Syntheses, Characterizations and Reactions of Acene-2,3-Dicarbaldehydes

Supporting Information

Qian Liu and Glen P. Miller*

Department of Chemistry, University of New Hampshire, 23 Academic Way, Durham, New Hampshire 03864-3598 USA

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1. Materials and Methods

Commercial reagents and solvents were purchased from Sigma Aldrich, Alfa Aesar, TCI America or Thermo Fisher Scientific, and used as received. Dry solvents were obtained using a solvent purification system (Innovative Technologies, Inc.) and handled under a nitrogen atmosphere, unless otherwise noted. Flash chromatography was performed using SiliaFlash® F60 40-63 μm (230-400 mesh) 60 Å silica from Silicycle Inc. and RediSep® Rf Silica Flash Columns (12 g, 24 g or 40 g) on a CombiFlash® Rf 200 instrument (Teledyne Isco, Inc.). Evaporation of solvents was accomplished using an IKA® RV 10 digital rotary evaporator. Baker-flex® silica gel IB2-F thin layer chromatography (TLC) plates were purchased from J.T. Baker. A 4-watt 254 nm lamp (Analytik Jena Co.) and a modified cardboard box were utilized for detection of TLC spots. Melting points were determined in open capillary tubes using a Mel-Temp apparatus, and are uncorrected. Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear

magnetic resonance (^{13}C NMR) spectra were recorded on either a Bruker 500 MHz or Bruker 700 MHz Nuclear Magnetic Resonance Spectrometer using 5 mm NMR tubes with plastic caps. High-resolution mass spectra (HRMS) were obtained on a Thermo Scientific Vanquish UHPLC and Exploris 120 Mass Spectrometer at the University of New Hampshire's University Instrumentation Center using a peak-matching protocol to determine the mass and error range of the molecular ion, and employing electrospray as the ionization technique. UV-vis absorption spectra were measured with a Varian Cary 50 Scan UV-Visible Spectrophotometer or SHIMADZU UV-2450 UV-Visible Spectrophotometer and corrected for background signal with a solvent-filled cuvette. Fluorescence spectra were measured on an FS5 Spectrofluorometer (150 W CW Ozone-free xenon arc lamp) from Edinburgh Instruments.

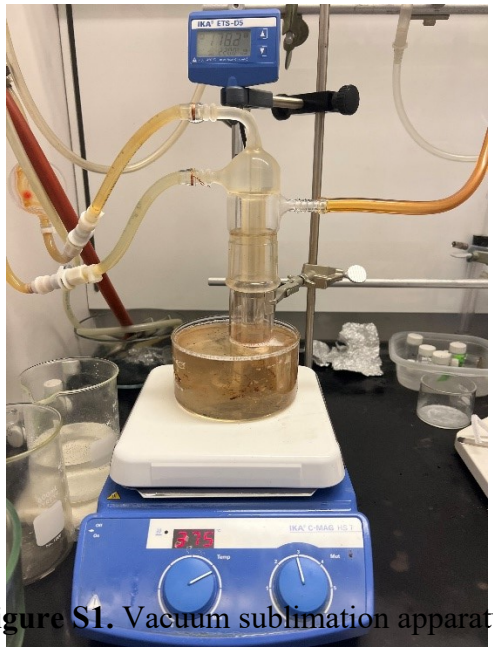
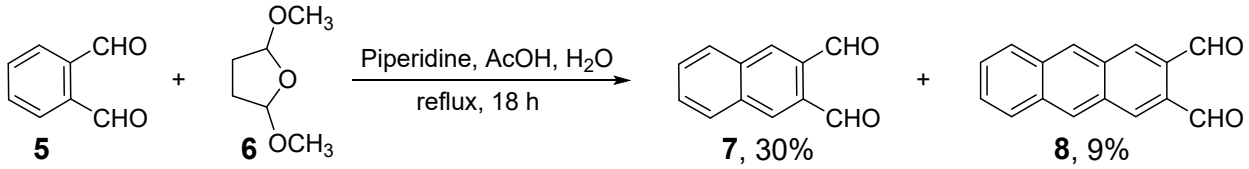


Figure S1. Vacuum sublimation apparatus

2. Syntheses of acene-2,3-dicarbaldehydes

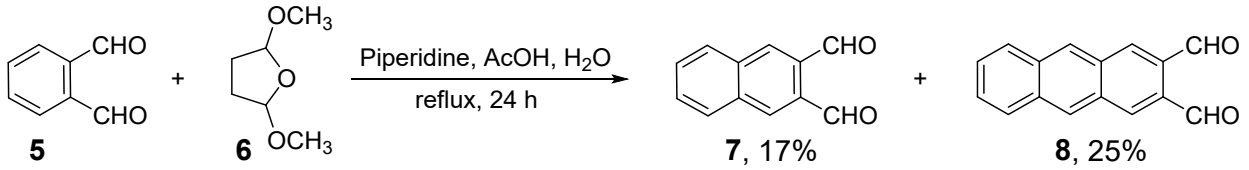
Exp. 1: naphthalene-2,3-dicarbaldehyde (7) and anthracene-2,3-dicarbaldehyde (8):



A modified literature procedure[1] was utilized. To a mixture of phthalaldehyde (2.0 g, 15 mmol) and 2,5-dimethoxytetrahydrofuran (2.0 g, 15 mmol) was added glacial acetic acid (AcOH) (1.0

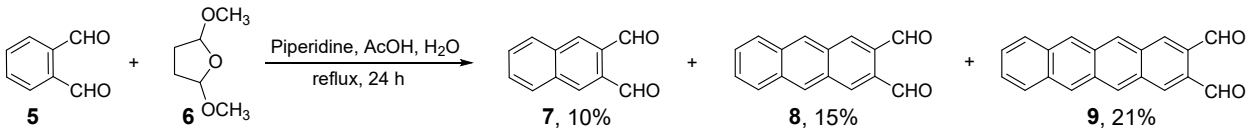
mL), H_2O (1.5 mL) and piperidine (2 drops). The resulting mixture was boiled for 18 h during which time the yellow solution turned brown and eventually dark-red. The reaction mixture was allowed to cool to rt and the dark-red precipitate was vacuum filtered. The filtrate suspension was set saved while the filtered solids were washed successively with 3 M HCl, water, methanol and diethyl ether (~10 mL each). The residue was air dried to give a red solid. A ^{1}H NMR spectrum showed that the red solid was a mixture of naphthalene-2,3-dicarbaldehyde, **7**, and anthracene-2,3-dicarbaldehyde, **8** (**7**:**8** = 1.65:1). A vacuum sublimation (132 ℃/0.1 Torr/4 hours) was performed to give **7** (0.48 g) as a bright yellow solid. The remaining, red residue was determined to be **8** (0.25 g). The filtrate suspension from above was then vacuum filtered a second time to obtain a dark brown, sticky solid. A ^{1}H NMR spectrum revealed a mixture of **7** and **8**. Vacuum sublimation was performed (132 ℃/0.1 Torr/6 hours) again to afford additional **7** (0.34 g), then again at higher temperature (220 ℃/0.1 Torr/4 hours) to obtain pure **8** (0.07 g). The combined isolated yield of **7** as a bright yellow solid was 0.82 g (30%, m.p. 119-120 ℃, lit.[1] m.p. 132 ℃). ^{1}H NMR (700 MHz, $CDCl_3$) δ 10.65 (s, 2H), 8.47 (s, 2H), 8.07 (m, J = 3.3, 6.1 Hz, 2H), 7.75 (m, J = 3.2, 6.2 Hz, 2H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 192.5, 134.5, 134.4, 132.9, 130.0, 129.7. UV–vis λ_{max} (1×10^{-4} M in CH_2Cl_2): 340 nm. HRMS (ESI): 185.0593 [calc'd for M+H$^+$: 185.0603]. The combined isolated yield of **8** was 0.32 g (9%, m.p. 214-216 ℃, lit.[1] m.p. 217 ℃) as an orange-red solid. ^{1}H NMR (700 MHz, $CDCl_3$) δ 10.66 (s, 2H), 8.65 (s, 2H), 8.63 (s, 2H), 8.13 – 8.09 (m, 2H), 7.67 – 7.63 (m, 2H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 192.5, 136.5, 133.8, 132.1, 130.9, 129.6, 128.7, 127.8. UV–vis λ_{max} (1×10^{-4} M in CH_2Cl_2): 410 nm. HRMS (ESI): 235.0751 [calc'd for M+H$^+$: 235.0759].

Exp. 2: naphthalene-2,3-dicarbaldehyde (7) and anthracene-2,3-dicarbaldehyde (8):



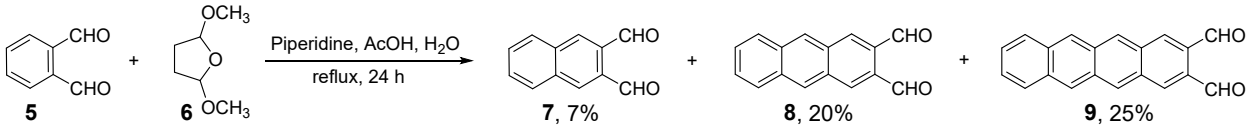
A modified literature procedure[1] was utilized. To a mixture of phthalaldehyde (2.0 g, 15 mmol) and 2,5-dimethoxytetrahydrofuran (4.0 g, 30 mmol) was added glacial acetic acid (AcOH) (1.5 mL), H_2O (1.5 mL) and piperidine (3 drops). The resulting mixture was boiled for ~24 h during which time the yellow solution turned brown and eventually dark-red. Following the same work-up described in Exp. 1 above, the solids collected from the first vacuum filtration were identified by ^{1}H NMR spectroscopy as mixture of naphthalene-2,3-dicarbaldehyde, **7**, and anthracene-2,3-dicarbaldehyde, **8** (**7**:**8** = 1:6.5). As in Exp. 1, the filtrate from the vacuum filtration was vacuum filtered a second time and a ^{1}H NMR spectrum revealed the collected solids to be a mixture of **7** and **8**. Vacuum sublimations were performed as described in Exp. 1. The combined yield of naphthalene-2,3-dicarbaldehyde, **7**, as a bright yellow solid was 0.47 g (17%) and of anthracene-2,3-dicarbaldehyde, **8**, as an orange-red solid was 0.88 g (25%).

Exp. 3: naphthalene-2,3-dicarbaldehyde (7), anthracene-2,3-dicarbaldehyde (8) and tetracene-2,3-dicarbaldehyde (9):



A modified literature procedure[1] was utilized. To a mixture of phthalaldehyde (2.0 g, 15 mmol) and 2,5-dimethoxytetrahydrofuran (7.9 g, 60 mmol) was added glacial acetic acid (AcOH) (3 mL), H_2O (1 mL) and piperidine (4 drops). The resulting mixture was boiled for ~24 h during which time the yellow solution turned brown and eventually dark-red. Following the same work-up described in Exp. 1 above, the solids collected from the first vacuum filtration were identified by ^{1}H NMR spectroscopy to be a mixture of naphthalene-2,3-dicarbaldehyde, **7**, anthracene-2,3-dicarbaldehyde, **8** and tetracene-2,3-dicarbaldehyde, **9** (**7**:**8**:**9** = 0.26:1:0.3). As before, the filtrate suspension was vacuum filtered a second time and identified as a mixture of **7**, **8** and **9**. Successive vacuum sublimations were performed for both the first and second batches of collected solids. At 132 °C/0.1 Torr, pure **7** was collected (0.27 g, 10%) as a bright yellow solid over 6 hours. At 180 °C and 0.1 Torr, pure **8** was collected over 4 hours (0.51 g, 15%) as an orange-red solid. At 220 °C and 0.1 Torr, a mixture of **8** and **9** was collected. Subsequently, this mixture was vacuum sublimed again at 180 °C and 0.1 Torr for an additional 4 hours to deplete the mixture of residual **8**. A final vacuum sublimation (220 °C/0.1 Torr/6 hours) afforded tetracene-2,3-dicarbaldehyde, **9** (0.89 g, 21%, m.p. 286 °C (subl.), lit.[1] m.p. 342 °C (subl.)) as a red solid. **9**: ^{1}H NMR (700 MHz, $CDCl_3$) δ 10.7 (s, 2H), 8.9 (s, 2H), 8.8 (s, 2H), 8.6 (s, 2H), 8.1 (m, J = 3.3, 6.5 Hz, 2H), 7.5 (m, J = 3.3, 6.7 Hz, 2H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 192.4, 137.5, 132.8, 131.8, 131.4, 130.6, 130.1, 128.5, 127.6, 126.7. UV-Vis λ_{max} (1×10^{-4} M in CH_2Cl_2): 503 nm. HRMS (ESI): 285.0905; 307.0725 [calc'd for M+H$^+$: 285.0916; M+Na$^+$: 307.0735].

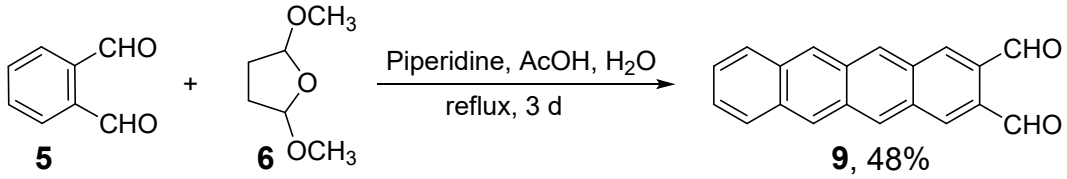
Exp. 4: naphthalene-2,3-dicarbaldehyde (7), anthracene-2,3-dicarbaldehyde (8) and tetracene-2,3-dicarbaldehyde (9):



A modified literature procedure[1] was utilized. To a mixture of phthalaldehyde (2.0 g, 15 mmol) and 2,5-dimethoxytetrahydrofuran (11.9 g, 90 mmol) was added glacial acetic acid (AcOH) (4 mL), H_2O (1 mL) and piperidine (5 drops). The resulting mixture was boiled for ~24 h during which time the yellow solution turned brown and eventually dark-red. After work-up as described in Exp. 1 above, a ^{1}H NMR spectrum of the solids collected from the first vacuum filtration were shown to be a mixture of **7**, **8** and **9** (**7**:**8**:**9** = 0.2:1:1.2). Successive vacuum sublimations were performed on both the first and second batches of solids collected from successive vacuum

filtrations, as before in Exps. 1, 2 and 3. At 132 ℃ and 0.1 Torr, pure **7** was collected over 6 hours (0.20 g, 7%) as a bright yellow solid. At 180 ℃ and 0.1 Torr, pure **8** was collected over 4 hours (0.71 g, 20%) as an orange-red solid. Lastly, at 220 ℃ and 0.1 Torr, pure **9** was collected over 6 hours (1.06 g, 25%) as a red solid.

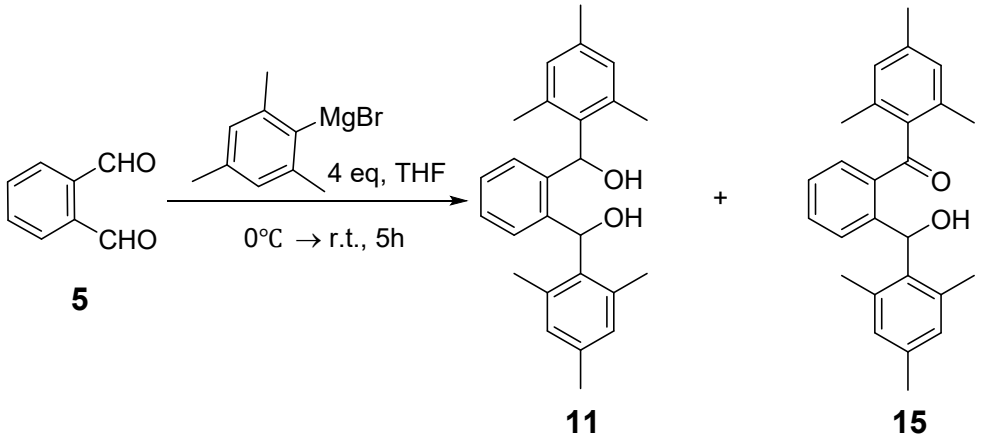
Exp. 5: tetracene-2,3-dicarbaldehyde (9):



A modified literature procedure[1] was utilized. To a mixture of phthalaldehyde (2.0 g, 15 mmol) and 2,5-dimethoxytetrahydrofuran (15.9 g, 120 mmol) was added glacial acetic acid (AcOH) (4 mL), H_2O (1 mL) and piperidine (5 drops). The resulting mixture was boiled for 72 hours during which time the yellow solution turned brown and eventually dark red. After work-up as described above, the first and second batches of solids collected by vacuum filtration were vacuum sublimed at 220 ℃ and 0.1 Torr for 12 hours to afford **9** (2.03 g, 48%) as a red solid.

3. Grignard reactions for the syntheses of diaryl diols

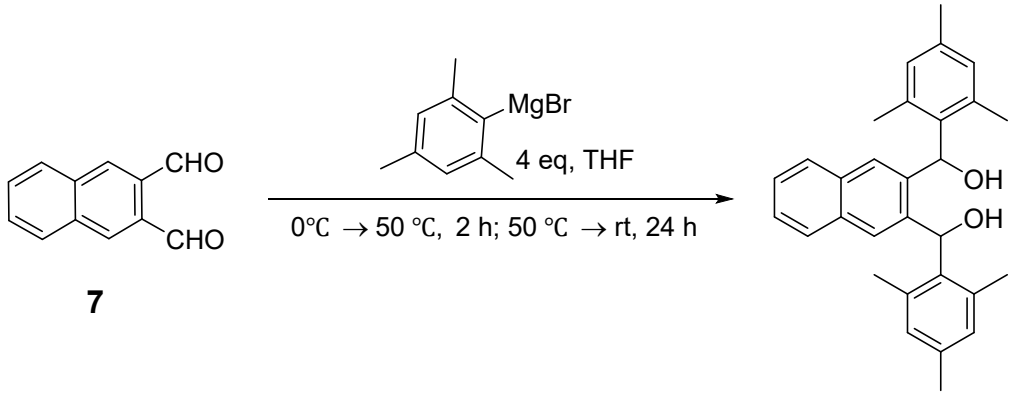
1,2-phenylenebis(mesitylmethanol) (11) and
(2-(hydroxy(mesityl)methyl)phenyl)(mesityl)methanone (15):



To a solution of *o*-phthalaldehyde, **5** (0.5 g, 5 mmol) in THF (5 mL) was added mesityl magnesium bromide (prepared from 2-bromomesitylene (2.3 mL, 14.91 mmol) and magnesium turnings (0.36

g, 14.91 mmol) in 10 mL THF as a brown, yellow solution) in an ice-bath (0 ℃). The reaction mixture was stirred for 5 h at room temperature. Then the reaction was quenched with 10 mL of a saturated aqueous solution of NH_4Cl and then extracted with 2×20 mL ethyl acetate. The extract was washed with 20 mL of brine solution and then dried over anhydrous Na_2SO_4. The solvent was rotary evaporated at reduced pressure to give an off-white crude product. The crude product was purified by silica gel CombiFlash chromatography (hexane/ethyl acetate = 85/15) to obtain two white solids: **11** (0.75 g, 54%). M.p. 180-181 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (m, 2H), 7.01 (m, 2H), 6.88 (s, 4H), 6.55 (s, 2H), 3.65 (s, 2H), 2.28 (s, 6H), 2.25 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.1, 137.0, 136.9, 134.6, 130.2, 128.3, 127.9, 71.1, 21.2, 20.8. HRMS (ESI): 237.1271; 357.2208 [calc'd for M+H$^+$-Mes-H_2O: 237.1279; M+H$^+$-H_2O: 357.2218]. **15** (0.11 g, 8%). M.p. 208-209 ℃, lit.[2] m.p. 220-221 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (m, 1H), 7.38 (m, 1H), 7.26 – 7.20 (m, 1H), 7.10 (m, 1H), 6.90 (s, 4H), 6.61 (d, 1H), 5.16 (d, 1H), 2.34 (s, 3H), 2.31 (s, 3H), 2.29 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 205.2, 144.3, 139.1, 137.8, 137.2, 137.2, 136.7, 134.2, 133.6, 133.3, 130.0, 129.0, 129.0, 128.7, 127.7, 70.5, 21.5, 21.2, 20.9, 19.6. HRMS (ESI): 355.2049 [calc'd for M+H$^+$-H_2O: 355.2062].

naphthalene-2,3-diylbis(mesitylmethanol) (12):

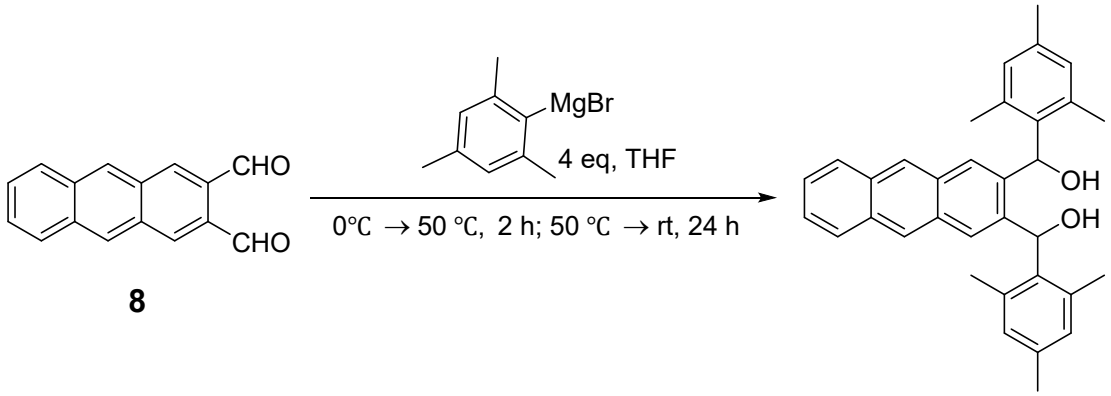


7 **12**

To a solution of naphthalene-2,3-dicarbaldehyde, **7** (0.10 g, 0.54 mmol), in THF (5 mL) was added mesityl magnesium bromide (2.2 mL, 1 M in THF) [prepared from 2-bromomesitylene (3.1 mL, 20 mmol) and magnesium turnings (0.49 g, 20 mmol) in 17 mL THF as a yellowish-brown solution] in an ice-bath (0 ℃). The reaction mixture was stirred for 2 h at 50 ℃, then cooled to rt and continued to stir for ~24 h. The reaction was quenched with 10 mL of a saturated aqueous solution of NH_4Cl and then extracted with 2×20 mL ethyl acetate. The extract was washed with 20 mL of brine solution and then dried over anhydrous Na_2SO_4. The solvent was rotary evaporated at reduced pressure to give a light-yellow oil. The oil was placed under vacuum for 12 h during

which time it solidified. The solid was recrystallized from hexane (5 mL), vacuum filtered and then washed with 2 mL cold hexane to give **12** as an off-white solid (0.17 g, 74%). M.p. 196-198 °C. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.64 (m, 2H), 7.50 (s, 2H), 7.37 (m, 2H), 6.92 (s, 4H), 6.67 (s, 2H), 3.62 (s, 2H), 2.32 (s, 6H), 2.27 (s, 12H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 137.8, 137.1, 137.0, 134.7, 132.6, 130.3, 127.9, 126.1, 71.3, 21.2, 20.9. HRMS (ESI): 287.1428; 407.2366 [calc'd for $M+H^+$-Mes-H_2O: 287.1436; $M+H^+$-H_2O: 407.2375].

