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Supporting Information

for

Alkyne Migrations in Alkylidene Carbenoid Species: A New Method of Polyyne Synthesis

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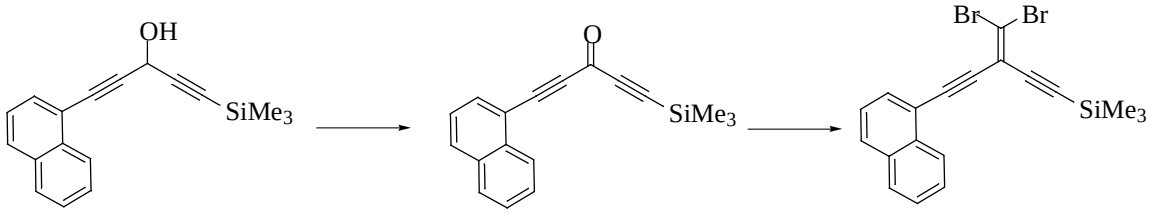
Structural data and procedures for the synthesis of compounds **5a-j, 6a-j, 7a-j, 12a-b, 13a-b, 15, 17-19, 21-23, 25-27.**

^{1}H and ^{13}C NMR spectra for compounds all new compounds



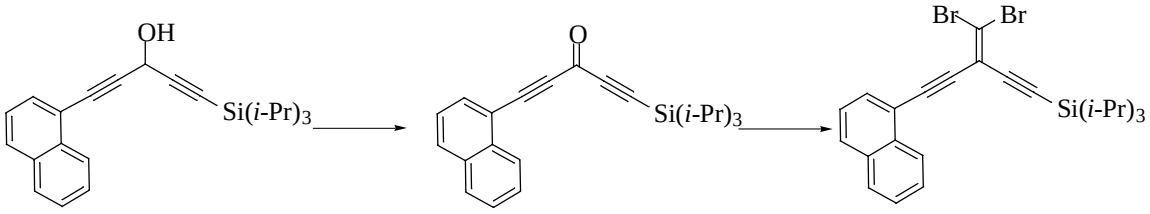
5d **6d** **7d**

5-(1-naphthyl)-1-trimethylsilylpenta-1,4-diyn-3-ol (5d). To 1-ethynylnaphthalene (0.600 g, 3.95 mmol) in THF (25 mL) at –78 °C was added BuLi (2.5 M in hexane, 1.6 mL, 4.0 mmol). After stirring for 30 min, 3-trimethylsilyl-1-propynal (0.504 g, 4.00 mmol) in Et_2O (5 mL) was added and stirring was continued for 2.5 h at –78 ˚C. The solution was quenched with satd. aq. NH_4Cl at –78 ˚C, extracted, and dried ($MgSO_4$). Chromatography (SiO_2, CH_2Cl_2) gave **5d** (663 mg, 60%) as a yellow oil: R_f = 0.4 (CH_2Cl_2); IR (CH_2Cl_2 cast) 3347, 3051, 2977, 2228, 2176, 1507 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.3 Hz, 1H), 7.88 (m, 2H), 7.74 (d, *J* = 7.3 Hz, 1H), 7.58 (m, 2H), 7.46 (dt, *J* = 7.3, 1.2Hz, 1H), 5.57 (s, 1H), 2.59 (s, 1H), 0.28 (s, 9 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 133.5, 133.1, 130.9, 129.4, 128.3, 127.0, 126.5, 126.1, 125.1, 119.6, 102.0, 90.9, 90.0, 82.8, 53.4, –0.3; MS (EI, 70 eV) *m/z* 278.1 (M^+, 100); HRMS calcd for $C_{18}H_{18}OSi$ (M^+) 278.1127, found 278.1123.

5-(1-naphthyl)-1-trimethylsilylpenta-1,4-diyn-3-one (6d). To **5d** (0.60 g, 2.2 mmol) in CH_2Cl_2 (50 mL) was added sequentially celite (0.6 g), molecular sieves (4 Å, 0.6 g), and PCC (0.58 g, 2.7 mmol). After stirring for 2 h at rt, the solution was filtered through a plug of silica gel (CH_2Cl_2) to give **6d** (0.32 g, 54%) as a yellow oil: R_f = 0.7 (CH_2Cl_2); IR (CH_2Cl_2 cast) 3059, 2961, 2197, 2176, 2152, 1623 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.3 Hz, 1H), 7.98 (d, *J* = 8.3 Hz, 1H), 7.87 (dd, *J* = 7.3, 1.1 Hz, 2H), 7.60 (m, 2H), 7.46 (dd, *J* = 8.3 Hz, 1H), 0.31 (s, 9H); ^{13}C NMR (125.3 MHz, $CDCl_3$) δ 160.5, 134.0, 133.8, 133.1, 132.2,

128.6, 127.9, 127.1, 125.7, 125.2, 117.0, 102.9, 99.6, 94.2, 90.6, –0.8; MS (EI, 70 eV) *m/z* 276.1 (M^+, 100); HRMS calcd for $C_{18}H_{16}OSi$ (M^+) 276.0971, found 276.0970.

3-(Dibromomethylidene)-5-(1-naphthyl)-1-trimethylsilylpenta-1,4-diyne (7d). CBr_4 (0.400 g, 1.21 mmol) and PPh_3 (0.680 g, 2.60 mmol) were added to CH_2Cl_2 (40 mL) and the mixture stirred for 5 min at rt. Ketone **6d** (0.276 g, 1.00 mmol) in CH_2Cl_2 (5 mL) was added in one portion and stirring continued until the reaction was complete (2-3 h) as monitored by TLC. The solution was concentrated to ca. 15 mL, hexanes (15 mL) was added, and the inhomogeneous mixture was filtered through celite. Evaporation gave a yellow oil that was further purified by column chromatography (SiO_2, hexanes/CH_2Cl_2 2:1) to give **7d** (231 mg, 54%) as a yellow oil that solidified under refrigeration: Mp 78 ˚C; R_f = 0.4 (hexanes/CH_2Cl_2 2:1); IR (CH_2Cl_2) 3058, 2959, 2199, 2153, 798 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.43 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 7.2 Hz, 1H), 7.57 (m, 2H), 7.44 (t, *J* = 7.8 Hz, 1H), 0.33 (s, 9H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 133.2 (2x), 131.0, 129.8, 128.4, 127.2, 126.7, 126.2, 125.2, 119.8, 114.6, 108.9, 102.8, 100.4, 94.4, 90.7, –0.3; MS (EI, 70 eV) *m/z* 431.9 (M^+, 100); HRMS calcd for $C_{19}H_{16}{}^{79}Br^{81}BrSi$ (M^+) 431.9368, found 431.9380; Anal. Calcd. for $C_{19}H_{16}Br_2Si$ (432.23): C, 52.80; H, 3.73. Found: C, 52.83; H, 3.72.



5e **6e** **7e**

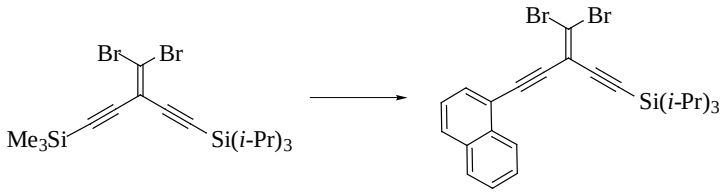
1-Naphthyl-5-triisopropylsilyl-1,4-pentadiyne-3-ol (5e). To a solution of 1-trimethylsilylacetylene-naphthalene (0.402 g, 1.79 mmol) in wet MeOH/THF (30 mL, 1:1 v/v) was added K_2CO_3 (0.06 g, 0.4 mmol), and the mixture stirred at rt for 2 h until TLC

showed complete desilylation. Et_2O and satd. aq. NH_4Cl were added, the solution extracted, dried over ($MgSO_4$), reduced to ca. 5 mL, and added to dried Et_2O (30 mL). The temperature was lowered to –78 ˚C and *n*-BuLi (2.5 M in hexanes, 0.70 mL, 1.8 mmol) was slowly added. After stirring for ca. 1 h, 3-triisopropylsilylpropynal (0.382 g, 1.82 mmol) was added and allowed to stir overnight. The reaction was quenched with aq. NH_4Cl and dried over $MgSO_4$. The solvent was reduced to give **5e** (0.359, 55%) as a yellow oil: R_f = 0.40 (hexanes/CH_2Cl_2 1:1); IR (CH_2Cl_2 cast) 3362, 2943, 2865, 2229, 2174, 1462 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.32 (m, 1H), 7.83 (m, 2H), 7.67 (dd, *J* = 7.1 Hz, 1.1 Hz, 1H), 7.52 (m, 2H), 7.41 (dd, *J* = 8.3 Hz, 7.2 Hz, 1H), 5.48 (d, *J* = 7.9 Hz, 1H), 2.37 (d, *J* = 7.9 Hz, 1H), 1.12 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$, APT) δ 133.5, 133.1, 130.8, 129.3, 128.3, 126.9, 126.5, 126.1, 125.1, 119.6, 104.1, 91.2, 86.4, 82.4, 53.3, 18.6, 11.2; MS (EI, 70 eV): *m/z*: 362 (M^+, 79); HRMS calcd. for $C_{24}H_{30}OSi$ 362.2066, found 362.2068.

1-Triisopropyl-5-naphthyl-1,4-pentadiyne-3-one (6e). To **5e** (0.351 g, 0.971 mmol) in CH_2Cl_2 (25 mL) was added sequentially celite (0.2 g), molecular sieves (4 Å, 0.2 g) and PCC (0.259 g, 1.20 mmol). After stirring for 2 h at rt, the solution was filtered through a plug of silica (CH_2Cl_2) and reduced to give **6e** as a yellow oil (0.166 g, 47%): R_f = 0.60 (hexanes/CH_2Cl_2 1:1). IR (CH_2Cl_2 cast) 2944, 2866, 2196, 2174, 2148, 1626 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.1 Hz, 1H), 7.98 (d, *J* = 8.3 Hz, 1H), 7.87 (m, 2H), 7.58 (m, 2H), 7.48 (dd, *J* = 8.1 Hz, 7.4 Hz, 1H), 1.17 (s, 21 H); ^{13}C NMR (100 MHz, $CDCl_3$, APT) δ 160.2, 134.0, 133.8, 133.1, 132.1, 128.6, 127.8, 127.0, 125.7, 125.2, 117.0, 105.4, 97.6, 94.5, 90.2, 18.5, 11.1; MS (EI, 70 eV,): *m/z*: 360 (M^+, 100); HRMS calcd. for $C_{24}H_{28}OSi$ 360.1910, found 360.1917.

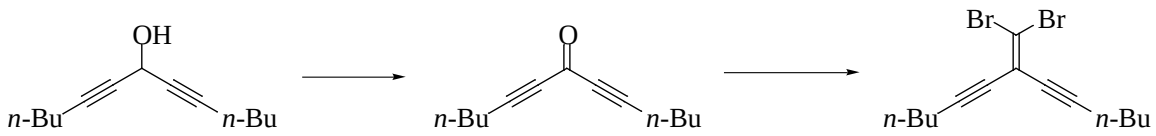
3-(Dibromomethylidene)-5-(1-naphthyl)-1-triisopropylsilylpenta-1,4-diyne (7e). CBr_4 (0.195 g, 0.589 mmol) and PPh_3 (0.334 g, 1.27 mmol) were added to CH_2Cl_2 (10 mL) and the mixture stirred for 5 min at rt. Ketone **6e** (0.166 g, 0.461 mmol) in CH_2Cl_2 (2 mL) was added in one portion and stirring continued until the reaction was complete (almost

immediately) as monitored by TLC. The solution was concentrated to ca. 2 mL, hexanes added and the inhomogeneous mixture filtered through silica. Evaporation gave **7e** (0.196 g, 82%) as a yellow oil. R_f = 0.5 (hexanes/CH_2Cl_2 2:1); IR (CH_2Cl_2 cast) 3059, 2942, 2199, 2151, 1585 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ), 8.37 (m, 1H), 7.85 (m, 2H), 7.73 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.53 (m, 2H), 7.42 (dd, *J* = 8.1, 7.2 Hz, 1H), 0.33 (s, 21H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 133.3, 133.2, 130.9, 129.8, 128.3, 127.1, 126.7, 126.2, 125.3, 119.9, 114.9, 108.1, 102.3, 99.8, 94.2, 91.1, 18.7, 11.3; MS (EI, 70 eV) *m/z* 516.0 (M^+, 100); HRMS calcd for $C_{25}H_{28}{}^{79}Br^{81}BrSi$ (M^+) 516.0306, found 516.0305.



7c **7e**

3-(Dibromomethylidene)-5-(1-naphthyl)-1-triisopropylsilylpenta-1,4-diyne (7e). To a solution of **7c** (1.50 g, 3.26 mmol) in wet MeOH (25 mL) was added K_2CO_3 (10 mg, 0.07 mmol), and the mixture stirred at rt for 2 h until TLC showed complete desilylation. Et_2O and satd. aq. NH_4Cl were added, the solution was extracted, dried with ($MgSO_4$), reduced to ca. 5 mL, and added to Et_3N (35 mL). This solution was degassed and 1-iodonaphthalene (0.828 g, 3.28 mmol), $PdCl_2(PPh_3)_2$ (200 mg, 0.28 mmol), and CuI (100 mg, 0.53 mmol) were added. Reaction for 5 h, followed by removal of the Et_3N in vacuo, and column chromatography (SiO_2, hexanes) gave **7e** (0.482 g, 29%) as a yellow oil. See above for spectral details.

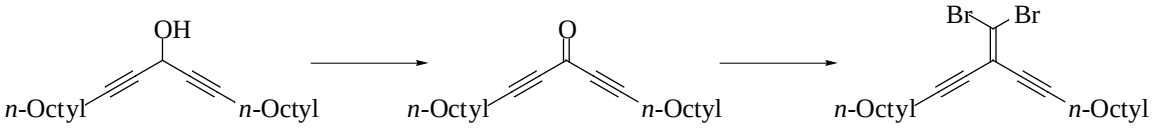


5f **6f** **7f**

Trideca-5,8-diyn-7-ol (5f). To 1-hexyne (1.48 g, 18.0 mmol) in Et_2O (50 mL) at –78 °C was added BuLi (2.5 M in hexanes, 7.20 mL, 18.0 mmol). After stirring for 30 min, ethyl formate (0.435 g, 7.50 mmol) in Et_2O (5 mL) was added in one portion and the solution warmed to rt. The solution was quenched with satd. aq. NH_4Cl, extracted, dried ($MgSO_4$) and reduced to give a yellow oil that was passed through a plug of silica, first with hexanes to remove unreacted starting materials and then with CH_2Cl_2 to give **5f** (1.33 g, 92%) as a yellow oil: R_f = 0.2 (hexanes/CH_2Cl_2 2:1); IR (CH_2Cl_2) 3381, 2926, 2286, 2226, 1120 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.03 (dp, *J* = 7.2 Hz, 2.1 Hz, 1H), 2.36 (d, *J* = 7.2 Hz, 1H), 2.17 (dt, *J* = 7.2 Hz, 2.1 Hz, 4H), 1.43 (m, 4H), 1.36 (m, 4H), 0.85 (m, 6H); ^{13}C NMR (75.5 MHz, APT, $CDCl_3$) δ 84.5, 78.1, 52.1, 30.3, 21.7, 18.2, 13.3; MS (EI, 70 eV) *m/z* 192.2 (M^+, 2), 107.5 ($[C_7H_7O]^+$, 100); HRMS calcd for $C_{13}H_{20}O$ (M^+) 192.1514, found 192.1488.

Trideca-5,8-diyn-7-one (6f). To **5f** (1.20 g, 6.24 mmol) in CH_2Cl_2 (50 mL) was added sequentially celite (2 g), molecular sieves (4 Å, 2 g), and PCC (2.00 g, 9.28 mmol). After stirring for 2 h at rt, the solution was filtered through a plug of silica (CH_2Cl_2) and reduced to give a yellow oil that was purified by flash chromatography (SiO_2, hexanes/CH_2Cl_2 2:1) to give **6f** (0.874 g, 73%) as a yellow oil: R_f = 0.4 (hexanes/CH_2Cl_2 2:1); IR (film) 2959, 2206, 1628, 1241 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.34 (t, *J* = 7.1 Hz, 4H), 1.52 (m, 4H), 1.39 (m, 4H), 0.87 (m, 6H); ^{13}C NMR (75.5 MHz, APT, $CDCl_3$) δ 161.3, 94.5, 82.3, 29.5, 21.9, 18.7, 13.4; MS (EI, 70 eV) *m/z* 190.1 (M^+, 3), 148.1 ($[M - C_3H_6]^+$, 85), 109.1 ($[M - C_6H_9]^+$, 100); HRMS calcd for $C_{13}H_{18}O$ (M^+) 190.1358, found 190.1352.

7-(1,1-Dibromomethylidene)-trideca-5,8-diyne (7f). CBr_4 (1.74 g, 5.26 mmol) and PPh_3 (2.75 g, 10.5 mmol) were added to CH_2Cl_2 (50 mL) and the mixture stirred for 5 min at rt. Ketone **6f** (0.800 g, 4.20 mmol) in CH_2Cl_2 (5 mL) was added in one portion and stirring continued until the reaction was complete (2-3 h) as monitored by TLC. The solution was concentrated to ca. 15 mL, hexanes (15 mL) added, and the inhomogeneous mixture filtered through celite. Evaporation gave a yellow oil that was further purified by column chromatography (SiO_2, hexane/CH_2Cl_2 2:1) to give **7f** (585 mg, 40%) as a yellow oil that slowly decomposes at rt. R_f = 0.7 (hexane/CH_2Cl_2 2:1); IR (CH_2Cl_2) 2957, 2219, 1331 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.31 (t, *J* = 7.0 Hz, 4H), 1.54 (m, 4H), 1.44 (m, 4H), 0.90 (m, 6H); ^{13}C NMR (75.5 MHz, APT, $CDCl_3$) δ 114.7, 105.0, 97.5, 78.1, 30.2, 21.9, 19.4, 13.6; MS (EI, 70 eV) *m/z* 346.0 (M^+, 100); HRMS calcd for $C_{14}H_{18}{}^{79}Br^{81}Br$ (M^+) 345.9755, found 345.9755.



5g **6g** **7g**

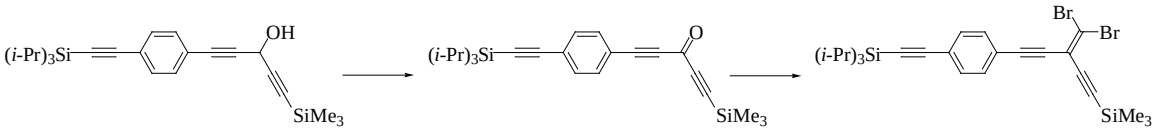
Heneicosa-9,12-diyn-11-ol (5g). To 1-decyne (2.50 g, 18.1 mmol) in Et_2O (25 mL) at –78 °C was added BuLi (2.5 M in hexane, 7.20 mL, 18.0 mmol). After stirring for 30 min, ethyl formate (0.435 g, 7.50 mmol) in Et_2O (5 mL) was added in one portion and the solution warmed to rt. The solution was quenched with satd. aq NH_4Cl, extracted, dried ($MgSO_4$), and reduced to give a yellow oil that was passed through a plug of silica, first with hexane to remove unreacted starting materials and then with CH_2Cl_2 to give **5g** (1.74 g, 76%) as a yellow oil. R_f = 0.2 (hexanes/CH_2Cl_2 2:1); IR (CH_2Cl_2) 3387, 2958, 2285, 2256, 2227, 1118 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.05 (p, *J* = 2.0 Hz, 1H), 2.38 (bs, 1H), 2.16 (dt, *J* = 7.1

Hz, 2.0 Hz, 4H), 1.46 (m, 4H), 1.30 (m, 4H), 1.23 (m, 16H), 0.83 (m, 6H); ^{13}C NMR (75.5 MHz, APT, $CDCl_3$) δ 85.1, 78.1, 52.5, 31.8, 29.2, 29.1, 28.9, 28.4, 22.6, 18.7, 14.1; MS (EI, 70 eV) *m/z* 304.3 (M^+, 2), 55 ($[C_4H_7]^+$, 100); HRMS calcd for $C_{21}H_{36}O$ (M^+) 304.2766, found 304.2750.

Heneicosa-9,12-diyn-11-one (6g). To **5g** (1.50 g, 4.93 mmol) in CH_2Cl_2 (50 mL) was added sequentially celite (1.5 g), molecular sieves (4 Å, 1.5 g), and PCC (1.58 g, 7.33 mmol). After stirring for 2 h at rt, the solution was filtered through a plug of silica (CH_2Cl_2), and reduced to give a yellow oil that was purified by flash chromatography (SiO_2, hexanes/CH_2Cl_2 2:1) to give **6g** (1.30 g, 87%) as a yellow oil. R_f = 0.4 (hexanes/CH_2Cl_2 2:1); IR (CH_2Cl_2 cast) 2927, 2208, 1629, 1241 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.33 (t, *J* = 7.1 Hz, 4H), 1.55 (m, 4H), 1.35 (m, 4H), 1.24 (m, 16H), 0.84 (m, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 161.3, 94.5, 82.3, 31.8, 29.1, 28.9, 28.8, 27.5, 22.6, 19.0, 14.0; MS (EI, 70 eV) *m/z* 302.3 (M^+, 6), 55 ($[C_4H_7]^+$, 100); HRMS calcd for $C_{21}H_{34}O$ (M^+) 302.2610, found 302.2608. Anal. Calcd. for $C_{21}H_{34}O$ (302.49): C, 83.38; H, 11.33. Found: C, 83.17; H, 11.30.

11-(1,1-Dibromomethylidene)-heneicosa-9,12-diyne (7g). CBr_4 (1.57 g, 4.74 mmol) and PPh_3 (2.49 g, 9.50 mmol) were added to CH_2Cl_2 (50 mL) and the mixture stirred for 5 min at rt. Ketone **6g** (1.15 g, 3.78 mmol) in CH_2Cl_2 (5 mL) was added in one portion and stirring continued until the reaction was complete (2-3 h) as monitored by TLC. The solution was concentrated to ca. 15 mL, hexanes (15 mL) added, and the inhomogeneous mixture filtered through celite. Evaporation gave a yellow oil that was further purified by column chromatography (SiO_2, hexanes/CH_2Cl_2 2:1) to give **7g** (935 mg, 54%) as a yellow oil that slowly decomposes at rt: R_f = 0.8 (hexanes/CH_2Cl_2 2:1); IR (CH_2Cl_2 cast) 2926, 2220 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.31 (t, *J* = 7.1 Hz, 4H), 1.54 (m, 4H), 1.41 (m, 4H), 1.25 (m, 16H), 0.86 (m, 6H); ^{13}C NMR (75.5 MHz, APT, $CDCl_3$) δ 114.8, 105.0, 97.6, 78.2, 31.9, 29.2, 29.1, 28.9, 28.2, 22.7, 19.8, 14.1; MS (EI, 70 eV) *m/z* 458.1 (M^+, 100); HRMS calcd for

$C_{22}H_{34}{}^{79}Br^{81}Br$ (M^+) 458.1007, found 458.1006; Anal. Calcd. for $C_{22}H_{34}Br_2$ (458.31): C, 57.65; H, 7.48. Found: C, 57.54; H, 7.71.

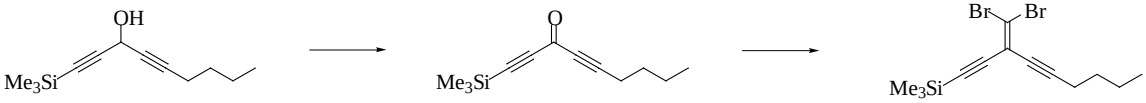


5h **6h** **7h**

1-(Trimethylsilyl)-5-((4-triisopropylsilylethynyl)-phenyl)-1,4-pentadiyne-3-ol (5h). K_2CO_3 (40 mg) was added to a MeOH/THF (10 mL, 1:1 v/v) solution of 1-triisopropylsilylethynyl-4-trimethylsilylethyl-benzene (0.749 g, 2.11 mmol) and stirred until TLC analysis showed removal of the TMS group (about 30 min). Ether (50 mL) was added and the solution washed with aqueous NH_4Cl and dried over $MgSO_4$. The ether was reduced in vacuo to ca. 5 mL, and the solution was then added to 10 mL of dried ether at –78 ˚C. *n*-BuLi (2.5 M in hexanes, 0.85 mL, 2.1 mmol) was added and the mixture stirred for 1 hr. 3-Trimethylsilylpropynal (0.218 g, 1.72 mmol) was added and the mixture was allowed to warm up to rt over the course of an hour. Aqueous work-up and flash chromatography (SiO_2, hexanes/CH_2Cl_2 1:1) gave alcohol **5h** (0.267, 31%) as a yellow oil: R_f = 0.38 (hexanes/CH_2Cl_2, 1:1); IR (CH_2Cl_2 cast) 3322, 2958, 2892, 2234, 2155, 1497 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (m, 4H), 5.32 (d, *J* = 7.2 Hz, 1H), 2.30 (d, *J* = 7.2 Hz, 1H), 1.11 (s, 21H), 0.19 (s, 9H); ^{13}C NMR (125 MHz, APT, $CDCl_3$) δ 131.8, 131.6, 124.0, 121.7, 106.4, 101.5, 93.1, 90.0, 87.5, 84.1, 53.2, 18.7, 11.4, –0.2; MS (EI, 70 eV) *m/z* 408, (M^+, 24), 365 ([M – *i*-Pr]$^+$, 100); HRMS calcd for $C_{25}H_{36}OSi_2$ 408.2305, found 408.2307.

1-(Trimethylsilyl)-5((4-triisopropylsilylethynyl)-phenyl)-3-(1,1-dibromomethylidene)-1,4-pentadiyne (7h). To alcohol **5h** (0.267 g, 0.652 mmol) in CH_2Cl_2 (10 mL) was added sequentially celite (0.2 g), molecular sieves (4 Å, 0.2 g) and PCC (0.225 g, 1.05 mmol). After an hour the reaction was complete and the mixture was filtered through

silica. The solvent was reduced to about 5 mL, and this solution ketone **6h** was added to a mixture of CBr_4 (0.250 g, 0.754 mmol) and PPh_3 (0.429 g, 1.64 mmol) in CH_2Cl_2 (10 mL). The bromination reaction was complete within a 0.5 hr (monitored by TLC, hexanes/CH_2Cl_2 1:1). The solution was concentrated to ca. 15 mL, hexanes (15 mL) added, and the inhomogeneous mixture filtered through celite. Column chromatography (SiO_2, hexanes) gave dibromide **7h** (0.194, 53%) as a yellow solid. Mp = 60-61 ˚C; R_f = 0.90 (hexanes/CH_2Cl 1:1); IR (CH_2Cl_2 cast) 2958, 2891, 2203, 2154, 1492 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.42 (m, 4H), 1.12 (s, 21H), 0.24 (s, 9H); ^{13}C NMR (125 MHz, APT, $CDCl_3$) δ 131.9, 131.3, 124.2, 121.8, 114.1, 109.4, 106.4, 102.7, 100.0, 95.3, 93.5, 87.5, 18.7, 11.4, –0.3; MS (EI, 70 eV) *m/z* 562, (M^+, 25), 518 ([M – *i*-Pr]$^+$, 100); HRMS calcd. for $C_{26}H_{34}Si_2{}^{79}Br^{81}Br$ 562.0545, found 562.0512. Anal. Calcd. for $C_{26}H_{34}Si_2Br_2$ (560.10): C, 55.51; H, 6.09. Found: C, 55.73; H, 5.99.



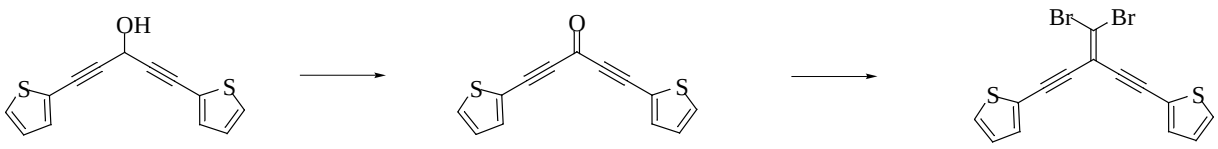
5i **6i** **7i**

1-Trimethylsilyl-1,4-nonadiyne-3-ol (5i). To 1-hexyne (0.389 g, 4.75 mmol) in Et_2O (25 mL) at –78 ˚C was added *n*-BuLi (2.5 M in hexanes, 1.80 mL, 4.50 mmol). After stirring for 0.5 h, 3-trimethylsilylpropynal (0.691 g, 5.47 mmol) was added in one portion and the solution allowed to warm up overnight. The reaction was quenched with NH_4Cl, extracted with Et_2O, and dried over $MgSO_4$. After passing through a plug of silica (CH_2Cl_2), **5i** (0.92 g, 98%) was isolated as a yellow oil: R_f = 0.43 (hexanes/CH_2Cl_2 1:1); IR (CH_2Cl_2 cast) 3377, 2959, 2293, 2232, 2178, 1466 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.07 (bs, 1H), 2.21 (dt, *J* = 2.1, 7.1 Hz, 2H), 2.12 (d, *J* = 6.5 Hz, 1H), 1.48 (m, 2H), 1.40 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H), 0.12 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, APT) δ 102.6, 88.8, 85.8, 52.8, 30.3, 21.9,

18.4, 13.5, -0.3 (one coincident peak not observed); MS (EI, 70 eV) *m/z* 208.1, (M^+, 0.8), 73.0 (Me_3Si^+, 100); HRMS calcd. for $C_{12}H_{20}OSi$ 208.1283, found 208.1272.

