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A Sidearm-Assisted Phosphine for Catalytic Ylide Intramolecular Cyclopropanation

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Supporting Information

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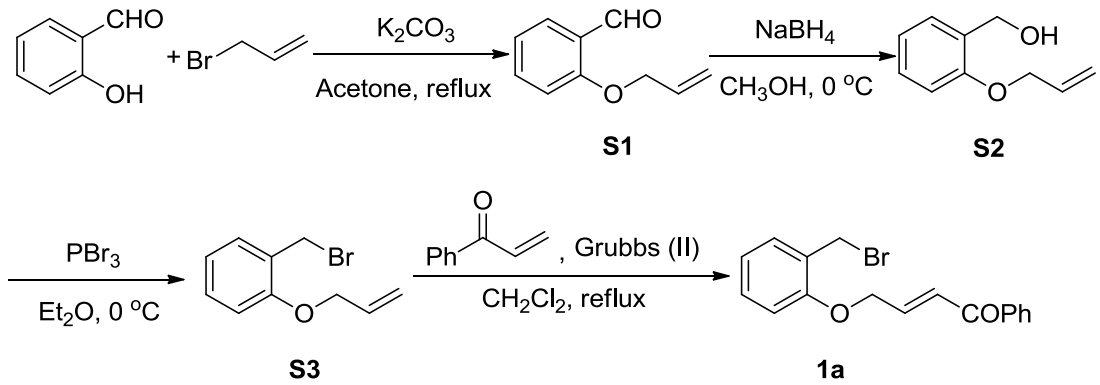
1. General Information

All reactions were carried out under N_2 unless otherwise noted. All 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 MHz or 100 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 7.0TESLA FTMS (ESI) mass spectrometers.

2. Synthesis of Substrates

Compounds **1a-q** are synthesized under the same procedures as shown in scheme S1. **1a** as an example[1]:

Scheme S1



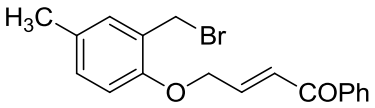
A mixture of salicylaldehyde (12.21 g, 100 mmol), allyl bromide (12.96 mL, 150 mmol), K_2CO_3 (15.2 g, 110 mmol), and acetone (100 mL) was stirred for 15 min, and then warmed to reflux. After the completion of the reaction (monitored by TLC, in 4 hours), the resulting mixture was cooled to room temperature, filtered rapidly through a funnel with a thin layer of silica gel and eluted with DCM. The filtrate was concentrated and the crude product **S1** was pure enough for the next step without the need of further purification.

A solution of the crude product **S1** (16.2 g, 100 mmol) in MeOH (150 mL) was cooled to 0 ℃, and then $NaBH_4$ (1.27 g, 33.3 mmol) was added slowly. After the completion of the reaction (monitored by TLC, in half an hour), saturated NH_4Cl solution was added. The solution was concentrated and the residue was extracted with EtOAc and dried with anhydrous Na_2SO_4. The solution was filtered and concentrated. The crude product **S2** was pure enough for the next step without the need of further purification.

The crude product **S2** (16.4 g, 100 mmol) was then dissolved in dry Et_2O (150 mL) and cooled to 0℃, and to this solution PBr_3 (3.8 mL, 40mmol) was added dropwise. After completion of the reaction (monitored by TLC, in half an hour), saturated aq. $NaHCO_3$ was added and the solution was extracted with Et_2O and dried with anhydrous Na_2SO_4. The solution was filtered and concentrated. The residue was

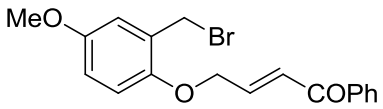
purified by column chromatography on silica gel (PE/EA = 50/1) to give **S3** (76% yield over three steps) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.35-7.32 (m, 1H), 7.29-7.24 (m, 1H), 6.94-6.85 (m, 2H), 6.13-6.03 (m, 1H), 5.51-5.45 (m, 1H), 5.32-5.28 (m, 1H), 4.63-4.60 (m, 4H).

Grubbs (II) catalyst (0.212 g, 0.25 mmol) was added to a mixture of **S3** (5.68 g, 25 mmol), Poly(vinyl phenyl ketone) (6.61 g, 50 mmol), and CH_2Cl_2 (40 mL) under a nitrogen atmosphere at room temperature, and then warmed to reflux. After completion of the reaction monitored by TLC, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EA = 20/1) to give **1a** (65% yield) as a pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 8.03-8.01 (m, 2H), 7.61-7.46 (m, 4H), 7.38-7.19 (m, 3H), 7.00-6.95 (m, 1H), 6.88 (d, *J* = 8.7 Hz, 1H), 4.91-4.90 (m, 2H), 4.66 (s, 2H);^{13}C NMR (100 MHz, $CDCl_3$) δ 189.7, 155.8, 141.7, 137.4, 133.0, 130.9, 130.3, 128.6(4), 128.6(0), 126.2, 125.2, 121.2, 111.8, 66.8, 29.2.



1b

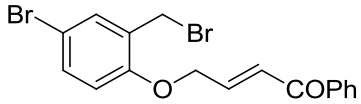
1b, pale yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 8.03-8.01 (m, 2H), 7.60-7.46 (m, 4H), 7.26-7.18 (m, 2H), 7.09 (d, *J* = 8.7 Hz, 1H), 6.77 (d, *J* = 8.1 Hz, 1H), 4.88-4.87 (m, 2H), 4.63 (s, 2H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.8, 153.8, 142.0, 137.4, 133.0, 131.6, 137.7(0), 136.6(7), 128.7, 128.6, 126.0, 125.2, 111.9, 67.0, 29.4, 20.3;



1c

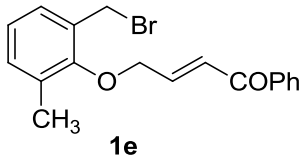
1c, pale yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 8.02-8.00 (m, 2H), 7.60-7.56 (m, 1H), 7.48-7.43 (m, 3H), 7.26-7.17 (m, 1H), 6.93 (s, 1H), 6.82 (s, 2H), 4.86-4.84 (m, 2H), 4.61 (s, 2H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.8, 153.8, 150.0, 142.1, 137.4, 133.0, 128.7, 128.6, 127.2, 125.1, 116.4, 115.0, 113.2, 67.6, 55.7, 29.0; IR ν/ cm^{-1} 2911 (m), 1673 (m), 1502 (m), 1229 (m), 809 (m);

HRMS (positive ESI) calcd for $C_{18}H_{18}BrO_3H^{+1}$ ($[M+H]^+$): 361.0434; Found: 361.0430.



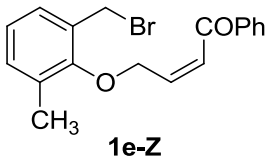
1d

1d, pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.02-7.99 (m, 2H), 7.60-7.56 (m, 1H), 7.50-7.38 (m, 5H), 7.22-7.16 (m, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 4.88-4.87 (m, 2H), 4.57 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.6, 155.0, 141.1, 137.3, 133.6, 133.2, 132.9, 128.7, 128.4, 125.4, 113.6, 113.2, 67.2, 27.7; IR ν/ cm^{-1} 2970 (m), 1738 (m), 1490 (m), 1216 (m), 649 (m); HRMS (positive ESI) calcd for $C_{17}H_{15}Br_2O_2^{+1}$ ($[M+H]^+$): 408.9433; Found: 408.9432.



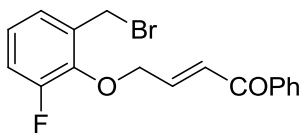
1e

1e, pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.05-8.03 (m, 2H), 7.61-7.48 (m, 4H), 7.26-7.17 (m, 3H), 7.07-7.04 (m, 1H), 4.79-4.77 (m, 2H), 4.58 (s, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.1, 155.3, 142.8, 137.5, 133.0, 132.2, 131.6, 131.2, 129.1, 128.7, 128.6, 124.8(4), 124.8(1), 124.8, 71.6, 28.4, 16.2; IR ν/ cm^{-1} 2987 (m), 2912 (m), 1672 (m), 1446 (m), 1242 (m), 753 (m), 667 (m); HRMS (positive ESI) calcd for $C_{18}H_{18}BrO_2^{+1}$ ($[M+H]^+$): 345.0485; Found: 345.0478.



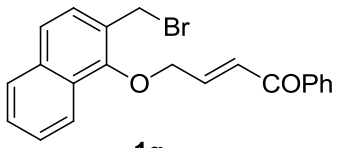
1e-Z

1e-Z, pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.04-8.02 (m, 2H), 7.61-7.57 (m, 1H), 7.52-7.47 (m, 3H), 7.27-7.18 (m, 3H), 7.09-7.06 (m, 1H), 4.75-4.73 (m, 2H), 4.67 (s, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.2, 155.4, 142.8, 137.5, 133.0, 132.2, 131.6, 130.9, 128.8, 128.7, 128.6, 124.8, 124.7, 72.2, 41.4, 16.2.



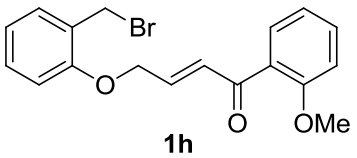
1f

1f, pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.03-8.01 (m, 2H), 7.61-7.57 (m, 1H), 7.52-7.40 (m, 3H), 7.22-7.15 (m, 2H), 7.12-7.00 (m, 2H), 5.01-5.00 (m, 2H), 4.58 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.0, 155.0 (d, $J_{C\text{-}F}$= 246.2 Hz), 144.3 (d, $J_{C\text{-}F}$= 11.0 Hz), 142.2, 137.4, 133.0, 132.4 (d, $J_{C\text{-}F}$= 2.8 Hz), 128.6(5), 128.5(9), 126.0 (d, $J_{C\text{-}F}$= 2.9 Hz), 125.3, 124.1 (d, $J_{C\text{-}F}$= 7.8 Hz), 117.6 (d, $J_{C\text{-}F}$= 19.6 Hz), 72.2 (d, $J_{C\text{-}F}$= 7.0 Hz), 27.4 (d, $J_{C\text{-}F}$= 2.9 Hz); IR ν/ cm^{-1} 2987 (m), 2914 (m), 1672 (m), 1478 (m), 1274 (m), 727 (m), 687 (m); HRMS (positive ESI) calcd for $C_{17}H_{15}BrFO_2^{+1}$ ($[M+H]^+$): 349.0234; Found: 349.0220.



1g

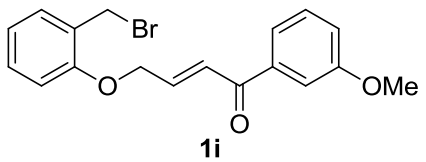
1g, pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.08-8.04 (m, 3H), 7.87-7.83 (m, 1H), 7.67-7.56 (m, 3H), 7.53-7.47 (m, 5H), 7.31 (dt, J = 15.6 and 4.0 Hz, 1H), 4.97-4.96 (m, 2H), 4.77 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.0, 152.6, 142.6, 137.5, 135.0, 133.0, 128.7, 128.6, 128.2, 127.7(9), 127.7(5), 127.0, 126.7(0), 126.6(9), 125.2, 124.9, 122.0, 73.3, 28.2; IR ν/ cm^{-1} 3028 (m), 2970 (m), 1739 (m), 1210 (m), 682 (m); HRMS (positive ESI) calcd for $C_{21}H_{21}BrNO_2^{+1}$ ($[M+NH_4]^+$): 398.0750; Found: 398.0735.



1h

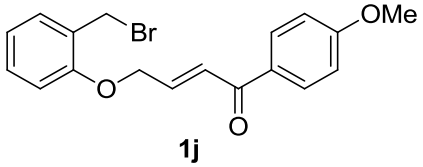
1h, pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.63 (dd, J = 7.6 and 2.0 Hz, 1H), 7.48-7.44 (m, 1H), 7.37-7.35 (m, 1H), 7.31-7.21 (m, 2H), 7.09-6.94 (m, 4H), 6.87 (d, J = 8.4 Hz, 1H), 4.87-4.86 (m, 2H), 4.62 (s, 2H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.8, 158.3, 155.8, 139.7, 133.3, 130.9, 130.5, 130.1, 129.9, 128.4, 126.2, 121.1, 120.5, 111.9, 111.4, 66.8, 55.5, 28.8; IR ν/ cm^{-1} 2926 (m),

1668 (m), 1598 (m), 1249 (m), 749 (m); HRMS (positive ESI) calcd for $C_{18}H_{18}BrO_3^{+1}$ ($[M+H]^+$): 361.0434; Found: 361.0431.



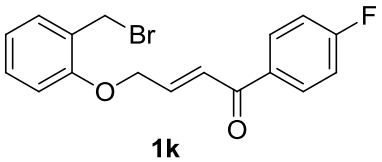
1i

1i, pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.61 (d, *J* = 7.6 Hz, 1H), 7.52-7.46 (m, 2H), 7.40-7.35 (m, 2H), 7.30-7.19 (m, 2H), 7.13-7.11 (m, 1H), 6.98-6.95 (m, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 4.90-4.89 (m, 2H), 4.65 (s, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.5, 159.8, 155.9, 141.7, 138.8, 131.0, 130.3, 129.6, 126.2, 125.2, 121.3(4), 121.2(7), 120.0, 112.5, 111.8, 66.8, 55.4, 29.2; IR ν/ cm^{-1} 2926 (m), 1668 (m), 1286 (m), 754 (m); HRMS (positive ESI) calcd for $C_{18}H_{18}BrO_3^{+1}$ ($[M+H]^+$): 361.0434; Found: 361.0429.



1j

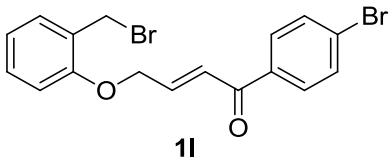
1j, pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.05-8.01 (m, 2H), 7.50 (dt, *J* = 15.6 and 2.2 Hz, 1H), 7.38-7.36 (m, 1H), 7.32-7.28 (m, 1H), 7.19 (dt, *J* = 15.2 and 3.6 Hz, 1H), 6.98-6.94 (m, 3H), 6.88 (d, *J* = 8.4 Hz, 1H), 4.90-4.88 (m, 2H), 4.66 (s, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.0, 163.5, 155.9, 140.7, 131.0, 130.9, 130.3, 126.2, 125.0, 121.2, 113.8, 111.8, 66.8, 55.4, 29.3; IR ν/ cm^{-1} 3015 (m), 2971 (m), 1739 (m), 1599 (m), 1217 (m), 749 (m); HRMS (positive ESI) calcd for $C_{18}H_{18}BrO_3^{+1}$ ($[M+H]^+$): 361.0434; Found: 361.0437.



1k

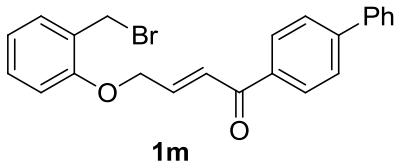
1k, pale yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 8.08-8.04 (m, 2H), 7.54-7.48 (m, 1H), 7.36-7.12 (m, 5H), 7.00-6.95 (m, 1H), 6.88 (d, *J* = 10.8 Hz, 1H), 4.91-4.90 (m, 2H), 4.66 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.0, 165.7 (d,

$J_{C\text{-}F}$= 253.3 Hz), 155.8, 141.8, 133.7 (d, $J_{C\text{-}F}$= 3.0 Hz), 131.3 (d, $J_{C\text{-}F}$= 9.3 Hz), 131.0, 130.4, 126.1, 124.7, 121.3, 115.7 (d, $J_{C\text{-}F}$= 21.8 Hz), 111.7, 66.6, 29.3; IR ν/ cm^{-1} 3022 (m), 2970 (m), 1739 (m), 1590 (m), 1214 (m), 745 (m); HRMS (positive ESI) calcd for $C_{17}H_{15}FO_2^{+1}$ ($[M+H]^+$): 349.0234; Found: 349.0223.



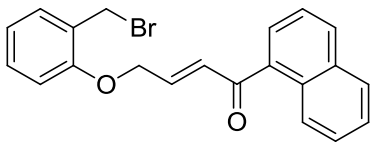
1l

1l, pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.90-7.87 (m, 2H), 7.64-7.61 (m, 2H), 7.49 (dt, *J* = 15.2 and 2.4 Hz, 1H), 7.39-7.36 (m, 1H), 7.33-7.29 (m, 1H), 7.27-7.21 (m, 1H), 7.00-6.96 (m, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 4.91-4.90 (m, 2H), 4.66 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.6, 155.8, 142.2, 136.1, 131.9, 131.0, 130.4, 130.2, 128.3, 126.1, 124.6, 121.3, 111.7, 66.6, 29.3; IR ν/ cm^{-1} 3027 (m), 2970 (m), 1739 (m), 1671 (m), 1216 (m), 752 (m); HRMS (positive ESI) calcd for $C_{17}H_{15}Br_2O_2^{+1}$ ($[M+H]^+$): 408.9433; Found: 408.9417.



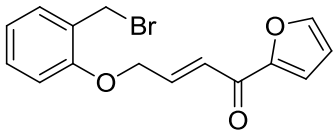
1m

1m, pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.10 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 7.2 Hz, 2H), 7.56 (dt, *J* = 15.6 and 2.0 Hz, 1H), 7.48-7.44 (m, 2H), 7.41-7.36 (m, 2H), 7.32-7.21 (m, 2H), 6.98-6.95 (m, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 4.91-4.90 (m, 2H), 4.67 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.2, 155.9, 145.7, 141.6, 139.8, 136.1, 131.0, 130.4, 129.3, 128.9, 128.2, 127.3, 127.2, 126.2, 125.2, 121.3, 111.8, 66.8, 29.2; IR ν/ cm^{-1} 2987 (m), 1667 (m), 1600 (m), 1492 (m), 1256 (m), 752 (m); HRMS (positive ESI) calcd for $C_{23}H_{20}BrO_2^{+1}$ ($[M+H]^+$): 407.0641; Found: 407.0635.



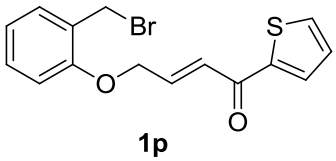
1n

1n, pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.41 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.89-7.87 (m, 1H), 7.80 (d, *J* = 6.8 Hz, 1H), 7.58-7.48 (m, 3H), 7.36-7.20 (m, 3H), 7.06 (dt, *J* = 15.6 and 3.6 Hz, 1H), 6.98-6.94 (m, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 4.86(4)-4.86(0) (m, 2H), 4.60 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 155.7, 142.7, 135.9, 133.7, 132.1, 131.0, 130.4, 130.2, 129.8, 128.4, 127.9, 127.5, 126.4, 126.3, 125.6, 124.4, 121.3, 111.8, 66.6, 28.9; IR ν/ cm^{-1} 2987 (m), 2901 (m), 1667 (m), 1600 (m), 1492 (m), 1250 (m), 751 (m); HRMS (positive ESI) calcd for $C_{21}H_{18}BrO_2^{+1}$ ([M+H]$^+$): 381.0485; Found: 381.0478.



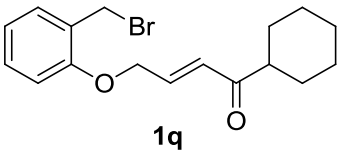
1o

1o, pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.66-7.65 (m, 1H), 7.38- 7.25 (m, 5H), 6.99-6.95 (m, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.58-6.56 (m, 1H), 4.90-4.88 (m, 2H), 4.66 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.2, 155.9, 153.0, 147.2, 141.1, 131.0, 130.4, 126.2, 124.6, 121.3, 118.6, 112.4, 111.8, 66.7, 29.2; IR ν/ cm^{-1} 3103 (m), 2970 (m), 1739 (m), 1494 (m), 1293 (m), 747 (m); HRMS (positive ESI) calcd for $C_{15}H_{14}BrO_3^{+1}$ ([M+H]$^+$): 321.0121; Found: 321.0125.



1p

1p, pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.86 (d, *J* = 3.6 Hz, 1H), 7.68 (d, *J* = 4.8 Hz, 1H), 7.45-7.36 (m, 2H), 7.33-7.22 (m, 2H), 7.17-7.15 (m, 1H), 6.99-6.88 (m, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 4.91-4.89 (m, 2H), 4.67 (s, 2H).



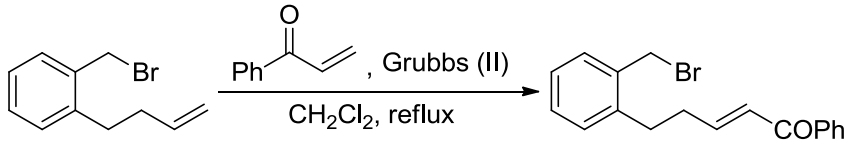
1q

1q, pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.37-7.35 (m, 1H), 7.31-7.26 (m, 1H), 7.03-6.94 (m, 2H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.69 (dt, *J* = 15.6 and 2.0 Hz, 1H), 4.82-4.80 (m, 2H), 4.62 (s, 2H), 2.58-2.51 (m, 1H), 1.88-1.67 (m, 5H), 1.43-1.19 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.6, 155.9, 139.3, 131.0, 130.2, 127.9, 126.3, 121.3, 111.9, 66.8, 49.4, 29.0, 28.3, 25.8, 25.6; IR ν/ cm^{-1} 2928 (m),

2854 (m), 1692 (m), 1492 (m), 1249 (m), 746 (m); HRMS (positive ESI) calcd for $C_{17}H_{22}BrO_2^{+1}$ ($[M+H]^+$): 337.0798; Found: 337.0798.

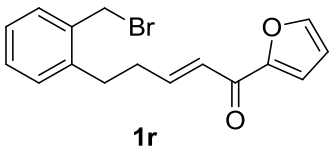
Compounds **1r-v** are synthesized under the same procedures as shown in scheme S2. **1t** as an example[1]

Scheme S2



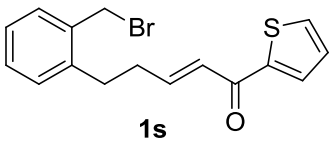
S4 **1t**

Grubbs (II) catalyst (0.093 g, 0.11 mmol) was added to a mixture of **S3** (1.23 g, 5.5 mmol), Poly(vinyl phenyl ketone) (1.81 g, 13.7 mmol), and CH_2Cl_2 (9 mL) under a nitrogen atmosphere at room temperature, and then warmed to reflux. After completion of the reaction monitored by TLC, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EA = 50/1) to give **1t** (83% yield) as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.91-7.89 (m, 2H), 7.58-7.54 (m, 1H), 7.48-7.45 (m, 2H), 7.36-7.34 (m, 1H), 7.30-7.19 (m, 3H), 7.16-7.09 (m, 1H), 6.95-6.90 (m, 1H), 4.55 (s, 2H), 3.00-2.96 (m, 2H), 2.74-2.69 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.6, 147.9, 139.6, 137.6, 135.4, 132.7, 130.7, 129.6, 129,1, 128.5, 126.8, 126.5, 33.6, 31.5, 30.6.



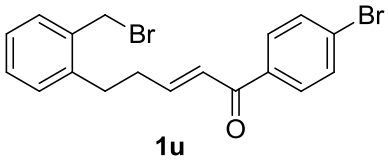
1r

1r, pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.62-7.61 (m, 1H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.29-7.18 (m, 5H), 6.87-6.83 (m, 1H), 6.55 (d, *J* = 4.2 Hz, 1H), 4.54 (s, 2H), 2.98-2.94 (m, 2H), 2.72-2.66 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8, 153.1, 147.2, 146.5, 139.6, 135.3, 130.6, 129.5, 129.1, 126.8, 125.4, 117.6, 112.3, 33.4, 31.5, 30.6; IR ν/ cm^{-1} 2987 (m), 1666 (m), 1622 (m), 1463 (m), 1215 (m), 754 (m); HRMS (positive ESI) calcd for $C_{16}H_{16}BrO_2^{+1}$ ($[M+H]^+$): 319.0328; Found: 319.0320.



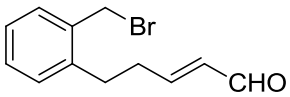
1s

1s, pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.72 (d, *J* = 3.2 Hz, 1H), 7.64-7.62 (m, 1H), 7.34-7.32 (m, 1H), 7.29-7.27 (m, 1H), 7.23-7.11 (m, 4H), 6.84 (dt, *J* = 15.2 and 1.4 Hz, 1H), 4.54 (s, 2H), 2.97-2.93 (m, 2H), 2.72-2.66 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.9, 147.0, 144.8, 139.5, 135.2, 133.8, 131.9, 130.6, 129.5, 129.0, 128.0, 126.7, 125.8, 33.2, 31.5, 30.6, 30.5; IR ν/ cm^{-1} 2987 (m), 1657 (m), 1602 (m), 1413 (m), 1215 (m), 723 (m); HRMS (positive ESI) calcd for $C_{16}H_{16}BrOS^{+1}$ ($[M+H]^+$): 335.0100; Found: 335.0093.



1u

1u, pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.77-7.74 (m, 2H), 7.60-7.58 (m, 2H), 7.36-7.33 (m, 1H), 7.29-7.25 (m, 1H), 7.22-7.19 (m, 2H), 7.16-7.09 (m, 1H), 6.86 (d, *J* = 15.6 Hz, 1H), 4.54 (s, 2H), 2.98-2.94 (m, 2H), 2.73-2.68 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.4, 148.5, 139.5, 136.4, 135.4, 131.8, 130.7, 130.0, 129.6, 129.1, 127.8, 126.9, 126.0, 33.5, 31.5, 30.6; IR ν/ cm^{-1} 2972 (m), 2924 (m), 1667 (m), 1617 (m), 1454 (m), 1208 (m), 754 (m); HRMS (positive ESI) calcd for $C_{18}H_{17}Br_2O^{+1}$ ($[M+H]^+$): 406.9641; Found: 406.9636.

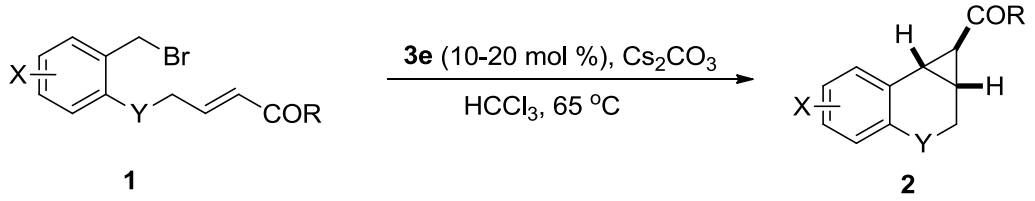


1v

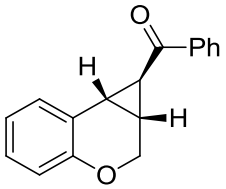
1v, pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 9.53 (d, *J* = 7.6 Hz, 1H), 7.36-7.19 (m, 4H), 6.96-6.88 (m, 1H), 6.22-6.16 (m, 1H), 4.54 (s, 2H), 2.98-2.94 (m, 2H), 2.77-2.72 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.9, 156.8, 139.2, 135.4, 133.4, 130.8, 129.5, 129.2, 127.1, 33.3, 31.4, 30.2.

3. General Procedure for the Intramolecular Cyclopropanation Reaction

Scheme S3

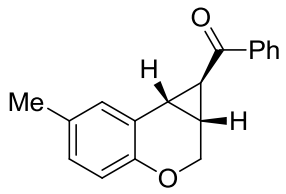


A mixture of **1** (0.3 mmol), **3e** (0.03-0.06 mmol), Cs_2CO_3 (0.6 mmol), and $HCCl_3$ (4 mL) was stirred under a nitrogen atmosphere at 65 ^{o}C. After completion of the reaction (monitored by TLC), the resulting mixture was filtered rapidly through a funnel with a thin layer of silica gel and eluted with DCM. The filtrate was concentrated and the residue was purified by chromatography on silica gel to afford the desired products.



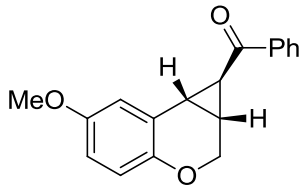
2a

2a, white solid, 90% yield; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 8.00-7.98 (m, 2H), 7.59-7.54 (m, 1H), 7.48-7.43 (m, 2H), 7.26-7.24 (m, 1H), 7.18-7.12 (m, 1H), 6.96-6.85 (m, 2H), 4.44 (d, *J* = 10.8 Hz, 1H), 4.02 (d, *J* = 10.8 Hz, 1H), 3.40-3.71 (m, 1H), 2.79 (dd, *J* = 9.0 and 3.3 Hz, 1H), 2.63-2.59 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.1, 152.8, 137.3, 133.0, 128.7, 128.5, 128.2, 127.4, 124.4, 121.9, 117.3, 61.9, 29.7, 28.8, 26.5; IR ν/ cm^{-1} 3056 (m), 2963 (m), 1660 (m), 1489 (m), 1254 (m), 697 (m); MS (EI, m/z, rel. intensity) 250 (24.3, M^+), 105 (100.0), 77 (54.1); HRMS (EI) calcd for $C_{17}H_{14}O_2$ (M^+): 250.0994; Found: 250.0997.



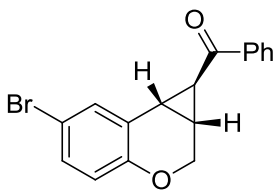
2b

2b, pale yellow solid, 92% yield; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.99 (d, *J* = 7.2 Hz, 2H), 7.58-7.54 (m, 1H), 7.48-7.43 (m, 2H), 7.06 (s, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 6.75 (d, *J* = 8.1 Hz, 1H), 4.41 (d, *J* = 11.4 Hz, 1H), 3.98 (d, *J* = 10.8 Hz, 1H), 3.78-3.35 (m, 1H), 2.74 (dd, *J* = 8.4 and 3.0 Hz, 1H), 2.61-2.57 (m, 1H), 2.27 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.1, 150.5, 137.3, 133.0, 131.2, 129.1, 128.5, 128.2, 127.8, 124.1, 117.0, 62.0, 29.6, 28.7, 26.6, 20.5; IR ν/ cm^{-1} 2974 (m), 2921 (m), 1658 (m), 1502 (m), 1206 (m), 691 (m); HRMS (positive ESI) calcd for $C_{18}H_{17}O_2^{+1}$ ([M+H]$^+$): 265.1223; Found: 265.1232.



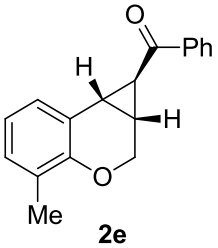
2c

2c, pale yellow oil, 84% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.98 (d, *J* = 7.2 Hz, 2H), 7.57-7.53 (m, 1H), 7.46-7.42 (m, 2H), 6.81-6.77 (m, 2H), 6.69-6.66 (m, 1H), 4.38 (d, *J* = 10.4 Hz, 1H), 3.94 (d, *J* = 11.2 Hz, 1H), 3.74 (s, 3H), 3.40-3.38 (m, 1H), 2.74 (dd, *J* = 9.2 and 2.4 Hz, 1H), 2.58-2.55 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 154.3, 146.5, 137.2, 133.0, 128.5, 128.2, 125.2, 117.8, 113.6, 112.7, 62.0, 55.6, 29.5, 28.5, 26.7; IR ν/ cm^{-1} 2928 (m), 1660 (m), 1495 (m), 1201 (m), 696 (m); HRMS (positive ESI) calcd for $C_{18}H_{17}O_3^{+1}$ ([M+H]$^+$): 281.1172; Found: 281.1176.



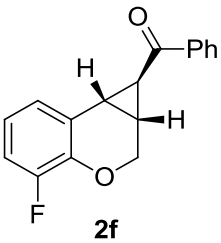
2d

2d, pale yellow oil, 83% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.98-7.96 (m, 2H), 7.59-7.55 (m, 1H), 7.48-7.44 (m, 2H), 7.36(4)-7.35(8) (m, 1H), 7.26-7.21 (m, 1H), 6.74 (d, *J* = 8.8 Hz, 1H), 4.43 (dd, *J* = 10.8 and 1.0 Hz, 1H), 3.99 (dd, *J* = 10.8 and 1.4 Hz, 1H), 3.35-3.33 (m, 1H), 2.72 (dd, *J* = 9.2 and 3.0 Hz, 1H), 2.61-2.57 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 151.8, 137.1, 133.2, 131.2, 130.2, 128.6, 128.2, 126.6, 119.0, 113.9, 62.0, 29.1, 28.7, 25.7; IR ν/ cm^{-1} 2925 (m), 2872 (m), 1662 (m), 1482 (m), 1251 (m), 699 (m); HRMS (positive ESI) calcd for $C_{17}H_{14}BrO_2^{+1}$ ([M+H]$^+$): 329.0172; Found: 329.0178.



2e

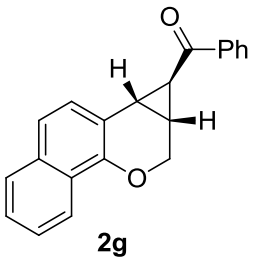
2e, pale yellow oil, 93% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.00-7.98 (m, 2H), 7.57-7.53 (m, 1H), 7.46-7.42 (m, 2H), 7.08 (d, *J* = 7.2 Hz, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.85-6.81 (m, 1H), 4.48 (d, *J* = 10.8 Hz, 1H), 3.99 (d, *J* = 11.2 Hz, 1H), 3.39-3.37 (m, 1H), 2.77 (dd, *J* = 8.8 and 3.2 Hz, 1H), 2.62-2.58 (m, 1H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 150.9, 137.3, 133.0, 128.8, 128.5, 128.2, 126.5, 126.3, 123.9, 121.3, 61.9, 29.8, 28.6, 26.8, 15.5; IR ν/ cm^{-1} 2921 (m), 1664 (m), 1475 (m), 1217 (m), 700 (m); HRMS (positive ESI) calcd for $C_{18}H_{17}O_2^{+1}$ ([M+H]$^+$): 265.1223; Found: 265.1231.



2f

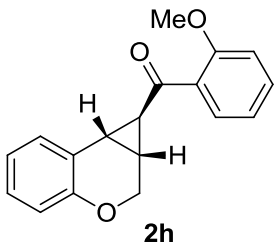
2f, white solid, 86% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.99-7.97 (m, 2H), 7.58-7.54 (m, 1H), 7.47-7.43 (m, 2H), 7.03-7.01 (m, 1H), 6.97-6.92 (m, 1H), 6.85-6.82 (m, 1H), 4.53 (d, *J* = 10.8 Hz, 1H), 4.04 (d, *J* = 10.8 Hz, 1H), 3.40-3.38 (m,

1H), 2.82-2.79 (m, 1H), 2.63-2.60 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 151.6 (d, $J_{C\text{-}F}$ = 244.4 Hz), 140.4 (d, $J_{C\text{-}F}$ = 12.1 Hz), 137.1, 133.2, 128.6, 128.2, 126.9, 123.7 (d, $J_{C\text{-}F}$ = 3.4 Hz), 121.5 (d, $J_{C\text{-}F}$ = 7.4 Hz), 114.3 (d, $J_{C\text{-}F}$ = 18.3 Hz), 62.1, 29.3, 28.8, 25.7 (d, $J_{C\text{-}F}$ = 3.0 Hz); IR ν/ cm^{-1} 2974 (m), 2877 (m), 1649 (m), 1482 (m), 1258 (m), 739 (m), 702 (m); HRMS (positive ESI) calcd for $C_{17}H_{14}FO_2^{+1}$ ($[M+H]^+$): 269.0972; Found: 269.0978.



2g

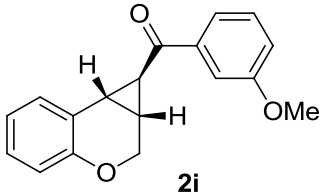
2g, pale yellow oil, 91% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.17-8.14 (m, 1H), 8.00-7.97 (m, 2H), 7.78-7.76 (m, 1H), 7.56-7.52 (m, 1H), 7.49-7.41 (m, 5H), 7.35 (d, *J* = 8.0 Hz, 1H), 4.65 (dd, *J* = 10.8 and 1.2 Hz, 1H), 4.14 (dd, *J* = 10.8 and 1.6 Hz, 1H), 3.47-3.45 (m, 1H), 2.86 (dd, *J* = 9.2 and 3.2 Hz, 1H), 2.76-2.72 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 147.8, 137.3, 133.2, 133.1, 128.5, 128.2, 127.6, 126.5, 125.8, 125.6, 125.2, 121.2, 121.1, 118.7, 62.3, 30.4, 30.0, 26.7; IR ν/ cm^{-1} 3055 (m), 2872 (m), 1661 (m), 1448 (m), 1217 (m), 703 (m), 689 (m); HRMS (positive ESI) calcd for $C_{21}H_{17}O_2^{+1}$ ($[M+H]^+$): 301.1223; Found: 301.1230.



2h

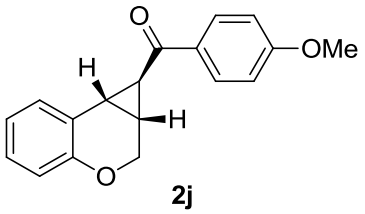
2h, pale yellow oil, 96% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.60 (dd, *J* = 7.6 and 0.8 Hz, 1H), 7.45-7.40 (m, 1H), 7.26-7.24 (m, 1H), 7.12-7.08 (m, 1H), 7.00-6.96 (m, 1H), 6.93-6.89 (m, 2H), 6.82 (d, *J* = 8.4 Hz, 1H), 4.41 (d, *J* = 11.2 Hz, 1H), 4.00 (d, *J* = 10.8 Hz, 1H), 3.74 (s, 3H), 3.38-3.36 (m, 1H), 2.76 (dd, *J* = 9.2 and 3.6 Hz, 1H), 2.59-2.56 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 158.6, 152.7,

133.4, 129.9, 128.8, 128.6, 127.0, 124.9, 121.6, 120.5, 117.1, 111.5, 62.1, 55.6, 33.8, 29.4, 26.3; IR ν/ cm^{-1} 2962 (m), 2938 (m), 1656 (m), 1486 (m), 1246 (m), 752 (m); HRMS (positive ESI) calcd for $C_{18}H_{17}O_3^{+1}$ ($[M+H]^+$): 281.1172; Found: 281.1173



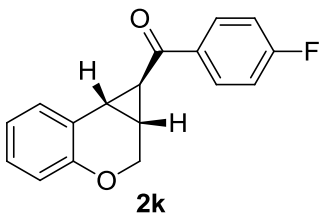
2i

2i, pale yellow solid, 94% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.58 (d, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 1.2 Hz, 1H), 7.38-7.34 (m, 1H), 7.26-7.23 (m, 1H), 7.16-7.09 (m, 2H), 6.95-6.91 (m, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 4.43 (d, *J* = 10.8 Hz, 1H), 4.02 (d, *J* = 11.2 Hz, 1H), 3.85 (s, 3H), 3.36-3.34 (m, 1H), 2.78 (dd, *J* = 9.2 and 3.2 Hz, 1H), 2.61-2.58 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 159.8, 152.8, 138.7, 129.5, 128.7, 127.4, 124.4, 121.9, 121.0, 119.6, 117.3, 112.3, 62.0, 55.4, 29.8, 29.0, 26.6; IR ν/ cm^{-1} 2919 (m), 1656 (m), 1428 (m), 1258 (m), 766 (m); HRMS (positive ESI) calcd for $C_{18}H_{17}O_3^{+1}$ ($[M+H]^+$): 281.1172; Found: 281.1163.



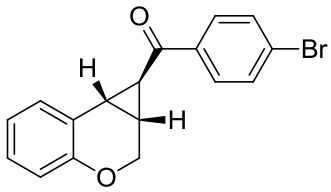
2j

2j, white solid, 91% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.99-7.95 (m, 2H), 7.25-7.22 (m, 1H), 7.15-7.11 (m, 1H), 6.94-6.89 (m, 3H), 6.85 (d, *J* = 8.0 Hz, 1H), 4.41 (dd, *J* = 11.2 and 1.2 Hz, 1H), 4.00 (dd, *J* = 11.2 and 1.2 Hz, 1H), 3.84 (s, 3H), 3.32-3.30 (m, 1H), 2.75 (dd, *J* = 8.8 and 3.2 Hz, 1H), 2.58-2.54 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.4, 163.5, 152.7, 130.5, 130.3, 128.7, 127.2, 124.6, 121.8, 117.2, 113.6, 62.0, 55.4, 29.3, 28.4, 26.0; IR ν/ cm^{-1} 2978 (m), 2923 (m), 1643 (m), 1593 (m), 1254 (m), 809 (m), 759 (m); HRMS (positive ESI) calcd for $C_{18}H_{17}O_3^{+1}$ ($[M+H]^+$): 281.1172; Found: 281.1177.



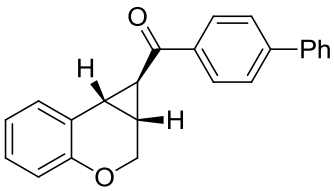
2k

2k, white solid, 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.03-7.98 (m, 2H), 7.25-7.23 (m, 1H), 7.16-7.08 (m, 3H), 6.95-6.91 (m, 1H), 6.87-6.85 (m, 1H), 4.42 (dd, *J* = 11.2 and 1.2 Hz, 1H), 4.01 (dd, *J* = 11.2 and 1.2 Hz, 1H), 3.33-3.31 (m, 1H), 2.78 (dd, *J* = 9.2 and 3.6 Hz, 1H), 2.62-2.58 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 165.7 (d, $J_{C\text{-}F}$ = 253.3 Hz), 152.8, 133.7 (d, $J_{C\text{-}F}$ = 3.0 Hz), 130.8 (d, $J_{C\text{-}F}$ = 9.1 Hz), 128.7, 127.5, 124.3, 122.0, 117.3, 115.6 (d, $J_{C\text{-}F}$ = 22 Hz), 61.9, 29.7, 28.6, 26.6; IR ν/ cm^{-1} 2977 (m), 1652 (m), 1487 (m), 1217 (m), 794 (m); HRMS (positive ESI) calcd for $C_{17}H_{14}FO_2^{+1}$ ([M+H]$^+$): 269.0972; Found: 269.0976.



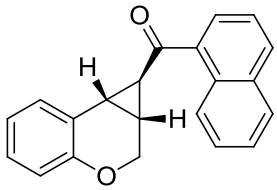
2l

2l, white solid, 66% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.84-7.82 (m, 2H), 7.58-7.55 (m, 2H), 7.24-7.22 (m, 1H), 7.16-7.11 (m, 1H), 6.95-6.91 (m, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 4.42 (d, *J* = 11.2 Hz, 1H), 4.00 (d, *J* = 11.2 Hz, 1H), 3.31-3.29 (m, 1H), 2.78 (dd, *J* = 8.8 and 3.2 Hz, 1H), 2.61-2.58 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 152.7, 136.0, 131.8, 129.7, 128.7, 128.2, 127.5, 124.2, 122.0, 117.3, 61.8, 29.9, 28.7, 26.8; IR ν/ cm^{-1} 2967 (m), 2924 (m), 1655 (m), 1487 (m), 1217 (m), 797 (m), 757 (m); HRMS (positive ESI) calcd for $C_{17}H_{14}BrO_2^{+1}$ ([M+H]$^+$): 329.0172; Found: 329.0173.



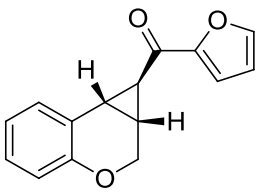
2m

2m, white solid, 84% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.08-8.04 (m, 2H), 7.69-7.66 (m, 2H), 7.63-7.60 (m, 2H), 7.48-7.43 (m, 2H), 7.41-7.37 (m, 1H), 7.27-7.25 (m, 1H), 7.17-7.13 (m, 1H), 6.96-6.92 (m, 1H), 6.88-6.86 (m, 1H), 4.40 (dd, *J* = 10.8 and 1.2 Hz, 1H), 4.03 (dd, *J* = 11.2 and 1.2 Hz, 1H), 3.42-3.40 (m, 1H), 2.81 (dd, *J* = 9.6 and 3.6 Hz, 1H), 2.64-2.61 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 152.8, 145.6, 139.7, 135.9, 128.9, 128.8, 128.7, 128.2, 127.4, 127.2, 127.1, 124.4, 121.9, 117.3, 61.9, 29.6, 28.8, 26.5; IR ν/ cm^{-1} 2926 (m), 1656 (m), 1220 (m), 764 (m), 730 (m); HRMS (positive ESI) calcd for $C_{23}H_{19}O_2^{+1}$ ($[M+H]^+$): 327.1380; Found: 327.1389.



2n

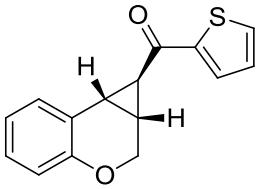
2n, white solid, 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.55-8.53 (m, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.94-7.92 (m, 1H), 7.88-7.86 (m, 1H), 7.59-7.46 (m, 3H), 7.33-7.31 (m, 1H), 7.16-7.12 (m, 1H), 6.98-6.94 (m, 1H), 6.85-6.83 (m, 1H), 4.57 (dd, *J* = 10.8 and 1.0 Hz, 1H), 4.06 (dd, *J* = 11.0 and 1.4 Hz, 1H), 3.32-3.30 (m, 1H), 2.91 (dd, *J* = 8.8 and 3.2 Hz, 1H), 2.76-2.72 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.6, 152.8, 136.4, 133.8, 132.6, 129.9, 128.7, 128.4, 128.1, 127.7, 127.4, 126.4, 125.6, 124.4, 124.3, 121.9, 117.3, 61.9, 32.9, 29.9, 27.1; IR ν/ cm^{-1} 2924 (m), 1657 (m), 1488 (m), 1220 (m), 1045 (m), 764 (m); HRMS (positive ESI) calcd for $C_{21}H_{17}O_2^{+1}$ ($[M+H]^+$): 301.1223; Found: 301.1227.



2o

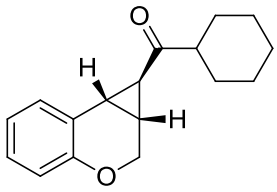
2o, pale yellow solid, 72% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.59 (s, 1H), 7.26-7.22 (m, 2H), 7.15-7.11 (m, 1H), 6.94-6.90 (m, 1H), 6.86-6.84 (m, 1H), 6.54-6.52 (m, 1H), 4.41 (d, *J* = 10.8 Hz, 1H), 3.99 (d, *J* = 10.8 Hz, 1H), 3.27-3.25 (m,

1H), 2.78 (dd, J = 8.8 and 4.0 Hz, 1H), 2.59-2.56 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.7, 152.8, 152.7, 146.7, 128.7, 127.4, 124.3, 121.9, 117.3(5), 117.2(6), 112.3, 61.8, 29.2, 28.8, 26.0; IR ν/ cm^{-1} 2923 (m), 2854 (m), 1650 (m), 1491 (m), 1054 (m), 775 (m), 760 (m); HRMS (positive ESI) calcd for $C_{15}H_{13}O_3^{+1}$ ([M+H]$^+$): 241.0859; Found: 241.0864.



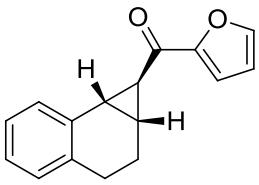
2p

2p, white solid, 84% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.79-7.78 (m, 1H), 7.66-7.64 (m, 1H), 7.26-7.23 (m, 1H), 7.16-7.11 (m, 2H), 6.95-6.91 (m, 1H), 6.86 (d, J = 8.4 Hz, 1H), 4.43 (d, J = 11.2 Hz, 1H), 4.00 (d, J = 11.2 Hz, 1H), 3.23-3.21 (m, 1H), 2.81 (dd, J = 8.8 and 3.2 Hz, 1H), 2.61-2.57 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.5, 152.7, 144.6, 133.9, 132.3, 128.7, 128.2, 127.4, 124.3, 121.9, 117.3, 61.8, 29.5, 29.4, 26.0; IR ν/ cm^{-1} 2957 (m), 1638 (m), 1255 (m), 1067 (m), 722 (m); HRMS (positive ESI) calcd for $C_{15}H_{13}O_2S^{+1}$ ([M+H]$^+$): 257.0631; Found: 257.0639.



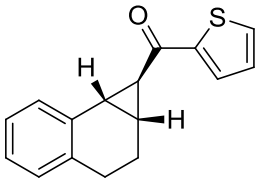
2q

2q. white solid, 94% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.21-7.19 (m, 1H), 7.13-7.08 (m, 1H), 6.93-6.89 (m, 1H), 6.81 (d, J = 8.4 Hz, 1H), 4.34 (dd, J = 11.2 and 1.0 Hz, 1H), 3.92 (dd, J = 10.8 and 1.0 Hz, 1H), 2.69-2.67 (m, 1H), 2.54-2.44 (m, 2H), 2.34-2.31 (m, 1H), 1.94-1.87 (m, 2H), 1.79-1.75 (m, 2H), 1.67-1.65 (m, 1H), 1.43-1.16 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.4, 152.6, 128.5, 127.2, 124.5, 121.8, 117.2, 61.8, 51.6, 30.7, 28.6, 28.1, 25.8, 25.6, 25.3; IR ν/ cm^{-1} 2919 (m), 1676 (m), 1251 (m), 755 (m); HRMS (positive ESI) calcd for $C_{17}H_{21}O_2^{+1}$ ([M+H]$^+$): 257.1536; Found: 257.1546.



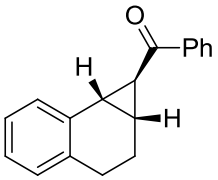
2r

2r, white solid, 92% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.56 (s, 1H), 7.28-7.26 (m, 1H), 7.19-7.14 (m, 3H), 7.08-7.06 (m, 1H), 6.53-6.52 (m, 1H), 3.10-3.08 (m, 1H), 2.81-2.71 (m, 2H), 2.67-2.58 (m, 1H), 2.47-2.45 (m, 1H), 2.25-2.21 (m, 1H), 1.93-1.84 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.9, 153.1, 146.2, 135.2, 133.8, 128.8, 128.5, 126.2, 126.0, 116.4, 112.2, 30.0, 28.0, 27.2, 25.4, 18.8; IR ν/ cm^{-1} 2933 (m), 1648 (m), 1417 (m), 1061 (m), 771 (m); HRMS (positive ESI) calcd for $C_{16}H_{15}O_2^{+1}$ ($[M+H]^+$): 239.1067; Found: 239.1070.



2s

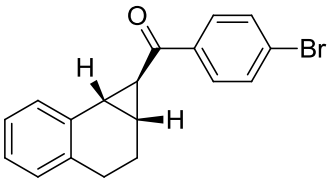
2s, white solid, 91% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.73-7.72 (m, 1H), 7.62-7.61 (m, 1H), 7.29-7.25 (m, 1H), 7.18-7.07 (m, 4H), 3.02-3.00 (m, 1H), 2.82-2.72 (m, 2H), 2.66-2.57 (m, 1H), 2.48-2.45 (m, 1H), 2.27-2.21 (m, 1H), 1.94-1.85 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.5, 144.9, 135.2, 133.8, 133.4, 131.6, 128.9, 128.6, 128.0, 126.3, 126.1, 30.0, 28.8, 27.3, 25.4, 18.8; IR ν/ cm^{-1} 2988 (m), 1625 (m), 1418 (m), 1248 (m), 765 (m); HRMS (positive ESI) calcd for $C_{16}H_{15}OS^{+1}$ ($[M+H]^+$): 255.0838; Found: 255.0850.



2t

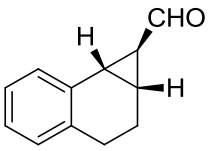
2t, white solid, 95% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.96-7.94 (m, 2H), 7.56-7.52 (m, 1H), 7.46-7.42 (m, 2H), 7.31-7.25 (m, 1H), 7.19-7.12 (m, 2H),

7.09-7.07 (m, 1H), 3.17-3.15 (m, 1H), 2.81-2.73 (m, 2H), 2.68-2.59 (m, 1H), 2.50-2.47 (m, 1H), 2.28-2.22 (m, 1H), 1.95-1.86 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3, 137.8, 135.4, 133.9, 132.7, 128.9, 128.7, 128.5, 128.0, 126.4, 126.1, 30.5, 28.3, 27.6, 25.6, 18.9.



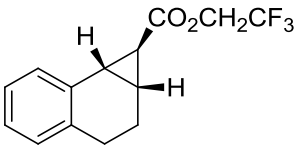
2u

2u, white solid, 93% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.29-7.25 (m, 1H), 7.18-7.13 (m, 2H), 7.09-7.07 (m, 1H), 3.10-3.08 (m, 1H), 2.80-2.73 (m, 2H), 2.67-2.58 (m, 1H), 2.50-2.48 (m, 1H), 2.27-2.22 (m, 1H), 1.95-1.86 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 136.5, 135.1, 133.8, 131.7, 129.6, 128.9, 128.7, 127.8, 126.4, 126.2, 30.8, 28.2, 27.8, 25.5, 18.9; IR ν/ cm^{-1} 2920 (m), 1655 (m), 1412 (m), 1224 (m), 1045 (m), 790 (m); HRMS (positive ESI) calcd for $C_{18}H_{16}BrO^{+1}$ ($[M+H]^+$): 327.0379; Found: 327.0387.



2v

2v, colourless oil, 81% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 9.35 (d, *J* = 4.4 Hz, 1H), 7.27-7.25 (m, 1H), 7.18-7.12 (m, 2H), 7.05-7.03 (m, 1H), 2.72-2.66 (m, 2H), 2.53-2.39 (m, 2H), 2.34-2.31 (m, 1H), 2.24-2.18 (m, 1H), 1.91-1.82 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 134.0, 133.7, 128.6(9), 128.6(7), 126.4, 126.3 33.0, 27.3, 25.2, 24.8, 18.6;

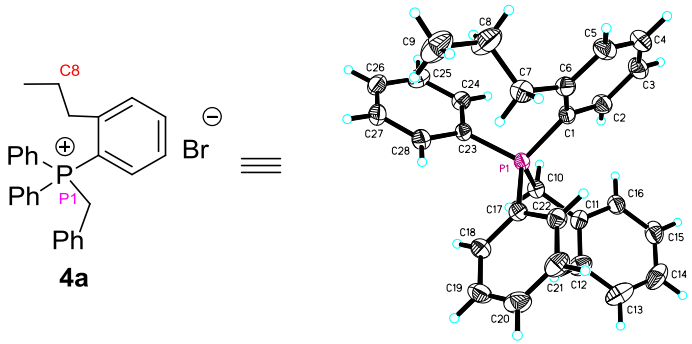


2w

A mixture of **1x** (0.3 mmol), **3e** (0.06 mmol), Cs_2CO_3 (0.6 mmol), and toluene (3 mL) was stirred under a nitrogen atmosphere at 110 ^{o}C. After completion of the reaction (monitored by TLC), 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 product **2x** as a colourless oil in 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.30-7.25 (m, 1H), 7.18-7.12 (m, 2H), 7.04-7.03 (m, 1H), 4.51-4.44 (m, 2H), 2.71-2.61 (m, 2H), 2.51-2.42 (m, 1H), 2.27-2.16 (m, 3H), 1.87-1.78 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 134.2, 133.7, 128.9, 128.7, 126.4, 126.3, 120.2 (q, $J_{C\text{-}F}$ = 275.8 Hz), 60.5 (q, $J_{C\text{-}F}$ = 36.7 Hz), 27.4, 25.2, 25.1, 22.4, 18.5. IR ν/ cm^{-1} 2928 (m), 1741 (m), 1423 (m), 1145 (m); MS (EI, m/z, rel. intensity) 270 (43.9, M^+), 187 (19.8), 141 (56.7), 128 (100.0); HRMS (EI) calcd for $C_{14}H_{13}O_2F_3$ (M^+): 270.0865; Found: 270.0868.

4. X-Ray structure of 4

4.1 X-Ray structure of 4a (CCDC 992015)



Bond precision: C-C = 0.0060 A Wavelength=0.71073

Cell: a=9.9037(7) b=21.1560(15) c=12.948(1)

alpha=90 beta=94.929(2) gamma=90

Temperature: 293 K

	Calculated	Reported
Volume	2702.9(3)	2702.9(3)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C28 H28 P, C H2 Cl2, Br	?
Sum formula	C29 H30 Br Cl2 P	C29 H30 Br Cl2 P
Mr	560.30	560.31
Dx,g cm-3	1.377	1.377
Z	4	4
Mu (mm-1)	1.793	1.793
F000	1152.0	1152.0
F000'	1152.75	
h,k,lmax	12,26,15	12,26,15
Nref	5306	5306
Tmin,Tmax	0.693,0.802	0.669,0.746
Tmin'	0.678	

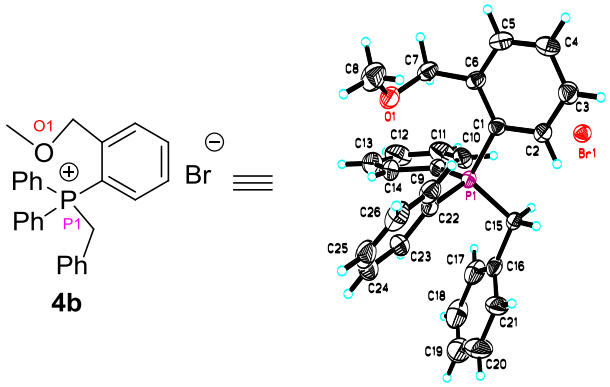
Correction method= MULTI-SCAN

Data completeness= 1.000 Theta(max)= 25.999

R(reflections)= 0.0524(3734) wR2(reflections)= 0.1490(5306)

S = 1.035 Npar= Npar = 299

4.2 X-Ray structure of 4b (CCDC 962019)



Bond precision: C-C = 0.0046 A Wavelength=0.71073

Cell: a=10.419(6) b=12.707(8) c=18.309(11)

alpha=90 beta=103.667(13) gamma=90

Temperature: 293 K

	Calculated	Reported
Volume	2355(2)	2355(2)
Space group	P 21/c	P2(1)/c
Hall group	-P 2ybc	?
Moiety formula	C27 H26 O P, Br	?
Sum formula	C27 H26 Br O P	C27 H26 Br O P
Mr	477.35	477.36
Dx,g cm-3	1.346	1.346
Z	4	4
Mu (mm-1)	1.829	1.829
F000	984.0	984.0
F000'	983.58	
h,k,lmax	12,15,22	12,15,22
Nref	4627	4627
Tmin,Tmax	0.671,0.784	0.425,1.000
Tmin'	0.622	

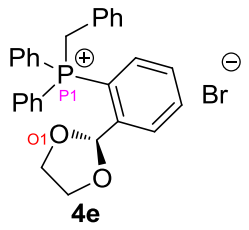
Correction method= EMPIRICAL

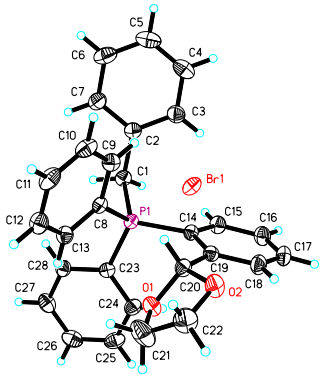
Data completeness= 1.000 Theta(max)= 26.000

R(reflections)= 0.0366(3766) wR2(reflections)= 0.0981(4627)

S = 1.022 Npar= 272

4.3 X-Ray structure of 4e (CCDC 962015)





Bond precision: C-C = 0.0037 A Wavelength=0.71073

Cell: a=10.9121(12) b=17.4195(19) c=12.6700(15)

alpha=90 beta=100.809(2) gamma=90

Temperature: 293 K

	Calculated	Reported
Volume	2365.6(5)	2365.6(5)
Space group	P 21/n	P2(1)/n
Hall group	-P 2yn	?
Moiety formula	C28 H26 O2 P, Br	?
Sum formula	C28 H26 Br O2 P	C28 H26 Br O2 P
Mr	505.36	505.37
Dx,g cm-3	1.419	1.419
Z	4	4
Mu (mm-1)	1.828	1.828
F000	1040.0	1040.0
F000'	1039.63	
h,k,lmax	14,23,16	14,23,16
Nref	5920	5874
Tmin,Tmax	0.651,0.760	0.658,0.771
Tmin'	0.627	

Correction method= MULTI-SCAN

Data completeness= 0.992 Theta(max)= 28.360

R(reflections)= 0.0419(3981) wR2(reflections)= 0.1169(5874)

S = 1.016 Npar= 289

5 Compitational Details

5.1 The hydrogen shift is a two-step process.

As shown in Figure 2 in the main text, the hydrogen shift of intermediate **B** assisted by $CsHCO_3$ is a two-step process, including protonation and deprotonation. The one-step concerted transition state cannot be located.

5.2 Structural analysis of PPh_3-TS-H-*Shift* and 3e-TS-H-*Shift*

The optimized structures of **PPh_3-TS-H-*Shift*** and **3e-TS-H-*Shift*** were shown in Figure S1, and the selected parameters were collected in Table S1.

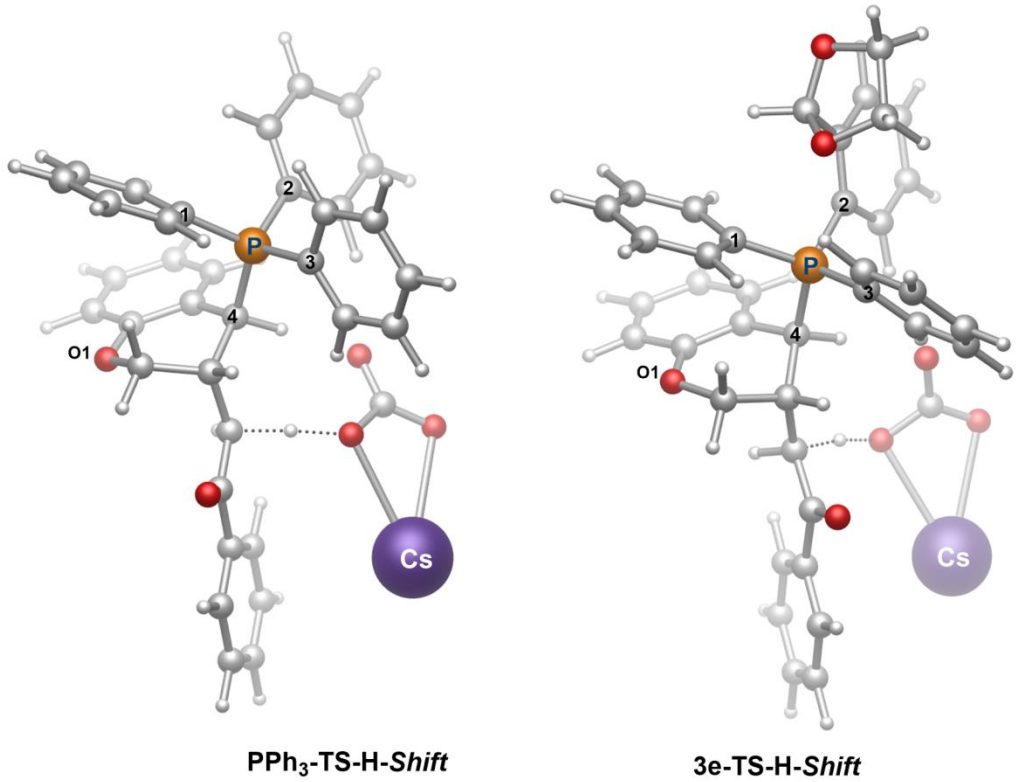


Figure S1. The optimized structures of **PPh_3-TS-H-*Shift*** and **3e-TS-H-*Shift***. Calculated at M06/6-31+G**/SDD level.

Table S1. Selected bond angles (in degree), relative entropies (in cal·mol^{-1}·K^{-1}), and relative entropy barriers (in kcal·mol^{-1}).

	A(C_1-P-C_4)	A(C_2-P-C_4)	A(C_3-P-C_4)	A(P-C_4-O_1)	ΔS	-TΔS
PPh_3-B	110.4	111.1	111.0	115.3	0.0	0.0

3e-B	107.3	109.2	109.1	115.1	0.0	0.0
PPh_3-TS-H-*Shift*	110.0	110.0	111.2	118.2	0.296	-0.1
3e-TS-H-*Shift*	107.1	108.1	107.1	106.9	-4.759	1.6

5.2.1 The three C-P bonds in 3e are more "flat".

As shown in Table S1, the three angles **A(C_1-P-C_4)**, **A(C_2-P-C_4)** and **A(C_3-P-C_4)** in **3e-B** and **3e-TS-H-*Shift*** are all smaller than those in **PPh_3-B** and **PPh_3-TS-H-*Shift***, indicating a more flat phosphonium group in **3e**.

