Electronic Supplementary Information(ESI)

CN - assisted oxidative cyclization of cyano cinnamates and styrene derivatives: a facile entry to 3-substituted chiral phthalides

R. Santhosh Reddy, I.N. Chaithanya Kiran and Arumugam Sudalai*

Chemical Engineering and Process Development Division, National Chemical Laboratoty Pashan Road, Pune 411008, India, Fax: (+) 91-02025902675.

E-mail: a.sudalai@ncl.res.in

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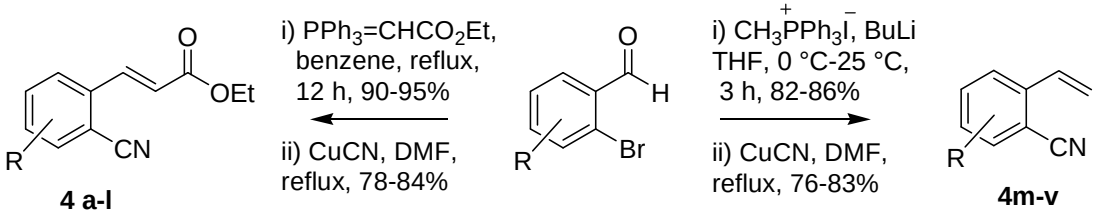
1. General Information

Solvents were purified and dried by standard procedures before use; petroleum ether of boiling range 60–80 ^{o}C was used. Melting points are uncorrected. Optical rotations were measured using sodium D line on a JASCO-181 digital polarimeter. Infrared spectra were recorded on Shimadzu FTIR-8400 spectrometer. ^{1}H NMR and ^{13}C NMR were recorded on Bruker AV-200, AV-400 & AV-500 NMR spectrometers, respectively. Elemental analysis was carried on a Carlo Erba CHNS-O analyzer. HPLC was performed on Dionex P680 with variable wavelength detector using Chiracel OJ-H column from Diacel.

2. Experimental Section

2.1. A general experimental procedure for the preparation of cyano cinnamates and styrenics (4a-z):



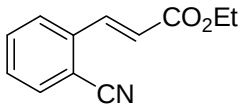
Scheme 1: Synthesis of o-Cyano olefins **4 a-l & 4 m-v**

2.1.1. General experimental procedure for the preparation of cyano cinnamates (4 a -l):

To a stirred solution of 2-bromobenzaldehydes (50 mmol) in benzene (100 mL), $Ph_3P{=}CHCO_2Et$ (55 mmol) was added. It was then refluxed for 4 h under N_2 atmosphere. After the completion of reaction, benzene was distilled out to give the crude product, which was purified by column chromatography [silica gel (230-400 mesh) and petrolium

ether: Ethyl acetate (90:10) as eluent] to afford pure product 2-bromo-ethyl cinnamtes in 94% yield. Which was taken in dry DMF (20 mL) and CuCN (15.6 mmol) was added and refluxed under N_2 for 18 h (monitored by TLC). The reaction mixture then cooled to room temperature, then diluted with water (30 mL) and EtOAc (25 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (2 x 20 mL). The combined organic extracts were washed with brine and dried over anhyd. Na_2SO_4 and concentrated under reduced pressure to give crude products which was purified by column chromatography [silica gel (230-400 mesh) and petroleum ether: EtOAc (70:30) as an eluent] gave 2-cyano-ethyl cinnamate in 82% yield.

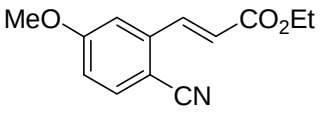
(*E*)-Ethyl 3-(2-cyanophenyl)acrylate (4a):



4a

Yield: 88% (for two steps)**,** colorless solid; mp 60 – 62 ºC; **IR** ($CHCl_3$): 765, 784, 1031, 1184, 1318, 1447, 1480, 1594, 1640, 1712, 2225, 2938, 2983 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): δ 1.36 (t, *J* = 7.3 Hz, 3H), 4.31 (q, *J* = 7.3 Hz, 2H), 6.60 (d, *J* = 16 Hz, 1H), 7.47 (td, *J* = 1.44, 7.55 Hz, 1H), 7.62 (td, *J* = 1.44, 7.55 Hz, 1H), 7.70-7.76 (m, 2H), 7.96 (d, *J* = 16 Hz, 1H); **^{13}C NMR** ($CDCl_3$): δ 14.1, 60.7, 112.5, 116.8, 122.9, 126.8, 129.9, 132.8, 133.3, 137.1, 139.1, 165.4; **Analysis**: $C_{12}H_{11}NO_2$ requires C 71.63, H 5.51, N 6.96 found C 71.59, H 5.56, N 6.93 %.

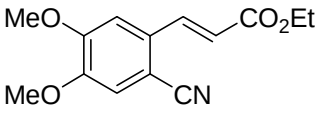
(E)-Ethyl 3-(2-cyano-5-methoxyphenyl)acrylate (4b):



4b

Yield: 86% (for two steps)**,** colorless solid; mp 130 – 132 ºC; **IR** ($CHCl_3$): 728, 868, 1026, 1256, 1490, 1594, 1607, 1640, 1712, 2228, 2853, 2923 3023 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): δ 1.36 (t, *J* = 7.08 Hz, 3H), 3.90 (s,3H), 4.29 (q, *J* = 7.08 Hz, 2H), 6.56 (d, *J* = 16 Hz, 1H), 6.97 (dd, *J* = 2.54, 8.73 Hz, 1H), 7.15 (d, *J* = 2.54 Hz, 1H), 7.63 (d, *J* = 8.79 Hz, 1H), 7.90 (d, *J* = 16 Hz, 1H) ; **^{13}C NMR** ($CDCl_3$): δ 14.2, 55.6, 60.8, 104.6, 112.1, 116.0, 117.3, 123.1, 135.0, 139.4, 162.7, 165.5; **Analysis**: $C_{13}H_{13}NO_3$ requires C 67.52, H 5.67, N 6.06 found C 67.49, H 5.61, N 6.01%.

(E)-Ethyl 3-(2-cyano-4,5-dimethoxyphenyl)acrylate (4c):

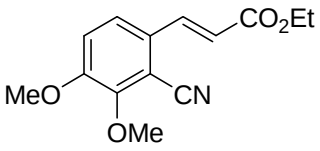


4c

Yield: 87% (for two steps)**,** colorless solid; mp 159 – 161 ºC; **IR** ($CHCl_3$): 761, 848, 1094, 1149, 1204, 1326, 1462, 1571, 1594, 1709, 2222, 2984, 3018 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): δ 1.36 (t, *J* = 7.36 Hz, 3H), 3.94 (s,3H), 3.97 (s, 3H), 4.29 (q, *J* = 7.36 Hz, 2H), 6.47 (d, *J* = 16.03 Hz, 1H), 7.07 (s, 1H), 7.11 (s, 1H), 7.89 (d, *J* = 16.03 Hz, 1H) ; **^{13}C NMR** ($CDCl_3$): δ 14.2, 55.9, 56.2, 60.7, 105.2, 108.2, 114.2, 117.1, 120.7, 131.5,

139.2, 150.5, 152.6, 165.8; **Analysis**: $C_{14}H_{15}NO_4$ requires C 64.36, H 5.79, N 5.36 found C 64.32, H 5.71, N 5.34 %.

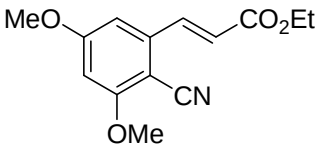
(E)-Ethyl 3-(2-cyano-3,4-dimethoxyphenyl)acrylate (4d):



4d

Yield: 88% (for two steps)**,** colorless solid; mp 145 – 147 ºC; **IR** ($CHCl_3$): 758, 894, 1078, 1138, 1208, 1318, 1326, 1462, 1571, 1594, 1608, 1710, 2222, 2984, 3018 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): δ 1.35 (t, *J* = 7.05 Hz, 3H), 3.93 (s,3H), 4.03 (s, 3H), 4.27 (q, *J* = 7.05 Hz, 2H), 6.48 (d, *J* = 16 Hz, 1H), 7.10 (d, *J* = 8.65 Hz, 1H), 7.40 (d, *J* = 8.65 Hz, 1H), 7.83 (d, *J* = 16 Hz, 1H) ; **^{13}C NMR** ($CDCl_3$): δ 14.3, 56.1, 60.6, 61.6, 107.9, 114.1, 116.4, 120.7, 122.9, 129.7, 139.2, 152.1, 153.5, 165.9; **Analysis**: $C_{14}H_{15}NO_4$ requires C 64.36, H 5.79, N 5.36 found C 64.34, H 5.71, N 5.32 %.

(E)-Ethyl 3-(2-cyano-3,5-dimethoxyphenyl)acrylate (4e):

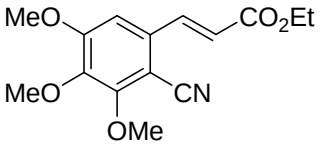


4e

Yield: 87% (for two steps)**,** colorless solid; mp 119 – 122 ºC; **IR** ($CHCl_3$): 734, 876, 1069, 1128, 1208, 1326, 1326, 1478, 1568, 1594, 1608, 1712, 2228, 2958, 3082 cm^{-1}; **^{1}H**

NMR (200 MHz, $CDCl_3$): δ 1.36 (t, *J* = 7.15 Hz, 3H), 3.89 (s,3H), 3.93 (s, 3H), 4.29 (q, *J* = 7.15 Hz, 2H), 6.47 (d, *J* = 2.13 Hz, 1H), 6.55 (d, *J* = 16 Hz, 1H), 6.73 (d, *J* = 2.13 Hz, 1H), 7.86 (d, *J* = 16 Hz, 1H) ; **^{13}C NMR** ($CDCl_3$): δ 14.3, 55.7, 56.1, 60.8, 94.9, 96.1 99.4, 103.4, 114.8, 123.3, 139.6, 140.1, 163.4, 163.9, 165.6; **Analysis**: $C_{14}H_{15}NO_4$ requires C 64.36, H 5.79, N 5.36 found C 64.32, H 5.71, N 5.34 %.

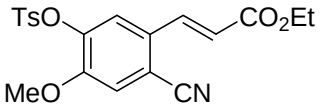
(E)-Ethyl 3-(2-cyano-3,4,5-trimethoxyphenyl)acrylate (4f):



4f

Yield: 88% (for two steps)**,** colorless solid; mp 150 – 152 ºC; **IR** ($CHCl_3$): 669, 703, 749, 940, 1260, 1311, 1573, 1607, 1640, 1708, 2210, 2979, 3016 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): δ 1.36 (t, *J* = 7.15 Hz, 3H), 3.90 (s,3H), 3.96 (s, 3H), 4.06 (s, 3H), 4.28 (q, *J* = 7.15 Hz, 2H), 6.50 (d, *J* = 16 Hz, 1H), 6.91 (s, 1H), 7.84 (d, *J* = 16 Hz, 1H); **^{13}C NMR** ($CDCl_3$): δ 14.3, 55.8, 60.3, 109.1, 115.4, 117.0, 118.5, 126.2, 142.5, 148.5, 151.1, 161.2; **Analysis**: $C_{15}H_{17}NO_5$ requires C 61.85, H 5.88, N 4.81 found C 61.82, H 5.79, N 4.75%.

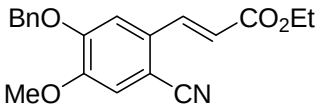
5-((E)-2-(Ethoxycarbonyl)vinyl)-4-cyano-2-methoxyphenyl 4-methylbenzenesulfonate (4g):



4g

Yield: 87% (for two steps)**,** colorless solid; mp 150 – 151 ºC; **IR** ($CHCl_3$): 742, 865, 1030, 1128, 1232, 1318, 1329, 1478, 1571, 1594, 1608, 1708, 2225, 2982, 3025 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): δ 1.35 (t, *J* = 6.90 Hz, 3H), 2.48 (s,3H), 3.73 (s, 3H), 4.30 (q, *J* = 6.90 Hz, 2H), 6.54 (d, *J* = 16 Hz, 1H), 7.09 (s, 1H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.39 (s, 1H), 7.77 (d, *J* = 8.5 Hz, 2H), 7.91 (d, *J* = 16 Hz, 1H); **^{13}C NMR** ($CDCl_3$): δ 14.2, 21.7, 56.0, 61.0, 104.5, 110.3, 116.0, 123.8, 128.3, 129.7, 132.6, 137.9, 138.4, 139.1, 145.8, 155.6, 165.2; **Analysis**: $C_{20}H_{19}NO_6S$ requires C 59.84, H 4.77, N 3.49 found C 59.78, H 4.69, N 3.42%.

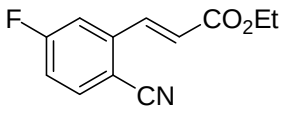
(E)-Ethyl 3-(5-(benzyloxy)-2-cyano-4-methoxyphenyl)acrylate (4h):



4h

Yield: 86% (for two steps)**,** colorless solid; mp 146 – 148 ºC; **IR** ($CHCl_3$): 738, 825, 1031, 1098, 1234, 1334, 1380, 1467, 1568, 1575, 1608, 1710, 2228, 2982, 3034 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): δ 1.35 (t, *J* = 7.23 Hz, 3H), 3.93 (s,3H), 4.28 (q, *J* = 7.33 Hz, 2H), 5.20 (s, 2H), 6.34 (d, *J* = 15.48 Hz, 1H), 7.08 (s, 2H), 7.34-7.43 (m, 5H), 7.84 (d, *J* = 15.48 Hz, 1H); **^{13}C NMR** ($CDCl_3$): δ 14.3, 56.2, 60.8, 71.0, 105.5, 110.5, 114.7, 117.2, 120.9, 127.3, 128.8, 131.5, 135.4, 139.3, 151.1, 151.8, 165.9; **Analysis**: $C_{20}H_{19}NO_4$ requires C 71.20, H 5.68, N 4.15 found C 71.14, H 5.61, N 4.09%.

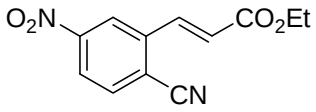
(E)-Ethyl 3-(2-cyano-5-fluorophenyl)acrylate (4i):



4i

Yield: 85% (for two steps)**,** colorless solid; mp 72 – 74 ºC; **IR** ($CHCl_3$): 756, 828, 866, 981, 1030, 1186, 1226, 1276, 1325, 1370, 1480, 1574, 1603, 1640, 1693, 2984, 3012 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): δ 1.36 (t, *J* = 7.27 Hz, 3H), 4.31 (q, *J* = 7.27 Hz, 2H), 6.58 (d, *J* = 15.9 Hz, 1H), 7.19 ((td, *J* = 2.8, 8.4 Hz, 1H), 7.41 ((dd, *J* = 2.61, 9.16 Hz, 1H), 7.74 (dd, *J* = 5.4, 8.47 Hz, 1H), 7.91 (d, *J* = 15.9 Hz, 1H); **^{13}C NMR** ($CDCl_3$): δ 14.1, 60.9, 108.8, 133.9 (d, *J* = 23.68 Hz), 116.0, 117.6 (d, *J* = 23.68 Hz), 124.2, 135.7 (d, *J* = 9.8 Hz), 140.2 (d, *J* = 8.8 Hz), 164.5 (d, *J* = 257.73 Hz), 164.9; **Analysis**: $C_{12}H_{10}FNO_2$ requires C 65.75, H 4.60, N 6.39 found C 65.68, H 4.56, N 6.36%.

(E)-Ethyl 3-(2-cyano-5-nitrophenyl)acrylate (4j):

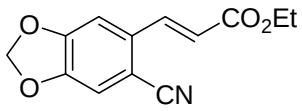


4j

Yield: 87% (for two steps)**,** colorless solid; mp 105 – 107 ºC; **IR** ($CHCl_3$): 739, 830, 968, 1032, 1106, 1346, 1540, 1708, 2233, 2980, 3087 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.38 (t, *J* = 7.04 Hz, 3H), 4.33 (q, *J* = 7.04 Hz, 2H), 6.78 (d, *J* = 15.87 Hz, 1H), 7.95 (d, *J* = 2.03 Hz, 1H), 7.98 (d, *J* = 15.87 Hz, 1H), 8.33 (dd, *J* = 2.03, 8.48 Hz, 1H) 8.59 (d, *J* = 2.03 Hz, 1H); **^{13}C NMR** ($CDCl_3$): δ 14.2, 61.3, 115.2, 117.8, 121.7, 124.1, 125.9, 134.7,

136.9, 139.5, 150.2, 164.8; **Analysis**: $C_{12}H_{10}N2O_4$ requires C 58.54, H 4.09, N 11.38 found C 58.48, H 4.02, N 11.31%.

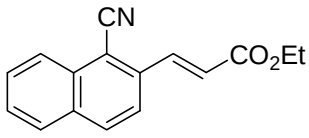
(E)-Ethyl 3-(5-cyanobenzo[d][1,3]dioxol-6-yl)acrylate (4k):



4k

Yield: 86%(for two steps)**,** white solid; mp 148 – 149 ºC; **IR** ($CHCl_3$): 728, 878, 1042, 1134, 1256, 1366, 1382, 1478, 1568, 1594, 1608, 1712, 2218, 2958, 3082 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): δ 1.35 (t, *J* = 7.06 Hz, 3H), 4.28 (q, *J* = 7.06 Hz, 2H), 6.12 (s, 2H), 6.41 (d, *J* = 15.88 Hz, 1H), 7.05 (s, 1H), 7.13 (s, 1H), 7.90 (d, *J* = 15.88 Hz, 1H) ; **^{13}C NMR** ($CDCl_3$): δ 14.3, 60.8, 102.8, 105.9, 106.8, 111.8, 116.9, 121.4, 133.9, 138.9, 149.2, 151.9, 165.7; **Analysis**: $C_{13}H_{11}NO_4$ requires C 63.67, H 4.52, N 5.71 found C 63.59, H 4.48, N 5.65 %.

(E)-Ethyl 3-(1-cyanonaphthalen-2-yl)acrylate (4l):



4l

Yield: 88% (for two steps)**,** colorless solid; mp 118 – 119 ºC; **IR** ($CHCl_3$): 784, 865, 989, 1030, 1106, 1210, 1275, 1291, 1319, 1368, 1573, 1607, 1712, 2218, 2978, 3084 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): δ 1.35 (t, *J* = 7.03 Hz, 3H), 4.32 (q, *J* = 7.03 Hz, 2H), 6.68 (d,

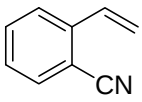
J = 16 Hz, 1H), 7.59-7.78 (m, 3H), 7.90 (d, *J* = 7.70 Hz, 1H), 8.04 (d, *J* = 8.78 Hz, 1H), 8.19 (d, *J* = 16 Hz, 1H), 8.28 (d, *J* = 8.78 Hz, 1H) ; **^{13}C NMR** ($CDCl_3$): δ 14.2, 60.8, 110.8, 115.5, 122.1, 123.5, 125.8, 128.3, 129.1, 132.5, 132.9, 137.0, 139.5, 165.5; **Analysis**: $C_{16}H_{13}NO_2$ requires C 76.48, H 5.21, N 5.57 found C 76.42, H 5.19, N 5.52 %.

2.1.2. General experimental procedure for the preparation of cyano styrenes (4m-v):

To a stirred solution of methyltriphenylphosphonium iodide (1.05 eq) in THF was added *n*-butyllithium in hexane (1.05 eq), the solution was stirred for 30 min at 0 °C and 2-bromo benzaldehydes (1.0 eq) in THF was added dropwise via syringe at the same temperature and the reaction mixture was allowed to stir for 90 min at room temperature (monitored by TLC). The reaction mixture then cooled to 0 °C, then diluted with sat.NH_4Cl (25mL) and EtOAc (25 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (2 x 20 mL). The combined organic extracts were washed with brine and dried over anhyd. Na_2SO_4 and concentrated under reduced pressure to give crude products which was purified by column chromatography [silica gel (230-400 mesh) and petroleum ether:EtOAc (90:10) as an eluent] gave 2-bromostyrenes in 86% yield. Which was taken in dry DMF (20 mL) and CuCN (15.6 mmol) was added and refluxed under N_2 for 18 h (monitored by TLC). The reaction mixture then cooled to room temperature, then diluted with water (30 mL) and EtOAc (25 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (2 x 20 mL). The combined organic extracts were washed with brine and dried over anhyd. Na_2SO_4 and concentrated under reduced pressure to give crude products which was purified by

column chromatography [silica gel (230-400 mesh) and petroleum ether: EtOAc (70:30) as an eluent] gave 2-cyano-ethyl cinnamates in 86% yield.

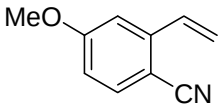
2-Vinylbenzonitrile (4m):



4m

Yield: 86% (for two steps)**,** Gum; **IR** ($CHCl_3$): 752, 839, 962, 1014, 1072, 1118, 1202, 1308, 1347, 1368, 1444, 1573, 1607, 1625, 1675, 2215, 2889, 2923, 3012 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): 5.54 (d, *J* = 10.64 Hz, 1H), 5.95 (d, *J* = 17.83 Hz, 1H), 7.08 (dd, *J* = 10.64, 17.83 Hz, 1H), 7.34 (td, *J* = 1.28, 7.59 Hz, 1H), 7.51-7.70 (m, 3H) ; **^{13}C NMR** ($CDCl_3$): δ 111.0, 117.4, 118.7, 125.2, 127.8, 132.5, 132.7, 140.4; **Analysis**: C_9H_7N requires C 83.69, H 5.46, N 10.84 found C 83.62, H 5.41, N 10.78 %.

4-Methoxy-2-vinylbenzonitrile (4n):

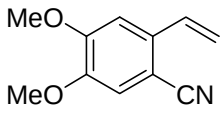


4n

Yield: 84% (for two steps), Gum, **IR** ($CHCl_3$): 752, 839, 1030, 1083, 1119, 1256, 1308, 1347, 1368, 1456, 1573, 1607, 1625, 1668, 2208, 2923, 3081 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): 3.88 (s, 3H), 5.53 (d, *J* = 11.10 Hz, 1H), 5.92 (d, *J* = 17.76 Hz, 1H), 6.85 (dd, *J* = 2.30, 8.54 Hz, 1H), 7.03 (dd, *J* = 11.10, 17.76 Hz, 1H), 7.11 (s, 1H), 7.55 (d, *J* = 8.54 Hz, 1H); **^{13}C NMR** ($CDCl_3$): δ 55.4, 103.2, 110.4, 114.1, 117.9, 118.7, 132.9, 134.4,

142.5, 162.7; **Analysis**: $C_{10}H_9NO$ requires C 75.45, H 5.70, N 8.80 found C 75.41, H 5.67, N 8.73 %.

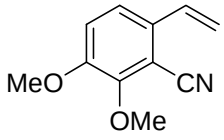
4,5-Dimethoxy-2-vinylbenzonitrile (4o):



4o

Yield: 88% (for two steps)**,** colorless solid; mp 106 – 107 ºC;**IR** ($CHCl_3$): 752, 839, 936, 1031, 1086, 1119, 1256, 1308, 1378, 1389, 1456, 1575, 1612, 1628, 1656, 2210, 2923, 3052 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): 3.91 (s, 3H), 3.97 (s, 3H), 5.45 (d, J = 11.08 Hz, 1H), 5.80 (d, J = 17.28 Hz, 1H), 6.94-7.08 (m, 3H); **^{13}C NMR** ($CDCl_3$): δ 55.7, 55.9, 102.7, 106.9, 113.5, 116.5, 117.7, 132.5, 134.9, 148.7, 152.5; **Analysis**: $C_{11}H_{11}NO_2$ requires C 69.83, H 5.86, N 7.40 found C 69.75, H 5.75, N 7.39 %.

2,3-Dimethoxy-6-vinylbenzonitrile (4p):

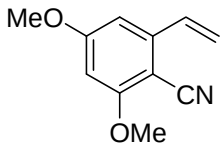


4p

Yield: 86% (for two steps)**,** colorless solid; mp 108 – 110 ºC; **IR** ($CHCl_3$): 748, 840, 936, 1028, 1086, 1119, 1256, 1308, 1378, 1389, 1456, 1575, 1612, 1628, 1656, 2202, 2981, 3029 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): 3.88 (s, 3H), 3.90 (s, 3H), 5.53 (d, J = 10.99 Hz, 1H), 5.90 (d, J = 17.31 Hz, 1H), 6.37 (d, J = 2.20 Hz, 1H), 6.69 (d, J = 2.20 Hz, 1H), 7.01 (dd, J = 10.99, 17.31 Hz, 1H); **^{13}C NMR** ($CDCl_3$): δ 56.1, 61.5, 106.7, 114.7, 116.7,

120.8, 132.4, 133.4, 151.5, 151.7; **Analysis**: $C_{11}H_{11}NO_2$ requires C 69.83, H 5.86, N 7.40 found C 69.73, H 5.78, N 7.39 %.

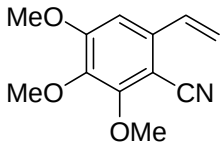
2,4-Dimethoxy-6-vinylbenzonitrile (4q):



4q

Yield: 83% (for two steps)**,** colorless solid; mp 76 – 79 ºC; **IR** ($CHCl_3$): 724, 867, 968, 1030, 1086, 1119, 1259, 1308, 1386, 1389, 1456, 1578, 1612, 1636, 1656, 2212, 2985, 3029 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): 3.90 (s, 3H), 4.00 (s, 3H), 5.40 (d, J = 10.83 Hz, 1H), 5.79 (d, J = 17.68 Hz, 1H), 6.94 (dd, J = 10.83, 17.68 Hz, 1H), 7.07 (d, J = 8.55 Hz, 1H), 7.32 (d, J = 8.55 Hz, 1H); **^{13}C NMR** ($CDCl_3$): δ 55.5, 55.9, 93.6, 97.5, 101.7, 115.5, 118.9, 133.1, 143.4, 163.0, 163.8; **Analysis**: $C_{11}H_{11}NO_2$ requires C 69.83, H 5.86, N 7.40 found C 69.79, H 5.78, N 7.39 %.

2,3,4-Trimethoxy-6-vinylbenzonitrile (4r):

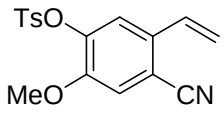


4r

Yield: 87% (for two steps)**,** white solid; mp 102 – 103 ºC; **IR** ($CHCl_3$): 771, 867, 1051, 1105, 1204, 1238, 1257, 1580, 1609, 1753, 2228, 2979, 3013 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): 3.86 (s, 3H), 3.95 (s, 3H), 4.04 (s, 3H), 5.48 (d, J = 11.28 Hz, 1H), 5.83 (d, J = 17.32 Hz, 1H), 6.85 (s, 1H), 6.97 (dd, J = 11.28, 17.32 Hz, 1H); **^{13}C NMR** ($CDCl_3$): δ

55.9, 60.8, 61.5, 98.7, 103.4, 114.8, 117.8, 132.6, 137.2, 141.1, 155.4, 157.2; **Analysis**: $C_{12}H_{13}NO_3$ requires C 65.74, H 5.98, N 6.39 found C 65.72, H 5.91, N 6.37 %.

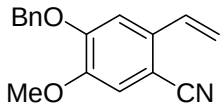
4-Cyano-2-methoxy-5-vinylphenyl 4-methylbenzenesulfonate (4s):



4s

Yield: 82% (for two steps)**,** colorless solid; mp 149 – 150 ºC; **IR** ($CHCl_3$): 746, 845, 938, 1034, 1086, 1119, 1256, 1308, 1378, 1389, 1456, 1575, 1612, 1628, 1656, 2220, 2978, 3075 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): 2.48 (s, 3H), 3.74 (s, 3H), 5.57 (d, J = 10.95 Hz, 1H), 5.86 (d, J = 17.62 Hz, 1H), 6.93-7.08 (m, 2H), 7.28 (s, 1H), 7.35 (d, J = 8.01 Hz, 2H), 7.77 (d, J = 8.24 Hz, 2H); **^{13}C NMR** ($CDCl_3$): δ 21.7, 55.8, 102.9, 108.9, 116.6, 119.7, 127.7, 128.5, 129.6, 132.3, 132.7, 137.7, 141.4, 145.6, 155.5; **Analysis**: $C_{17}H_{15}NO_4S$ requires C 61.99, H 4.59, N 4.25 found C 61.89, H 4.53, N 4.23%.

4-(Benzyloxy)-5-methoxy-2-vinylbenzonitrile (4t):

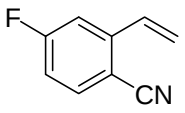


4t

Yield: 84% (for two steps)**,** colorless solid; mp 111 – 113 ºC; **IR** ($CHCl_3$): 747, 858, 934, 1028, 1065, 1119, 1232, 1308, 1394, 1389, 1456, 1574, 1612, 1631, 1656, 2220, 2988, 3086 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): 3.90 (s, 3H), 5.21 (s, 2H), 5.39 (d, J = 11.15 Hz, 1H), 5.66 (d, J = 17.45 Hz, 1H), 6.89-7.04 (m, 2H), 7.10 (s, 1H), 7.32-7.47 (m, 5H); **^{13}C NMR** ($CDCl_3$): δ 56.0, 70.8, 103.1, 109.2, 114.0, 116.6, 117.8, 127.2, 128.2, 128.6,

132.6, 134.9, 135.7, 149.3, 151.8; **Analysis**: $C_{17}H_{15}NO_2$ requires C 76.96, H 5.70, N 5.28 found C 76.91, H 5.67, N 5.27 %.

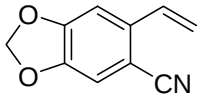
4-Fluoro-2-vinylbenzonitrile (4u):



4u

Yield: 86% (for two steps)**,** colorless solid; mp 105 – 107 ºC; **IR** ($CHCl_3$): 752, 839, 962, 1014, 1072, 1118, 1202, 1308, 1347, 1368, 1444, 1573, 1607, 1625, 1675, 2853, 2923, 3012 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): 5.62 (d, *J* = 11.00 Hz, 1H), 5.96 (d, *J* = 17.30 Hz, 1H), 7.02-7.08 (m, 2H), 7.34 (dd, *J* = 2.29, 9.49 Hz, 1H), 7.64 (dd, *J* = 5.56, 8.51 Hz, 1H); **^{13}C NMR** ($CDCl_3$): δ 107.6, 112.6 (d, *J* = 23.70 Hz), 115.8 (d, *J* = 23.70 Hz), 116.8, 120.2, 132.2, 143.8 (d, *J* = 9.51 Hz), 165.1 (d, *J* = 243.84 Hz); **Analysis**: C_9H_6FN requires C 73.46, H 4.11, N 9.52 found C 73.44, H 4.08, N 9.49 %.

6-Vinylbenzo[d][1,3]dioxole-5-carbonitrile (4v):

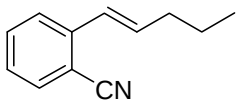


4v

Yield: 88% (for two steps)**,** colorless solid; mp 88 – 91 ºC; **IR** ($CHCl_3$): 756, 868, 930, 1038, 1162, 1263, 1359, 1486, 1505, 1604, 1615, 2219, 2916, 3018 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): 5.44 (d, *J* = 11.10 Hz, 1H), 5.77 (d, *J* = 17.36 Hz, 1H), 6.07 (s, 2H), 6.95-7.04 (m, 2H), 7.09 (s, 1H); **^{13}C NMR** ($CDCl_3$): δ 102.3, 104.0, 104.8, 110.9, 117.2,

117.7, 132.5, 137.5, 147.4, 151.8; **Analysis**: $C_{10}H_7NO_2$ requires C 69.36, H 4.07, N 8.09 found C 69.34, H 4.02, N 7.99 %.

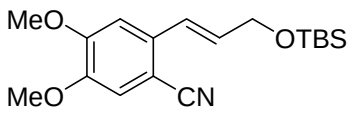
2-((E)-Pent-1-enyl)benzonitrile (4w):



4w

Yield: 87% (for two steps)**,** colorless solid; mp 126 – 128 ºC; **IR** ($CHCl_3$): 756, 857, 974, 1037, 1095, 1184, 1202, 1216, 1251, 1275, 1291, 1319, 1347, 1368, 1393, 1444, 1477, 1573, 1607, 1640, 1716, 2984, 3023, 3415 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): 0.98 (t, *J* = 7.31 Hz, 3H), 1.45-1.63 (m, 2H), 2.22-2.33 (m, 2H), 6.43 (dt, *J* = 15.36, 6.89 Hz, 1H), 6.74 (d, *J* = 15.36 Hz, 1H), 7.25 (dd, *J* = 15.36, 1.45 Hz, 1H), 7.45-7.62 (m, 3H); **^{13}C NMR** ($CDCl_3$): δ 13.7, 22.2, 35.2, 110.5, 117.9, 125.2, 126.0, 126.8, 132.5, 132.7, 136.4, 141.1; **Analysis**: $C_{12}H_{13}N$ requires C 84.17, H 7.65, N 8.18 found C 84.14, H 7.61, N 8.15.

4,5-Dimethoxy-2-((E)-3-*tert*-butyldimethylsillyloxyprop-1-enyl)benzonitrile (4x):

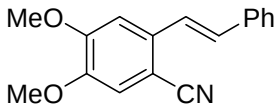


4x

Yield: 85% (for two steps), Gum; **IR** ($CHCl_3$): 748, 876, 932, 1032, 1098, 1276, 1339, 1486, 1505, 1604, 1615, 2220, 2989, 3054 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): 0.12 (s, 6H), 0.94 (s, 9H), 3.88 (s, 3H), 3.94 (s, 3H), 4.39 (dd, *J* = 1.75, 4.73 Hz, 2H), 6.27-6.39 (m, 1H), 6.89 (d, *J* = 15.54 Hz, 1H), 6.98 (s, 1H), 7.00 (s, 1H); **^{13}C NMR** ($CDCl_3$): δ -

5.3, 18.3, 25.9, 55.8, 55.9, 63.3, 102.6, 107.4, 113.7, 117.9, 124.9, 132.4, 134.8, 148.4, 152.5; **Analysis**: $C_{18}H_{27}NO_3Si$ requires C 64.83, H 8.16, N 4.20 found C 64.79, H 8.09, N 4.13%.

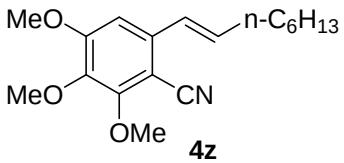
4,5-Dimethoxy-2-styrylbenzonitrile (4y):



4y

Yield: 83% (for two steps)**,** colorless solid; mp 158 – 159 ºC; **IR** ($CHCl_3$): 696, 761, 1149, 1204, 1326, 1462, 1571, 1594, 2215, 2984, 3023 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): 3.91 (s, 3H), 4.01 (s, 3H), 7.01-7.17 (m, 3H), 7.26-7.42 (m, 4H), 7.54 (d, *J* = 6.91 Hz, 2H); **^{13}C NMR** ($CDCl_3$): δ 55.9, 102.9, 106.8, 113.6, 118.0, 123.8, 126.7, 128.7, 128.6, 131.2, 134.9, 136.1, 148.5, 152.6; **Analysis**: $C_{17}H_{15}NO_2$ requires C 76.96, H 5.70, N 5.28 found C 76.89, H 5.57, N 5.19 %.

2,3,4-Trimethoxy-6-((E)-oct-1-enyl)benzonitrile (4z):

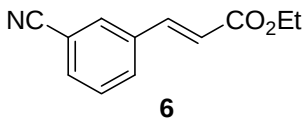


4z

Yield: 86% (for two steps)**,** colorless solid; mp 172 – 174 ºC; **IR** ($CHCl_3$): 694, 755, 878, 969, 989, 1097, 1216, 1271, 1452, 1464, 1513, 1600, 2220, 2970, 3025, 3059 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): 0.87-0.93 (m, 3H), 1.26-1.46 (m, 8H), 2.21-2.31 (m, 2H), 3.85 (s, 3H), 3.94 (s, 3H), 4.03 (s, 3H), 6.23-6.36 (m, 1H), 6.63 (d, *J* = 15.66 Hz, 1H), 6.78 (s,

1H); **^{13}C NMR** ($CDCl_3$): δ 14.1, 22.6, 28.9, 29.0, 31.6, 33.1, 56.0, 61.1, 61.6, 98.3, 103.3, 115.4, 125.8, 135.9, 138.1, 140.5, 155.6, 157.2; **Analysis**: $C_{18}H_{25}NO_3$ requires C 71.26, H 8.31, N 4.62 found C 71.22, H 8.28, N 4.58%.

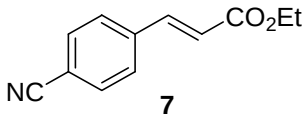
(E)-Ethyl 3-(3-cyanophenyl)acrylate (6):



6

Yield: 93%; colorless solid; mp 62 – 65 ºC; **IR** ($CHCl_3$): 710, 765, 977, 1032, 1185, 1278, 1318, 1447, 1480, 1640, 1712, 2225, 2938, 2983 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): δ 1.35 (d, *J* = 7.06 Hz, 3H), 4.28 (d, *J* = 7.06 Hz, 2H), 6.48 (d, *J* = 16.11 Hz, 1H), 7.48-7.80 (m, 5H); **^{13}C NMR** ($CDCl_3$): δ 14.1, 60.5, 113.2, 117.8, 120.8, 129.6, 131.1, 131.6, 132.8, 135.5, 141.5, 165.7; **Analysis**: $C_{12}H_{11}NO_2$ requires C 71.63, H 5.51, N 6.96 found C 71.59, H 5.45, N 6.85%.

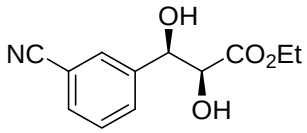
(E)-Ethyl 3-(4-cyanophenyl)acrylate (7):



7

Yield: 93%; colorless solid; mp 68 – 70 ºC; **IR** ($CHCl_3$): 730, 795, 955, 1065, 1194, 1268, 1375, 1445, 1495, 1652, 1721, 2226, 2983 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): δ 1.35 (d, *J* = 7.15 Hz, 3H), 4.28 (d, *J* = 7.15 Hz, 2H), 6.51 (d, *J* = 15.85 Hz, 1H), 7.59-7.71 (m, 5H); **^{13}C NMR** ($CDCl_3$): δ 14.1, 60.6, 113.2, 117.9, 121.6, 128.2, 132.4, 138.5, 141.8, 165.7; **Analysis**: $C_{12}H_{11}NO_2$ requires C 71.63, H 5.51, N 6.96 found C 71.58, H 5.48, N 6.88%.

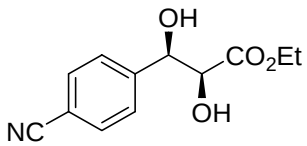
(2S,3R)-Ethyl 3-(3-cyanophenyl)-2,3-dihydroxypropanoate (8):



8

Yield: 93%; Gum; $[\alpha]^{D}_{25}$ -36.06 (*c* 1.20, $CHCl_3$); **IR** ($CHCl_3$): 680, 725, 954, 1057, 1118, 1214, 1291, 1734, 2229, 2985, 3443 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): δ 1.30 (d, *J* = 7.16 Hz, 3H), 3.26 (d, *J* = 7.51 Hz, 1H), 3.43 (d, *J* = 5.89 Hz, 1H), 4.24-4.34 (m, 3H), 5.02 (dd, *J* = 2.38, 7.51 Hz, 1H), 7.49 (d, *J* = 7.52 Hz, 1H), 7.57-7.67 (m, 2H), 7.72 (s, 1H); **^{13}C NMR** ($CDCl_3$): δ 14.1, 62.3, 73.5, 74.5, 112.2, 118.6, 129.0, 130.2, 130.9, 131.3, 141.9, 172.3; **Analysis**: $C_{12}H_{13}NO_4$ requires C 61.27, H 5.57, N 5.95 found C 61.26, H 5.54, N 5.89.

(2S,3R)-Ethyl 3-(4-cyanophenyl)-2,3-dihydroxypropanoate (9):

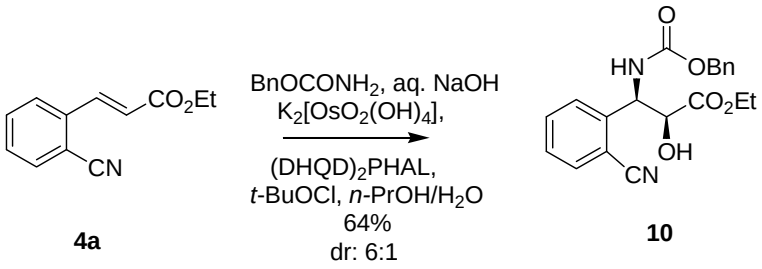


9

Yield: 93%; colorless solid; mp 102 – 103 ºC; $[\alpha]^{D}_{25}$ -36.42 (*c* 1.10, $CHCl_3$); **IR** ($CHCl_3$): 685, 765, 1017, 1050, 1105, 1204, 1257, 1752, 2228, 2978, 3332 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): δ 1.31 (d, *J* = 7.06 Hz, 3H), 3.03 (d, *J* = 7.63 Hz, 1H), 3.27 (d, *J* = 5.36 Hz, 1H), 4.24-4.35 (m, 3H), 5.05 (dd, *J* = 2.38, 7.51 Hz, 1H), 7.49 (d, *J* = 7.52 Hz, 1H), 7.57-7.67 (m, 2H), 7.72 (s, 1H); **^{13}C NMR** ($CDCl_3$+CD_3OD): δ 12.9, 60.6, 73.2,

74.2, 110.0, 117.9, 126.7, 131.0, 146.2, 171.4; **Analysis**: $C_{12}H_{13}NO_4$ requires C 61.27, H 5.57, N 5.95 found C 61.23, H 5.52, N 5.84%.

Benzyl(1R,2S)-2-(ethoxycarbonyl)-1-(2-cyanophenyl)-2-hydroxyethylcarbamate(10):



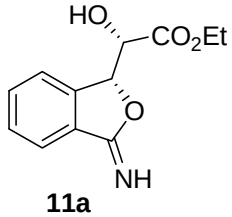
4a **10**

Sodium hydroxide (60 mg, 1.5 mmol) was dissolved in water (4 mL), and 0.5 mL of this NaOH solution was transferred to a small vial containing $K_2OsO_2(OH)_4$ (0.020 mmol for 4 mol %) for later use. To the remainder of the NaOH solution were added the carbamate (1.55 mmol) and *n*-PrOH (2 mL). The mixture was stirred for 2-3 min and placed in a water bath before *tert*-butylhypochlorite16 (175 μL, 1.52 mmol) was slowly added with vigorous stirring. Then, the resulting solution was sequentially treated with a solution of $(DHQD)_2PHAL$ (0.025 mmol for 5 mol %) in *n*-PrOH (1 mL), the o-cyano ethylcinnamate (0.50 mmol), the previously prepared solution of $K_2OsO_2(OH)_4$, and *n*-PrOH (1 mL). The reaction mixture was monitored by TLC to establish completion, quenched by the addition of saturated aqueous sodium sulfite (4 mL) while being cooled in an ice-water bath, and stirred for an additional 30 min. The separated aqueous phase was extracted with EtOAc (3 X 5 mL), and the combined organic extracts were washed with water (3 mL) followed by brine (5 mL), dried over Na_2SO_4, and concentrated under reduced pressure to give crude products which was purified by column chromatography

[silica gel (230-400 mesh) and petroleum ether: EtOAc (60:40) as an eluent] gave product **10** in 64% yield with dr 6:1.

Gum; $[\alpha]^{D}_{25}$ -36.06 (*c* 1.10, $CHCl_3$); **IR** ($CHCl_3$): 756, 857, 974, 1037, 1095, 1184, 1202, 1275, 1291, 1319, 1347, 1368, 1393, 1477, 1573, 1607, 1640, 1716, 2219, 2984, 3023, 3415 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): δ 1.28 (t, *J* = 7.16 Hz, 3H), 3.34 (d, *J* = 7.51 Hz, 1H), 4.29 (q, *J* = 7.16 Hz, 2H), 4.50 (s, 1H), 5.06 (dd, *J* = 2.38, 7.51 Hz, 1H), 5.62 (d, *J* = 8.9 Hz, 1H), 5.85 (d, *J* = 8.9 Hz, 1H), 7.32-7.36 (m, 5H), 7.39-7.56 (m, 3H), 7.66-7.77 (m, 1H); **^{13}C NMR** ($CDCl_3$): δ 14.2, 55.3, 60.3, 62.8, 72.5, 111.1, 117.0, 122.0, 128.4, 132.8, 133.2, 142.9, 145.8, 155.3, 172.0; **Analysis**: $C_{12}H_{13}NO_4$ requires C 61.27, H 5.57, N 5.95 found C 61.26, H 5.54, N 5.89.

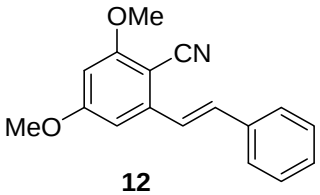
Ethyl 2-(1,3-dihydro-1-iminoisobenzofuran-3-yl)-2-hydroxyacetate (11a):



11a

IR ($CHCl_3$): 687, 728, 975, 1050, 1320, 1385, 1468, 1498, 1678, 1758, 2874, 2958, 3413cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): δ 1.29 (t, *J* = 6.85 Hz, 3H), 4.29 (d, *J* = 6.85 Hz, 2H), 4.73 (d, *J* = 2.33 Hz, 1H), 6.10 (s, 1H), 7.59 (t, *J* = 6.60 Hz, 2H), 7.75 (t, *J* = 6.60 Hz, 1H), 7.92 (d, *J* = 8.48 Hz, 1H); **^{13}C NMR** ($CDCl_3$): δ 12.4, 60.9, 69.4, 88.2, 121.5, 123.8, 128.2, 128.9, 134.1, 144.4, 167.8, 169.6; ESI-MS: *m*/*z* 235.01$[M+Na]^+$.

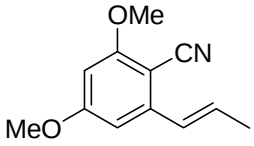
2, 4-Dimethoxy-6-styrylbenzonitrile (12):



12

Yield: 79%; colorless solid; mp 147 – 148 ºC; **IR** ($CHCl_3$): 694, 831, 953, 1045, 1073, 1150, 1203, 1326, 1460, 1570, 1595, 2216 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.90 (s, 6H), 6.34 (d, *J* = 2.3 Hz, 1H), 6.80 (d, *J* = 2.3 Hz, 1H), 7.20 (d, *J* = 16.4 Hz, 1H), 7.26-7.30 (m, 1H), 7.32-7.38 (m, 3H), 7.55 (d, *J* = 7.38 Hz, 2H); **^{13}C NMR** ($CDCl_3$): δ 55.6, 56.0, 94.1, 97.4, 101.4, 115.7, 124.4, 127.2, 128.8, 133.5, 136.1, 143.4, 163.2, 163.9; **Analysis**: $C_{17}H_{15}NO_2$ requires C 76.96, H 5.70, N 5.28 found C 76.92, H 5.68, N 5.24%.

