Supporting Information

Catalytic Redox-Neutral C–H functionalisation with TEMPO in Water to access Aminomethyl-substituted Pyrroles

Guilherme Cariello Silva, Gabriela F. P. de Souza and Airton G. Salles, Jr

Department of Organic Chemistry, Institute of Chemistry, University of Campinas, P.O. Box 6154, Campinas, SP 13084-862, Brazil

Table of contents

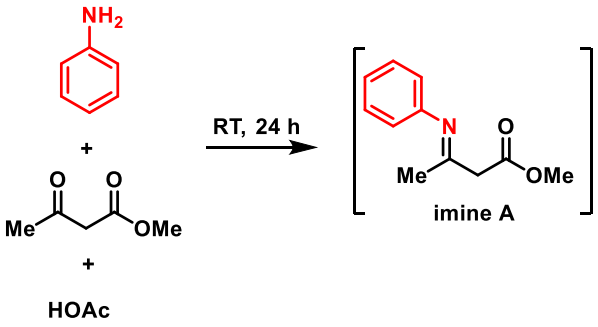
1. General Information

All reagents were purchased from commercial suppliers (Sigma-Aldrich, Oakwood and Combi-Blocks) and used without further purification, all solvents were analytical grade. Temperatures above room temperature were maintained by using an aluminium block heated on a hotplate, and reaction temperatures are reported as the temperature of the block surrounding the vessel. Thin layer chromatography (TLC) was performed using silica gel GF254, 0.25 mm thickness, visualization was accomplished with short wave UV light or $KMnO_4$ staining solution followed by heating. Hydrogen nuclear magnetic resonance spectra (^{1}H NMR) were obtained at 500 MHz in $CDCl_3$ solutions, at ambient temperature. Carbon-13 nuclear magnetic resonance spectra (^{13}C NMR) were obtained at 125 MHz in $CDCl_3$ solutions, at ambient temperature. Chemicals shifts (δ) are given in ppm and the residual solvent signals were used as references for ^{1}H and ^{13}C NMR spectra ($CDCl_3$: δH = 7.27 ppm, δC = 77.00 ppm). High resolution mass spectra were recorded on Thermo Scientific LTQ FT Ultra and Q Exactive Orbitrap spectrometers working with an electronspray ionization (ESI). The Gas Chromatography coupled to Mass Spectrometry (CG-MS) analyses were performed using a Network GC system 6890N (Agilent Technologies Inc., Palo Alto, CA, USA), equipped with a HP-5MS 5% Phenyl Methyl Silox (25.0 m × 250 µm × 0.25 µ nominal) capillary column. The GC analyses were carried out in split mode (ratio 150:1) using helium as carrier gas at a flow rate of 504 mL/min (7.65 psi). The injection port temperature was 250 °C; the oven was maintained at an initial temperature of 50 °C for 3 minutes, then programmed at 40 °C/min to a temperature of 280 °C, where it was held, post-run, for 2 minutes. The MS detector was at 250 °C, using H_2 flow at 40.00 mL/min, air at 400 mL/min and He makeup flow at 45.0 mL/min.

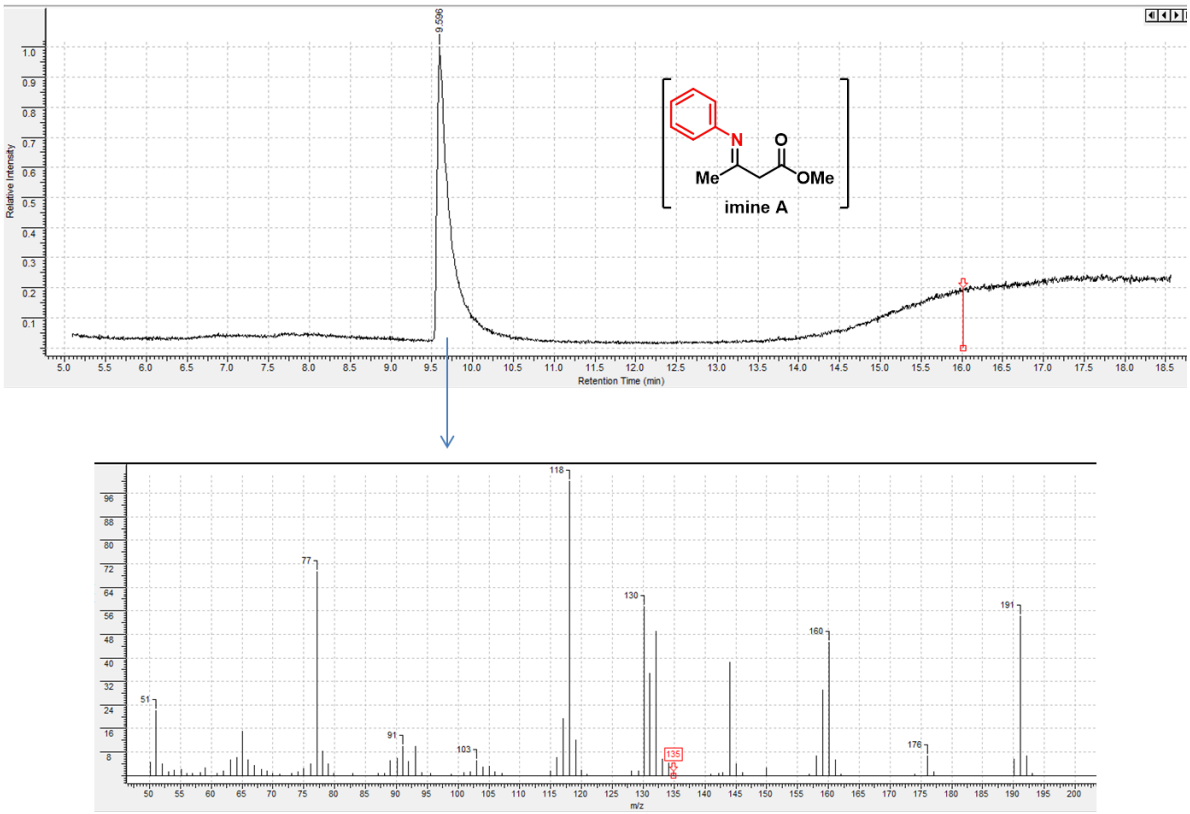
2. General Procedure

Following this sequence, acetic acid (1.0 mmol, 1.0 equiv), ketoesters (2.0 mmol, 2.0 equiv), anilines (2.0 mmol, 2.0 equiv) and TEMPO (30 mol%) were added to 4 ml of water. The resulting suspension was capped with a rubber septum and stirred at 70 ^{o}C for 72 h. The stirring speed of the reaction mixture was kept at 1150 rpm to ensure a proper diffusion of reaction components. Then, the suspension was extracted with ethyl acetate (2×2 mL) and the combined organic layers were concentrated. The crude mixture was added to silica column and eluted using ethyl acetate/n-hexane (20:80) to afford the targeted product.

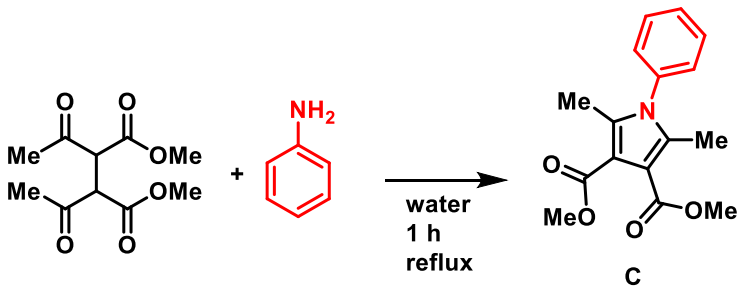
3. Synthesis of imine A



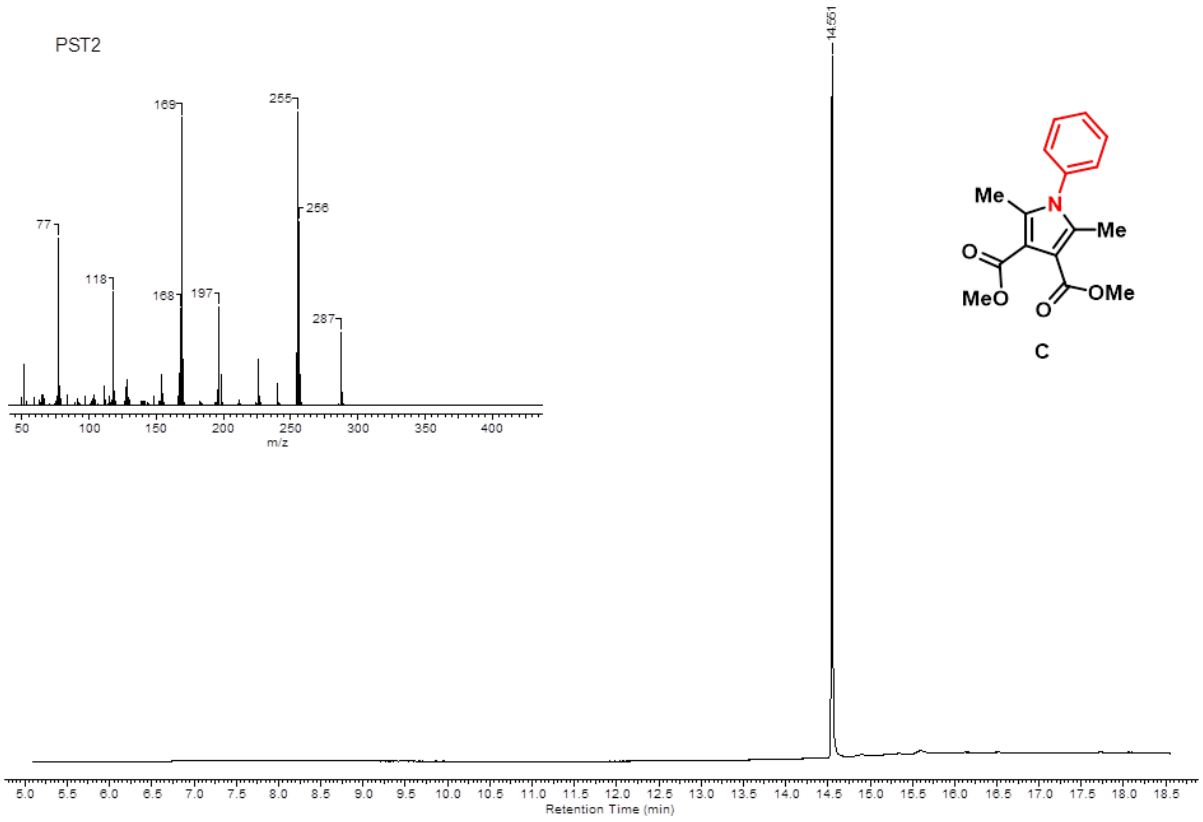
Aniline (1.0 mmol, 1.0 equiv), methyl acetoacetate (1.0 mmol, 1 equiv) and acetic acid (1.0 mmol, 1 equiv) were mixed together neat (solvent-free) and stirred at room temperature for 24 h. The crude mixture was added to the top of a silica gel column and eluted using ethyl acetate/n-hexane (20:80) to afford imine **A**:



4. Synthesis of pyrrole C



3,4-diacetylhexane-2,5-dione (1.0 mmol, 1 equiv) and aniline (1.0 mmol, 1 equiv) were added to 1mL of water and refluxed for 1h. Then, the mixture was extracted with ethyl acetate (3×5 mL) and dried with anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and pyrrole **C** was recrystallized from ethanol:



5. Scheme 3 in the manuscript, item I, Figure S1

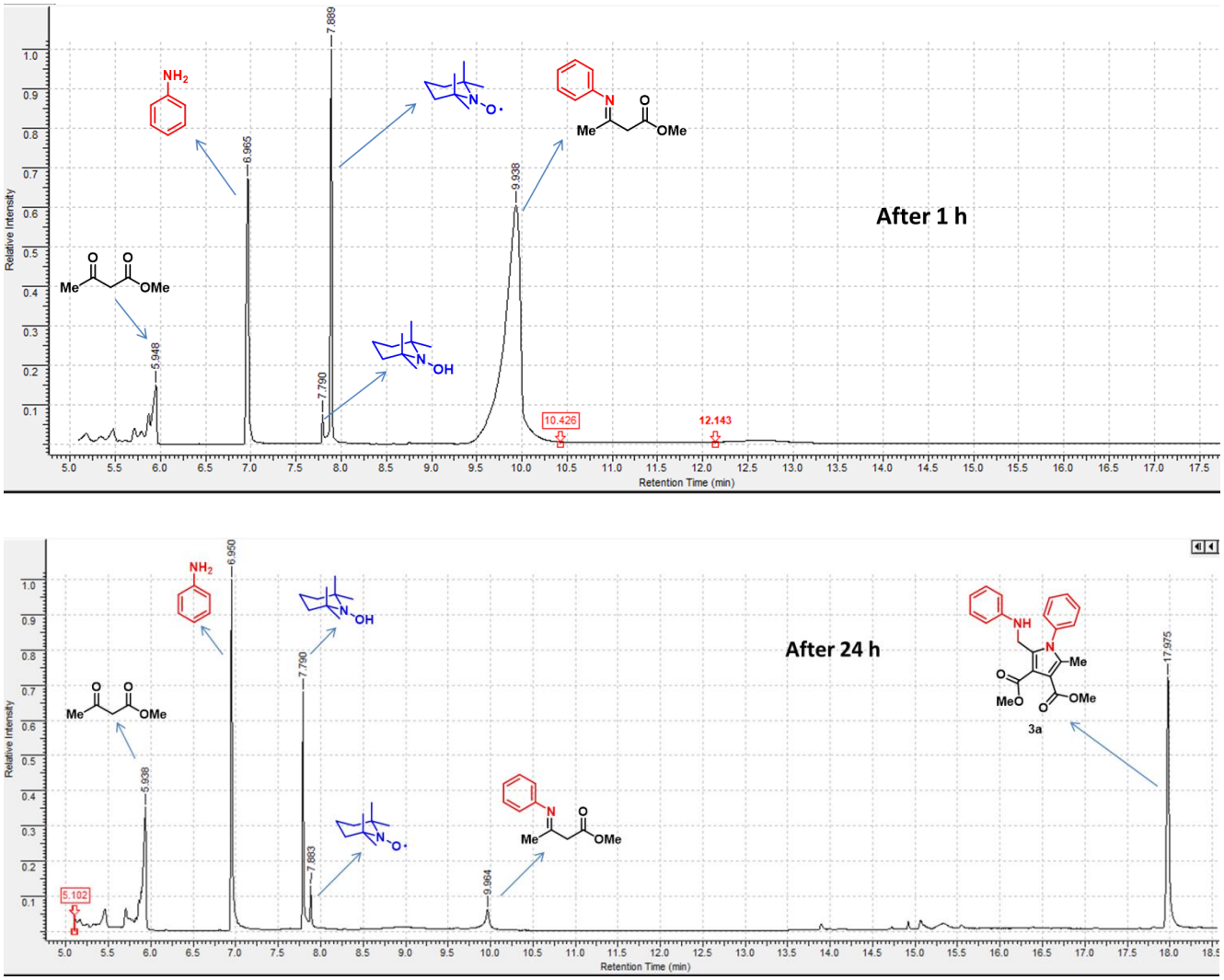


Figure S1

6. Scheme 3 in the manuscript, item III, Figure S2

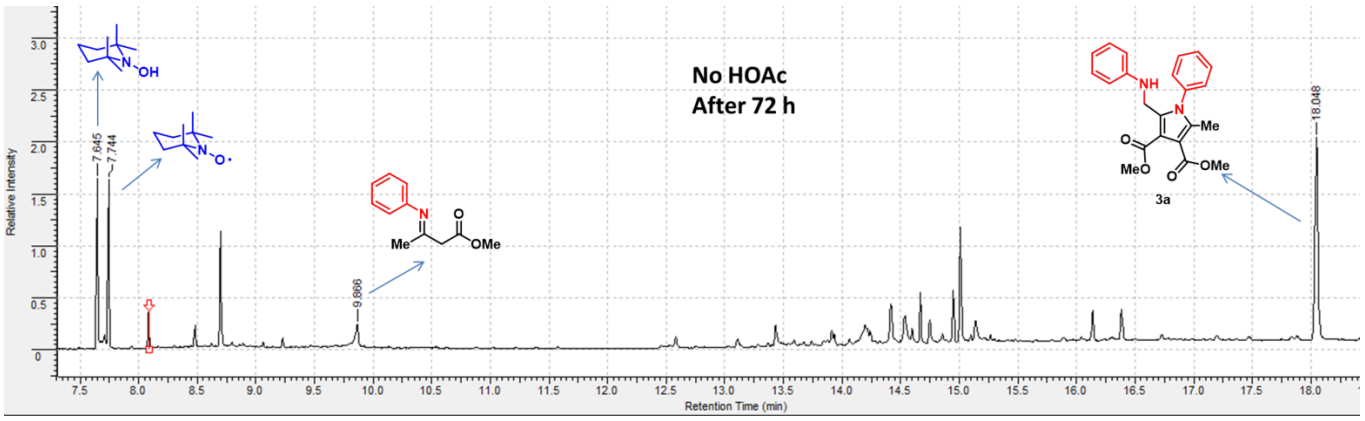


Figure S2

7. Scheme 4 in the manuscript, item III, Figure S3

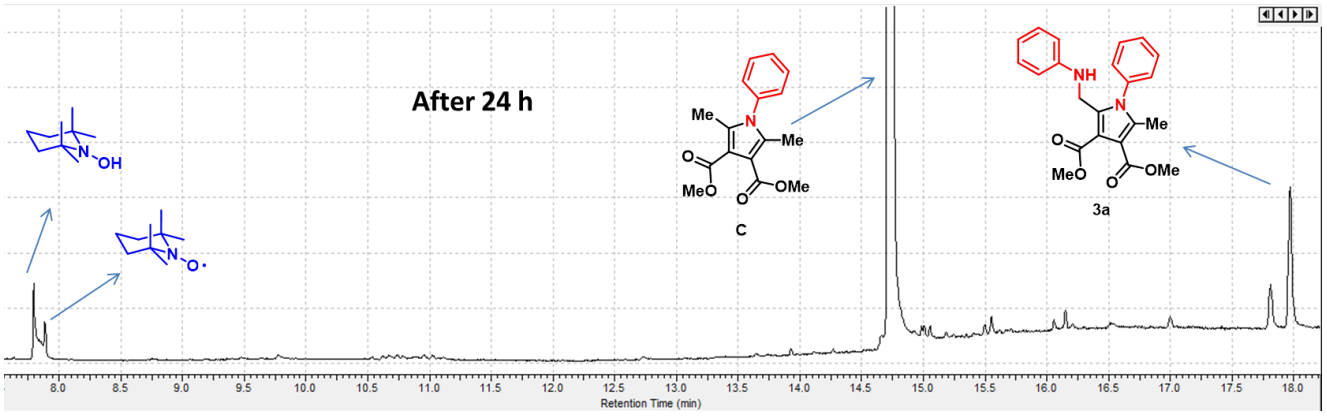


Figure S3

8. Scheme 5 in the manuscript, item II, Figure S4

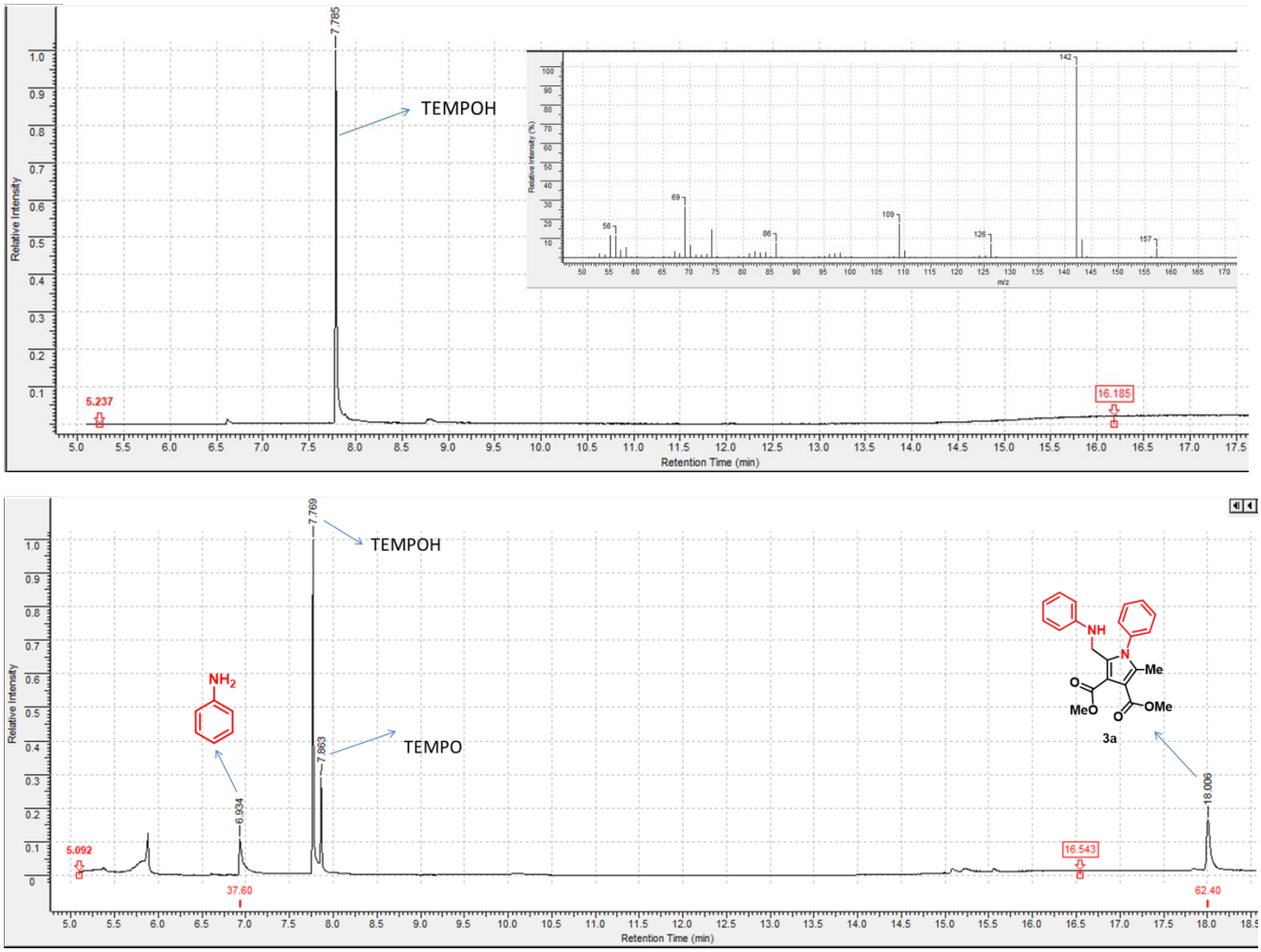


Figure S4

9. Scheme 5 in the manuscript, item III, Figure S5

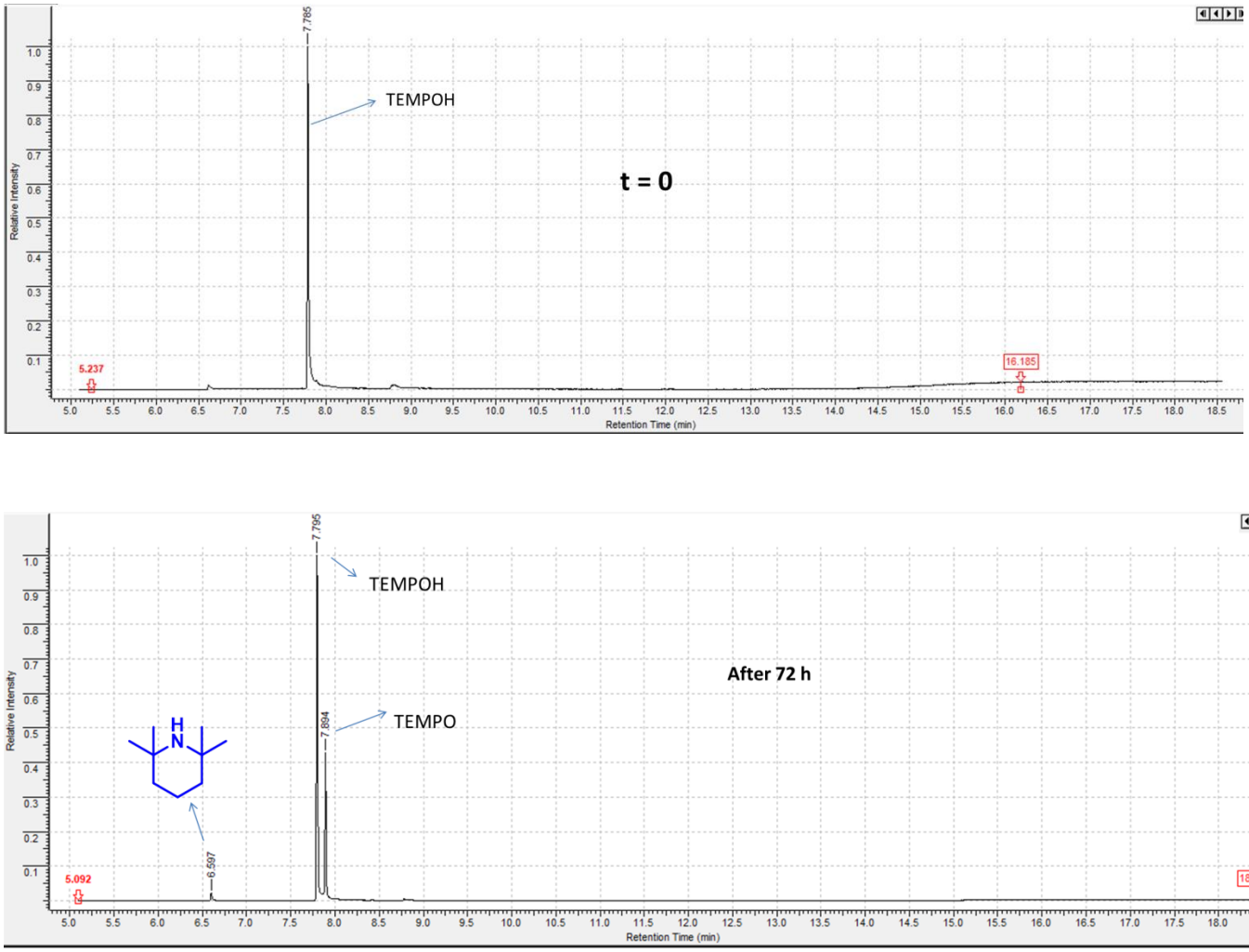
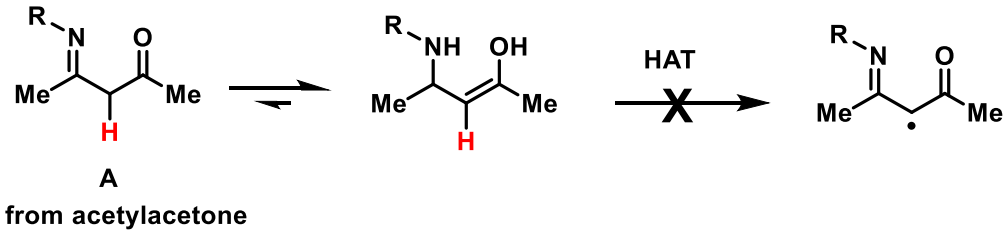