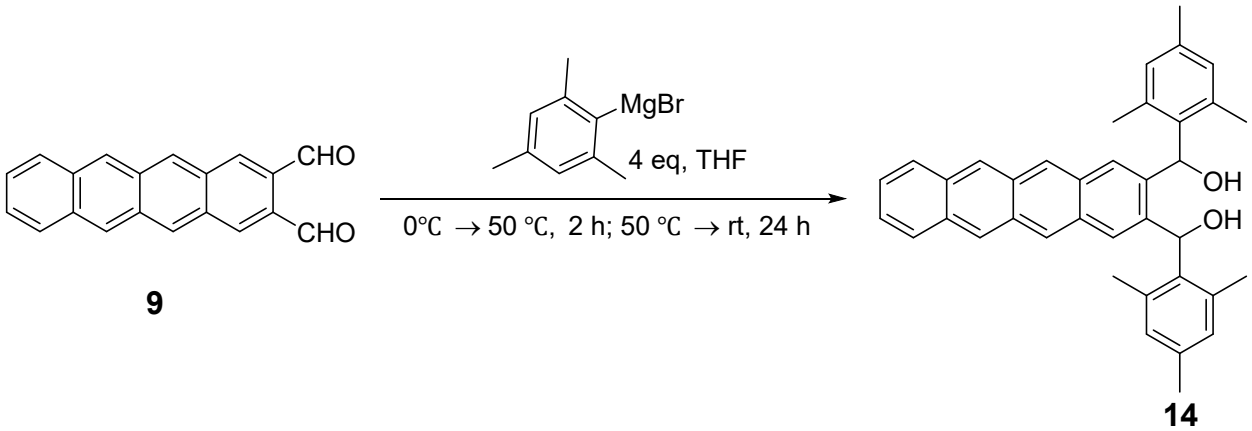
anthracene-2,3-diylbis(mesitylmethanol) (13):



8 **13**

To a solution of anthracene-2,3-dicarbaldehyde, **8** (0.10 g, 0.43 mmol), in THF (5 mL) was added mesityl magnesium bromide (1.7 mL, 1 M in THF) [prepared from 2-bromomesitylene (3.1 mL, 20 mmol) and magnesium turnings (0.49 g, 20 mmol) in 17 mL THF as a yellowish-brown solution] in an ice-bath (0 ℃). The reaction mixture was stirred for 2 h at 50 ℃, then cooled to rt and stir for ~24 h. The reaction was quenched with 10 mL of a saturated aqueous solution of NH_4Cl and then extracted with 2×20 mL ethyl acetate. The extract was washed with 20 mL of brine solution and then dried over anhydrous Na_2SO_4. The solvent was rotary evaporated at reduced pressure to give a yellow oil. The oil was placed under vacuum for ~12h during which time it solidified. The solid was recrystallized from hexane (10 mL), vacuum filtered and washed with 5 mL cold hexane to give **13** as a yellow solid (0.15 g, 73%). M.p. 180-182 ℃. ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.23 (s, 2H), 7.88 (m, 2H), 7.66 (s, 2H), 7.39 (m, 2H), 6.93 (s, 4H), 6.68 (s, 2H), 3.72 (s, 2H), 2.33 (s, 6H), 2.29 (s, 12H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 137.4, 137.1, 137.0, 134.7, 131.9, 130.8, 130.3, 128.1, 128.0, 126.3, 125.4, 71.3, 21.2, 20.9. HRMS (ESI): 337.1583; 457.2521 [calc'd for $M+H^+$-Mes-H_2O: 337.1592; $M+H^+$-H_2O: 457.2531].

tetracene-2,3-diylbis(mesitylmethanol) (14):

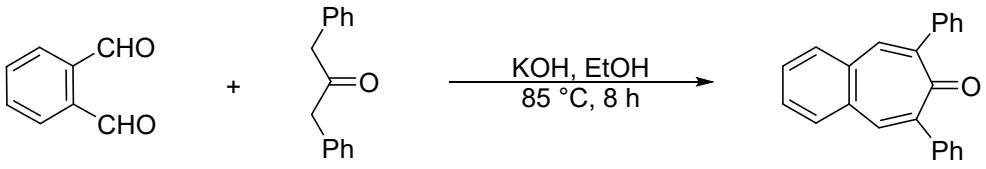


9 **14**

To a solution of tetracene-2,3-dicarbaldehyde, **9** (0.10 g, 0.35 mmol), in THF (5 mL) was added mesityl magnesium bromide (1.4 mL, 1 M in THF) [prepared from 2-bromomesitylene (3.1 mL, 20 mmol) and magnesium turnings (0.49 g, 20 mmol) in 17 mL THF as a yellowish-brown solution] in an ice-bath (0 ℃). The reaction mixture was stirred for 2 h at 50 ℃, then cooled to rt and continued to stir for ~24 h. The reaction was quenched with 10 mL of a saturated aqueous solution of NH_4Cl and then extracted with 2×20 mL ethyl acetate. The extract was washed with 20 mL of brine solution and then dried over anhydrous Na_2SO_4. The solvent was rotary evaporated at reduced pressure to give a brown solid. The solid was recrystallized from hexane (10 mL), vacuum filtered and washed with 5 mL of cold hexane to give a tan solid (0.13 g, 71%). M.p. 220-222 ℃. ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.53 (s, 2H), 8.46 (s, 2H), 7.94 (m, 2H), 7.67 (s, 2H), 7.36 (m, 2H), 6.95 (s, 4H), 6.70 (s, 2H), 3.62 (s, 2H), 2.35 (s, 6H), 2.33 (s, 12H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 137.2, 137.1, 137.1, 134.7, 131.5, 130.6, 130.44, 130.3, 128.3, 128.2, 126.5, 126.3, 125.2, 71.4, 21.3, 20.9. HRMS (ESI): 387.1740; 507.2677; 524.2706 [calc'd for $M+H^+$-Mes-H_2O: 387.1749; $M+H^+$-H_2O: 507.2688; M^+: 524.2715].

4. One-pot, double aldol condensations for the syntheses of acenotropones

6,8-diphenyl-7*H*-benzo[7]annulen-7-one (16):

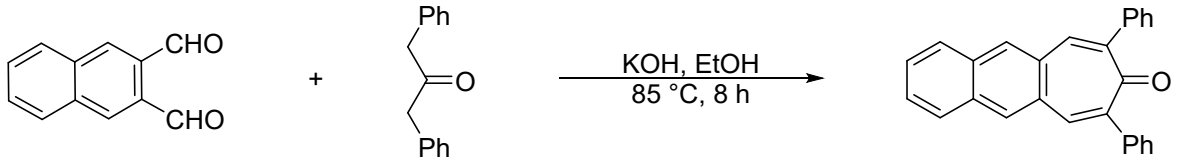


5 **16**

To a solution of *o*-phthalaldehyde, **5** (0.50 g, 3.72 mmol), and 1,3-diphenylacetone (0.78 g, 3.72 mmol) in ethanol (20 mL) was added powdery KOH (0.42 g, 7.46 mmol). With the addition of KOH, the reaction mixture color changed from light yellow to orange, and then to bright yellow. The reaction mixture was then heated to 85 °C for 8 h. The resulting light yellowish precipitate

was cooled in an ice bath, vacuum filtered, washed with cold ethanol and air dried to obtain a pale yellowish solid, **16** (0.92 g, 80%). M.p. 117-118 °C, lit.[3] m.p. 117-119 °C. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.75 – 7.70 (m, 4H), 7.60 – 7.54 (m, 6H), 7.44 – 7.35 (m, 6H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 187.3, 145.8, 140.8, 139.5, 134.7, 133.5, 129.7, 129.3, 128.1, 127.8. UV–vis λ_{max} (1×10^{-5} M in CH_2Cl_2): 284 nm.

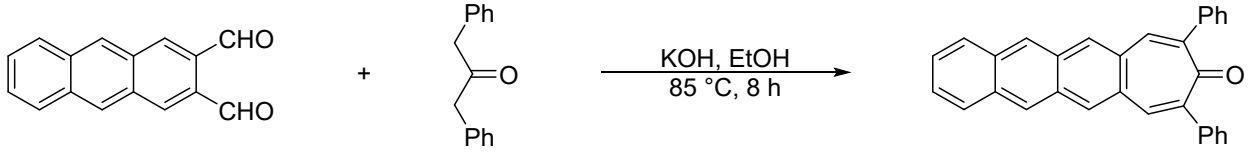
7,9-diphenyl-8*H*-cyclohepta[*b*]naphthalen-8-one (17):



7 **17**

To a solution of naphthalene-2,3-dicarbaldehyde, **7** (0.10 g, 0.54 mmol), and 1,3-diphenylacetone (0.11 g, 0.54 mmol) in ethanol (10 mL) was added powdery KOH (0.06 g, 1.08 mmol). With the addition of KOH, the reaction mixture color changed from yellow to brown, then to yellow. The reaction mixture was then heated to 85 °C for 8 h. The resulting yellow precipitate was cooled in an ice bath, vacuum filtered, washed with cold ethanol and air dried to obtain a yellow solid, **17** (0.15 g, 77%). M.p. 189-190 °C, lit.[4] m.p. 196-197 °C. ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.20 (s, 2H), 7.96 (m, 2H), 7.84 (s, 2H), 7.61 (m, 2H), 7.58 (d, 4H), 7.43 (t, 4H), 7.38 (t, 2H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 188.0, 144.2, 141.0, 140.0, 133.7, 133.2, 132.1, 129.3, 128.0, 128.0, 127.9, 127.7. UV–vis λ_{max} (1×10^{-5} M in CH_2Cl_2): 306 nm. HRMS (ESI): 359.1429 [calc'd for $M+H^+$: 359.1436].

8,10-diphenyl-9*H*-cyclohepta[*b*]anthracen-9-one (18):

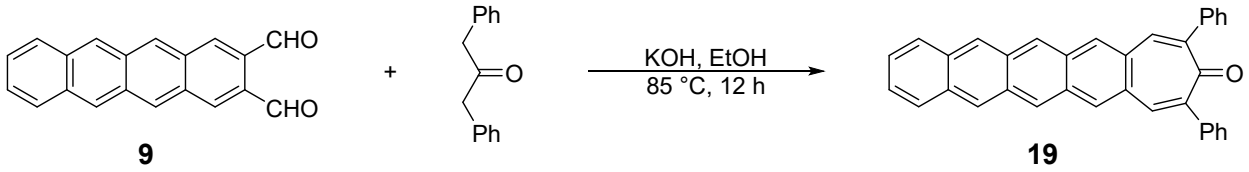


8 **18**

To a solution of anthracene-2,3-dicarbaldehyde, **8** (100 mg, 0.43 mmol), and 1,3-diphenylacetone (90 mg, 0.43 mmol) in ethanol (10 mL) was added powdery KOH (48 mg, 0.85 mmol). With the addition of KOH, the reaction mixture color changed from orange red to red. The reaction mixture was then heated to 85 °C for 8 h. The resulting dark red precipitate was cooled in an ice bath, vacuum filtered, washed with cold ethanol and air dried to obtain an orange solid, **18** (110 mg, 63%). m.p. 196 °C (subl.). ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.54 (s, 2H), 8.36 (s, 2H), 8.05 (m, 2H), 7.83 (s, 2H), 7.57 (m, 4H), 7.54 (m, 2H), 7.43 (t, 4H), 7.39 – 7.35 (m, 2H). ^{13}C NMR (176 MHz, CDCl3) δ 188.4, 143.4, 141.1, 140.1, 134.4, 132.8, 131.5, 130.7, 129.3, 128.3, 128.0, 127.6, 126.9,

126.5. UV–vis λ_{max} (1×10^{-5} M in CH_2Cl_2): 332 nm. HRMS (ESI): 409.1583 [calc'd for $M+H^+$: 409.1592].

9,11-diphenyl-10*H*-cyclohepta[*b*]tetracen-10-one (19):

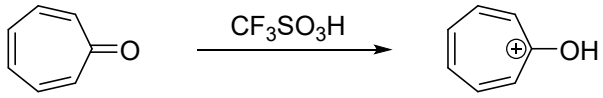


9 **19**

To a solution of tetracene-2,3-dicarbaldehyde, **9** (50 mg, 0.18 mmol), and 1,3-diphenylacetone (37 mg, 0.18 mmol) in ethanol (10 mL) was added powdery KOH (20 mg, 0.35 mmol). The reaction mixture was then heated to 85 °C for 12 h during which time the reaction mixture color changed from red to dark-red. The resulting dark-red precipitate was cooled in an ice bath, vacuum filtered, washed with cold ethanol and air dried to obtain a red solid, **19** (44 mg, 53%). Due to the instability of **19** in solution phase, we did not obtain a ^{13}C NMR spectrum. ^1H NMR (700 MHz, $CDCl_3$) δ 8.78 (s, 2H), 8.71 (s, 2H), 8.34 (s, 2H), 8.03 – 7.99 (m, 2H), 7.79 (s, 2H), 7.58 – 7.54 (m, 4H), 7.47 – 7.41 (m, 6H), 7.40 – 7.35 (m, 2H). HRMS (ESI): 459.1740 [calc'd for $M+H^+$: 459.1749].

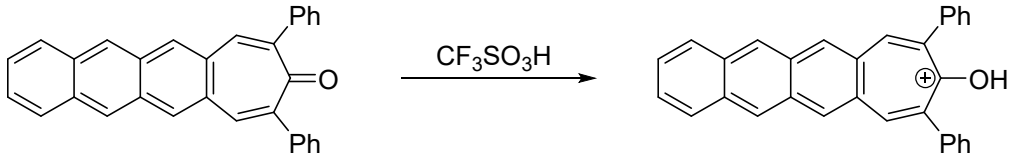
5. Hydroxytropylium ions formation for NMR characterization

tropone to hydroxytropylium ion:



To a solution of commercially available tropone (13 mg, 0.12 mmol) in $CDCl_3$ (2 mL) was added 10 drops of triflic acid (CF_3SO_3H) with shaking to form the hydroxytropylium ion as a yellow solution. **Tropone** NMR: ^1H NMR (700 MHz, $CDCl_3$) δ 7.09 (m, 2H), 7.03 – 6.99 (m, 2H), 6.97 – 6.93 (m, 2H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 188.2, 142.2, 136.1, 134.7. **Hydroxytropylium ion** NMR: ^1H NMR (700 MHz, $CDCl_3$) δ 8.19 – 8.13 (m, 2H), 8.01 (m, 2H), 7.78 (d, 2H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 181.0, 151.9, 147.8, 140.0.

anthracenotropone (18) to hydroxyanthracenotropylium ion (22):