1-Trimethylsilyl-1,4-nonadiyne-3-one (6i). To **5i** (0.791 g, 3.79 mmol) in CH_2Cl_2 (70 mL) was added sequentially celite (1.0 g), molecular sieves (4 Å, 1.0 g), and PCC (1.07 g, 4.98 mmol). After stirring for 1 h at rt, the solution was filtered through a plug of silica (CH_2Cl_2), and reduced to give a yellow oil that was purified by flash chromatography (SiO_2, hexanes/CH_2Cl_2 1:1) to give **6i** (0.448 g, 57%): R_f = 0.62 (hexanes/CH_2Cl_2 1:1); IR (CH_2Cl_2 cast) 2961, 2231, 2212, 2148, 1629 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.39 (t, *J* = 7.1 Hz, 2H), 1.57 (m, 2H), 1.42 (tq, *J* = 7.3, 7.5 Hz, 2H), 0.91 (t, *J* = 7.3 Hz, 3H), 0.23 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, APT) δ 160.8, 102.8, 97.9, 96.1, 82.2, 29.5, 22.0, 18.9, 13.4, –0.9; MS (EI, 70 eV) *m/z* 206, (M^+, 2), 191 ($[M - CH_3]^+$, 82); HRMS calcd. for $C_{12}H_{18}OSi$ 206.1127, found 206.1129.

3-Dibromomethylidene-1-trimethylsilyl-1,4-nonadiyne (7i). CBr_4 (0.848 g, 2.56 mmol) and PPh_3 (1.28 g, 4.88 mmol) were added to CH_2Cl_2 (25 mL) and the mixture stirred for 5 min at rt. **6i** (0.412 g, 2.00 mmol) in CH_2Cl_2 (5 mL) was added in one portion and stirring continued until the reaction was complete (15 min) as monitored by TLC. The solution was concentrated to ca. 5 mL, hexanes added, and the inhomogeneous mixture filtered through celite. Evaporation gave **7i** (0.437 g, 60%) as a yellow oil: R_f = 0.91 (hexanes/CH_2Cl_2 1:1); IR (CH_2Cl_2 cast) 2959, 2222, 2147 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.32 (t, *J* = 7.0 Hz, 2H), 1.55 (m, 2H), 1.44 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H), 0.20 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, APT) δ 114.5, 107.7, 101.7, 100.7, 98.4, 77.5, 30.1, 21.9, 19.4, 13.5, -0.4; MS (EI, 70 eV) *m/z* 362, (M^+, 100); HRMS calcd. for $C_{13}H_{18}Si^{79}Br^{81}Br$ 361.9524, found 361.9525.

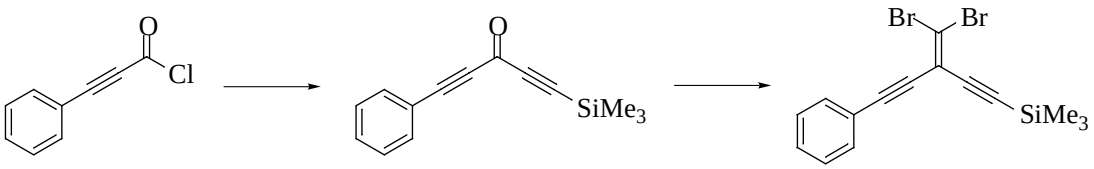


5j **6j** **7j**

1,5-Bis(2-thienyl)-1,4-pentadiyne-3-ol (5j). 2-Trimethylsilylethynylthiophene (0.878 g, 4.87 mmol) and K_2CO_3 (0.14 g, 1.0 mmol) in wet THF (10 mL) and MeOH (10 mL) was stirred for 2 h until TLC showed complete desilylation. After work-up with Et_2O and saturated aqueous NH_4Cl, the terminal acetylene was dried over $MgSO_4$. The solvent was reduced to ca. 5 mL and the acetylene added to 20 mL of dried Et_2O. *n*-BuLi (2.5 M in hexanes, 2.00 mL, 5.00 mmol) was subsequently added at –78 ˚C and allowed to stir for an hour. Ethyl formate (0.180 g, 2.43 mmol) was added and the mixture warmed to rt. The reaction was quenched with NH_4Cl, extracted with Et_2O, and dried over $MgSO_4$. The alcohol was purified by flash chromatography (SiO_2, hexanes/CH_2Cl_2 1:1) to give a brown oil (0.231 g, 40%): R_f = 0.25 (hexanes/CH_2Cl_2 1:1); IR (CH_2Cl_2 cast) 3335, 3105, 2224, 1517 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.27 (m, 4H), 6.96 (dd, *J* = 3.7, 5.1 Hz, 2H), 5.60 (bs, 1H), 2.79 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, APT) δ 133.1, 133.0, 128.0, 127.9, 127.0, 126.9, 121.6, 89.4, 78.3, 53.3; MS (EI, 70 eV) *m/z* 244, (M^+, 54), 108 ($[C_6H_4S]^+$, 100).

1,5-Bis(2-thienyl)-1,4-pentadiyne-3-one (6j). To **5j** (0.172 g, 0.705 mmol) in CH_2Cl_2 (10 mL) was added sequentially celite (0.2 g), molecular sieves (4Å, 0.2 g), and PCC (0.231 g, 1.07 mmol). After stirring for 2 h at rt, the solution was filtered through a plug of silica (CH_2Cl_2) and further purified by flash chromatography (SiO_2, hexanes/CH_2Cl_2 1:1) to give **6j** (0.0853 g, 50%) as a brown solid: Mp 99–101 ˚C. R_f = 0.33 (hexanes/CH_2Cl_2 1:1); IR (CH_2Cl_2 cast) 3093, 2170, 1599 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 1.0, 3.8 Hz, 2H), 7.53 (dd, *J* = 1.1, 5.1 Hz, 2H), 7.08 (dd, *J* = 3.8, 5.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, APT) δ 159.6, 137.5, 132.6, 127.9, 119.3, 93.9, 86.0; MS (EI, 70 eV) *m/z* 242, (M^+, 100); HRMS calcd. for $C_{13}H_6OS_2$ 241.9860, found 241.9847.

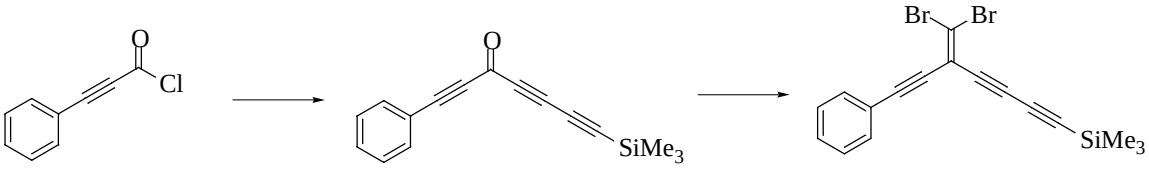
3-Dibromomethylidene-1,5-bis(2-thienyl)-1,4-pentadiyne (7j). CBr_4 (0.154 g, 0.464 mmol) and PPh_3 (0.277 g, 1.06 mmol) were added to CH_2Cl_2 (10 mL) and the mixture stirred for 5 min at rt. **6j** (0.0853 g, 0.352 mmol) in CH_2Cl_2 (5 mL) was added in one portion and stirring continued until the reaction was complete (0.5 h) as monitored by TLC. The solution was concentrated to ca. 1 mL, hexanes (15 mL) added, and the inhomogeneous mixture filtered through celite. Evaporation gave **7j** (0.066 g, 47%) as a brown solid: Mp 60 - 63 ˚C; R_f = 0.76 (hexanes/CH_2Cl_2 1:1); IR (CH_2Cl_2 cast) 3104, 2023, 2197, 1419 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.35 (dd, J = 1.1, 5.1 Hz, 2H), 7.34 (dd, *J* = 1.1, 3.7 Hz, 2H), 7.01 (dd, *J* = 3.7, 5.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, APT) δ 133.1, 128.7, 127.2, 121.8, 113.8, 107.6, 89.3, 89.3; MS (EI, 70 eV) *m/z* 397, (M^+, 100); HRMS calcd. for $C_{14}H_6{}^{79}Br^{81}BrS_2$ 397.8257, found 397.8250.



11 **12a** **13a**

5-Phenyl-1-trimethylsilyl-1,4-pentadiyne-3-one (12a). To **11** (0.999 g, 6.84 mmol) was added thionyl chloride (7 mL) and the reaction stirred overnight. The excess thionyl chloride was removed in vacuo and the acid chloride was dissolved in CH_2Cl_2 (50 mL) and bis-trimethylsilylacetylene (1.18 g, 6.90 mmol) was added. The temperature lowered to 0 ˚C, $AlCl_3$ (1.07 g, 8.04 mmol) was carefully added, and the reaction stirred for 3 h. Aqueous work-up (10% HCl, $NaHCO_3$, NaCl) and purification by column chromatography (SiO_2, hexanes/CH_2Cl_2 1:1) yielded **12a** (0.729 g, 47%). Spectra date consistent with those reported (D. H. Wadsworth, S. M. Geer, M. R. Detty, *J. Org. Chem.* **1987**, *52*, 3662-3668.)

5-Phenyl-trimethylsilyl-3-dibromomethylidene-1,4-pentadiyne (13a). CBr_4 (1.26 g, 3.80 mmol) and PPh_3 (2.14 g, 8.18 mmol) were added to CH_2Cl_2 (100 mL) and the mixture stirred for 5 min at rt. Ketone **12a** (0.669 g, 2.96 mmol) in CH_2Cl_2 (5 mL) was added and the reaction monitored by TLC until complete (0.5 h). The solution was concentrated to ca. 5 mL, hexanes added, and the inhomogeneous mixture filtered through celite. Evaporation gave **13a** (0.806 g, 71%) as a yellow solid: Mp 76 - 78 ˚C; R_f = 0.74 (hexanes/CH_2Cl_2 1:1); IR (CH_2Cl_2 cast) 2960, 2203, 2153, 1597 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.34 (m, 3H), 0.24 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, APT) δ 131.7, 129.2, 128.4, 122.2, 114.3, 109.1, 102.6, 100.2, 95.8, 85.9, -0.4; MS (EI, 70 eV) *m/z* 382, (M^+, 100); HRMS calcd. for $C_{15}H_{14}Si^{79}Br^{81}Br$ 381.9211, found 381.9233.

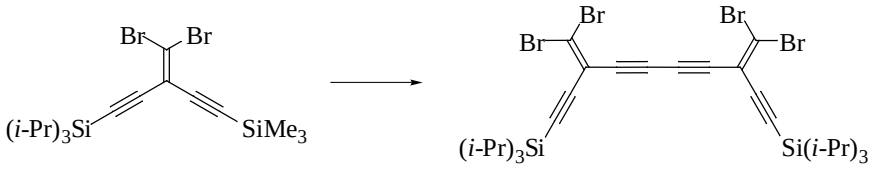


11 **12b** **13b**

7-phenyl-1-trimethylsilyl-1,3,6-heptatriyne-5-one (12b). To **11** (1.01 g, 6.91 mmol) was added thionyl chloride (7 mL) and the reaction stirred overnight. The excess thionyl chloride was removed in vacuo, the acid chloride dissolved in CH_2Cl_2 (50 mL), bis-trimethylsilylbutadiyne (1.29 g, 6.62 mmol) was added, and the temperature lowered to 0 ˚C. $AlCl_3$ (0.938 g, 7.04 mmol) was carefully added and the reaction stirred for 3 h. Aqueous work-up (10% HCl, $NaHCO_3$, NaCl) and purification by column chromatography (SiO_2, hexanes/CH_2Cl_2 1:1) yielded **12b** (0.959 g, 55%) as an unstable light brown oil: R_f = 0.56 (hexanes/CH_2Cl_2 1:1); IR (CH_2Cl_2 cast) 2962, 2196, 2098, 1622 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.59 (m, 2H), 7.48 (m, 1H), 7.38 (t, *J* = 7.7, 2H), 0.24 (s, 9H); ^{13}C NMR (125 MHz, APT, $CDCl_3$) δ 159.2, 133.3, 131.4, 128.6, 119.0, 99.2, 92.6, 89.1, 85.8, 75.7, 74.1, –0.7; MS

(EI, 70 eV) *m/z* 250.1 (M^+, 24), 207.1 ([$C_{14}H_{11}Si[^+$, 100); HRMS calcd. for $C_{16}H_{14}OSi$ 250.0814, found 250. 0808.

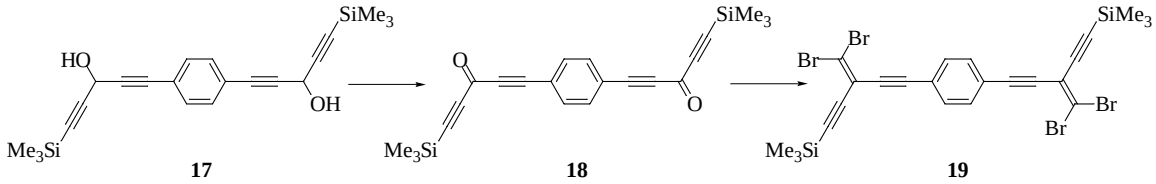
7-phenyl-1-trimethylsilyl-(5-dibromomethylidene)-1,3,6-heptatriyne (13b). CBr_4 (1.69 g, 5.09 mmol) and PPh_3 (2.67 g, 10.2 mmol) were added to CH_2Cl_2 (100 mL) and the mixture stirred for 5 min at rt. Ketone **12b** (0.959 g, 4.09 mmol) in CH_2Cl_2 (5 mL) was added and the reaction monitored by TLC until complete (0.5 h). The solution was concentrated to ca. 5 mL, hexanes added, and the inhomogeneous mixture filtered through celite. Evaporation gave **13b** (0.804 g, 48%) as a brown solid: Mp 35 - 37 ˚C; R_f = 0.69 (hexanes/CH_2Cl_2 1:1). IR (CH_2Cl_2 cast) 2960, 2222, 2197, 2097, 1487 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (m, 2H), 7.34 (m, 3H), 0.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, APT) δ 131.7, 129.4, 128.4, 121.8, 113.3, 110.9, 96.5, 95.2, 87.2, 85.2, 80.3, 72.2, -0.6; MS (EI, 70 eV) *m/z* 406, (M^+, 100). HRMS calcd. for $C_{17}H_{14}Si^{79}Br^{81}Br$ 405.9211, found 405.9219.



7c **15**

1,10-bis(triisopropylsilyl)-3,8-bis(1,1-dibromomethylene)deca-1,4,6,9-tetrayne (15). A mixture of compound **7c** (0.190 g, 0. 411 mmol) and K_2CO_3 (30 mg, 0.217 mmol) in MeOH/THF (20 mL, 1:1 v/v) was stirred for 0.5h. After work-up, the deprotected vinyl bromide was oxidatively homocoupled in CH_2Cl_2 (20 mL) using TMEDA (1 mL, 6.6 mmol) and CuI (0.0485 g, 0.25 mmol) (A. S. Hay, *J. Org. Chem.* **1962**, *27*, 3320-3321). Work-up and column chromatography (silica gel, hexanes) gave **15** (0.0873 g, 55%) as an off-white solid: Mp 64-65 °C; R_f = 0.71 (hexane); IR (CH_2Cl_2 cast) 2943, 2152, 1462 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2) δ 1.2 (s); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 113.9, 113.3, 102.0, 101.0, 80.9,

79.3, 18.7, 11.5; MS (EI, 70 eV) *m/z* 778, (M^+, 100); HRMS calcd. for $C_{30}H_{42}Si_2{}^{79}Br_2{}^{81}Br_2$ 777.9518 (M^+), found 777.9527; Anal. Calcd. for $C_{30}H_{42}Si_2Br_4$ (773.96): C, 46.29; H, 5.44. Found: C, 46.67; H, 5.55.

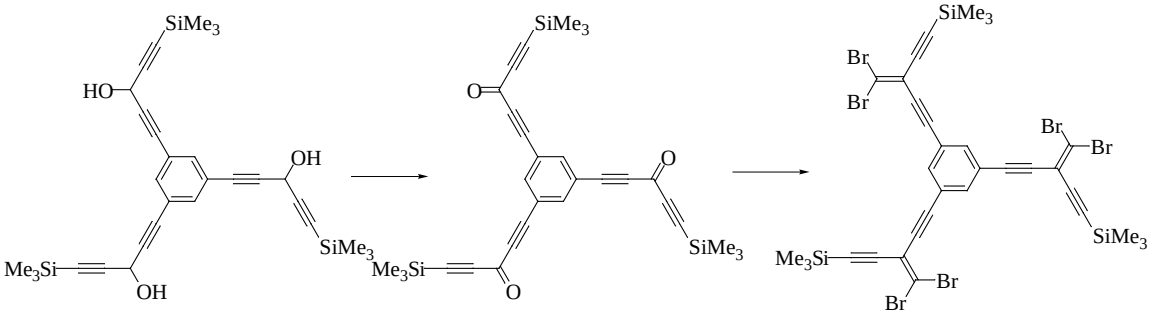


Compound (17). To 1,4-diethynylbenzene (0.949 g, 7.53 mmol) in THF (25 mL) at –78 °C was added BuLi (2.5 M in hexanes, 6.00 mL, 15.0 mmol). After stirring for 30 min, 3-trimethylsilyl-1-propynal (2.00 g, 15.8 mmol) in Et_2O (5 mL) was added and stirring was continued for 2.5 h at –78 ˚C. The solution was quenched with satd. aq NH_4Cl at –78 ˚C and then extracted with Et_2O, dried ($MgSO_4$), evaporation, and crystallization from hexanes at 4 ˚C to give **17** (1.19 g, 42%) as a white solid that is presumably a mixture of stereoisomers: Mp 99 ˚C; R_f = 0.2 (CH_2Cl_2); IR (μscope) 3314, 2959, 2237, 2177, 1500 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.42 (s, 4H), 5.34 (d, *J* = 6 Hz, 2H), 2.41 (d, *J* = 6 Hz, 2H), 0.21 (s, 18H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 131.7, 122.4, 101.6, 90.0, 87.8, 83.8, 53.0, –0.3; MS (EI, 70 eV) *m/z* 378.1 (M^+, 72), 73.0 (Me_3Si^+, 100); HRMS calcd for $C_{22}H_{26}O_2Si_2$ (M^+) 378.1471, found 378.1468. Anal. Calcd. for $C_{22}H_{26}O_2Si_2$ (378.61): C, 69.79; H, 6.92. Found: C, 69.61; H, 7.02.

1,4-Bis-(5-trimethylsilyl-3-one-penta-1,4-diyne)-benzene (18). To diol **17** (1.0 g, 2.6 mmol) in CH_2Cl_2 (100 mL) was added sequentially celite (1.5 g), molecular sieves (4 Å, 1.5 g), and PCC (1.43 g, 6.63 mmol). After stirring for 2 h at rt, the solution was filtered through a plug of silica (CH_2Cl_2), evaporation, and crystallization from hexanes at –4 ˚C gave **18** (0.78 g, 80%) as a yellow solid: Mp 101 ˚C; R_f = 0.3 (CH_2Cl_2); IR (μscope) 3090, 2961, 2208, 2151, 1613, 1143 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.65 (s, 4H), 0.28 (s, 18H); ^{13}C NMR

(75.5 MHz, $CDCl_3$) δ 160.1, 133.3, 122.2, 102.5, 100.3, 91.1, 89.3, –0.9; MS (EI, 70 eV) *m/z* 374.1 (M^+, 100); HRMS calcd for $C_{22}H_{22}O_2Si_2$ (M^+) 374.1158, found 374.1150. Anal. Calcd. for $C_{22}H_{22}O_2Si_2$ (374.58): C, 70.54; H, 5.92. Found: C, 70.32; H, 5.94.

Compound (19). CBr_4 (1.51 g, 4.56 mmol) and PPh_3 (2.40 g, 9.16 mmol) were added to CH_2Cl_2 (80 mL) and the mixture stirred for 5 min at rt. Dione **18** (0.681 g, 1.82 mmol) in CH_2Cl_2 (5 mL) was added in one portion and stirring continued until the reaction was complete (2-3 h) as monitored by TLC. The solution was concentrated to ca. 15 mL, hexanes (10 mL) added, and the inhomogeneous mixture filtered through celite. Evaporation gave a yellow oil that was purified by column chromatography (SiO_2, hexanes) to give **19** (1.05 g, 85%) as a yellow solid: Mp 68-69 ˚C; R_f = 0.3 (hexanes); IR (μscope) 3044, 2898, 2207, 2157, 1515, 1249 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.49 (s, 4H), 0.25 (s, 18H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 131.7, 122.9, 114.1, 109.8, 103.0, 100.0, 95.1, 88.1, –0.4; MS (EI, 70 eV) *m/z* 685.8 (M^+, 100); HRMS calcd for $C_{24}H_{22}{}^{79}Br_2{}^{81}Br_2Si_2$ (M^+) 685.7953, found 685.7945; Anal. Calcd. for (686.23): $C_{24}H_{22}Br_4Si_2$ C, 42.01; H, 3.23. Found: C, 42.12; H, 3.37.



21 **22** **23**

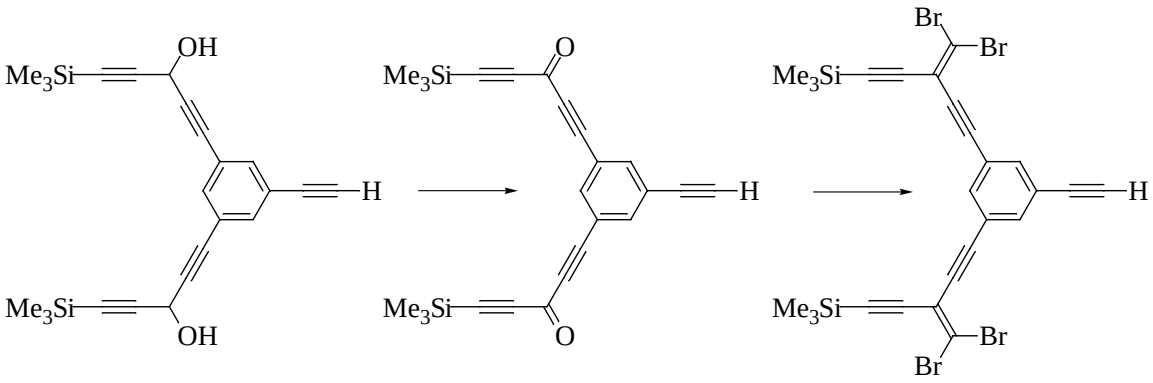
Compound (21). To 1,3,5-triethynylbenzene (1.49 g, 4.06 mmol) in Et_2O (50 mL) at –78 °C was added BuLi (2.5 M in hexane, 4.90 mL, 12.2 mmol). After stirring for 30 min, 3-trimethylsilyl-1-propynal (1.90 g, 15.1 mmol) in Et_2O (5 mL) was added and stirring was

continued for 2.5 h at –78 ˚C The solution was quenched with satd. aq NH_4Cl at –78 ˚C and then extracted with Et_2O. Drying ($MgSO_4$), evaporation, and column chromatography (hexane/Et_2O 7:3) gave **21** (891 mg, 42%) as a viscous light yellow oil, presumably a mixture of stereoisomers, that solidified under refrigeration: Mp 59 ˚C; R_f = 0.3 (hexanes/Et_2O 95:5); IR (CH_2Cl_2 cast) 3313, 2959, 2225, 2179 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.51 (s, 3H), 5.35 (d, *J* = 7.3 Hz, 3H), 2.62 (d, *J* = 7.3 Hz, 3H), 0.25 (s, 27H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 135.0, 122.7, 101.3, 90.2, 87.3, 82.3, 52.9, –0.4; MS (EI, 70 eV) *m/z* 528.2 (M^+, 5), 73.0 (Me_3Si^+, 100); HRMS calcd for $C_{30}H_{36}O_3Si_3$ (M^+) 528.1972, found 528.1959.

Compound (22). To triol **21** (0.851 g, 1.61 mmol) in CH_2Cl_2 (150 mL) was added sequentially celite (1.2 g), molecular sieves (4 Å, 1.2 g), and PCC (2.19 g, 10.2 mmol). After stirring for 2.5 h at rt, the solution was filtered through a plug of silica (CH_2Cl_2), and column chromatography (CH_2Cl_2) gave **22** (0.665 g, 79%) as a light yellow oil: R_f = 0.2 (hexanes/CH_2Cl_2 2:1); IR (CH_2Cl_2 cast) 2962, 2200, 2154, 1632, 1583 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.83 (s, 3H), 0.26 (s, 27H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 159.5, 138.6, 121.5, 102.2, 100.8, 90.0, 86.2, –0.6; MS (EI, 70 eV) *m/z* 522.2 (M^+, 56), 73.0 (Me_3Si^+, 100); HRMS calcd. for $C_{30}H_{30}O_3Si_3$ (M^+) 522.1503, found 522.1499.

Compound (23). CBr_4 (1.62 g, 4.89 mmol) and PPh_3 (2.57 g, 9.82 mmol) were added to CH_2Cl_2 (150 mL) and the mixture stirred for 5 min at rt. Trione **22** (0.665 g, 1.27 mmol) in CH_2Cl_2 (5 mL) was added in one portion and stirring continued until the reaction was complete (2-3 h) as monitored by TLC. The solution was concentrated to ca. 15 mL, hexanes (50 mL) added, and the inhomogeneous mixture filtered through celite. Evaporation gave a yellow oil that was purified by column chromatography (SiO_2, hexanes/CH_2Cl_2 2:1) to give **23** (0.806 g, 64%) as a yellow oil: R_f = 0.7 (hexane/CH_2Cl_2 2:1); IR (CH_2Cl_2 cast) 2960, 2216, 2153, 1582, 1250 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.61 (s, 3H), 0.24 (s, 27H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 134.6, 123.2, 113.8, 110.4, 103.2, 99.8, 93.2, 87.3, –0.5; MS (ESI,

CH_2Cl_2, with AgOTf added) *m/z* 1098.6 ([M + Ag]$^+$, 100); HRMS calcd for $C_{33}H_{30}{}^{79}Br_3{}^{81}Br_3Si_3{}^{109}Ag$ ([M + Ag]$^+$) 1098.5742, found 1098.5750.



25 **26** **27**

Compound (25). 1,3,5-Tris-(1-trimethylsilylethynyl)benzene (1.56 g, 4.25 mmol) and K_2CO_3 (0.4 g, 2 mmol) were added to wet THF/MeOH (50 mL, 1:1 v/v) and stirred for 2 h until TLC showed complete desilylation. Et_2O was added, the solution washed with saturated aqueous NH_4Cl, and dried over $MgSO_4$. The solvent was reduced to ca. 10 mL and added to dried Et_2O (250 mL). *n*-BuLi (2.5 M in hexanes, 5.1 mL, 13 mmol) was subsequently added at –78 ˚C and allowed to stir for an hour. 3-Trimethylsilylpropynal (1.67g, 13.2 mmol) was added and the mixture allowed to warm to rt overnight. Aqueous work-up, solvent removal, and column chromatography (silica gel, hexanes/CH_2Cl_2 8:2), gave **25** (0.623g, 36%) as an orange oil: R_f = 0.13 (hexanes/CH_2Cl_2 4:1); IR (CH_2Cl_2 cast) 3291(OH and ≡C–H), 2960, 2235, 2179, 1584 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (m, 3H), 5.30 (s, 2H), 3.08 (s, 2H), 2.51 (s, 1H), 0.19 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.3, 135.0, 122.9, 122.8, 101.3, 90.2, 87.3, 82.3, 81.6, 78.8, 52.9, -0.4; MS (EI, 70 eV) *m/z* 402.1 (M^+, 9), 73.0 (Me_3Si^+, 100); HRMS calcd. for $C_{24}H_{26}O_2Si_2$ 402.1471, found 402.1459.

Compound (26). To **25** (0.0220 g, 0.0546 mmol) in CH_2Cl_2 (20 mL) was added sequentially celite (0.1 g), molecular sieves (4 Å, 0.1 g), and PCC (0.037 g, 0.17 mmol). After stirring for 6 h at rt, the solution was filtered through a plug of silica (CH_2Cl_2) to give **26** (0.0142 g, 65%) as a white solid: Mp 72 - 74 ˚C; R_f = 0.71 (hexanes/Et_2O 7:3); IR (CH_2Cl_2 cast) 3289, 2962, 2210, 2153, 2103, 1631 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (m, 1H), 7.76 (m, 2H), 3.18 (s, 1H), 0.27 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, APT) δ 159.8, 138.2, 137.0, 124.1, 121.0, 102.3, 100.6, 89.7, 87.3, 80.4, -0.9 (one coincident signal not observed); MS (EI, 70 eV) *m/z* 398.1 (M^+, 100); HRMS calcd. for $C_{24}H_{22}O_2Si_2$ 398.1158, found 398.1160.

Compound (27). CBr_4 (0.316 g, 0.954 mmol) and PPh_3 (0.514 g, 1.96 mmol) were added to CH_2Cl_2 (50 mL) and the mixture stirred for 5 min at rt. Ketone **26** (0.156 g, 0.392 mmol) in CH_2Cl_2 (3 mL) was added and the reaction was complete within 0.5 h as monitored by TLC. The solution was concentrated to ca. 5 mL, hexanes (15 mL) was added and the mixture filtered through celite. Evaporation gave **27** (0.151 g, 56%) as a white solid: Mp 118-120 ˚C. R_f = 0.78 (hexanes/CH_2Cl_2 1:1); IR (CH_2Cl_2 cast) 3298, 2959, 2211, 2153, 1581 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (m, 3H), 3.10 (s, 1H), 0.24 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, APT) δ 135.3, 134.4, 123.2, 123.1, 113.8, 110.3, 103.2, 102.5, 99.8, 93.3, 87.2, 81.4, 79.0, -0.5; MS (EI, 70 eV) *m/z* 402.1 (M^+, 40), 73.0 (Me_3Si^+, 100); HRMS calcd. for $C_{26}H_{22}{}^{79}Br_2{}^{81}Br_2Si_2$ 709.7953, found 709.7975.

