Supplementary Information

Intramolecular 5-*exo*, 7-*endo*-dig Transition Metal-Free Cyclization Sequence of (2-Alkynylphenyl) Benzyl Ethers: Synthesis of Seven-Membered Fused Benzo[*b*]furans

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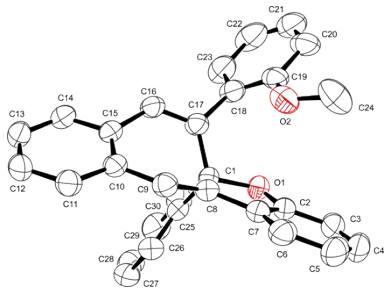
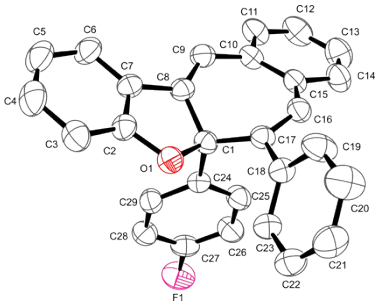
Materials and Methods

Proton nuclear magnetic resonance spectra (^{1}H NMR) were obtained on a NMR spectrometer at 400 MHz. Spectra were recorded in $CDCl_3$ solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of $CDCl_3$ or tetramethylsilane (TMS) as the external reference. Data are reported as follows: chemical shift (δ), multiplicity, coupling constant *(J)* in Hertz and integrated intensity. Carbon-13 nuclear magnetic resonance spectra (^{13}C NMR) were obtained on a 400 NMR spectrometer at 100 MHz. Spectra were recorded in $CDCl_3$ solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of $CDCl_3$. Abbreviations to denote the multiplicity of a particular signal are s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sex (sextet), dt (double triplet), td (triple doublet) and m (multiplet). High resolution mass spectra were recorded on a mass spectrometer using electrospray ionization (ESI). Column chromatography was performed using Silica Gel (230-400 mesh) following the methods described by Still.[1] Thin layer chromatography (TLC) was performed using Gel GF_{254}, 0.25 mm thickness. For visualization, TLC plates were either placed under ultraviolet light, or stained with iodine vapor, or acidic vanillin. Most reactions were monitored by TLC for disappearance of starting material. The following solvents were dried and purified by distillation from the reagents indicated: tetrahydrofuran from sodium with a benzophenone ketyl indicator. All other solvents were ACS or HPLC grade unless otherwise noted. Air- and moisture-sensitive reactions were conducted in flame-dried or oven dried glassware equipped with tightly fitted rubber septa and under a positive atmosphere of dry nitrogen or argon. Reagents and solvents were handled using standard syringe techniques. Spectroscopic grade solvents (Sigma-Aldrich) were used for fluorescence and UV-Vis measurements. UV-Vis electronic absorption spectra in solution were performed on a UV-2600 spectrophotometer at a concentration of 1.0×10^{-4} - 1.0×10^{-5} M range. Steady state fluorescence spectra were taken with an Cary Eclipse spectrofluorometer. The maximum absorption wavelength was used as excitation wavelength for fluorescence measurements. The quantum yield of fluorescence (Φ_F) was measured at 25 ºC using spectroscopic grade solvents within solutions with absorbance intensity lower than A = 0.2. 9,10-Diphenylanthracene (DPA, Aldrich) in $CHCl_3$ was used as fluorescence quantum yield standard (Φ_F = 0.65). Cyclic voltammograms were recorded on potenciostat/galvanostat system at room temperature under argon atmosphere, using

dry dichloromethane solution (Sigma-Aldrich). Electrochemical grade tetrabutylammonium hexafluorophosphate ($TBAPF_6$, Sigma-Aldrich) was used as supporting electrolyte. These experiments were carried out by employing a standard three component system: a glassy carbon working electrode; a platinum wire auxiliary electrode and a platinum wire *pseudo*-reference electrode. To monitor the reference electrode, the Fc/Fc^+ couple was used as an internal reference. All measurements were performed at room temperature (25 ºC).



cyclohepta[*b*]furan **2g**



cyclohepta[*b*]furan **2m**

Figure S1. The molecular structure with the atom-labeling scheme of the compounds 2g (CCDC 1485827) and 2m (CCDC 1485825) with 50% thermal ellipsoids (using ORTEP software[2]).

Description of the Solution of the X-ray Structure

Data were collected with a CCD area-detector diffractometer and graphite–monochromatized Mo–*K* radiation. The structure was solved by direct methods using SHELXS.[1] Subsequent Fourier-difference map analyses yielded the positions of the non-hydrogen atoms. Refinements were carried out with the SHELXL package.[1] All refinements were made by full-matrix least squares on F^2 with anisotropic displacement parameters for all non–hydrogen atoms. Hydrogen atoms were included in the refinement in calculated positions but the atoms (of hydrogens) that are commenting performing special bond were located in the Fourier map. Illustration of complexes was done using *ORTEP3* for Windows.[2]

Electrochemical Cyclic Voltammogram analysis

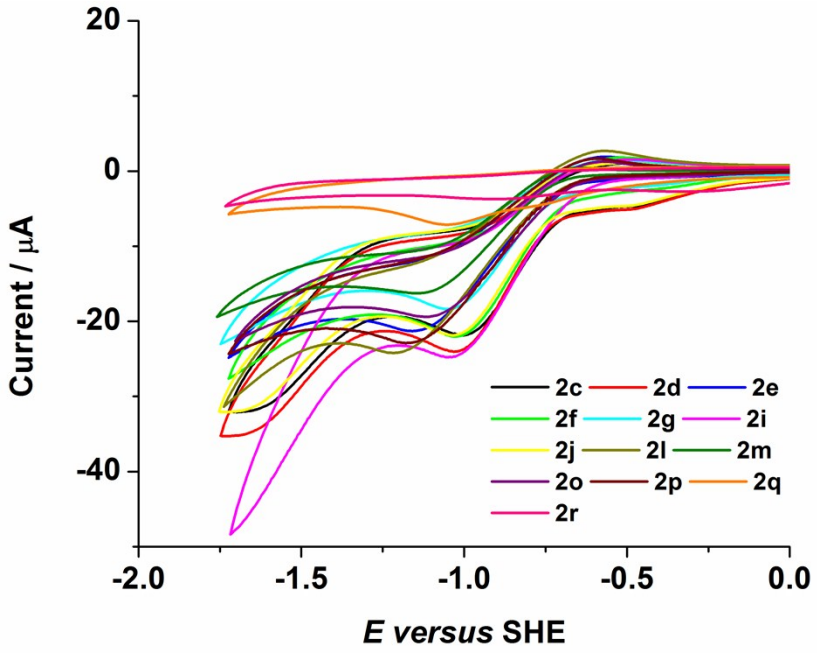


Figure S2. Cyclic voltammogram of related compounds in dry dichloromethane solution, containing 0.1 M $TBAPF_6$, as support electrolyte, using scan rate at 100 mV/s at the cathodic range.

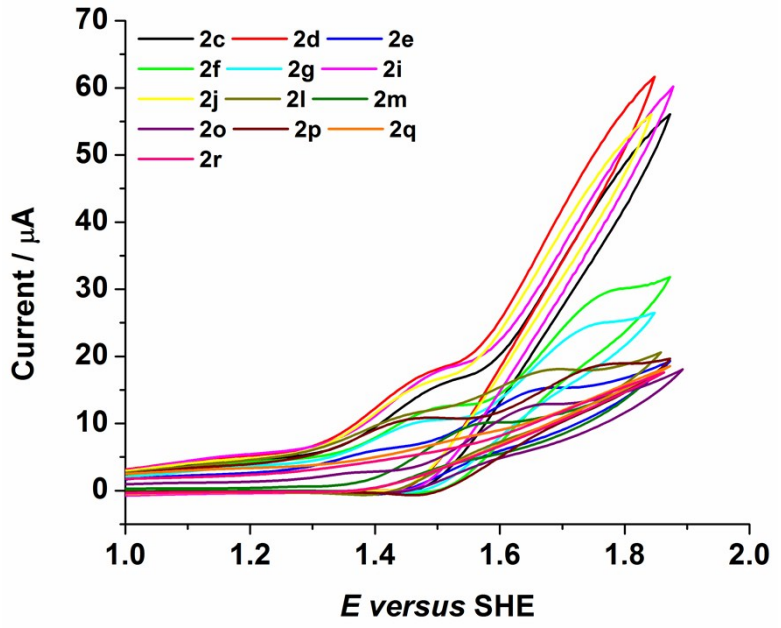
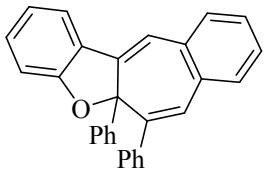


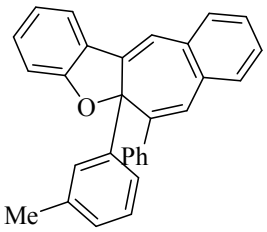
Figure S3. Cyclic voltammogram of related compounds in dry dichloromethane solution, containing 0.1 M $TBAPF_6$, as support electrolyte, using scan rate at 100 mV/s, at the anodic range.

General Procedure for the Preparation of *H*-benzo[4,5]cyclohepta[1,2-*b*]benzofurans Derivatives 2a-v

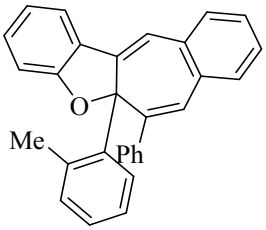
To a tube, under argon, containing the substrate **1** (0.25 mmol) and DMSO (2 mL), was added *t*-BuOK. The reaction mixture was allowed to stir for 1 h. After this time, the mixture was diluted with ethyl acetate (20 mL) and washed saturated solution of NH_4Cl (2 x 20 mL). The organic phase was separated, dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by column chromatography on silica gel.



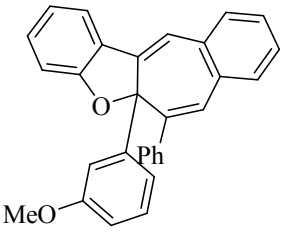
5a,6-diphenyl-5a*H*-benzo[4,5]cyclohepta[1,2-*b*]benzofuran (2a): Isolated by column chromatography (hexane as eluent) as a white yellow solid. Yield: 0.086 g (90 %), mp 76-79 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.52-7.50 (m, 1H), 7.48-7.40 (m, 2H), 7.30-7.23 (m, 7H), 7.20 (s, 1H), 7.17-7.02 (m, 6H), 6.93-6.90 (m, 2H), 6.71 (d, *J* = 8.0 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): *δ* 161.3, 142.6, 140.9, 140.6, 140.4, 135.0, 134.1, 131.3, 130.6, 129.9, 129.4, 129.3, 128.1, 127.9, 127.5, 127.3, 126.8, 126.2, 126.1, 126.0, 121.0, 120.7, 116.5, 110.5, 91.5. MS (EI, 70 eV; *m/z* (relative intensity)): 385 ([M + 1], 8), 384 (28), 307 (100), 276 (10), 205 (3), 169 (3), 153 (11), 138 (4). HRMS (ESI-TOF) *m/z* calcd for $C_{29}H_{21}O$ [M + H]$^+$: 385.1592. Found: 385.1602.



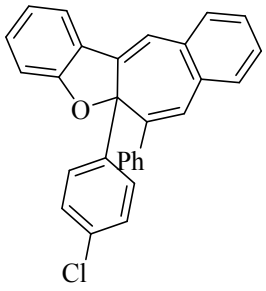
6-phenyl-5a-(*m*-tolyl)-5a*H*-benzo[4,5]cyclohepta[1,2-*b*]benzofuran (2c): Isolated by column chromatography (hexane as eluent) as a white yellow viscous oil. Yield: 0.069 g (70 %). ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.56-7.52 (m, 1H), 7.49-7.42 (m, 2H), 7.36-7.25 (m, 5H), 7.22 (s, 1H), 7.20-7.07 (m, 5H), 6.99-6.91 (m, 3H), 6.90-6.86 (m, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 2.12 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): *δ* 161.3, 142.6, 140.9, 140.7, 140.3, 137.5, 135.1, 134.2, 131.2, 130.6, 129.9, 129.4, 129.3, 128.9, 127.7, 127.5, 127.2, 126.9, 126.7, 126.2, 126.1, 123.4, 121.0, 120.7, 116.4, 110.5, 91.5, 21.4. MS (EI, 70 eV; *m/z* (relative intensity)): 400 ([M + 2], 3), 399 ([M + 1], 19), 398 (60), 383 (4), 321 (68), 307 (100), 276 (11), 205 (4), 160 (10), 138 (4). HRMS (ESI-TOF) *m/z* calcd for $C_{30}H_{23}O$ [M + H]$^+$: 399.1749. Found: 399.1752.



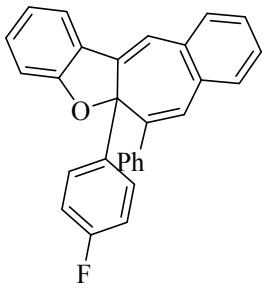
6-phenyl-5a-(*o*-tolyl)-5a*H*-benzo[4,5]cyclohepta[1,2-*b*]benzofuran (2d): Isolated by column chromatography (hexane as eluent) as a yellow viscous oil. Yield: 0.054 g (55 %). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.51-7.42 (m, 4H), 7.35-7.21 (m, 5H), 7.20-7.02 (m, 4H), 6.99-6.87 (m, 4H), 6.85-6.79 (m, 1H), 6.65 (d, J = 8.0 Hz, 1H), 2.19 (s, 3H). ^{13}C NMR {^{1}H} ($CDCl_3$, 100 MHz): δ 161.9, 141.8, 141.7, 139.9, 138.2, 135.3, 135.2, 134.3, 132.2, 130.6, 130.2, 129.4, 129.1, 129.0, 128.7, 128.2, 127.5, 127.2, 126.4, 126.3, 125.8, 124.6, 121.1, 120.5, 114.6, 109.9, 92.7, 21.7. MS (EI, 70 eV; *m/z* (relative intensity)): 400 ([M + 2], 3), 399 ([M + 1], 33), 398 (100), 383 (7), 321 (24), 307 (67), 276 (17), 205 (11), 176 (12). HRMS (ESI-TOF) *m/z* calcd for $C_{30}H_{23}O$ $[M + H]^+$: 399.1749. Found: 399.1755.