Figure S5

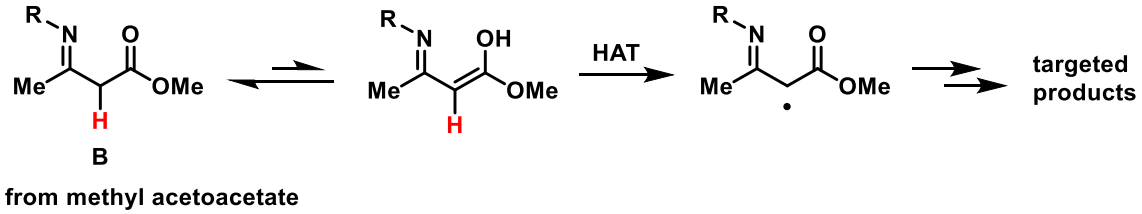
10. Possible reason for reaction failure when using either acetylacetone or dimethyl malonate.

Following the **General Procedure** with acetylacetone and aniline, we could observe by GC-MS the formation of the corresponding imine in accordance to the mechanistic studies described in the manuscript. However, no product was obtained after 72 h and the imine remained unreacted. We hypothesize that, under our conditions, the enol form of imine **A** is favoured and considering that HAT parallels bond dissociation energies[1], hydrogen transfer from sp^2 carbon becomes more difficult compared to the same transfer from sp^3 carbons:

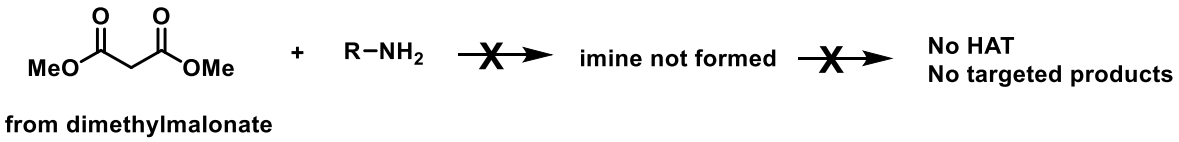
[1] J. M. Mayer, *Acc. Chem. Res.*, 2011, **44**, 36–46.



On the other hand, the keto form of imine **B**, coming from methyl acetoacetate, might be favoured due to higher pK_a of α-hydrogens next to an ester group. In this scenario, imine **B** undergoes HAT more easily (from sp^3 carbon) allowing the transformation reach completion:

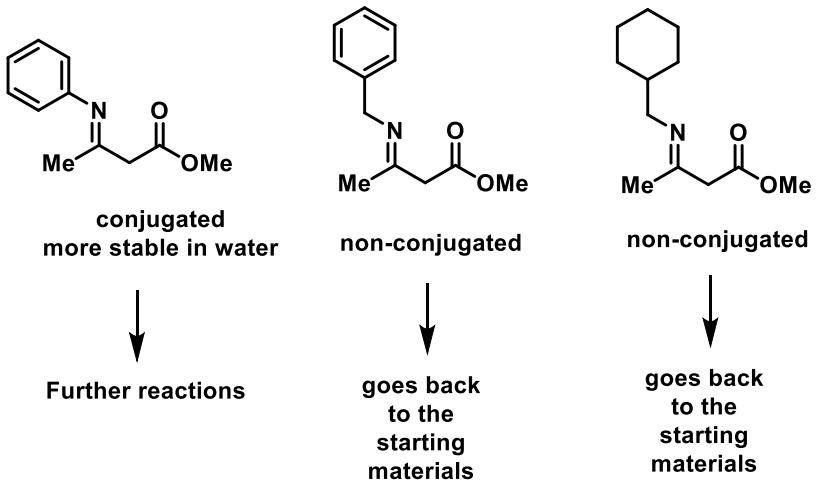


When employing dimethyl malonate, the imine is not formed at all and the process is shut down. This result emphasizes the necessity of imine formation to carry the transformation on.



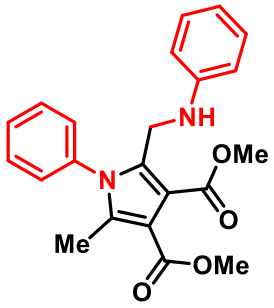
11. Possible reason for reaction failure when using either benzylamines or aliphatic amines.

The formation of imines takes place by a mechanism that is the reverse of the hydrolysis. Conjugated C=N systems are more stable to aqueous hydrolysis than non-conjugated imines and, for many cases, the equilibrium constants for formation are high, even in aqueous solution.[2] Therefore, we believe that, under our conditions, conjugated imines formed from anilines are very stable and allow the transformation to carry on. On the other hand, non-conjugated imines coming from benzylamines or aliphatic amines hydrolyse easily, thus preventing the reaction to move forward:



[2] W. P. Jencks, *Prog. Phys. Org. Chern.*, **1964**, 2, 63; J. M. Sayer, M. Peskin, and W. P. Jencks, *J. Am. Chern. Soc.*, **1973**, 95, 4277.

12. Characterization of the products

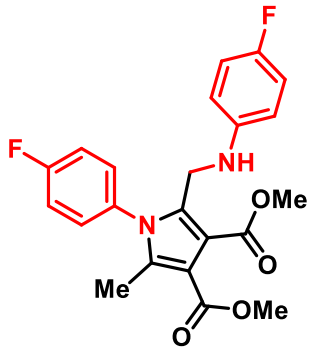


3a

Prepared from aniline and methyl acetoacetate following the general procedure to give the product as pale yellow oil (89% yield).[3]

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.51–7.48 (m, 3H), 7.23–7.19 (m, 2H), 7.09 (appt t, 2H, J = 8.24 Hz), 6.70 (appt t, 1H, J = 7.32 Hz), 6.41 (d, 2H, J = 8.24 Hz), 4.14 (s, 2H), 3.85 (s, 6H), 2.16 (s, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*): δ 165.89, 165.68, 147.41, 136.15, 135.32, 135.05, 129.65, 129.04, 128.07, 118.02, 114.52, 113.64, 112.67, 51.83, 51.54, 38.92, 11.91.



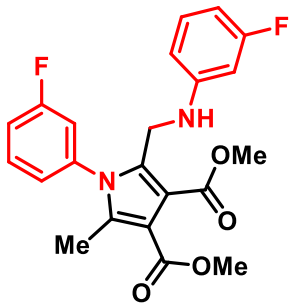
3b

Prepared from 4-fluoroaniline and methyl acetoacetate following the general procedure to give the product as pale yellow oil (92% yield).[3]

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.20–7.18 (m, 4H), 6.81 (t, 2H, J = 8.80 Hz), 6.38–6.38 (m, 2H), 4.05 (s, 2H), 3.86 (s, 3H), 3.85 (s, 3H), 2.15 (s, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*): δ 165.76, 165.54, 163.75, 161.75, 157.23, 143.72, 135.33, 135.05, 132.01, 129.94, 129.87, 116.77, 116.58, 115.64, 115.45, 114.90, 114.86, 114.63, 112.88, 51.89, 51.60, 39.83, 11.89.

[3] M. Zhao, Z. Zhang, Z. Ren, D. Yang and Z. Guan, *Org. Lett.*, 2018, **20**, 3088–3091.



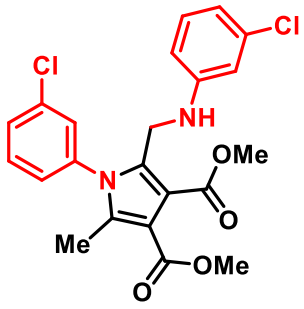
3c

Prepared from 3-fluoroaniline and methyl acetoacetate following the general procedure to give the product as pale yellow oil (90% yield).

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.48 (m, 1H), 7.26–7.23 (m, 1H), 7.05–6.96 (m, 3H), 6.37 (td, 1H, *J* = 8.49, 1.57 Hz), 6.17 (dd, 1H, *J* = 7.23, 1.26 Hz), 6.04 (dt, 1H, *J* = 11.32, 2.20 Hz), 4.13 (s, 2H), 3.86 (s, 6H), 2.18 (s, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*): δ 165.65, 165.40, 164.79, 163.70, 162.86, 161.71, 148.98, 148.90, 137.35, 137.27, 135.13, 134.47, 130.99, 130.14, 130.06, 124.01, 123.98, 116.93, 116.76, 115.86, 115.69, 114.87, 113.00,109.39, 104.57, 104.41, 100.16, 99.95, 51.89, 51.59, 38.62, 11.80.

HRMS m/z (ESI): calcd. for $C_{22}H_{21}F_2N_2O_4$ $[M+H]^+$ 415.14639, found 415.14492.

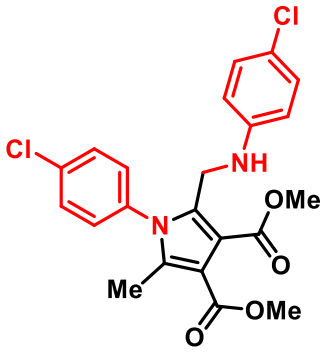


3d

Prepared from 3-chloroaniline and methyl acetoacetate following the general procedure to give the product as pale orange oil (85% yield).[3]

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.53–7.50 (m, 1H), 7.45 (t, 1H, *J* = 7.86 Hz), 7.23 (t, 1H, *J* = 1.89 Hz), 7.12–7.13 (m, 1H), 6.99 (t, 1H, *J* = 7.86 Hz), 6.65 (dd, 1H, *J* = 7.86, 1.26 Hz), 6.33 (t, 1H, *J* = 1.89 Hz), 6.29 (dd, 1H, *J* = 7.86, 1.89 Hz), 4.14 (d, 1H, *J* = 14.46 Hz), 4.13 (d, 1H, *J* = 14.46 Hz), 3.87 (s, 3H), 3.85 (s, 3H), 2.17 (s, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*): δ 165.70, 165.43, 148.15, 137.09, 135.45, 135.16, 134.87, 134.60, 130.72, 130.08, 129.98, 128.45, 126.42, 118.12, 114.89, 113.13, 113.10, 112.09, 51.97, 51.65, 38.65, 11.88.

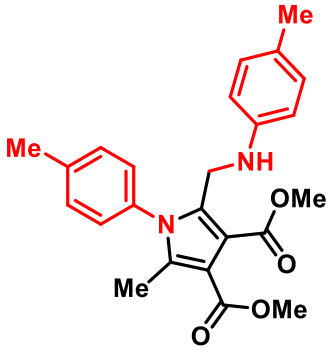


3e

Prepared from 4-chloroaniline and methyl acetoacetate following the general procedure to give the product as pale orange oil (86% yield).[3]

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.46 (d, 2H, *J* = 8.80 Hz), 7.14 (d, 2H, *J* = 8.31 Hz), 7.03 (d, 2H, *J* = 8.80 Hz), 6.35 (d, 2H, *J* = 8.80 Hz), 4.09 (s, 2H), 3.85 (s, 6H), 2.15 (s, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*): δ 165.70, 165.40, 145.59, 135.65, 135.24, 134.46, 129.90, 129.31, 128.95, 123.02, 114.86, 113.04, 51.91, 51.60, 39.11, 11.86.



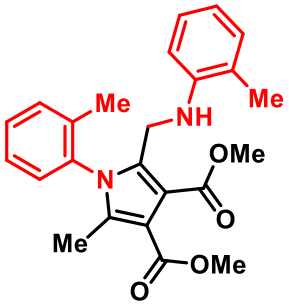
3f

Prepared from 4-methylaniline and methyl acetoacetate following the general procedure to give the product as pale yellow oil (88% yield).

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.28 (d, 2H, *J* = 8.17 Hz), 7.09 (d, 2H, *J* = 8.17 Hz), 6.89 (d, 2H, *J* = 8.17 Hz), 6.34 (d, 2H, *J* = 8.80 Hz), 4.11 (s, 2H), 3.84 (s, 6H), 2.44 (s, 3H), 2.21 (s, 3H), 2.15 (s, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*): δ 165.92, 165.75, 145.22, 139.49, 135.41, 133.51, 130.19, 129.50, 127.76, 127.24, 114.35, 113.93, 112.49, 51.78, 51.49, 39.32, 21.22, 20.37, 11.89.

HRMS m/z (ESI): calcd. for $C_{24}H_{27}N_2O_4$ $[M+H]^+$ 407,19653, found 407,19525.

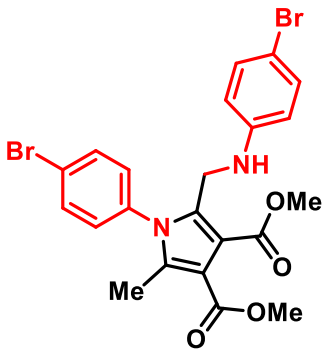


3g

Prepared from 2-methylaniline and methyl acetoacetate following the general procedure to give the product as pale yellow oil (84% yield).[3]

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.44–7.30 (m, 3H), 7.06 (d, 1H, J = 7.02 Hz), 6.98 (appt t, 2H, J = 8.24 Hz), 6.65 (t, 1H, J = 7.02 Hz), 6.32 (d, 1H, J = 7.63 Hz), 4.16 (d, 1H, J = 14.04 Hz), 4.01 (d, 1H, J = 14.04 Hz), 3.86 (s, 6H), 2.08 (s, 3H), 2.03 (s, 3H), 1.92 (s, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*): δ 166.05, 165.60, 136.69, 135.27, 135.16, 131.28, 130.10, 129.84, 128.50, 127.17, 126.88, 114.63, 112.64, 51.87, 51.51, 38.97, 17.36, 17.16, 11.46.

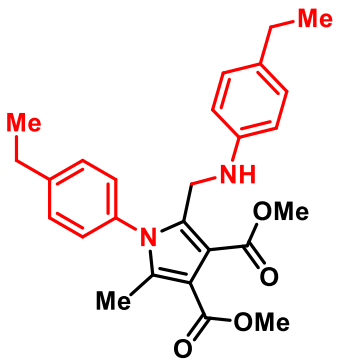


3h

Prepared from 4-bromoaniline and methyl acetoacetate following the general procedure to give the product as pale orange oil (87% yield).[3]

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.61 (d, 2H, J = 8.80 Hz), 7.17 (d, 2H, J = 8.80 Hz), 7.07 (d, 2H, J = 8.80 Hz), 6.31 (d, 2H, J = 8.80 Hz), 4.09 (s, 2H), 3.85 (s, 6H), 2.15 (s, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*): δ 165.73, 165.38, 145.86, 135.22, 134.95, 134.30, 132.94, 131.87, 129.60, 123.74, 115.45, 114.95, 113.10, 110.29, 51.95, 51.63, 39.10, 11.89.



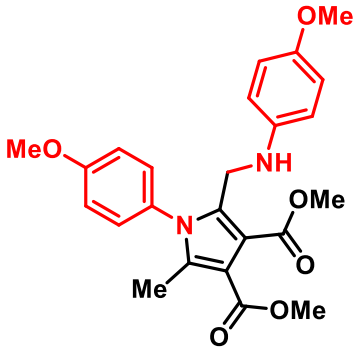
3i

Prepared from 4-ethyl aniline and methyl acetoacetate following the general procedure to give the product as pale brown oil (90% yield).

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.29 (d, 2H, *J* = 8.31 Hz), 7.09 (d, 2H, *J* = 8.31 Hz), 6.92 (d, 2H, *J* = 8.31 Hz), 6.39 (d, 2H, *J* = 8.31 Hz), 4.12 (s, 2H), 3.85 (s, 6H), 2.73 (q, 2H, *J* = 7.34 Hz), 2.51 (q, 2H, *J* = 7.34 Hz), 2.15 (s, 3H), 1.30 (t, 3H, *J* = 7.83 Hz), 1.17 (t, 3H, *J* = 7.83 Hz).

^{13}C NMR (125 MHz, Chloroform-*d*): δ 166.02, 165.71, 145.70, 135.52, 133.56, 128.99, 128.37, 127.85, 114.37, 112.50, 51.83, 51.50, 39.67, 28.51, 27.91, 15.85, 15.29, 11.92.

HRMS m/z (ESI): calcd. for $C_{26}H_{31}N_2O_4$ $[M+H]^+$ 435,22783, found 435,22632.



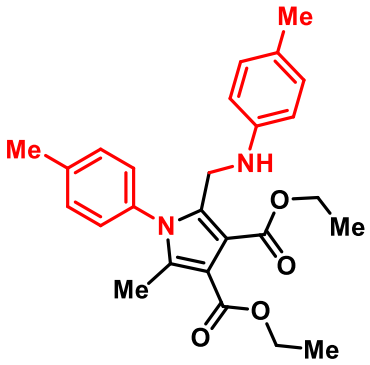
3j

Prepared from 4-methoxyaniline and methyl acetoacetate following the general procedure to give the product as pale yellow oil (83% yield).

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.11 (d, 2H, *J* = 8.80 Hz), 6.96 (d, 2H, *J* = 8.80 Hz), 6.68 (d, 2H, *J* = 8.80 Hz), 6.40 (d, 2H, *J* = 8.80 Hz), 4.07 (s, 2H), 3.87 (s, 3H), 3.84 (s, 6H), 3.72 (s, 3H), 2.14 (s, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*): δ 165.76, 165.57, 159.84, 152.47, 141.42, 135.48, 135.40, 128.96, 128.47, 115.37, 114.44, 113.96, 112.25, 55.52, 55.39, 51.59, 51.31, 40.09, 11.70.

HRMS m/z (ESI): calcd. for $C_{24}H_{27}N_2O_6$ $[M+H]^+$ 439,18636, found 439,18489.



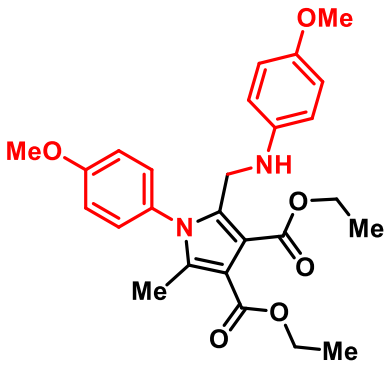
3k

Prepared from 4-methyl aniline and ethyl acetoacetate following the general procedure to give the product as pale brown oil (89% yield).

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.26 (d, 2H, *J* = 8.24 Hz), 7.06 (d, 2H, *J* = 8.24 Hz), 6.89 (d, 2H, *J* = 8.24 Hz), 6.37 (d, 2H, *J* = 8.24 Hz), 4.30 (q, 4H, *J* = 7.32 Hz), 4.10 (s, 2H), 2.44 (s, 3H), 2.22 (s, 2H), 2.15 (s, 3H), 1.26–1.38 (t+t, 6H, *J* = 7.32 Hz).

^{13}C NMR (125 MHz, Chloroform-*d*): δ 165.56, 165.32, 139.44, 135.19, 134.66, 133.48, 130.18, 129.52, 127.76, 115.24, 114.70, 114.15, 112.78, 60.63, 60.26, 39.57, 21.20, 20.37, 14.29, 14.24, 11.84.

HRMS m/z (ESI): calcd. for $C_{24}H_{31}N_2O_4$ $[M+H]^+$ 435,22783, found 435,22637.



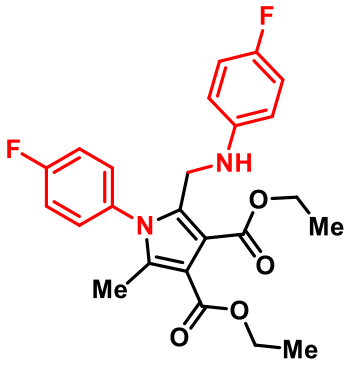
3l

Prepared from 4-methoxy aniline and ethyl acetoacetate following the general procedure to give the product as pale yellow oil (86% yield).

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.10 (d, 2H, *J* = 8.80 Hz), 6.96 (d, 2H, *J* = 8.80 Hz), 6.69 (d, 2H, *J* = 8.80 Hz), 6.44 (d, 2H, *J* = 8.80 Hz), 4.30 (q, 4H, *J* = 7.23 Hz), 4.07 (s, 2H), 3.87 (s, 3H), 3.73 (s, 3H), 2.14 (s, 3H), 1.37–1.30 (t+t, 6H, *J* = 7.23 Hz).

^{13}C NMR (125 MHz, Chloroform-*d*): δ 165.56, 165.33, 159.98, 152.83, 135.33, 135.05, 129.14, 128.64, 115.70, 114.63, 114.49, 112.75, 60.61, 60.28, 55.71, 55.55, 40.44, 14.30, 14.24, 11.83.

HRMS m/z (ESI): calcd. for $C_{26}H_{31}N_2O_6$ $[M+H]^+$ 467.21766, found 467.21656.



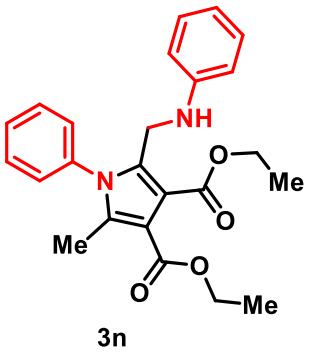
3m

Prepared from 4-fluoroaniline and ethyl acetoacetate following the general procedure to give the product as pale yellow oil (91% yield).

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.22–7.16 (m, 4H), 6.81 (appt. t, 2H, J = 8.80 Hz), 6.38 (appt. dd, 2H, J = 8.80, 4.40 Hz), 4.34–4.29 (q+q, 4H, J = 7.23 Hz), 4.05 (s, 2H), 2.15 (s, 3H), 1.37–1.30 (t+t, 6H, J = 7.23 Hz).

^{13}C NMR (125 MHz, Chloroform-*d*): δ 165.35, 165.14, 163.74, 161.74, 157.33, 155.45, 143.51, 135.08, 134.55, 132.01, 129.95, 129.87, 116.74, 116.57, 115.66, 115.48, 115.02, 114.95, 113.21, 60.76, 60.44, 39.99, 14.30, 14.22, 11.84.