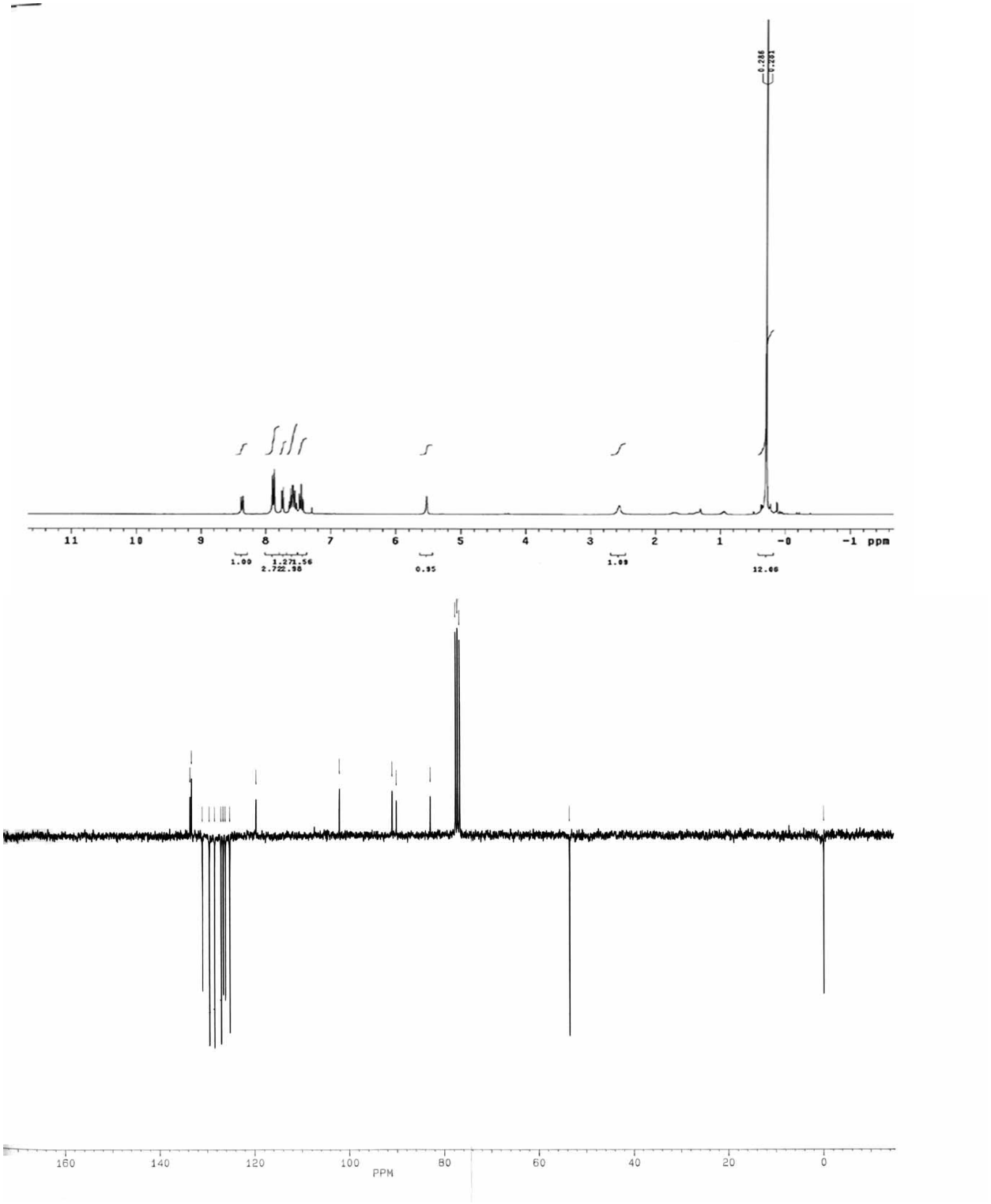


Figure S1-^{1}H and ^{13}C NMR spectra of **5d**

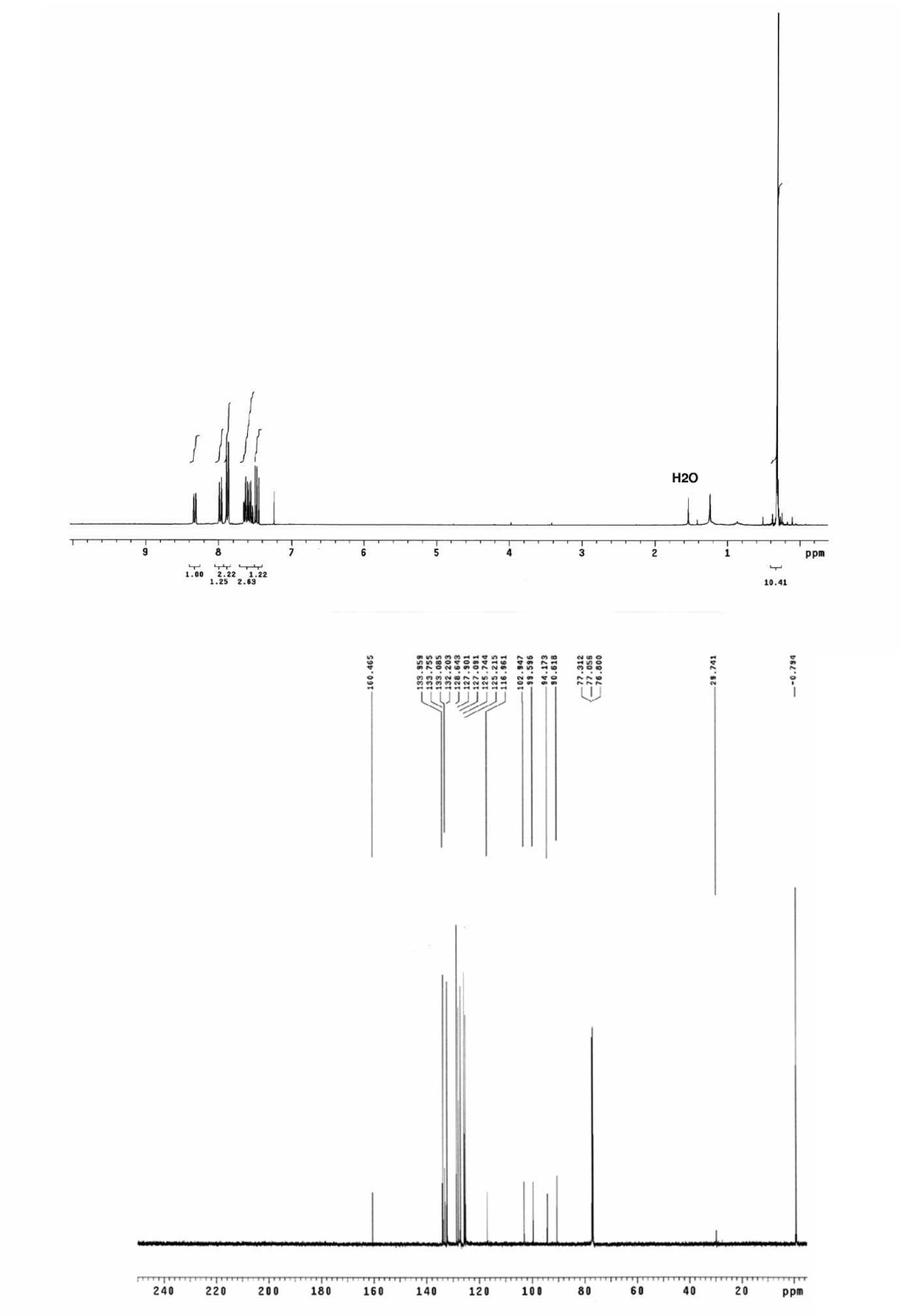


Figure S2- ^{1}H NMR and ^{13}C NMR spectra of **6d**

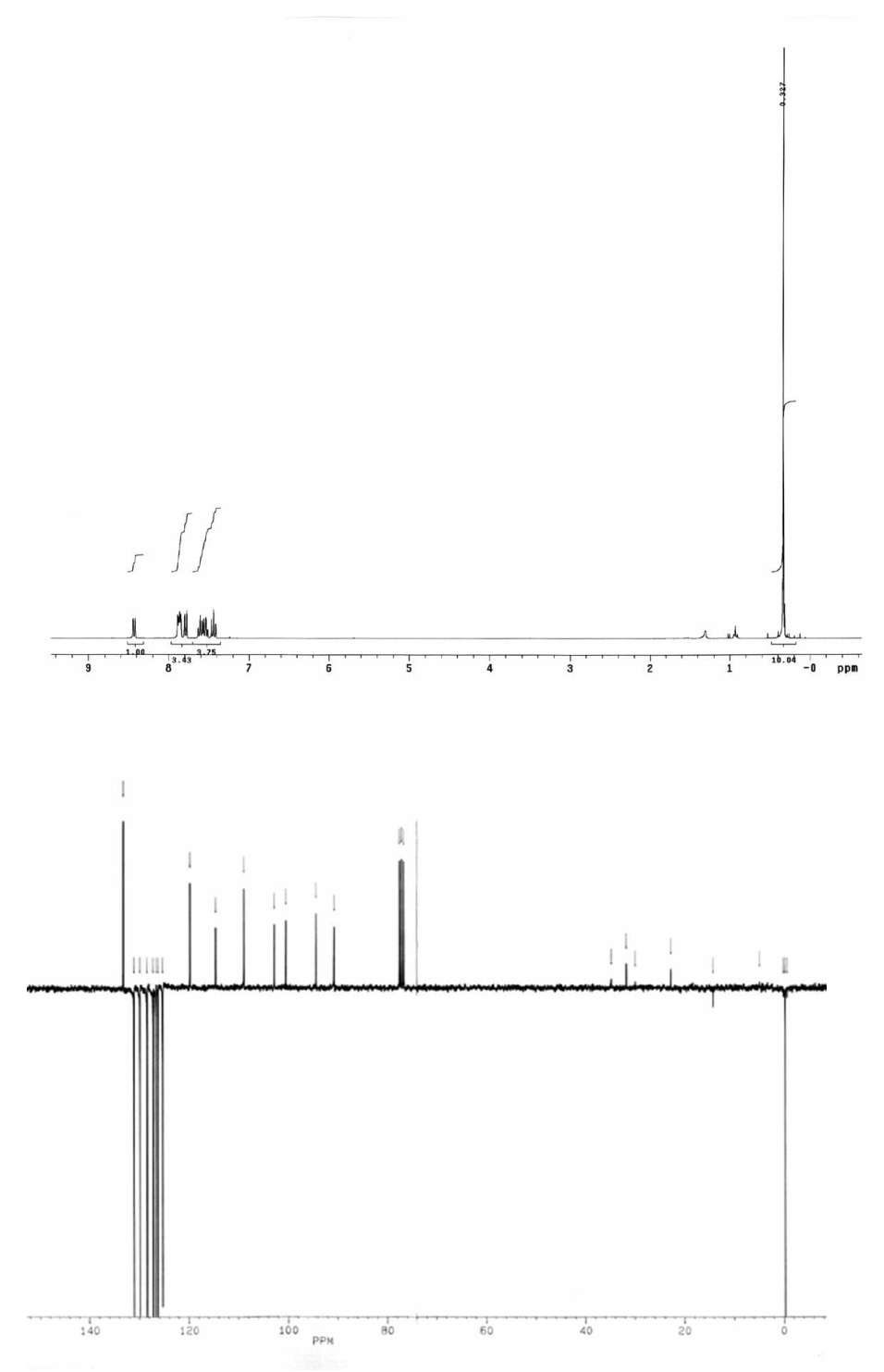


Figure S3 - ^{1}H NMR and ^{13}C NMR spectra of **7d**

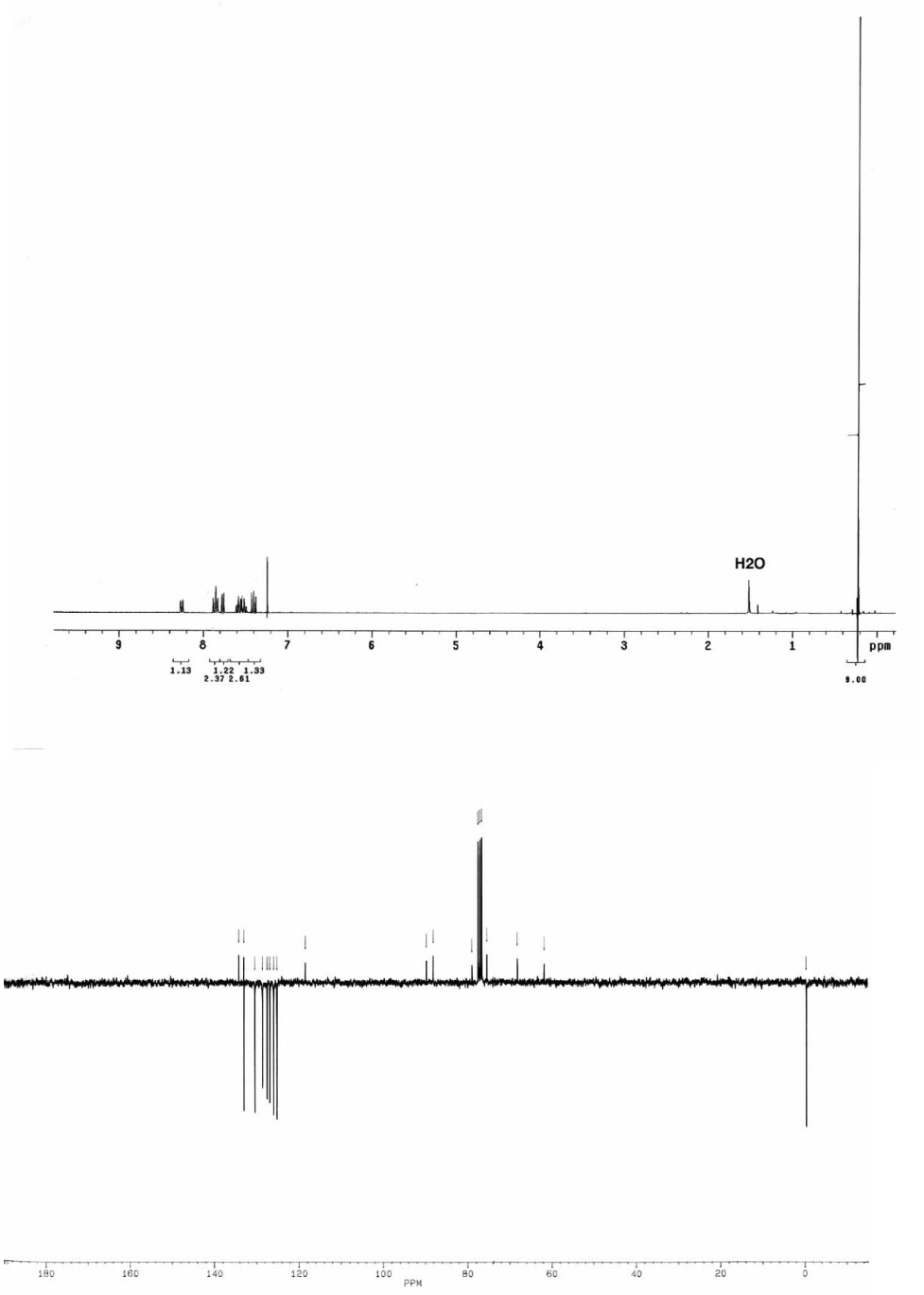


Figure S4 - ^{1}H NMR ^{13}C NMR spectra of **4d**

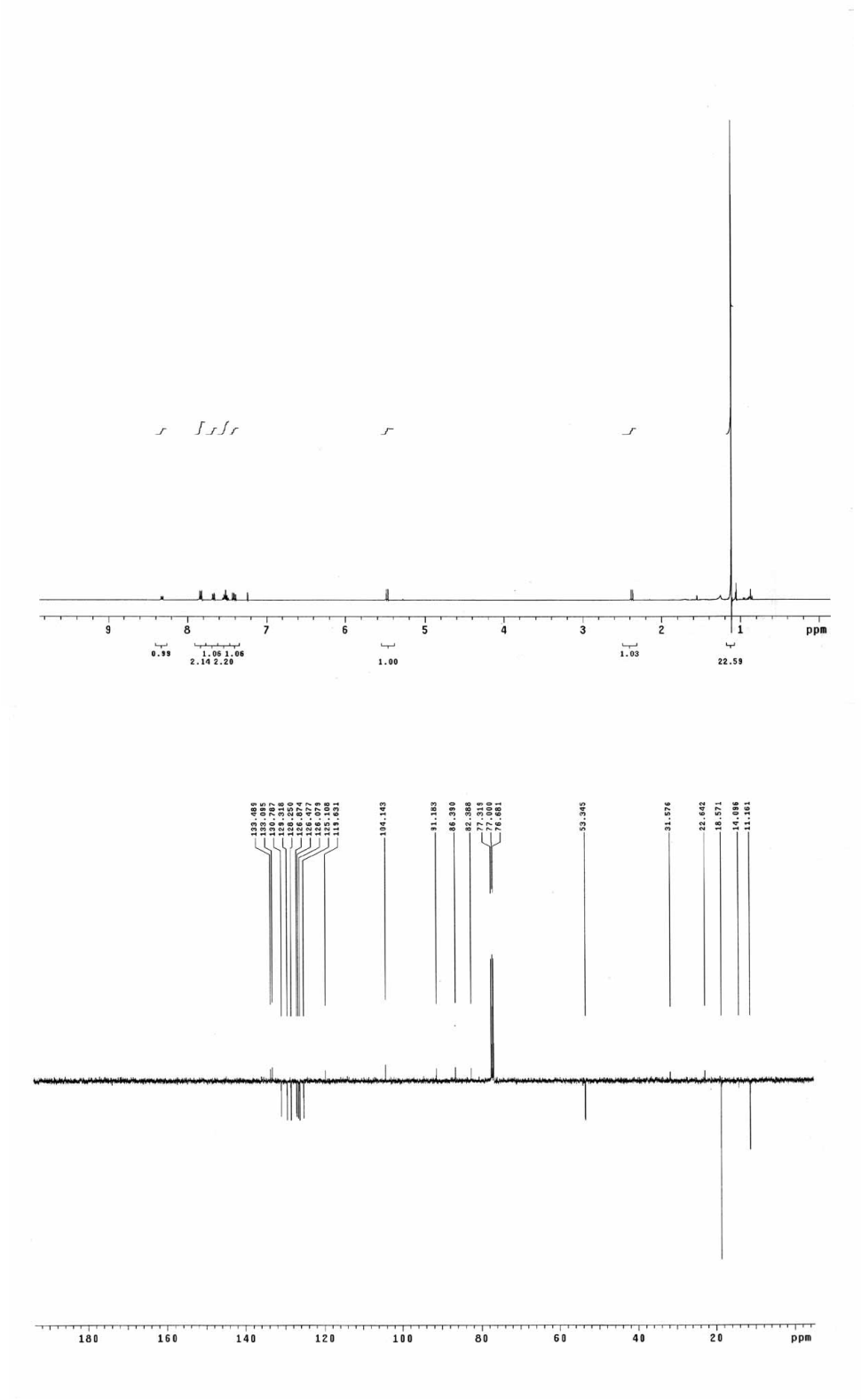


Figure S5 - ^{1}H NMR and ^{13}C NMR spectra of **5e**

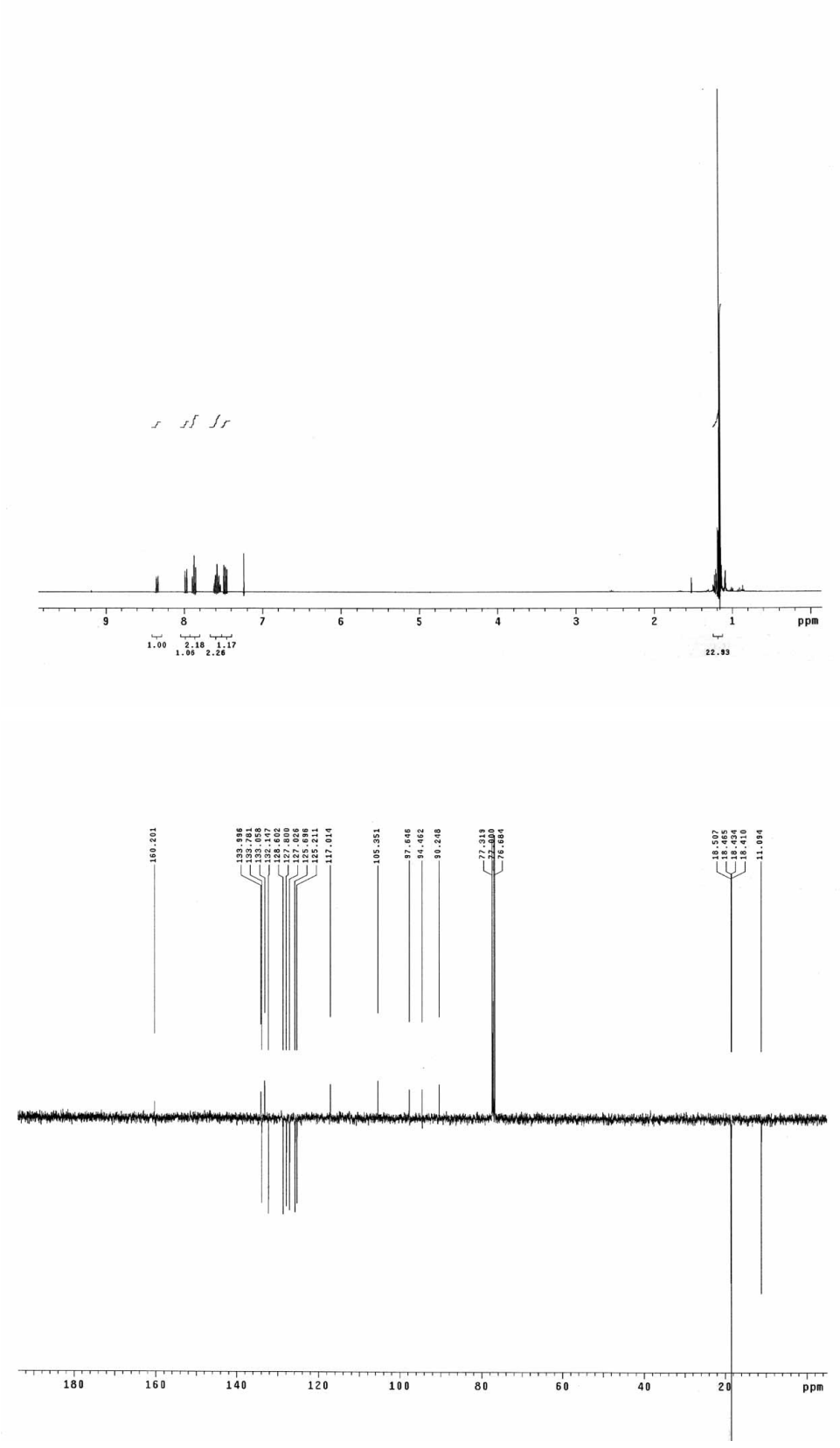


Figure S6 - ^{1}H NMR and ^{13}C NMR spectra of **6e**

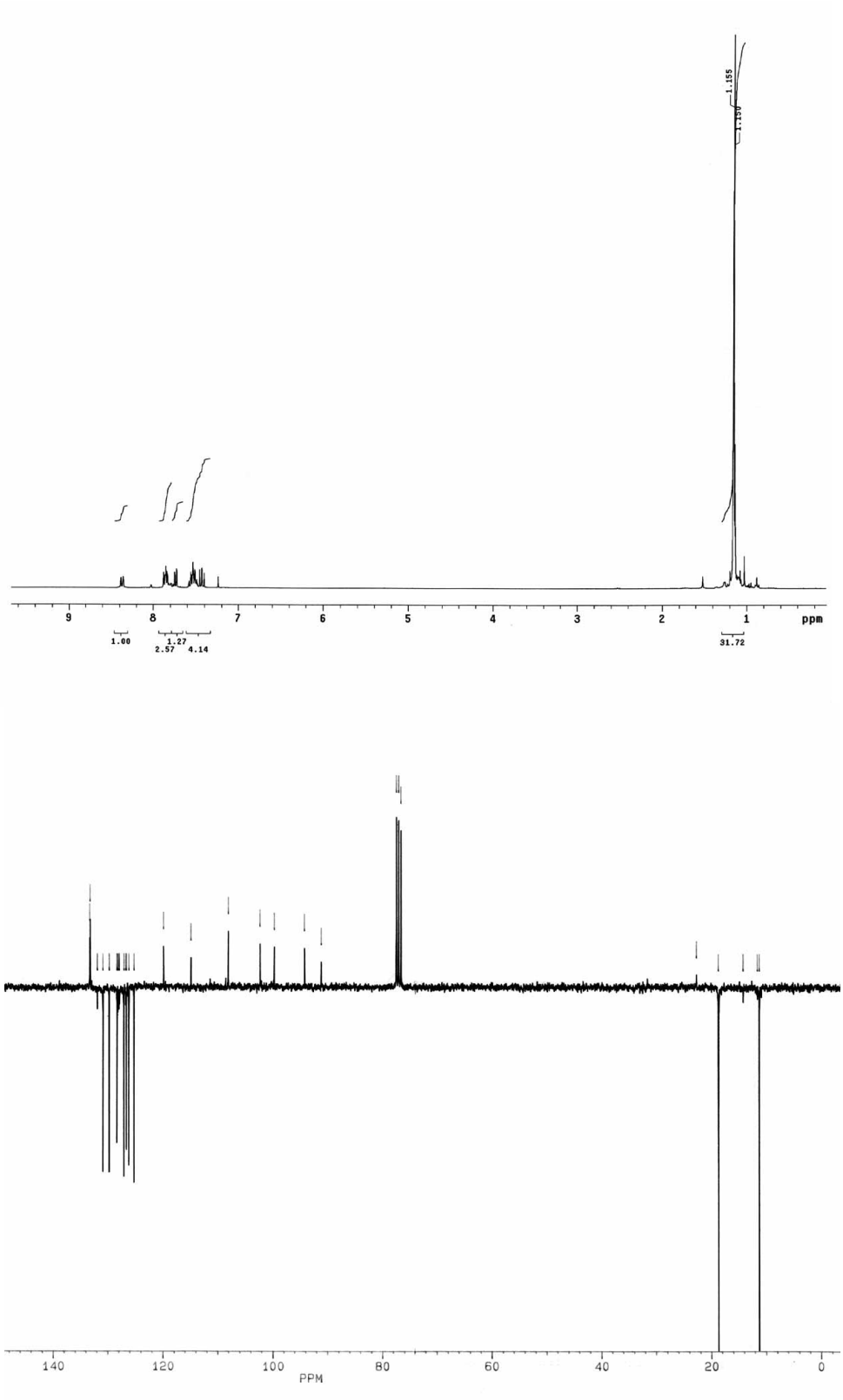


Figure S7 - ^{1}H NMR and ^{13}C NMR spectra of **7e**

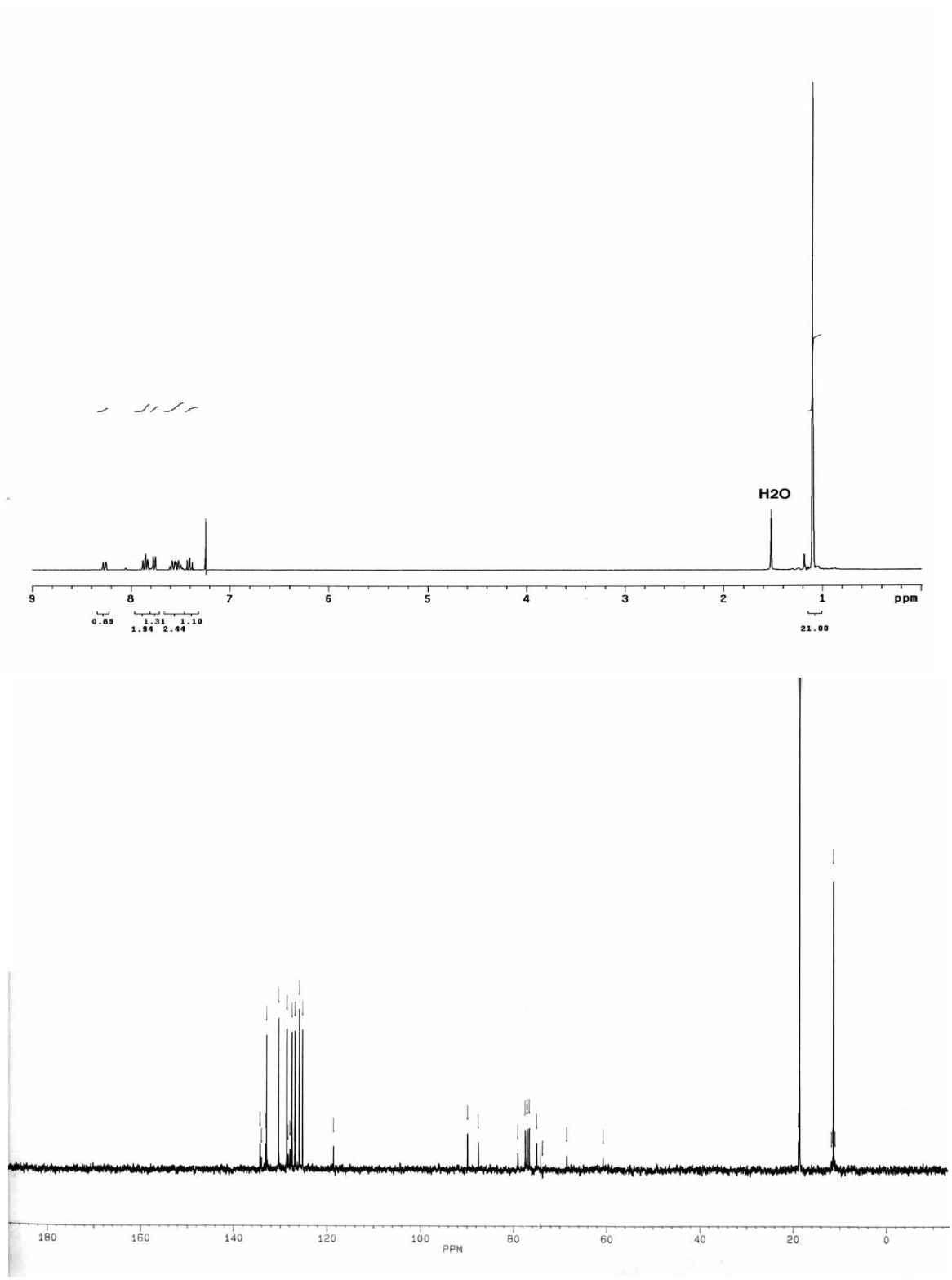


Figure S8 - ^{1}H NMR and ^{13}C NMR spectra of **4e**