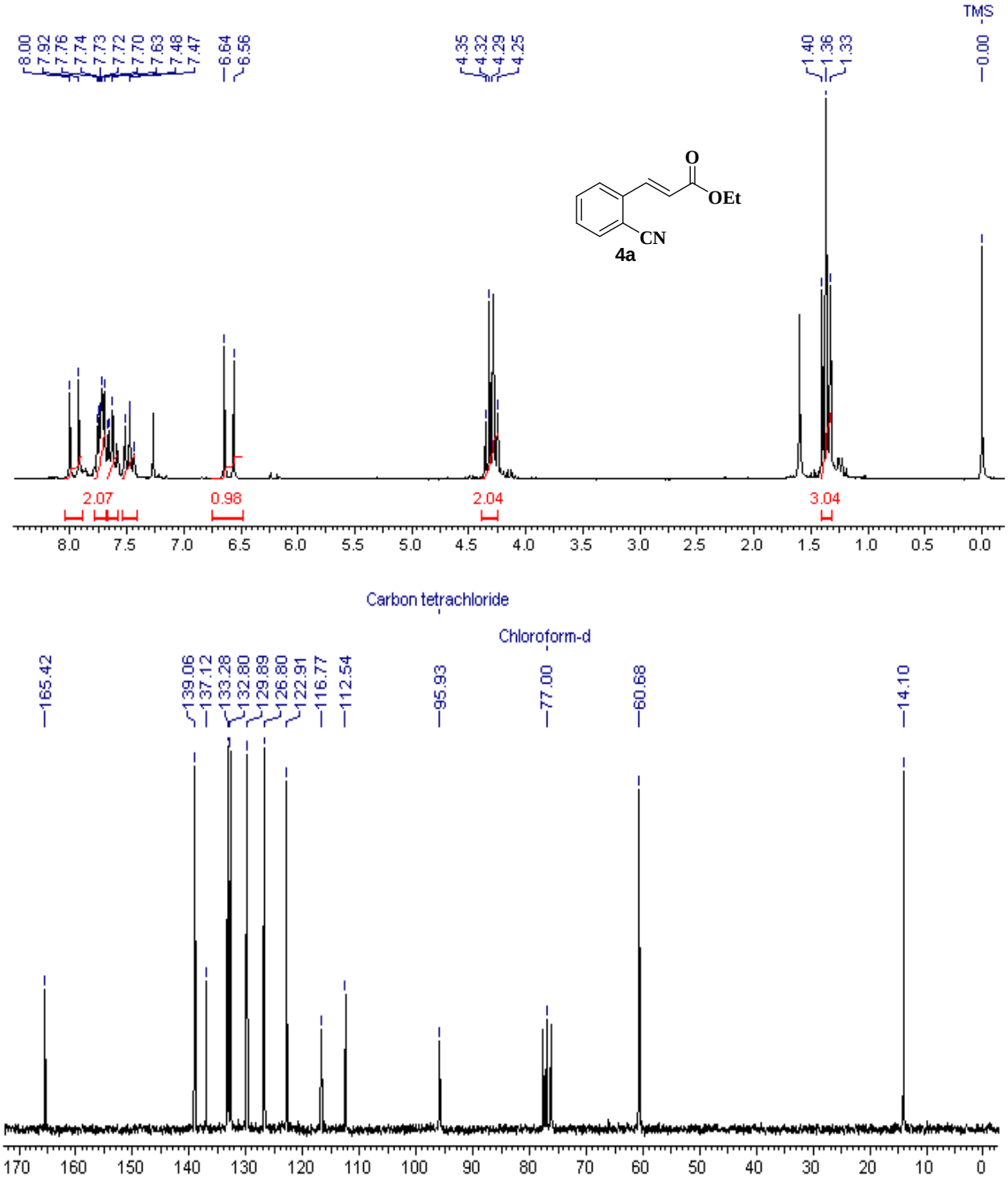
2,4-Dimethoxy-6-((E)-prop-1-enyl)-benzonitrile (14):



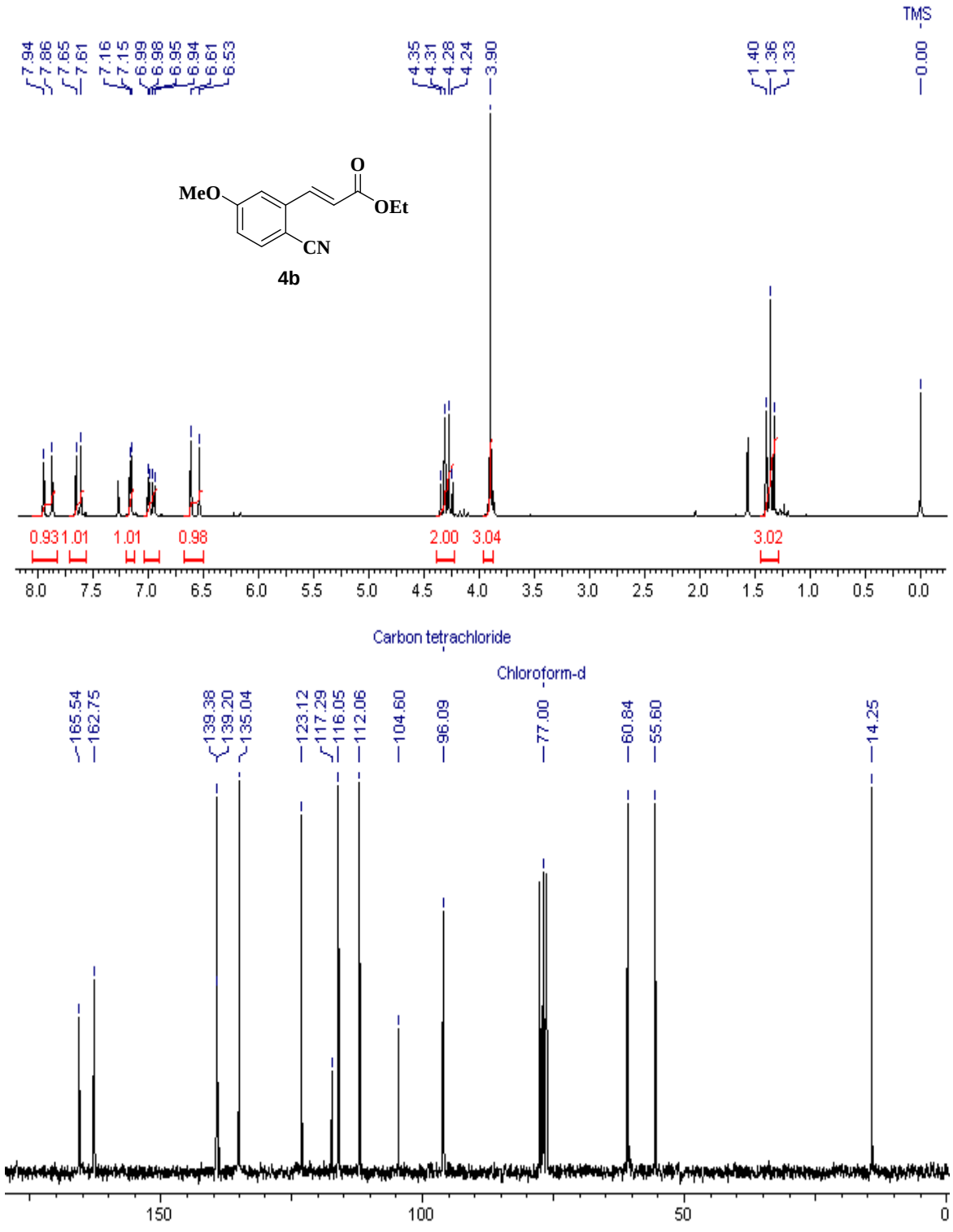
14

Yield: 72%; Gum; **IR** ($CHCl_3$): 720, 857, 9662, 1036, 1092, 1129, 1260, 1318, 1381, 1386, 1450, 1576, 1616, 1629, 1647, 2216, 2982, 3030 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): δ 1.95 (d, *J* = 6.4 Hz, 3H), 3.86 (s, 3H), 3.89 (s, 3H), 6.29-6.30 (m, 1H), 6.39-6.46 (m, 1H), 6.60 (d, *J* = 1.8 Hz, 1H), 6.69 (d, *J* = 15.5 Hz, 1H); **^{13}C NMR** ($CDCl_3$): δ 18.7, 55.5, 55.9, 96.8, 101.5, 106.4, 115.7, 126.6, 127.6, 131.4, 144.1, 163.1, 163.8; **Analysis**: $C_{12}H_{13}NO_2$ requires C 70.92, H 6.45, N 6.89 found C 70.89, H 6.40, N 6.85%.