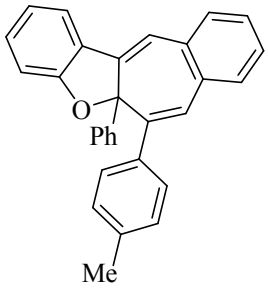
5a-(3-methoxyphenyl)-6-phenyl-5a*H*-benzo[4,5]cyclohepta[1,2-*b*]benzofuran (2e): Isolated by column chromatography (hexane as eluent) as a white yellow viscous oil. Yield: 0.083 g (81 %). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52 (ddd, J = 7.6 Hz, J = 1.3 Hz, J = 0.5 Hz, 1H), 7.48-7.42 (m, 2H), 7.35-7.26 (m, 5H), 7.21 (s, 1H), 7.20-7.11 (m, 3H), 6.99 (t, J = 8.0 Hz, 1H), 6.96-6.92 (m, 2H), 6.90 (ddd, J = 7.8 Hz, J = 1.7 Hz, J = 1.1 Hz, 1H), 6.86-6.83 (m, 1H), 6.77-6.73 (m, 1H), 6.62 (ddd, J = 8.0 Hz, J = 3.0 Hz, J = 1.0 Hz, 1H), 3.52 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$. 100 MHz): δ 161.2, 159.2, 142.3, 142.2, 140.9, 140.7, 135.0, 134.1, 131.3, 130.6, 130.0, 129.5, 129.3, 128.9, 127.5, 127.3, 126.8, 126.2, 126.0, 121.0, 120.8, 118.5, 116.6, 113.6, 112.1, 110.5, 91.2, 55.0. MS (EI, 70 eV; *m/z* (relative intensity)): 415 ([M + 1], 14), 414 (42), 337 (58), 321 (10), 307 (100), 276 (10), 207 (4), 163 (6), 138 (4). HRMS (ESI-TOF) *m/z* calcd for $C_{30}H_{23}O_2$ $[M + H]^+$: 415.1698. Found: 415.1704.



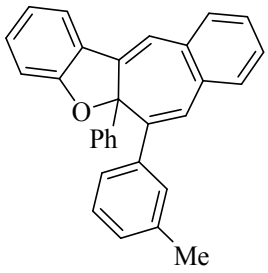
5a-(4-chlorophenyl)-6-phenyl-5a*H*-benzo[4,5]cyclohepta[1,2-*b*]benzofuran (2f): Isolated by column chromatography (hexane as eluent) as a white yellow solid. Yield: 0.068 g (65 %), mp 174-176 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.54 (ddd, *J* = 7.6 Hz, *J* = 1.3 Hz, *J* = 0.6 Hz, 1H), 7.46-7.40 (m, 2H), 7.38-7.11 (m, 11H), 7.03 (d, *J* = 9.0 Hz, 2H), 6.98-6.92 (m, 2H), 6.77-6.72 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): *δ* 161.1, 142.3, 140.6, 140.3, 139.1, 134.9, 134.0, 133.9, 131.3, 130.8, 130.0, 129.5, 129.3, 128.1, 127.8, 127.6, 127.4, 127.0, 126.4, 125.9, 121.2, 120.8, 116.7, 110.5, 90.8. MS (EI, 70 eV; *m/z* (relative intensity)): 420 ([M + 2], 13), 419 ([M + 1], 13), 418 (38), 383 (3), 341 (72), 307 (100), 276 (22), 207 (8), 152 (16). HRMS (ESI-TOF) *m/z* calcd for $C_{29}H_{20}ClO$ $[M + H]^+$: 419.1203. Found: 419.1210.



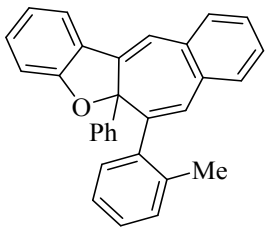
5a-(4-fluorophenyl)-6-phenyl-5a*H*-benzo[4,5]cyclohepta[1,2-*b*]benzofuran (2g): Isolated by column chromatography (hexane as eluent) as a white yellow solid. Yield: 0.087 g (87 %), mp 183-185 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.54 (ddd, *J* = 7.6 Hz, *J* = 1.3 Hz, *J* = 0.5 Hz, 1H), 7.47-7.42 (m, 2H), 7.36-7.25 (m, 7H), 7.23 (s, 1H), 7.21-7.11 (m, 3H), 6.97-6.92 (m, 2H), 6.78-6.69 (m, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): *δ* 162.3 (d, *J* = 247.0 Hz), 161.0, 142.5, 140.7, 140.3, 136.3 (d, *J* = 3.0 Hz), 134.8, 134.0, 131.2, 130.7, 129.8, 129.4, 129.3, 128.2 (d, *J* = 8.0 Hz), 127.6, 127.4, 126.9, 126.3, 125.8, 121.1, 120.7, 116.5, 114.7 (d, *J* = 21.0 Hz), 110.5, 90.8. MS (EI, 70 eV; *m/z* (relative intensity)): 403 ([M + 1], 20), 402 (61), 325 (100), 307 (95), 276 (12), 205 (5), 162 (11), 153 (12). HRMS (ESI-TOF) *m/z* calcd for $C_{29}H_{20}FO$ $[M + H]^+$: 403.1498. Found: 403.1503.



5a-phenyl-6-(*p*-tolyl)-5a*H*-benzo[4,5]cyclohepta[1,2-*b*]benzofuran (2h): Isolated by column chromatography (hexane as eluent) as a white yellow solid. Yield: 0.069 g (70 %), mp 170-173 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.56 (d, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.33-7.24 (m, 4H), 7.23 (s, 1H), 7.21-7.01 (m, 8H), 6.99-6.90 (m, 2H), 6.75 (d, *J* = 8.0 Hz, 1H), 2.36 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): *δ* 161.3, 142.5, 140.7, 140.4, 137.8, 137.0, 135.0, 134.0, 131.2, 130.5, 129.8, 129.2, 128.9, 128.2, 128.0, 127.8, 126.6, 126.2, 126.1, 120.9, 120.6, 116.5, 110.5, 91.5, 21.1. MS (EI, 70 eV; *m/z* (relative intensity)): 399 ([M+1], 10), 398 (47), 321 (100), 307 (72), 276 (14), 253 (16), 207 (15), 177 (9). HRMS (ESI-TOF) *m/z* calcd for $C_{30}H_{23}O$ [M + H]$^{+}$: 399.1749. Found: 399.1758.

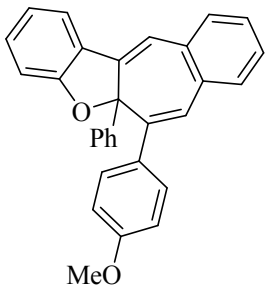


5a-phenyl-6-(*m*-tolyl)-5a*H*-benzo[4,5]cyclohepta[1,2-*b*]benzofuran (2i): Isolated by column chromatography (hexane as eluent) as a white yellow viscous oil. Yield: 0.080 g (80 %). ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.57-7.47 (m, 1H), 7.36-6.99 (m, 15H), 6.97-6.89 (m, 2H), 6.77-6.71 (m, 1H), 2.33 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): *δ* 161.3, 142.7, 140.9, 140.5, 140.4, 137.1, 135.0, 134.1, 131.2, 130.6, 129.9, 129.8, 129.2, 128.1, 128.0, 127.9, 127.4, 126.7, 126.6, 126.3, 126.1, 126.0, 121.0, 120.7, 116.4, 110.5, 91.5, 21.4. MS (EI, 70 eV; *m/z* (relative intensity)): 399 ([M + 1], 13), 398 (47), 321 (100), 307 (83), 276 (15), 207 (11), 163 (6), 153 (8). HRMS (ESI-TOF) *m/z* calcd for $C_{30}H_{23}O$ [M + H]$^{+}$: 399.1749. Found: 399.1755.

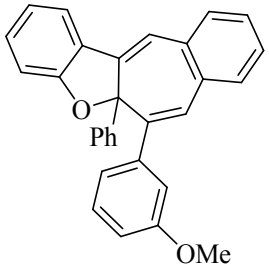


5a-phenyl-6-(*o*-tolyl)-5a*H*-benzo[4,5]cyclohepta[1,2-*b*]benzofuran (2j): Isolated by column chromatography (hexane as eluent) as a white

yellow viscous oil. Yield: 0.089 g (90 %). ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.53 (d, *J* = 7.6 Hz, 1H), 7.40-7.10 (m, 12H), 7.09-6.98 (m, 3H), 6.91 (td, *J* = 7.6 Hz, *J* = 0.7 Hz, 1H), 6.74-6.67 (m, 2H), 1.96 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): *δ* 161.5, 142.0, 140.9, 140.5, 140.0, 137.1, 134.8, 134.4, 131.3, 130.7, 130.2, 129.8, 129.5, 128.9, 127.9, 127.8, 127.2, 126.9, 126.3, 126.1, 125.9, 124.9, 121.0, 120.8, 117.0, 110.5, 91.7, 20.2. MS (EI, 70 eV; *m/z* (relative intensity)): 400 ([M + 2], 3), 399 ([M + 1], 19), 398 (59), 321 (100), 307 (39), 276 (10), 205 (3), 169 (6), 138 (4). HRMS (ESI-TOF) *m/z* calcd for $C_{30}H_{23}O$ [M + H]$^+$: 399.1749. Found: 399.1753.

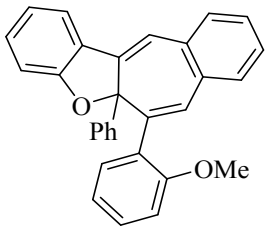


6-(4-methoxyphenyl)-5a-phenyl-5a*H*-benzo[4,5]cyclohepta[1,2-*b*]benzofuran (2k): Isolated by column chromatography (hexane as eluent) as a white yellow solid. Yield: 0.081 g (79 %), mp 163-166 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.50 (d, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 8.7 Hz, 2H), 7.34-7.22 (m, 4H), 7.20 (s, 1H), 7.18-7.00 (m, 6H), 6.95-6.88 (m, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.74 (d, *J* = 8.0 Hz, 1H), 3.76 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): *δ* 161.2, 159.0, 142.4, 140.5, 140.3, 135.1, 134.0, 133.2, 131.2, 130.6, 130.5, 129.8, 128.5, 128.0, 127.9, 126.5, 126.2, 126.1, 126.0, 121.0, 120.7, 116.5, 113.0, 110.4, 91.6, 55.2. MS (EI, 70 eV; *m/z* (relative intensity)): 415 ([M + 1], 15), 414 (48), 337 (100), 307 (65), 293 (19), 276 (8), 207 (7), 163 (7). HRMS (ESI-TOF) *m/z* calcd for $C_{30}H_{23}O_2$ [M + H]$^+$: 415.1698. Found: 415.1708.

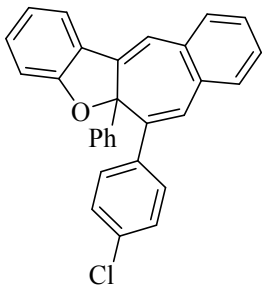


6-(3-methoxyphenyl)-5a-phenyl-5a*H*-benzo[4,5]cyclohepta[1,2-*b*]benzofuran (2l): Isolated by column chromatography (hexane as eluent) as a yellow viscous oil. Yield: 0.072 g (70 %). ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.56-7.50 (m, 1H), 7.34-7.02 (m, 13H), 7.00-6.97 (m, 1H), 6.96-6.90 (m, 2H), 6.85 (ddd, *J* = 8.2 Hz, *J* = 2.6 Hz, *J* = 1.0 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 3.73 (s, 3H).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 161.3, 159.0, 142.7, 142.1, 140.8, 140.5, 134.9, 134.3, 131.4, 130.7, 130.0, 129.4, 128.5, 128.1, 128.0, 126.9, 126.3, 126.2, 126.1, 122.1, 121.1, 120.8, 116.6, 115.1, 113.1, 110.6, 91.5, 55.3. MS (EI, 70 eV; *m/z* (relative intensity)): 415 ([M + 1], 18), 414 (65), 337 (99), 307 (100), 293 (17), 276 (11), 207 (13), 163 (9). HRMS (ESI-TOF) *m/z* calcd for $C_{30}H_{23}O_2$ $[M + H]^+$: 415.1698. Found: 415.1703.

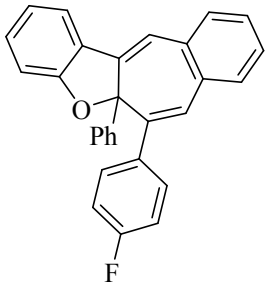


6-(2-methoxyphenyl)-5a-phenyl-5a*H*-benzo[4,5]cyclohepta[1,2-*b*]benzofuran (2m): Isolated by column chromatography (hexane as eluent) as a white solid. Yield: 0.084 g (82 %), mp 138-140 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.57 (d, *J* = 7.3 Hz, 1H), 7.42 (s*l*, 1H), 7.36-7.23 (m, 5H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.18-6.88 (m, 8H), 6.79 (s, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 3.19 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 162.4, 157.8, 142.9, 139.9, 139.2, 134.8, 134.7, 130.7, 130.6, 130.5, 130.3, 129.7, 128.8, 128.2, 127.6, 127.5, 126.4, 126.3, 125.8, 120.6, 120.4, 120.1, 115.9, 110.1, 109.8, 91.4, 54.6. MS (EI, 70 eV; *m/z* (relative intensity)): 416 ([M + 2], 4), 415 ([M + 1], 23), 414 (69), 337 (100), 321 (52), 307 (60), 292 (8), 276 (8), 207 (6), 168 (9). HRMS (ESI-TOF) *m/z* calcd for $C_{30}H_{23}O_2$ $[M + H]^+$: 415.1698. Found: 415.1700.

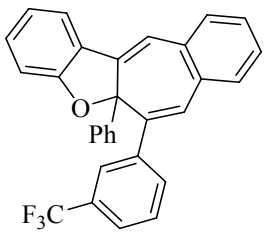


6-(4-chlorophenyl)-5a-phenyl-5a*H*-benzo[4,5]cyclohepta[1,2-*b*]benzofuran (2n): Isolated by column chromatography (hexane as eluent) as a white yellow viscous oil. Yield: 0.086 g (83 %). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.55-7.51 (m, 1H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.34-7.23 (m, 6H), 7.22-7.00 (m, 7H), 6.94 (td, *J* = 7.5 Hz, *J* = 0.9 Hz, 1H), 6.91 (s, 1H), 6.77-6.72 (m, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 161.1, 142.5, 140.2, 139.5, 138.9, 134.7, 134.1, 133.3, 131.3, 130.7, 130.6, 129.9, 129.6, 128.2, 128.0, 127.7, 127.0, 126.3, 126.1, 126.0, 121.2, 120.8, 116.6, 110.5, 91.2. MS (EI, 70 eV; *m/z* (relative intensity)): 420 ([M + 2], 18), 419 ([M + 1], 18), 418

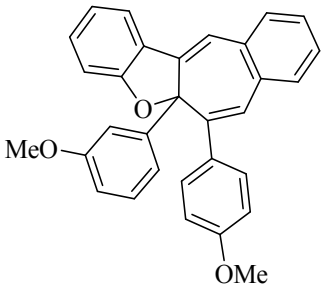
(56), 341 (100), 307 (85), 276 (27), 205 (9), 176 (12), 153 (25). HRMS (ESI-TOF) *m/z* calcd for $C_{29}H_{20}ClO$ $[M + H]^+$: 419.1203. Found: 419.1225.



