Supporting Information

Selenium Dioxide-Mediated Oxidative Annulation of Sufonyl *o*-Hydroxyacetophenones with Acetophenones. One-pot Synthesis of Aurone Analogs

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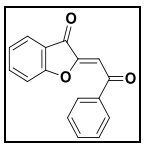
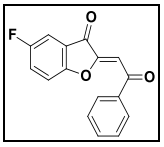
Experimental Section

General. All reagents and solvents were obtained from commercial sources and used without further purification. Reactions were routinely carried out under an atmosphere of dry air with magnetic stirring. Products in organic solvents were dried with anhydrous $MgSO_4$ before concentration in vacuo. Melting points were determined with a SMP3 melting apparatus. ^1H and ^{13}C NMR spectra were recorded on a Varian INOVA-400 spectrometer operating at 400/600 and at 100/150 MHz, respectively. Chemical shifts (δ) are reported in ppm. Multiplicity data are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, br s = broad singlet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, and m = multiplet. The multiplicity is followed by the coupling constant(s) in Hz and integration. In $^{13}C\{^1H\}$ NMR data, (2x) = some carbons. High resolution mass spectra (HRMS) were measured with a mass spectrometer Finnigan/Thermo Quest MAT 95XL. X-ray crystal structures were obtained with an Enraf-Nonius FR-590 diffractometer (CAD4, Kappa CCD).

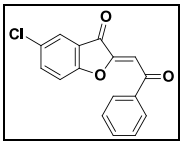
A representative synthetic procedure of skeleton 4 is as follows: To a 50 mL two-necked flame-dried flask equipped with a magnetic stir bar, SeO_2 (222 mg, 1.0 mmol) was sequentially added to a solution of **3** (0.5 mmol) in dioxane (10 mL) at 25 ^oC. The reaction flask was sealed with a rubber stopper. Then, the flask was flushed with dry air. The reaction mixture was stirred at reflux for 2 h with a condenser and then cooled to 25 ^oC. **2** (0.5 mmol) in dioxane (10 mL) and 80% $H_2SO_{4(aq)}$ (1 mL) was added to the reaction mixture at 25 ^oC via a syringe. The reaction mixture was stirred at reflux for 13 h with a condenser. The reaction mixture was cooled to 25 ^oC and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 30/1~1/1) afforded **4**.



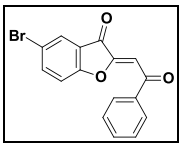
(*Z*)-2-(2-Oxo-2-phenylethylidene)benzofuran-3(2*H*)-one (4a). Yield = 91% (114 mg); Yellowish solid; mp = 126-128 ^oC (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{16}H_{11}O_3$ 251.0708, found 251.0710; ^1H NMR (400 MHz, $CDCl_3$): δ 8.07-8.04 (m, 2H), 7.80 (dd, *J* = 0.8, 7.6 Hz, 1H), 7.70 (dt, *J* = 1.2, 8.4 Hz, 1H), 7.64-7.60 (m, 1H), 7.54-7.50 (m, 2H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.27 (dt, *J* = 0.8, 7.6 Hz, 1H), 7.12 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 188.8, 185.8, 167.7, 152.2, 138.4, 137.7, 133.7, 128.8 (2x), 128.6 (2x), 125.1, 124.5, 120.1, 113.6, 102.5.



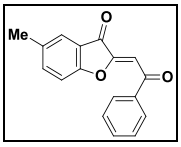
(*Z*)-5-Fluoro-2-(2-oxo-2-phenylethylidene)benzofuran-3(2*H*)-one (4b). Yield = 90% (121 mg); Yellowish solid; mp = 184-186 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{16}H_{10}FO_3$ 269.0614, found 269.0615; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05-8.02 (m, 2H), 7.64-7.60 (m, 1H), 7.53-7.50 (m, 2H), 7.45-7.39 (m, 2H), 7.33 (ddd, *J* = 0.8, 4.0, 8.4 Hz, 1H), 7.11 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 188.6, 185.2 (d, *J* = 3.1 Hz), 163.7 (d, *J* = 1.5 Hz), 159.2 (d, *J* = 244.8 Hz), 152.5, 137.5, 133.8, 128.8 (2x), 128.6 (2x), 125.7 (d, *J* = 25.7 Hz), 120.8 (d, *J* = 8.3 Hz), 114.9 (d, *J* = 7.6 Hz), 110.7 (d, *J* = 25.0 Hz), 103.7; ^{19}F{^{1}H} NMR (564 MHz, $CDCl_3$): δ -118.41~-118.45 (m, 1F). Single-crystal X-Ray diagram: crystal of compound **4b** was grown by slow diffusion of EtOAc into a solution of compound **4b** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group $P2_1/n$, *a* = 8.1097(2) Å, *b* = 5.22990(10) Å, *c* = 27.2462(5) Å, *V* = 1155.23(4) Å^3, *Z* = 4, d_{calcd} = 1.542 g/cm^3, *F*(000) = 552.0, 2*θ* range 5.206~54.162^{o}, R indices (all data) R1 = 0.0368, wR2 = 0.0876.



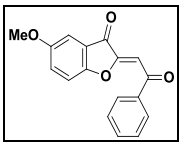
(*Z*)-5-Chloro-2-(2-oxo-2-phenylethylidene)benzofuran-3(2*H*)-one (4c). Yield = 93% (132 mg); Yellowish solid; mp = 179-181 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{16}H_{10}ClO_3$ 285.0319, found 285.0320; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05-8.03 (m, 2H), 7.75 (d, *J* = 2.0 Hz, 1H), 7.66-7.60 (m, 2H), 7.54-7.50 (m, 2H), 7.32 (d, *J* = 8.8 Hz, 1H), 7.12 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 188.6, 184.6, 165.9, 152.0, 138.1, 133.9, 129.2, 128.9 (2x), 128.6 (2x), 128.5, 125.2, 124.6, 120.0, 103.5.



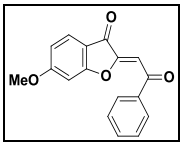
(*Z*)-5-Bromo-2-(2-oxo-2-phenylethylidene)benzofuran-3(2*H*)-one (4d). Yield = 90% (148 mg); Yellowish solid; mp = 195-197 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{16}H_{10}BrO_3$ 328.9813, found 328.9815; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06-8.03 (m, 2H), 7.91 (d, *J* = 2.4 Hz, 1H), 7.78 (dd, *J* = 2.4, 8.4 Hz, 1H), 7.65-7.61 (m, 1H), 7.55-7.50 (m, 2H), 7.28 (d, *J* = 8.4 Hz, 1H), 7.13 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 188.6, 184.4, 166.3, 151.8, 140.9, 137.5, 133.9, 128.9 (2x), 128.6 (2x), 127.7, 121.8, 117.4, 115.3, 103.5.



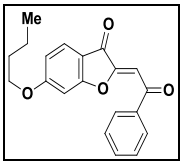
(*Z*)-5-Methyl-2-(2-oxo-2-phenylethylidene)benzofuran-3(2*H*)-one (4e). Yield = 84% (111 mg); Yellowish solid; mp = 160-162 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{17}H_{13}O_3$ 265.0865, found 265.0866; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07-8.04 (m, 2H), 7.64-7.60 (m, 1H), 7.58 (br s, 1H), 7.54-7.49 (m, 3H), 7.25 (d, *J* = 8.4 Hz, 1H), 7.09 (s, 1H), 2.41 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 188.9, 185.9, 166.2, 152.7, 139.5, 137.8, 134.4, 133.6, 128.8 (2x), 128.6 (2x), 124.7, 120.0, 113.2, 102.2, 20.8.



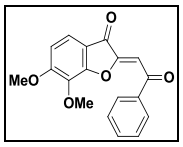
(*Z*)-5-Methoxy-2-(2-oxo-2-phenylethylidene)benzofuran-3(2*H*)-one (4f). Yield = 85% (119 mg); Yellowish solid; mp = 150-152 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{17}H_{13}O_4$ 281.0814, found 281.0815; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06-8.03 (m, 2H), 7.63-7.58 (m, 1H), 7.52-7.48 (m, 2H), 7.26 (d, *J* = 1.2 Hz, 2H), 7.18 (t, *J* = 1.6 Hz, 1H), 7.08 (s, 1H), 3.82 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 188.8, 186.0, 162.8, 156.7, 153.0, 137.7, 133.6, 128.8 (2x), 128.5 (2x), 127.3, 120.2, 114.4, 105.7, 102.4, 55.9. Single-crystal X-Ray diagram: crystal of compound **4f** was grown by slow diffusion of EtOAc into a solution of compound **4f** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group $P2_1/c$, *a* = 5.3211(2) Å, *b* = 8.1869(2) Å, *c* = 29.8283(8) Å, *V* = 1298.38(7) Å^3, *Z* = 4, d_{calcd} = 1.434 g/cm^3, *F*(000) = 584.0, 2*θ* range 5.16~49.998^{o}, R indices (all data) R1 = 0.0527, wR2 = 0.1252.



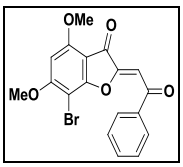
(*Z*)-6-Methoxy-2-(2-oxo-2-phenylethylidene)benzofuran-3(2*H*)-one (4g). Yield = 86% (120 mg); Yellowish solid; mp = 127-129 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{17}H_{13}O_4$ 281.0814, found 281.0818; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07-8.04 (m, 2H), 7.70 (d, *J* = 8.8 Hz, 1H), 7.64-7.60 (m, 1H), 7.54-7.50 (m, 2H), 7.08 (s, 1H), 6.81 (d, *J* = 2.0 Hz, 1H), 6.78 (dd, *J* = 2.0, 8.4 Hz, 1H), 3.92 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 188.9, 183.5, 170.3, 168.6, 153.6, 137.8, 133.6, 129.3, 128.8 (2x), 128.6 (2x), 126.3, 113.1, 101.8, 97.4, 56.2.



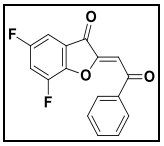
(*Z*)-6-*n*-butoxy-2-(2-oxo-2-phenylethylidene)benzofuran-3(2*H*)-one (4h). Yield = 90% (145 mg); Yellowish solid; mp = 108-110 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{20}H_{19}O_4$ 323.1283, found 323.1287; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.07-8.05 (m, 2H), 7.68 (d, *J* = 9.0 Hz, 1H), 7.63-7.60 (m, 1H), 7.53-7.50 (m, 2H), 7.06 (s, 1H), 6.78 (d, *J* = 1.8 Hz, 1H), 6.76 (dd, *J* = 2.4, 8.4 Hz, 1H), 4.07 (t, *J* = 6.6 Hz, 2H), 1.84-1.79 (m, 2H), 1.54-1.49 (m, 2H), 0.99 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 188.9, 183.4, 170.4, 168.2, 153.7, 137.9, 133.6, 128.8 (2x), 128.6 (2x), 126.3, 113.5, 113.1, 101.7, 97.7, 69.0, 30.8, 19.1, 13.7.



(*Z*)-6,7-Dimethoxy-2-(2-oxo-2-phenylethylidene)benzofuran-3(2*H*)-one (4i). Yield = 87% (135 mg); Yellowish solid; mp = 156-158 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{18}H_{15}O_5$ 311.0920, found 311.0923; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03-8.00 (m, 2H), 7.62 (m 1H), 7.52-7.47 (m, 3H), 7.00 (s, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 4.11 (s, 3H), 3.97 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 188.9, 183.8, 159.7, 157.7, 153.0, 137.8, 134.0, 133.5, 128.7 (2x), 128.5 (2x), 119.8, 115.2, 108.5, 102.0, 61.0, 56.9.

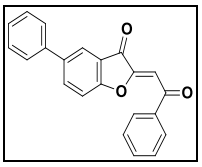


(*Z*)-7-Bromo-4,6-dimethoxy-2-(2-oxo-2-phenylethylidene)benzofuran-3(2*H*)-one (4j). Yield = 85% (165 mg); Yellowish solid; mp = 236-238 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{18}H_{14}BrO_5$ 389.0025, found 389.0023; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.05-8.03 (m, 2H), 7.62-7.59 (m, 1H), 7.52-7.49 (m, 2H), 7.04 (s, 1H), 6.20 (s, 1H), 4.04 (s, 3H), 4.03 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 188.6, 180.7, 165.8, 165.6, 159.4, 153.4, 137.8, 133.5, 128.7 (2x), 128.6 (2x), 105.1, 102.3, 91.2, 86.2, 57.2, 56.7.

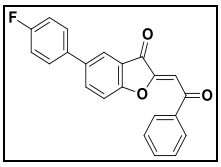


(*Z*)-5,7-Difluoro-2-(2-oxo-2-phenylethylidene)benzofuran-3(2*H*)-one (4k). Yield = 86% (123 mg); Yellowish solid; mp = 156-158 ^{o}C (recrystallized from hexanes and EtOAc); HRMS

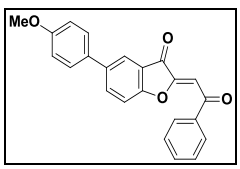
(ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{16}H_9F_2O_3$ 287.0520, found 287.0523; ^1H NMR (400 MHz, $CDCl_3$): δ 8.04-8.00 (m, 2H), 7.66-7.61 (m, 1H), 7.54-7.50 (m, 2H), 7.31-7.22 (m, 2H), 7.15 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 188.2, 184.0, 158.5 (dd, *J* = 6.9, 247.2 Hz), 151.4, 151.1 (d, *J* = 9.9 Hz), 147.8 (dd, *J* = 11.3, 257.7 Hz), 137.2, 134.0 (2x), 128.9, 128.6, 123.0 (d, *J* = 11.4 Hz), 113.4 (dd, *J* = 19.7, 28.1 Hz), 106.3 (dd, *J* = 4.5, 24.3 Hz), 105.2 (2x); $^{19}F\{^1H\}$ NMR (564 MHz, $CDCl_3$): δ -114.54~-114.57 (m, 1F), -130.68~-130.70 (m, 1F).



(*Z*)-2-(2-Oxo-2-phenylethylidene)-5-phenylbenzofuran-3(2*H*)-one (4l). Yield = 84% (137 mg); Yellowish solid; mp = 179-181 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{22}H_{15}O_3$ 327.1021, found 327.1023; ^1H NMR (400 MHz, $CDCl_3$): δ 8.08-8.06 (m, 2H), 7.99-7.98 (m, 1H), 7.92 (dd, *J* = 2.0, 8.4 Hz, 1H), 7.65-7.61 (m, 1H), 7.58-7.37 (m, 8H), 7.14 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 188.8, 185.8, 167.1, 152.6, 139.0, 138.2, 137.7, 137.5, 133.7, 129.0 (2x), 128.8 (2x), 128.6 (2x), 127.9, 126.9 (2x), 123.1, 120.6, 113.8, 102.7.

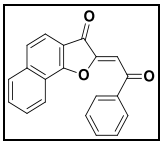


(*Z*)-5-(4-Fluorophenyl)-2-(2-oxo-2-phenylethylidene)benzofuran-3(2*H*)-one (4m). Yield = 93% (160 mg); Yellowish solid; mp = 202-204 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{22}H_{14}FO_3$ 345.0927, found 345.0931; ^1H NMR (400 MHz, $CDCl_3$): δ 8.08-8.06 (m, 2H), 7.93 (d, *J* = 2.0 Hz, 1H), 7.87 (dd, *J* = 2.0, 8.8 Hz, 1H), 7.65-7.61 (m, 1H), 7.55-7.50 (m, 4H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.08-7.13 (m, 2H), 7.14 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 188.8, 185.7, 167.0, 162.8 (d, *J* = 246.4 Hz), 152.5, 137.6, 137.3, 137.2, 135.2 (d, *J* = 3.8 Hz), 133.8, 128.9 (2x), 128.63 (d, *J* = 9.1 Hz, 2x), 128.59 (2x), 122.9, 120.6, 116.0 (d, *J* = 21.3 Hz, 2x), 113.9, 102.8; $^{19}F\{^1H\}$ NMR (564 MHz, $CDCl_3$): δ -115.59~-115.64 (m, 1F).

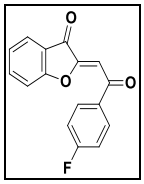


(*Z*)-5-(4-Methoxyphenyl)-2-(2-oxo-2-phenylethylidene)benzofuran-3(2*H*)-one (4n). Yield = 86% (153 mg); Yellowish solid; mp = 171-173 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{23}H_{17}O_4$ 357.1127, found 357.1131; ^1H NMR (400

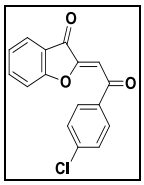
MHz, $CDCl_3$): δ 8.08-8.06 (m, 2H), 7.93 (d, *J* = 2.0 Hz, 1H), 7.88 (dd, *J* = 2.0, 8.8 Hz, 1H), 7.65-7.61 (m, 1H), 7.55-7.48 (m, 4H), 7.40 (dd, *J* = 0.4, 8.4 Hz, 1H), 7.13 (s, 1H), 6.99 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 188.8, 185.9, 166.7, 159.6, 152.6, 137.9, 137.7, 137.1, 133.7, 131.5, 128.8 (2x), 128.6 (2x), 128.0 (2x), 122.4, 120.5, 114.5 (2x), 113.7, 102.6, 55.4.



(*Z*)-2-(2-Oxo-2-phenylethylidene)naphtho[1,2-*b*]furan-3(2*H*)-one (4o). Yield = 84% (126 mg); Yellowish solid; mp = 138-140 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{20}H_{13}O_3$ 301.0865, found 301.0868; ^1H NMR (400 MHz, $CDCl_3$): δ 8.30 (dd, *J* = 0.8, 8.0 Hz, 1H), 8.11-8.08 (m, 2H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.73 (dt, *J* = 1.6, 8.4 Hz, 1H), 7.68-7.60 (m, 4H), 7.56-7.52 (m, 2H), 7.17 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 189.0, 185.1, 168.2, 152.5, 138.9, 137.6, 133.7, 131.3, 128.8 (2x), 128.7 (2x), 128.5, 127.5, 124.6, 122.4, 120.5, 118.7, 115.4, 103.6.

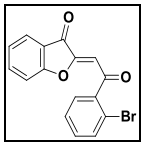


(*Z*)-2-(2-(4-Fluorophenyl)-2-oxoethylidene)benzofuran-3(2*H*)-one (4p). Yield = 82% (110 mg); Yellowish solid; mp = 128-130 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{16}H_{10}FO_3$ 269.0614, found 269.0612; ^1H NMR (400 MHz, $CDCl_3$): δ 8.10-8.05 (m, 2H), 7.78 (ddd, *J* = 0.4, 1.2, 8.0 Hz, 1H), 7.69 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.26 (dt, *J* = 0.4, 8.4 Hz, 1H), 7.20-7.15 (m, 2H), 7.04 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 187.2, 185.6, 167.6, 166.1 (d, *J* = 254.7 Hz), 152.2, 138.4, 134.1 (d, *J* = 3.1 Hz), 131.3 (d, *J* = 9.1 Hz, 2x), 125.0, 124.5, 120.0, 116.0 (d, *J* = 22.0 Hz, 2x), 113.5, 102.2; $^{19}F\{^1H\}$ NMR (564 MHz, $CDCl_3$): δ -104.97~-105.01 (m, 1F).

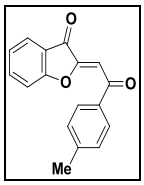


(*Z*)-2-(2-(4-Chlorophenyl)-2-oxoethylidene)benzofuran-3(2*H*)-one (4q). Yield = 80% (114 mg); Yellowish solid; mp = 164-166 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{16}H_{10}ClO_3$ 285.0319, found 285.0322; ^1H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.8 Hz, 2H), 7.78 (dd, *J* = 0.8, 7.6 Hz, 1H), 7.69 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.02 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 187.5, 185.6, 167.6, 152.3, 140.2, 138.5, 136.0, 129.9 (2x), 129.1

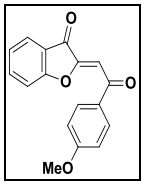
(2x), 125.1, 124.5, 120.0, 113.5, 101.9.



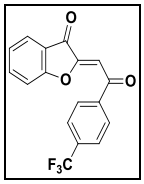
(*Z*)-2-(2-(2-Bromophenyl)-2-oxoethylidene)benzofuran-3(2*H*)-one (4r). Yield = 82% (134 mg); Yellowish solid; mp = 104-106 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{16}H_{10}BrO_3$ 328.9813, found 328.9815; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (dd, *J* = 0.4, 8.0 Hz, 1H), 7.69 (dt, *J* = 1.6, 7.6 Hz, 1H), 7.64 (dd, *J* = 1.2, 8.0 Hz, 1H), 7.54 (dd, *J* = 1.6, 7.6 Hz, 1H), 7.42 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.36 (dt, *J* = 2.0, 7.6 Hz, 1H), 7.29-7.24 (m, 2H), 6.81 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 191.3, 185.7, 167.5, 151.6, 141.0, 138.4, 133.6, 132.3, 129.6, 127.6, 125.1, 124.6, 120.0, 119.6, 113.5, 104.9.



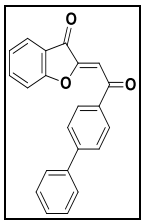
(*Z*)-2-(2-(4-Methylphenyl)-2-oxoethylidene)benzofuran-3(2*H*)-one (4s). Yield = 90% (119 mg); Yellowish solid; mp = 163-165 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{17}H_{13}O_3$ 265.0865, found 265.0862; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.78 (dd, *J* = 1.2, 7.6 Hz, 1H), 7.68 (dt, *J* 1.6, 7.6 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.09 (s, 1H), 2.42 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 188.3, 185.8, 167.6, 152.0, 144.7, 138.3, 135.2, 129.5 (2x), 128.7 (2x), 125.0, 124.3, 120.1, 113.6, 102.8, 21.7.



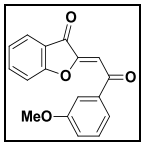
(*Z*)-2-(2-(4-Methoxyphenyl)-2-oxoethylidene)benzofuran-3(2*H*)-one (4t). Yield = 90% (126 mg); Yellowish solid; mp = 161-163 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{17}H_{13}O_4$ 281.0814, found 281.0816; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.8 Hz, 2H), 7.79 (dd, *J* = 1.2, 7.6 Hz, 1H), 7.69 (dt, *J* = 1.6, 7.6 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.26 (dt, *J* = 0.8, 8.0 Hz, 1H), 7.09 (s, 1H), 6.98 (d, *J* = 9.2 Hz, 2H), 3.89 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 187.2, 185.8, 167.7, 164.1, 151.8, 138.3, 131.0 (2x), 130.9, 125.0, 124.3, 120.2, 114.0 (2x), 113.6, 103.1, 55.6.



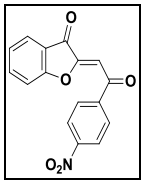
(*Z*)-2-(2-Oxo-2-(4-(trifluoromethyl)phenyl)ethylidene)benzofuran-3(2*H*)-one (4u). Yield = 86% (137 mg); Yellowish solid; mp = 185-187 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{17}H_{10}F_3O_3$ 319.0582, found 319.0588; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, *J* = 8.0 Hz, 2H), 7.81-7.78 (m, 1H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.71 (dt, *J* = 1.6, 7.6 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.28 (dt, *J* = 0.4, 8.0 Hz, 1H), 7.06 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 187.8, 185.6, 167.7, 152.7, 140.3, 138.6, 134.8 (q, *J* = 32.6 Hz), 128.8 (2x), 125.9 (q, *J* = 3.8 Hz, 2x), 125.2, 124.7, 123.5 (q, *J* = 271.4 Hz), 119.9, 113.6, 101.5; ^{19}F{^{1}H} NMR (564 MHz, $CDCl_3$): δ -64.38 (s, 3F).



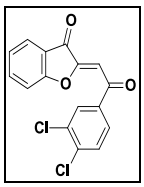
(*Z*)-2-(2-([1,1'-Biphenyl]-4-yl)-2-oxoethylidene)benzofuran-3(2*H*)-one (4v). Yield = 84% (137 mg); Yellowish solid; mp = 209-211 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{22}H_{15}O_3$ 327.1021, found 327.1023; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, *J* = 8.4 Hz, 2H), 7.91 (ddd, *J* = 0.8, 1.2, 7.6 Hz, 1H), 7.86-7.75 (m, 5H), 7.61-7.57 (m, 2H), 7.54-7.47 (m, 2H), 7.38 (dt, *J* = 0.8, 8.0 Hz, 1H), 7.36 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 188.3, 185.9, 167.7, 152.2, 146.4, 139.7, 138.4, 136.4, 129.2 (2x), 129.0 (2x), 128.4, 127.4 (2x), 127.3 (2x), 125.1, 124.5, 120.2, 113.6, 102.6.



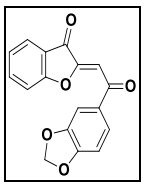
(*Z*)-2-(2-(3-Methoxyphenyl)-2-oxoethylidene)benzofuran-3(2*H*)-one (4w). Yield = 83% (116 mg); Yellowish solid; mp = 128-130 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{17}H_{13}O_4$ 281.0814, found 281.0816; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.78 (ddt, *J* = 0.6, 1.2, 7.8 Hz, 1H), 7.68 (dt, *J* = 1.2, 8.4 Hz, 1H), 7.61 (ddt, *J* = 0.6, 1.2, 7.8 Hz, 1H), 7.55 (dd, *J* = 1.2, 2.4 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.34 (dt, *J* = 0.6, 8.4 Hz, 1H), 7.25 (dt, *J* = 0.6, 7.8 Hz, 1H), 7.15 (ddd, *J* = 1.2, 2.4, 8.4 Hz, 1H), 7.07 (s, 1H), 3.86 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 188.5, 185.7, 167.6, 160.0, 152.1, 139.0, 138.3, 129.8, 125.0, 124.4, 121.3, 120.4, 120.1, 113.5, 112.5, 102.6, 55.4.



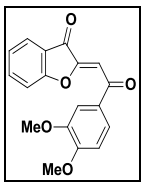
(*Z*)-2-(2-(4-Nitrophenyl)-2-oxoethylidene)benzofuran-3(2*H*)-one (4x). Yield = 82% (121 mg); Yellowish solid; mp = 230-232 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{16}H_{10}NO_5$ 296.0559, found 296.0563; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (d, *J* = 8.8 Hz, 2H), 8.20 (d, *J* = 8.8 Hz, 2H), 7.82 (dd, *J* = 0.4, 7.6 Hz, 1H), 7.73 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.05 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 187.3, 185.5, 167.7, 153.0, 150.5, 142.1, 138.8, 130.4, 129.5 (2x), 125.3, 124.9, 124.0 (2x), 113.6, 101.1.



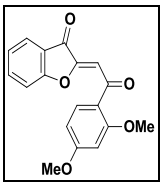
(*Z*)-2-(2-(3,4-Dichlorophenyl)-2-oxoethylidene)benzofuran-3(2*H*)-one (4y). Yield = 90% (143 mg); Yellowish solid; mp = 194-196 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{16}H_9Cl_2O_3$ 318.9929, found 318.9930; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, *J* = 2.0 Hz, 1H), 7.87 (dd, *J* = 2.0, 8.4 Hz, 1H), 7.80 (ddd, *J* = 0.4, 1.2, 7.6 Hz, 1H), 7.72 (dt, *J* = 1.6, 8.4 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.29 (dt, *J* = 0.8, 7.6 Hz, 1H), 6.99 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 186.5, 185.6, 167.7, 152.7, 138.6, 138.3, 137.2, 133.6, 130.9, 130.4, 127.5, 125.2, 124.7, 119.9, 113.6, 101.3.



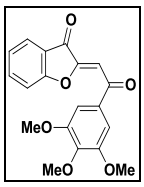
(*Z*)-2-(2-(Benzo[*d*][1,3]dioxol-5-yl)-2-oxoethylidene)benzofuran-3(2*H*)-one (4z). Yield = 90% (132 mg); Yellowish solid; mp = 216-218 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{17}H_{11}O_5$ 295.0607, found 295.0611; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (ddd, *J* = 0.4, 1.6, 7.6 Hz, 1H), 7.71-7.65 (m, 2H), 7.53 (d, *J* = 2.0 Hz, 1H), 7.35 (dd, *J* = 0.8, 8.0 Hz, 1H), 7.26 (dt, *J* = 0.8, 7.6 Hz, 1H), 7.03 (s, 1H), 6.89 (d, = 8.0 Hz, 1H), 6.08 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 186.8, 185.8, 167.7, 152.5, 151.9, 148.6, 138.4, 132.7, 125.5, 125.0, 124.4, 120.2, 113.6, 108.1, 108.0, 102.9, 102.1.



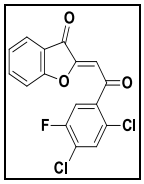
(*Z*)-2-(2-(3,4-Dimethoxyphenyl)-2-oxoethylidene)benzofuran-3(2*H*)-one (4aa). Yield = 89% (138 mg); Yellowish solid; mp = 192-194 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^{+}$ calcd for $C_{18}H_{15}O_5$ 311.0920, found 311.0924; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (ddd, *J* = 0.4, 1.6, 7.6 Hz, 1H), 7.69-7.65 (m, 2H), 7.59 (d, *J* = 2.0 Hz, 1H), 7.32 (dt, *J* = 0.8, 7.6 Hz, 1H), 7.23 (dt, *J* = 0.8, 7.6 Hz, 1H), 7.07 (s, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 3.95 (s, 3H), 3.94 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 187.1, 185.7, 167.6, 154.0, 151.8, 149.3, 138.3, 131.0, 124.9, 124.3, 123.7, 120.2, 113.5, 110.2, 110.0, 102.9, 56.1, 56.0.



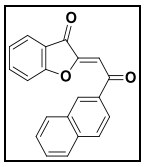
(*Z*)-2-(2-(2,4-Dimethoxyphenyl)-2-oxoethylidene)benzofuran-3(2*H*)-one (4ab). Yield = 86% (133 mg); Yellowish solid; mp = 123-125 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^{+}$ calcd for $C_{18}H_{15}O_5$ 311.0920, found 311.0923; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.4 Hz, 1H), 7.77 (ddd, *J* = 0.4, 1.2, 7.6 Hz, 1H), 7.67 (dt, *J* = 1.2, 8.4 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.26-7.21 (m, 2H), 6.57 (dd, *J* = 2.4, 8.8 Hz, 1H), 6.47 (d, *J* = 2.4 Hz, 1H), 3.92 (s, 3H), 3.87 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 187.7, 186.4, 167.7, 165.2, 161.0, 150.5, 138.0, 133.3, 124.8, 124.0, 121.7, 120.5, 113.6, 108.2, 105.7, 98.3, 55.8, 55.6.



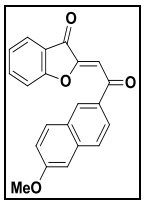
(*Z*)-2-(2-(3,4,5-Trimethoxyphenyl)-2-oxoethylidene)benzofuran-3(2*H*)-one (4ac). Yield = 88% (150 mg); Yellowish solid; mp = 146-148 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^{+}$ calcd for $C_{19}H_{17}O_6$ 341.1025, found 341.1030; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.69 (dt, *J* = 1.6, 8.0 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.28 (s, 2H), 7.25 (t, *J* = 8.0 Hz, 1H), 7.05 (s, 1H), 3.93 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 187.5, 185.7, 167.6, 153.2 (2x), 152.1, 143.2, 138.4, 132.9, 125.0, 124.4, 120.1, 113.5, 106.0 (2x), 102.6, 61.0, 56.3 (2x). Single-crystal X-Ray diagram: crystal of compound **4ac** was grown by slow diffusion of EtOAc into a solution of compound **4ac** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group Pc, *a* = 12.7257(3) Å, *b* = 4.69060(10) Å, *c* = 13.7330(5) Å, *V* = 786.38(4) Å^3, *Z* = 3, d_{calcd} = 1.437 g/cm^3, *F*(000) = 356.0, 2θ range 3.336~54.122^{o}, R indices (all data) R1 = 0.0409, wR2 = 0.0978.



(*Z*)-2-(2-(5-Fluoro-2,4-dichlorophenyl)-2-oxoethylidene)benzofuran-3(2*H*)-one (4ad). Yield = 86% (144 mg); Yellowish solid; mp = 162-164 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{16}H_8Cl_2FO_3$ 336.9835, found 336.9838; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (dd, *J* = 1.2, 7.6 Hz, 1H), 7.71 (dt, *J* = 1.6, 7.6 Hz, 1H), 7.53 (d, *J* = 6.0 Hz, 1H), 7.41 (d, *J* = 8.8 Hz, 1H), 7.31-7.26 (m, 2H), 6.79 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 188.2 (d, *J* = 1.5 Hz), 185.4, 167.5, 157.9 (d, *J* = 250.9 Hz), 152.1, 138.6, 138.5 (d, *J* = 5.3 Hz), 132.2, 127.2 (d, *J* = 3.8 Hz), 125.4, 125.2, 124.8, 119.9, 117.7 (d, *J* = 23.5 Hz), 113.5, 104.3; ^{19}F{^{1}H} NMR (564 MHz, $CDCl_3$): δ -116.94~-116.99 (m, 1F).

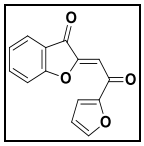


(*Z*)-2-(2-(Naphthalen-2-yl)-2-oxoethylidene)benzofuran-3(2*H*)-one (4ae). Yield = 92% (138 mg); Yellowish solid; mp = 165-167 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{20}H_{13}O_3$ 301.0865, found 301.0867; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (d, *J* = 1.2 Hz, 1H), 8.11 (dd, *J* = 2.0, 8.8 Hz, 1H), 7.99 (dd, *J* = 0.4, 8.0 Hz, 1H), 7.93 (d, *J* = 8.8 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.82-7.79 (m, 1H), 7.69 (dt, *J* = 1.6, 8.4 Hz, 1H), 7.62 (dt, *J* = 1.2, 8.0 Hz, 1H), 7.56 (dt, *J* = 1.2, 8.0 Hz, 1H), 7.36 (dd, *J* = 0.8, 8.4 Hz, 1H), 7.264 (dt, *J* = 0.4, 7.6 Hz, 1H), 7.263 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 188.5, 185.8, 167.7, 152.2, 138.4, 132.4, 131.4, 130.7, 130.3, 129.7, 128.9, 128.8, 127.8, 127.0, 125.0, 124.4, 123.8, 120.1, 113.6, 102.7.

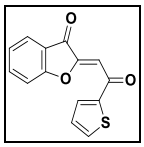


(*Z*)-2-(2-(6-Methoxynaphthalen-2-yl)-2-oxoethylidene)benzofuran-3(2*H*)-one (4af). Yield = 82% (135 mg); Yellowish solid; mp = 185-187 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{21}H_{15}O_4$ 331.0970, found 331.0973; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (d, *J* = 1.6 Hz, 1H), 8.10 (dd, *J* = 1.6, 8.4 Hz, 1H), 7.89 (d, *J* = 9.2 Hz, 1H), 7.83-7.80 (m, 2H), 7.70 (dt, *J* = 1.6, 8.8 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.28 (dd, *J* = 0.8, 8.0 Hz, 1H), 7.26-7.24 (m, 1H), 7.22 (dd, *J* = 2.4, 8.8 Hz, 1H), 7.17 (d, *J* = 2.8 Hz, 1H), 3.96 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 188.2, 185.9, 167.7, 160.2, 152.0, 138.4, 137.7, 133.3, 131.4, 130.7, 127.8, 127.5, 125.0, 124.6, 124.4, 120.2, 119.9, 113.6, 105.9,

103.0, 55.5.

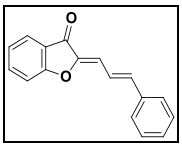


(*Z*)-2-(2-(Furan-2-yl)-2-oxoethylidene)benzofuran-3(2*H*)-one (4ag). Yield = 86% (103 mg); Yellowish solid; mp = 178-180 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^{+}$ calcd for $C_{14}H_9O_4$ 241.0501, found 241.0506; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (dd, *J* = 0.8, 7.6 Hz, 1H), 7.71 (dt, *J* = 1.2, 8.0 Hz, 1H), 7.68 (dd, *J* = 0.8, 2.0 Hz, 1H), 7.40 (d, *J* = 7.6 Hz, 1H), 7.38 (dd, *J* = 0.8, 4.0 Hz, 1H), 7.27 (dt, *J* = 0.8, 8.0 Hz, 1H), 7.03 (s, 1H), 6.62 (dd, *J* = 2.0, 4.0 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 185.8, 176.2, 167.8, 153.7, 152.4, 147.3, 138.5, 125.1, 124.6, 120.0, 118.4, 113.7, 112.9, 101.7.



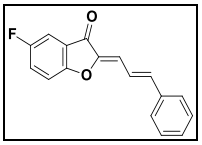
(*Z*)-2-(2-Oxo-2-(thiophen-2-yl)ethylidene)benzofuran-3(2*H*)-one (4ah). Yield = 80% (102 mg); Yellowish solid; mp = 194-196 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^{+}$ calcd for $C_{14}H_9O_3S$ 257.0272, found 257.0273; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (dd, *J* = 1.2, 4.0 Hz, 1H), 7.79 (ddd, *J* = 0.4, 1.6, 8.4 Hz, 1H), 7.74 (dd, *J* = 1.2, 5.2 Hz, 1H), 7.70 (dt, *J* = 1.2, 8.4 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.26 (dt, *J* = 0.4, 8.0 Hz, 1H), 7.19 (dd, *J* = 4.0, 5.2 Hz, 1H), 6.98 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 185.8, 180.6, 167.7, 152.0, 145.7, 138.5, 135.3, 132.8, 128.5, 125.0, 124.5, 120.0, 113.6, 102.3.

A representative synthetic procedure of skeleton 6 is as follows: To a 50 mL two-necked flame-dried flask equipped with a magnetic stir bar, SeO_2 (233 mg, 1.1 mmol) was sequentially added to a solution of **5** (0.5 mmol) in dioxane (10 mL) at 25 ^{o}C. The reaction flask was sealed with a rubber stopper. Then, the flask was flushed with dry air. The reaction mixture was stirred at reflux for 2 h with a condenser and then cooled to 25 ^{o}C. **2** (0.5 mmol) in dioxane (10 mL) and 80% $H_2SO_{4(aq)}$ (1 mL) was added to the reaction mixture at 25 ^{o}C via a syringe. The reaction mixture was stirred at reflux for 10 h with a condenser. The reaction mixture was cooled to 25 ^{o}C and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 30/1~1/1) afforded **6**.

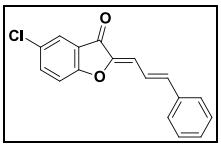


(*Z*)-2-((*E*)-3-Phenylallylidene)benzofuran-3(2*H*)-one (6a). Yield = 90% (112 mg); Yellowish

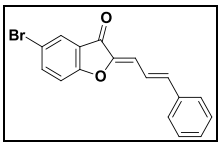
solid; mp = 103-105 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{17}H_{13}O_2$ 249.0916, found 249.0921; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (dd, *J* = 1.2, 7.6 Hz, 1H), 7.62 (dt, *J* = 1.2, 8.4 Hz, 1H), 7.56-7.54 (m, 2H), 7.40-7.26 (m, 5H), 7.18 (dt, *J* = 0.4, 7.6 Hz, 1H), 7.01 (d, *J* = 15.2 Hz, 1H), 6.78 (dd, *J* = 0.8, 11.6 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 183.7, 165.4, 147.4, 141.3, 136.6, 136.2, 129.3, 128.8 (2x), 127.4 (2x), 124.4, 123.1, 122.4, 120.6, 114.2, 112.7.



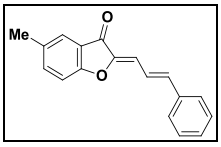
(*Z*)-5-Fluoro-2-((*E*)-3-phenylallylidene)benzofuran-3(2*H*)-one (6b). Yield = 85% (113 mg); Yellowish solid; mp = 122-124 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{17}H_{12}FO_2$ 267.0821, found 267.0818; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.55 (m, 2H), 7.44-7.23 (m, 7H), 7.05 (d, *J* = 16.0 Hz, 1H), 6.81 (dd, *J* = 0.8, 11.6 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 183.1, 161.4, 148.0, 128.7 (d, *J* = 242.6 Hz), 142.0, 136.2, 129.5, 128.9 (2x), 127.5 (2x), 124.0 (d, *J* = 25.7 Hz), 121.9 (d, *J* = 14.4 Hz), 120.5, 115.2, 113.9 (d, *J* = 7.6 Hz), 110.0 (d, *J* = 24.2 Hz); ^{19}F{^{1}H} NMR (564 MHz, $CDCl_3$): δ -120.42~-120.45 (m, 1F).



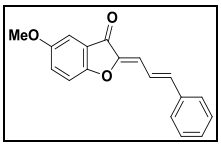
(*Z*)-5-Chloro-2-((*E*)-3-phenylallylidene)benzofuran-3(2*H*)-one (6c). Yield = 82% (116 mg); Yellowish solid; mp = 164-166 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{17}H_{12}ClO_2$ 283.0526, found 283.0524; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 2.0 Hz, 1H), 7.58-7.54 (m, 3H), 7.41-7.26 (m, 4H), 7.22 (d, *J* = 8.8 Hz, 1H), 7.05 (d, *J* = 15.6 Hz, 1H), 6.81 (d, *J* = 11.6 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 182.4, 163.5, 147.5, 142.2, 136.4, 136.1, 129.6, 128.9 (2x), 128.8, 127.5 (2x), 124.0, 123.6, 120.4, 115.3, 114.0.



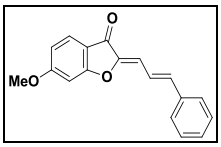
(*Z*)-5-Bromo-2-((*E*)-3-phenylallylidene)benzofuran-3(2*H*)-one (6d). Yield = 83% (135 mg); Yellowish solid; mp = 180-182 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{17}H_{12}BrO_2$ 327.0021, found 327.0026; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (dd, *J* = 0.4, 2.4 Hz, 1H), 7.70 (dd, *J* = 2.4, 8.8 Hz, 1H), 7.56-7.54 (m, 2H), 7.39-7.29 (m, 4H), 7.17 (dd, *J* = 0.4, 8.8 Hz, 1H), 7.04 (d, *J* = 15.6 Hz, 1H), 6.81 (dd, *J* = 0.8, 11.6 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 182.1, 163.9, 147.3, 142.3, 139.1, 136.1, 129.6, 128.9 (2x), 127.5 (2x), 127.1, 124.2, 120.4, 116.0, 115.3, 114.5.



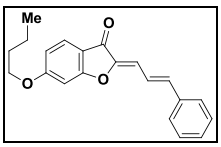
(*Z*)-5-Methyl-2-((*E*)-3-phenylallylidene)benzofuran-3(2*H*)-one (6e). Yield = 83% (109 mg); Yellowish solid; mp = 141-143 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^{+}$ calcd for $C_{18}H_{15}O_2$ 263.1072, found 263.1078; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.55 (m, 3H), 7.43-7.26 (m, 5H), 7.16 (d, *J* = 8.4 Hz, 1H), 7.01 (d, *J* = 15.6 Hz, 1H), 6.76 (dd, *J* = 0.8, 11.6 Hz, 1H), 2.39 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 183.9, 163.9, 147.9, 141.1, 137.8, 136.3, 132.9, 129.2, 128.8 (2x), 127.4 (2x), 124.1, 122.4, 120.7, 113.9, 112.3, 20.8.



(*Z*)-5-Methoxy-2-((*E*)-3-phenylallylidene)benzofuran-3(2*H*)-one (6f). Yield = 80% (111 mg); Yellowish solid; mp = 158-160 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^{+}$ calcd for $C_{18}H_{15}O_3$ 279.1021, found 279.1026; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.54 (m, 2H), 7.38-7.17 (m, 7H), 7.03 (d, *J* = 15.6 Hz, 1H), 6.78 (dd, *J* = 0.8, 11.6 Hz, 1H), 3.82 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 183.9, 160.5, 155.9, 148.2, 141.3, 136.3, 129.3, 128.8 (2x), 127.4 (2x), 126.0, 122.5, 120.7, 114.3, 113.5, 105.0, 55.9.

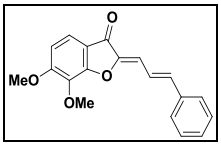


(*Z*)-6-Methoxy-2-((*E*)-3-phenylallylidene)benzofuran-3(2*H*)-one (6g). Yield = 86% (120 mg); Yellowish solid; mp = 197-199 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^{+}$ calcd for $C_{18}H_{15}O_3$ 279.1021, found 279.1025; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.4 Hz, 1H), 7.55-7.53 (m, 2H), 7.39-7.25 (m, 4H), 6.98 (d, *J* = 15.6 Hz, 1H), 6.74-6.70 (m, 3H), 3.91 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 182.1, 167.8, 167.3, 148.4, 140.5, 136.4, 129.1, 128.8 (2x), 127.3 (2x), 125.6, 120.6, 115.7, 113.1, 111.8, 96.4, 56.0.

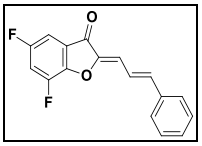


(*Z*)-6-*n*-Butoxy-2-((*E*)-3-phenylallylidene)benzofuran-3(2*H*)-one (6h). Yield = 85% (136 mg); Yellowish solid; mp = 100-102 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^{+}$ calcd for $C_{21}H_{21}O_3$ 321.1491, found 321.1495; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.4 Hz, 1H), 7.55-7.53 (m, 2H), 7.37-7.26 (m, 4H), 7.16 (d, *J* = 15.6 Hz, 1H), 6.73-6.68 (m, 3H), 4.06 (t, *J* = 7.2 Hz, 2H), 1.84-1.79 (m, 2H), 1.53-1.50 (m, 2H), 1.00 (t,

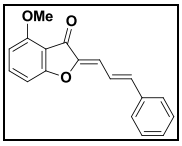
J = 7.2 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 182.1, 167.8, 166.9, 148.4, 140.4, 136.4, 129.1, 128.8 (2x), 127.3 (2x), 125.6, 120.6, 115.5, 112.9, 112.3, 96.8, 68.6, 30.9, 19.1, 13.7.



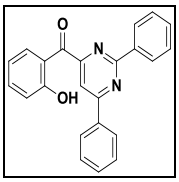
(*Z*)-6,7-Dimethoxy-2-((*E*)-3-phenylallylidene)benzofuran-3(2*H*)-one (6i). Yield = 80% (123 mg); Yellowish solid; mp = 127-129 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{19}H_{17}O_4$ 309.1127, found 309.1129; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.47 (m, 3H), 7.37-7.30 (m, 4H), 7.00 (d, *J* = 15.6 Hz, 1H), 6.78-6.71 (m, 2H), 4.12 (s, 3H), 3.97 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 182.3, 158.9, 157.3, 148.1, 140.8, 136.2, 133.7, 129.2, 128.8 (2x), 127.3 (2x), 120.5, 119.5, 117.6, 113.3, 107.9, 61.2, 56.7.



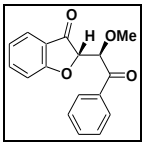
(*Z*)-5,7-Difluoro-2-((*E*)-3-phenylallylidene)benzofuran-3(2*H*)-one (6j). Yield = 81% (115 mg); Yellowish solid; mp = 142-144 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{17}H_{11}F_2O_2$ 285.0727, found 285.0732; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59-7.57 (m, 2H), 7.42-7.31 (m, 4H), 7.28-7.26 (m, 1H), 7.18 (dd, *J* = 0.8, 11.2 Hz, 1H), 7.09 (d, *J* = 15.6 Hz, 1H), 6.89 (dd, *J* = 0.8, 11.2 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 181.8, 157.9 (dd, *J* = 6.8, 245.6 Hz), 157.7 (dd, *J* = 6.8, 246.0 Hz), 149.1 (d, *J* = 12.1 Hz), 146.5 (d, *J* = 11.3 Hz), 143.3, 135.9, 129.8, 128.93 (2x), 128.88, 127.7 (2x), 120.1, 116.8, 111.5 (dd, *J* = 19.7, 28.8 Hz), 105.8 (dd, *J* = 4.6, 23.5 Hz); $^{19}F\{^{1}H\}$ NMR (564 MHz, $CDCl_3$): δ -116.69~-116.72 (m, 1F), -133.49~-133.52 (m, 1F).



(*Z*)-4-Methoxy-2-((*E*)-3-phenylallylidene)benzofuran-3(2*H*)-one (6k). Yield = 83% (115 mg); Yellowish solid; mp = 172-174 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{18}H_{15}O_3$ 279.1021, found 279.1023; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.54 (m, 3H), 7.37-7.29 (m, 4H), 6.99 (d, *J* = 16.0 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 6.74 (dd, *J* = 1.2, 12.0 Hz, 1H), 6.59 (d, *J* = 8.4 Hz, 1H), 3.99 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 181.5, 166.4, 158.4, 147.4, 140.6, 138.2, 136.4, 129.7, 129.1, 128.8 (2x), 127.3 (2x), 120.7, 113.2, 104.8, 104.6, 56.2.

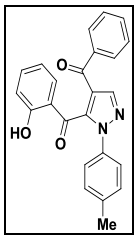


(2,6-Diphenylpyrimidin-4-yl)(2-hydroxyphenyl)methanone (7). To a 50 mL two-necked flame-dried flask equipped with a magnetic stir bar, benzamidine (40 mg, 0.33 mmol) was sequentially added to a solution of **4a** (75 mg, 0.3 mmol) in *t*BuOH (10 mL) at 25 °C. The reaction flask was sealed with a rubber stopper. Then, the flask was flushed with dry air. The reaction mixture was stirred at reflux for 20 h with a condenser. The reaction mixture was cooled to 25 °C and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 30/1~1/1) afforded **7**. Yield = 85% (90 mg); Yellowish solid; mp = 198-200 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{23}H_{17}N_2O_2$ 353.1290, found 353.1295; ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.00 (br s, 1H), 8.64-8.62 (m, 2H), 8.33-8.30 (m, 2H), 8.25 (dd, *J* = 1.6, 8.4 Hz, 1H), 8.07 (s, 1H), 7.61-7.53 (m, 7H), 7.12 (dd, *J* = 0.8, 8.4 Hz, 1H), 6.95 (dt, *J* = 0.8, 8.4 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 197.0, 166.1, 164.1, 163.8, 162.9, 137.4, 137.1, 136.4, 134.2, 131.6, 131.3, 129.1 (2x), 128.7 (2x), 128.6 (2x), 127.4 (2x), 119.1, 118.5, 118.3, 113.3. Single-crystal X-Ray diagram: crystal of compound **7** was grown by slow diffusion of EtOAc into a solution of compound **7** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the triclinic crystal system, space group P-1, *a* = 3.8702(6) Å, *b* = 13.0697(10) Å, *c* = 16.8646(8) Å, *V* = 845.21(15) Å^3, *Z* = 2, d_{calcd} = 1.385 g/cm^3, *F*(000) = 368.0, 2*θ* range 3.144~49.998°, R indices (all data) R1 = 0.1245, wR2 = 0.2751.

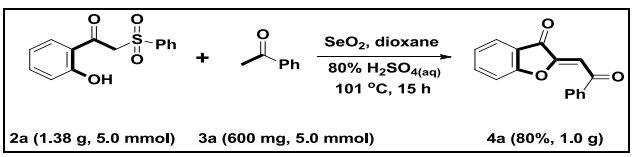


2-(1-Methoxy-2-oxo-2-phenylethyl)benzofuran-3(2*H*)-one (8). To a 50 mL two-necked flame-dried flask equipped with a magnetic stir bar, K_2CO_3 (140 mg, 1.0 mmol) was sequentially added to a solution of **4a** (75 mg, 0.3 mmol) in MeOH (10 mL) at 25 °C. The reaction flask was sealed with a rubber stopper. Then, the flask was flushed with dry air. The reaction mixture was stirred at reflux for 20 h with a condenser. The reaction mixture was cooled to 25 °C and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 15/1~1/1) afforded **8**. Yield = 80% (68 mg); Viscous oil; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{17}H_{15}O_4$ 283.0970, found 283.0978; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89-7.86 (m, 2H), 7.73 (ddd, *J* = 0.8, 1.6, 7.6 Hz, 1H), 7.64 (dt, *J* = 1.6, 8.4 Hz, 1H), 7.58-7.53 (m, 1H), 7.45-7.41 (m, 2H), 7.13 (dt, *J* = 0.8, 7.6

Hz, 1H), 7.06 (d, *J* = 8.4 Hz, 1H), 4.02 (d, *J* = 17.2 Hz, 1H), 3.71 (d, *J* = 17.6 Hz, 1H), 3.27 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 198.2, 194.4, 170.8, 138.5, 136.0, 133.6, 128.6 (2x), 128.3 (2x), 124.1, 122.3, 121.4, 112.5, 105.0, 51.6, 44.9.



(4-Benzoyl-1-(*p*-tolyl)-1*H*-pyrazol-5-yl)(2-hydroxyphenyl)methanone (9). To a 50 mL two-necked flame-dried flask equipped with a magnetic stir bar, excess *p*TolN=N=CH (100 mg, 0.76 mmol) was sequentially added to a solution of **4a** (75 mg, 0.3 mmol) in $CHCl_3$ (10 mL) at 0 °C. The reaction flask was sealed with a rubber stopper. Then, the flask was flushed with dry nitrogen. The reaction mixture was stirred at 0 °C for 20 h. The reaction mixture was was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 30/1~10/1) afforded **9**. Yield = 73% (84 mg); Yellowish solid; mp = 135-137 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{24}H_{19}N_2O_3$ 383.1396, found 383.1399; ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.38 (s, 1H), 8.08 (s, 1H), 7.83-7.80 (m, 2H), 7.59-7.55 (m, 1H), 7.47-7.41 (m, 3H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.28 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.95 (dd, *J* = 0.8, 8.4 Hz, 1H), 6.77 (dt, *J* = 0.8, 8.0 Hz, 1H), 2.35 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 193.0, 188.2, 162.6, 141.4, 141.2, 139.3, 138.1, 137.6, 136.2, 132.9, 131.6, 130.0 (2x), 128.9 (2x), 128.6 (2x), 124.4, 123.9 (2x), 120.3, 119.6, 118.5, 21.1. Single-crystal X-Ray diagram: crystal of compound **9** was grown by slow diffusion of EtOAc into a solution of compound **9** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group $P2_1/n$, *a* = 10.7895(6) Å, *b* = 11.0470(6) Å, *c* = 16.5159(10) Å, *V* = 1912.78(19) $Å^3$, *Z* = 4, d_{calcd} = 1.331 g/cm^3, *F*(000) = 584.0, 2*θ* range 4.108~54.116°, R indices (all data) R1 = 0.0956, wR2 = 0.1772.



Gram-scale synthesis of compound 4a. To a 50 mL two-necked flame-dried flask equipped with a magnetic stir bar, SeO_2 (2.22 g, 10.0 mmol) was sequentially added to a solution of **3a** (600 mg, 5.0 mmol) in dioxane (50 mL) at 25 °C. The reaction flask was sealed with a rubber stopper. Then, the flask was flushed with dry air. The reaction mixture was stirred at reflux for 2 h with a condenser and then cooled to 25 °C. **2a** (1.38 g, 5.0 mmol) in dioxane (50 mL) and 80% $H_2SO_{4(aq)}$ (5 mL) was added to the reaction mixture at 25 °C via a syringe. The reaction

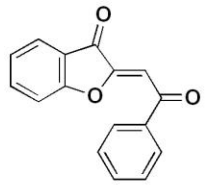
mixture was stirred at reflux for 13 h with a condenser. The reaction mixture was cooled to 25 ^{o}C and the solvent was concentrated. The residue was diluted with water (50 mL) and the mixture was extracted with CH_2Cl_2 (3 x 100 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 8/1~2/1) afforded **4a** (80%, 1.0 g).

