

Supporting Information

Dichlorination of Olefins with Trichloroisocyanuric Acid (TCCA) and Tetrabutylammonium Chloride (TBACl)

Ramazan Koçak^{*1,2}

Address: ¹Department of Chemistry, Faculty of Arts and Sciences, Amasya University, Amasya, Turkey, ²Department of Chemistry, Faculty of Science, Ataturk University, Erzurum, Turkey.

Email: ramazan.kocak@amasya.edu.tr, ramazan.kocak@atauni.edu.tr

Table of contents

Experimental	S2
General procedure.....	S2
References.....	S9
¹ H NMR, ¹³ C NMR, and HRMS Spectra.....	S10

Experimental

General

Compounds **1d** and **1o** were synthesized following the procedures reported in the literature.¹⁻² All chemicals and solvents, purchased from Sigma-Aldrich, were used without further purification. Reactions that require heating were carried out under oil bath conditions. Reactions were monitored by thin layer chromatography using Merck TLC Silica gel 60 F254 and the plates were inspected by 254 nm or 365 nm UV-light and/or by acquiring ¹H-NMR spectra. Column chromatography was performed over Merck Silica gel 60F (70-230 mesh ASTM). The one and two dimensional ¹H- and ¹³C NMR spectra were recorded on a Varian-400 or a Bruker-400 spectrometer in CDCl₃ using tetramethylsilane as the internal reference. All spectra were recorded at 25 °C and coupling constants (*J* values) are given in Hz. Chemical shifts are given in parts per million (ppm). Abbreviations used to define the multiplicities are as follows: s = singlet; d = doublet; dd = doublet of doublets; m = multiplet. Mass spectra of the compounds (**2e**, **3u**, **3w** and **2ac**) that are unknown and/or whose data cannot be accessed were recorded on the Agilent Technologies 6530 Accurate-Mass Q-TOF-LC/MS.

General procedure

For Chlorination of Olefins with TCCA/TBACl

Olefine (**1**) (0,5 mmol) and TBACl (153 mg, 0.55 mmol) were dissolved in 2 mL CH₂Cl₂ in a 10 mL reaction tube. Then, TCCA (81 mg, 0.35 mmol) was added to the reaction mixture (Caution: When the TCCA is added before TBACl, the yield of some products decreases). The reaction mixture was stirred at room temperature for 10 minutes. 2 mL *n*- hexane was added and stirred at room temperature. After about 5 minutes, a dense viscous part formed at the bottom of the tube, and the CH₂Cl₂/*n*- hexane phase containing chlorinated compounds was transferred to a short silica gel column with a pipette. Dichlorinated compounds were purified by eluting with *n*- hexane/CH₂Cl₂ (1:1).

For Regioselective Chlorobromination and Dibromination Reactions of Bicyclic Alkene Benzonorbornadiene with TCCA/TBA₂Br Redox Reactions

TCCA (0.5-1.1 equiv) and TBA₂Br (0.5-3.0 equiv) were dissolved in 2 mL CH₂Cl₂ in a 10 mL reaction tube and stirred for 5 min at room temperature. Then, olefine (**1**) (0,5 mmol) was added to the reaction mixture. The reaction mixture was stirred at room temperature for an additional 10 minutes. 2 mL *n*- hexane was added and stirred at room temperature. After about 5 minutes, a dense viscous part formed at the bottom of the tube, and the CH₂Cl₂/*n*- hexane phase containing chlorinated compounds was transferred to a short silica gel column with a pipette. Regioselective chlorobromination and dibromination redox products were purified by eluting with *n*- hexane/CH₂Cl₂ (1:1).

For Control experiments: Regioselective Chlorobromination and Dibromination Reactions of Bicyclic Alkene Benzonorbornadiene with DBI/TBA₂X (Cl, Br).

Benzonorbornadiene (**1o**) (0,5 mmol) and TBACl (153 mg, 0.55 mmol) or TBA₂Br (177 mg, 0.55 mmol) were dissolved in 2 mL CH₂Cl₂ in a 10 mL reaction tube. Then, DBI (158 mg, 0.55 mmol) was added to the reaction mixture. The reaction mixture was stirred at room temperature for 10 minutes. 2 mL *n*- hexane was added and stirred at room temperature. After about 5 minutes, a dense viscous part

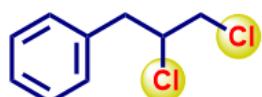
formed at the bottom of the tube, and the $\text{CH}_2\text{Cl}_2/n$ - hexane phase containing chlorinated compounds was transferred to a short silica gel column with a pipette. Dichlorinated compounds were purified by eluting with n - hexane/ CH_2Cl_2 (1:1).

1,2-Dichlorononane (2a)³



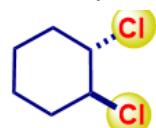
Colorless oil (94 mg, 95%). ^1H NMR (400 MHz, CDCl_3) δ 4.08 – 3.99 (m, 1H), 3.76 (dd, $J = 11.3, 5.2$ Hz, 1H), 3.65 (dd, $J = 11.3, 7.4$ Hz, 1H), 2.05 – 1.92 (m, 1H), 1.79 – 1.64 (m, 1H), 1.48 – 1.21 (m, 10H), 0.89 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 61.4, 48.4, 35.2, 31.9, 29.2, 29.1, 26.0, 22.8, 14.2.

(2,3-Dichloropropyl)benzen (2b)⁴



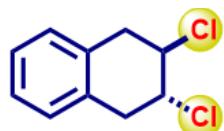
Colorless oil (85 mg, 90%). ^1H NMR (400 MHz, CDCl_3) δ 7.30 – 7.16 (m, 5H), 4.23 – 4.13 (m, 1H), 3.66 (dd, $J = 11.5, 4.8$ Hz, 1H), 3.58 (dd, $J = 11.5, 6.9$ Hz, 1H), 3.24 (dd, $J = 14.2, 5.7$ Hz, 1H), 2.99 (dd, $J = 14.2, 7.3$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 136.4, 129.7, 128.7, 127.3, 61.1, 47.6, 41.1.

trans-1,2-Dichlorocyclohexane (2c)⁵



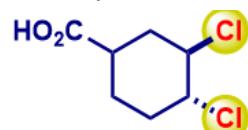
Colorless oil (71 mg, 93%). ^1H NMR (400 MHz, CDCl_3) δ 4.10 – 3.87 (m, 2H), 2.38 – 2.27 (m, 2H), 1.86 – 1.65 (m, 4H), 1.51 – 1.34 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 63.3, 33.6, 23.2.

trans-2,3-Dichloro-1,2,3,4-tetrahydronaphthalene (2d)⁶



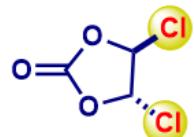
White crystal (88 mg, 87%). Mp: 84–85 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.25 – 7.18 (AA' part of AA'BB' system, 2H), 7.16 – 7.09 (BB' part of AA'BB' system, 2H), 4.53 – 4.44 (m, 2H), 3.69 (dd, $J = 18.4, 3.2$ Hz, 2H), 3.20 – 3.10 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 131.3, 129.0, 126.9, 58.0, 34.8.

trans-3,4-Dichlorocyclohexane-1-carboxylic acid (2e)



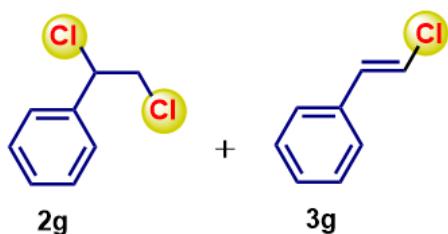
White solid (95 mg, 96%). Mp: 128–129 °C. ^1H NMR (400 MHz, CDCl_3) δ 4.78 – 4.74 (t, J = 5.2 Hz, 1H), 4.33 (t, J = 4.7 Hz, 1H), 2.69–2.63 (m, 1H), 2.52 (d, J = 12.3 Hz, 1H), 2.34 – 2.21 (m, 2H), 2.07 (dd, J = 16.1, 5.4 Hz, 1H), 1.99 – 1.79 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 177.7, 79.0, 53.5, 38.2, 31.9, 27.9, 22.4. HRMS (ESI) m/z: [M - HCl + H] $^+$ calcd for $\text{C}_7\text{H}_{10}\text{ClO}_2$: 161.0364, found: 161.0365.

trans-4,5-Dichloro-1,3-dioxolan-2-one (2f)⁷



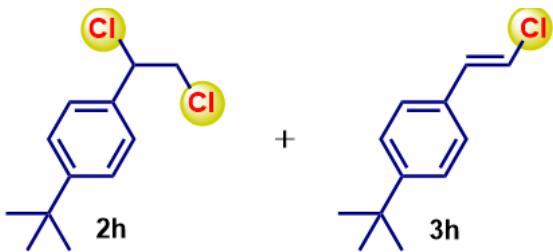
Colorless viscous (74 mg, 94%). ^1H NMR (400 MHz, CDCl_3) δ 6.33 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 149.9, 90.5.

(1,2-Dichloroethyl)benzene (2g)⁸ and (E)-(2-chlorovinyl)benzene (3g)⁹



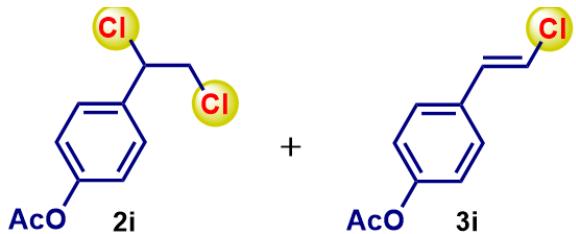
Mixture of **2g** (79%) and **3g** (9%, was not isolated). **2g**: colorless oil (69 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.48 – 7.33 (m, 5H), 5.01 (dd, J = 7.9, 6.6 Hz, 1H), 4.01 (dd, J = 11.3, 6.6 Hz, 1H), 3.94 (dd, J = 11.3, 7.9 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 138.1, 129.3, 129.0, 127.5, 61.9, 48.5.

1-(tert-Butyl)-4-(1,2-dichloroethyl)benzene (2h)⁸ and (E)-1-(tert-butyl)-4-(2-chlorovinyl)benzene (3h)¹⁰



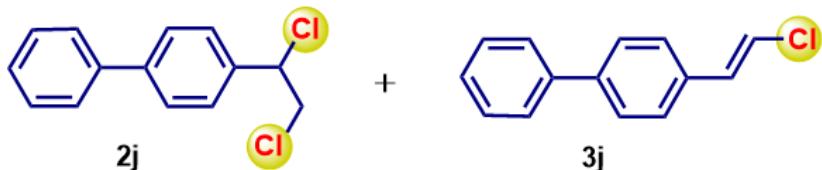
Mixture of **2h** (72%) and **3h** (9%, was not isolated). **2h**: colorless oil (83 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.41 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 5.00 (t, J = 7.2 Hz, 1H), 4.02 – 3.90 (m, 2H), 1.33 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 152.4, 135.1, 127.2, 125.9, 62.0, 48.6, 34.8, 31.4.

4-(1,2-Dichloroethyl)phenyl acetate (2i**)¹¹ and (*E*)-4-(2-chlorovinyl)phenyl acetate (**3i**)¹²**



Mixture of **2i** (72%) and **3i** (14%, was not isolated). **2i**: colorless oil (84 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.42 (d, *J* = 8.7 Hz, 2H), 7.12 (d, *J* = 8.7 Hz, 2H), 5.00 (dd, *J* = 7.8, 6.6 Hz, 1H), 3.98 (dd, *J* = 11.4, 6.6 Hz, 1H), 3.89 (dd, *J* = 11.4, 7.8 Hz, 1H), 2.31 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 169.2, 151.1, 135.5, 128.6, 122.0, 61.2, 48.4, 21.1.

4-(1,2-Dichloroethyl)-1,1'-biphenyl (2j**)¹¹ and (*E*-4-(2-chlorovinyl)-1,1'-biphenyl (**3j**)¹³**



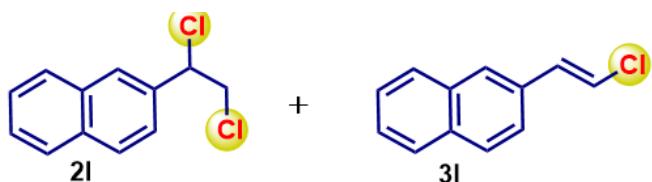
Mixture of **2j** (83%) and **3j** (8%, was not isolated). **2j**: white crystal (105 mg). Mp: 101–103 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.67 – 7.55 (m, 4H), 7.54 – 7.42 (m, 4H), 7.42 – 7.34 (m, 1H), 5.06 (dd, *J* = 7.9, 6.6 Hz, 1H), 4.11 – 3.92 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 142.3, 140.4, 137.0, 129.0, 128.0, 127.8, 127.7, 127.3, 61.7, 48.4.

trans-1,2-Dichlorocyclohexylbenzene (2k**)¹⁴**



Colorless oil (109 mg, 95%). ¹H NMR (400 MHz, CDCl₃) δ 7.57 – 7.50 (m, 2H), 7.43 – 7.36 (m, 2H), 7.35 – 7.29 (m, 1H), 4.81–4.77 (m, 1H), 2.74 – 2.59 (m, 2H), 2.34 – 2.25 (m, 1H), 2.09 – 1.92 (m, 2H), 1.90 – 1.75 (m, 2H), 1.70 – 1.60 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 144.1, 128.4, 128.2, 126.1, 73.8, 65.1, 31.1, 30.1, 21.4, 18.6.

2-(1,2-Dichloroethyl)naphthalene (2l**)¹¹ and (*E*-2-(2-chlorovinyl)naphthalene (**3l**)¹⁵**



Mixture of **2l** (80%) and **3l** (8%, was not isolated). **2l**: white crystal (90 mg). Mp: 66–67 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.92 – 7.84 (m, 4H), 7.58 – 7.49 (m, 3H), 5.19 (dd, *J* = 8.0, 6.6 Hz, 1H), 4.15 – 4.00 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 135.2, 133.6, 133.0, 129.1, 128.3, 127.9, 127.4, 127.0, 126.8, 124.3, 62.2, 48.3.

***trans*-1,2-Dichloro-2,3-dihydro-1H-indene (2m)⁸**



Colorless oil (81 mg, 87%). ^1H NMR (400 MHz, CDCl_3) δ 7.49 – 7.44 (m, 1H), 7.40 – 7.27 (m, 3H), 5.36 (d, J = 3.0 Hz, 1H), 4.67 (dt, J = 6.1, 3.2 Hz, 1H), 3.71 (dd, J = 16.8, 6.1 Hz, 1H), 3.19 (dd, J = 16.7, 3.4 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.0, 129.8, 128.1, 125.6, 125.2, 67.8, 64.6, 40.9.

***trans*-10,11-Dichloro-10,11-dihydro-5H-dibenzo[a,d][7]annulen-5-one (2n)¹⁶**



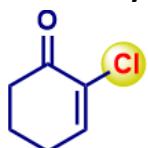
Brown crystal (94 mg, 91%). Mp: 188–191 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.06 (dd, J = 7.7, 1.5 Hz, 2H), 7.57 (dt, J = 7.4, 1.5 Hz, 2H), 7.50 (dt, J = 7.6, 1.4 Hz, 2H), 7.43 (dd, J = 7.5, 1.2 Hz, 2H), 5.58 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 192.8, 137.9, 135.3, 132.9, 131.4, 131.2, 129.8, 62.4.

(1*R* (*S*),2*S*(*R*),4*R*(*S*),9*R*(*S*))-2,9-dichloro-1,2,3,4-tetrahydro-1,4-methanonaphthalene (2o)¹⁶



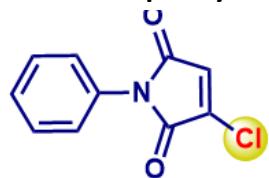
White crystal (101 mg, 95%). Mp: 48–49 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.26 – 7.14 (m, 4H), 4.13 – 4.09 (m, 1H), 3.86 (ddd, J = 7.9, 4.3, 1.1 Hz, 1H), 3.66 – 3.63 (m, 1H), 3.53 – 3.49 (m, 1H), 2.70 (dt, A part of AB system, J = 13.2, 4.0 Hz, 1H), 2.19 (dd, B part of AB system, J = 13.2, 7.9 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.9, 142.3, 128.0, 127.4, 122.0, 122.0, 66.4, 56.9, 56.9, 50.6, 36.4.

2-Chlorocyclohex-2-en-1-one (3p)¹⁴



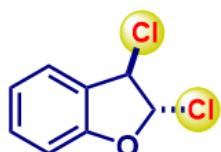
White crystal (61 mg, 94%). Mp: 60–71 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.14 (t, J = 4.5 Hz, 1H), 2.62 – 2.57 (m, 2H), 2.50 – 2.45 (m, 2H), 2.10 – 2.01 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 191.7, 146.8, 132.3, 38.6, 27.2, 22.7.

3-Chloro-1-phenyl-1H-pyrrole-2,5-dione (3q)¹⁷



White crystal (84 mg, 81%). Mp: 164–165 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.51 – 7.44 (m, 2H), 7.42 – 7.37 (m, 1H), 7.36 – 7.31 (m, 2H), 6.82 – 6.75 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 166.8, 164.0, 141.4, 131.0, 129.4, 128.5, 126.9, 126.2.

***trans*-2,3-Dichloro-2,3-dihydrobenzofuran (2r)¹⁸**



Colorless viscous (81 mg, 86%). ¹H NMR (400 MHz, CDCl₃) δ 7.50 (d, J = 7.6 Hz, 1H), 7.39 (t, J = 7.5 Hz, 1H), 7.13 (t, J = 7.5 Hz, 1H), 7.05 (d, J = 8.1 Hz, 1H), 6.51 (s, 1H), 5.48 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 157.6, 131.8, 126.1, 125.1, 123.9, 112.2, 98.3, 64.2.

3-Chloro-1-tosyl-1H-indole (3s)¹⁹



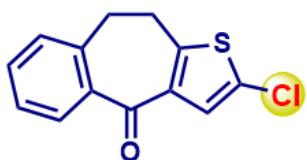
White crystal (152 mg, 89%). Mp: 122–123 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, J = 8.3 Hz, 1H), 7.77 (d, J = 8.4 Hz, 2H), 7.59 – 7.52 (m, 2H), 7.38 (dt, J = 7.8, 1.2 Hz, 1H), 7.31 (dt, J = 7.8, 0.9 Hz, 1H), 7.23 (d, J = 8.4 Hz, 2H), 2.34 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 145.5, 134.9, 134.2, 130.1, 128.5, 127.0, 125.9, 123.9, 122.5, 119.2, 114.0, 113.9, 21.8.

3-Chlorobenzo[b]thiophene (3t)²⁰



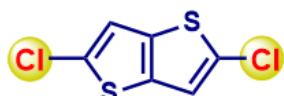
Colorless oil (96 mg, 81%). ¹H NMR (400 MHz, CDCl₃) δ 7.94 – 7.80 (m, 2H), 7.52 – 7.38 (m, 2H), 7.32 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 138.52, 136.23, 125.46, 124.98, 123.03, 121.97, 121.28, 120.88, 77.48, 77.16, 76.84.

2-Chloro-9,10-dihydro-4H-benzo[4,5]cyclohepta[1,2-b]thiophen-4-one (3u)



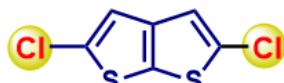
Brown viscous (116 mg, 93%). ^1H NMR (400 MHz, CDCl_3) δ 7.91 (dd, $J = 7.7, 1.5$ Hz, 1H), 7.48 – 7.40 (m, 2H), 7.35 (dt, $J = 7.7, 1.2$ Hz, 1H), 7.22 (d, $J = 7.4$ Hz, 1H), 3.23 – 3.17 (m, 2H), 3.16 – 3.09 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 186.7, 151.5, 139.5, 138.5, 138.4, 132.6, 130.8, 129.4, 128.9, 127.4, 126.2, 35.3, 29.2. HRMS (ESI) m/z: [M + H] $^+$ calcd for $\text{C}_{13}\text{H}_{10}\text{ClOS}$: 249.0141, found: 249.0132.

2,5-Dichlorothieno[3,2-b]thiophene (3v)²¹



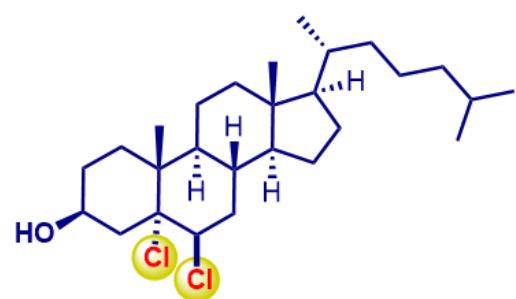
White crystal (95 mg, 91%). Mp: 99–100 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.03 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 134.6, 131.0, 118.7.