HRMS m/z (ESI): calcd. for $C_{24}H_{25}F_2N_2O_4$ $[M+H]^+$ 443,17769, found 443,17607.

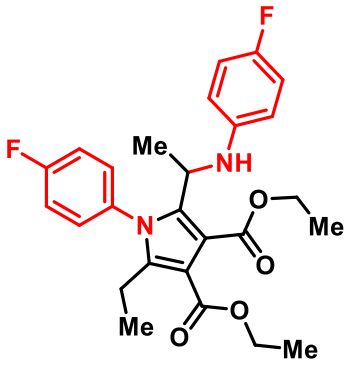


3n

Prepared from aniline and ethyl acetoacetate following the general procedure to give the product as pale yellow oil (92% yield).[3]

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.51–7.47 (m, 3H), 7.22 (m, 2H), 7.08 (dd, 2H, J = 8.17, 7.23 Hz), 6.69 (t, 1H, J = 7.23 Hz), 6.41 (d, 2H, J = 7.86 Hz), 4.34–4.29 (q+q, 4H, J = 7.23 and 6.92 Hz), 4.13 (s, 2H), 2.16 (s, 3H), 1.37–1.30 (t+t, 6H, J = 6.92 Hz).

^{13}C NMR (125 MHz, Chloroform-*d*): δ 165.48, 165.27, 147.19, 136.15, 135.06, 134.54, 129.62, 129.36, 129.04, 128.07, 118.16, 114.84, 113.77, 112.96, 60.68, 60.32, 39.10, 14.29, 14.22, 11.86.



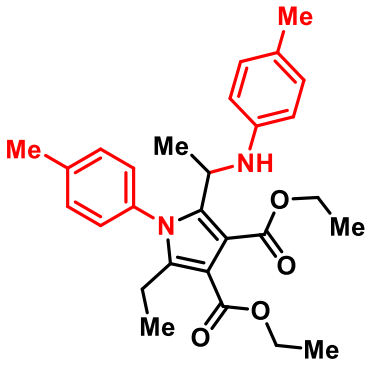
3o

Prepared from 4-fluoroaniline and ethyl propionylacetate following the general procedure to give the product as pale yellow oil (74% yield).

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.25–7.10 (m, 4H), 6.80 (t, 2H, *J* = 8.54 Hz), 6.32 (dd, 2H, *J* = 8.24, 3.66 Hz), 4.37–4.24 (m, 5H), 2.47 (q, 2H, *J* = 7.63 Hz), 1.46 (d, 3H, *J* = 6.71 Hz), 1.34 (t+t, 6H, *J* = 7.32 Hz), 0.93 (t, 3H, *J* = 7.63 Hz).

^{13}C NMR (125 MHz, Chloroform-*d*): δ 166.60, 165.07, 164.87, 160.88, 140.01, 138.82, 132.32, 132.26, 130.46, 130.40, 130.31, 130.27, 116.69, 116.33, 115.75, 115.40, 115.03, 112.97, 112.64, 60.90, 60.32, 47.21, 21.53, 18.76, 14.31, 14.27, 14.11.

HRMS m/z (ESI): calcd. for $C_{26}H_{29}F_2N_2O_4$ $[M+H]^+$ 471,20899, found 471,20854.



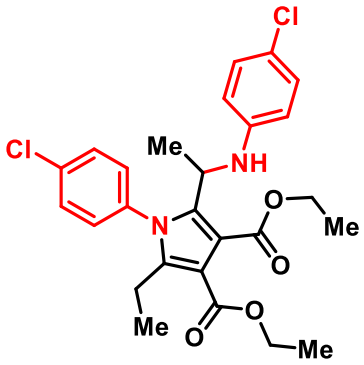
3p

Prepared from 4-methylaniline and ethyl propionylacetate following the general procedure to give the product as pale yellow oil (70% yield).

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.30 (d, 2H, *J* = 8.34 Hz), 7.05 (m, 2H), 6.88 (d, 2H, *J* = 7.93 Hz), 6.32 (d, 2H, *J* = 7.32 Hz), 4.39–4.17 (m, 5H), 2.53–2.44 (s+m, 5H), 2.21 (s, 3H), 1.43 (d, 3H, *J* = 6.71 Hz), 1.32 (t+t, 6H, *J* = 7.02 Hz), 0.93 (t, 3H, *J* = 7.32 Hz).

^{13}C NMR (125 MHz, Chloroform-*d*): δ 166.77, 165.29, 140.02, 139.72, 133.71, 130.03, 129.96, 129.53, 128.40, 128.30, 113.89, 112.53, 112.20, 60.71, 60.13, 46.29, 21.68, 21.27, 20.36, 18.77, 14.36, 14.27, 14.12.

HRMS m/z (ESI): calcd. for $C_{28}H_{35}N_2O_4$ $[M+H]^+$ 463,25913, found 463,25848.



3q

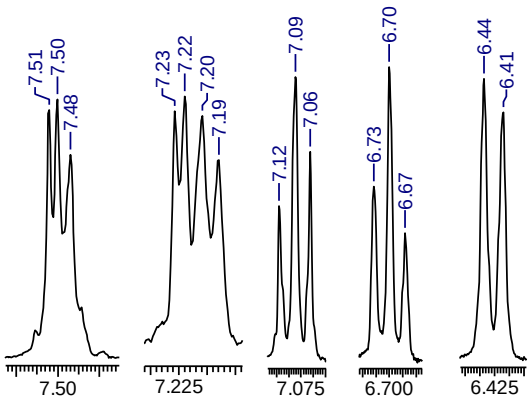
Prepared from 4-chloroaniline and ethyl propionylacetate following the general procedure to give the product as orange yellow oil (76% yield).

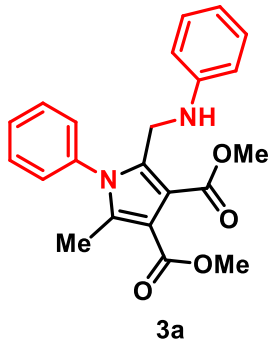
^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.54–7.47 (m, 2H), 7.19–7.02 (m, 4H), 6.26 (d, 2H, J = 8.85 Hz), 4.38–4.24 (m, 5H), 2.47 (q, 2H, J = 7.32 Hz), 1.42 (d, 3H, J = 6.71 Hz), 1.33 (t+t, 6H, J = 7.02 Hz), 0.93 (t, 3H, J = 7.32 Hz).

^{13}C NMR (125 MHz, Chloroform-*d*): δ 166.47, 165.00, 145.15, 139.92, 138.51, 135.86, 134.89, 129.87, 129.83, 129.72, 128.99, 122.36, 114.67, 113.17, 112.76, 60.92, 60.33, 46.21, 21.61, 18.73, 14.34, 14.25, 14.11.

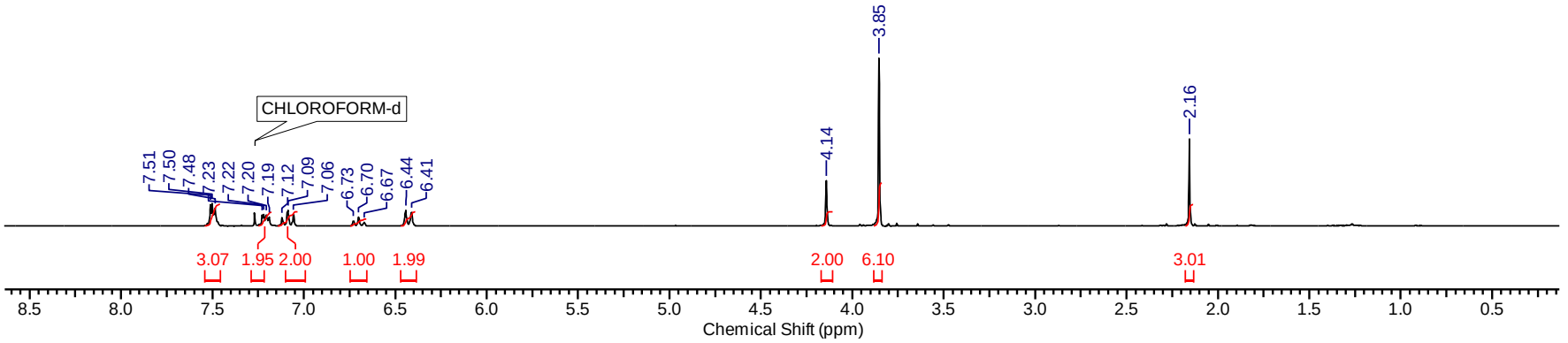
HRMS m/z (ESI): calcd. for $C_{26}H_{29}Cl_2N_2O_4$ $[M+H]^+$ 503,14989, found 503,14910.

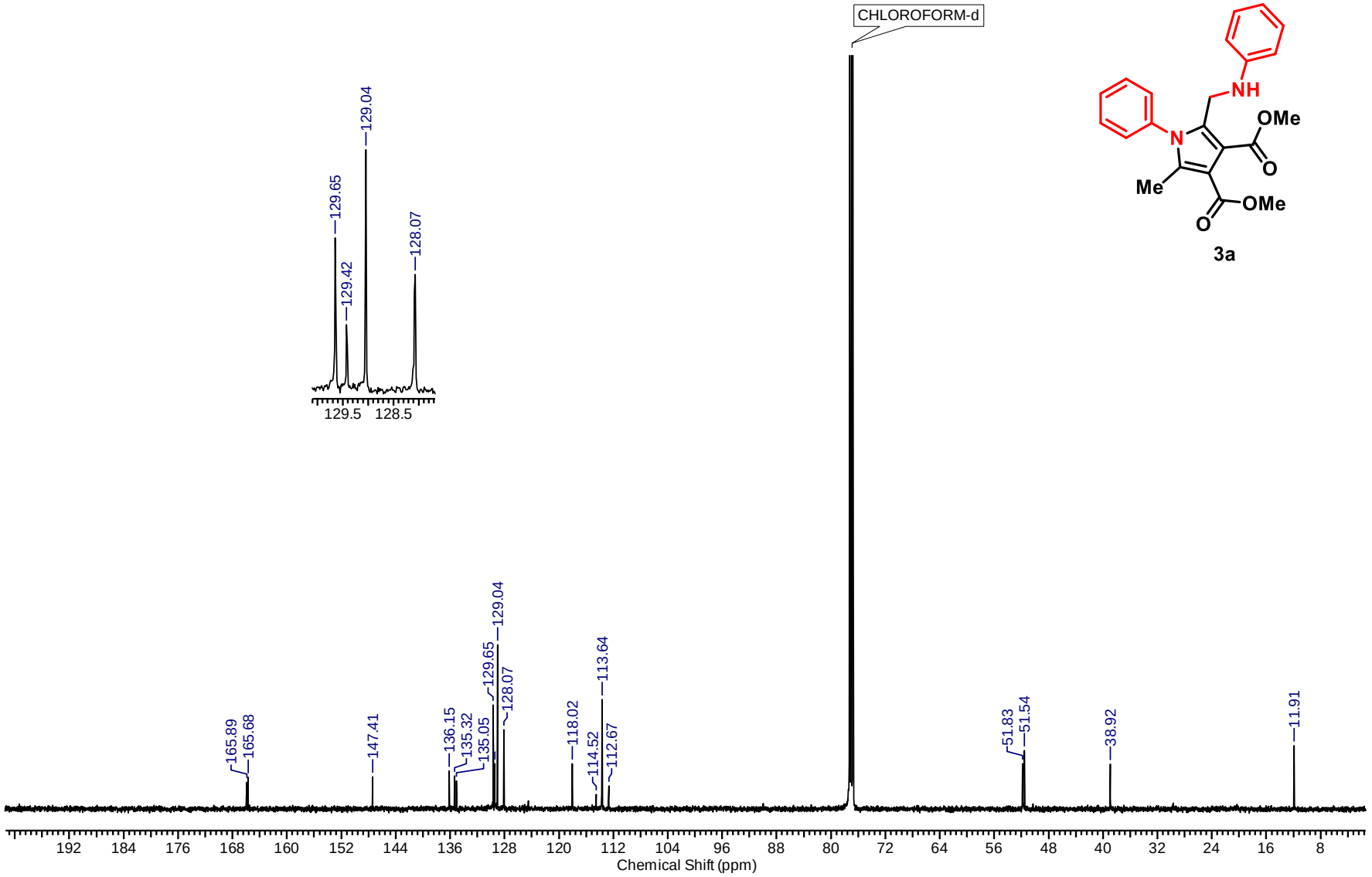
13. Spectral data

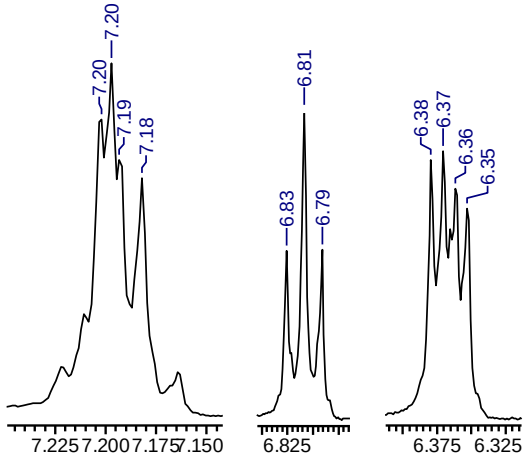

7.51
7.50
7.48
7.23
7.22
7.20
7.19
7.12
7.09
7.06
6.73
6.70
6.67
6.44
6.41
7.50
7.225
7.075
6.700
6.425

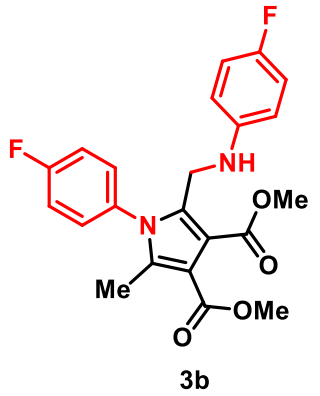

NH
OMe
N
O
Me
OMe
O

3a

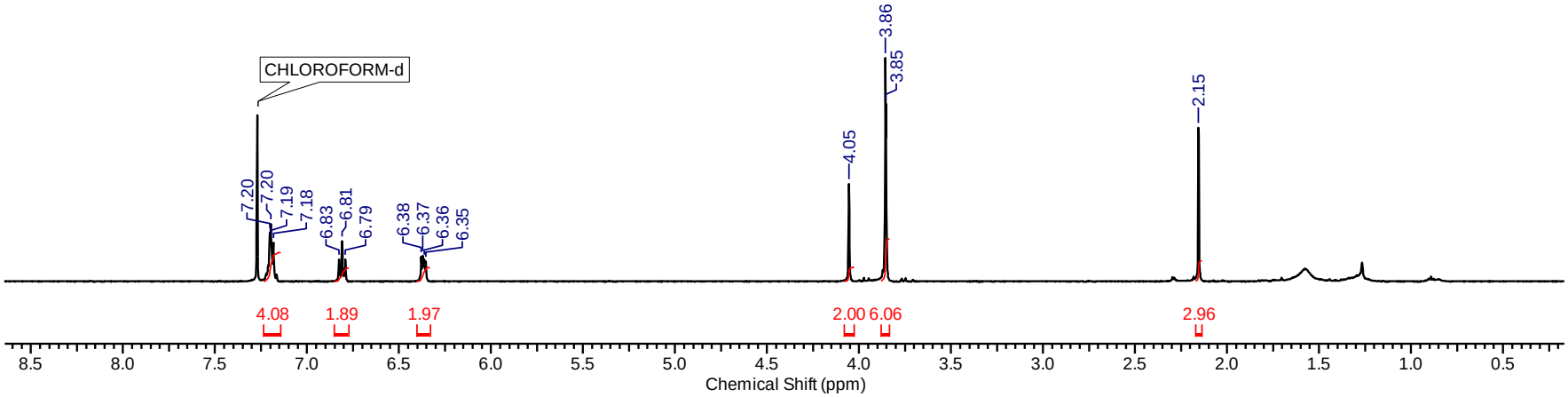

CHLOROFORM-d
7.51
7.50
7.48
7.23
7.22
7.20
7.19
7.12
7.09
7.06
6.73
6.70
6.67
6.44
6.41
4.14
3.85
2.16
3.07
1.95
2.00
1.00
1.99
2.00
6.10
3.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

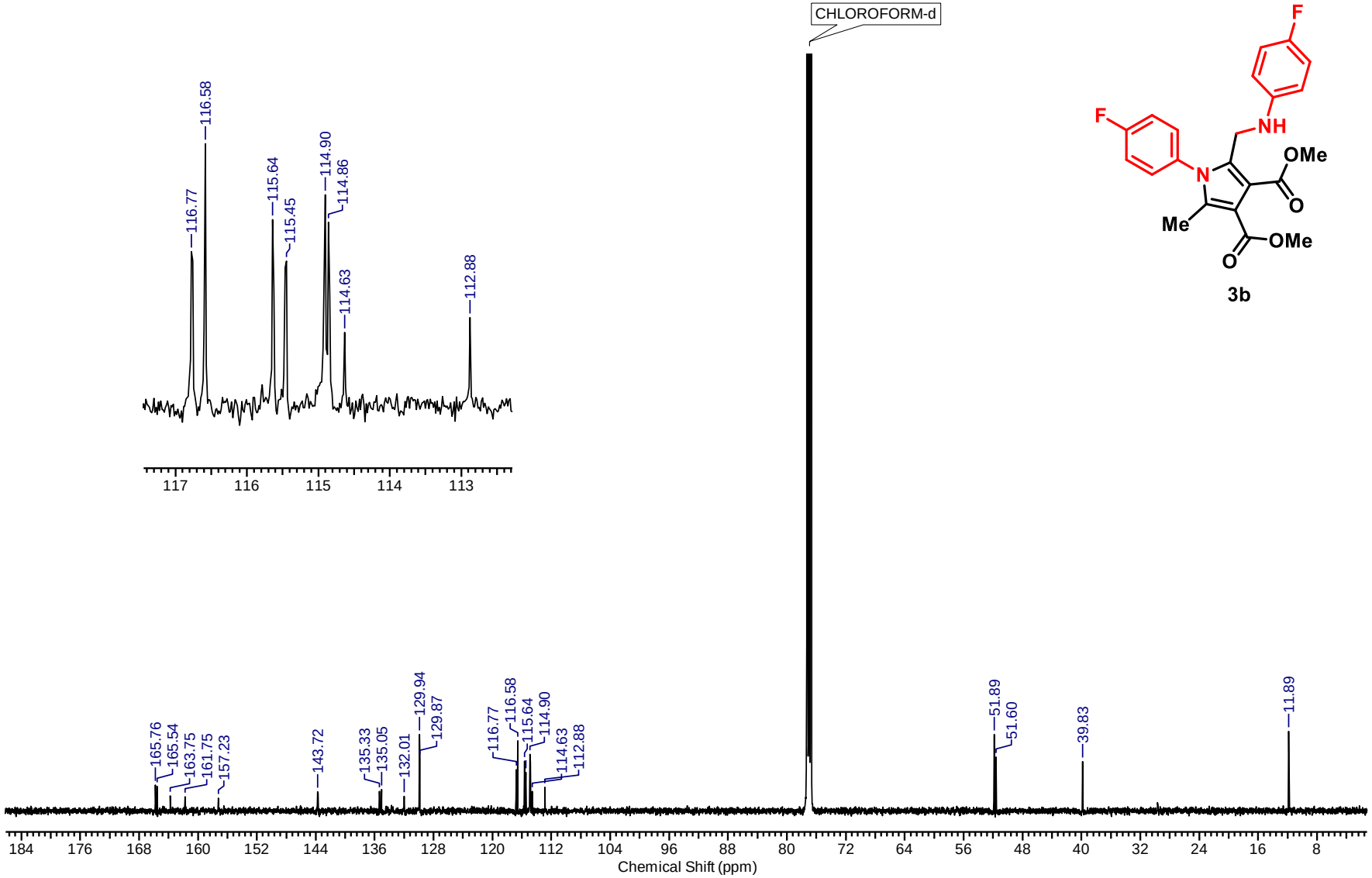

CHLOROFORM-d
129.65
129.42
129.04
128.07
129.5
128.5
NH
OMe
N
O
Me
OMe
O
3a
165.89
165.68
147.41
136.15
135.32
135.05
129.65
129.04
128.07
118.02
114.52
113.64
112.67
51.83
51.54
38.92
11.91
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

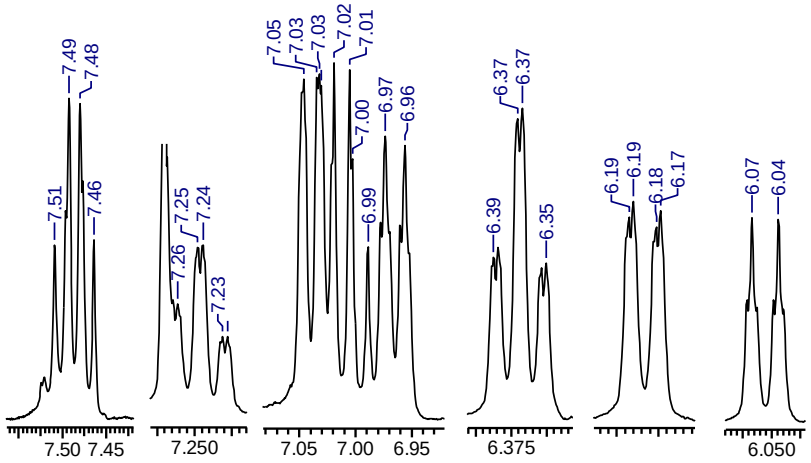

7.20
7.20
7.19
7.18
6.81
6.83
6.79
6.38
6.37
6.36
6.35
7.225 7.200 7.175 7.150
6.825
6.375 6.325

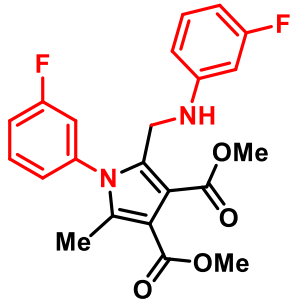

F
F
NH
N
OMe
O
Me
OMe
O

3b

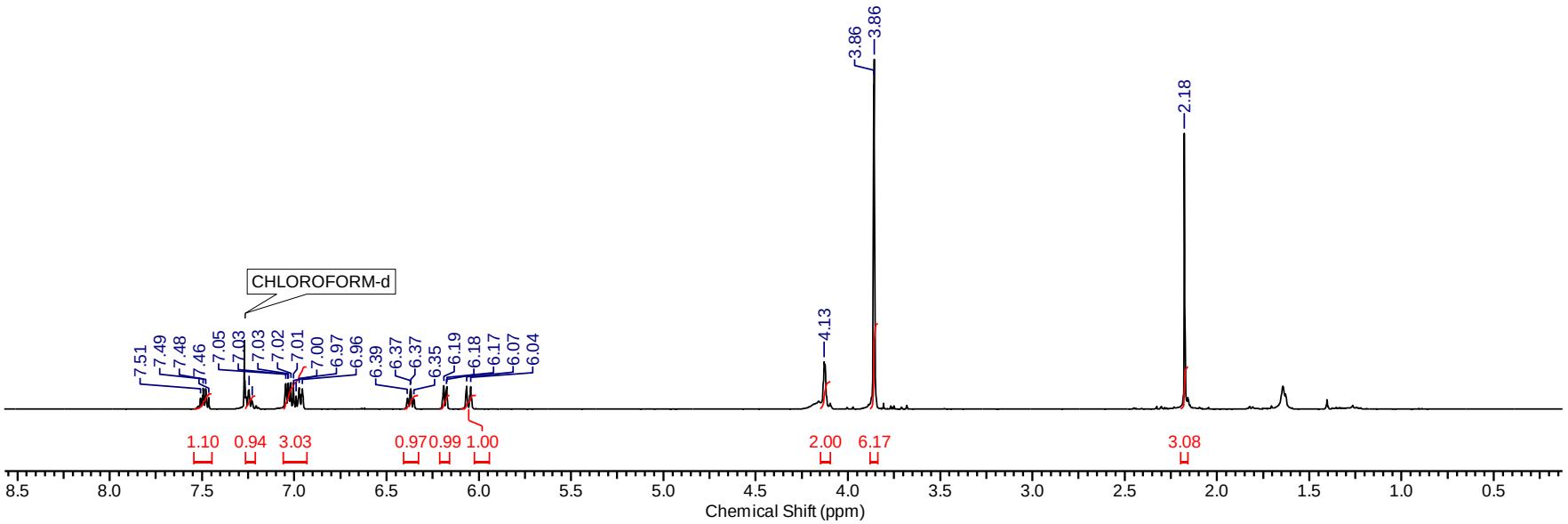

CHLOROFORM-d
7.20
7.20
7.19
7.18
6.83
6.81
6.79
6.38
6.37
6.36
6.35
4.05
3.86
3.85
2.15
4.08
1.89
1.97
2.00
6.06
2.96
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
Chemical Shift (ppm)