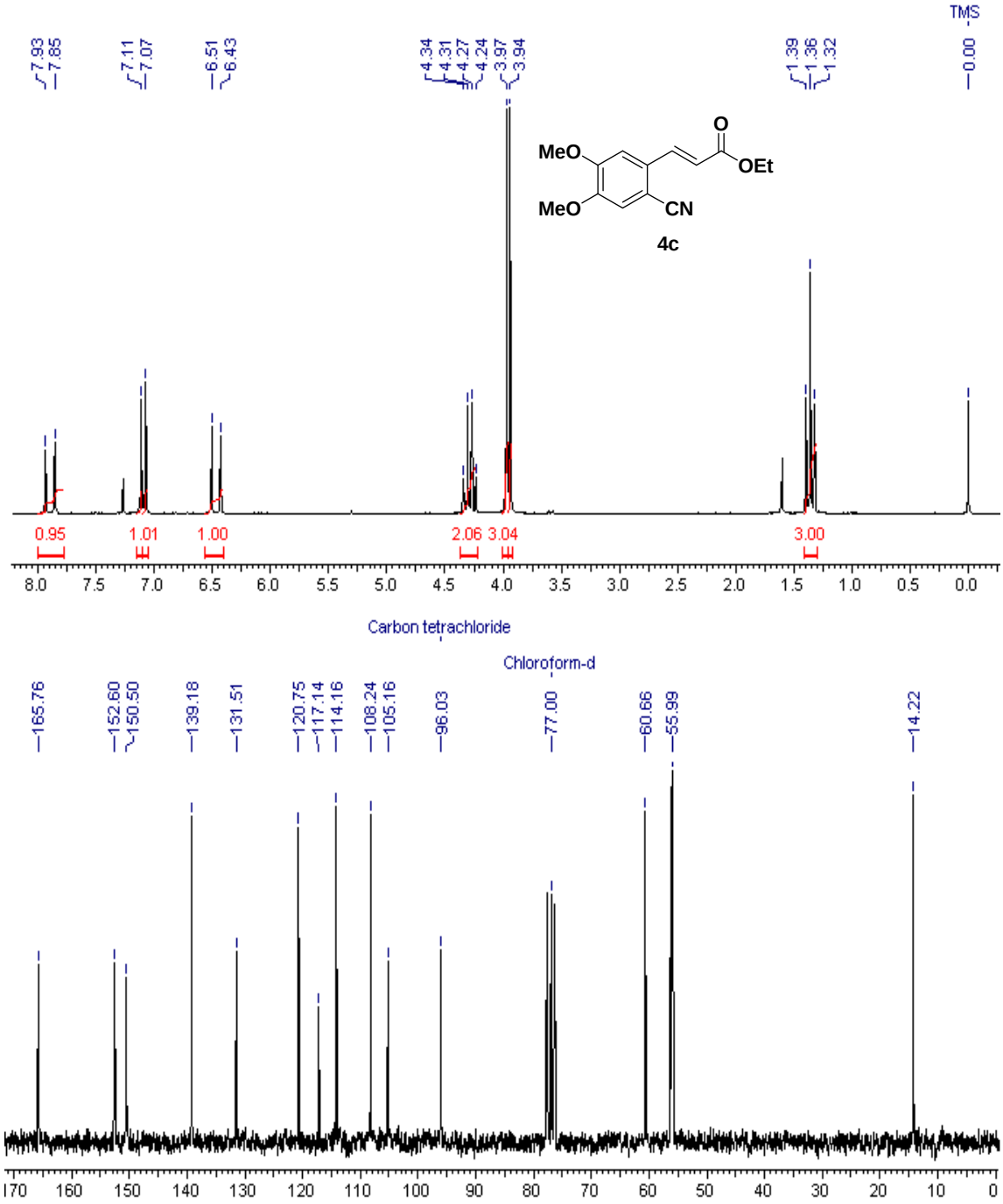
2. Spectra



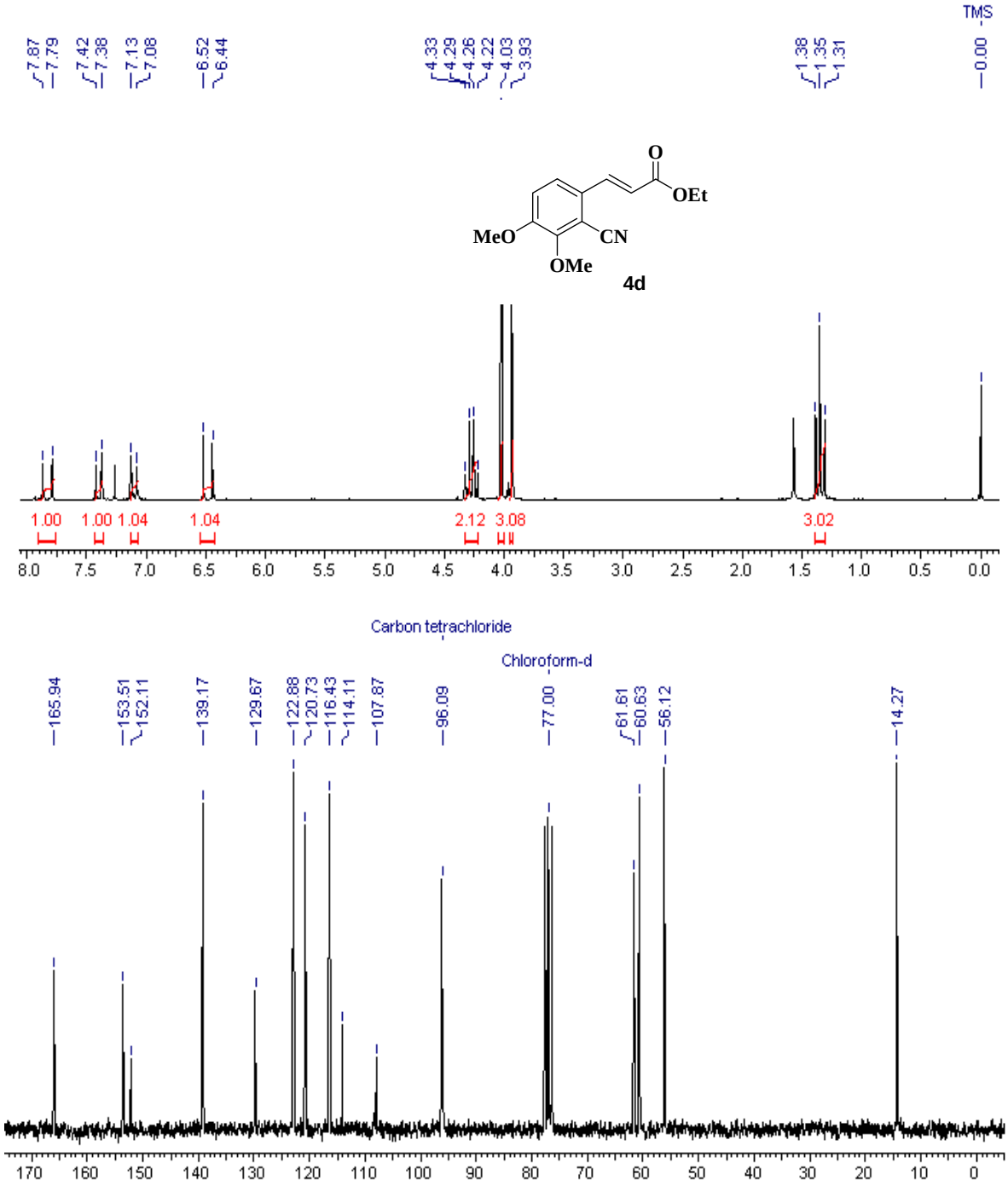
^{1}H and ^{13}C NMR spectra of 4a



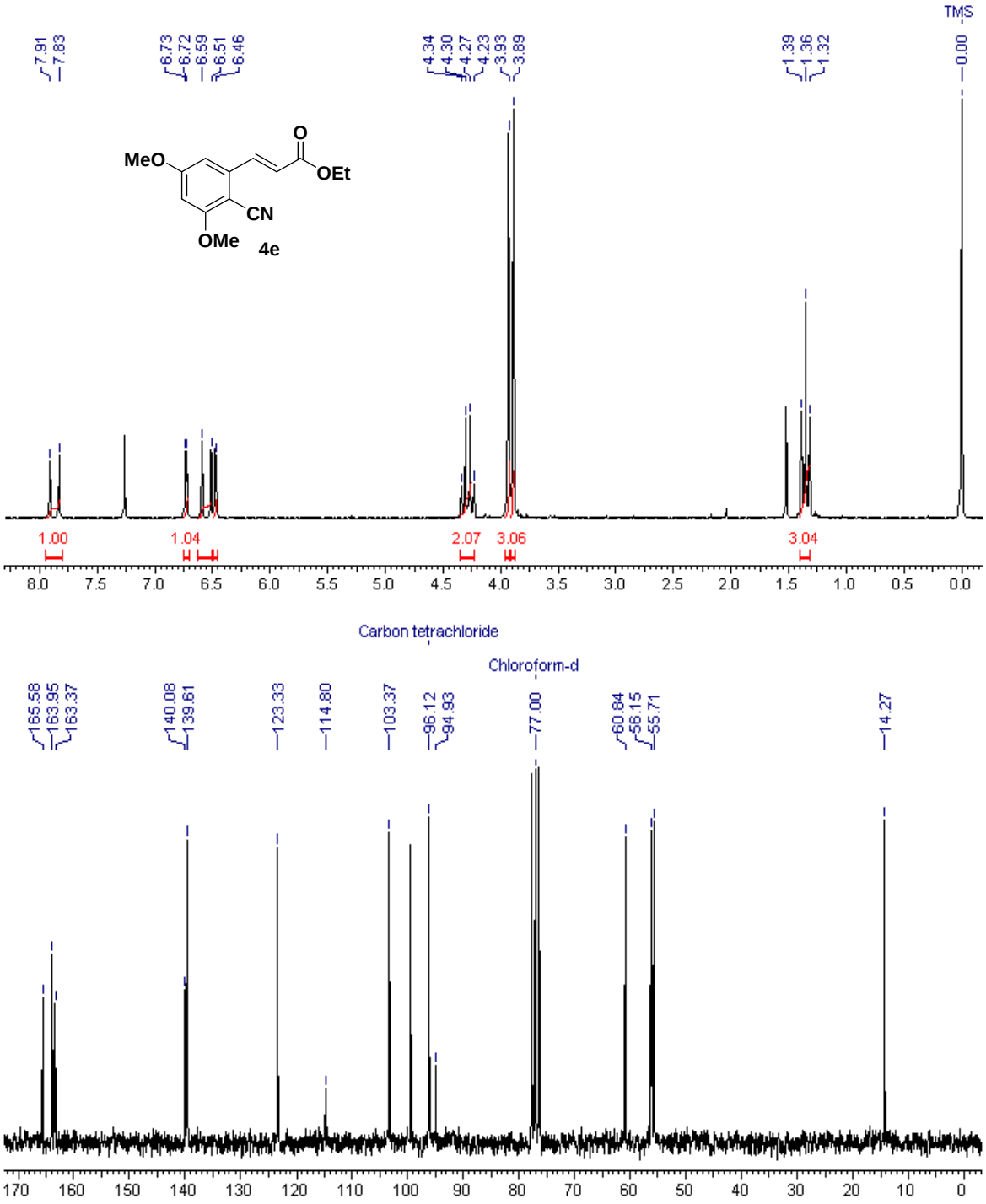
^{1}H and ^{13}C NMR spectra of 4b



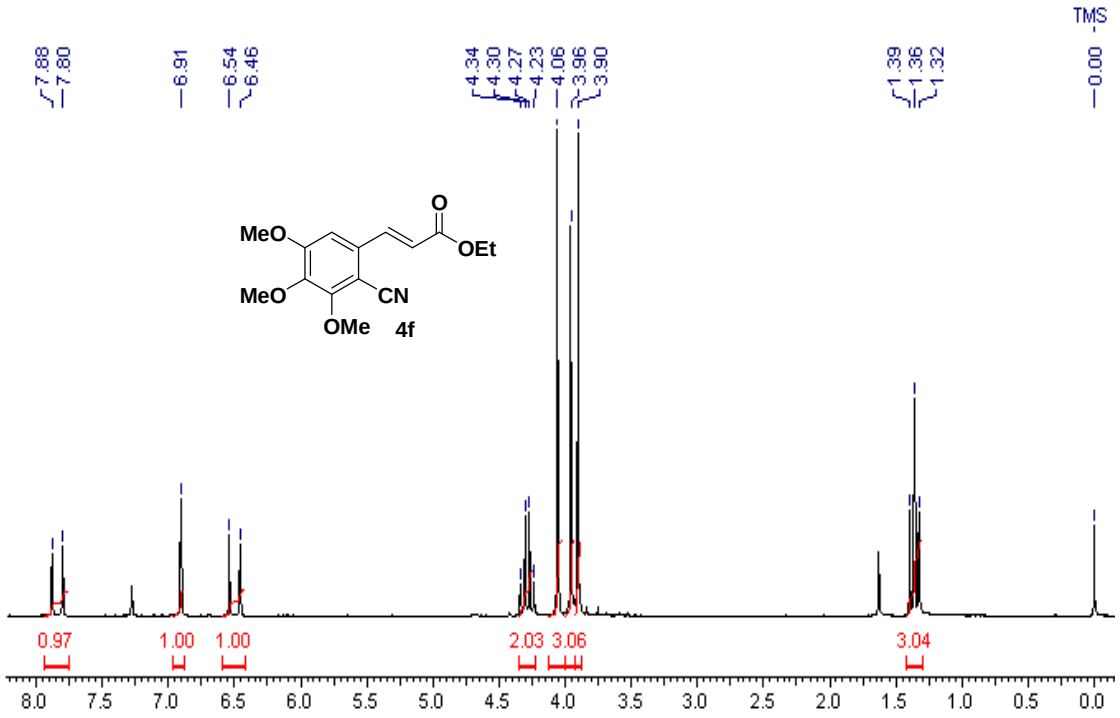
^{1}H and ^{13}C NMR spectra of 4c

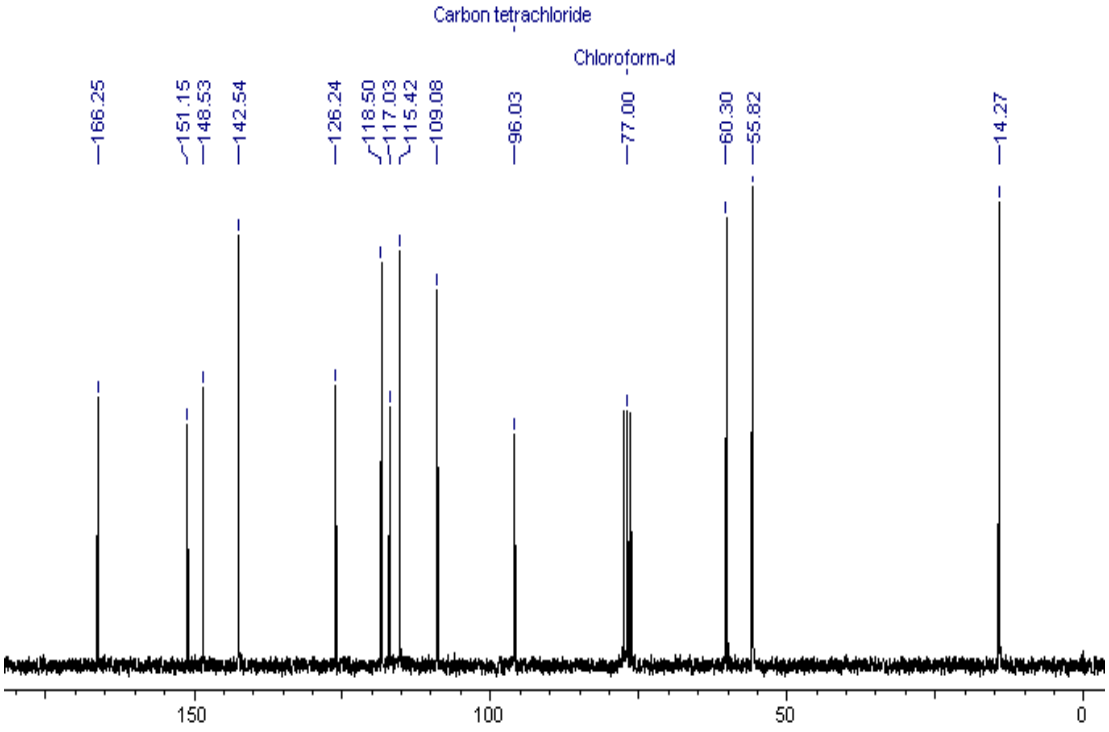


^{1}H and ^{13}C NMR spectra of 4d

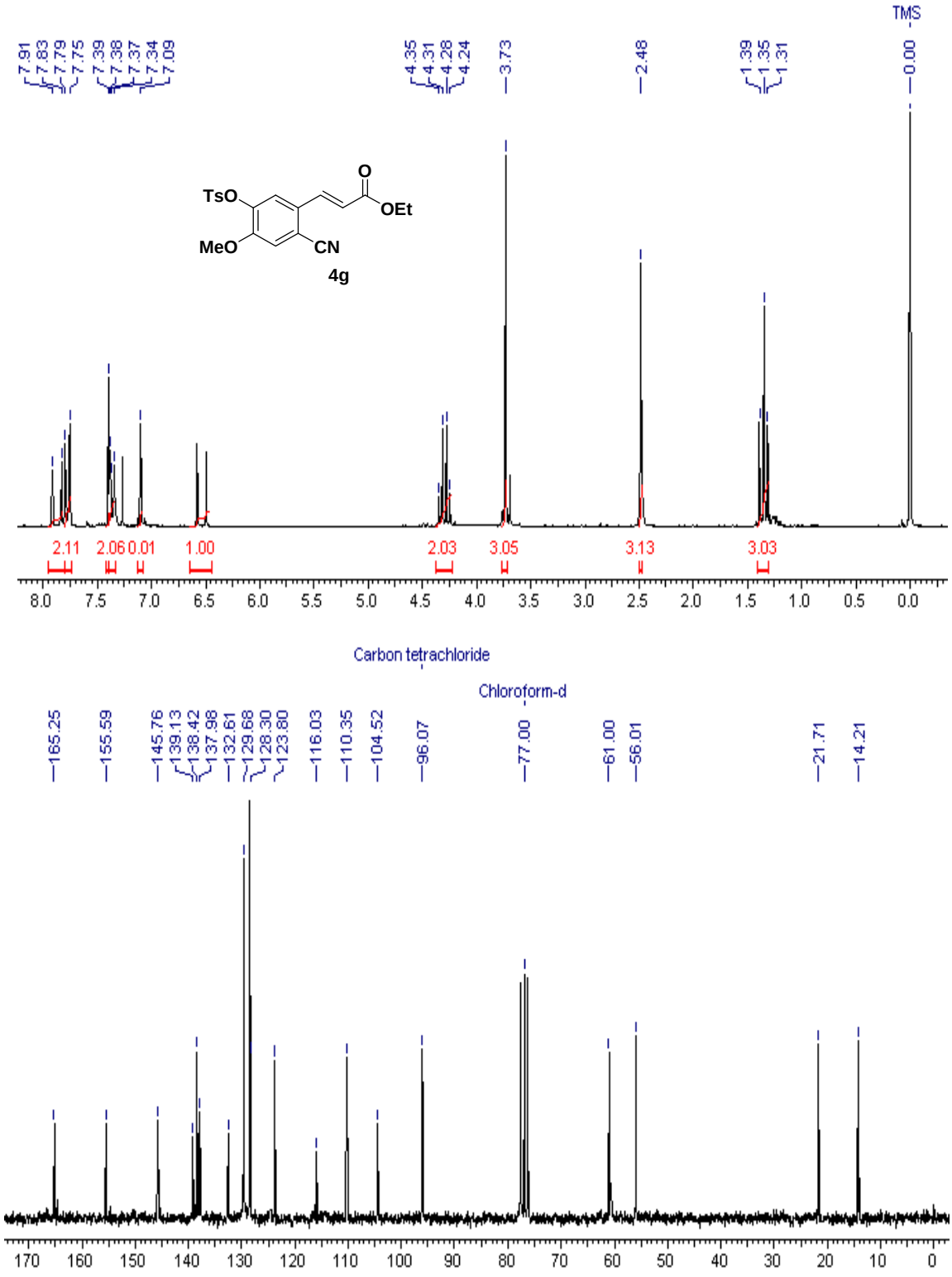


^{1}H and ^{13}C NMR spectra of 4e

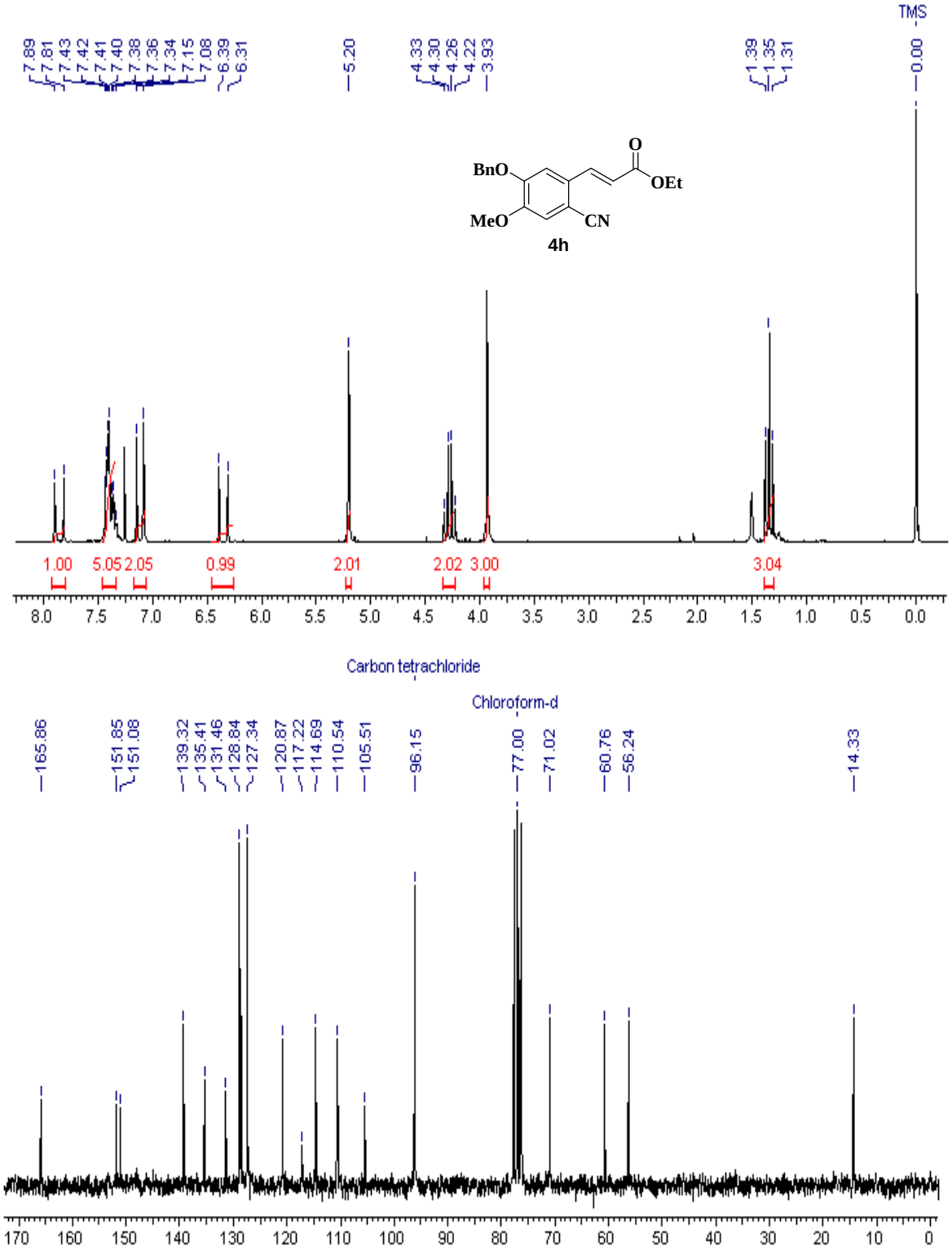




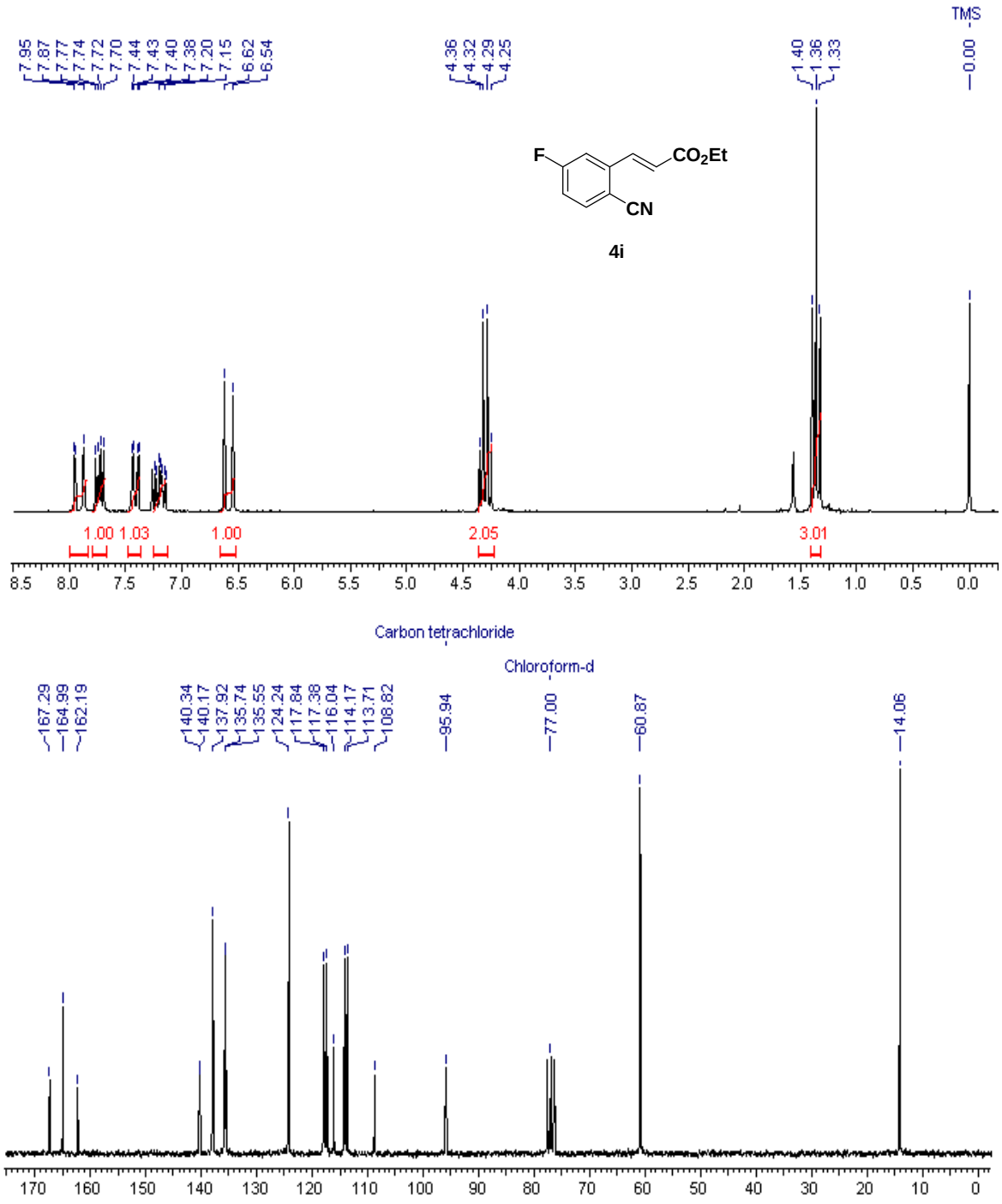
^{1}H and ^{13}C NMR spectra of 4f



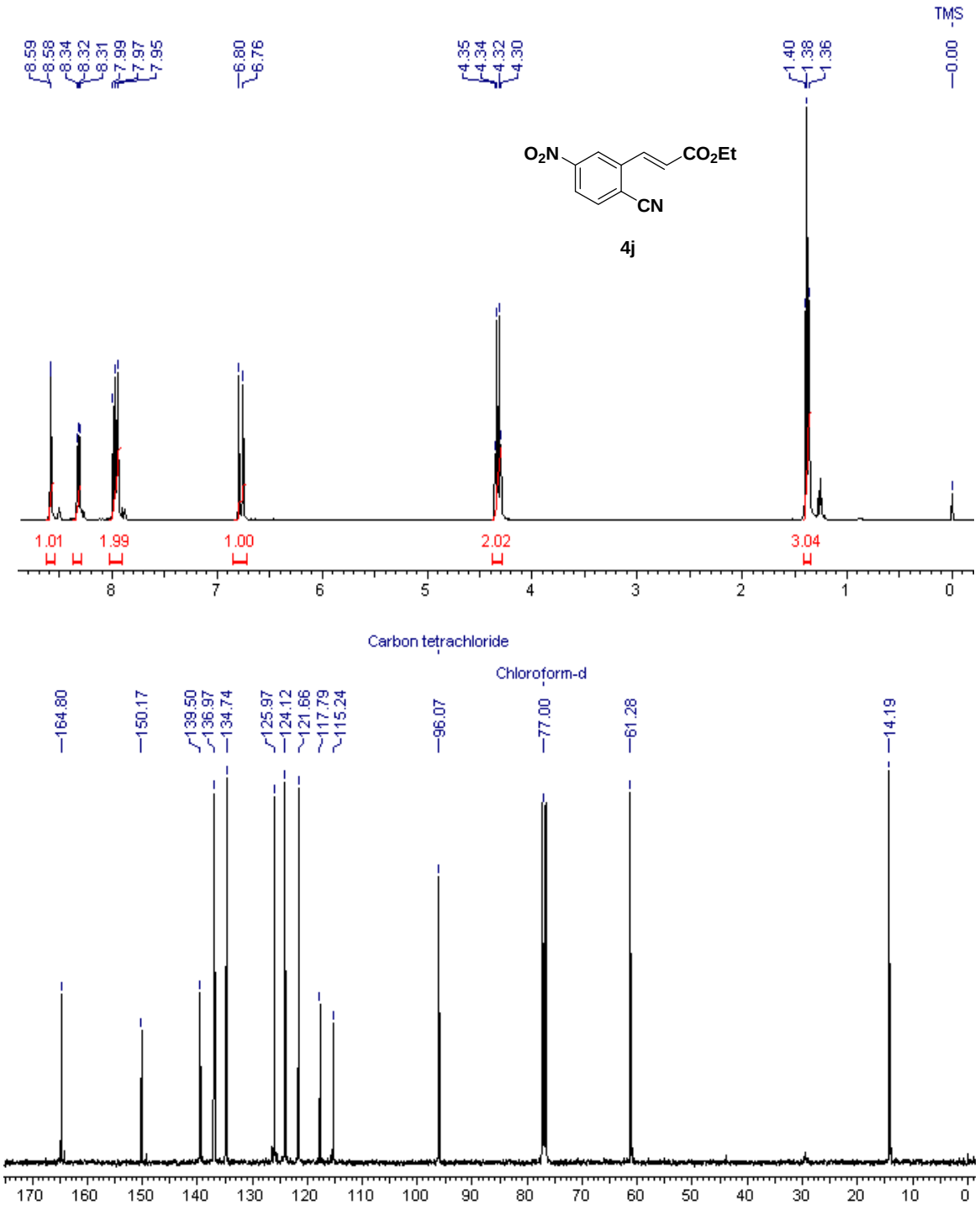
^{1}H and ^{13}C NMR spectra of 4g



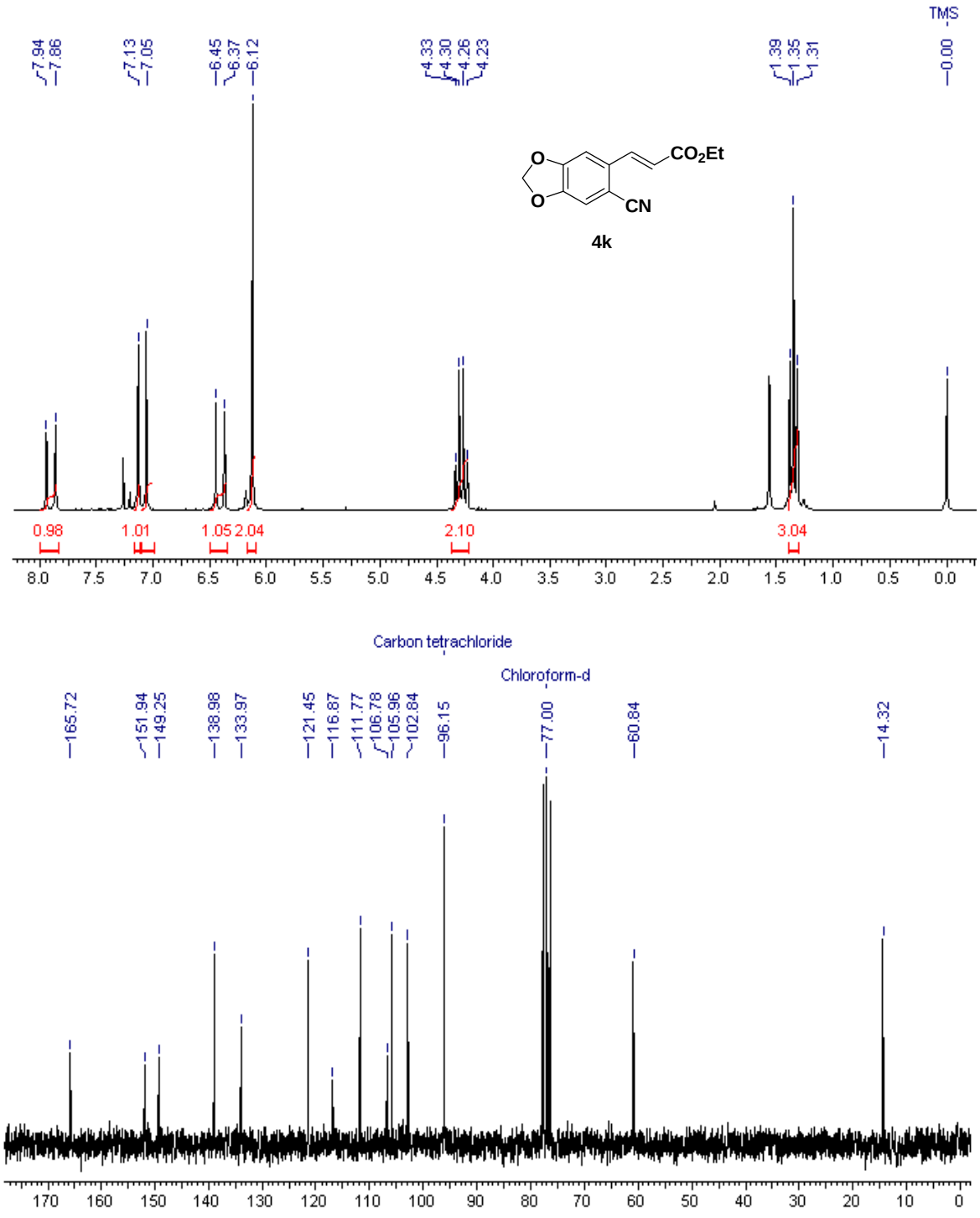
^{1}H and ^{13}C NMR spectra of 4h



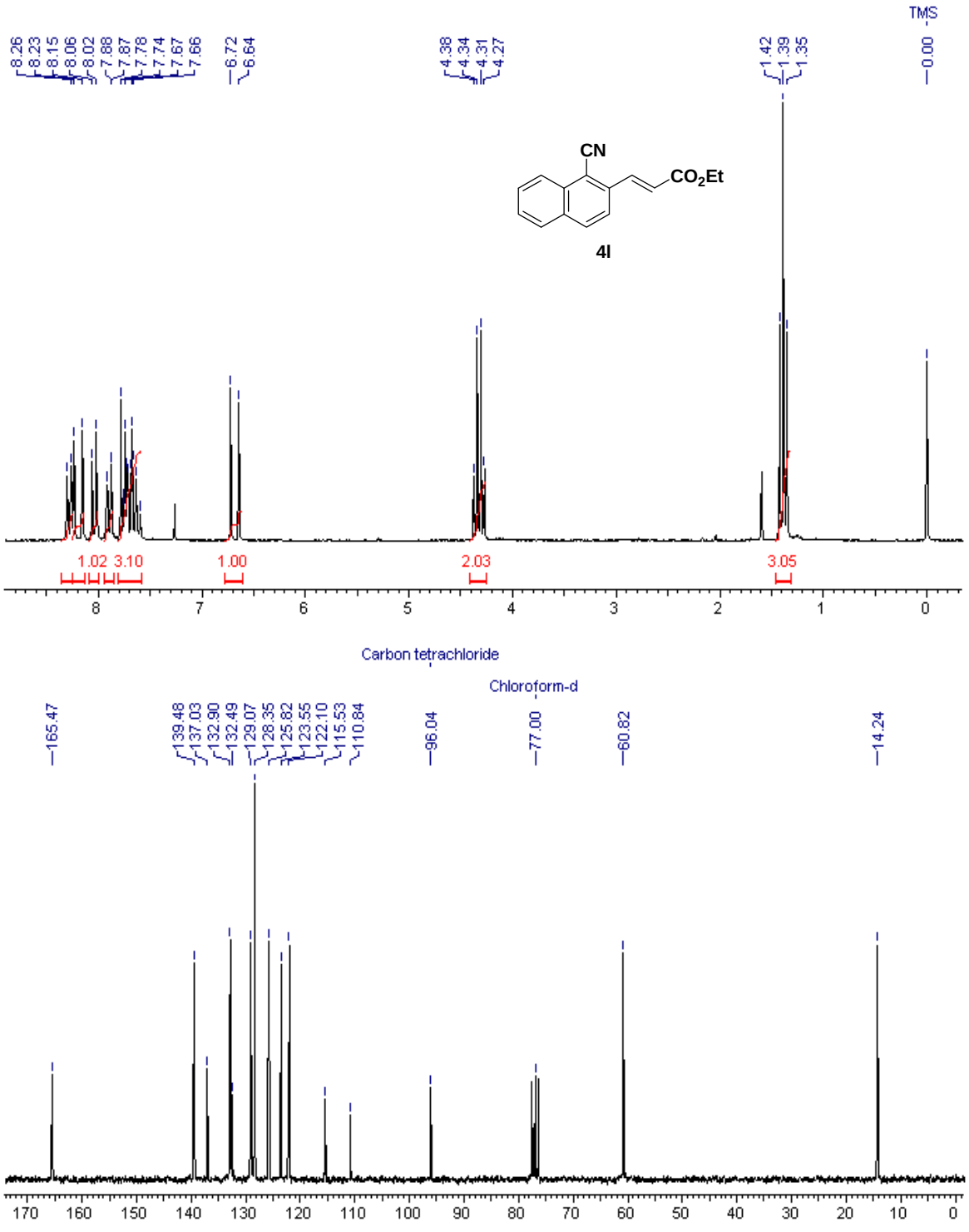
^{1}H and ^{13}C NMR spectra of 4i



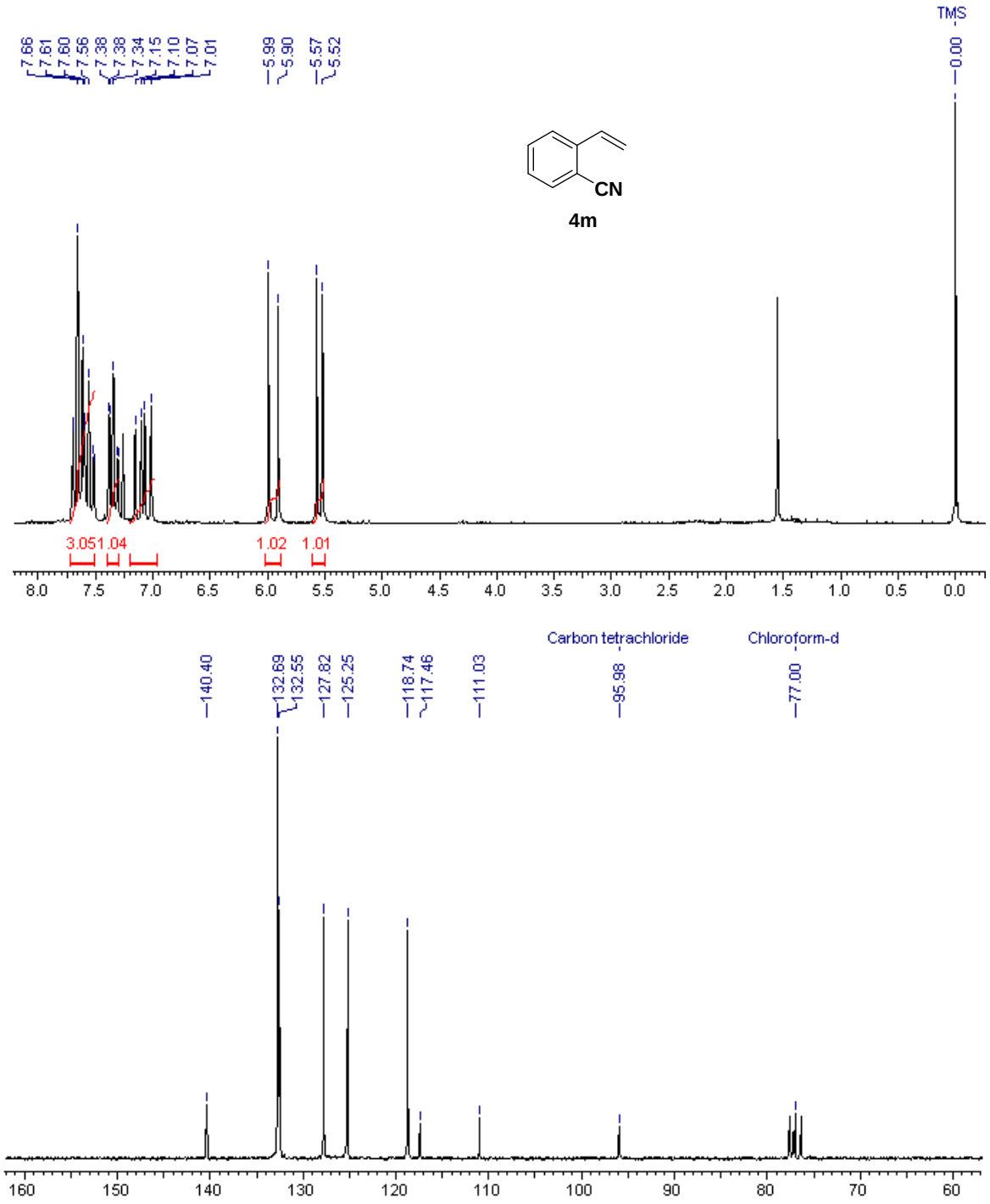
^{1}H and ^{13}C NMR spectra of 4j



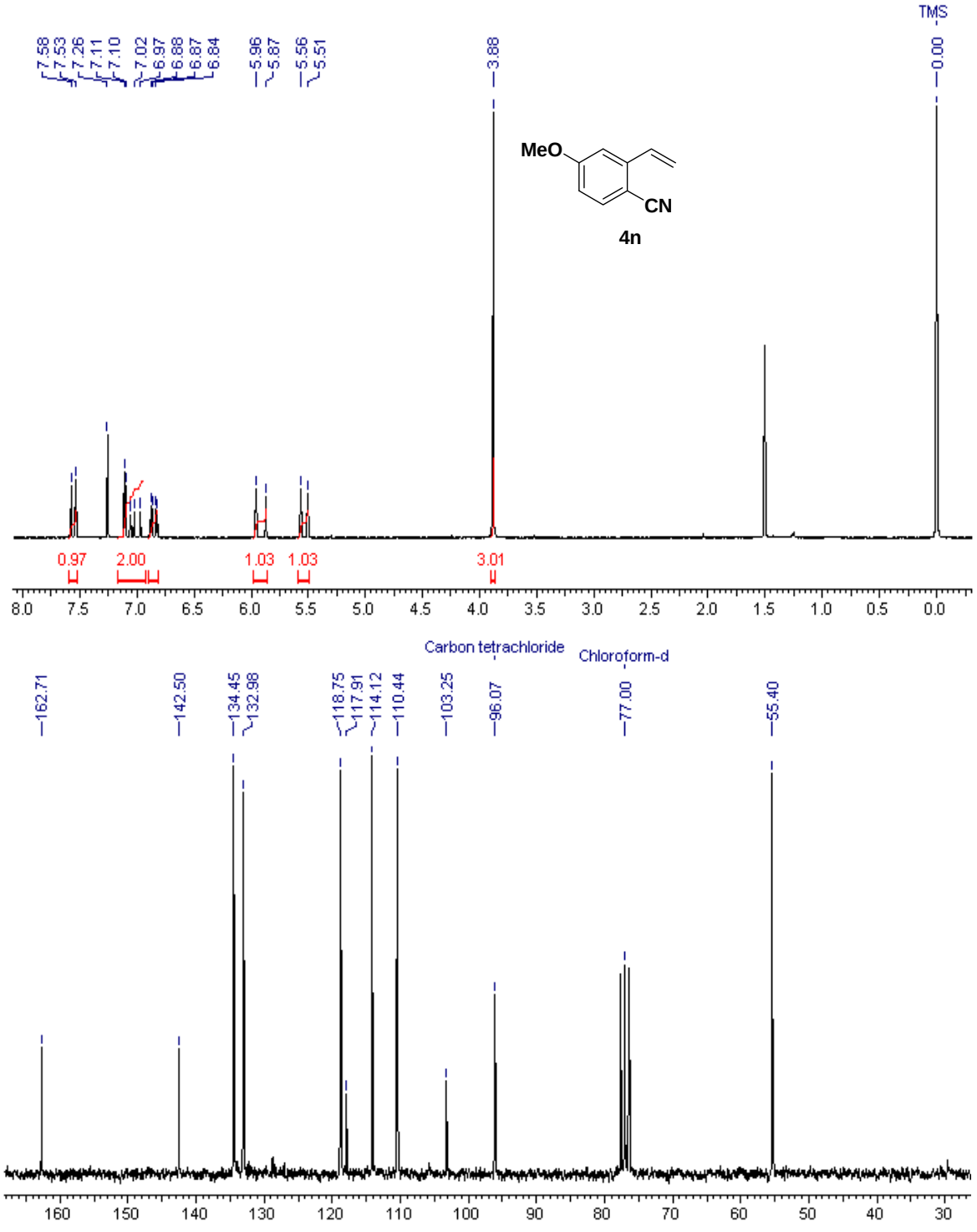
^{1}H and ^{13}C NMR spectra of 4k



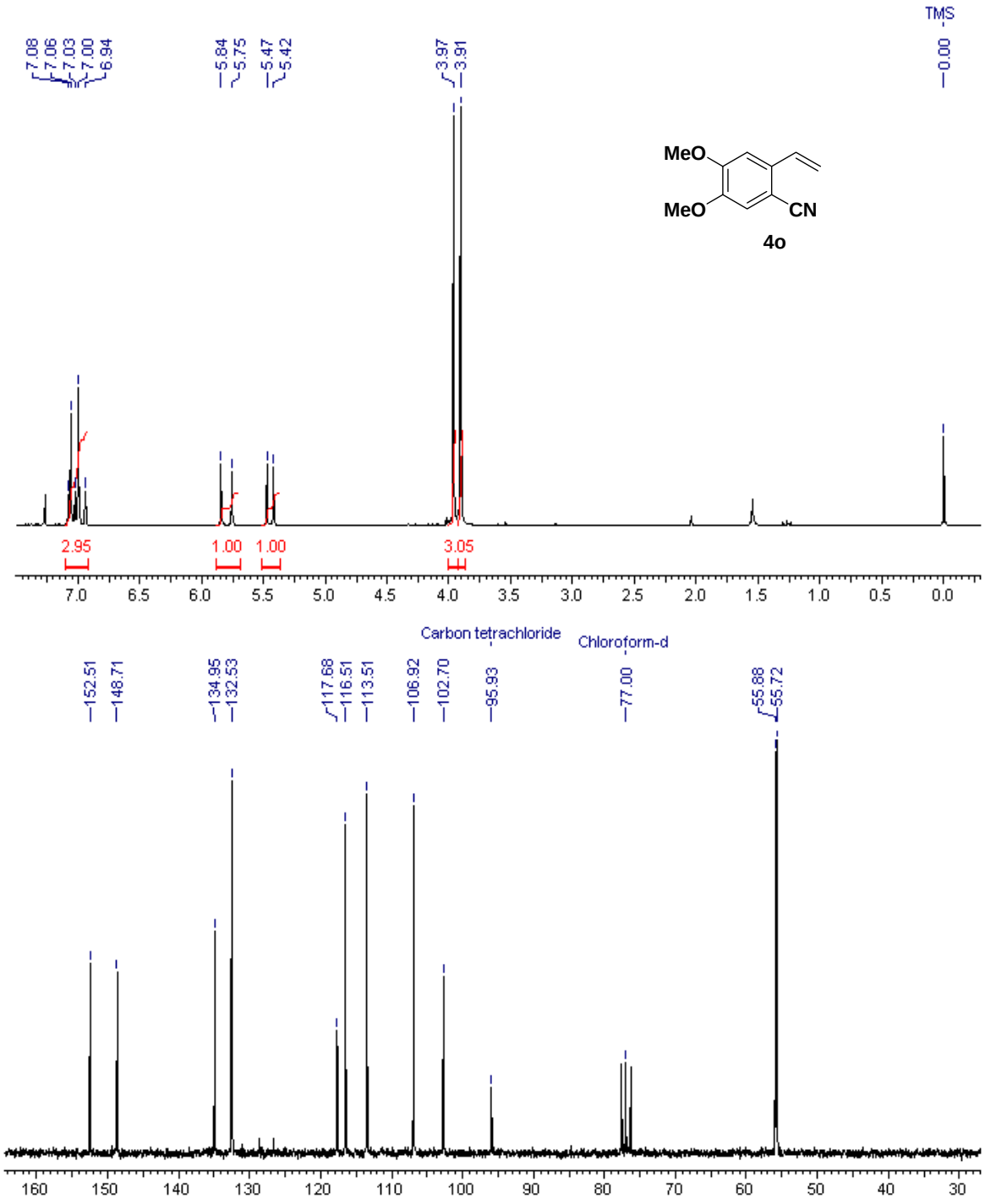
^{1}H and ^{13}C NMR spectra of 4l



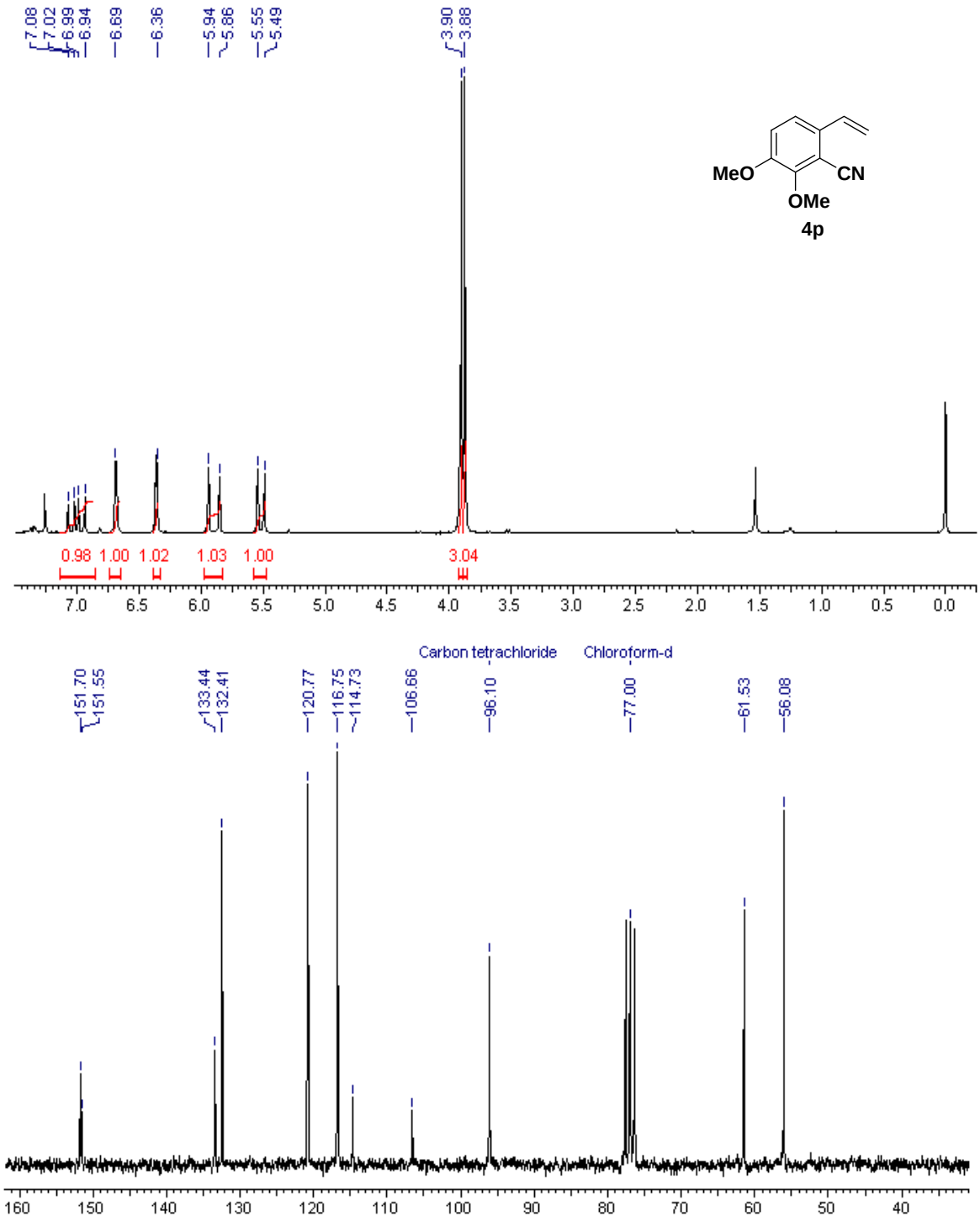
^{1}H and ^{13}C NMR spectra of 4m



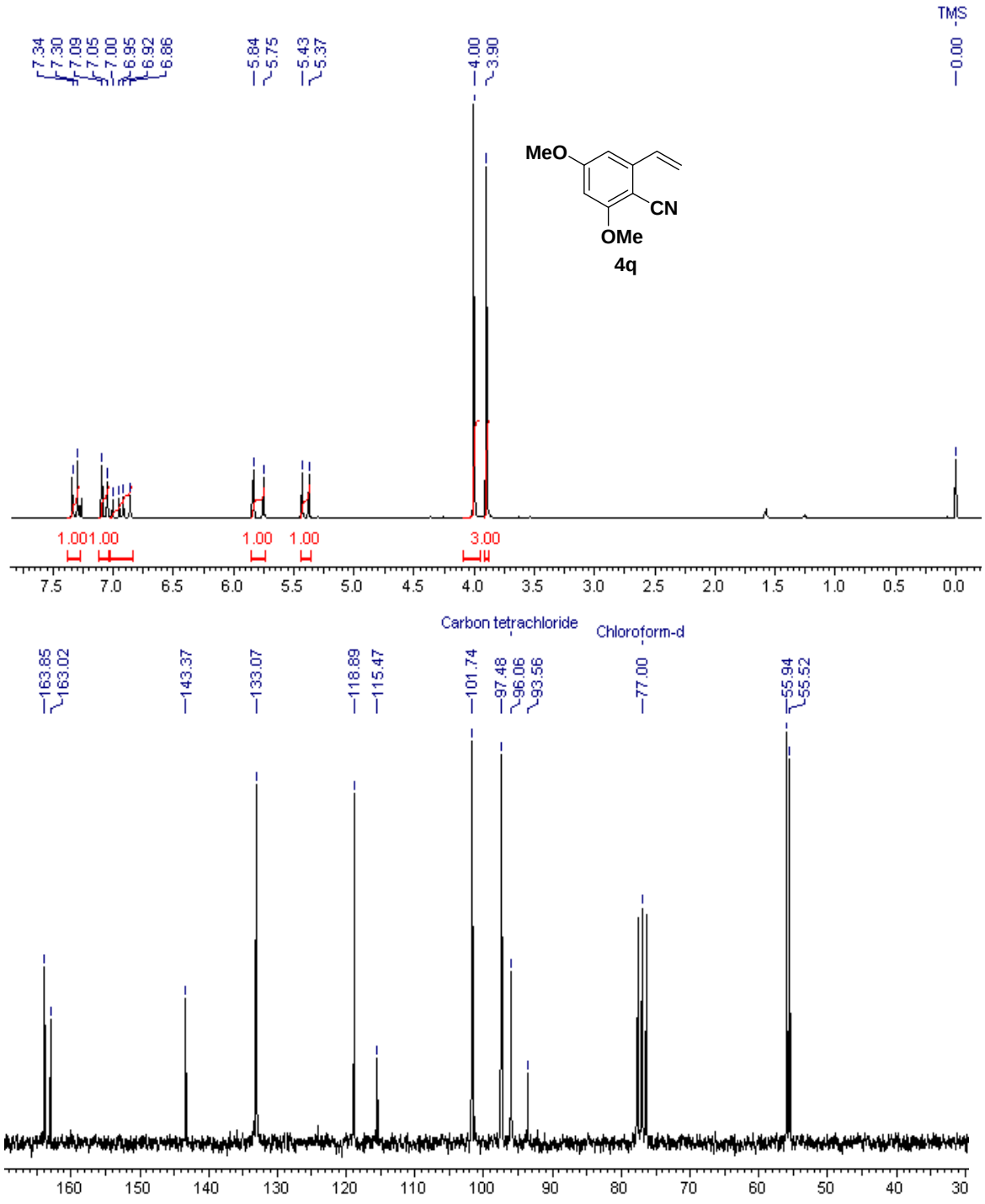
^{1}H and ^{13}C NMR spectra of 4n



