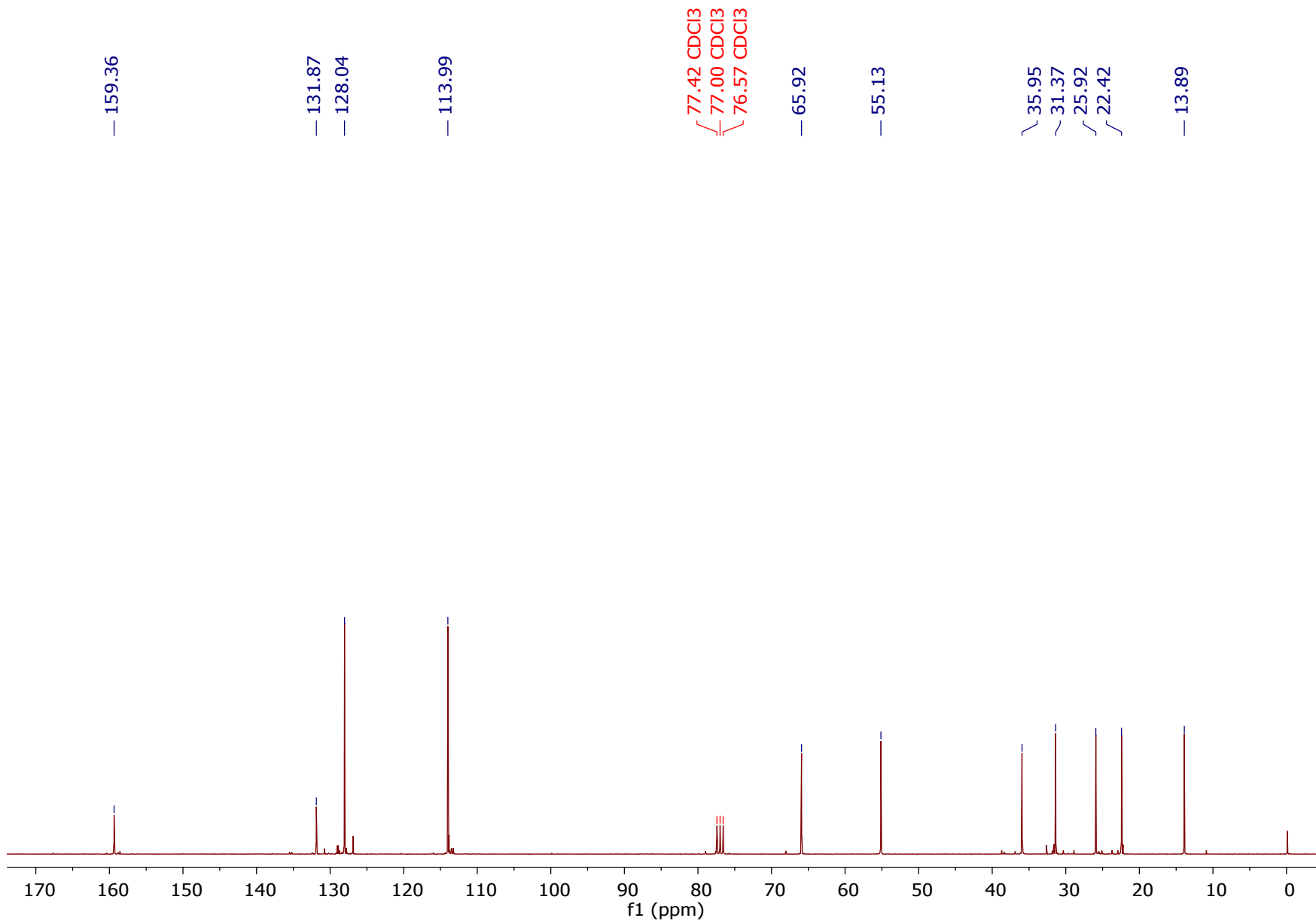
[36]



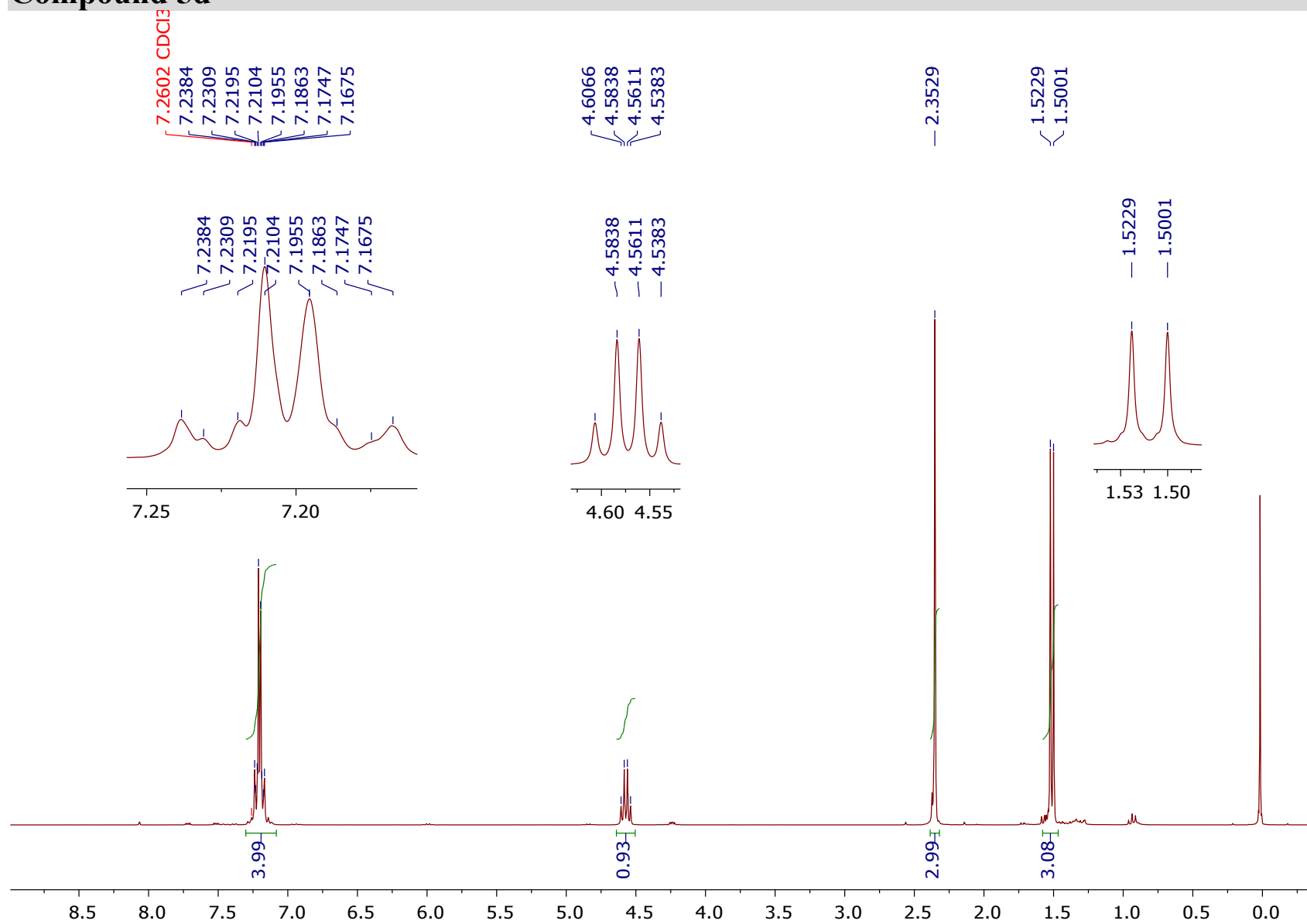
Compound 5c



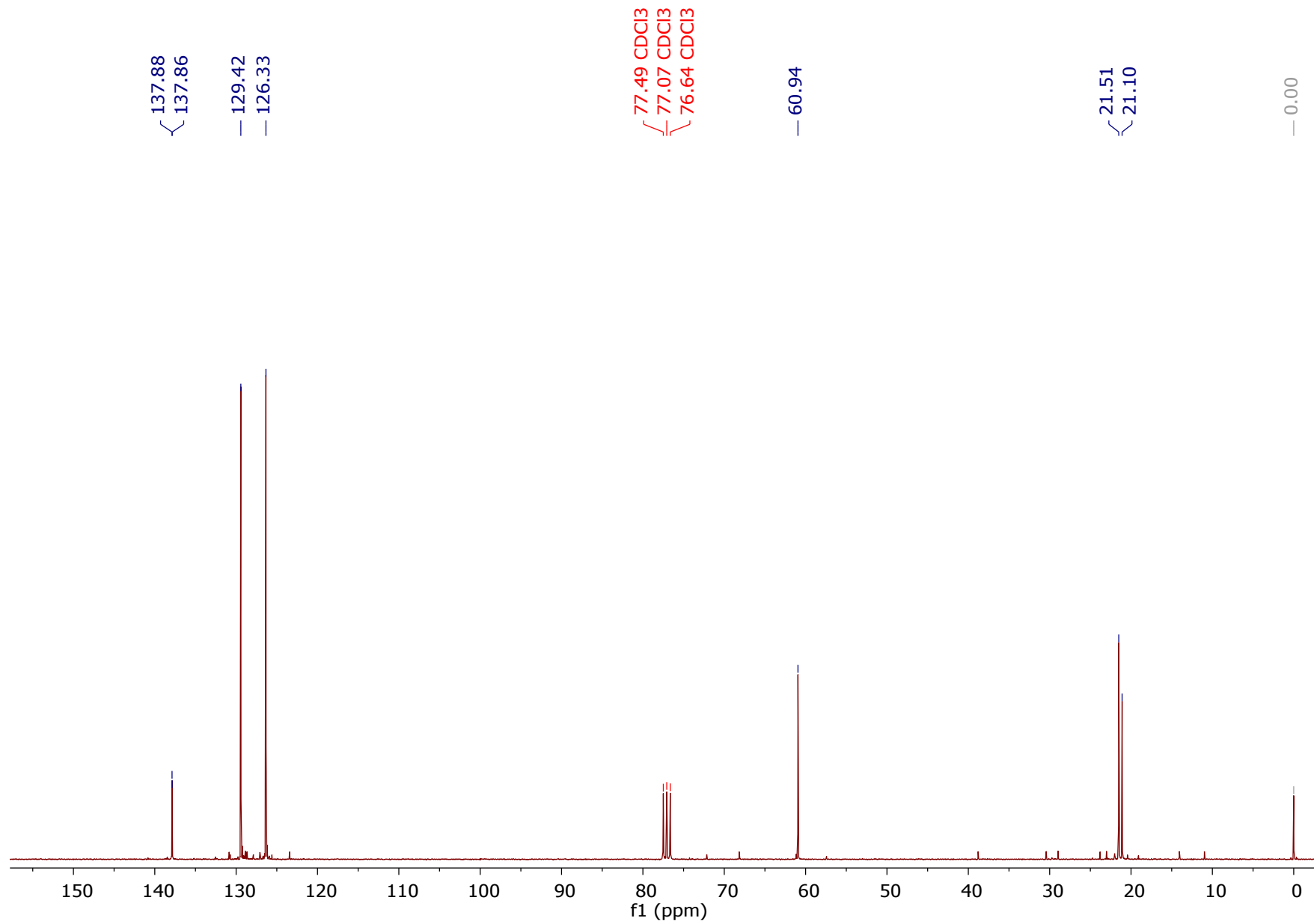
[38]



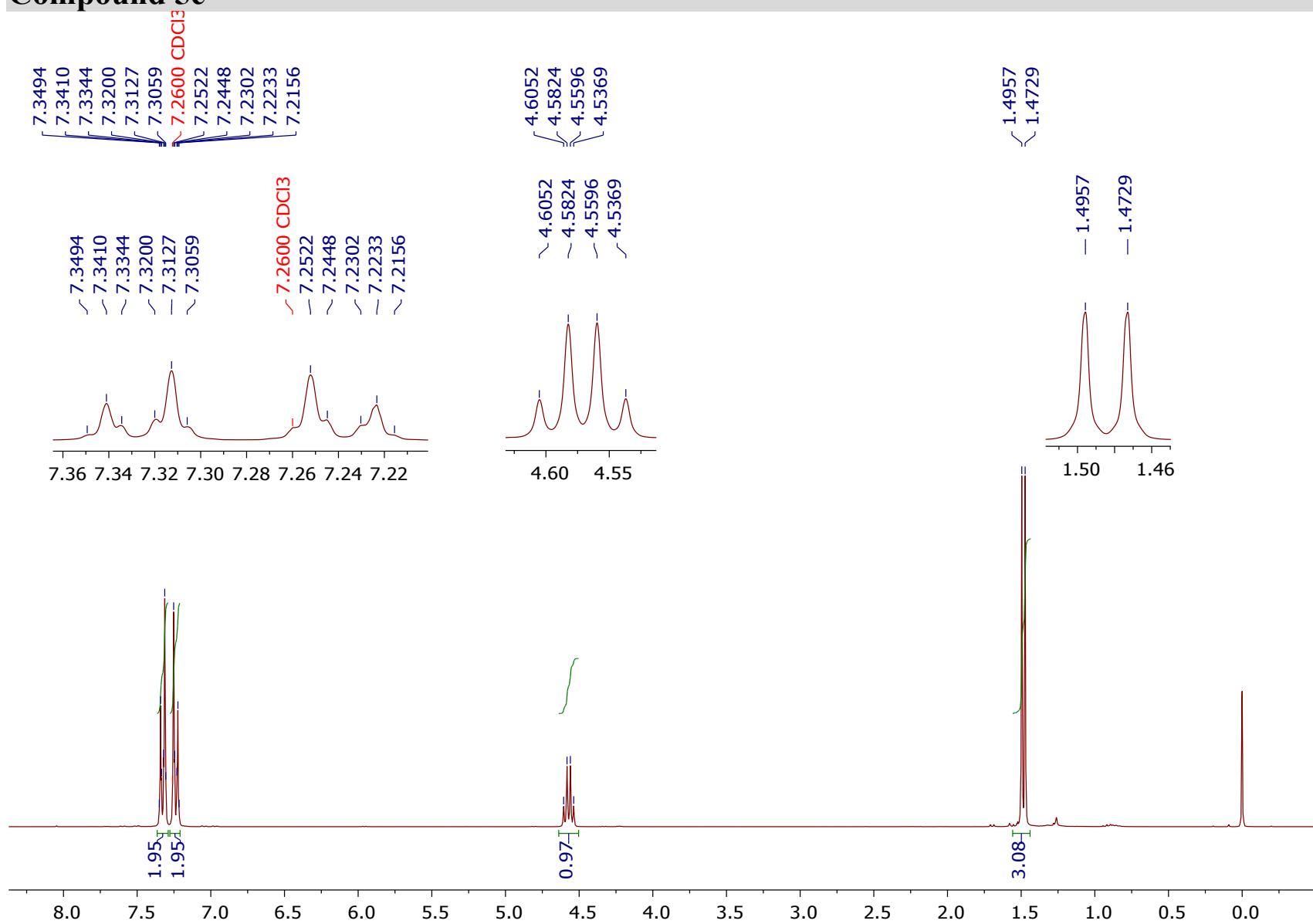
Compound 5d



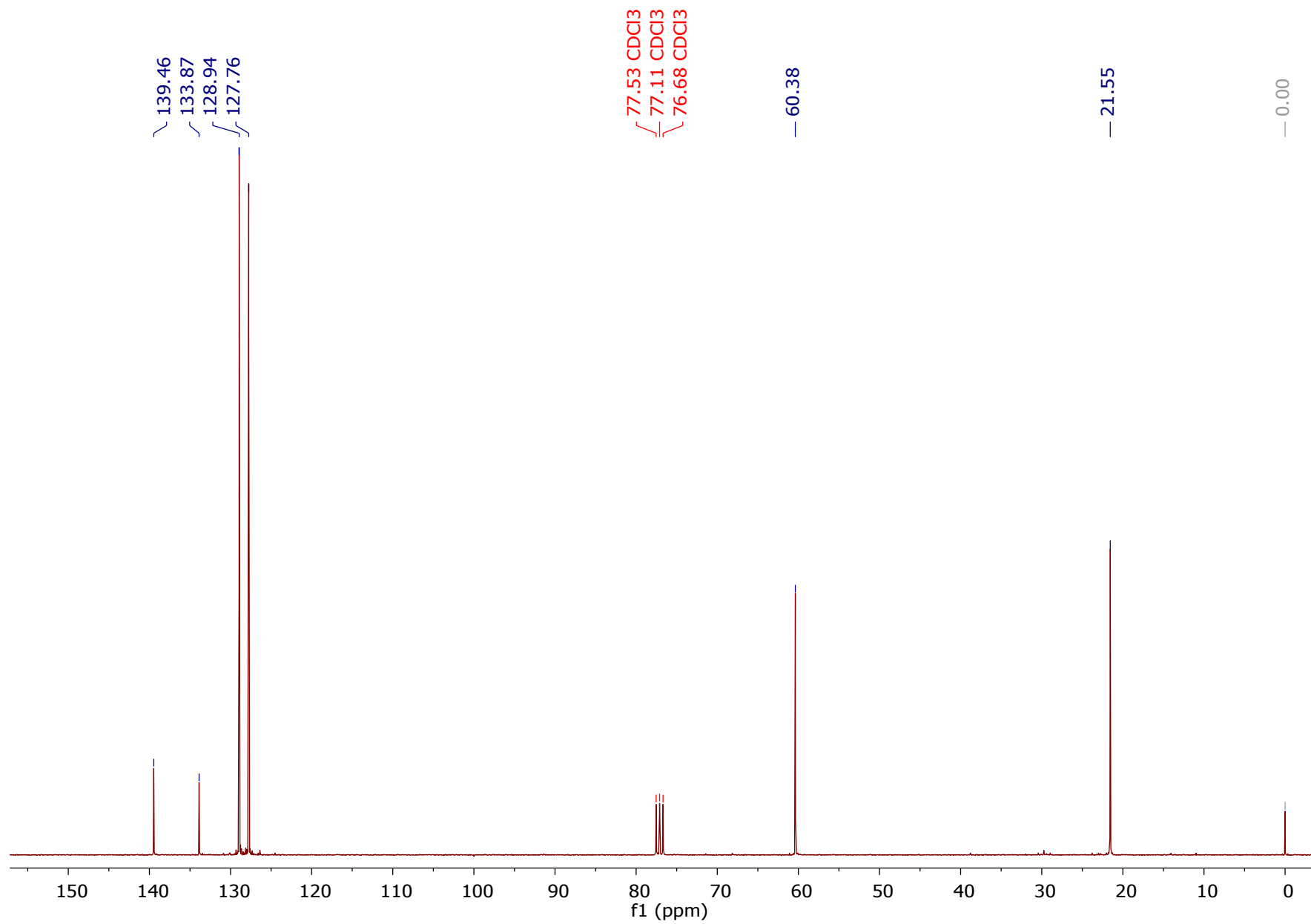
[40]



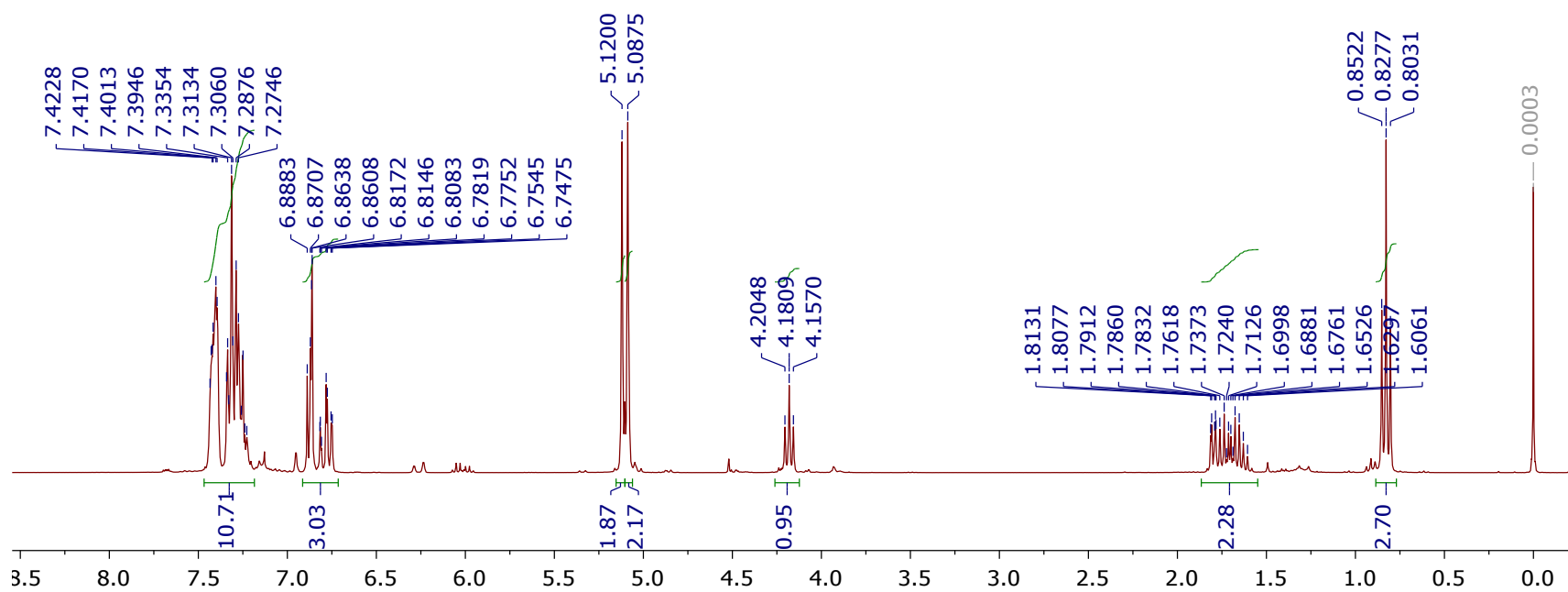
Compound 5e



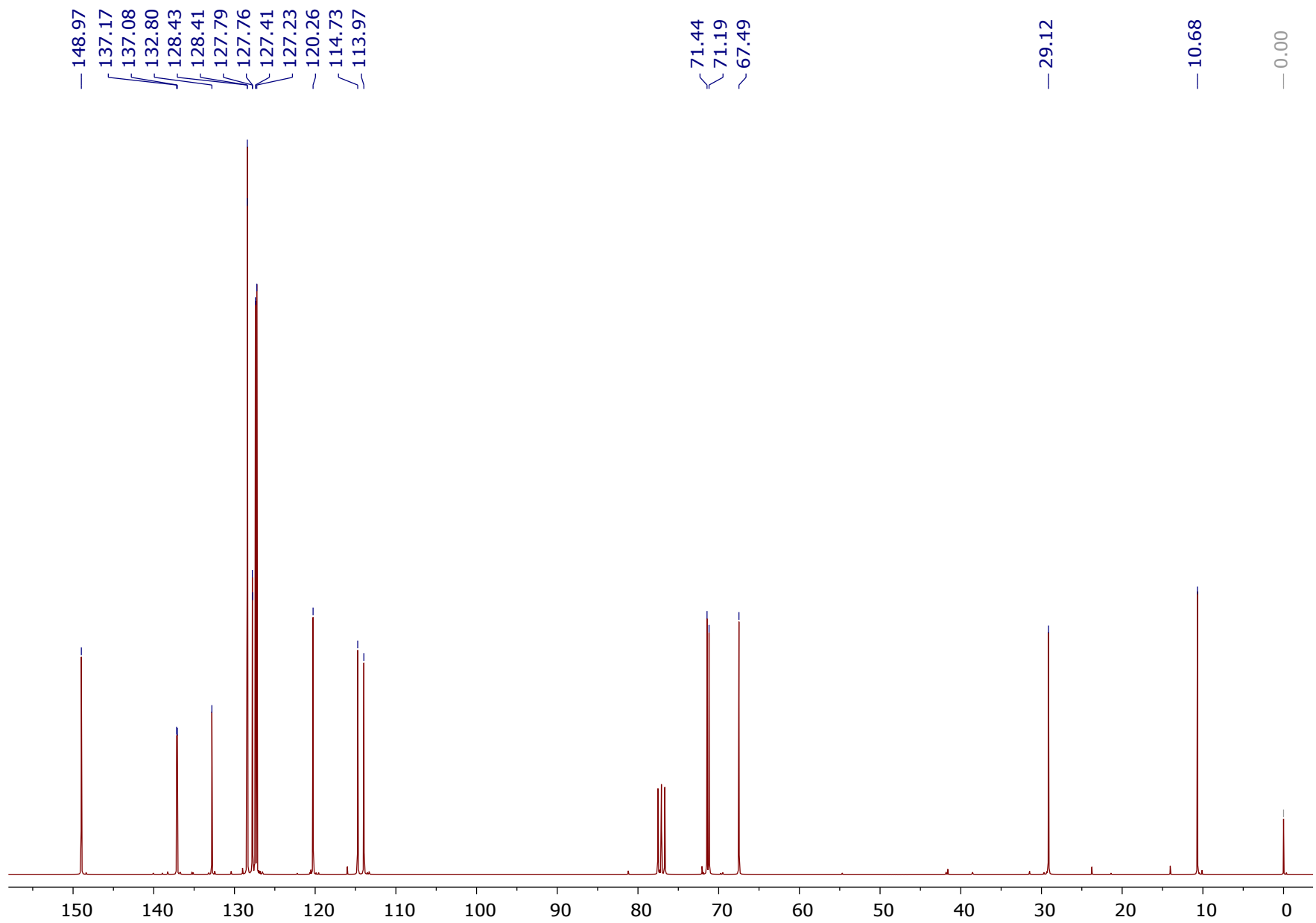
[42]



