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Supporting Information

A Base-promoted Tandem Approach to Bicyclic 8-Membered Ring Ketones.

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1. General Information

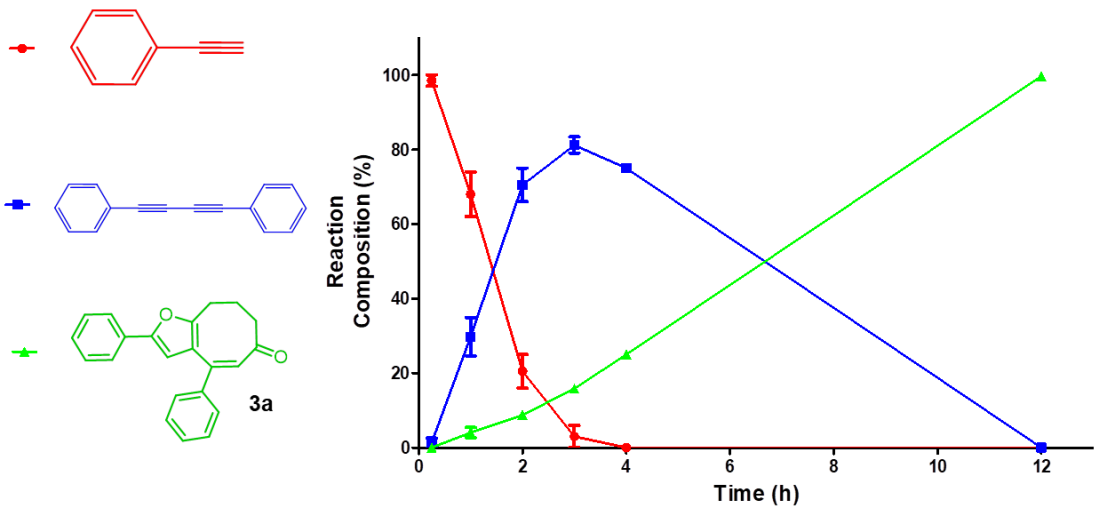
All reagents were purchased from commercial suppliers (Sigma-Aldrich, Oakwood and Combi-Blocks) and used without further purification, all solvents were analytical grade. Thin layer chromatography (TLC) was performed using silica gel GF254, 0.25 mm thickness, visualization was accomplished with short wave UV light or $KMnO_4$ staining solution followed by heating. Melting points were measured on Buchi M-560 melting point apparatus and are uncorrected. Hydrogen nuclear magnetic resonance spectra (^{1}H NMR) were obtained at 400, 500 and 250 MHz in $CDCl_3$ solutions, at ambient temperature. Carbon-13 nuclear magnetic resonance spectra (^{13}C NMR) were obtained at 100, 125 e 62.5 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 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.

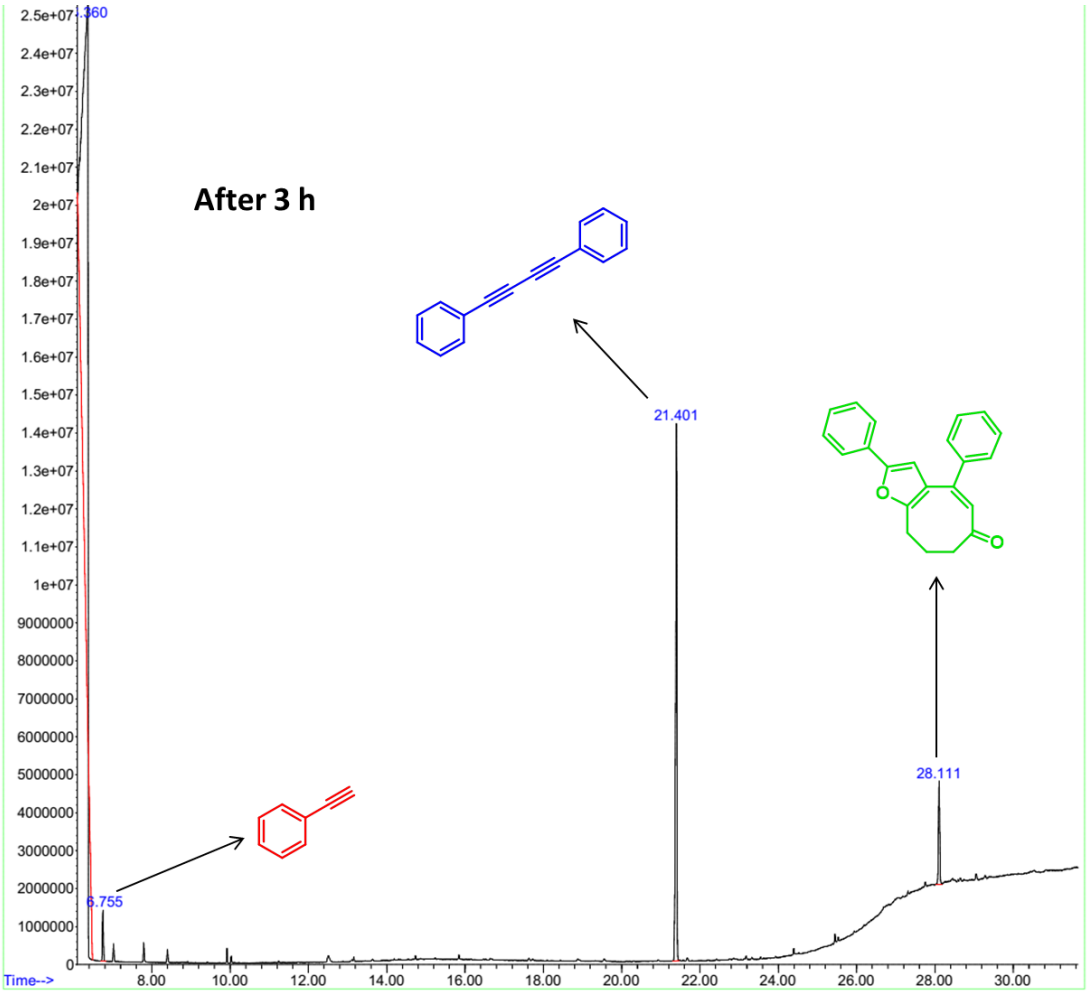
2. General procedure to obtain bicyclic furan/8-membered ring ketones

Sequentially, phenylacetylenes (1.0 mmol, 2.0 equiv), 1,3-diketones (0.5 mmol, 1.0 equiv), CuI (12 mol %) and K_2CO_3 (0.7 mmol, 1.4 equiv) were added to 2 ml of DMSO (from the bottle). It was capped with a rubber septum and constant supply of O_2 was allowed using a balloon. The resulting mixture was heated to 140 ^oC for 12 h. After completion of the reaction (followed by TLC), the whole mixture was added to the top of a silica column and eluted using ethyl acetate/*n*-hexane (10:90) to afford the targeted product.

3. Kinetic profile and intermediate determination

Phenylacetylene (1.0 mmol), cyclohexane-1,3-dione (0.5 mmol), CuI (12 mol %) and K_2CO_3 (0.7 mmol) and 2 ml of DMSO (from the bottle) were employed following the **General procedure to obtain bicyclic furan/8-membered ring ketones**. Aliquots of the reaction mixture were taken (1 h, 2 h, 3 h, 4 h and 12 h) and analysed by GC-MS (Figure S1).


3a
Reaction Composition (%)
Time (h)


After 3 h
6.755
21.401
28.111
Time-->

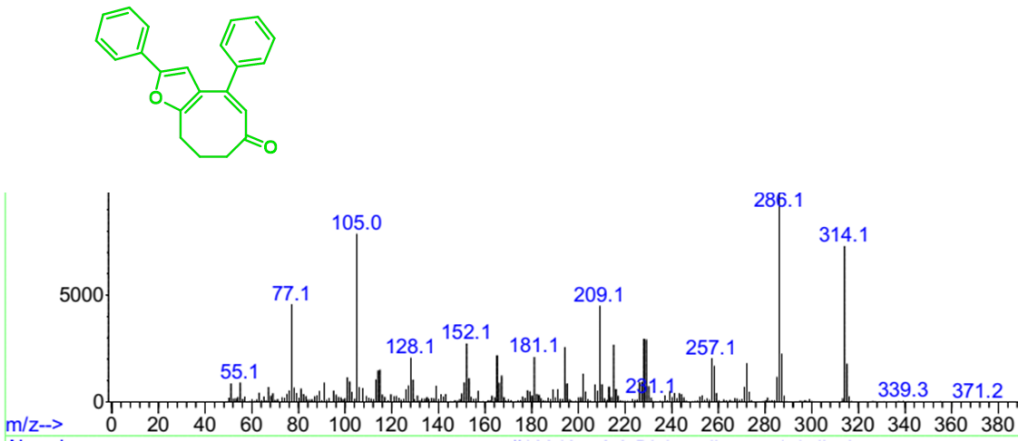


Figure S1. Kinetic profile and intermediate determination using GC-MS.

Here, it is possible to pin down three reaction components: phenylacetylene, 1,4-diphenylbuta-1,3-diyne and product **3a**. One can observe that, after 3 h, the peak relative to 1,4-diphenylbuta-1,3-diyne reaches a maximum concentration and then decreases. Concomitantly, there is an increase in the intensity of the peak relative to the product **3a**. It suggests that 1,4-diphenylbuta-1,3-diyne is a potential intermediate in this transformation.

4. Reaction employing 1,4-diphenylbuta-1,3-diyne as an intermediate

Sequentially, 1,4-diphenylbuta-1,3-diyne (0.5 mmol), cyclohexane-1,3-dione (0.5 mmol) and K_2CO_3 (0.7 mmol) were added to 2 ml of DMSO (from the bottle). It was capped with a rubber septum and the resulting mixture was heated to 140 ^oC for 12 h. After completion of the reaction (followed by TLC), the whole mixture was added to the top of a silica column and eluted using ethyl acetate/*n*-hexane (10:90) to afford product **3a** in 88% yield.

5. Radical trapping experiment

The reaction was carried out following the sequence: 2.0 mL of DMSO, TEMPO (0.5 mmol, 1.0 equiv.), 1,4-diphenylbuta-1,3-diyne (0.5 mmol, 1.0 equiv), cyclohexane-1,3-dione (0.5 mmol, 1.0 equiv) and K_2CO_3 (0.7 mmol, 1.4 equiv). The resulting mixture was heated to 140 ^oC for 12 h. After completion of the reaction (followed by TLC), the whole mixture was added to the top of a silica column and eluted using ethyl acetate/*n*-hexane (10:90) to afford product **3a** in 80% yield.

6. Characterization of products

2,4-diphenyl-8,9-dihydrocycloocta[*b*]furan-6(7*H*)-one (3a). Prepared from phenylacetylene and cyclohexane-1,3-dione following the general procedure to give the product as a white solid (91% yield, 368 mg, m.p. = 92–94 ^oC).

^{1}H NMR (500 MHz, Chloroform-d): δ 7.67–7.63 (m, 2H), 7.44–7.36 (m, 7H), 7.32–7.25 (m, 1H), 6.42 (s, 1H), 6.25 (s, 1H), 2.98 (t, *J* = 6.95, 2H), 2.61 (t, *J* = 6.63 Hz, 2H); 2.35 (quint, *J* = 6.95 Hz, 2H).

^{13}C NMR (125 MHz, Chloroform-d): δ 204.77, 157.33, 152.41, 146.99, 141.04, 129.53, 129.14, 128.75, 128.40, 127.80, 127.68, 123.64, 121.82, 107.18, 38.36, 32.98, 25.31.

HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{19}O_2$ 315.1385; Found 315.1379.

8,8-dimethyl-2,4-diphenyl-8,9-dihydrocycloocta[*b*]furan-6(7*H*)-one (3b). Prepared from phenylacetylene and 5,5-dimethylcyclohexane-1,3-dione following the general procedure to give the product as a white solid (84% yield, 420 mg, m.p. = 80–82 ^oC).

^{1}H NMR (500 MHz, Chloroform-d): δ 7.65 (d, *J* = 7.55 Hz, 2H), 7.45–7.38 (m, 7H), 7.29 (t, *J* = 7.55 Hz, 1H), 6.43 (s, 1H), 6.28 (s, 1H), 2.80–2.00 (s+m, 4H), 1.18 (s, 6H).

^{13}C NMR (125 MHz, Chloroform-d): δ 201.84, 157.54, 152.31, 146.80, 141.24, 130.09, 129.40, 129.16, 128.79, 128.73, 128.32, 127.67, 123.67, 121.89, 107.27, 51.66, 45.02, 38.74, 28.77.

HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{23}O_2$ 343.1698; Found 343.1688.

2,4,8-triphenyl-8,9-dihydrocycloocta[*b*]furan-6(7*H*)-one (3c). Prepared from phenylacetylene and 5-phenylcyclohexane-1,3-dione following the general procedure to give the product as a white solid (86% yield, 312 mg, m.p. = 75–77 ^{o}C).

^{1}H NMR (500 MHz, Chloroform-d): δ 7.55 (d, *J* = 7.34 Hz, 2H), 7.47–7.27 (m, 11H), 7.16 (d, *J* = 6.85 Hz, 2H), 6.49 (s, 1H), 6.35 (s, 1H), 3.87 (sext, *J* = 4.89, 1H), 3.33 (dd, *J* = 6.36, 14.67 Hz, 1H), 3.17 (m+dd, *J* = 4.89, 14.18 Hz, 2H), 2.69 (m, 1H).

^{13}C NMR (125 MHz, Chloroform-d): δ 202.73, 155.88, 152.60, 147.04, 143.08, 141.07, 129.97, 129.58, 129.19, 128.74, 128.45, 127.73, 127.09, 127.04, 123.70, 122.46, 107.33, 50.63, 44.24, 32.27.

HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{28}H_{23}O_2$ 391.1698; Found 391.1677.

2,4-*bis*(4-fluorophenyl)-8,9-dihydrocycloocta[*b*]furan-6(*7H*)-one (3d). Prepared from 1-ethynyl-4-fluorobenzene and cyclohexane-1,3-dione following the general procedure to give the product as a white solid (92% yield, 489 mg, m.p. = 110–112 ^{o}C).

^{1}H NMR (500 MHz, Chloroform-d): δ 7.62 (dd, *J* = 5.38, 8.80 Hz, 2H), 7.40 (dd, *J* = 5.38, 8.80 Hz, 2H), 7.09 (t, *J* = 8.80 Hz, 4H), 6.33 (s, 1H), 6.19 (s, 1H), 2.96 (t, *J* = 6.85 Hz, 2H), 2.59 (m, 2H), 2.34 (quint, *J* = 6.85 Hz, 2H).

^{13}C NMR (125 MHz, Chloroform-d): δ 204.49, 164.88, 163.57, 162.38, 161.10, 157.35, 151.74, 145.68, 137.01, 130.98, 130.89, 127.70, 126.31, 125.52, 125.44, 121.66, 115.95, 115.73, 115.60, 115.38, 106.58, 38.32, 32.89, 25.27.

HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{17}F_2O_2$ 351.1197; Found 351.1176.

(2,4-*bis*(4-fluorophenyl)-8,8-dimethyl-8,9-dihydrocycloocta[*b*]furan-6(*7H*)-one (3e).

Prepared from 1-ethynyl-4-fluorobenzene and 5,5-dimethylcyclohexane-1,3-dione following the general procedure to give the product as a pale yellow oil (80% yield).

^{1}H NMR (500 MHz, Chloroform-d): δ 7.61 (dd, *J* = 5.38, 8.80 Hz, 2H), 7.38 (dd, *J* = 5.38, 8.80 Hz, 2H), 7.08 (td, *J* = 3.91, 8.80 Hz, 4H), 6.34 (s, 1H), 6.23 (s, 1H), 2.75–2.25 (s+m, 4H), 1.17 (s, 6H).

^{13}C NMR (125 MHz, Chloroform-d): δ 201.62, 164.81, 163.57, 162.33, 161.10, 157.60, 151.65, 145.50, 137.20, 131.01, 130.92, 128.73, 126.38, 125.55, 125.48, 121.76, 115.95, 115.73, 115.54, 115.33, 106.69, 51.63, 45.00, 38.71, 28.75.

HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{21}F_2O_2$ 379.1510; Found 37.1491.

2,4-*bis*(4-fluorophenyl)-8-phenyl-8,9-dihydrocycloocta[*b*]furan-6(*7H*)-one (3f).

Prepared from 1-ethynyl-4-fluorobenzene and 5-phenylcyclohexane-1,3-dione following the general procedure to give the product as a pale yellow oil (89% yield).

^{1}H NMR (500 MHz, Chloroform-d): δ 7.51 (dd, *J* = 5.66, 8.80 Hz, 2H), 7.45–7.42 (m, 2H), 7.35–7.29 (m, 3H), 7.14–7.05 (m, 6H), 6.39 (s, 1H), 6.29 (s, 1H), 3.85 (sext, *J* = 5.03 Hz, 1H), 3.30 (dd, *J* = 5.66, 14.46 Hz, 1H), 3.16–3.12 (m+dd, *J* = 4.40, 13.83 Hz, 2H), 2.69 (bs, 1H).
^{13}C NMR (125 MHz, Chloroform-d): δ 202.50, 164.65, 163.34, 162.66, 161.36, 155.89, 151.92, 145.75, 142.94, 137.01, 136.98, 131.02, 130.96, 128.45, 127.11, 127.04, 126.21, 125.58, 125.51, 122.28, 115.91, 115.45, 106.71, 50.52, 44.08, 32.27.
HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{28}H_{21}F_2O_2$ 427.1494; Found 427.1510.

2,4-*bis*(4-(trifluoromethyl)phenyl)-8,9-dihydrocycloocta[*b*]furan-6(*7H*)-one (3g)

Prepared from 1-ethynyl-4-(trifluoromethyl)benzene and cyclohexane-1,3-dione following the general procedure to give the product as a pale yellow oil (80% yield).

^{1}H NMR (500 MHz, Chloroform-d): δ 7.74 (d, *J* = 8.17 Hz, 2H), 7.67 (d, *J* = 8.17 Hz, 2H), 7.63 (d, *J* = 8.17 Hz, 2H), 7.52 (d, *J* = 8.17 Hz, 2H), 6.49 (s, 1H), 6.24 (s, 1H), 3.01 (t, *J* = 6.92 Hz, 2H), 2.63 (d, *J* = 6.29 Hz, 2H), 2.38 (quint, *J* = 6.29 Hz, 2H).
^{13}C NMR (125 MHz, Chloroform-d): δ 204.28, 158.42, 151.34, 144.78, 144.47, 132.94, 131.85, 131.58, 131.33, 131.07, 129.60, 129.31, 128.99, 125.80, 125.50, 125.46, 125.08, 124.95, 123.72, 122.92, 122.80, 121.57, 108.55, 38.25, 32.74, 25.33.
HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{17}F_6O_2$ 451.1133; Found 451.1131.

8,8-dimethyl-2,4-*bis*(4-(trifluoromethyl)phenyl)-8,9-dihydrocycloocta[*b*]furan-6(*7H*)-one (3h).

Prepared from 1-ethynyl-4-(trifluoromethyl)benzene and 5,5-dimethylcyclohexane-1,3-dione following the general procedure to give the product as a pale yellow oil (81% yield).

^{1}H NMR (500 MHz, Chloroform-d): δ 7.75 (d, *J* = 8.17 Hz, 2H), 7.66 (d, *J* = 8.17 Hz, 2H), 7.63 (d, *J* = 8.17 Hz, 2H), 7.51 (d, *J* = 8.17 Hz, 2H), 6.51 (s, 1H), 6.27 (s, 1H), 2.78 (s, 2H), 2.44 (m, 2H), 1.20 (s, 6H).

^{13}C NMR (125 MHz, Chloroform-d): δ 201.35, 158.64, 151.26, 144.63, 132.99, 131.74, 131.49, 131.23, 130.97, 129.95, 129.58, 129.36, 125.80, 125.77, 125.73, 125.43, 125.40, 125.06, 124.95, 123.75, 122.91, 122.80, 121.66, 108.66, 51.52, 44.97, 38.71, 28.71.

HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{26}H_{21}F_6O_2$ 479.1446; Found 479.1442.

2,4-di-*p*-tolyl-8,9-dihydrocycloocta[*b*]furan-6(*7H*)-one (3i)

Prepared from 1-ethynyl-4-methylbenzene and cyclohexane-1,3-dione following the general procedure to give the product as a pale yellow oil (79% yield).

^{1}H NMR (500 MHz, Chloroform-d): δ 7.53 (d, *J* = 8.31 Hz, 2H), 7.31 (d, *J* = 8.31 Hz, 2H), 7.19 (dd, *J* = 0.98, 8.31 Hz, 4H), 6.37 (s, 1H), 6.24 (s, 1H), 2.96 (t, *J* = 6.85 Hz, 2H), 2.59 (m, 2H), 2.41 (s, 3H), 2.38 (s, 3H), 2.33(quint, *J* = 6.85 Hz, 2H).

