Supporting Information

Substituent-controlled Chemoselective Synthesis of Multi-substituted Pyridones via One-pot Three-component Cascade Reaction

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Table of Contents

EXPERIMENTAL SECTION

General Methods

All reagents were obtained from commercial suppliers and used without further purification. All compounds were characterized by full spectroscopic data. The ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance III 400MHz (^{1}H NMR: 400 MHz, ^{13}C NMR: 100 MHz) using $CDCl_3$ and DMSO-d_6 as solvent with TMS as internal standard. Chemical shifts are given in ppm (δ) referenced to $CDCl_3$ with 7.26 for ^{1}H and 76.01 for ^{13}C, DMSO-d_6 with 2.50 for ^{1}H and 39.46 for ^{13}C. Signals are abbreviated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, and coupling constants are expressed in hertz. The melting points were determined on Tech X-5 melting point apparatus and are uncorrected. IR spectra (KBr pellet) were detected by a Thermo Nicolet S10 FT-IR instrument. HRMS were performed on an Agilent LC/MSD TOF instrument.

General experimental procedure for the synthesis of Pyridone.

Cascade raction process : anilines **1** (1.2 mmol), alkyne diester **2a** (1.2 mmol), diethyl ethoxymethylenemalonate **3a** (1.0 mmol) and Cs_2CO_3 (0.5 mmol) were placed into a 5.0 mL reaction tube, closed the tube and stirred for 5 h at room temperature to make the raw materials mix well. The reaction was monitored by thin-layer chromatography (TLC) until all the substrate disappeared. The mixture was then washed with water and extracted with ethyl acetate. The mixture was purified by flash

column chromatography on silica gel (Eluent: Ethyl acetate/Petroleum ether = 1:4 (v/v)) to give the final product pyridone derivatives. All the other compounds were synthesized according to this typical procedure. The products were further identified by FTIR, NMR, HRMS and X-ray, being in good agreement with the assigned structures.

Characterization Data of Compounds 4a-4ff, 6a-6j and intermediate I, II, III, IV and 7

6-Oxo-1-phenyl-1,6-dihydro-pyridine-2,3,5-tricarboxylic acid triethyl ester (**4a**). Pale yellow solid; yield 85%; mp: 92-94 ^{o}C; ^{1}H NMR (DMSO-d_6, 400 MHz, TMS) δ 8.49 (s, 1H, CH), 7.52 (q, J = 3.2 Hz, 3H, Ph-H), 7.36-7.34 (m, 2H, Ph-H), 4.27 (q, J = 7.2 Hz, 4H, OCH_2), 3.92 (q, J = 7.2 Hz, 2H, OCH_2), 1.28-1.23 (m, 6H, CH_3), 0.85 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 163.1, 162.2, 160.1, 157.3, 148.9, 143.1, 136.1, 129.8, 128.9, 128.8, 120.6, 104.5, 62.3, 61.6, 61.0, 14.0, 13.8, 13.0; IR (KBr) (ν_{max}, cm^{-1}): 3059, 2988, 1743, 1707, 1604, 1400, 1232, 757, 699; HRMS (ESI-TOF^{+}) *m/z*: calcd for $C_{20}H_{22}NO_7^{+}$ [(M + H)$^{+}$], 388.1391; found, 388.1400.

6-Oxo-1-p-tolyl-1,6-dihydro-pyridine-2,3,5-tricarboxylic acid triethyl ester (**4b**). Pale yellow solid; yield 82%; mp: 100-102 ^{o}C; ^{1}H NMR (DMSO-d_6, 400 MHz, TMS) δ 8.47 (s, 1H, CH), 7.32 (d, J = 8.4 Hz, 2H, Ph-H), 7.22 (d, J = 8.4 Hz, 2H, Ph-H), 4.26 (q, J = 7.2 Hz, 4H, OCH_2), 3.93 (q, J = 7.2 Hz, 2H, OCH_2), 2.36 (s, 3H, CH_3), 1.28-1.23 (m, 6H, CH_3), 0.88 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ

163.2, 162.2, 160.1, 157.4, 149.1, 143.0, 139.5, 133.5, 129.3, 128.4, 120.5, 104.4, 62.3, 61.5, 61.0, 20.7, 14.0, 13.8, 13.0; IR (KBr) (ν_{max}, cm^{-1}): 2978, 2922, 1741, 1686, 1605, 1403, 802; HRMS (ESI-TOF$^+$) *m/z*: calcd for $C_{21}H_{24}NO_7^+$ [(M + H)$^+$], 402.1547; found, 402.1570.

6-(4-Methoxy-phenyl)-5-oxo-cyclohexa-1,3-diene-1,2,4-tricarboxylic acid triethyl ester (**4c**). Pale yellow solid; yield 80%; mp: 83-85 ^oC; ^1H NMR (DMSO-d_6, 400 MHz, TMS) δ 8.47 (s, 1H, CH), 7.26 (q, J = 4.4 Hz, 2H, Ph-H), 7.04 (q, J = 4.8 Hz, 2H, Ph-H), 4.26 (q, J = 7.2 Hz, 4H, OCH_2), 3.95 (q, J = 7.2 Hz, 2H, OCH_2), 3.80 (s, 3H, OCH_3), 1.28-1.23 (m, 6H, CH_3), 0.90 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 163.2, 162.2, 160.1, 159.9, 157.5, 149.4, 143.0, 130.0, 128.5, 120.4, 114.0, 104.3, 62.3, 61.5, 61.0, 55.4, 14.0, 13.9, 13.1; IR (KBr) (ν_{max}, cm^{-1}): 2977, 2929, 1743, 1705, 1607, 1463, 1241, 865; HRMS (ESI-TOF$^+$) *m/z*: calcd for $C_{21}H_{24}NO_8^+$ [(M + H)$^+$], 418.1496; found, 418.1522.

6-Oxo-1-o-tolyl-1,6-dihydro-pyridine-2,3,5-tricarboxylic acid triethyl ester (**4d**). Yellow oil; yield 83%; ^1H NMR (DMSO-d_6, 400 MHz, TMS) δ 8.53 (s, 1H, CH), 7.45-7.38 (m, 2H, Ph-H), 7.35-7.31 (m, 1H, Ph-H), 7.26 (t, J = 7.2 Hz 1H, Ph-H), 4.29-4.23 (m, 4H, OCH_2), 3.94-3.86 (m, 2H, OCH_2), 2.04 (s, 3H, CH_3), 1.27 (q, J = 6.4 Hz, 6H, CH_3), 0.83 (t, J = 6.8 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 163.1, 162.1, 160.0, 156.7, 148.8, 143.4, 136.2, 135.3, 130.5, 130.1, 128.8, 126.6, 120.5, 104.8, 62.4, 61.6, 61.1, 16.9, 14.0, 13.8, 12.9; IR (KBr) (ν_{max}, cm^{-1}): 2983, 2933, 1747, 1719, 1605, 1403, 1242, 762; HRMS (ESI-TOF$^+$) *m/z*: calcd for $C_{21}H_{24}NO_7^+$ [(M + H)$^+$], 402.1547; found, 402.1569.

6-(2-Methoxy-phenyl)-5-oxo-cyclohexa-1,3-diene-1,2,4-tricarboxylic acid triethyl ester (**4e**). Yellow oil; yield 80%; ^{1}H NMR (DMSO-d_6, 400 MHz, TMS) δ 8.50 (s, 1H, CH), 7.51 (q, J = 7.2 Hz, 1H, Ph-H), 7.28 (q, J = 6.0 Hz, 1H, Ph-H), 7.22 (d, J = 8.0 Hz, 1H, Ph-H), 7.07 (q, J = 7.2 Hz, 1H, Ph-H), 4.29-4.23 (m, 4H, OCH_2), 3.93-3.88 (m, 2H, OCH_2), 3.75 (s, 3H, OCH_3), 1.27 (q, J = 7.6 Hz, 6H, CH_3), 0.86 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 163.1, 162.1, 159.9, 156.6, 154.7, 149.6, 143.3, 131.7, 129.8, 124.5, 120.3, 120.2, 112.2, 104.6, 62.2, 61.6, 61.0, 55.8, 14.0, 13.8, 13.0; IR (KBr) (ν_{max}, cm^{-1}): 2981, 2927, 1722, 1603, 1404, 1243, 757; HRMS (ESI-TOF$^+$) *m/z*: calcd for $C_{21}H_{24}NO_8^+$ [(M + H)$^+$], 418.1496; found, 418.1520.

1-(2-Tert-Butyl-phenyl)-6-oxo-1,6-dihydro-pyridine-2,3,5-tricarboxylic acid triethyl ester (**4f**). Yellow oil; yield 75%; ^{1}H NMR (DMSO-d_6, 400 MHz, TMS) δ 8.50 (s, 1H, CH), 7.68 (q, J = 7.2 Hz, 1H, Ph-H), 7.48-7.43 (m, 1H, Ph-H), 7.30-7.26 (m, 1H, Ph-H), 7.07 (q, J = 6.4 Hz, 1H, Ph-H), 4.29-4.23 (m, 4H, OCH_2), 3.97-3.91 (m, 2H, OCH_2), 1.29-1.23 (m, 6H, CH_3), 1.20 (s, 9H, CH_3), 0.84 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 163.0, 162.1, 160.2, 158.4, 149.2, 146.6, 143.2, 132.6, 130.8, 130.2, 129.9, 126.3, 120.4, 104.7, 62.5, 61.7, 61.1, 36.4, 31.0, 14.0, 13.8, 12.9; IR (KBr) (ν_{max}, cm^{-1}): 2980, 1745, 1722, 1604, 1402, 1241, 764; HRMS (ESI-TOF$^+$) *m/z*: calcd for $C_{24}H_{30}NO_7^+$ [(M + H)$^+$], 444.2017; found, 444.2040.

6-Oxo-1-m-tolyl-1,6-dihydro-pyridine-2,3,5-tricarboxylic acid triethyl ester (**4g**). Pale yellow solid; yield 80%; mp: 102-104 ^{o}C; ^{1}H NMR (DMSO-d_6, 400 MHz, TMS) δ 8.48 (s, 1H, CH), 7.39 (t, J = 7.6 Hz, 1H, Ph-H), 7.34 (d, J = 8.0 Hz, 1H, Ph-H),

7.14 (t, J = 7.6 Hz, 2H, Ph-H), 4.26 (q, J = 7.2 Hz, 4H, OCH_2), 3.97-3.89 (m, 2H, OCH_2), 2.33 (s, 3H, CH_3), 1.28-1.23 (m, 6H, CH_3), 0.85 (t, J = 6.8 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 163.2, 162.2, 160.1, 157.3, 148.9, 143.0, 138.5, 135.9, 130.3, 129.0, 128.7, 125.7, 120.5, 104.4, 62.3, 61.6, 61.0, 20.5, 14.0, 13.8, 13.0; IR (KBr) (ν_{max}, cm^{-1}): 2986, 2925, 1744, 1708, 1605, 1404, 1233, 860, 784; HRMS (ESI-TOF$^+$) *m/z*: calcd for $C_{21}H_{24}NO_7^+$ [(M + H)$^+$], 402.1547; found, 402.1570.

1-(3-Methoxy-phenyl)-6-oxo-1,6-dihydro-pyridine-2,3,5-tricarboxylic acid triethyl ester (**4h**). Yellow oil; yield 79%; ^1H NMR (DMSO-d_6, 400 MHz, TMS) δ 8.48 (s, 1H, CH), 7.41 (t, J = 8.0 Hz, 1H, Ph-H), 7.10-7.07 (m, 1H, Ph-H), 6.99 (t, J = 2.4 Hz, 1H, Ph-H), 6.91-6.89 (m, 1H, Ph-H), 4.26 (q, J = 7.2 Hz, 4H, OCH_2), 3.98-3.92 (m, 2H, OCH_2), 3.75 (s, 3H, OCH_3), 1.26 (q, J = 5.6 Hz, 6H, CH_3), 0.88 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 163.1, 162.2, 160.1, 159.4, 157.2, 148.9, 143.0, 137.0, 129.7, 120.8, 120.5, 115.5, 114.5, 104.5, 62.3, 61.6, 61.0, 55.4, 14.0, 13.8, 13.0; IR (KBr) (ν_{max}, cm^{-1}): 2983, 1746, 1718, 1605, 1403, 1244, 864, 783; HRMS (ESI-TOF$^+$) *m/z*: calcd for $C_{21}H_{24}NO_8^+$ [(M + H)$^+$], 418.1496; found, 418.1529.

1-(2,3-Dimethyl-phenyl)-6-oxo-1,6-dihydro-pyridine-2,3,5-tricarboxylic acid triethyl ester (**4i**). Yellow oil; yield 75%; ^1H NMR (DMSO-d_6, 400 MHz, TMS) δ 8.53 (s, 1H, CH), 7.32 (d, J = 7.6 Hz, 1H, Ph-H), 7.21 (t, J = 7.6 Hz, 1H, Ph-H), 7.08 (d, J = 7.6 Hz, 1H, Ph-H), 4.29-4.23 (m, 4H, OCH_2), 3.96-3.85 (m, 2H, OCH_2), 2.29 (s, 3H, CH_3), 1.90 (s, 3H, CH_3), 1.27 (q, J = 6.8 Hz, 6H, CH_3), 0.81 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 163.1, 162.1, 159.9, 156.8, 148.9, 143.4, 137.6,

135.2, 134.7, 131.1, 126.3, 125.9, 120.3, 104.7, 62.2, 61.6, 61.0, 19.6, 14.0, 13.9, 13.8 12.9; IR (KBr) (ν_{max}, cm^{-1}): 2983, 1748, 1719, 1604, 1403, 1238, 783, 720, 672; HRMS (ESI-TOF$^+$) *m/z*: calcd for $C_{22}H_{26}NO_7^+$ [(M + H)$^+$], 416.1704; found, 416.1735.

1-(2,4-Dimethyl-phenyl)-6-oxo-1,6-dihydro-pyridine-2,3,5-tricarboxylic acid triethyl ester (**4j**). Yellow oil; yield 73%; ^{1}H NMR (DMSO-d_6, 400 MHz, TMS) δ 8.52 (s, 1H, CH), 7.19 (s, 1H, Ph-H), 7.14-7.09 (m, 2H, Ph-H), 4.28-4.23 (m, 4H, OCH_2), 3.95-3.87 (m, 2H, OCH_2), 2.32 (s, 3H, CH_3), 1.99 (s, 3H, CH_3), 1.27 (q, J = 6.4 Hz, 6H, CH_3), 0.87 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 163.1, 162.1, 160.0, 156.7, 149.0, 143.3, 139.7, 135.7, 132.8, 131.0, 128.5, 127.0, 120.4, 104.7, 62.3, 61.6, 61.0, 20.6, 16.8, 14.0, 13.8, 12.9; IR (KBr) (ν_{max}, cm^{-1}): 2983, 1748, 1719, 1610, 1403, 1242, 863, 802; HRMS (ESI-TOF$^+$) *m/z*: calcd for $C_{22}H_{26}NO_7^+$ [(M + H)$^+$], 416.1704; found, 416.1738.

1-(2,5-Dimethyl-phenyl)-6-oxo-1,6-dihydro-pyridine-2,3,5-tricarboxylic acid triethyl ester (**4k**). Yellow oil; yield 76%; ^{1}H NMR (DMSO-d_6, 400 MHz, TMS) δ 8.52 (s, 1H, CH), 7.27-7.22 (m, 2H, Ph-H), 7.06 (s, 1H, Ph-H), 4.27 (q, J = 7.2 Hz, 4H, OCH_2), 3.95-3.90 (m, 2H, OCH_2), 2.28 (s, 3H, CH_3), 1.98 (s, 3H, CH_3), 1.27 (q, J = 6.4 Hz, 6H, CH_3), 0.84 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 163.1, 162.1, 160.0, 156.6, 148.8, 143.3, 136.0, 135.1, 132.9, 130.6, 130.3, 129.0, 120.4, 104.7, 62.3, 61.6, 61.0, 20.1, 16.5, 14.0, 13.8, 12.9; IR (KBr) (ν_{max}, cm^{-1}): 2982, 2927, 1748, 1720, 1604, 1403, 1240, 862; HRMS (ESI-TOF$^+$) *m/z*: calcd for $C_{22}H_{26}NO_7^+$ [(M + H)$^+$], 416.1704; found, 416.1752.

1-(2,6-Dimethyl-phenyl)-6-oxo-1,6-dihydro-pyridine-2,3,5-tricarboxylic acid triethyl ester (**4l**). Yellow oil; yield 65%; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 8.80 (s, 1H, CH), 7.23 (d, J = 7.6 Hz, 1H, Ph-H), 7.12 (d, J = 7.6 Hz, 2H, Ph-H), 4.41-4.30 (m, 4H, OCH_2), 3.99 (q, J = 7.2 Hz, 2H, OCH_2), 2.11 (s, 6H, CH_3), 1.39-1.33 (m, 6H, CH_3), 0.95 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.0, 161.7, 159.5, 156.2, 148.6, 143.8, 135.4, 134.0, 128.9, 127.4, 119.8, 105.0, 61.7, 60.8, 60.7, 16.8, 13.2, 13.1, 12.2; IR (KBr) (ν_{max}, cm^{-1}): 2982, 2931, 1739, 1611, 1471, 1272, 777; HRMS (ESI-TOF$^+$) *m/z*: calcd for $C_{22}H_{26}NO_7^+$ [(M + H)$^+$], 416.1704; found, 416.1734.

1-(3,5-Dimethyl-phenyl)-6-oxo-1,6-dihydro-pyridine-2,3,5-tricarboxylic acid triethyl ester (**4m**). Pale yellow solid; yield 76%; mp: 128-130 ^{o}C; ^{1}H NMR (DMSO-d_6, 400 MHz, TMS) δ 8.47 (s, 1H, CH), 7.15 (s, 1H, Ph-H), 6.94 (s, 2H, Ph-H), 4.26 (q, J = 7.2 Hz, 4H, OCH_2), 3.96 (q, J = 7.2 Hz, 2H, OCH_2), 2.29 (s, 6H, CH_3), 1.28-1.23 (m, 6H, CH_3), 0.87 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 163.2, 162.2, 160.1, 157.2, 148.9, 143.0, 138.3, 135.8, 130.9, 126.1, 120.5, 104.4, 62.2, 61.6, 61.0, 20.5, 14.0, 13.8, 13.0; IR (KBr) (ν_{max}, cm^{-1}): 2987, 2920, 1745, 1709, 1610, 1403, 1227, 862; HRMS (ESI-TOF$^+$) *m/z*: calcd for $C_{22}H_{26}NO_7^+$ [(M + H)$^+$], 416.1704; found, 416.1734.

1-(3,4-Dimethyl-phenyl)-6-oxo-1,6-dihydro-pyridine-2,3,5-tricarboxylic acid triethyl ester (**4n**). Pale yellow solid; yield 73%; mp: 114-115 ^{o}C; ^{1}H NMR (DMSO-d_6, 400 MHz, TMS) δ 8.47 (s, 1H, CH), 7.27 (d, J = 8.0 Hz, 1H, Ph-H), 7.10 (d, J = 2.0 Hz, 1H, Ph-H), 7.03 (q, J = 5.6 Hz, 1H, Ph-H), 4.26 (q, J = 6.8 Hz, 4H, OCH_2), 3.98-3.89

(m, 2H, OCH_2), 2.26 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 1.28-1.23 (m, 6H, CH_3), 0.88 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 163.2, 162.2, 160.1, 157.3, 149.1, 142.9, 138.1, 137.1, 133.6, 129.7, 129.2, 125.8, 120.5, 104.4, 62.2, 61.5, 61.0, 19.1, 19.0, 14.0, 13.8, 13.0; IR (KBr) (ν_{max}, cm^{-1}): 2985, 1742, 1710, 1607, 1404, 1235, 801, 716; HRMS (ESI-TOF$^+$) *m/z*: calcd for $C_{22}H_{26}NO_7^+$ [(M + H)$^+$], 416.1704; found, 416.1742.

6-Oxo-1-(2,4,6-trimethyl-phenyl)-1,6-dihydro-pyridine-2,3,5-tricarboxylic acid triethyl ester (**4o**). White solid; yield 66%; mp: 131-132 ^{o}C; ^{1}H NMR (DMSO-d_6, 400 MHz, TMS) δ 8.56 (s, 1H, CH), 7.02 (s, 2H, Ph-H), 4.29-4.23 (m, 4H, OCH_2), 3.93 (q, J = 6.8 Hz, 2H, OCH_2), 2.28 (s, 3H, CH_3), 1.96 (s, 6H, CH_3), 1.27 (q, J = 7.2 Hz, 6H, CH_3), 0.86 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 163.0, 162.0, 159.8, 156.3, 148.9, 143.6, 139.4, 135.5, 132.2, 128.8, 120.5, 105.2, 62.4, 61.7, 61.1, 20.5, 17.1, 14.0, 13.8, 12.9; IR (KBr) (ν_{max}, cm^{-1}): 2984, 2932, 1747, 1720, 1606, 1404, 1218, 868; HRMS (ESI-TOF$^+$) *m/z*: calcd for $C_{23}H_{28}NO_7^+$ [(M + H)$^+$], 430.1860; found, 430.1879.

6-Oxo-1-(3,4,5-trimethyl-phenyl)-1,6-dihydro-pyridine-2,3,5-tricarboxylic acid triethyl ester (**4p**). Pale yellow solid; yield 75%; mp: 147-148 ^{o}C; ^{1}H NMR (DMSO-d_6, 400 MHz, TMS) δ 8.46 (s, 1H, CH), 6.94 (s, 2H, Ph-H), 4.26 (q, J = 6.8 Hz, 4H, OCH_2), 3.96 (q, J = 7.2 Hz, 2H, OCH_2), 2.25 (s, 6H, CH_3), 2.16 (s, 3H, CH_3), 1.28-1.23 (m, 6H, CH_3), 0.88 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 163.2, 162.2, 160.1, 157.3, 149.1, 142.9, 136.8, 136.6, 132.8, 127.0, 120.5, 104.3, 62.2, 61.5, 61.0, 19.9, 14.9, 14.0, 13.8, 13.0; IR (KBr) (ν_{max}, cm^{-1}): 2986, 2910, 1743,

1709, 1605, 1405, 1231, 781; HRMS (ESI-TOF$^+$) *m/z*: calcd for $C_{23}H_{28}NO_7^+$ [(M + H)$^+$], 430.1860; found, 430.1871.

1-Naphthalen-1-yl-6-oxo-1,6-dihydro-pyridine-2,3,5-tricarboxylic acid triethyl ester (**4q**). Drak green oil; yield 70%; ^{1}H NMR (DMSO-d_6, 400 MHz, TMS) δ 8.64 (s, 1H, CH), 8.13 (d, J = 8.0 Hz, 1H, Ph-H), 8.06 (t, J = 7.2 Hz, 1H, Ph-H), 7.65-7.55 (m, 4H, Ph-H), 7.52 (d, J = 8.0 Hz, 1H, Ph-H), 4.30-4.25 (m, 4H, OCH_2), 3.72-3.66 (m, 2H, OCH_2), 1.27 (q, J = 6.8 Hz, 6H, CH_3), 0.41 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 163.1, 162.2, 159.9, 157.3, 149.5, 143.7, 133.4, 132.8, 130.4, 129.5, 128.1, 127.4, 127.4, 126.7, 125.1, 122.5, 120.5, 105.1, 62.0, 61.6, 61.0, 14.0, 13.8, 12.5; IR (KBr) (ν_{max}, cm^{-1}): 3063, 2980, 1748, 1706, 1601, 1405, 1243, 796, 773; HRMS (ESI-TOF$^+$) *m/z*: calcd for $C_{24}H_{24}NO_7^+$ [(M + H)$^+$], 438.1547; found, 438.1592.

1-Naphthalen-2-yl-6-oxo-1,6-dihydro-pyridine-2,3,5-tricarboxylic acid triethyl ester (**4r**). Drak green oil; yield 72%; ^{1}H NMR (DMSO-d_6, 400 MHz, TMS) δ 8.54 (s, 1H, CH), 8.04-7.93 (m, 4H, Ph-H), 7.65-7.57 (m, 2H, Ph-H), 7.44 (q, J = 6.4 Hz, 1H, Ph-H), 4.28-4.23 (m, 4H, OCH_2), 3.85-3.77 (m, 2H, OCH_2), 1.25 (q, J = 6.8 Hz, 6H, CH_3), 0.66 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 163.2, 162.2, 160.1, 157.6, 149.0, 143.2, 133.7, 132.8, 132.3, 128.7, 128.0, 127.6, 127.6, 127.0, 126.0, 120.6, 104.8, 62.3, 61.7, 61.1, 13.9, 13.8, 12.8; IR (KBr) (ν_{max}, cm^{-1}): 2923, 2853, 1738, 1721, 1633, 1403, 1247, 605; HRMS (ESI-TOF$^+$) *m/z*: calcd for $C_{24}H_{24}NO_7^+$ [(M + H)$^+$], 438.1547; found, 438.1582.

1-(4-Fluoro-phenyl)-6-oxo-1,6-dihydro-pyridine-2,3,5-tricarboxylic acid triethyl ester (**4s**). Pale yellow solid; yield 79%; mp: 113-114 ^{o}C; ^{1}H NMR (DMSO-d_6, 400 MHz, TMS) δ 8.48 (s, 1H, CH), 7.47-7.43 (m, 2H, Ph-H), 7.40 (q, J = 6.0 Hz, 2H, Ph-H), 4.29-4.23 (m, 4H, OCH_2), 3.96 (q, J = 7.2 Hz, 2H, OCH_2), 1.28-1.23 (m, 6H, CH_3), 0.90 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 163.1, 162.2, 160.1, 157.4, 148.9, 143.1, 132.3, 132.2, 131.3, 131.2, 120.6, 116.0, 115.8, 104.6, 62.5, 61.6, 61.0, 14.0, 13.9, 13.0; IR (KBr) (ν_{max}, cm^{-1}): 3076, 2991, 1740, 1604, 1403, 1240, 850; HRMS (ESI-TOF^{+}) *m/z*: calcd for $C_{20}H_{21}FNO_7^{+}$ [(M + H)$^{+}$], 406.1297; found, 406.1366.

1-(4-Chloro-phenyl)-6-oxo-1,6-dihydro-pyridine-2,3,5-tricarboxylic acid triethyl ester (**4t**). White solid; yield 78%; mp: 106-108 ^{o}C; ^{1}H NMR (DMSO-d_6, 400 MHz, TMS) δ 8.48 (s, 1H, CH), 7.63 (d, J = 8.8 Hz, 2H, Ph-H), 7.44 (d, J = 8.8 Hz, 2H, Ph-H), 4.29-4.23 (m, 4H, OCH_2), 3.97 (q, J = 7.2 Hz, 2H, OCH_2), 1.28-1.23 (m, 6H, CH_3), 0.90 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 163.1, 162.1, 160.1, 157.2, 148.7, 143.1, 135.0, 134.5, 130.8, 129.1, 120.6, 104.7, 62.5, 61.6, 61.0, 14.0, 13.9, 13.0; IR (KBr) (ν_{max}, cm^{-1}): 3071, 2986, 1740, 1715, 1608, 1405, 1238, 857; HRMS (ESI-TOF^{+}) *m/z*: calcd for $C_{20}H_{21}ClNO_7^{+}$ [(M + H)$^{+}$], 422.1001; found, 422.1026.

1-(4-Bromo-phenyl)-6-oxo-1,6-dihydro-pyridine-2,3,5-tricarboxylic acid triethyl ester (**4u**). Pale yellow solid; yield 80%; mp: 110-111 ^{o}C; ^{1}H NMR (DMSO-d_6, 400 MHz, TMS) δ 8.48 (s, 1H, CH), 7.76 (d, J = 8.8 Hz, 2H, Ph-H), 7.37 (d, J = 8.8 Hz, 2H, Ph-H), 4.29-4.23 (m, 4H, OCH_2), 3.98 (q, J = 7.2 Hz, 2H, OCH_2), 1.28-1.23 (m,

6H, CH_3), 0.91 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 163.1, 162.1, 160.1, 157.2, 148.6, 143.1, 135.4, 132.0, 131.0, 123.2, 120.6, 104.7, 62.5, 61.6, 61.0, 14.0, 13.9, 13.0; IR (KBr) (ν_{max}, cm^{-1}): 3093, 2985, 1742, 1711, 1540, 1405, 1240, 857; HRMS (ESI-TOF$^+$) *m/z*: calcd for $C_{20}H_{21}BrNO_7^+$ [(M + H)$^+$], 466.0496; found, 466.0493.

1-(4-Iodo-phenyl)-6-oxo-1,6-dihydro-pyridine-2,3,5-tricarboxylic acid triethyl ester (**4v**). Pale yellow solid; yield 80%; mp: 128-129 ^{o}C; ^{1}H NMR (DMSO-d_6, 400 MHz, TMS) δ 8.47 (s, 1H, CH), 7.91 (d, J = 8.8 Hz, 2H, Ph-H), 7.19 (d, J = 8.4 Hz, 2H, Ph-H), 4.27 (q, J = 7.2Hz, 4H, OCH_2), 3.97 (q, J = 7.2 Hz, 2H, OCH_2), 1.28-1.23 (m, 6H, CH_3), 0.90 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 163.1, 162.1, 160.1, 157.1, 148.6, 143.1, 137.9, 135.9, 130.9, 120.6, 104.7, 96.5, 62.5, 61.6, 61.0, 14.0, 13.8, 13.0; IR (KBr) (ν_{max}, cm^{-1}): 3088, 2985, 1742, 1710, 1606, 1406, 1270, 858; HRMS (ESI-TOF$^+$) *m/z*: calcd for $C_{20}H_{21}INO_7^+$ [(M + H)$^+$], 514.0357; found, 514.0380.

6-Oxo-1-(4-trifluoromethyl-phenyl)-1,6-dihydro-pyridine-2,3,5-tricarboxylic acid triethyl ester (**4w**). White solid; yield 68%; mp: 164-166 ^{o}C; ^{1}H NMR (DMSO-d_6, 400 MHz, TMS) δ 8.50 (s, 1H, CH), 7.95 (d, J = 8.4 Hz, 2H, Ph-H), 7.68 (d, J = 8.0 Hz, 2H, Ph-H), 4.29-4.24 (m, 4H, OCH_2), 3.95 (q, J = 6.8 Hz, 2H, OCH_2), 1.28-1.24 (m, 6H, CH_3), 0.83 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 163.0, 162.1, 160.0, 157.2, 148.3, 143.2, 139.8, 130.1, 126.2, 120.8, 105.0, 62.6, 61.7, 61.1, 14.0, 13.8, 12.8; IR (KBr) (ν_{max}, cm^{-1}): 3081, 2988, 1742, 1610, 1404, 1245, 851;

HRMS (ESI-TOF$^+$) *m/z*: calcd for $C_{21}H_{21}F_3NO_7^+$ [(M + H)$^+$], 456.1265; found, 456.1296.