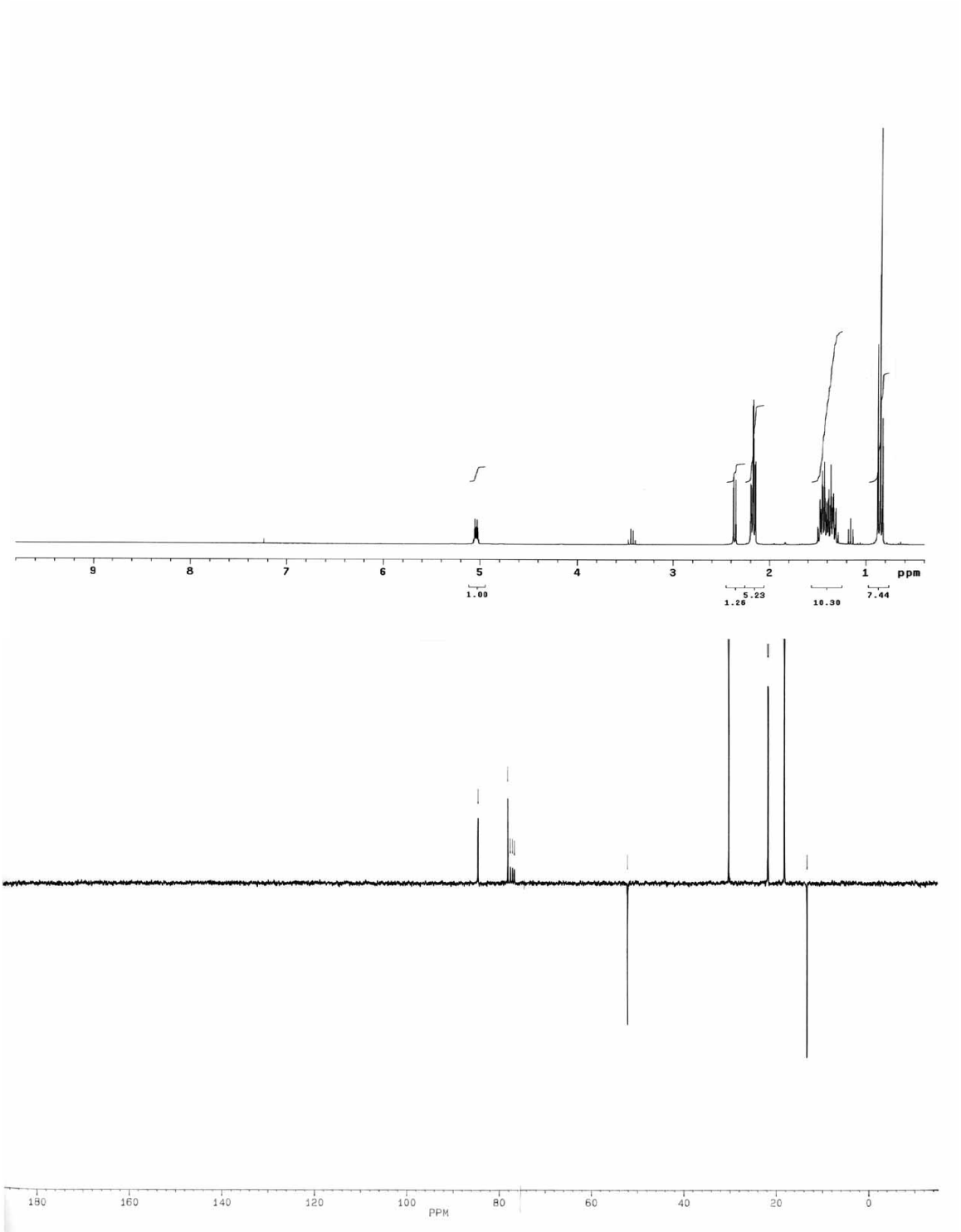


Figure S9 - ^{1}H NMR and ^{13}C NMR spectra of **5f**

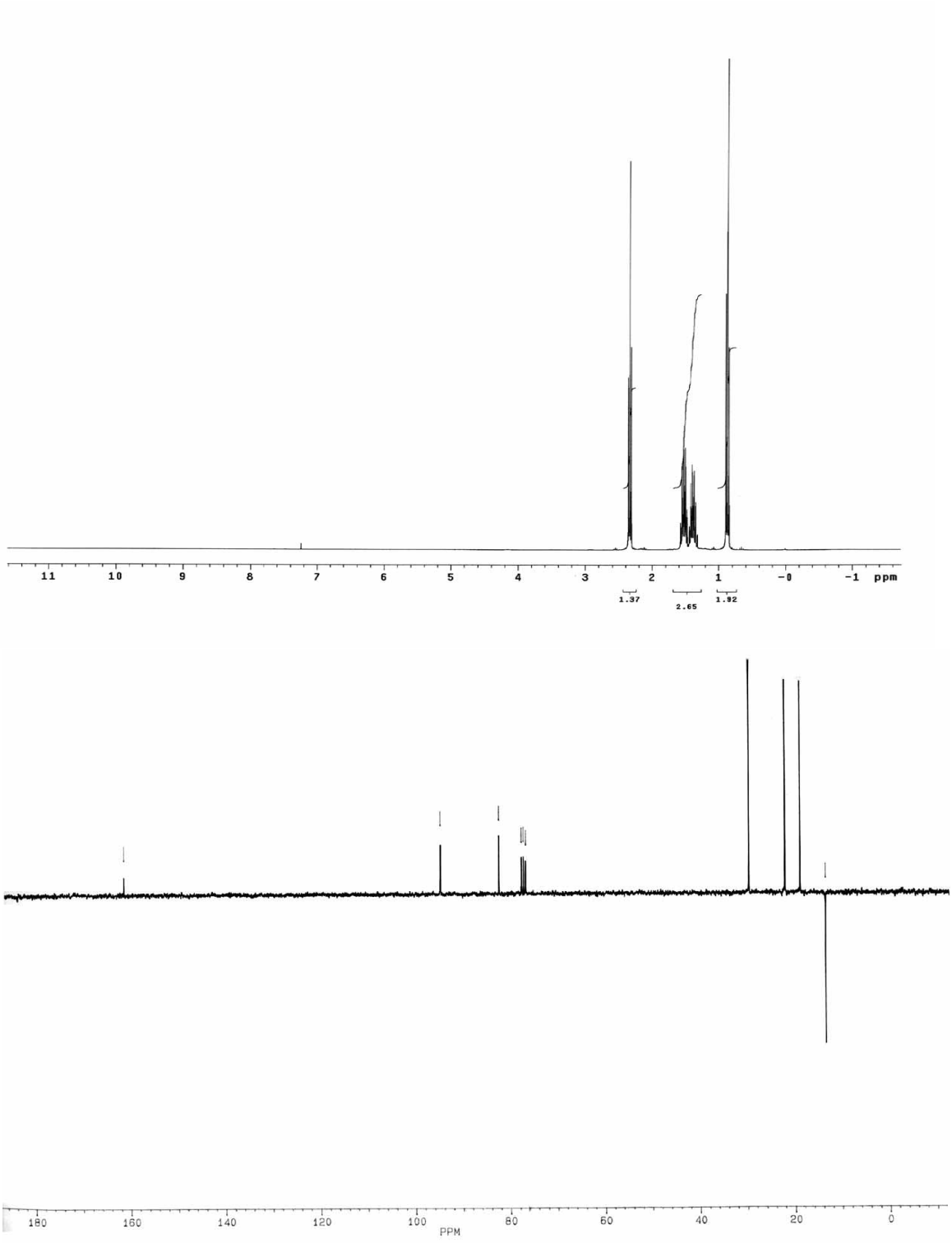


Figure S10 - ^{1}H NMR and ^{13}C NMR spectra of **6f**

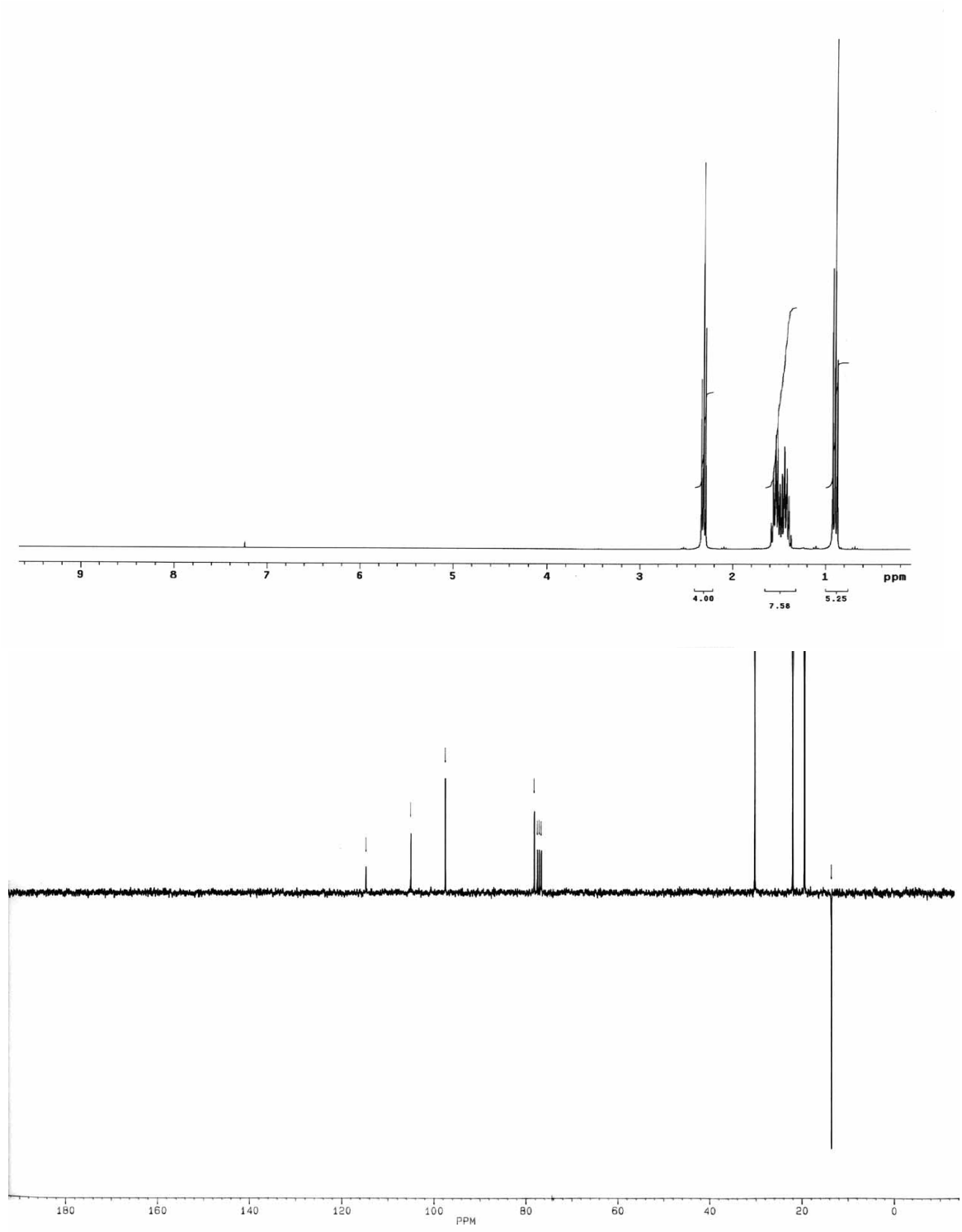


Figure S11 - ^{1}H NMR and ^{13}C NMR spectra of **7f**

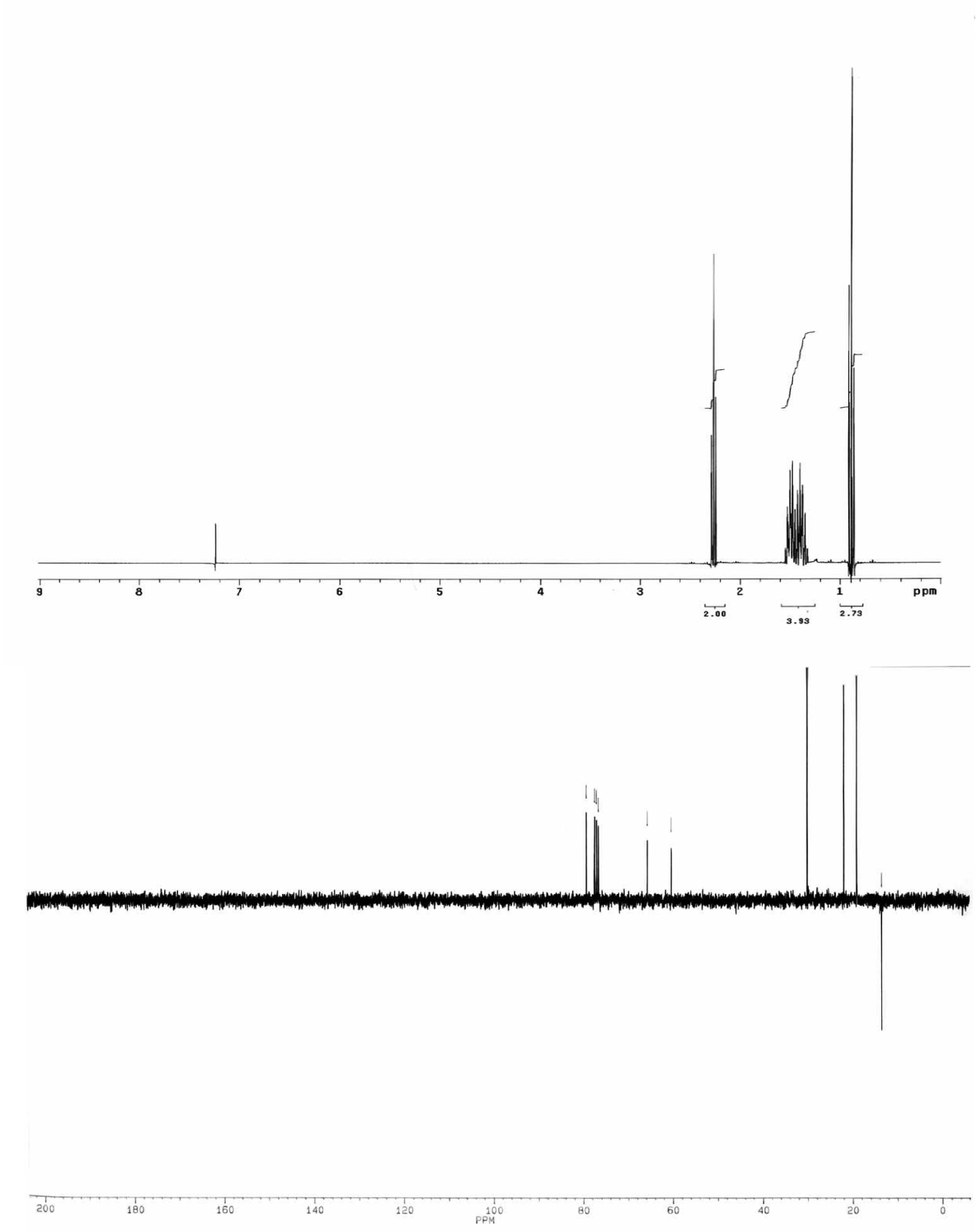


Figure S12 - ^{1}H NMR and ^{13}C NMR spectra of **4f**

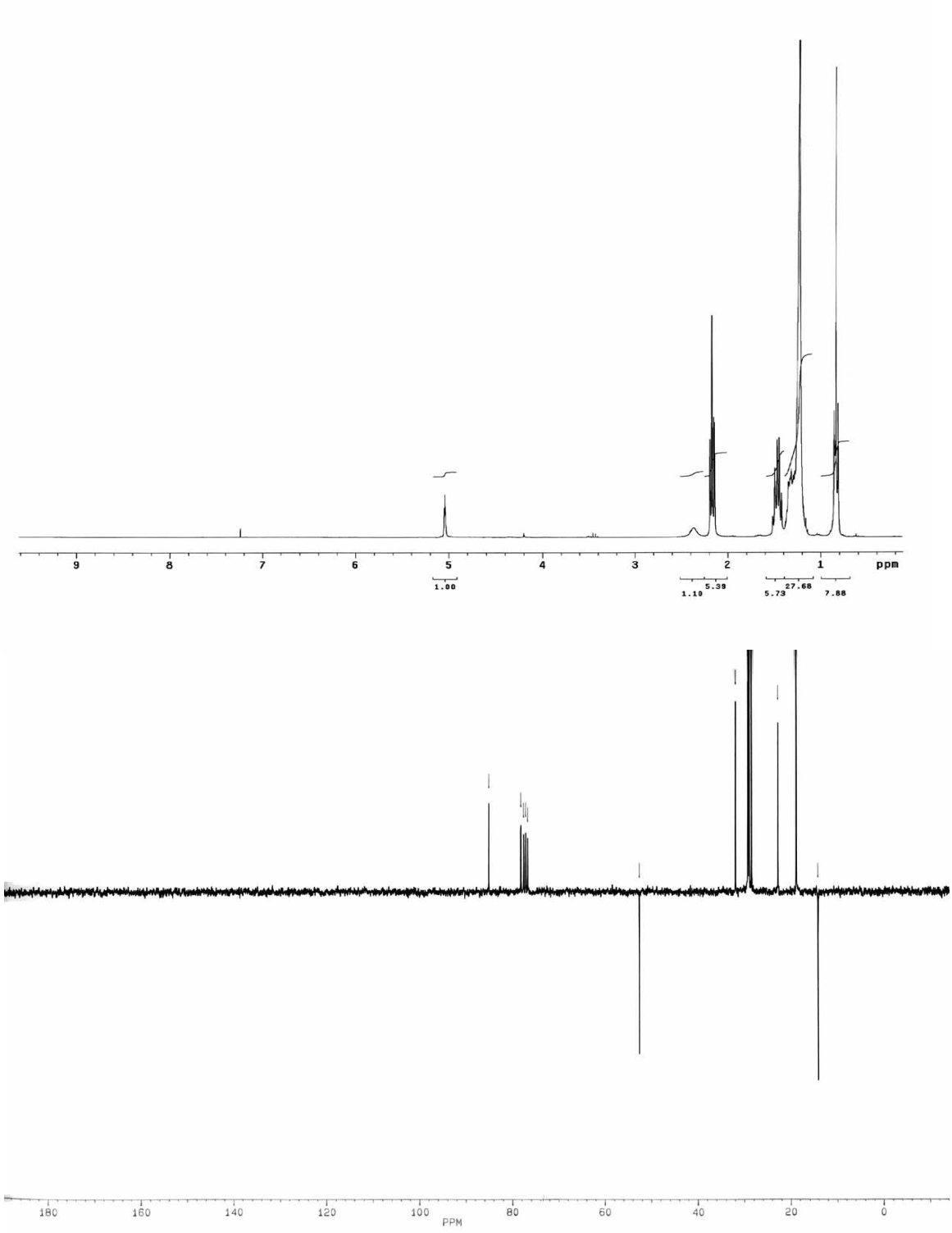


Figure S13 - ^{1}H NMR and ^{13}C NMR spectra of **5g**

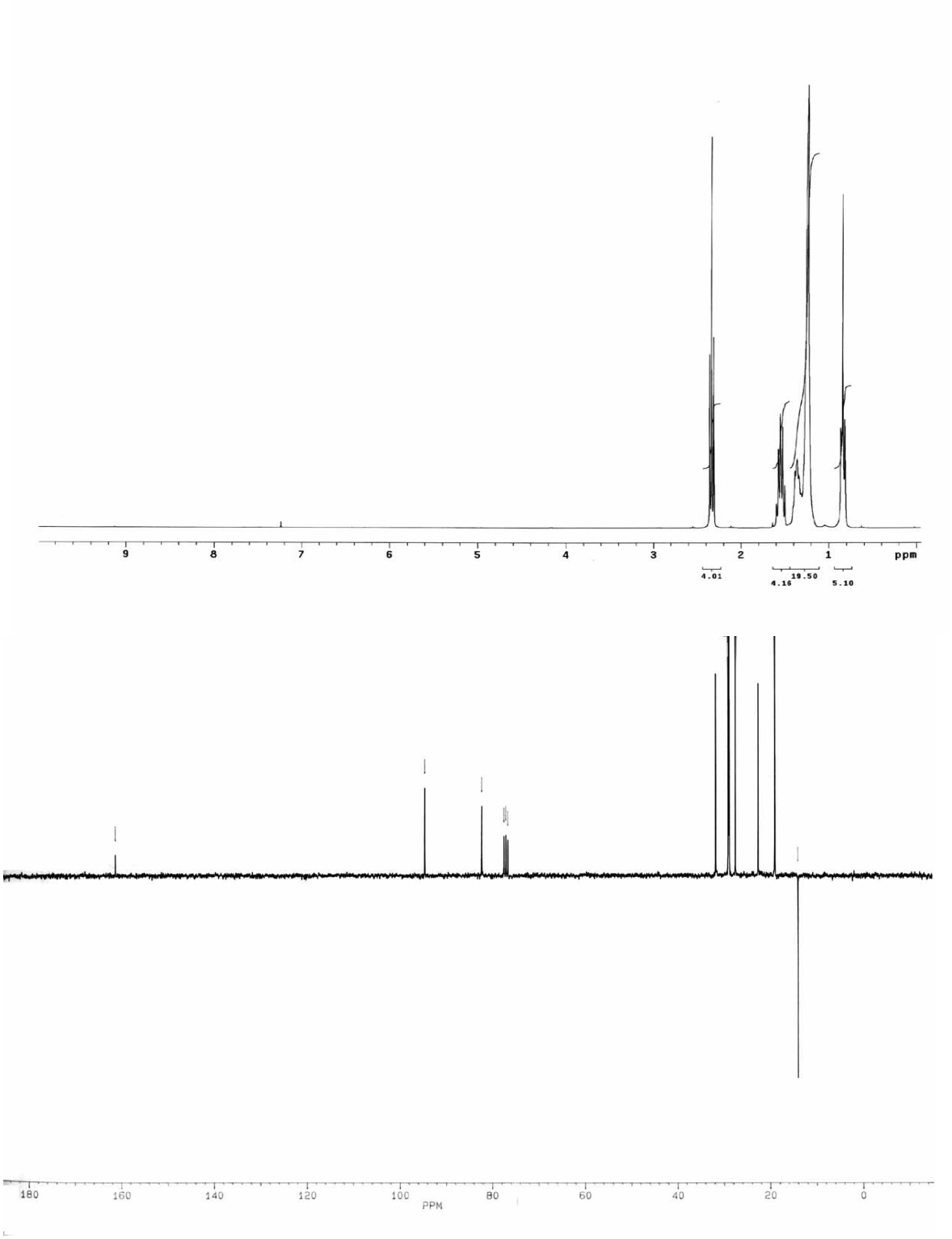


Figure S14 - ^{1}H NMR and ^{13}C NMR spectra of **6g**

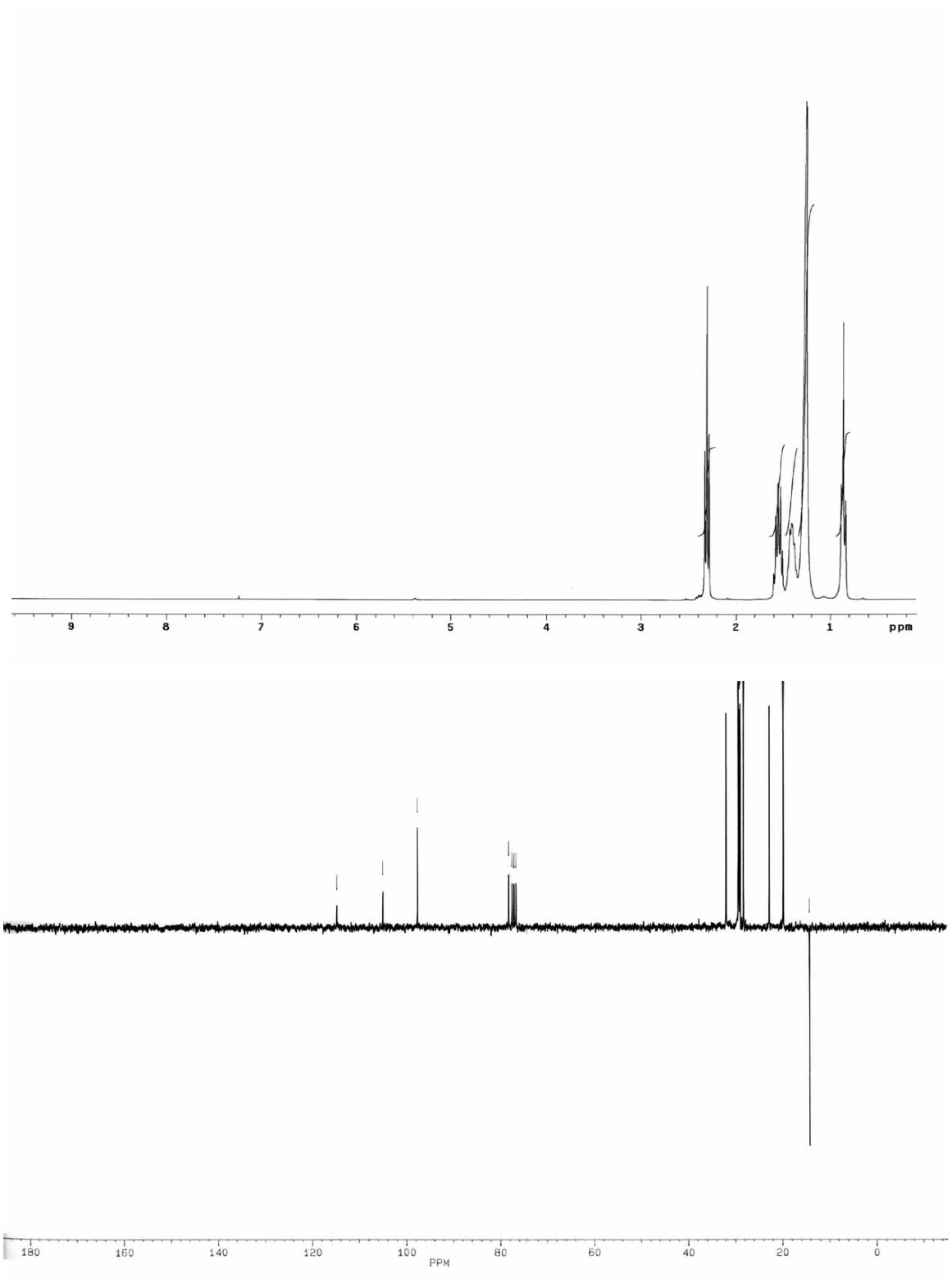


Figure S15 - ^{1}H NMR and ^{13}C NMR spectra of **7g**

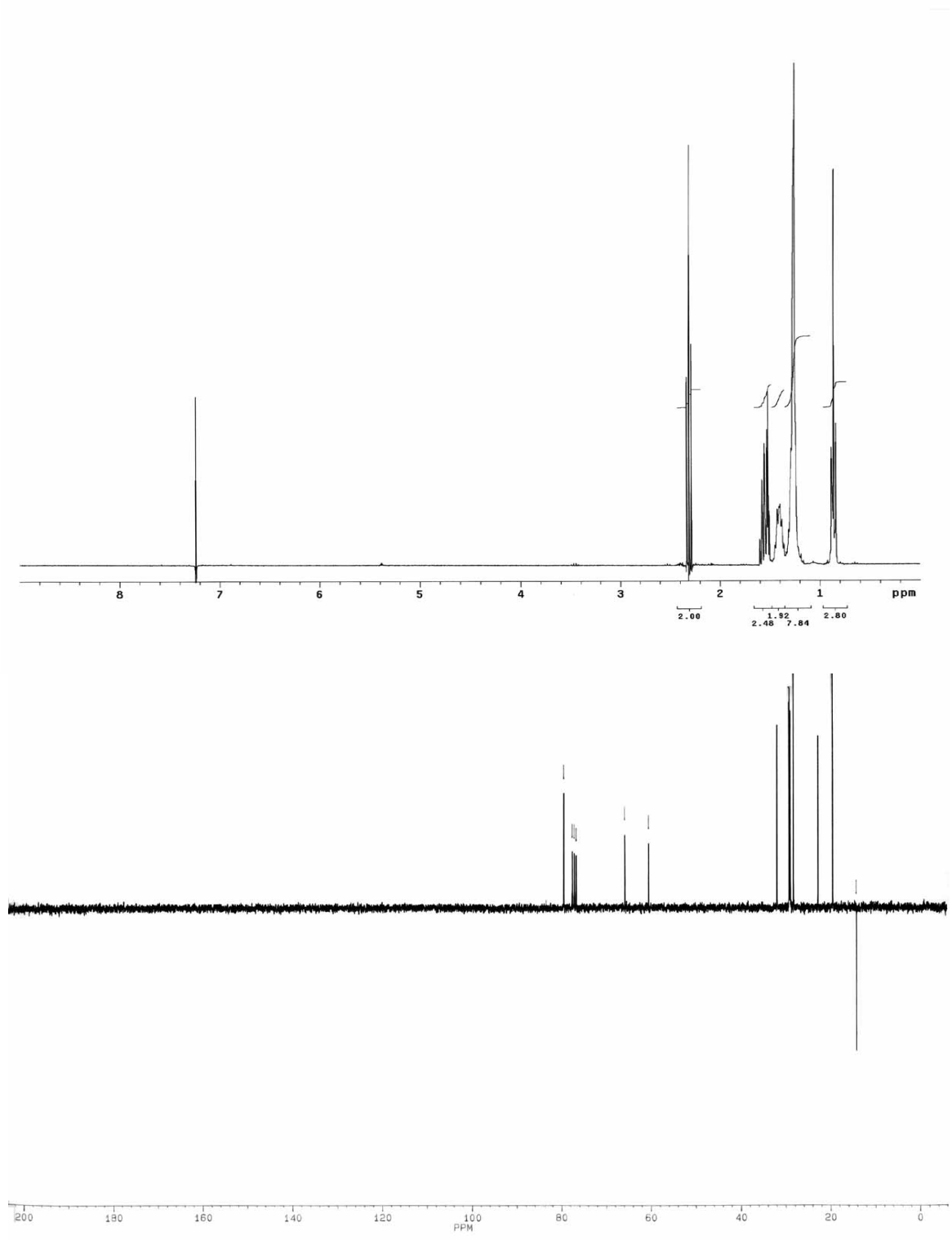
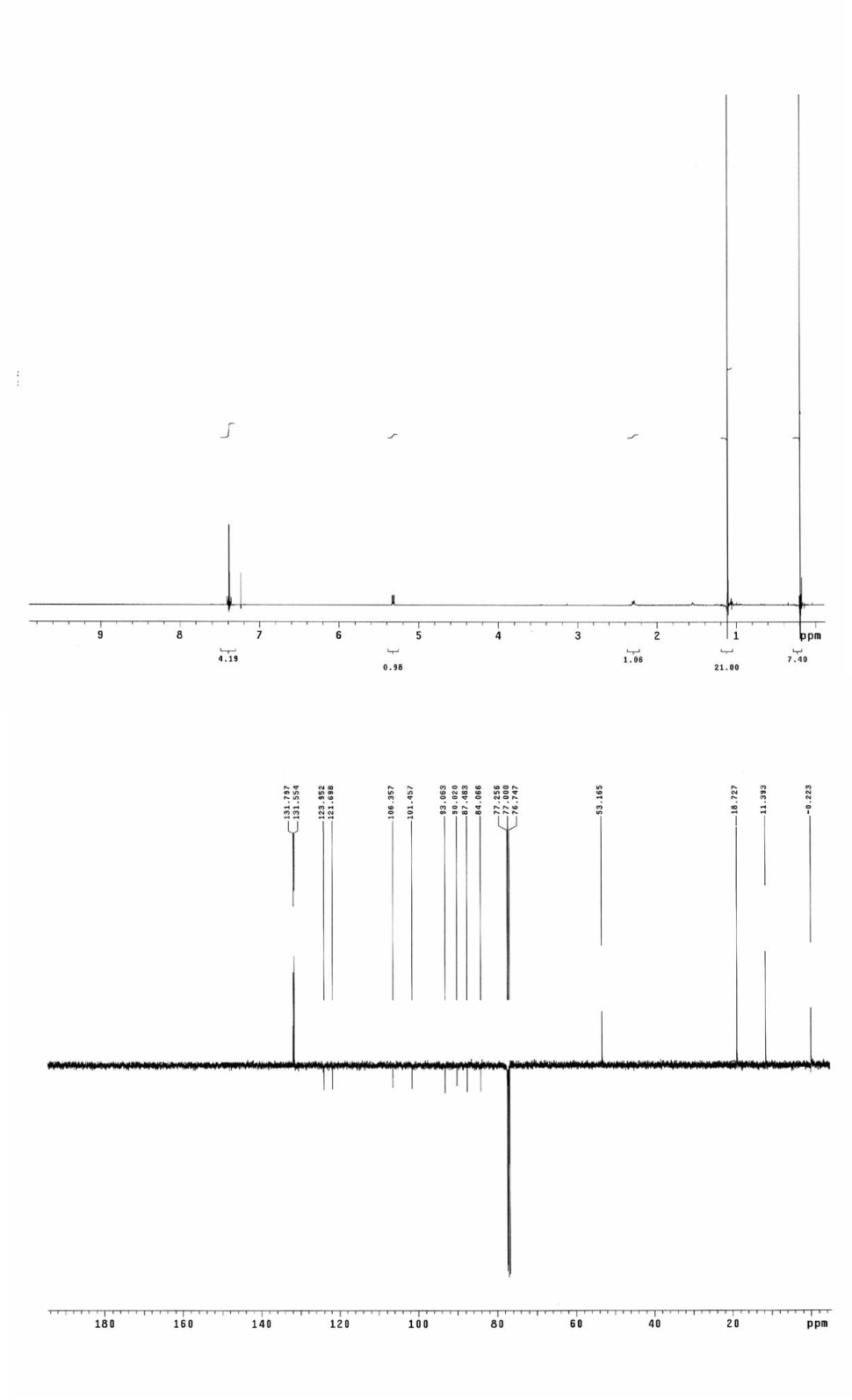