^{13}C NMR (125 MHz, Chloroform-d): δ 204.80, 156.96, 152.53, 147.13, 139.76, 138.18, 137.55, 129.42, 129.13, 127.43, 127.14, 123.60, 121.81, 106.57, 99.96, 38.39, 33.01, 25.28, 21.27.

HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{23}O_2$ 343.1698; Found 343.1682.

8,8-dimethyl-2,4-di-*p*-tolyl-8,9-dihydrocycloocta[*b*]furan-6(*7H*)-one (3j)

Prepared from 1-ethynyl-4-methylbenzene and 5,5-dimethylcyclohexane-1,3-dione following the general procedure to give the product as a pale yellow oil (77% yield).

^{1}H NMR (500 MHz, Chloroform-d): δ 7.54 (d, *J* = 8.31 Hz, 2H), 7.30 (d, *J* = 8.31 Hz, 2H), 7.19 (d, *J* = 7.82 Hz, 4H), 6.39 (s, 1H), 6.28 (s, 1H), 2.73–2.45 (s+m, 4H), 2.41 (s, 3H), 2.38 (s, 3H), 1.18 (bs, 6H).

^{13}C NMR (125 MHz, Chloroform-d): δ 201.94, 157.22, 152.44, 146.96, 139.62, 138.41, 137.57, 129.42, 129.17, 129.05, 128.16, 127.49, 123.66, 121.91, 106.69, 51.73, 45.02, 38.74, 28.78, 21.26.

HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{26}H_{27}O_2$ 371.2011; Found 371.1982.

8-phenyl-2,4-di-*p*-tolyl-8,9-dihydrocycloocta[*b*]furan-6(*7H*)-one (3k)

Prepared from 1-ethynyl-4-methylbenzene and 5-phenylcyclohexane-1,3-dione following the general procedure to give the product as a pale yellow oil (88% yield).

^{1}H NMR (500 MHz, Chloroform-d): δ 7.43 (d, *J* = 7.83 Hz, 2H), 7.36–7.30 (m, 6H), 7.24–7.15 (m, 5H), 6.44 (s, 1H), 6.33 (s, 1H), 3.84 (sext, *J* = 4.89 Hz, 1H), 3.30 (dd, *J* = 5.87, 14.18 Hz, 1H), 3.16–3.12 (m+dd, *J* = 4.40, 14.18 Hz, 2H), 2.67 (bs, 1H), 2.43 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (125 MHz, Chloroform-d): δ 202.82, 155.51, 152.70, 147.22, 143.19, 139.84, 137.70, 137.64, 129.41, 129.20, 129.15, 128.43, 127.35, 127.14, 127.00, 123.67, 122.46, 106.74, 50.71, 44.29, 32.26, 21.30, 21.25.

HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{30}H_{27}O_2$ 419.2011; Found 419.1994.

2,4-di-*m*-tolyl-8,9-dihydrocycloocta[*b*]furan-6(*7H*)-one (3l)

Prepared from 1-ethynyl-3-methylbenzene and cyclohexane-1,3-dione following the general procedure to give the product as a pale yellow oil (85% yield).

^{1}H NMR (500 MHz, Chloroform-d): δ 7.49–7.46 (m, 2H), 7.31–7.27 (m, 2H), 7.26–7.21 (m, 3H), 7.10 (d, *J* = 7.55 Hz, 1H), 6.43 (s, 1H), 6.25 (s, 1H), 2.98 (t, *J* = 6.92 Hz, 2H), 2.61 (m, 2H), 2.39 (s, 6H), 2.36(quint, *J* = 6.92 Hz, 2H).

^{13}C NMR (125 MHz, Chloroform-d): δ 204.69, 157.11, 152.46, 147.17, 141.02, 138.34, 138.02, 130.24, 129.70, 128.63, 128.43, 128.19, 127.62, 126.29, 124.22, 121.81, 120.77, 107.08, 38.31, 32.95, 25.23, 21.33.

HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{23}O_2$ 343.1698; Found 343.1685.

8,8-dimethyl-2,4-di-*m*-tolyl-8,9-dihydrocycloocta[*b*]furan-6(*7H*)-one (3m)

Prepared from 1-ethynyl-3-methylbenzene and 5,5-dimethylcyclohexane-1,3-dione following the general procedure to give the product as a pale yellow oil (80% yield).

^{1}H NMR (500 MHz, Chloroform-d): δ 7.51–7.49 (m, 2H), 7.34–7.27 (m, 4H), 7.22 (d, *J* = 7.34 Hz, 1H), 7.13 (d, *J* = 7.34 Hz, 1H), 6.46 (s, 1H), 6.32 (s, 1H), 2.78 (s, 2H), 2.75–2.00 (s+s+m, 8H), 1.22 (bs, 6H).

^{13}C NMR (125 MHz, Chloroform-d): δ 201.87, 157.38, 152.40, 147.05, 141.29, 138.37, 138.01, 130.15, 130.04, 129.75, 128.64, 128.46, 128.16, 126.37, 124.27, 121.94, 120.84, 107.23, 51.67, 45.01, 38.71, 28.78, 21.40, 21.33.

HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{26}H_{27}O_2$ 371.2011; Found 371.2000.

2,4-di-*o*-tolyl-8,9-dihydrocycloocta[*b*]furan-6(*7H*)-one (3n)

Prepared from 1-ethynyl-2-methylbenzene and cyclohexane-1,3-dione following the general procedure to give the product as a pale yellow oil (78% yield).

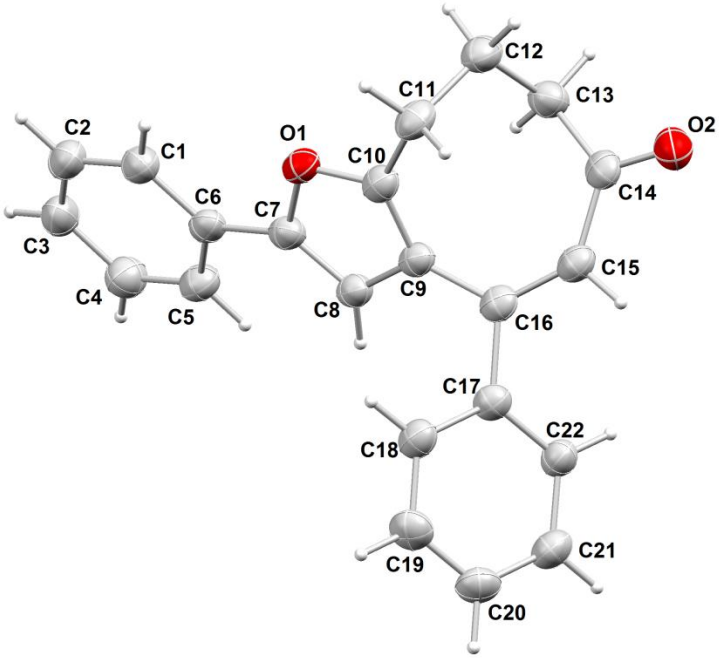
^{1}H NMR (500 MHz, Chloroform-d): δ 7.64 (d, *J* = 6.85 Hz, 1H), 7.31–7.27 (m, 1H), 7.25–7.19 (m, 6H), 6.03 (s, 1H), 5.98 (s, 1H), 3.00 (t, *J* = 6.85 Hz, 2H), 2.70 (t, *J* = 6.85 Hz, 2H), 2.40 (quint, *J* = 6.85 Hz, 2H), 2.37 (s, 3H), 2.12 (s, 3H).
^{13}C NMR (125 MHz, Chloroform-d): δ 205.60, 155.68, 152.29, 147.51, 141.21, 135.53, 134.56, 131.18, 130.51, 129.29, 128.94, 128.64, 128.48, 127.80, 126.84, 125.99, 125.79, 122.77, 109.91, 38.35, 33.59, 25.52, 21.77, 19.77.
HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{23}O_2$ 343.1698; Found 343.1681.

2,4-*bis*(4-methoxyphenyl)-8,9-dihydrocycloocta[*b*]furan-6(*7H*)-one (3o)

Prepared from 1-ethynyl-4-methoxybenzene and cyclohexane-1,3-dione following the general procedure to give the product as a pale yellow oil (69% yield).

^{1}H NMR (500 MHz, Chloroform-d): δ 7.57 (d, *J* = 8.80 Hz, 2H), 7.36 (d, *J* = 8.80 Hz, 2H), 6.92 (dd, *J* = 5.38, 8.80 Hz, 4H), 6.31 (s, 1H), 6.22 (s, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 2.94 (t, *J* = 6.85 Hz, 2H), 2.57 (m, 2H), 2.32 (quint, *J* = 6.85 Hz, 2H).
^{13}C NMR (125 MHz, Chloroform-d): δ 204.64, 160.84, 159.24, 156.70, 152.31, 146.80, 133.25, 130.61, 126.41, 125.07, 123.12, 121.72, 114.18, 113.74, 105.67, 55.29, 38.36, 32.94, 25.21.
HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{23}O_4$ 375.1596; Found 375.1572.

7. X-Ray data



The crystal structure of **3a** was determined by single crystal X-ray diffraction on a Bruker APEX II DUO area detector diffractometer, equipped with a low-temperature device (Oxford Cryosystems CRYOSTREAM 700). Data were collected at 150 K crystal temperature, using Cu*K*α radiation (λ = 1.54184 Å; Incoatec microfocus X-ray source), based on a strategy combining omega and phi scans, width of 0.5º and acquisition time of 30 s per frame. Cell refinement and data reduction were performed using SAINT[1] and multi-scan absorption correction was performed with SADABS-2014/5[1] . The structure was solved by direct methods using SHELXTL XT-2014/4[2] and refined by leastsquares methods against F^2, using SHELXle[3], with all non-hydrogen atoms refined anisotropically. All hydrogen atoms were placed by the refinement program with site location inferred from neighbouring sites. 271 parameters were

[1] Bruker, APEX2, SAINT and SADABS, Bruker AXS Inc., Madison, Wisconsin, USA, 2010.
[2] G.M. Sheldrick, A short history of SHELX, Acta Crystallogr. A. A64 (2008) 112-122, https://doi.org/10.1107/S0108767307043930.
[3] G.M. Sheldrick, SHELXT - integrated space-group and crystal-structure determination, Acta Crystallogr. A. A71 (2015) 3-8, https://doi.org/10.1107/S2053273314026370.

refined, $R[F^2 > 2\sigma(F^2)]$ = 0.058, $wR^2(F^2)$ = 0.133, S = 1.13, with maximum and minimum residual electron density of 0.15 e Å^{-3} and -0.18 e Å^{-3}, respectively. Details about the analyzed crystal and data collection are presented in Tables S1 and S2, respectively.

Table S1: selected crystallographic data for cystal.

$C_{22}H_{18}O_2$	$F(000)$ = 664
M_r = 314.36	D_x = 1.254 Mg m^{-3}
Monoclinic, $P2_1/c$	Cu $K\alpha$ radiation, λ = 1.54178 Å
a = 8.6541 (5) Å	Cell parameters from 92 reflections
b = 5.7809 (3) Å	θ = 9.3–36.8°
c = 33.543 (2) Å	μ = 0.62 mm^{-1}
b = 97.281 (4)°	T = 150 K
V = 1664.55 (16) Å^3	Plate, colorless
Z = 4	0.24 × 0.18 × 0.03 mm

Table S2: selected crystallographic data for data collection.

Absorption correction: multi-scan	R_{int} = 0.060
T_{min} = 0.611, T_{max} = 0.753	θ_{max} = 68.8°, θ_{min} = 5.2°
6055 measured reflections	h = -10→9
2583 independent reflections	k = -5→6
2018 reflections with $I > 2s(I)$	l = -39→39

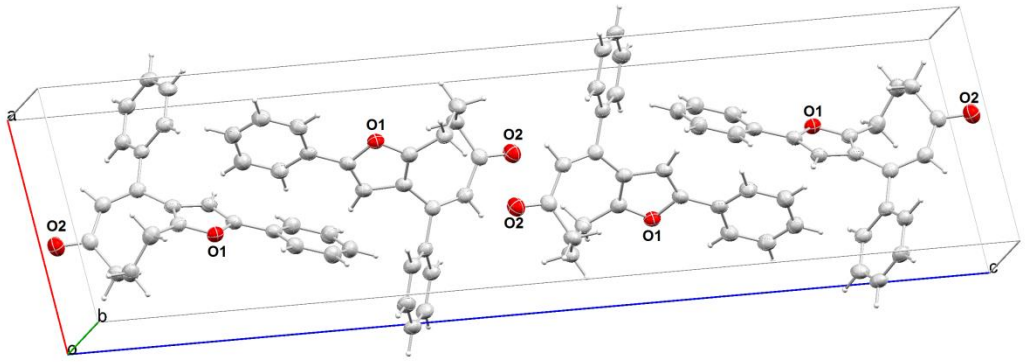


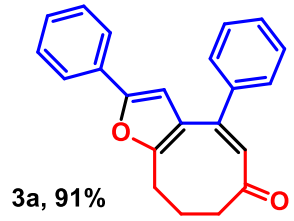
Fig. S2 Crystal packing, showing the unit cell of **3a** with four molecules, oxygen atoms labels and 50% probability displacement ellipsoids.

It is important to mention that it was too difficult to obtain suitable crystals of bicyclic 8-membered ring ketone and the ones that had been formed presented severe

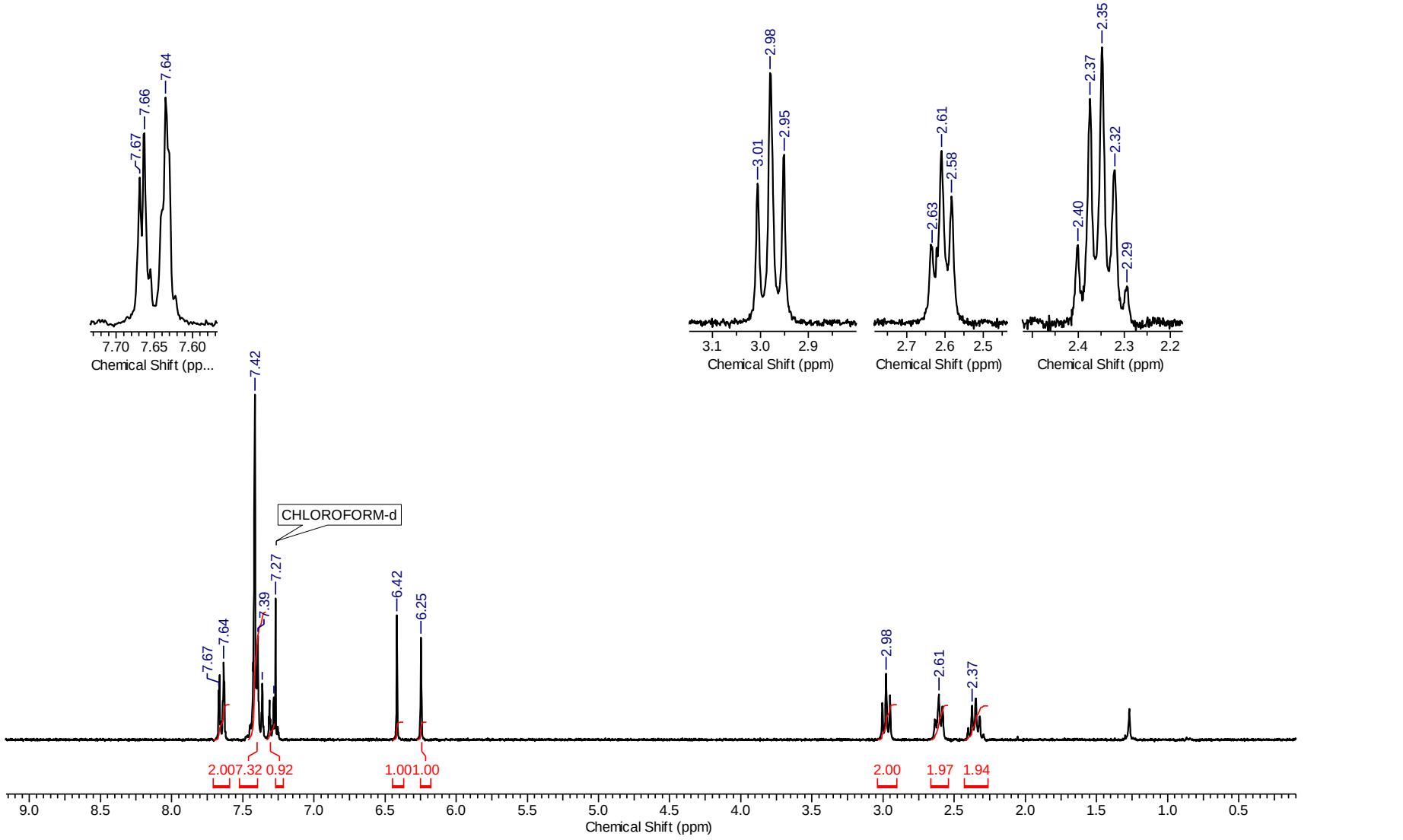
limitation to diffract X-ray radiation. Considering this, both data collection strategy and data reduction were optimized to favour completeness. In spite of our efforts, alerts level A (PLAT 029 – 3A) and level B (PLAT 911 – 2B) are indicated in checkcif, both of them related to the absence of reflections. As the structure refinement converged and the proposed structure is corroborated by the results of other analysis (^{1}H and ^{13}C NMR, 2D NMR and HRMS), the authors have no doubt about its identity.

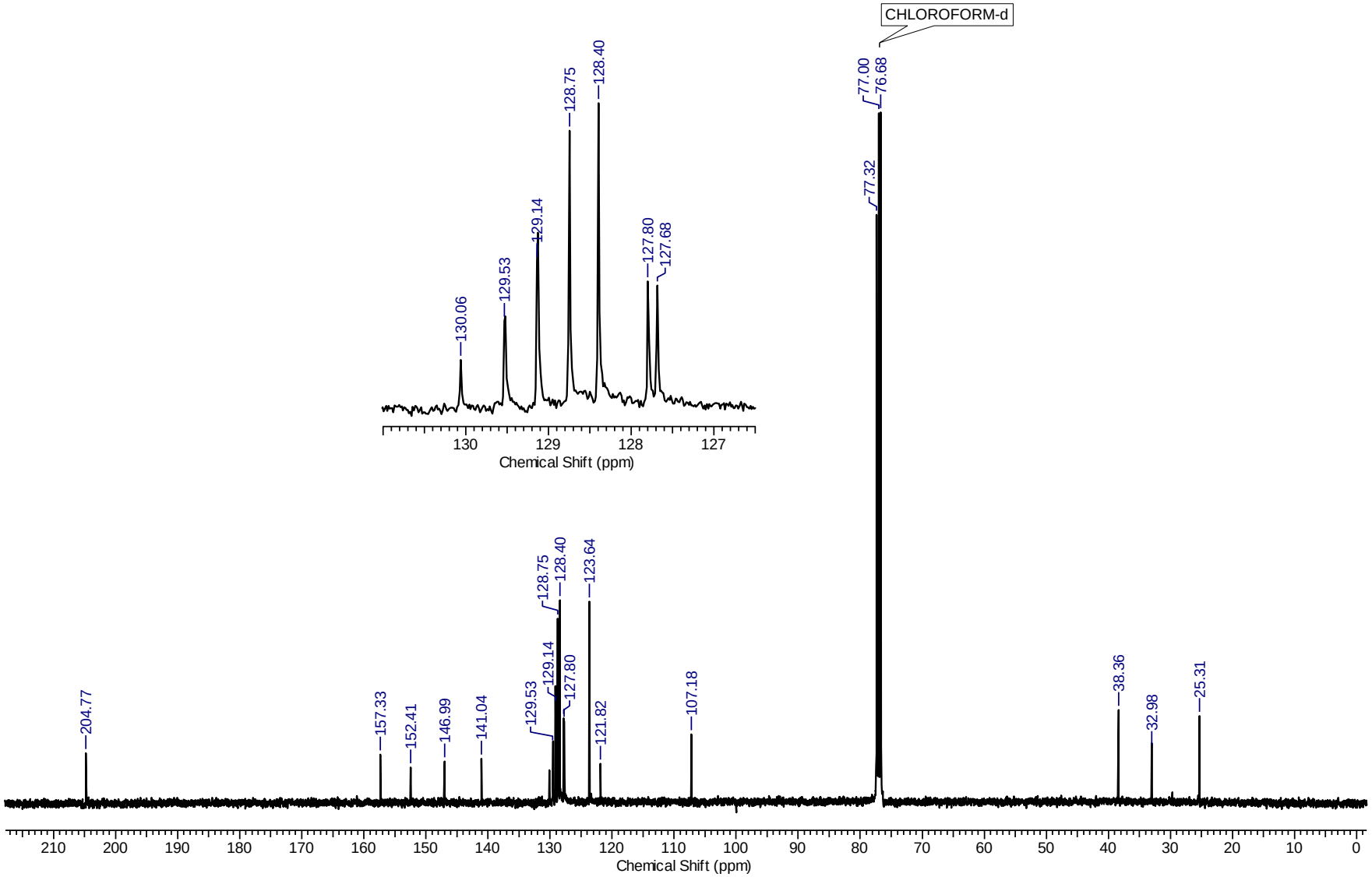
8. ^{1}H NMR and ^{13}C NMR spectral data