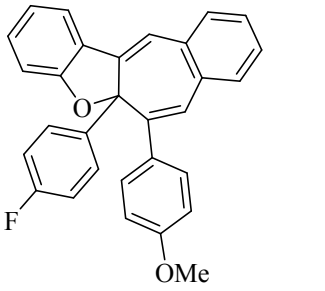
6-(4-fluorophenyl)-5a-phenyl-5a*H*-benzo[4,5]cyclohepta[1,2-*b*]benzofuran (2o): Isolated by column chromatography (hexane as eluent) as a yellow viscous oil. Yield: 0.088 g (88 %). ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.53 (ddd, *J* = 7.6 Hz, *J* = 1.3 Hz, *J* = 0.6 Hz, 1H), 7.45-7.38 (m, 2H), 7.33-7.24 (m, 4H), 7.22 (s, 1H), 7.21-7.12 (m, 3H), 7.11-7.04 (m, 3H), 7.03-6.91 (m, 3H), 6.91 (s, 1H), 6.75-6.72 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): *δ* 162.2 (d, *J* = 247.0 Hz), 161.1, 142.5, 140.2, 139.6, 136.5 (d, *J* = 3.0 Hz), 134.8, 134.1, 131.3, 131.0 (d, *J* = 8.0 Hz), 130.7, 129.9, 129.3, 128.2, 128.0, 126.9, 126.2, 126.1, 126.0, 121.1, 120.7, 116.6, 114.4 (d, *J* = 21.0 Hz), 110.4, 91.3. MS (EI, 70 eV; *m/z* (relative intensity)): 403 ([M + 1], 16), 402 (50), 325 (100), 307 (58), 276 (8), 205 (5), 176 (4), 153 (13). HRMS (ESI-TOF) *m/z* calcd for $C_{29}H_{20}FO$ $[M + H]^+$: 403.1498. Found: 403.1503.



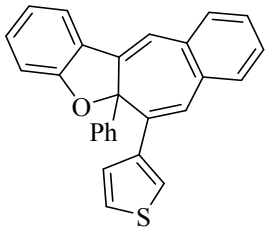
5a-phenyl-6-(3-(trifluoromethyl)phenyl)-5a*H*-benzo[4,5]cyclohepta[1,2-*b*]benzofuran (2p): Isolated by column chromatography (hexane as eluent) as a white yellow solid. Yield: 0.061 g (54 %), mp 59-61 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.71 (s, 1H), 7.63 (d, *J* = 7.5 Hz, 1H), 7.56 (d, *J* = 7.5 Hz, 2H), 7.46-7.37 (m, 1H), 7.36-7.02 (m, 11H), 7.01-6.90 (m, 2H), 6.73 (d, *J* = 8.0 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): *δ* 161.1, 142.8, 141.3, 140.2, 139.5, 134.7, 134.5, 132.9, 131.4, 130.9, 130.3 (quart, *J* = 32.0 Hz), 130.2, 130.0, 128.3, 128.0, 127.9, 127.2, 126.3, 126.2 (2C), 126.0, 124.3 (quart, *J* = 272.0 Hz), 124.0 (quart, *J* = 4.0 Hz), 121.3, 120.8, 116.7, 110.6, 91.2. MS (EI, 70 eV; *m/z* (relative intensity)): 453 ([M + 1], 14), 452 (45), 375 (100), 307 (69), 276 (11), 205 (5), 176 (5), 153 (20). HRMS (ESI-TOF) *m/z* calcd for $C_{30}H_{20}F_3O$ $[M + H]^+$: 453.1466. Found: 453.1471.



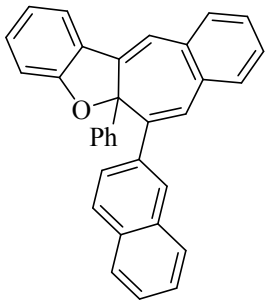
5a-(3-methoxyphenyl)-6-(4-methoxyphenyl)-5a*H*-benzo[4,5]cyclohepta[1,2-*b*]benzofuran (2q): Isolated by column chromatography (hexane as eluent) as a yellow solid. Yield: 0.083 g (75 %), mp 156-159 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52 (ddd, J = 7.6 Hz, J = 1.3 Hz, J = 0.6 Hz, 1H), 7.41 (d, J = 8.9 Hz, 2H), 7.35-7.26 (m, 2H), 7.21 (s, 1H), 7.20-7.10 (m, 3H), 7.02-6.96 (m, 1H), 6.95-6.89 (m, 3H), 6.88-6.82 (m, 3H), 6.78-6.74 (m, 1H), 6.62 (ddd, J = 8.0 Hz, J = 2.6 Hz, J = 1.0 Hz, 1H), 3.80 (s, 3H), 3.53 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 161.2, 159.1, 159.0, 142.2, 142.1, 140.4, 135.1, 134.0, 133.3, 131.3, 130.6, 130.5, 129.9, 128.9, 128.6, 126.6, 126.2, 126.1, 121.0, 120.7, 118.6, 116.6, 113.5, 113.0, 112.2, 110.4, 91.4, 55.2, 55.0. MS (EI, 70 eV; *m/z* (relative intensity)): 446 ([M + 2], 2), 445 ([M + 1], 16), 444 (50), 429 (2), 413 (3), 337 (100), 321 (6), 293 (15), 265 (4), 163 (4). HRMS (ESI-TOF) *m/z* calcd for $C_{31}H_{25}O_3$ [M + H]$^{+}$: 445.1804. Found: 445.1810.



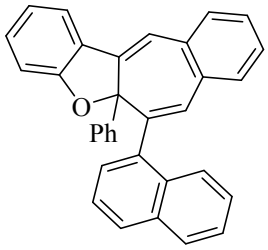
5a-(4-fluorophenyl)-6-(4-methoxyphenyl)-5a*H*-benzo[4,5]cyclohepta[1,2-*b*]benzofuran (2r): Isolated by column chromatography (hexane as eluent) as a white yellow solid. Yield: 0.064 g (60 %), mp 75-78 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.53 (ddd, J = 7.6 Hz, J = 1.3 Hz, J = 0.5 Hz, 1H), 7.40 (d, J = 8.9 Hz, 2H), 7.35-7.09 (m, 8H), 6.94 (td, J = 7.6 Hz, J = 0.9 Hz, 1H), 6.91 (s, 1H), 6.86 (d, J = 8.9 Hz, 2H), 6.78-6.70 (m, 3H), 3.81 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 162. 3 (d, J = 247. 0 Hz), 161.1, 159.1, 142.5, 140.3, 136.4 (d, J = 3.0 Hz), 135.0, 133.9, 133.0, 131.2, 130.7, 130.6, 129.8, 128.5, 128.2 (d, J = 8.0 Hz), 126.7, 126.2, 125.9, 121.1, 120.7, 116.5, 114.7 (d, J = 22.0 Hz), 113.0, 110.5, 91.0, 55.2. MS (EI, 70 eV; *m/z* (relative intensity)): 434 ([M + 2], 4), 433 ([M + 1], 30), 432 (96), 417 (3), 401 (3), 337 (100), 325 (99), 294 (20), 276 (4), 168 (11). HRMS (ESI-TOF) *m/z* calcd for $C_{30}H_{22}FO_2$ [M + H]$^{+}$: 433.1604. Found: 433.1609.



5a-phenyl-6-(thiophen-3-yl)-5a*H*-benzo[4,5]cyclohepta[1,2-*b*]benzofuran (2s): Isolated by column chromatography (hexane as eluent) as a white yellow viscous oil. Yield: 0.073 g (75 %). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.55 (ddd, J = 7.6 Hz, J = 1.3 Hz, J = 0.6 Hz, 1H), 7.48 (dd, J = 3.0 Hz, J = 1.3 Hz, 1H), 7.40-7.00 (m, 14H), 6.95 (td, J = 7.6 Hz, J = 0.9 Hz, 1H), 6.84-6.77 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 161.0, 142.2, 141.1, 140.2, 135.5, 134.8, 134.3, 131.2, 130.7, 129.8, 129.2, 128.1, 128.0, 127.9, 126.7, 126.3, 126.2, 126.1, 124.2, 124.0, 121.0, 120.7, 116.7, 110.5, 91.5. MS (EI, 70 eV; *m/z* (relative intensity)): 392 ([M + 2], 5), 391 ([M + 1], 17), 390 (54), 357 (6), 313 (100), 285 (7), 252 (7), 205 (4), 153 (5). HRMS (ESI-TOF) *m/z* calcd for $C_{27}H_{19}OS$ [M + H]$^{+}$: 391.1157. Found: 391.1163.

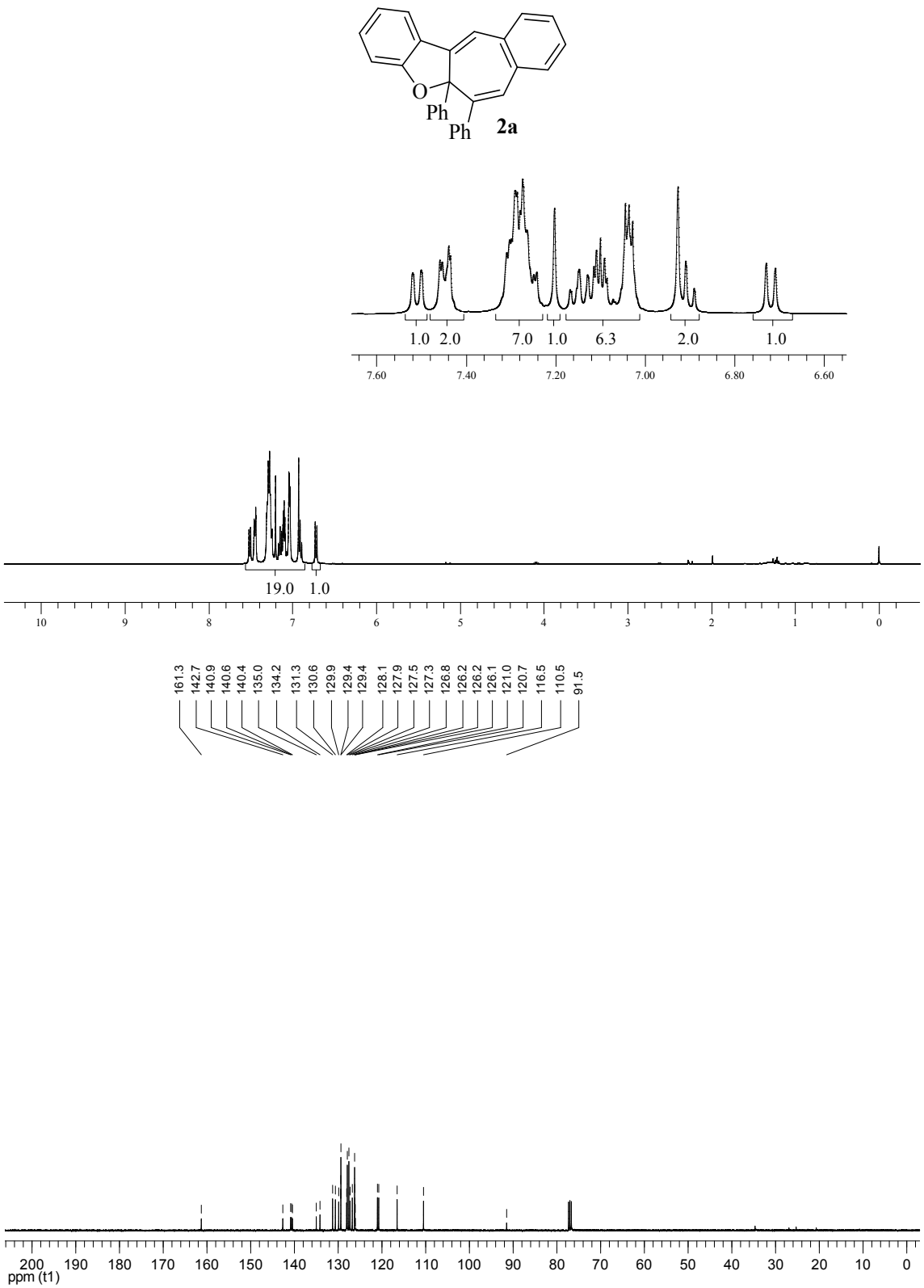


6-(naphthalen-2-yl)-5a-phenyl-5a*H*-benzo[4,5]cyclohepta[1,2-*b*]benzofuran (2t): Isolated by column chromatography (hexane as eluent) as a white yellow viscous oil. Yield: 0.097 g (90 %). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.92-7.88 (m, 1H), 7.84-7.77 (m, 2H), 7.75 (d, J = 8.6 Hz, 1H), 7.60 (dd, J = 8.6 Hz, J = 1.8 Hz, 1H), 7.55 (ddd, J = 7.6 Hz, J = 1.3 Hz, J = 0.5 Hz, 1H), 7.46-7.39 (m, 2H), 7.38-7.27 (m, 4H), 7.25 (s, 1H), 7.19-7.06 (m, 6H), 7.05 (s, 1H), 6.93 (td, J = 7.6 Hz, J = 0.9 Hz, 1H), 6.71-6.67 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 161.4, 142.9, 140.9, 140.5, 138.5, 135.1, 134.3, 133.3, 132.8, 131.3, 130.7, 129.9, 129.7, 128.3, 128.2, 128.1, 128.0, 127.9, 127.6, 126.8, 126.6, 126.4, 126.2, 126.1, 126.0, 125.9, 121.1, 120.8, 116.5, 110.6, 91.7. MS (EI, 70 eV; *m/z* (relative intensity)): 436 ([M + 2], 5), 435 ([M + 1], 30), 434 (87), 357 (100), 307 (88), 276 (7), 178 (19), 163 (10), 77 (6). HRMS (ESI-TOF) *m/z* calcd for $C_{33}H_{23}O$ [M + H]$^{+}$: 435.1749. Found: 435.1758.