Figure S16 - ^{1}H NMR and ^{13}C NMR spectra of **4g**



"Figure S17 - ^{1}H NMR and ^{13}C NMR spectra of **5h**

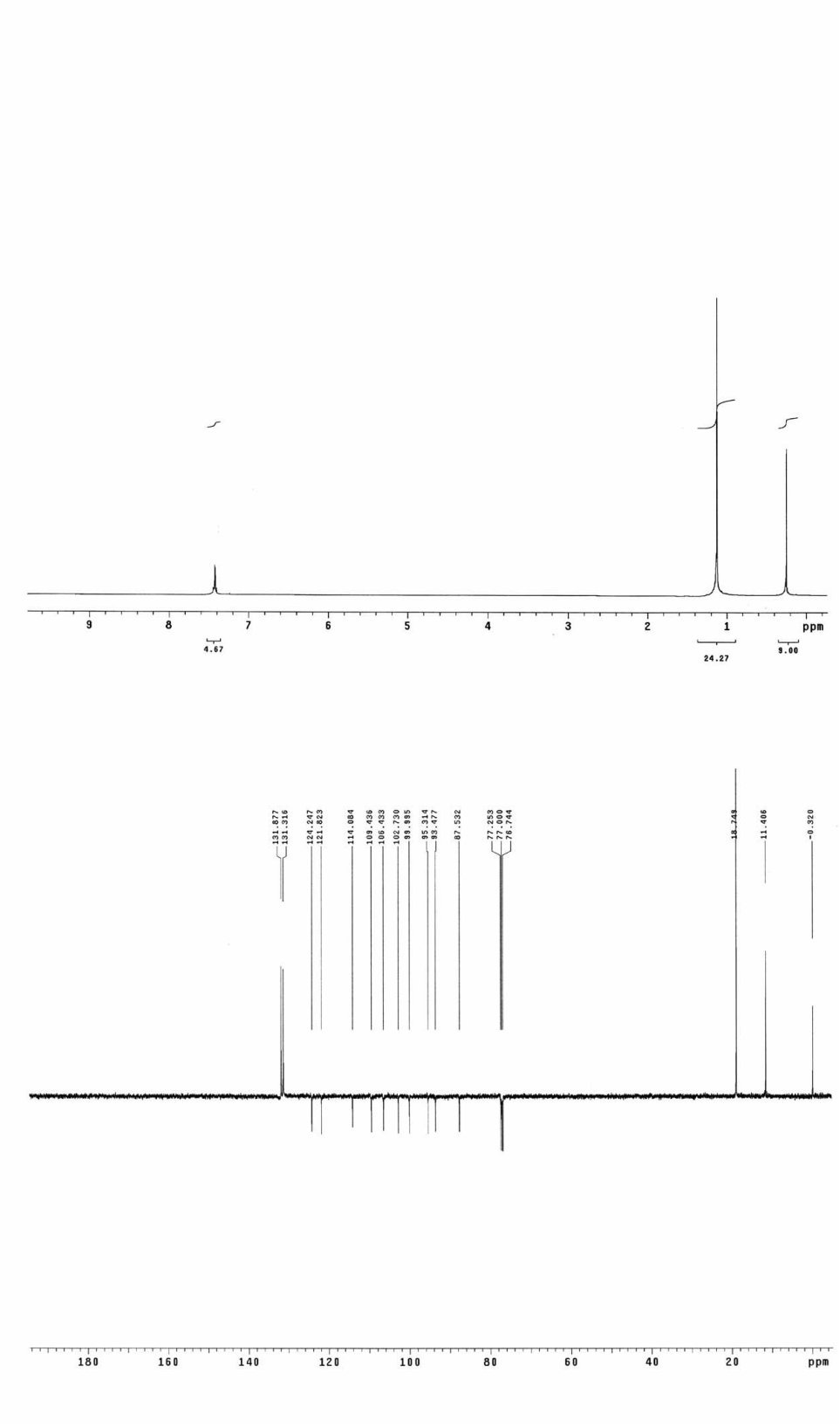


Figure S18 - ^{1}H NMR and ^{13}C NMR spectra of **7h**

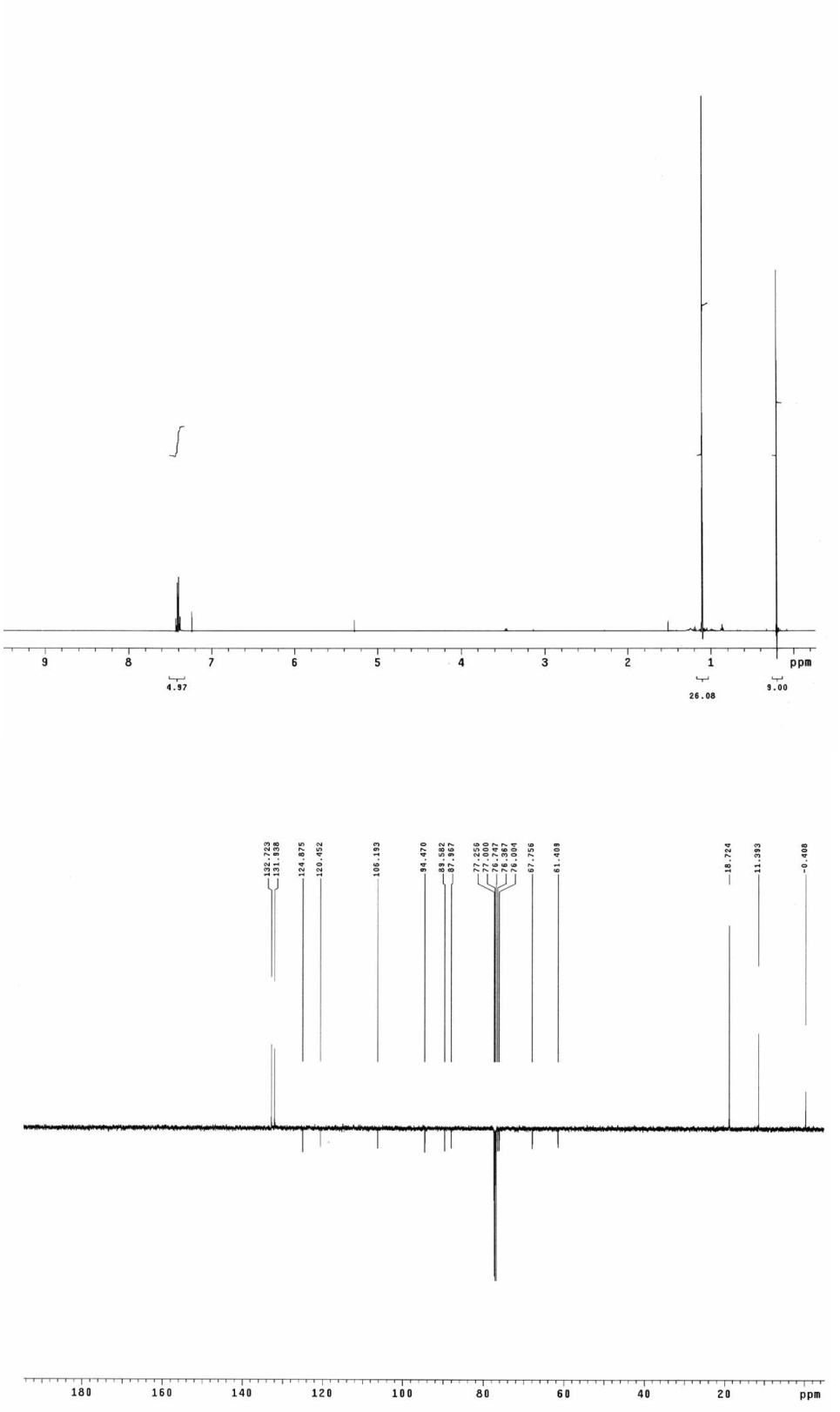


Figure S19 - ^{1}H NMR and ^{13}C NMR spectra of **4h**

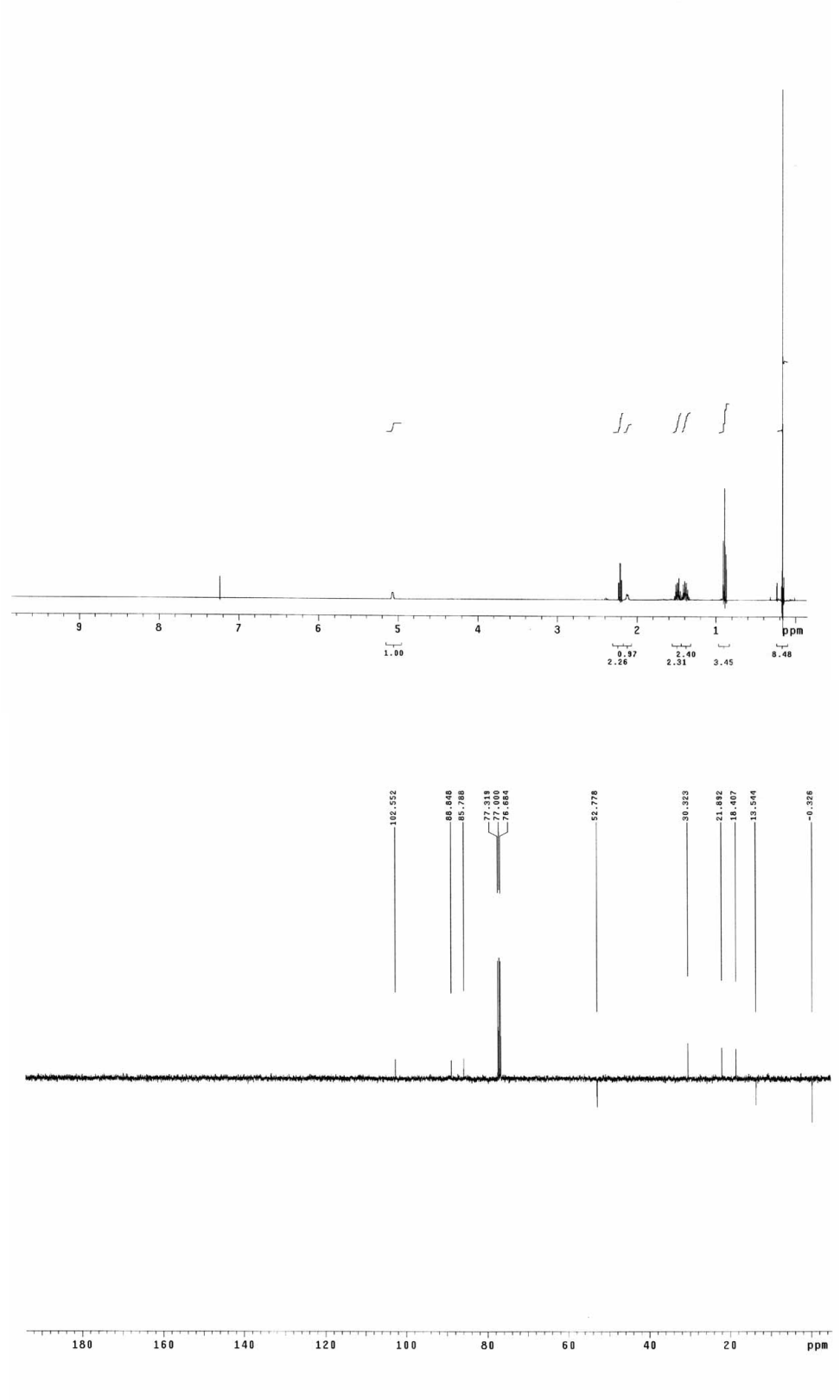


Figure S20 - ^{1}H NMR and ^{13}C NMR spectra of **5i**

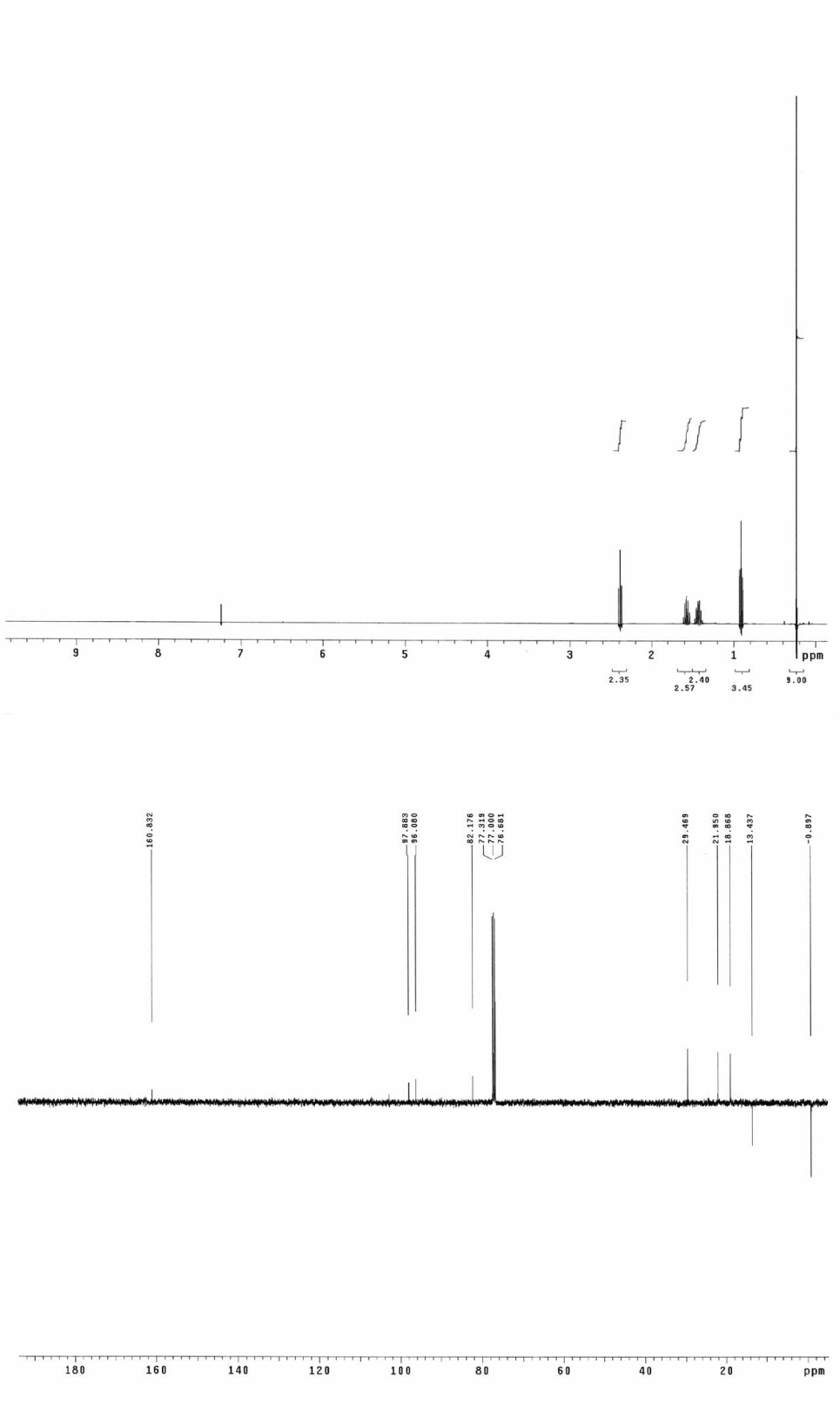


Figure S21 - ^{1}H NMR and ^{13}C NMR spectra of **6i**

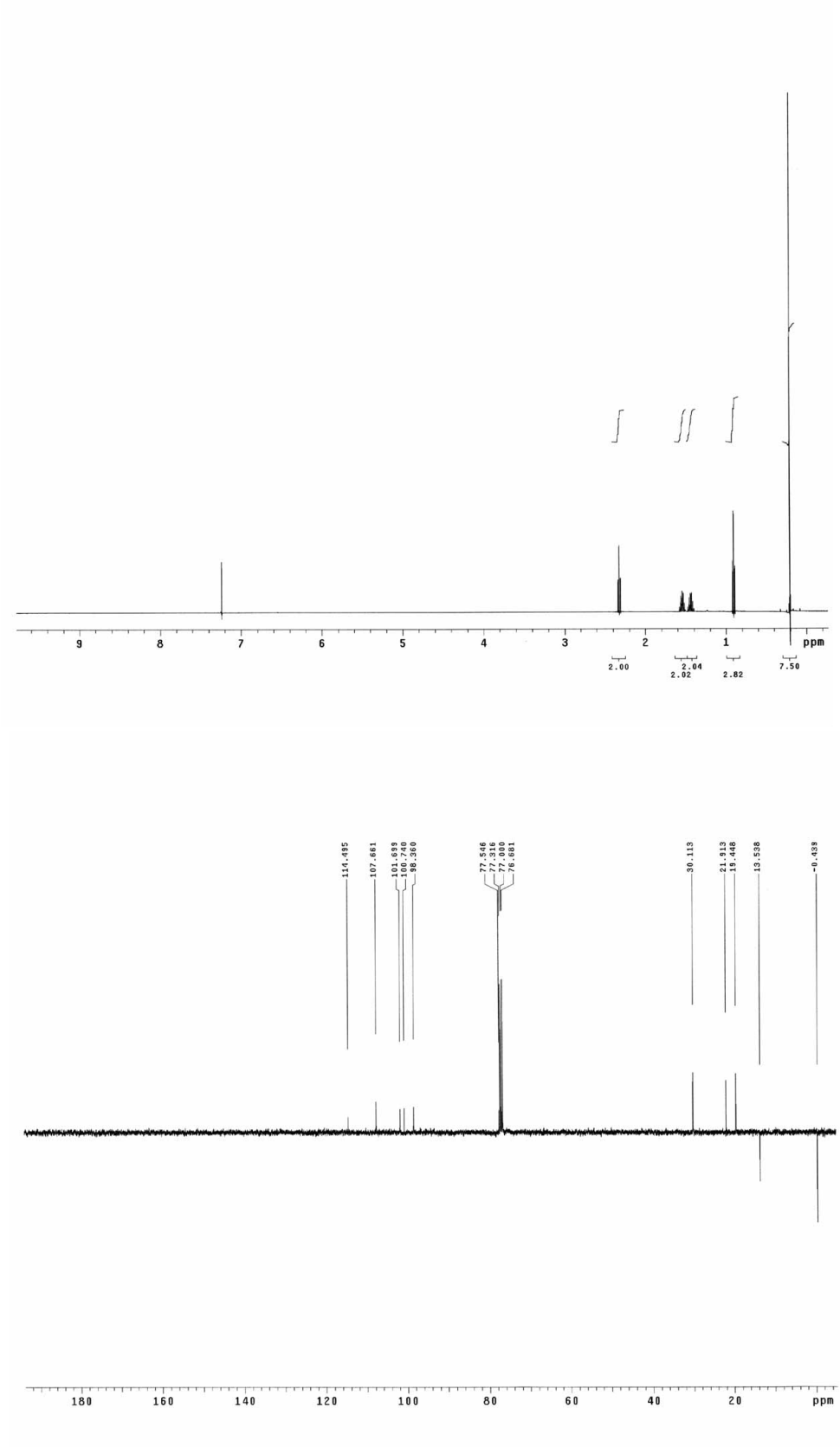


Figure S22 - ^{1}H NMR and ^{13}C NMR spectra of **7i**

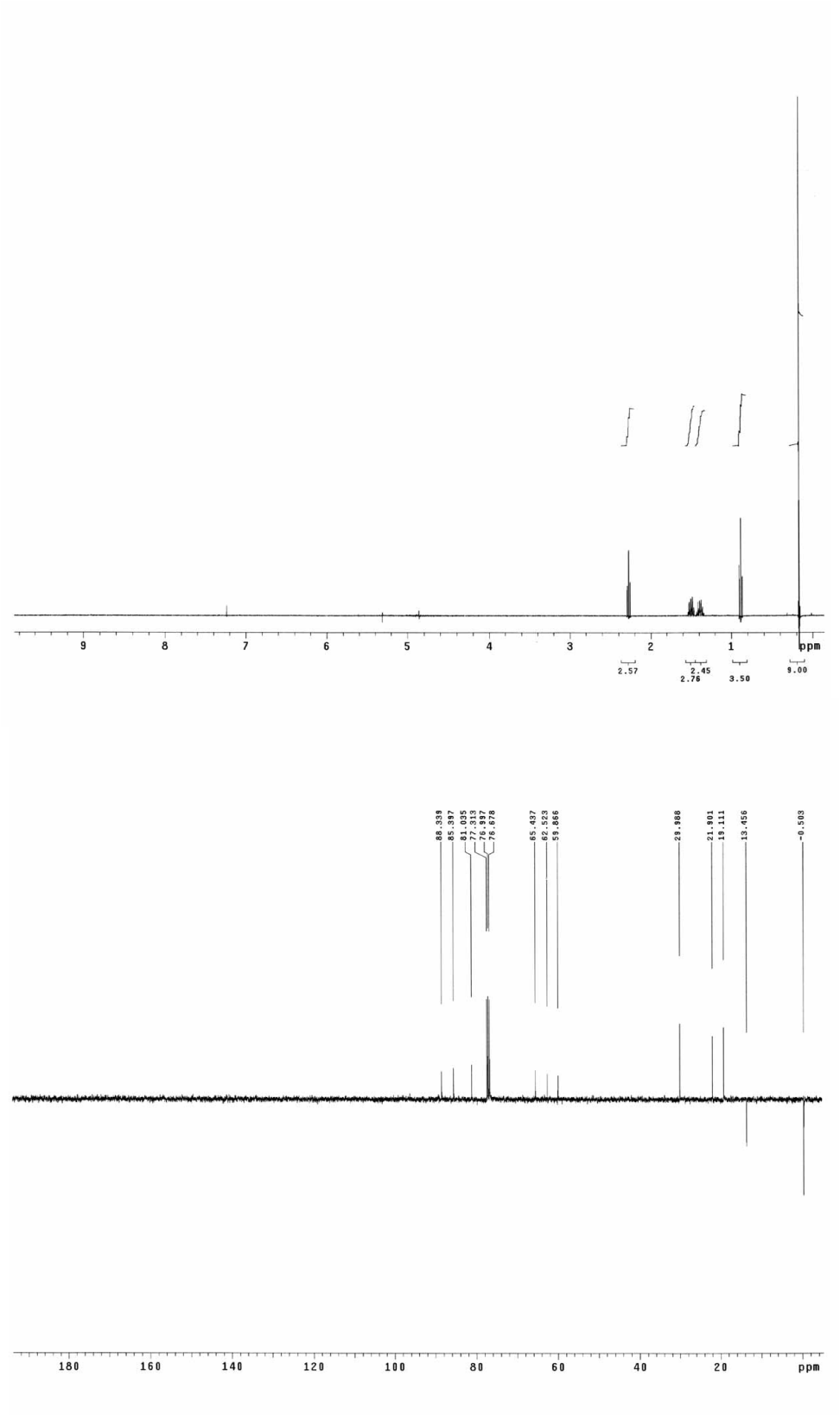


Figure S23 - ^{1}H NMR and ^{13}C NMR spectra of **4i**

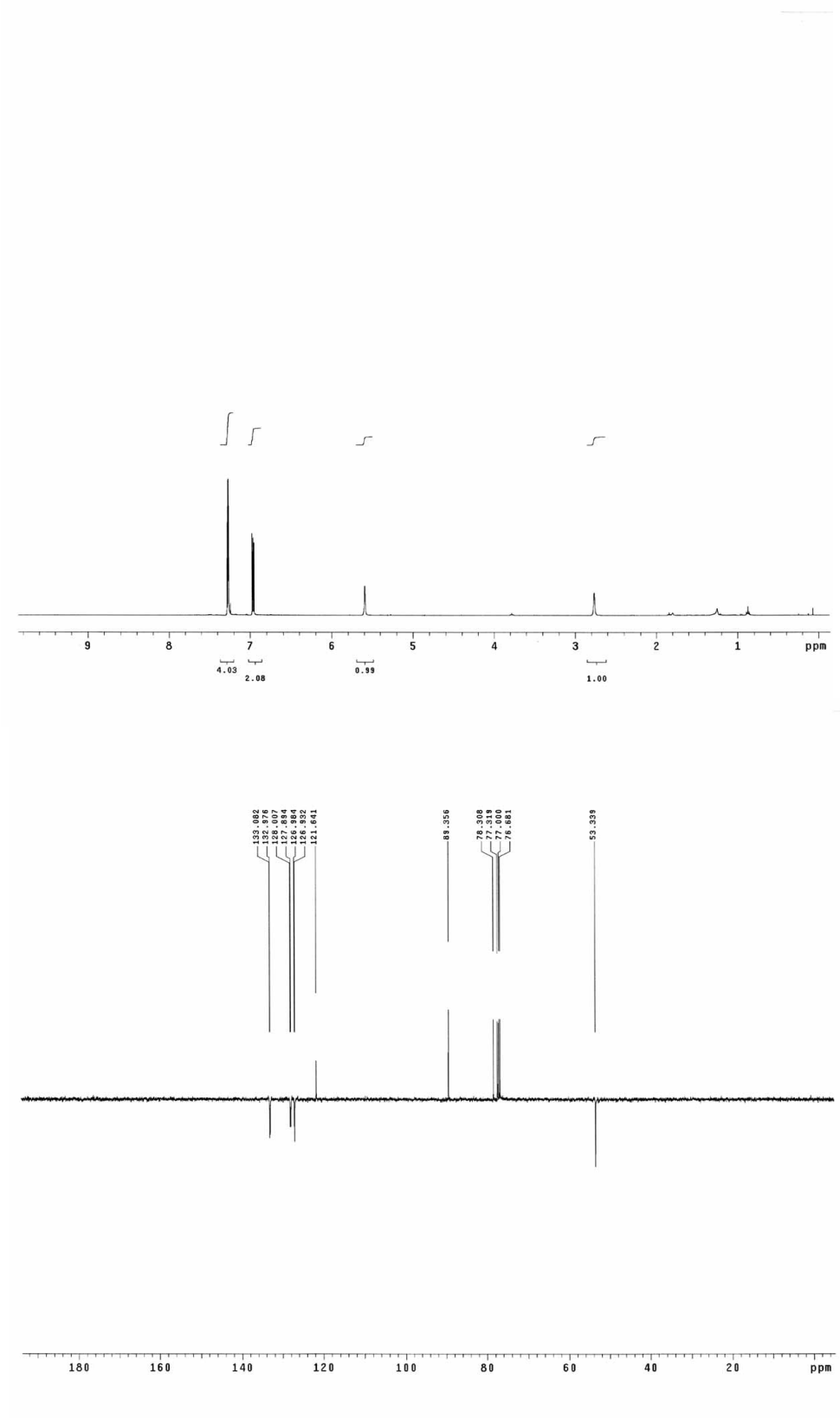


