Support Information

Reaction of Trisubstituted Alkenes with Iron Porphyrin Carbenes: Facile Synthesis of Tetrasubstituted Dienes and Cyclopentadienes

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General Information All reactions were carried out under N_2 unless otherwise noted. All carbonyl compounds and solvents were purified according to standard methods unless otherwise noted.

^{1}H NMR spectra were recorded on a VARIAN Mercury 300 MHz or VARIAN Mercury 400 MHz spectrometer in chloroform-d. All signals are reported in ppm with the internal TMS signal at 0.0 ppm or chloroform signal at 7.26 ppm as a standard. The data are reported as (s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet or unresolved, coupling constant(s) in Hz, integration). ^{13}C NMR spectra were recorded on a VARIAN Mercury 75.5 MHz spectrometer in chloroform-d. All signals are reported in ppm with the internal chloroform signal at 77.0 ppm as a standard. IR spectra were recorded on a Perkin–Elmer 983, Digital FT–IR spectrometer or Bruker–Tensor 27; frequencies are given in reciprocal centimeters (cm^{-1}) and only selected absorbance is reported; Mass spectra were determined on an Agilent 5973N MSD (EI) and Shimadzu LCMS-2010EV (ESI) mass spectrometer or Agilent G6100 LC/MSD (ESI) single Quand mass spectrometer. High resolution mass spectra were recorded on Waters Micromass GCT Premier (EI) and Bruker Daltonics, Inc. APEXIII 7.0 TESLA FTMS (ESI) mass spectrometers.

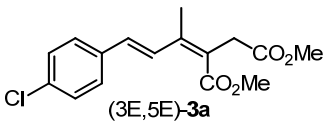
Fe(TCP)Cl was synthesized according to literature procedure.[1]

2. General Procedures for the Substituent Effect

To a stirred suspension of phosphonium salt **1** (0.5 mmol) in dry $PhCH_3$ (2.0 mL) under N_2 at room temperature was added LiHMDS (0.6 mL, 1.0 M in THF, 0.6 mmol) in one portion. 10 minutes later, Fe(TCP)Cl (1.7 mg, 0.002 mmol) and MDA (50 μL, 0.6 mmol) were added to the system respectively (Caution! N_2 Release!), then washed the Schlenk tube with dry $PhCH_3$ (1.0 mL), and the mixture stirred at room temperature for another 10 minutes. PCBA (56.0 mg, 0.4 mmol) and $PhCH_3$ (1.0 mL) were added and the resulting mixture was stirred at room temperature. After the reaction was complete, the resulting mixture was filtered rapidly through a funnel with a thin layer of silica gel and eluted with DCM. The filtrate was concentrated and analyzed by ^1H NMR, and then the residue was purified by chromatography on silica gel to afford the desired products.

For **1a** and **1b**, No desired products were formed.

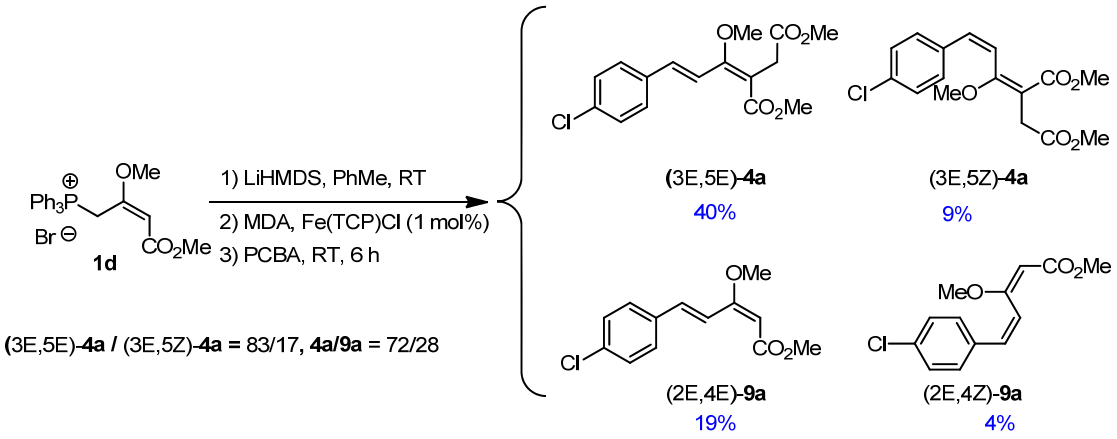
For **1c**, desired product **3a** was isolated in 13% yield, 3E,5E/3E,5Z = 69/31.

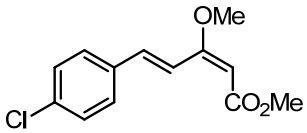


(3E,5E)-**3a**

(3E, 5E)-**3a**, white solid, ^1H NMR ($CDCl_3$, 400 MHz) δ 8.03 (d, J = 16.0 Hz, 1H), 7.41 (d, J = 8.8 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 6.82 (d, J = 16.0 Hz, 1H), 3.80 (s, 3H), 3.70 (s, 3H), 3.55 (s, 2H), 2.09 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 171.2, 167.9, 145.5, 135.6, 133.9, 132.3, 128.8, 128.6, 128.3, 123.1, 52.1, 51.9, 36.1, 16.2; IR (neat) ν 2951 (m), 2847 (m), 1736 (s), 1706 (s), 1489 (m), 1433 (m), 1191 (s), 1166 (m), 965 (m), 812 (s); MS (EI, m/z, rel. intensity) 308 (52, M^+), 293 (2.5), 277 (12), 248 (13), 235 (15), 217 (24), 203 (57), 189 (60), 171 (9.7), 153 (31), 127 (32), 113 (33), 99 (31), 84 (57), 71 (68), 57 (100), 43 (60), 41 (24); HRMS (EI) calcd for $C_{16}H_{17}ClO_4$ (M^+): 308.0815; Found: 308.0811.

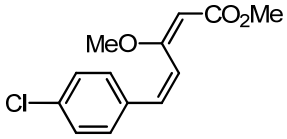
For **1d,** desired product **4a** was isolated in 49% yield, 3E,5E/3E,5Z = 83/17, the direct Wittig reaction of phosphonium salt **1d** was also observed.





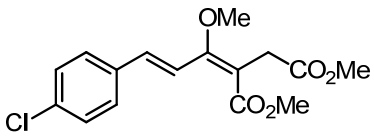
(2E, 4E)-**9a**

19% yield，white solid, ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.07 (d, *J* = 16.0 Hz, 1H), 7.46 (dt, *J* =2.2, 8.8 Hz, 2H), 7.30 (dt, *J* = 2.2, 8.4 Hz, 2H), 7.22 (d, *J* = 16.0 Hz, 1H), 5.16 (s, 1H), 3.74 (s, 3H), 3.72 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.7, 166.5, 134.6, 134.5, 133.8, 128.8, 128.7, 120.6, 92.1, 55.4, 50.9; IR (neat) ν 2951 (m), 2847 (m), 1703 (s), 1639 (m), 1583 (s), 1566 (m), 1490 (m), 1433 (m), 1145 (s), 970 (s); MS (EI, m/z, rel. intensity) 252 (28, M^+), 221 (17), 192 (100), 178 (20), 158 (61), 149 (14), 127 (22), 115 (36), 101 (17), 89 (5.5), 75 (12), 59 (13); HRMS (EI) calcd for $C_{13}H_{13}ClO_3$ (M^+): 252.0553; Found: 252.0556.



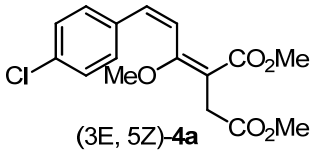
(2E, 4Z)-**9a**

4% yield, White solid, ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.25 (d, *J* = 8.8 Hz, 2H), 7.18 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 12.8 Hz, 1H), 6.68 (d, *J* = 12.8 Hz, 1H), 5.19 (s, 1H), 3.71 (s, 3H), 3.54 (s, 3H).



(3E, 5E)-**4a**

40% yield, colorless liquid, ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.78 (d, *J* = 16.0 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 7.2 Hz, 2H), 6.98 (d, *J* = 16.4 Hz, 1H), 3.76 (s, 3H), 3.73 (s, 3H), 3.70 (s, 3H), 3.54 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 171.8, 167.5, 164.9, 134.5, 134.4, 128.8, 128.5, 121.1, 113.4, 60.5, 51.9, 51.7, 32.6; IR (neat) ν 2954 (m), 1735 (s), 1610 (m), 1589 (m), 1565 (m), 1491 (m), 1436 (m); MS (EI, m/z, rel. intensity) 324 (1.2, M^+), 310 (2.3), 293 (1.8), 279 (2.7), 265 (4.1), 251 (12), 233 (9.6), 219 (36), 205 (14), 165 (100), 137 (20), 102 (24), 75 (8.7), 59 (11); HRMS (EI) calcd for $C_{16}H_{17}ClO_5$ (M^+): 324.0765; Found: 324.0763.

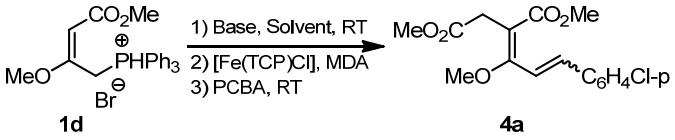


(3E, 5Z)-**4a**

9% yield, colorless liquid, ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40-7.38 (m, 2H), 7.29-7.27 (m, 2H), 6.68 (d, *J* = 12.4 Hz, 1H), 6.45 (d, *J* = 12.8 Hz, 1H), 3.72 (s, 3H), 3.68 (s, 3H), 3.48 (s, 2H), 3.46 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.1, 167.5, 164.1, 134.2, 133.0, 130.1, 128.6, 121.7, 106.2, 56.5, 51.8, 51.4, 31.5； IR (neat) ν 2953 (m), 1738 (s), 1587 (m), 1491 (m), 1437 (m); MS (EI, m/z, rel. intensity) 324 (0.7, M^+), 293 (5.1), 265 (10), 251 (31), 233 (26), 219 (100), 205 (38), 165 (9.8), 139 (12), 102 (10), 75 (8.1), 59 (17); HRMS (EI) calcd for $C_{16}H_{17}ClO_5$ (M^+): 324.0765; Found: 324.0773.

3. Reaction Conditions for Synthesis of Tetrasubstituted Dienes

Table *S1*. Base and solvent effect on the reaction.



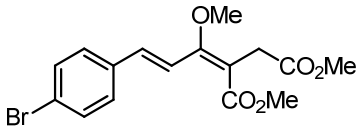
1d **4a**

Entry [a]	Base	Solvent	*3E, 5E*-**4a** (%) [b]	3E, 5E/3E, 5Z [c]
1	LiHMDS	THF	13	83/17
2	NaHMDS	THF	39	97/3
3	CH_3ONa	THF	48	98/2
4	K_2CO_3	THF	30	84/16
5	*t*-BuOK	THF	78	97/3
6	*t*-BuOK	DME	85	98/2
7	*t*-BuOK	CH_2Cl_2	84	99/1
8	*t*-BuOK	$PhCH_3$	81	95/5
9	*t*-BuOK	*n*-Hexane	21	---
10	*t*-BuOK	CH_3CN	89	99/1
11 [d]	*t*-BuOK	CH_3CN	85	98/2

[a] Phosphonium salt **1d** (235.5 mg, 0.5 mmol), base (0.6 mmol), MDA (50 µL, 0.6 mmol), PCBA (56 mg, 0.4 mmol), Fe(TCP)Cl (1.7 mg, 0.002 mmol), solvent (4.0 mL). [b] Isolated yield of single isomer. [c] Determined by ^{1}H NMR. [d] Using 0.1 mol% [Fe(TCP)Cl] as catalyst.

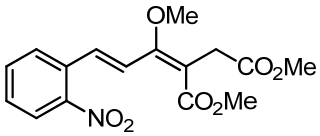
4. General Procedure for Synthesis of Tetrasubstituted Dienes

To a stirred suspension of phosphonium salt **1d** (236 mg, 0.5 mmol) in 2.0 mL dry CH_3CN under N_2 at room temperature was added *t*-BuOK (67.2 mg, 0.60 mmol) in one portion. After 10 min, Fe(TCP)Cl (1.7 mg, 0.002 mmol) and MDA (50 μL, 0.6 mmol) were added to the system respectively (Caution! N_2 Release!), washed the Schlenk tube with 1.0 mL dry CH_3CN, and the mixture stirred for another 10 min. Aldehyde (0.4 mmol) and CH_3CN (1.0 mL) were added and the resulting mixture was stirred at room temperature. After the reaction was complete, the resulting mixture was filtered rapidly through a funnel with a thin layer of silica gel and eluted with DCM. The filtrate was concentrated and the residue was purified by chromatography on silica gel to afford the desired products.



(3E, 5E)-**4b**

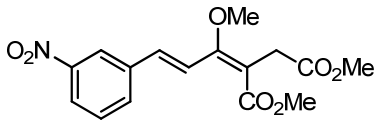
86% yield, white solid, ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.79 (d, *J* = 16.2 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.7 Hz, 2H), 6.97 (d, *J* = 15.9 Hz, 1H), 3.77 (s, 3H), 3.74 (s, 3H), 3.71 (s, 3H), 3.53 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 171.8, 167.5, 164.9, 134.9, 134.5, 131.7, 128.8, 122.8, 121.2, 113.4, 60.5, 51.8, 51.7, 32.5; IR (KBr) ν 2954 (m), 1734 (s), 1609 (m), 1584 (m), 1487 (m), 1438 (m), 1256 (m), 1205 (m), 1170 (m); MS (EI, m/z, rel. intensity) 369 (4, M^+), 337 (12), 309 (13), 295 (45), 279 (23), 265 (100), 249 (30), 235 (4.6), 211 (5.4), 198 (8.4), 183 (8.7), 171 (8.5), 155 (8.2), 141 (10), 128 (18), 115 (10), 102 (19), 75 (7.3), 59 (32), 45 (5.3); HRMS (EI) calcd for $C_{16}H_{17}BrO_5$ (M^+): 368.0259; Found: 368.0251.



(3E, 5E)-**4c**

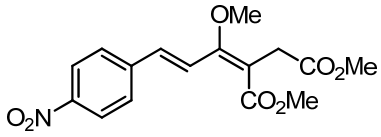
78% yield, light yellow solid, ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.01-7.99 (m, 1H), 7.80-7.71 (m, 2H), 7.65-7.61 (m, 1H), 7.49-7.43 (m, 2H), 3.83 (s, 3H), 3.77 (s, 3H),

3.72 (s, 3H), 3.56 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 171.7, 167.4, 164.3, 148.0, 133.3, 132.0, 130.9, 128.96, 128.90, 125.2, 124,6, 114.2, 60.4, 51.9, 51.8, 32.4; IR (KBr) ν 2952 (m), 1741 (s), 1710 (s), 1586 (m), 1524 (m), 1435 (s), 1346 (m); MS (EI, m/z, rel. intensity) 335 (19, M^+), 318 (35), 304 (25), 276 (10), 262 (22), 244 (22), 230 (98), 216 (19), 200 (100), 188 (6.0), 170 (8.2), 156 (17), 141 (45), 128 (35), 120 (46), 102 (12), 92 (12), 77 (14), 59 (37), 45 (9.1); HRMS (EI) calcd for $C_{16}H_{17}NO_7$ (M^+): 335.1005; Found: 335.1004.



(3E, 5E)-**4d**

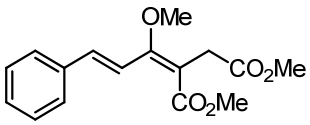
83% yield, light yellow solid, ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.32 (t, *J* = 2.0 Hz, 1H), 8.15-8.13 (m, 1H), 7.92-7.86 (m, 2H), 7.57-7.53 (m, 1H), 7.08 (d, *J* = 16.8 Hz, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 3.72 (s, 3H), 3.56 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 171.5, 167.2, 164.0, 148.5, 137.8, 133.0, 132.5, 129.6, 123.5, 123.0, 122.0, 114.8, 60.5, 51.9, 51.8, 32.6; IR (KBr) ν 2953 (m), 1732 (s), 1737 (s), 1705 (s), 1600 (m), 1519 (s), 1435 (m), 1443 (s); MS (EI, m/z, rel. intensity) 335 (6.7, M^+), 304 (12), 276 (19), 262 (24), 244 (16), 230 (100), 216 (38), 200 (6.2), 184 (3.4), 170 (4.7), 155 (4.3), 141 (5.1), 128 (11), 115 (8.2), 102 (5.9), 89 (1.7), 75 (3.2), 59 (13), 45 (3.2); HRMS (EI) calcd for $C_{16}H_{17}NO_7$ (M^+): 335.1005; Found: 335.1009.



(3E, 5E)-**4e**

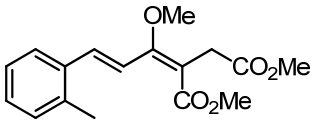
90% yield, light yellow solid, ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.20 (d, *J* = 8.4 Hz, 2H), 7.96 (d, *J* = 16.4 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 16.0 Hz, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 3.72 (s, 3H), 3.57 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 171.5, 167.2, 164.0, 147.3, 142.4, 132.9, 127.8, 124.8, 123.9, 115.4, 60.6, 51.91, 51.87, 32.6; IR (KBr) ν 2953 (m), 1732 (s), 1737 (s), 1705 (s), 1600 (m), 1519 (s), 1435 (m), 1443 (s); MS (EI, m/z, rel. intensity) 335 (6.7, M^+), 304 (12), 276 (19), 262

(24), 244 (16), 230 (100), 216 (38), 198 (5.9), 186 (3.0), 170 (5.5), 155 (3.3), 141 (3.7), 128 (10), 102 (6.8), 89 (2.0), 75 (2.8), 59 (15), 45 (3.5); HRMS (EI) calcd for $C_{16}H_{17}NO_7$ (M^+): 335.1005; Found: 335.1009.



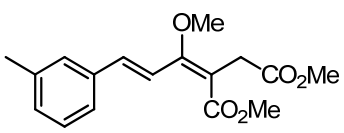
(3E, 5E)-**4f**

90% yield, white solid, ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.78 (d, *J* = 16.4 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 2H), 7.37-7.27 (m, 3H), 7.04 (d, *J* = 16.0 Hz, 1H), 3.76 (s, 3H), 3.74 (s, 3H), 3.70 (s, 3H), 3.54 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.0, 167.6, 165.2, 136.0, 128.8, 128.6, 127.4, 120.4, 112.9, 60.4, 51.8, 51.7, 32.6; IR (KBr) ν 2955(m), 1732 (s), 1689 (m), 1607 (m), 1575 (m), 1437 (m); MS (EI, m/z, rel. intensity) 290 (3.8, M^+), 259 (9.6), 231 (16), 217 (46), 199 (32), 185 (100), 171 (43), 157 (6.5), 141 (13), 128 (21), 115 (15), 103 (12), 91 (4.0), 77 (9.8), 59 (14), 45 (3.2); HRMS (EI) calcd for $C_{16}H_{18}O_5$ (M^+): 290.1154; Found: 290.1157.



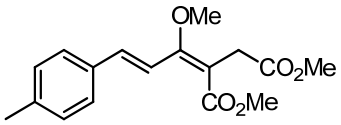
(3E, 5E)-**4g**

71% yield, colorless liquid, ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.67-7.63 (m, 2H), 7.30 (d, *J* = 16.0 Hz, 1H), 7.22-7.17 (m, 3H), 3.76 (m, 6H), 3.71 (s, 3H), 3.54 (s, 2H), 2.40 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.0, 167.6, 165.4, 136.4, 134.9, 133.6, 130.4, 128.6, 126.2, 126.0, 121.3, 112.7, 60.4, 51.8, 51.7, 32.6, 19.7; IR (KBr) ν 2950 (m), 1741(s), 1710 (s), 1619 (m), 1587 (m), 1435 (m); MS (EI, m/z, rel. intensity) 304 (1.2, M^+), 273 (6.7), 245 (12), 231 (47), 213 (19), 199 (100), 185 (32), 153 (26), 128 (12), 115 (24), 105 (4.2), 84 (43), 59 (18), 45 (4.5); HRMS (EI) calcd for $C_{17}H_{20}O_5$ (M^+): 304.1311; Found: 304.1310.



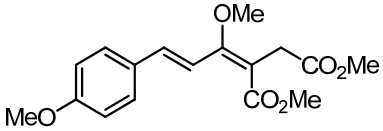
(3E, 5E)-**4h**

77% yield, colorless liquid, ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.78 (d, *J* = 16.0 Hz, 1H), 7.34-7.32 (m, 2H), 7.24 (t, *J* = 8.0 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 7.02(d, *J* = 16.4 Hz, 1H), 3.76 (s, 3H), 3.73 (s, 3H), 3.70 (s, 3H), 3.54 (s, 2H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.0, 167.6, 165.4, 138.2, 136.2, 135.8, 129.7, 128.5, 127.9, 124.6, 120.1, 112.6, 60.4, 51.8, 51.6, 32.5, 21.2; IR (KBr) ν 2950 (s), 2842 (m), 1743(s), 1712 (s), 1621 (m), 1588 (m), 1435 (m); MS (EI, m/z, rel. intensity) 304 (1.9, M^+), 273 (4.8), 245 (10), 230 (52), 213 (36), 199 (100), 185 (40), 171 (5.2), 155 (7.9), 141 (10.9), 128 (13), 115 (17), 105 (2.2), 84 (10), 59 (14), 51 (5.3), 45 (2.5); HRMS (EI) calcd for $C_{17}H_{20}O_5$ (M^+): 304.1311; Found: 304.1319.



(3E, 5E)-**4i**

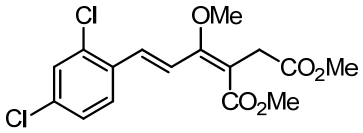
77% yield, colorless liquid, ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.75 (d, *J* = 16.0 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 16.0 Hz, 1H), 3.76 (s, 3H), 3.74 (s, 3H), 3.70 (s, 3H), 3.53 (s, 2H), 2.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.1, 167.7, 165.6, 139.0, 136.0, 133.2, 129.4, 127.4, 119.4, 112.4, 60.5, 51.8, 51.7, 32.6, 21.2; IR (KBr) ν 2950 (s), 2842 (m), 1741(s), 1710 (s), 1620 (m), 1585 (m), 1435 (m); MS (EI, m/z, rel. intensity) 304 (2.1, M^+), 273 (4.9), 245 (10), 231 (35), 213 (34), 199 (100), 185 (44), 171 (9.2), 155 (14), 128 (16), 115 (24), 105 (4.7), 84 (91), 71 (9.5), 59 (22), 43 (11); HRMS (EI) calcd for $C_{17}H_{20}O_5$ (M^+): 304.1311; Found: 304.1304.



(3E, 5E)-**4j**

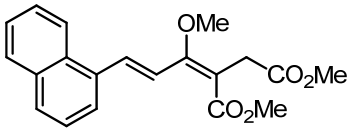
55% yield, colorless liquid, ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.67 (d, *J* = 16.0 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 16.4 Hz, 1H), 6.89 (d, *J* = 9.2 Hz, 2H), 3.83 (s, 3H), 3.76 (s, 3H), 3.74 (s, 3H), 3.70 (s, 3H), 3.53 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.2, 167.8, 165.8, 160.3, 135.8, 128.9, 128.8, 118.3, 114.1, 112.0, 60.6,

55.3, 51.9, 51.7, 32.7; IR (KBr) ν 2951(m), 2840 (m), 1741 (s), 1709 (s), 1602 (m), 1512 (m), 1435 (m); MS (EI, m/z, rel. intensity) 320 (7.2, M^+), 289 (3.9), 261 (11), 246 (57), 229 (51), 215 (100), 201 (30), 187 (5.6), 171 (6.4), 161 (6.5), 145 (4.9), 128 (9.2), 115 (8.8), 103 (2.2), 89 (3.1), 77 (3.7), 59 (11), 45 (2.9); HRMS (EI) calcd for $C_{17}H_{20}O_6$ (M^+): 320.1260; Found: 320.1262.



(3E, 5E)-**4k**

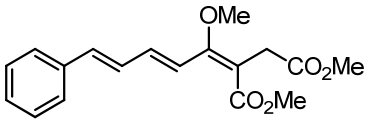
95% yield, white solid, ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.73 (d, J = 16.8 Hz, 1H), 7.65 (d, J = 8.1 Hz, 1H), 7.41-7.24 (m, 3H), 3.78 (s, 3H), 3.77 (s, 3H), 3.72 (s, 3H), 3.55 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 171.7, 167.4, 164.6, 134.7, 134.5, 132.8, 130.5, 129.4, 127.9, 127.3, 123.2, 114.1, 60.5, 51.9, 51.7, 32.5; IR (KBr) ν 2954(m), 1734 (s), 1696 (m), 1608 (m), 1581 (m), 1437 (m), 1368 (m); MS (EI, m/z, rel. intensity) 358 (4.3, M^+), 327 (7.2), 299 (24), 285 (34), 267 (22), 253 (100), 239 (52), 225 (6.4), 211 (4.9), 199 (7.2), 173 (8.8), 162 (11), 139 (11), 113 (7.7), 99 (10), 86 (5.8), 75 (8.8), 59 (44), 49 (10); HRMS (EI) calcd for $C_{16}H_{16}Cl_2O_5$ (M^+): 358.0375; Found: 358.0381.



(3E, 5E)-**4l**

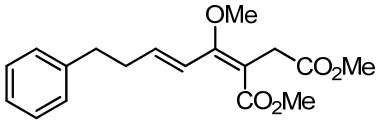
86% yield, colorless liquid, ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.15 (d, J = 7.5 Hz, 1H), 7.90-7.82 (m, 5H), 7.58-7.46 (m, 3H), 3.85 (s, 3H), 3.77 (s, 3H), 3.73 (s, 3H), 3.58 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.0, 167.6, 165.2, 133.6, 133.3, 132.8, 131.2, 129.1, 128.6, 126.3, 125.8, 125.5, 124.4, 123.2, 123.0, 113.0, 60.5, 51.9, 51.7, 32.6; IR (KBr) ν 2950(m), 2841 (m), 1742 (s), 1613 (m), 1582 (m), 1508 (m), 1435 (m), 797 (m), 775 (m); MS (EI, m/z, rel. intensity) 341 (2.3, M^+), 309 (5.6), 267 (40), 249 (14). 235 (100), 221 (24), 206 (5.1), 189 (16), 178 (7.8), 165 (4.6), 152 (10), 127 (2.0), 113 (1.8), 101 (0.5), 89 (1.1), 76 (1.6), 59 (11), 45 (1.8); HRMS (EI) calcd for

$C_{20}H_{20}O_5$ (M^+): 340.1311; Found: 340.1314.



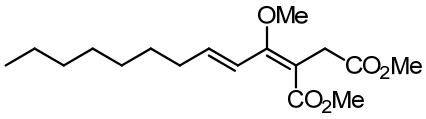
(3E, 5E)-**4m**

64%, yield, white solid, ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.44 (d, *J* = 7.2 Hz, 2H), 7.36-7.24 (m, 4H), 7.01-6.95 (m, 1H), 6.90-6.83 (m, 1H), 6.75 (d, *J* = 15.2 Hz, 1H), 3.75 (s, 3H), 3.71 (s, 3H), 3.70 (s, 3H), 3.52 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.0, 167.6, 165.2, 136.7, 136.63, 136.60, 128.6, 128.27, 128.23, 126.7, 124.3, 112.8, 60.6, 51.9, 51.7, 32.6; IR (KBr) ν 2950(m), 2850 (m), 1738 (s), 1707 (s), 1605 (m), 1256 (m), 1054 (s), 998 (s), 788 (m), 751 (m), 738 (m), 693 (m); MS (EI, m/z, rel. intensity) 316 (23, M^+), 285 (4.5), 270 (5.5), 256 (5.6), 242 (27), 225 (20), 211 (100), 197 (62), 181 (19), 157 (88), 153 (33), 128 (89), 115 (51), 105 (84), 91 (91), 84 (78). 59 (100), 43 (78); HRMS (EI) calcd for $C_{18}H_{20}O_5$ (M^+): 316.1311; Found: 316.1305.



(3E, 5E)-**4n**

72% yield, colorless liquid, ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.31-7.26 (m, 2H), 7.20-7.19 (m, 3H), 6.95 (d, *J* = 15.6 Hz, 1H), 6.29-6.20 (m, 1H), 3.71 (s, 3H), 3.68 (s, 3H), 3.58 (s, 3H), 3.45 (s, 2H), 2.82-2.77 (m, 2H), 2.60-2.53 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.1, 167.8, 165.1, 141.2, 138.9, 128.32, 128.31, 125.9, 122.7, 110.8, 59.9, 51.8, 51.6, 35.0, 34.5, 32.4; IR (KBr) ν 2949 (m), 2850 (m), 1739 (s), 1712 (s), 1589 (m), 1435 (m), 1193 (s), 1053 (s), 1015 (s), 801 (s), 736 (s), 700 (s); MS (EI, m/z, rel. intensity) 318 (17, M^+), 286 (5.6), 254 (8.4), 227 (22), 213 (100), 195 (5.9), 173 (9.8), 167 (12), 139 (8.3), 117 (10), 109 (12), 91 (68), 77 (4.8), 65 (10.2), 59 (9.4), 41 (2.9); HRMS (EI) calcd for $C_{18}H_{22}O_5$ (M^+): 318.1467; Found: 318.1469.

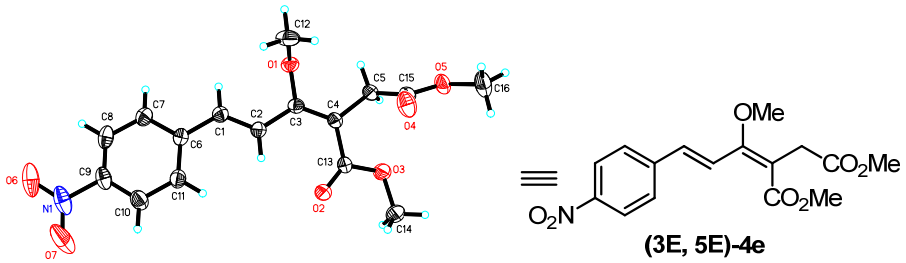


(3E, 5E)-**4o**

49% yield, colorless liquid, ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.92 (d, *J* = 16.0 Hz,

1H), 6.28-6.20 (m, 1H), 3.72 (s, 3H), 3.69 (s, 3H), 3.66 (s, 3H), 3.46 (s, 2H), 2.26-2.20 (m, 2H), 1.48-1.45 (m, 2H), 1.30-1.28 (m, 8H), 0.88-0.87 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.2, 167.8, 165.4, 140.3, 122.0, 110.4, 60.0, 51.8, 51.5, 32.8, 32.4, 31.7, 29.1, 29.0, 28.7, 22.5, 14.0; IR (KBr) ν 2926(m), 2855 (m), 1742 (s), 1715 (s), 1640 (m), 1590 (m), 1435 (m), 1194 (m), 1117 (m), 1059 (m), 978 (m), 800 (m); MS (EI, m/z, rel. intensity) 312 (8.4, M^+), 281 (5.8), 253 (5.0), 213 (100), 196 (5.7), 177 (4.8), 164 (16), 149 (3.1), 137 (4.0), 123 (8.1), 109 (9.3), 95 (9.1), 79 (6.1), 59 (7.7), 41 (13); HRMS (EI) calcd for $C_{17}H_{28}O_5$ (M^+): 312.1937; Found: 312.1941.

X-Ray Structure of (3E, 5E)-4e (CCDC 932306)



Bond precision: C-C = 0.0026 A Wavelength=0.71073

Cell: a=7.5752(9) b=9.2925(12) c=11.9191(15)
alpha=90.060(2) beta=98.984(2) gamma=95.356(2)

Temperature: 293 K

	Calculated	Reported
Volume	825.00(18)	825.00(18)
Space group	P -1	P-1
Hall group	-P 1	?
Moiety formula	C16 H17 N O7	?
Sum formula	C16 H17 N O7	C16 H17 N O7
Mr	335.31	335.31
Dx,g cm-3	1.350	1.350
Z	2	2
Mu (mm-1)	0.107	0.107
F000	352.0	352.0
F000'	352.22	
h,k,lmax	9,11,14	9,11,14
Nref	3260	3205
Tmin,Tmax	0.958,0.974	0.786,1.000
Tmin'	0.958	

Correction method= EMPIRICAL

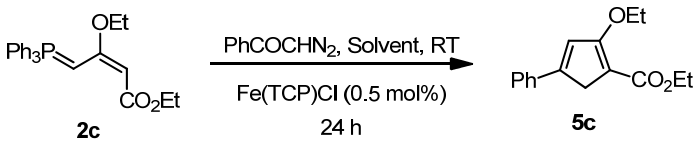
Data completeness= 0.983 Theta(max)= 26.000

R(reflections)= 0.0571(2472) wR2(reflections)= 0.1731(3205)

S = 1.032 Npar= 221

5. Reaction Conditions for Synthesis of Cyclopentadienes

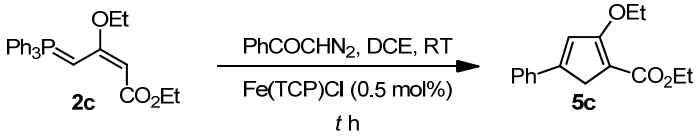
Table *S2* Solvent effects



Entry [a]	Solvent	Yield (%) [b]	Entry	Solvent	Yield (%)[b]
1	THF	44	7	$PhCH_3$	47
2	DME	54	8	PhCl	48
3	MTBE	23	9	EtOAc	46
4	1,4-Dioxane	44	10	*i*-PrOAc	47
5	DCM	45	11	CH_3CN	33
6	DCE	60	12	DMF	trace

[a] Condition: ylide **2c** (167.4 mg, 0.4 mmol), $PhCOCHN_2$ (116.8 mg, 0.8 mmol), Fe(TCP)Cl (1.7 mg, 0.002 mmol), solvent (4.0 mL), RT; [b] Isolated yield.

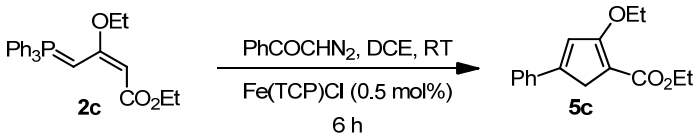
Table *S3* Reaction time



Entry [a]	t (h)	Yield (%) [b]	Entry	t (h)	Yield (%)[b]
1	6	69	4	36	47
2	15	60	5	48	52
3	24	60			

[a] Condition: ylide **2c** (167.4 mg, 0.4 mmol), $PhCOCHN_2$ (116.8 mg, 0.8 mmol), Fe(TCP)Cl (1.7 mg, 0.002 mmol), DCE (4.0 mL); [b] Isolated yield.

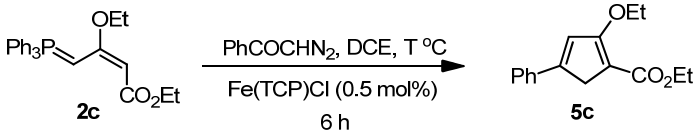
Table *S4* Loading of diazo phenylethanone



Entry [a]	Ylide/Diazo	Yield (%) [b]	Entry	Ylide/Diazo	Yield (%) [b]
1	1.0/1.0	45	4	1.0/1.5	67
2	1.0/1.2	55	5	1.0/2.0	69
3	1.0/1.4	67	6	1.0/2.5	54

[a] Condition: ylide **2c** (167.4 mg, 0.4 mmol), $PhCOCHN_2$, Fe(TCP)Cl (1.7 mg, 0.002 mmol), DCE (4.0 mL), 6 h; [b] Isolated yield.

Table *S5* Reaction temperature

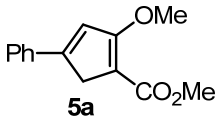


Entry [a]	T (℃)	Yield (%) [b]	Entry [a]	T (℃)	Yield (%) [b]
1	0	70	5	45	62
2	10	74	6	55	59
3	20	76	7 [c]	20	65
4	35	68			

[a] Condition: ylide **2c** (167.4 mg, 0.4 mmol), $PhCOCHN_2$ (81.8 mg, 0.56 mmol), Fe(TCP)Cl (1.7 mg, 0.002 mmol), DCE (4.0 mL), 6 h; [b] Isolated yield; [c] Under the same condition, t = 12 h.

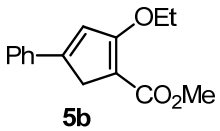
6. General Procedure for Synthesis of Cyclopentadienes

General procedure: To a stirred suspension of ylide **2** (0.4 mmol) in dry DCE (2.0 mL) under N_2 at room temperature was added Fe(TCP)Cl (1.7 mg, 0.002 mmol) and $RCOCHN_2$ (0.56 mmol) sequentially at 20 ^oC. (Caution! N_2 Release!) The resulting mixture was stirred at 20 ^oC for 6 hours. After the reaction was complete, the resulting mixture was concentrated and the residue was purified by chromatography on silica gel to afford the desired products.



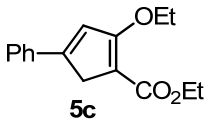
5a

65% yield, light yellow solid, ^1H NMR ($CDCl_3$, 400 MHz) δ 7.58 (d, J = 6.8 Hz, 2H), 7.39-7.29 (m, 3H), 6.93 (s, 1H), 4.04 (s, 3H), 3.78 (s, 3H), 3.70 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.2, 164.3, 152.9, 134.3, 128.80, 128.79, 125.5, 119.0, 104.6, 58.6, 50.8, 38.3; IR (KBr) ν 2946 (m), 1697 (s), 1673 (s), 1610 (m), 1456 (m), 1392 (m), 1209 (s), 1079 (s); MS (EI, m/z, rel. intensity) 230 (81, M^+), 199 (21), 171 (100), 155 (13), 142 (10), 128 (48), 115 (17), 105 (17), 91 (5.5), 77 (16), 57 (4); HRMS (EI) calcd for $C_{14}H_{14}O_3$ (M^+): 230.0943; Found: 230.0947.



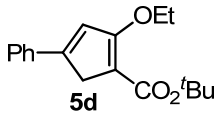
5b

74% yield, light yellow solid, ^1H NMR ($CDCl_3$, 300 MHz) δ 7.58 (d, J = 7.5 Hz, 2H), 7.40-7.29 (m, 3H), 6.90 (s, 1H), 4.32 (q, J = 7.1 Hz, 2H), 3.78 (s, 3H), 3.70 (s, 2H), 1.47 (t, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.7, 164.4, 152.7, 134.4, 128.8, 128.76, 125.5, 119.7, 104.8, 67.1, 50.7, 38.1, 15.2; IR (KBr) ν 2983 (m), 2945 (m), 1697 (s), 1674 (s), 1609 (m), 1448 (m), 1386 (m), 1208 (s), 1074 (s); MS (EI, m/z, rel. intensity) 244 (83, M^+), 213 (17), 185 (38), 157 (77), 128 (100), 115 (18), 108 (12), 102 (21), 91 (5.5), 77 (16); HRMS (EI) calcd for $C_{15}H_{16}O_3$ (M^+): 244.1099; Found: 244.1100.



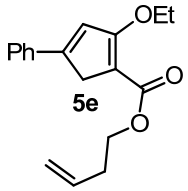
5c

76% yield, light yellow solid, ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.57 (d, J = 6.9 Hz, 2H), 7.40-7.30 (m, 3H), 6.89 (s, 1H), 4.35-4.20 (m, 4H), 3.69 (s, 2H), 1.47 (t, J = 7.0 Hz, 3H), 1.33 (t, J = 7.0 Hz, 3H).