1-(4-Cyano-phenyl)-6-oxo-1,6-dihydro-pyridine-2,3,5-tricarboxylic acid triethyl ester (**4x**). Yellow oil; yield 54%; ^{1}H NMR (DMSO-d_6, 400 MHz, TMS) δ 8.49 (s, 1H, CH), 8.06 (d, J = 8.8 Hz, 2H, Ph-H), 7.66 (d, J = 8.4 Hz, 2H, Ph-H), 4.30-4.24 (m, 4H, OCH_2), 3.96 (q, J = 7.2 Hz, 2H, OCH_2), 1.28-1.24 (m, 6H, CH_3), 0.89 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 163.0, 162.1, 160.0, 157.1, 148.1, 143.2, 140.3, 133.2, 130.3, 120.9, 117.8, 112.8, 105.1, 62.7, 61.7, 61.1, 13.9, 13.8, 13.0; IR (KBr) (ν_{max}, cm^{-1}): 2985, 2228, 1740, 1689, 1600, 1424, 1260, 856; HRMS (ESI-TOF$^+$) *m/z*: calcd for $C_{21}H_{21}N_2O_7^+$ [(M + H)$^+$], 413.1343; found, 413.1374.

1-(3,4-Dichloro-phenyl)-6-oxo-1,6-dihydro-pyridine-2,3,5-tricarboxylic acid triethyl ester (**4y**). White solid; yield 70%; mp: 142-144 ^{o}C; ^{1}H NMR (DMSO-d_6, 400 MHz, TMS) δ 8.48 (s, 1H, CH), 7.88 (q, J = 10.0 Hz, 2H, Ph-H), 7.47 (q, J = 6.0 Hz, 1H, Ph-H), 4.29-4.23 (m, 4H, OCH_2), 4.06-3.96 (m 2H, OCH_2), 1.28-1.23 (m, 6H, CH_3), 0.92 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 163.0, 162.1, 160.0, 157.1, 148.4, 143.2, 135.9, 132.9, 131.4, 131.2, 130.9, 129.4, 120.8, 104.9, 62.6, 61.7, 61.1, 14.0, 13.8, 13.0; IR (KBr) (ν_{max}, cm^{-1}): 2988, 1741, 1709, 1605, 1404, 1233, 801, 781; HRMS (ESI-TOF$^+$) *m/z*: calcd for $C_{20}H_{20}Cl_2NO_7^+$ [(M + H)$^+$], 456.0611; found, 456.0605.

1-(3-Bromo-phenyl)-6-oxo-1,6-dihydro-pyridine-2,3,5-tricarboxylic acid triethyl ester (**4aa**). White solid; yield 75%; mp: 107-108 ^{o}C; ^{1}H NMR (DMSO-d_6, 400 MHz, TMS) δ 8.48 (s, 1H, CH), 7.74 (t, J = 1.2 Hz, 2H, Ph-H), 7.49 (t, J = 8.0 Hz, 1H, Ph-H), 7.41 (t, J = 1.2 Hz, 1H, Ph-H), 4.29-4.23 (m, 4H, OCH_2), 4.02-3.93 (m, 2H, OCH_2), 1.28-1.23 (m, 6H, CH_3), 0.89 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 163.0, 162.1, 160.0, 157.2, 148.5, 143.1, 137.4, 132.8, 131.8, 130.8, 128.1, 121.2, 120.7, 104.7, 62.5, 61.6, 61.0, 14.0, 13.8, 13.0; IR (KBr) (ν_{max}, cm^{-1}): 3075, 2984, 1741, 1716, 1580, 1403, 1258, 800, 782; HRMS (ESI-TOF^{+}) *m/z*: calcd for $C_{20}H_{21}BrNO_7^{+}$ [(M + H)$^{+}$], 466.0496; found, 466.0486.

6-Oxo-1-(3-trifluoromethyl-phenyl)-1,6-dihydro-pyridine-2,3,5-tricarboxylic acid triethyl ester (**4bb**). White solid; yield 70%; mp: 160-162 ^{o}C; ^{1}H NMR (DMSO-d_6, 400 MHz, TMS) δ 8.49 (s, 1H, CH), 7.90 (t, J = 6.0 Hz, 2H, Ph-H), 7.77 (t, J = 8.0 Hz, 1H, Ph-H), 7.72 (d, J = 8.4 Hz, 1H, Ph-H), 4.26 (q, J = 7.2 4H, OCH_2), 3.92 (q, J = 7.2 Hz, 2H, OCH_2), 1.27-1.22 (m, 6H, CH_3), 0.82 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 163.1, 162.2, 160.1, 157.4, 148.4, 143.3, 136.8, 133.2, 130.4, 130.0, 129.6, 126.7, 126.1, 126.0, 124.8, 122.1, 120.8, 105.0, 62.6, 61.7, 61.1, 13.9, 13.8, 12.8; IR (KBr) (ν_{max}, cm^{-1}): 2989, 1746, 1712, 1610, 1414, 1231, 804, 703; HRMS (ESI-TOF^{+}) *m/z*: calcd for $C_{21}H_{21}F_3NO_7^{+}$ [(M + H)$^{+}$], 456.1265; found, 456.1297.

1-(3-Cyano-phenyl)-6-oxo-1,6-dihydro-pyridine-2,3,5-tricarboxylic acid triethyl ester (**4cc**). Pale yellow solid; yield 68%; mp: 153-155 ^{o}C; ^{1}H NMR (DMSO-d_6, 400 MHz, TMS) δ 8.49 (s, 1H, CH), 8.05-8.03 (m, 2H, Ph-H), 7.82-7.74 (m, 2H, Ph-H),

4.30-4.24 (m, 4H, OCH_2), 4.01-3.92 (m, 2H, OCH_2), 1.28-1.24 (m, 6H, CH_3), 0.88 (t, J = 6.8 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 163.0, 162.1, 160.0, 157.2, 148.3, 143.2, 136.9, 134.2, 133.8, 132.9, 130.5, 120.9, 117.5, 111.9, 105.0, 62.6, 61.7, 61.1, 14.0, 13.8, 13.0; IR (KBr) (ν_{max}, cm^{-1}): 2985, 1740, 1642, 1611, 1424, 1258, 832, 714; HRMS (ESI-TOF$^+$) *m/z*: calcd for $C_{21}H_{21}N_2O_7^+$ [(M + H)$^+$], 413.1343; found, 413.1400.

1-(3-Nitro-phenyl)-6-oxo-1,6-dihydro-pyridine-2,3,5-tricarboxylic acid triethyl ester (**4dd**). White solid; yield 52%; mp: 123-124 ^{o}C; ^{1}H NMR (DMSO-d_6, 400 MHz, TMS) δ 8.49 (s, 1H, CH), 8.44 (t, J = 1.6 Hz, 1H, Ph-H), 8.42-8.39 (m, 1H, Ph-H), 7.94-7.91 (m, 1H, Ph-H), 7.85 (t, J = 8.0 Hz, 1H, Ph-H), 4.30-4.24 (m, 4H, OCH_2), 3.99-3.91 (m, 2H, OCH_2), 1.29-1.24 (m, 6H, CH_3), 0.86 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 163.0, 162.2, 160.1, 157.3, 148.3, 147.8, 143.2, 137.1, 135.9, 130.6, 124.8, 124.3, 120.9, 105.1, 62.6, 61.7, 61.0, 14.0, 13.8, 13.0; IR (KBr) (ν_{max}, cm^{-1}): 2981, 1723, 1689, 1654, 1406, 1260, 856, 769; HRMS (ESI-TOF$^+$) *m/z*: calcd for $C_{21}H_{21}N_2O_9^+$ [(M + H)$^+$], 433.1242; found, 433.1292.

5-Ethyl 2,3-dimethyl 6-oxo-1-phenyl-1,6-dihydropyridine-2,3,5-tricarboxylate (**4ee**). Pale yellow solid; yield 80%; mp: 99-101 ^{o}C; ^{1}H NMR (DMSO-d_6, 400 MHz, TMS) δ 8.49 (s, 1H, CH), 7.54-7.50 (m, 3H, Ph-H), 7.36-7.33 (m, 2H, Ph-H), 4.27 (q, J = 7.2 Hz, 2H, OCH_2), 3.81 (s, 3H, CH_3), 3.45 (s, 3H, CH_3), 1.27 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 163.5, 163.2, 161.2, 157.8, 149.4, 143.5, 136.6, 130.3, 129.5, 129.0, 121.1, 104.9, 61.5, 53.5, 53.2, 14.5; IR (KBr) (ν_{max}, cm^{-1}): 3010,

2968, 1711, 1701, 1623, 1426, 1223, 748, 692; HRMS (ESI-TOF$^+$) *m/z*: calcd for $C_{18}H_{18}NO_7^+$ [(M + H)$^+$], 360.1078; found, 360.1092.

2,3-Diethyl 5-methyl 6-oxo-1-phenyl-1,6-dihydropyridine-2,3,5-tricarboxylate (**4ff**). White solid; yield 78%; mp: 106-107 ^oC; ^1H NMR (DMSO-d_6, 400 MHz, TMS) δ 8.51 (s, 1H, CH), 7.52 (t, J = 3.2 Hz, 3H, Ph-H), 7.36-7.33 (m, 2H, Ph-H), 4.27 (q, J = 6.8 Hz, 2H, OCH_2), 3.92 (q, J = 7.2 Hz, 2H, OCH_2), 3.79 (s, 3H, CH_3), 1.25 (t, J = 7.2 Hz, 3H, CH_3), 0.86 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 163.5, 162.2, 160.1, 157.3, 149.0, 143.3, 136.0, 129.8, 128.9, 128.7, 120.3, 104.5, 62.4, 61.6, 52.2, 13.9, 13.0; IR (KBr) (ν_{max}, cm^{-1}): 3025, 2998, 1726, 1702, 1602, 1400, 1222, 751, 682; HRMS (ESI-TOF$^+$) *m/z*: calcd for $C_{19}H_{20}NO_7^+$ [(M + H)$^+$], 374.1234; found, 374.1259.

1-(2-Bromo-phenyl)-6-oxo-1,6-dihydro-pyridine-2,3,5-tricarboxylic acid triethyl ester (**6a**). Yellow oil; yield 70%; ^1H NMR (DMSO-d_6, 400 MHz, TMS) δ 6.93 (s, 1H, CH), 7.81 (t, J = 7.6 Hz, 1H, Ph-H), 7.54 (q, J = 3.6 Hz, 2H, Ph-H), 7.49-7.44 (m, 1H, Ph-H), 4.30 (q, J = 7.2 Hz, 2H, OCH_2), 4.20-4.16 (m, 2H, OCH_2), 3.93-3.87 (m, 2H, OCH_2), 1.29 (t, J = 7.2 Hz, 3H, CH_3), 1.19 (t, J = 7.2 Hz, 3H, CH_3), 0.86 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 164.7, 162.6, 159.8, 158.8, 144.7, 143.4, 135.5, 133.0, 131.8, 130.7, 128.6, 122.7, 120.7, 106.0, 62.5, 62.1, 62.0, 13.7, 13.5, 13.0; IR (KBr) (ν_{max}, cm^{-1}): 2984, 2932, 1738, 1690, 1623, 1423, 1264, 762; HRMS (ESI-TOF$^+$) *m/z*: calcd for $C_{20}H_{21}BrNO_7^+$ [(M + H)$^+$], 466.0496; found, 466.0490.

6-Oxo-1-(2-trifluoromethyl-phenyl)-1,6-dihydro-pyridine-2,3,5-tricarboxylic acid triethyl ester (**6b**). Yellow oil; yield 66%; ^{1}H NMR (DMSO-d_6, 400 MHz, TMS) δ 6.90 (s, 1H, CH), 7.92 (q, J = 6.8 Hz, 1H, Ph-H), 7.85-7.75 (m, 2H, Ph-H), 7.60 (d, J = 7.6 Hz, 1H, Ph-H), 4.29 (q, J = 6.8 Hz, 2H, OCH_2), 4.19-4.14 (m, 2H, OCH_2), 3.88 (q, J = 7.2 Hz, 2H, OCH_2), 1.27 (t, J = 7.2 Hz, 3H, CH_3), 1.18 (t, J = 7.2 Hz, 3H, CH_3), 0.82 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 164.5, 162.8, 159.8, 159.8, 144.4, 143.3, 133.7, 133.0, 131.7, 131.0, 127.8, 127.7, 127.2, 126.9, 124.1, 121.4, 120.6, 115.3, 106.8, 62.7, 62.3, 62.1, 13.6, 13.4, 12.9; IR (KBr) (ν_{max}, cm^{-1}): 2986, 1739, 1692, 1604, 1422, 1218, 772; HRMS (ESI-TOF$^+$) *m/z*: calcd for $C_{21}H_{21}F_3NO_7^+$ [(M + H)$^+$], 456.1265; found,456.1291.

1-(2-Cyano-phenyl)-4-oxo-1,4-dihydro-pyridine-2,3,5-tricarboxylic acid triethyl ester (**6c**). Yellow oil; yield 60%; ^{1}H NMR (DMSO-d_6, 400 MHz, TMS) δ 7.00 (s, 1H, CH), 8.12 (q, J = 6.8 Hz, 1H, Ph-H), 7.93-7.88 (m, 1H, Ph-H), 7.77-7.71 (m, 2H, Ph-H), 4.32 (q, J = 7.2 Hz, 2H, OCH_2), 4.25-4.16 (m, 2H, OCH_2), 3.95-3.89 (m, 2H, OCH_2), 1.29 (t, J = 7.2 Hz, 3H, CH_3), 1.20 (t, J = 7.2 Hz, 3H, CH_3), 0.86 (t, J = 6.8 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 164.4, 162.6, 159.8, 159.2, 144.1, 143.4, 138.4, 134.6, 133.5, 130.9, 129.8, 121.1, 115.2, 112.6, 106.9, 62.9, 62.2, 62.1, 13.6, 13.5, 13.0; IR (KBr) (ν_{max}, cm^{-1}): 2980, 2942, 1741, 1689, 1670, 1404, 1252, 750; HRMS (ESI-TOF$^+$) *m/z*: calcd for $C_{21}H_{21}N_2O_7^+$ [(M + H)$^+$], 413.1343; found, 413.1394.

Triethyl 1-(2-fluorophenyl)-4-oxo-1,4-dihydropyridine-2,3,5-tricarboxylate (**6d**). Yellow oil; yield 66%; ^{1}H NMR (DMSO-d_6, 400 MHz, TMS) δ 6.91 (s, 1H, CH),

7.62-7.57 (m, 1H, Ph-H), 7.52-7.43 (m, 2H, Ph-H), 7.34 (t, J = 7.6 Hz, 1H, Ph-H), 4.30 (q, J = 7.2 Hz, 2H, OCH_2), 4.23-4.17 (m, 2H, OCH_2), 3.93 (q, J = 7.2 Hz, 2H, OCH_2), 1.28 (t, J = 7.2 Hz, 3H, CH_3), 1.19 (t, J = 7.2 Hz, 3H, CH_3), 0.87 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 164.5, 162.6, 160.0, 159.0, 156.1, 144.9, 143.3, 132.5, 130.3, 125.1, 123.8, 120.6, 116.1, 106.4, 62.7, 62.1, 62.0, 13.6, 13.5, 13.0; ^{19}F NMR (DMSO-d_6, 311 MHz) δ -120.9 (s, 1F); IR (KBr) (ν_{max}, cm^{-1}): 3030, 2998, 1732, 1601, 1412, 1238, 762; HRMS (ESI-TOF$^+$) *m/z*: calcd for $C_{20}H_{21}FNO_7^+$ [(M + H)$^+$], 406.1297; found, 406.1345.

Triethyl 1-(2-chlorophenyl)-4-oxo-1,4-dihydropyridine-2,3,5-tricarboxylate (**6e**). Yellow oil; yield 68%; ^1H NMR (DMSO-d_6, 400 MHz, TMS) δ 6.92 (s, 1H, CH), 7.70-7.67 (m, 1H, Ph-H), 7.58-7.54 (m, 2H, Ph-H), 7.52-7.48 (m, 1H, Ph-H), 4.30 (q, J = 7.2 Hz, 2H, OCH_2), 4.21-4.16 (m, 2H, OCH_2), 3.93-3.88 (m, 2H, OCH_2), 1.28 (t, J = 7.2 Hz, 3H, CH_3), 1.19 (t, J = 7.2 Hz, 3H, CH_3), 0.85 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 165.1, 163.1, 160.3, 159.3, 145.3, 143.9, 134.4, 132.6, 132.3, 131.1, 130.3, 128.6, 121.2, 106.6, 63.1, 62.7, 62.5, 14.2, 14.0, 13.5; IR (KBr) (ν_{max}, cm^{-1}): 2994, 2912, 1710, 1658, 1610, 1452, 1286, 756; HRMS (ESI-TOF$^+$) *m/z*: calcd for $C_{20}H_{21}ClNO_7^+$ [(M + H)$^+$], 422.1001; found, 422.1012.

Triethyl 1-(2-iodophenyl)-4-oxo-1,4-dihydropyridine-2,3,5-tricarboxylate (**6f**). Yellow oil; yield 65%; ^1H NMR (DMSO-d_6, 400 MHz, TMS) δ 6.91 (s, 1H, CH), 7.99 (q, J = 6.8 Hz, 1H, Ph-H), 7.55-7.47 (m, 2H, Ph-H), 7.28-7.24 (m, 1H, Ph-H), 4.31 (q, J = 7.2 Hz, 2H, OCH_2), 4.21-4.11 (m, 2H, OCH_2), 3.92-3.86 (m, 2H, OCH_2), 1.29 (t, J = 7.2 Hz, 3H, CH_3), 1.19 (t, J = 7.2 Hz, 3H, CH_3), 0.87 (t, J = 6.8 Hz, 3H,

CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 164.7, 162.7, 159.7, 158.8, 144.7, 143.4, 139.2, 139.1, 131.4, 130.0, 129.1, 120.9, 106.0, 100.2, 62.4, 62.1, 62.0, 13.7, 13.5, 13.0; IR (KBr) (ν_{max}, cm^{-1}): 3011, 2985, 1742, 1714, 1602, 1406, 1270, 762; HRMS (ESI-TOF$^+$) *m/z*: calcd for $C_{20}H_{21}INO_7^+$ [(M + H)$^+$], 514.0357; found, 514.0382.

Triethyl 1-(3-chloro-2-fluorophenyl)-4-oxo-1,4-dihydropyridine-2,3,5-tricarboxylate (**6g**). Yellow oil; yield 56%; ^1H NMR (DMSO-d_6, 400 MHz, TMS) δ 6.97 (s, 1H, CH), 7.85-7.81 (m, 1H, Ph-H), 7.60-7.54 (m, 1H, Ph-H), 7.43-7.38 (m, 1H, Ph-H), 4.32-4.26 (m, 2H, OCH_2), 4.21-4.16 (m, 2H, OCH_2), 4.01-3.94 (m, 2H, OCH_2), 1.28 (t, J = 7.2 Hz, 3H, CH_3), 1.19 (t, J = 7.2 Hz, 3H, CH_3), 0.88 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 164.9, 163.1, 160.4, 159.4, 155.0, 144.8, 143.8, 133.2, 129.8, 125.9, 121.4, 120.9, 107.4, 63.3, 62.7, 62.6, 14.1, 14.0, 13.4; ^{19}F NMR (DMSO-d_6, 311 MHz) δ -122.2 (s, 1F); IR (KBr) (ν_{max}, cm^{-1}): 2992, 1722, 1701, 1602, 1435, 1211, 822, 786; HRMS (ESI-TOF$^+$) *m/z*: calcd for $C_{20}H_{20}ClFNO_7^+$ [(M + H)$^+$], 440.0907; found, 440.0935.

Trimethyl 1-(2-bromophenyl)-4-oxo-1,4-dihydropyridine-2,3,5-tricarboxylate (**6h**). Yellow oil; yield 72%; ^1H NMR (DMSO-d_6, 400 MHz, TMS) δ 6.96 (s, 1H, CH), 7.81 (t, J = 1.2 Hz, 1H, Ph-H), 7.56-7.51 (m, 2H, Ph-H), 7.48-7.44 (m, 1H, Ph-H), 3.85 (s, 3H, CH_3), 3.74 (s, 3H, CH_3), 3.45 (s, 3H, CH_3), ^{13}C NMR (DMSO-d_6, 100 MHz) δ 165.2, 163.1, 160.4, 158.8, 144.7, 143.0, 135.5, 133.0, 131.8, 130.4, 128.6, 122.4, 121.0, 105.9, 53.3, 53.2, 53.1; IR (KBr) (ν_{max}, cm^{-1}): 3045, 2998, 1735, 1711, 1605, 1406, 1248, 760; HRMS (ESI-TOF$^+$) *m/z*: calcd for $C_{17}H_{15}BrNO_7^+$ [(M + H)$^+$], 424.0026; found, 424.0056.

Triethyl 4-oxo-1-phenyl-1,4-dihydropyridine-2,3,5-tricarboxylate **(6i)**. Yellow oil; yield 70%; ^{1}H NMR (DMSO-d_6, 400 MHz, TMS) δ 6.84 (s, 1H, CH), 7.52-7.49 (m, 3H, Ph-H), 7.37-7.34 (m, 2H, Ph-H), 4.30 (q, J = 6.8 Hz, 2H, OCH_2), 4.18 (q, J = 7.2 Hz, 2H, OCH_2), 3.88 (q, J = 6.8 Hz, 2H, OCH_2), 1.28 (t, J = 6.8 Hz, 3H, CH_3), 1.18 (t, J = 6.8 Hz, 3H, CH_3), 0.85 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 164.8, 162.8, 160.2, 159.7, 145.2, 142.9, 136.3, 129.6, 129.0, 128.5, 120.6, 105.6, 62.4, 62.0, 61.8, 13.7, 13.5, 13.0; IR (KBr) (ν_{max}, cm^{-1}): 3032, 2922, 1704, 1683, 1604, 1432, 1258, 742, 654; HRMS (ESI-TOF^{+}) *m/z*: calcd for $C_{20}H_{22}NO_7^{+}$ [(M + H)$^{+}$], 388.1391; found, 388.1411.

Triethyl 4-oxo-1-(o-tolyl)-1,4-dihydropyridine-2,3,5-tricarboxylate **(6j)**. Yellow oil; yield 52%; ^{1}H NMR (DMSO-d_6, 400 MHz, TMS) δ 6.87 (s, 1H, CH), 7.43-7.37 (m, 2H, Ph-H), 7.33-7.29 (m, 1H, Ph-H), 7.26 (d, J = 8.0 Hz, 2H, Ph-H), 4.30 (q, J = 6.8 Hz, 2H, OCH_2), 4.22-4.14 (m, 2H, OCH_2), 3.87 (q, J = 7.2 Hz, 2H, OCH_2), 2.06 (s, 3H, CH_3), 1.29 (t, J = 6.8 Hz, 3H, CH_3), 1.19 (t, J = 7.2 Hz, 3H, CH_3), 0.83 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 164.8, 162.7, 160.1, 159.1, 145.2, 143.3, 136.1, 135.5, 130.5, 130.0, 128.5, 126.7, 120.5, 105.6, 62.4, 62.1, 61.9, 16.9, 13.7, 13.5, 12.9; IR (KBr) (ν_{max}, cm^{-1}): 3012, 2903, 1769, 1711, 1622, 1407, 1258, 760; HRMS (ESI-TOF^{+}) *m/z*: calcd for $C_{21}H_{24}NO_7^{+}$ [(M + H)$^{+}$], 402.1547; found, 402.1582.

2-Phenylamino-but-2-enedioic acid diethyl ester (**Ⅰ**).

Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 9.70 (s, 1H, NH), 7.28 (d, J = 15.2 Hz, 2H, Ph-H), 7.08 (t, J = 7.2 Hz, 1H, Ph-H), 6.93 (d, J = 7.6 Hz, 2H, Ph-H), 5.39 (s, 1H, CH), 4.22-4.12 (m, 4H, OCH_2), 1.29 (t, J = 7.6 Hz, 3H, CH_3), 1.08 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.5, 164.3, 148.4, 140.4, 129.0, 124.2, 121.0, 93.7, 61.9, 59.8, 14.3, 13.6.

2-[(2-Bromo-phenylamino)-methylene]-malonic acid diethyl ester (Ⅱ).

White solid; mp: 84-85 ^{o}C; ^{1}H NMR (DMSO-d_6, 400 MHz, TMS) δ 11.1 (d, J = 13.2 Hz, 1H, NH), 8.51 (d, J = 34.8 Hz, 1H, CH), 7.71 (q, J = 6.8 Hz, 1H, Ph-H), 7.63 (t, J = 7.2 Hz, 1H, Ph-H), 7.46-7.42 (m, 1H, Ph-H), 7.12-7.08 (m, 1H, Ph-H), 4.23 (q, J = 6.8 Hz, 2H, OCH_2), 4.15 (q, J = 7.2 Hz, 2H, OCH_2), 1.28-1.23 (m, 6H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 167.6, 164.5, 150.4, 136.9, 133.1, 129.2, 125.7, 116.9, 112.6, 94.8, 60.0, 59.6, 14.1, 14.1.

Diethyl 2-((2-bromophenyl)amino)fumarate (**III**).

Yellow oil; ^{1}H NMR (DMSO-d_6, 400 MHz, TMS) δ 9.77 (s, 1H, NH), 7.63 (d, J = 8.0 Hz, 1H, Ph-H), 7.28 (t, J = 7.6 Hz, 1H, Ph-H), 7.01 (t, J = 7.6 Hz, 1H, Ph-H), 6.84 (q, J = 7.2 Hz, 1H, Ph-H), 5.45 (d, J = 0.8 Hz, 1H, CH), 4.18-4.11 (m, 4H, OCH_2), 1.22 (t, J = 7.2 Hz, 3H, CH_3), 1.06 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 168.4, 162.9, 146.6, 138.0, 132.6, 128.1, 125.2, 121.3, 114.8, 95.2, 62.0, 59.9, 13.9, 13.3.

3-{[(1,2-Bis-ethoxycarbonyl-vinyl)-(2-nitro-phenyl)-amino]-methylene}-2,4-dioxo-pentanedioic acid diethyl ester (**IV**).

Yellow oil; ^{1}H NMR (DMSO-d_6, 400 MHz, TMS) δ 8.34 (q, J = 6.8 Hz, 1H, Ph-H), 7.94-7.89 (m, 1H, Ph-H), 7.83-7.79 (m, 1H, Ph-H), 7.61 (q, J = 6.4 Hz, 1H, Ph-H), 7.55 (s, 1H, CH), 5.21 (s, 1H, CH), 4.20-4.02 (m, 8H, OCH_2), 1.17-1.1.12 (m, 9H, CH_3), 0.94 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 164.3, 163.9, 163.1, 162.1, 148.9, 144.8, 139.4, 135.8, 132.5, 132.0, 129.6, 126.4, 107.5, 102.2, 62.4, 60.9, 60.7, 60.4, 13.8, 13.8, 13.3, 13.2.

2-Phenylaminomethylene-malonic acid diethyl ester (**7**).

Yellow oil; ^{1}H NMR (DMSO-d_6, 400 MHz, TMS) δ 10.73 (t, J = 6.0 Hz, 1H, NH), 8.42 (d, J = 14.0 Hz, 1H, CH), 7.38-7.30 (m, 4H, Ph-H), 7.14 (q, J = 6.0 Hz, 1H, Ph-H), 4.22-4.09 (m, 4H, OCH_2), 1.25 (q, J = 6.8 Hz, 6H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 167.4, 164.8, 151.0, 139.2, 129.5, 124.4, 117.3, 93.1, 59.5, 59.3, 14.1, 14.0.

X-Ray Crystallography structures of Compound **4a**

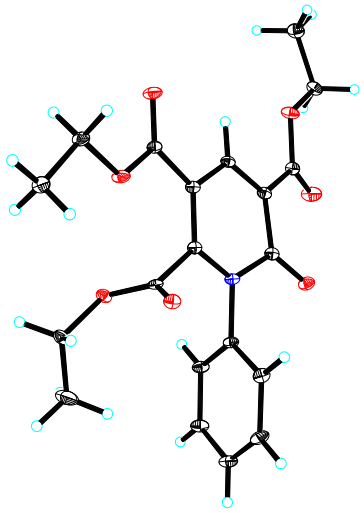


Figure S1. X-ray crystal structure of **4a**

Crystal data for md_lst1: $C_{20}H_{21}NO_7$, M = 387.38, a = 20.3966(5) Å, b = 5.58400(10) Å, c = 17.3130(4) Å, α = 90°, β = 108.5690(10)°, γ = 90°, V = 1869.20(7) Å^3, T = 100.(2) K, space group $P121/c1$, Z = 4, μ(Cu Kα) = 0.880 mm^{-1}, 20590 reflections measured, 3693 independent reflections (R_{int} = 0.0668). The final R_1 values were 0.0429 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1048 ($I > 2\sigma(I)$). The final R_1 values were 0.0525 (all data). The final $wR(F^2)$ values were 0.1122 (all data). The goodness of fit on F^2 was 1.053. **CCDC-1965346**.

View of a molecule of md_lst1 with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

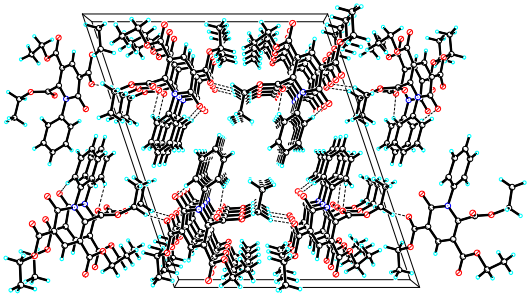


Figure S2. Crystal data and structure refinement for md_lst1_0m.

View of the pack drawing of md_lst1.

Hydrogen-bonds are shown as dashed lines.