5.2.2 The phosphonium group in 3e-TS-H-Shift bears larger steric repulsion.

When the phosphonium group is hardly pushed by the side-attacking $CsHCO_3$, the angle **A(P-C_4-O_1)** will become smaller. Therefore, **A(P-C_4-O_1)** can be used to indicate the steric repulsion subjected on the phosphonium group. In **PPh_3-B** and **3e-B**, **A(P-C_4-O_1)** has similar values (115.3 º and 115.1 º). In **PPh_3-TS-H-*Shift***, **A(P-C_4-O_1)** increases slightly to 118.2 º, indicating that there is no noticeable steric interaction with the attacking of $CsHCO_3$. However, in **3e-TS-H-*Shift***, **A(P-C_4-O_1)** decreases in large scale to 106.9 º, showing that the phosphonium group bears large steric repulsion.

5.2.3 The entropy effect.

Large steric interaction implies a more rigid structure, which means entropy loss and energy increase. For **PPh_3-TS-H-*Shift***, the relative entropy increases 0.296 cal·mol^{-1}·K^{-1}, which is consistent well with the former conclusion that there is no noticeable steric interaction increase. For **3e-TS-H-*Shift***, the relative entropy decreases 4.759 cal·mol^{-1}·K^{-1}, which equivalent to 1.6 kcal/mol energy increase.

5.2.4 Calculations for phosphine 3a, 3b and 3f.

Table S2. Key transition states of ***Path-a*** and ***Path-b*** for phosphine **3a**, **3b** and **3f**.

Transition States	**ΔG_{sol}**
3a-TS-*Cyc*	0.0
3a-TS-H-*Shift*	-1.2
3b-TS-*Cyc*	0.0
3b-TS-H-*Shift*	1.1
3f-TS-H-*Cyc*	0.0
3f-TS-H-*Shift*	-0.5

As shown in Table S2, for **3a** and **3f**, the hydrogen shift pathway is favorable, which is consistent with the experiment results that only small amount of cyclopropanation product was formed. For **3b**, the cyclopropanation pathway is favorable, which agree with the experiment results that the yield of the cyclopropanation product can reach 64%.

6 Calculated total energies and geometrical coordinates

*Calculated at the M06/6-31+G**/SDD level in CH3Cl with SMD method.*

PPh_3-B

SCF Done: E(RM06) = -2126.44234078 A.U.

Sum of electronic and thermal Free Energies= -2125.965272 A.U.

C,0,-2.0158838916,3.7640246099,2.0624611234

C,0,-1.7473297161,2.9198035695,0.9787253884

C,0,-1.4371604964,1.5660093736,1.1900740348

C,0,-1.3492825618,1.1124497592,2.5133010795

C,0,-1.6220238158,1.9420983254,3.5931052378

C,0,-1.9684620762,3.2751401319,3.359505344

H,0,-2.2557463698,4.8049187254,1.8551752858

H,0,-1.0455020163,0.0820374608,2.6895437614

H,0,-1.5502932069,1.5571212729,4.6074365123

H,0,-2.1856783863,3.9402995592,4.1928811681

C,0,-1.6663465419,2.6826758651,-1.4028940984

C,0,-0.7360415475,1.4977179834,-1.2148213441

C,0,-1.1678489435,0.6555455478,0.0196115662

H,0,-0.8115901282,0.8872653373,-2.1278649018

H,0,-2.6800912728,2.3761435023,-1.6937018052

H,0,-1.2763248222,3.3380540204,-2.188936332

H,0,-0.3529990925,-0.0494041675,0.2682184006

O,0,-1.7708880574,3.5096230978,-0.2402488341

P,0,-2.605474846,-0.4918059612,-0.2667306829

C,0,0.6878242887,1.9389329146,-1.0461053356

H,0,0.8662125,2.9041015434,-0.5749149451

C,0,1.7279657502,1.1573328191,-1.4841816875

C,0,3.1380964274,1.6457539545,-1.2983588845

C,0,4.1406418801,1.1430941328,-2.1393115919

C,0,3.5114976217,2.571205952,-0.3119916456

C,0,5.4599391708,1.5787731601,-2.0304499659

H,0,3.8570771831,0.4066250369,-2.8891179837

C,0,4.8305138855,3.0034634259,-0.1947395006

H,0,2.7629314433,2.9505820824,0.3813934871

C,0,5.8130274099,2.515387672,-1.0584873808

H,0,6.2151436742,1.1897390181,-2.7121388662

H,0,5.0931658454,3.7251223456,0.5772666123

H,0,6.8415697676,2.8617706456,-0.9739353174

O,0,1.5804087567,0.0225980314,-2.0875539324

C,0,-2.1806462417,-1.7771636864,-1.4644042232

C,0,-3.1419531896,-2.7630092892,-1.7341865556

C,0,-0.9092364437,-1.8546013844,-2.0354047203

C,0,-2.834798446,-3.8099942777,-2.5929018604

H,0,-4.1267383508,-2.7162427093,-1.2687258583

C,0,-0.6112409422,-2.9139615352,-2.8922507572

H,0,-0.1338434598,-1.1125024507,-1.8323136182

C,0,-1.566392602,-3.8851590036,-3.1726154798

H,0,-3.5805345252,-4.5732567689,-2.8024127284

H,0,0.3825083365,-2.9719354422,-3.3319094718

H,0,-1.3243549826,-4.7108758058,-3.8383977091

C,0,-4.0445374808,0.4350422863,-0.8504583733

C,0,-4.6619634369,1.366016515,-0.0007535794

C,0,-4.4601786815,0.3266217522,-2.1820597538

C,0,-5.6844620005,2.1741345651,-0.4845956992

H,0,-4.3357579686,1.4784249726,1.0329444056

C,0,-5.4863955386,1.1386229779,-2.6576793677

H,0,-3.9744238993,-0.3765877511,-2.8562464433

C,0,-6.0963773627,2.0616796001,-1.8120073722

H,0,-6.1554404893,2.8973615245,0.1767854507

H,0,-5.8026700006,1.0526866024,-3.6944005121

H,0,-6.8935426391,2.6989923573,-2.1879328132

C,0,-3.0383953885,-1.3851915622,1.2511274546

C,0,-2.0426084592,-2.1869591963,1.8260449147

C,0,-4.3185564577,-1.3437478164,1.8098781361

C,0,-2.3298248387,-2.9168072384,2.9742648206

H,0,-1.0360572446,-2.2227247947,1.3998480403

C,0,-4.5952422992,-2.0811024956,2.9588807994

C,0,-3.6016291844,-2.8618003062,3.5437474898

H,0,-1.552186973,-3.5295634169,3.4241825068

H,0,-5.5917197013,-2.0447997735,3.3930521401

H,0,-3.8199249596,-3.4342187003,4.4428032844

C,0,2.0912688066,-2.0167259504,0.7074013967

O,0,0.9104265954,-1.6143871861,0.8226210365

O,0,2.7090202536,-1.8262023239,-0.5139896205

O,0,2.8183444671,-2.5644149318,1.5668530234

Cs,0,5.272498865,-0.8454174519,0.8240040447

H,0,2.1709224265,-1.2174572612,-1.0899412888

H,0,-5.1073648256,-0.748650973,1.3555061705

PPh_3-TS-H-*Shift*

SCF Done: E(RM06) = = -2126.42039642 A.U.

Sum of electronic and thermal Free Energies= -2125.948599 A.U.

C,0,-2.0854839063,3.7920461006,1.9625259315

C,0,-1.6434526242,2.8622941627,1.0142898334

C,0,-1.6265018436,1.4895320578,1.3139923442

C,0,-2.0037330548,1.0988764985,2.6069505804

C,0,-2.4496809668,2.0153204535,3.550457534

C,0,-2.4995726504,3.3707958514,3.2171086841

H,0,-2.085766369,4.8445879257,1.6865706103

H,0,-1.9328178735,0.0468263984,2.8761632017

H,0,-2.7386568721,1.6770367045,4.5425453398

H,0,-2.8446413782,4.1034828116,3.9438752986

C,0,-0.9607387826,2.4845160681,-1.2385953259

C,0,-0.3133033192,1.1790450663,-0.8041966008

C,0,-1.1536863178,0.4862864256,0.2899835933

H,0,-0.2637029337,0.5619025722,-1.7148667901

H,0,-1.9152574102,2.3129772101,-1.7585099749

H,0,-0.2965283851,3.0199542568,-1.9233483858

H,0,-0.5180910584,-0.2728718579,0.8009432292

O,0,-1.2039619612,3.3829574969,-0.1550971995

P,0,-2.5504398486,-0.5208605012,-0.3669043026

C,0,1.0962855851,1.3343360175,-0.2641503352

H,0,1.5317972852,0.1068158524,-0.0681235935

C,0,2.1105331711,1.7776785177,-1.1837082589

C,0,3.4724588721,2.1050898961,-0.6239386236

C,0,3.7994869904,1.9486006448,0.730445644

C,0,4.4639472794,2.5534786562,-1.503954604

C,0,5.0823354234,2.2395137948,1.1892405899

H,0,3.0575176788,1.5808286804,1.4366169228

C,0,5.7472771374,2.8427384114,-1.0487577967

H,0,4.2047844911,2.670428499,-2.5542243772

C,0,6.0611453319,2.6854893558,0.3011801468

H,0,5.3174787428,2.1147977819,2.2446064501

H,0,6.5038096309,3.1965531263,-1.7467135756

H,0,7.0621635796,2.9162905093,0.6607531857

O,0,1.9595453828,1.7866513401,-2.4196834998

C,0,-1.9572642958,-1.7999572805,-1.5008861541

C,0,-2.9119301891,-2.5636399591,-2.187886531

C,0,-0.6002594922,-2.1209712484,-1.5925448829

C,0,-2.5047903656,-3.6199728658,-2.992947639

H,0,-3.9741707216,-2.3394535602,-2.089066632

C,0,-0.2046399751,-3.1878666053,-2.3975573224

H,0,0.1652997756,-1.5791391304,-1.0340932843

C,0,-1.1484381361,-3.9300167286,-3.1005843123

H,0,-3.2467369634,-4.2074575626,-3.5286825783

H,0,0.8524644085,-3.4364078378,-2.4612859193

H,0,-0.8313393754,-4.760649525,-3.7273728424

C,0,-3.7436143985,0.5486228233,-1.1998433475

C,0,-4.4708998114,1.4771523749,-0.4396703058

C,0,-3.8187862087,0.5822462425,-2.5969487595

C,0,-5.2662542628,2.4229032911,-1.0776727345

H,0,-4.409096134,1.4768186786,0.6479373843

C,0,-4.6223028033,1.5280954659,-3.2268336054

H,0,-3.2359489447,-0.1118275488,-3.1992980985

C,0,-5.3422219565,2.4489287472,-2.4693863768

H,0,-5.8225594023,3.144275822,-0.4840759987

H,0,-4.6749445007,1.5508282324,-4.3125771948

H,0,-5.9619811382,3.1928959661,-2.9646763273

C,0,-3.3445202254,-1.4317691427,0.9810712335

C,0,-2.5186574839,-2.2194942977,1.7962679258

C,0,-4.7298421566,-1.4389725062,1.1583010576

C,0,-3.0910181332,-2.989252417,2.8028062619

H,0,-1.4309875631,-2.2147770874,1.6686248827

C,0,-5.2910477764,-2.2157774298,2.1695136449

C,0,-4.4730330907,-2.985831386,2.9920819534

H,0,-2.450548943,-3.5916100308,3.4426059451

H,0,-6.3692745752,-2.2172540684,2.3113598069

H,0,-4.9139209933,-3.5891225923,3.7827117344

C,0,1.7707242214,-1.7789237921,1.1154906364

O,0,0.6774570917,-1.5386262608,1.721415281

O,0,2.6437844414,-2.6135998723,1.5021996497

O,0,2.0288521447,-1.1050717035,-0.0151566769

H,0,1.1356279945,1.7878870562,0.7317427993

Cs,0,4.9735404293,-1.4935208538,-0.0998831474

H,0,-5.3770261078,-0.8469690743,0.5139466338

PPh_3-INT

SCF Done: E(RM06) = -2126.43267625 A.U.

Sum of electronic and thermal Free Energies= -2125.955404 A.U.

C,0,-2.668688965,4.0539327878,1.0902720819

C,0,-2.061473437,3.0124697948,0.3810423472

C,0,-1.8401514497,1.7658018095,0.9905106447

C,0,-2.1932398272,1.6240344614,2.3394954368

C,0,-2.8034219213,2.6511778305,3.0481848848

C,0,-3.0507525213,3.8694548602,2.4109885299

H,0,-2.8255873592,5.0017818721,0.5793364043

H,0,-1.9706241409,0.6830254167,2.8393865584

H,0,-3.0685874849,2.5089857813,4.093002606

H,0,-3.526681933,4.6851809203,2.9514432786

C,0,-1.1888583176,2.2650051761,-1.7234323687

C,0,-0.3923466373,1.2222370833,-0.9631608175

C,0,-1.2021201668,0.6459836891,0.2100539066

H,0,-0.1371159771,0.4374861655,-1.6863385123

H,0,-2.042409881,1.8208819474,-2.2537180212

H,0,-0.5552975177,2.758241666,-2.4697900617

H,0,-0.494138061,0.0730770206,0.8661572479

O,0,-1.679188189,3.3143952319,-0.8858003271

P,0,-2.4577525692,-0.6174798594,-0.2610643981

C,0,0.9166395616,1.8015524229,-0.4169227638

H,0,1.1011191946,1.4296720717,0.5961688424

C,0,2.1126572813,1.489781301,-1.274233814

C,0,3.4683566387,1.8305074053,-0.736925498

C,0,3.7174772586,2.0353645585,0.6252518281

C,0,4.5258700822,1.9493492285,-1.6471648116

C,0,5.0020118035,2.3439303383,1.0661435662

H,0,2.9216901758,1.9218577232,1.3578706562

C,0,5.8078214126,2.264921971,-1.2085453753

H,0,4.3225806305,1.7940216472,-2.704784063

C,0,6.0486075419,2.4600615161,0.1520837634

H,0,5.1843045937,2.4864358175,2.128946173

H,0,6.618739602,2.3653871567,-1.9273126439

H,0,7.0499675561,2.707958129,0.4988062962

O,0,1.997405762,1.0778730258,-2.4223651937

C,0,-1.7211477666,-1.9747069162,-1.201489487

C,0,-2.5754431941,-2.914361289,-1.7981563061

C,0,-0.3364207009,-2.166172739,-1.2100424194

C,0,-2.0409124229,-4.0227009201,-2.4425453949

H,0,-3.6572389187,-2.7885054275,-1.7547140506

C,0,0.1833513952,-3.2869759019,-1.8584284196

H,0,0.3695156079,-1.4916925009,-0.7010482743

C,0,-0.6575063422,-4.2052039474,-2.4788814687

H,0,-2.7036485702,-4.7479042219,-2.9091502464

H,0,1.2613607847,-3.4360586358,-1.8636853354

H,0,-0.2395737993,-5.0747392139,-2.982112106

C,0,-3.7942213886,0.147774025,-1.2095112067

C,0,-4.6431308499,1.0626351959,-0.5690574236

C,0,-3.880331393,-0.0248617842,-2.5961493518

C,0,-5.5651399788,1.7919824441,-1.3126064336

H,0,-4.5817553823,1.2194903431,0.5072397445

C,0,-4.8110579581,0.7027565797,-3.3316704046

H,0,-3.2084481892,-0.709196301,-3.1107143128

C,0,-5.6493861223,1.6133421749,-2.6922372397

H,0,-6.2147881851,2.5047310988,-0.8101505166

H,0,-4.8719317883,0.5636872115,-4.4083688603

H,0,-6.3696619929,2.1873772933,-3.2707481854

C,0,-3.1252792318,-1.3859678266,1.2369360278

C,0,-2.2119737703,-1.849221946,2.195199945

C,0,-4.4937626342,-1.627868362,1.3850057841

C,0,-2.6876012807,-2.5306784923,3.3109757328

H,0,-1.1360181394,-1.6647164176,2.0878632406

C,0,-4.9553951083,-2.3130704332,2.5060510933

C,0,-4.0540152462,-2.7603857894,3.4689084506

H,0,-1.9819366513,-2.881957229,4.0600967064

H,0,-6.0207785599,-2.4975708801,2.6234155047

H,0,-4.4171712483,-3.2937350665,4.344847208

C,0,1.9220025142,-0.9754363747,1.425472717

O,0,0.7843468999,-0.7022246418,1.9792036444

O,0,2.9299190396,-1.3476803173,2.1301085301

O,0,2.0412782375,-0.861827003,0.1319609441

H,0,0.8585425268,2.9006434113,-0.336008579

Cs,0,4.90680957,-1.4670542253,-0.0789615826

H,0,-5.2040577109,-1.2912120318,0.6319503193

PPh_3-TS-H-*Shift2*

SCF Done: E(RM06) = -2126.42270472 A.U.

Sum of electronic and thermal Free Energies= -2125.948890 A.U.

C,0,-2.5999397995,4.0137517548,1.2452667278

C,0,-2.0170739809,2.9922339528,0.4891092513

C,0,-1.7879188814,1.7171256714,1.0434322536

C,0,-2.1284676315,1.5385936388,2.3939684413

C,0,-2.7244433471,2.5423469607,3.1480370033

C,0,-2.9673571412,3.7875889607,2.5646371495

H,0,-2.7595417056,4.9788539088,0.7677329854

H,0,-1.9047017947,0.5811781224,2.8596444617

H,0,-2.9795048775,2.3602007488,4.1895980963

H,0,-3.4281804583,4.5870951417,3.14139693

C,0,-1.2373259074,2.3075416564,-1.6702145453

C,0,-0.4058858657,1.2488654105,-0.9667159756

C,0,-1.1611863079,0.6259950464,0.2219599979

H,0,-0.1673551158,0.4913593217,-1.7246089844

H,0,-2.1199192245,1.8750800094,-2.1612331633

H,0,-0.6450714553,2.8185651037,-2.4398182874

H,0,-0.2569927212,0.0008612772,0.985871246

O,0,-1.6706292354,3.3378172012,-0.7804563087

P,0,-2.3978173019,-0.5999880314,-0.2397743026

C,0,0.9146181536,1.8600832611,-0.474887318

H,0,1.1026366718,1.5839510178,0.5663982128

C,0,2.1081485136,1.5007688846,-1.3153953227

C,0,3.4707076086,1.8376388241,-0.7870320562

C,0,3.7080423701,2.1729275729,0.5515114095

C,0,4.5462640557,1.8261308233,-1.6839039358

C,0,4.994887831,2.4888229874,0.98136372

H,0,2.896903409,2.1728810264,1.2761129417

C,0,5.8313918398,2.1443802589,-1.2568125019

H,0,4.3533498596,1.5703749679,-2.7237497166

C,0,6.0584875436,2.4755686397,0.0798216427

H,0,5.1648206665,2.7427967566,2.0253571149

H,0,6.6556466748,2.1433134002,-1.9674574119

H,0,7.061597304,2.7305098902,0.416159349

O,0,1.9909567201,1.0512853236,-2.4486793414

C,0,-1.6891951003,-1.9872938853,-1.1690529122

C,0,-2.5580611075,-2.9658543461,-1.6741919467

C,0,-0.3069991291,-2.1482348495,-1.285745357

C,0,-2.0458925173,-4.0800767118,-2.3269633095

H,0,-3.6364325633,-2.8633207665,-1.5520963733

C,0,0.1953892525,-3.2733306385,-1.9403278869

H,0,0.401199941,-1.4383427897,-0.8446184893

C,0,-0.6651829757,-4.2312445517,-2.4664219724

H,0,-2.7235681037,-4.8346525344,-2.7198843712

H,0,1.2734064836,-3.3949105634,-2.027032833

H,0,-0.2642689957,-5.1051532224,-2.9758576605

C,0,-3.7482076514,0.115266154,-1.2277175416

C,0,-4.5891412613,1.0658417156,-0.628246799

C,0,-3.8307463945,-0.100166028,-2.6082525762

C,0,-5.4986678679,1.780486619,-1.400890291

H,0,-4.5294392031,1.2628099865,0.4419216504

C,0,-4.7476777161,0.6138416161,-3.3753968927

H,0,-3.1659252571,-0.8108603917,-3.0959687875

C,0,-5.5790272934,1.5561780267,-2.774528406

H,0,-6.1415415402,2.5184885672,-0.9265377984

H,0,-4.8033939037,0.4381759901,-4.4473040587

H,0,-6.2885333028,2.1191432642,-3.3768874091

C,0,-3.1315741706,-1.3818371695,1.2288006081

C,0,-2.2638772384,-1.9024853379,2.1983915557

C,0,-4.5099702941,-1.5759654452,1.348748184

C,0,-2.784431459,-2.588225269,3.29070133

H,0,-1.1852621127,-1.74926175,2.1155186693

C,0,-5.0222846103,-2.2652821913,2.4459847771

C,0,-4.1615174401,-2.7678323444,3.4179662505

H,0,-2.1079239242,-2.9809334848,4.0462676546

H,0,-6.0967021724,-2.4079990416,2.5372787345

H,0,-4.5634512206,-3.3035321218,4.2753523775

C,0,1.7840484165,-0.817820608,1.4291680178

O,0,0.5897388317,-0.4441853018,1.861036195

O,0,2.6568678925,-1.1767557281,2.2786466764

O,0,2.0163840045,-0.7956536305,0.1661820633

H,0,0.8582223764,2.9627785533,-0.479250417

Cs,0,4.9102172839,-1.4032228473,0.2988042716

H,0,-5.1925563299,-1.1961047223,0.5911574616

PPh_3-C

SCF Done: E(RM06) = -2126.43680919 A.U.

Sum of electronic and thermal Free Energies= -2125.960437 A.U.

C,0,-2.6804927029,4.0949970943,0.7456560292

C,0,-1.8734132285,3.069227777,0.2747560568

C,0,-1.9469422277,1.7451625447,0.7811468523

C,0,-2.9576075852,1.5293658348,1.7460304145

C,0,-3.773871497,2.552426808,2.2192688605

C,0,-3.6309892221,3.8527328878,1.7376676735

H,0,-2.5510410524,5.0858845501,0.3128917851

H,0,-3.1097481693,0.5276834217,2.1495638649

H,0,-4.5261463578,2.3248615678,2.9727660577

H,0,-4.257631479,4.6604080128,2.1090268071

C,0,-0.7434439266,2.2949358197,-1.6116536752

C,0,-0.1186256922,1.1140173161,-0.8911342837

C,0,-1.0070486297,0.7482839355,0.3019811176

H,0,-0.0960468411,0.2967731357,-1.6273820287

H,0,-1.6987202723,2.0067051914,-2.0807832622

H,0,-0.078521711,2.6847767597,-2.3905200412

H,0,0.4294504153,1.4719155123,2.0099180857

O,0,-0.9750900285,3.3790143948,-0.7154800707

P,0,-1.2155246933,-0.9289640302,0.6753615882

C,0,1.3310760669,1.4306787117,-0.5182449405

H,0,1.6485128193,0.8470228542,0.3584669407

C,0,2.3436467795,1.167477072,-1.5944549835

C,0,3.7881202401,1.3005713736,-1.2209198273

C,0,4.1954617313,1.9016854112,-0.022968666

C,0,4.7581140204,0.8063485679,-2.1008872051

C,0,5.5500889283,2.0169456608,0.2788385175

H,0,3.4612584667,2.2970895474,0.6761644054

C,0,6.1095848525,0.9056923925,-1.7912968768

H,0,4.431249266,0.3411084541,-3.0287779457

C,0,6.5082822457,1.5160809272,-0.6013028307

H,0,5.8555046868,2.5144608576,1.1977443717

H,0,6.8552462923,0.5146295902,-2.4803049343

H,0,7.5667458859,1.609168962,-0.3657826304

O,0,2.0301427047,0.8116037444,-2.7244130298

C,0,-0.0636403252,-1.889168864,-0.3558121145

C,0,-0.5040726195,-2.5713996705,-1.4918041493

C,0,1.3006850418,-1.8692439217,-0.0369777606

C,0,0.4149104436,-3.2212282577,-2.3141278579

H,0,-1.5628086587,-2.5954798574,-1.7454555432

C,0,2.2119223357,-2.5190967828,-0.8641910084

H,0,1.6469619352,-1.335221379,0.8506729595

C,0,1.7719306512,-3.1910411488,-2.0042698642

H,0,0.0670221702,-3.7478607728,-3.199902948

H,0,3.2725243134,-2.4931841101,-0.6203629393

H,0,2.4882641136,-3.6922035176,-2.6517635521

C,0,-2.9013705043,-1.5667615451,0.3226156217

C,0,-3.5180521645,-2.5724462186,1.0723531425

C,0,-3.5795486326,-1.0043844282,-0.764616558

C,0,-4.7899139047,-3.0228530935,0.7244808713

H,0,-3.0158720613,-3.0039470707,1.9365382182

C,0,-4.8486152844,-1.4569937376,-1.1118057323

H,0,-3.1093608135,-0.2013979356,-1.3338633482

C,0,-5.4538751944,-2.468689205,-0.3678138009

H,0,-5.2646757542,-3.8049510991,1.3130802234

H,0,-5.3686889654,-1.0116077174,-1.9569874195

H,0,-6.4490545222,-2.8183660297,-0.6341208455

C,0,-0.8473124361,-1.4705367334,2.3856990076

C,0,-0.8788735527,-0.5677413538,3.4510455117

C,0,-0.4874900225,-2.8023463307,2.6271804854

C,0,-0.5572057879,-0.9883710982,4.7387506881

H,0,-1.1356492729,0.475801195,3.2847926186

C,0,-0.165815435,-3.221724419,3.9148731594

C,0,-0.1990465361,-2.3138187882,4.9723275141

H,0,-0.5763810329,-0.271229291,5.5564531987

H,0,0.1154302127,-4.2581339717,4.0898577155

H,0,0.0566238786,-2.6400475425,5.9784153793

C,0,2.0748066925,1.2704711659,2.9850494269

O,0,0.9391485495,1.9812963161,2.6718868382

O,0,2.8262928238,1.808135153,3.8241190159

O,0,2.2457928838,0.1711510121,2.3924343808

H,0,1.4188007505,2.4814066583,-0.1949855269

Cs,0,5.0021010954,-0.3128370979,3.5726863721

H,0,-0.4473694452,-3.5174442517,1.8055544132

PPh_3-TS-*Cyc*

SCF Done: E(RM06) = -2126.41471053 A.U.

Sum of electronic and thermal Free Energies= -2125.946779 A.U.

C,0,-3.7020586886,3.2969355062,1.8438240123

C,0,-2.9016899063,2.8026420011,0.8118663921

C,0,-1.9207687224,1.8290567377,1.0786659388

C,0,-1.7573257561,1.3738732895,2.3970722211

C,0,-2.5629468522,1.8490454275,3.4199452675

C,0,-3.5371828025,2.8138654049,3.1359275704

H,0,-4.4469030668,4.0547681493,1.6102219781

H,0,-0.9751373931,0.6386000758,2.588771703

H,0,-2.4317251548,1.4832643952,4.4353511549

H,0,-4.1714852886,3.196440417,3.9331162892

C,0,-2.5669743099,2.6280320699,-1.5485061312

C,0,-1.2084544557,2.0076948281,-1.313215855

C,0,-1.1074260975,1.3096166435,-0.0084842687

H,0,-0.9330577544,1.3773331846,-2.1693238097

H,0,-3.3026961816,1.8565799729,-1.8191047024

H,0,-2.5203526961,3.3628078112,-2.3585657688

H,0,-0.1800509158,0.7910330589,0.2382272667

O,0,-3.0705612234,3.3480511558,-0.4158959435

P,0,-2.136680354,-0.9353553236,-0.2962441349

C,0,-0.1152711906,2.9593677402,-0.9418547335

H,0,-0.3828948739,3.9178451677,-0.5042735996

C,0,1.211206487,2.5453516251,-1.0820294478

C,0,2.3219146685,3.4433309652,-0.6337921935

C,0,3.5974960747,3.2559029576,-1.1799003117

C,0,2.145347095,4.4503711157,0.3236864821

C,0,4.6638728319,4.0645379132,-0.7981765287

H,0,3.73359534,2.4651080409,-1.9152901004

C,0,3.2126931636,5.2541129549,0.7137978402

H,0,1.1719066719,4.5911802733,0.7896006935

C,0,4.4749494036,5.0685981529,0.1507568636

H,0,5.6457046355,3.913716432,-1.2438494312

H,0,3.0599699176,6.0245786237,1.4671356313

H,0,5.3074963422,5.7002717534,0.4545104304

O,0,1.5218644856,1.4195077863,-1.5919957532

C,0,-1.227545549,-1.9914612917,-1.4814959235

C,0,-1.656823753,-3.2907909836,-1.7841208309

C,0,-0.0566269012,-1.4953156559,-2.0624444681

C,0,-0.9317622225,-4.0767527849,-2.6727635495

H,0,-2.5612406352,-3.687542982,-1.3219469616

C,0,0.6696856549,-2.2903527562,-2.9499596008

H,0,0.3086319107,-0.4943579423,-1.8224678694

C,0,0.2332013875,-3.5753213812,-3.2571782391

H,0,-1.2706326929,-5.0840459183,-2.9063411756

H,0,1.5828969523,-1.8970775667,-3.3926475325

H,0,0.8020086375,-4.1938237866,-3.9486952519

C,0,-3.7835898892,-0.6520440352,-1.0195874496

C,0,-4.7501625799,-0.0126568528,-0.2260074238

C,0,-4.0512974662,-0.8664163899,-2.3764279608

C,0,-5.962924316,0.3867901139,-0.7769843495

H,0,-4.5496575797,0.1815697482,0.8286965246

C,0,-5.2674198701,-0.4619540362,-2.9253324369

H,0,-3.3064907929,-1.3430877457,-3.0125066046

C,0,-6.2237922779,0.1643166115,-2.1294992157

H,0,-6.7021124208,0.8807983666,-0.1497091081

H,0,-5.4649329326,-0.6362025963,-3.9810052839

H,0,-7.1701346613,0.4825174207,-2.5614402513

C,0,-2.3958965517,-2.0391750534,1.1420173901

C,0,-1.2777316463,-2.2835521304,1.9524508506

C,0,-3.6154965837,-2.6550088365,1.4427407511

C,0,-1.383078603,-3.144996241,3.0408433835

H,0,-0.325798955,-1.788732576,1.7371294864

C,0,-3.7142056488,-3.5114107043,2.5375291388

C,0,-2.5994533924,-3.7593069754,3.3361685406

H,0,-0.5084846833,-3.3301812438,3.6611520162

H,0,-4.6654218047,-3.9904070065,2.7614265987

H,0,-2.679655065,-4.4295124014,4.1897020256

C,0,2.2545202461,-0.8129422431,1.0268240993

O,0,1.1749218784,-0.240784345,1.2931106227

O,0,2.923485314,-0.3966366535,-0.1143146657

O,0,2.8377508836,-1.721949465,1.6581922819

Cs,0,5.6099689347,-1.7533297109,0.5077127862

H,0,2.3913798524,0.2949329292,-0.5805572838

H,0,-4.4908182169,-2.4807455269,0.8187593586

PPh_3-D

SCF Done: E(RM06) = -2126.46094479 A.U.

Sum of electronic and thermal Free Energies= -2125.987716 A.U.

C,0,-2.6947380275,4.488833223,-1.0968341461

C,0,-2.6769917285,3.3094746255,-0.3576102005

C,0,-2.1319178535,2.1343135314,-0.8898687689

C,0,-1.5709534805,2.1674452357,-2.1681396755

C,0,-1.5723630318,3.3459018087,-2.9113967918

C,0,-2.142197483,4.502441444,-2.3761540153

H,0,-3.1317283842,5.3824086084,-0.6549774037

H,0,-1.1394987019,1.2471049294,-2.5650454537

H,0,-1.1326108555,3.3611709365,-3.9061099452

H,0,-2.1517763193,5.424602853,-2.9539837785

C,0,-2.6348565888,2.4648098217,1.8629020168

C,0,-2.4106600303,1.0610423461,1.371155298

C,0,-2.1305537758,0.909272049,-0.0721185245

H,0,-1.8826085163,0.4021003568,2.0612963331

H,0,-1.6652414205,2.8998978966,2.158673021

H,0,-3.3044910325,2.4949650048,2.728551951

H,0,-1.4733500831,0.1111515445,-0.4119148721

O,0,-3.2471473387,3.3128386607,0.886627671

P,0,1.4125095177,0.8537081532,0.175969108

C,0,-3.4658548171,0.4043874078,0.5145377375

H,0,-4.3488472611,0.9950279982,0.286153416

C,0,-3.5849121842,-1.0630704061,0.5815441762

C,0,-4.8715879815,-1.7141627633,0.2162845137

C,0,-5.0409131465,-3.0675521811,0.5384066295

C,0,-5.9029658395,-1.0369979805,-0.446353758

C,0,-6.2195494346,-3.7272285542,0.2170080001

H,0,-4.2326443564,-3.5890635509,1.0456855259

C,0,-7.0788644584,-1.7024942434,-0.7796322834

H,0,-5.7895514708,0.0062381852,-0.7295912825

C,0,-7.2414406691,-3.044710323,-0.4441876723

H,0,-6.3432482436,-4.7761464084,0.4773629411

H,0,-7.8687873186,-1.1711399275,-1.3054569221

H,0,-8.1638024382,-3.5616030957,-0.7010228407

O,0,-2.6239986191,-1.7518529347,0.9376197123

C,0,2.2312922522,-0.2656355216,1.3983490786

C,0,3.6135540358,-0.3382506756,1.6088934056

C,0,1.38851703,-1.0763652408,2.1716221727

C,0,4.140290875,-1.1908235965,2.5790223084

H,0,4.2869573324,0.2822978096,1.0175508651

C,0,1.9115024849,-1.9192684011,3.1509945162

H,0,0.311200848,-1.0490587471,1.9999444578

C,0,3.2901578974,-1.9794795321,3.3545591487

H,0,5.2166112205,-1.2309316995,2.7362615815

H,0,1.2417000252,-2.5336766694,3.7493612421

H,0,3.7013060444,-2.6379028791,4.1172198301

C,0,1.2825549011,2.4081115225,1.165509746

C,0,0.7484571058,3.5329723298,0.5181735374

C,0,1.6007994889,2.5060756181,2.5244503965

C,0,0.5606241805,4.7281715086,1.2054163081

H,0,0.4778070302,3.4718258005,-0.5379188058

C,0,1.3988808366,3.7010242218,3.2170401162

H,0,2.0139734931,1.6493806393,3.0558228393

C,0,0.8822450307,4.8149828514,2.5605850284

H,0,0.1492760905,5.589868076,0.6826926438

H,0,1.6526923834,3.7585636632,4.2739848003

H,0,0.7267697728,5.7461702018,3.1015095675

C,0,2.7996768859,1.2460144071,-0.9738171333

C,0,2.8891599174,0.4617611749,-2.133126222

C,0,3.7430916347,2.2579613709,-0.7598028321

C,0,3.9215968747,0.6749138544,-3.0464082529

H,0,2.1431497219,-0.3163945336,-2.3293085251

C,0,4.7670391469,2.4743952721,-1.6794173769

C,0,4.8605853251,1.6799960485,-2.8217928947

H,0,3.9789007012,0.0641253991,-3.9453386504

H,0,5.4936958391,3.2654313194,-1.5037681725

H,0,5.6582791236,1.8521600086,-3.5416837853

C,0,-0.1636050549,-1.9645773332,-1.8185213411

O,0,-1.1278222174,-1.2735461898,-2.1883148038

O,0,-0.2689630188,-2.5680228569,-0.5575127531

O,0,0.9176675111,-2.2175589967,-2.3969876225

Cs,0,2.7318875648,-3.424952924,-0.3899406928

H,0,-1.1152782304,-2.2919353656,-0.1590634682

H,0,3.6793907296,2.8829517149,0.1311297017

3e-B

SCF Done: E(RM06) = -2393.45370084 A.U.

Sum of electronic and thermal Free Energies= -2392.909235 A.U.

C,0,1.3319288452,4.0977598007,-2.05130498

C,0,1.0698952916,3.2477790621,-0.9701517861

C,0,0.8904500372,1.8686964249,-1.17396637

C,0,0.9169629367,1.3954858599,-2.4930561203

C,0,1.1822094824,2.2314729734,-3.5699468521

C,0,1.402624887,3.5914698791,-3.3404003476

H,0,1.4714410847,5.1574218456,-1.8471548945

H,0,0.7126404603,0.3418465189,-2.6727853679

H,0,1.2005771115,1.8286915299,-4.5797097467

H,0,1.6130544469,4.2619735037,-4.17121228

C,0,0.8592799526,3.0446067128,1.4083123844

C,0,0.0509412684,1.7798877402,1.1843557305

C,0,0.6333309168,0.9544625693,-0.0026245267

H,0,0.1068607638,1.1906948886,2.1122053311

H,0,1.8730215731,2.8396596713,1.7753972654

H,0,0.3556419017,3.6760099382,2.1481078237

H,0,-0.1208011145,0.200586401,-0.2827602124

O,0,0.9718532868,3.8560008101,0.2347941735

P,0,2.1538358386,-0.0629228191,0.419262054

C,0,-1.3887639368,2.0953862187,0.903009951

H,0,-1.6076454382,3.0036554036,0.3433138444

C,0,-2.3995485095,1.2591621876,1.3072985151

C,0,-3.8156055002,1.6167208025,0.9504810046

C,0,-4.8530405734,1.2029181077,1.797552344

C,0,-4.1552457905,2.328988456,-0.2088025979

C,0,-6.1790698273,1.5324663931,1.5260524518

H,0,-4.5936688474,0.6242913983,2.6823761015

C,0,-5.4814580466,2.6528934573,-0.4892382336

H,0,-3.3717589024,2.6205808519,-0.9066576158

C,0,-6.5010879245,2.2622094532,0.3802420264

H,0,-6.9653744097,1.2222264254,2.2131317043

H,0,-5.7193488065,3.2100899614,-1.3940521135

H,0,-7.5359341033,2.5250748096,0.1672035876

O,0,-2.2316236965,0.1821285472,2.0031571045

C,0,1.7459905048,-1.2127655362,1.7584896249

C,0,2.7642426801,-1.9125124889,2.4229464006

C,0,0.4049771838,-1.4894194222,2.0397870454

C,0,2.4351732529,-2.8666327274,3.3783131121

H,0,3.8081367246,-1.71277917,2.1903954999

C,0,0.0879774357,-2.4489954607,2.9991429185

H,0,-0.411613163,-0.962348835,1.5457910174

C,0,1.0965320539,-3.1353680489,3.6676731881

H,0,3.2263643948,-3.4034028773,3.8970510042

H,0,-0.9590400541,-2.6503675671,3.2163635939

H,0,0.8432255049,-3.8837725314,4.4155709631

C,0,3.4529367231,1.0924508208,0.9119038248

C,0,3.9591420319,1.9853674829,-0.0418431549

C,0,3.8363939363,1.2148412061,2.2510465313

C,0,4.8450859734,2.9857341007,0.3441527352

H,0,3.6606525376,1.9106061112,-1.0876801811

C,0,4.7283310222,2.2136604457,2.6289186681

H,0,3.4289572331,0.5474997618,3.0075015024

C,0,5.2304069287,3.1001668529,1.6784892662

H,0,5.2287590002,3.6788752054,-0.4007759666

H,0,5.0228654796,2.3035474025,3.6717742234

H,0,5.9202446675,3.8855209591,1.9788687014

C,0,2.586590449,-1.1197402215,-1.0128228591

C,0,1.4641239192,-1.7718802481,-1.5428915856

C,0,3.8598873021,-1.3724572792,-1.5696898839

C,0,1.5708007913,-2.6060751425,-2.6496627875

H,0,0.4683060747,-1.6308777877,-1.1171118984

C,0,3.9377176285,-2.1921867228,-2.6975531229

C,0,2.8103672871,-2.7963272908,-3.2460972068

H,0,0.6764243797,-3.0878518997,-3.0383198598

H,0,4.9160091317,-2.3647936357,-3.1387899588

H,0,2.9103604055,-3.4299550482,-4.1245221892

C,0,5.162785635,-0.8644231713,-0.9640406951

C,0,6.6469829571,-2.5999259321,-0.7918298652

C,0,5.7051917379,-2.5481591002,0.4093096291

H,0,6.5151259417,-3.5145477215,-1.3845072982

H,0,7.70158474,-2.5048789035,-0.5100214907

H,0,4.8591593994,-3.2446445386,0.2975595367

H,0,6.1997172977,-2.7350767292,1.3663976544

O,0,5.2419696502,-1.1999950118,0.4027629249

O,0,6.2895908317,-1.4495407419,-1.5630011465

H,0,5.2640255965,0.2224384676,-1.0557805243

C,0,-2.6120183242,-1.9043188971,-0.7248526726

O,0,-1.5325406598,-1.2898485174,-0.8889443849

O,0,-3.2231973506,-1.7944595498,0.5076903998

O,0,-3.2430885153,-2.6045450971,-1.5496661392

Cs,0,-5.9075831566,-1.2375118389,-0.9017514495

H,0,-2.7635205399,-1.1027206485,1.0623317172

3e-TS-H-*Shift*

SCF Done: E(RM06) = -2393.43052064 A.U.

Sum of electronic and thermal Free Energies= -2392.888658A.U.

C,0,0.6341193466,4.123400607,-1.5573918559

C,0,0.5136755514,3.0296389498,-0.6946949281

C,0,0.6057496579,1.7201154743,-1.192800934

C,0,0.7619519577,1.5417421262,-2.5709910943

C,0,0.8879119608,2.6237849451,-3.4347096695

C,0,0.8356516835,3.9195553028,-2.9160663489

H,0,0.5658268834,5.1245681885,-1.13654972

H,0,0.7821022962,0.5259830322,-2.9647014589

H,0,1.0128092368,2.4594113357,-4.5022800856

H,0,0.9329287084,4.7782443333,-3.5774745183

C,0,0.0477472904,2.2727693039,1.5573301245

C,0,-0.4388957654,0.9818374623,0.9250779933

C,0,0.4874616583,0.5692505217,-0.2356184772

H,0,-0.4297428402,0.2213476905,1.7160049301

H,0,0.9705371699,2.1235994197,2.1342946627

H,0,-0.7083213138,2.6654678744,2.2473841065

H,0,0.0116366151,-0.3023493157,-0.7203219078

O,0,0.2915652927,3.3240627538,0.6095251608

P,0,2.1788107524,-0.0421169959,0.2911630601

C,0,-1.8686993823,1.1008077663,0.4208926281

H,0,-2.1942494,0.1425936457,-0.4342055712

C,0,-2.8889688499,0.9359648775,1.4321789359

C,0,-4.2962858612,1.3709150899,1.102208635

C,0,-4.6739890113,1.8654776345,-0.1534450403

C,0,-5.2751651663,1.2502332794,2.0958663062

C,0,-5.9947614322,2.230895992,-0.4036875401

H,0,-3.9416312217,1.948234286,-0.9531877112

C,0,-6.5949324453,1.617598088,1.8499766588

H,0,-4.974856141,0.8644337113,3.0678149188

C,0,-6.9595347649,2.1088170774,0.5963546891

H,0,-6.2710462981,2.6119564226,-1.3849764219

H,0,-7.3403113071,1.5254561172,2.6378700007

H,0,-7.9897099686,2.4004485903,0.4006642713

O,0,-2.693340422,0.3771148608,2.5260773251

C,0,1.9268944625,-1.171343847,1.691987398

C,0,2.7500422537,-1.2301820271,2.8220199525

C,0,0.8575874416,-2.0701961945,1.558053128

C,0,2.4927336081,-2.1660536131,3.8192041725

H,0,3.612588649,-0.5785146061,2.9178110082

C,0,0.6175709761,-3.0077249525,2.5586174951

H,0,0.2001327051,-2.0569131822,0.6816825454

C,0,1.4272820286,-3.0542080033,3.6903343445

H,0,3.135985224,-2.203311057,4.6957065301

H,0,-0.2125795923,-3.7008835156,2.446151785

H,0,1.2318985637,-3.785601377,4.4715435693

C,0,3.1928046083,1.4226100308,0.6330037155

C,0,3.6391793016,2.1583424016,-0.4727658272

C,0,3.4250718249,1.9133725598,1.9222486326

C,0,4.3146313591,3.3607327043,-0.2885676632

H,0,3.4646447389,1.7993275451,-1.4864574903

C,0,4.1036201348,3.1142695954,2.1006905298

H,0,3.0635049793,1.3793174116,2.7968189391

C,0,4.5474706658,3.8402940914,0.997510991

H,0,4.6492195663,3.9239396239,-1.1566981998

H,0,4.2784597938,3.484742145,3.1079562637

H,0,5.0721684118,4.7820458237,1.1414715973

C,0,2.906920876,-0.9814289196,-1.1061742334

C,0,1.9987527914,-1.6250858,-1.958211338

C,0,4.2949155304,-1.1351475997,-1.3362894981

C,0,2.4426989569,-2.3515308123,-3.0599399689

H,0,0.9239665458,-1.6049314242,-1.7689207672

C,0,4.7127778719,-1.8428950608,-2.4620944745

C,0,3.8008295931,-2.4389144322,-3.3289933157

H,0,1.7127509214,-2.8440704114,-3.6977817935

H,0,5.7807253213,-1.9416299951,-2.6408601277

H,0,4.1586494783,-2.9896534725,-4.1961055593

C,0,5.365828085,-0.6139599344,-0.3854723518

C,0,6.6127018919,-2.4171906752,0.2301672983

C,0,5.4007528113,-2.2471407686,1.1516036618

H,0,6.5326097642,-3.3190395707,-0.3911627607

H,0,7.5642165824,-2.4404506478,0.771488133

H,0,4.5769354885,-2.9240259993,0.8775338327

H,0,5.6328744391,-2.3799874476,2.2118975569

O,0,5.0145990941,-0.8879043616,0.9493320943

O,0,6.6026305243,-1.2424123896,-0.5848911953

H,0,5.5199887277,0.4679488248,-0.4848964119

C,0,-2.1816468192,-1.9106564365,-1.3703318796

O,0,-0.9516624475,-2.0412802202,-1.0520054517

O,0,-2.9194065523,-2.870187721,-1.7494340541

O,0,-2.7360367825,-0.7027817949,-1.2865684369

H,0,-2.0250531113,1.9839604352,-0.2093055983

Cs,0,-5.4624723945,-1.7335528103,-0.5600768953

3e-TS-H-*Shift2*

SCF Done: E(RM06) = -2393.43295844 A.U.

Sum of electronic and thermal Free Energies= -2392.890534 A.U.

C,0,-1.4493024332,4.4068269729,1.515699593

C,0,-1.0183464197,3.3654202987,0.6874768186

C,0,-1.0031829581,2.0305125286,1.1412113986

C,0,-1.4061914768,1.8105258278,2.4694416

C,0,-1.8552183957,2.8357188122,3.2925037391

C,0,-1.880830695,4.1452761746,2.8082734331

H,0,-1.4433493819,5.4177968198,1.1120300999

H,0,-1.3495092884,0.7993664781,2.865827946

H,0,-2.162442328,2.6163587881,4.3126554432

H,0,-2.2221565936,4.9625545835,3.4405238403

C,0,-0.3616590086,2.7343636333,-1.5226280318

C,0,0.293678711,1.5054207948,-0.9162069896

C,0,-0.5285907596,0.9156745578,0.2512756124

H,0,0.3994583083,0.7784667786,-1.7323222455

H,0,-1.3090148682,2.497496038,-2.0226044456

H,0,0.30078344,3.1941355122,-2.2672215021

H,0,0.3348743829,0.1862910791,0.9972188599

O,0,-0.5998831256,3.7507676175,-0.548857044

P,0,-1.9181535898,-0.1151650172,-0.3039750827

C,0,1.7055429517,1.8734116511,-0.4326978402

H,0,1.8607960577,1.5478878477,0.5998031902

C,0,2.8130616657,1.3392205172,-1.2989605968

C,0,4.2226453051,1.4985681593,-0.8098038506

C,0,4.5353897806,1.8327659449,0.5135215907

C,0,5.2642120681,1.3287903382,-1.7299920215

C,0,5.862345597,1.9940096302,0.9054373205

H,0,3.7494933847,1.9526213646,1.2559282762

C,0,6.5899652039,1.4950391254,-1.3416106087

H,0,5.0128832043,1.0752405016,-2.7578289403

C,0,6.8919168435,1.8278677222,-0.0202237681

H,0,6.0901108217,2.2492262445,1.9380661571

H,0,7.3887610535,1.3739017767,-2.0707728538

H,0,7.9274662171,1.9642411842,0.2855650125

O,0,2.6059873239,0.894429097,-2.420931793

C,0,-1.3312321342,-1.4723495203,-1.362085267

C,0,-2.2513737402,-2.2517784504,-2.0784118146

C,0,0.0257554617,-1.8061780106,-1.3761638216

C,0,-1.810307063,-3.3380024545,-2.8255527928

H,0,-3.3113837777,-2.0095369043,-2.0478880731

C,0,0.4553819272,-2.8992741238,-2.1280090769

H,0,0.7731229316,-1.2528597052,-0.7981308289

C,0,-0.4535211468,-3.6615603852,-2.8550502681

H,0,-2.5291146358,-3.9347193891,-3.38318307

H,0,1.5148063563,-3.1488515059,-2.1339710731

H,0,-0.110530345,-4.5120760519,-3.4407640051

C,0,-3.0961011338,0.9083080923,-1.237018308

C,0,-3.7428788468,1.9579654114,-0.5685102018

C,0,-3.1965654929,0.8192072248,-2.6293045664

C,0,-4.4928303302,2.8874977017,-1.2817299062

H,0,-3.6572937876,2.06174802,0.5133059239

C,0,-3.9522501177,1.7488130581,-3.3382342356

H,0,-2.6722255119,0.0361510429,-3.1728090271

C,0,-4.6001035138,2.7837152477,-2.6675272694

H,0,-4.9873661357,3.6978781349,-0.7508889416

H,0,-4.025664215,1.6671883961,-4.420324829

H,0,-5.1834668188,3.5134753581,-3.2245724897

C,0,-2.6947230927,-0.965990316,1.1314681761

C,0,-1.7372705179,-1.5449859056,1.9779007467

C,0,-4.0660680877,-1.1554617751,1.4193533397

C,0,-2.1045267209,-2.2477867526,3.1192248847

H,0,-0.6729177605,-1.4226531625,1.775623944

C,0,-4.4103870239,-1.8430500038,2.58643552

C,0,-3.4496653302,-2.3802540824,3.436473355

H,0,-1.3323830801,-2.6718252282,3.756555439

H,0,-5.4653724408,-1.9579645009,2.8206774795

H,0,-3.7575938811,-2.9102843815,4.3351292398

C,0,2.2725541343,-0.8554202658,1.4543401636

O,0,1.143395747,-0.2997611852,1.8690716788

O,0,3.0938476777,-1.281694462,2.3225327612

O,0,2.4938942216,-0.930037077,0.1928214969

H,0,1.8362839565,2.9693061705,-0.4125417018

Cs,0,5.2984766395,-1.8673344611,0.3572156211

C,0,-5.2011045024,-0.703291387,0.5064426737

C,0,-6.7913037903,-2.3441423249,0.2786775958

C,0,-5.6240624277,-2.554411405,-0.6787879187

H,0,-6.903534478,-3.1701118201,0.9928756875

H,0,-7.7427615599,-2.191051398,-0.2441563367

H,0,-4.8823997163,-3.2611578306,-0.2733038

H,0,-5.9236071056,-2.8819786554,-1.6780146886

O,0,-5.0624954965,-1.2500250731,-0.7852584208

O,0,-6.4581096865,-1.1357131872,0.9663954869

H,0,-5.2384808155,0.3866821275,0.4104239901

3e-TS-*Cyc*

SCF Done: E(RM06) = -2393.42812813 A.U.

Sum of electronic and thermal Free Energies= -2392.890402 A.U.

C,0,-2.2410078465,4.3377177178,1.8835365128

C,0,-1.5918111809,3.6719109613,0.8414824964

C,0,-0.9030991288,2.4680311057,1.0865350032

C,0,-0.8698849955,1.9630527923,2.3971502138

C,0,-1.5288743804,2.6120832542,3.4292653148

C,0,-2.2172905461,3.8025019735,3.1648815594

H,0,-2.7600162894,5.2687079255,1.6647302282

H,0,-0.3036528668,1.0497844305,2.580301836

H,0,-1.5006392044,2.2059369375,4.4373604598

H,0,-2.7339279341,4.3214609785,3.96979952

C,0,-1.2922412657,3.4742664676,-1.5210638571

C,0,-0.1411751566,2.5194480607,-1.2957984495

C,0,-0.2488125216,1.7782757628,-0.0124628137

H,0,-0.0268515792,1.8639612188,-2.1693171453

H,0,-2.2003676543,2.9290023848,-1.8146005061

H,0,-1.0467077738,4.1910125113,-2.3111204908

H,0,0.5275230621,1.0512413532,0.23211917

O,0,-1.6026684919,4.2718778505,-0.3714152166

P,0,-1.8445326712,-0.113589558,-0.4113147761

C,0,1.1513377523,3.1624886854,-0.9032740314

H,0,1.1177220491,4.139210782,-0.4276022205

C,0,2.3414415066,2.4510577717,-1.0569495662

C,0,3.6313539772,3.0466147279,-0.583115735

C,0,4.831154228,2.5397424882,-1.0971163124

C,0,3.6940288421,4.0765296966,0.3646469035

C,0,6.0580670372,3.0572903885,-0.6924285829

H,0,4.7810276443,1.7329943948,-1.8260114247

C,0,4.9199695513,4.5917445497,0.7749607376

H,0,2.7787052745,4.4642051136,0.8073526337

C,0,6.1075589694,4.0880185102,0.2448785652

H,0,6.9799425663,2.6567691841,-1.1108634876

H,0,4.9485708329,5.3848393775,1.5198198526

H,0,7.065441427,4.4923449944,0.5663938905

O,0,2.3816167761,1.298903883,-1.6018214282

C,0,-1.1890169026,-1.2323619855,-1.7037647314

C,0,-1.9216586756,-2.3061203811,-2.229146409

C,0,0.1305405886,-1.0283515603,-2.1214719771

C,0,-1.3434433635,-3.1492653975,-3.1722971606

H,0,-2.9450372104,-2.4703729845,-1.8967255688

C,0,0.7062470327,-1.8806468632,-3.0634528845

H,0,0.7298292534,-0.2068137354,-1.7253869572

C,0,-0.028378616,-2.9377573671,-3.5911724757

H,0,-1.9193346405,-3.9773669293,-3.5809005531

H,0,1.7345589724,-1.7079568322,-3.376581666

H,0,0.4197983819,-3.6018266352,-4.327704918

C,0,-3.3501906059,0.6816372335,-1.0393302156

C,0,-4.0306482675,1.5482116569,-0.169162349

C,0,-3.7240981603,0.6366359759,-2.3863530295

C,0,-5.0804528245,2.3331895063,-0.6329912966

H,0,-3.7374992989,1.6087902476,0.880656156

C,0,-4.774383283,1.4275822237,-2.8484355474

H,0,-3.1957757786,-0.0156132641,-3.0801753055

C,0,-5.4537761264,2.2754749014,-1.9759835676

H,0,-5.5992773792,2.99834504,0.0545181713

H,0,-5.0610118835,1.380292948,-3.8969107466

H,0,-6.2704065887,2.8942128679,-2.3415269917

C,0,-2.2056704188,-1.2238246674,1.013765146

C,0,-1.0213847594,-1.528445492,1.7039646355

C,0,-3.4261095072,-1.7657526771,1.4774564242

C,0,-1.0212875809,-2.3473783356,2.8274074856

H,0,-0.069326561,-1.1036137249,1.3745921515

C,0,-3.4075848158,-2.5626034693,2.6260042146

C,0,-2.225044304,-2.85690928,3.2988506752

H,0,-0.0817233255,-2.5598216711,3.3327379256

H,0,-4.3513925242,-2.9562524477,2.9955145225

H,0,-2.2507983192,-3.4827270687,4.1885475115

C,0,-4.7556307682,-1.5548043631,0.7658818229

C,0,-6.048736646,-3.4558944133,0.7418924727

C,0,-5.0257998661,-3.4558618167,-0.3871584987

H,0,-5.9118767766,-4.2955066171,1.4355573299

H,0,-7.0813760041,-3.4620038624,0.3723665115

H,0,-4.1157800594,-4.0155708046,-0.1165994763

H,0,-5.4123448951,-3.8367958485,-1.3362693141

O,0,-4.7329813158,-2.0727936301,-0.5458862559

O,0,-5.8169564108,-2.2171848273,1.4150792304

H,0,-5.0136679103,-0.4920249911,0.6973199512

C,0,2.6095970026,-0.9696372031,1.0408841577

O,0,1.8518685489,-0.035295614,1.3818655443

O,0,3.2619661666,-0.8399060007,-0.1759996486

O,0,2.8762899591,-2.0284898091,1.6528954105

Cs,0,5.2880146065,-3.1168429589,0.2469726496

H,0,2.9602888446,-0.0094972605,-0.6229641373

3a-TS-H-*Shift*

SCF Done: E(RM06) = -2244.26492787 A.U.

Sum of electronic and thermal Free Energies= -2243.714282 A.U.

C,0,0.5218070647,4.47059906,-0.9881838599

C,0,0.4295412201,3.2382972871,-0.3346468527

C,0,0.5817528466,2.0413641785,-1.053500196

C,0,0.7732249708,2.1154986855,-2.4359241266

C,0,0.8599507725,3.3371808912,-3.0943194212

C,0,0.7451763159,4.5177556587,-2.3580230094

H,0,0.4056140285,5.3785216269,-0.3997106871

H,0,0.8576856927,1.186800058,-2.9999446487

H,0,1.0104043286,3.3686222416,-4.1708093113

H,0,0.815054908,5.4826162984,-2.8564309372

C,0,0.0131479766,2.0752098987,1.7429555804

C,0,-0.4166000516,0.8898619274,0.9030164678

C,0,0.5179986185,0.738062765,-0.3088046022

H,0,-0.3558144118,0.0034067355,1.5473170797

H,0,0.9649257678,1.8746168043,2.2557351261

H,0,-0.7322381595,2.2931122477,2.5154256061

H,0,0.0940976377,-0.0825305959,-0.9099484294

O,0,0.1602250035,3.289611711,0.9934258799

P,0,2.2556780079,0.1598924124,0.0837049787

C,0,-1.8496593284,1.0040678961,0.411790147

H,0,-2.106629657,0.056087573,-0.4651364811

C,0,-2.8647805247,0.7491453779,1.4084262236

C,0,-4.2924336491,1.105522775,1.0758159364

C,0,-4.6892902226,1.5859723222,-0.1792378977

C,0,-5.270232791,0.9097312387,2.0584786581

C,0,-6.0292800903,1.8623711651,-0.4409725372

H,0,-3.9550549725,1.7254673354,-0.9694132485

C,0,-6.6092482671,1.189707416,1.8014070019

H,0,-4.9548283947,0.5341412131,3.0296996313

C,0,-6.9935300742,1.664927288,0.5474134642

H,0,-6.3213621154,2.2319563594,-1.4220624802

H,0,-7.3547597693,1.0398290373,2.5801963231

H,0,-8.0393264439,1.8857397606,0.3423436218

O,0,-2.6438349141,0.1653341216,2.4842108132

C,0,2.2406671507,-0.8849705899,1.5647481653

C,0,3.0656503697,-0.6888601796,2.6765818225

C,0,1.3613301064,-1.9768470569,1.5194184453

C,0,3.0011803154,-1.5739695216,3.7490590218

H,0,3.7779447677,0.1318671434,2.7102772646

C,0,1.31192318,-2.8577526861,2.5956677075

H,0,0.7042550355,-2.1345368119,0.6562539199

C,0,2.1256852614,-2.6569761479,3.7090267249

H,0,3.6440741732,-1.4190065092,4.6124796236

H,0,0.6276189639,-3.7019972615,2.5598277872

H,0,2.0796898238,-3.348929629,4.5471406031

C,0,3.3170049612,1.6325095152,0.2293153876

C,0,3.9101720464,2.1191921655,-0.9439936519

C,0,3.4510412981,2.3650594006,1.4146096096

C,0,4.6251482909,3.3117044311,-0.9280131278

H,0,3.8095275586,1.5740548864,-1.880873801

C,0,4.175486296,3.5534586738,1.4269191007

H,0,2.9868574918,2.0313145035,2.3388573135

C,0,4.7610256713,4.0301369582,0.2575003193

H,0,5.0714560566,3.6803641799,-1.8485559722

H,0,4.271832282,4.1100746077,2.3560085586

H,0,5.3188452053,4.9637314885,0.268829515

C,0,2.9046584677,-0.8384203824,-1.302031796

C,0,2.0292002621,-1.2284645353,-2.3264032863

C,0,4.2674663866,-1.2120842627,-1.3552311941

C,0,2.4934719146,-1.9327303147,-3.4301882852

H,0,0.962660283,-1.0341696412,-2.2519778862

C,0,4.7074547243,-1.8971215542,-2.4924371731

C,0,3.8442801684,-2.2480375019,-3.5234013967

H,0,1.7940932679,-2.2345958823,-4.2055513261

H,0,5.7596476617,-2.1693567492,-2.5625919301

H,0,4.2260679753,-2.7833556501,-4.3902358719

C,0,5.2816831824,-0.9423235021,-0.269262692

C,0,5.0656861089,-3.2505941168,0.8008148031

H,0,4.331844989,-3.5922050484,0.0584693266

H,0,5.6208760353,-4.1312453745,1.1442045187

H,0,6.0264860497,-0.226500807,-0.6495647765

C,0,-1.8766476908,-2.0080807499,-1.3125870369

O,0,-0.6542771113,-2.0056991816,-0.9525035316

O,0,-2.5198967106,-3.0499376514,-1.6500885688

O,0,-2.5382603289,-0.848368594,-1.3290556041

H,0,-2.0352861434,1.9081775207,-0.1796024398

Cs,0,-5.1785544004,-2.078855774,-0.5764500142

C,0,6.0026636832,-2.2012898246,0.2246789899

H,0,4.816680983,-0.4532388803,0.5936226088

H,0,6.7305553171,-1.8931987203,0.9880873771

H,0,6.5932129957,-2.6378350044,-0.5928957811

H,0,4.50502936,-2.856159949,1.6591189759

3a-TS-*Cyc*

SCF Done: E(RM06) = -2244.26150074 A.U.

Sum of electronic and thermal Free Energies= -2243.712407 A.U.

