Supporting Information

Synthesis of multisubstituted cycloalkenes through carbomagnesiation of strained cycloalkynes

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Contents

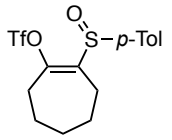
General Remarks

All reactions were performed in a dry glassware under atmosphere of argon otherwise noted. Analytical thin-layer chromatography (TLC) was performed on precoated (0.25 mm) silica-gel plates (Merck Chemicals, Silica Gel 60 F_{254}, Cat. No. 1.05715). Column chromatography was conducted using silica-gel (Kanto Chemical Co., Inc., Silica Gel 60N, spherical neutral, particle size 40–50 μm, Cat. No. 37563-85 or particle size 63–210 μm, Cat. No. 37565-85). Preparative thin-layer chromatography (PTLC) was performed on silica-gel (Wako Pure Chemical Industries Ltd., Wakogel B5-F, Cat. No. 230-00043). Melting points (Mp) were measured on a YANACO MP-J3 instrument or an OptiMelt MPA100 (Stanford Research Systems), and are uncorrected. ^{1}H and ^{13}C NMR spectra were obtained with a Bruker AVANCE 500 spectrometer at 500 or 126 MHz, respectively. ^{19}F NMR spectra were obtained with a Bruker AVANCE 400 spectrometer at 376 MHz. Chemical shifts (δ) are given in parts per million (ppm) downfield from $(CH_3)_4Si$ (δ 0.00 for ^{1}H NMR in $CDCl_3$) or the solvent peak (δ 77.0 for ^{13}C NMR in $CDCl_3$ and δ 4.87 for ^{1}H NMR in CD_3OD) as an internal reference, or α,α,α-trifluorotoluene (δ –63.0 ppm for ^{19}F NMR in $CDCl_3$) as an external standard with coupling constants (*J*) in hertz (Hz). The abbreviations s, d, t, q, quin, sept, m, and br signify singlet, doublet, triplet, quartet, quintet, septet, multiplet, and broad, respectively. IR spectra were measured by diffuse reflectance method on a Shimadzu IRPrestige-21 spectrometer attached with DRS-8000A with the absorption band given in cm^{-1}. High-resolution mass spectra (HRMS) were measured on a Bruker micrOTOF mass spectrometer under positive electrospray ionization (ESI^+) conditions. Elemental analyses were carried out at A Rabbit Science Japan Co., Ltd.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. 2-(4-Tolylsulfinyl)cyclohept-1-en-1-yl triflate (**1a**),[S1] 8-(4-tolylsulfinyl)-6,7-dihydro-5*H*-benzocyclohepten-9-yl triflate (**1b**),[S1] 6-(4-tolylsulfinyl)-7*H*-benzocyclohepten-5-yl triflate,[S1] 5-(4-tolylsulfinyl)-7,8-dihydro-6*H*-cyclohepta[*b*]thiophen-4-yl triflate,[S1] 2-(4-tolylsulfinyl)cyclohex-1-en-1-yl triflate,[S1] *S*-(4-tolyl) 4-toluenethiosulfonate,[S2] and *S*-(2-bromophenyl) 4-toluenethiosulfonate[S3] were prepared according to the reported methods. 3,4-Dihydro-1-benzoxepin-5(2*H*)-one,[S4] 7-methoxy-3,4-dihydro-1-benzoxepin-5(2*H*)-one,[S4] 7-bromo-3,4-dihydro-1-

benzoxepin-5(2*H*)-one,[S4] and 8-fluoro-3,4-dihydro-1-benzoxepin-5(2*H*)-one[S5] were prepared according to the typical reported procedure. Phenylmagnesium bromide (1.05 M in Et_2O), 4-methoxyphenylmagnesium bromide (0.92 M in THF), 4-trifluoromethylphenylmagnesim bromide (0.88 M in THF), and 2-methoxyphenylmagnesium bromide (1.09 M in THF) were prepared from the reaction of the corresponding bromoarenes with magnesium. 2-Chlorophenylmagnesium chloride lithium chloride was prepared in situ from 1-bromo-2-chlorobenzene with isopropylmagnesium chloride lithium chloride complex solution (1.3 M in THF).[S6] Organolithium and organomagnesium reagents were used after titrimetric determination of the concentration by the 1,10-phenanthroline method.[S7]

Structures of Cycloalkyne Precursors



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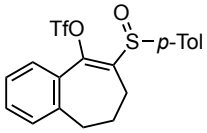

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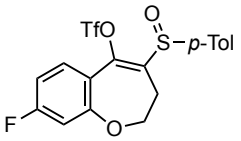
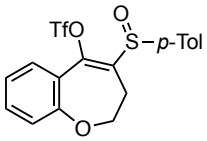


1c



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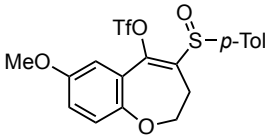

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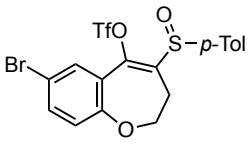

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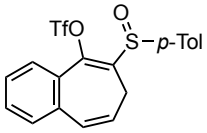

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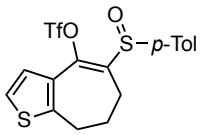

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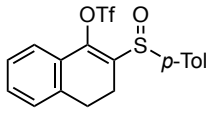

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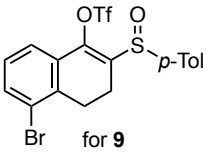

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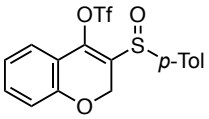

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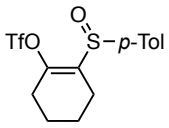
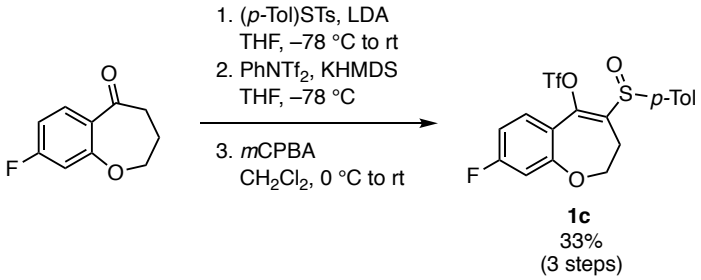


for **11**

Experimental Procedures

*General procedure for the synthesis of 2-sulfinylcycloalkenyl triflates **1***

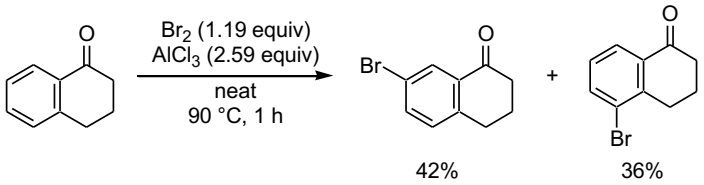


To a solution of 3,4-dihydro-8-fluoro-1-benzoxepin-5(2*H*)-one (901 mg, 5.00 mmol)[S5] in THF (10.0 mL) was added lithium diisopropylamide (0.391 M, THF/*n*-hexane solution, 12.8 mL, 5.00 mmol) at –78 ºC. After stirring for 2 h at –78 ºC, the mixture was transferred into a solution of *S*-*p*-tolyl *p*-toluenethiosulfonate (1.53 g, 5.50 mmol) in THF (10.0 mL) at –78 ºC. After gradually warming to room temperature, the mixture was stirred for 14 h, and to this was added an aqueous saturated solution of ammonium chloride. The mixture was extracted with EtOAc, and the combined organic extract was washed with brine, dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica-gel 45 g, *n*-hexane/EtOAc = 91/9 to 70/30) to give 3,4-dihydro-4-(*p*-tolylthio)-8-fluoro-1-benzoxepin-5(2*H*)-one (988 mg, *ca.* 90% purity judged from ^{1}H NMR analysis).

To a solution of the mixture containing the above product (988 mg) prepared as above in THF (15.0 mL) was added potassium bis(trimethylsilyl)amide (11% in toluene, *ca.* 0.5 M, 6.60 mL, *ca*. 3 mmol) at –78 ºC. After stirring for 30 min at the same temperature, to this was added a solution of bis(trifluoromethanesulfonyl)aniline (1.16 g, 3.24 mmol) in THF (15.0 mL) at the same temperature. After stirring for 16 h at the same temperature, to this was added an aqueous saturated solution of ammonium chloride. The mixture was diluted with water and extracted with EtOAc, and the combined organic extract was washed with brine, dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica-gel 30 g, *n*-hexane/EtOAc = 100/0 to 90/10) to give a mixture containing 8-fluoro-4-(4-tolylthio)-2,3-dihydro-1-benzoxepin-5-yl triflate (973 mg, *ca.* 87% purity judged from ^{1}H NMR analysis).

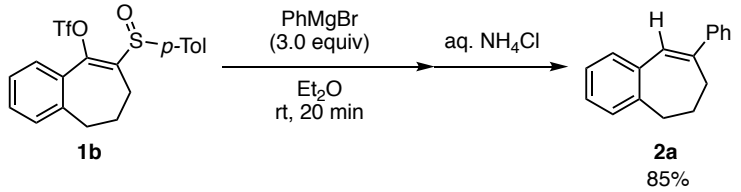
To a solution of the mixture containing the triflate (918 mg) prepared as above in dichloromethane (20.0 mL) was slowly added *m*CPBA (>65%, 509 mg, >1.74 mmol) at 0 ºC. After gradually warming to room temperature, the mixture was stirred for 15 h, and to this was added an aqueous saturated solution of sodium thiosulfate and an aqueous saturated solution of potassium carbonate. The mixture was extracted with dichloromethane, and the combined organic extract was washed with brine, dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica-gel 45 g, *n*-hexane/EtOAc = 88/12 to 67/33) to give 8-fluoro-4-(4-tolylsulfinyl)-2,3-dihydro-1-benzoxepin-5-yl triflate (**1c**) (739 mg, 1.64 mmol, 35% in 3 steps from the starting material) as a pale yellow solid.

Bromination of 3,4-dihydro-1(2H)-naphthalenone[S8]



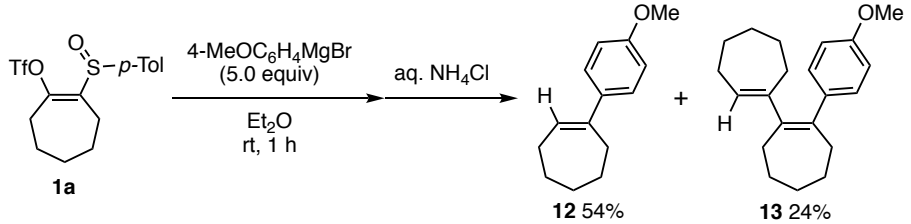
3,4-Dihydro-1(2*H*)-naphthalenone (2.91 g, 19.9 mmol) was added to trichloroaluminium (6.86 g, 51.5 mmol) at 0 ºC. After stirring at 90 ºC for 45 min, bromine (3.87 g, 24.2 mmol) was added to this mixture and the resultant mixture was stirred for 1 h. The reaction mixture was poured into ice water and to this was added an aqueous saturated solution of sodium thiosulfate. The mixture was extracted with EtOAc, and the combined organic extract was washed with brine, dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica-gel 200 g, *n*-hexane/EtOAc = 20/1) to give 7-bromo-3,4-dihydro-1(2*H*)-naphthalenone (1.88 g, 8.36 mmol, 42%) and 5-bromo-3,4-dihydro-1(2*H*)-naphthalenone (1.60 g, 7.09 mmol, 36%), respectively.

General procedure for carbomagnesiation of cycloalkynes followed by protonation



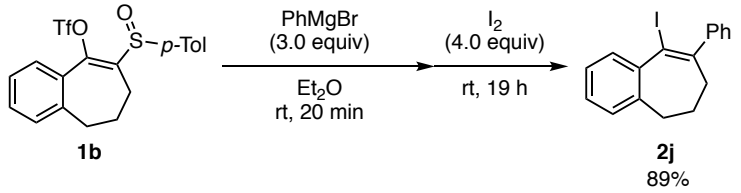
To a solution of phenylmagnesium bromide in diethyl ether (1.31 M, 0.460 mL, 0.603 mmol) were added diethyl ether (1.0 mL) and 8-(4-tolylsulfinyl)-6,7-dihydro-5*H*-benzocyclohepten-9-yl triflate (**1b**) (86.0 mg, 0.200 mmol) in diethyl ether (2.5 mL) at room temperature. After stirring for 20 min at the same temperature, to the mixture was added an aqueous saturated solution of ammonium chloride. The mixture was extracted with EtOAc, and the combined organic extract was washed with brine, dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane only) to give 8-phenyl-6,7-dihydro-5*H*-benzocycloheptene (**2a**) (37.4 mg, 0.170 mmol, 85%) as a pale yellow oil.

Carbomagnesiation of cycloheptyne



To a solution of *p*-methoxyphenylmagnesium bromide in diethyl ether (1.59 M, 1.26 mL, 2.00 mmol) were added diethyl ether (2.0 mL) and 2-(4-tolylsulfinyl)cyclohept-1-en-1-yl triflate (**1a**) (145 mg, 0.379 mmol) in diethyl ether (5.0 mL) at room temperature. After stirring for 1 h at the same temperature, to the mixture was added an aqueous saturated solution of ammonium chloride. The mixture was extracted with EtOAc, and the combined organic extract was washed with brine, dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane only) to give 1-(*p*-methoxyphenyl)cycloheptene (**12**) (41.7 mg, 0.206 mmol, 54%) as a colorless oil and 1-(1-cycloheptenyl)-2-(*p*-methoxyphenyl)cycloheptene (**13**) (13.5 mg, 45.5 μmol, 24%) as a colorless oil, respectively.

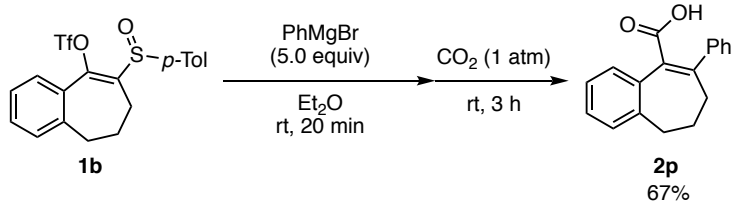
General procedure for carbomagnesiation of cycloheptynes and subsequent bond formations with electrophiles



1b **2j** 89%

To a solution of phenylmagnesium bromide in diethyl ether (1.05 M, 1.15 mL, 1.21 mmol) were added diethyl ether (2.0 mL) and 8-(4-tolylsulfinyl)-6,7-dihydro-5*H*-benzocyclohepten-9-yl triflate (**1b**) (172 mg, 0.400 mmol) in diethyl ether (5.0 mL) at room temperature. After stirring for 20 min at the same temperature, to the mixture was added molecular iodine (406 mg, 1.60 mmol) and diethyl ether (4.0 mL). After the resultant mixture was stirred for 19 h at room temperature, to the mixture was added an aqueous saturated solution of ammonium chloride and an aqueous saturated solution of sodium thiosulfate. The mixture was extracted with EtOAc, and the combined organic extract was washed with brine, dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane only) to give 9-iodo-8-phenyl-6,7-dihydro-5*H*-benzocycloheptene (**2j**) (124 mg, 0.357 mmol, 89%) as a colorless solid.

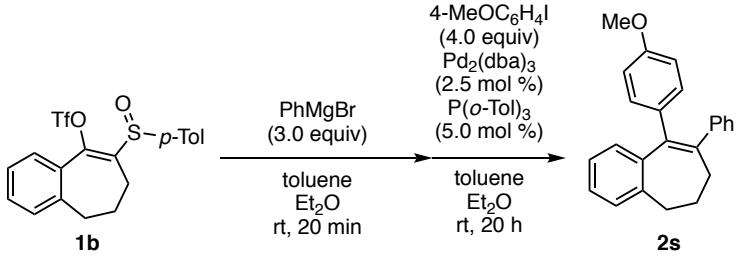
General procedure for carbomagnesiation of cycloheptynes and subsequent carboxylation with carbon dioxide



1b **2p** 67%

To a solution of phenylmagnesium bromide in diethyl ether (1.02 M, 4.90 mL, 5.00 mmol) were added diethyl ether (5.0 mL) and 8-(4-tolylsulfinyl)-6,7-dihydro-5*H*-benzocyclohepten-9-yl triflate (**1b**) (429 mg, 1.00 mmol) in diethyl ether (12.0 mL) at room temperature. After stirring for 20 min at the same temperature, the resultant mixture was exposed under an atmosphere of carbon dioxide filled in balloon. After the resultant mixture was stirred for 3 h at room temperature, to the mixture was added an aqueous saturated solution of ammonium chloride. The mixture was extracted with EtOAc, and the combined organic extract was washed with brine, dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica-gel 40 g, dichloromethane/methanol = 10/1) to give 8-phenyl-6,7-dihydro-5*H*-benzocycloheptene-9-carboxylic acid (**2p**) (177 mg, 0.670 mmol, 67%) as a yellow solid.

*Procedure for carbomagnesiation of cycloheptyne generated from **1b** followed by the palladium-catalyzed cross-coupling*

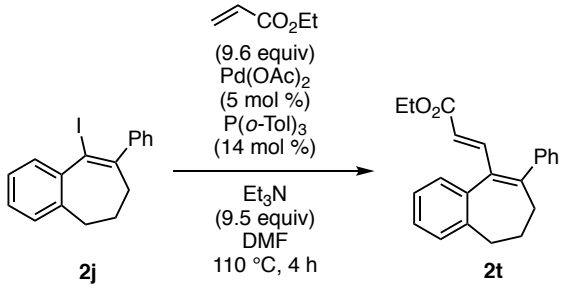


1b **2s** 39%

To a solution of phenylmagnesium bromide in diethyl ether (1.20 M, 0.500 mL, 0.600 mmol) were added toluene (1.0 mL) and 8-(4-tolylsulfinyl)-6,7-dihydro-5*H*-benzocyclohepten-9-yl triflate (**1b**) (86.8 mg, 0.202 mmol) in toluene (2.0 mL) at room temperature. After stirring for 20 min at the same

temperature, the resultant mixture was added to the mixture of tris(dibenzylideneacetone)dipalladium (4.6 mg, 5.0 μmol), tri(*o*-tolyl)phosphine (3.1 mg, 10 μmol), 4-iodoanisole (187 mg, 0.801 mmol), and toluene (3.0 mL) by cannulation transfer technique. After the resultant mixture was stirred for 20 h at room temperature, to the mixture was added an aqueous saturated solution of ammonium chloride. The mixture was extracted with EtOAc, and the combined organic extract was washed with brine, dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/$CHCl_3$ = 3/1) to give 9-(4-methoxyphenyl)-8-phenyl-6,7-dihydro-5*H*-benzocycloheptene (**2p**) (25.6 mg, 78.5 μmol, 39%) as a pale yellow solid.

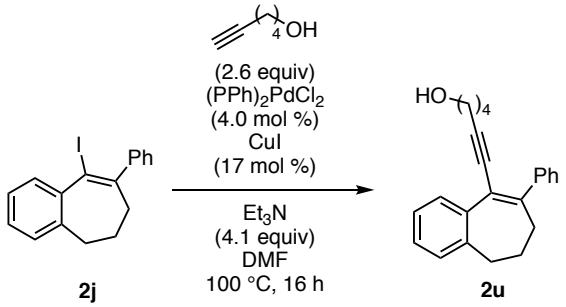
*Procedure for Mizoroki–Heck reaction of 9-iodo-8-phenyl-6,7-dihydro-5H-benzocycloheptene (**2j**) with ethyl acrylate*



2j **2t** 91%

To a mixture of palladium acetate (0.7 mg, 3 μmol), tri(*o*-tolyl)phosphine (2.6 mg, 8.5 μmol), 9-iodo-8-phenyl-6,7-dihydro-5*H*-benzocycloheptene (**2j**) (21.8 mg, 63.0 μmol), and DMF (0.60 mL) were added triethylamine (84.0 μL, 0.601 mmol) and ethyl acrylate (66.0 μL, 0.605 mmol) at room temperature. After stirring for 4 h at 110 °C, the reaction mixture was filtered through Celite and the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 5/1) to give ethyl β-(*E*)-(8-phenyl-6,7-dihydro-5*H*-benzocyclohepten-9-yl)acrylate (**2t**) (18.3 mg, 57.5 μmol, 91%) as a pale yellow solid.

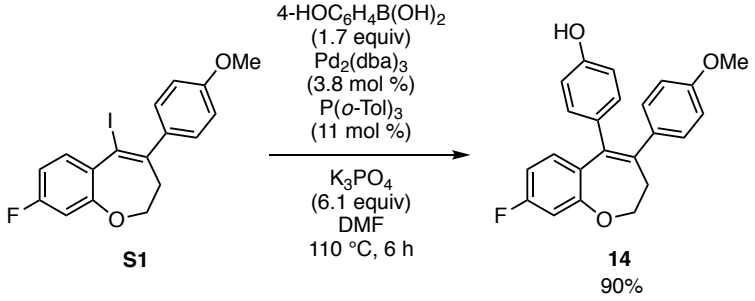
*Procedure for Sonogashira coupling of 9-iodo-8-phenyl-6,7-dihydro-5H-benzocycloheptene (**2j**) with 1-hydroxy-5-hexyne*



2j **2u** 49%

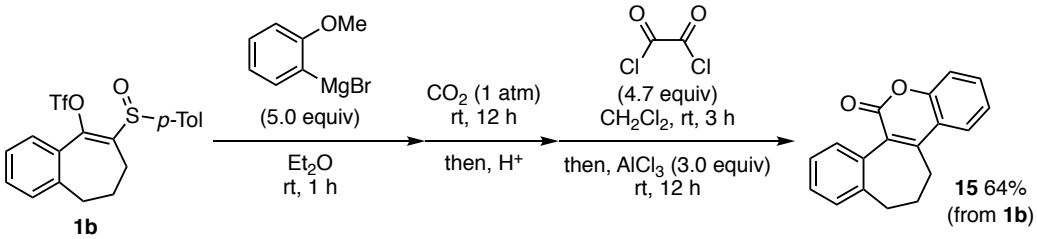
To a mixture of dichlorobis(triphenylphosphine)palladium (1.4 mg, 2.0 μmol), copper(I) iodide (1.6 mg, 8.4 μmol), 9-iodo-8-phenyl-6,7-dihydro-5*H*-benzocycloheptene (17.1 mg, 49.4 μmol), and DMF (0.30 mL) were added triethylamine (28.0 μL, 0.200 mmol) and 1-hydroxy-5-hexyne (14.0 μL, 0.127 mmol) at room temperature. After stirring for 16 h at 100 °C, the reaction mixture was filtered through Celite and the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane only) to give 6-(8-phenyl-6,7-dihydro-5*H*-benzocyclohepten-9-yl)-1-hydroxy-5-hexyne (**2u**) (7.7 mg, 24 μmol, 49%) as a green oil.

*Procedure for Suzuki–Miyaura cross-coupling of 8-fluoro-5-iodo-4-(p-anisyl)-2,3-dihydro-5-benzoxepin (**S1**) with 4-hydroxyphenylboronic acid*



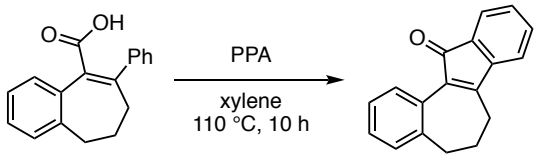
To a mixture of tris(dibenzylideneacetone)dipalladium (1.4 mg, 1.5 μmol), tri(*o*-tolyl)phosphine (1.3 mg, 4.3 μmol), potassium phosphate (52.0 mg, 0.245 mmol), 8-fluoro-5-iodo-4-(*p*-methoxyphenyl)-2,3-dihydro-5-benzoxepin (**S1**) (16.0 mg, 40.4 μmol), and 4-hydroxyphenylboronic acid (9.7 mg, 70 μmol) was added DMF (0.40 mL) at room temperature. After stirring for 6 h at 110 °C, the reaction mixture was filtered through Celite and the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 5/1) to give ethyl 8-fluoro-5-(4-hydroxyphenyl)-4-(4-methoxyphenyl)-2,3-dihydro-1-benzoxepin (**14**) (13.2 mg, 36.4 mmol, 90%) as a colorless solid.

*Synthesis of 11,12-dihydro-benzo[b]benzo[6,7]cyclohepta[2,1-d]pyran-6(13H)-one (**15**)*



To a solution of *o*-anisylmagnesium bromide in THF (1.00 M, 1.00 mL, 1.00 mmol) were added diethyl ether (1.0 mL) and 8-(4-tolylsulfinyl)-6,7-dihydro-5*H*-benzocyclohepten-9-yl triflate (87.2 mg, 0.203 mmol) in diethyl ether (2.4 mL) at room temperature. After stirring for 1 h at the same temperature, the resultant mixture was exposed under an atmosphere of carbon dioxide filled in balloon. After the resultant mixture was stirred for 12 h at room temperature, an aqueous saturated solution of ammonium chloride was added to the reaction mixture. The mixture was extracted with EtOAc, and the combined organic extract was washed with brine, dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was reprecipitated from methanol/*n*-hexane followed by filtration and dried under reduced pressure to get a colorless solid. Dichloromethane (2.0 mL) and oxalyl chloride (81.0 μL, 0.945 mmol) were added to this solid and the resultant mixture was stirred for 3 h at room temperature. After the mixture was concentrated under reduced pressure, trichloroaluminium (83.1 mg, 0.623 mmol) and dichloromethane (2.0 mL) were added to the resultant colorless solid. After stirring for 12 h at room temperature, the reaction mixture was filtered through Celite and the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*hexane/EtOAc = 10/1) to give 11,12-dihydro-benzo[*b*]benzo[6,7]cyclohepta[2,1-*d*]pyran-6(13*H*)-one (**15**) (33.9 mg, 0.129 mmol, 64%) as a pale yellow solid.

*Cyclization of 8-phenyl-6,7-dihydro-5H-benzocycloheptene-9-carboxylic acid (**2p**)*



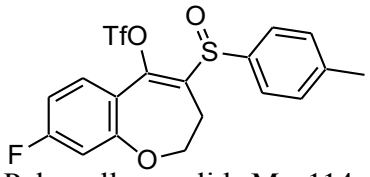
2p **16**
59%

To a mixture of polyphosphoric acid (PPA, 269 mg) and xylene (16.0 mL) was added 8-phenyl-6,7-dihydro-5*H*-benzocycloheptene-9-carboxylic acid (**2p**) (93.5 mg, 0.354 mmol) at room temperature. After stirring for 10 h at 110 °C, water was added to the reaction mixture. The mixture was extracted with EtOAc and the combined organic extract was washed with brine, dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 5/1) to give 6,7-dihydrodibenzo[*a*,*e*]azulen-12(5*H*)-one (**16**) (51.1 mg, 0.207 mmol, 59%) as a red solid.

Characterization Data of New Compounds

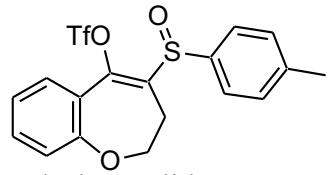
3-Phenyl-1,2-dihydronaphthalene (**8**),[S9] 3-phenyl-2*H*-chromene (**10**),[S10] 1-phenylcyclohexene (**11**),[S11] 1-(*p*-methoxyphenyl)cycloheptene (**12**),[S12] and 9-(4-methoxyphenyl)-8-phenyl-6,7-dihydro-5*H*-benzo[7]annulene (**2s**)[S13] were identical in spectra data with those reported in the literature.

8-Fluoro-4-(*p*-tolylsulfinyl)-2,3-dihydrobenzo[*b*]oxepin-5-yl trifluoromethanesulfonate (**1c**)



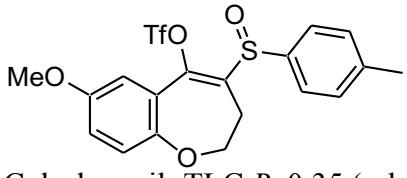
Pale yellow solid; Mp 114–117 °C; TLC R_f 0.56 (*n*-hexane/EtOAc = 5/2); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.33 (ddd, 1H, J = 16.5, 7.0, 4.0 Hz), 2.42 (s, 3H), 2.74 (ddd, 1H, J = 16.5, 7.0, 4.0 Hz), 4.10 (ddd, 1H, J = 10.5, 7.0, 4.0 Hz), 4.34 (ddd, 1H, J = 10.5, 7.0, 4.0 Hz), 6.79 (dd, 1H, J = 9.5, 2.0 Hz), 6.92 (ddd, 1H, J = 10.0, 8.0, 2.0 Hz), 7.36 (d, 2H, J = 8.0 Hz), 7.58 (dd, 1H, J = 8.0, 4.0 Hz), 7.62 (d, 2H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 21.4 (1C), 22.9 (1C), 76.7 (1C), 110.0 (d, 1C, $J_{C–F}$ = 23.7 Hz), 111.3 (d, 1C, $J_{C–F}$ = 22.6 Hz), 118.4 (q, 1C, $J_{C–F}$ = 322 Hz), 119.3 (d, 1C, $J_{C–F}$ = 3.3 Hz), 124.3 (2C), 130.1 (d, 1C, $J_{C–F}$ = 10.5 Hz), 130.3 (2C), 138.0 (1C), 138.6 (1C), 142.0 (1C), 143.5 (1C), 158.4 (d, 1C, $J_{C–F}$ = 12.1 Hz), 164.8 (d, 1C, $J_{C–F}$ = 255.3 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –72.4 (s, 3F), –105.27 to –105.34 (m, 1F); IR (KBr, cm^{-1}) 606, 748, 764, 826, 1136, 1223, 1425, 1493, 1580, 1609, 1638; HRMS (ESI$^+$) *m*/*z* 473.0098 ([M+Na]$^+$, $C_{18}H_{14}F_4NaO_5S_2^+$ requires 473.0111).

4-(*p*-Tolylsulfinyl)-2,3-dihydrobenzo[*b*]oxepin-5-yl trifluoromethanesulfonate



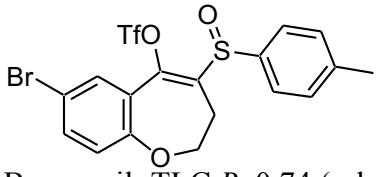
Colorless solid; Mp 80–82 ºC; TLC R_f 0.32 (*n*-hexane/EtOAc = 3/1); ^{1}H NMR (CD_3OD, 500 MHz) δ 2.28–2.34 (m, 1H), 2.43 (s, 3H), 2.64–2.72 (m, 1H), 4.03–4.10 (m, 1H), 4.35–4.42 (m, 1H), 7.13 (dd, 1H, J = 8.1, 1.0 Hz), 7.26 (ddd, 1H, J = 8.1, 8.1, 1.0 Hz), 7.44–7.51 (m, 3H), 7.60–7.65 (m, 3H); ^{13}C NMR (CD_3OD, 126 MHz) δ 21.5 (1C), 24.3 (1C), 79.2 (1C), 120.0 (q, 1C, $J_{C–F}$ = 320 Hz), 124.0 (1C), 125.0 (1C), 125.1 (1C), 125.6 (2C), 129.6 (1C), 131.7 (2C), 134.5 (1C), 138.8 (1C), 139.7 (1C), 144.2 (1C), 146.6 (1C), 158.6 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –72.6 (s); IR (KBr, cm^{-1}) 797, 837, 912, 1040, 1136, 1219, 1423; Anal. calcd. for $C_{18}H_{15}F_3O_5S_2$: C, 50.00; H, 3.50; N, 0.00; Found: C, 50.03; H, 3.41, N, 0.00.

7-Methoxy-4-(*p*-tolylsulfinyl)-2,3-dihydrobenzo[*b*]oxepin-5-yl trifluoromethanesulfonate



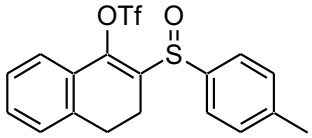
Colorless oil; TLC R_f 0.35 (*n*-hexane/EtOAc = 3/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.35 (ddd, 1H, J = 16.1, 5.1, 5.1 Hz), 2.43 (s, 3H), 2.59 (ddd, 1H, J = 16.1, 8.4, 5.1 Hz), 3.81 (s, 3H), 3.90 (ddd, 1H, J = 10.8, 8.4, 5.1 Hz), 4.31 (ddd, 1H, J = 10.8, 5.1, 5.1 Hz), 7.04 (dd, 1H, J = 8.9, 3.0 Hz), 7.01 (d, 1H, J = 8.9 Hz), 7.04 (dd, 1H, J = 3.0 Hz), 7.33–7.38 (AA'BB', 2H), 7.62–7.68 (AA'BB', 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 21.4 (1C), 23.1 (1C), 55.7 (1C), 78.3 (1C), 115.6 (1C), 119.3.0 (q, 1C, $J_{C–F}$ = 321 Hz), 119.5 (1C), 123.7 (1C), 124.4 (2C), 124.7 (1C), 130.2 (2C), 138.1 (1C), 138.7 (1C), 141.9 (1C), 144.5 (1C), 150.5 (1C), 155.7 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –72.8 (s); IR (KBr, cm^{-1}) 814, 870, 1007, 1038, 1082, 1136, 1211, 1420, 1493; Anal. calcd. for $C_{19}H_{17}F_3O_6S_2$: C, 49.35; H, 3.71; N, 0.00; Found: C, 49.46; H, 3.71, N, 0.00.