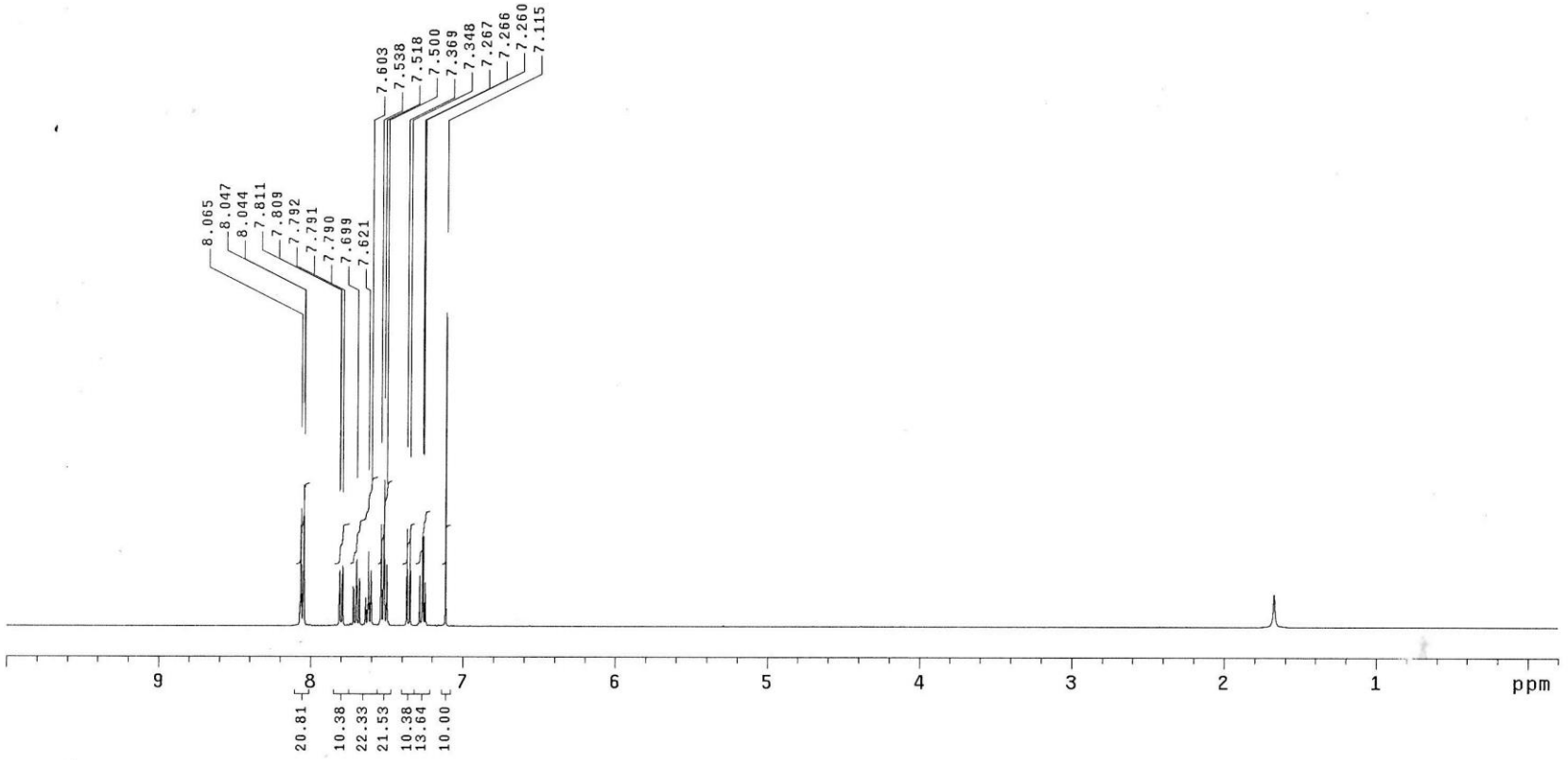
Compound 4a (^{1}H-NMR spectral data)

LYK1833

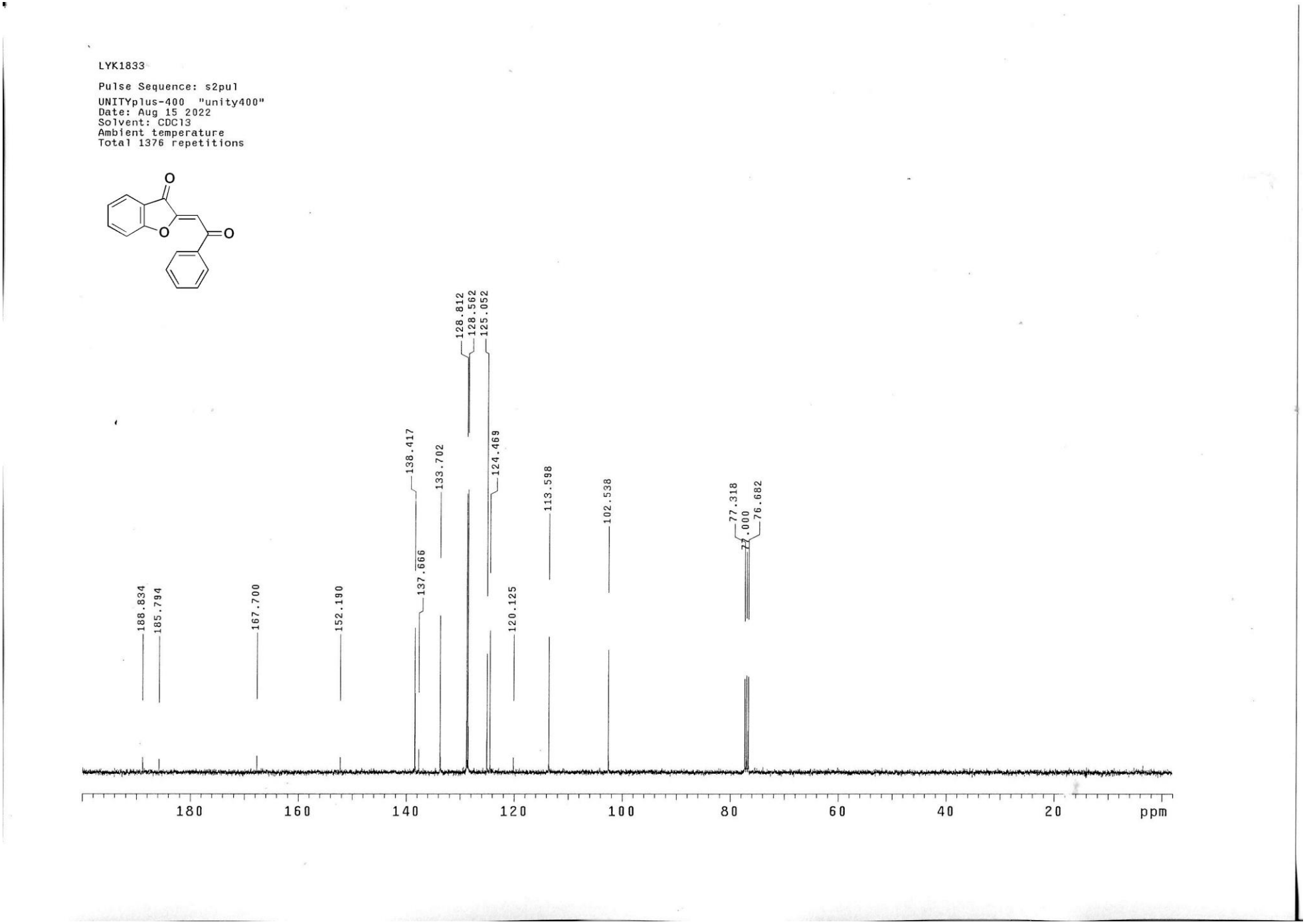
Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Aug 15 2022
Solvent: CDCl3
Ambient temperature
Total 32 repetitions

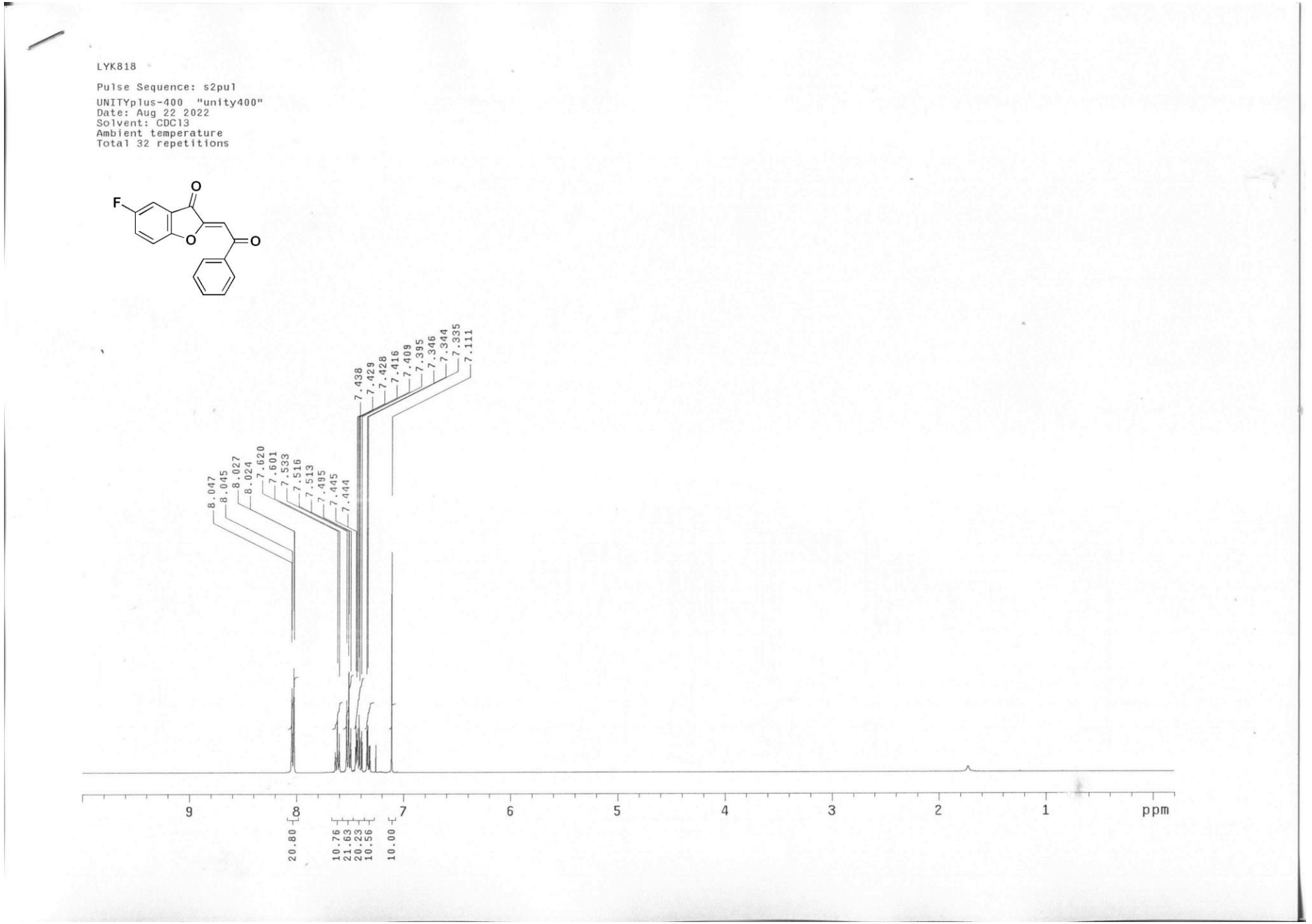




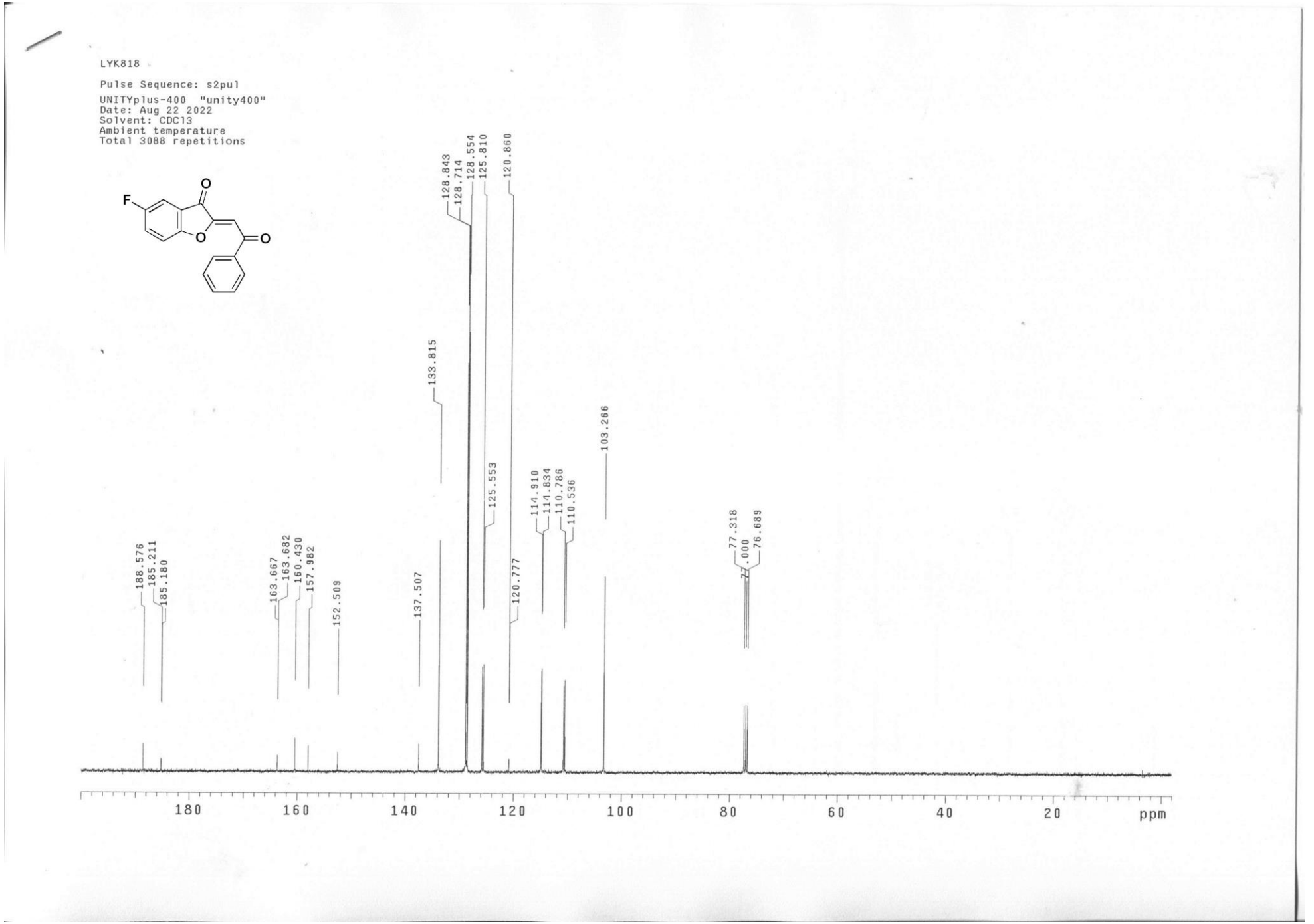
Compound 4a (^{13}C-NMR spectral data)



Compound 4b (^{1}H-NMR spectral data)

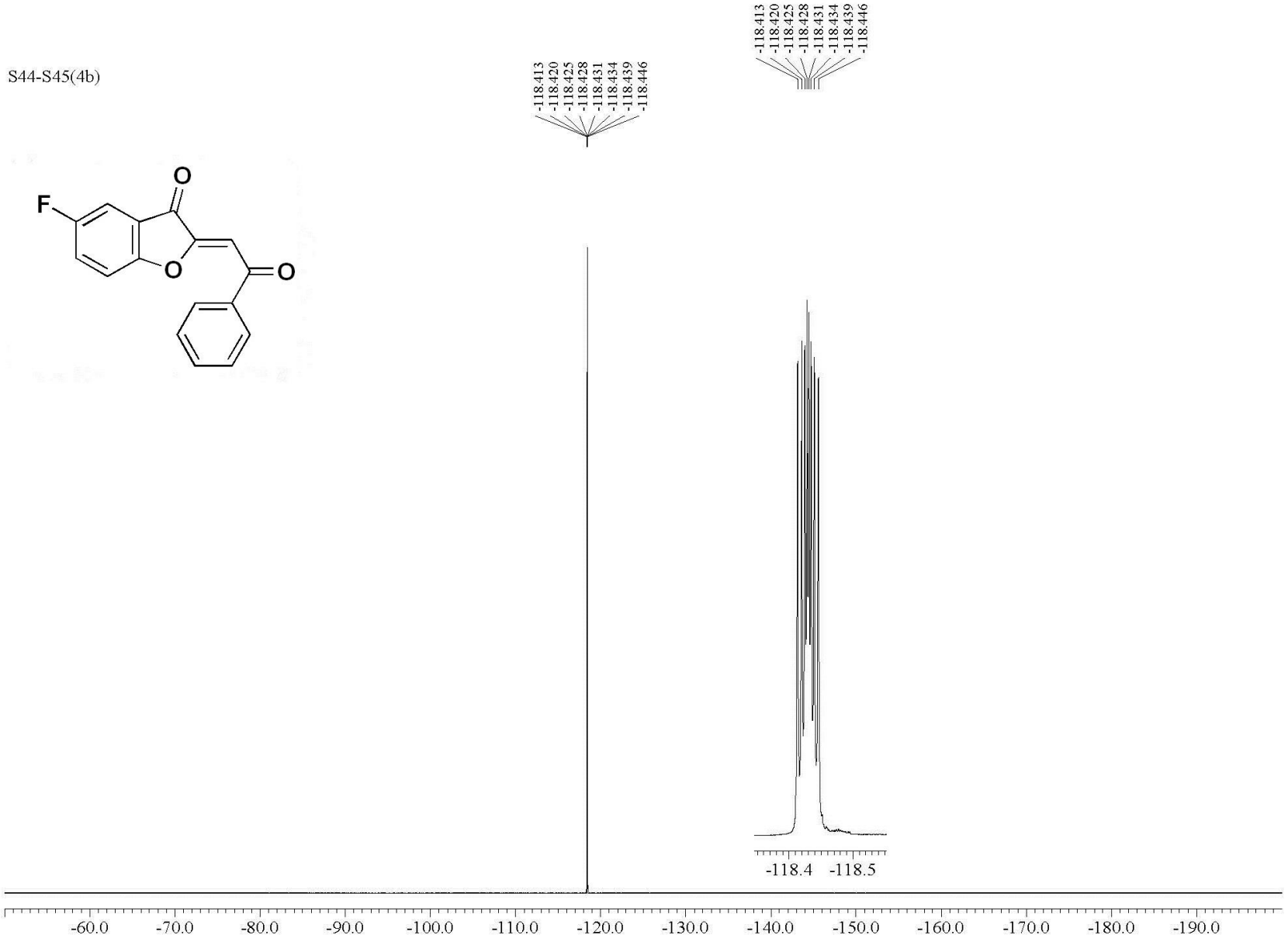


Compound 4b (^{13}C-NMR spectral data)

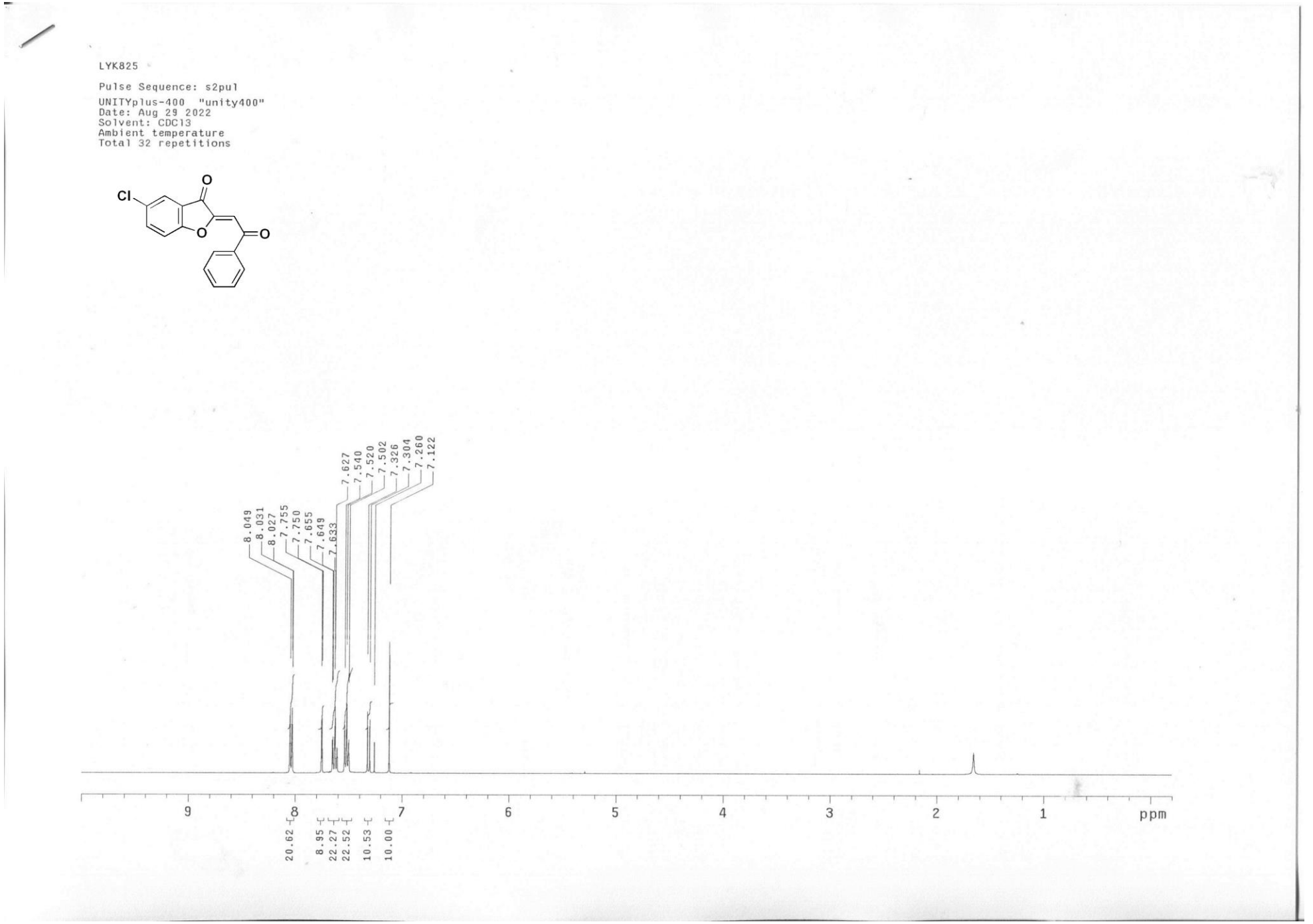


Compound 4b (^{19}F-NMR spectral data)

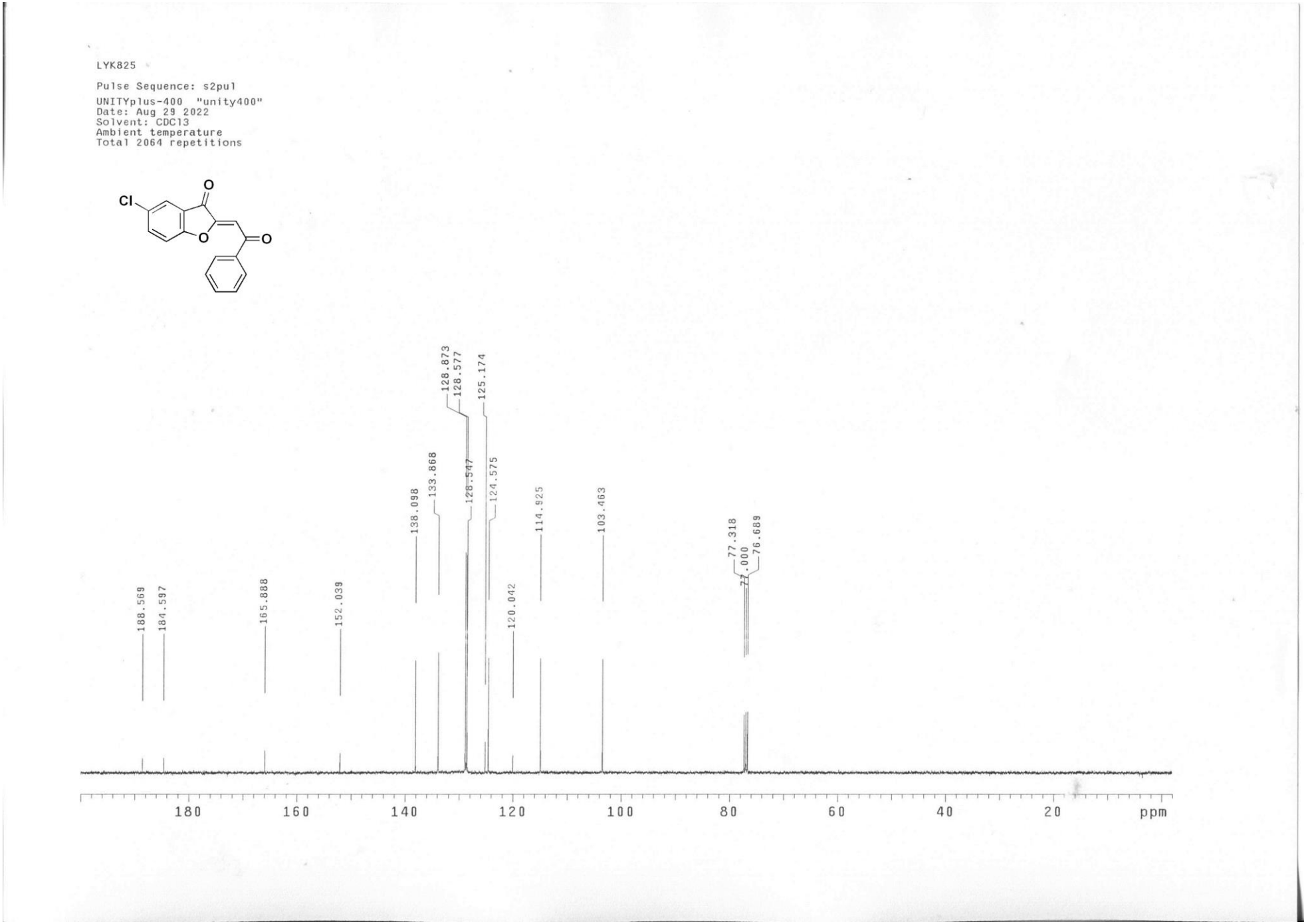
S44-S45(4b)



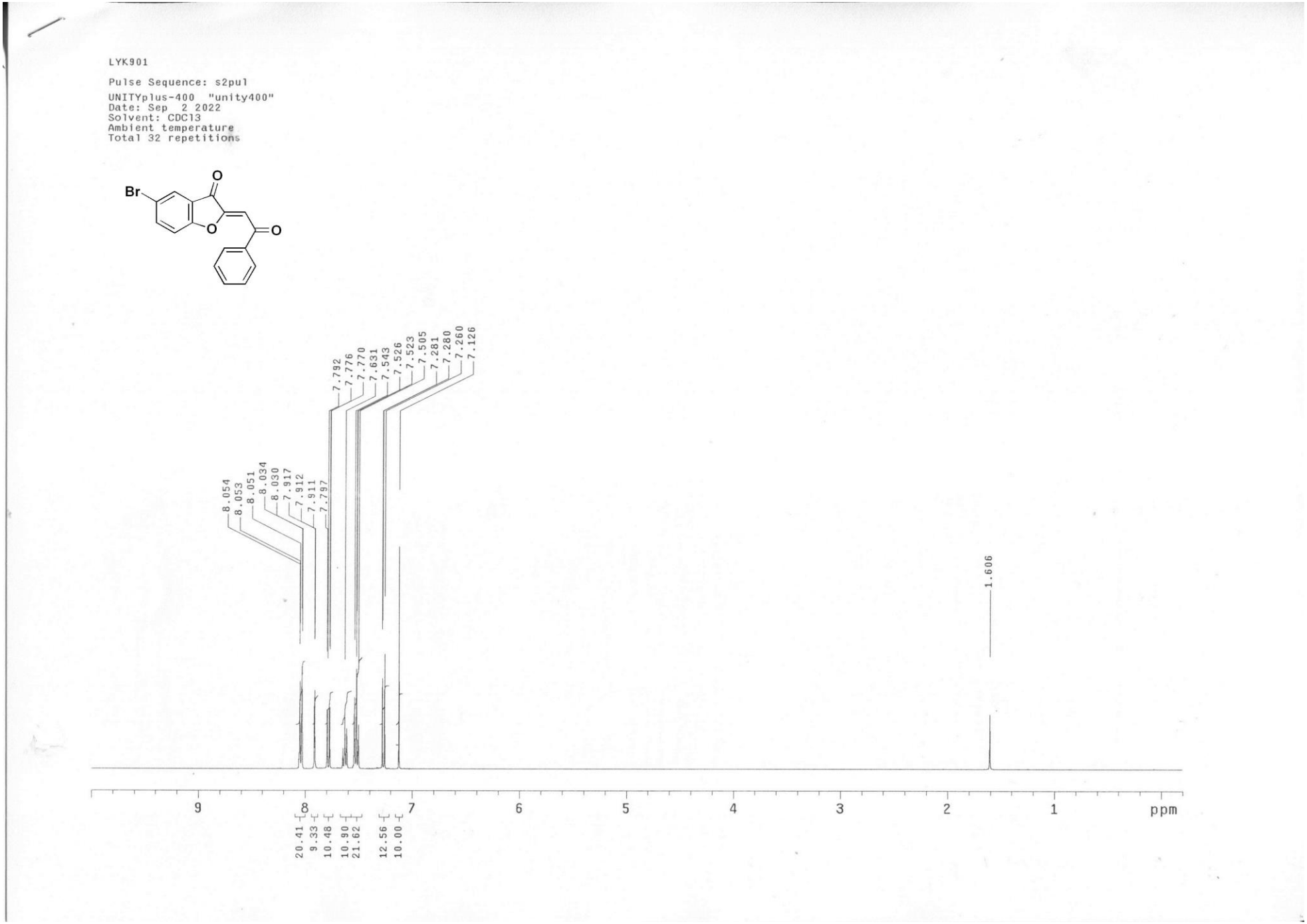
Compound 4c (^{1}H-NMR spectral data)



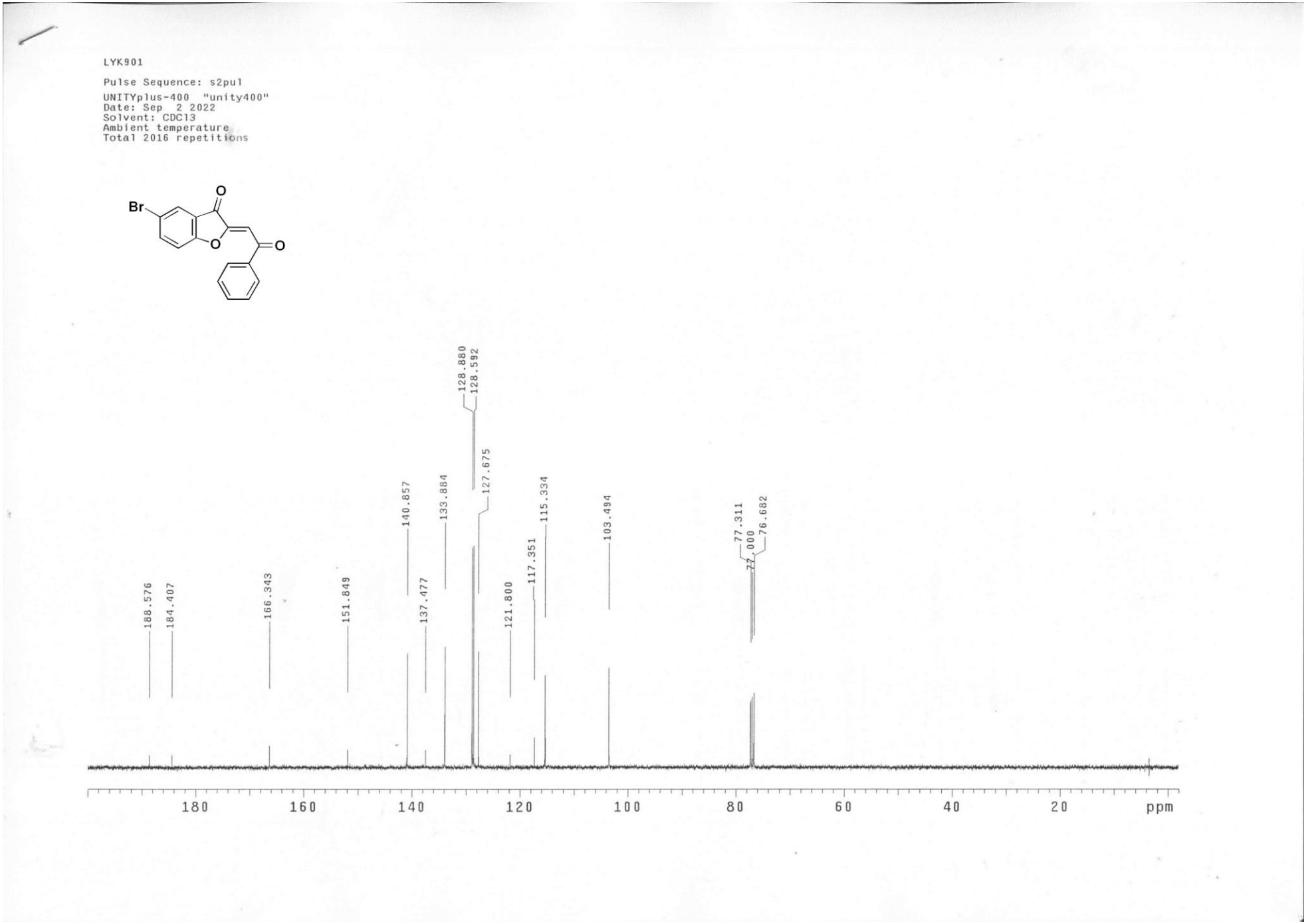
Compound 4c (^{13}C-NMR spectral data)



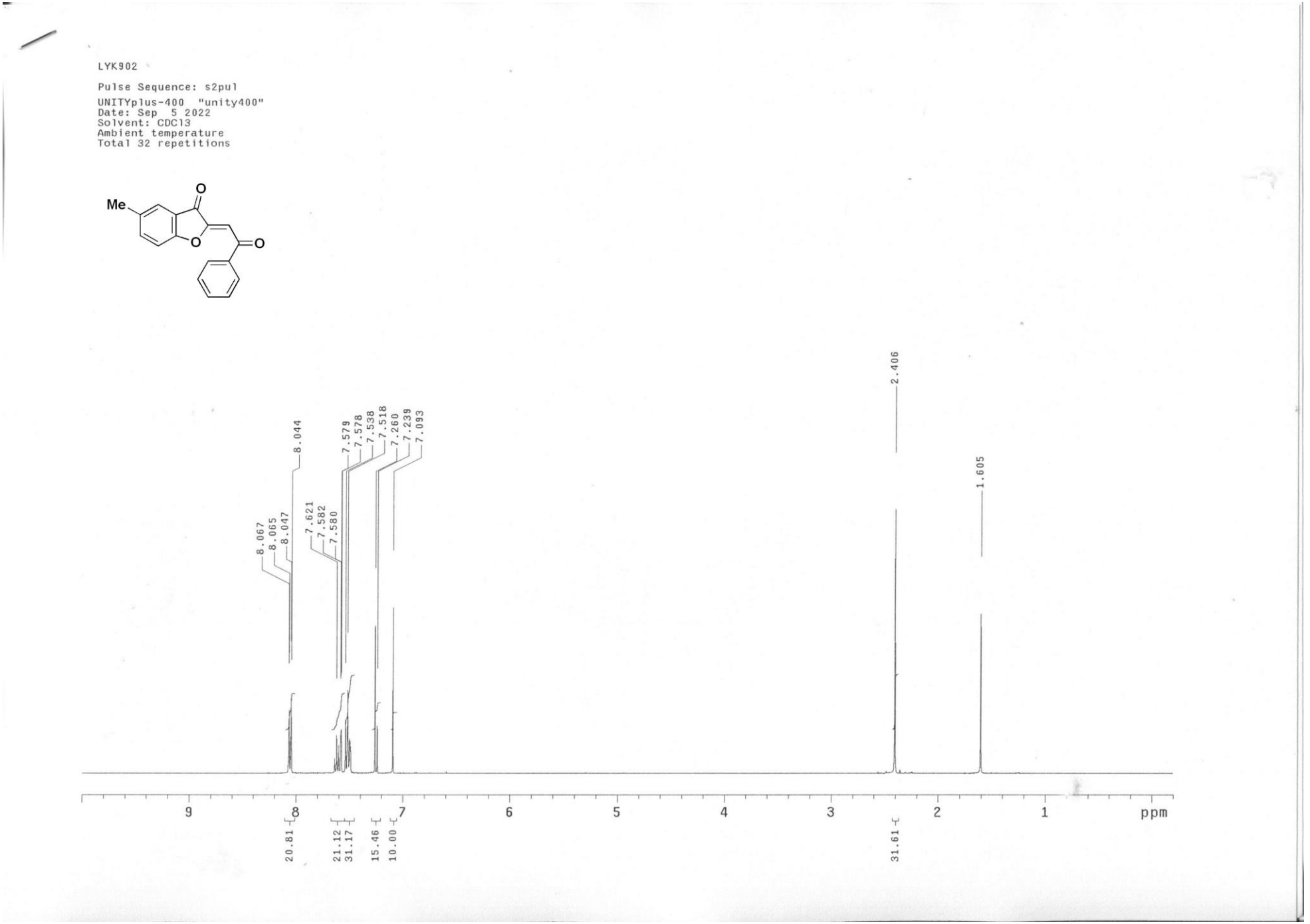
Compound 4d (^{1}H-NMR spectral data)



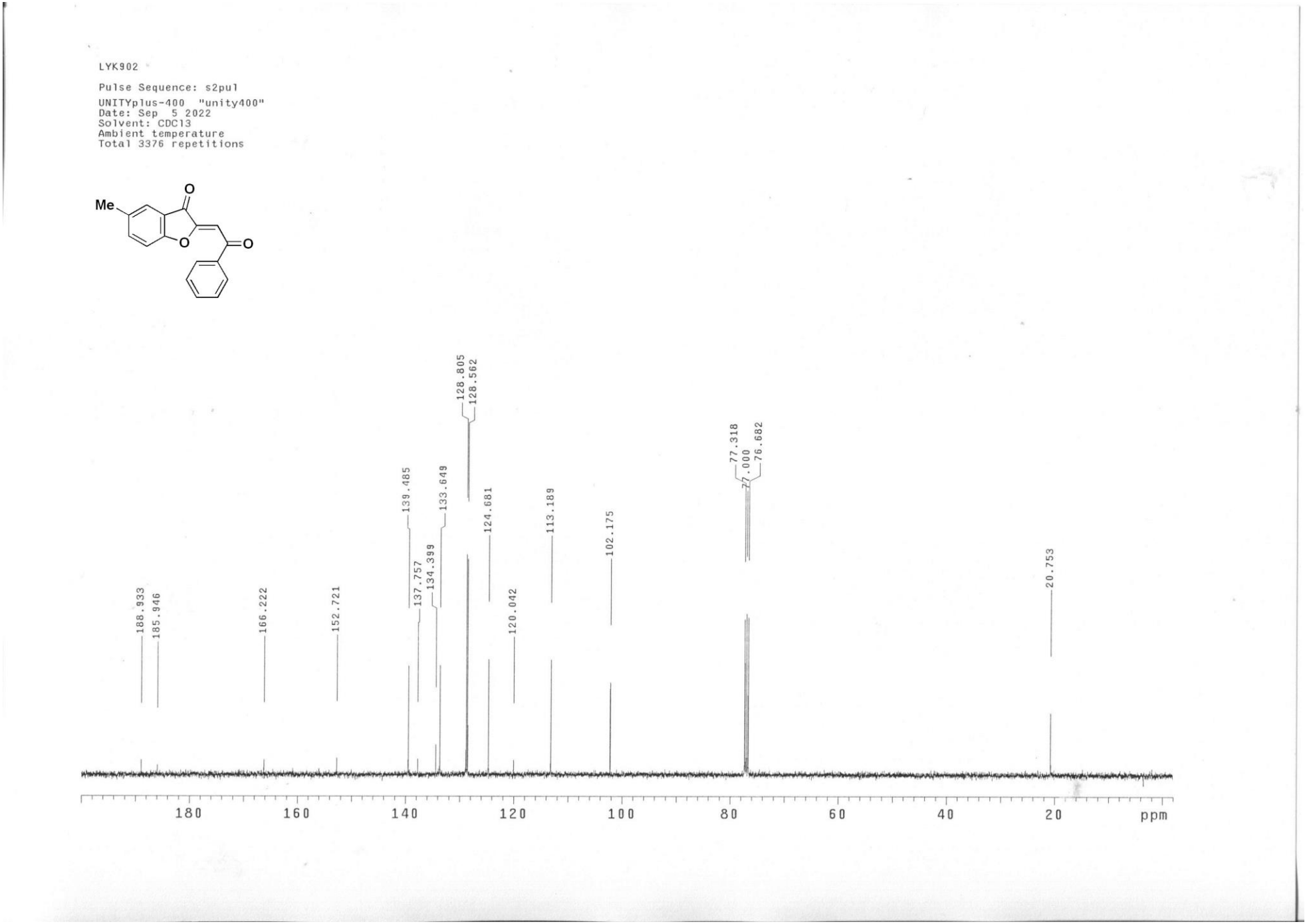
Compound 4d (^{13}C-NMR spectral data)



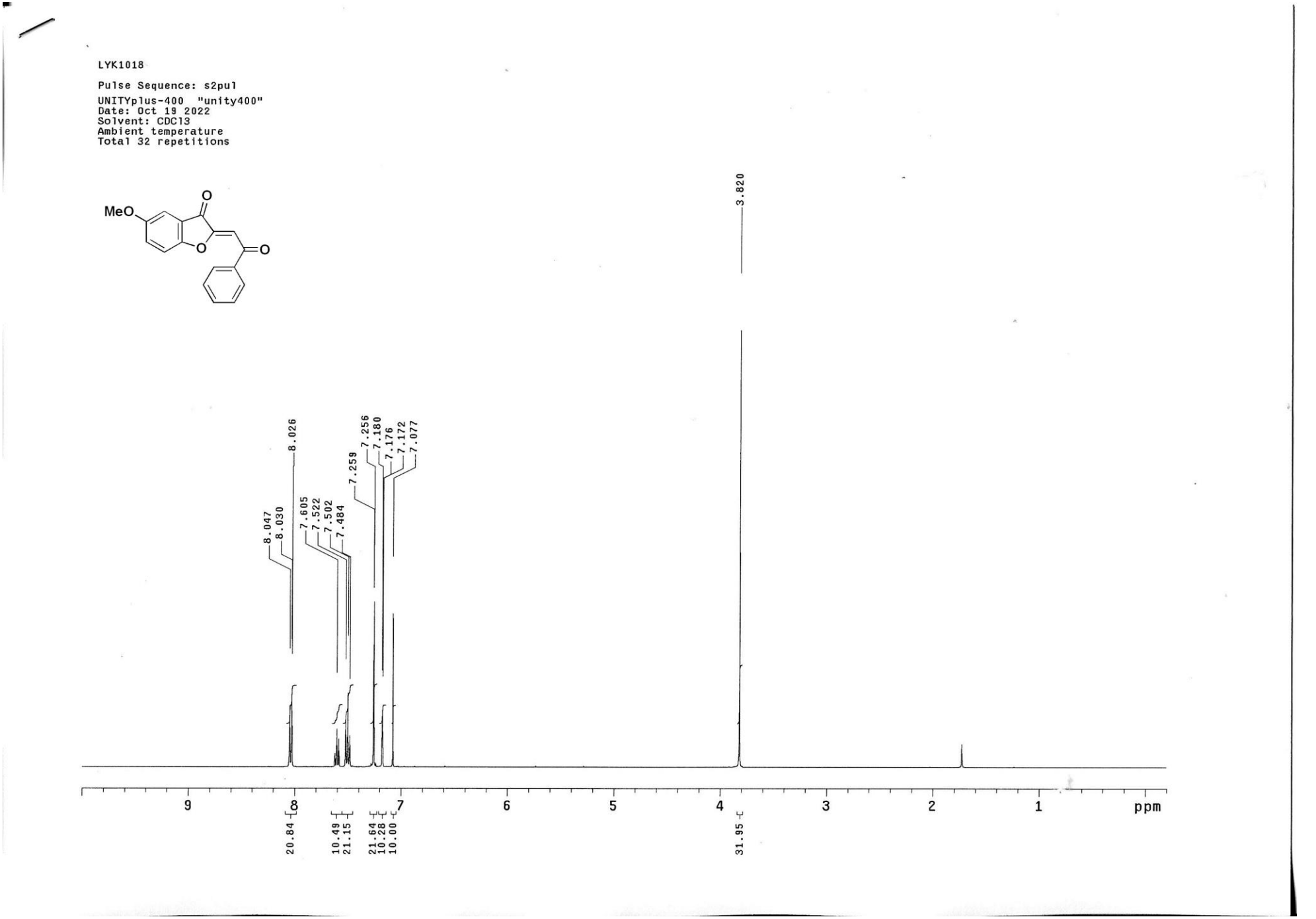
Compound 4e (^{1}H-NMR spectral data)



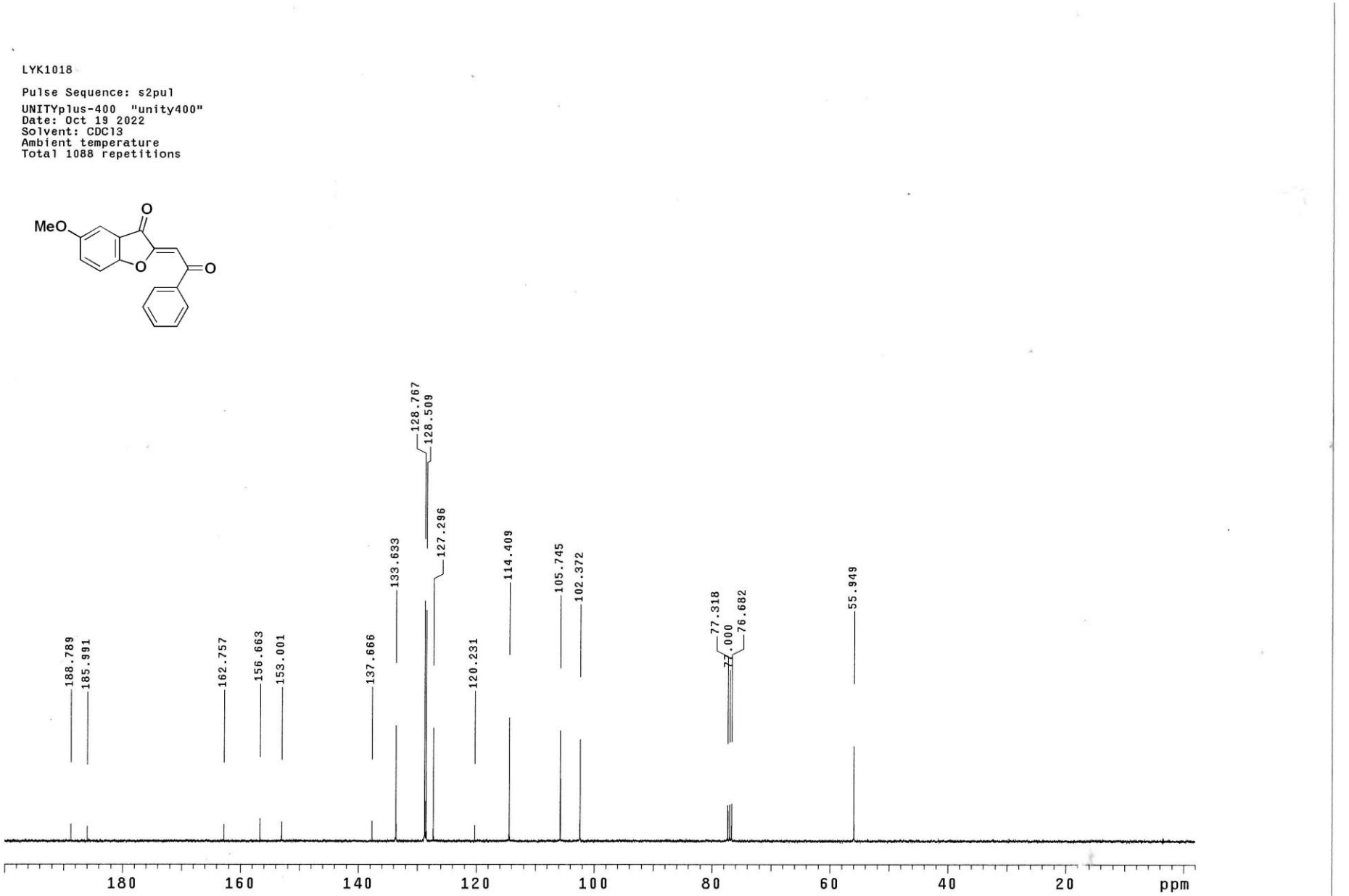
Compound 4e (^{13}C-NMR spectral data)



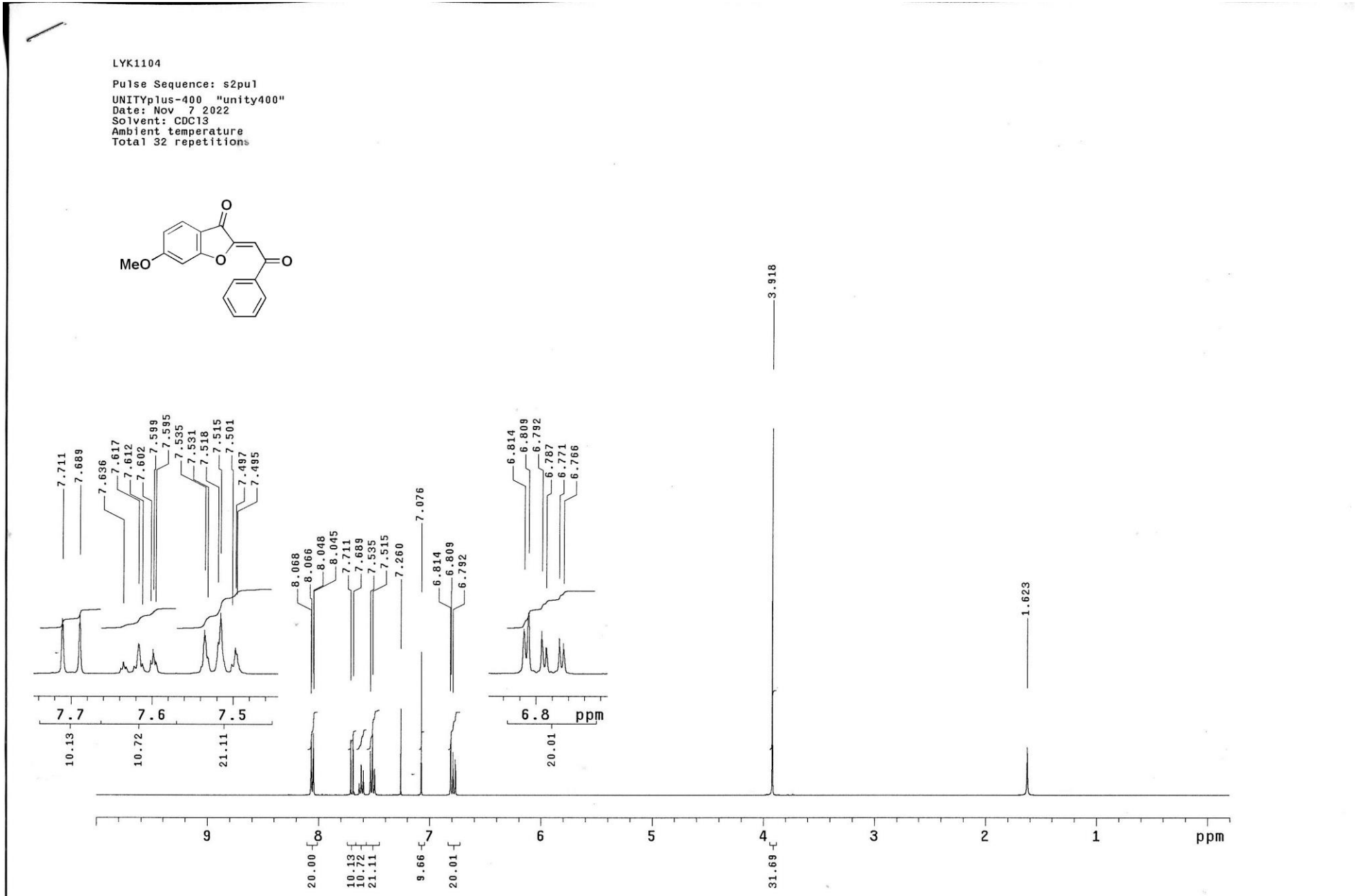
Compound 4f (^{1}H-NMR spectral data)



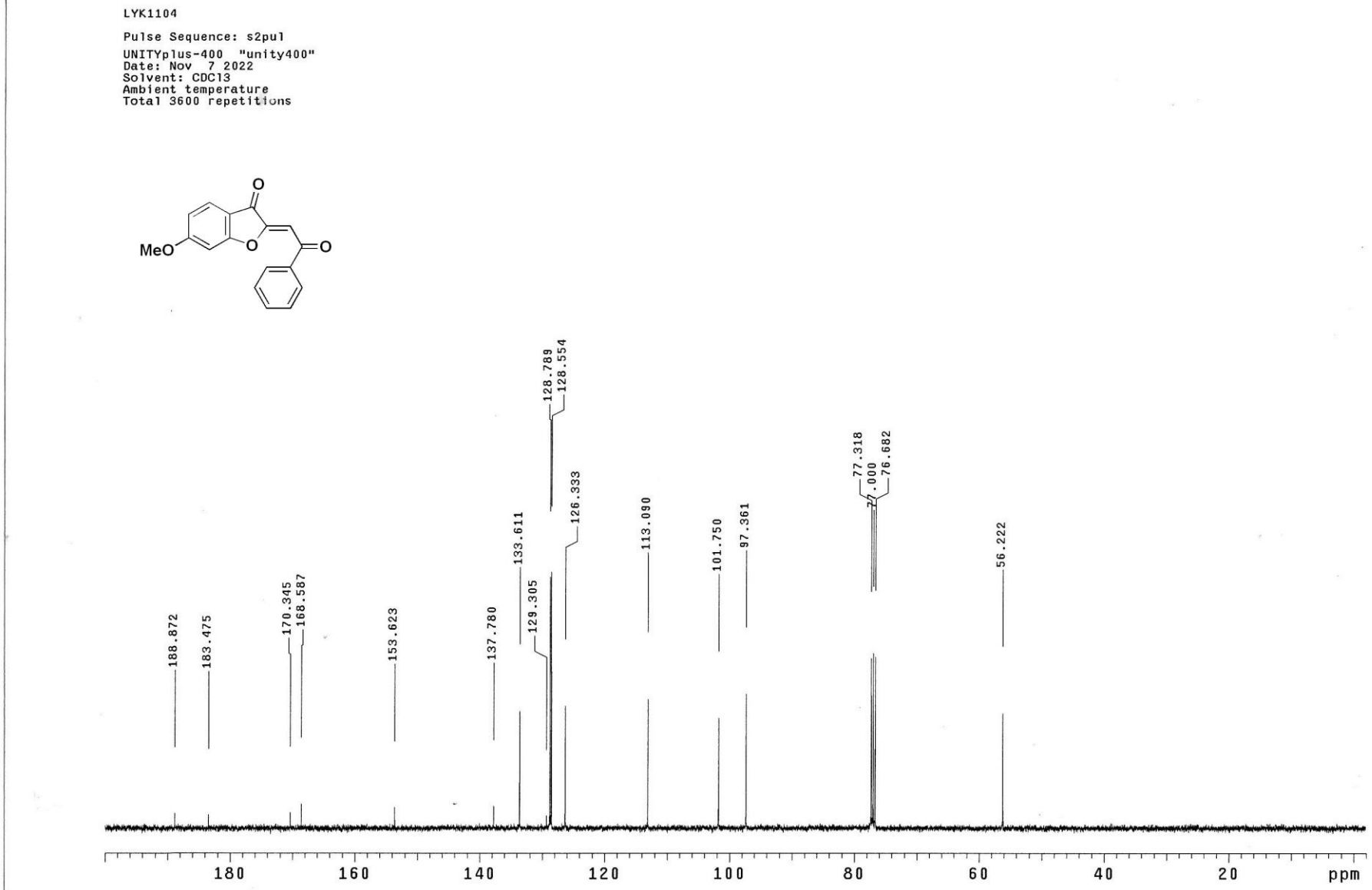
Compound 4f (^{13}C-NMR spectral data)