Identification code	global	
Empirical formula	C20 H21 N O7	
Formula weight	387.38	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 20.3966(5) Å	α= 90°.
	b = 5.58400(10) Å	β= 108.5690(10)°.
	c = 17.3130(4) Å	γ = 90°.
Volume	1869.20(7) Å^3	
Z	4	
Density (calculated)	1.377 Mg/m^3	
Absorption coefficient	0.880 mm^{-1}	
F(000)	816	

Crystal size	0.600 x 0.060 x 0.030 mm^3
Theta range for data collection	2.29 to 72.37°.
Index ranges	-25<=h<=25, -5<=k<=6, -21<=l<=21
Reflections collected	20590
Independent reflections	3693 [R(int) = 0.0668]
Completeness to theta = 72.37°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.97 and 0.75
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3693 / 0 / 256
Goodness-of-fit on F^2	1.053
Final R indices [I>2sigma(I)]	R1 = 0.0429, wR2 = 0.1048
R indices (all data)	R1 = 0.0525, wR2 = 0.1122
Largest diff. peak and hole	0.430 and -0.333 $e.Å^{-3}$

^{1}H NMR and ^{13}C NMR spectra for Pyridones

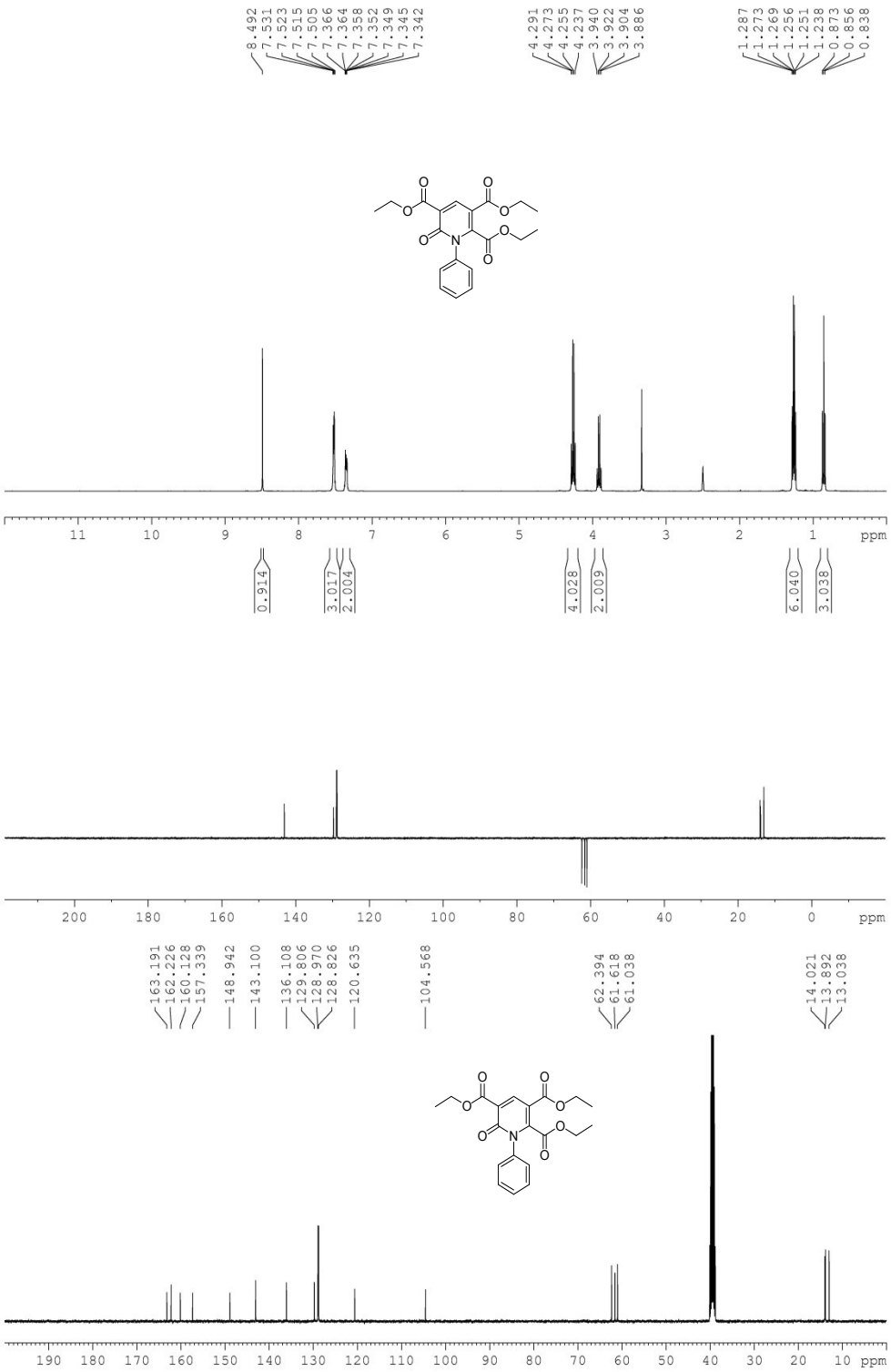


Figure S3. ^{1}H and ^{13}C NMR spectra of compound **4a**

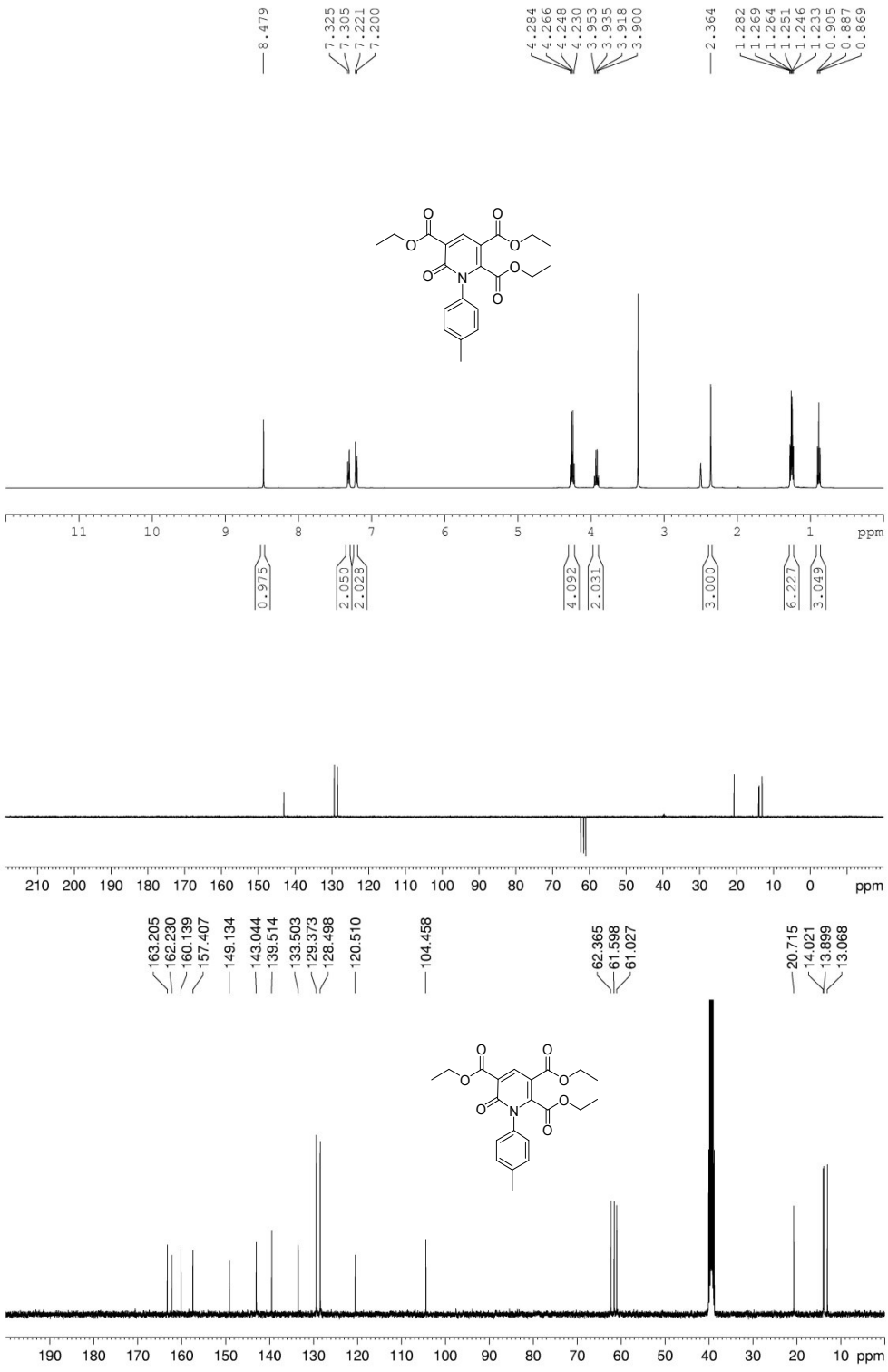


Figure S4. ^{1}H and ^{13}C NMR spectra of compound **4b**

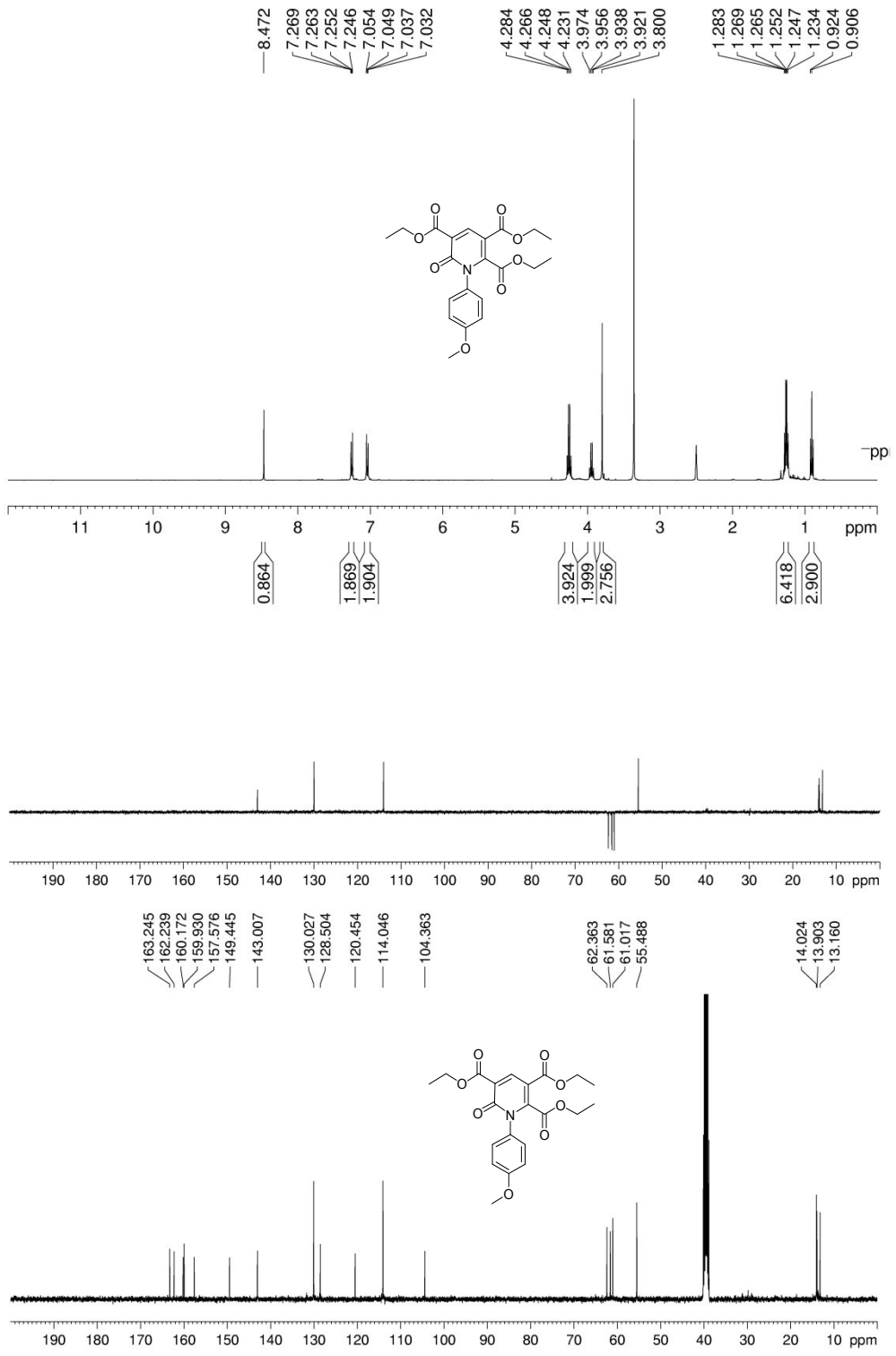