C,0,-2.1409460599,4.5495685032,1.8221278616

C,0,-1.5349181165,3.8040802559,0.8080197421

C,0,-0.8756739641,2.5963986824,1.1094663861

C,0,-0.8257457997,2.17102322,2.4478286075

C,0,-1.4408189231,2.8997471323,3.4531360726

C,0,-2.1015183019,4.0922078522,3.132419205

H,0,-2.6358401706,5.4820773875,1.5587749711

H,0,-0.2777812845,1.2563913746,2.6737765083

H,0,-1.3981663634,2.555103748,4.4833788078

H,0,-2.582643809,4.6744312112,3.9158180114

C,0,-1.2715915055,3.4735277684,-1.5450759732

C,0,-0.1461813681,2.4981836663,-1.2809542267

C,0,-0.2560875331,1.8296444788,0.041819578

H,0,-0.0646512538,1.7931652656,-2.1189156091

H,0,-2.1972674906,2.9424573491,-1.8068862506

H,0,-1.0114981756,4.142486508,-2.3716986916

H,0,0.5036642242,1.0957432245,0.3156037985

O,0,-1.5530702735,4.3357144161,-0.4355514248

P,0,-1.9029791509,-0.0308557235,-0.244557059

C,0,1.1731630646,3.1201161036,-0.9483298051

H,0,1.1796443435,4.1223951716,-0.5280754341

C,0,2.3357553108,2.3619228703,-1.0879727826

C,0,3.656070647,2.9449863188,-0.6876848617

C,0,4.8253493413,2.3663393803,-1.1958847698

C,0,3.7761603383,4.0314532343,0.1887957977

C,0,6.07815539,2.8715068301,-0.8604531297

H,0,4.7305935541,1.5144501176,-1.8665447575

C,0,5.0279149066,4.5343406118,0.5304506365

H,0,2.8860940562,4.4767751534,0.6286177406

C,0,6.1846437319,3.9597515975,0.0041413604

H,0,6.97549089,2.4141875969,-1.2738860941

H,0,5.1010973526,5.3731723143,1.22017344

H,0,7.1628141939,4.3550192092,0.2714413147

O,0,2.3250284147,1.178730055,-1.564383361

C,0,-1.3620820137,-1.1804119769,-1.5606542713

C,0,-2.182472701,-2.1986464478,-2.064514407

C,0,-0.0412857596,-1.0759156461,-2.0087474025

C,0,-1.693255258,-3.0877245301,-3.0149423216

H,0,-3.2081586375,-2.2983977841,-1.7118681077

C,0,0.4465604349,-1.9720150749,-2.9602276612

H,0,0.6223621959,-0.2968453747,-1.628338918

C,0,-0.3760791552,-2.9742889077,-3.4649174077

H,0,-2.3386961284,-3.8737966816,-3.4022686743

H,0,1.4762017508,-1.8770943965,-3.3006539886

H,0,0.0050029276,-3.6721045363,-4.2078925518

C,0,-3.4123716335,0.8085836431,-0.8051409511

C,0,-4.0754943075,1.6255984089,0.1230976789

C,0,-3.8160497545,0.8288606335,-2.1452324433

C,0,-5.1388764161,2.4265106337,-0.2791992415

H,0,-3.7575684154,1.6365570002,1.1670703511

C,0,-4.8826131267,1.6327054695,-2.5434452807

H,0,-3.295640225,0.2205626521,-2.8840405433

C,0,-5.5459564227,2.4314230658,-1.613667997

H,0,-5.6439571897,3.0561720825,0.4507019362

H,0,-5.1917773551,1.6377311922,-3.5866376815

H,0,-6.3743694274,3.0622738083,-1.9283321615

C,0,-2.2775908728,-1.1229908358,1.1883547044

C,0,-1.1323140247,-1.3434716091,1.9721204554

C,0,-3.5016037424,-1.7410282541,1.5362828784

C,0,-1.1729134562,-2.1463401859,3.1050059402

H,0,-0.1821602116,-0.876233783,1.6989385905

C,0,-3.5162689014,-2.5208196285,2.7009917872

C,0,-2.3813296664,-2.7241656027,3.4790575699

H,0,-0.2662035044,-2.3029631147,3.6851006159

H,0,-4.4463776317,-2.998595703,3.003294576

H,0,-2.4446204695,-3.3429617605,4.3721945545

C,0,2.4496548041,-0.9632069706,1.1946919569

O,0,1.7955093335,0.0548004649,1.5102035505

O,0,3.0682478849,-0.9528637537,-0.0469657669

O,0,2.6350452183,-2.0124005164,1.8507862902

Cs,0,4.8338342313,-3.4316105912,0.3949590421

H,0,2.828961076,-0.1192494516,-0.5240921992

C,0,-4.7798780371,-1.5972128787,0.7391022712

H,0,-4.5408812321,-1.3135272362,-0.2927605458

H,0,-5.3546016315,-0.7482517972,1.1423509754

C,0,-5.6852628358,-2.8277581767,0.6901266719

C,0,-5.0527574085,-4.018022476,-0.0144395371

H,0,-5.71900438,-4.8889060618,-0.0078684487

H,0,-4.8336115709,-3.7817390113,-1.0650973537

H,0,-4.1079164276,-4.3196801323,0.4569596521

H,0,-6.0098040112,-3.114114735,1.6998521822

H,0,-6.6040885311,-2.5397406671,0.1609598527

3b-TS-H-*Shift*

SCF Done: E(RM06) = -2280.15623352 A.U.

Sum of electronic and thermal Free Energies= -2279.624634 A.U.

C,0,0.6325936982,4.1182092258,-1.653999139

C,0,0.5094022835,3.0482808489,-0.7617504097

C,0,0.604544633,1.7254572315,-1.2230863103

C,0,0.7670860314,1.5103736241,-2.5957897145

C,0,0.8973001028,2.5681922173,-3.4880203179

C,0,0.8409710377,3.877898815,-3.0054596327

H,0,0.5613576695,5.130212069,-1.260353579

H,0,0.7878270191,0.4847153426,-2.9623296326

H,0,1.026953833,2.3744962807,-4.5500530267

H,0,0.940568555,4.7182502901,-3.689652641

C,0,0.0513113931,2.354472876,1.5109341843

C,0,-0.4348088129,1.0440887099,0.9182111147

C,0,0.482310778,0.5979960506,-0.2384039007

H,0,-0.4193555041,0.3082523835,1.7319480865

H,0,0.9786653809,2.229187092,2.0859771187

H,0,-0.7036493809,2.7622521099,2.1934374704

H,0,0.0005300665,-0.2807316274,-0.7049183778

O,0,0.282003599,3.379859531,0.5320059358

P,0,2.1695633299,-0.0212631943,0.2883232038

C,0,-1.8685564443,1.1466673043,0.4203072649

H,0,-2.191796682,0.1784658729,-0.423170532

C,0,-2.8838264065,0.9841238127,1.4370180968

C,0,-4.2969420459,1.401729035,1.1080920045

C,0,-4.6830912208,1.8908102838,-0.1472253542

C,0,-5.2723314963,1.273307661,2.1044366277

C,0,-6.0081100121,2.2429294458,-0.394732878

H,0,-3.9538908277,1.9828736726,-0.9487260383

C,0,-6.5963721557,1.6272148559,1.8612647724

H,0,-4.9657401828,0.8927387105,3.0764636724

C,0,-6.9691498773,2.1128230483,0.6078599231

H,0,-6.2901601572,2.620774067,-1.3755863762

H,0,-7.3386412328,1.5292880479,2.6513564499

H,0,-8.0026119053,2.3941212444,0.4145325599

O,0,-2.6787243184,0.4385896701,2.5359964671

C,0,1.9275869838,-1.1674827119,1.6754877203

C,0,2.8267492442,-1.2961247021,2.7403254745

C,0,0.8082826049,-2.0104812232,1.597559041

C,0,2.5895902335,-2.2376603931,3.7370359453

H,0,3.7307546662,-0.695680792,2.7778581559

C,0,0.5890120428,-2.9545368057,2.5966287838

H,0,0.1057967141,-1.9553720507,0.7591786543

C,0,1.4700918551,-3.0641275464,3.6693719297

H,0,3.2915793821,-2.3297130031,4.5629629149

H,0,-0.2798454492,-3.6046656897,2.5286352727

H,0,1.2901473762,-3.8001313334,4.4499767496

C,0,3.1758943954,1.4351260115,0.6775874468

C,0,3.5948351969,2.2303166411,-0.3984272274

C,0,3.4184407975,1.8661972692,1.9857948566

C,0,4.2543754747,3.4323701901,-0.1652590213

H,0,3.4152203099,1.9139843994,-1.4253904865

C,0,4.0827078379,3.0675771807,2.2129927992

H,0,3.0724254401,1.2862340438,2.8373945164

C,0,4.4991122971,3.8522710664,1.1399959191

H,0,4.5690918482,4.0421996813,-1.0089812188

H,0,4.2664140841,3.3922527072,3.2343344262

H,0,5.0119385298,4.7940126087,1.3219987112

C,0,2.9094493311,-0.949157673,-1.1069126116

C,0,2.0057328861,-1.6348327199,-1.9310974471

C,0,4.299219361,-1.0733587621,-1.3452388409

C,0,2.4529767049,-2.3784038361,-3.0199390476

H,0,0.9322336946,-1.6290265061,-1.7306288764

C,0,4.715848071,-1.8172100168,-2.4504172228

C,0,3.8110901818,-2.451103607,-3.2970184527

H,0,1.7271289079,-2.900940045,-3.6382700158

H,0,5.7852839532,-1.9151900176,-2.6341139933

H,0,4.1721792075,-3.0240347113,-4.1482032271

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H,0,5.3835271586,0.5578813224,-0.3949590129

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O,0,-2.9270363883,-2.8398682735,-1.7344570391

O,0,-2.7341253701,-0.6738358546,-1.2676130726

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3b-TS-*Cyc*

SCF Done: E(RM06) = -2280.15450399 A.U.

Sum of electronic and thermal Free Energies= -2279.626359 A.U.

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C,0,-0.11205132,2.5039396774,-1.3113052006

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H,0,-4.7755987432,-4.2032374504,-1.4097895996

O,0,-4.7558389764,-2.3565431924,-0.5733488622

H,0,-5.0000692954,-0.6186862497,0.4035306854

C,0,2.5015890784,-1.0280157295,1.040726442

O,0,1.8220182639,-0.0449175526,1.4088126785

O,0,3.1979569138,-0.9019979856,-0.1516020023

O,0,2.6503222114,-2.1346789344,1.6065703389

Cs,0,4.8419598926,-3.4888773263,0.0885227236

H,0,2.9583179483,-0.0435480884,-0.58272193

H,0,-5.5745475793,-2.0367284508,1.2932871562

H,0,-5.4289989598,-4.1443389807,0.2501844764

3f-TS-H-*Shift*

SCF Done: E(RM06) = -2603.13625698 A.U.

Sum of electronic and thermal Free Energies= -2602.614795 A.U.

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C,0,0.9889030134,1.5173139991,-1.4352833972

C,0,1.2836157505,1.0634002994,-2.7284686048

C,0,1.5245594102,1.942139382,-3.776634638

C,0,1.4453505843,3.3179186361,-3.546895021

H,0,1.0170296974,4.8606420658,-2.0898401863

H,0,1.3117069764,-0.0101738872,-2.9103196398

H,0,1.7536510417,1.5577858237,-4.7675994149

H,0,1.6287774695,4.0211247427,-4.3567609451

C,0,0.4176901728,2.6409786543,1.1023519701

C,0,-0.1070163342,1.2473056556,0.7959719666

C,0,0.7436907646,0.563386058,-0.2972390651

H,0,-0.0575482201,0.6851697017,1.7389273275

H,0,1.4018756007,2.6247381203,1.5885169735

H,0,-0.2769198053,3.1577288447,1.7745212846

H,0,0.1773886113,-0.3173257915,-0.6646285587

O,0,0.5120954806,3.4716344491,-0.0594247013

P,0,2.3266285126,-0.1876444946,0.340270357

C,0,-1.5672338658,1.3060220546,0.3669556832

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C,0,-3.959323494,1.5888770851,1.1690314874

C,0,-4.3823602109,2.162449514,-0.0378494709

C,0,-4.9033729411,1.4054109841,2.1868341564

C,0,-5.7085700596,2.5511595479,-0.2140058586

H,0,-3.6809063279,2.3020327527,-0.8567406406

C,0,-6.2297287973,1.7910364817,2.0136373312

H,0,-4.5692606402,0.9604476427,3.1217639737

C,0,-6.6368686649,2.3691340264,0.8110519485

H,0,-6.0163031889,3.0005764125,-1.1562252391

H,0,-6.9461540653,1.6483184603,2.8204462712

H,0,-7.6706516246,2.6809887133,0.6749178341

O,0,-2.2789366527,0.6311797374,2.5282554403

C,0,1.9341762125,-1.3874221213,1.6444618723

C,0,2.9720726301,-1.9209970461,2.4228518719

C,0,0.6269526648,-1.8604036201,1.8041220362

C,0,2.693903844,-2.8885258632,3.3809084429

H,0,3.9989792187,-1.5874469866,2.2715962938

C,0,0.3607531028,-2.8306649586,2.7675940478

H,0,-0.1799495809,-1.5269896373,1.1519179455

C,0,1.3856521749,-3.337270719,3.560590737

H,0,3.5019218525,-3.2947828312,3.9852102738

H,0,-0.6575579781,-3.1929204337,2.885536754

H,0,1.1693841594,-4.0936659154,4.31196565

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C,0,3.7836076651,2.1583138391,0.117995658

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H,0,3.1804426502,0.5571200154,3.0707928831

C,0,4.6584041466,3.4128769958,1.9828597081

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H,0,4.3672990777,2.5339695211,3.9299548655

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C,0,2.1721377188,-2.0781713203,-1.5482232006

C,0,4.4234866137,-1.147664763,-1.4807659358

C,0,2.5270177743,-2.9309129133,-2.5859950135

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C,0,4.7431900517,-2.01156371,-2.5370189594

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H,0,1.7847973959,-3.6152960099,-2.9894719499

H,0,5.7630306558,-1.9973869741,-2.9194981681

H,0,4.1155369537,-3.5373777222,-3.9143394995

C,0,5.5676571446,-0.3427999713,-0.9348488653

C,0,6.3871406384,-2.5988340163,0.4982886607

H,0,5.448678981,-3.1167143899,0.2658579083

H,0,6.7805738019,-2.996276421,1.4390571885

H,0,5.353843072,0.7259206591,-0.8585492478

C,0,-2.0717069688,-1.7307210089,-1.3602942703

O,0,-0.8820221162,-1.9579022537,-0.9591910087

O,0,-2.8532831619,-2.6276366238,-1.8031429003

O,0,-2.5381982304,-0.4849040958,-1.2937033851

H,0,-1.7651355367,2.164375735,-0.2851760949

Cs,0,-5.3606908489,-1.3531880064,-0.720522186

H,0,6.4244517583,-0.443268227,-1.6109131572

H,0,7.1206752678,-2.7853783487,-0.2941257057

S,0,6.1193509263,-0.8211904401,0.7480489893

3f-TS-*Cyc*

SCF Done: E(RM06) = -2603.13566575 A.U.

Sum of electronic and thermal Free Energies= -2602.615513 A.U.

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C,0,-1.2607050647,1.8257827885,2.4020784128

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C,0,-0.6464291592,1.6740111304,-0.0102907405

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H,0,6.1933475042,5.4703696805,0.3549702438

O,0,2.0067319032,1.5633922581,-1.6562641568

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C,0,-1.6318857042,-2.7487433379,-1.9485008362

C,0,0.1145604383,-1.0783247031,-2.0502193029

C,0,-0.9332464317,-3.5320559864,-2.8611201513

H,0,-2.5875756997,-3.0907774225,-1.5502502862

C,0,0.8126158903,-1.8704843564,-2.9618345301

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H,0,0.8336758119,-3.7094582211,-4.0846441406

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O,0,3.1924844234,-0.4291647595,-0.242472797

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H,0,-5.295227949,-4.9656386058,1.0042867595

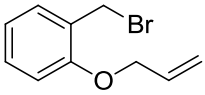
S,0,-5.0234153318,-2.9977216508,-0.4085085734

7. References

1 (a) L.-W. Ye, X.-L. Sun, C.-Y. Li, Y. Tang, *J. Org. Chem.* **2007**, *72*, 1335;

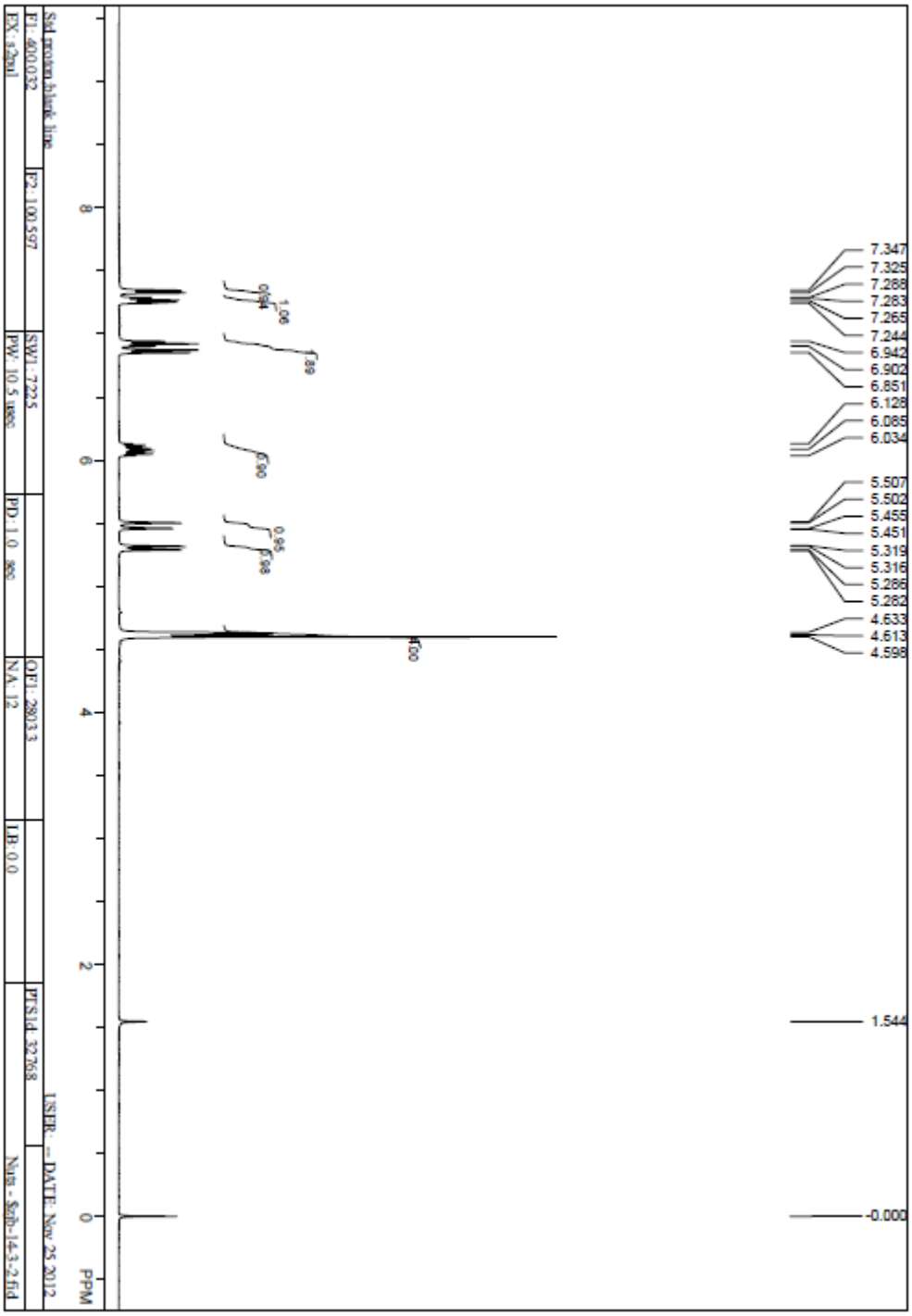
(b) J.-B. Zhu, P. Wang, S. Liao, Y. Tang, *Chem. Commun.* **2013,** *49*, 4570.

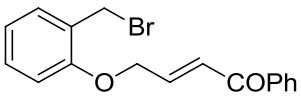
8. NMR Spectra



S3

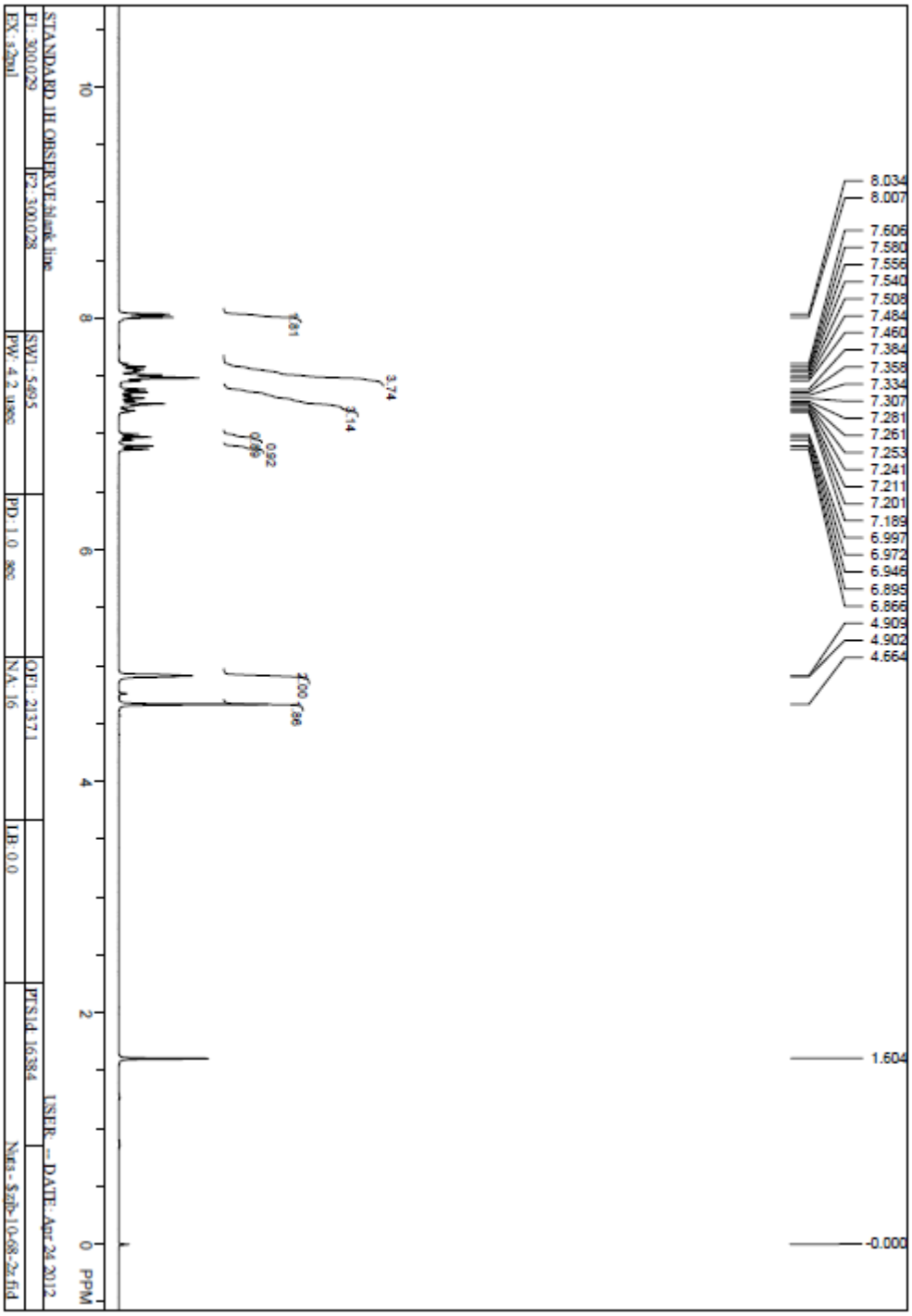
^{1}H NMR (400 M Hz in $CDCl_3$)

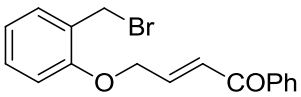




1a

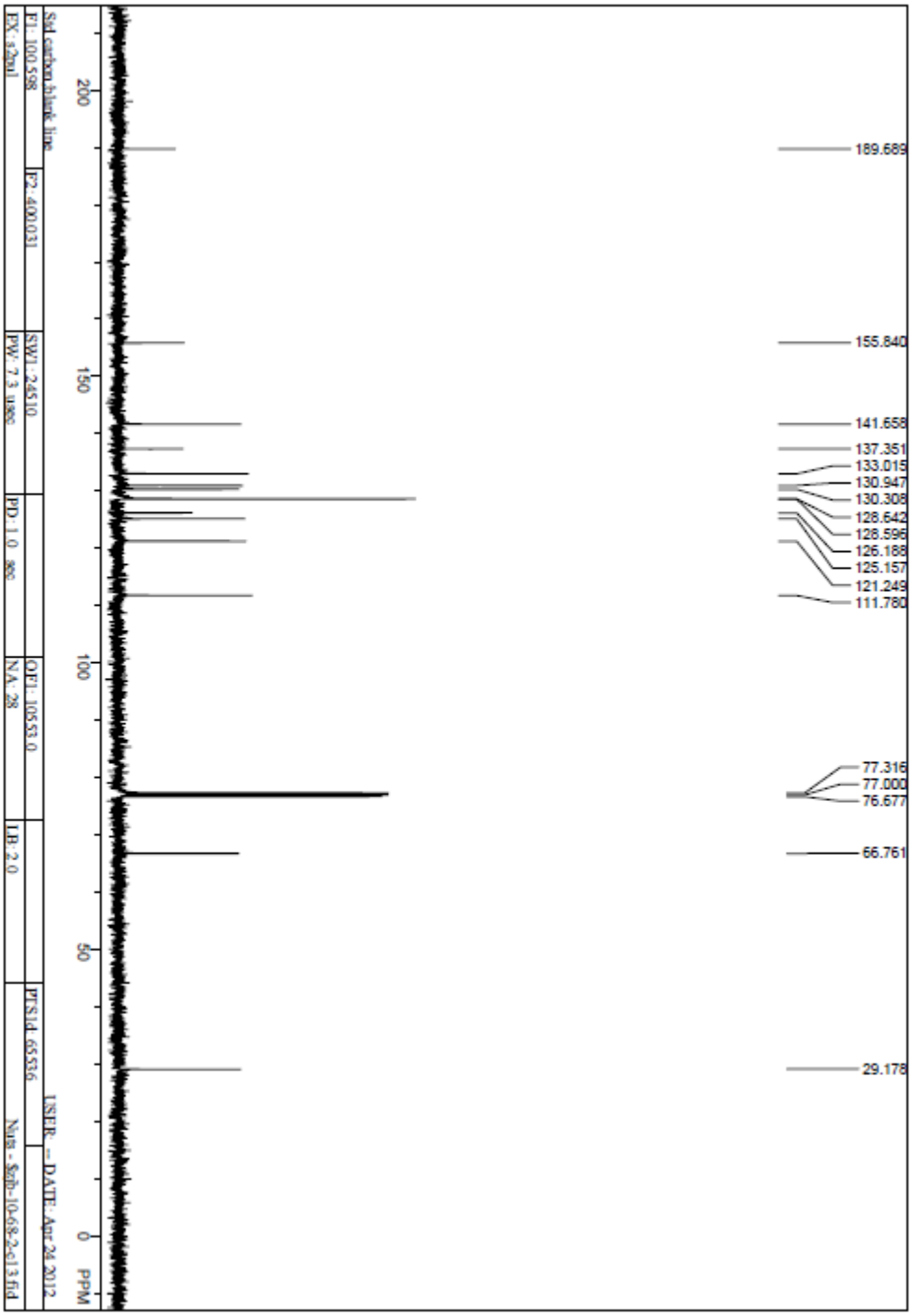
^{1}H NMR (300 M Hz in $CDCl_3$)

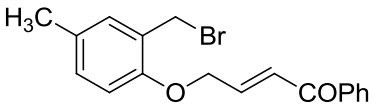




1a

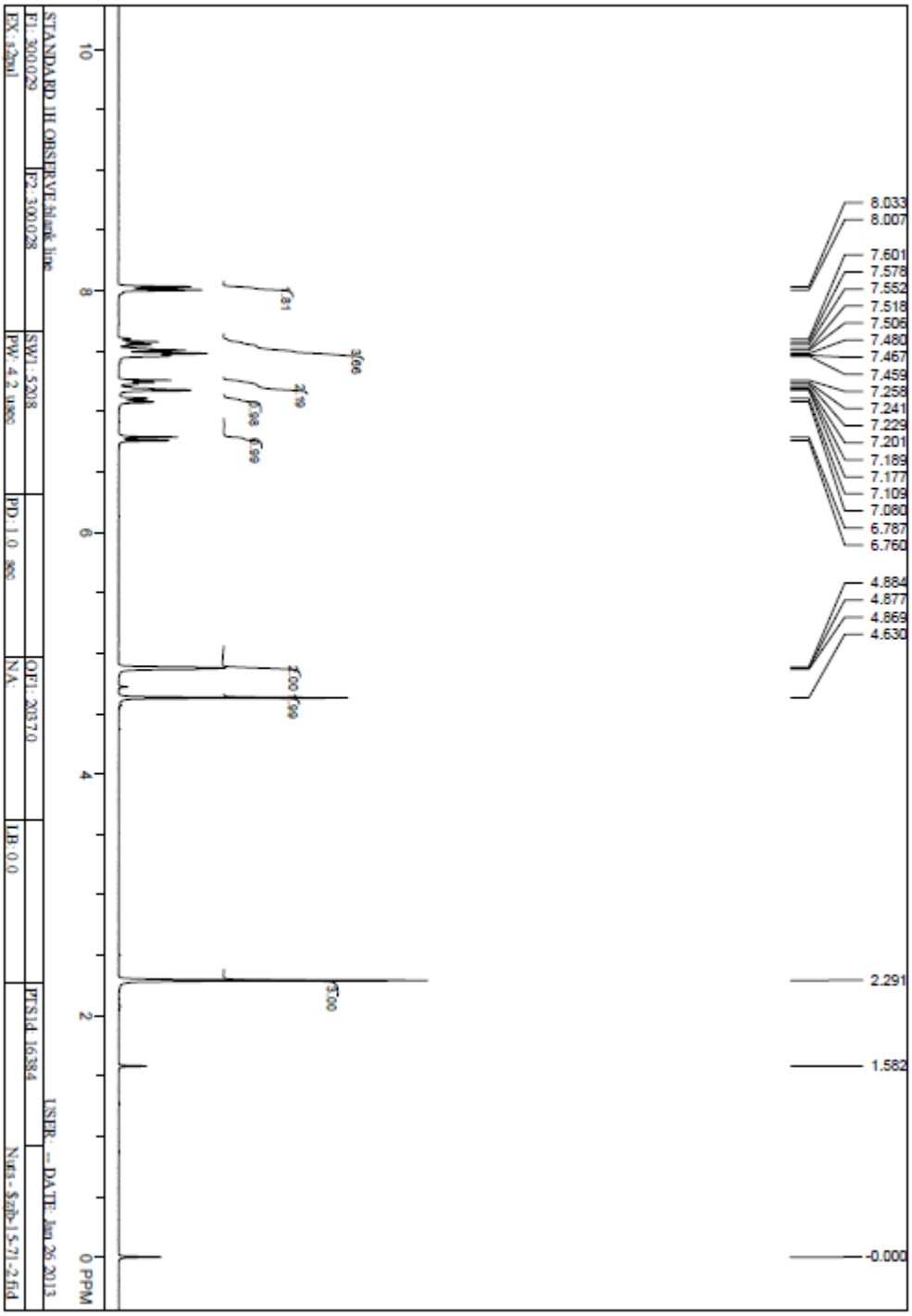
^{13}C NMR (100 M Hz in $CDCl_3$)

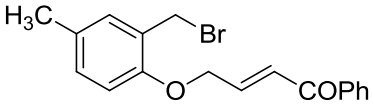




1b

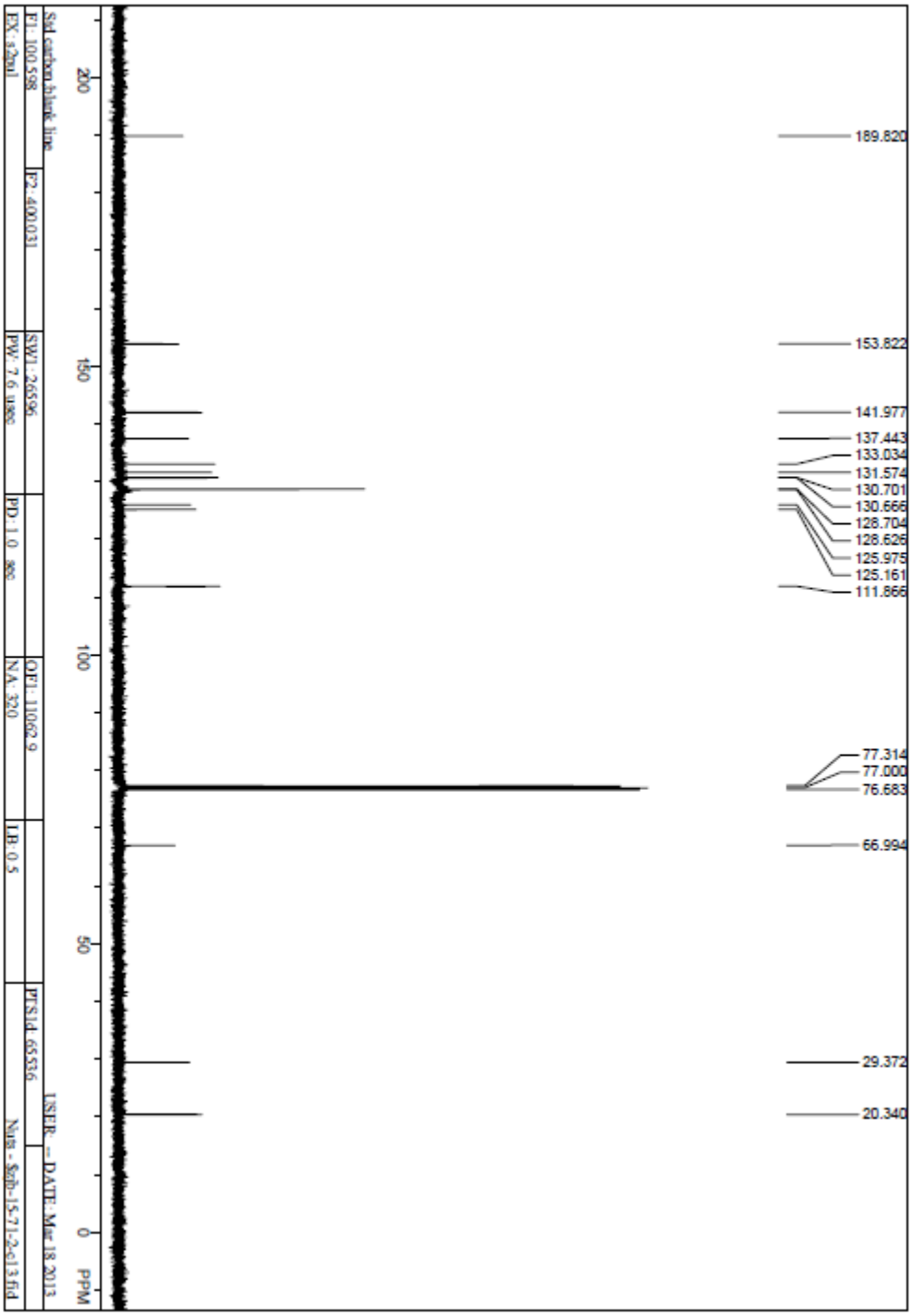
^{1}H NMR (300 M Hz in $CDCl_3$)

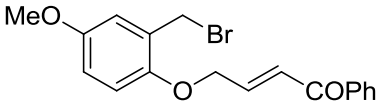




1b

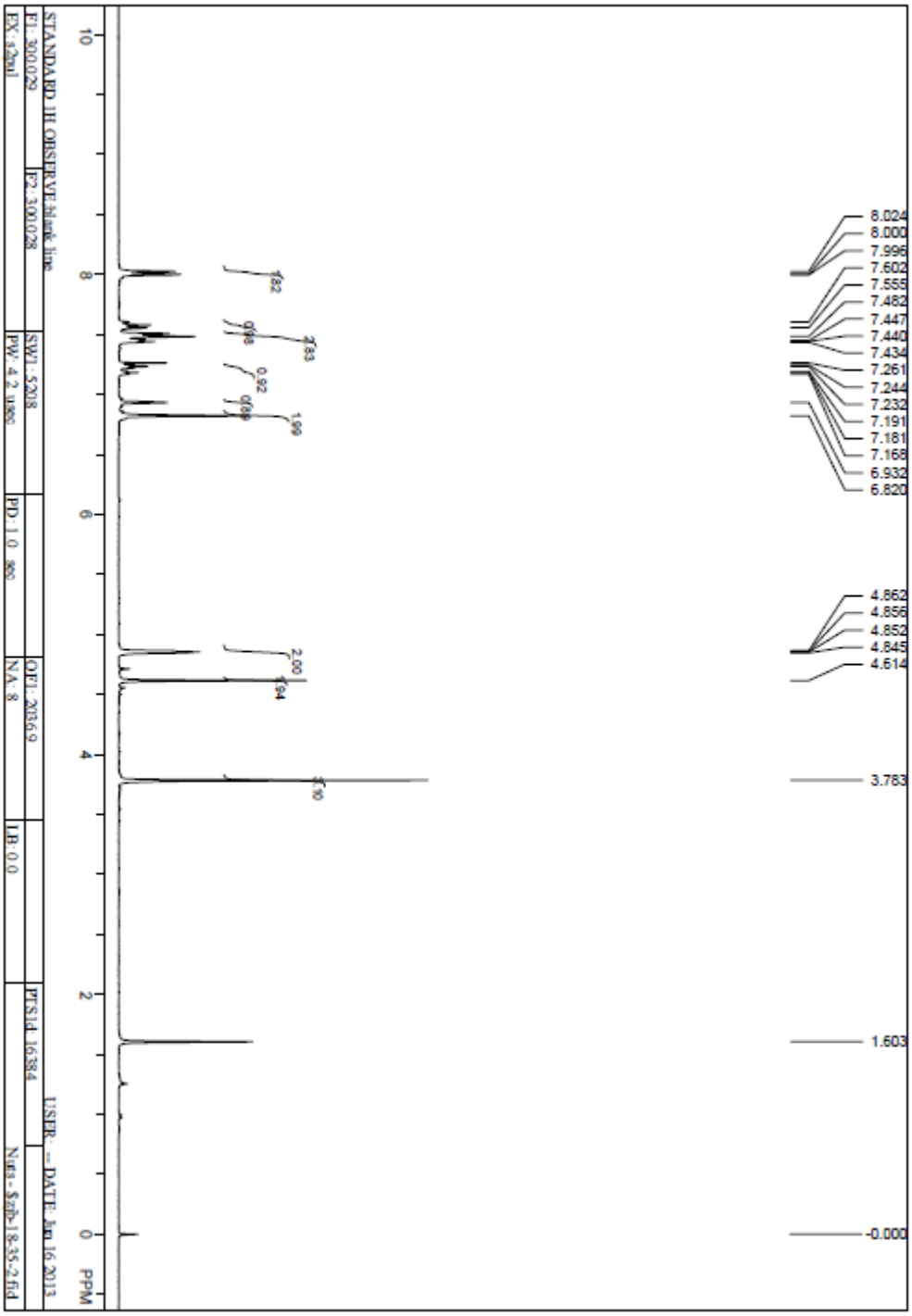
^{13}C NMR (100 M Hz in $CDCl_3$)

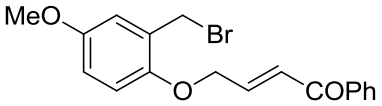




1c

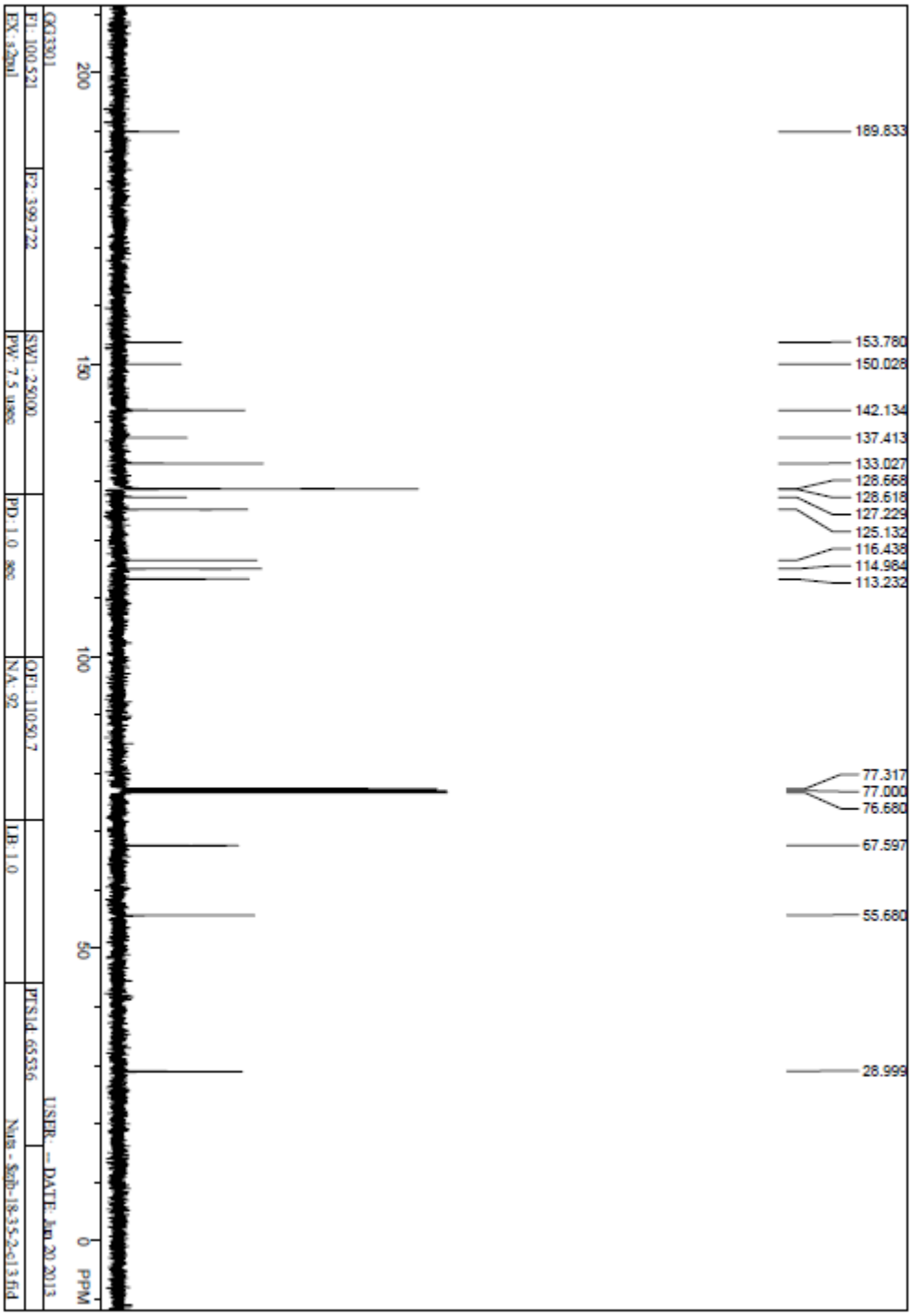
^{1}H NMR (300 M Hz in $CDCl_3$)

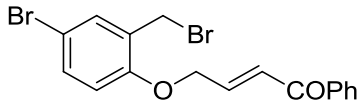




1c

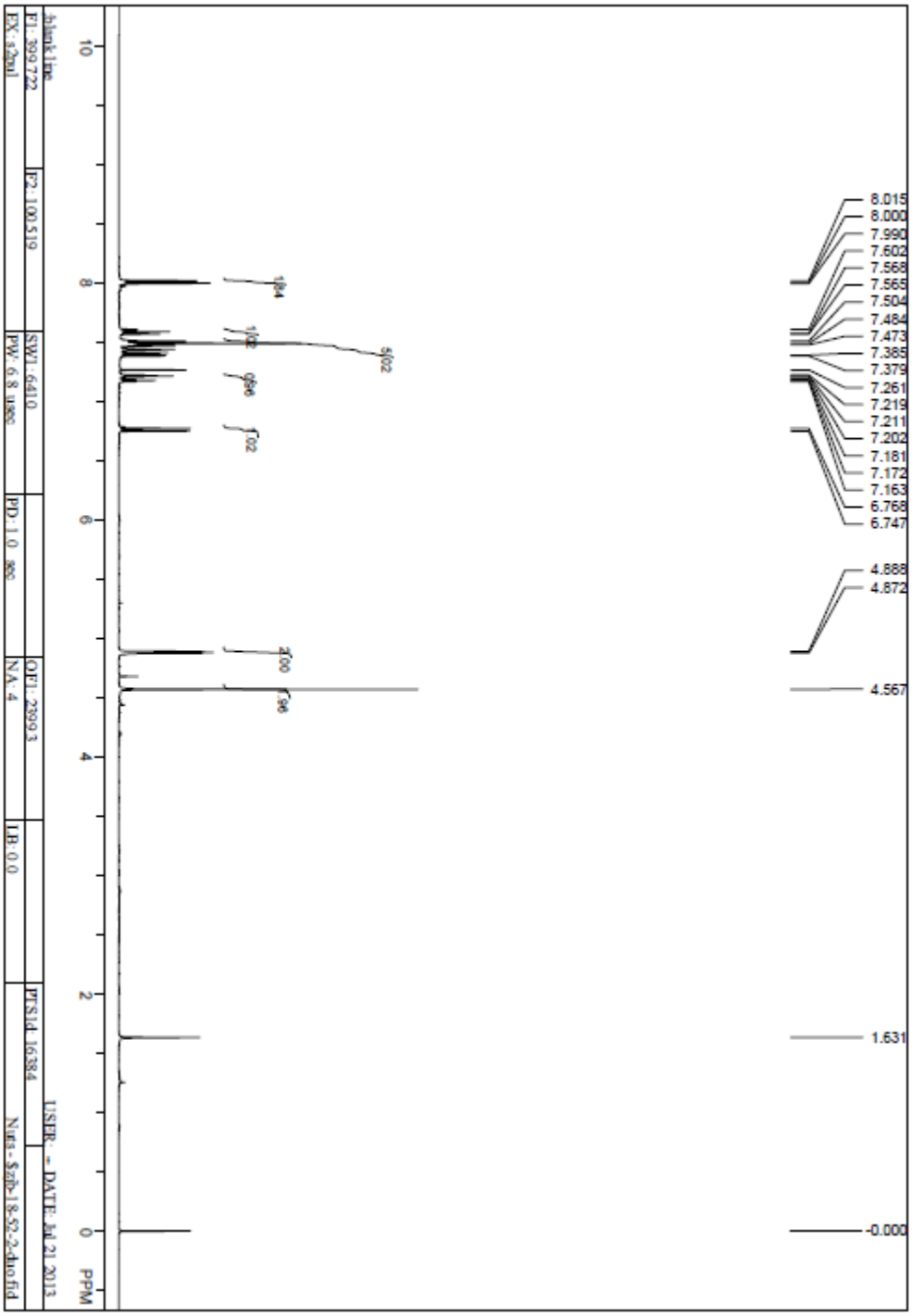
^{13}C NMR (100 M Hz in $CDCl_3$)

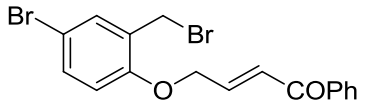




1d

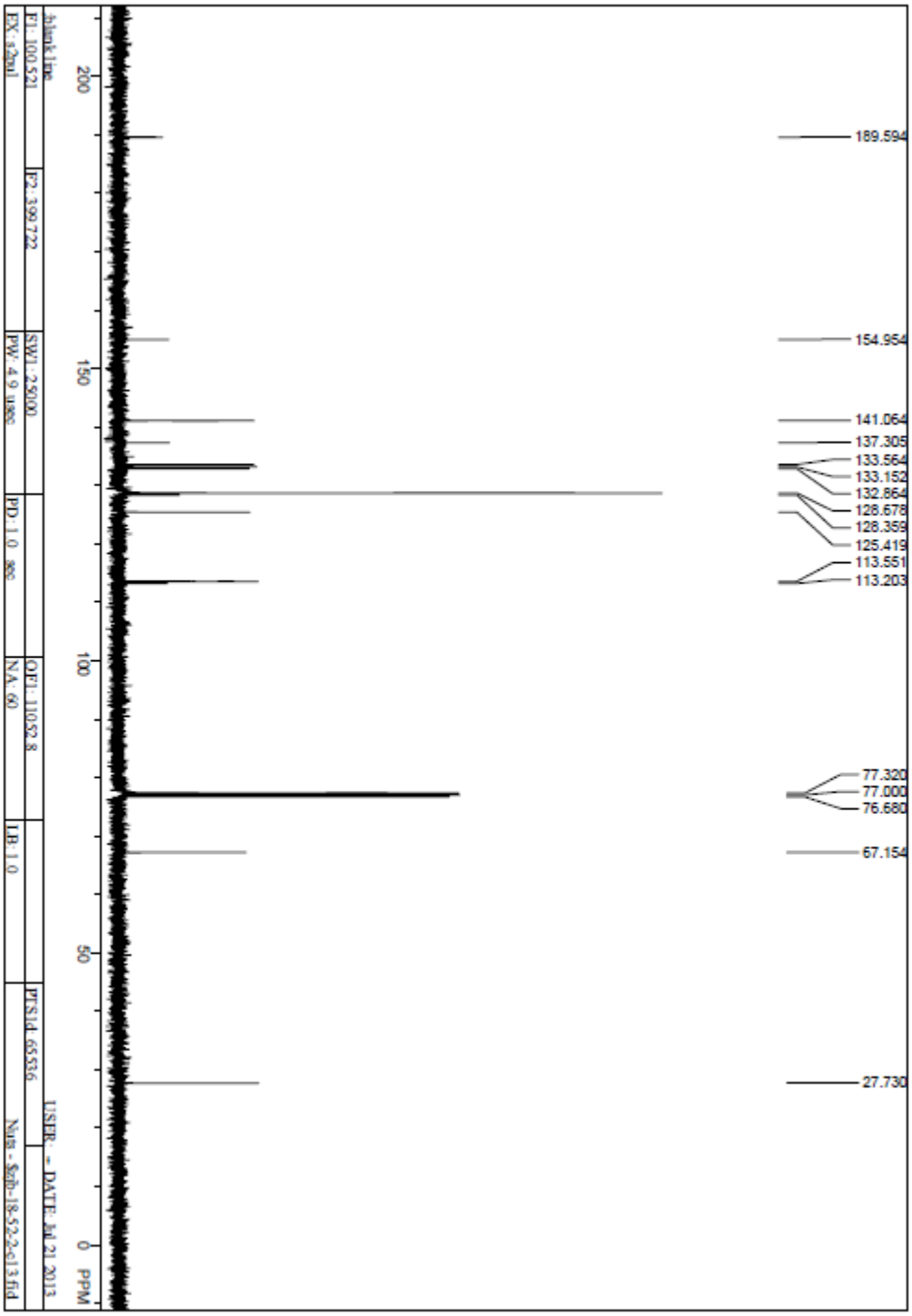
^{1}H NMR (400 M Hz in $CDCl_3$)

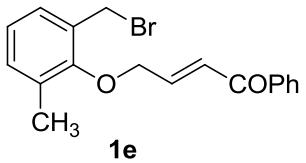




1d

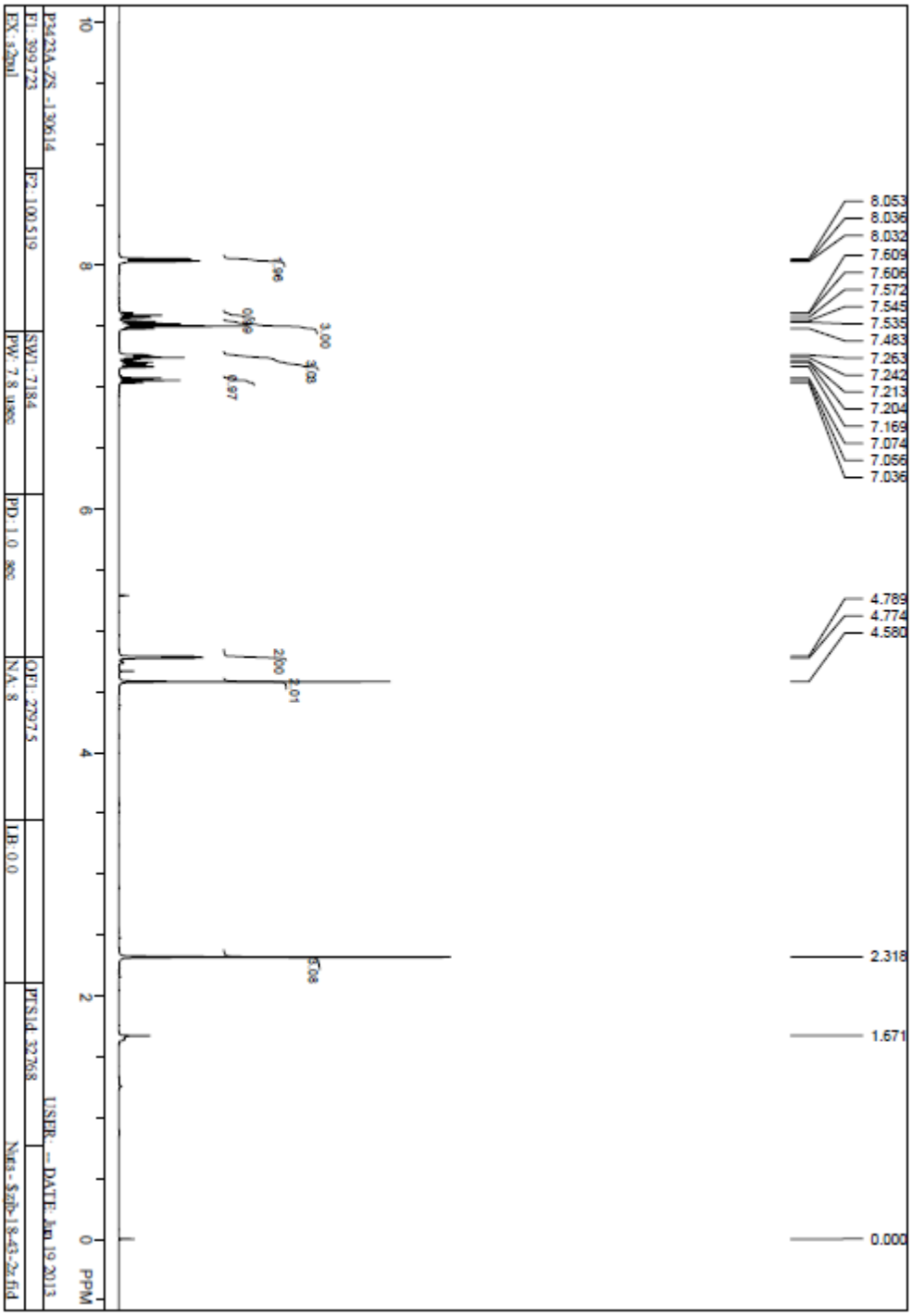
^{13}C NMR (100 M Hz in $CDCl_3$)

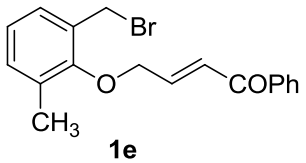




1e

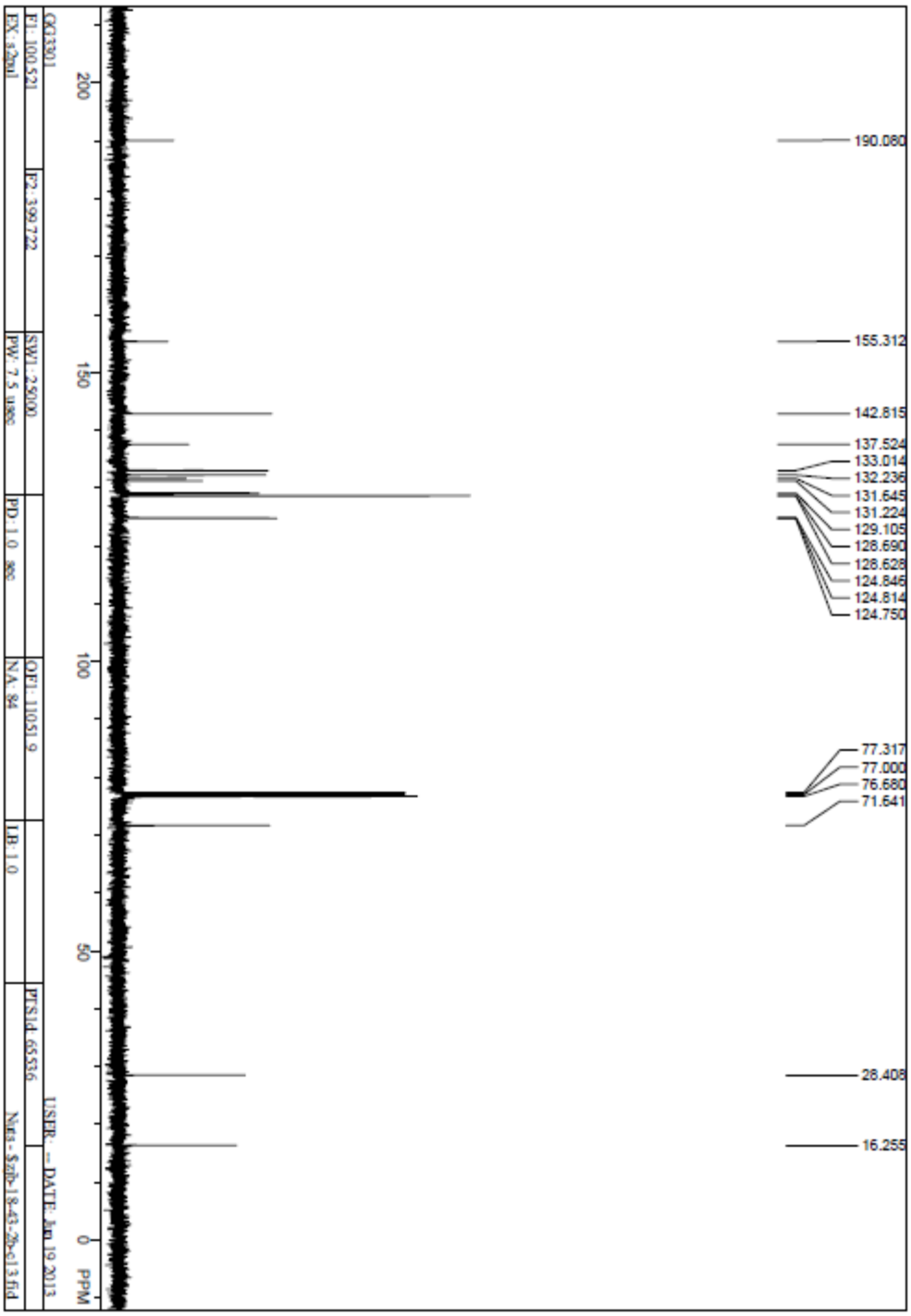
^{1}H NMR (400 M Hz in $CDCl_3$)

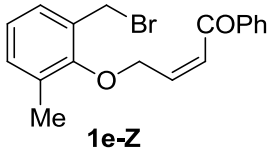




1e

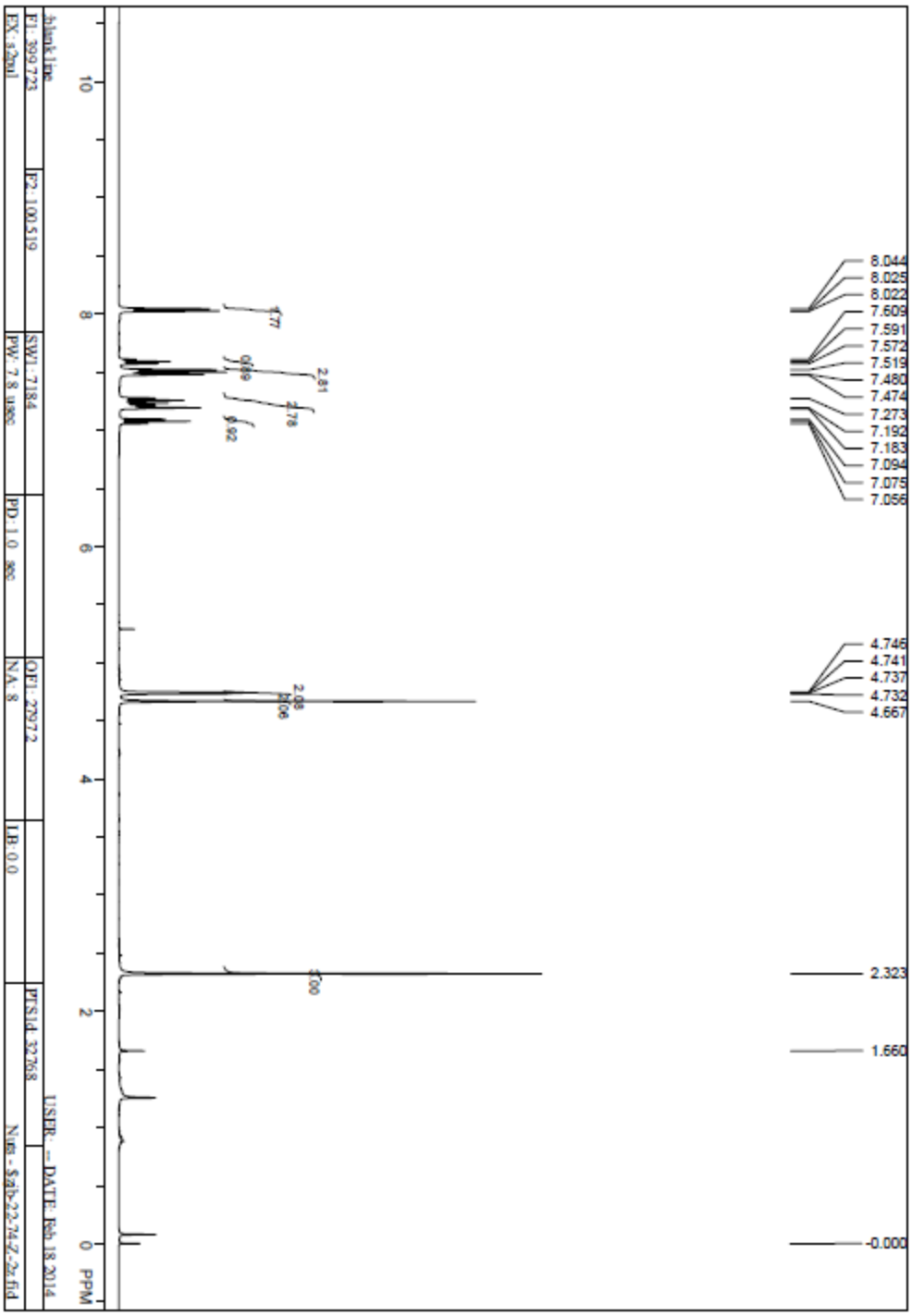
^{13}C NMR (100 M Hz in $CDCl_3$)

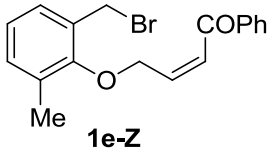




1e-Z

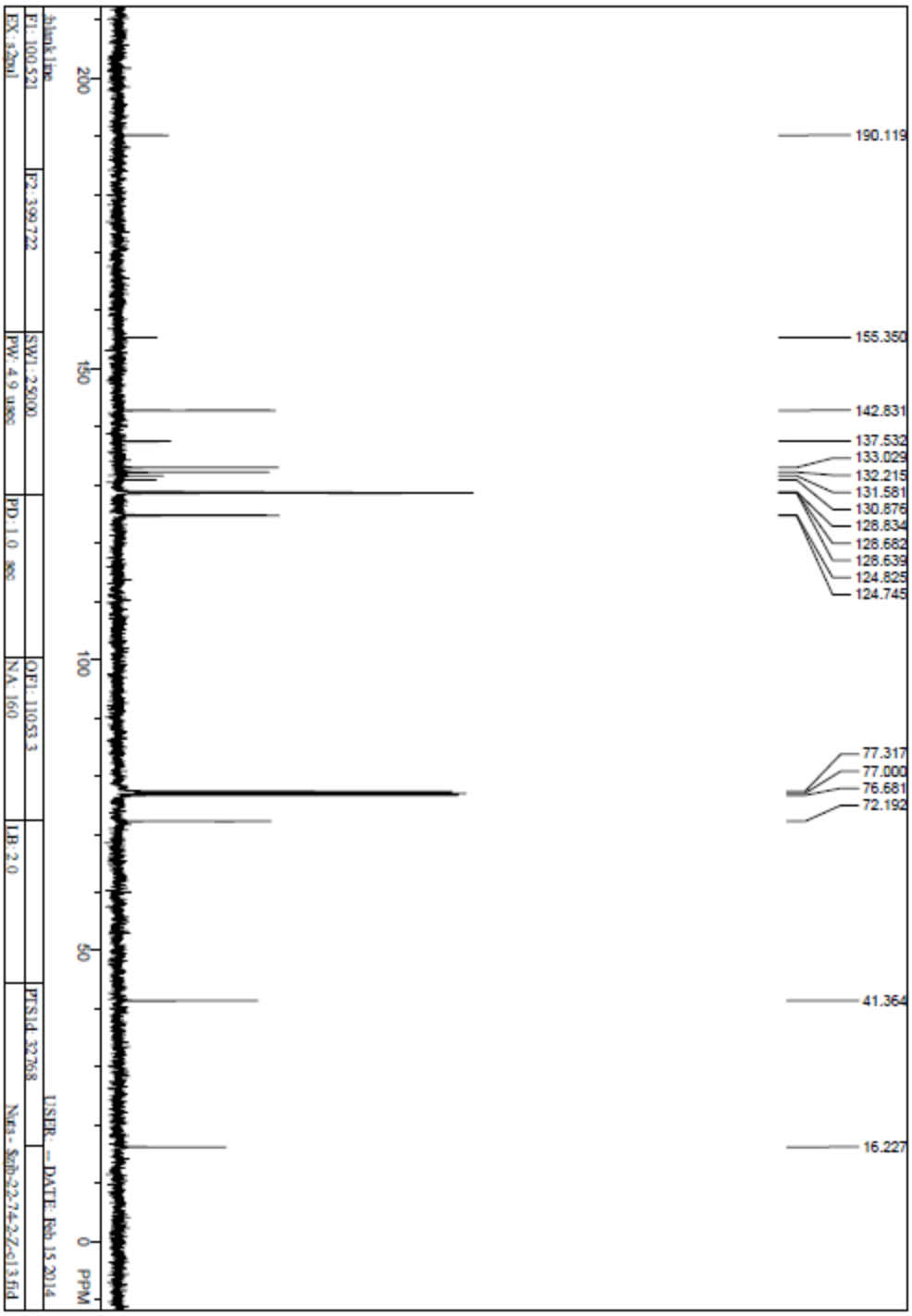
^{1}H NMR (400 M Hz in $CDCl_3$)