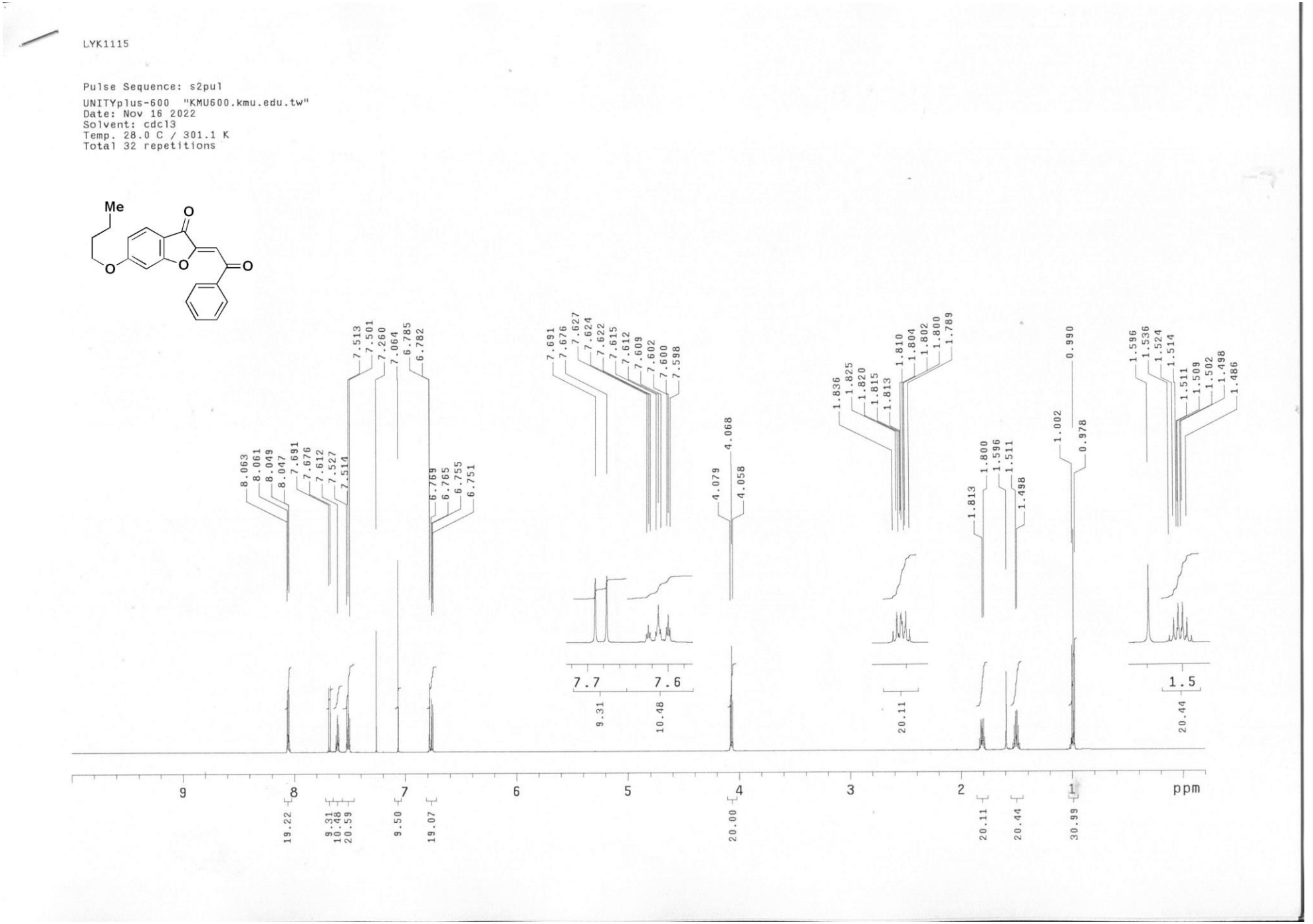
Compound 4g (^{1}H-NMR spectral data)



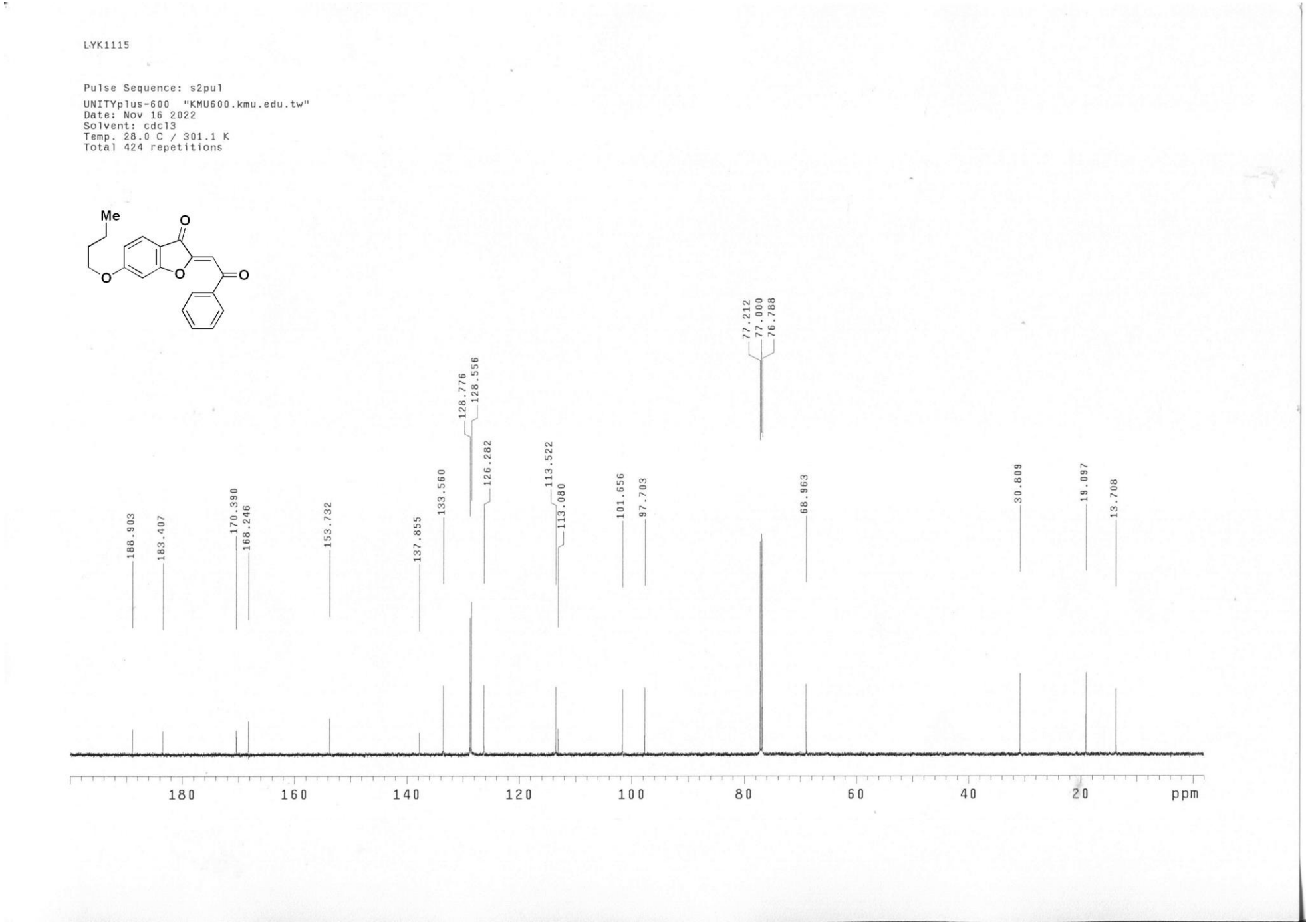
Compound 4g (^{13}C-NMR spectral data)



Compound 4h (^{1}H-NMR spectral data)



Compound 4h (^{13}C-NMR spectral data)

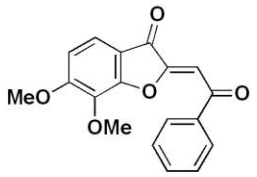


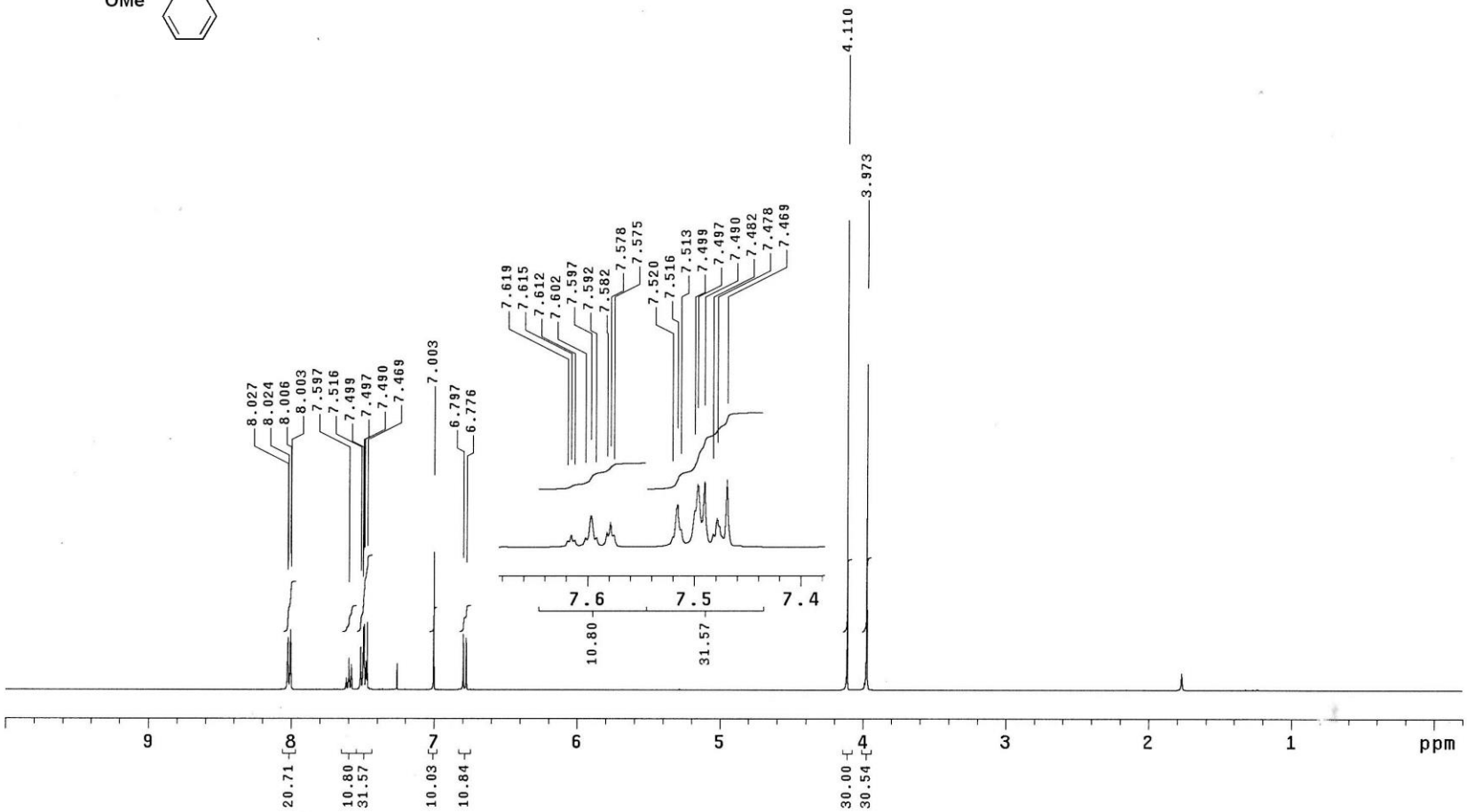
Compound 4i (^{1}H-NMR spectral data)

LYK1102

Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Nov 3 2022
Solvent: CDCl3
Ambient temperature
Total 32 repetitions



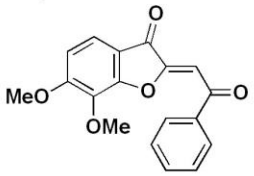


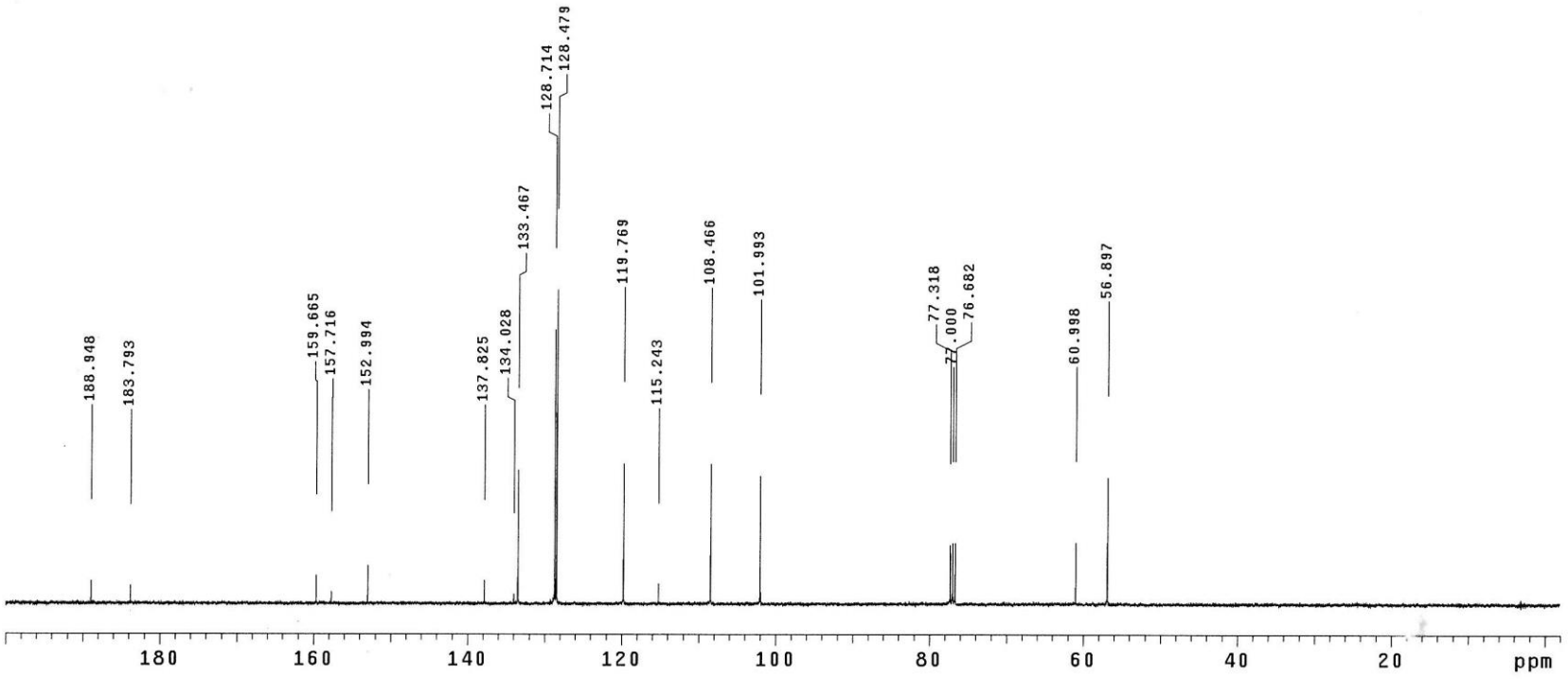
Compound 4i (^{13}C-NMR spectral data)

LYK1102

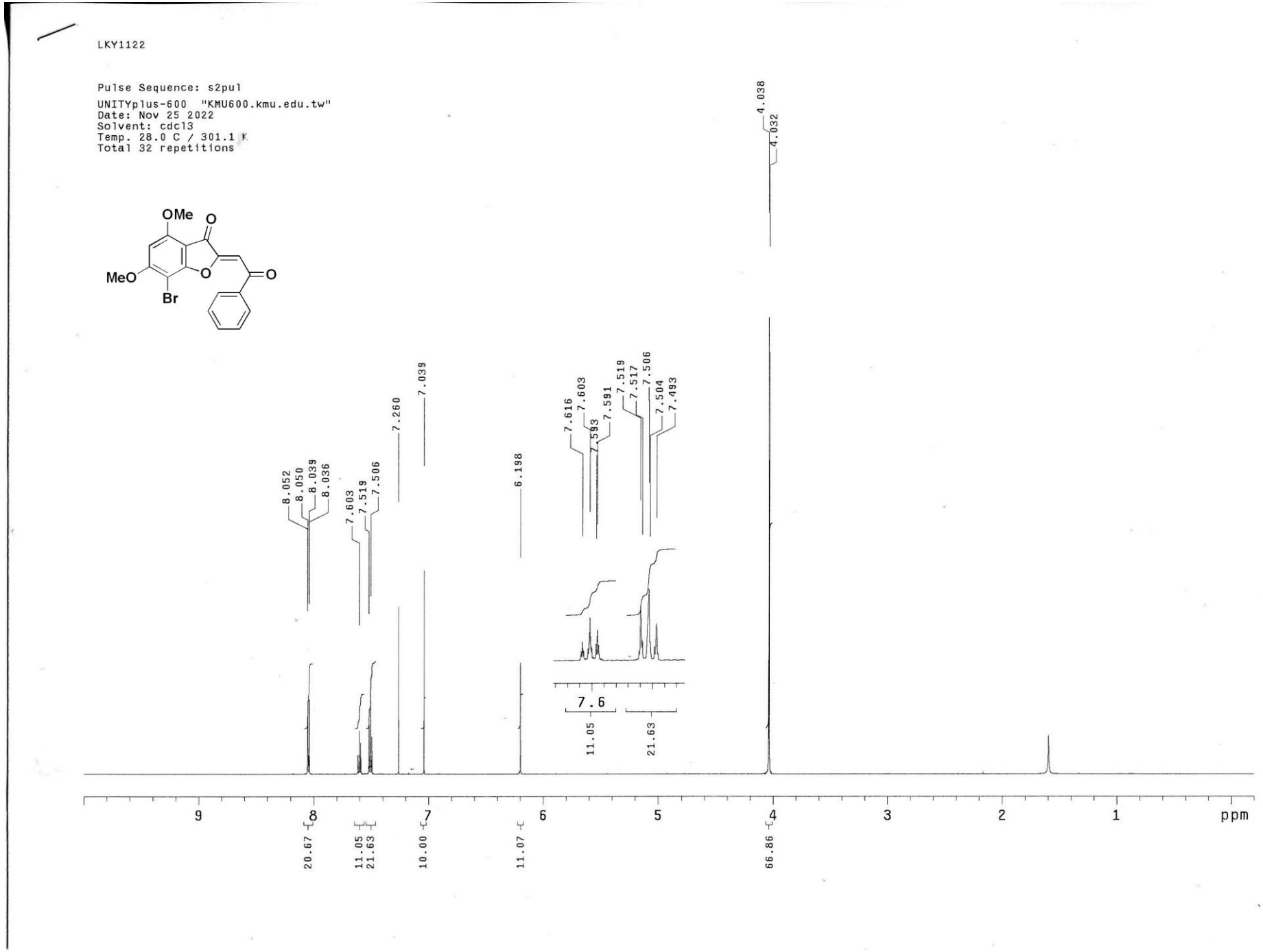
Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Nov 3 2022
Solvent: CDCl3
Ambient temperature
Total 1808 repetitions

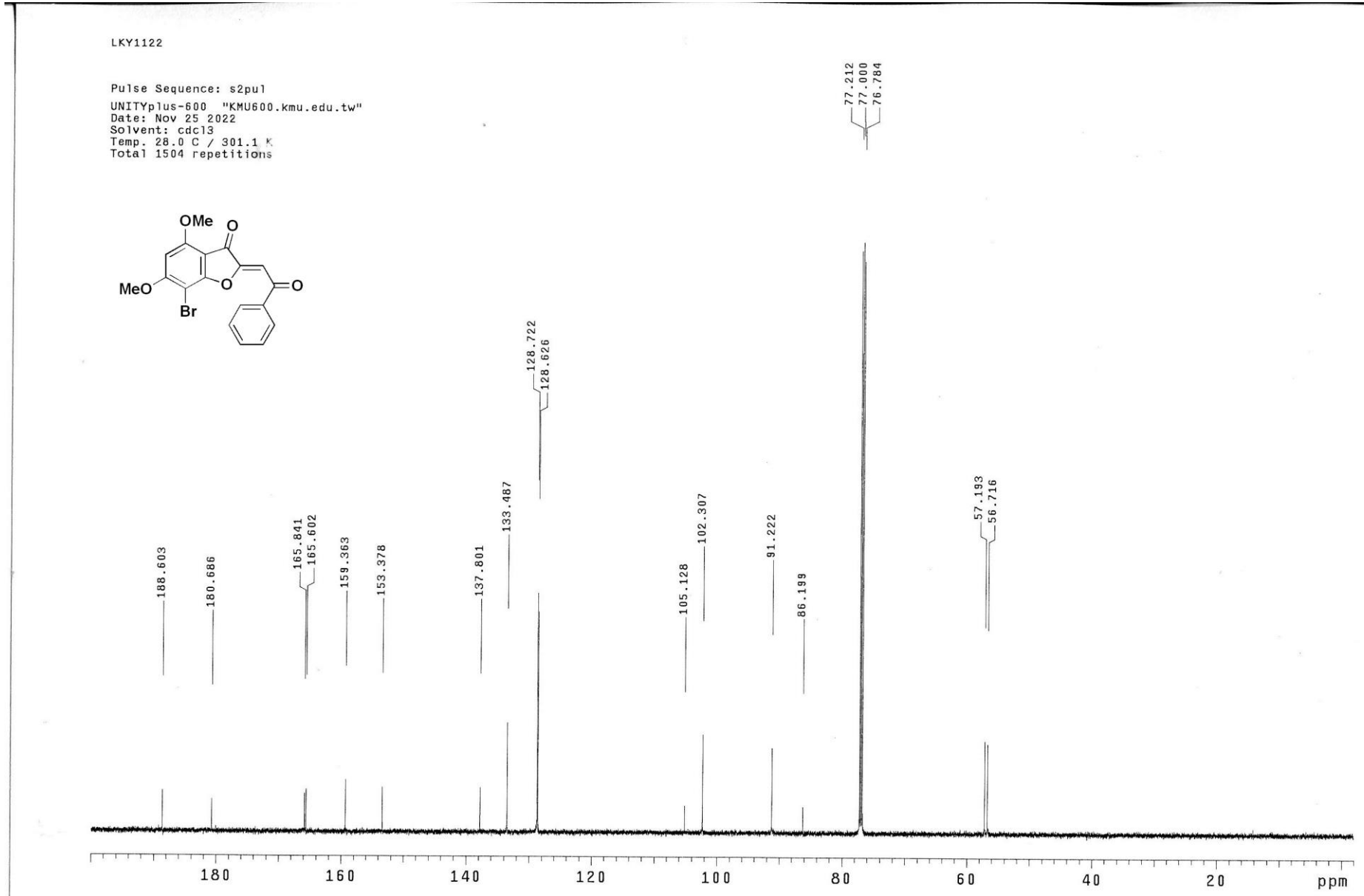




Compound 4j (^{1}H-NMR spectral data)



Compound 4j (^{13}C-NMR spectral data)

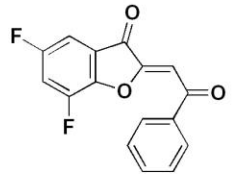


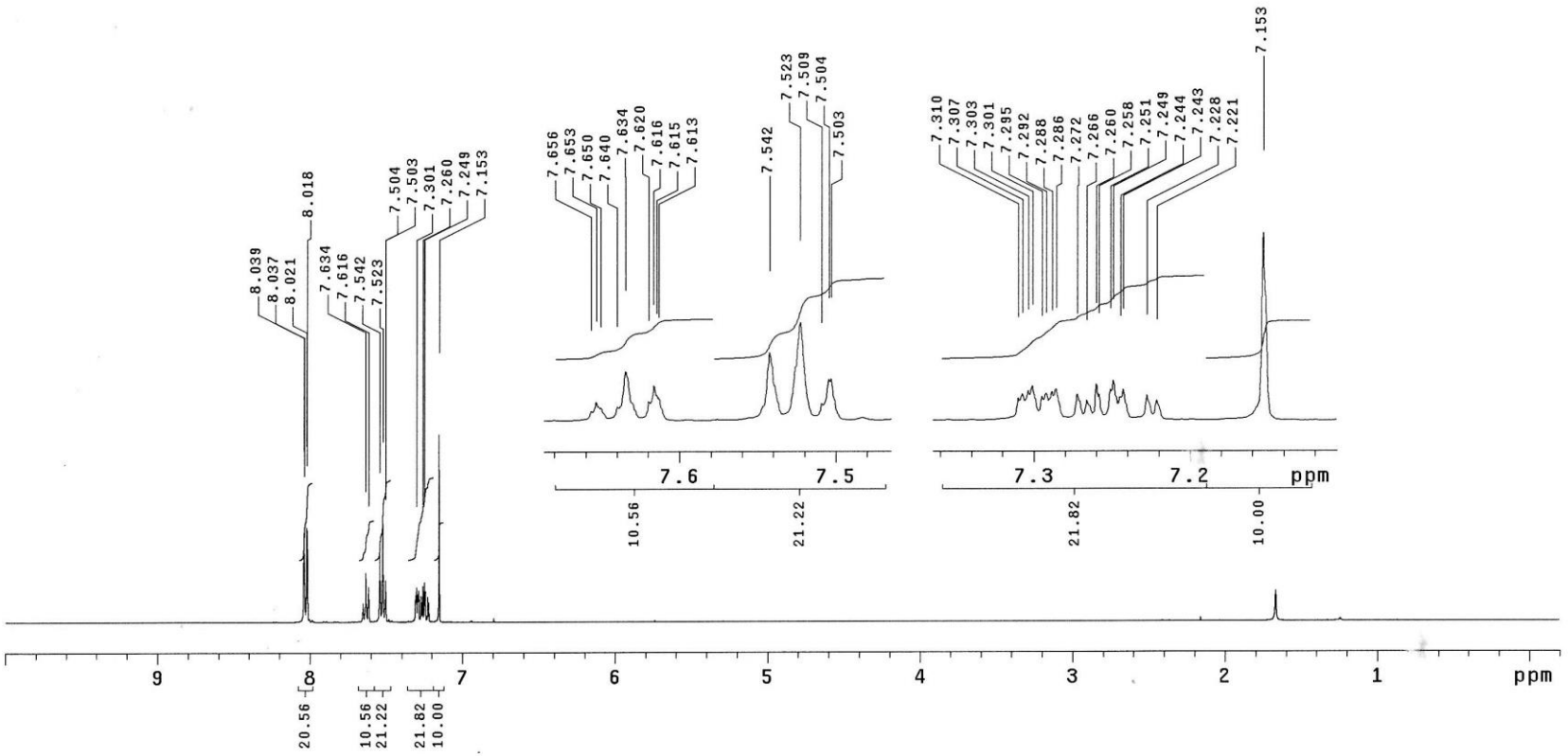
Compound 4k (^{1}H-NMR spectral data)

LYK1117

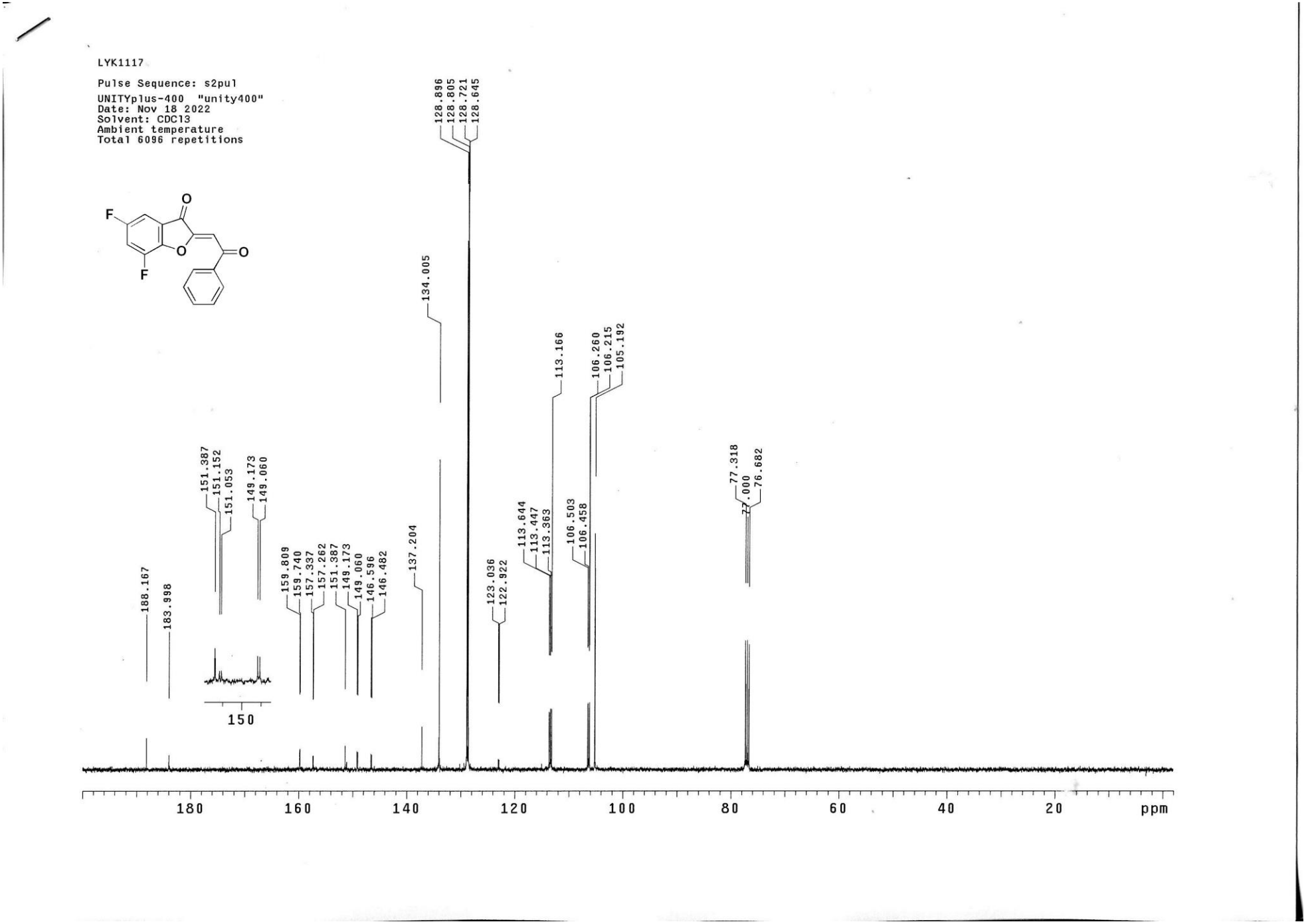
Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Nov 18 2022
Solvent: CDCl3
Ambient temperature
Total 32 repetitions

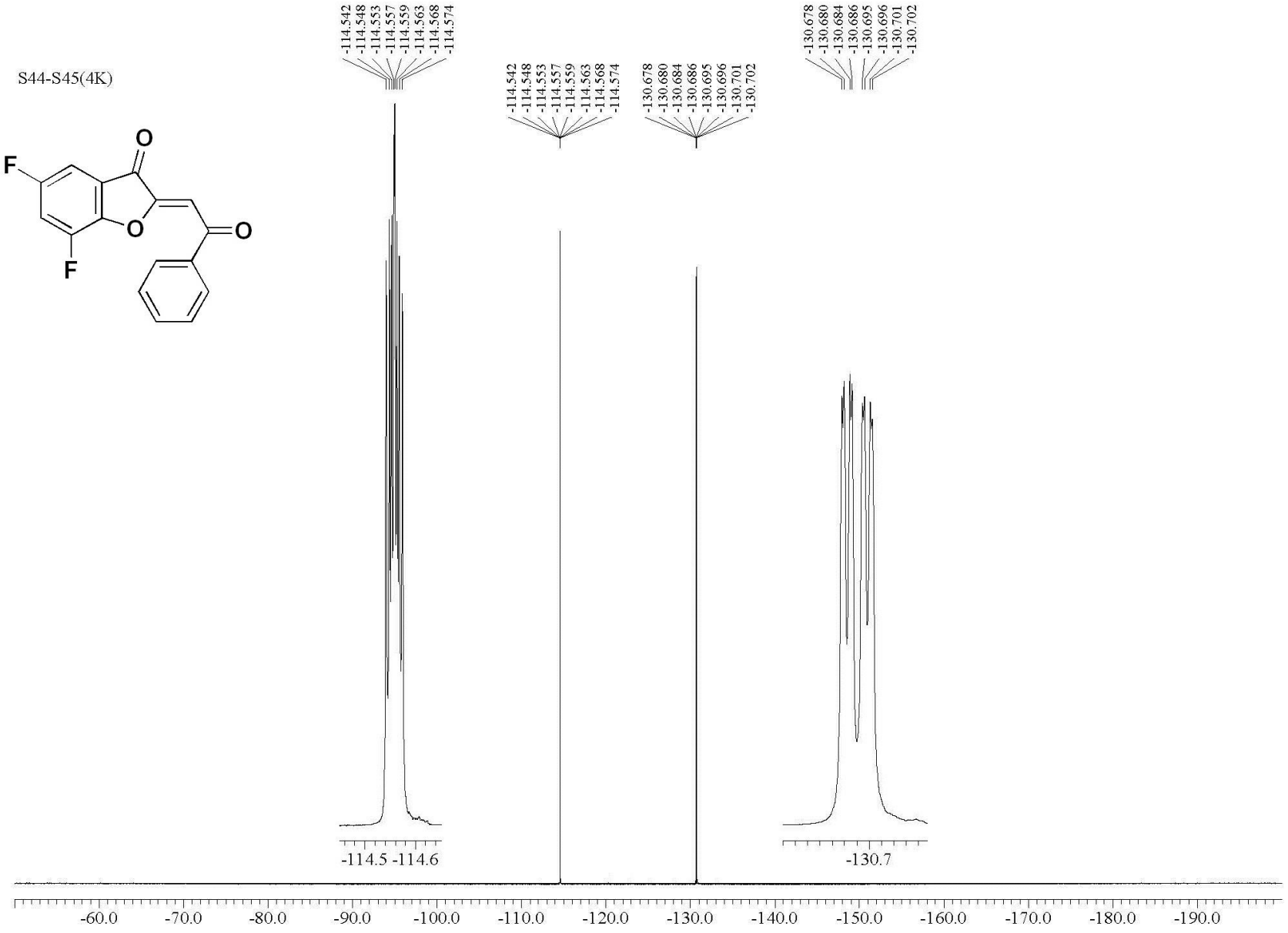




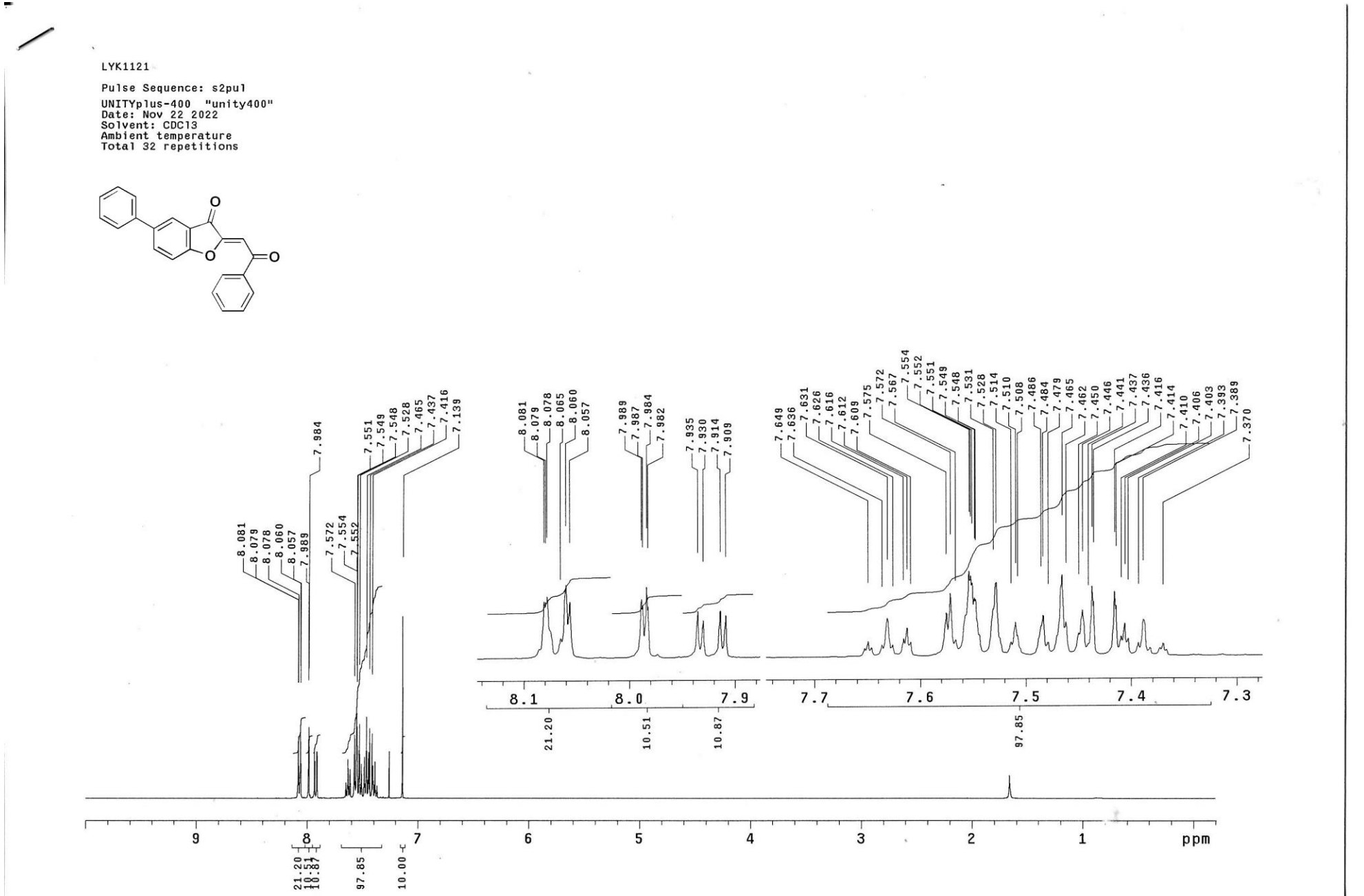
Compound 4k (^{13}C-NMR spectral data)



Compound 4k (^{19}F-NMR spectral data)



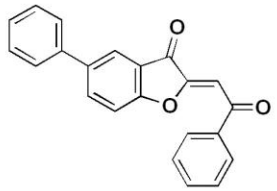
Compound 4l (^{1}H-NMR spectral data)

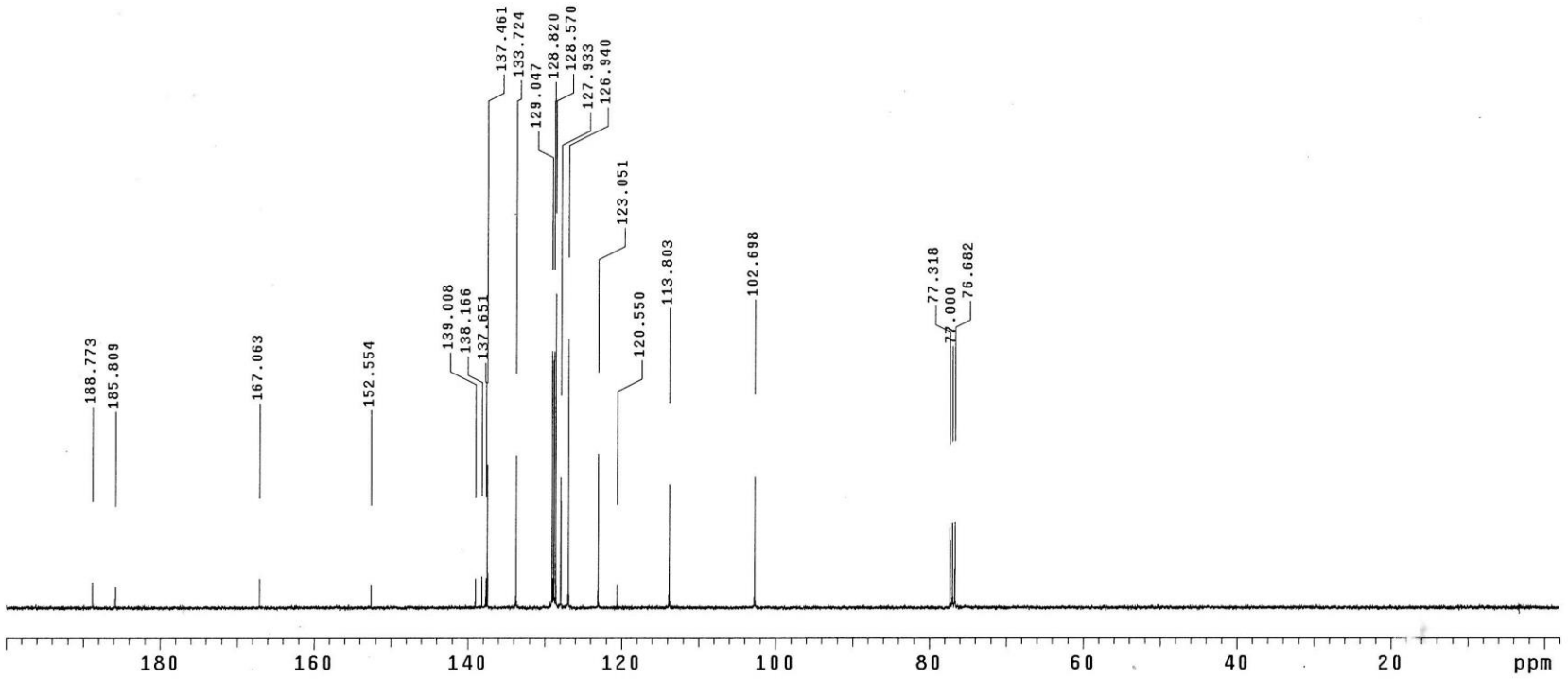


Compound 4l (^{13}C-NMR spectral data)

LYK1121

Pulse Sequence: s2pul
UNITYplus-400 "unity400"
Date: Nov 22 2022
Solvent: CDCl3
Ambient temperature
Total 2688 repetitions



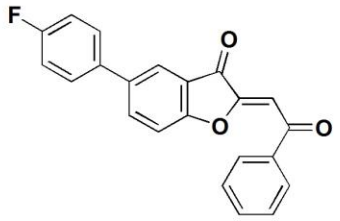


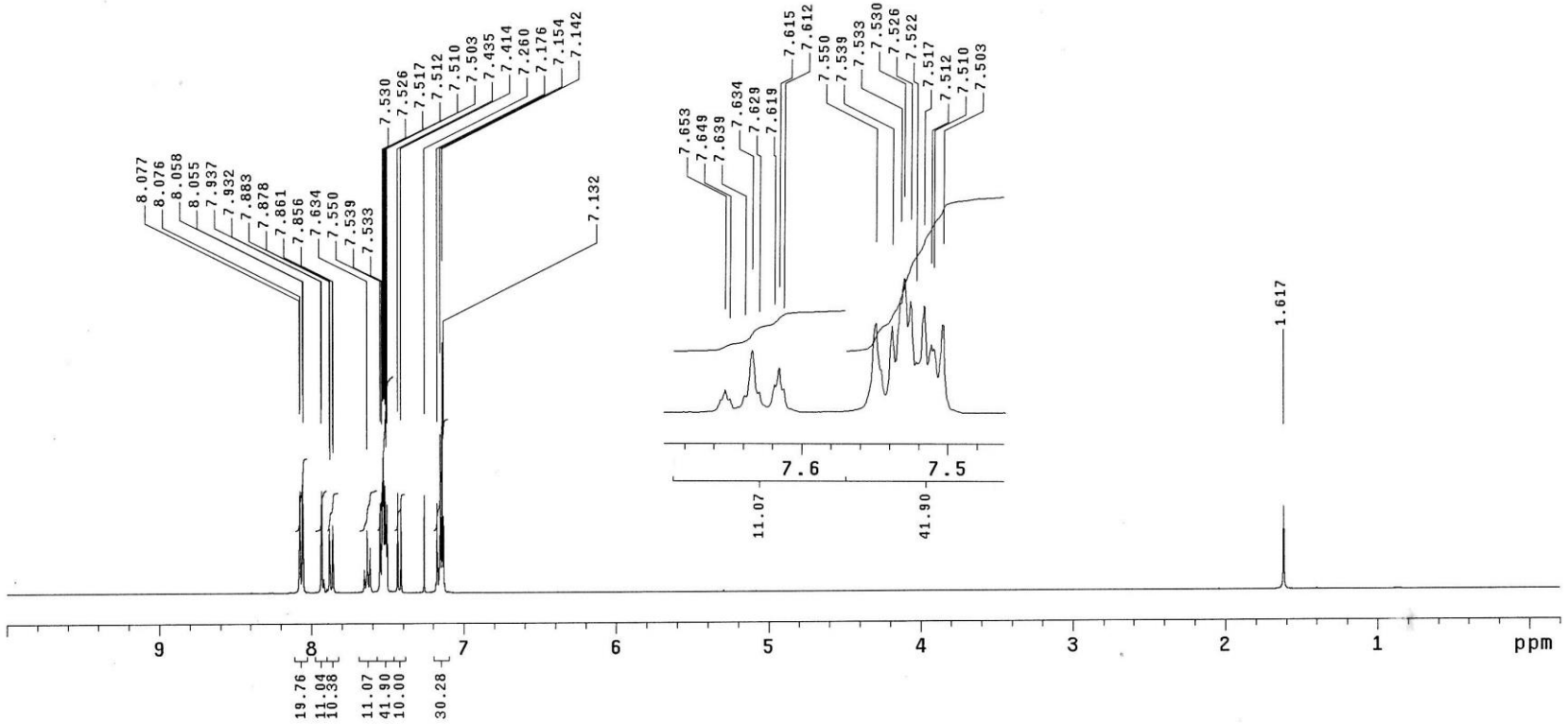
Compound 4m (^{1}H-NMR spectral data)

LYK1124

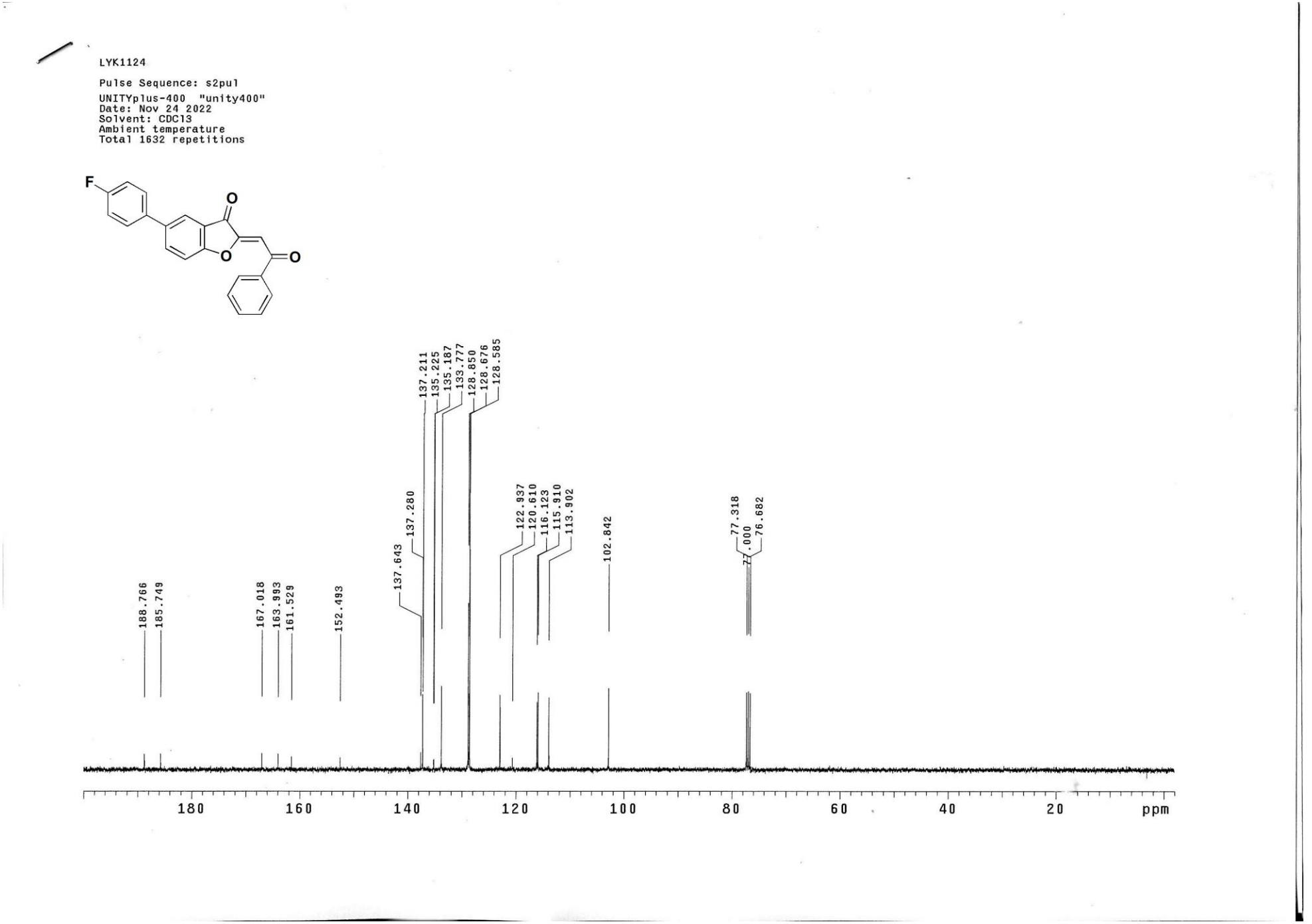
Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Nov 24 2022
Solvent: CDCl3
Ambient temperature
Total 32 repetitions



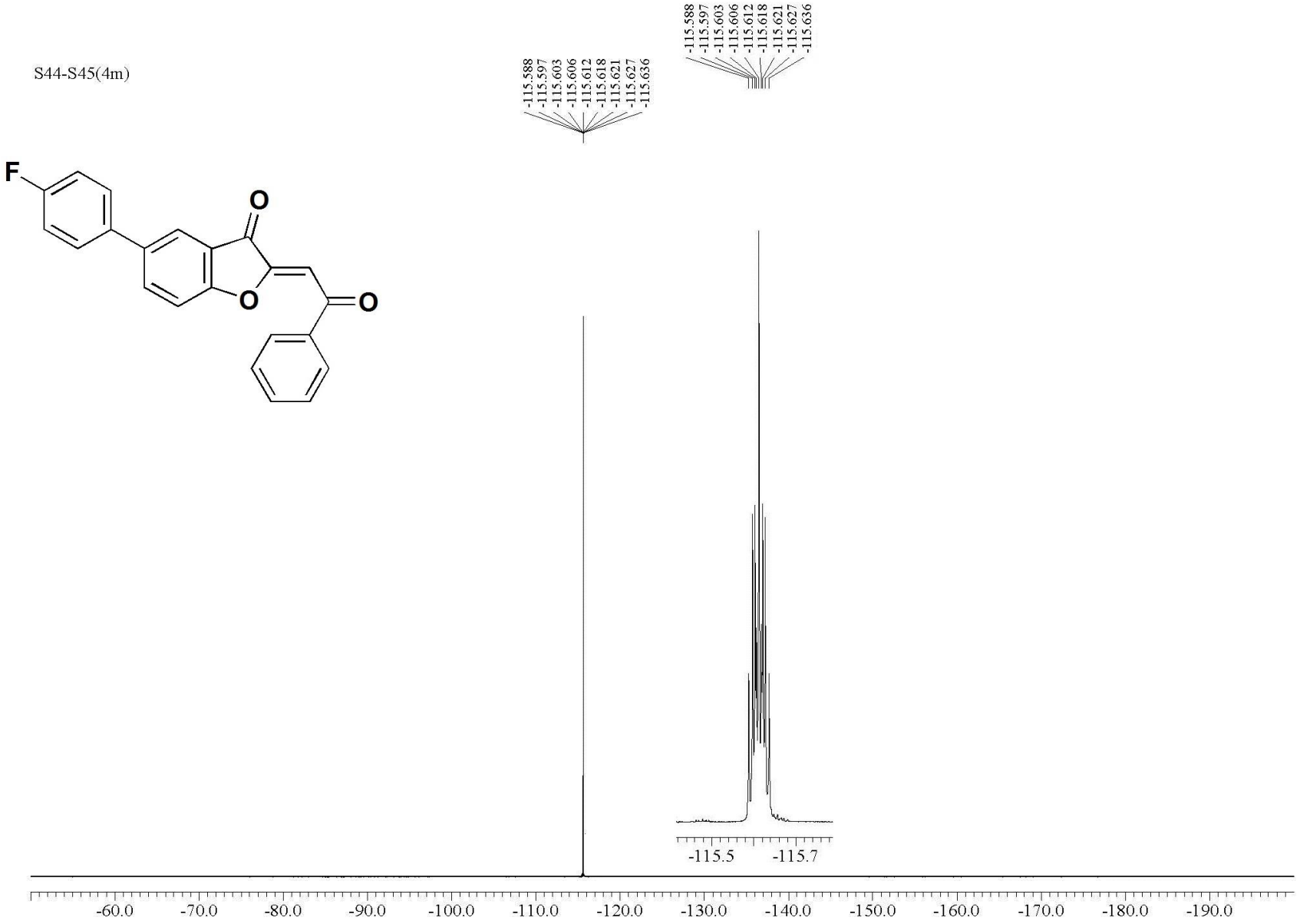


Compound 4m (^{13}C-NMR spectral data)



Compound 4m (^{19}F-NMR spectral data)

S44-S45(4m)

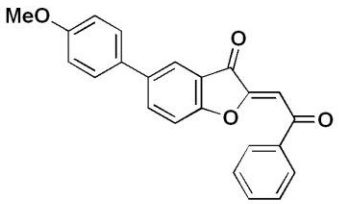


Compound 4n (^{1}H-NMR spectral data)