Figure S5. ^{1}H and ^{13}C NMR spectra of compound **4c**

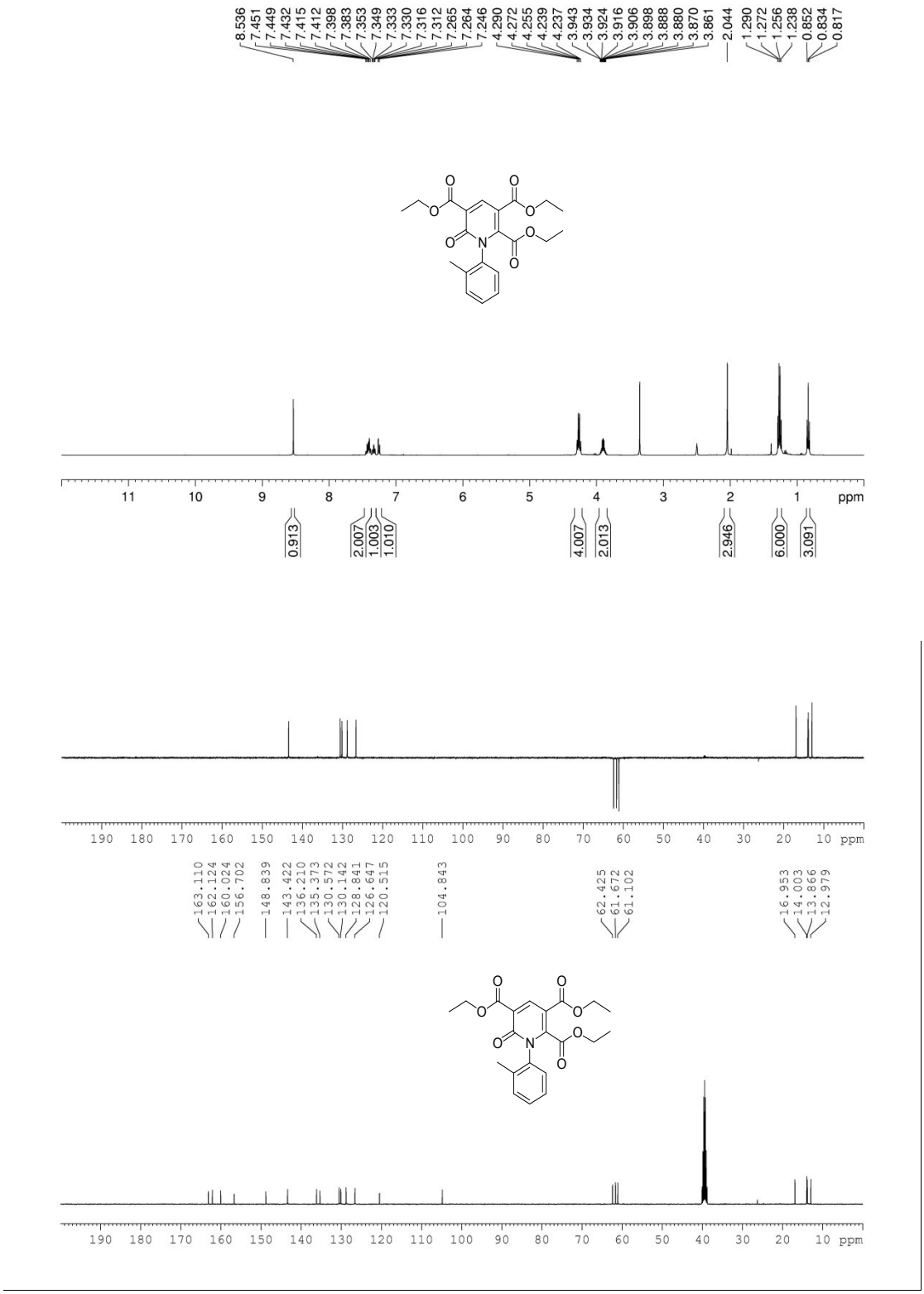


Figure S6. ^{1}H and ^{13}C NMR spectra of compound **4d**

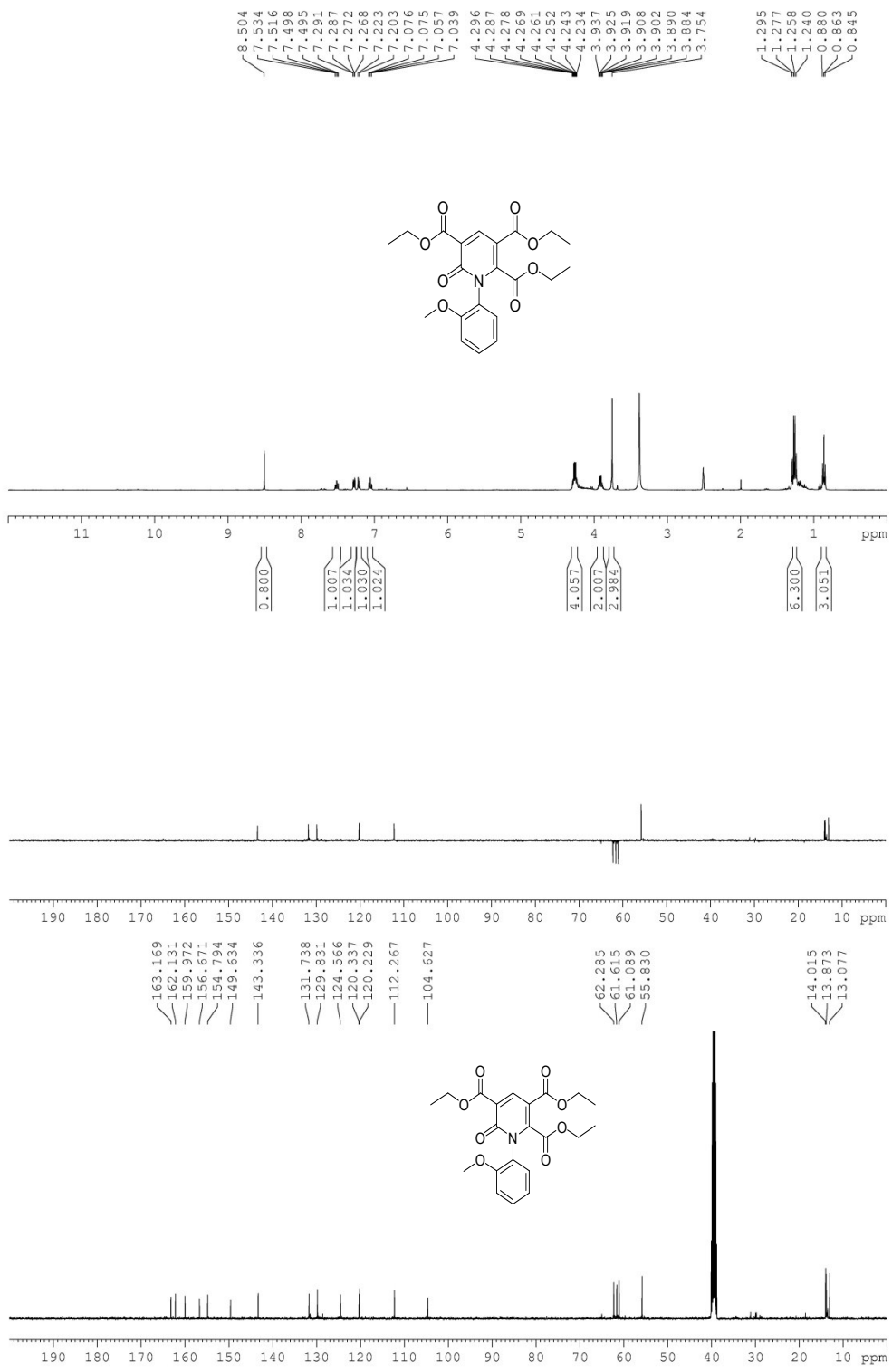


Figure S7. ^{1}H and ^{13}C NMR spectra of compound **4e**

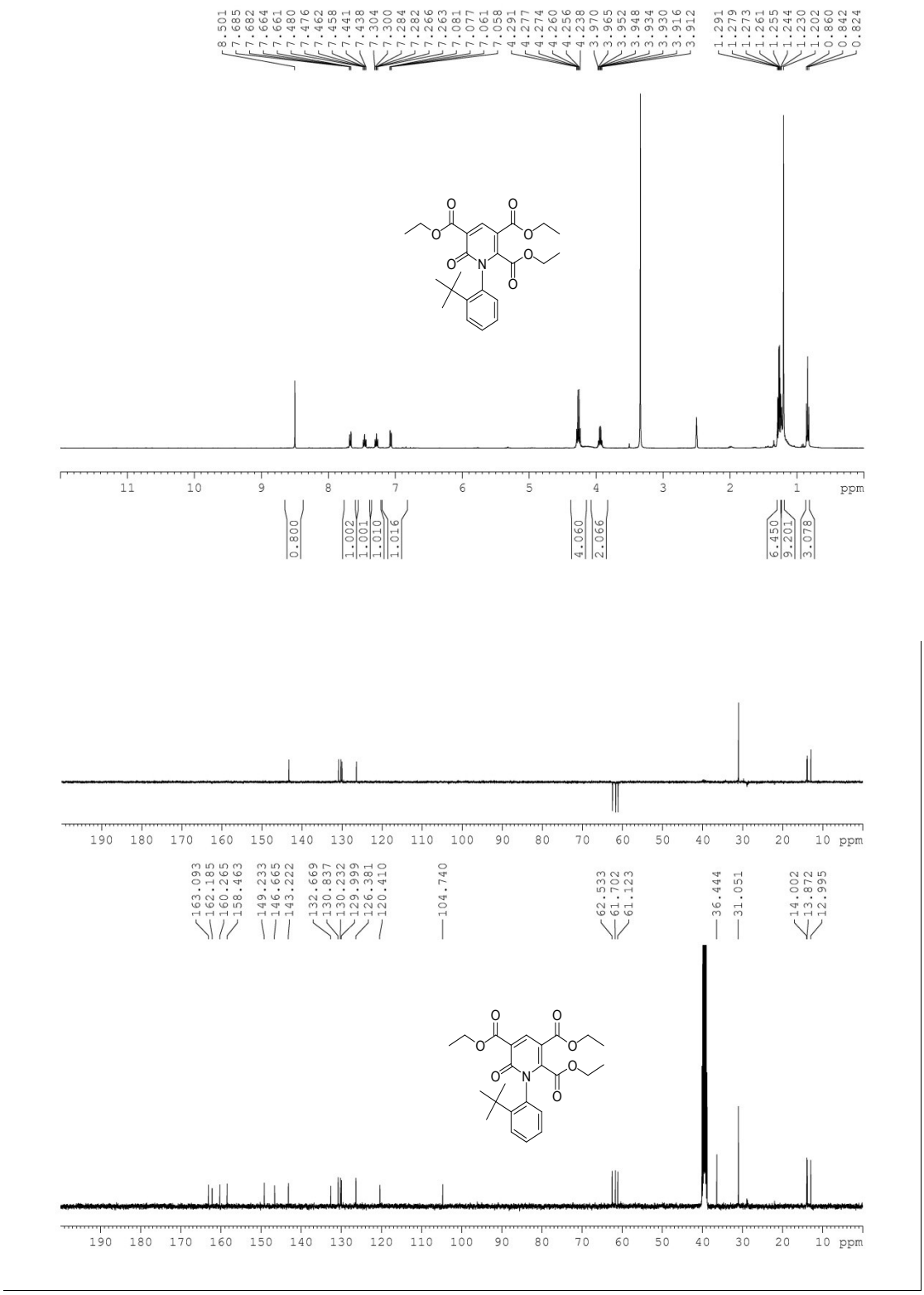


Figure S8. ^{1}H and ^{13}C NMR spectra of compound **4f**

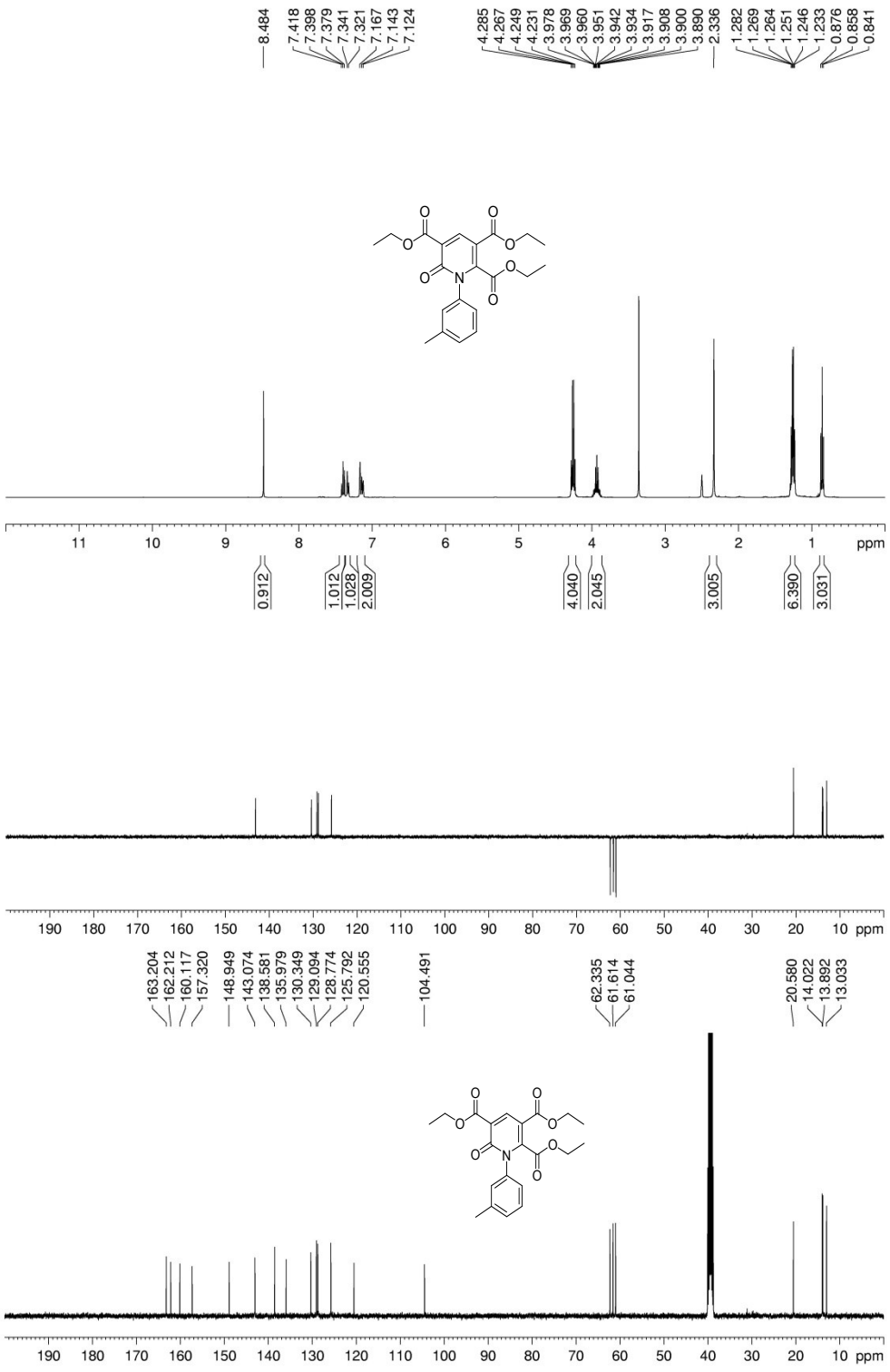


Figure S9. ^{1}H and ^{13}C NMR spectra of compound **4g**

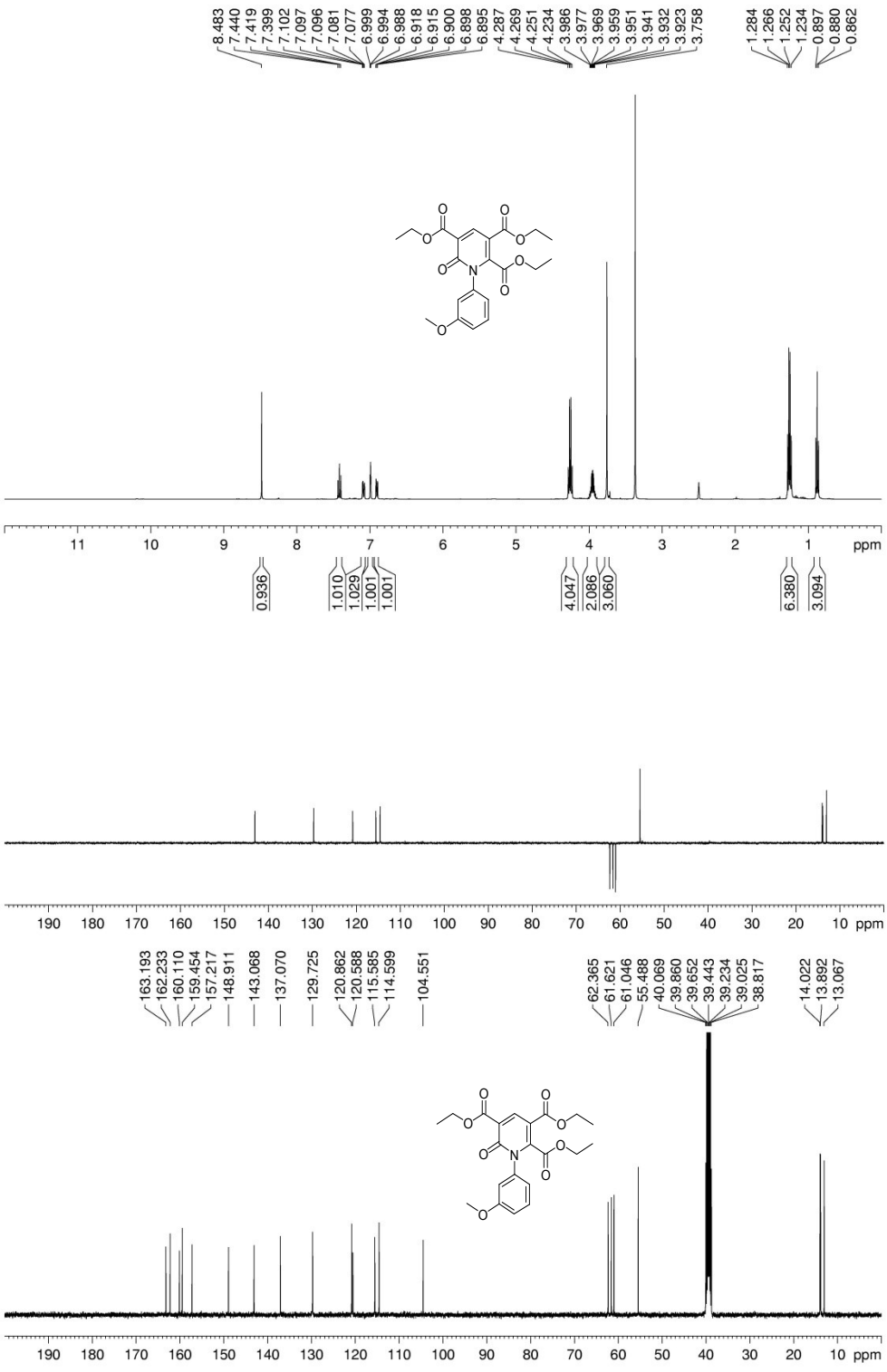


Figure S10. ^{1}H and ^{13}C NMR spectra of compound **4h**

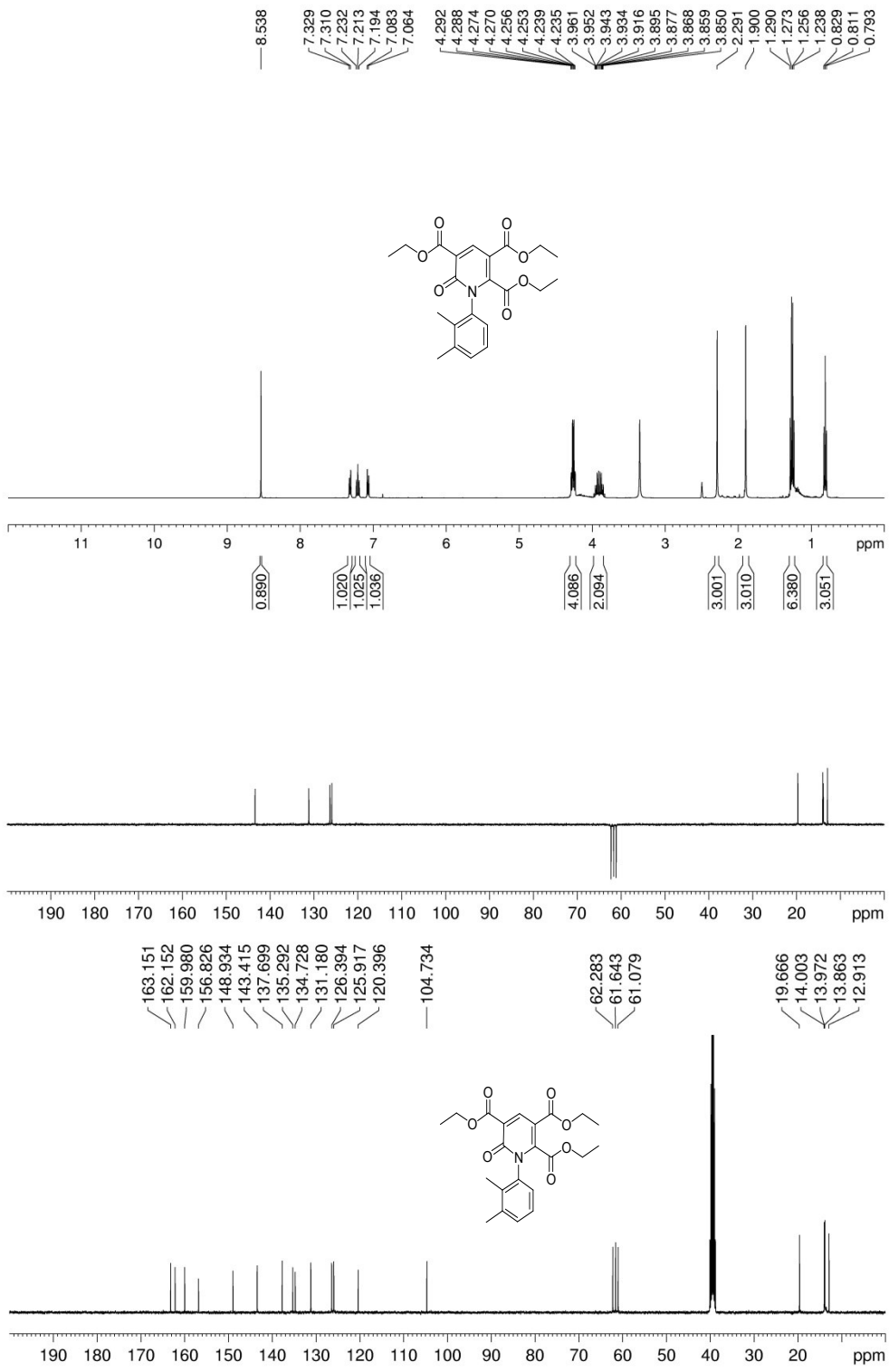


Figure S11. ^{1}H and ^{13}C NMR spectra of compound **4i**

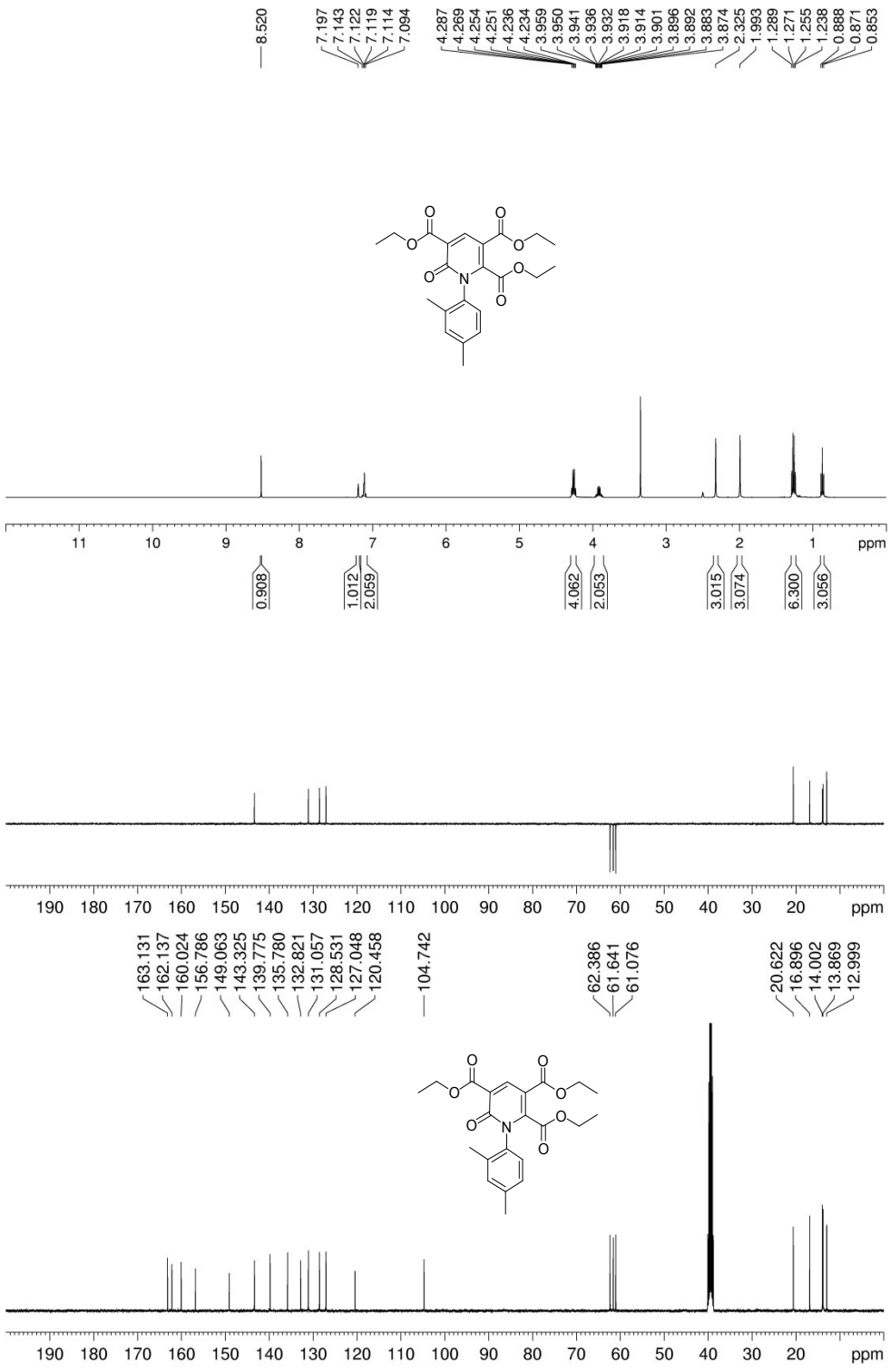


Figure S12. ^{1}H and ^{13}C NMR spectra of compound **4j**

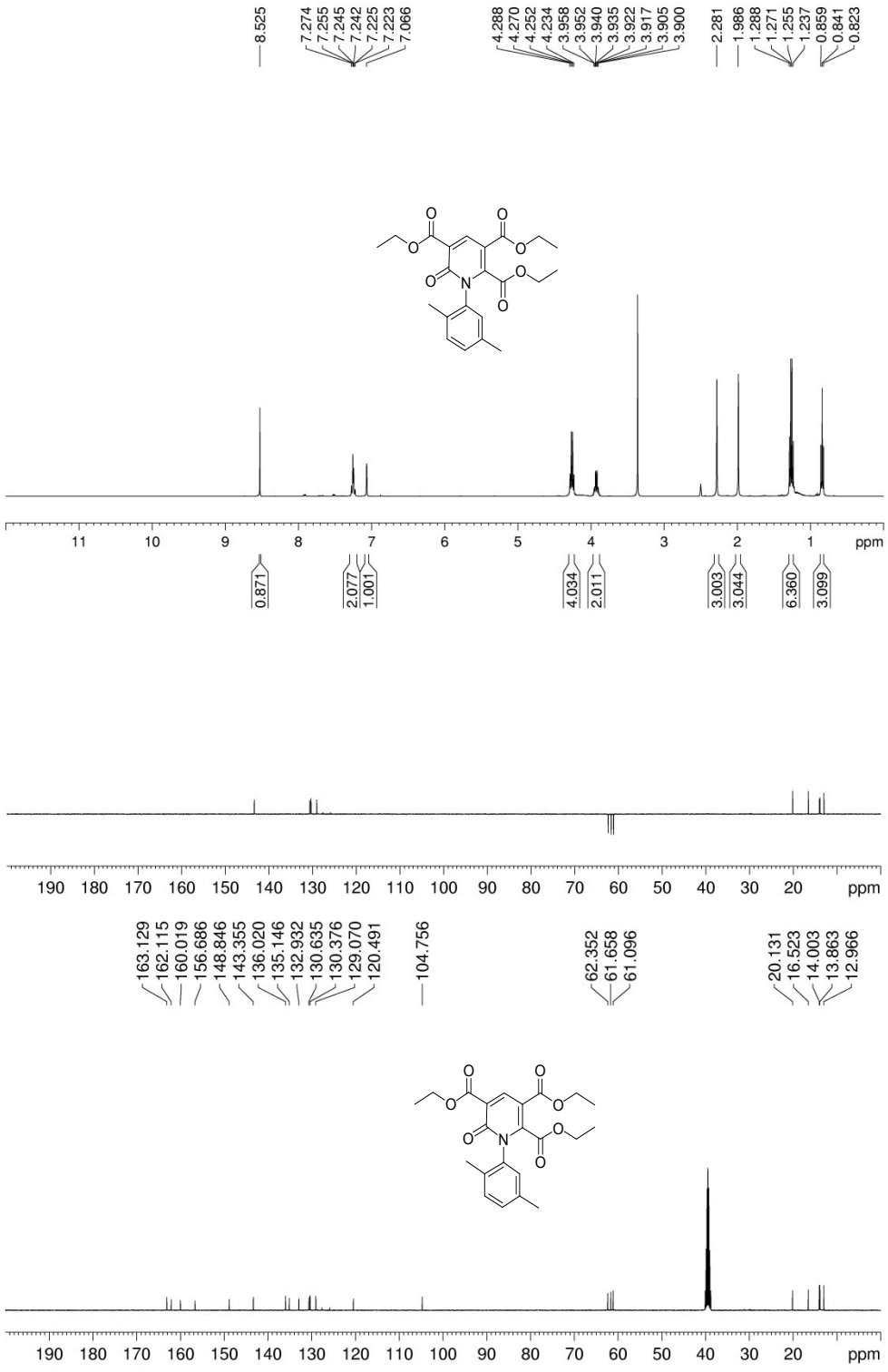


Figure S13. ^{1}H and ^{13}C NMR spectra of compound **4k**

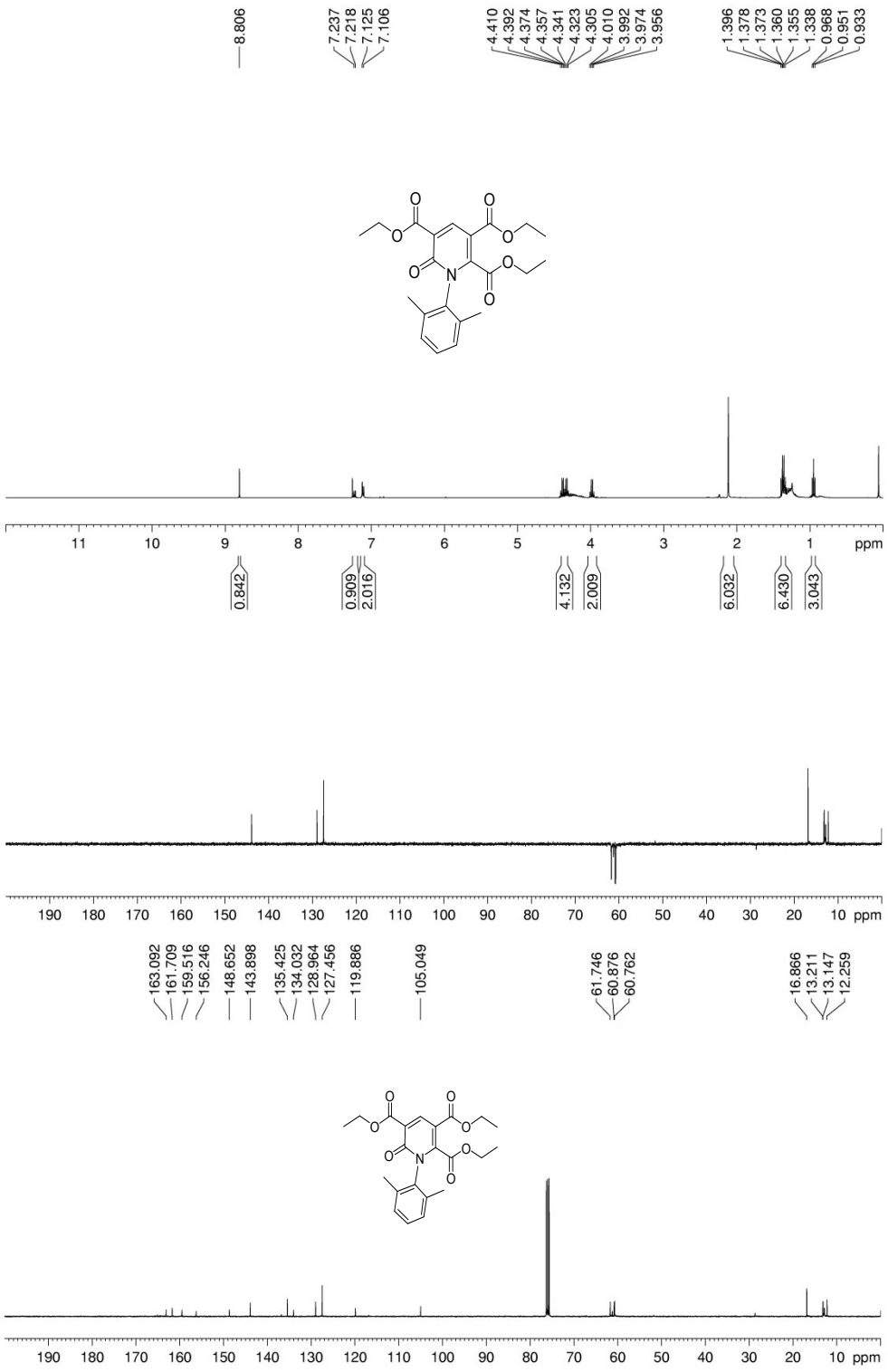


Figure S14. ^{1}H and ^{13}C NMR spectra of compound **4l**

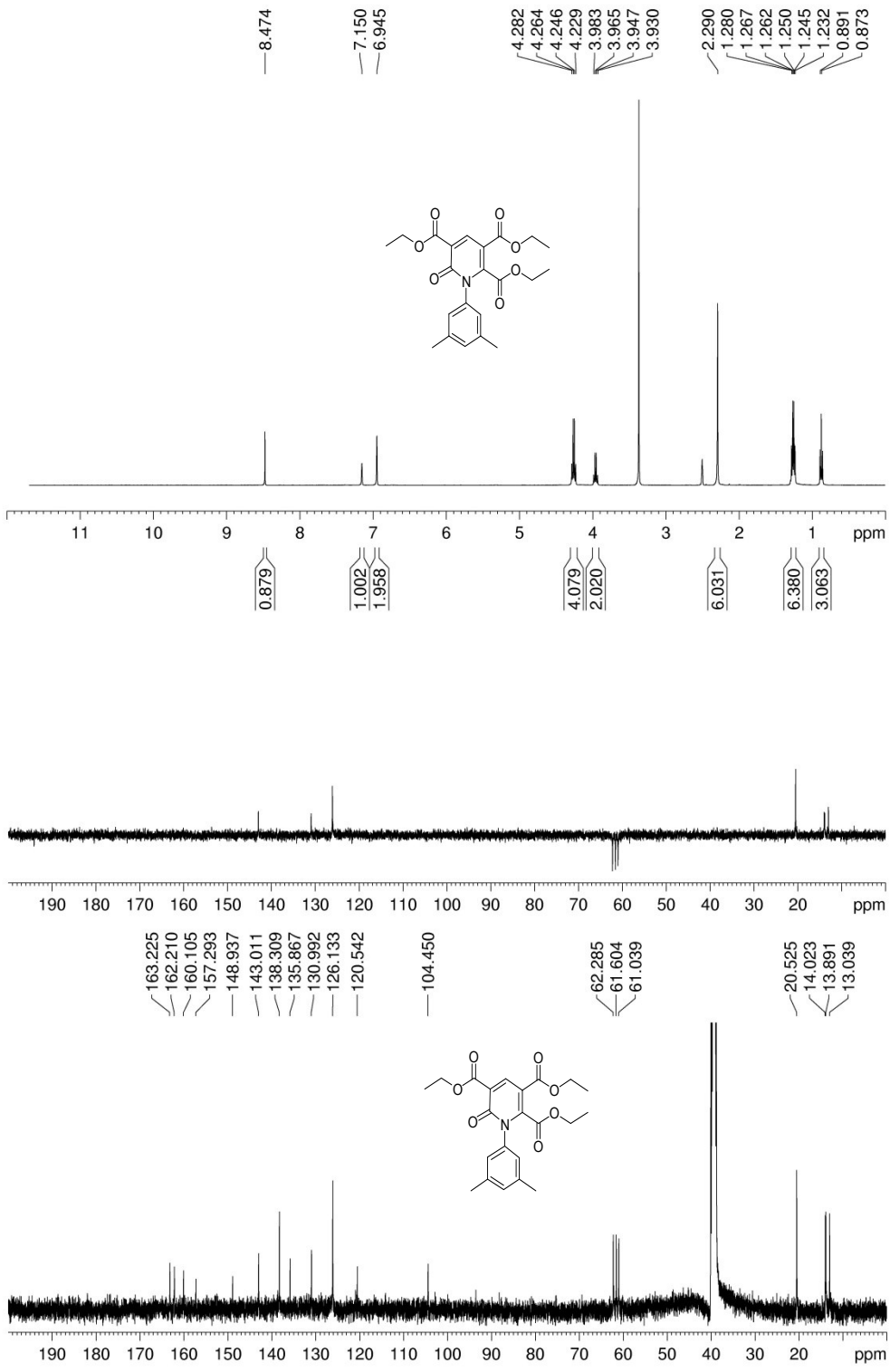


Figure S15. ^{1}H and ^{13}C NMR spectra of compound **4m**

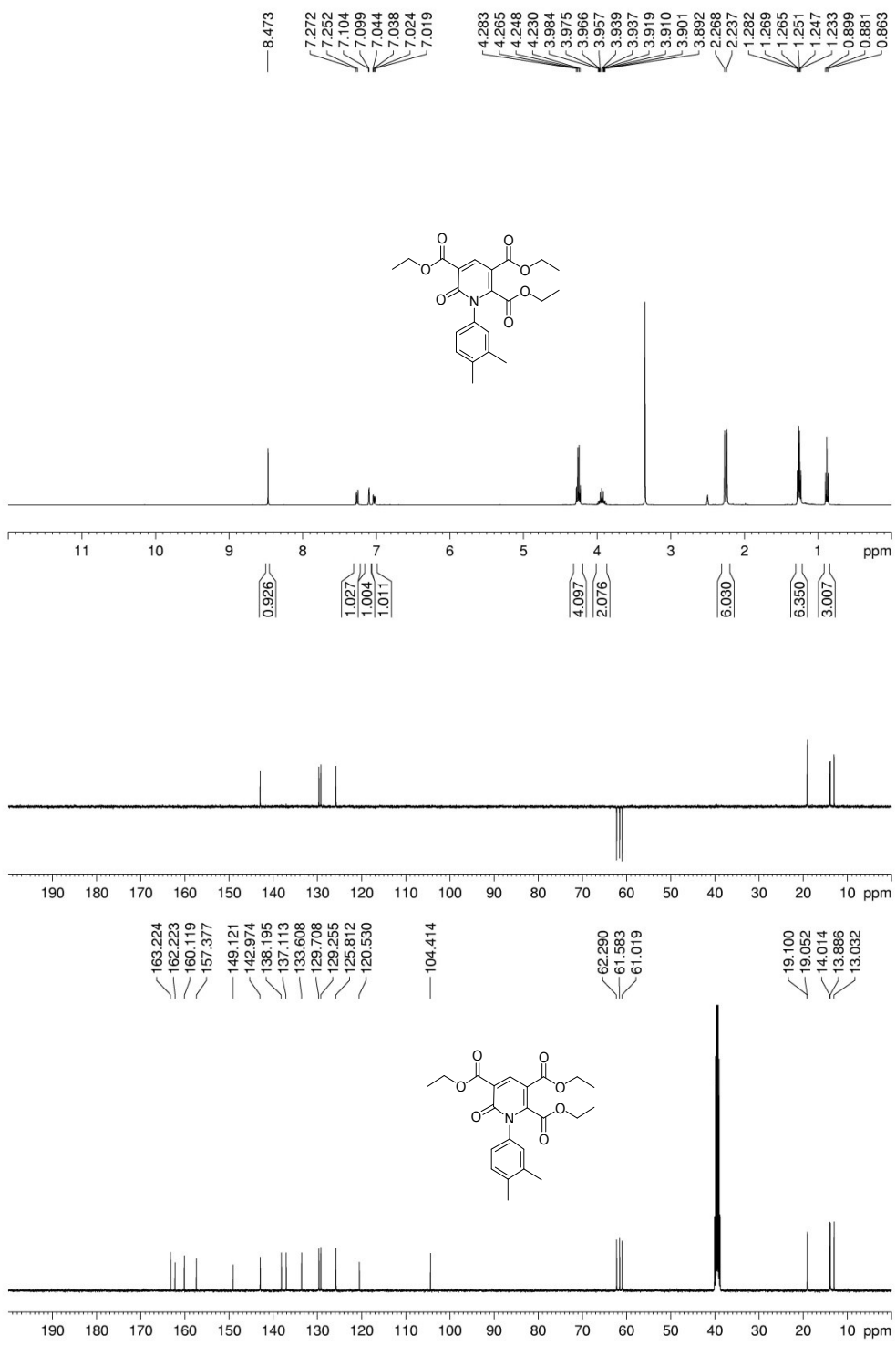


Figure S16. ^{1}H and ^{13}C NMR spectra of compound **4n**

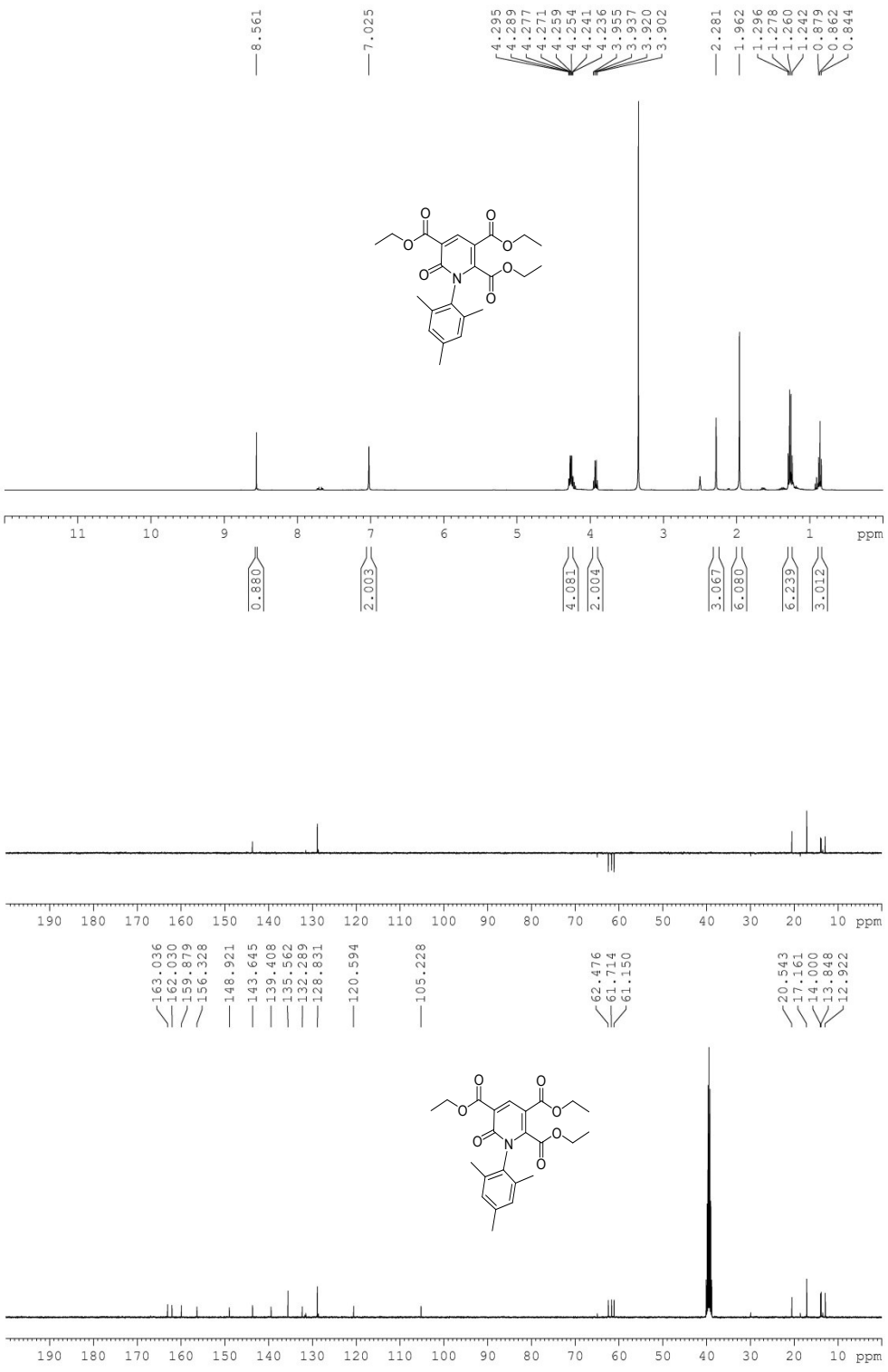