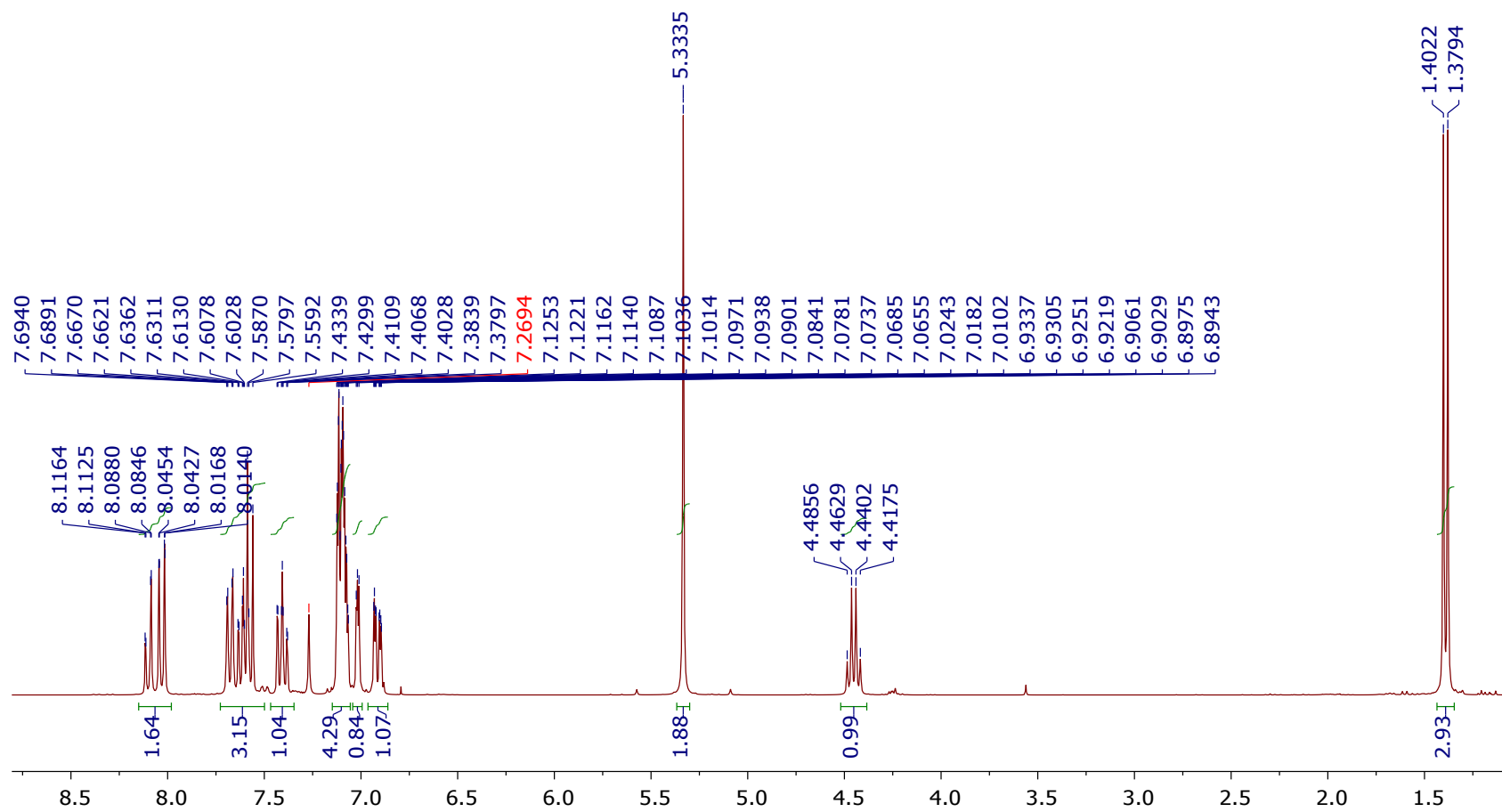
Compound 5f



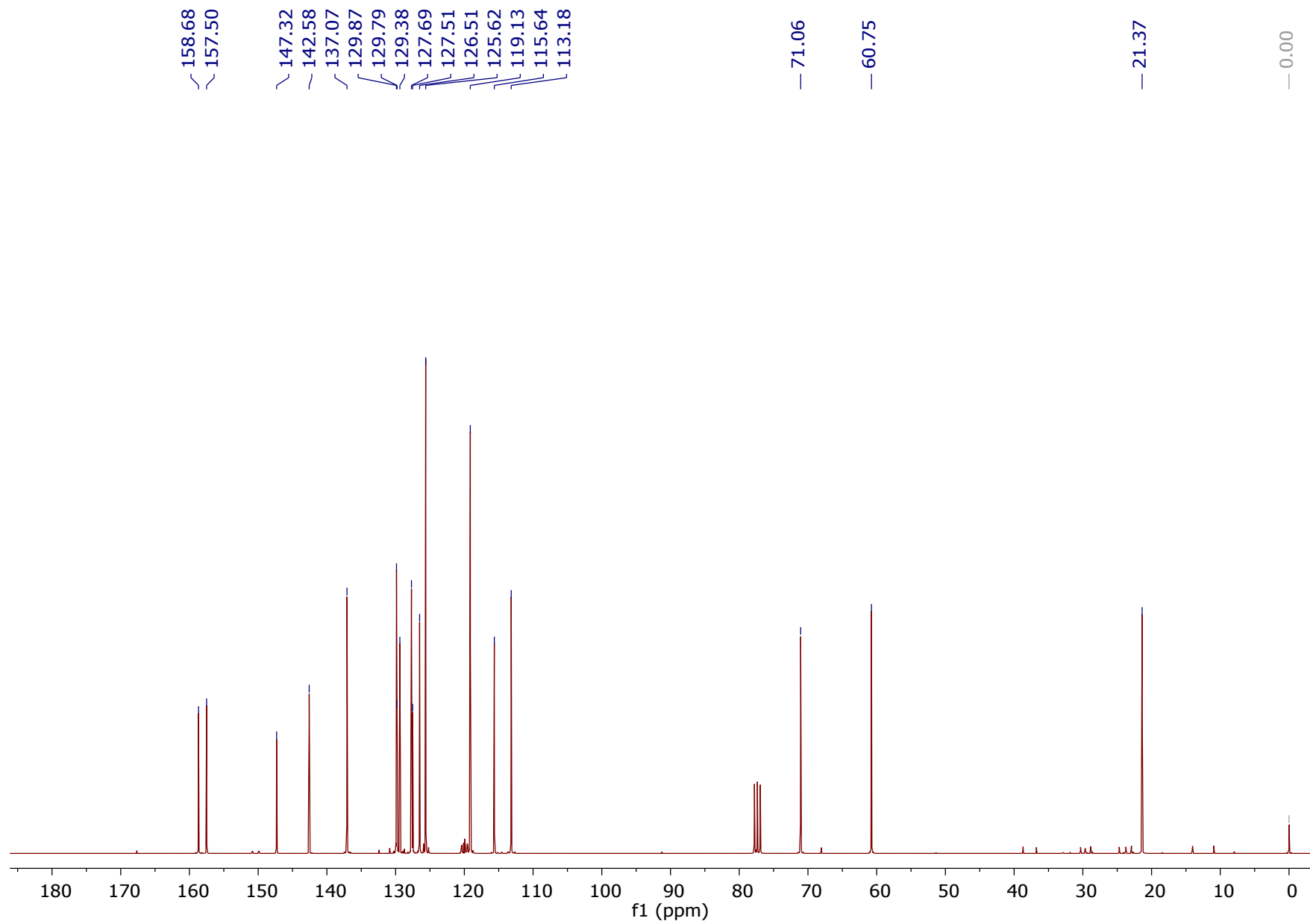
[44]



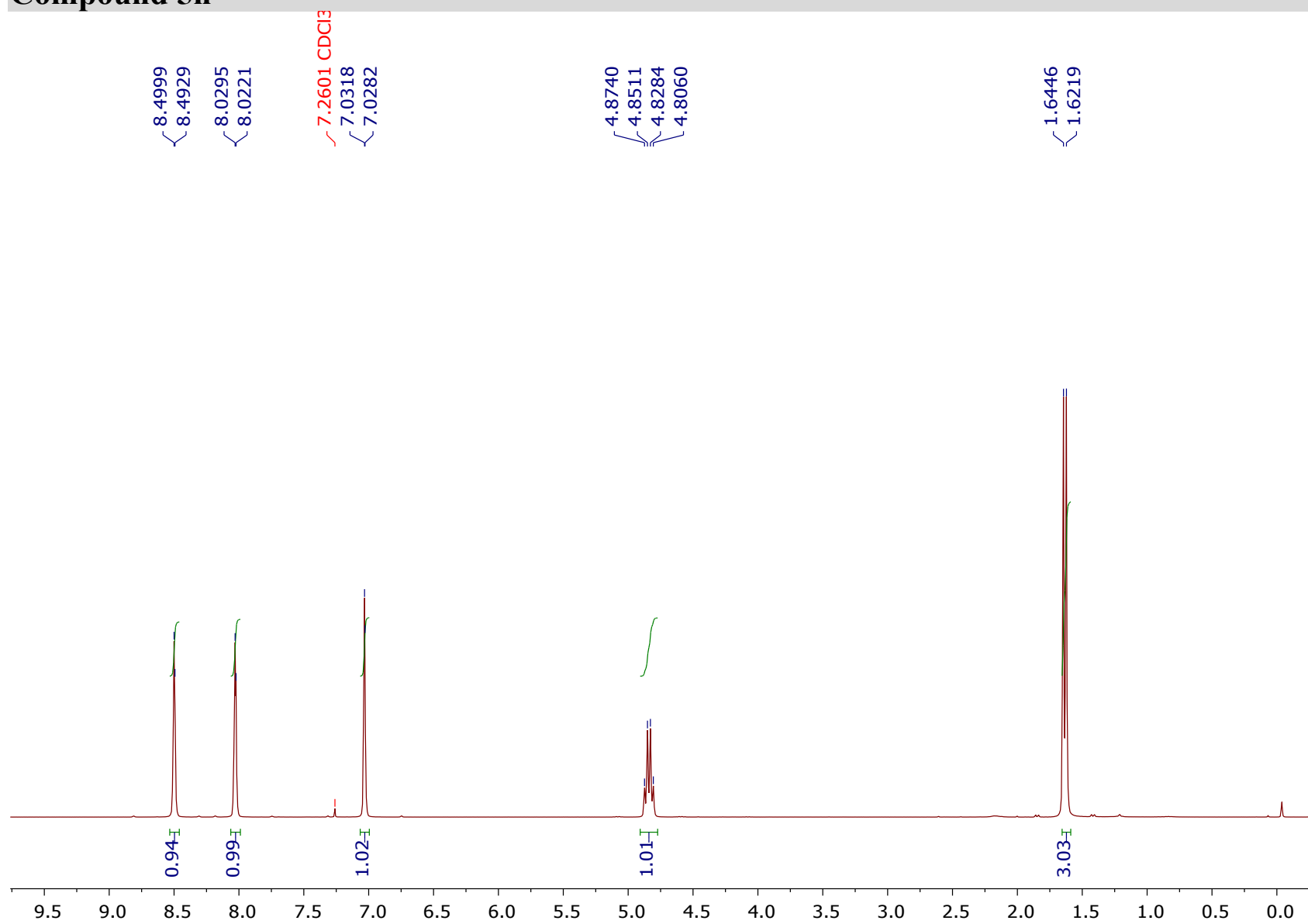
Compound 5g



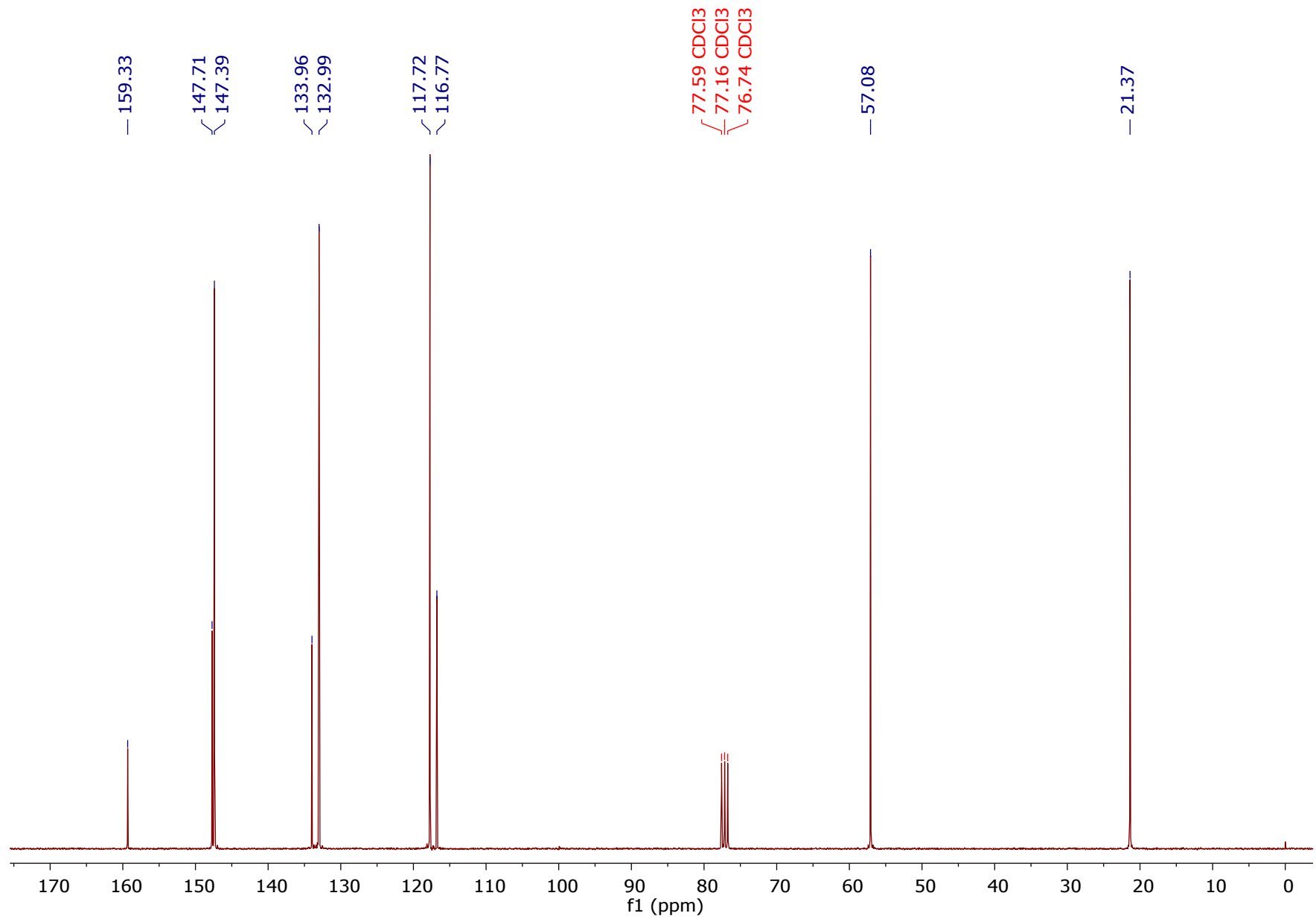
[46]



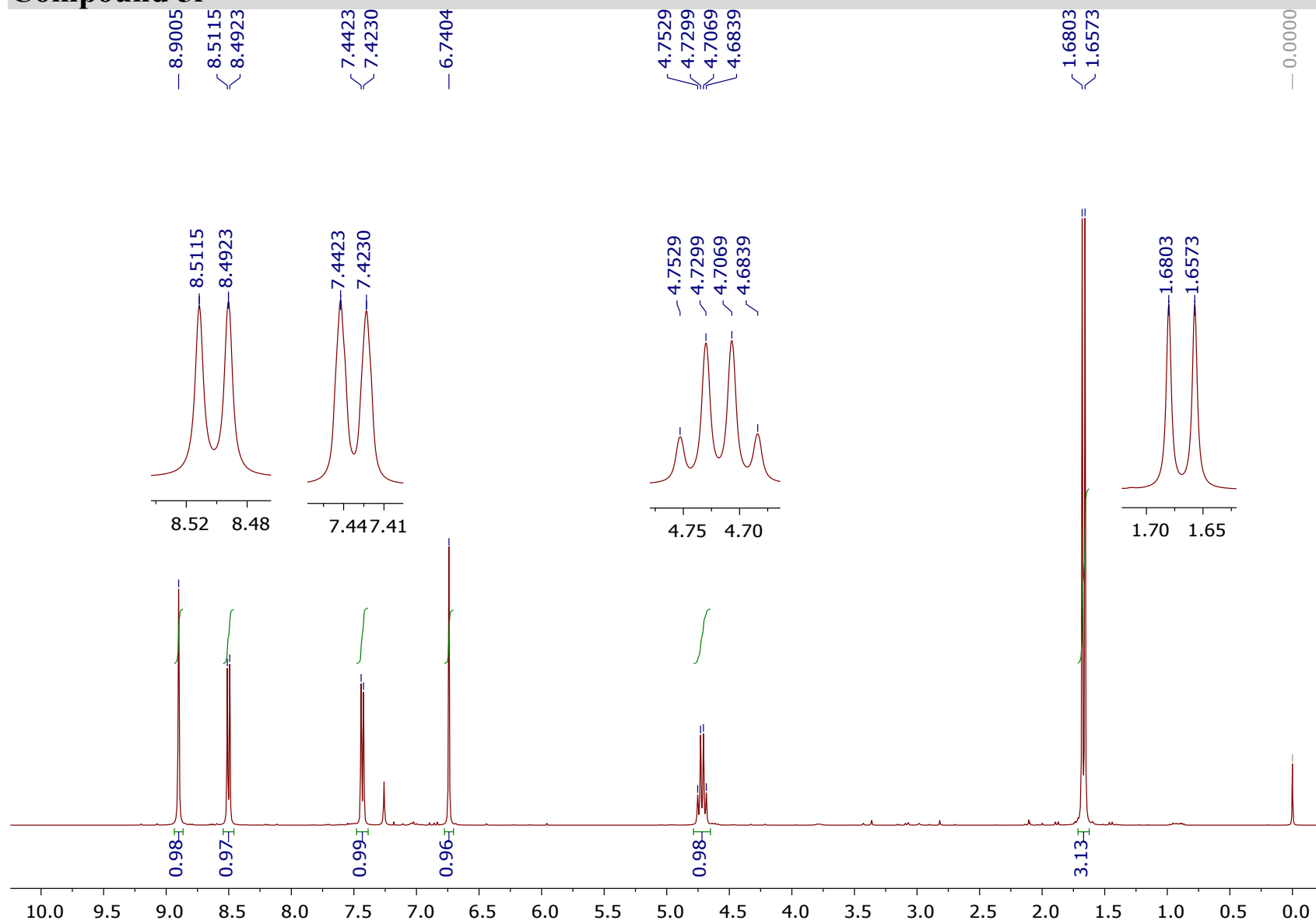
Compound 5h

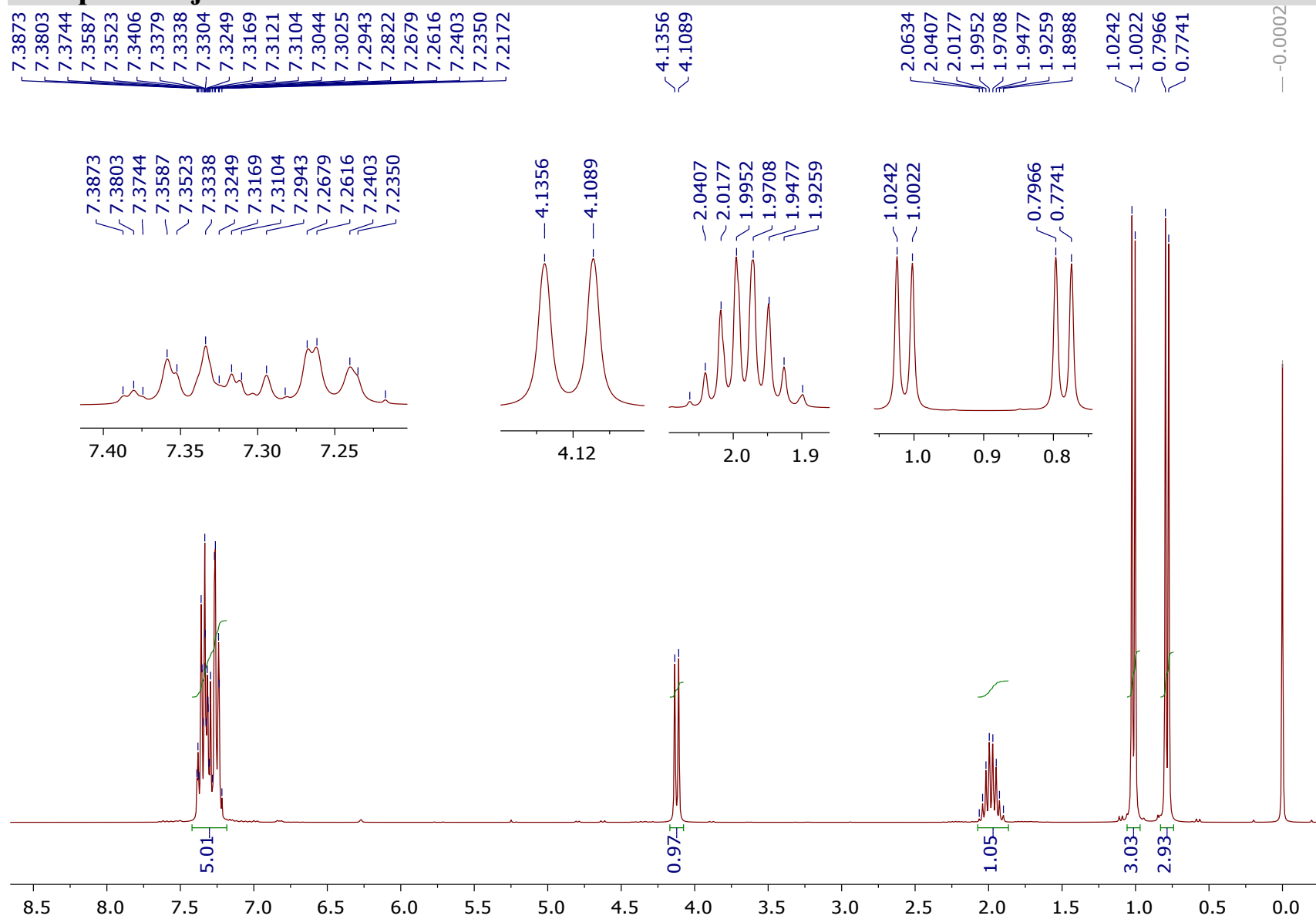


[48]