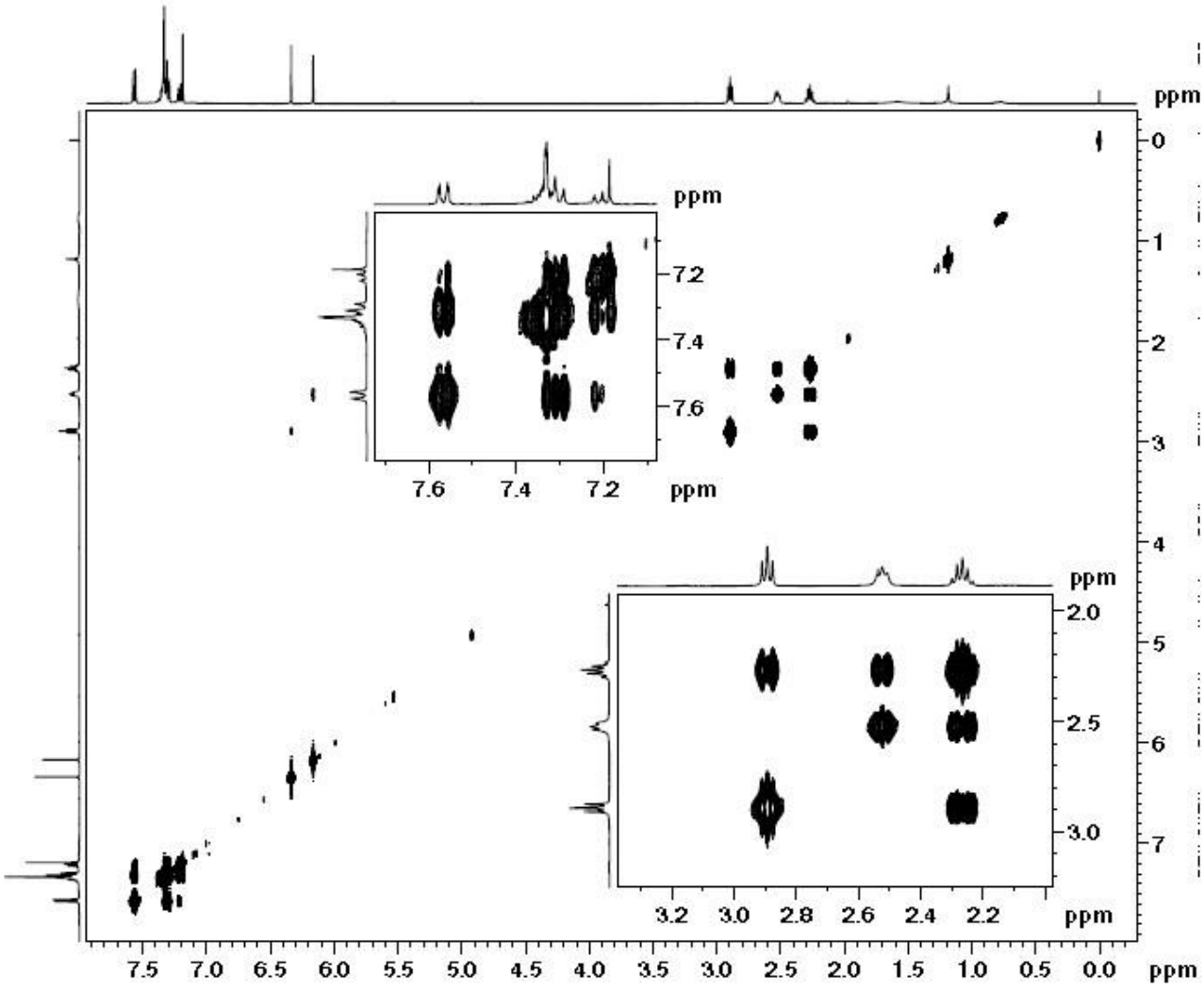
2,4-diphenyl-8,9-dihydrocycloocta[*b*]furan-6(7*H*)-one



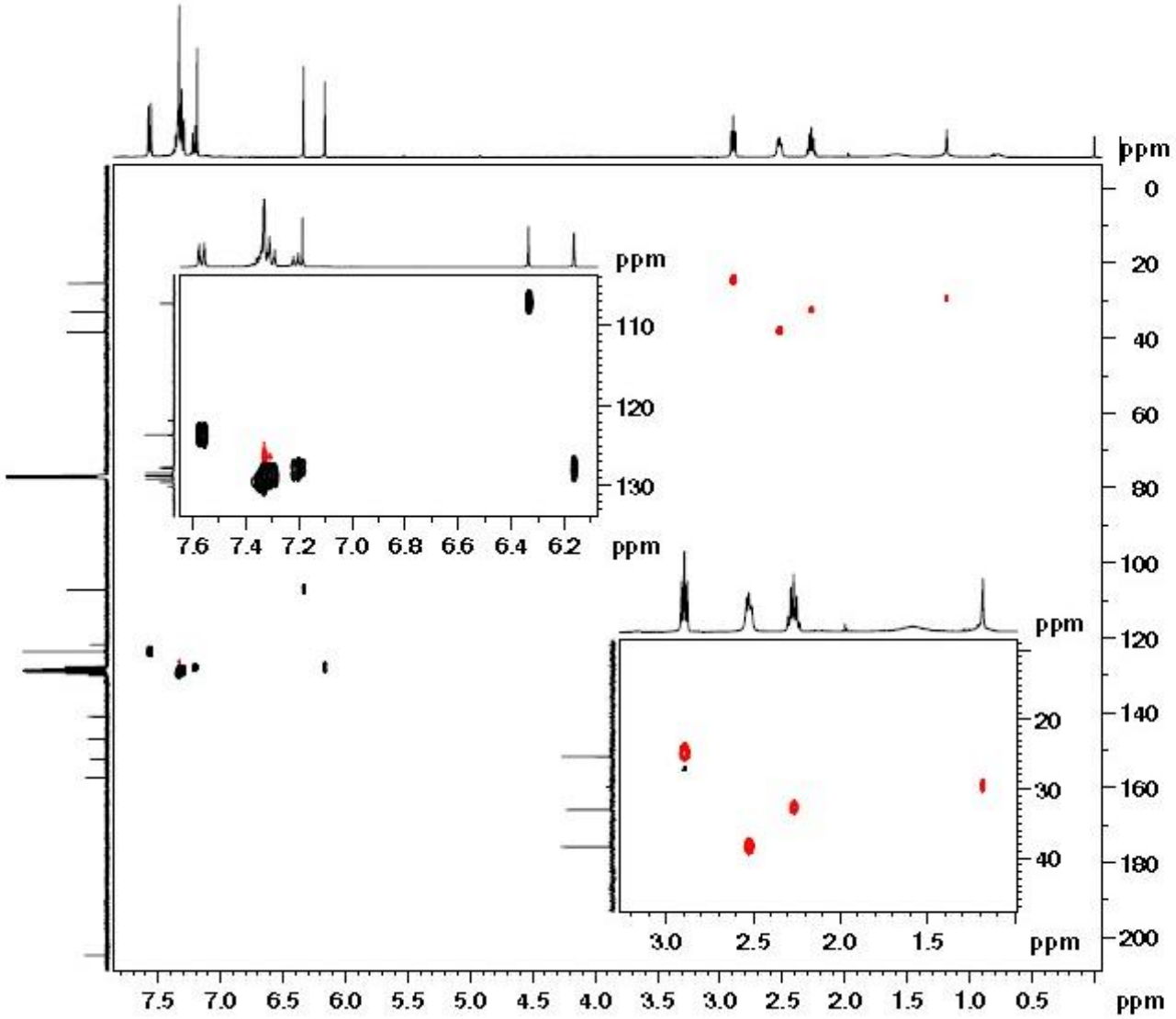
3a, 91%



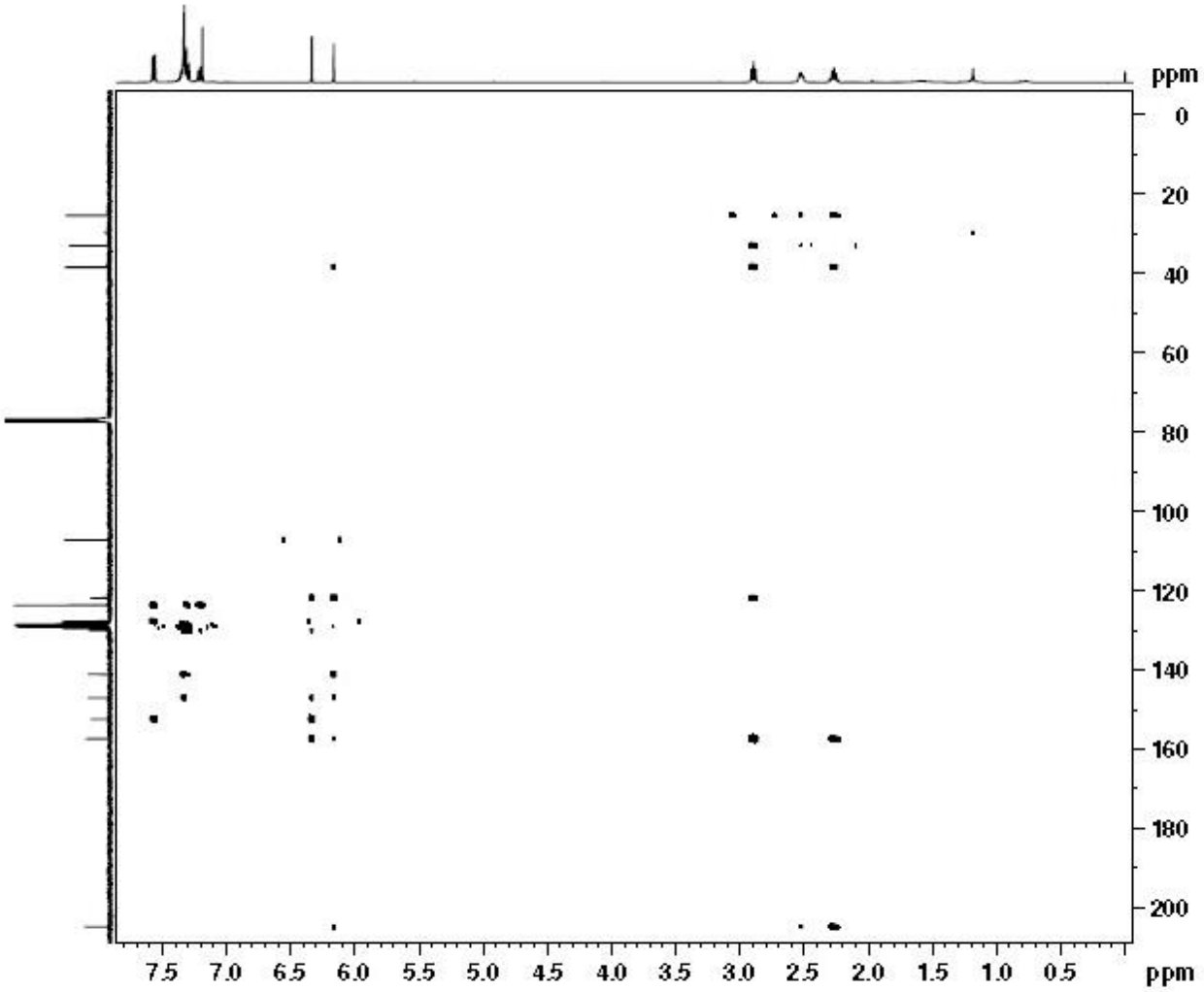

CHLOROFORM-d
77.00
76.68
77.32
128.75
128.40
129.14
129.53
127.80
127.68
130.06
204.77
157.33
152.41
146.99
141.04
123.64
121.82
107.18
38.36
32.98
25.31
Chemical Shift (ppm)
Chemical Shift (ppm)