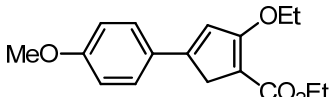
5d

50% yield, light yellow solid, ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.56 (d, J = 6.9 Hz, 2H), 7.38-7.26 (m, 3H), 6.87 (s, 1H), 4.29 (q, J = 7.1 Hz, 2H), 3.62 (s, 2H), 1.54 (s, 9H), 1.46 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.0, 163.8, 151.8, 134.7, 128.8, 128.5, 125.5, 119.8, 106.9, 79.0, 66.8, 38.2, 28.5, 15.2; IR (KBr) ν 2976 (m), 2928 (m), 1693 (s), 1670 (s), 1610 (m), 1413 (m), 1389 (m), 1168 (s), 1063 (m); MS (EI, m/z, rel. intensity) 286 (30, M^+), 244 (26), 230 (48), 213 (24), 184 (55), 157 (74), 128 (100), 115 (17), 108 (26), 91 (9), 77 (20), 57 (36); HRMS (EI) calcd for $C_{18}H_{22}O_3$ (M^+): 286.1569; Found: 286.1565.



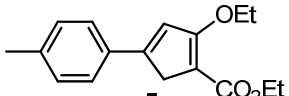
5e

40% yield, light yellow liquid, ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.57 (d, J = 7.5 Hz, 2H), 7.40-7.28 (m, 3H), 6.90 (s, 1H), 5.96-5.82 (m, 1H), 5.13 (m, 2H), 4.34-4.22 (m, 4H), 3.68 (s, 2H), 2.47 (q, J = 6.8 Hz, 2H), 1.47 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.8, 164.0, 152.6, 134.7, 134.4, 128.8, 128.7, 125.5, 119.7, 116.8, 104.9, 67.0, 62.5, 37.9, 33.4, 15.2; IR (KBr) ν 2979 (m), 2927 (m), 1698 (s), 1672 (s), 1609 (m), 1205 (s), 1071 (s); MS (EI, m/z, rel. intensity) 284 (30, M^+), 255 (5.6), 230 (10), 213 (30), 199 (15), 186 (50), 157 (100), 128 (85), 115 (20), 108 (63), 102 (21), 91 (11), 77 (23), 55 (46); HRMS (EI) calcd for $C_{18}H_{20}O_3$ (M^+): 284.1412; Found: 284.1413.



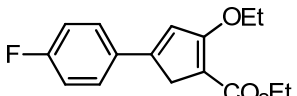
5f

45% yield, light yellow solid, ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.49 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H), 6.89 (s, 1H), 4.33-4.21 (m, 4H), 3.84 (s, 3H), 3.64 (s, 2H), 1.46 (t, *J* = 7.0 Hz, 3H), 1.32 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.2, 164.1, 160.1, 152.5, 127.4, 127.0, 117.7, 114.1, 104.0, 67.0, 59.2, 55.3, 38.0, 15.2, 14.6; IR (neat) ν 2926 (m), 2853 (m), 1667 (s), 1605 (s), 1506 (m), 1425 (m), 1254 (s), 1207 (s), 1074 (s), 1025 9s), 811 (m), 738 (m); MS (EI, m/z, rel. intensity) 288 (43, M^+), 259 (4.8), 243 (11), 231 (4.3), 215 (36), 203 (5.0), 187 (70), 172 (11), 158 (14), 144 (21), 128 (27), 115 (100), 102 (13), 89 (42), 77 (29), 63 (26), 55 (17), 43 (19); HRMS (EI) calcd for $C_{17}H_{20}O_4$ (M^+): 288.1362; Found: 288.1366.



5g

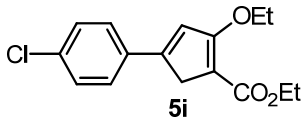
49% yield, light yellow solid, ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.46 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 6.83 (s, 1H), 4.33-4.20 (m, 4H), 3.66 (s, 2H), 2.36 (s, 3H), 1.46 (t, *J* = 7.0 Hz, 3H), 1.32 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.9, 164.1, 152.7, 138.8, 131.8, 129.4, 125.4, 118.8, 104.5, 67.0, 59.2, 38.0, 21.3, 15.2, 14.5; IR (KBr) ν 2984 (m), 2892 (m), 1674 (s), 1610 (s), 1425 (m), 1281 (m), 1200 (s), 1074 (m), 801 (m); MS (EI, m/z, rel. intensity) 272 (61, M^+), 227 (23), 199 (31), 191 (100), 171 (84), 141 (40), 128 (22), 115 (48), 91 (14); HRMS (EI) calcd for $C_{17}H_{20}O_3$ (M^+): 272.1412; Found: 272.1413.



5h

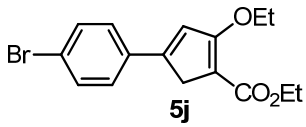
57% yield, light yellow solid, ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.57-7.52 (m, 2H), 7.08-7.03 (m, 2H), 6.82 (s, 1H), 4.34-4.20 (m, 4H), 3.65 (s, 2H), 1.46 (t, *J* = 7.0 Hz, 3H), 1.32 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.6, 164.0 (d, *J* = 14.8 Hz, 1C), 161.6, 151.2, 130.8 (d, *J* = 4.0 Hz, 1C), 127.3 (d, *J* = 7.5 Hz, 1C), 119.6,

115.8 (d, J = 22.6 Hz, 1C), 105.0, 67.0, 59.2, 38.2, 15.1, 14.5; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -112.2 – -112.3 (m, 1F); IR (neat) ν 2982 (m), 2926 (m), 1691 (s), 1610 (s), 1503 (s), 1207 (s), 1097 (s), 823 (s), 736 (s); MS (EI, m/z, rel. intensity) 337 (22, M^+), 308 (8.0), 276 (48), 248 (4.7), 231 (17), 203 (41), 175 (100), 146 (84), 133 (19), 120 (24), 101 (8.2), 83 (13), 57 (7.6), 43 (13); HRMS (EI) calcd for $C_{16}H_{17}FO_3$ (M^+): 276.1162; Found: 276.1163.



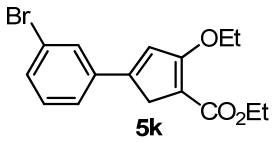
5i

48% yield, light yellow solid, ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.49 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.8 Hz, 2H), 6.87 (s, 1H), 4.33-4.21 (m, 4H), 3.64 (s, 2H), 1.46 (t, J = 7.2 Hz, 3H), 1.32 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.4, 163.9, 150.9, 134.4, 133.0, 129.0, 126.7, 120.3, 105.4, 67.1, 59.3, 38.1, 15.2, 15.0; IR (KBr) ν 2979 (m), 2929 (m), 1662 (s), 1610 (m), 1434 (m), 1206 (s), 1103 (m), 813 (m); MS (EI, m/z, rel. intensity) 292 (90, M^+), 264 (8.1), 247 (25), 220 (60), 191 (100), 155 (25), 127 (46), 115 (13), 101 (12), 75 (10), 43 (10); HRMS (EI) calcd for $C_{16}H_{17}ClO_3$ (M^+): 292.0866; Found: 292.0867.



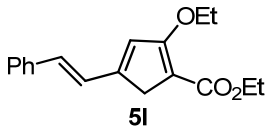
5j

48% yield, light yellow solid, ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.49 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.8 Hz, 2H), 6.89 (s, 1H), 4.33-4.21 (m, 4H), 3.64 (s, 2H), 1.46 (t, J = 7.0 Hz, 3H), 1.32 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.4, 163.9, 150.9, 133.3, 131.9, 126.9, 122.6, 120.4, 105.5, 67.1, 59.3, 38.0, 15.1, 14.5; IR (neat) ν 2982 (m), 2854 (m), 1689 (s), 1664 (s), 1610 (s), 1206 (s), 1069 (s), 810 (s), 736 (s); MS (EI, m/z, rel. intensity) 337 (22, M^+), 308 (8.0), 291 (21), 264 (92), 235 (100), 155 (42), 128 (79), 115 (27), 101 (22), 75 (20), 43 (15); HRMS (EI) calcd for $C_{16}H_{17}BrO_3$ (M^+): 336.0361; Found: 336.0358.



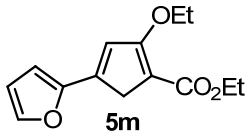
5k

70% yield, light yellow solid, ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.70 (s, 1H), 7.49-7.40 (m, 2H), 7.26-7.20 (m, 1H), 6.90 (s, 1H), 4.34-4.20 (m, 4H), 3.64 (s, 2H), 1.46 (t, J = 6.9 Hz, 3H), 1.33 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.2, 163.8, 150.5, 136.5, 131.4, 130.3, 128.4, 124.0, 123.0, 121.1, 105.8, 67.1, 59.3, 38.0, 15.1, 14.5; IR (KBr) ν 2982 (m), 2929 (m), 1693 (s), 1610 (s), 1561 (m), 1209 (s), 1070 (s), 737 (s); MS (EI, m/z, rel. intensity) 338 (19, M^+), 293 (9.1), 264(34), 235 (33), 153 (92), 127 (31), 110 (52), 97 (95), 81 (61), 57 (100), 43 (97); HRMS (EI) calcd for $C_{16}H_{17}BrO_3$ (M^+): 336.0361; Found: 336.0366.



5l

46% yield, light yellow solid, ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.46 (d, J = 8.2 Hz, 2H), 7.35 (t, J = 8.2 Hz, 2H), 7.29-7.24 (m, 1H), 7.00 (d, J = 16.2 Hz, 1H), 6.90 (d, J = 15.9 Hz, 1H), 6.52 (s, 1H), 4.28-4.20 (m, 4H), 3.54 (s, 2H), 1.44 (t, J = 7.0 Hz, 3H), 1.32 (t, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.7, 164.0, 151.8, 136.5, 131.7, 128.8, 128.2, 126.6, 123.8, 123.3, 104.5, 67.0, 59.2, 36.5, 15.1, 14.6; IR (KBr) ν 2986 (m), 2939 (m), 1669(s), 1693 (s), 1595 (s), 1524 (m), 1210 (s), 1147 (m), 1069 (s); MS (EI, m/z, rel. intensity) 284 (93, M^+), 239 (30), 210 (52), 183 (80), 165 (100), 153 (78), 141 (37), 128 (35), 115 (26), 102 (9.0), 91 (12), 77 (16), 55(19); HRMS (EI) calcd for $C_{18}H_{20}O_3$ (M^+): 284.1412; Found: 284.1415.

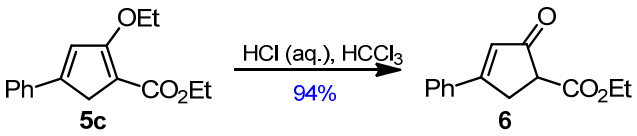


5m

70% yield, light yellow solid, ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.42 (s, 2H), 6.75 (s, 1H), 6.55 (d, J = 3.0 Hz, 1H), 6.46-6.44 (m, 1H), 4.32-4.19 (m, 4H), 3.60 (s, 2H), 1.45 (t, J = 6.9 Hz, 3H), 1.32 (t, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.8, 164.0, 150.9, 142.9, 141.5, 118.1, 111.9, 108.7, 103.7, 67.0, 59.2, 36.9, 15.1, 14.5; IR

(KBr) ν 2980 (m), 2934 (m), 1697(s), 1620 (m), 1577 (s), 1523 (m), 1217 (s), 1199 (m), 1068 (s); MS (EI, m/z, rel. intensity) 248 (48, M^+), 175 (47), 147 (100), 118 (16), 91 (19), 77 (5.4), 65 (11), 55(3.7); HRMS (EI) calcd for $C_{14}H_{16}O_4$ (M^+): 248.1049; Found: 248.1052.

7. Procedure for Chemical Transformation[2]



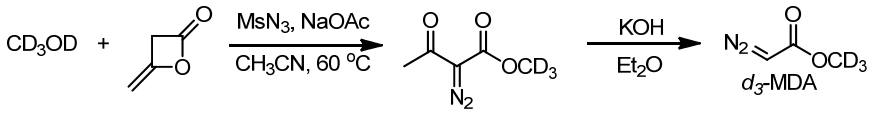
5c **6**

To a solution of **5c** (103.3 mg, 0.4 mmol) in $CHCl_3$ (8.0 mL) was added aq. HCl (8.0 mL, 2.0 M in H_2O) at room temperature. After stirred at the same temperature for 24 hours, the aqueous layer was extracted with $CHCl_3$ (3 × 10 mL). The combined organic layer was dried over Mg_2SO_4, filtered and concentrated. The residue was purified by chromatography on silica gel to afford the desired product **6** (85.6 mg, 94% yield).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.69-7.67 (m, 2H), 7.53-7.45 (m, 3H), 6.53 (t, J = 1.8 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 3.63 (dd, J = 2.2, 10.5Hz, 1H), 3.55 (ddd, J = 1.9, 2.9, 18.0 1H), 3.25 (ddd, J = 1.7, 3.3, 18.2 Hz, 1H), 1.32 (t, J = 7.0 Hz, 3H).

8. General Procedure for Deuterium Experiment

Synthesis of d_3-MDA[3,4]

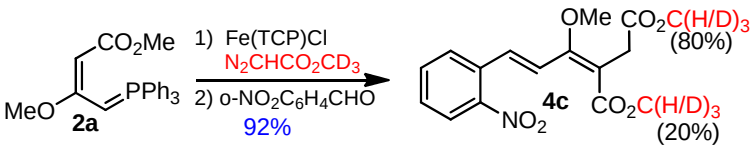


To a mixture of MsN_3 (9.1 g, 75 mmol)，NaOAc (492 mg, 6 mmol) in CH_3CN (60 mL) was added CD_3OD (2.7 mL, 60 mmol) under N_2. The resulting mixture was heated to 60 ℃, and then diketene (9.2 mL, 120 mmol) in CH_3CN (10 mL) was added dropwise in 7 hours. After refluxed for 20 hours, the reaction system was cooled to room temperature and diluted with brine (50 mL). The aqueous layer was extracted with Et_2O (3 × 50 mL), and the combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was subjected to the next step without further purification.

To a solution of upper products in Et_2O (200 mL) was added KOH (150 mL, 7 wt% in water, 210 mmol) at 0 °C, and then he reaction was warmed up to room temperature. After the reaction was complete, the organic layer was separated and the aqueous layer was extracted with Et_2O (3 × 50 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by distillation under vacuum to afford d_3-MDA as a light yellow liquid (2.2 g, 43% for two steps).

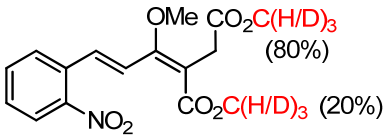
^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.76 (brs, 1H).

Deuterium Experiment



To a stirred suspension of phosphorus ylide **2a** (195 mg, 0.5 mmol) in dry CH_3CN (2.0 mL) under N_2 at room temperature was added Fe(TCP)Cl (1.7 mg, 0.002 mmol), d_3-MDA (50 μL, 0.6 mmol) and CH_3CN (1.0 mL) were added to the system

sequentially (Caution! N_2 Release!). Ten minutes later, *o*-$NO_2C_6H_4CHO$ (60.4 mg, 0.4 mmol) and CH_3CN (1.0 mL) were added and the resulting mixture was stirred at room temperature for 6 hours. After the reaction was complete, the resulting mixture was filtered rapidly through a funnel with a thin layer of silica gel and eluted with CH_2Cl_2. The filtrate was concentrated and the residue was purified by chromatography on silica gel to afford the desired products **(3E, 5E)-4c** as a light yellow solid (123.8 mg, 92% yield).



4c

92% yield, light yellow solid, ^1H NMR ($CDCl_3$, 400 MHz) δ 8.01 (d, *J* = 8.4 Hz, 1 H), 7.81-7.71 (m, 2H), 7.63 (t, *J* = 7.0 Hz, 1H), 7.50-7.43 (m, 2H), 3.83 (s, 3H), 3.77 (s, 2.4 H), 3.72 (s, 0.6 H), 3.56 (s, 2H).

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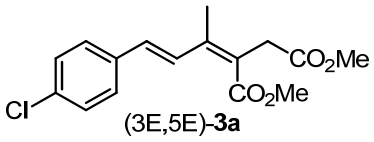
2. M. Hatanaka, Y. Himeda, R. Imashiro, Y. Tanaka, I. Ueda, *J. Org. Chem.* **1994**, *59*, 111.

3. a) H. M. L. Davies, J. H. Houser, G. Thornley, *J. Org. Chem.* **1995**, *60*, 7529. b) K. Ohtaka, M. Kajiwara, *J. Label. Compd. Radiopharm.* **2003**, *46*, 1177.

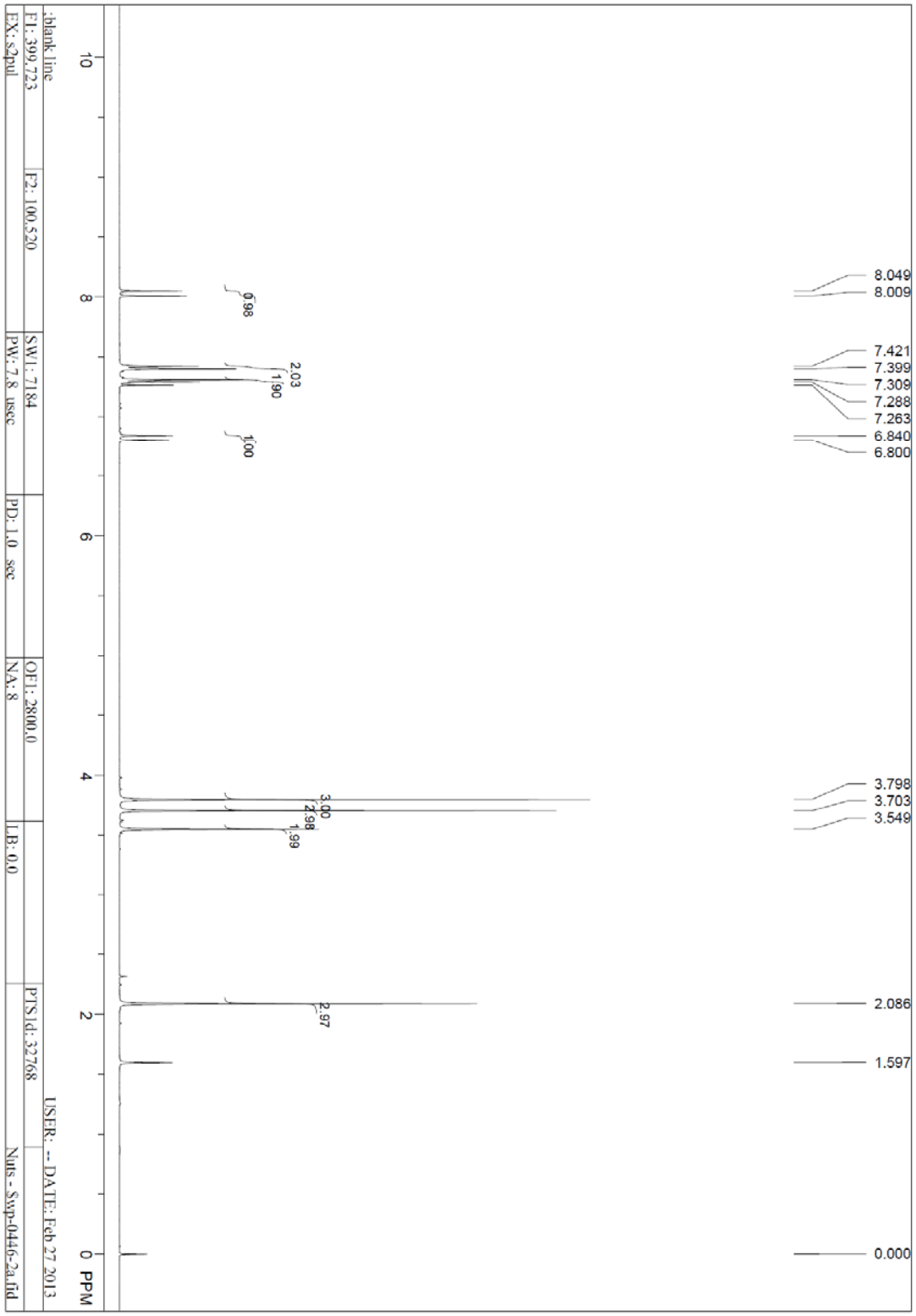
4. L. McElwee-White, D. A. Dougherty, *J. Am. Chem. Soc.* **1984**, *106*, 3466.

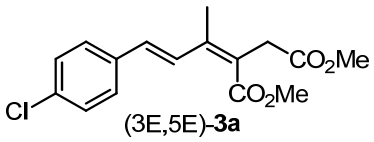
9. NMR Spectra of the Compounds



(3E,5E)-**3a**

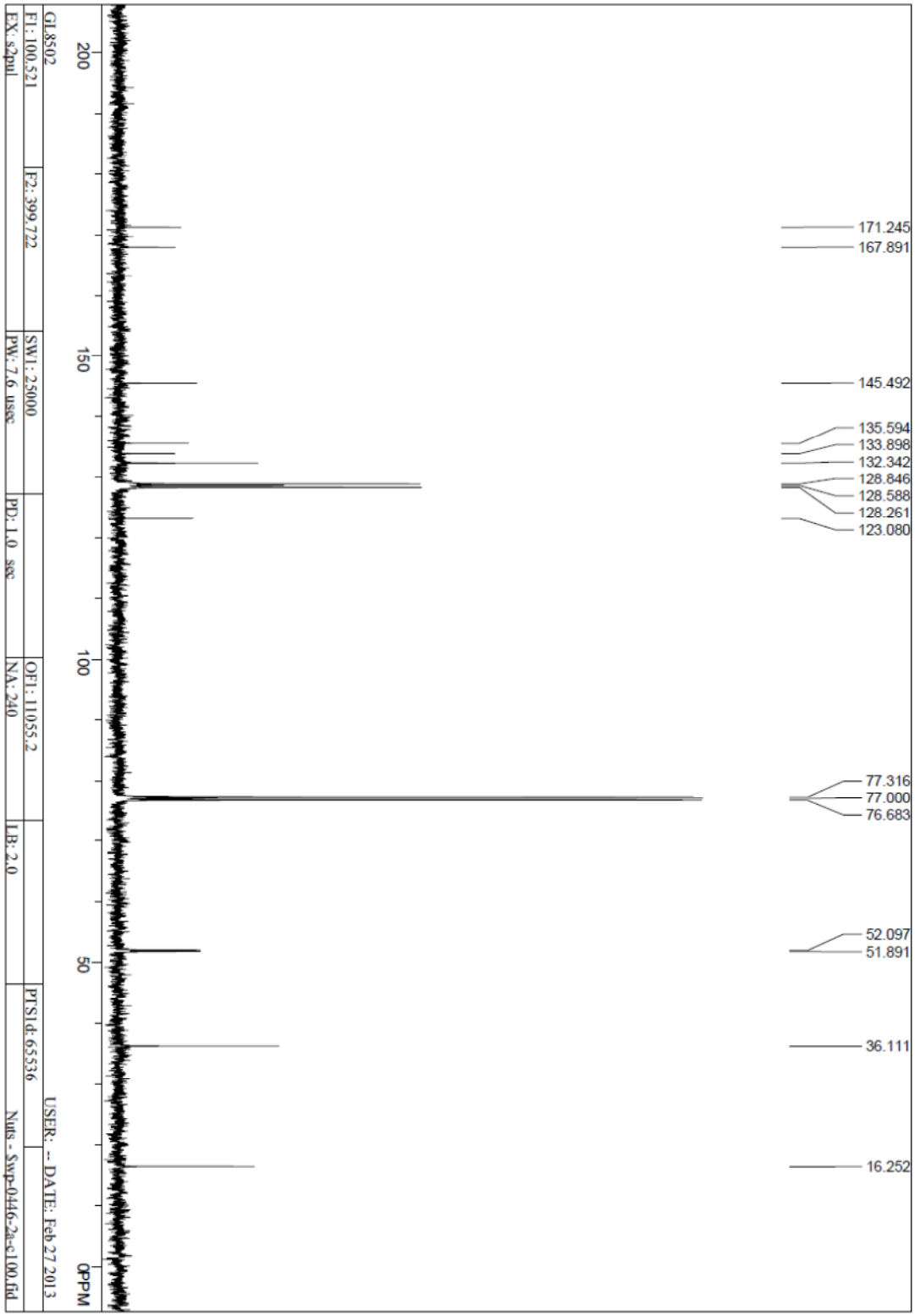
^{1}H NMR (400 M Hz in $CDCl_3$)

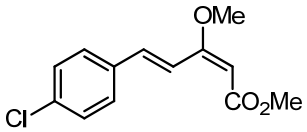




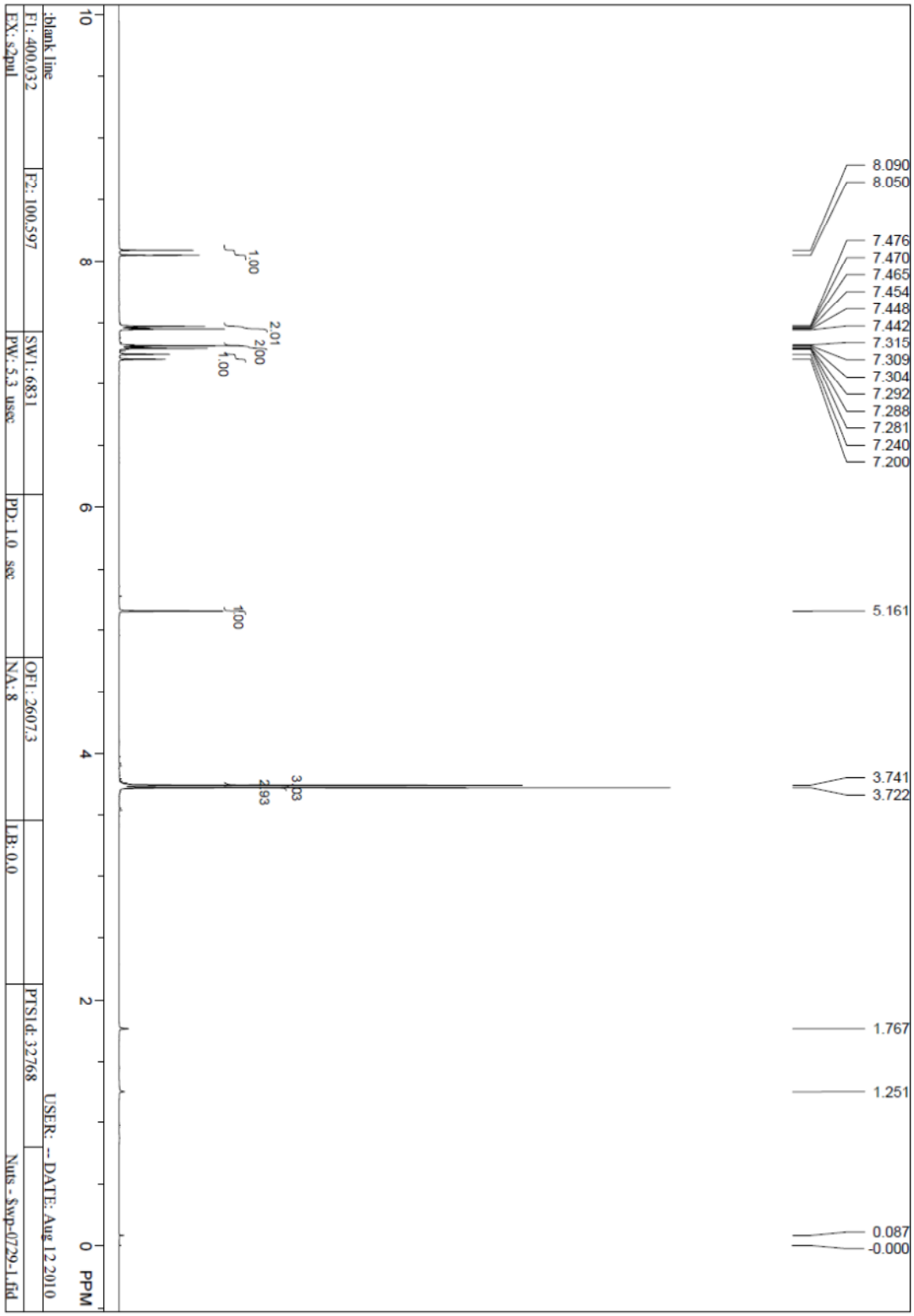
(3E,5E)-**3a**

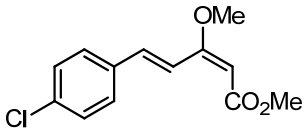
^{13}C NMR (100 M Hz in $CDCl_3$)





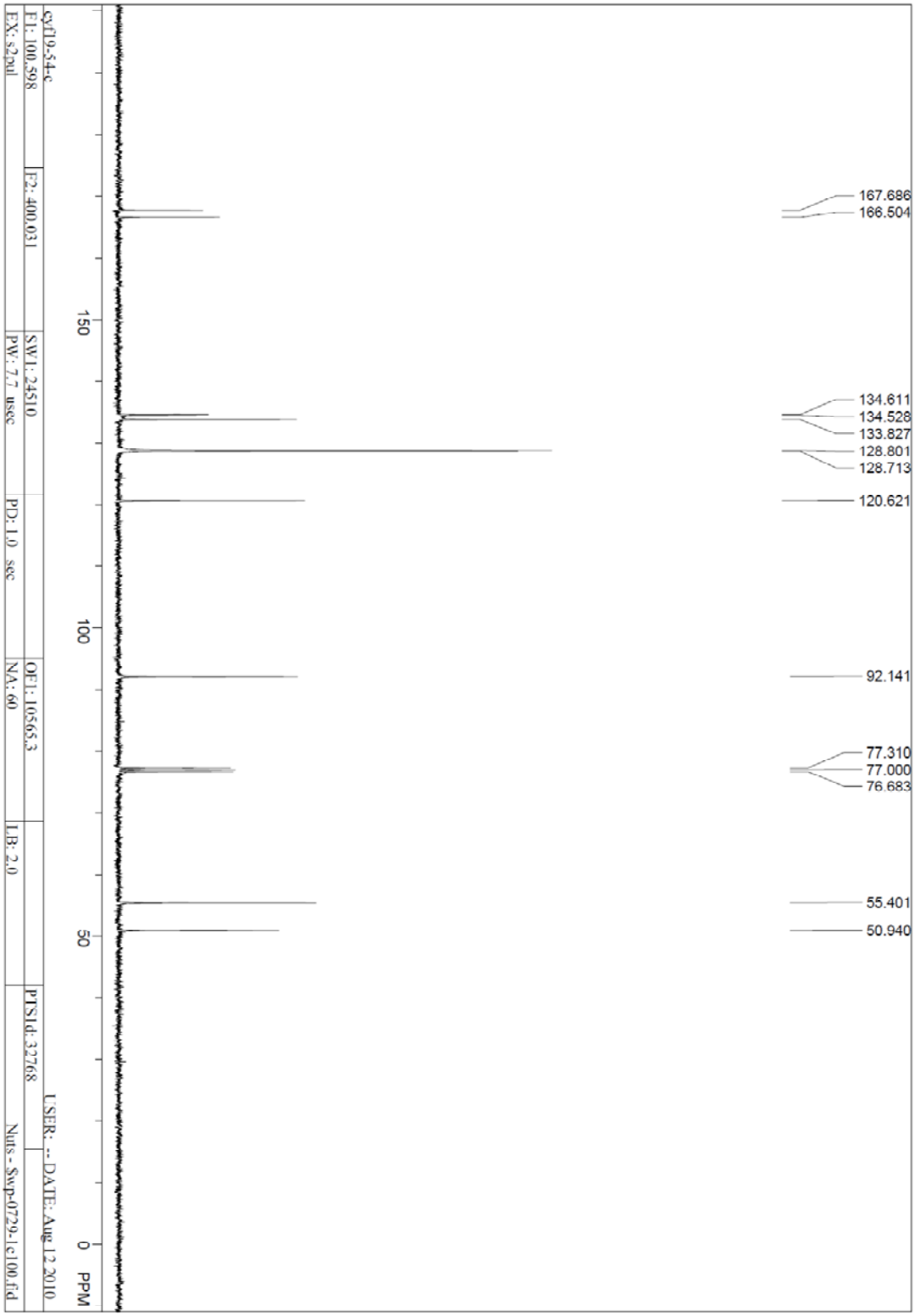
(2E, 4E)-**9a** ^{1}H NMR (400 M Hz in $CDCl_3$)

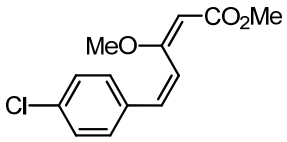




(2E, 4E)-**9a**

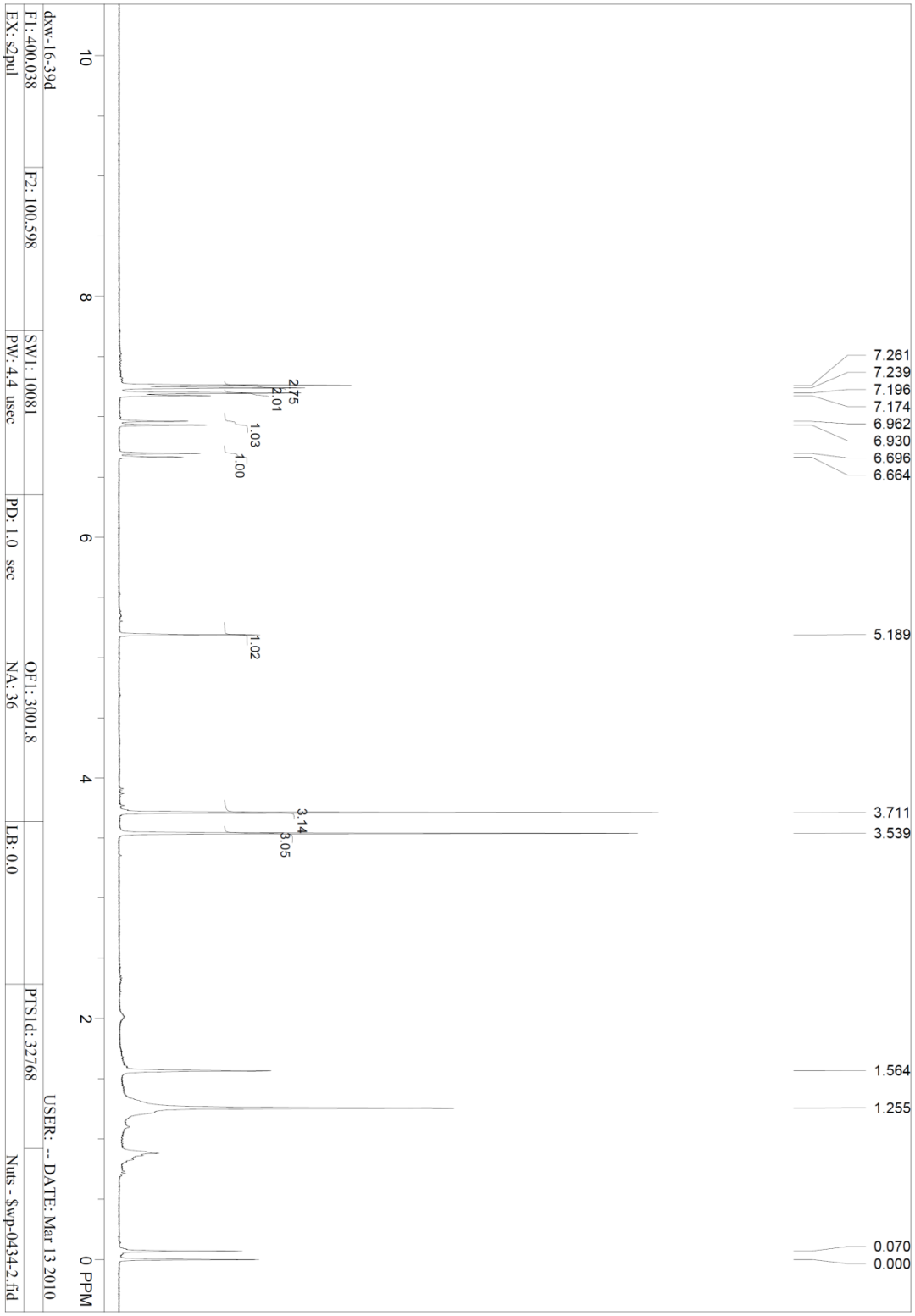
^{13}C NMR (100 M Hz in $CDCl_3$)

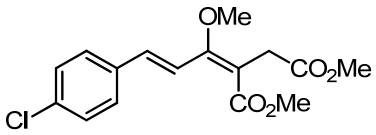




(2E, 4Z)-**9a**

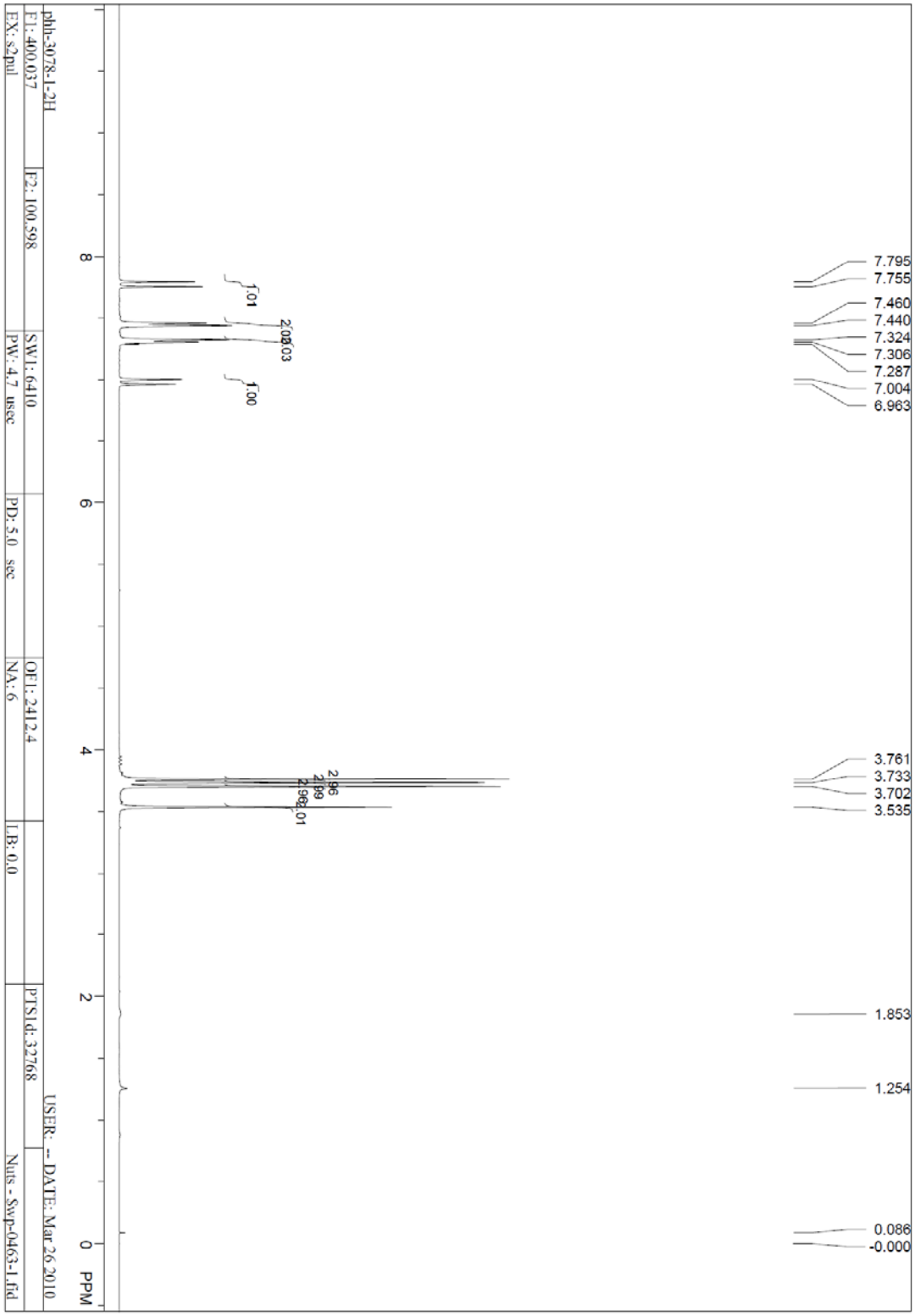
^{1}H NMR (400 M Hz in $CDCl_3$)