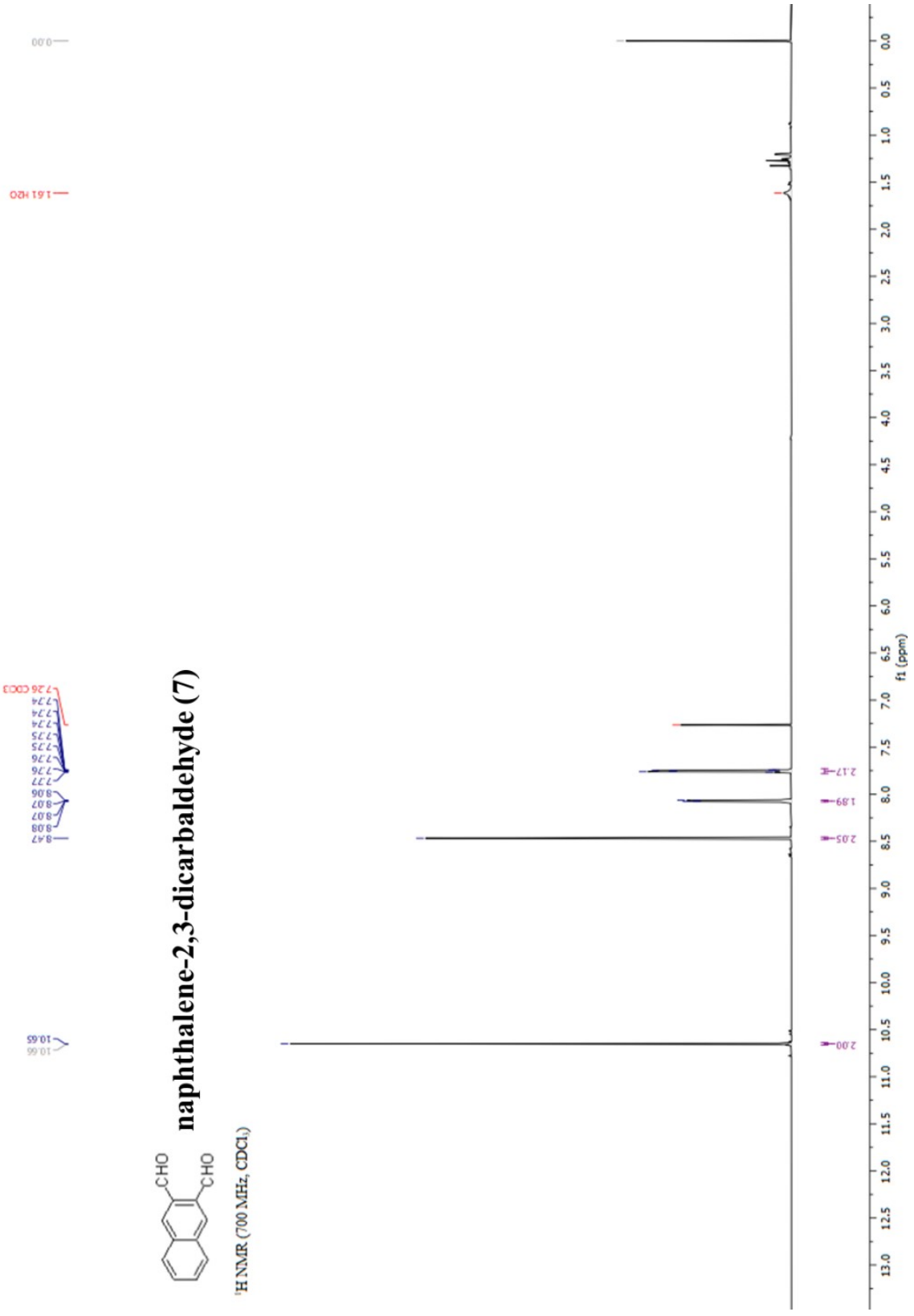


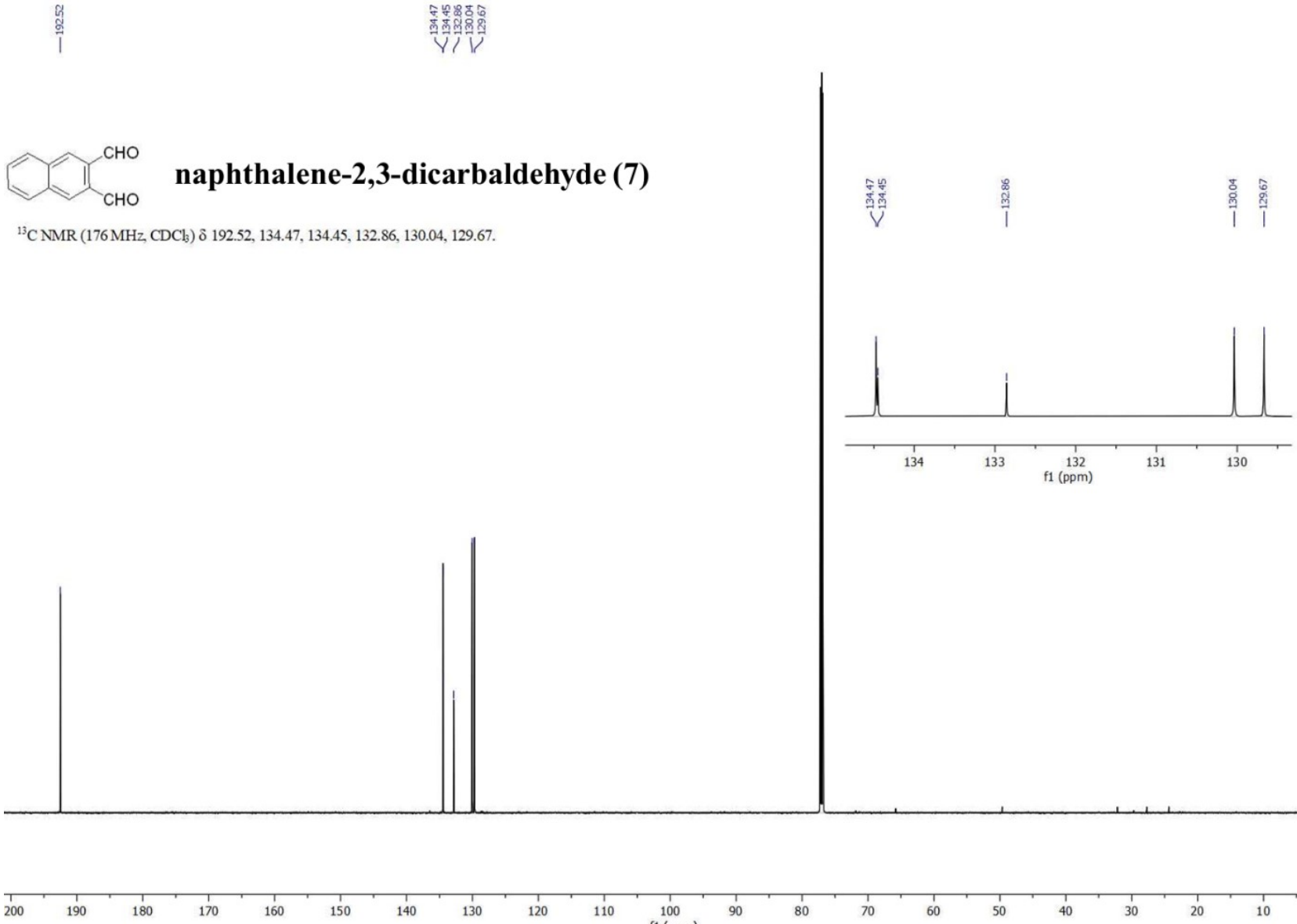
18 **22**

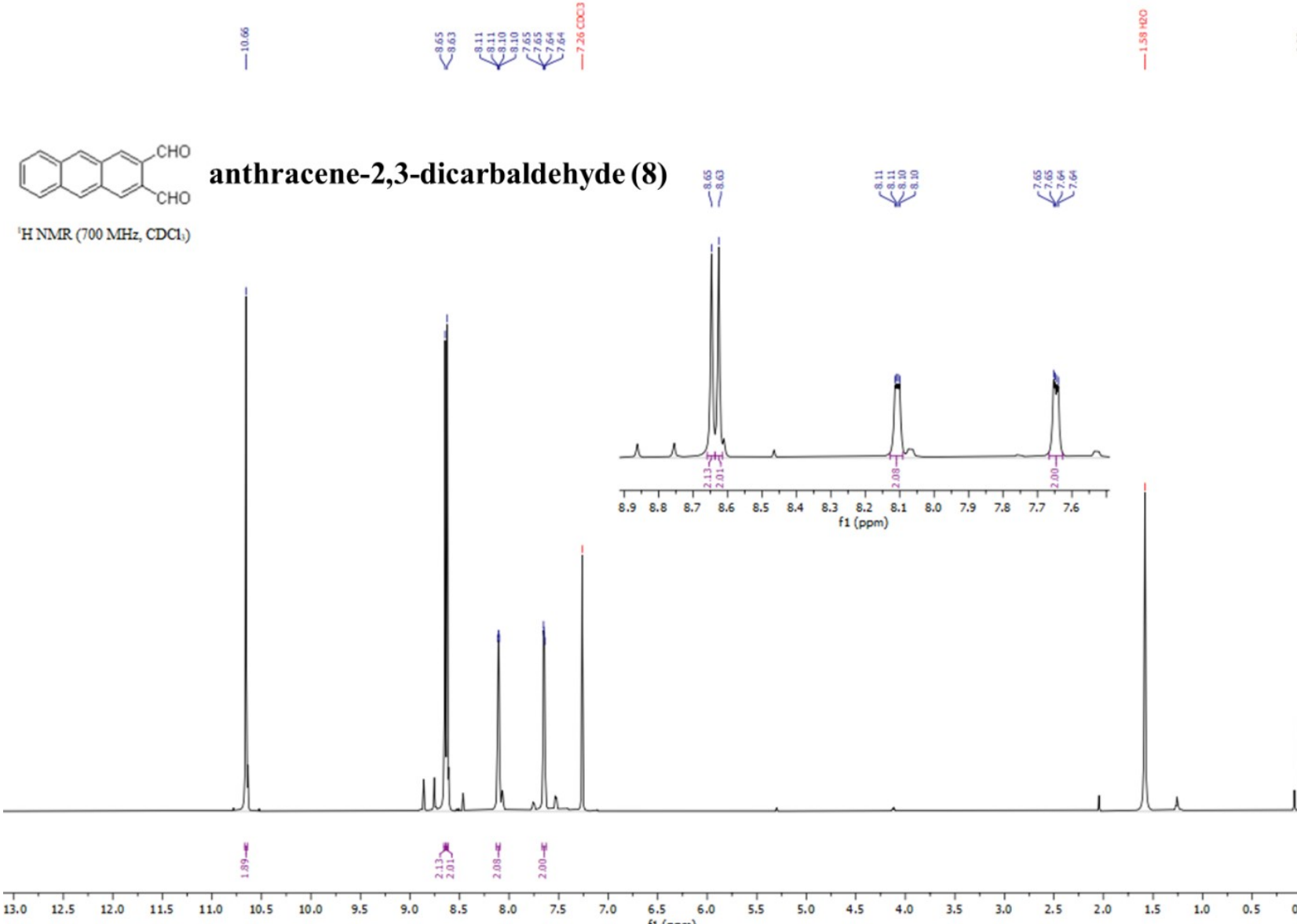
To a solution of anthracenotropone (7 mg, 0.017 mmol) in $CDCl_3$ (2 mL) was added 5 drops of triflic acid (CF_3SO_3H) with shaking to form the hydroxyanthracenotropylium ion, **22**, as a green solution. ^1H NMR (700 MHz, $CDCl_3$) δ 9.33 (s, 2H), 9.26 (s, 2H), 9.11 (s, 2H), 8.32 (s, 2H), 7.84

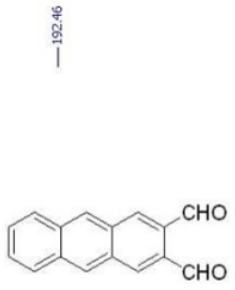
(s, 2H), 7.73 – 7.65
141.9, 136.0, 135.4

6. ^{1}H and ^{13}C N



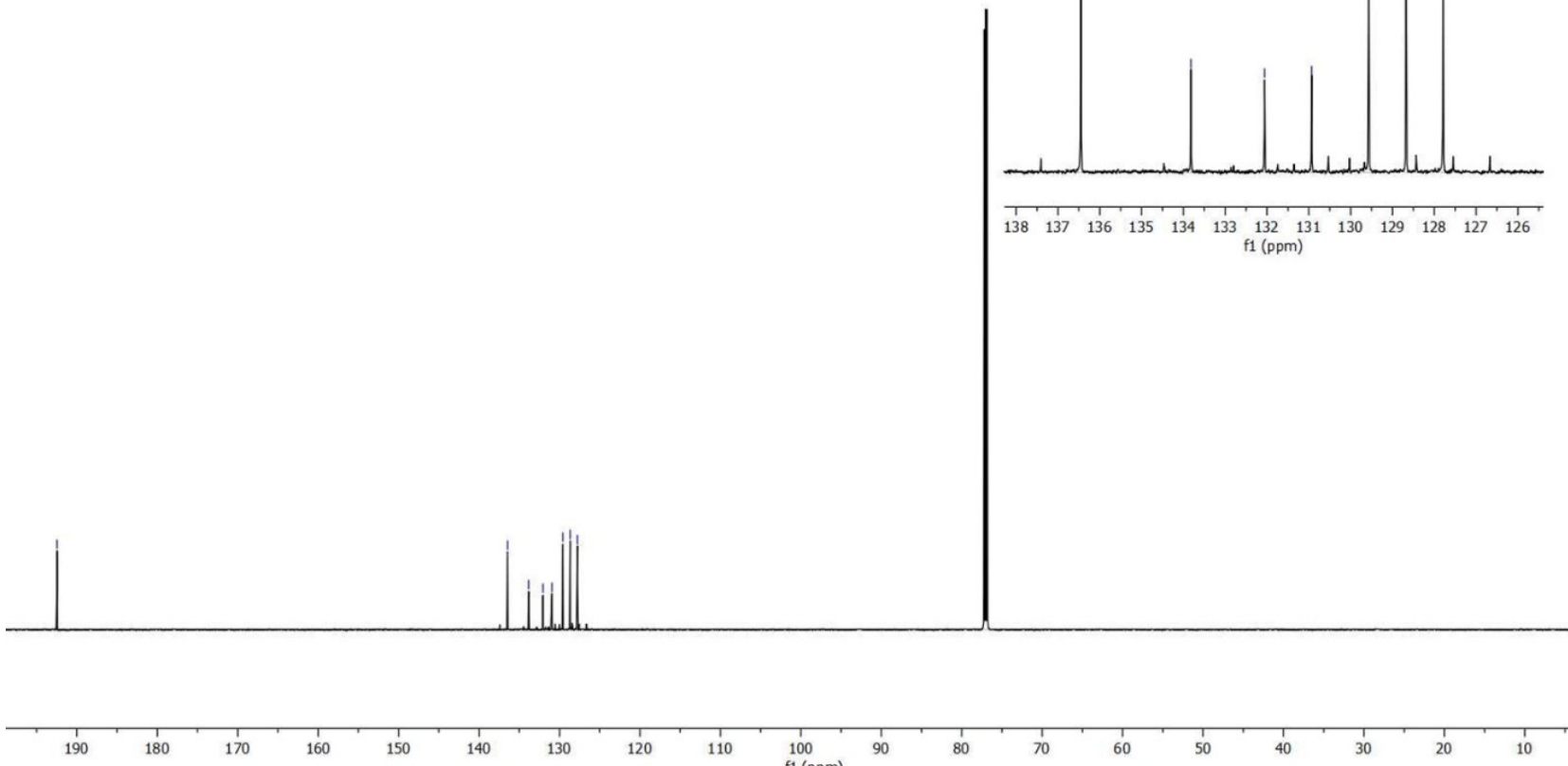

192.52
134.47
134.45
132.86
130.04
129.67
CHO
CHO
naphthalene-2,3-dicarbaldehyde (7)
^{13}C NMR (176 MHz, CDCl$_3$) δ 192.52, 134.47, 134.45, 132.86, 130.04, 129.67.
f1 (ppm)

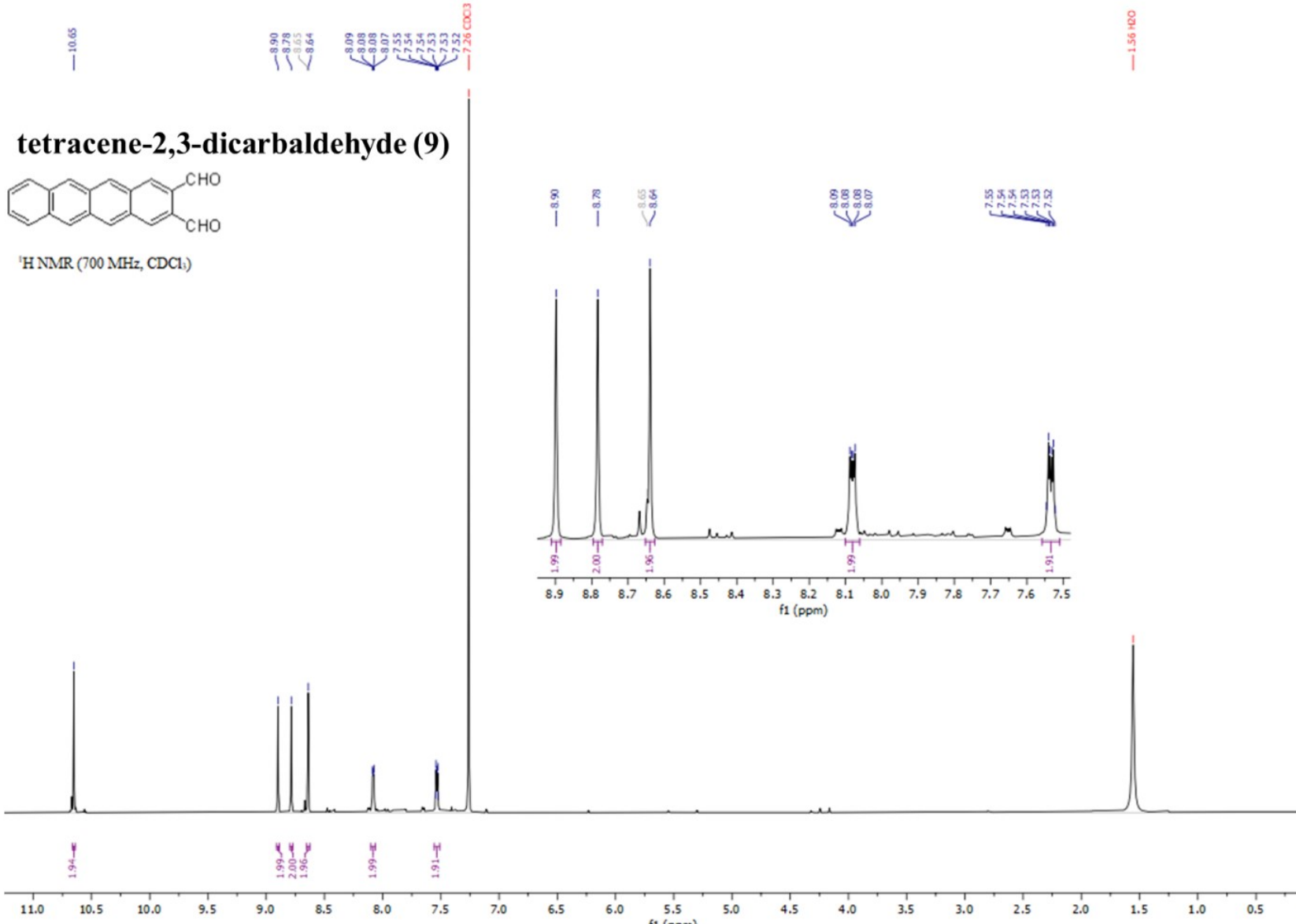

anthracene-2,3-dicarbaldehyde (8)
CHO
CHO
^{1}H NMR (700 MHz, CDCl$_3$)
10.66
8.65
8.63
8.11
8.11
8.10
8.10
7.65
7.65
7.64
7.64
7.26 CDCl3
1.58 H2O
f1 (ppm)

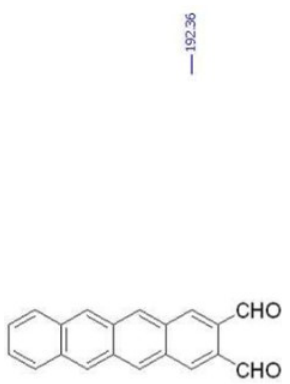


anthracene-2,3-dicarbaldehyde (8)

^{13}C NMR (176 MHz, $CDCl_3$) δ 192.46, 136.45, 133.82, 132.06, 130.93, 129.57, 128.67, 127.79.

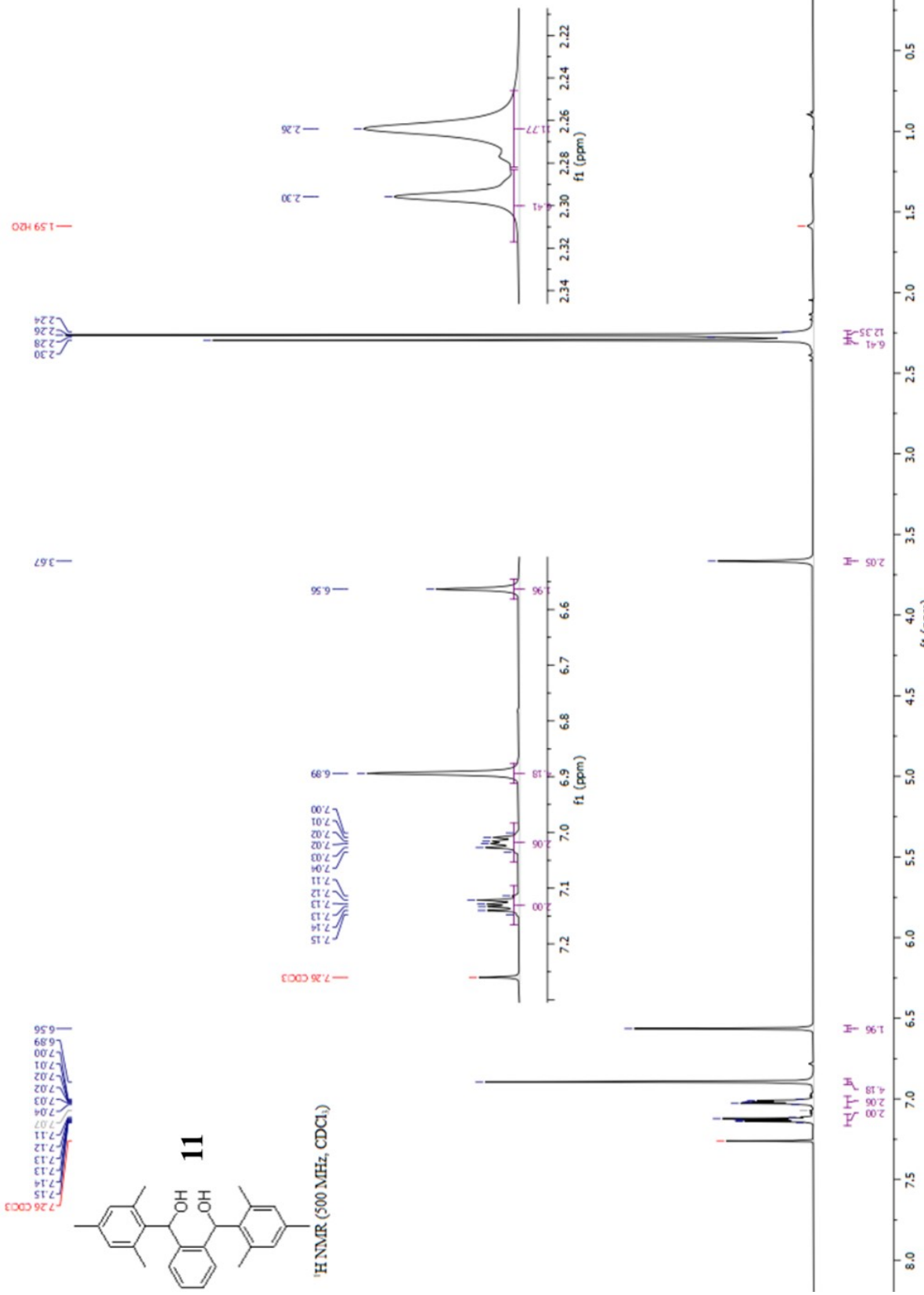


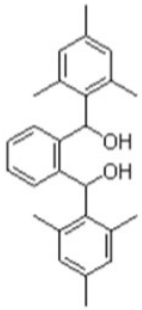

tetracene-2,3-dicarbaldehyde (9)
CHO
CHO
^{1}H NMR (700 MHz, CDCl$_3$)
10.65
8.90
8.78
8.65
8.64
8.09
8.08
8.08
8.07
7.55
7.54
7.54
7.53
7.53
7.52
7.26 CDCl3
1.56 H2O
1.94
1.99
2.00
1.96
1.99
1.91
f1 (ppm)



tetracene-2,3-dicarbaldehyde (9)

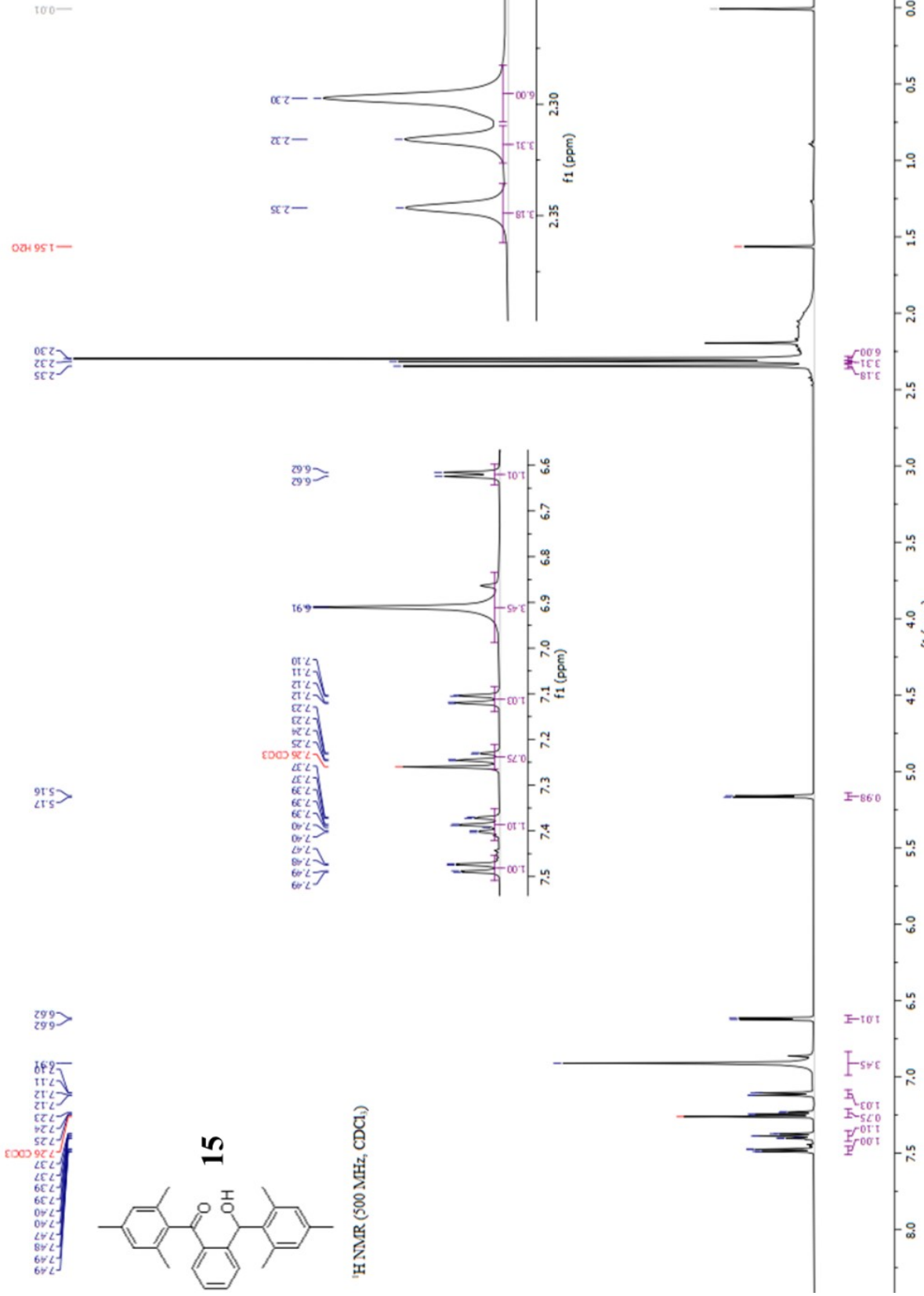
^{13}C NMR (176 MHz, $CDCl_3$) δ 192.36, 137.45, 132.83, 131.78, 131.40, 130.58, 130.08, 128.45, 127.58, 126.67.