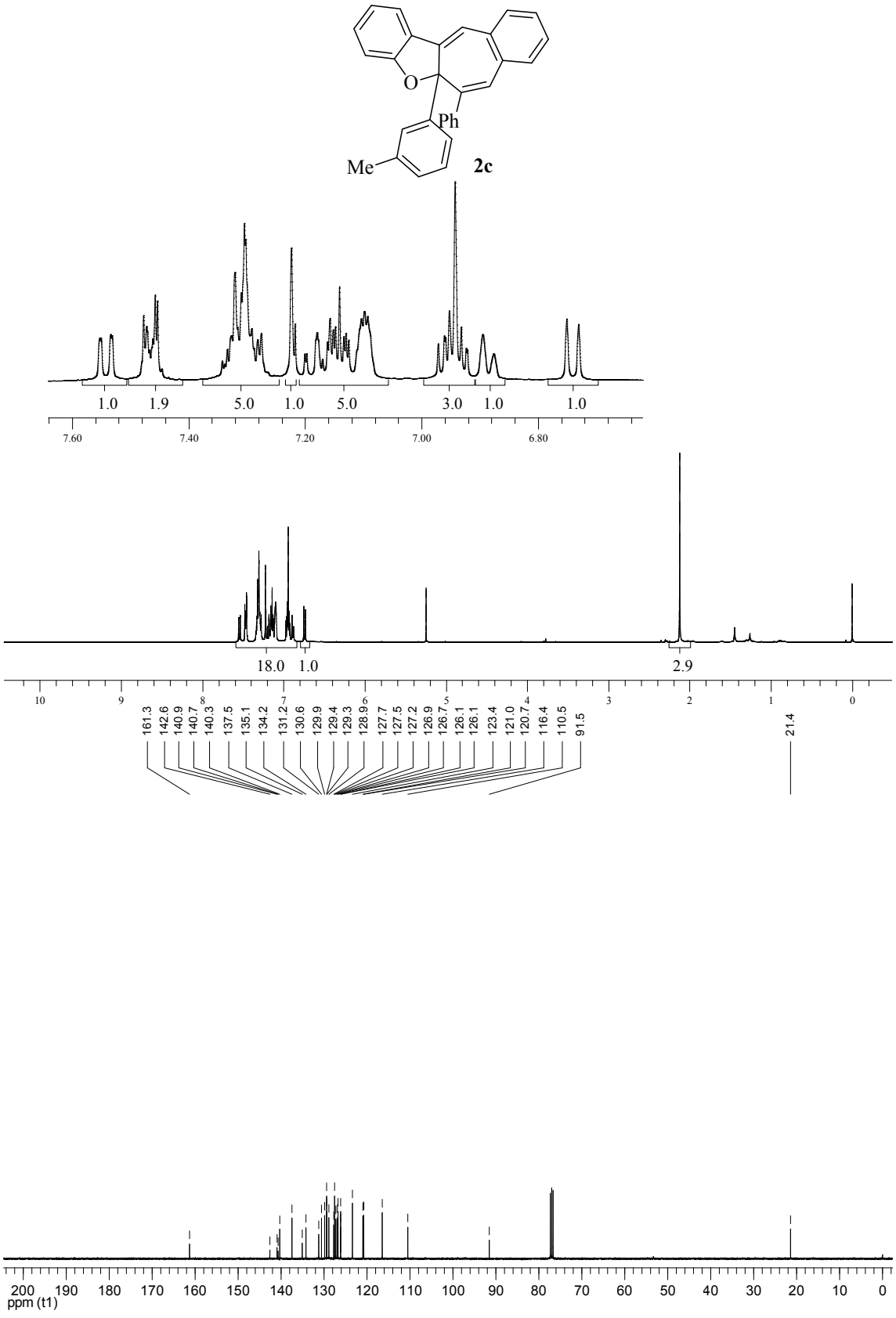


6-(naphthalen-1-yl)-5a-phenyl-5a*H*-benzo[4,5]cyclohepta[1,2-*b*]benzofuran (2u): Compounds **2u** and **2u'** exist as an inseparable mixture (**2u**:**2u'** / 5:1, determined by ^{1}H NMR) isolated by column chromatography (hexane as eluent) as a white yellow viscous oil. Total yield: 0.084 g (78 %). The combined chemical shifts are reported. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.02-7.96 (m, 0, 2H), 7.88-7.84 (m, 0.2H), 7.83-7.75 (m, 2.3H), 7.63-7.58 (m, 2H), 7.57-7.54 (m, 1H), 7.52-6.84 (m, 20.7H), 6.67-6.62 (m, 0.2H), 6.39-6.33 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 161.5, 161.0, 142.1, 140.4, 139.7, 139.3, 139.0, 138.5, 138.1, 134.8, 134.7, 134.5, 133.9, 133.3, 132.9, 132.6, 131.3, 131.1, 130.7, 130.6, 130.3, 130.2, 130.1, 130.0, 128.6, 128.3, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.1, 127.0, 126.9, 126.8, 126.7, 126.4, 126.2, 126.1, 126.0, 125.9, 125.8, 125.4, 125.3, 124.9, 124.6, 121.1, 121.0, 120.9, 120.7, 117.1, 116.8, 110.6, 110.5, 91.8. MS (EI, 70 eV; *m/z* (relative intensity)): 436 ([M + 2], 4), 435 ([M + 1], 26), 434 (75), 357 (100), 326 (11), 307 (35), 217 (3), 178 (13), 163 (10). HRMS (ESI-TOF) *m/z* calcd for $C_{33}H_{23}O$ [M + H]$^{+}$: 435.1749. Found: 435.1760.

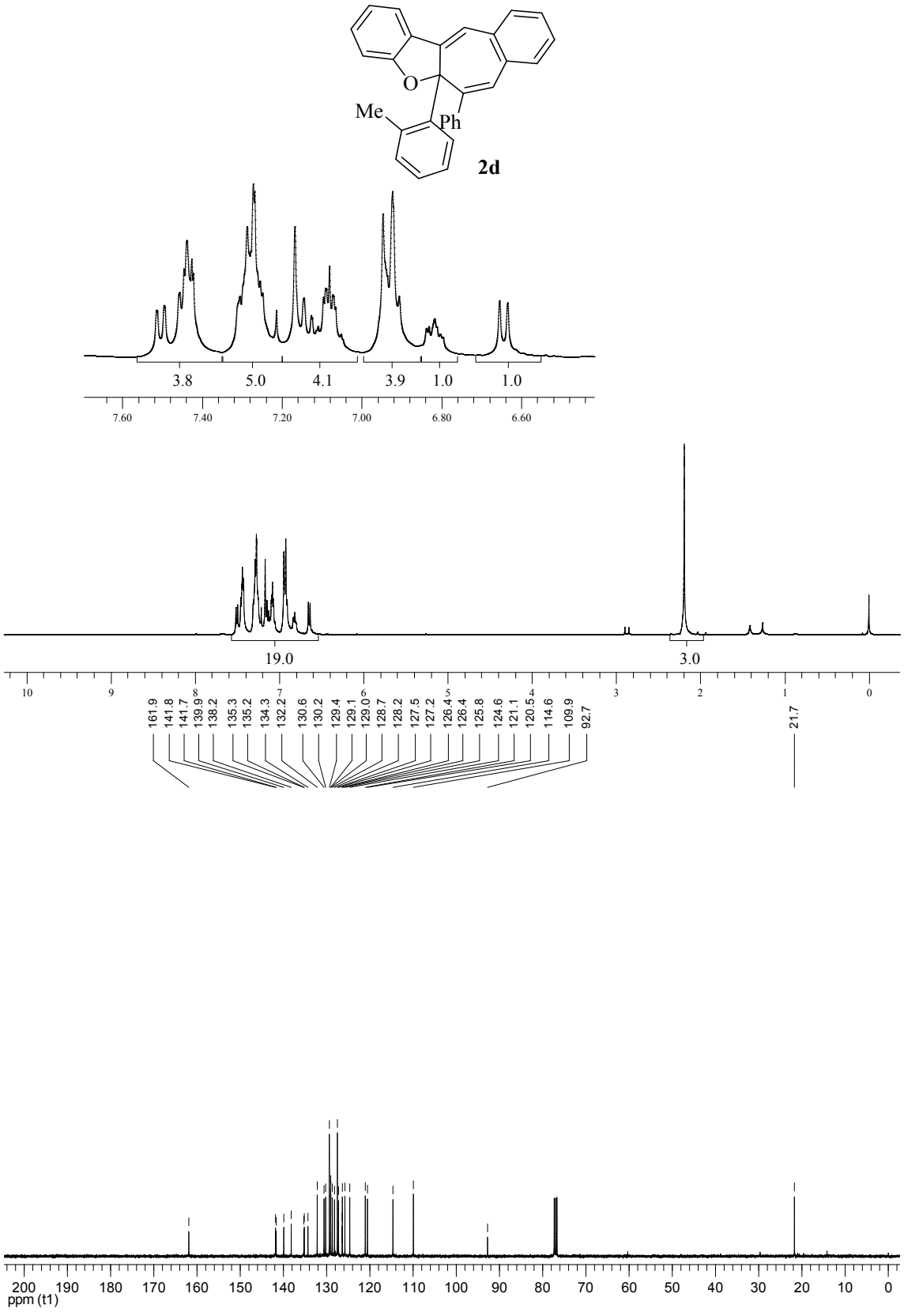
NMR Spectra



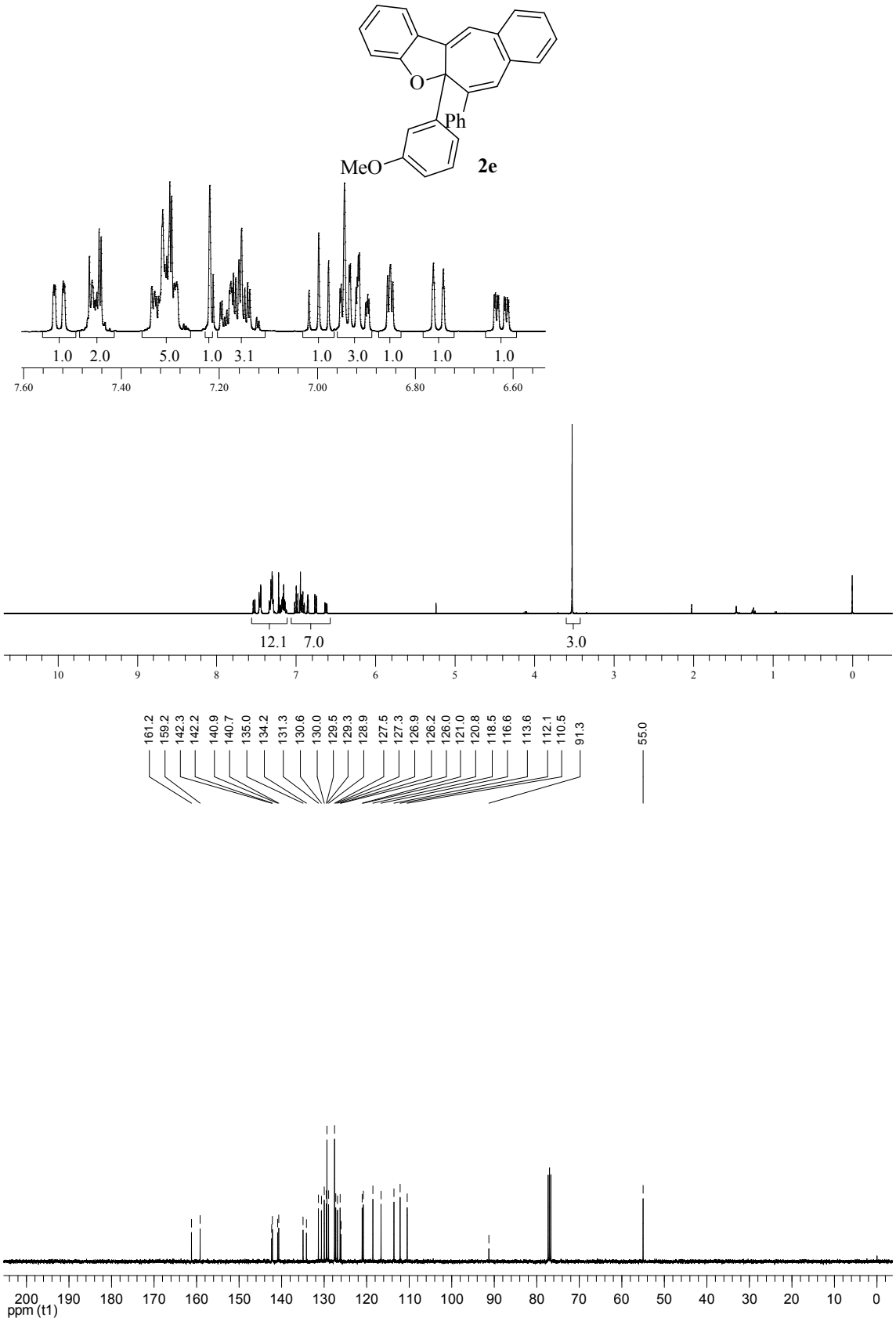
The ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **2a** in $CDCl_3$



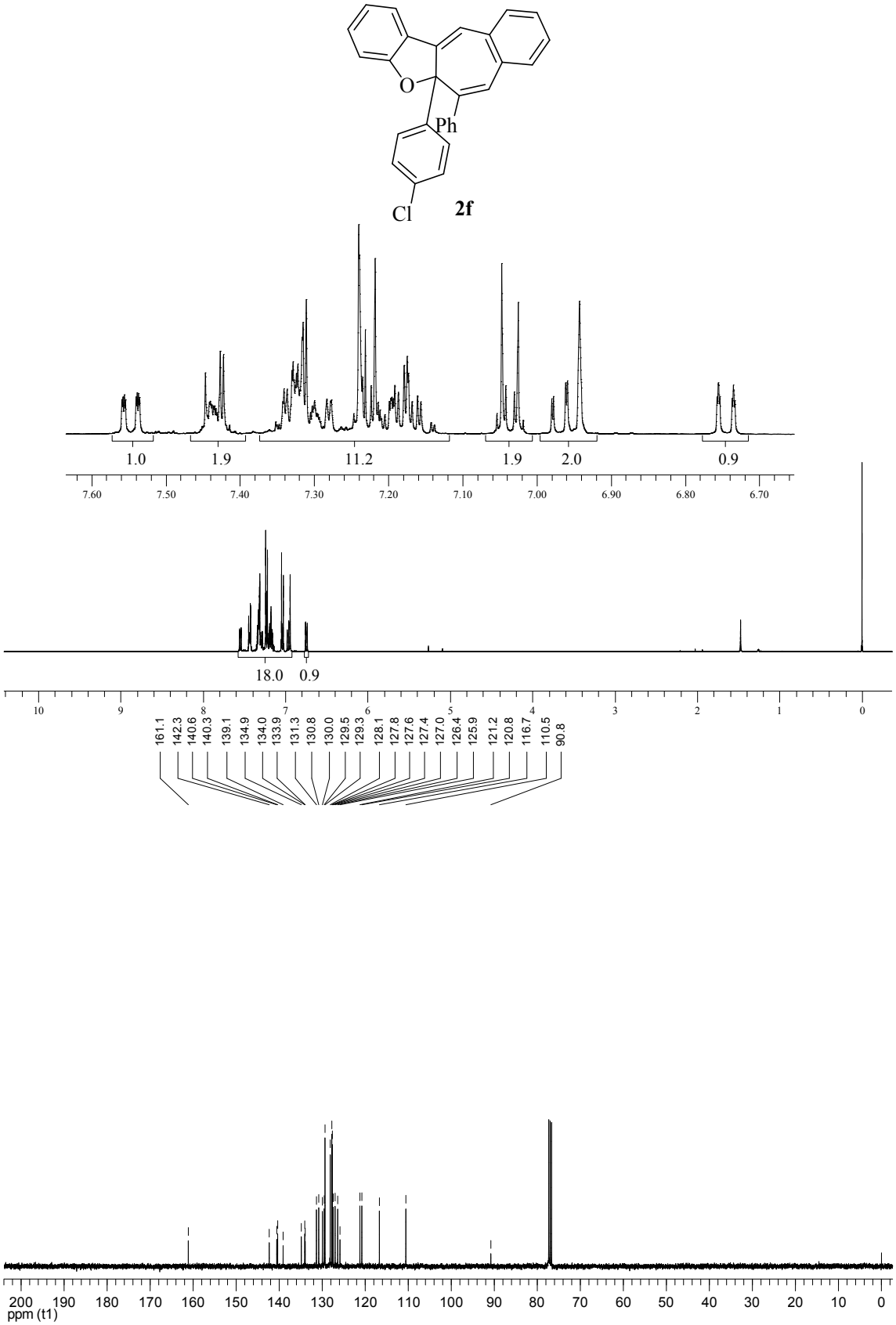
The ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **2c** in $CDCl_3$