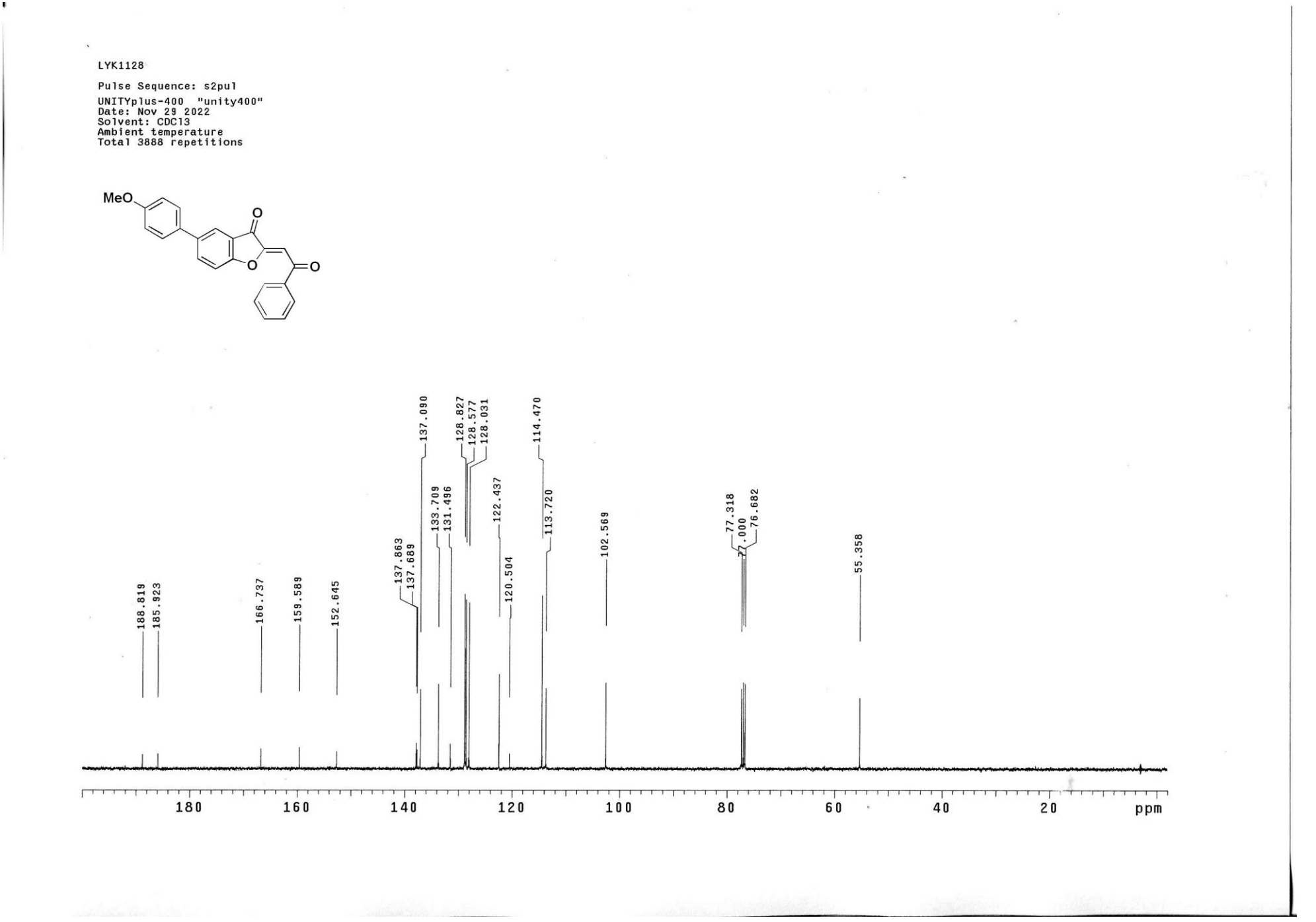
LYK1128

Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Nov 29 2022
Solvent: CDCl3
Ambient temperature
Total 32 repetitions



Compound 4n (^{13}C-NMR spectral data)

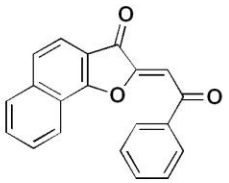


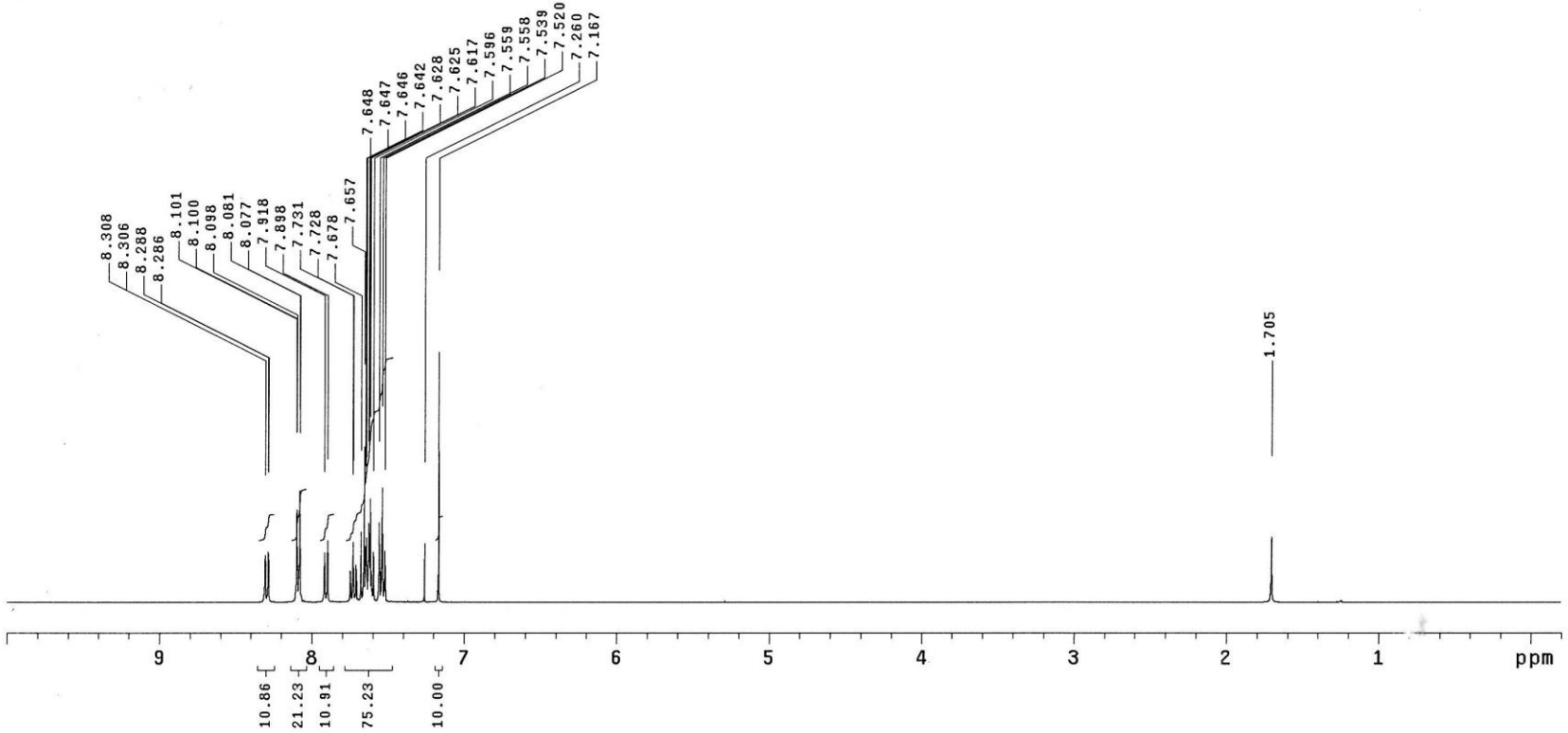
Compound 4o (^{1}H-NMR spectral data)

LYK1019

Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Oct 20 2022
Solvent: CDCl3
Ambient temperature
Total 32 repetitions



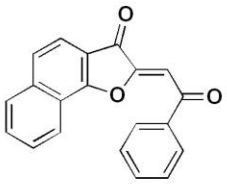


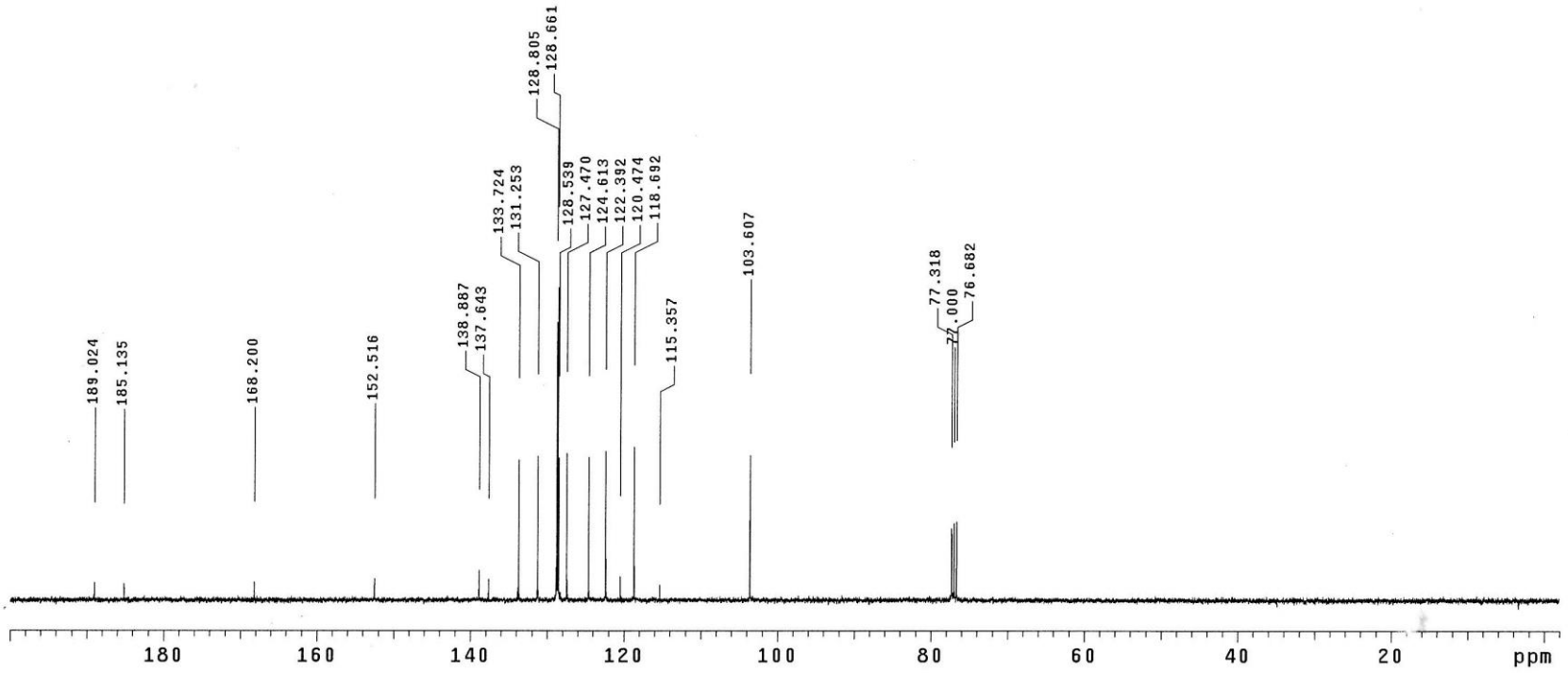
Compound 4o (^{13}C-NMR spectral data)

LYK1019

Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Oct 20 2022
Solvent: CDCl3
Ambient temperature
Total 1296 repetitions



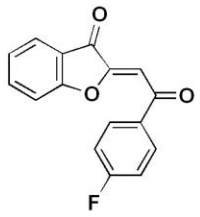


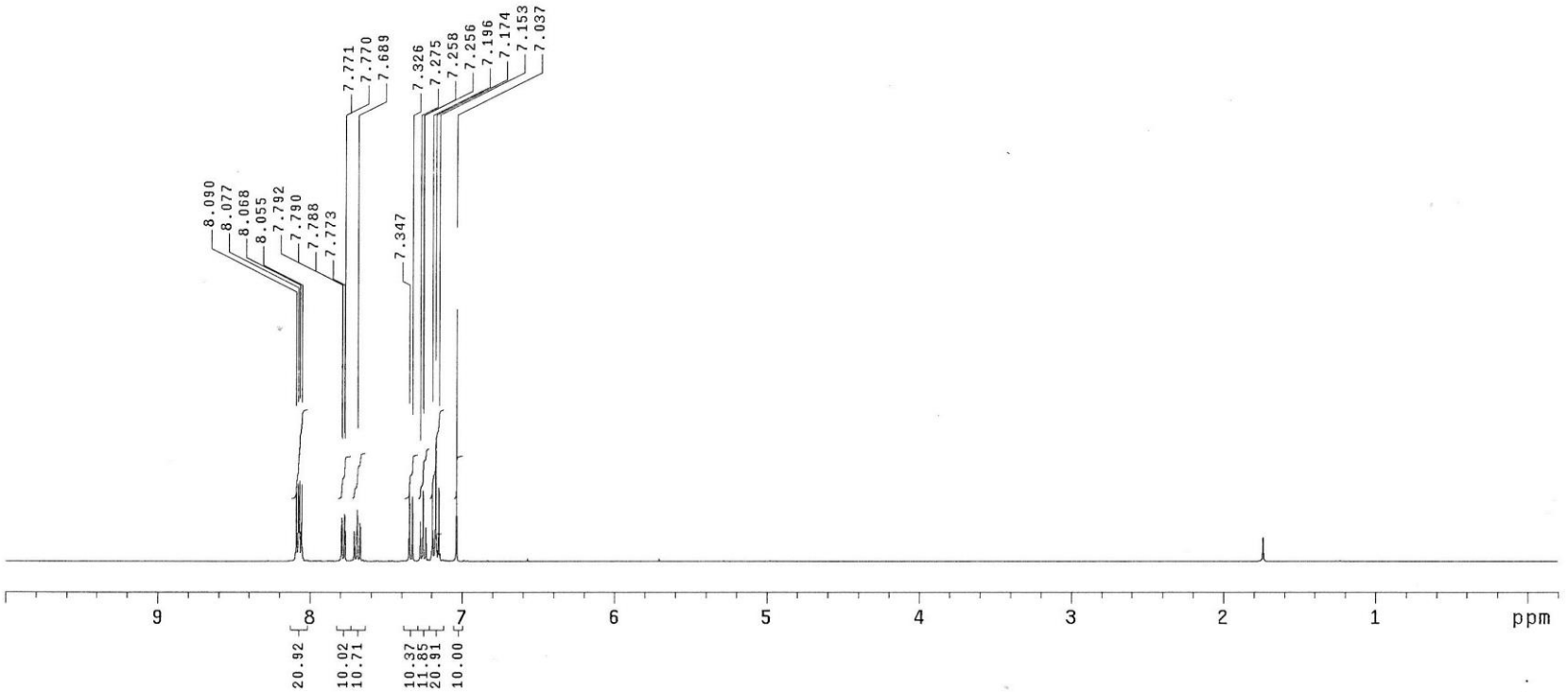
Compound 4p (^{1}H-NMR spectral data)

LYK928

Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Sep 29 2022
Solvent: CDCl3
Ambient temperature
Total 32 repetition



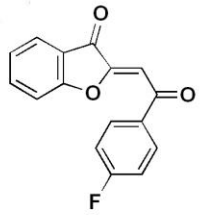


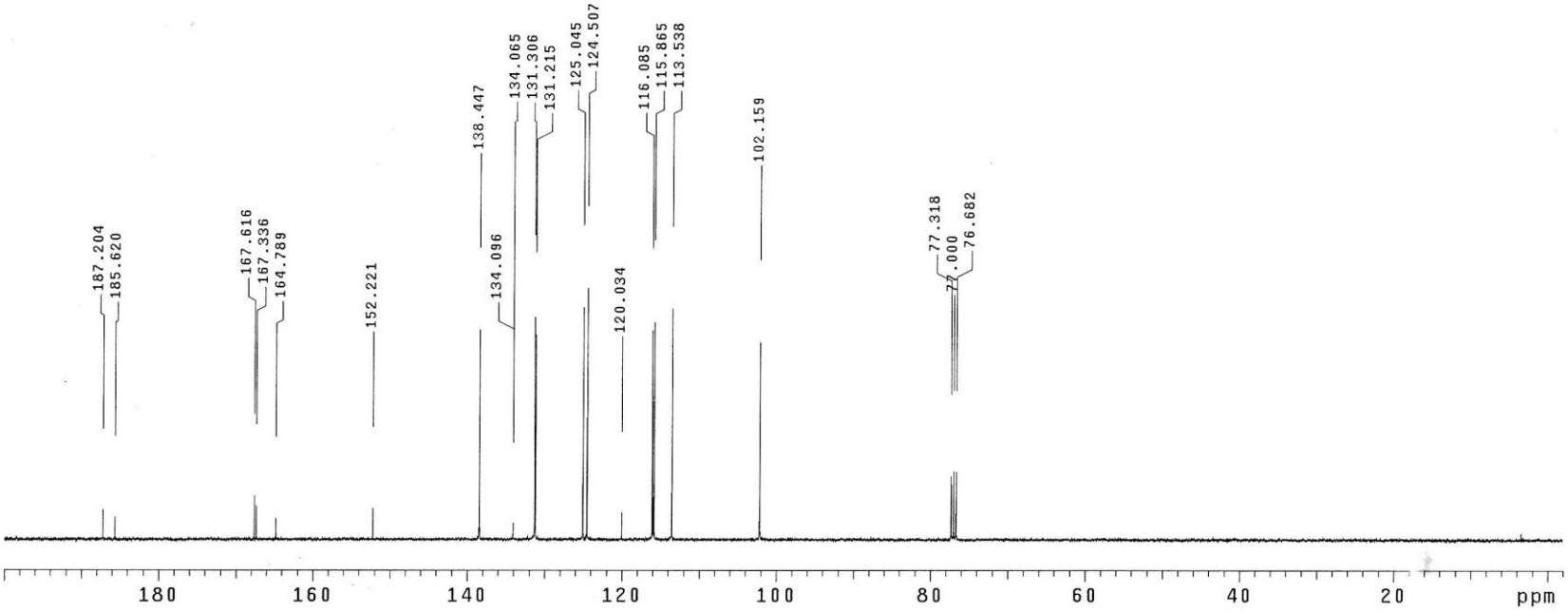
Compound 4p (^{13}C-NMR spectral data)

LYK928

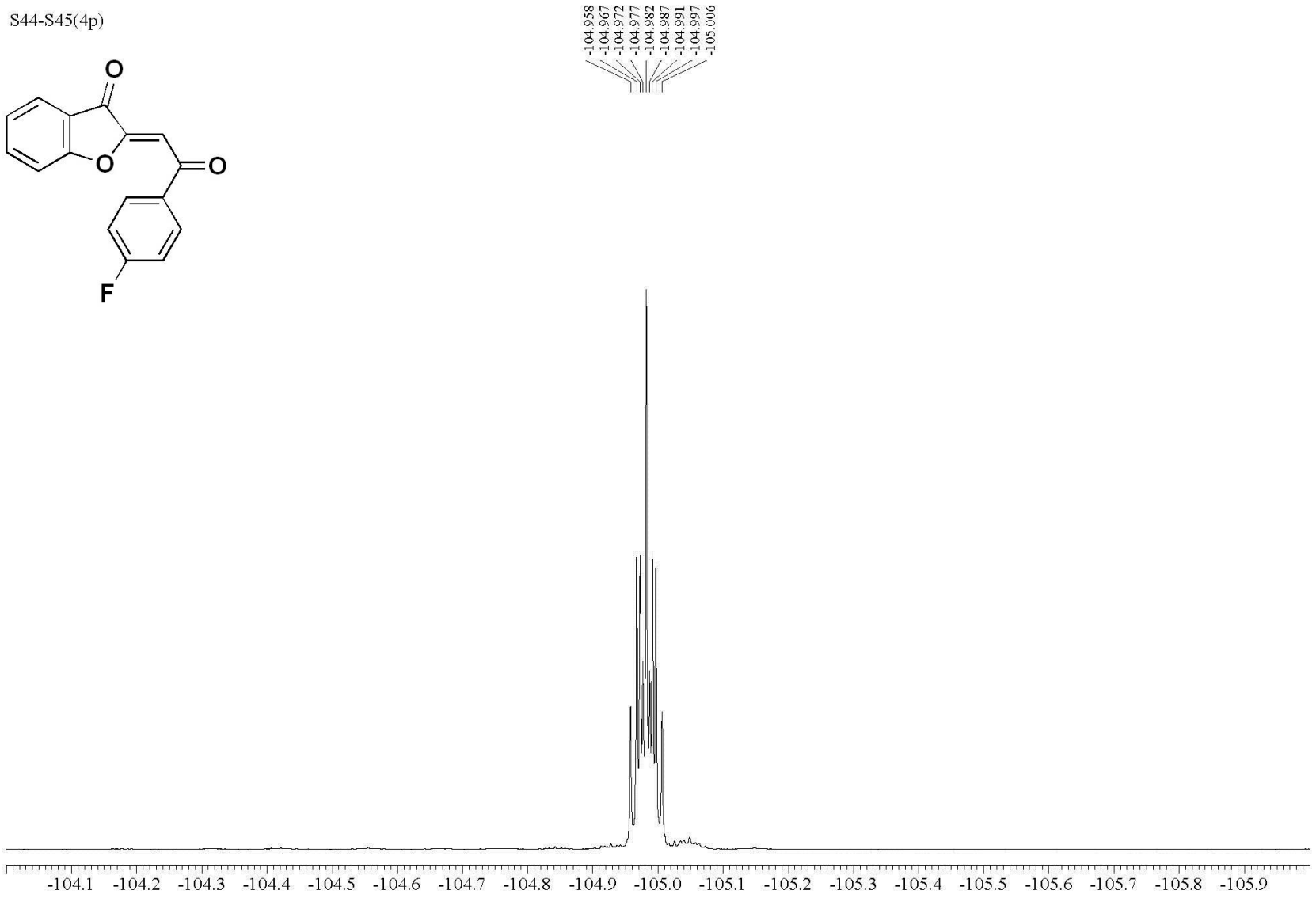
Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Sep 29 2022
Solvent: CDCl3
Ambient temperature
Total 1872 repetitions



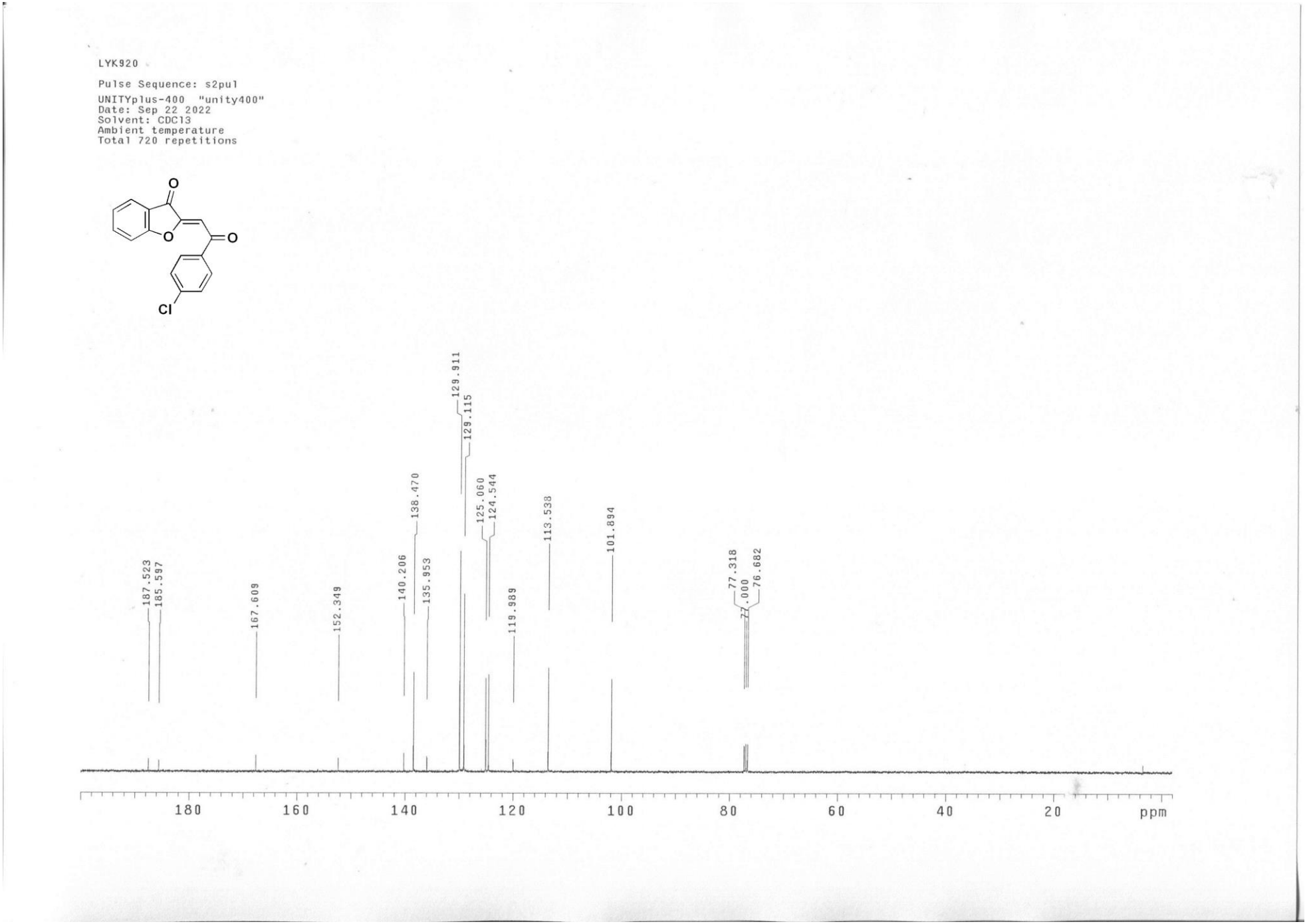


Compound 4p (^{19}F-NMR spectral data)

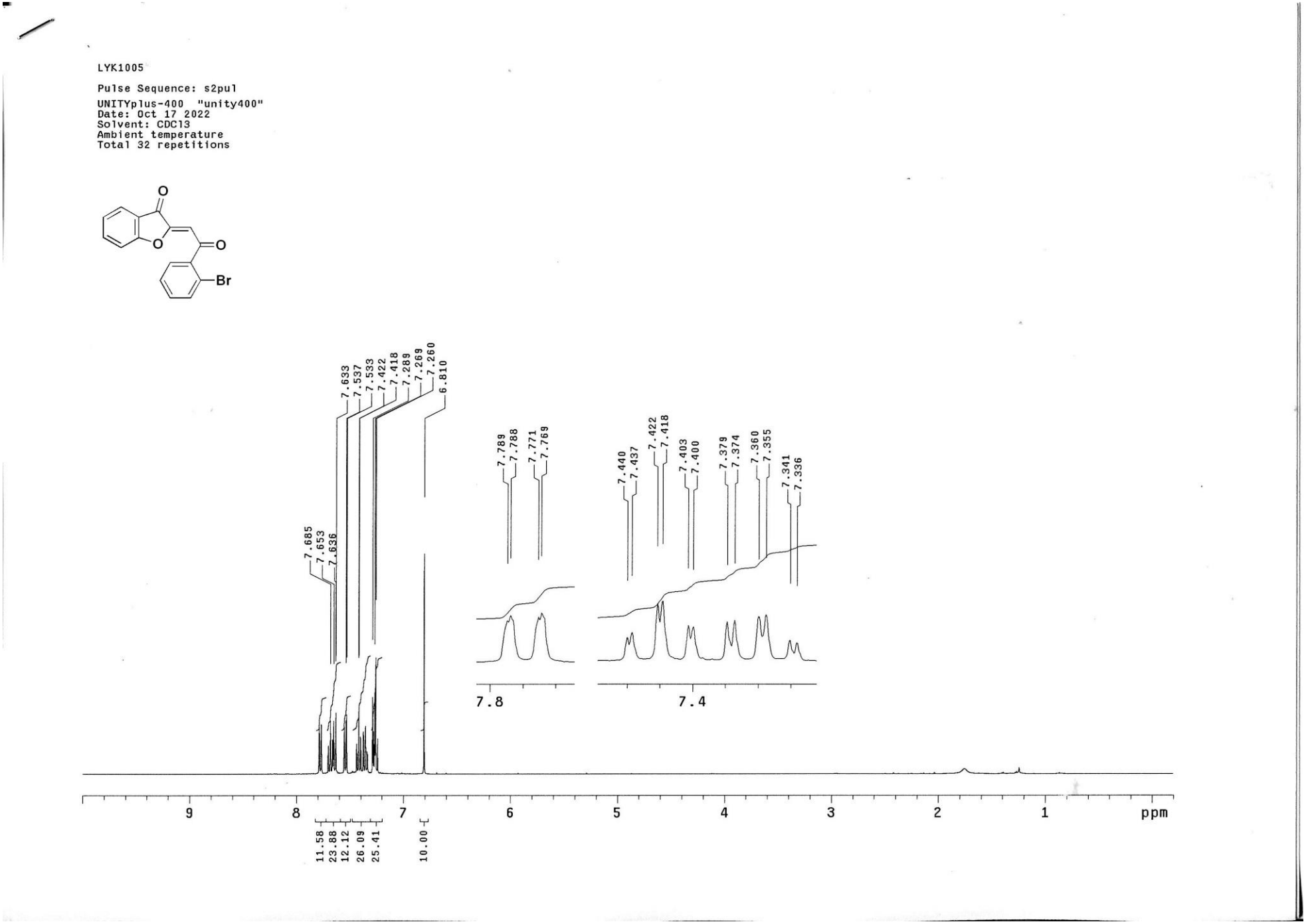


Compound 4q (^{1}H-NMR spectral data)

Compound 4q (^{13}C-NMR spectral data)



Compound 4r (^{1}H-NMR spectral data)

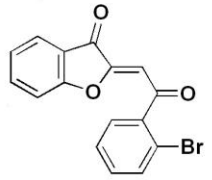


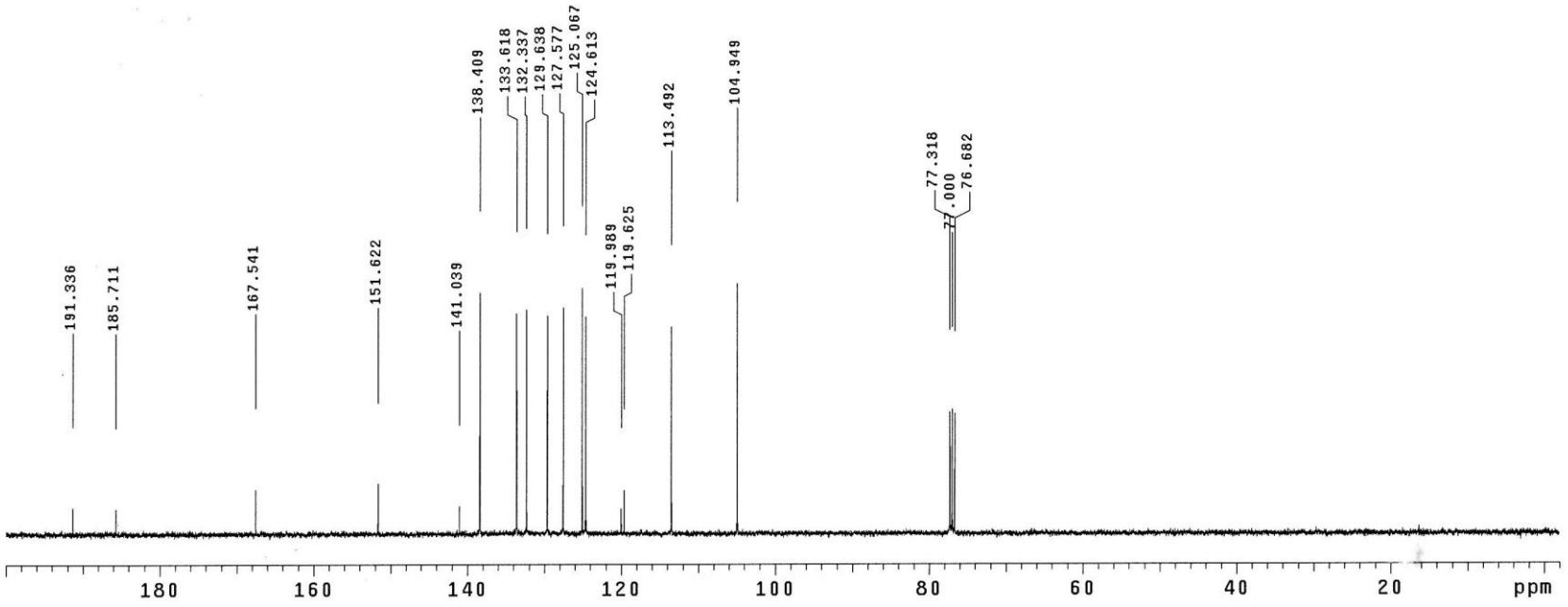
Compound 4r (^{13}C-NMR spectral data)

LYK1005

Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Oct 17 2022
Solvent: CDCl3
Ambient temperature
Total 2144 repetitions



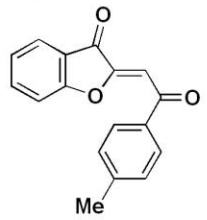


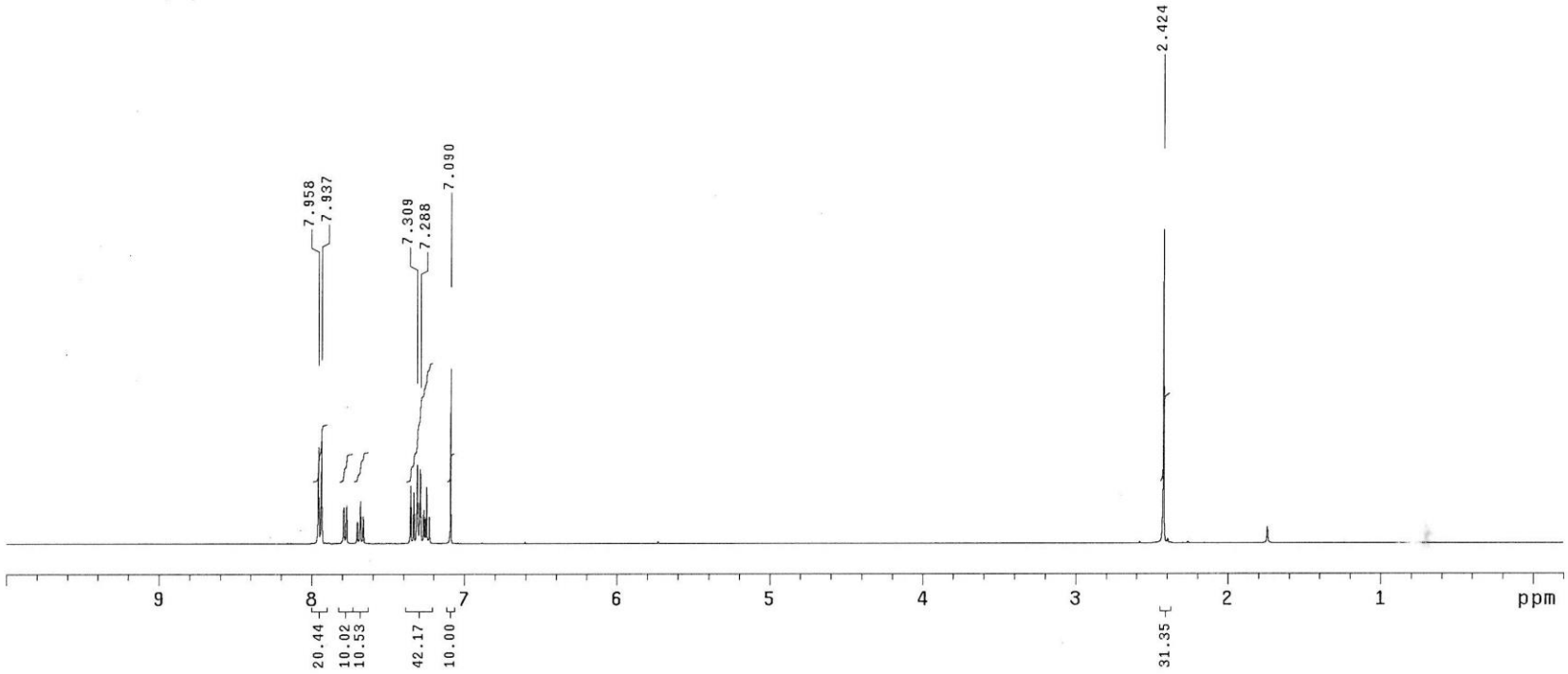
Compound 4s (^{1}H-NMR spectral data)

LYK929

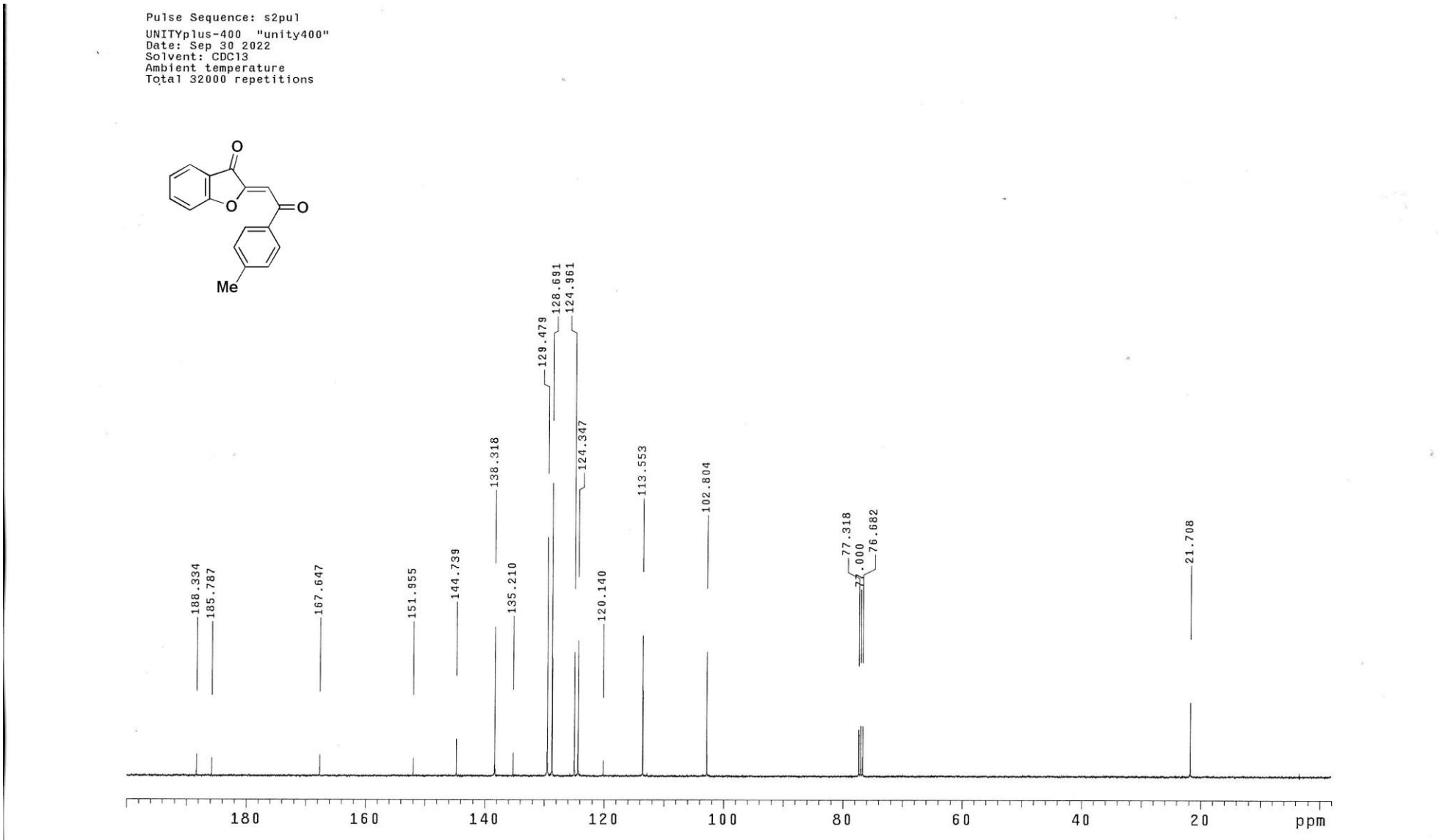
Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Sep 30 2022
Solvent: CDCl3
Ambient temperature
Total 32 repetitions





Compound 4s (^{13}C-NMR spectral data)

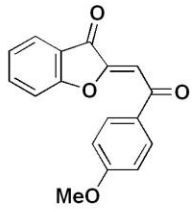


Compound 4t (^{1}H-NMR spectral data)

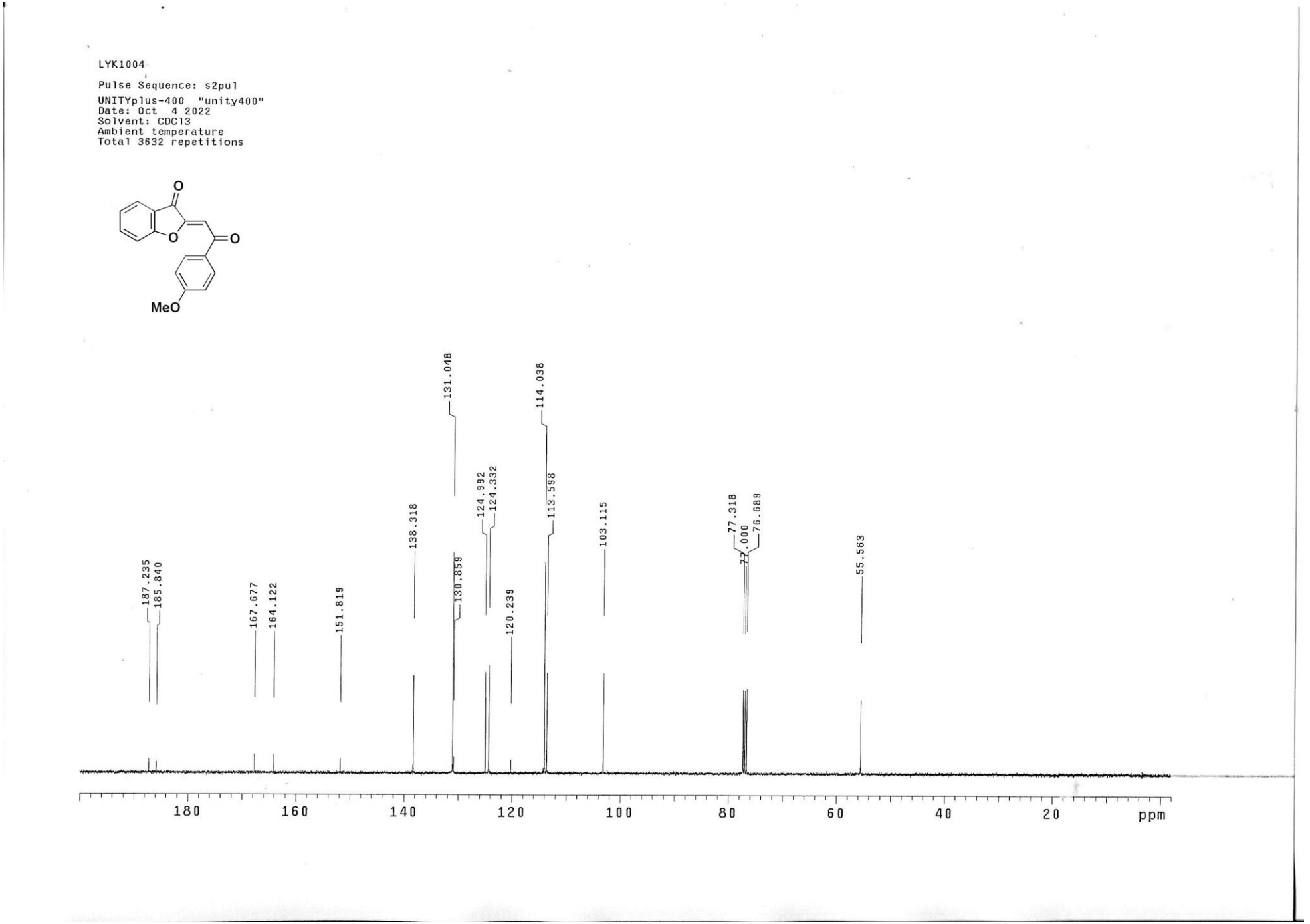
LYK1004

Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Oct 4 2022
Solvent: CDCl3
Ambient temperature
Total 32 repetitions



Compound 4t (^{13}C-NMR spectral data)

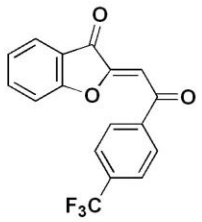


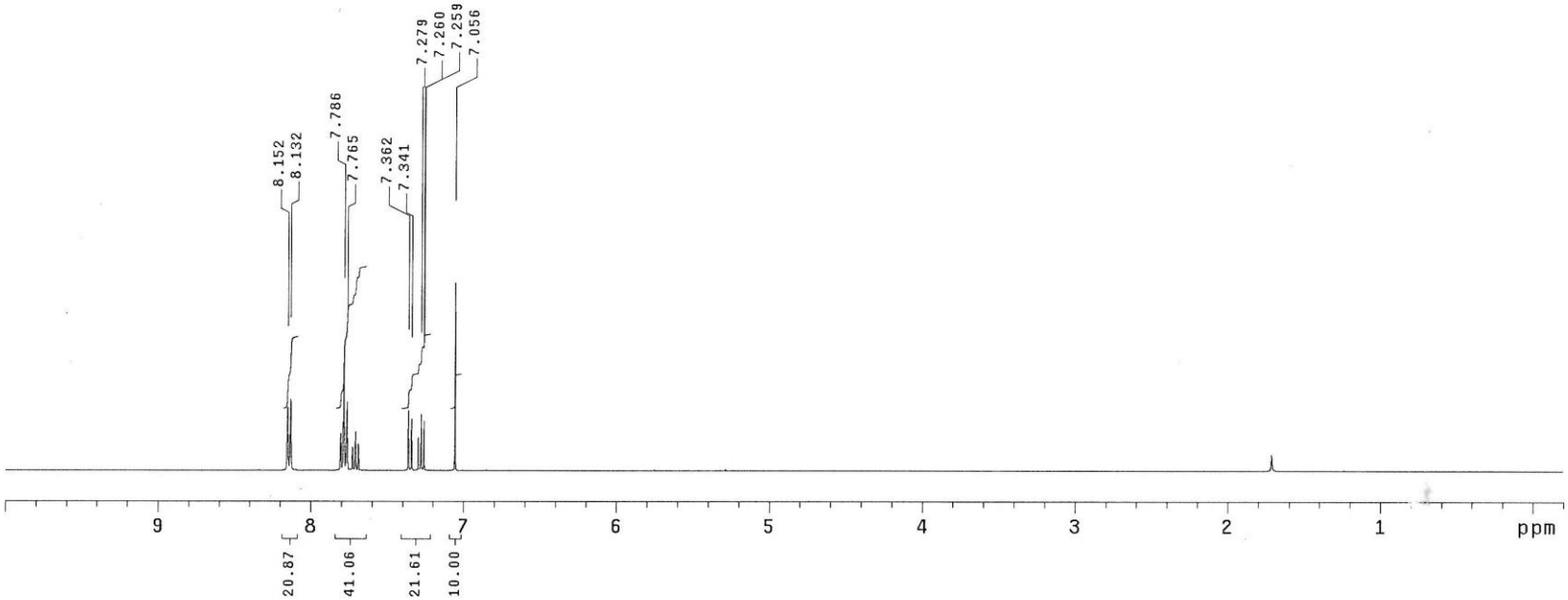
Compound 4u (^{1}H-NMR spectral data)

LYK1006

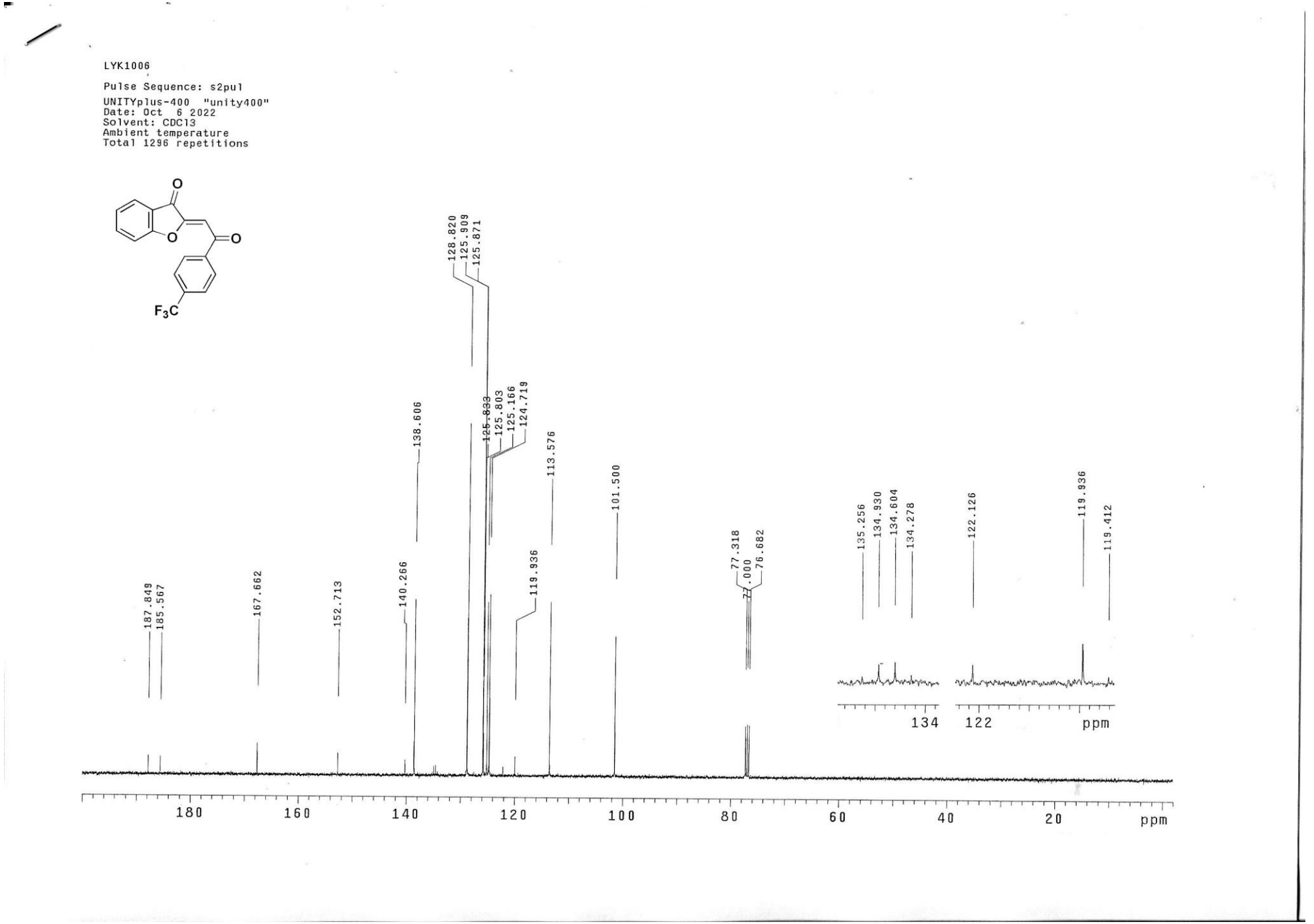
Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Oct 6 2022
Solvent: CDCl3
Ambient temperature
Total 32 repetitions

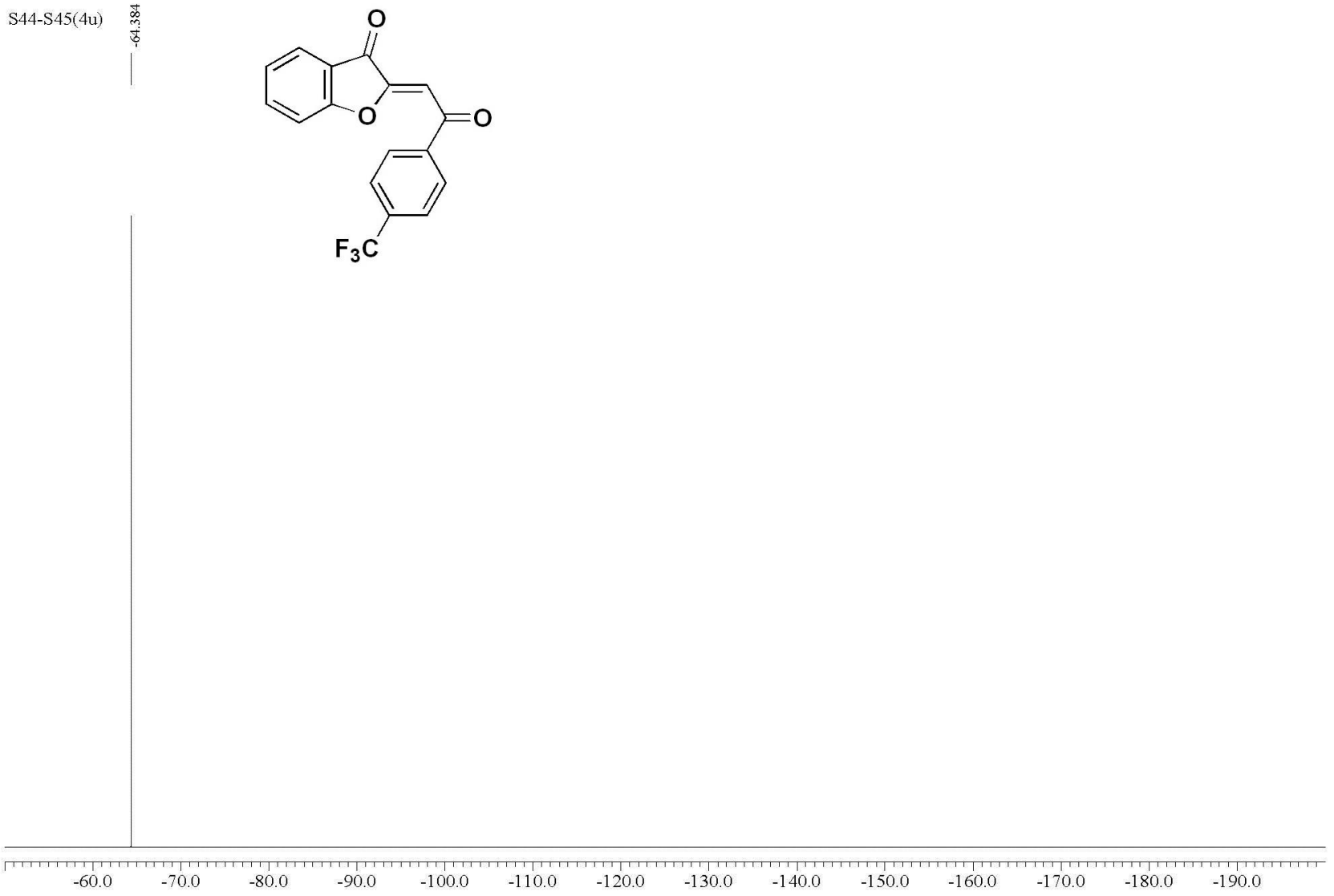




Compound 4u (^{13}C-NMR spectral data)



Compound 4u (^{19}F-NMR spectral data)