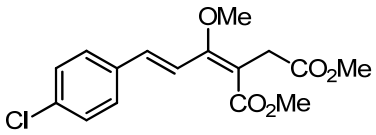




(3E, 5E)-**4a**

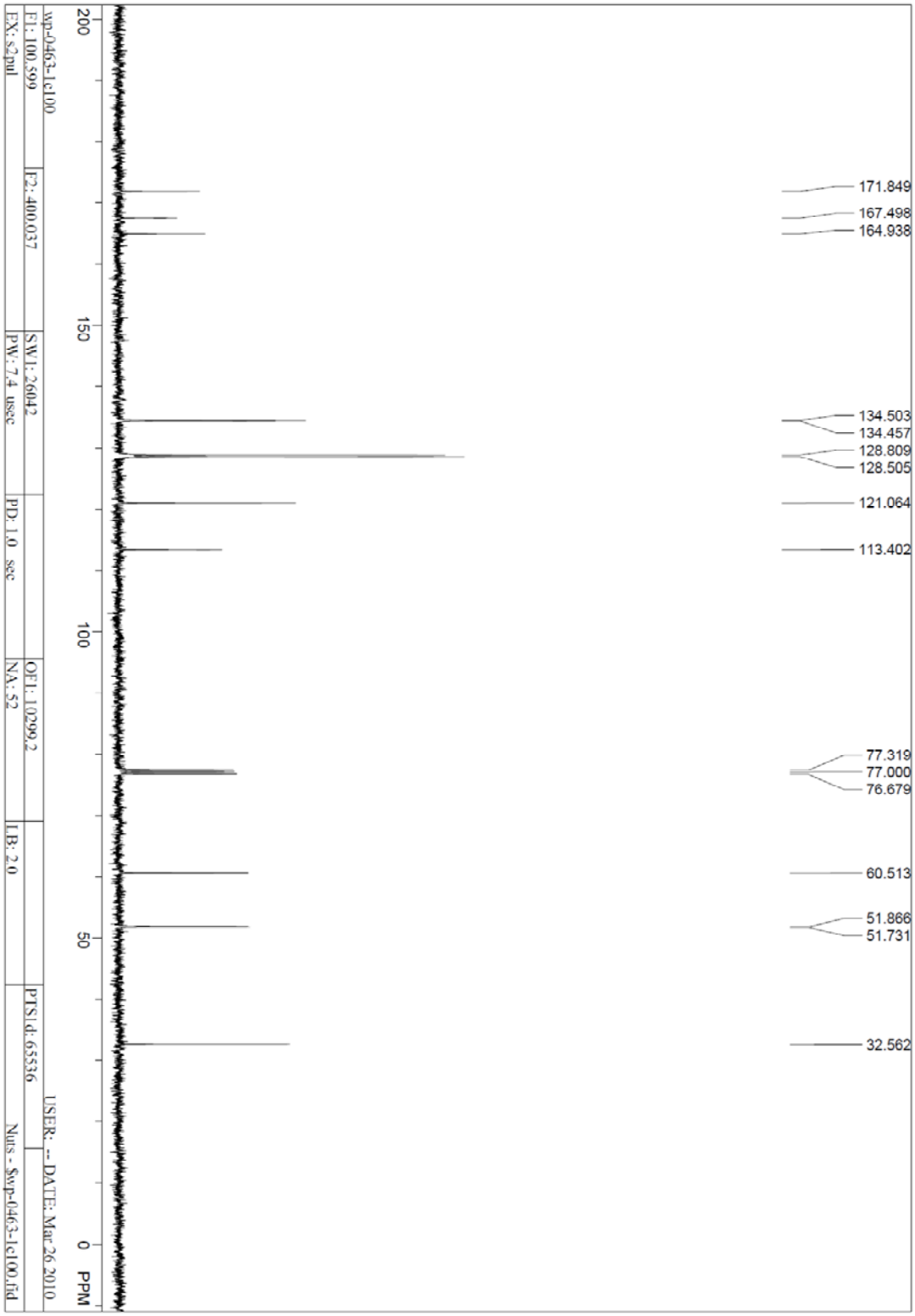
^{1}H NMR (400 M Hz in $CDCl_3$)

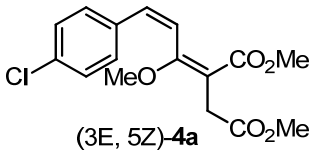




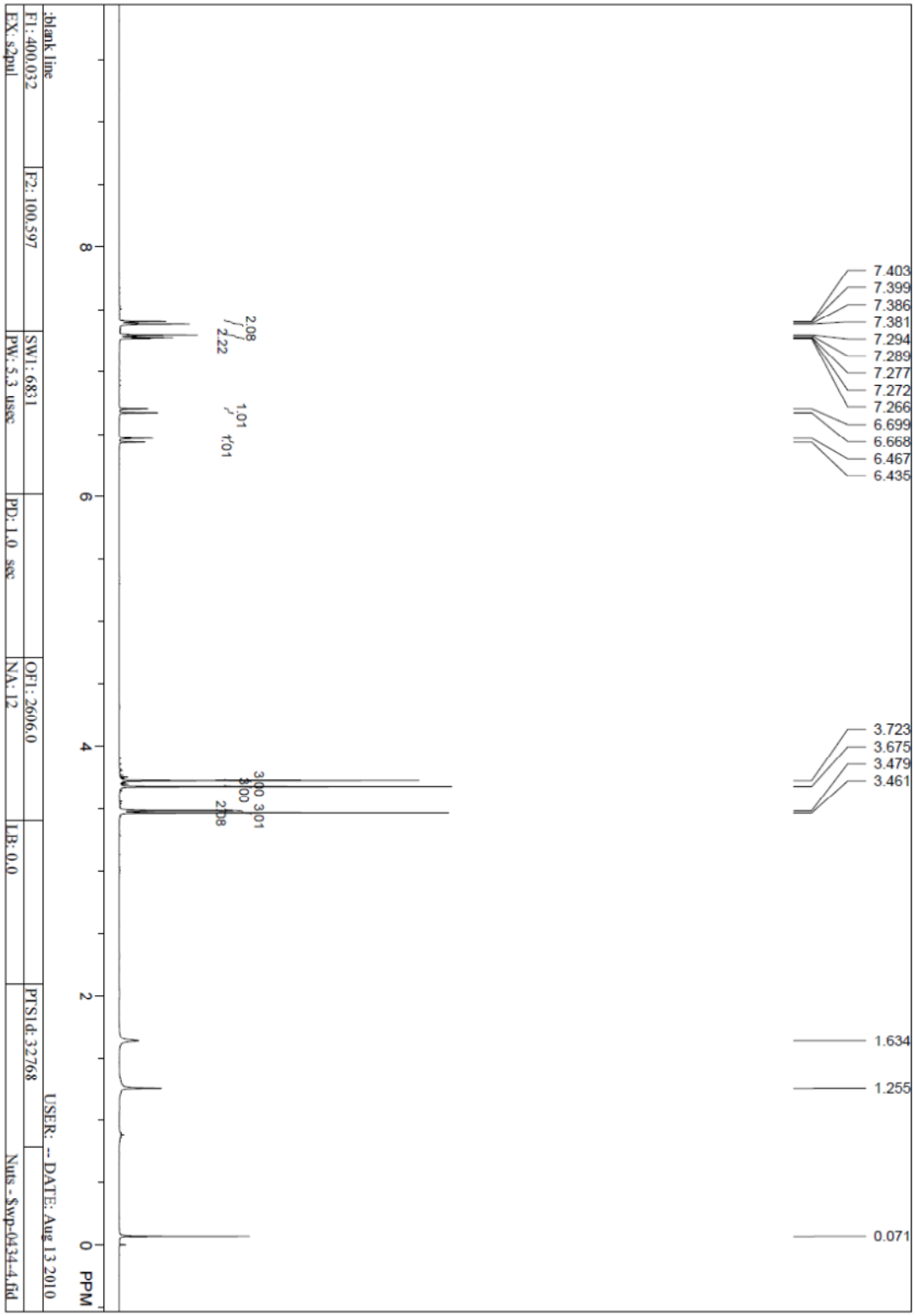
(3E, 5E)-**4a**

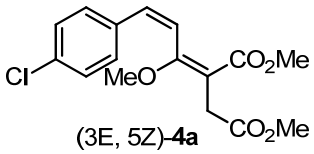
^{13}C NMR (100 M Hz in $CDCl_3$)



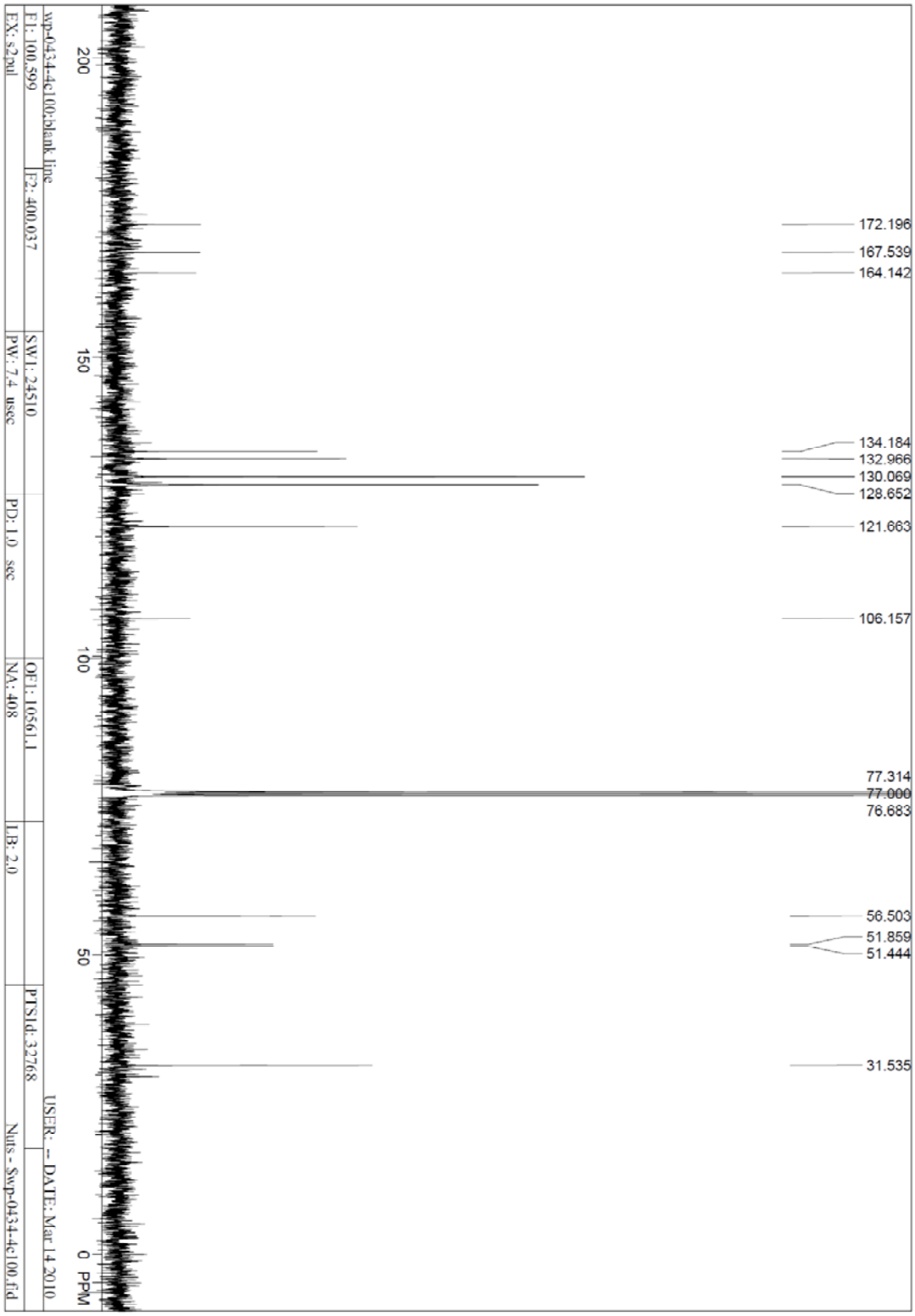


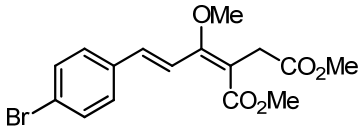
(3E, 5Z)-**4a** ^{1}H NMR (400 M Hz in $CDCl_3$)





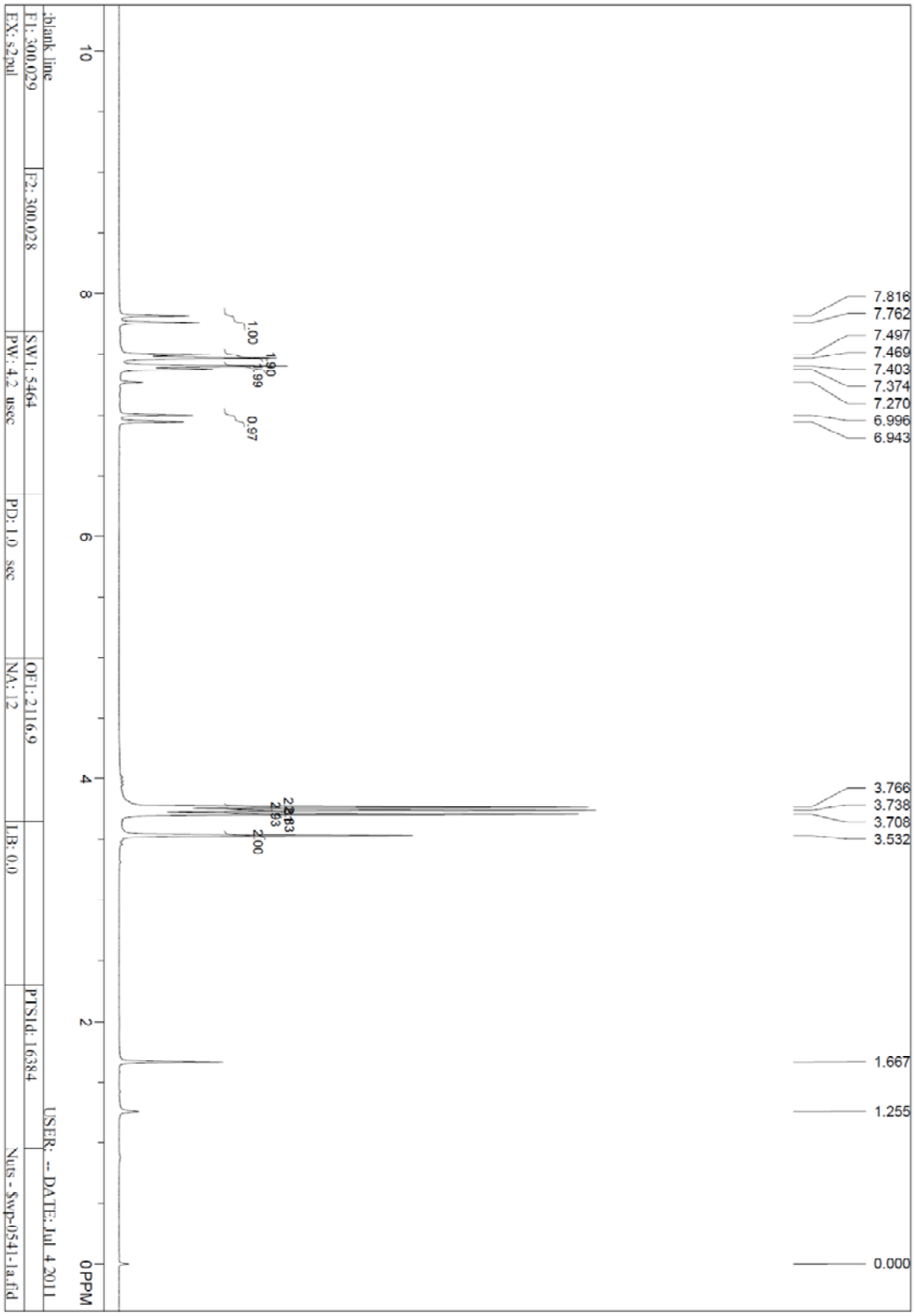
(3E, 5Z)-**4a** ^{13}C NMR (100 M Hz in $CDCl_3$)

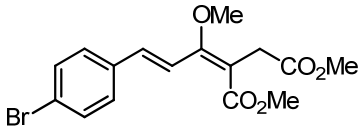




(3E, 5E)-**4b**

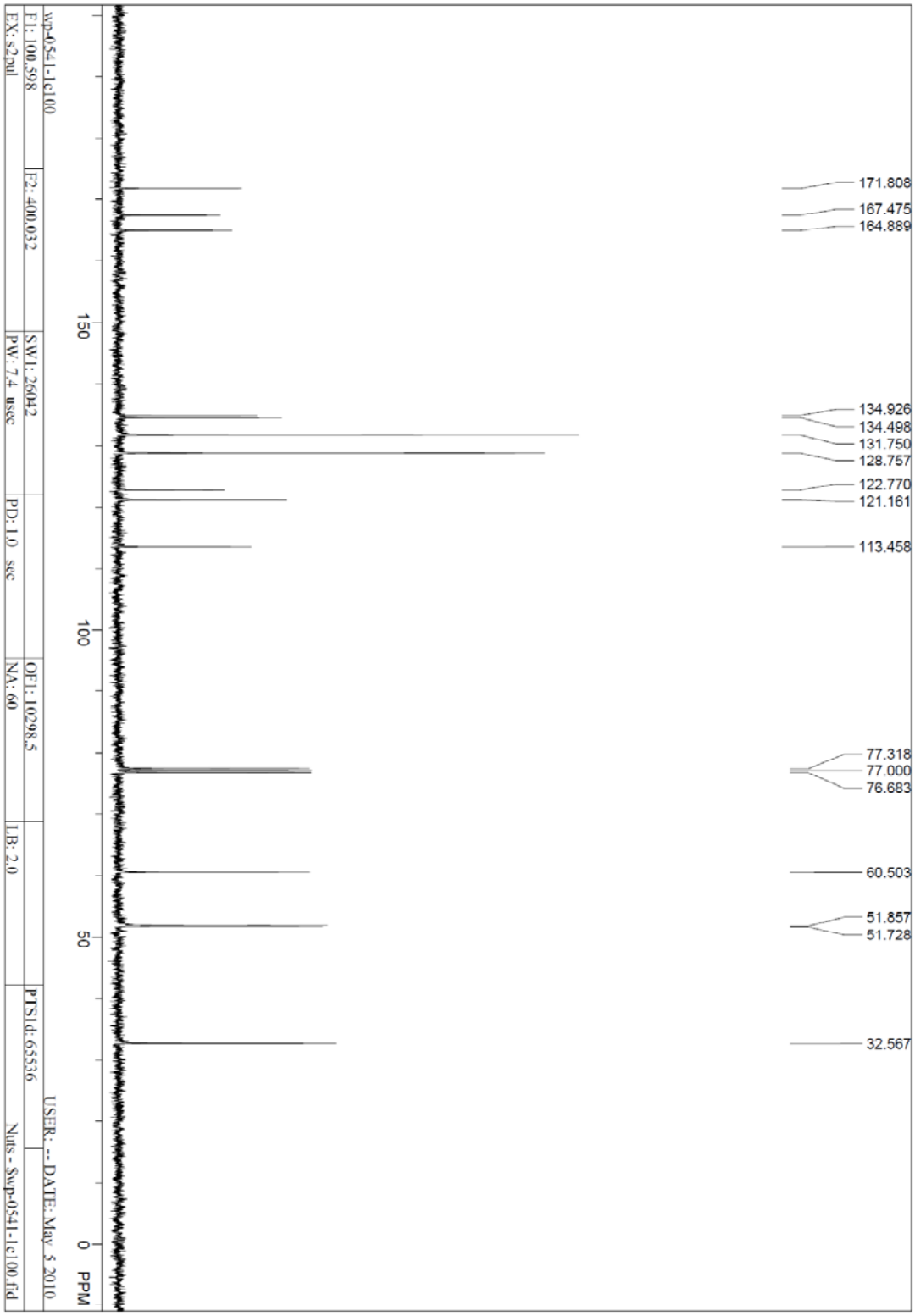
^{1}H NMR (400 M Hz in $CDCl_3$)

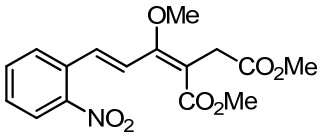




(3E, 5E)-**4b**

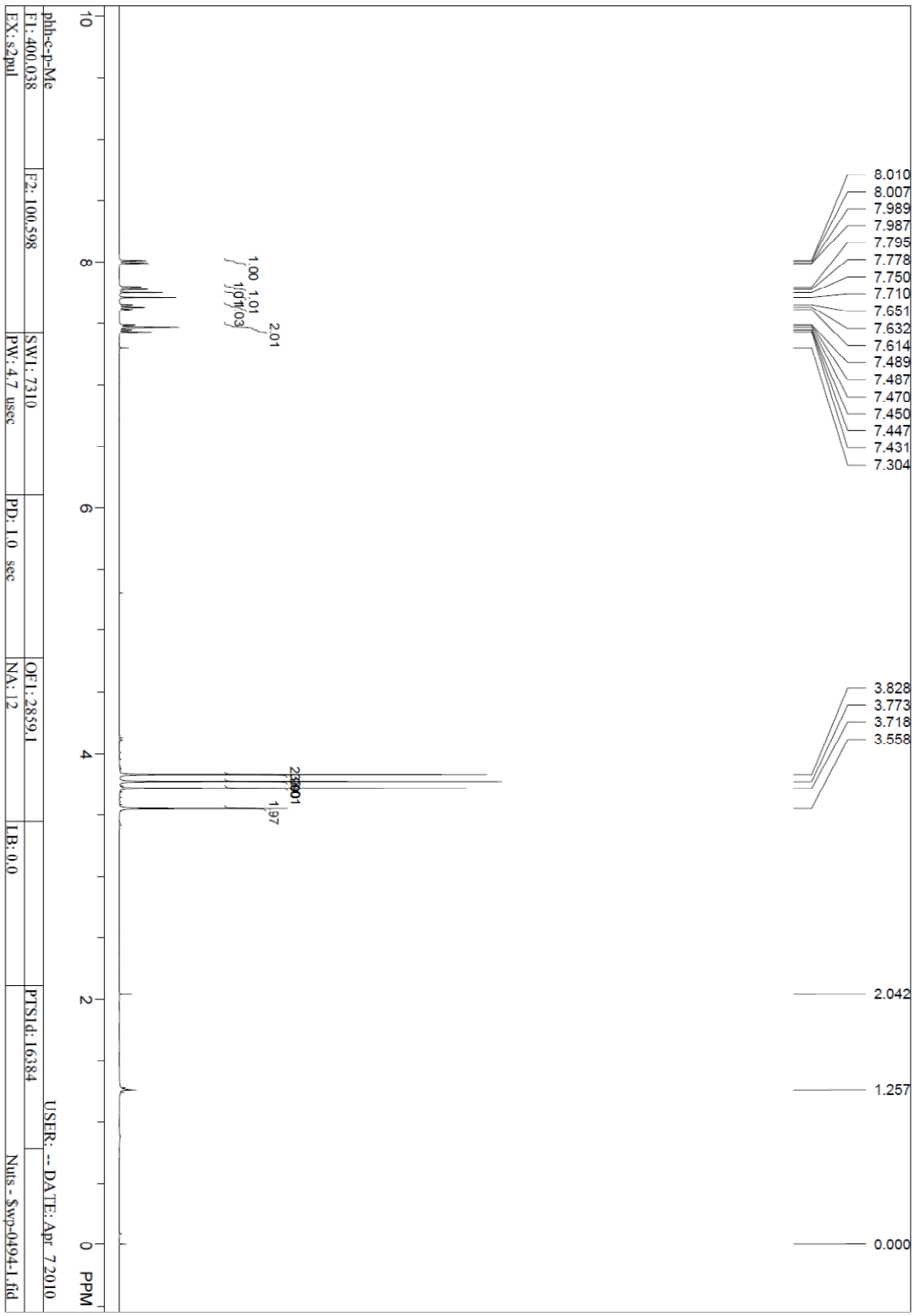
^{13}C NMR (100 M Hz in $CDCl_3$)

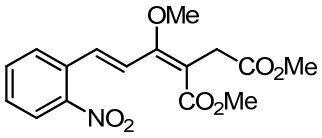




(3E, 5E)-**4c**

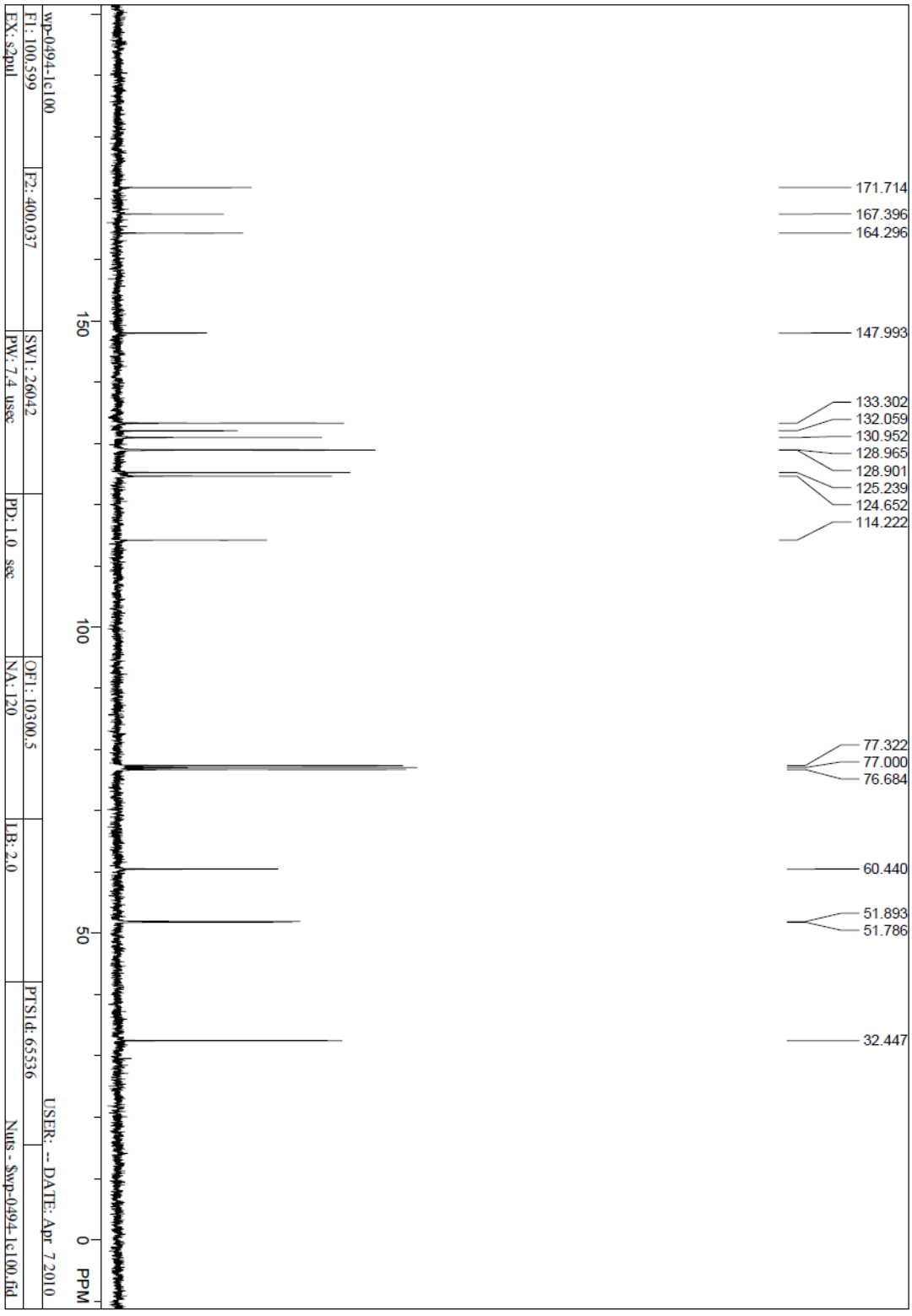
^{1}H NMR (400 M Hz in $CDCl_3$)

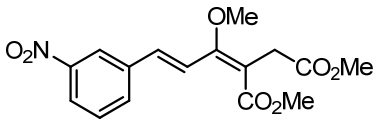




(3E, 5E)-**4c**

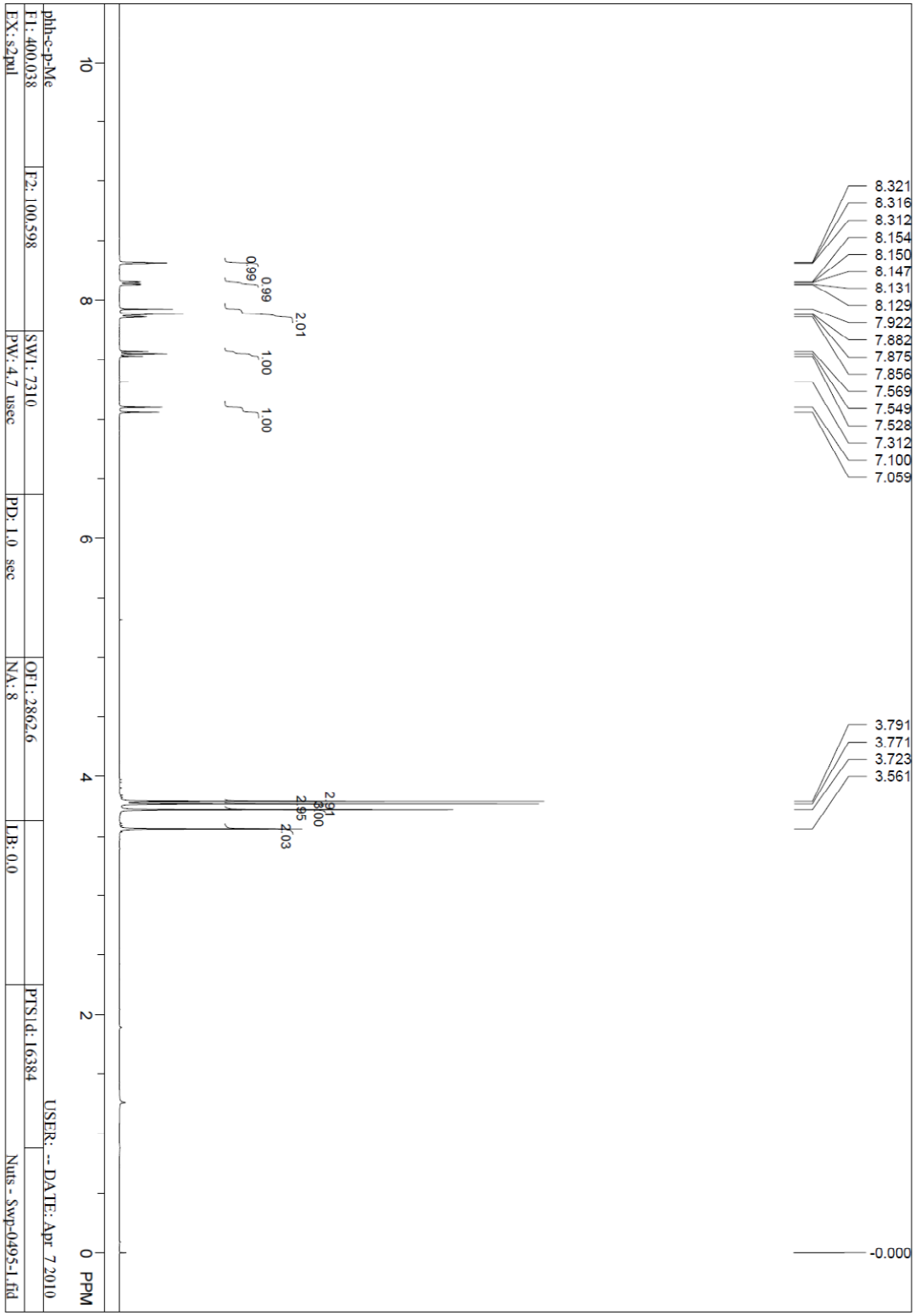
^{13}C NMR (100 M Hz in $CDCl_3$)

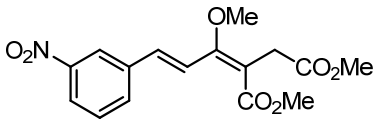




(3E, 5E)-**4d**

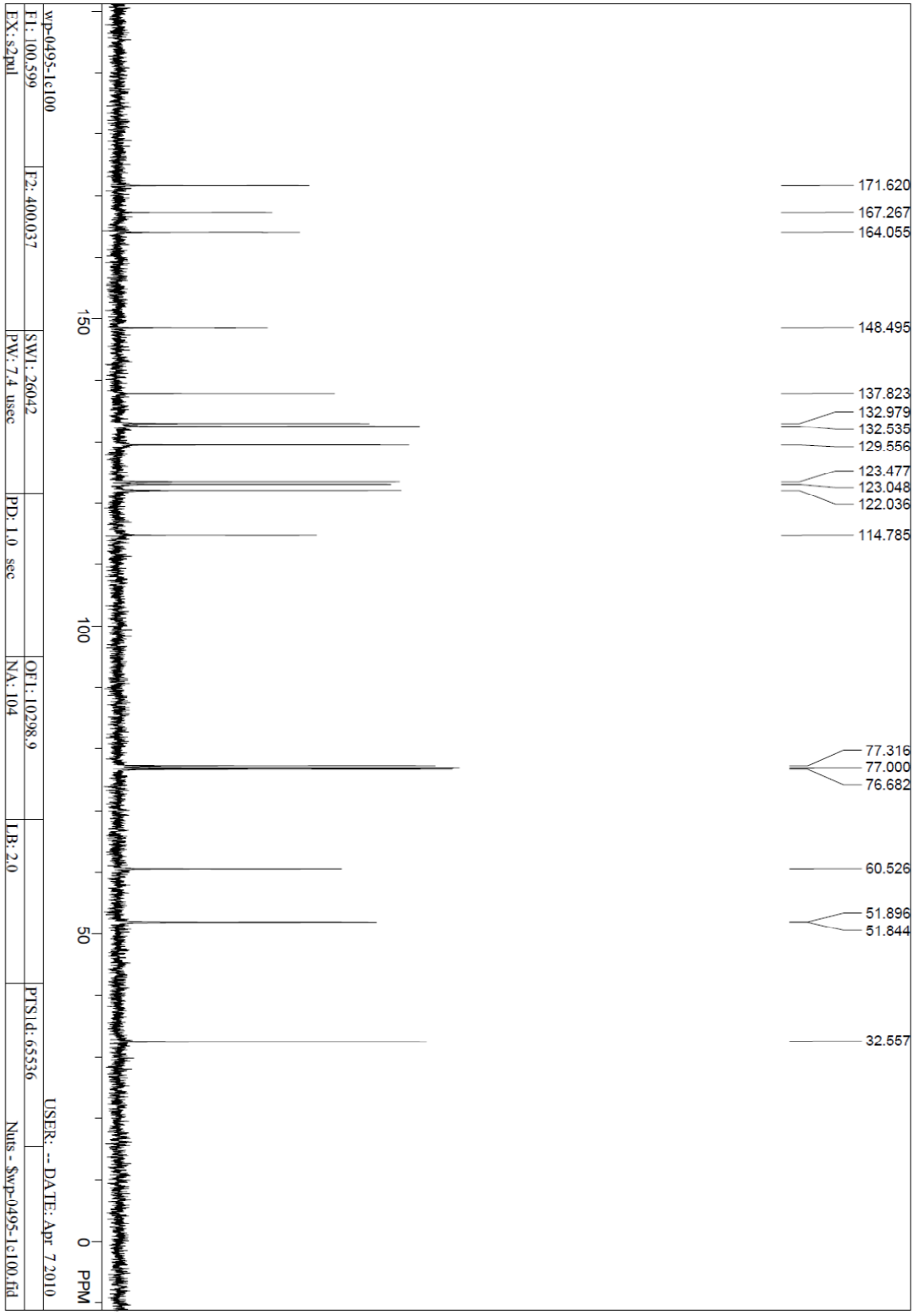
^{1}H NMR (400 M Hz in $CDCl_3$)

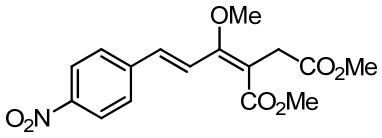




(3E, 5E)-**4d**

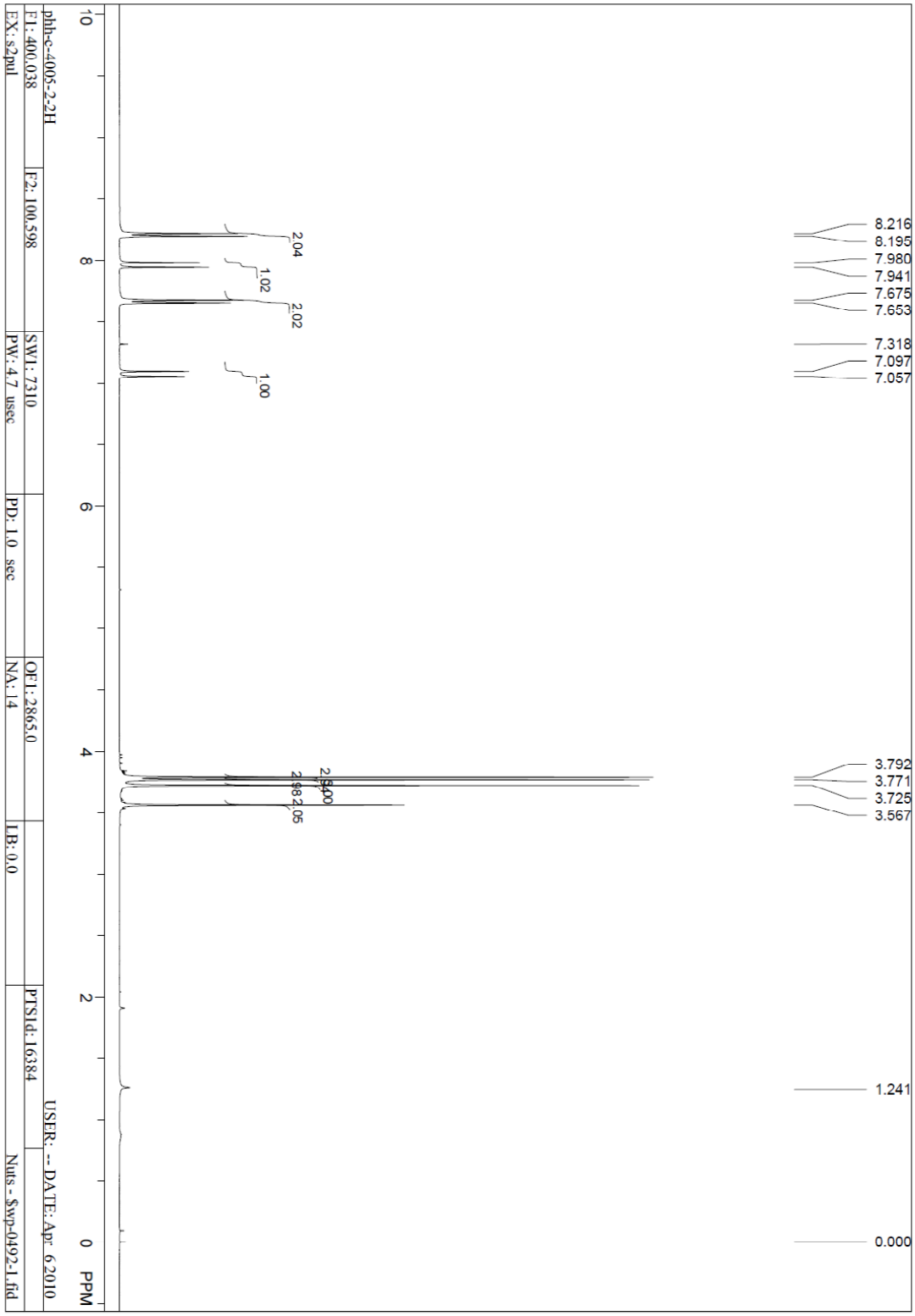
^{13}C NMR (100 M Hz in $CDCl_3$)