Cosy spectrum of 3a

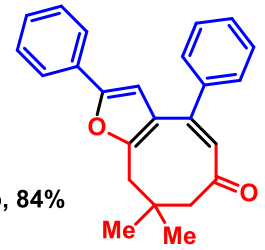


HSQC spectrum of 3a

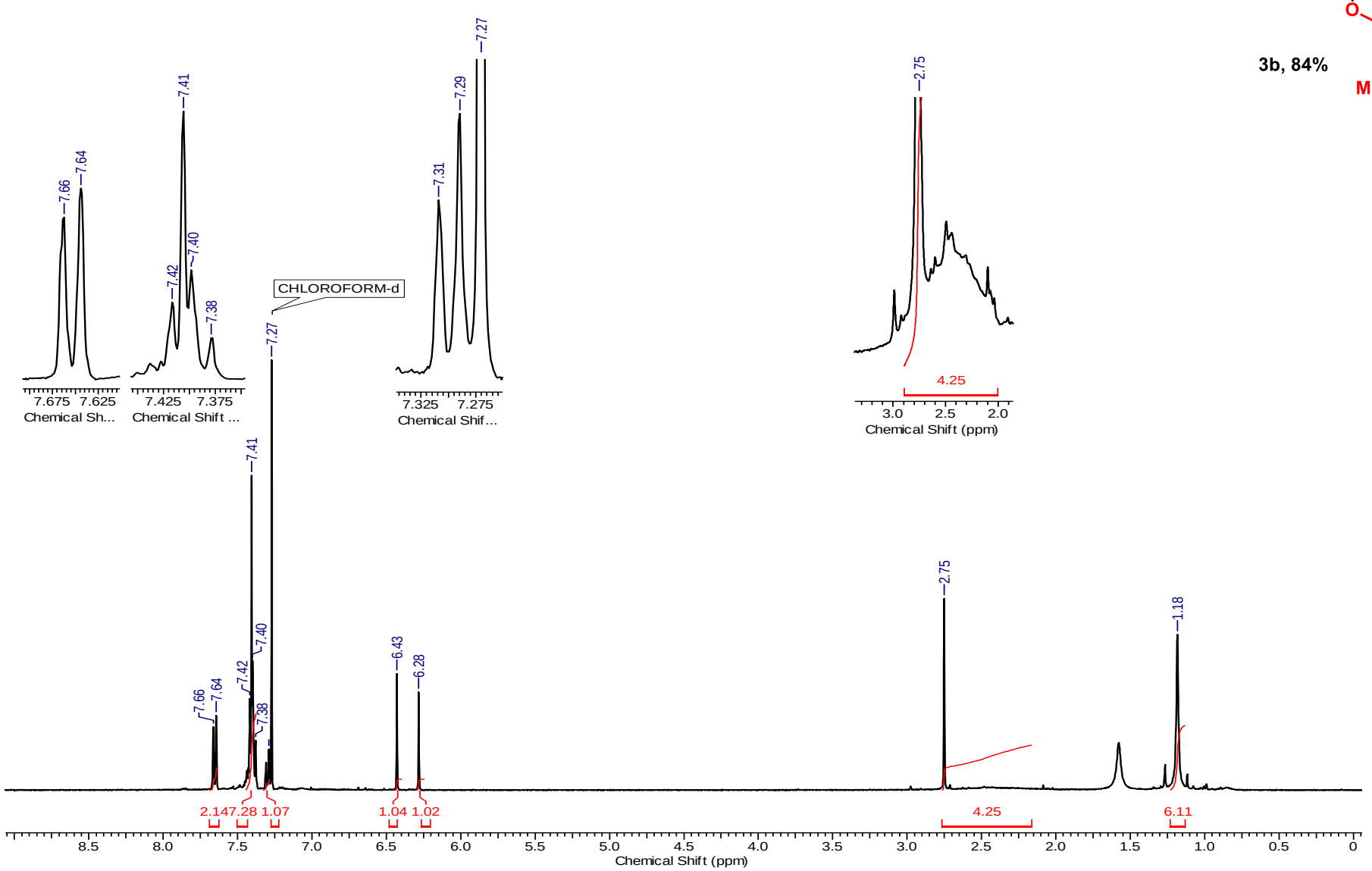


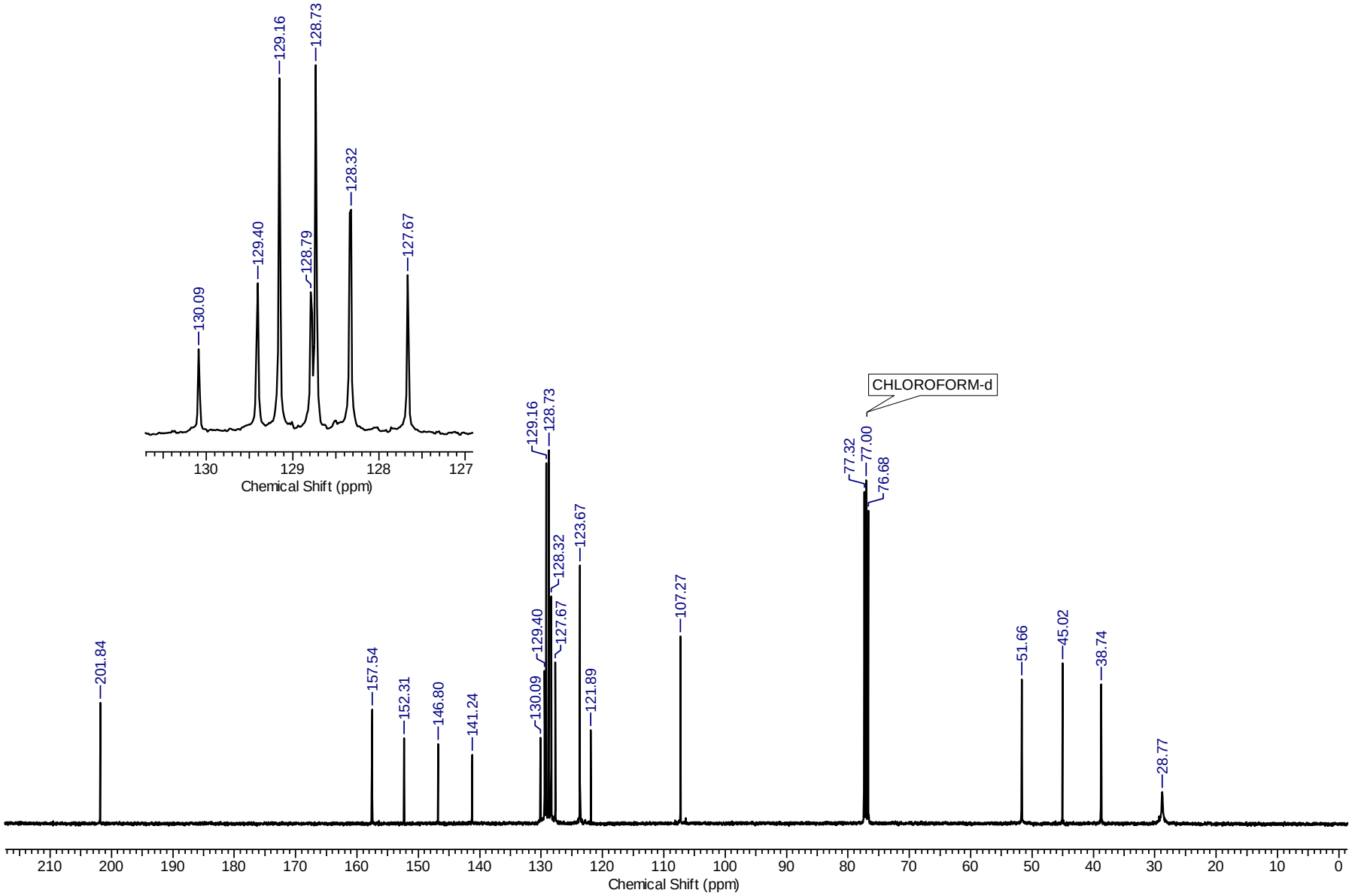
HMBC spectrum of 3a

8,8-dimethyl-2,4-diphenyl-8,9-dihydrocycloocta[*b*]furan-6(7*H*)-one

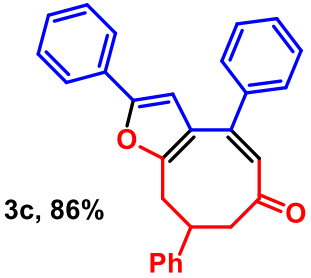


3b, 84%

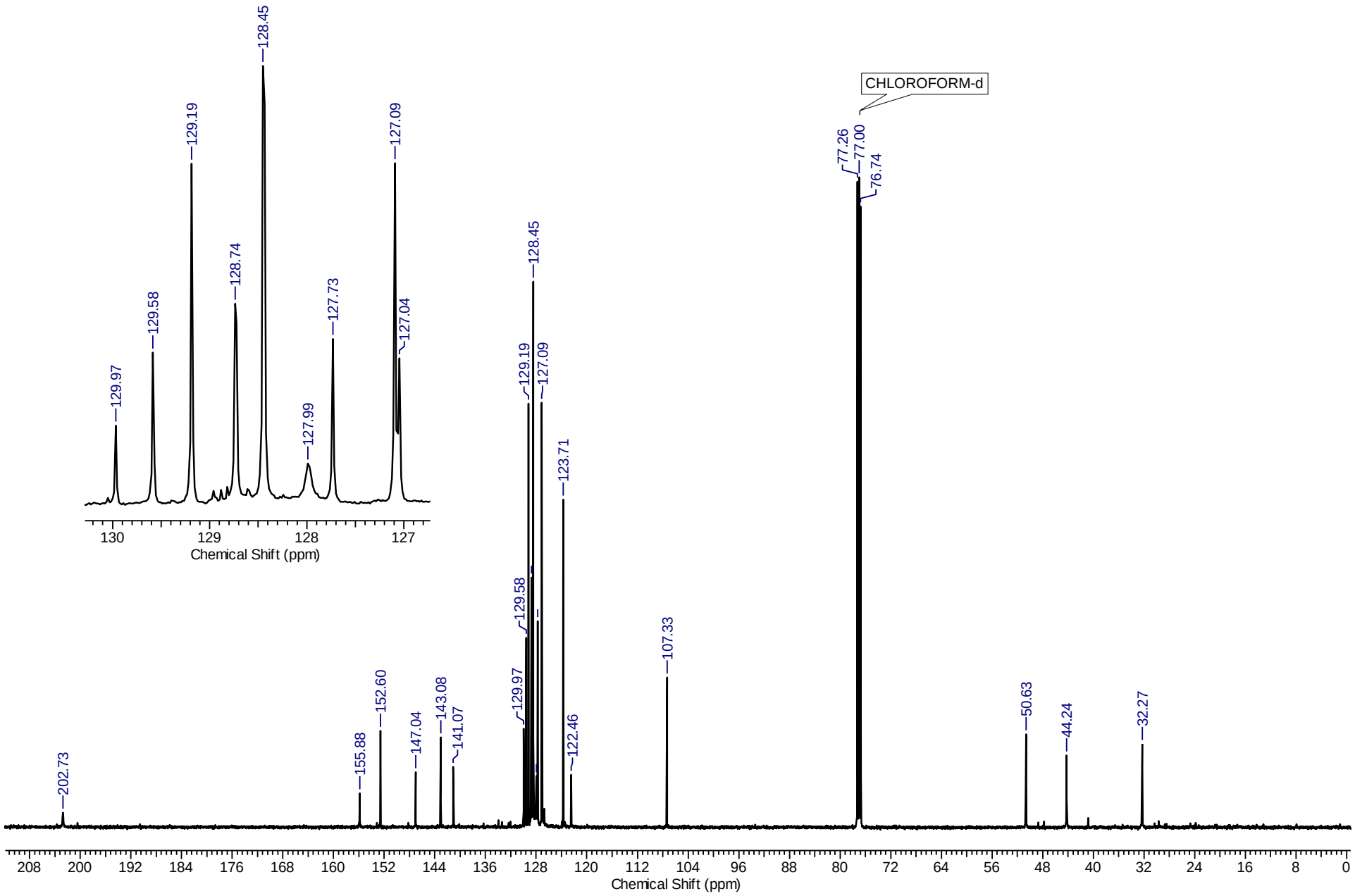



130.09
129.40
129.16
128.79
128.73
128.32
127.67
130
129
128
127
Chemical Shift (ppm)
CHLOROFORM-d
201.84
157.54
152.31
146.80
141.24
130.09
129.40
129.16
128.73
128.32
127.67
123.67
121.89
107.27
77.32
77.00
76.68
51.66
45.02
38.74
28.77
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

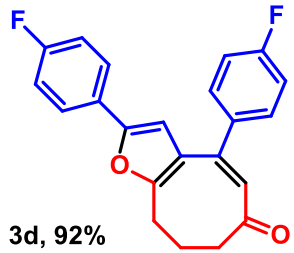
2,4,8-triphenyl-8,9-dihydrocycloocta[*b*]furan-6(7*H*)-one



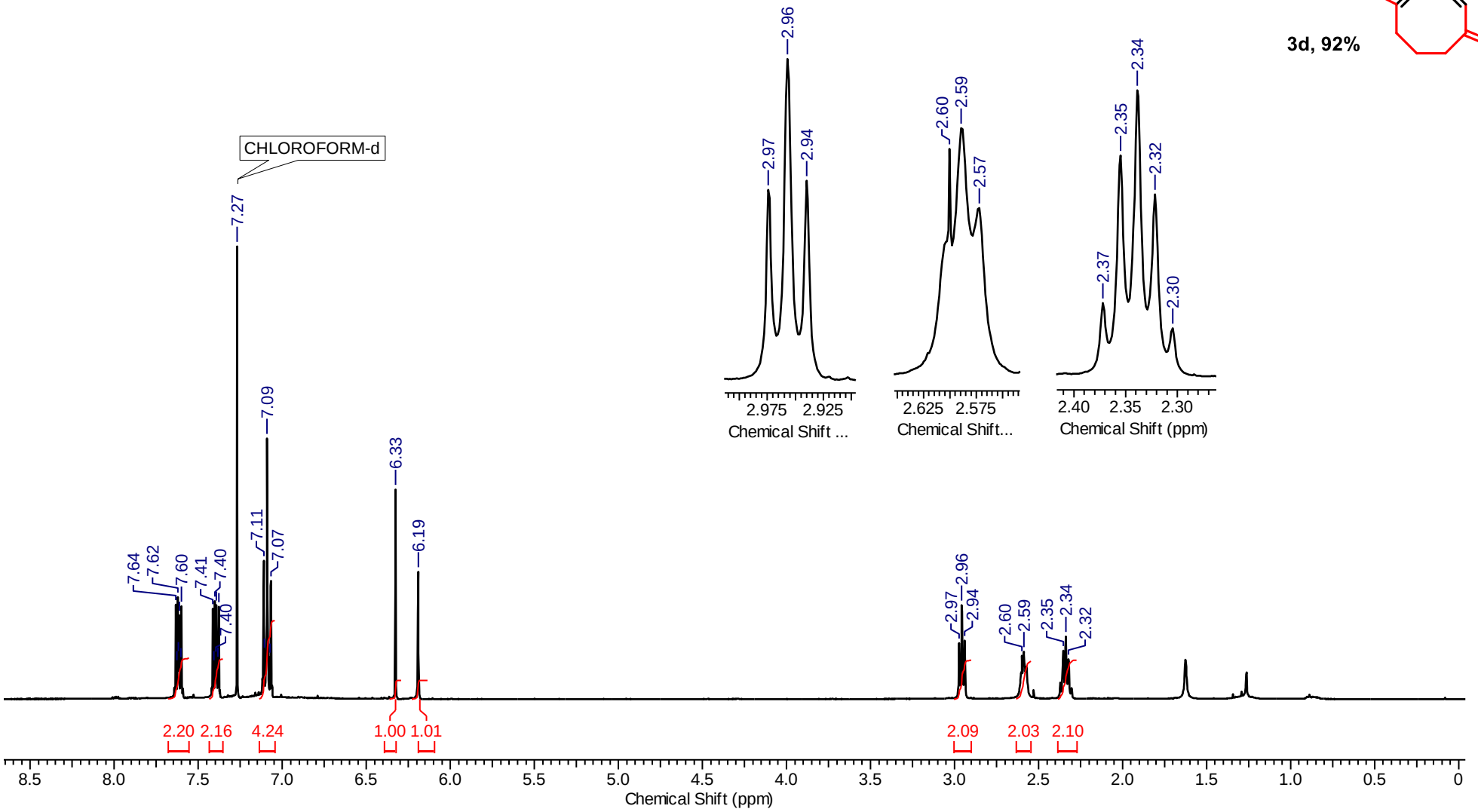
3c, 86%

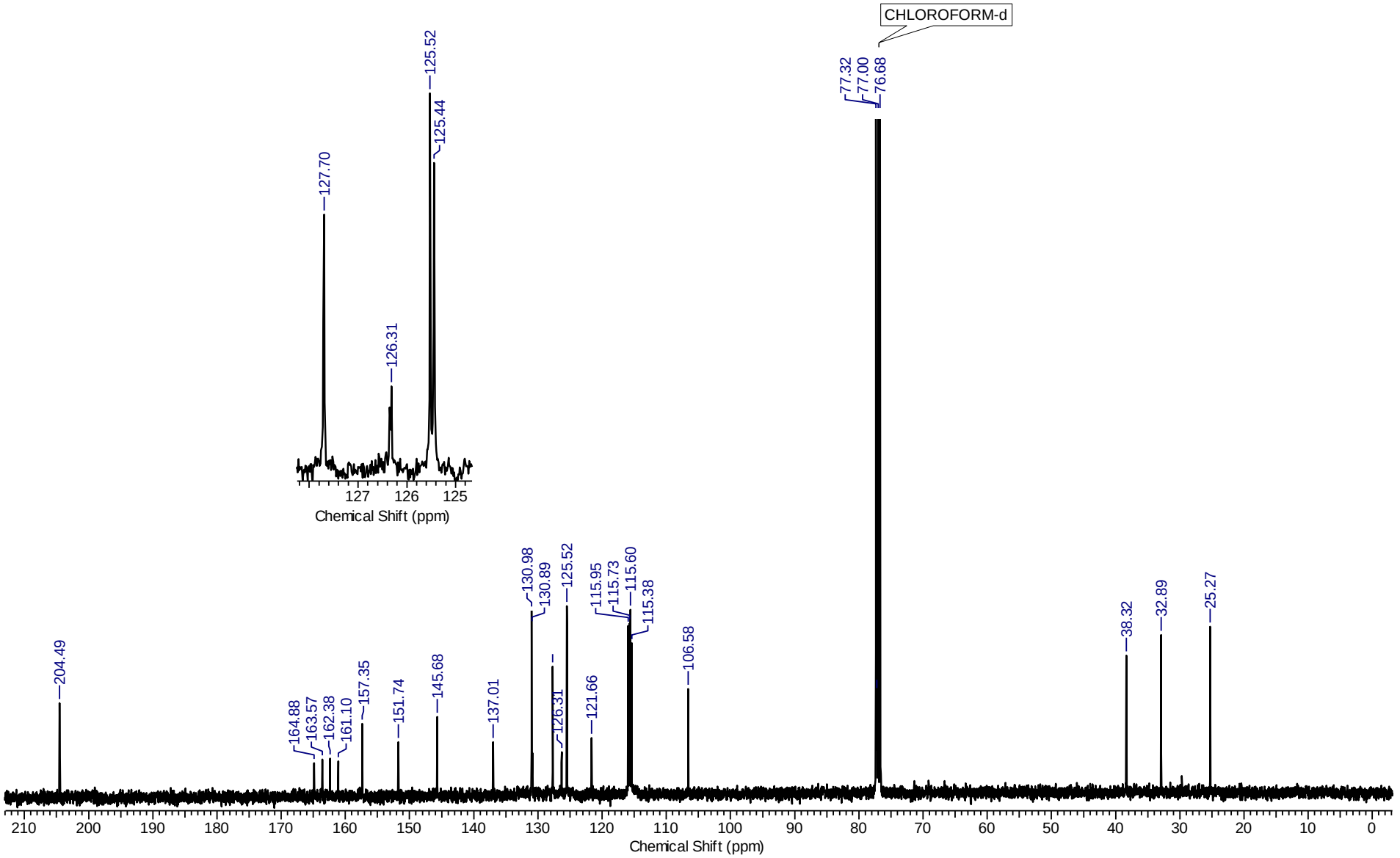

CHLOROFORM-d
77.26
77.00
76.74
128.45
129.19
127.09
129.58
128.74
127.73
127.04
129.97
127.99
123.71
107.33
202.73
155.88
152.60
147.04
143.08
141.07
122.46
50.63
44.24
32.27
Chemical Shift (ppm)
Chemical Shift (ppm)

2,4-*bis*(4-fluorophenyl)-8,9-dihydrocycloocta[*b*]furan-6(*7H*)-one

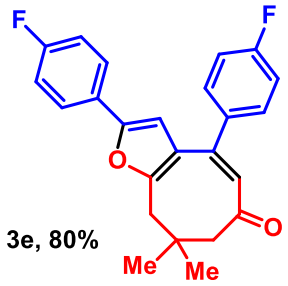


3d, 92%

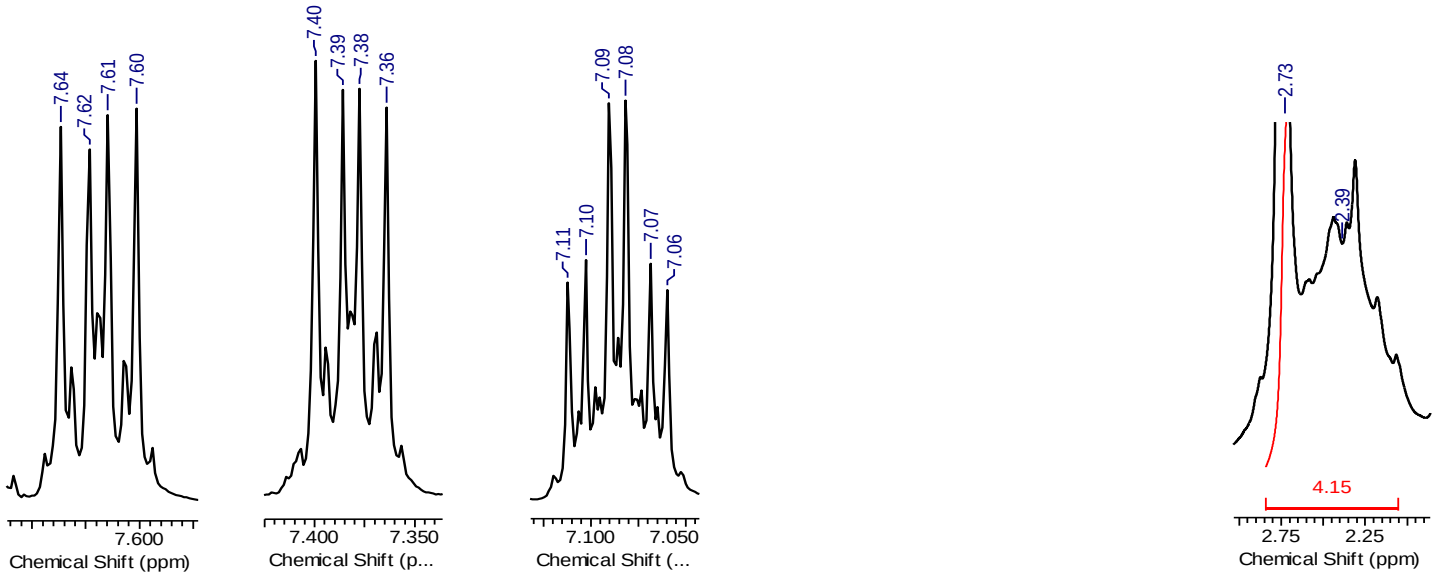


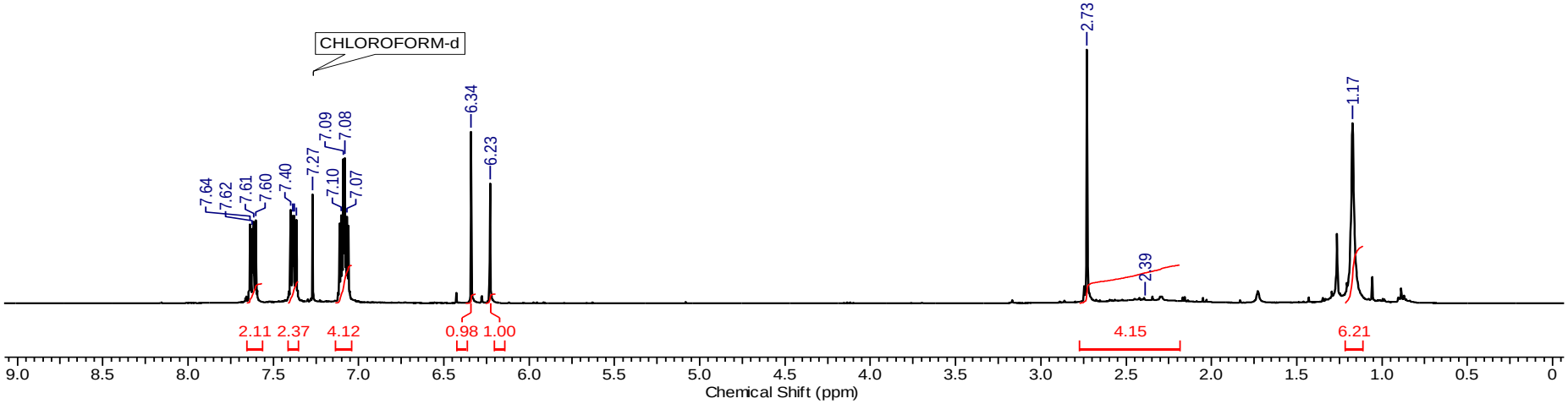

CHLOROFORM-d
77.32
77.00
76.68
204.49
164.88
163.57
162.38
161.10
157.35
151.74
145.68
137.01
130.98
130.89
126.31
125.52
125.44
121.66
115.95
115.73
115.60
115.38
106.58
38.32
32.89
25.27
127.70
126.31
125.52
125.44
127
126
125
Chemical Shift (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

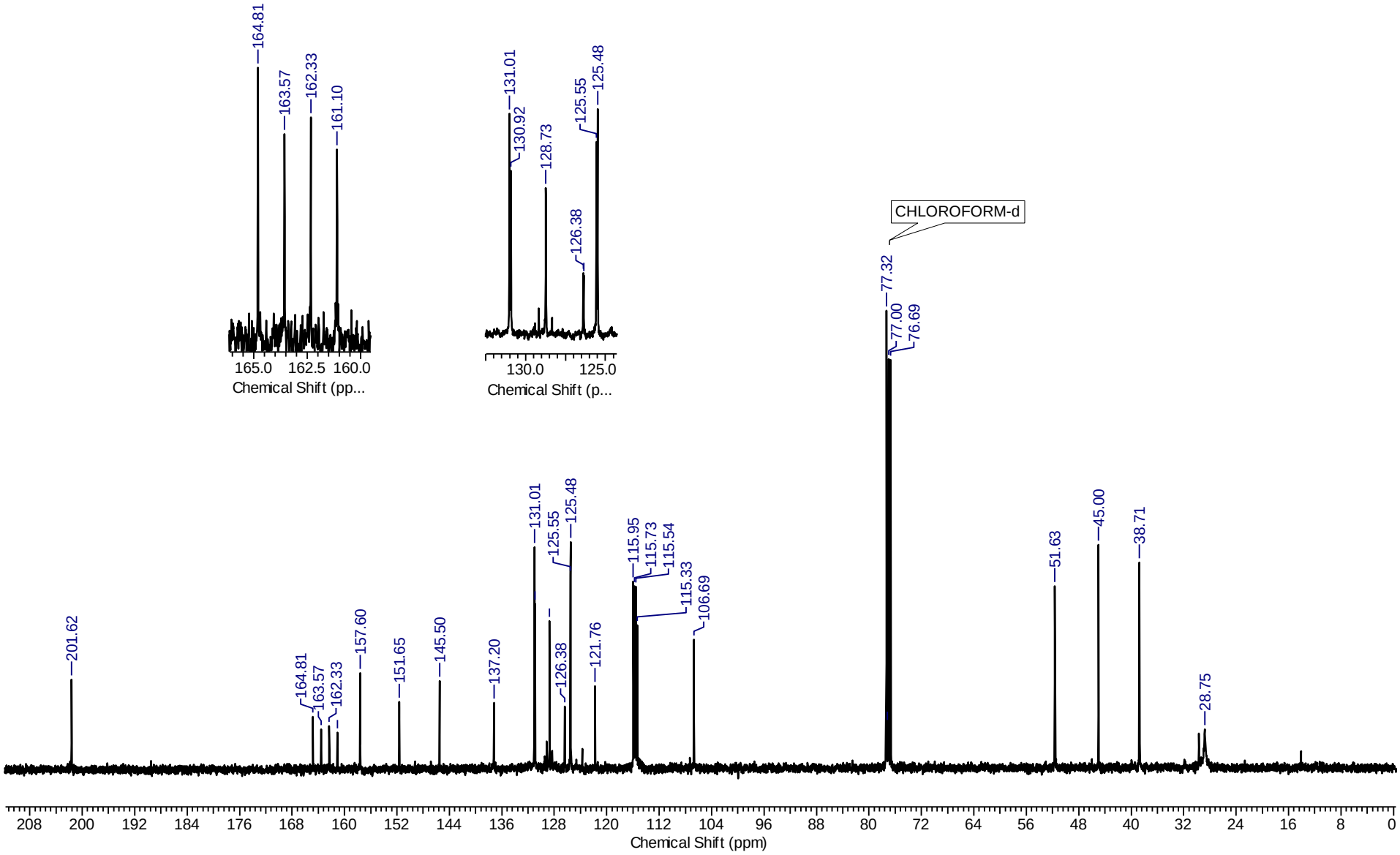
(2,4-*bis*(4-fluorophenyl)-8,8-dimethyl-8,9-dihydrocycloocta[*b*]furan-6(*7H*)-one