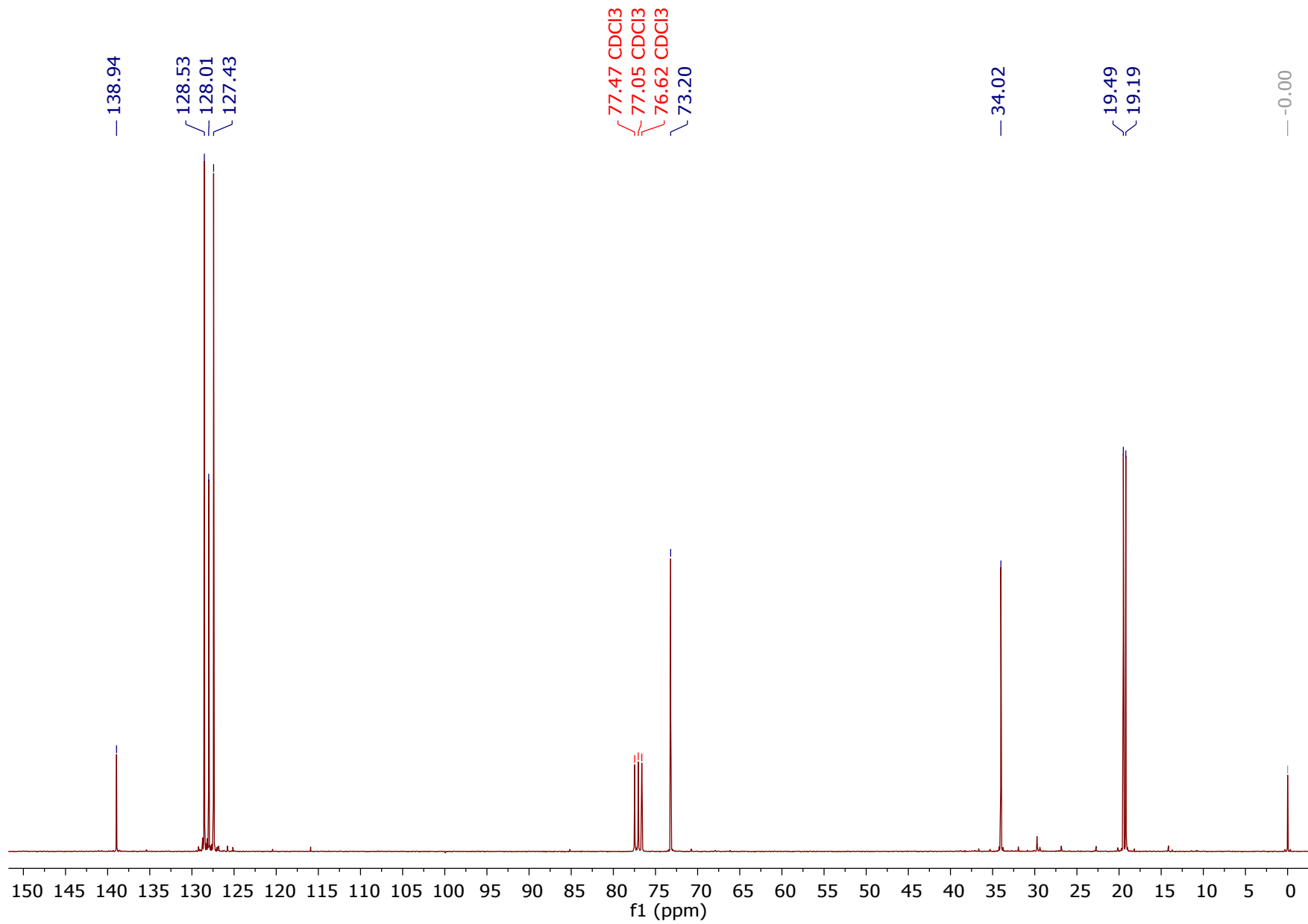


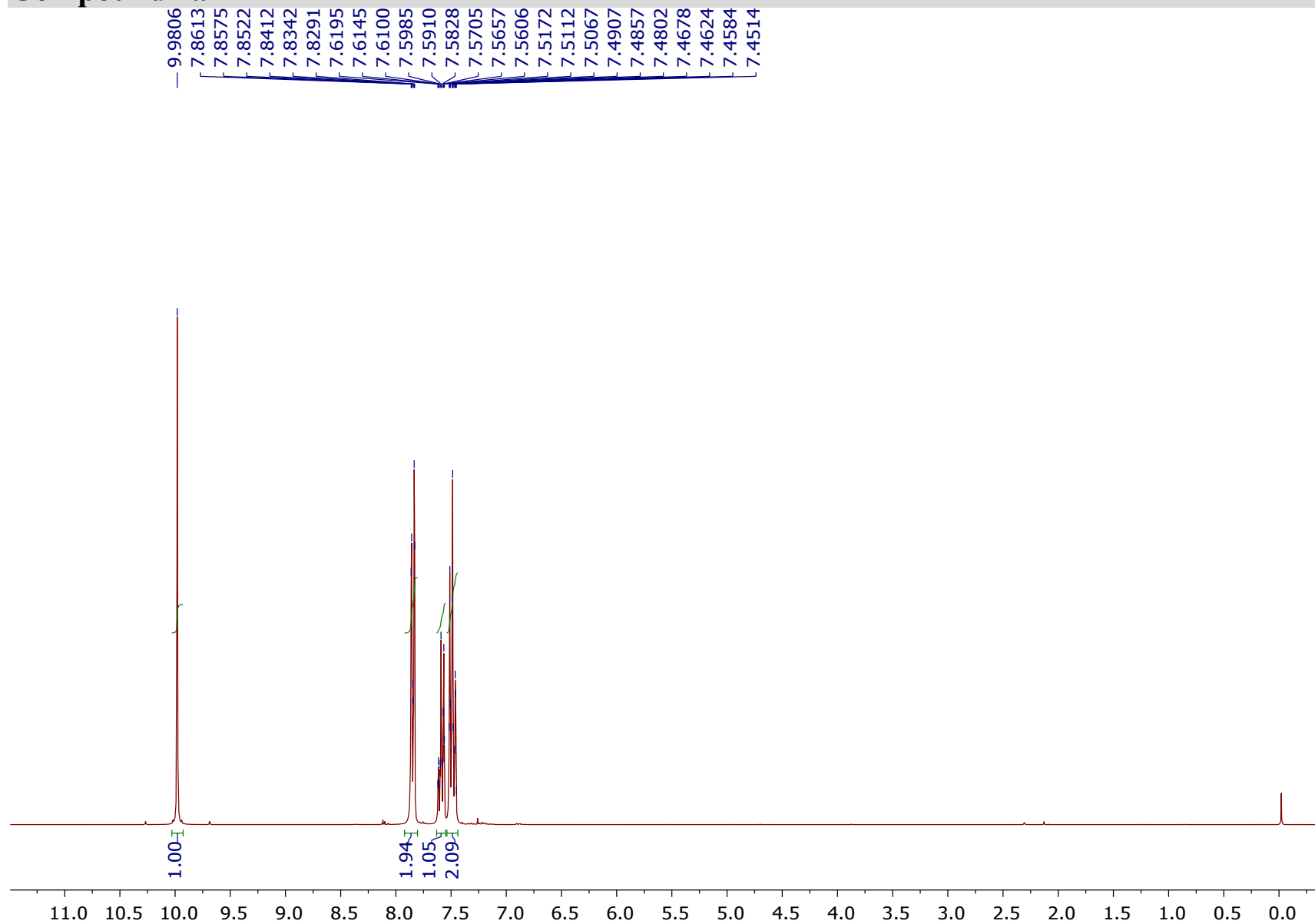
Compound 5i



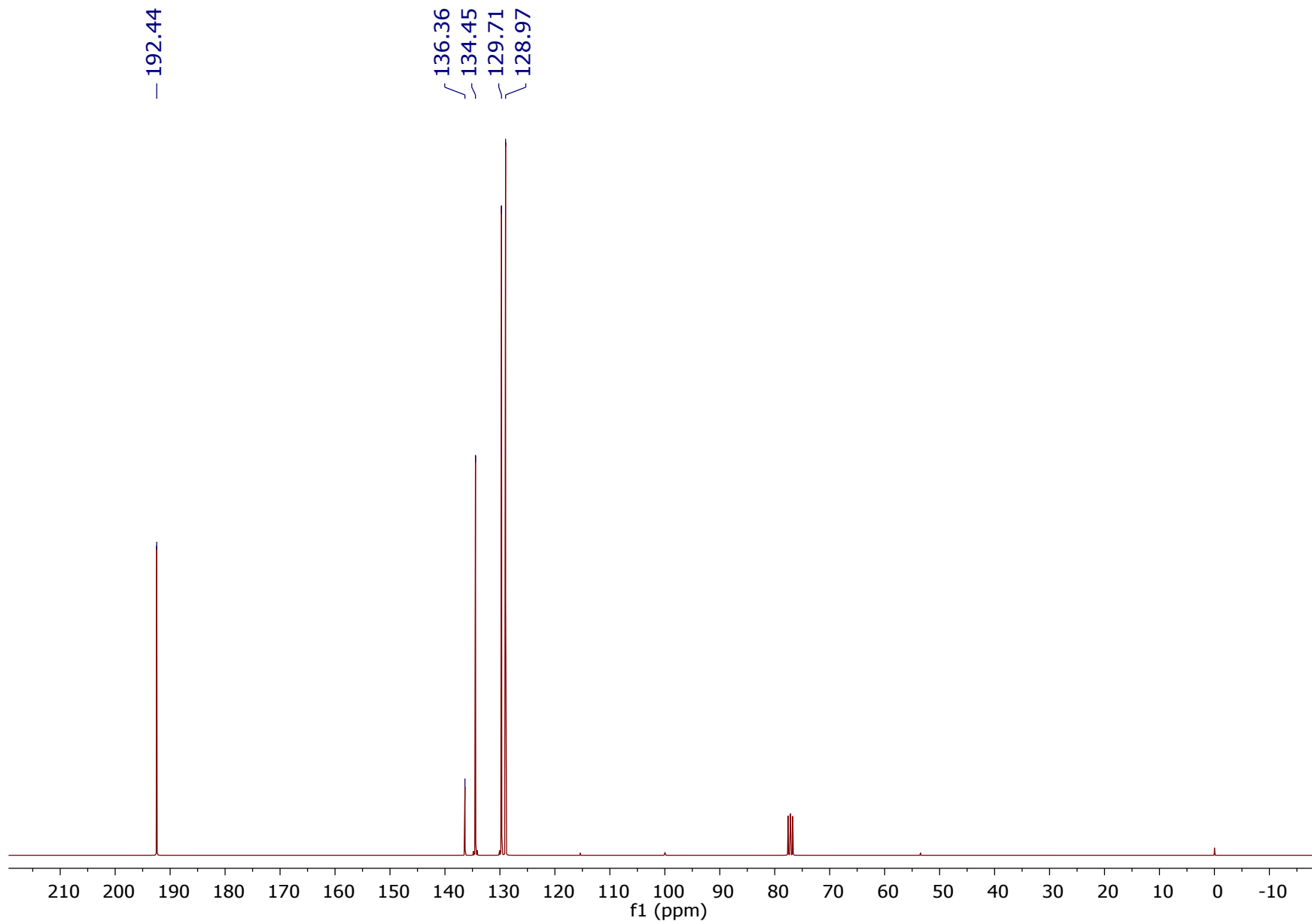
Compound 5j

[51]

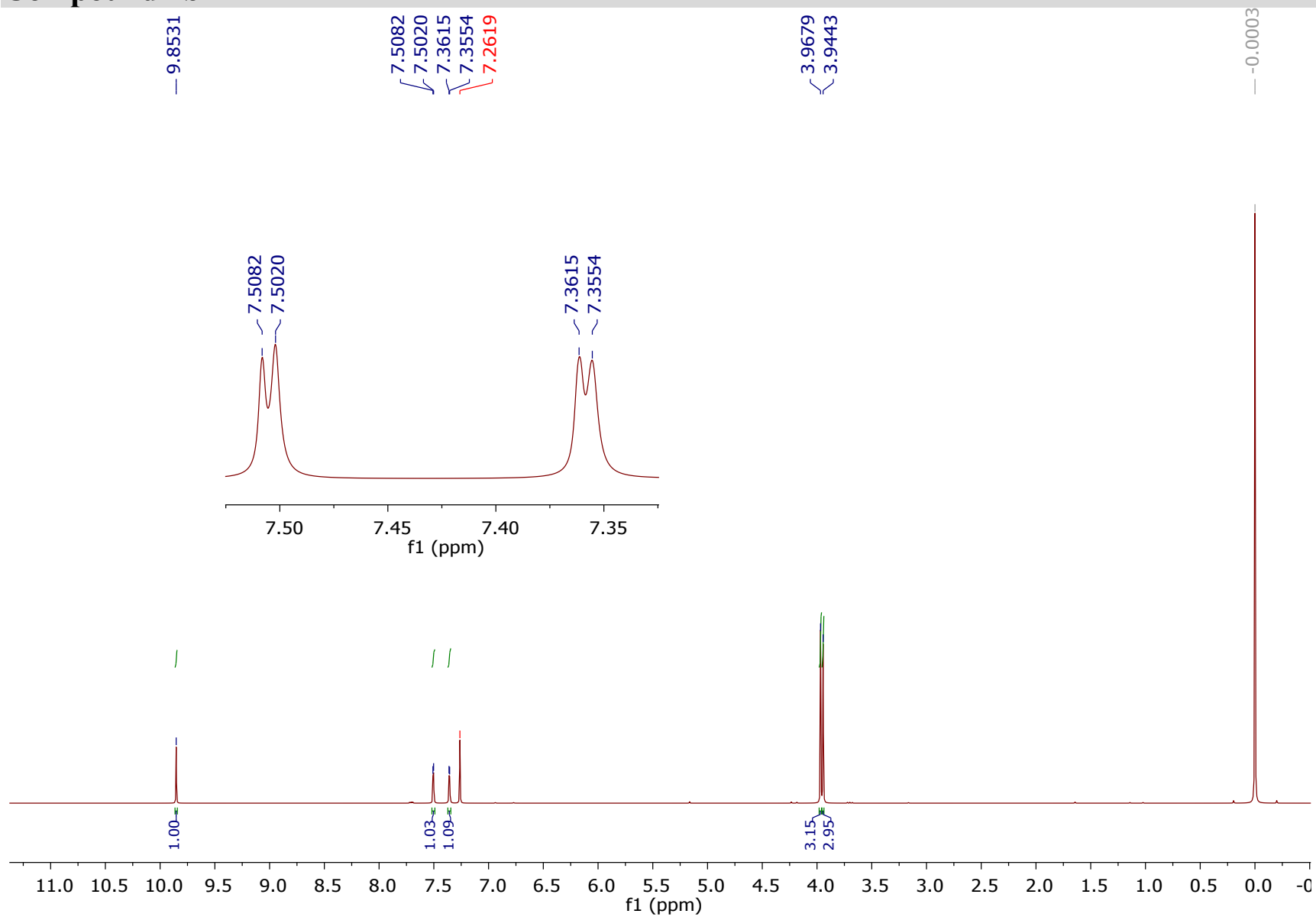


Compound 4a

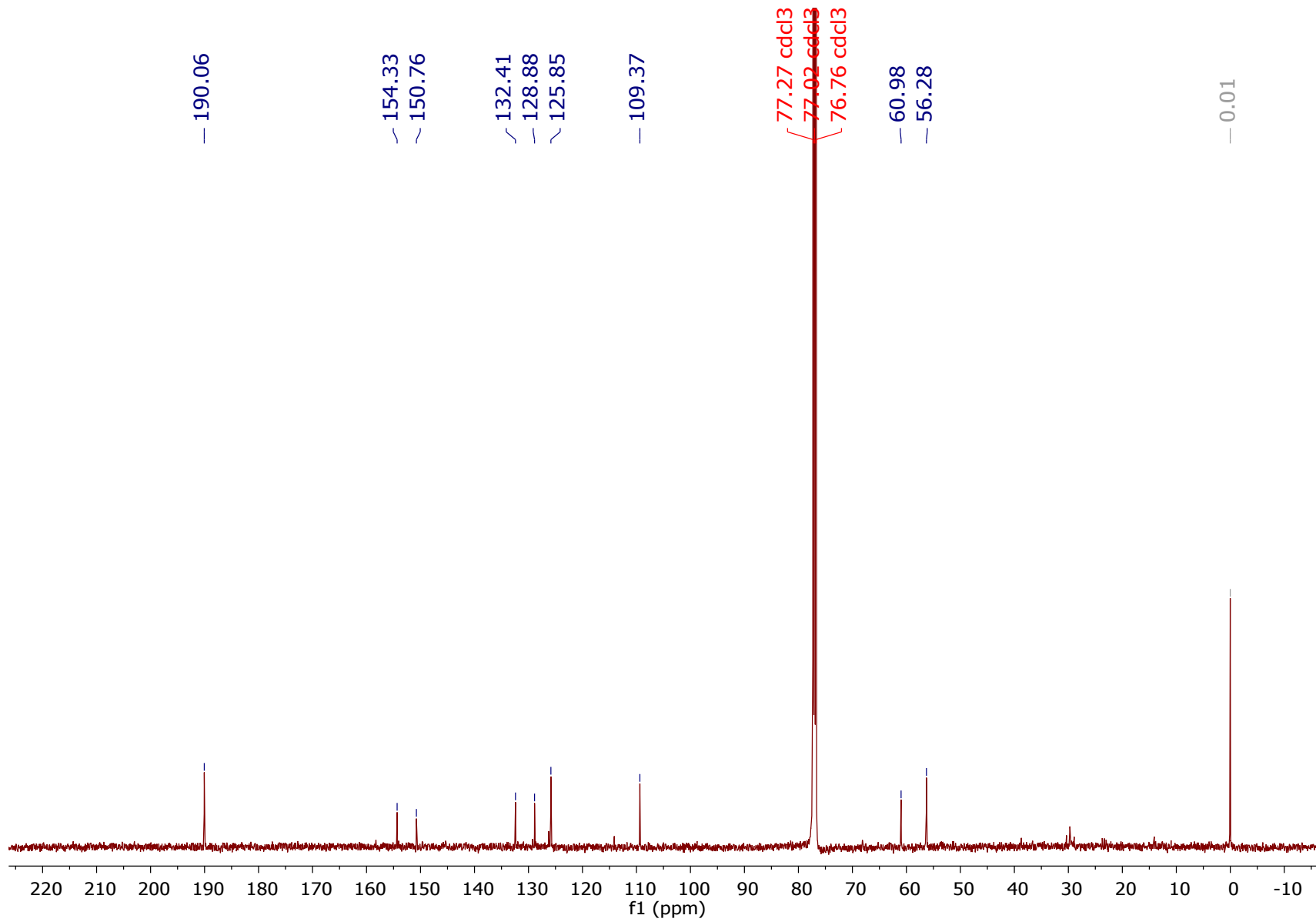
[53]



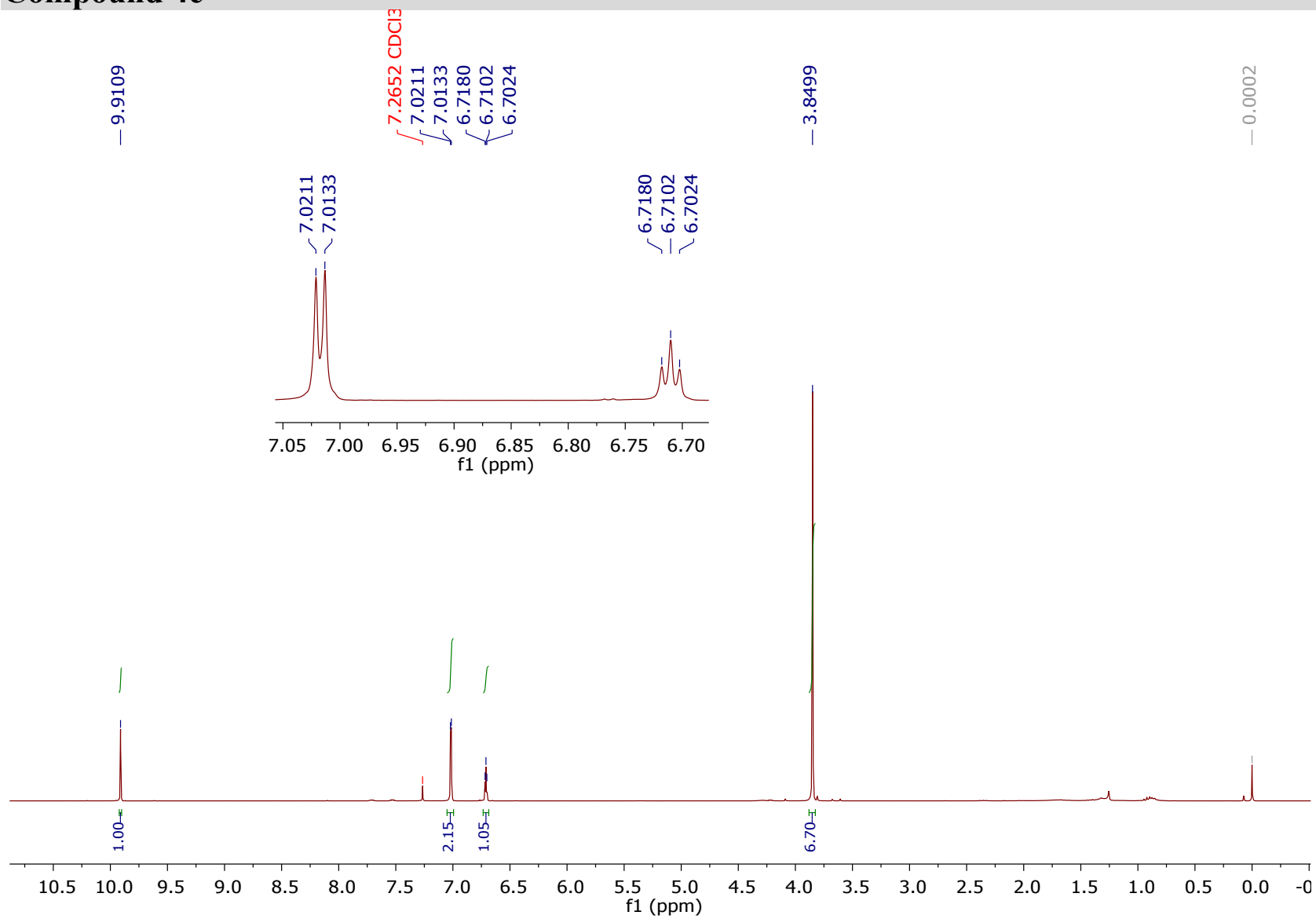
Compound 4b



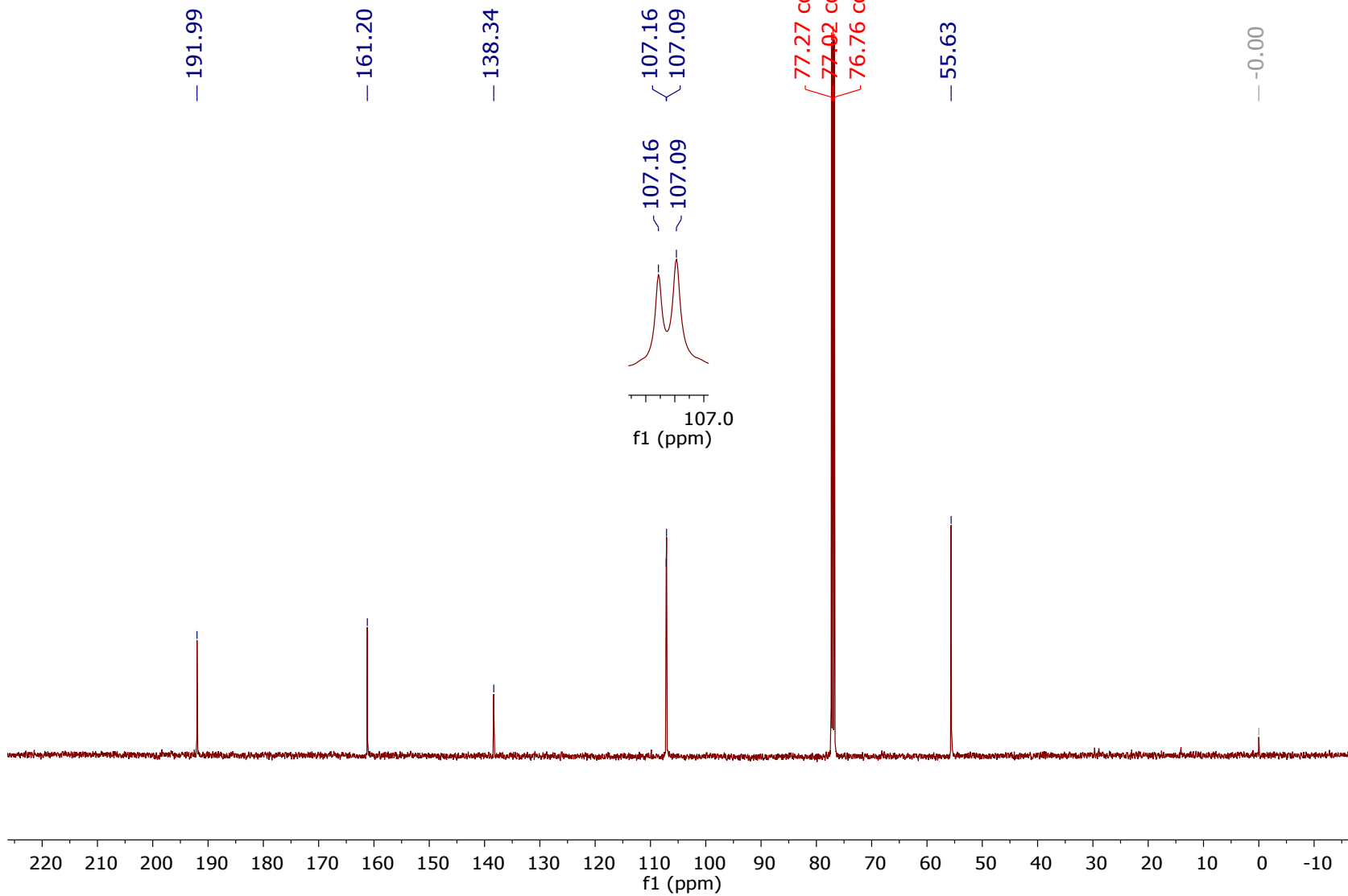
[55]



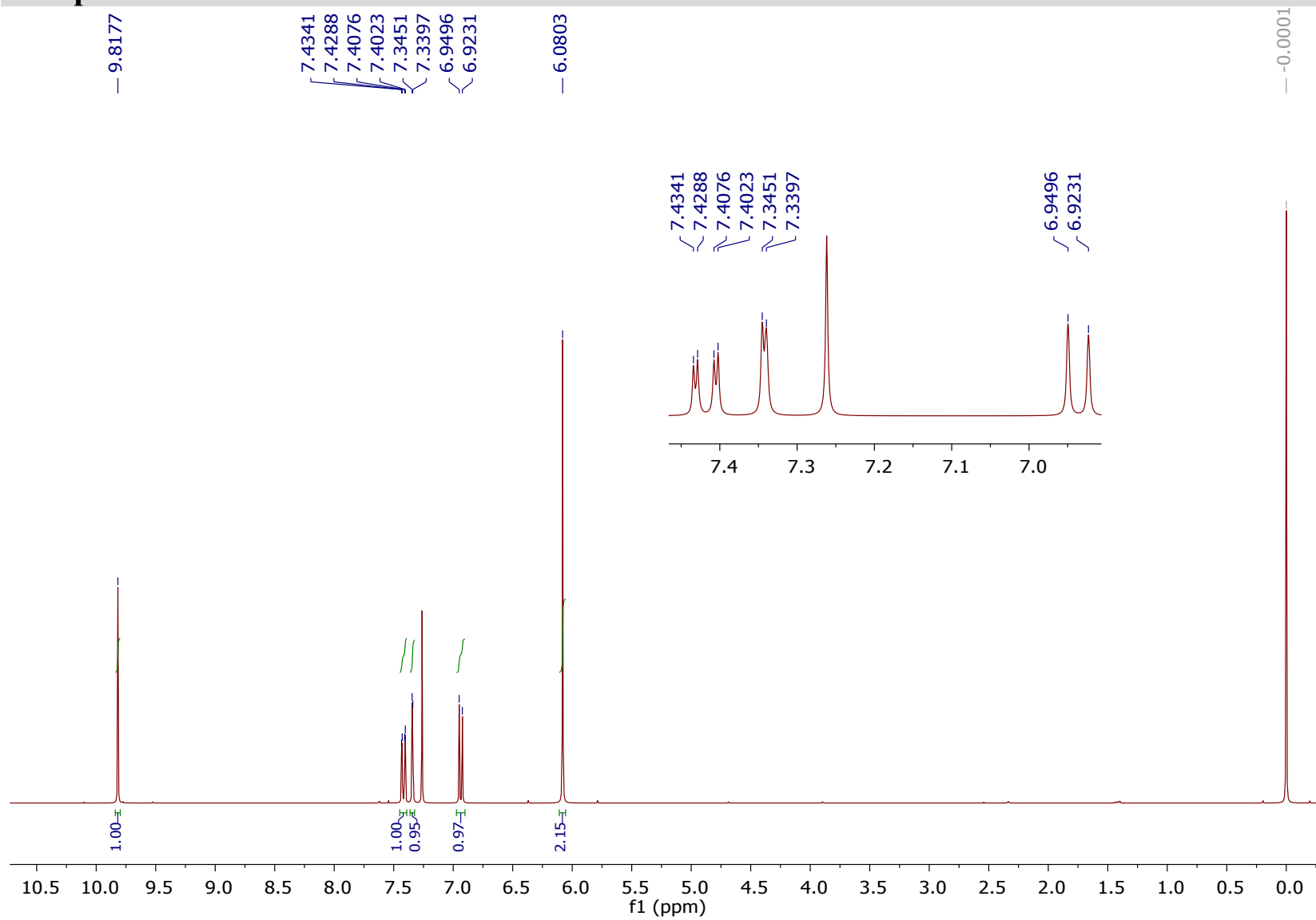
Compound 4c



[57]