Figure S24 - ^{1}H NMR and ^{13}C NMR spectra of **5j**

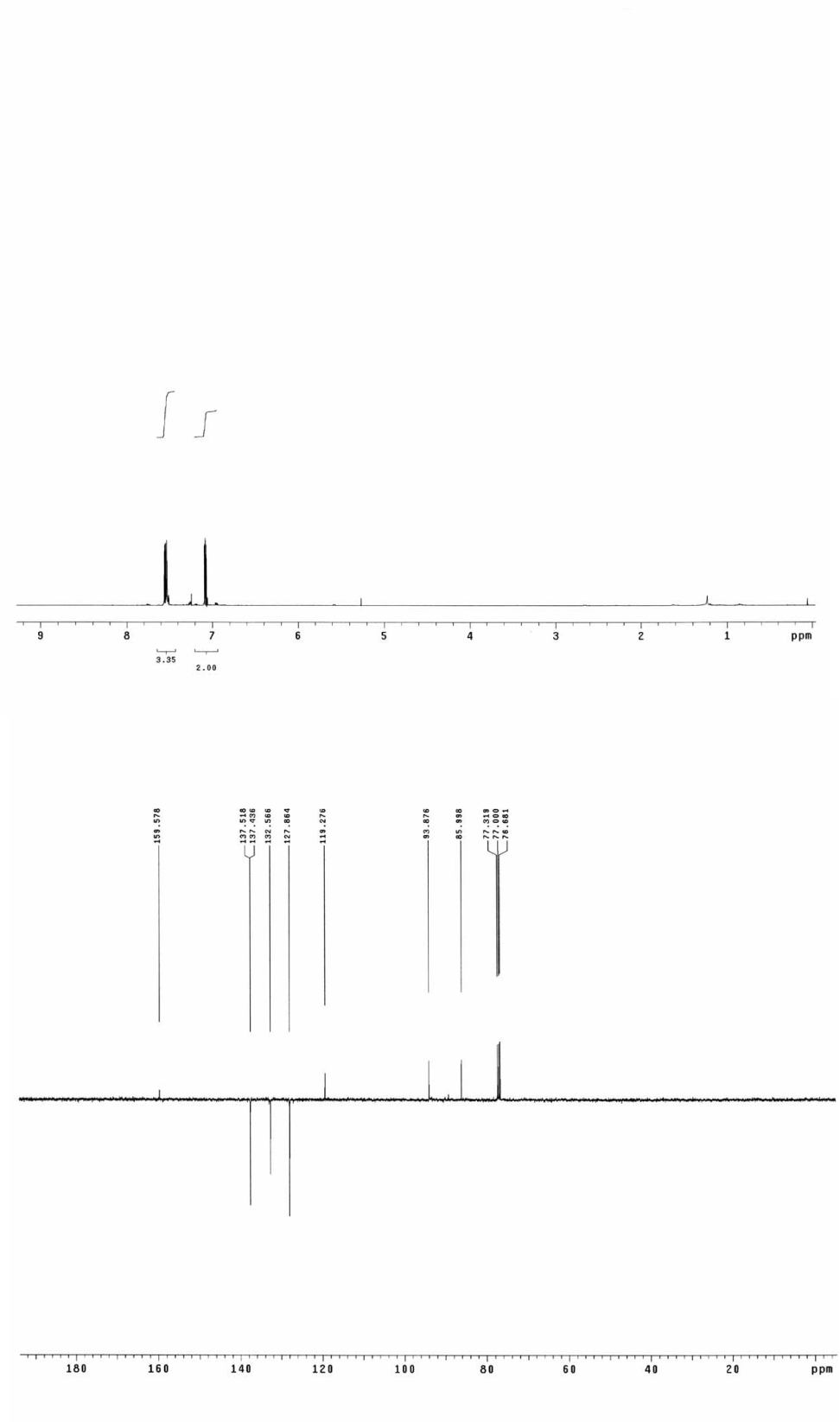


Figure S25 - ^{1}H NMR and ^{13}C NMR spectra of **6j**

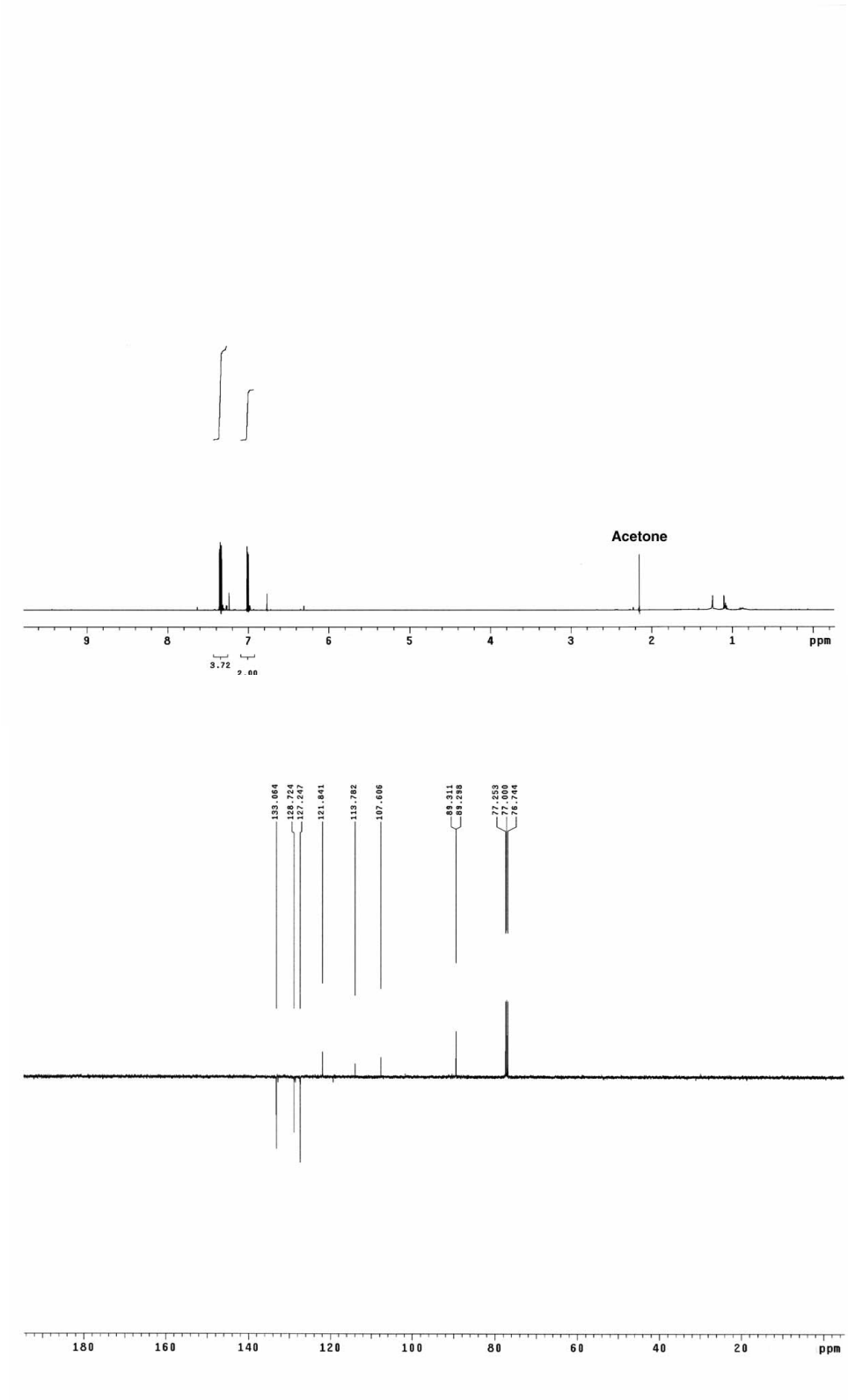


Figure S26 - ^{1}H NMR and ^{13}C NMR spectra of **7j**

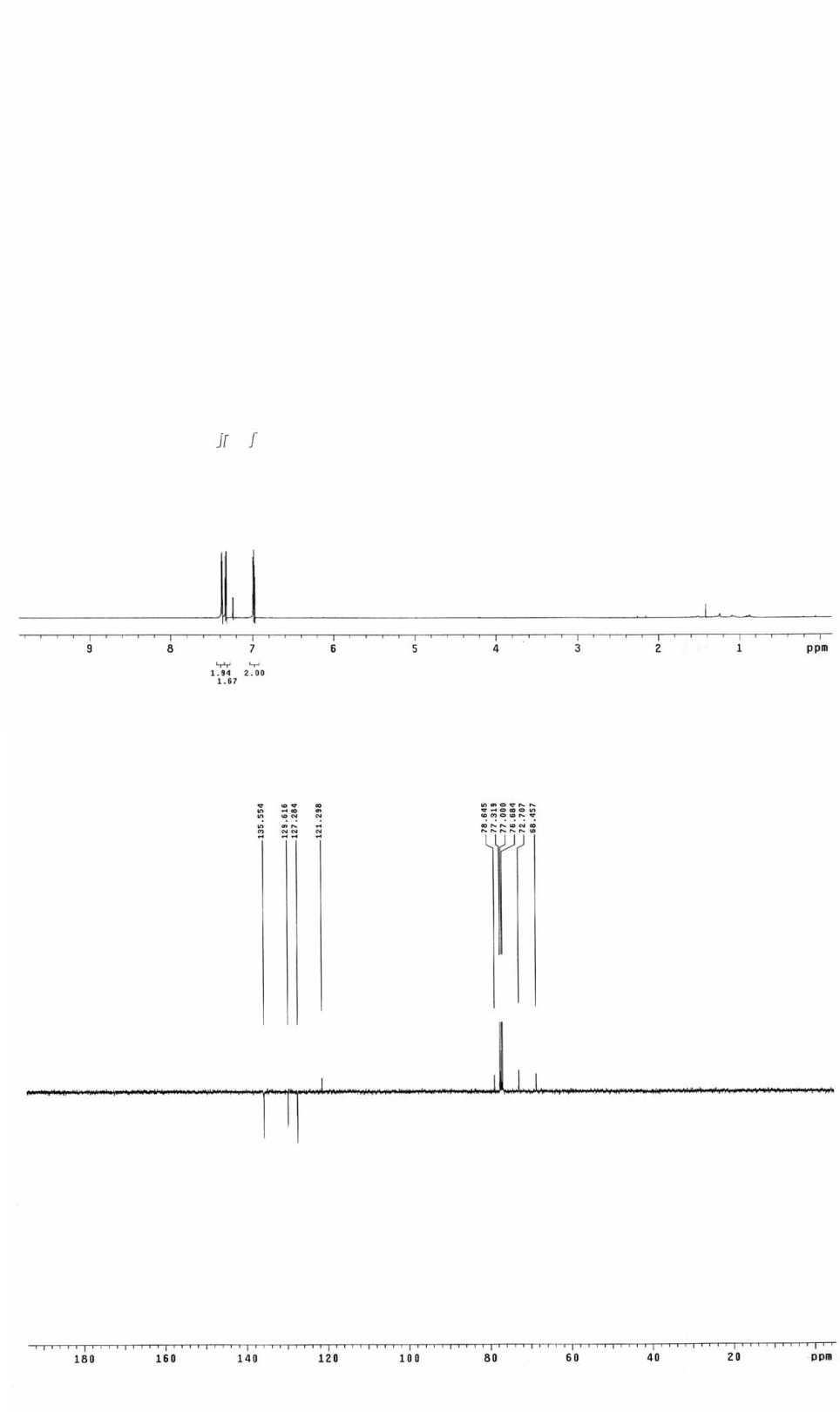


Figure S27 - ^{1}H NMR and ^{13}C NMR spectra of **4j**

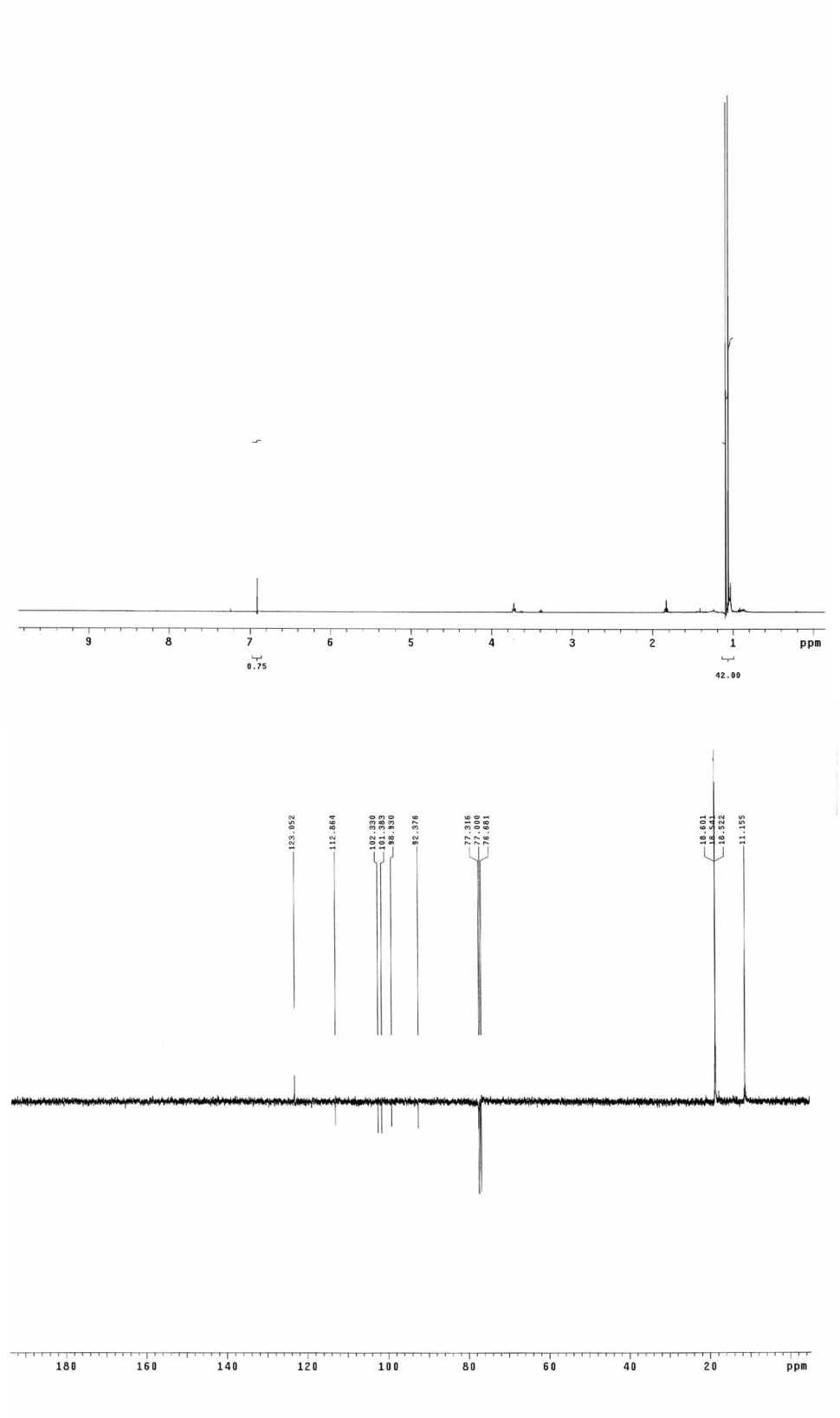


Figure S28 - ^{1}H NMR and ^{13}C NMR spectra of **10a**

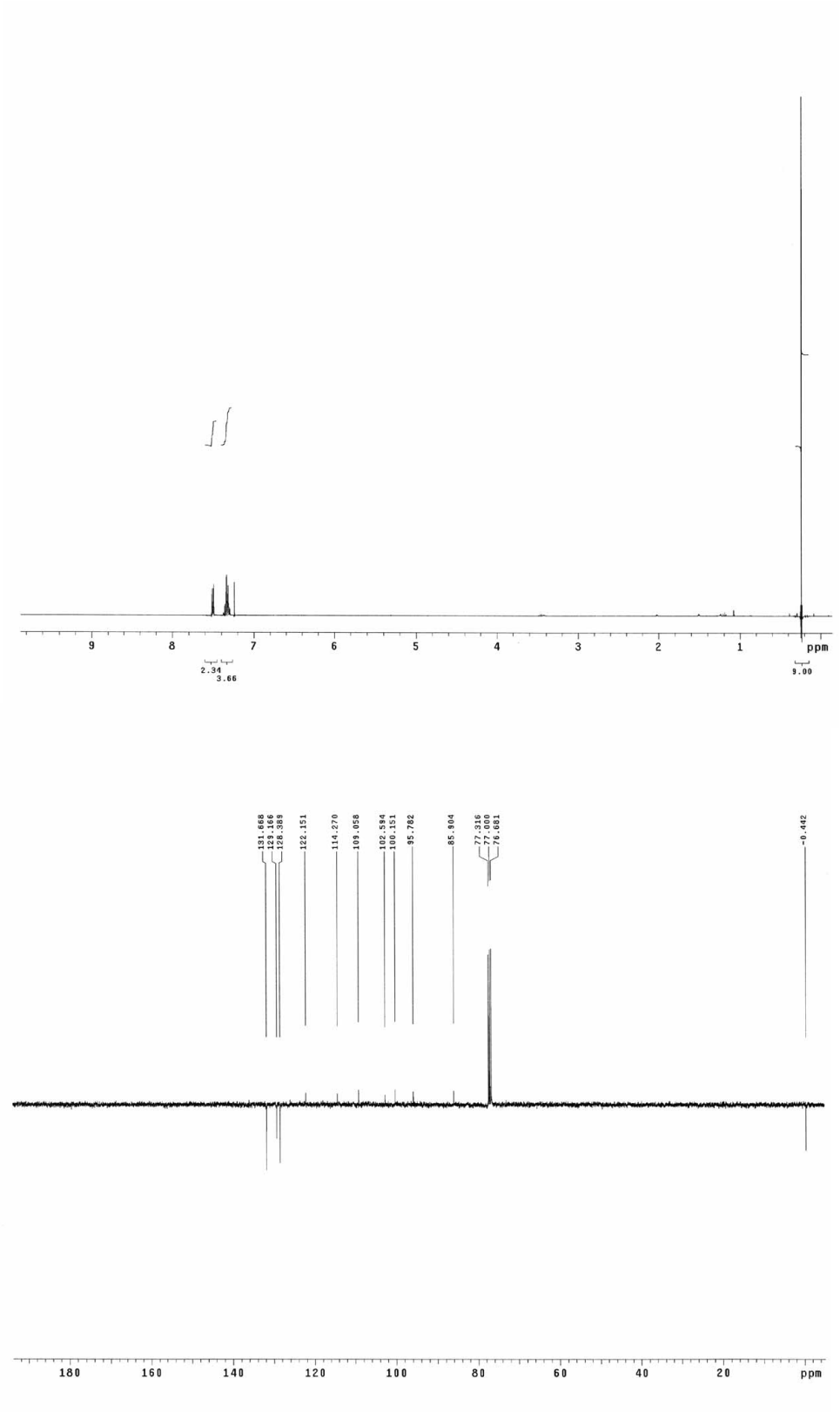


Figure S29 - ^{1}H NMR and ^{13}C NMR spectra of **13a**

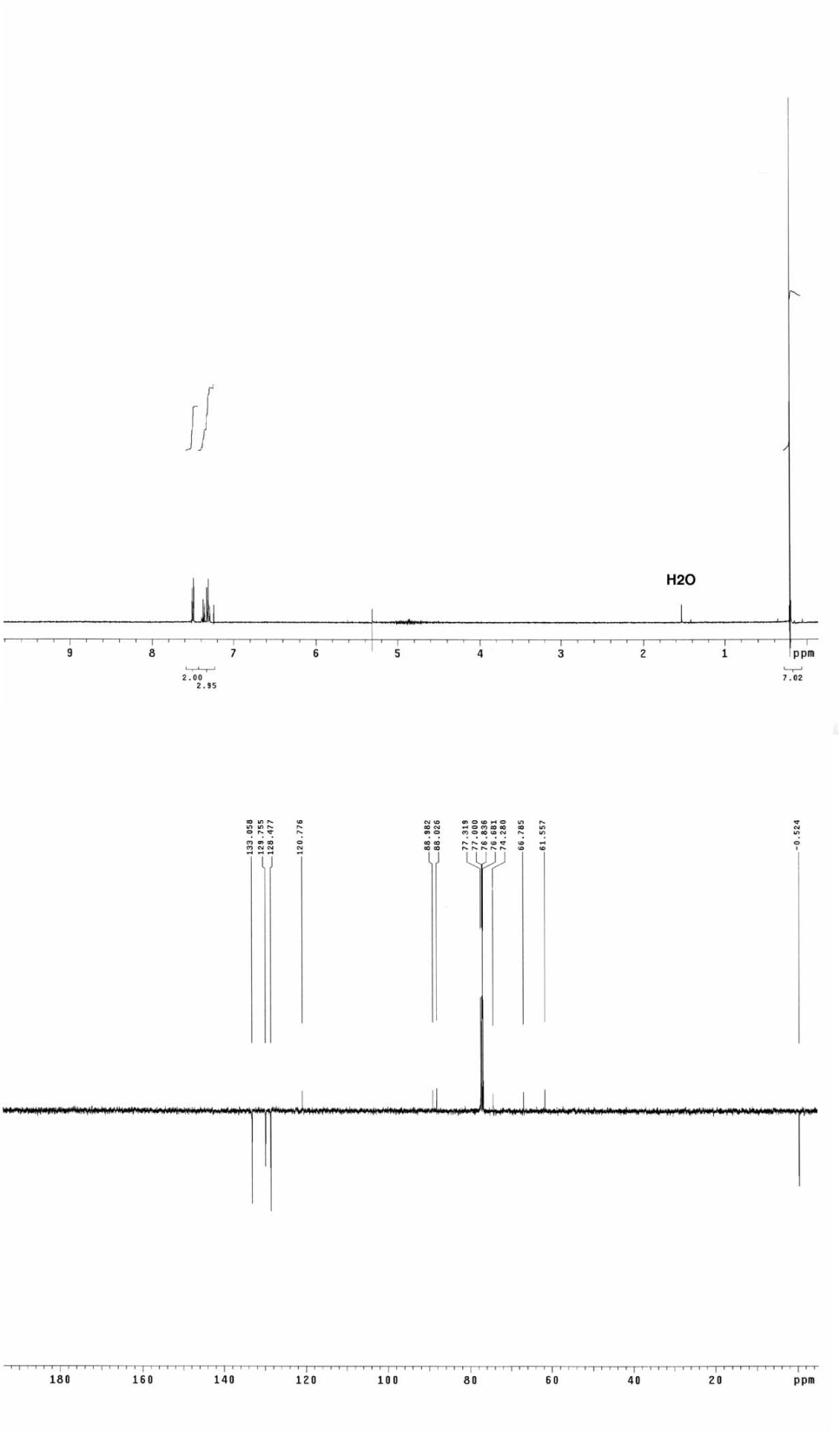


Figure S30 - ^{1}H NMR and ^{13}C NMR spectra of **14a**

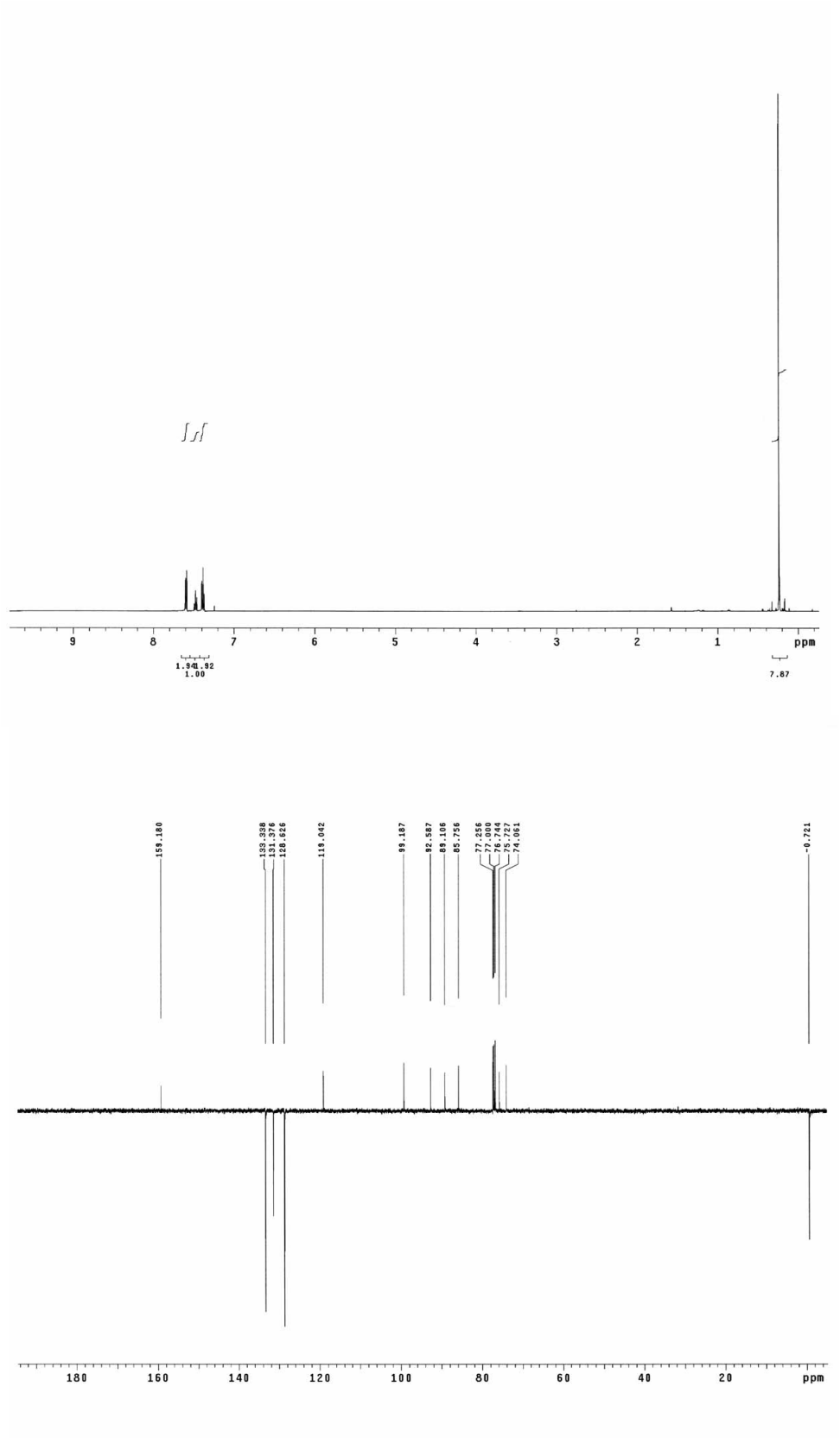


Figure S31 - ^{1}H NMR and ^{13}C NMR spectra of **12b**

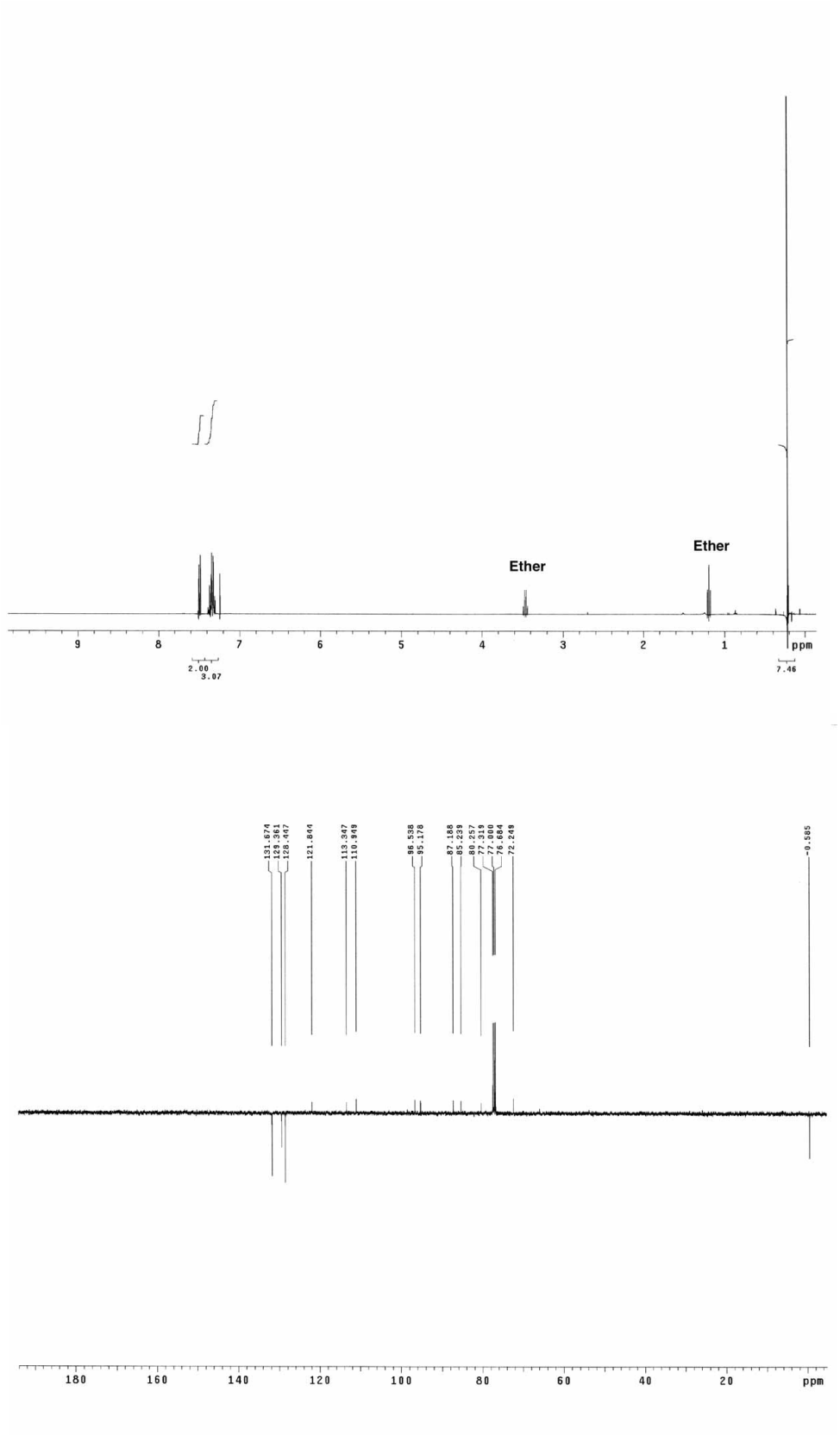