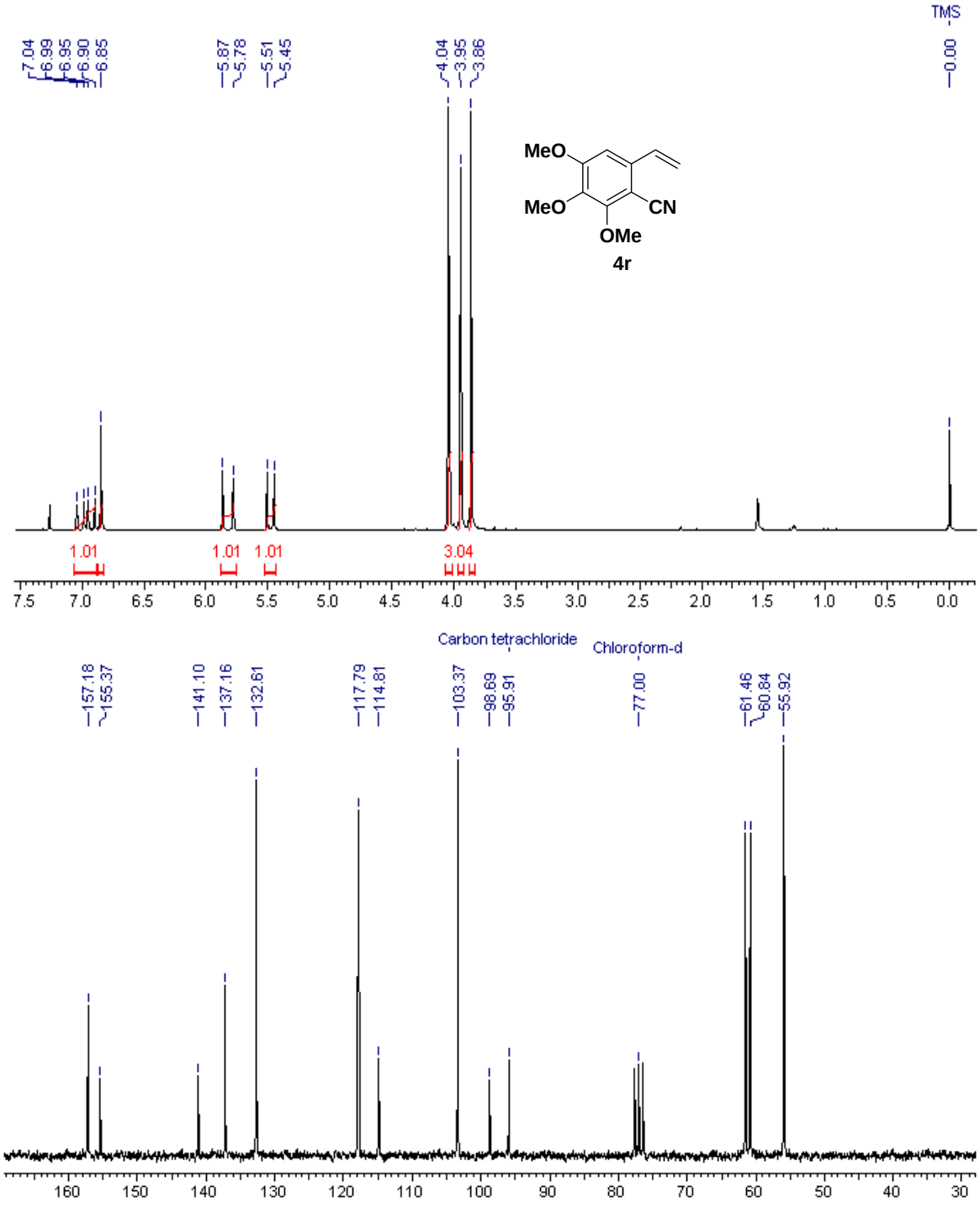
^{1}H and ^{13}C NMR spectra of 4o



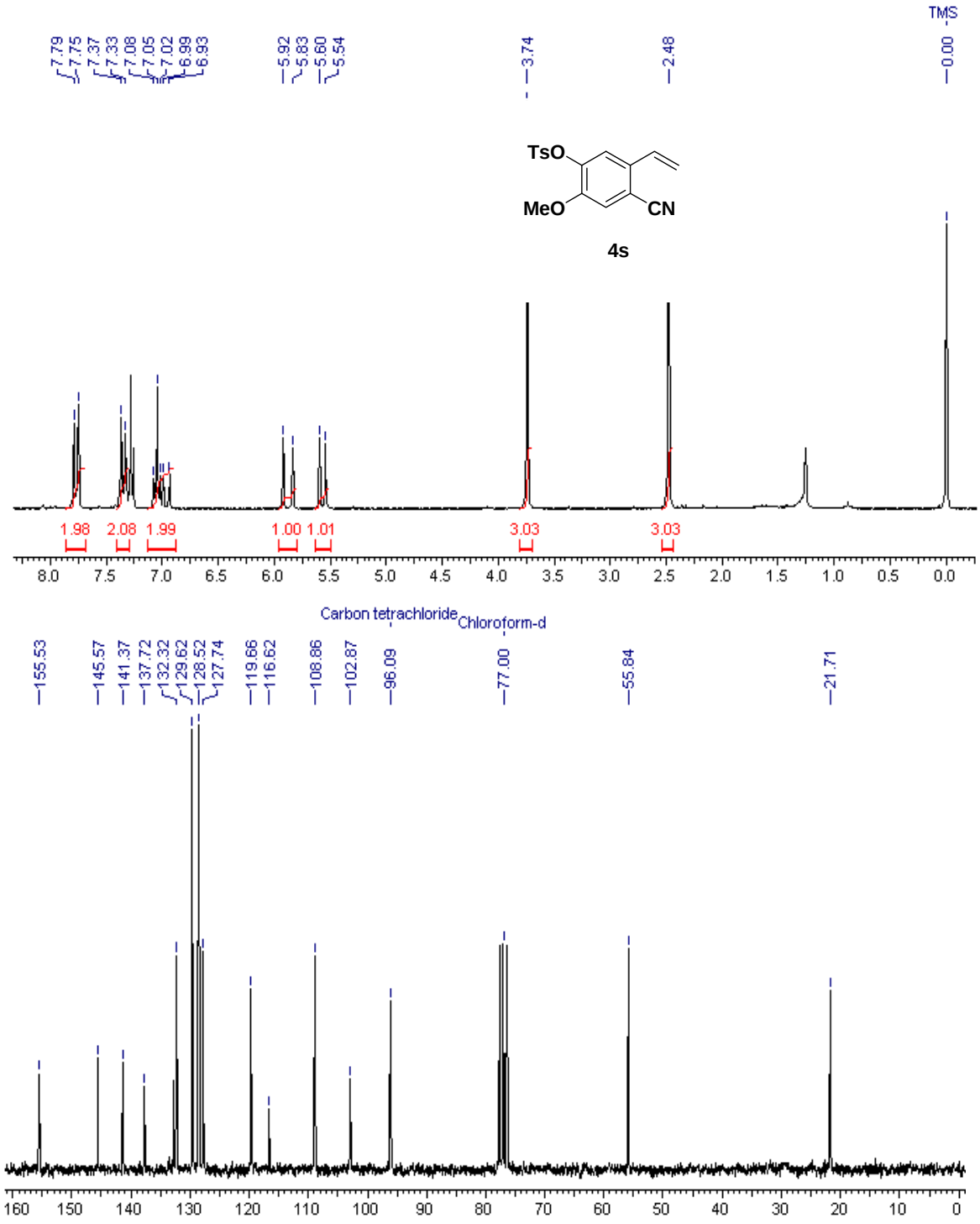
^{1}H and ^{13}C NMR spectra of 4p



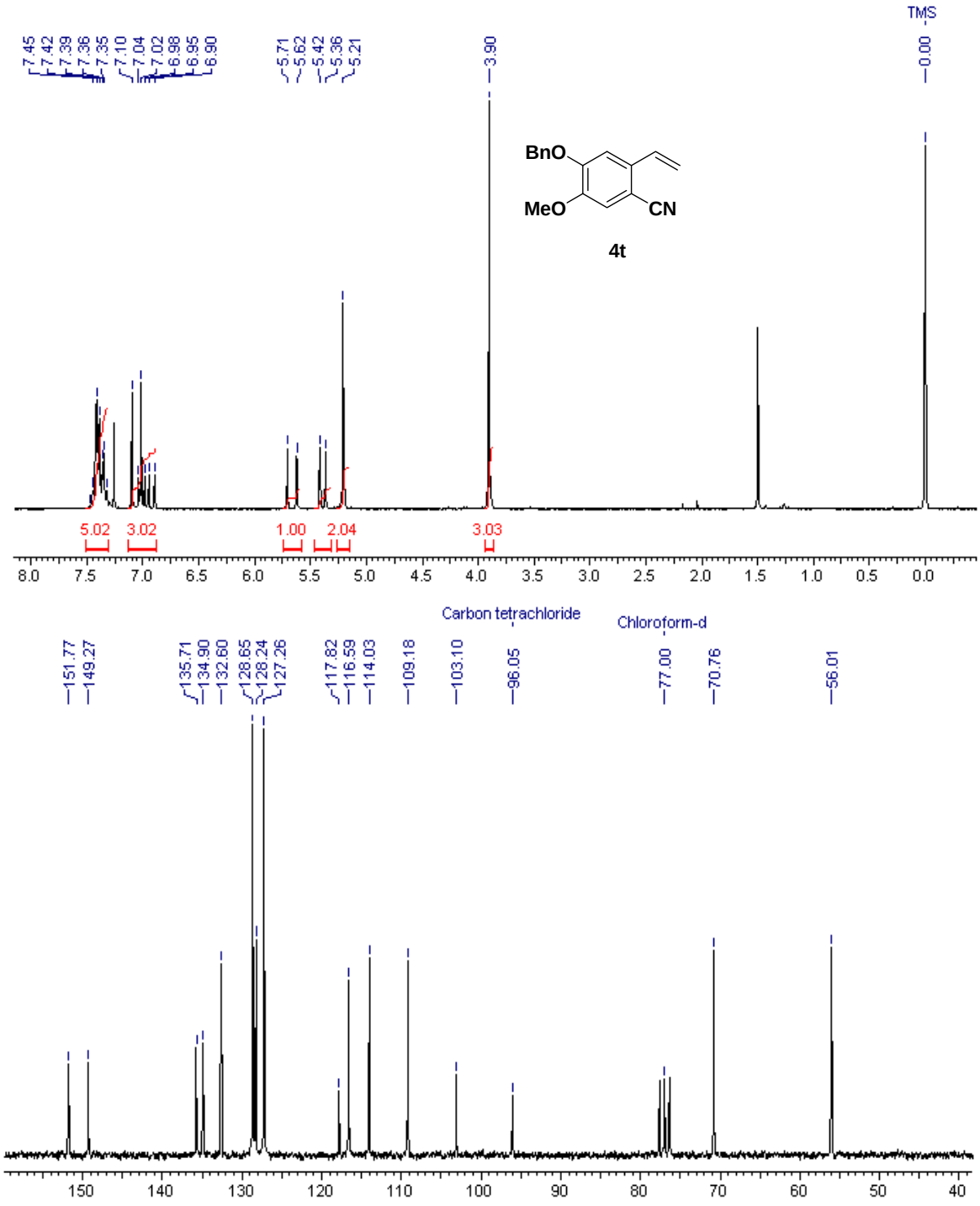
^{1}H and ^{13}C NMR spectra of 4q



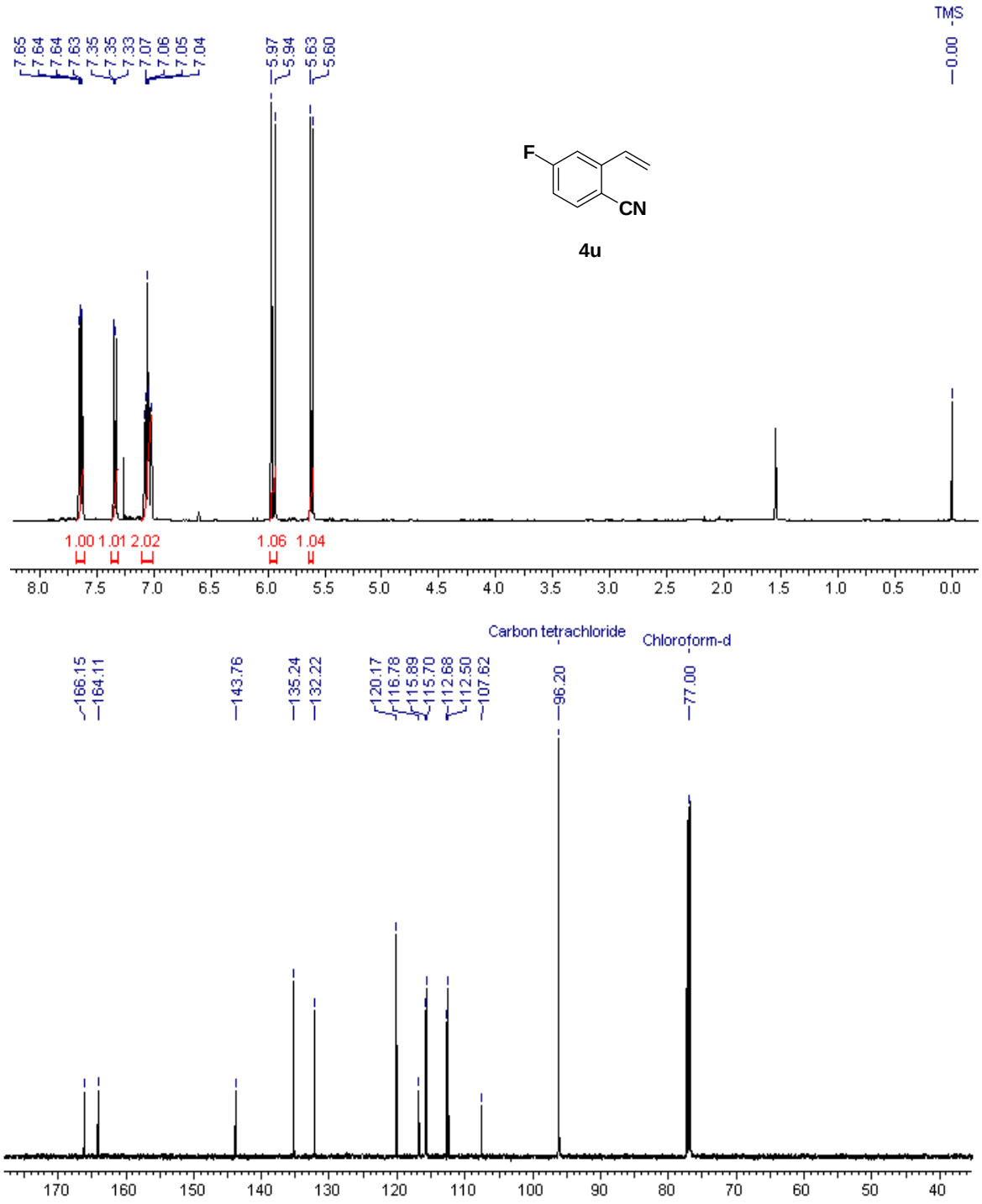
^{1}H and ^{13}C NMR spectra of 4r



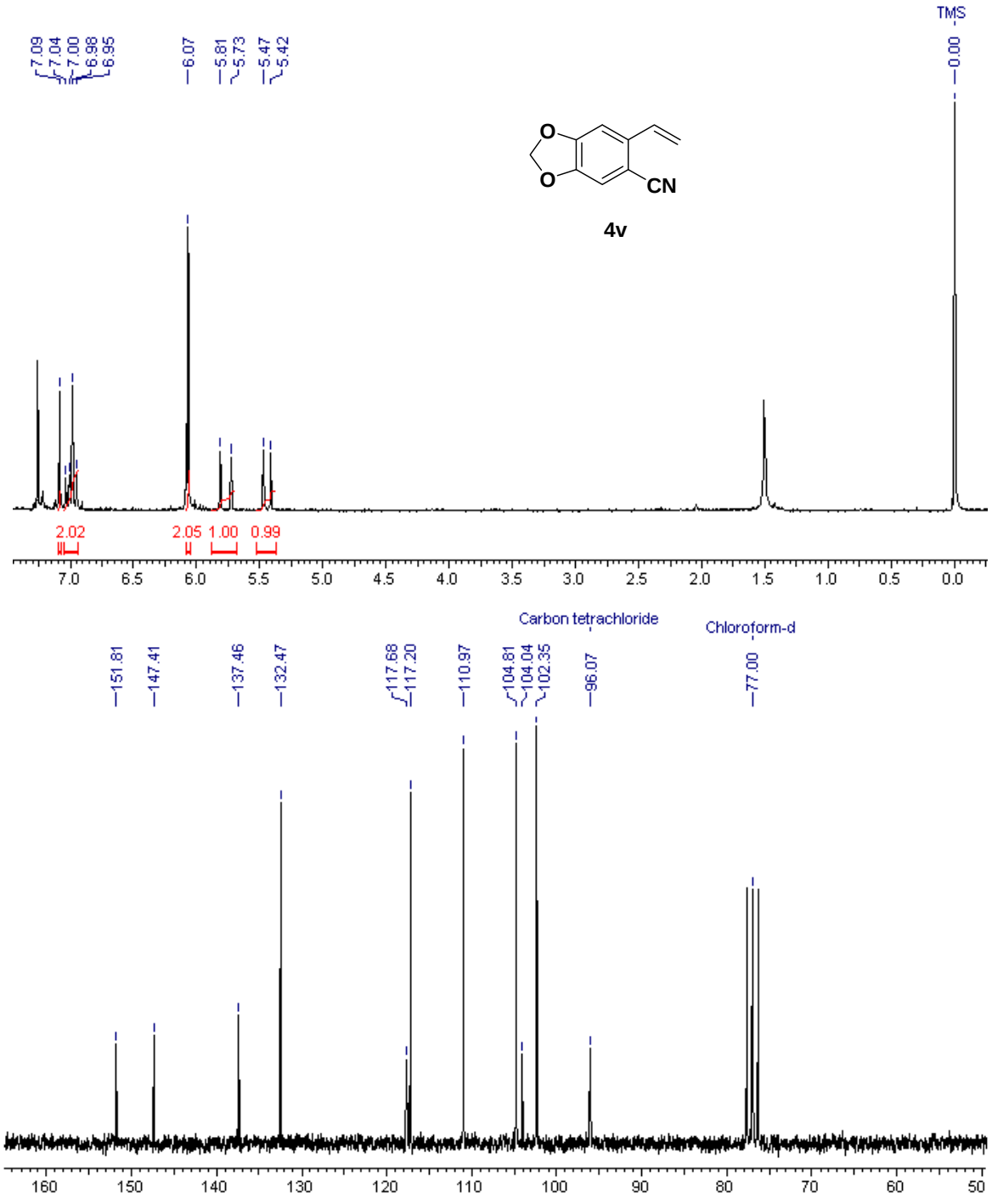
^{1}H and ^{13}C NMR spectra of 4s



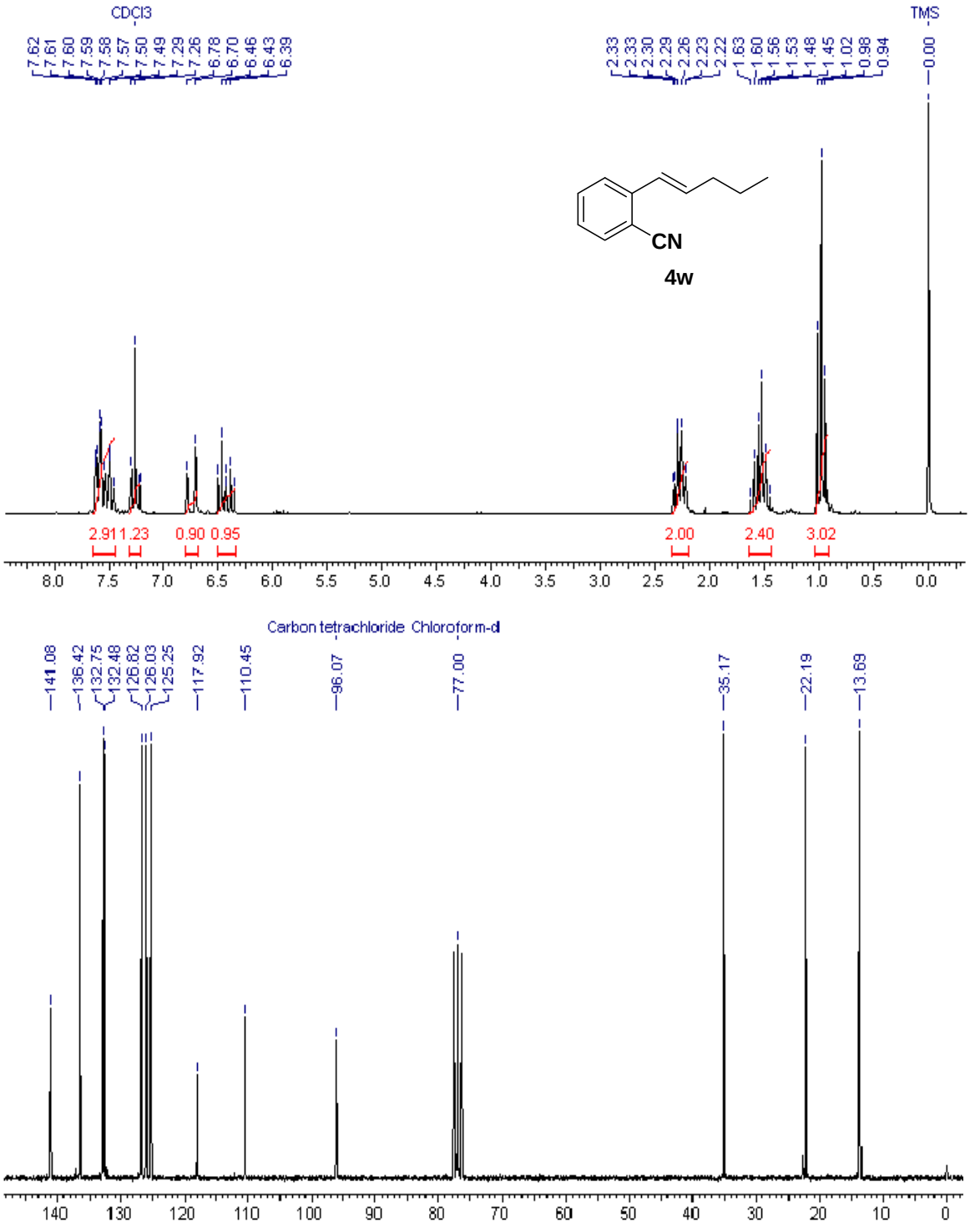
^{1}H and ^{13}C NMR spectra of 4t



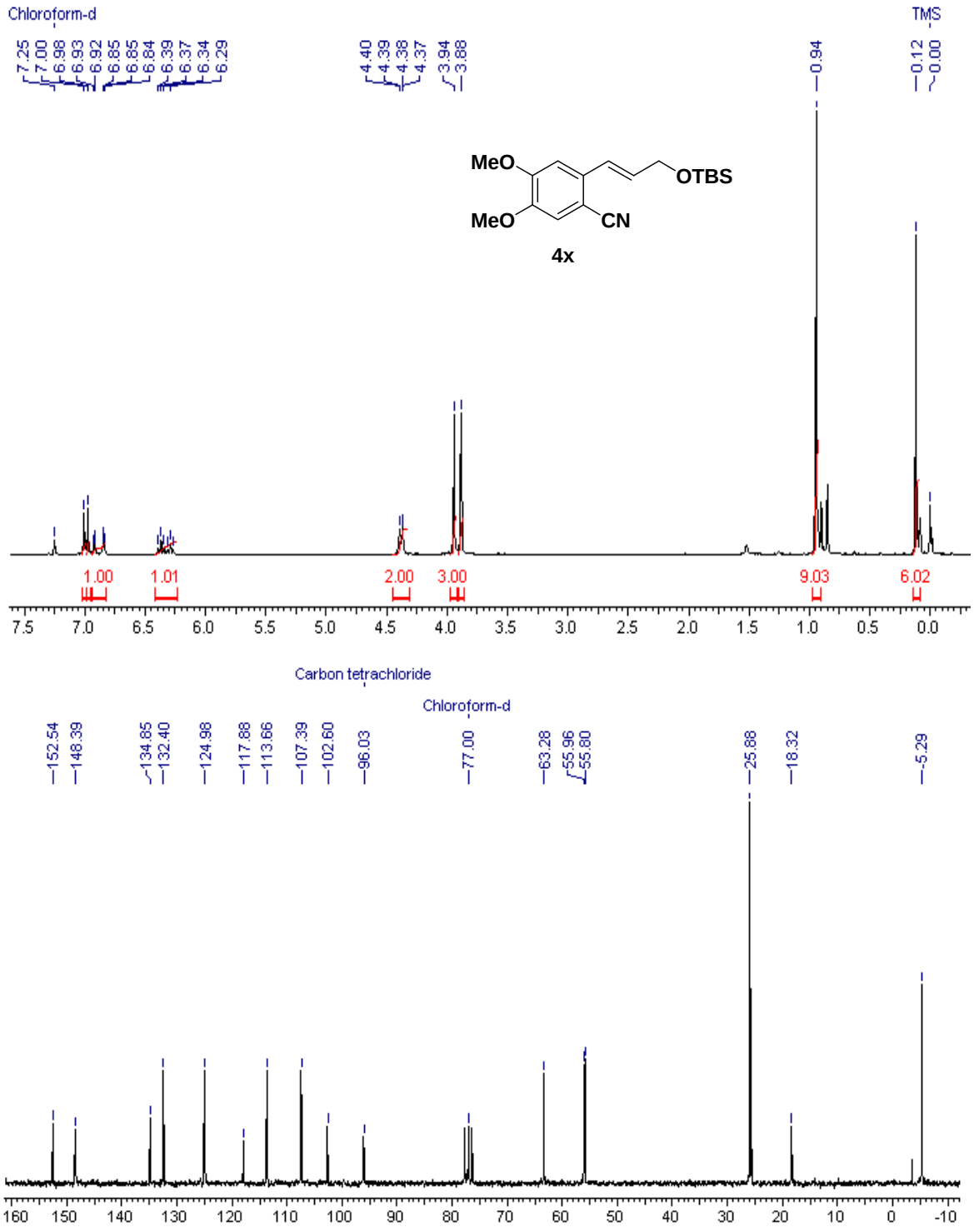
^{1}H and ^{13}C NMR spectra of 4u



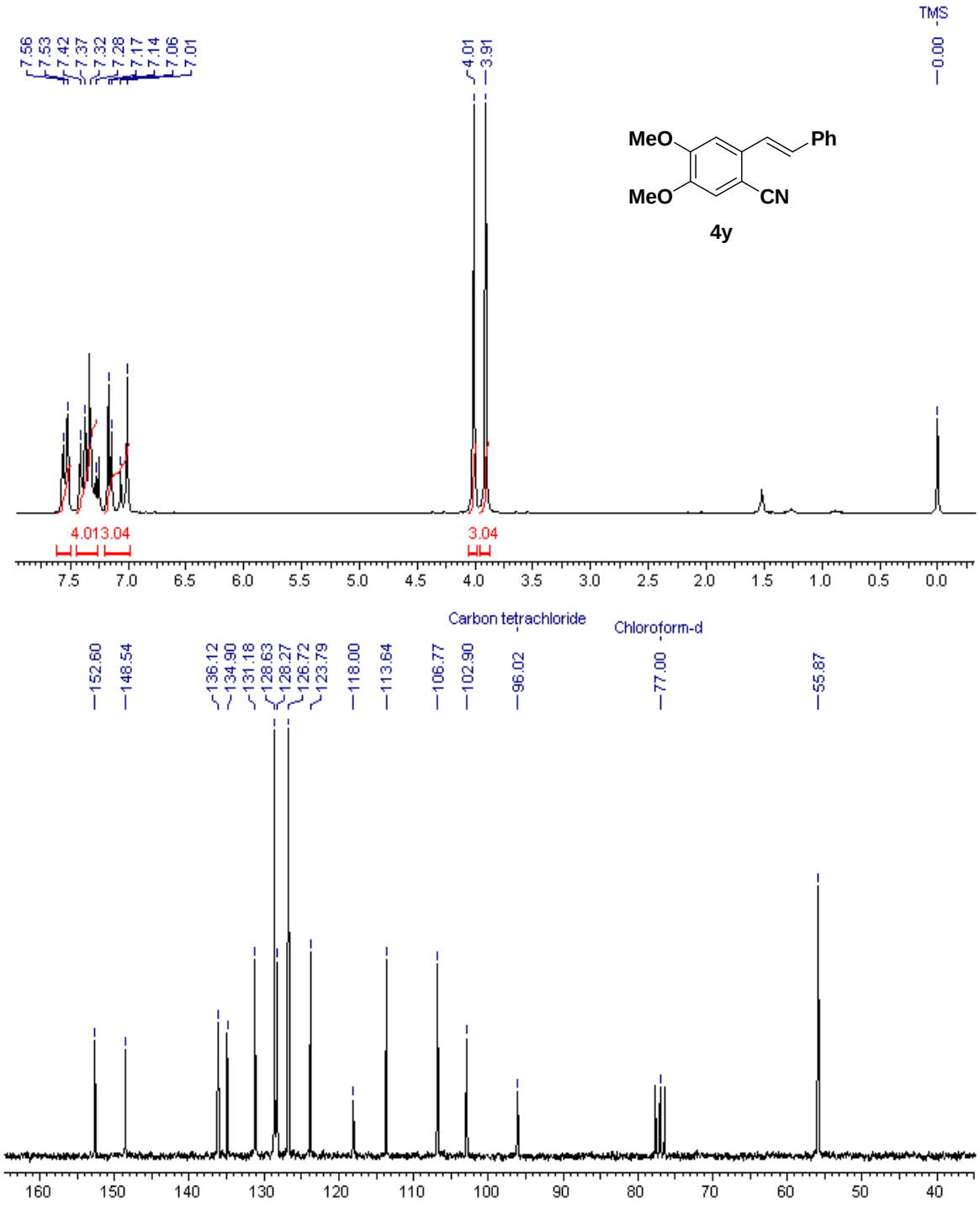
^{1}H and ^{13}C NMR spectra of 4v



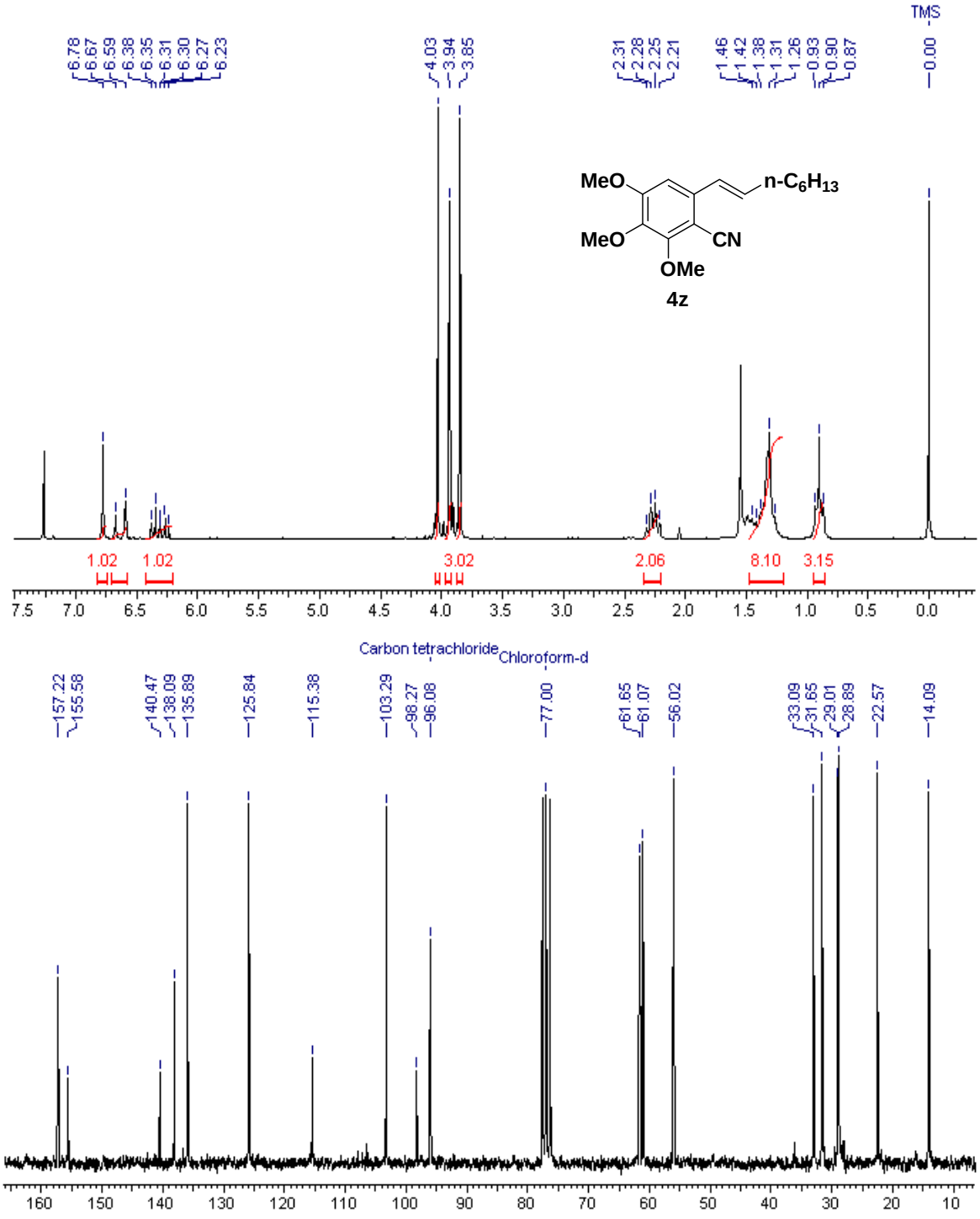
^{1}H and ^{13}C NMR spectra of 4w



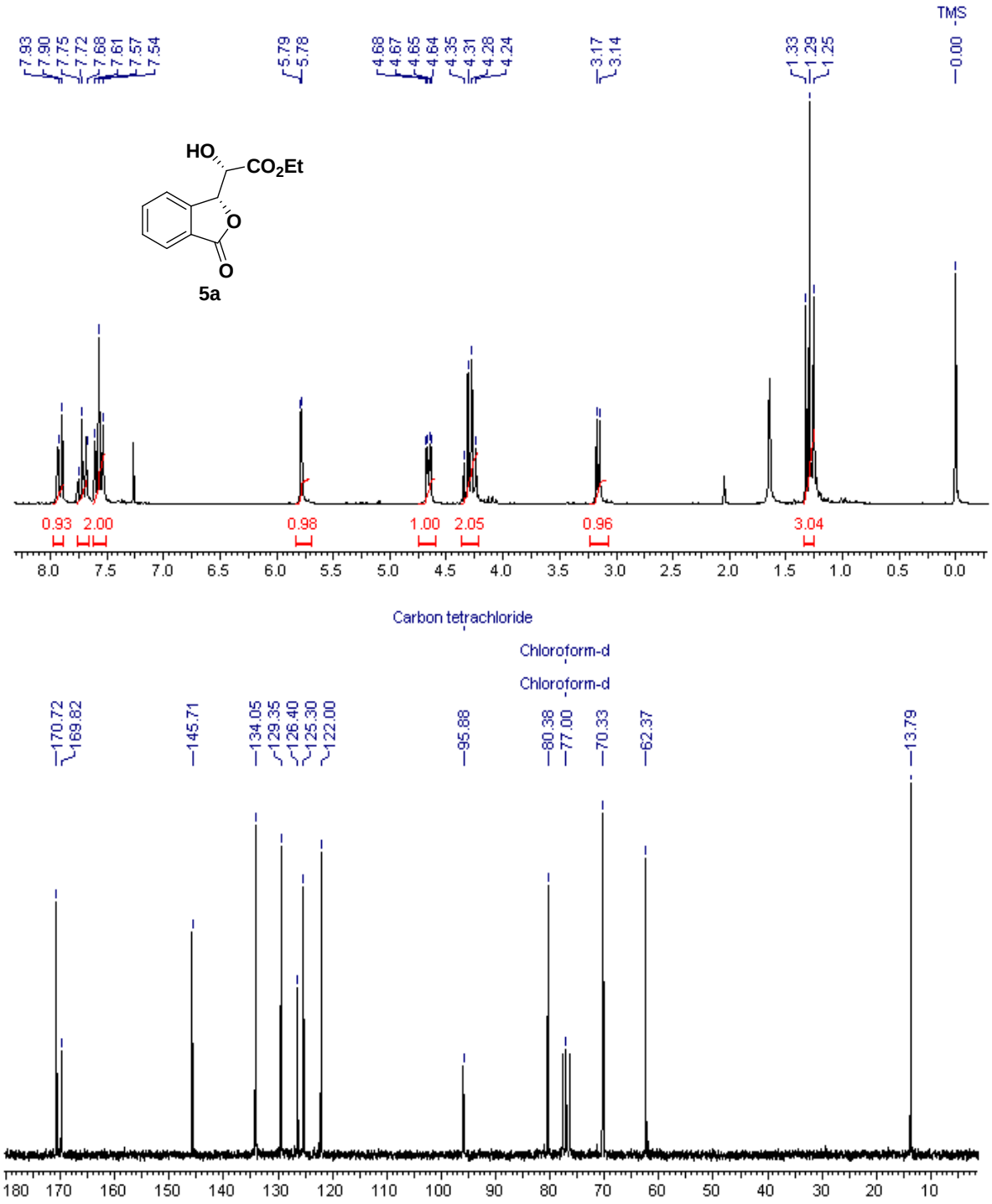
^{1}H and ^{13}C NMR spectra of 4x



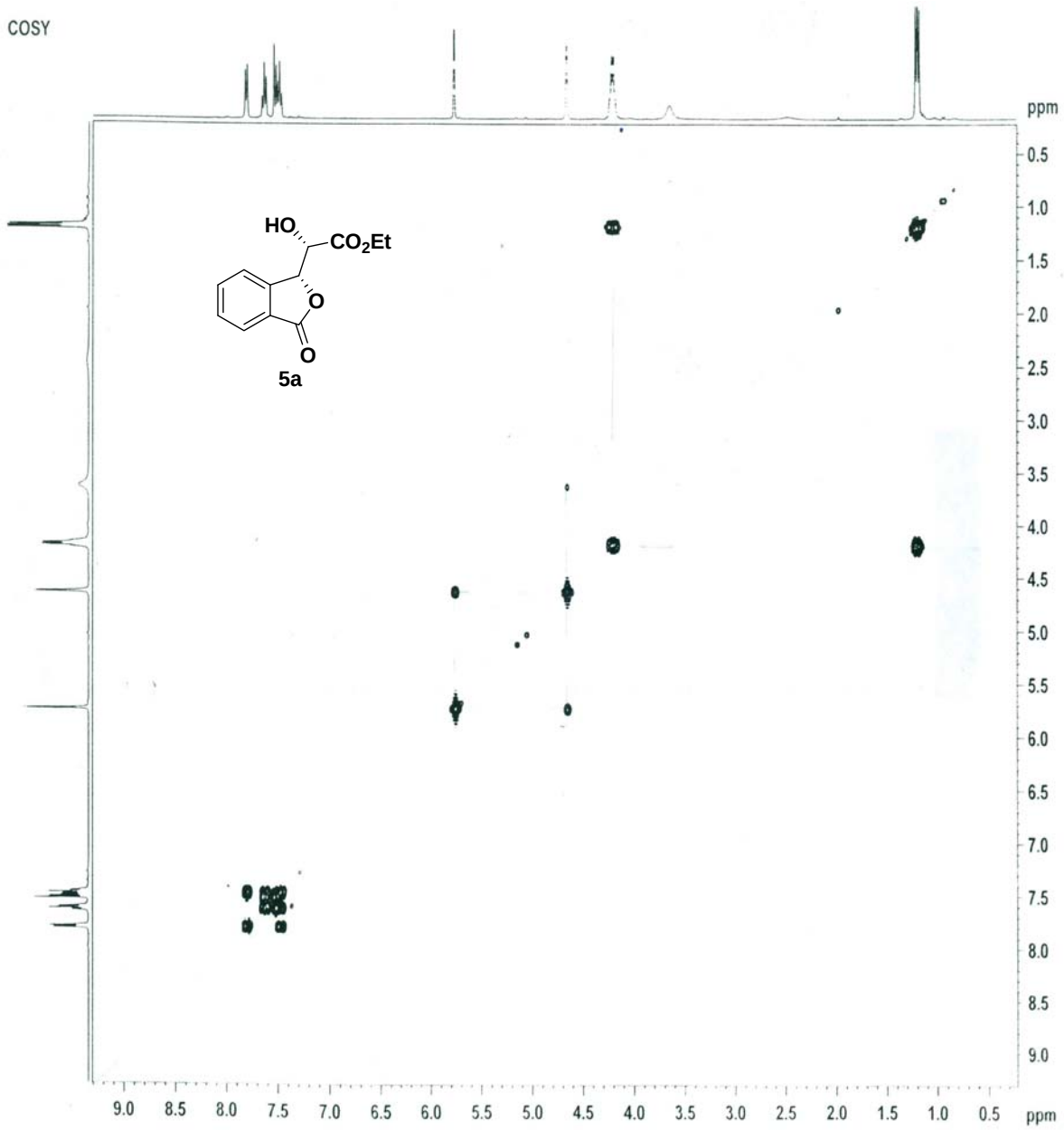
^{1}H and ^{13}C NMR spectra of 4y



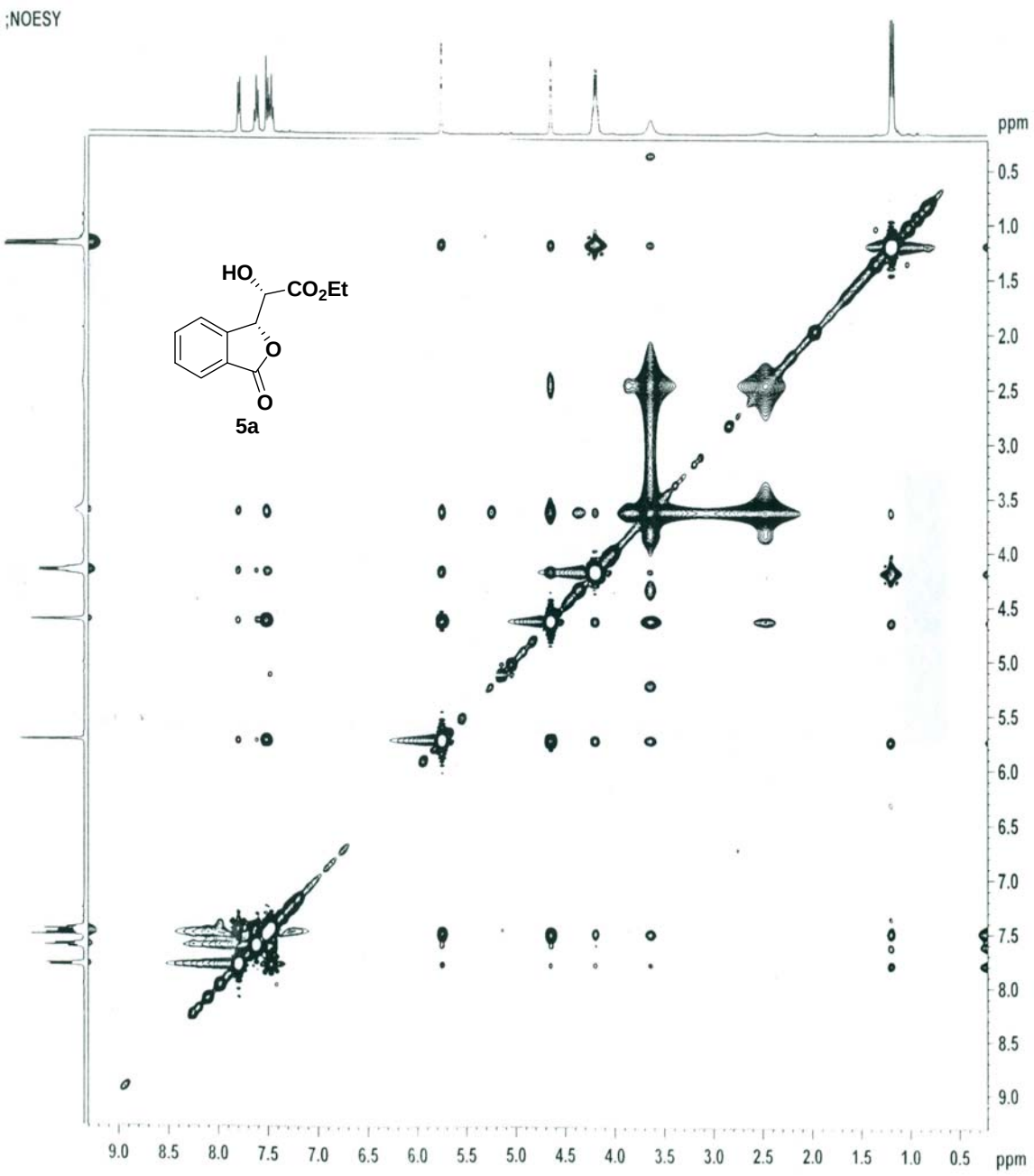
^{1}H and ^{13}C NMR spectra of 4z



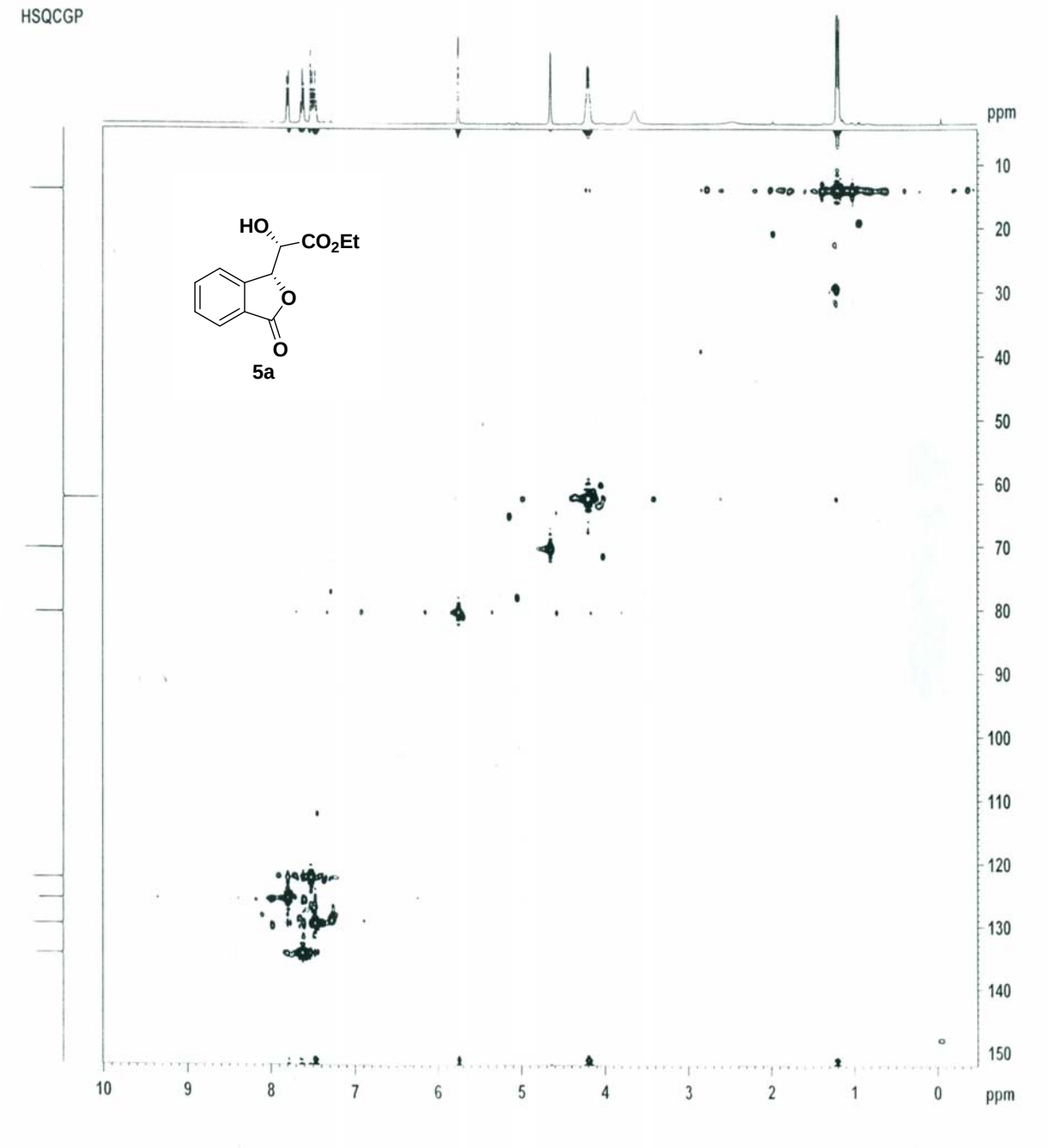
^{1}H and ^{13}C NMR spectra of 5a



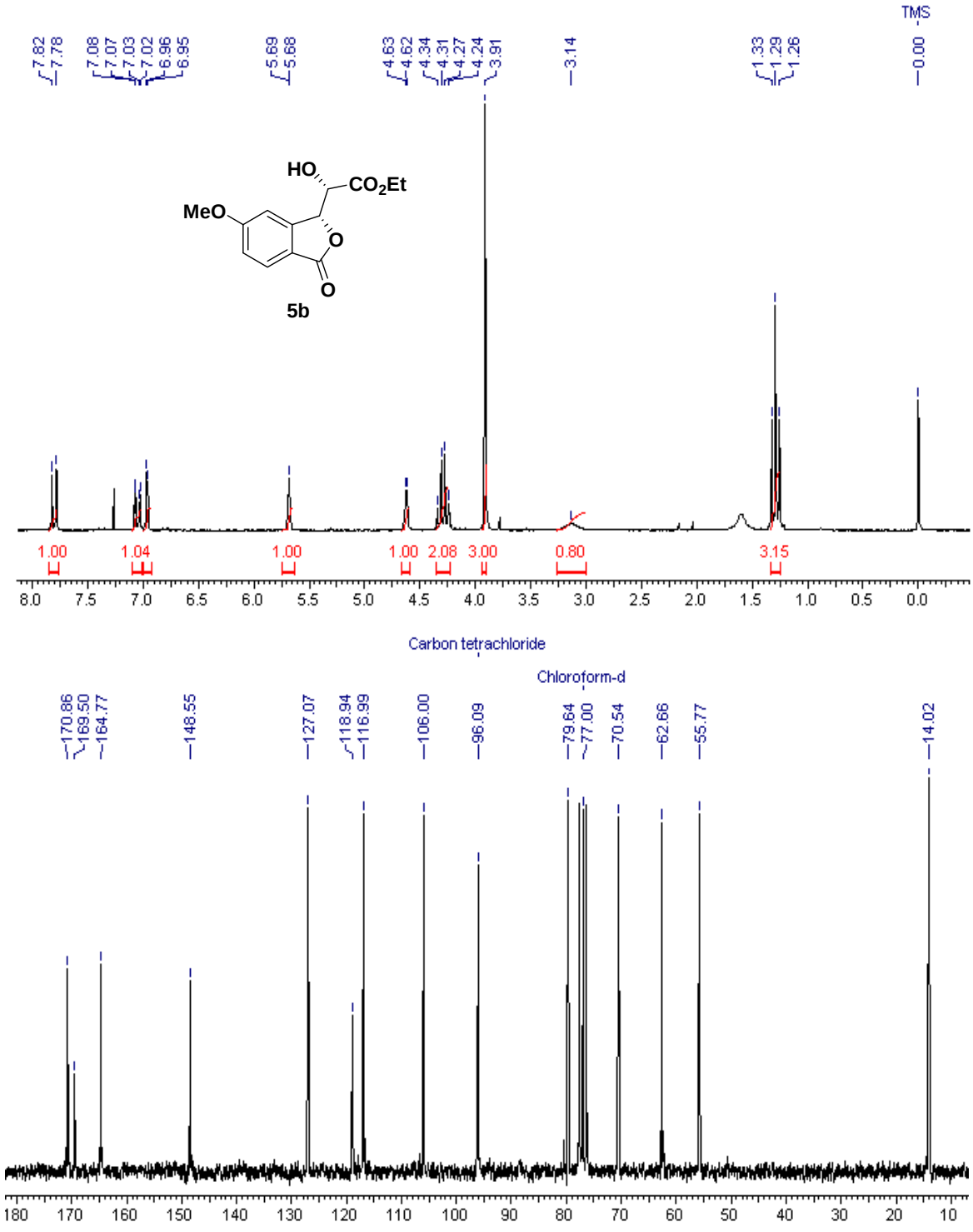
COSY spectra of 5a



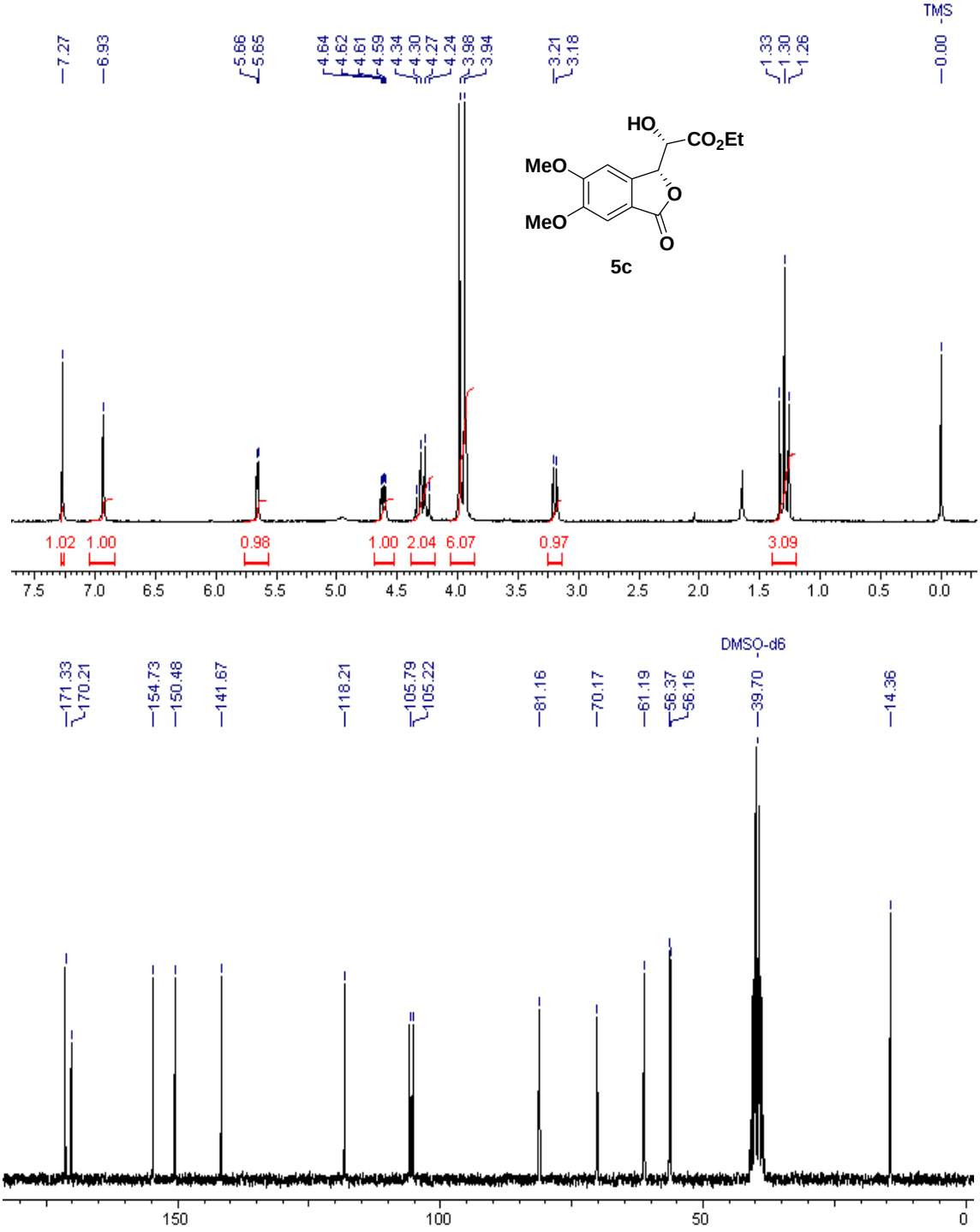
NOESY spectra of 5a



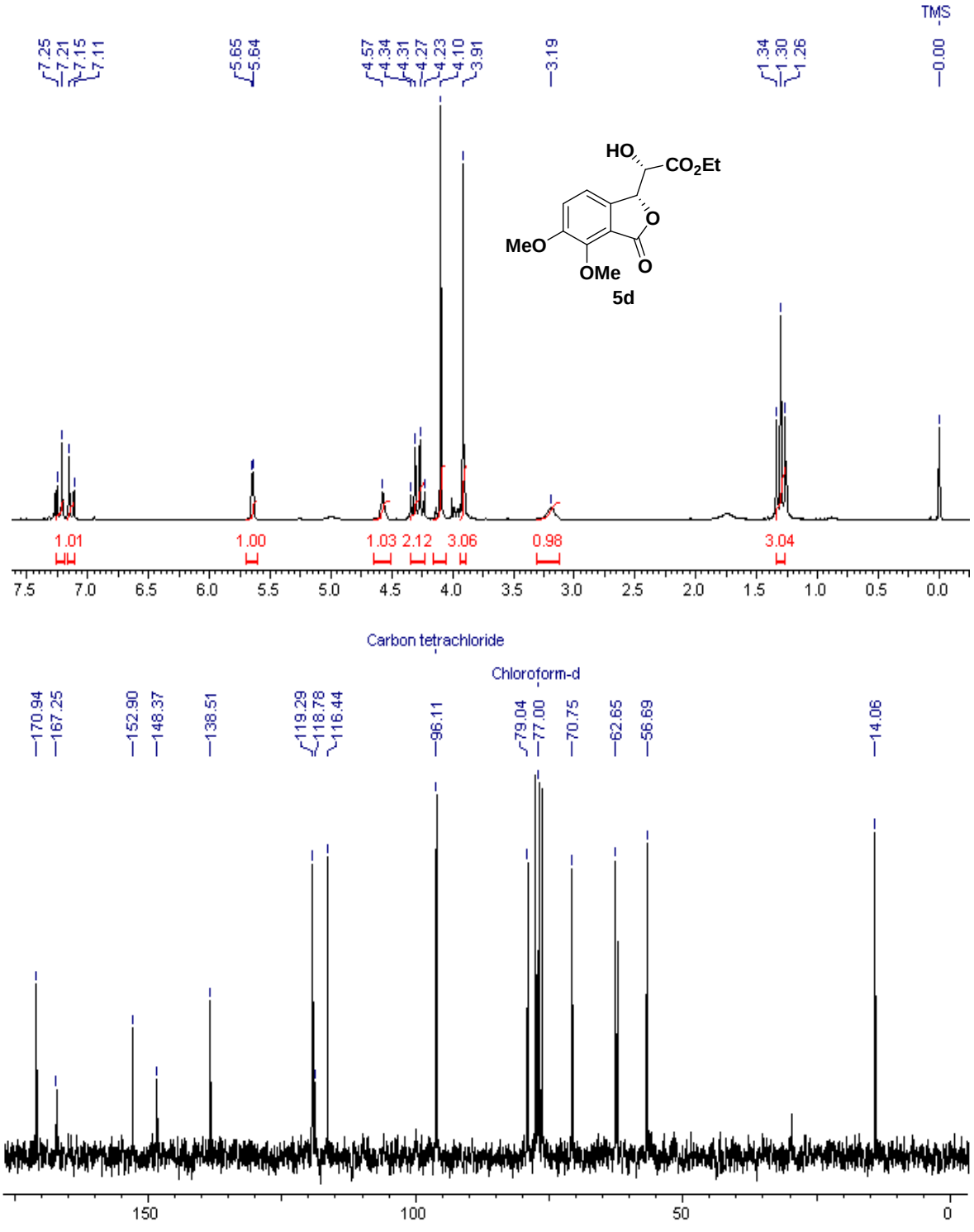