Figure S17. ^{1}H and ^{13}C NMR spectra of compound **4o**

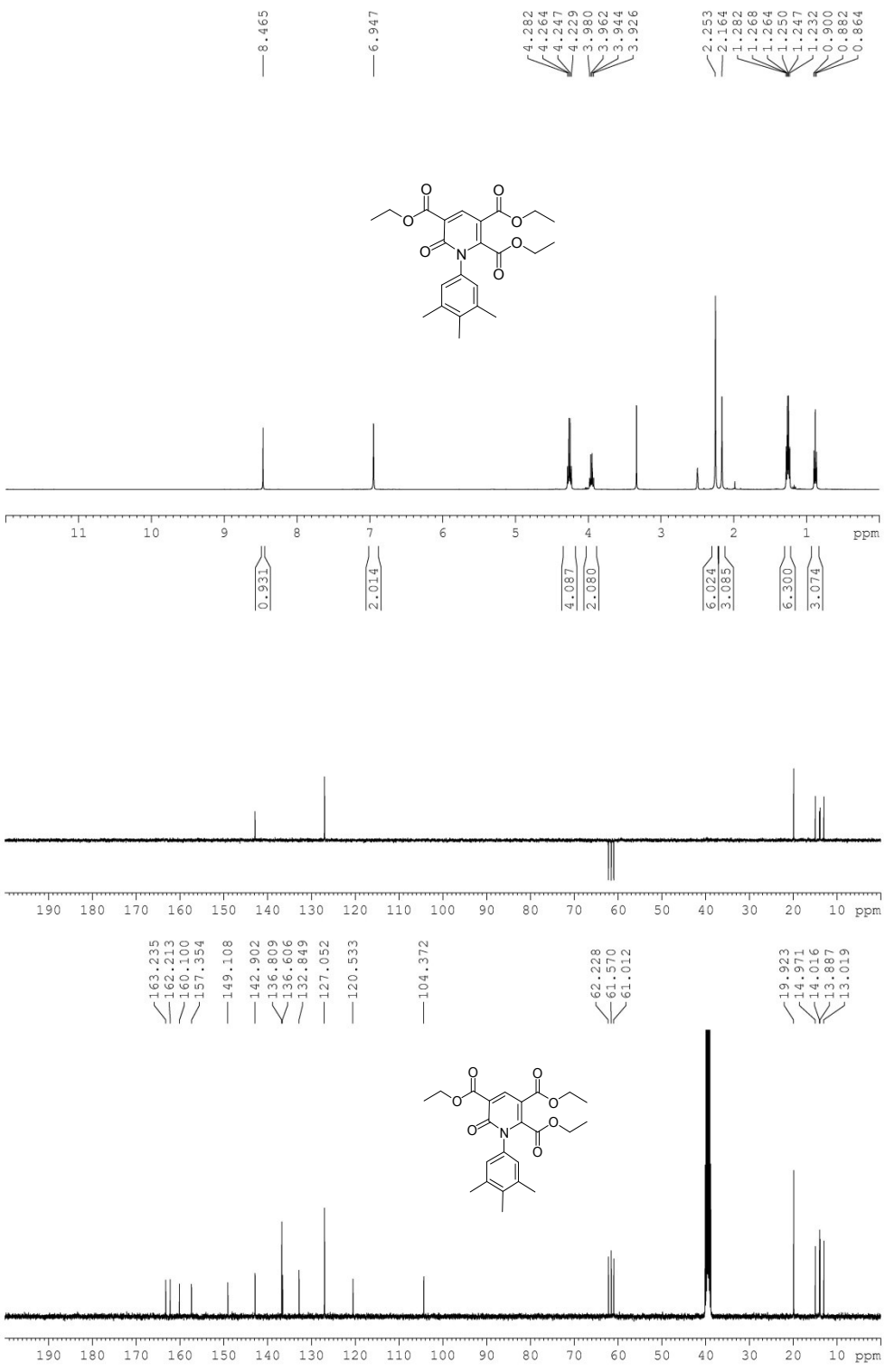


Figure S18. ^{1}H and ^{13}C NMR spectra of compound **4p**

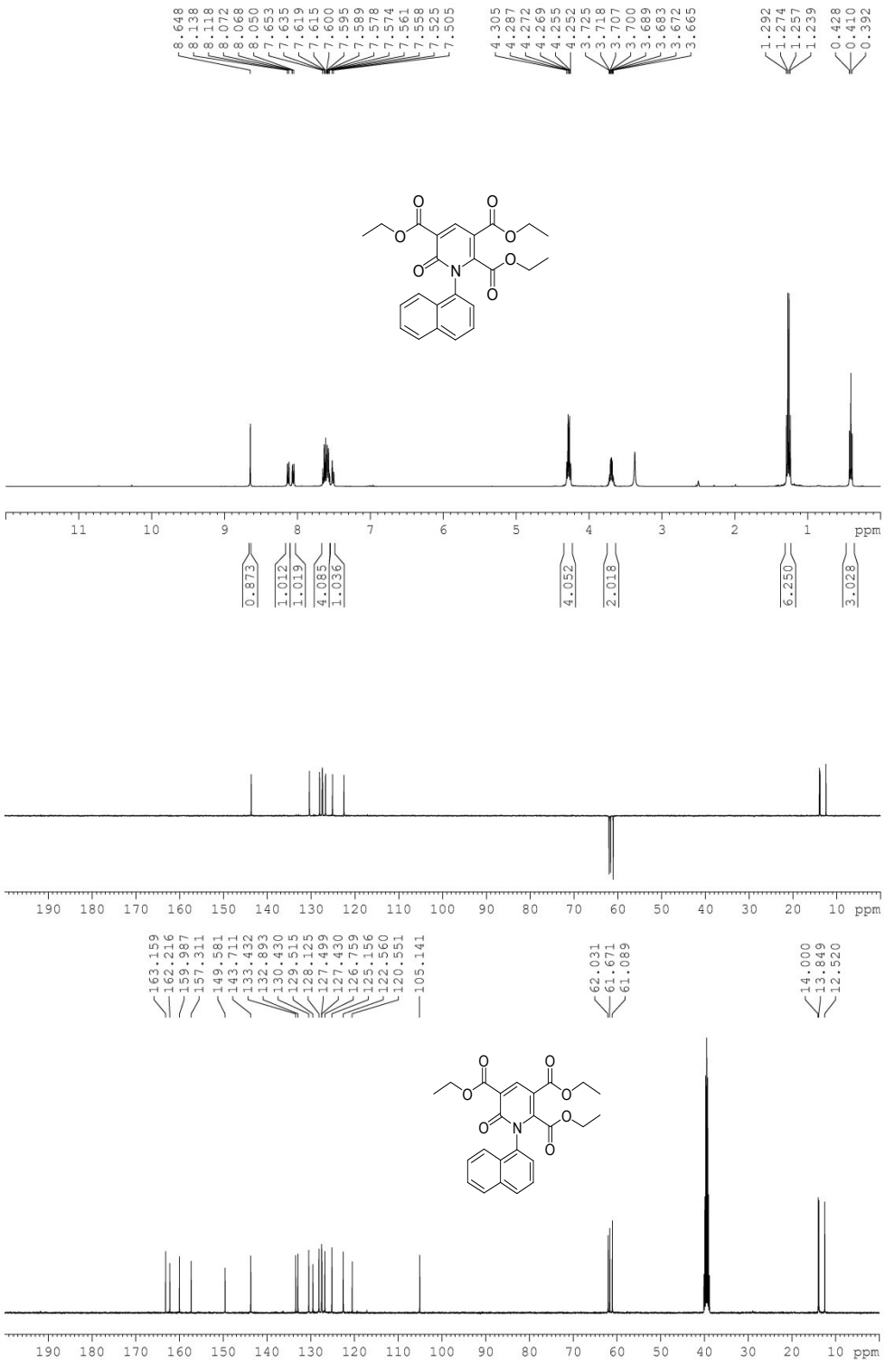


Figure S19. ^{1}H and ^{13}C NMR spectra of compound **4q**

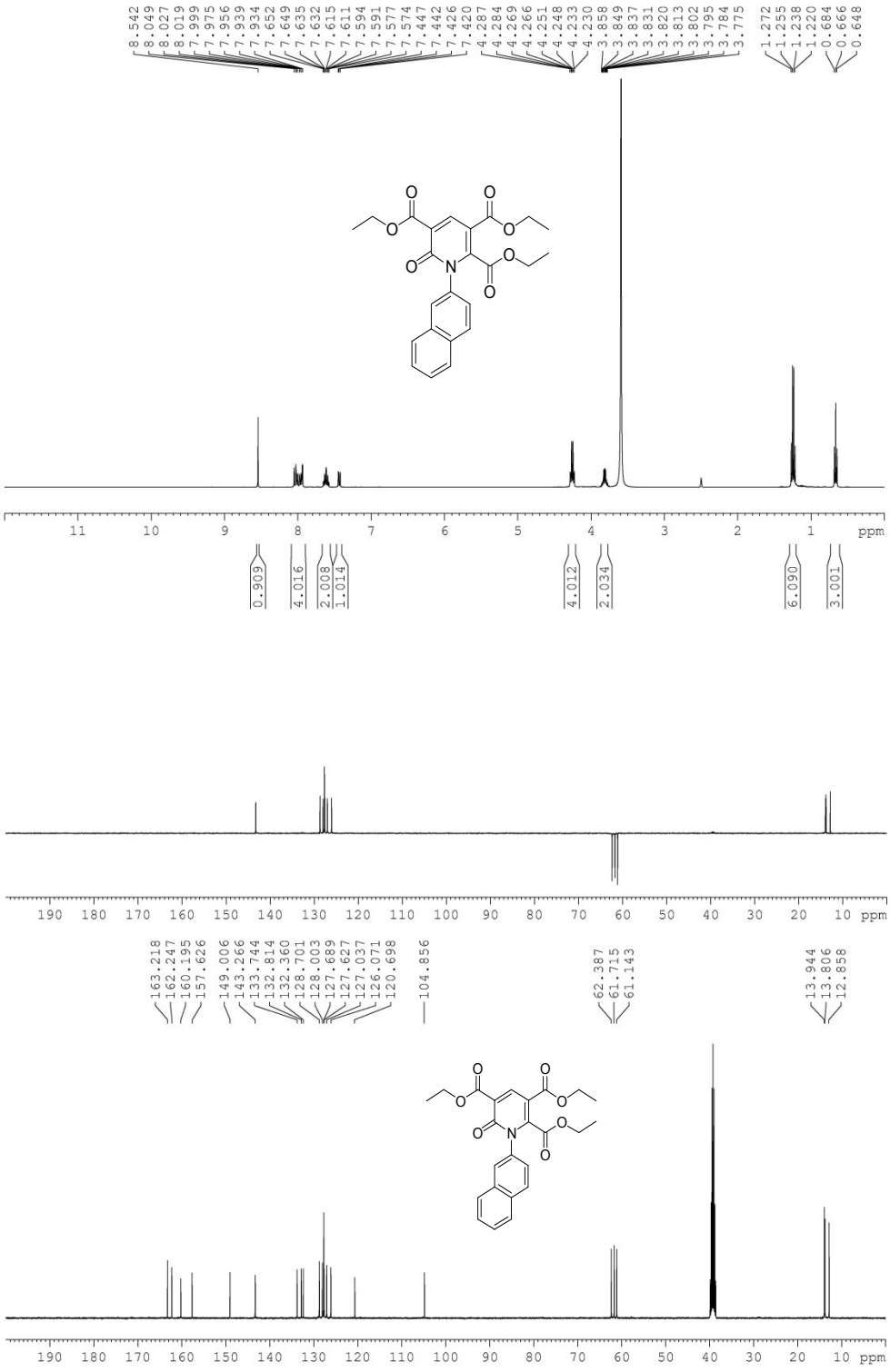


Figure S20. ^{1}H and ^{13}C NMR spectra of compound **4r**

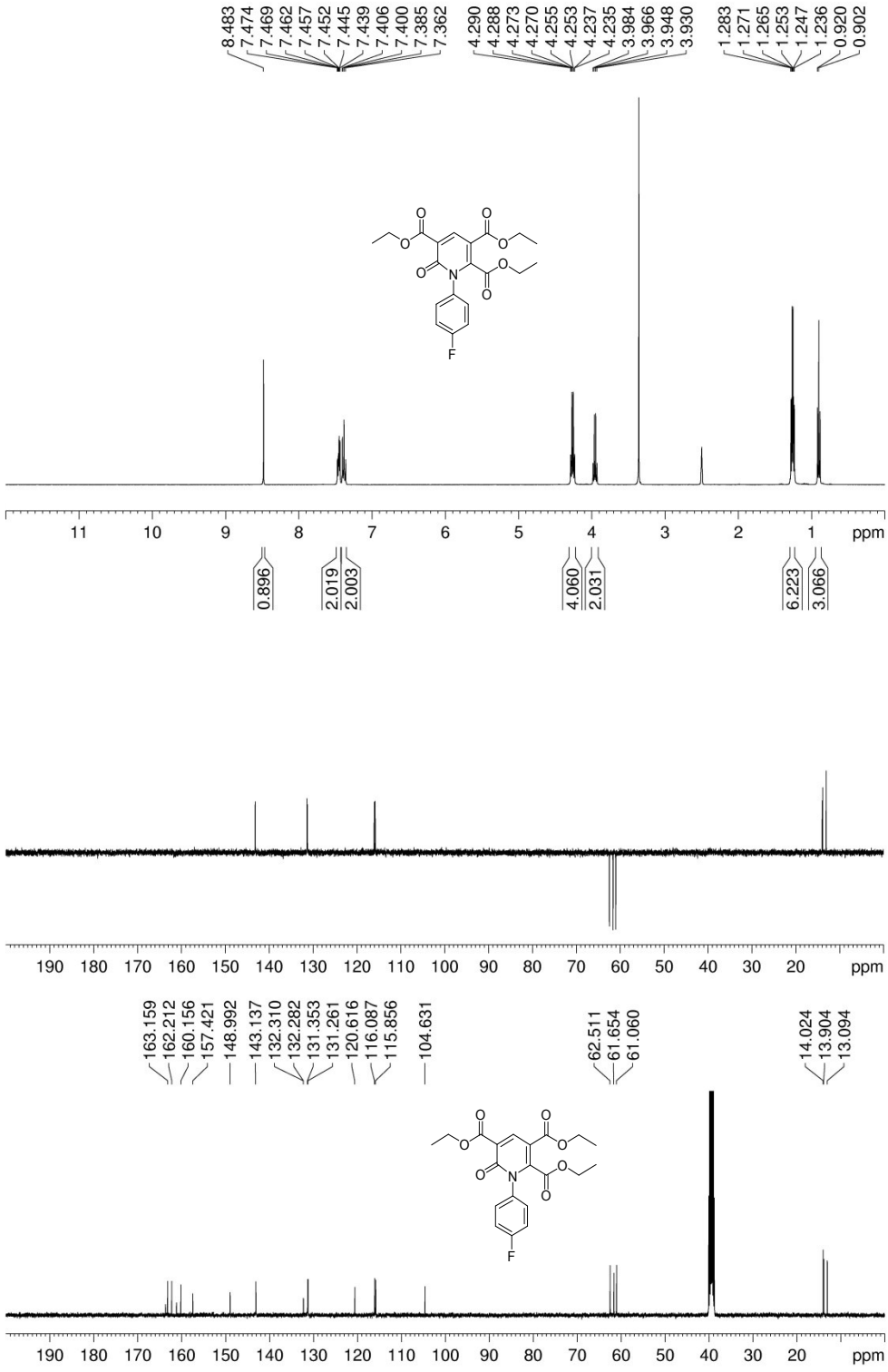


Figure S21. ^{1}H and ^{13}C NMR spectra of compound **4s**

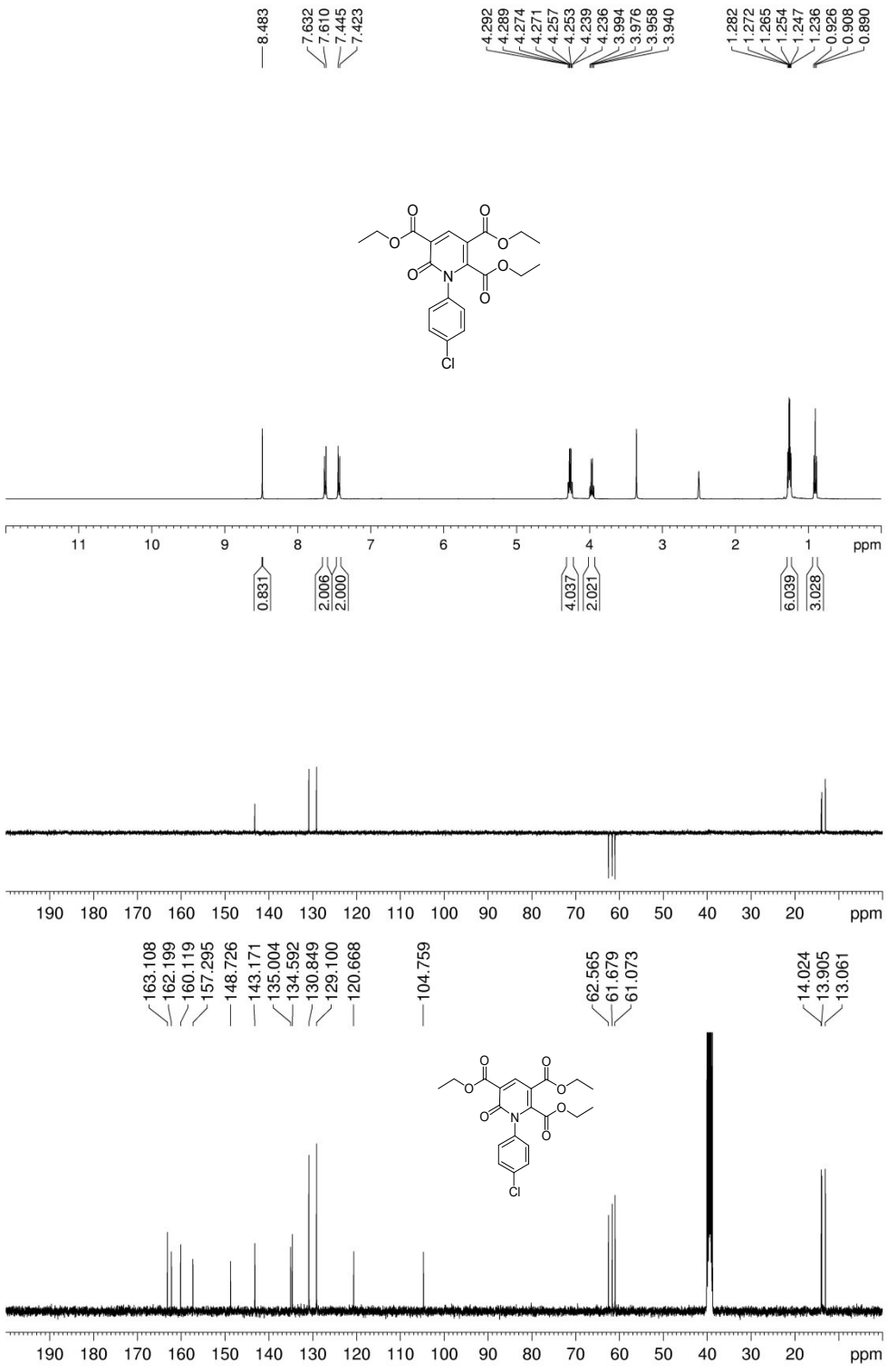


Figure S22. ^{1}H and ^{13}C NMR spectra of compound **4t**

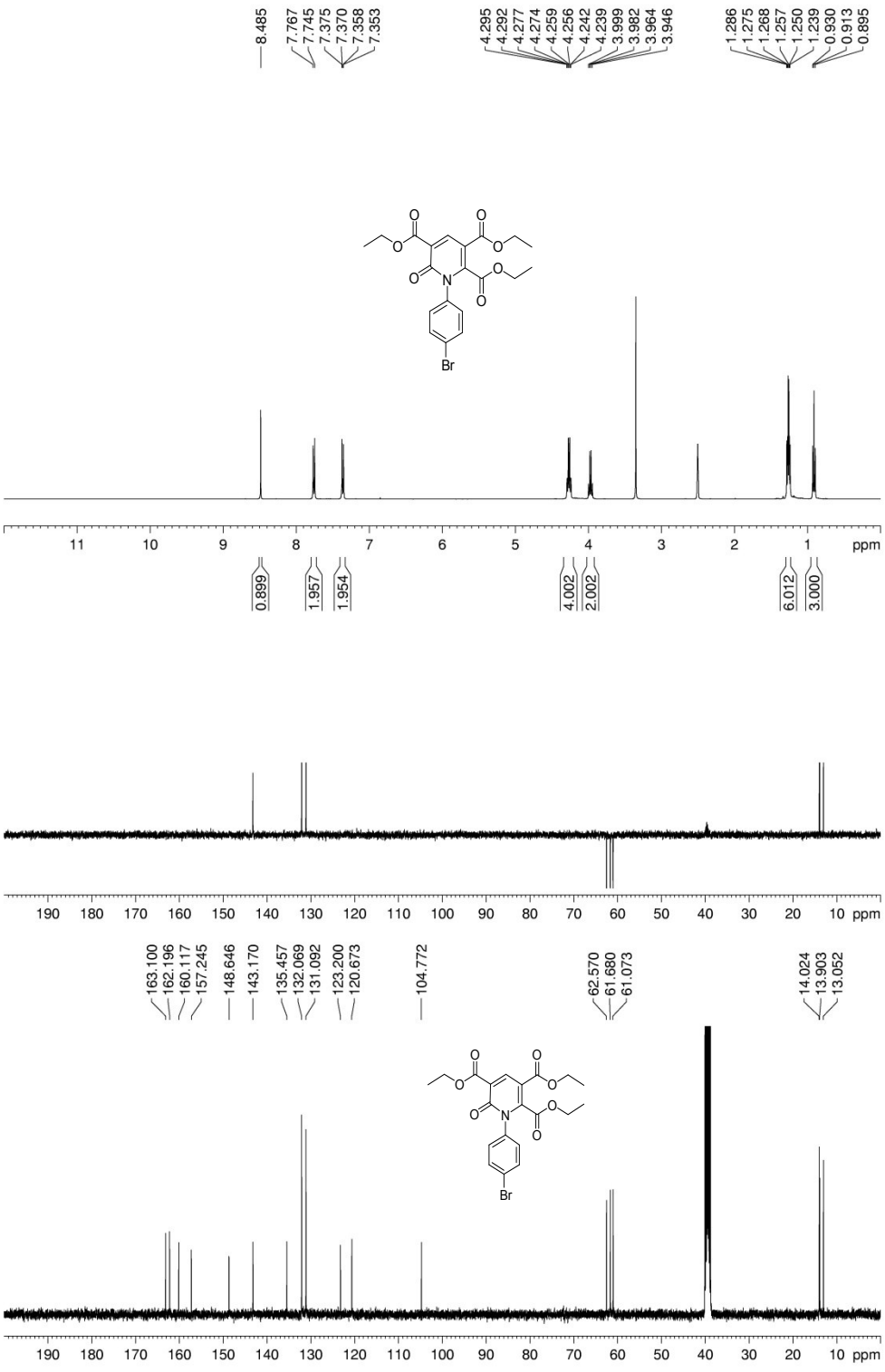


Figure 23. ^{1}H and ^{13}C NMR spectra of compound **4u**

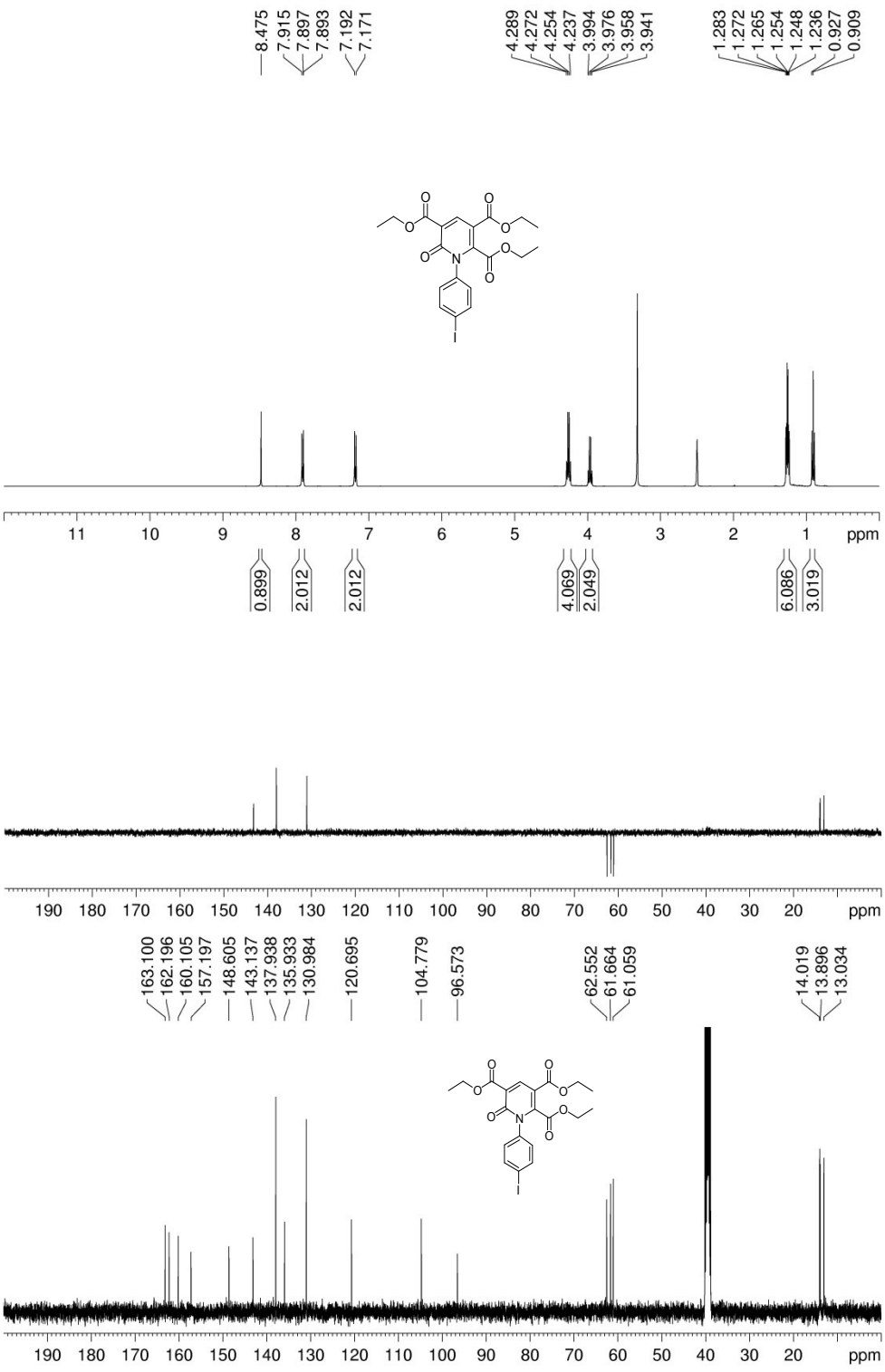


Figure S24. ^{1}H and ^{13}C NMR spectra of compound **4v**

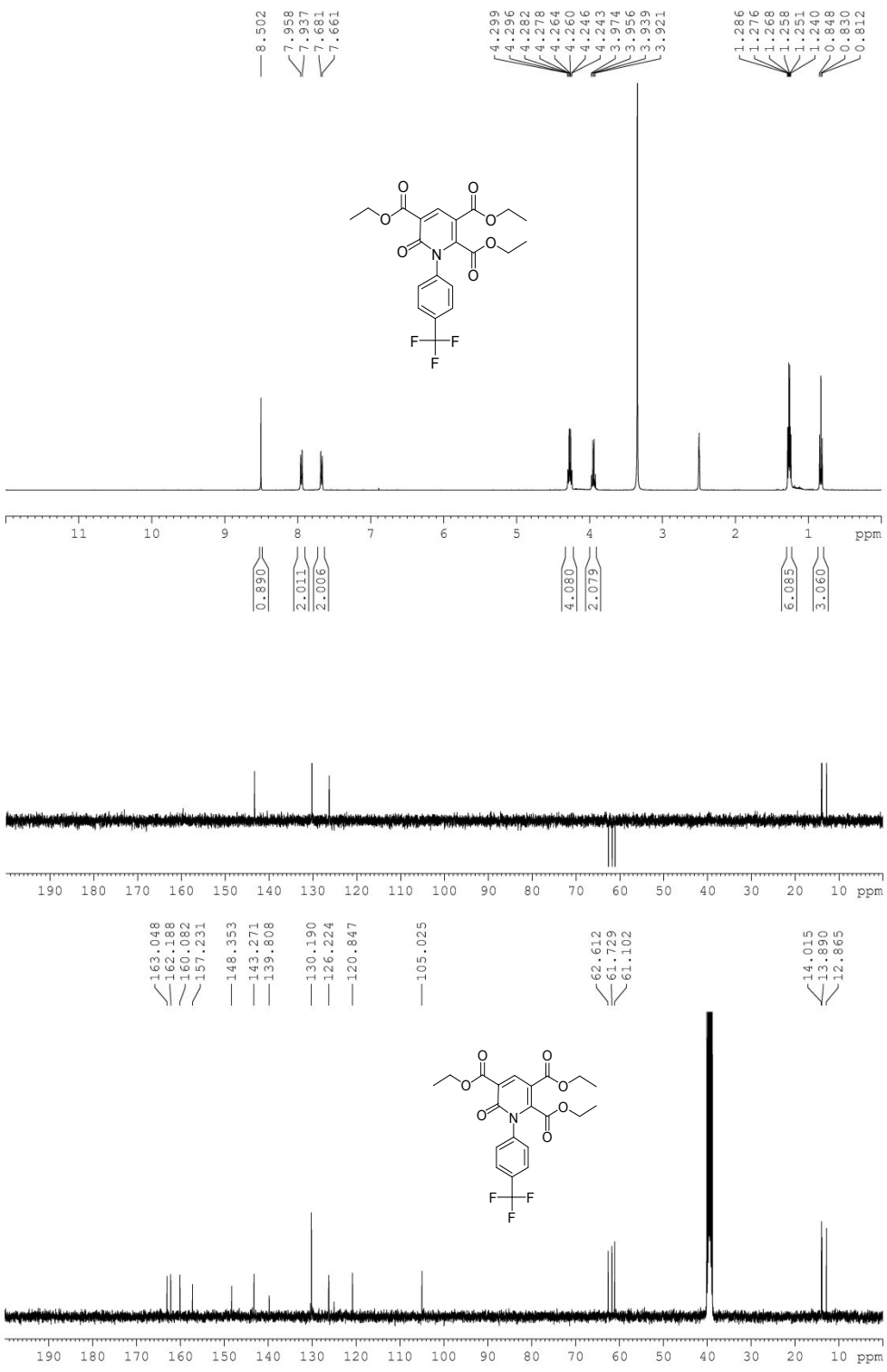


Figure S25. ^{1}H and ^{13}C NMR spectra of compound **4w**

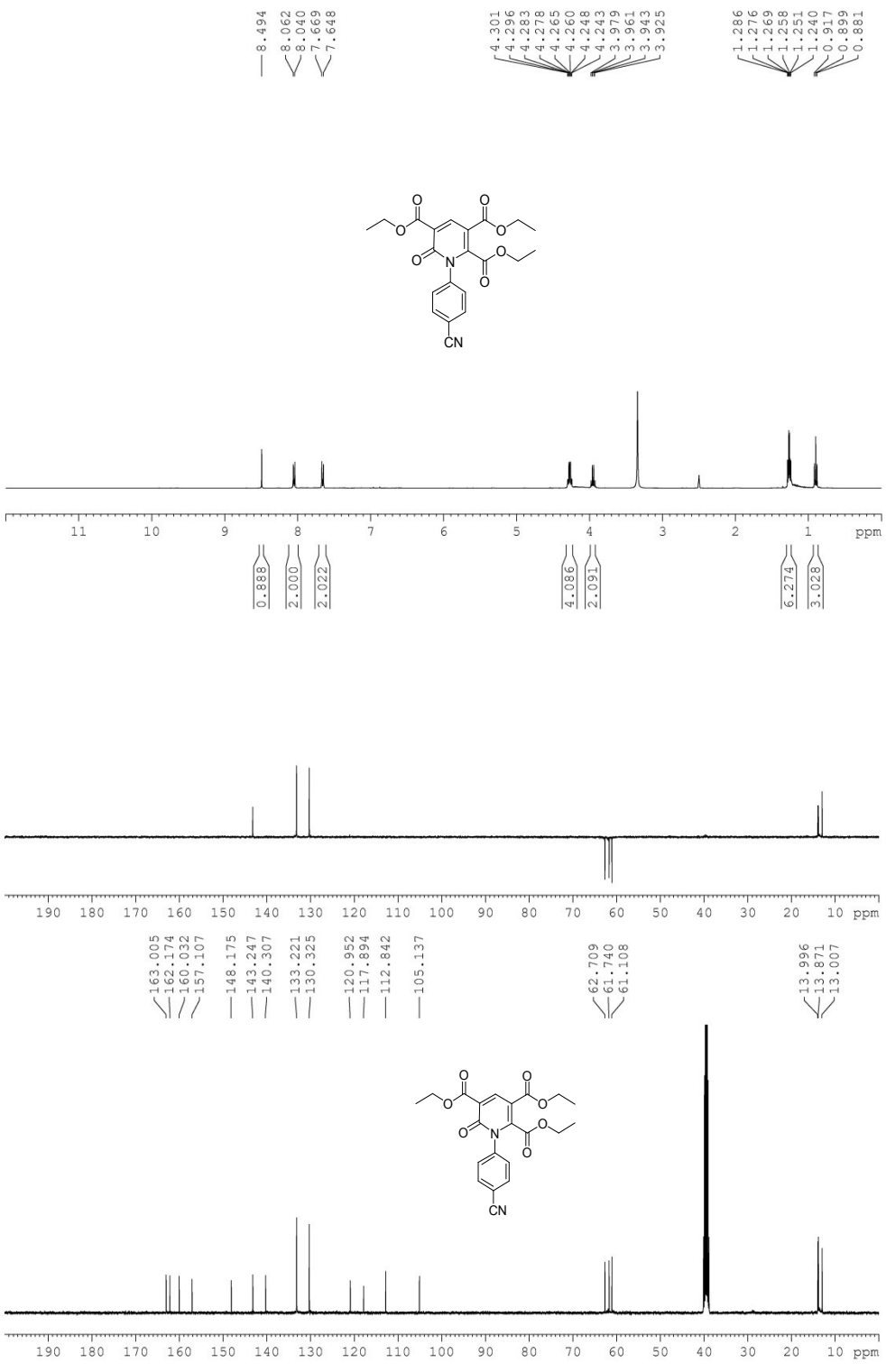


Figure S26. ^{1}H and ^{13}C NMR spectra of compound **4x**

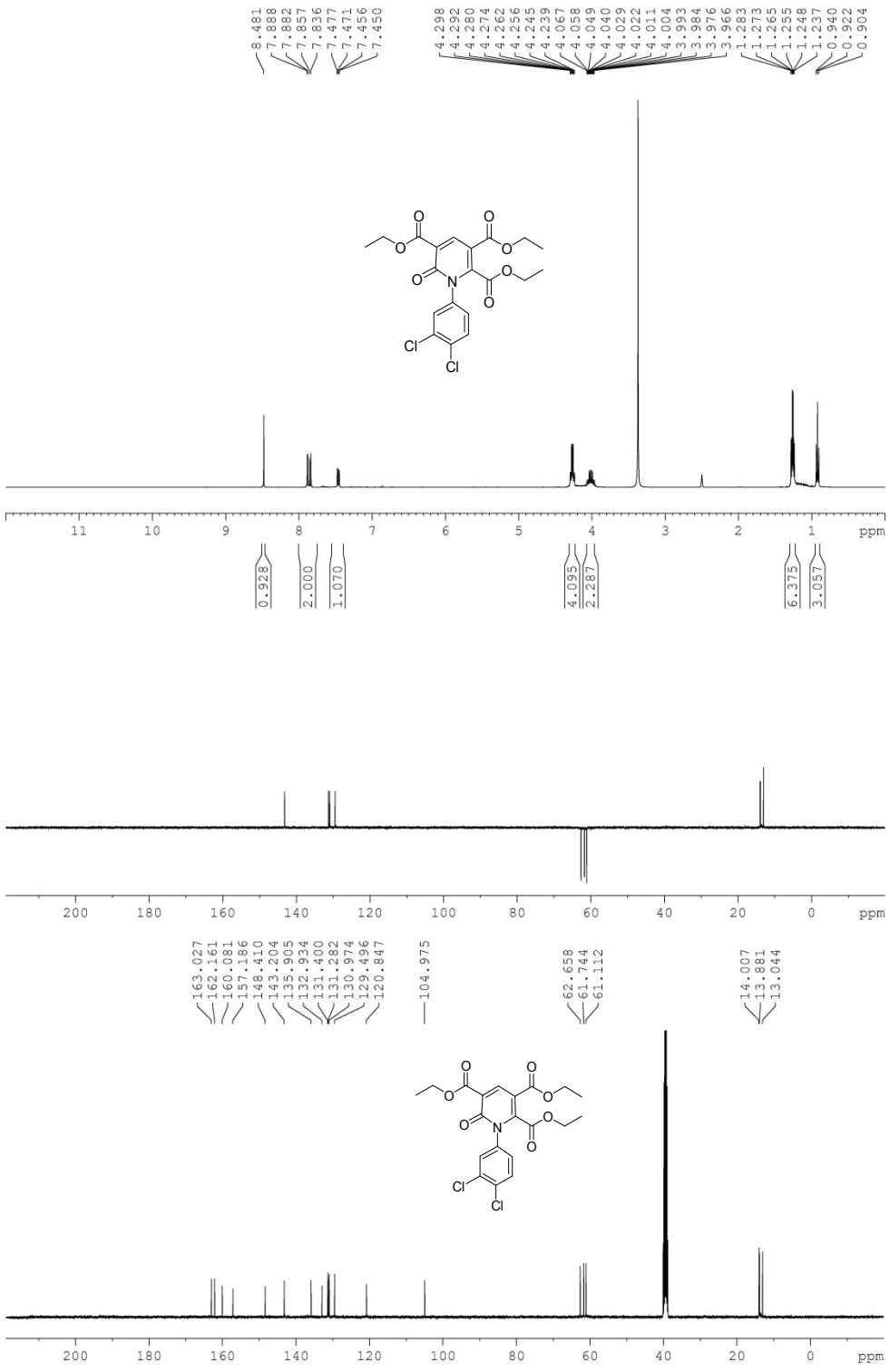


Figure S27. ^{1}H and ^{13}C NMR spectra of compound **4y**

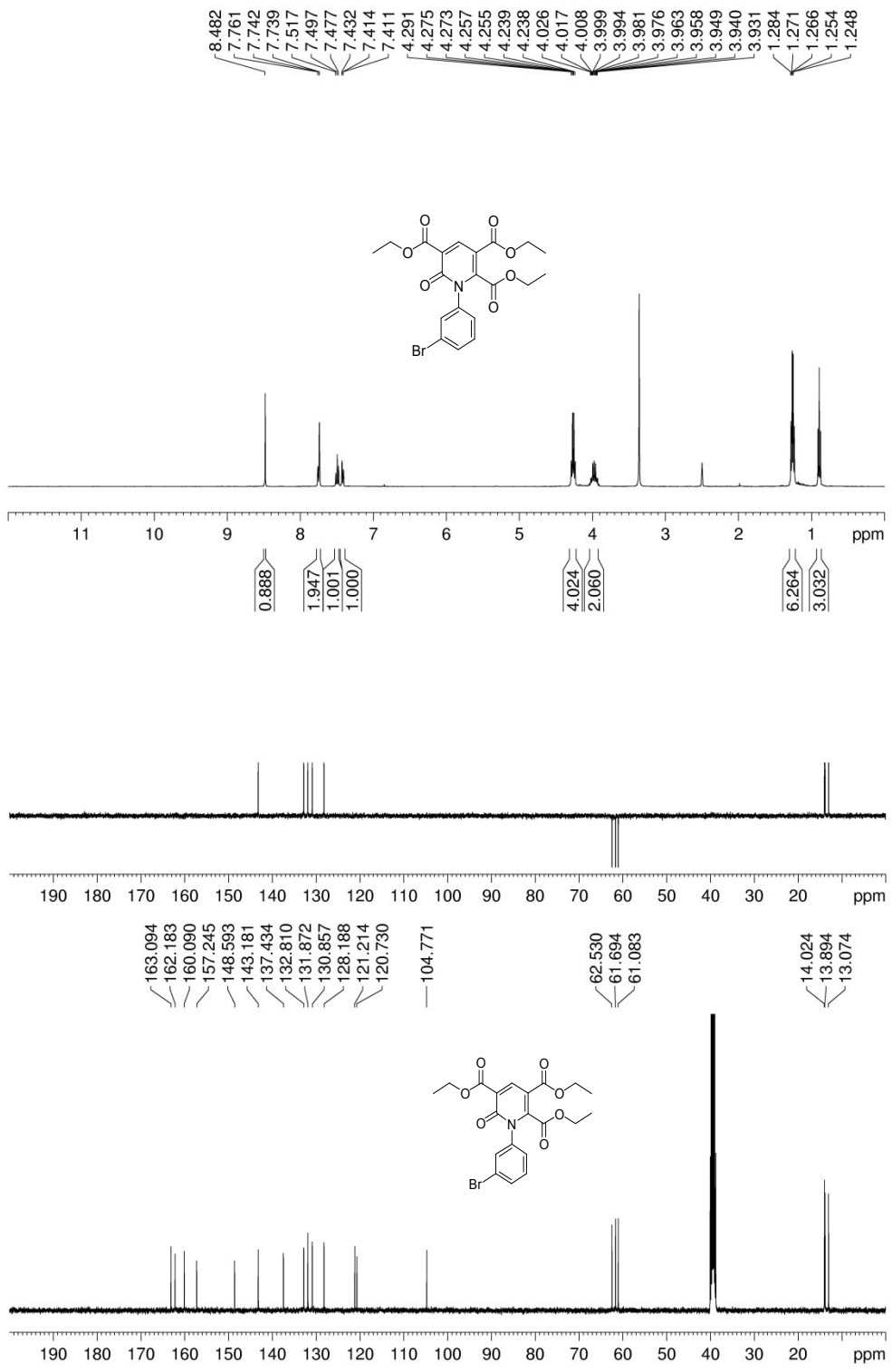


Figure S28. ^{1}H and ^{13}C NMR spectra of compound **4aa**