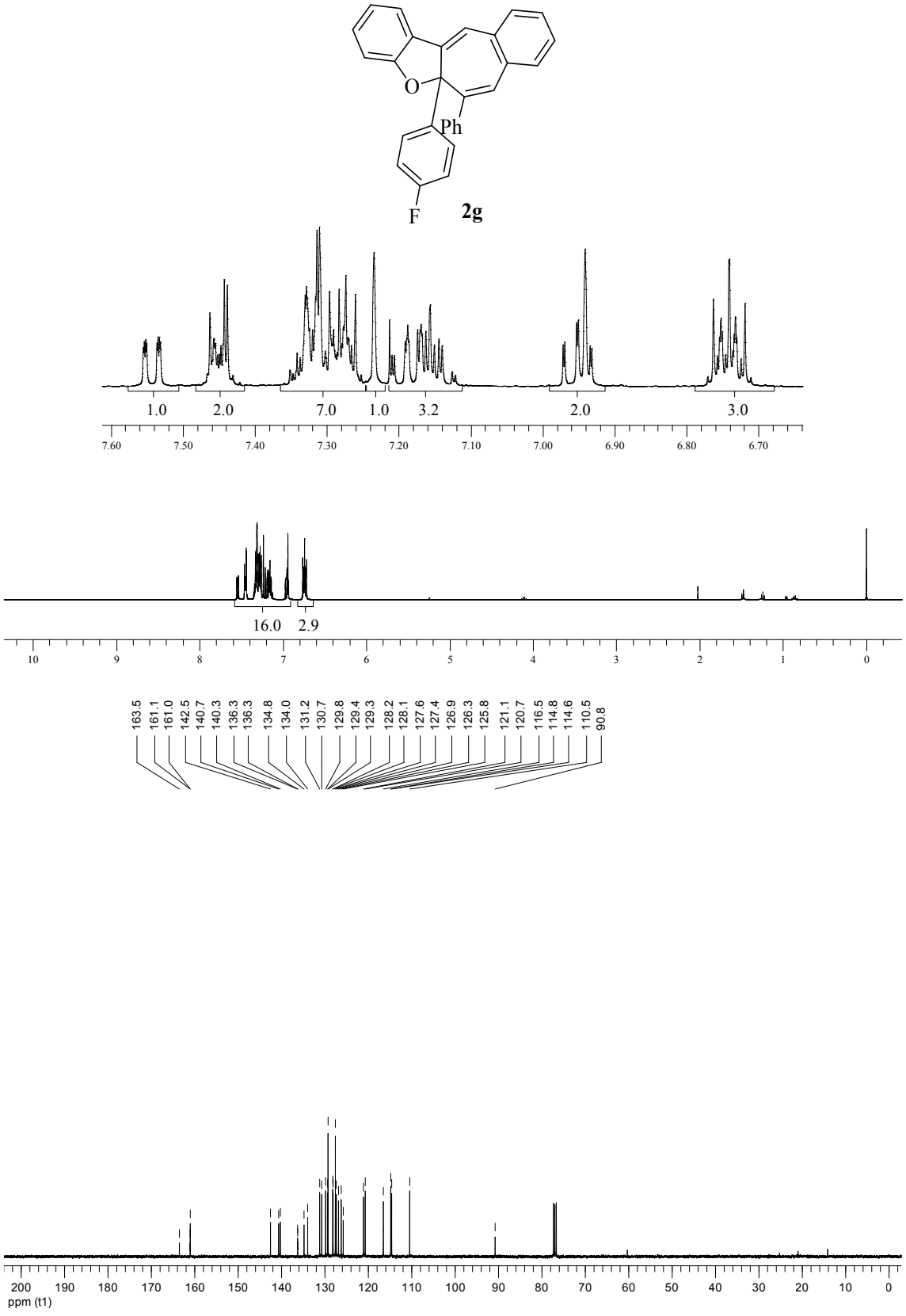
The ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **2d** in $CDCl_3$



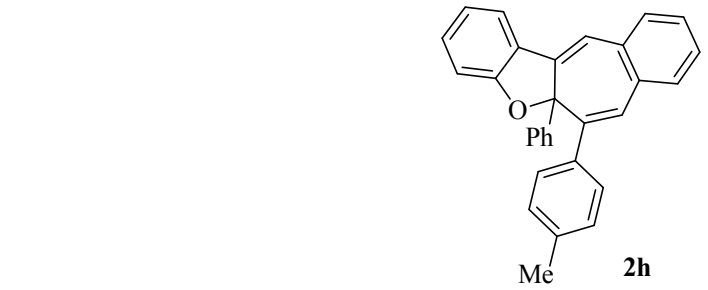
The ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **2e** in $CDCl_3$



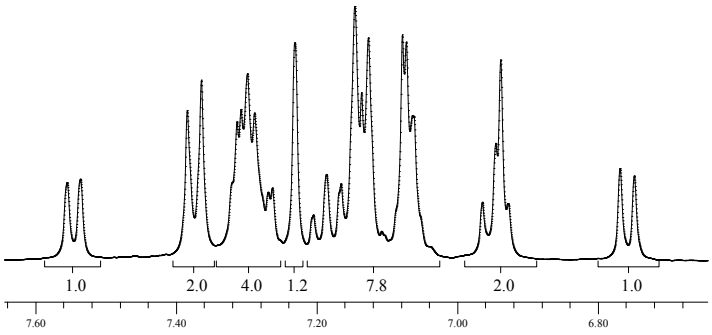
The ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **2f** in $CDCl_3$

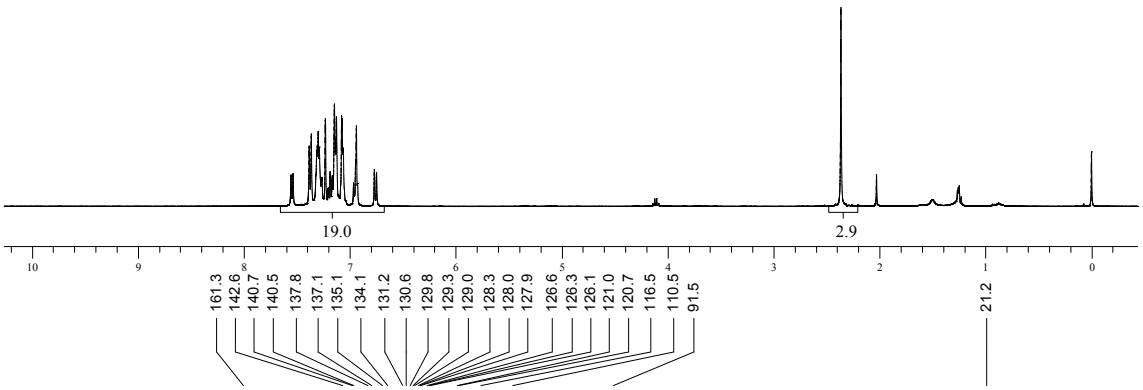


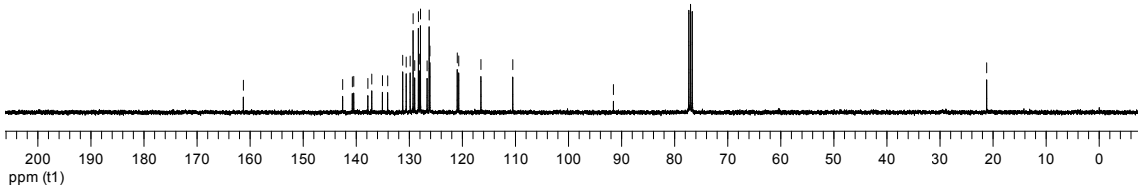
The ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **2g** in $CDCl_3$