2,5-Dichlorothieno[2,3-b]thiophene (3w)



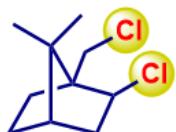
White crystal (92 mg, 88%). Mp: 54–55 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.01 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 142.2, 131.4, 131.1, 119.5. HRMS (APCI): m/z [M] $^+$ calcd for $\text{C}_6\text{H}_2\text{Cl}_2\text{S}_2$: 207.8969, found: 207.8968.

Dichloro-cholesterol (2x)²²



White crystal (146 mg, 64%). Mp: 140–142 °C. ^1H NMR (400 MHz, CDCl_3) δ 4.89 (d, $J = 4.1$ Hz, 1H), 4.77 (dd, $J = 11.8, 4.8$ Hz, 1H), 4.64 – 4.49 (m, 1H), 2.20 – 0.82 (m, 59H), 0.63 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 86.7, 67.3, 67.1, 61.4, 56.1, 55.7, 47.5, 43.5, 42.9, 39.6, 39.5, 37.9, 36.2, 35.9, 35.6, 32.4, 28.3, 28.2, 26.6, 24.1, 23.9, 22.9, 22.7, 20.7, 18.8, 18.3, 12.2.

(1*S*,2*S*,4*S*)-2-Chloro-1-(chloromethyl)-7,7-dimethylbicyclo[2.2.1]heptane (2y)^{23,24}



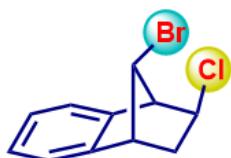
Colorless oil (27 mg, 69%). ^1H NMR (400 MHz, CDCl_3) δ 4.18 (dd, $J = 8.5, 4.5$ Hz, 1H), 3.95 (d, $J = 10.8$ Hz, 1H), 3.52 (d, $J = 10.8$ Hz, 1H), 2.28 – 2.20 (m, 1H), 2.08 (dd, $J = 14.0, 8.5$ Hz, 1H), 1.93 – 1.70 (m, 3H), 1.55 – 1.45 (m, 1H), 1.20 – 1.14 (m, 4H), 0.93 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) 64.3, 54.3, 48.9, 47.6, 46.1, 41.8, 33.0, 26.6, 21.1, 20.4.

***trans*-9,10-Dichlorooctadecanoic acid (2z)²⁵**



White viscous (134 mg, 95%). ^1H NMR (400 MHz, CDCl_3) δ 4.03 (dd, $J = 8.8, 3.2$ Hz, 2H), 2.35 (t, $J = 7.5$ Hz, 2H), 2.01 – 1.19 (m, 26H), 0.88 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 180.2, 65.8, 65.7, 34.54, 34.50, 34.1, 32.0, 29.5, 29.4, 29.2 (2C), 29.0, 28.9, 26.9, 26.8, 24.7, 22.8, 14.3.

(1*R*(*S*),2*S*(*R*),4*R*(*S*),9*R*(*S*))-9-bromo-2-chloro-1,2,3,4-tetrahydro-1,4-methanonaphthalene (2ab)



Yellowish viscous (116 mg, 90%). ^1H NMR (400 MHz, CDCl_3) δ 7.25 – 7.12 (m, 4H), 4.16 – 4.13 (m, 1H), 3.87 (ddd, $J = 8.1, 4.4, 1.3$ Hz, 1H), 3.69 (bs, 1H), 3.56 – 3.52 (m, 1H), 2.76 (dt, A part of AB system, $J = 13.1, 4.0$ Hz, 1H), 2.21 (dd, B part of AB system, $J = 13.1, 8.1$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 144.2, 142.7, 128.0, 127.4, 121.9, 121.7, 57.1, 56.9, 55.5, 51.0, 36.7. HRMS (ESI) m/z: [M - HCl + H]⁺ calcd for $\text{C}_{11}\text{H}_{10}\text{Br}$: 220.9960, found: 220.9957.

(1*R*,2*S*,4*R*,9*R*)-2,9-dibromo-1,2,3,4-tetrahydro-1,4-methanonaphthalene (2ac)^{16,26}



White crystal (137 mg, 91%). Mp: 77–78 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.25 – 7.11 (m, 4H), 4.16 – 4.15 (m, 1H), 3.80 (ddd, $J = 8.0, 4.6, 1.3$ Hz, 1H), 3.76 (bs, 1H), 3.54 – 3.49 (m, 1H), 2.87 (dt, A part of AB system, $J = 13.4, 4.2$ Hz, 1H), 2.21 (dd, B part of AB system, $J = 13.4, 8.0$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.7, 143.1, 128.0, 127.5, 122.0, 121.5, 56.6, 55.7, 51.2, 45.3, 36.8.

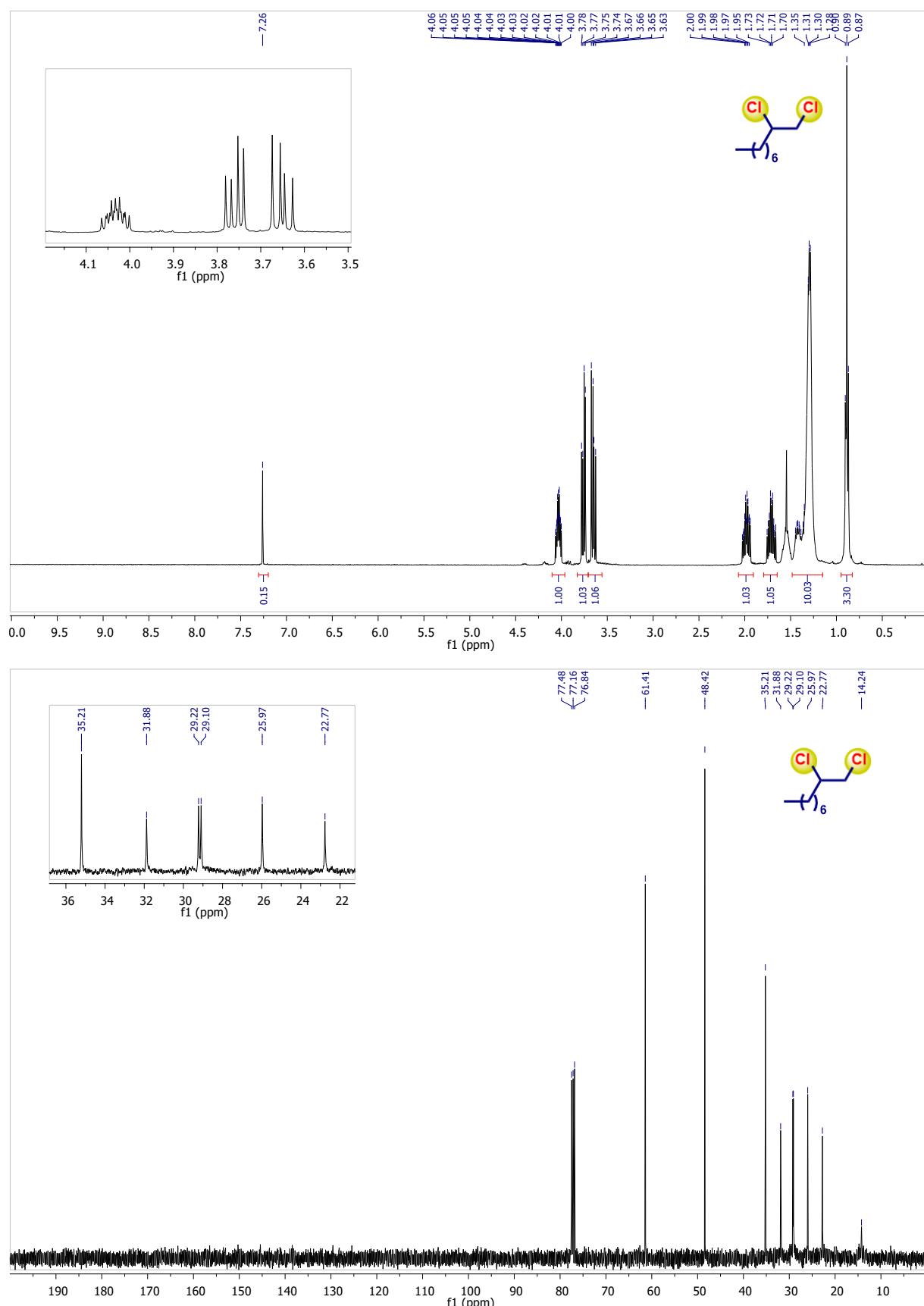
References

1. Agarwal, J., & Peddinti, R. K. (2019). Water-Mediated, Highly-Efficient and Improved Protocol for the Synthesis of Vesamicol, Its Analogues and β -Blockers through the Highly-Chemoselective Aminolysis of Epoxides. *ChemistrySelect*, 4(26), 7745-7750.
2. Goll, J. M., & Fillion, E. (2008). Tuning the reactivity of palladium carbenes derived from diphenylketene. *Organometallics*, 27(14), 3622-3625.
3. Dieter, R. K., Nice, L. E., & Velu, S. E. (1996). Oxidation of α , β -enones and alkenes with oxone and sodium halides: A convenient laboratory preparation of chlorine and bromine. *Tetrahedron letters*, 37(14), 2377-2380.
4. Li, M., Qiu, M., Ren, Y. L., Li, H., & An, W. K. (2024). Light-Induced Vicinal Dichlorination of Alkenes Using FeCl₃ as the Dichlorination Reagent. *ChemistrySelect*, 9(6), e202304488.
5. Stodulski, M., Goetzinger, A., Kohlhepp, S. V., & Gulder, T. (2014). Halocarbocyclization versus dihalogenation: substituent directed iodine (III) catalyzed halogenations. *Chemical Communications*, 50(26), 3435-3438.
6. Wedek, V., Van Lommel, R., Daniliuc, C. G., De Proft, F., & Hennecke, U. (2019). Organocatalytic, enantioselective dichlorination of unfunctionalized alkenes. *Angewandte Chemie International Edition*, 58(27), 9239-9243.
7. Kasakado, T., Fukuyama, T., Nakagawa, T., Taguchi, S., & Ryu, I. (2022). High-speed C–H chlorination of ethylene carbonate using a new photoflow setup. *Beilstein Journal of Organic Chemistry*, 18(1), 152-158.
8. Fu, N., Sauer, G. S., & Lin, S. (2017). Electrocatalytic radical dichlorination of alkenes with nucleophilic chlorine sources. *Journal of the American Chemical Society*, 139(43), 15548-15553.
9. Loginova, I. Y. Chukicheva and A. Kuchin, Reaction of styrene with chlorine dioxide, Russian Journal of General Chemistry, 2018, 88, 825-828.

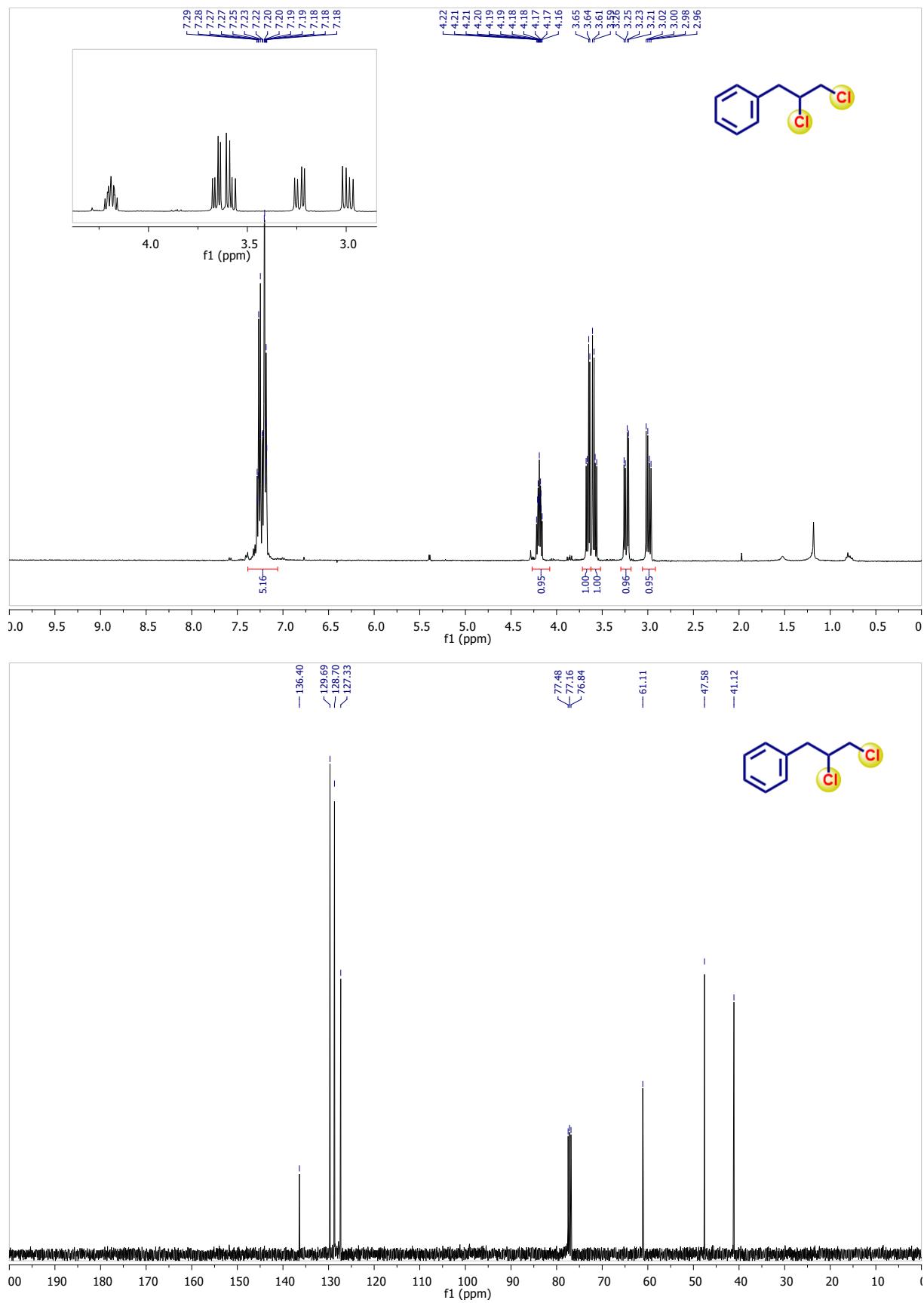
10. J. Zhang, J. Wang, Z. Qiu and Y. Wang, Highly regio-and diastereoselective halohydroxylation of olefins: a facile synthesis of vicinal halohydrins, *Tetrahedron*, 2011, 67, 6859-6867.
11. Lian, P., Long, W., Li, J., Zheng, Y., & Wan, X. (2020). Visible-Light-Induced Vicinal Dichlorination of Alkenes through LMCT Excitation of CuCl₂. *Angewandte Chemie*, 132(52), 23809-23814.
12. T. T. Nguyen, M. J. Koh, X. Shen, F. Romiti, R. R. Schrock and A. H. Hoveyda, Kinetically controlled E-selective catalytic olefin metathesis, *Science*, 2016, 352, 569-575.
13. T. Matsuda, K. Suzuki and N. Miura, Rhodium-Catalyzed Cross-Coupling of Alkenyl Halides with Arylboron Compounds, *Advanced Synthesis & Catalysis*, 2013, **355**, 3396-3400.
14. Saju, A., Griffiths, J. R., MacMillan, S. N., & Lacy, D. C. (2022). Synthesis of a bench-stable manganese (III) chloride compound: Coordination chemistry and alkene dichlorination. *Journal of the American Chemical Society*, 144(37), 16761-16766.
15. Dagalan, Z., Koçak, R., Dastan, A., & Nişancı, B. (2022). Selectfluor and TBAX (Cl, Br) Mediated Oxidative Chlorination and Bromination of Olefins. *Organic Letters*, 24(45), 8261-8264.
16. Pyriadi, T. M., & Kaleefa, H. (1984). Synthesis and attempted polymerization of N-arylmaleimides substituted with allylamino or cyclopropylamino groups at 2-position. *Journal of Polymer Science: Polymer Chemistry Edition*, 22(1), 129-134.
17. Baciocchi, E., Clementi, S., & Sebastiani, G. V. (1977). Identification of the addition products formed in the chlorination of benzofuran. *Journal of Heterocyclic Chemistry*, 14(2), 359-360.
18. Zheng, T., Xu, J., Cheng, S., Ye, J., Ma, S., & Tong, R. (2023). Green Halogenation of Indoles with Oxone–Halide. *The Journal of Organic Chemistry*, 88(16), 11497-11503.
19. Kuriyama, M., Hamaguchi, N., Yano, G., Tsukuda, K., Sato, K., & Onomura, O. (2016). Deuterodechlorination of aryl/heteroaryl chlorides catalyzed by a palladium/unsymmetrical NHC system. *The Journal of Organic Chemistry*, 81(19), 8934-8946.
20. Kunz, T., & Knochel, P. (2011). Selective Multiple Magnesiations of the Thieno [3, 2-b] thiophene Scaffold. *Chemistry—A European Journal*, 17(3), 866-872.
21. KIMURA, M., TOHMA, M., & TOMITA, T. (1973). Metal Ion Catalyzed Oxidation of Steroids. III. Reactions of Cholesterol with Ferrous Ions-and Titanous Ions-Hydrogen Peroxide Systems in Acetonitrile. *Chemical and Pharmaceutical Bulletin*, 21(11), 2521-2528.
22. Moreno-Dorado, F. J., Guerra, F. M., Manzano, F. L., Aladro, F. J., Jorge, Z. D., & Massanet, G. M. (2003). CeCl₃/NaClO: a safe and efficient reagent for the allylic chlorination of terminal olefins. *Tetrahedron letters*, 44(35), 6691-6693.
23. Izmost' ev, E. S., Lezina, O. M., Grebyonkina, O. N., Patov, S. A., Rubtsova, S. A., & Kutchin, A. V. (2014). Oxidative transformations of diisobornyl disulfide. *Russian Chemical Bulletin*, 63, 2067-2073.

24. Denton, R. M., Tang, X., & Przeslak, A. (2010). Catalysis of phosphorus (V)-mediated transformations: dichlorination reactions of epoxides under Appel conditions. *Organic Letters*, 12(20), 4678-4681.
25. Dastan, A., Demir, U., & Balci, M. (1994). Functionalization of benzonorbornadiene: hightemperaturebromination and electrochemical oxidation. *The Journal of Organic Chemistry*, 59(22), v6534-6538.