Compound 4d



[59]

77.25 cdcl3
76.99 cdcl3
76.74 cdcl3

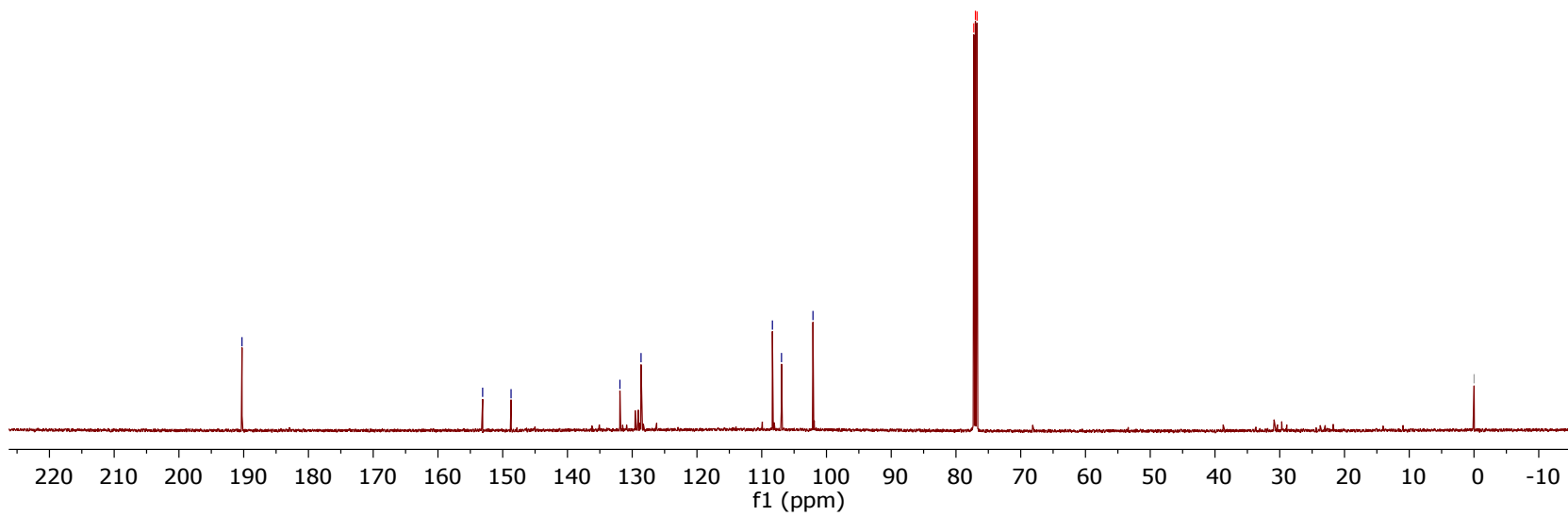
190.26

153.10
148.71

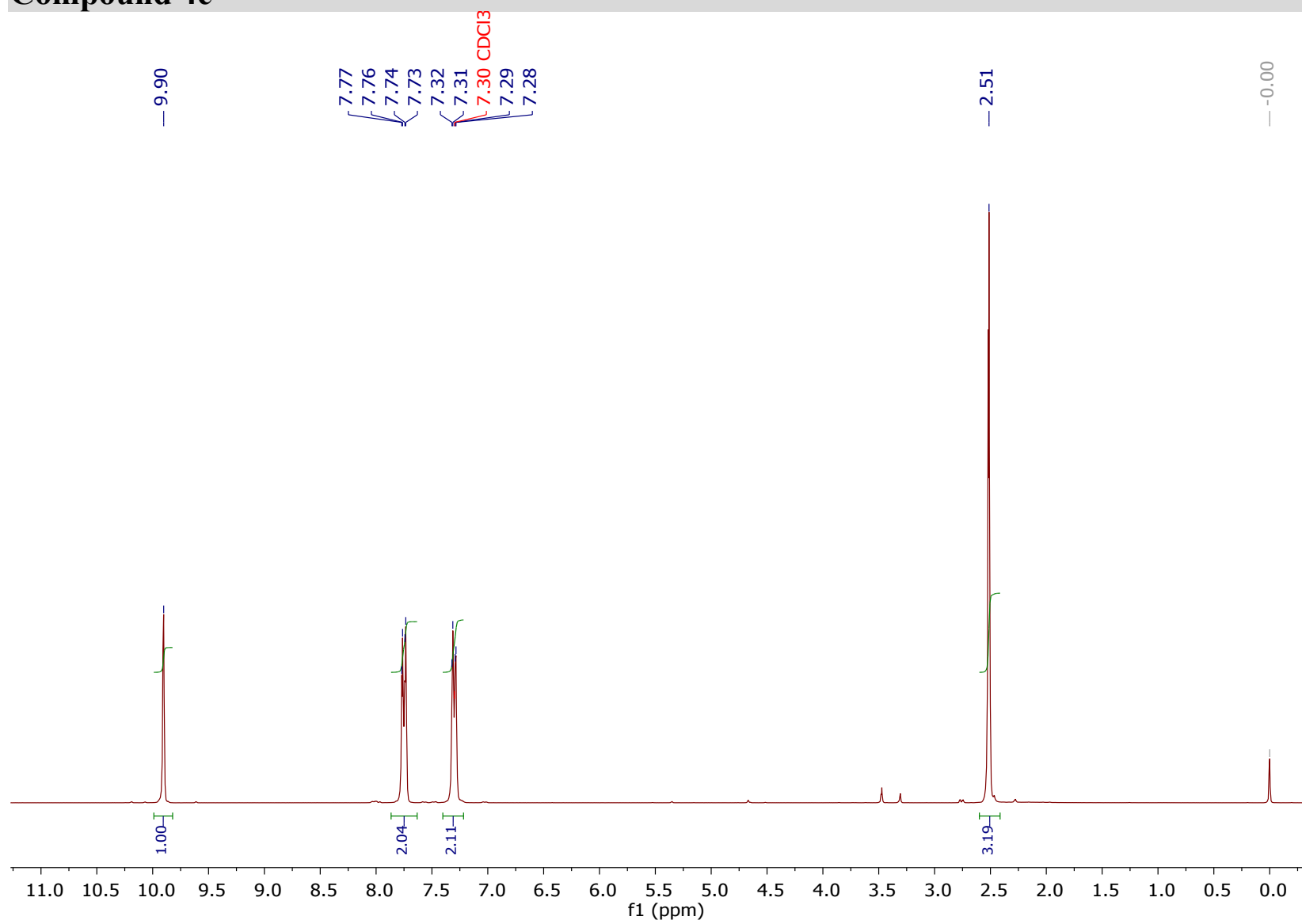
131.90
128.63

108.35
106.94
102.09

-0.02



Compound 4e



[61]

77.44 cdcl3
77.18 cdcl3
76.93 cdcl3

191.18

147.89

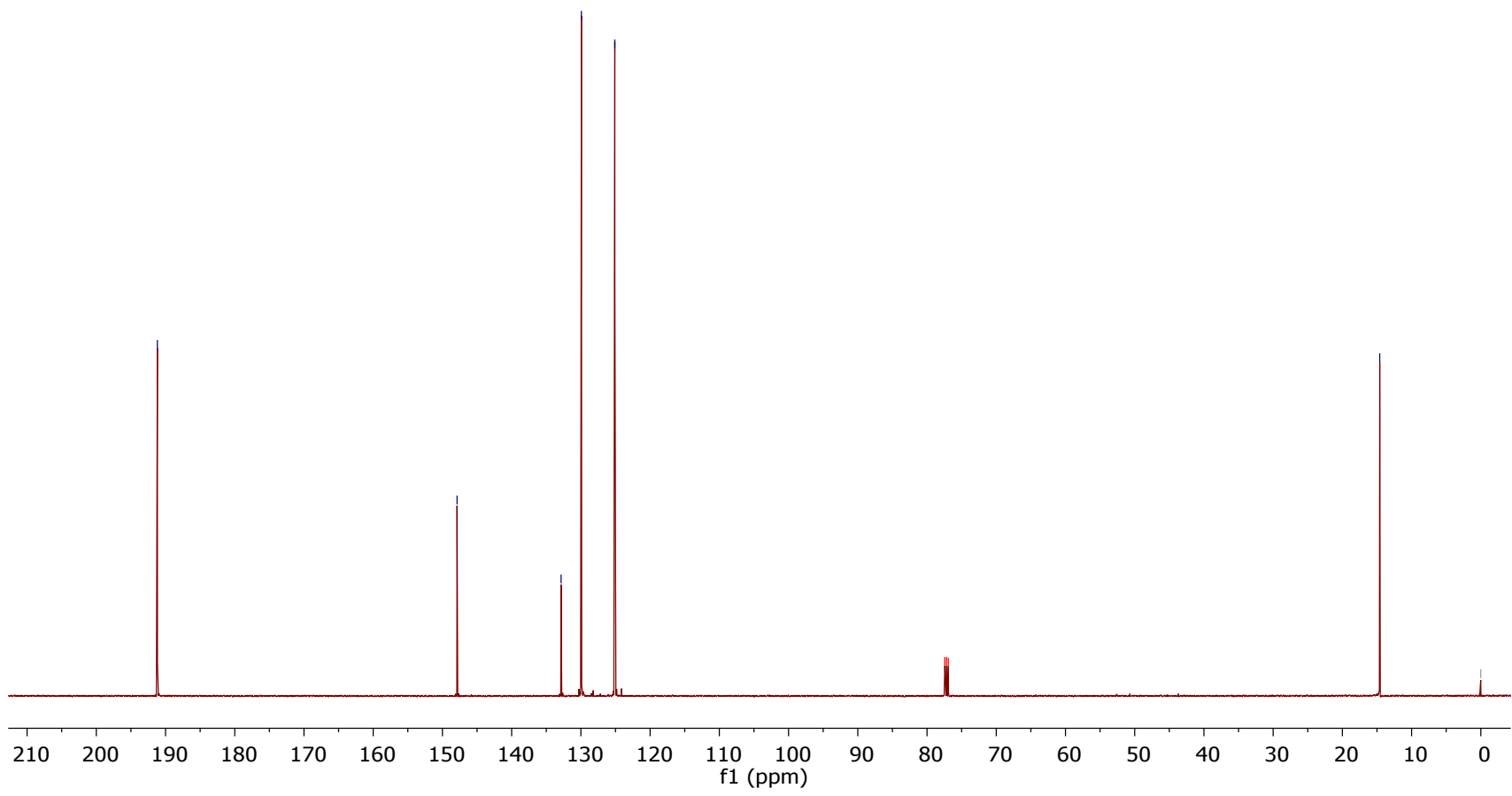
132.86

129.93

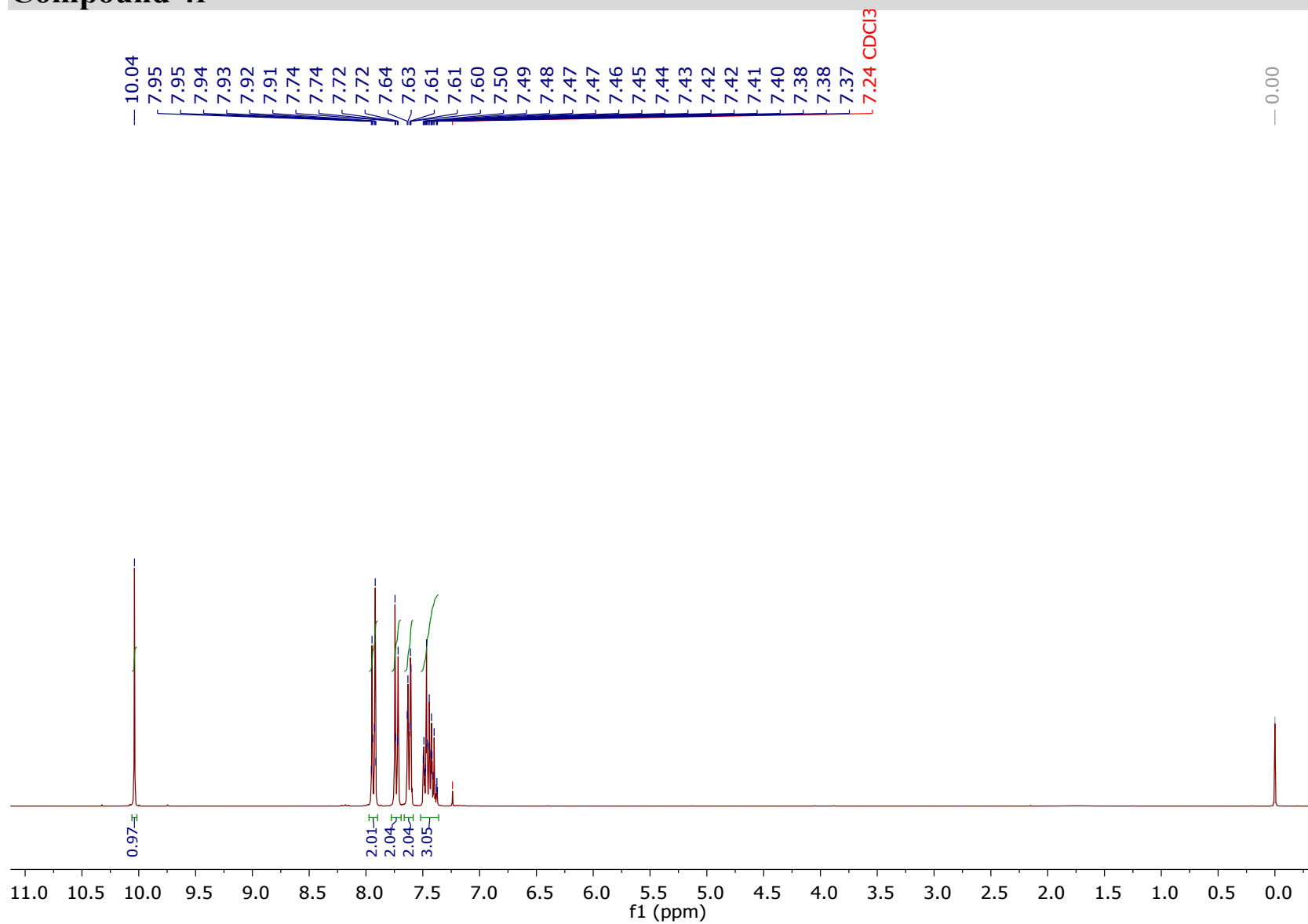
125.10

14.60

0.01



Compound 4f



[63]

77.47 CDCl₃
77.05 CDCl₃
76.63 CDCl₃

-0.00

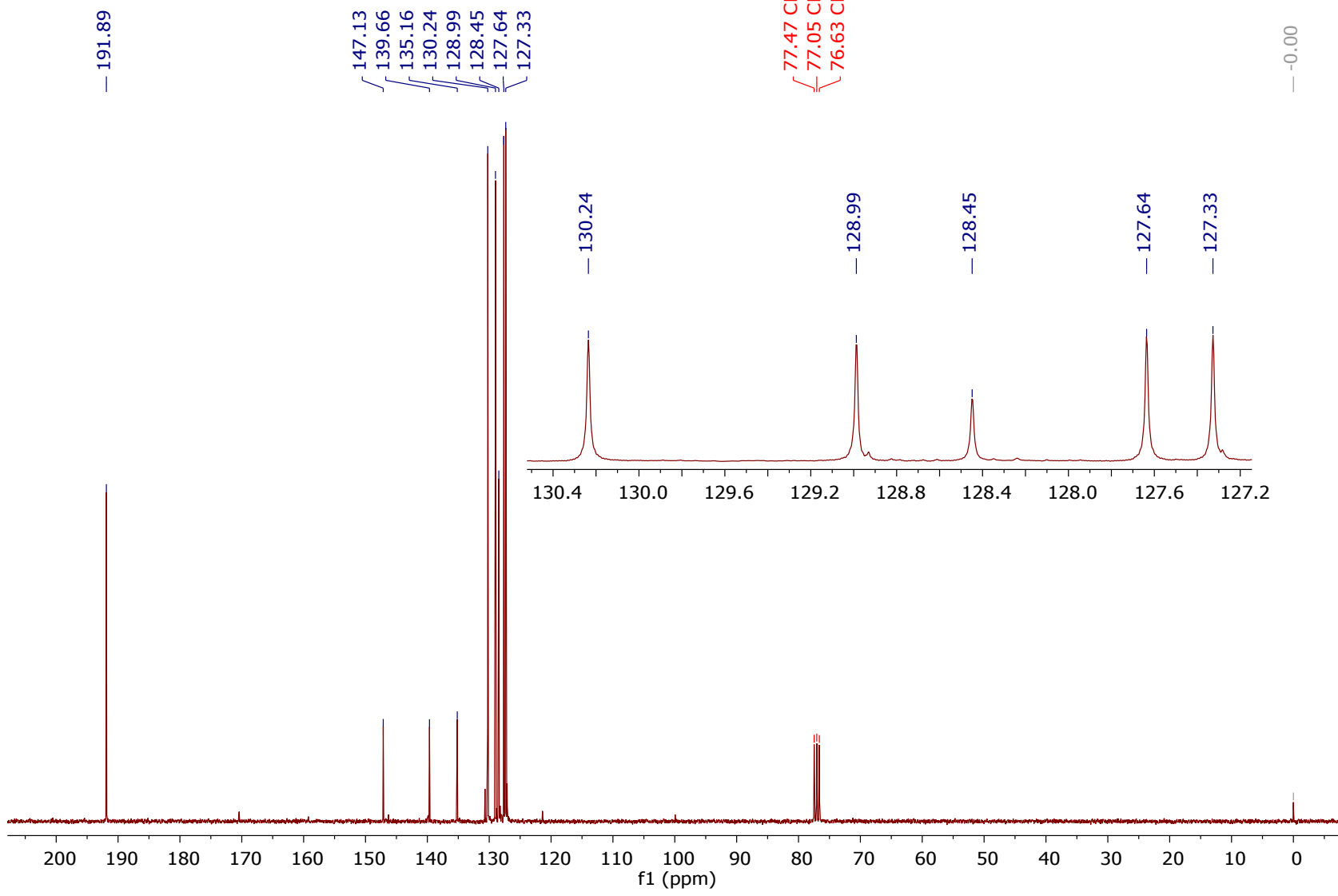
147.13
139.66
135.16
130.24
128.99
128.45
127.64
127.33

191.89

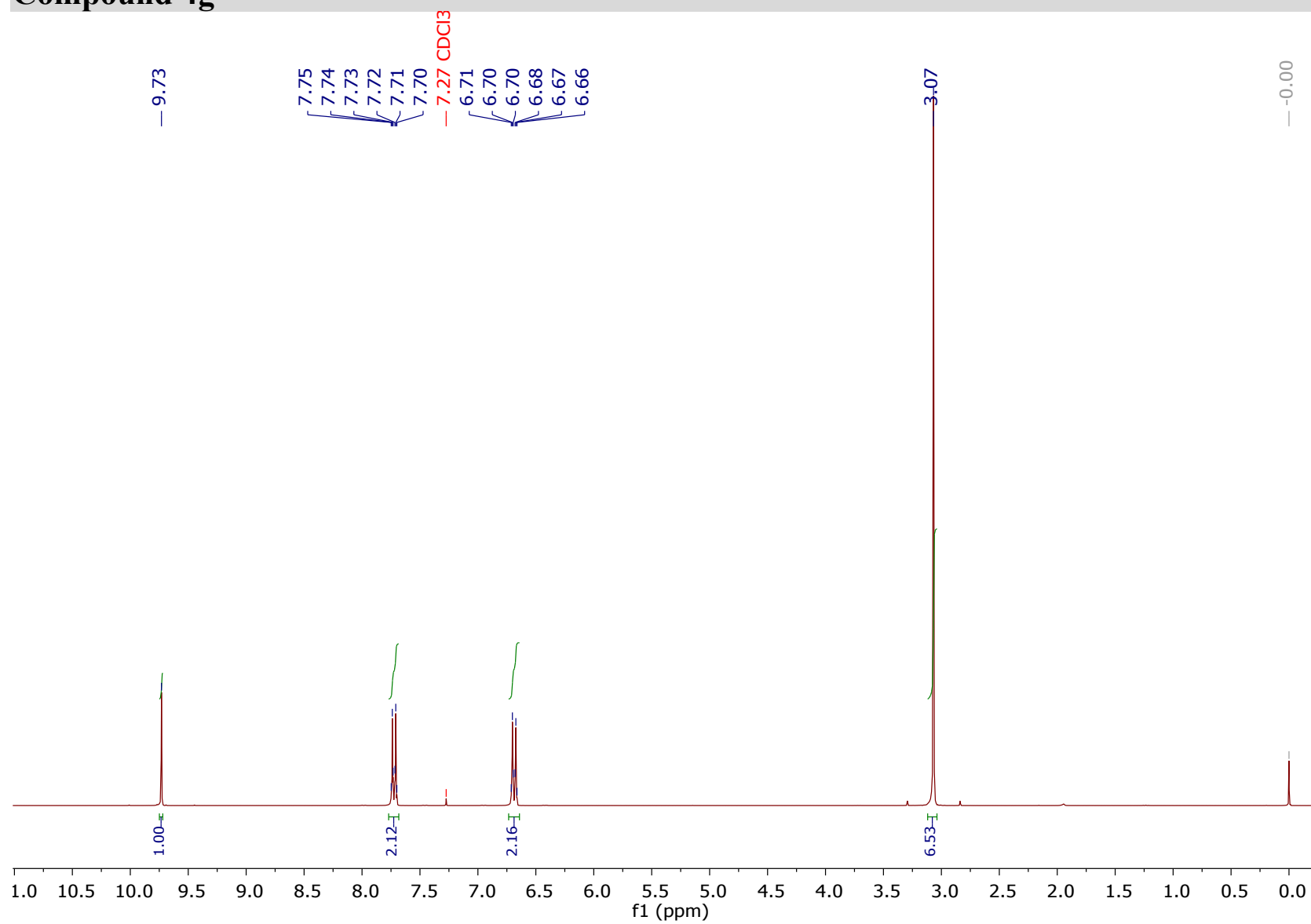
130.24
128.99
128.45
127.64
127.33

130.4 130.0 129.6 129.2 128.8 128.4 128.0 127.6 127.2

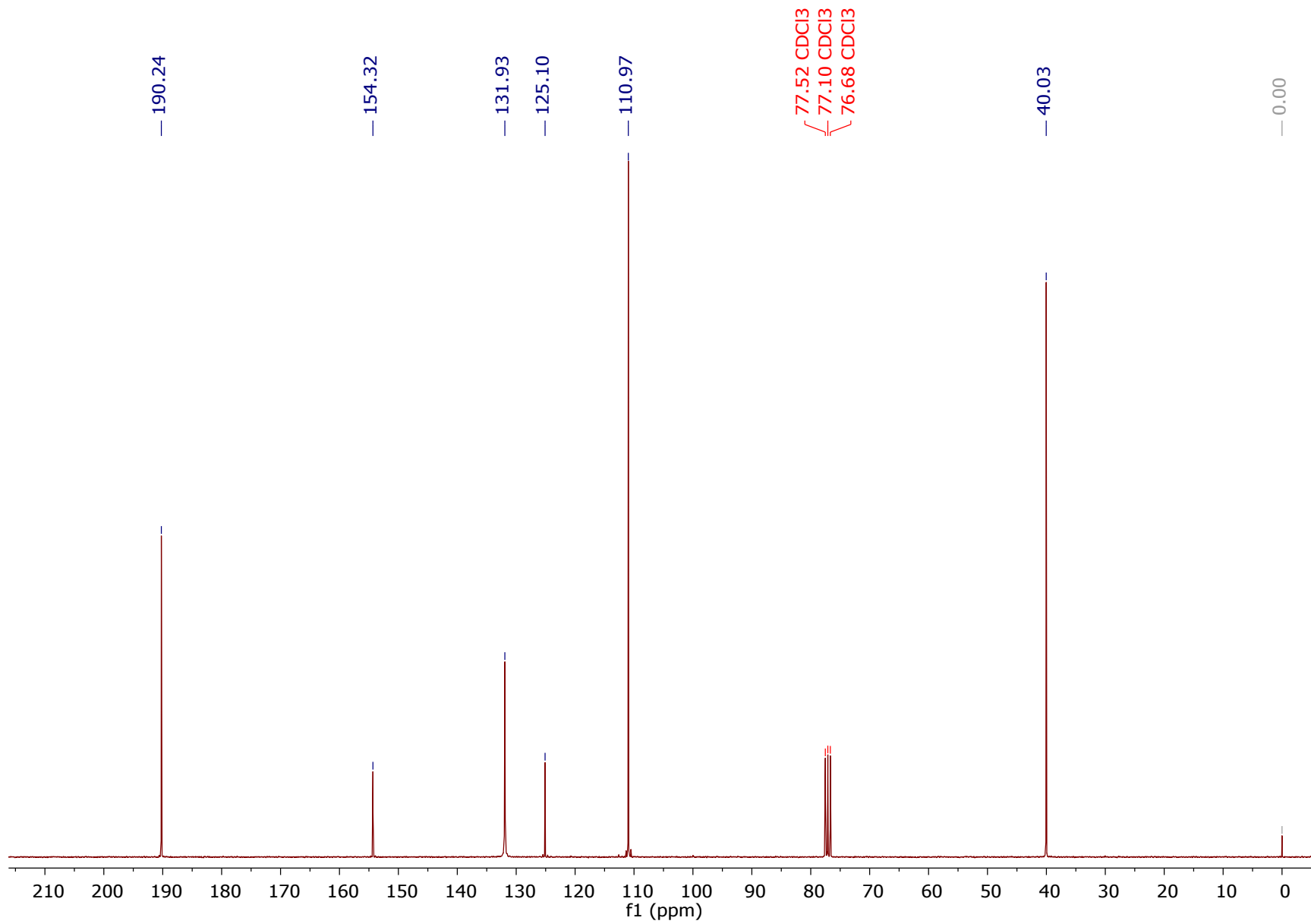
f1 (ppm)