7-Bromo-4-(*p*-tolylsulfinyl)-2,3-dihydrobenzo[*b*]oxepin-5-yl trifluoromethanesulfonate



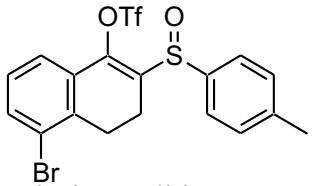
Brown oil; TLC R_f 0.74 (*n*-hexane/EtOAc = 3/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.32 (ddd, 1H, J = 16.6, 6.8, 4.3 Hz), 2.42 (s, 3H), 2.79 (ddd, 1H, J = 16.6, 7.4, 4.3 Hz), 4.10 (ddd, 1H, J = 11.0, 7.4, 4.3 Hz), 4.34 (ddd, 1H, J = 11.0, 6.8, 4.3 Hz), 6.95 (d, 1H, J = 8.7 Hz), 7.33–7.38 (AA'BB', 2H), 7.48 (dd, 1H, J = 8.7, 2.4 Hz), 7.59–7.64 (AA'BB', 2H), 7.68 (d, 1H, J = 2.4 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 21.2 (1C), 32,4 (1C), 76,2 (1C), 114.5 (1C), 115.8 (1C), 118.3 (q, 1C, $J_{C–F}$ = 321 Hz), 123.8 (1C), 126,6 (1C), 126.7 (1C), 130.0 (1C), 130.3 (2C), 133.8 (1C), 134.2 (2C), 138.1 (1C), 139.6 (1C) 154.4 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –72.4 (s); IR (KBr, cm^{-1}) 602, 808, 851, 1030, 1055, 1082, 1134, 1215, 1425, 1479; Anal. calcd. for $C_{18}H_{14}BrF_3O_5S_2$: C, 42.28; H, 2.76; N, 0.00; Found: C, 41.98; H, 2.87, N, 0.00.

2-(*p*-Tolylsulfinyl)-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate



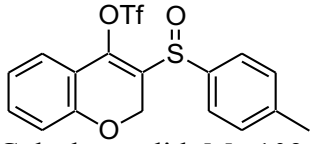
Colorless solid; Mp 82–84 ºC; TLC R_f 0.28 (*n*-hexane/EtOAc = 3/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.98–2.07 (m, 1H), 2.40 (s, 3H), 2.75–2.83 (m, 1H), 2.89–3.01 (m, 2H), 7.17 (dd, 1H, J = 6.6, 1.6 Hz), 7.29–7.32 (AA'BB', 2H) 7.32–7.37 (m, 2H), 7.52 (dd, 1H, J = 8.9, 1.9 Hz), 7.54–7.58 (AA'BB', 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 17.9 (1C), 21.4 (1C), 27.2 (1C), 118.6 (q, 1C, $J_{C–F}$ = 321 Hz), 123.6 (1C), 124.2 (2C), 127.2 (1C), 127.90 (1C), 127.94 (1C), 130.1 (2C), 131.1 (1C), 136.2 (1C), 137.3 (1C), 138.1 (1C), 141.7 (1C), 145.1 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –72.6 (s); IR (KBr, cm^{-1}) 600, 762, 800, 835, 899, 1013, 1084, 1136, 1217, 1423; Anal. calcd. for $C_{18}H_{15}F_3O_4S_2$: C, 51.92; H, 3.63; N, 0.00; Found: C, 52.05; H, 3.64, N, 0.00.

5-Bromo-2-(*p*-tolylsulfinyl)-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate



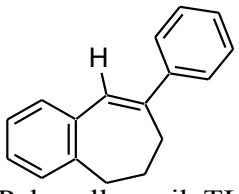
Colorless solid; Mp 92–94ºC; TLC R_f 0.50 (*n*-hexane/EtOAc = 3/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.00–2.10 (m, 1H), 2.40 (s, 3H), 2.86–2.95 (m, 1H), 2.95–3.04 (m, 1H), 3.05–3.13 (m, 1H), 7.19 (dd, 1H, J = 8.0, 8.0 Hz), 7.29–7.34 (AA'BB', 2H) 7.48 (d, J = 8.0 Hz, 2H), 7.54–7.57 (AA'BB', 2H), 7.58 (d, J = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 17.3 (1C), 21.4 (1C), 26.8 (1C), 118.5 (q, 1C, $J_{C–F}$ = 321 Hz), 122.8 (1C), 123.9 (1C), 124.2 (2C), 128.2 (1C), 129.9 (1C), 130.2 (2C), 135.1 (1C), 136.6 (1C), 137.3 (1C), 137.9 (1C), 142.0 (1C), 143.8 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –72.5 (s); IR (KBr, cm^{-1}) 602, 797, 845, 895, 1084, 1136, 1217, 1414, 1425; Anal. calcd. for $C_{18}H_{15}F_3O_4S_2$: C, 43.65; H, 2.85; N, 0.00; Found: C, 43.63; H, 2.79, N, 0.00.

3-(*p*-Tolylsulfinyl)-2*H*-chromen-4-yl trifluoromethanesulfonate



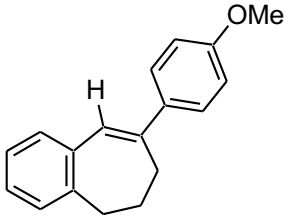
Colorless solid; Mp 109–110 ºC; TLC R_f 0.50 (*n*-hexane/EtOAc = 3/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.42 (s, 3H), 4.54 (d, 1H, J = 14.1 Hz), 5.12 (d, 1H, J = 14.1 Hz), 6.87 (dd, 1H, J = 7.9, 0.7 Hz), 7.06 (ddd, 1H, J = 7.9, 7.9, 0.7 Hz), 7.32–7.38 (m, 3H), 7.45 (dd, 1H, J = 7.9, 1.4 Hz), 7.58–7.63 (AA'BB', 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 21.4 (1C), 62.0 (1C), 116.9 (1C), 117.1 (1C), 118.5 (q, 1C, $J_{C–F}$ = 321 Hz), 122.4 (1C), 124.0 (1C), 124.4 (2C), 126.4 (1C), 130.4 (2C), 133.6 (1C), 136.7 (1C), 142.2 (1C), 142.9 (1C), 156.0 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –72.1 (s); IR (KBr, cm^{-1}) 600, 762, 849, 1043, 1136, 1223, 1420, 1427; Anal. calcd. for $C_{17}H_{13}F_3O_5S_2$: C, 48.80; H, 3.18; N, 0.00; Found: C, 48.75; H, 3.18, N, 0.00.

8-Phenyl-6,7-dihydro-5*H*-benzo[7]annulene (**2a**)



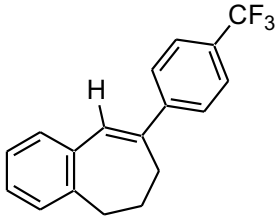
Pale yellow oil; TLC R_f 0.60 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.22 (tt, 2H, *J* = 7.0, 6.5 Hz), 2.64 (t, 2H, *J* = 7.0 Hz), 2.81 (t, 2H, *J* = 6.5 Hz), 6.80 (s, 1H), 7.12–7.18 (m, 2H), 7.20–7.22 (m, 2H), 7.26–7.29 (m, 1H), 7.36 (dd, 2H, *J* = 8.0, 8.0 Hz), 7.52 (d, 2H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 30.8 (1C), 32.6 (1C), 34.4 (1C), 126.0 (1C), 126.3 (2C), 126.6 (1C), 127.1 (1C), 128.4 (2C), 128.7 (1C), 129.0 (1C), 130.4 (1C), 137.5 (1C), 141.3 (1C), 142.3 (1C), 144.3 (1C); IR (KBr, cm^{-1}) 702, 748, 895, 1262, 1447, 1597, 2934, 3051; HRMS (ESI^+) *m*/*z* 221.1321 ($[M+H]^+$, $C_{17}H_{17}^+$ requires 221.1325).

8-(4-Methoxyphenyl)-6,7-dihydro-5*H*-benzo[7]annulene (**2b**)



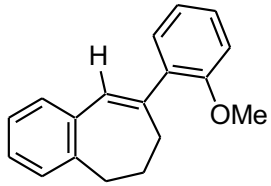
Pale yellow oil; TLC R_f 0.44 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.17–2.24 (m, 2H), 2.62 (t, 2H, *J* = 6.5 Hz), 2.77–2.82 (m, 2H), 3.84 (s, 3H), 6.75 (s, 1H), 6.88–6.93 (AA'BB', 2H), 7.10–7.22 (m, 4H), 7.43–7.47 (AA'BB', 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 30.8 (1C), 32.5 (1C), 34.3 (1C), 55.3 (1C), 113.7 (2C), 125.9 (1C), 126.4 (1C), 127.2 (1C), 127.3 (2C), 128.9 (1C), 130.2 (1C), 136.6 (1C), 137.7 (1C), 141.1 (1C), 142.3 (1C), 158.9 (1C); IR (KBr, cm^{-1}) 810, 1042, 1206, 1277, 1418, 1458, 1489, 1674; HRMS (ESI^+) *m*/*z* 273.1256 ($[M+Na]^+$, $C_{18}H_{18}NaO^+$ requires 273.1250).

8-(4-Trifluoromethylphenyl)-6,7-dihydro-5*H*-benzo[7]annulene (**2c**)



Colorless solid; Mp 51–53 ºC; TLC R_f 0.50 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.19–2.27 (m, 2H), 2.65 (t, 2H, *J* = 7.1 Hz), 2.82 (t, 2H, *J* = 6.1 Hz), 6.84 (s, 1H), 7.15–7.20 (m, 2H), 7.20–7.25 (m, 2H), 7.57–7.64 (m, 4H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 30.4 (1C), 32,6 (1C), 34.3 (1C), 124.3 (q, 1C, J_{C-F} = 279 Hz), 125.2 (1C), 125.3 (1C), 126.1 (1C), 126.5 (2C), 127.1 (1C), 129.0 (q, 2C, J_{C-F} = 32.4 Hz), 129.1 (1C), 130.4 (1C), 130.6 (1C), 136.8 (1C), 141.6 (1C), 147.8 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –63.0 (s); IR (KBr, cm^{-1}) 748, 895, 1261, 1422, 2886, 3053; HRMS (ESI^+) *m*/*z* 311.1023 ($[M+Na]^+$, $C_{18}H_{15}F_3Na^+$ requires 311.1018).

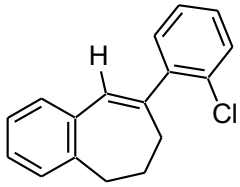
8-(2-Methoxyphenyl)-6,7-dihydro-5*H*-benzo[7]annulene (**2d**)



Yellow oil; TLC R_f 0.20 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.19 (tt, 2H, *J* = 6.6, 6.6 Hz), 2.54 (t, 2H, *J* = 6.6 Hz), 2.85 (t, 2H, *J* = 6.6 Hz), 3.83 (s, 3H), 6.55 (s, 1H), 6.90 (dd, 1H, *J* = 8.2, 1.0 Hz), 6.95 (ddd, 1H, *J* = 7.4, 7.4, 1.0 Hz), 7.09–7.14 (m, 1H), 7.14–7.20 (m, 3H), 7.25–7.30 (m, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 30.7 (1C), 33.5 (1C), 34.7 (1C), 55.4 (1C), 110.8 (1C), 120.6 (1C), 125.8 (1C), 126.3 (1C), 128.2 (1C), 129.0 (1C), 129.7 (1C), 129.8 (1C), 130.1 (1C), 134.8 (1C), 137.5 (1C), 141.4 (1C), 143.1 (1C), 156.6 (1C); IR (KBr, cm^{-1}) 752, 1028, 1117, 1244, 1433, 1462, 1487, 2930;

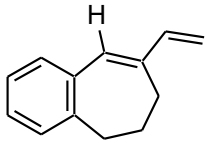
HRMS (ESI$^+$) *m*/*z* 273.1261 ([M+Na]$^+$, $C_{18}H_{18}NaO^+$ requires 273.1250).

8-(2-Chlorophenyl)-6,7-dihydro-5*H*-benzo[7]annulene (**2e**)



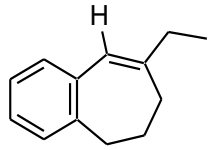
Colorless solid; Mp >300 ºC; TLC R_f 0.54 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.14–2.21 (m, 2H), 2.56–2.61 (m, 2H), 2.89–2.95 (m, 2H), 6.45 (s, 1H), 7.13–7.26 (m, 6H), 7.30–7.39 (m, 1H), 7.80–7.41 (m, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 29.2 (1C), 29.7 (1C), 35.0 (1C), 126.0 (1C), 126.7 (1C), 126.8 (1C), 128.1 (1C), 129.1 (1C), 129.6 (1C), 130.2 (1C), 130.8 (1C), 131.0 (1C), 132.3 (1C), 136.3 (1C), 141.5 (1C), 142.5 (1C), 144.6 (1C); IR (KBr, cm^{-1}) 739, 752, 1034, 1059, 1472, 2849, 2920; HRMS (ESI$^+$) *m*/*z* 277.0761 ([M+Na]$^+$, $C_{17}H_{15}{}^{35}ClNa^+$ requires 277.0754).

8-Ethenyl-6,7-dihydro-5*H*-benzo[7]annulene (**2f**)



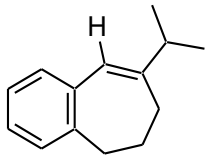
Colorless oil; TLC R_f 0.45 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.03–2.09 (m, 2H), 2.51 (t, 2H, *J* = 6.6 Hz), 2.79–2.84 (m, 2H), 5.06 (d, 1H, *J* = 10.9 Hz), 5.27 (d, 1H, *J* = 17.5 Hz), 6.50–6.58 (m, 2H), 7.08–7.13 (m, 2H), 7.08–7.20 (m, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 27.3 (1C), 29.4 (1C), 35.3 (1C), 111.8 (1C), 125.9 (1C), 126.9 (1C), 128.9 (1C), 131.3 (1C), 132.8 (1C), 136.2 (1C), 140.1 (1C), 141.7 (1C), 142.2 (1C); IR (KBr, cm^{-1}) 737, 754, 887, 986, 2924; HRMS (ESI$^+$) *m*/*z* 193.0988 ([M+Na]$^+$, $C_{13}H_{14}Na^+$ requires 193.0988).

8-Ethyl-6,7-dihydro-5*H*-benzo[7]annulene (**2g**)



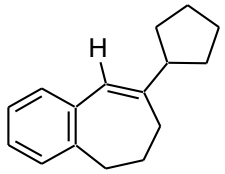
Colorless oil; TLC R_f 0.67 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.13 (t, 3H, *J* = 7.4 Hz), 1.98–2.05 (m, 2H), 2.21 (q, 2H, *J* = 7.4 Hz), 2.26 (t, 2H, *J* = 6.8 Hz), 2.72–2.76 (m, 2H), 6.28 (s, 1H), 7.03–7.16 (m, 4H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 13.6 (1C), 28.9 (1C), 33.4 (1C), 33.7 (1C), 35.0 (1C), 124.5 (1C), 125.7 (1C), 125.8 (1C), 128.8 (1C), 129.9 (1C), 137.2 (1C), 141.1 (1C), 146.1 (1C); IR (KBr, cm^{-1}) 737, 750, 1449, 2853, 2872, 2926, 2961; HRMS (ESI$^+$) *m*/*z* 195.1143 ([M+Na]$^+$, $C_{13}H_{16}Na^+$ requires 195.1144).

8-Isopropyl-6,7-dihydro-5*H*-benzo[7]annulene (**2h**)



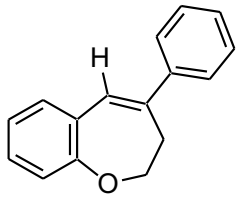
Colorless oil; TLC R_f 0.64 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.13 (d, 6H, *J* = 6.9 Hz), 2.04–2.10 (m, 2H), 2.14 (t, 2H, *J* = 6.6 Hz), 2.46 (sept, 1H, *J* = 6.9 Hz), 2.65–2.69 (t, 2H, *J* = 6.3 Hz), 6.31 (s, 1H), 7.04–7.13 (m, 3H), 7.15 (ddd, 1H, *J* = 7.4, 7.4, 1.6 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 22.0 (2C), 29.8 (1C), 31.4 (1C), 34.2 (1C), 37.4 (1C), 123.2 (1C), 125.7 (1C), 125.8 (1C), 128.8 (1C), 129.3 (1C), 138.1 (1C), 141.0 (1C), 150.5 (1C); IR (KBr, cm^{-1}) 749, 895, 1261, 1422, 1551, 1603, 2986, 3053; HRMS (ESI$^+$) *m*/*z* 209.1297 ([M+Na]$^+$, $C_{14}H_{18}Na^+$ requires 209.1301).

8-Cyclopentyl-6,7-dihydro-5*H*-benzo[7]annulene (**2i**)



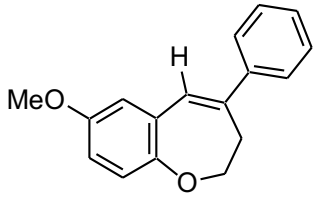
Colorless oil; TLC R_f 0.69 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.44–1.54 (m, 2H), 1.58–1.67 (m, 2H), 1.67–1.77 (m, 2H), 1.82–1.91 (m, 2H), 2.05–2.10 (m, 2H), 2.14 (t, 2H, J = 6.5 Hz), 2.60 (quin, 1H, J = 8.1 Hz), 2.68 (t, 2H, J = 6.3 Hz), 6.34 (s, 1H), 7.04–7.13 (m, 3H), 7.16 (ddd, 1H, J = 7.3, 7.3, 1.6 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 25.3 (2C), 30.5 (1C), 31.5 (1C), 31.9 (2C), 34.2 (1C), 49.5 (1C), 123.7 (1C), 125.69 (1C), 125.75 (1C), 128.1 (1C), 129.3 (1C), 138.1 (1C), 141.0 (1C), 147.7 (1C); IR (KBr, cm^{-1}) 752, 895, 1261, 1422, 1551, 1605, 2934, 3051; HRMS (ESI$^+$) *m*/*z* 235.1452 ([M+Na]$^+$, $C_{16}H_{20}Na^+$ requires 235.1457).

4-Phenyl-2,3-dihydrobenzo[*b*]oxepine (**3**)



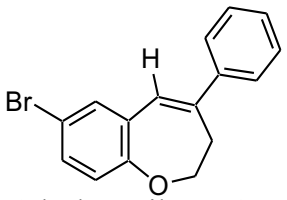
Colorless oil; TLC R_f 0.46 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.09 (t, 2H, J = 4.8 Hz), 4.39 (t, 2H, J = 4.8 Hz), 6.66 (s, 1H), 6.96–7.02 (m, 2H), 7.14 (ddd, 1H, J = 7.8, 7.8, 1.6 Hz), 7.24–7.31 (m, 2H), 7.34–7.40 (AA'BB'C, 2H), 7.45–7.50 (AA'BB'C, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 36.8 (1C), 68.9 (1C), 119.7 (1C), 122.3 (1C), 125.8 (1C), 125.9 (2C), 127.2 (1C), 127.5 (1C), 128.0 (1C), 128.4 (2C), 133.7 (1C), 140.8 (1C), 143.5 (1C), 158.7 (1C); IR (KBr, cm^{-1}) 696, 758, 822, 874, 897, 1229, 1260, 1483; HRMS (ESI$^+$) *m*/*z* 245.0939 ([M+Na]$^+$, $C_{16}H_{14}NaO^+$ requires 245.0937).

7-Methoxy-4-phenyl-2,3-dihydrobenzo[*b*]oxepine (**4**)



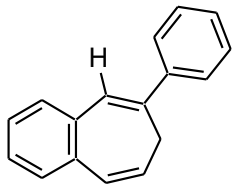
Colorless oil; TLC R_f 0.42 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.08 (t, 2H, J = 4.8 Hz), 3.79 (s, 3H), 4.34 (t, 2H, J = 4.8 Hz), 6.60 (s, 1H), 6.71 (dd, 1H, J = 8.8, 3.1 Hz), 6.77 (d, 1H, J = 3.1 Hz), 6.90 (d, 1H, J = 8.8 Hz), 7.27–7.31 (AA'BB'C, 1H), 7.34–7.39 (AA'BB'C, 2H), 7.45–7.49 (AA'BB'C, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 36.9 (1C), 55.7 (1C), 69.1 (1C), 113.8 (1C), 117.4 (1C), 120.4 (1C), 125.9 (2C), 126.7 (1C), 127.30 (1C), 127.32 (1C), 128.4 (2C), 141.5 (1C), 143.5 (1C), 152.9 (1C), 154.6 (1C); IR (KBr, cm^{-1}) 750, 895, 1261, 1422, 1497, 1607, 2986, 3051; HRMS (ESI$^+$) *m*/*z* 275.1030 ([M+Na]$^+$, $C_{17}H_{16}NaO_2^+$ requires 275.1043).

7-Bromo-4-phenyl-2,3-dihydrobenzo[*b*]oxepine (**5**)



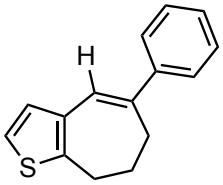
Colorless oil; TLC R_f 0.26 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.08 (t, 2H, J = 4.8 Hz), 4.35 (t, 2H, J = 4.8 Hz), 6.54 (s, 1H), 6.84 (d, 1H, J = 8.6 Hz), 7.20 (dd, 1H, J = 8.6, 2.5 Hz), 7.27–7.33 (AA'BB'C, 1H), 7.34–7.40 (m, 3H), 7.42–7.47 (AA'BB'C, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 36.7 (1C), 68.9 (1C), 114.4 (1C), 121.5 (1C), 125.8 (2C), 126.1 (1C), 127.6 (1C), 127.9 (1C), 128.5 (2C), 130.5 (1C), 135.6 (1C), 142.5 (1C), 143.0 (1C), 157.7 (1C); IR (KBr, cm^{-1}) 696, 758, 820, 897, 1229, 1260, 1304, 1483; HRMS (ESI$^+$) *m*/*z* 323.0038 ([M+Na]$^+$, $C_{16}H_{13}{}^{79}BrNaO^+$ requires 323.0042).

6-Phenyl-7*H*-benzo[7]annulene (**6**)



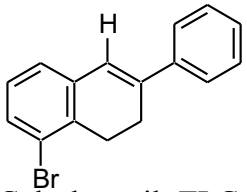
Colorless solid; Mp 42–44 ºC; TLC R_f 0.56 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.90 (d, 2H, J = 7.1 Hz), 6.00 (dt, 1H, J = 10.0, 7.1 Hz), 6.70 (d, 1H, J = 10.0 Hz), 6.90 (s, 1H), 7.26–7.32 (m, 3H), 7.37–7.41 (m, 3H), 7.41–7.45 (m, 1H) 7.53–7.57 (AA'BB', 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 29.7 (1C), 125.9 (1C), 126.1 (1C), 126.8 (3C), 127.3 (1C), 127.8 (1C), 128.4 (2C), 130.0 (1C), 130.4 (1C), 130.8 (1C), 136.5 (1C), 137.0 (1C), 140.4 (1C), 142.1 (1C); IR (KBr, cm^{-1}) 694, 745, 787, 820, 854, 1445, 1481, 1493, 3021, 3053; HRMS (ESI^+) *m*/*z* 217.1014 ($[M–H]^+$, $C_{17}H_{13}^+$ requires 217.1012).

5-Phenyl-7,8-dihydro-6*H*-cyclohepta[*b*]thiophene (**7**)



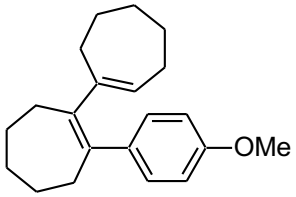
Colorless oil; TLC R_f 0.43 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.18 (tt, 2H, J = 5.9, 5.9 Hz), 2.87 (t, 2H, J = 5.9 Hz), 3.12 (t, 2H, J = 5.9 Hz), 6.63 (s, 1H), 6.86 (d, 1H, J = 5.2 Hz), 7.00 (d, 1H, J = 5.2 Hz), 7.22–7.28 (AA'BB'C, 1H), 7.31–7.36 (AA'BB'C, 2H), 7.41–7.45 (AA'BB'C, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 25.3 (1C), 30.4 (1C), 34.4 (1C), 121.2 (1C), 122.5 (1C), 126.0 (2C), 126.8 (1C), 128.2 (2C), 131.5 (1C), 134.8 (1C), 139.6 (1C), 141.1 (1C), 145.0 (1C); IR (KBr, cm^{-1}) 633, 696, 721, 758, 889, 1435, 1445, 1491, 2924; HRMS (ESI^+) *m*/*z* 227.0898 ($[M+H]^+$, $C_{15}H_{15}S^+$ requires 227.0889).

8-Bromo-3-phenyl-1,2-dihydronaphthalene (**9**)



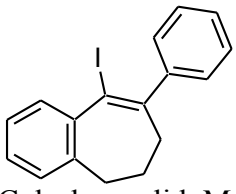
Colorless oil; TLC R_f 0.41 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.79 (t, 2H, J = 7.9 Hz), 3.08 (t, 2H, J = 7.9 Hz), 6.79 (s, 1H), 7.01–7.09 (m, 2H), 7.28–7.32 (AA'BB'C, 1H), 7.34–7.41 (m, 3H), 7.51–7.57 (AA'BB'C, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 25.9 (1C), 27.7 (1C), 123.7 (1C), 123.8 (1C), 125.2 (2C), 125.9 (1C), 127.7 (1C), 127.8 (1C), 128.5 (2C), 130.9 (1C), 134.0 (1C), 136.8 (1C), 139.3 (1C), 140.4 (1C); IR (KBr, cm^{-1}) 692, 710, 750, 764, 783, 858, 962, 1445, 1493, 1551; HRMS (ESI^+) *m*/*z* 285.0268 ($[M+H]^+$, $C_{16}H_{14}{}^{79}Br^+$ requires 285.0273)

1-(1-Cycloheptenyl)-2-(*p*-methoxyphenyl)cycloheptene (**13**)



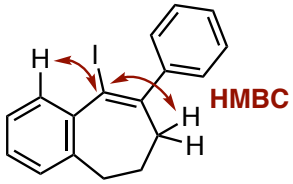
Colorless oil; TLC R_f 0.66 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.28–1.32 (m, 2H), 1.40–1.45 (m, 2H), 1.54–1.65 (m, 6H), 1.78–1.83 (m, 2H), 1.85–1.89 (m, 2H), 2.05–2.08 (m, 2H), 2.31–2.33 (m, 2H), 2.48–2.50 (m, 2H), 3.79 (s, 3H), 5.27 (t, 1H, J = 7.0 Hz), 6.75–6.78 (AA'BB', 2H), 7.02–7.04 (AA'BB', 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 26.7 (1C+1C, two signals overlapped), 26.83 (1C), 28.84 (1C), 28.7 (1C), 32.6 (1C), 32.8 (1C), 33.3 (1C), 34.1 (1C), 36.2 (1C), 55.2 (1C), 112.8 (2C), 129.3 (2C), 129.6 (1C), 136.9 (1C), 138.8 (1C), 145.0 (1C), 146.9 (1C), 157.3 (1C); IR (KBr, cm^{-1}) 700, 750, 895, 1261, 1242, 2986, 3051; HRMS (ESI^+) *m*/*z* 319.2035 ($[M+Na]^+$, $C_{21}H_{28}NaO^+$ requires 319.2032).

9-Iodo-8-phenyl-6,7-dihydro-5*H*-benzocycloheptene (**2j**)

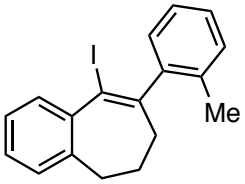


Colorless solid; Mp 136–138 ºC; TLC R_f 0.37 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.18 (tt, 2H, *J* = 7.1, 7.1Hz), 2.29 (t, 2H, *J* = 7.1 Hz), 2.78 (t, 2H, *J* = 7.1 Hz), 7.14 (d, 1H, *J* = 7.4 Hz), 7.19 (dd, 1H, *J* = 7.4, 7.4 Hz), 7.29–7.35 (m, 4H), 7.37–7.43 (AA'BB'C, 2H), 7.62 (d, 1H, *J* = 7.8 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 32.0 (1C), 33.4 (1C), 34.1 (1C), 95.4 (1C), 126.3 (1C), 127.3 (1C), 127.9 (2C), 128.1 (1C), 128.2 (2C+1C, two signals overlapped), 131.3 (1C), 138.1 (1C), 142.9 (1C), 146.9 (1C), 149.8 (1C); IR (KBr, cm^{-1}) 573, 648, 698, 745, 887, 1443, 1489, 2855, 2932; Anal. calcd. for $C_{17}H_{15}I$: C, 58.98; H, 4.37; N, 0.00; Found: C, 58.82; H, 4.29; N, 0.00.

The regiochemistry of **2j** was determined by the HMBC experiment.

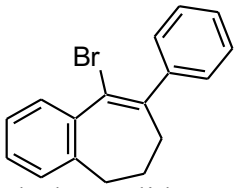


9-Iodo-8-(*o*-tolyl)-6,7-dihydro-5*H*-benzocycloheptene (**2k**)



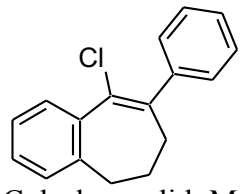
Yellow solid; Mp 122–123 ºC; TLC R_f 0.63 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.13–2.21 (m, 2H), 2.22–2.31 (m, 2H), 2.32 (s, 3H), 2.77–2.81 (m, 1H), 2,85–2.90 (m, 1H), 7.10–7.12 (m, 1H), 7.16 (dd, 1H, *J* = 7.5, 1.0 Hz), 7.18–7.26 (m, 4H), 7.32 (ddd, 1H, *J* = 8.0, 8.0, 1.5 Hz), 7.62 (dd, 1H, *J* = 8.0, 1.5 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 19.8 (1C), 32.2 (1C), 32.5 (1C), 33.9 (1C), 97.1 (1C), 125.9 (1C), 126.3 (1C), 127.4 (1C), 127.8 (1C), 128.0 (1C), 128.4 (1C), 130.2 (1C), 131.2 (1C), 133.9 (1C), 138.9 (1C), 142.4 (1C), 147.4 (1C), 150.1 (1C); IR (KBr, cm^{-1}) 746, 895, 1260, 1416, 1551, 1603, 2934, 3051; HRMS (ESI$^+$) *m*/*z* 383.0269 ([M+Na]$^+$, $C_{18}H_{17}INa^+$ requires 383.0267).

9-Bromo-8-phenyl-6,7-dihydro-5*H*-benzocycloheptene (**2l**)



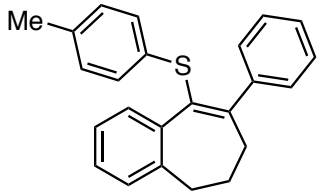
Colorless solid; Mp 93–96 ºC; TLC R_f 0.37 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.22 (tt, 2H, *J* = 7.0, 7.0 Hz), 2.28 (t, 2H, *J* = 7.0 Hz), 2.79 (t, 2H, *J* = 7.0 Hz), 7.19 (d, 2H, *J* = 7.4 Hz), 7.29–7.35 (AA'BB'C, 2H), 7.38–7.42 (m, 4H), 7.64 (d, 1H, *J* = 7.7 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 31.9 (1C), 33.7 (1C), 34.2 (1C), 116.2 (1C), 126.4 (1C), 127.3 (1C), 128.3 (2C+2C, two signals overlapped), 128.3 (1C), 128.4 (1C), 129.6 (1C), 139.8 (1C), 140.3 (1C), 142.7 (1C), 143.5 (1C); IR (KBr, cm^{-1}) 654, 698, 746, 897, 1447, 1479, 1489, 2855, 2932; HRMS (ESI$^+$) *m*/*z* 321.0245 ([M+Na]$^+$, $C_{17}H_{15}{}^{79}BrNa^+$ requires 321.0249).