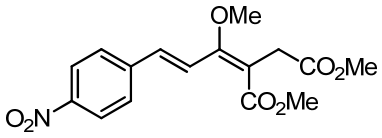




(3E, 5E)-**4e**

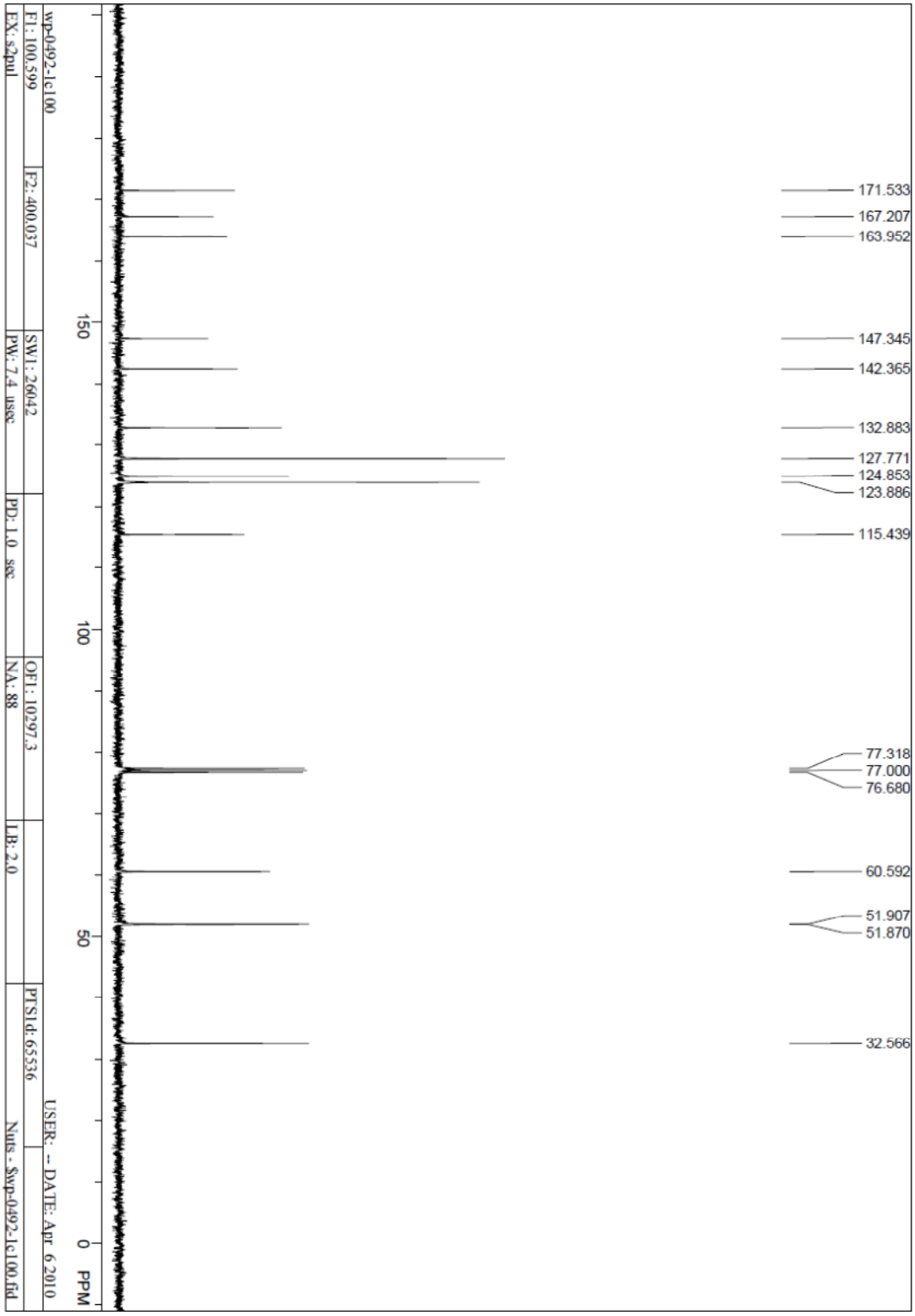
^{1}H NMR (400 M Hz in $CDCl_3$)

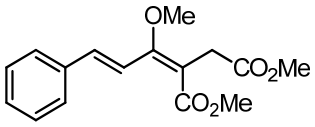




(3E, 5E)-**4e**

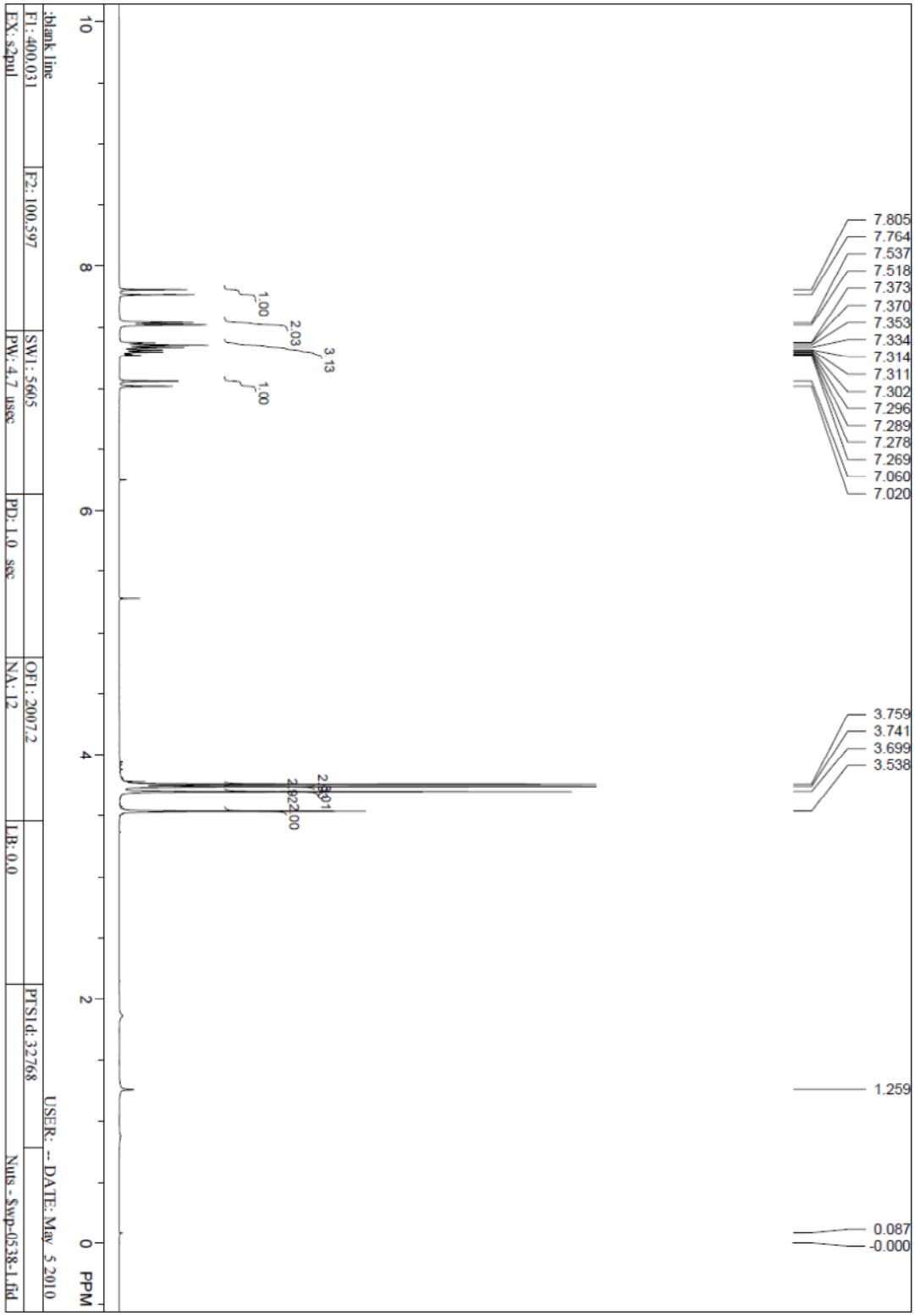
^{13}C NMR (100 M Hz in $CDCl_3$)

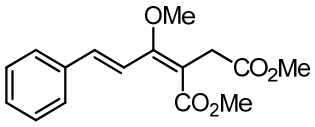




(3E, 5E)-**4f**

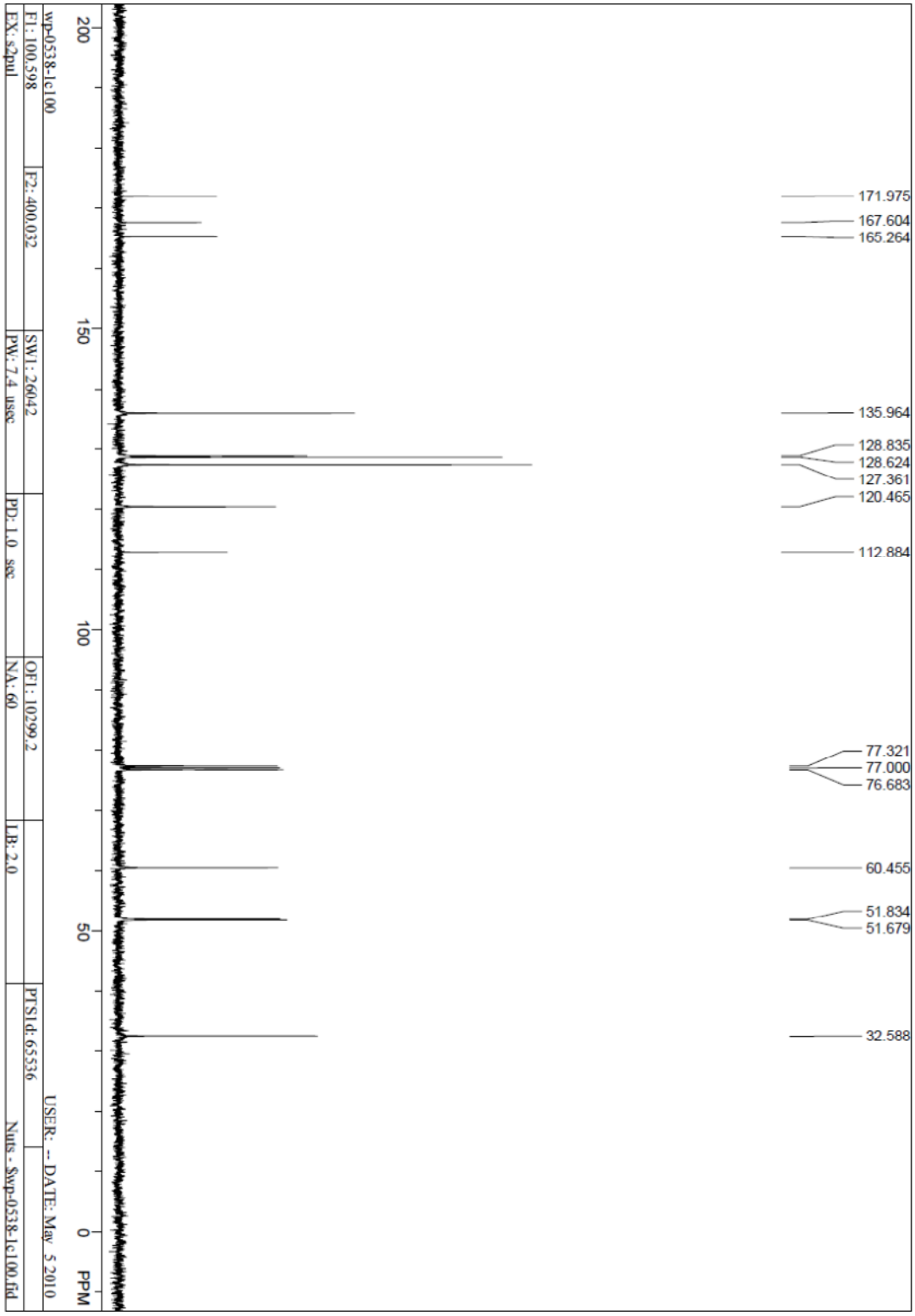
^{1}H NMR (400 M Hz in $CDCl_3$)

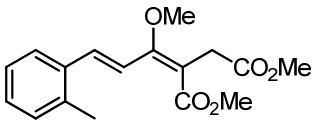




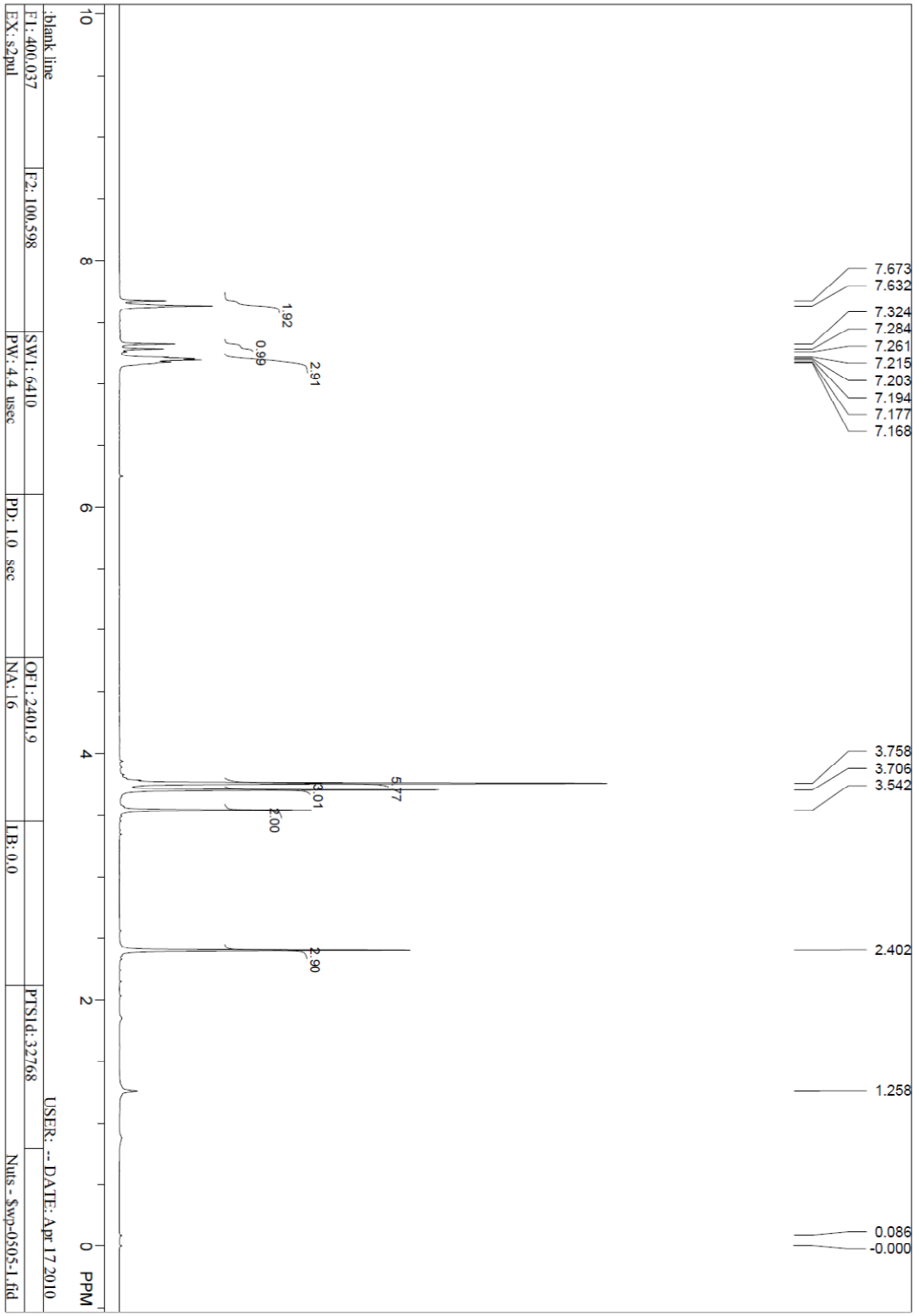
(3E, 5E)-**4f**

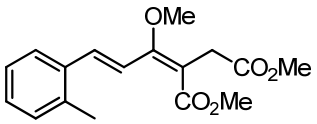
^{13}C NMR (100 M Hz in $CDCl_3$)





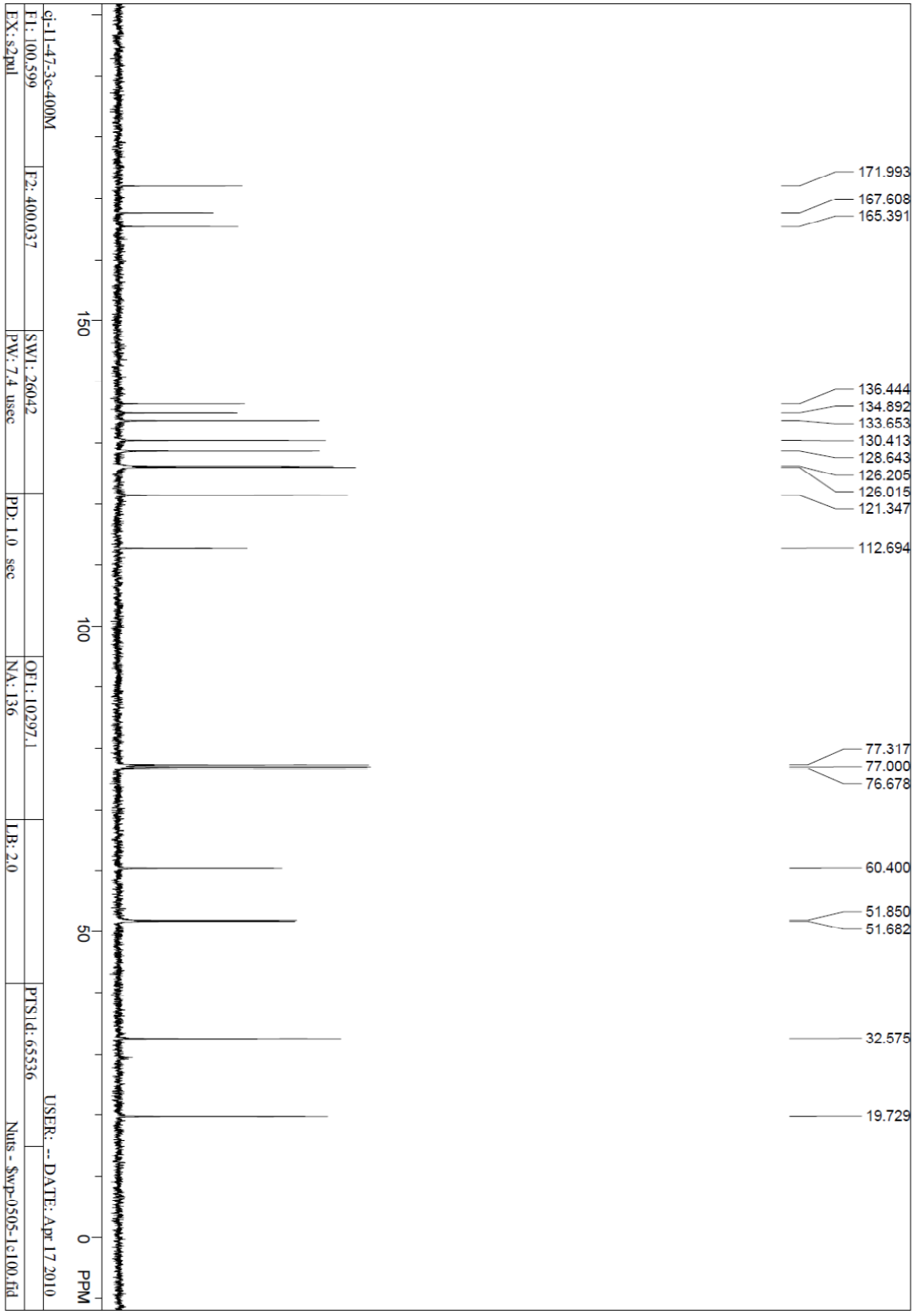
(3E, 5E)-**4g** ^{1}H NMR (400 M Hz in $CDCl_3$)

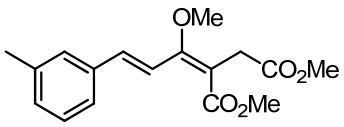




(3E, 5E)-**4g**

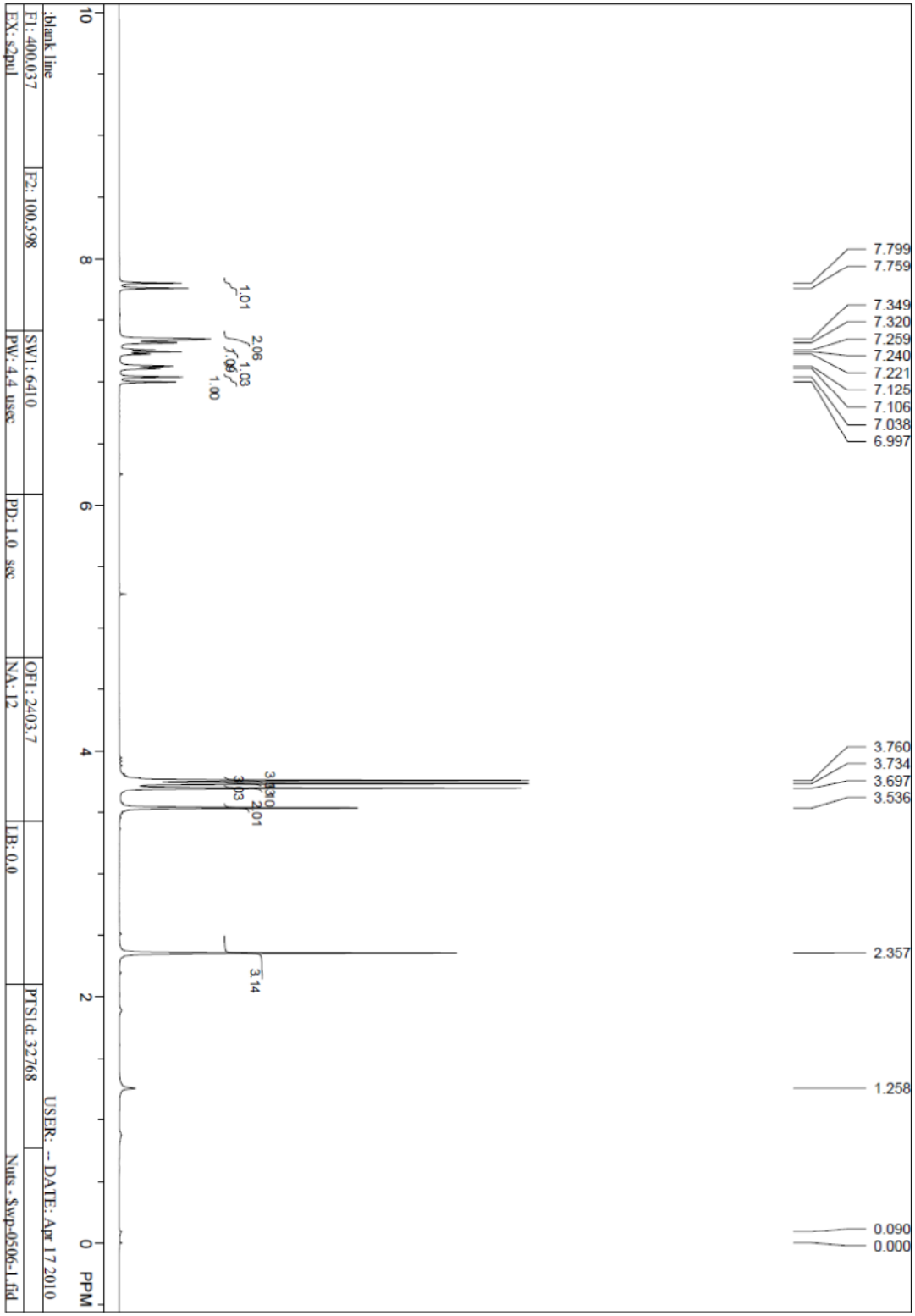
^{13}C NMR (100 M Hz in $CDCl_3$)

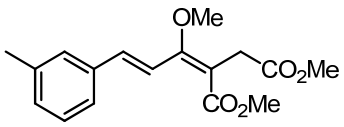




(3E, 5E)-**4h**

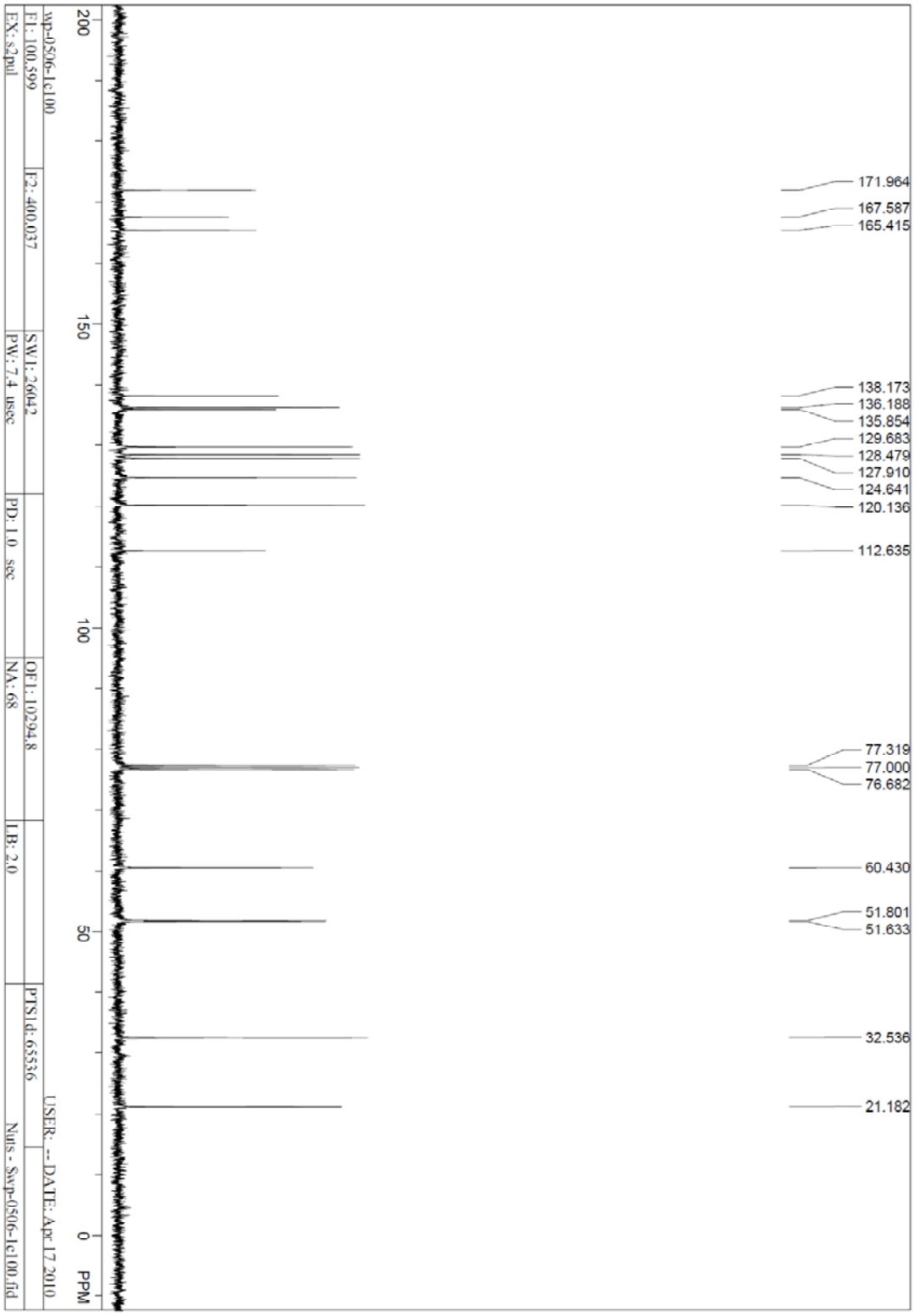
^{1}H NMR (400 M Hz in $CDCl_3$)

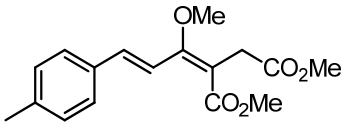




(3E, 5E)-**4h**

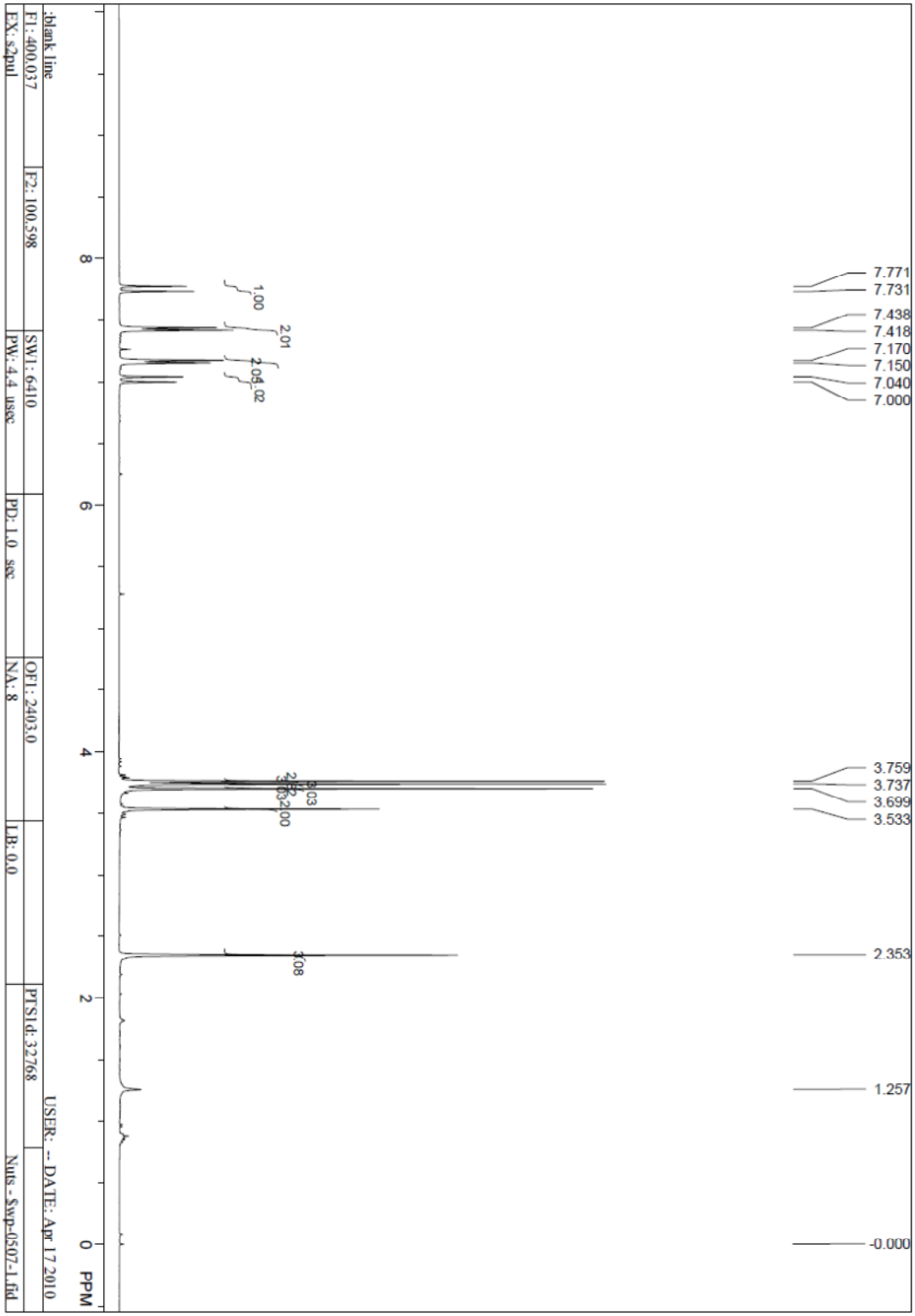
^{13}C NMR (100 M Hz in $CDCl_3$)

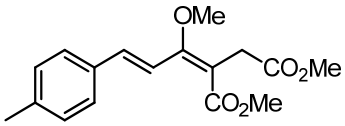




(3E, 5E)-**4i**

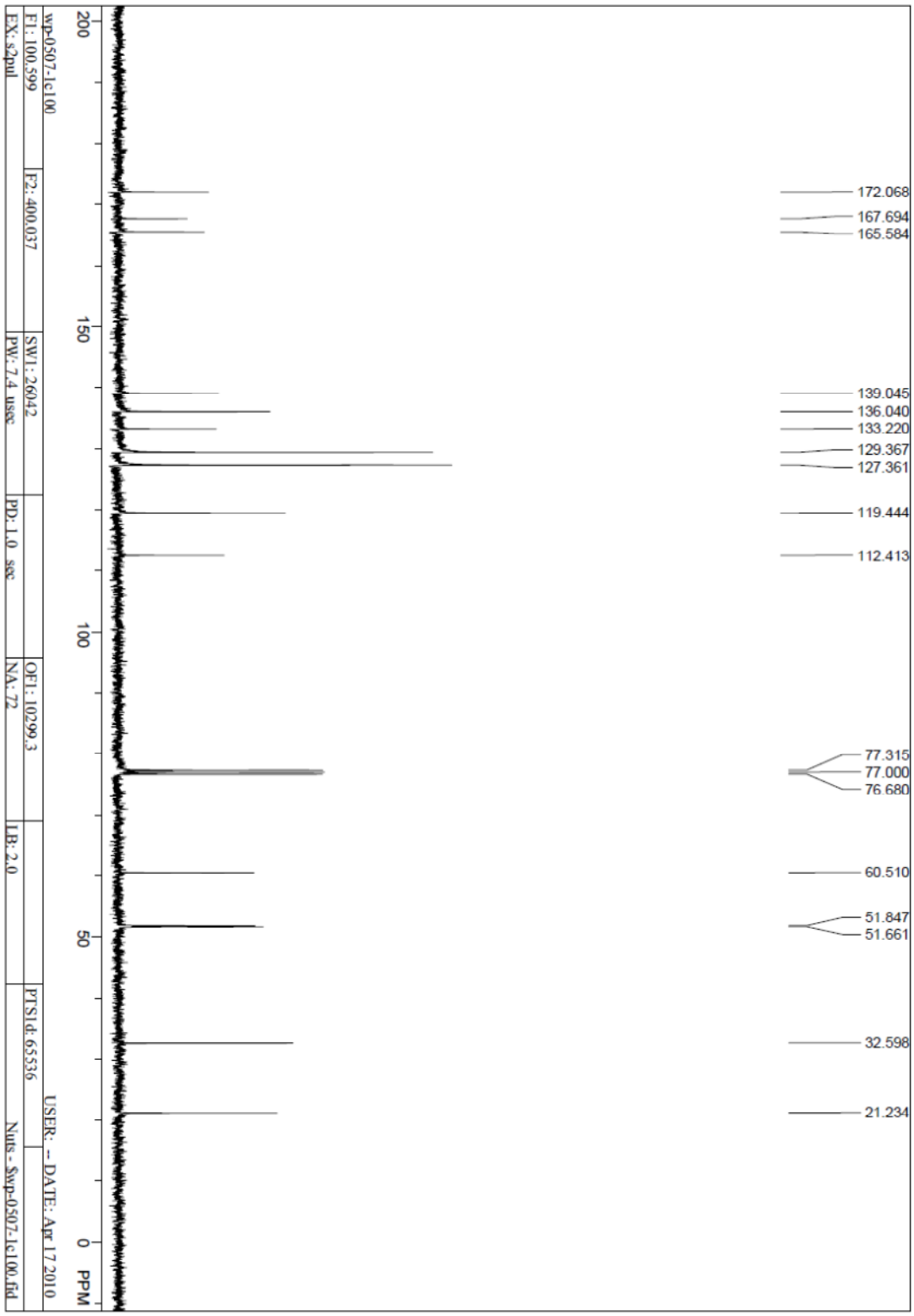
^{1}H NMR (400 M Hz in $CDCl_3$)