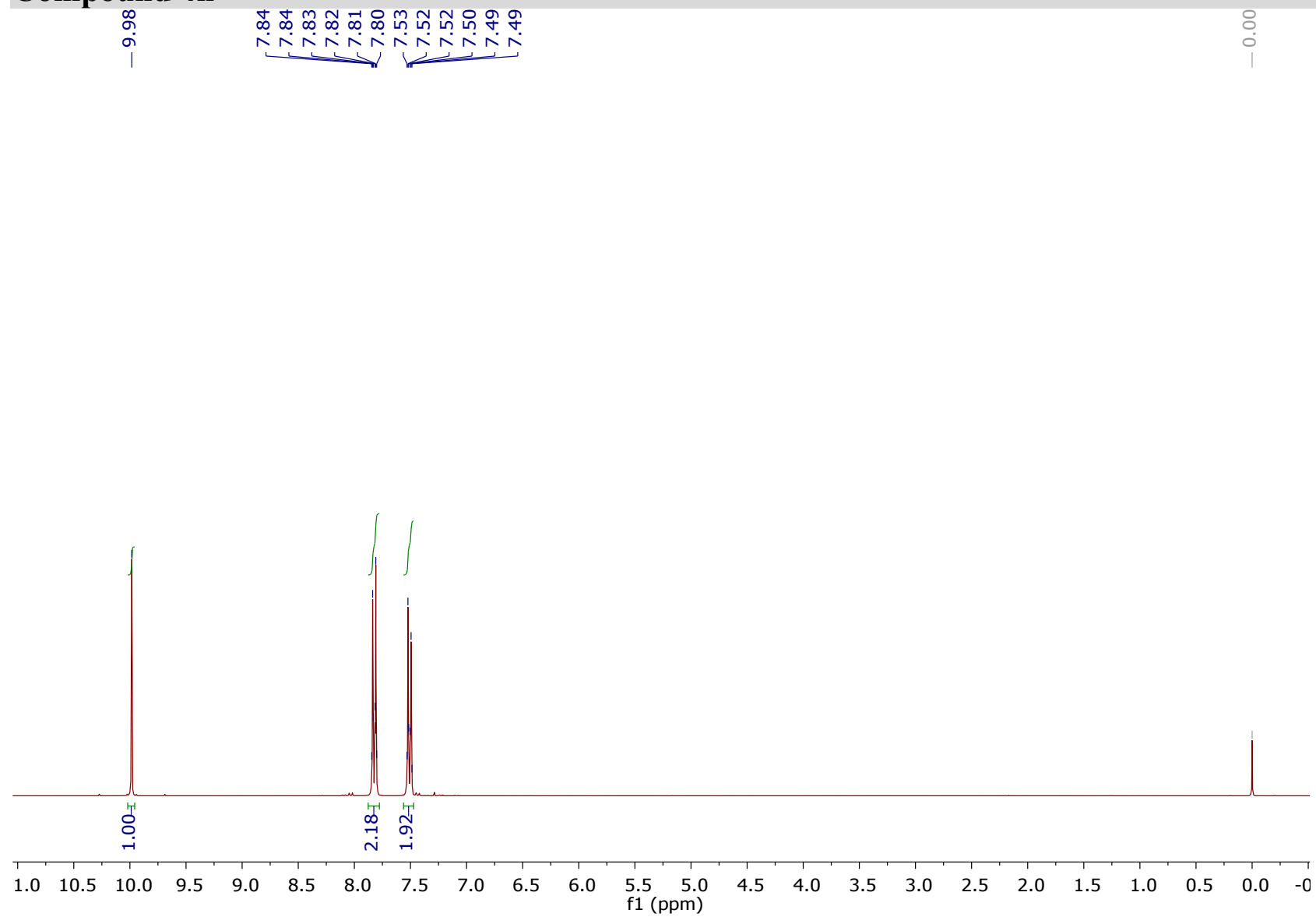
Compound 4g



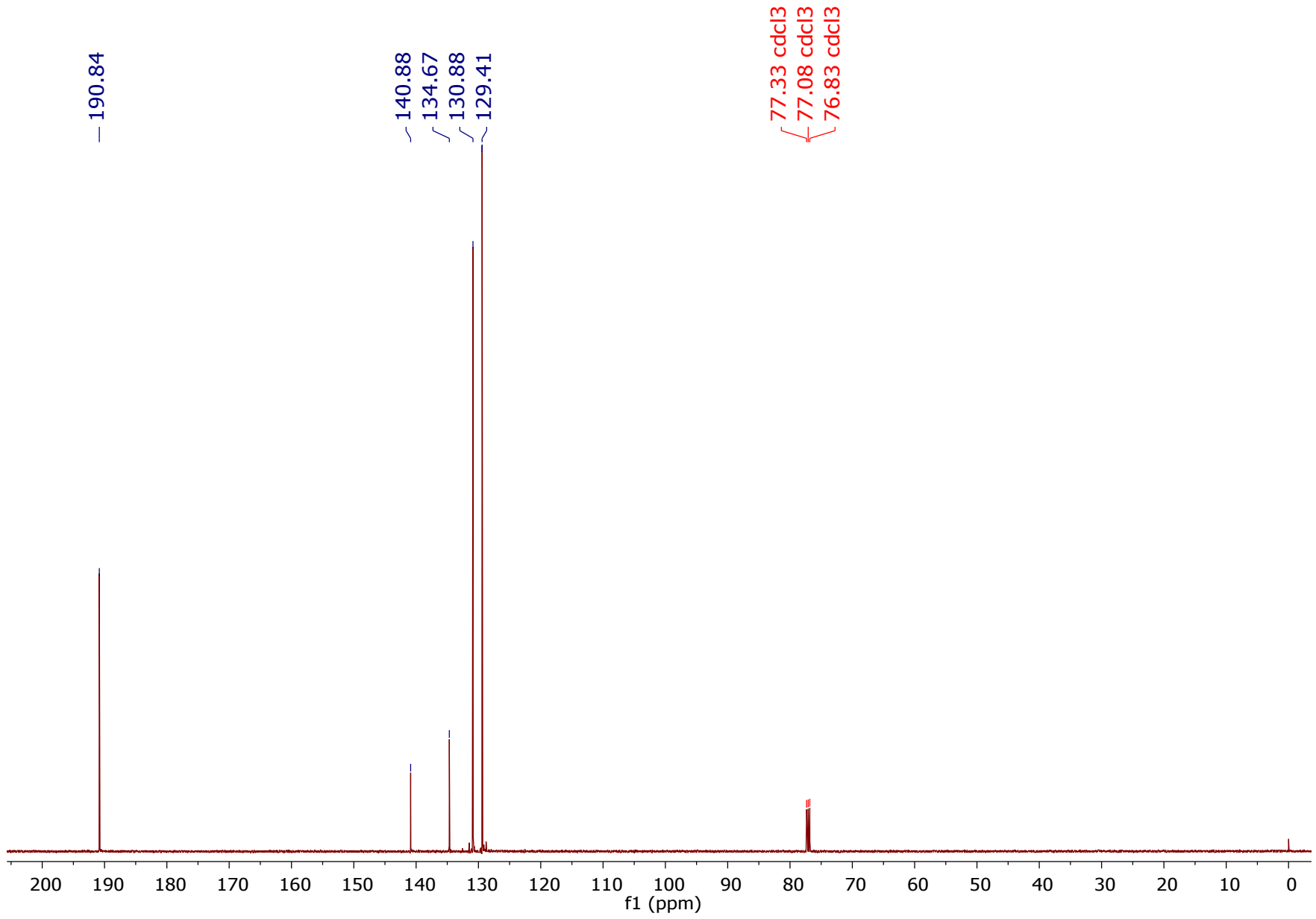
[65]



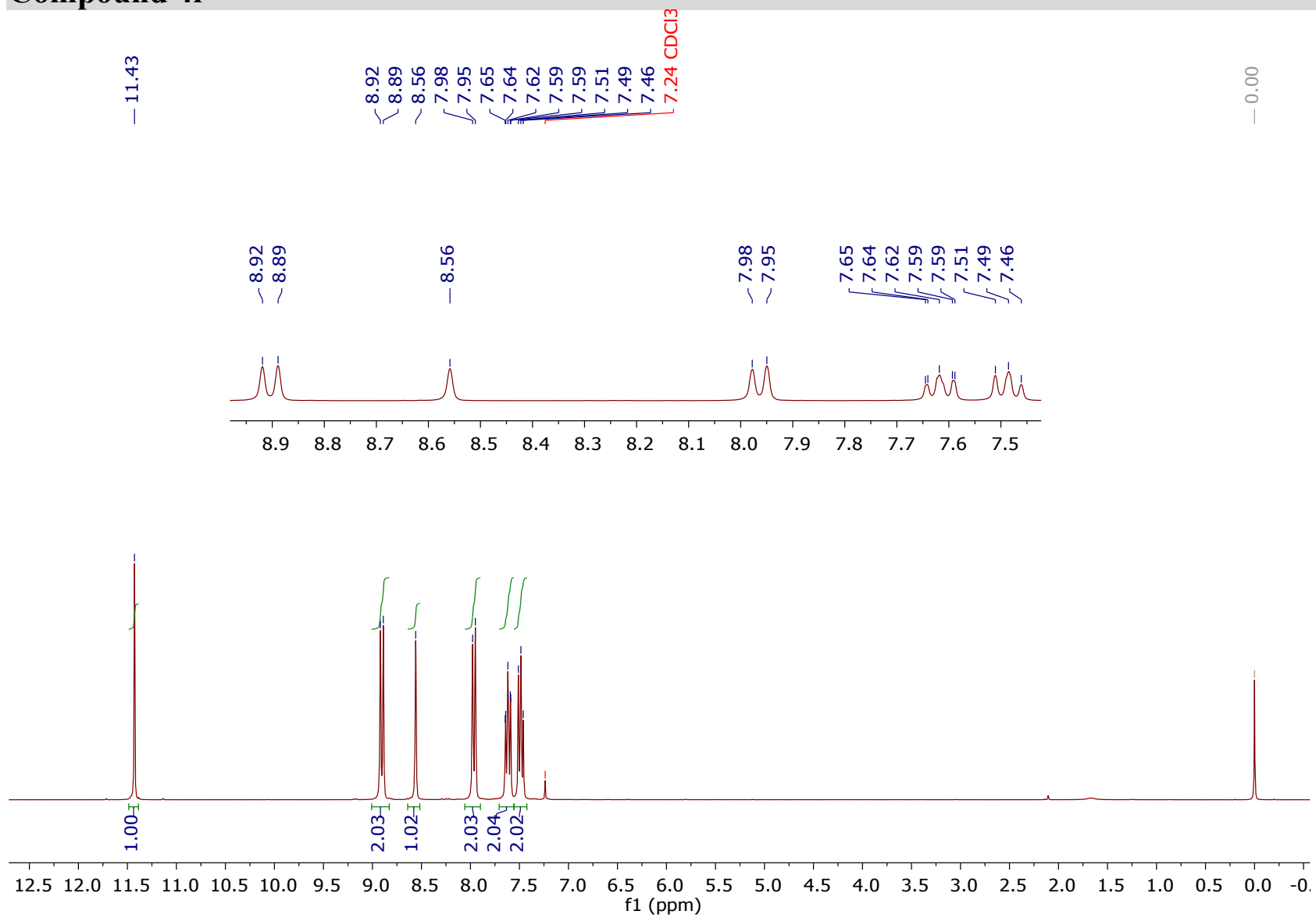
Compound 4h



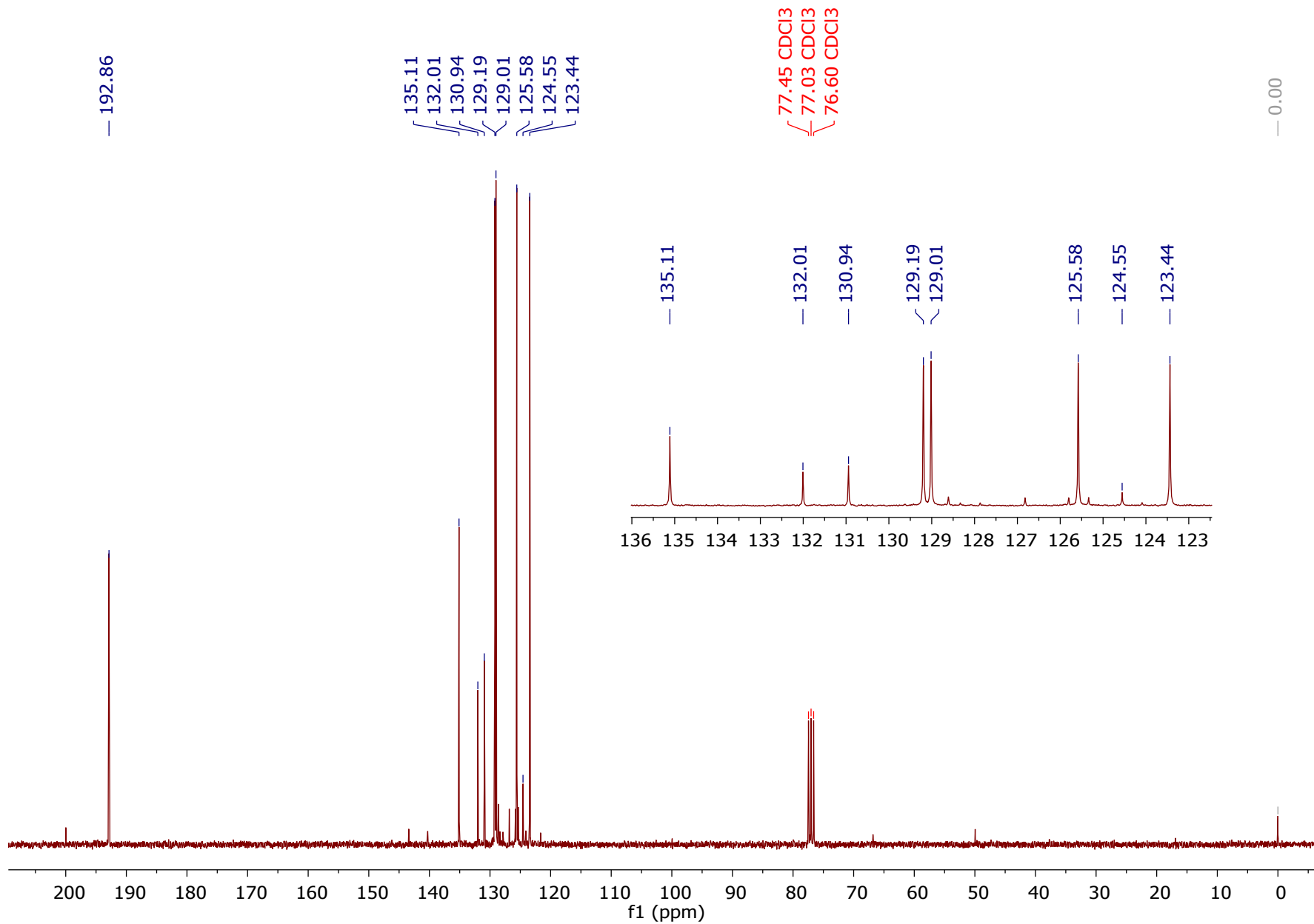
[67]



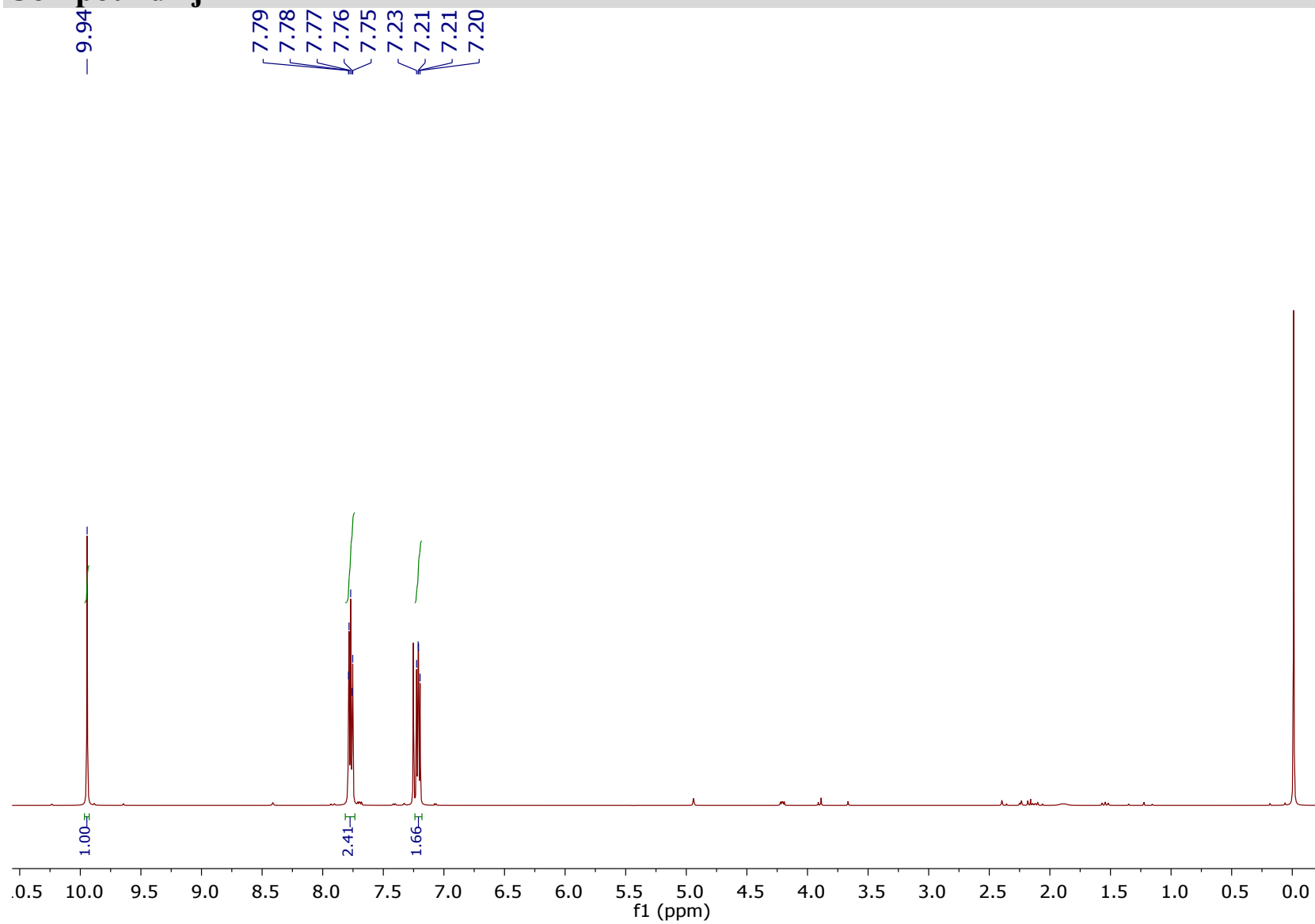
Compound 4i

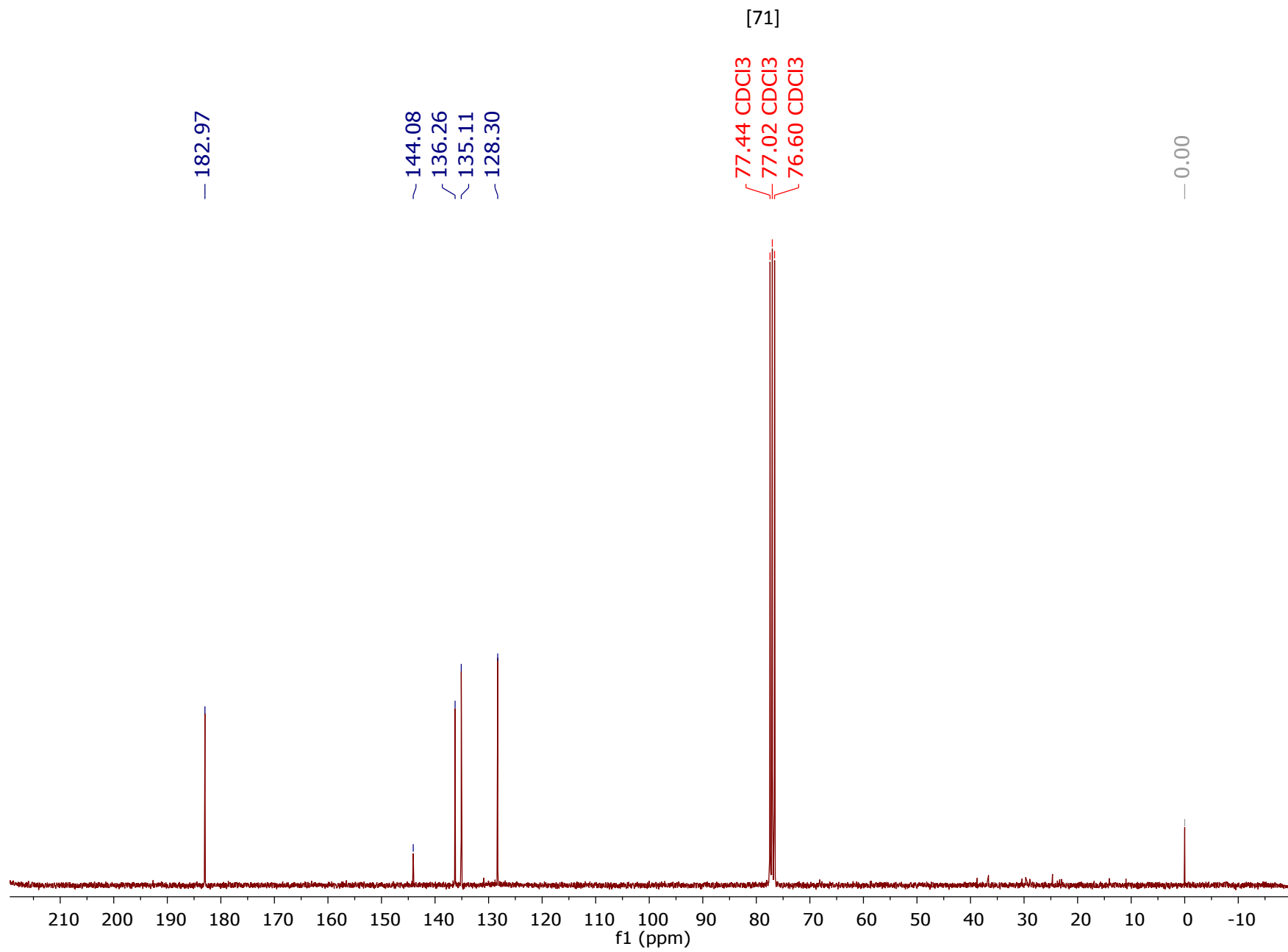


[69]