HSQCGP spectra of 5a



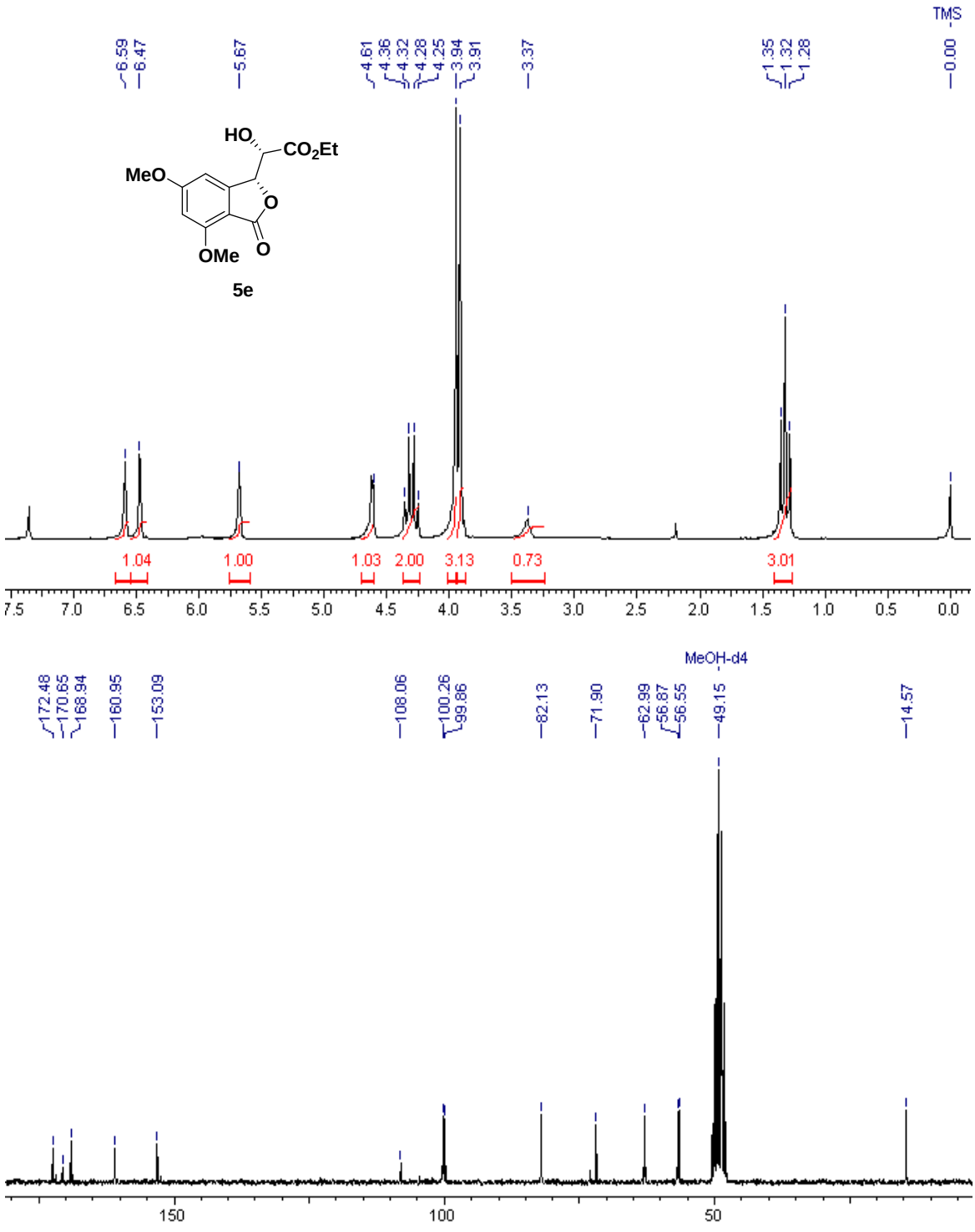
^{1}H and ^{13}C NMR spectra of 5b



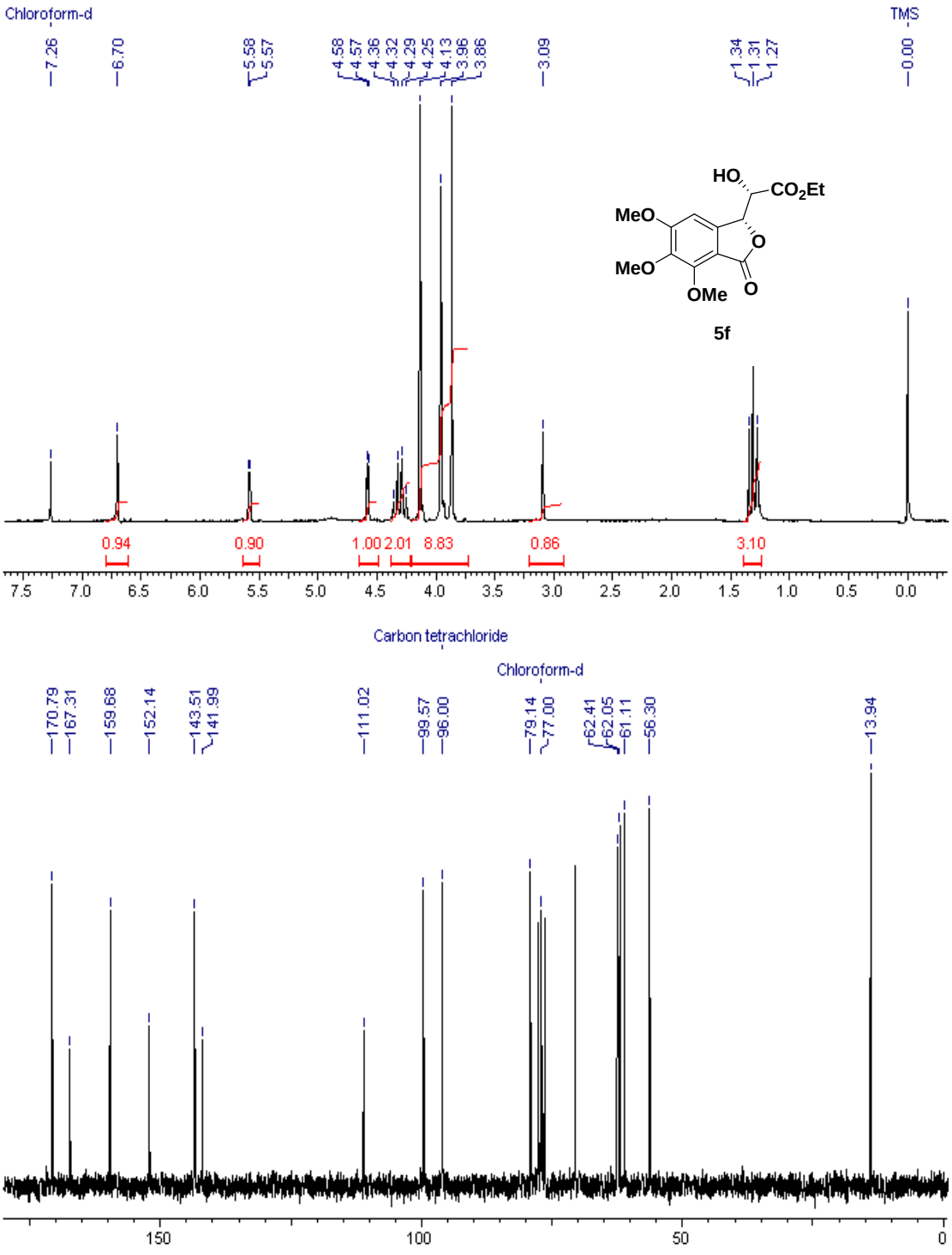
^{1}H and ^{13}C NMR spectra of 5c



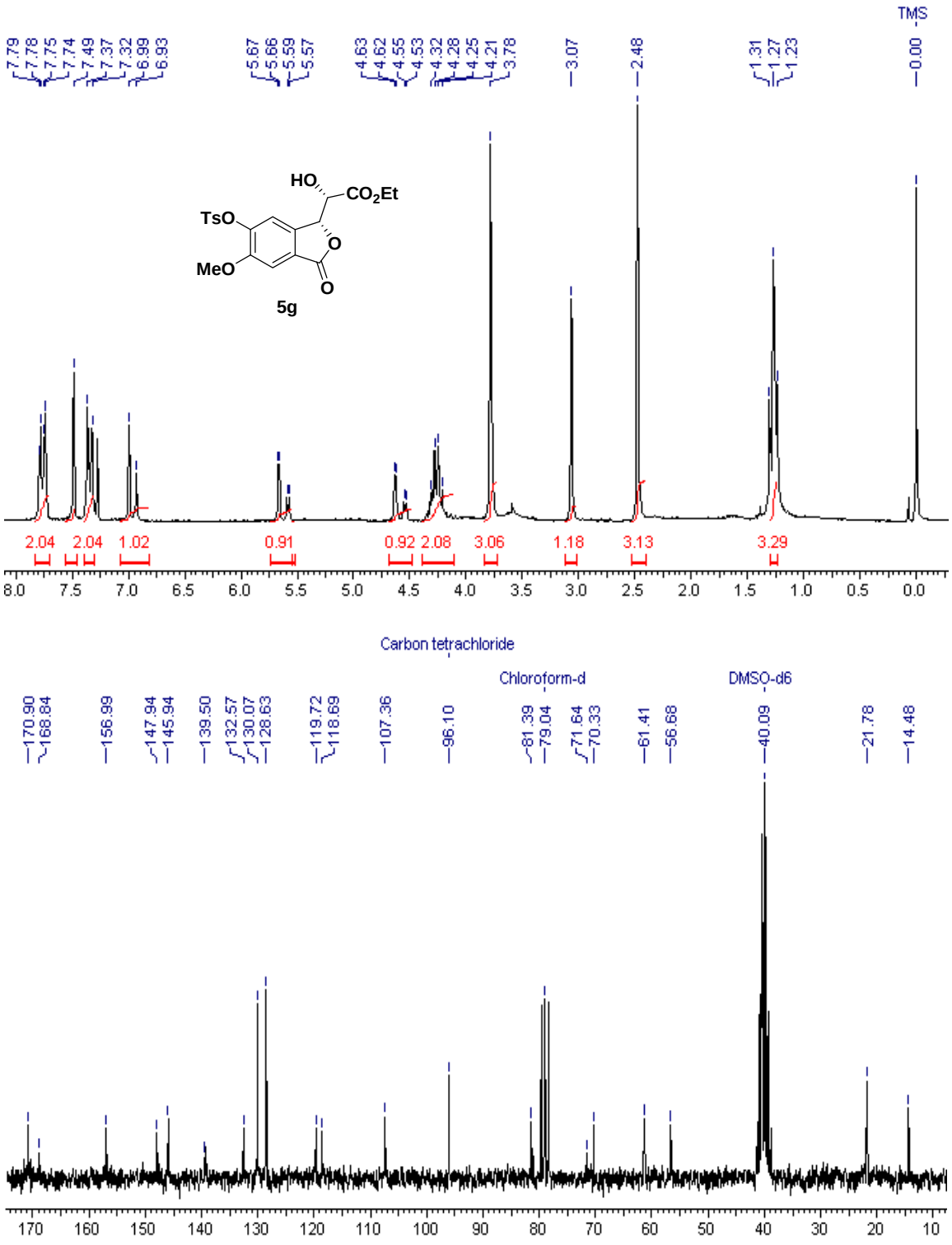
^{1}H and ^{13}C NMR spectra of 5d



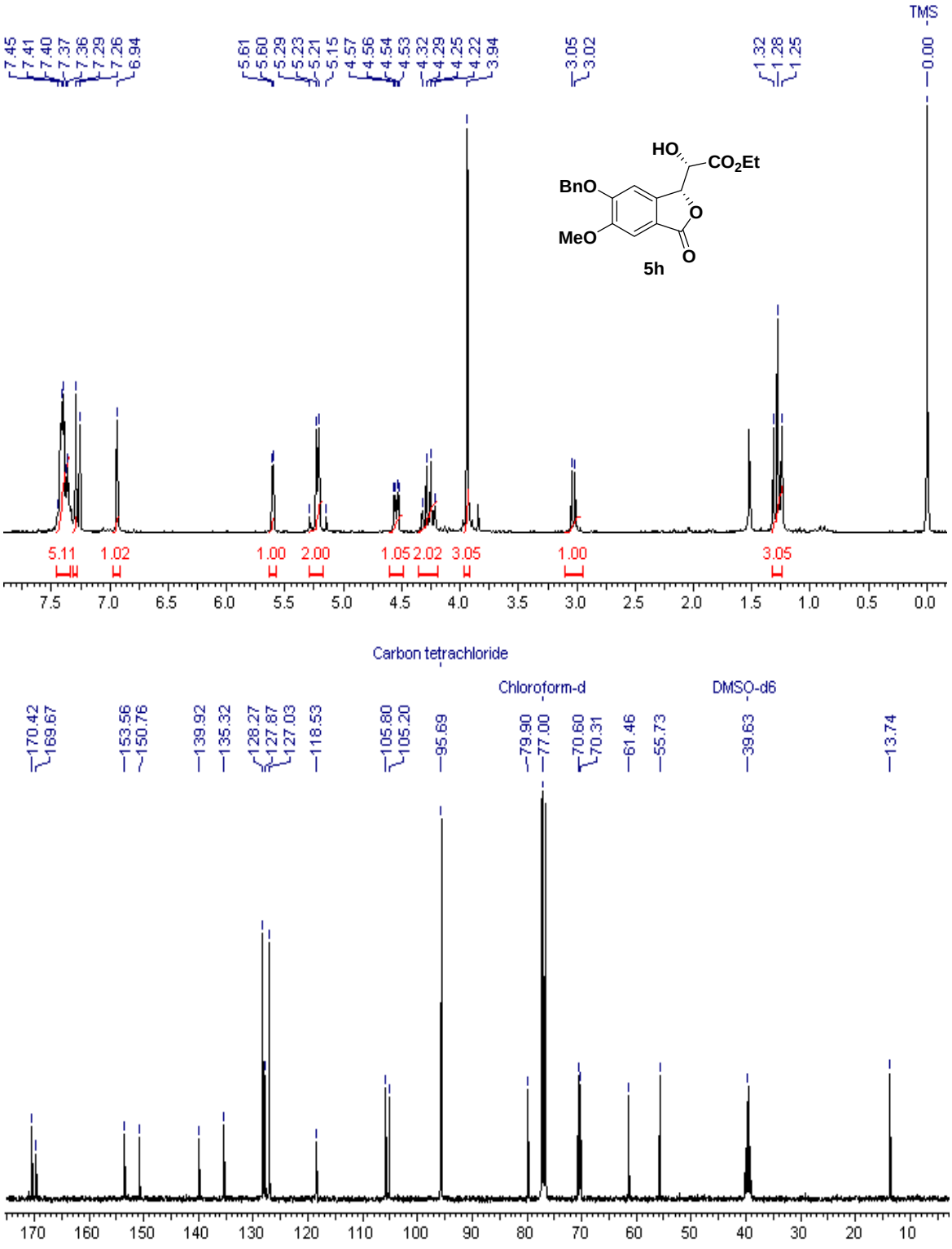
^{1}H and ^{13}C NMR spectra of 5e



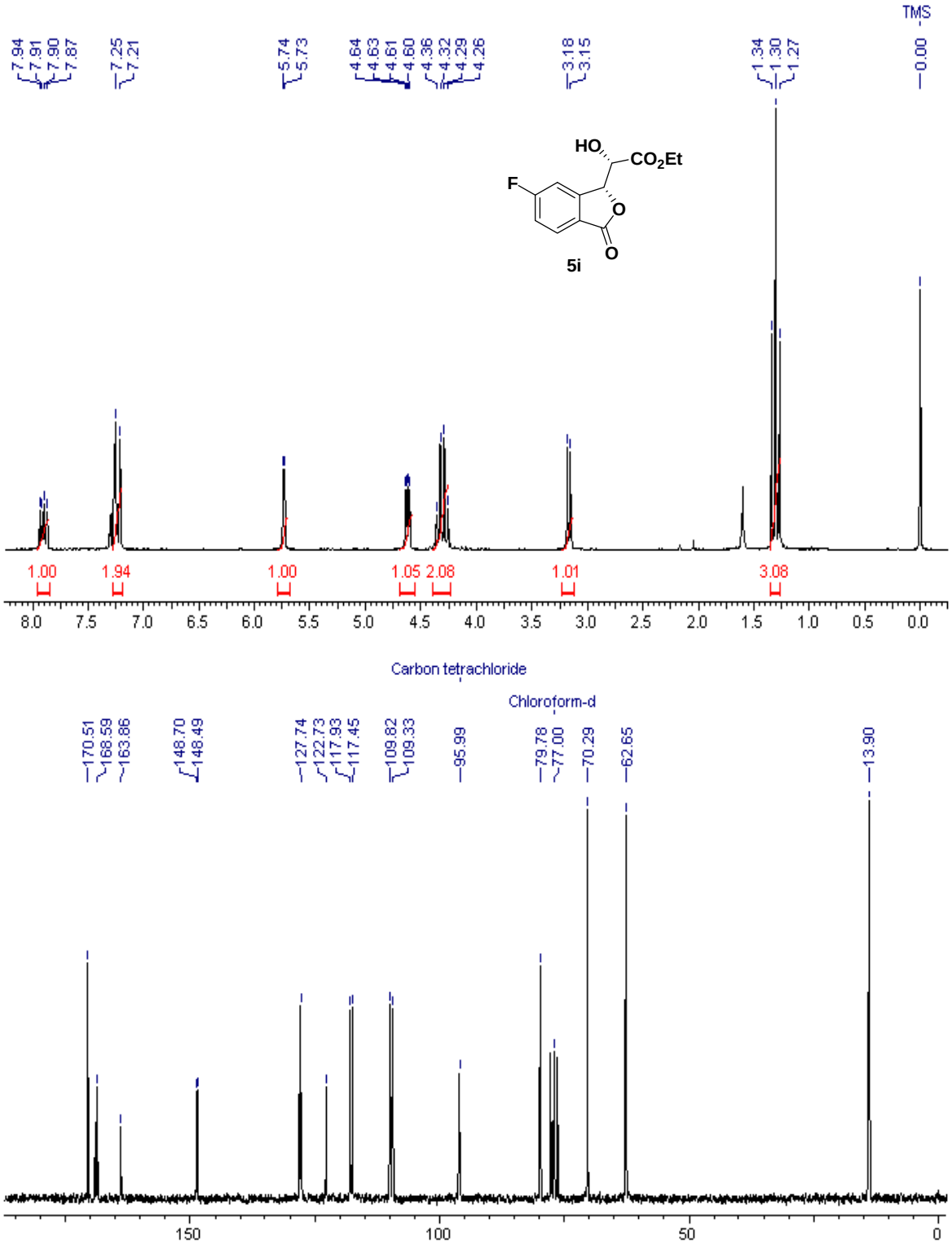
^{1}H and ^{13}C NMR spectra of 5f



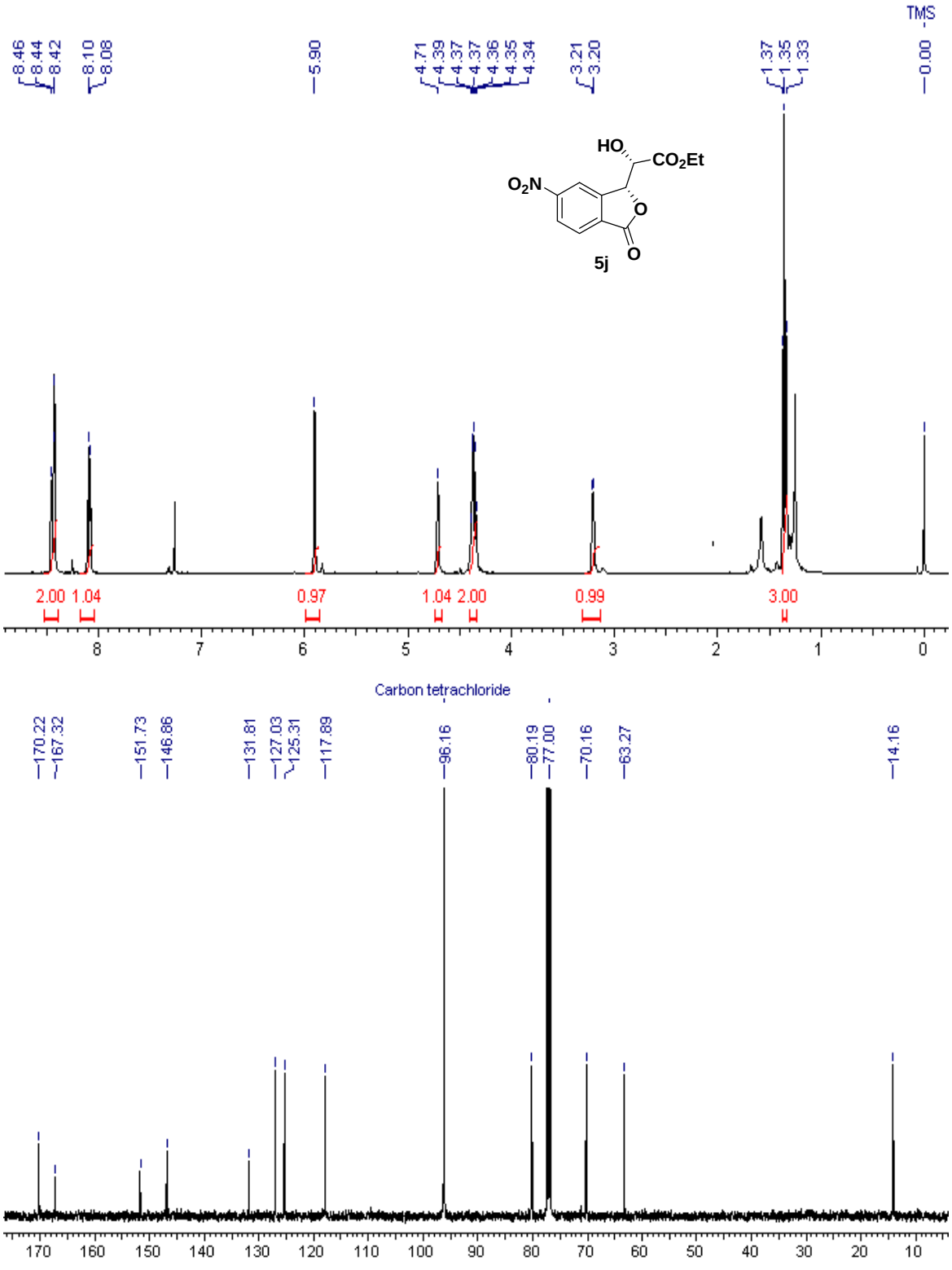
^{1}H and ^{13}C NMR spectra of 5g



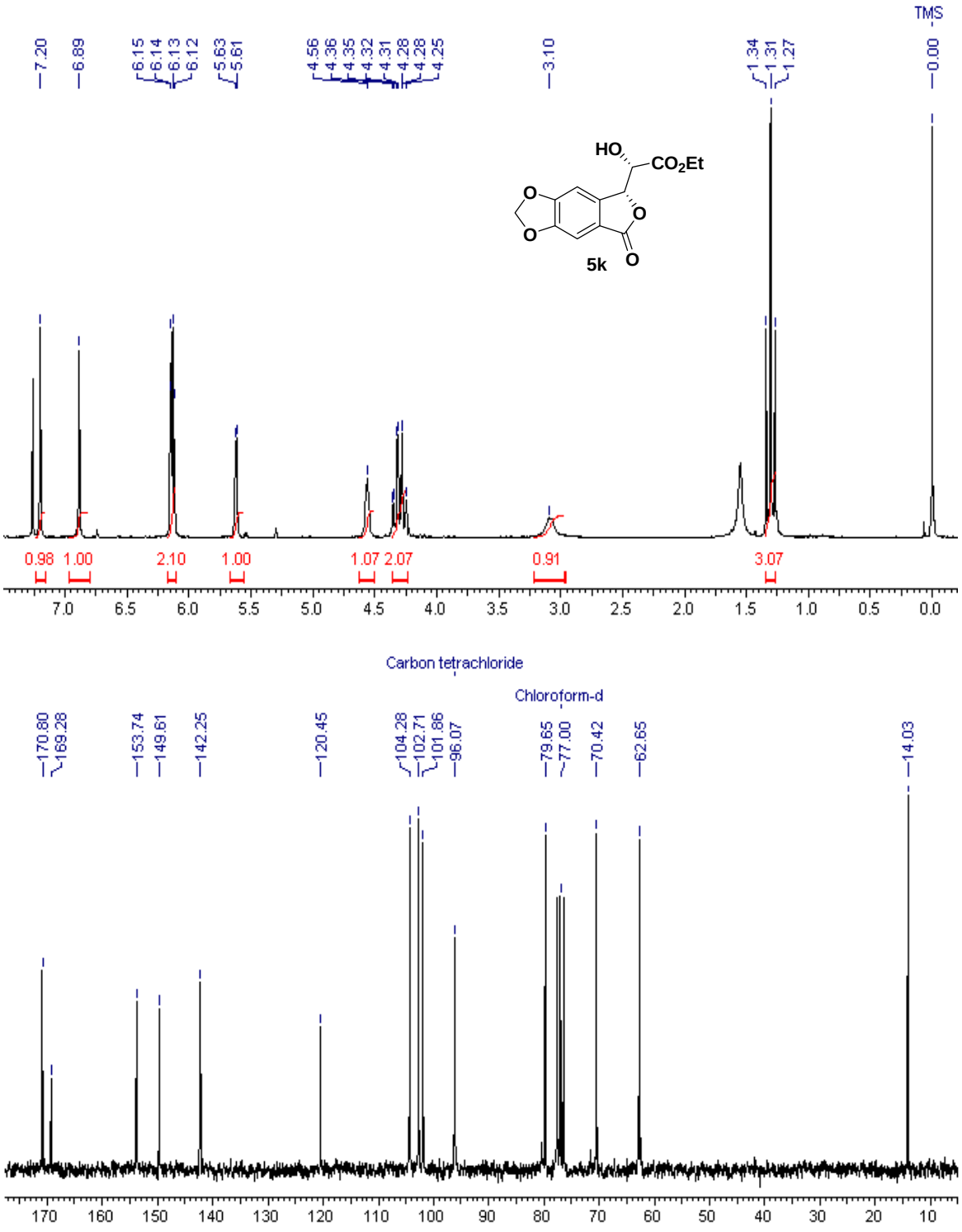
^{1}H and ^{13}C NMR spectra of 5h



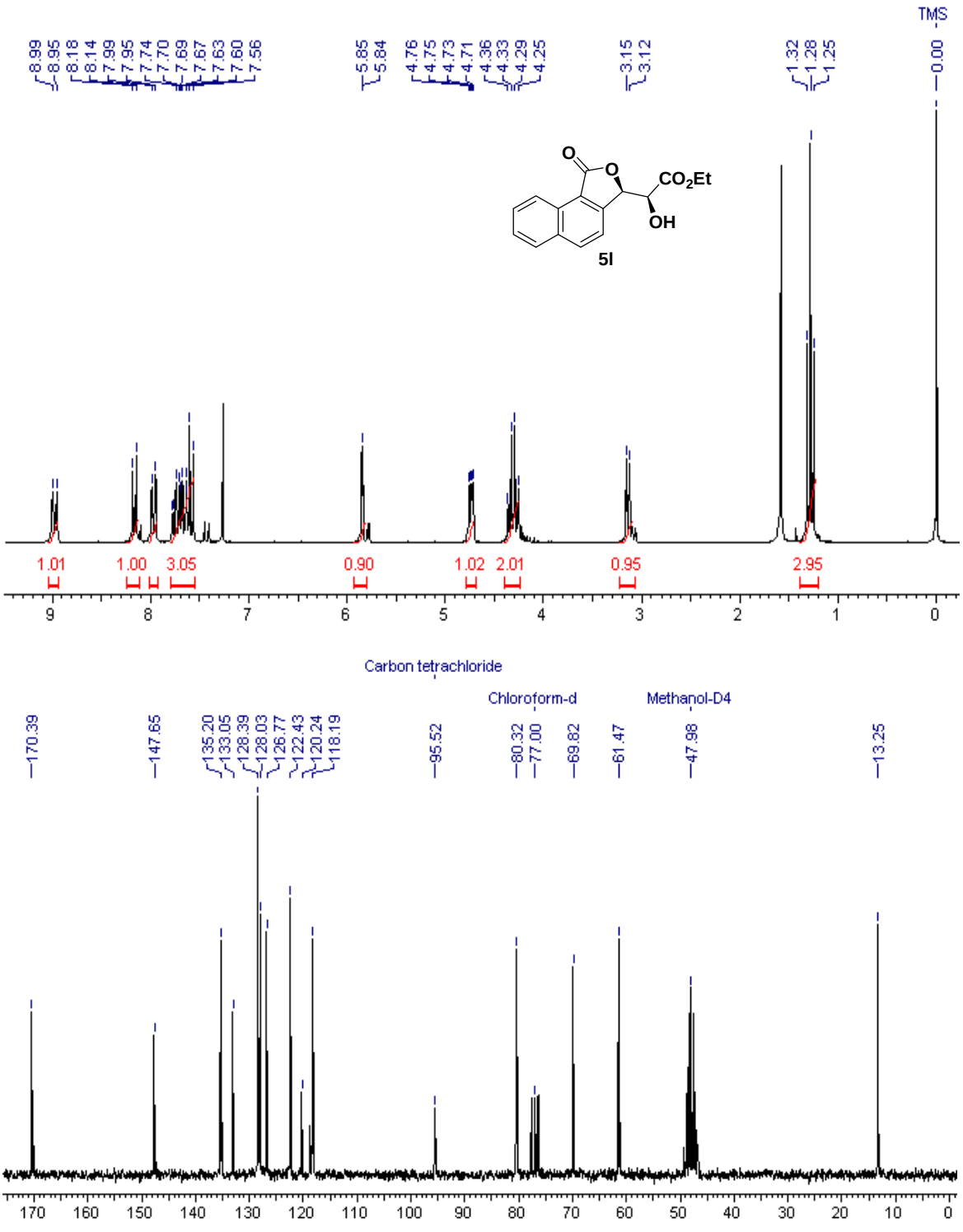
^{1}H and ^{13}C NMR spectra of 5i



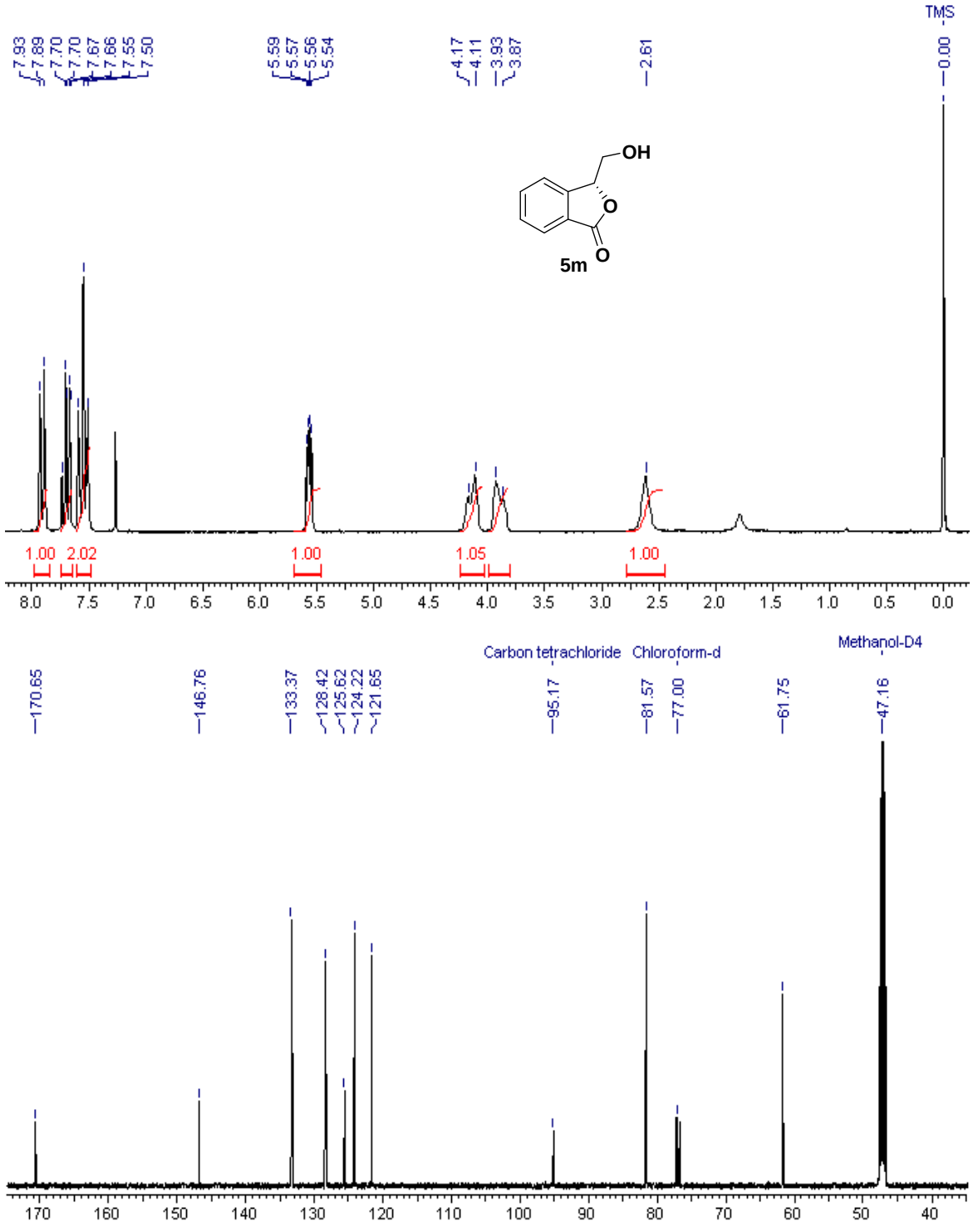
^{1}H and ^{13}C NMR spectra of 5j



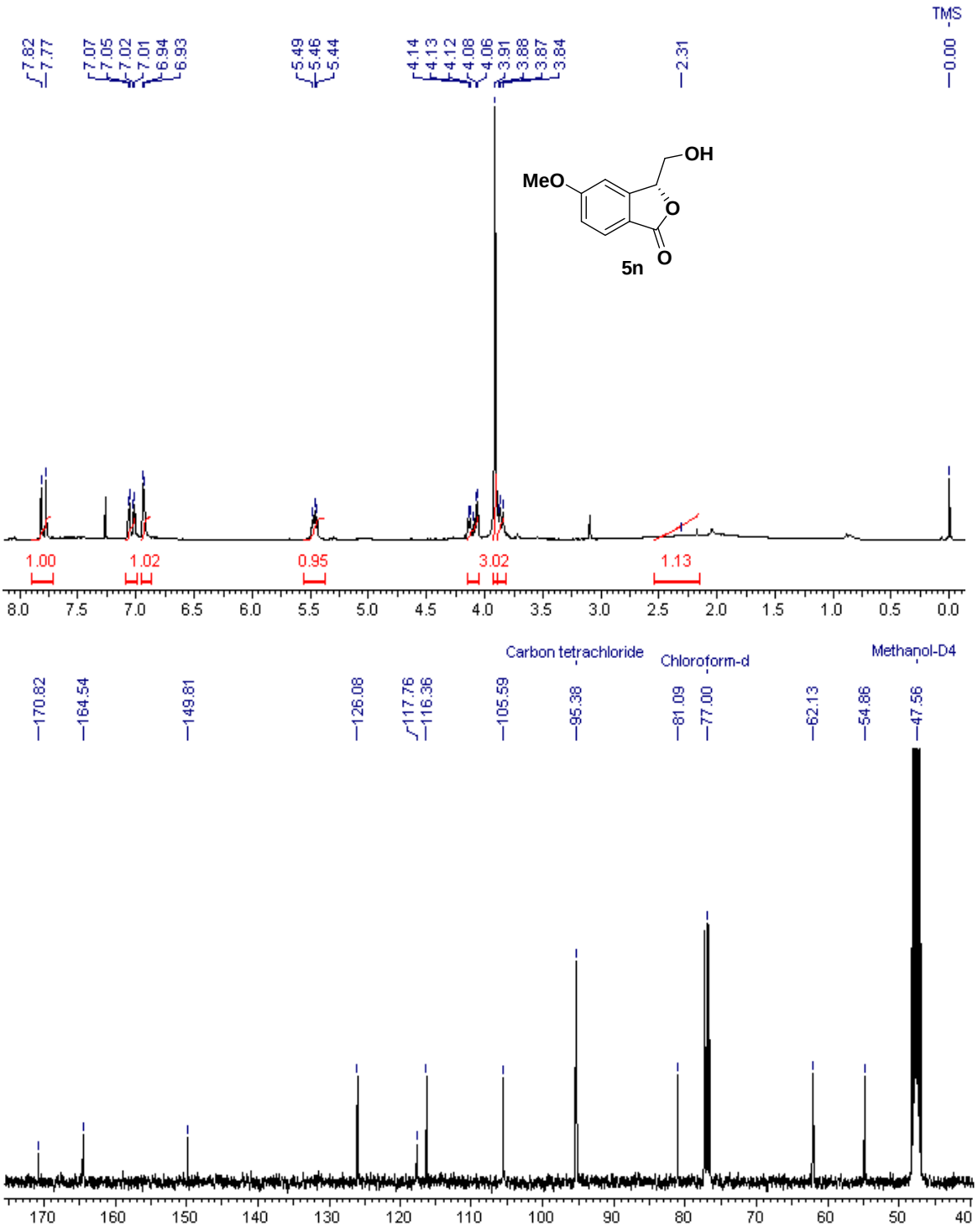
^{1}H and ^{13}C NMR spectra of 5k



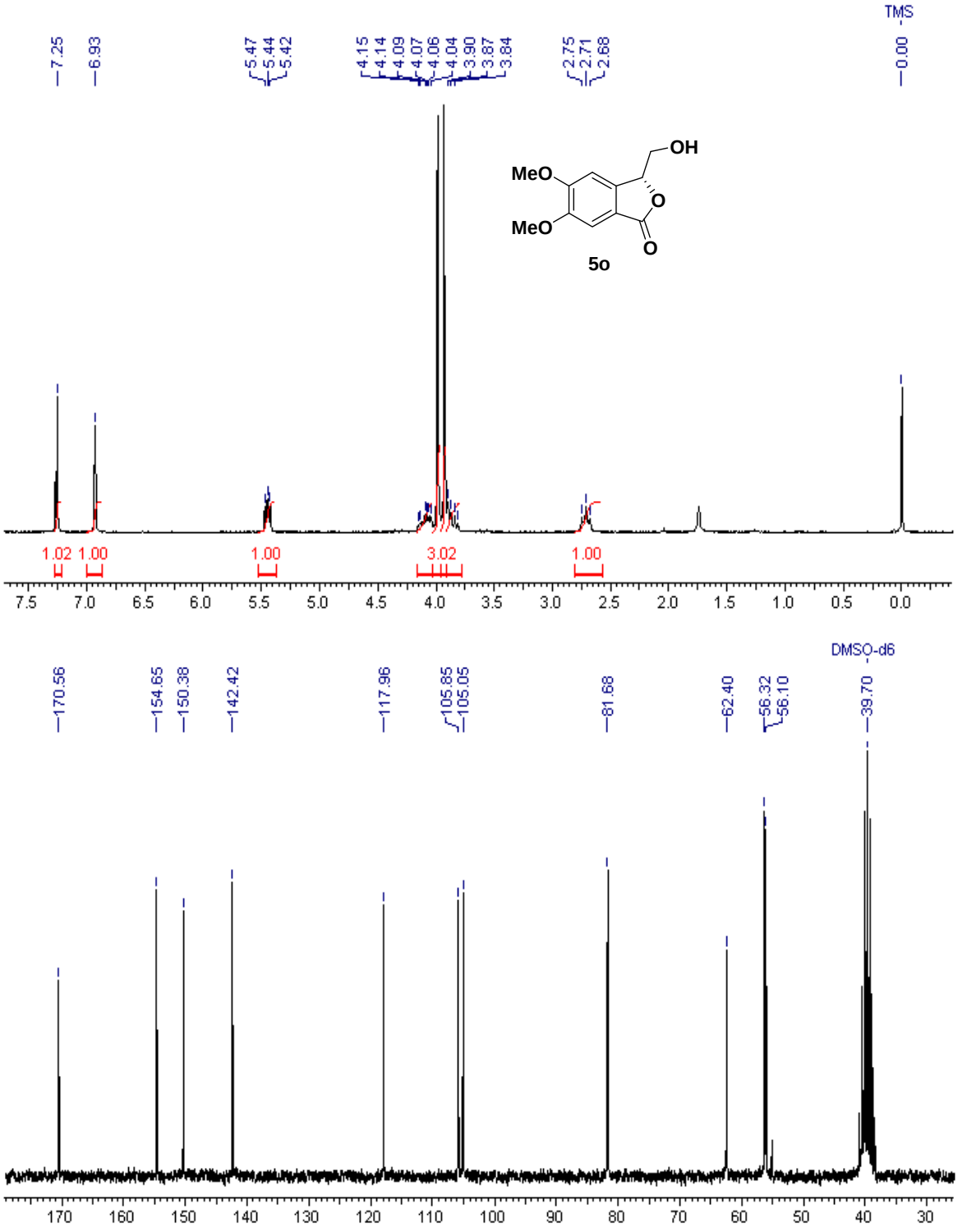
^{1}H and ^{13}C NMR spectra of 5l



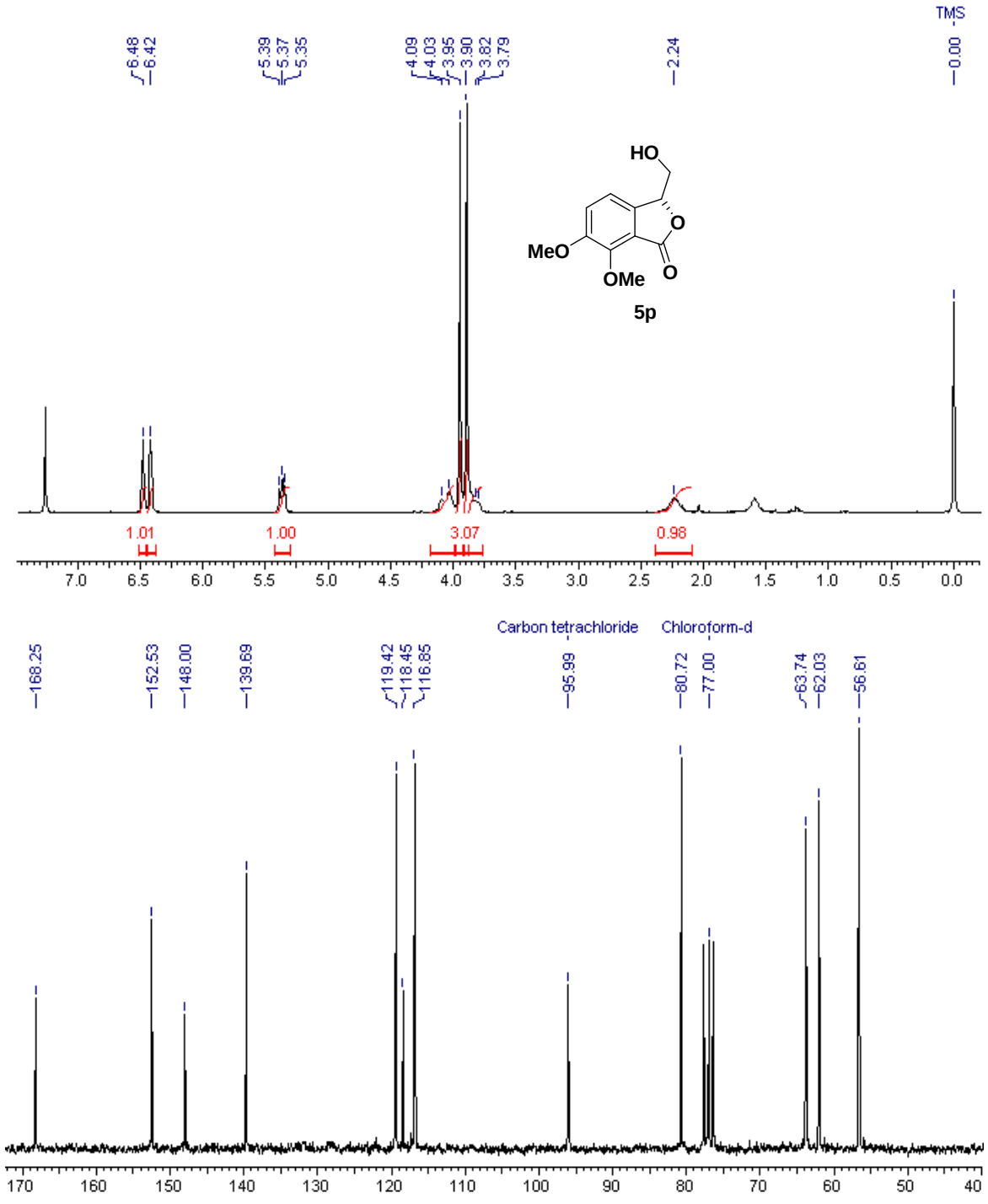
^{1}H and ^{13}C NMR spectra of 5m



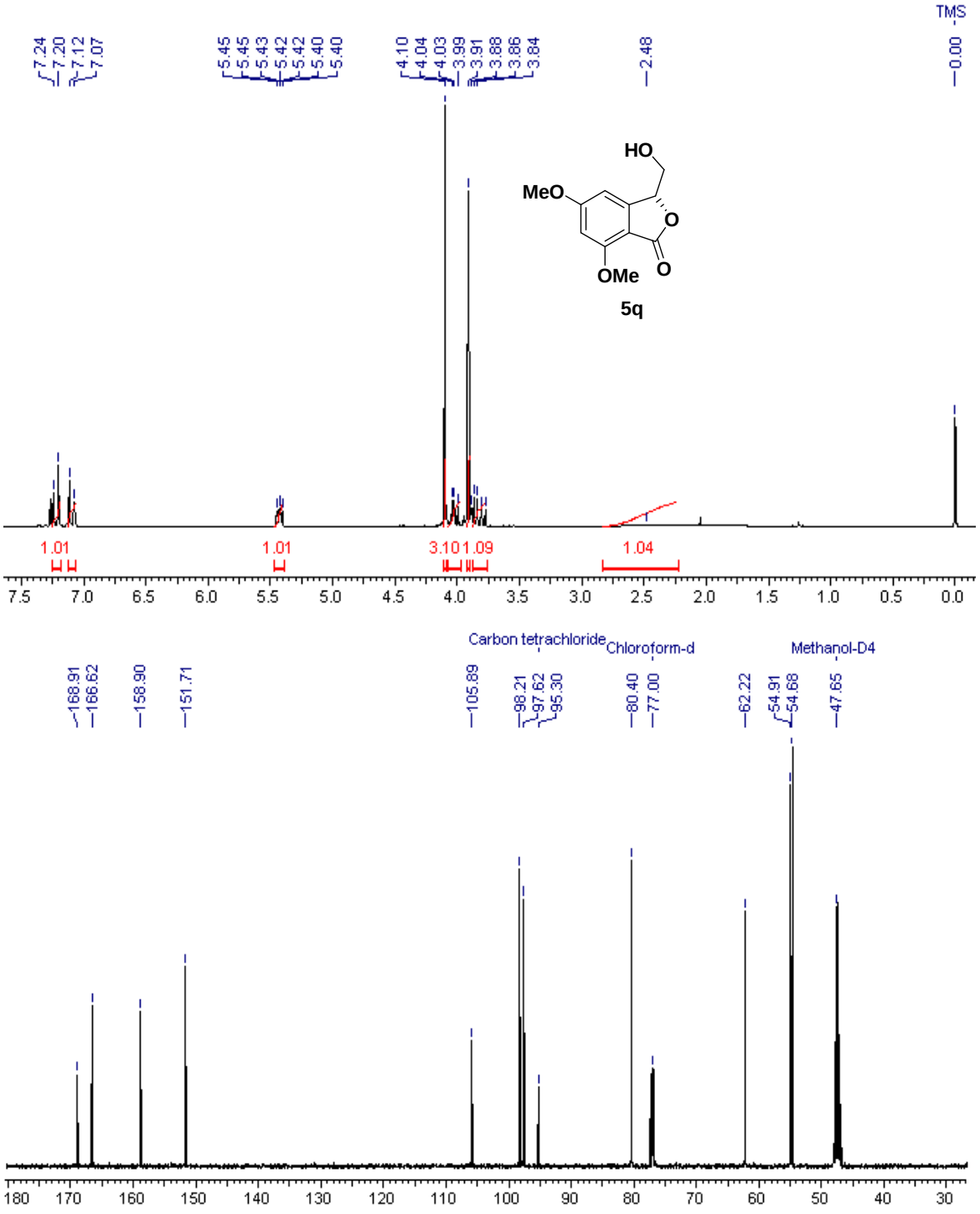
^{1}H and ^{13}C NMR spectra of 5n



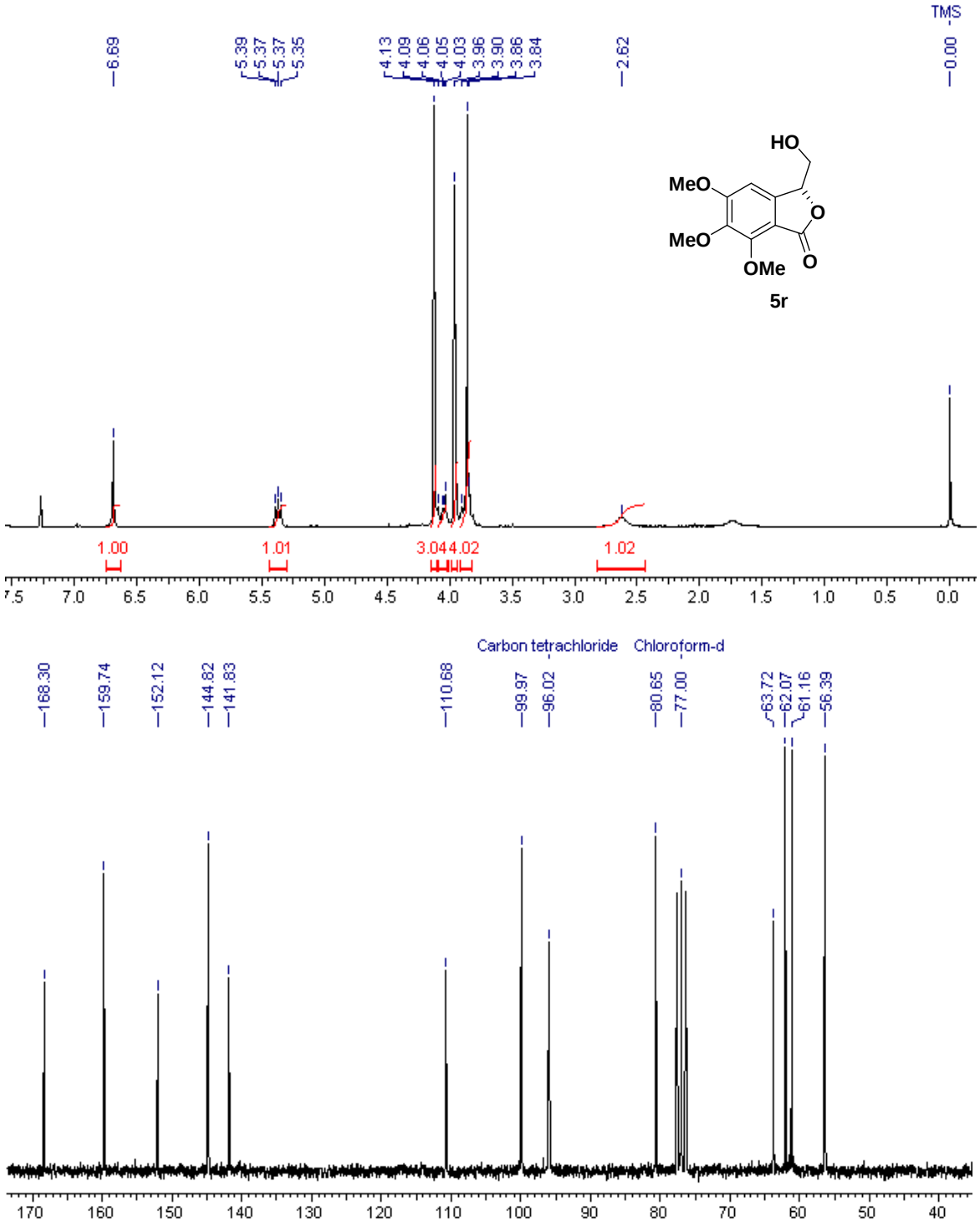
^{1}H and ^{13}C NMR spectra of 5o



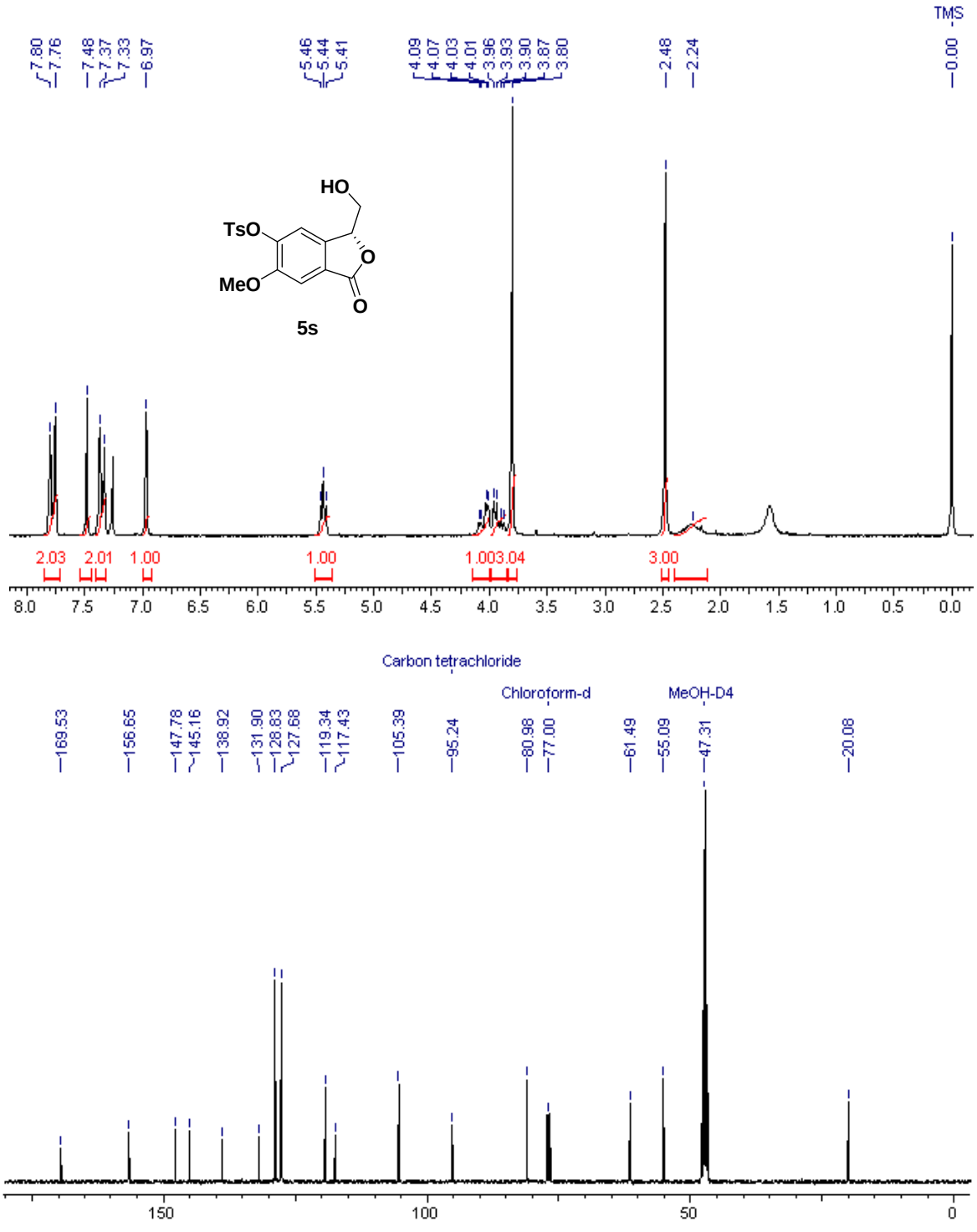