9-Chloro-8-phenyl-6,7-dihydro-5*H*-benzocycloheptene (**2m**)



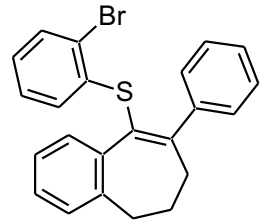
Colorless solid; Mp 62–64 ºC; TLC R_f 0.37 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.20–2.26 (m, 2H), 2.26–2.31 (m, 2H), 2.76–2.80 (m, 2H), 7.21–7.24 (m, 1H), 7.24–7.29 (m, 1H), 7.29–7.35 (m, 2H), 7.38–7.46 (m, 4H), 7.61–7.64 (m, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 31.9 (1C), 33.2 (1C), 34.5 (1C), 126.4 (1C), 127.2 (1C), 128.10 (1C), 128.13 (1C), 128.3 (2C), 128.4 (2C), 128.5 (1C), 139.1 (1C), 139.2 (1C), 140.1 (1C), 141.7 (1C), 152.0 (1C); IR (KBr, cm^{-1}) 700, 752, 1227, 1244, 1277, 1306, 1449, 1690, 2855, 2928, 2947; HRMS (ESI$^+$) *m*/*z* 277.0776 ([M+Na]$^+$, $C_{17}H_{15}{}^{35}ClNa^+$ requires 277.0754).

8-Phenyl-6,7-dihydro-5*H*-benzo[7]annulen-9-yl *p*-tolyl sulfide (**2n**)



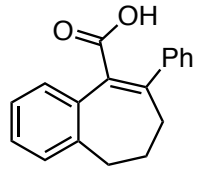
Colorless solid; Mp 127–129 ºC; TLC R_f 0.21 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.17 (s, 3H), 2.25–2.35 (m, 4H), 2.82 (t, 2H, *J* = 6.8 Hz), 6.83–6.88 (AA'BB', 2H), 6.93–6.97 (AA'BB', 2H), 7.07–7.16 (m, 3H), 7.26–7.31 (AA'BB'C, 1H), 7.33–7.38 (AA'BB', 2H), 7.38–7.43 (AA'BB'C, 2H), 7.69 (dd, 1H, *J* = 7.2, 2.1 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 20.9 (1C), 32.4 (1C), 34.1 (1C), 35.3 (1C), 126.2 (1C), 127.0 (1C), 127.3 (1C), 128.0 (2C), 128.3 (2C), 128.4 (1C), 128.7 (1C), 129.0 (2C), 129.2 (2C), 129.9 (1C), 133.1 (1C), 135.3 (1C), 139.5 (1C), 141.3 (1C), 143.5 (1C), 146.8 (1C); IR (KBr, cm^{-1}) 698, 750, 802, 1449, 1489, 2855, 2926, 3017; HRMS (ESI$^+$) *m*/*z* 365.1338 ([M+Na]$^+$, $C_{24}H_{22}NaS^+$ requires 365.1334).

8-Phenyl-6,7-dihydro-5*H*-benzo[7]annulen-9-yl *o*-bromophenyl sulfide (**2o**)



Colorless solid; Mp 105–107 ºC; TLC R_f 0.64 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.27–2.40 (m, 4H), 2.89 (t, 2H, *J* = 7.0 Hz), 6.82 (ddd, 1H, *J* = 7.9, 7.9, 1.9 Hz), 6.95–7.02 (m, 2H), 7.10–7.15 (m, 2H), 7.17 (dd, 1H, *J* = 1.9, 7.2 Hz), 7.25–7.30 (AA'BB'C, 1H), 7.31–7.37 (m, 3H), 7.37–7.42 (AA'BB'C, 2H), 7.69 (dd, 1H, *J* = 7.7, 1.9 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 32.5 (1C), 34.3 (1C), 35.3 (1C), 122.6 (1C), 126.4 (2C), 127.2 (1C), 127.3 (1C), 127.6 (1C), 127.98 (2C), 128.04 (2C), 128.3 (1C), 128.6 (1C), 128.9 (1C), 129.5 (1C), 132.6 (1C), 138.3 (1C), 139.1 (1C), 141.4 (1C), 143.1 (1C), 149.0 (1C); IR (KBr, cm^{-1}) 698, 748, 908, 1020, 1425, 1445, 1489, 2855, 2932; HRMS (ESI$^+$) *m*/*z* 429.0292 ([M+Na]$^+$, $C_{23}H_{19}{}^{79}BrNaS^+$ requires 429.0283).

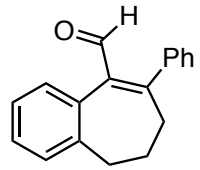
8-Phenyl-6,7-dihydro-5*H*-benzo[7]annulene-9-carboxylic acid (**2p**)



Yellow solid; Mp 105–107 ºC; TLC R_f 0.44 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.21(tt, 2H, *J* = 7.1, 7.1 Hz), 2.32 (t, 2H, *J* = 7.1 Hz), 2.74 (t, 2H, *J* = 7.1 Hz), 7.23–7.37 (m, 9H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 31.6 (1C), 34.0 (1C+1C, two signals overlapped), 126.2 (1C), 127.2 (2C), 127.9 (1C), 128.1 (1C), 128.3 (2C), 128.6 (1C), 128.8 (1C), 130.0 (1C), 136.7 (1C), 140.7 (1C), 142.0 (1C), 151.3 (1C), 173.3 (1C); IR (KBr, cm^{-1}) 750, 1275, 1489, 1684, 2852, 2924, 3055; HRMS

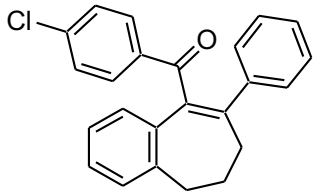
(ESI$^+$) *m*/*z* 265.1213 ([M+H]$^+$, $C_{18}H_{17}O_2^+$ requires 265.1223).

8-Phenyl-6,7-dihydro-5*H*-benzo[7]annulene-9-carbaldehyde (**2q**)



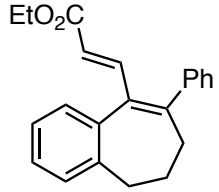
Colorless solid; Mp 115–117 ºC, TLC R_f 0.44 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.27 (tt, 2H, *J* = 7.2, 7.2 Hz), 2.48 (t, 2H, *J* = 7.2 Hz), 2.66 (t, 2H, *J* = 7.2 Hz), 7.23–7.31 (m, 2H), 7.31–7.36 (m, 2H), 7.37–7.46 (m, 2H), 7.41–7.46 (m, 3H), 9.72 (s, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 31.5 (1C), 34.0 (1C), 35.1 (1C), 126.0 (1C), 128.1 (2C), 128.3 (1C), 128.6 (1C), 129.0 (1C), 129.3 (2C), 130.0 (1C), 134.2 (1C), 137.8 (1C), 138.8 (1C), 140.6 (1C), 163.1 (1C), 191.9 (1C); IR (KBr, cm^{-1}) 644, 702, 754, 1304, 1445, 1670, 2857, 2934; HRMS (ESI$^+$) *m*/*z* 249.1285 ([M+H]$^+$, $C_{18}H_{17}O^+$ requires 249.1274).

8-Phenyl-6,7-dihydro-5*H*-benzo[7]annulene-9-yl *p*-chlorophenyl ketone (**2r**)



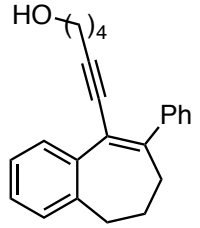
Colorless solid; Mp 124–127 ºC, TLC R_f 0.47 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.34 (tt, 2H, *J* = 7.0, 7.0 Hz), 2.48 (t, 2H, *J* = 7.0 Hz), 2.90 (t, 2H, *J* = 7.0 Hz), 7.05 (dd, 1H, *J* = 7.5, 1.0 Hz), 7.13–7.18 (m, 4H), 7.19–7.24 (m, 5H), 7.31 (dd, 1H, *J* = 7.5, 1.0 Hz), 7.64–7.69 (AA'BB', 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 32.3 (1C), 33.0 (1C), 34.8 (1C), 126.5 (1C), 127.88 (1C), 127.92 (1C), 128.0 (1C), 128.2 (2C+2C, two signals overlapped), 128.5 (2C), 129.4 (1C), 130.8 (2C), 136.3 (1C), 138.0 (1C), 138.3 (1C), 138.9 (1C), 140.6 (1C), 141.4 (1C), 146.5 (1C), 197.6 (1C); IR (KBr, cm^{-1}) 750, 1265, 1586, 1659, 2932, 3053; HRMS (ESI$^+$) *m*/*z* 381.1002 ([M+Na]$^+$, $C_{24}H_{19}{}^{35}ClNaO^+$ requires 381.1017).

Ethyl β-(*E*)-(8-phenyl-6,7-dihydro-5*H*-benzocyclohepten-9-yl)acrylate (**2t**)



Yellow oil; TLC R_f 0.46 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.21 (t, 3H, *J* = 7.0 Hz), 2.12 (tt, 2H, *J* = 7.0, 7.0 Hz), 2.31 (t, 2H, *J* = 7.0 Hz), 2.65 (t, 2H, *J* = 7.0 Hz), 4.12 (q, 2H, *J* = 7.0 Hz), 5.75 (d, 1H, *J* = 15.5 Hz), 7.24–7.26 (m, 2H), 7.28–7.33 (m, 4H), 7.34–7.36 (m, 1H), 7.39–7.40 (AA'BB'C, 2H), 7.64 (d, 1H, *J* = 15.5 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 14.2 (1C), 31.3 (1C), 33.3 (1C), 33.9 (1C), 60.1 (1C), 120.0 (1C), 126.0 (1C), 127.7 (1C), 127.8 (2C), 128.2 (1C), 128.5 (1C), 129.1 (2C), 129.2 (1C), 134.0 (1C), 137.6 (1C), 140.8 (1C), 141.2 (1C), 143.8 (1C), 149.6 (1C), 167.7 (1C); IR (KBr, cm^{-1}) 746, 895, 1261, 1422, 1614, 1703, 2986, 3053; HRMS (ESI$^+$) *m*/*z* 341.1496 ([M+Na]$^+$, $C_{22}H_{22}NaO_2^+$ requires 341.1512).

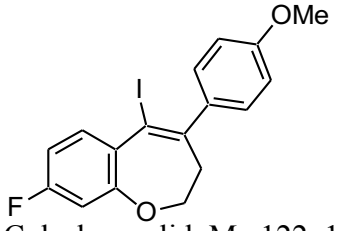
6-(8-Phenyl-6,7-dihydro-5*H*-benzocyclohepten-9-yl)-1-hydroxy-5-hexyne (**2u**)



Green oil; TLC R_f 0.51 (*n*-hexane/EtOAc = 5/2); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.10 (t, 1H, *J* = 5.0 Hz), 1.50–1.53 (m, 4H), 2.23 (tt, 2H, *J* = 7.0, 7.0 Hz), 2.29–2.33 (m, 4H), 2.71 (t, 2H, *J* = 7.0 Hz), 3.56–3.57 (br, 2H), 7.20–7.22 (m, 2H), 7.27–7.32 (m, 2H), 7.36–7.39 (AA'BB'C, 2H), 7.58 (d, 1H,

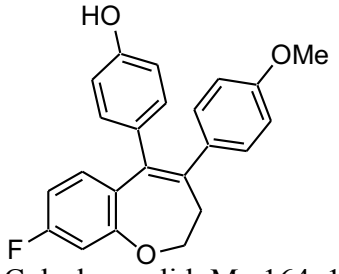
J = 7.5 Hz), 7.61–7.65 (AA'BB'C, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 19.4 (1C), 24.7 (1C), 31.75 (1C), 31.79 (1C), 32.2 (1C), 34.9 (1C), 62.5 (1C), 81.6 (1C), 91.8 (1C), 120.2 (1C), 126.2 (1C), 127.1 (1C), 127.3 (1C), 127.7 (1C), 128.4 (2C), 128.45 (1C), 128.54 (2C), 139.9 (1C), 140.4 (1C), 142.7 (1C), 147.3 (1C); IR (KBr, cm^{-1}) 698, 752, 1059, 1449, 1481, 2857, 2934, 3055, 3341; HRMS (ESI^+) m/z 339.1707 ($[M+Na]^+$, $C_{23}H_{24}NaO^+$ requires 339.1719).

8-Fluoro-5-iodo-4-(*p*-methoxyphenyl)-2,3-dihydrobenzo[*b*]oxepine (**S1**)



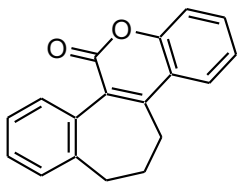
Colorless solid; Mp 122–123 ºC; TLC R_f 0.39 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.63 (t, 2H, J = 6.0 Hz), 3.85 (s, 3H), 4.60 (t, 2H, J = 6.0 Hz), 6.75 (dd, 1H, J = 9.5, 2.5 Hz), 6.74–6.96 (m, 3H), 7.29–7.32 (AA'BB', 2H), 7.63 (dd, 1H, J = 9.0, 2.5 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 35.2 (1C), 55.3 (1C), 80.2 (1C), 93.7 (1C), 109.3 (d, 1C, $J_{C–F}$ = 22.6 Hz), 111.2 (d, 1C, $J_{C–F}$ = 21.5 Hz), 113.7 (2C), 129.2 (2C), 133.4 (d, 1C, $J_{C–F}$ = 3.3 Hz), 134.2 (d, 1C, $J_{C–F}$ = 9.9 Hz), 138.1 (1C), 147.5 (1C), 154.4 (d, 1C, $J_{C–F}$ = 11.1 Hz), 159.1 (1C), 162.6 (d, 1C, $J_{C–F}$ = 250 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –111.11 to –111.17 (m); IR (KBr, cm^{-1}) 708, 748, 764, 895, 1261, 1242, 1605, 2986, 3053; HRMS (ESI^+) m/z 418.9934 ($[M+Na]^+$, $C_{17}H_{14}FINaO_2^+$ requires 418.9915).

8-Fluoro-5-(*p*-hydroxyphenyl)-4-(*p*-methoxyphenyl)-2,3-dihydrobenzo[*b*]oxepine (**14**)



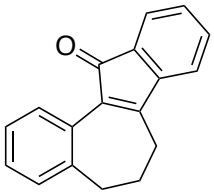
Colorless solid; Mp 164–167 ºC; TLC R_f 0.58 (*n*-hexane/EtOAc = 5/2); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.69 (t, 2H, J = 6.0 Hz), 3.76 (s, 3H), 4.61 (t, 2H, J = 6.0 Hz), 4.86 (br s, 1H), 6.57–6.59 (AA'BB', 2H), 6.71–6.75 (m, 3H), 6.80–6.85 (m, 4H), 7.07–7.05 (AA'BB', 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 35.6 (1C), 55.2 (1C), 80.9 (1C), 109.4 (d, 1C, $J_{C–F}$ = 22.1 Hz), 110.7 (d, 1C, $J_{C–F}$ = 21.2 Hz), 113.4 (2C), 114.7 (2C), 130.6 (2C), 131.9 (d, 1C, $J_{C–F}$ = 9.7 Hz), 132.6 (2C), 133.3 (d, 1C, $J_{C–F}$ = 3.4 Hz), 134.0 (1C), 134.5 (1C), 135.6 (1C), 137.3 (1C), 154.1 (1C), 157.0 (d, 1C, $J_{C–F}$ = 11.0 Hz), 158.1 (1C), 162.1 (d, 1C, $J_{C–F}$ = 248 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –113.46 to –113.52 (m); IR (KBr, cm^{-1}) 704, 895, 1261, 1242, 1607, 2986, 3053; HRMS (ESI^+) m/z 385.1200 ($[M+Na]^+$, $C_{23}H_{19}FNaO_3^+$ requires 385.1210).

12,13-Dihydrobenzo[*b*]benzo[6,7]cyclohepta[2,1-*d*]pyran-6(11*H*)-one (**15**)



Pale yellow solid; Mp 149–152 ºC; TLC R_f 0.22 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.25–2.45 (br, 3H), 2.50–2.68 (br, 2H), 2.95–3.10 (br, 1H), 7.26 (dd, 1H, J = 7.5, 1.0 Hz), 7.29–7.34 (m, 2H), 7.36 (dd, 1H, J = 7.5, 7.5, 1.5 Hz), 7.39 (dd, 1H, J = 8.5, 1.5 Hz), 7.52–7.56 (m, 1H), 7.71 (dd, 1H, J = 7.5, 1.5 Hz), 7.75 (dd, 1H, J = 7.5, 1.5 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 25.6 (1C), 31.3 (1C), 33.3 (1C), 117.2 (1C), 119.5 (1C), 124.1 (1C), 124.3 (1C), 124.5 (1C), 126.2 (1C), 128.6 (1C), 128.7 (1C), 130.1 (1C), 131.4 (1C), 134.0 (1C), 140.2 (1C), 151.2 (1C), 153.3 (1C), 160.1 (1C); IR (KBr, cm^{-1}) 746, 895, 1263, 1422, 1601, 1715, 2305, 2986, 3053; HRMS (ESI^+) m/z 285.0879 ($[M+Na]^+$, $C_{18}H_{14}NaO_2^+$ requires 285.0886).

6,7-Dihydrodibenzo[*a*,*e*]azulen-12(5*H*)-one (**16**)



Colorless solid, Mp 110–112 ºC; TLC R_f 0.59 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.13–2.21 (m, 2H), 2.79–2.84 (m, 2H), 2.86 (t, 2H, *J* = 7.0 Hz), 7.13–7.18 (m, 2H), 7.21 (ddd, 1H, *J* = 7.5, 7.5, 1.1 Hz), 7.26 (ddd, 1H, *J* = 7.5, 7.5, 1.1 Hz), 7.30 (ddd, 1H, *J* = 7.5, 7.5, 1.1 Hz), 7.39 (ddd, 1H, *J* = 7.5, 7.5, 1.1 Hz), 7.49 (d, 1H, *J* = 7.5 Hz), 7.94 (dd, 1H, *J* = 7.5, 1.1 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 27.5 (1C), 29.1 (1C), 34.8 (1C), 118.8 (1C), 122.1 (1C), 126.1 (1C), 127.6 (1C), 128.76 (1C), 128.79 (1C), 130.1 (1C), 130.2 (1C), 130.4 (1C), 130.6 (1C), 133.6 (1C), 143.1 (1C), 145.9 (1C), 158.3 (1C), 197.0 (1C); IR (KBr, cm^{-1}) 712, 735, 810, 1300, 1465, 1454, 1582, 1601, 2932; Anal. calcd. for $C_{18}H_{14}O$: C, 87.78; H, 5.73; N, 0.00; Found: C, 87.69; H, 5.85, N, 0.00.

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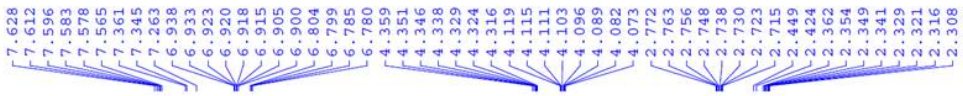
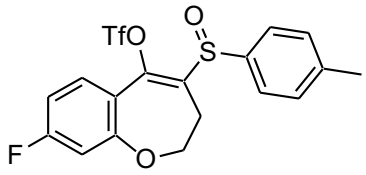
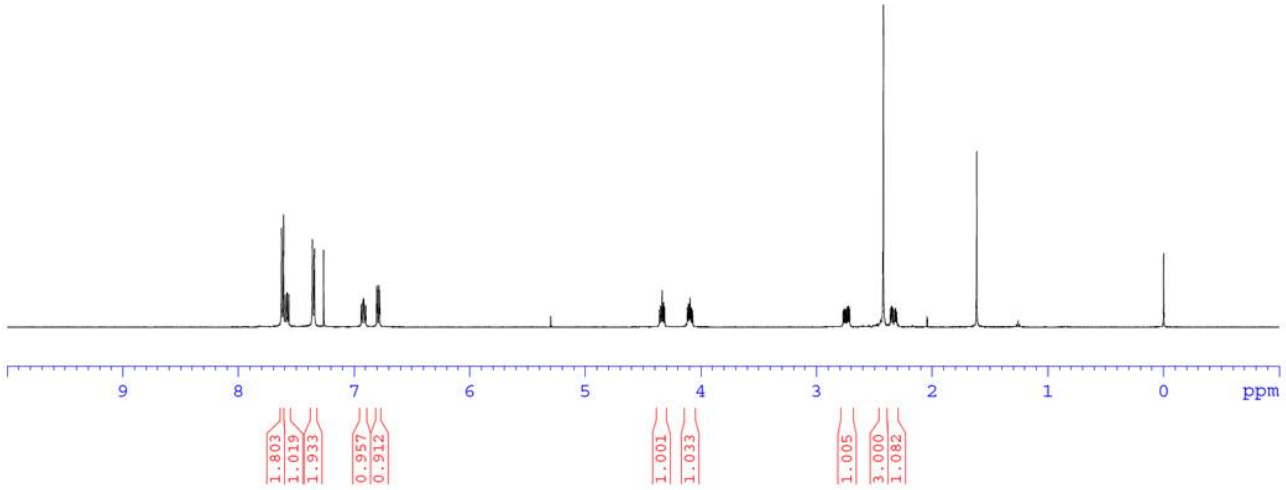
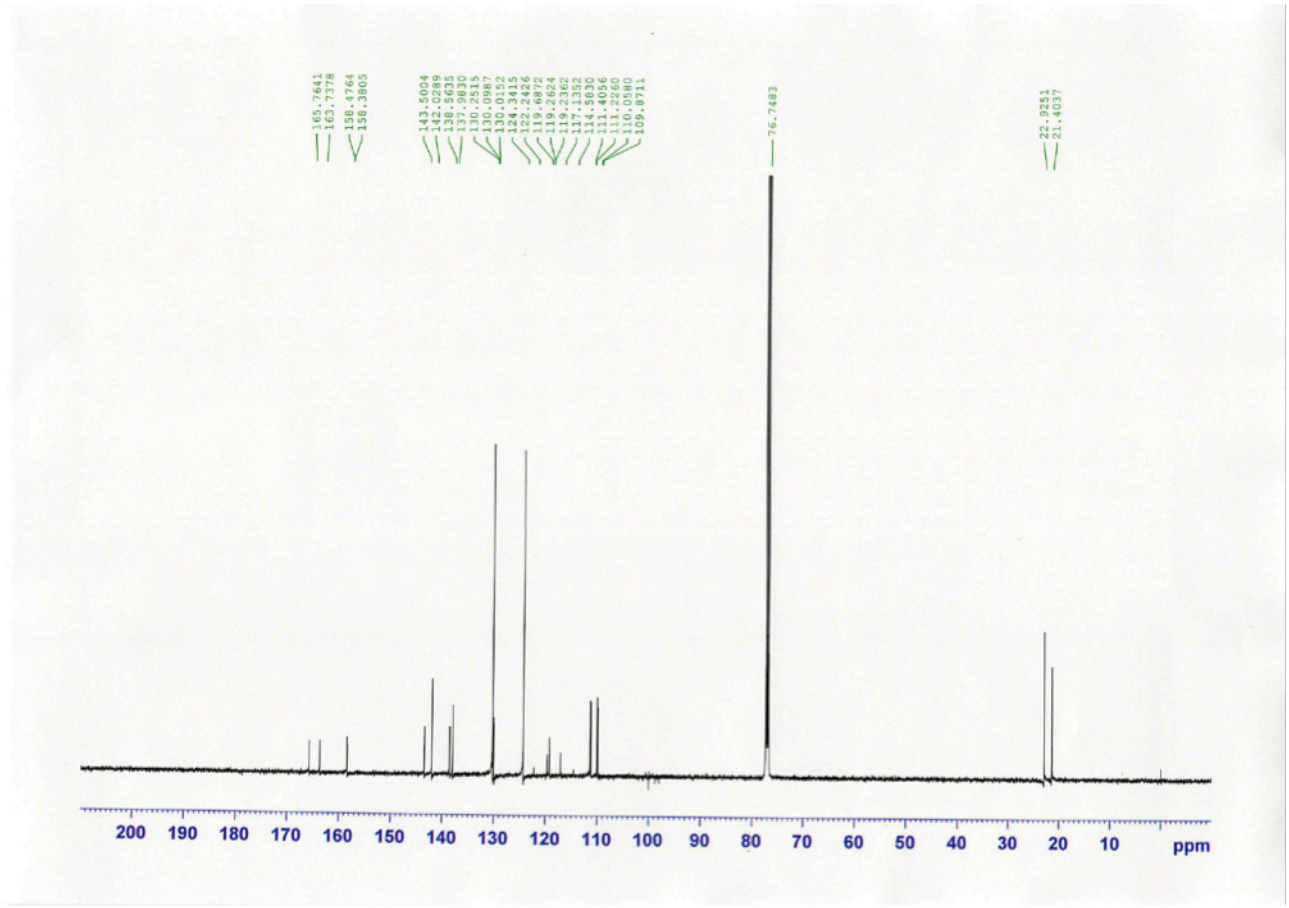
NMR Spectra of New Compounds

^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 8-fluoro-4-(*p*-tolylsulfinyl)-2,3-dihydrobenzo[*b*]oxepin-5-yl trifluoromethanesulfonate (**1c**) ($CDCl_3$)

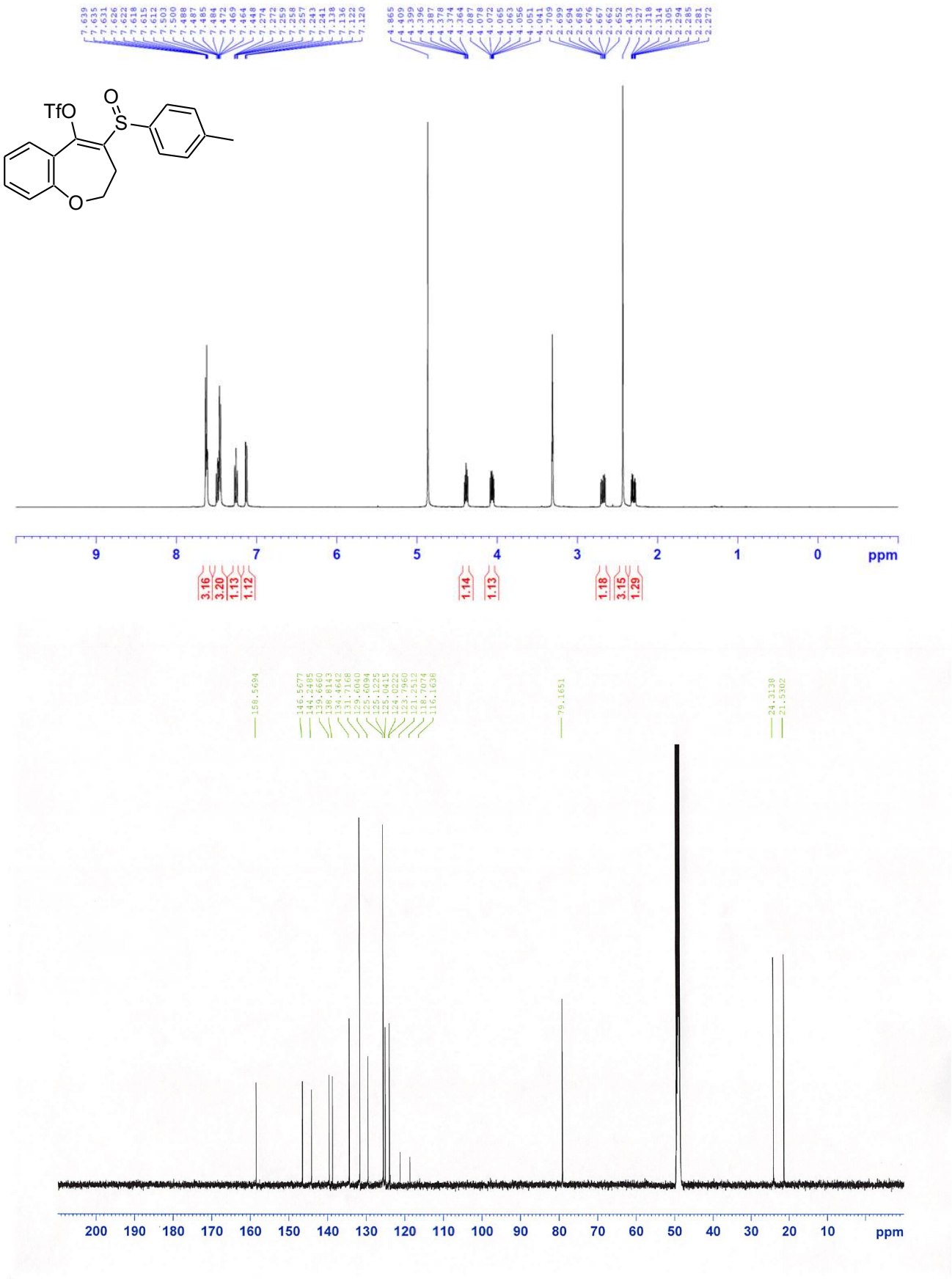




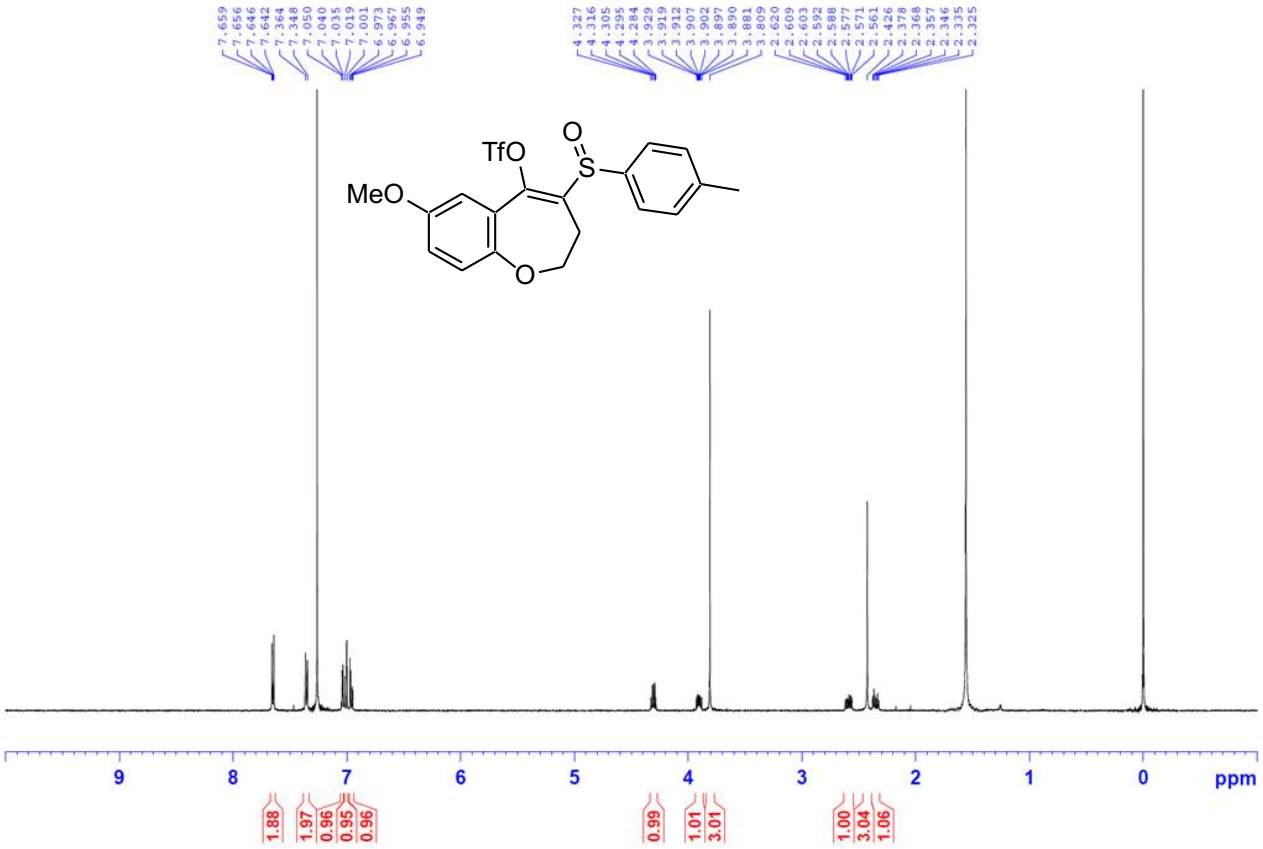


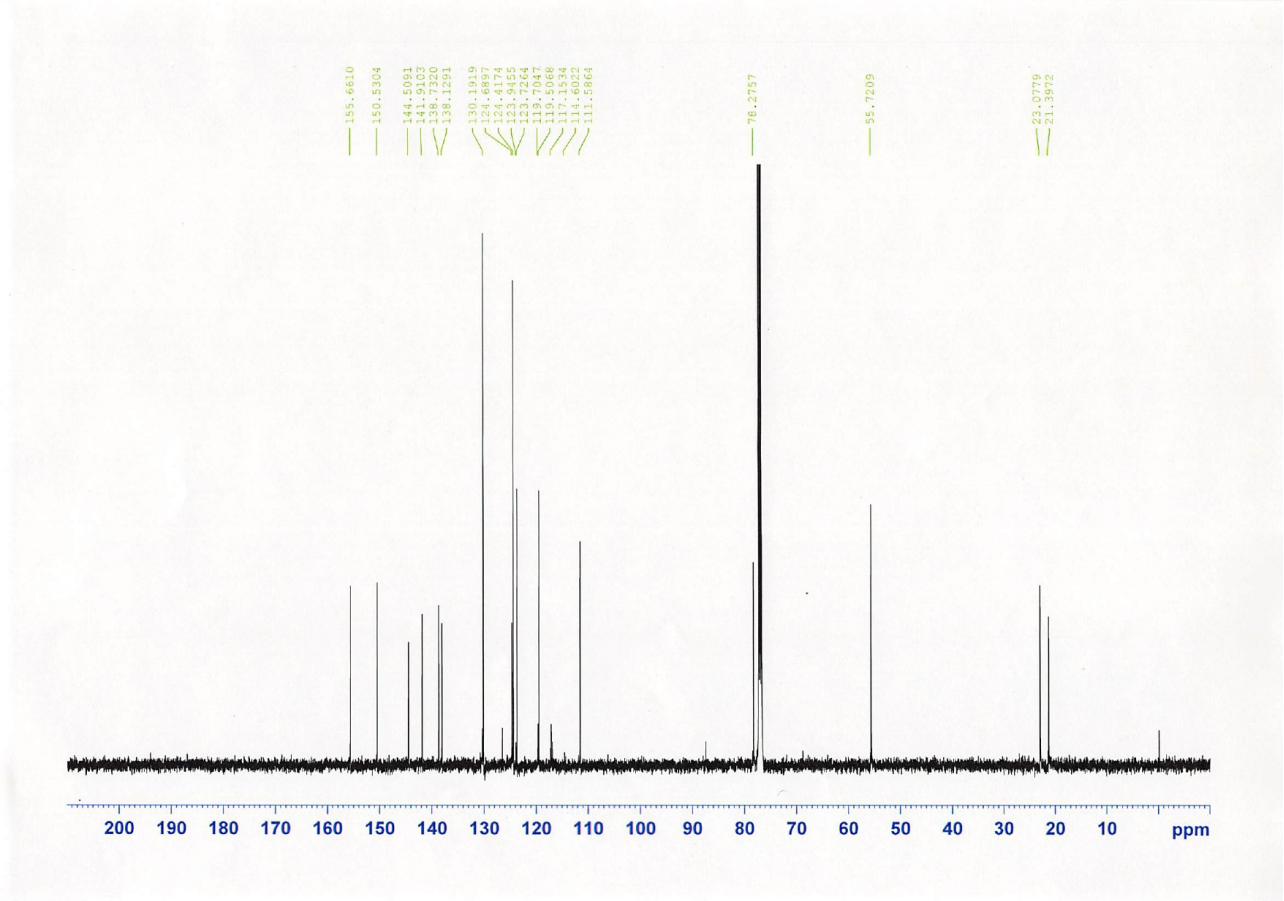


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 4-(*p*-tolylsulfinyl)-2,3-dihydrobenzo[*b*]oxepin-5-yl trifluoromethanesulfonate (CD_3OD)