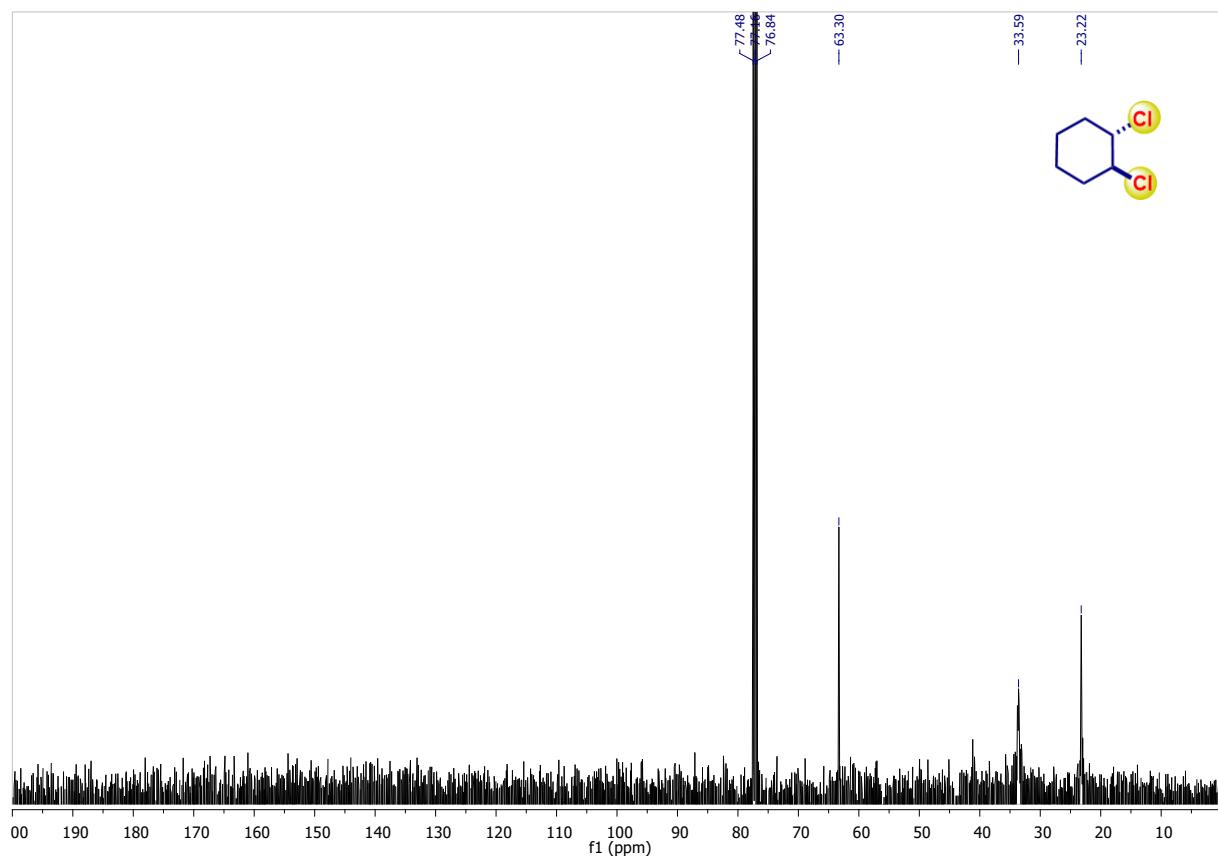
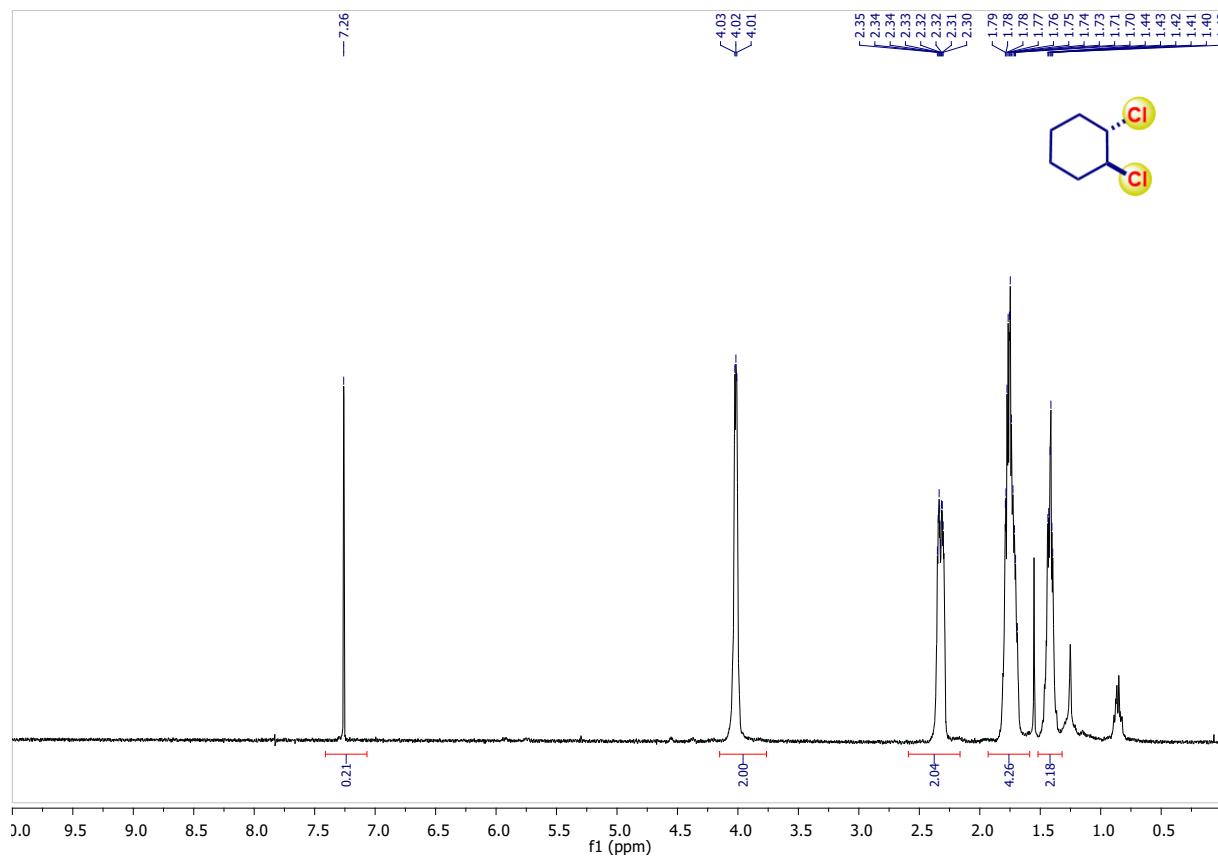
¹H NMR, ¹³C NMR, and HRMS Spectra



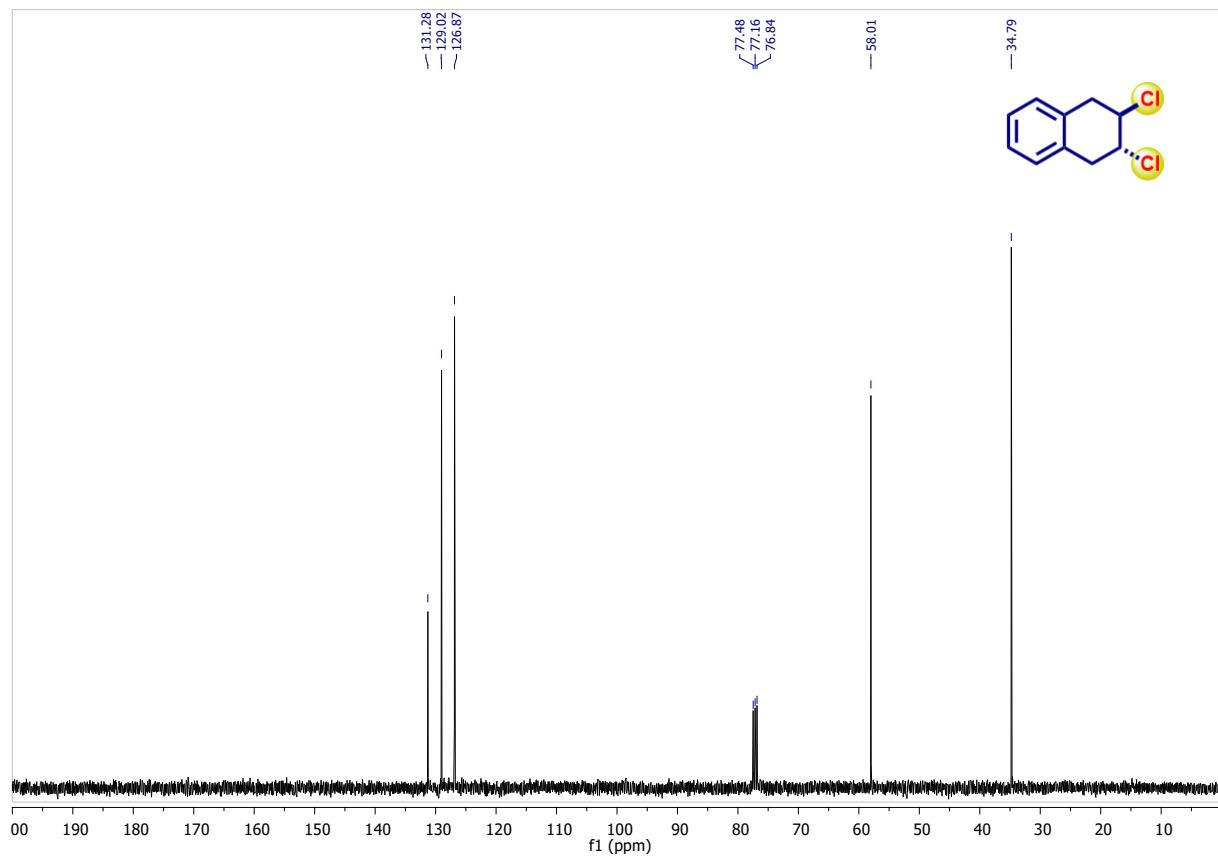
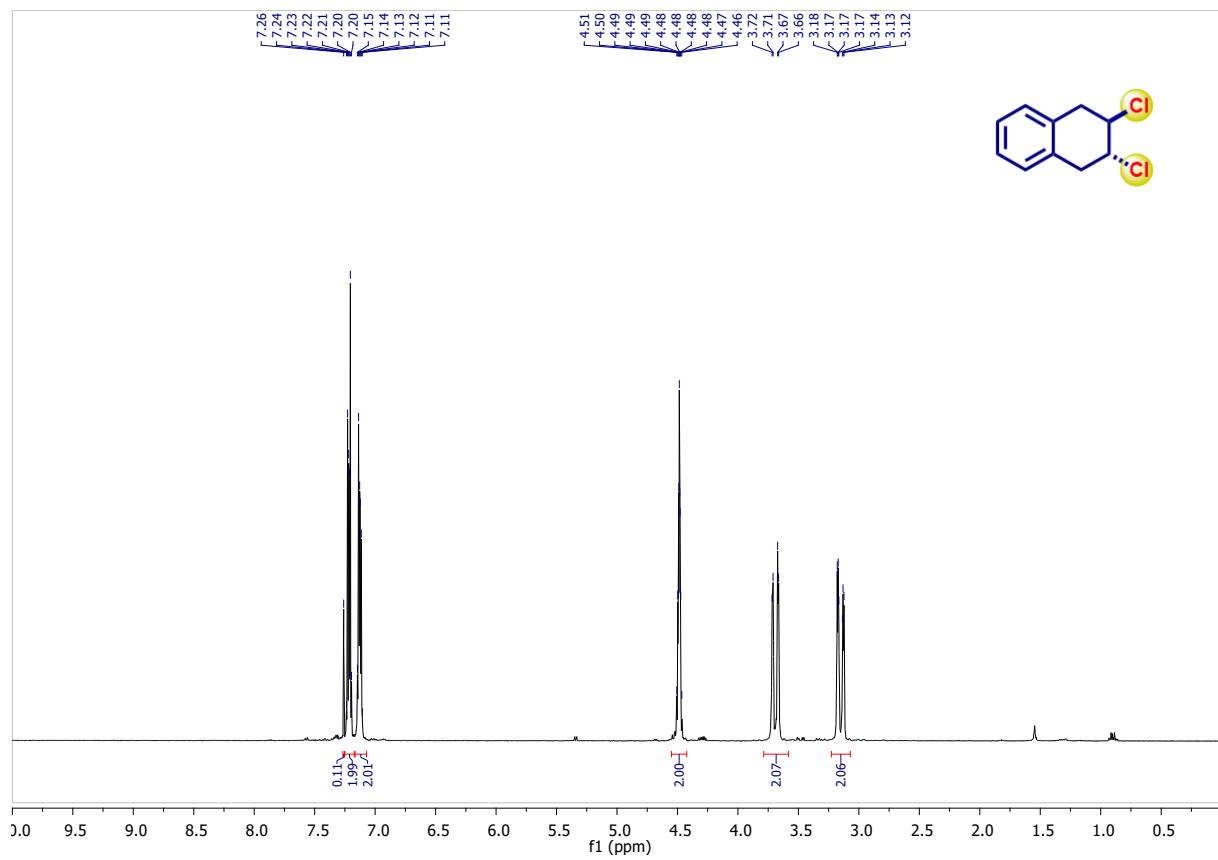
400 MHz ¹H-NMR (top) and 101 MHz ¹³C-NMR (bottom) spectra of **2a** (CDCl_3)



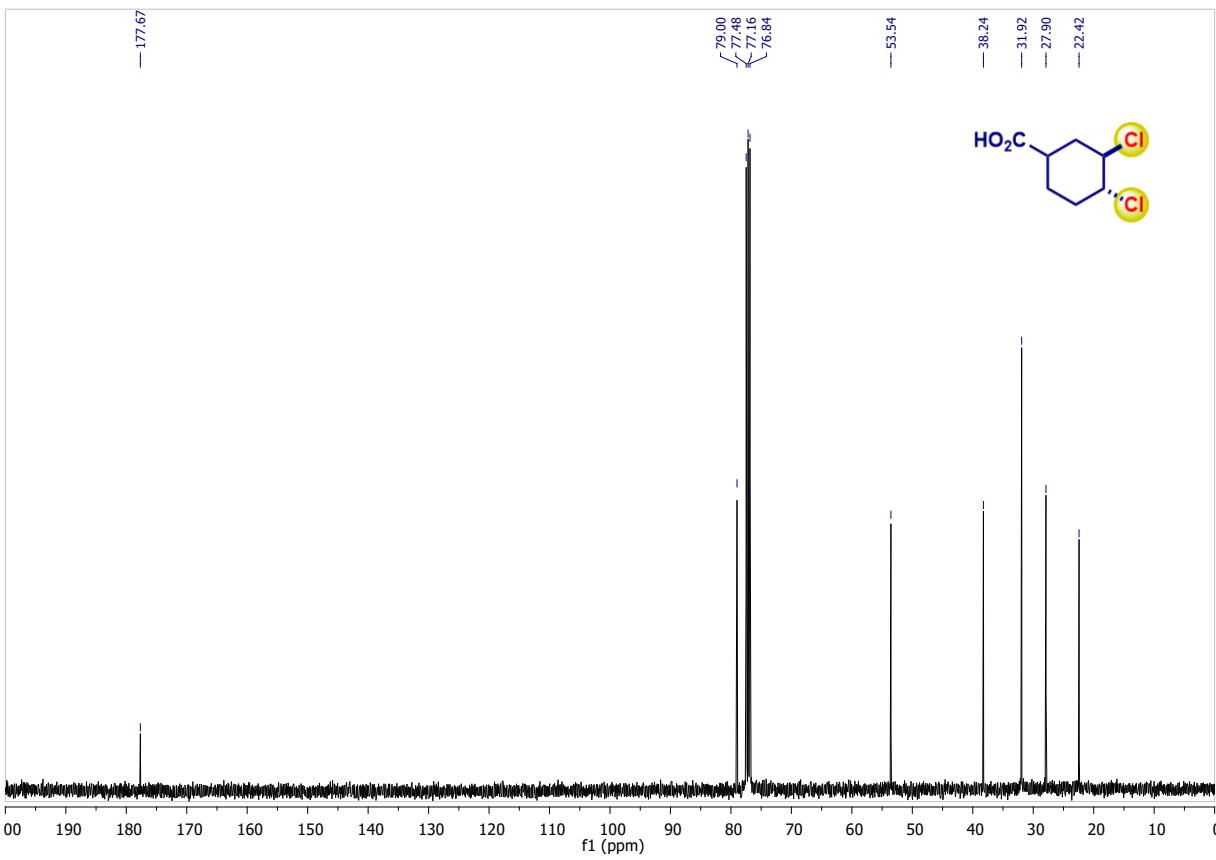
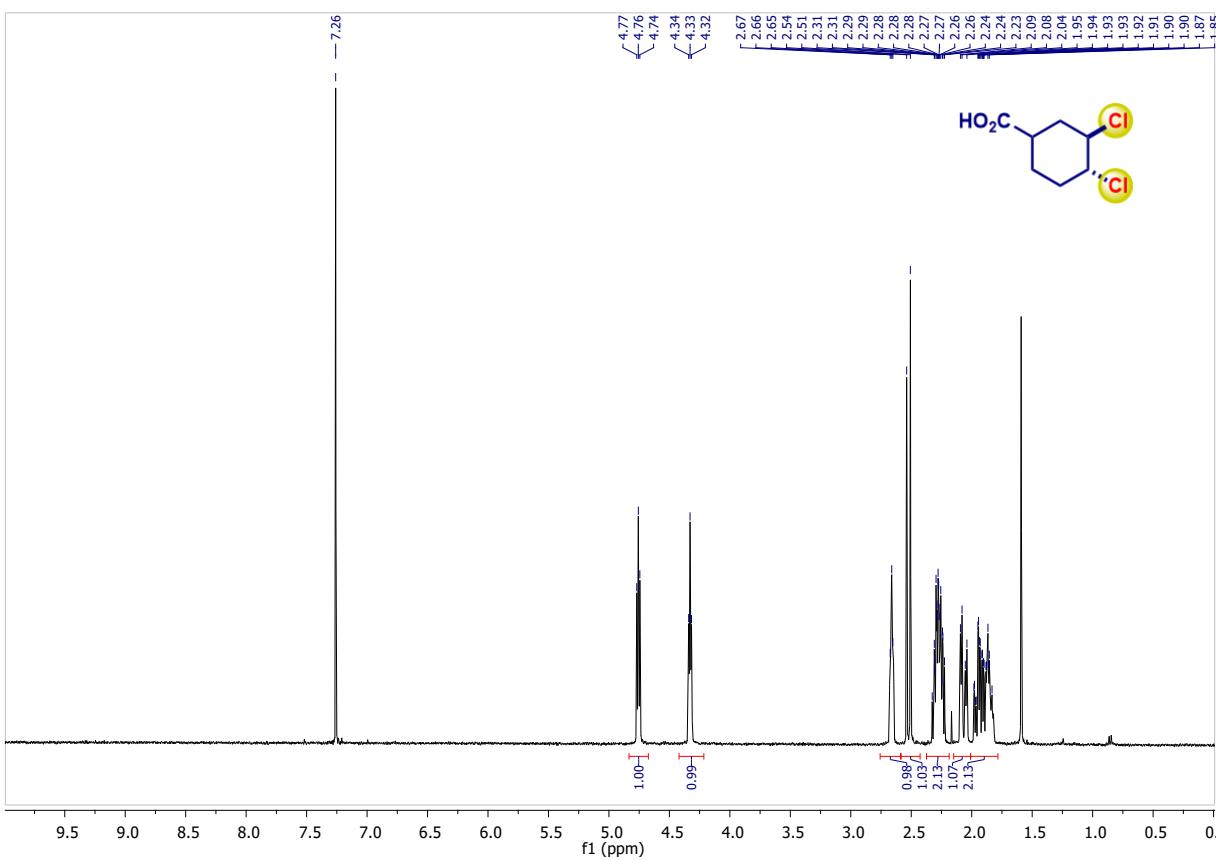
400 MHz ^1H -NMR (top) and 101 MHz ^{13}C -NMR (bottom) spectra of **2b** (CDCl_3)