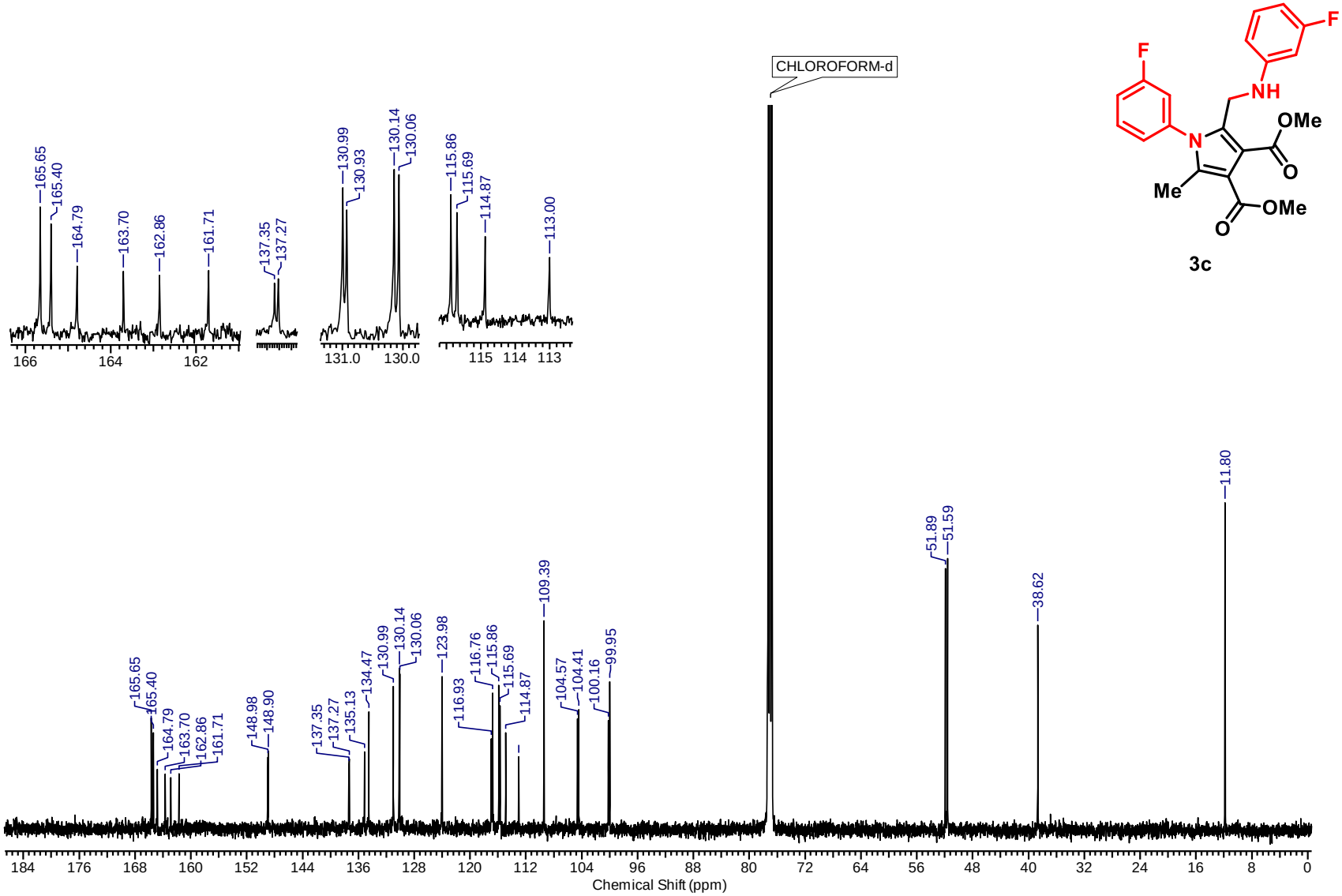

CHLOROFORM-d
116.77
116.58
115.64
115.45
114.90
114.86
114.63
112.88
117
116
115
114
113
F
NH
F
N
OMe
O
Me
OMe
O
3b
165.76
165.54
163.75
161.75
157.23
143.72
135.33
135.05
132.01
129.94
129.87
116.77
116.58
115.64
114.90
114.63
112.88
51.89
51.60
39.83
11.89
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

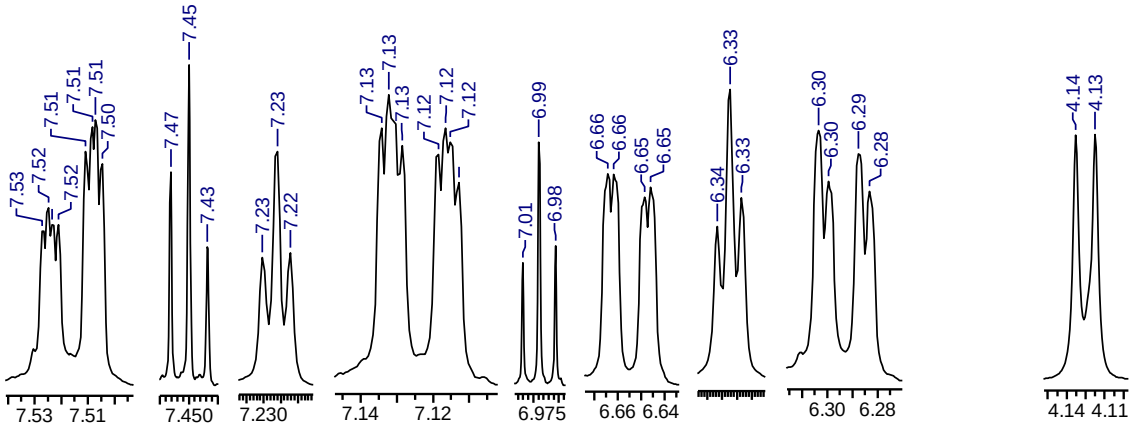

7.51
7.49
7.48
7.46
7.26
7.25
7.24
7.23
7.05
7.03
7.03
7.02
7.01
7.00
6.99
6.97
6.96
6.39
6.37
6.37
6.35
6.19
6.19
6.18
6.17
6.07
6.04
7.50 7.45
7.250
7.05 7.00 6.95
6.375
6.050

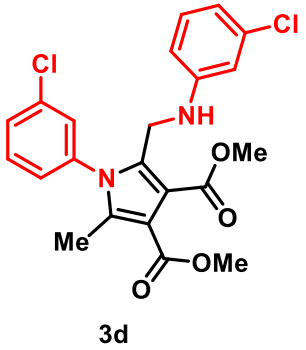

F
F
NH
N
OMe
O
Me
O
OMe

3c

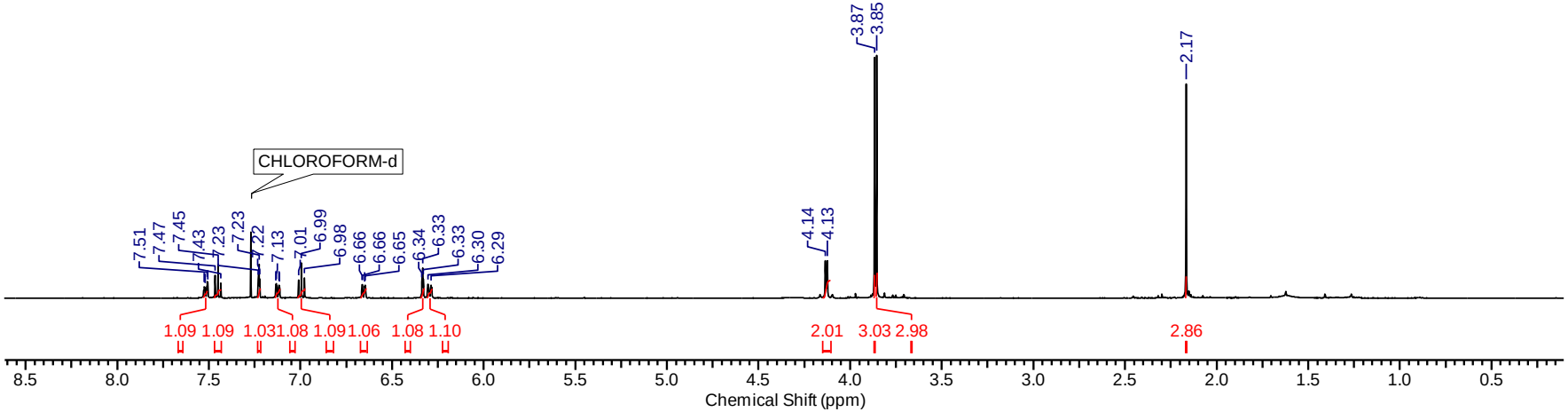

CHLOROFORM-d
7.51
7.49
7.48
7.46
7.05
7.03
7.03
7.02
7.01
7.00
6.97
6.96
6.39
6.37
6.37
6.35
6.19
6.18
6.17
6.07
6.04
4.13
3.86
3.86
2.18
1.10
0.94
3.03
0.97
0.99
1.00
2.00
6.17
3.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

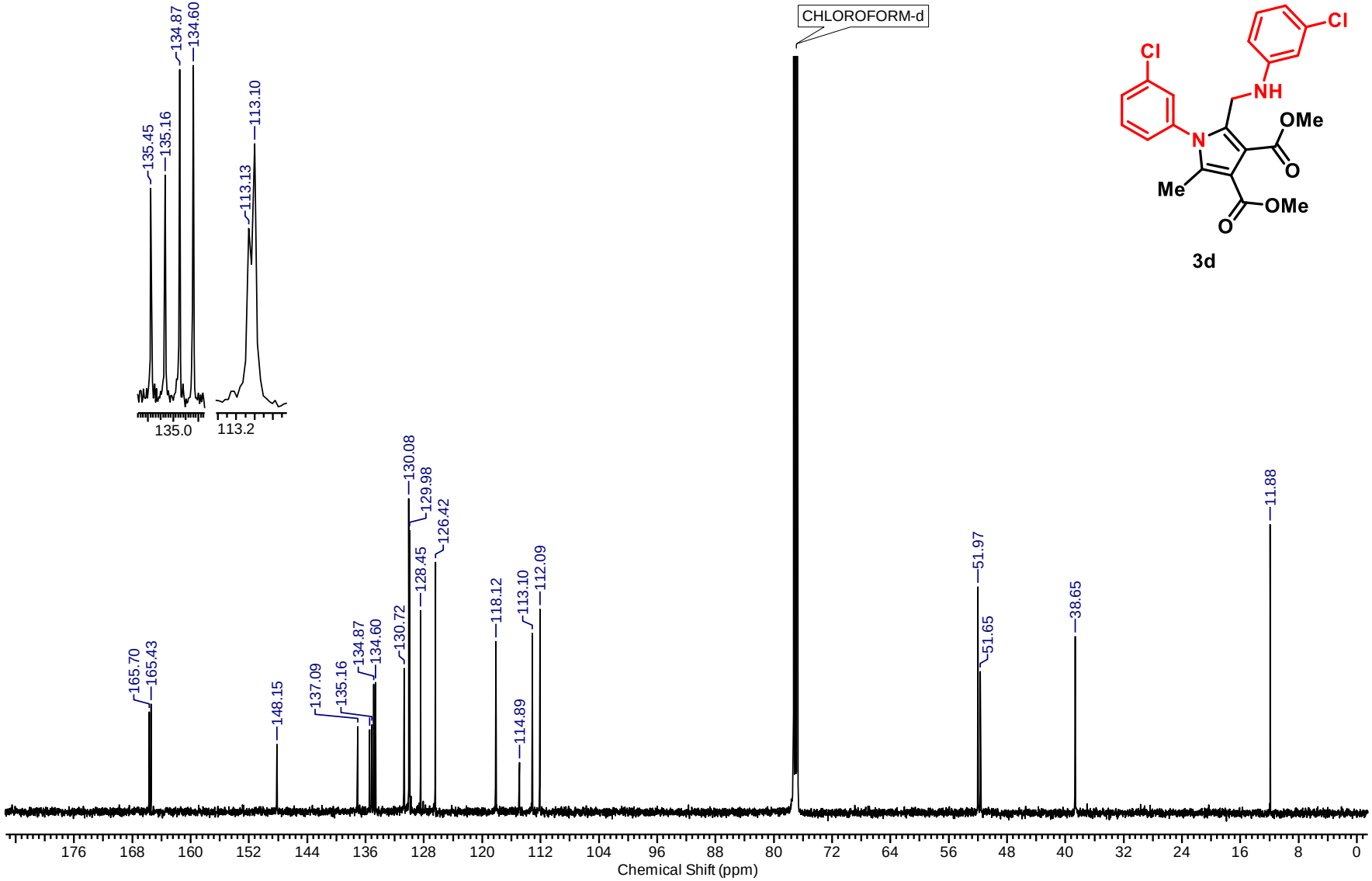

CHLOROFORM-d
F
F
NH
OMe
O
N
Me
OMe
O
3c
165.65
165.40
164.79
163.70
162.86
161.71
137.35
137.27
130.99
130.93
130.14
130.06
115.86
115.69
114.87
113.00
148.98
148.90
135.13
134.47
123.98
116.93
116.76
109.39
104.57
104.41
100.16
99.95
51.89
51.59
38.62
11.80
166
164
162
131.0
130.0
115
114
113
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

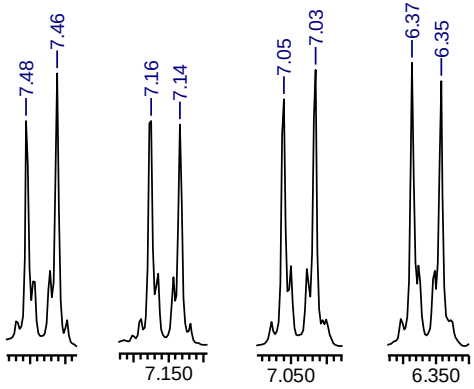

7.53
7.52
7.51
7.51
7.51
7.50
7.52
7.47
7.45
7.43
7.23
7.23
7.22
7.13
7.13
7.13
7.12
7.12
7.12
7.01
6.99
6.98
6.66
6.66
6.65
6.65
6.34
6.33
6.33
6.30
6.30
6.29
6.28
4.14
4.13
7.53 7.51
7.450
7.230
7.14 7.12
6.975
6.66 6.64
6.30 6.28
4.14 4.11

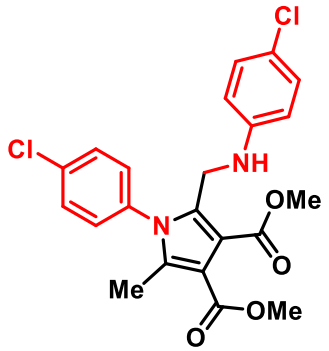

Cl
Cl
NH
N
OMe
O
Me
OMe
O

3d

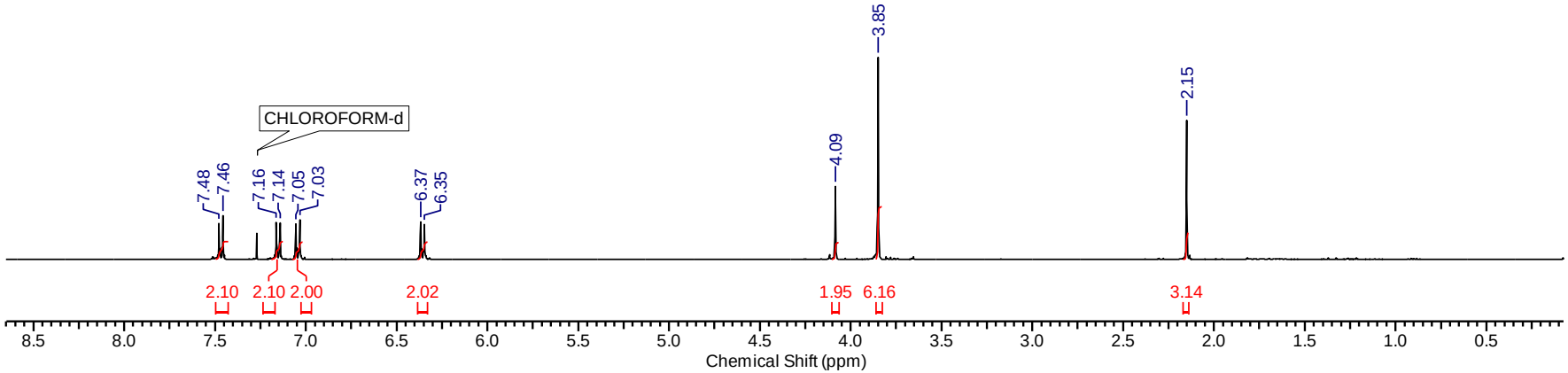

CHLOROFORM-d
7.51
7.47
7.45
7.43
7.23
7.22
7.13
7.01
6.99
6.98
6.66
6.66
6.65
6.34
6.33
6.33
6.30
6.29
4.14
4.13
3.87
3.85
2.17
1.09 1.09 1.03 1.08 1.09 1.06 1.08 1.10
2.01 3.03 2.98
2.86
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
Chemical Shift (ppm)

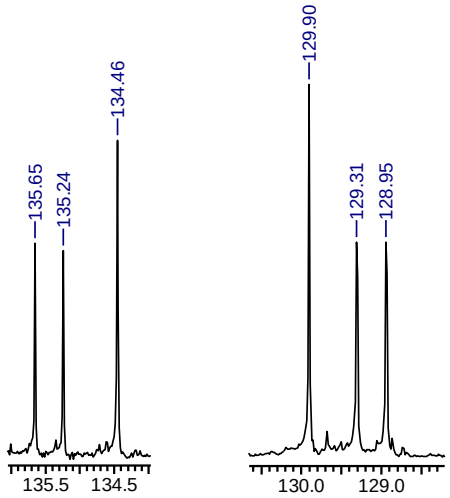

CHLOROFORM-d
Cl
Cl
NH
N
OMe
O
Me
OMe
O
3d
135.45
135.16
134.87
134.60
113.13
113.10
135.0
113.2
165.70
165.43
148.15
137.09
135.16
134.87
134.60
130.72
130.08
129.98
128.45
126.42
118.12
114.89
113.10
112.09
51.97
51.65
38.65
11.88
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


7.48
7.46
7.16
7.14
7.05
7.03
6.37
6.35
7.150
7.050
6.350

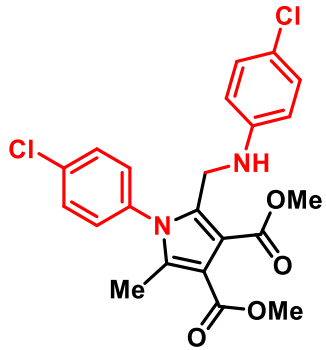

Cl
Cl
NH
N
OMe
O
Me
O
OMe

3e

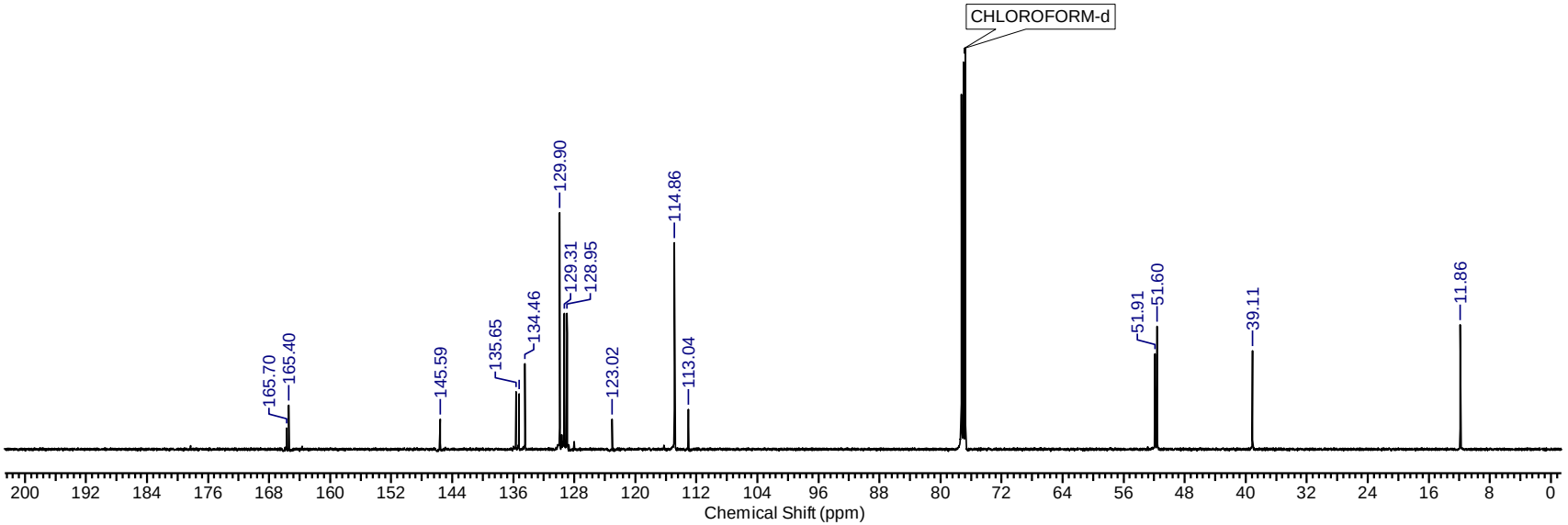

CHLOROFORM-d
7.48
7.46
7.16
7.14
7.05
7.03
6.37
6.35
4.09
3.85
2.15
2.10
2.10
2.00
2.02
1.95
6.16
3.14
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