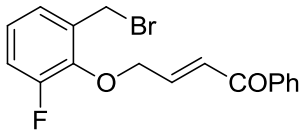




1e-Z

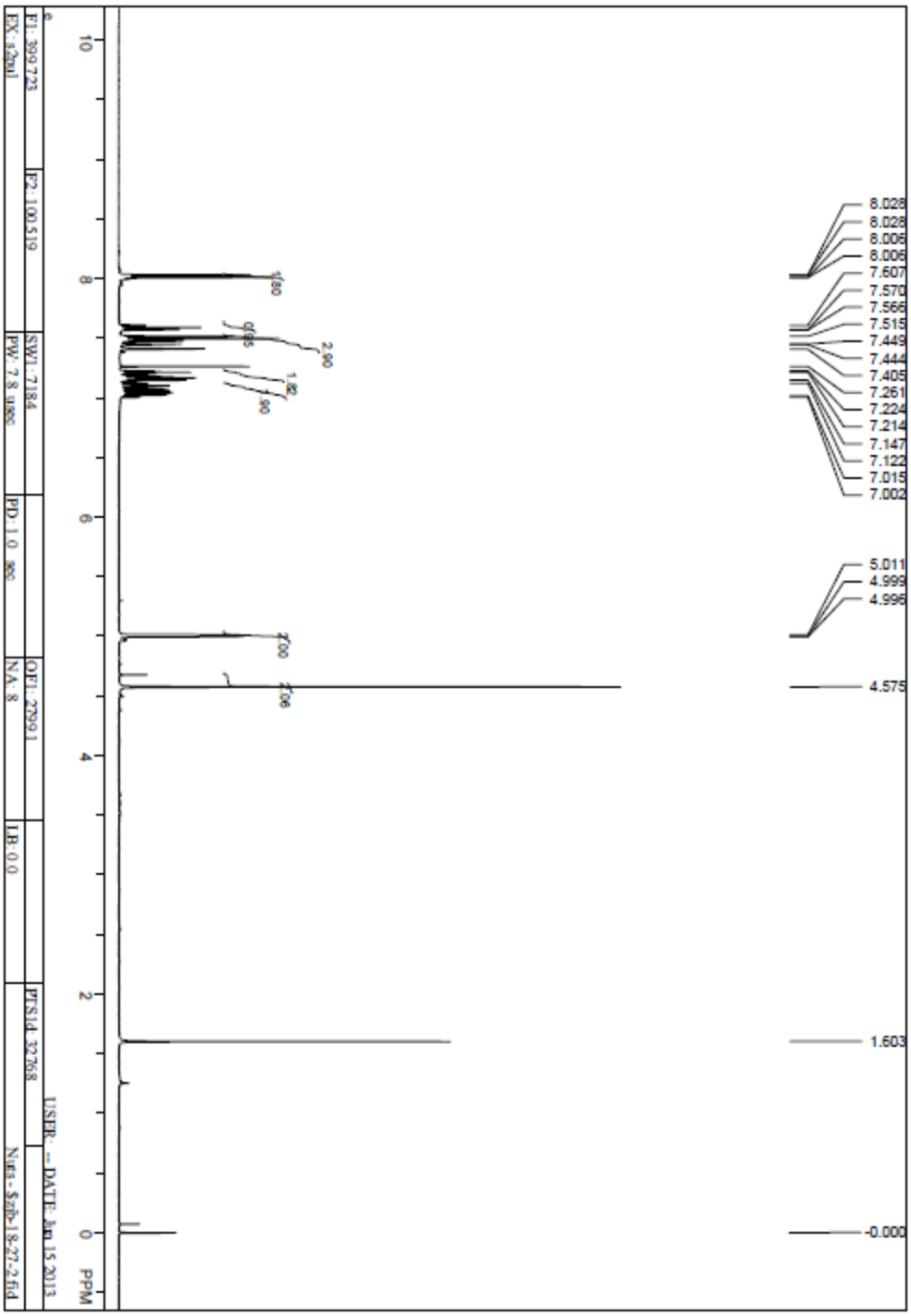
^{13}C NMR (100 M Hz in $CDCl_3$)

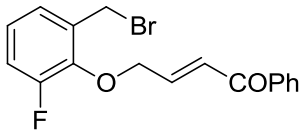




1f

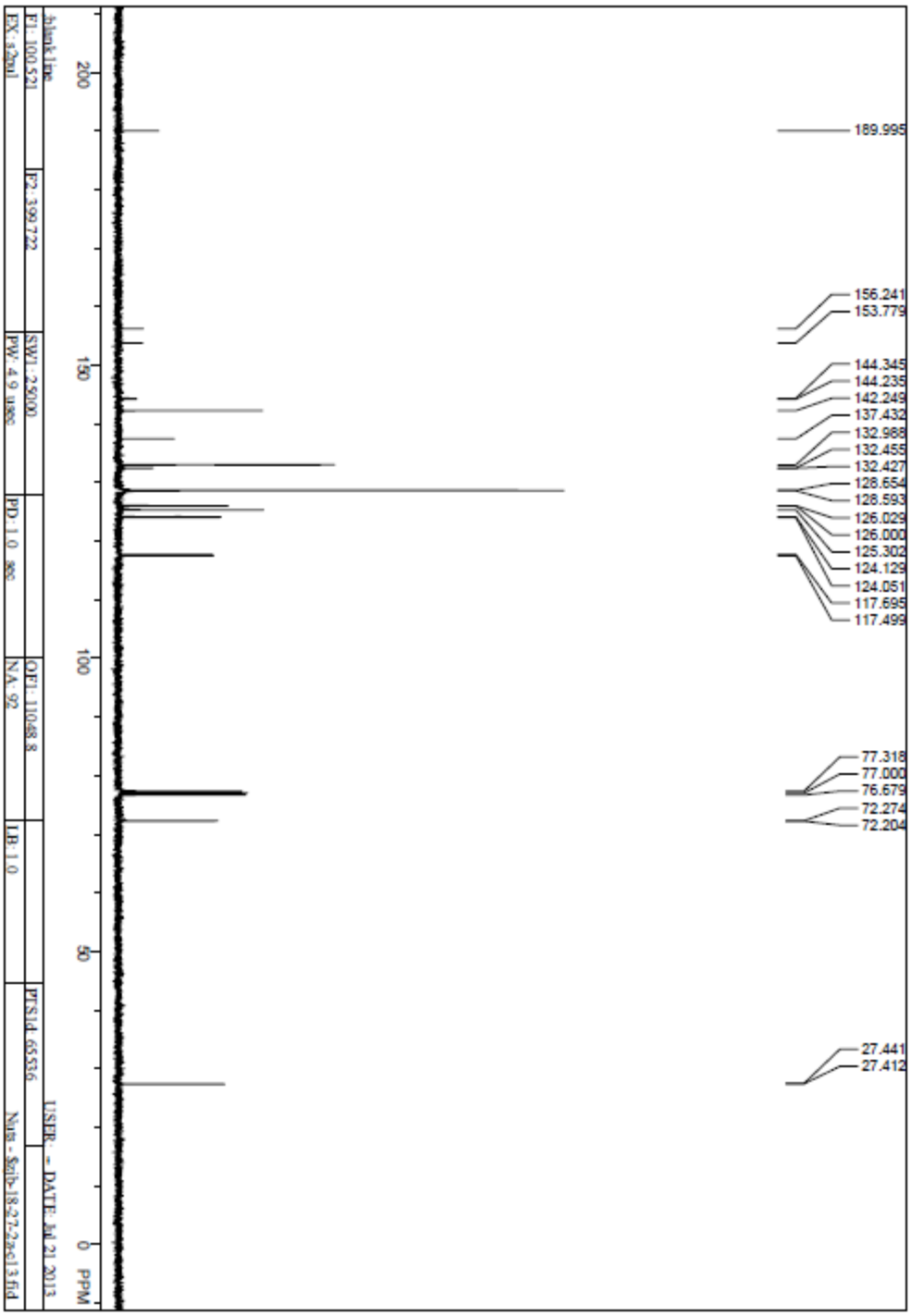
^{1}H NMR (400 M Hz in $CDCl_3$)

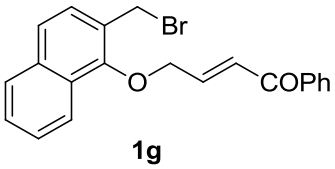




1f

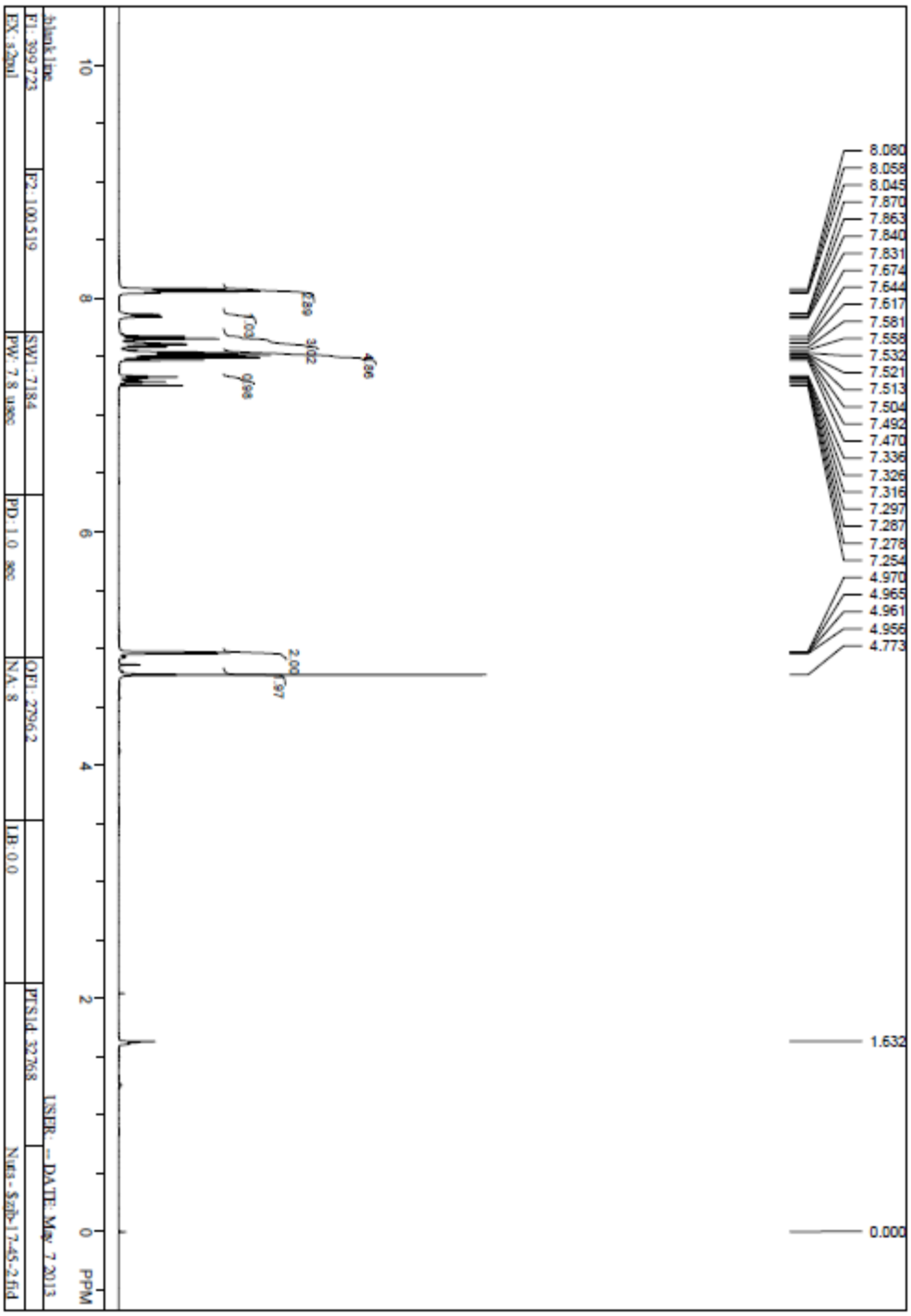
^{13}C NMR (100 M Hz in $CDCl_3$)

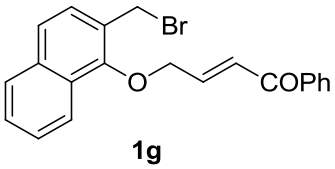




1g

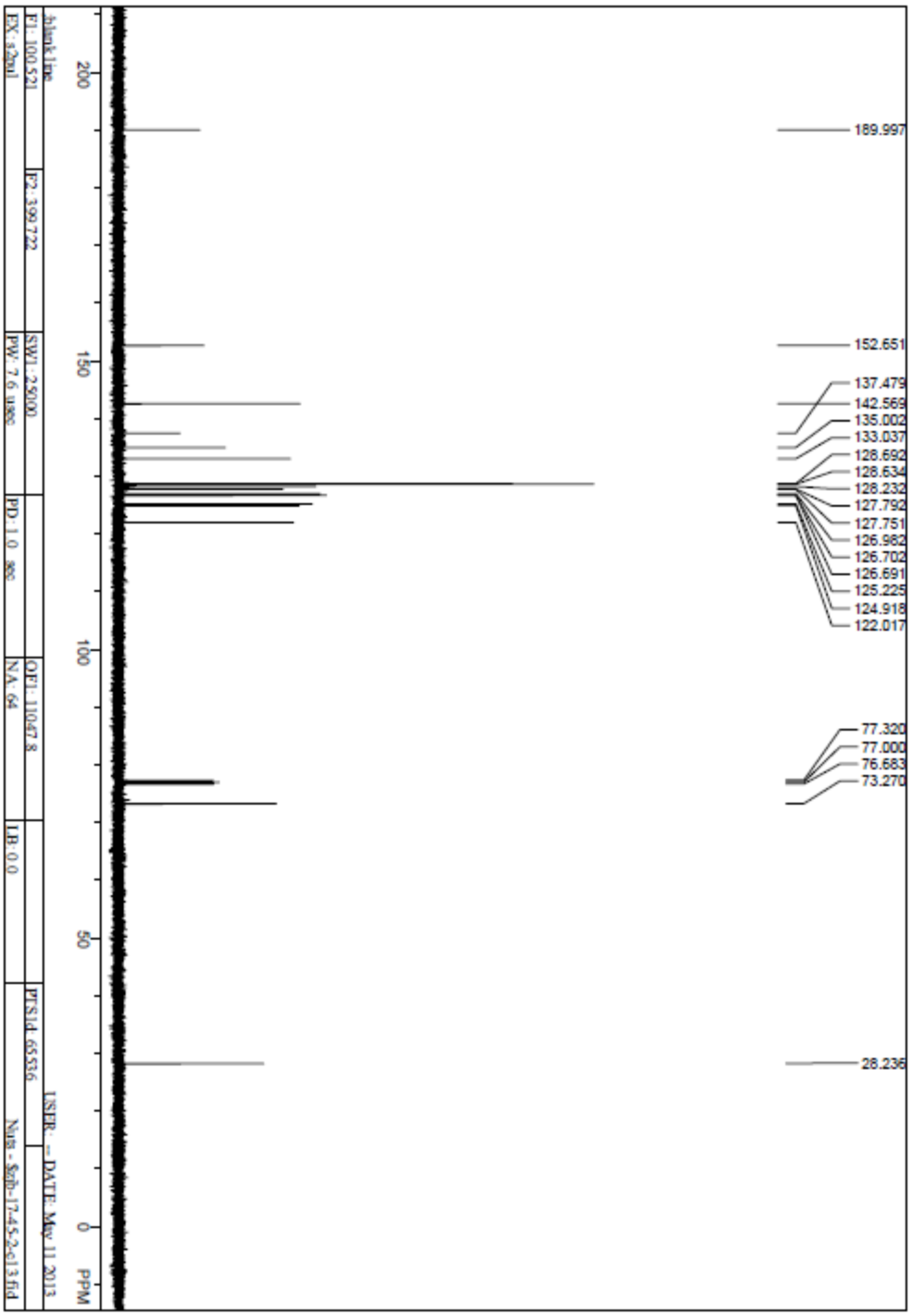
^{1}H NMR (400 M Hz in $CDCl_3$)

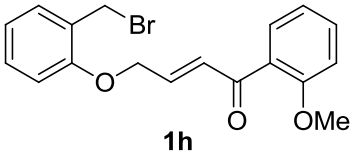




1g

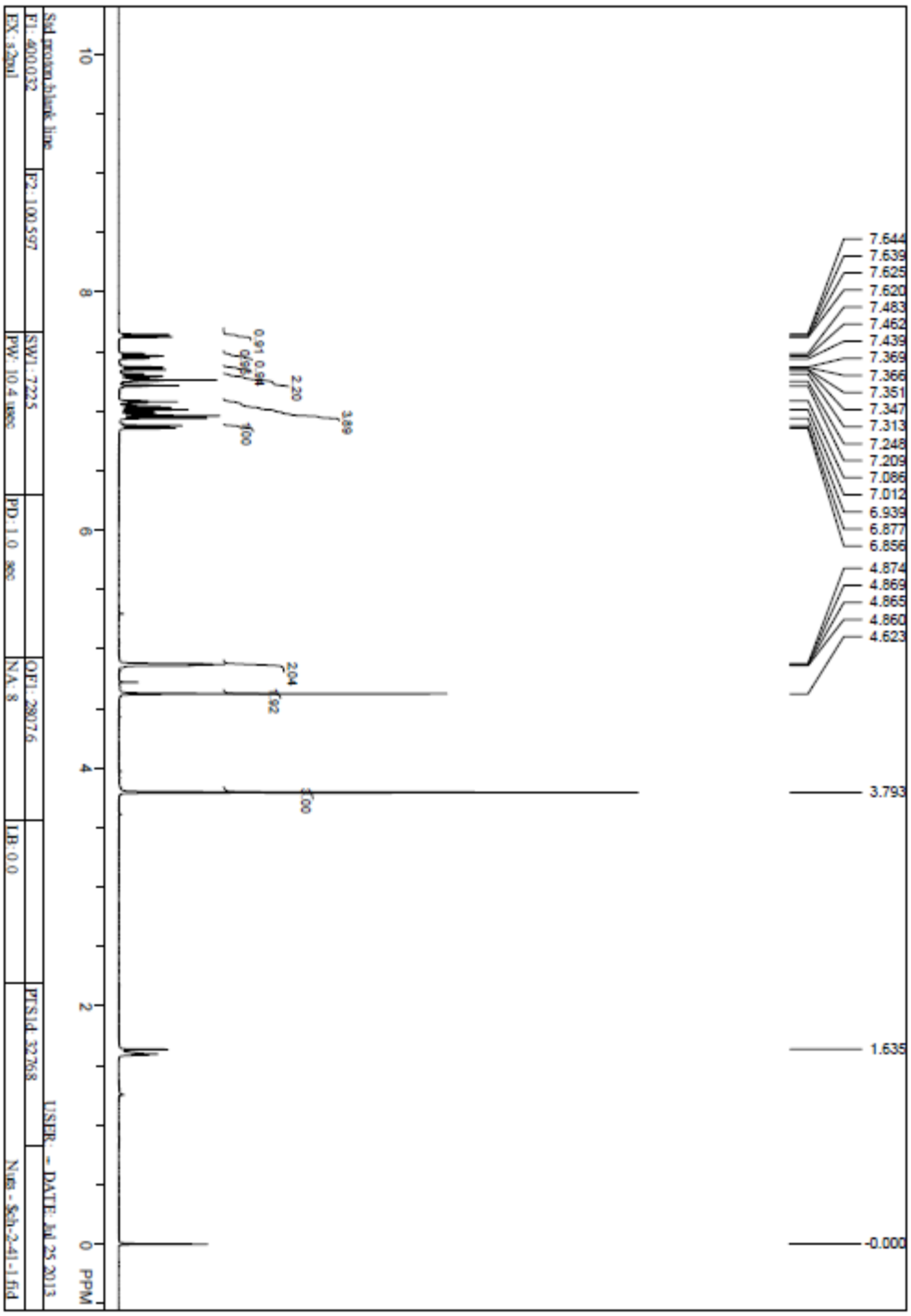
^{13}C NMR (100 M Hz in $CDCl_3$)

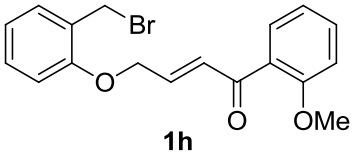




1h

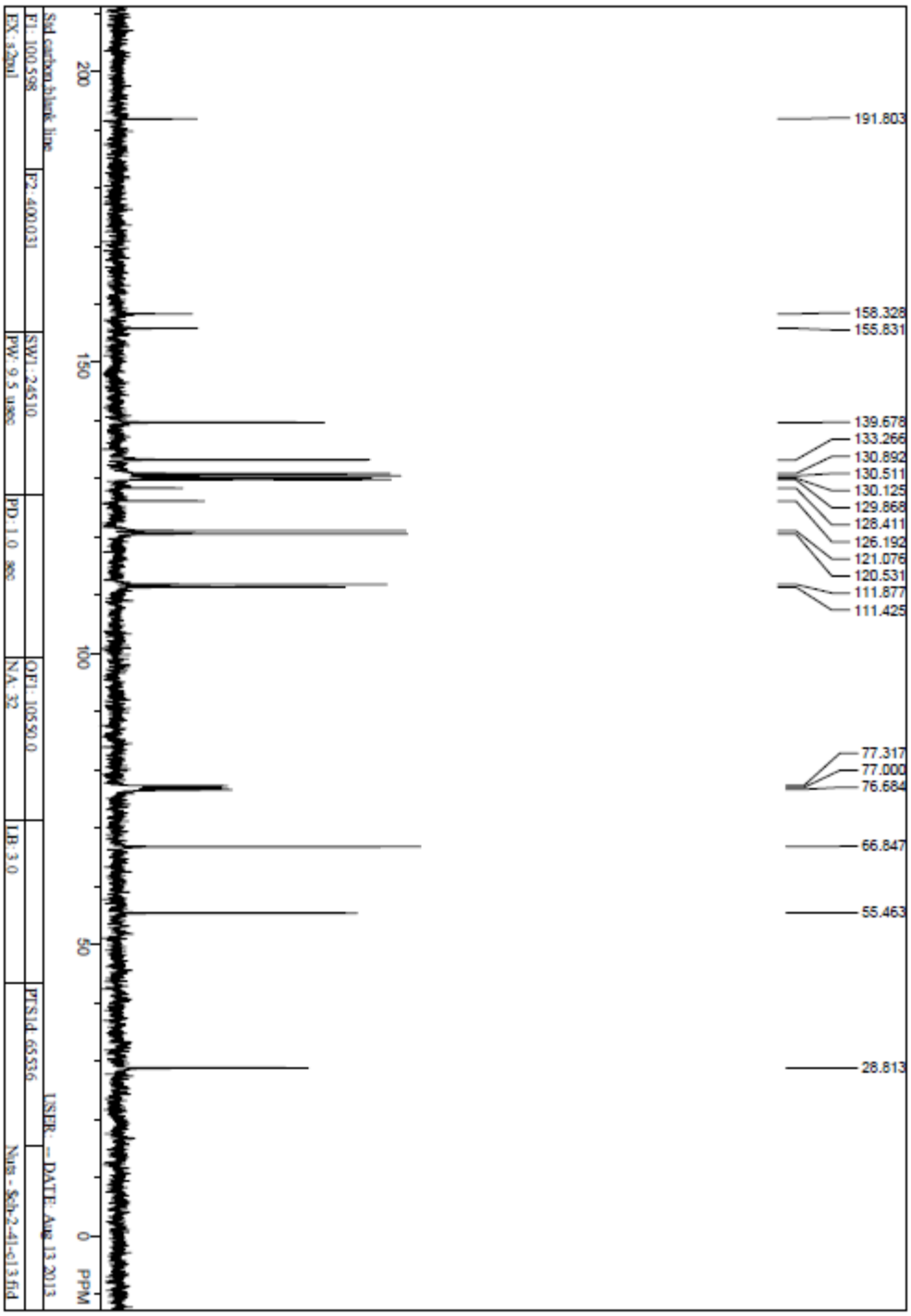
^{1}H NMR (400 M Hz in $CDCl_3$)

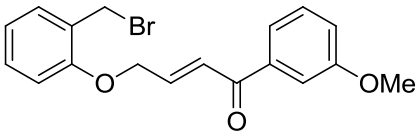




1h

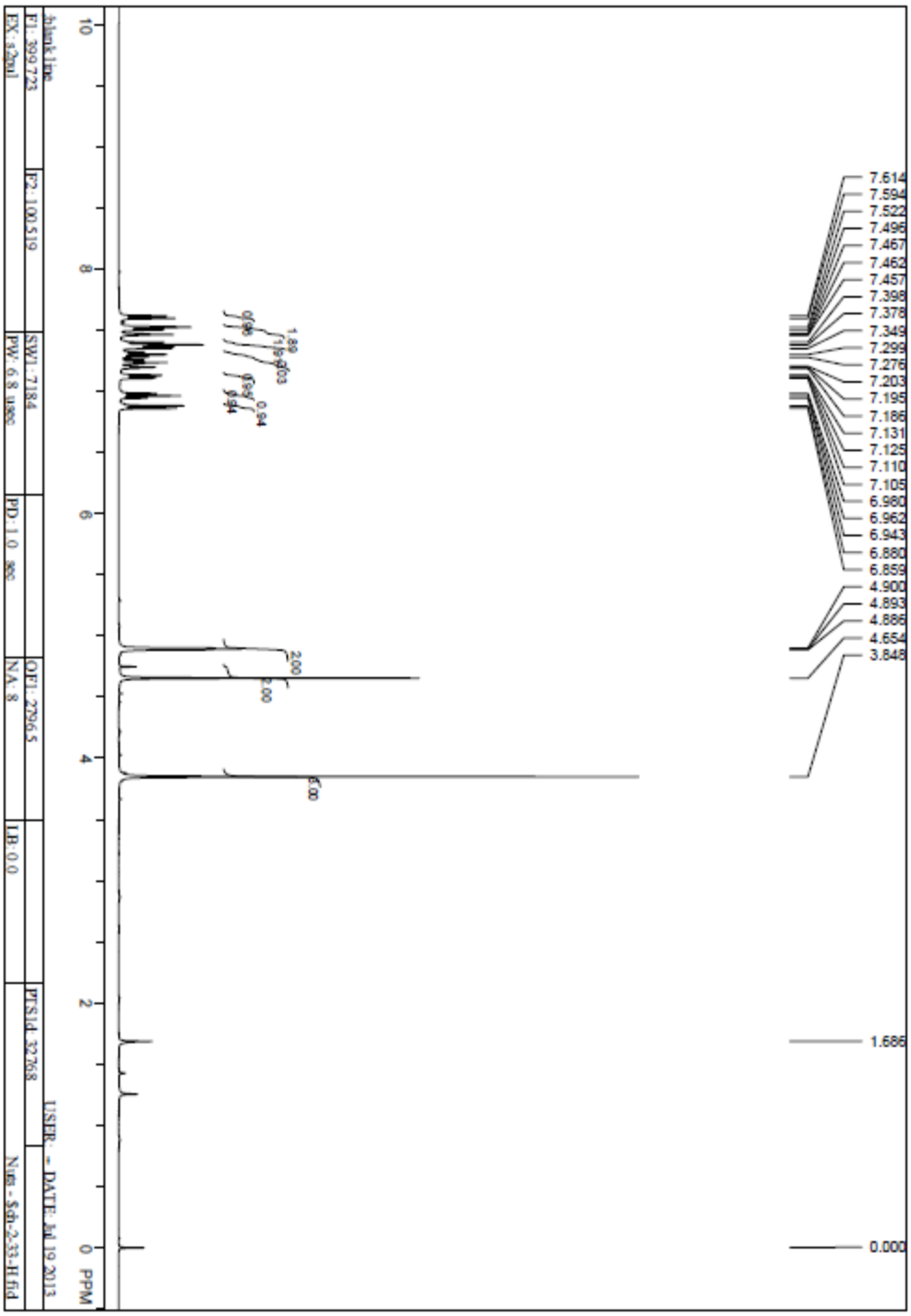
^{13}C NMR (100 M Hz in $CDCl_3$)

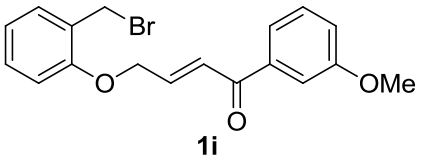




1i

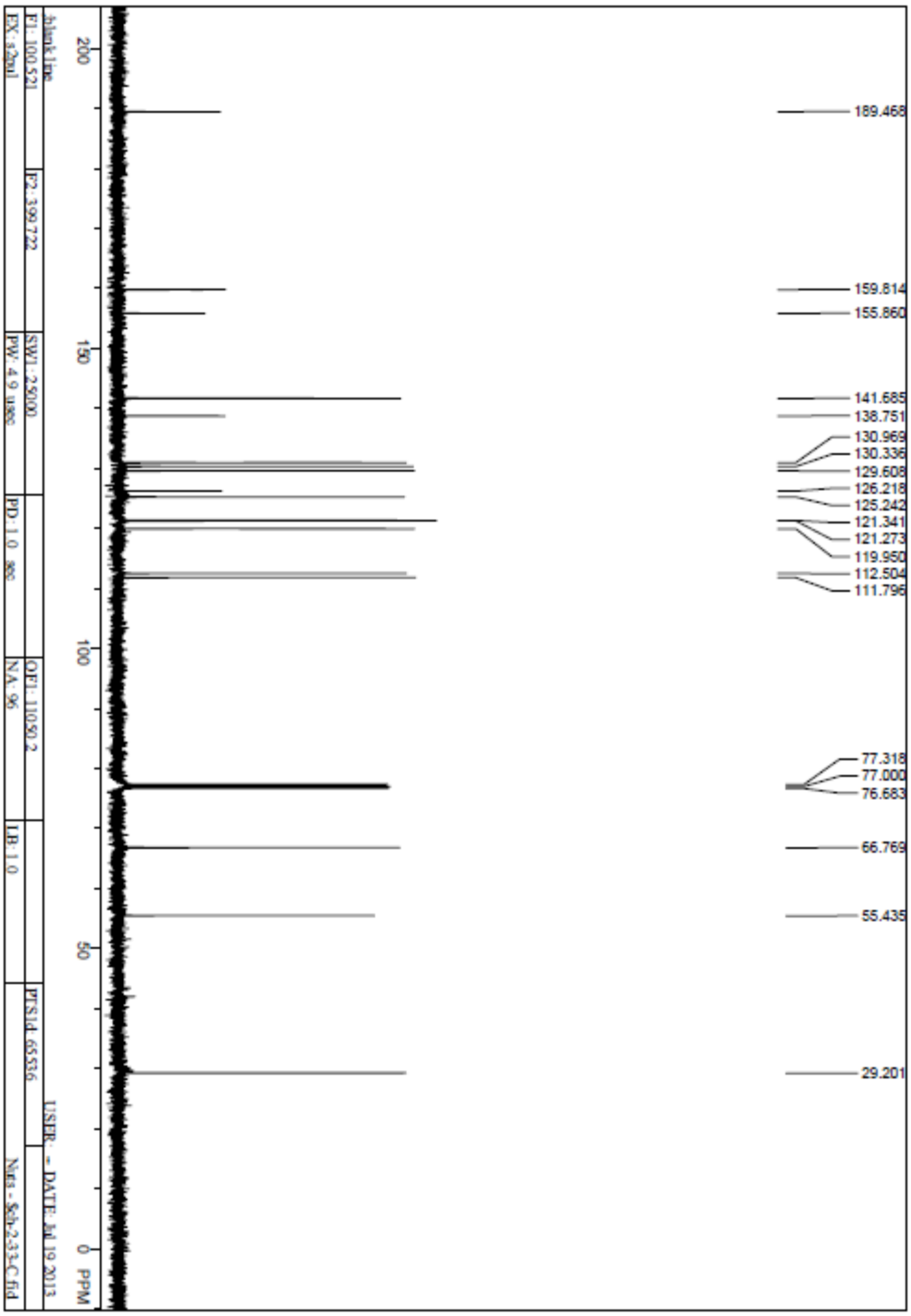
^{1}H NMR (400 M Hz in $CDCl_3$)

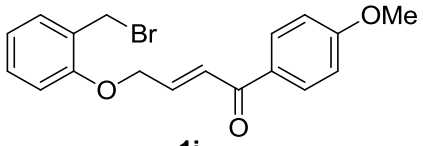




1i

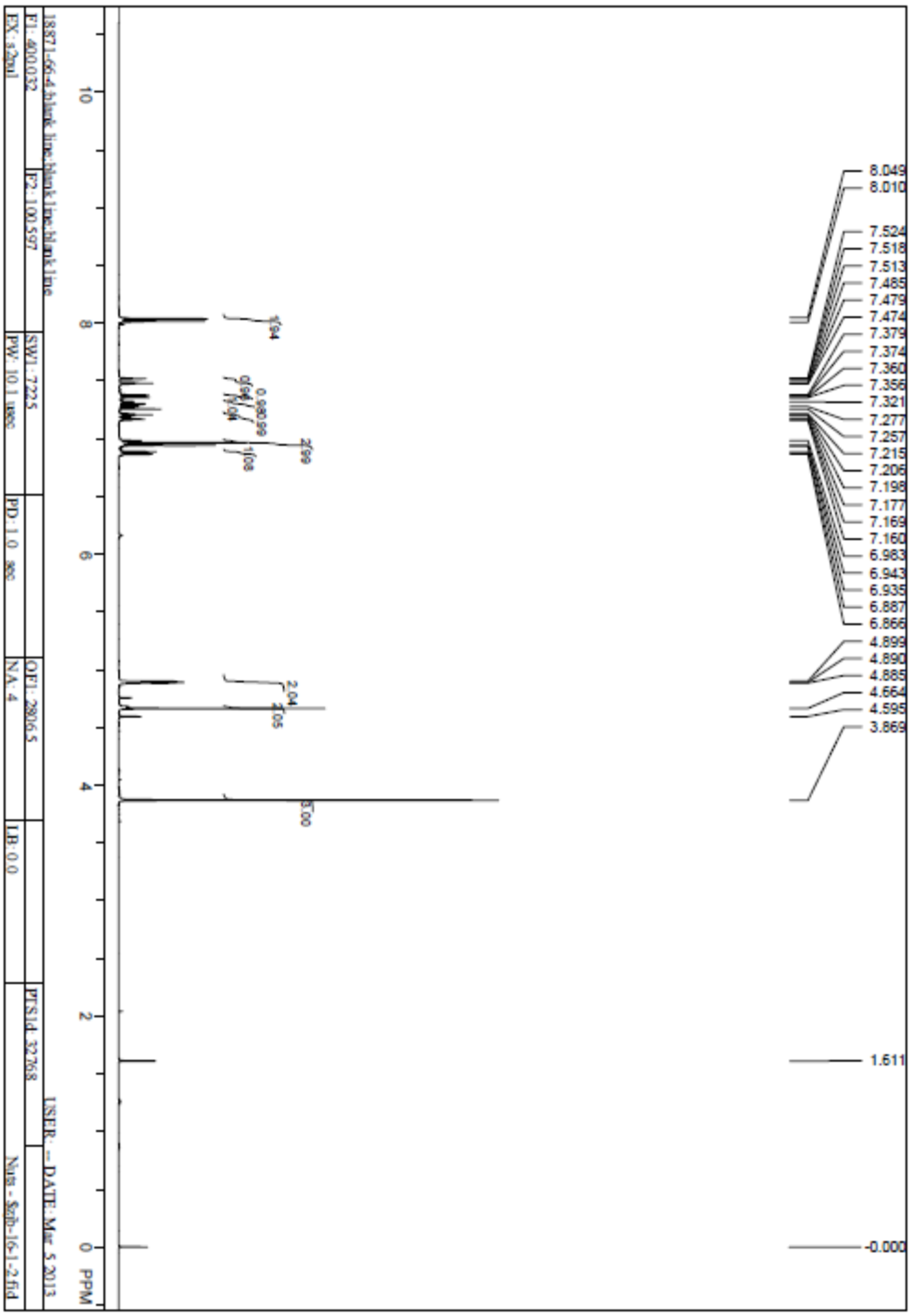
^{13}C NMR (100 M Hz in $CDCl_3$)

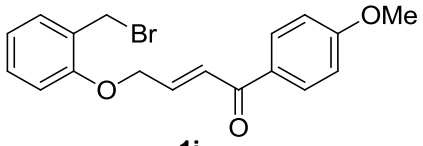




1j

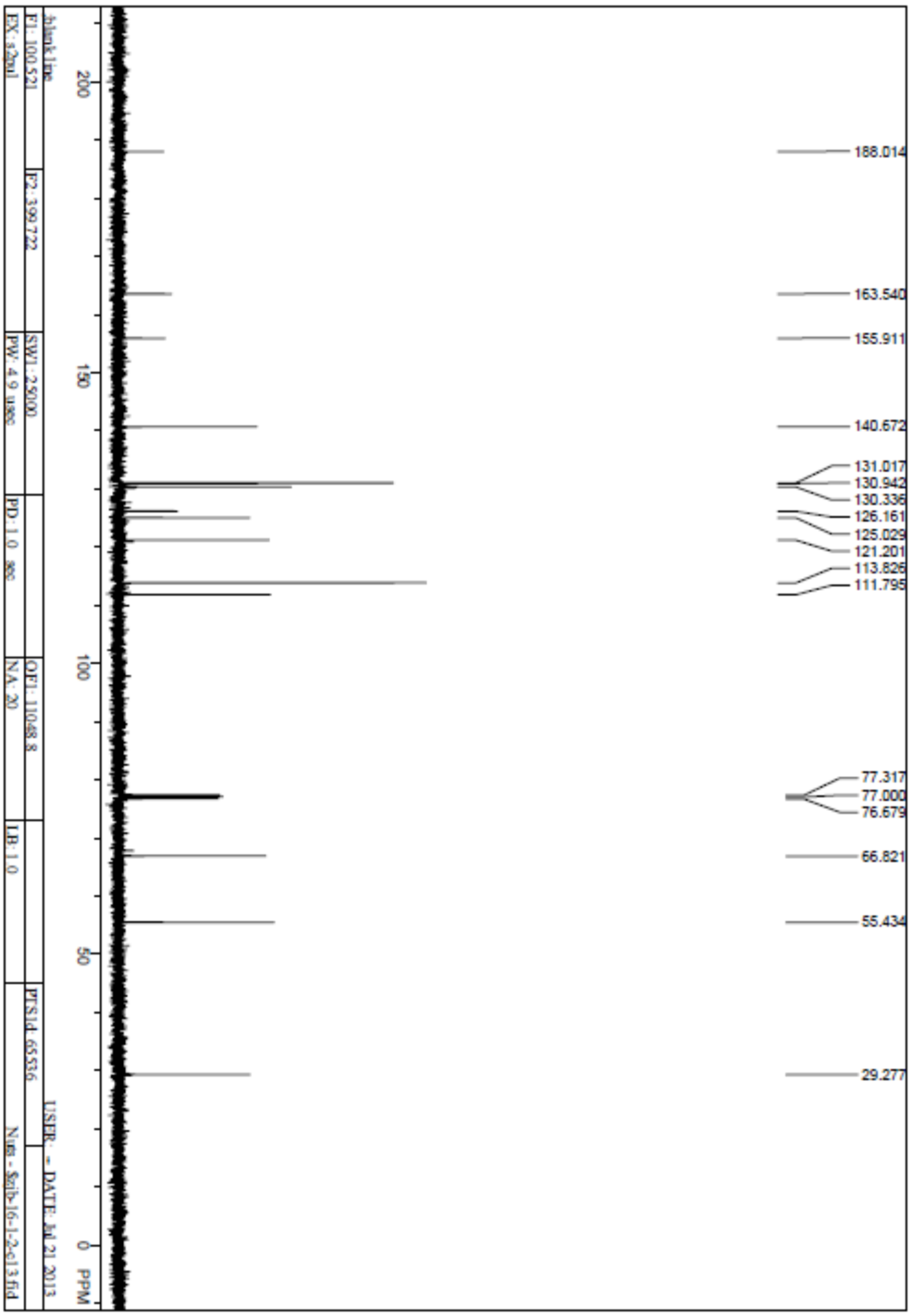
^{1}H NMR (400 M Hz in $CDCl_3$)

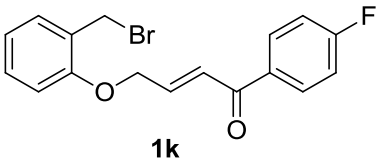




1j

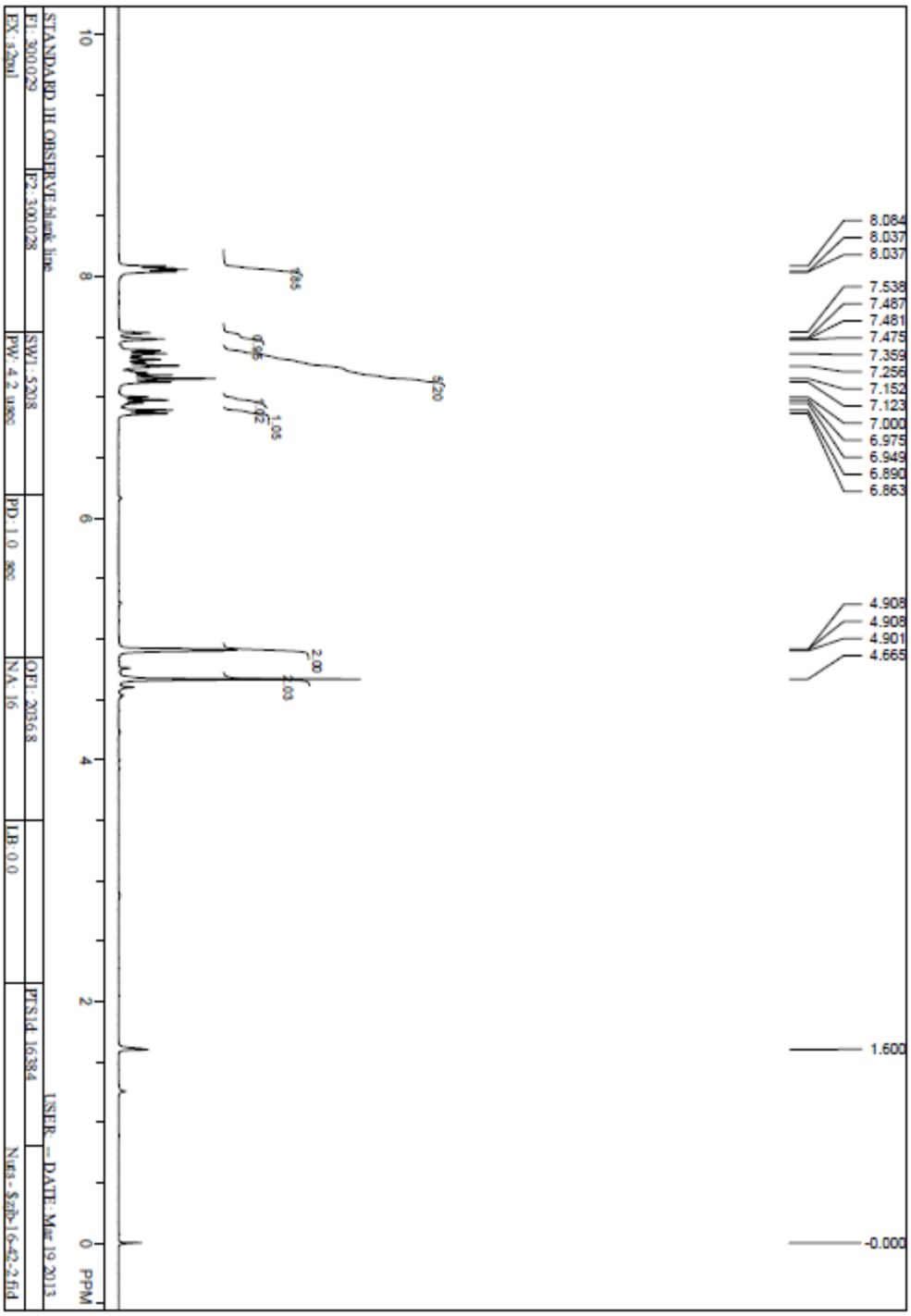
^{13}C NMR (100 M Hz in $CDCl_3$)

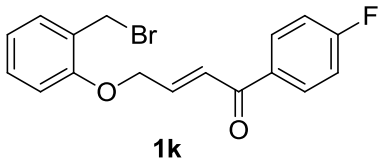




1k

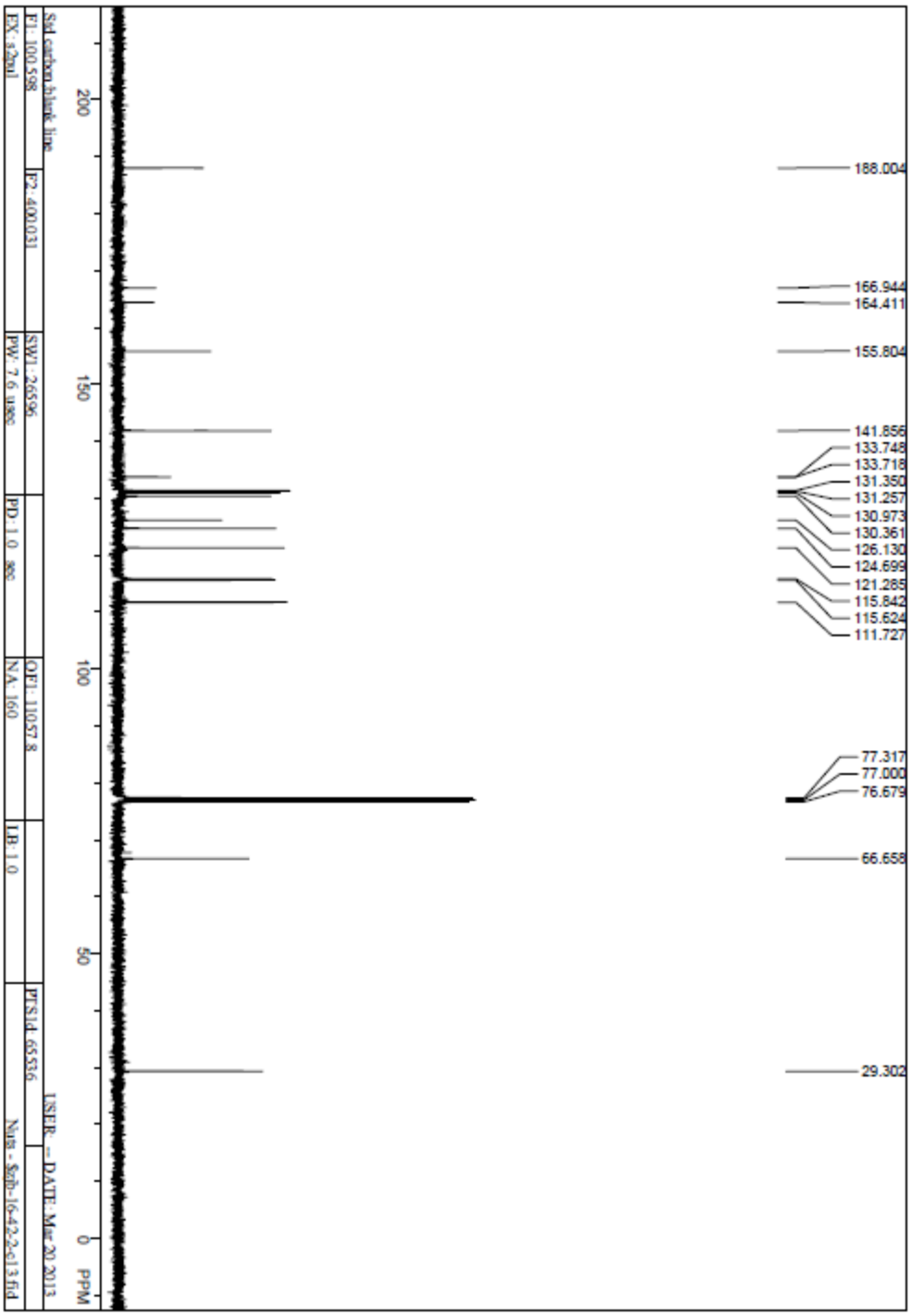
^{1}H NMR (300 M Hz in $CDCl_3$)

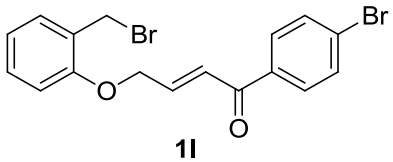




1k

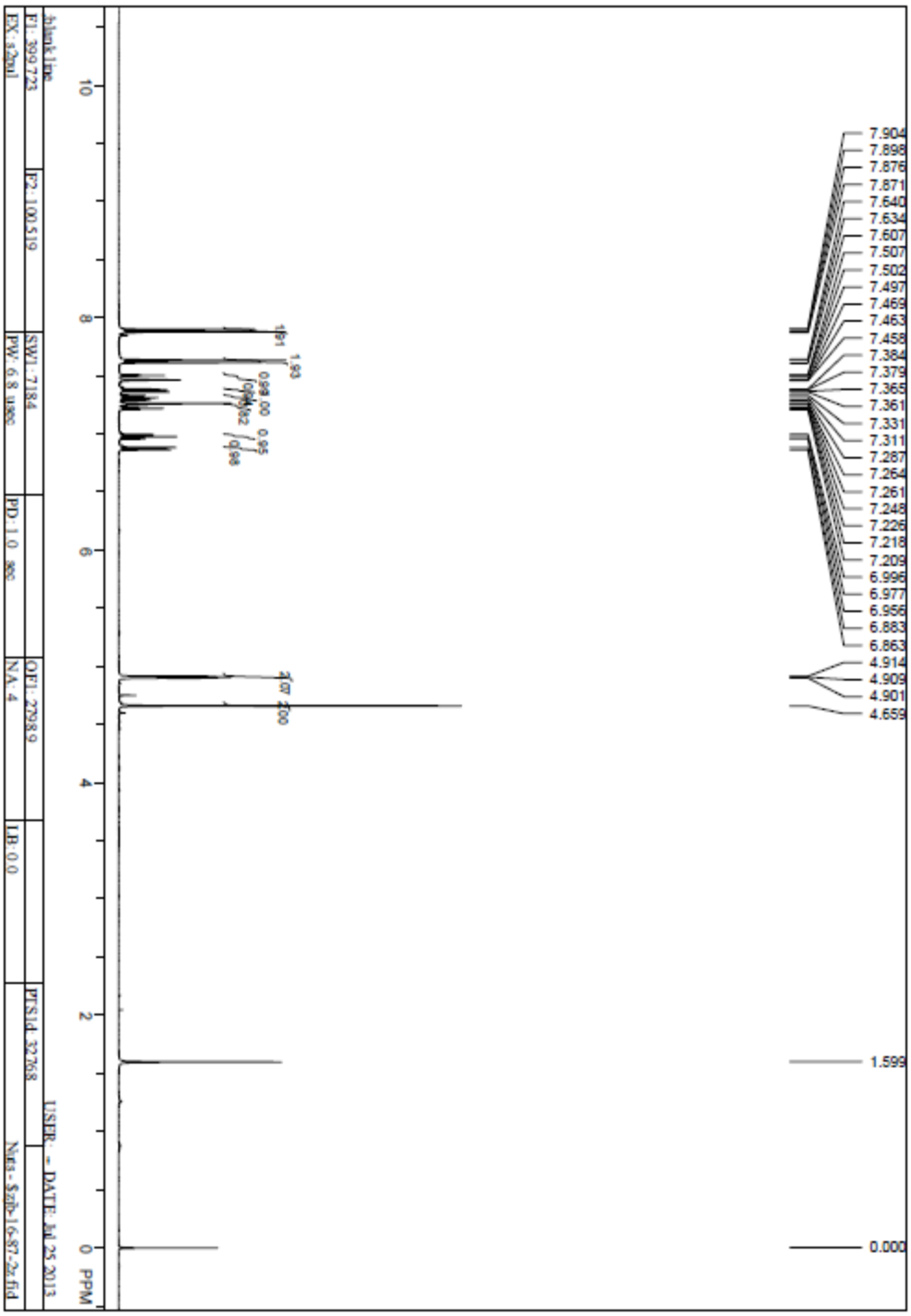
^{13}C NMR (100 M Hz in $CDCl_3$)

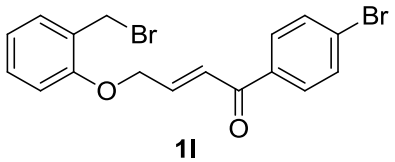




1l

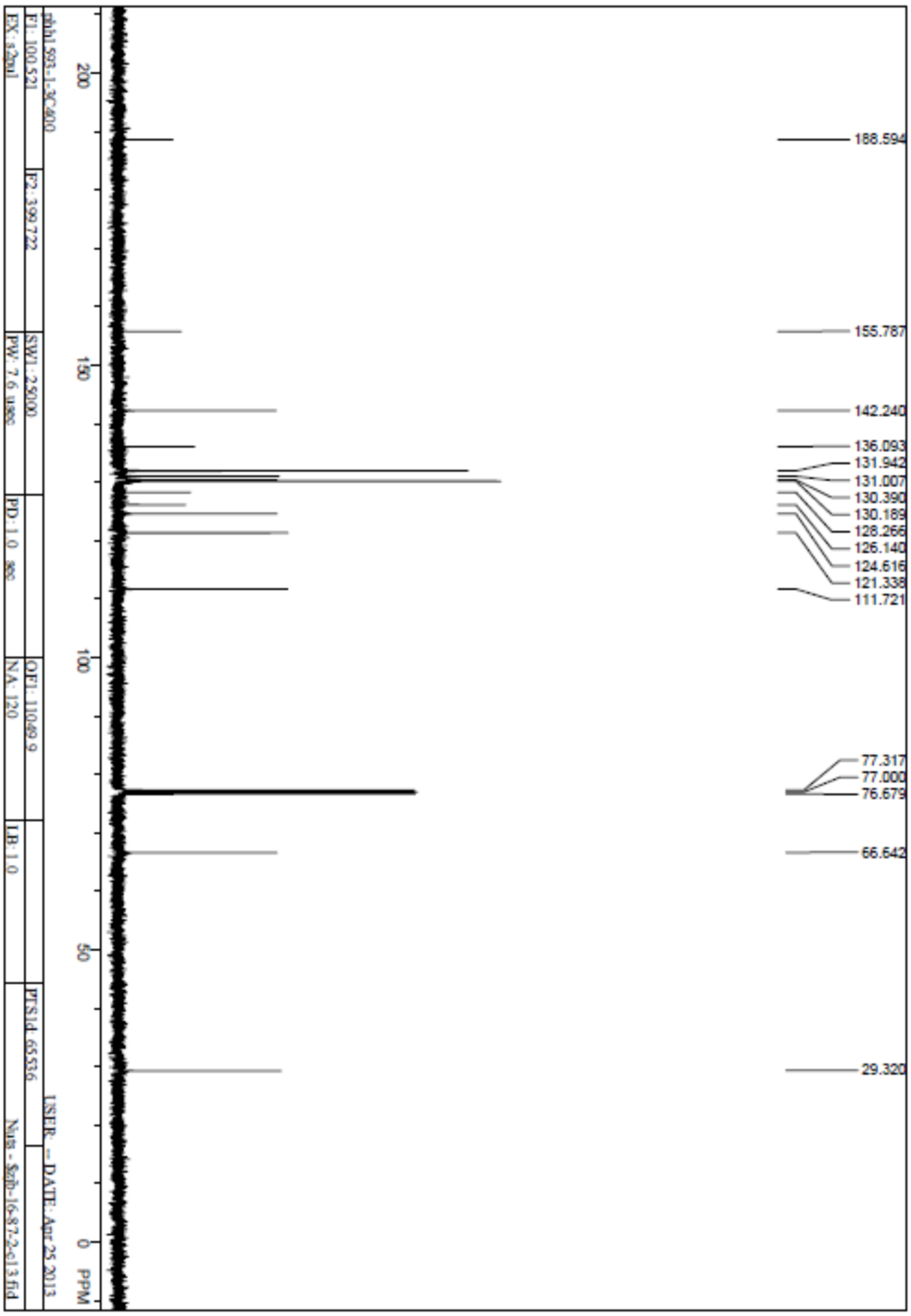
^{1}H NMR (400 M Hz in $CDCl_3$)

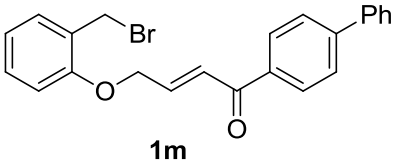




1l

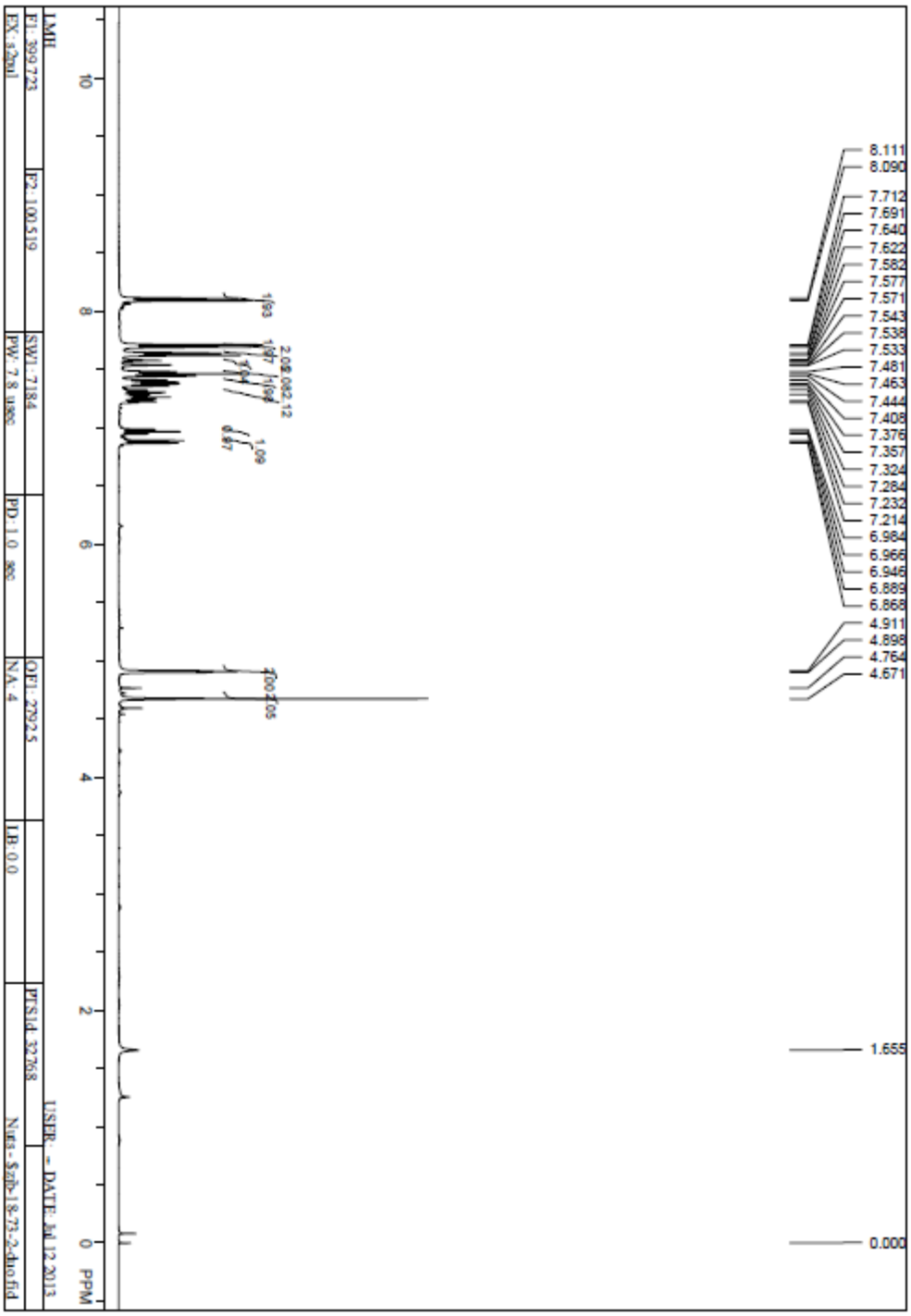
^{13}C NMR (100 M Hz in $CDCl_3$)

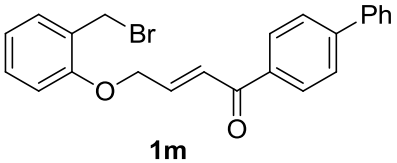




1m

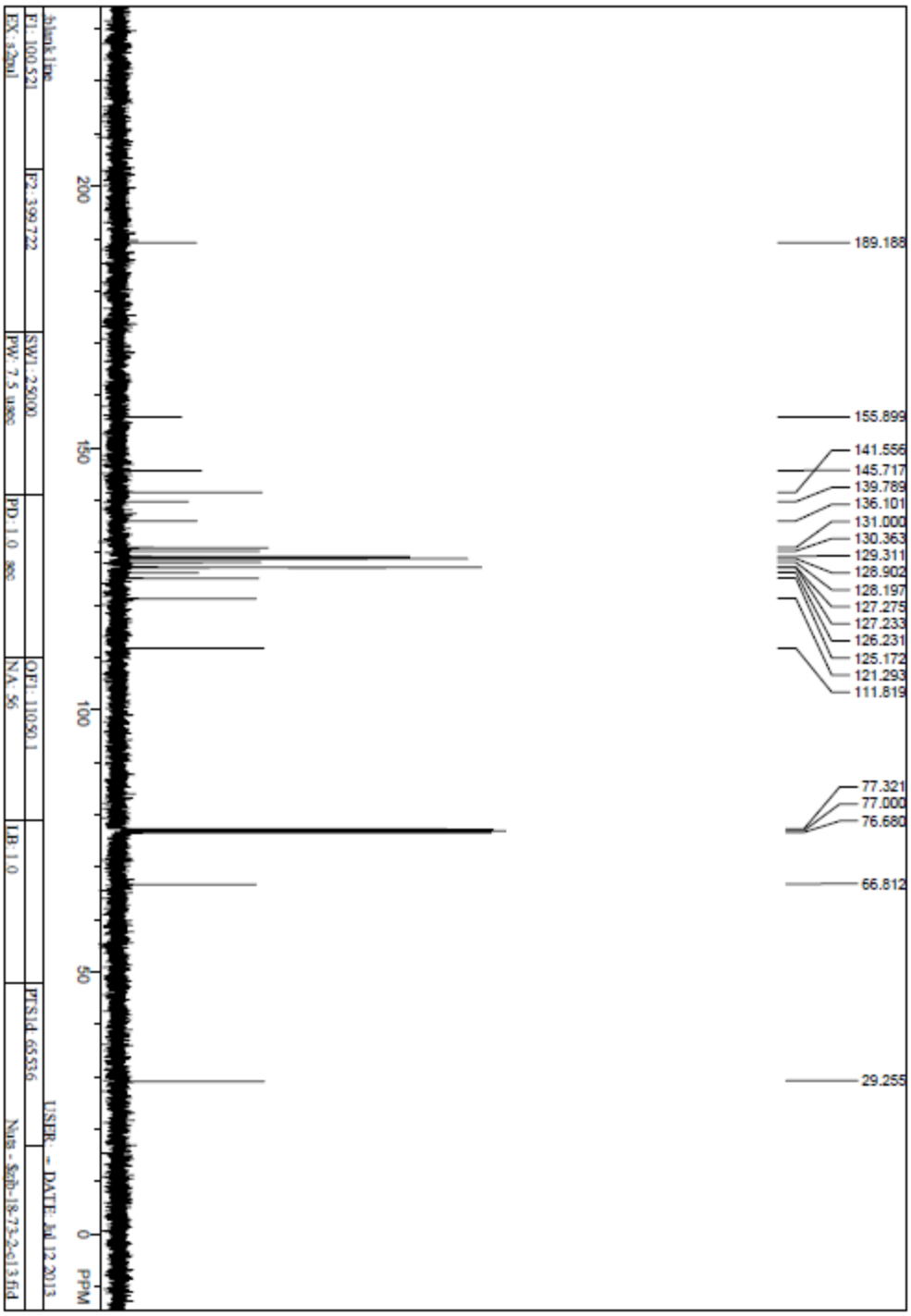
^{1}H NMR (400 M Hz in $CDCl_3$)