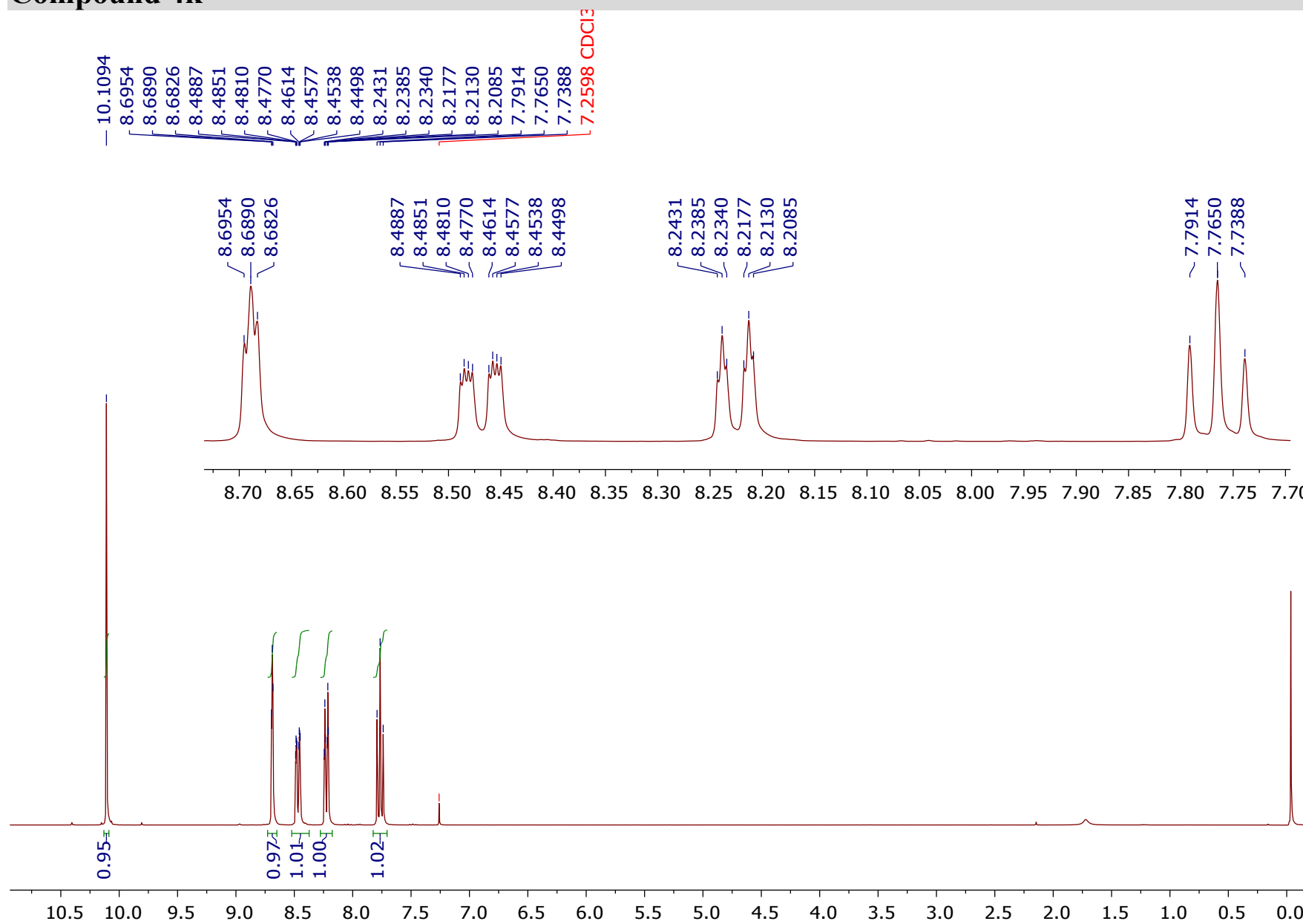


Compound 4j

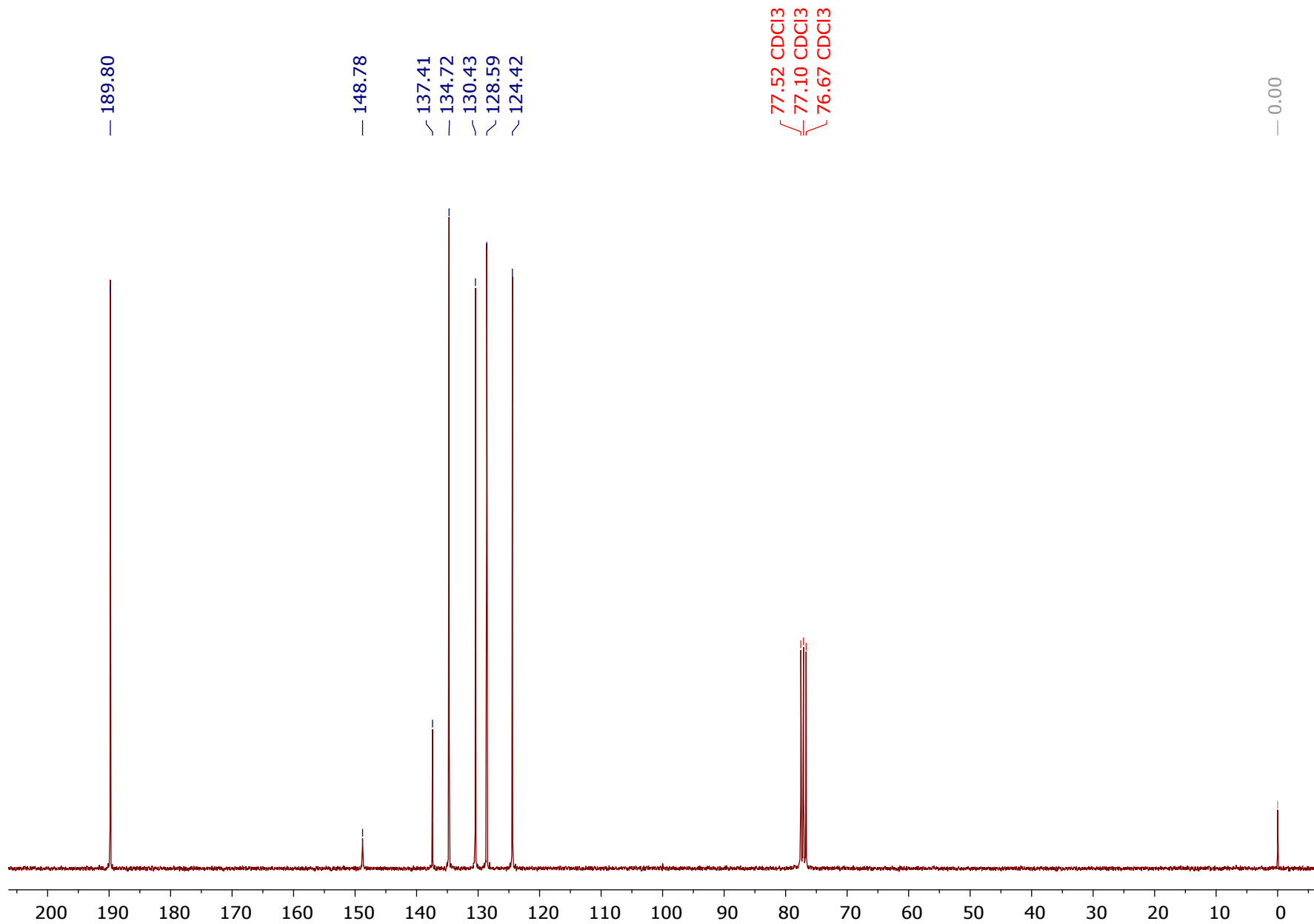




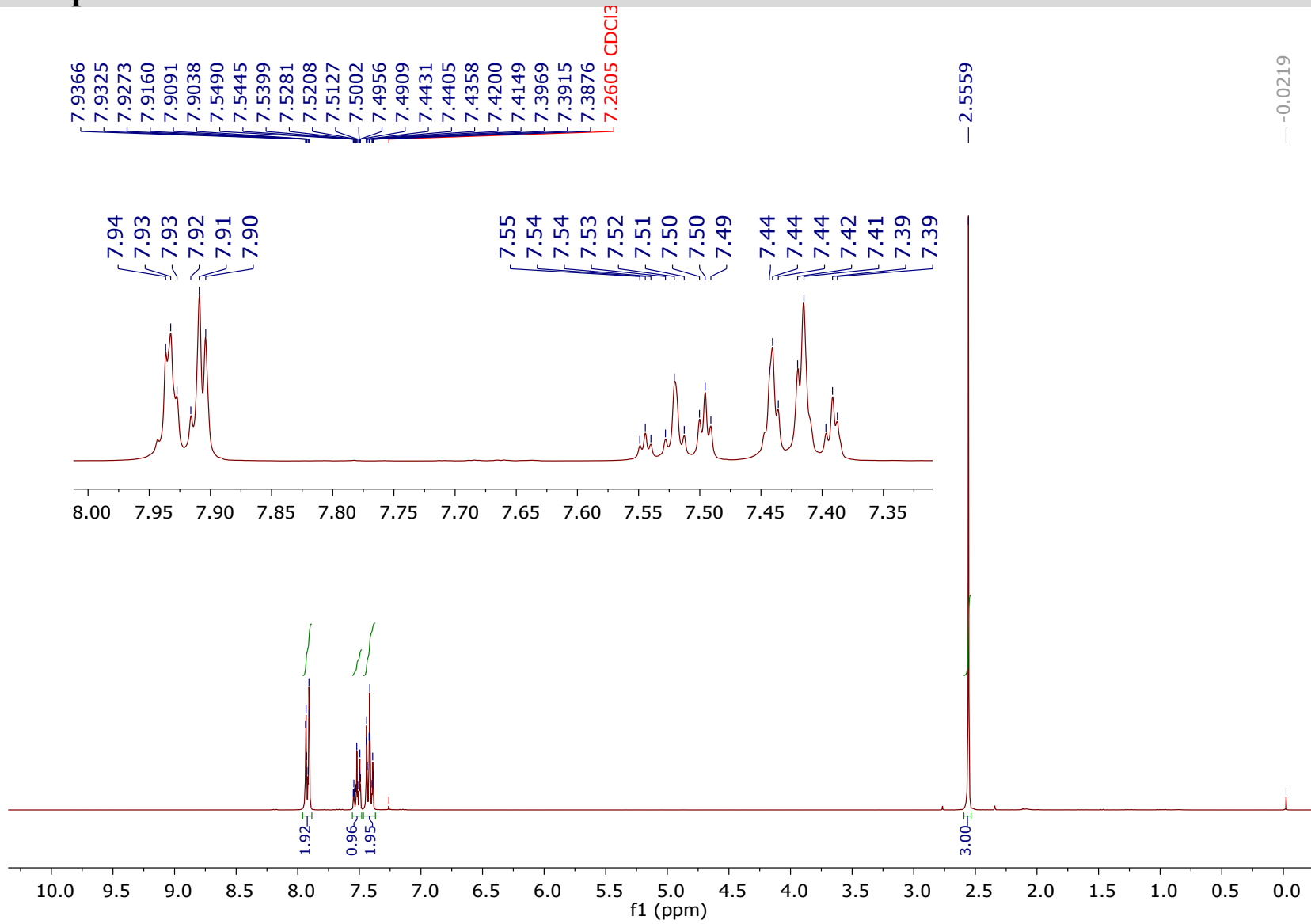
Compound 4k



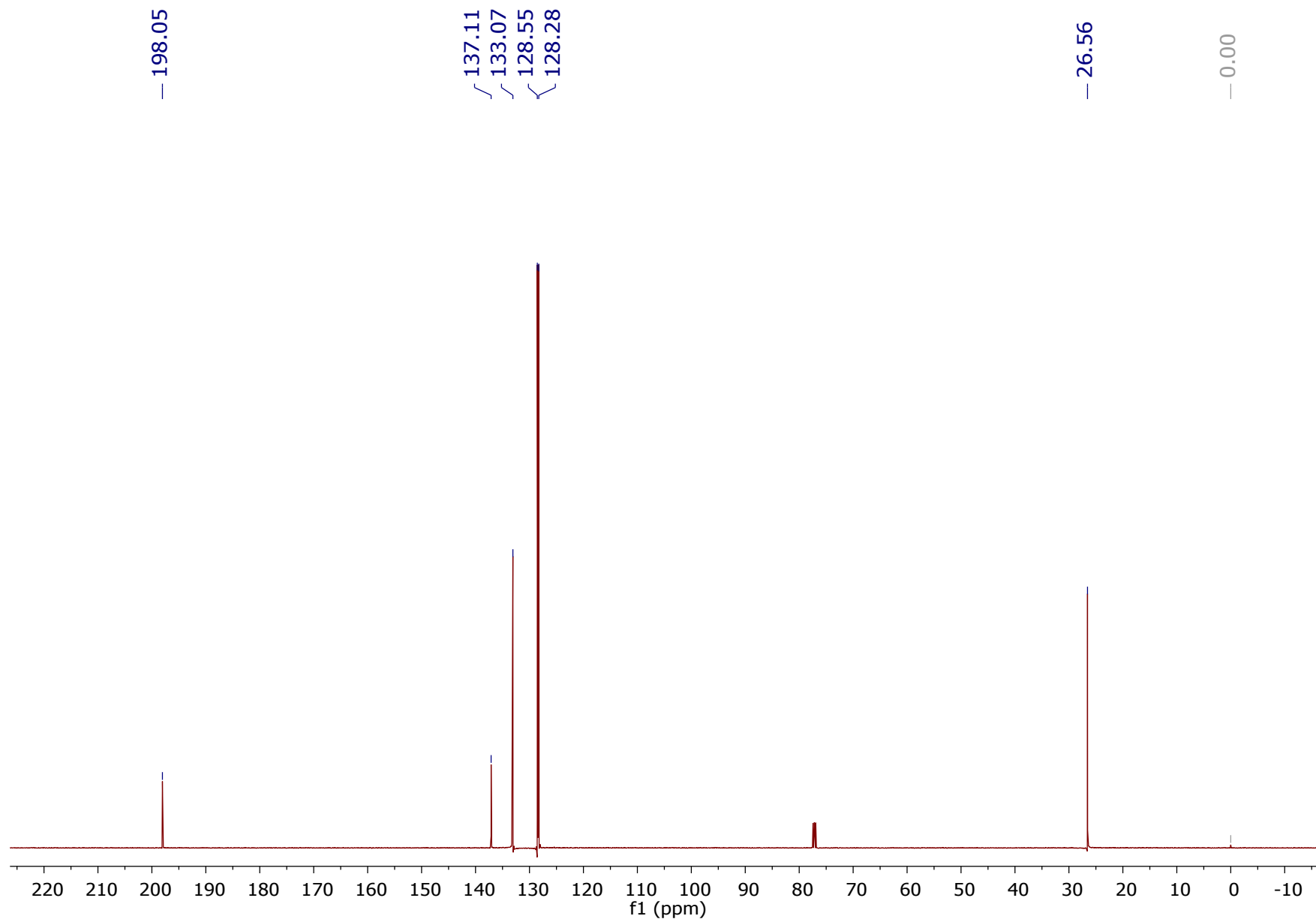
[73]



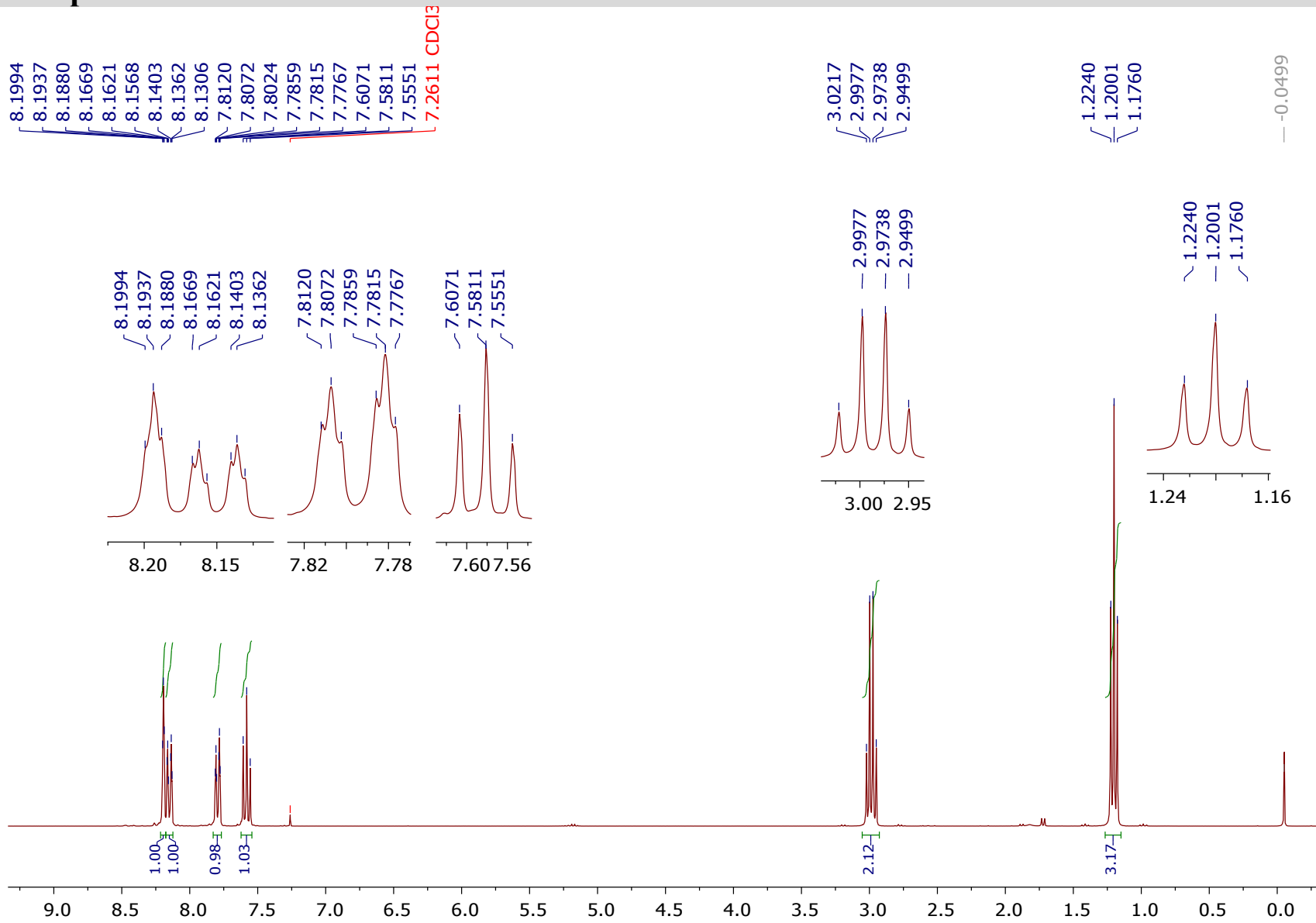
Compound 6a



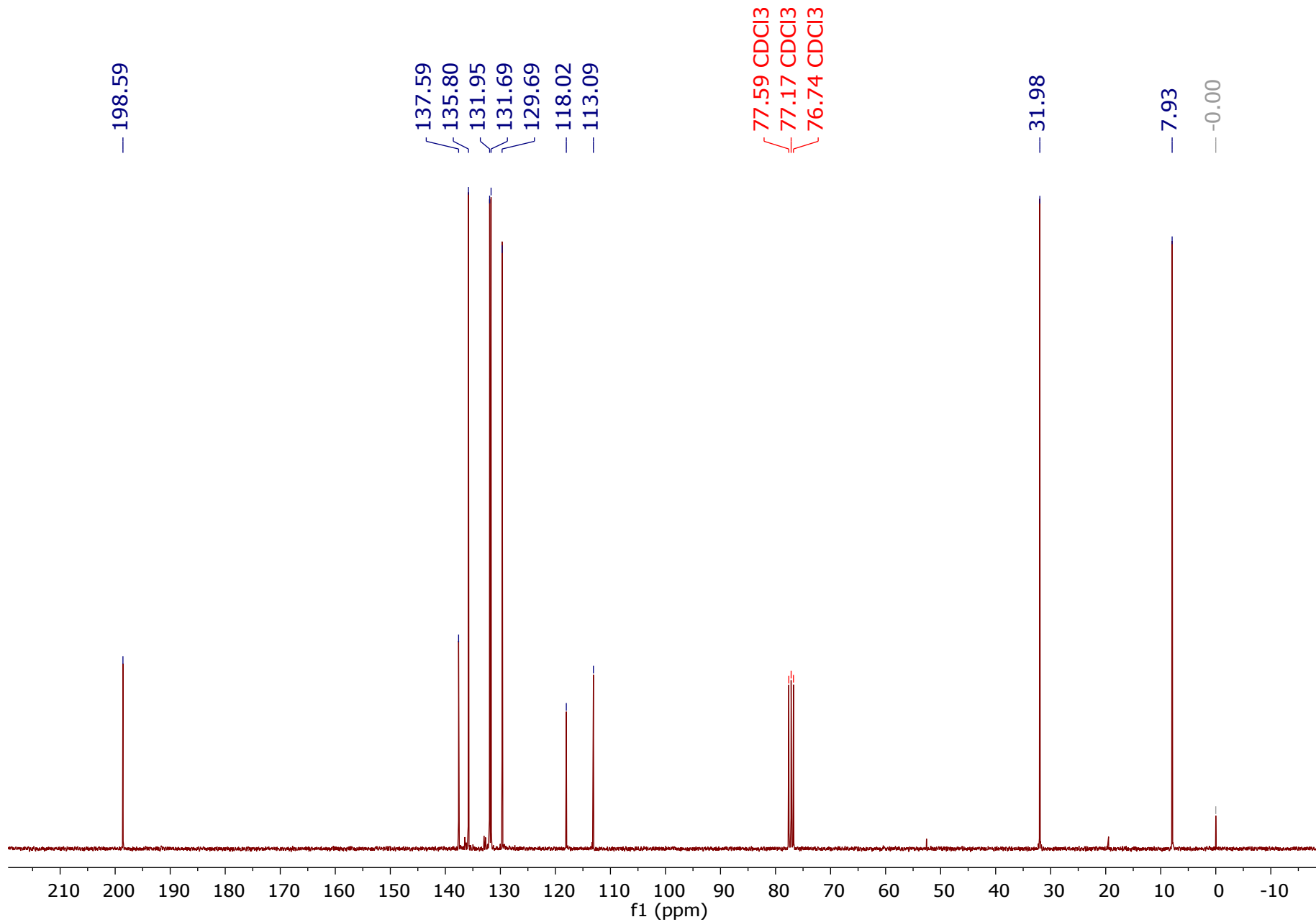
[75]



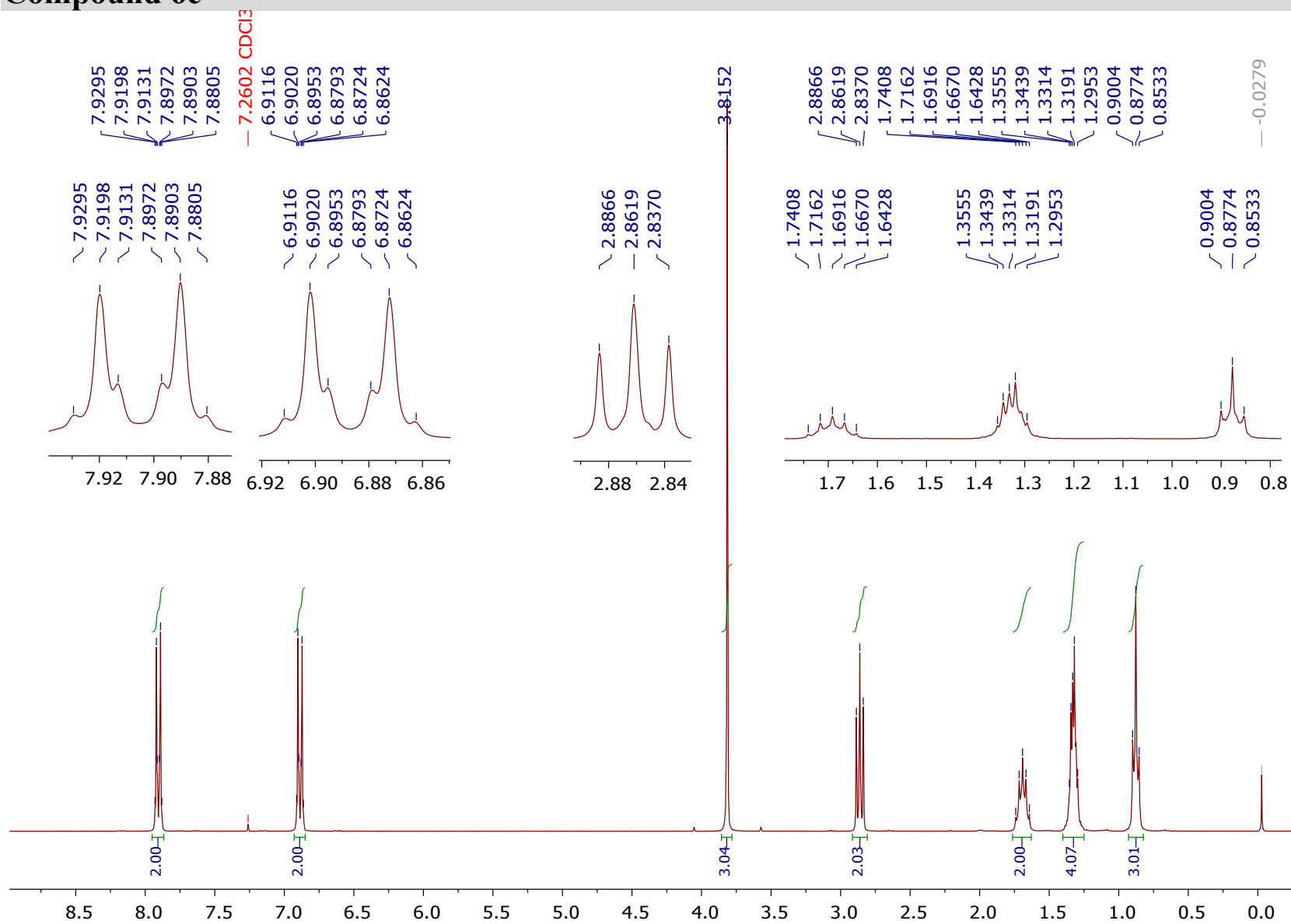
Compound 6b



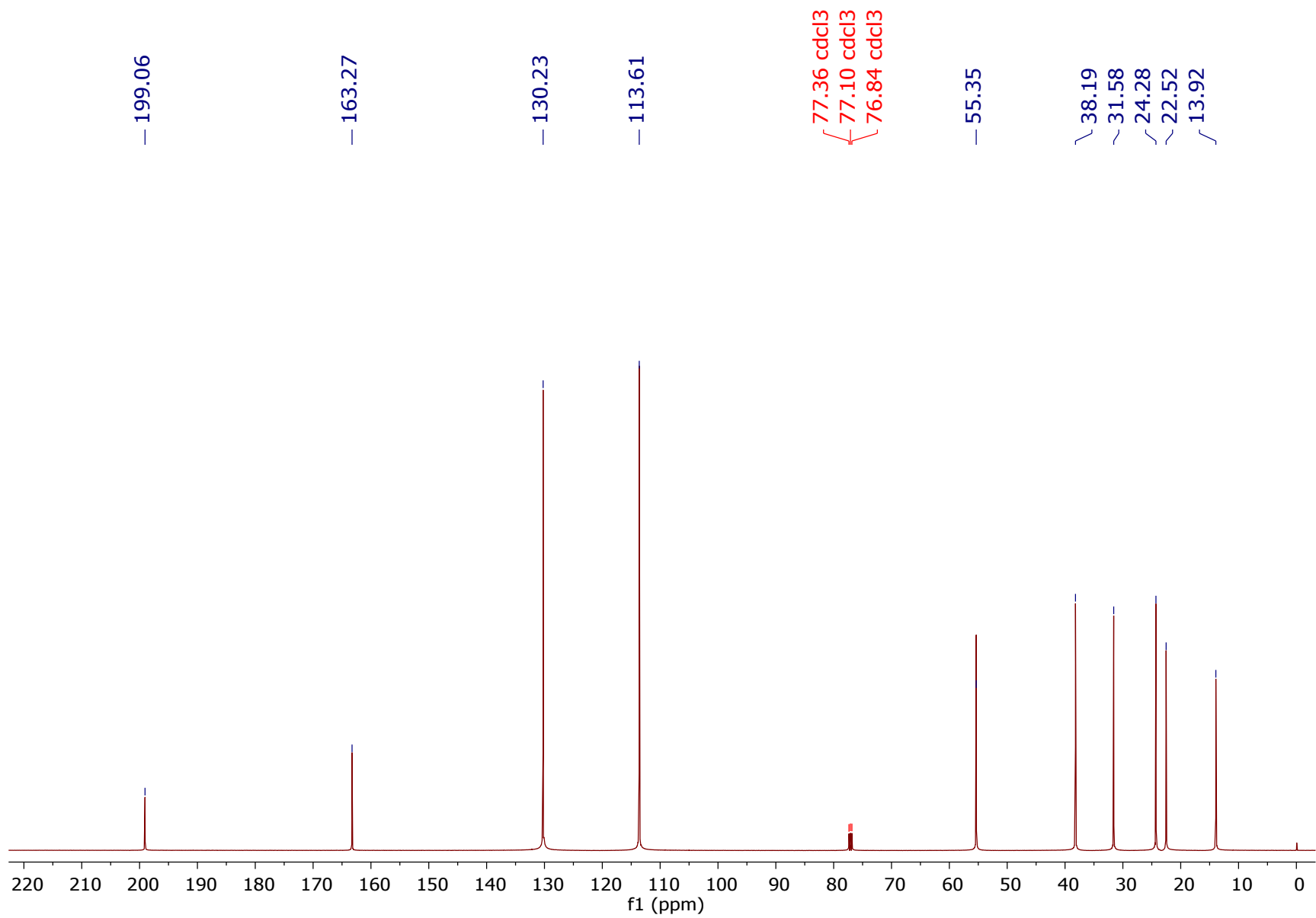
[77]