3e, 80%



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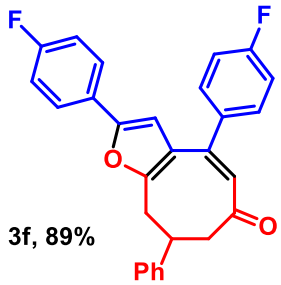
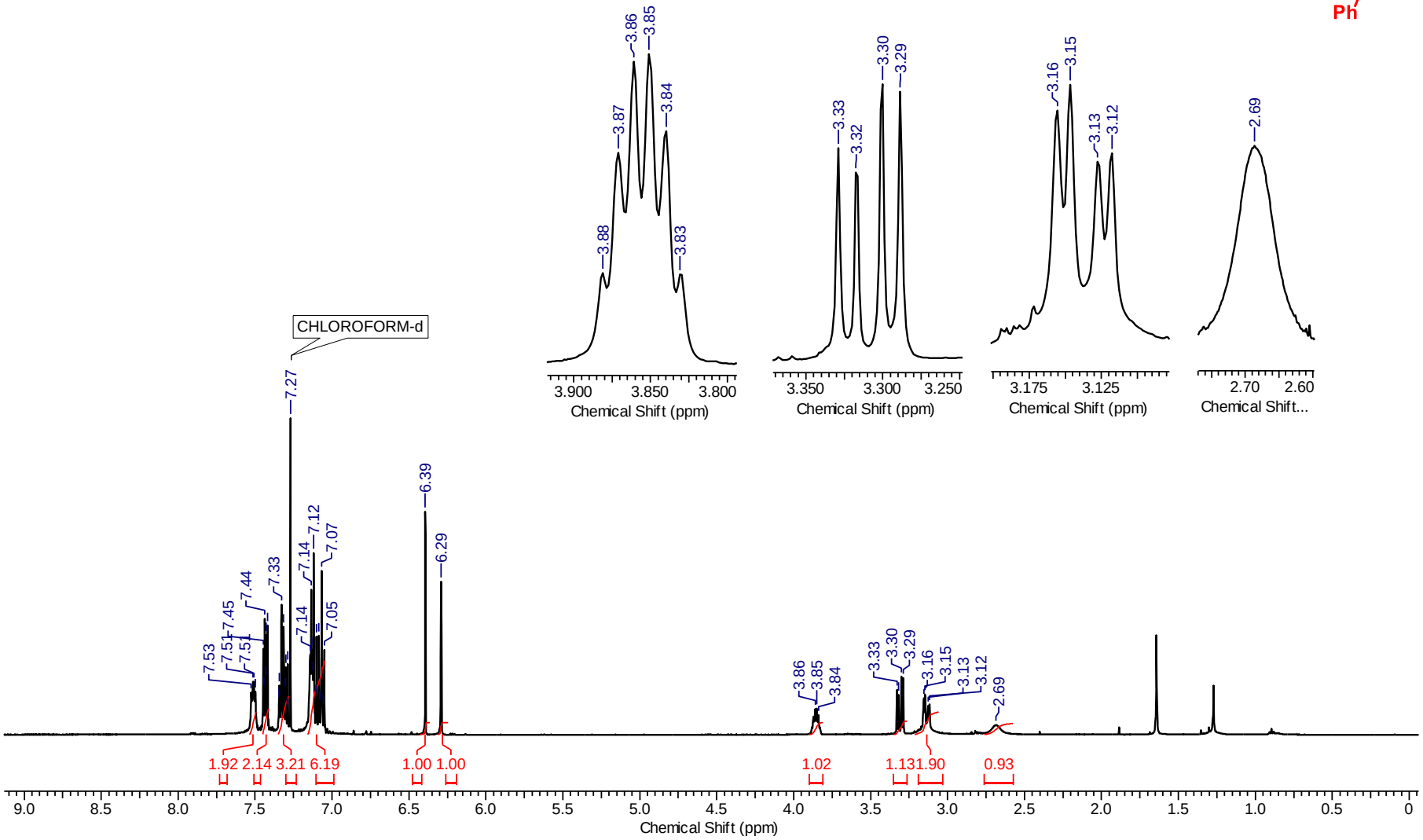
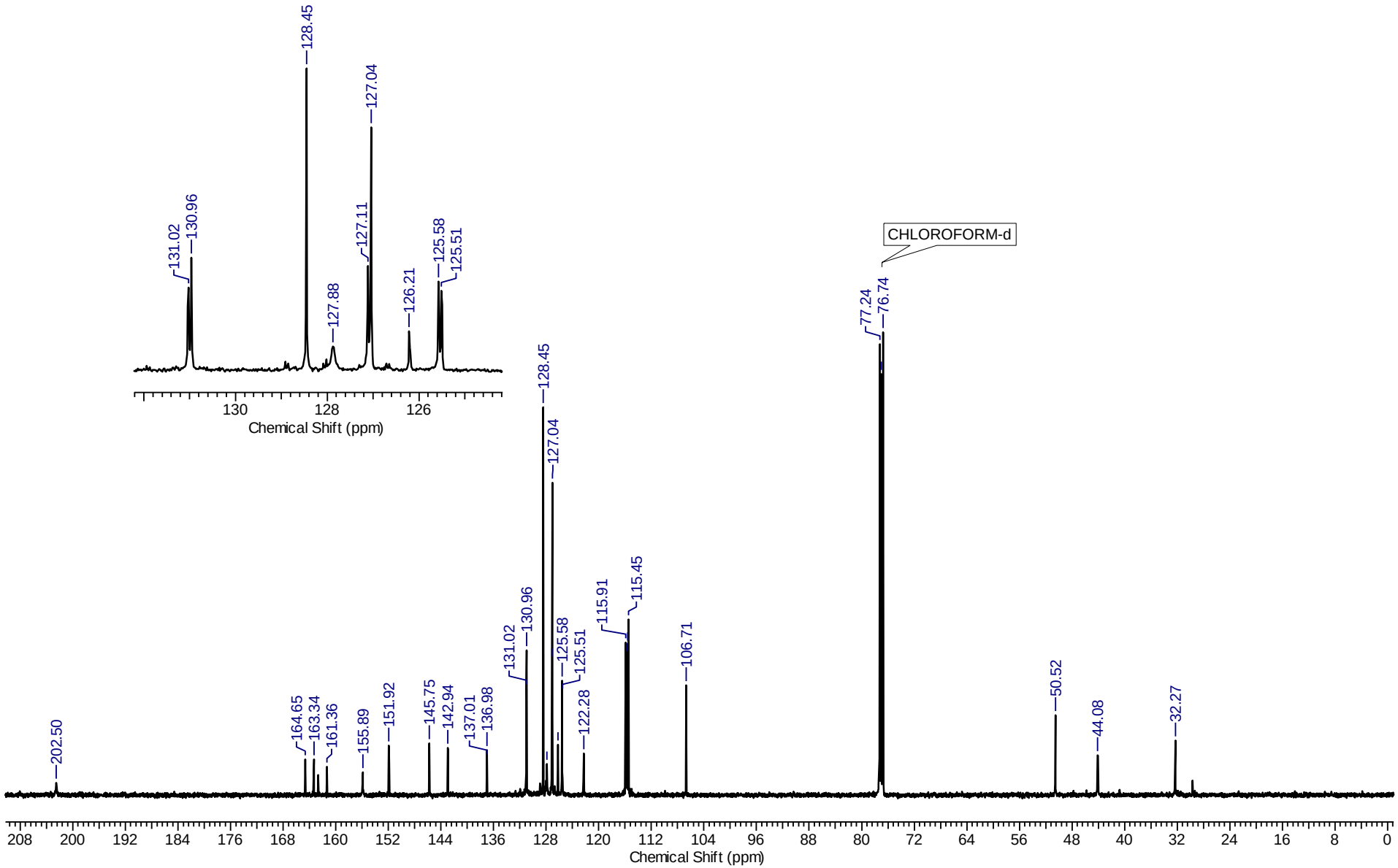
163.57
162.33
161.10
165.0
162.5
160.0
Chemical Shift (pp...
131.01
130.92
128.73
126.38
125.55
125.48
130.0
125.0
Chemical Shift (p...
CHLOROFORM-d
77.32
77.00
76.69
201.62
164.81
163.57
162.33
157.60
151.65
145.50
137.20
131.01
125.55
126.38
125.48
121.76
115.95
115.73
115.54
115.33
106.69
51.63
45.00
38.71
28.75
208
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)

2,4-*bis*(4-fluorophenyl)-8-phenyl-8,9-dihydrocycloocta[*b*]furan-6(*7H*)-one

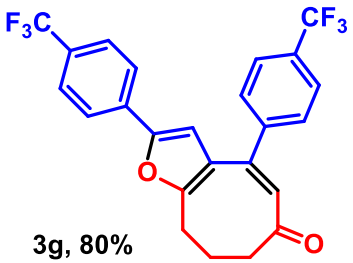


3f, 89%

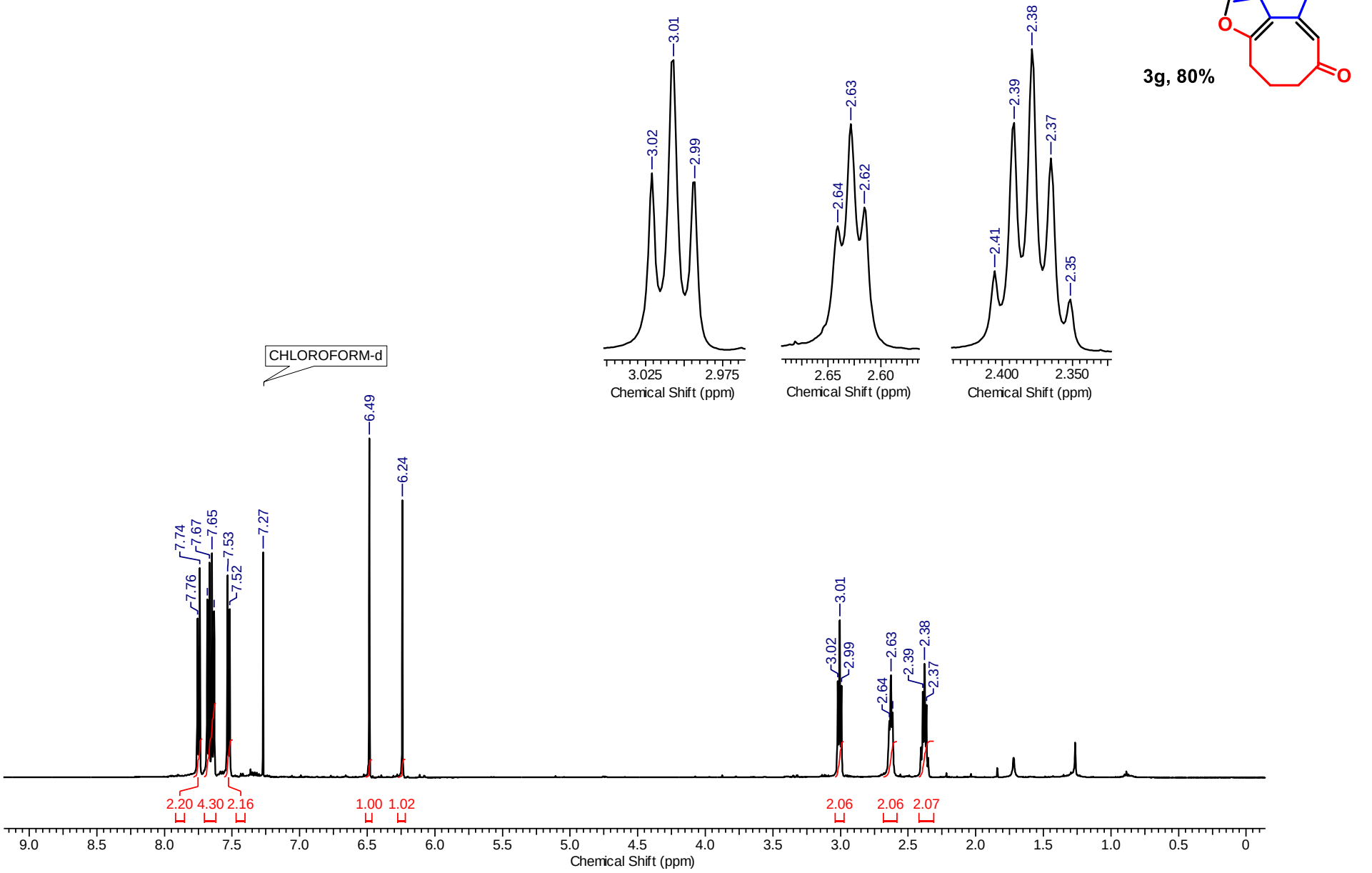


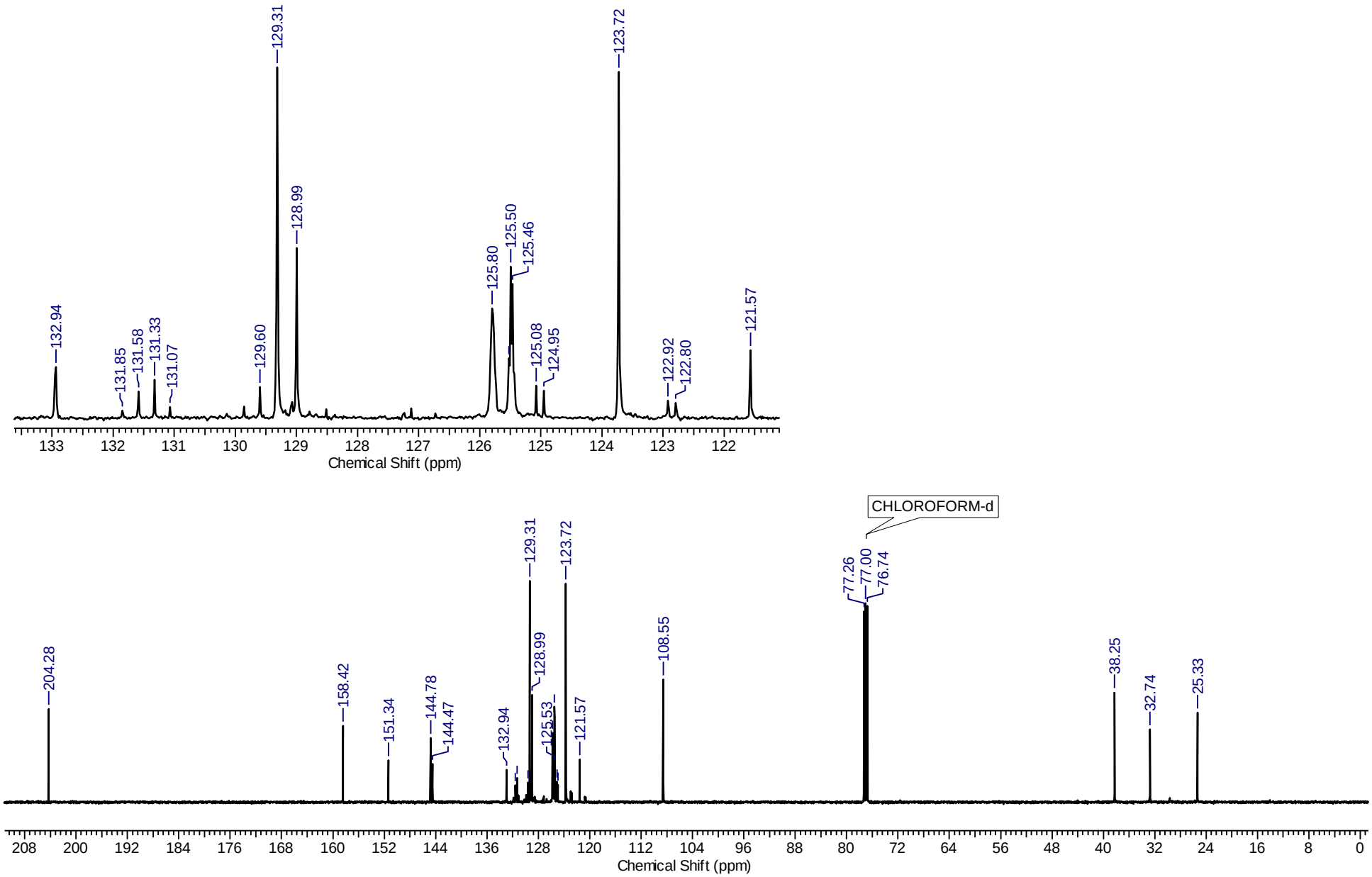

128.45
127.04
131.02
130.96
127.11
127.88
126.21
125.58
125.51
130
128
126
Chemical Shift (ppm)
CHLOROFORM-d
77.24
76.74
128.45
127.04
131.02
130.96
125.58
125.51
115.91
115.45
106.71
202.50
164.65
163.34
161.36
155.89
151.92
145.75
142.94
137.01
136.98
122.28
50.52
44.08
32.27
208
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