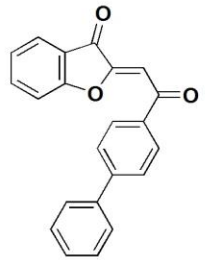


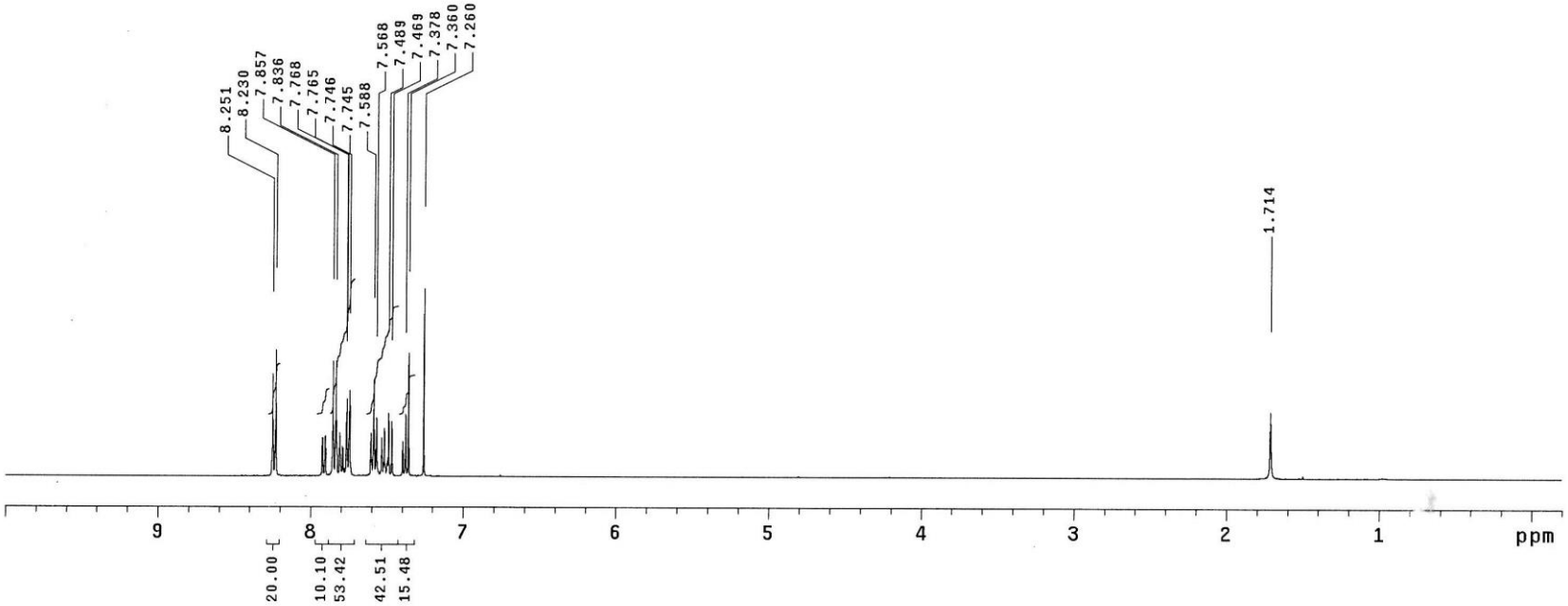
Compound 4v (^{1}H-NMR spectral data)

LYK1020

Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Oct 20 2022
Solvent: CDCl3
Ambient temperature
Total 32 repetitions

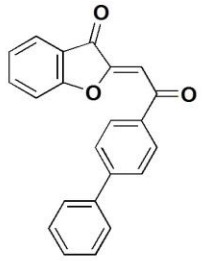


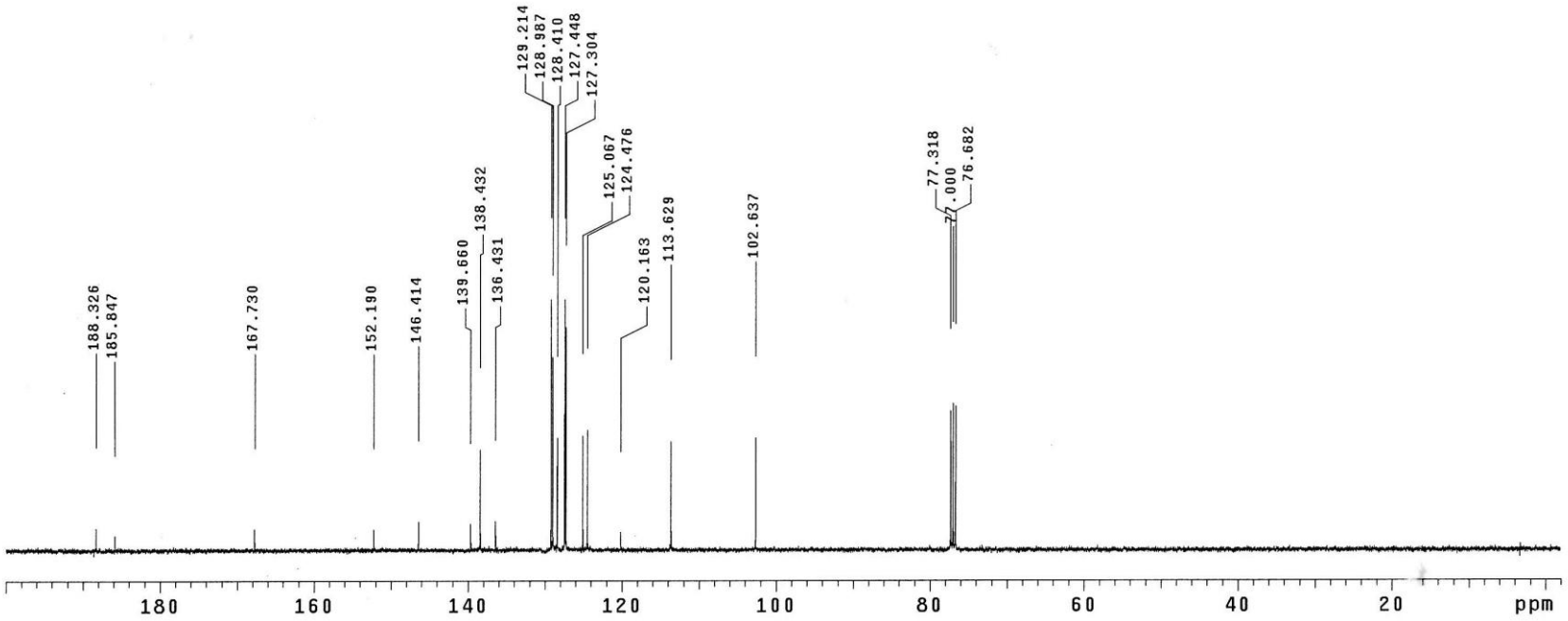


Compound 4v (^{13}C-NMR spectral data)

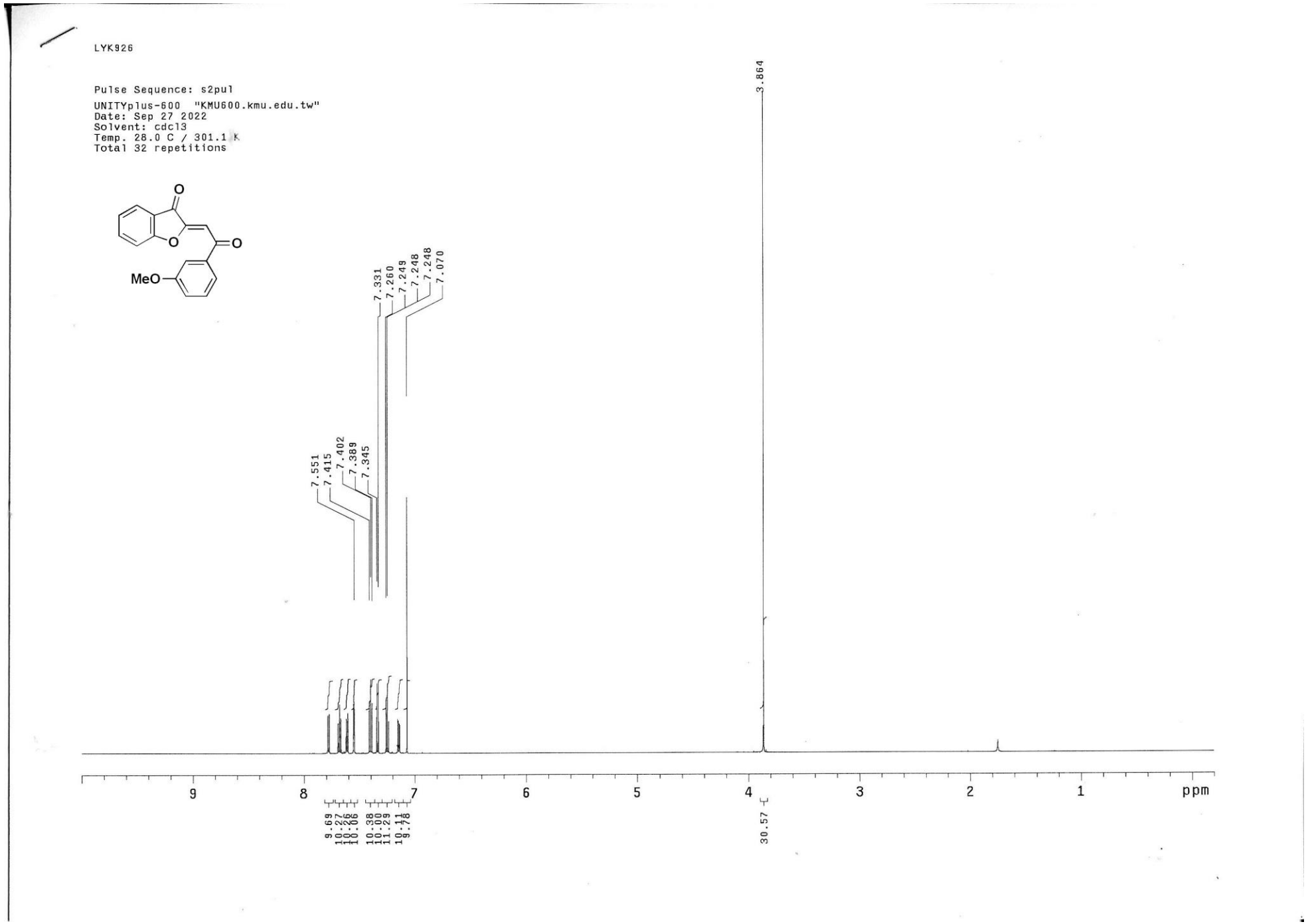
LYK1020

Pulse Sequence: s2pul
UNITYplus-400 "unity400"
Date: Oct 20 2022
Solvent: CDCl3
Ambient temperature
Total 5200 repetitions

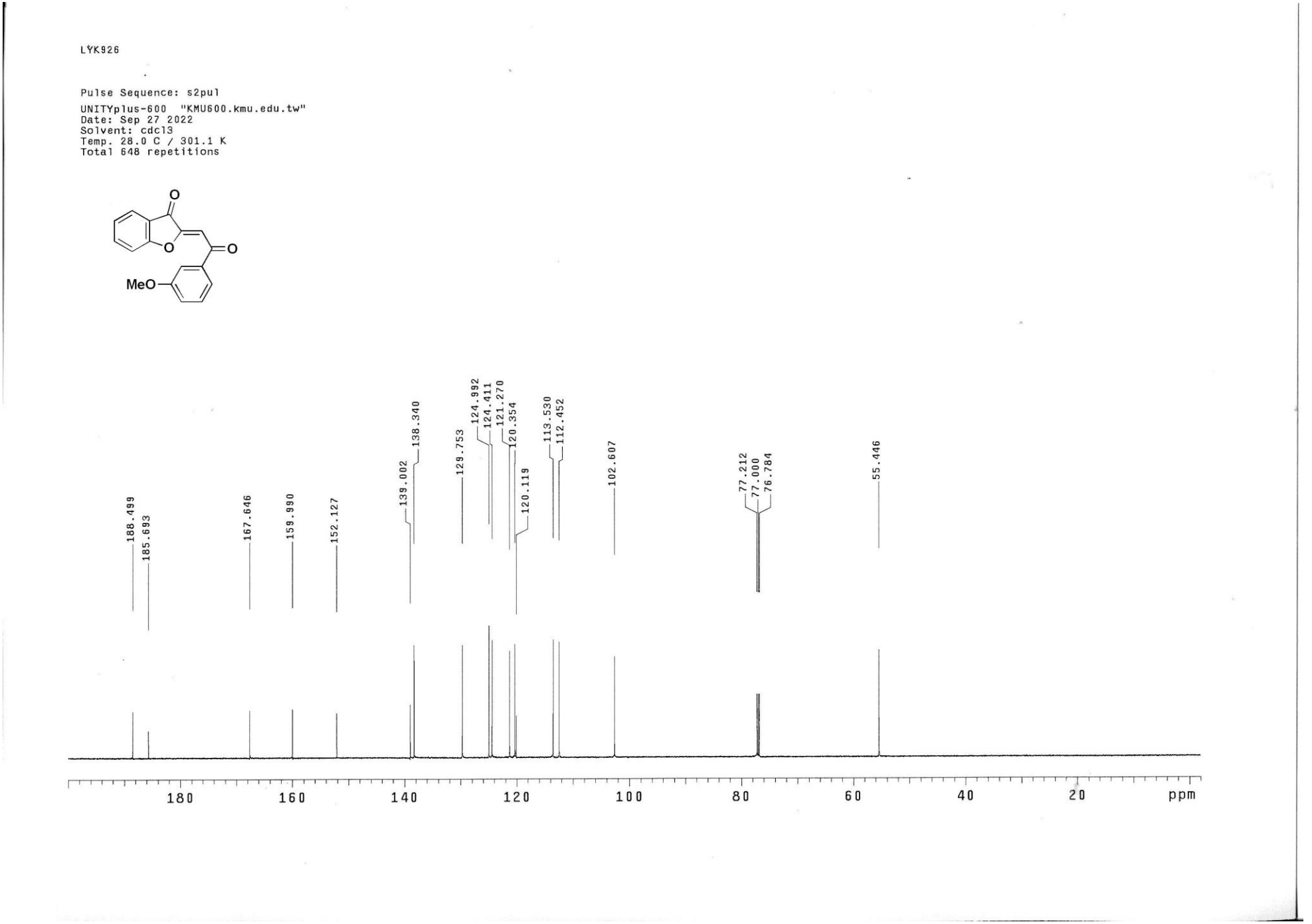




Compound 4w (^{1}H-NMR spectral data)



Compound 4w (^{13}C-NMR spectral data)

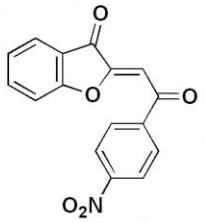


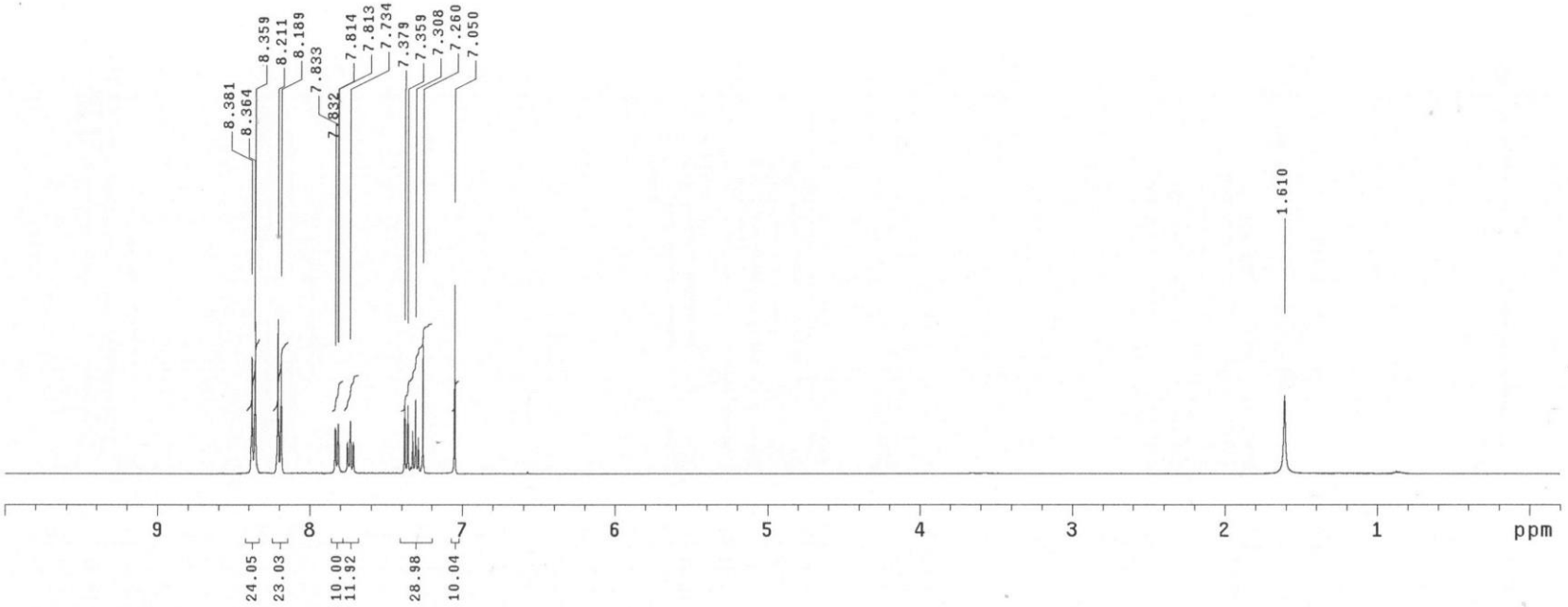
Compound 4x (^{1}H-NMR spectral data)

LYK1021

Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Oct 24 2022
Solvent: CDCl3
Ambient temperature
Total 32 repetitions



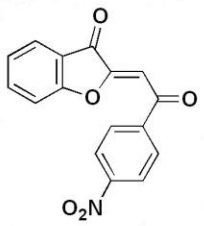


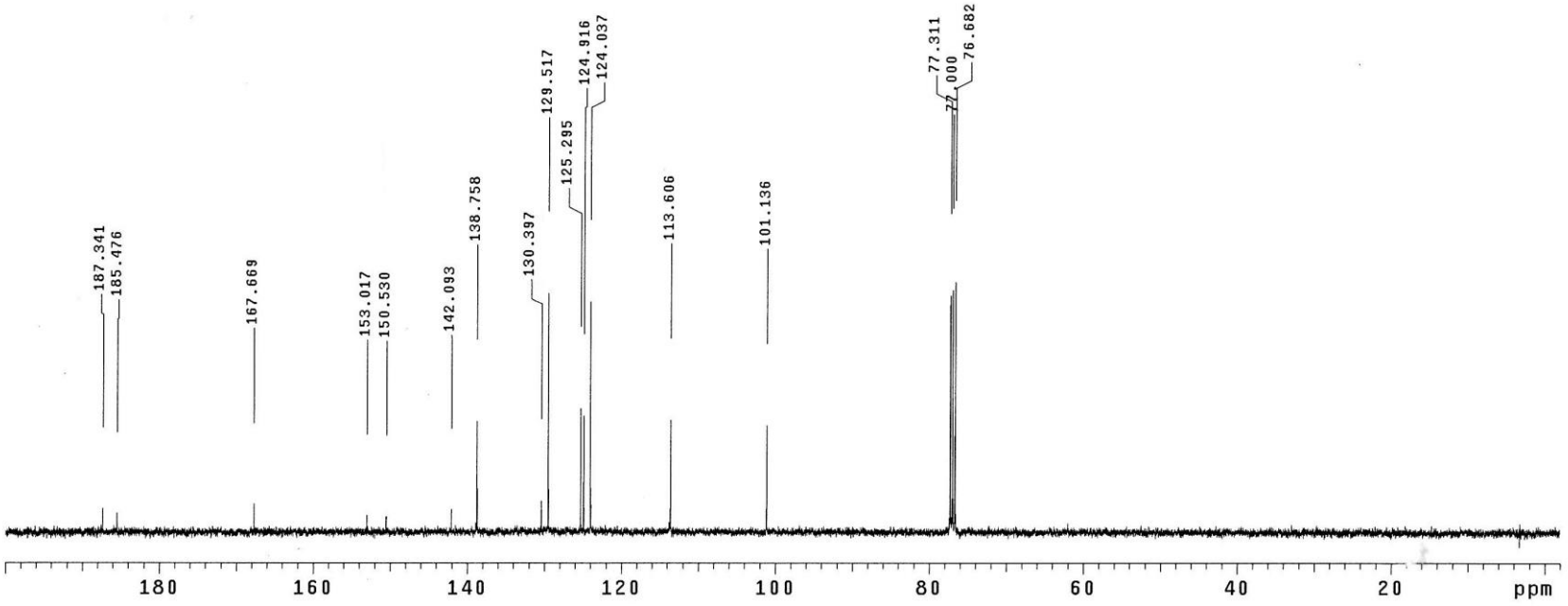
Compound 4x (^{13}C-NMR spectral data)

LYK1021

Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Oct 24 2022
Solvent: CDCl3
Ambient temperature
Total 6816 repetitions



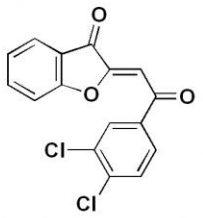


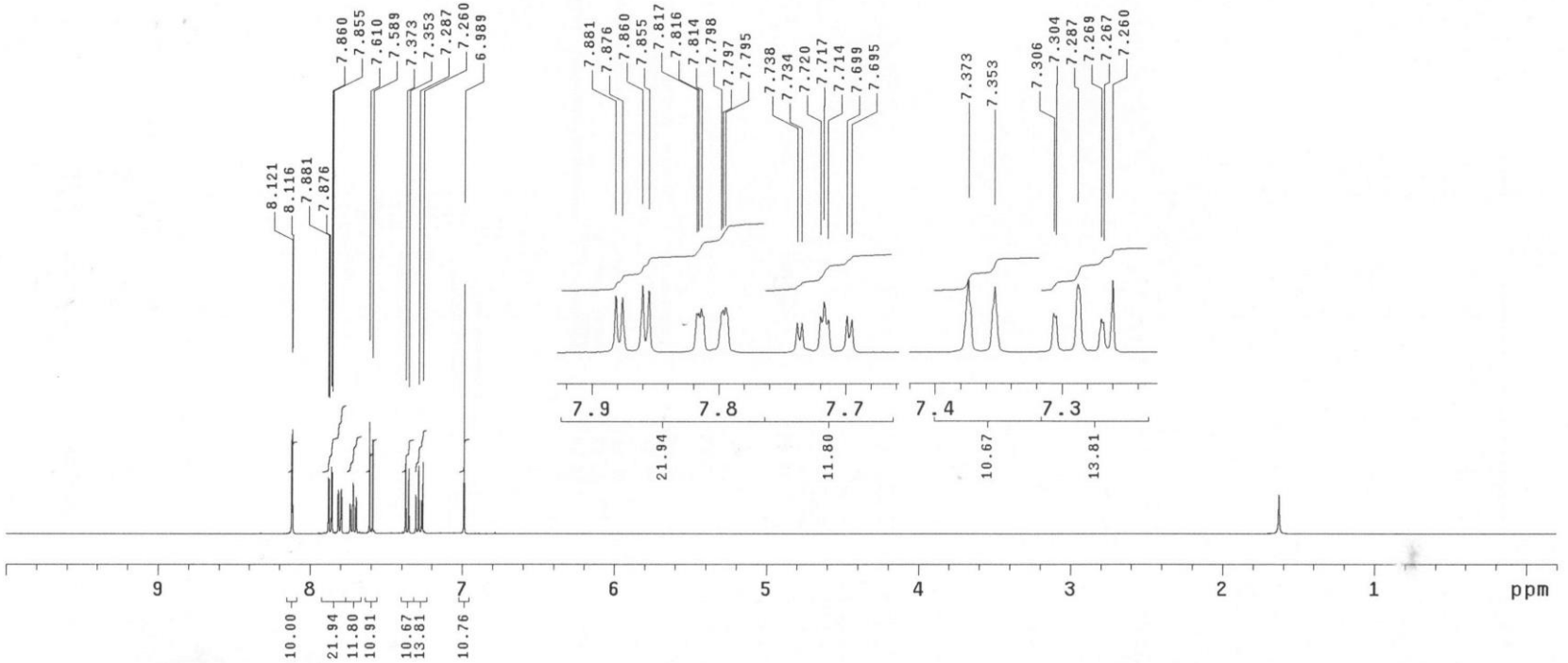
Compound 4y (^{1}H-NMR spectral data)

LYK1027

Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Oct 28 2022
Solvent: CDCl3
Ambient temperature
Total 32 repetitions



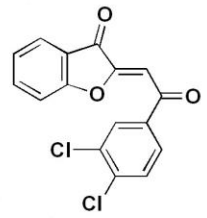


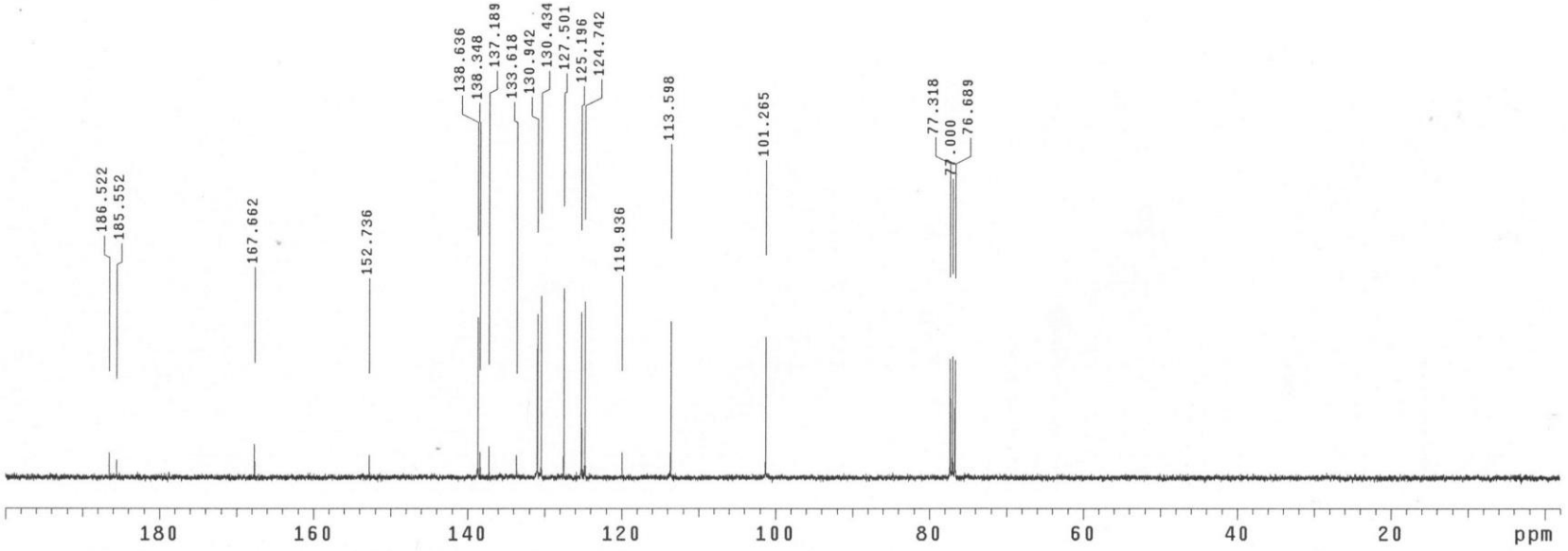
Compound 4y (^{13}C-NMR spectral data)

LYK1027

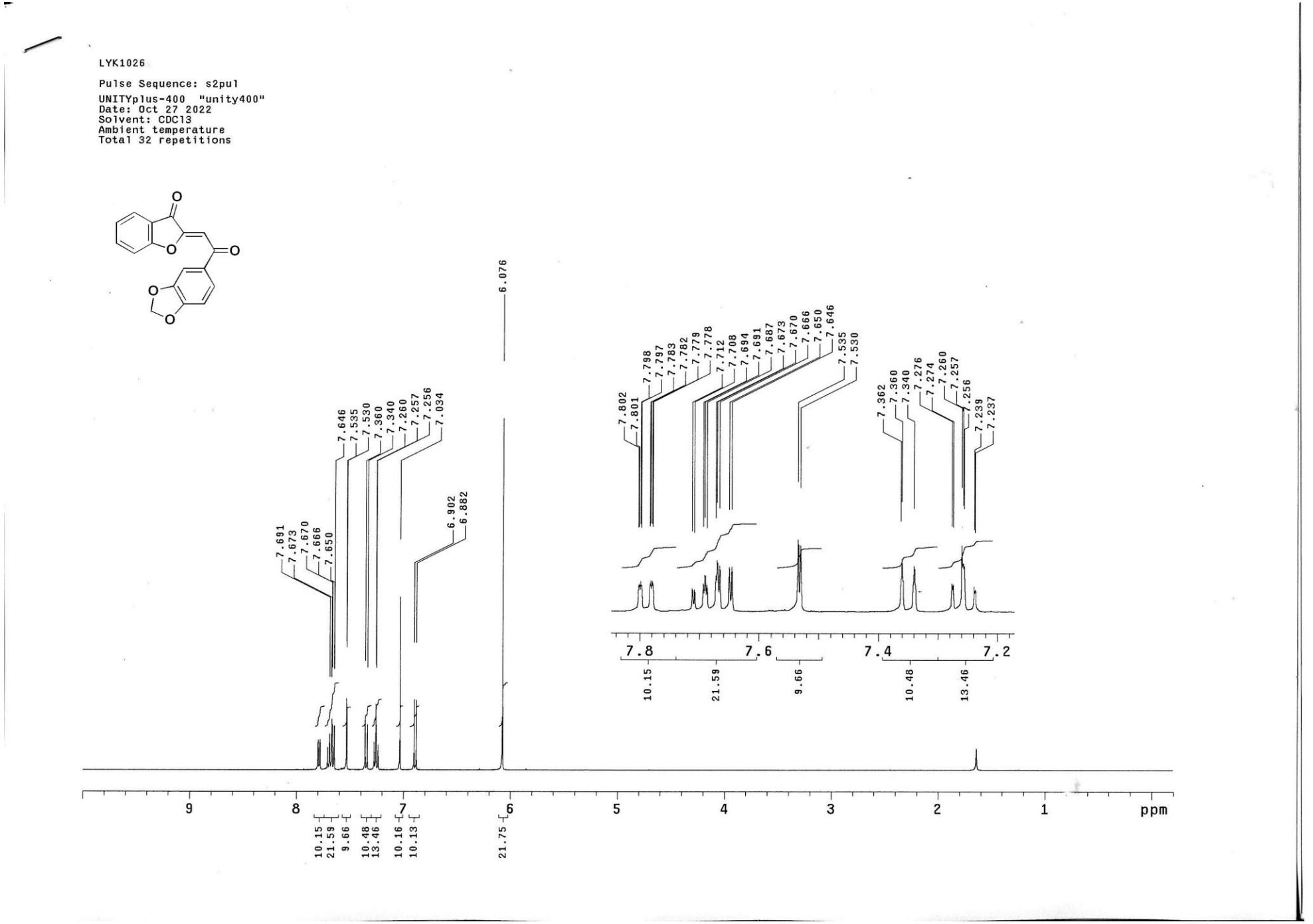
Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Oct 28 2022
Solvent: CDCl3
Ambient temperature
Total 2640 repetitions





Compound 4z (^{1}H-NMR spectral data)

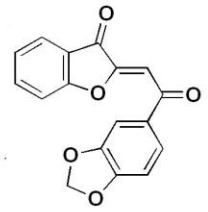


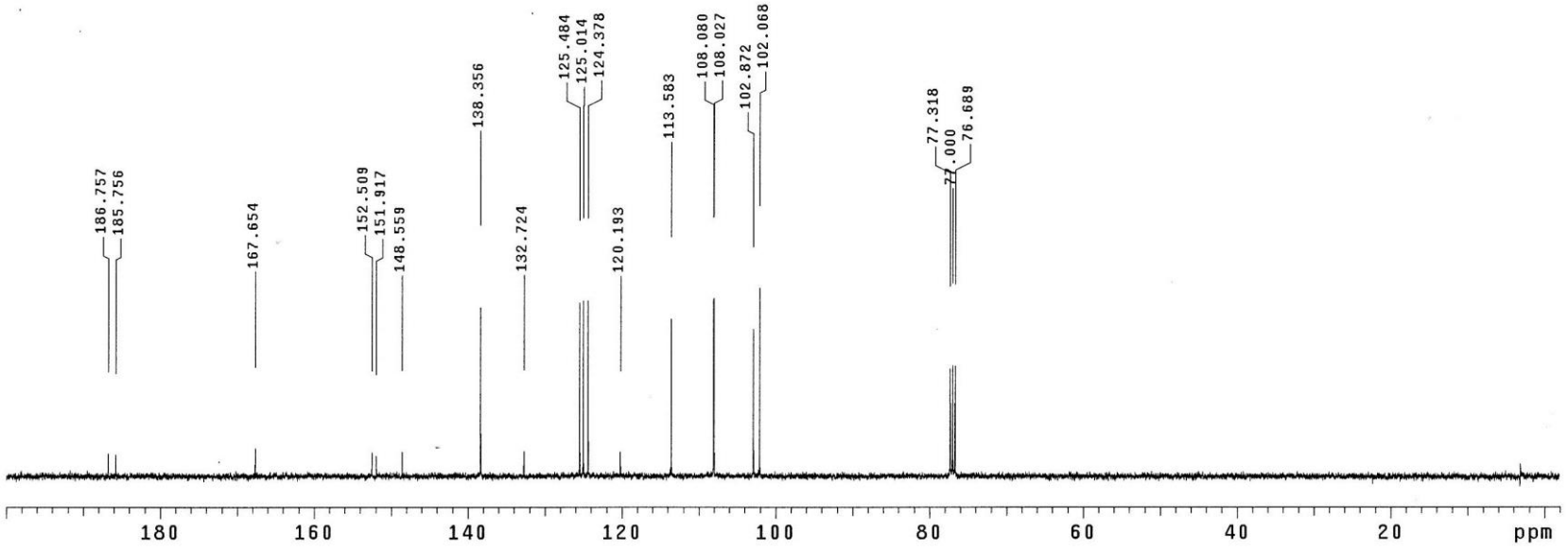
Compound 4z (^{13}C-NMR spectral data)

LYK1026

Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Oct 27 2022
Solvent: CDCl3
Ambient temperature
Total 2640 repetitions



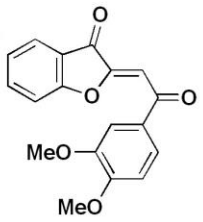


Compound 4aa (^{1}H-NMR spectral data)

LYK1024

Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Oct 25 2022
Solvent: CDCl3
Ambient temperature
Total 32 repetitions

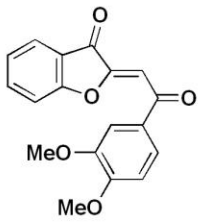


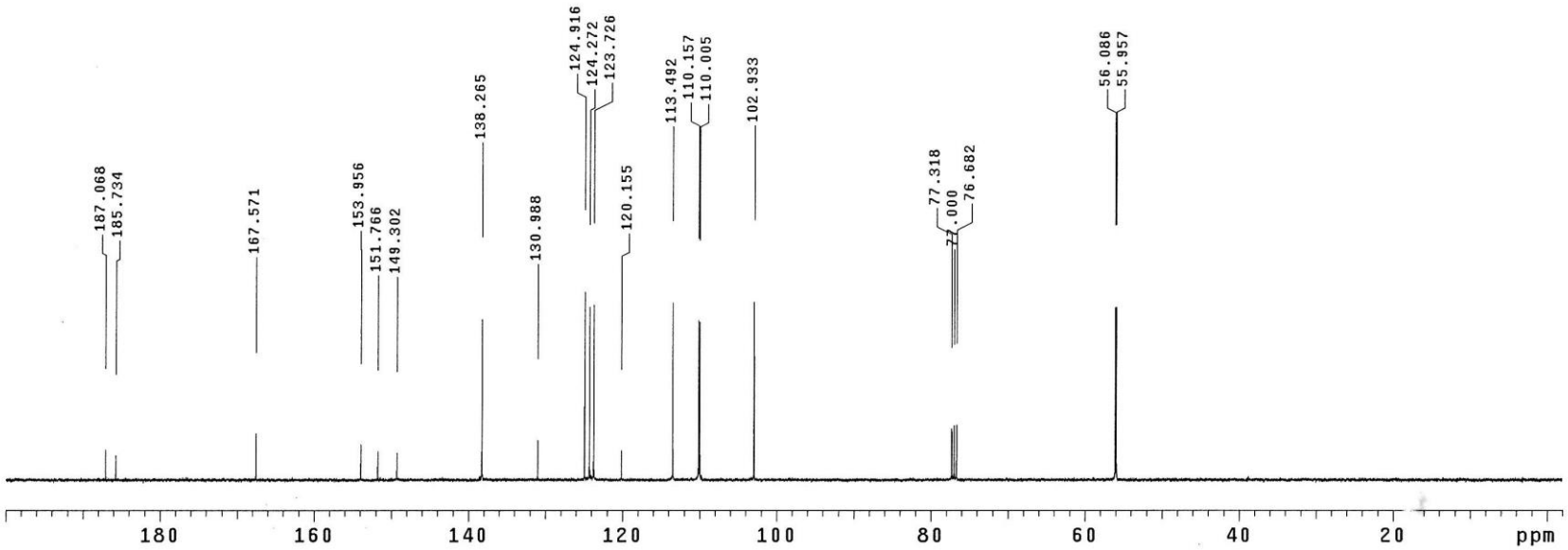
Compound 4aa (^{13}C-NMR spectral data)

LYK1024

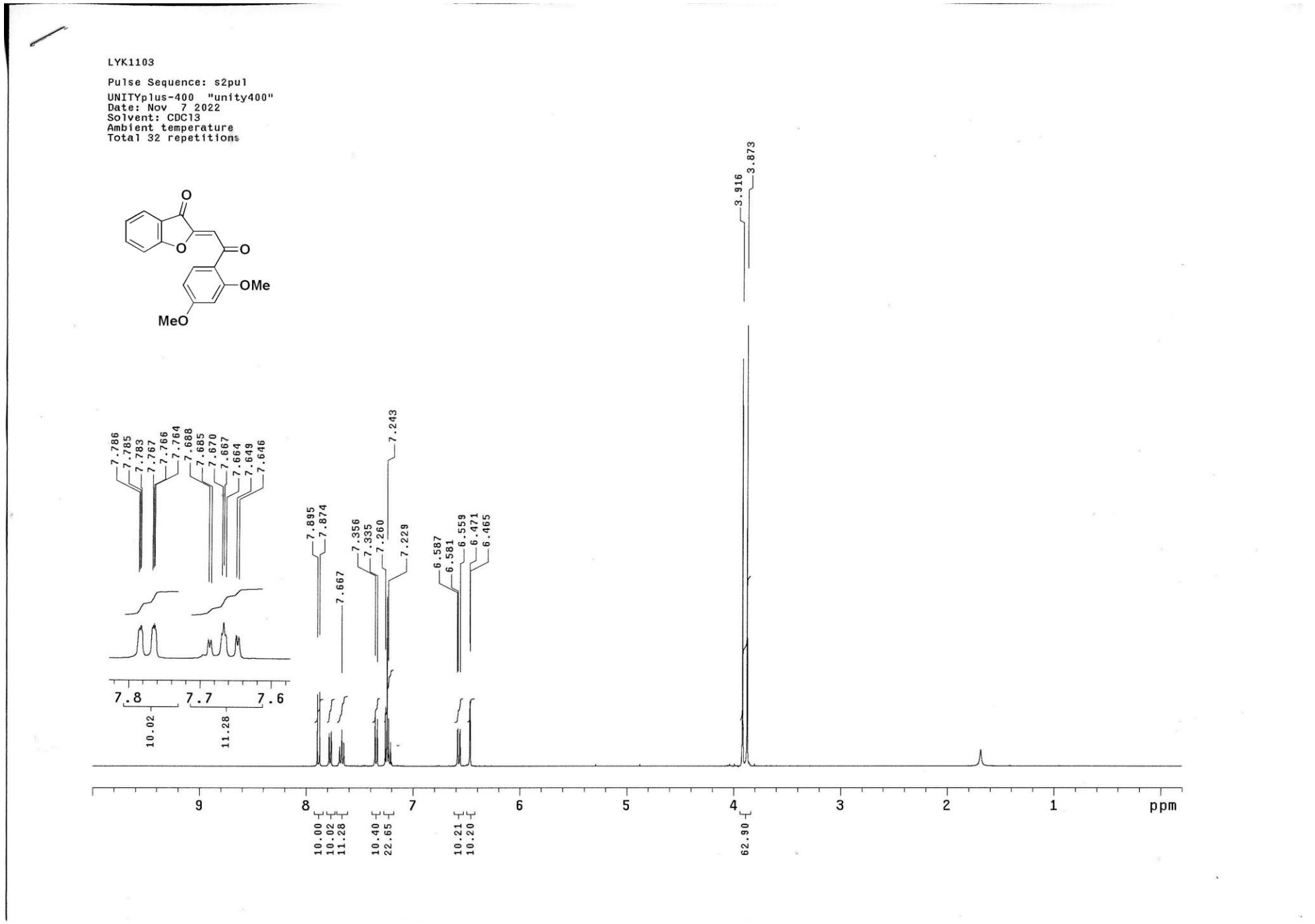
Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Oct 25 2022
Solvent: CDCl3
Ambient temperature
Total 1760 repetitions





Compound 4ab (^{1}H-NMR spectral data)

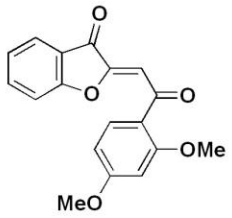


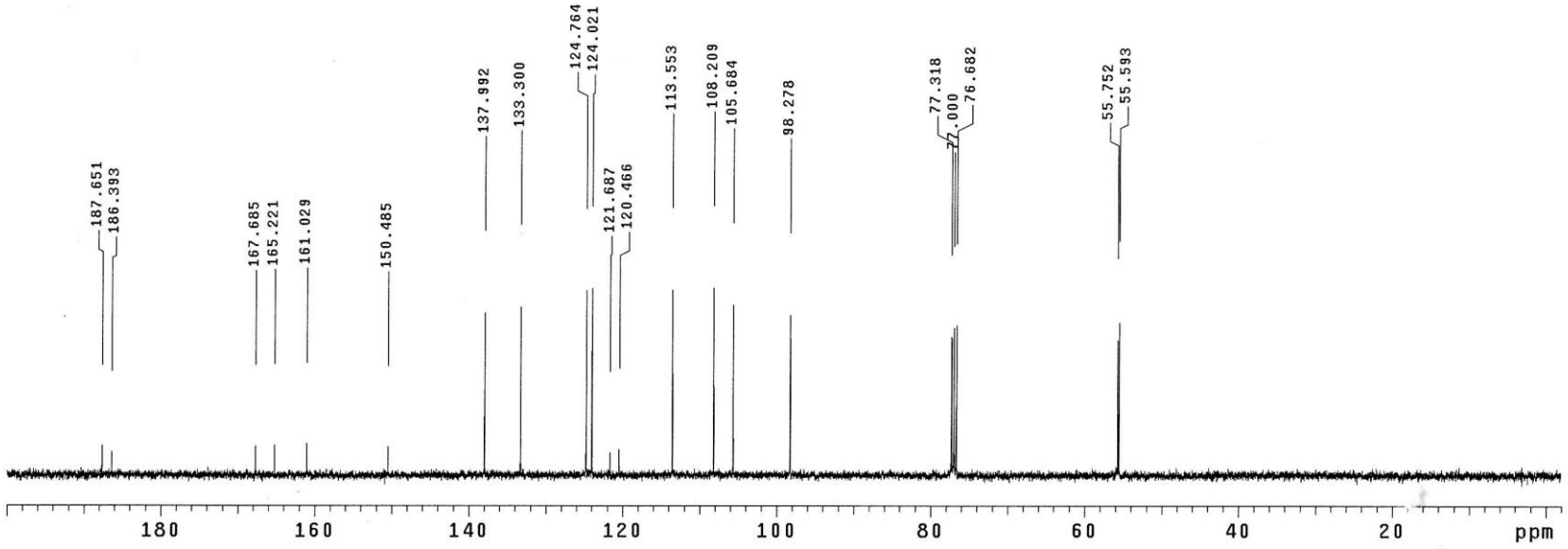
Compound 4ab (^{13}C-NMR spectral data)

LYK1103

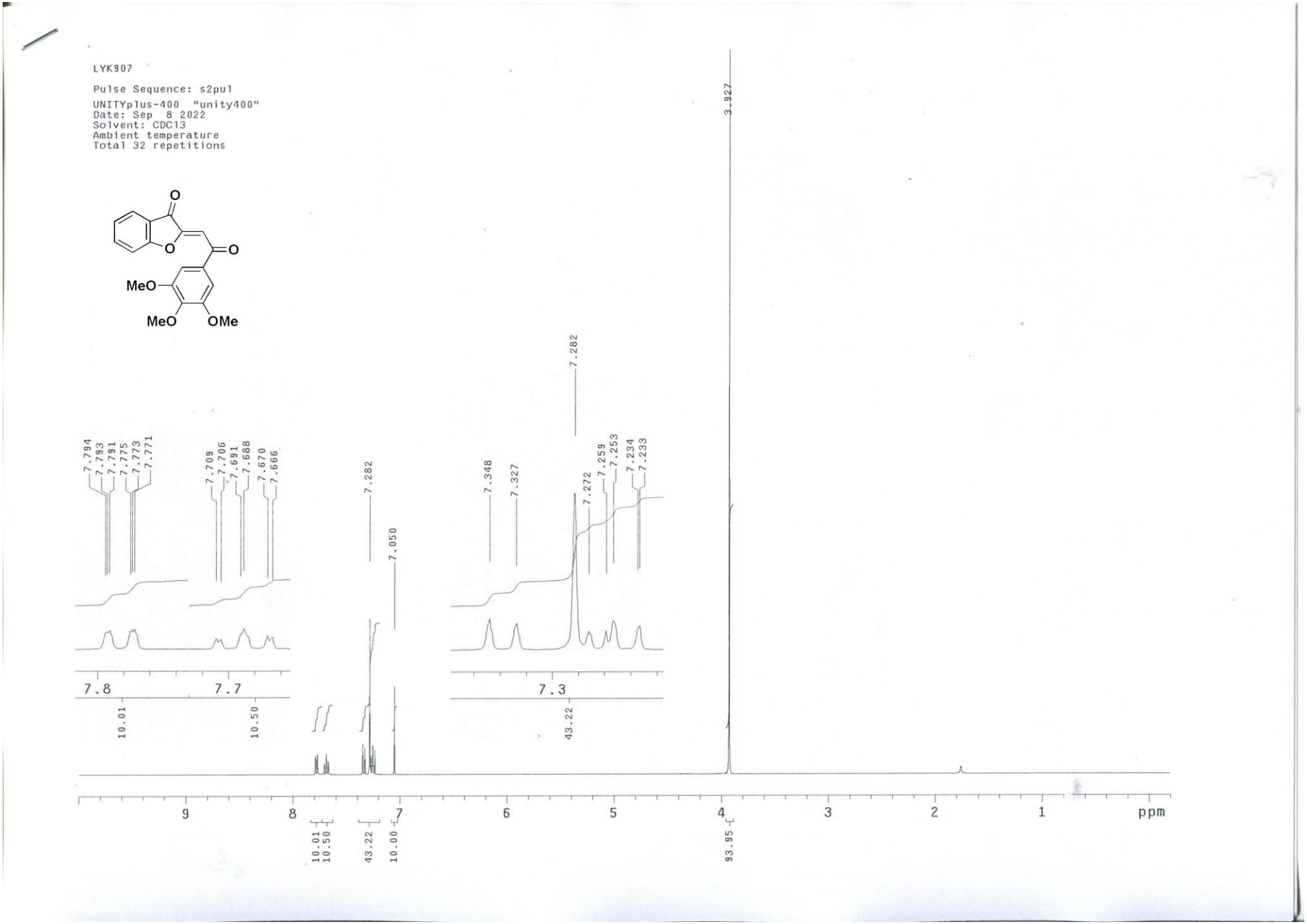
Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Nov 7 2022
Solvent: CDCl3
Ambient temperature
Total 1472 repetitions





Compound 4ac (^{1}H-NMR spectral data)

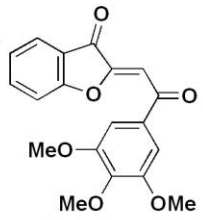


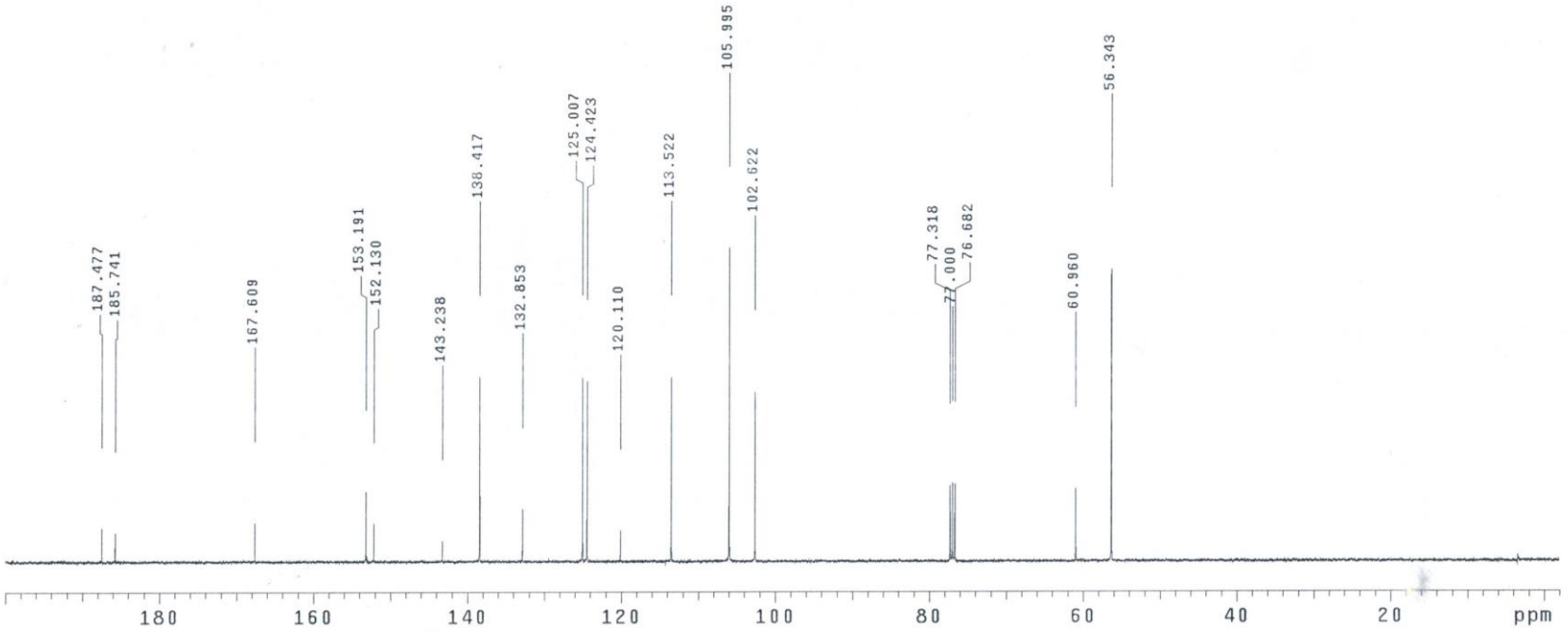
Compound 4ac (^{13}C-NMR spectral data)

LYK907

Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Sep 8 2022
Solvent: CDCl3
Ambient temperature
Total 2848 repetitions



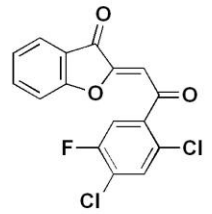


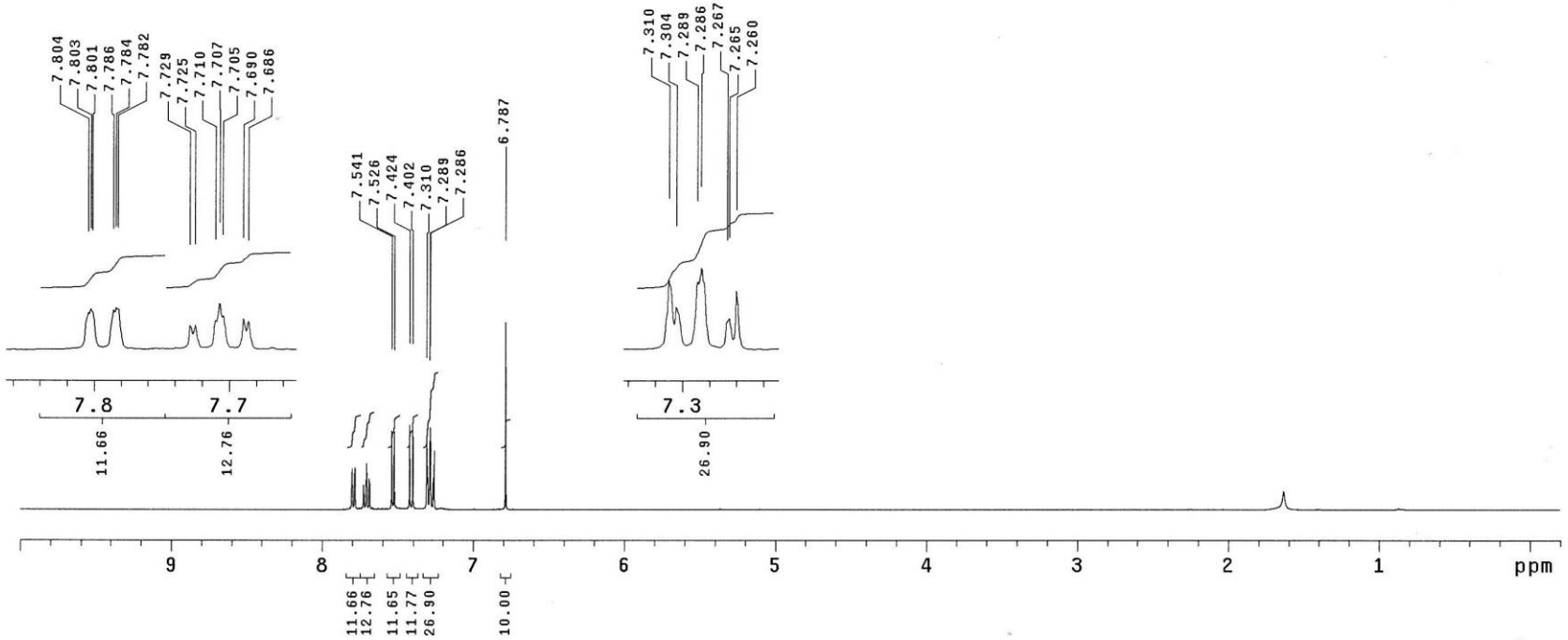
Compound 4ad (^{1}H-NMR spectral data)

LYK1108

Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Nov 9 2022
Solvent: CDCl3
Ambient temperature
Total 32 repetitions