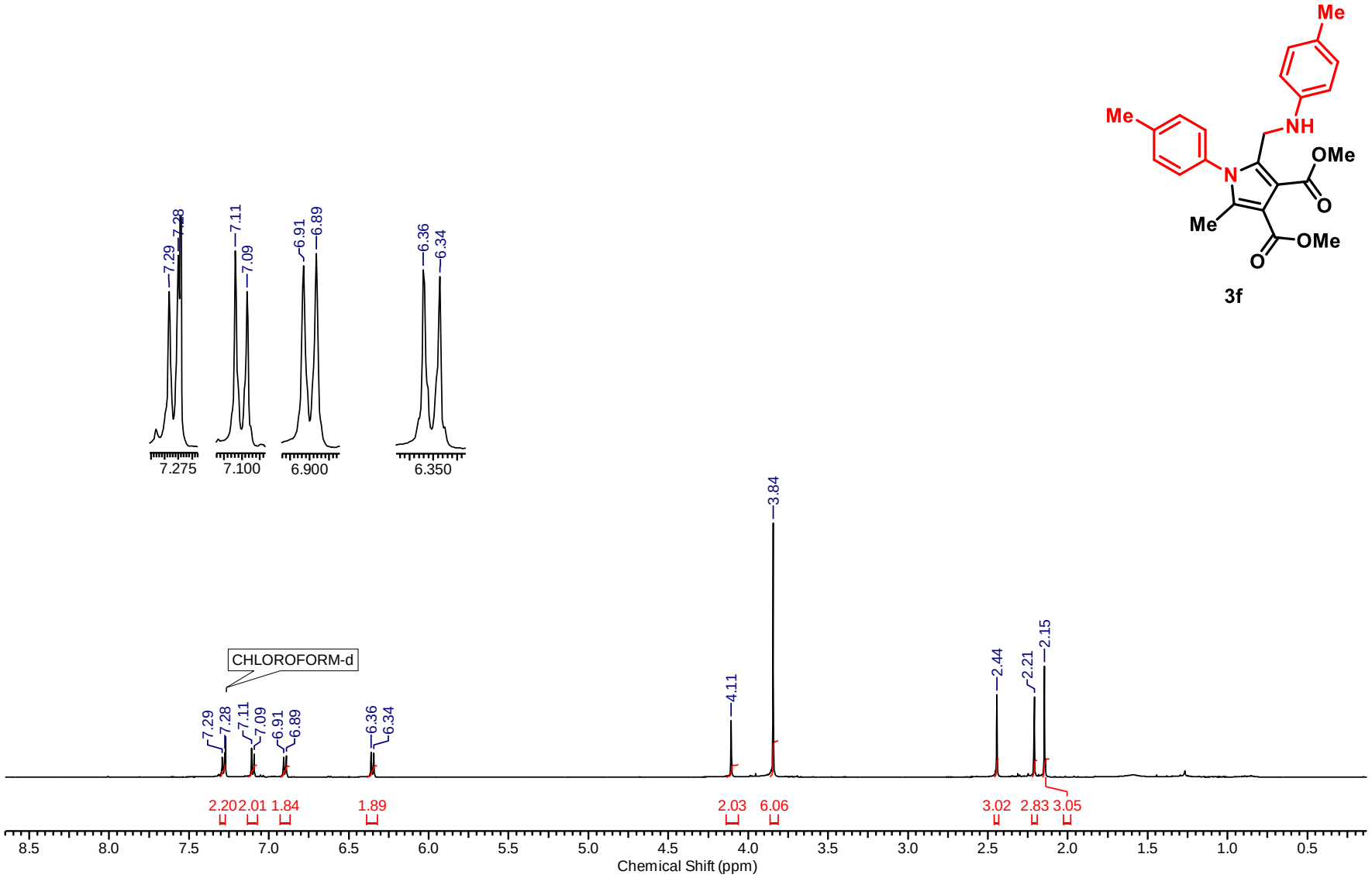

135.65
135.24
134.46
135.5
134.5

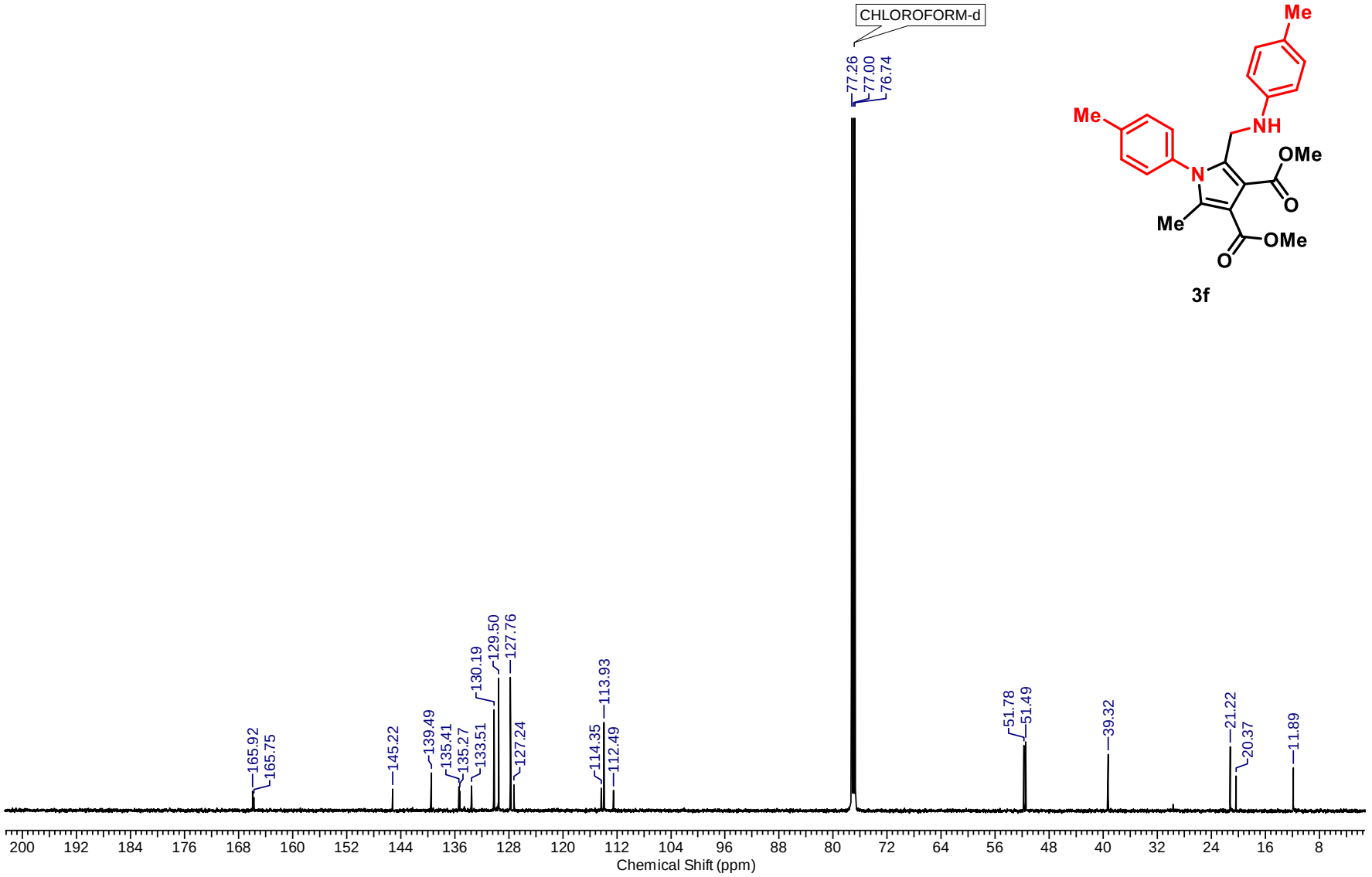
129.90
129.31
128.95
130.0
129.0

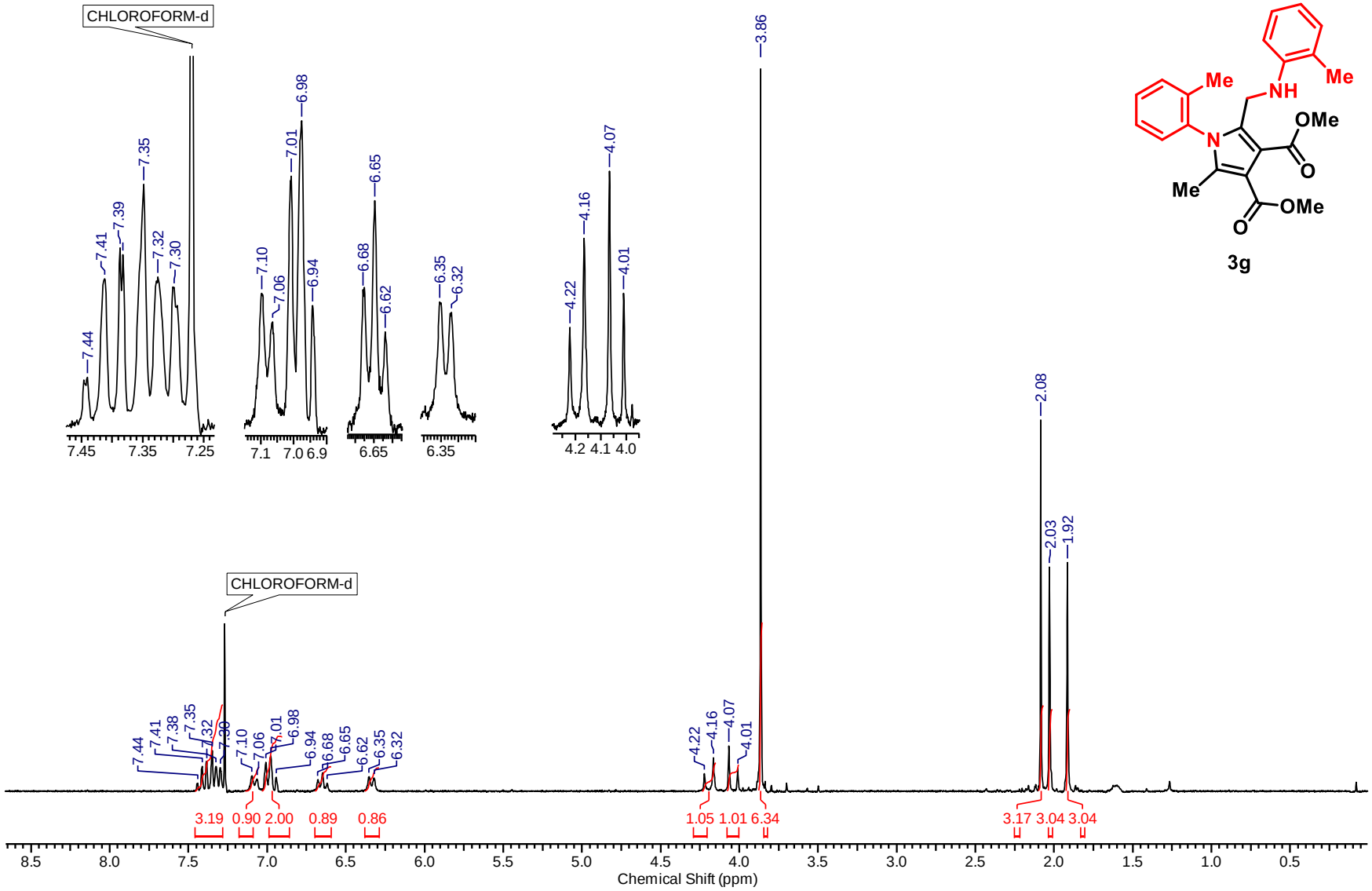

Cl
Cl
NH
N
OMe
O
Me
OMe
O

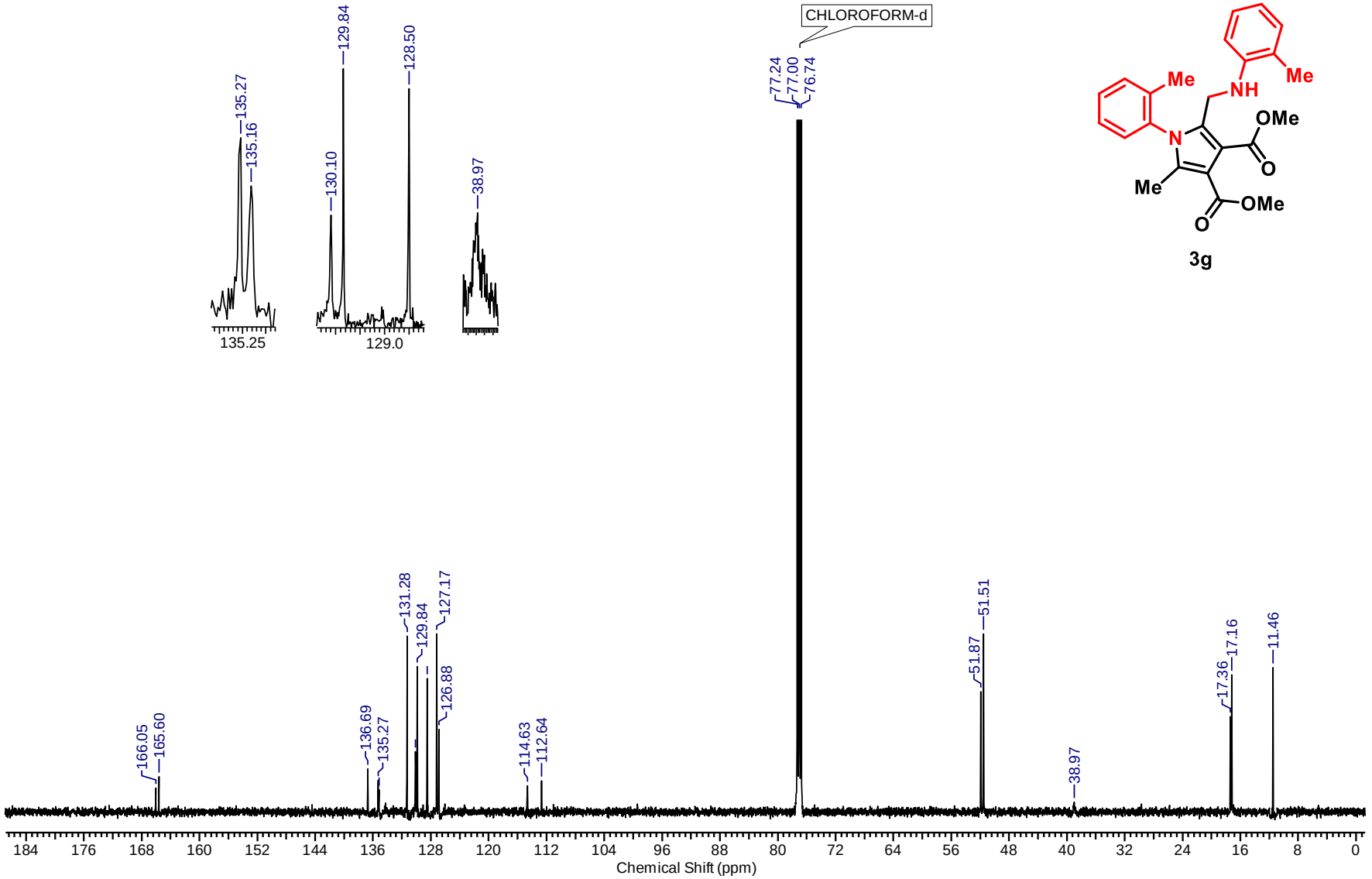
3e

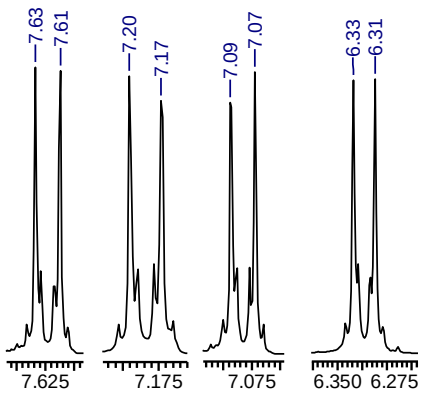

CHLOROFORM-d
165.70
165.40
145.59
135.65
134.46
129.90
129.31
128.95
123.02
114.86
113.04
51.91
51.60
39.11
11.86
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

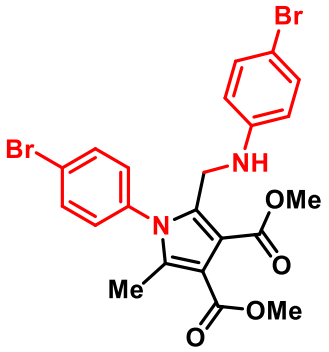

Me
Me
NH
N
OMe
O
Me
OMe
O
3f
7.29
7.28
7.11
7.09
6.91
6.89
6.36
6.34
7.275
7.100
6.900
6.350
CHLOROFORM-d
3.84
4.11
2.44
2.21
2.15
2.20
2.01
1.84
1.89
2.03
6.06
3.02
2.83
3.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)


CHLOROFORM-d
77.26
77.00
76.74
165.92
165.75
145.22
139.49
135.41
135.27
133.51
130.19
129.50
127.76
127.24
114.35
113.93
112.49
51.78
51.49
39.32
21.22
20.37
11.89
Me
NH
N
OMe
O
Me
OMe
O
Me
3f
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8
Chemical Shift (ppm)

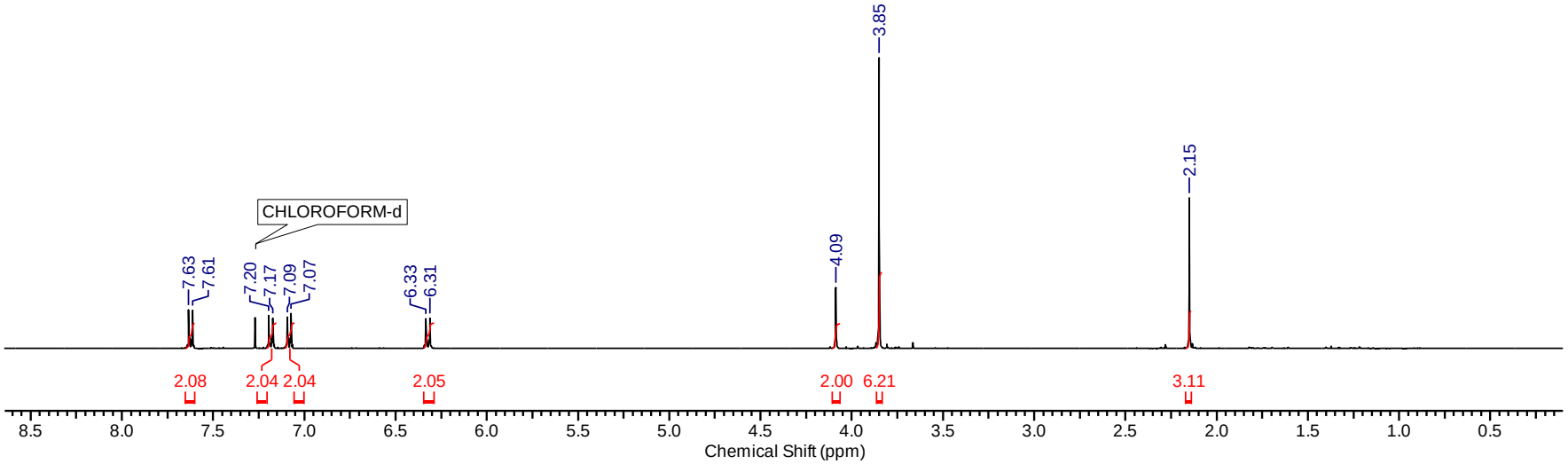

CHLOROFORM-d
7.44
7.41
7.39
7.35
7.32
7.30
7.10
7.06
6.98
7.01
6.94
6.68
6.65
6.62
6.35
6.32
4.22
4.16
4.07
4.01
3.86
2.08
2.03
1.92
3.19
0.90
2.00
0.89
0.86
1.05
1.01
6.34
3.17
3.04
3.04
Chemical Shift (ppm)
Me
NH
Me
N
OMe
O
Me
OMe
O
3g

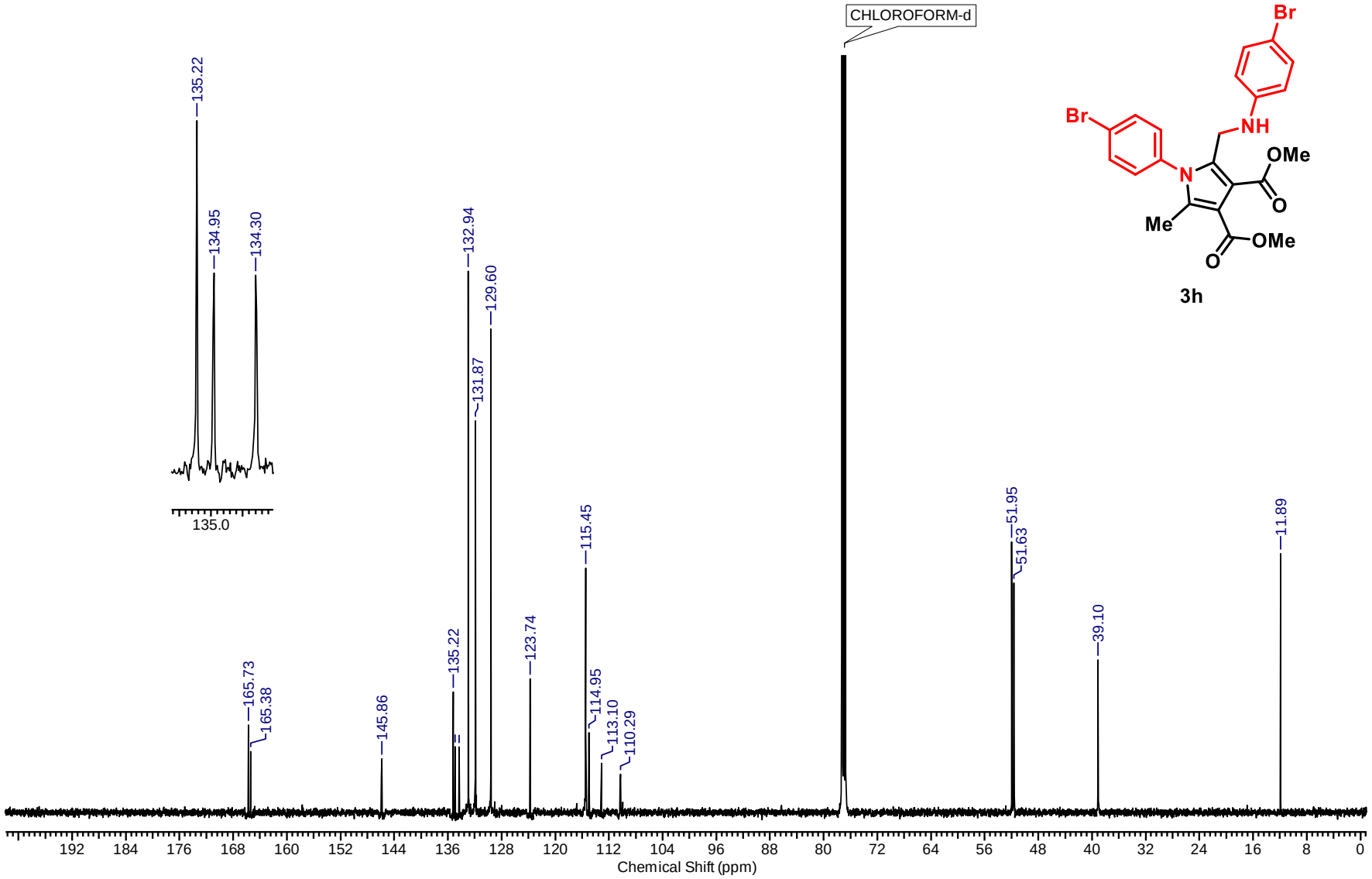

CHLOROFORM-d
77.24
77.00
76.74
135.27
135.16
130.10
129.84
128.50
38.97
135.25
129.0
Me
NH
Me
N
OMe
O
Me
OMe
O
3g
166.05
165.60
136.69
135.27
131.28
129.84
127.17
126.88
114.63
112.64
51.87
51.51
38.97
17.36
17.16
11.46
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

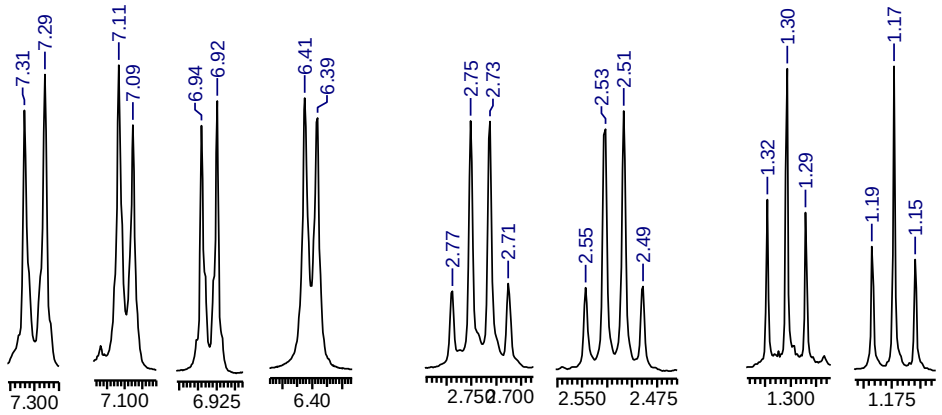

7.63
7.61
7.20
7.17
7.09
7.07
6.33
6.31
7.625
7.175
7.075
6.350 6.275

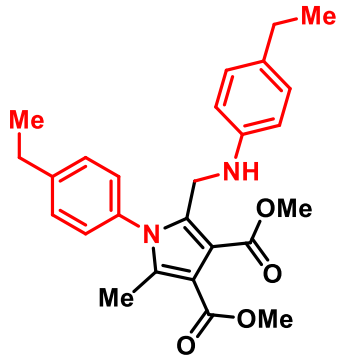

Br
Br
NH
N
OMe
O
Me
OMe
O

3h

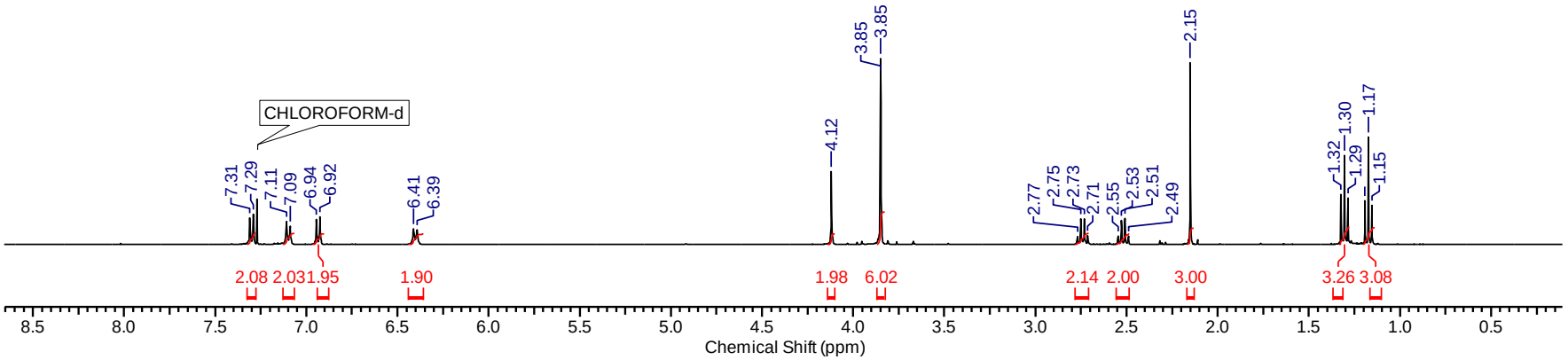

CHLOROFORM-d
7.63
7.61
7.20
7.17
7.09
7.07
6.33
6.31
4.09
3.85
2.15
2.08
2.04
2.04
2.05
2.00
6.21
3.11
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