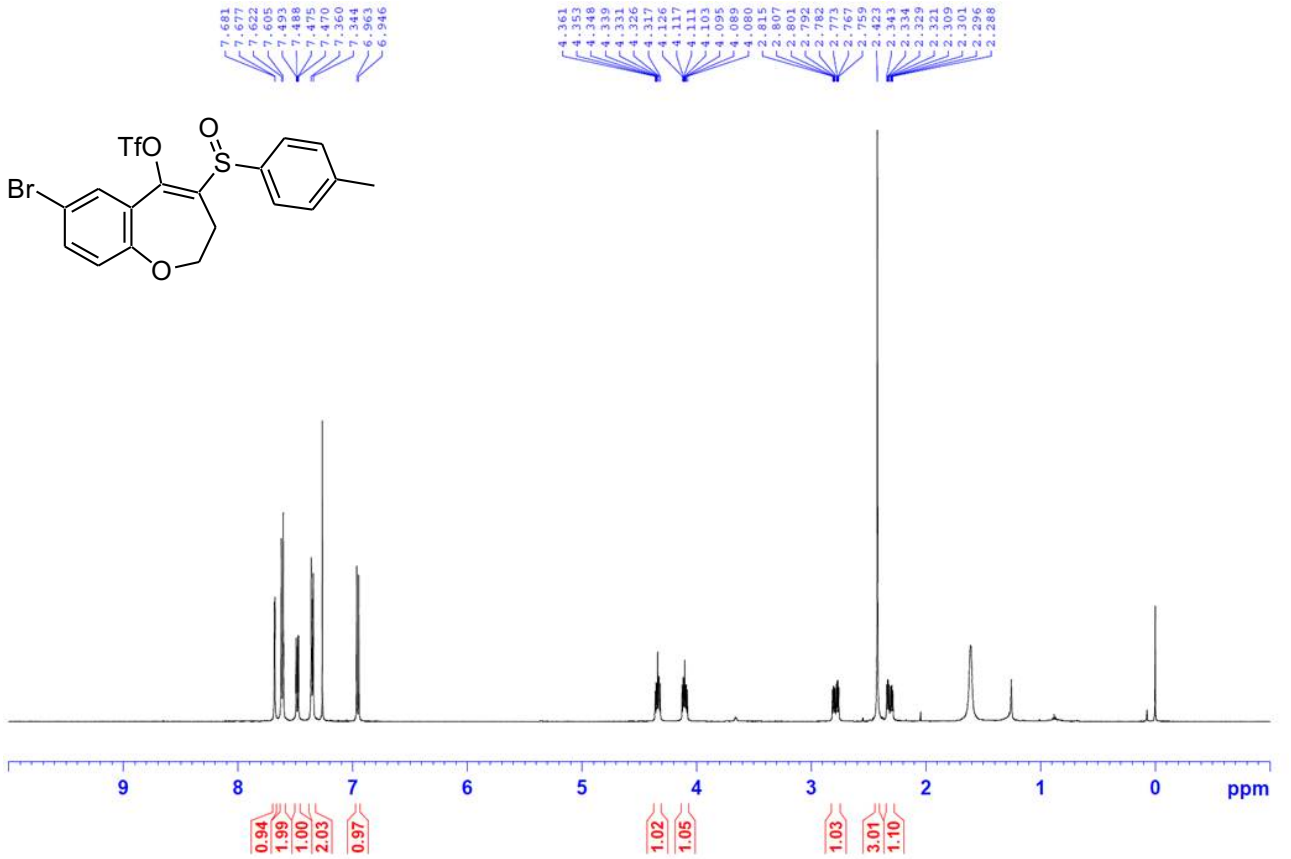


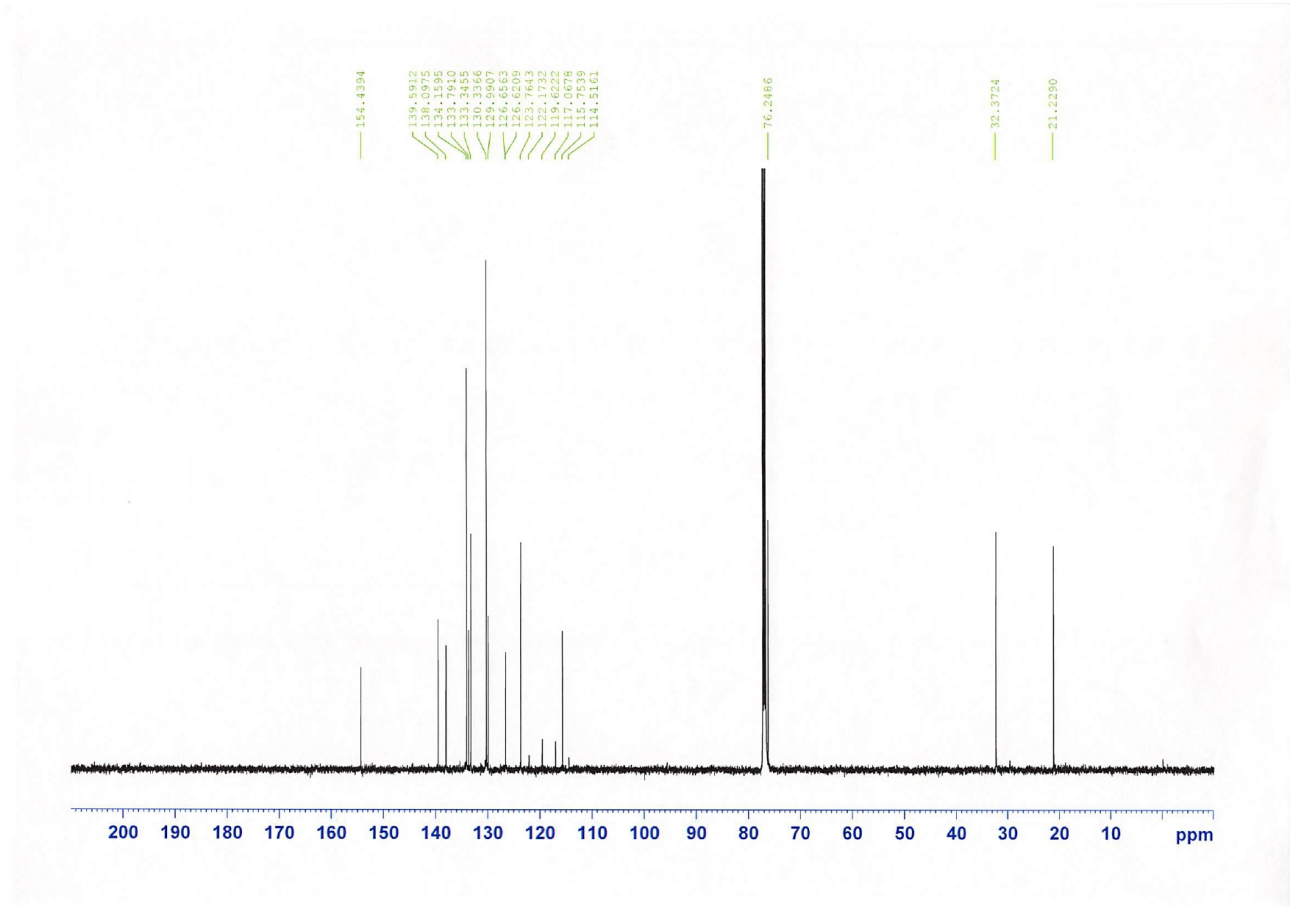
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 7-methoxy-4-(*p*-tolylsulfinyl)-2,3-dihydrobenzo[*b*]oxepin-5-yl trifluoromethanesulfonate ($CDCl_3$)



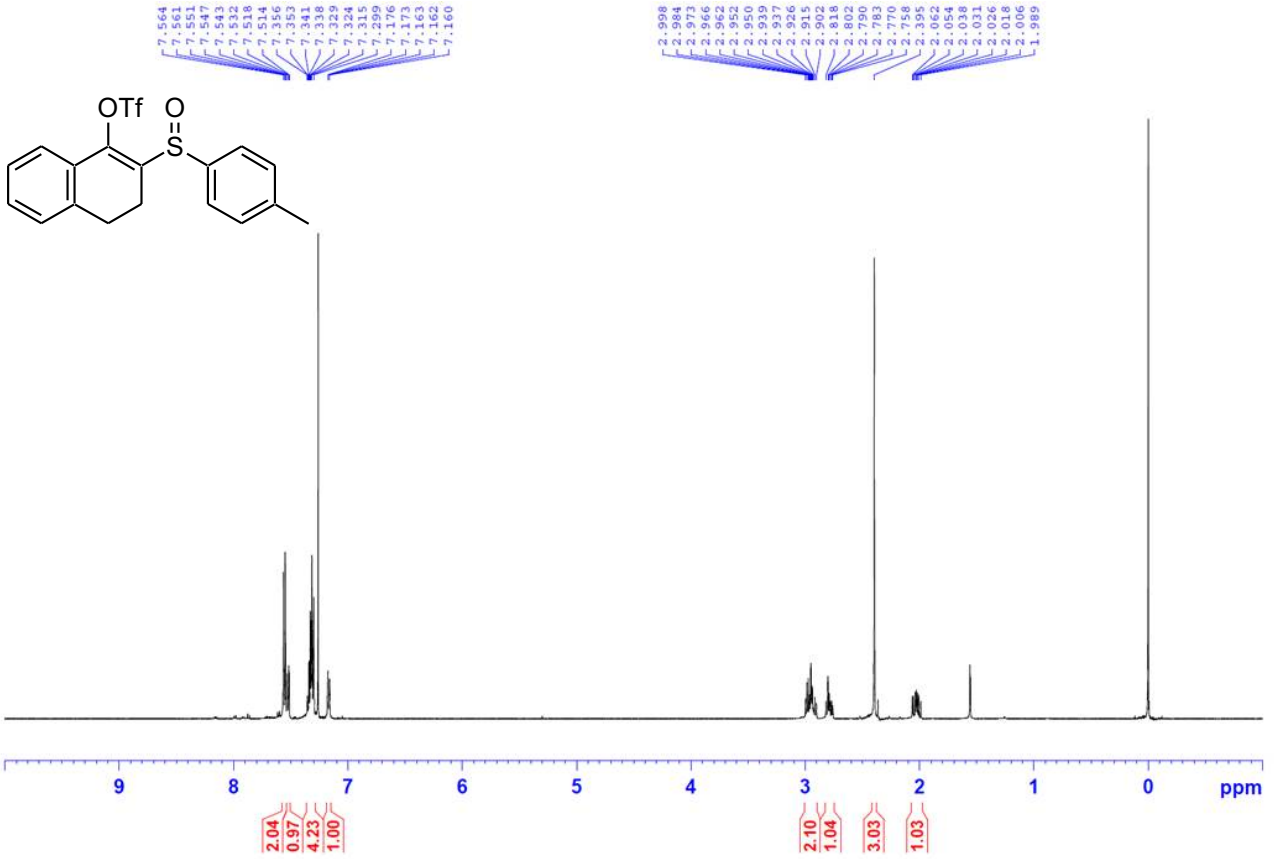


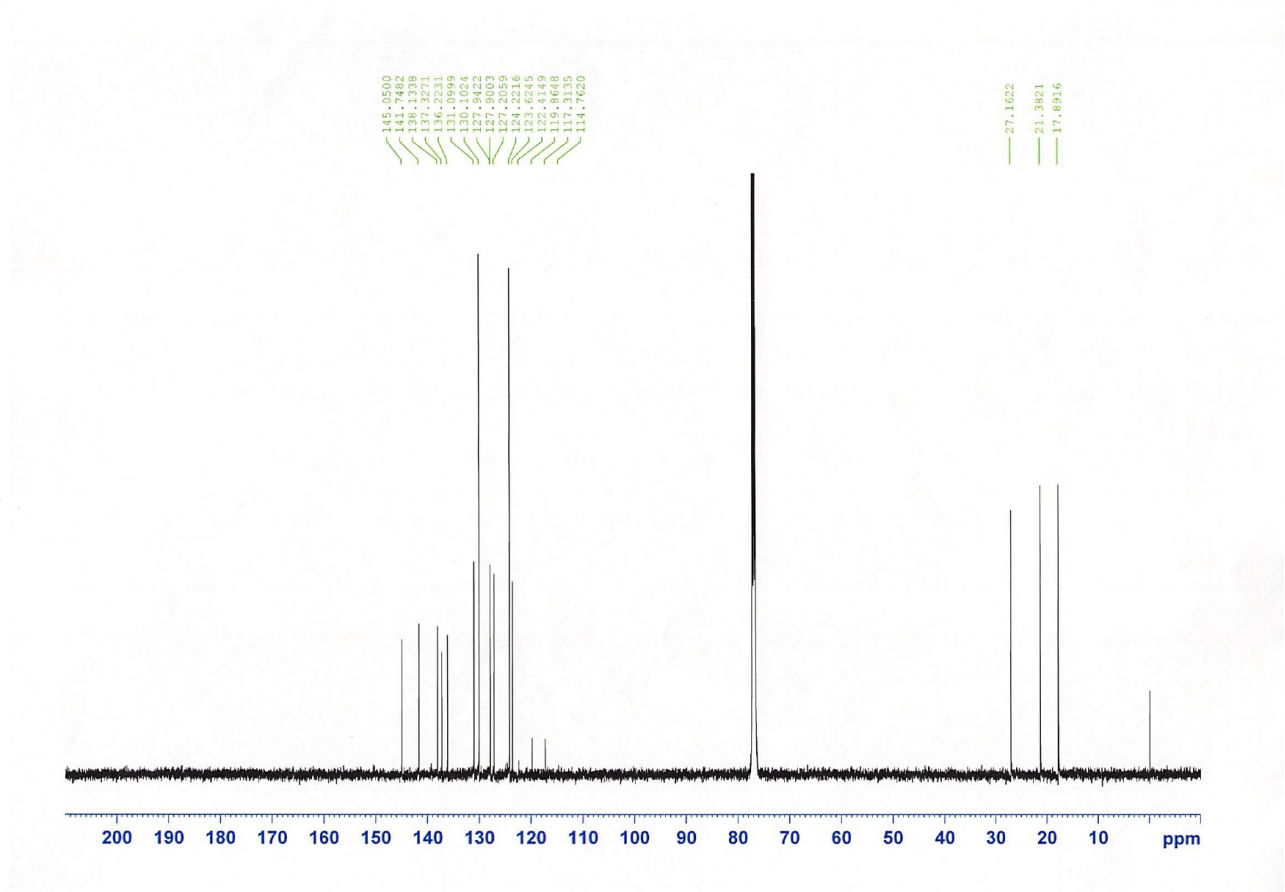
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 7-bromo-4-(*p*-tolylsulfinyl)-2,3-dihydrobenzo[*b*]oxepin-5-yl trifluoromethanesulfonate ($CDCl_3$)



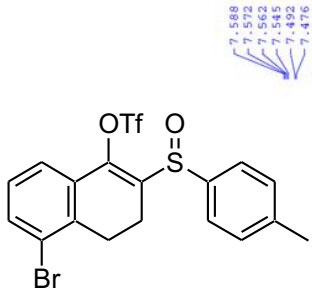


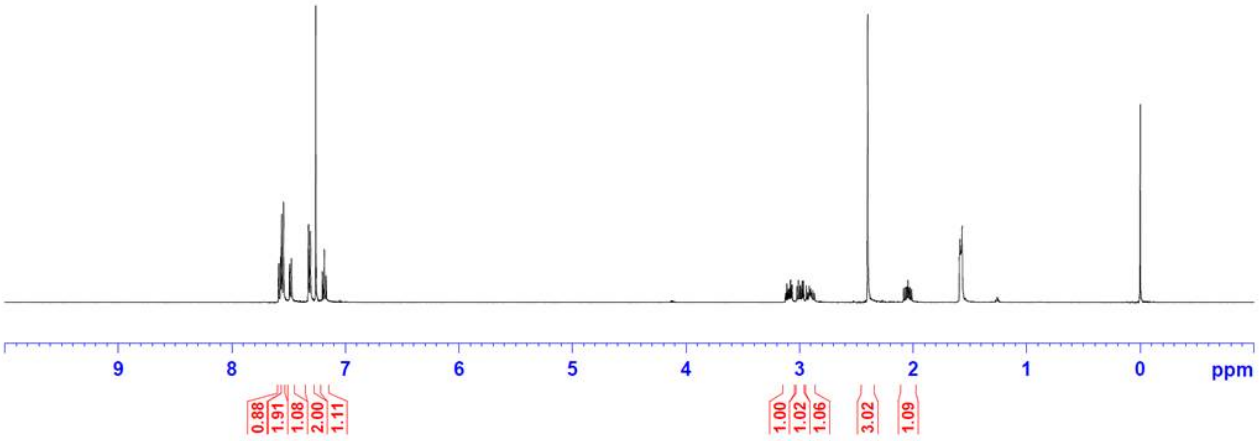
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 2-(*p*-Tolylsulfinyl)-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate ($CDCl_3$)

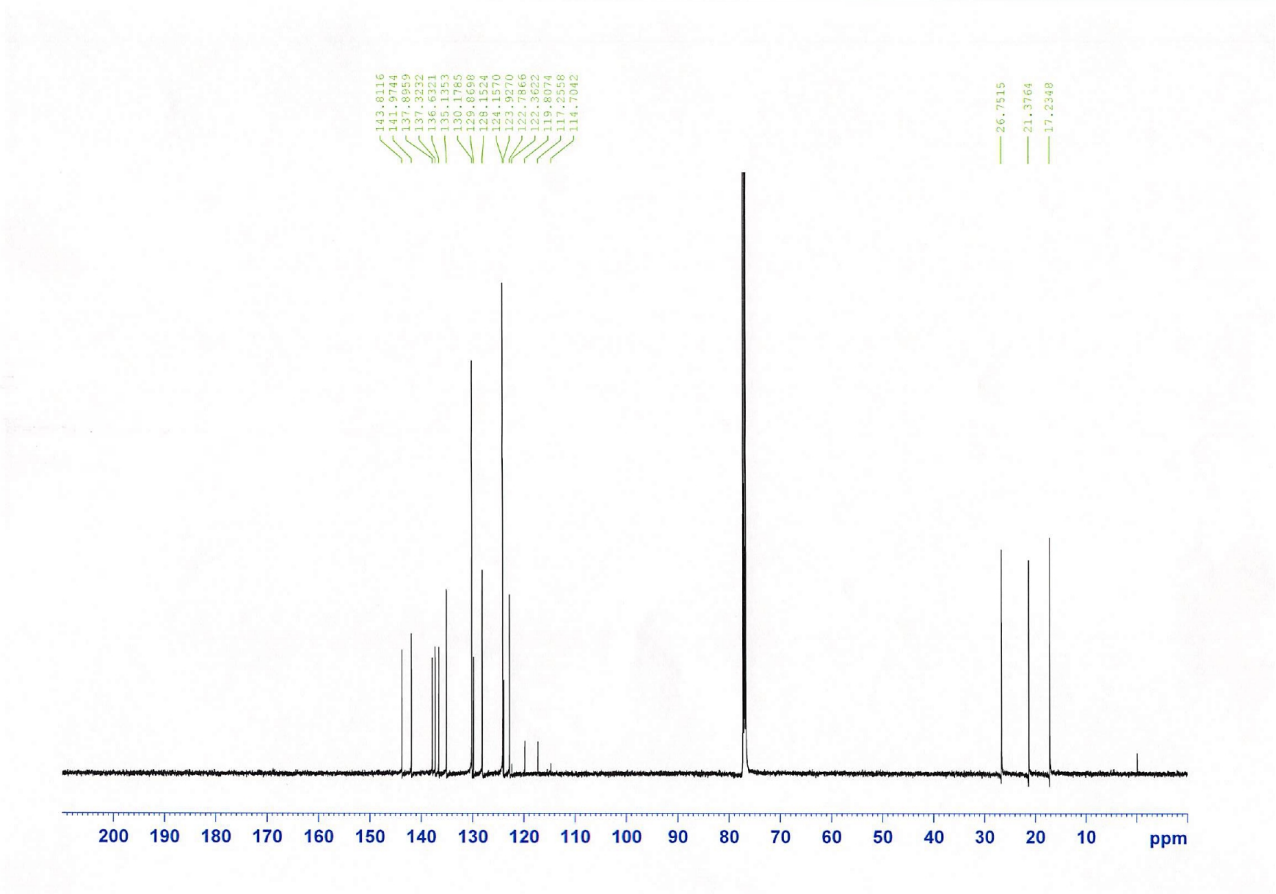




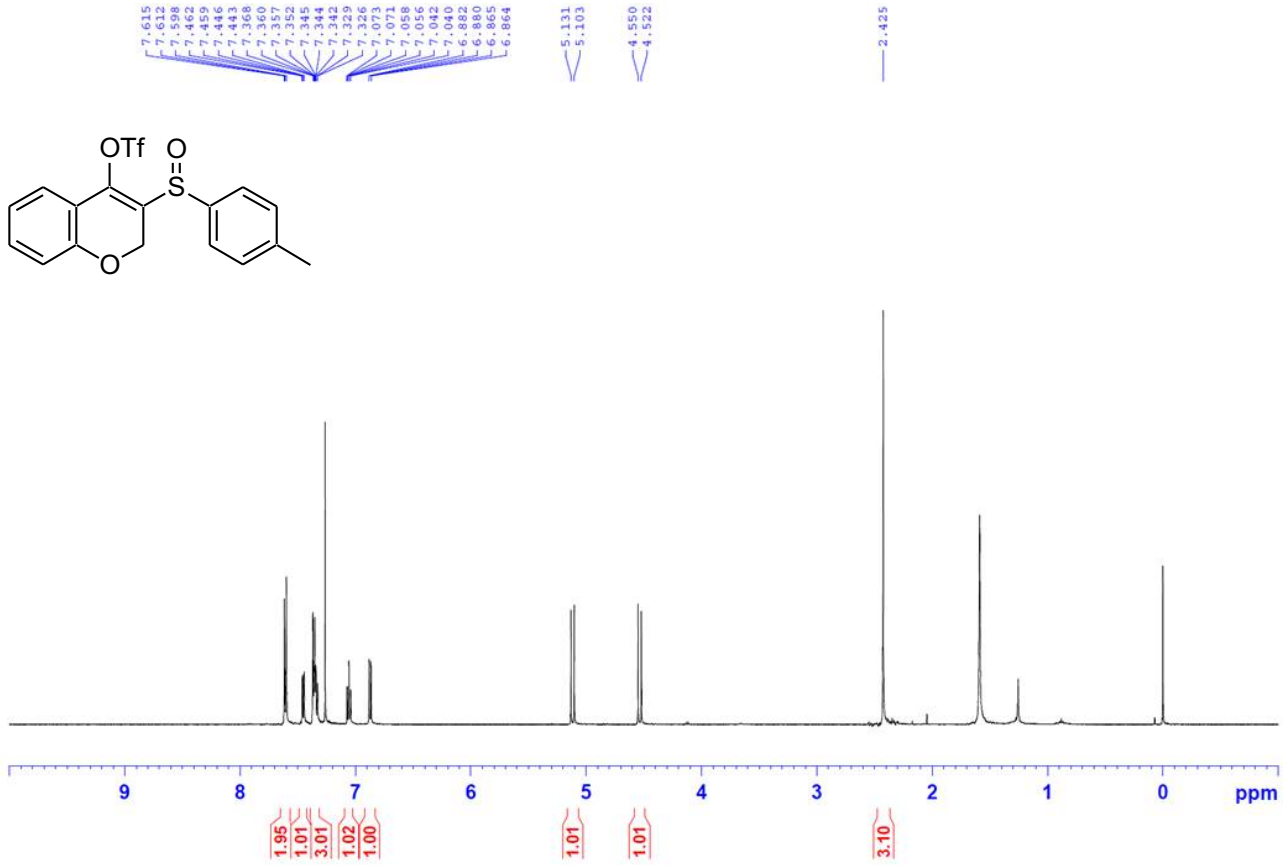
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 5-bromo-2-(*p*-tolylsulfinyl)-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate ($CDCl_3$)

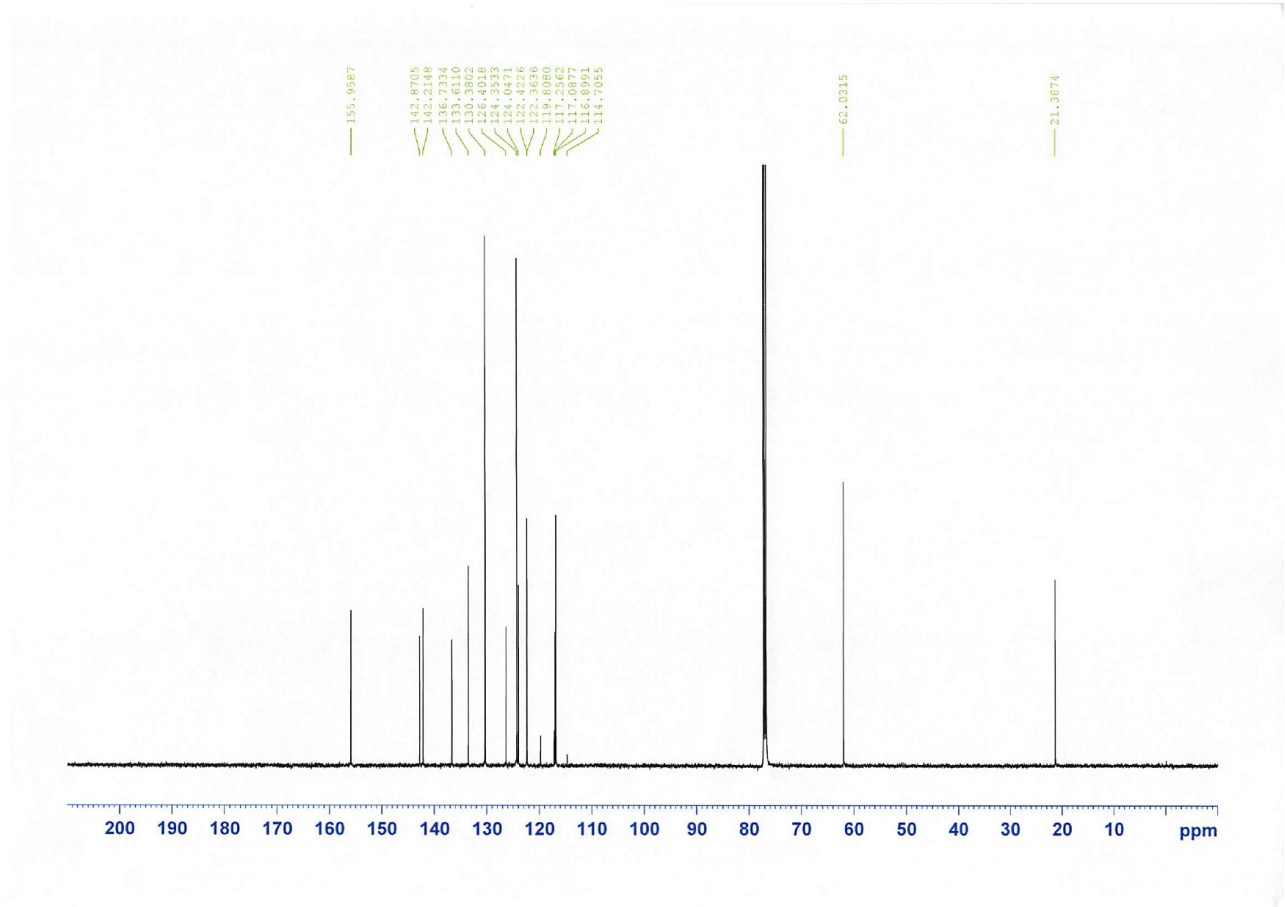




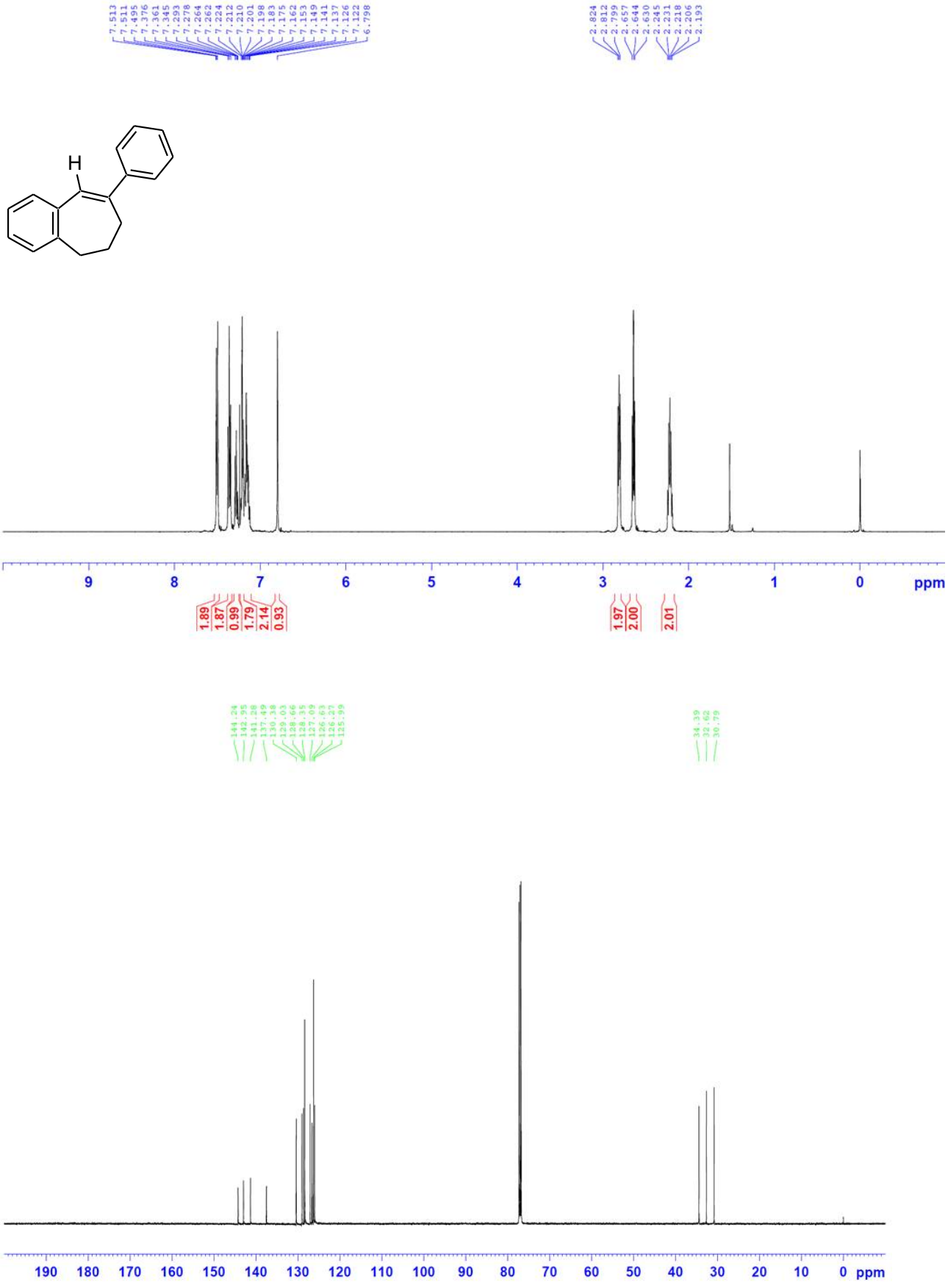


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 3-(*p*-tolylsulfinyl)-2*H*-chromen-4-yl trifluoromethanesulfonate ($CDCl_3$)