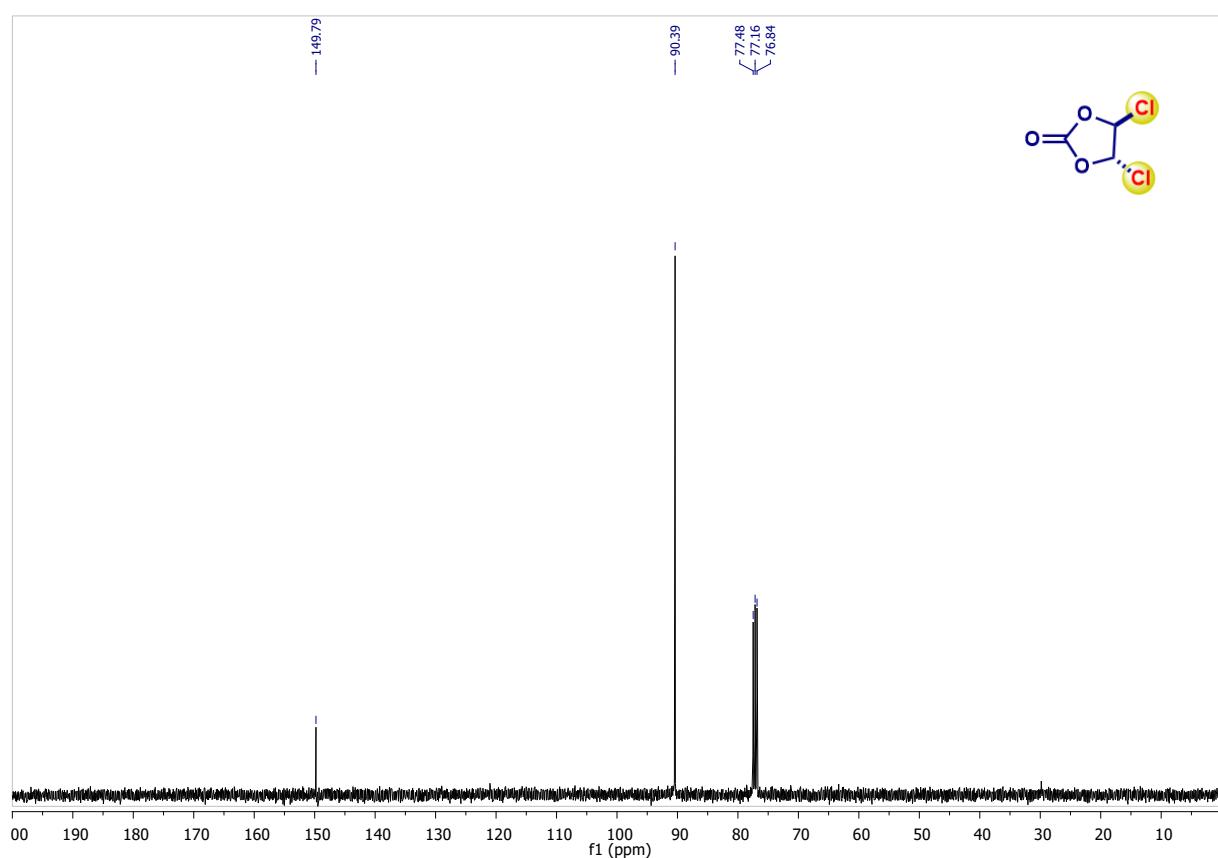
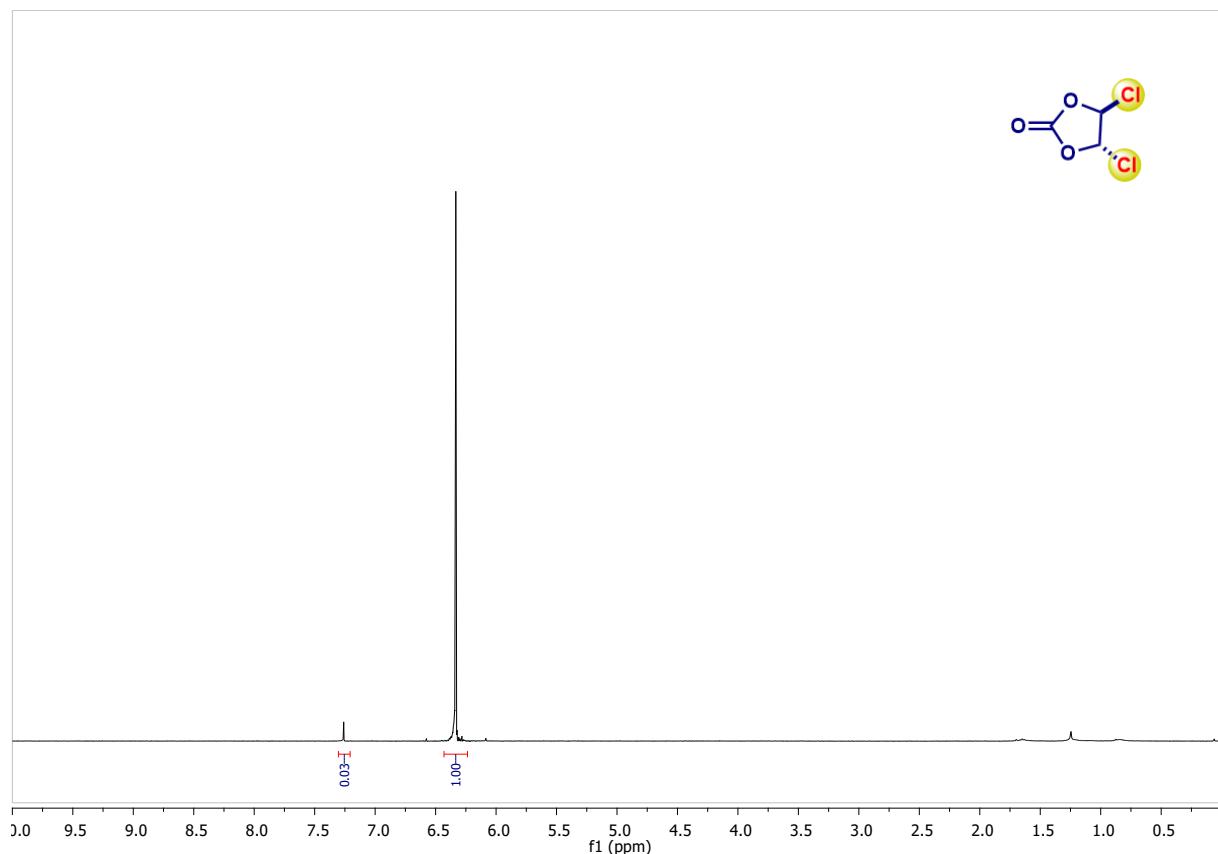
400 MHz ^1H -NMR (top) and 101 MHz ^{13}C -NMR (bottom) spectra of **2c** (CDCl_3)



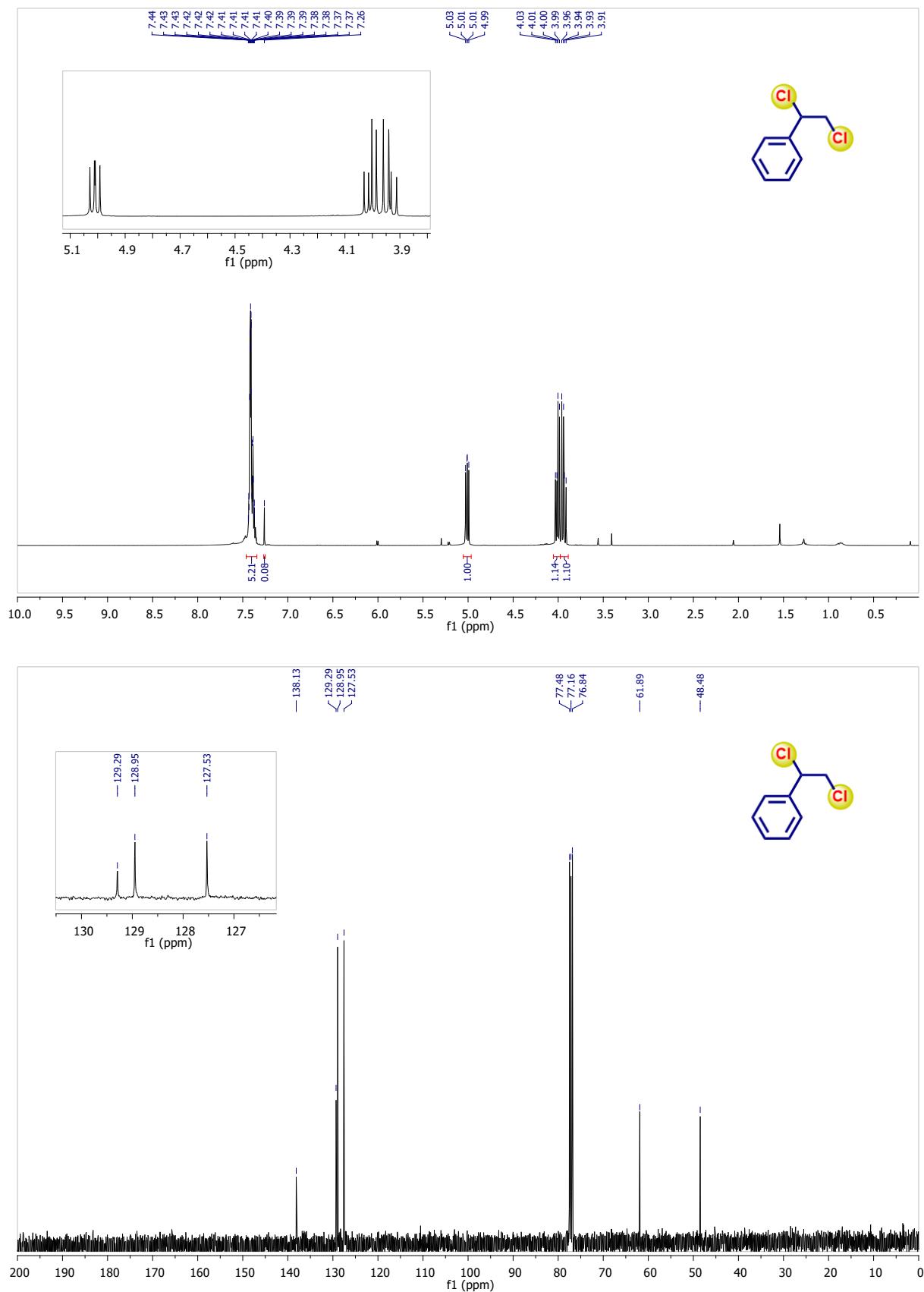
400 MHz ^1H -NMR (top) and 101 MHz ^{13}C -NMR (bottom) spectra of **2d** (CDCl_3)



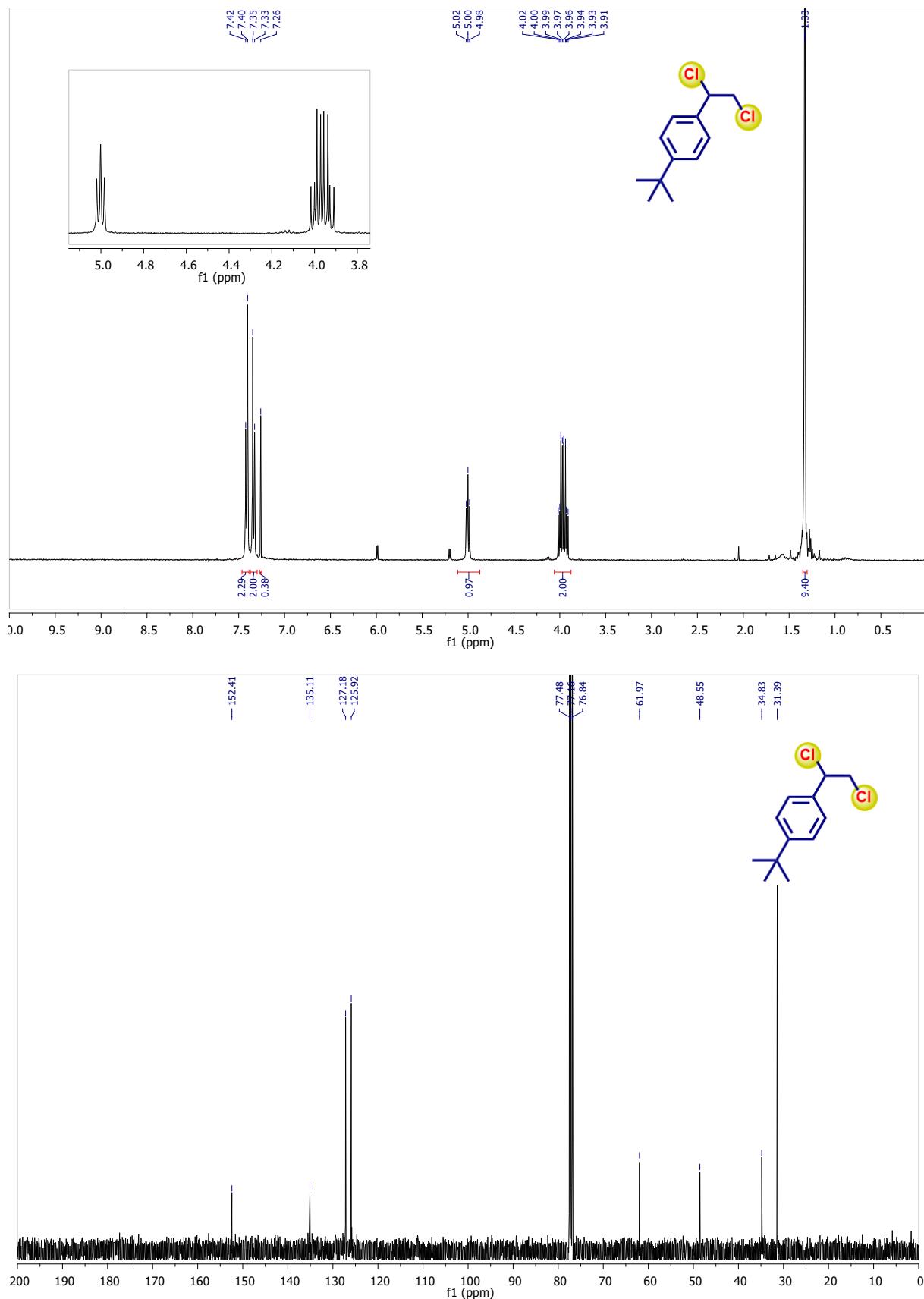
400 MHz ^1H -NMR (top) and 101 MHz ^{13}C -NMR (bottom) spectra of **2e** (CDCl_3)