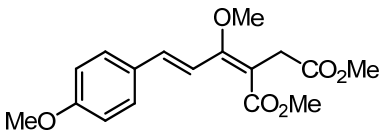




(3E, 5E)-**4i**

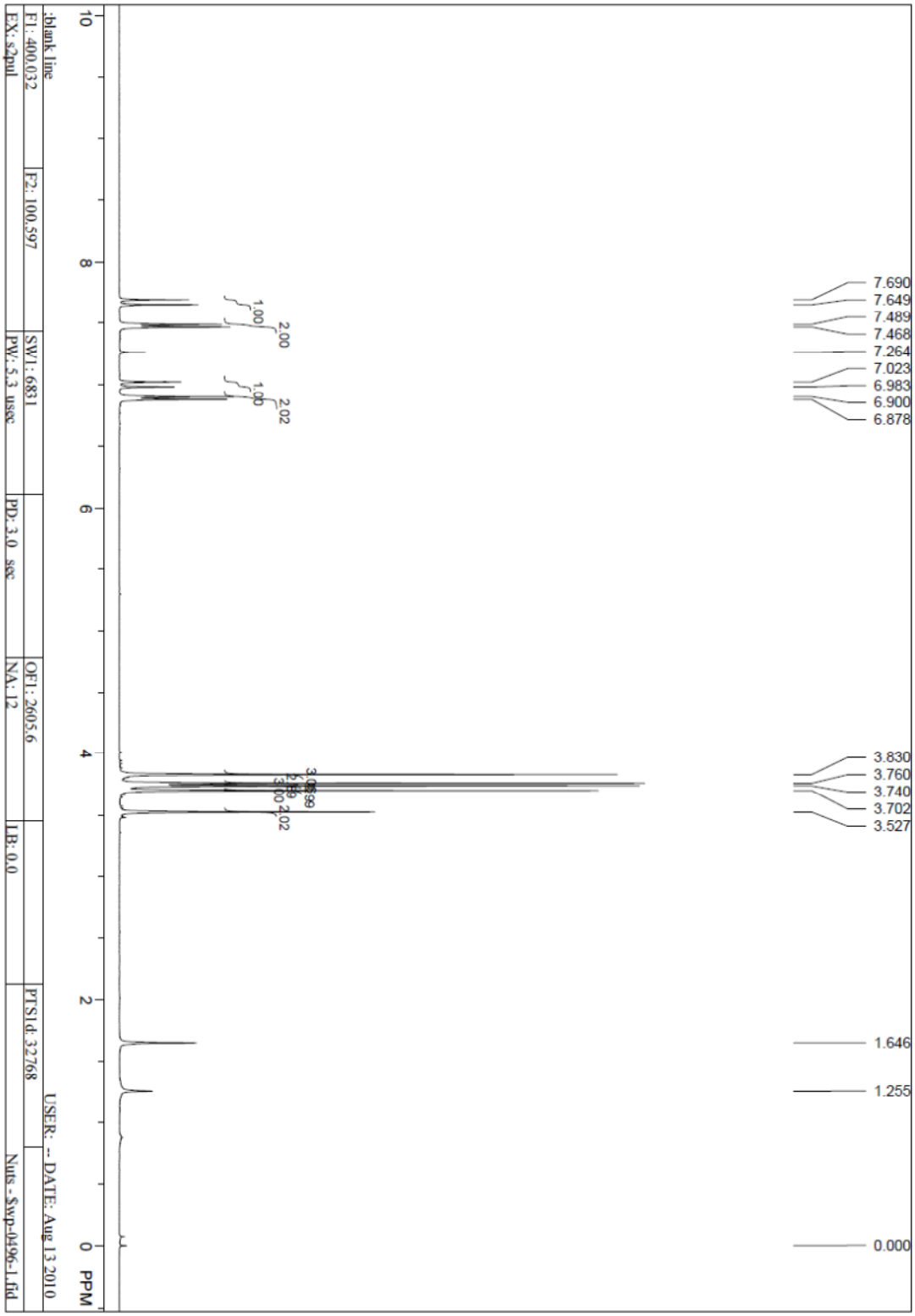
^{13}C NMR (100 M Hz in $CDCl_3$)

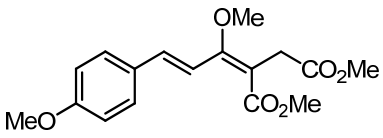




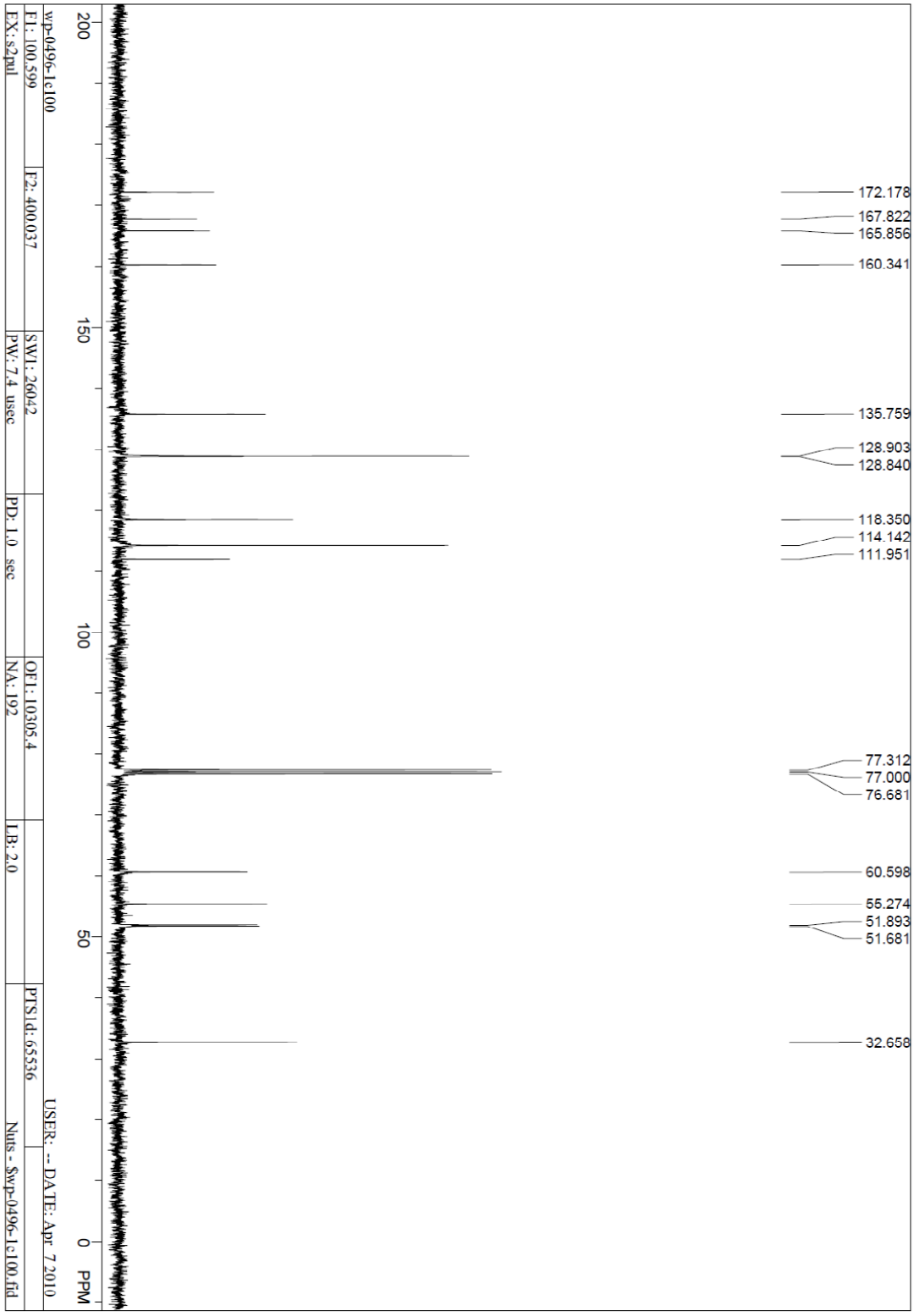
(3E, 5E)-**4j**

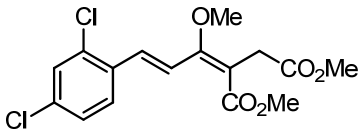
^{1}H NMR (400 M Hz in $CDCl_3$)





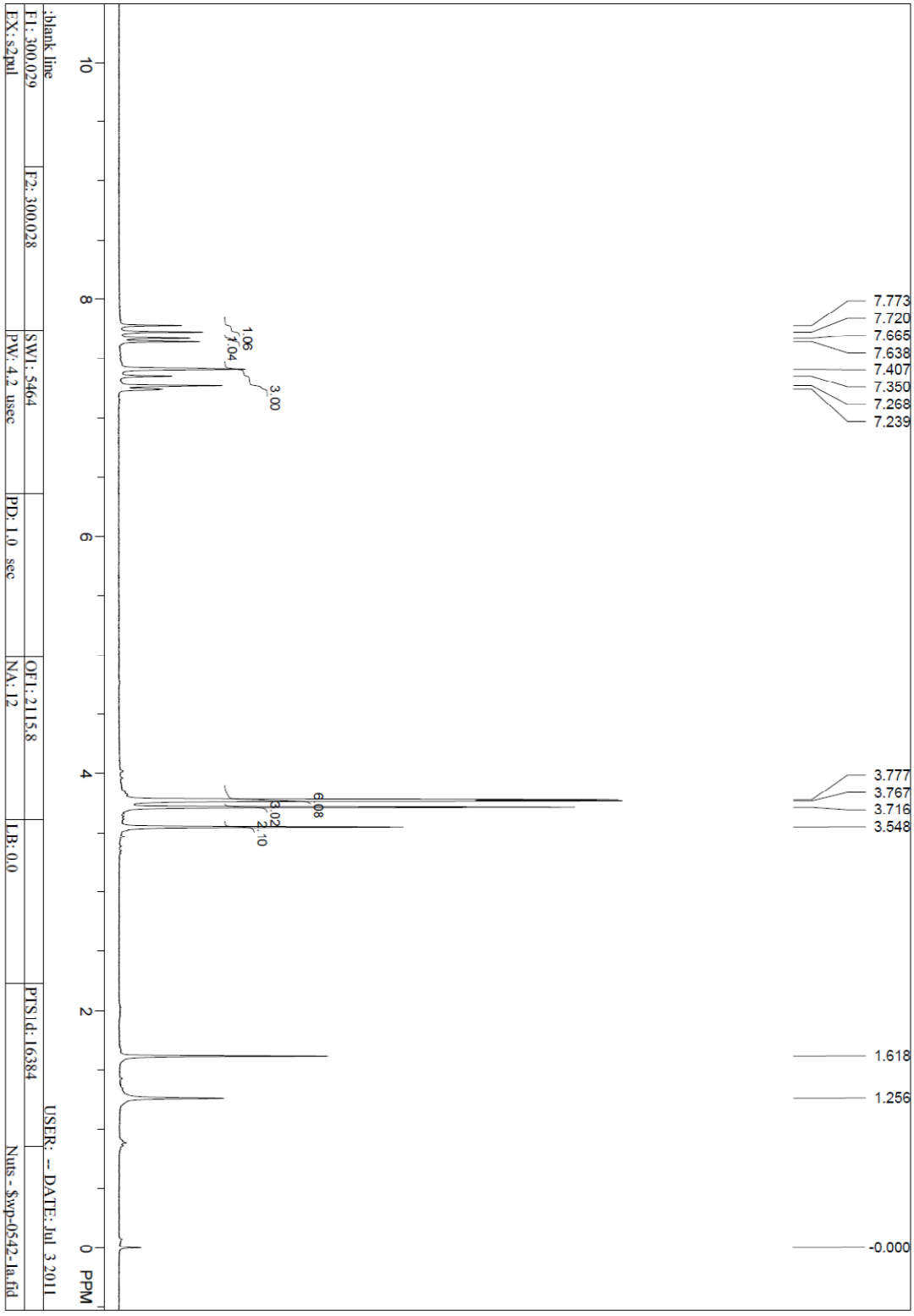
(3E, 5E)-**4j** ^{13}C NMR (100 M Hz in $CDCl_3$)

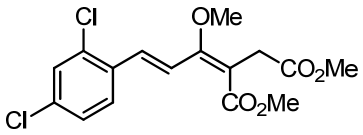




(3E, 5E)-**4k**

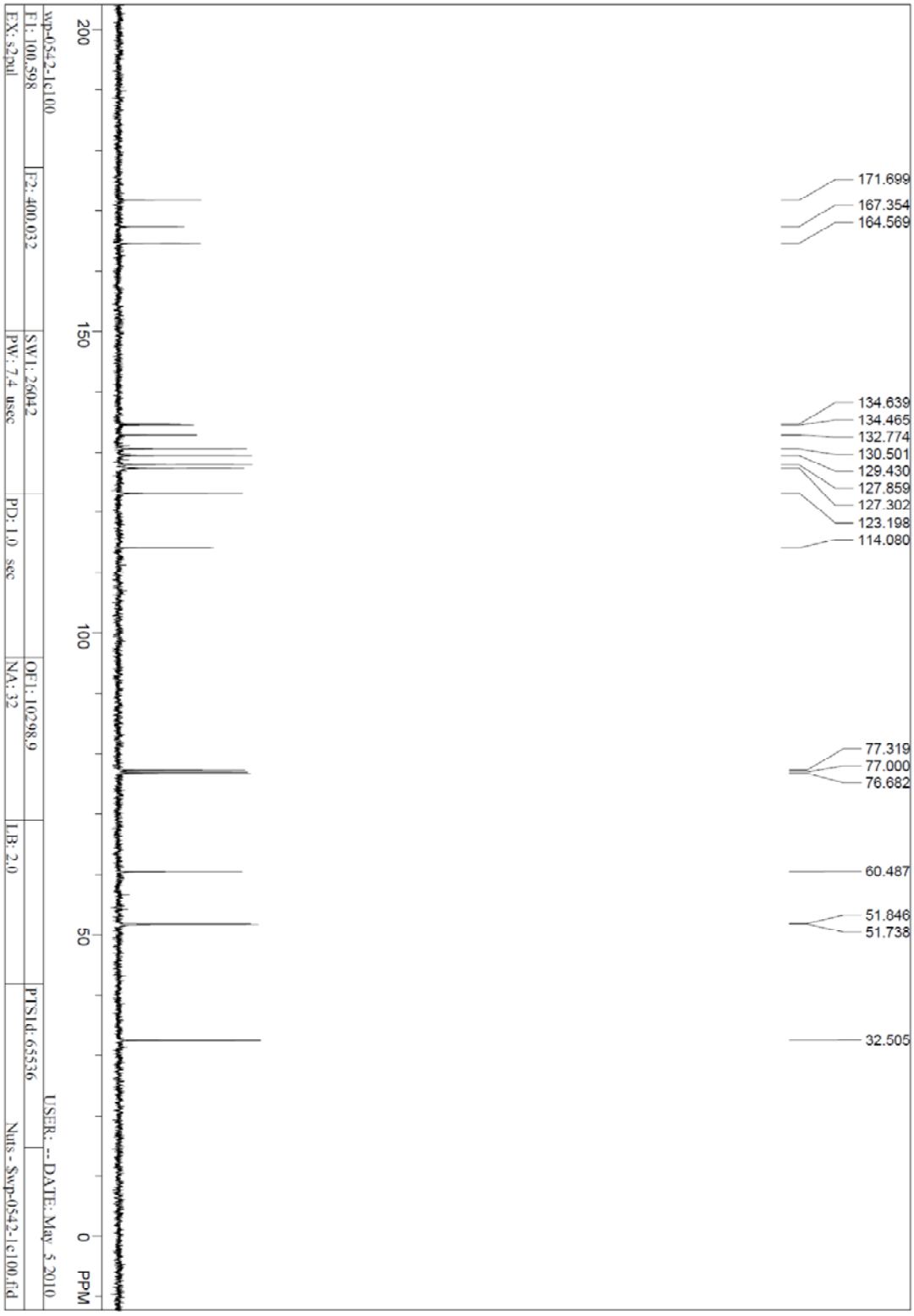
^{1}H NMR (300 M Hz in $CDCl_3$)

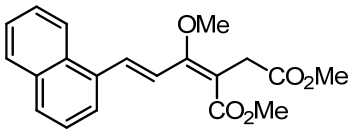




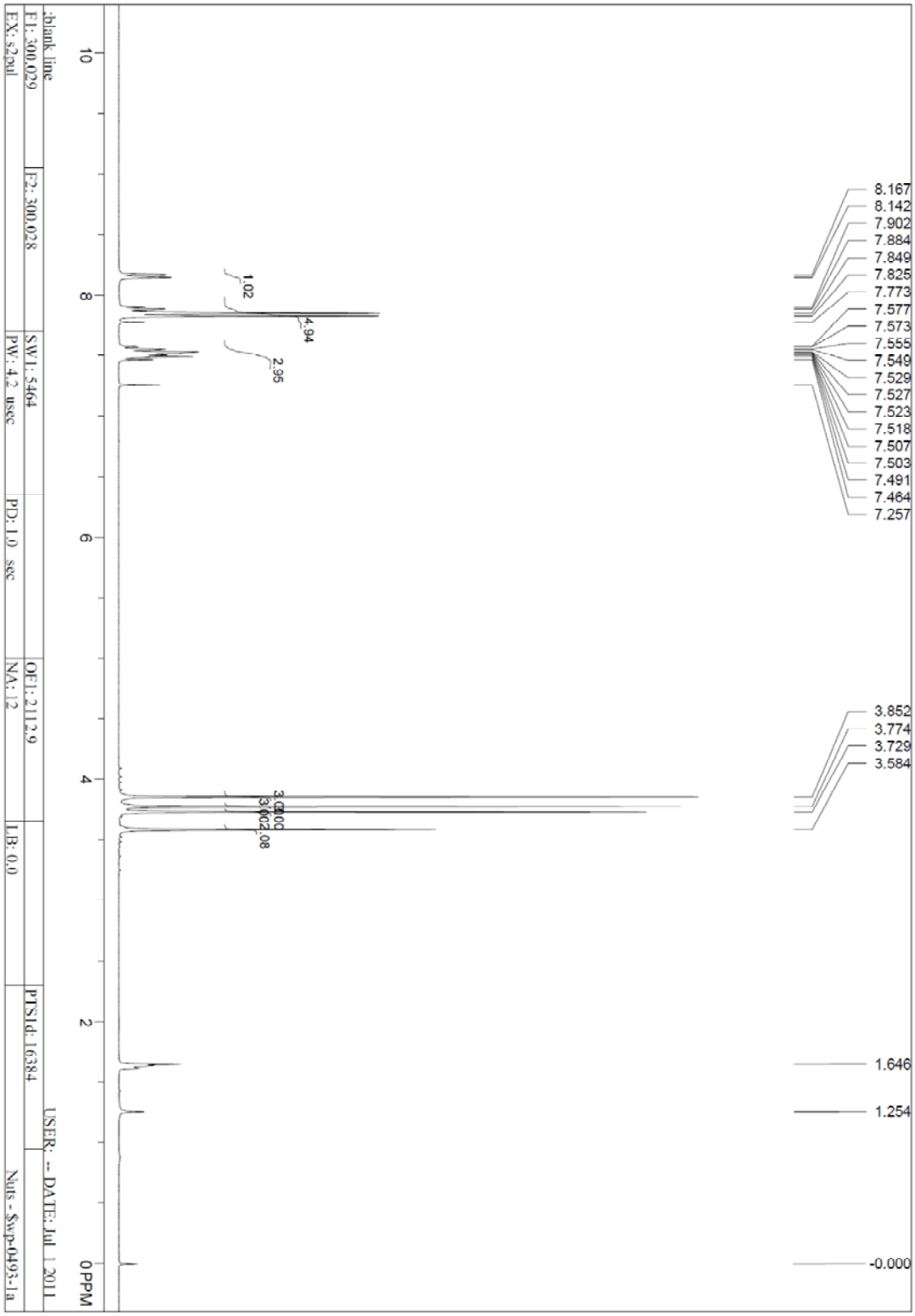
(3E, 5E)-**4k**

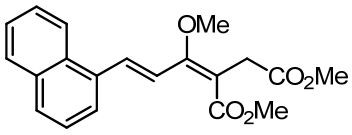
^{13}C NMR (100 M Hz in $CDCl_3$)





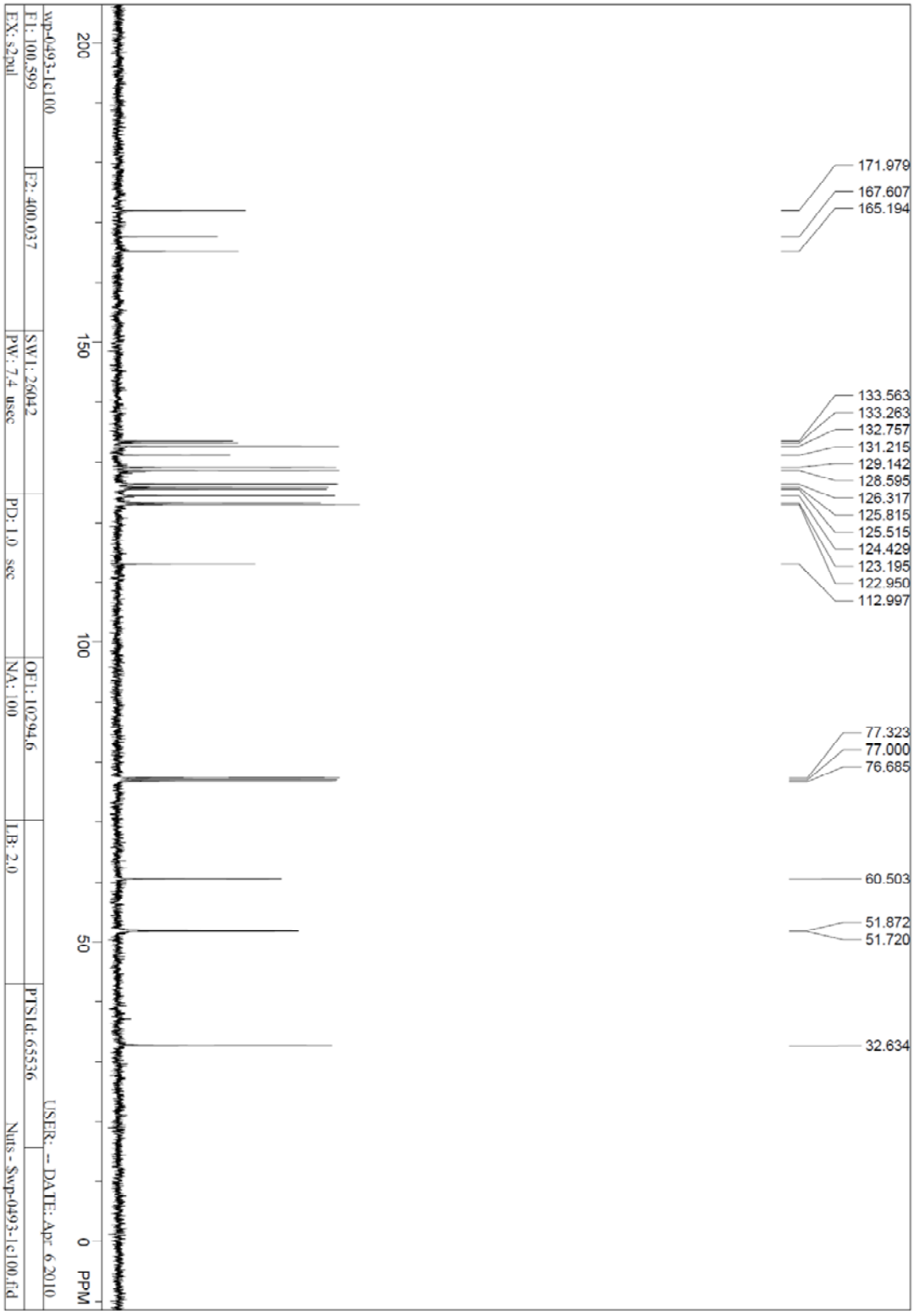
(3E, 5E)-**4l** ^{1}H NMR (300 M Hz in $CDCl_3$)

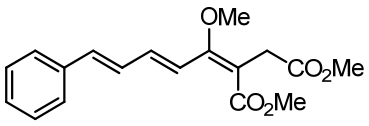




(3E, 5E)-**4l**

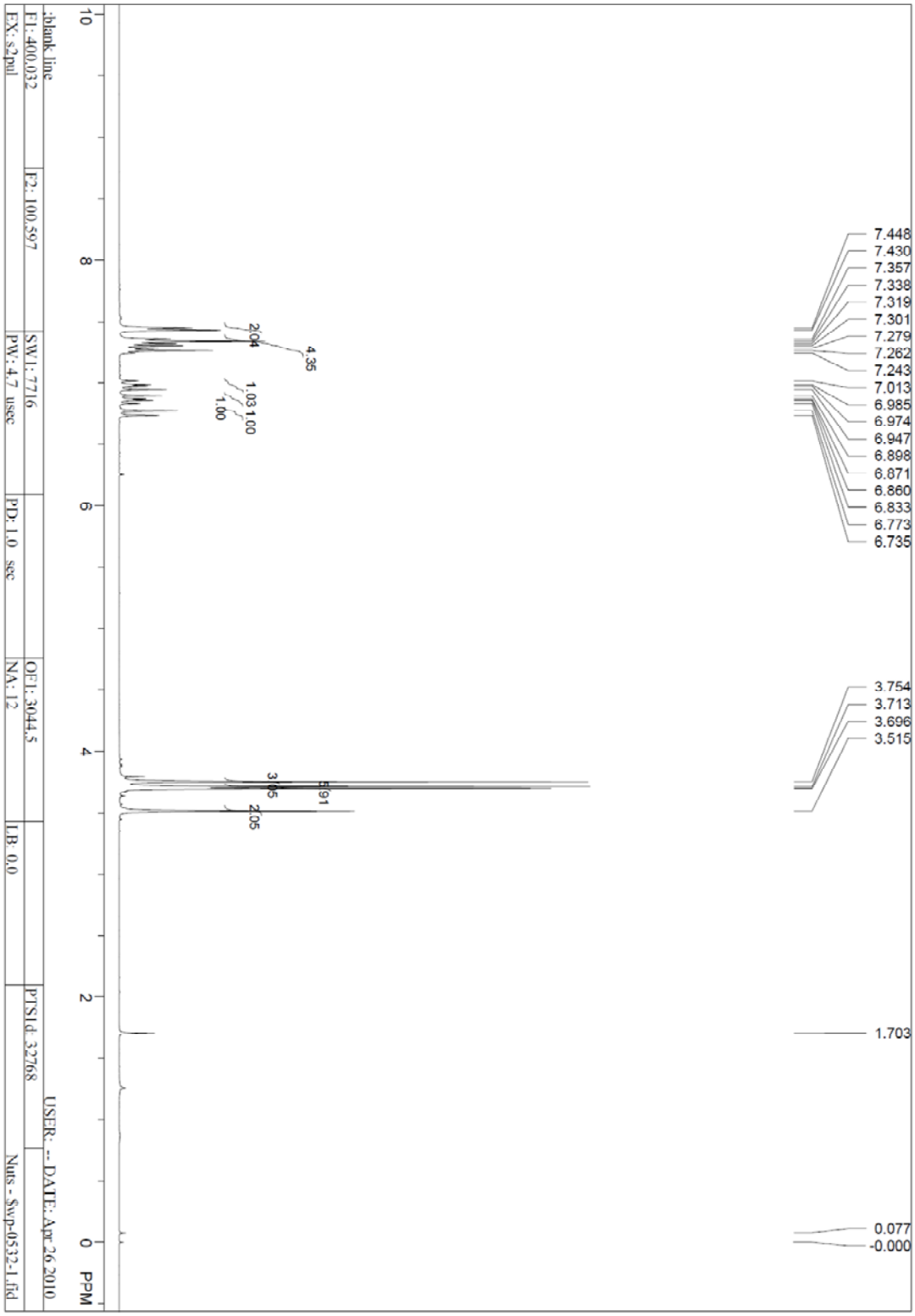
^{13}C NMR (100 M Hz in $CDCl_3$)

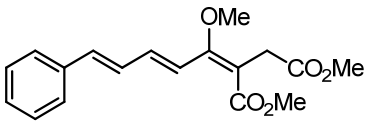




(3E, 5E)-**4m**

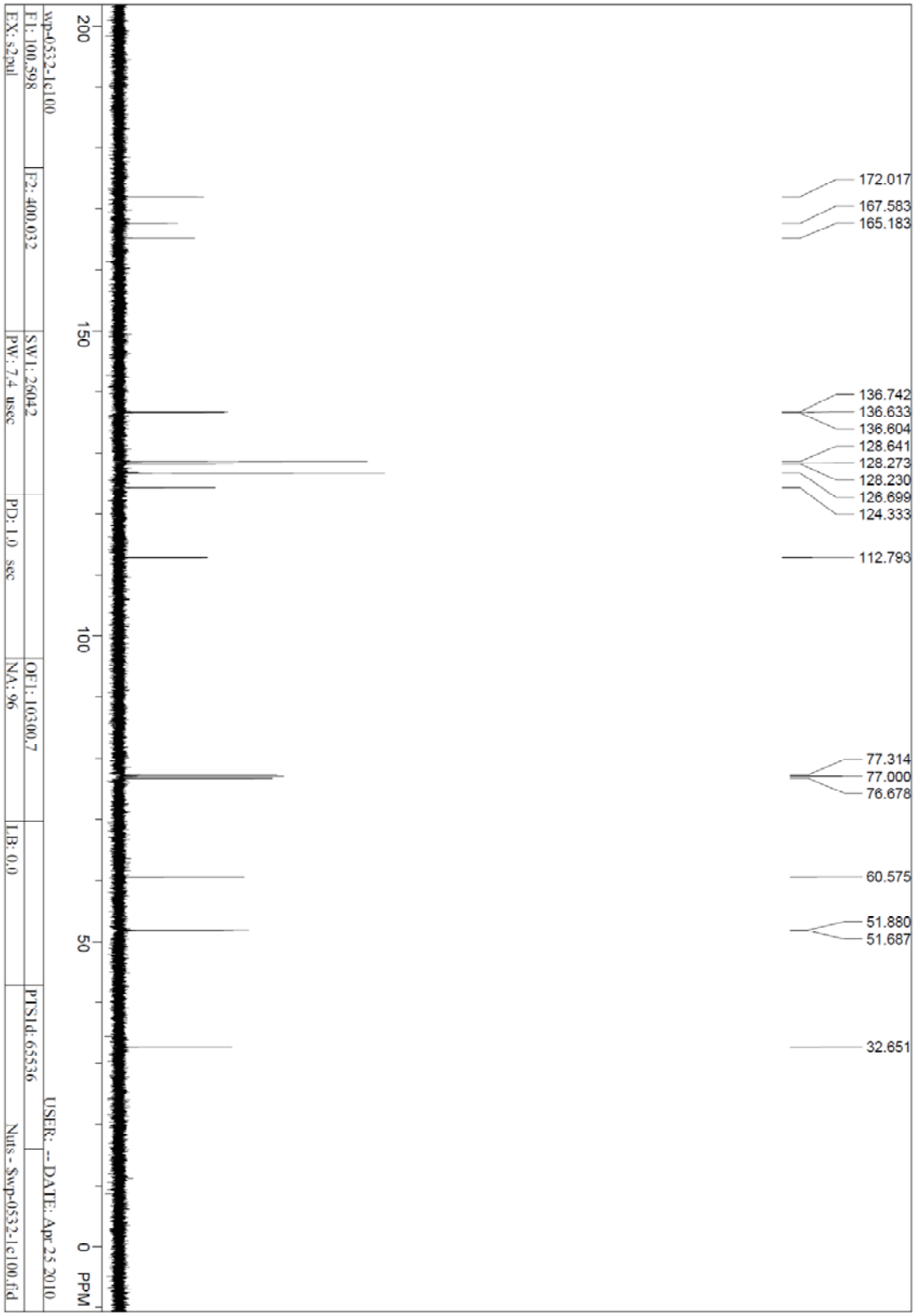
^{1}H NMR (400 M Hz in $CDCl_3$)

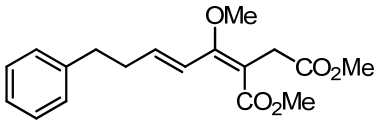




(3E, 5E)-**4m**

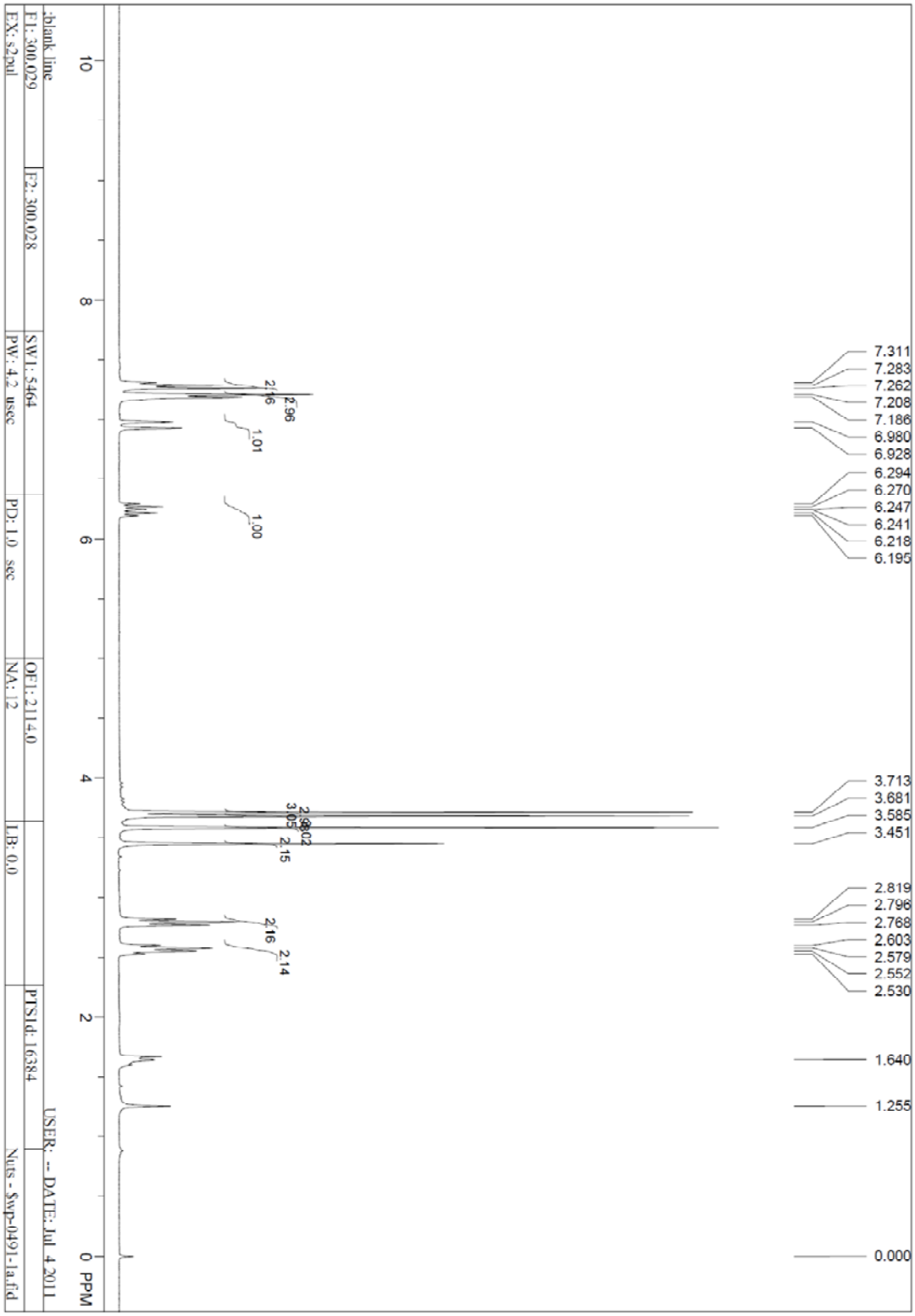
^{13}C NMR (100 M Hz in $CDCl_3$)

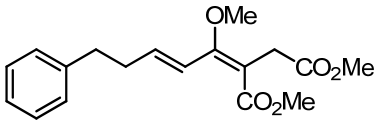




(3E, 5E)-**4n**

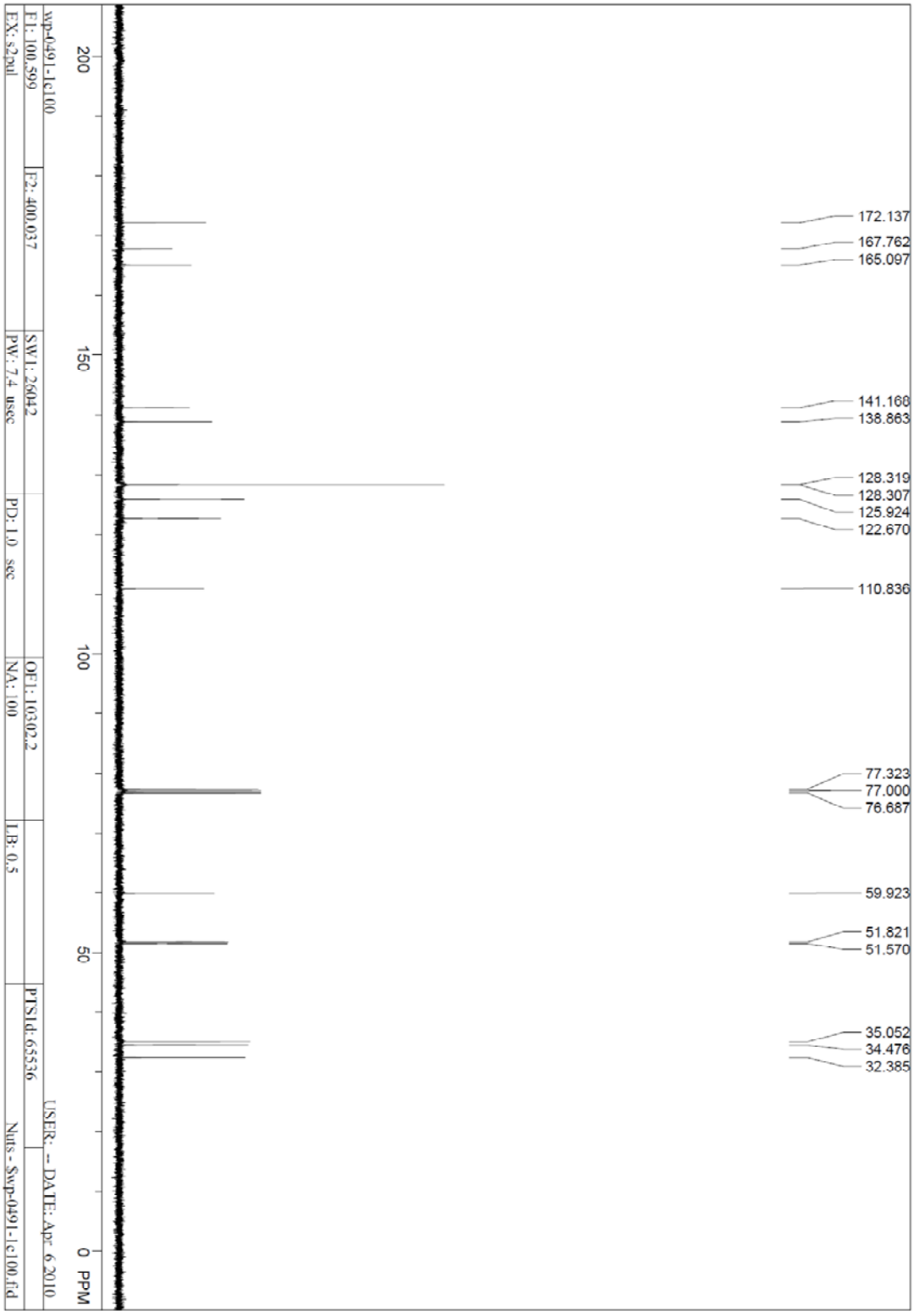
^{1}H NMR (300 M Hz in $CDCl_3$)