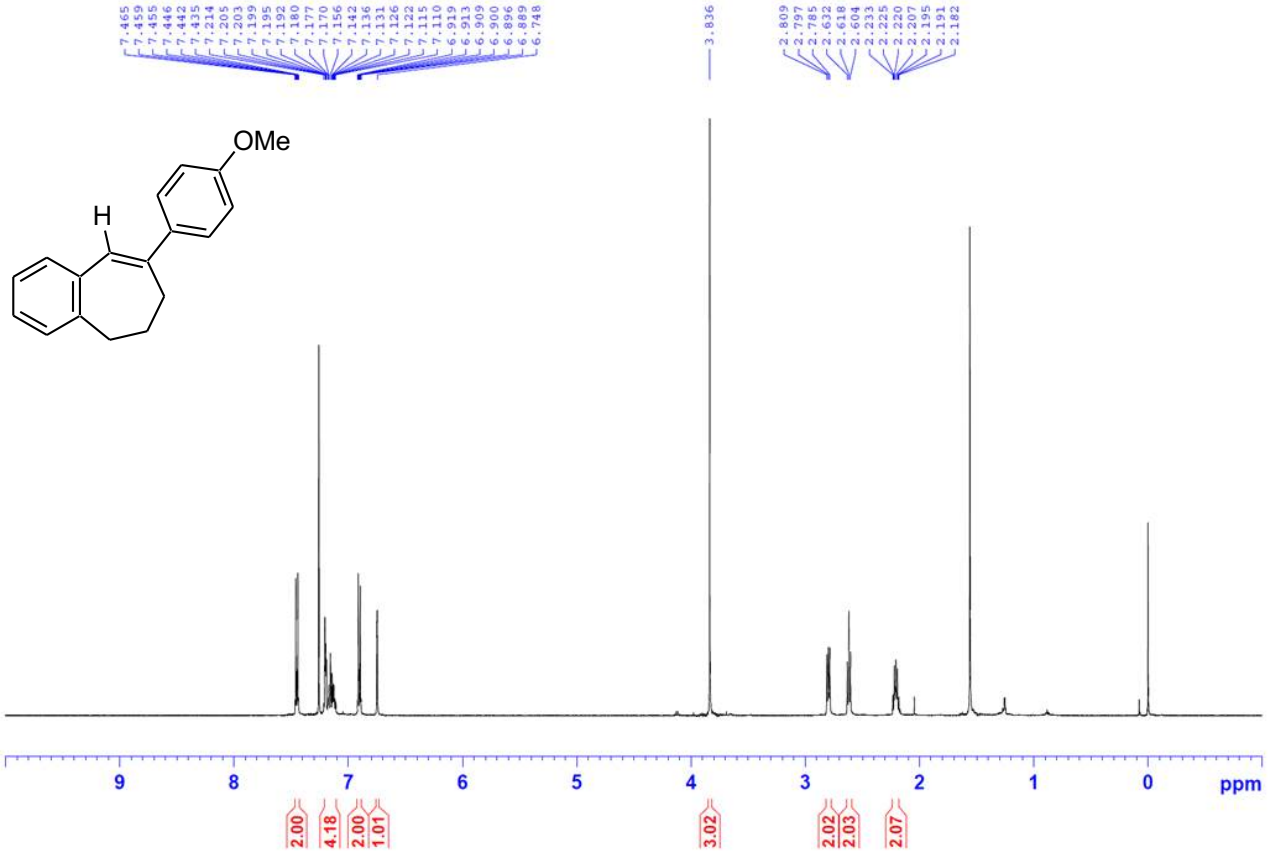


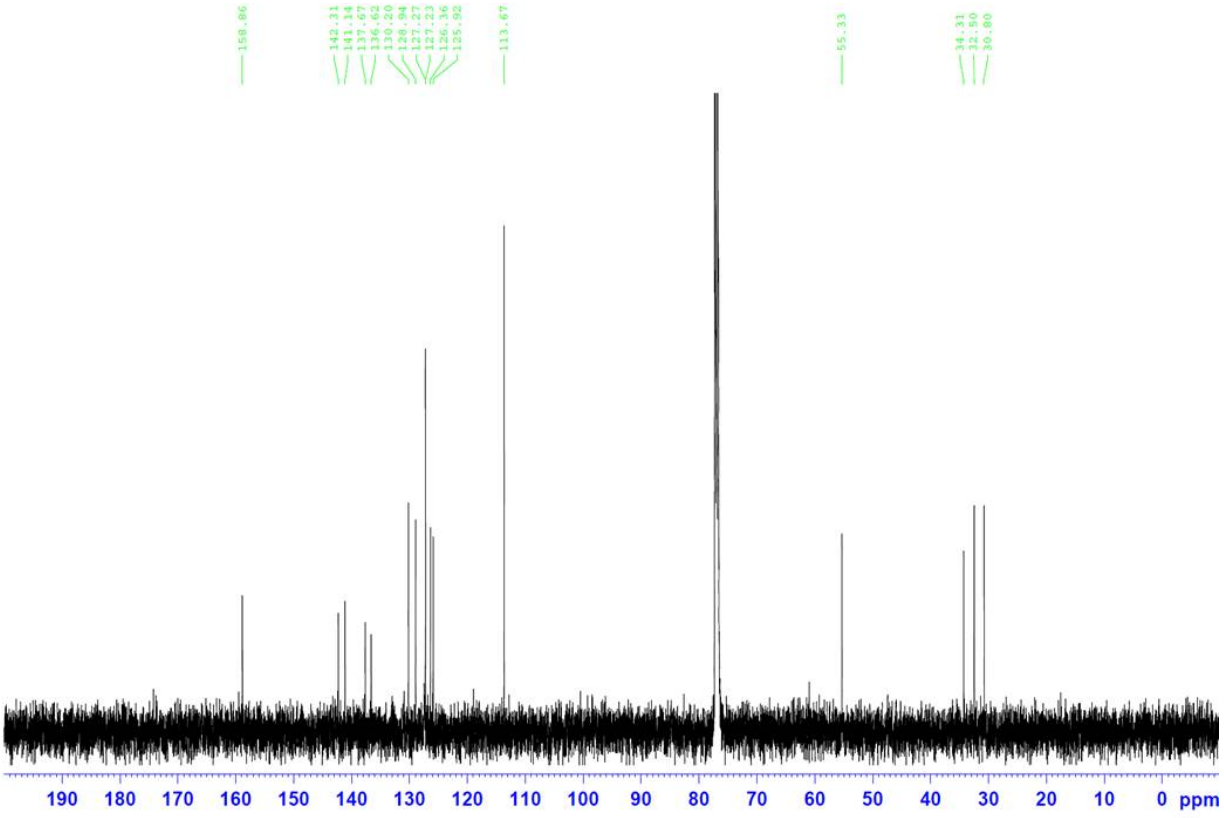


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 8-phenyl-6,7-dihydro-5*H*-benzo[7]annulene (**2a**) ($CDCl_3$)

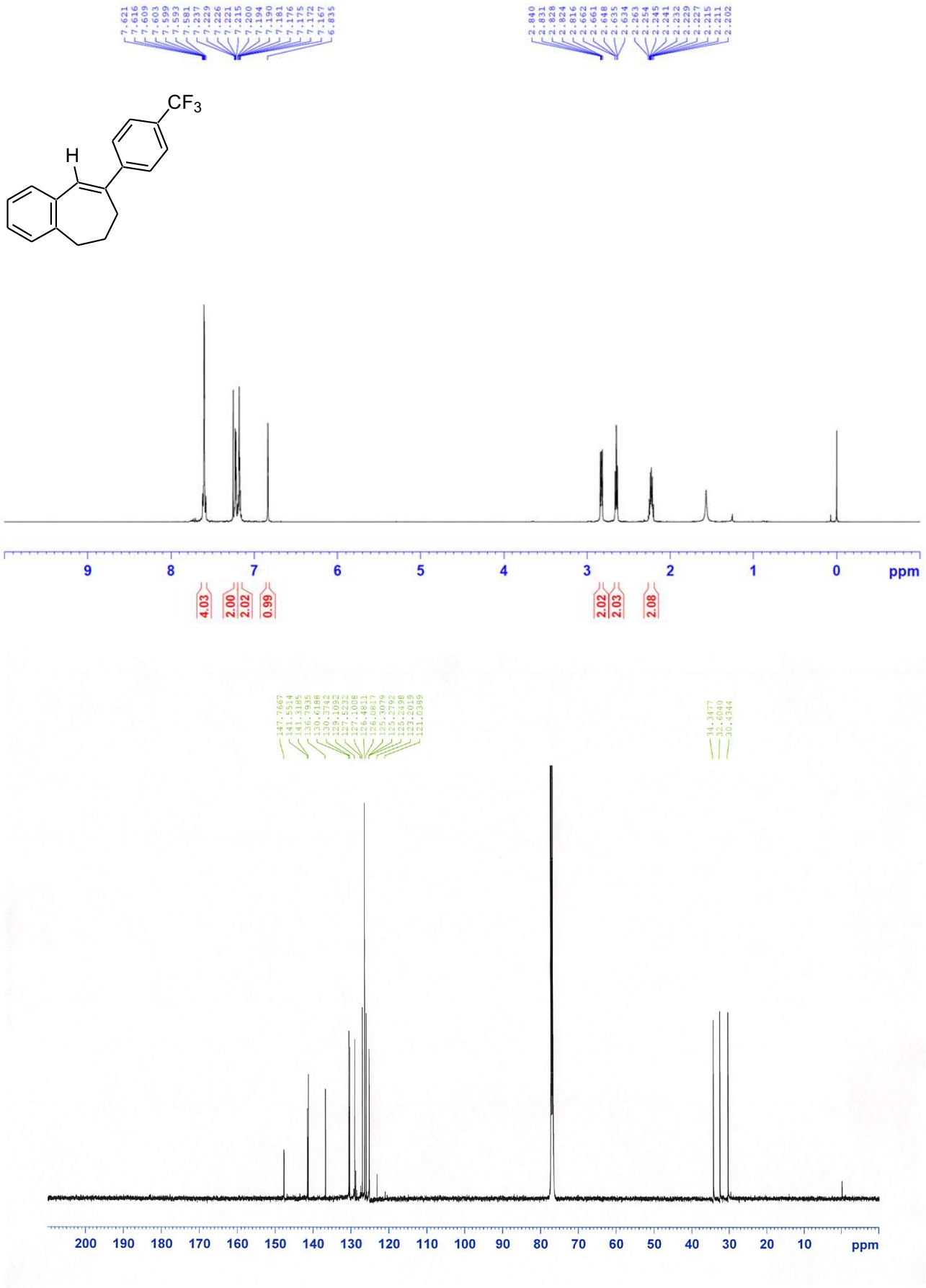


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 8-(4-methoxyphenyl)-6,7-dihydro-5*H*-benzo[7]annulene (**2b**) ($CDCl_3$)

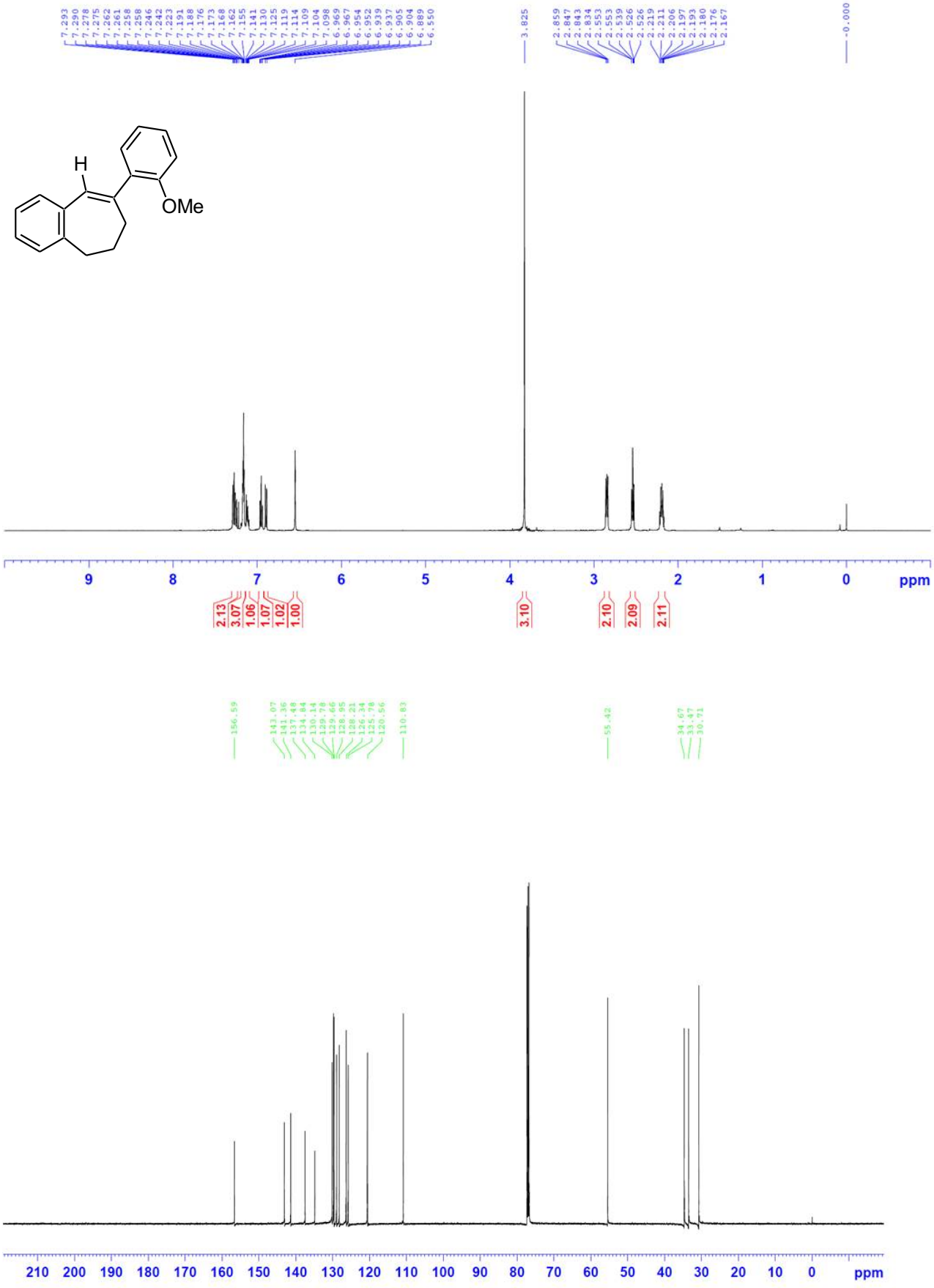




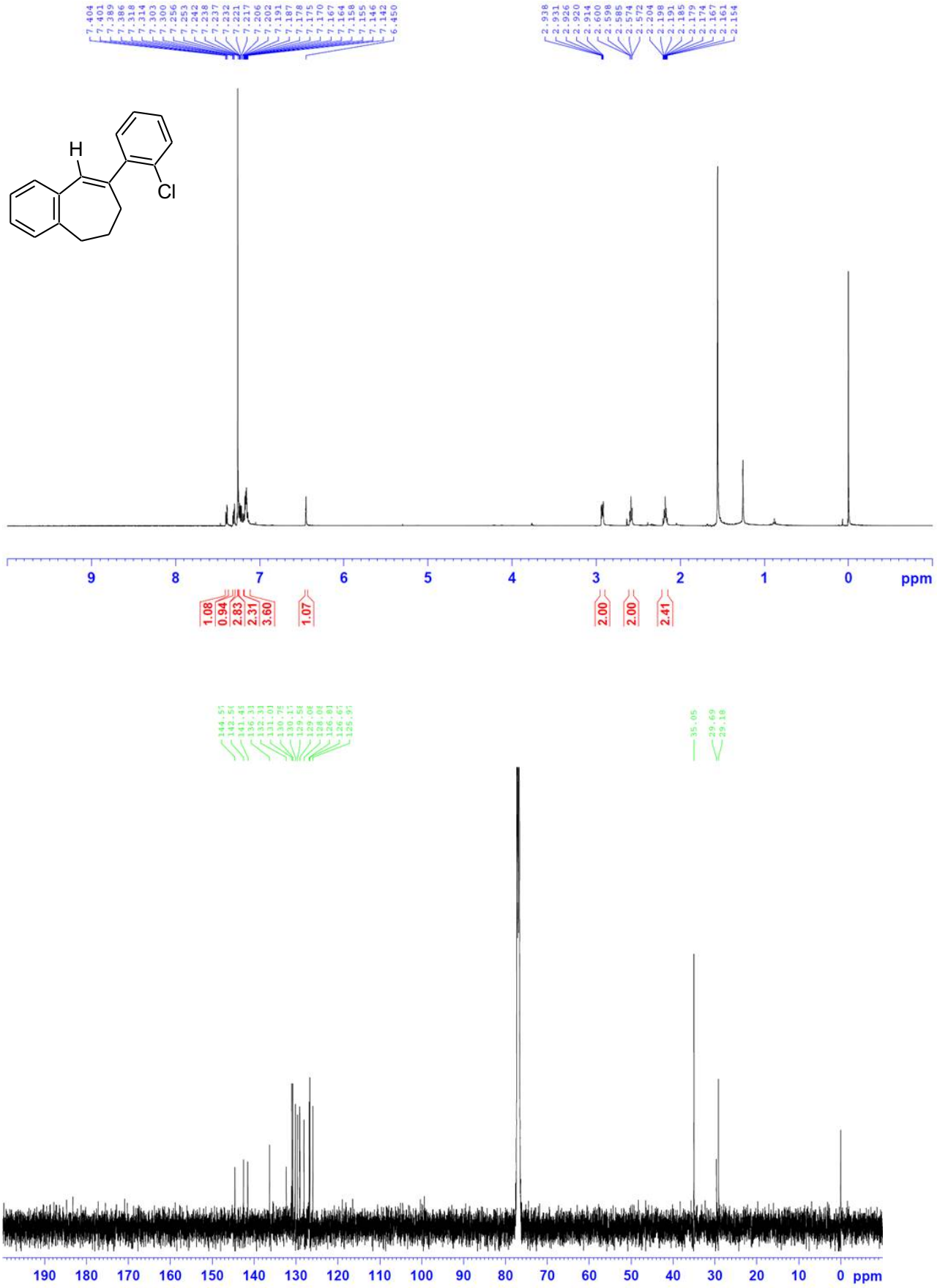
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 8-(4-trifluoromethylphenyl)-6,7-dihydro-5*H*-benzo[7]annulene (**2c**) ($CDCl_3$)



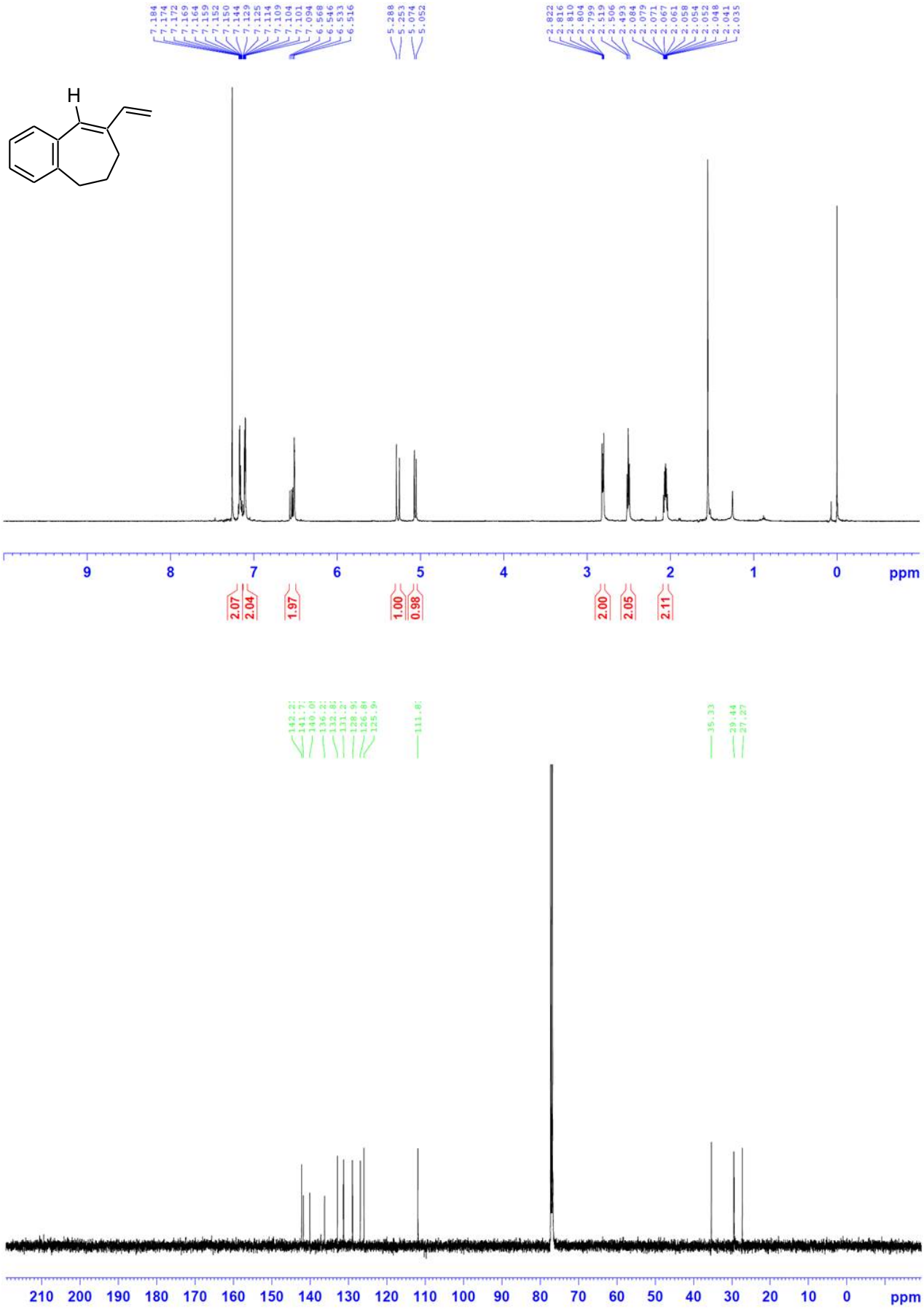
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 8-(2-methoxyphenyl)-6,7-dihydro-5*H*-benzo[7]annulene (**2d**) ($CDCl_3$)



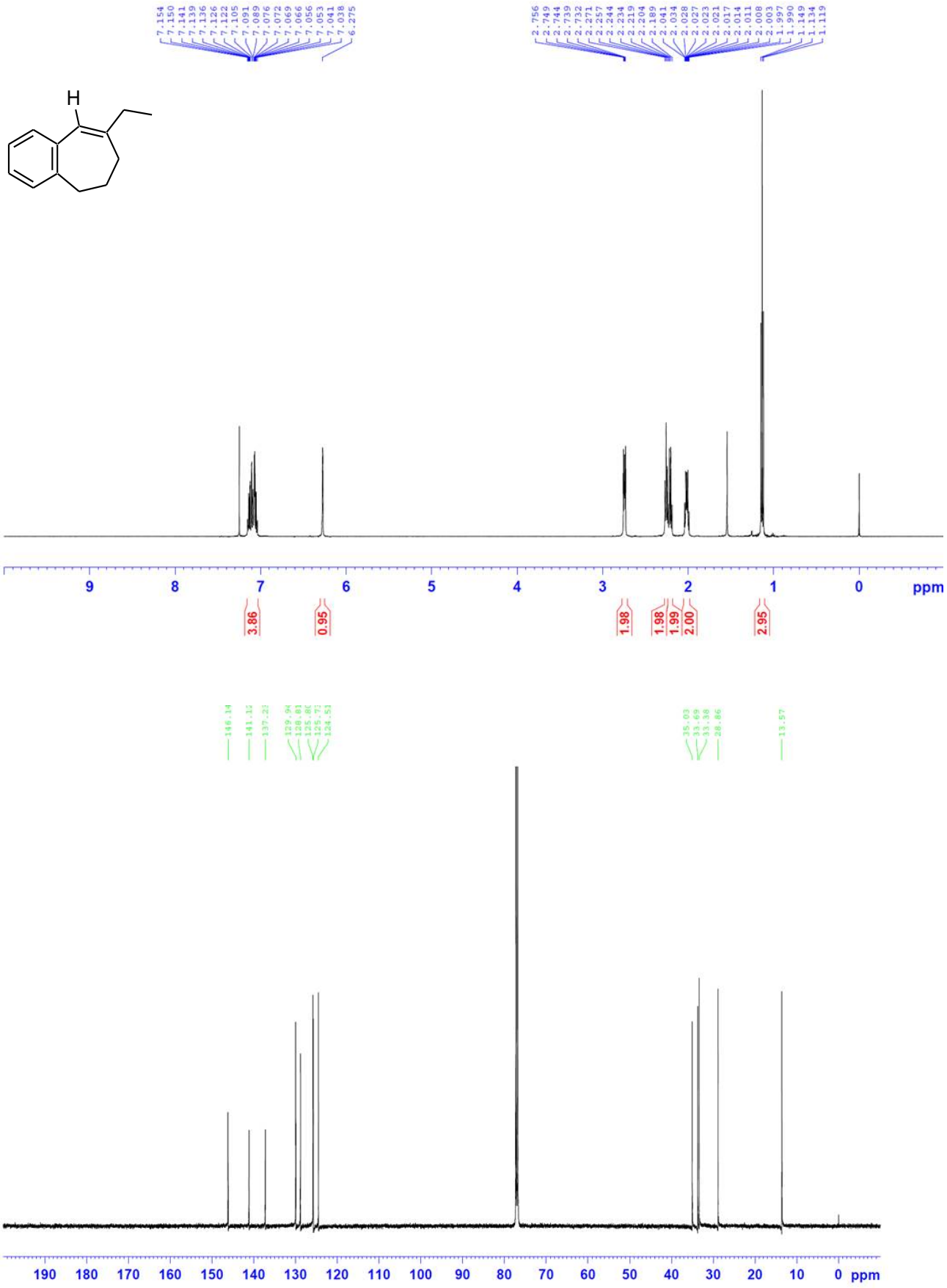
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 8-(2-chlorophenyl)-6,7-dihydro-5*H*-benzo[7]annulene (**2e**) ($CDCl_3$)



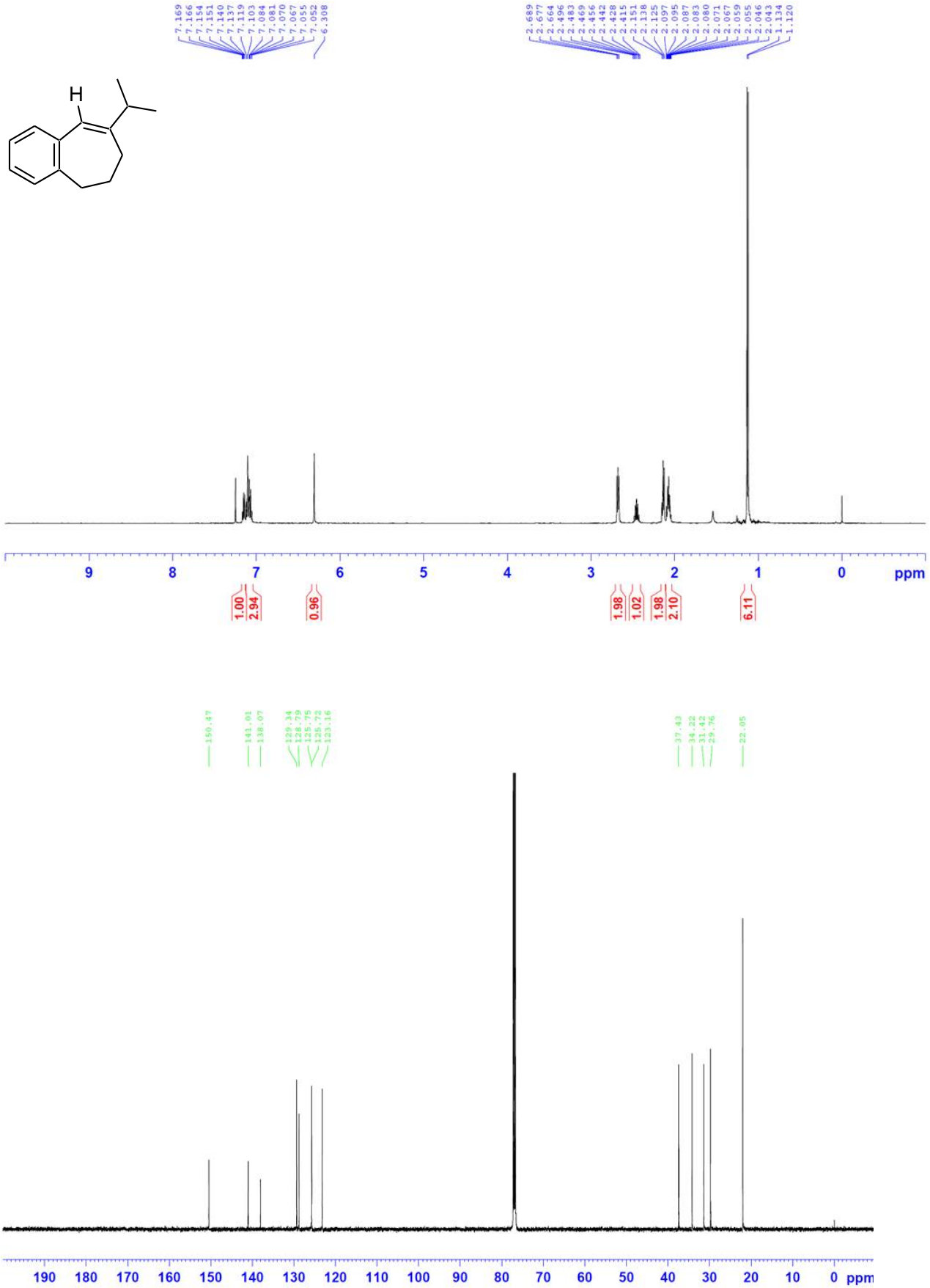
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 8-ethenyl-6,7-dihydro-5*H*-benzo[7]annulene (**2f**) ($CDCl_3$)