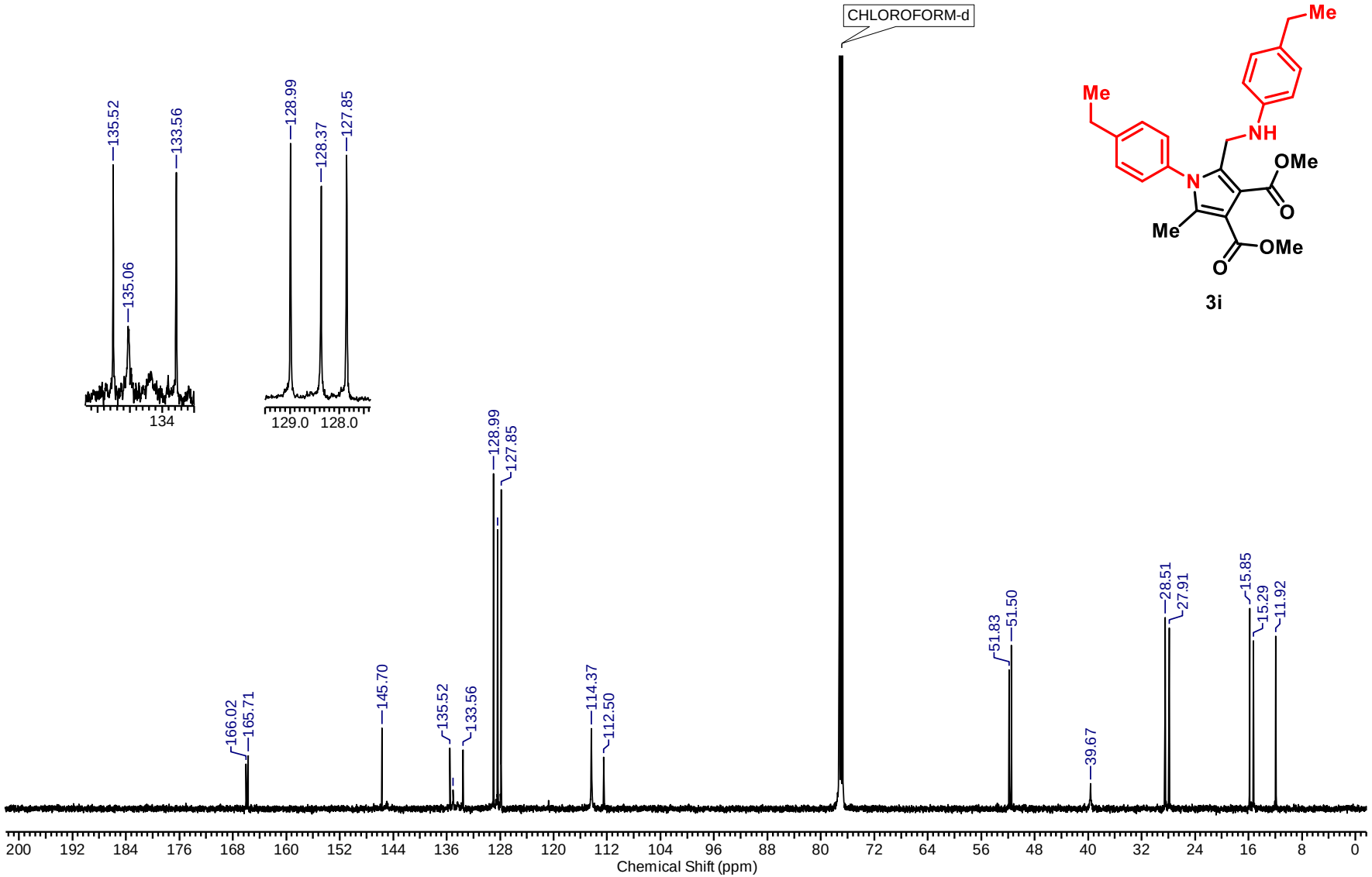

CHLOROFORM-d
135.22
134.95
134.30
135.0
132.94
129.60
131.87
115.45
123.74
51.95
51.63
11.89
39.10
165.73
165.38
145.86
135.22
114.95
113.10
110.29
Br
Br
NH
OMe
O
N
Me
O
OMe
3h
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

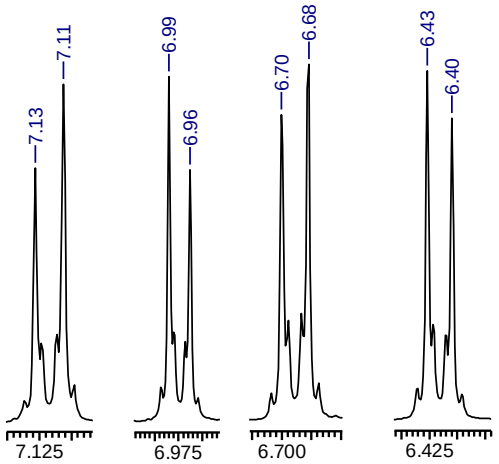

7.31
7.29
7.11
7.09
6.94
6.92
6.41
6.39
2.77
2.75
2.73
2.71
2.55
2.53
2.51
2.49
1.32
1.30
1.29
1.19
1.17
1.15
7.300
7.100
6.925
6.40
2.750
2.700
2.550
2.475
1.300
1.175

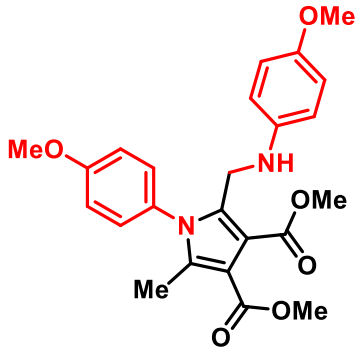

Me
Me
NH
N
OMe
O
Me
OMe
O

3i

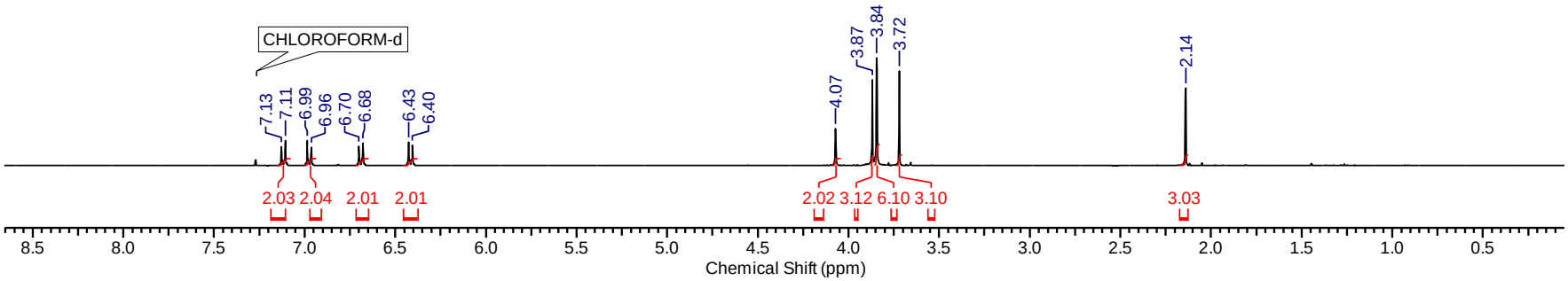

CHLOROFORM-d
7.31
7.29
7.11
7.09
6.94
6.92
6.41
6.39
4.12
3.85
3.85
2.77
2.75
2.73
2.71
2.55
2.53
2.51
2.49
2.15
1.32
1.30
1.29
1.17
1.15
2.08
2.03
1.95
1.90
1.98
6.02
2.14
2.00
3.00
3.26
3.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

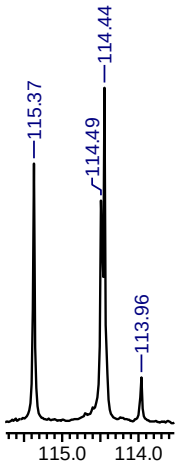

CHLOROFORM-d
135.52
135.06
133.56
128.99
128.37
127.85
134
129.0
128.0
Me
Me
NH
N
OMe
O
Me
O
OMe
3i
166.02
165.71
145.70
135.52
133.56
128.99
127.85
114.37
112.50
51.83
51.50
39.67
28.51
27.91
15.85
15.29
11.92
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

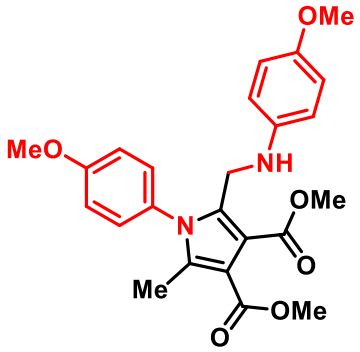

7.13
7.11
6.99
6.96
6.70
6.68
6.43
6.40
7.125
6.975
6.700
6.425


OMe
MeO
NH
N
OMe
O
Me
OMe
O

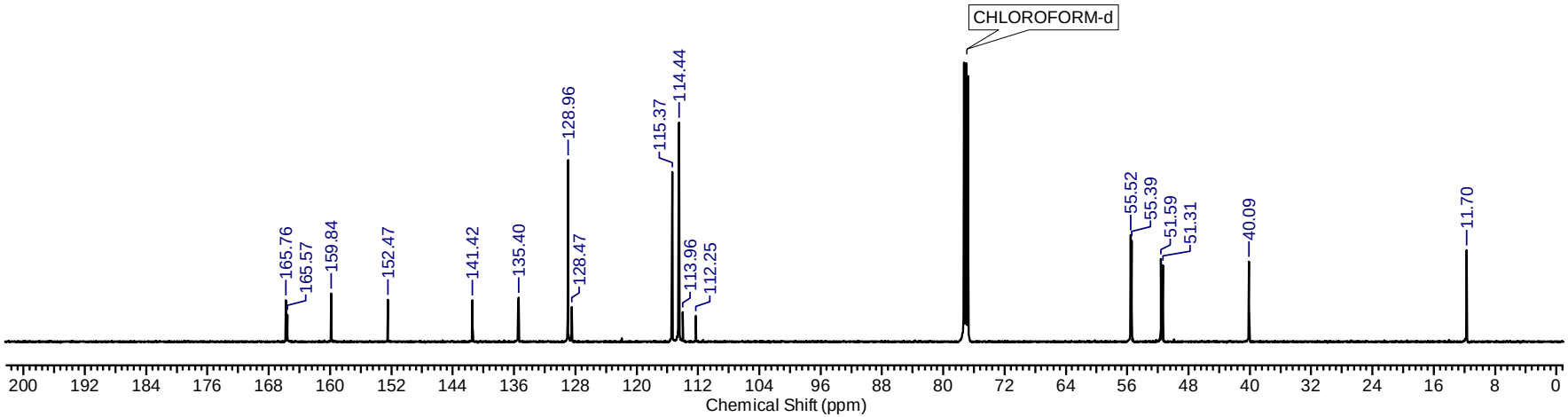
3j

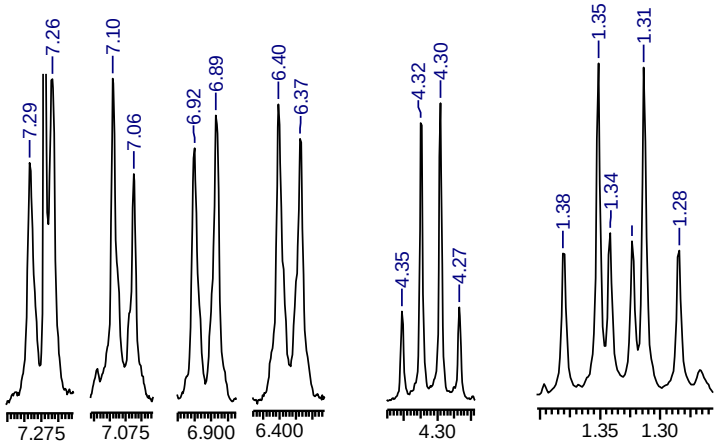

CHLOROFORM-d
7.13
7.11
6.99
6.96
6.70
6.68
6.43
6.40
4.07
3.87
3.84
3.72
2.14
2.03 2.04 2.01 2.01
2.02 3.12 6.10 3.10
3.03
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
Chemical Shift (ppm)

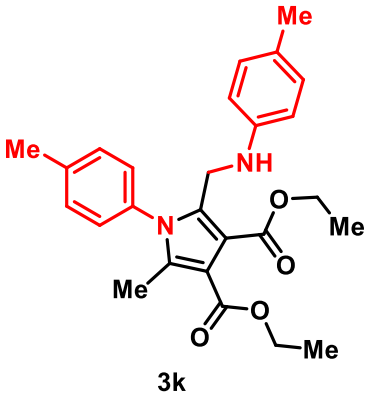

115.37
114.49
114.44
113.96
115.0
114.0


OMe
MeO
NH
N
OMe
O
Me
OMe
O

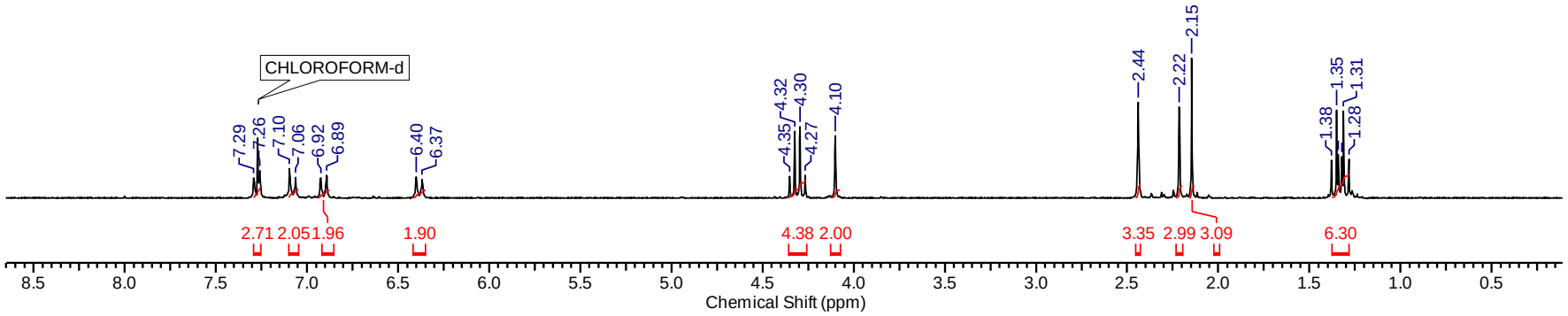
3j

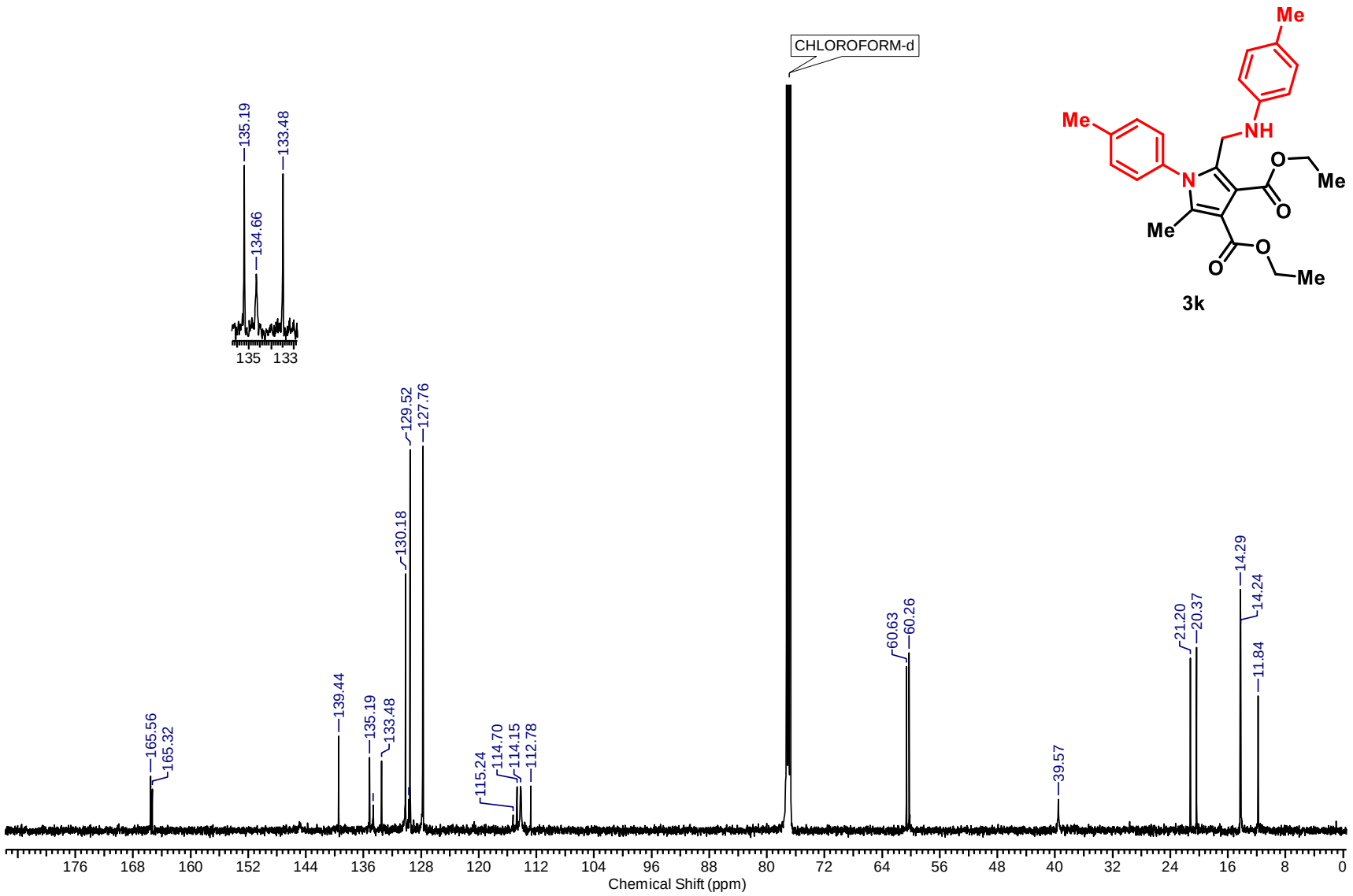

CHLOROFORM-d
165.76
165.57
159.84
152.47
141.42
135.40
128.96
128.47
115.37
114.44
113.96
112.25
55.52
55.39
51.59
51.31
40.09
11.70
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

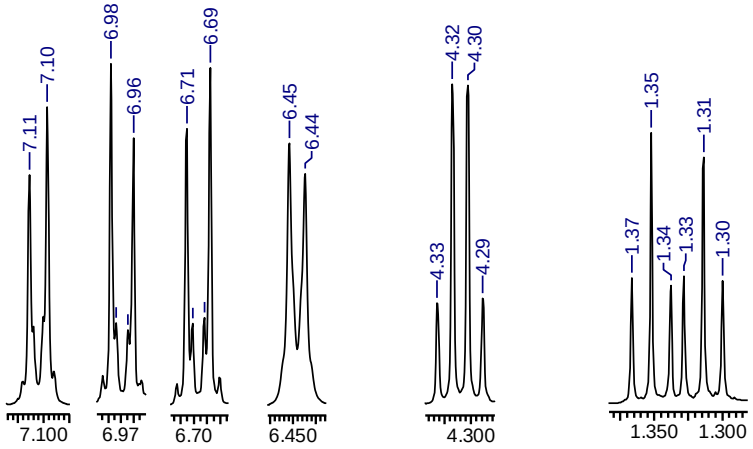

7.29
7.26
7.10
7.06
6.92
6.89
6.40
6.37
4.35
4.32
4.30
4.27
1.38
1.35
1.34
1.31
1.28
7.275
7.075
6.900
6.400
4.30
1.35
1.30

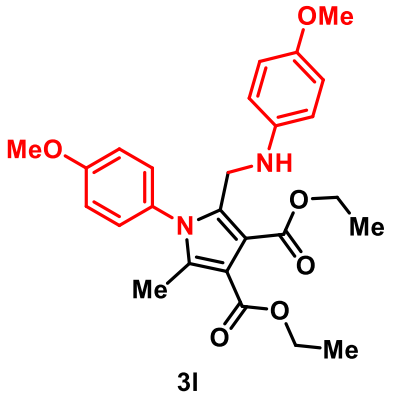

Me
NH
Me
N
Me
O
Me
O
O
O
Me

3k

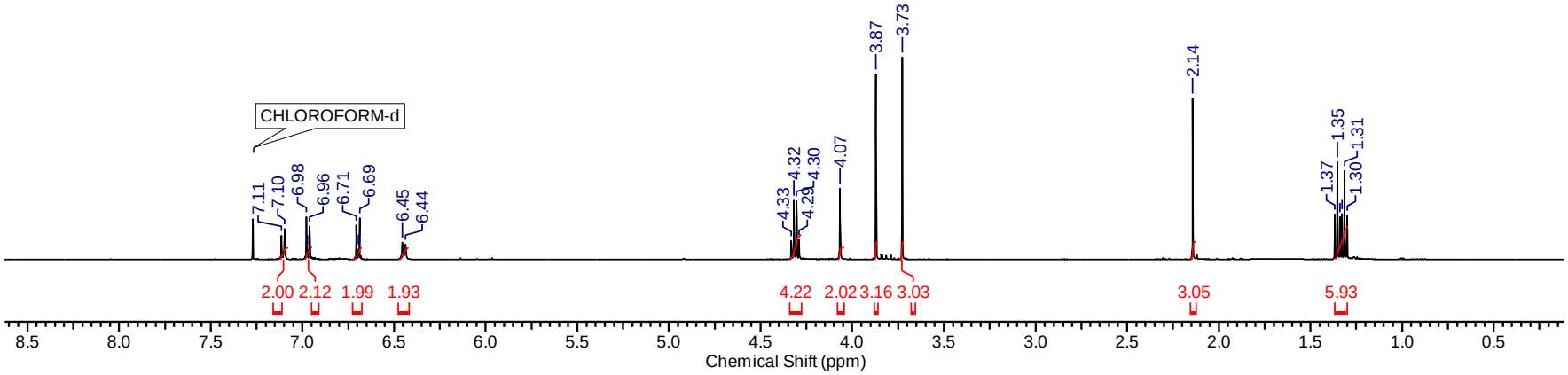

CHLOROFORM-d
7.29
7.26
7.10
7.06
6.92
6.89
6.40
6.37
4.35
4.32
4.30
4.27
4.10
2.44
2.22
2.15
1.38
1.35
1.31
1.28
2.71 2.05 1.96
1.90
4.38 2.00
3.35 2.99 3.09
6.30
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
Chemical Shift (ppm)