Figure S32 - ^{1}H NMR and ^{13}C NMR spectra of **13b**

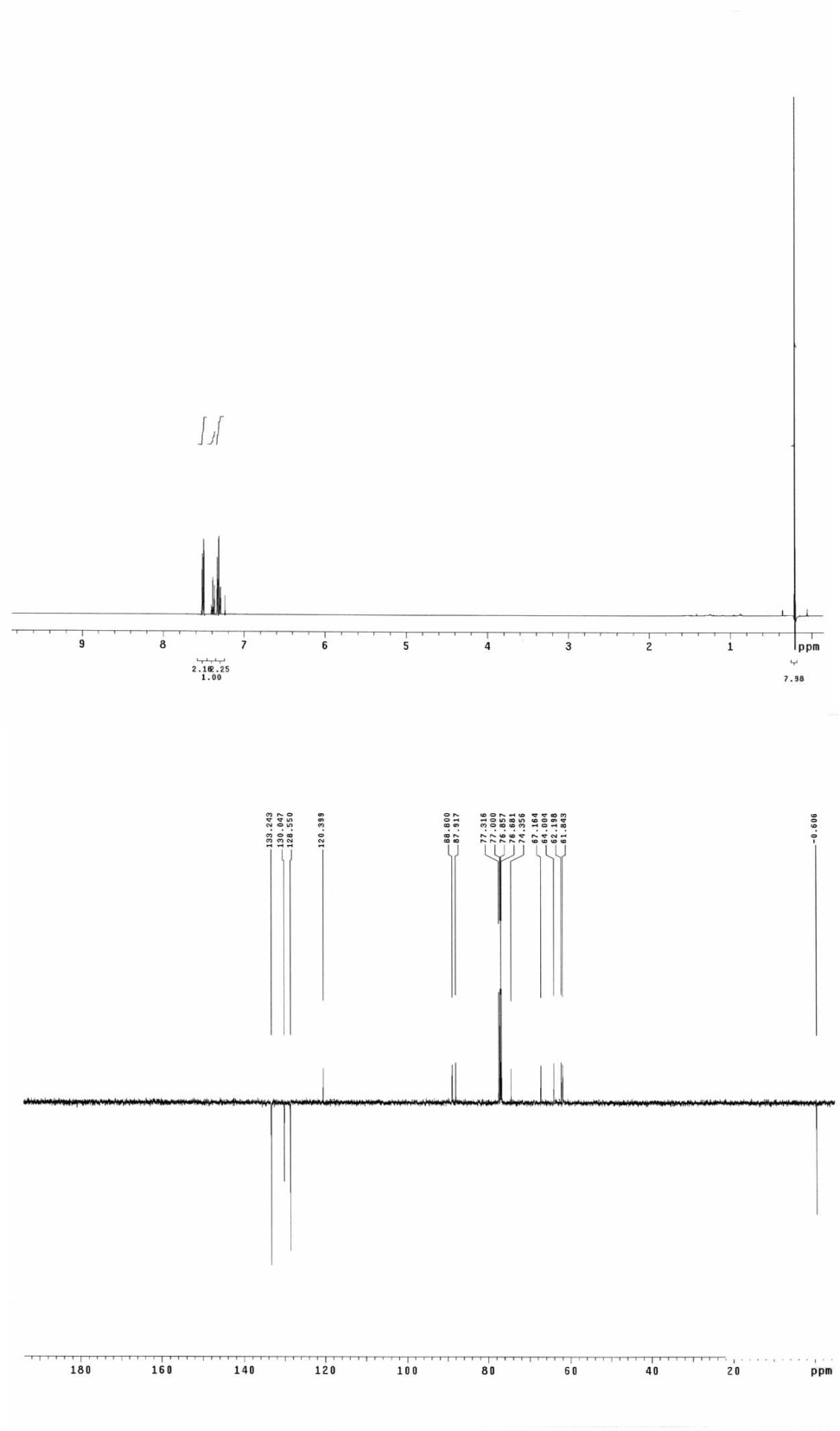


Figure S33 - ^{1}H NMR and ^{13}C NMR spectra of **14b**

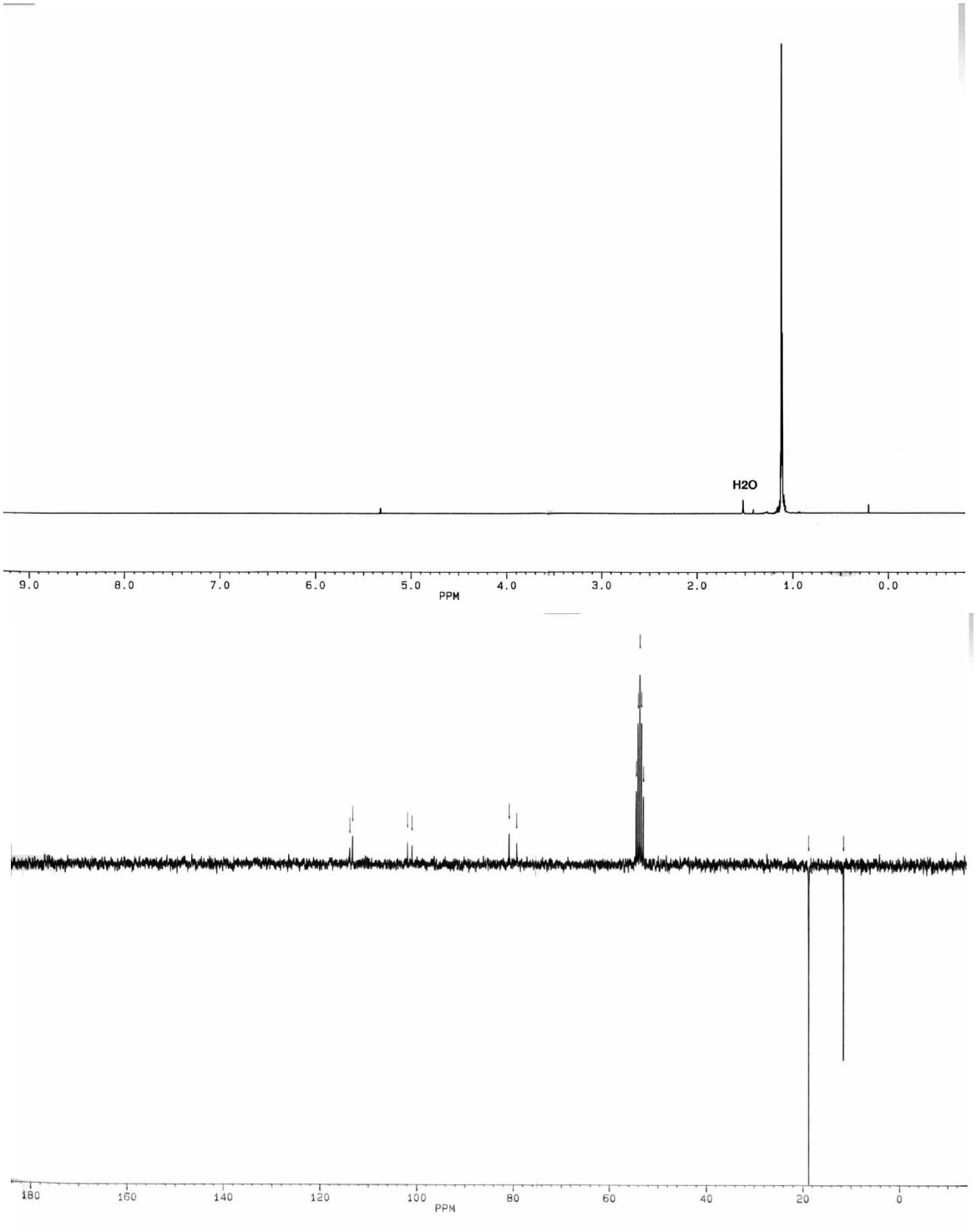


Figure S34 - ^{1}H NMR and ^{13}C NMR spectra of **15**

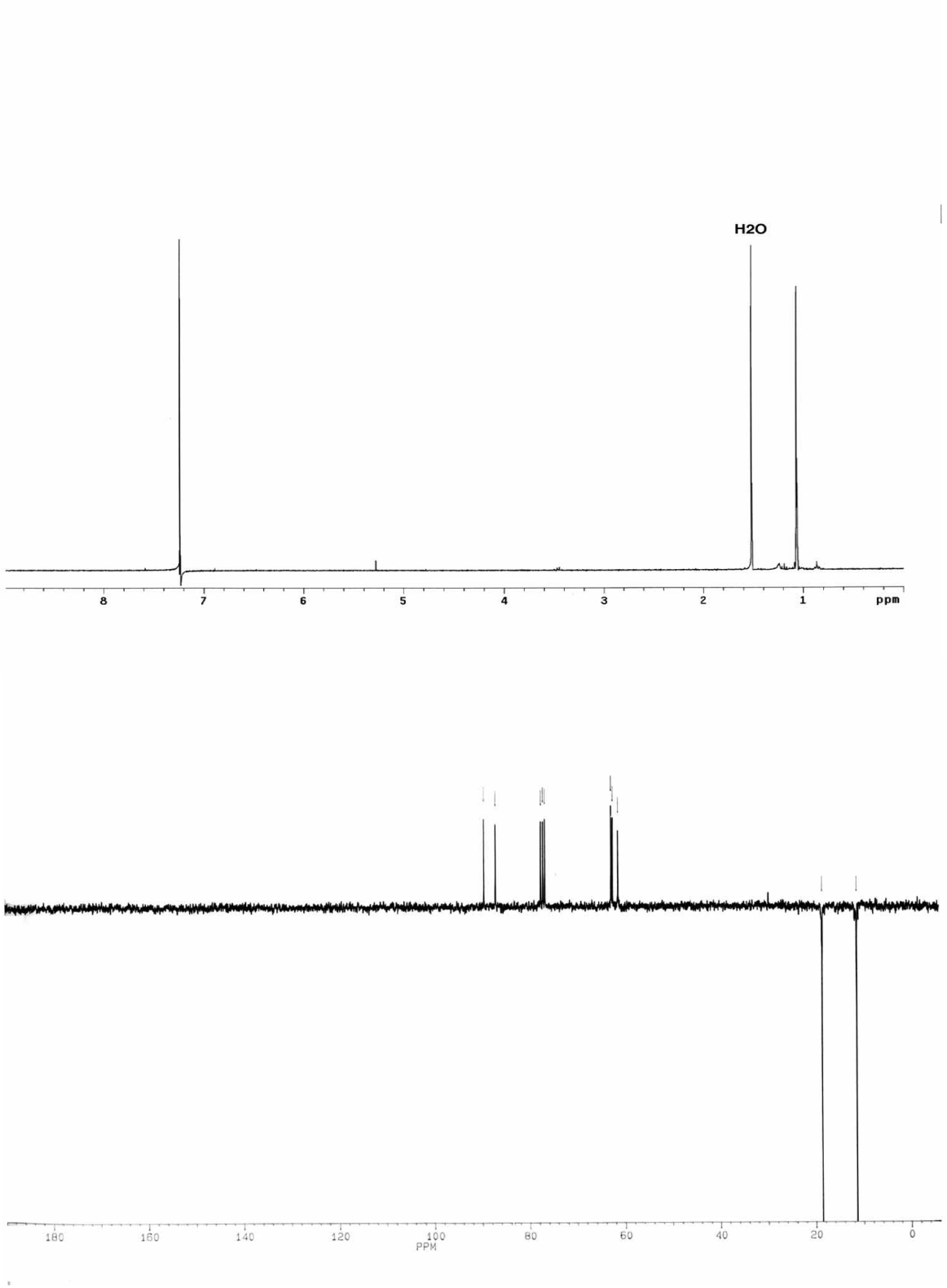


Figure S35 - ^{1}H NMR and ^{13}C NMR spectra of **16**

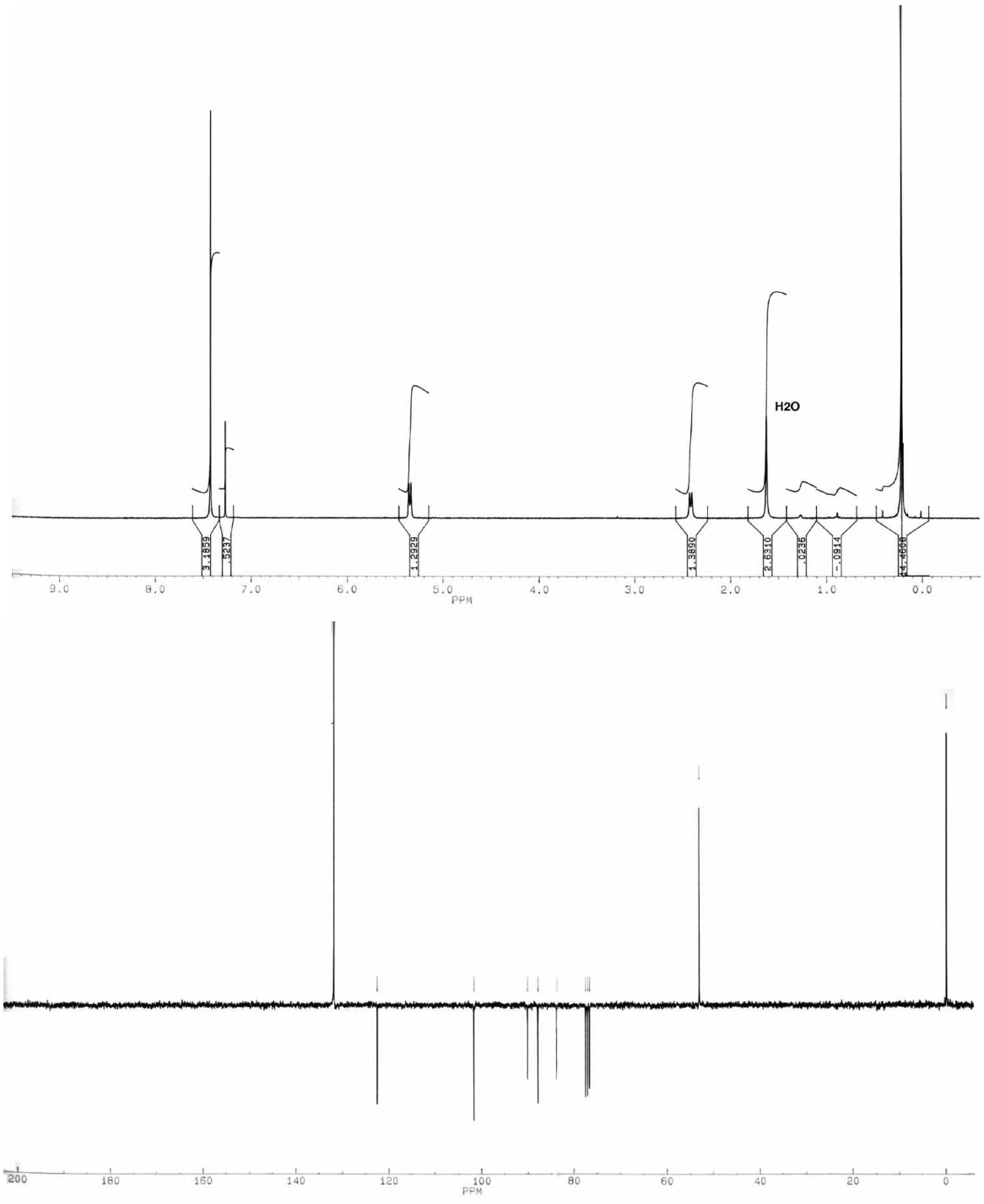


Figure S36 - ^{1}H NMR and ^{13}C NMR spectra of **17**

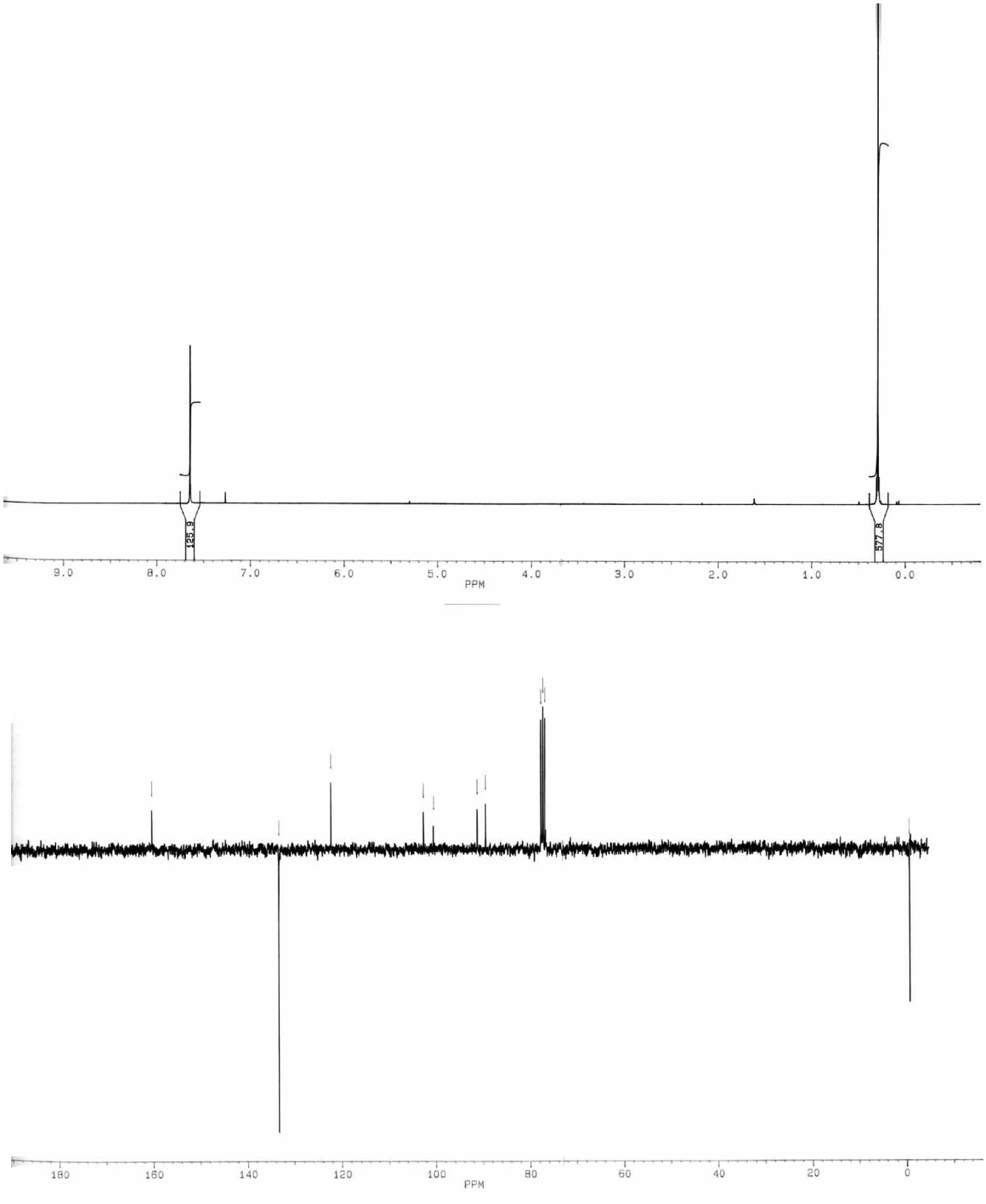


Figure S37 - ^{1}H NMR and ^{13}C NMR spectra of **18**

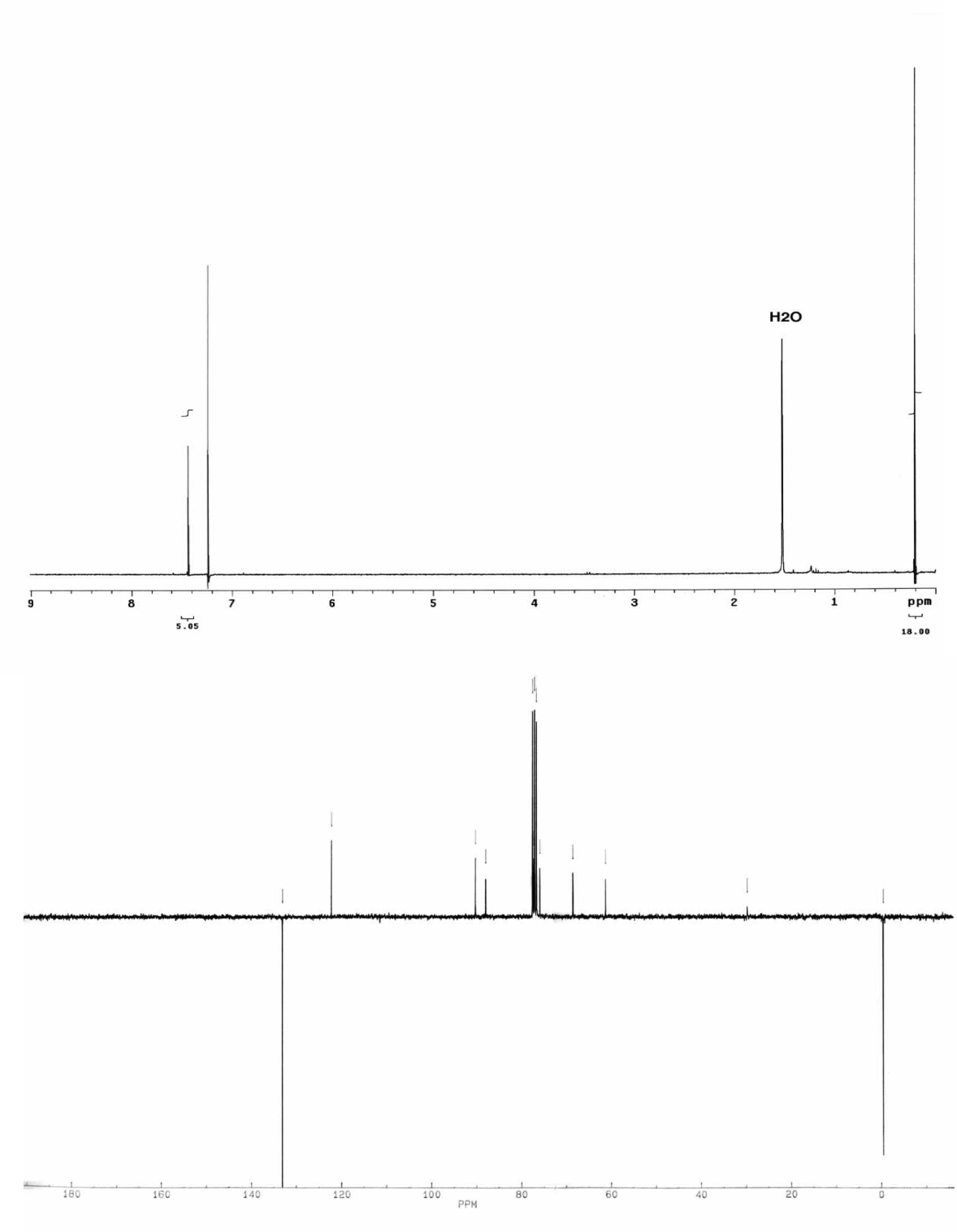


Figure S38 - ^{1}H NMR and ^{13}C NMR spectra of **20**

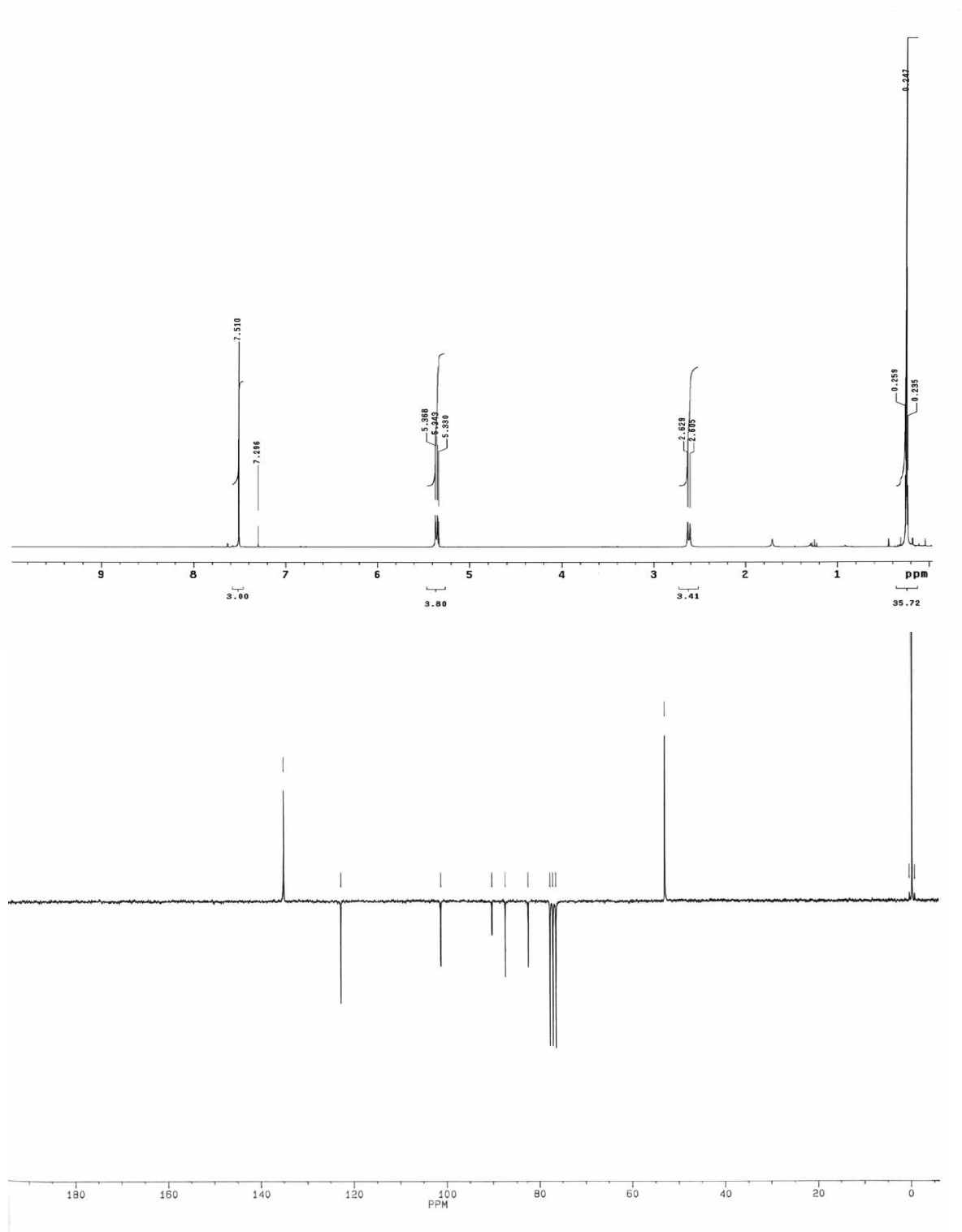


Figure S39 - ^{1}H NMR and ^{13}C NMR spectra of **21**