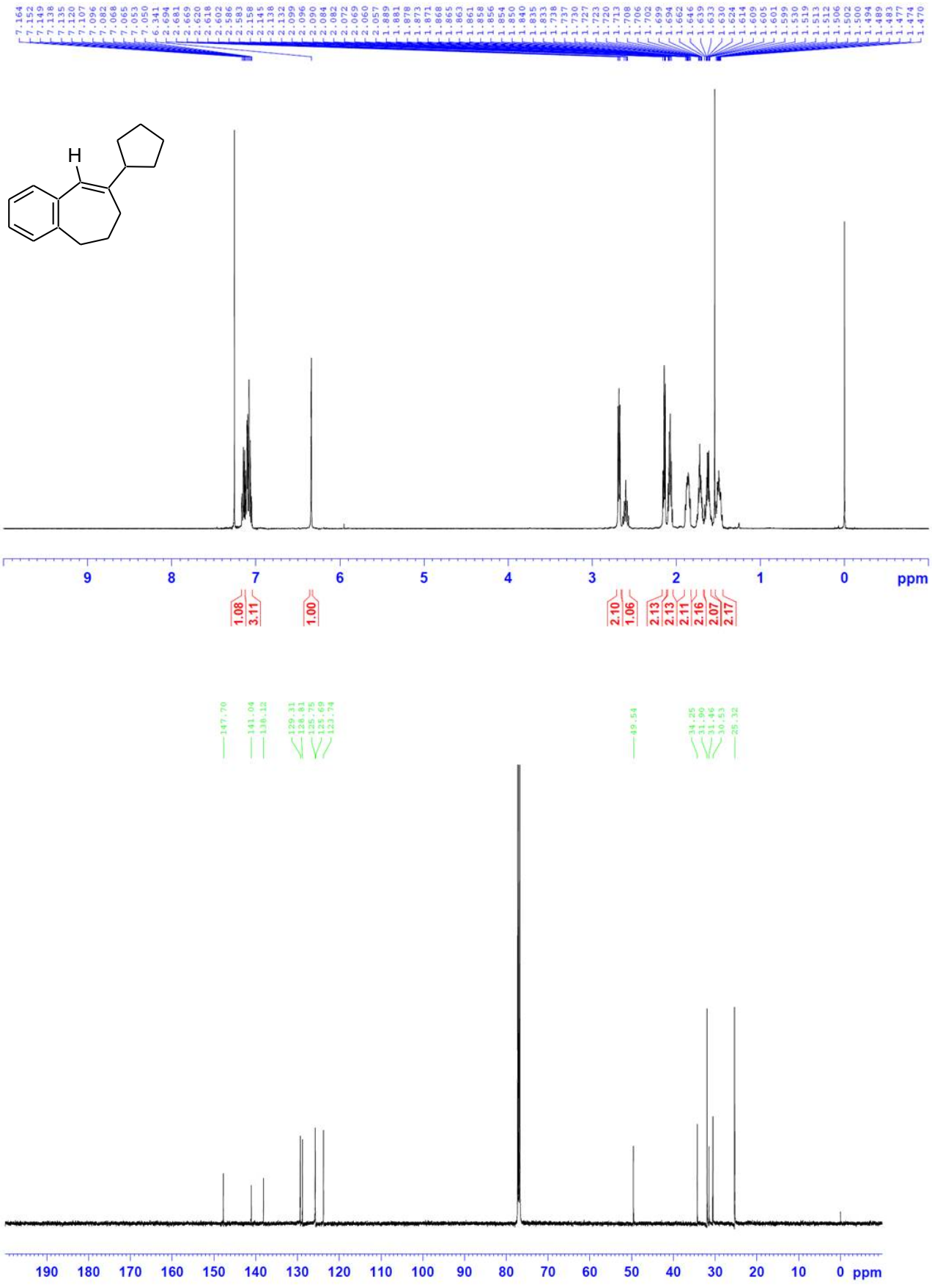
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 8-ethyl-6,7-dihydro-5*H*-benzo[7]annulene (**2g**) ($CDCl_3$)



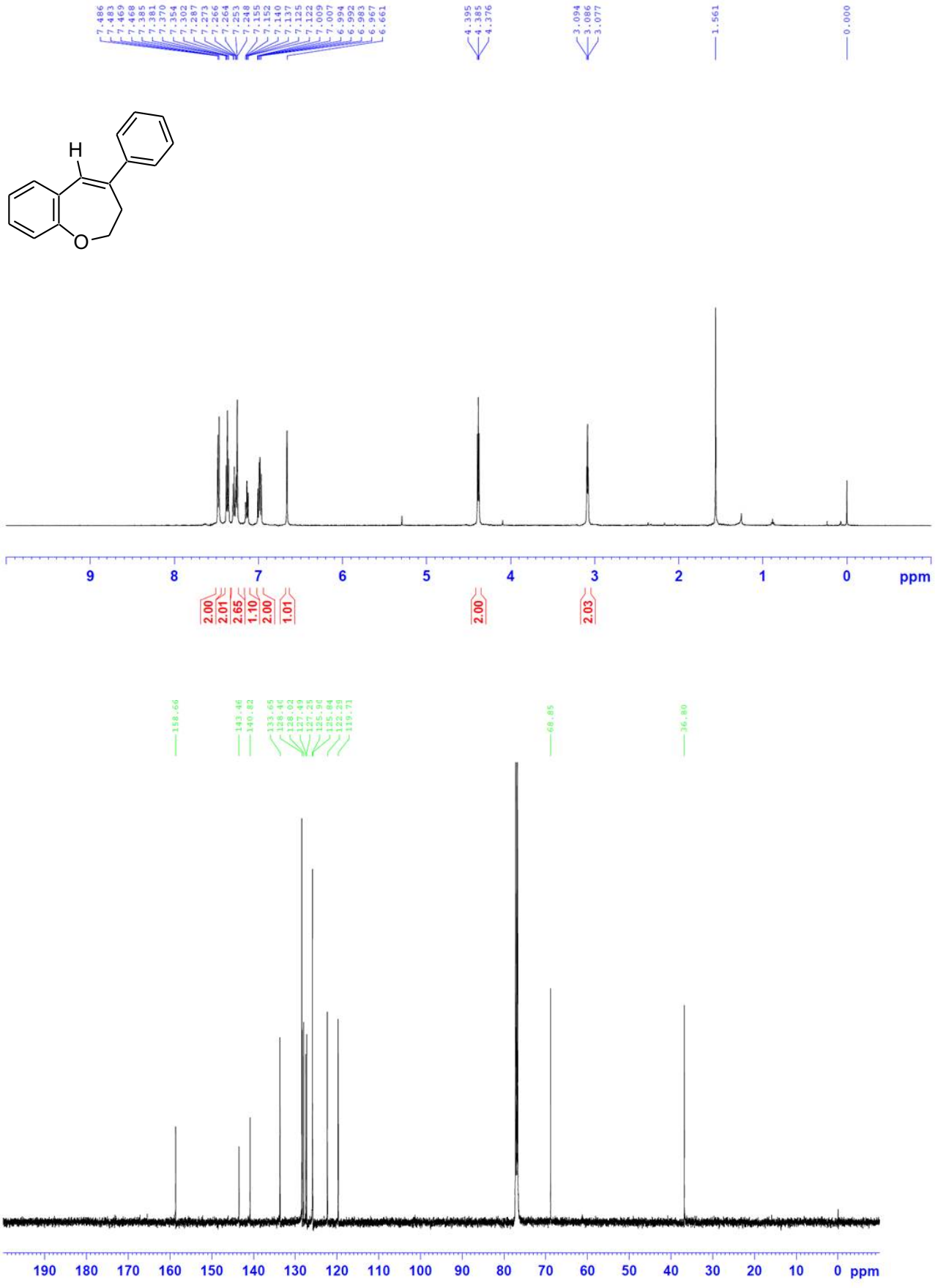
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 8-isopropyl-6,7-dihydro-5*H*-benzo[7]annulene (**2h**) ($CDCl_3$)



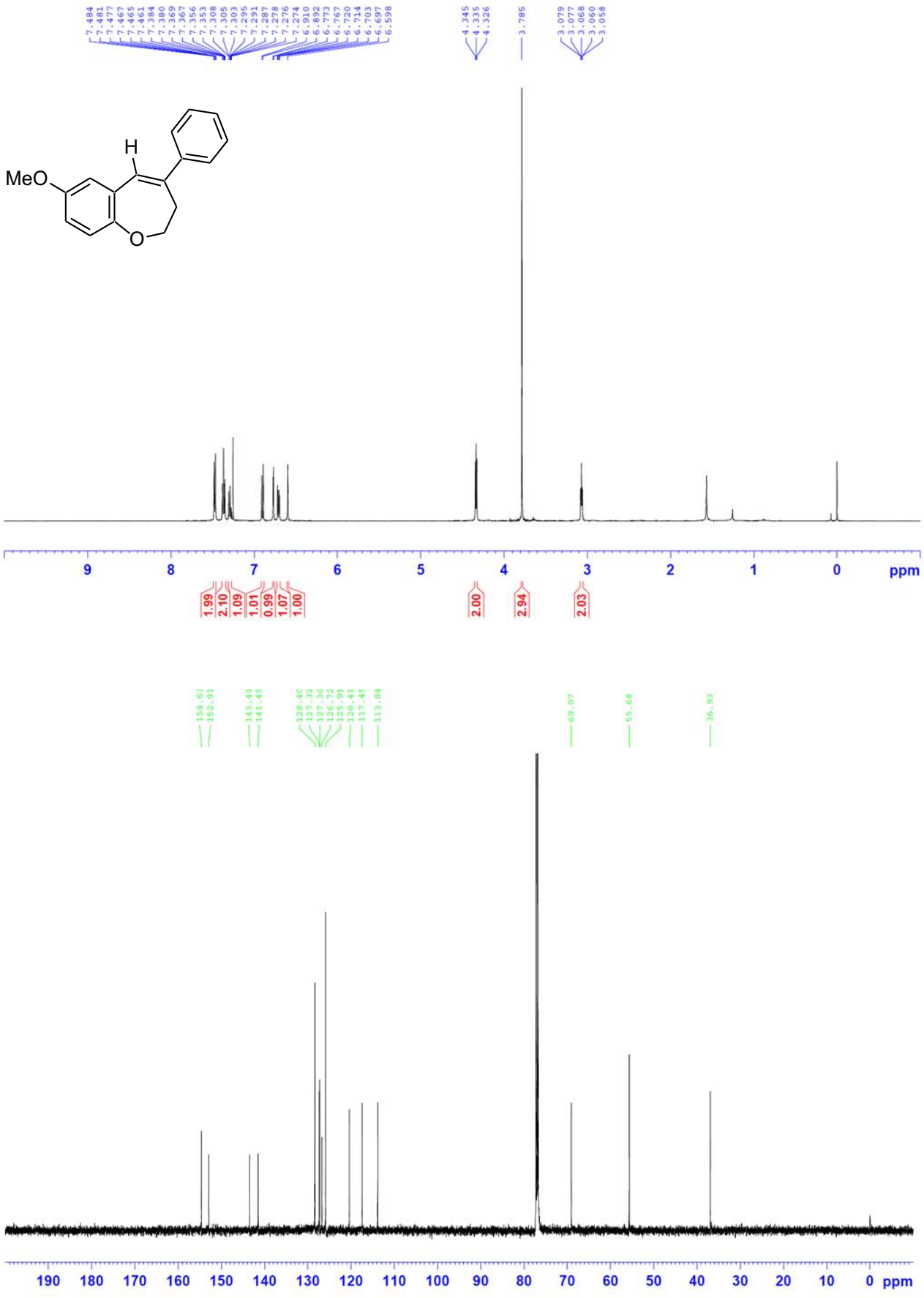
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 8-cyclopentyl-6,7-dihydro-5*H*-benzo[7]annulene (**2i**) ($CDCl_3$)



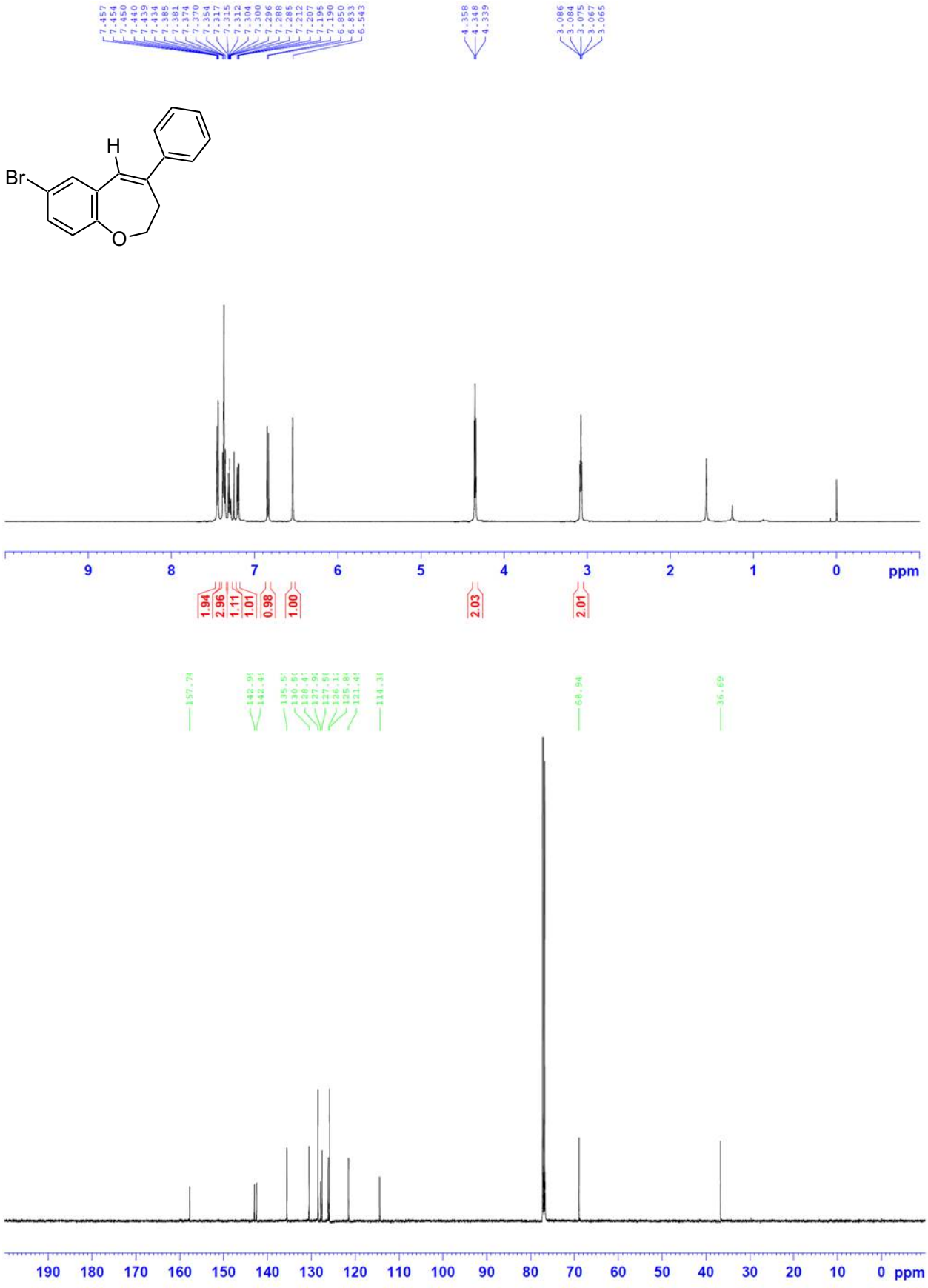
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 4-phenyl-2,3-dihydrobenzo[*b*]oxepine (**3**) ($CDCl_3$)



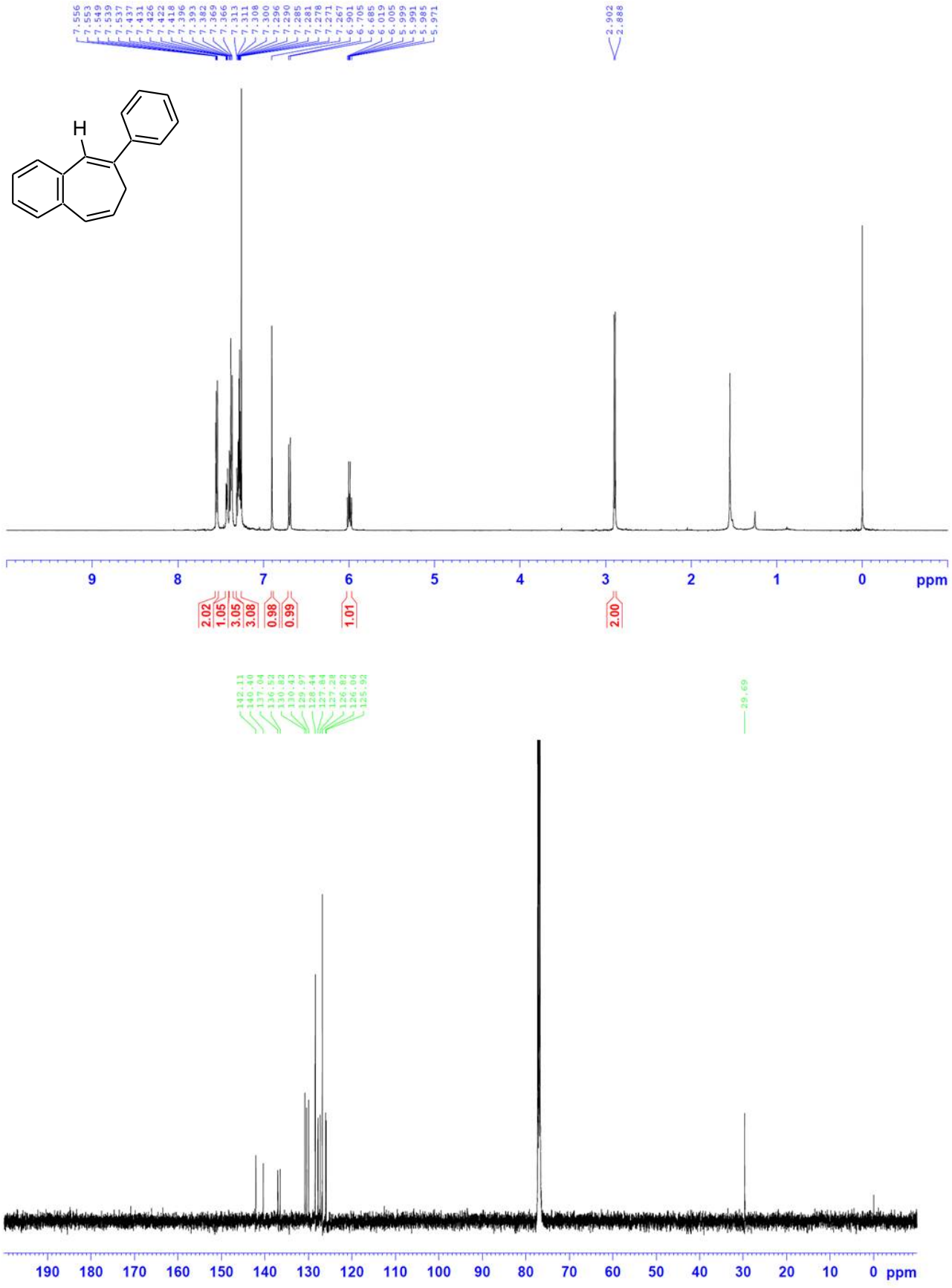
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 7-methoxy-4-phenyl-2,3-dihydrobenzo[*b*]oxepine (**4**) ($CDCl_3$)



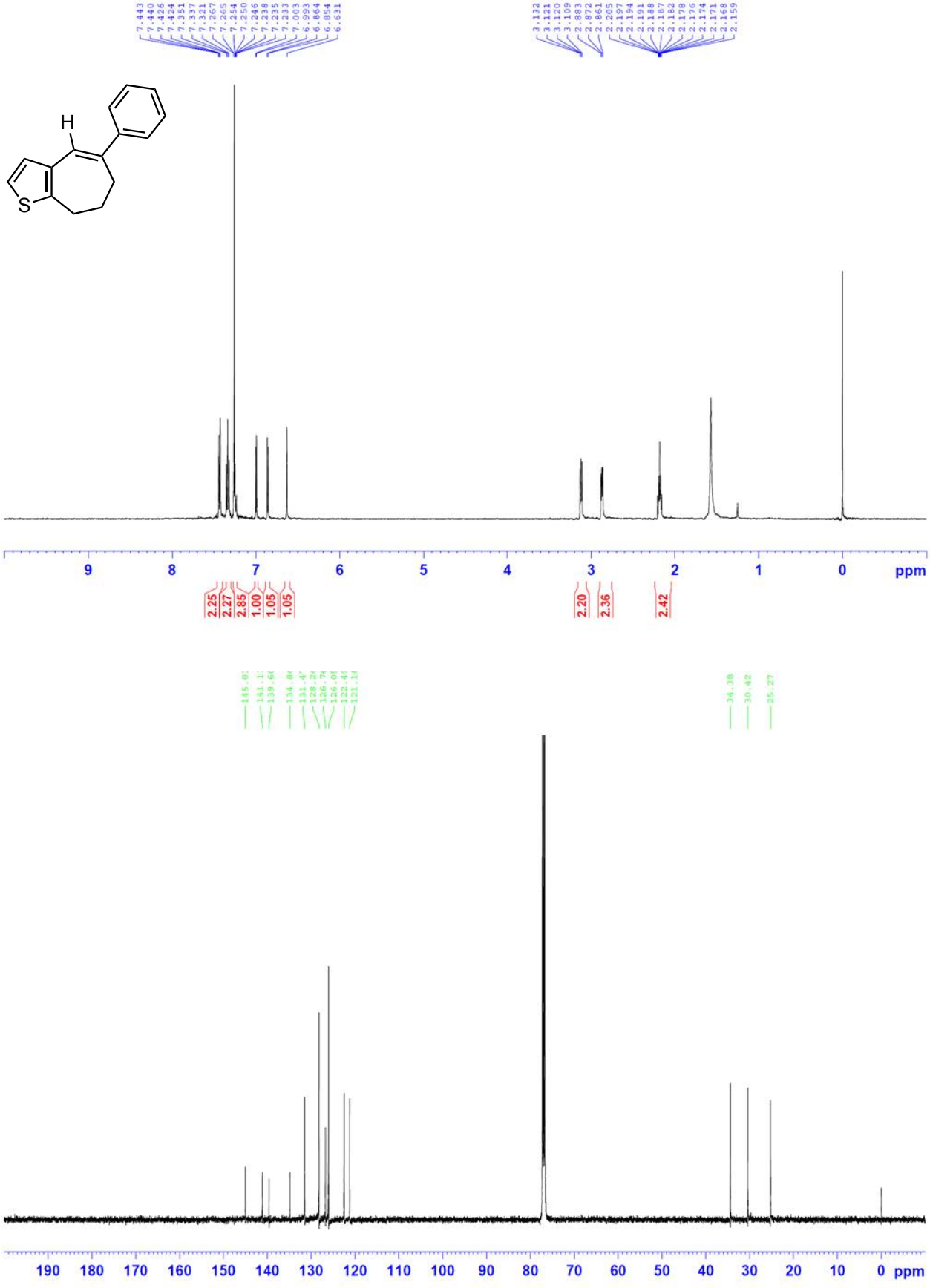
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 7-bromo-4-phenyl-2,3-dihydrobenzo[*b*]oxepine (**5**) ($CDCl_3$)



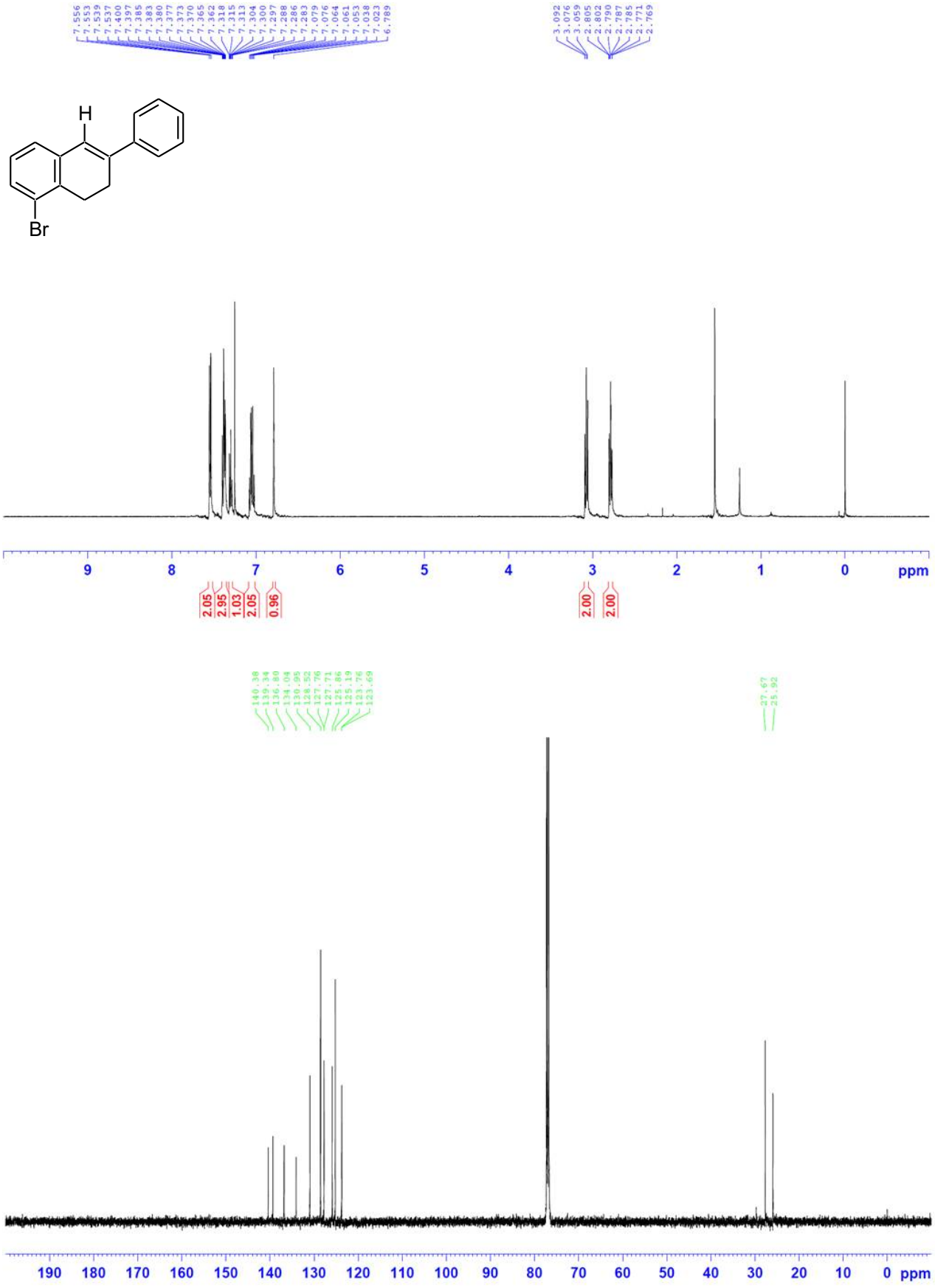
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 6-phenyl-7*H*-benzo[7]annulene (**6**) ($CDCl_3$)



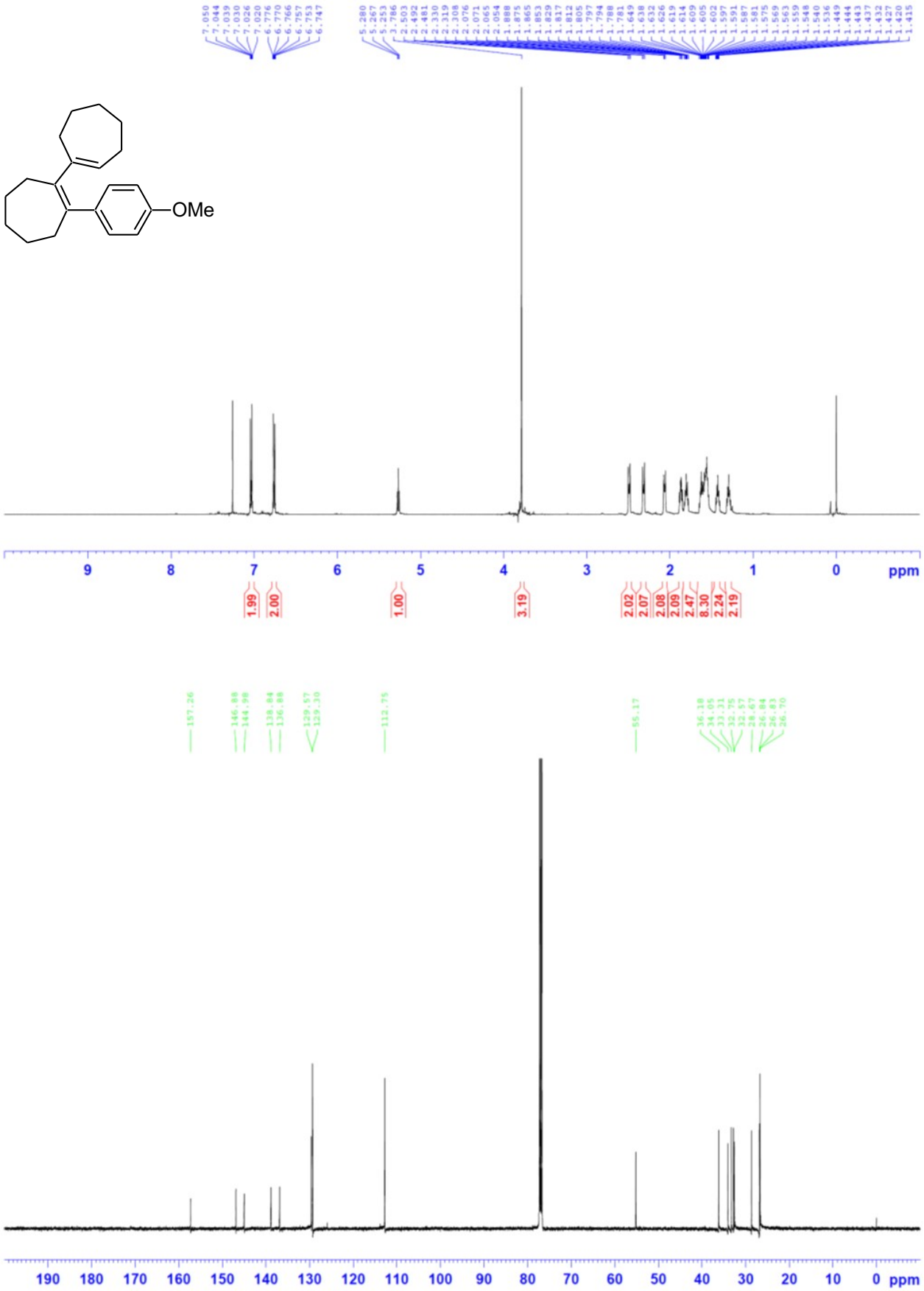
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 5-phenyl-7,8-dihydro-6*H*-cyclohepta[*b*]thiophene (**7**) ($CDCl_3$)