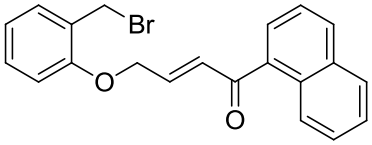




1m

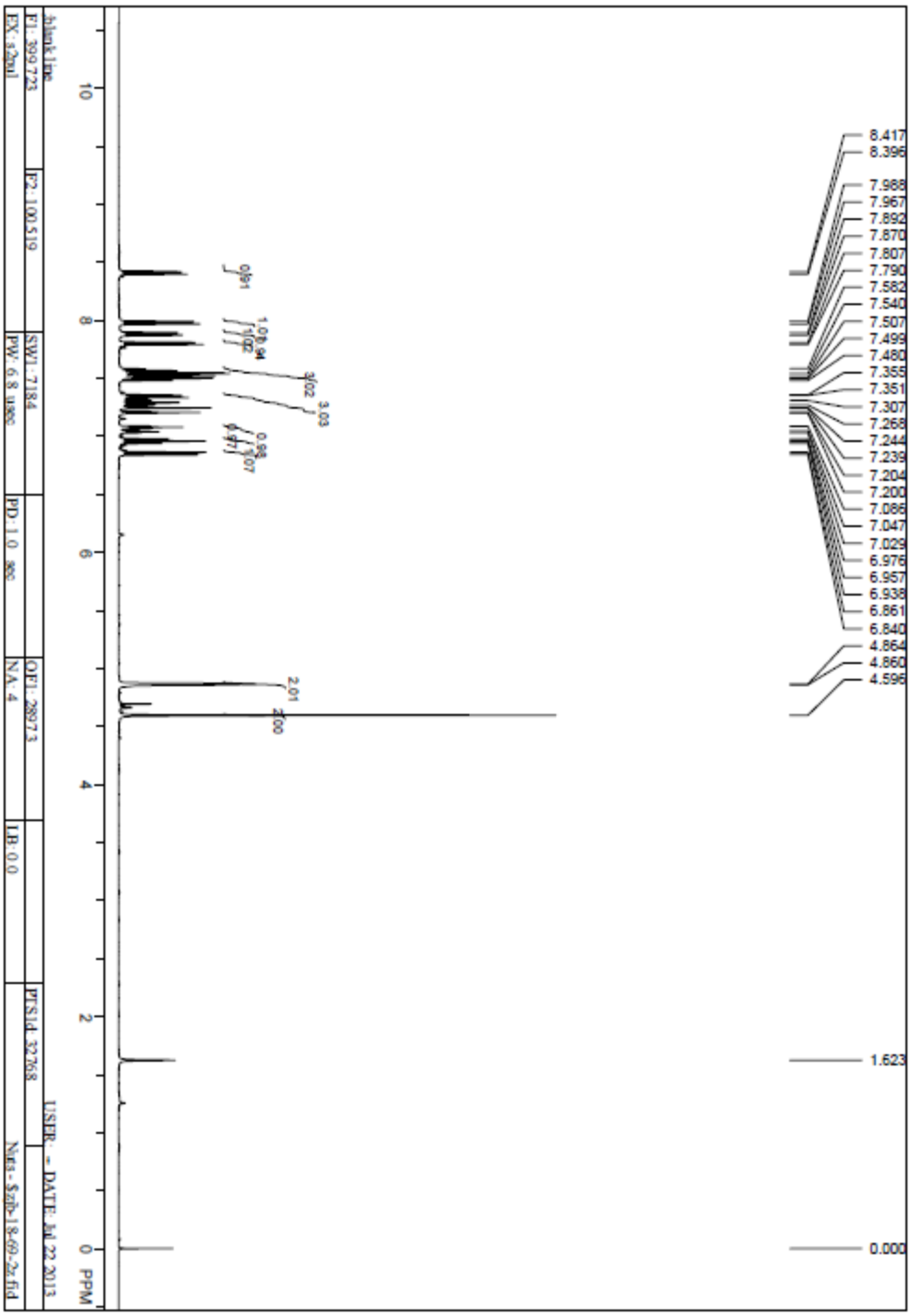
^{13}C NMR (100 M Hz in $CDCl_3$)

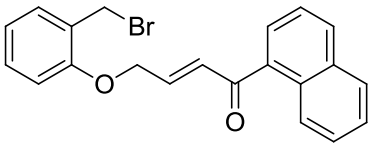




1n

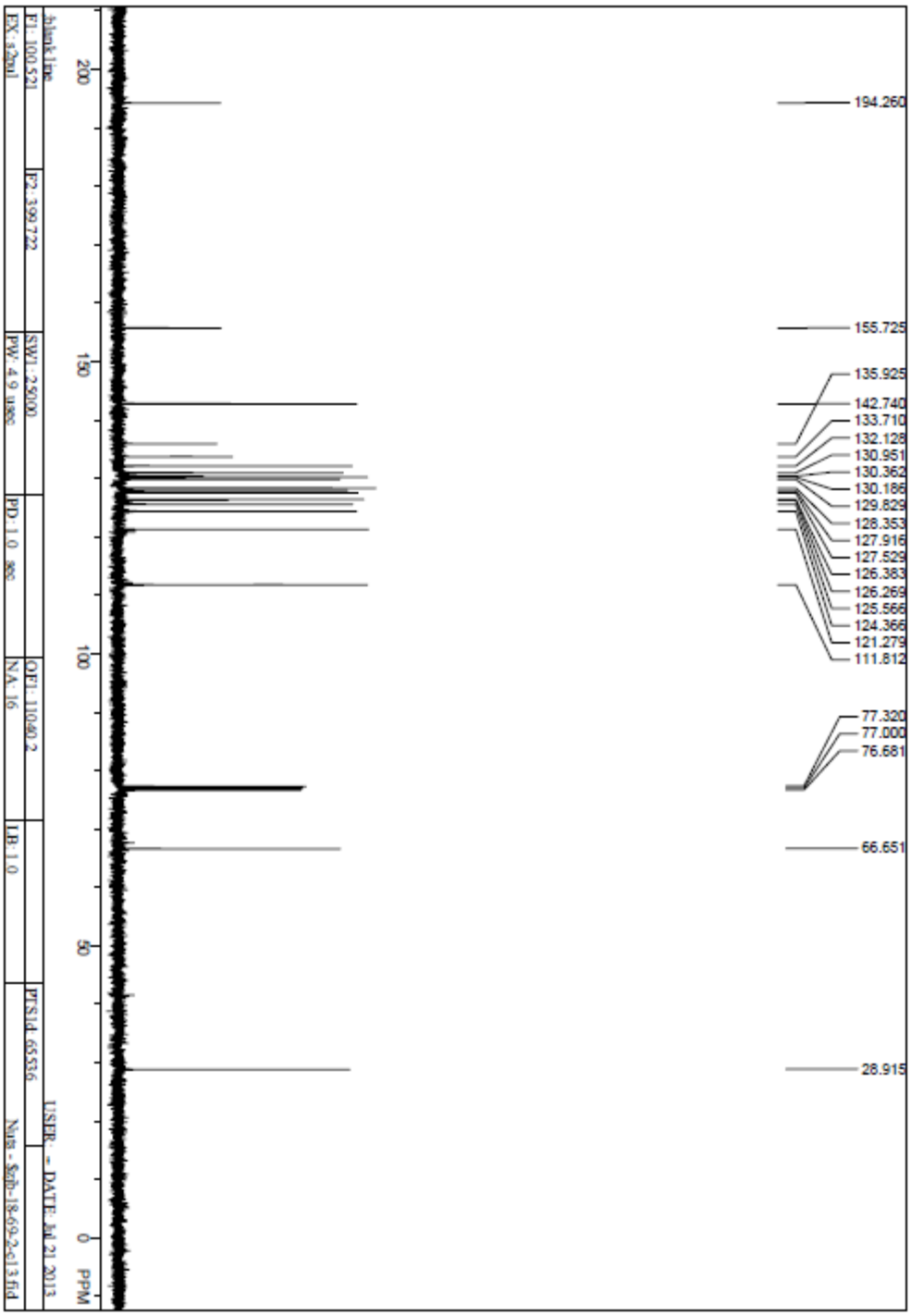
^{1}H NMR (400 M Hz in $CDCl_3$)

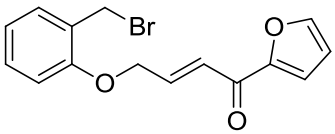




1n

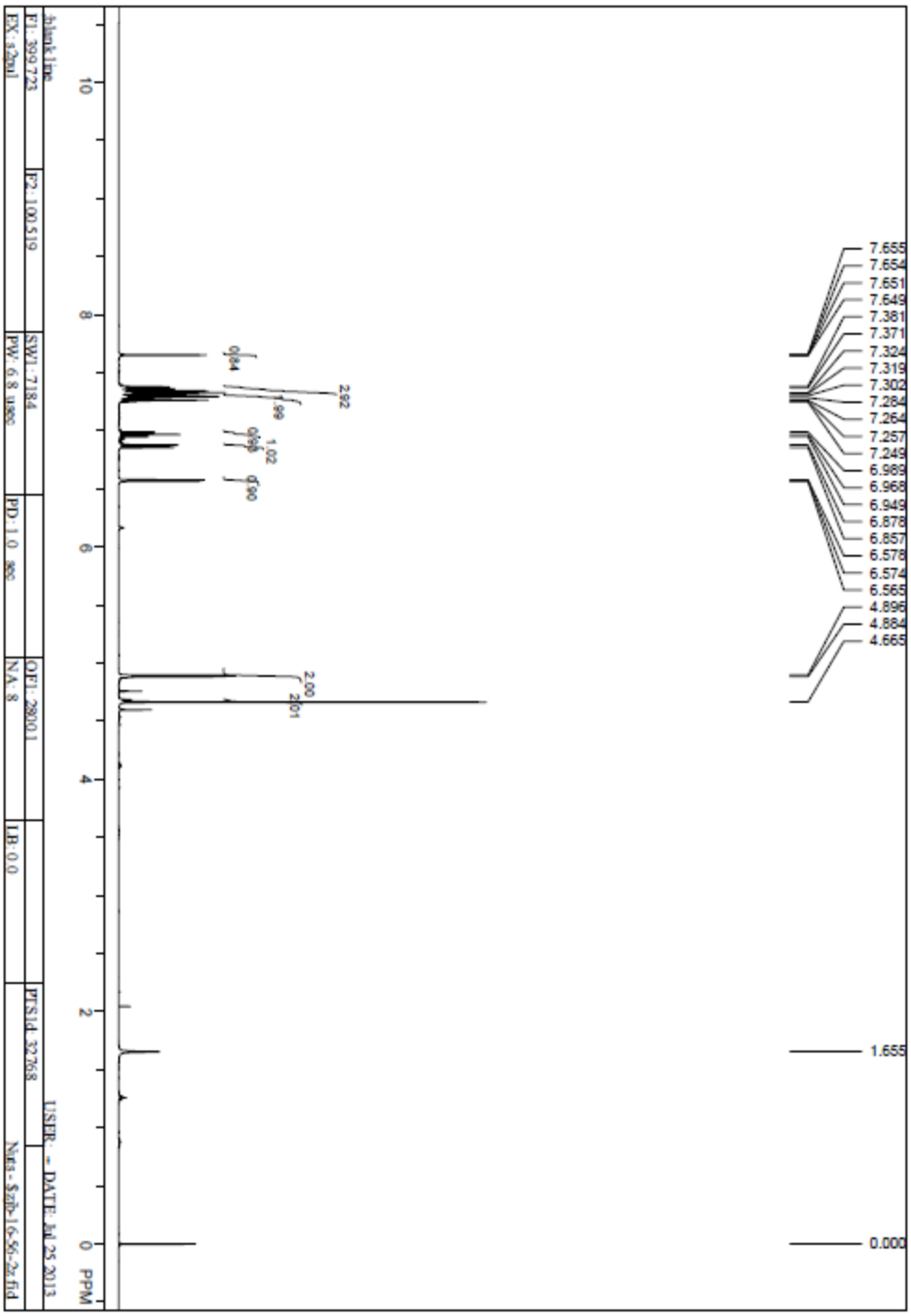
^{13}C NMR (100 M Hz in $CDCl_3$)

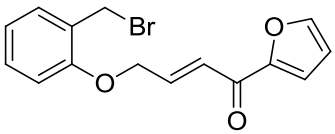




1o

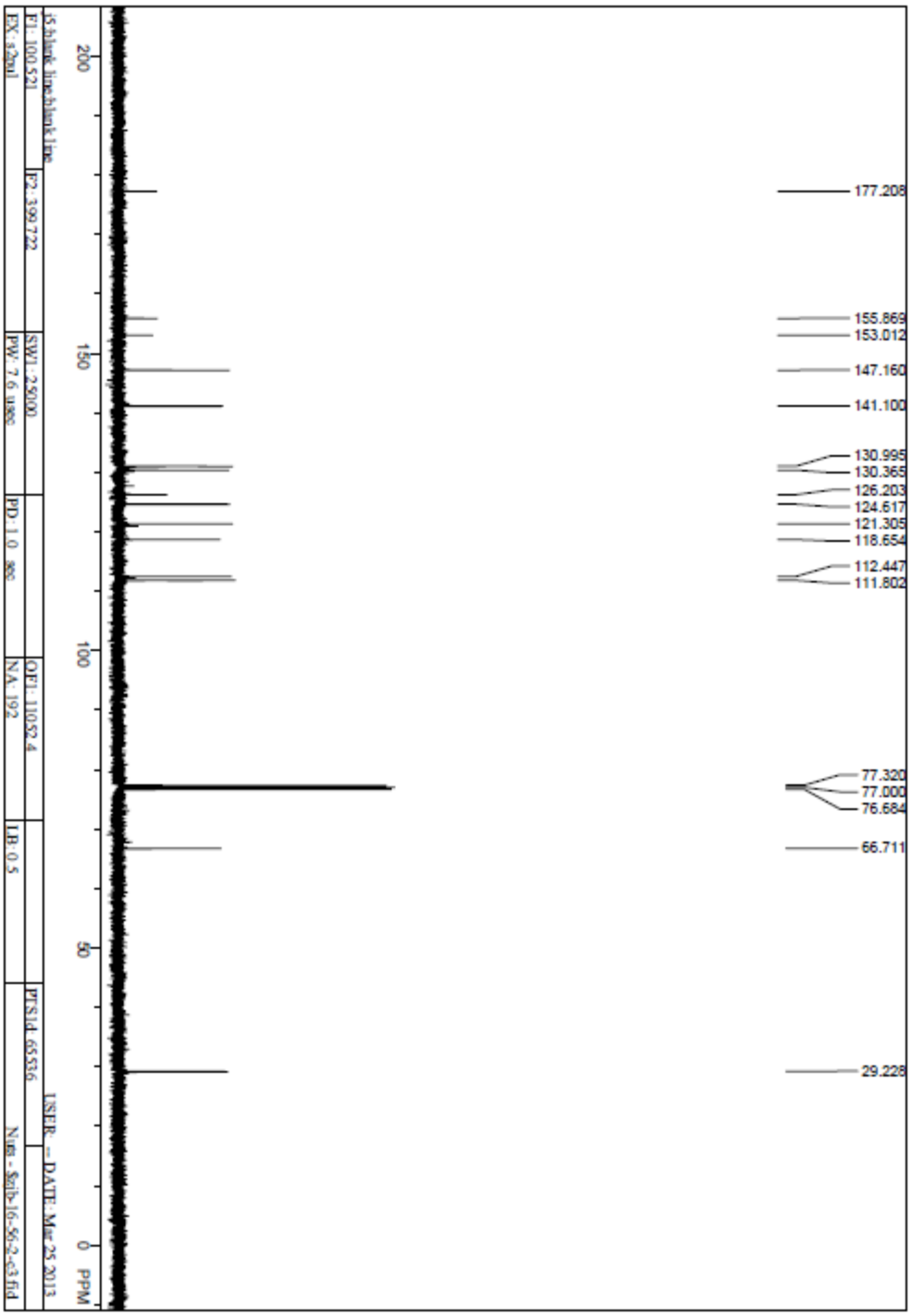
^{1}H NMR (400 M Hz in $CDCl_3$)

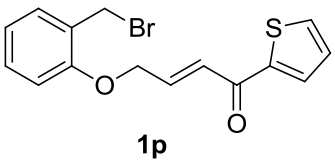




1o

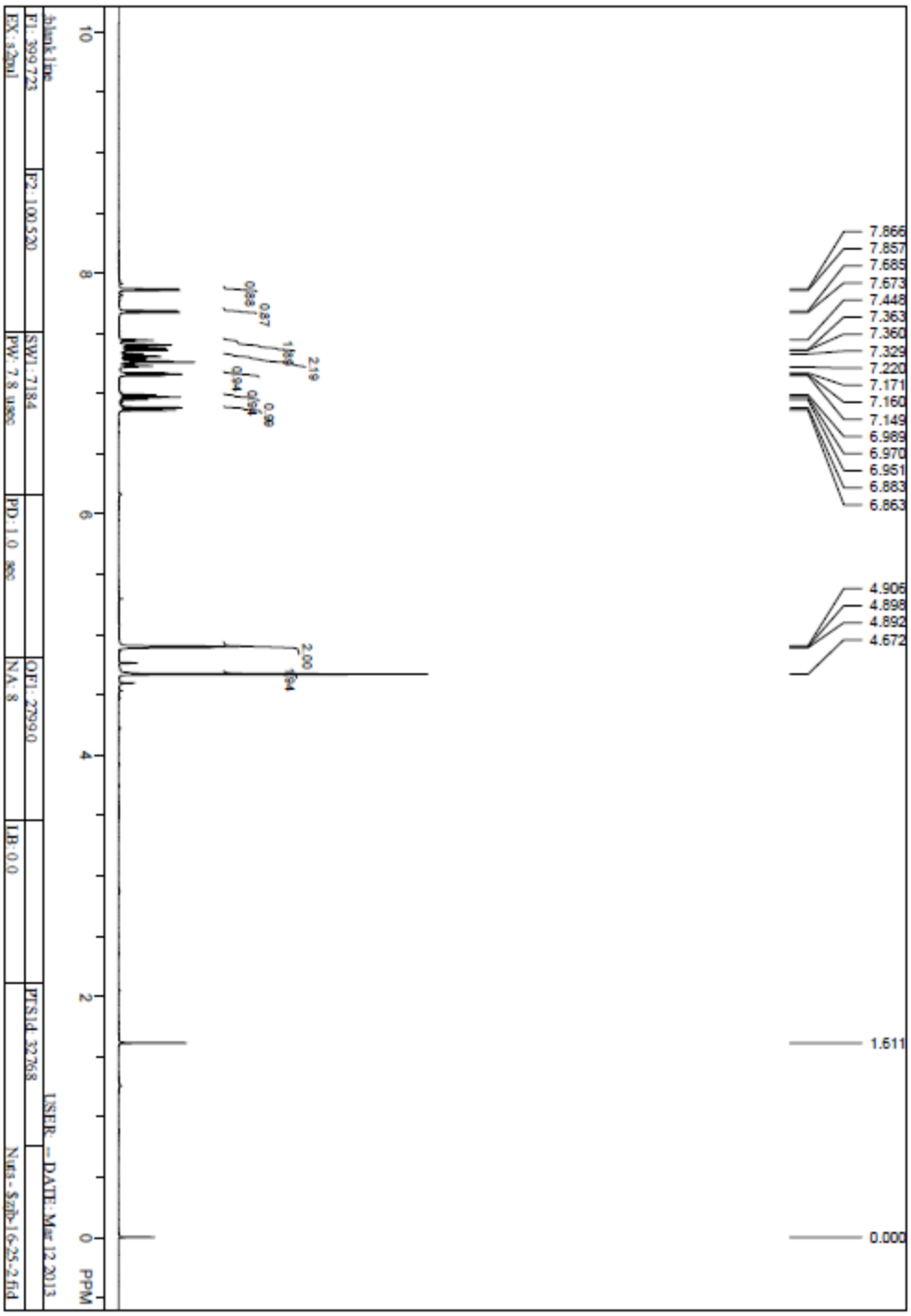
^{13}C NMR (100 M Hz in $CDCl_3$)

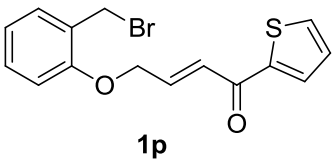




1p

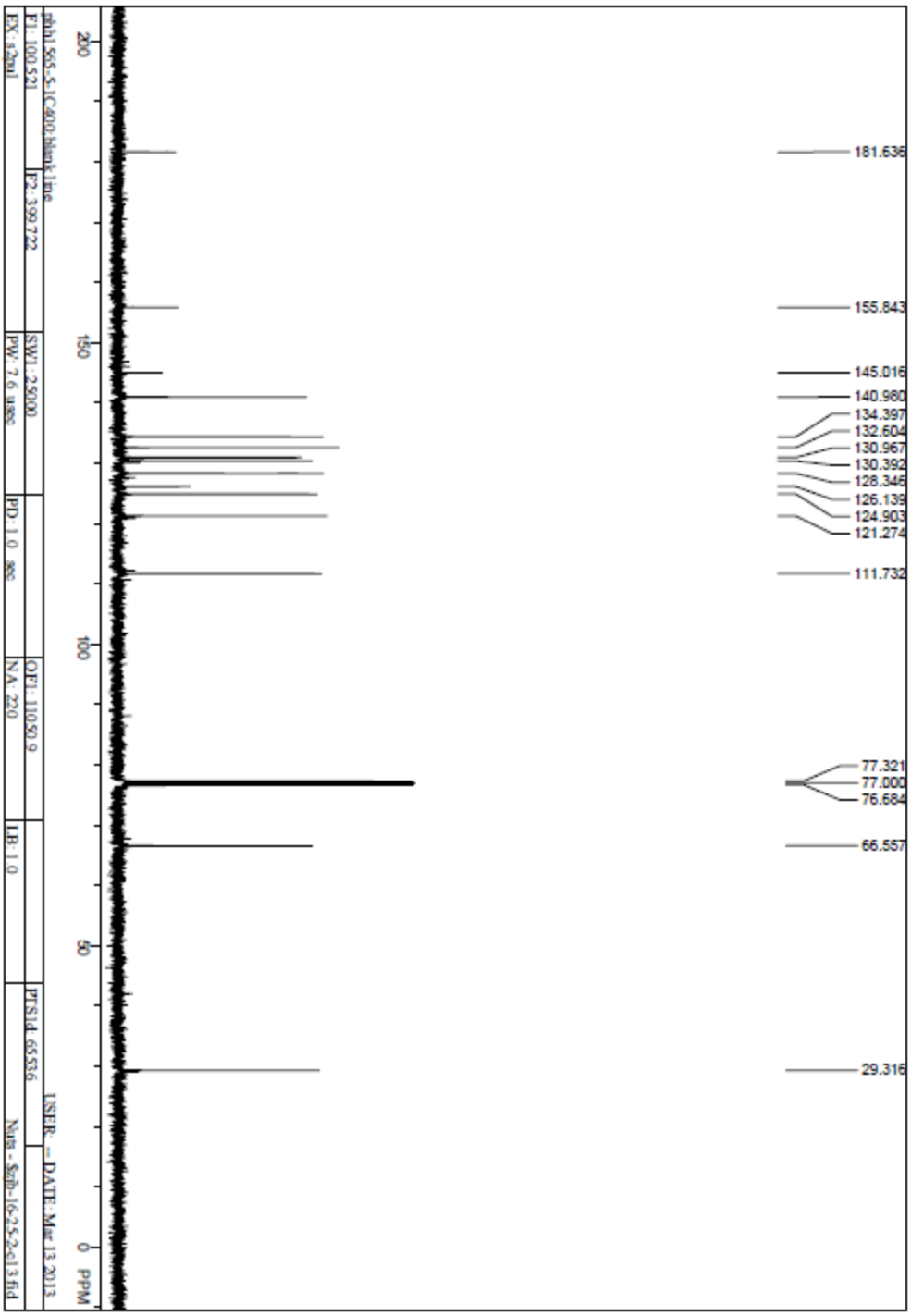
^{1}H NMR (400 M Hz in $CDCl_3$)

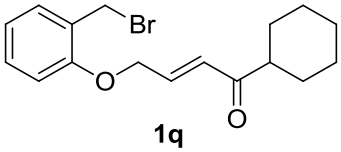




1p

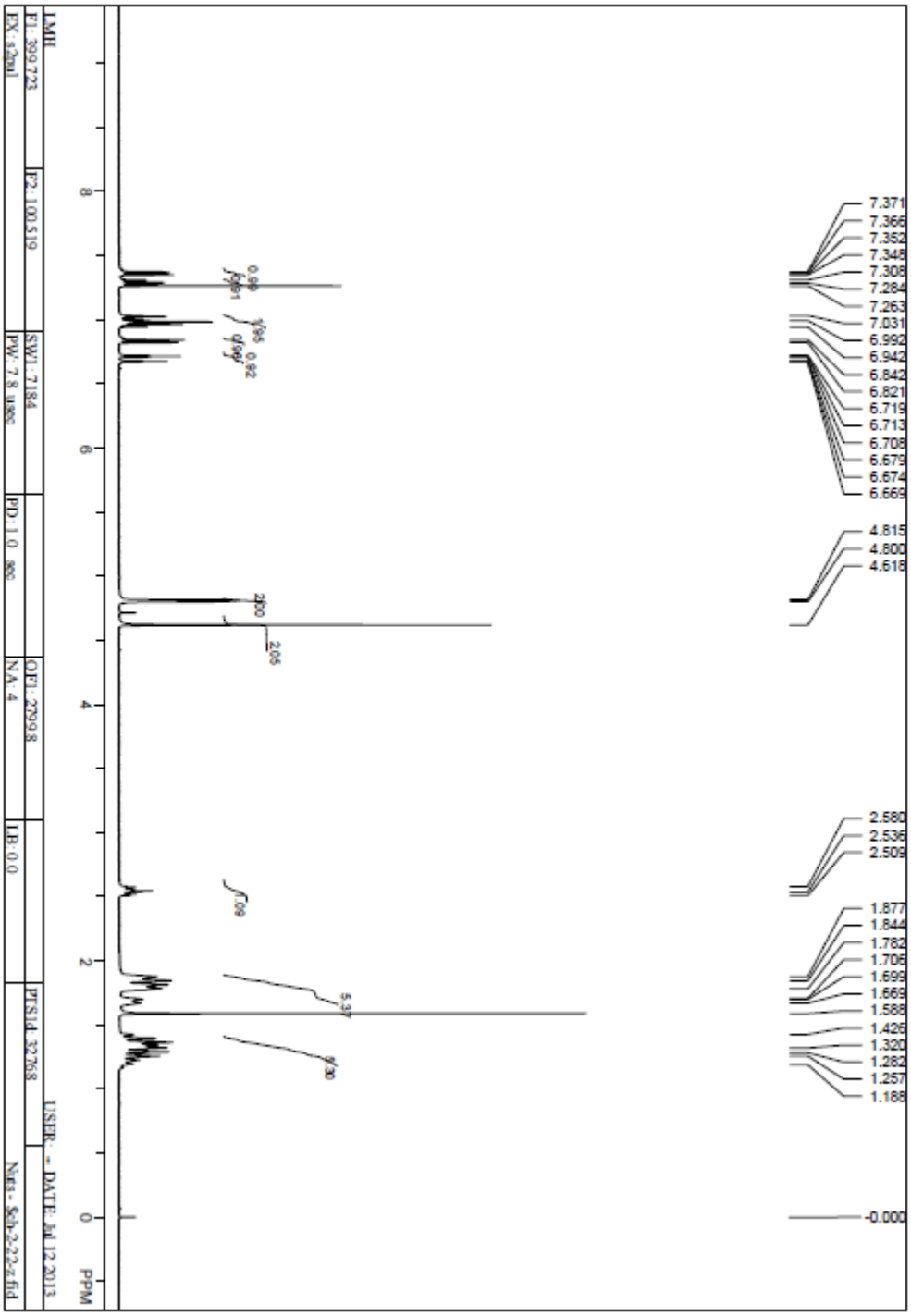
^{13}C NMR (100 M Hz in $CDCl_3$)

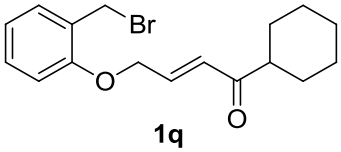




1q

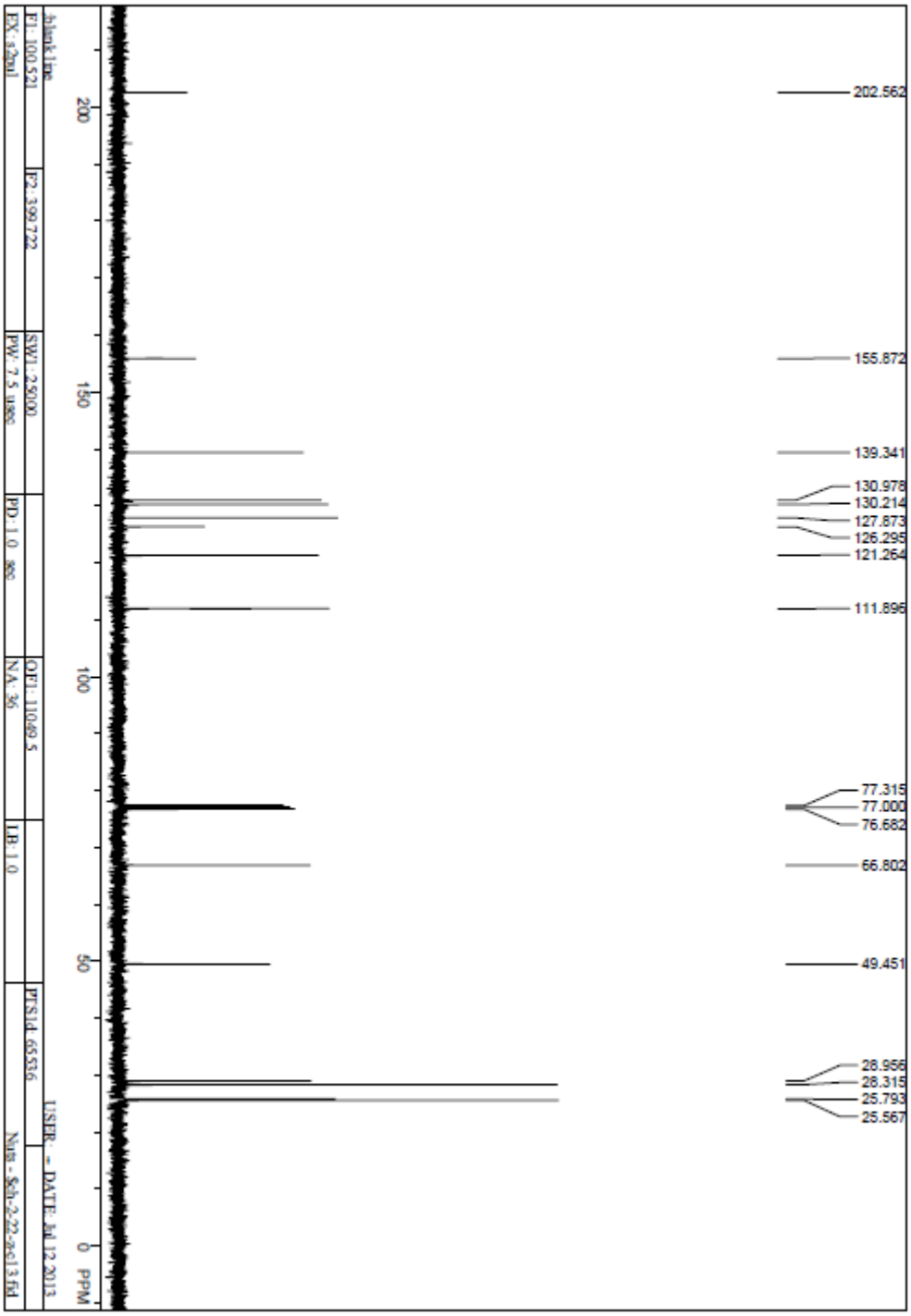
^{1}H NMR (400 M Hz in $CDCl_3$)

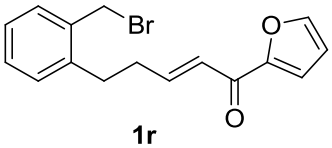




1q

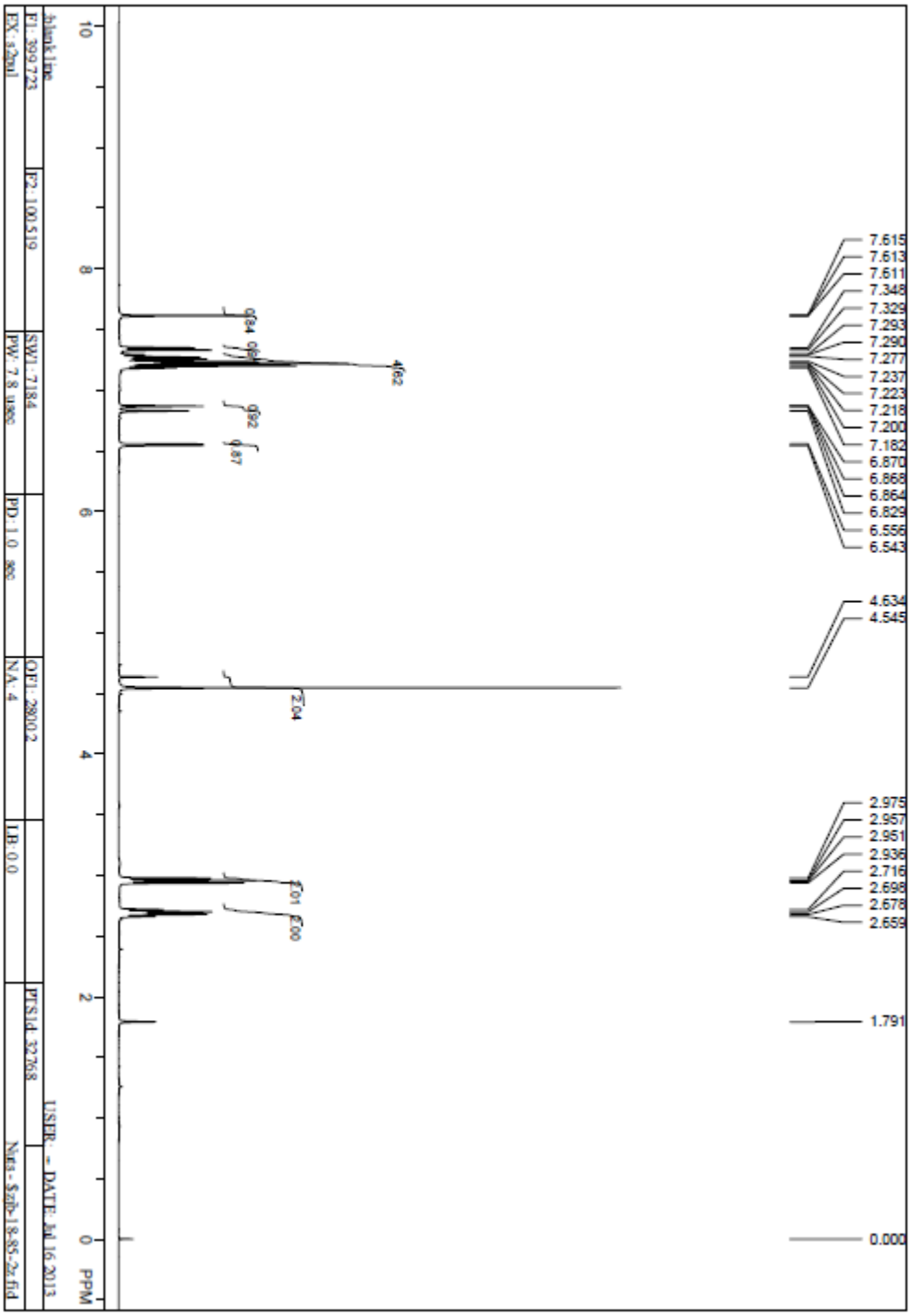
^{13}C NMR (100 M Hz in $CDCl_3$)

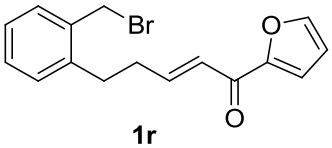




1r

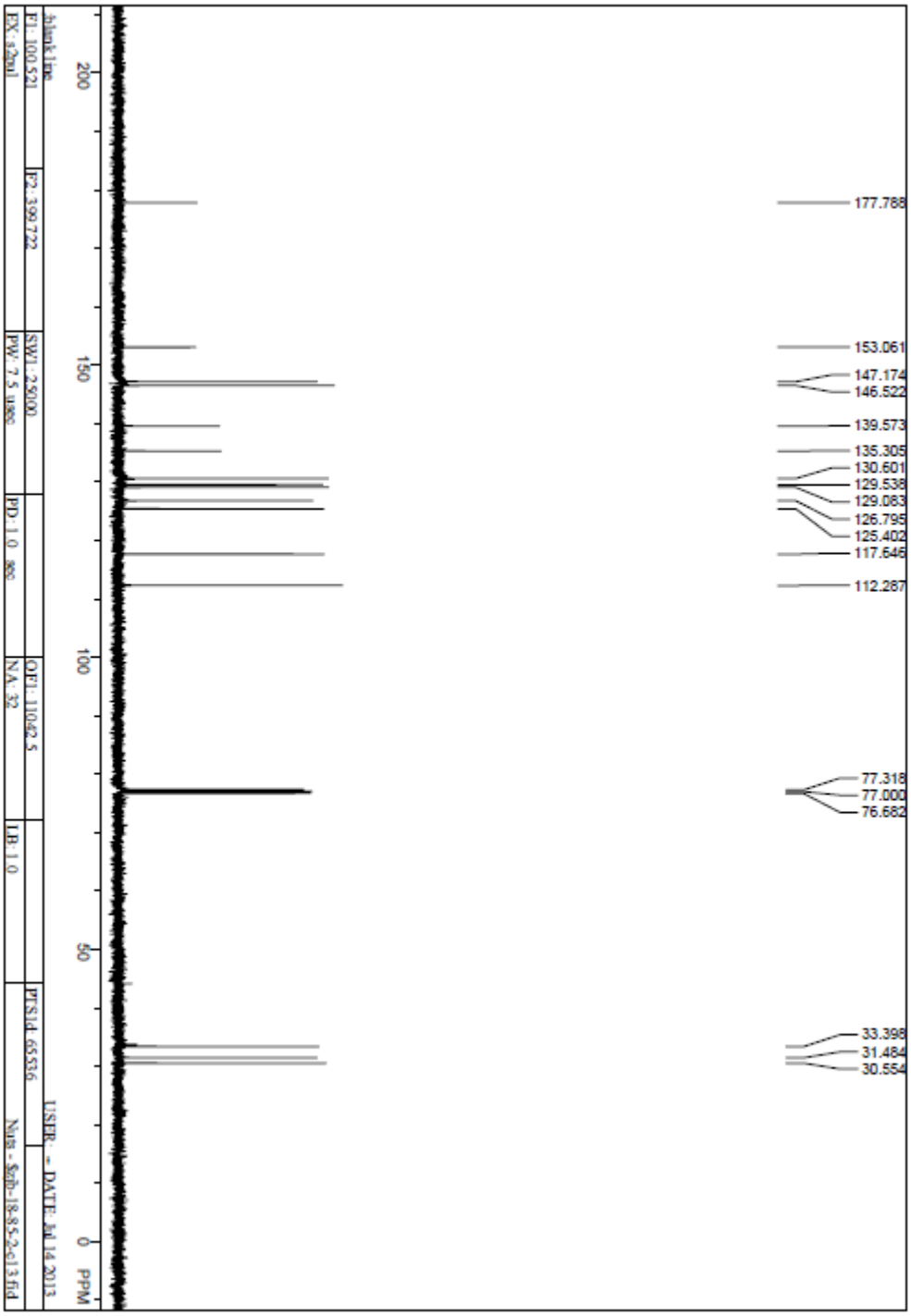
^{1}H NMR (400 M Hz in $CDCl_3$)

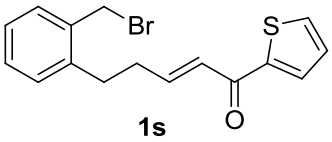




1r

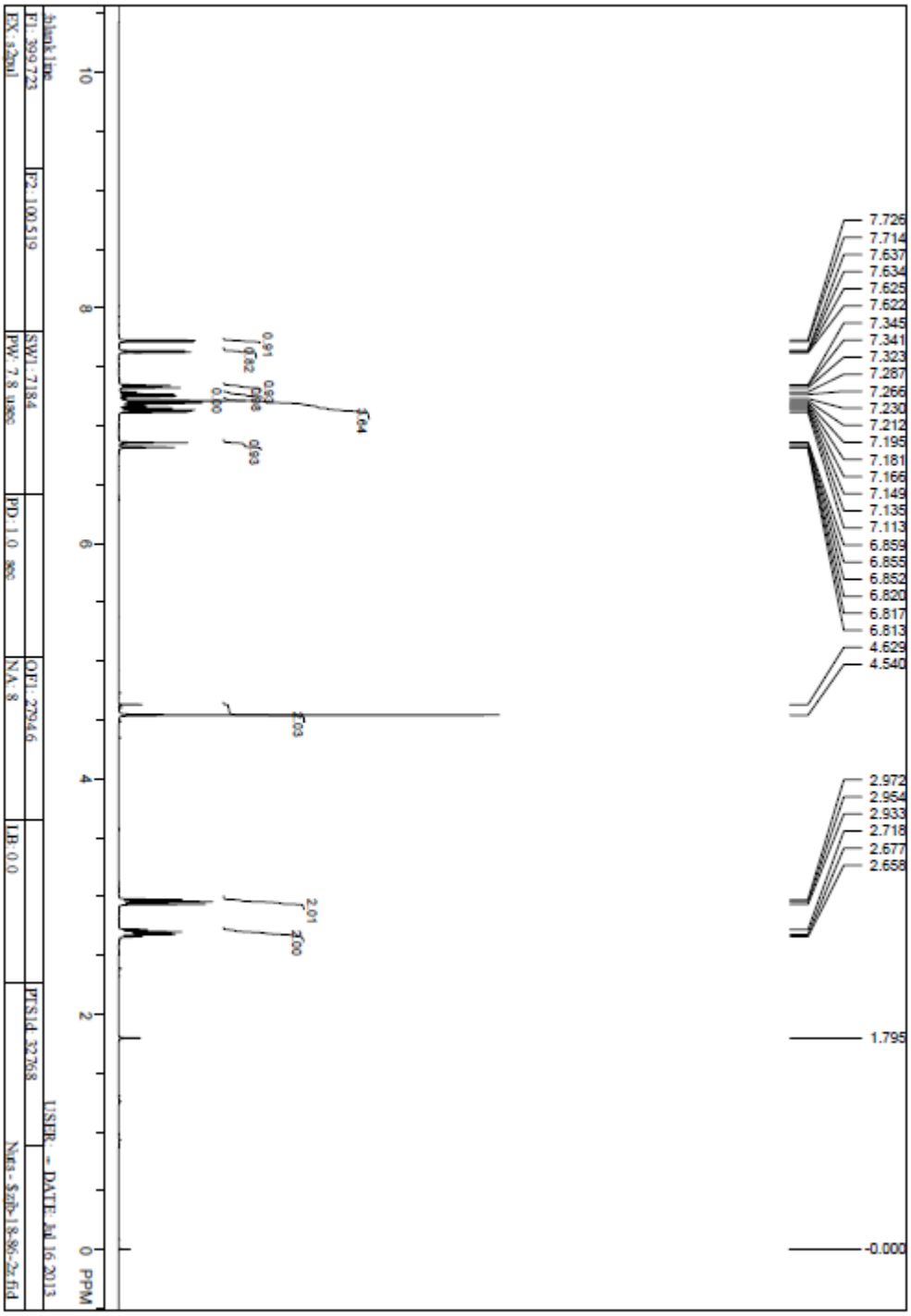
^{13}C NMR (100 M Hz in $CDCl_3$)

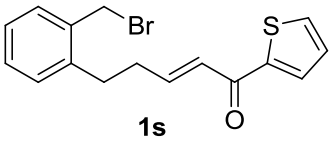




1s

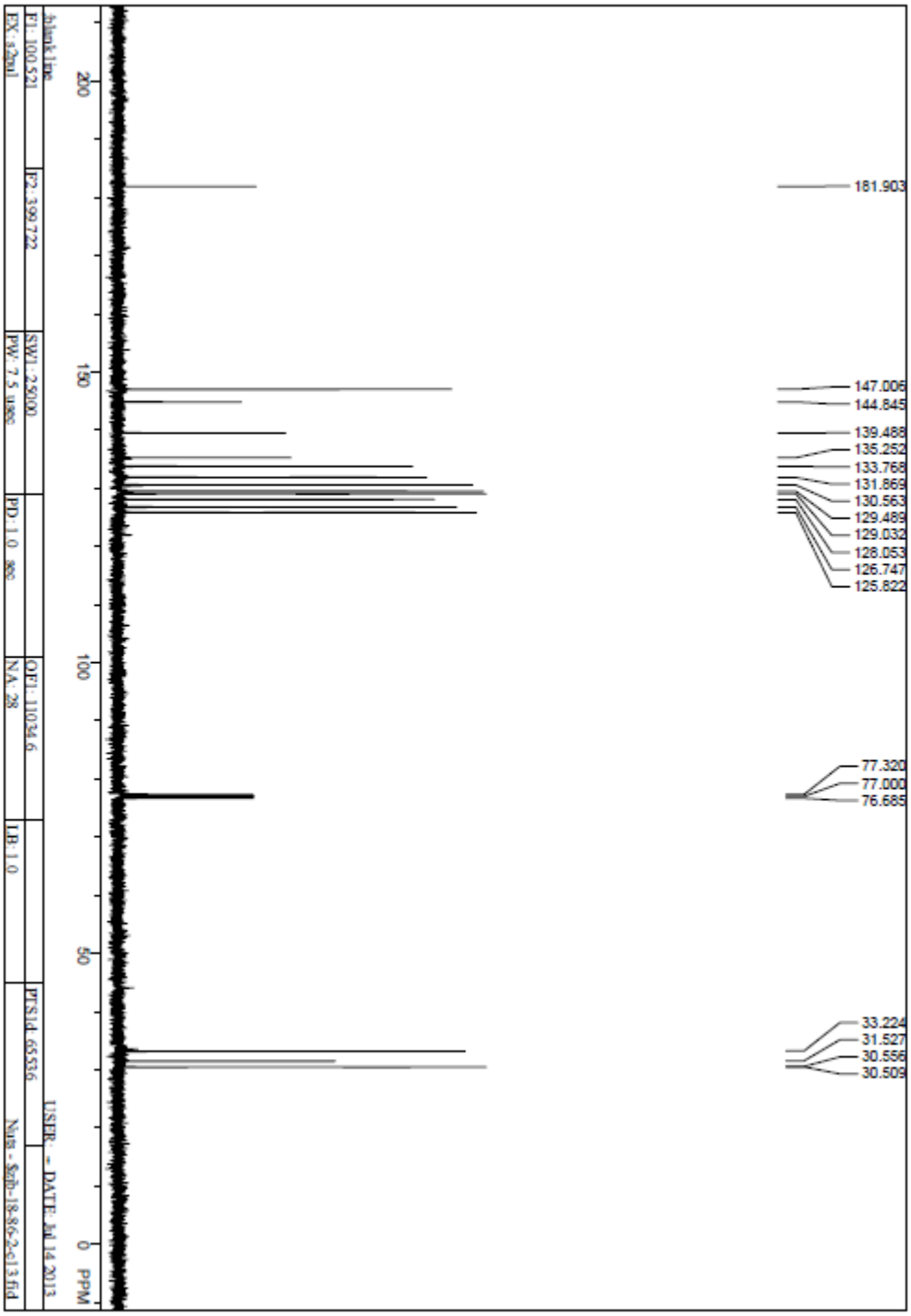
^{1}H NMR (400 M Hz in $CDCl_3$)

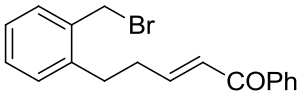




1s

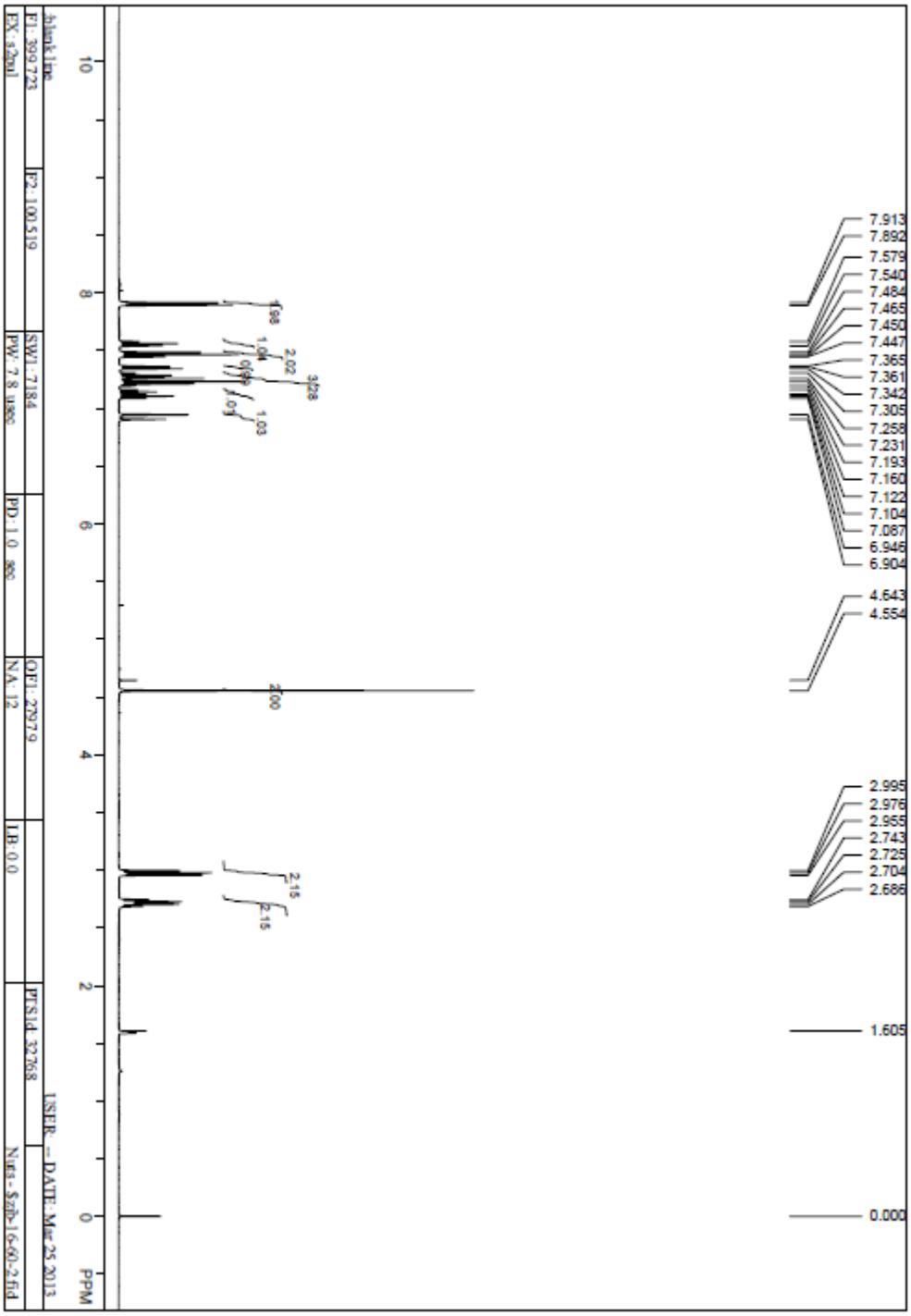
^{13}C NMR (100 M Hz in $CDCl_3$)

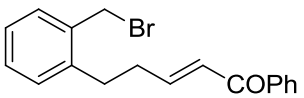




1t

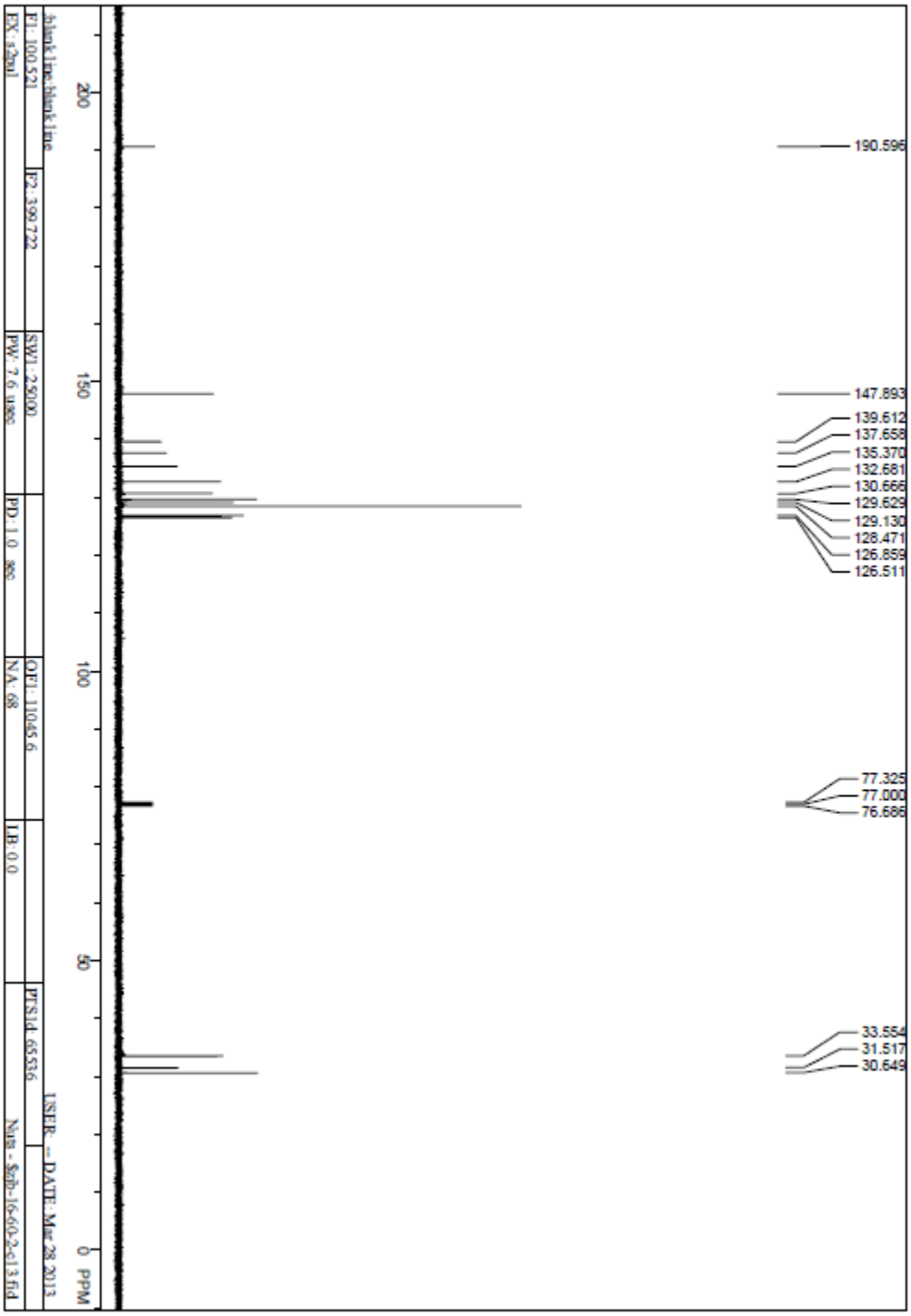
^{1}H NMR (400 M Hz in $CDCl_3$)

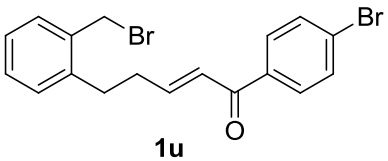




1t

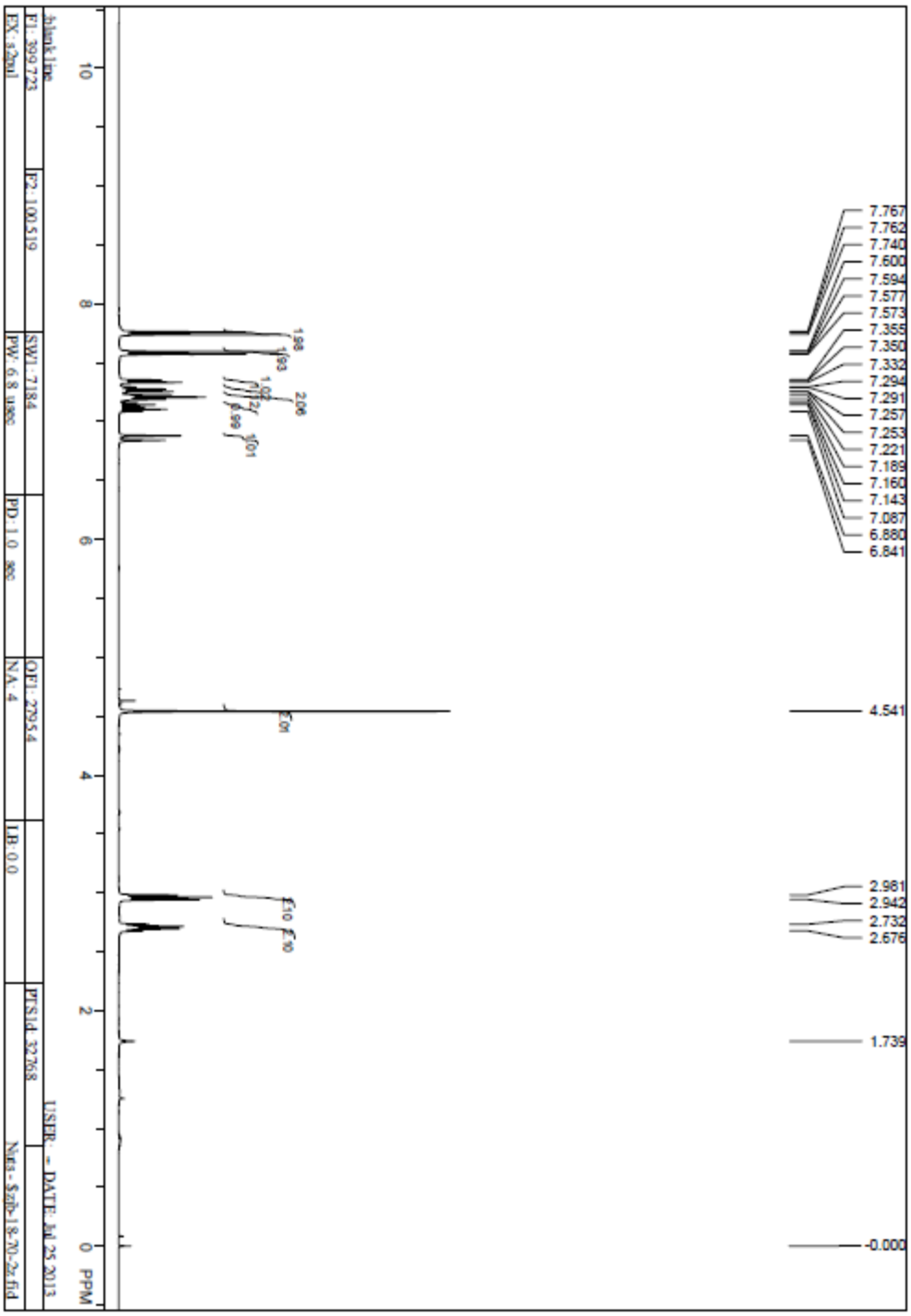
^{13}C NMR (100 M Hz in $CDCl_3$)

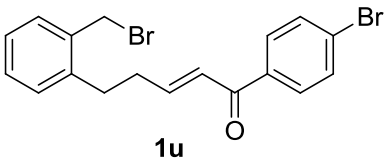




1u

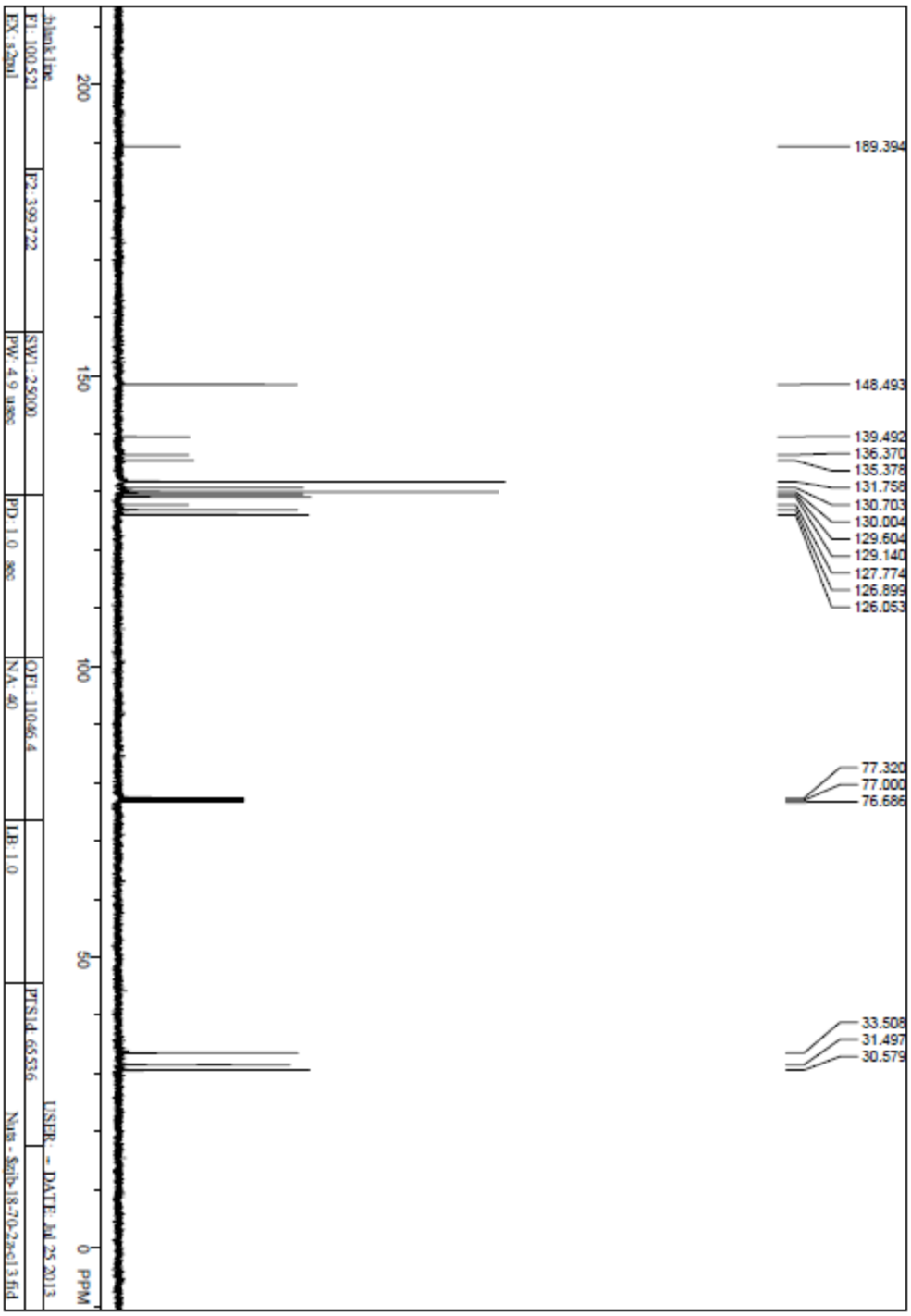
^{1}H NMR (400 M Hz in $CDCl_3$)