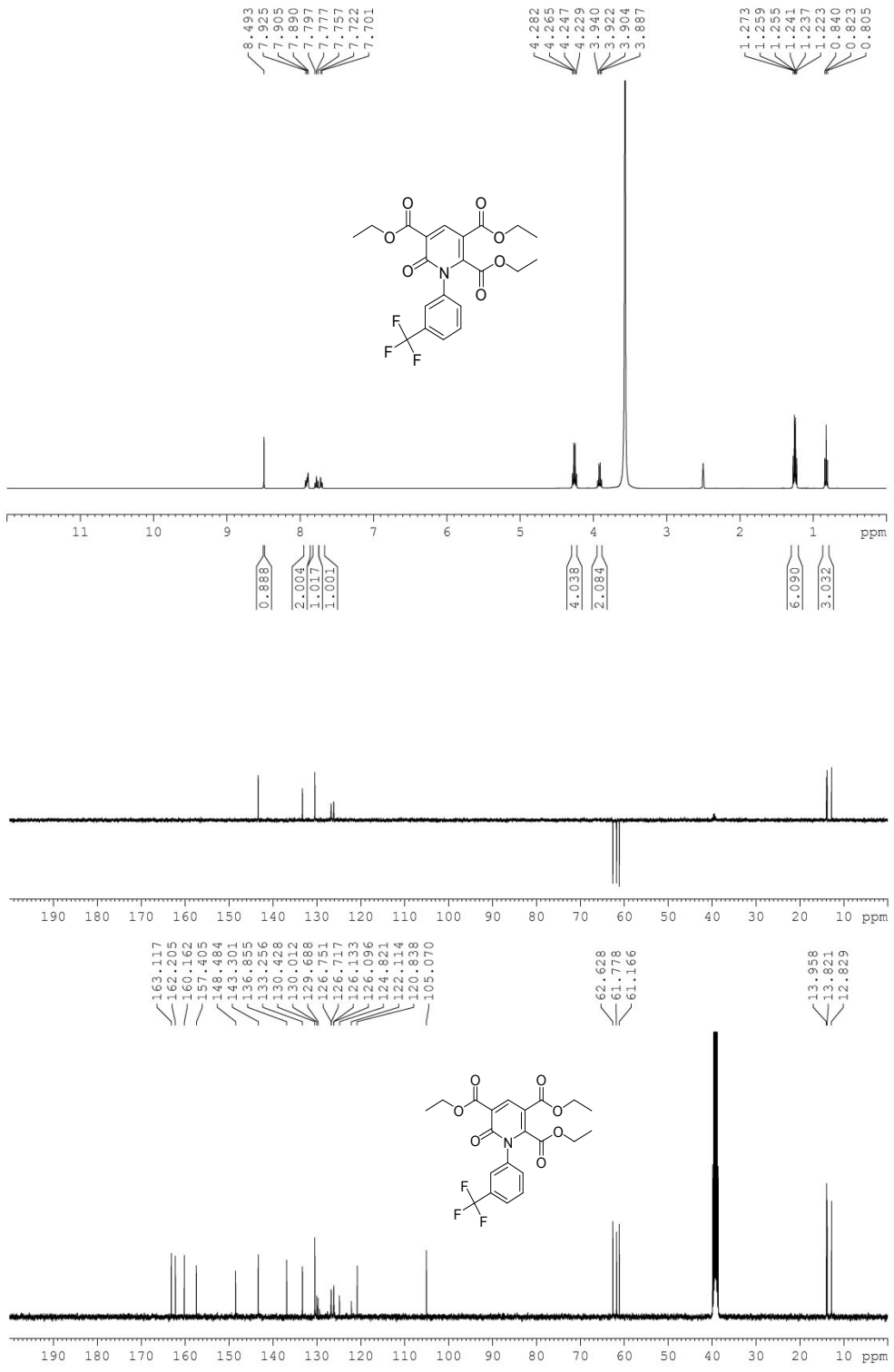


Figure S29. ^{1}H and ^{13}C NMR spectra of compound **4bb**

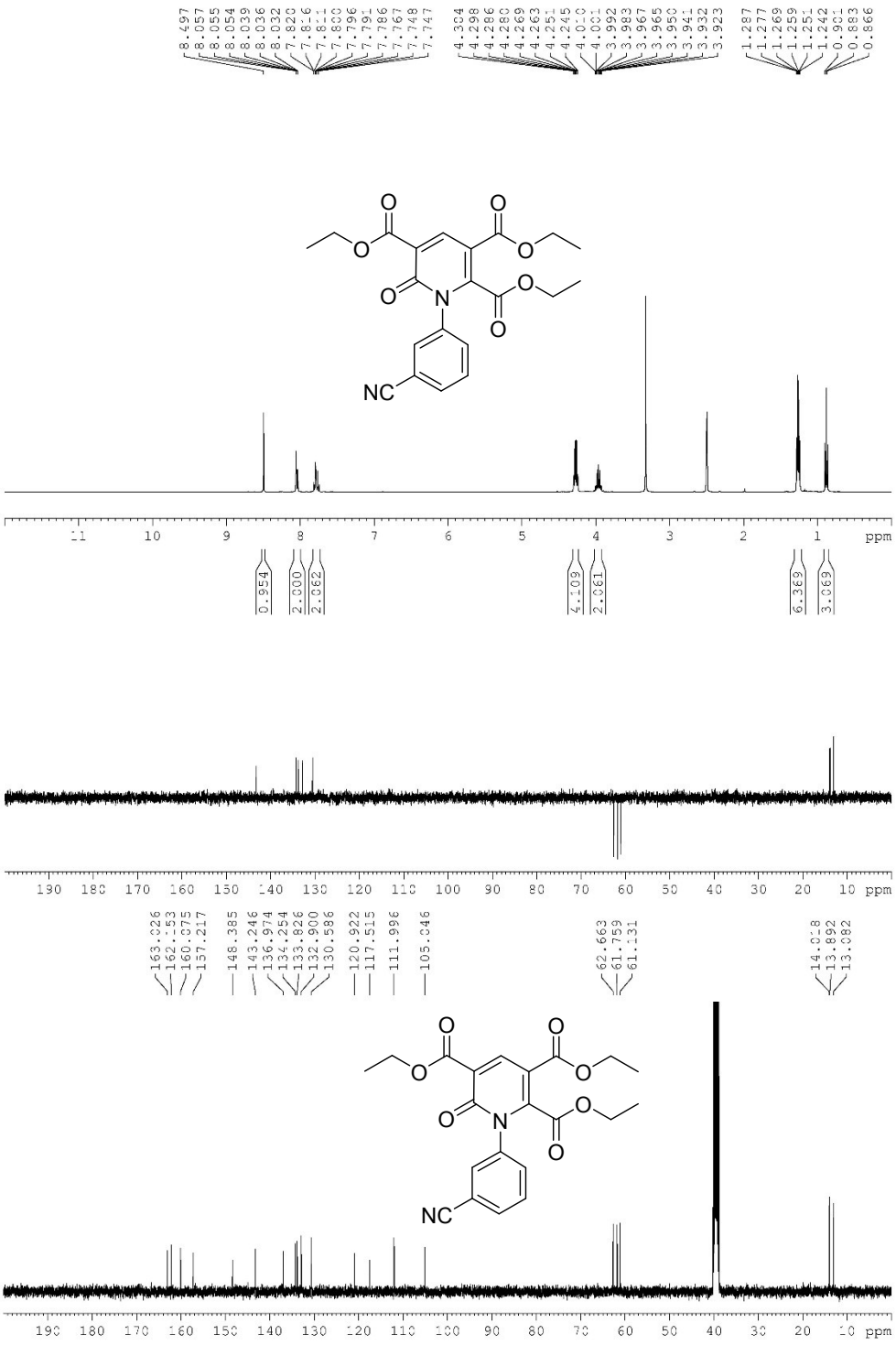


Figure S30. ^{1}H and ^{13}C NMR spectra of compound **4cc**

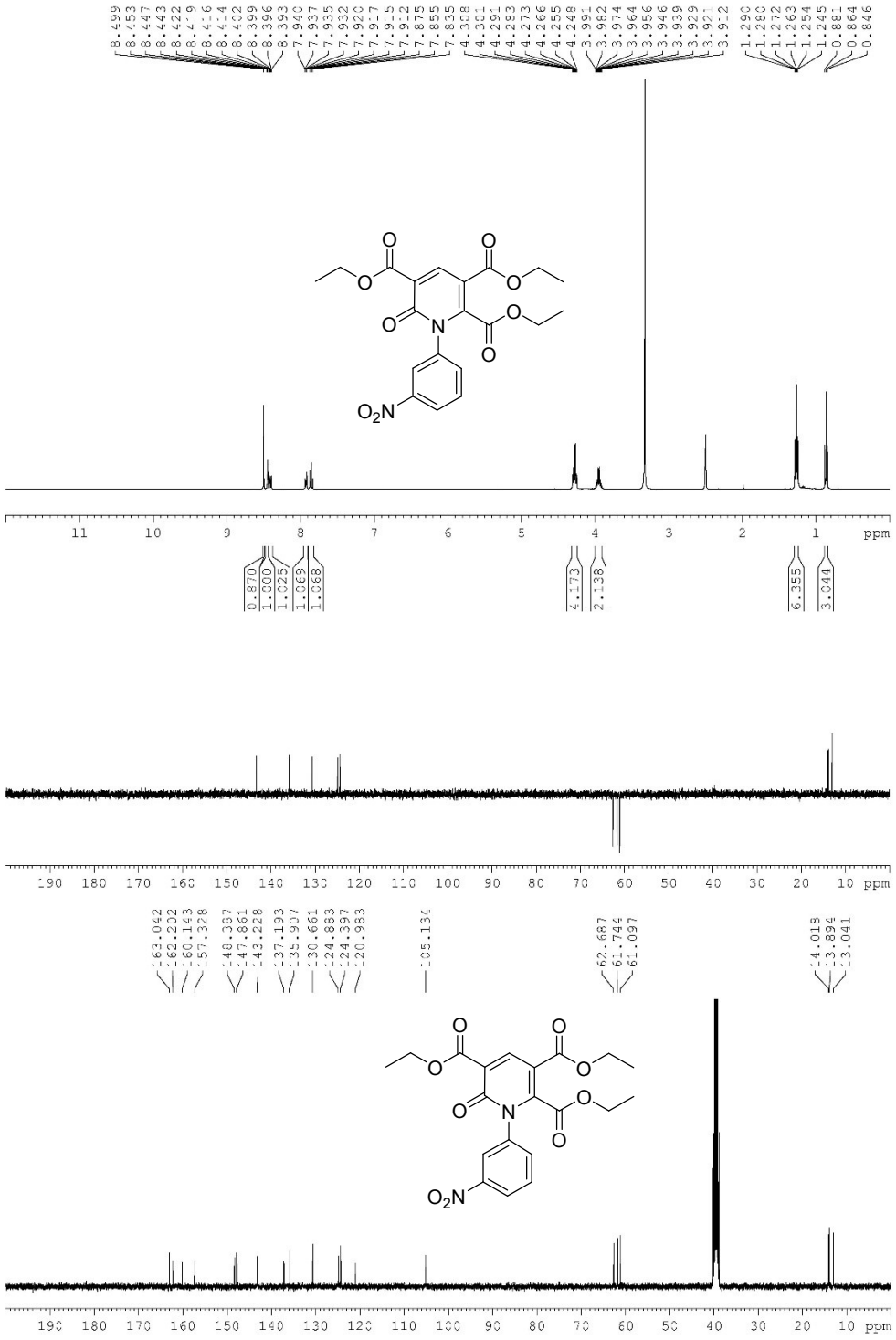


Figure S31. ^{1}H and ^{13}C NMR spectra of compound **4dd**

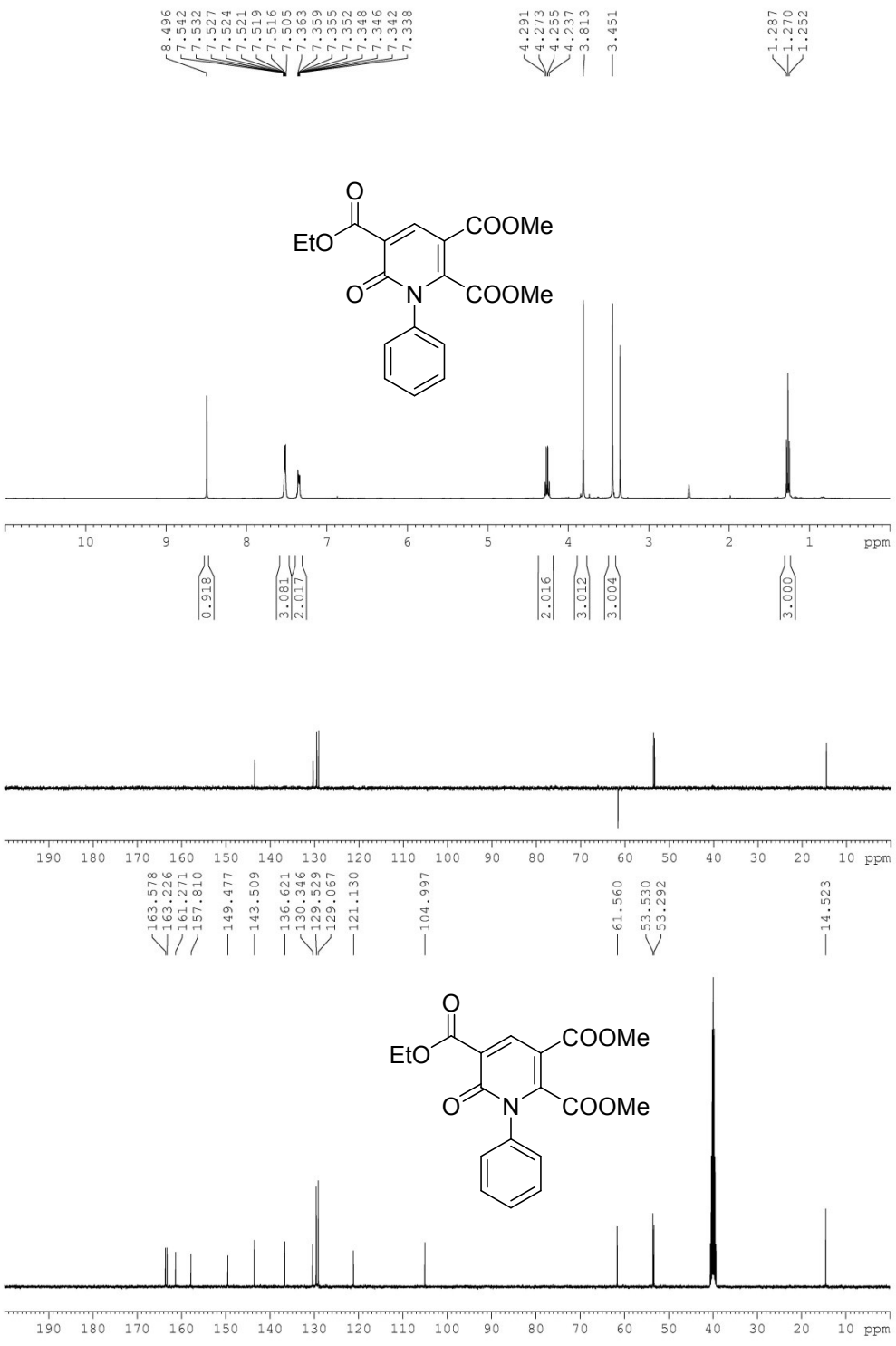


Figure S32. ^{1}H and ^{13}C NMR spectra of compound **4ee**

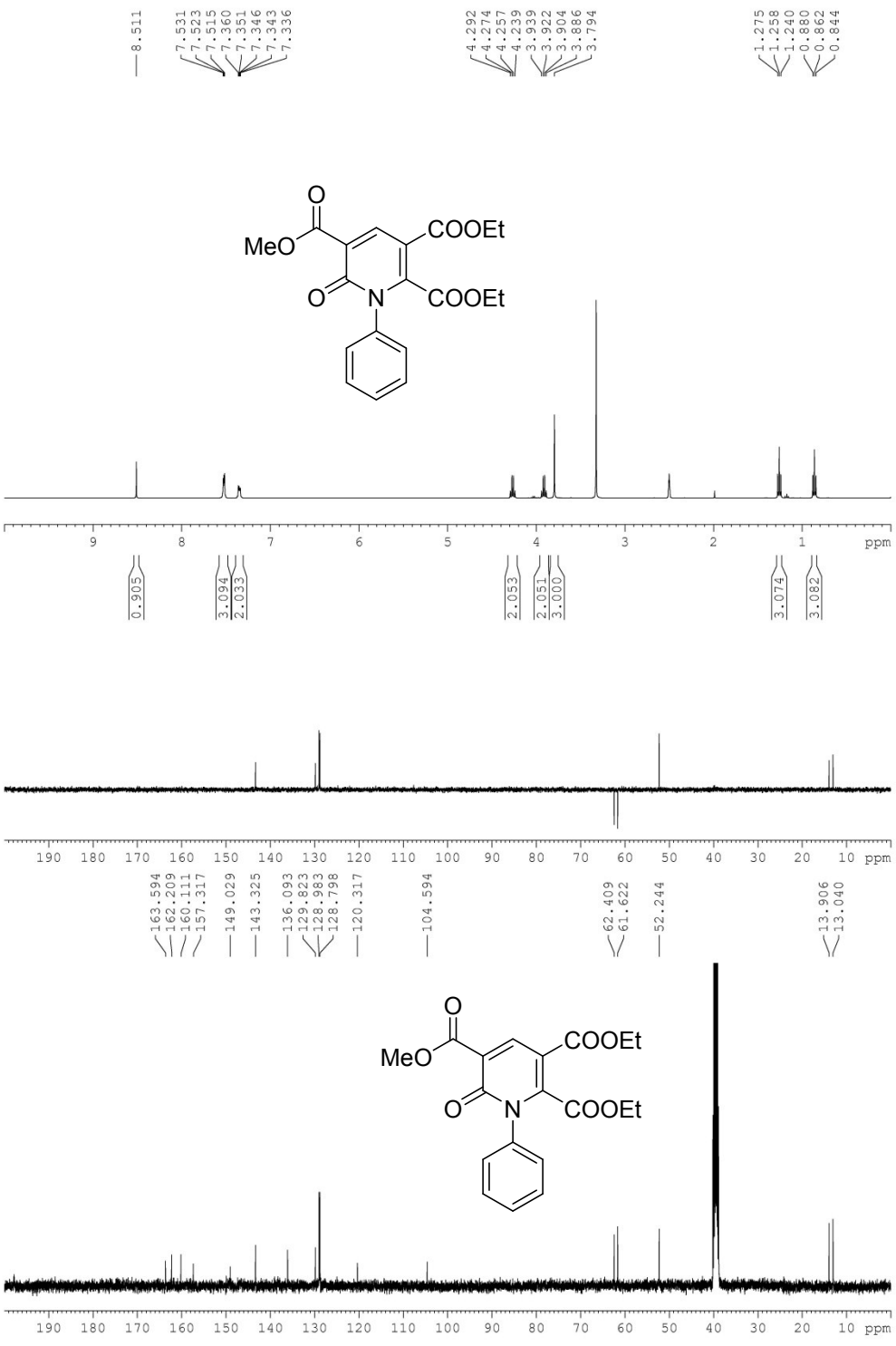


Figure S33. ^{1}H and ^{13}C NMR spectra of compound **4ff**

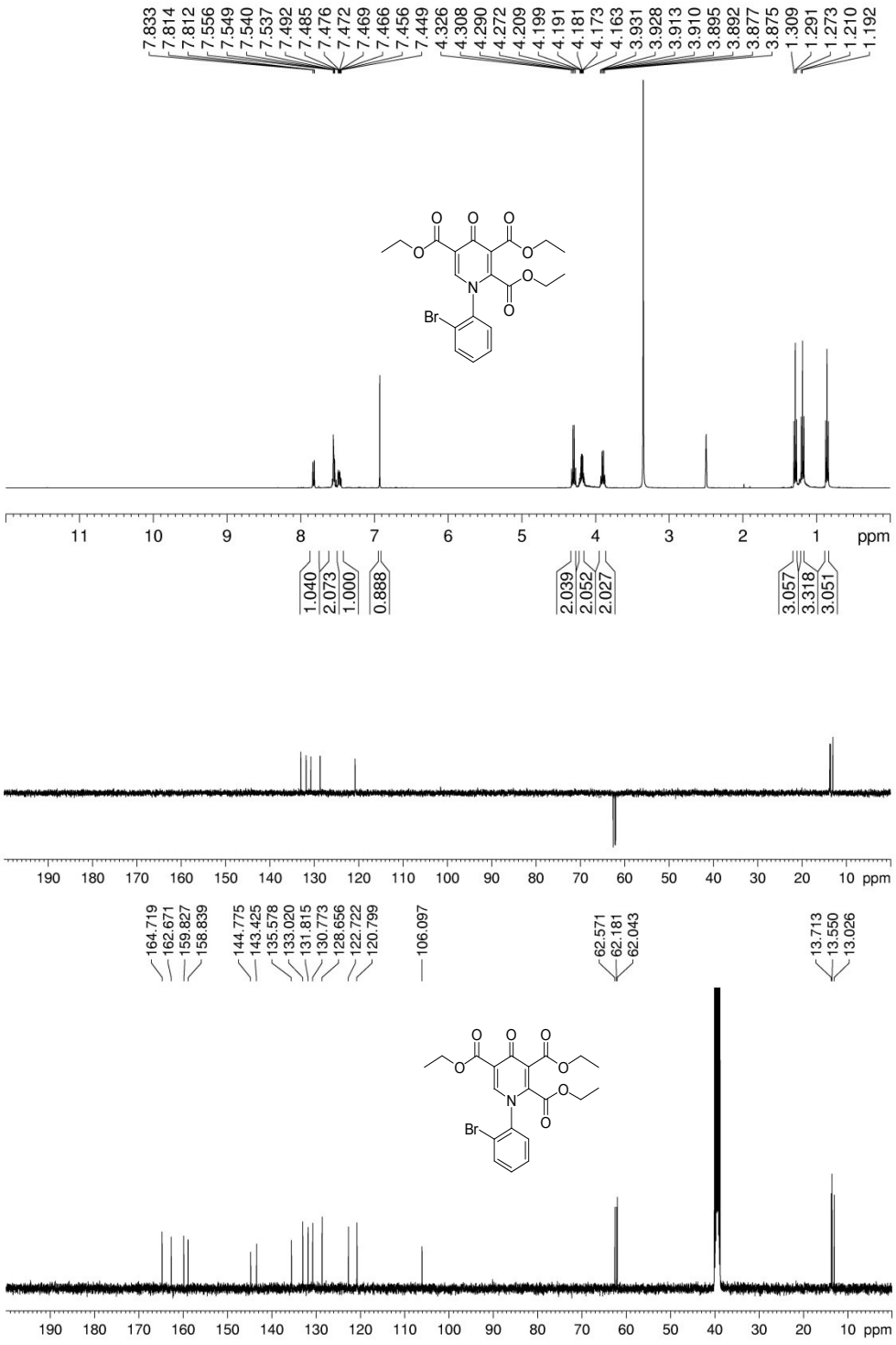


Figure S34. ^{1}H and ^{13}C NMR spectra of compound **6a**

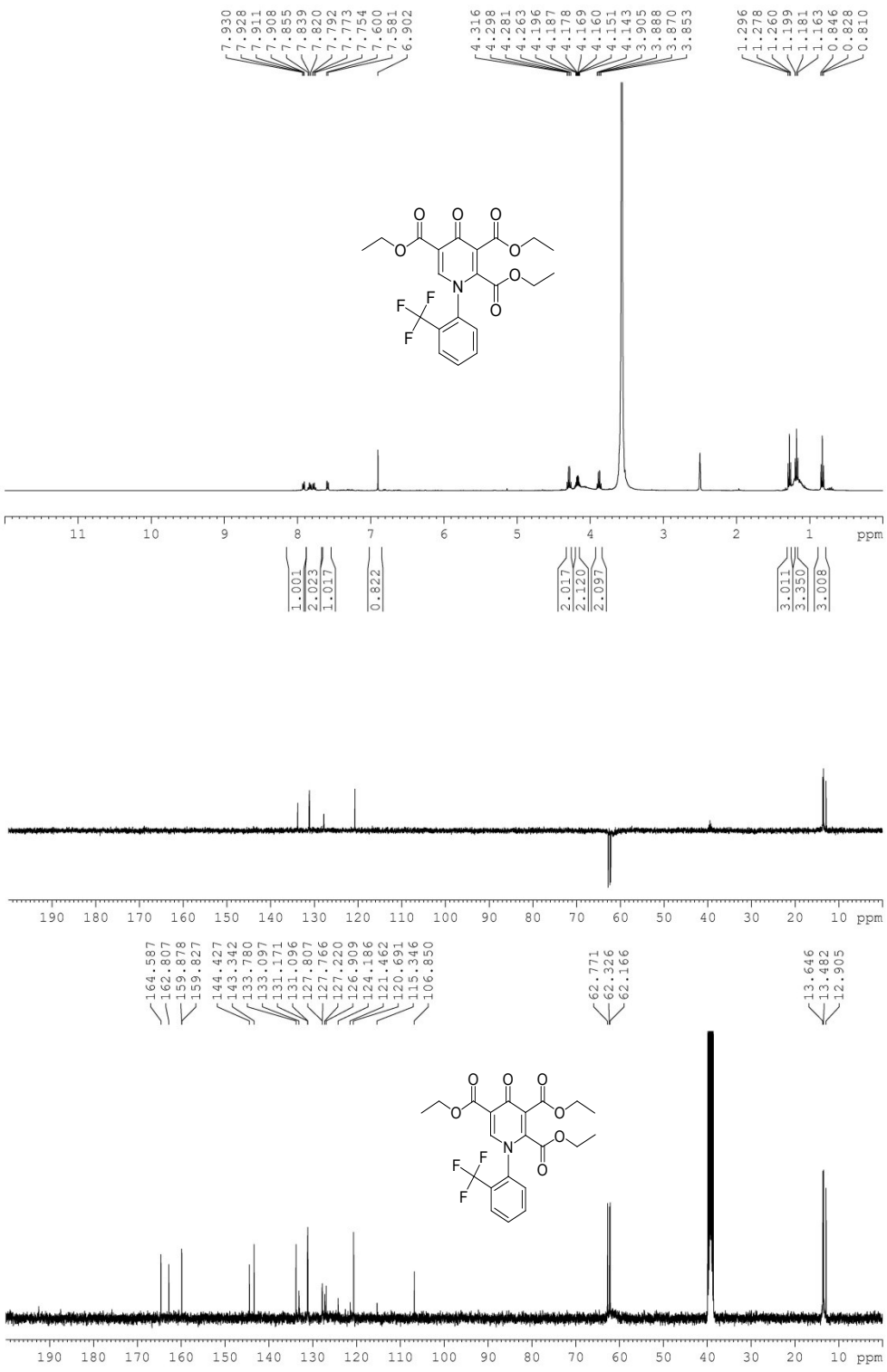


Figure S35. ^{1}H and ^{13}C NMR spectra of compound **6b**

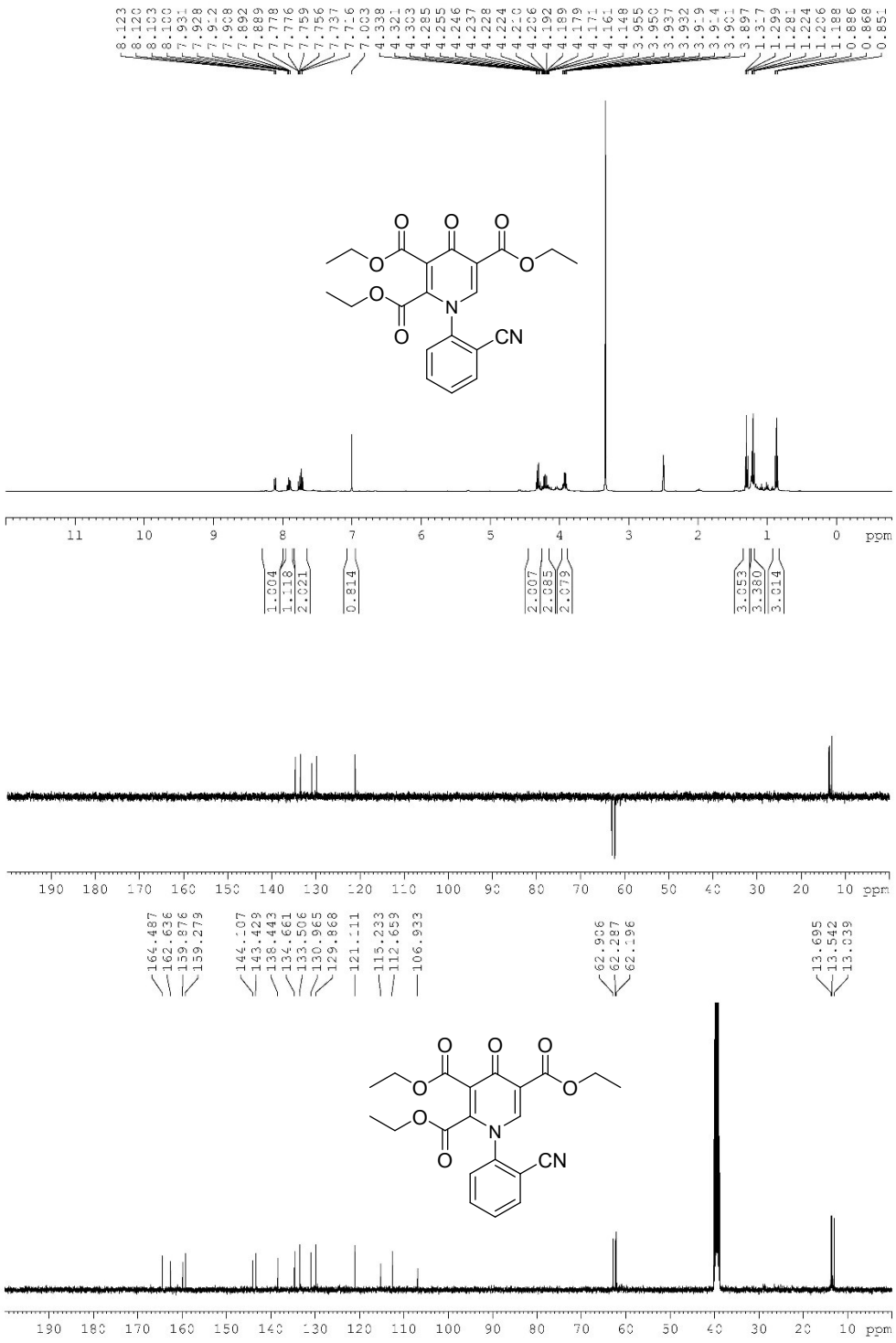
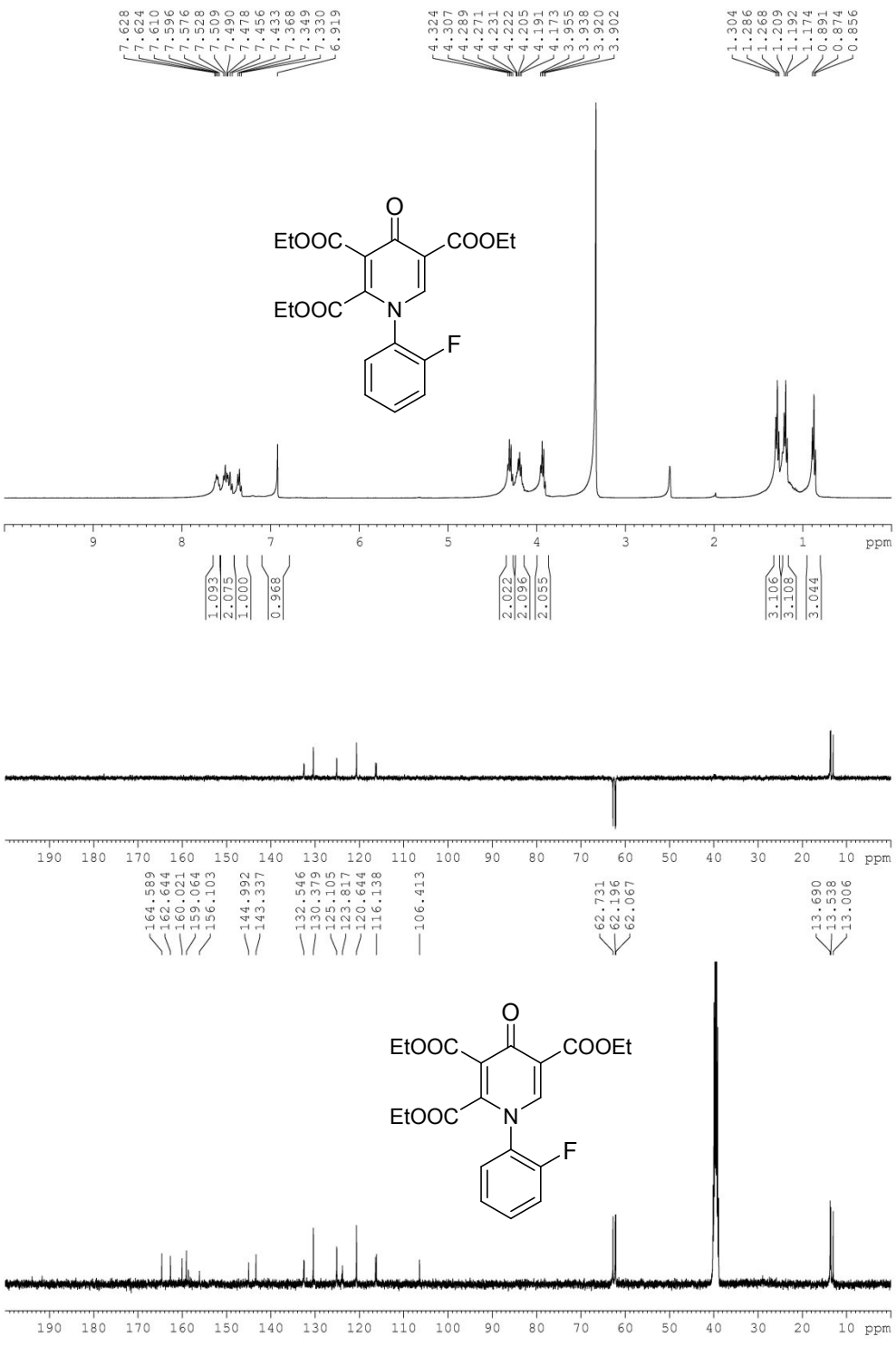


Figure S36. ^{1}H and ^{13}C NMR spectra of compound **6c**


7.628
7.624
7.610
7.596
7.576
7.528
7.509
7.490
7.478
7.456
7.433
7.368
7.349
7.330
6.919
4.324
4.307
4.289
4.271
4.231
4.222
4.205
4.191
4.173
3.955
3.938
3.920
3.902
1.304
1.286
1.268
1.209
1.192
1.174
0.891
0.874
0.856
O
EtOOC
COOEt
EtOOC
N
F
ppm
1.093
2.075
1.000
0.968
2.022
2.096
2.055
3.106
3.108
3.044
ppm
164.589