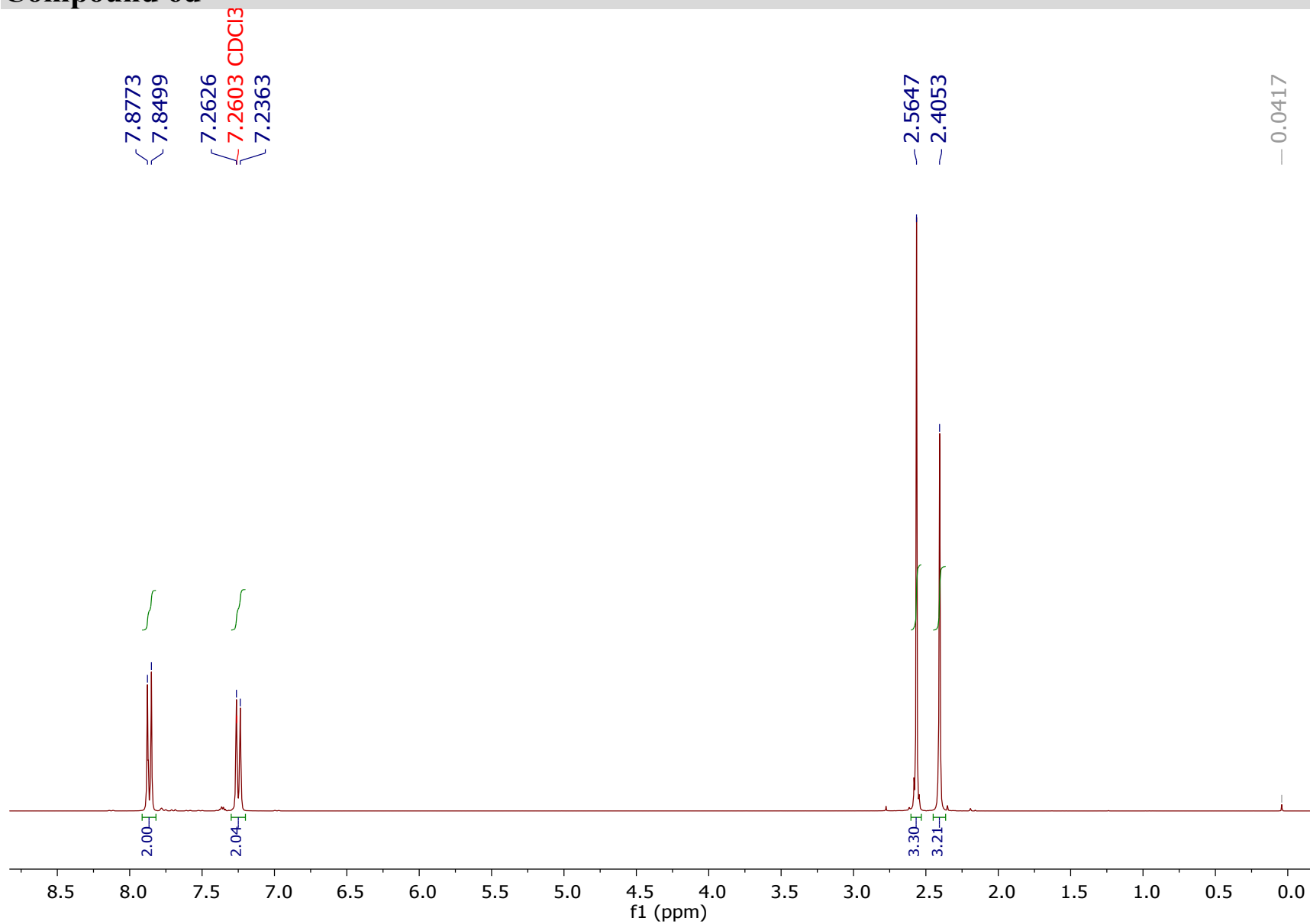
Compound 6c



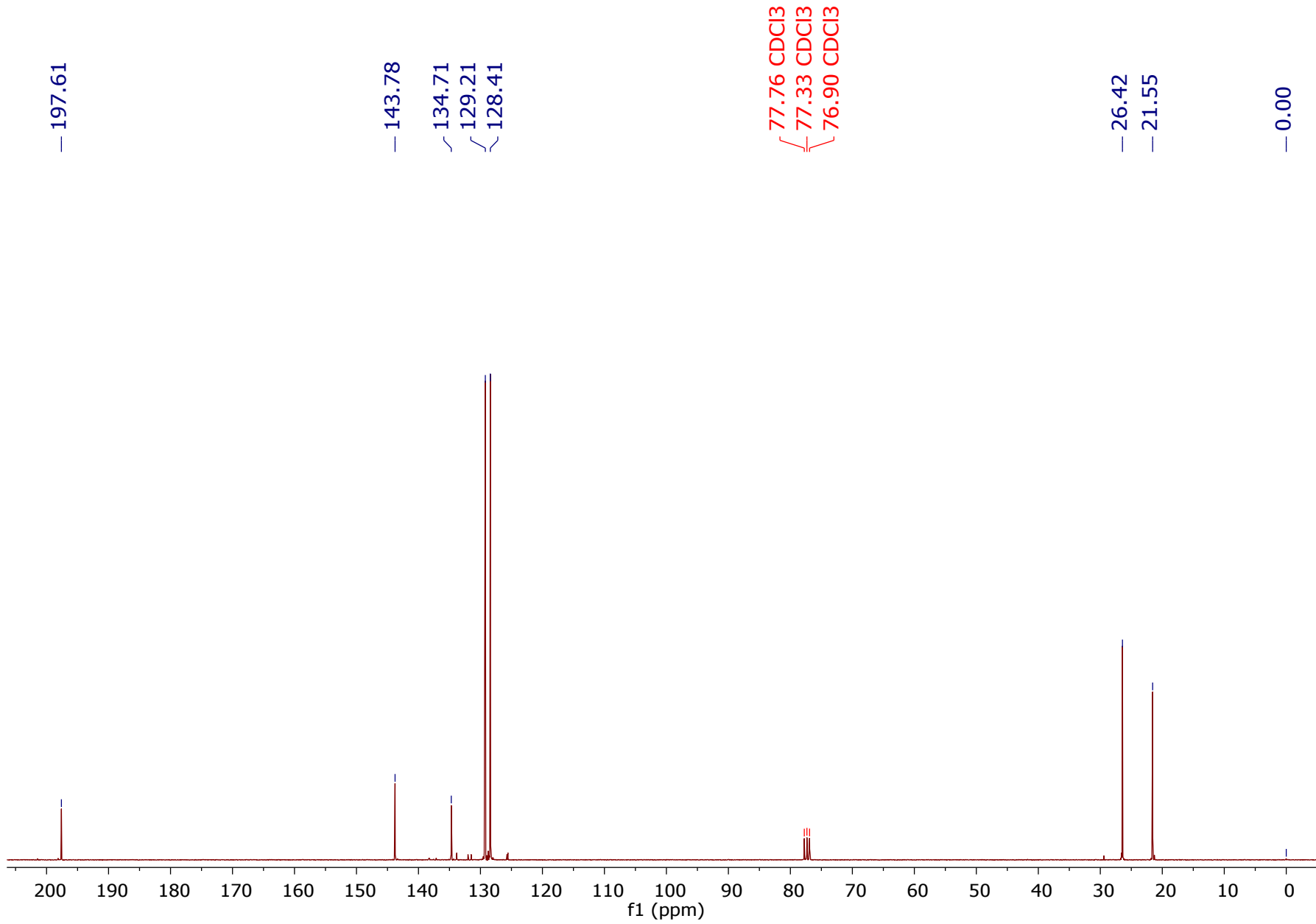
[79]



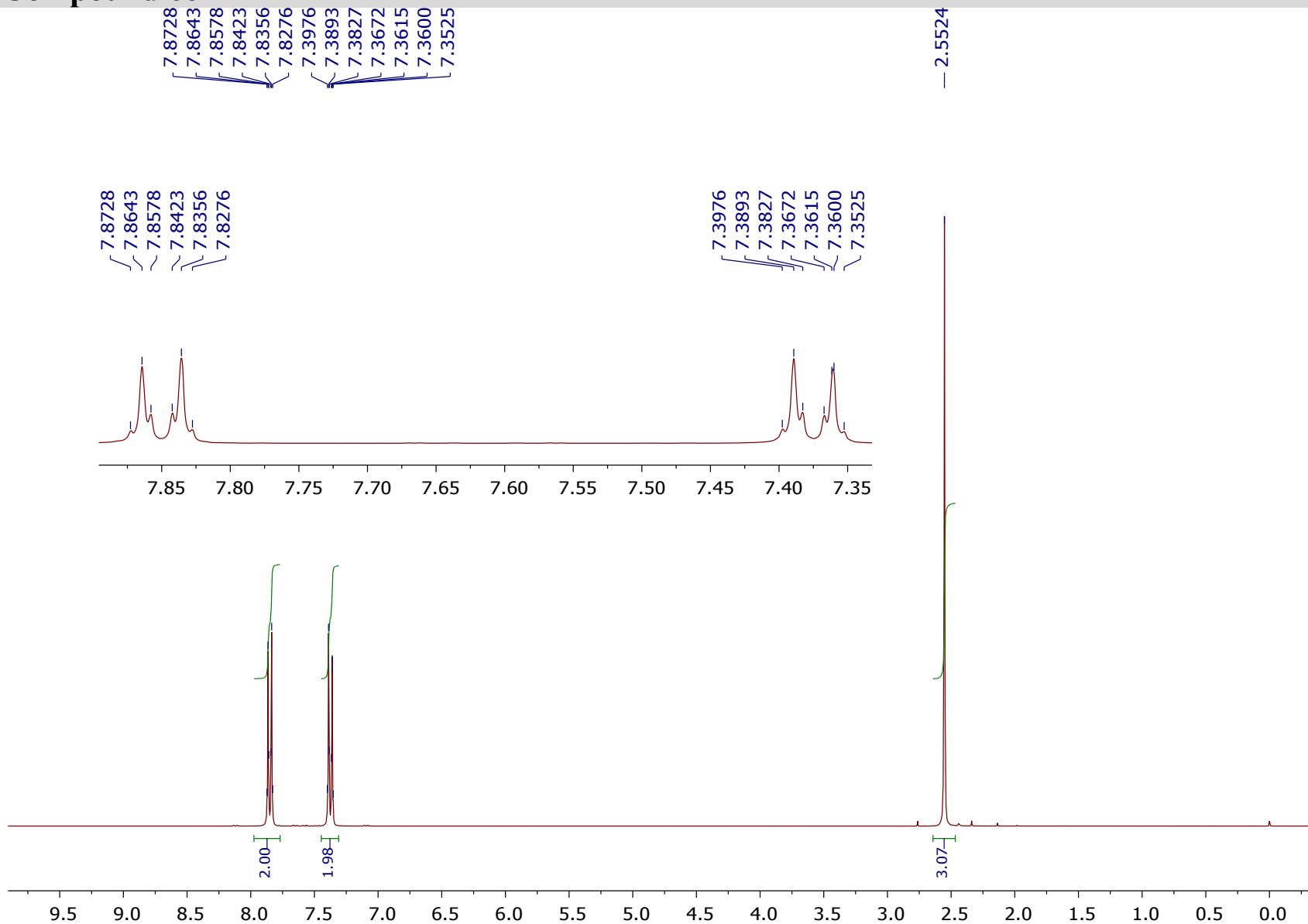
Compound 6d



[81]



Compound 6e



[83]