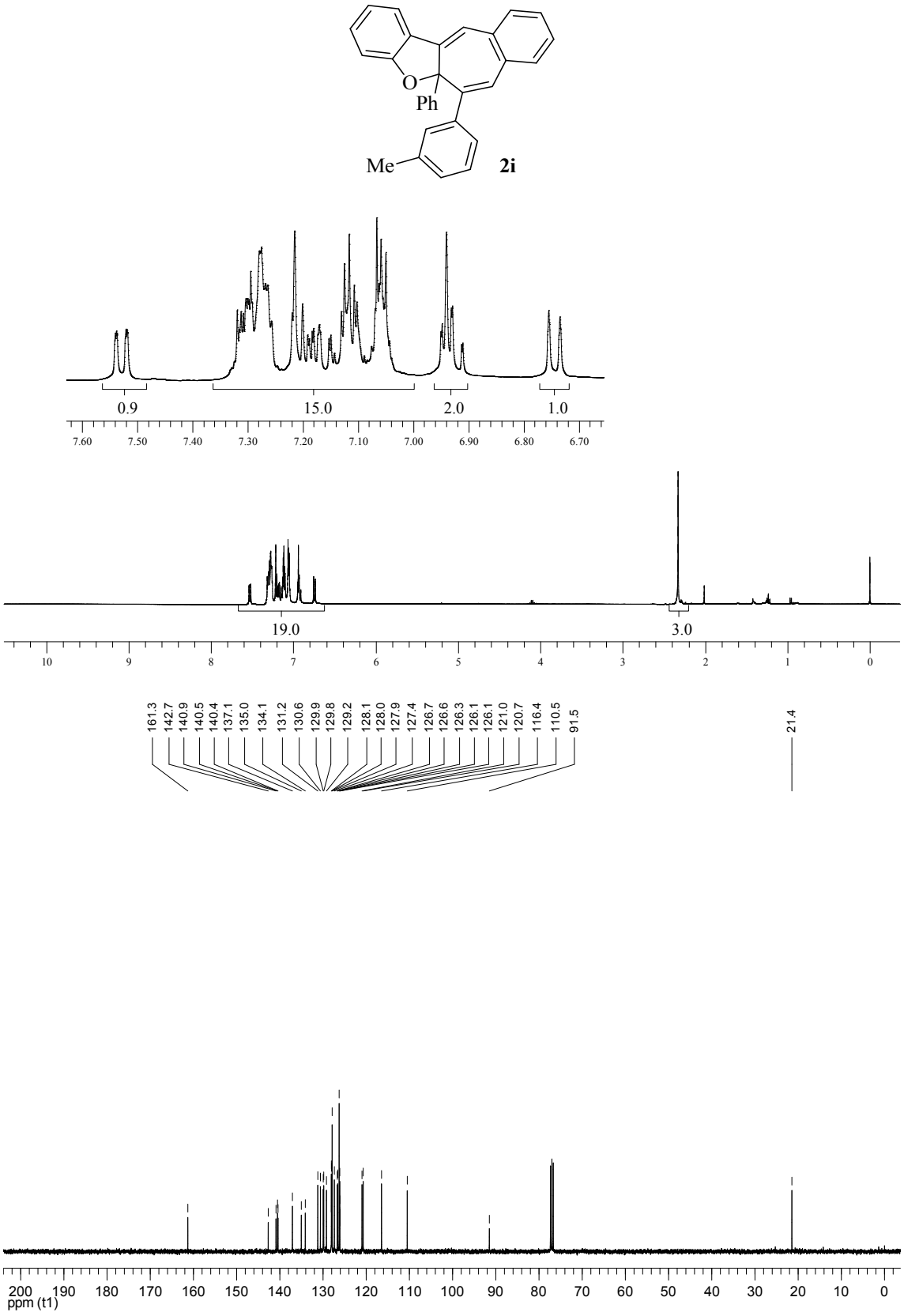
2h



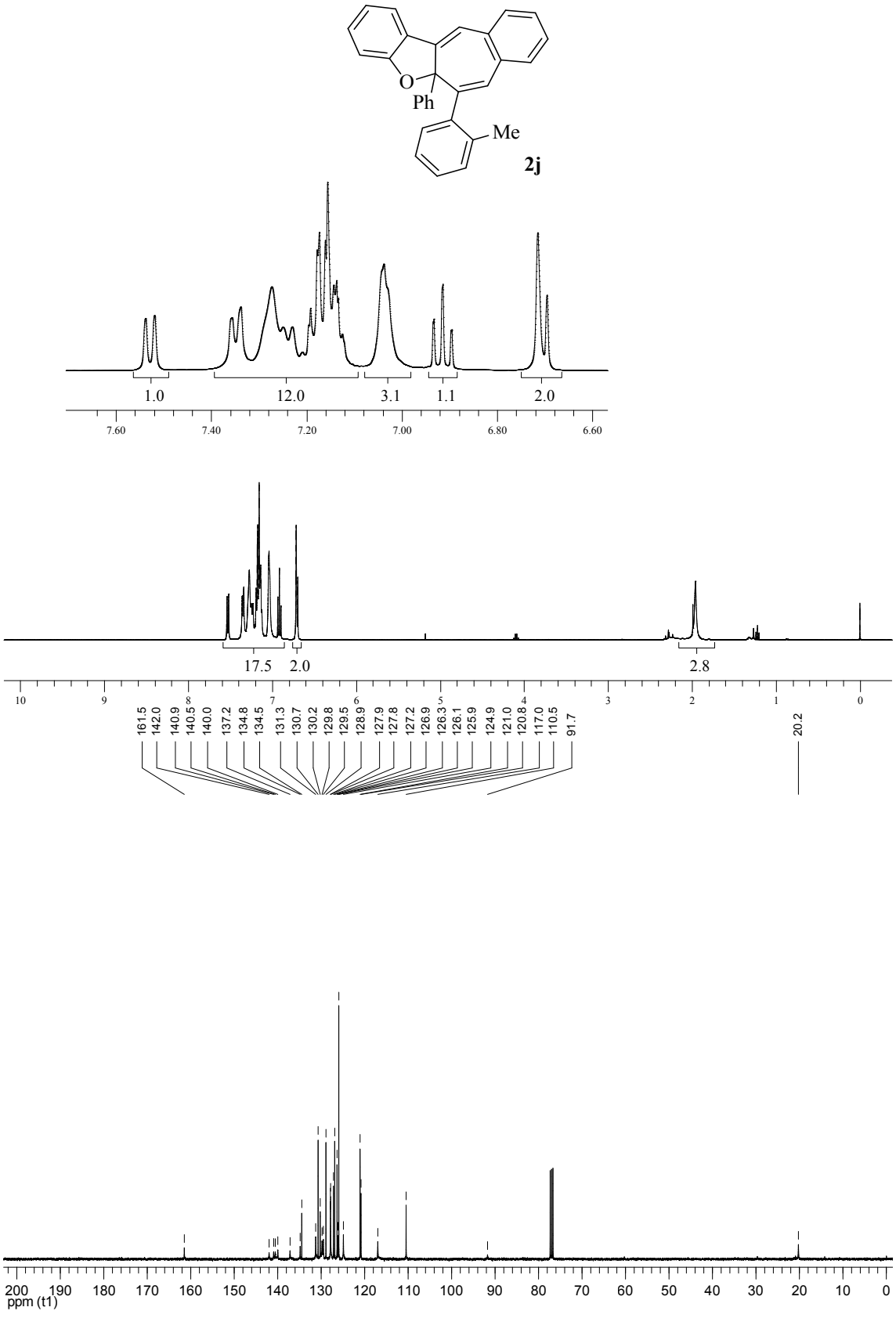




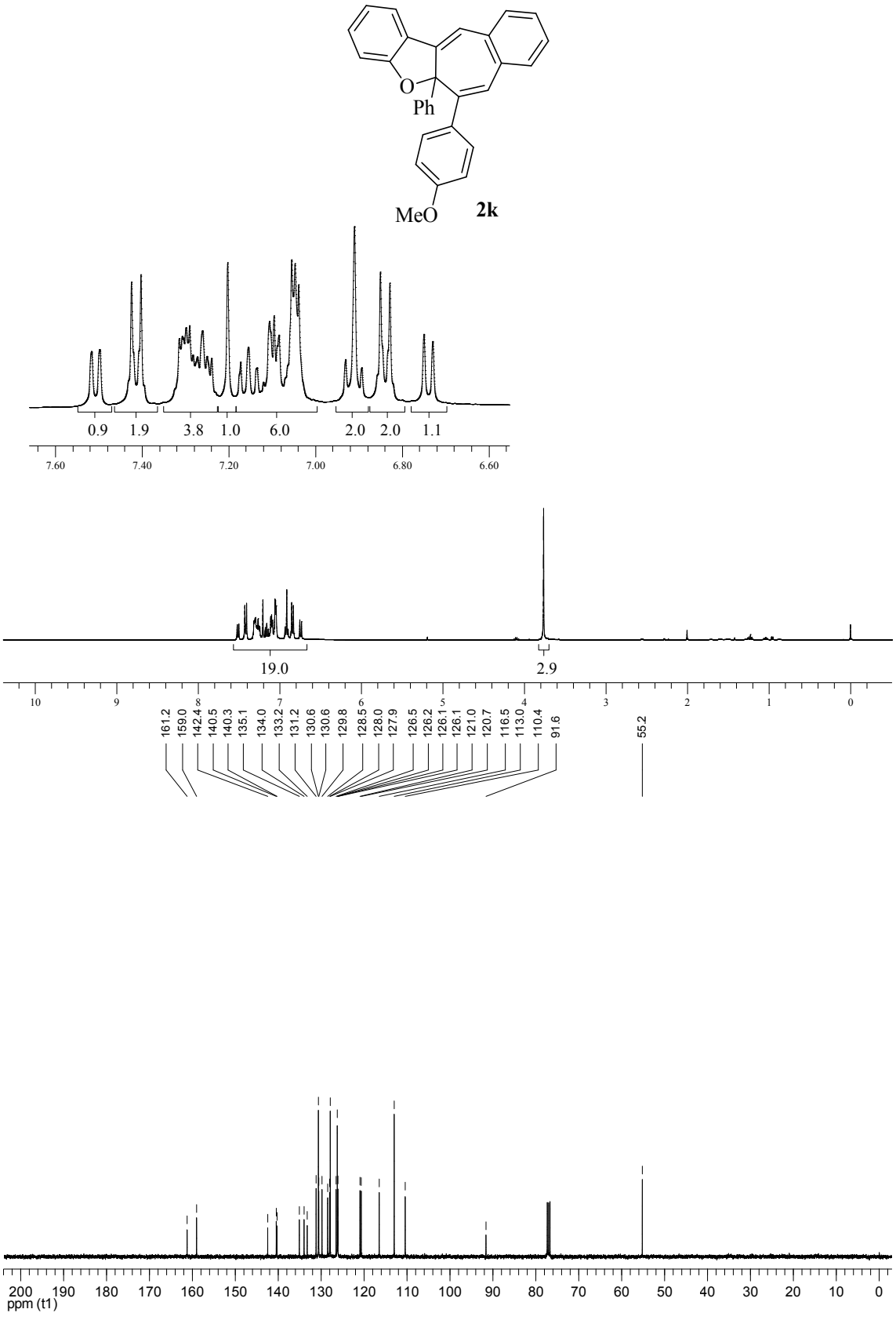
The ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **2h** in $CDCl_3$



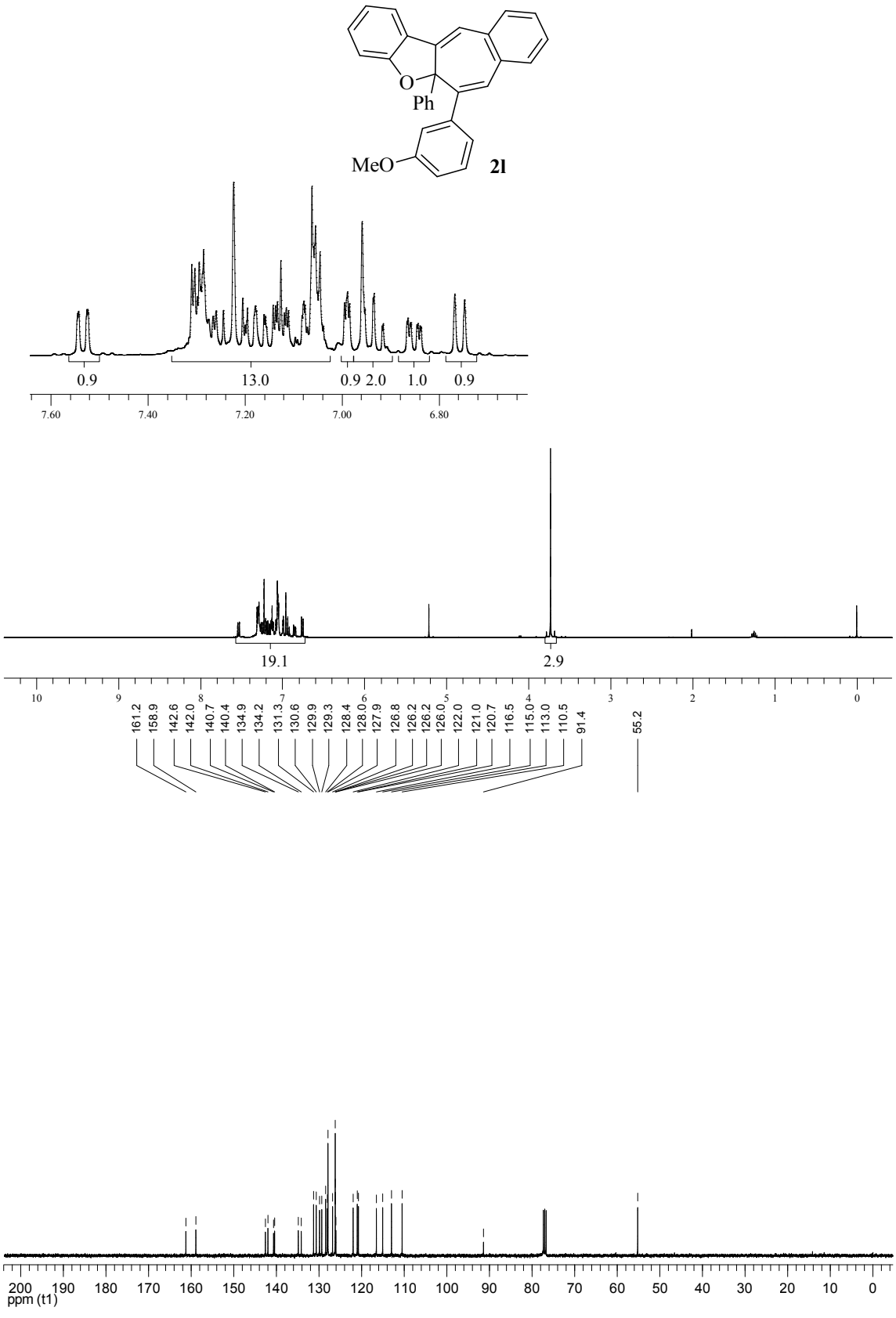
The ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **2i** in $CDCl_3$



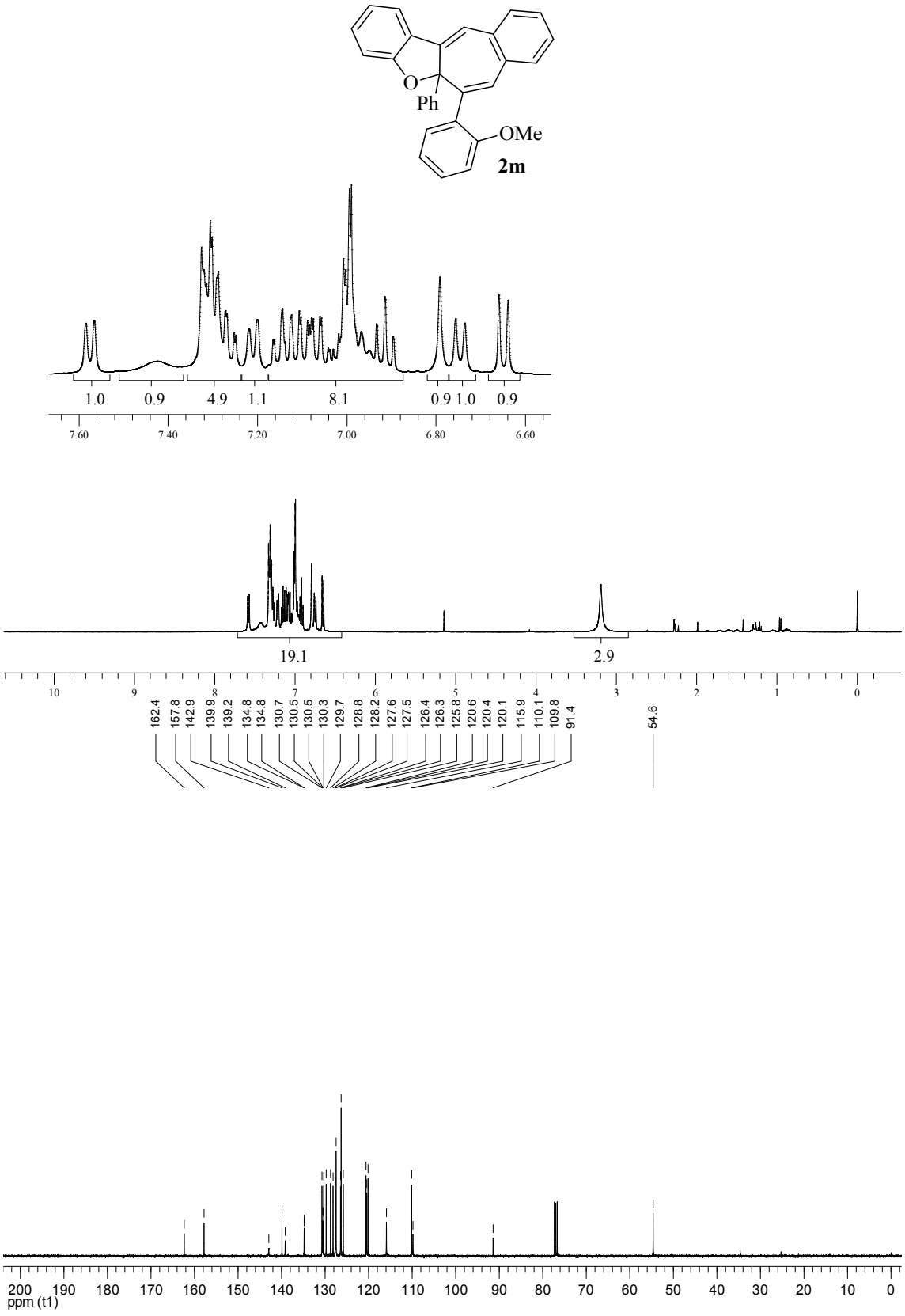
The ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **2j** in $CDCl_3$