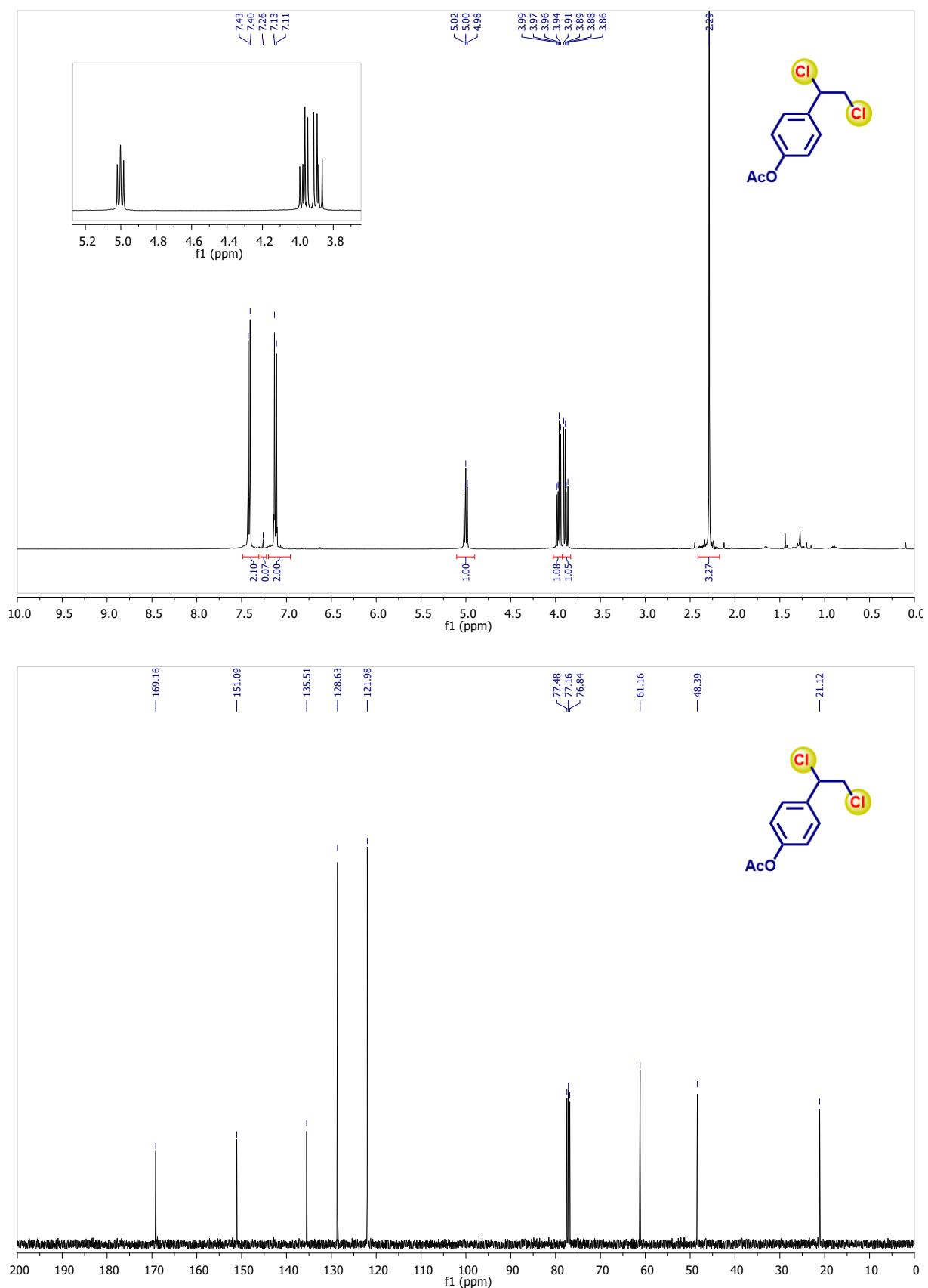


400 MHz ¹H-NMR (top) and 101 MHz ¹³C-NMR (bottom) spectra of **2f** (CDCl₃)

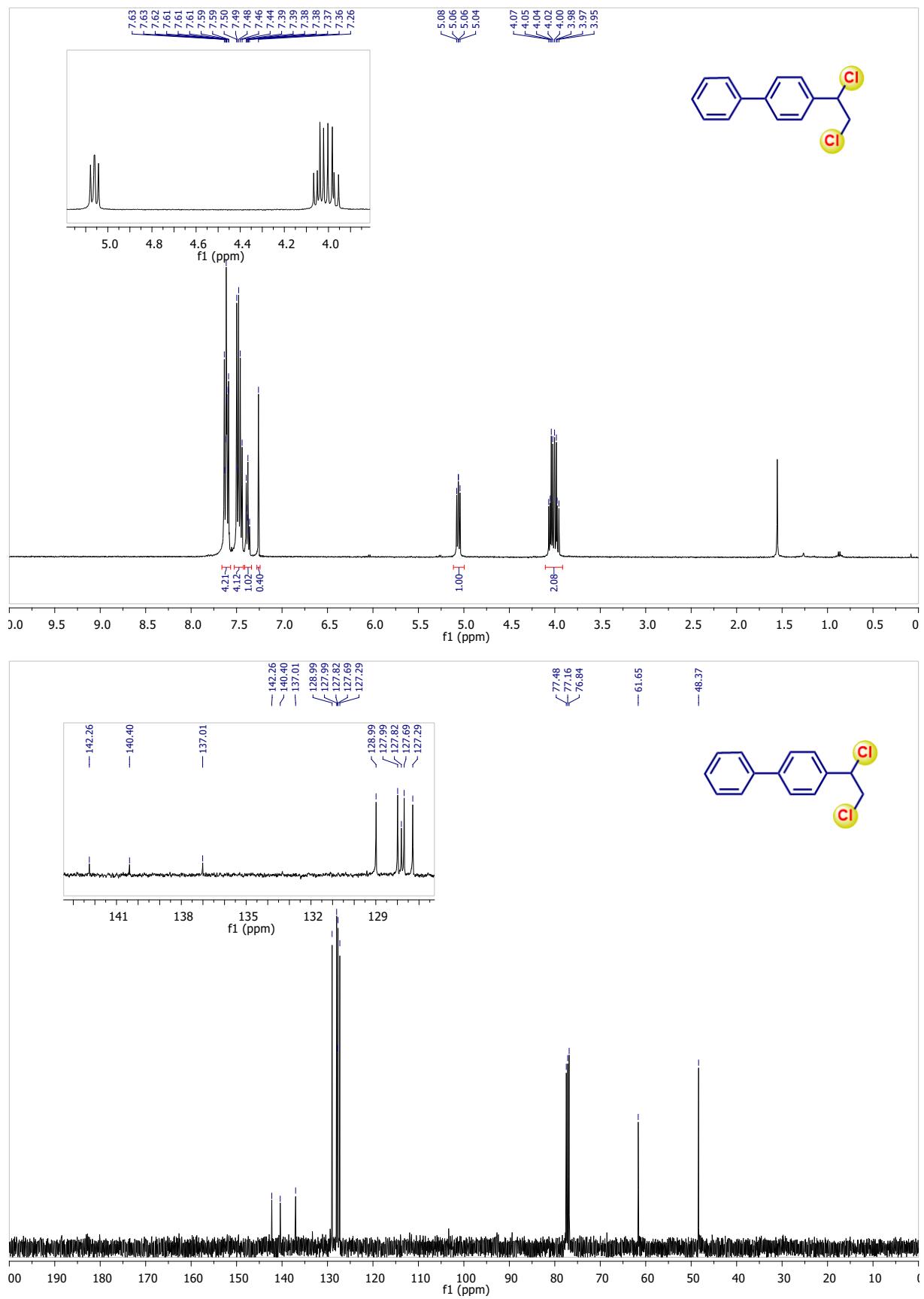


400 MHz ¹H-NMR (top) and 101 MHz ¹³C-NMR (bottom) spectra of **2g** (CDCl₃)

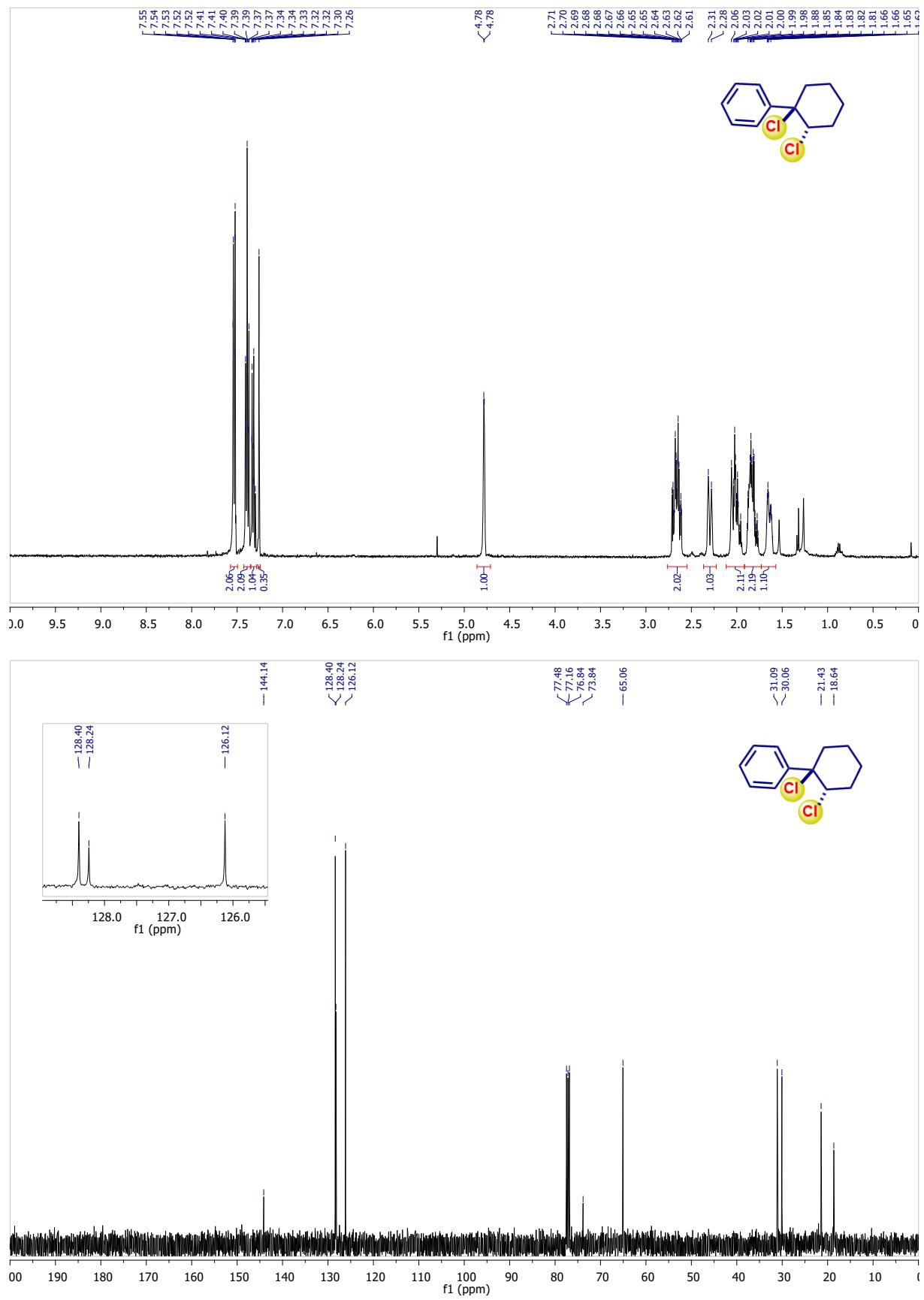




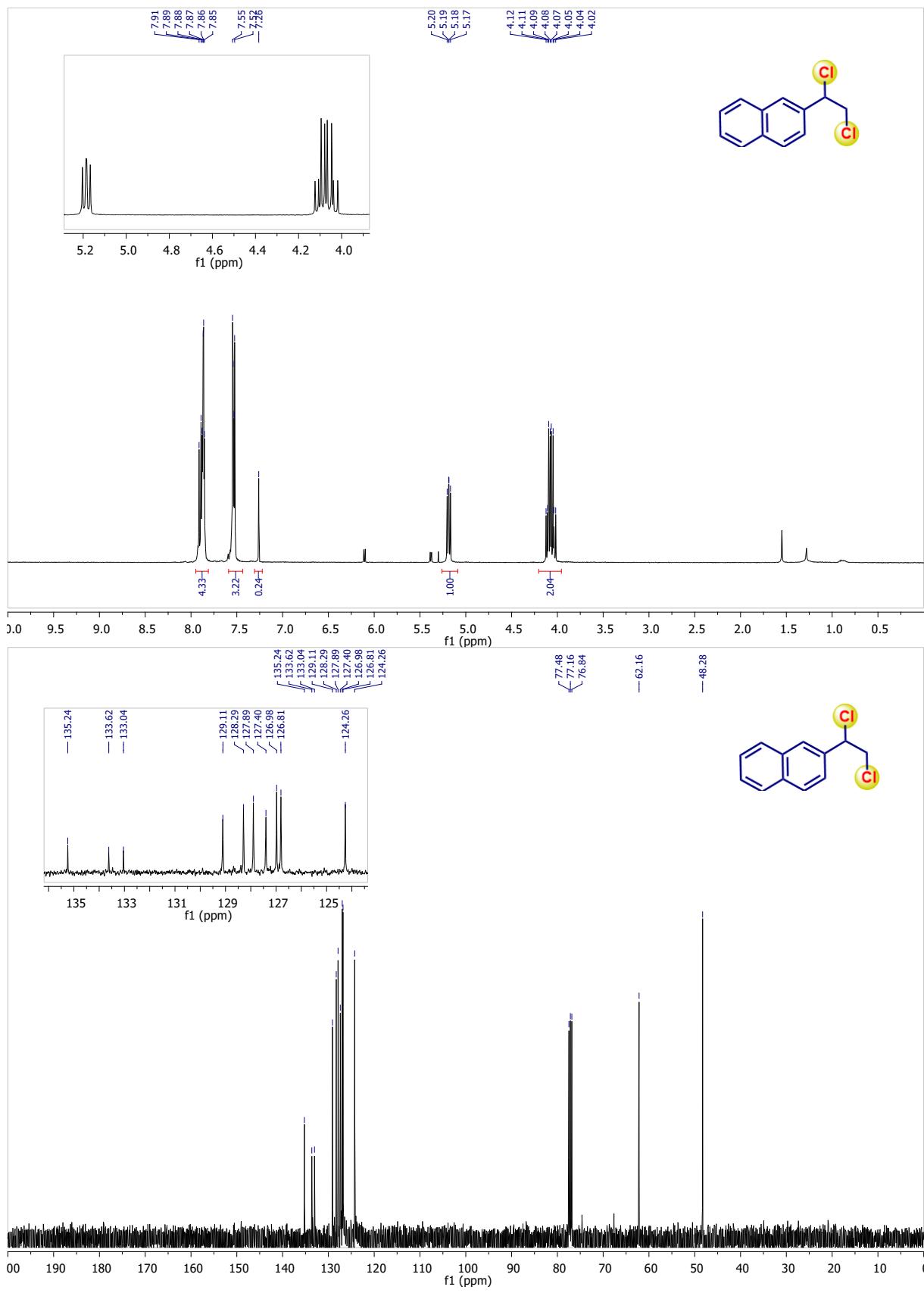
400 MHz ^1H -NMR (top) and 101 MHz ^{13}C -NMR (bottom) spectra of **2i** (CDCl_3)



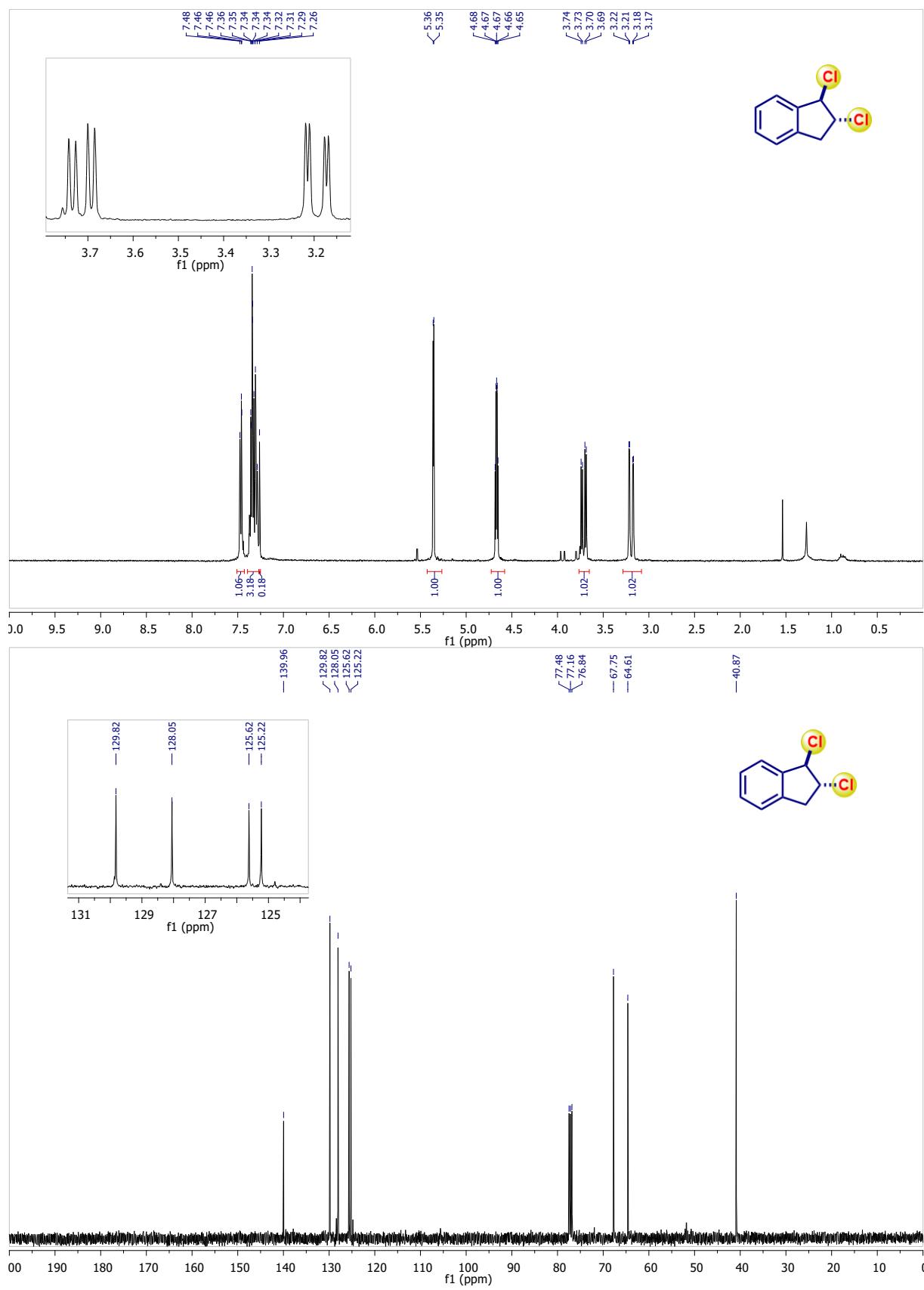
400 MHz ¹H-NMR (top) and 101 MHz ¹³C-NMR (bottom) spectra of **2j** (CDCl_3)



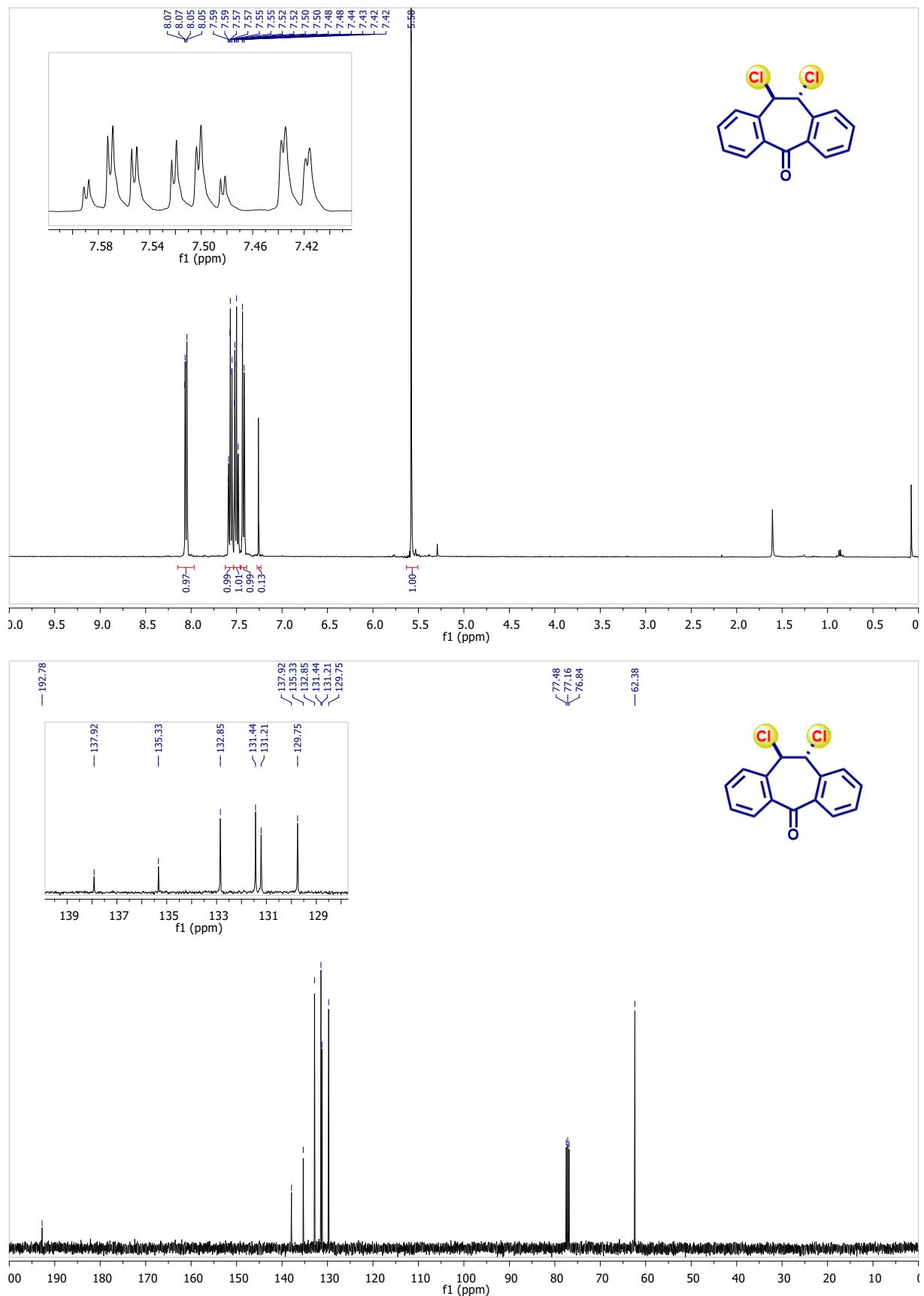
400 MHz ^1H -NMR (top) and 101 MHz ^{13}C -NMR (bottom) spectra of **2k** (CDCl₃)



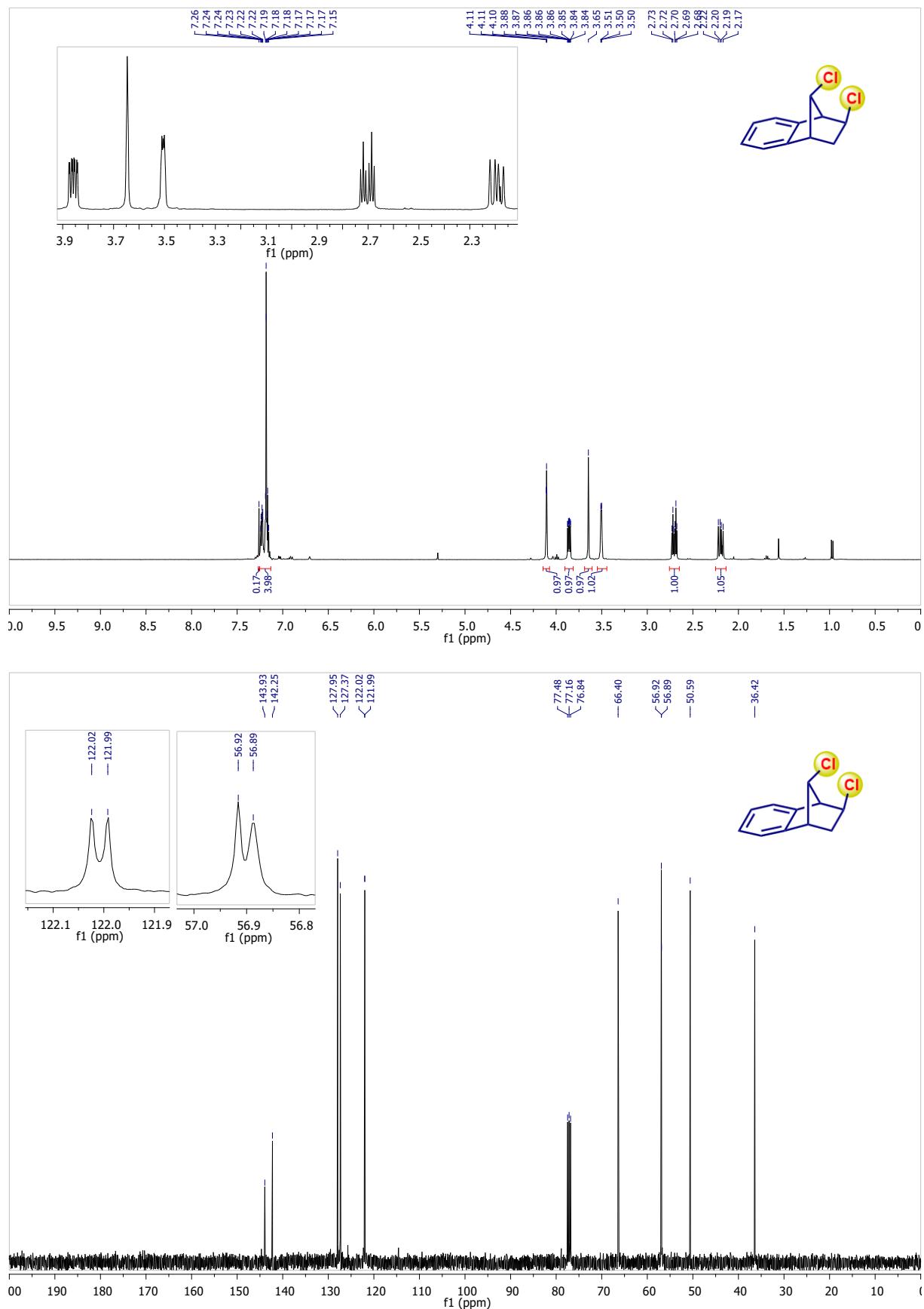
400 MHz ^1H -NMR (top) and 101 MHz ^{13}C -NMR (bottom) spectra of **2l** (CDCl_3)