^{1}H and ^{13}C NMR spectra of 5p



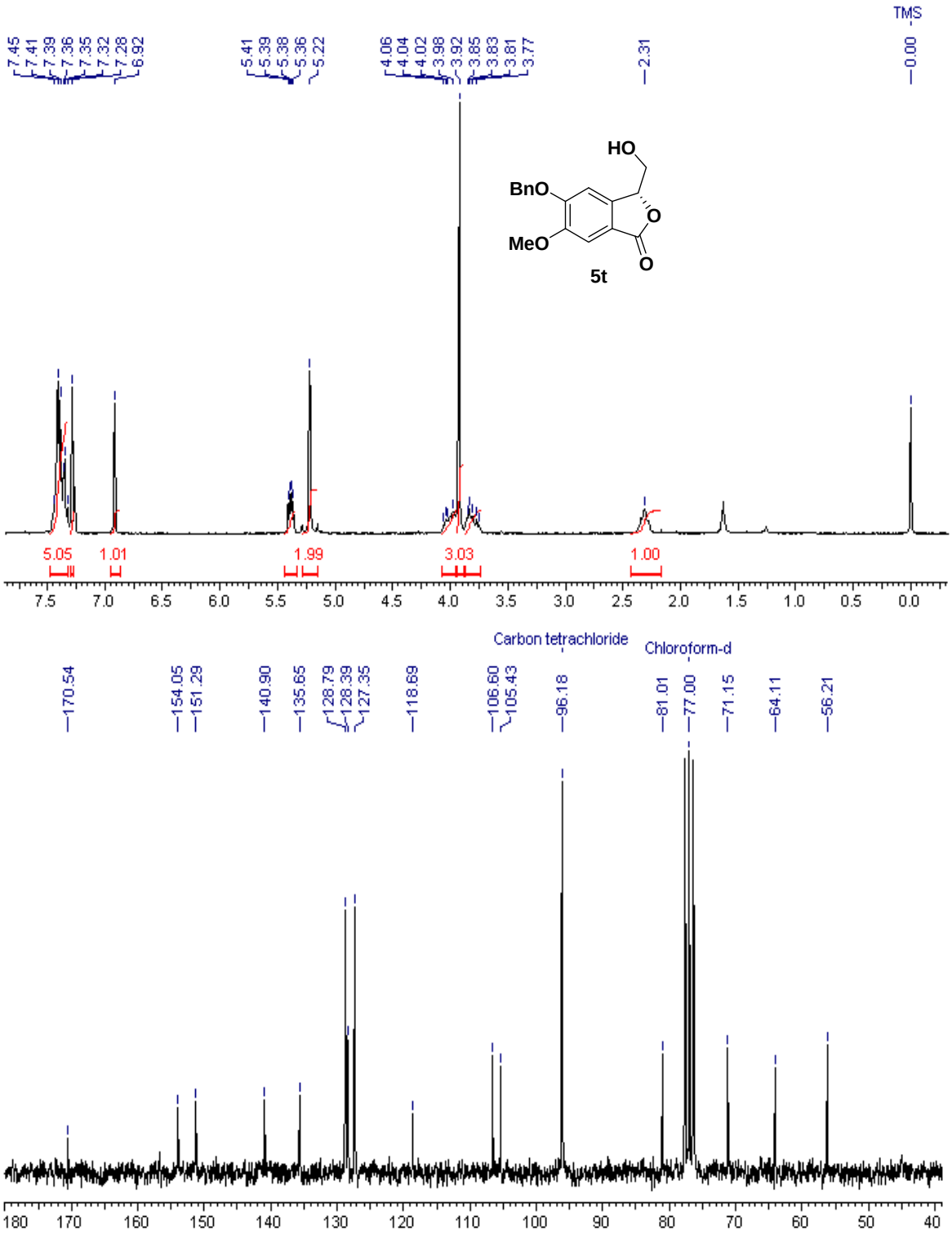
^{1}H and ^{13}C NMR spectra of 5q



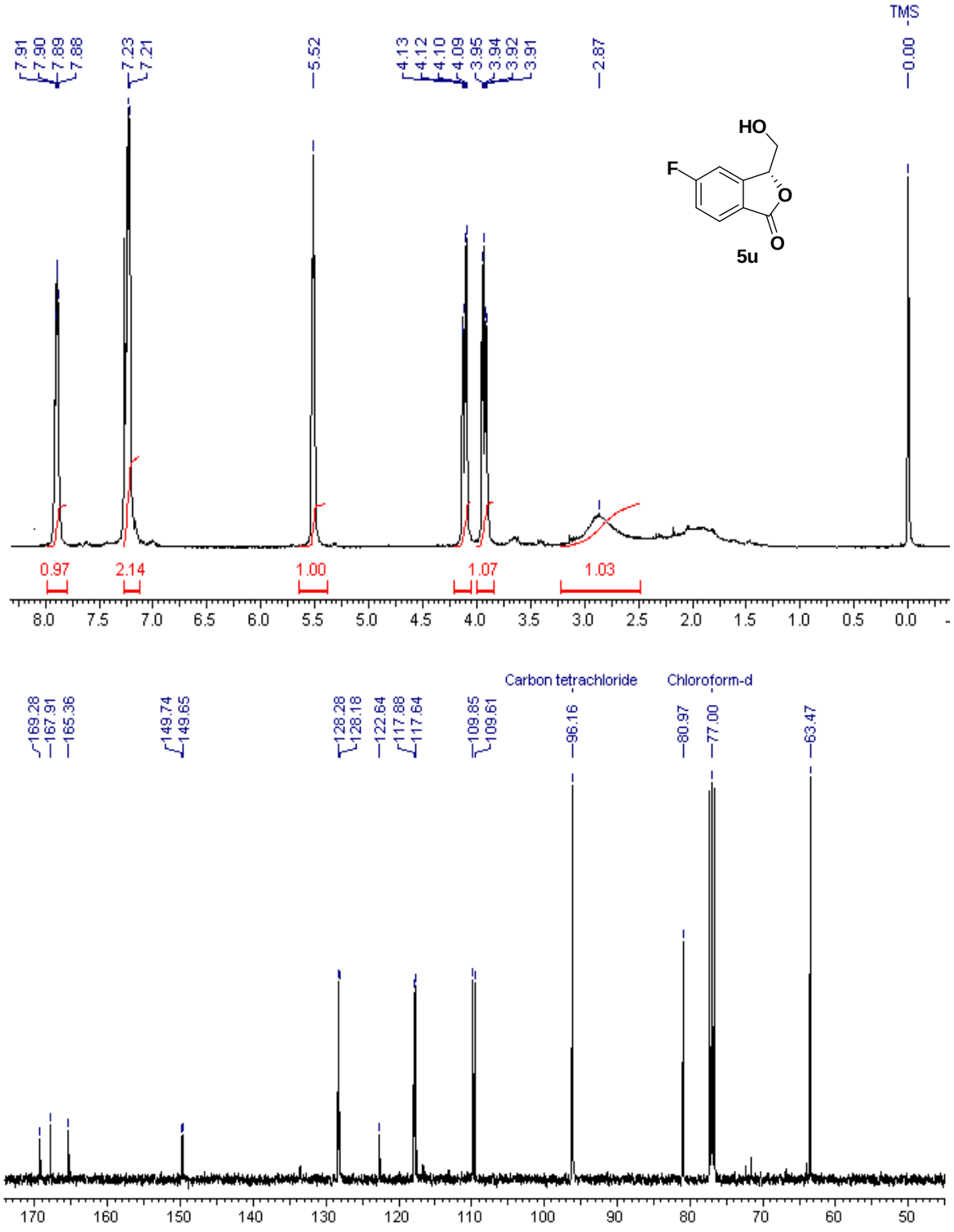
^{1}H and ^{13}C NMR spectra of 5r



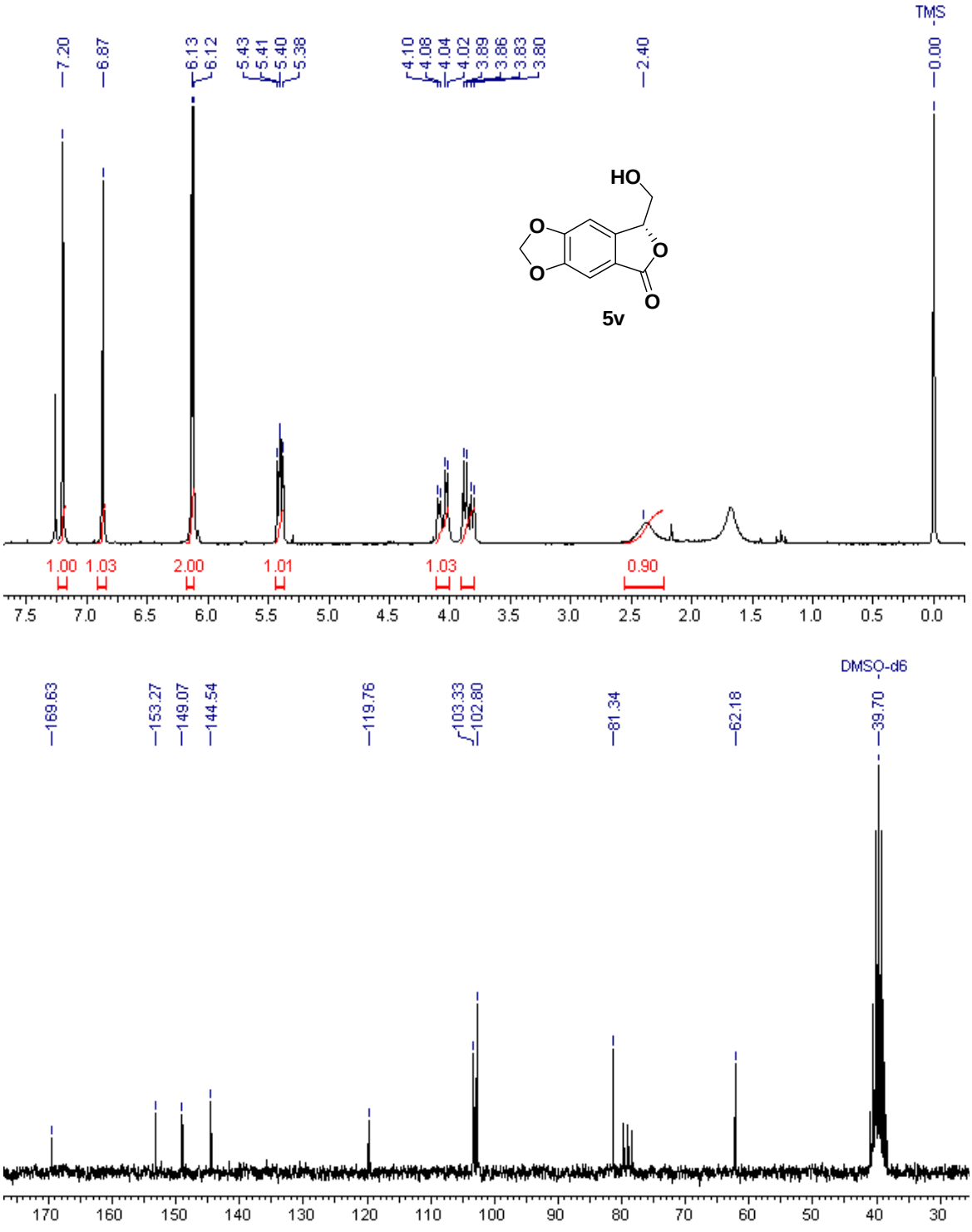
^{1}H and ^{13}C NMR spectra of 5s



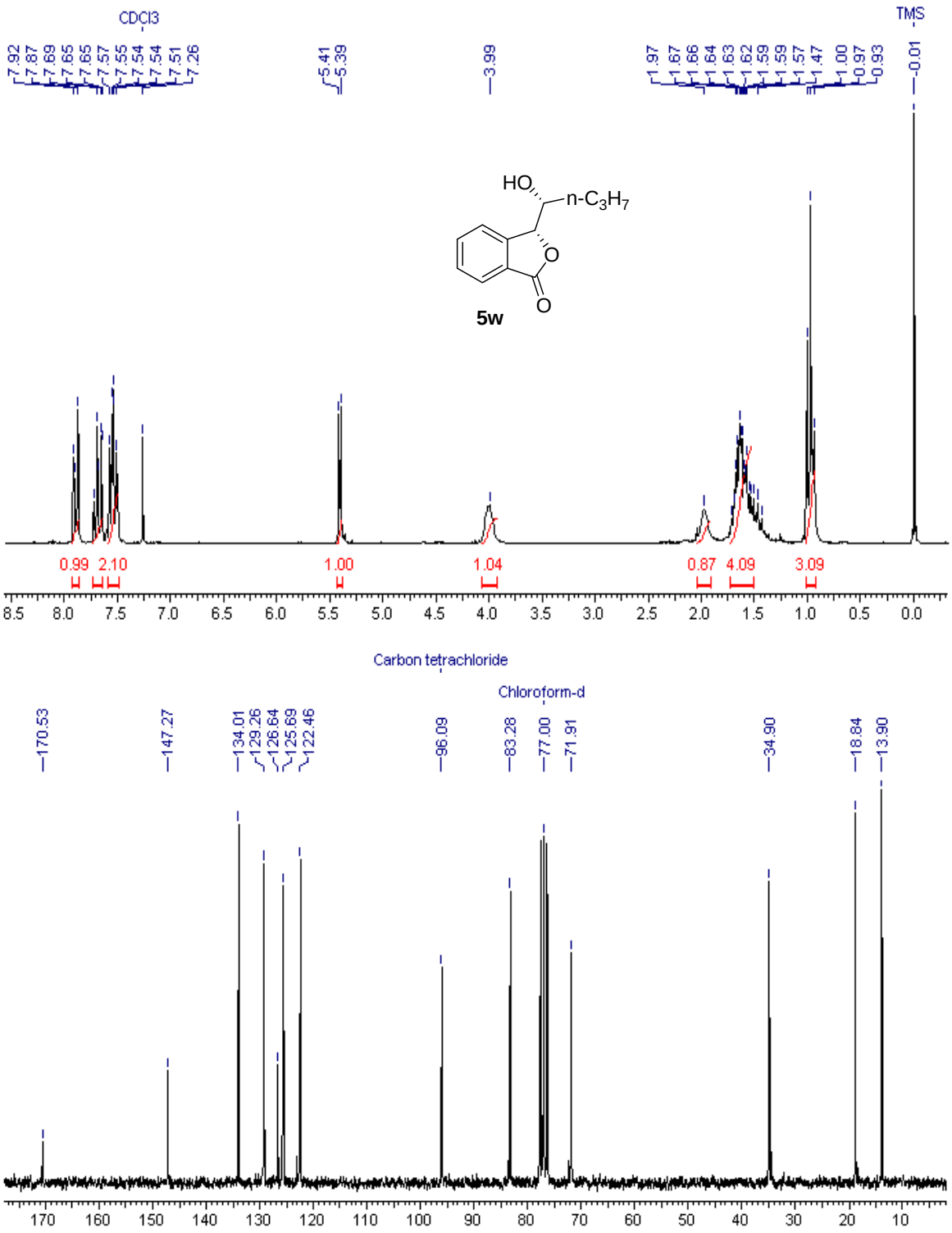
^{1}H and ^{13}C NMR spectra of 5t



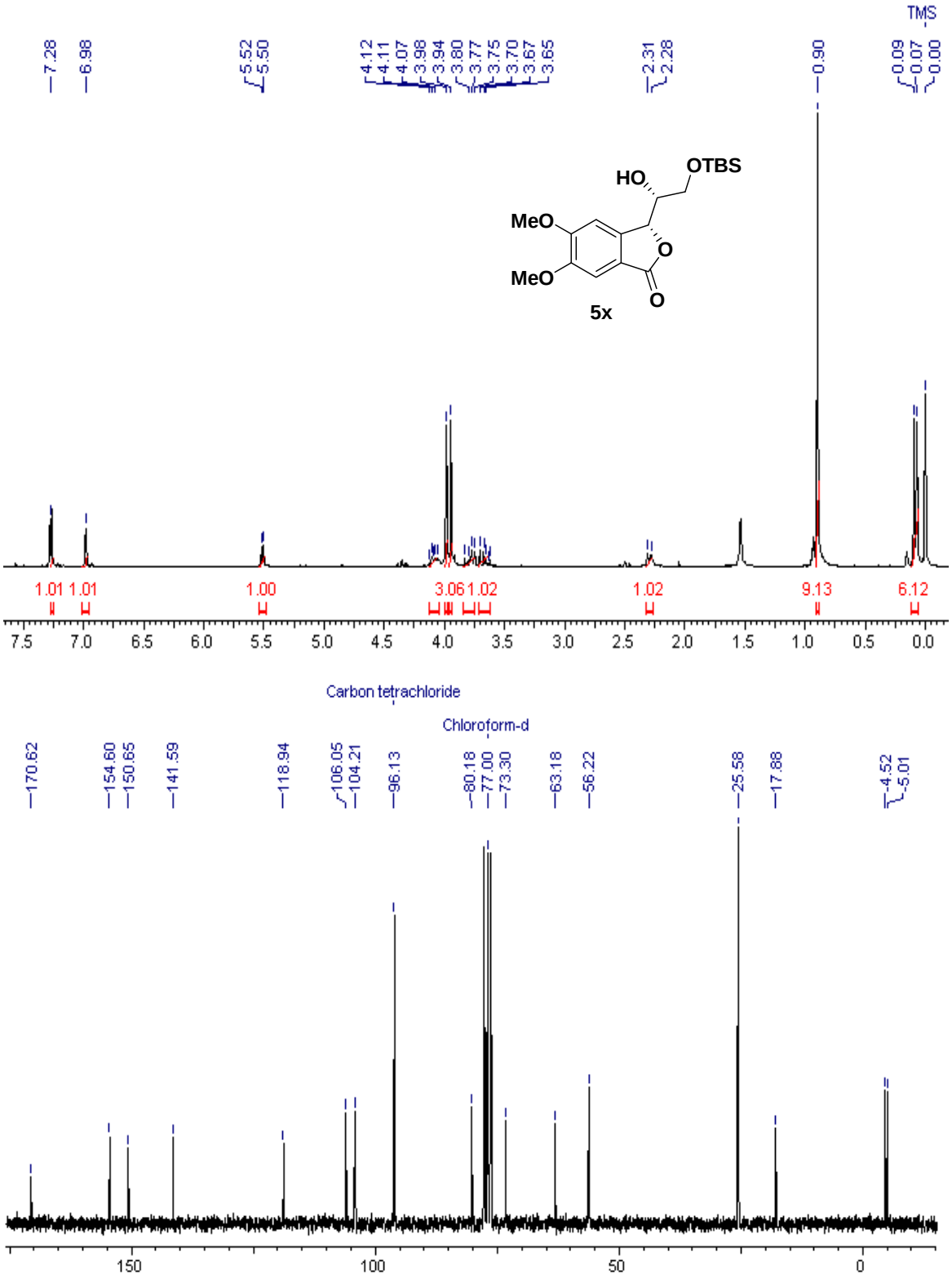
^{1}H and ^{13}C NMR spectra of 5u



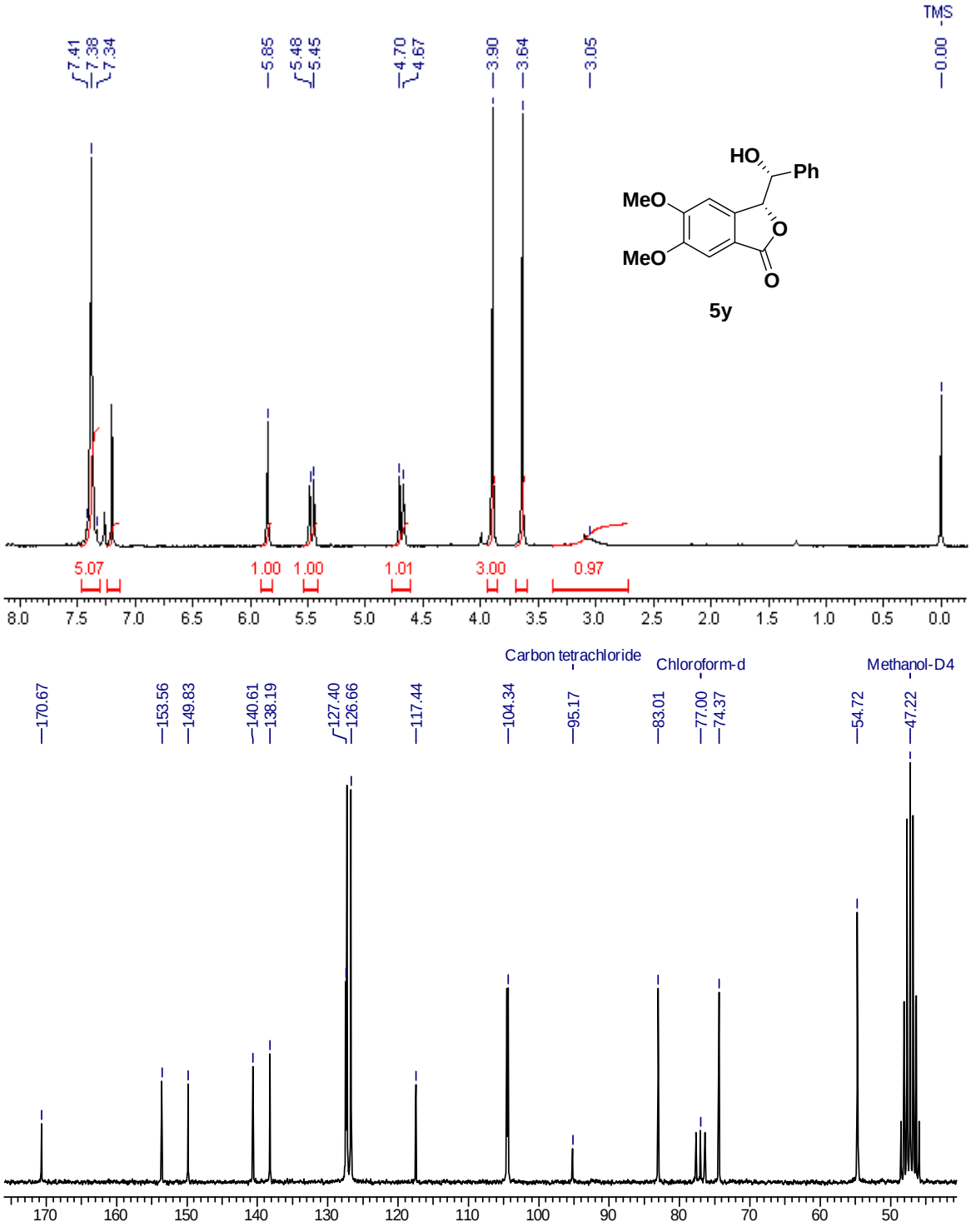
^{1}H and ^{13}C NMR spectra of 5v



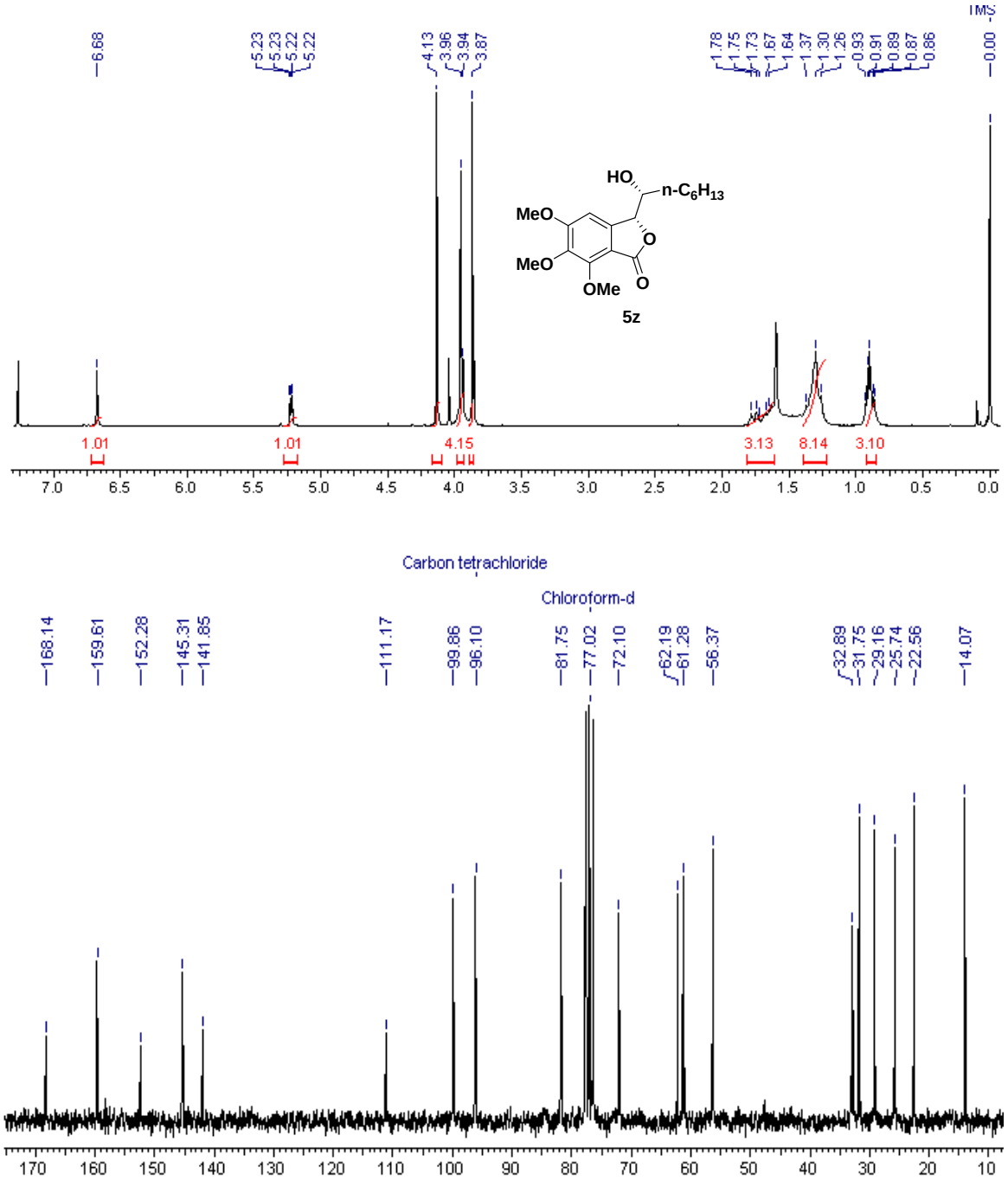
^{1}H and ^{13}C NMR spectra of 5w



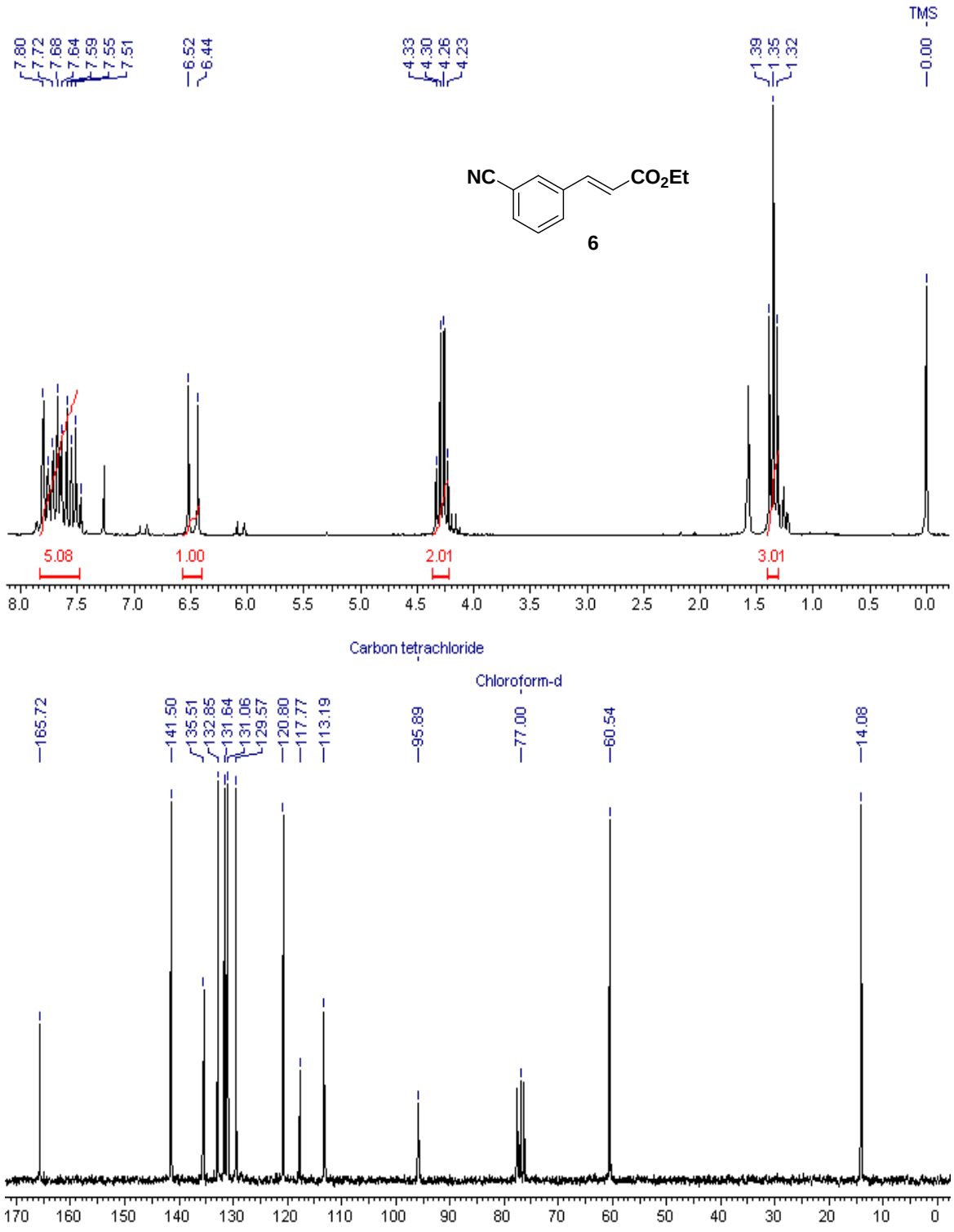
^{1}H and ^{13}C NMR spectra of 5x



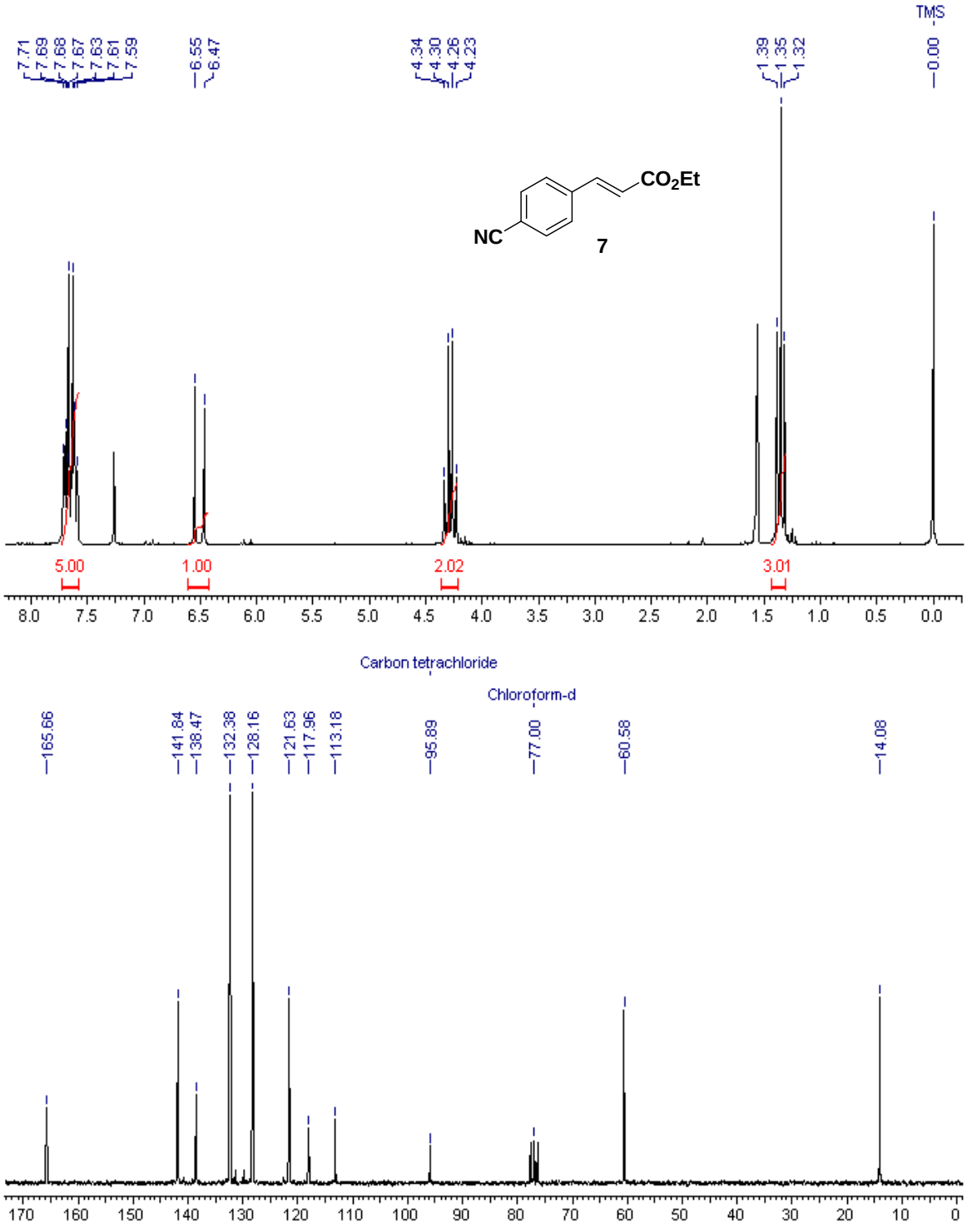
^{1}H and ^{13}C NMR spectra of 5y



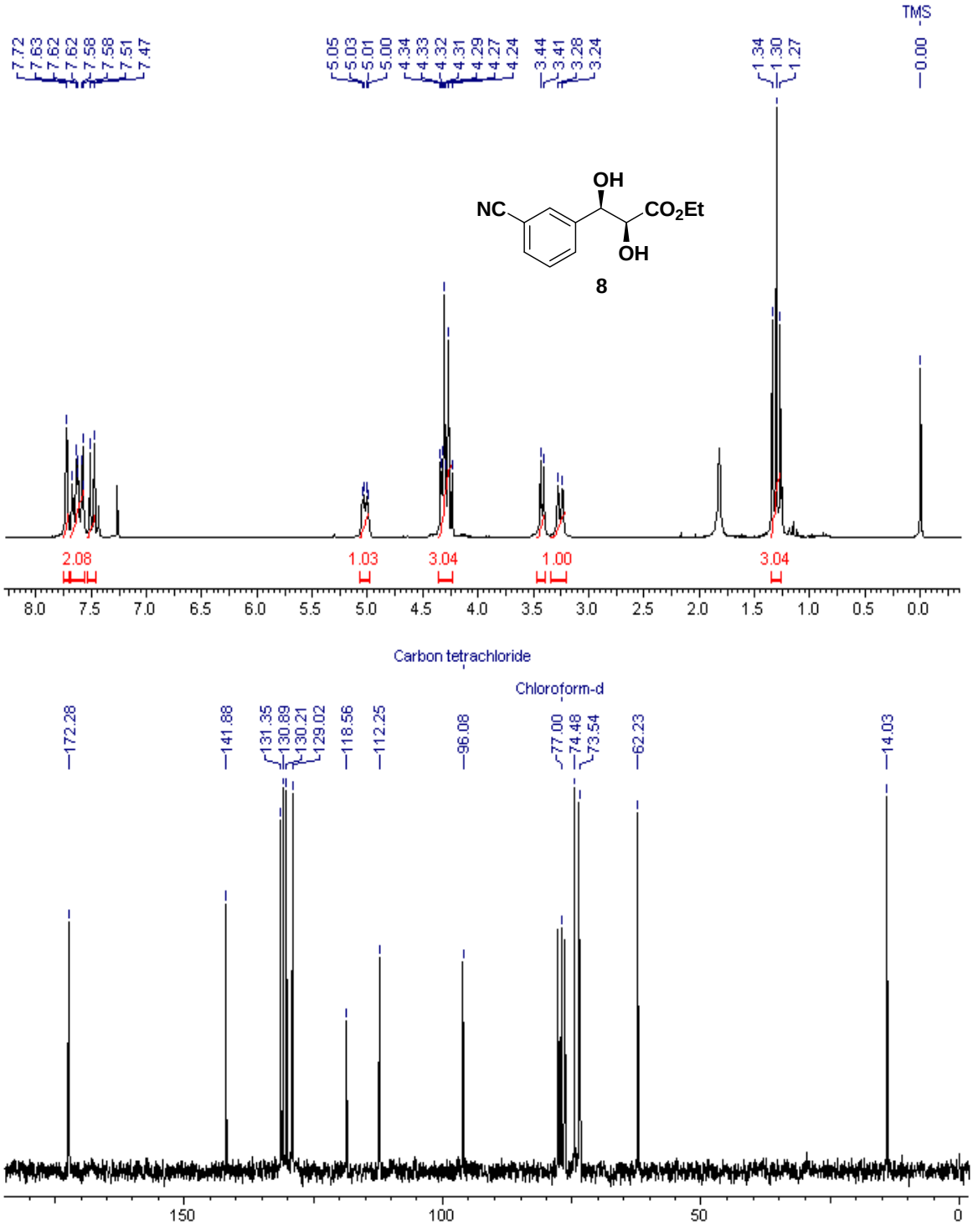
^{1}H and ^{13}C NMR spectra of 5z



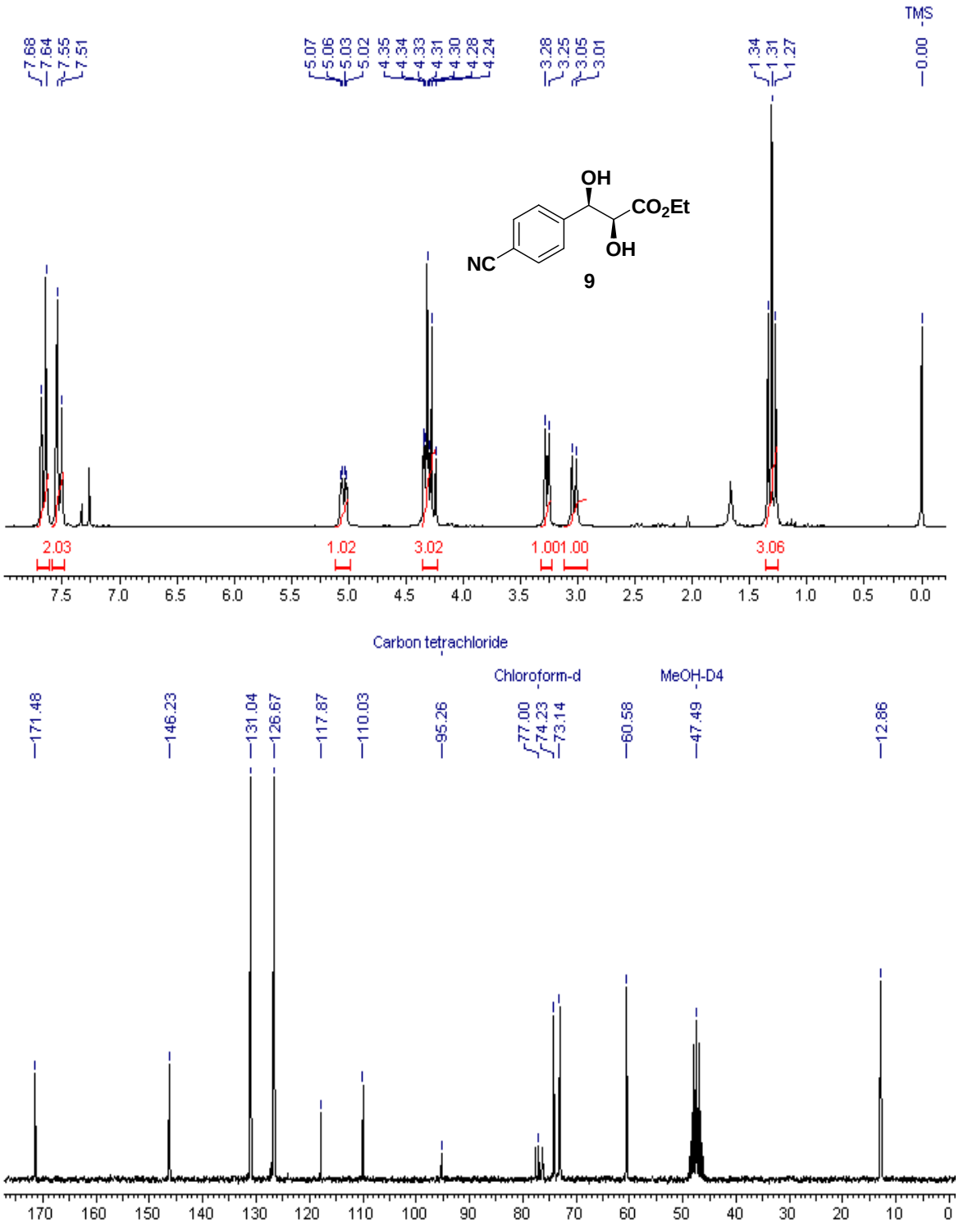
^{1}H and ^{13}C NMR spectra of 6



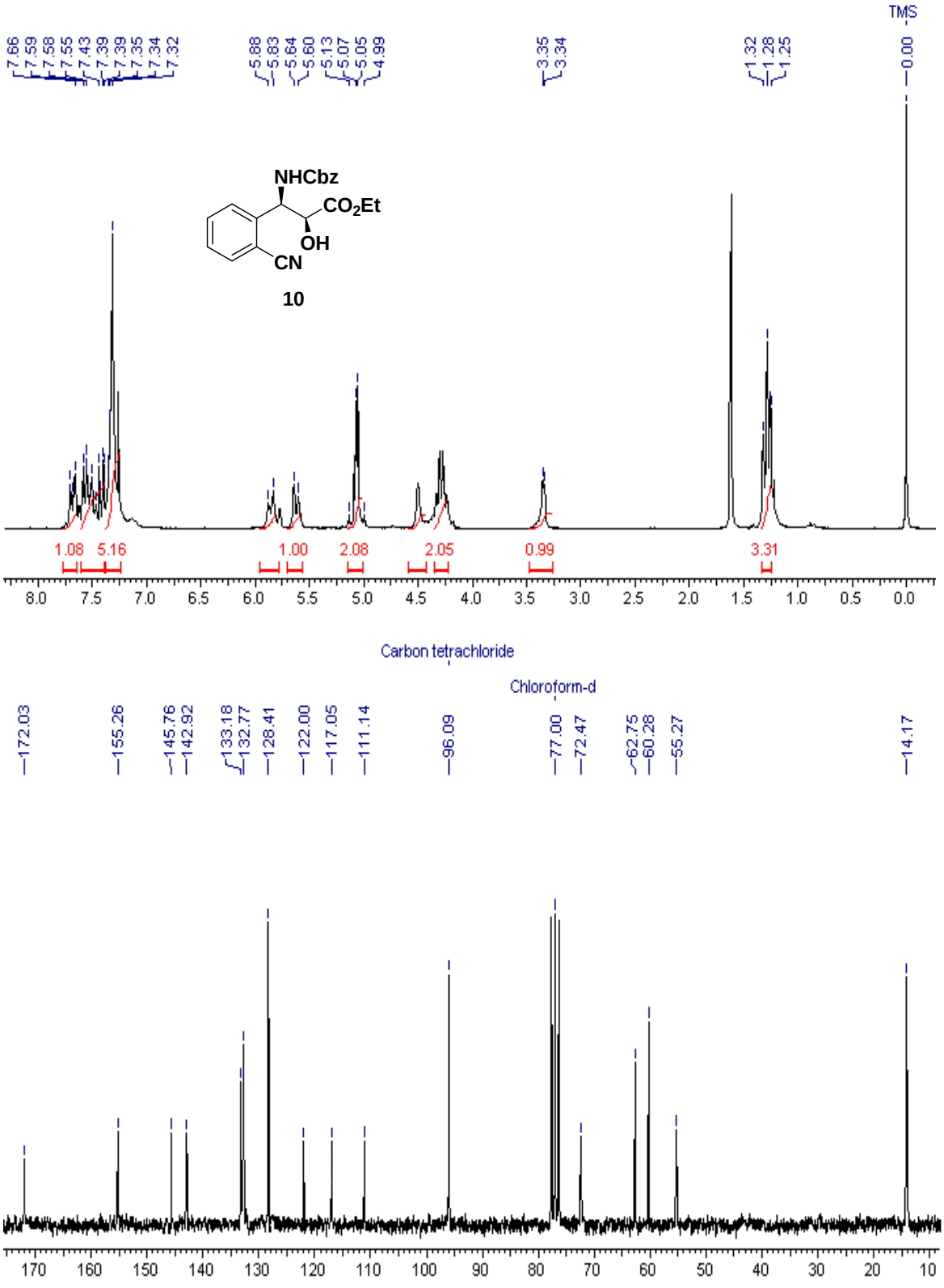
^{1}H and ^{13}C NMR spectra of 7



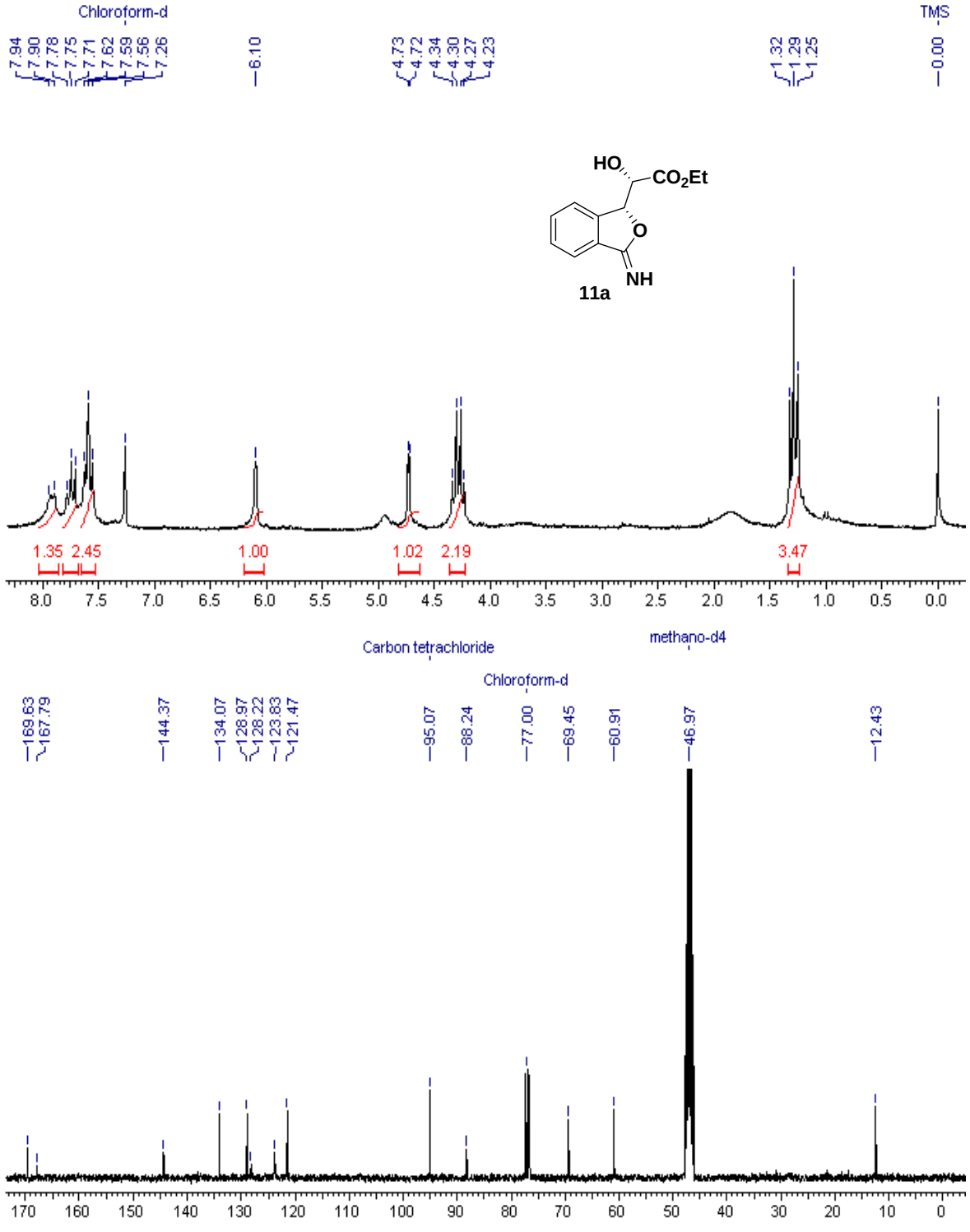
^{1}H and ^{13}C NMR spectra of 8



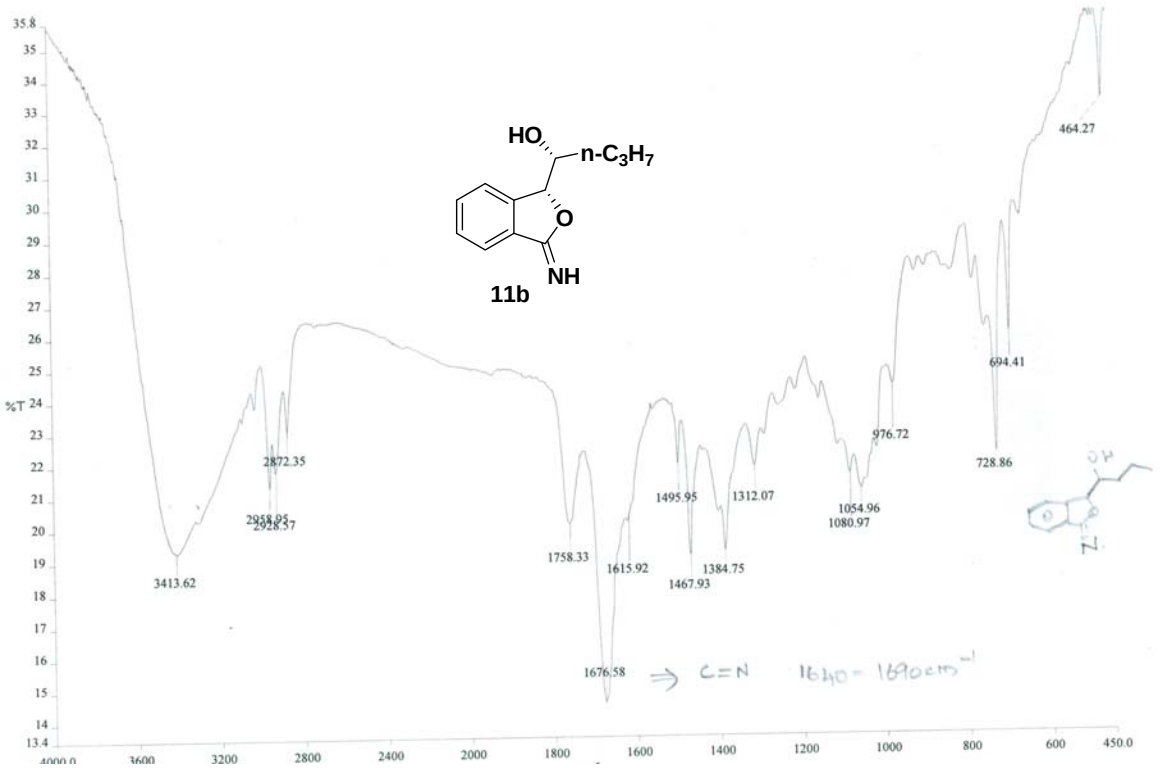
^{1}H and ^{13}C NMR spectra of 9

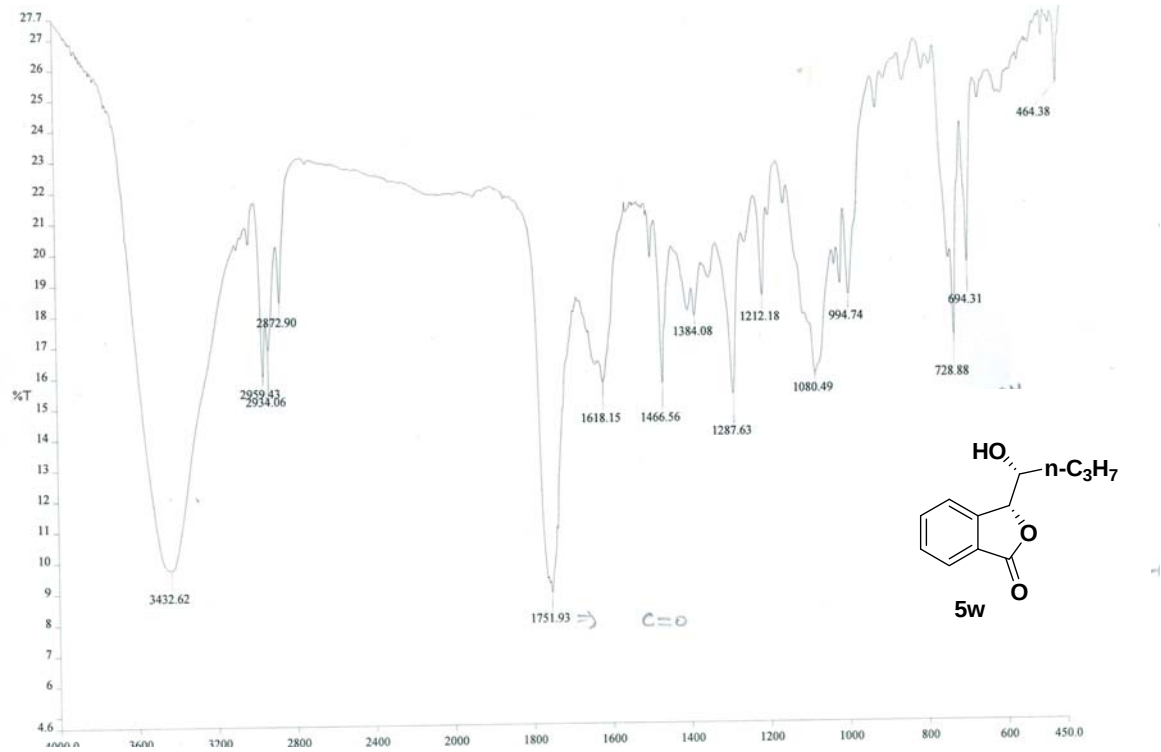