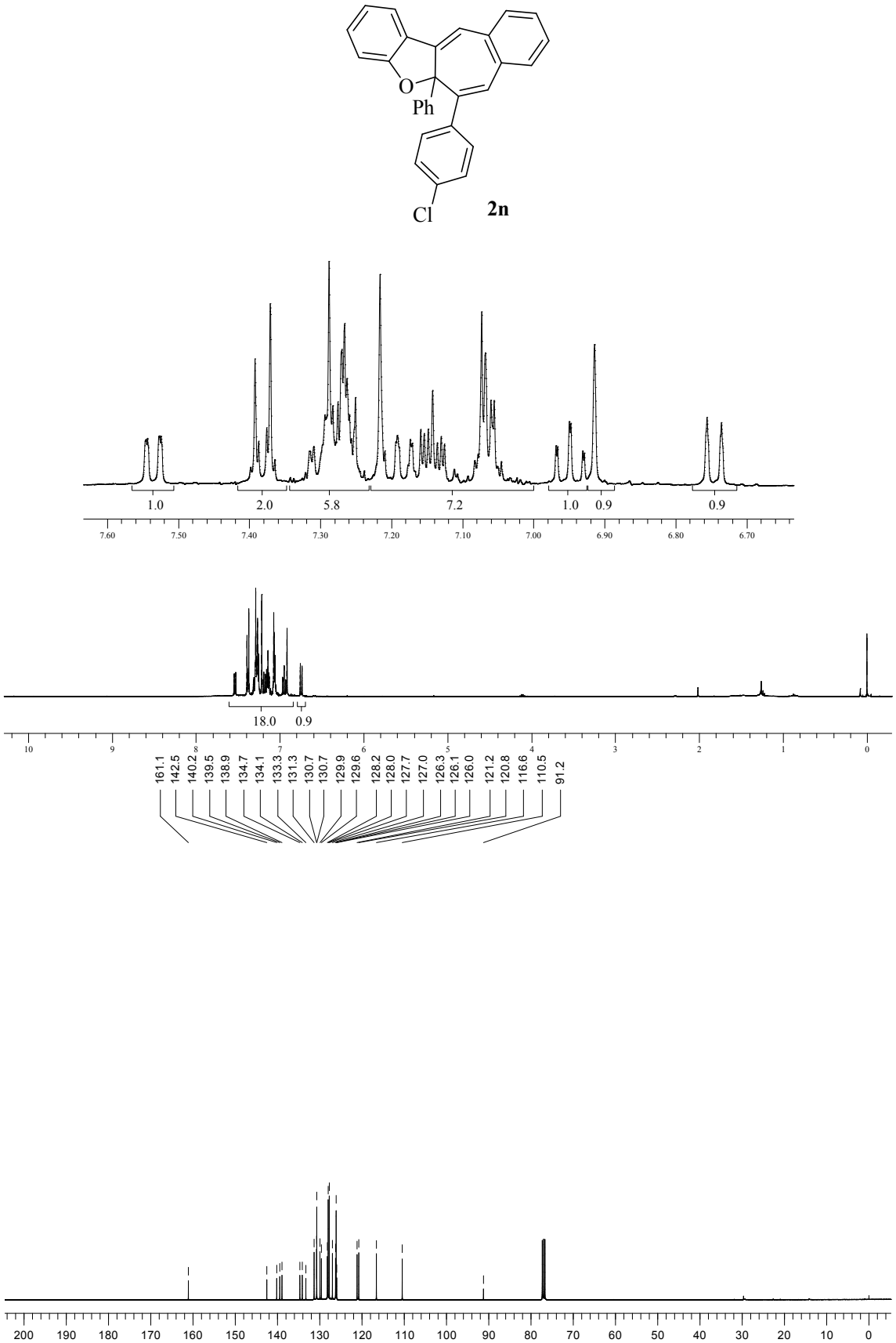
The ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **2k** in $CDCl_3$



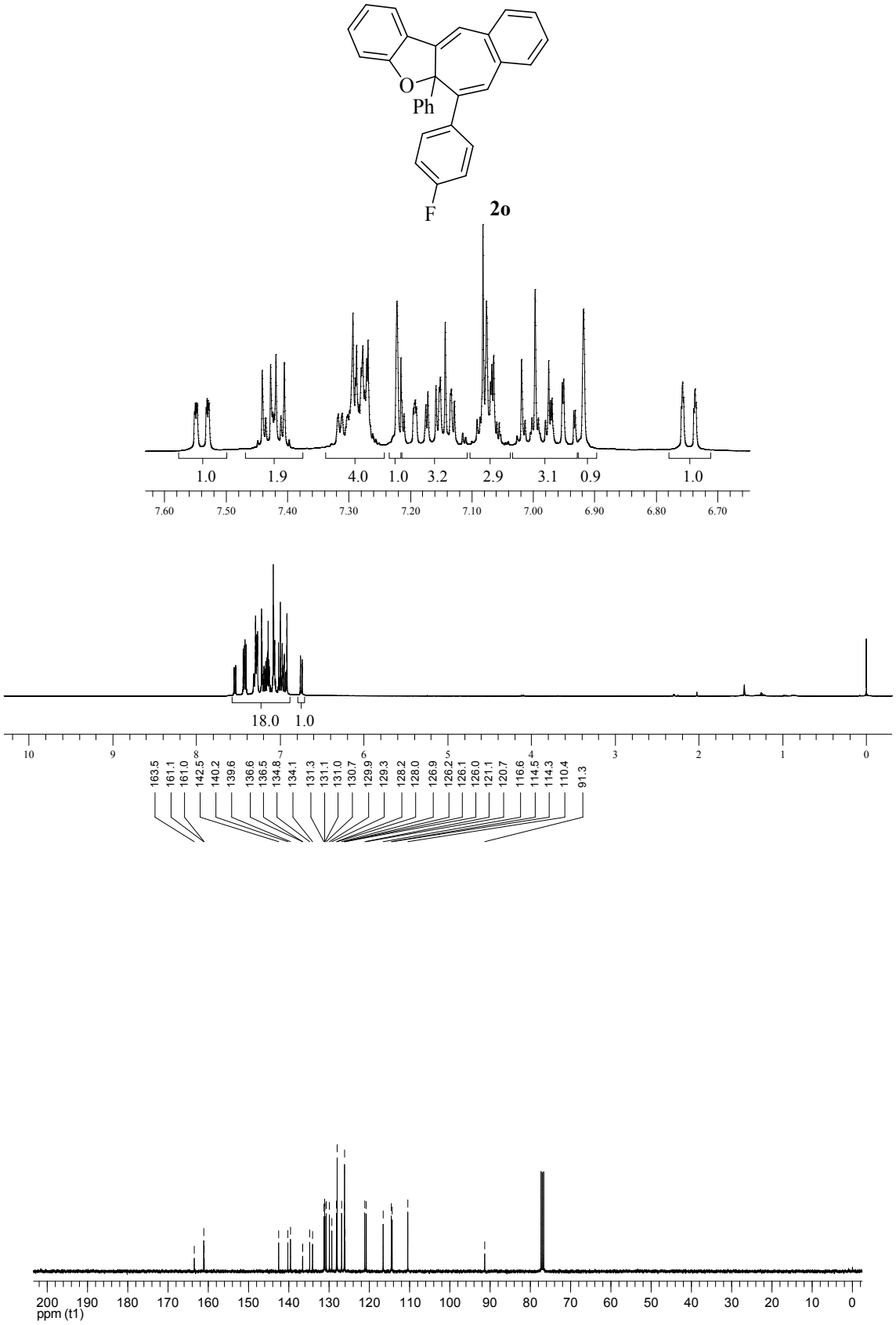
The ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **2l** in $CDCl_3$



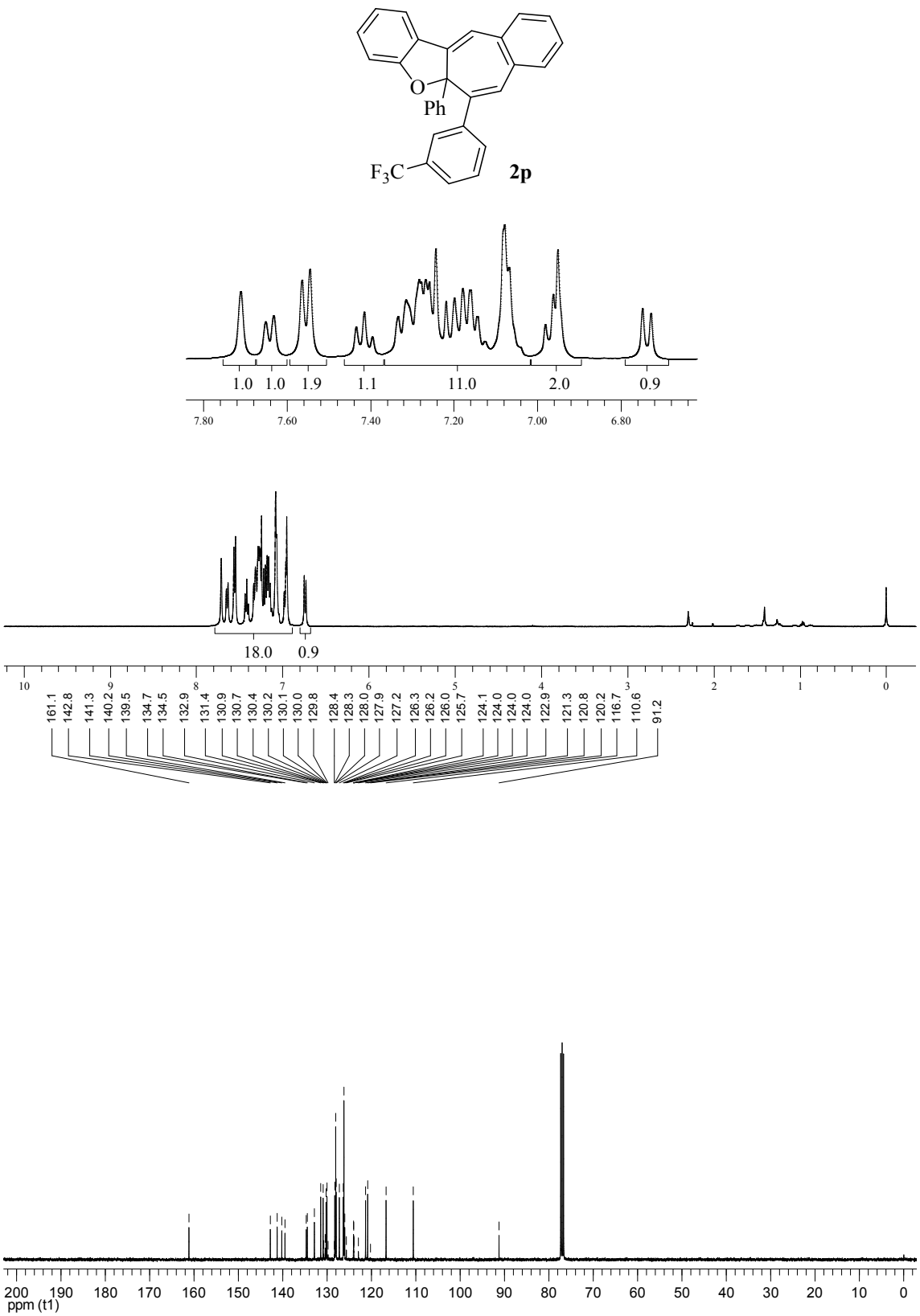
The ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **2m** in $CDCl_3$



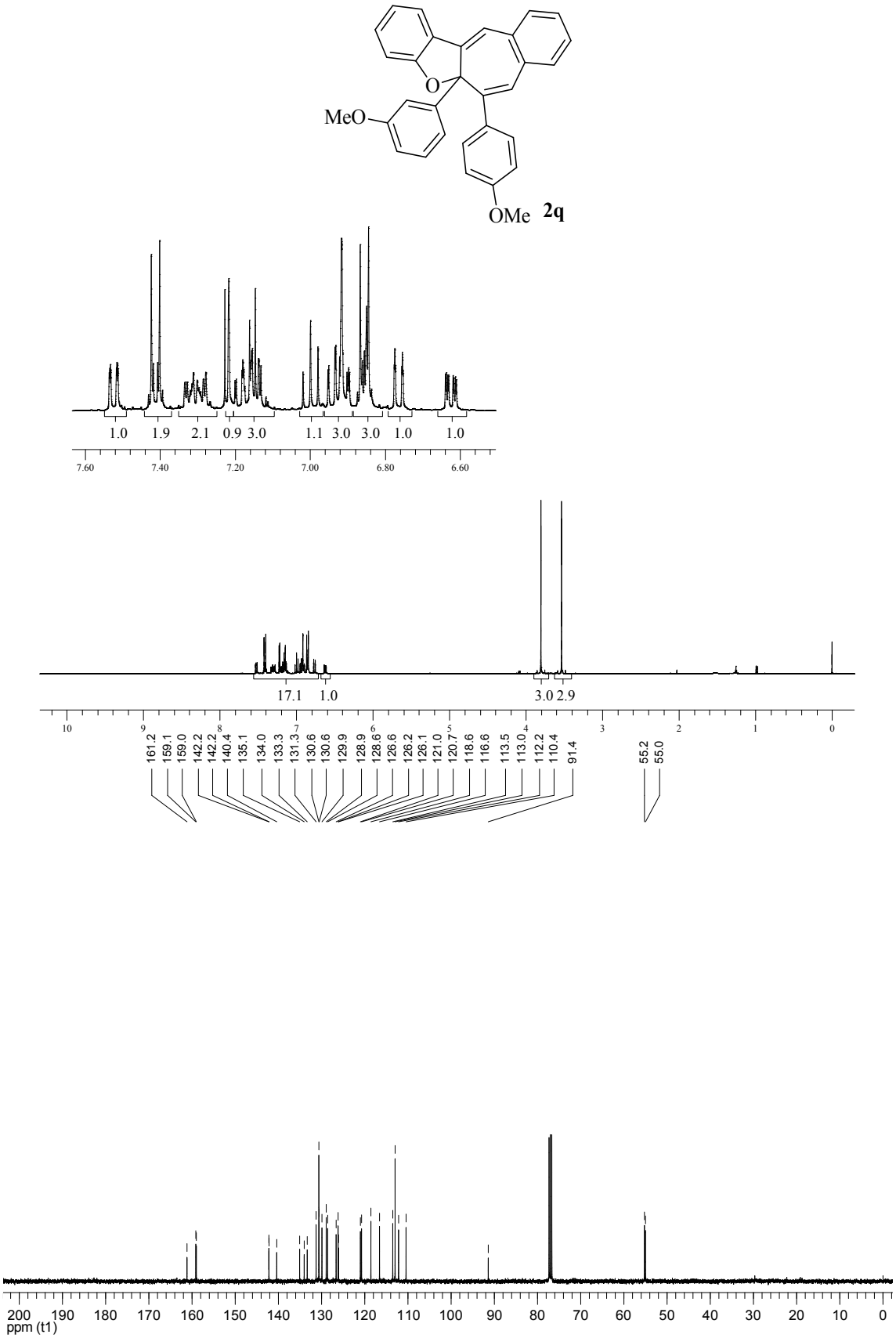
The ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **2n** in $CDCl_3$