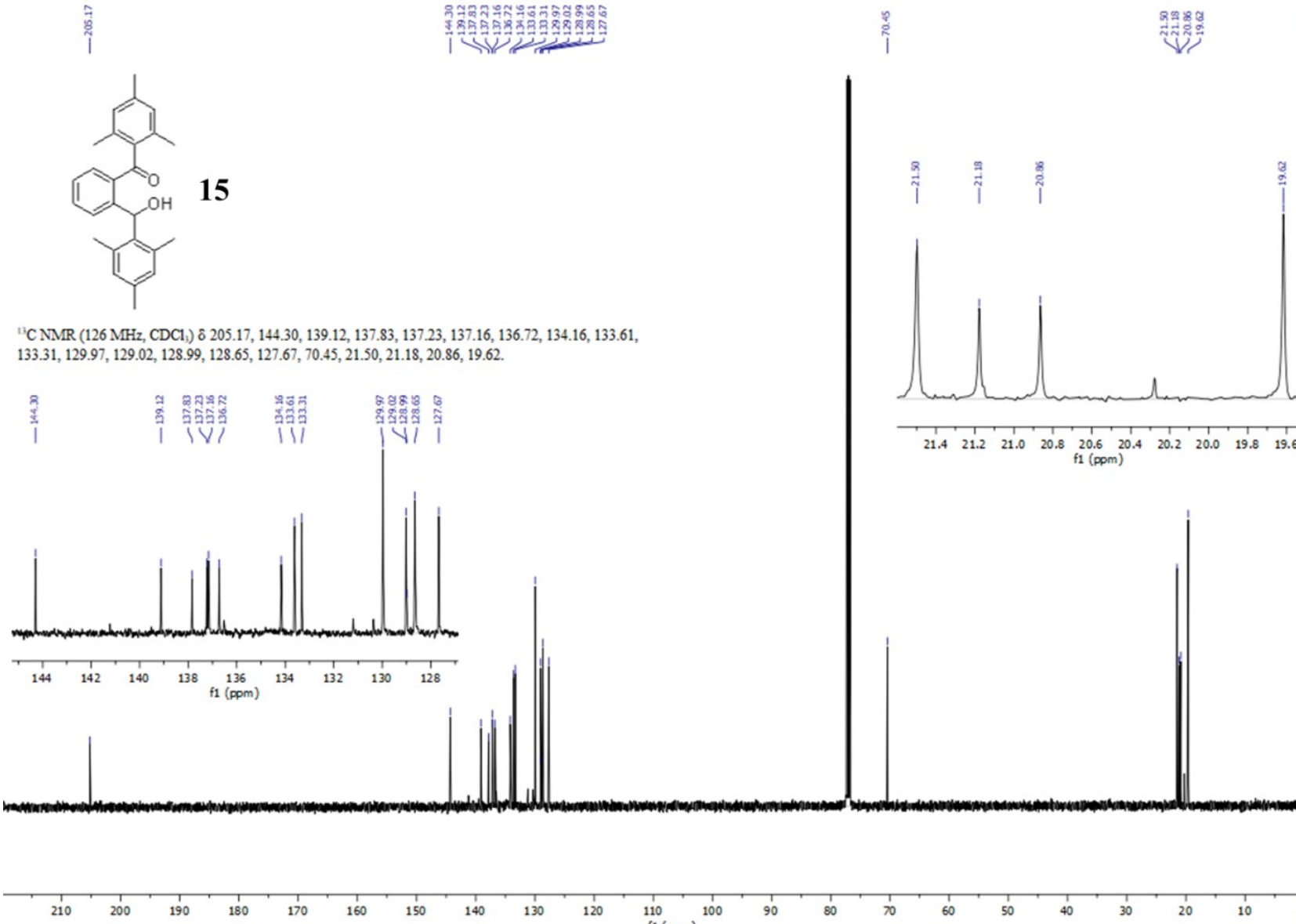

11
OH
OH
^{1}H NMR (500 MHz, CDCl$_3$)
f1 (ppm)



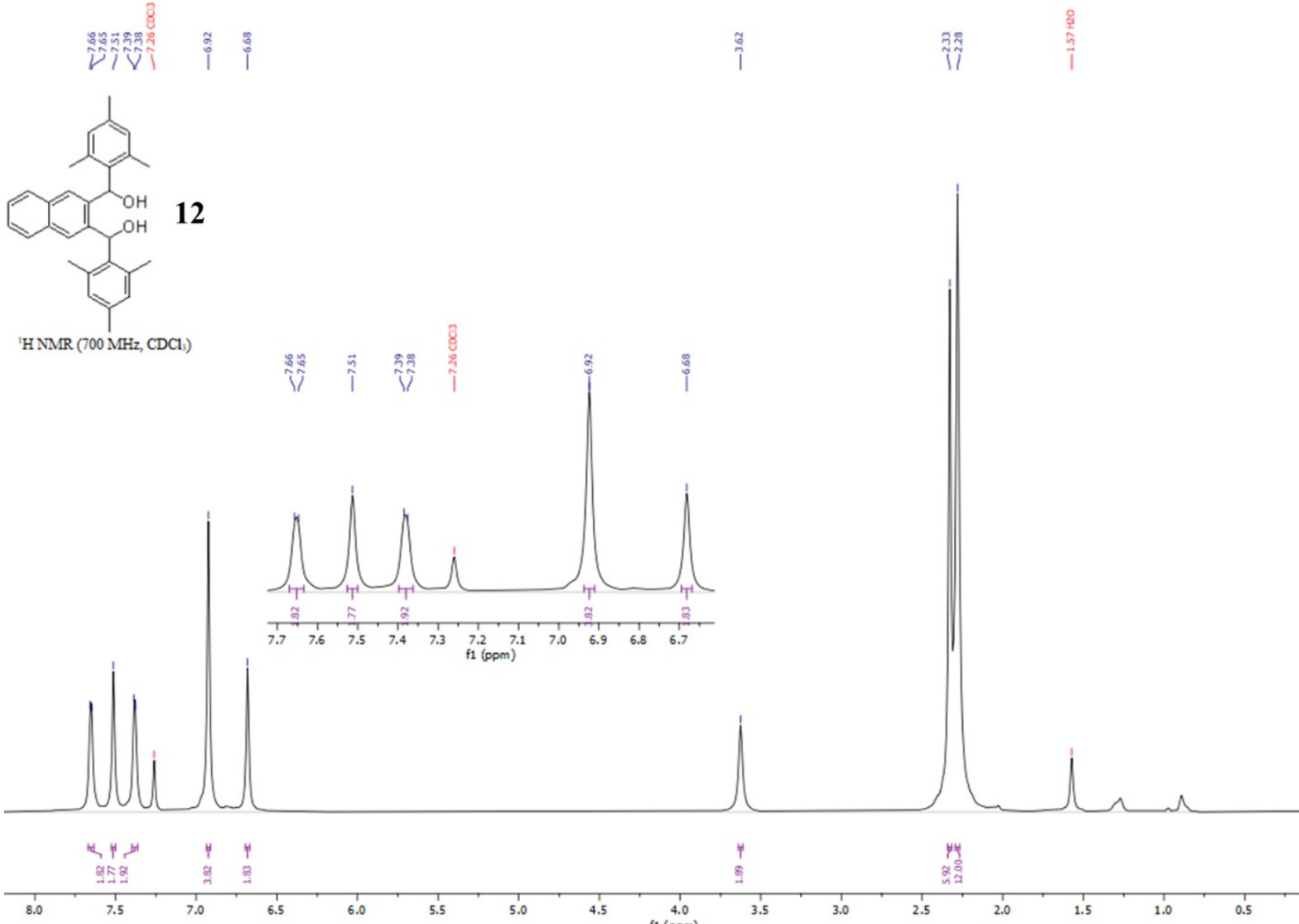
11

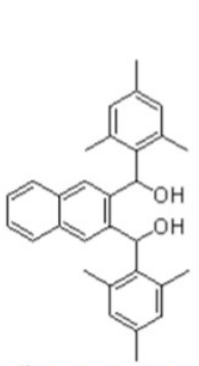
^{13}C NMR (126 MHz, $CDCl_3$) δ 140.07, 136.95, 136.89, 134.56, 130.15, 128.28, 127.87, 71.12, 21.22, 20.80.


15
^{1}H NMR (500 MHz, CDCl$_3$)
f1 (ppm)



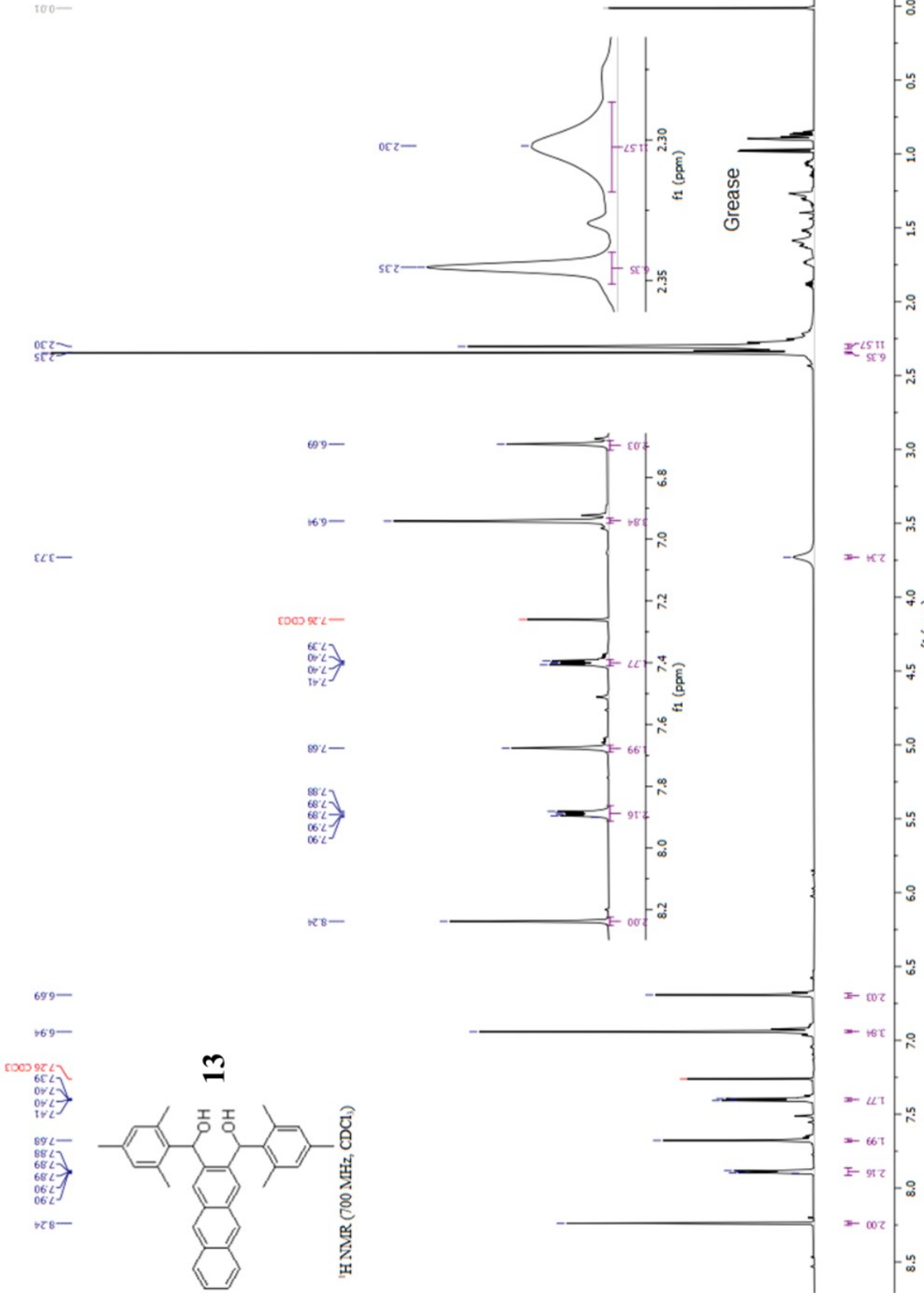
^{13}C NMR (126 MHz, $CDCl_3$) δ 205.17, 144.30, 139.12, 137.83, 137.23, 137.16, 136.72, 134.16, 133.61, 133.31, 129.97, 129.02, 128.99, 128.65, 127.67, 70.45, 21.50, 21.18, 20.86, 19.62.

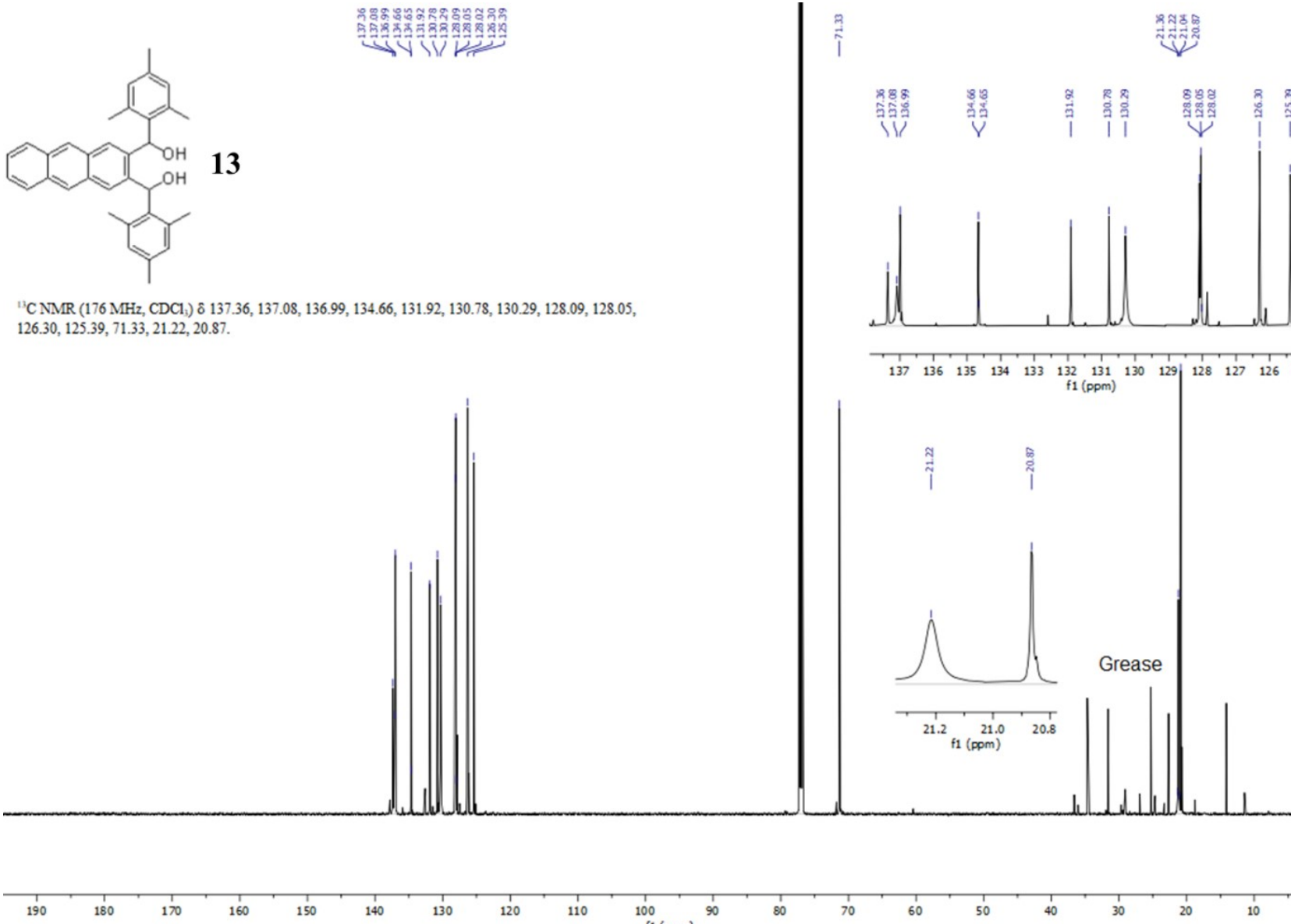

7.66
7.65
7.51
7.39
7.38
7.26 CDCl3
6.92
6.68
3.62
2.33
2.28
1.57 H2O
OH
OH
12
1H NMR (700 MHz, CDCl3)
1.82
1.77
1.92
3.82
1.83
1.89
5.92
12.00
f1 (ppm)



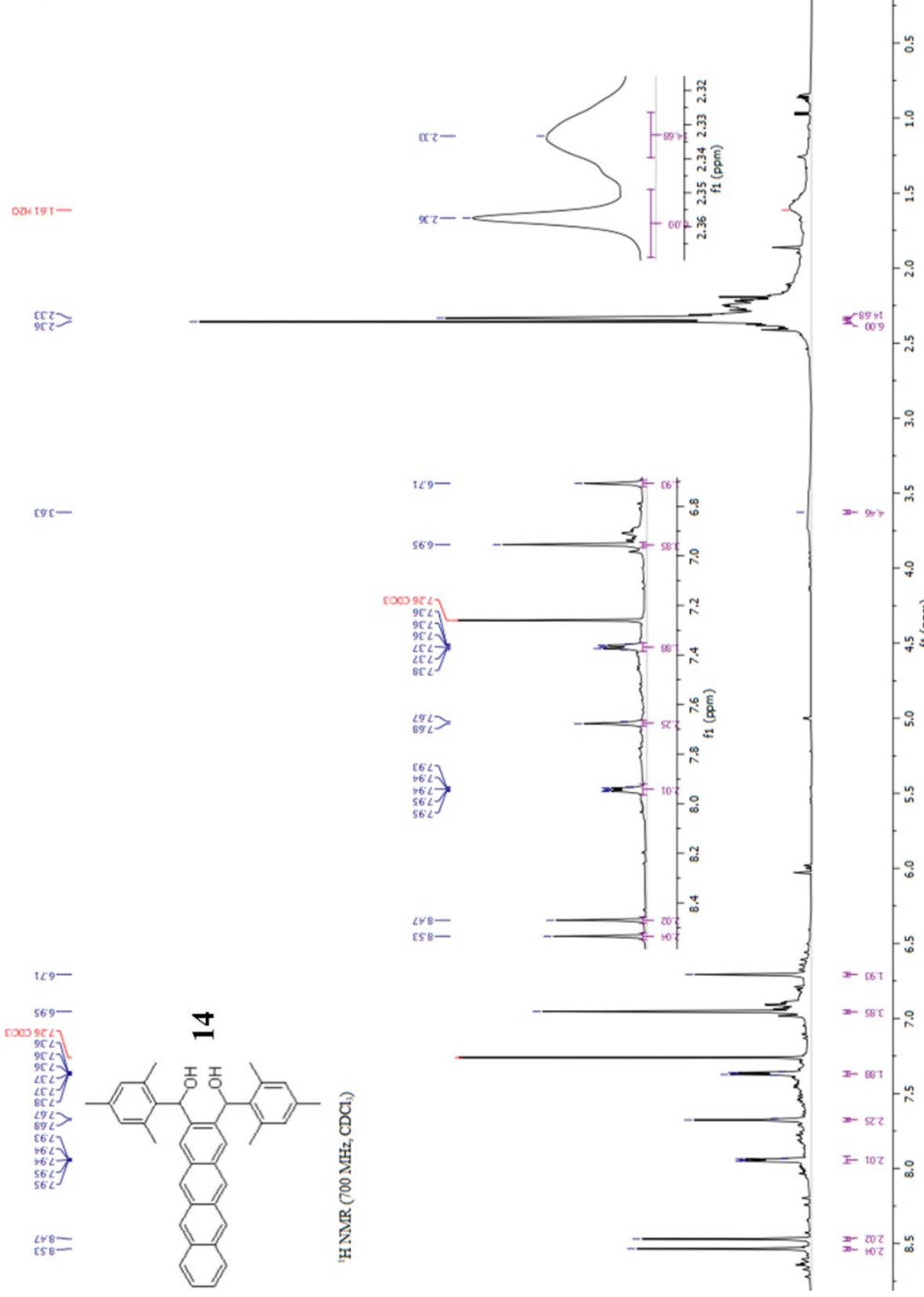
12

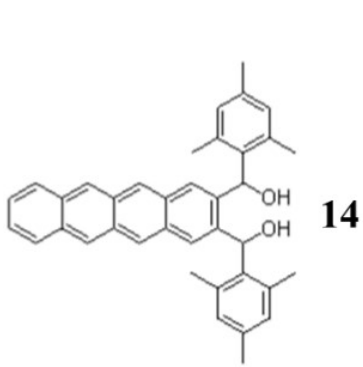
^{13}C NMR (176 MHz, CDCl$_3$) δ 137.80, 137.04, 136.97, 134.66, 132.60, 130.25, 127.87, 126.13, 71.27, 21.22, 20.85.