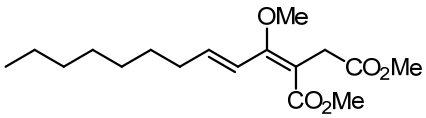




(3E, 5E)-**4n**

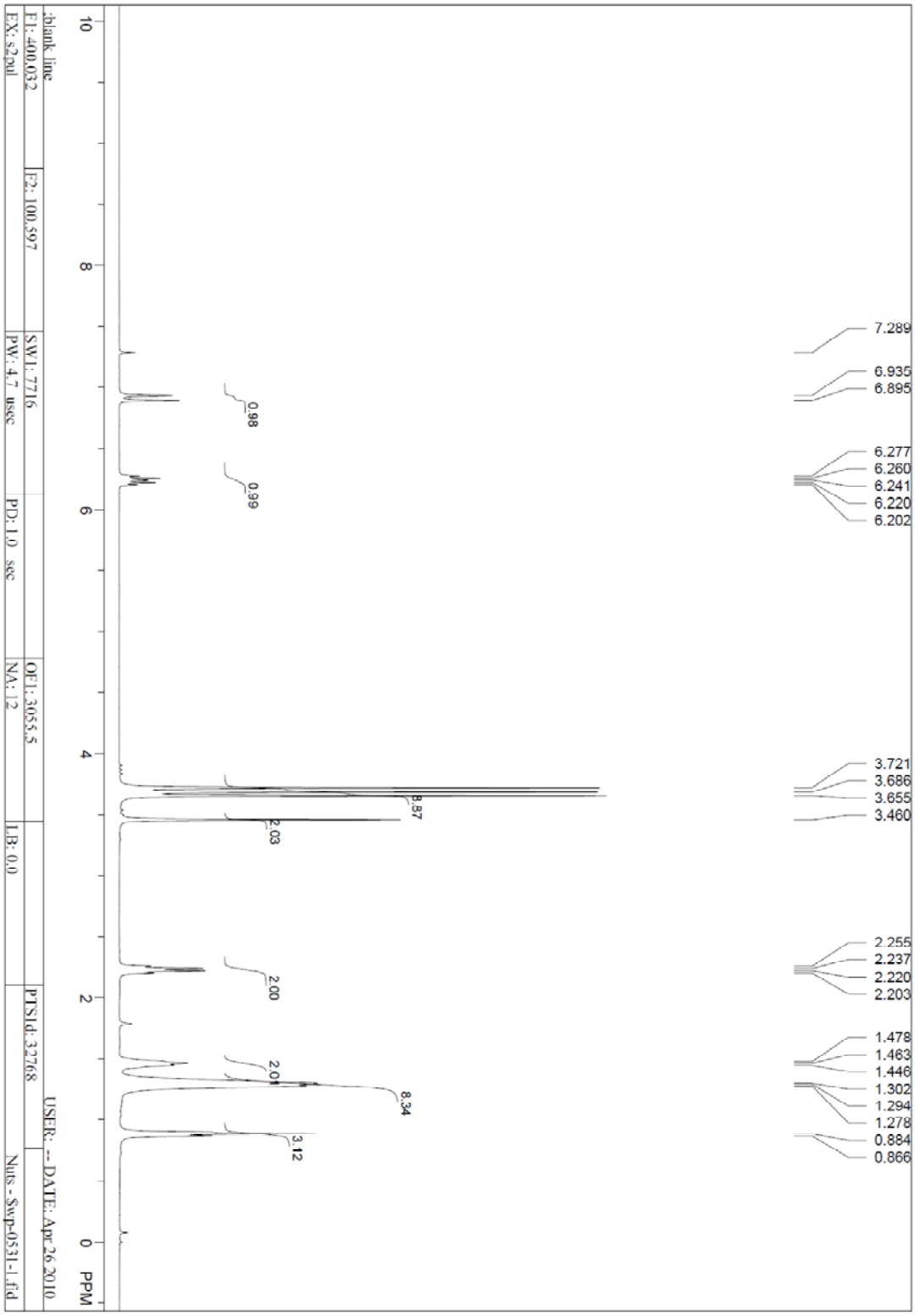
^{13}C NMR (100 M Hz in $CDCl_3$)

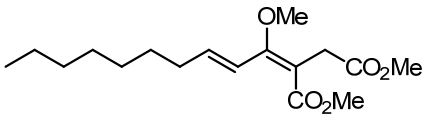




(3E, 5E)-**4o**

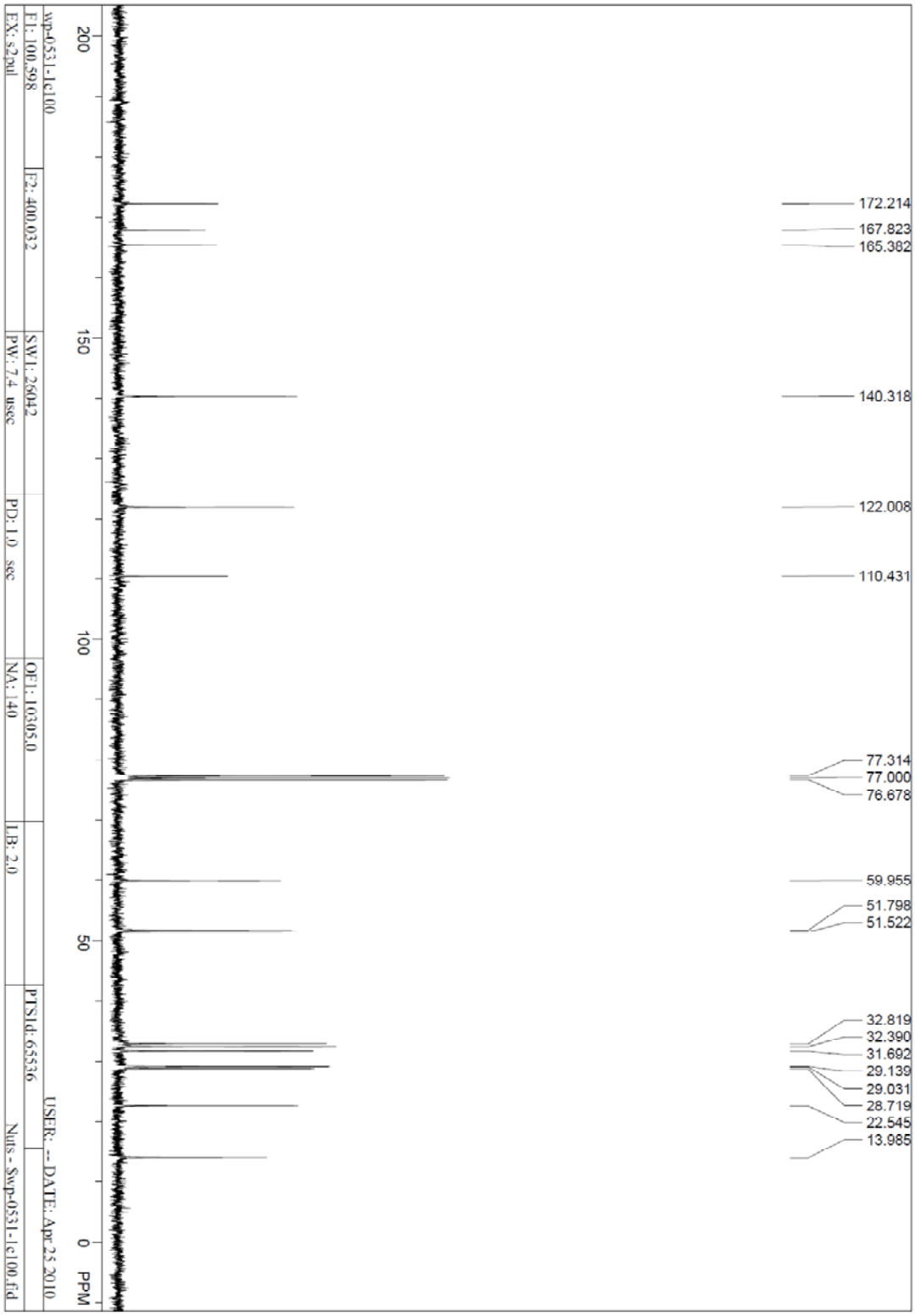
^{1}H NMR (400 M Hz in $CDCl_3$)

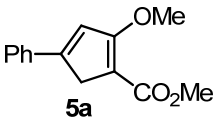




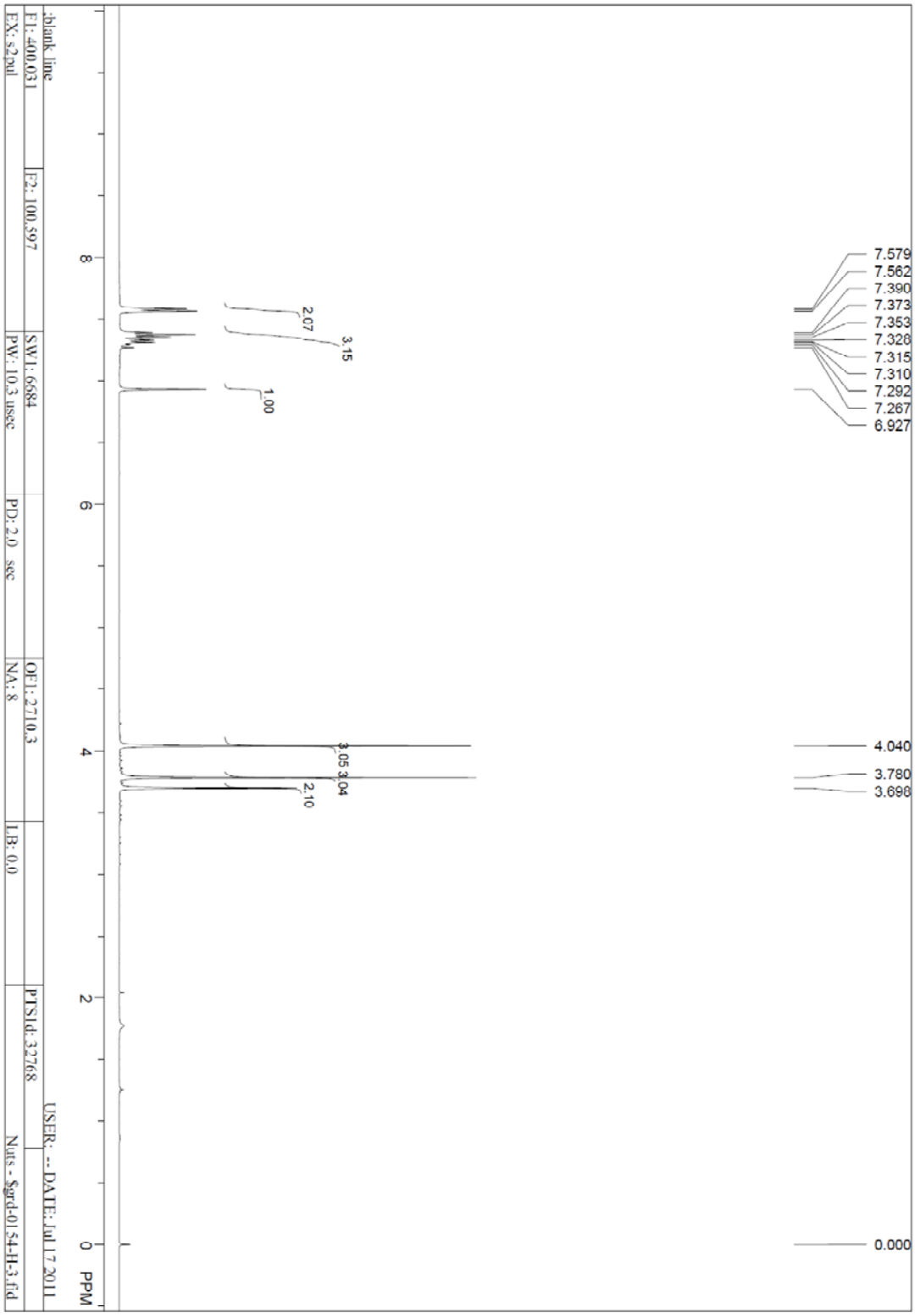
(3E, 5E)-**4o**

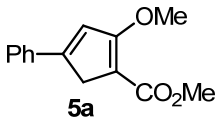
^{13}C NMR (100 M Hz in $CDCl_3$)



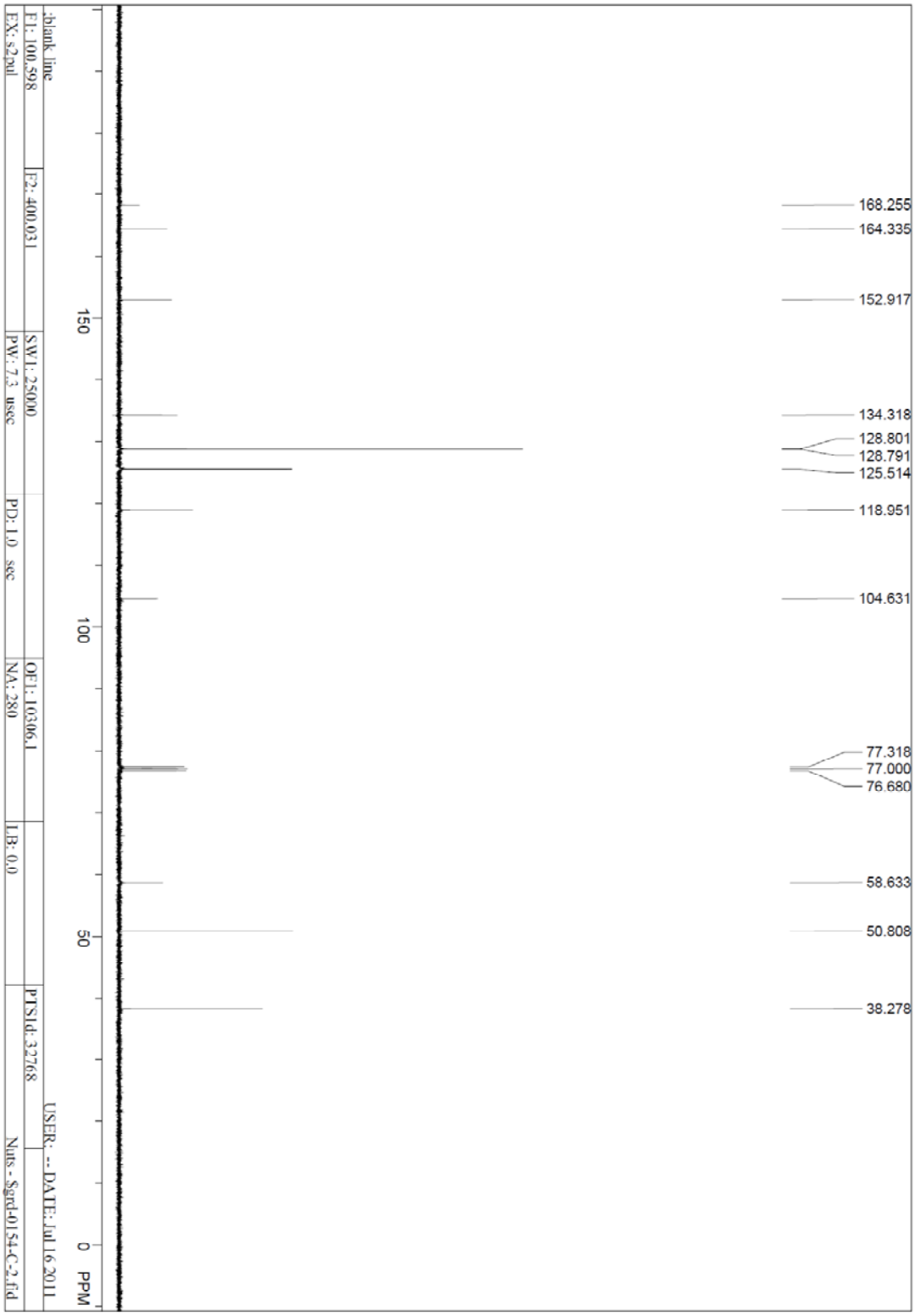


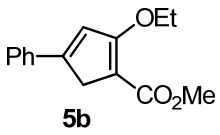
5a ^{1}H NMR (400 M Hz in $CDCl_3$)





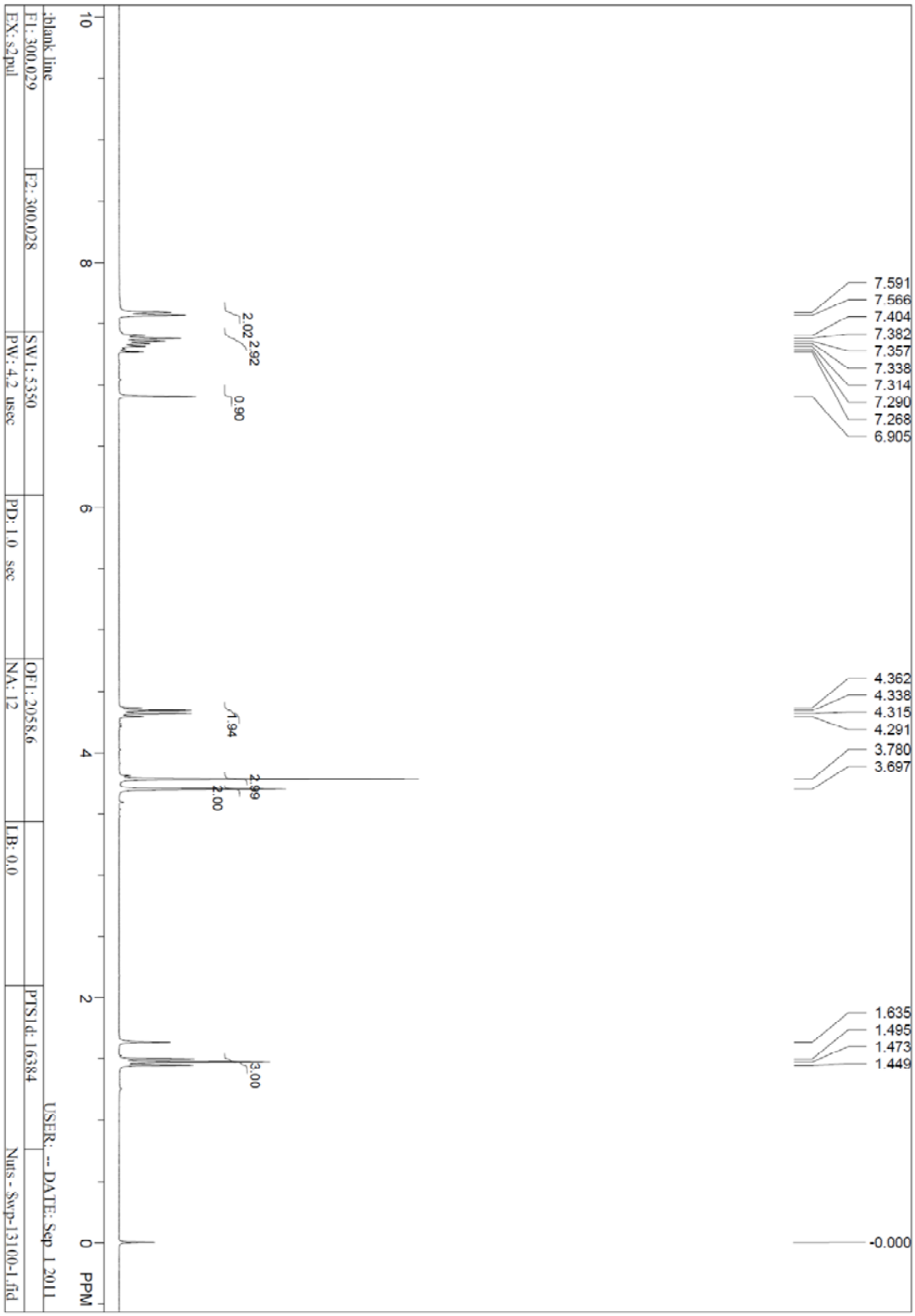
5a ^{13}C NMR (100 M Hz in $CDCl_3$)

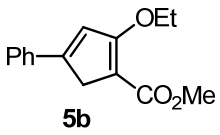




5b

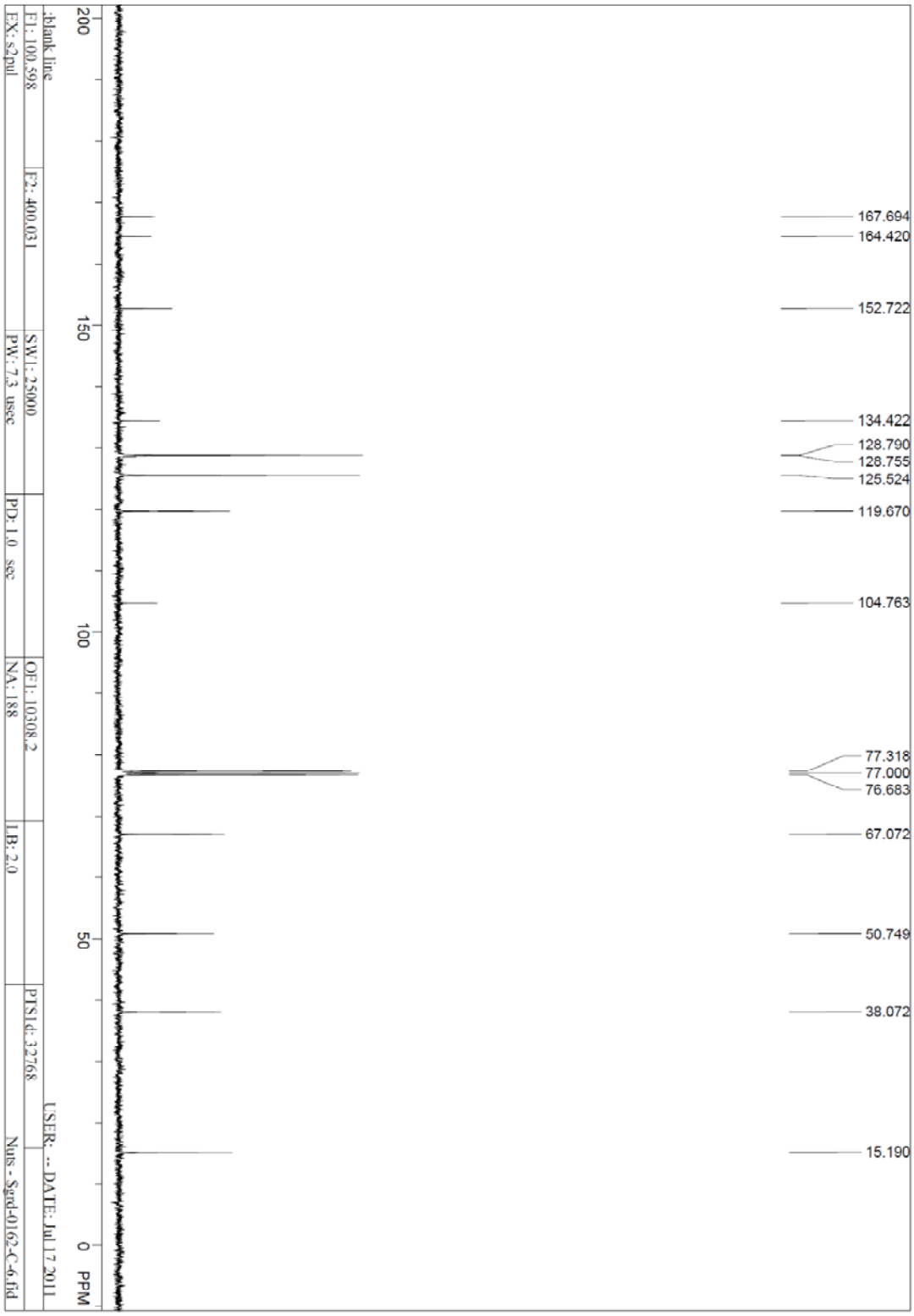
^{1}H NMR (300 M Hz in $CDCl_3$)

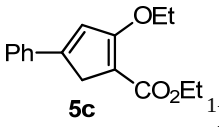




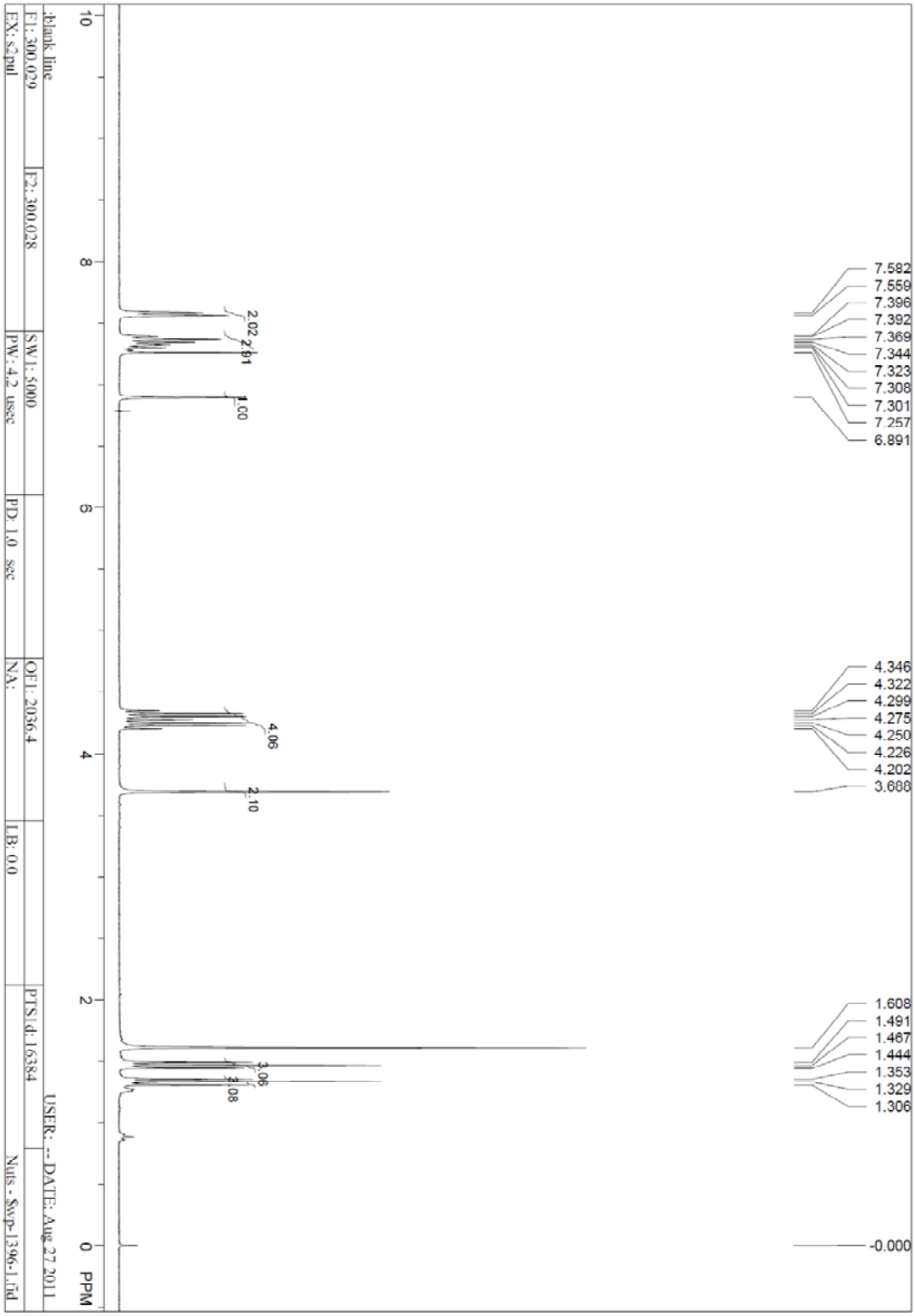
5b

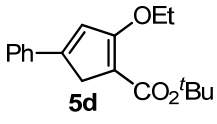
^{13}C NMR (100 M Hz in $CDCl_3$)



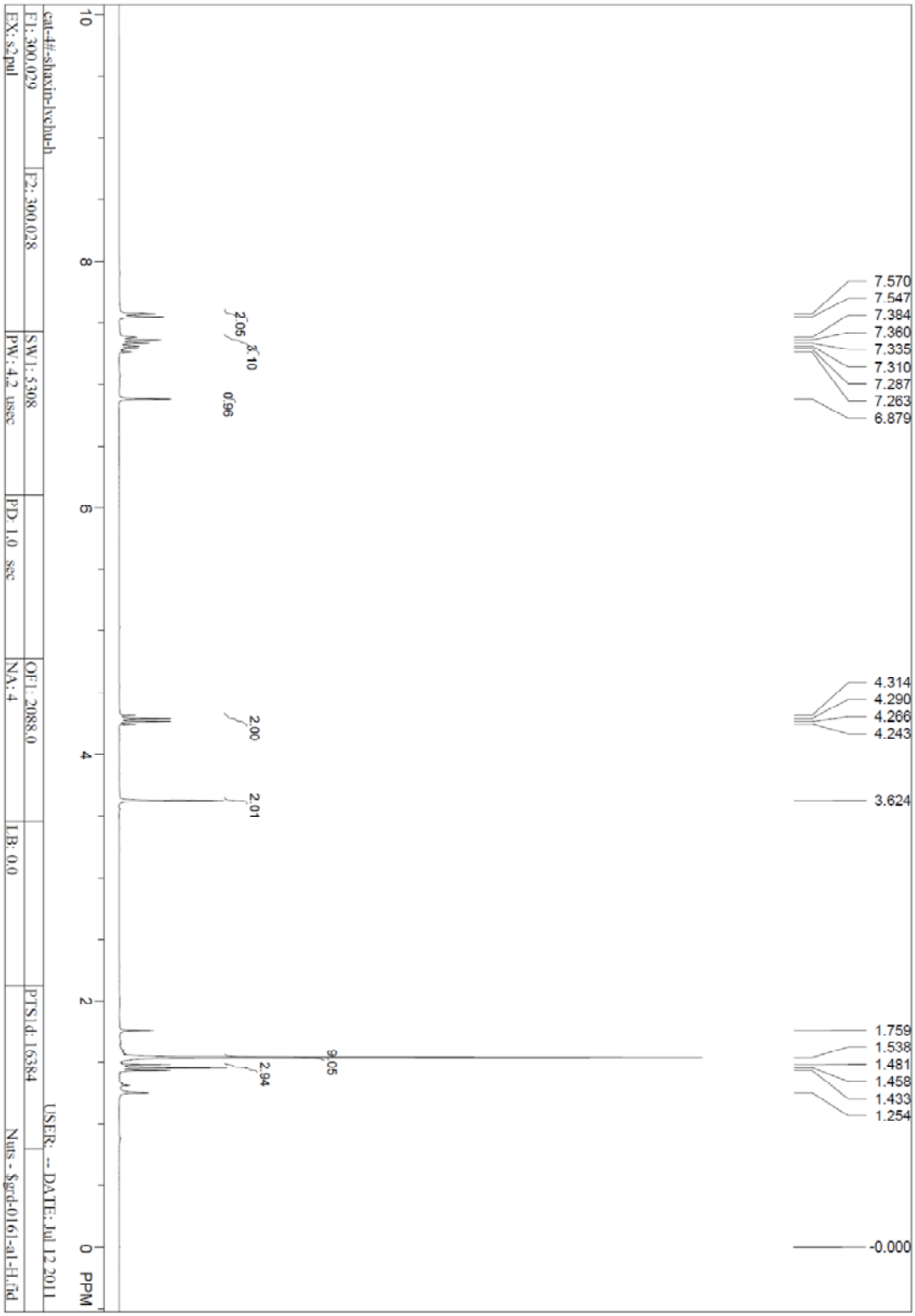


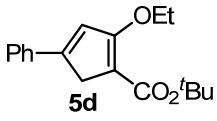
5c ^{1}H NMR (300 M Hz in $CDCl_3$)



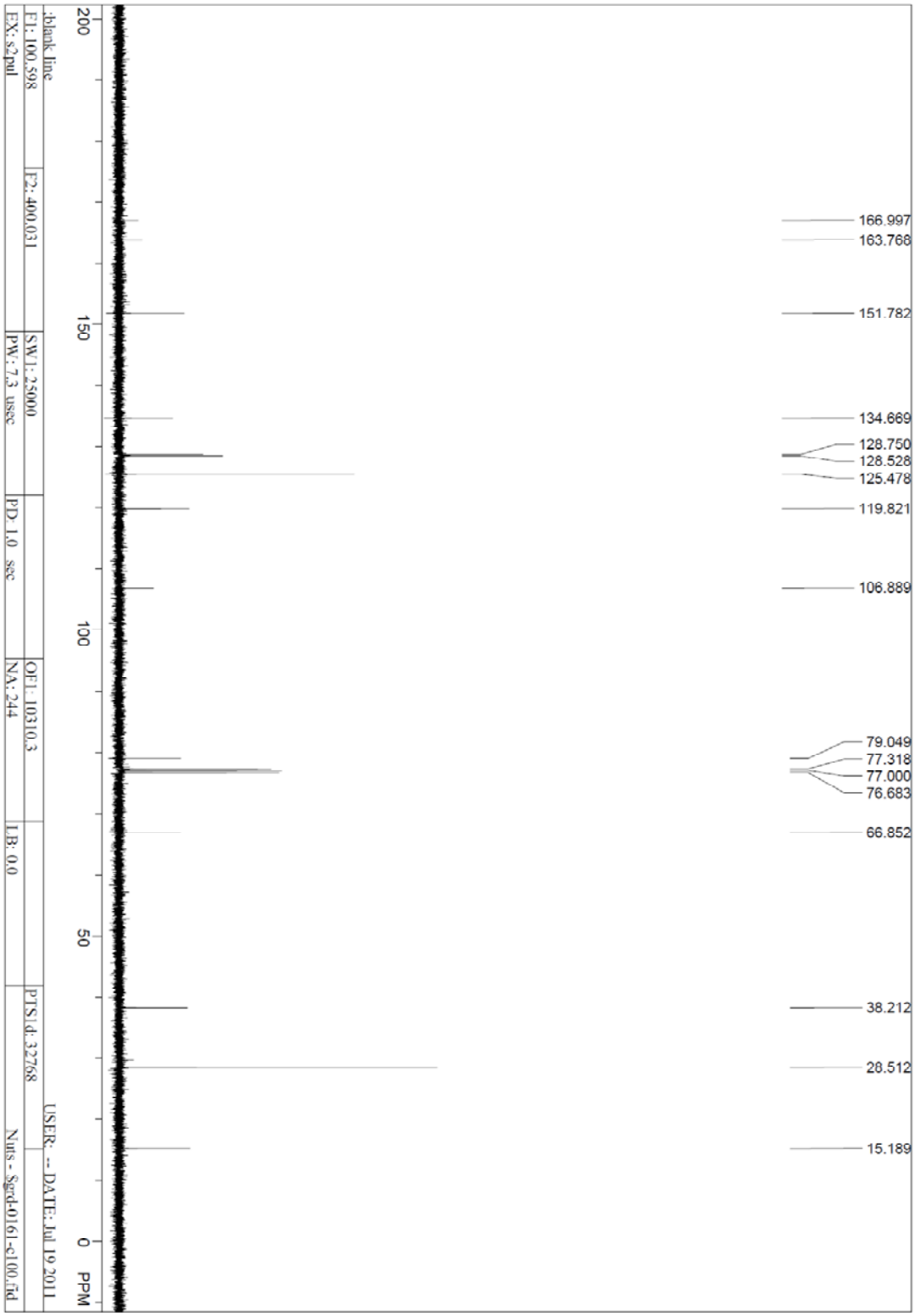


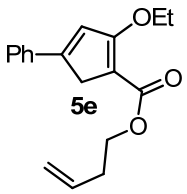
5d ^{1}H NMR (300 M Hz in $CDCl_3$)



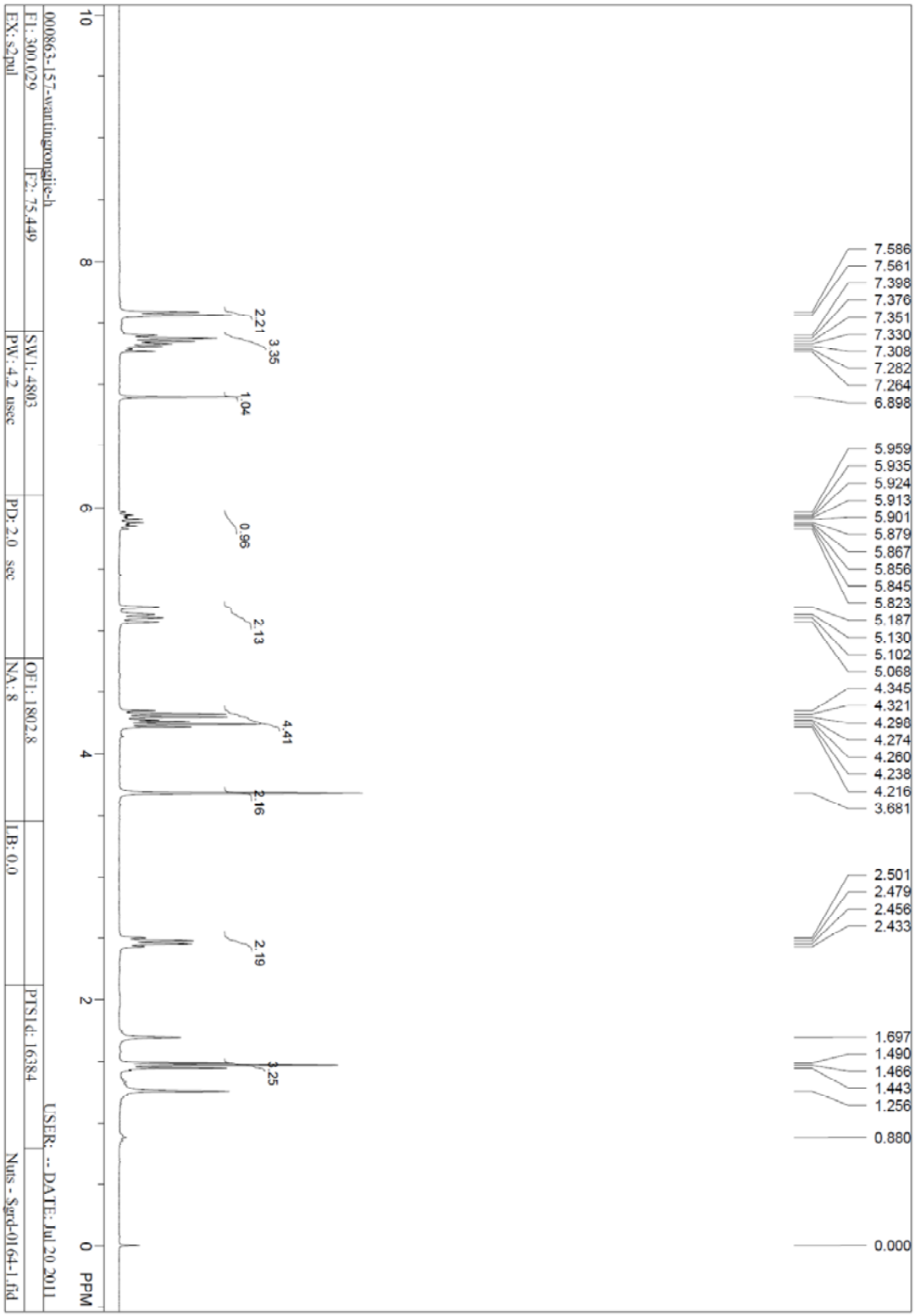


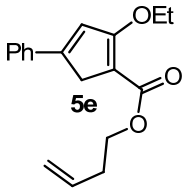
5d ^{13}C NMR (100 M Hz in $CDCl_3$)