162.644
160.021
159.064
156.103
144.992
143.337
132.546
130.379
125.105
123.817
120.644
116.138
106.413
62.731
62.196
62.067
13.690
13.538
13.006
O
EtOOC
COOEt
EtOOC
N
F
ppm

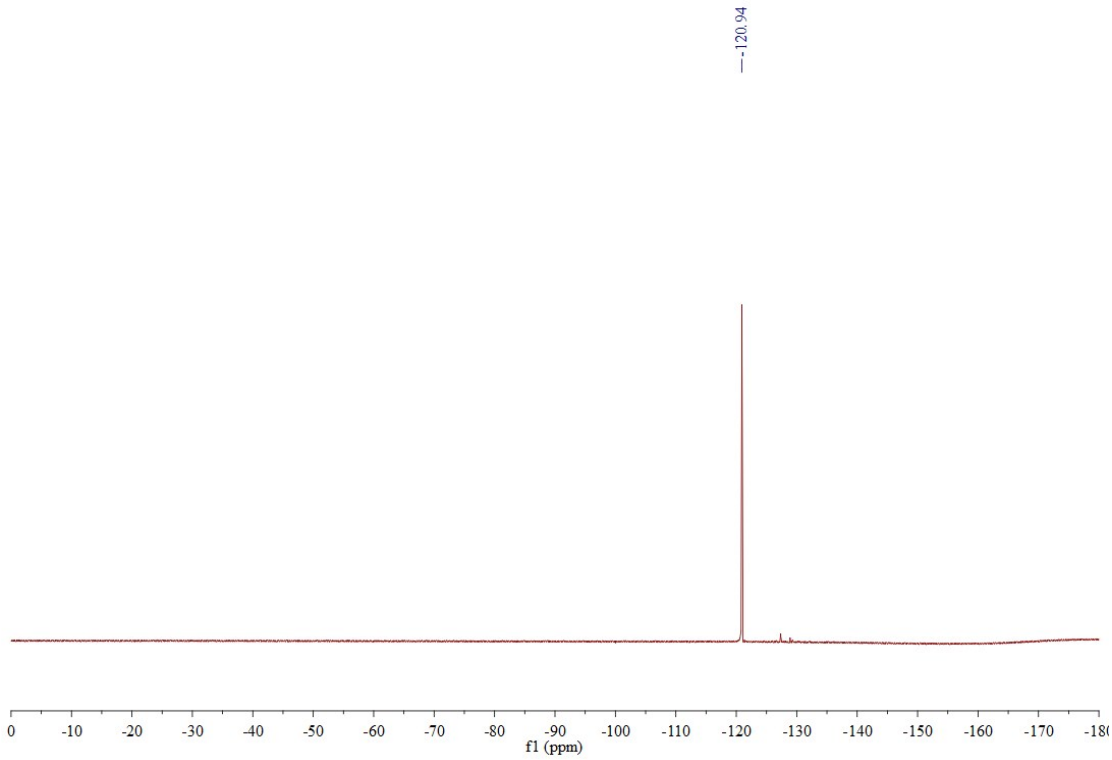


Figure S37. ^{1}H, ^{13}C and ^{19}F NMR spectra of compound **6d**

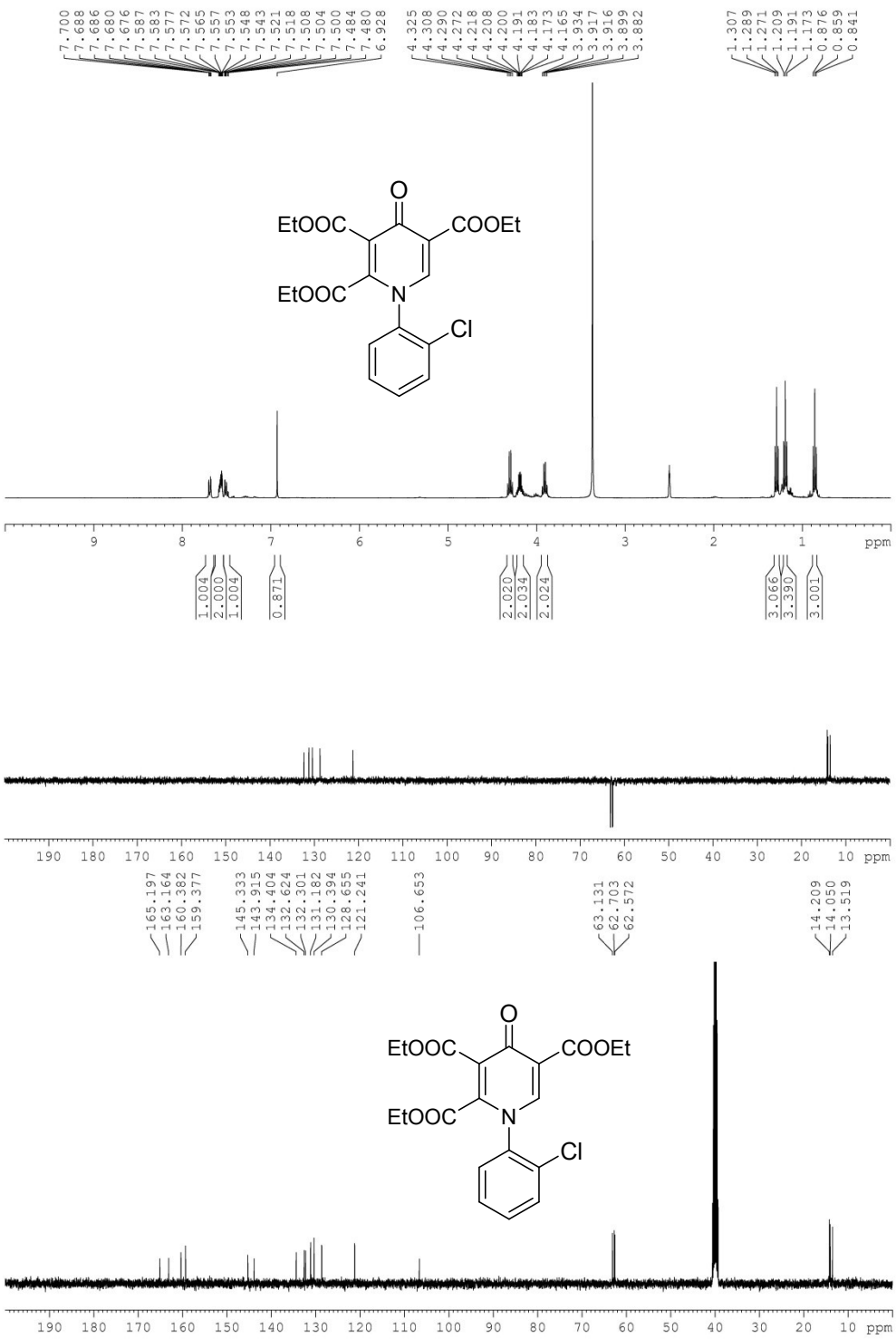
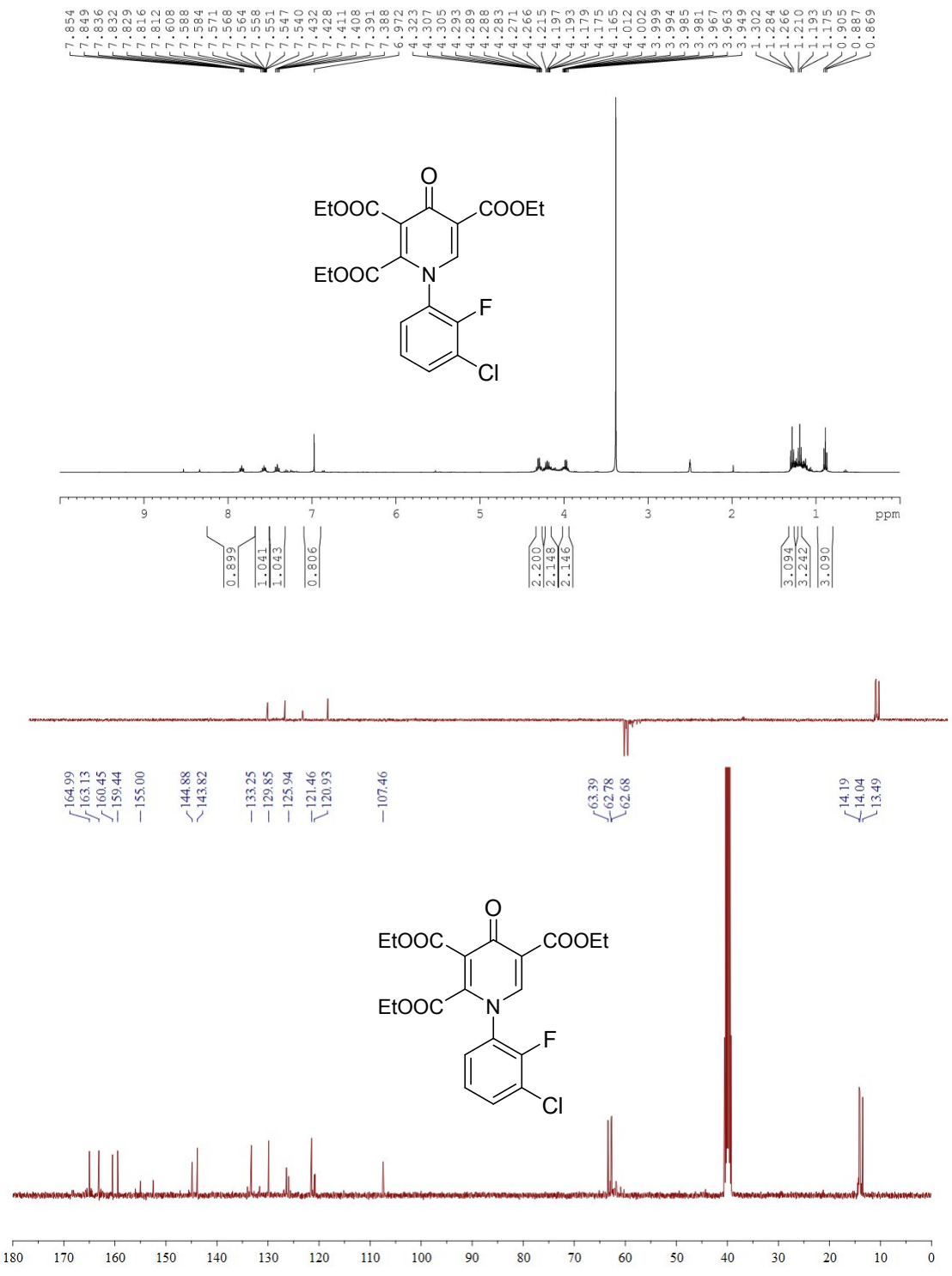


Figure S38. ^{1}H and ^{13}C NMR spectra of compound **6e**

Figure S39. ^{1}H and ^{13}C NMR spectra of compound **6f**


7.854
7.849
7.836
7.832
7.829
7.816
7.812
7.608
7.588
7.584
7.571
7.568
7.564
7.558
7.551
7.547
7.540
7.432
7.428
7.411
7.408
7.391
7.388
6.972
4.323
4.307
4.305
4.293
4.289
4.288
4.283
4.271
4.266
4.215
4.197
4.193
4.179
4.175
4.165
4.012
4.002
3.999
3.994
3.985
3.981
3.967
3.963
3.949
1.302
1.284
1.266
1.210
1.193
1.175
0.905
0.887
0.869
O
EtOOC
COOEt
EtOOC
N
F
Cl
9
8
7
6
5
4
3
2
1
ppm
0.899
1.041
1.043
0.806
2.200
2.148
2.146
3.094
3.242
3.090
164.99
163.13
160.45
159.44
155.00
144.88
143.82
133.25
129.85
125.94
121.46
120.93
107.46
63.39
62.78
62.68
14.19
14.04
13.49
O
EtOOC
COOEt
EtOOC
N
F
Cl
180
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150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