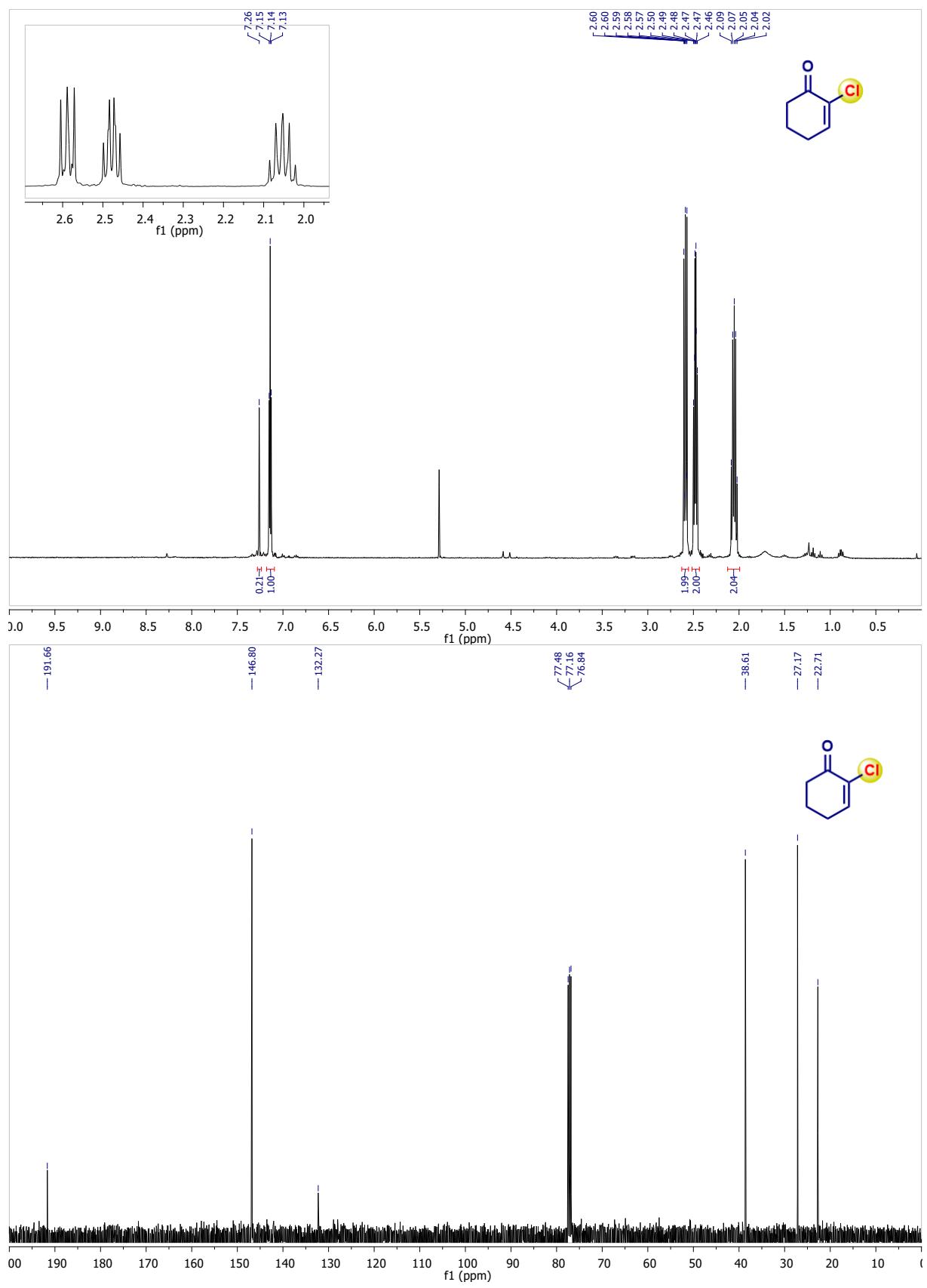
400 MHz ^1H -NMR (top) and 101 MHz ^{13}C -NMR (bottom) spectra of **2m** (CDCl_3)



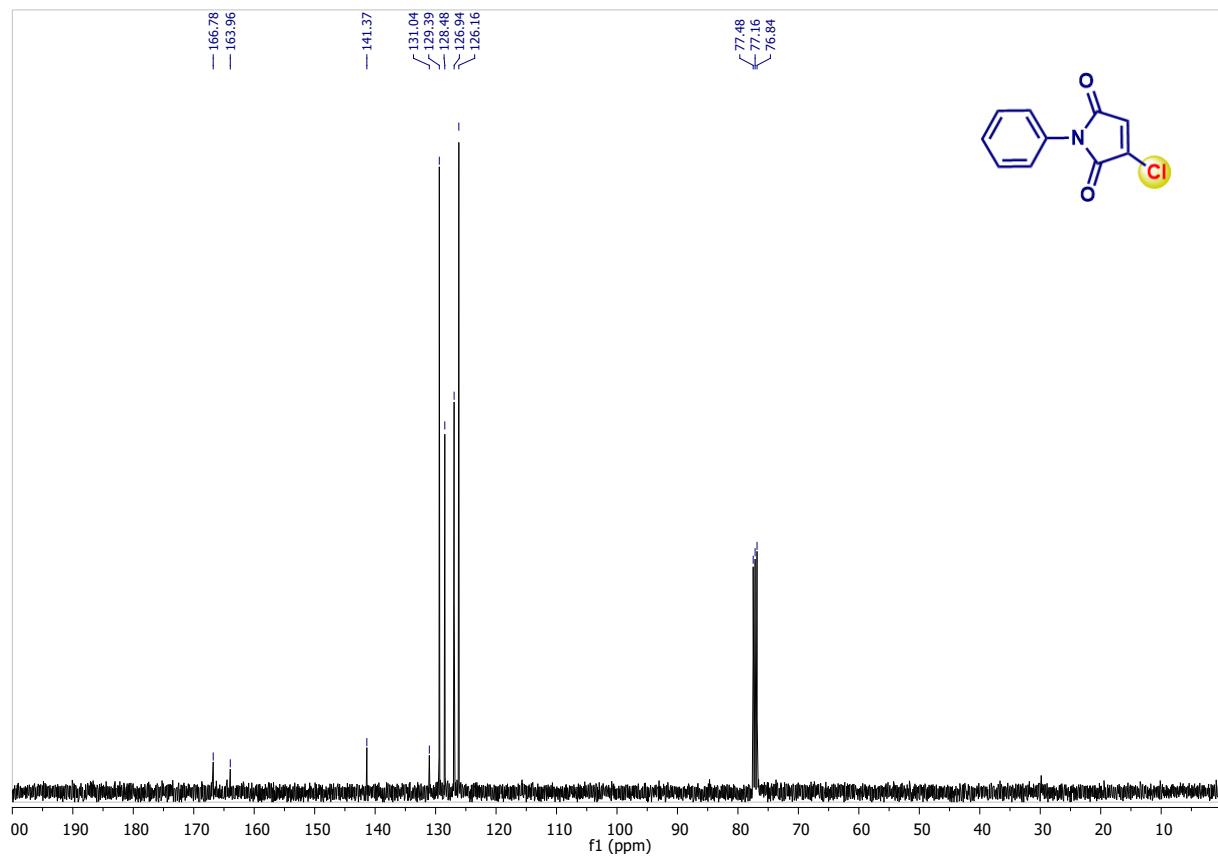
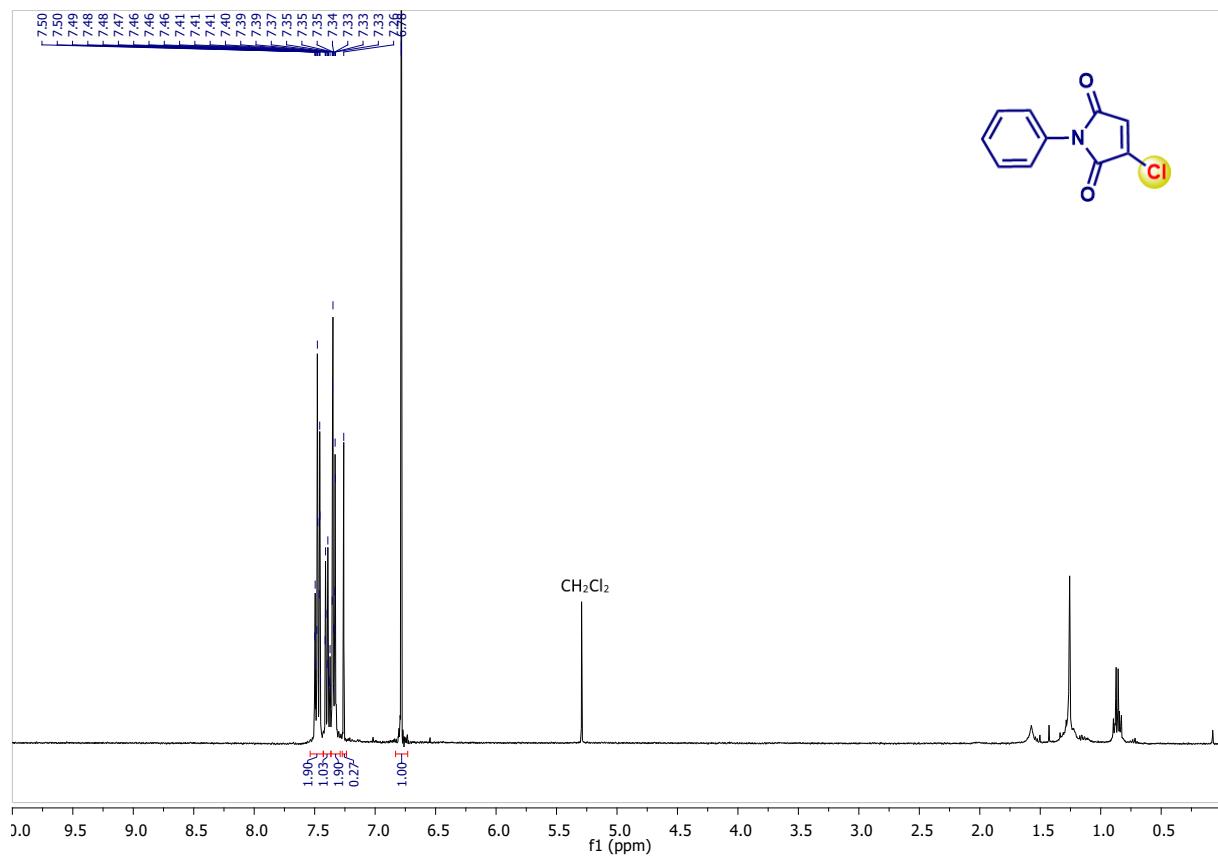
400 MHz ¹H-NMR (top) and 101 MHz ¹³C-NMR (bottom) spectra of **2n** (CDCl_3)



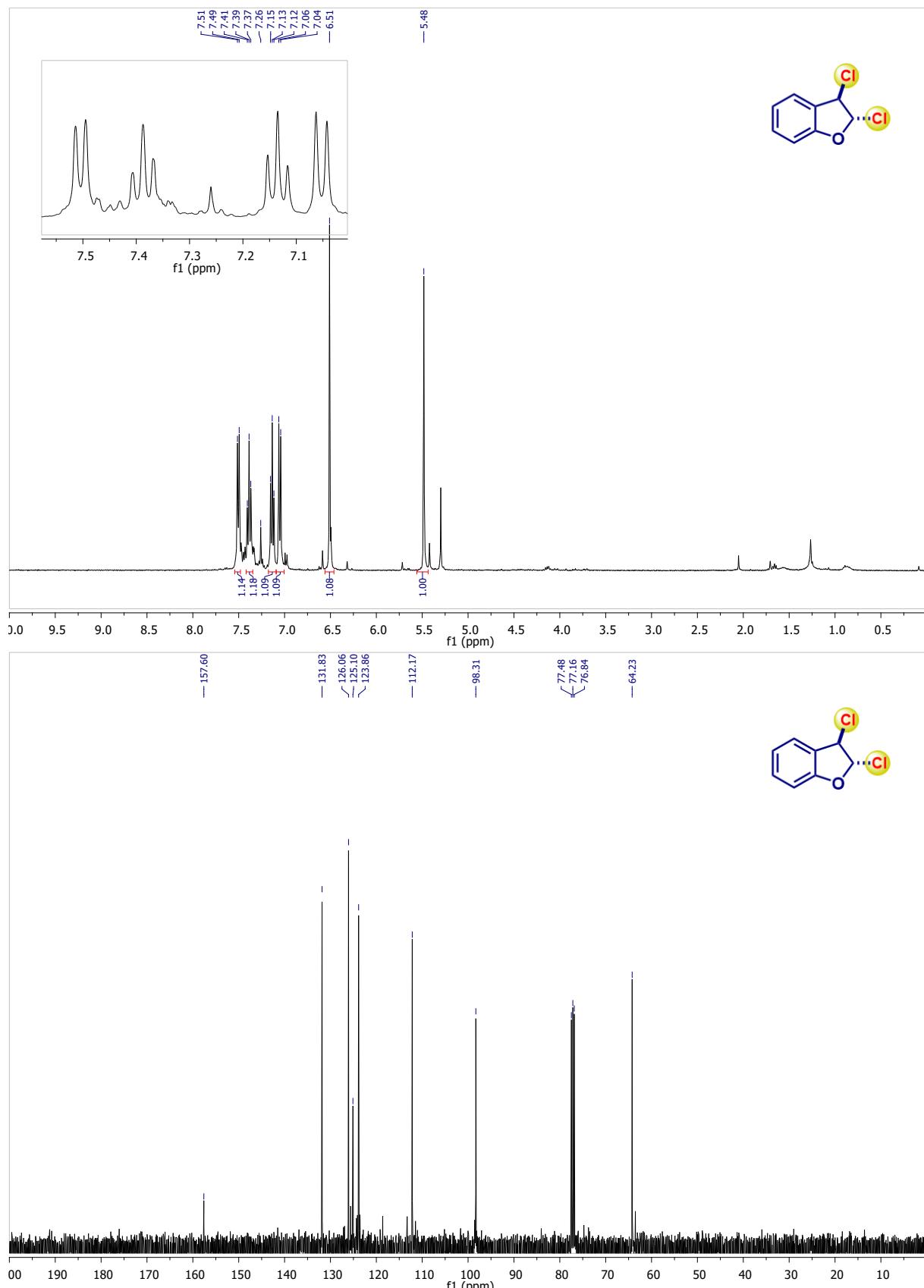
400 MHz ^1H -NMR (top) and 101 MHz ^{13}C -NMR (bottom) spectra of **2o** (CDCl_3)



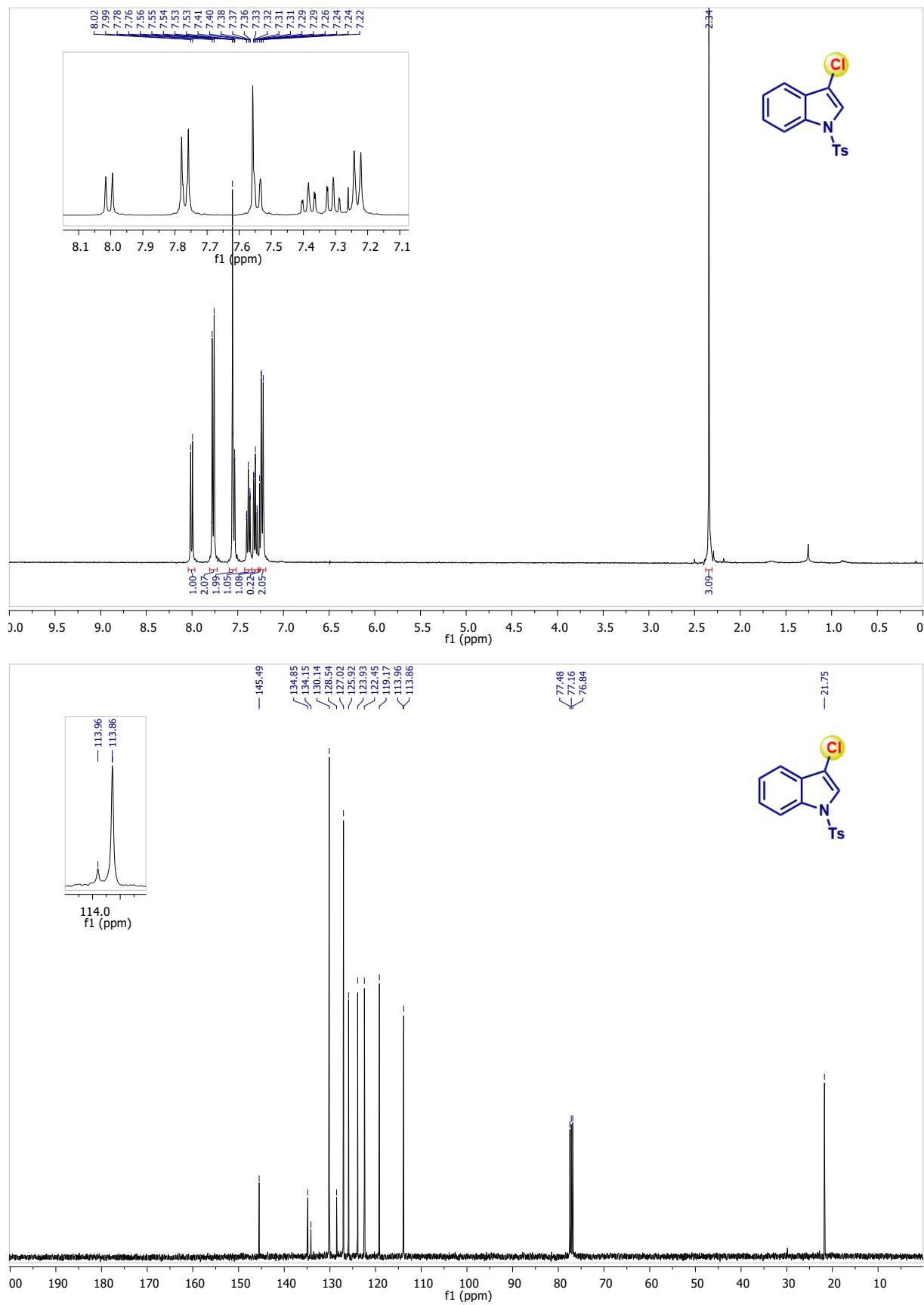
400 MHz ^1H -NMR (top) and 101 MHz ^{13}C -NMR (bottom) spectra of **2p** (CDCl_3)



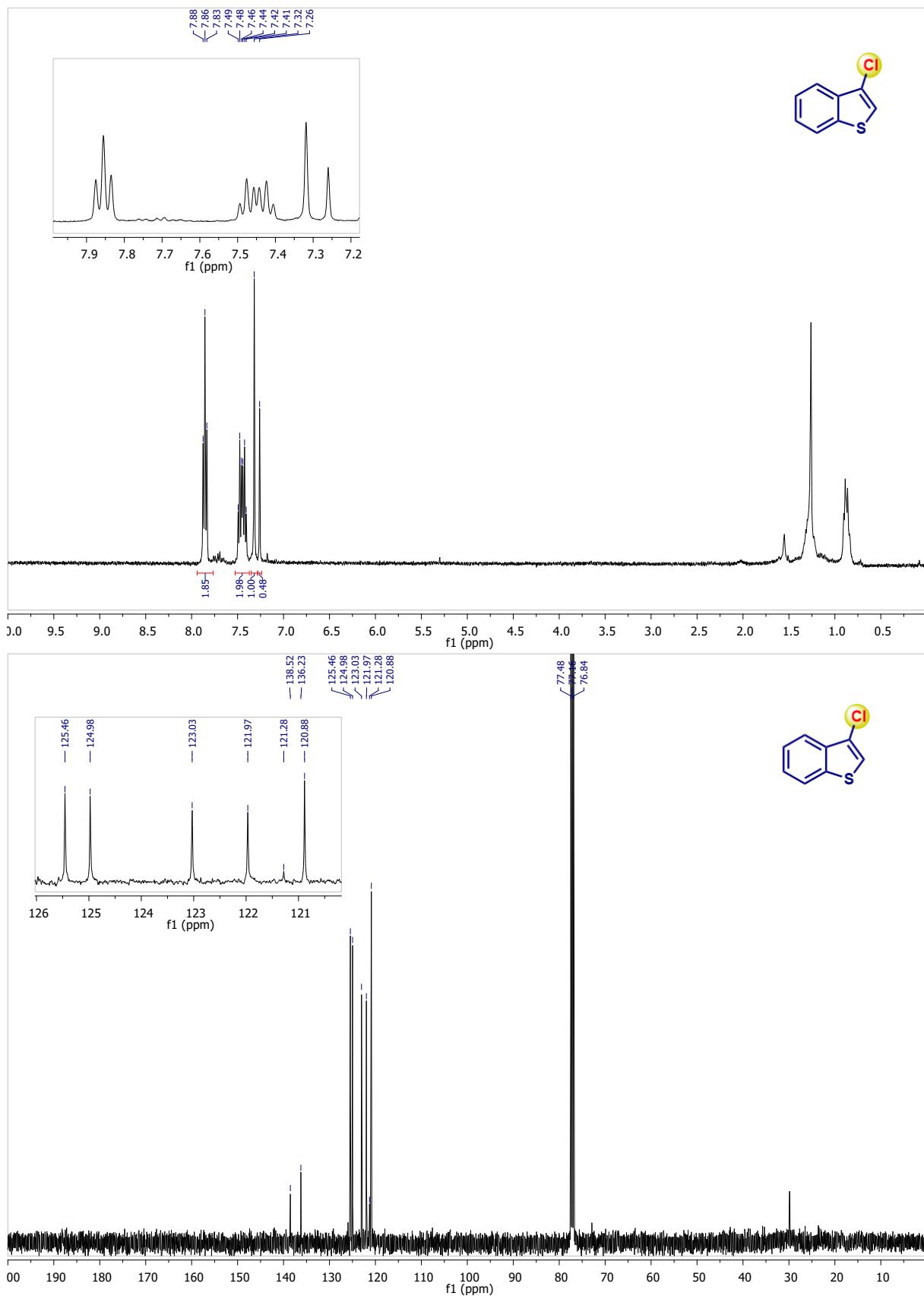
400 MHz ^1H -NMR (top) and 101 MHz ^{13}C -NMR (bottom) spectra of **2q** (CDCl_3)