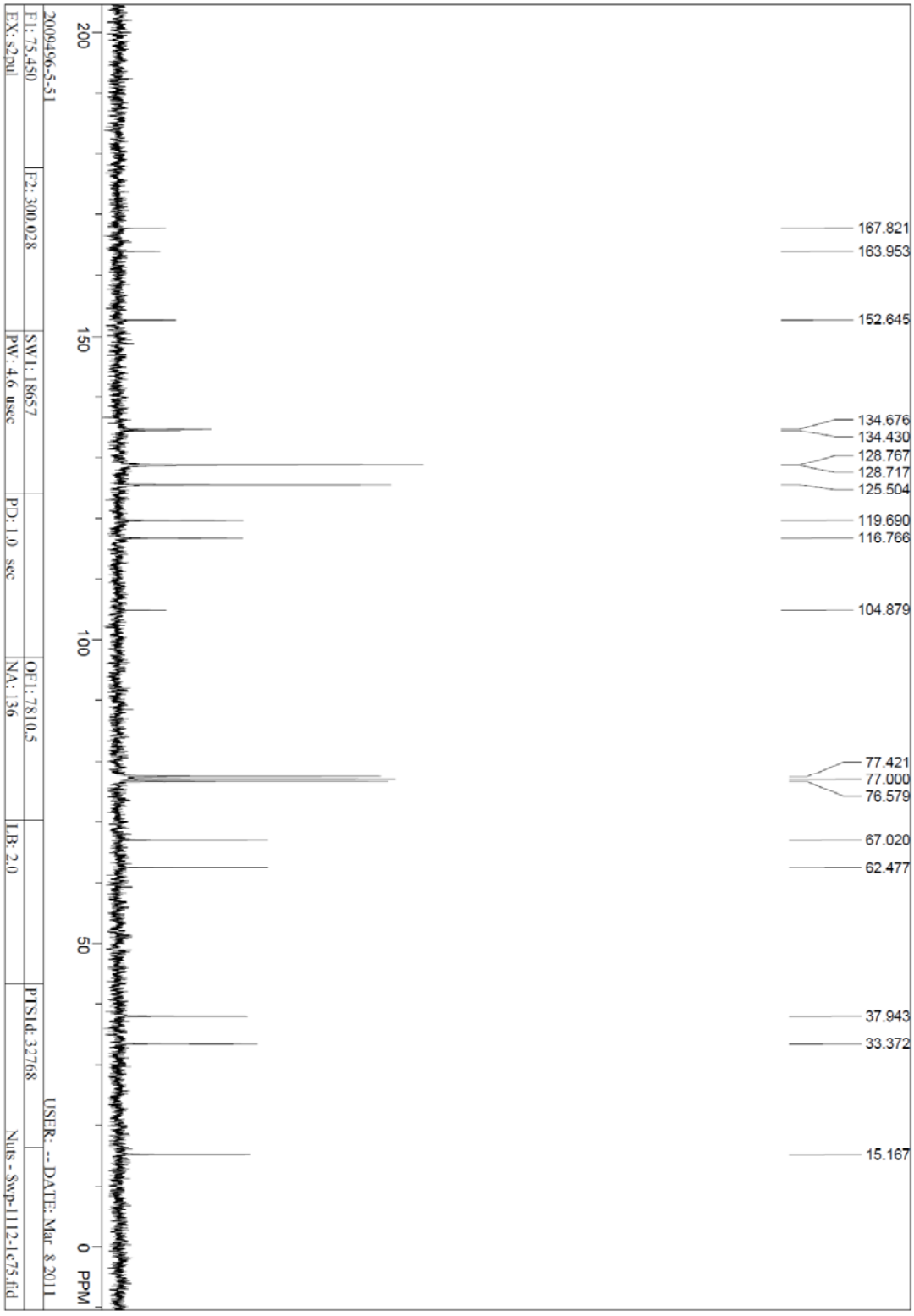


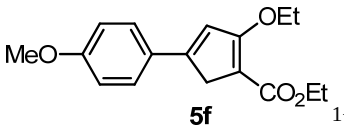
^{1}H NMR (300 M Hz in $CDCl_3$)





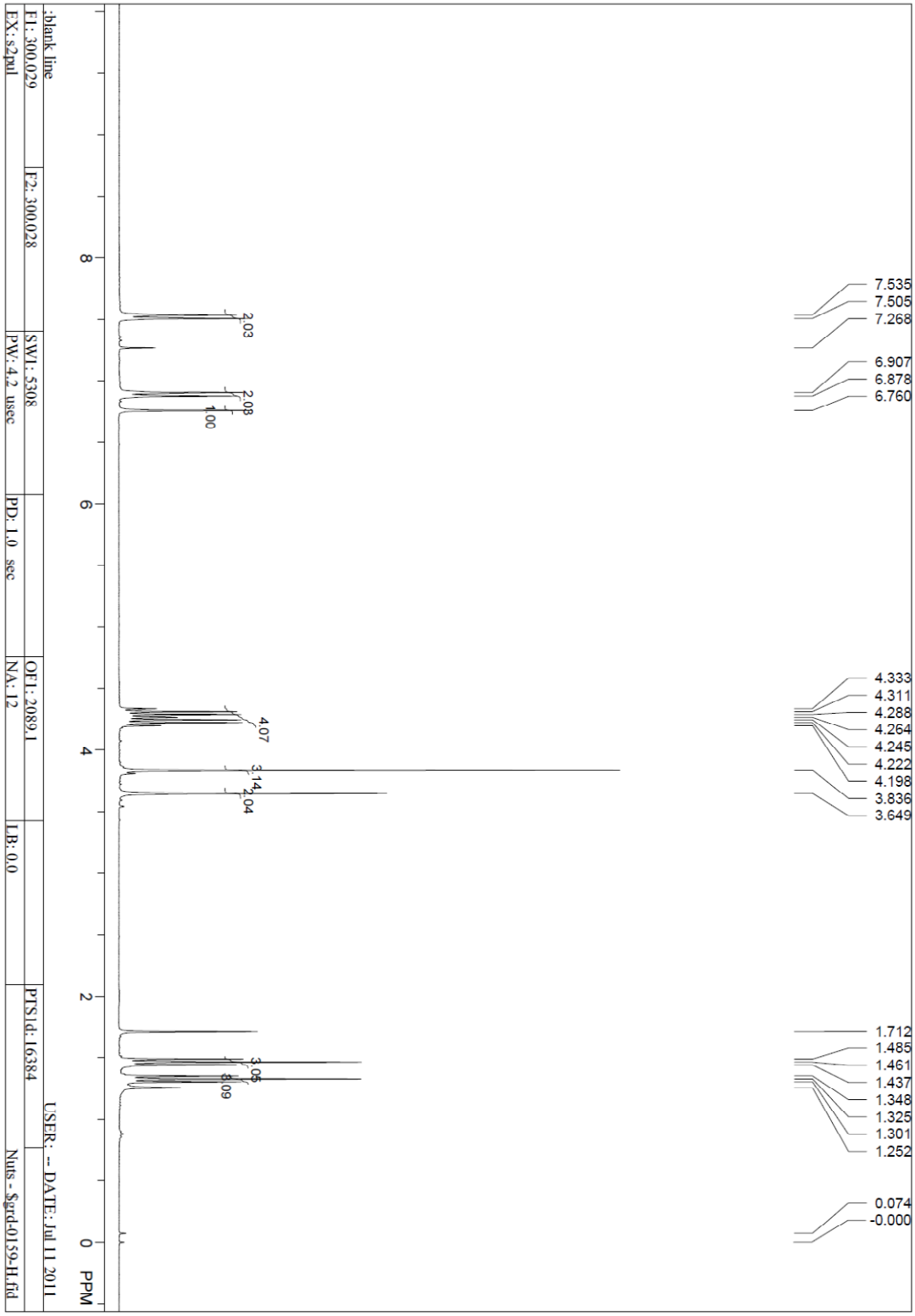
^{13}C NMR (75 M Hz in $CDCl_3$)

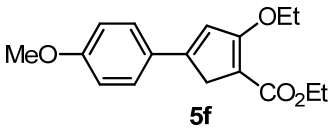




5f

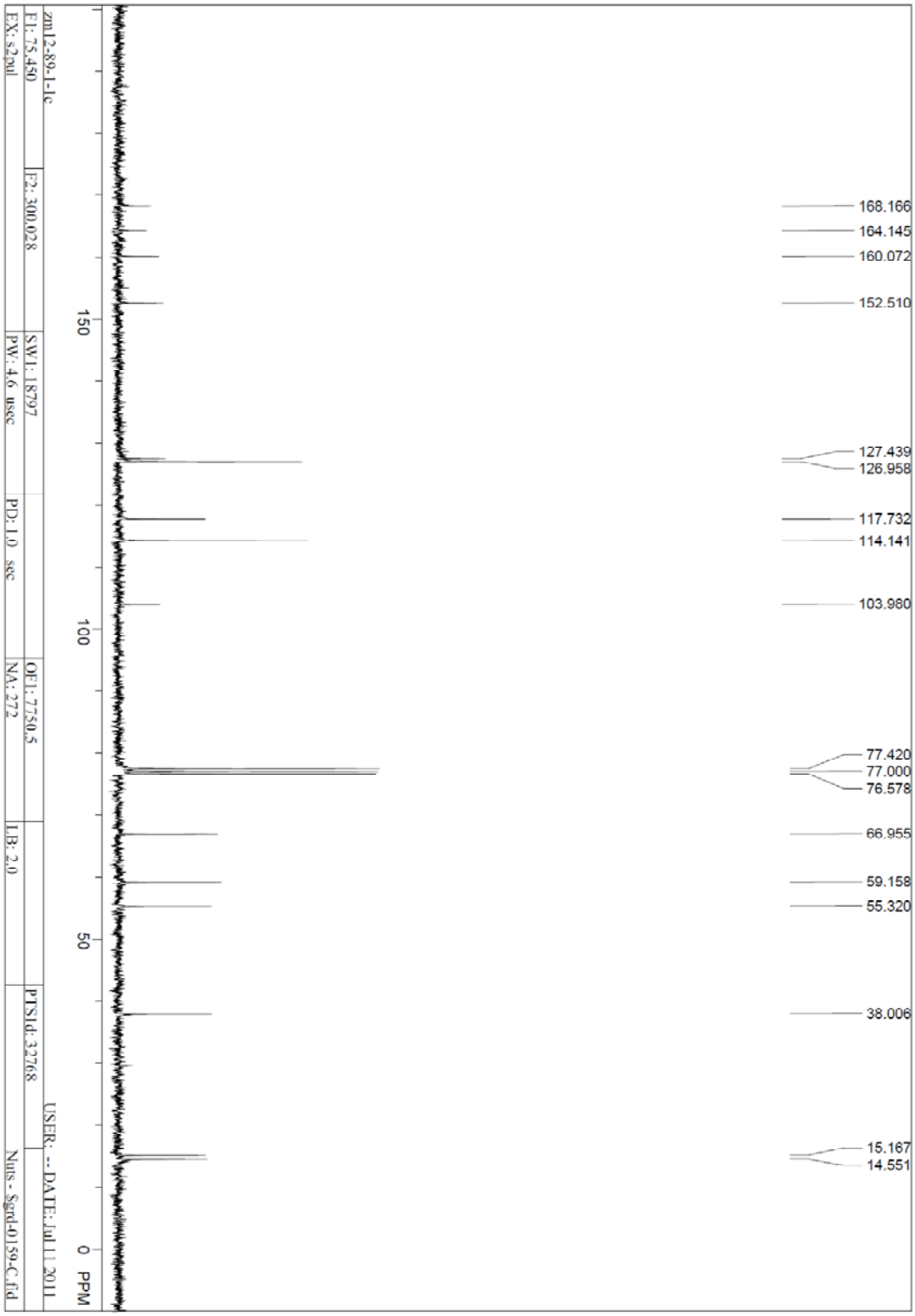
^{1}H NMR (400 M Hz in $CDCl_3$)

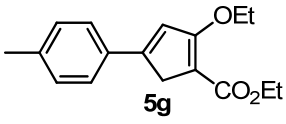




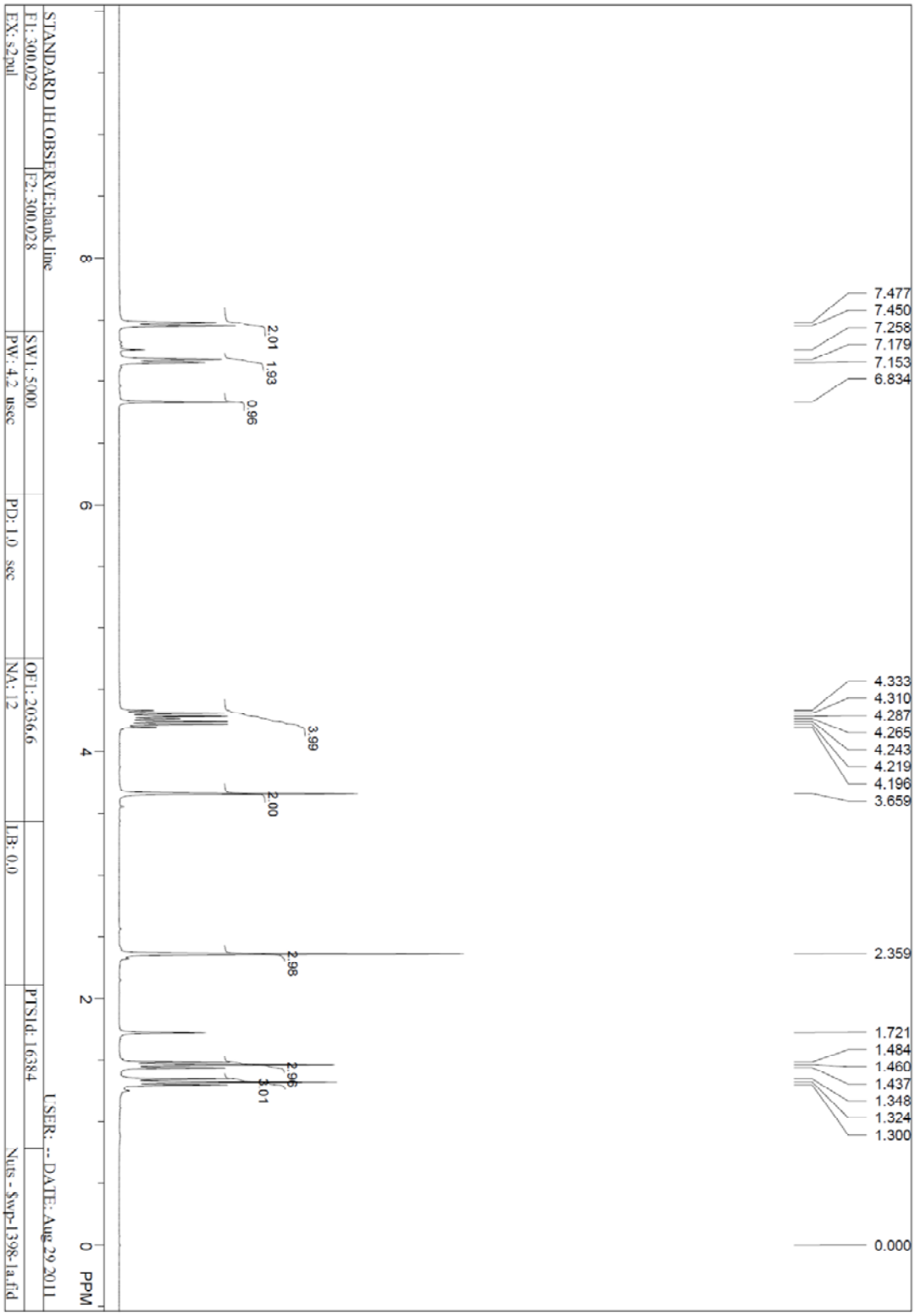
5f

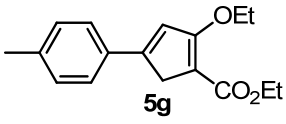
^{13}C NMR (100 M Hz in $CDCl_3$)



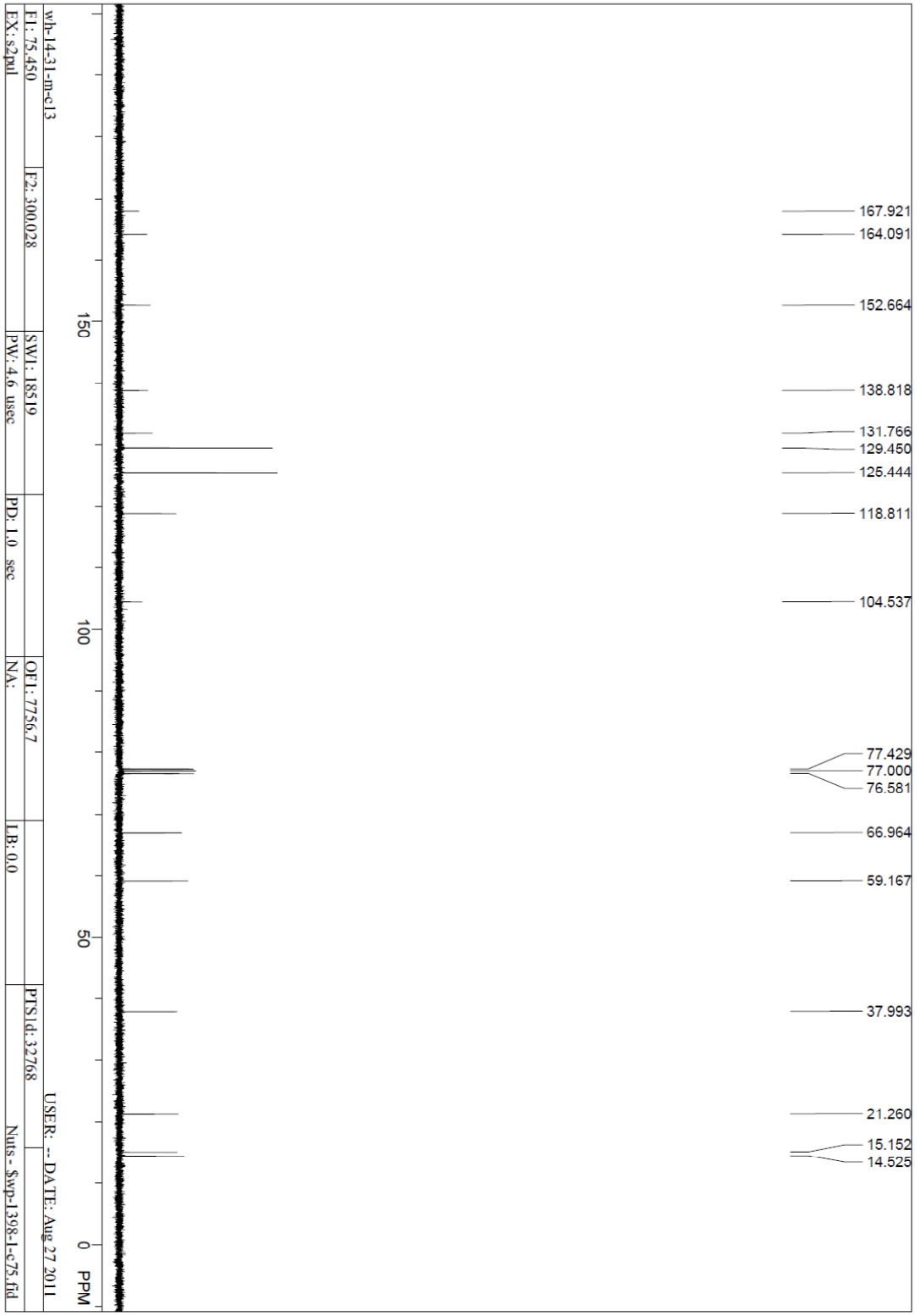


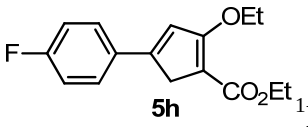
5g ^{1}H NMR (300 M Hz in $CDCl_3$)



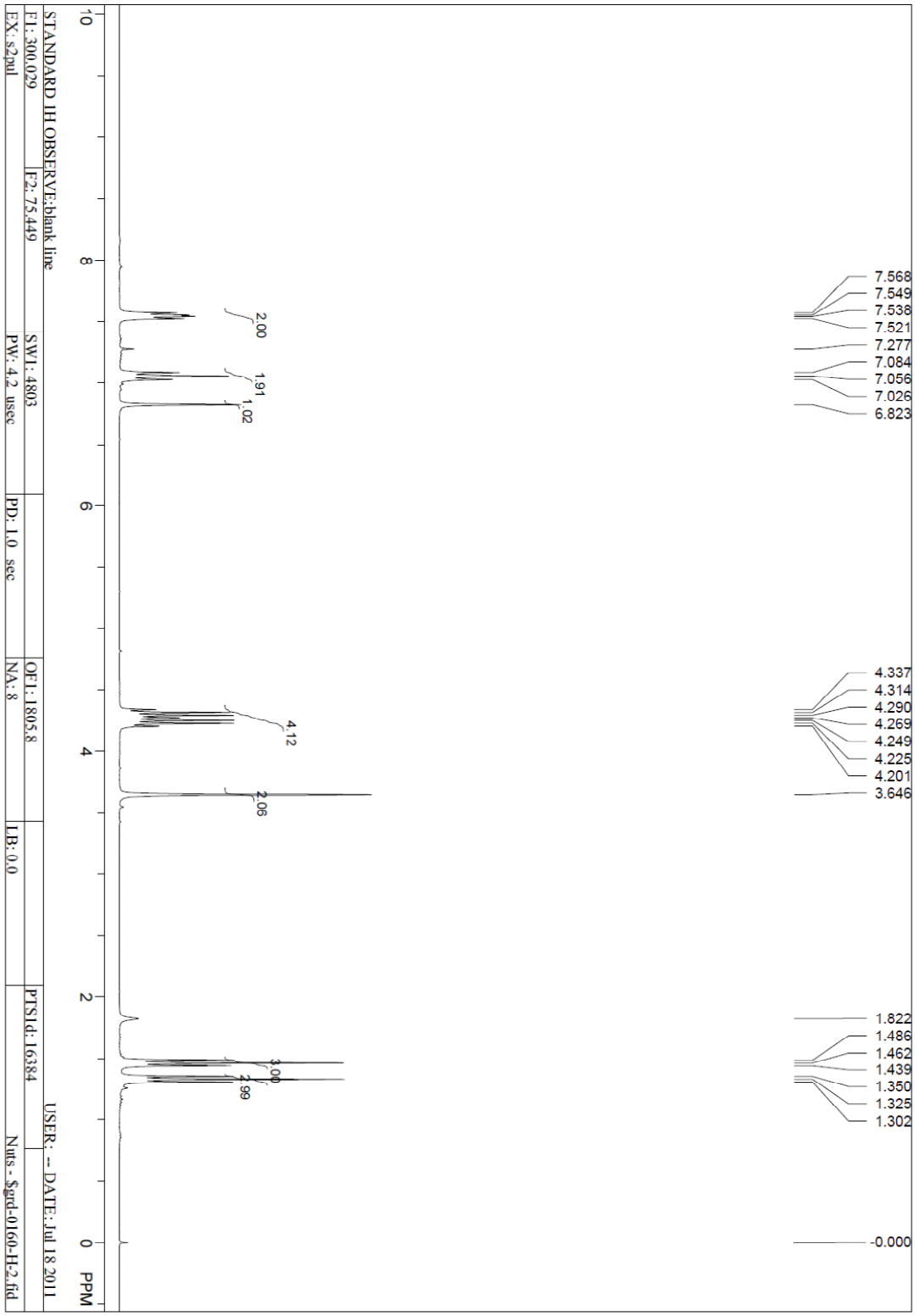


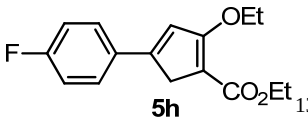
5g ^{13}C NMR (75 M Hz in $CDCl_3$)



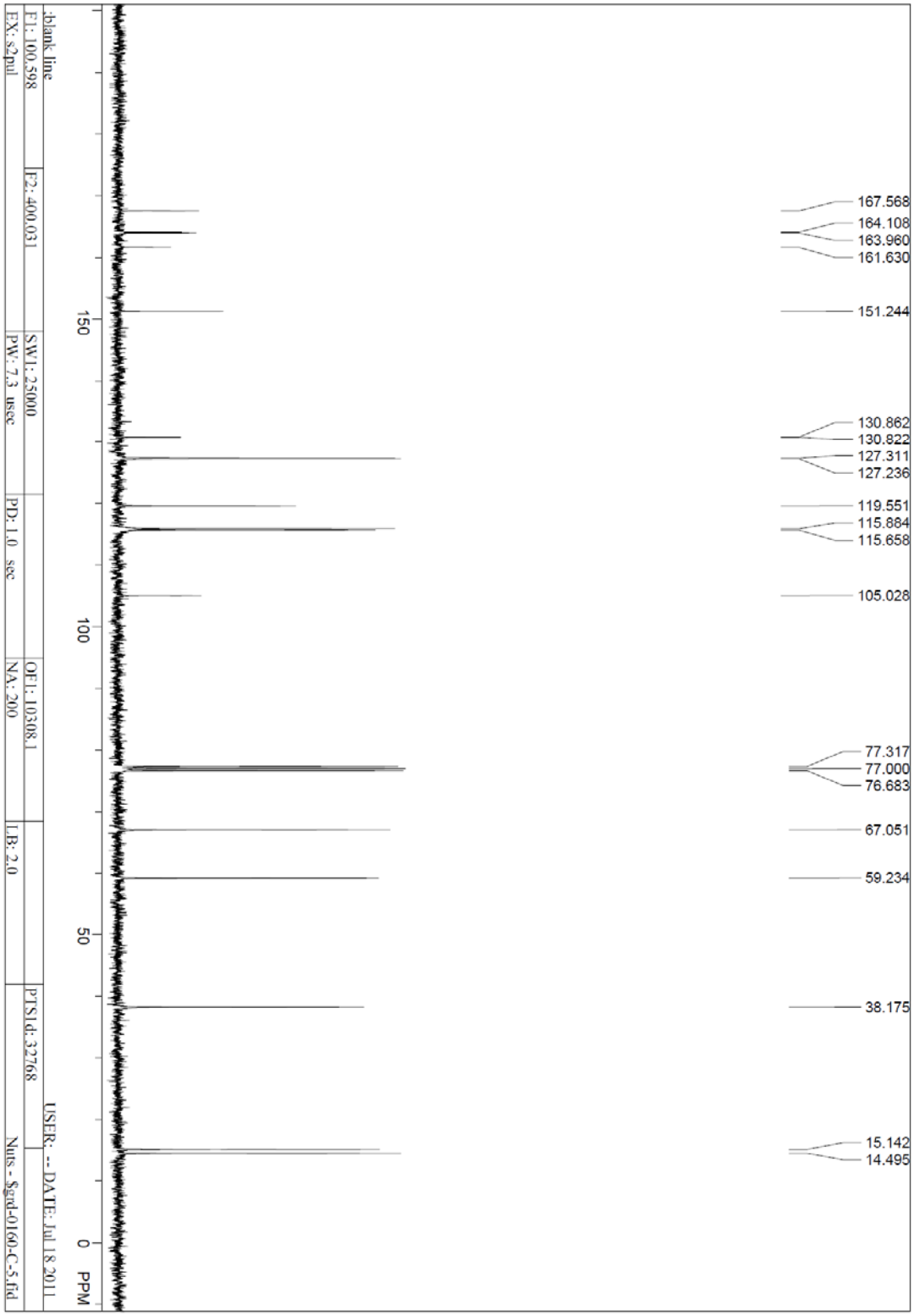


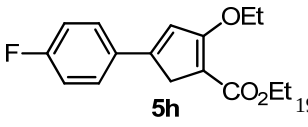
5h ^{1}H NMR (300 M Hz in $CDCl_3$)





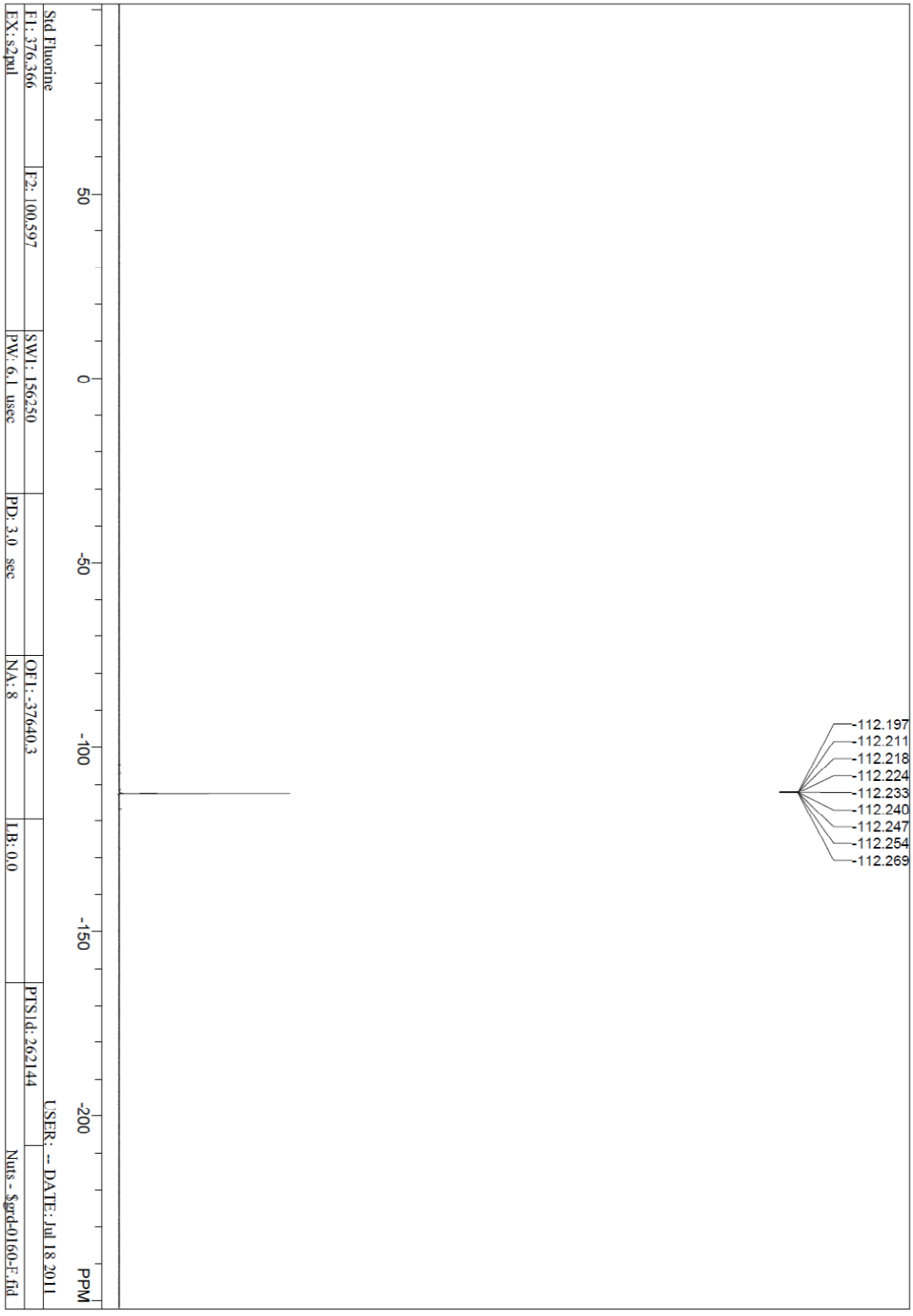
5h ^{13}C NMR (100 M Hz in $CDCl_3$)

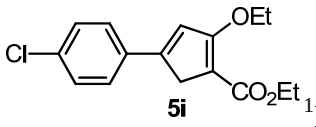




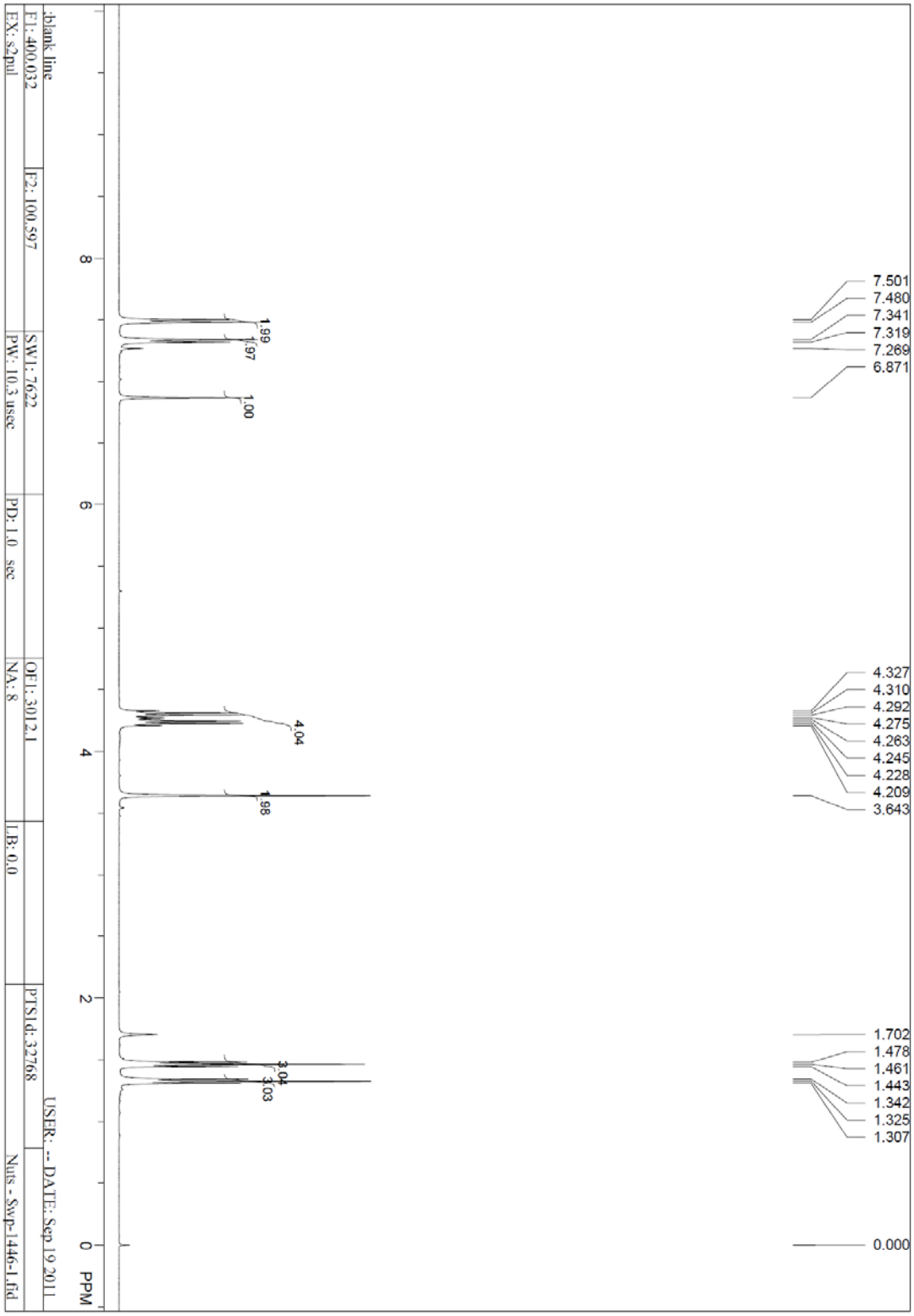
5h

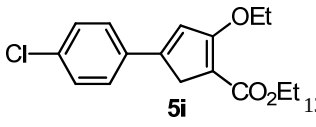
^{19}F NMR (376 M Hz in $CDCl_3$)





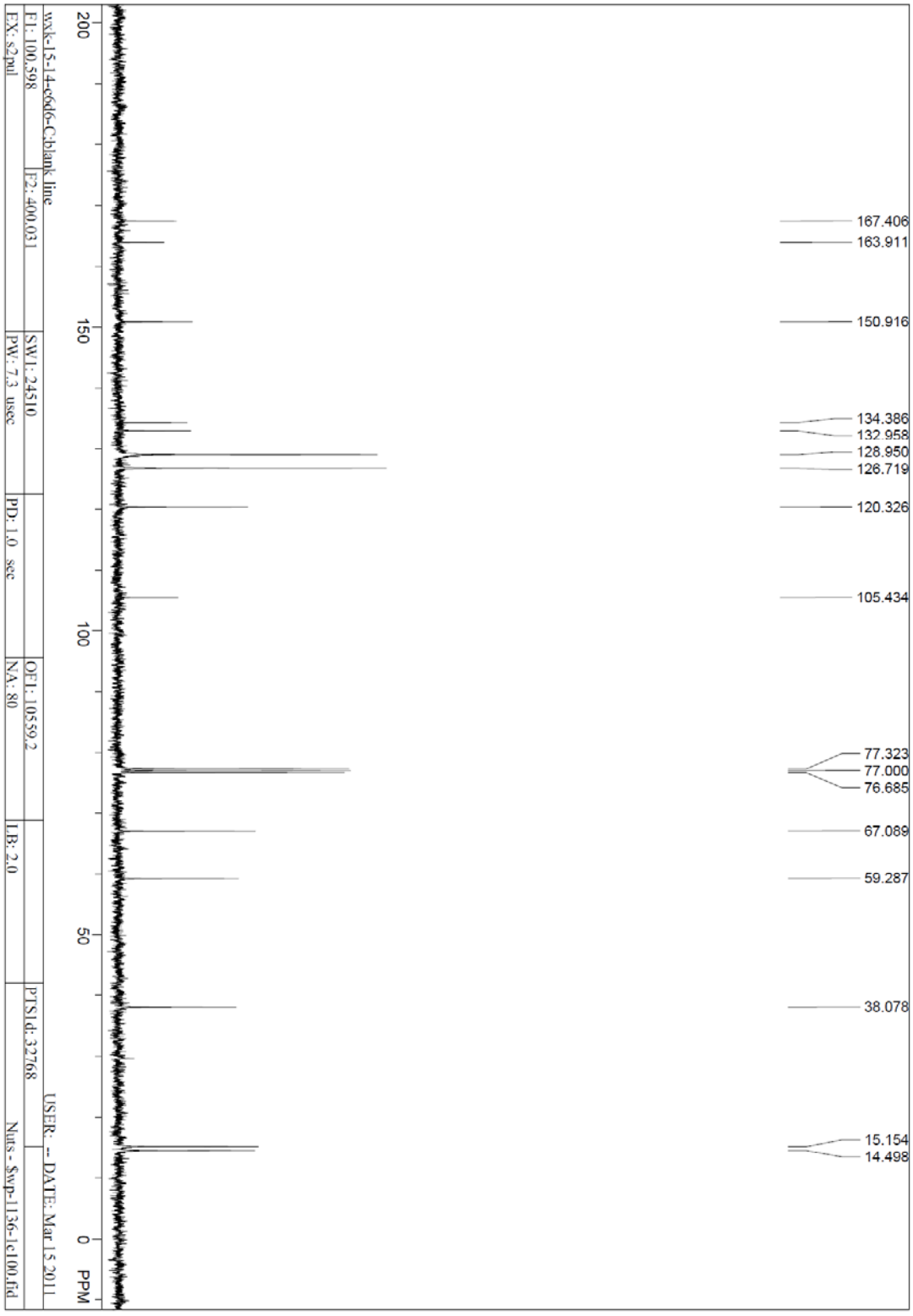
5i ^{1}H NMR (400 M Hz in $CDCl_3$)