13
^{1}H NMR (700 MHz, CDCl$_3$)
Grease
f1 (ppm)



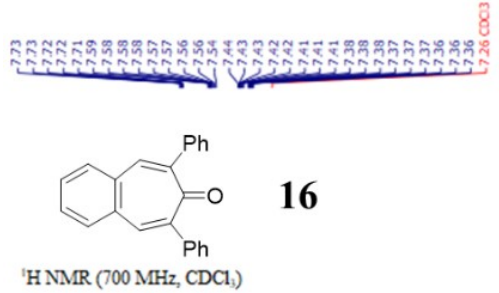
^{13}C NMR (176 MHz, $CDCl_3$) δ 137.36, 137.08, 136.99, 134.66, 131.92, 130.78, 130.29, 128.09, 128.05, 126.30, 125.39, 71.33, 21.22, 20.87.


14
OH
OH
^{1}H NMR (700 MHz, CDCl$_3$)
f1 (ppm)



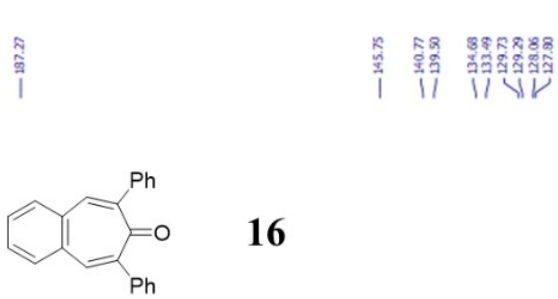
14

^{13}C NMR (176 MHz, $CDCl_3$) δ 137.17, 137.10, 137.07, 134.65, 131.50, 130.62, 130.44, 130.34, 128.28, 128.25, 126.48, 126.26, 125.16, 71.39, 21.25, 20.90.



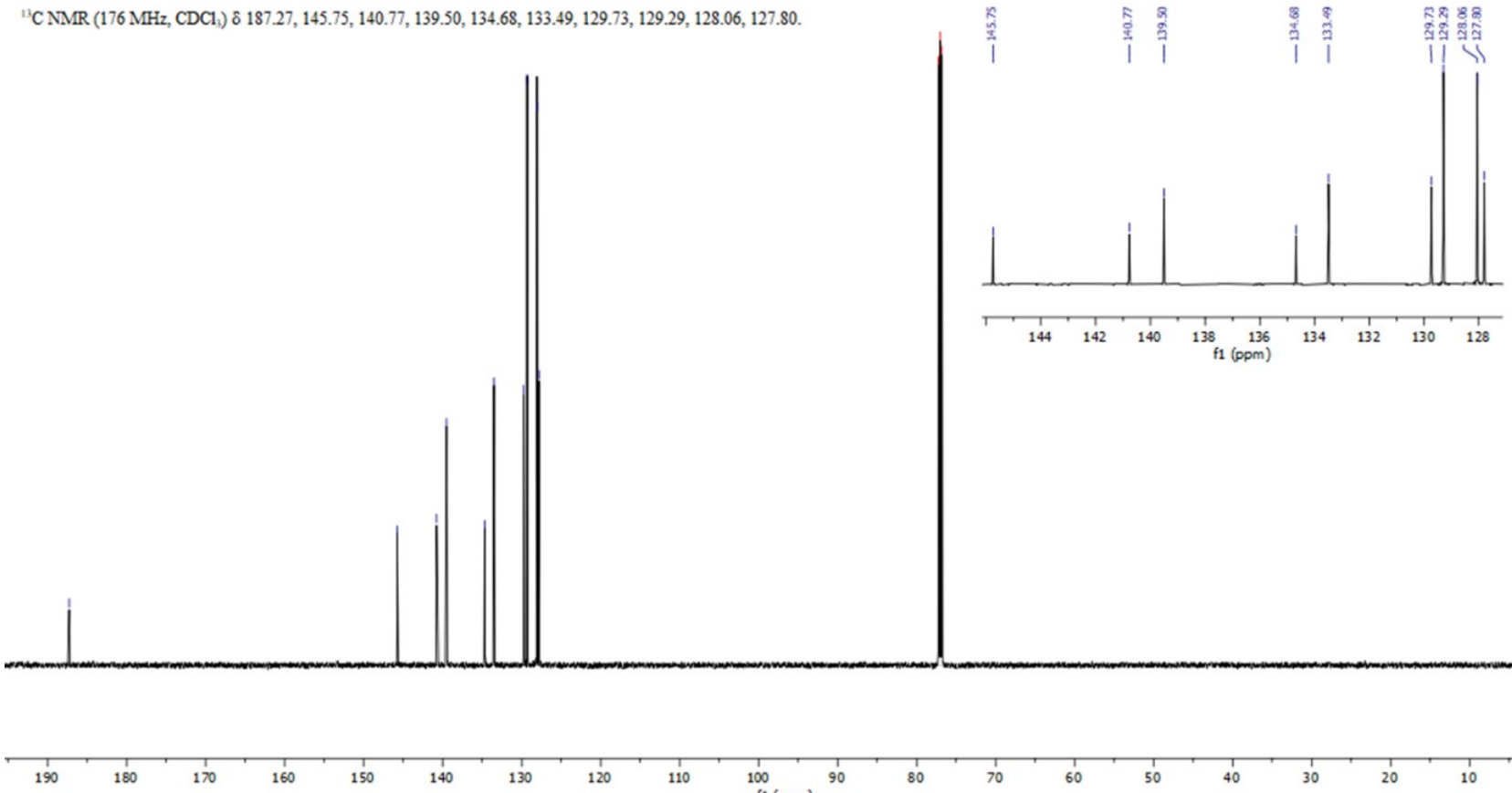
16

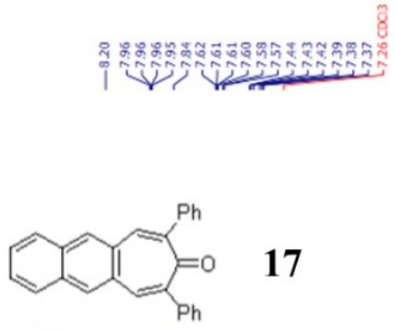
^{1}H NMR (700 MHz, $CDCl_3$)



16

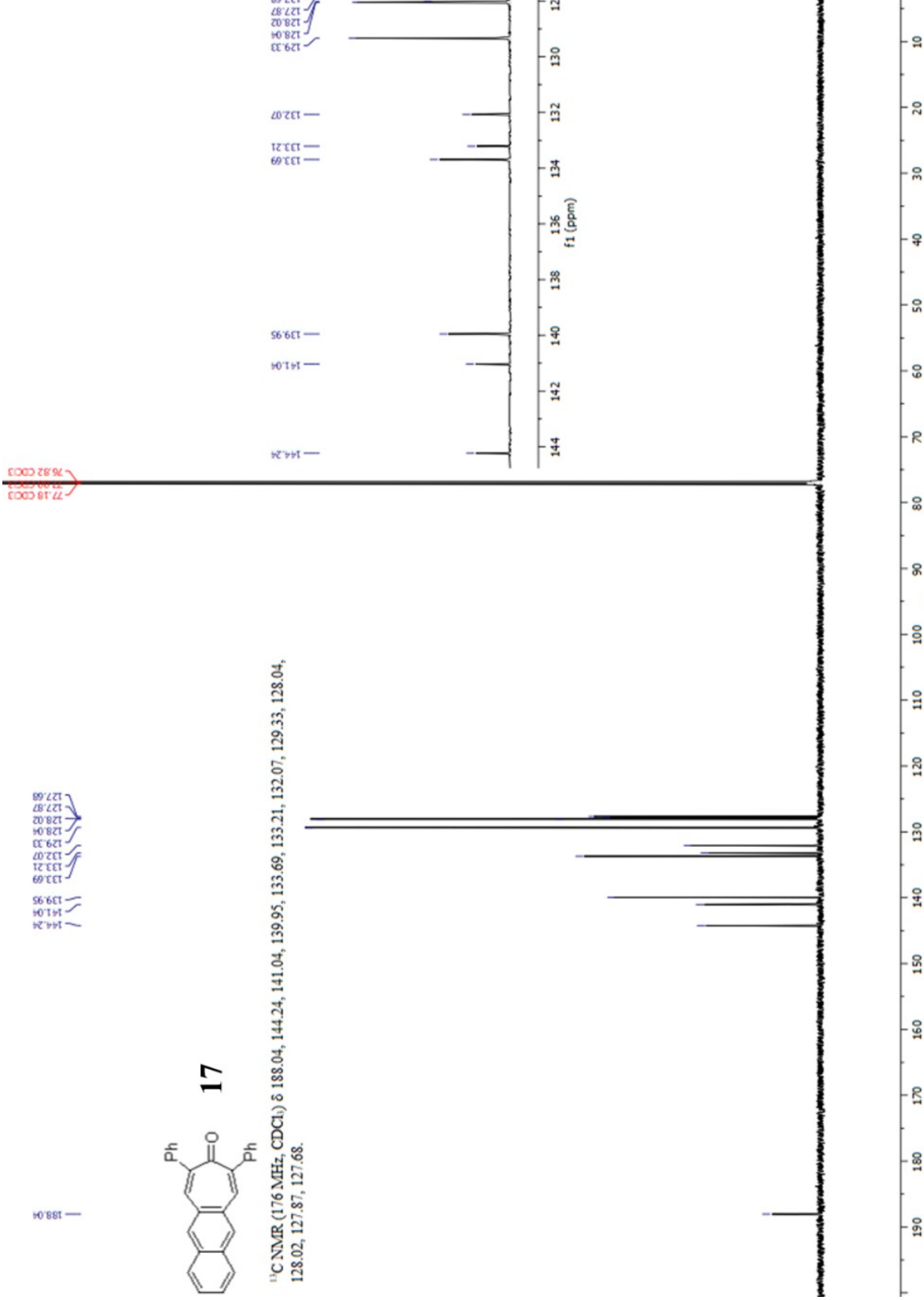
^{13}C NMR (176 MHz, $CDCl_3$) δ 187.27, 145.75, 140.77, 139.50, 134.68, 133.49, 129.73, 129.29, 128.06, 127.80.

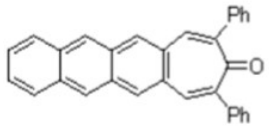




17

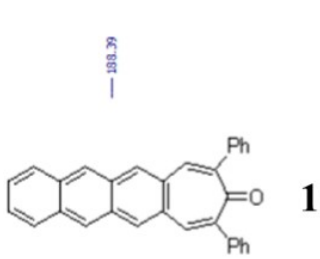
^{1}H NMR (700 MHz, $CDCl_3$)


17
Ph
Ph
O
^{13}C NMR (176 MHz, CDCl$_3$) δ 188.04, 144.24, 141.04, 139.95, 133.69, 133.21, 132.07, 129.33, 128.04, 128.02, 127.87, 127.68.
77.18 CDCl3
76.82 CDCl3
144.24
141.04
139.95
133.69
133.21
132.07
129.33
128.04
128.02
127.87
127.69
188.04
f1 (ppm)



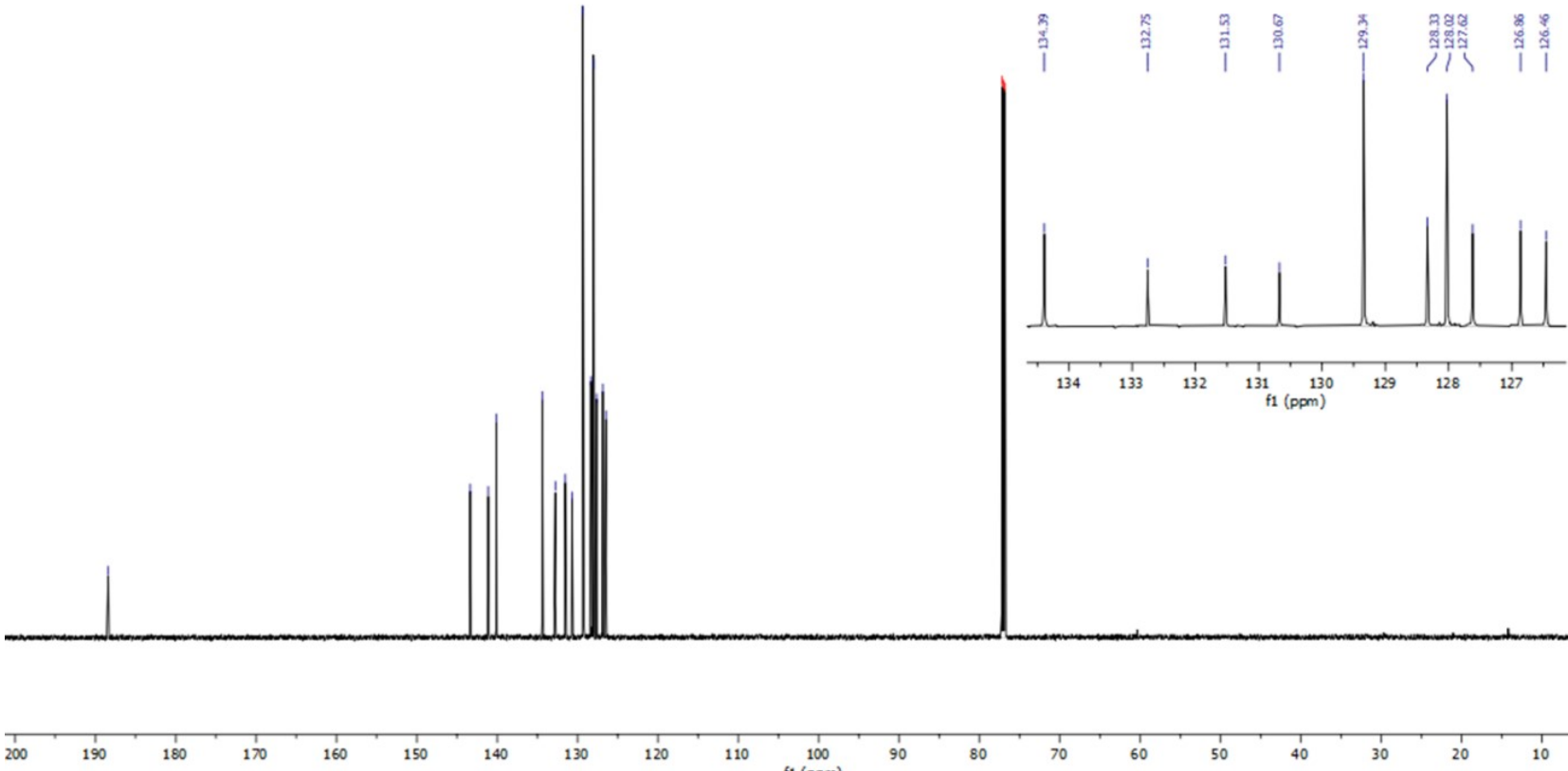
18

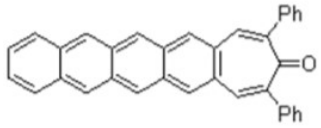
^{1}H NMR (700 MHz, $CDCl_3$)



18

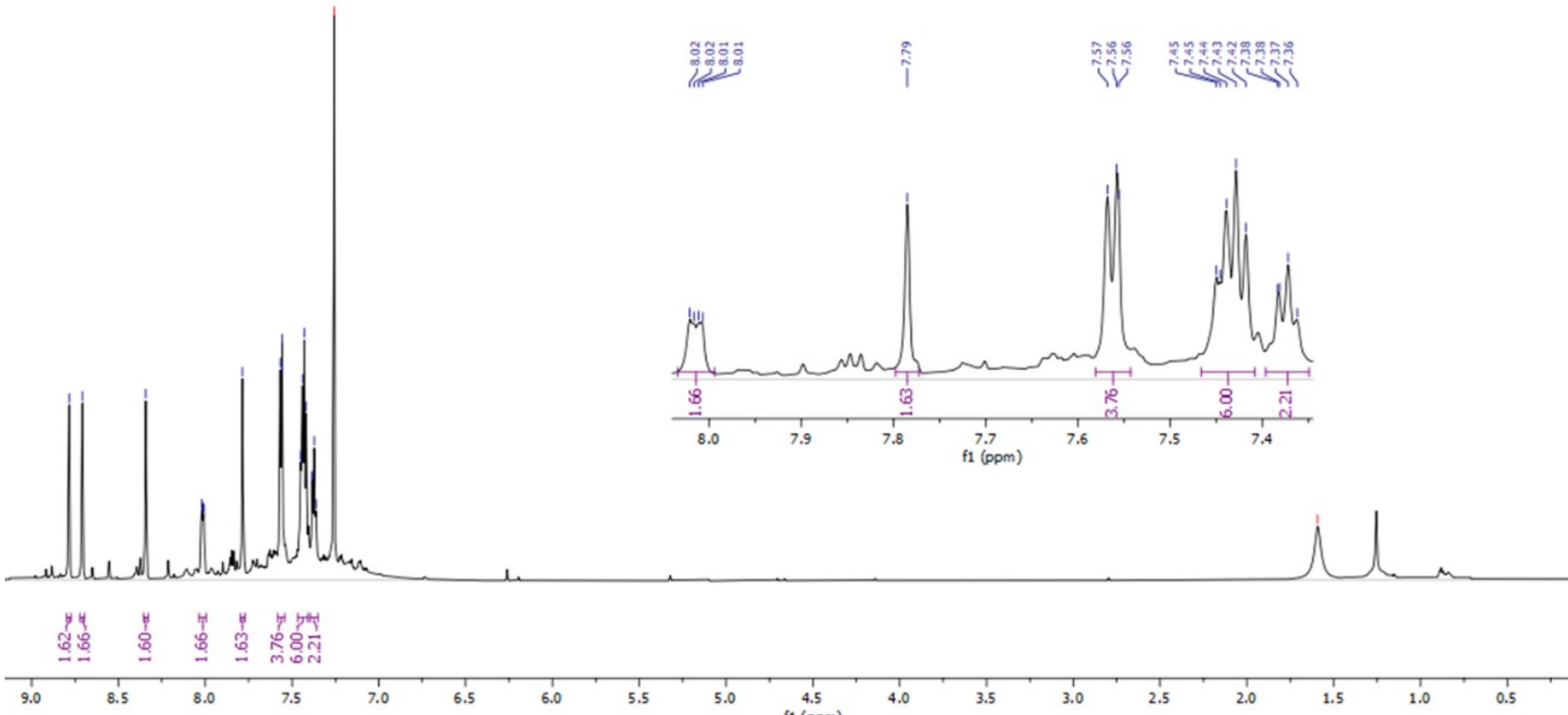
^{13}C NMR (176 MHz, $CDCl_3$) δ 188.39, 143.36, 141.12, 140.12, 134.39, 132.75, 131.53, 130.67, 129.34, 128.33, 128.02, 127.62, 126.86, 126.46.