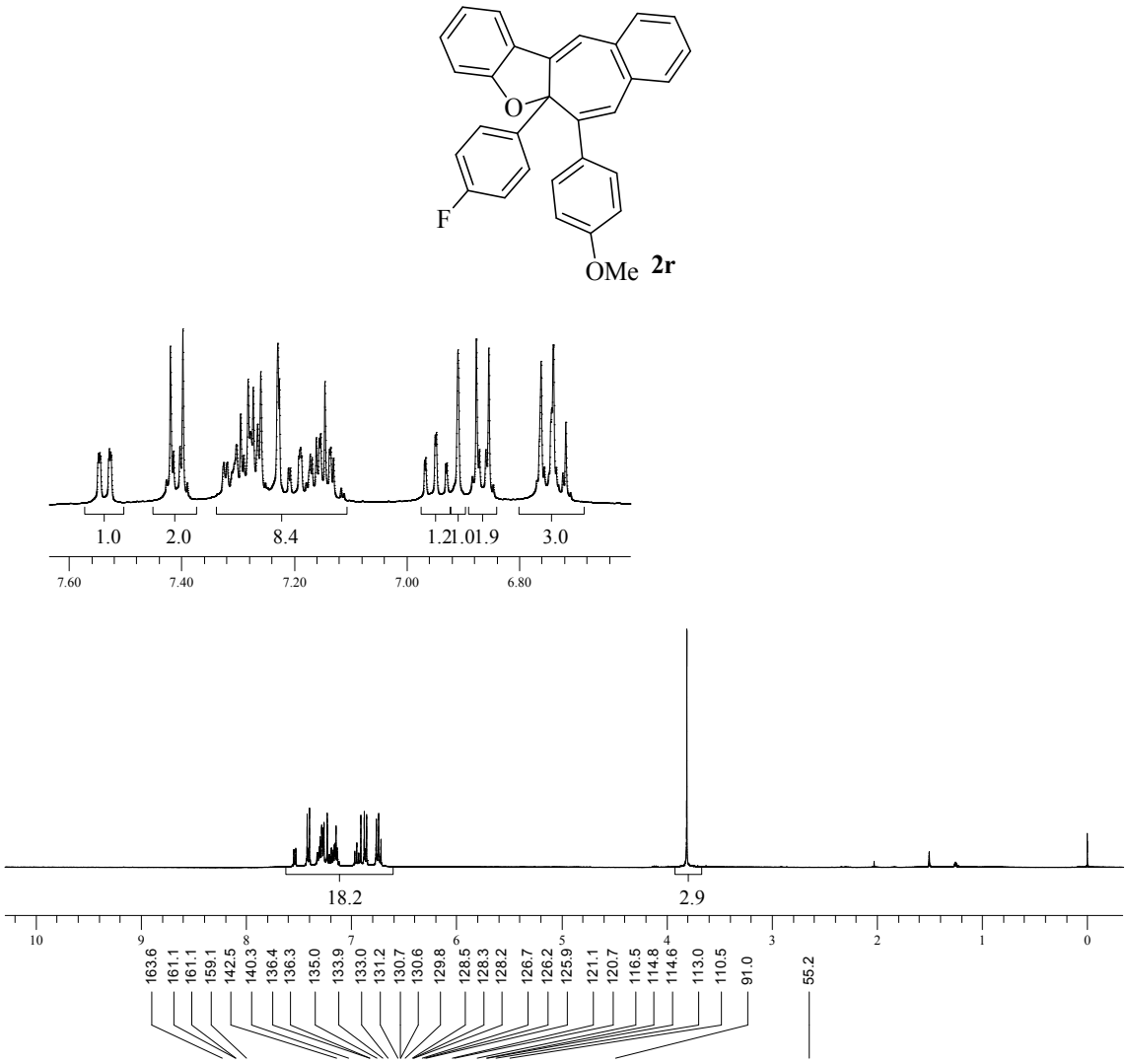
The ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **2o** in $CDCl_3$



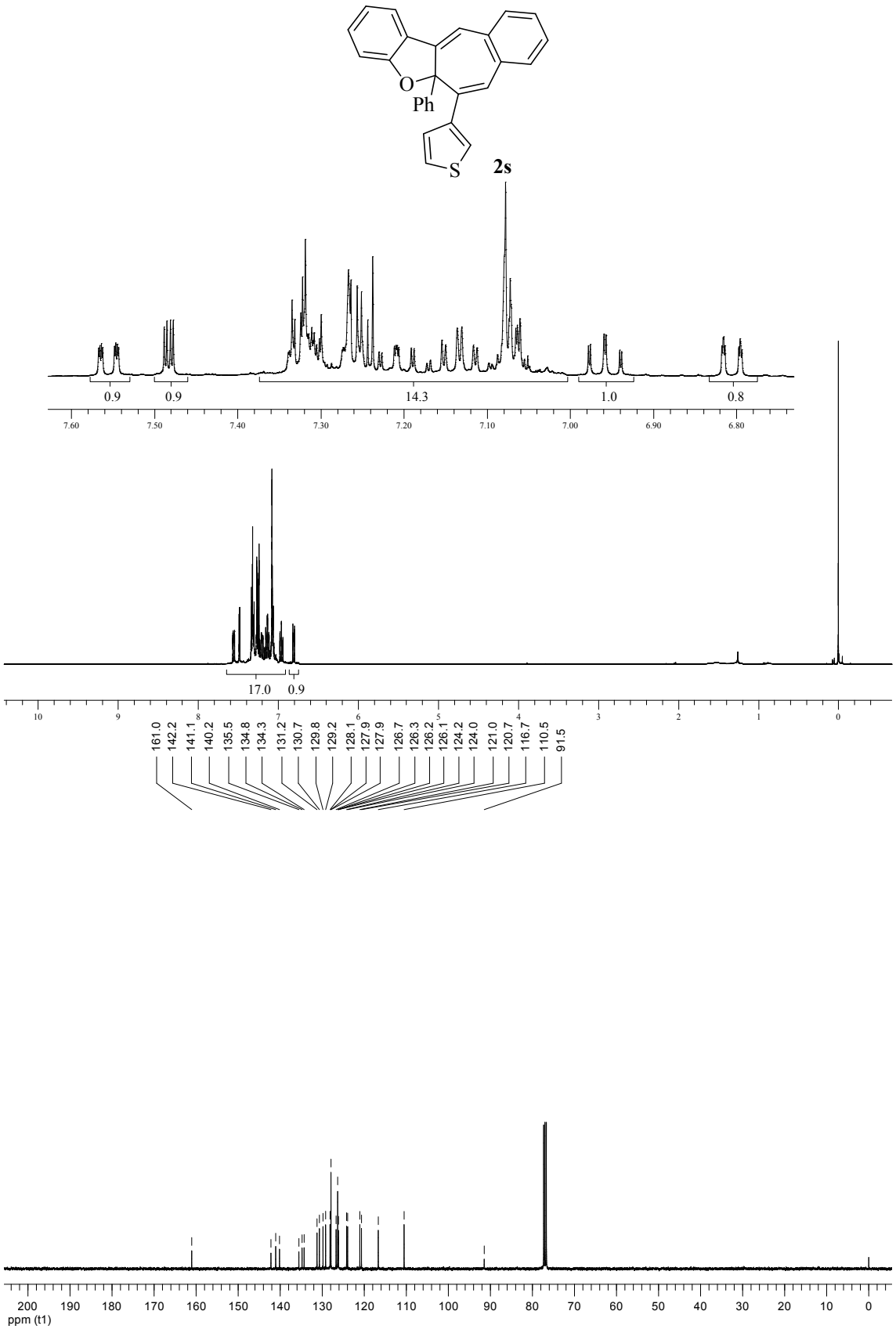
The ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **2p** in $CDCl_3$



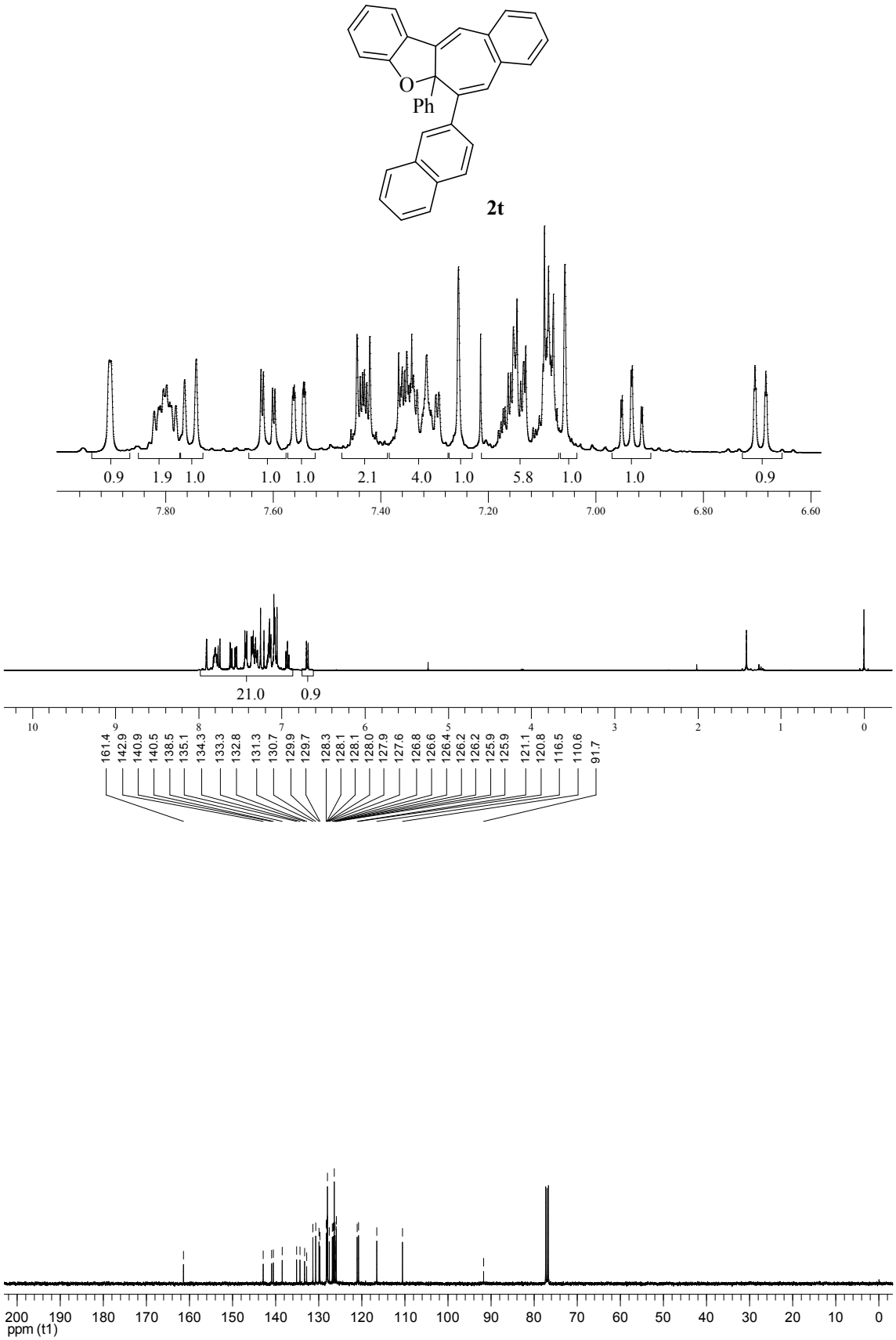
The ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **2q** in $CDCl_3$



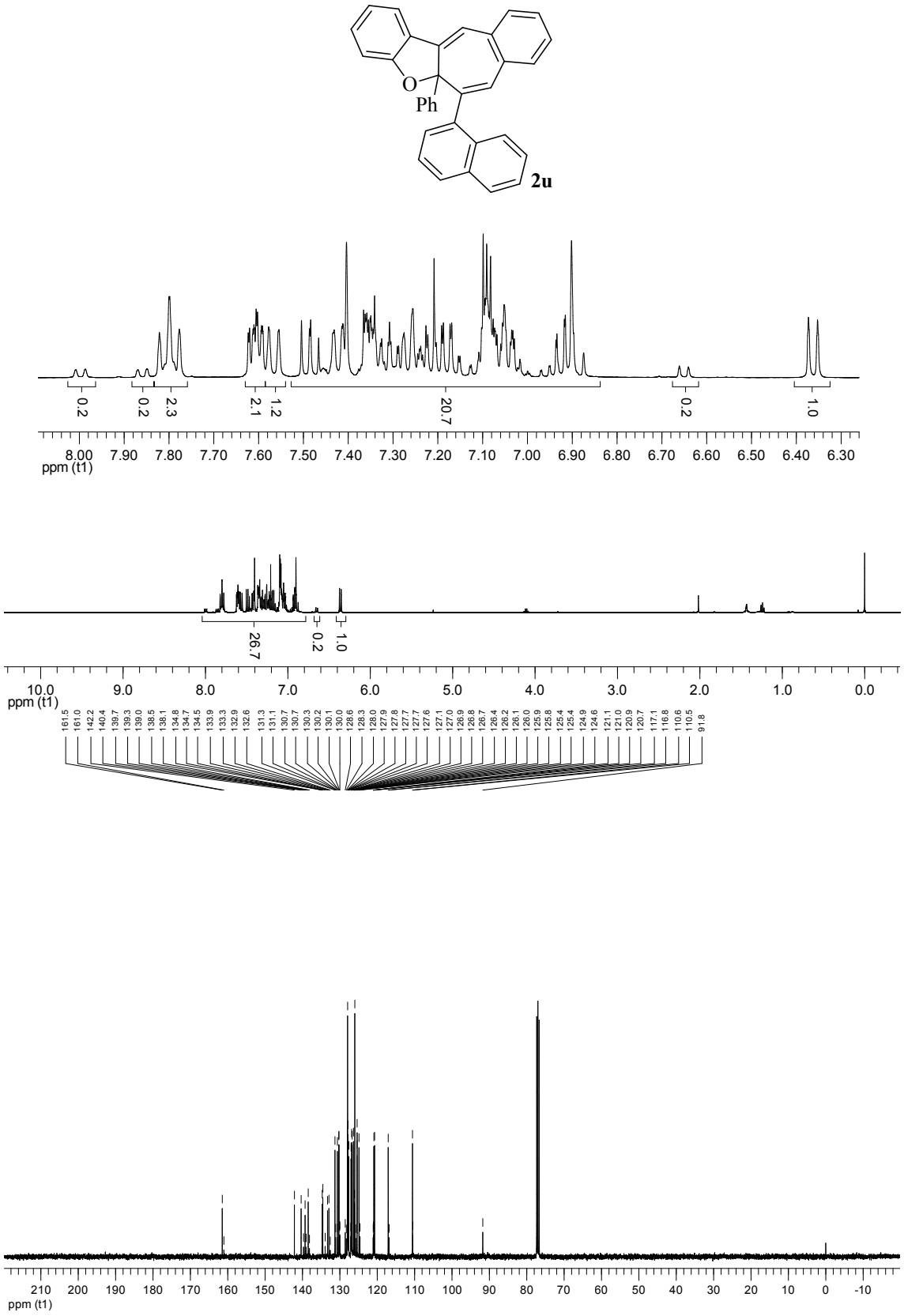
The ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **2r** in $CDCl_3$



The ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **2s** in $CDCl_3$



The ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **2t** in $CDCl_3$



The ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **2u** in $CDCl_3$