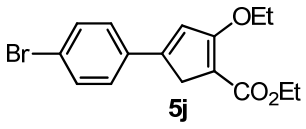




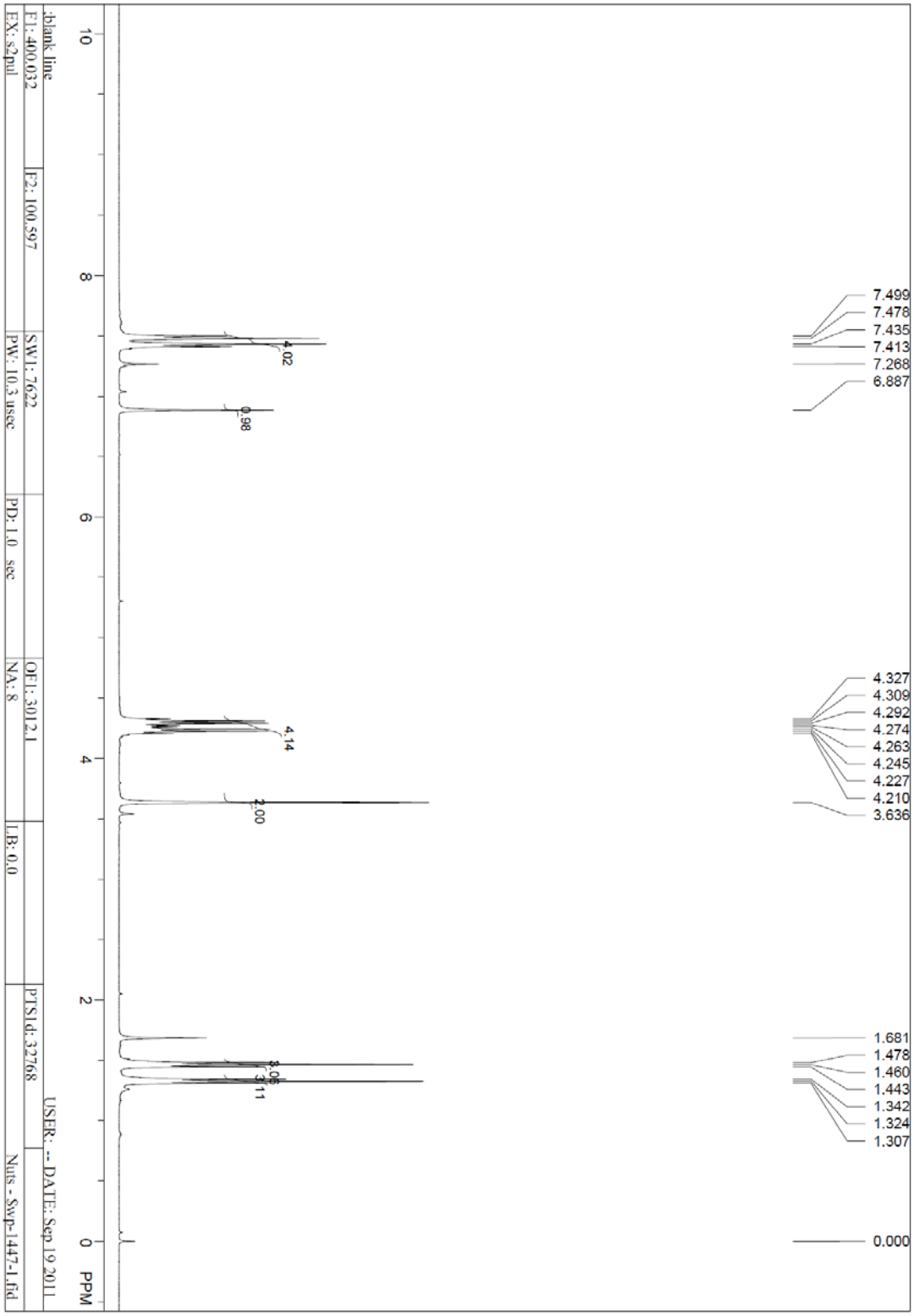
5i

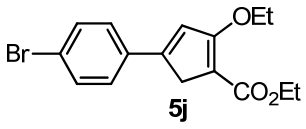
^{13}C NMR (100 M Hz in $CDCl_3$)





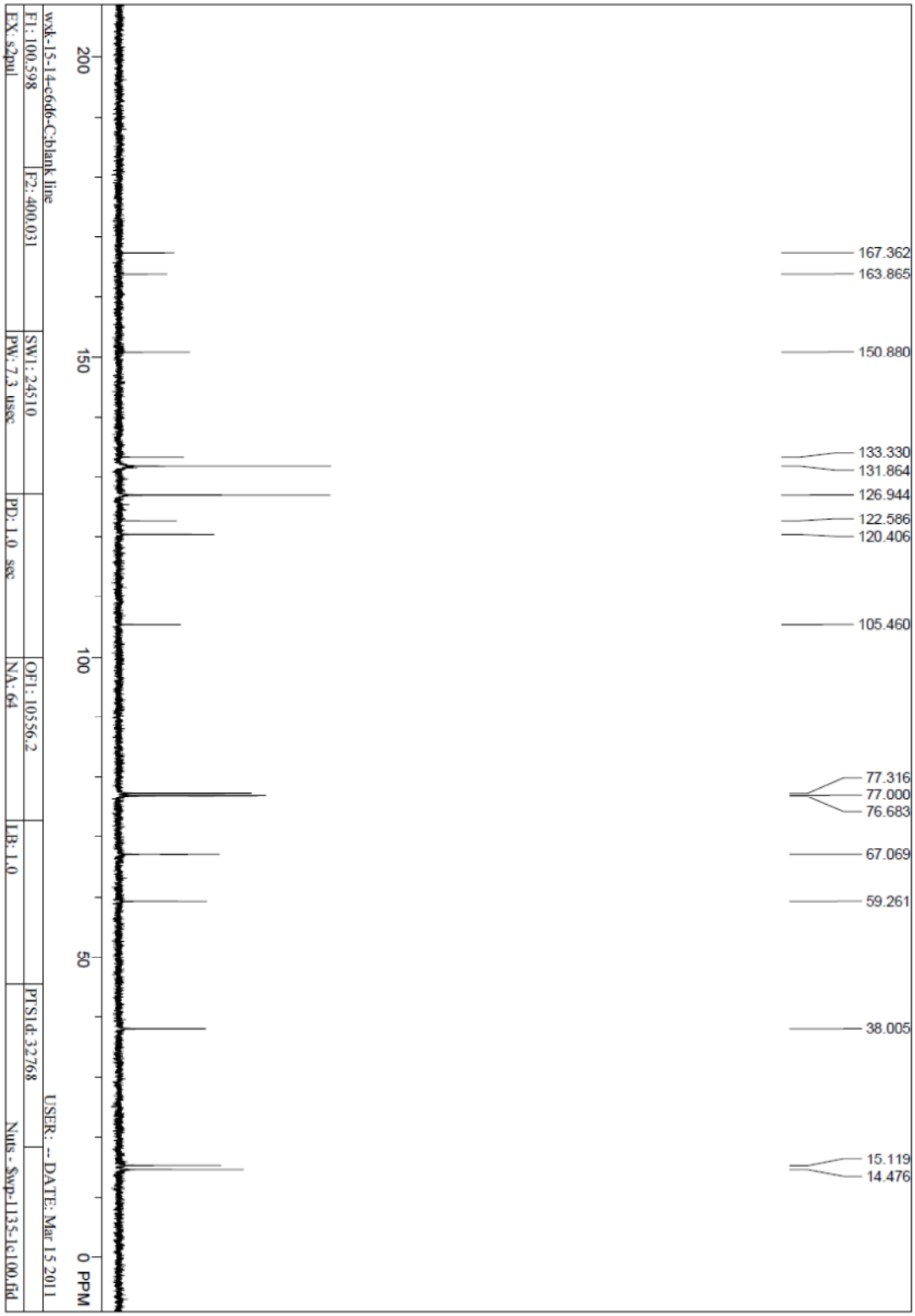
5j ^{1}H NMR (400 M Hz in $CDCl_3$)

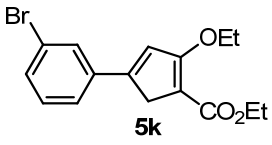




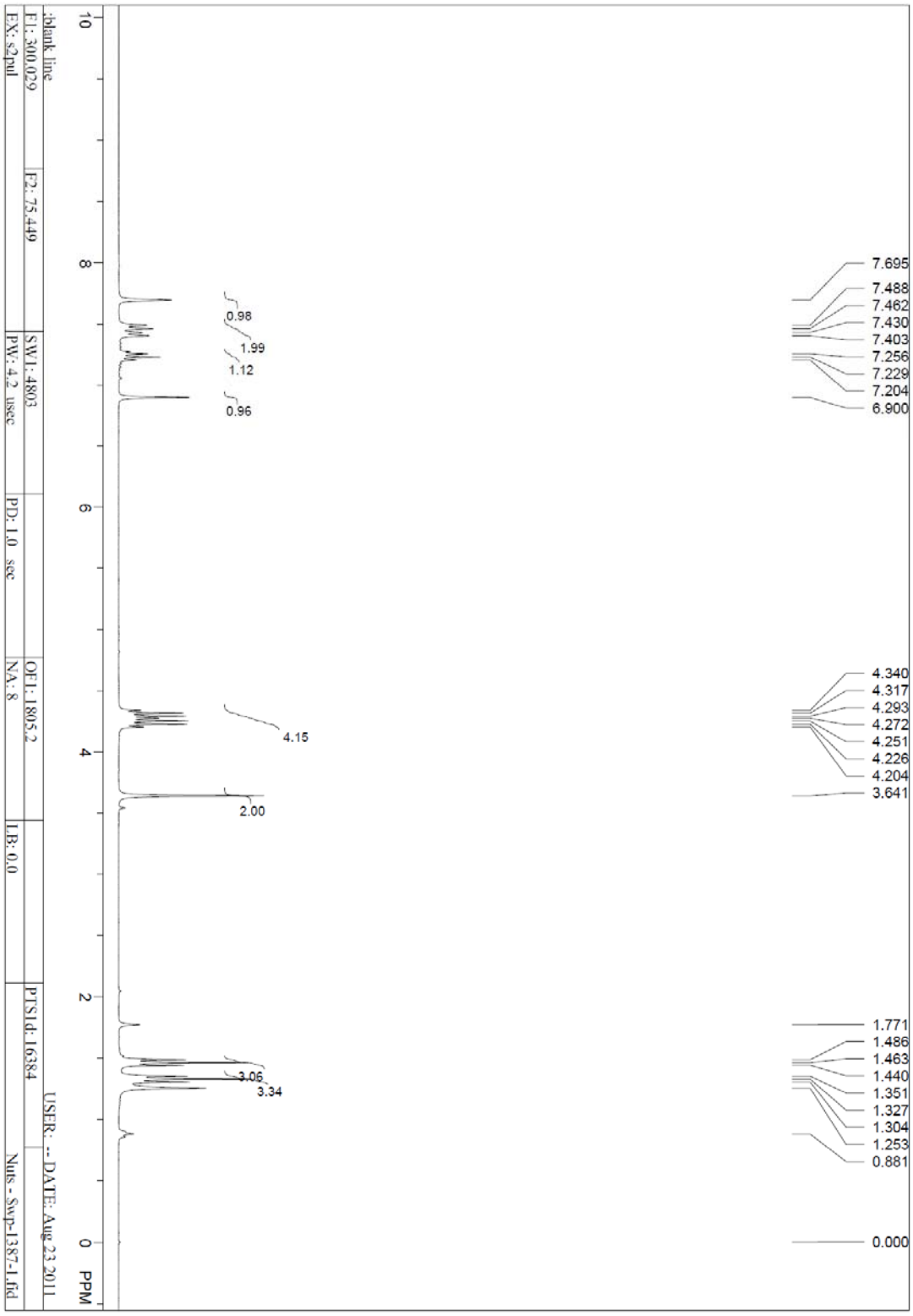
5j

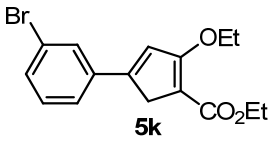
^{13}C NMR (100 M Hz in $CDCl_3$)



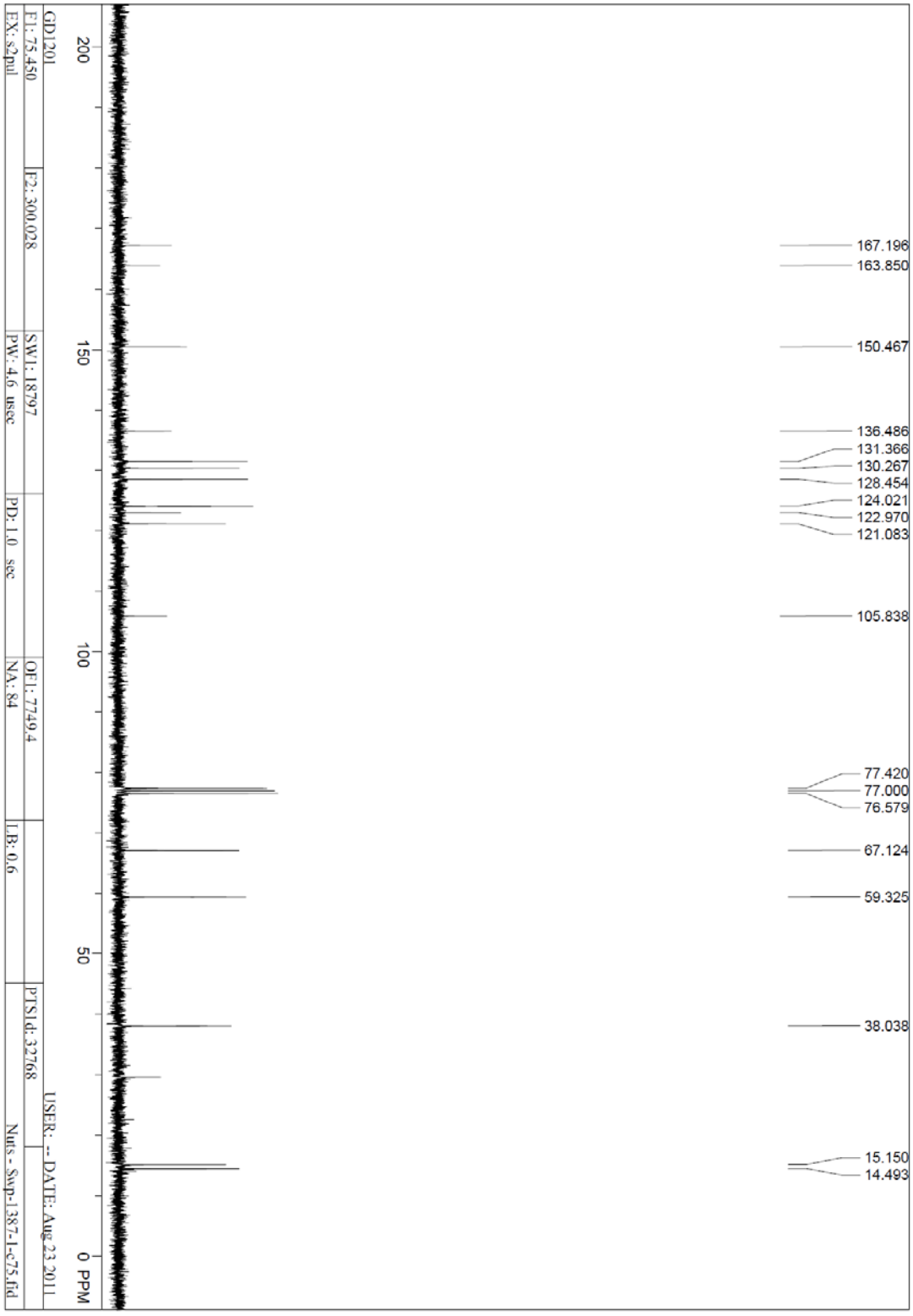


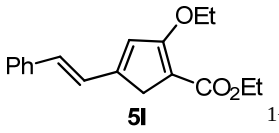
5k ^{1}H NMR (300 M Hz in $CDCl_3$)





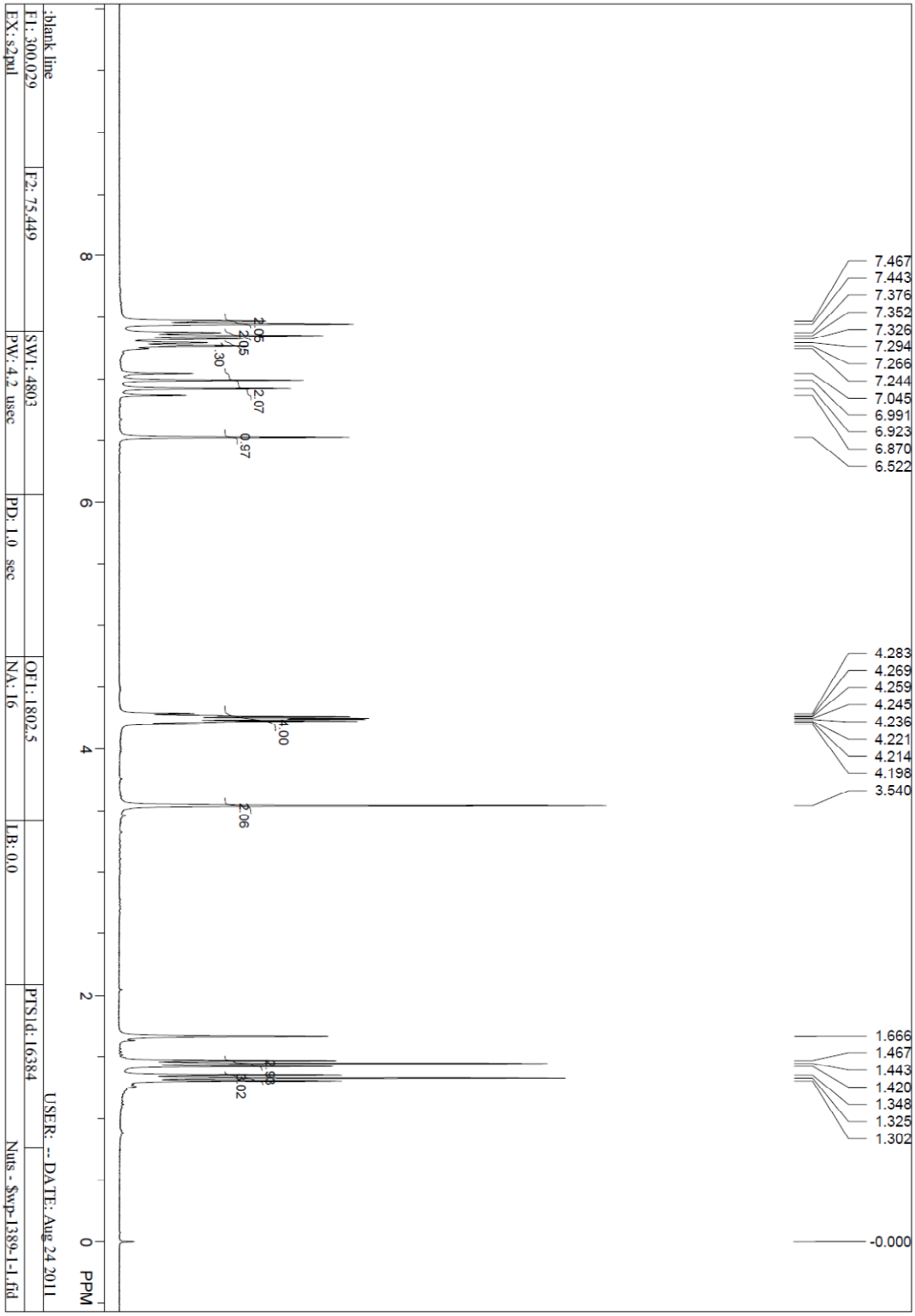
5k ^{13}C NMR (75 M Hz in $CDCl_3$)

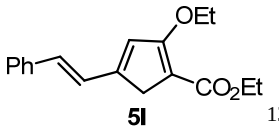




5l

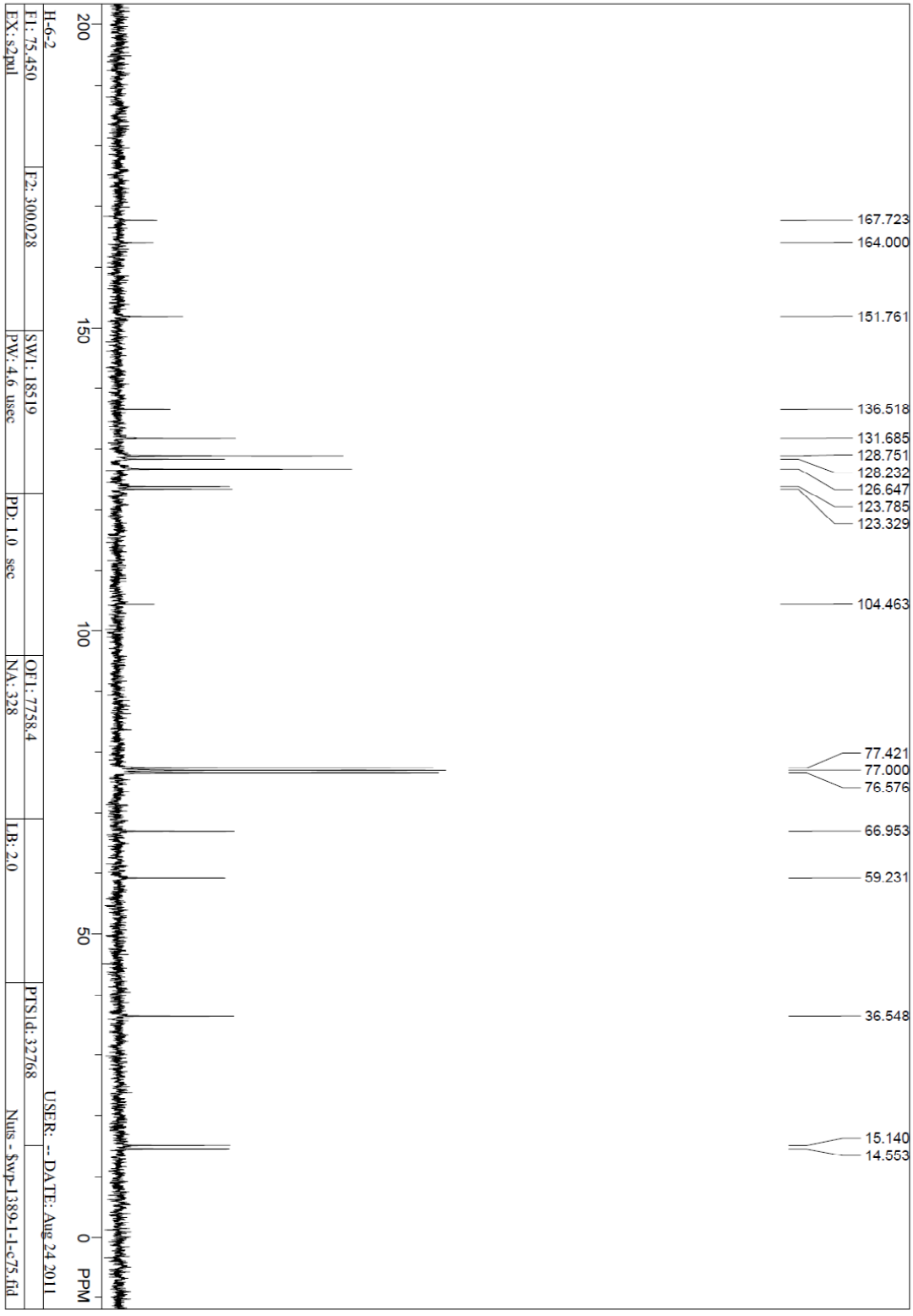
^{1}H NMR (300 M Hz in $CDCl_3$)

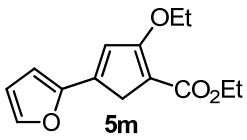




5l

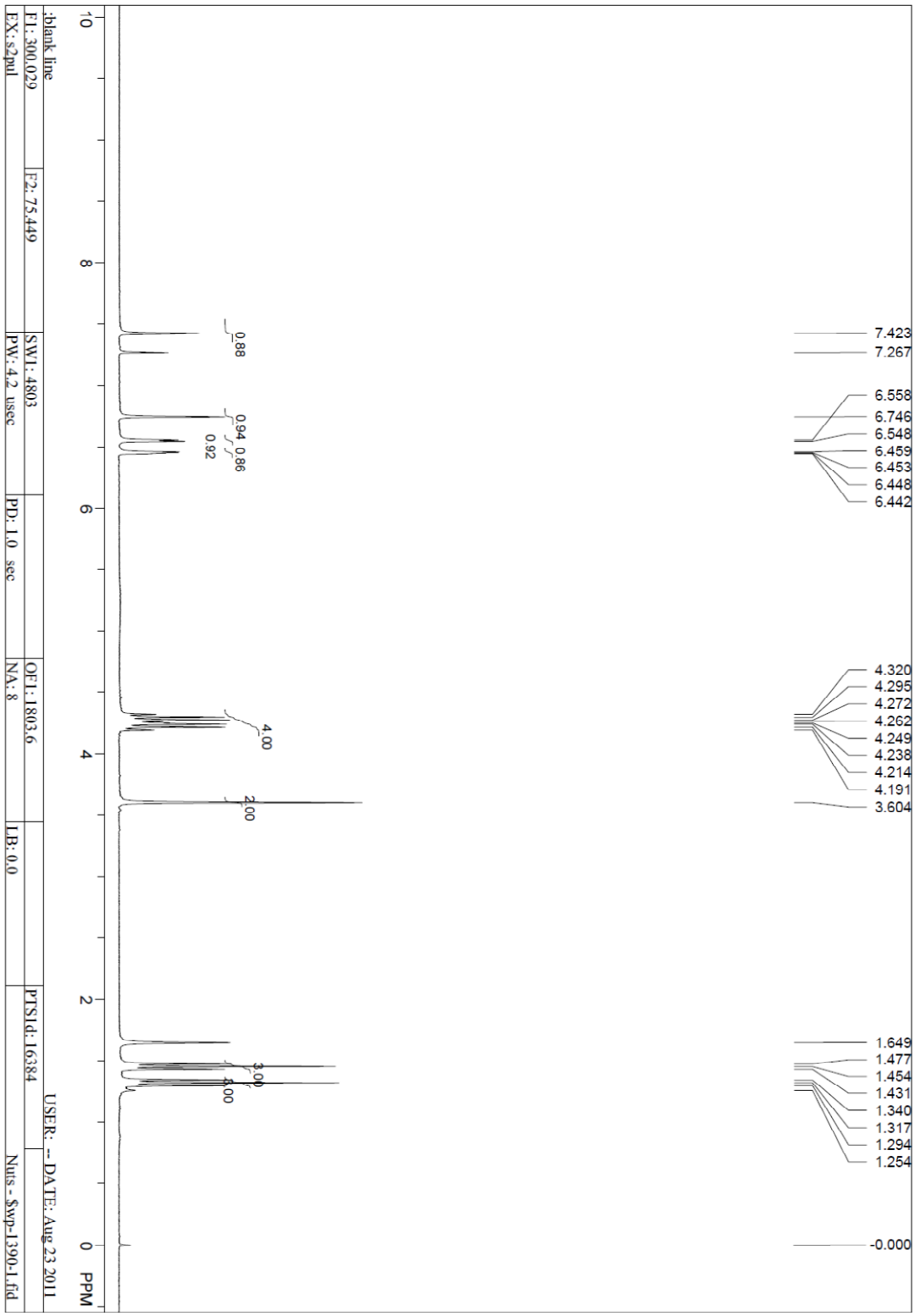
^{13}C NMR (75 M Hz in $CDCl_3$)

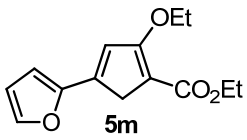




5m

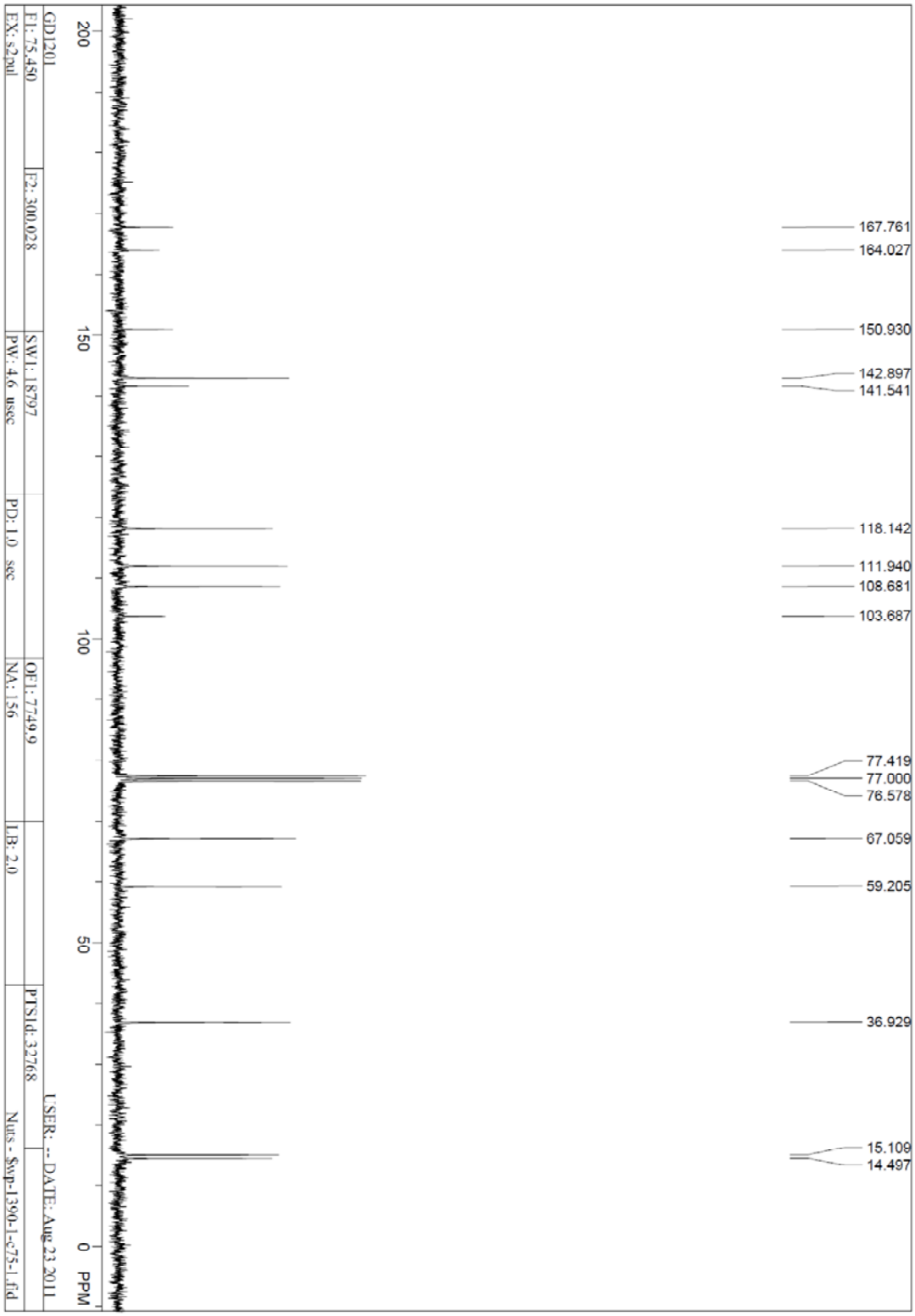
^{1}H NMR (300 M Hz in $CDCl_3$)

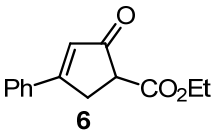




5m

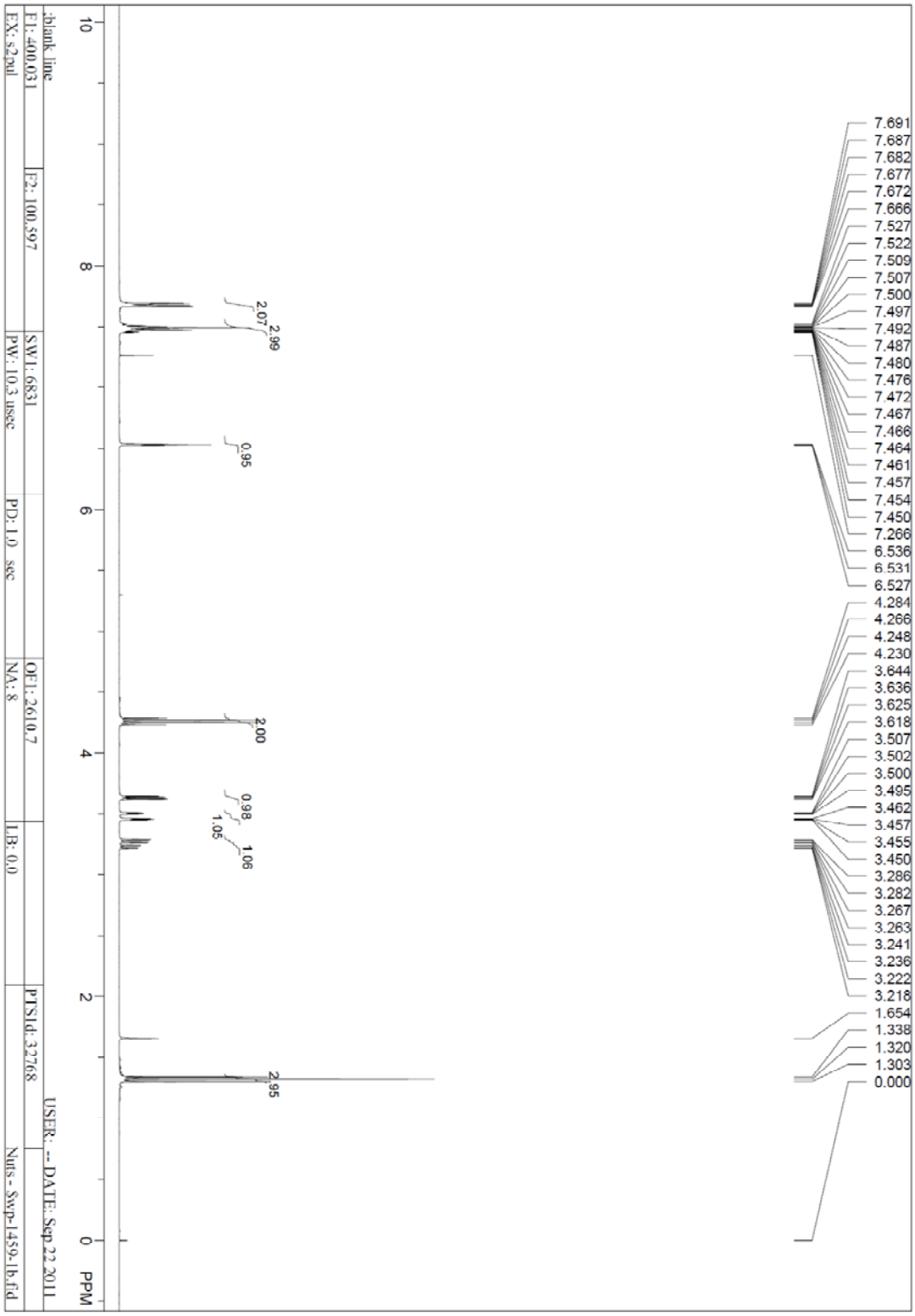
^{13}C NMR (75 M Hz in $CDCl_3$)

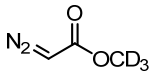




6

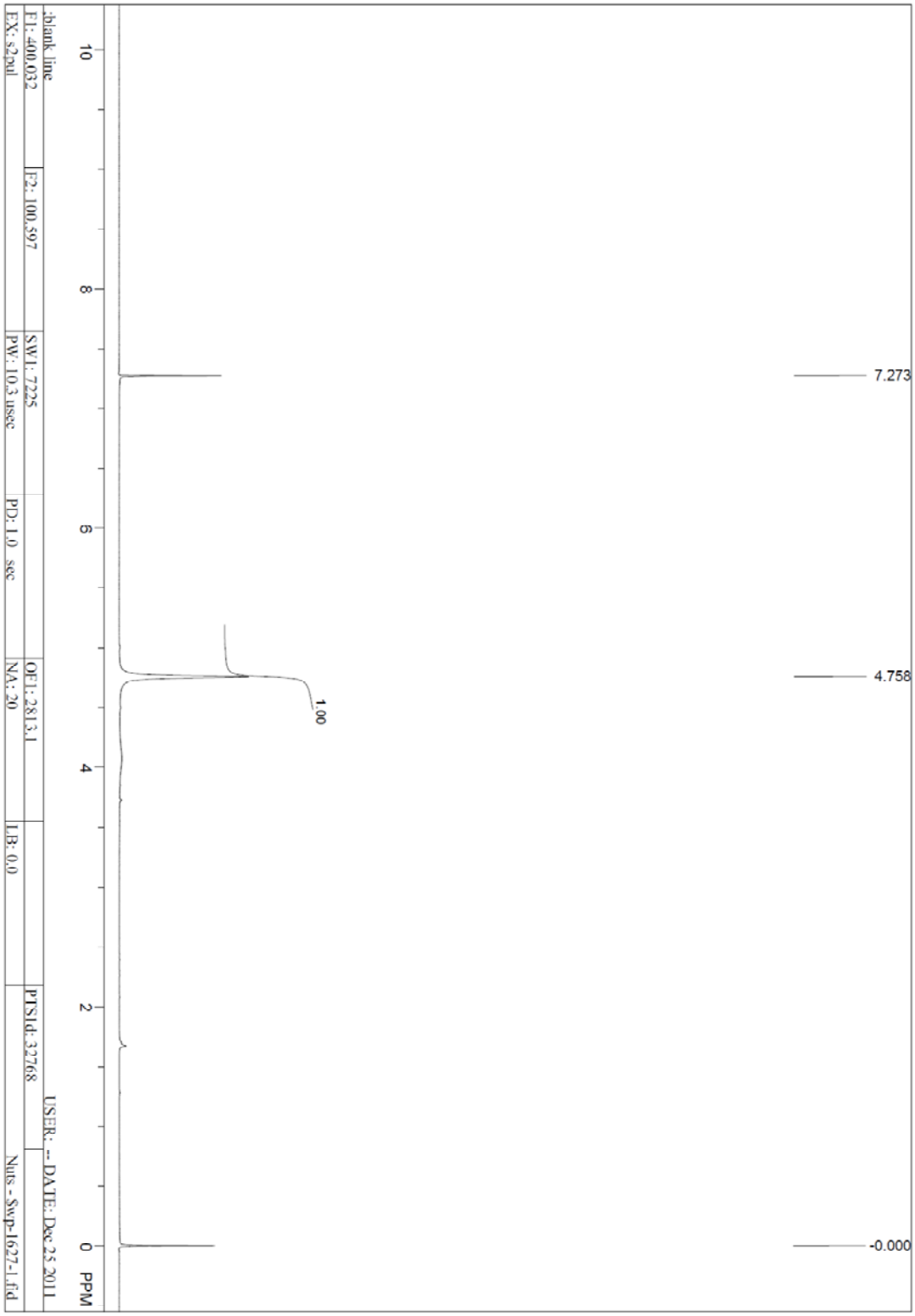
^{1}H NMR (400 M Hz in $CDCl_3$)

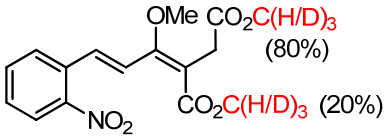




d$_3$-MDA

^{1}H NMR (400 M Hz in $CDCl_3$)





4c

^{1}H NMR (300 M Hz in $CDCl_3$)