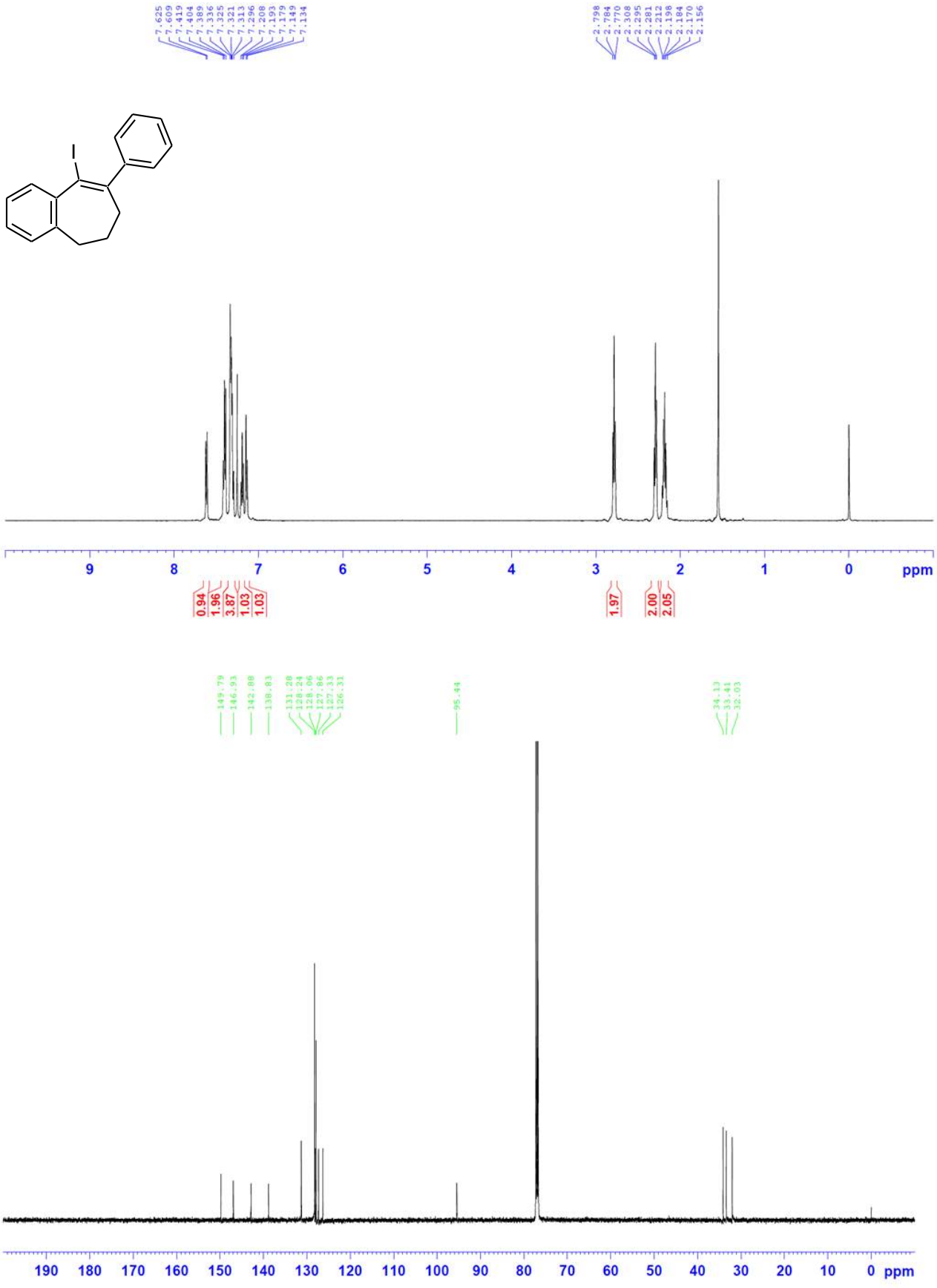
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 8-bromo-3-phenyl-1,2-dihydronaphthalene (**9**) ($CDCl_3$)



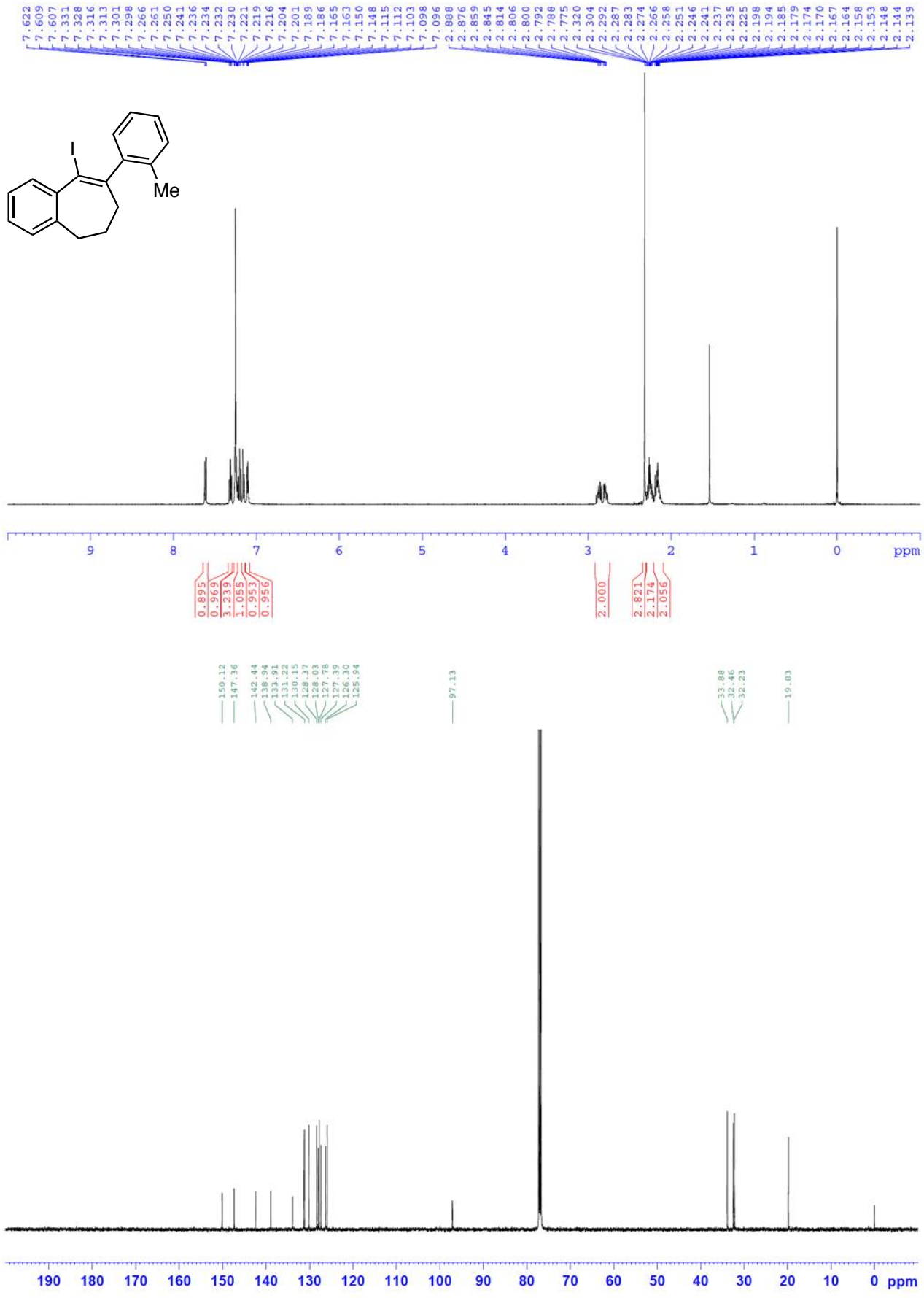
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 1-(1-cycloheptenyl)-2-(*p*-methoxyphenyl)cycloheptene (**13**) ($CDCl_3$)



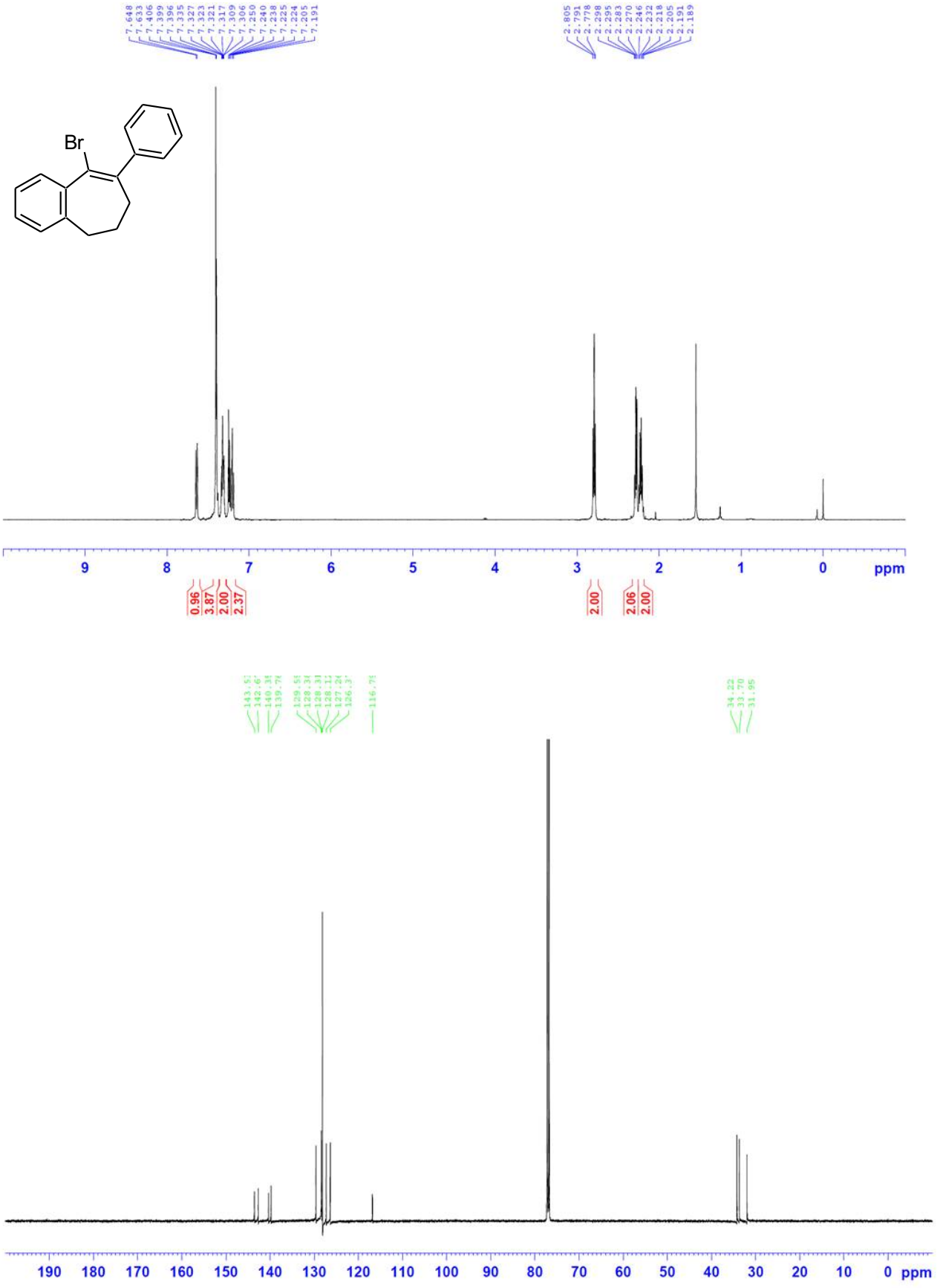
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 9-iodo-8-phenyl-6,7-dihydro-5*H*-benzocycloheptene (**2j**) ($CDCl_3$)



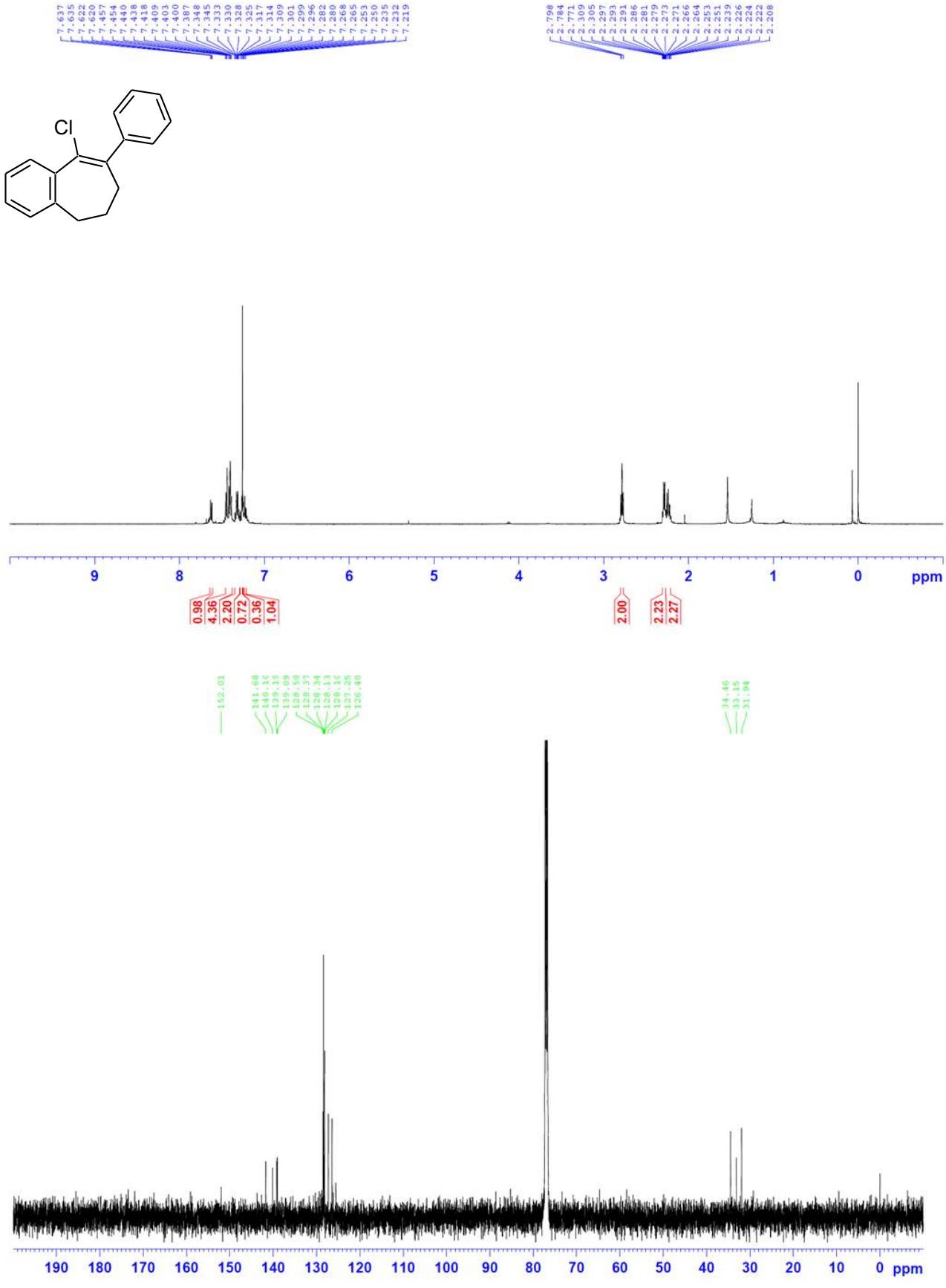
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 9-iodo-8-(*o*-tolyl)-6,7-dihydro-5*H*-benzocycloheptene (**2k**) ($CDCl_3$)



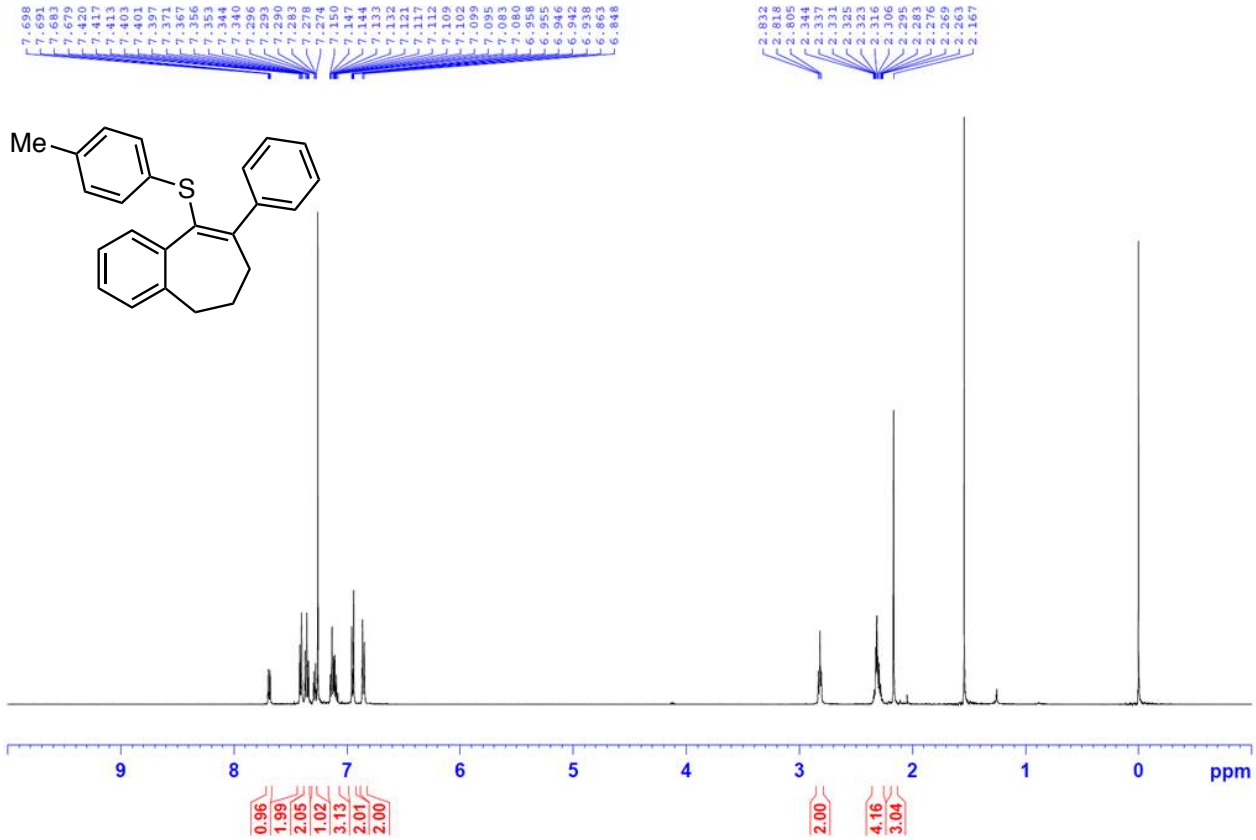
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 9-bromo-8-phenyl-6,7-dihydro-5*H*-benzocycloheptene (**2l**) ($CDCl_3$)

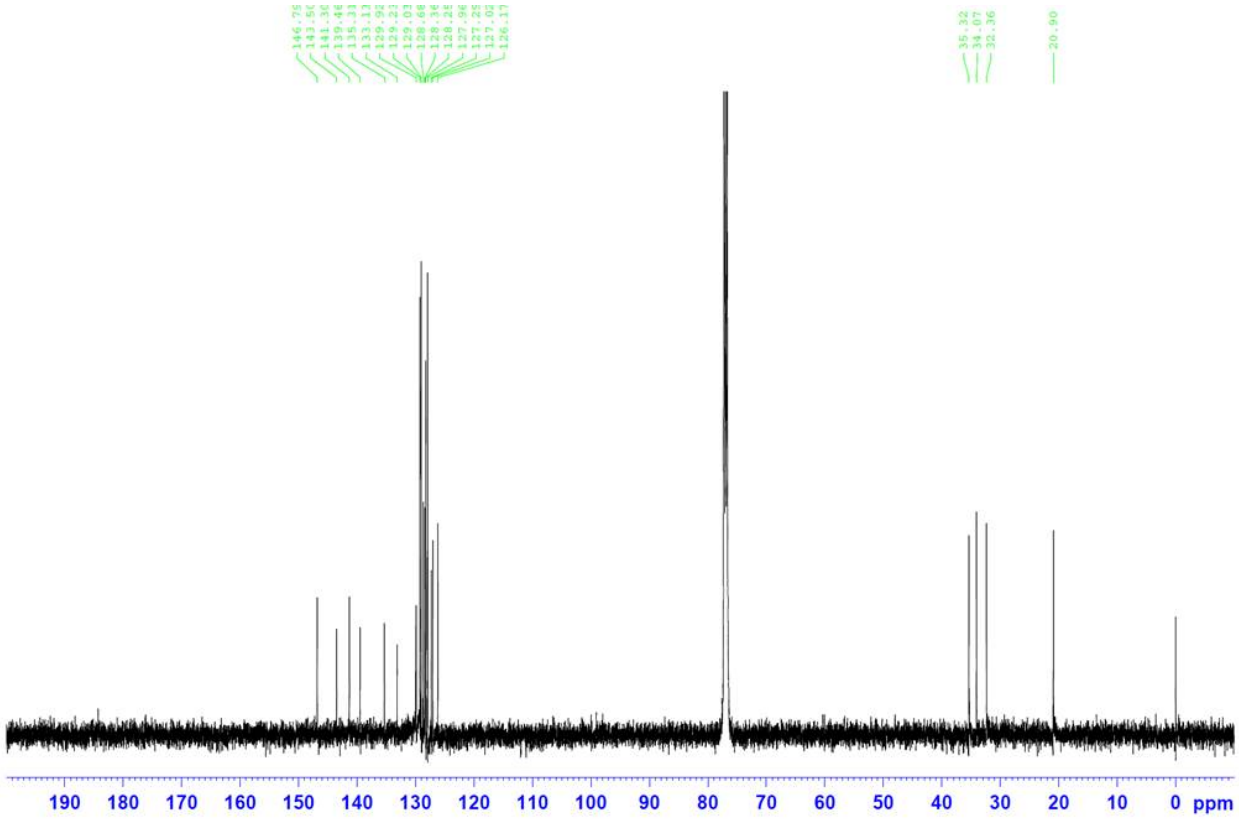


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 9-chloro-8-phenyl-6,7-dihydro-5*H*-benzocycloheptene (**2m**) ($CDCl_3$)

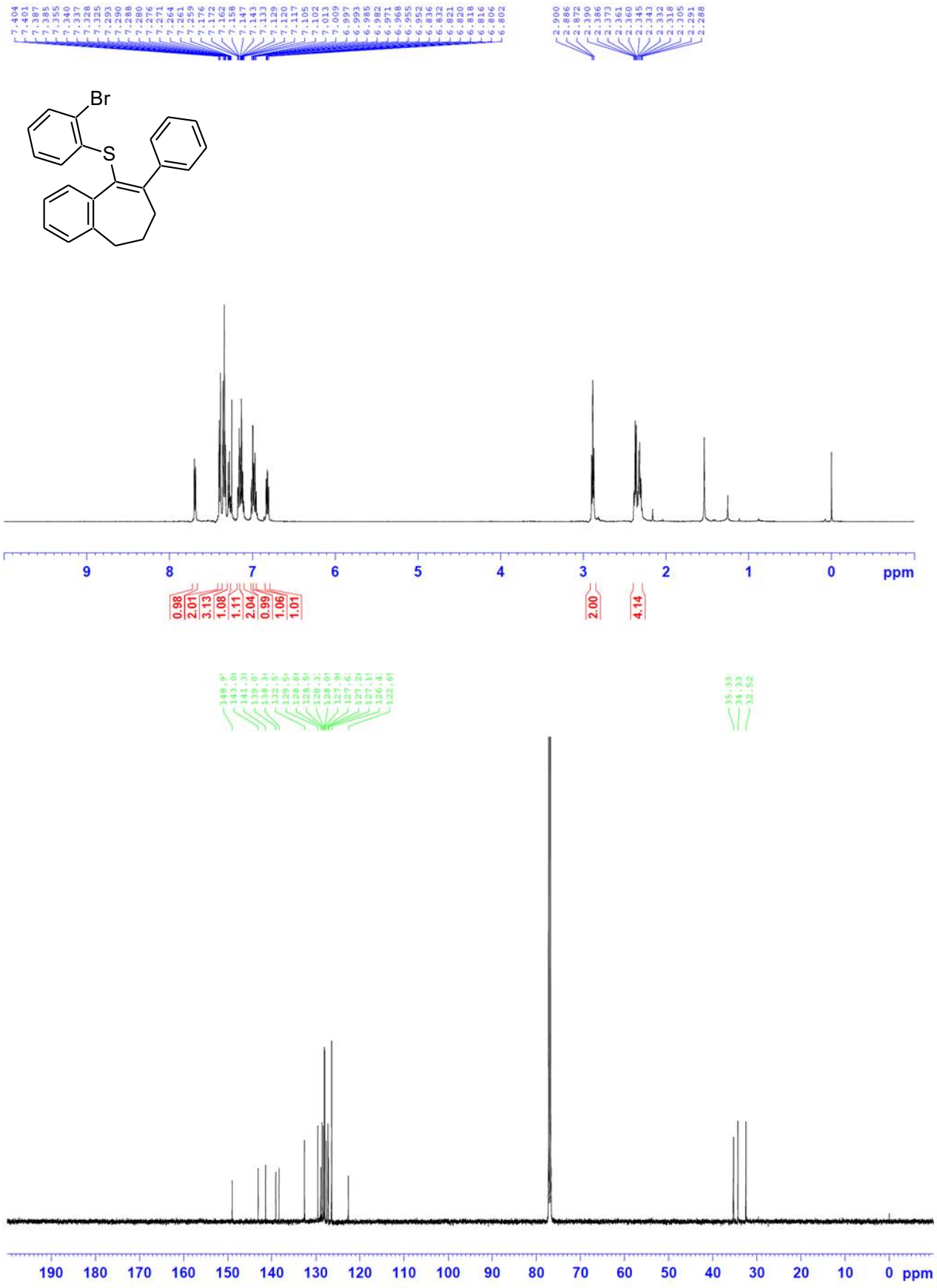


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 8-phenyl-6,7-dihydro-5*H*-benzo[7]annulen-9-yl *p*-tolyl sulfide (**2n**) ($CDCl_3$)

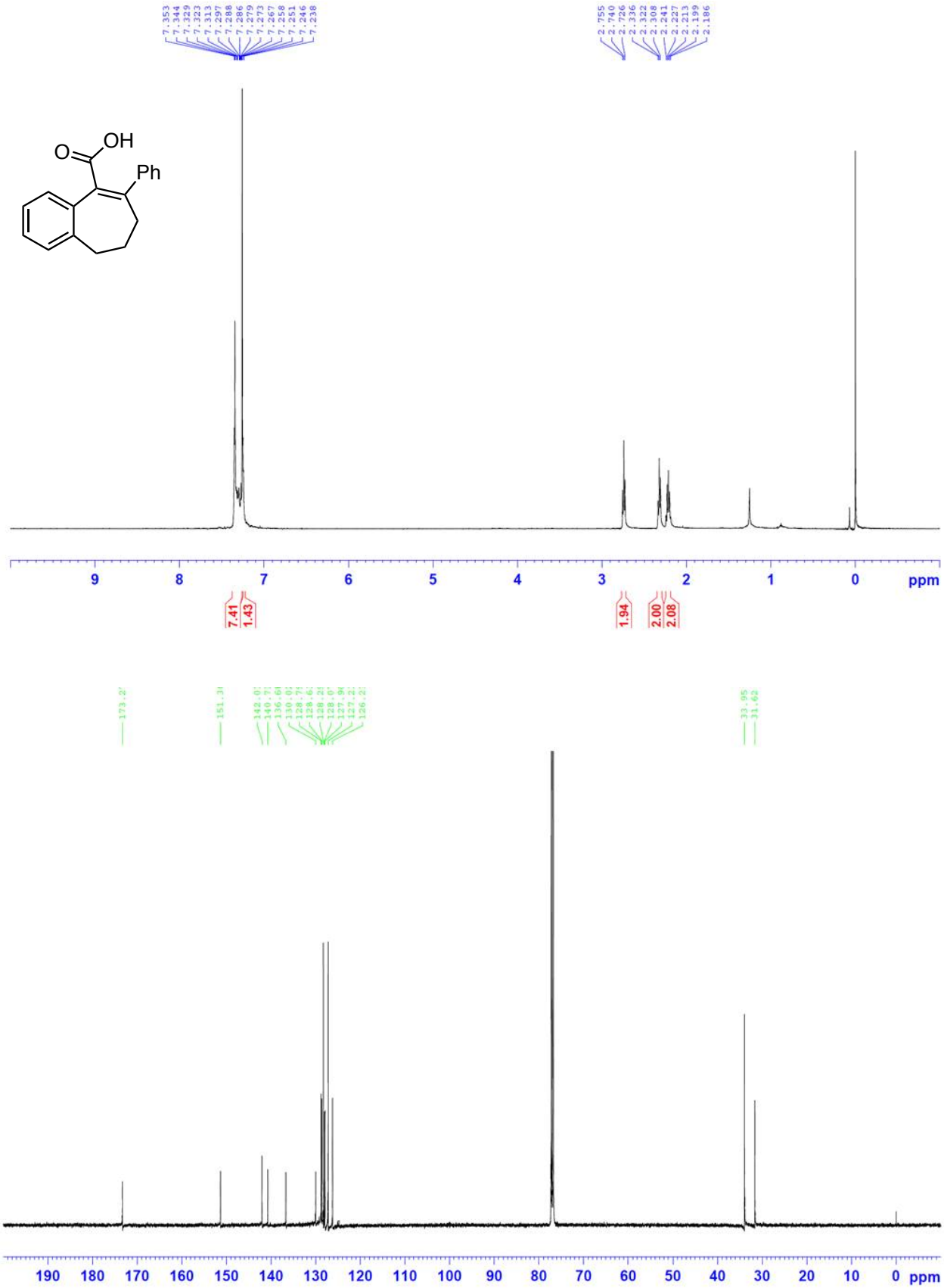




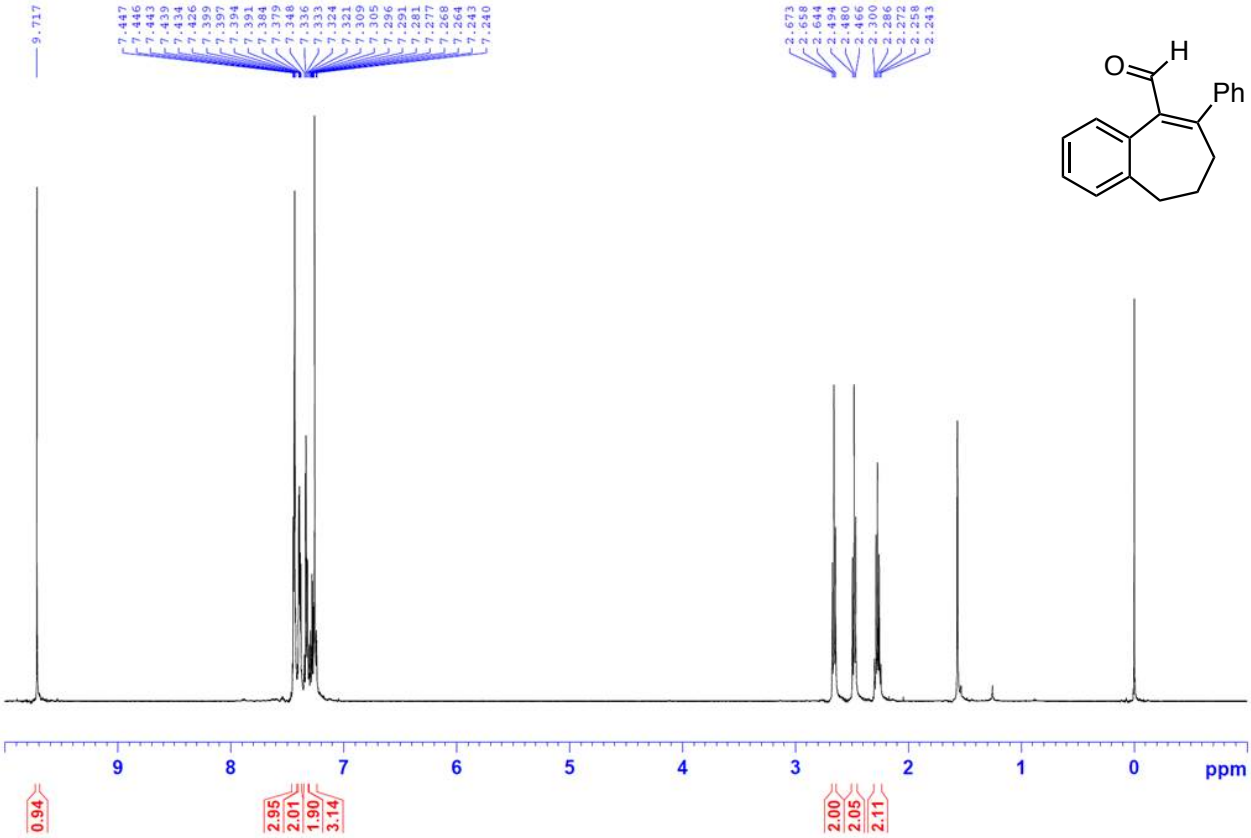
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 8-phenyl-6,7-dihydro-5*H*-benzo[7]annulen-9-yl *o*-bromophenyl sulfide (**2o**) ($CDCl_3$)