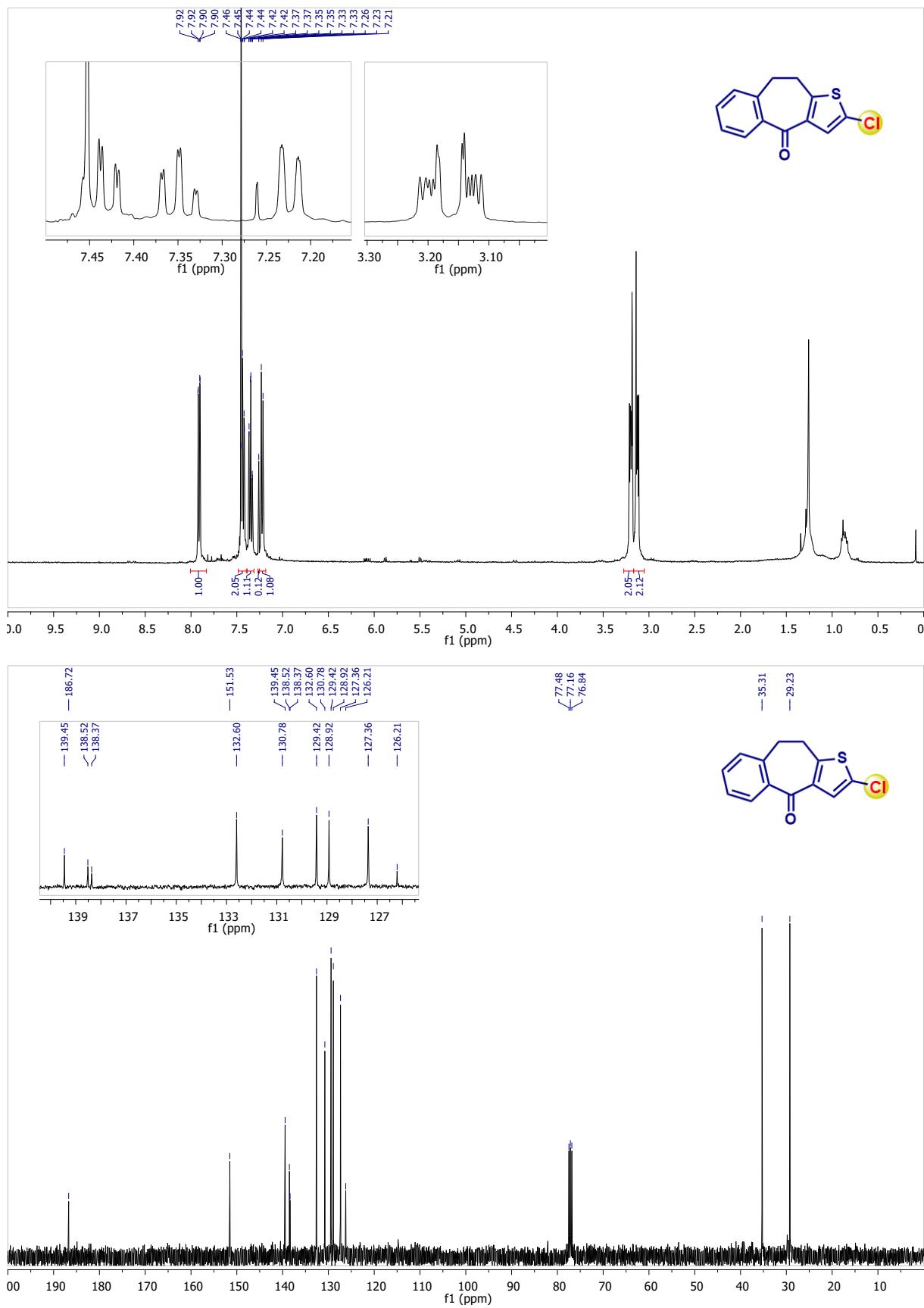
400 MHz ^1H -NMR (top) and 101 MHz ^{13}C -NMR (bottom) spectra of **2r** (CDCl_3)



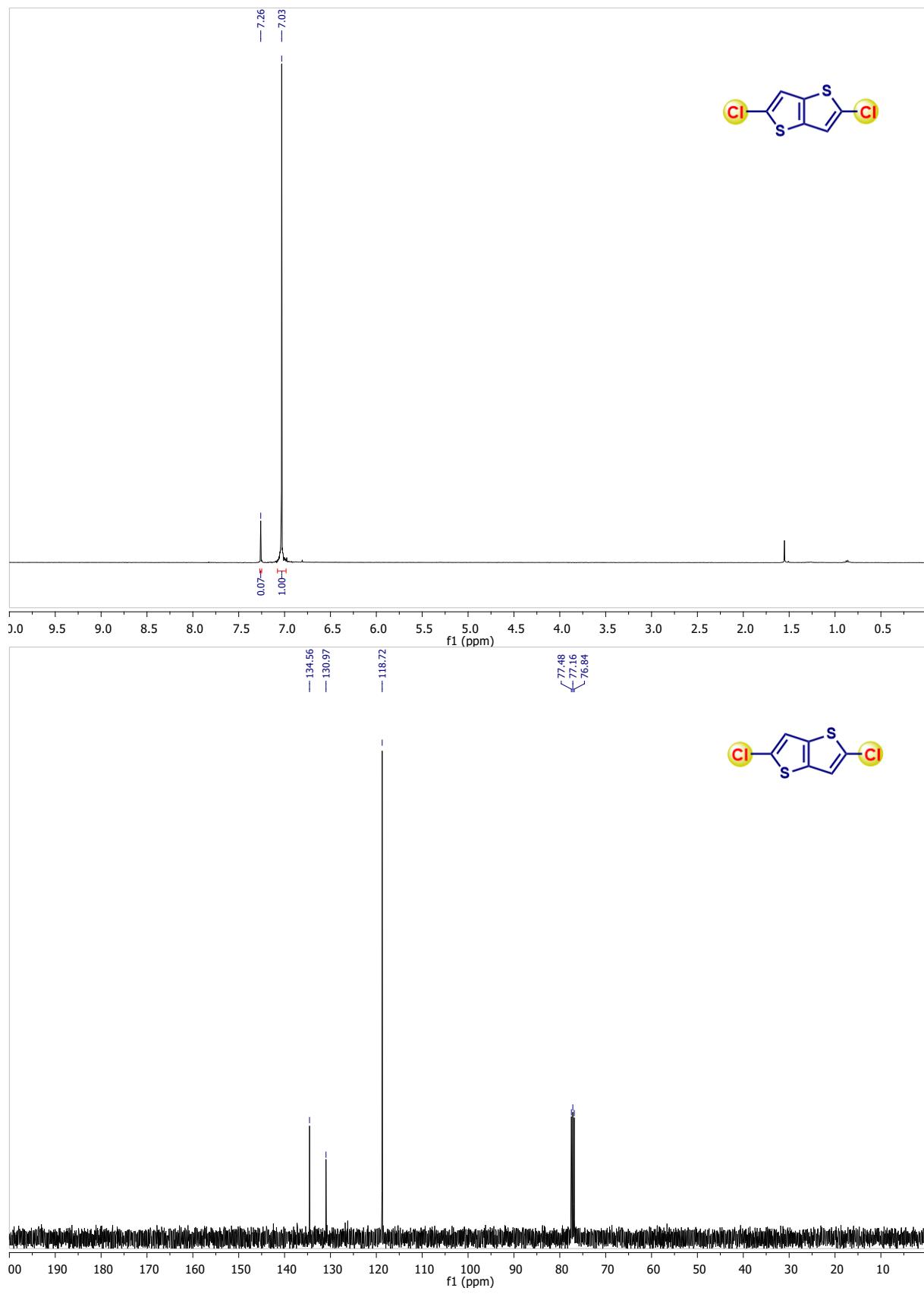
400 MHz ^1H -NMR (top) and 101 MHz ^{13}C -NMR (bottom) spectra of **2s** (CDCl_3)



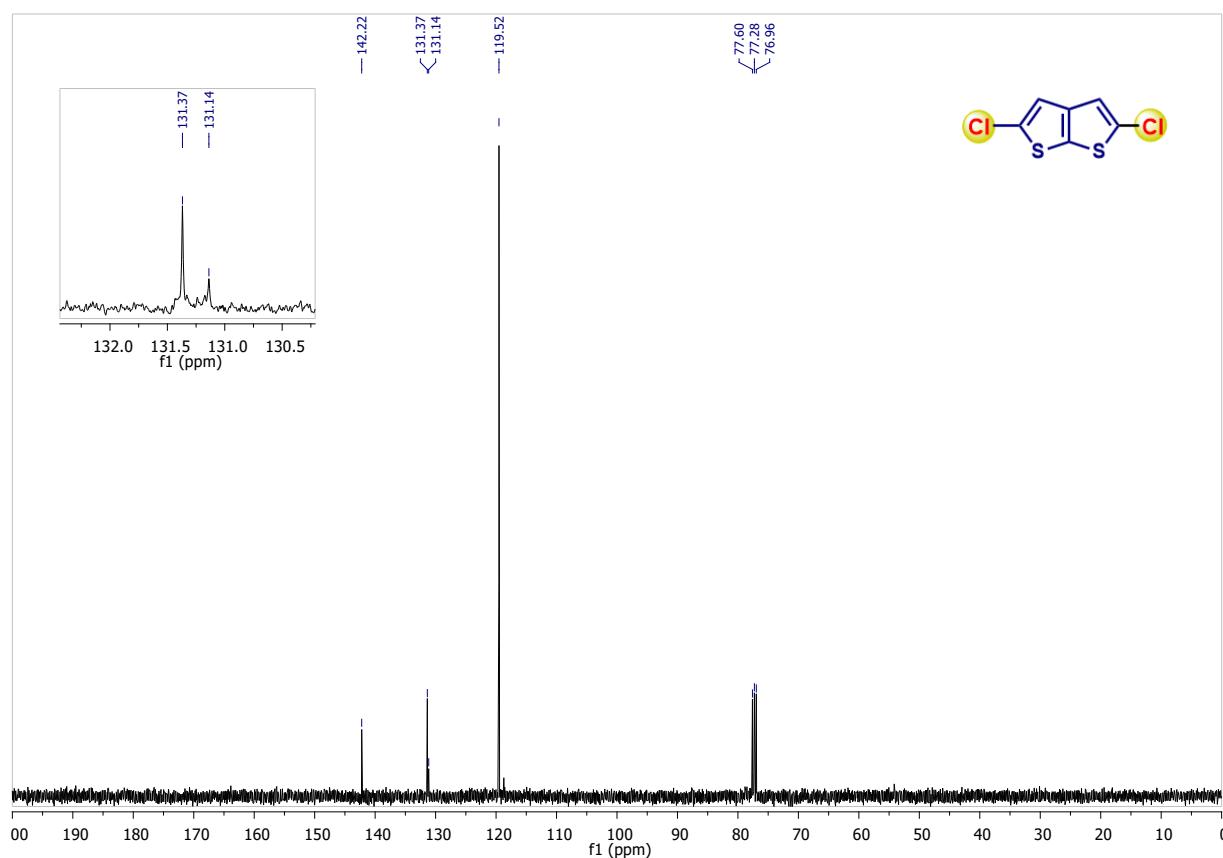
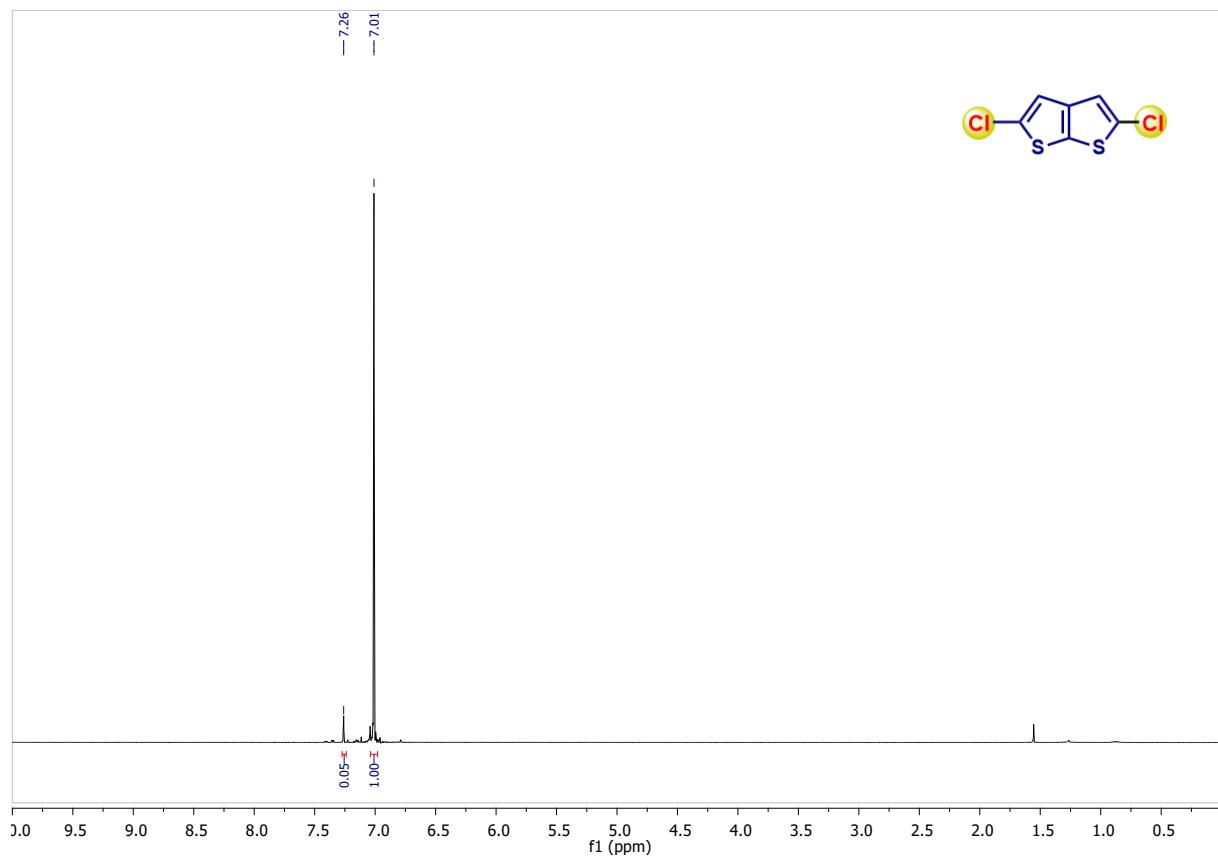
400 MHz ^1H -NMR (top) and 101 MHz ^{13}C -NMR (bottom) spectra of **2t** (CDCl_3)



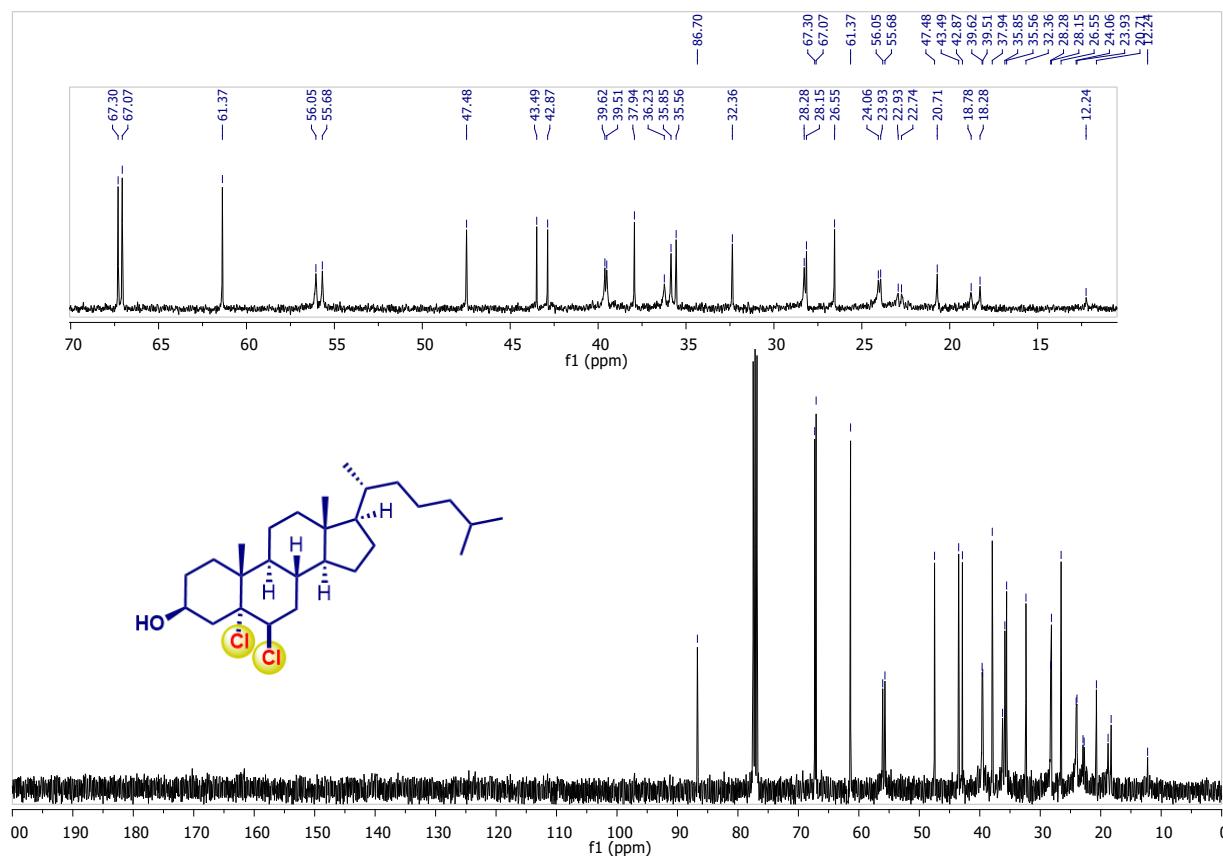
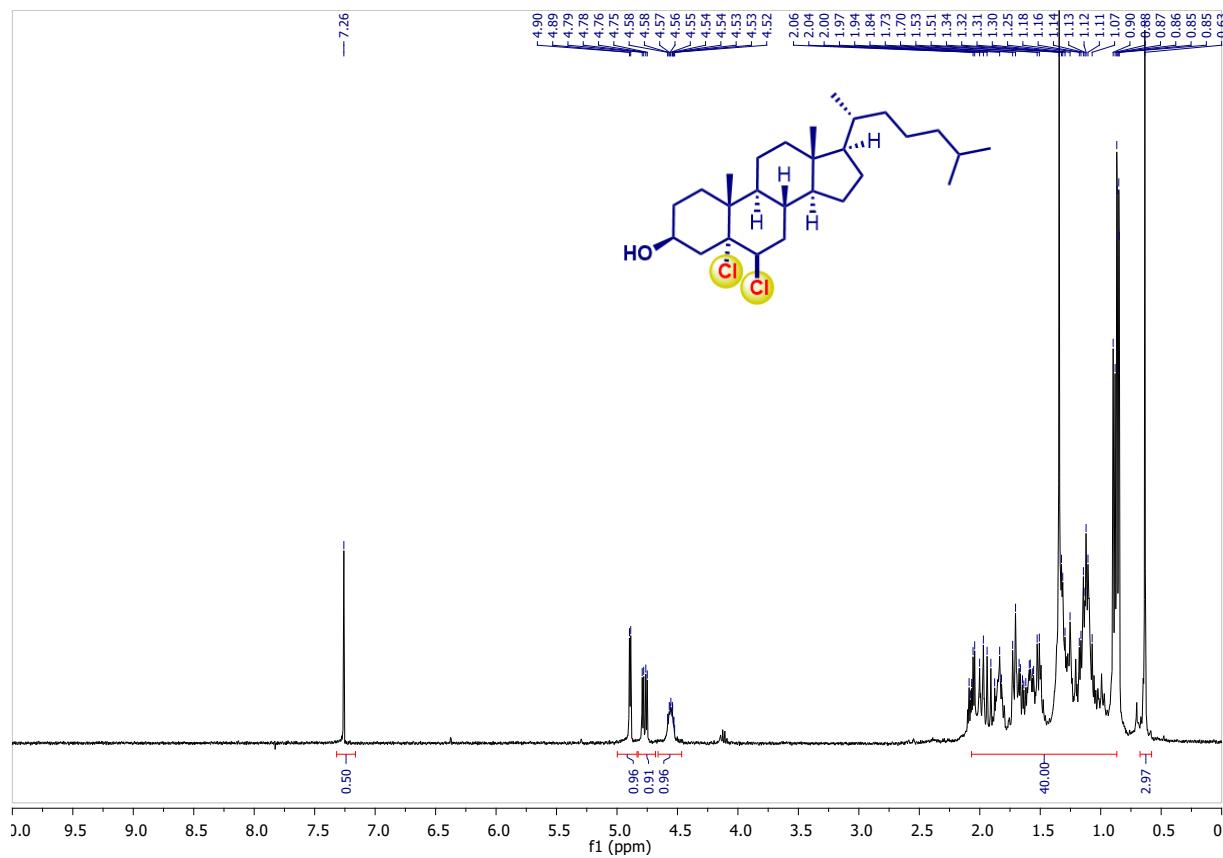
400 MHz ^1H -NMR (top) and 101 MHz ^{13}C -NMR (bottom) spectra of **2u** (CDCl_3)