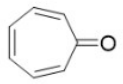




19

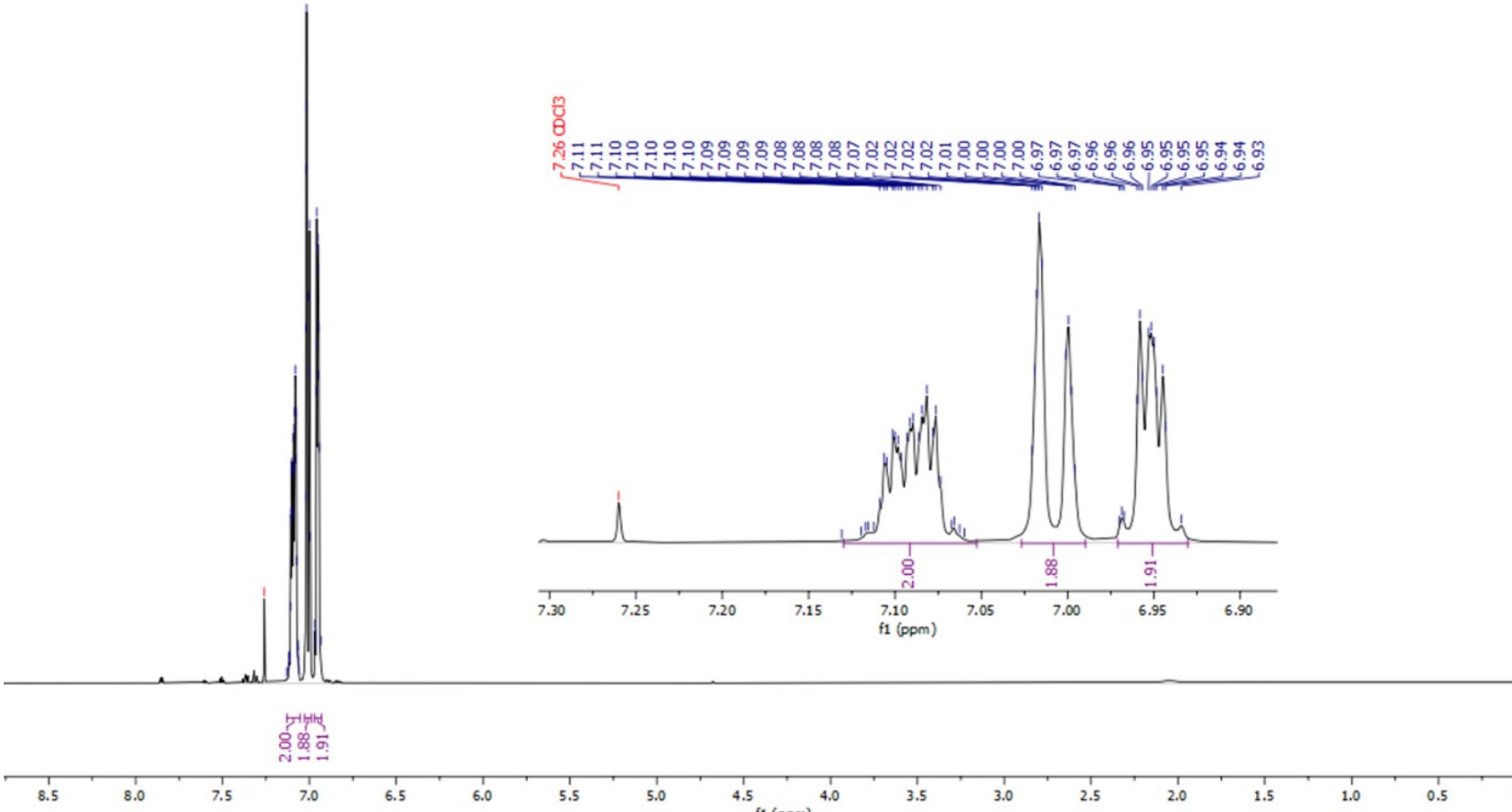
^{1}H NMR (700 MHz, $CDCl_3$)





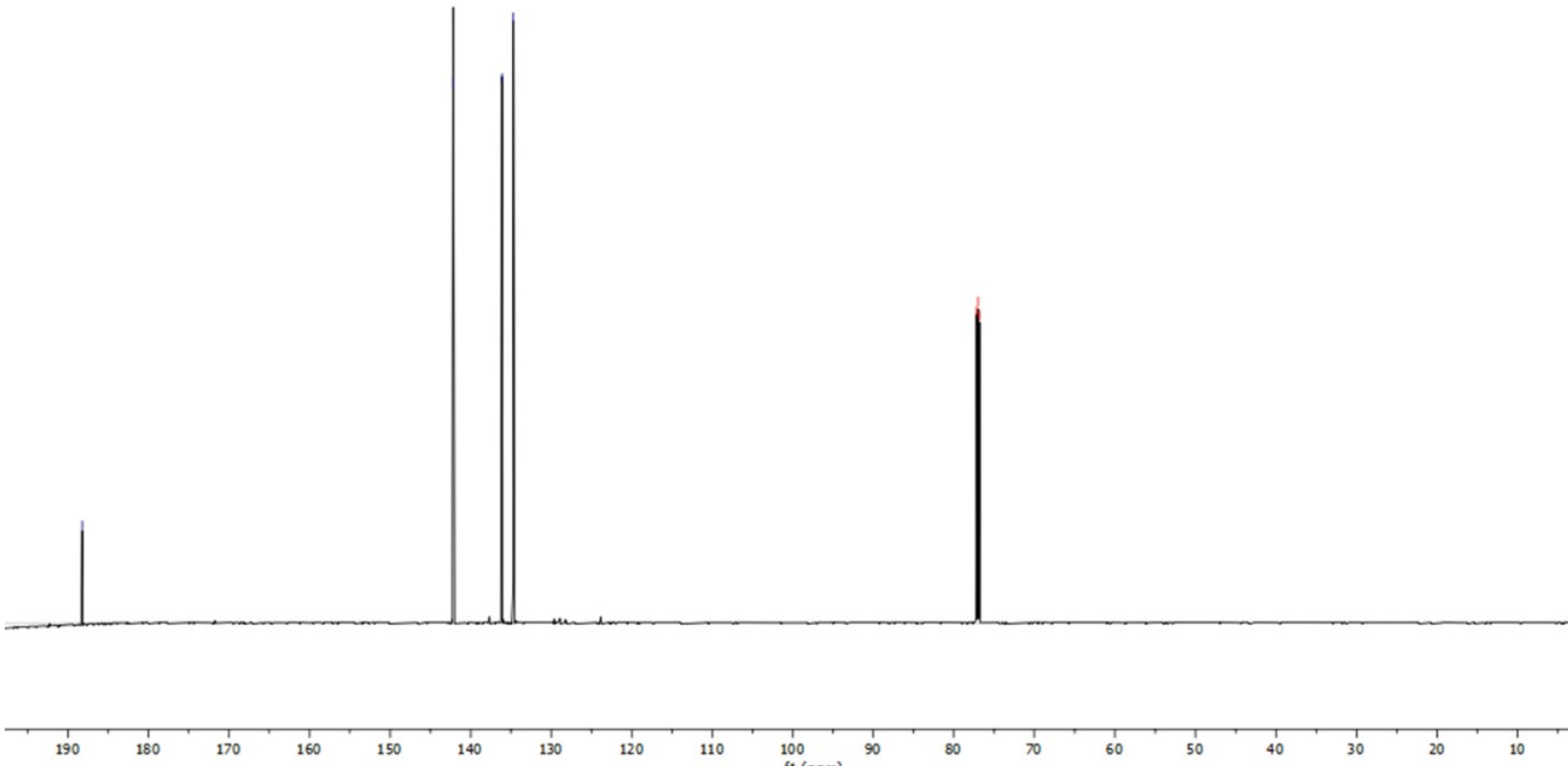
Tropone

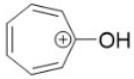
^{1}H NMR (700 MHz, $CDCl_3$)



Tropone

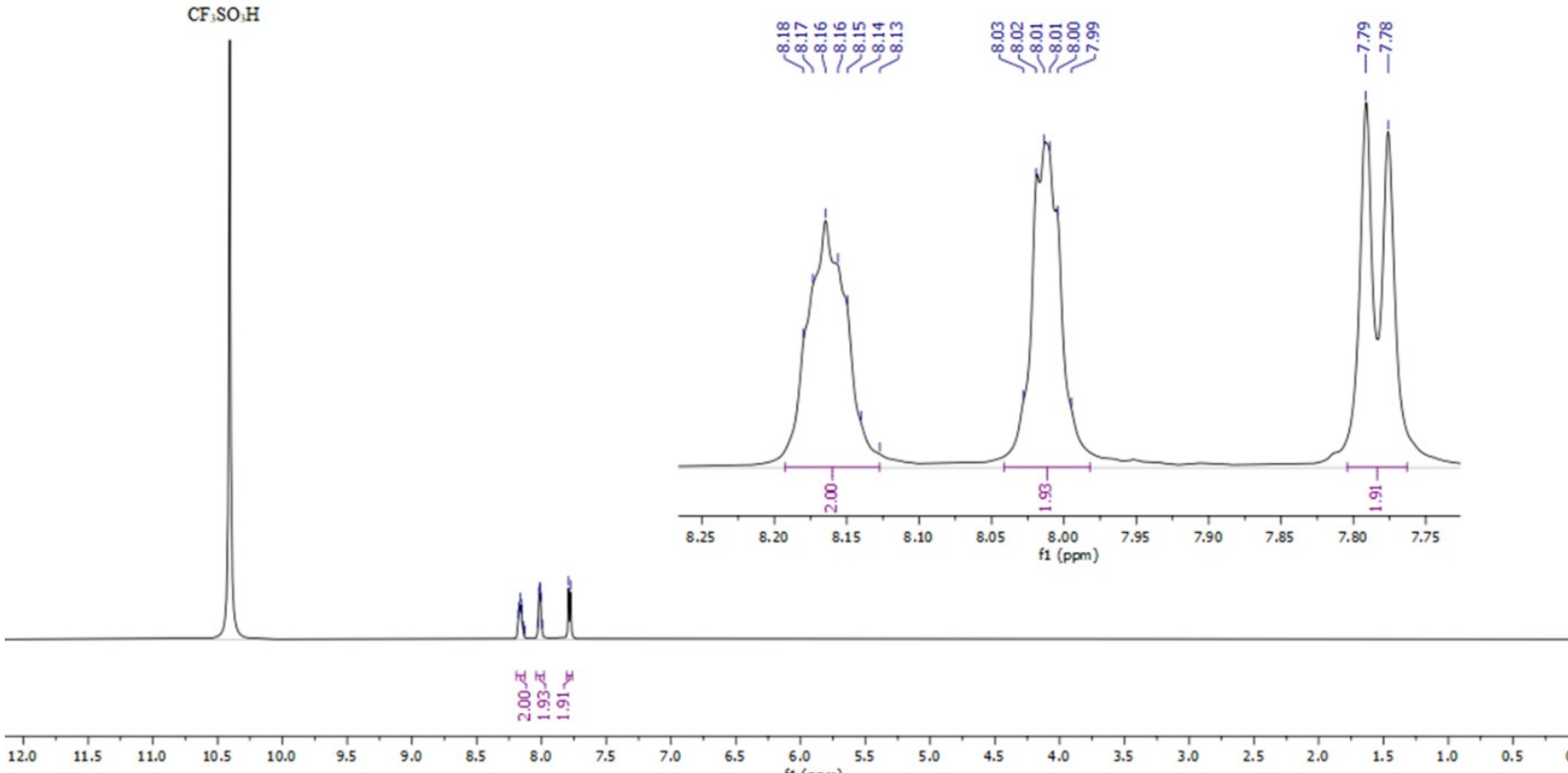
^{13}C NMR (176 MHz, $CDCl_3$) δ 188.22, 142.18, 136.10, 134.70.