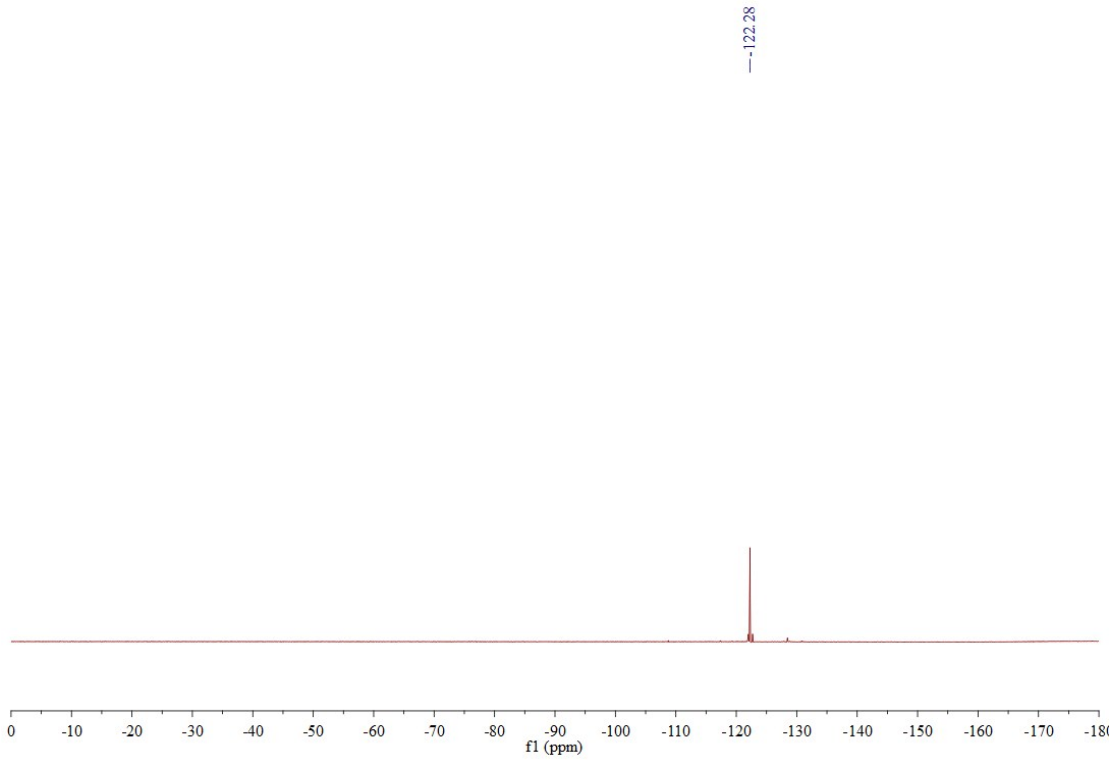

Figure S40. ^{1}H, ^{13}C and ^{19}F NMR spectra of compound **6g**

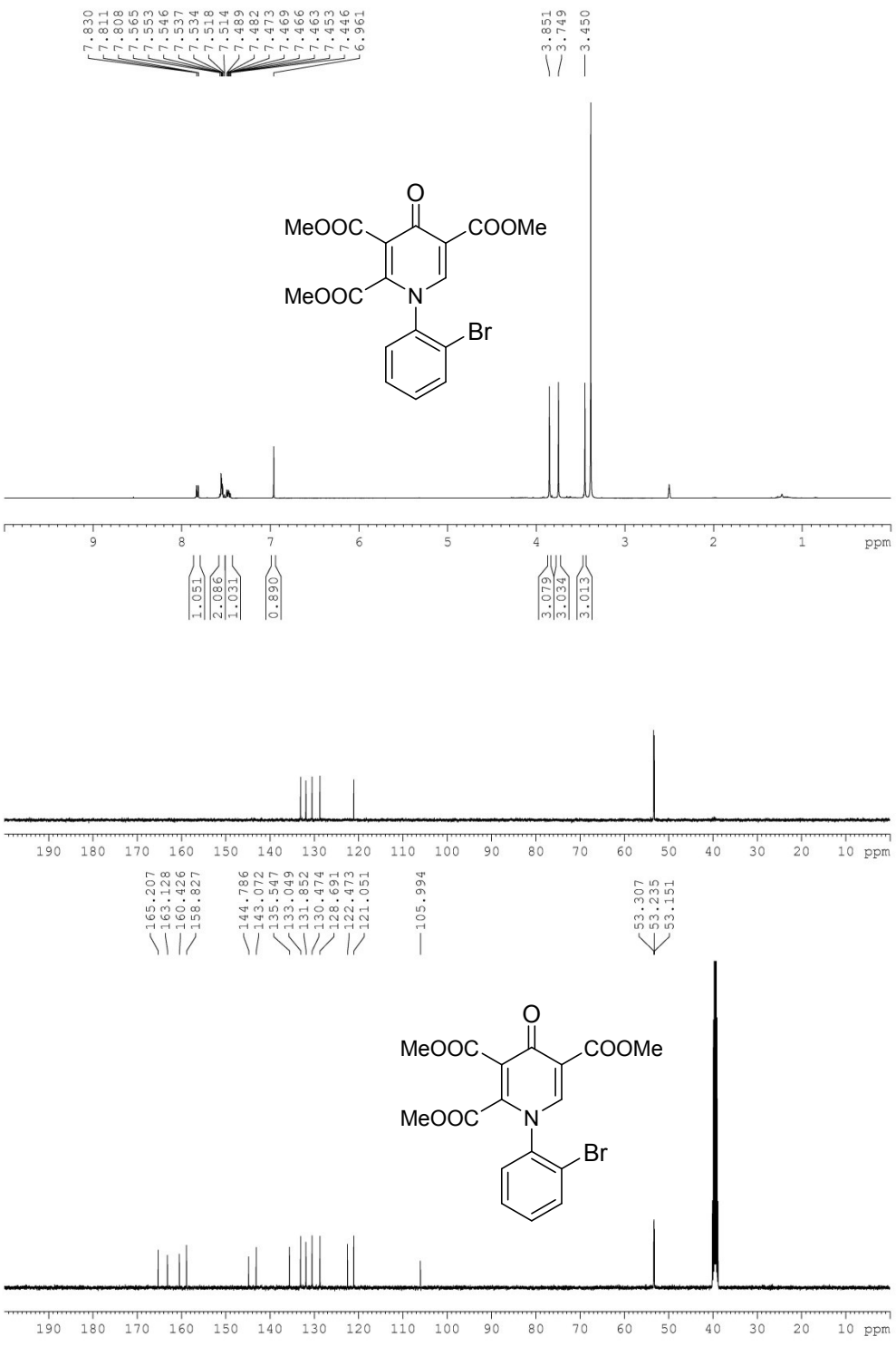

Figure S41. ^{1}H and ^{13}C NMR spectra of compound **6h**

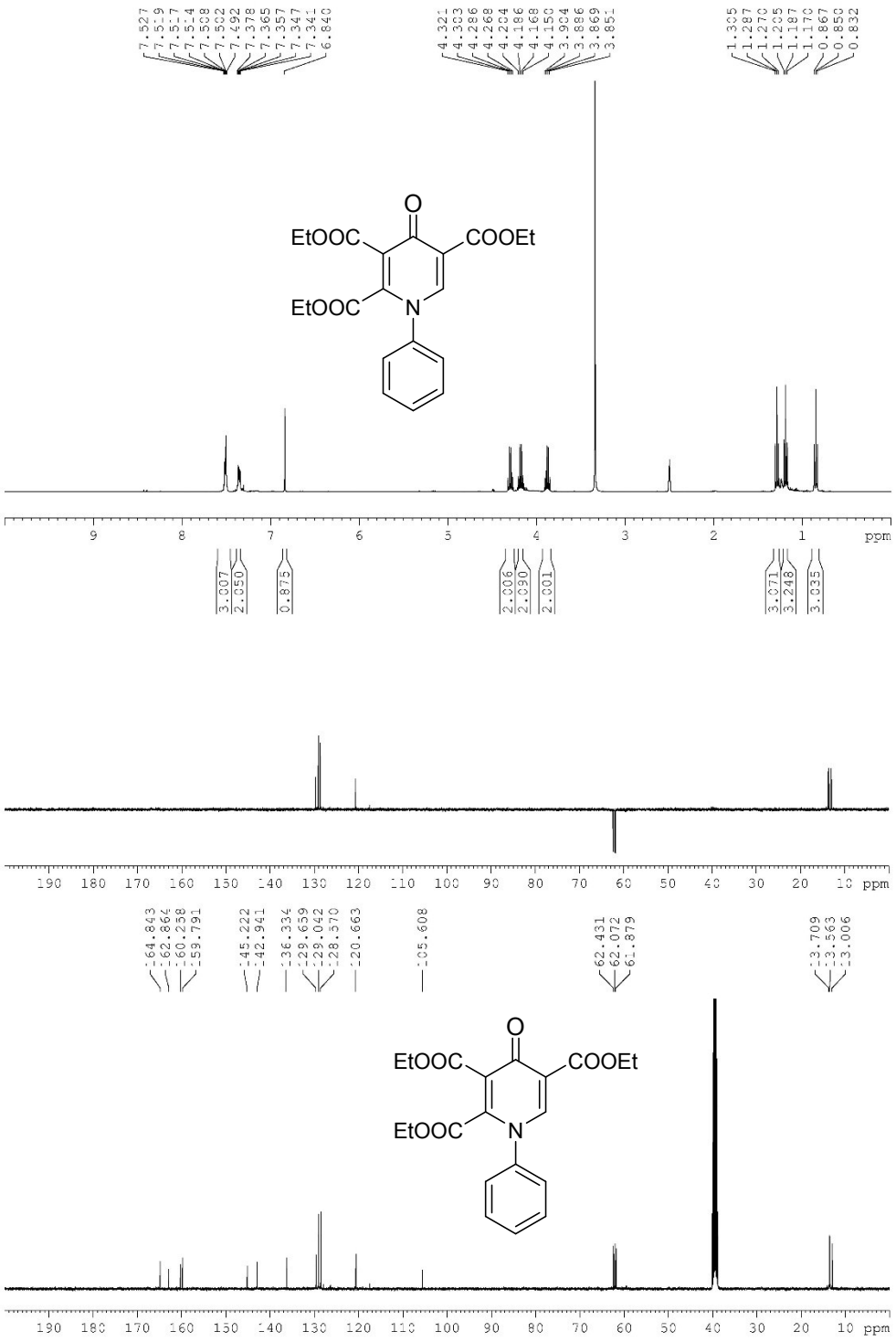

Figure S42. ^{1}H and ^{13}C NMR spectra of compound **6i**

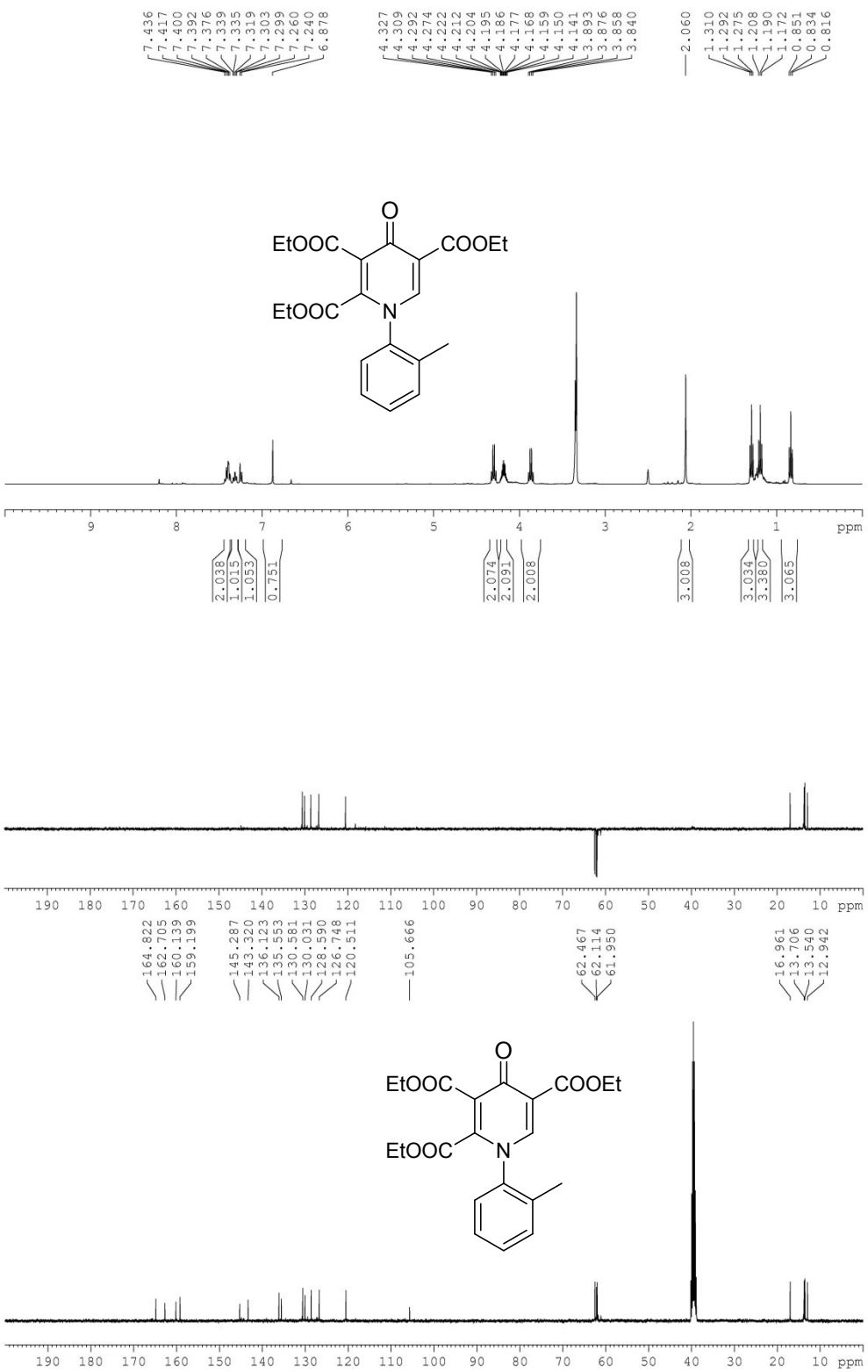

Figure S43. ^{1}H and ^{13}C NMR spectra of compound **6j**

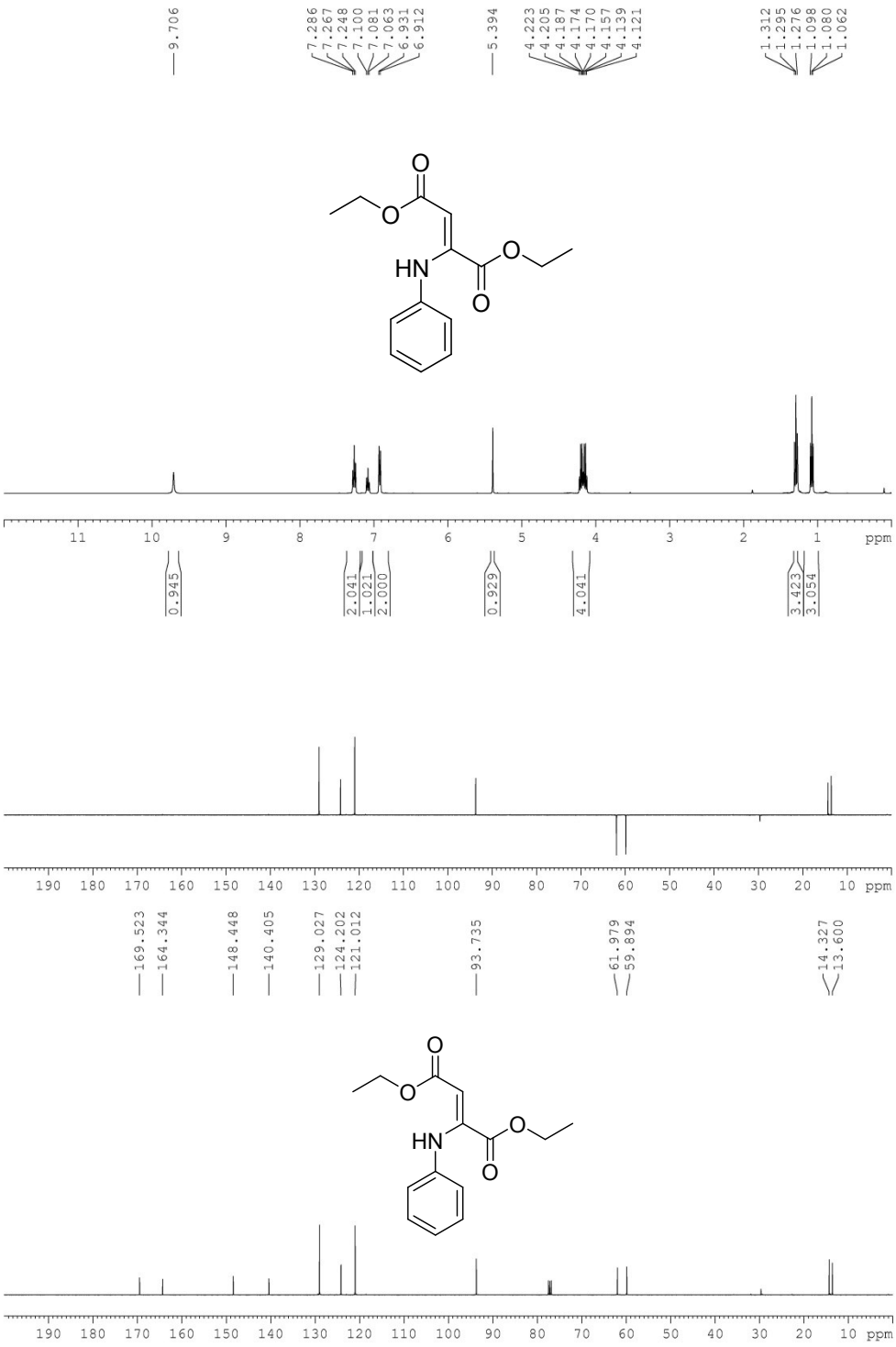

Figure S44. ^{1}H and ^{13}C NMR spectra of intermediate **I**

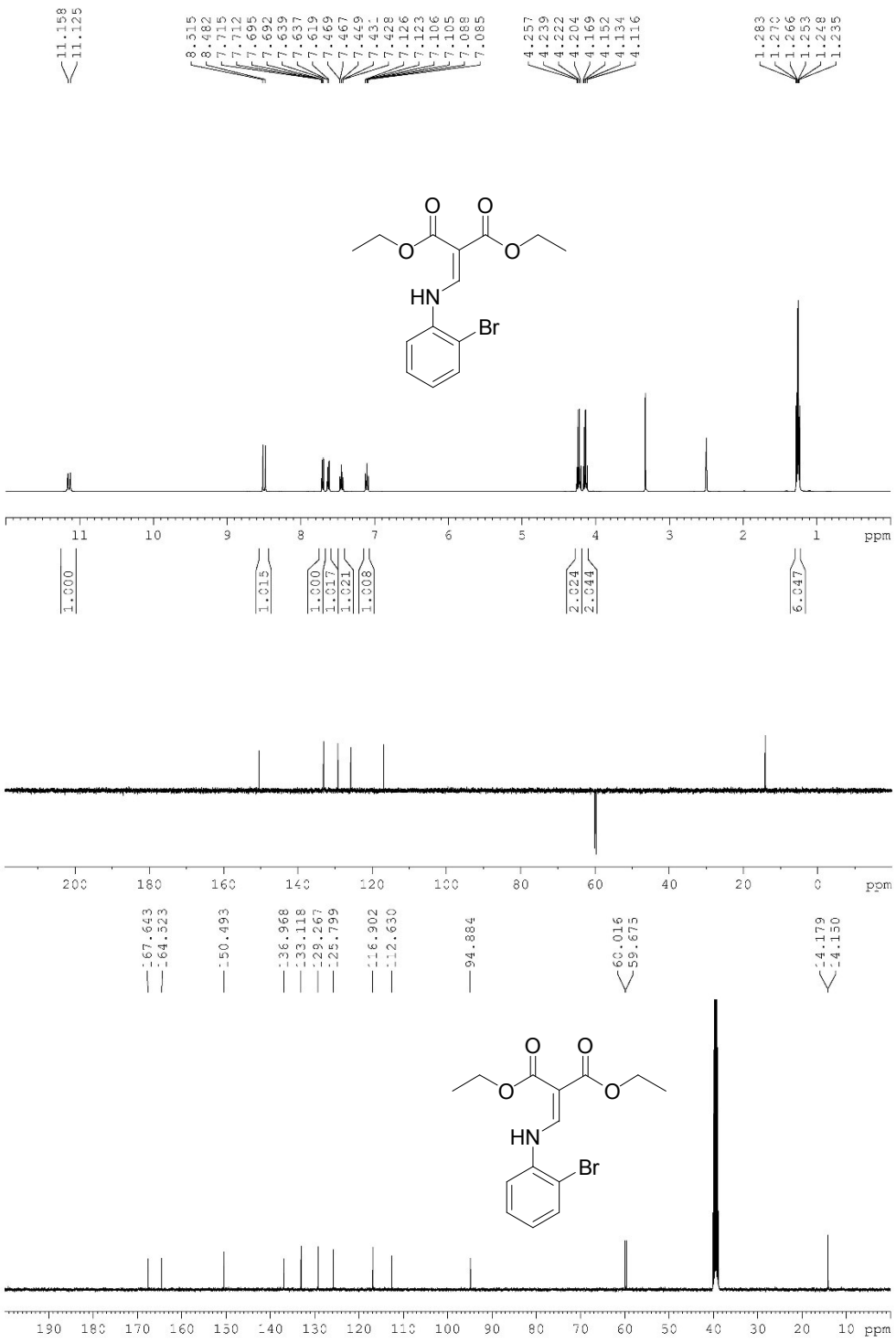

Figure S45. ^{1}H and ^{13}C NMR spectra of intermediate **II**

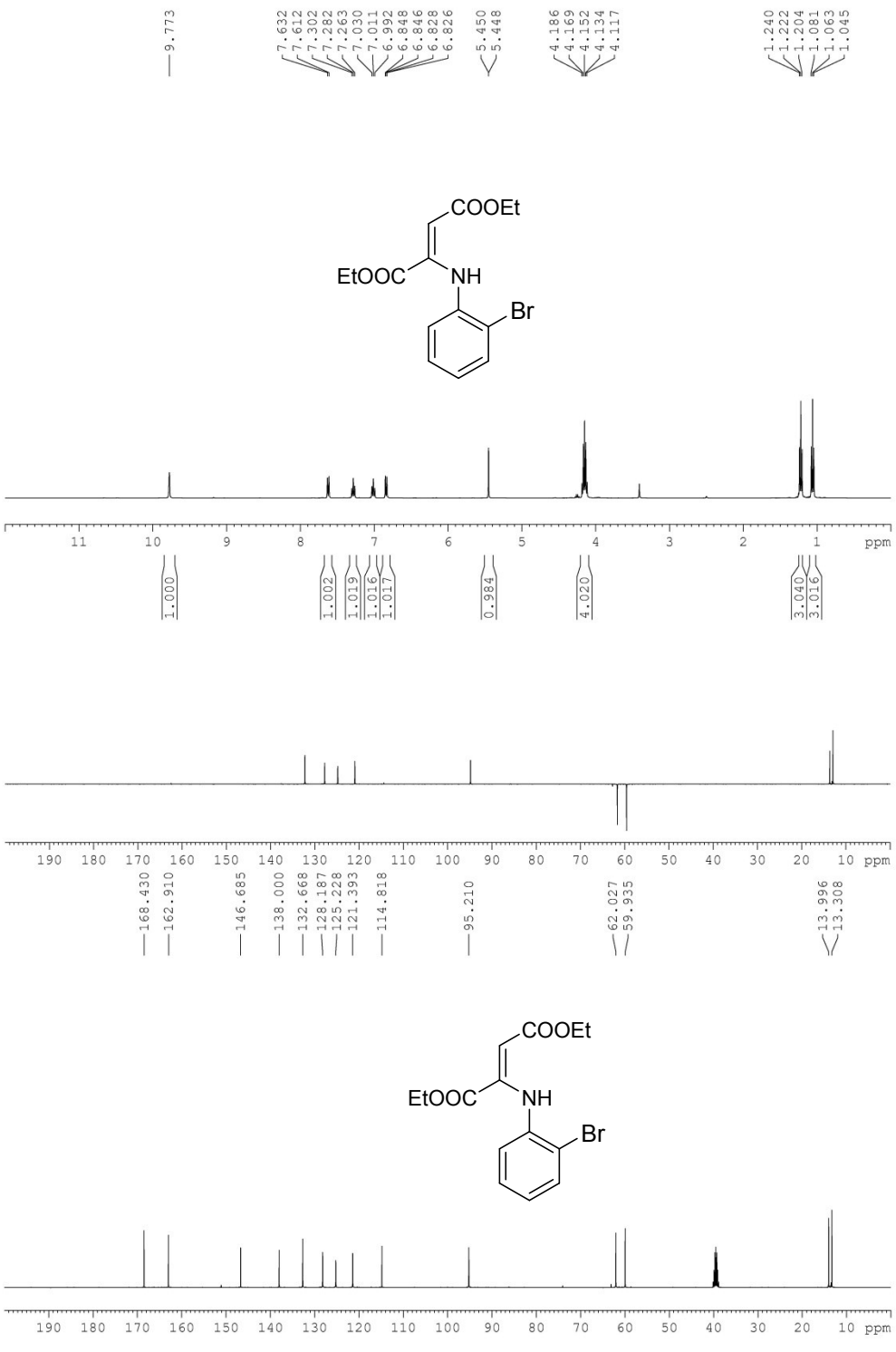

Figure S46. ^{1}H and ^{13}C NMR spectra of intermediate **III**

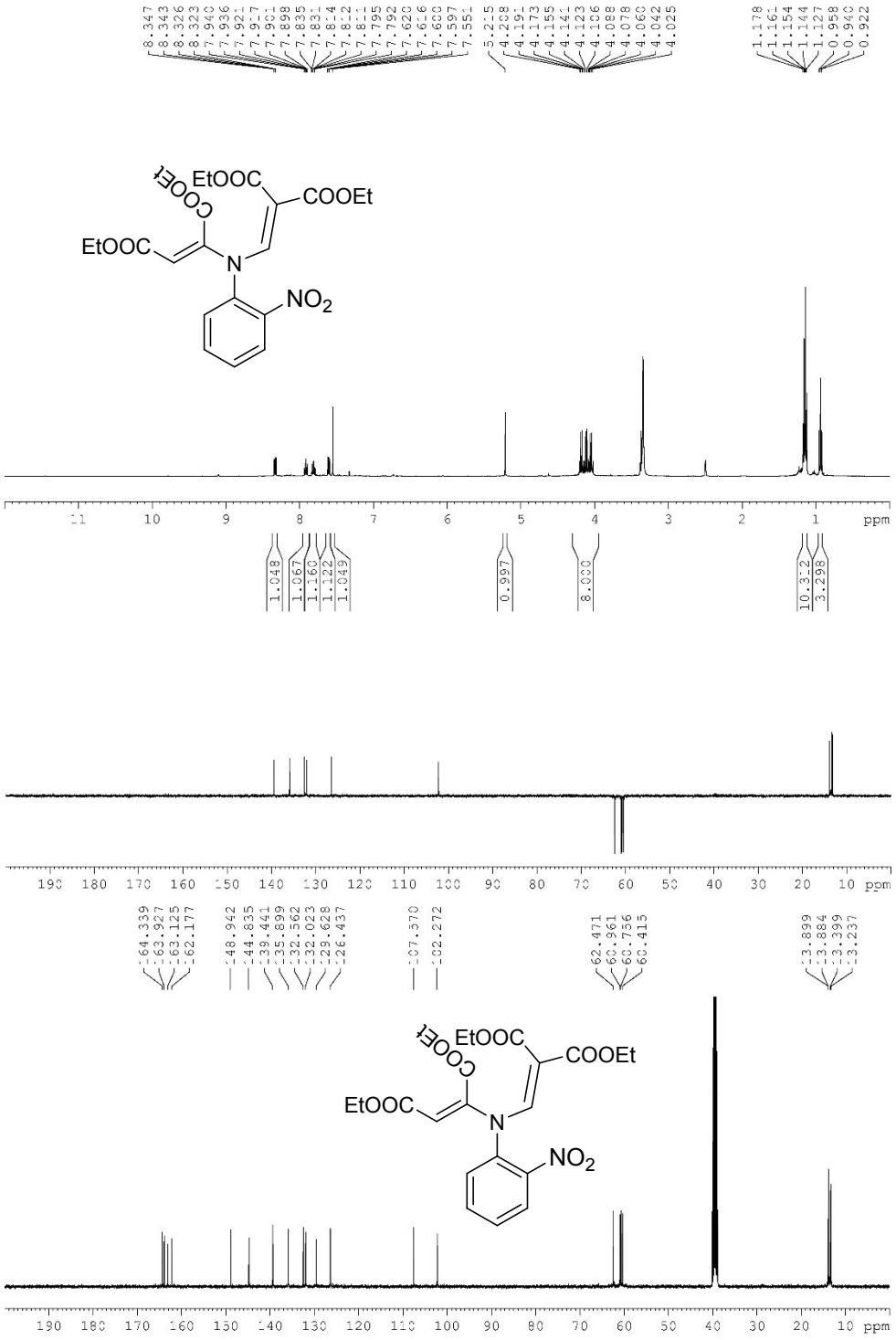

Figure S47. ^{1}H and ^{13}C NMR spectra of intermediate **IV**

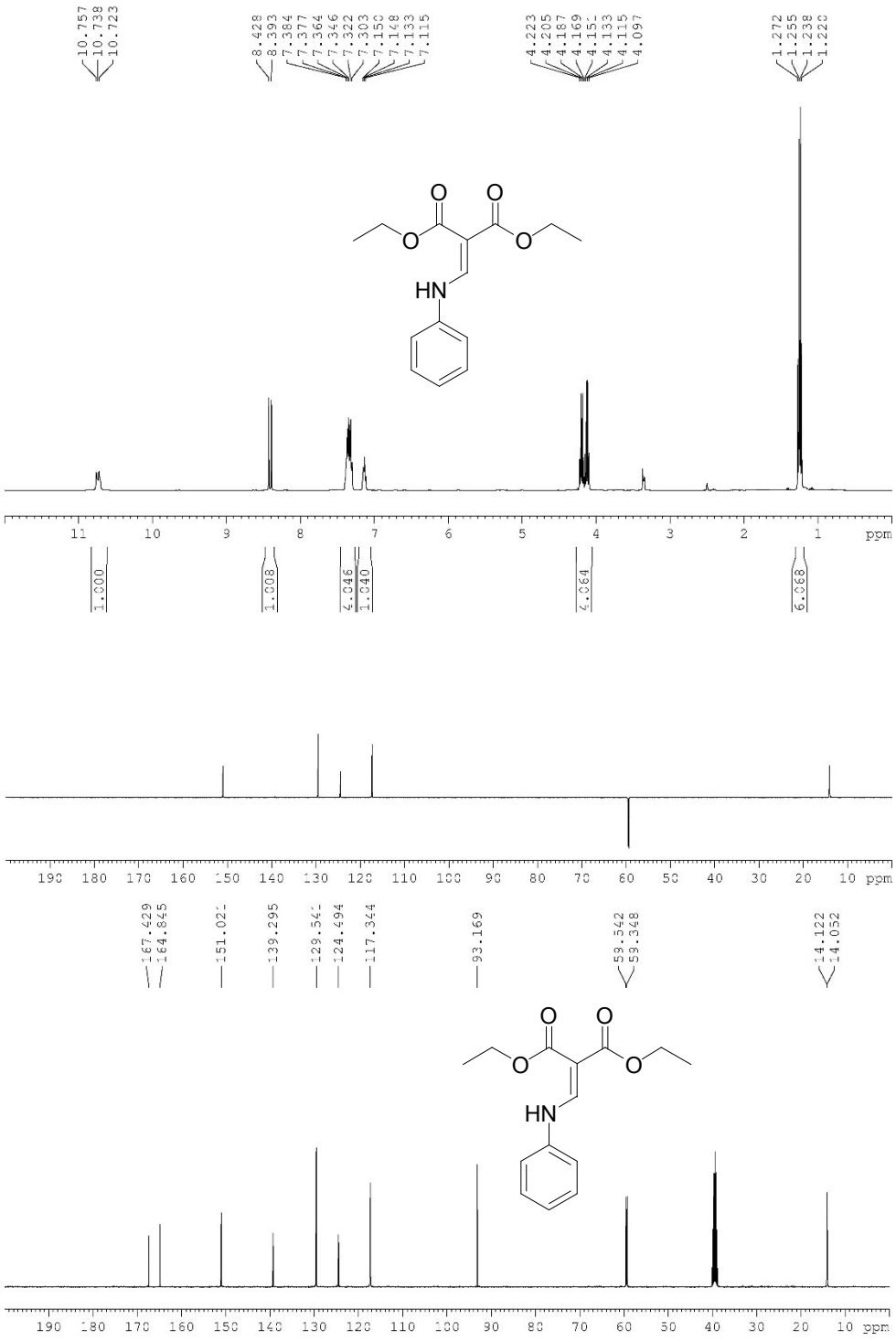

Figure S48. ^{1}H and ^{13}C NMR spectra of intermediate **7**