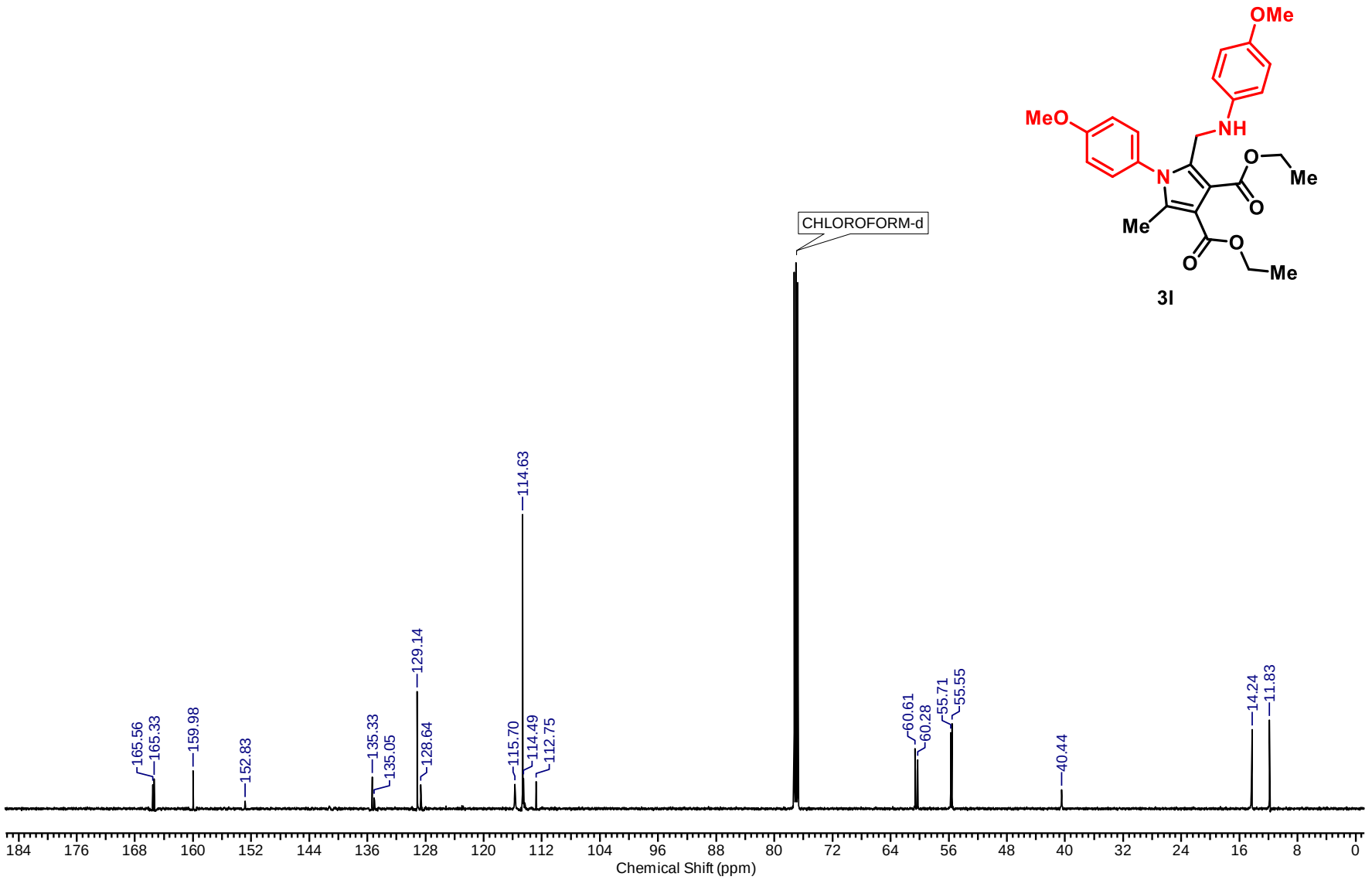

CHLOROFORM-d
135.19
133.48
134.66
135
133
Me
NH
N
Me
O
O
Me
Me
O
O
Me
3k
165.56
165.32
139.44
135.19
133.48
130.18
129.52
127.76
115.24
114.70
114.15
112.78
60.63
60.26
39.57
21.20
20.37
14.29
14.24
11.84
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

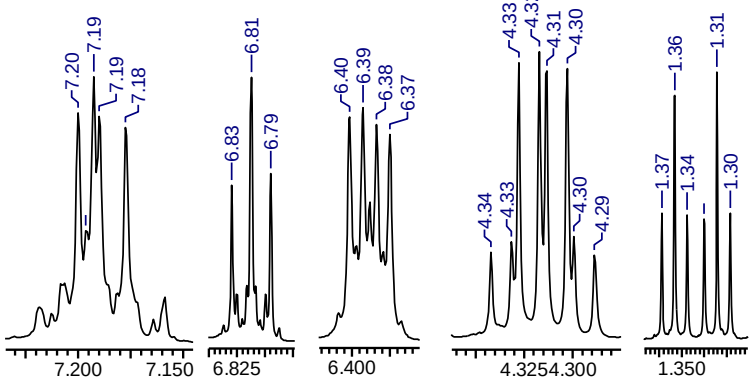

7.11
7.10
6.98
6.96
6.71
6.69
6.45
6.44
4.33
4.32
4.30
4.29
1.37
1.35
1.34
1.33
1.31
1.30
7.100
6.97
6.70
6.450
4.300
1.350
1.300

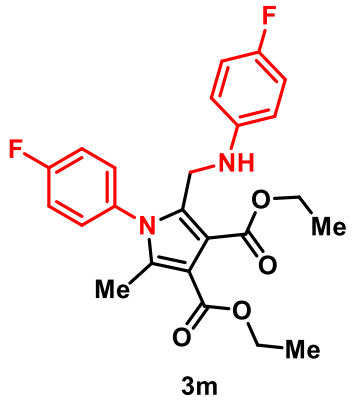

OMe
MeO
NH
N
Me
O
Me
O
O
O
Me

3l

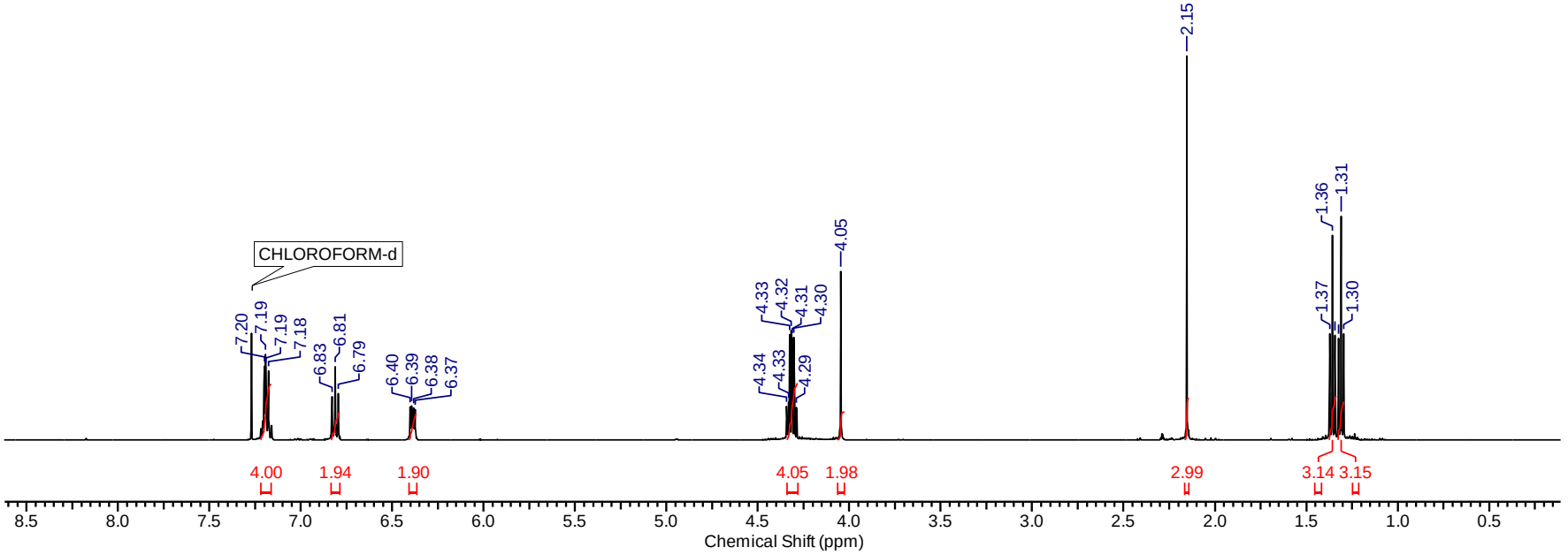

CHLOROFORM-d
7.11
7.10
6.98
6.96
6.71
6.69
6.45
6.44
4.33
4.32
4.30
4.29
4.07
3.87
3.73
2.14
1.37
1.35
1.31
1.30
2.00
2.12
1.99
1.93
4.22
2.02
3.16
3.03
3.05
5.93
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

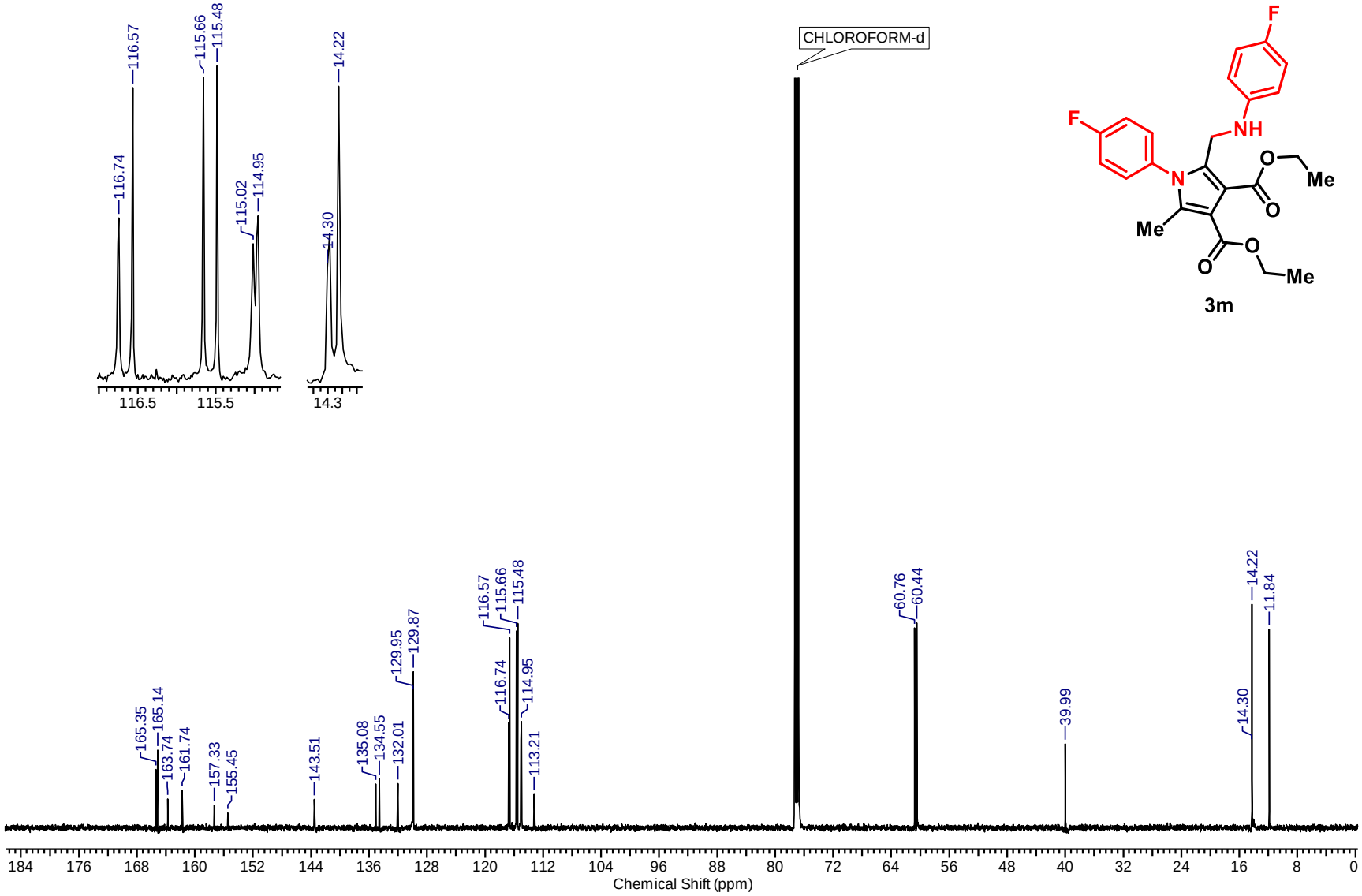

OMe
MeO
NH
N
O
Me
O
Me
O
O
O
Me
3l
CHLOROFORM-d
165.56
165.33
159.98
152.83
135.33
135.05
129.14
128.64
114.63
115.70
114.49
112.75
60.61
60.28
55.71
55.55
40.44
14.24
11.83
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

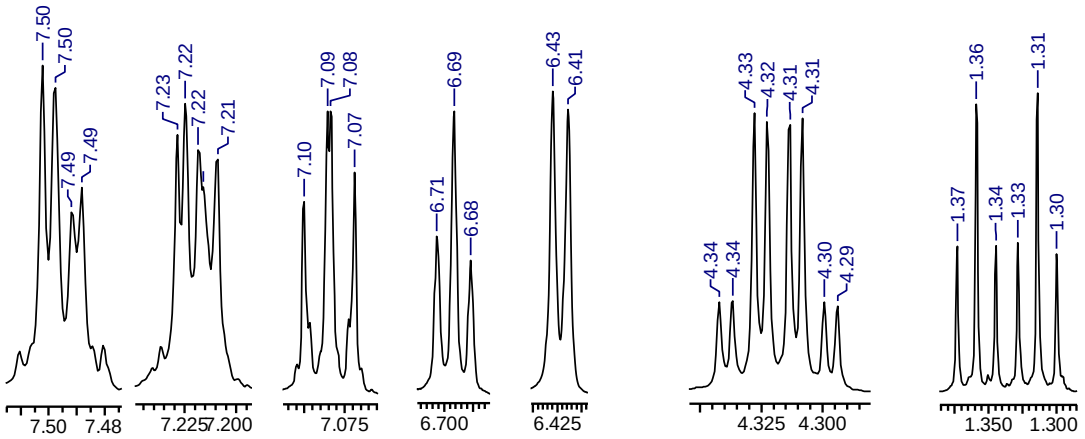

7.20
7.19
7.19
7.18
6.83
6.81
6.79
6.40
6.39
6.38
6.37
4.34
4.33
4.33
4.32
4.31
4.30
4.30
4.29
1.37
1.36
1.34
1.31
1.30
7.200
7.150
6.825
6.400
4.325
4.300
1.350

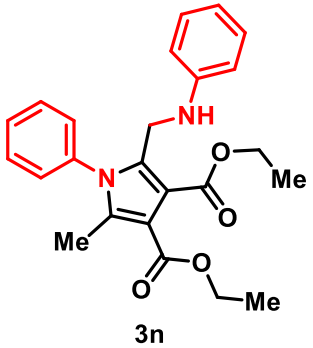

F
F
NH
N
O
Me
Me
O
O
O
Me

3m

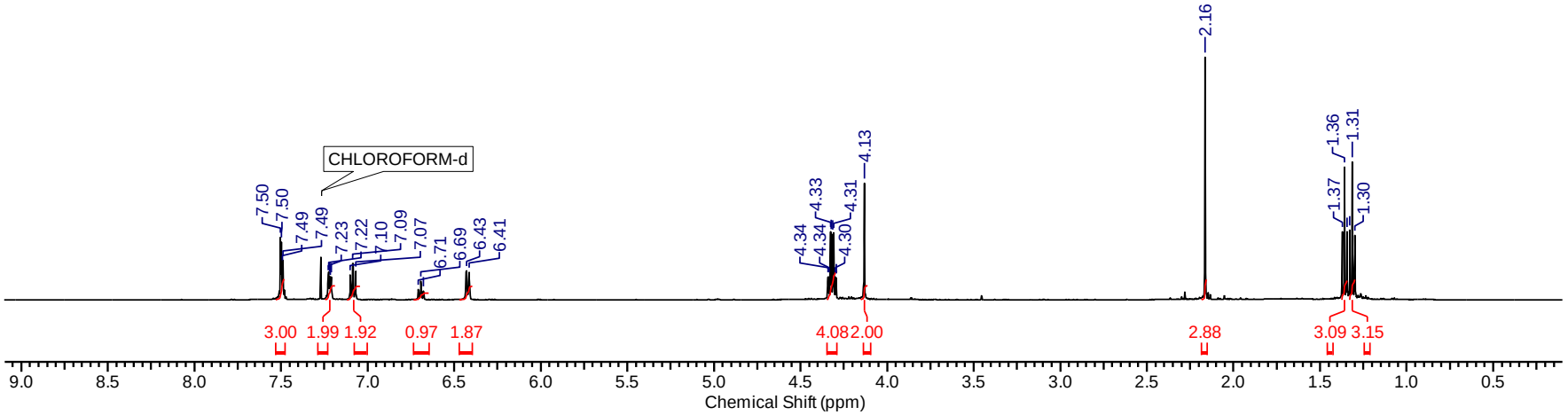

CHLOROFORM-d
7.20
7.19
7.19
7.18
6.83
6.81
6.79
6.40
6.39
6.38
6.37
4.34
4.33
4.33
4.32
4.31
4.30
4.29
4.05
2.15
1.37
1.36
1.31
1.30
4.00
1.94
1.90
4.05
1.98
2.99
3.14
3.15
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

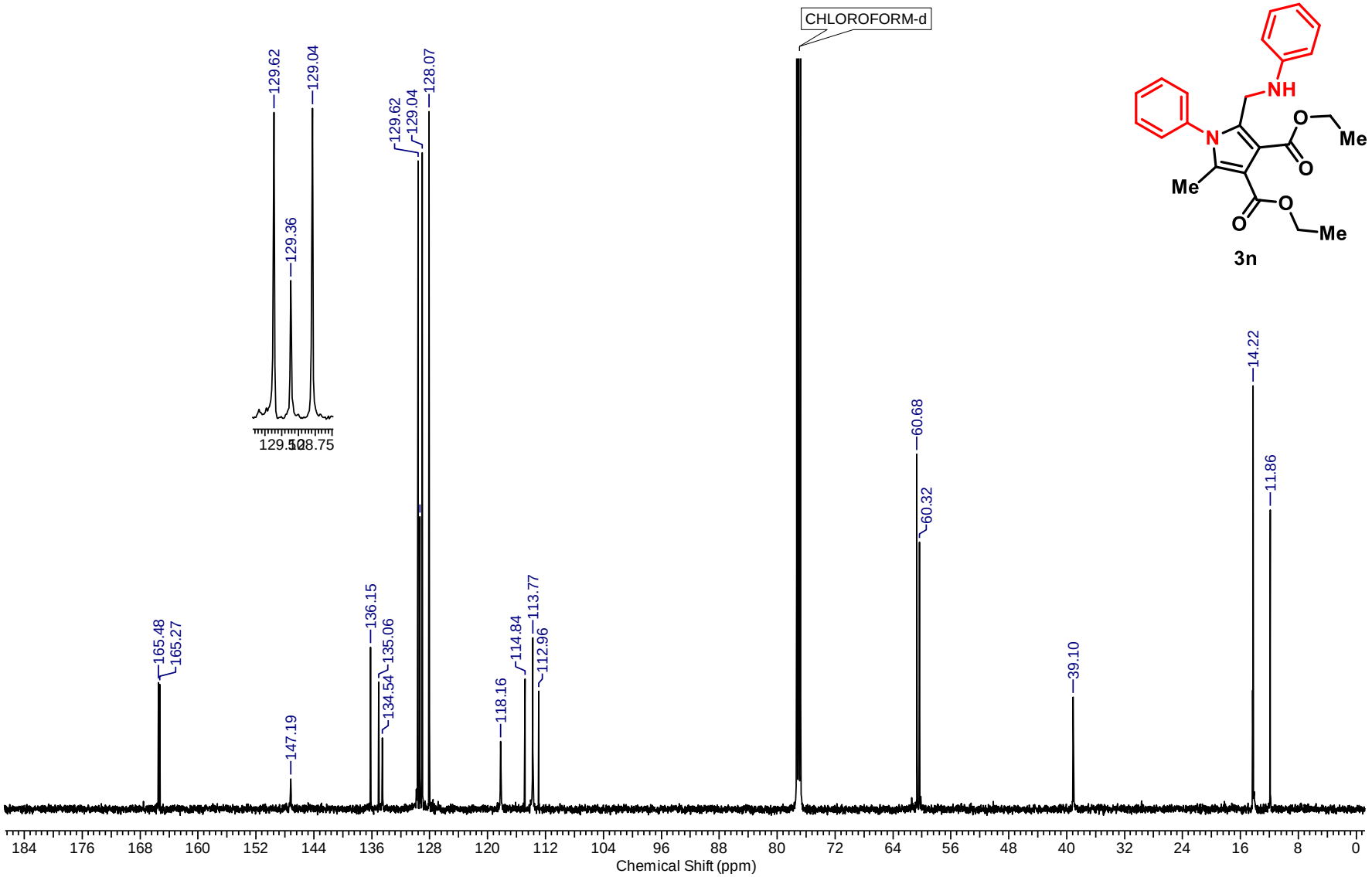

116.57
115.66
115.48
116.74
115.02
114.95
14.30
14.22
116.5
115.5
14.3
CHLOROFORM-d
F
F
NH
N
Me
O
O
Me
O
O
Me
3m
165.35
165.14
163.74
161.74
157.33
155.45
143.51
135.08
134.55
132.01
129.95
129.87
116.57
115.66
115.48
116.74
114.95
113.21
60.76
60.44
39.99
14.30
14.22
11.84
184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

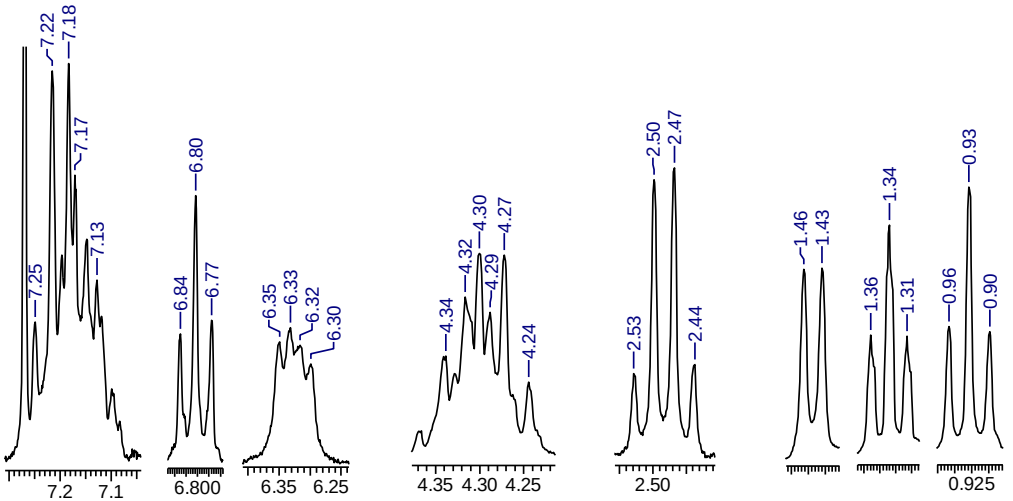

7.50
7.50
7.49
7.49
7.23
7.22
7.22
7.21
7.10
7.09
7.08
7.07
6.71
6.69
6.68
6.43
6.41
4.34
4.34
4.33
4.32
4.31
4.31
4.30
4.29
1.37
1.36
1.34
1.33
1.31
1.30
7.50 7.48
7.225 7.200
7.075
6.700
6.425
4.325 4.300
1.350 1.300

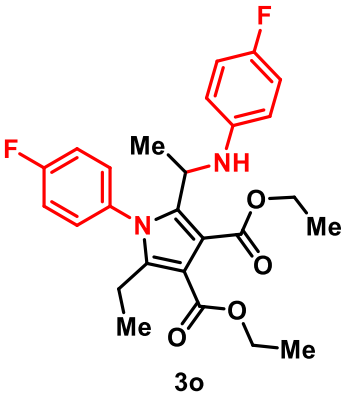

NH
N
O
Me
Me
O
O
O
Me

3n

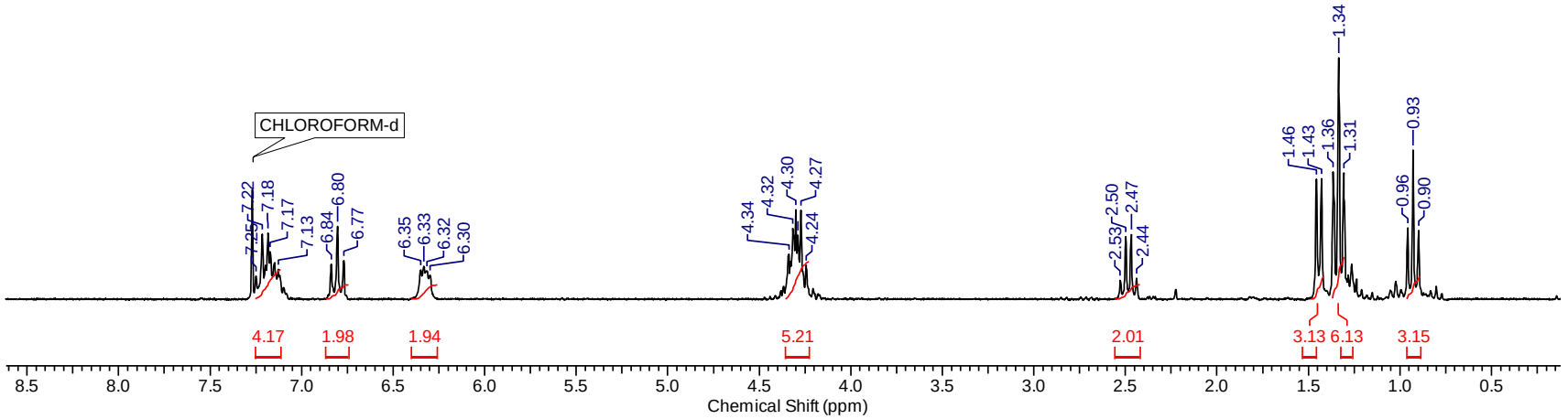

CHLOROFORM-d
7.50
7.50
7.49
7.49
7.23
7.22
7.10
7.09
7.07
6.71
6.69
6.43
6.41
4.34
4.34
4.33
4.31
4.30
4.13
2.16
1.37
1.36
1.31
1.30
3.00 1.99 1.92 0.97 1.87
4.08 2.00
2.88
3.09 3.15
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
Chemical Shift (ppm)