2,4-*bis*(4-(trifluoromethyl)phenyl)-8,9-dihydrocycloocta[*b*]furan-6(*7H*)-one



3g, 80%

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125.46
132.94
131.85
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131.33
131.07
129.60
125.08
124.95
122.92
122.80
121.57
133
132
131
130
129
128
127
126
125
124
123
122
Chemical Shift (ppm)
CHLOROFORM-d
204.28
158.42
151.34
144.78
144.47
132.94
129.31
128.99
125.53
123.72
121.57
108.55
77.26
77.00
76.74
38.25
32.74
25.33
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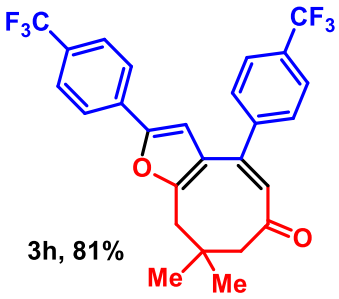
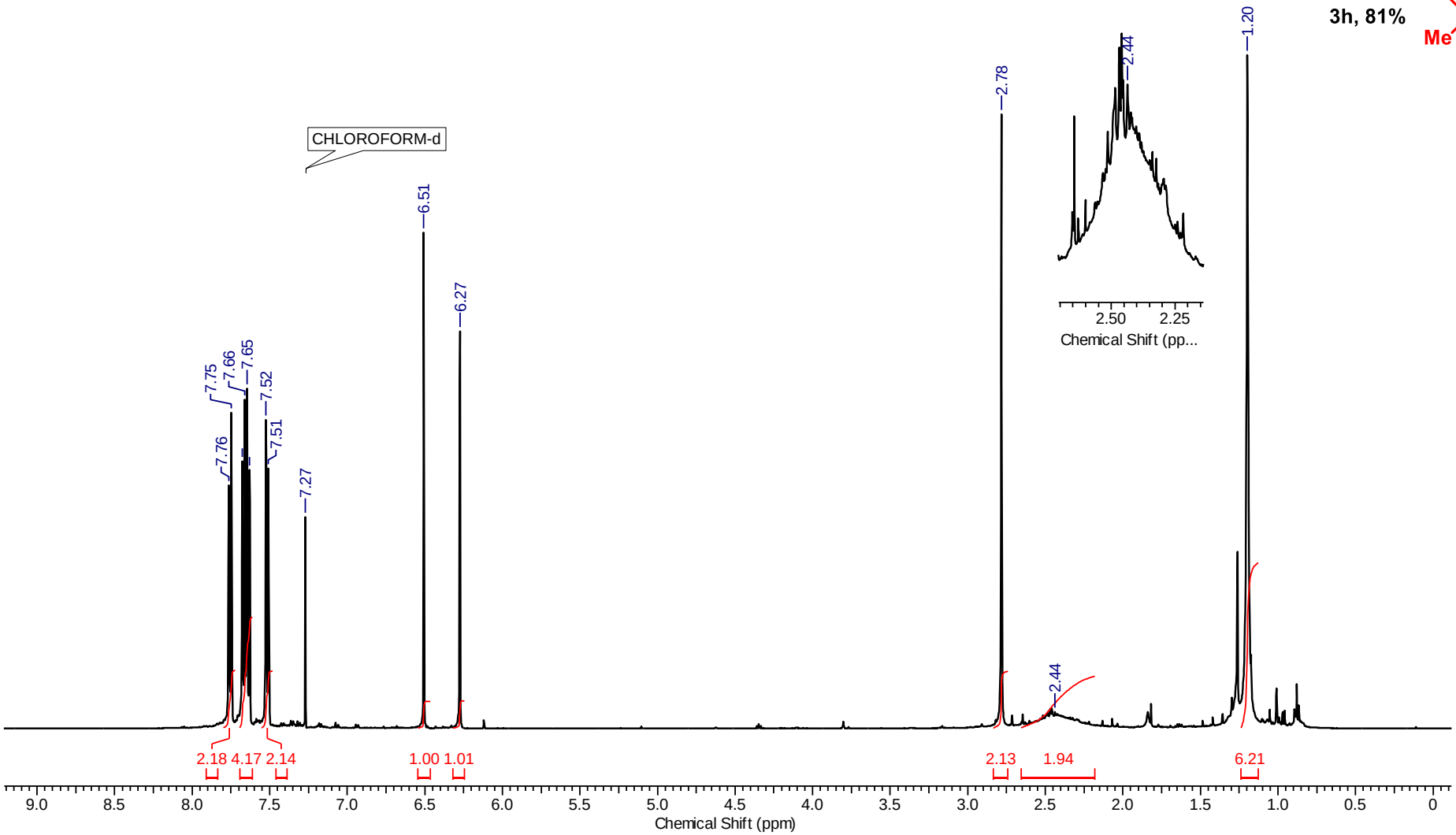
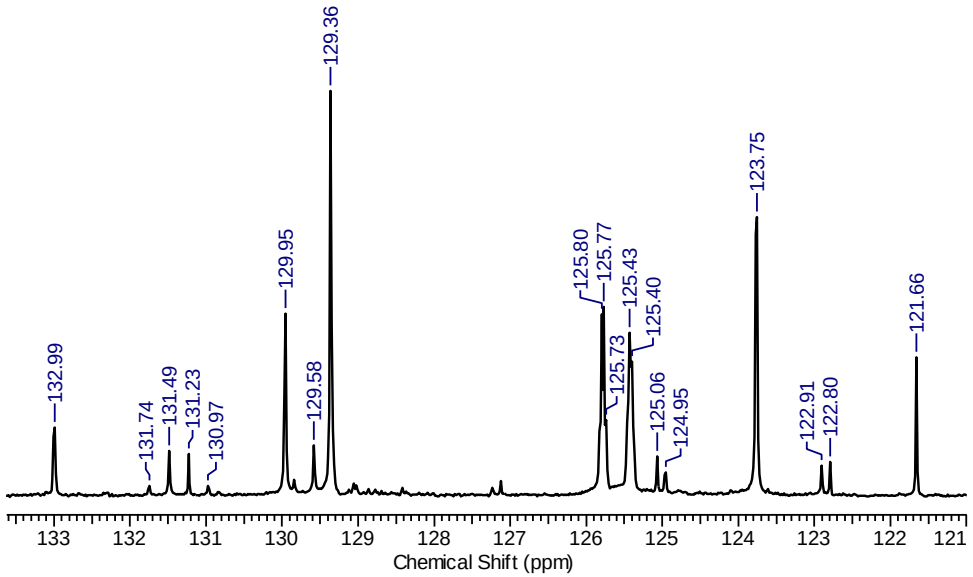
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

8,8-dimethyl-2,4-*bis*(4-(trifluoromethyl)phenyl)-8,9-dihydrocycloocta[*b*]furan-6(*7H*)-one



3h, 81%

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131.49
131.23
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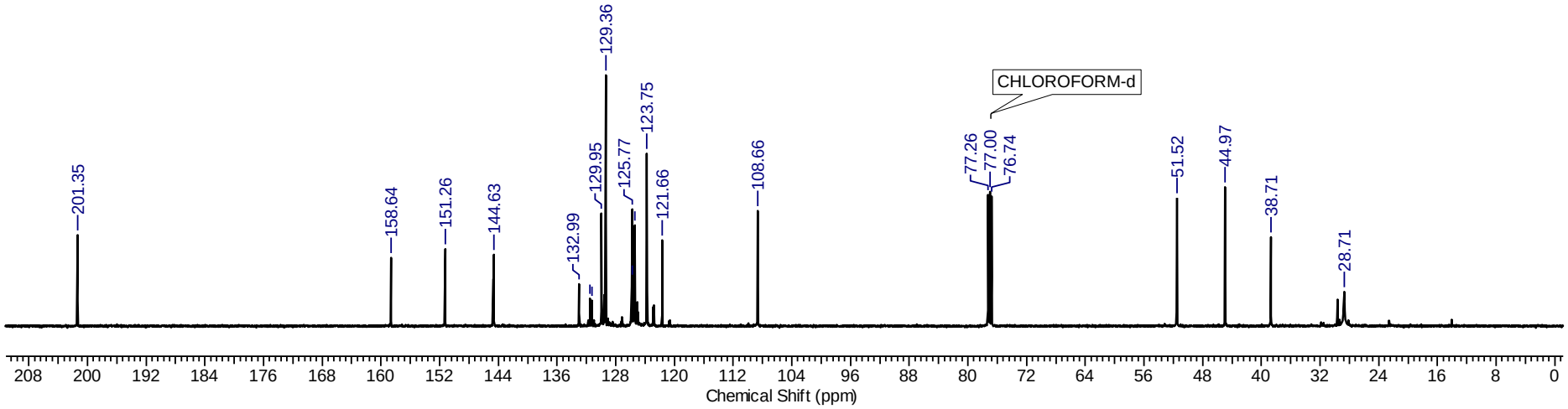
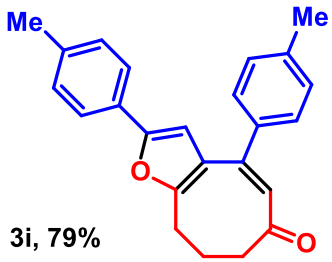
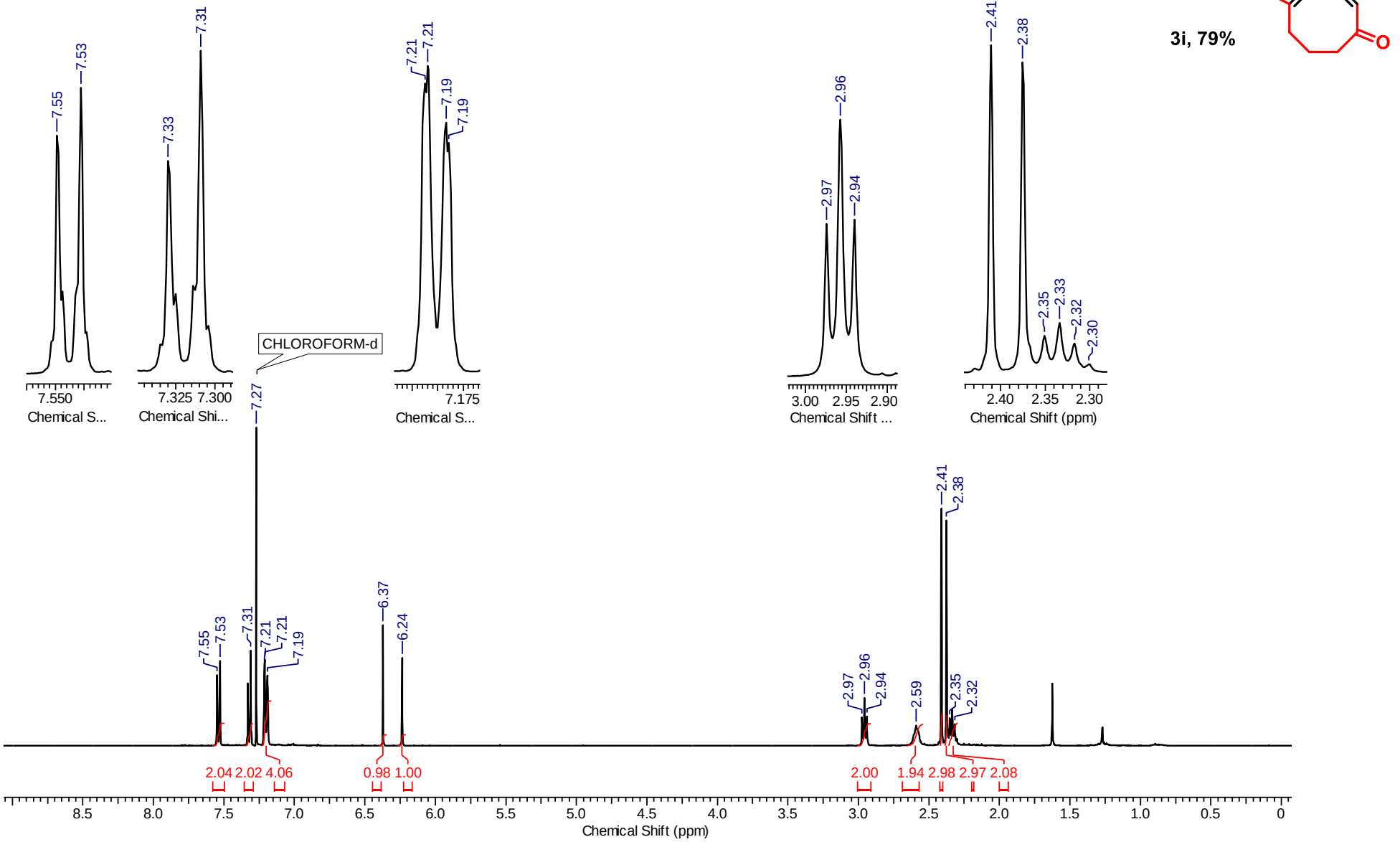
129.95
129.58
129.36
125.80
125.77
125.73
125.43
125.40
125.06
124.95
123.75
122.91
122.80
121.66
133
132
131
130
129
128
127
126
125
124
123
122
121
Chemical Shift (ppm)

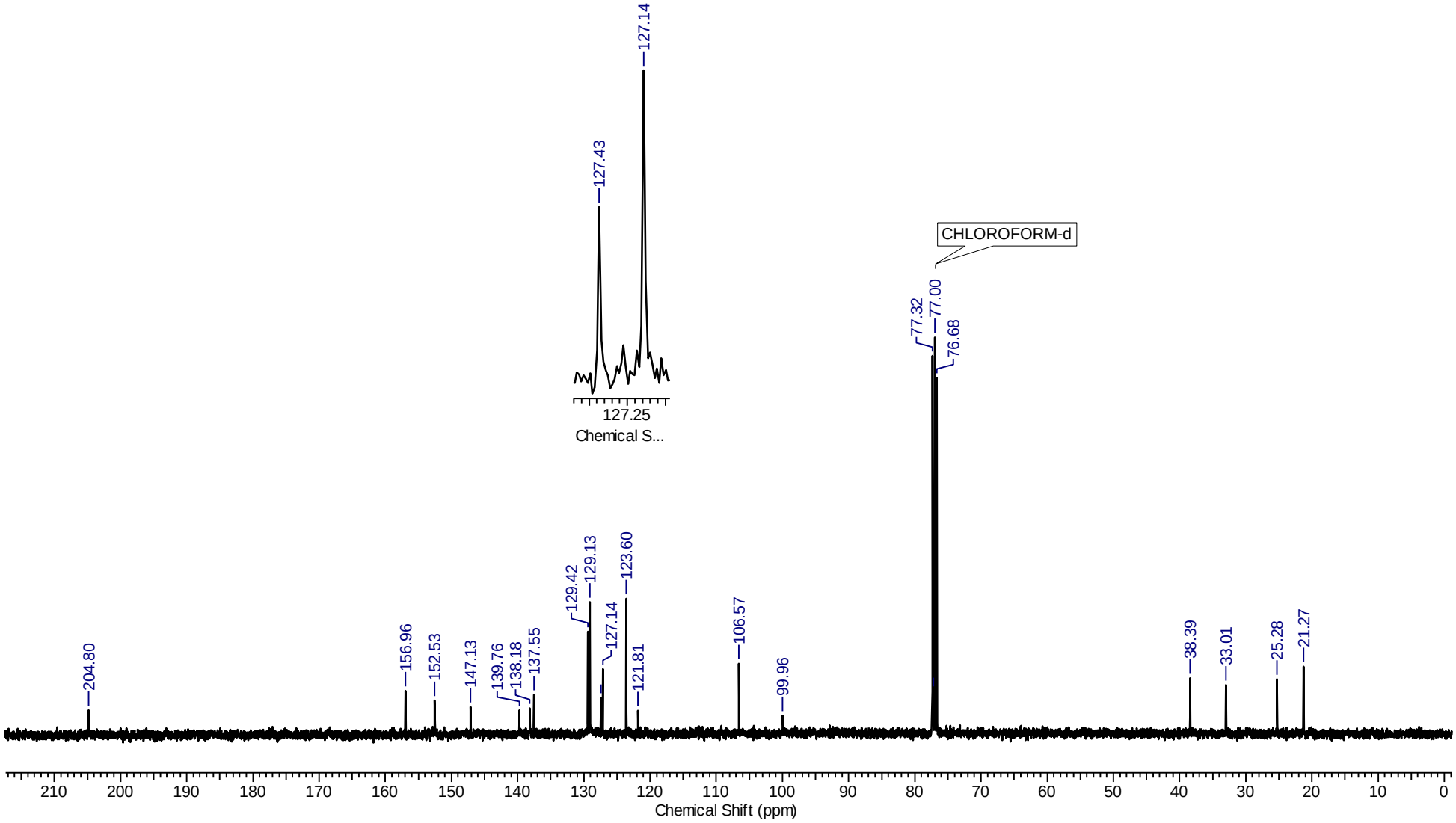

201.35
158.64
151.26
144.63
132.99
129.95
129.36
125.77
123.75
121.66
108.66
CHLOROFORM-d
77.26
77.00
76.74
51.52
44.97
38.71
28.71
208
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

2,4-di-*p*-tolyl-8,9-dihydrocycloocta[*b*]furan-6(*7H*)-one

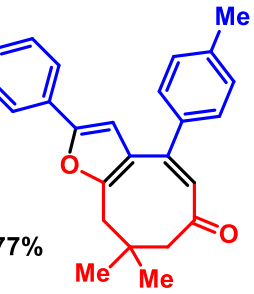


3i, 79%

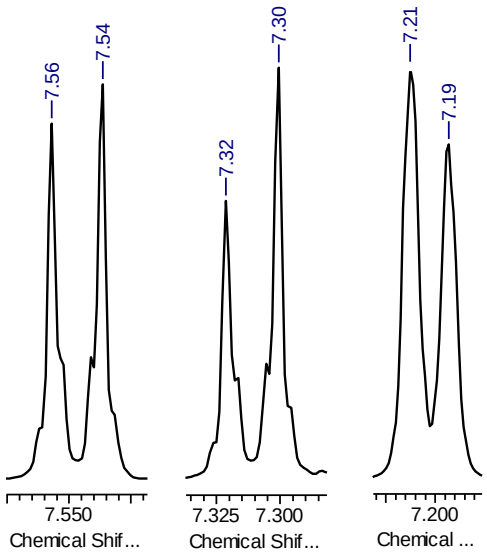


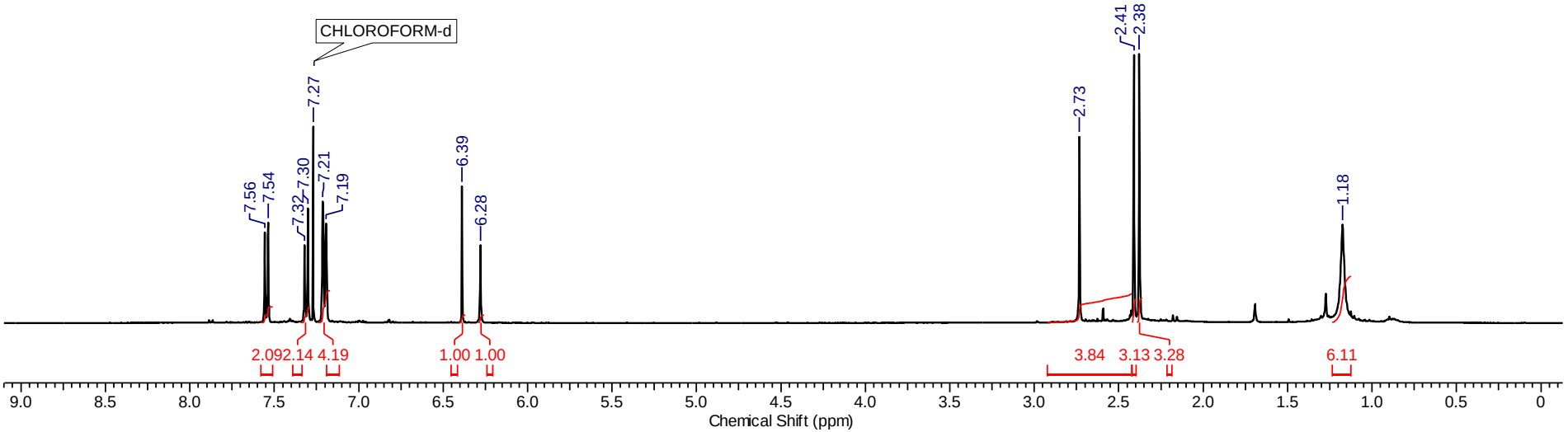

127.14
127.43
127.25
Chemical S...
CHLOROFORM-d
77.32
77.00
76.68
204.80
156.96
152.53
147.13
139.76
138.18
137.55
129.42
129.13
127.14
123.60
121.81
106.57
99.96
38.39
33.01
25.28
21.27
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)

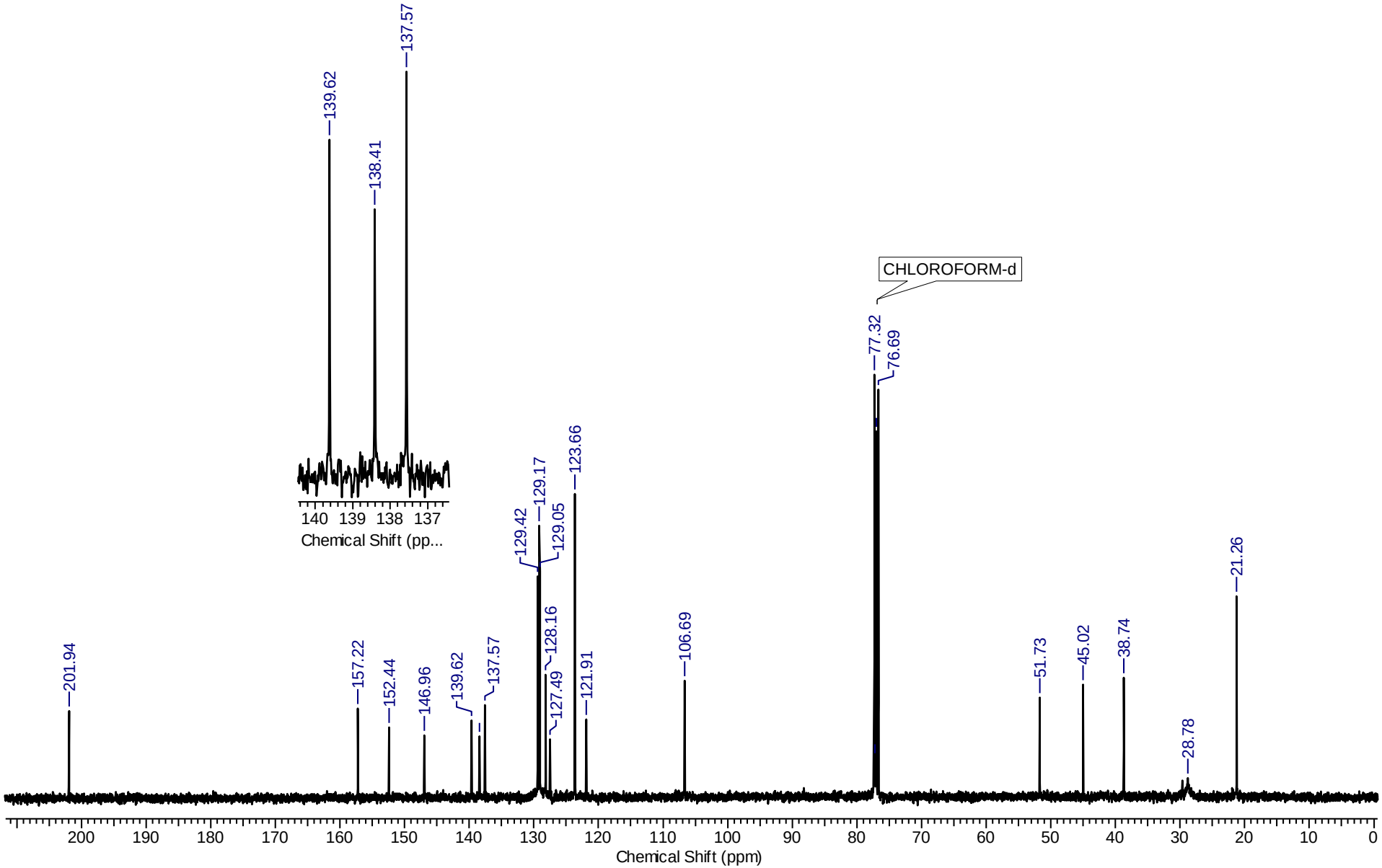
8,8-dimethyl-2,4-di-*p*-tolyl-8,9-dihydrocycloocta[*b*]furan-6(*7H*)-one