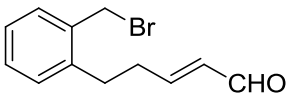




1u

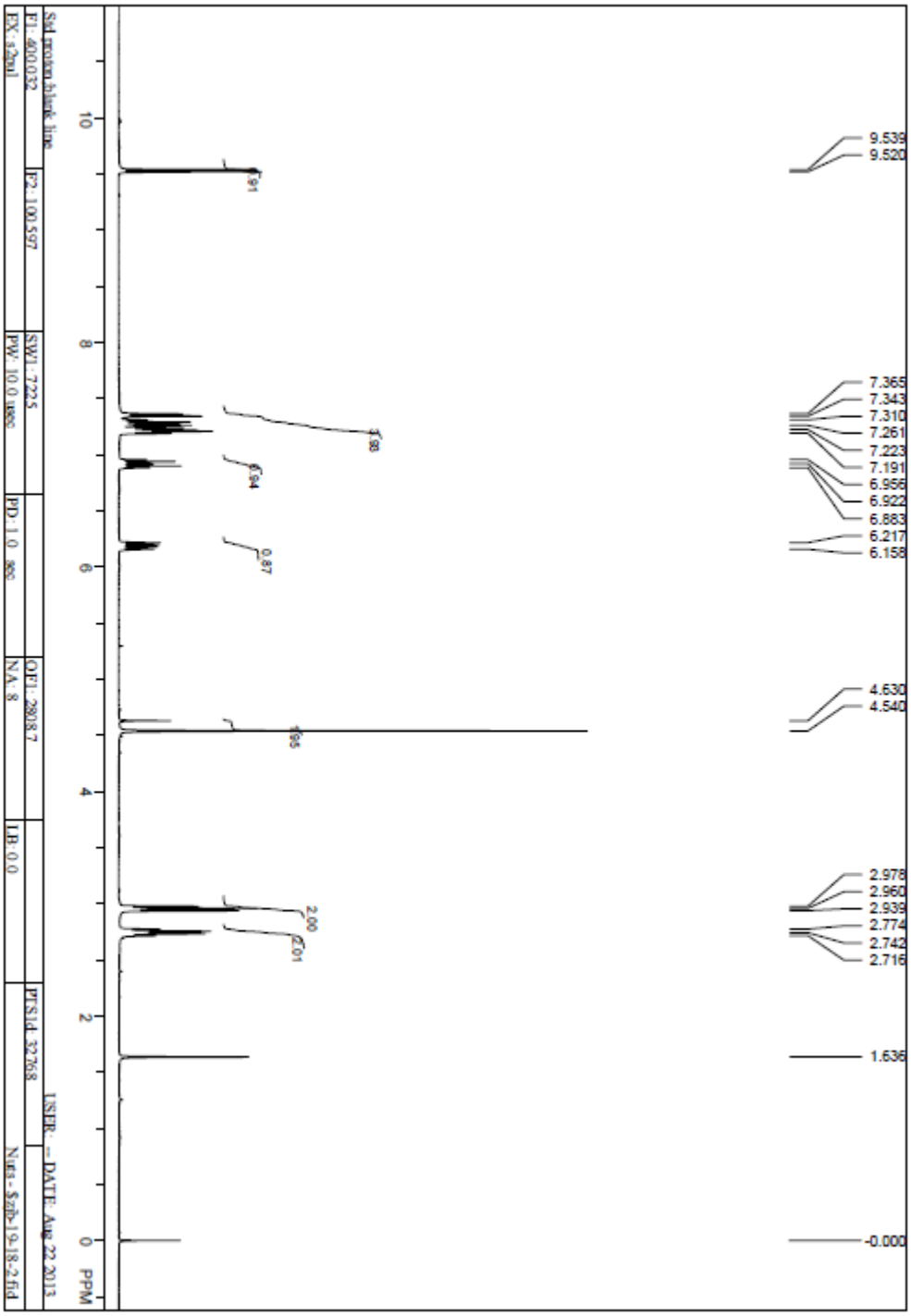
^{13}C NMR (100 M Hz in $CDCl_3$)

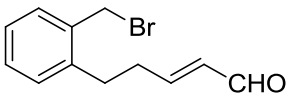




1v

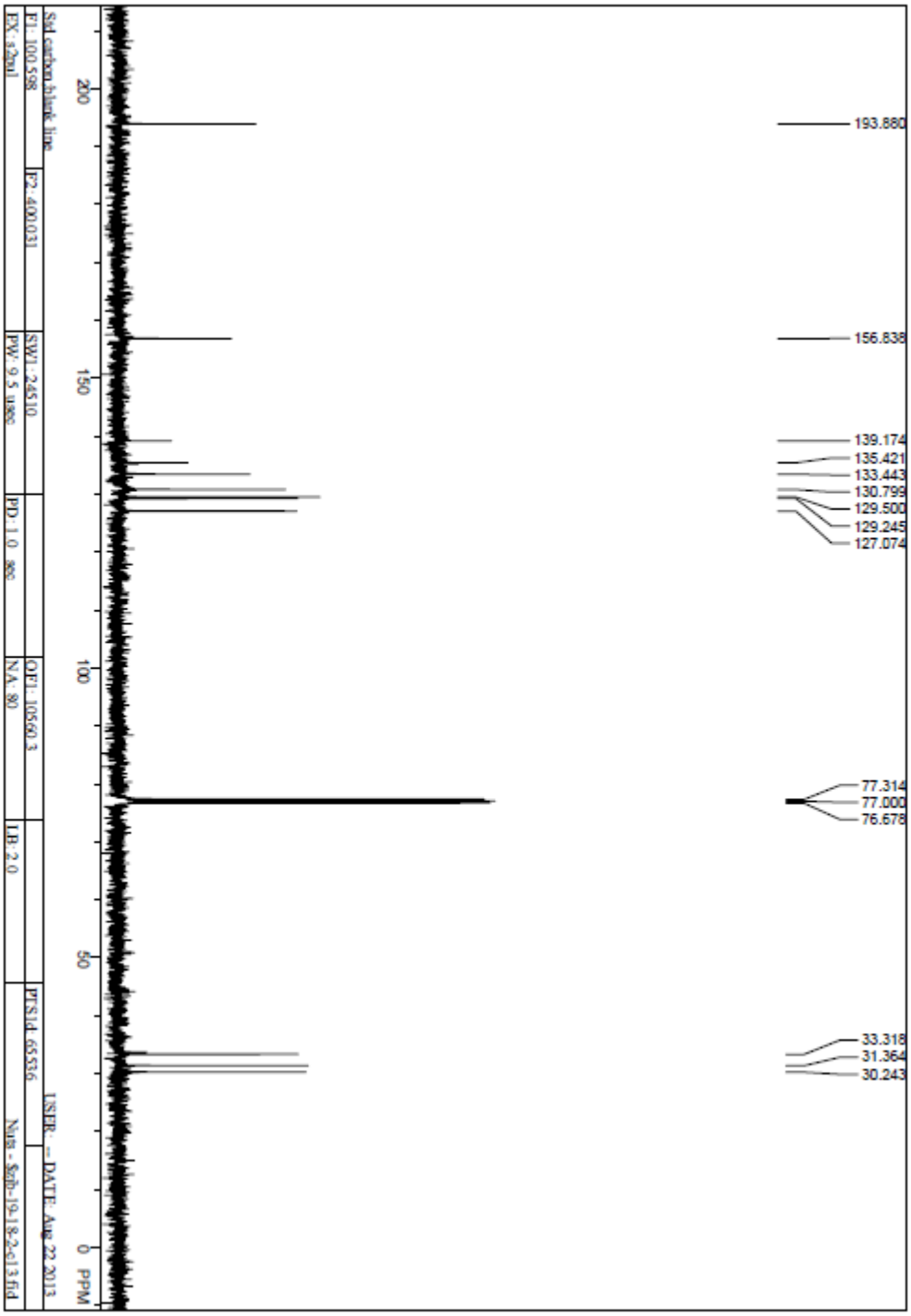
^{1}H NMR (400 M Hz in $CDCl_3$)

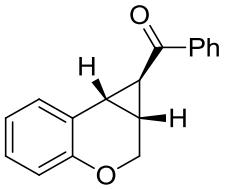




1v

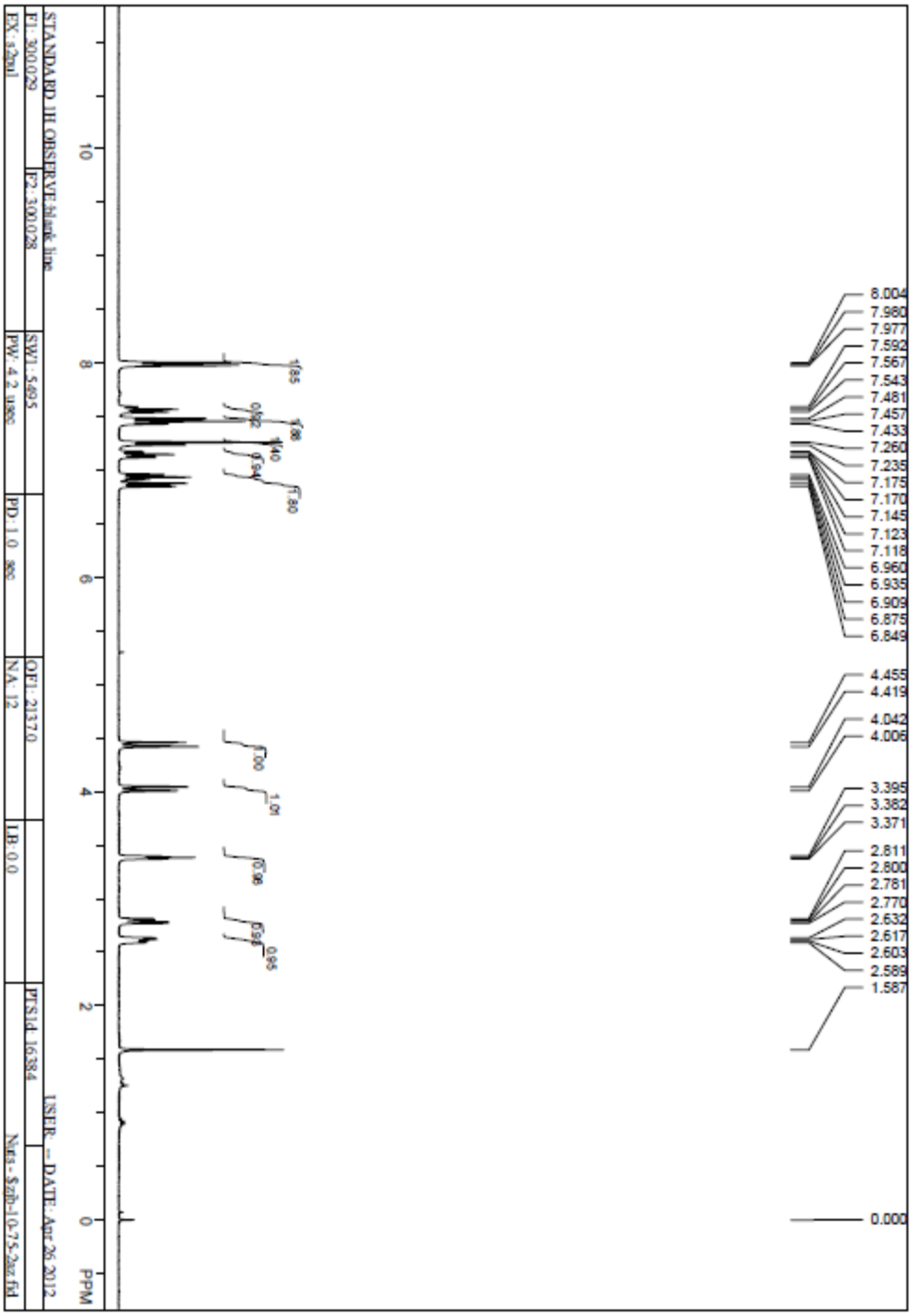
^{13}C NMR (100 M Hz in $CDCl_3$)

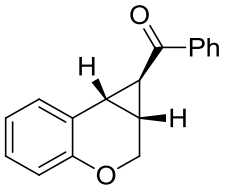




2a

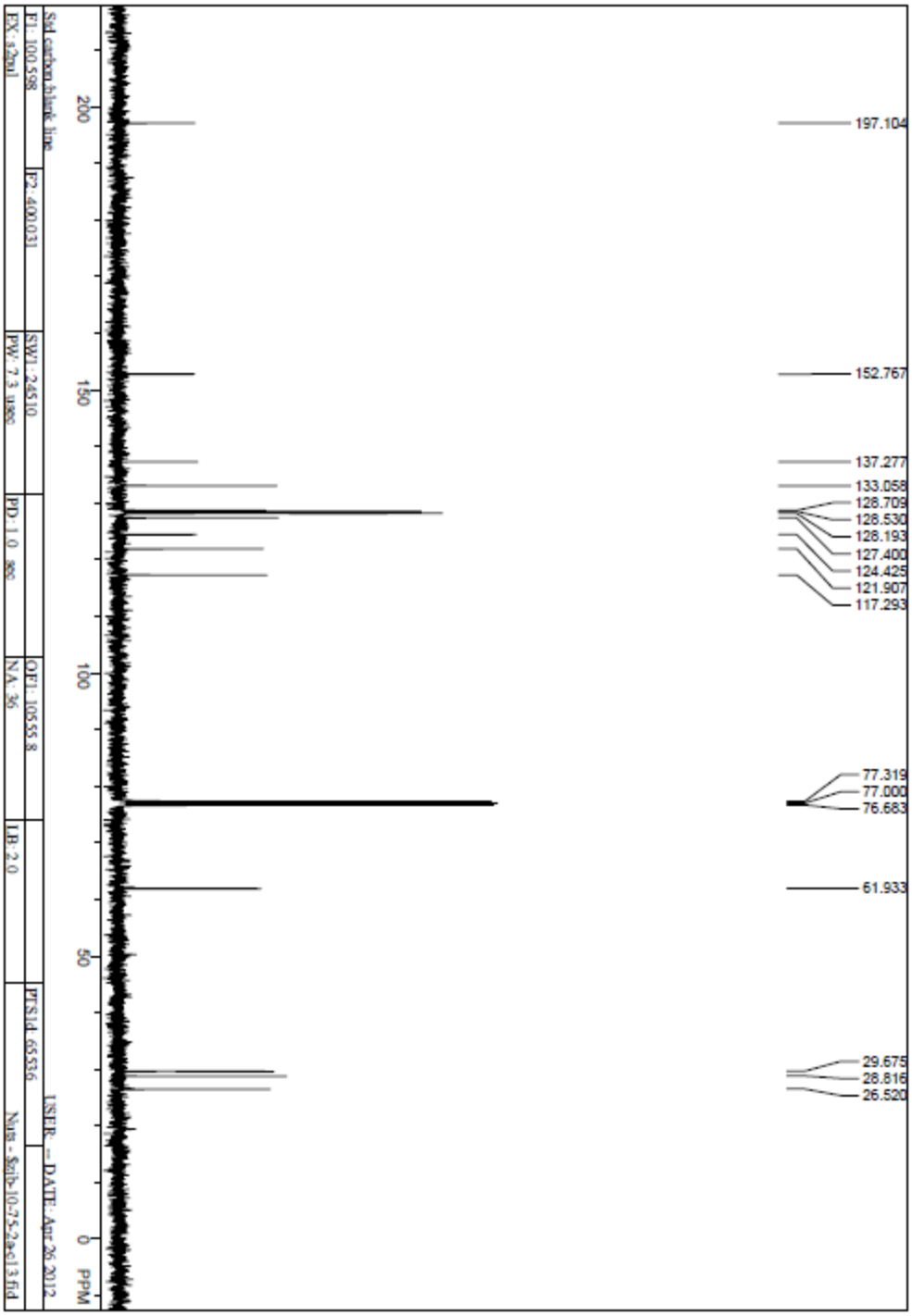
^{1}H NMR (300 M Hz in $CDCl_3$)

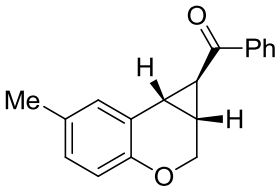




2a

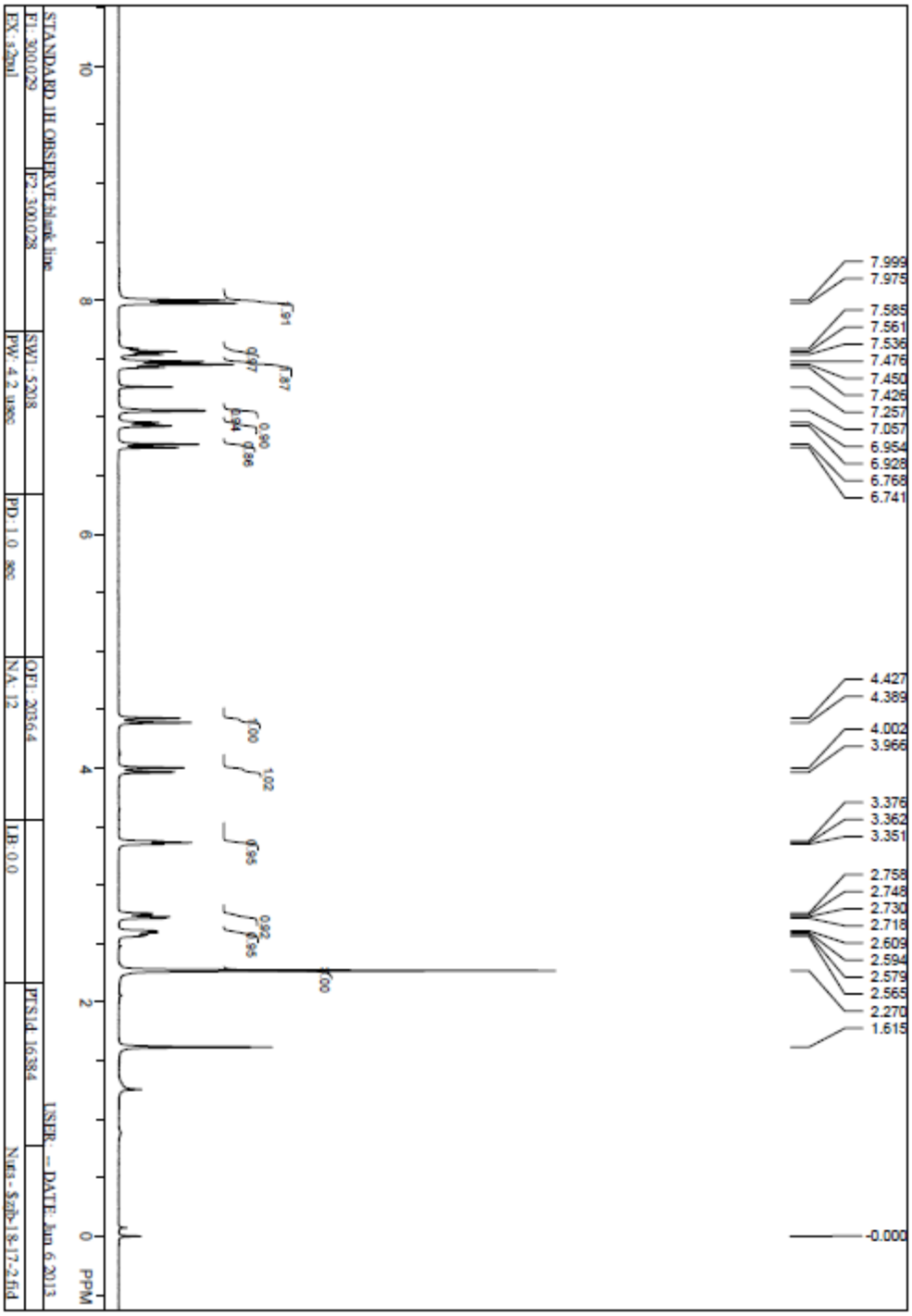
^{13}C NMR (100 M Hz in $CDCl_3$)

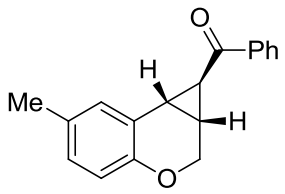




2b

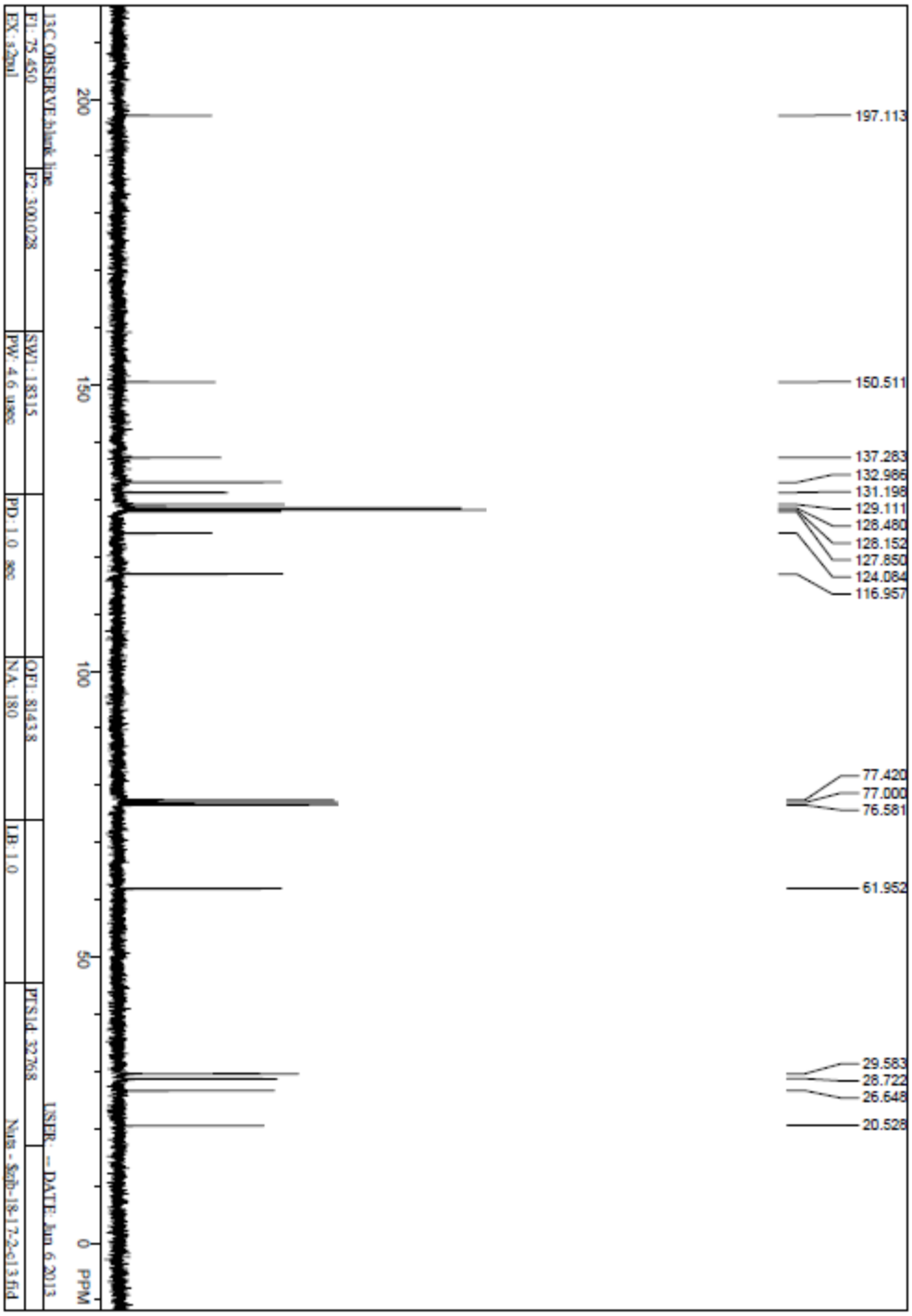
^{1}H NMR (300 M Hz in $CDCl_3$)

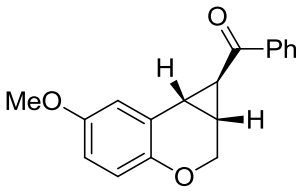




2b

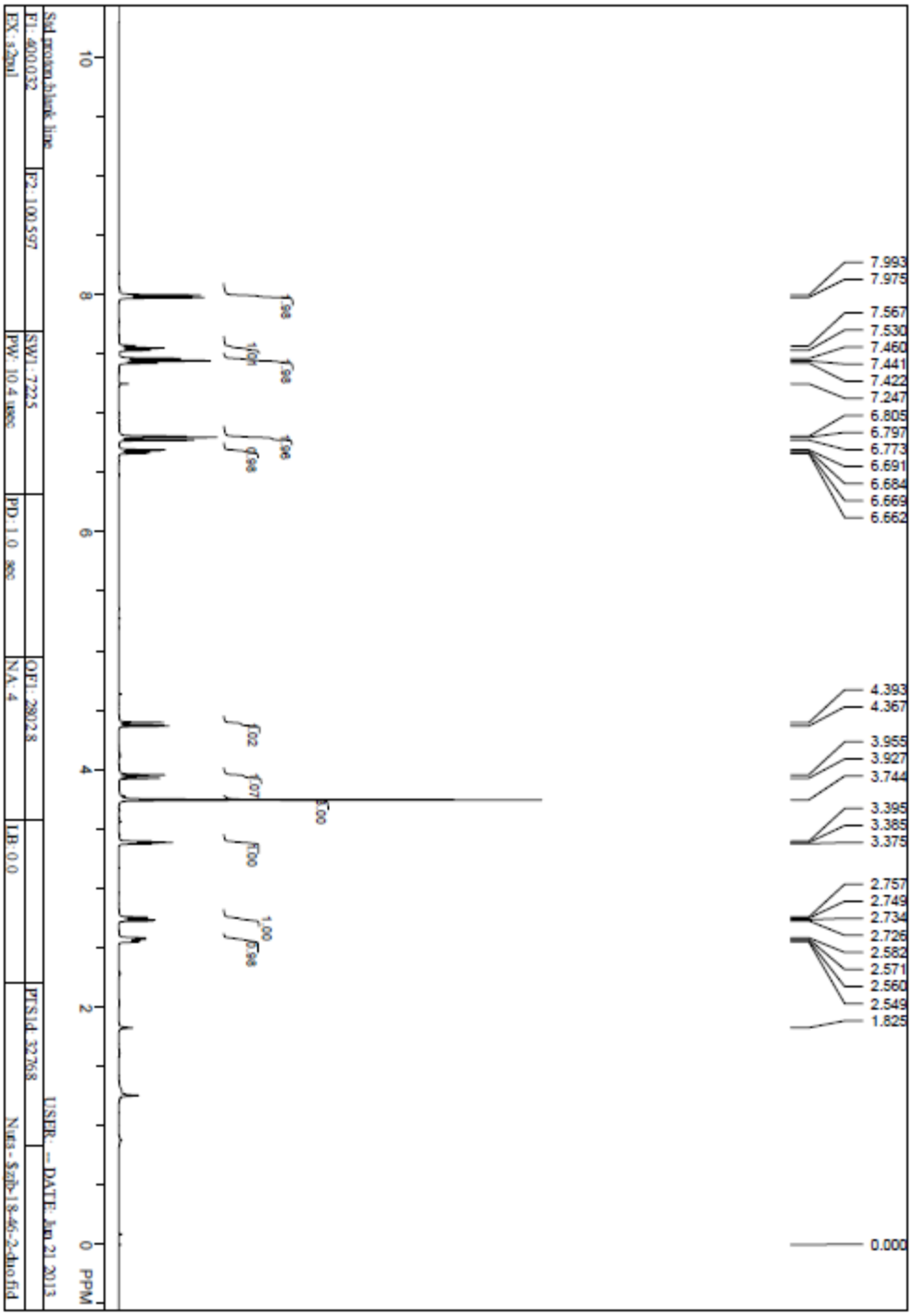
^{13}C NMR (75 M Hz in $CDCl_3$)

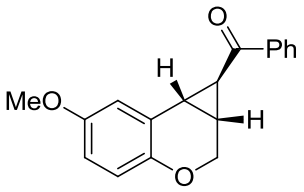




2c

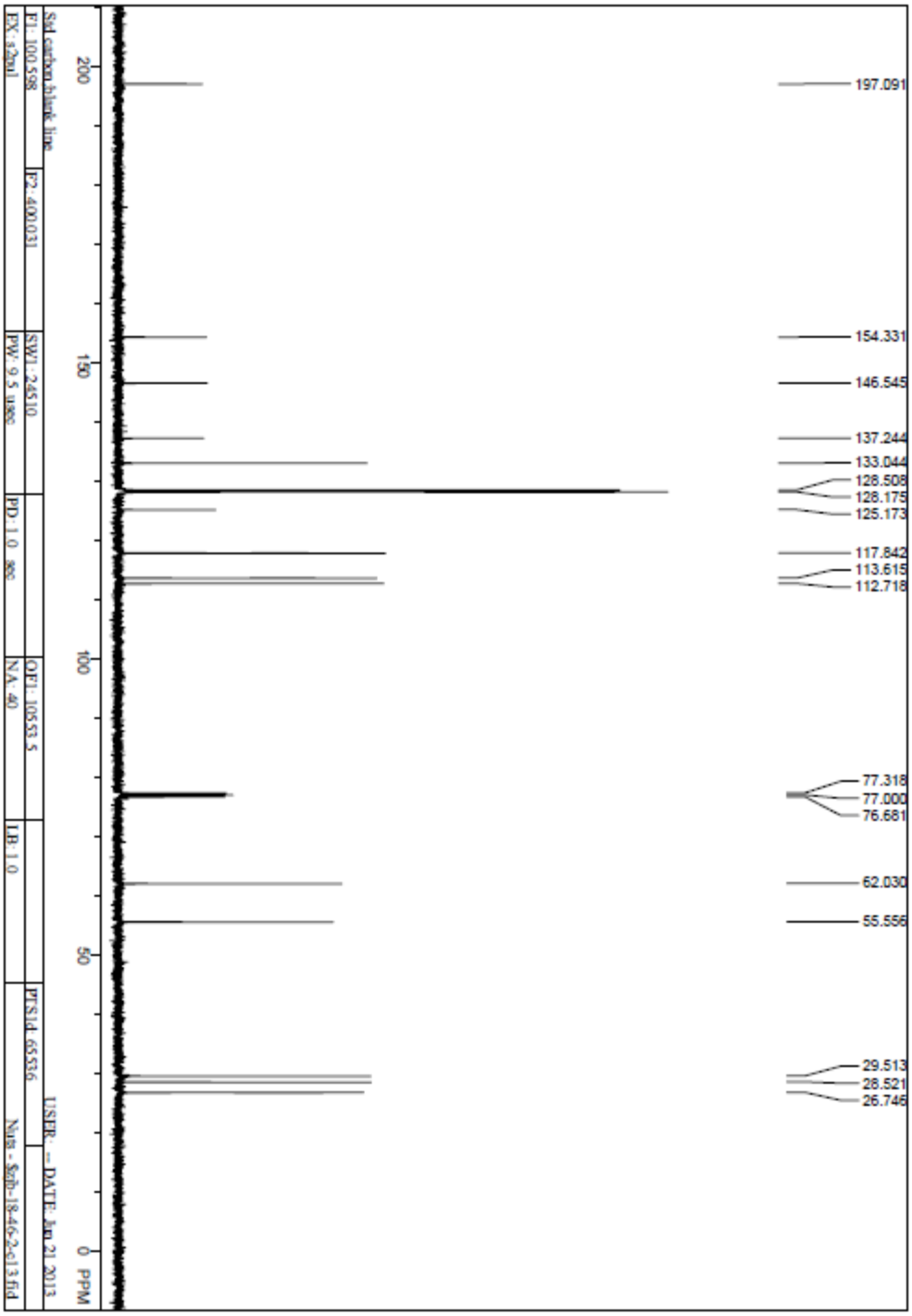
^{1}H NMR (400 M Hz in $CDCl_3$)

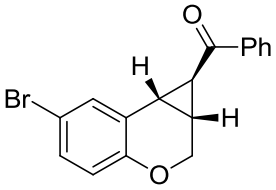




2c

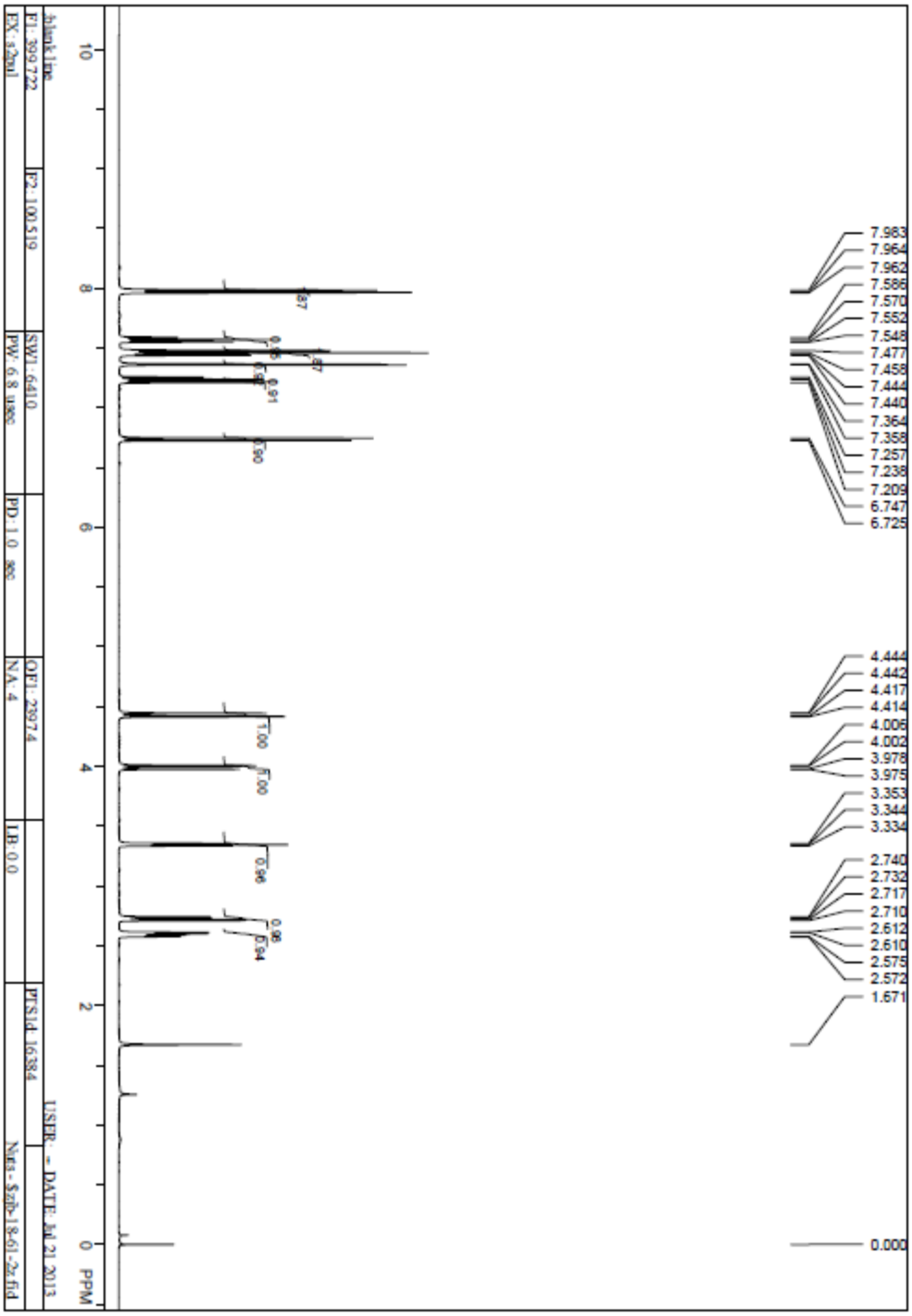
^{13}C NMR (100 M Hz in $CDCl_3$)

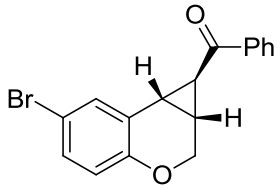




2d

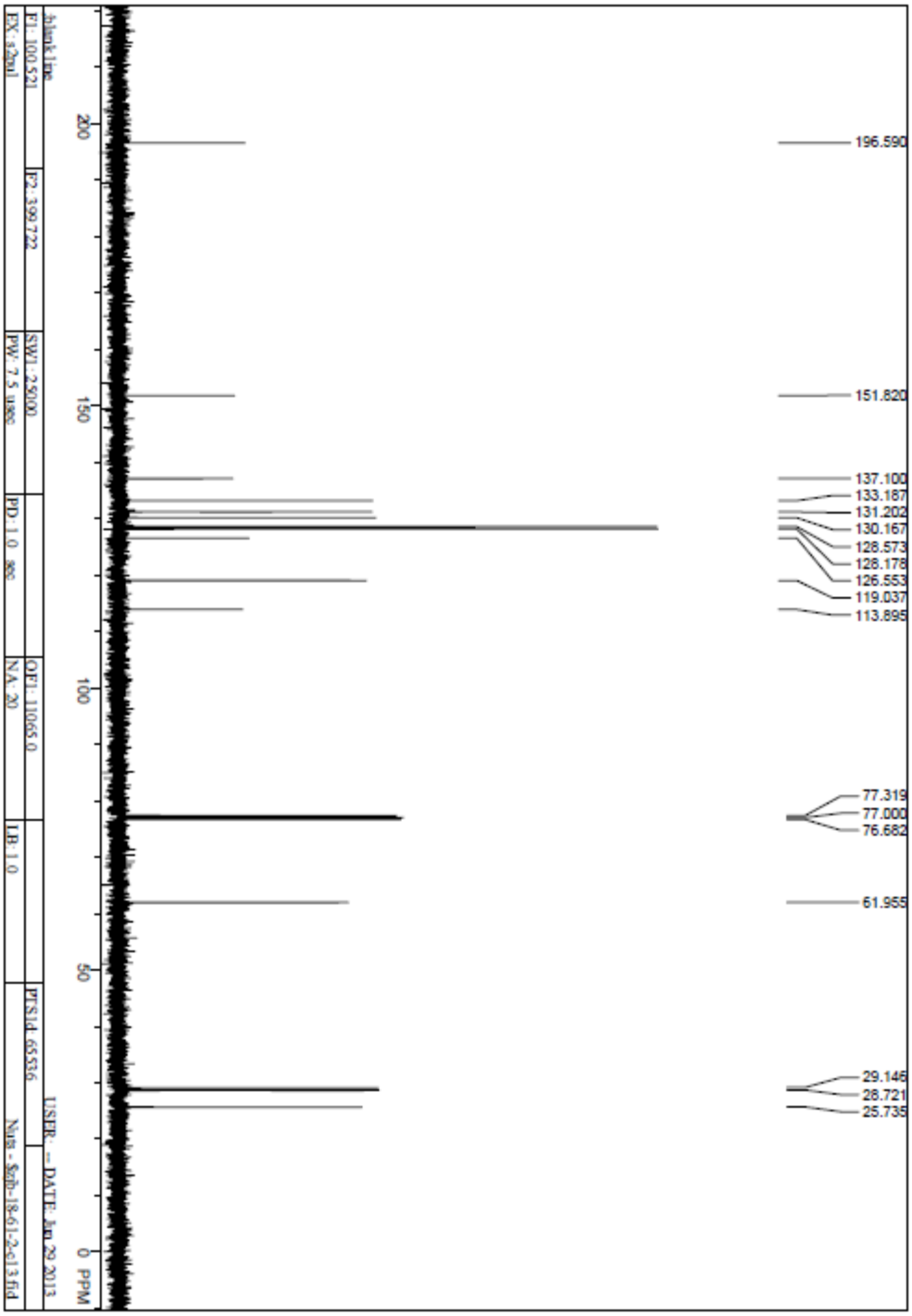
^{1}H NMR (400 M Hz in $CDCl_3$)

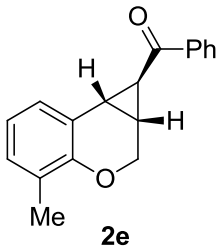




2d

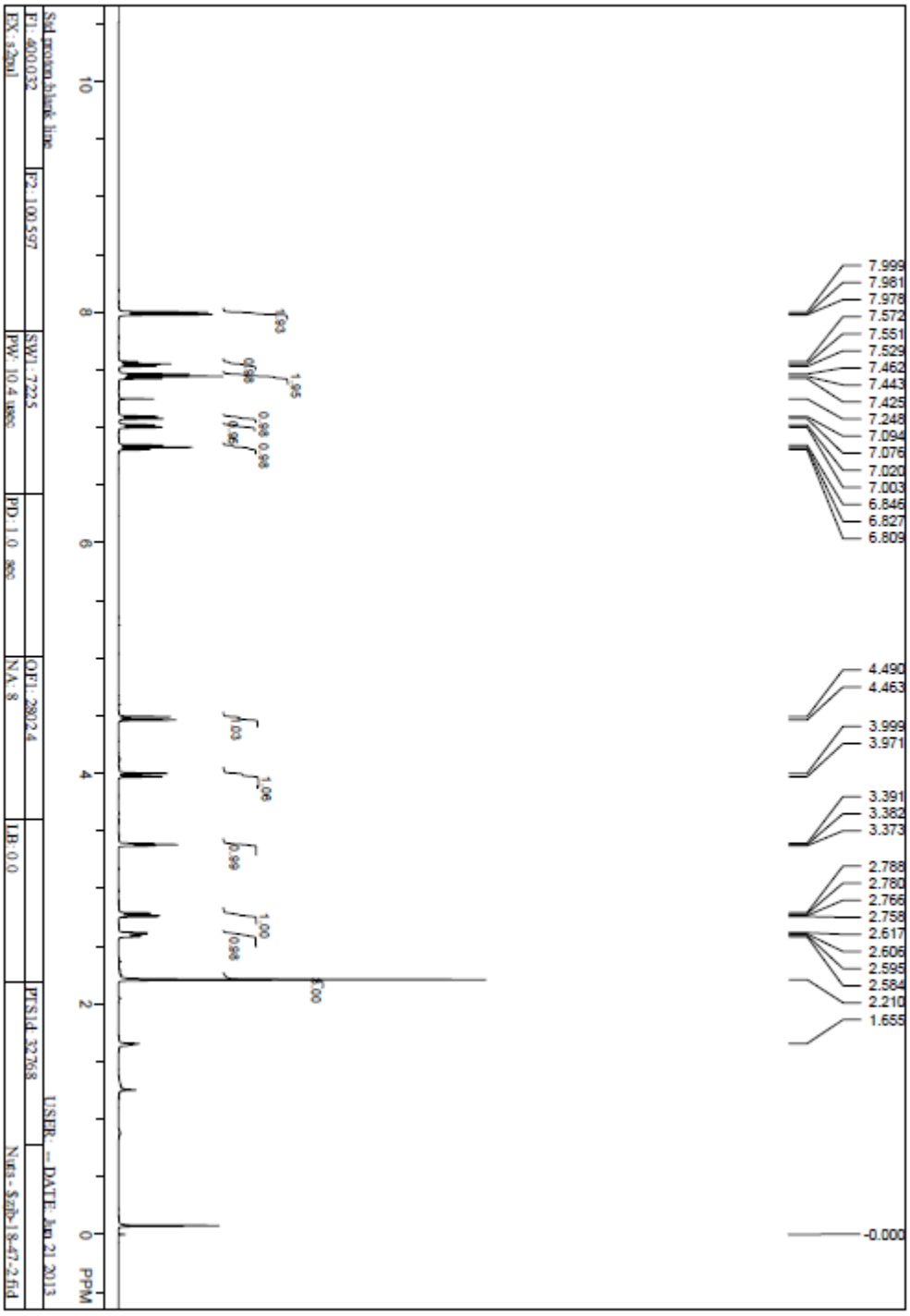
^{13}C NMR (100 M Hz in $CDCl_3$)

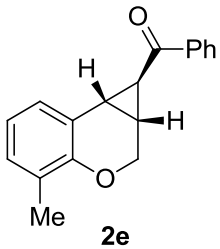




2e

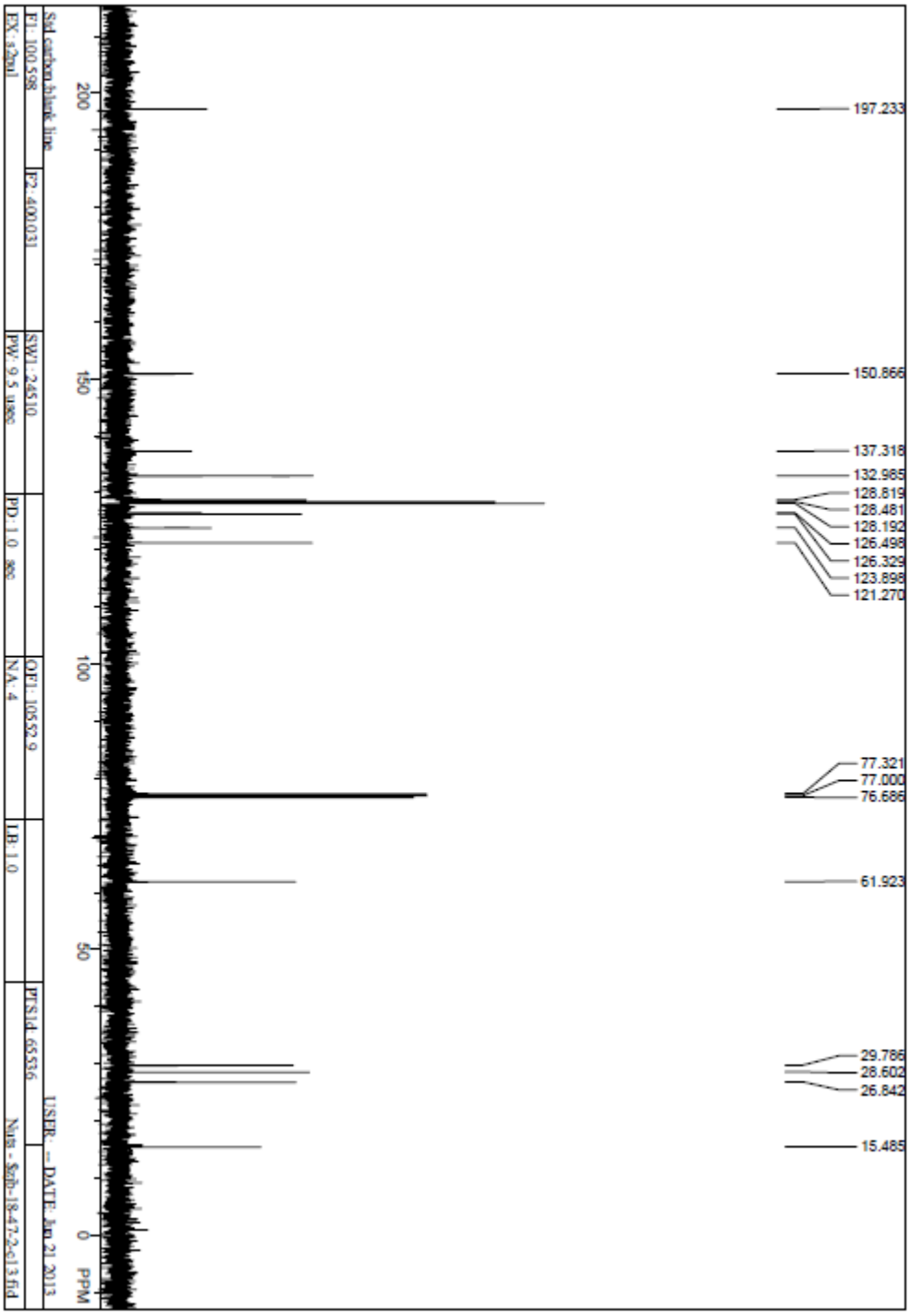
^{1}H NMR (400 M Hz in $CDCl_3$)

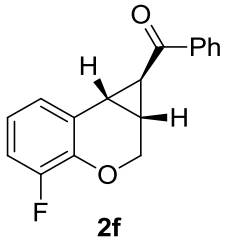




2e

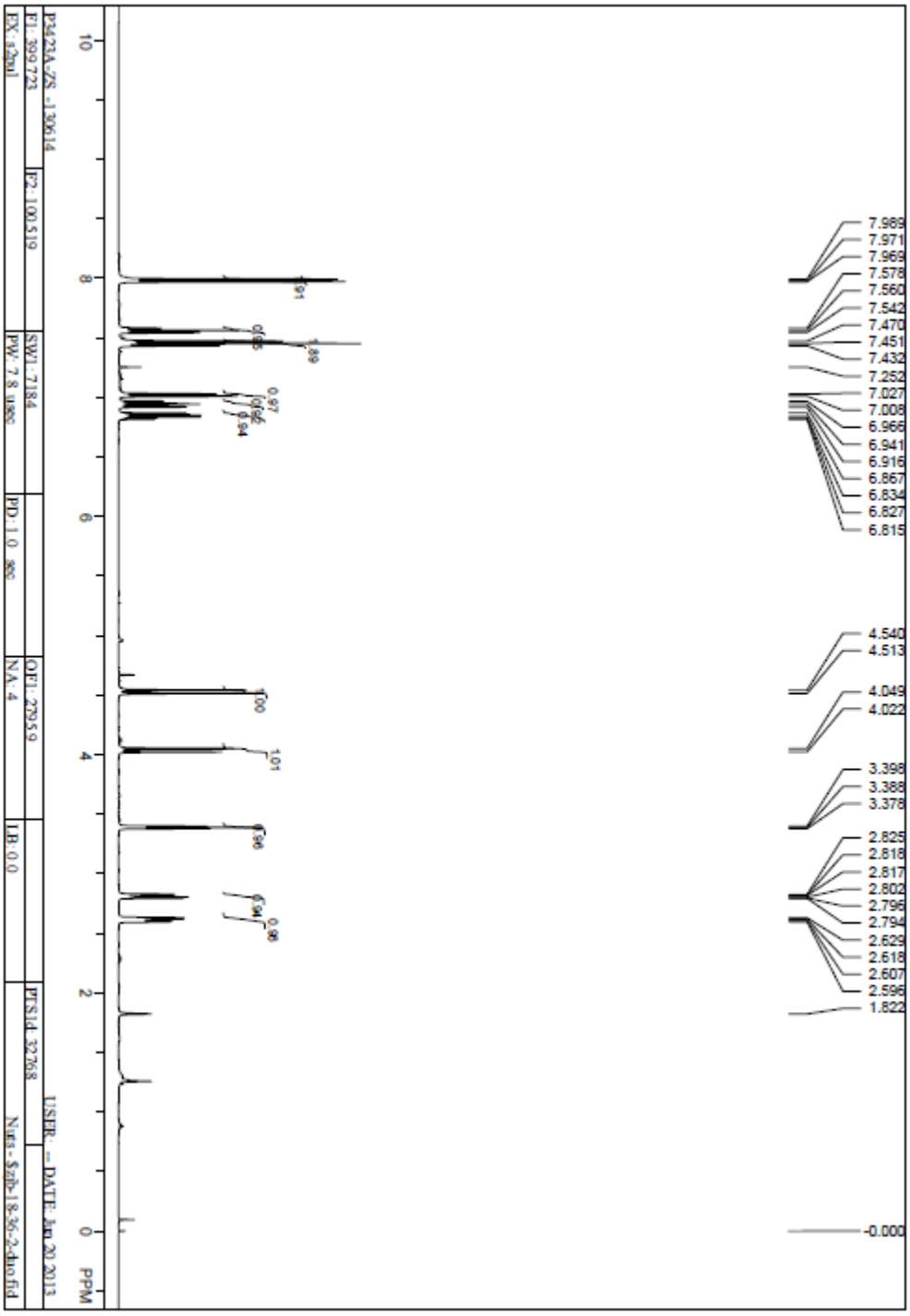
^{13}C NMR (100 M Hz in $CDCl_3$)

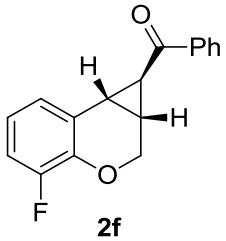




2f

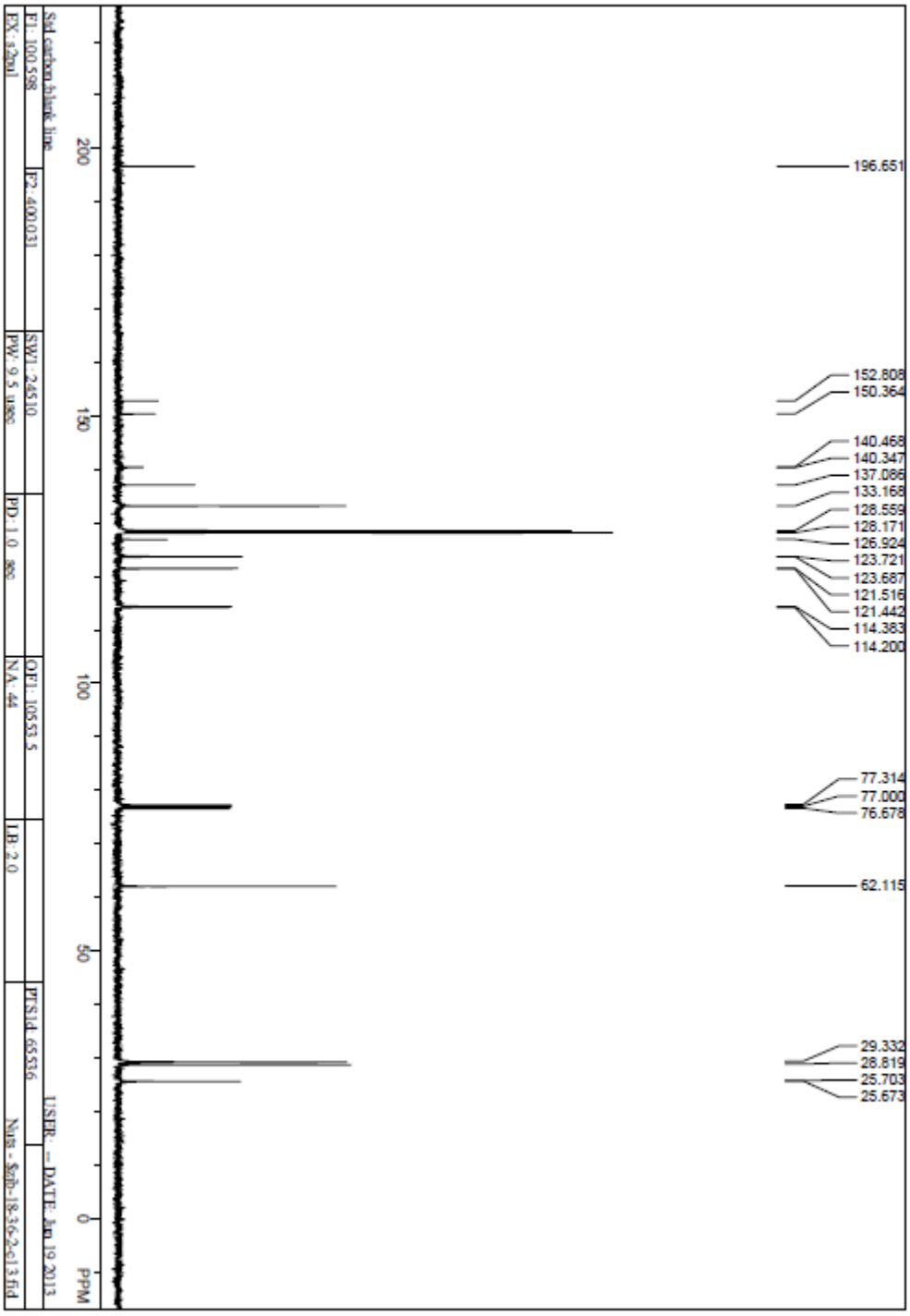
^{1}H NMR (400 M Hz in $CDCl_3$)

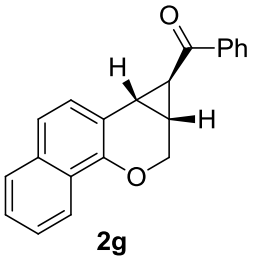




2f

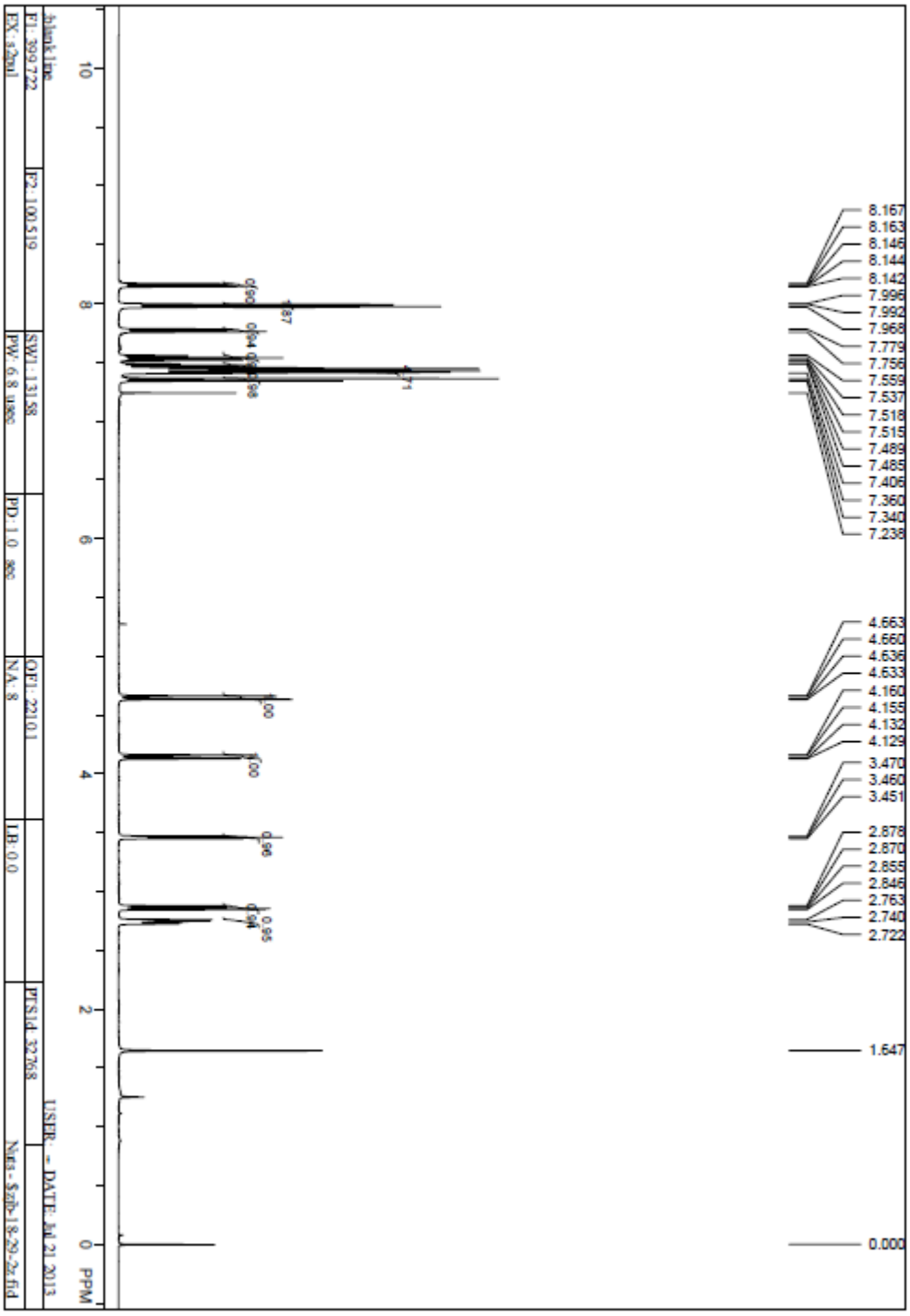
^{13}C NMR (100 M Hz in $CDCl_3$)