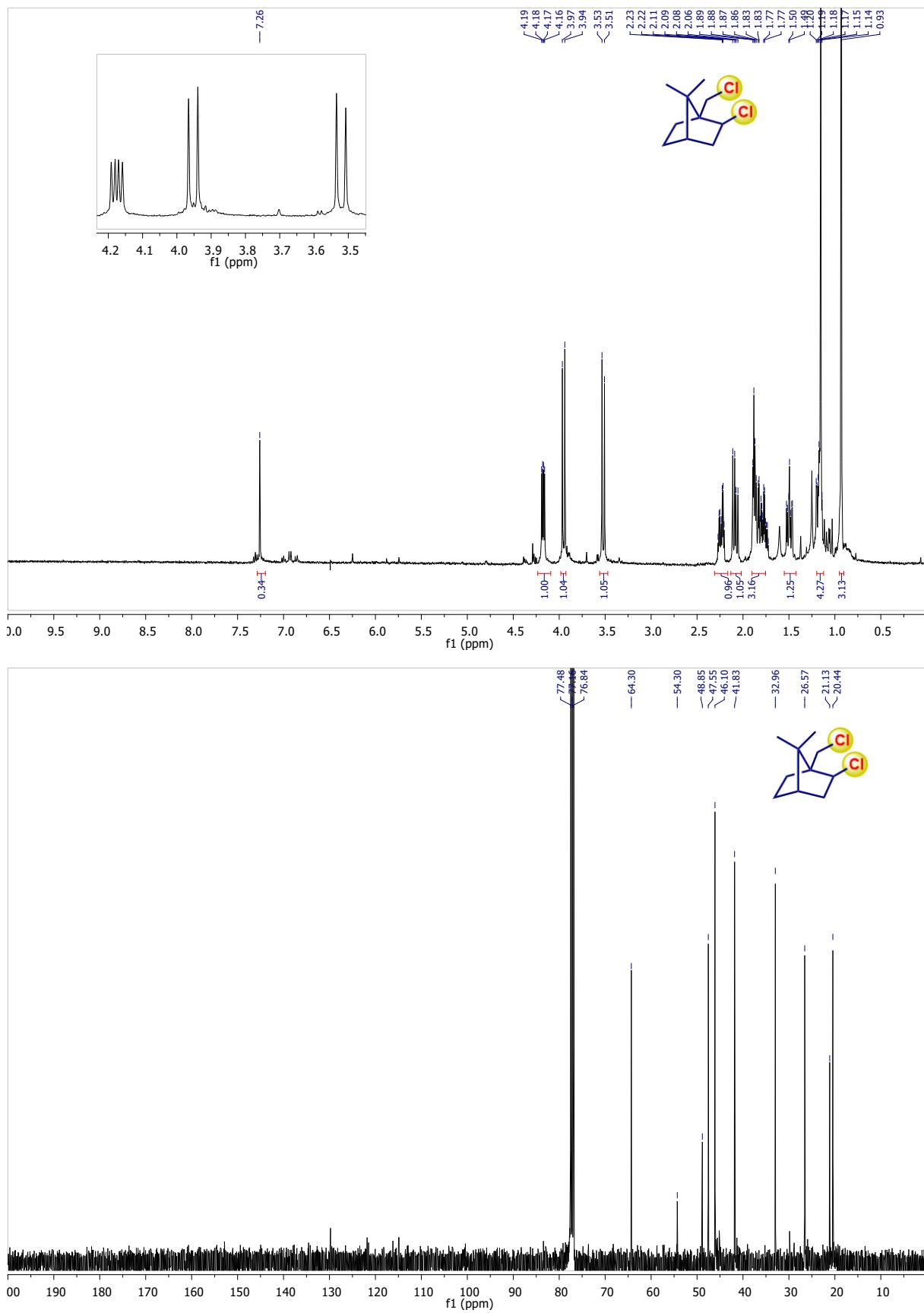
400 MHz ^1H -NMR (top) and 101 MHz ^{13}C -NMR (bottom) spectra of **2v** (CDCl_3)



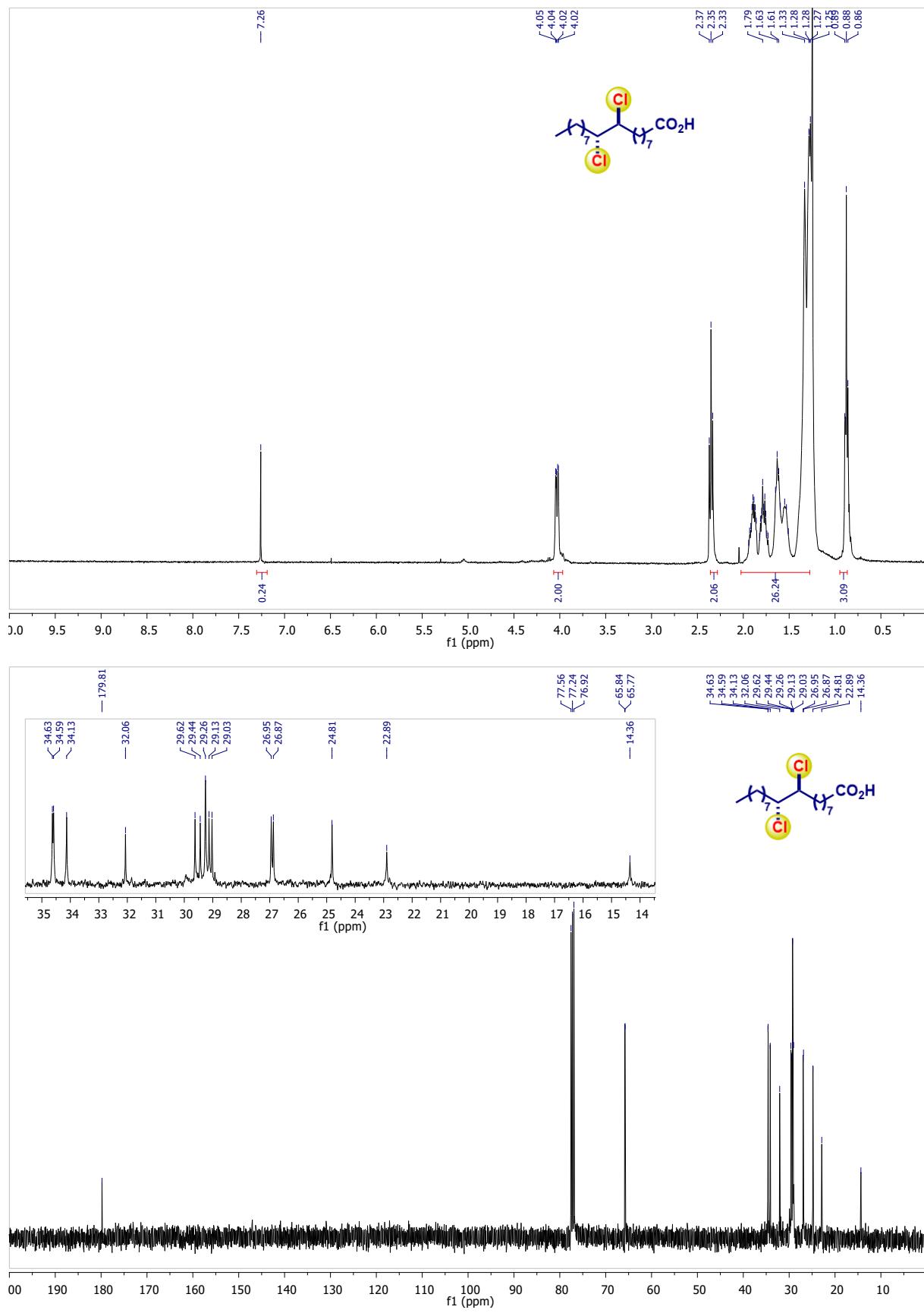
400 MHz ^1H -NMR (top) and 101 MHz ^{13}C -NMR (bottom) spectra of **2w** (CDCl_3)

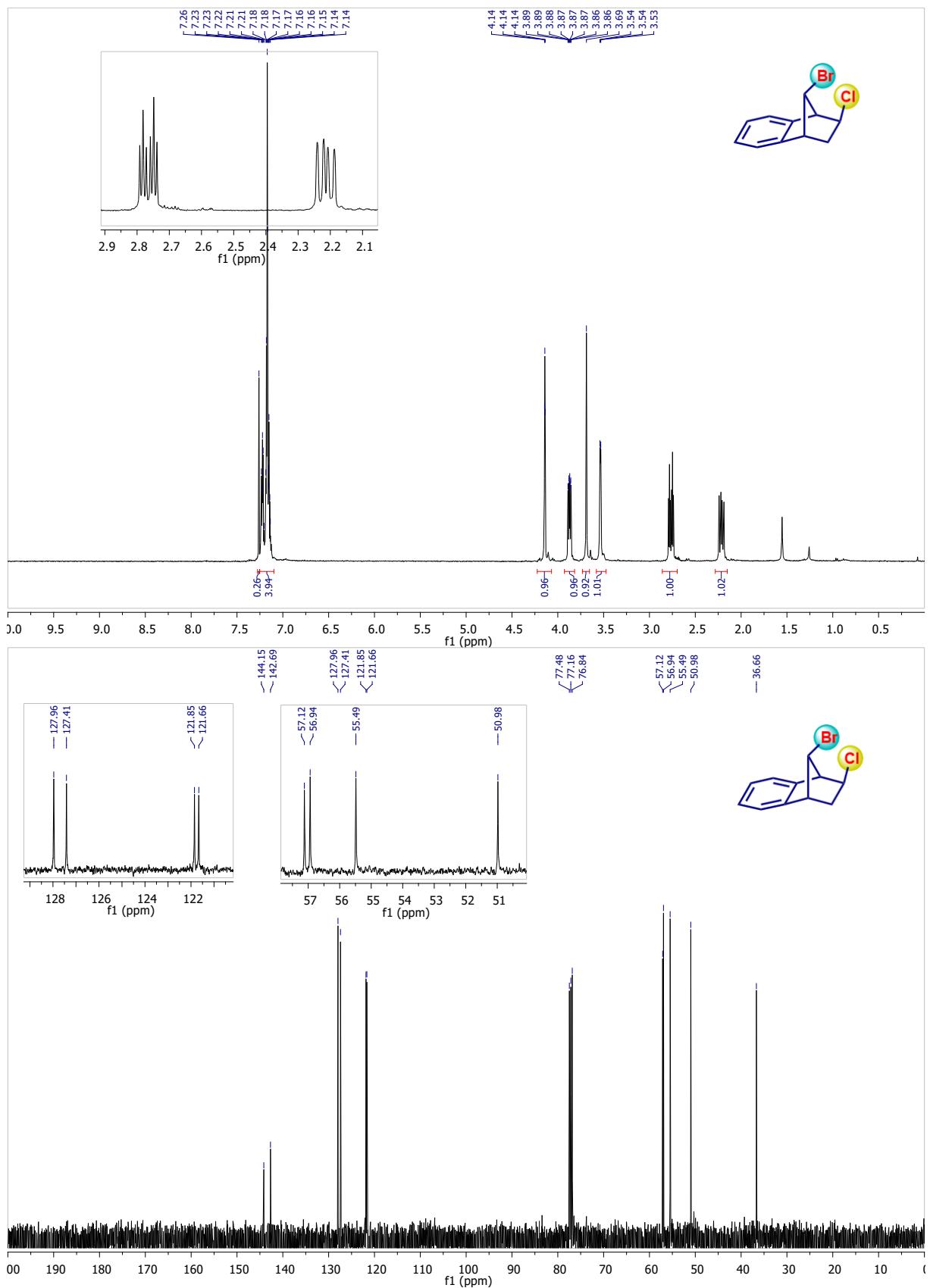


400 MHz ^1H -NMR (top) and 101 MHz ^{13}C -NMR (bottom) spectra of **2x** (CDCl_3)

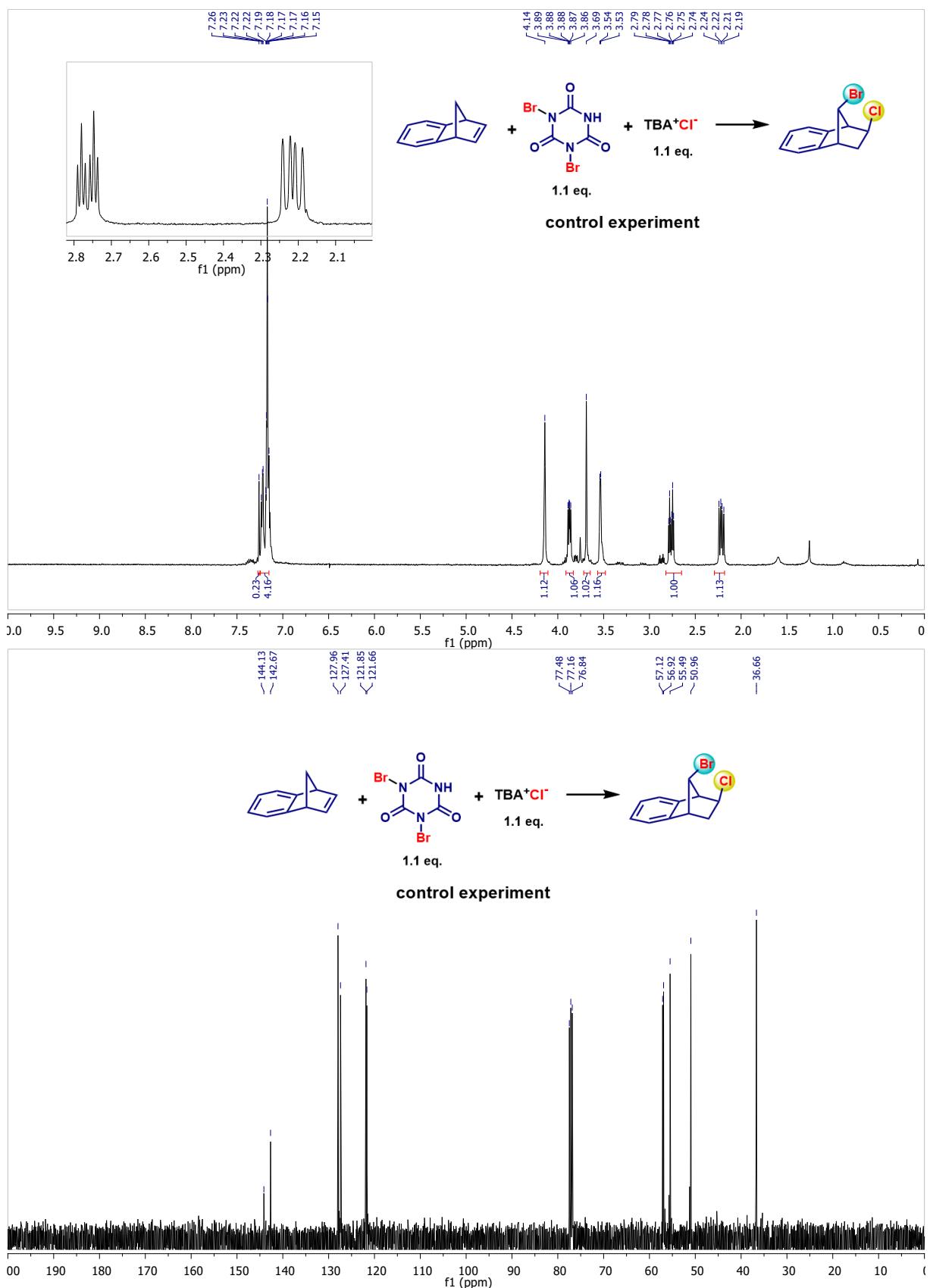


400 MHz ¹H-NMR (top) and 101 MHz ¹³C-NMR (bottom) spectra of **2y** (CDCl₃)

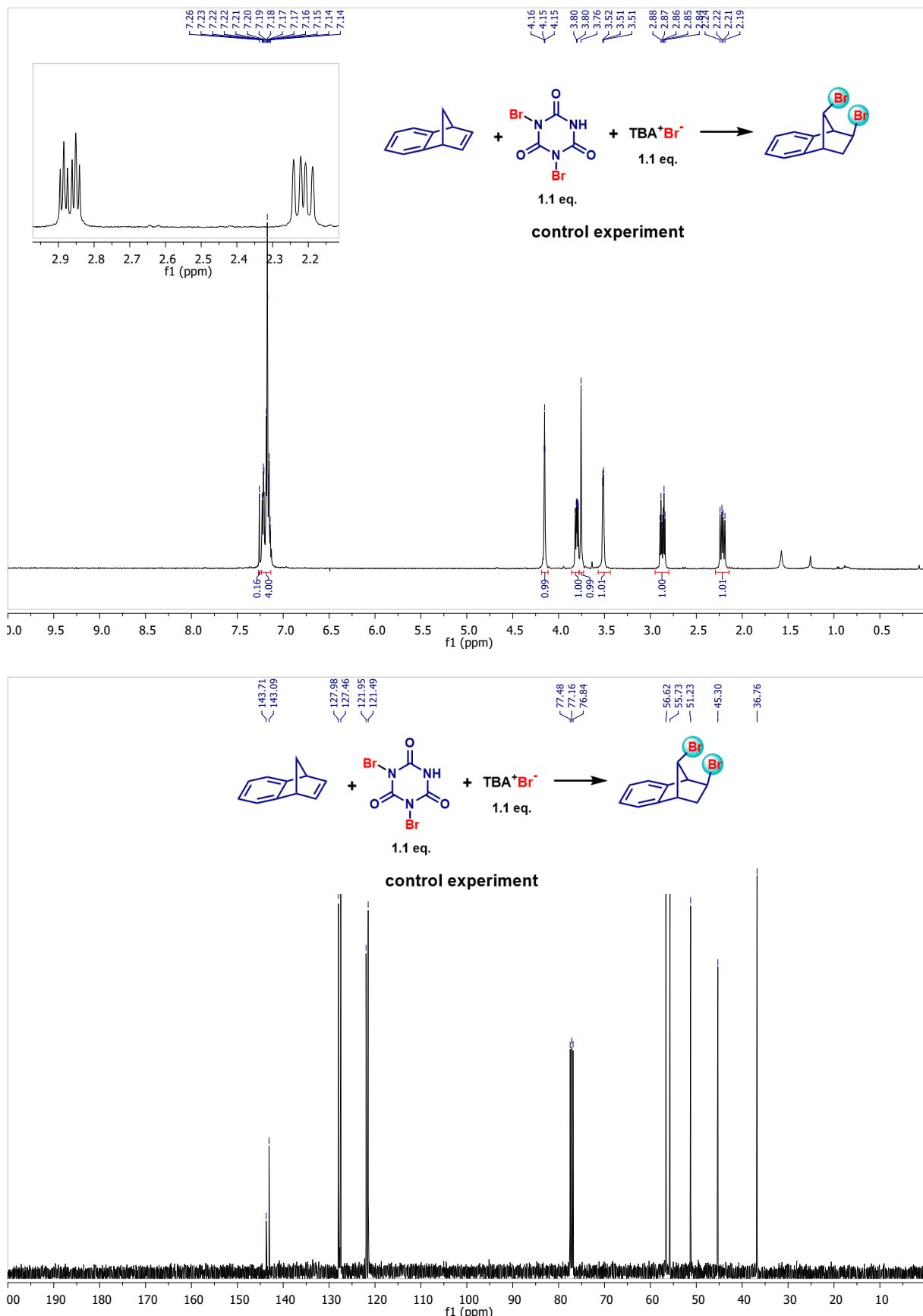




400 MHz ¹H-NMR (top) and 101 MHz ¹³C-NMR (bottom) spectra of **2ab** (CDCl_3)



400 MHz $^1\text{H-NMR}$ (top) and 101 MHz $^{13}\text{C-NMR}$ (bottom) spectra of **2ab** (from control experimental) (CDCl_3)



400 MHz ^1H -NMR (top) and 101 MHz ^{13}C -NMR (bottom) spectra of **2ac** (from control experimental) (CDCl_3)