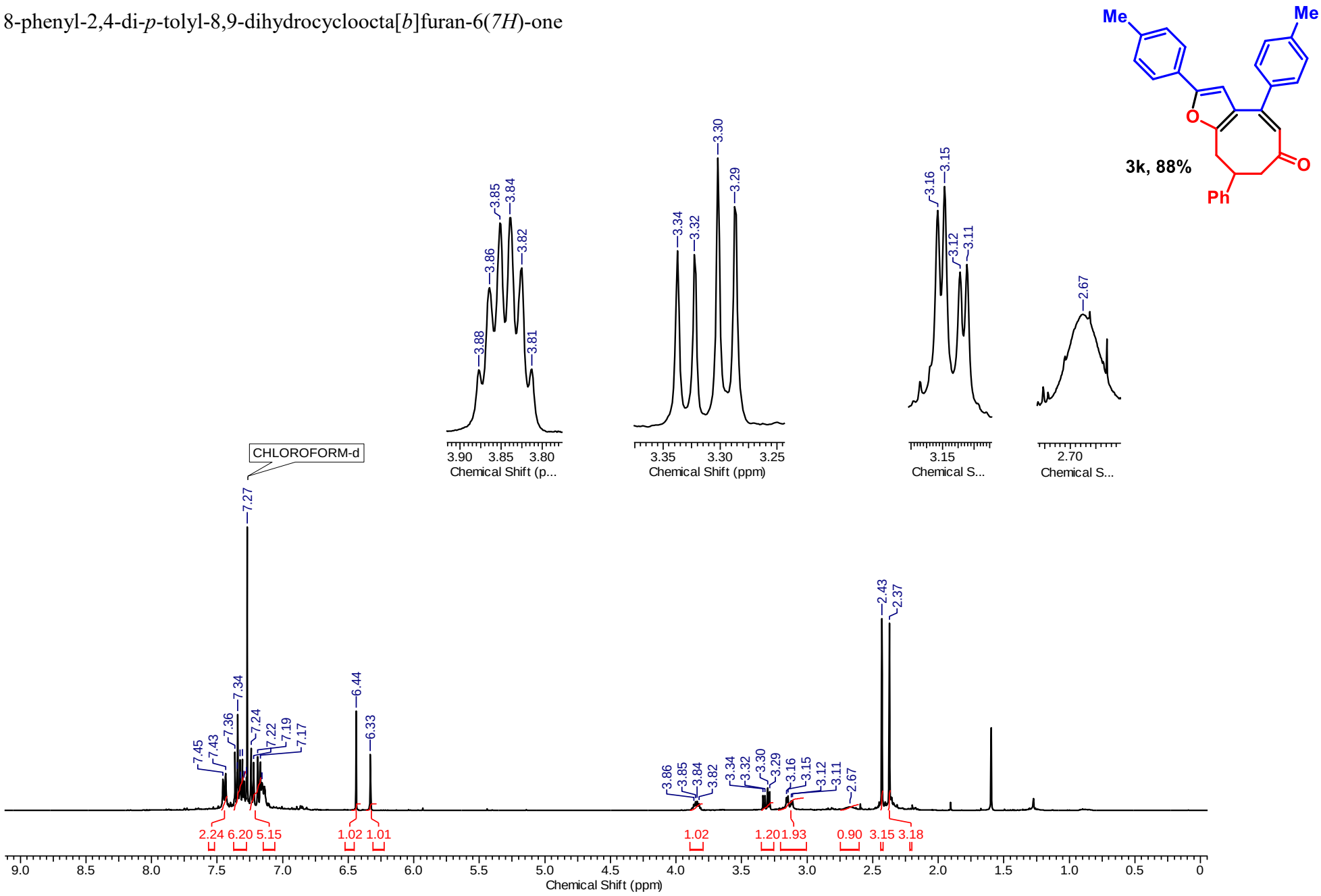
3j, 77%

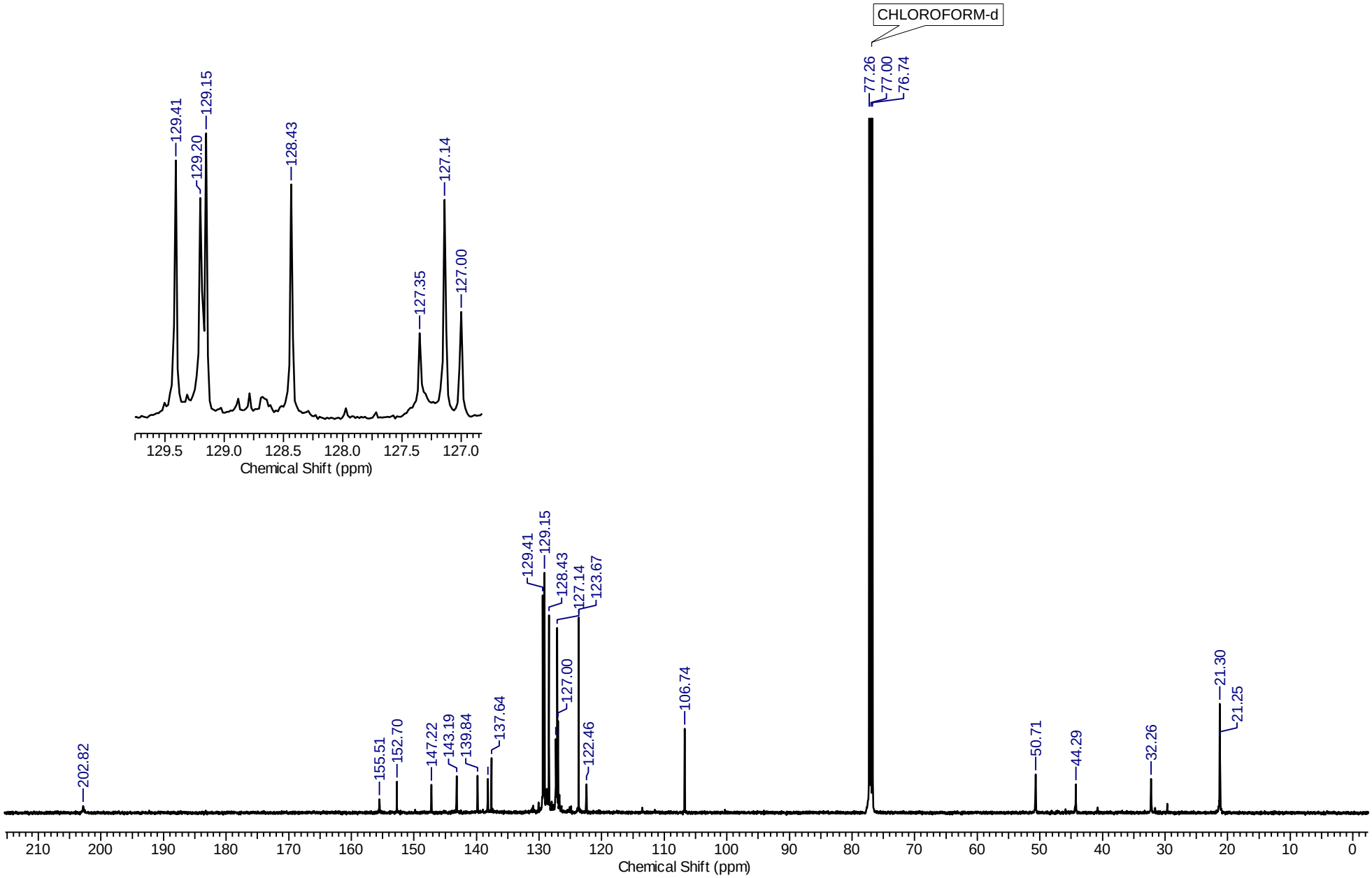




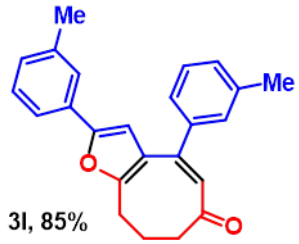

139.62
138.41
137.57
140 139 138 137
Chemical Shift (pp...
CHLOROFORM-d
77.32
76.69
123.66
129.17
129.42
129.05
128.16
127.49
121.91
106.69
201.94
157.22
152.44
146.96
139.62
137.57
51.73
45.02
38.74
28.78
21.26
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)

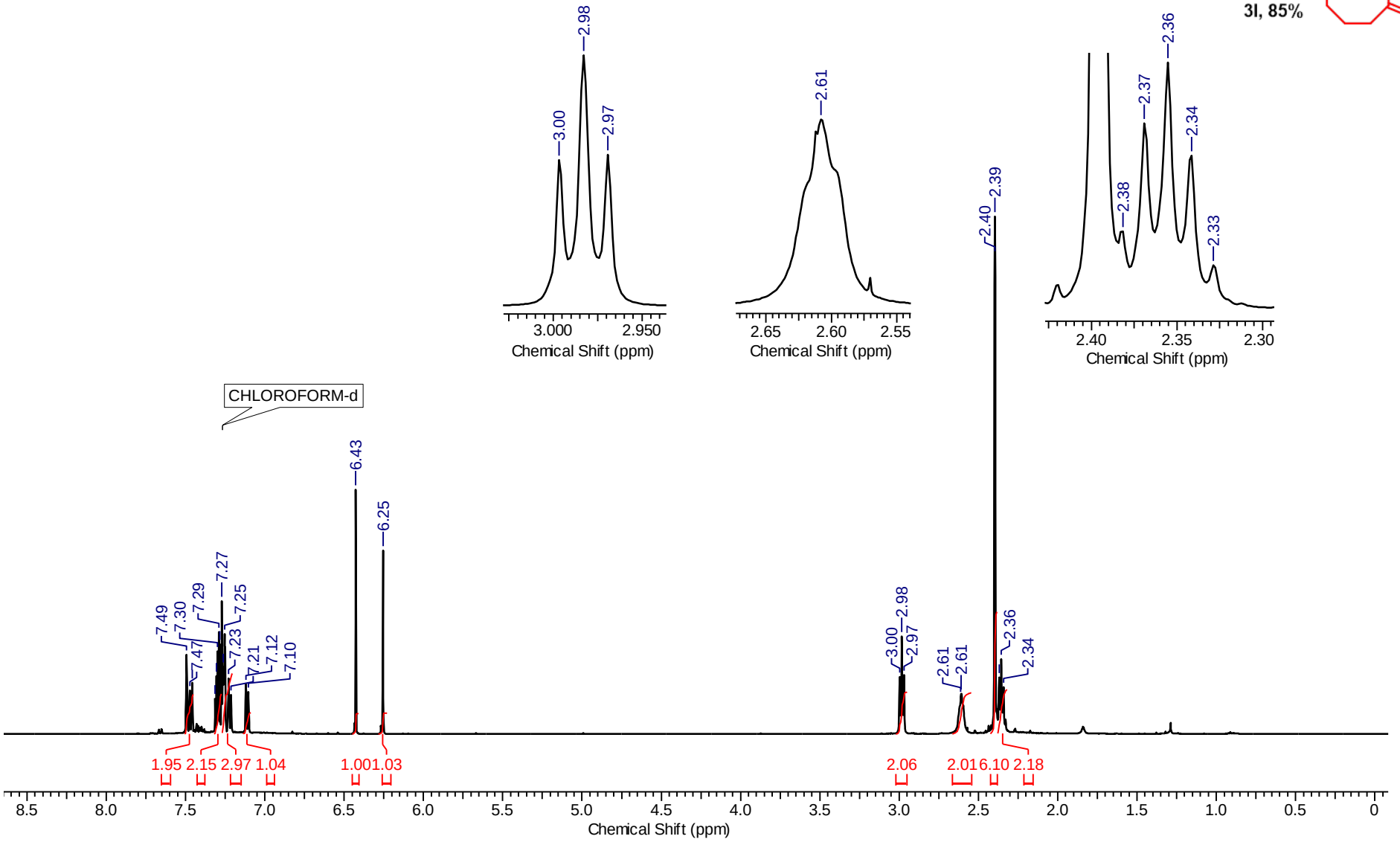
8-phenyl-2,4-di-*p*-tolyl-8,9-dihydrocycloocta[*b*]furan-6(*7H*)-one

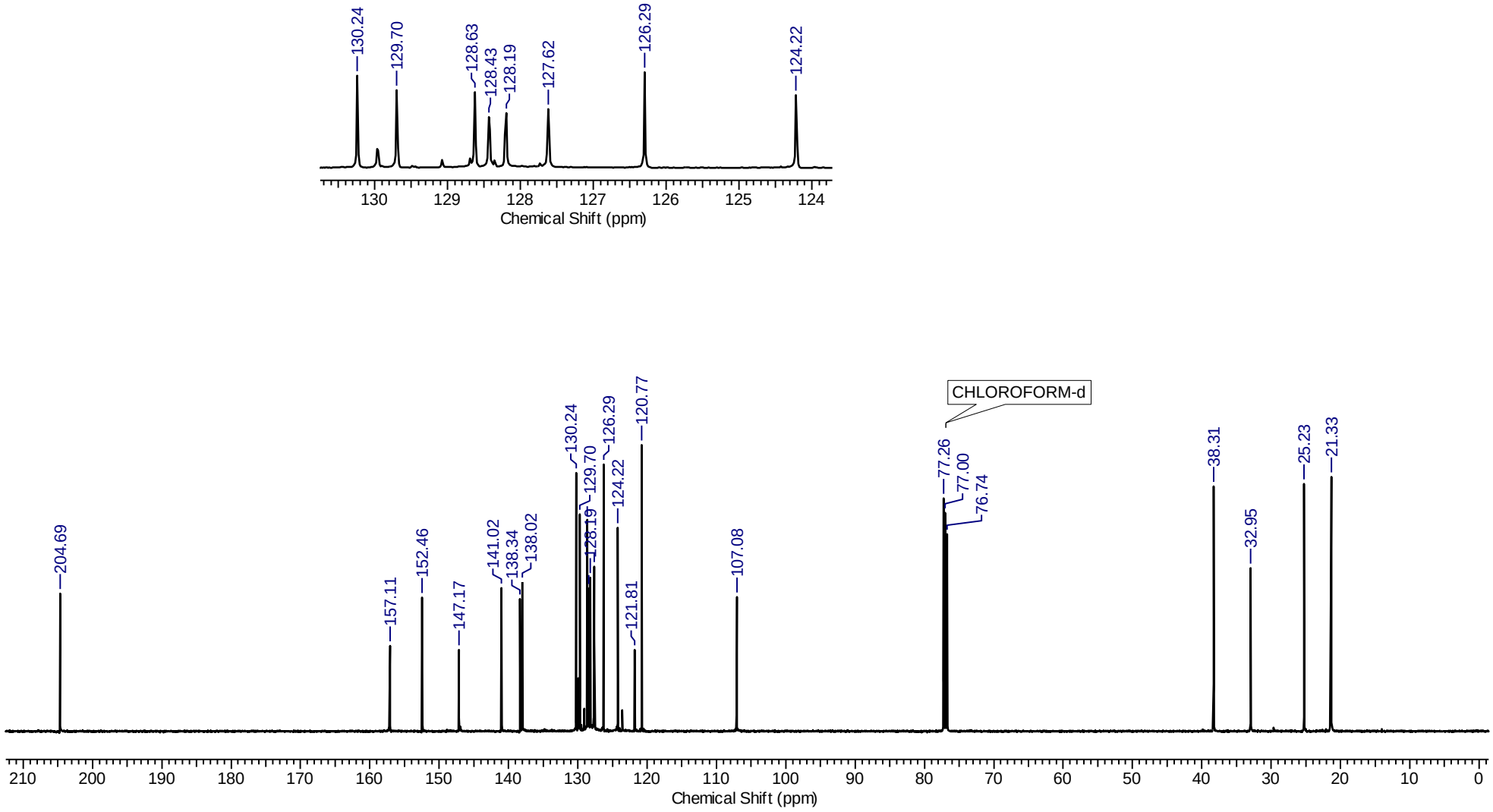



CHLOROFORM-d
77.26
77.00
76.74
129.41
129.15
128.43
127.14
127.00
127.35
129.5
129.0
128.5
128.0
127.5
127.0
Chemical Shift (ppm)
202.82
155.51
152.70
147.22
143.19
139.84
137.64
129.41
129.15
128.43
127.14
123.67
127.00
122.46
106.74
50.71
44.29
32.26
21.30
21.25
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

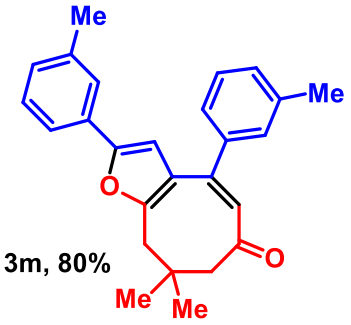
2,4-di-*m*-tolyl-8,9-dihydrocycloocta[*b*]furan-6(*7H*)-one