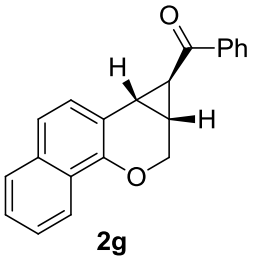




2g

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





2g

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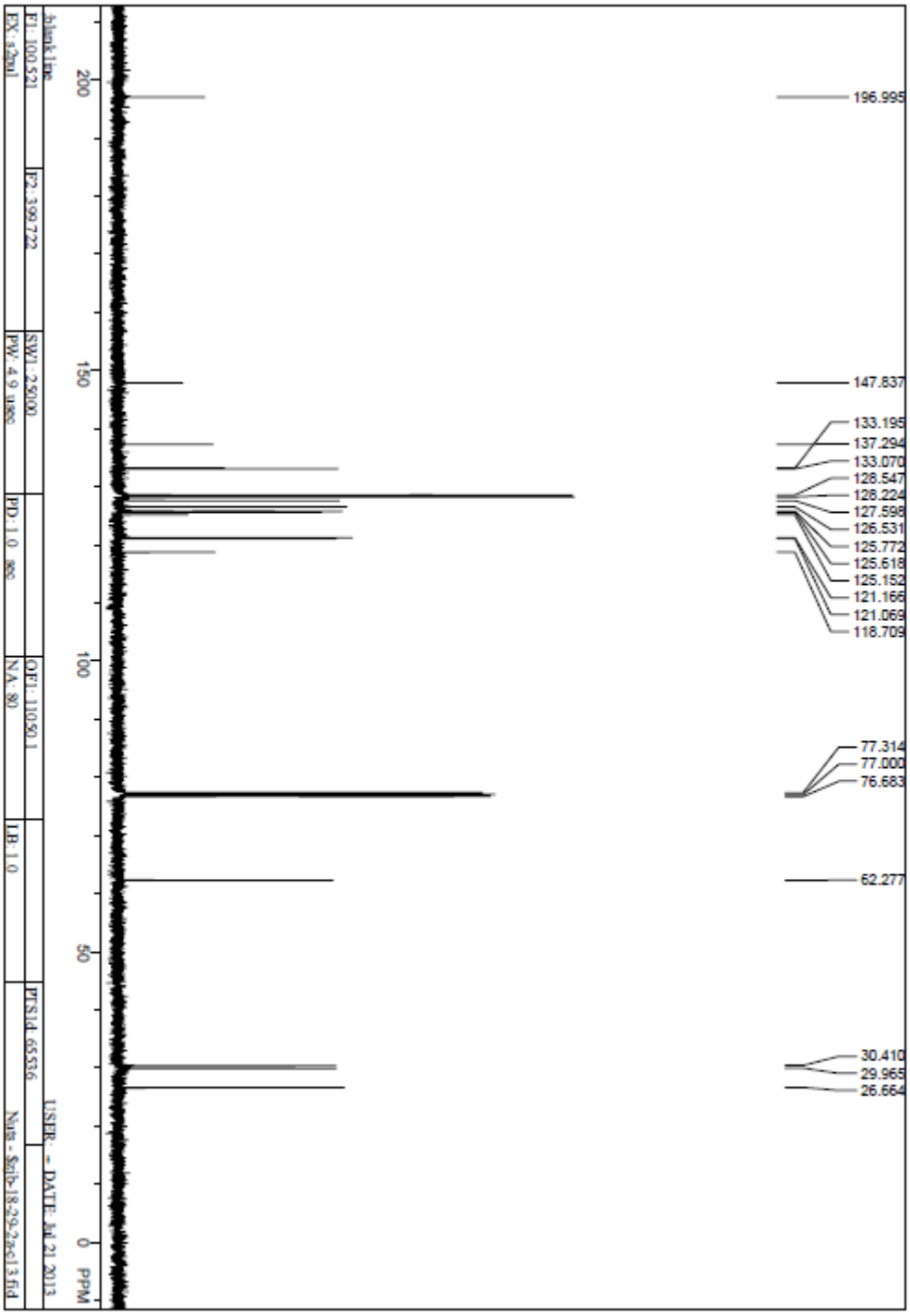
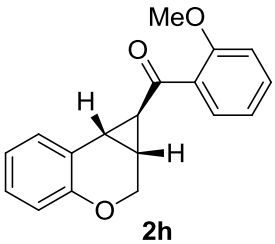
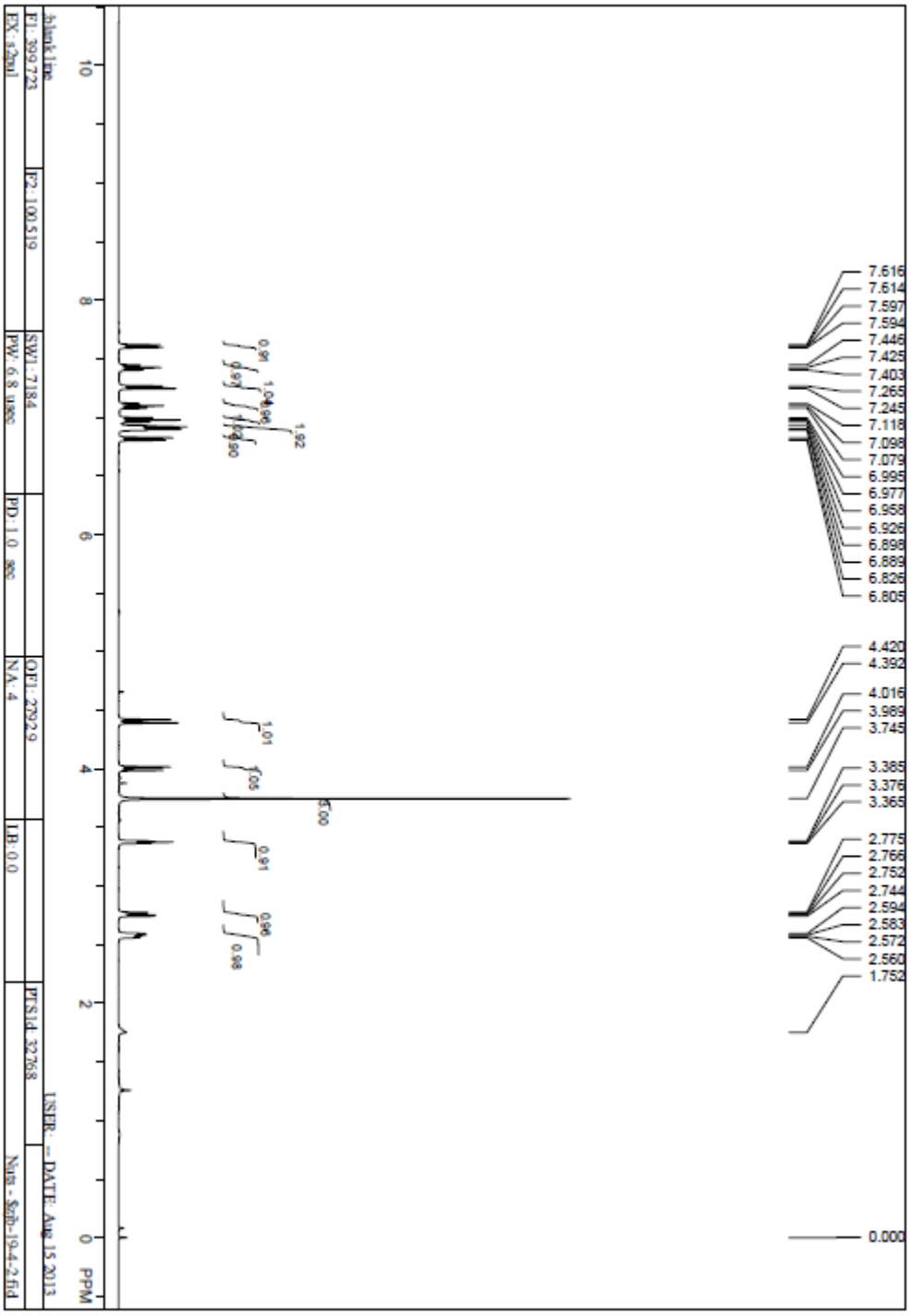
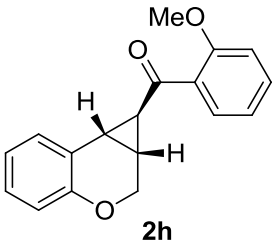




2h

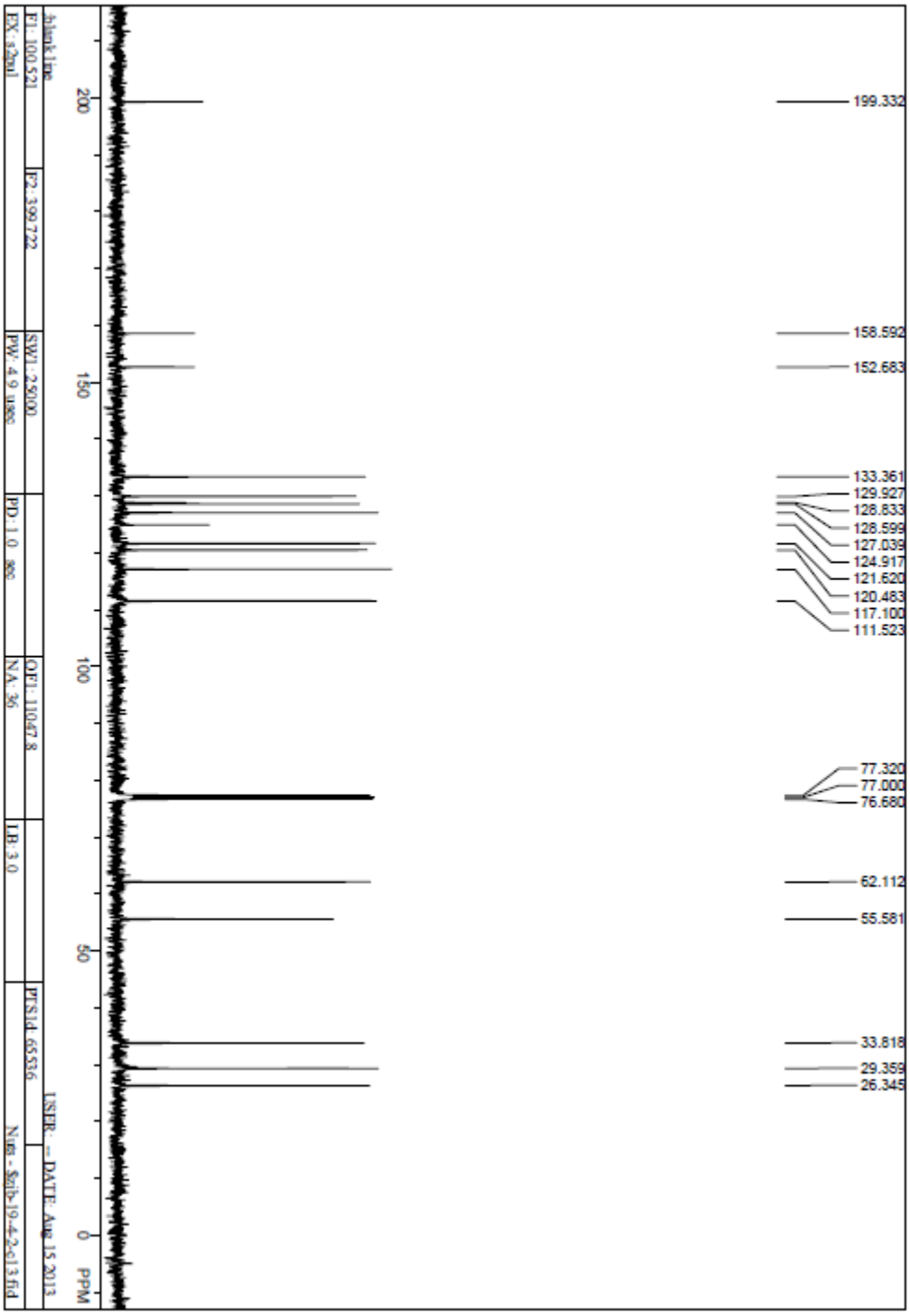
^{1}H NMR (400 M Hz in $CDCl_3$)

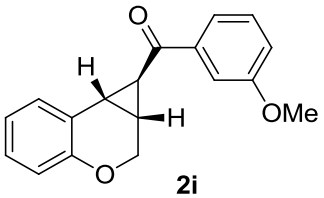




2h

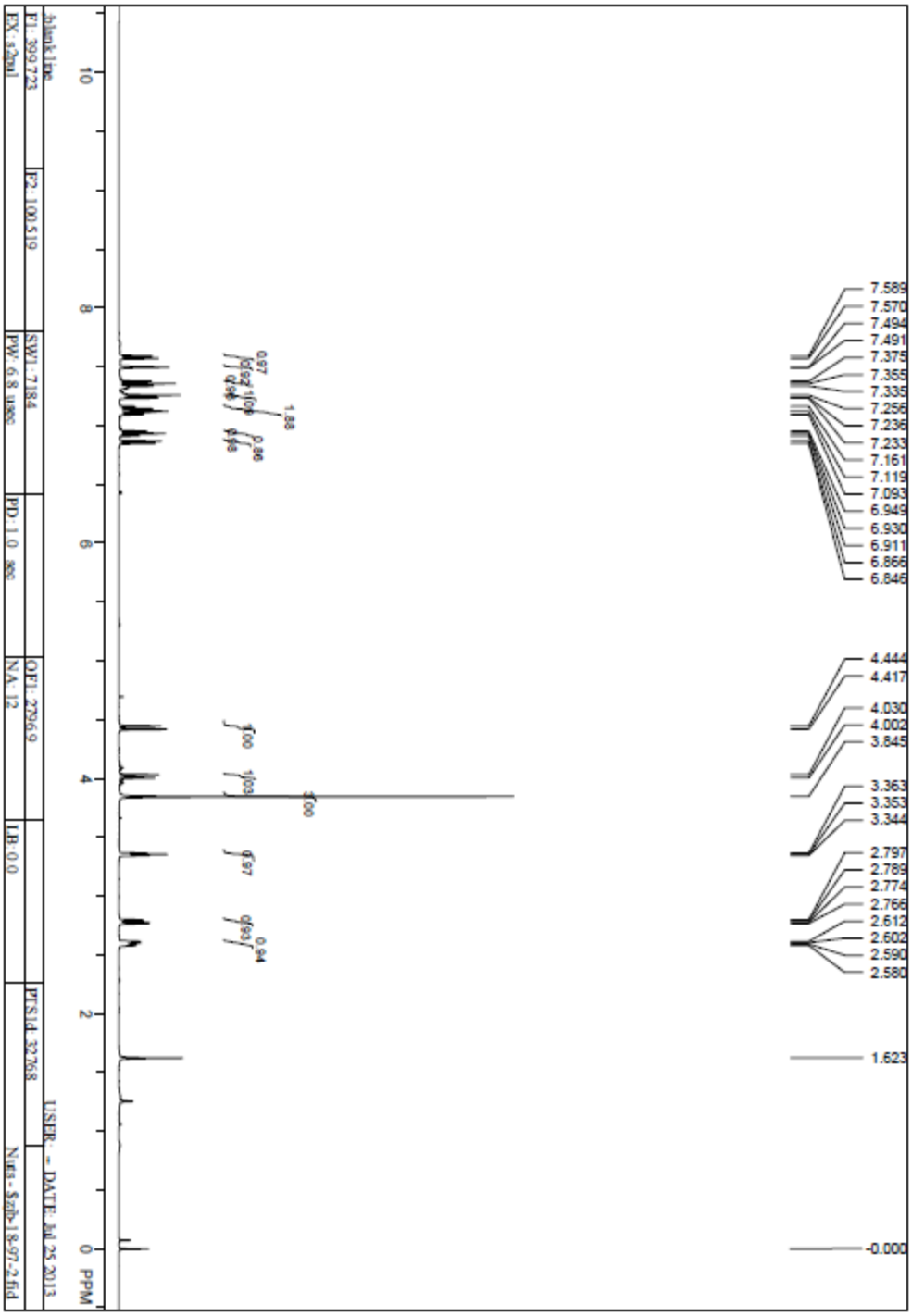
^{13}C NMR (100 M Hz in $CDCl_3$)

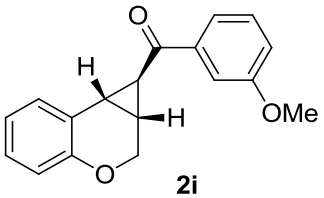




2i

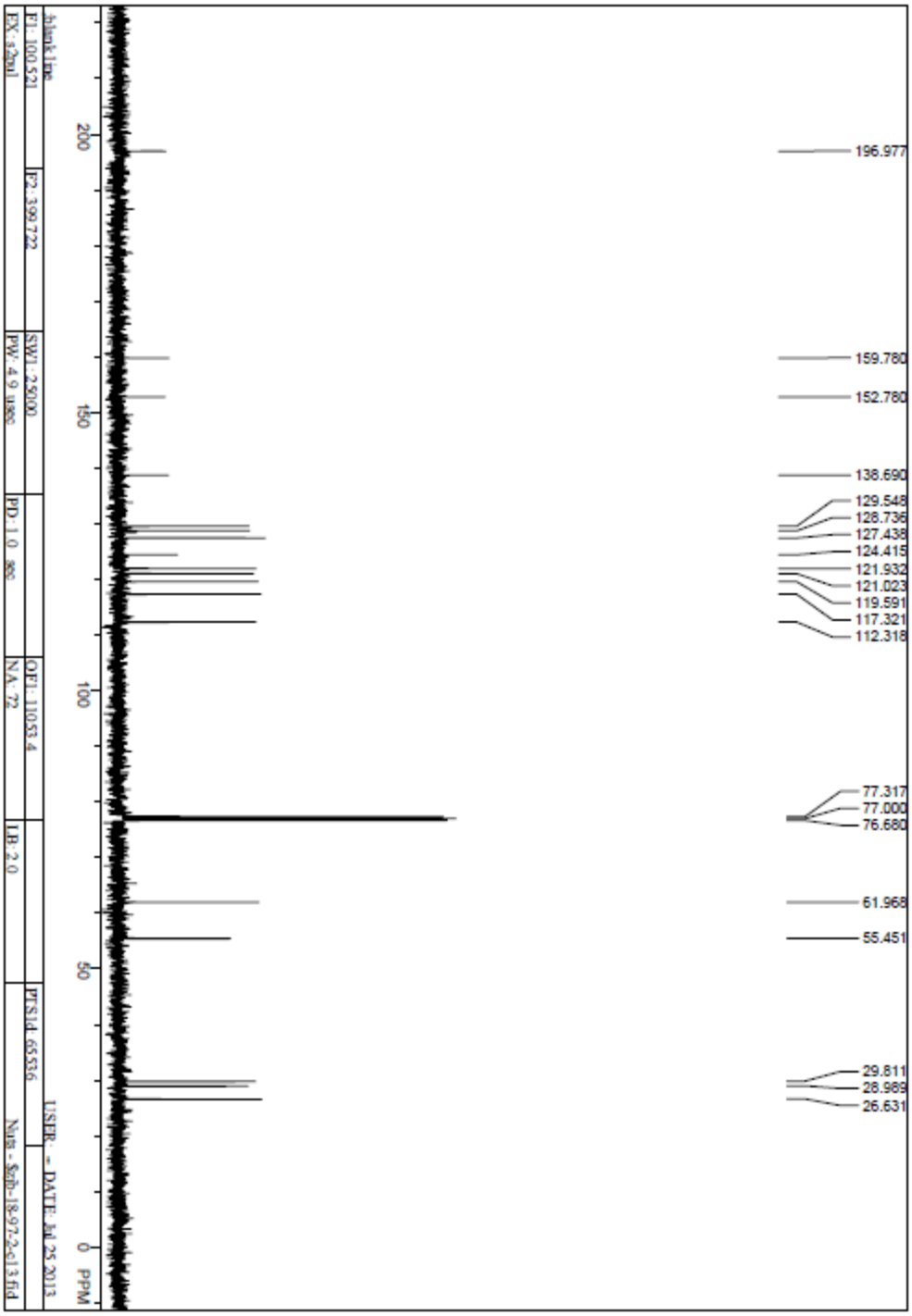
^{1}H NMR (400 M Hz in $CDCl_3$)

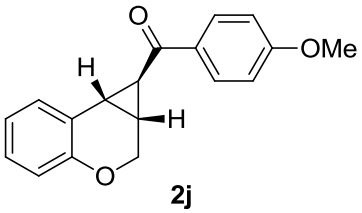




2i

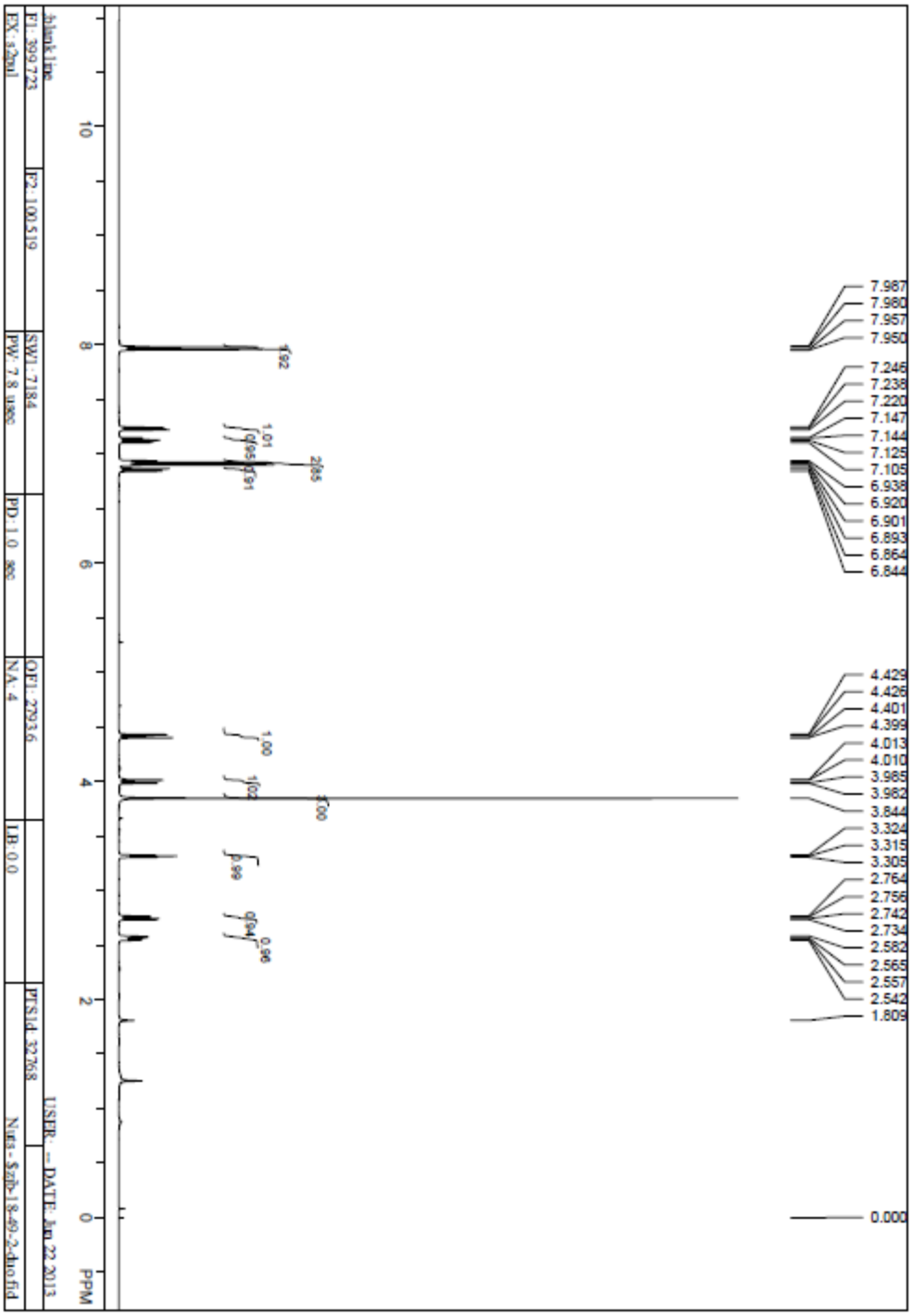
^{13}C NMR (100 M Hz in $CDCl_3$)

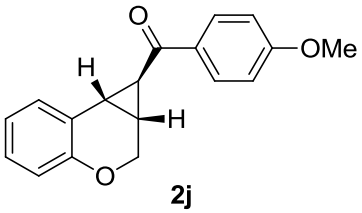




2j

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





2j

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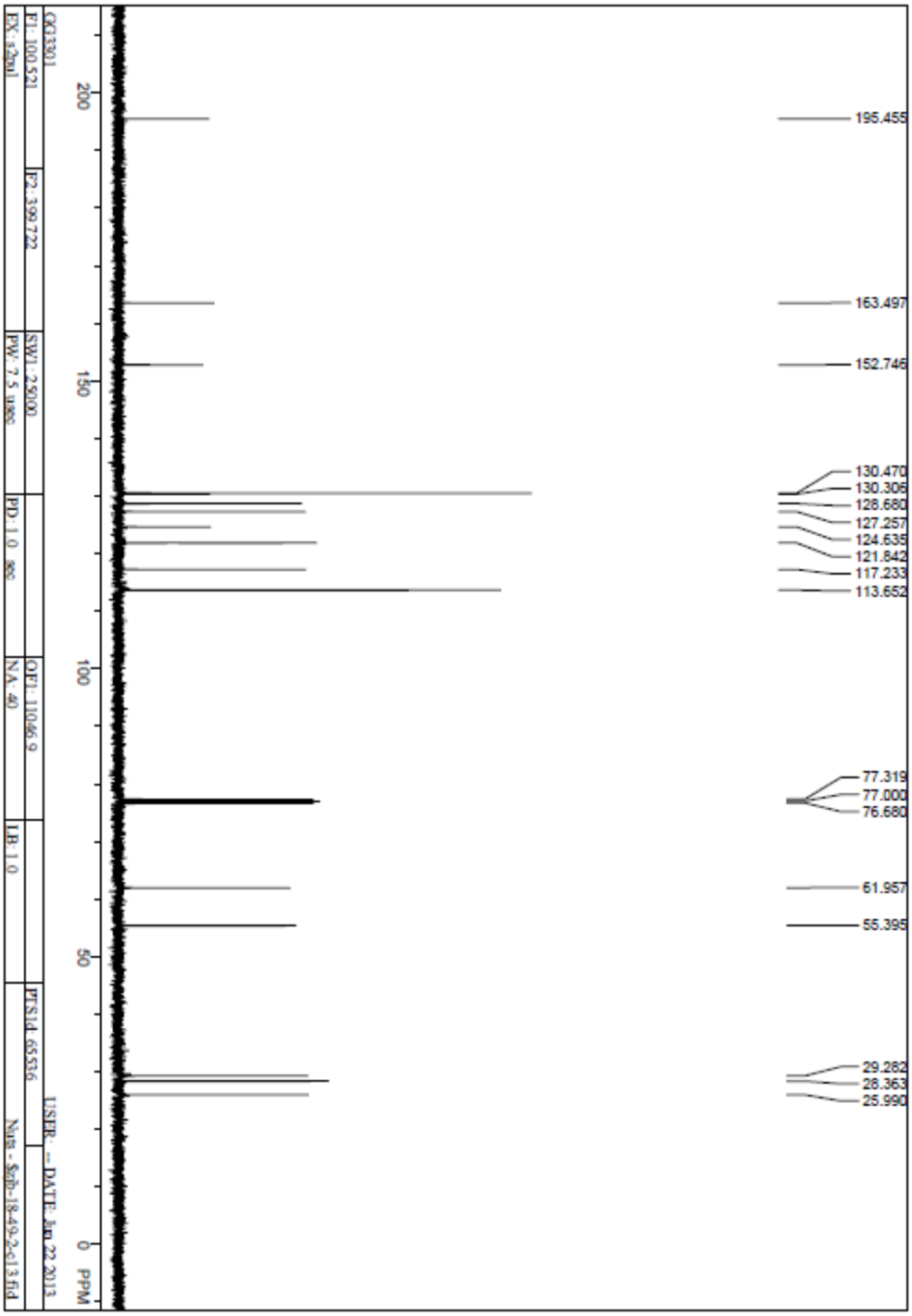

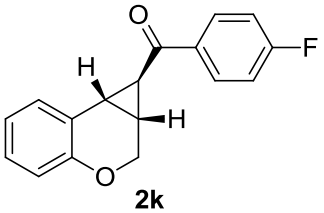

2k

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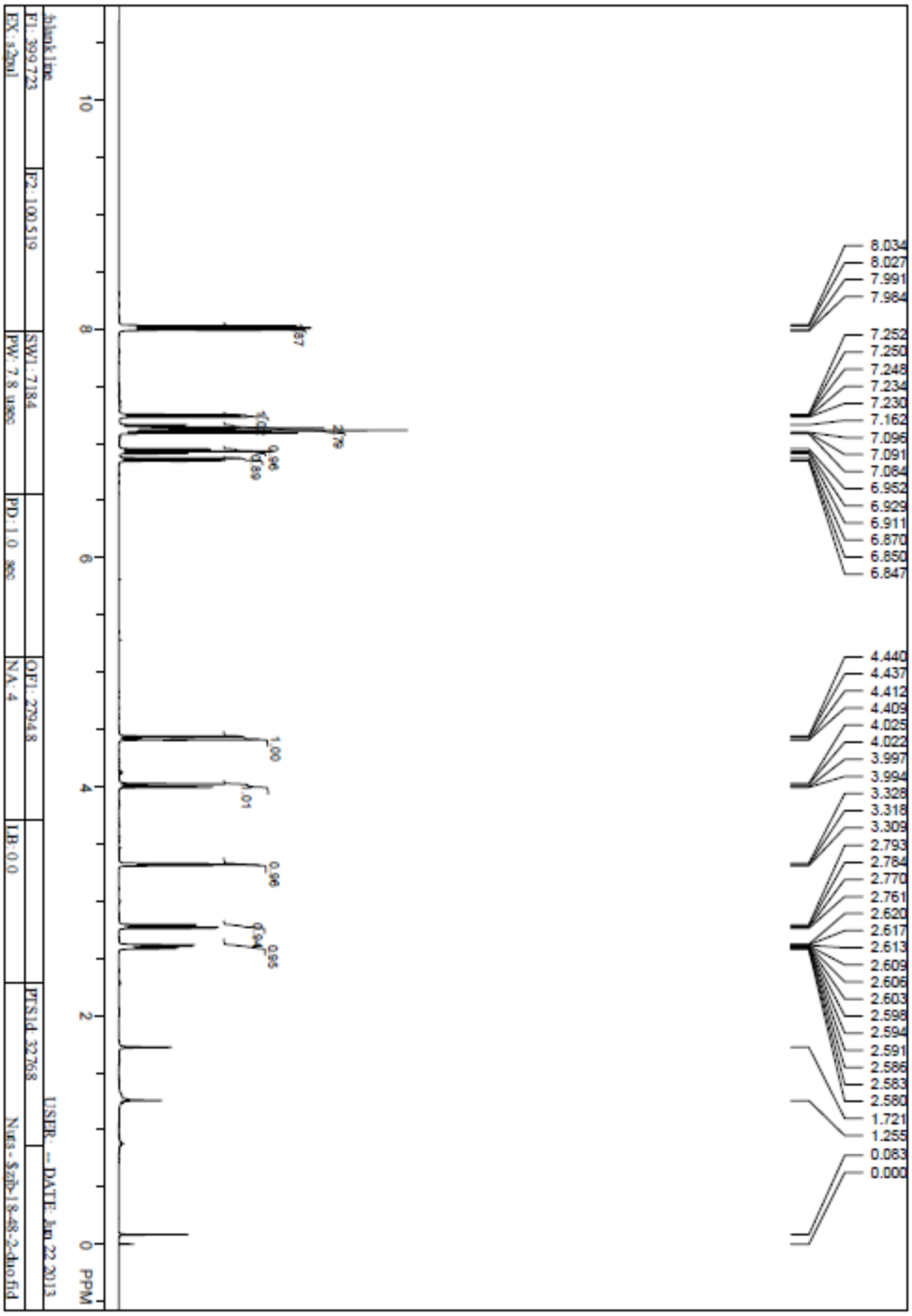

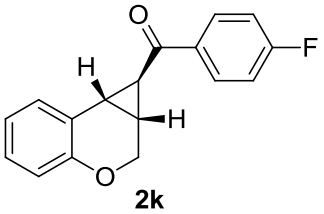

2k

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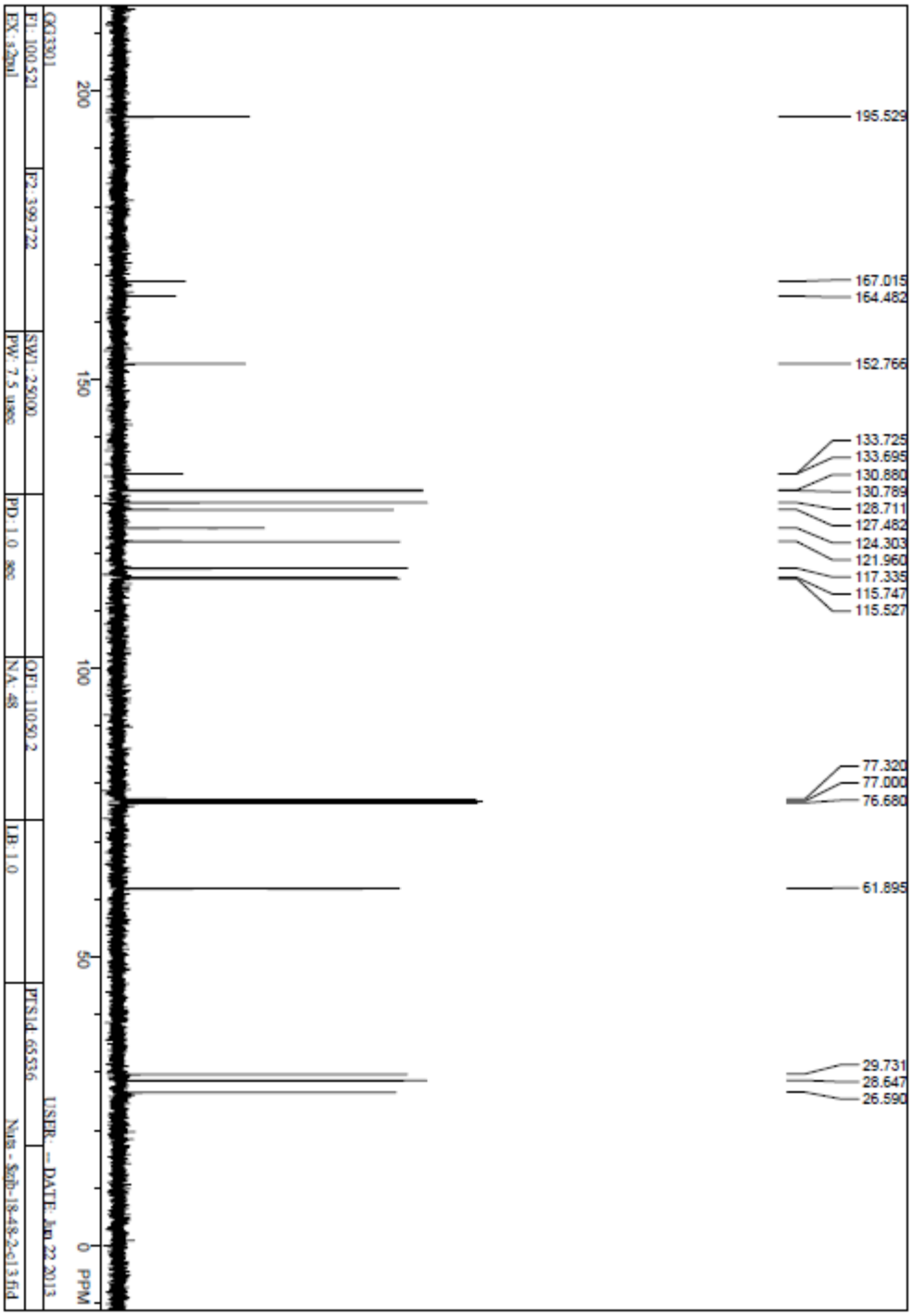

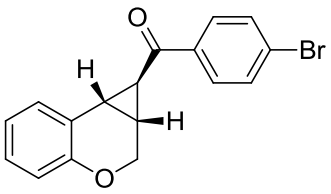

2l

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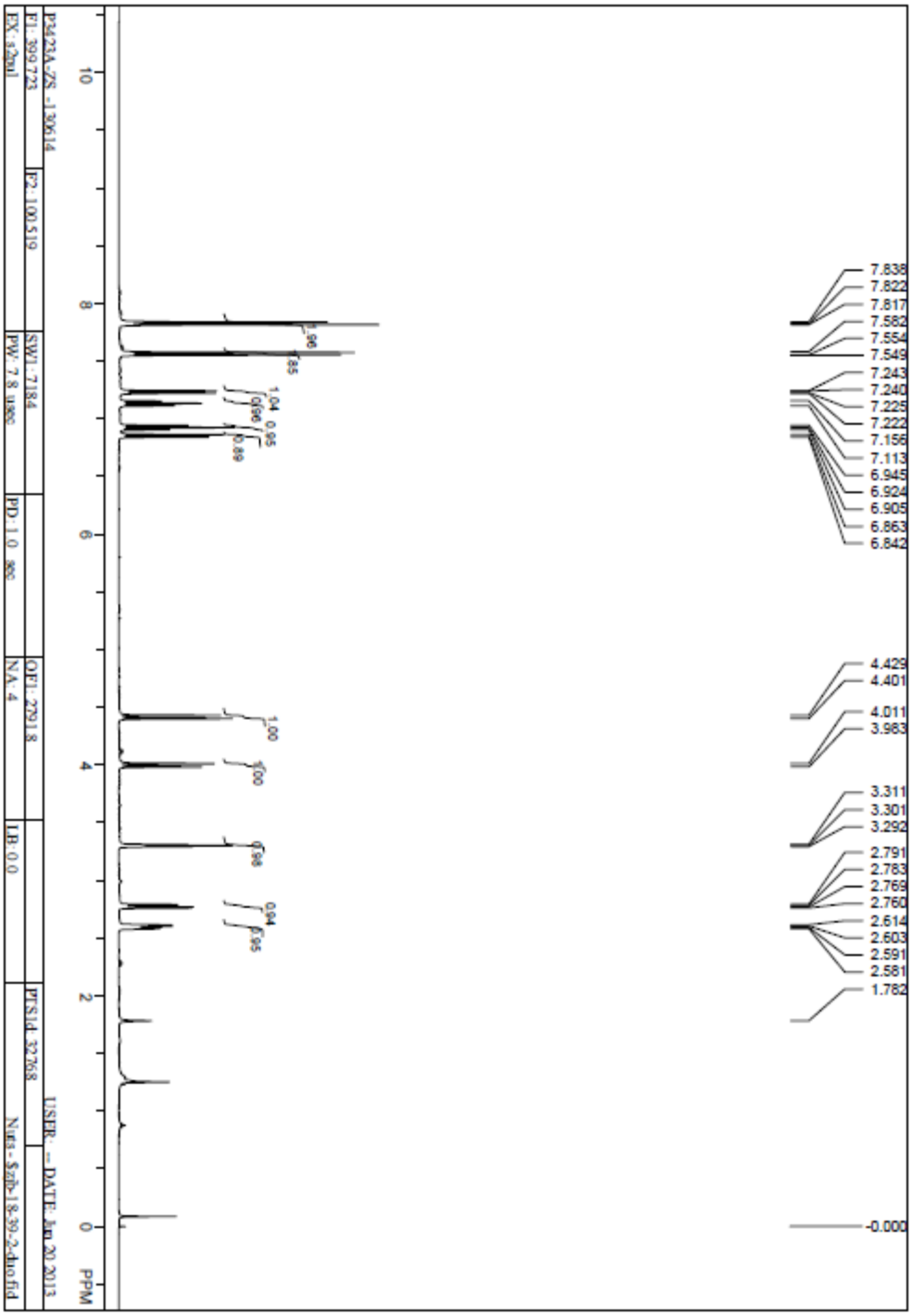
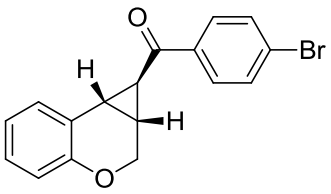
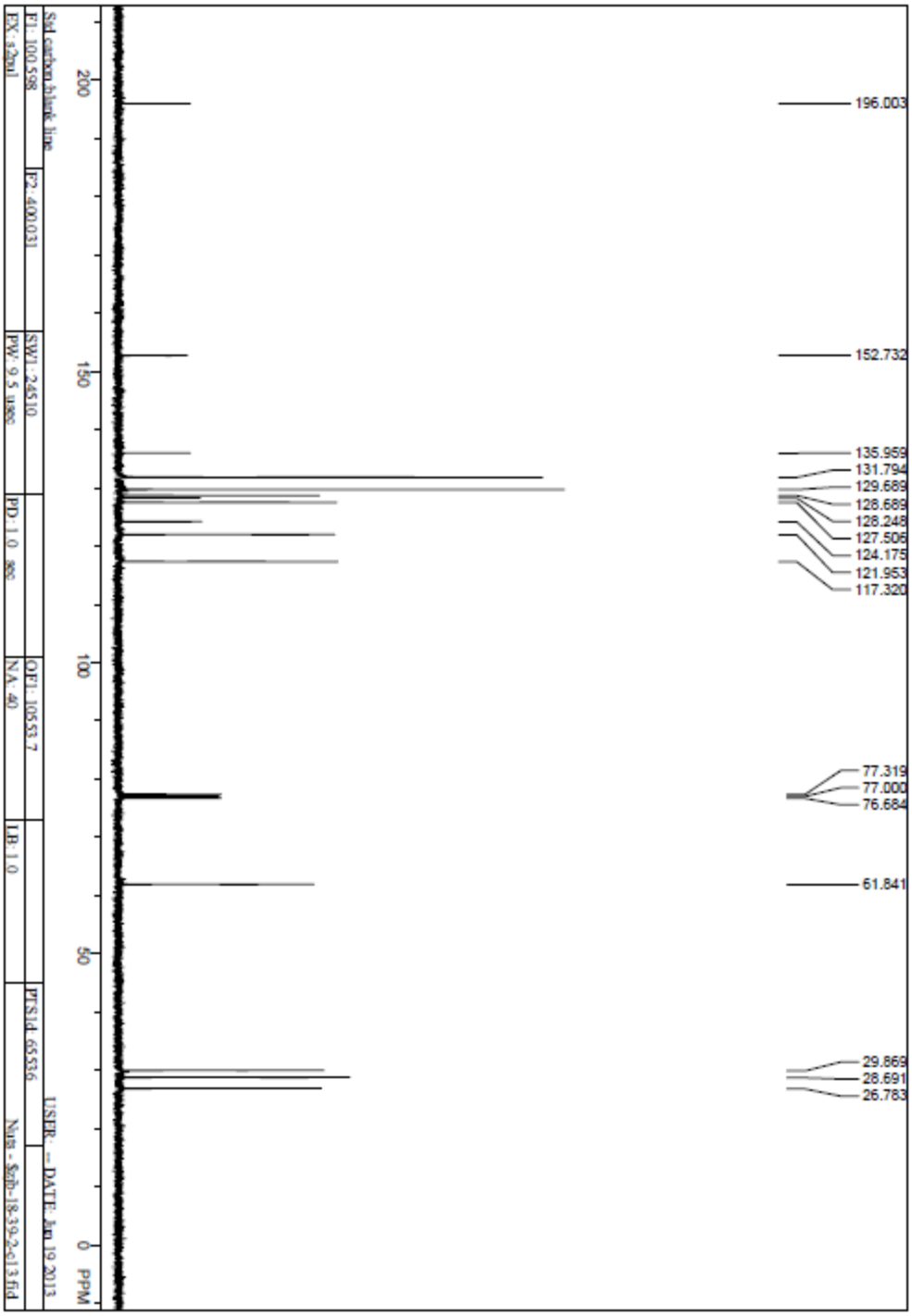
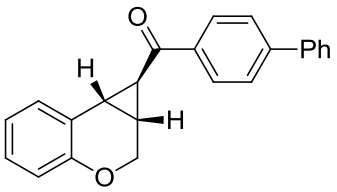




2l

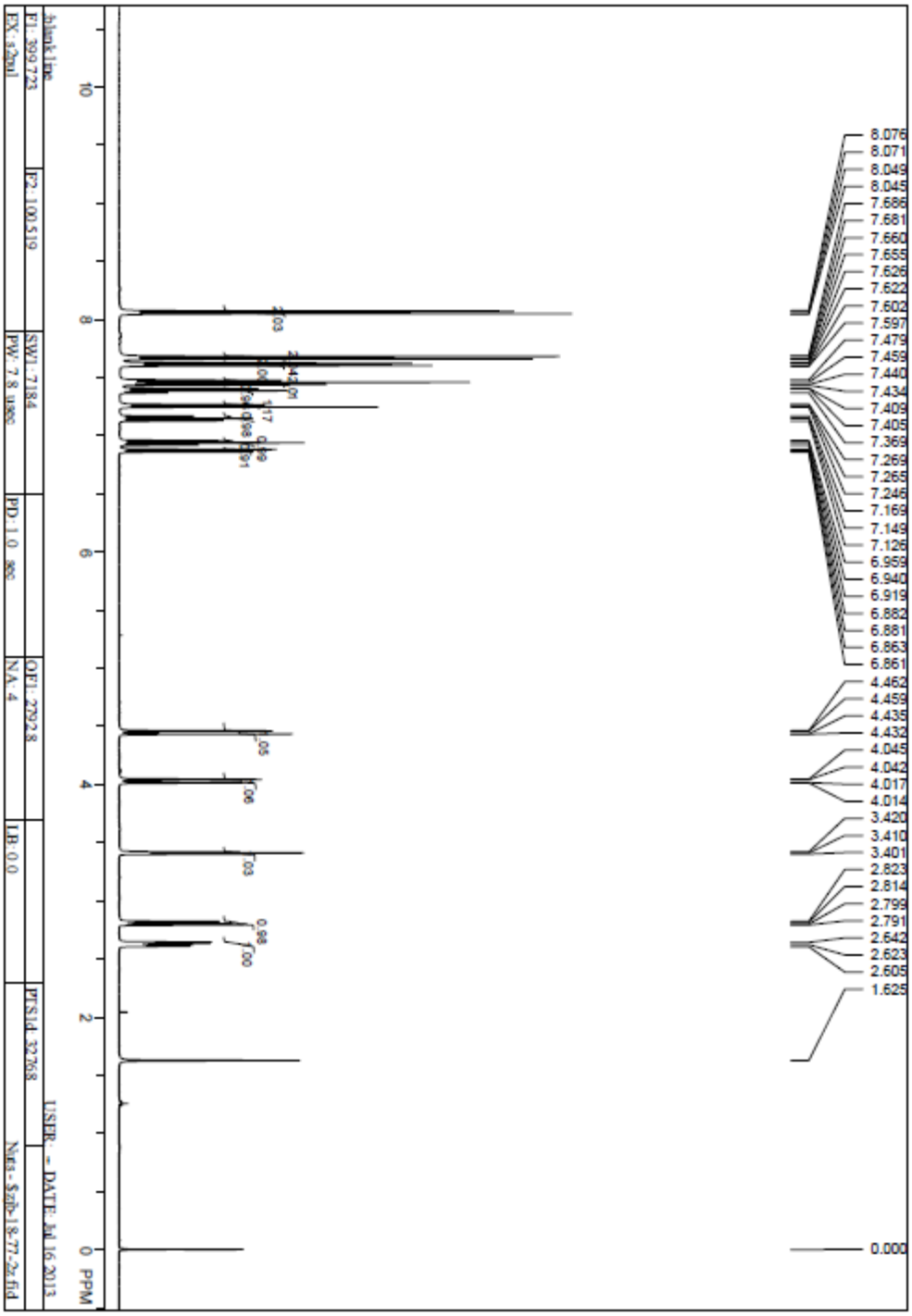
^{13}C NMR (100 M Hz in $CDCl_3$)

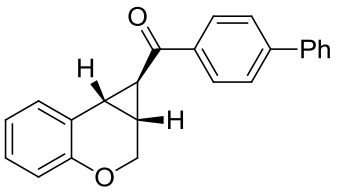




2m

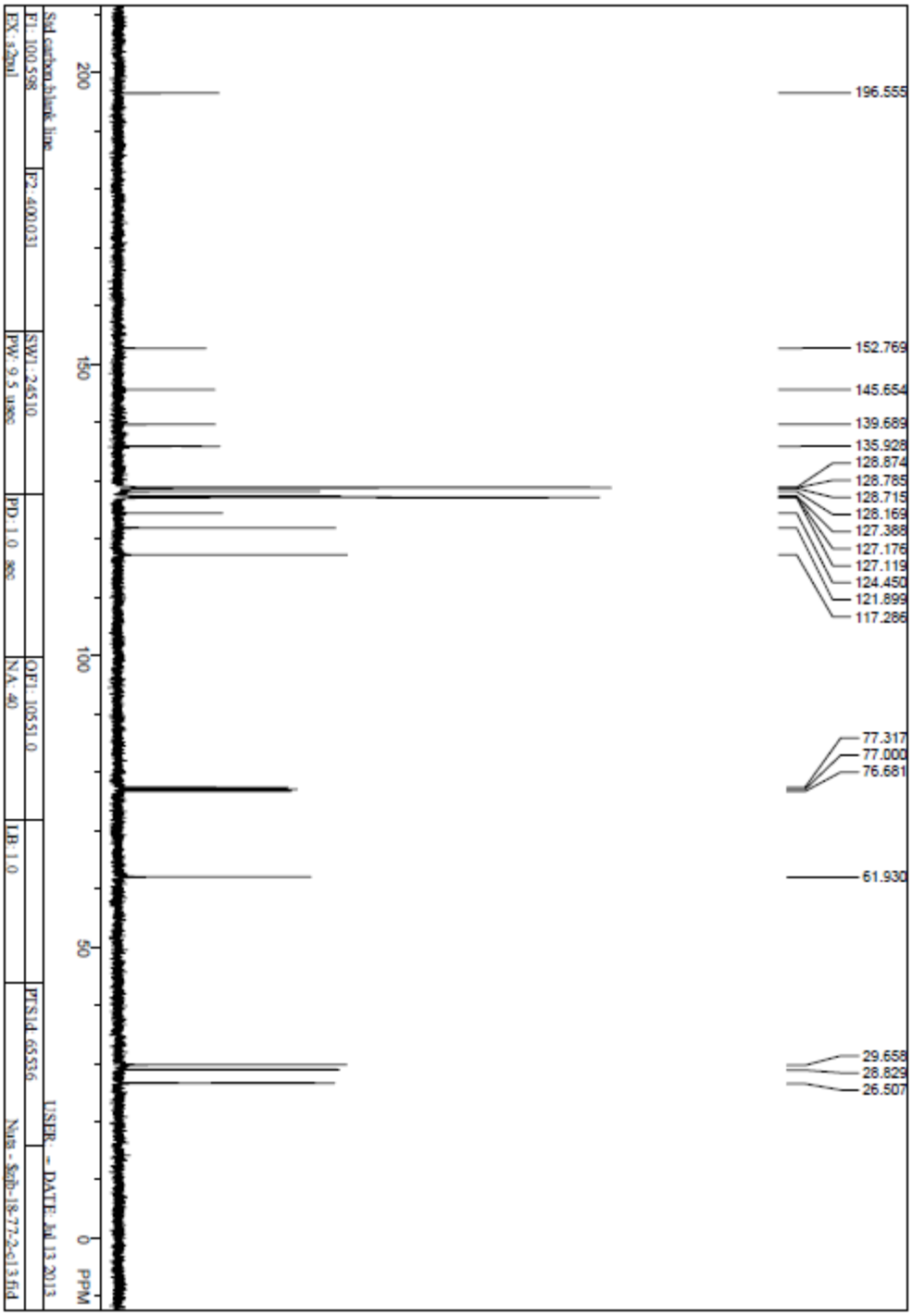
^{1}H NMR (400 M Hz in $CDCl_3$)

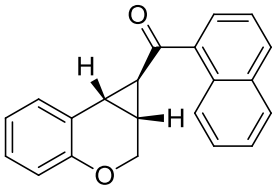




2m

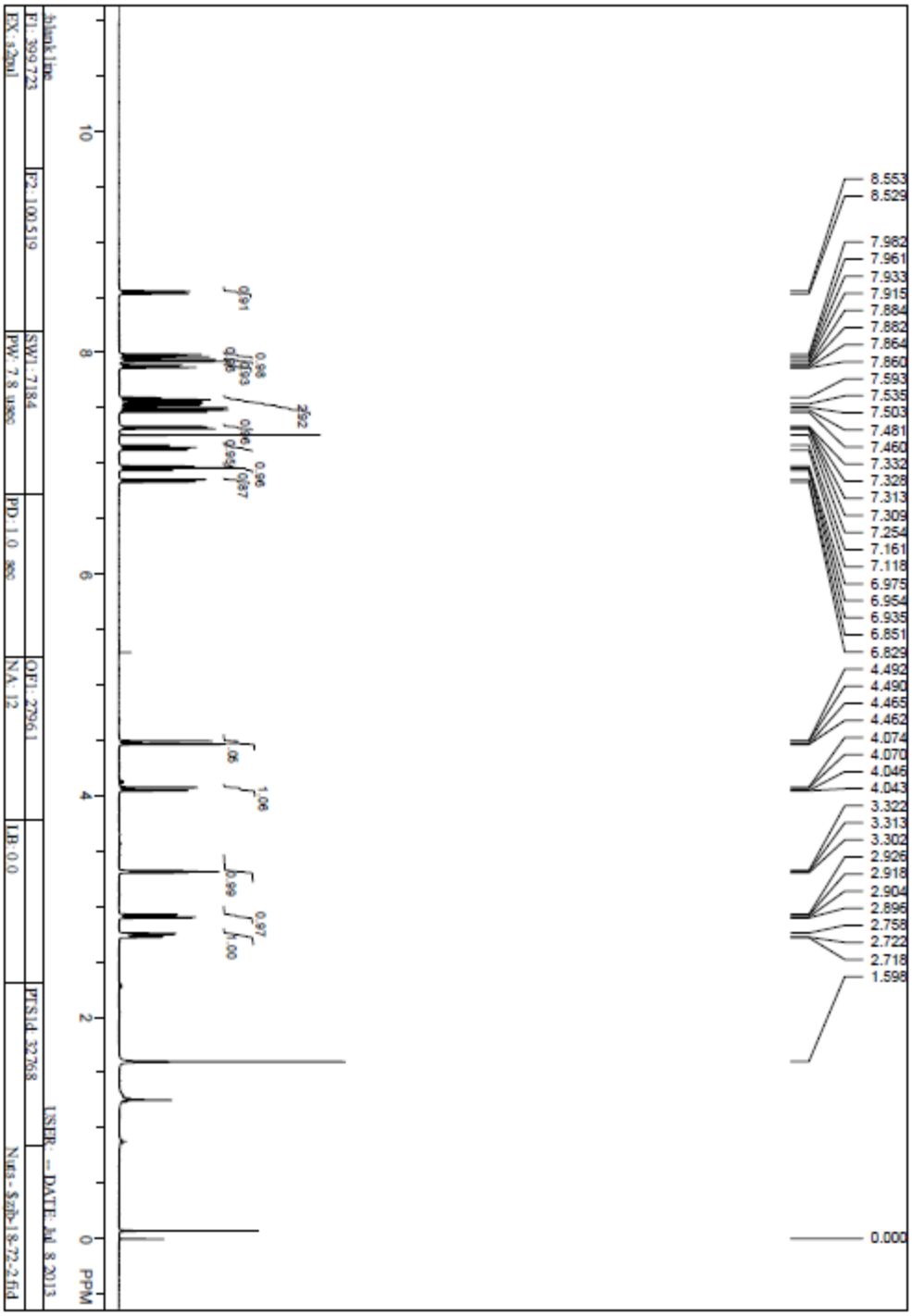
^{13}C NMR (100 M Hz in $CDCl_3$)

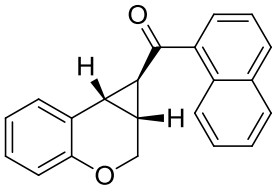




2n

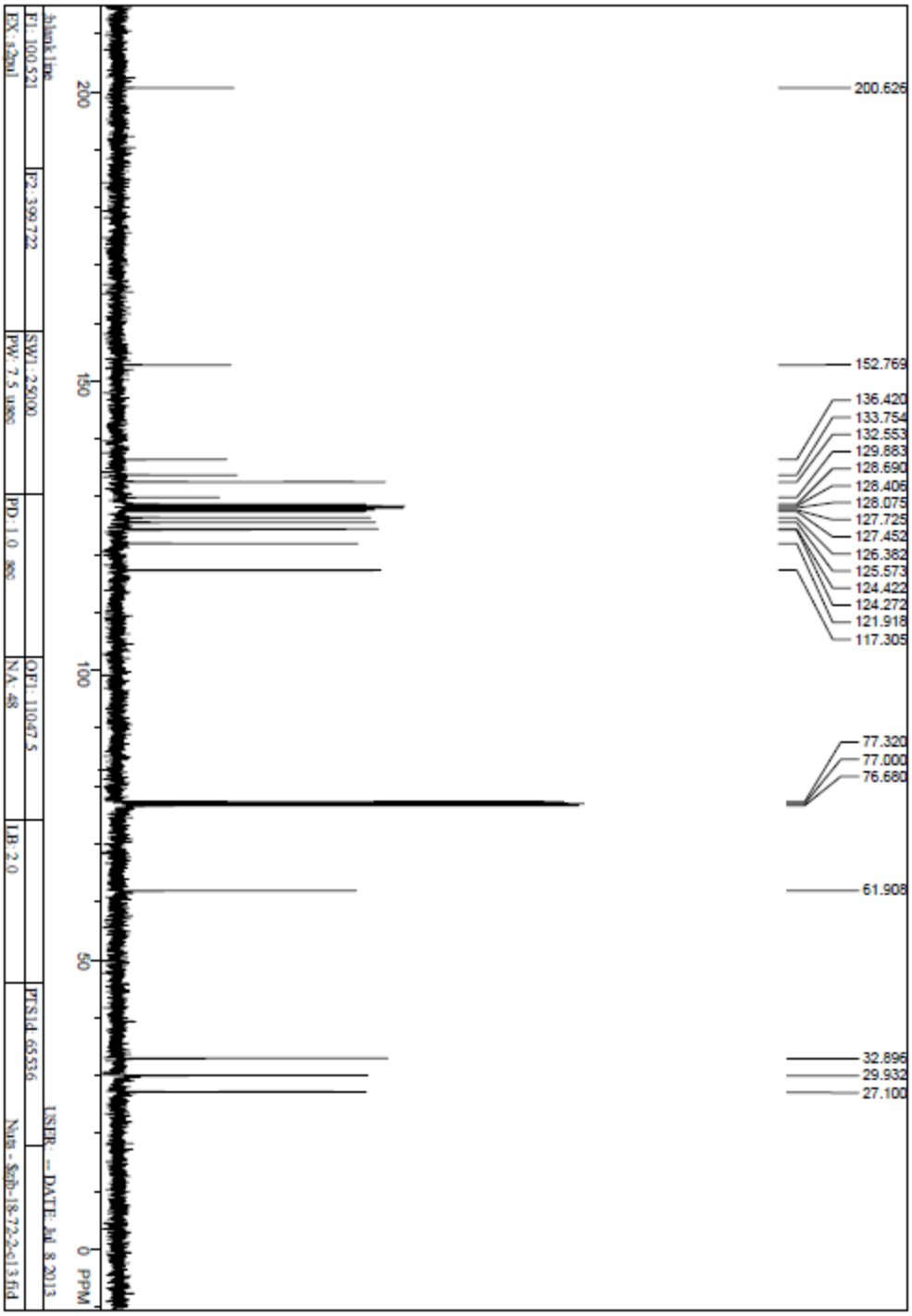
^{1}H NMR (400 M Hz in $CDCl_3$)

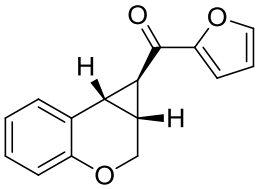




2n

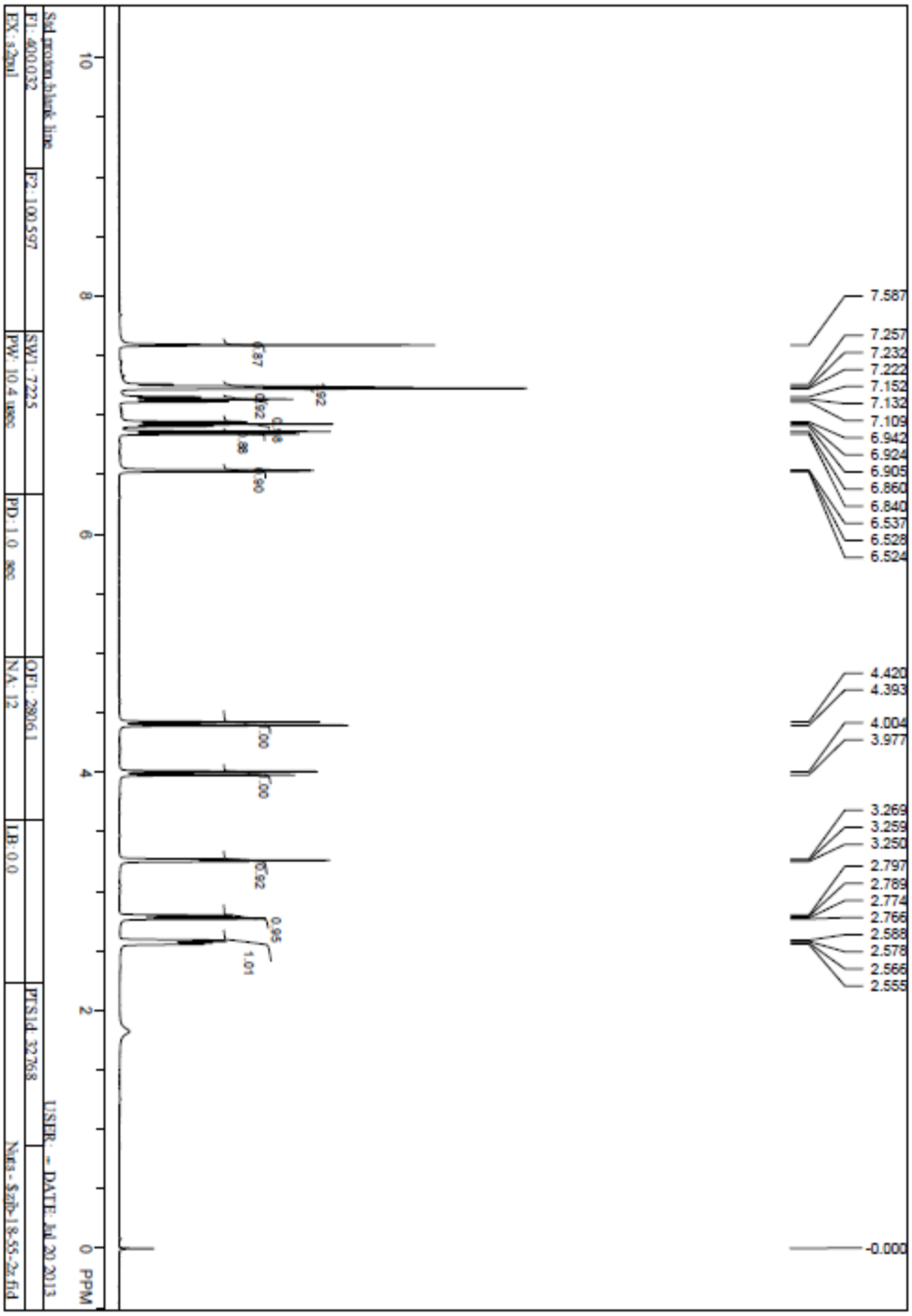
^{13}C NMR (100 M Hz in $CDCl_3$)

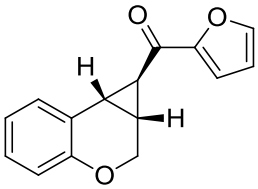




2o

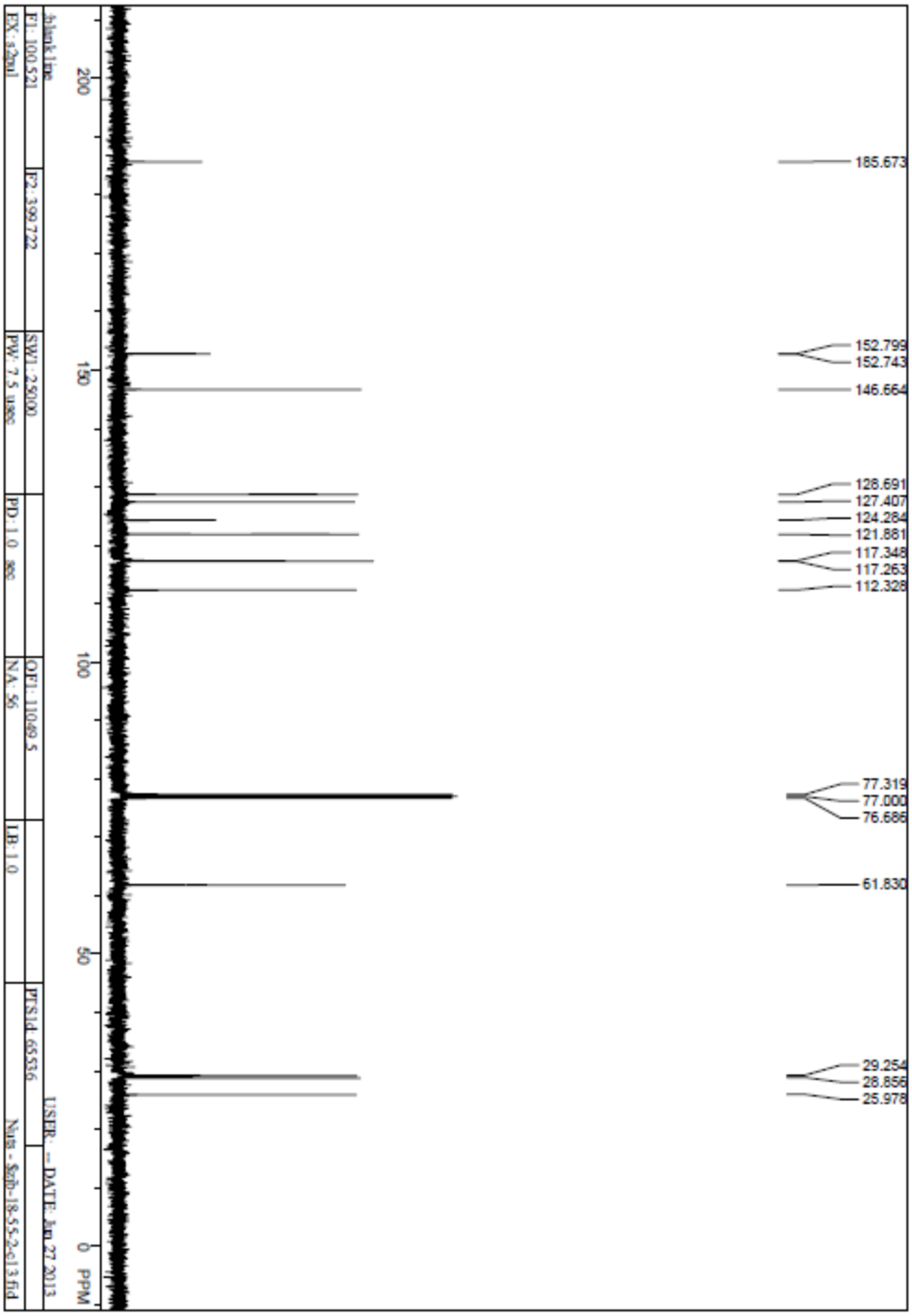
^{1}H NMR (400 M Hz in $CDCl_3$)