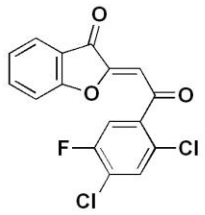


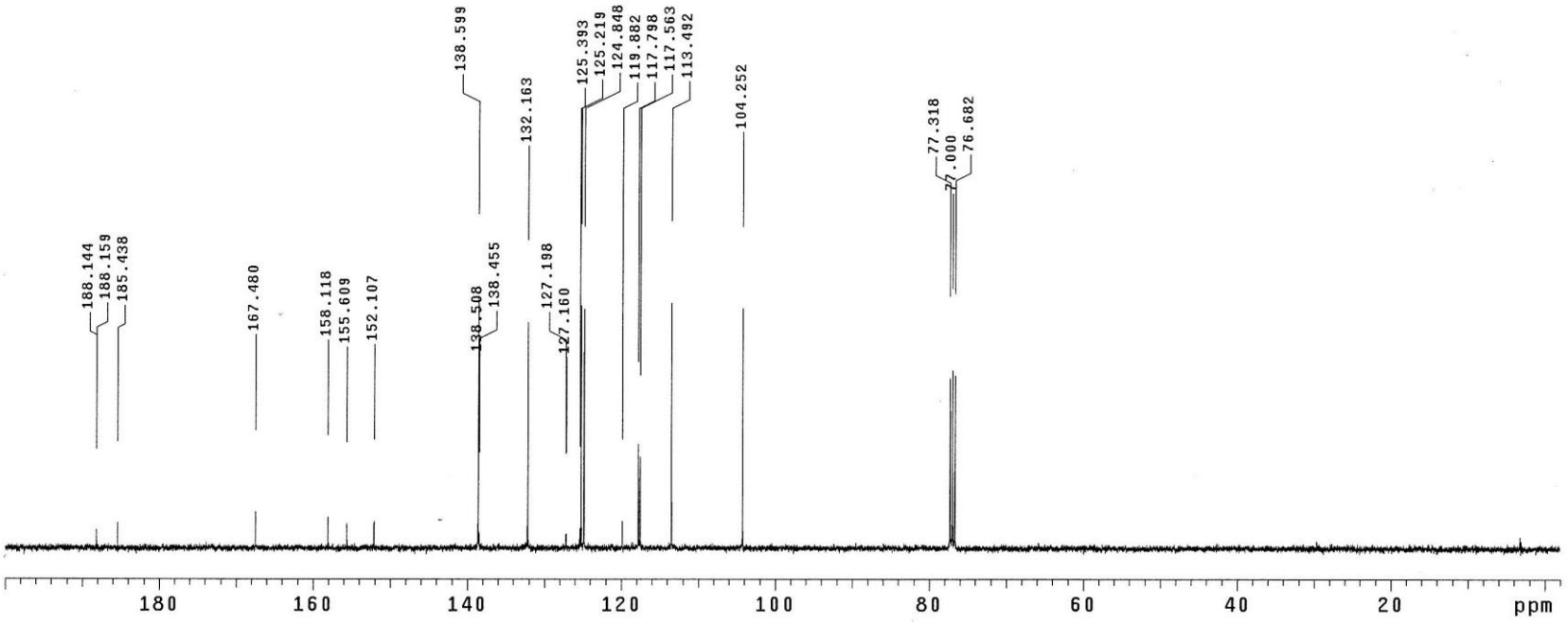
Compound 4ad (^{13}C-NMR spectral data)

LYK1108

Pulse Sequence: s2pul

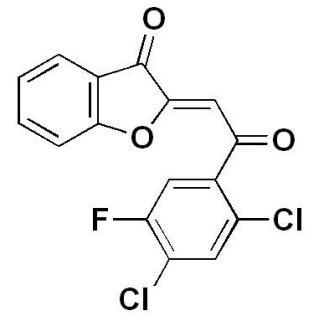
UNITYplus-400 "unity400"
Date: Nov 9 2022
Solvent: CDCl3
Ambient temperature
Total 4256 repetitions





Compound 4ad (^{19}F-NMR spectral data)

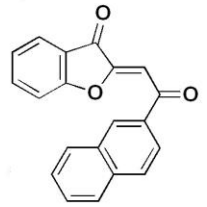
S44-S45(4ad)

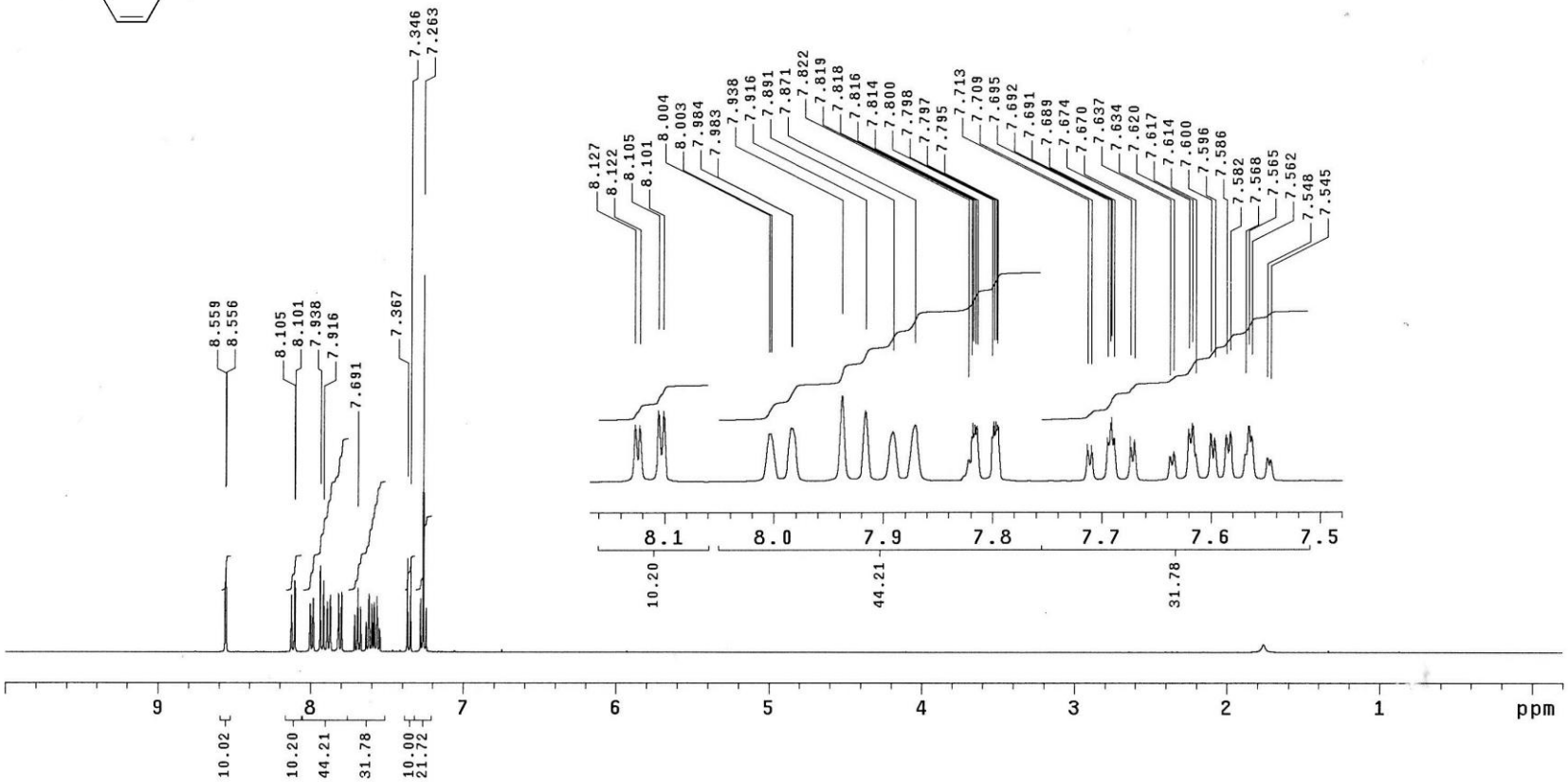


Compound 4ae (^{1}H-NMR spectral data)

LYK1110

Pulse Sequence: s2pul
UNITYplus-400 "unity400"
Date: Nov 11 2022
Solvent: CDCl3
Ambient temperature
Total 32 repetitions



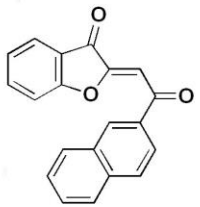


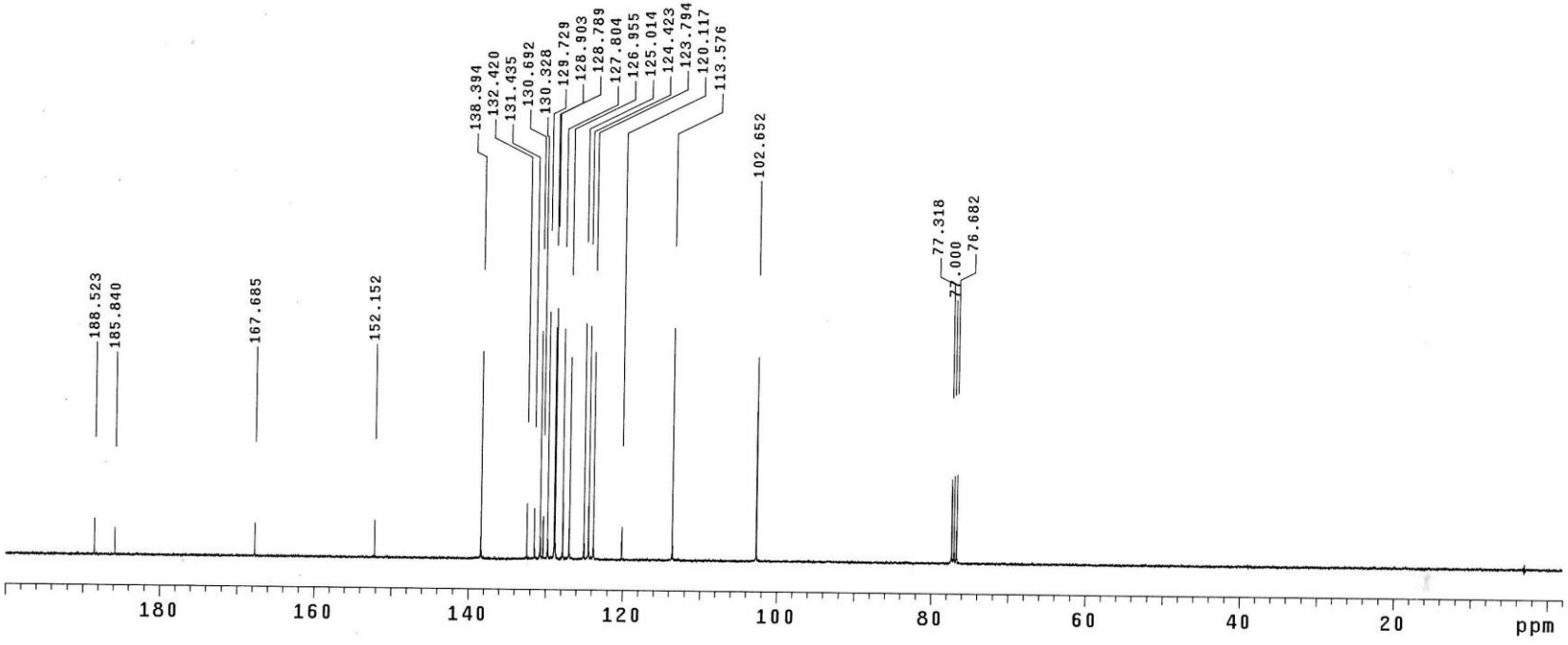
Compound 4ae (^{13}C-NMR spectral data)

LYK1110

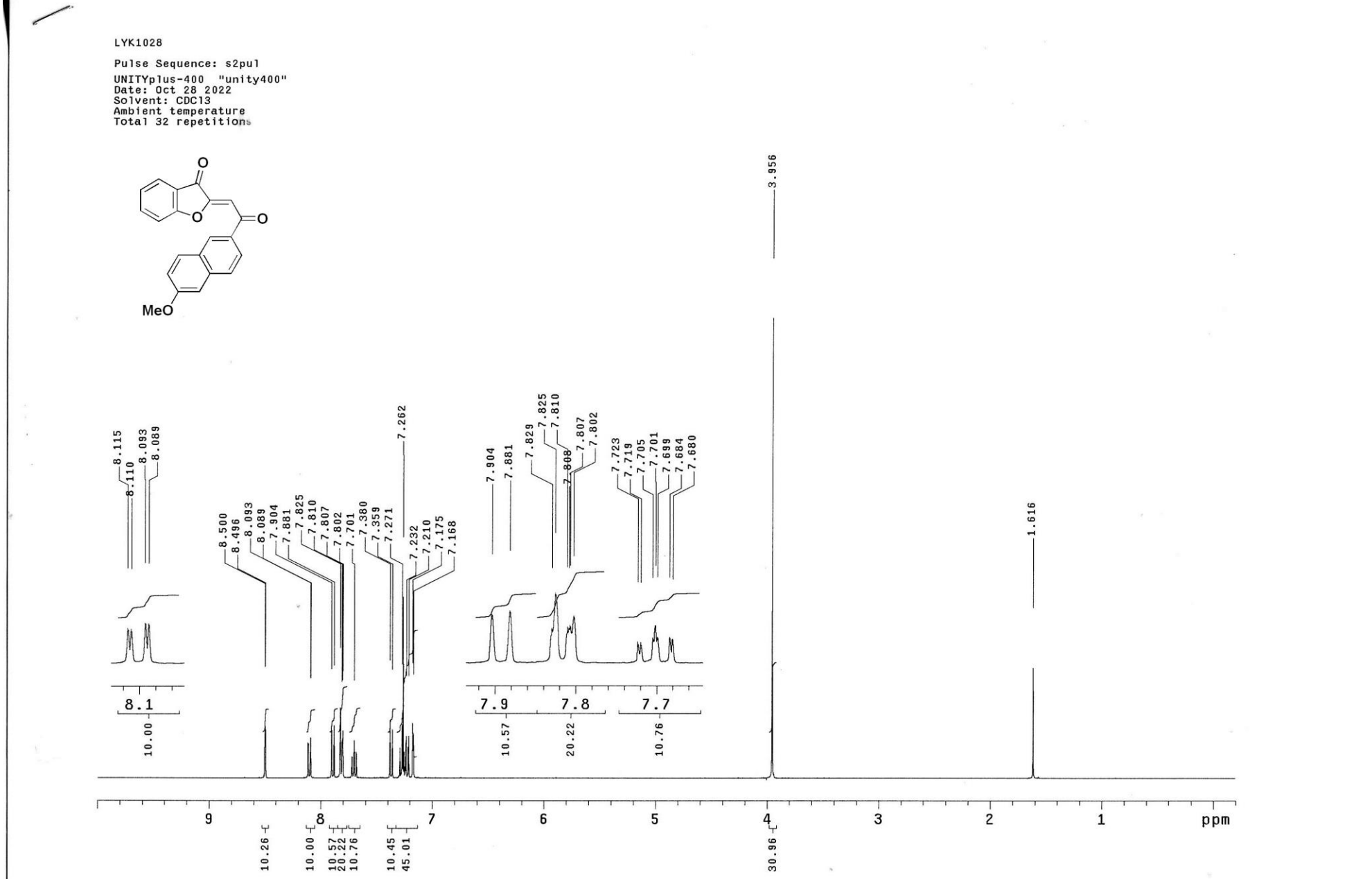
Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Nov 11 2022
Solvent: CDCl3
Ambient temperature
Total 5264 repetitions





Compound 4af (^{1}H-NMR spectral data)

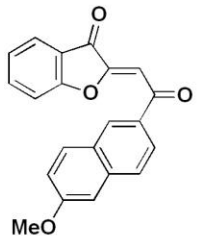


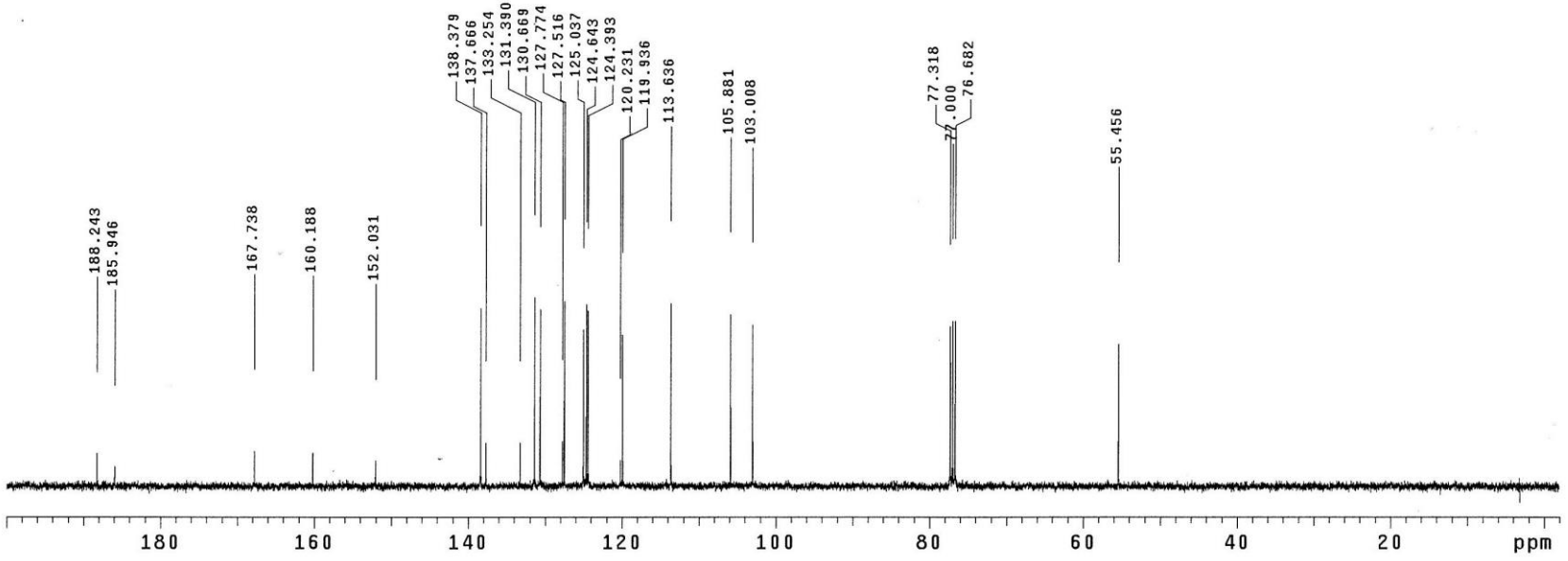
Compound 4af (^{13}C-NMR spectral data)

LYK1028

Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Oct 28 2022
Solvent: CDCl3
Ambient temperature
Total 2624 repetitions



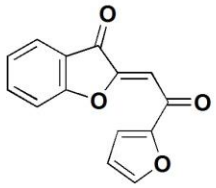


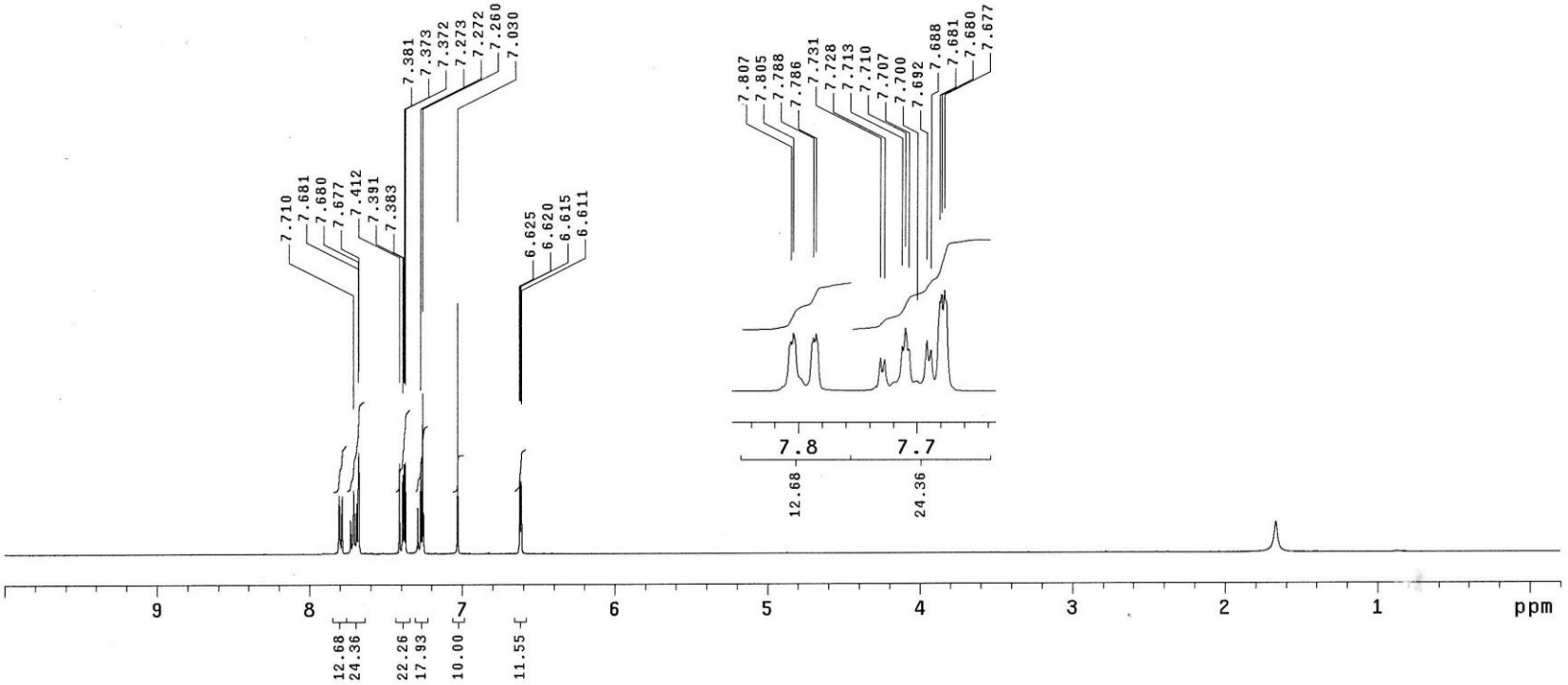
Compound 4ag (^{1}H-NMR spectral data)

LYK1123

Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Nov 24 2022
Solvent: CDCl3
Ambient temperature
Total 32 repetitions



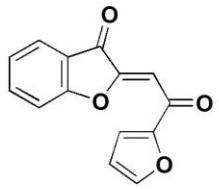


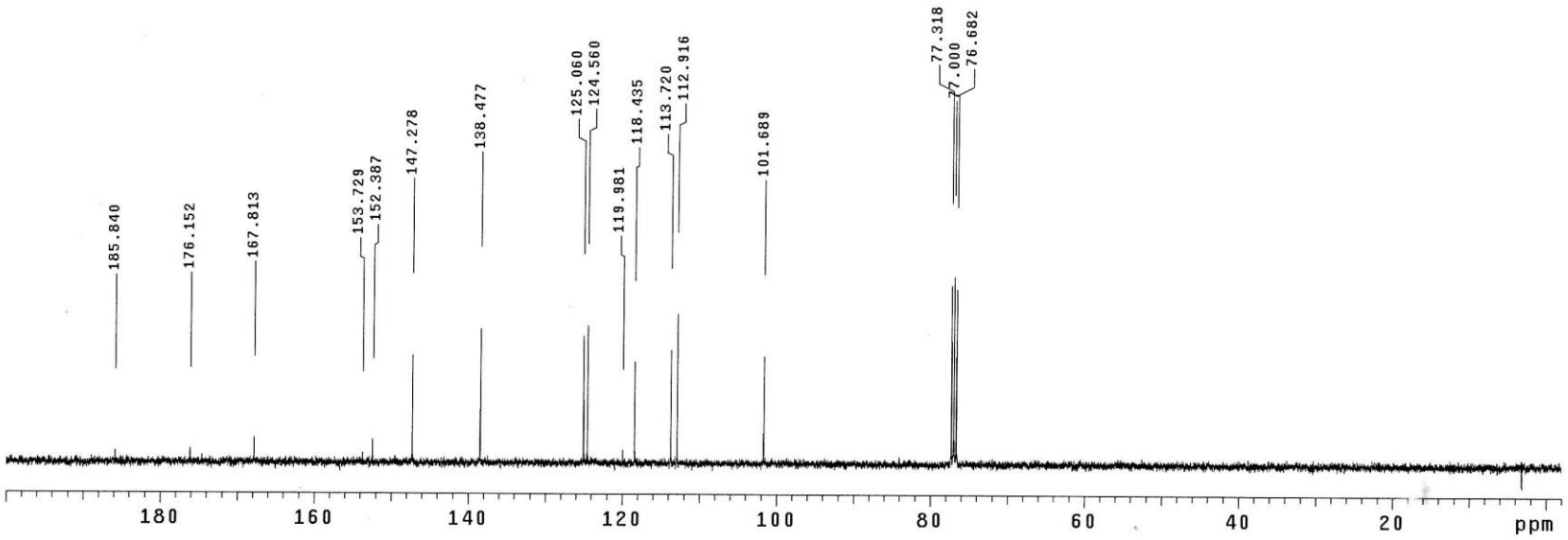
Compound 4ag (^{13}C-NMR spectral data)

LYK1123

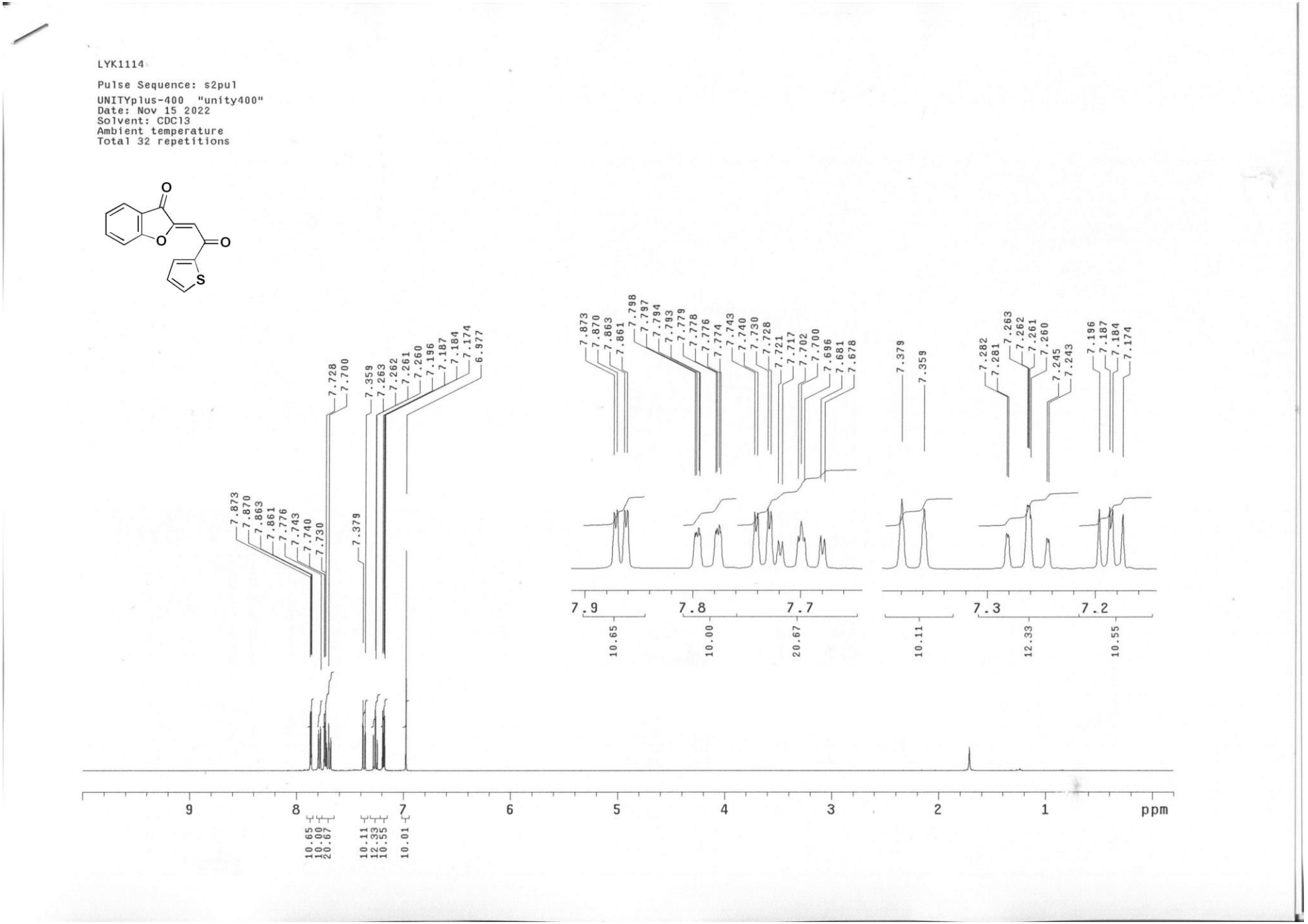
Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Nov 24 2022
Solvent: CDCl3
Ambient temperature
Total 2832 repetitions





Compound 4ah (^{1}H-NMR spectral data)

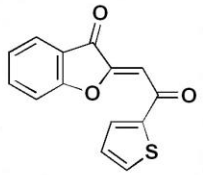


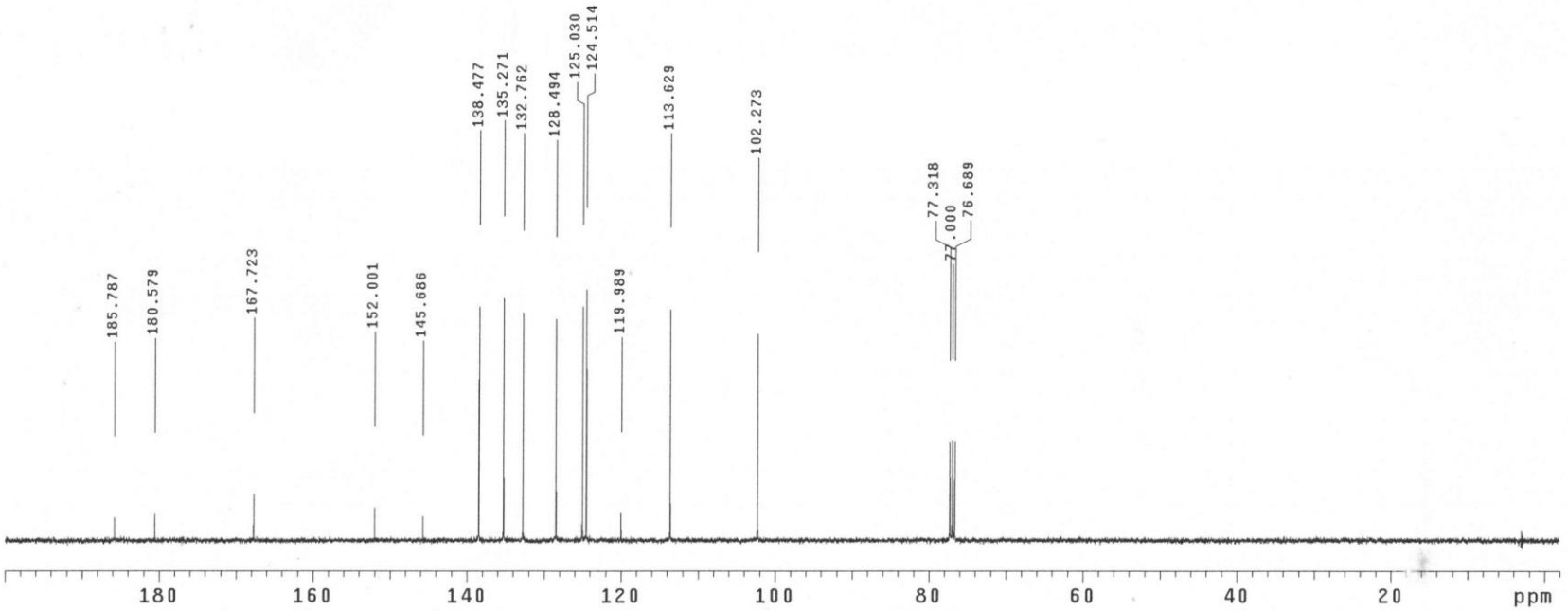
Compound 4ah (^{13}C-NMR spectral data)

LYK1114

Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Nov 15 2022
Solvent: CDCl3
Ambient temperature
Total 2112 repetitions



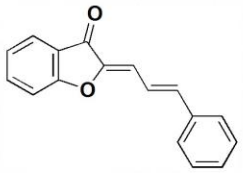


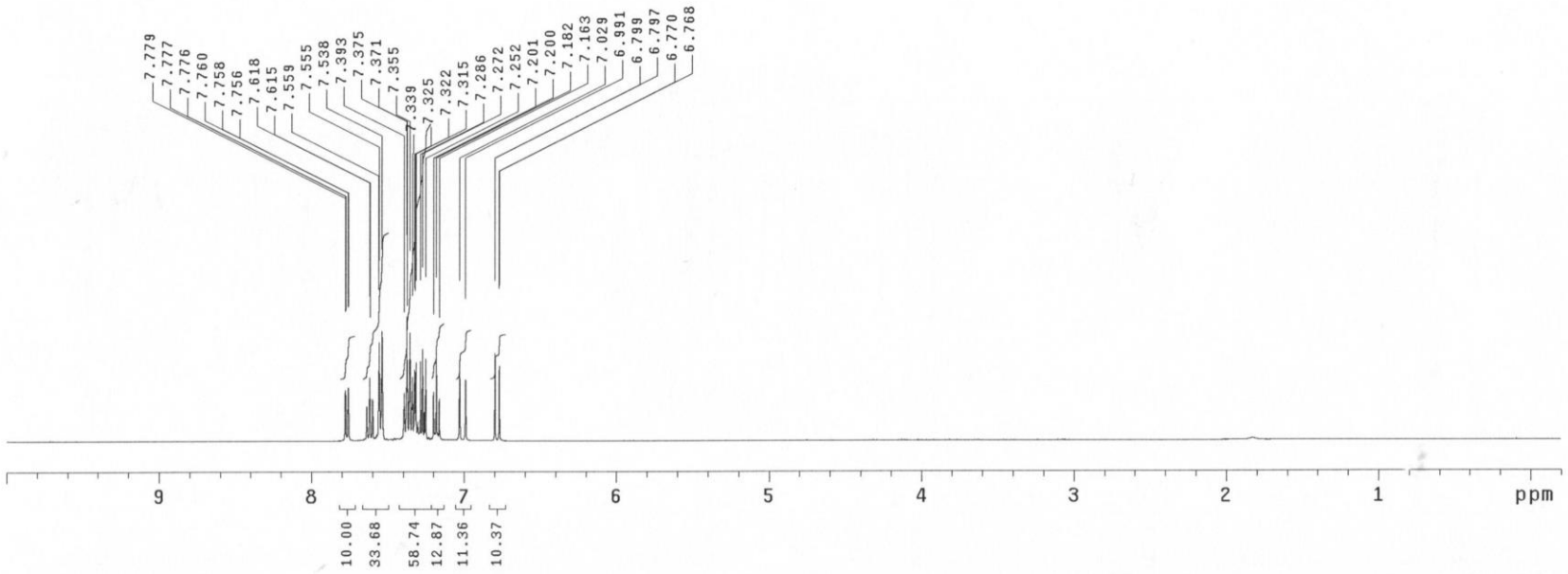
Compound 6a (^{1}H-NMR spectral data)

CRC0112

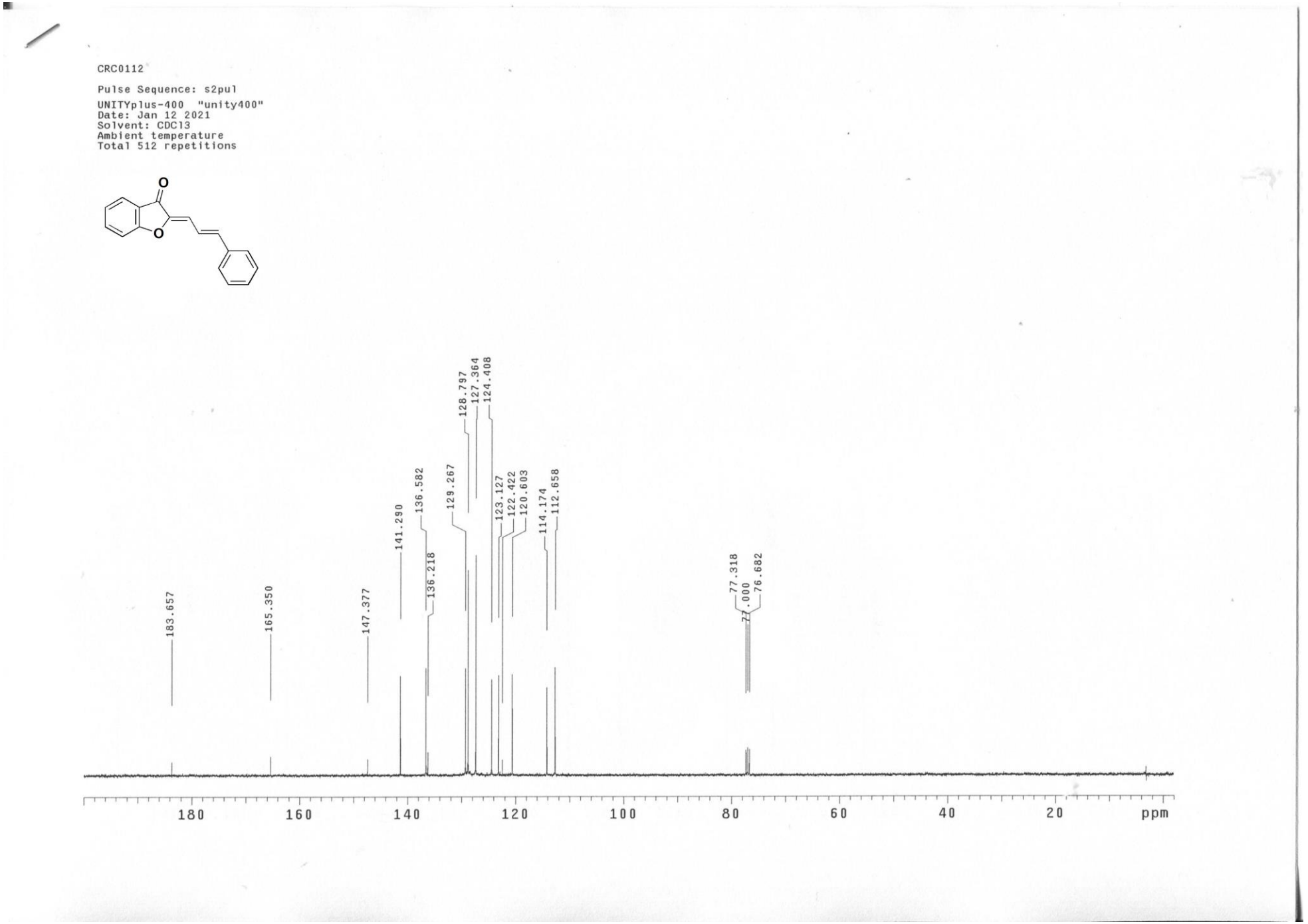
Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Jan 12 2021
Solvent: CDCl3
Ambient temperature
Total 32 repetitions





Compound 6a (^{13}C-NMR spectral data)

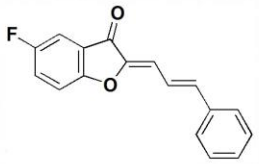


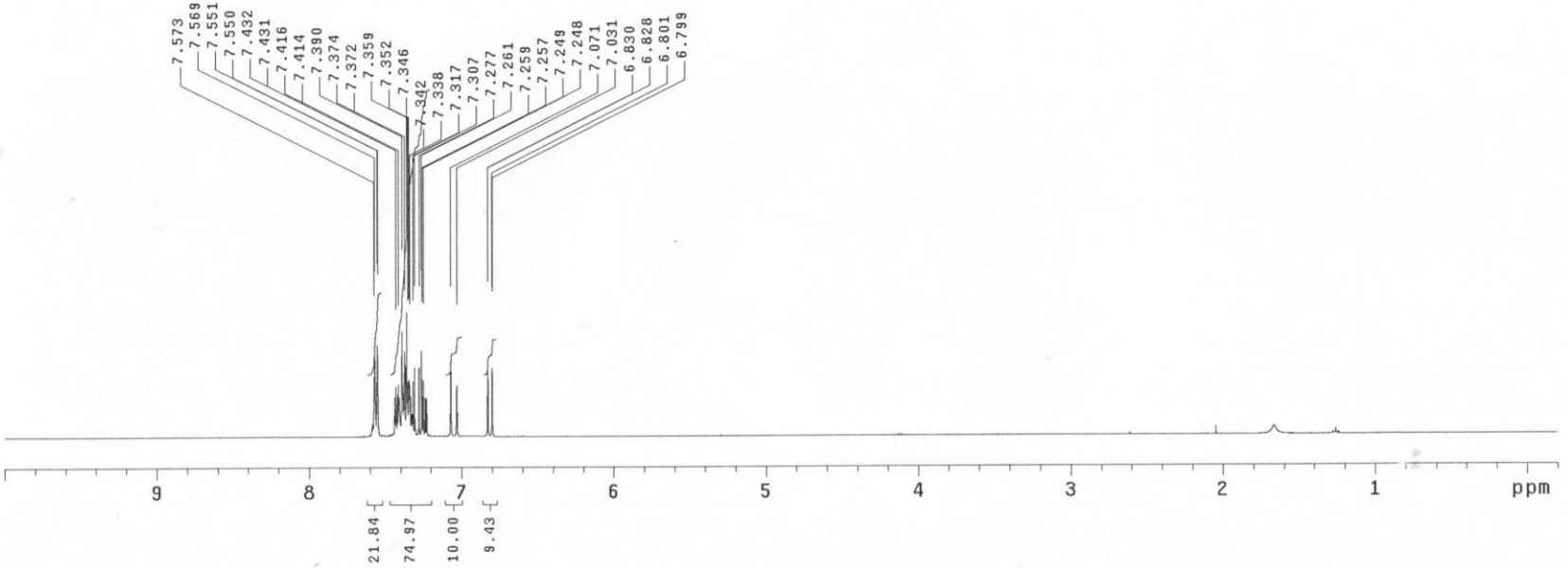
Compound 6b (^{1}H-NMR spectral data)

CRC0119

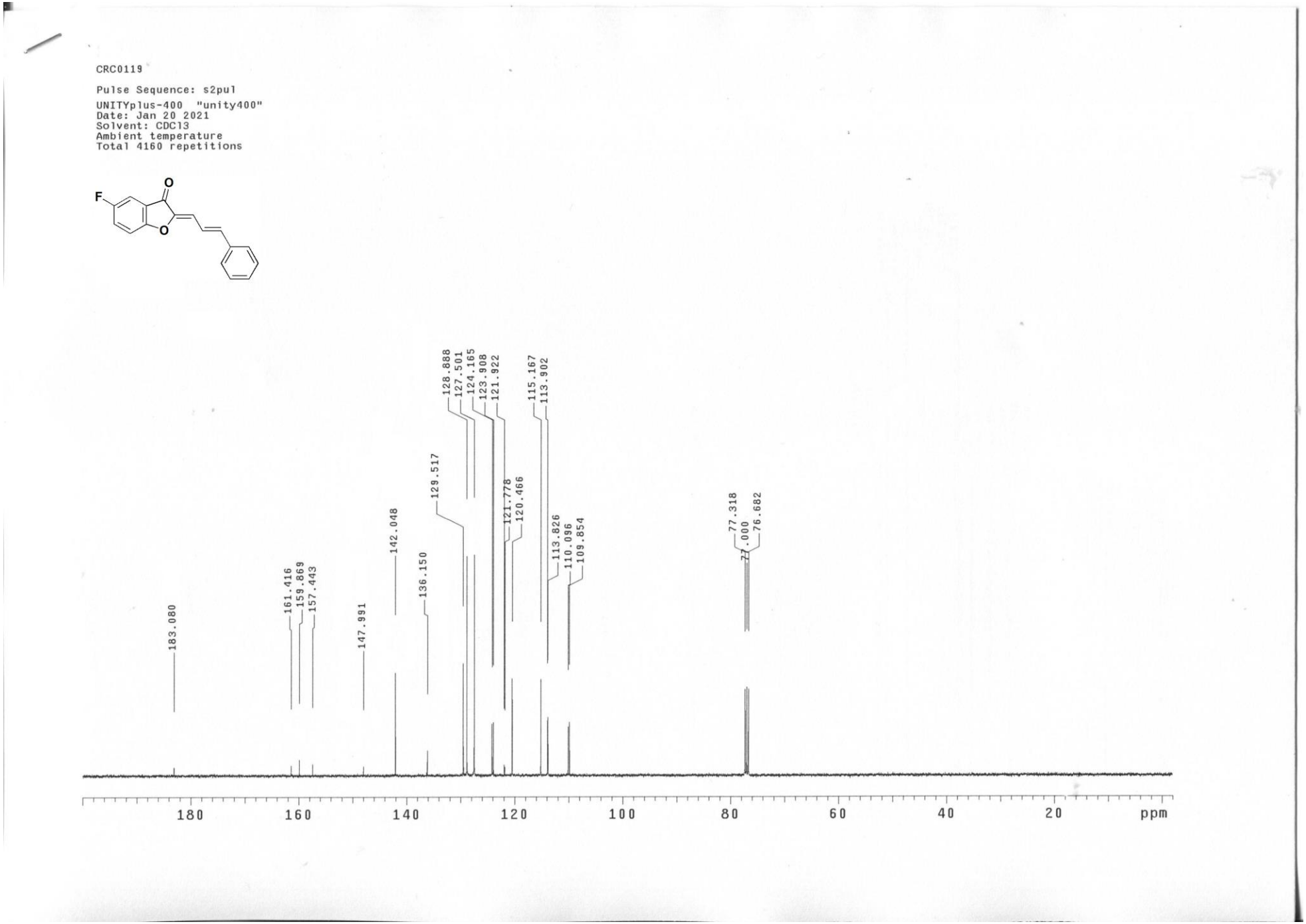
Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Jan 20 2021
Solvent: CDCl3
Ambient temperature
Total 32 repetitions



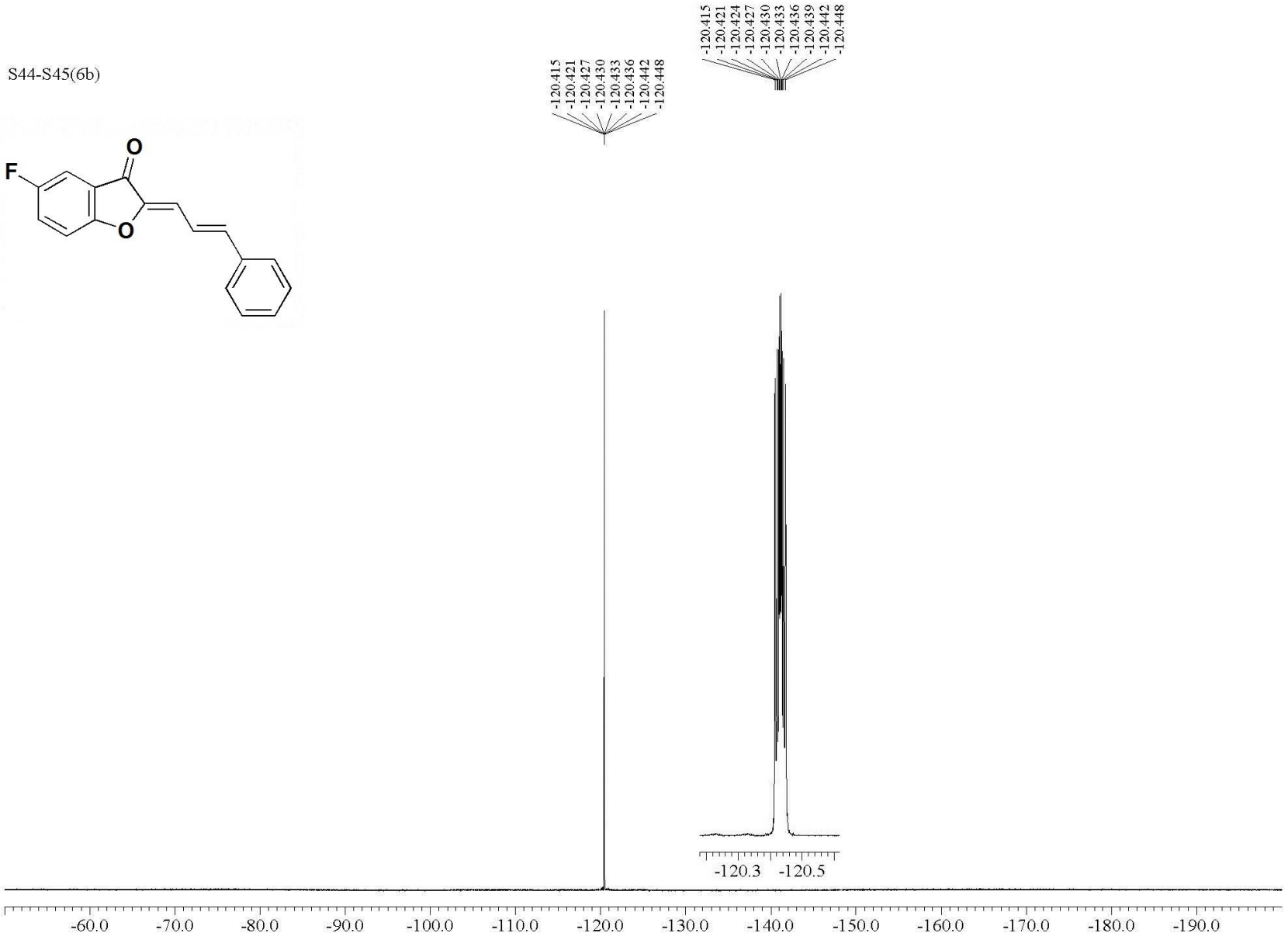


Compound 6b (^{13}C-NMR spectral data)



Compound 6b (^{19}F-NMR spectral data)

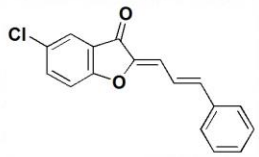
S44-S45(6b)

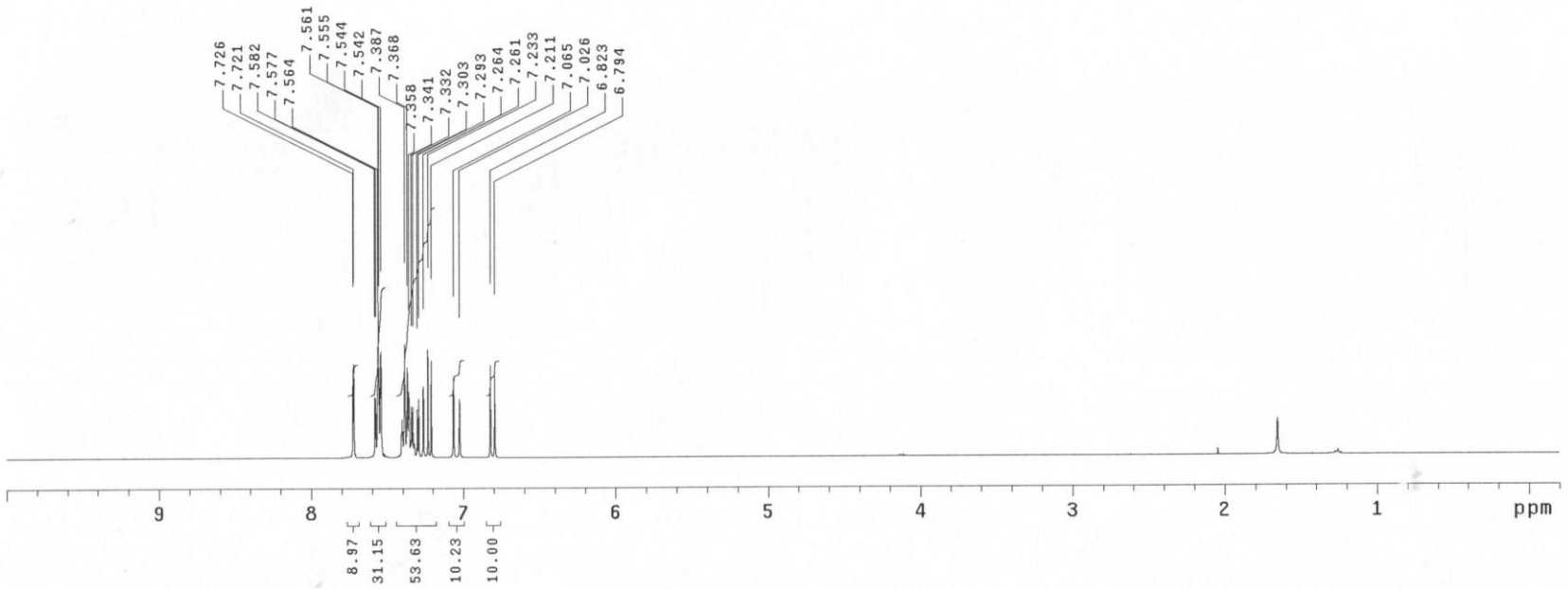


Compound 6c (^{1}H-NMR spectral data)

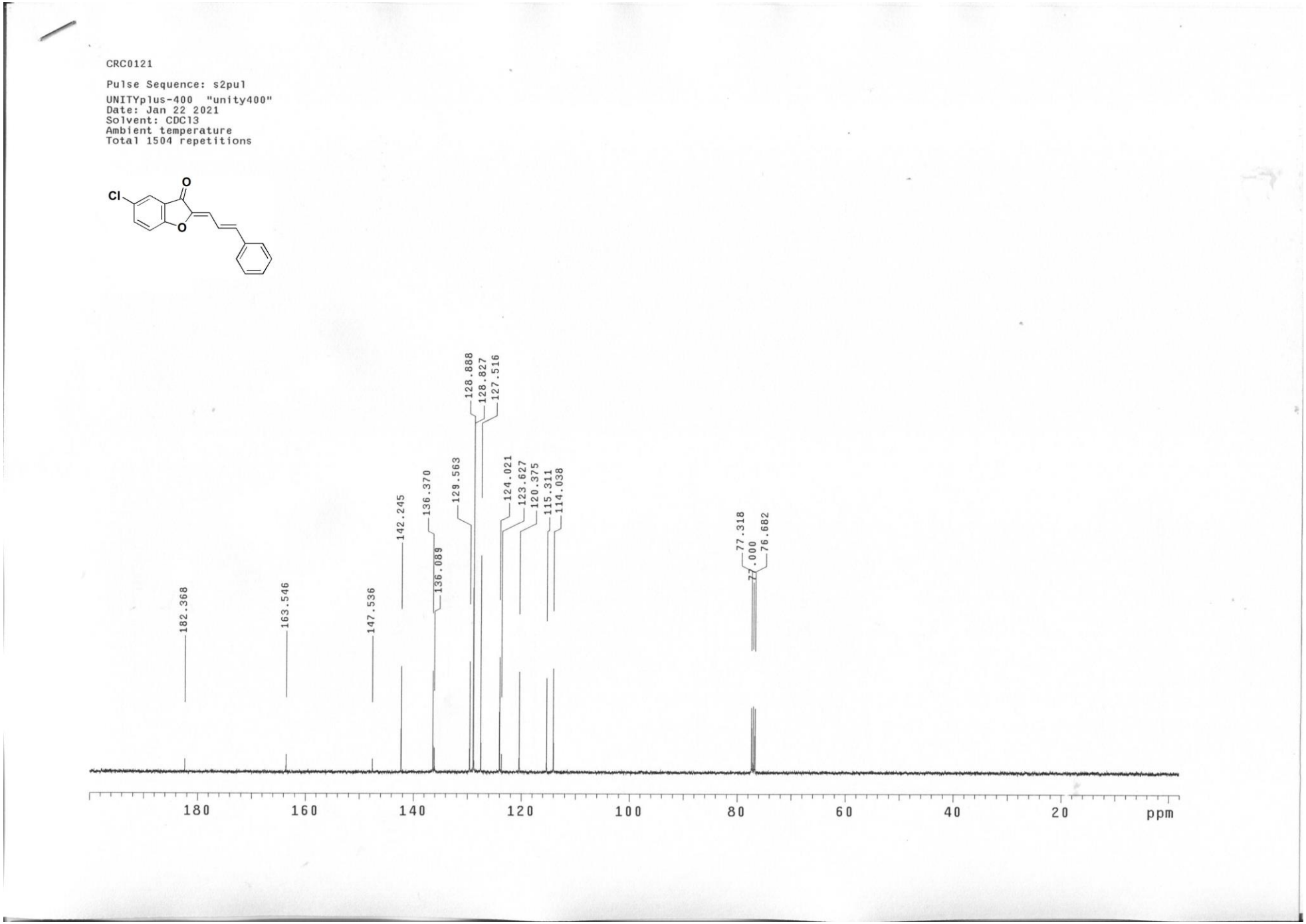
CRC0121

Pulse Sequence: s2pul
UNITYplus-400 "unity400"
Date: Jan 22 2021
Solvent: CDCl3
Ambient temperature
Total 32 repetitions