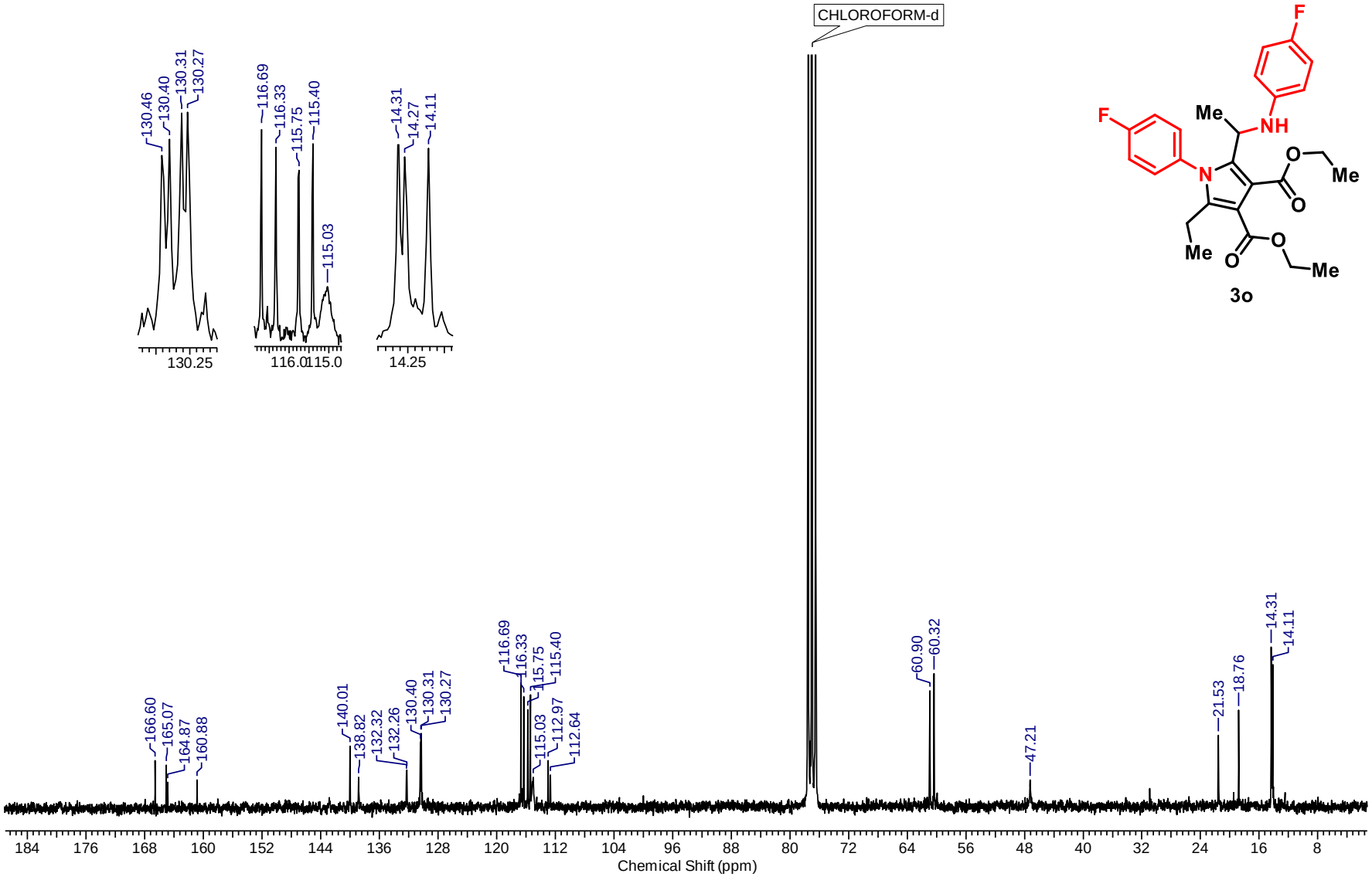

CHLOROFORM-d
129.62
129.36
129.04
129.62
129.04
128.07
165.48
165.27
147.19
136.15
135.06
134.54
118.16
114.84
113.77
112.96
60.68
60.32
39.10
14.22
11.86
NH
N
O
O
Me
Me
O
O
Me
3n
Chemical Shift (ppm)

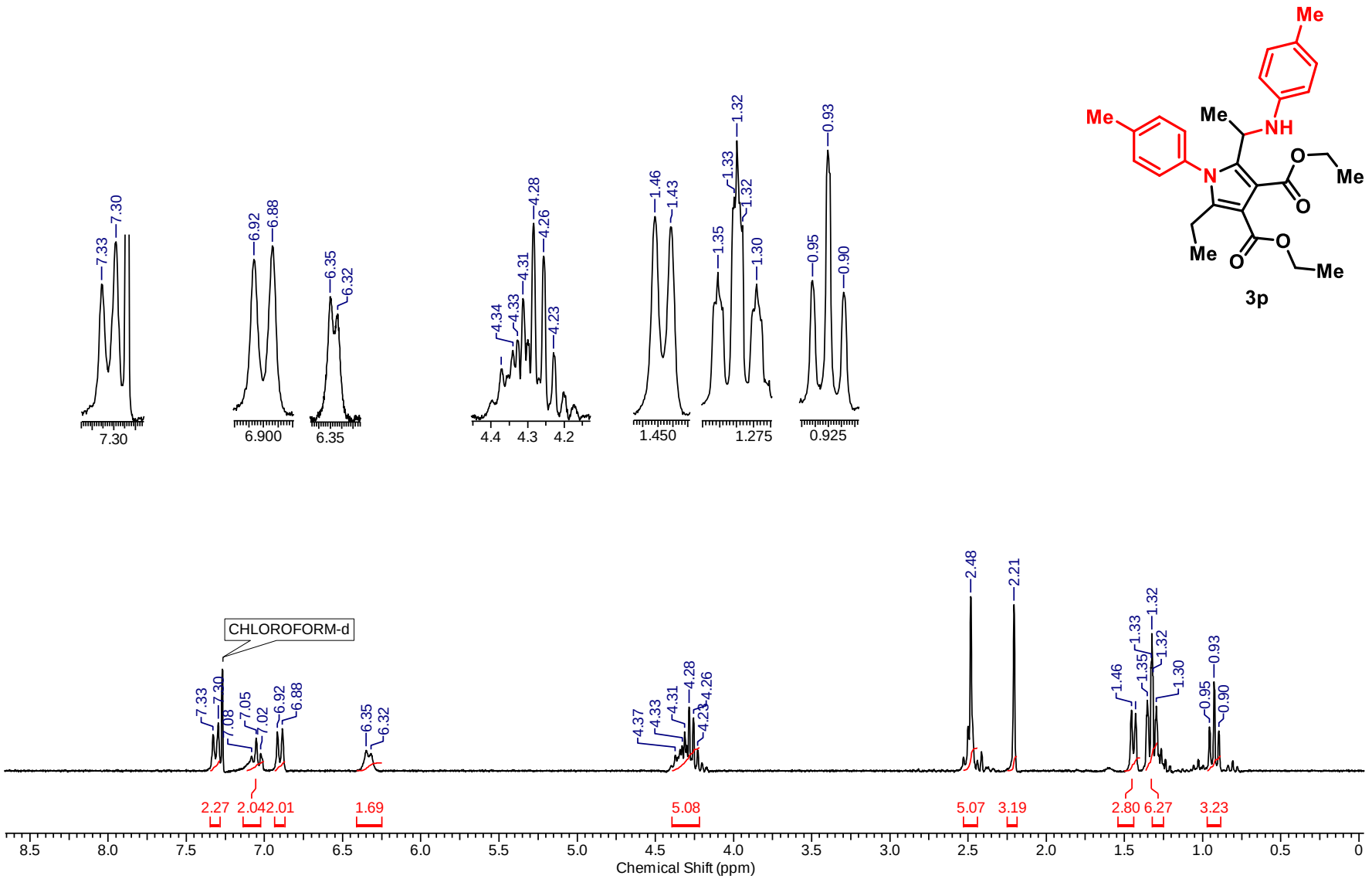

7.22
7.18
7.17
7.25
7.13
6.80
6.84
6.77
6.35
6.33
6.32
6.30
4.34
4.32
4.30
4.29
4.27
4.24
2.50
2.47
2.53
2.44
1.46
1.43
1.36
1.34
1.31
0.96
0.90
0.93
7.2
7.1
6.800
6.35
6.25
4.35
4.30
4.25
2.50
0.925

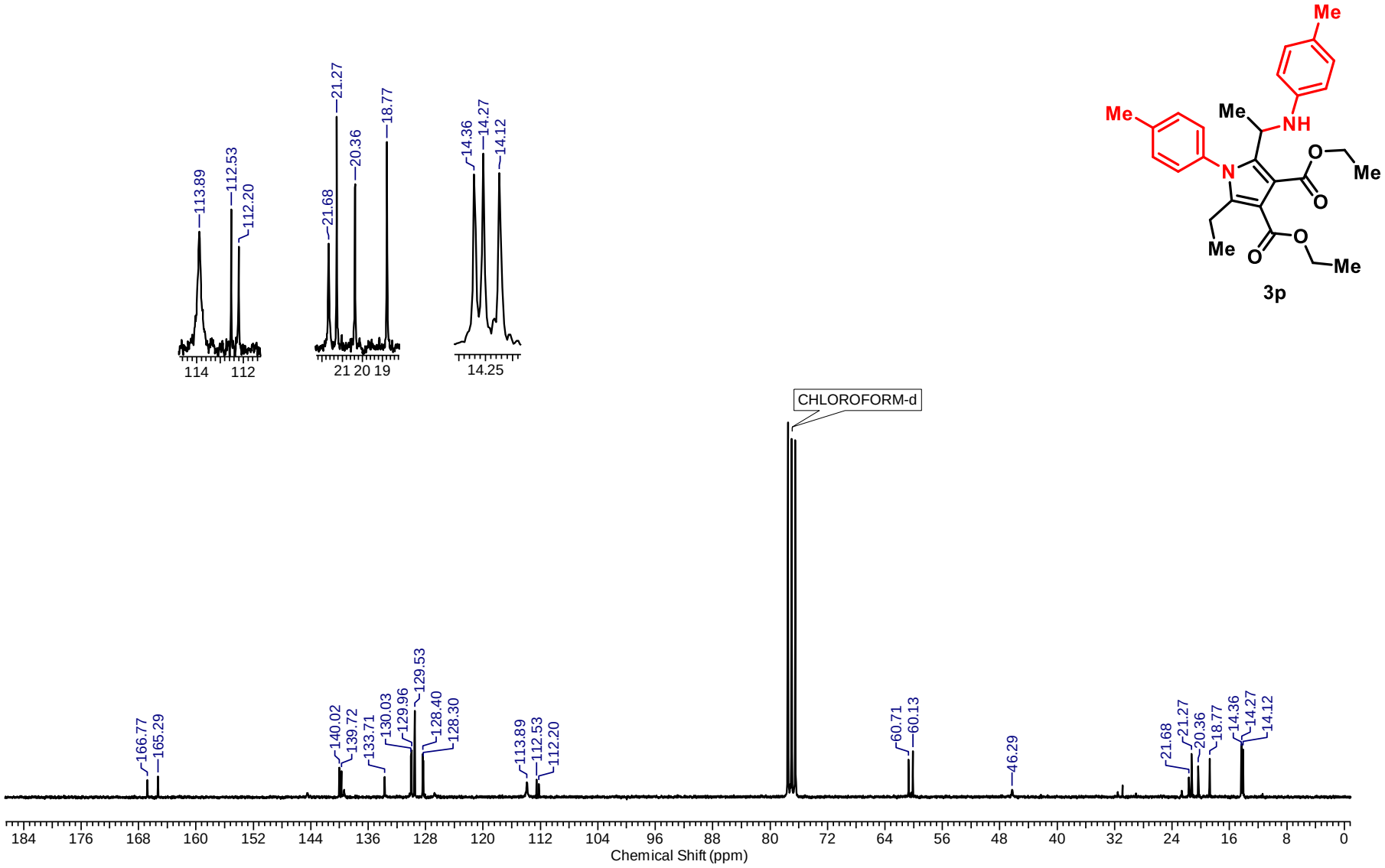

F
Me
NH
F
N
O
Me
O
Me
O
O
Me

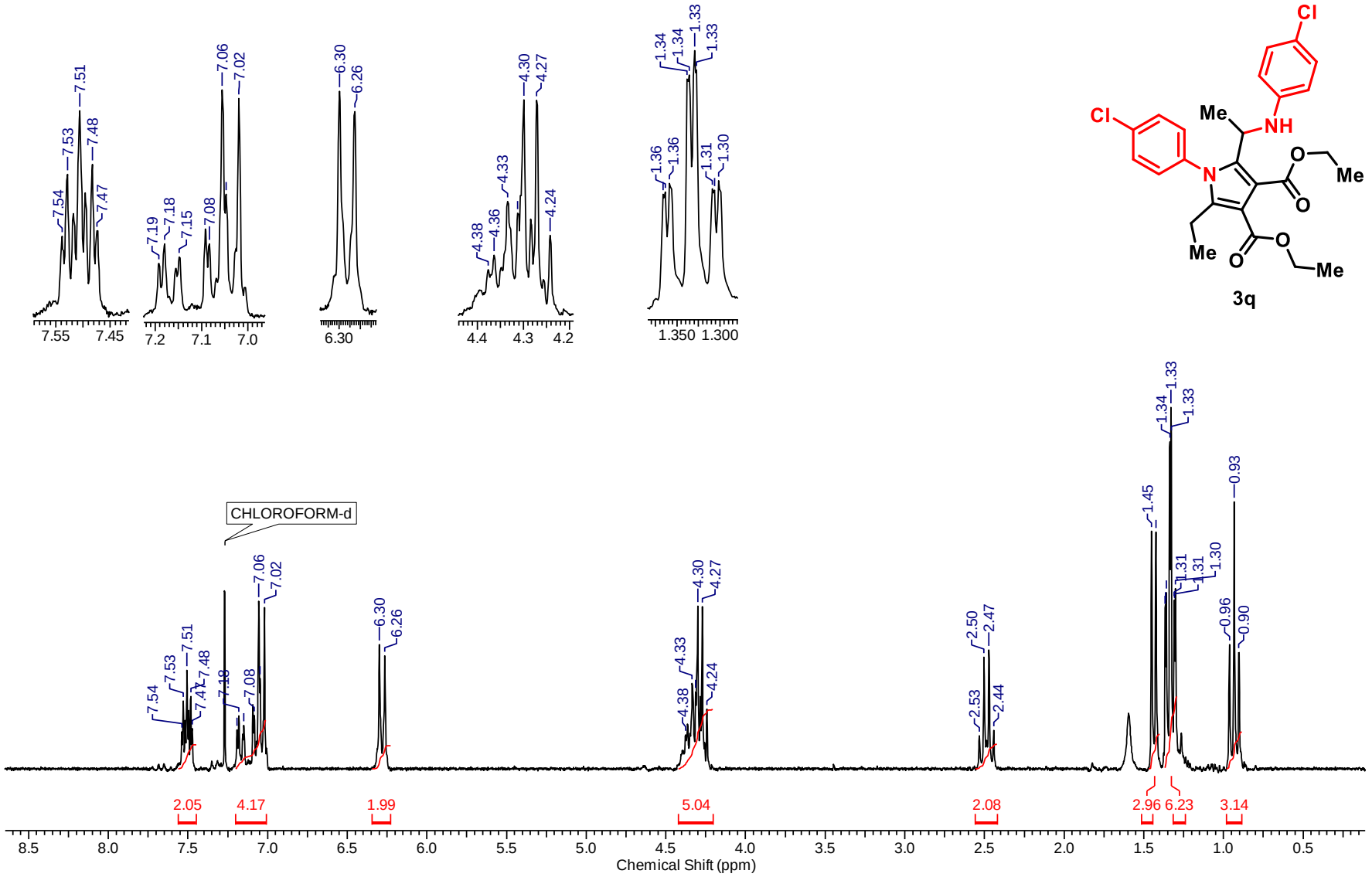
3o

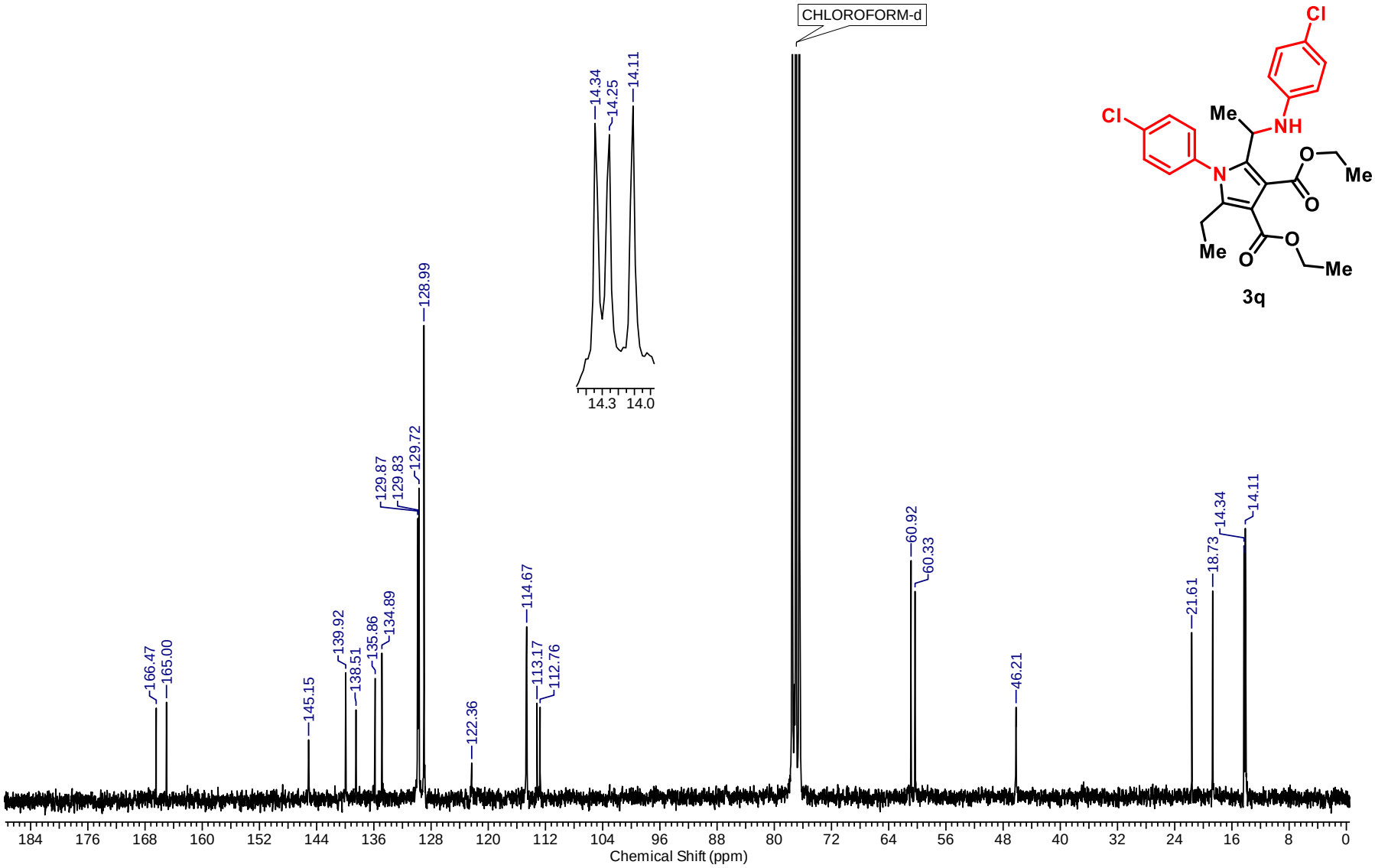

CHLOROFORM-d
7.25
7.22
7.18
7.17
7.13
6.84
6.80
6.77
6.35
6.33
6.32
6.30
4.34
4.32
4.30
4.27
4.24
2.53
2.50
2.47
2.44
1.46
1.43
1.36
1.34
1.31
0.96
0.90
0.93
4.17
1.98
1.94
5.21
2.01
3.13
6.13
3.15
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)


CHLOROFORM-d
130.46
130.40
130.31
130.27
116.69
116.33
115.75
115.40
115.03
14.31
14.27
14.11
130.25
116.0
115.0
14.25
F
Me
NH
F
N
O
Me
O
Me
O
O
Me
3o
166.60
165.07
164.87
160.88
140.01
138.82
132.32
132.26
130.40
130.31
130.27
116.69
116.33
115.75
115.40
115.03
112.97
112.64
60.90
60.32
47.21
21.53
18.76
14.31
14.11
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)


Me
Me
NH
N
O
O
Me
Me
O
O
Me
3p
7.33
7.30
6.92
6.88
6.35
6.32
4.34
4.33
4.31
4.28
4.26
4.23
1.46
1.43
1.35
1.33
1.32
1.30
0.95
0.90
0.93
7.30
6.900
6.35
4.4
4.3
4.2
1.450
1.275
0.925
CHLOROFORM-d
7.33
7.30
7.08
7.05
7.02
6.92
6.88
6.35
6.32
4.37
4.33
4.31
4.28
4.26
4.23
2.48
2.21
1.46
1.35
1.33
1.32
1.30
0.95
0.90
0.93
2.27
2.04
2.01
1.69
5.08
5.07
3.19
2.80
6.27
3.23
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


Me
Me
NH
Me
N
O
O
Me
Me
O
O
Me
3p
113.89
112.53
112.20
114
112
21.68
21.27
20.36
18.77
21 20 19
14.36
14.27
14.12
14.25
CHLOROFORM-d
166.77
165.29
140.02
139.72
133.71
130.03
129.96
129.53
128.40
128.30
113.89
112.53
112.20
60.71
60.13
46.29
21.68
21.27
20.36
18.77
14.36
14.27
14.12
184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)


7.54
7.53
7.51
7.48
7.47
7.55
7.45
7.19
7.18
7.15
7.08
7.06
7.02
7.2
7.1
7.0
6.30
6.26
6.30
4.38
4.36
4.33
4.30
4.27
4.24
4.4
4.3
4.2
1.34
1.34
1.33
1.33
1.36
1.36
1.31
1.30
1.350
1.300
Cl
Cl
Me
NH
N
O
Me
O
Me
O
O
Me
3q
CHLOROFORM-d
7.54
7.53
7.51
7.48
7.47
7.19
7.08
7.06
7.02
6.30
6.26
4.38
4.33
4.30
4.27
4.24
2.53
2.50
2.47
2.44
1.45
1.34
1.33
1.33
1.31
1.31
1.30
0.96
0.93
0.90
2.05
4.17
1.99
5.04
2.08
2.96
6.23
3.14
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)


CHLOROFORM-d
166.47
165.00
145.15
139.92
138.51
135.86
134.89
129.87
129.83
129.72
128.99
122.36
114.67
113.17
112.76
60.92
60.33
46.21
21.61
18.73
14.34
14.11
14.34
14.25
14.11
14.3
14.0
Cl
Cl
Me
NH
N
O
Me
O
Me
O
O
Me
3q
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)