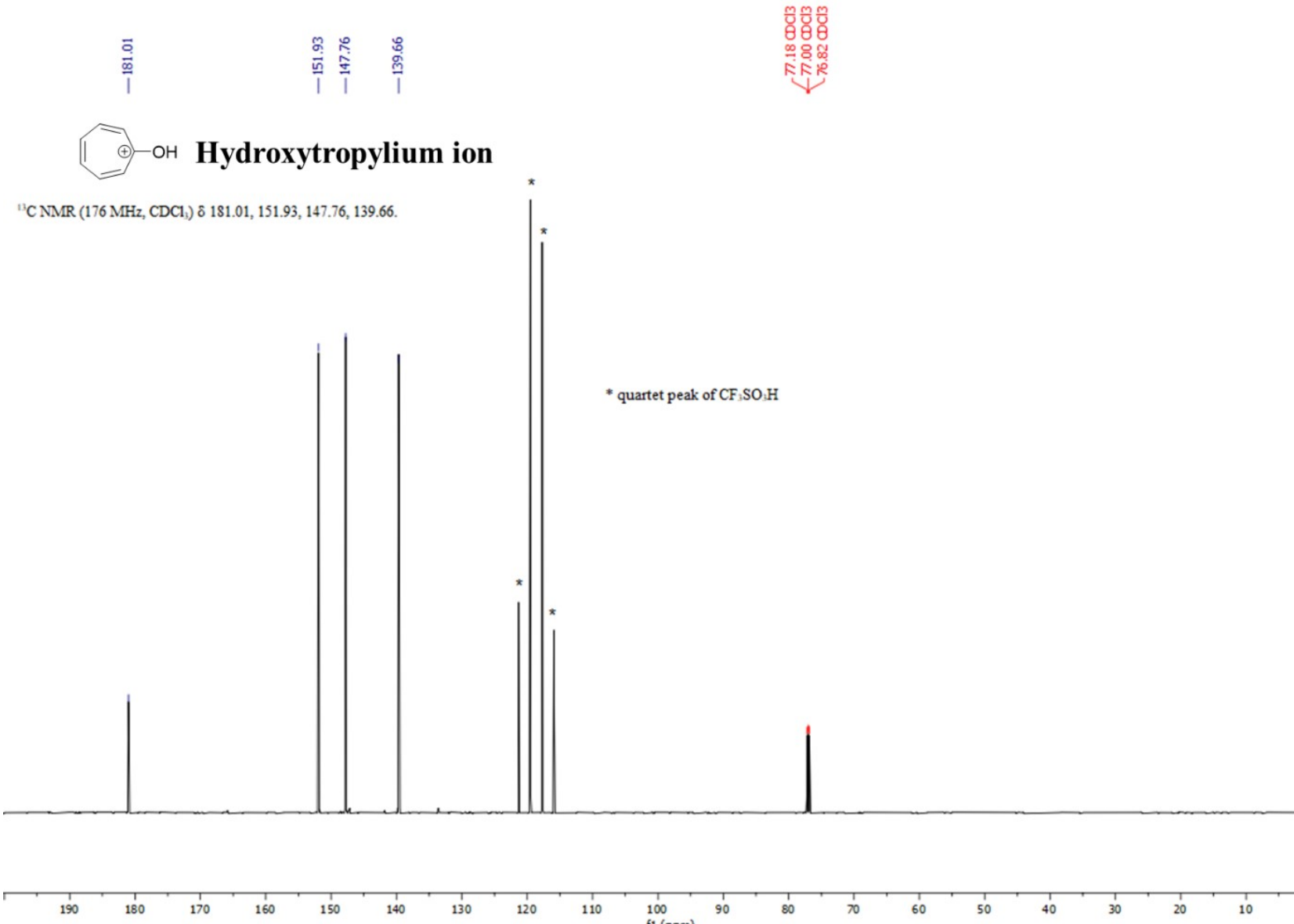


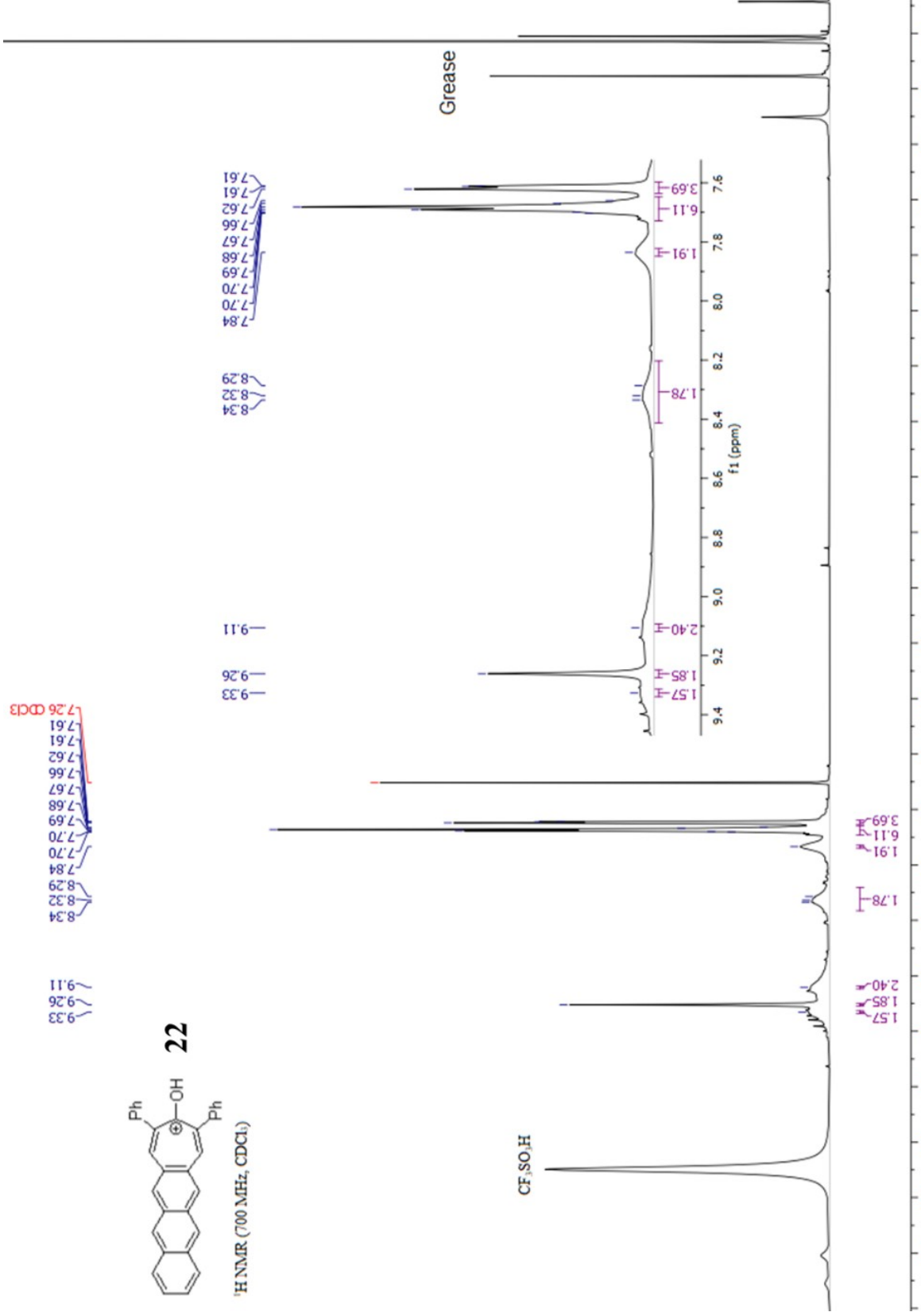


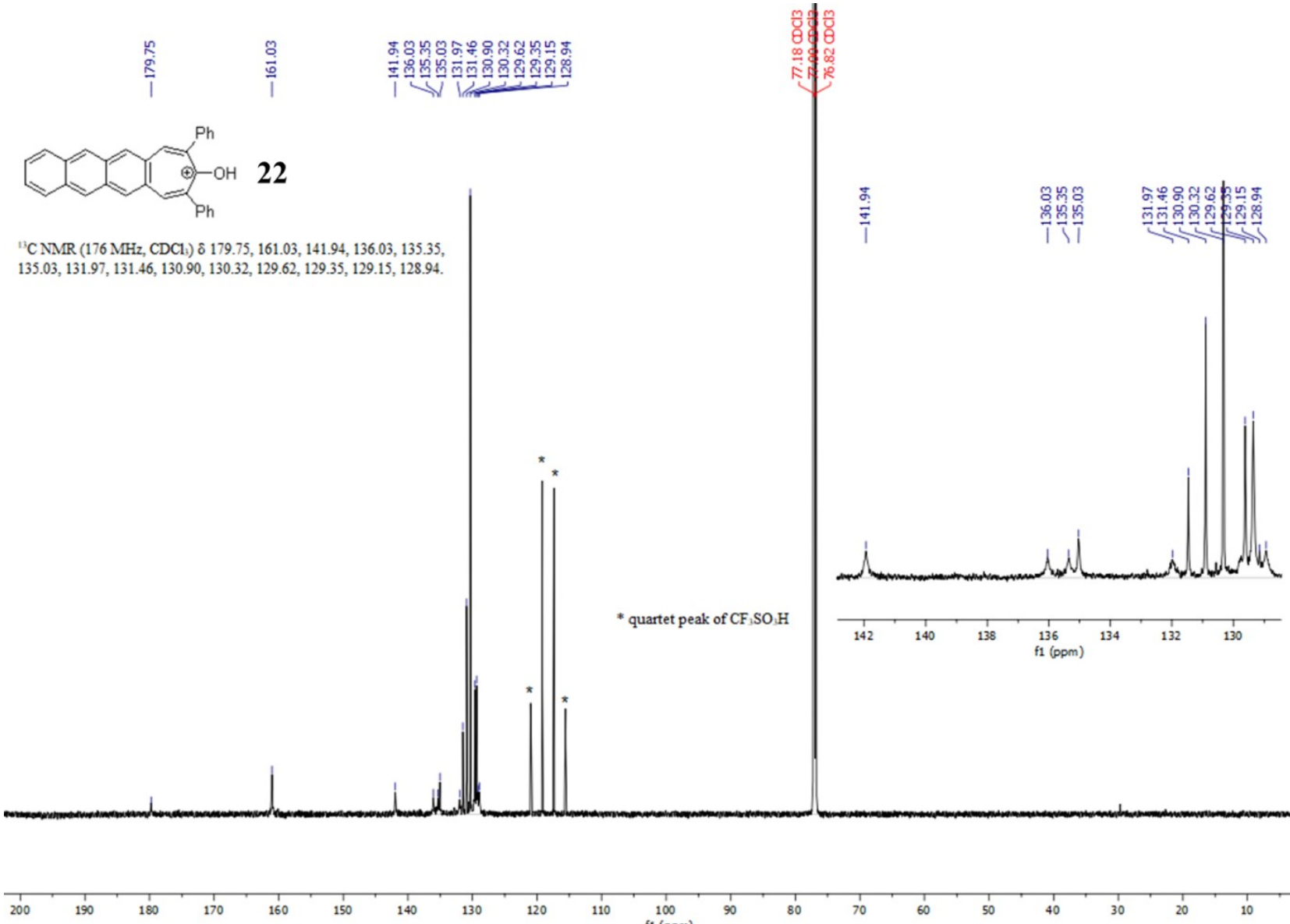
Hydroxytropylium ion

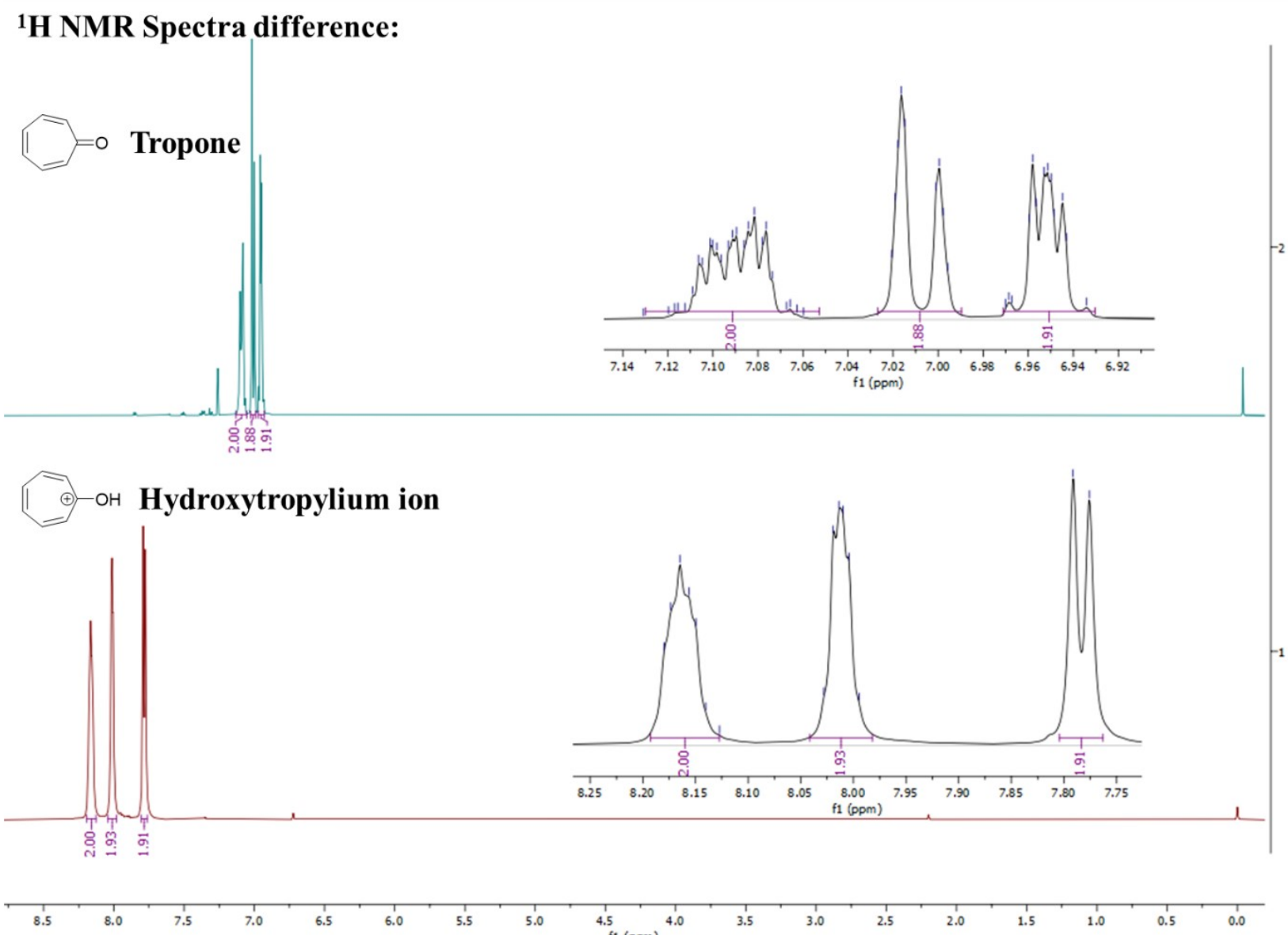
^{1}H NMR (700 MHz, $CDCl_3$)



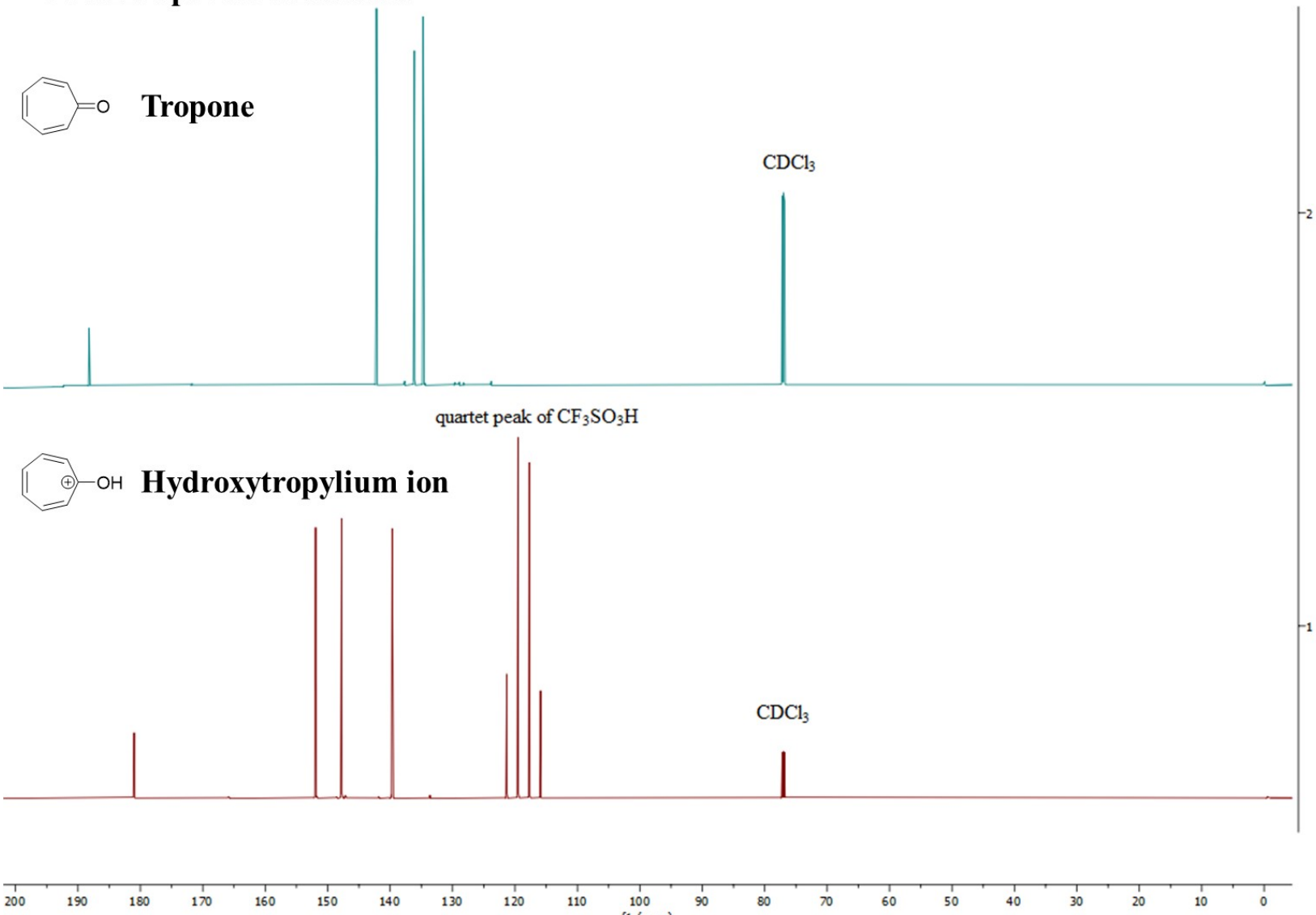

181.01
151.93
147.76
139.66
77.18 CDCl3
77.00 CDCl3
76.82 CDCl3
OH
Hydroxytropylium ion
13C NMR (176 MHz, CDCl3) δ 181.01, 151.93, 147.76, 139.66.
* quartet peak of CF3SO3H
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


22
Ph
OH
Ph
^{1}H NMR (700 MHz, CDCl$_3$)
CF$_3$SO$_3$H
Grease
f1 (ppm)
7.26 CDCl3

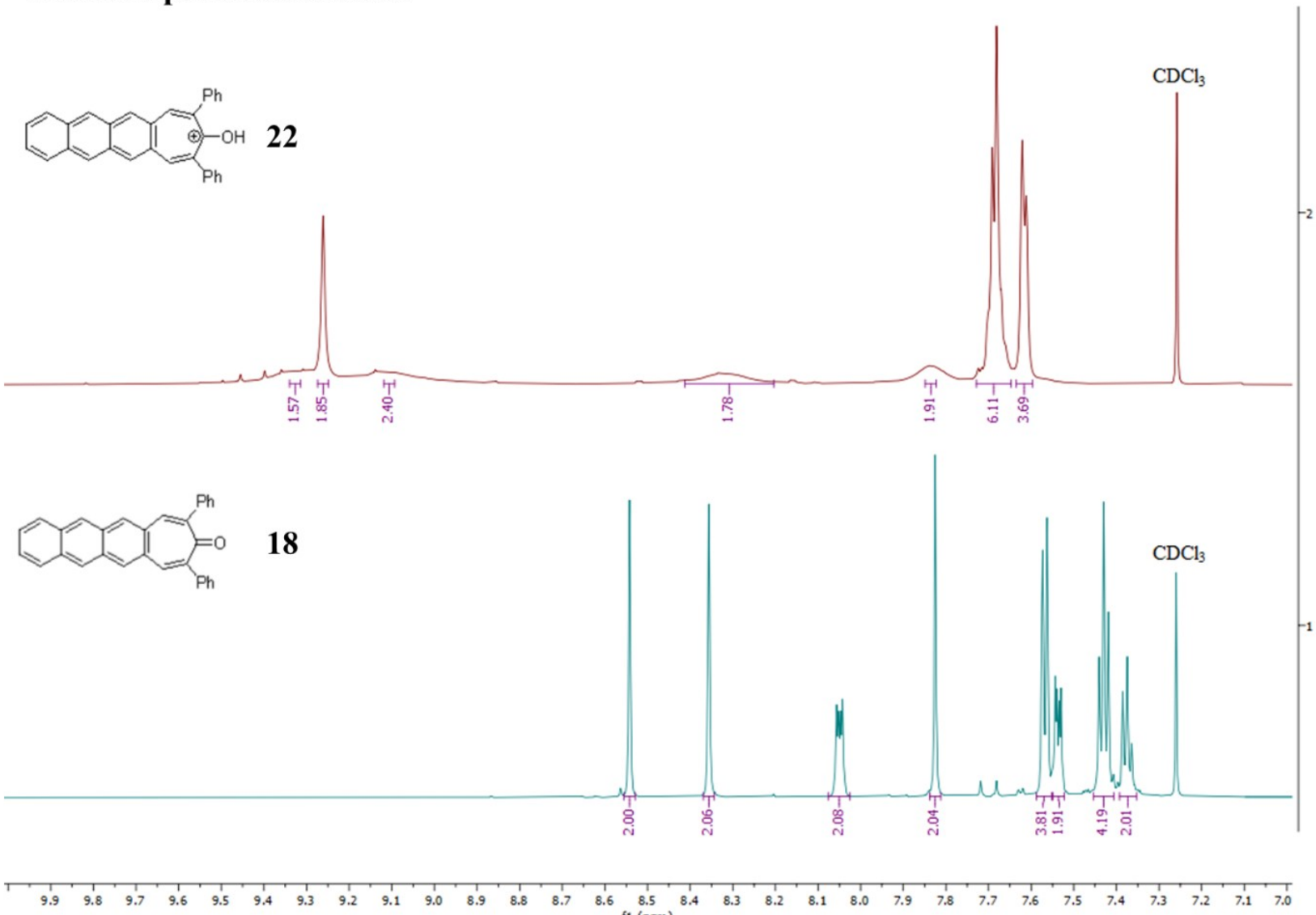

179.75
161.03
141.94
136.03
135.35
135.03
131.97
131.46
130.90
130.32
129.62
129.35
129.15
128.94
77.18 CDCl3
77.00 CDCl3
76.82 CDCl3
Ph
OH
Ph
22
^{13}C NMR (176 MHz, CDCl$_3$) δ 179.75, 161.03, 141.94, 136.03, 135.35, 135.03, 131.97, 131.46, 130.90, 130.32, 129.62, 129.35, 129.15, 128.94.
* quartet peak of CF_3SO_3H
f1 (ppm)


¹H NMR Spectra difference:
Tropone
2.00
1.88
1.91
f1 (ppm)
Hydroxytropylium ion
2.00
1.93
1.91
f1 (ppm)

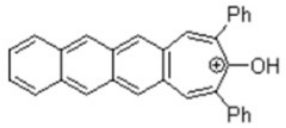
^{13}C NMR Spectra difference:



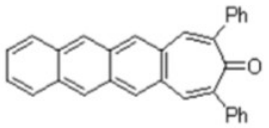
^{1}H NMR Spectra difference:



^{13}C NMR Spectra difference:

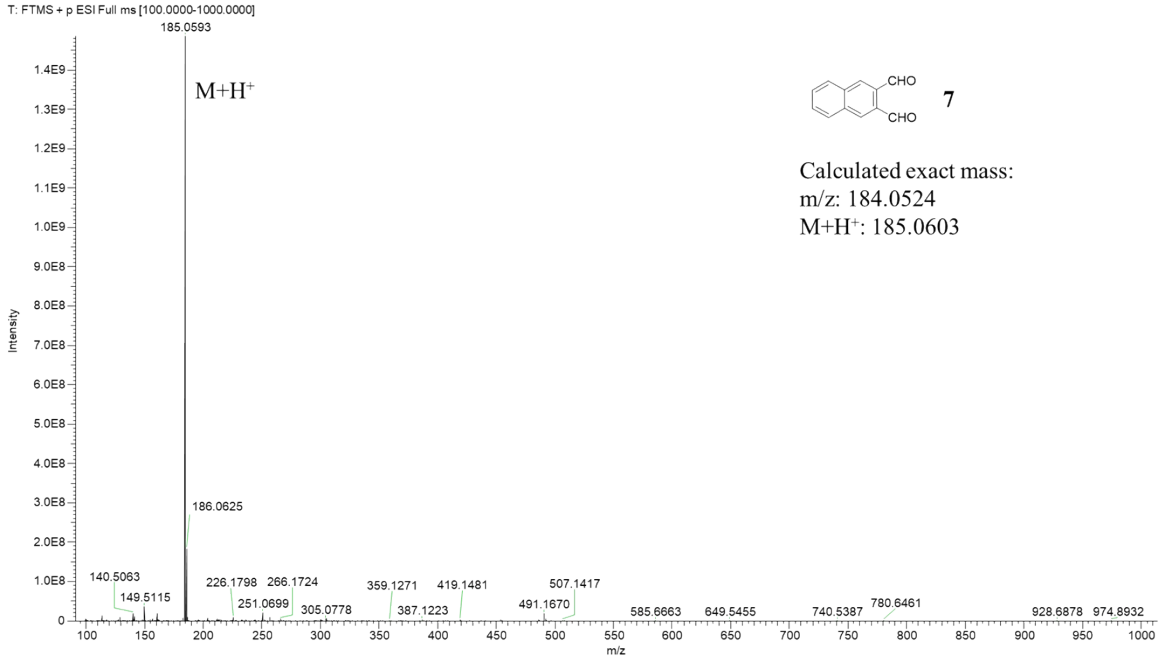


22



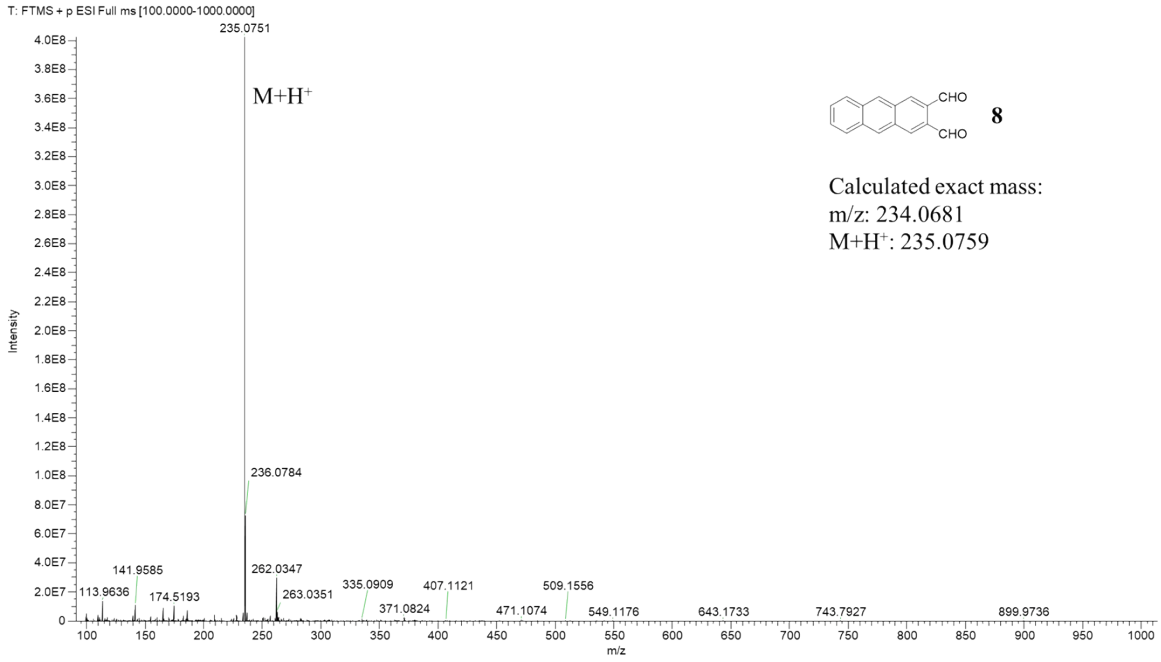
18

7. HRMS Spectra



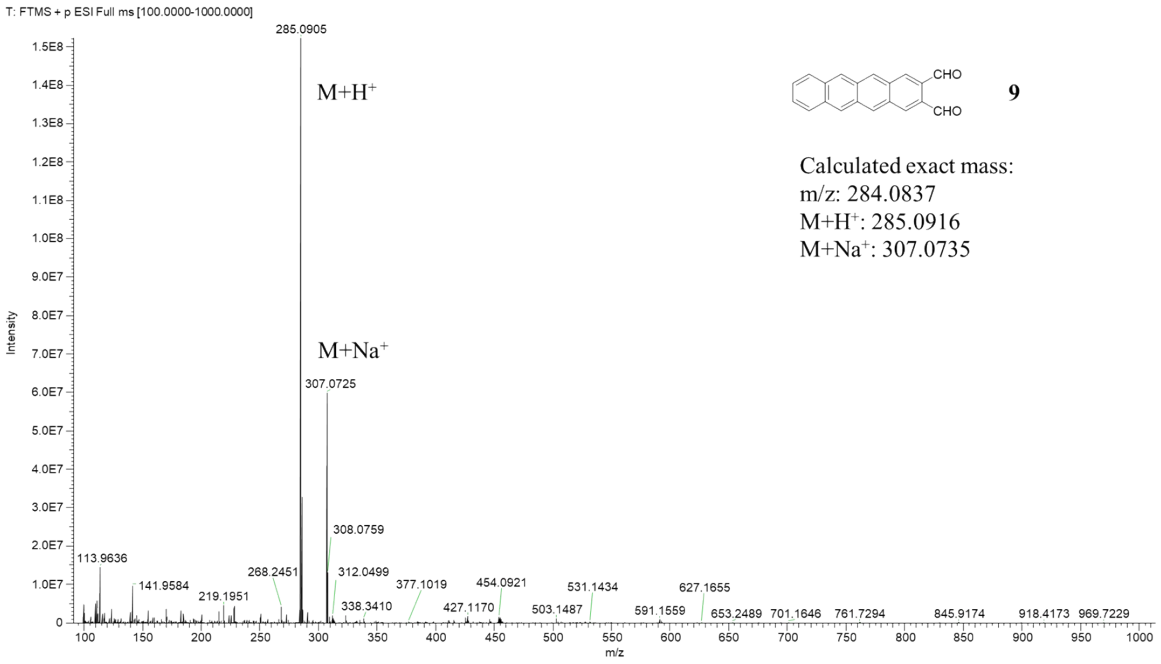
7

Calculated exact mass:
m/z: 184.0524
$M+H^+$: 185.0603



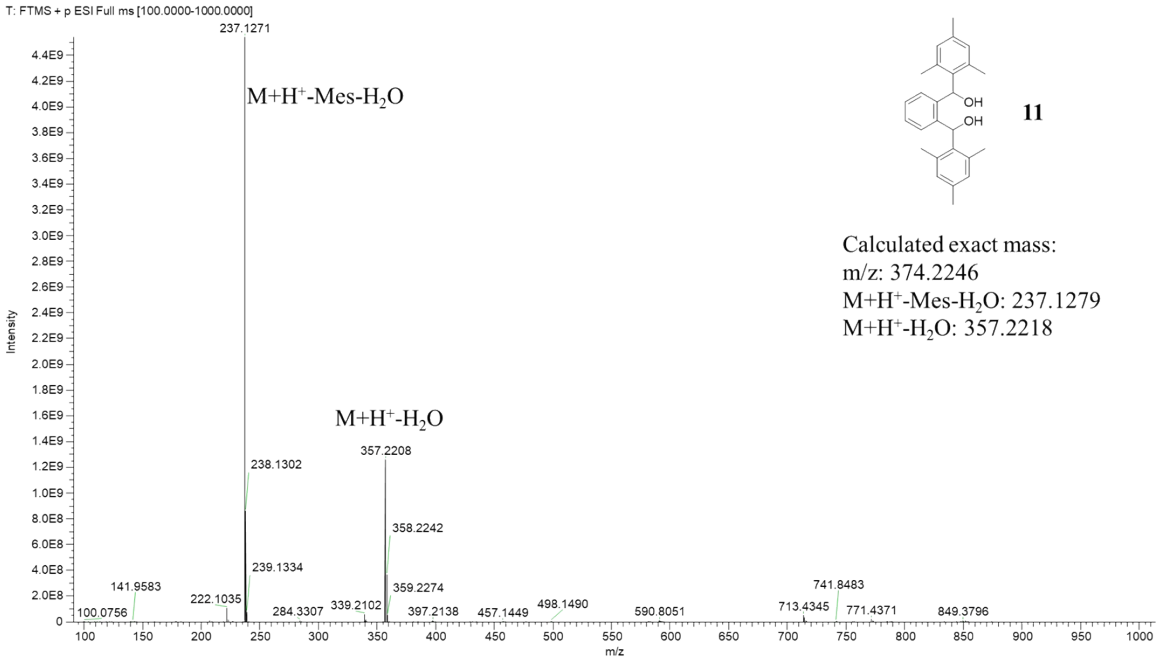
8

Calculated exact mass:
m/z: 234.0681
$M+H^+$: 235.0759



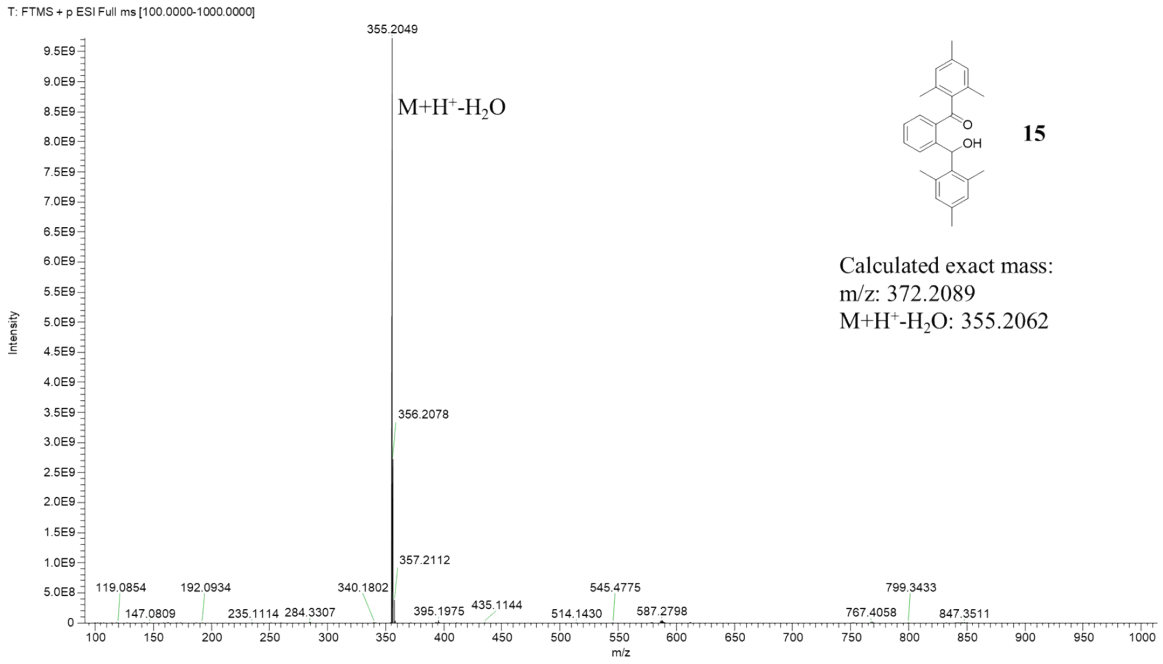
9

Calculated exact mass:
m/z: 284.0837
$M+H^+$: 285.0916
$M+Na^+$: 307.0735



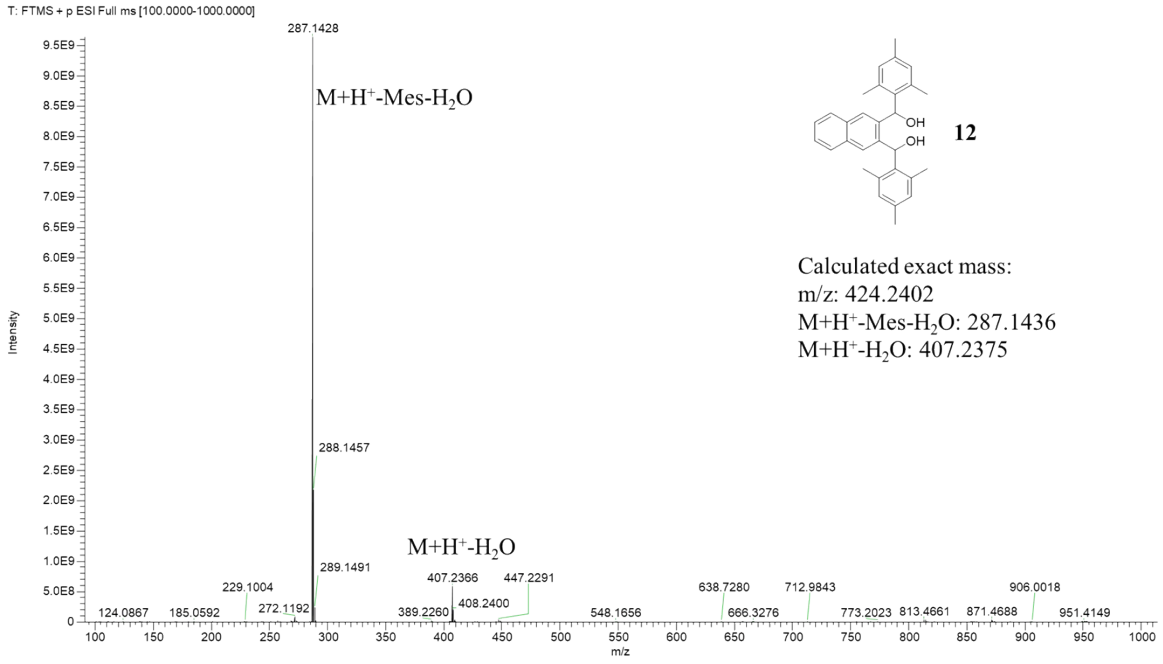
11

Calculated exact mass:
m/z: 374.2246
$M+H^+-Mes-H_2O$: 237.1279
$M+H^+-H_2O$: 357.2218



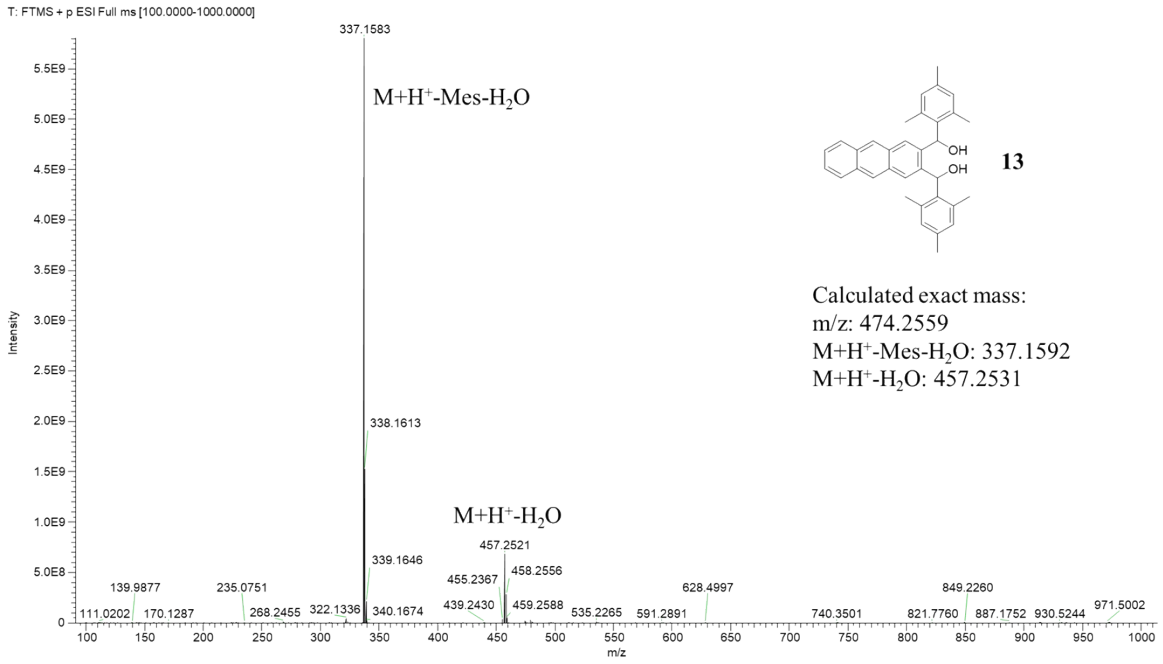
15

Calculated exact mass:
m/z: 372.2089
$M+H^+-H_2O$: 355.2062



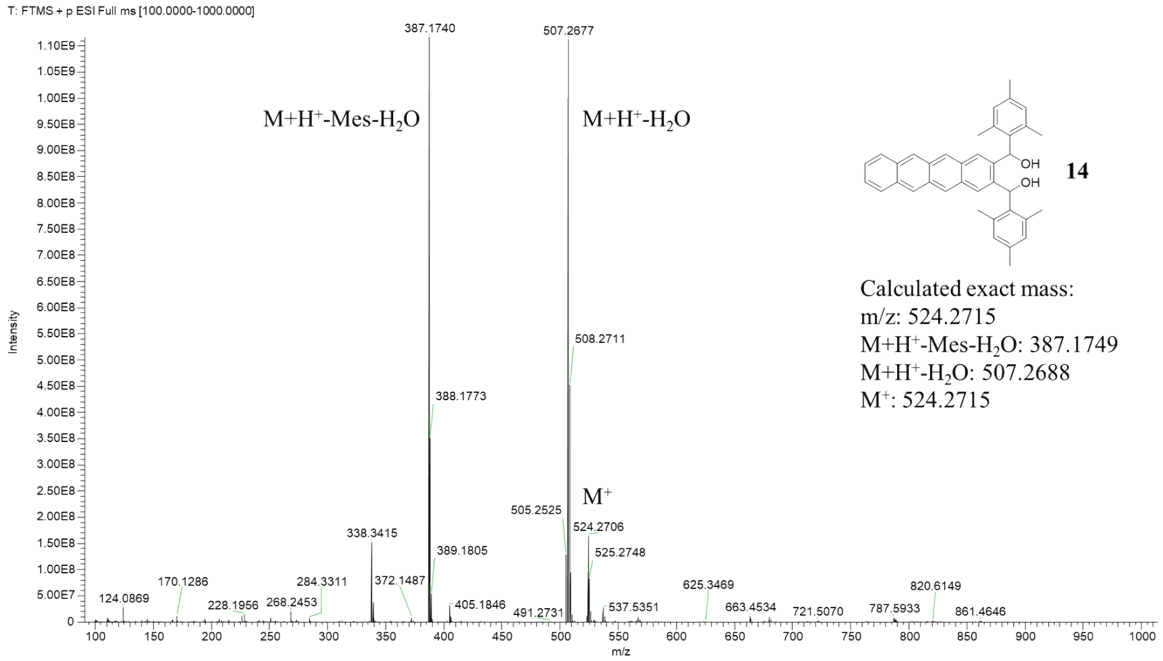
12

Calculated exact mass:
m/z: 424.2402
$M+H^+-Mes-H_2O$: 287.1436
$M+H^+-H_2O$: 407.2375



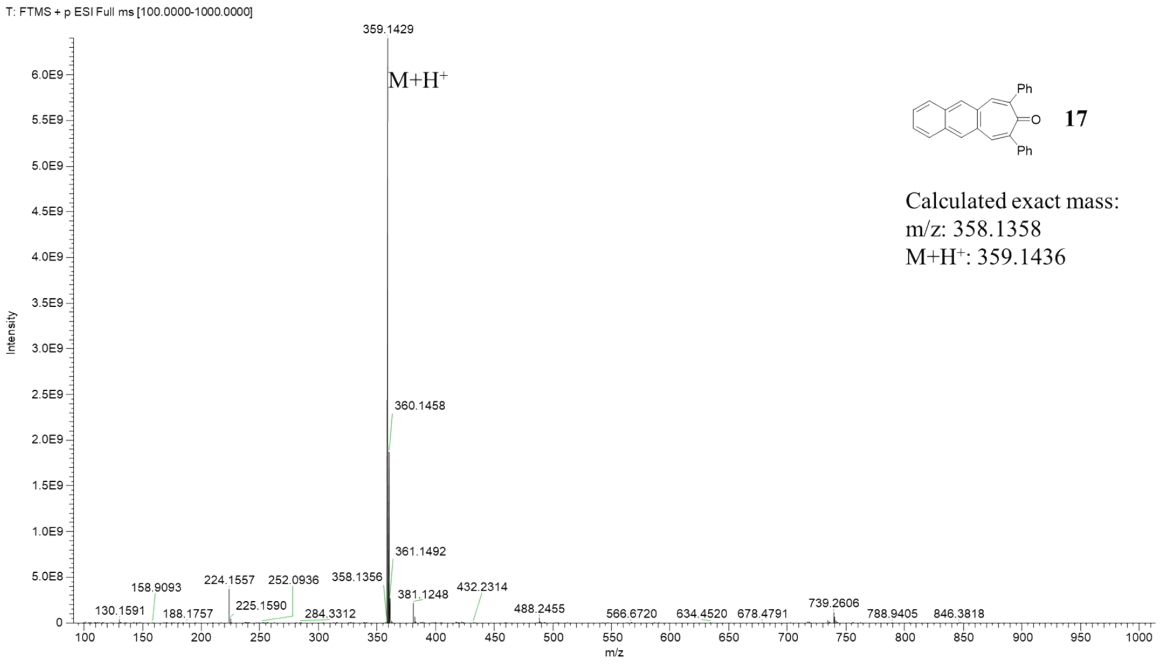
13

Calculated exact mass:
m/z: 474.2559
M+H+-Mes-H2O: 337.1592
M+H+-H2O: 457.2531



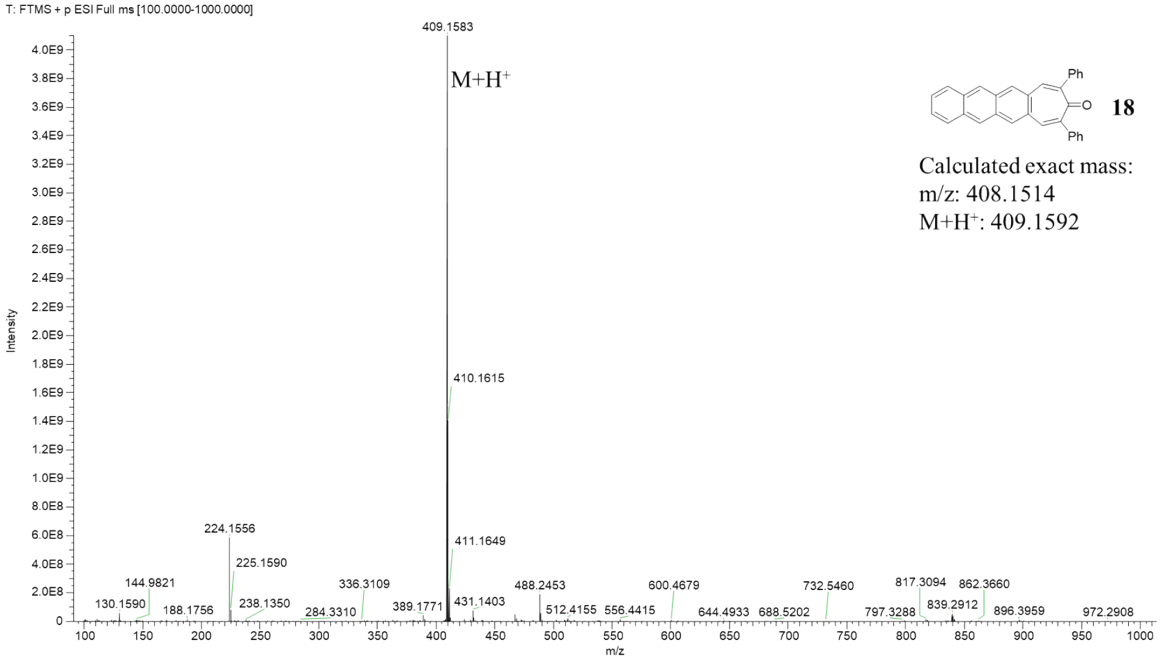
14

Calculated exact mass:
m/z: 524.2715
M+H+-Mes-H2O: 387.1749
M+H+-H2O: 507.2688
M+: 524.2715



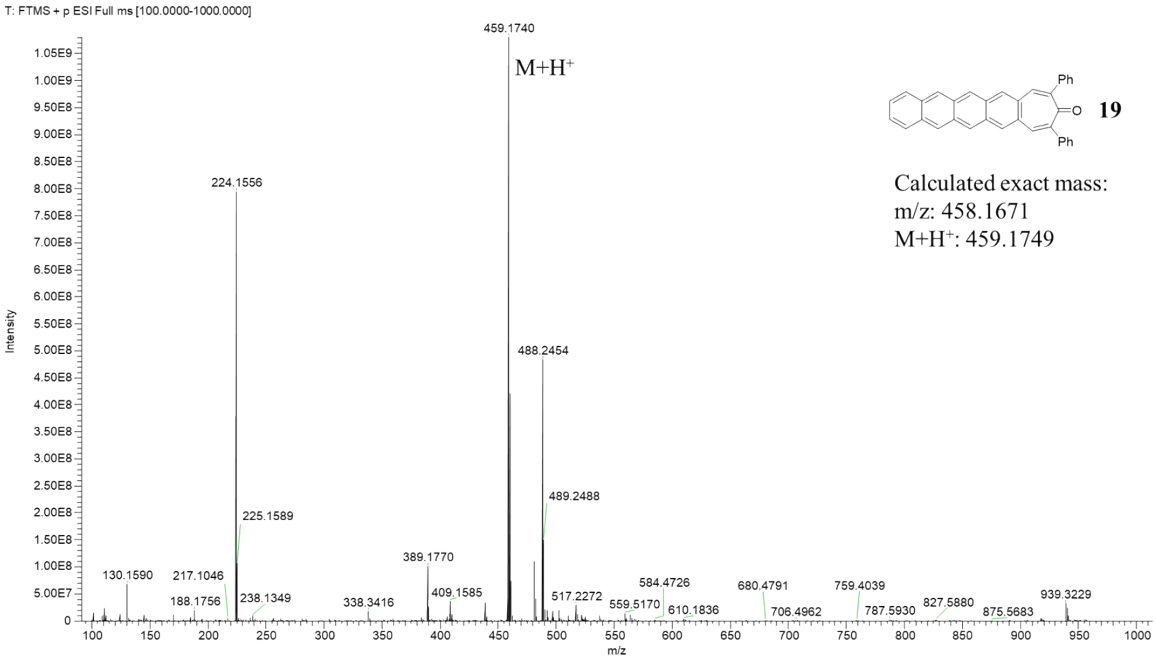
17

Calculated exact mass:
m/z: 358.1358
$M+H^+$: 359.1436



18

Calculated exact mass:
m/z: 408.1514
$M+H^+$: 409.1592



8. References

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