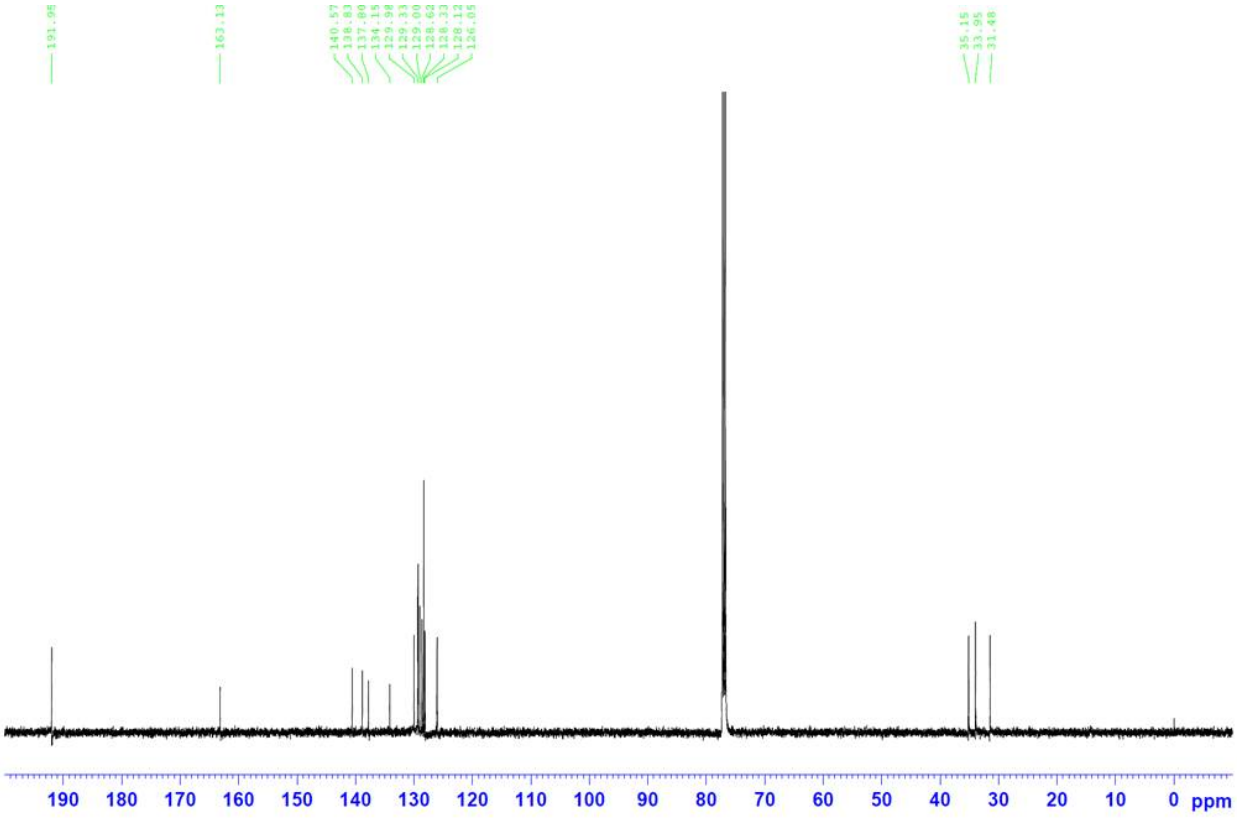


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 8-phenyl-6,7-dihydro-5*H*-benzo[7]annulene-9-carboxylic acid (**2p**) ($CDCl_3$)

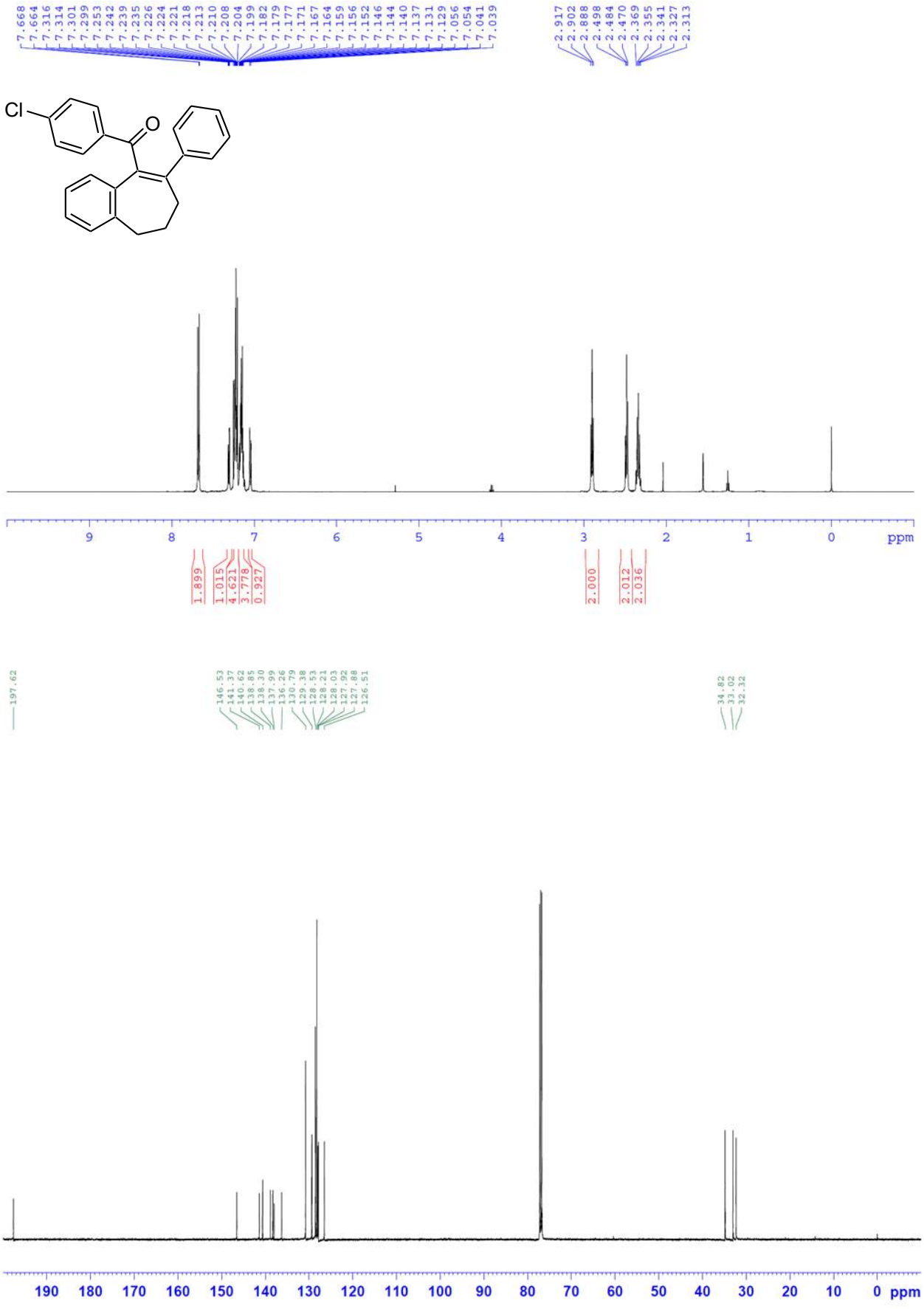


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 8-phenyl-6,7-dihydro-5*H*-benzo[7]annulene-9-carbaldehyde (**2q**) ($CDCl_3$)

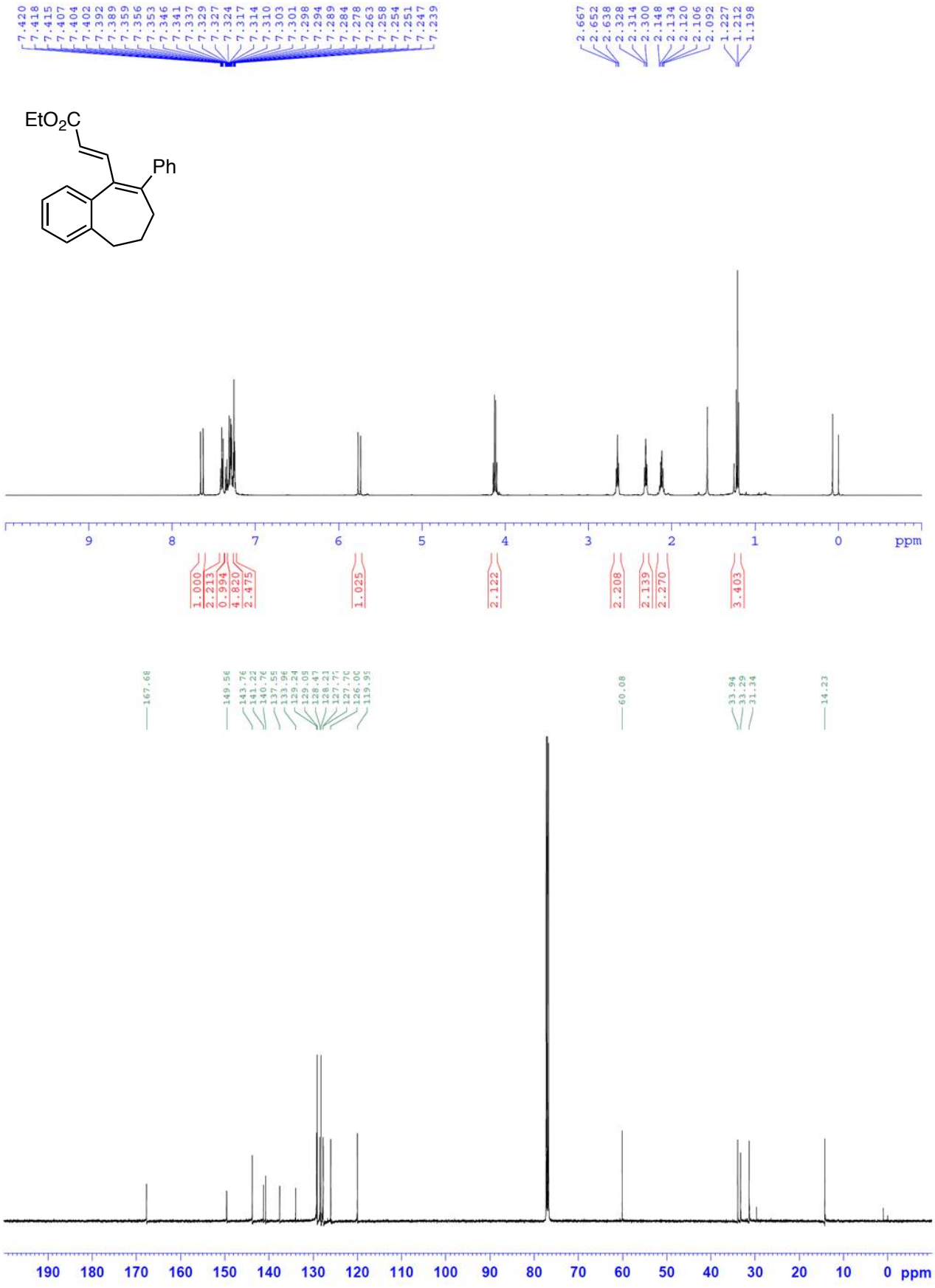




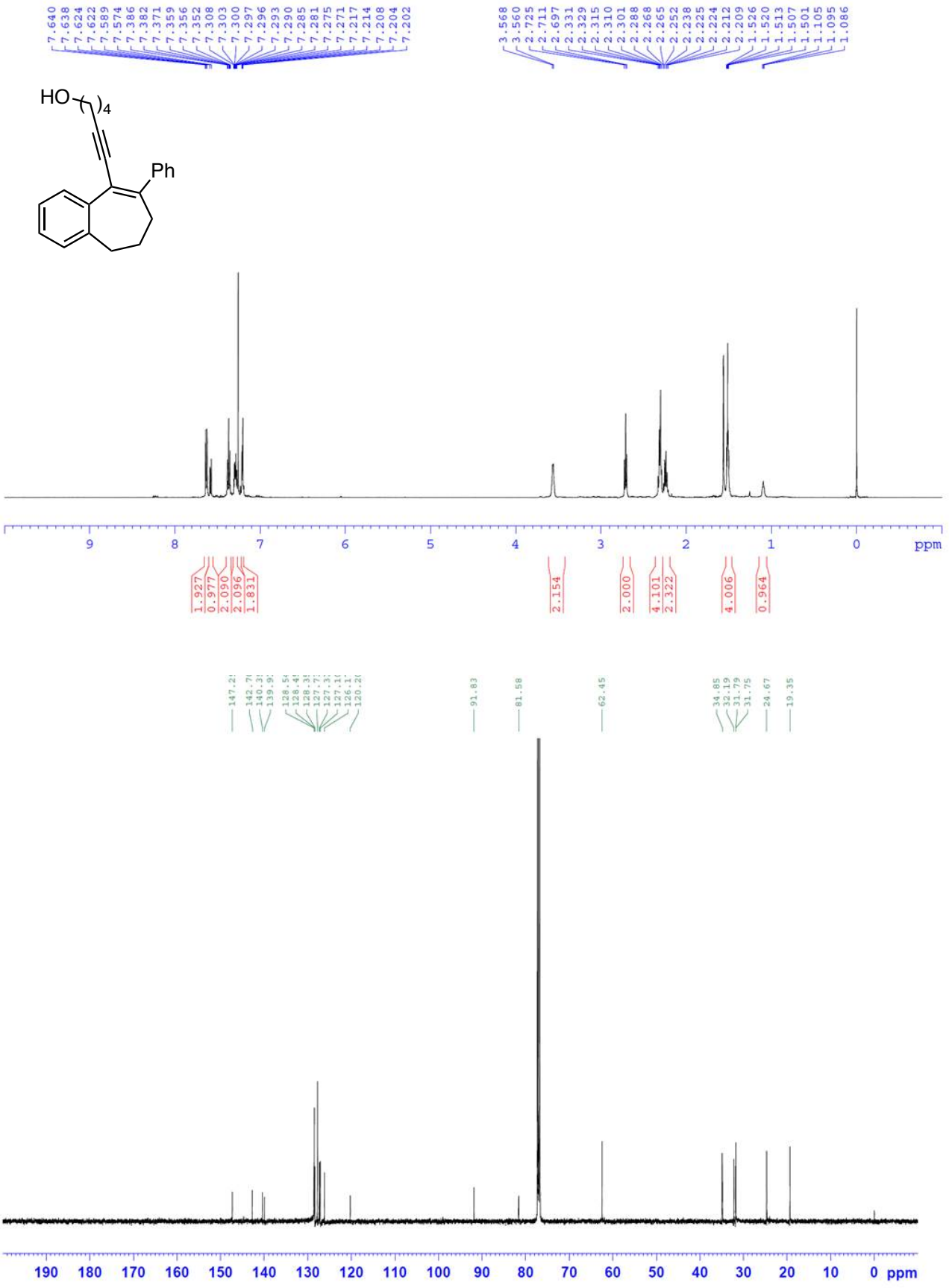
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 8-phenyl-6,7-dihydro-5*H*-benzo[7]annulene-9-yl *p*-chlorophenyl ketone (**2r**) ($CDCl_3$)



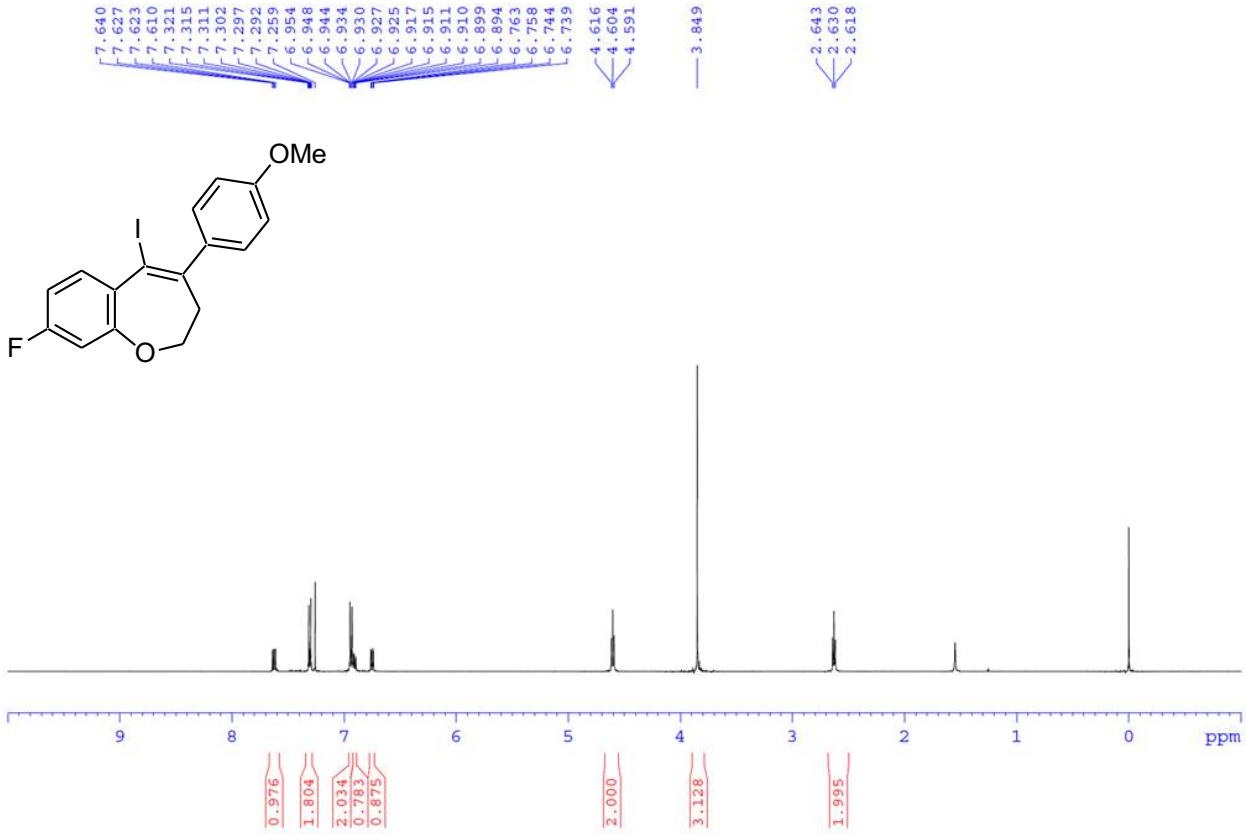
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of ethyl β-(*E*)-(8-phenyl-6,7-dihydro-5*H*-benzocyclohepten-9-yl)acrylate (**2t**) ($CDCl_3$)

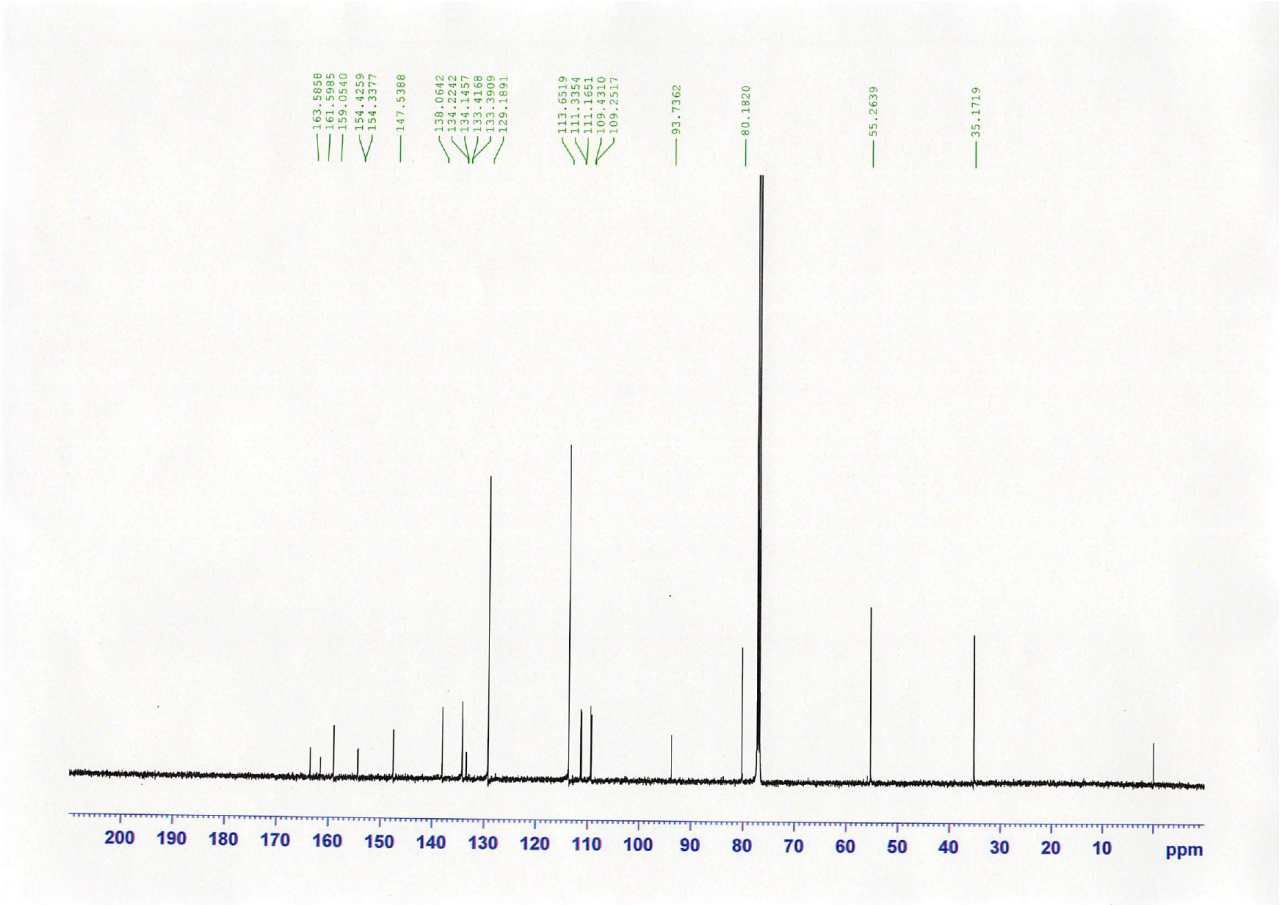


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 6-(8-phenyl-6,7-dihydro-5*H*-benzocyclohepten-9-yl)-1-hydroxy-5-hexyne (**2u**) ($CDCl_3$)

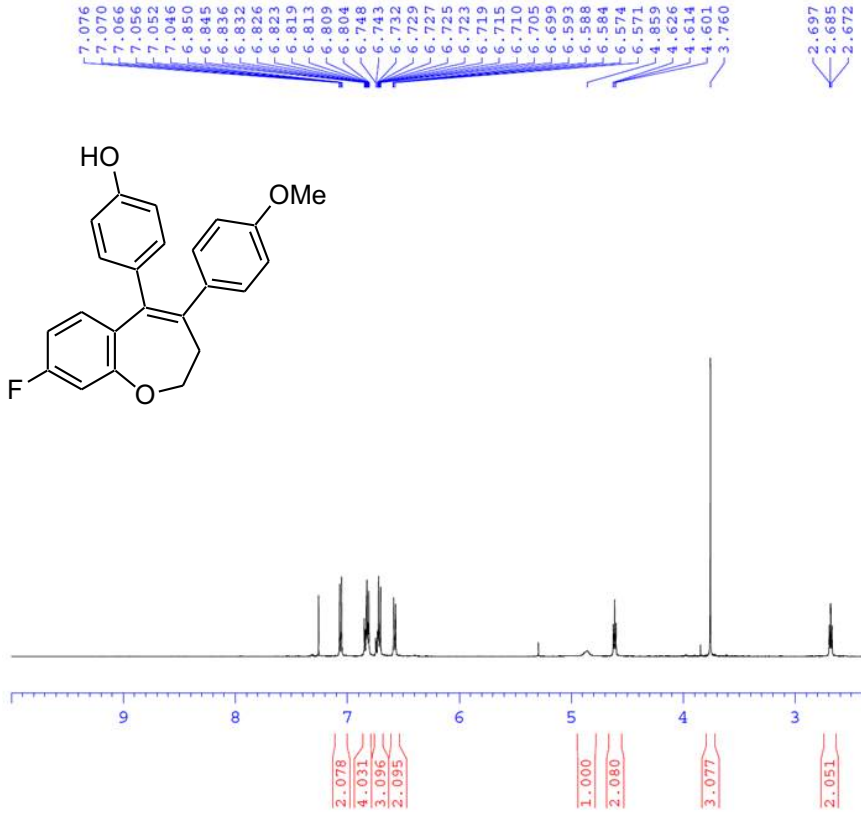


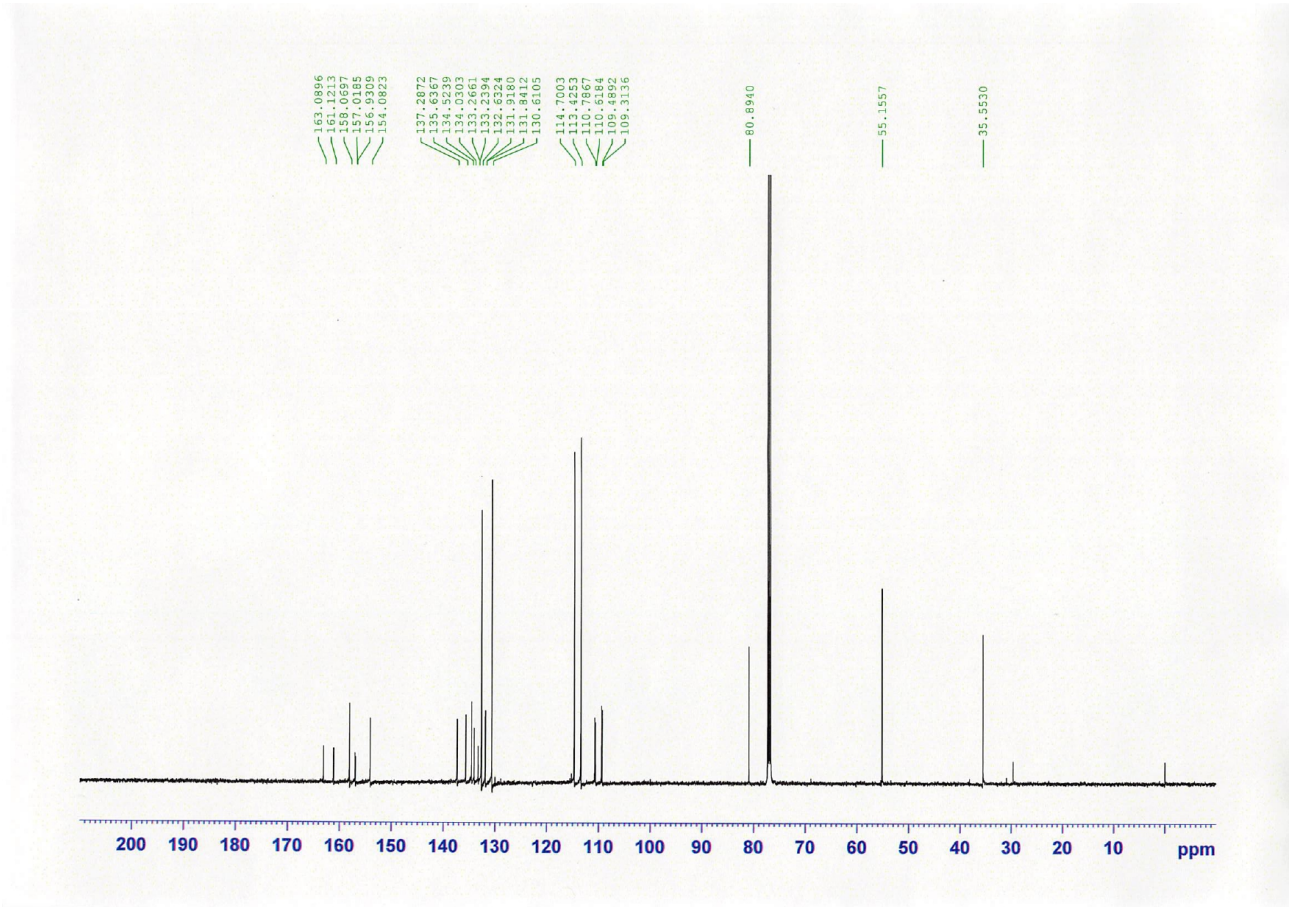
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 8-fluoro-5-iodo-4-(*p*-methoxyphenyl)-2,3-dihydrobenzo[*b*]oxepine (**S1**) ($CDCl_3$)



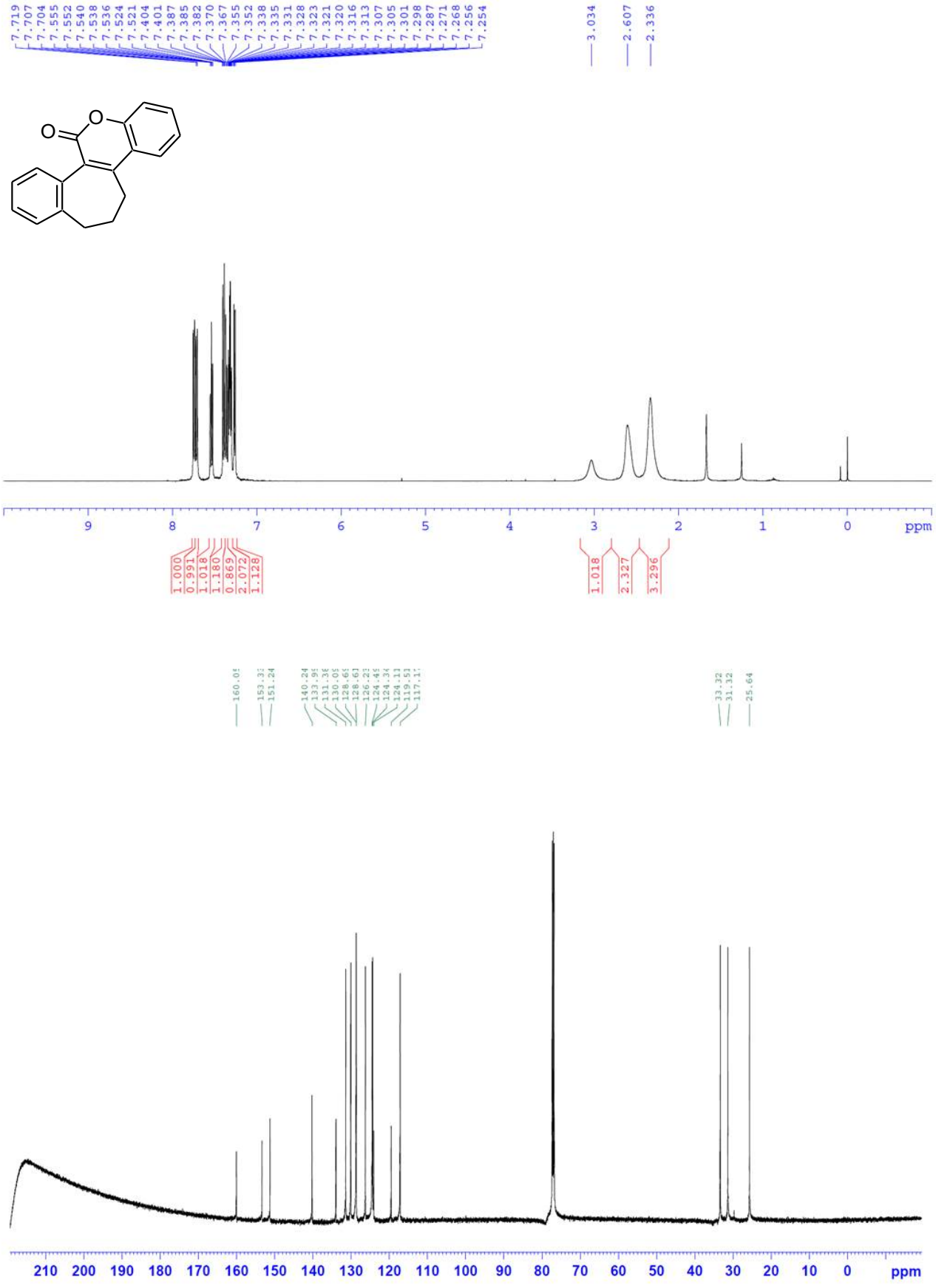


H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 8-fluoro-5-(4-hydroxyphenyl)-4-(4-methoxyphenyl)-2,3-dihydrobenzo[*b*]oxepine (**14**) ($CDCl_3$)





^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 12,13-dihydro-benzo[*b*]benzo[6,7]cyclohepta[2,1-*d*]pyran-6(11*H*)-one (**15**) ($CDCl_3$)



^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 6,7-dihydrodibenzo[*a*,*e*]azulen-12(5*H*)-one (**16**) ($CDCl_3$)