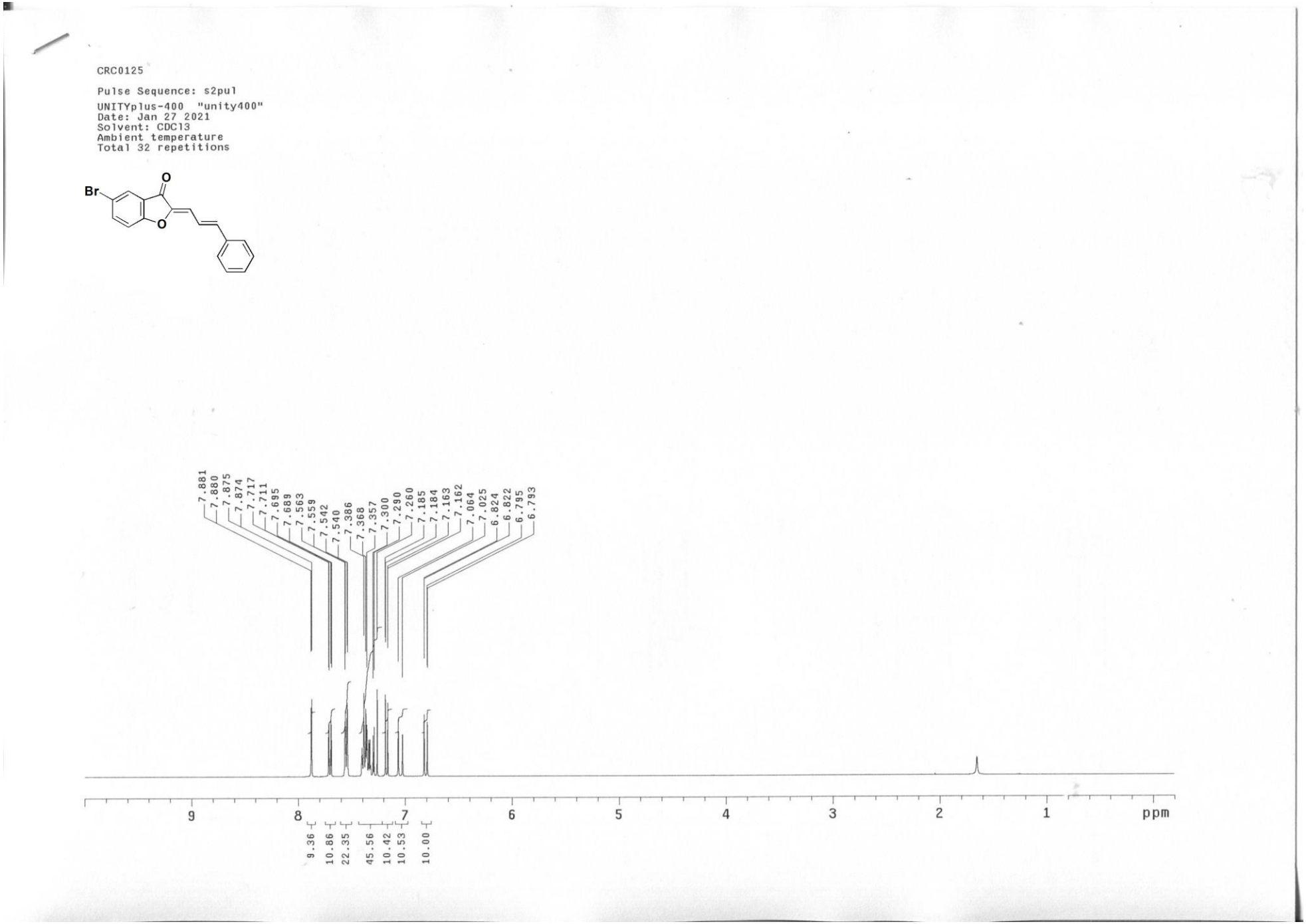




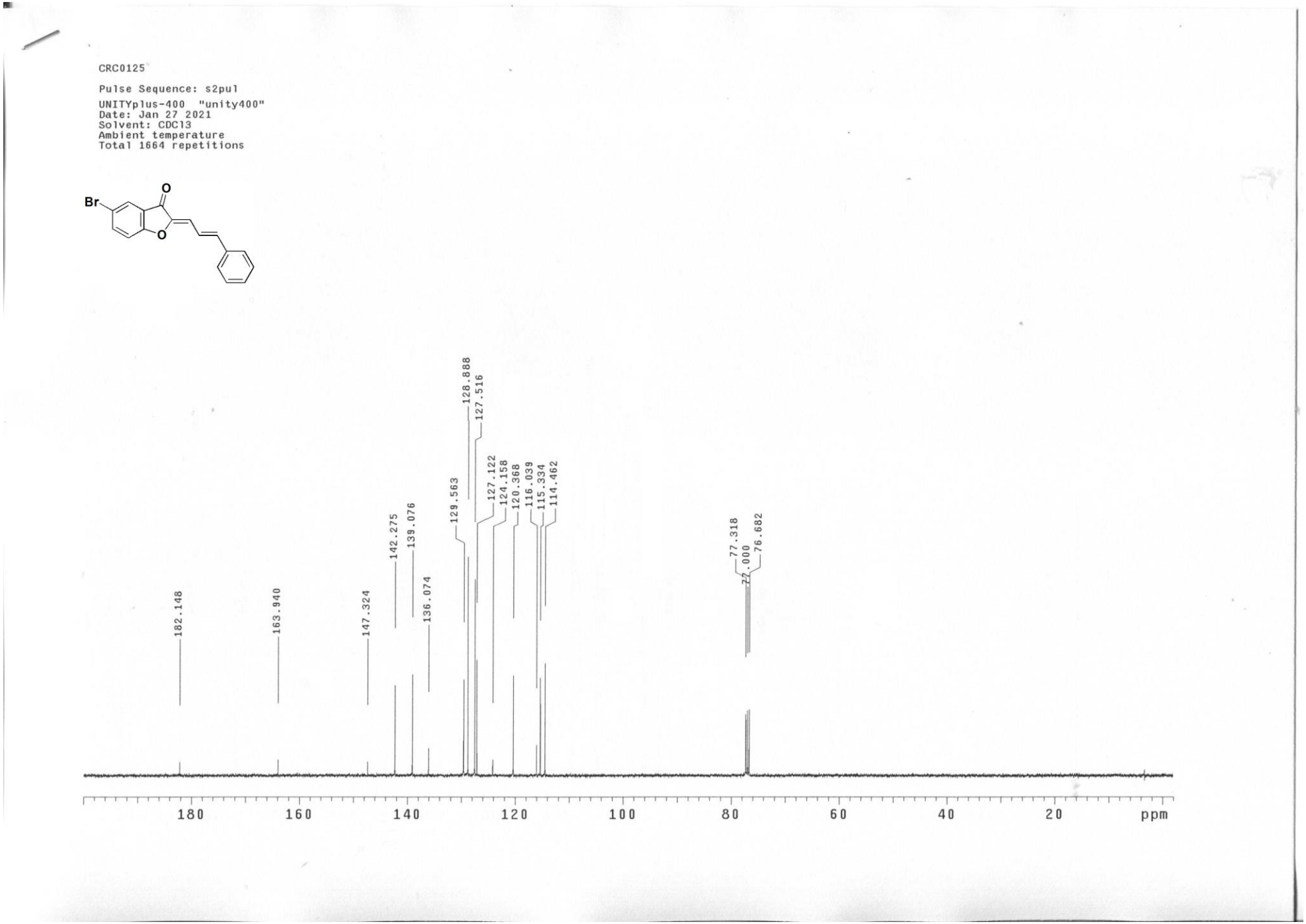
Compound 6c (^{13}C-NMR spectral data)



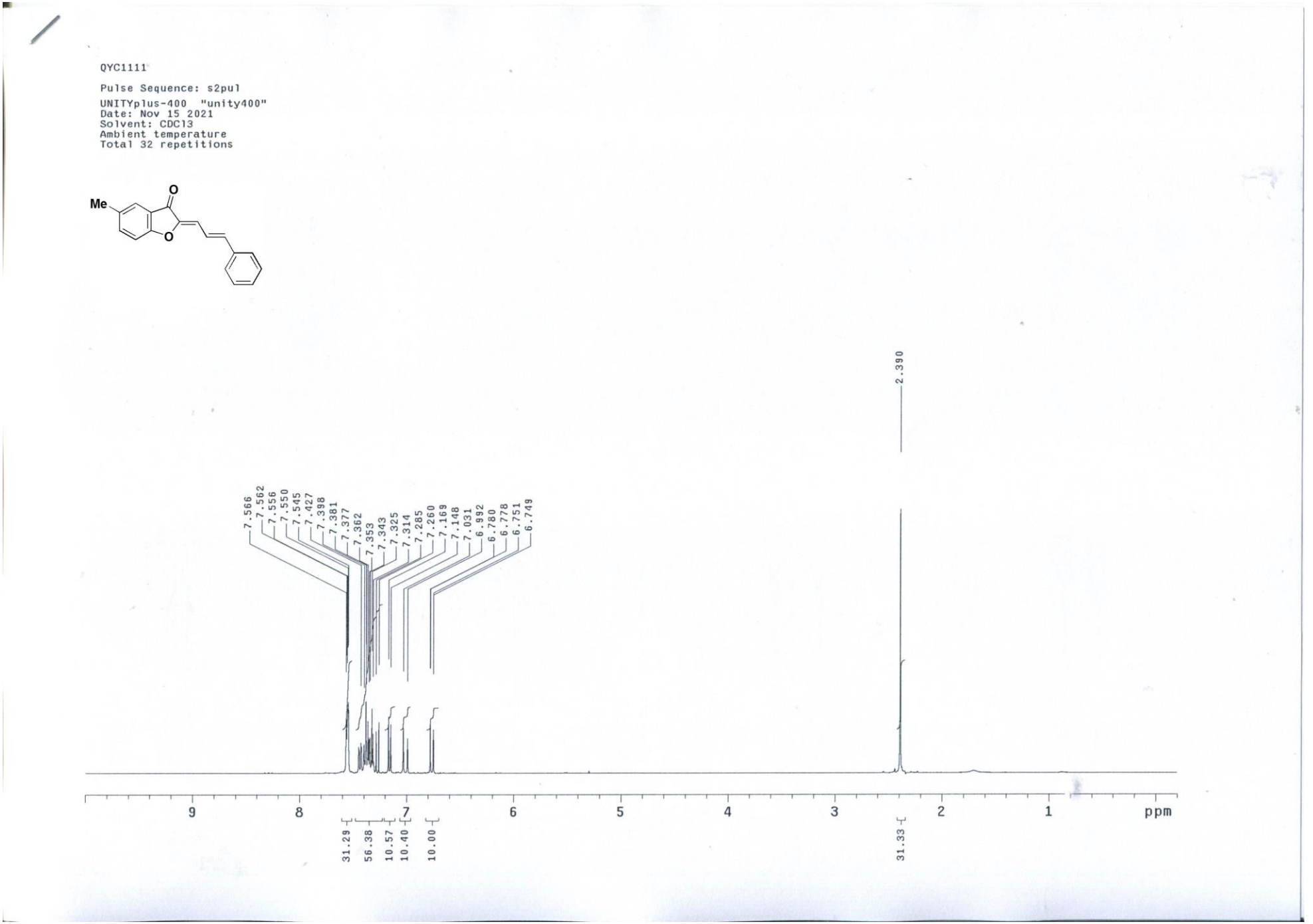
Compound 6d (^{1}H-NMR spectral data)



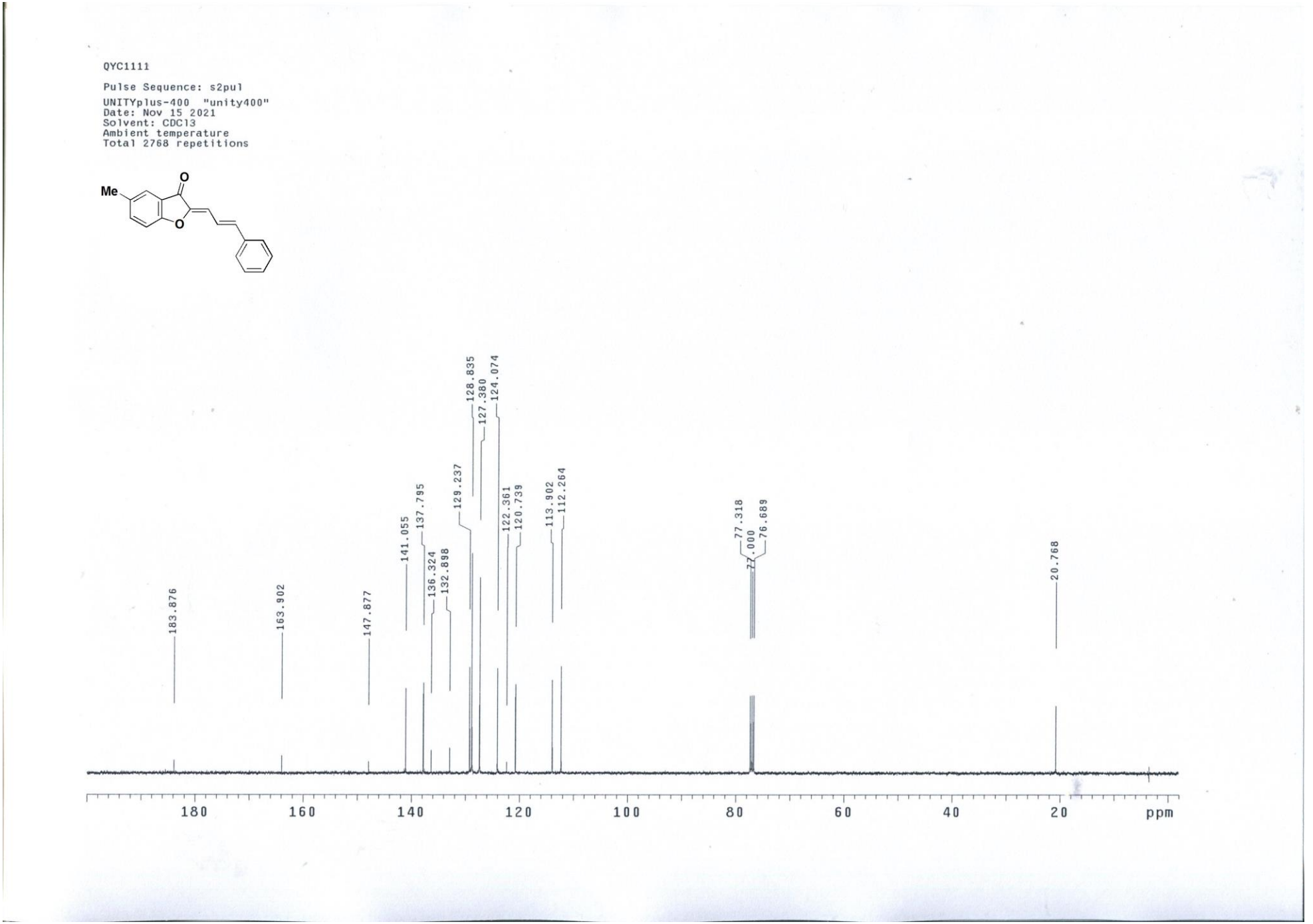
Compound 6d (^{13}C-NMR spectral data)



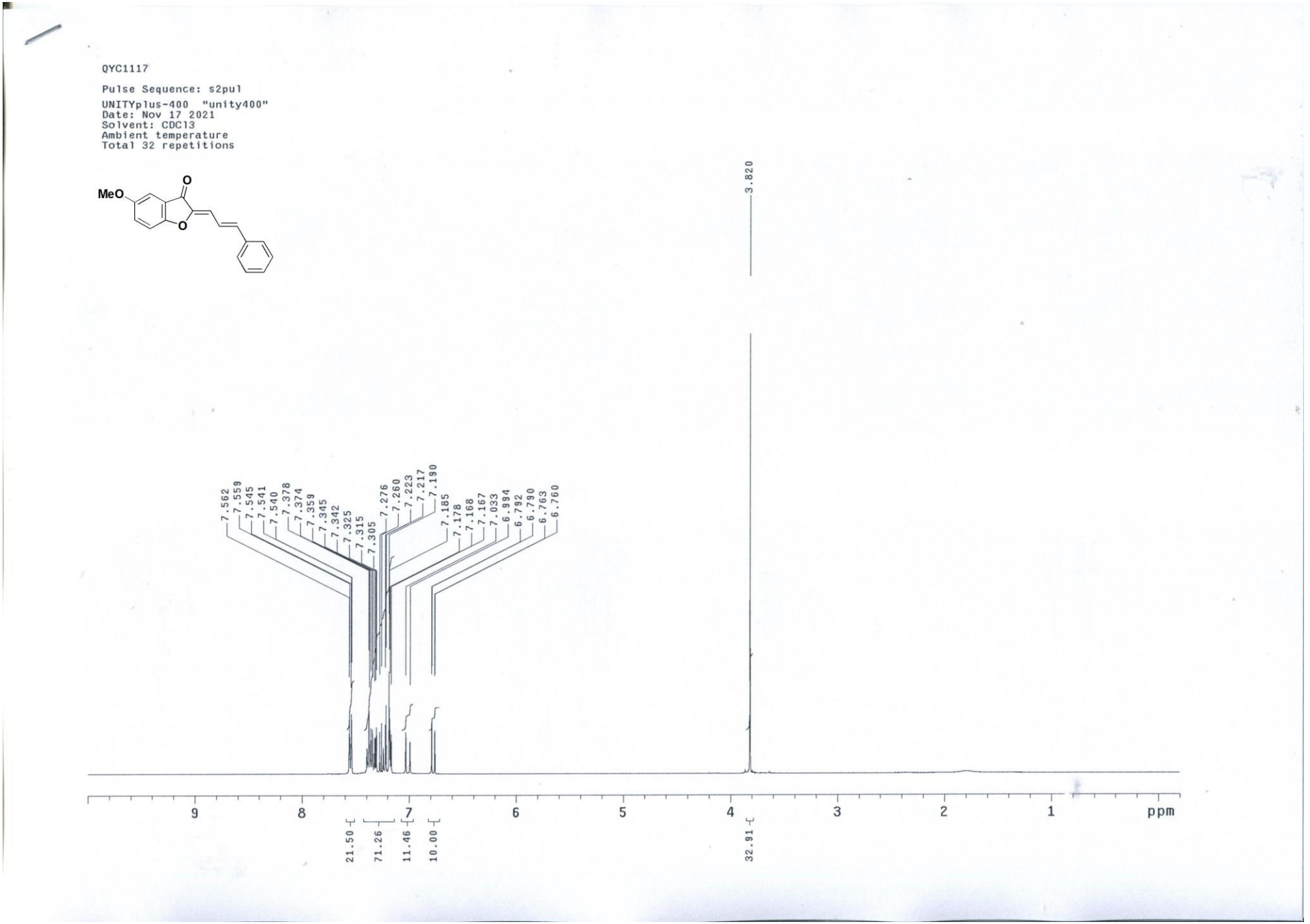
Compound 6e (^{1}H-NMR spectral data)



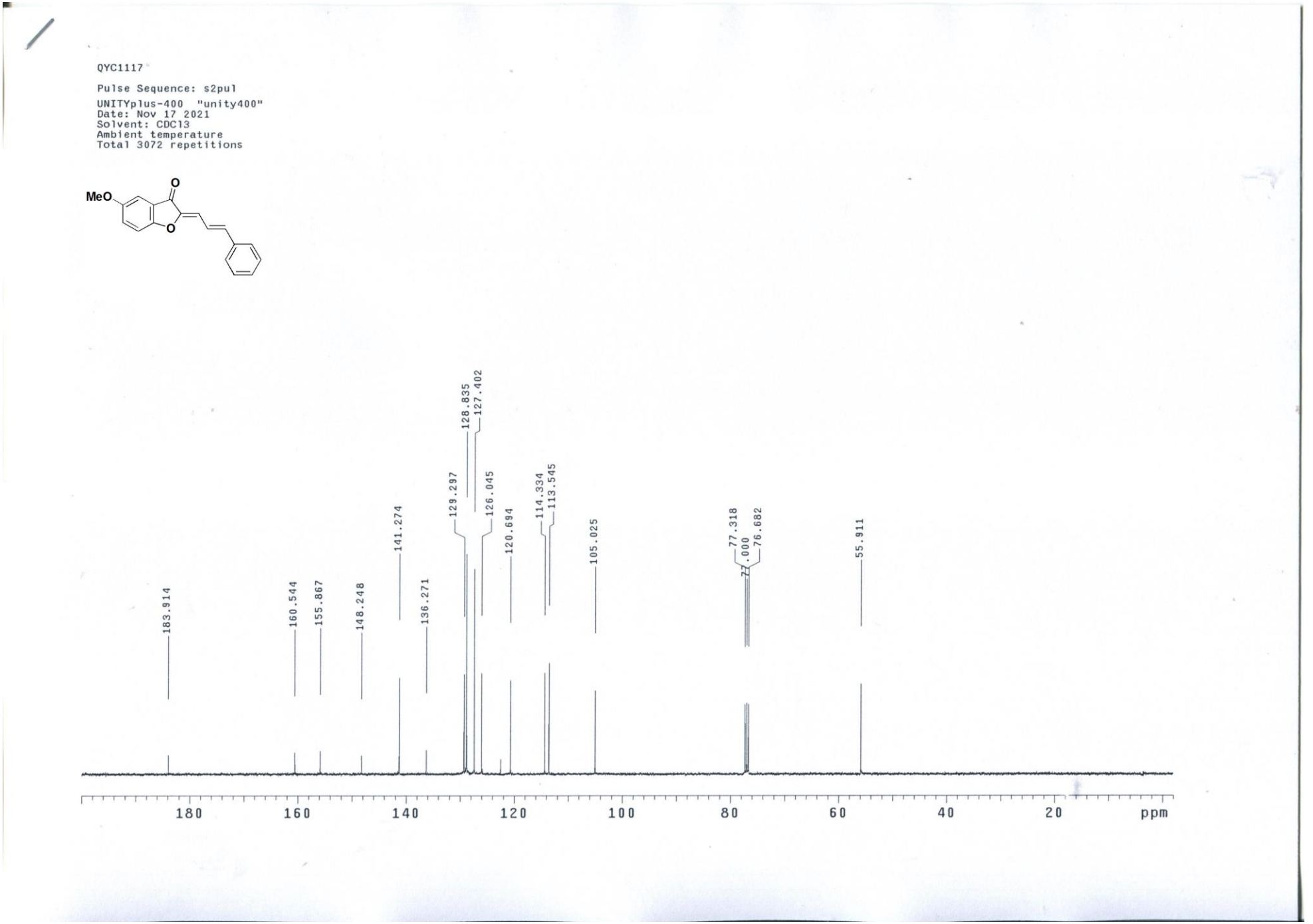
Compound 6e (^{13}C-NMR spectral data)



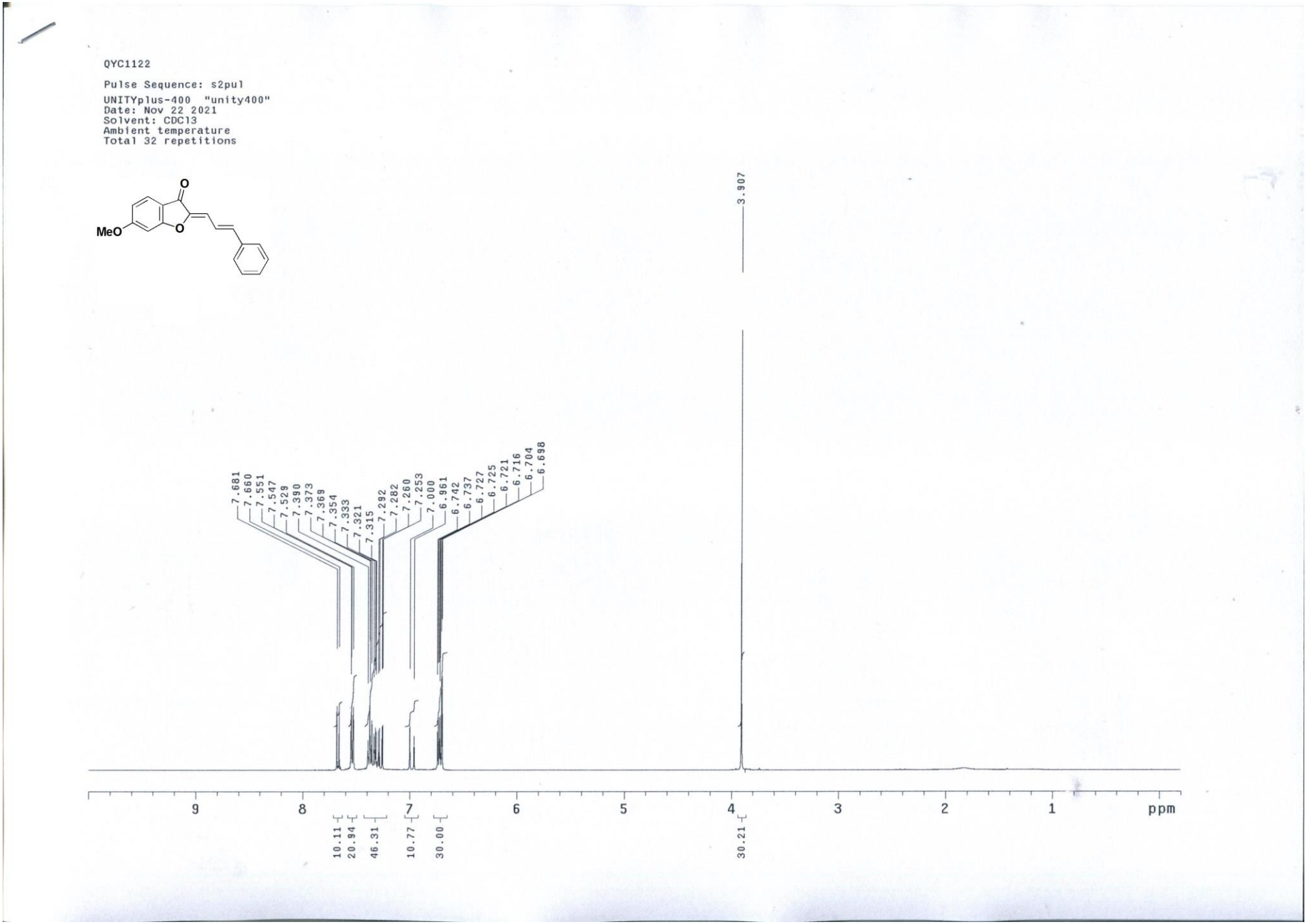
Compound 6f (^{1}H-NMR spectral data)



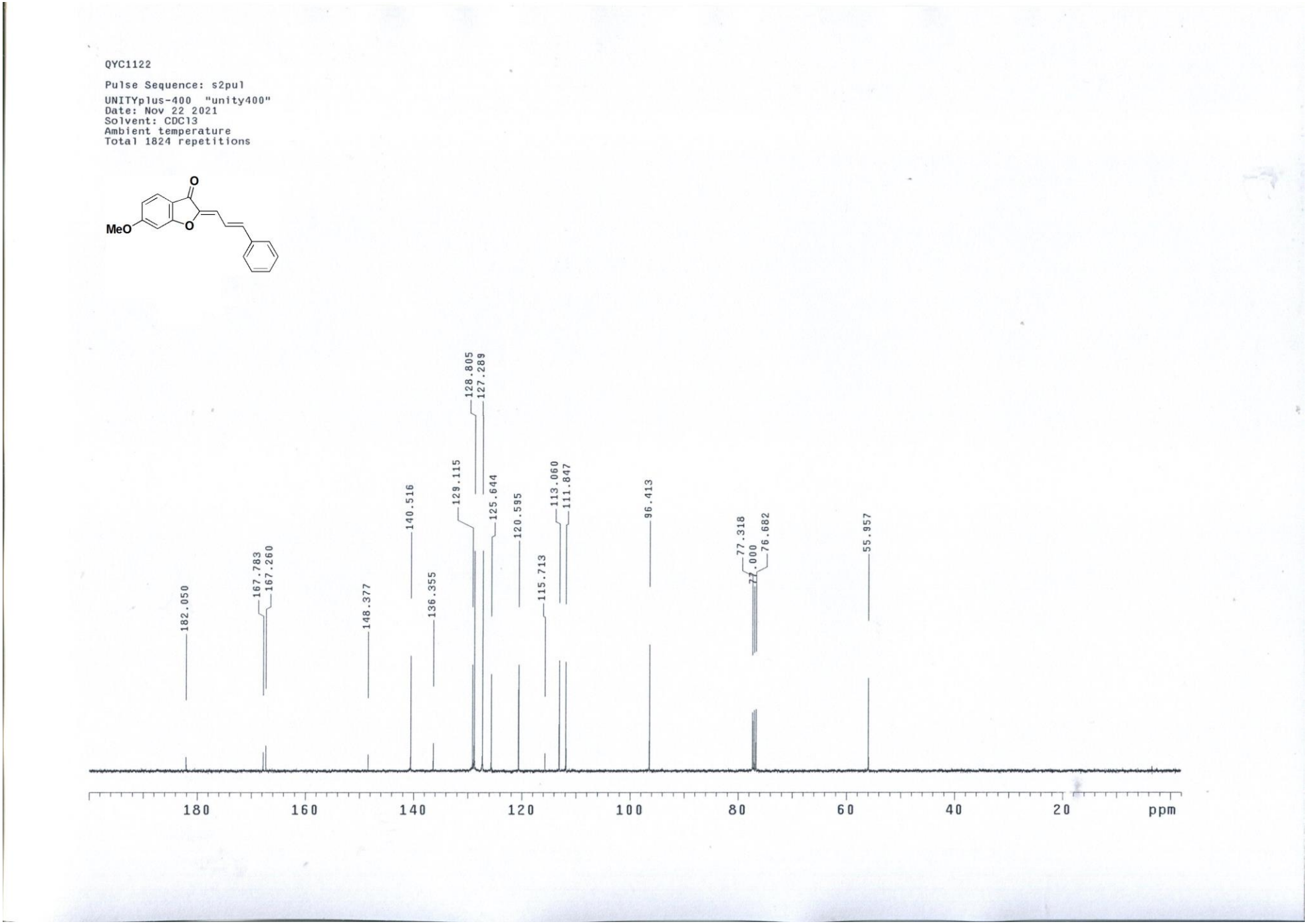
Compound 6f (^{13}C-NMR spectral data)



Compound 6g (^{1}H-NMR spectral data)



Compound 6g (^{13}C-NMR spectral data)

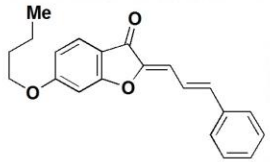


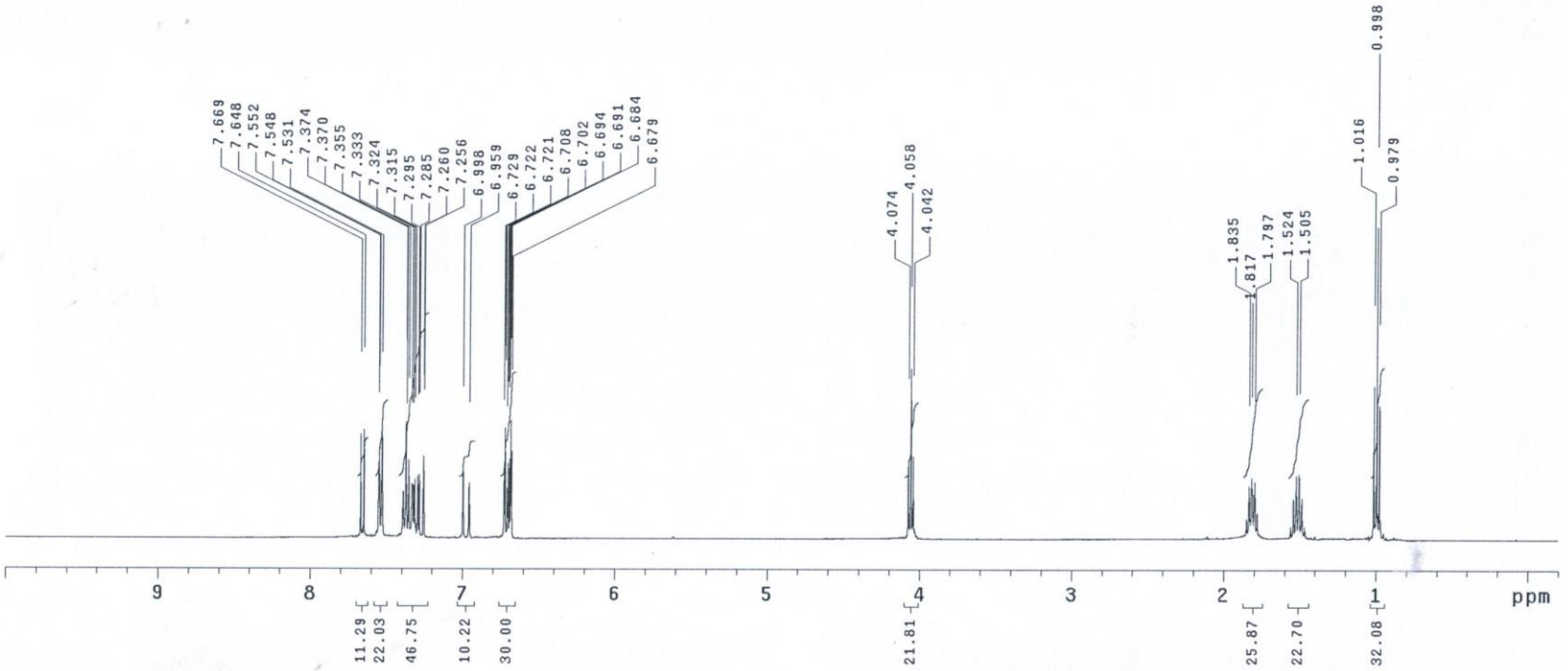
Compound 6h (^{1}H-NMR spectral data)

QYC1118

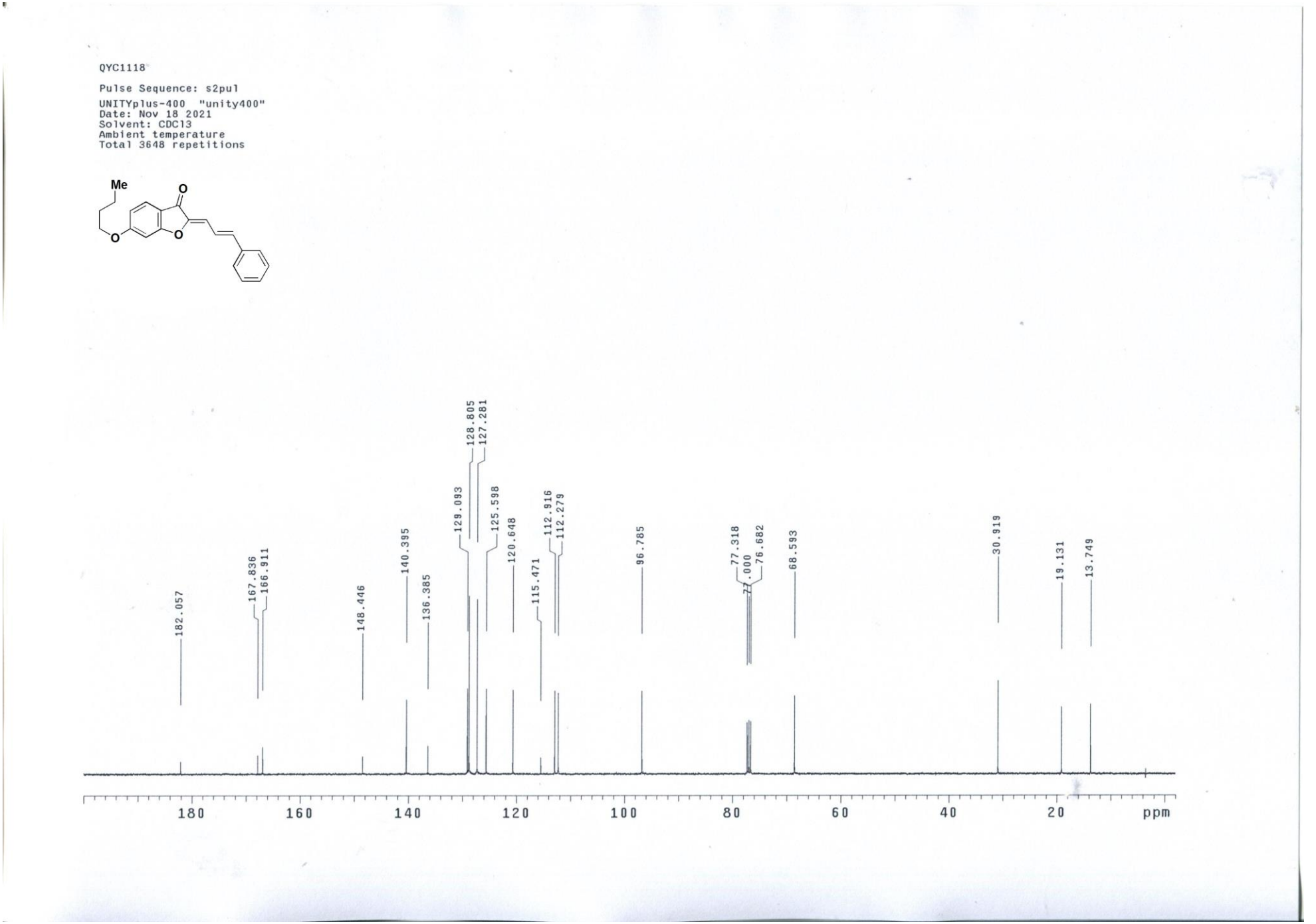
Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Nov 18 2021
Solvent: CDCl3
Ambient temperature
Total 32 repetitions

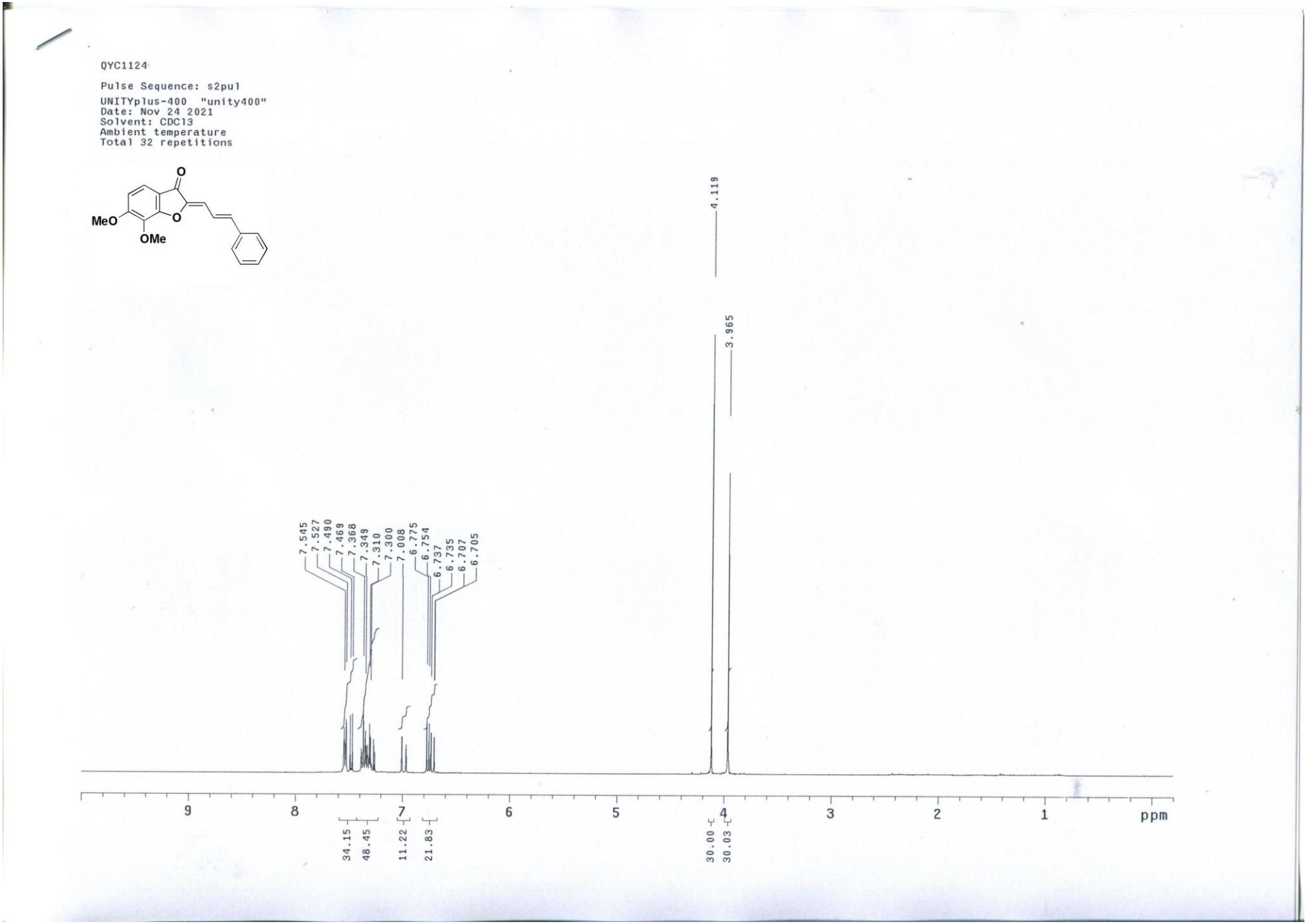




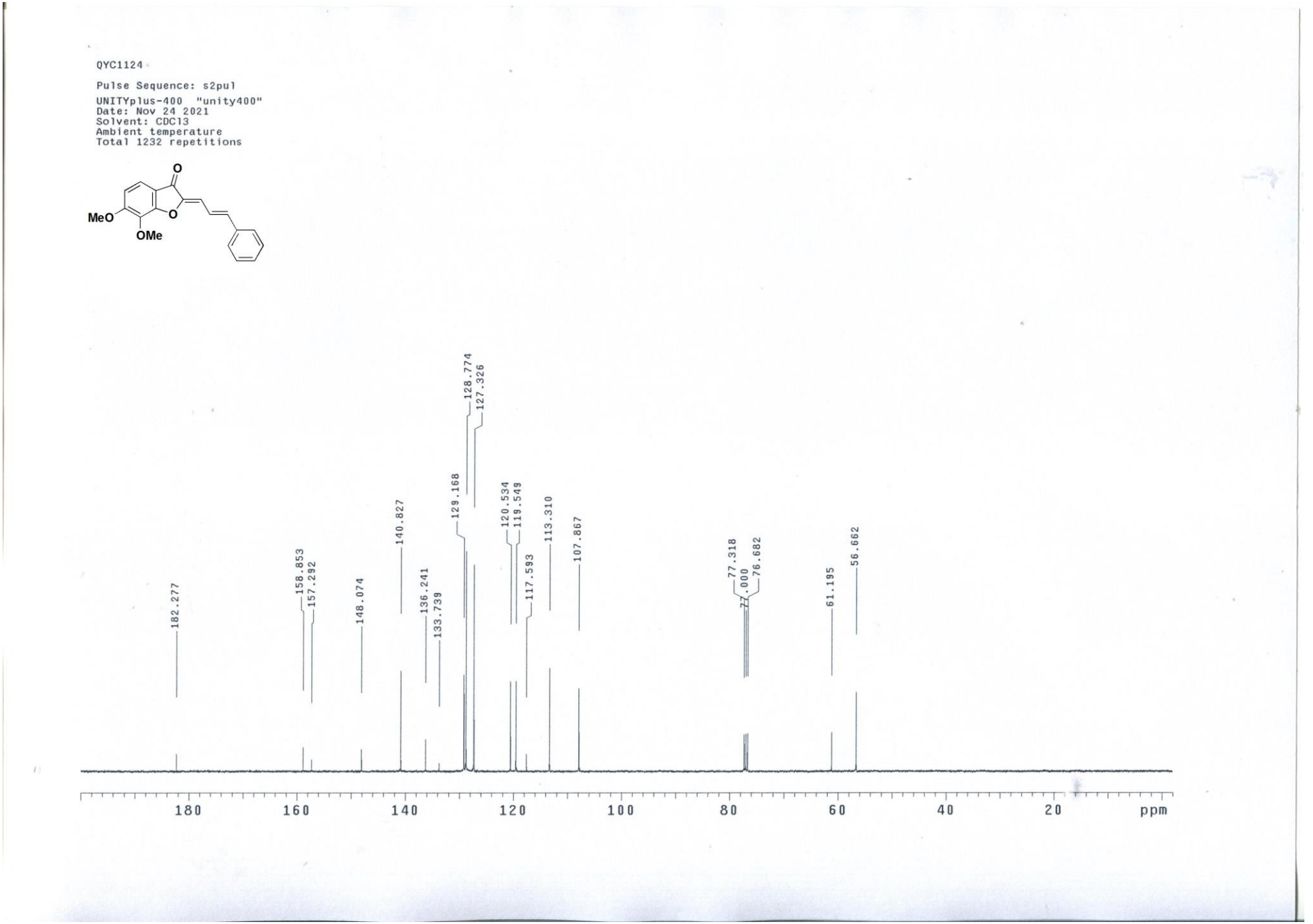
Compound 6h (^{13}C-NMR spectral data)



Compound 6i (^{1}H-NMR spectral data)



Compound 6i (^{13}C-NMR spectral data)

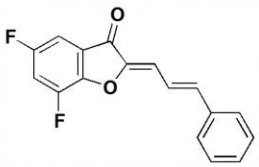


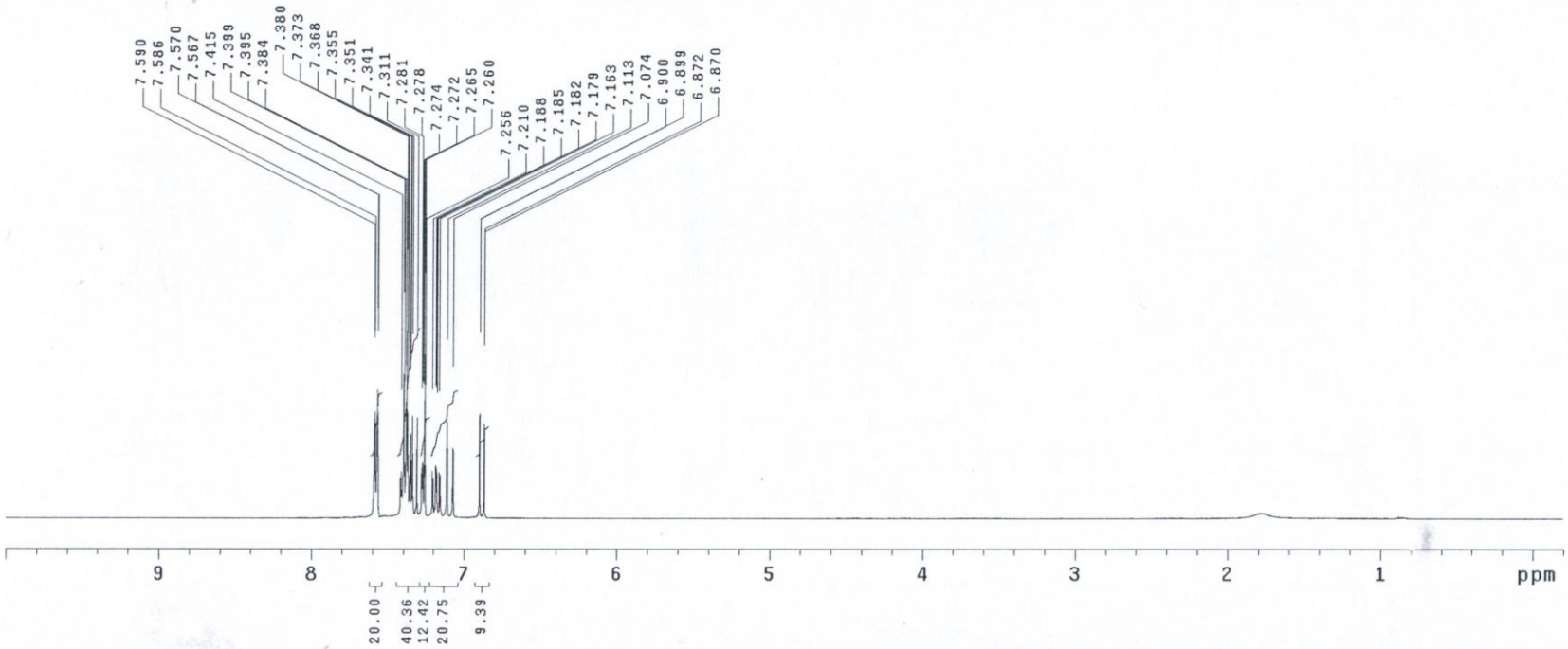
Compound 6j (^{1}H-NMR spectral data)

QYC1217

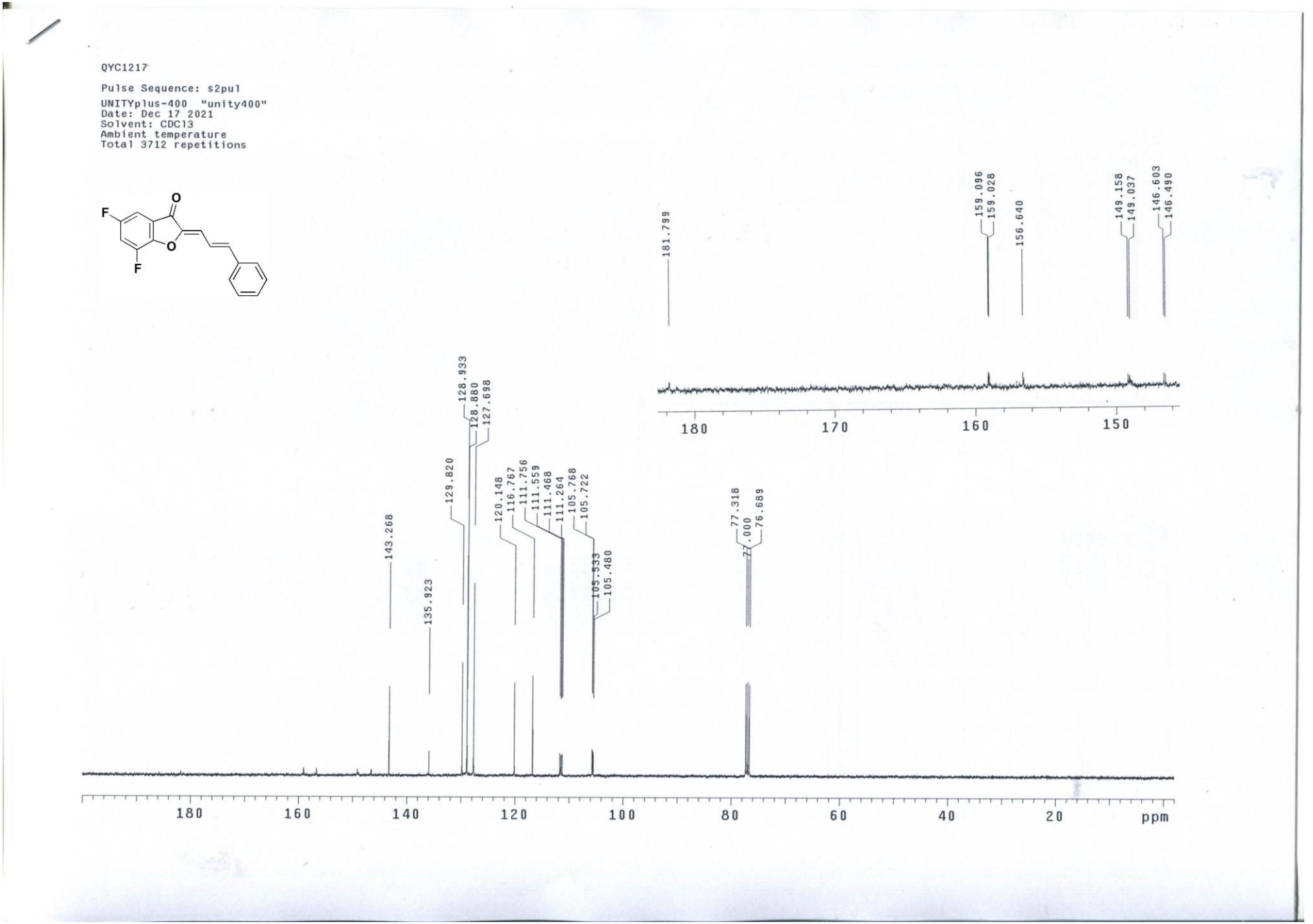
Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Dec 17 2021
Solvent: CDCl3
Ambient temperature
Total 32 repetitions