^{1}H and ^{13}C NMR spectra of 10

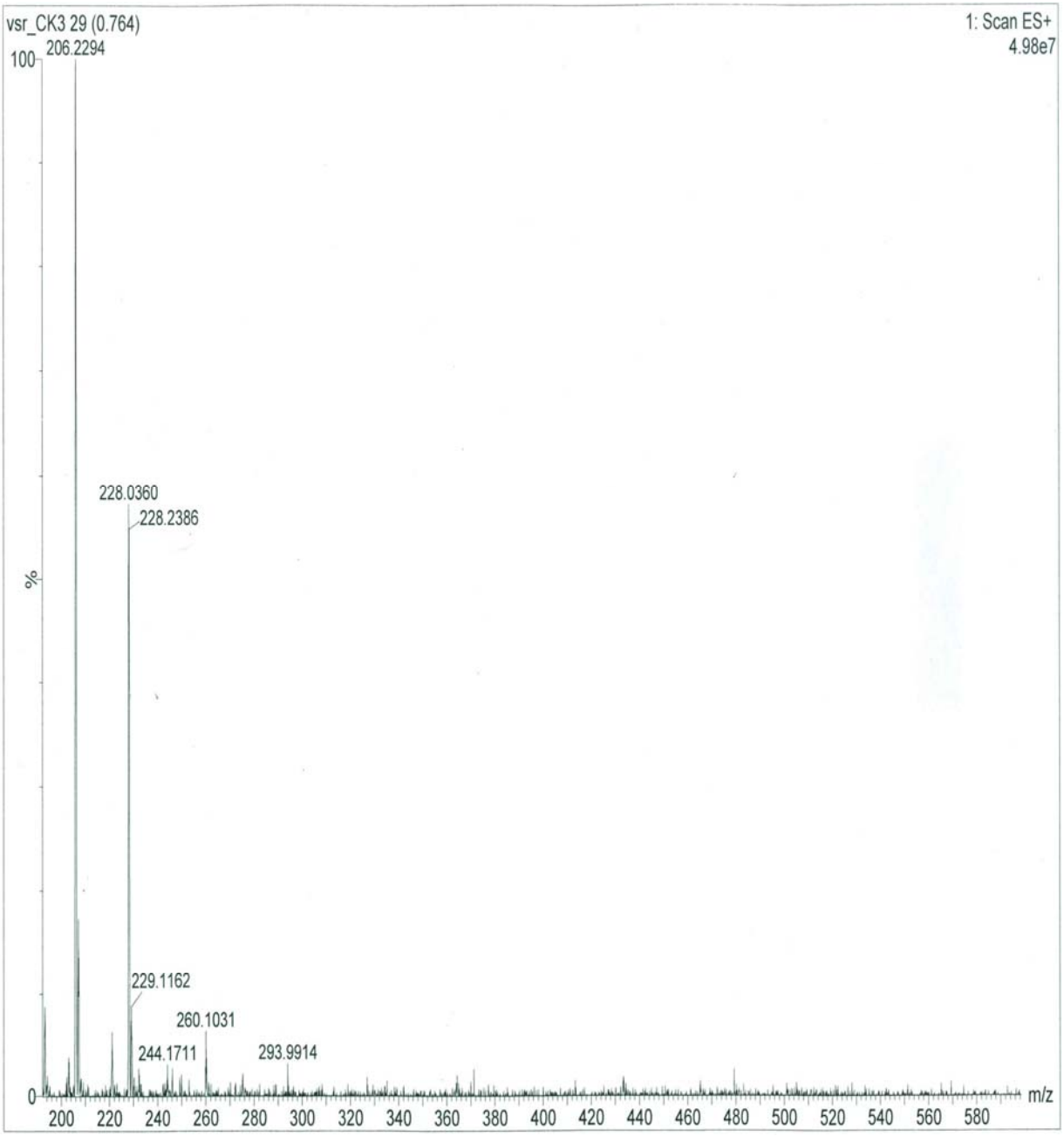


^{1}H and ^{13}C NMR spectra of 11a

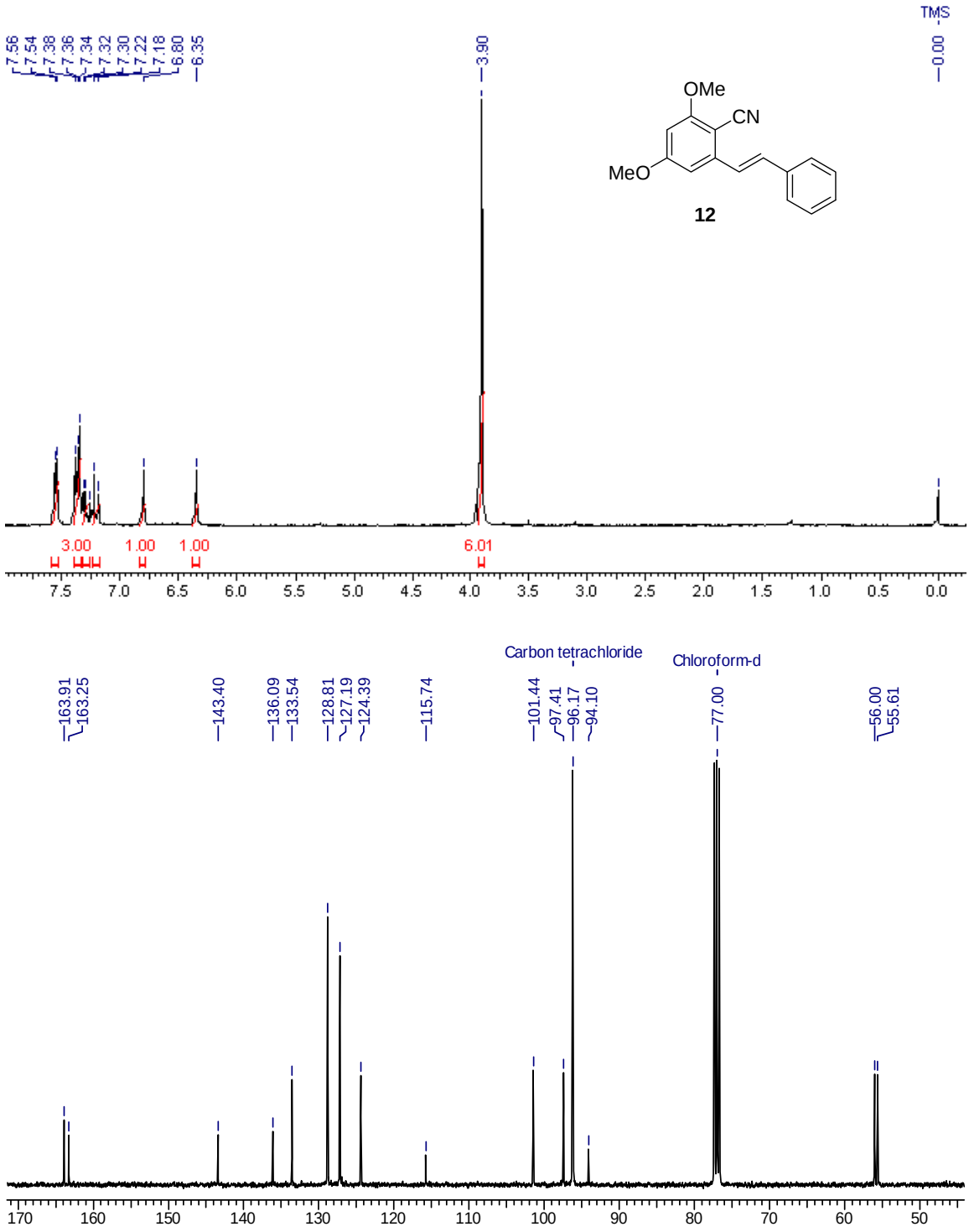




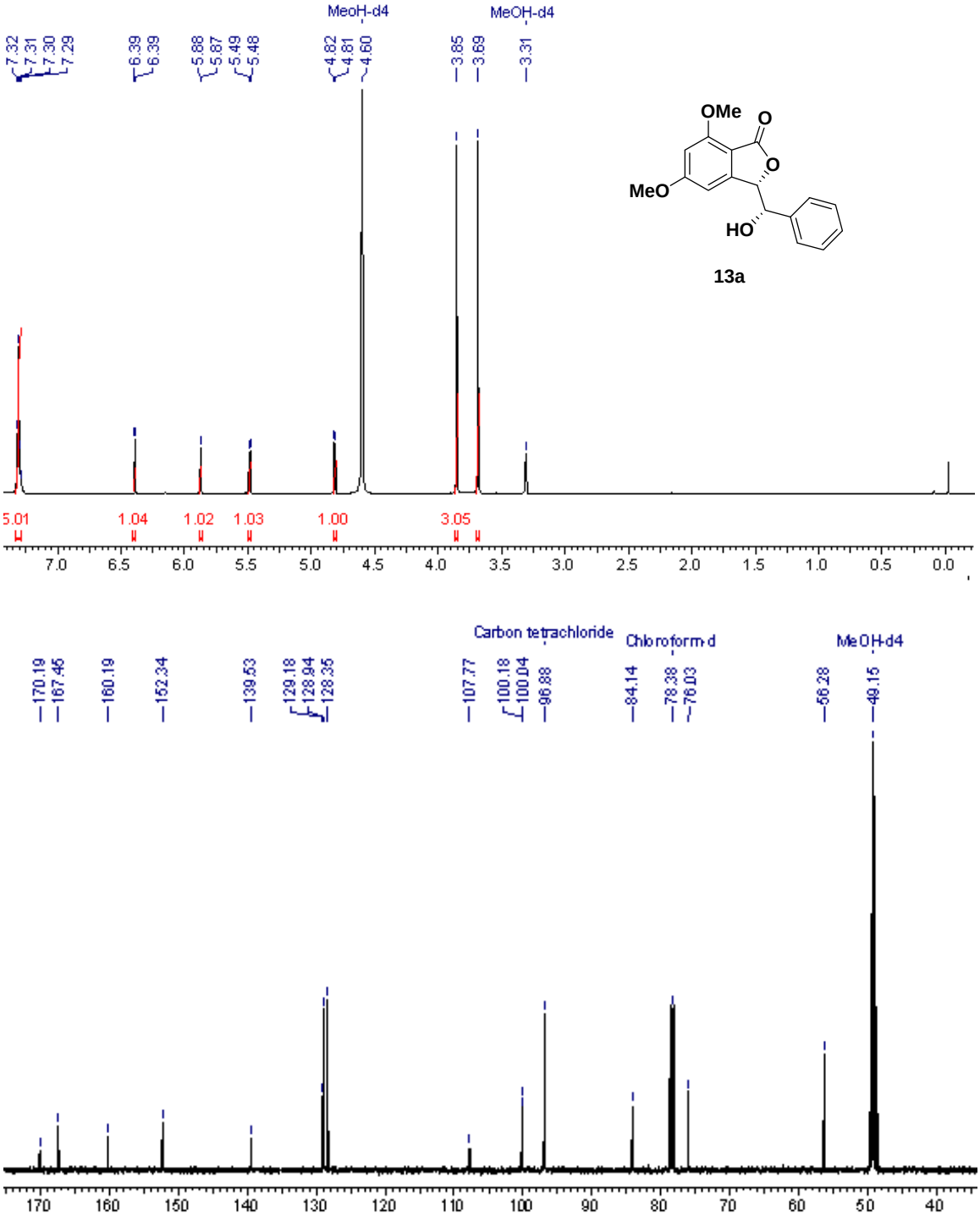
IR spectra of 11b and 5w



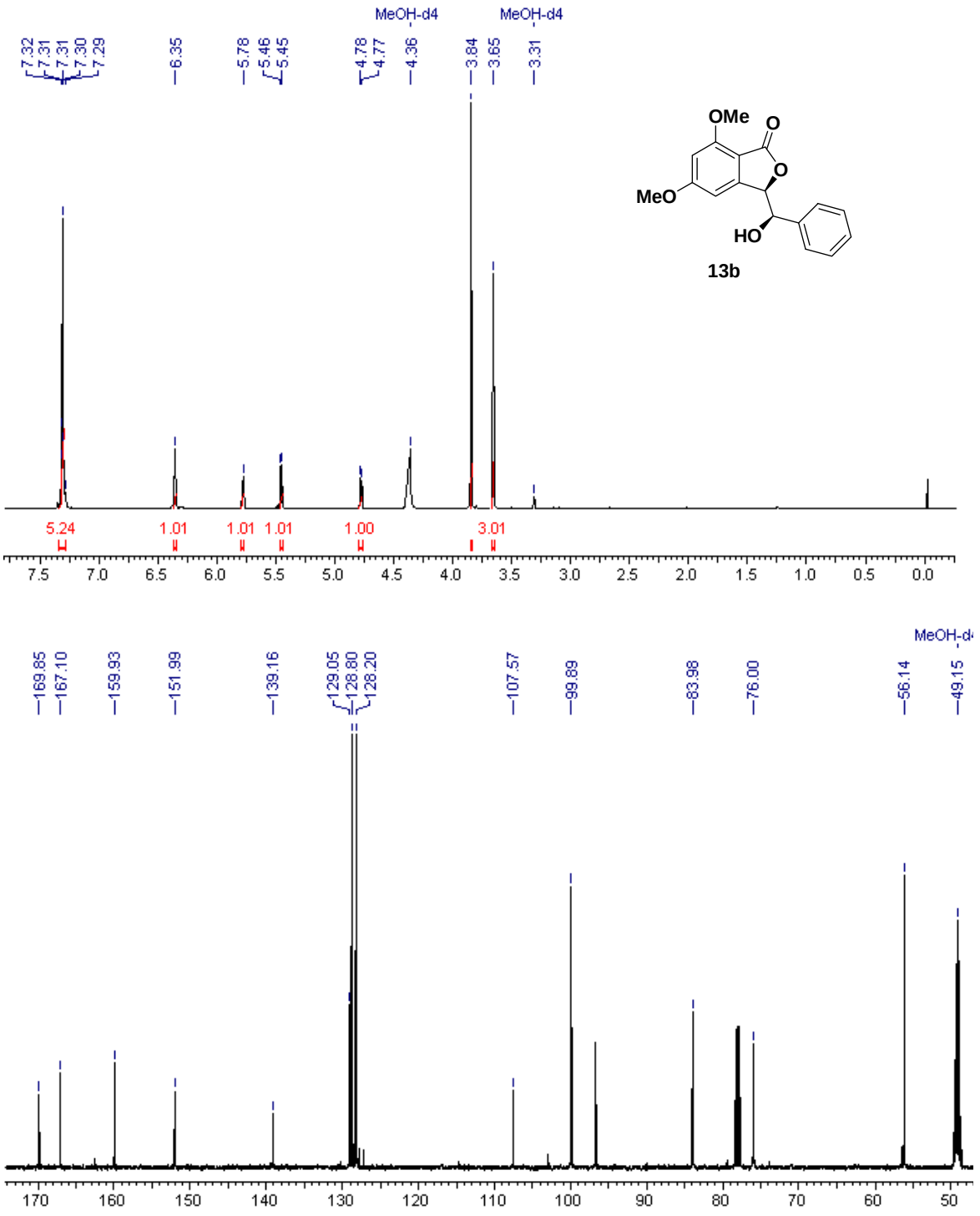
Mass spectrum of 11b



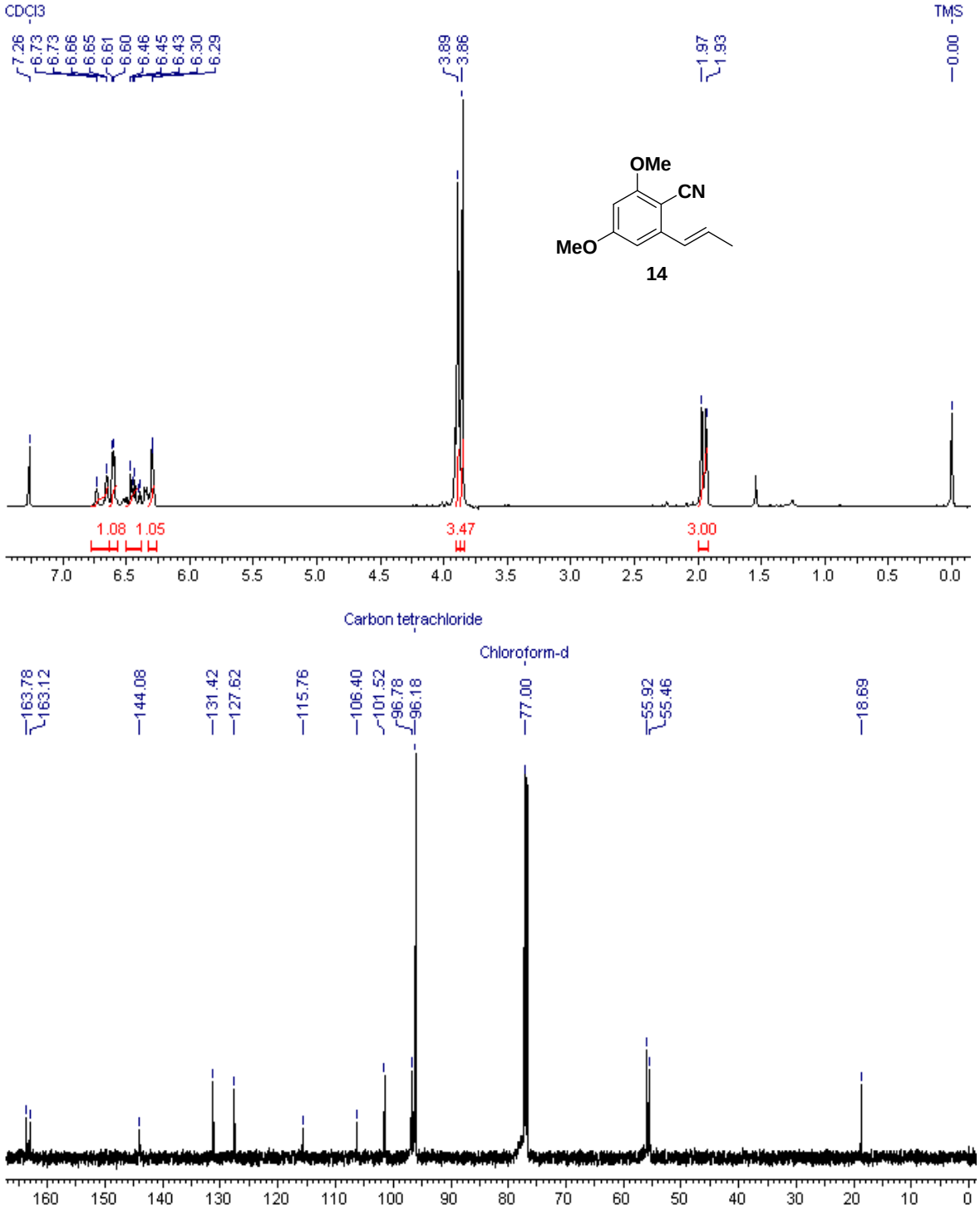
^{1}H and ^{13}C NMR spectra of 12



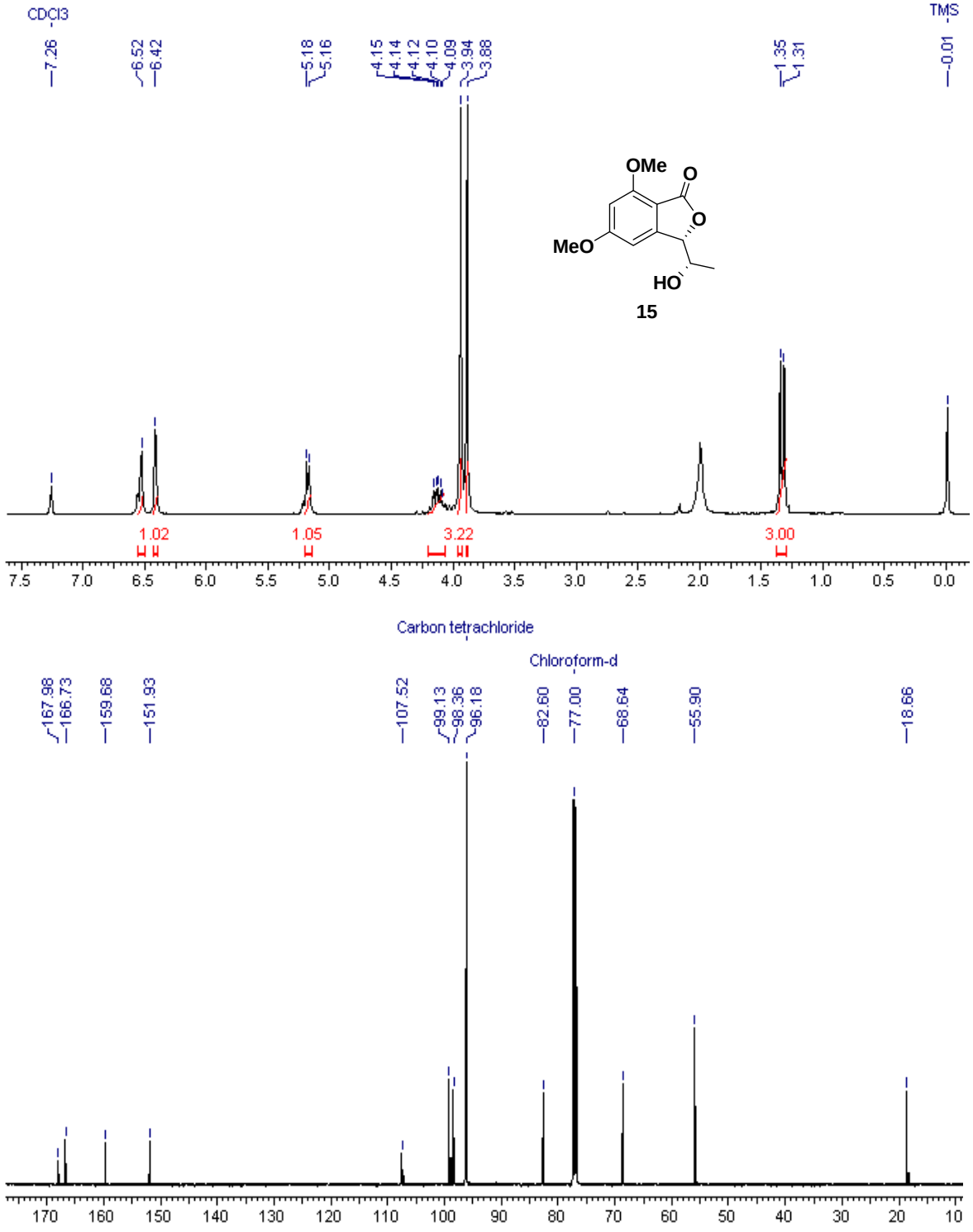
^{1}H and ^{13}C NMR spectra of 13a



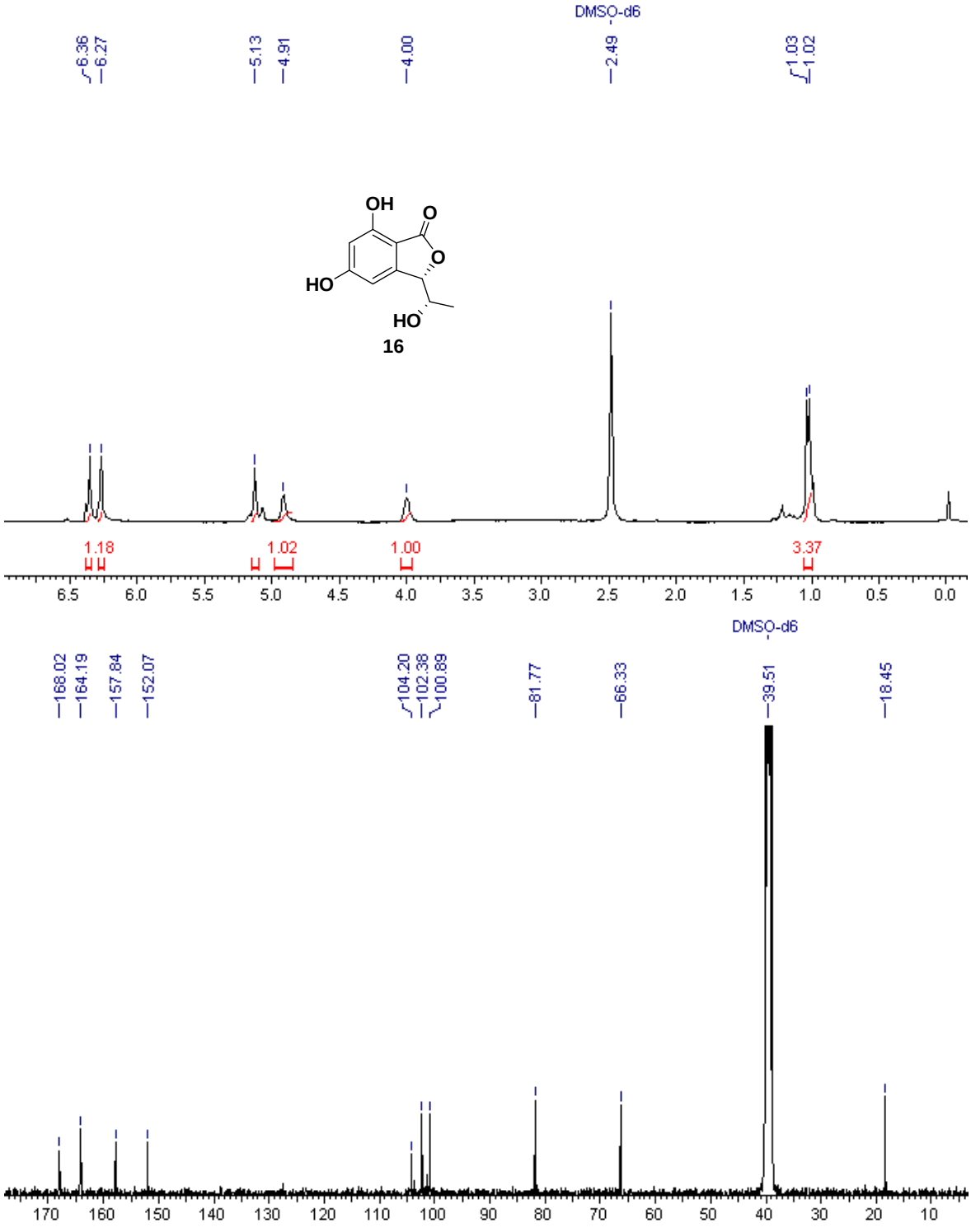
^{1}H and ^{13}C NMR spectra of 13b



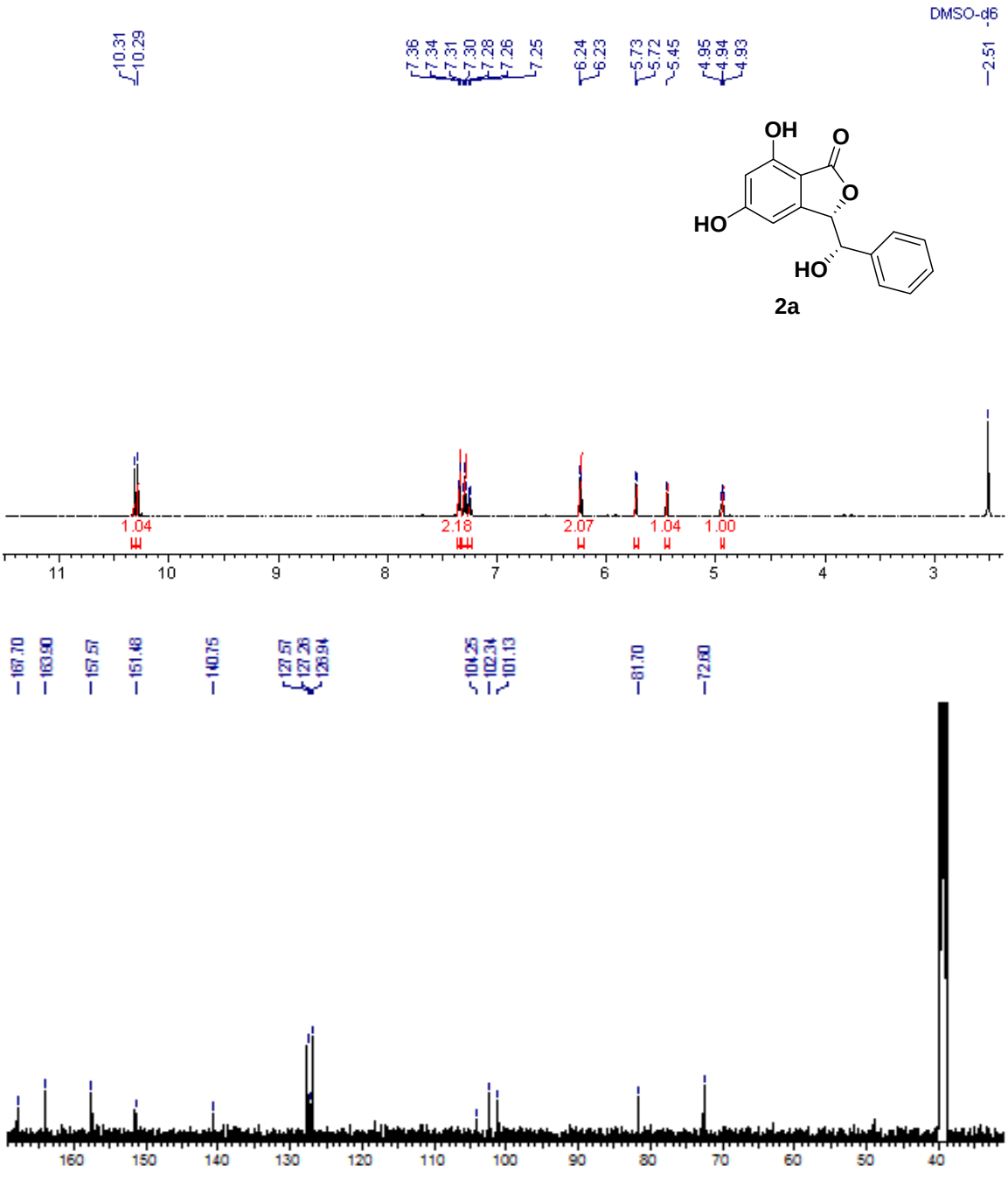
^{1}H and ^{13}C NMR spectra of 14



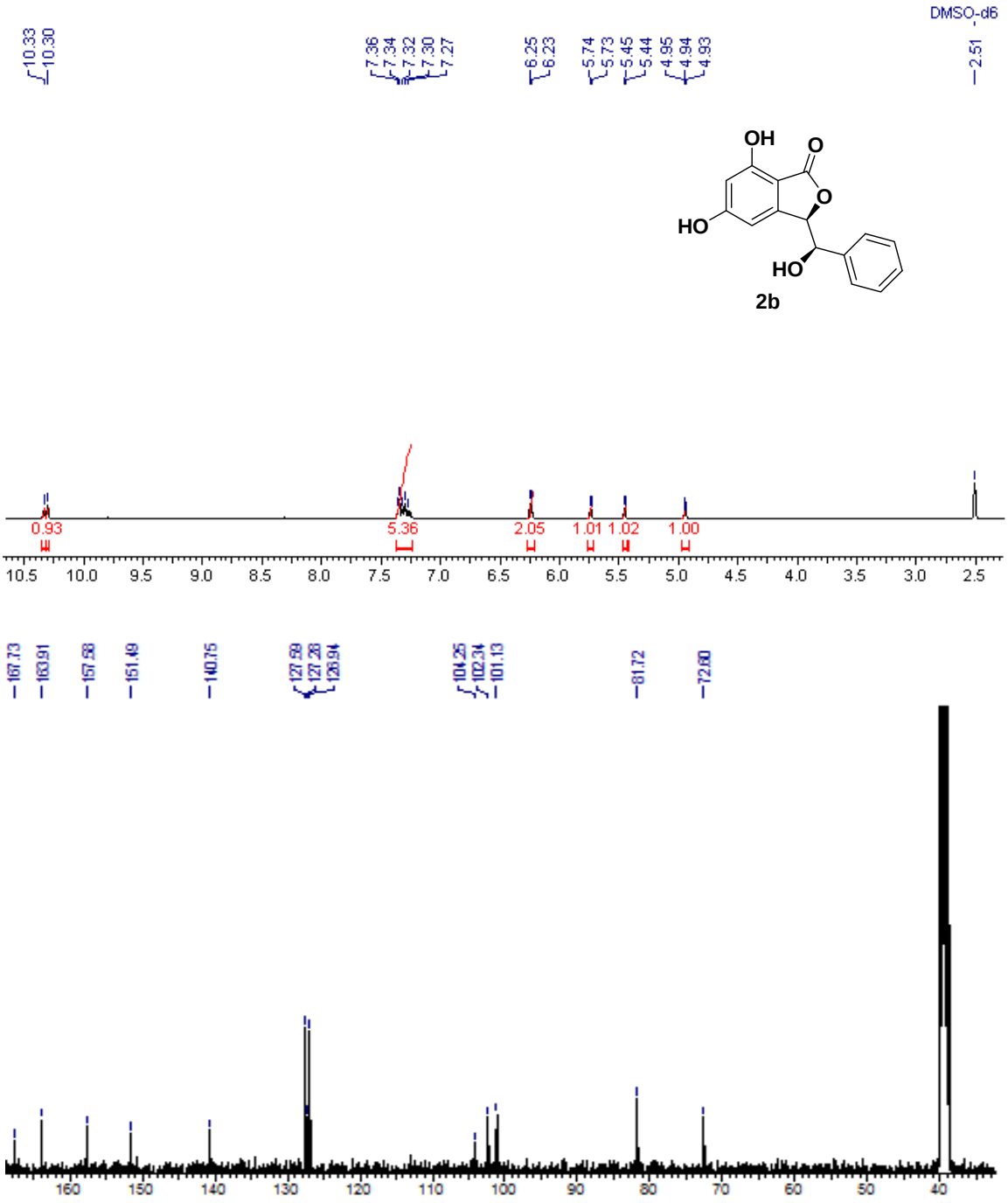
^{1}H and ^{13}C NMR spectra of 15



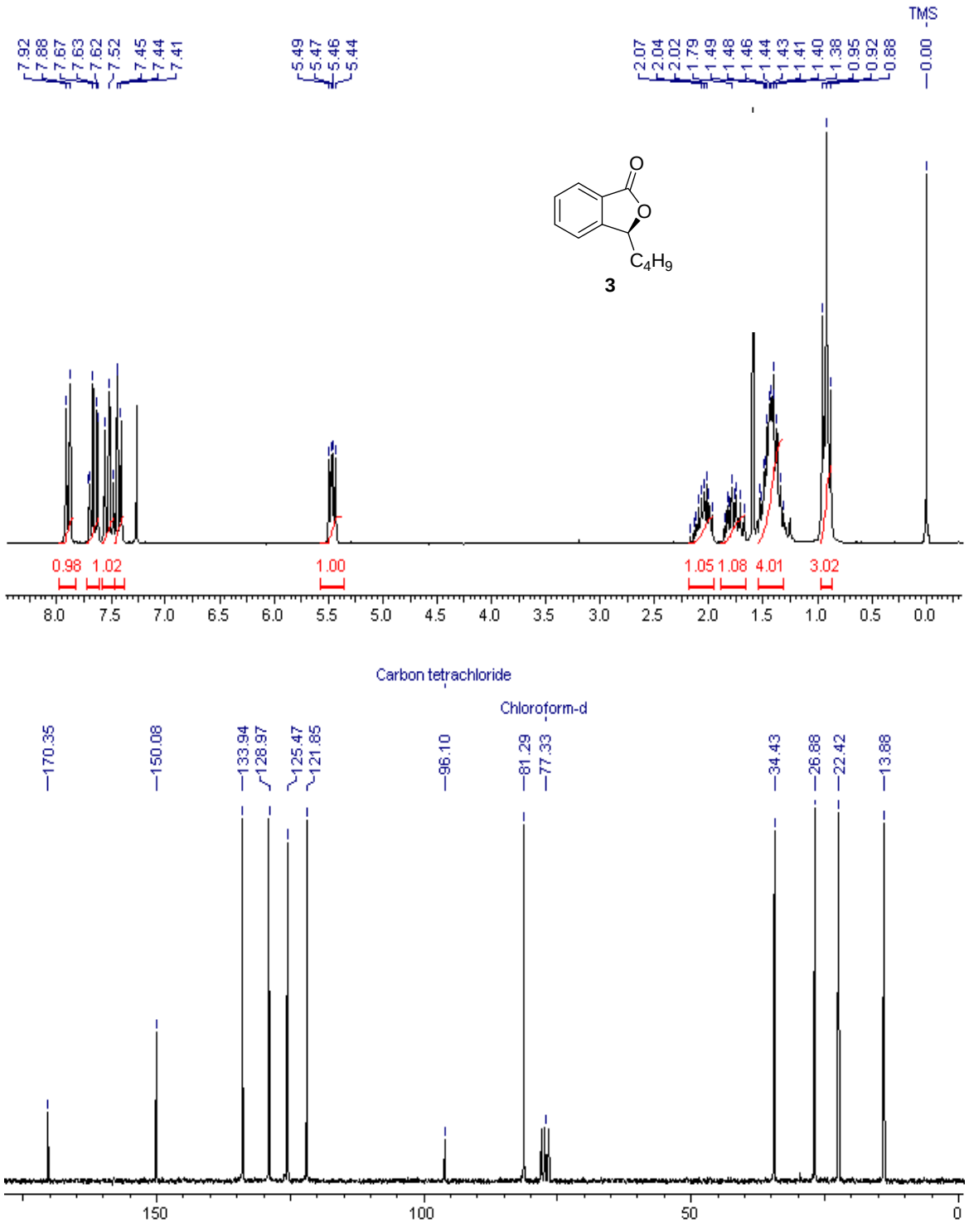
^{1}H and ^{13}C NMR spectra of 16



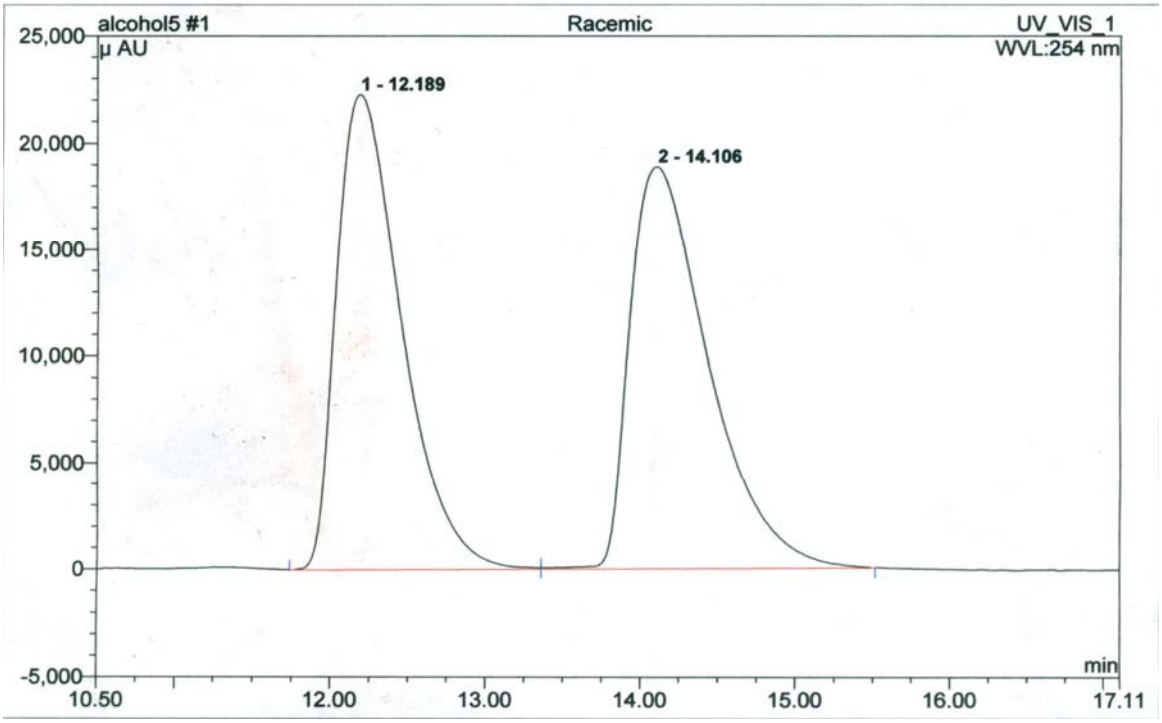
^{1}H and ^{13}C NMR spectra of 2a

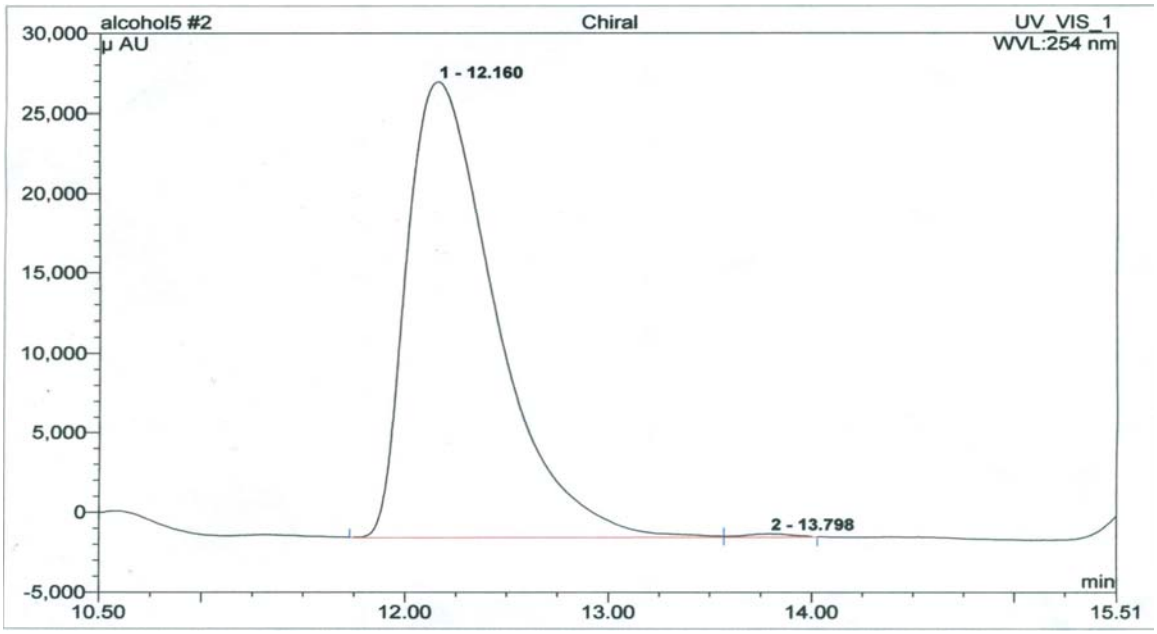


^{1}H and ^{13}C NMR spectra of 2b



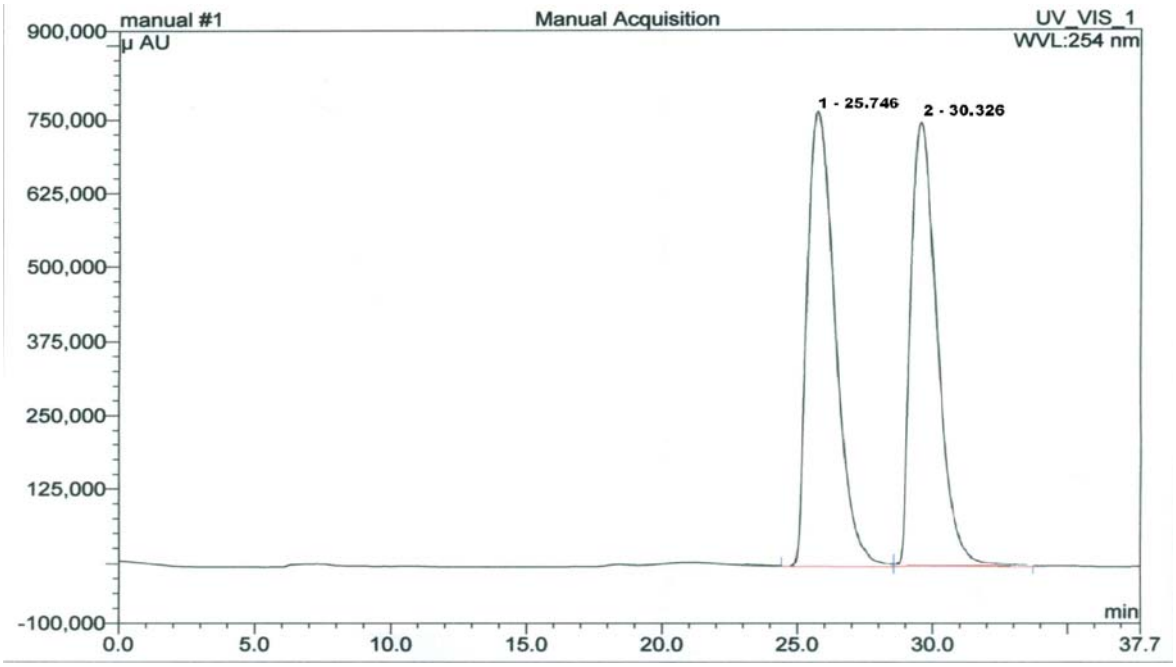
^{1}H and ^{13}C NMR spectra of 3

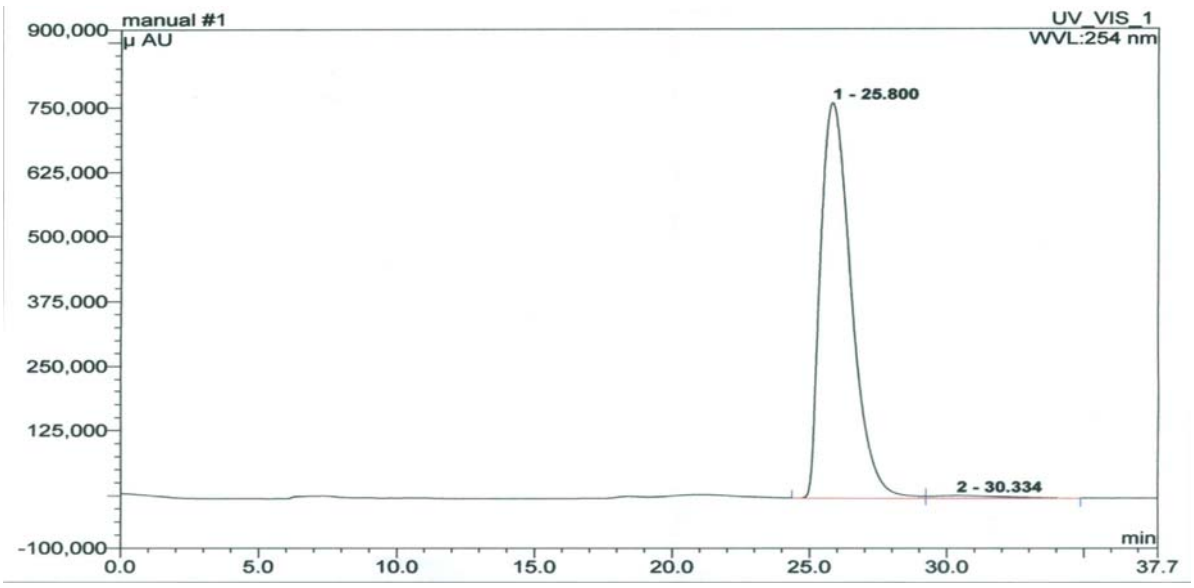




No	Ret. Time min	Height µ AU	Area µ AU* min	Rel. Area %	Amount	Type
1	12.16	28495.075	14410.126	99.65	n. a.	BMB
2	13.80	189.662	50.523	0.35	n. a.	BMB