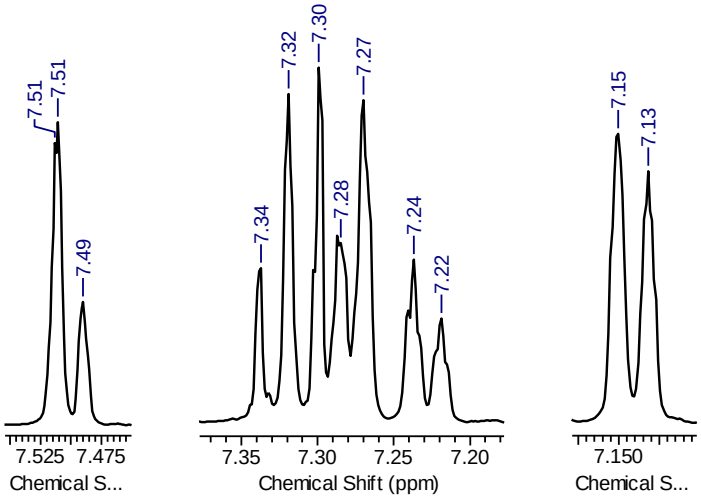


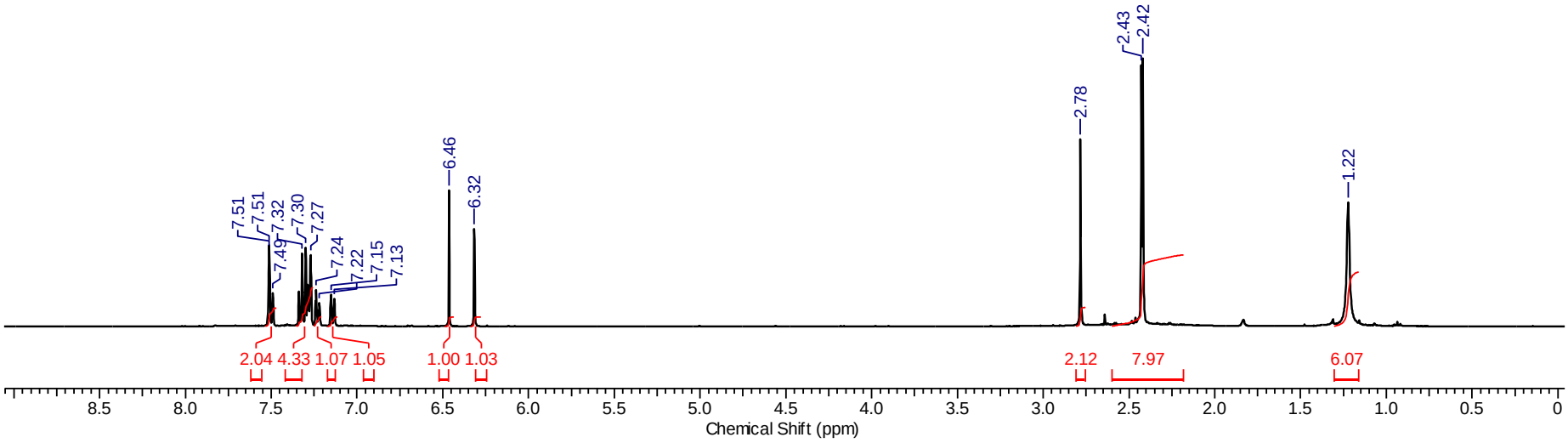


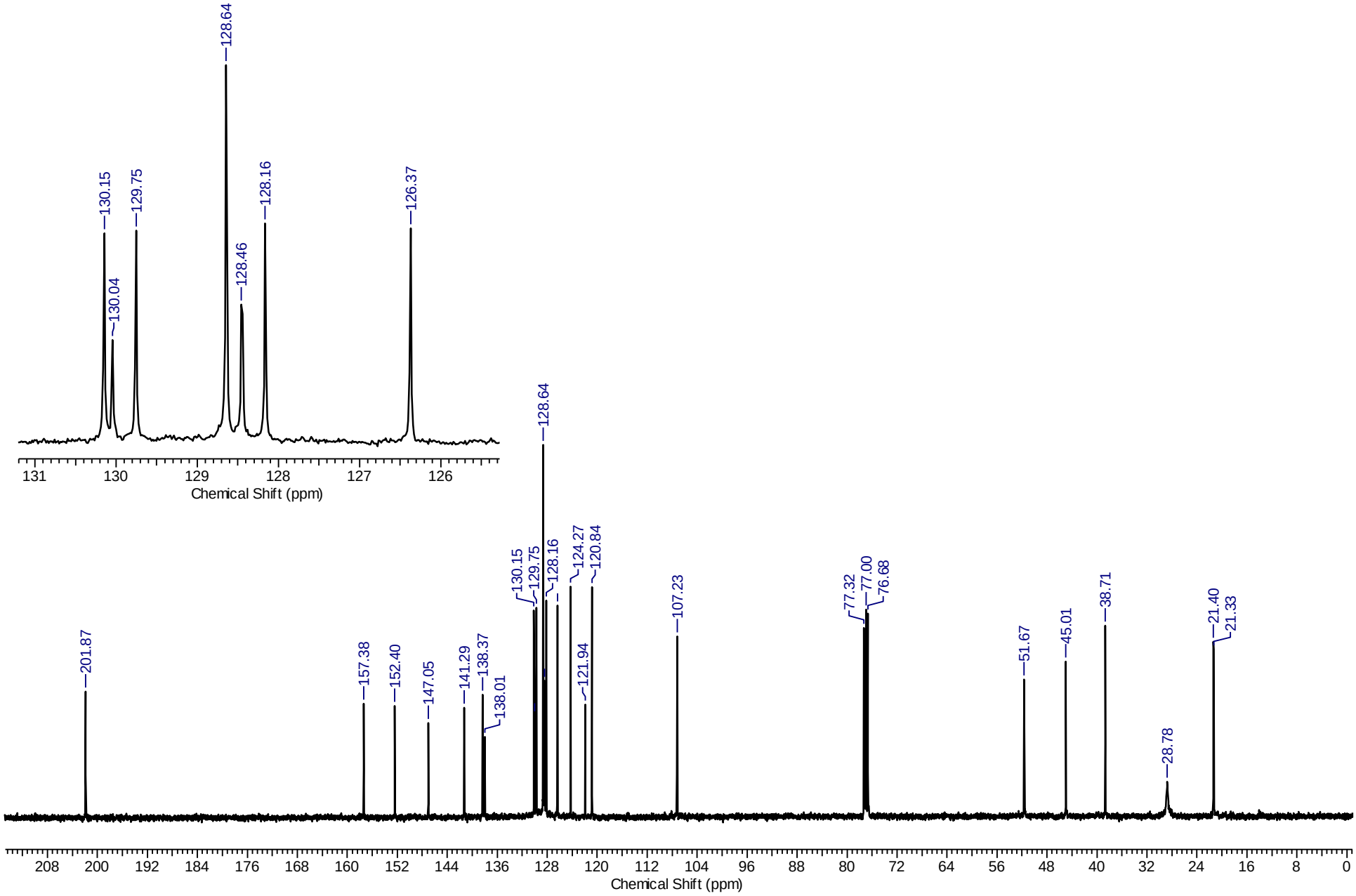

130.24
129.70
128.63
128.43
128.19
127.62
126.29
124.22
130
129
128
127
126
125
124
Chemical Shift (ppm)
204.69
157.11
152.46
147.17
141.02
138.34
138.02
130.24
129.70
128.19
126.29
124.22
121.81
120.77
107.08
CHLOROFORM-d
77.26
77.00
76.74
38.31
32.95
25.23
21.33
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

8,8-dimethyl-2,4-di-*m*-tolyl-8,9-dihydrocycloocta[*b*]furan-6(*7H*)-one

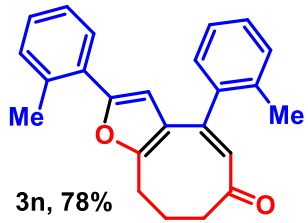




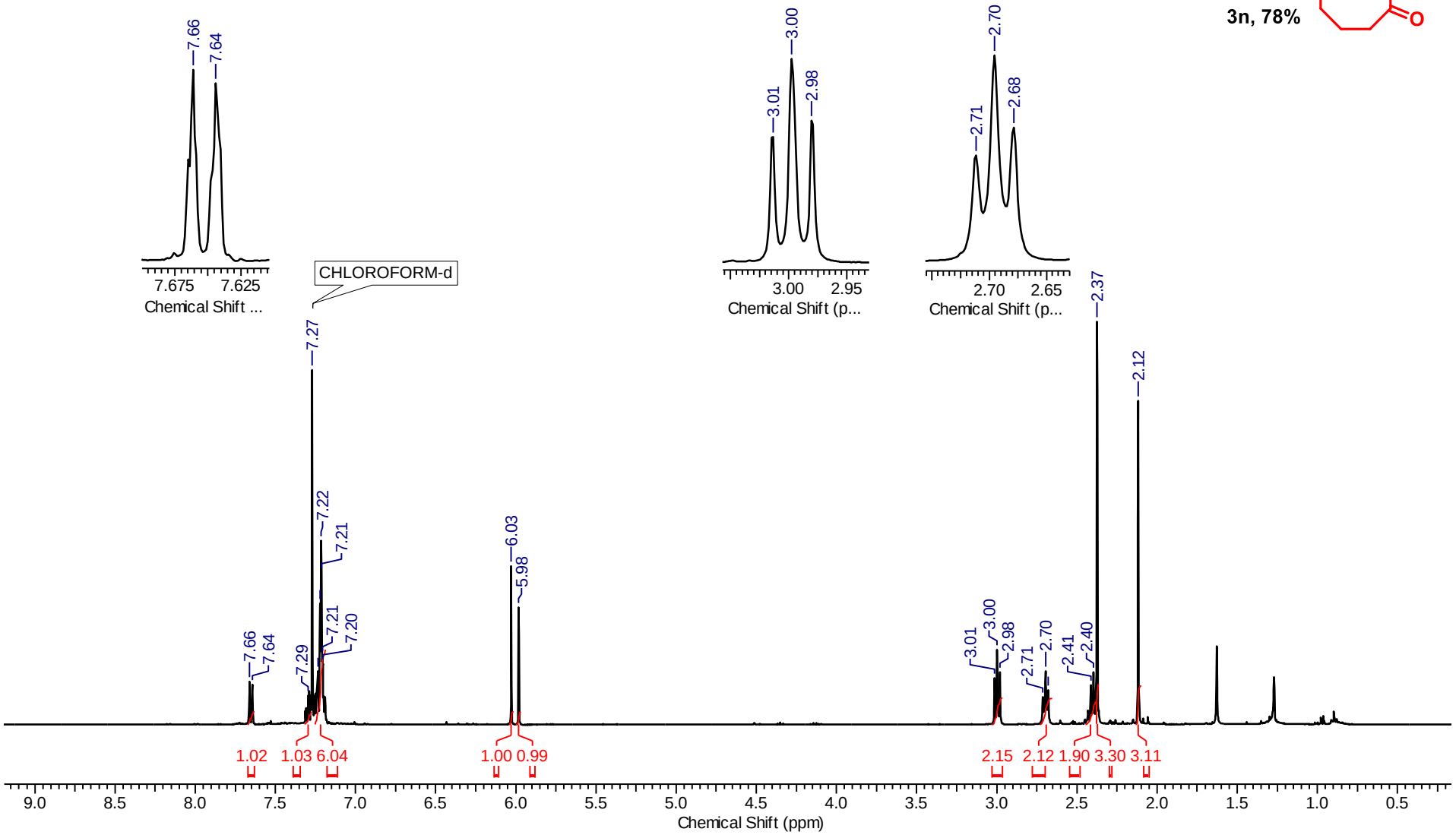


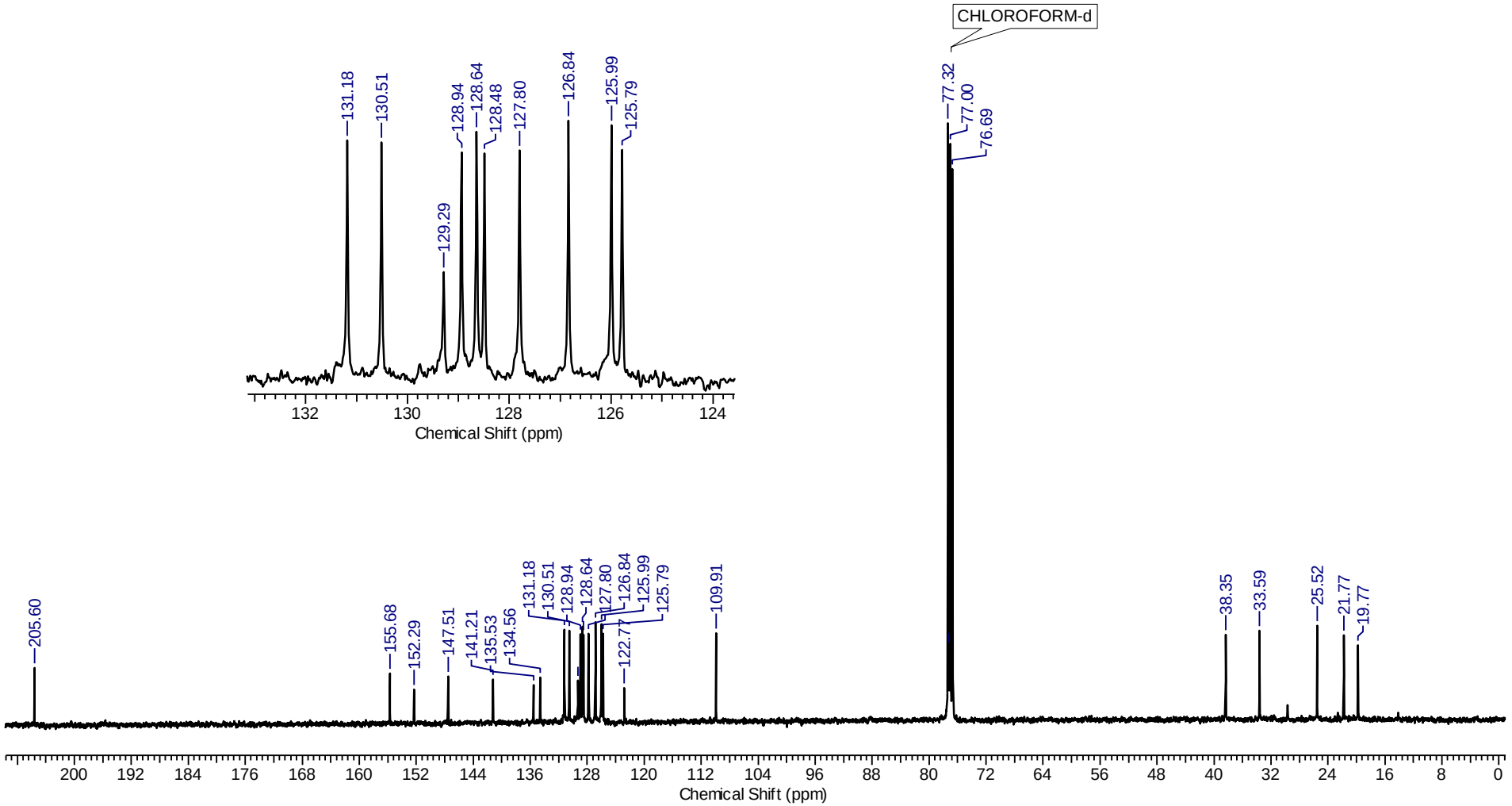

128.64
130.15
129.75
128.16
126.37
130.04
128.46
131
130
129
128
127
126
Chemical Shift (ppm)
128.64
130.15
129.75
128.16
124.27
120.84
77.32
77.00
76.68
201.87
157.38
152.40
147.05
141.29
138.37
138.01
121.94
107.23
51.67
45.01
38.71
28.78
21.40
21.33
208
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

2,4-di-*o*-tolyl-8,9-dihydrocycloocta[*b*]furan-6(*7H*)-one

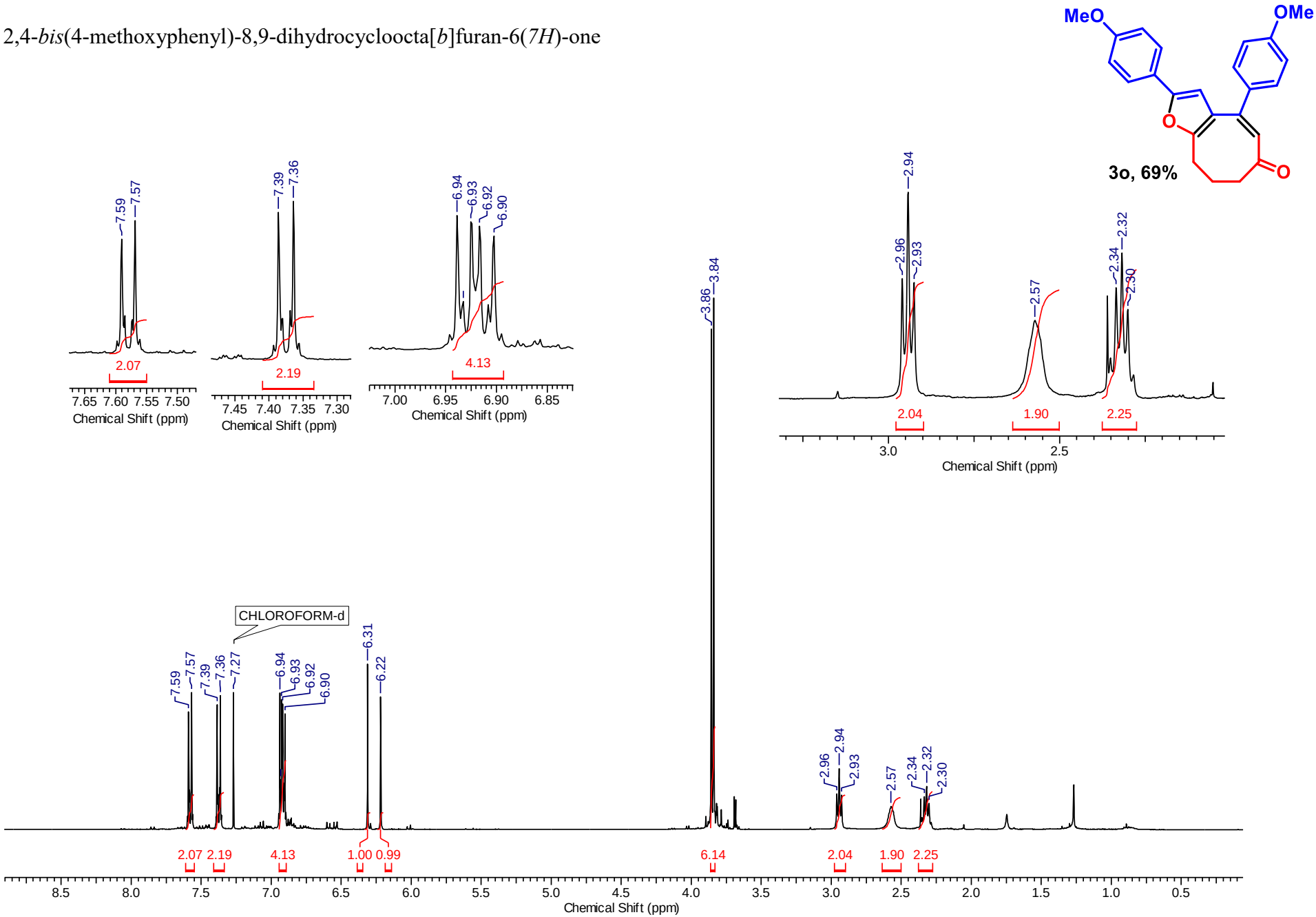


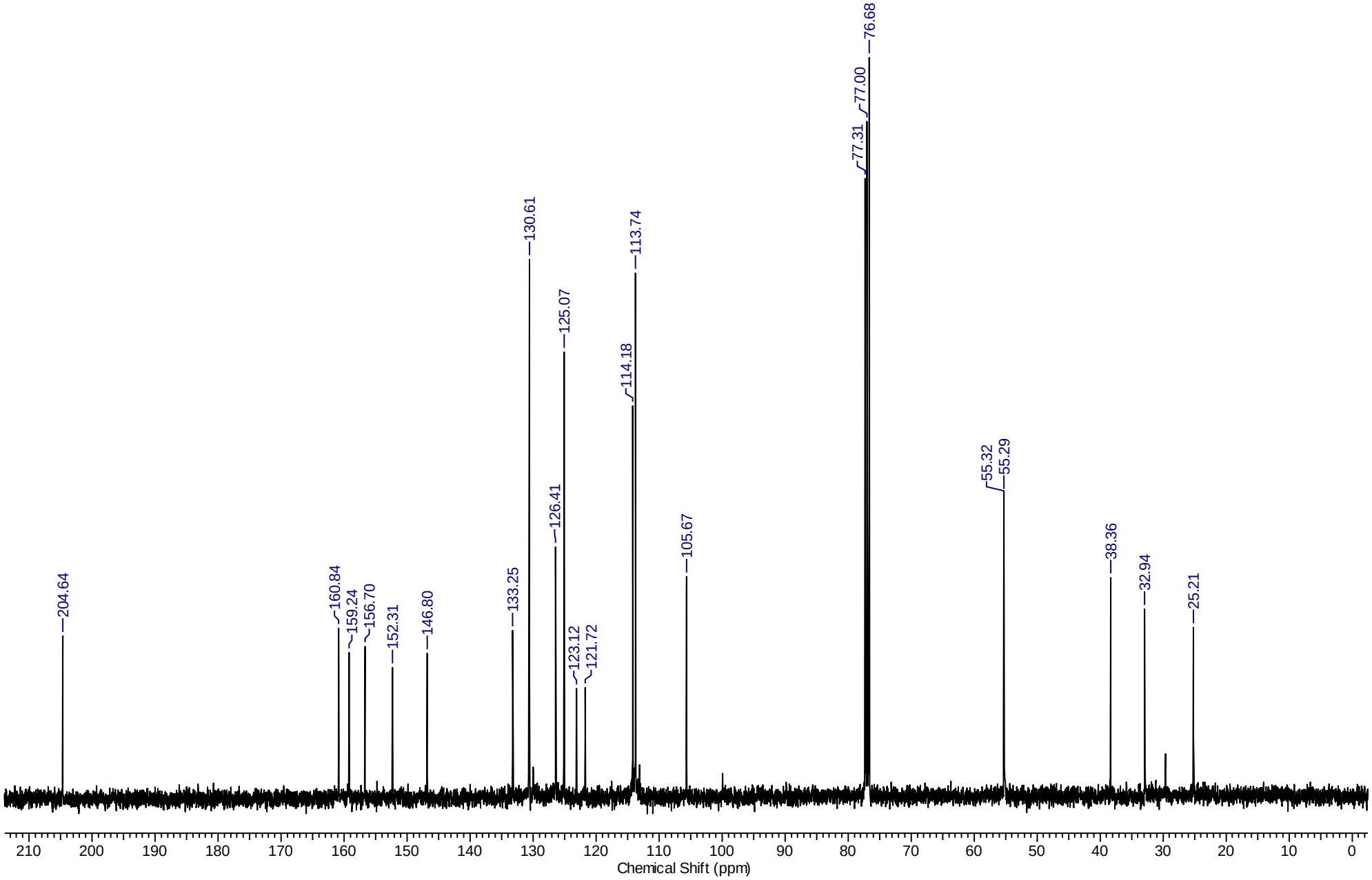
3n, 78%




CHLOROFORM-d
77.32
77.00
76.69
205.60
155.68
152.29
147.51
141.21
135.53
134.56
131.18
130.51
128.94
128.64
128.48
127.80
126.84
125.99
125.79
122.77
109.91
38.35
33.59
25.52
21.77
19.77
Chemical Shift (ppm)
131.18
130.51
128.94
128.64
128.48
127.80
126.84
125.99
125.79
129.29
Chemical Shift (ppm)

2,4-*bis*(4-methoxyphenyl)-8,9-dihydrocycloocta[*b*]furan-6(*7H*)-one




204.64
160.84
159.24
156.70
152.31
146.80
133.25
130.61
126.41
125.07
123.12
121.72
114.18
113.74
105.67
77.31
77.00
76.68
55.32
55.29
38.36
32.94
25.21
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)