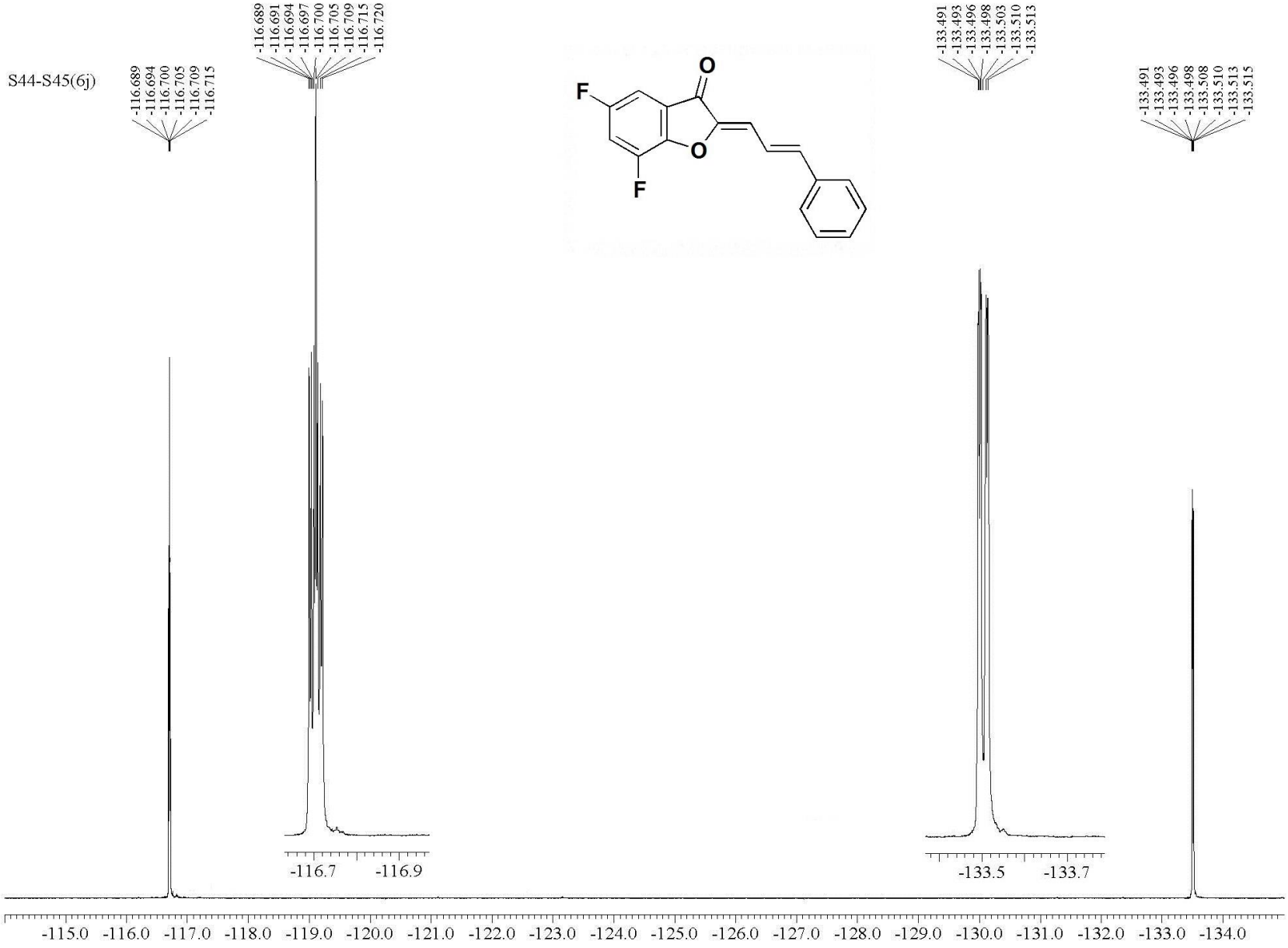




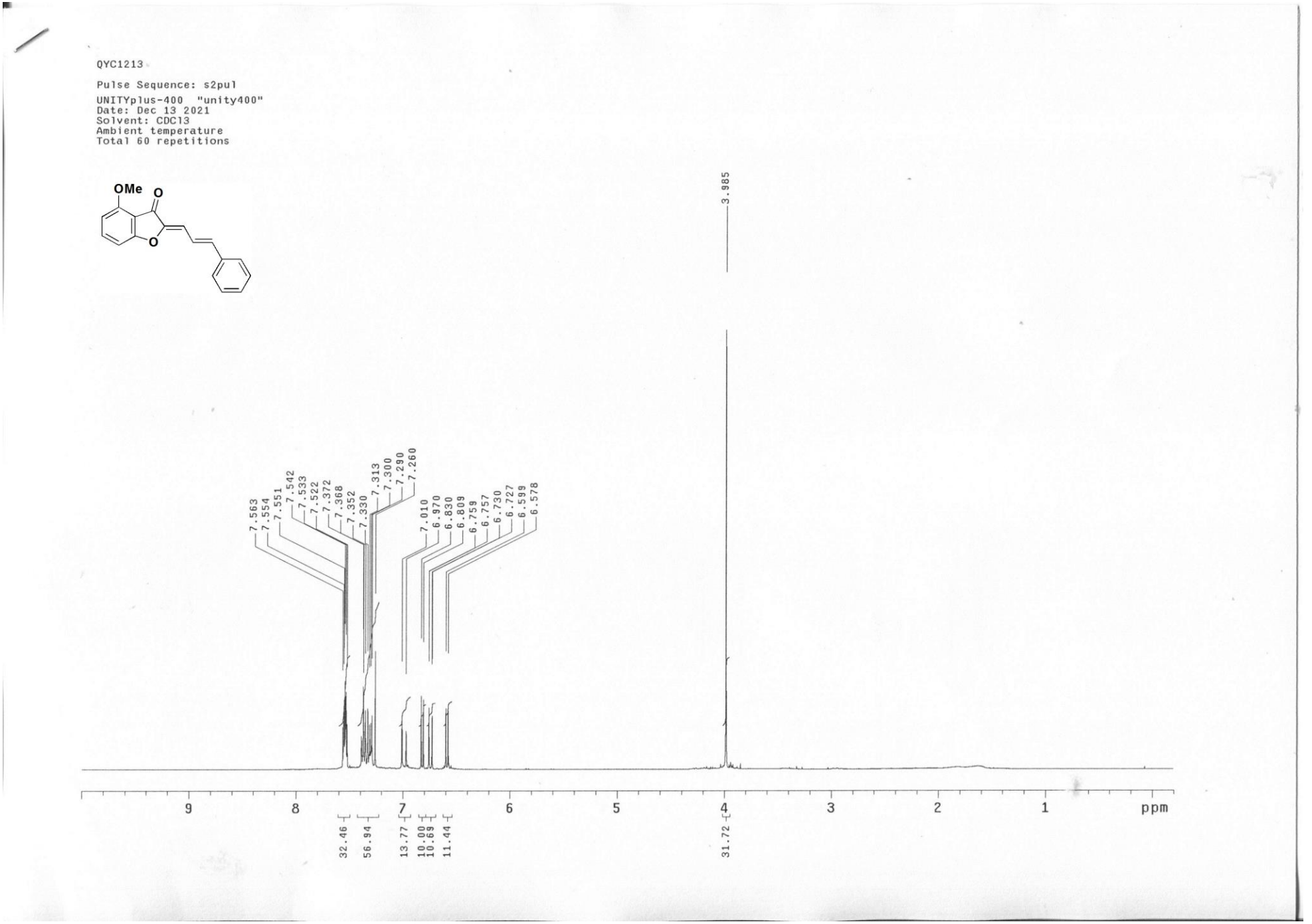
Compound 6j (^{13}C-NMR spectral data)



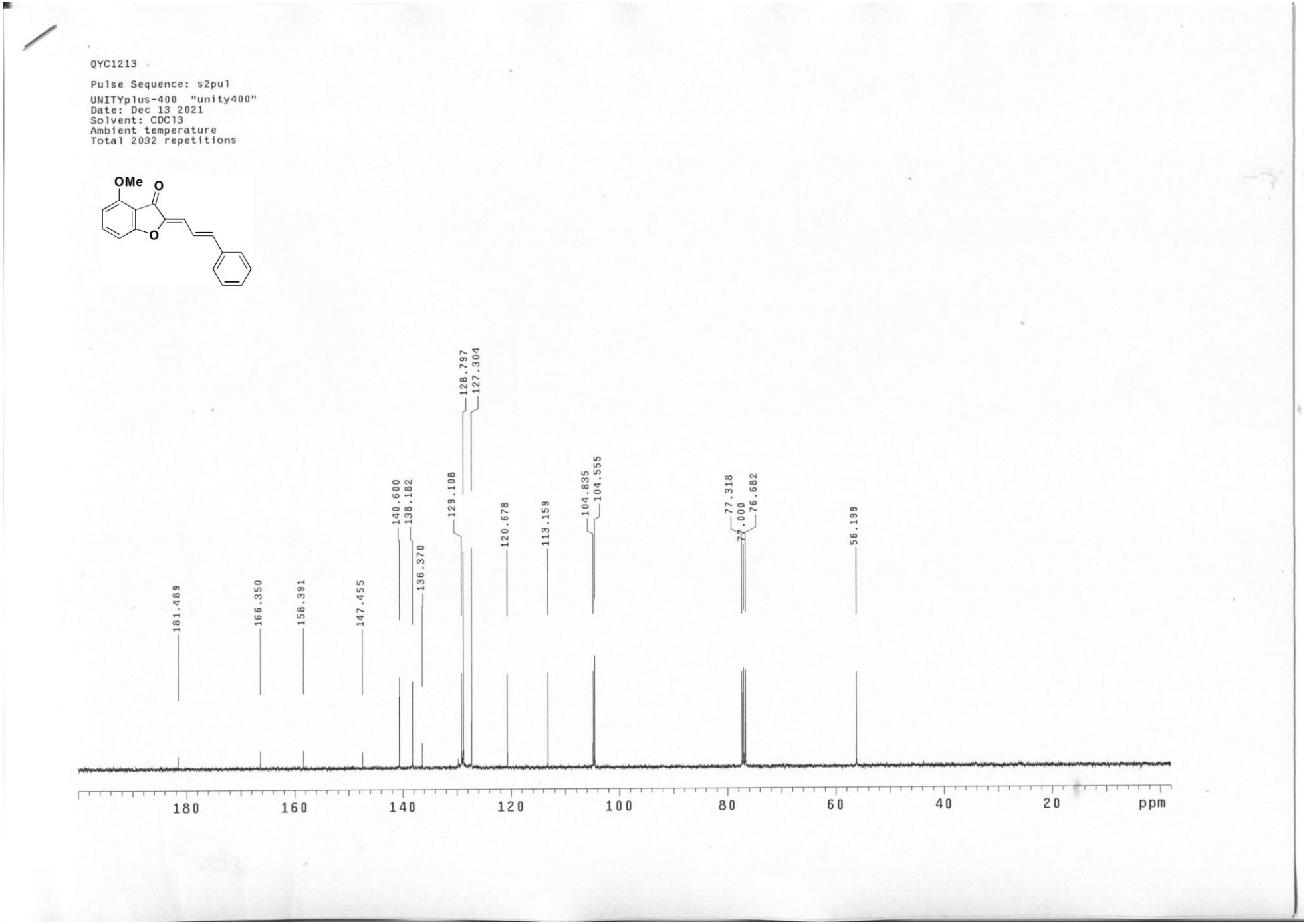
Compound 6j (^{19}F-NMR spectral data)



Compound 6k (^{1}H-NMR spectral data)



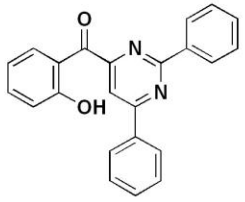
Compound 6k (^{13}C-NMR spectral data)

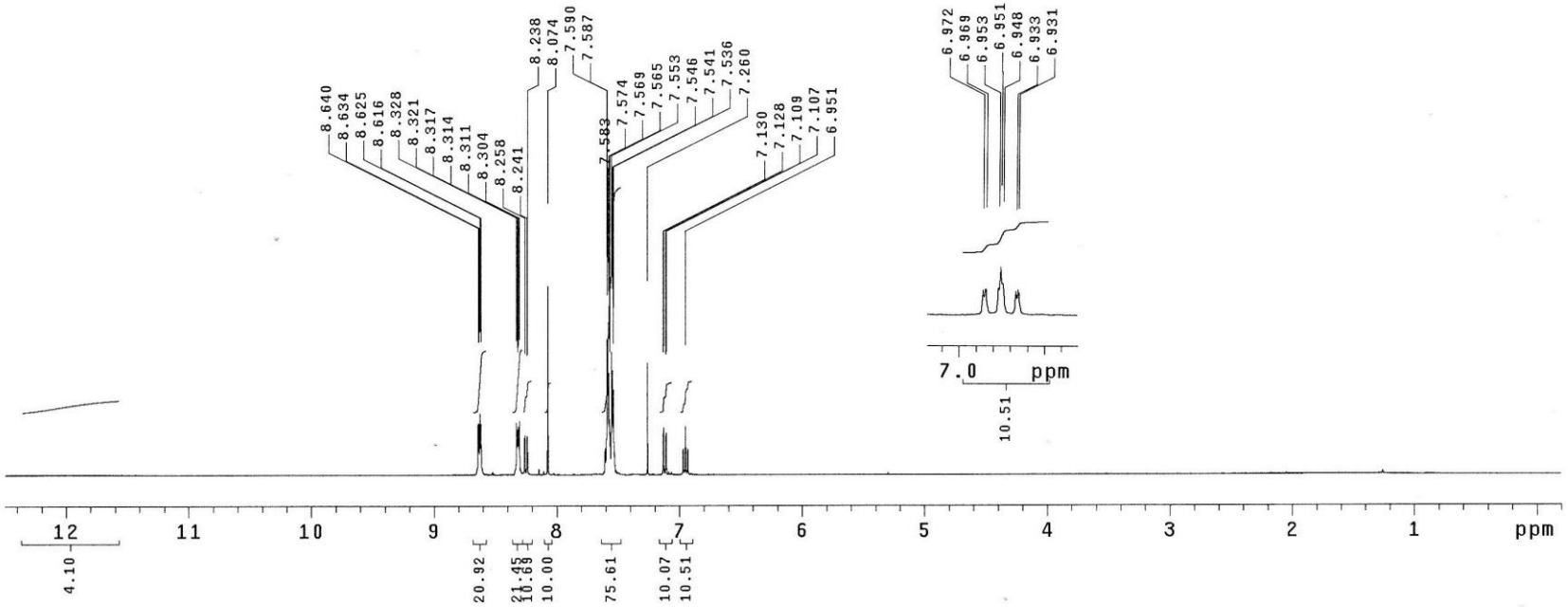


Compound 7 (^{1}H-NMR spectral data)

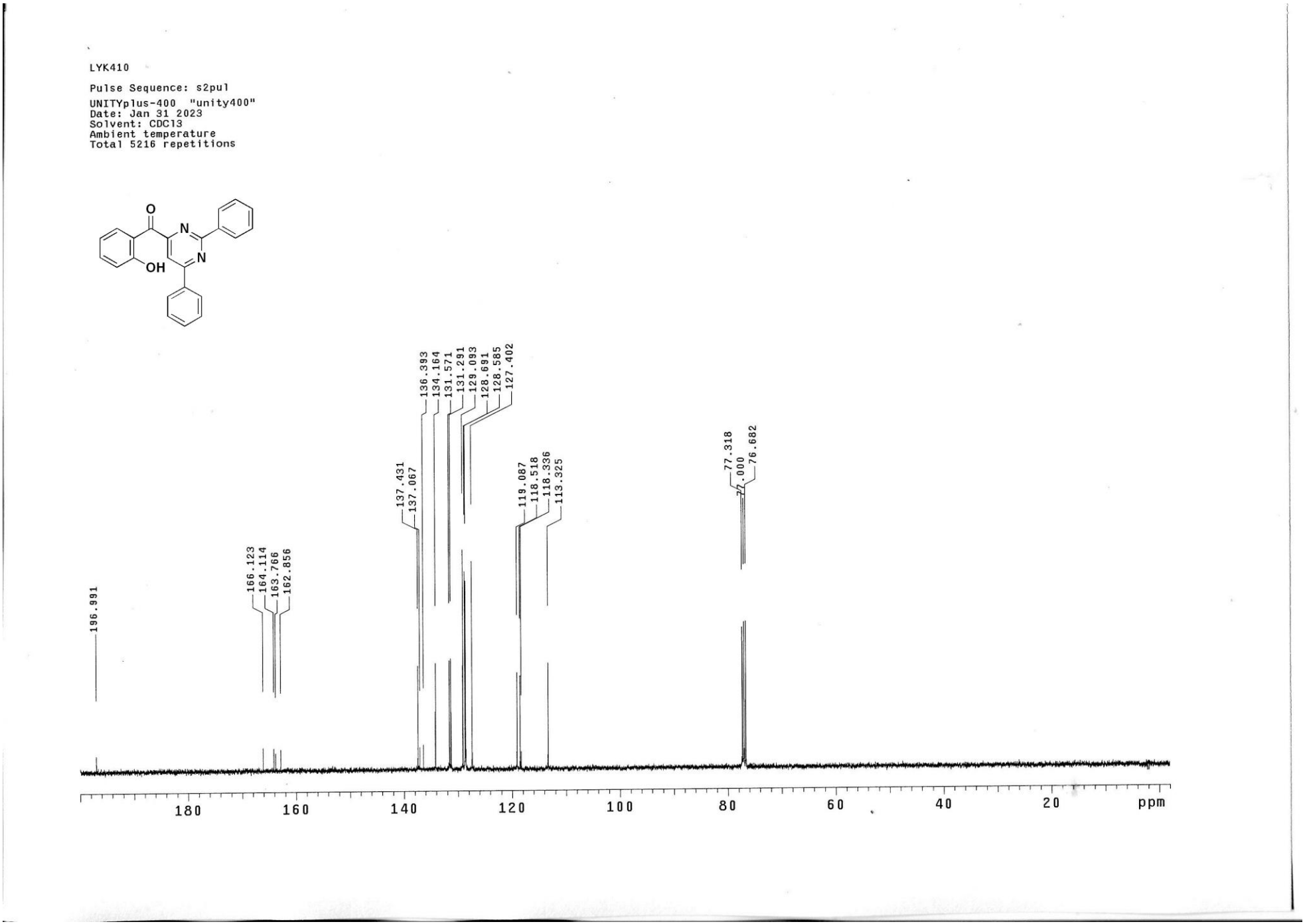
LYK410

Pulse Sequence: s2pul
UNITYplus-400 "unity400"
Date: Jan 31 2023
Solvent: CDCl3
Ambient temperature
Total 32 repetitions

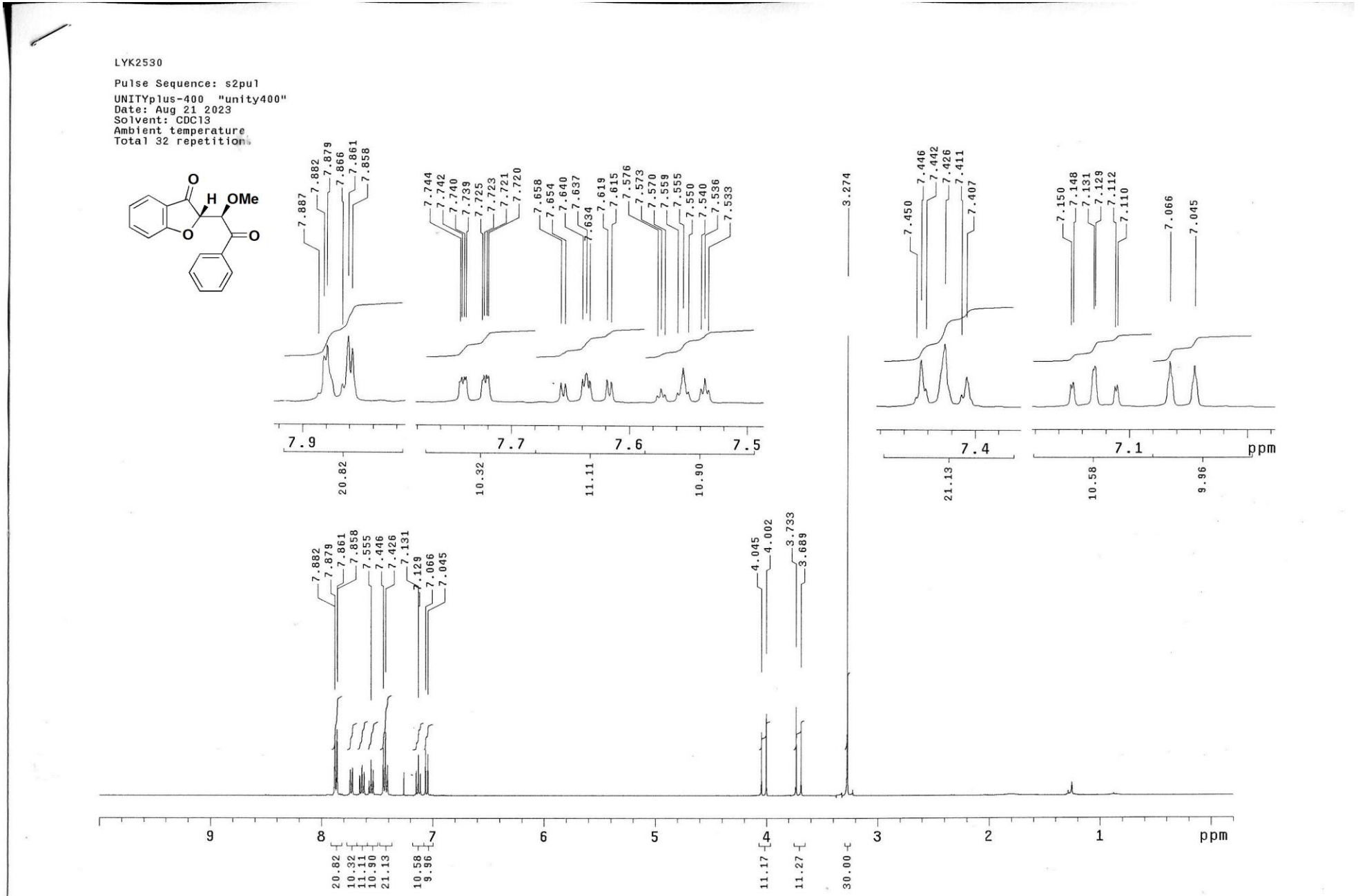




Compound 7 (^{13}C-NMR spectral data)



Compound 8 (^{1}H-NMR spectral data)

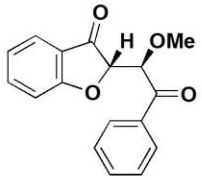


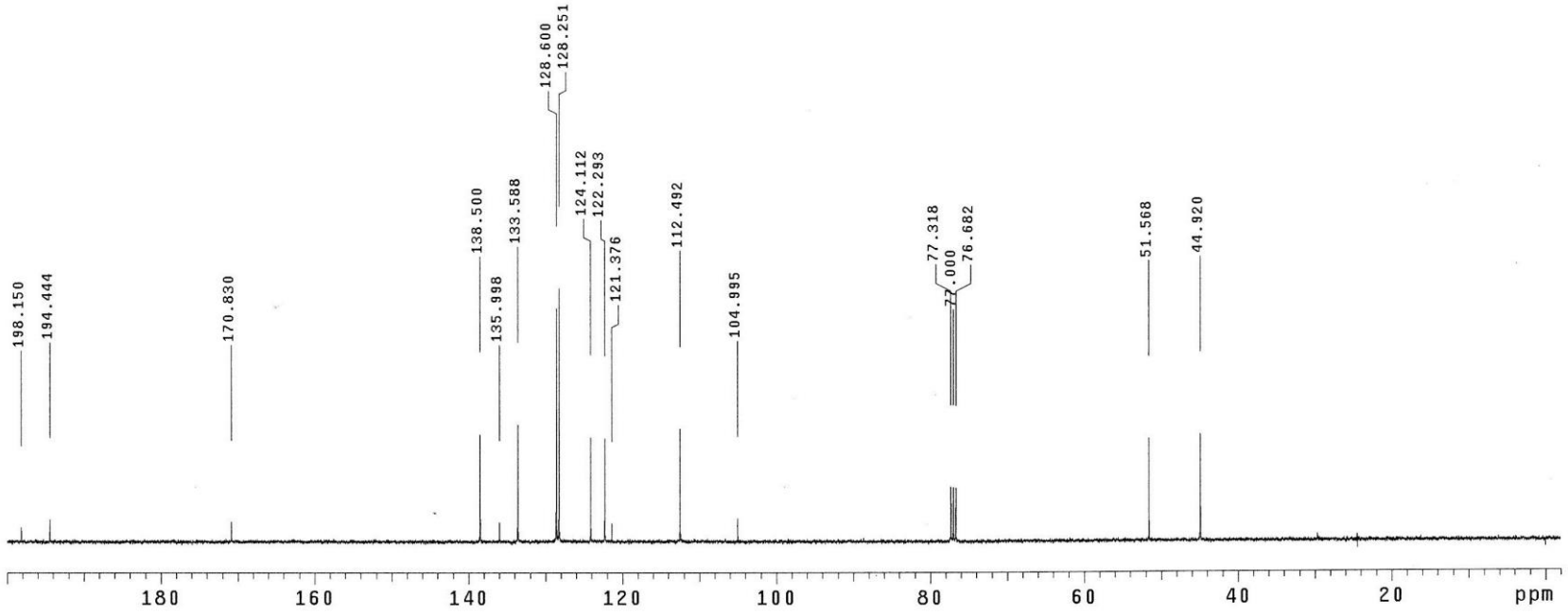
Compound 8 (^{13}C-NMR spectral data)

LYK2530

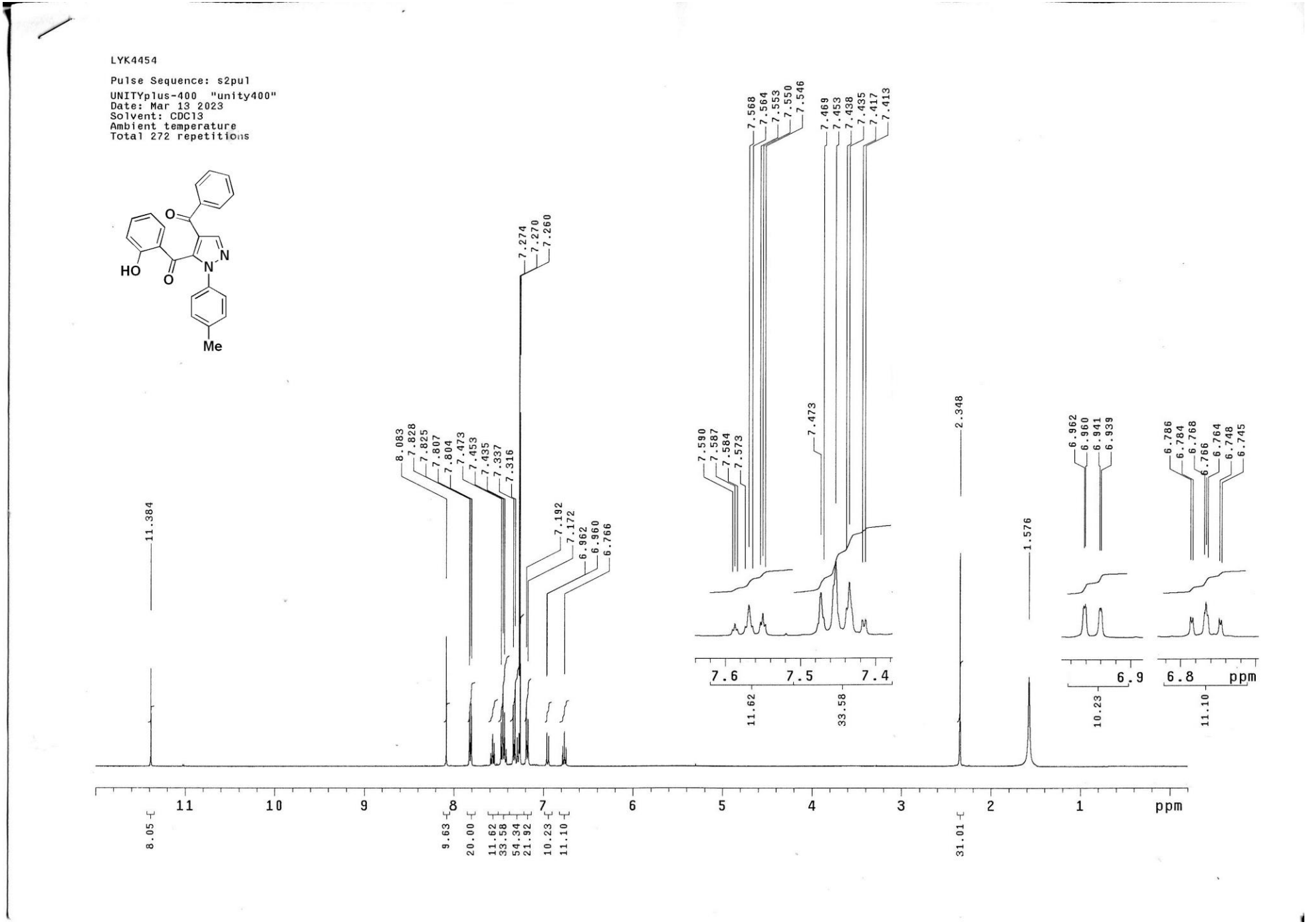
Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Aug 21 2023
Solvent: CDCl3
Ambient temperature
Total 1280 repetitions

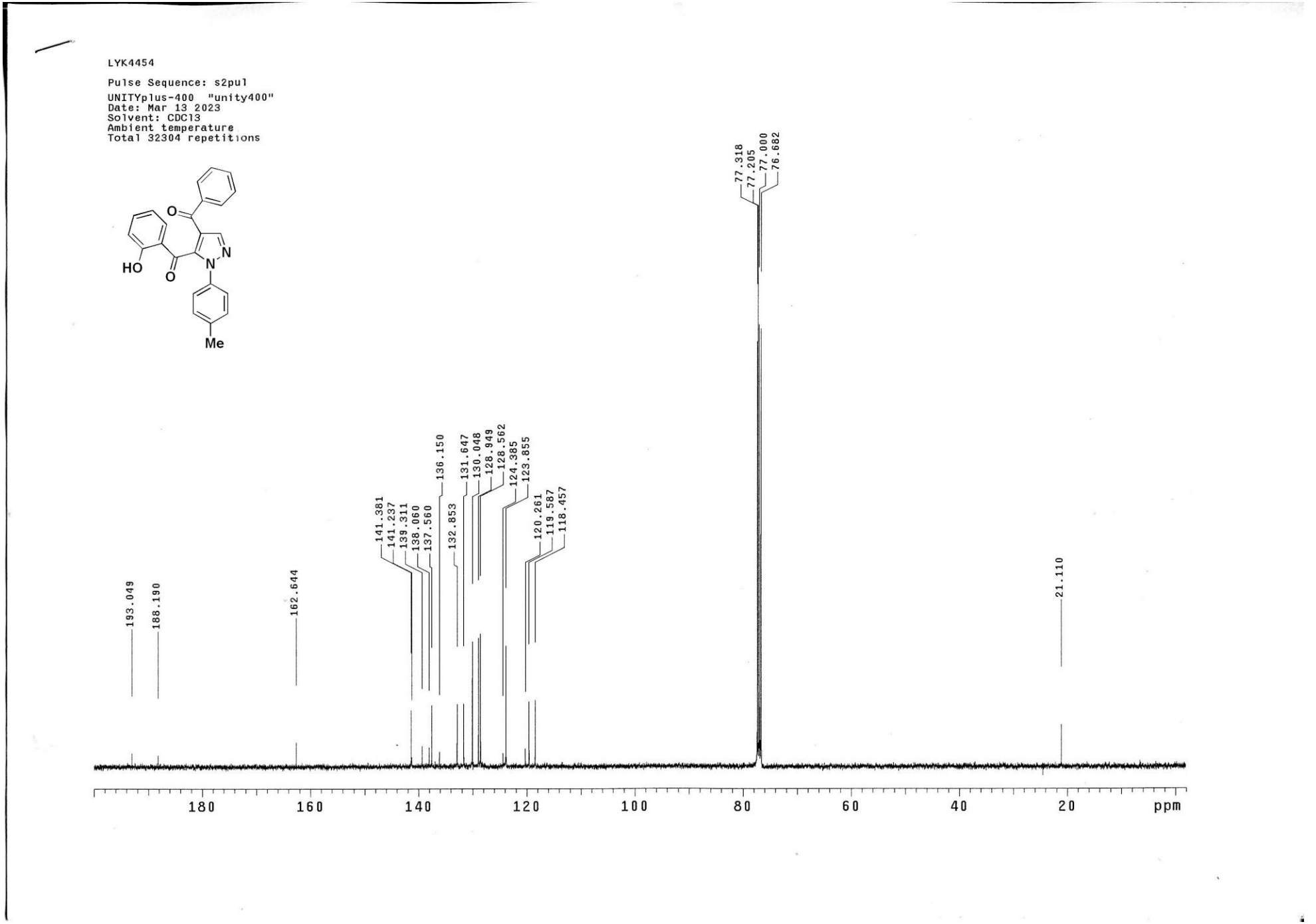




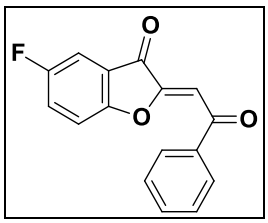
Compound 9 (^{1}H-NMR spectral data)



Compound 9 (^{13}C-NMR spectral data)

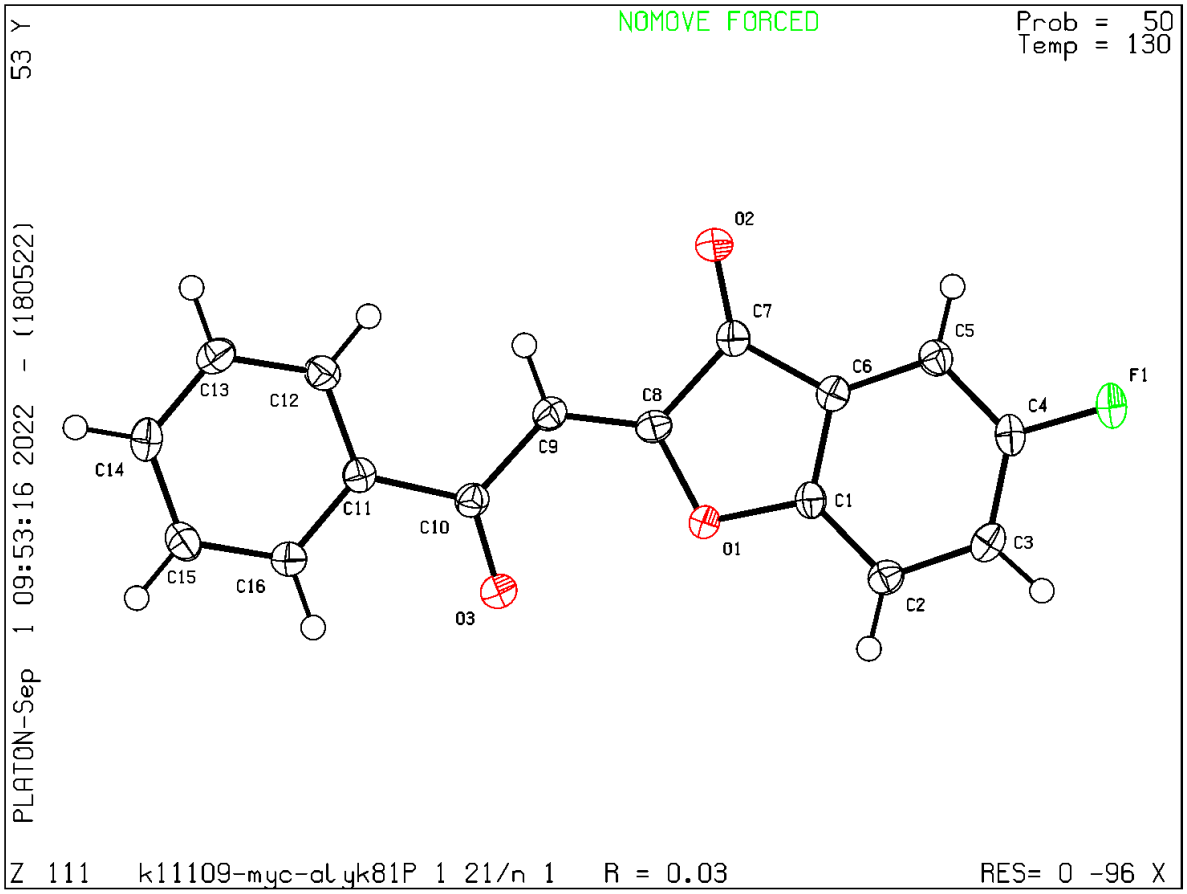


X-ray crystal data of compound 4b



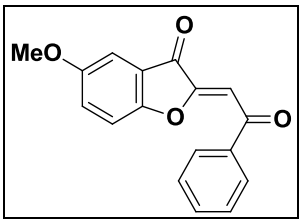
Sample preparation : A solution of compound **4b** (30 mg) in CH_2Cl_2 (10 mL) was placed in a tube (10 mL). EtOAc (2 mL) was added slowly to the vial with a dropper. The vial was closed with little cotton and kept at room temperature for 2 days. Then, colorless prisms were observed.

Crystal measurement : X-ray crystal structures were determined with a Bruker Enraf-Nonius single-crystal diffractometer (CAD4, Kappa CCD). Thermal ellipsoids are drawn at 50% probability level.



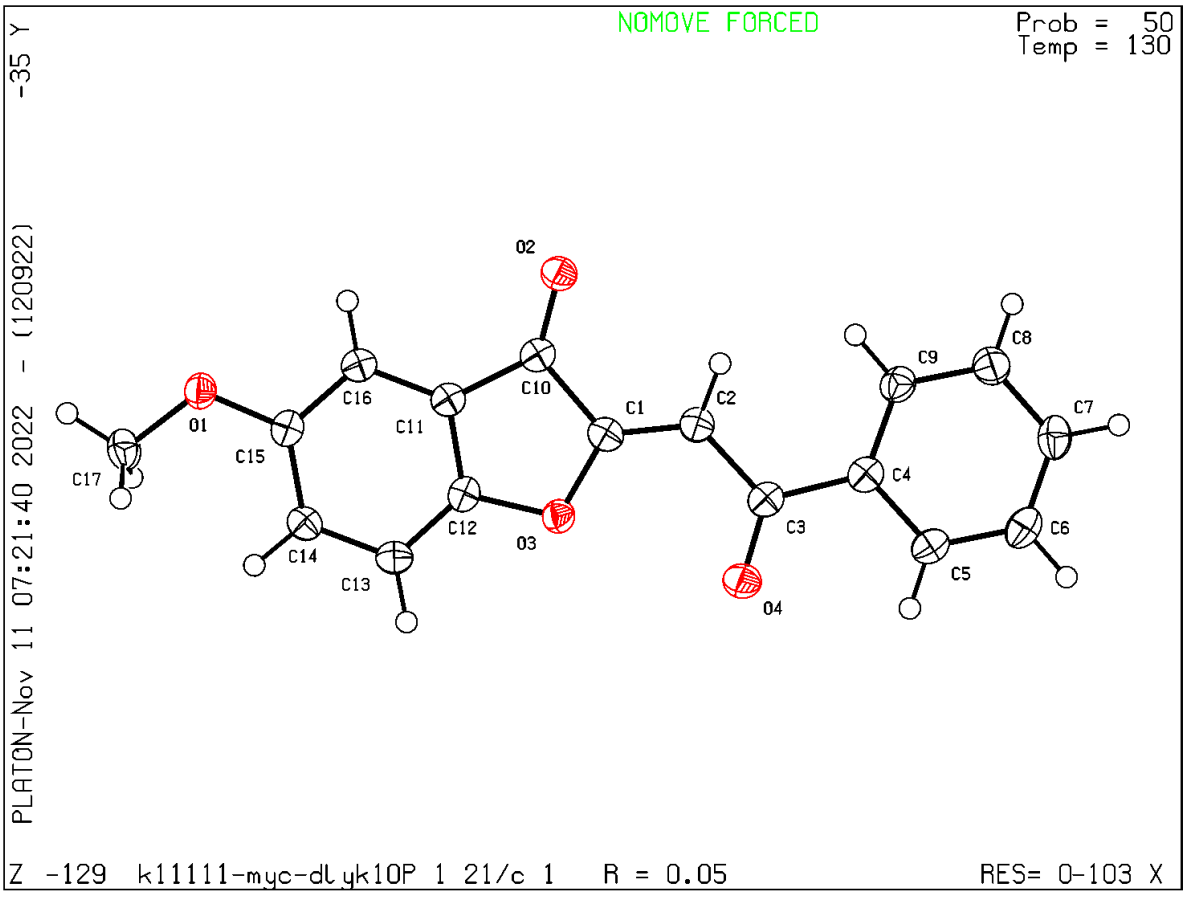
Empirical formula	$C_{16}H_9FO_3$
Formula weight	268.23
Temperature/K	130(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.1097(2)
b/Å	5.22990(10)
c/Å	27.2462(5)
α/°	90
β/°	91.430(2)
γ/°	90
Volume/Å ^{3}	1155.23(4)
Z	4
ρ_{calc}g/cm^3	1.542
μ/mm^{-1}	0.117
F(000)	552.0
Crystal size/mm^3	0.5 × 0.2 × 0.2
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.206 to 54.162
Index ranges	$-10 \leq h \leq 10$, $-6 \leq k \leq 5$, $-34 \leq l \leq 33$
Reflections collected	23940
Independent reflections	2444 [R_{int} = 0.0274, R_{sigma} = 0.0156]
Data/restraints/parameters	2444/0/182
Goodness-of-fit on F^2	1.064
Final R indexes [I>=2σ (I)]	R_1 = 0.0327, wR_2 = 0.0845
Final R indexes [all data]	R_1 = 0.0368, wR_2 = 0.0876
Largest diff. peak/hole / e Å $^{-3}$	0.29/-0.19

X-ray crystal data of compound 4f



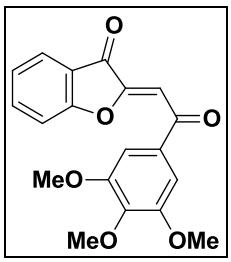
Sample preparation : A solution of compound **4f** (30 mg) in CH_2Cl_2 (10 mL) was placed in a tube (10 mL). EtOAc (2 mL) was added slowly to the vial with a dropper. The vial was closed with little cotton and kept at room temperature for 2 days. Then, colorless prisms were observed.

Crystal measurement : X-ray crystal structures were determined with a Bruker Enraf-Nonius single-crystal diffractometer (CAD4, Kappa CCD). Thermal ellipsoids are drawn at 50% probability level.



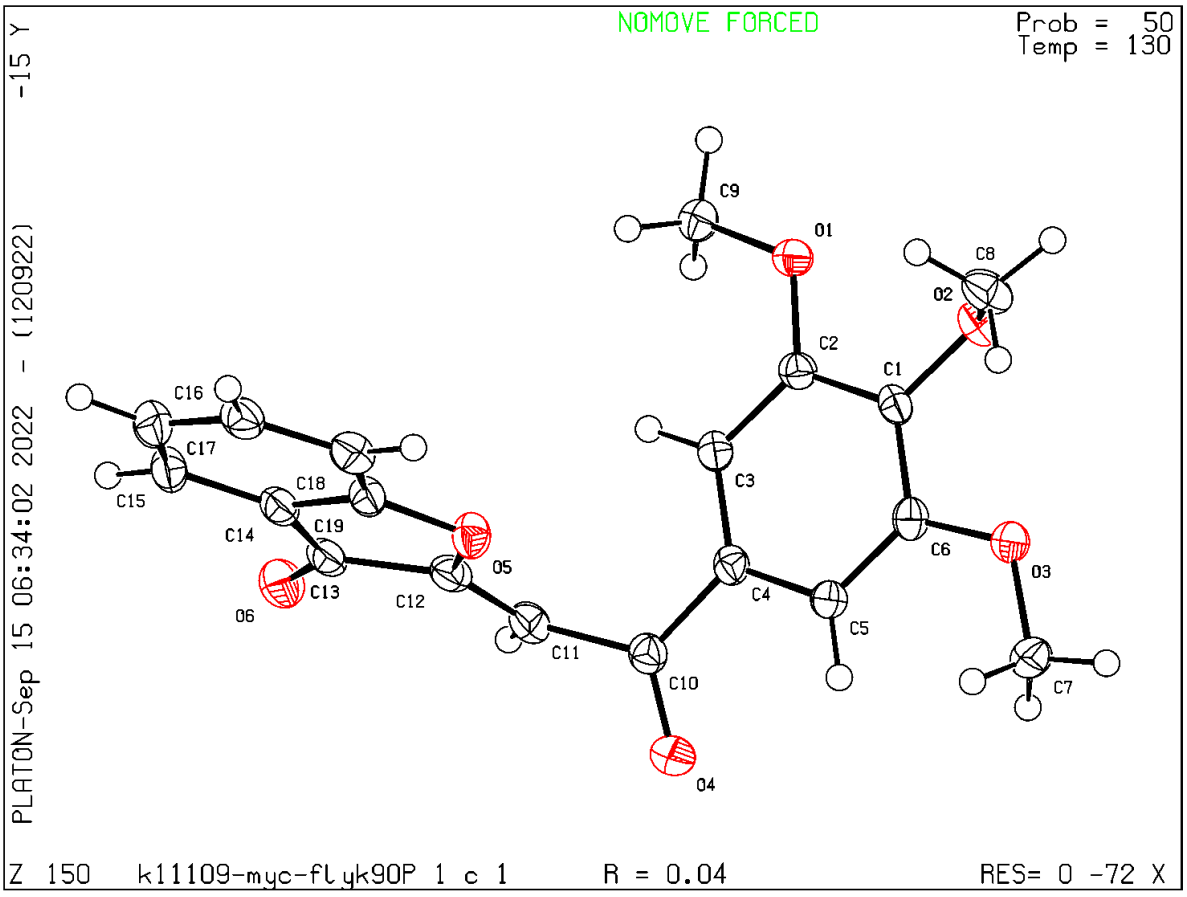
Empirical formula	$C_{17}H_{12}O_4$
Formula weight	280.27
Temperature/K	130(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	5.3211(2)
b/Å	8.1869(2)
c/Å	29.8283(8)
α/°	90
β/°	92.288(3)
γ/°	90
Volume/Å ^{3}	1298.38(7)
Z	4
ρ_{calc}g/cm^3	1.434
μ/mm^{-1}	0.103
F(000)	584.0
Crystal size/mm^3	0.2 × 0.2 × 0.2
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.16 to 49.998
Index ranges	$-6 \leq h \leq 6$, $-9 \leq k \leq 9$, $-35 \leq l \leq 35$
Reflections collected	19804
Independent reflections	2288 [R_{int} = 0.0383, R_{sigma} = 0.0233]
Data/restraints/parameters	2288/0/191
Goodness-of-fit on F^2	1.133
Final R indexes [I>=2σ (I)]	R_1 = 0.0465, wR_2 = 0.1220
Final R indexes [all data]	R_1 = 0.0527, wR_2 = 0.1252
Largest diff. peak/hole / e Å $^{-3}$	0.24/-0.20

X-ray crystal data of compound 4ac



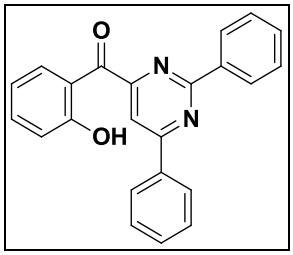
Sample preparation : A solution of compound **4ac** (30 mg) in CH_2Cl_2 (10 mL) was placed in a tube (10 mL). EtOAc (2 mL) was added slowly to the vial with a dropper. The vial was closed with little cotton and kept at room temperature for 2 days. Then, colorless prisms were observed.

Crystal measurement : X-ray crystal structures were determined with a Bruker Enraf-Nonius single-crystal diffractometer (CAD4, Kappa CCD). Thermal ellipsoids are drawn at 50% probability level.



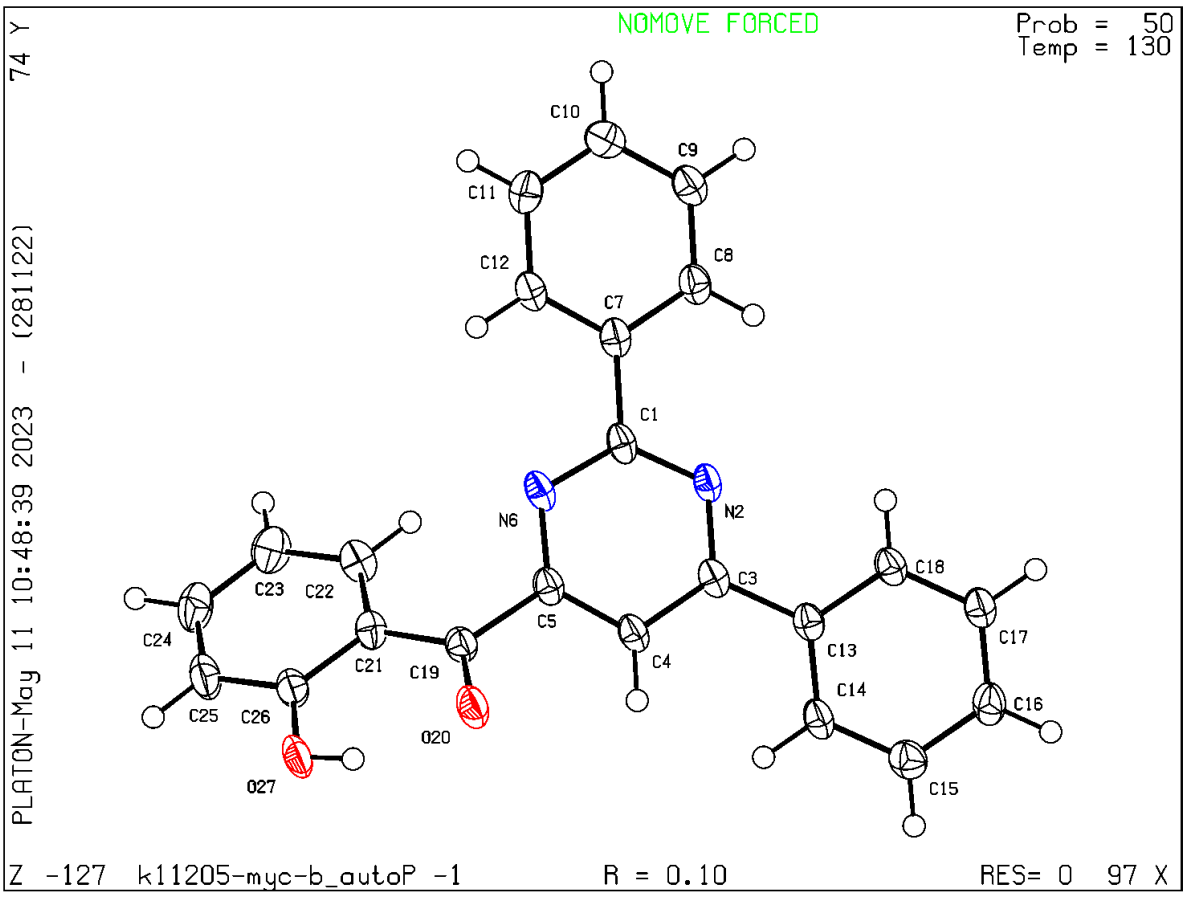
Formula weight	226.88
Temperature/K	130(2)
Crystal system	monoclinic
Space group	Pc
a/Å	12.7257(3)
b/Å	4.69060(10)
c/Å	13.7330(5)
α/°	90
β/°	106.401(3)
γ/°	90
Volume/Å ^{3}	786.38(4)
Z	3
ρ_{calc}g/cm^3	1.437
μ/mm^{-1}	0.108
F(000)	356.0
Crystal size/mm^3	0.6 × 0.5 × 0.5
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.336 to 54.122
Index ranges	-15 ≤ h ≤ 15, -5 ≤ k ≤ 5, -16 ≤ l ≤ 17
Reflections collected	8968
Independent reflections	3023 [R_{int} = 0.0471, R_{sigma} = 0.0451]
Data/restraints/parameters	3023/2/229
Goodness-of-fit on F^2	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0388, wR_2 = 0.0960
Final R indexes [all data]	R_1 = 0.0409, wR_2 = 0.0978
Largest diff. peak/hole / e Å $^{-3}$	0.20/-0.26
Flack parameter	-0.3(5)

X-ray crystal data of compound 7



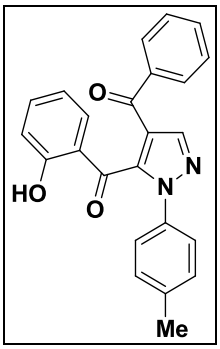
Sample preparation : A solution of compound **7** (30 mg) in CH_2Cl_2 (10 mL) was placed in a tube (10 mL). EtOAc (2 mL) was added slowly to the vial with a dropper. The vial was closed with little cotton and kept at room temperature for 2 days. Then, colorless prisms were observed.

Crystal measurement : X-ray crystal structures were determined with a Bruker Enraf-Nonius single-crystal diffractometer (CAD4, Kappa CCD). Thermal ellipsoids are drawn at 50% probability level.



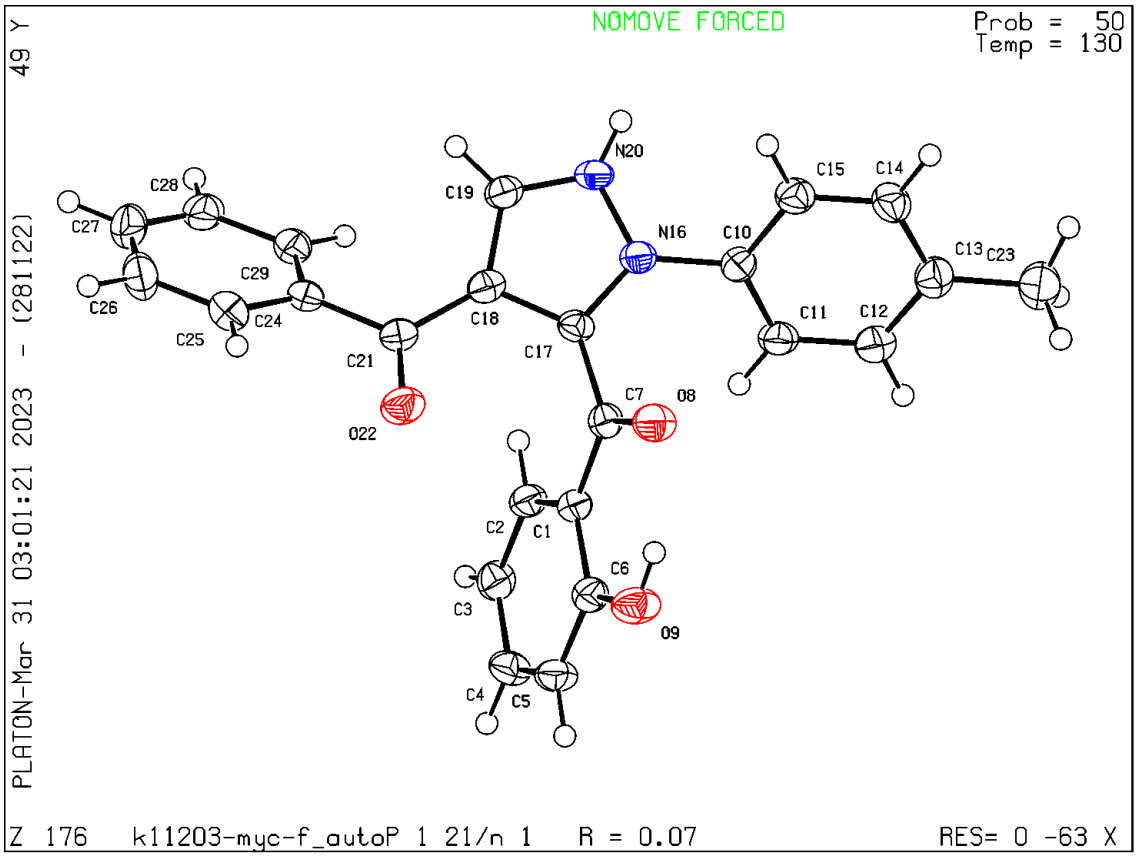
Empirical formula	$C_{23}H_{16}N_2O_2$
Formula weight	352.38
Temperature/K	130(2)
Crystal system	triclinic
Space group	P-1
a/Å	3.8702(6)
b/Å	13.0697(10)
c/Å	16.8646(8)
α/°	96.863(5)
β/°	90.517(9)
γ/°	93.533(9)
Volume/Å ^{3}	845.21(15)
Z	2
ρ_{calc}g/cm^3	1.385
μ/mm^{-1}	0.090
F(000)	368.0
Crystal size/mm^3	0.5 × 0.4 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.144 to 49.998
Index ranges	-4 ≤ h ≤ 4, -15 ≤ k ≤ 15, -20 ≤ l ≤ 20
Reflections collected	20747
Independent reflections	2962 [R_{int} = 0.1676, R_{sigma} = 0.0714]
Data/restraints/parameters	2962/138/245
Goodness-of-fit on F^2	1.063
Final R indexes [I>=2σ (I)]	R_1 = 0.0975, wR_2 = 0.2493
Final R indexes [all data]	R_1 = 0.1245, wR_2 = 0.2751
Largest diff. peak/hole / e Å $^{-3}$	0.66/-0.50

X-ray crystal data of compound 9



Sample preparation : A solution of compound **9** (30 mg) in CH_2Cl_2 (10 mL) was placed in a tube (10 mL). EtOAc (2 mL) was added slowly to the vial with a dropper. The vial was closed with little cotton and kept at room temperature for 2 days. Then, colorless prisms were observed.

Crystal measurement : X-ray crystal structures were determined with a Bruker Enraf-Nonius single-crystal diffractometer (CAD4, Kappa CCD). Thermal ellipsoids are drawn at 50% probability level.



Empirical formula	$C_{24}H_{19}N_2O_3$
Formula weight	383.41
Temperature/K	130(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.7895(6)
b/Å	11.0470(6)
c/Å	16.5159(10)
α/°	90
β/°	103.671(6)
γ/°	90
Volume/Å ^{3}	1912.78(19)
Z	4
ρ_{calc}g/cm^3	1.331
μ/mm^{-1}	0.089
F(000)	804.0
Crystal size/mm^3	0.4 × 0.4 × 0.3
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.108 to 54.116
Index ranges	$-13 \leq h \leq 13$, $-13 \leq k \leq 14$, $-16 \leq l \leq 20$
Reflections collected	21618
Independent reflections	4016 [R_{int} = 0.0964, R_{sigma} = 0.0639]
Data/restraints/parameters	4016/0/264
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0673, wR_2 = 0.1631
Final R indexes [all data]	R_1 = 0.0956, wR_2 = 0.1772
Largest diff. peak/hole / e Å $^{-3}$	0.32/-0.59