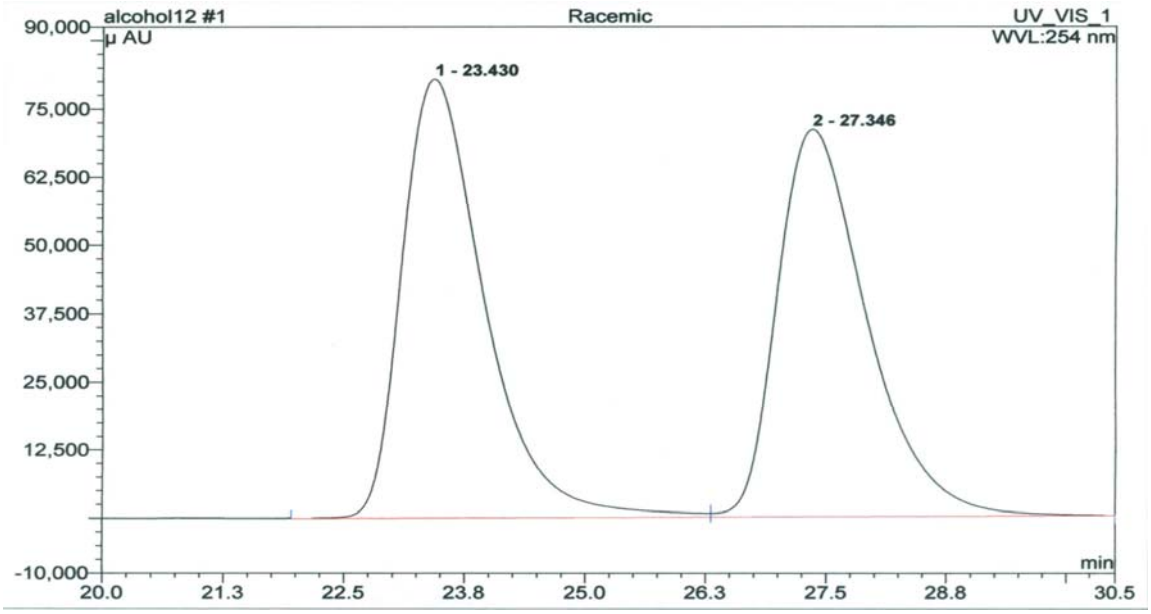
HPLC chromatogram of 5a

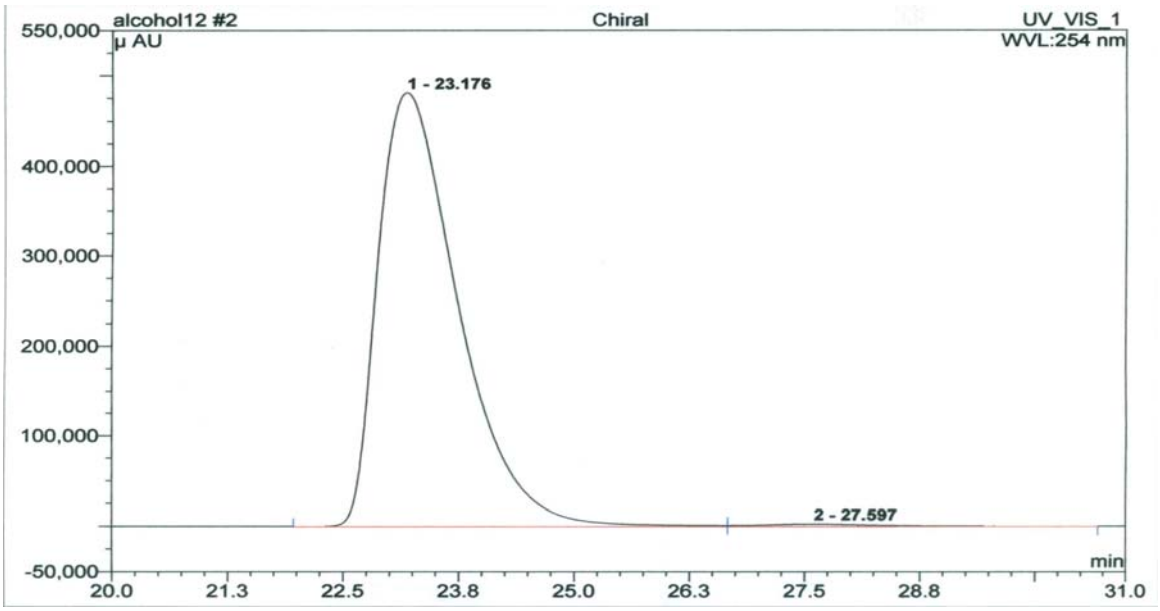




No	Ret. Time min	Height µ AU	Area µ AU* min	Rel. Area %	Amount	Type
1	25.80	761537.955	992808.305	99.55	n. a.	BMB
2	30.33	4531.145	4477.146	0.45	n. a.	BMB

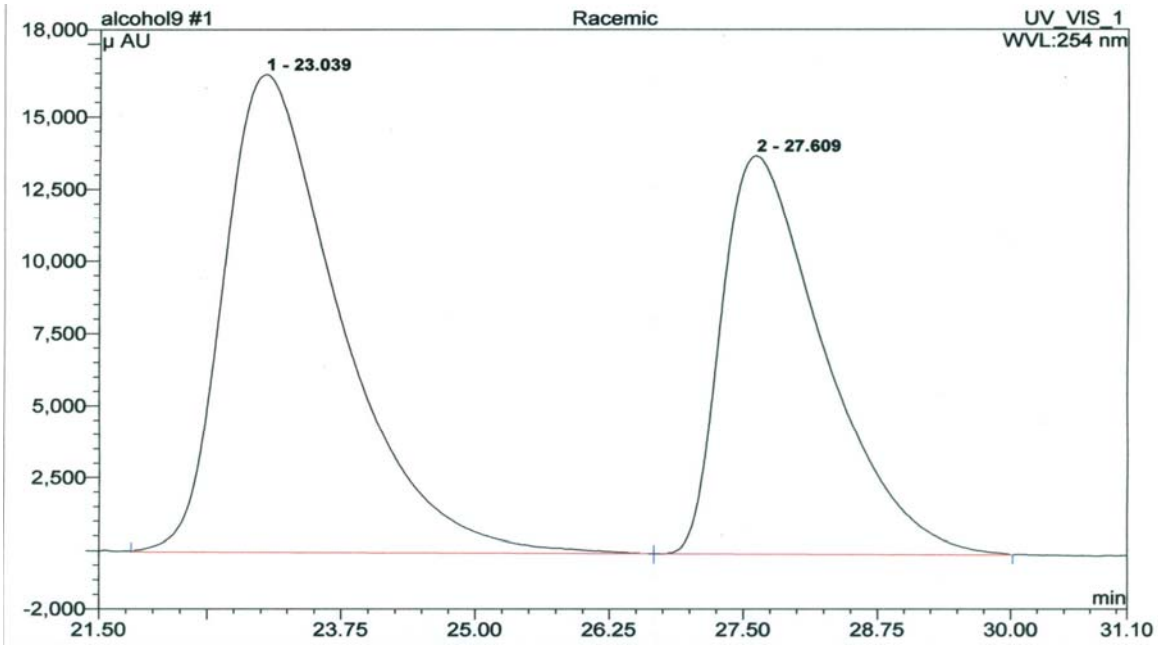
HPLC chromatogram of 5b

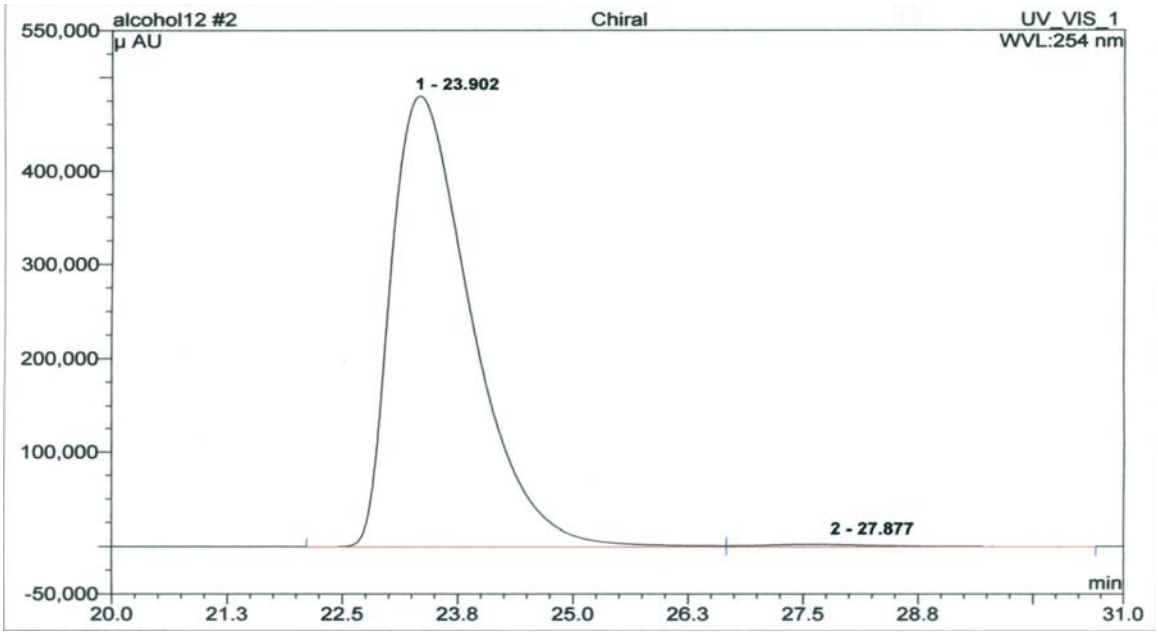




No	Ret. Time min	Height µ AU	Area µ AU* min	Rel. Area %	Amount	Type
1	23.18	48063.355	484381.220	99.36	n. a.	BMB
2	27.60	2265.930	3105.222	0.64	n. a.	BMB

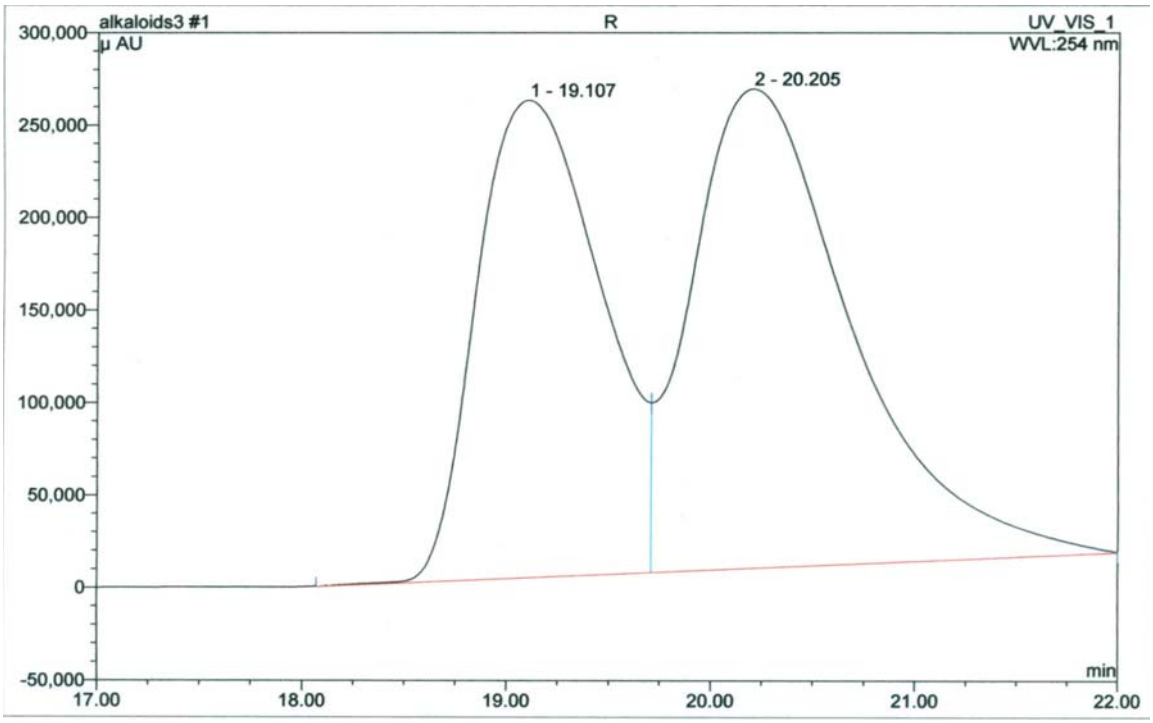
HPLC chromatogram of 5c

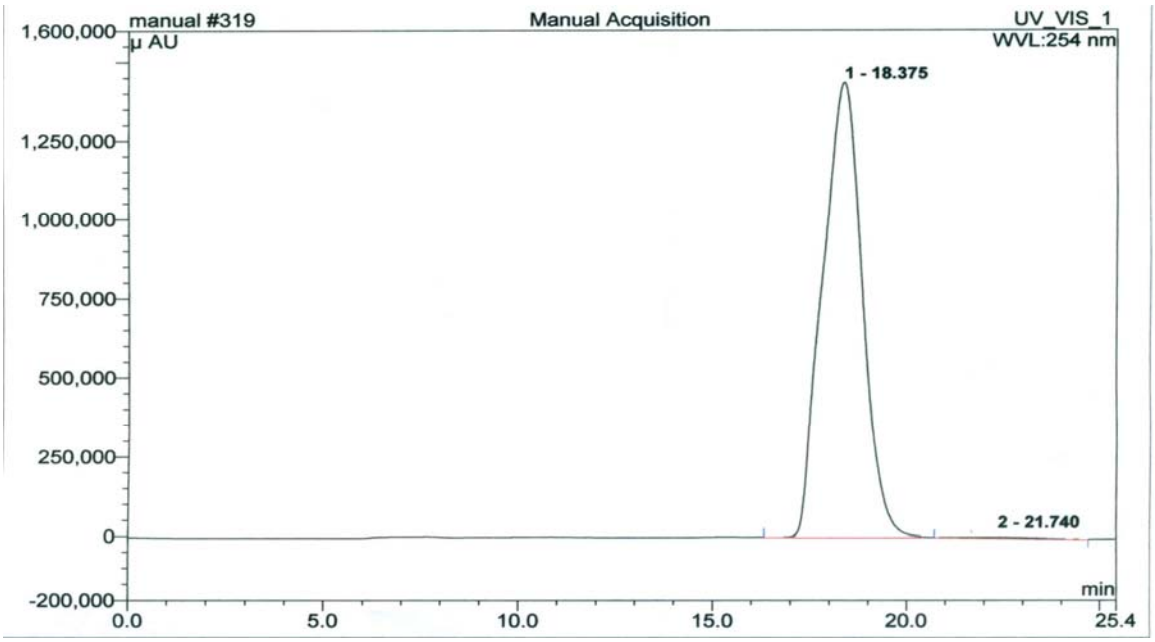




No	Ret. Time min	Height µ AU	Area µ AU* min	Rel. Area %	Amount	Type
1	23.90	48072.355	484390.220	99.44	n. a.	BMB
2	27.87	2273.930	3113.222	0.56	n. a.	BMB

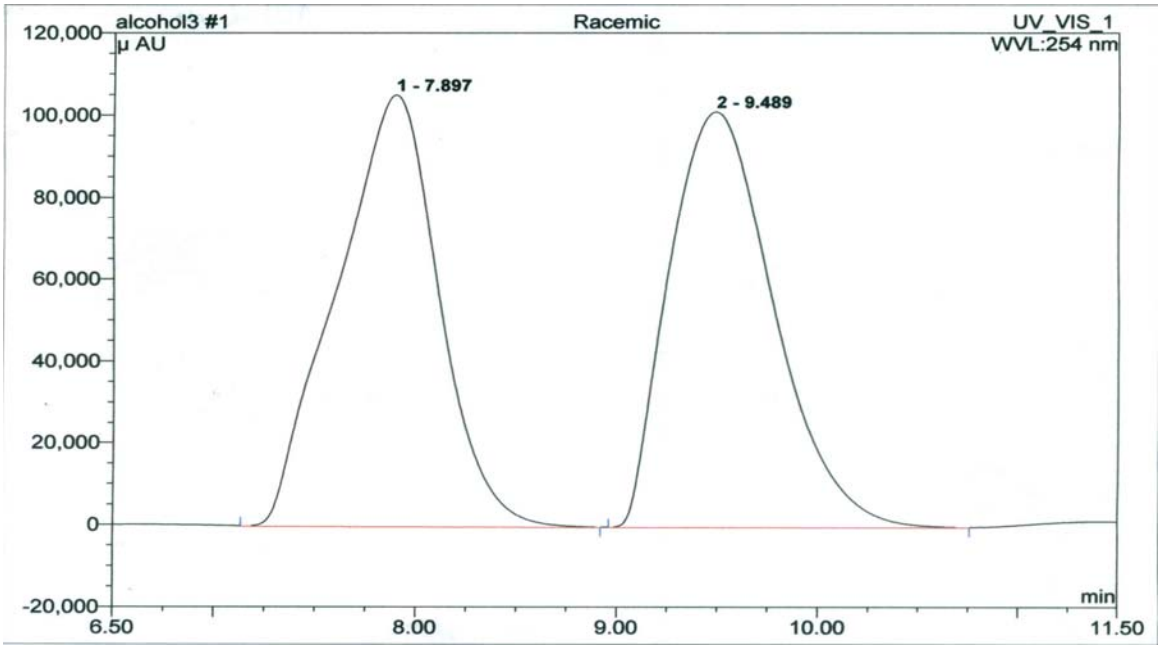
HPLC chromatogram of 5d

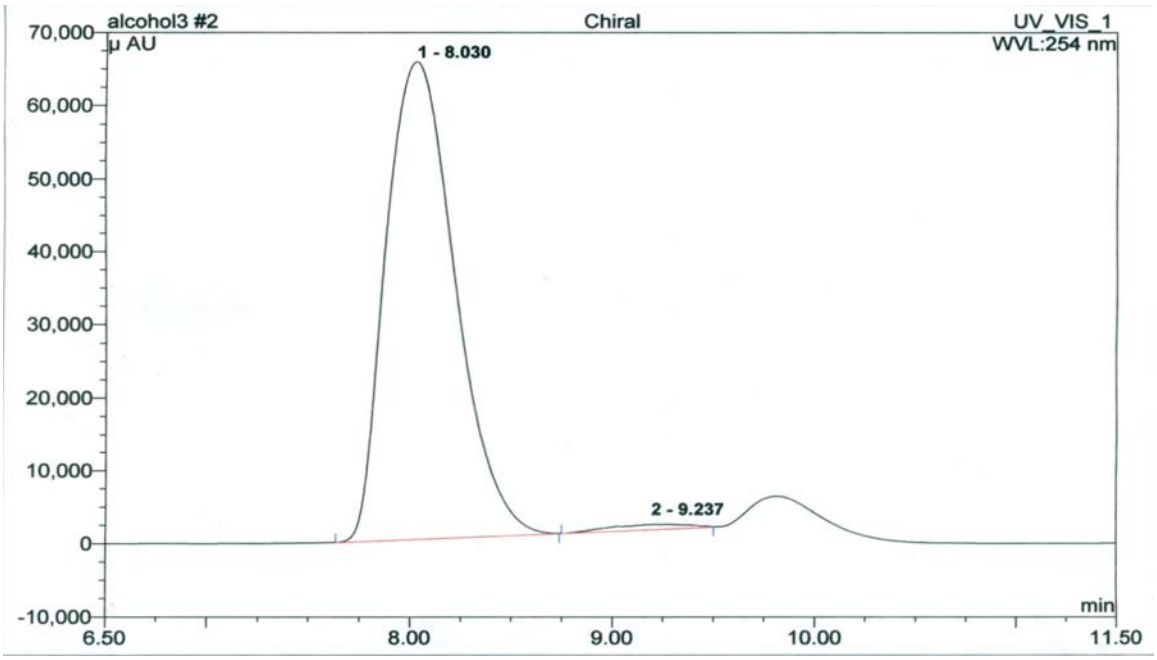




No	Ret. Time min	Height µ AU	Area µ AU* min	Rel. Area %	Amount	Type
1	18.37	1436573.591	1817973.860	99.60	n. a.	BMB
2	21.74	106560.833	7299.549	0.40	n. a.	BMB

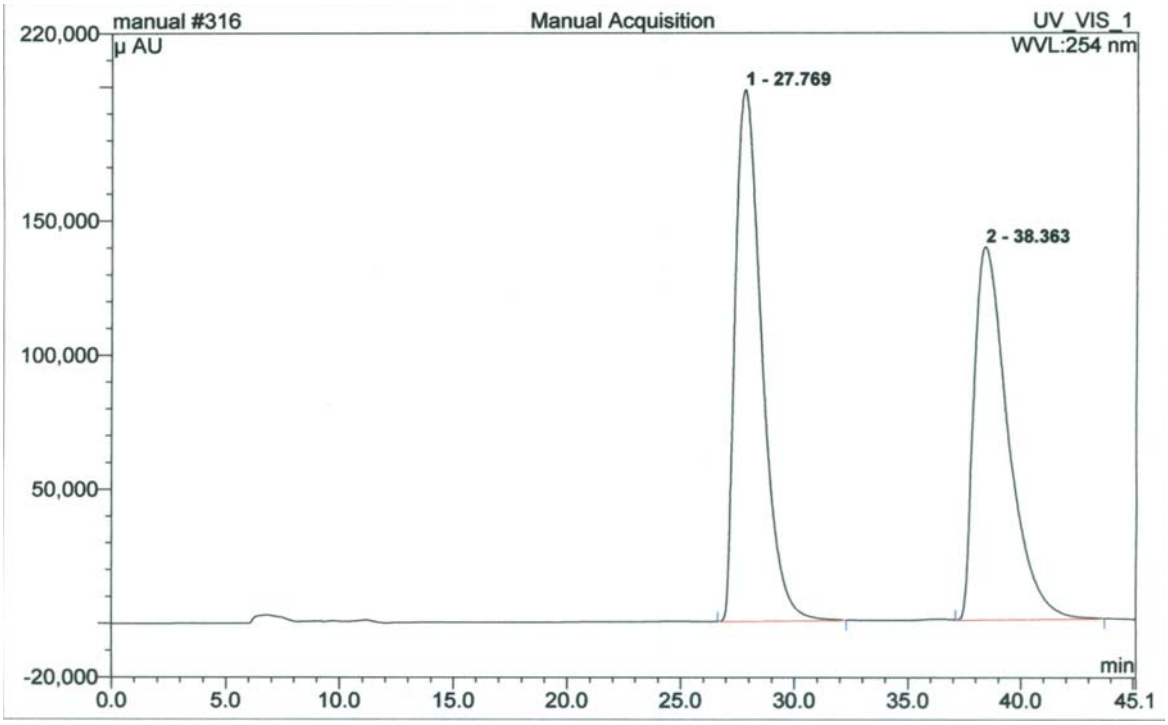
HPLC chromatogram of 5e

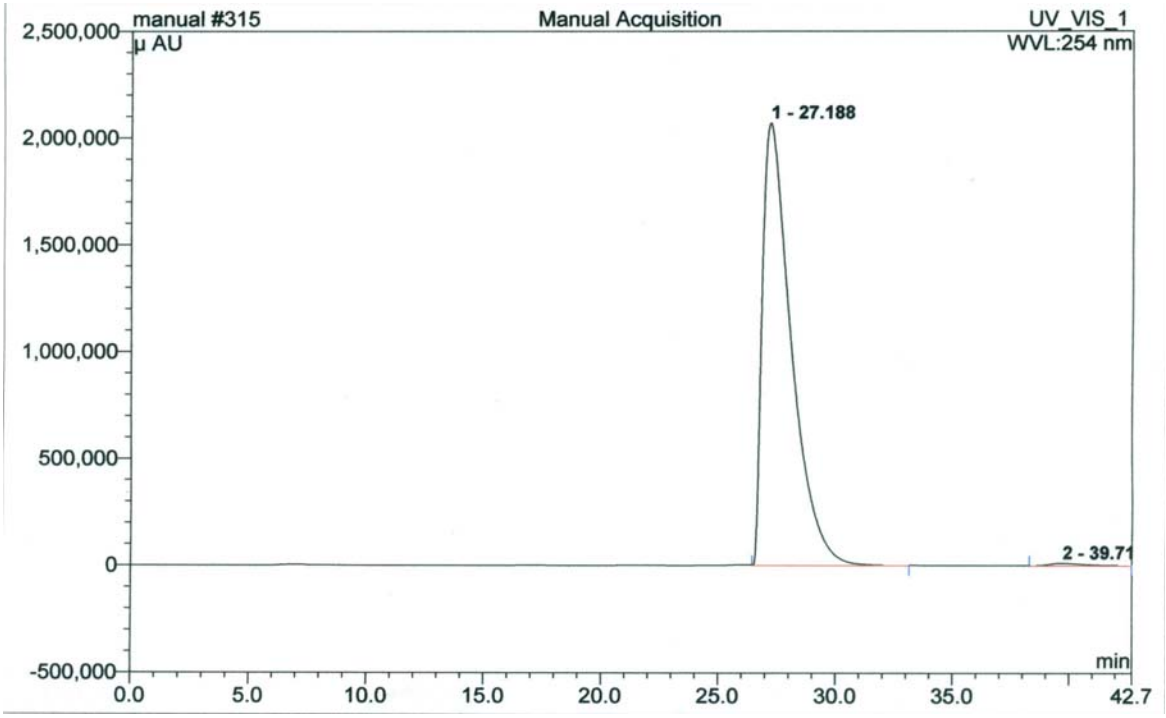




No	Ret. Time min	Height µ AU	Area µ AU* min	Rel. Area %	Amount	Type
1	8.03	65330.509	26133.285	99.36	n. a.	BMB
2	9.24	895.500	168.309	0.64	n. a.	BMB

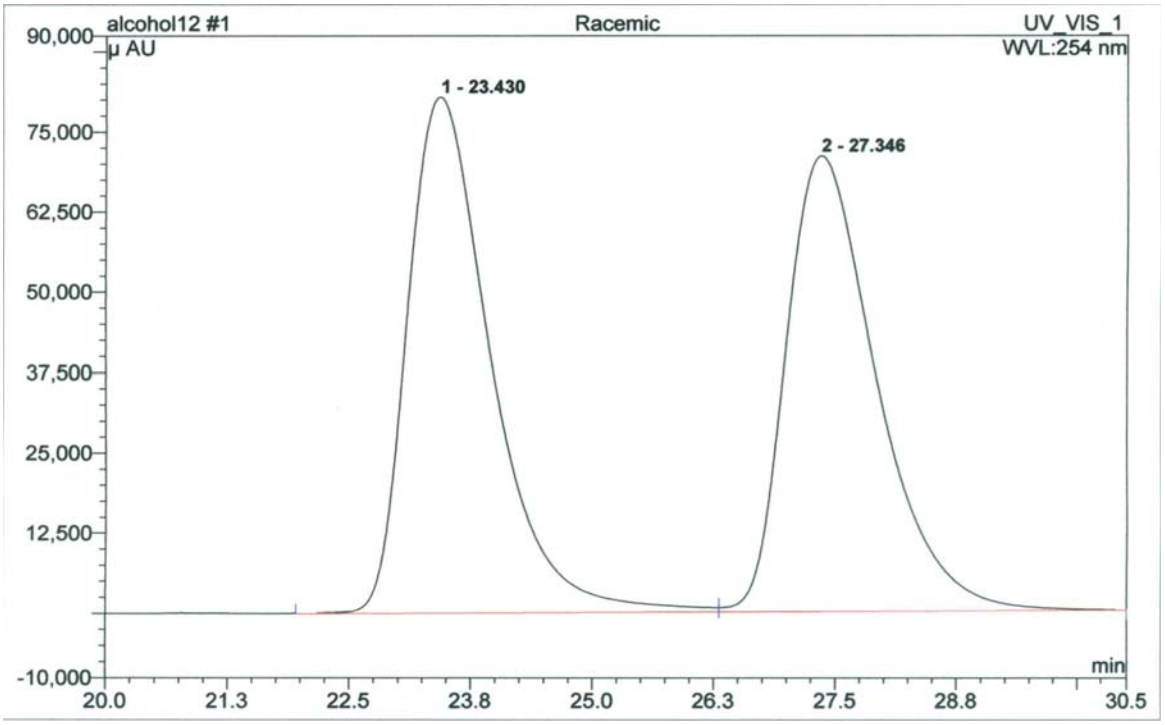
HPLC chromatogram of 5m

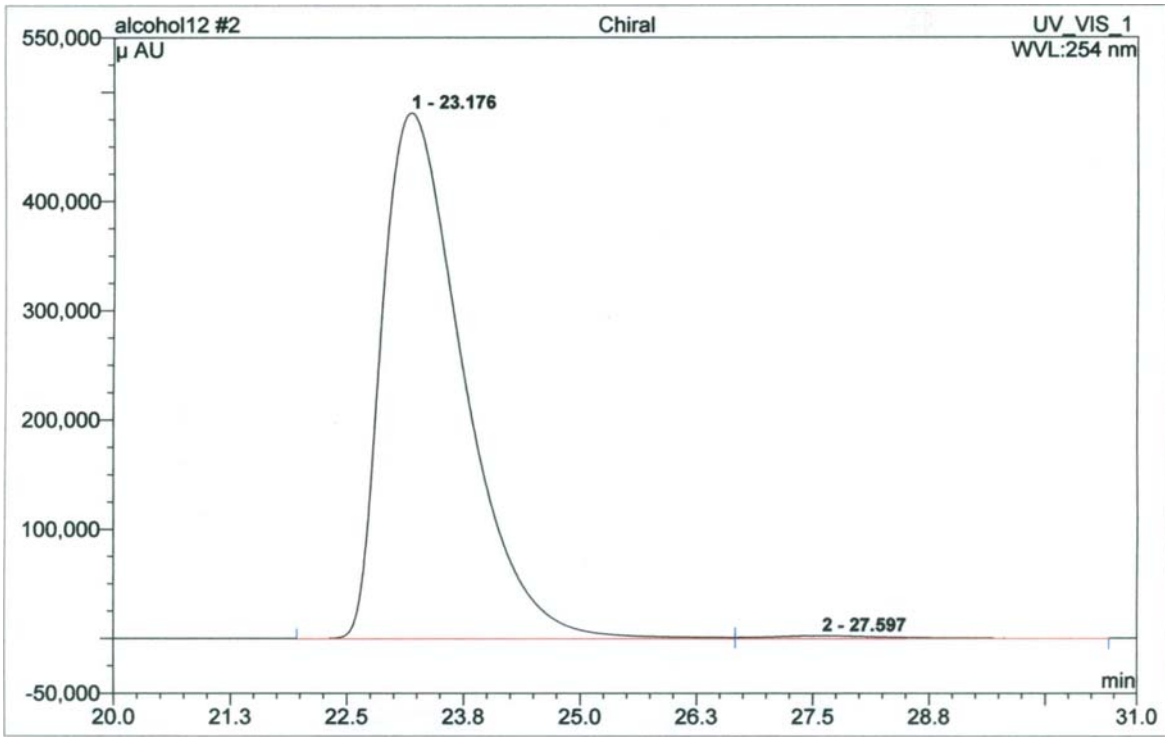




No	Ret. Time min	Height μ AU	Area μ AU* min	Rel. Area %	Amount	Type
1	27.19	2066521.172	26133.285	99.36	n. a.	BMB
2	39.72	10209.799	168.309	0.64	n. a.	BMB

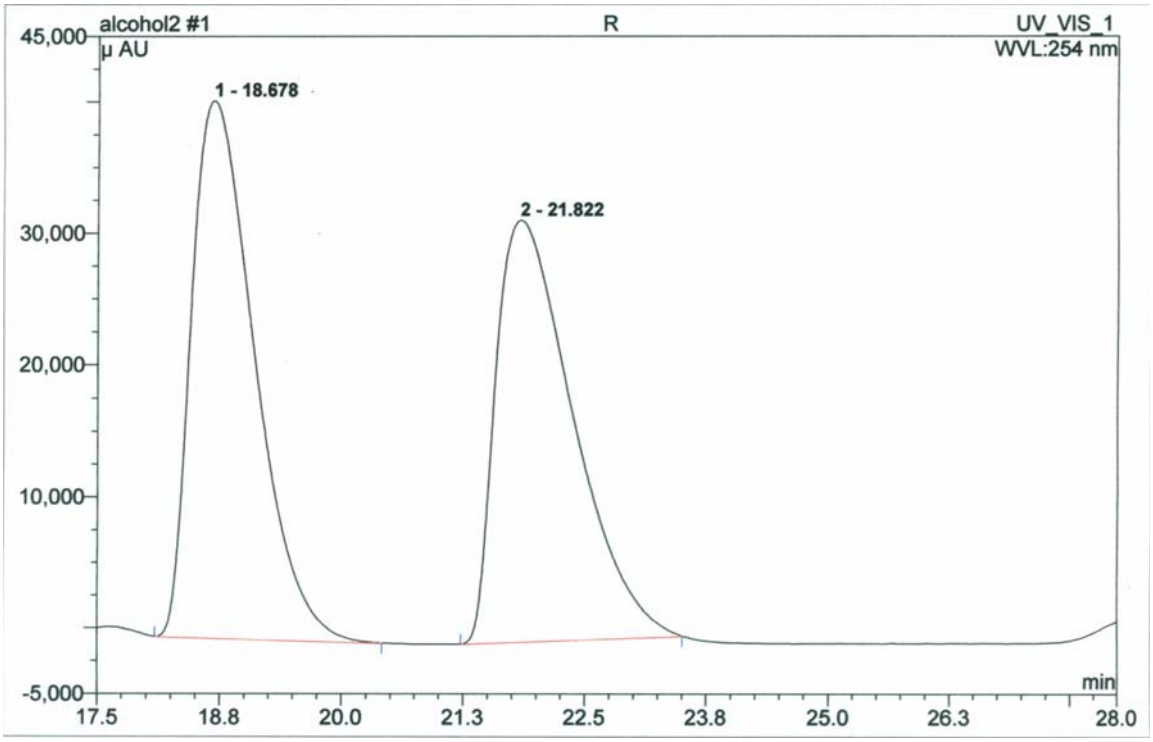
HPLC chromatogram of 5n

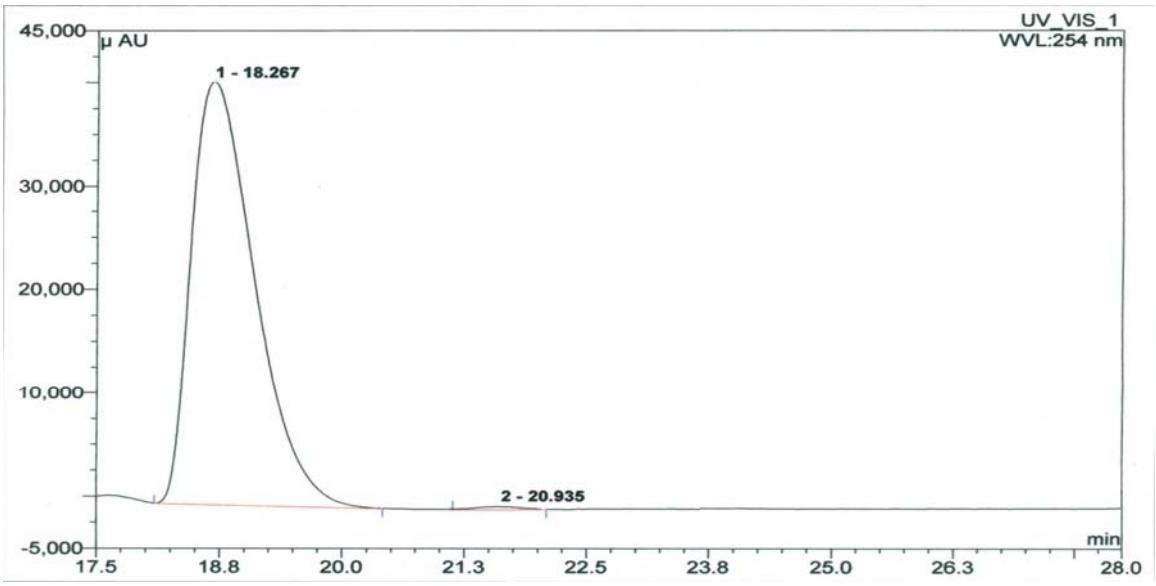




No	Ret. Time min	Height µ AU	Area µ AU* min	Rel. Area %	Amount	Type
1	23.18	480683.355	484381.220	99.36	n. a.	BMB
2	27.60	2265.930	3105.222	0.64	n. a.	BMB

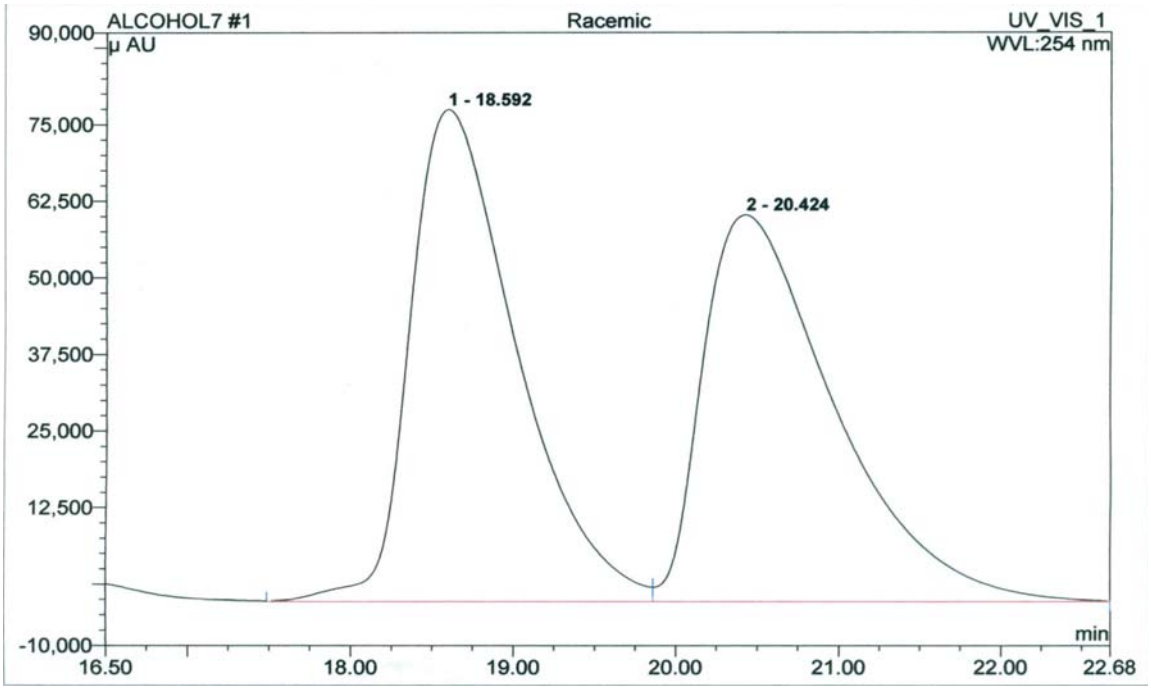
HPLC chromatogram of 5o

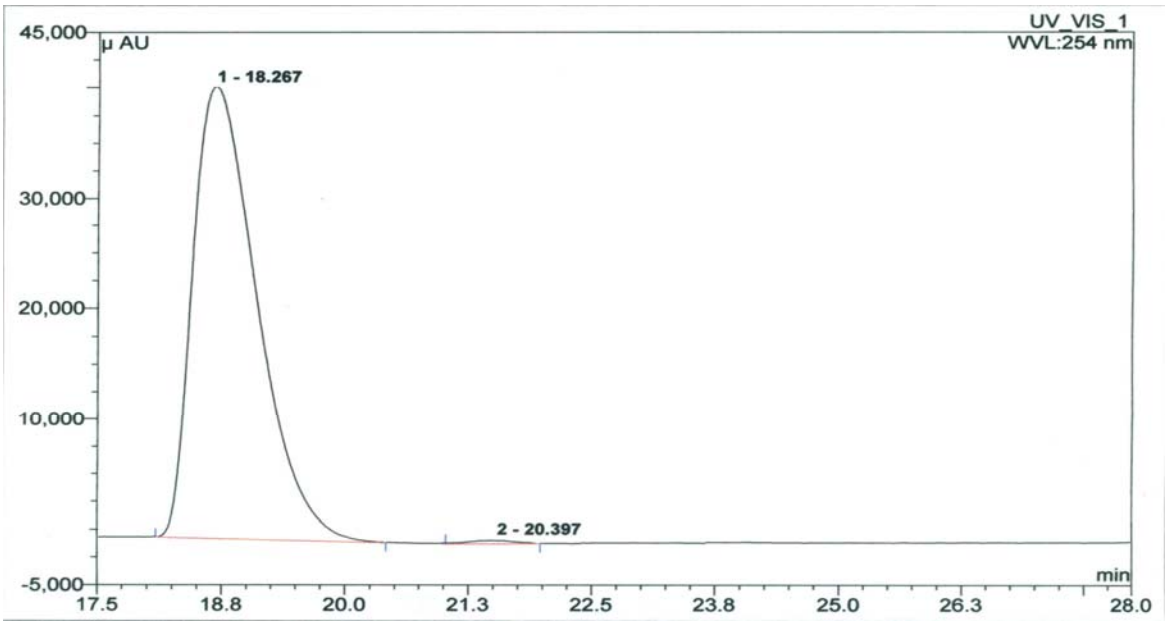




No	Ret. Time min	Height µ AU	Area µ AU* min	Rel. Area %	Amount	Type
1	18.27	40869.477	30535.089	99.36	n. a.	BMB
2	20.93	2265.930	196.683	0.64	n. a.	BMB

HPLC chromatogram of 5p





No	Ret. Time min	Height µ AU	Area µ AU* min	Rel. Area %	Amount	Type
1	18.27	40895.238	30456.124	99.36	n. a.	BMB
2	20.40	2196.930	195.138	0.64	n. a.	BMB

HPLC chromatogram of 5q