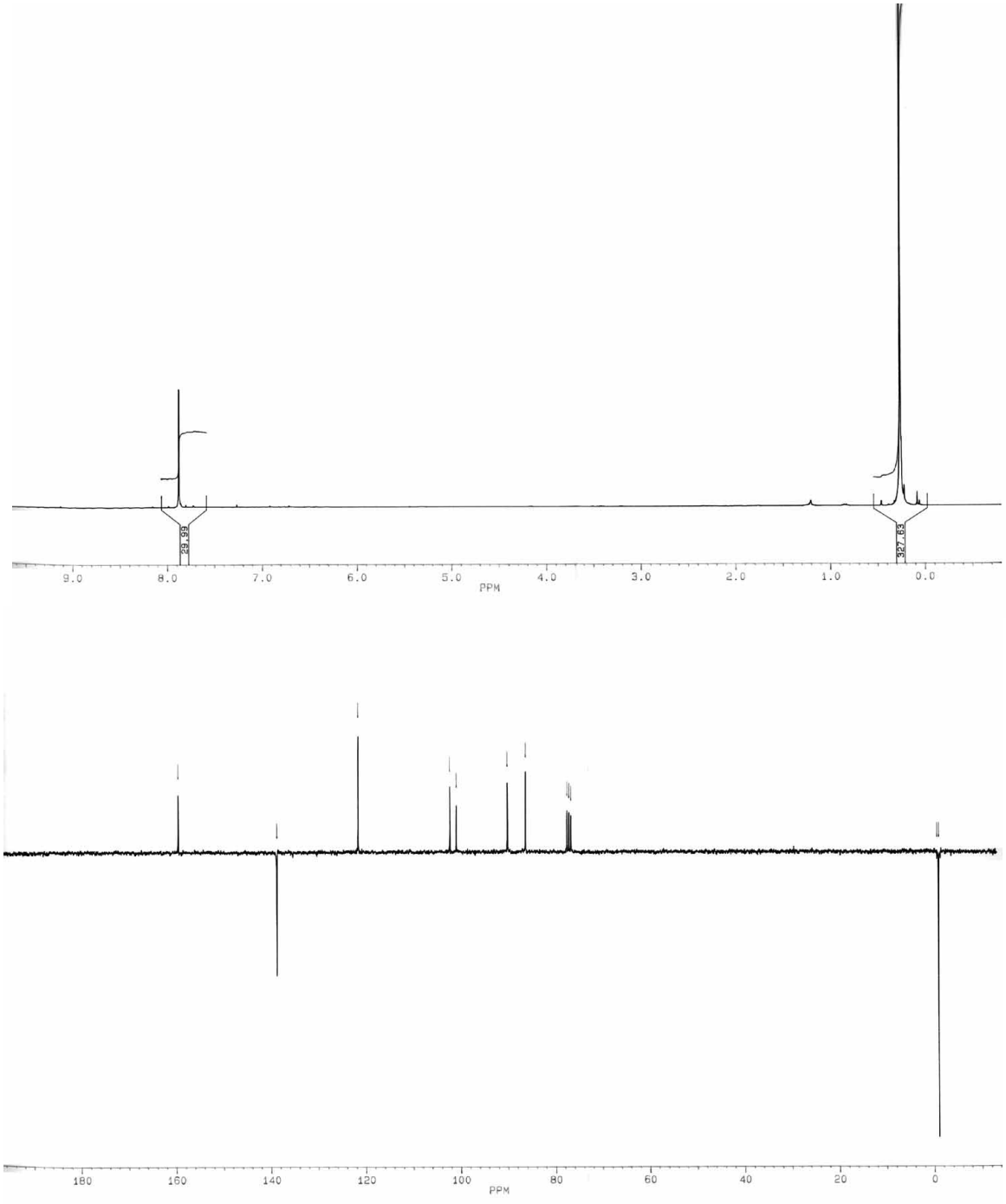


Figure S40 - ^{1}H NMR and ^{13}C NMR spectra of **22**

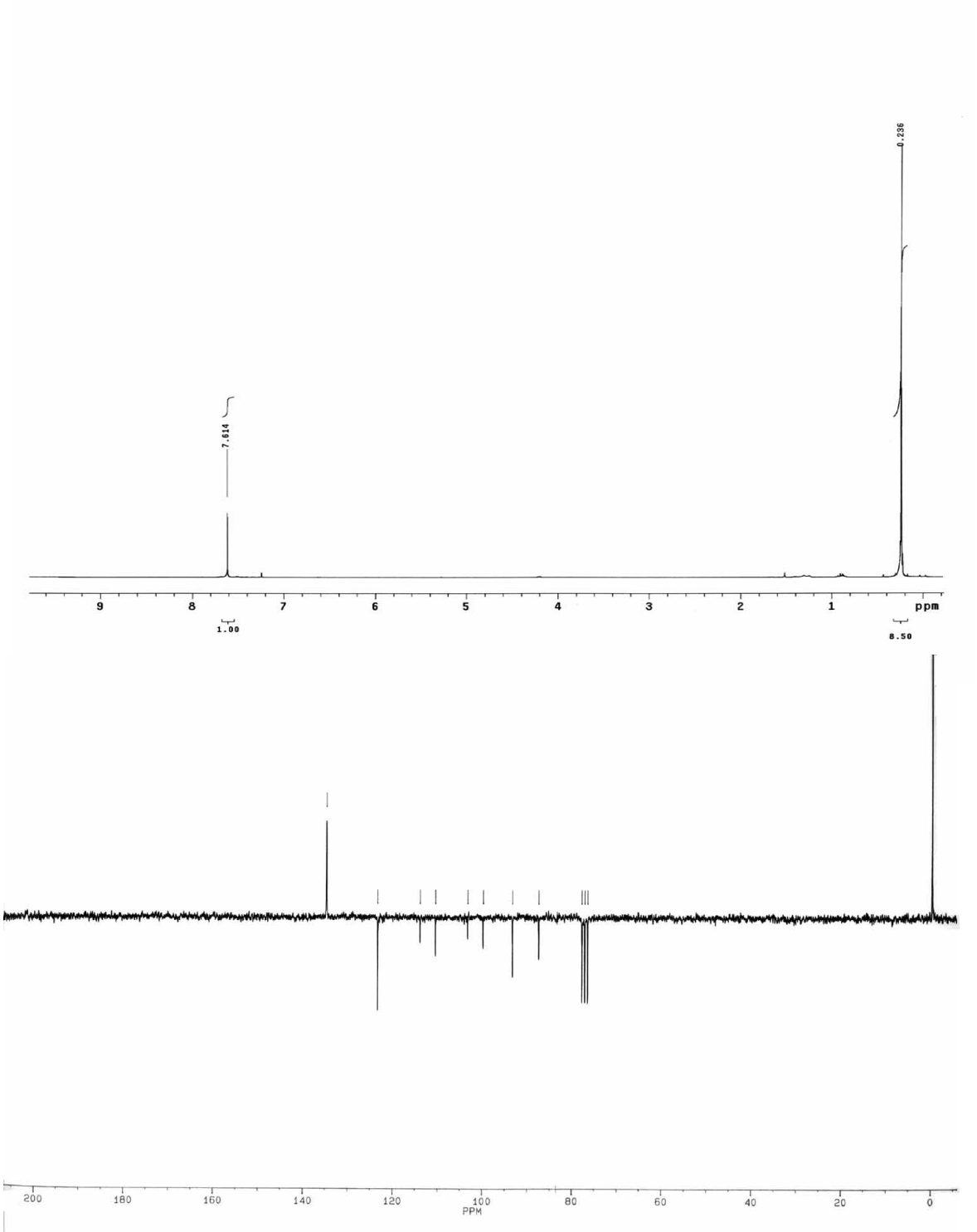


Figure S41 - ^{1}H NMR and ^{13}C NMR spectra of **23**

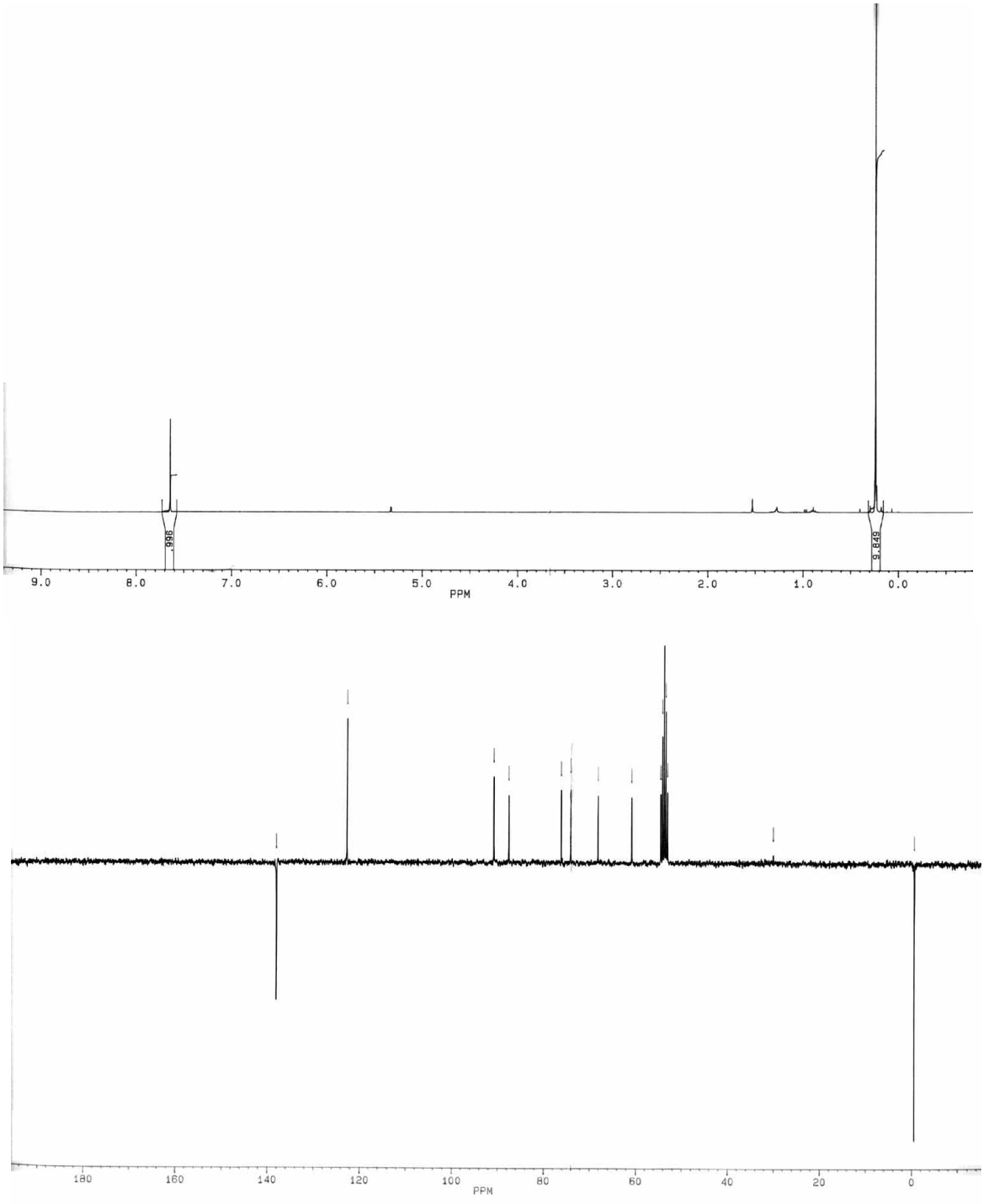


Figure S42 - ^{1}H NMR and ^{13}C NMR spectra of **24**

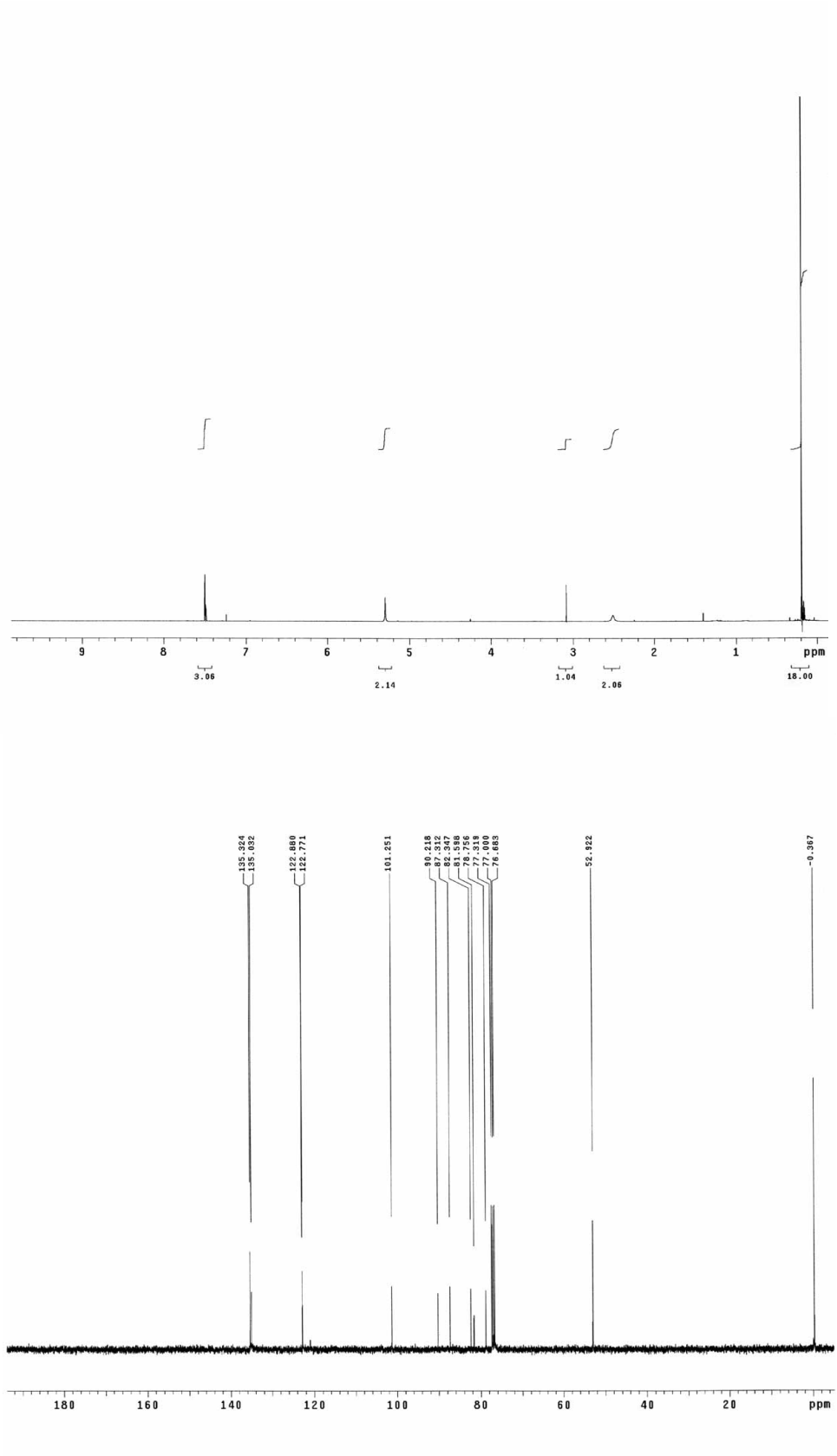


Figure S43 - ^{1}H NMR and ^{13}C NMR spectra of **25**

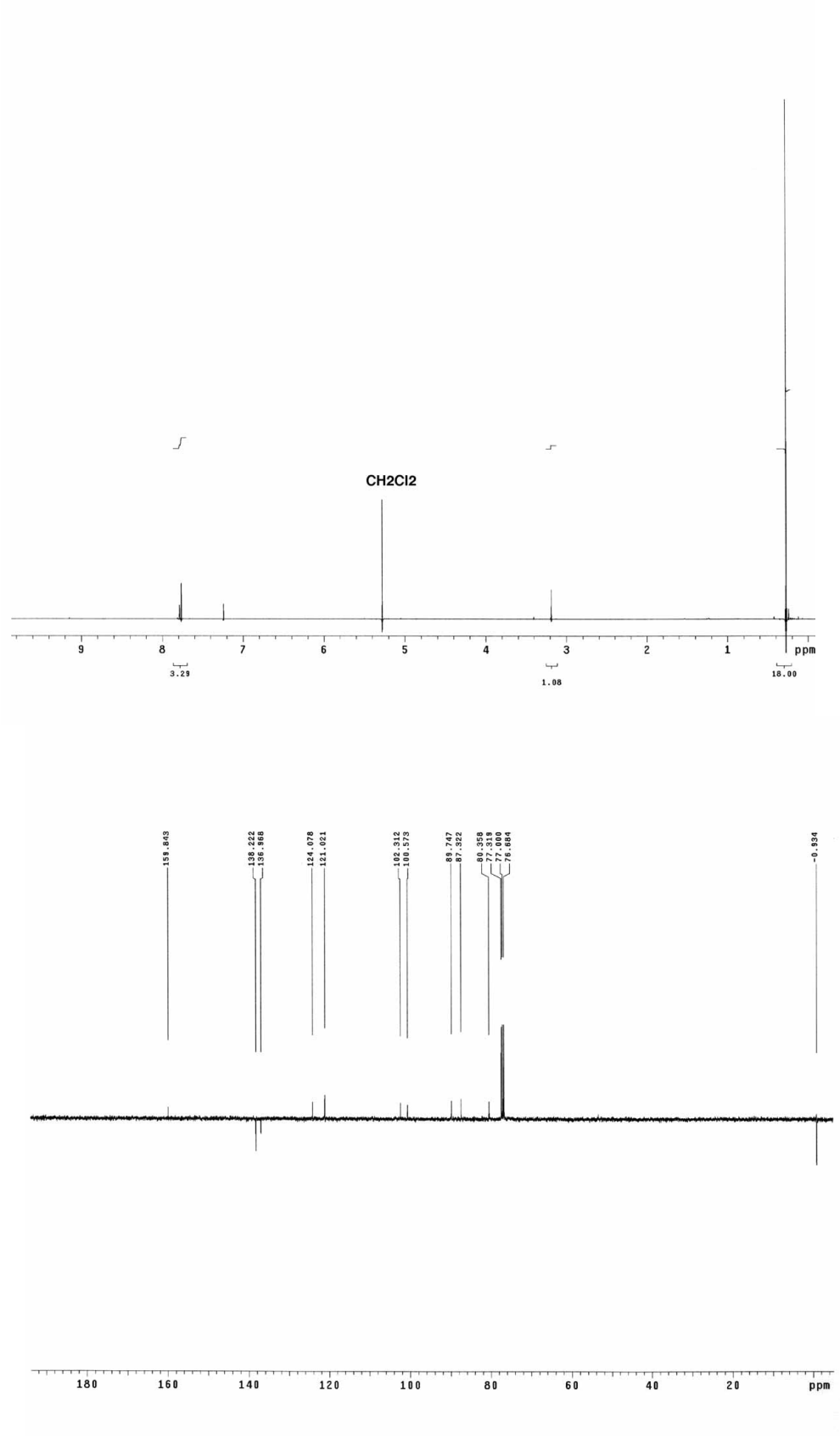


Figure S44 - ^{1}H NMR and ^{13}C NMR spectra of **26**

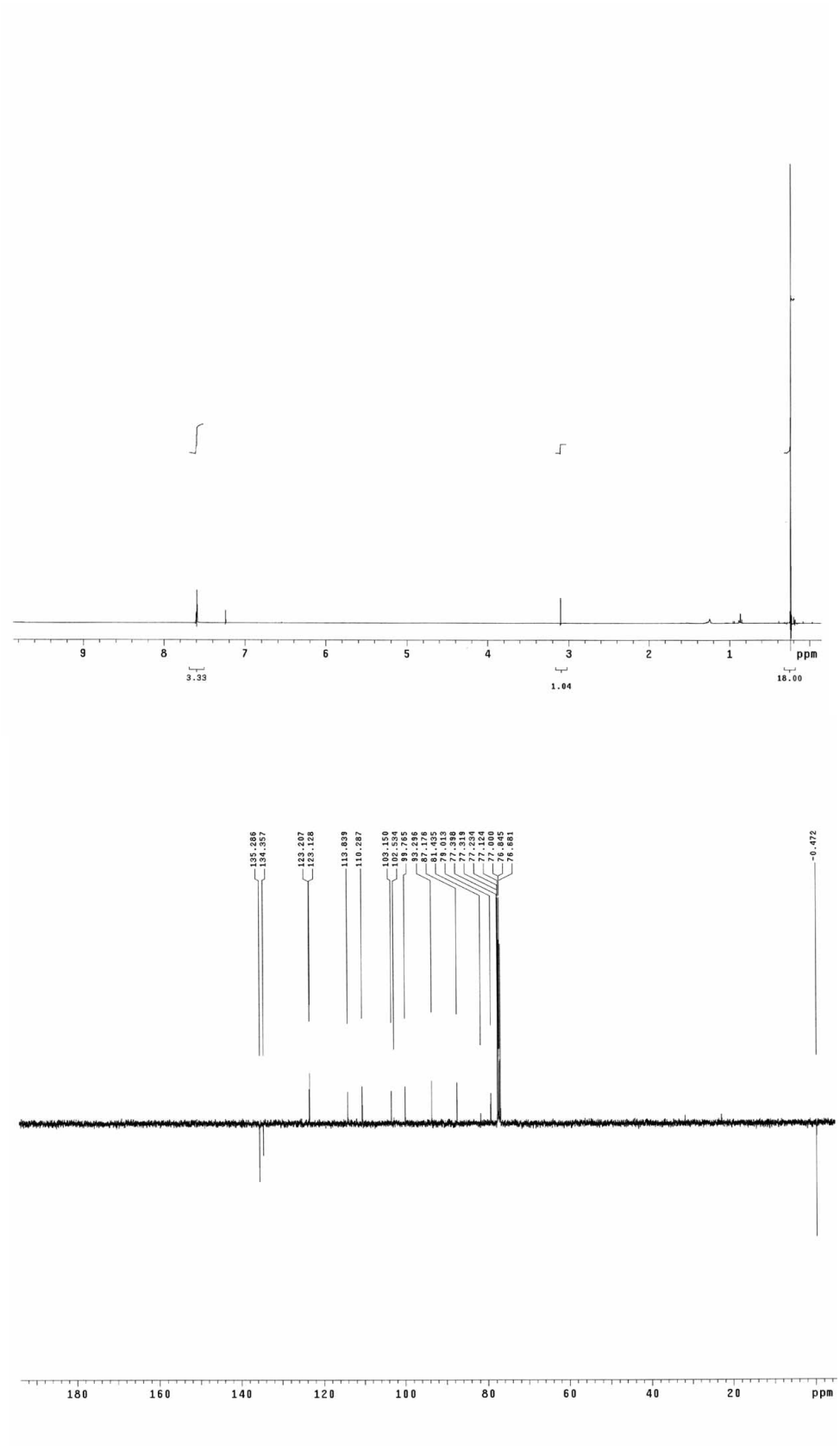


Figure S45 - ^{1}H NMR and ^{13}C NMR spectra of **27**

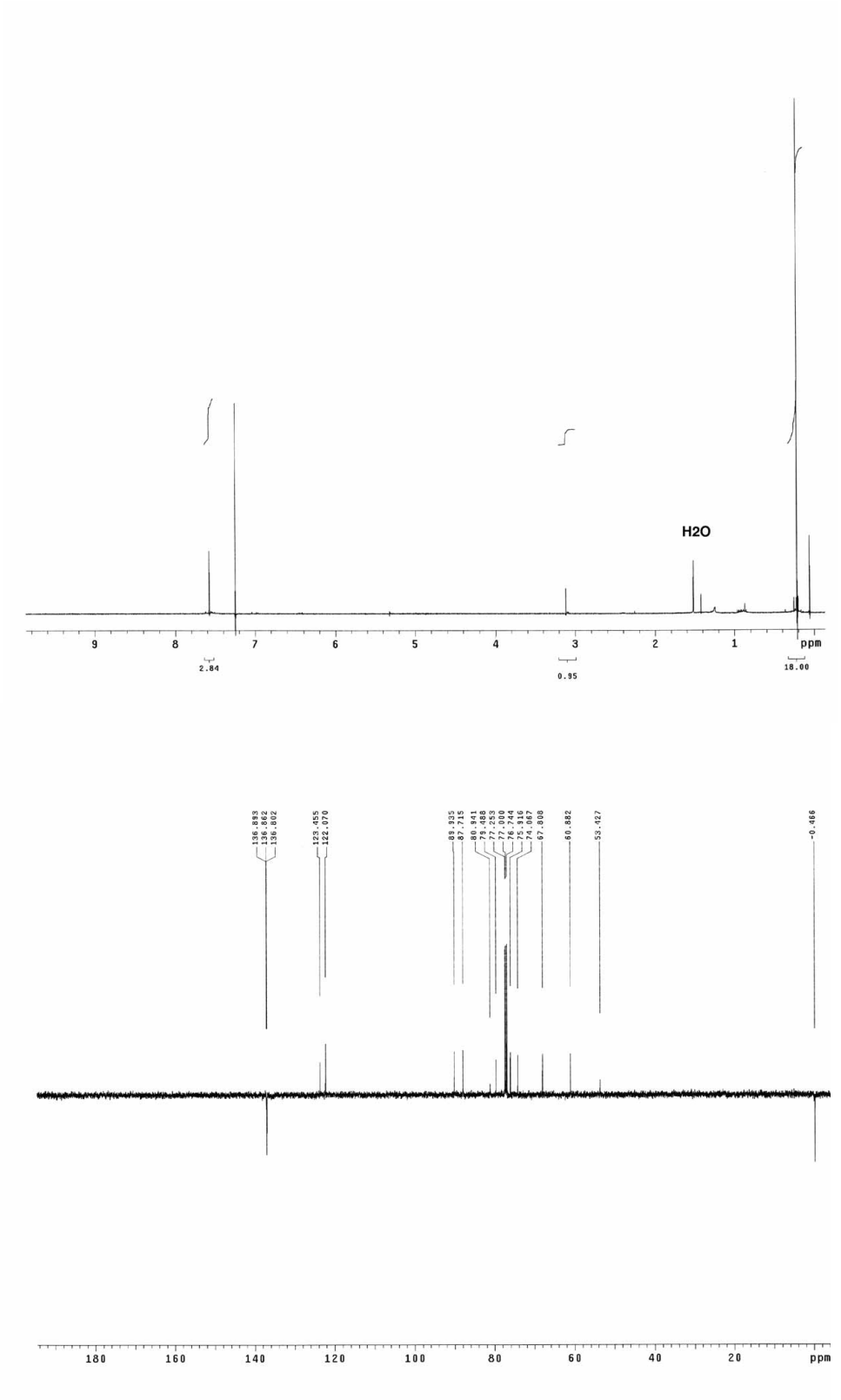


Figure S46 - ^{1}H NMR and ^{13}C NMR spectra of **28**

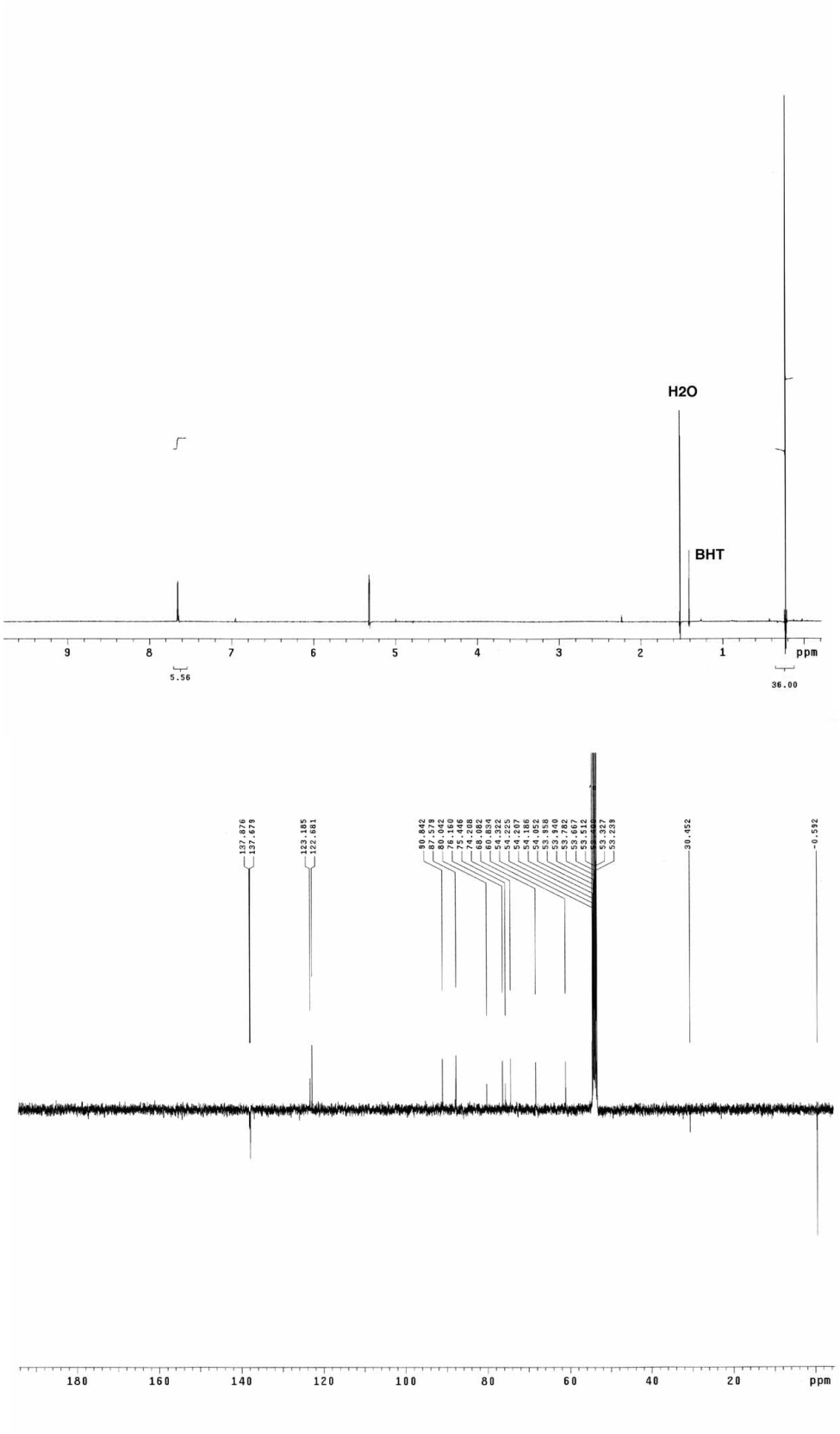


Figure S47 - ^{1}H NMR and ^{13}C NMR spectra of **29**