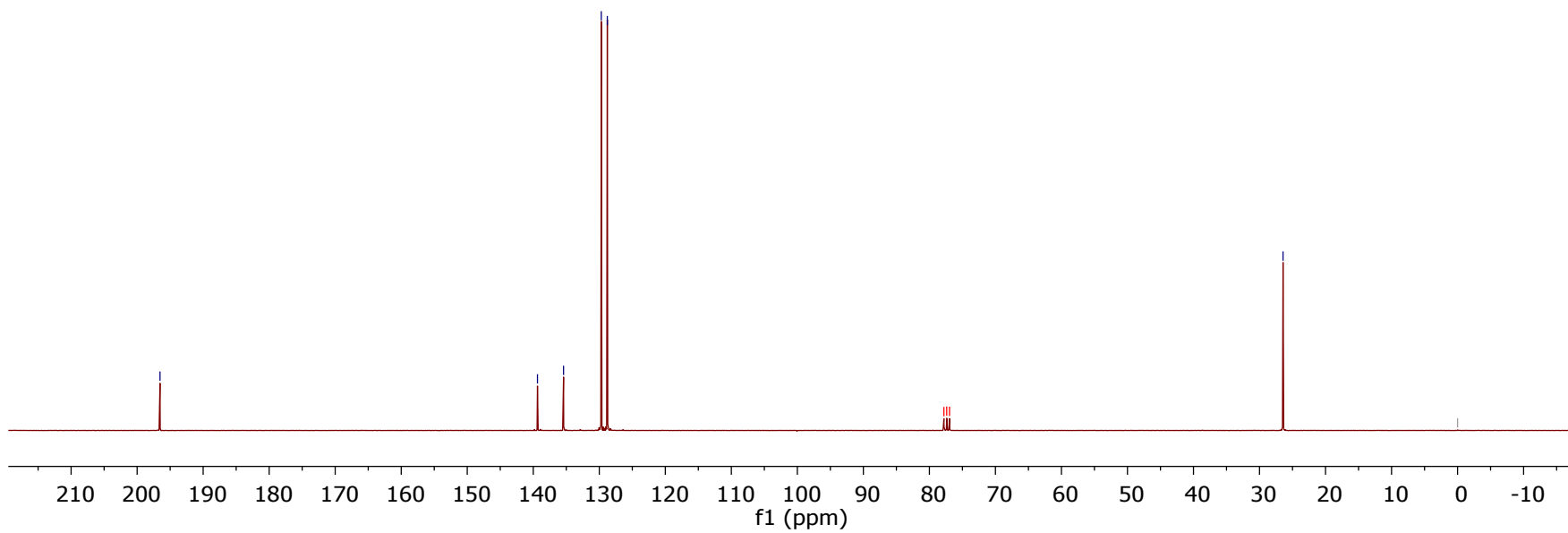
77.80 CDCI3
77.38 CDCI3
76.95 CDCI3

196.54

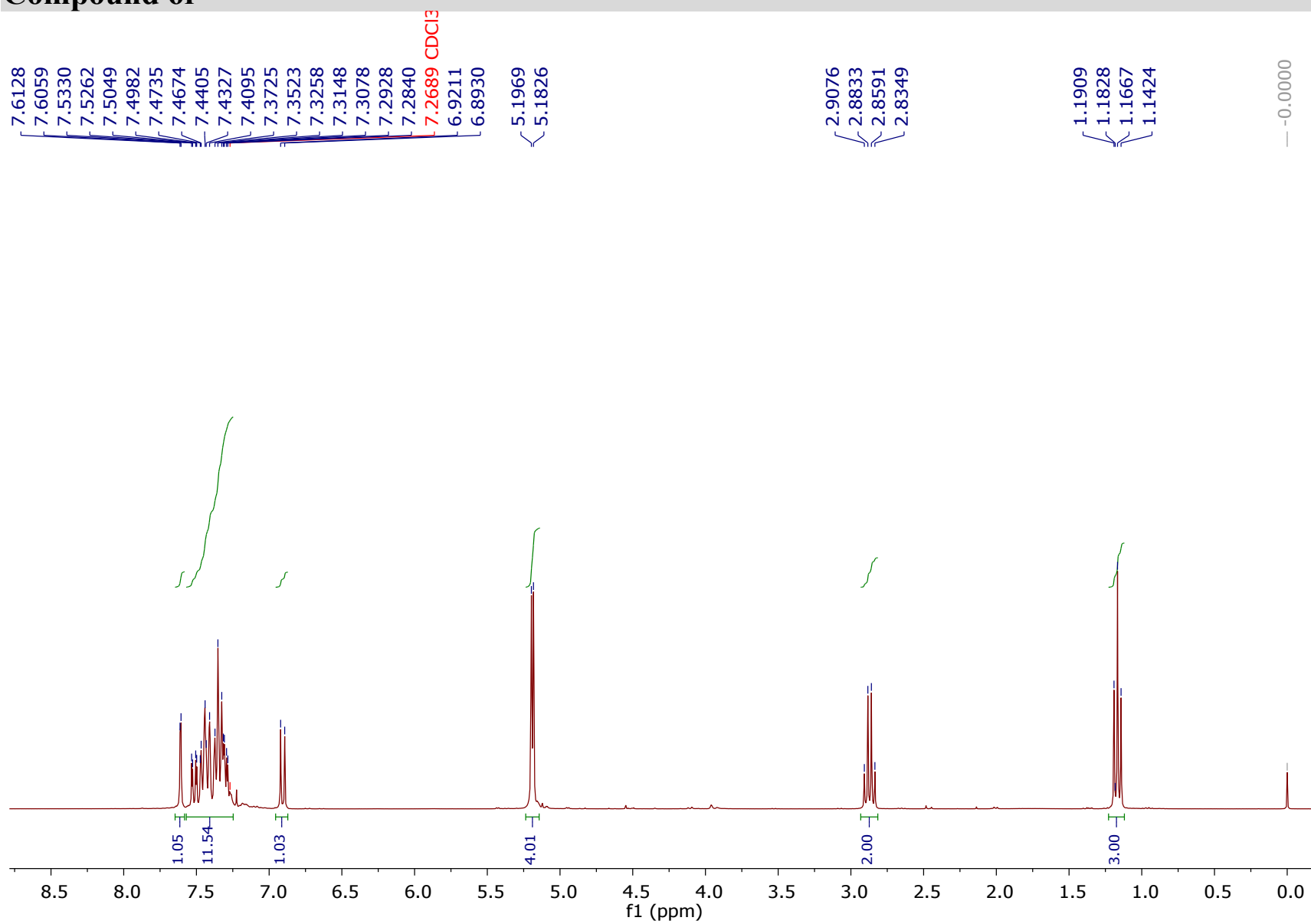
139.36
135.41
129.70
128.78

26.44

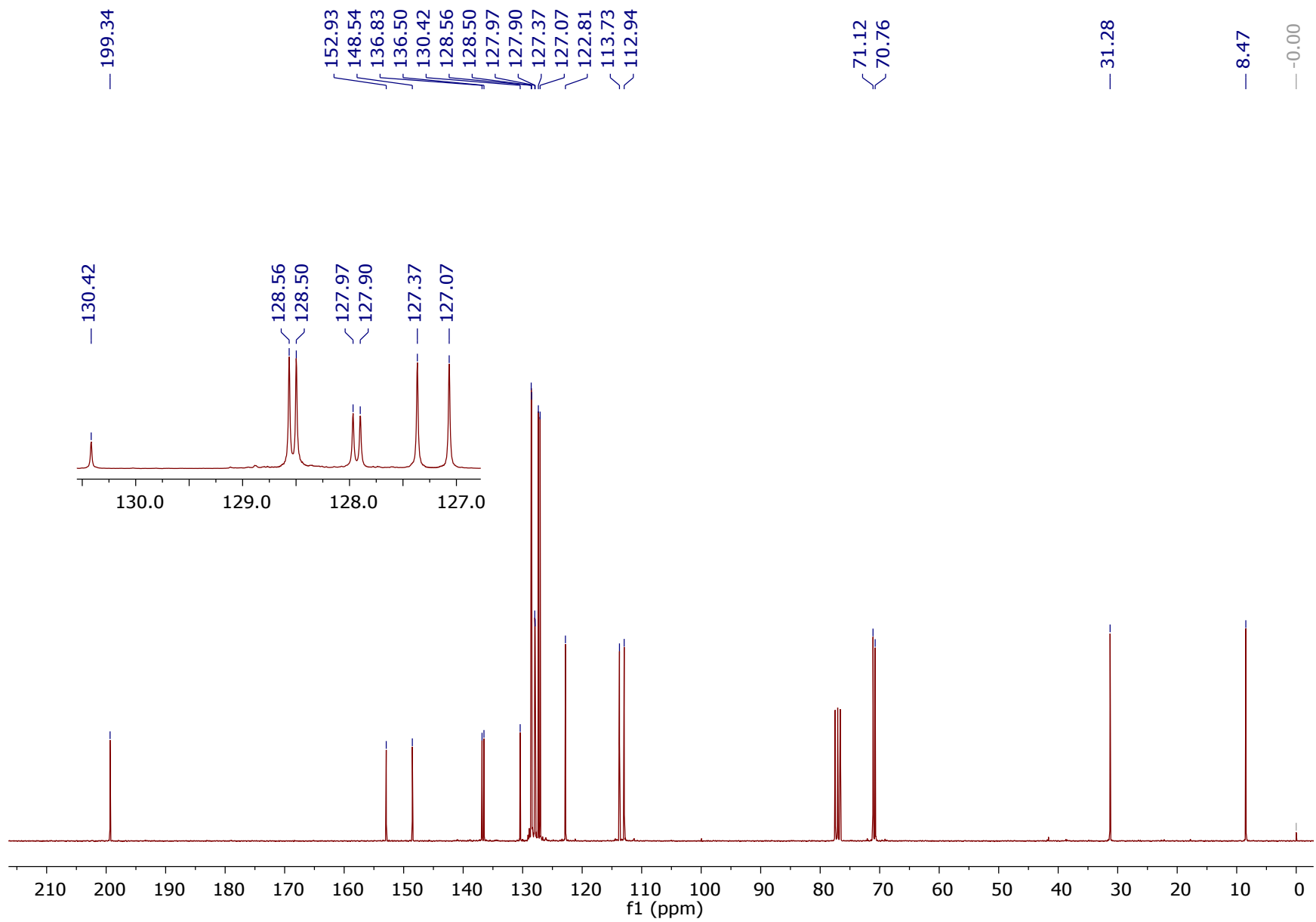
0.00



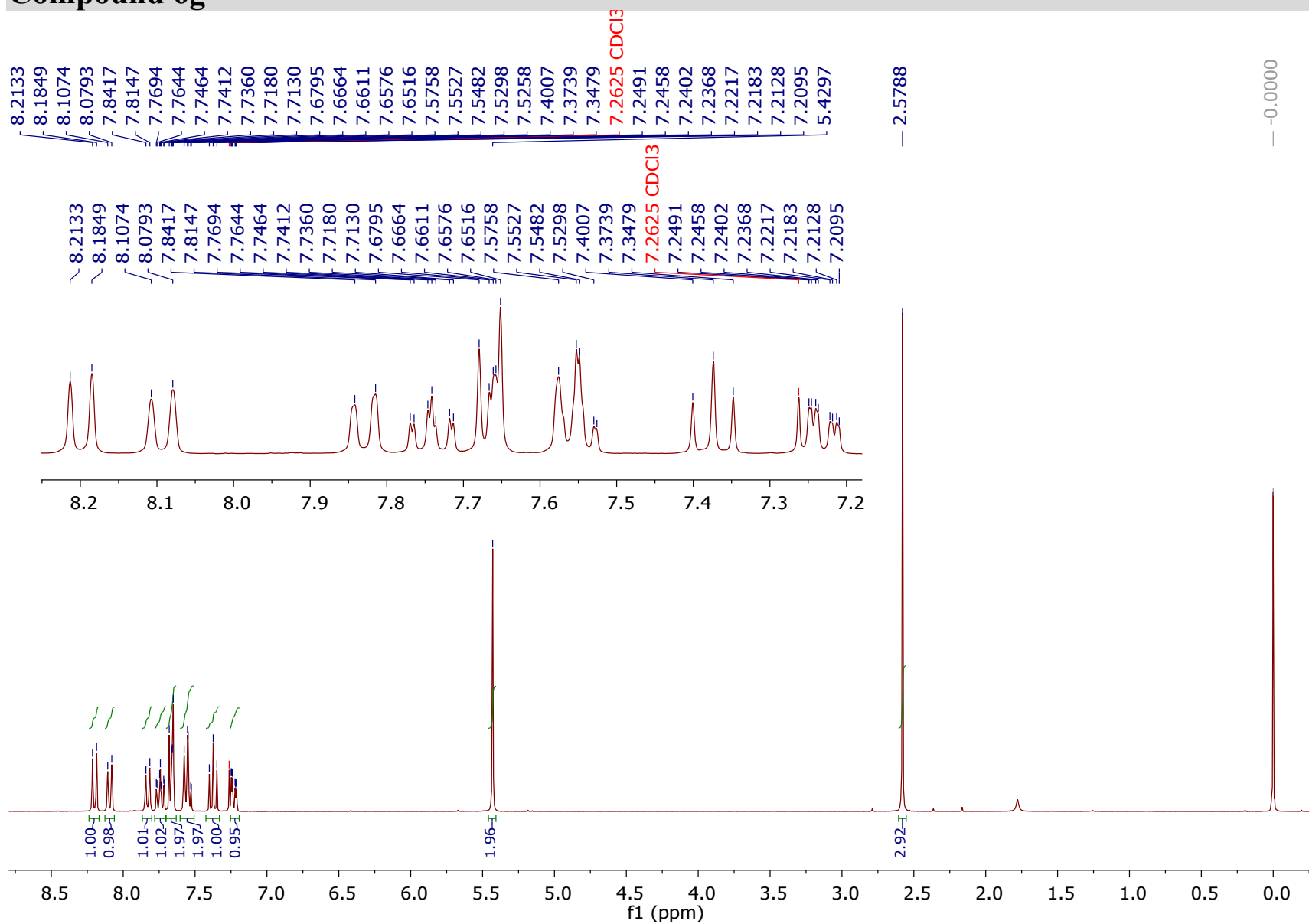
Compound 6f



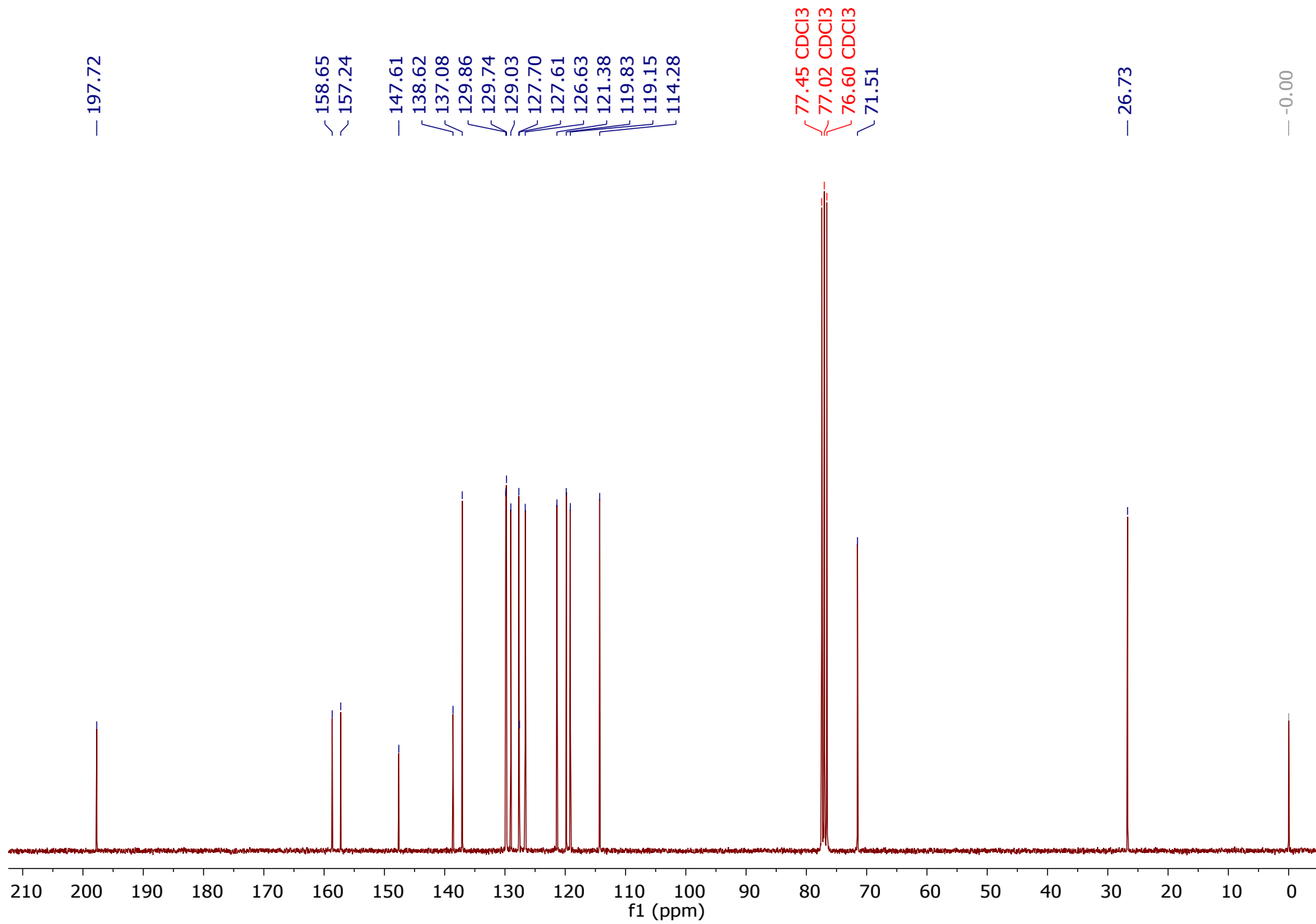
[85]



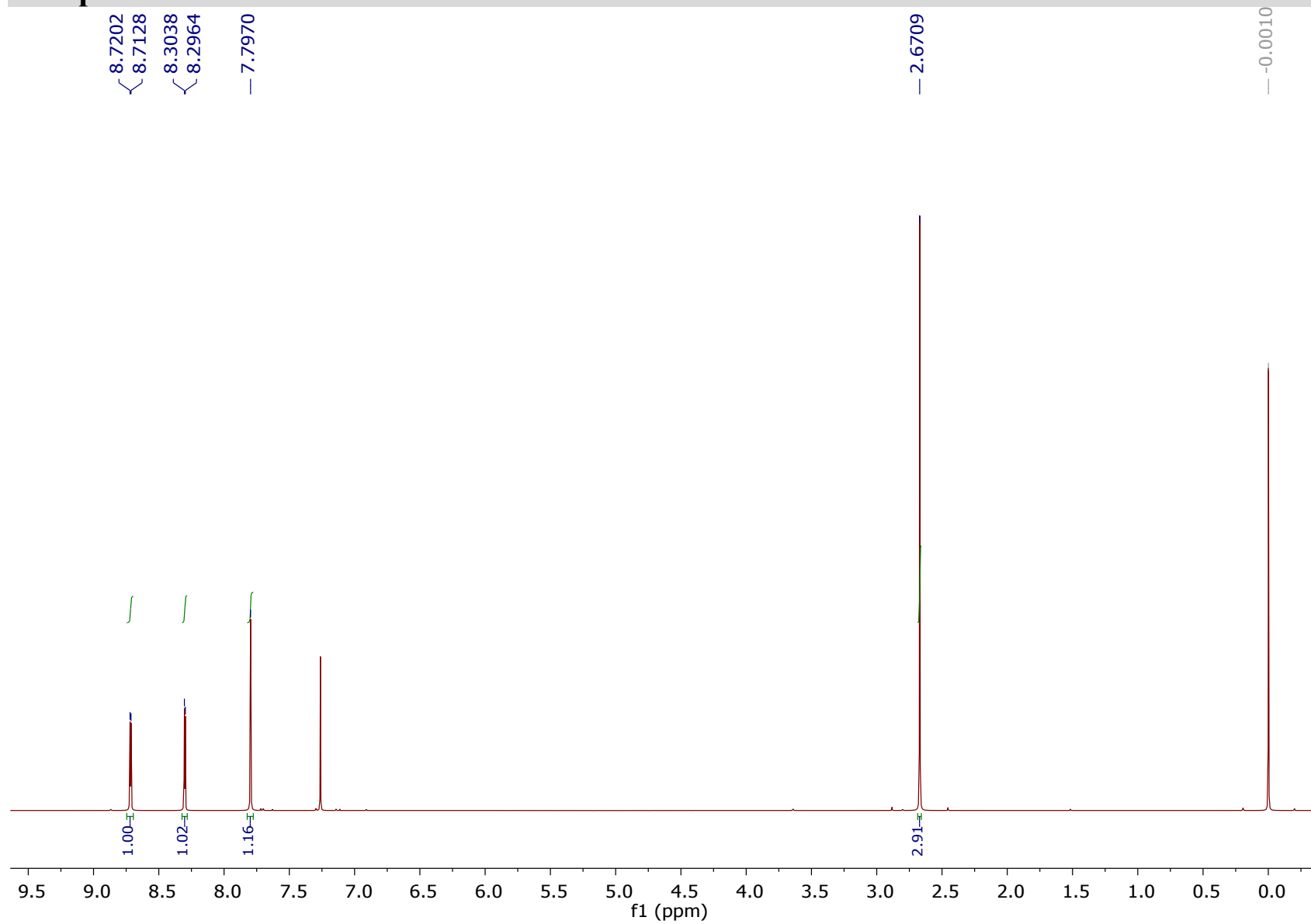
Compound 6g



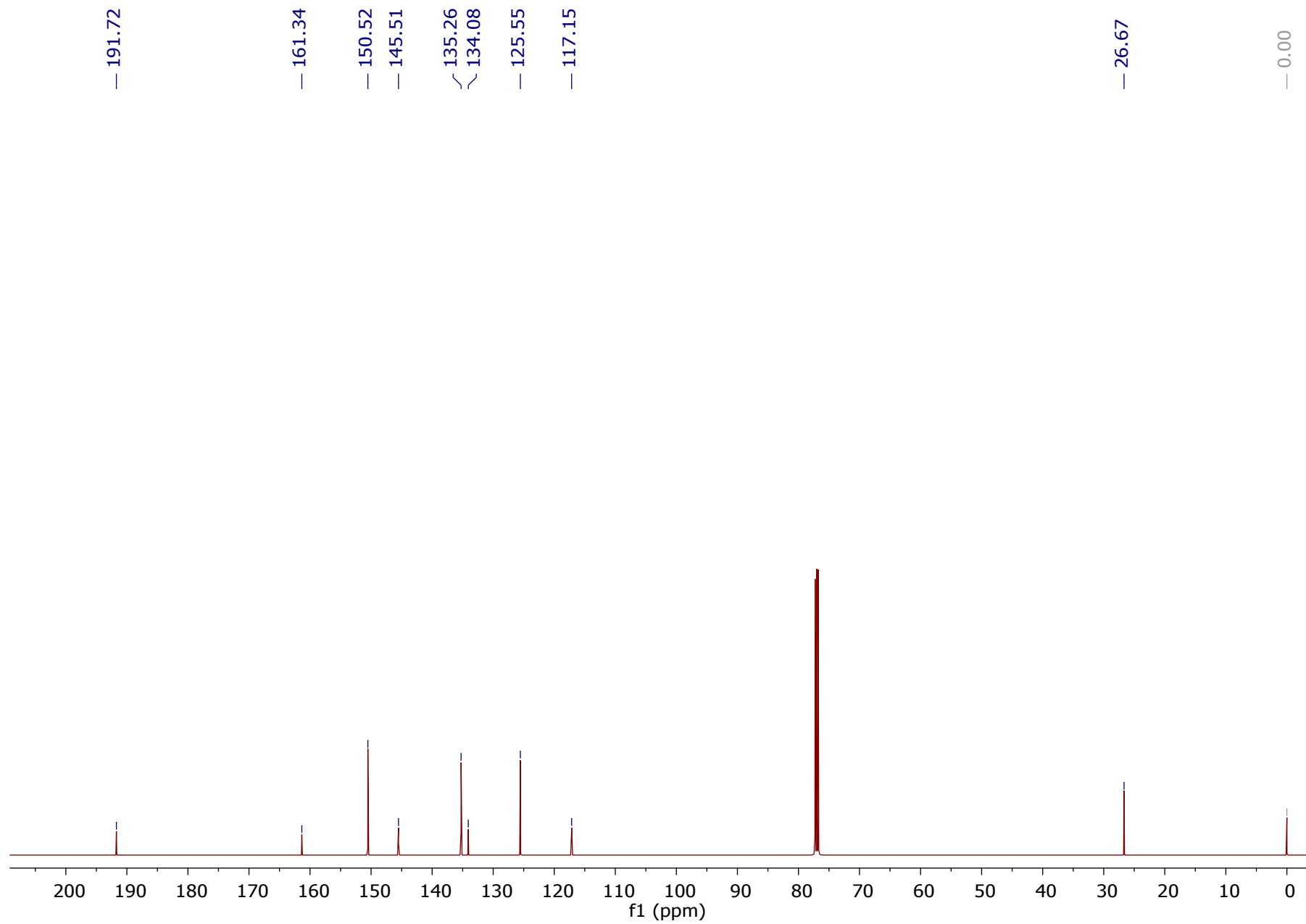
[87]

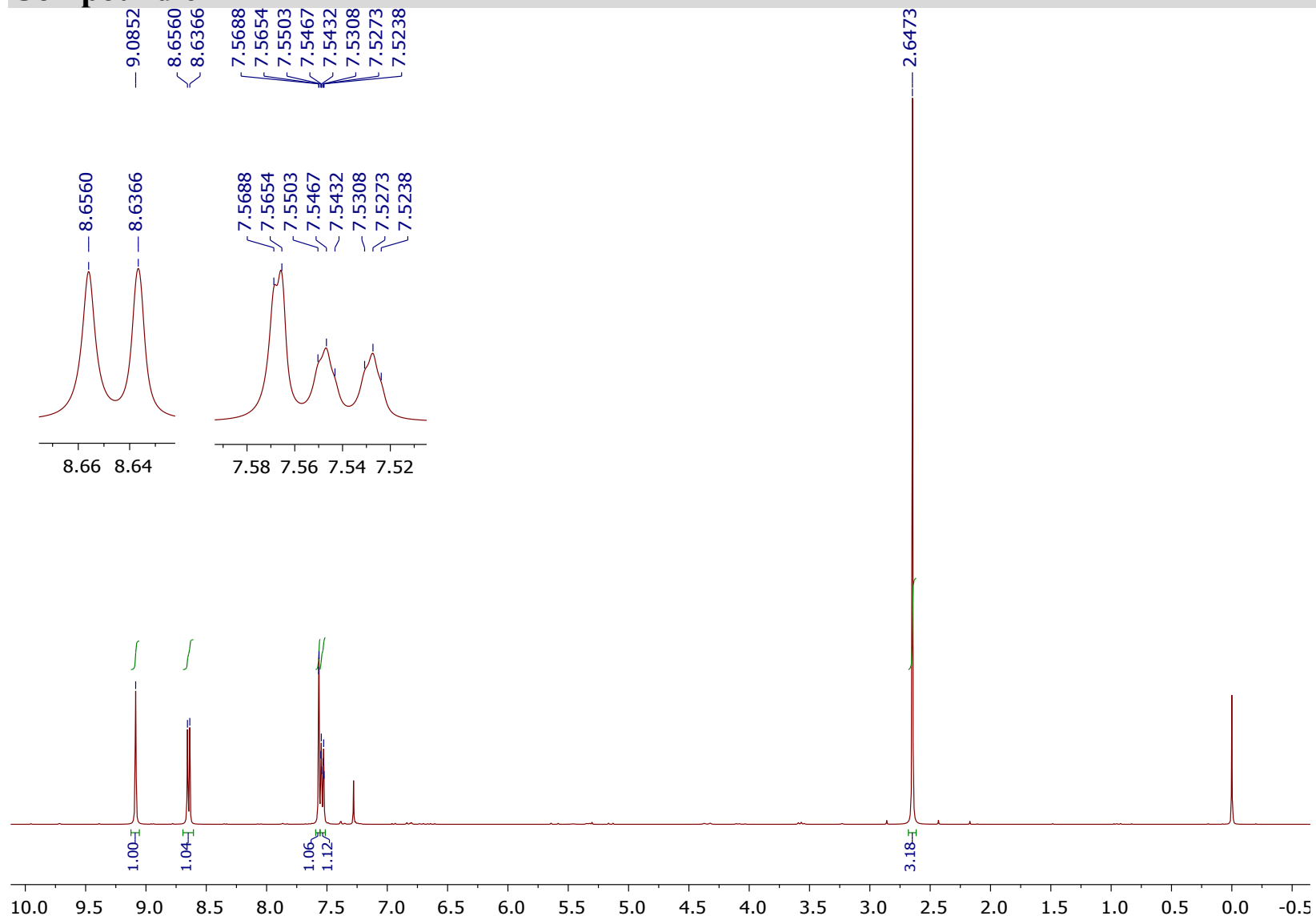


Compound 6h

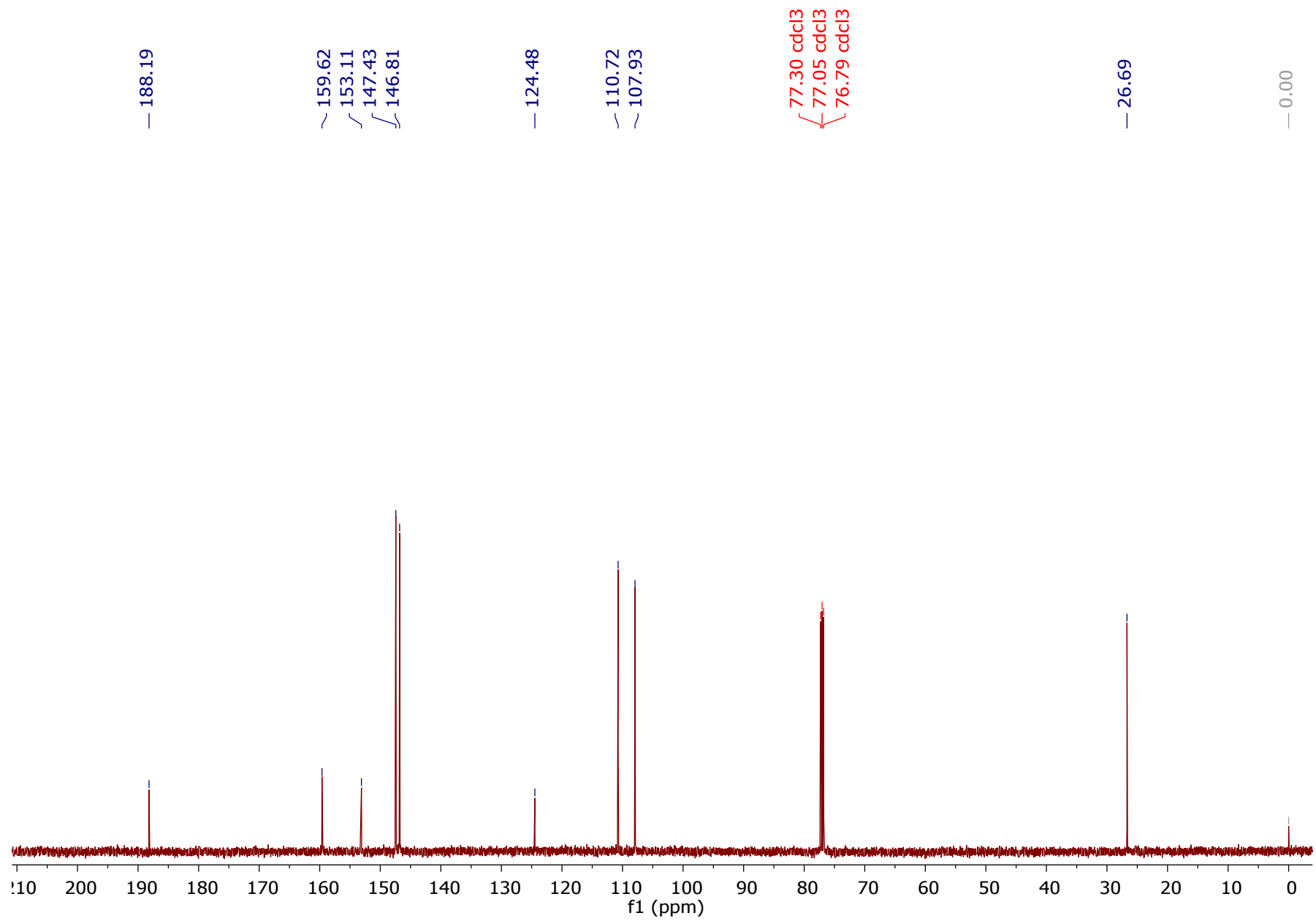


[89]

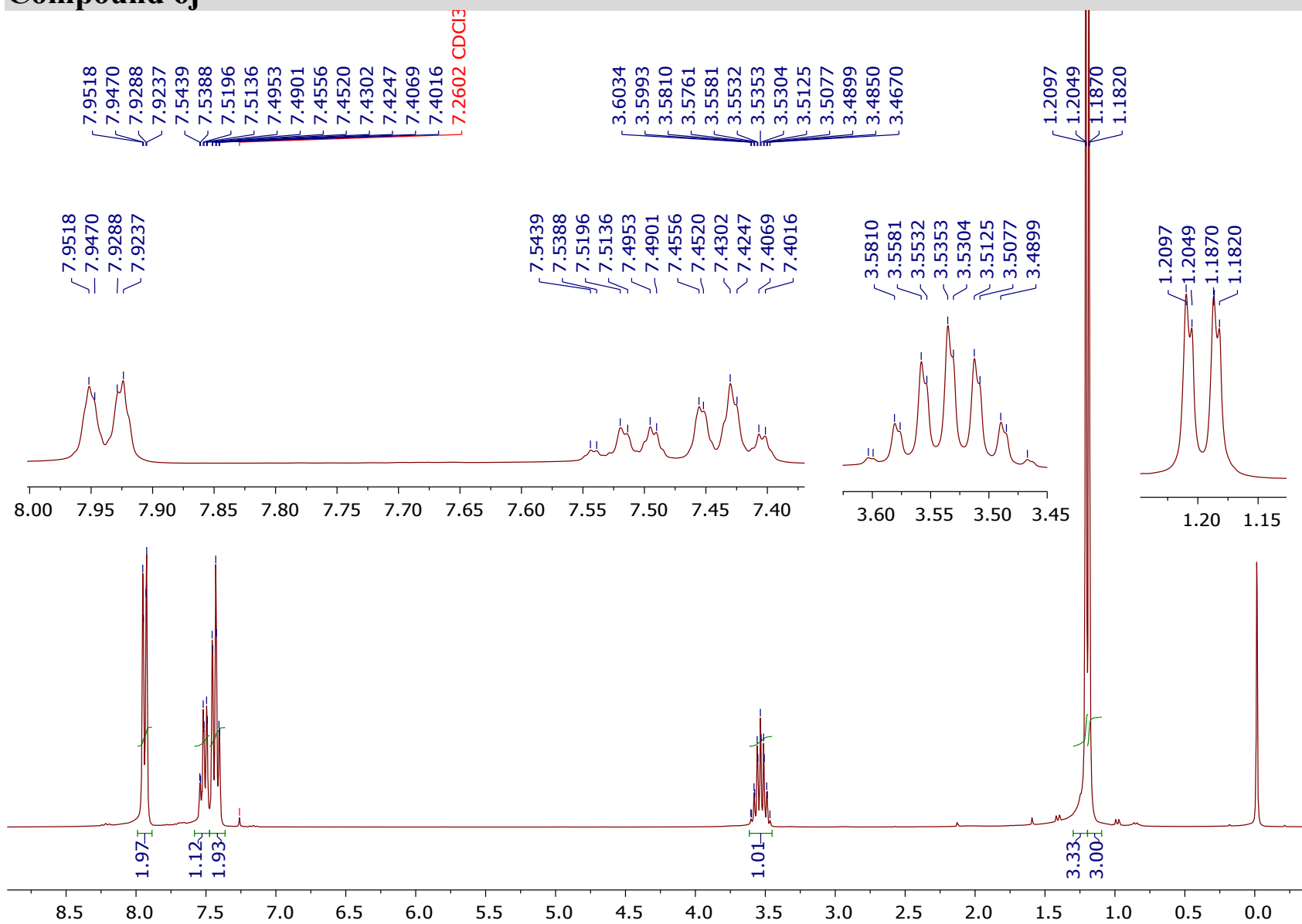


Compound 6i

[91]



Compound 6j



[93]