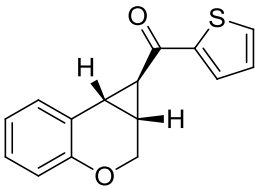




2o

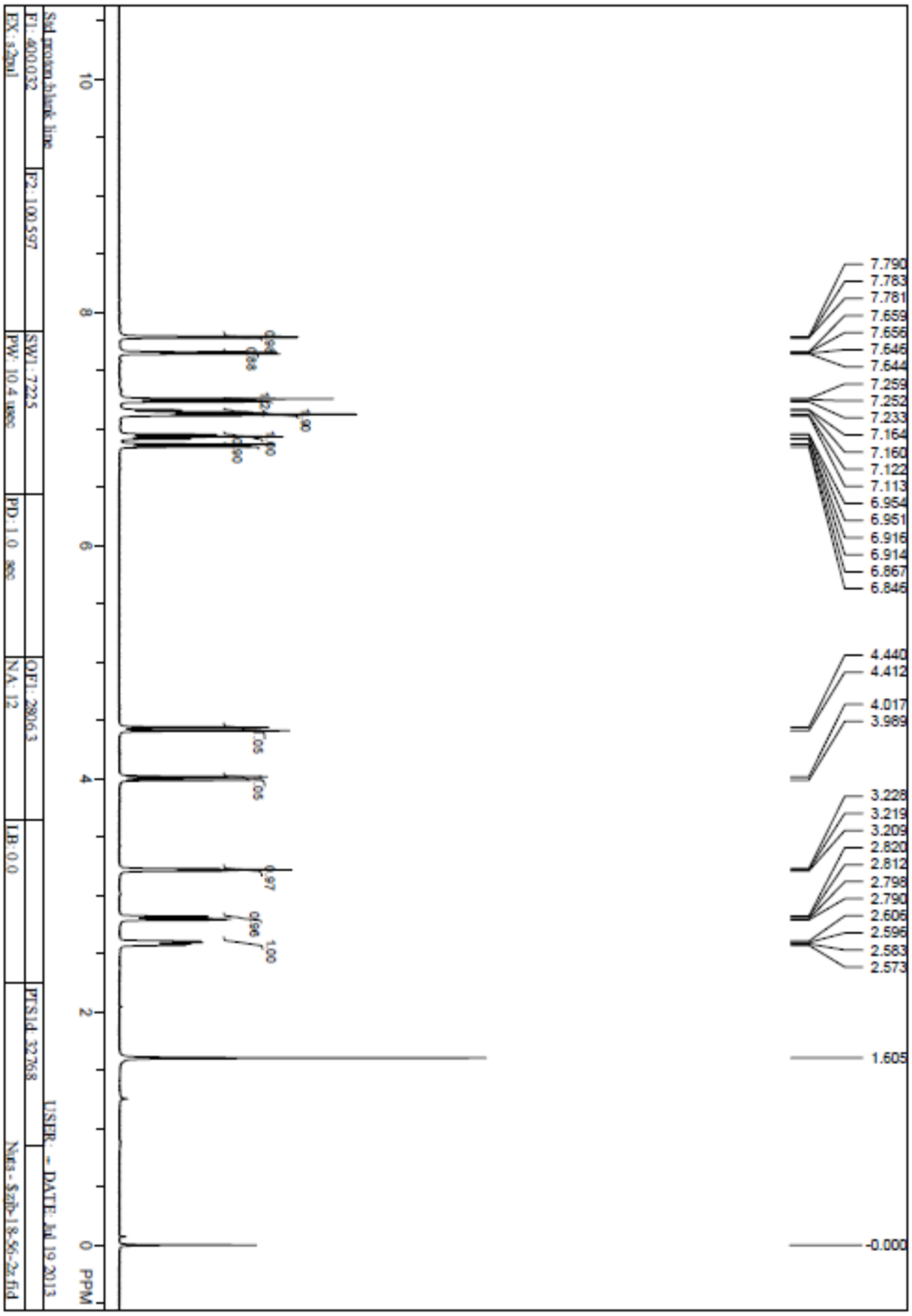
^{13}C NMR (100 M Hz in $CDCl_3$)

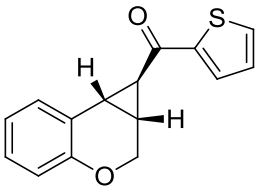




2p

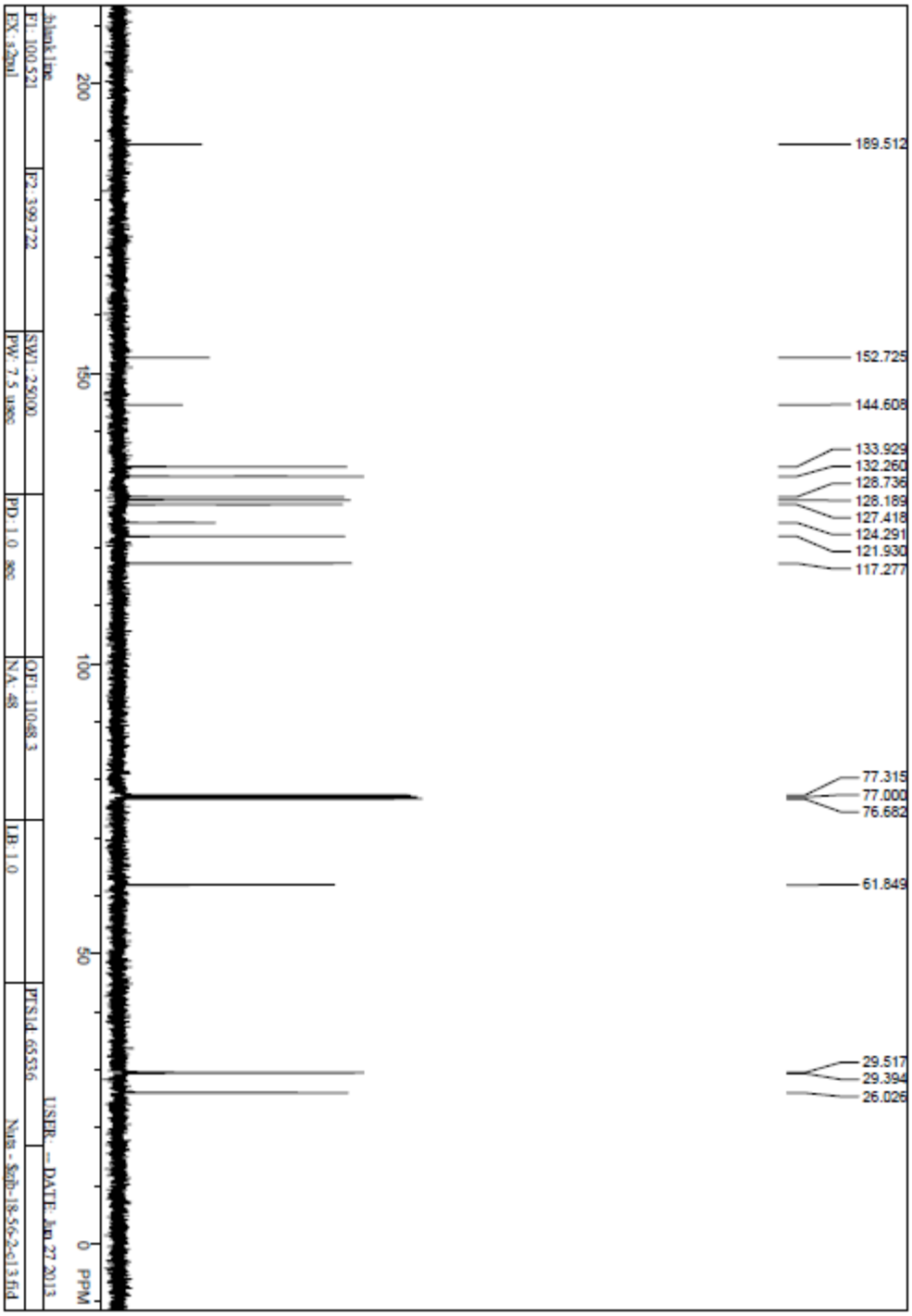
^{1}H NMR (400 M Hz in $CDCl_3$)

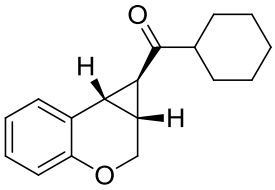




2p

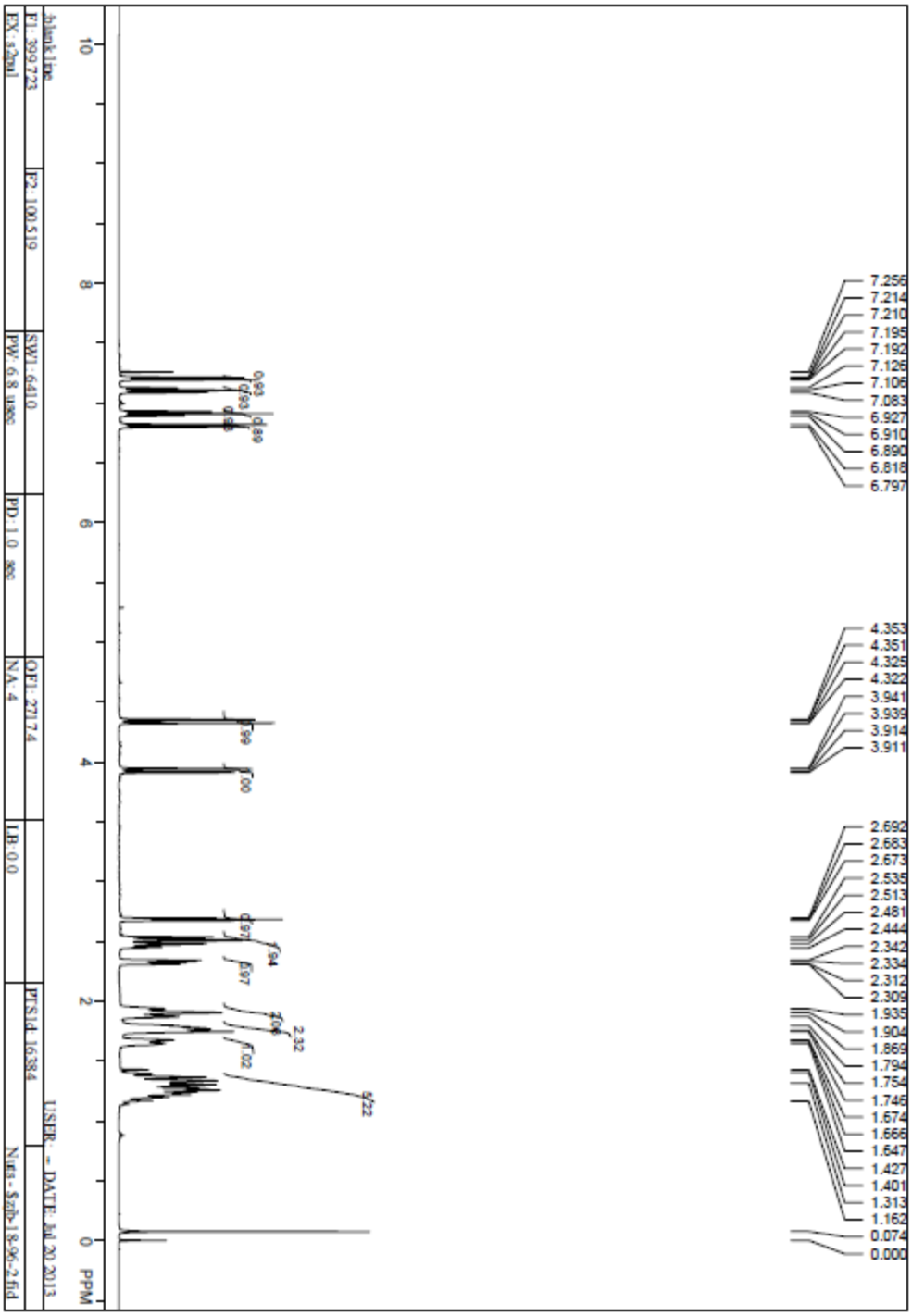
^{13}C NMR (100 M Hz in $CDCl_3$)

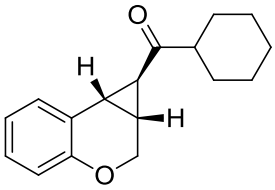




2q

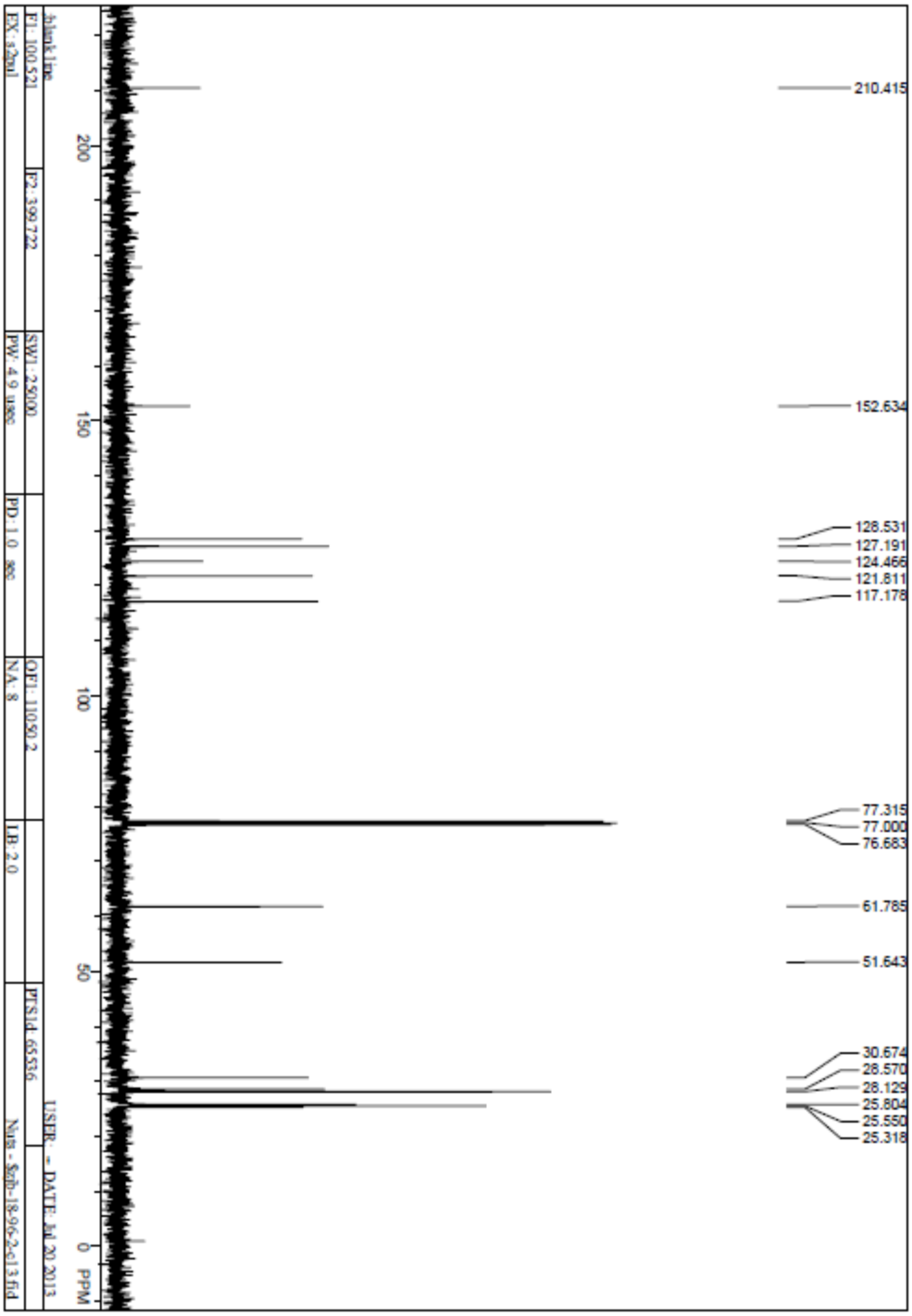
^{1}H NMR (400 M Hz in $CDCl_3$)

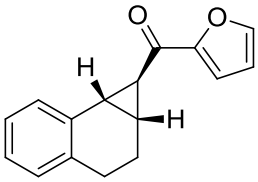




2q

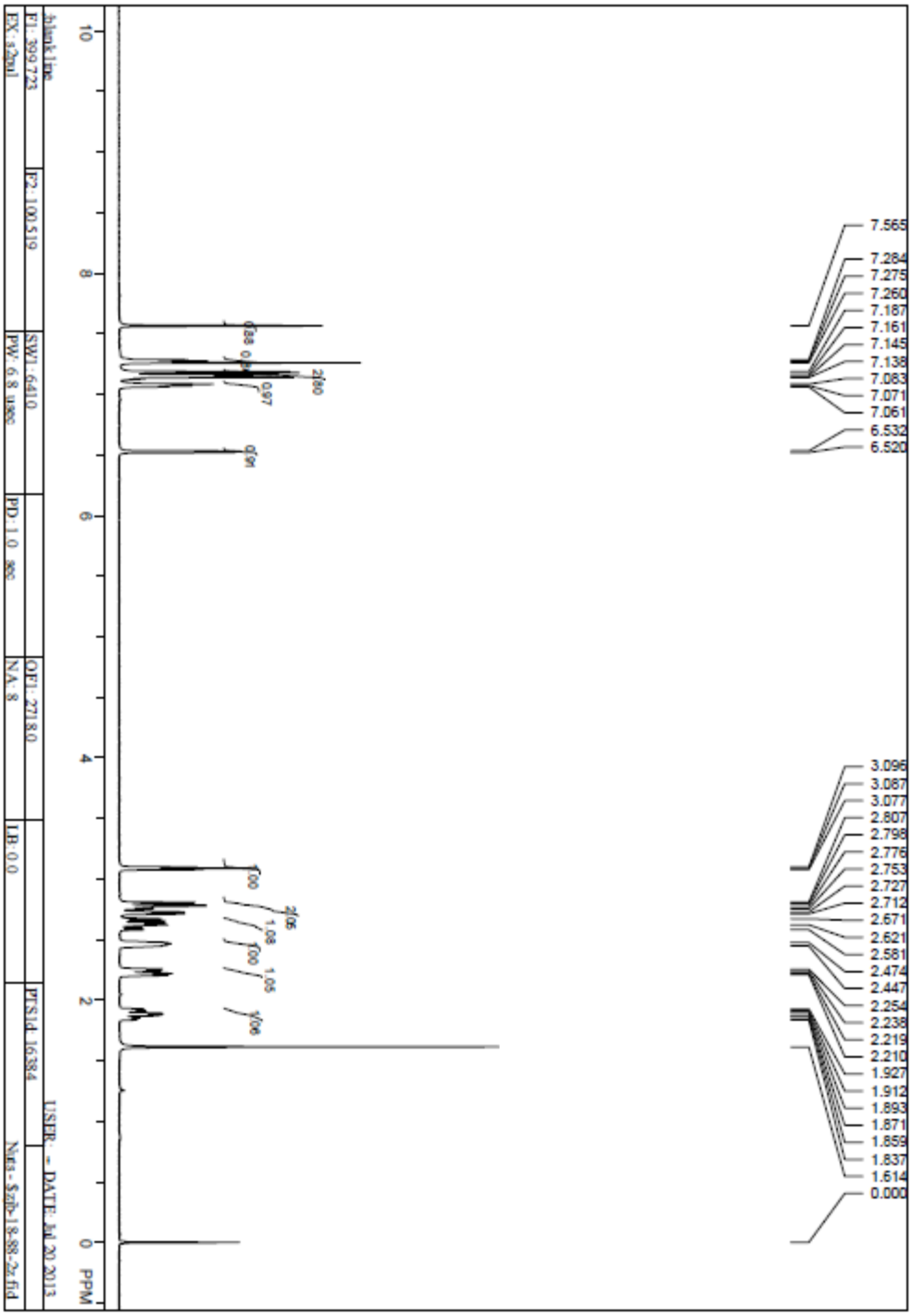
^{13}C NMR (100 M Hz in $CDCl_3$)

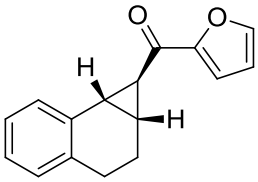




2r

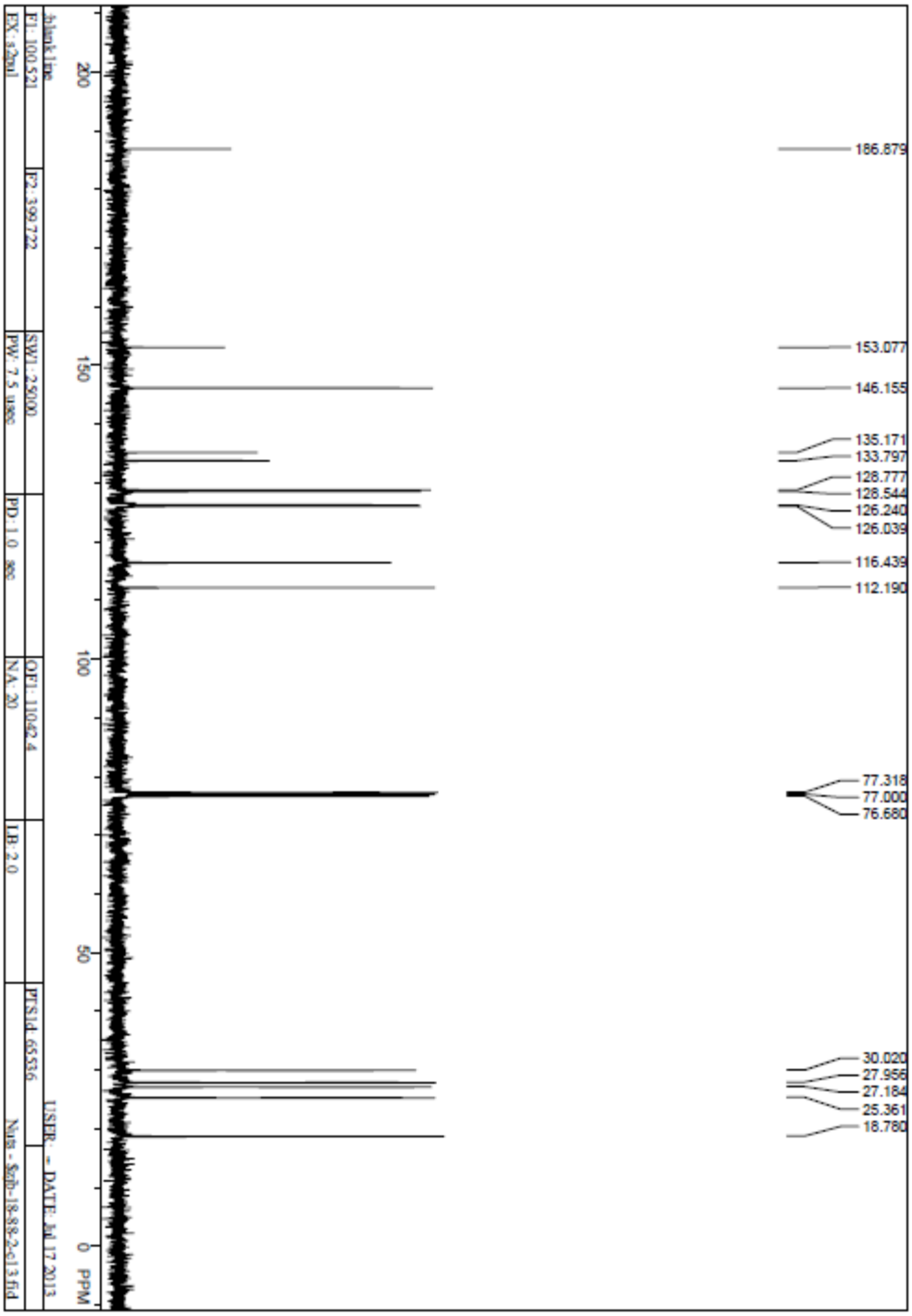
^{1}H NMR (400 M Hz in $CDCl_3$)

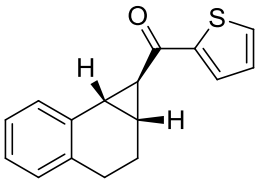




2r

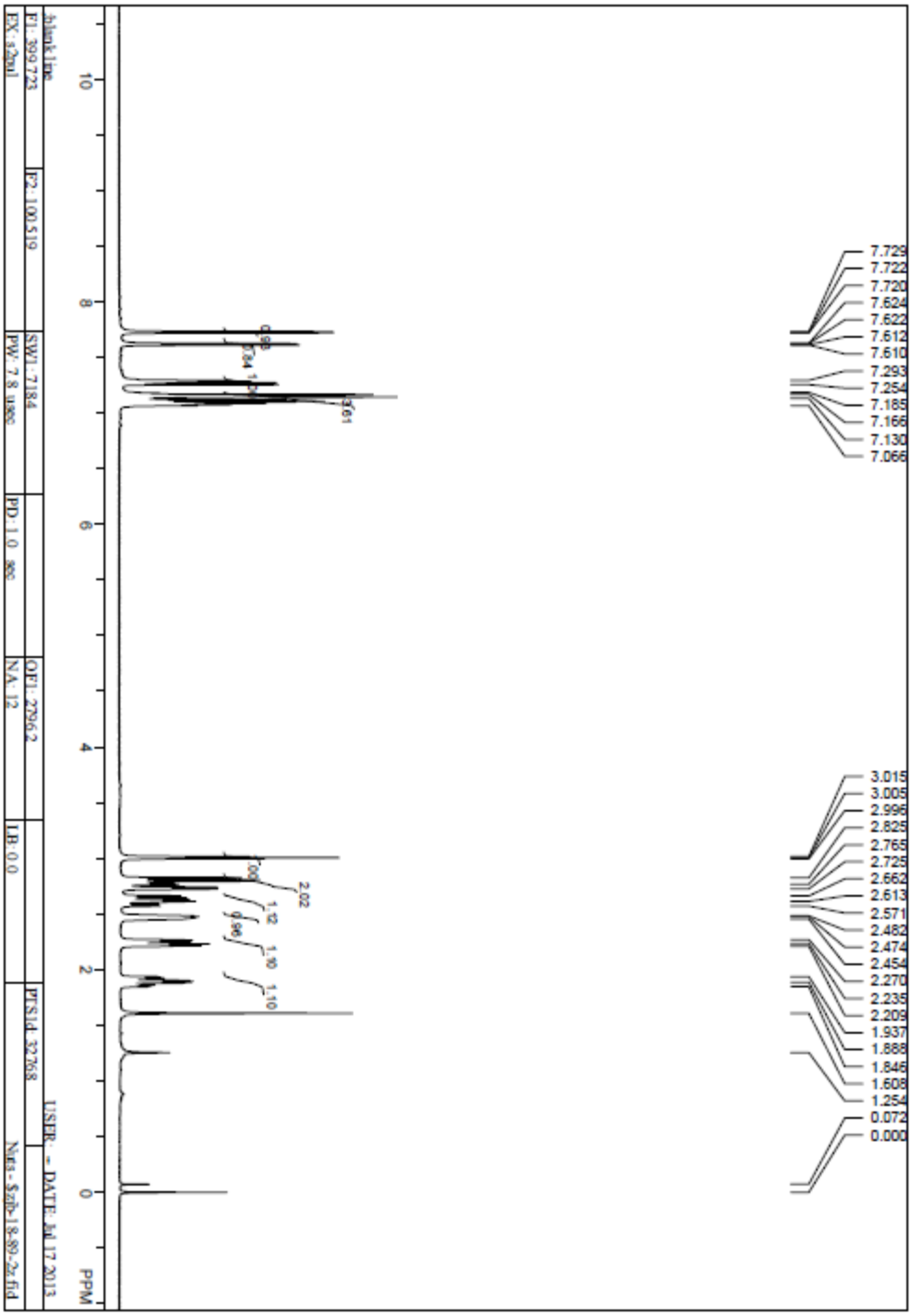
^{13}C NMR (100 M Hz in $CDCl_3$)

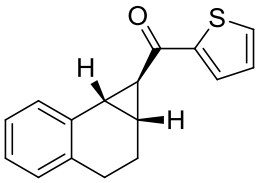




2s

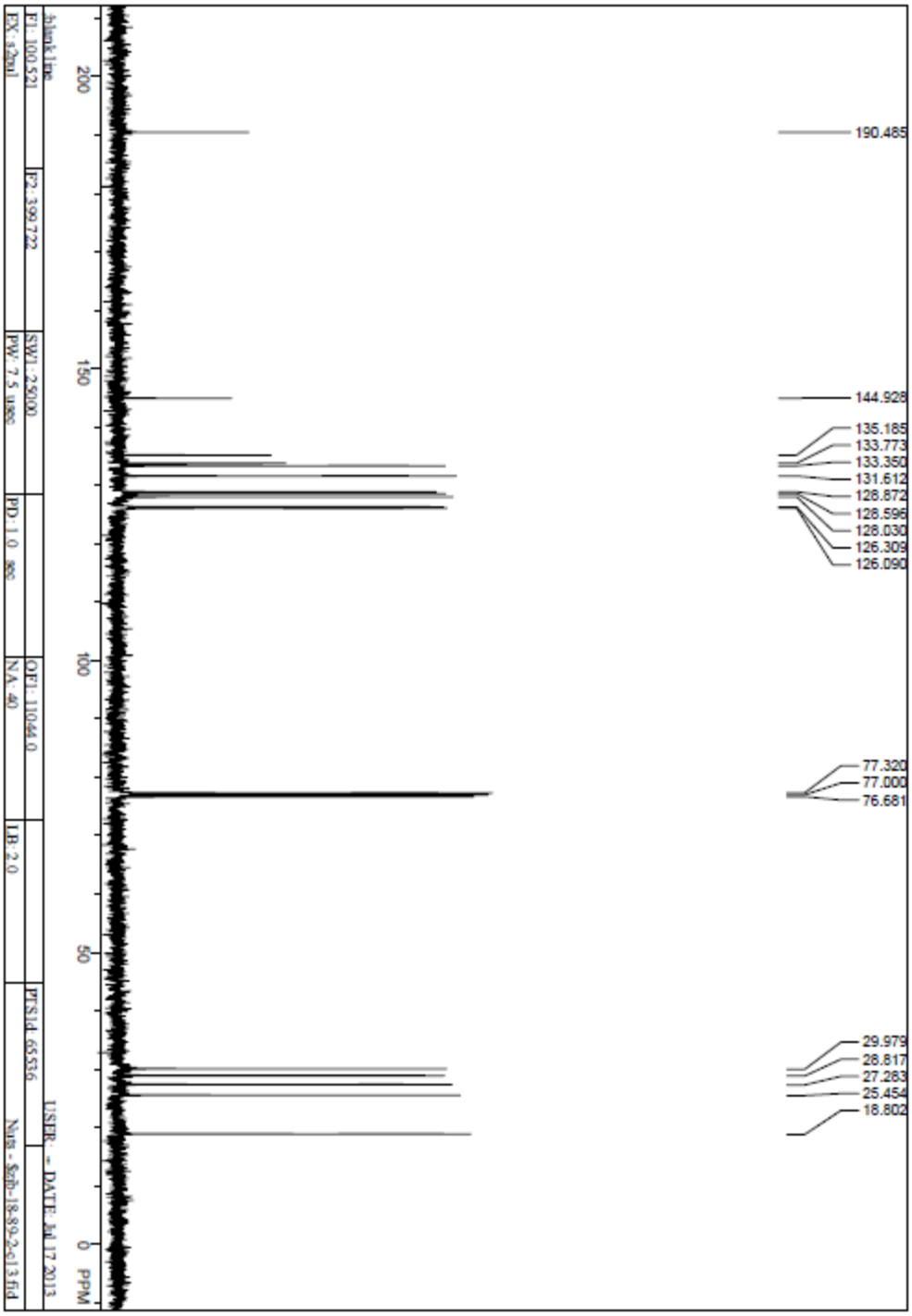
^{1}H NMR (400 M Hz in $CDCl_3$)

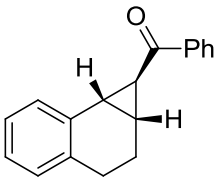




2s

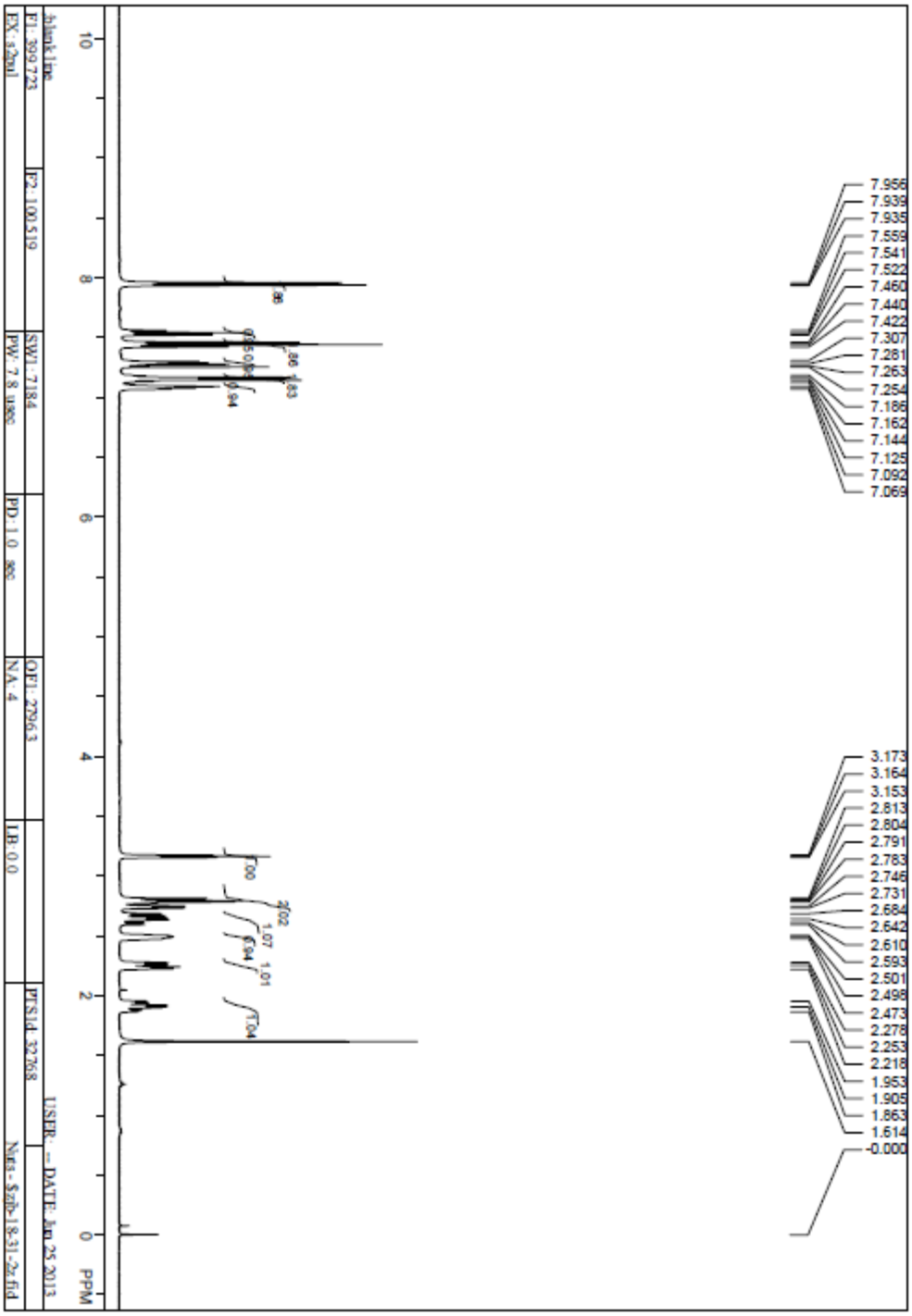
^{13}C NMR (100 M Hz in $CDCl_3$)

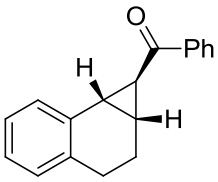




2t

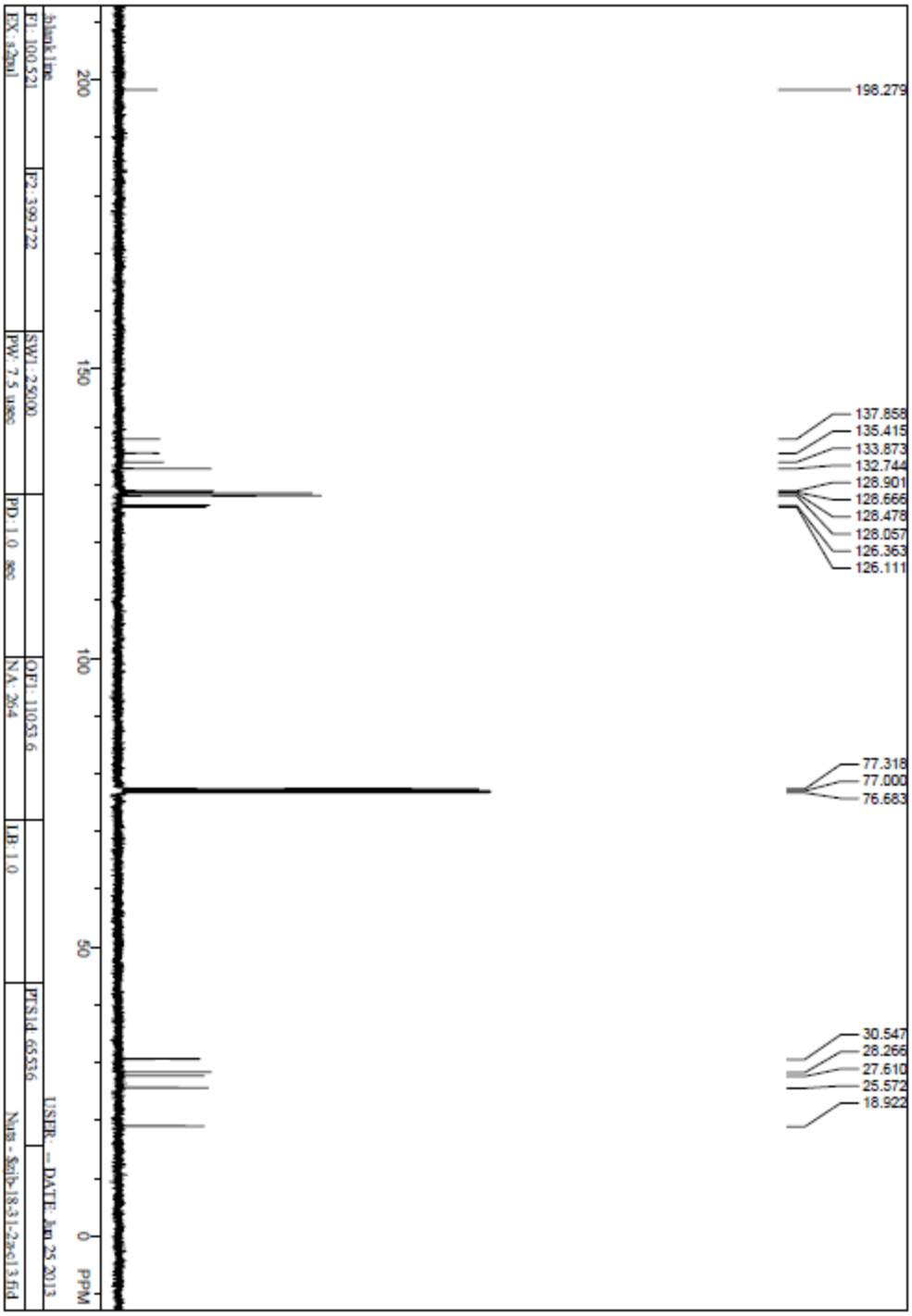
^{1}H NMR (400 M Hz in $CDCl_3$)

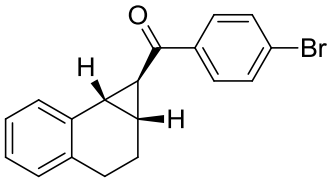




2t

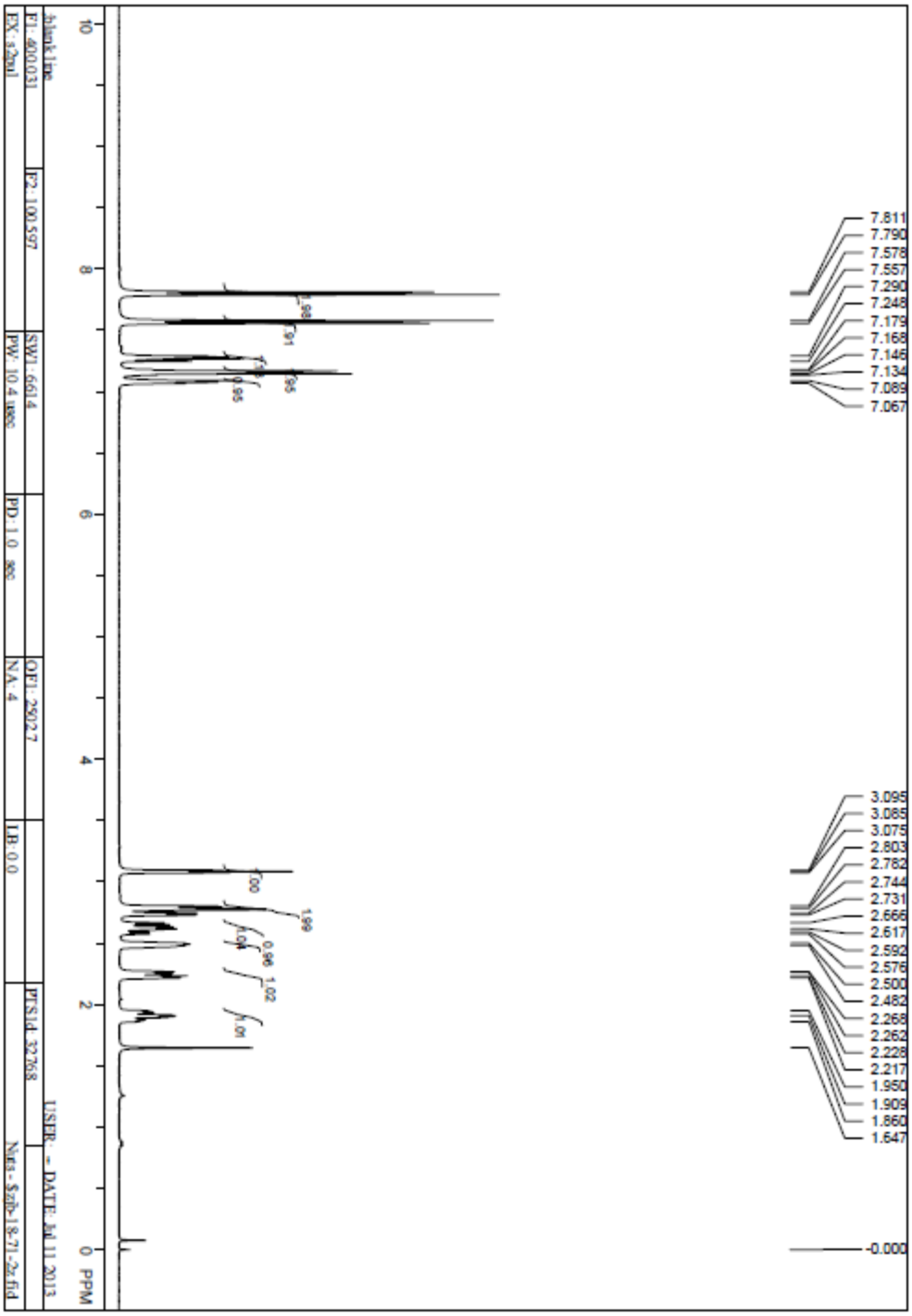
^{13}C NMR (100 M Hz in $CDCl_3$)

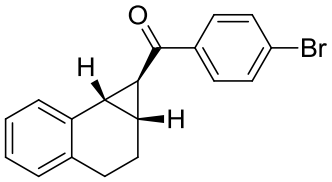




2u

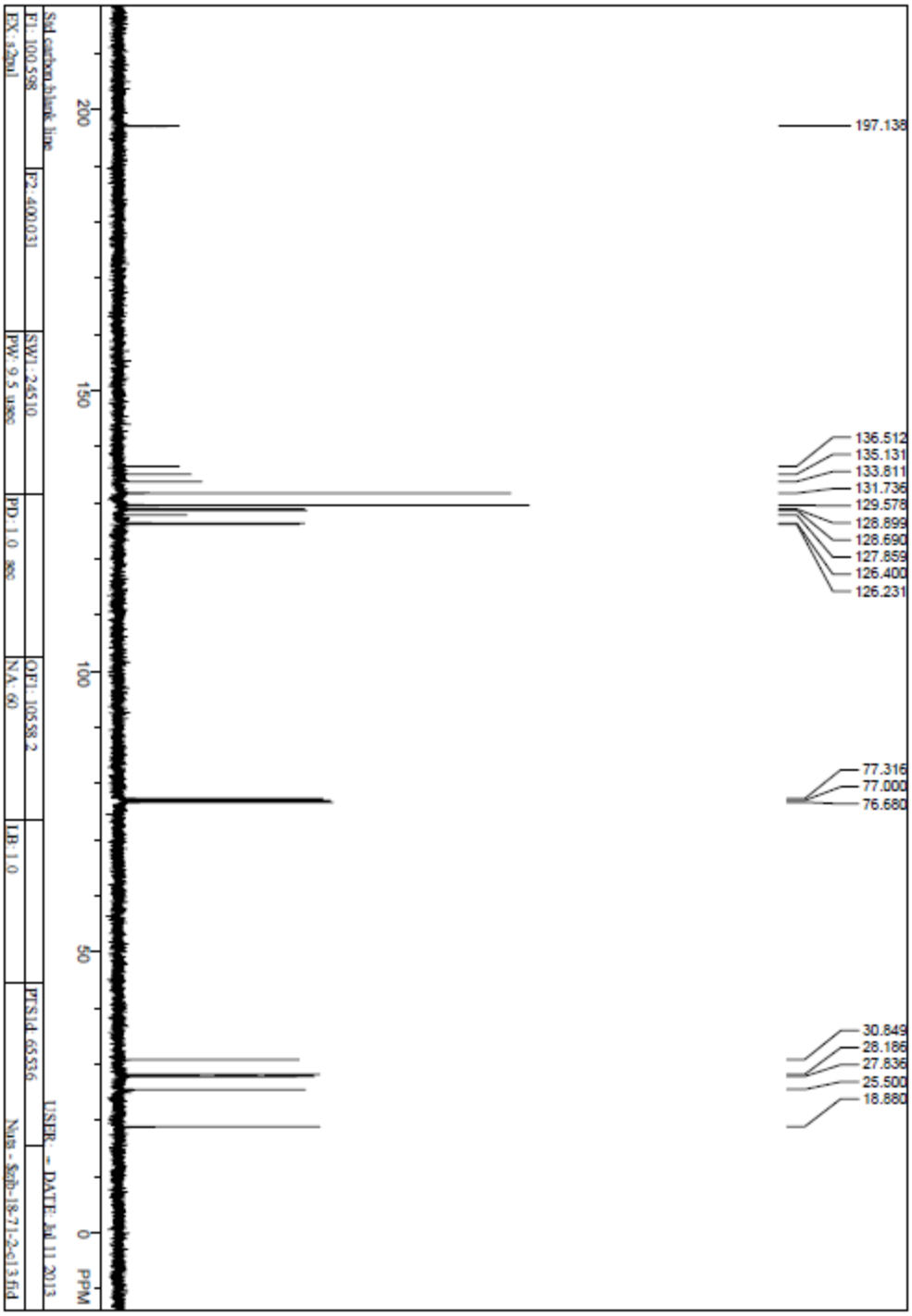
^{1}H NMR (400 M Hz in $CDCl_3$)

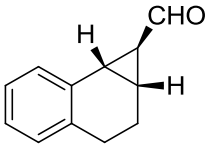




2u

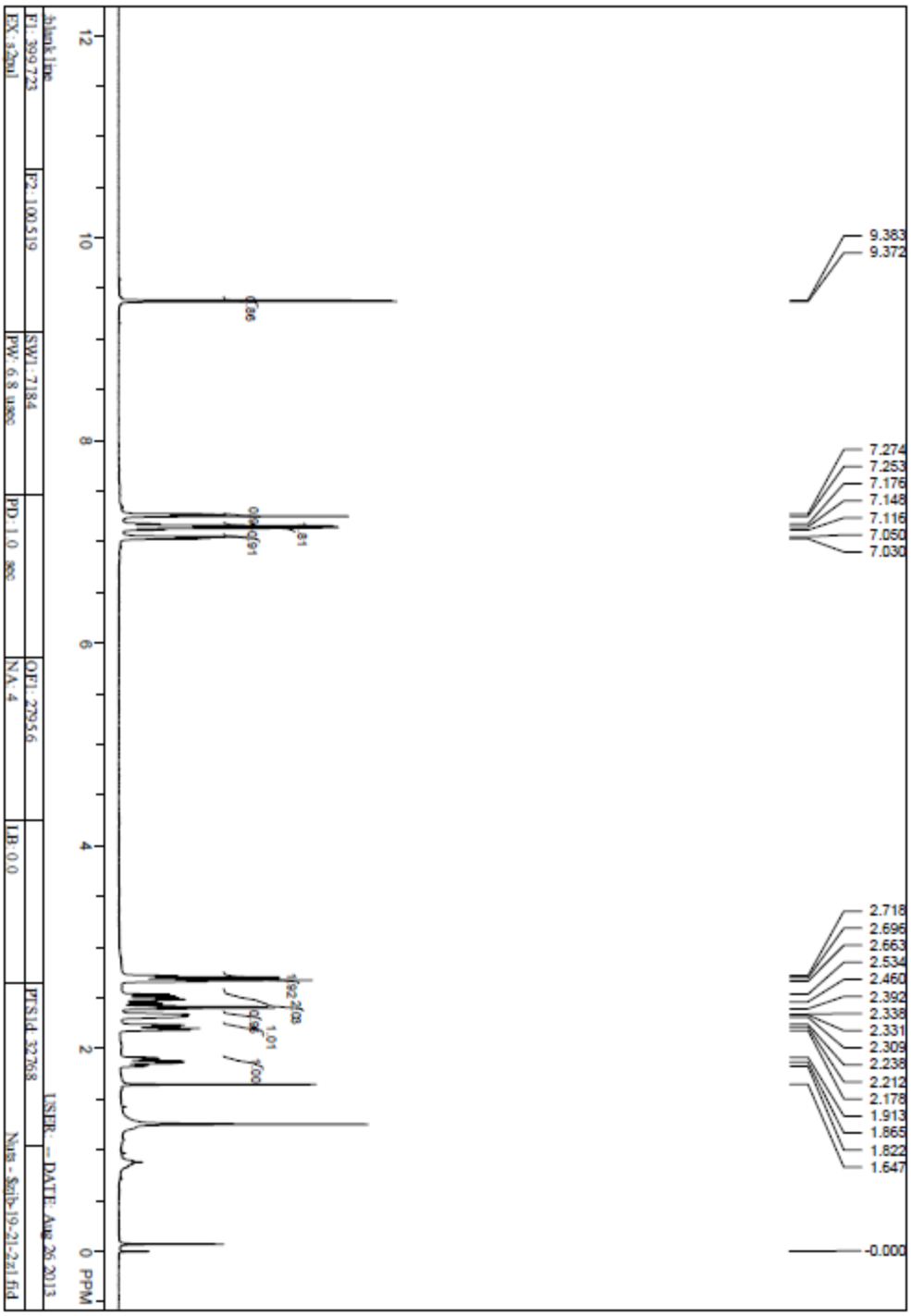
^{13}C NMR (100 M Hz in $CDCl_3$)

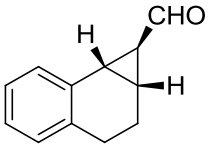




2v

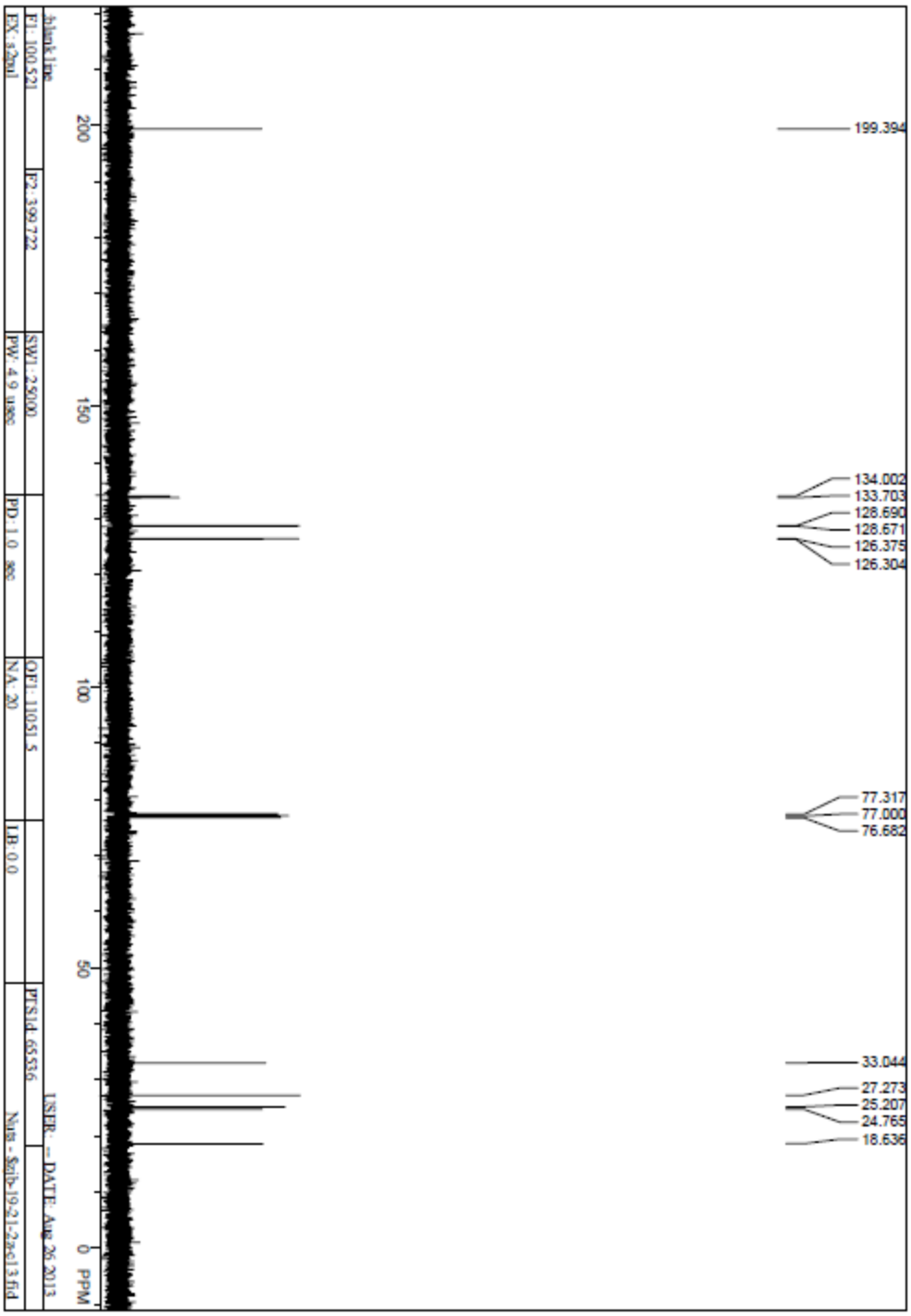
^{1}H NMR (400 M Hz in $CDCl_3$)

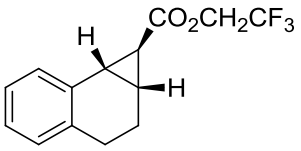




2v

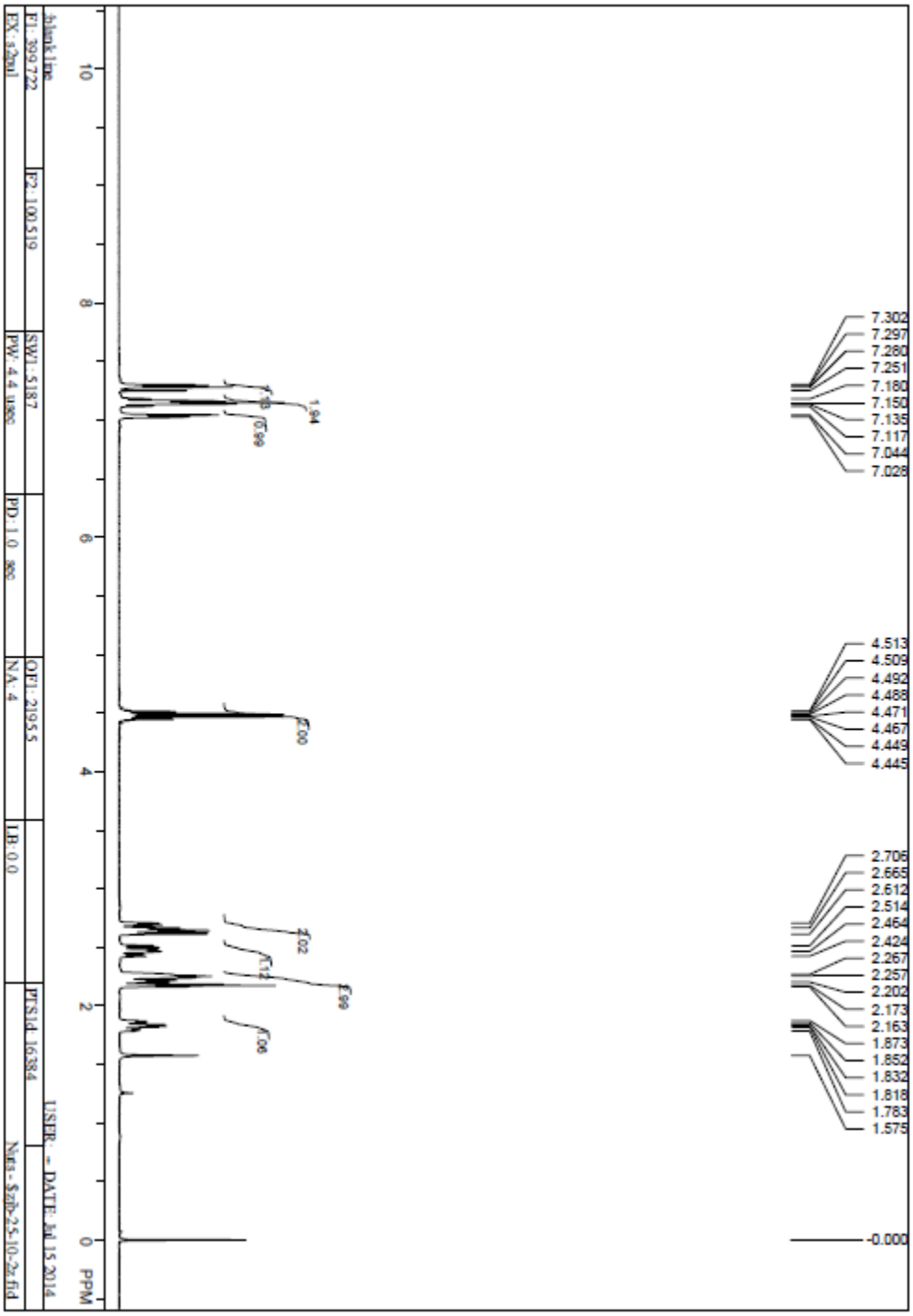
^{13}C NMR (100 M Hz in $CDCl_3$)

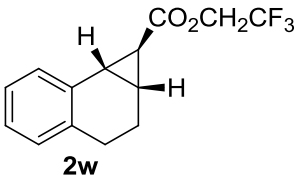




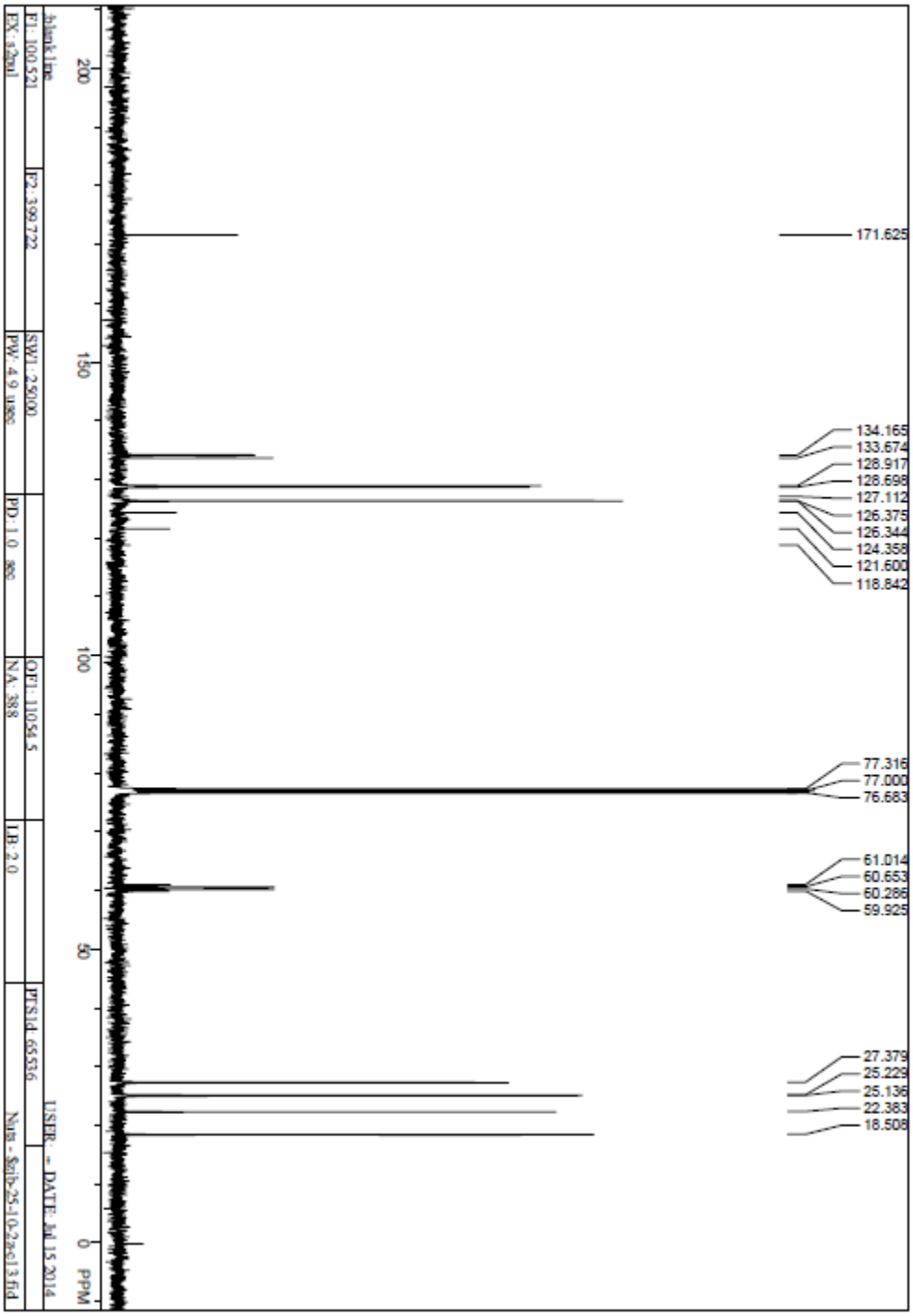
2w

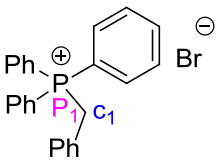
^{1}H NMR (400 M Hz in $CDCl_3$)



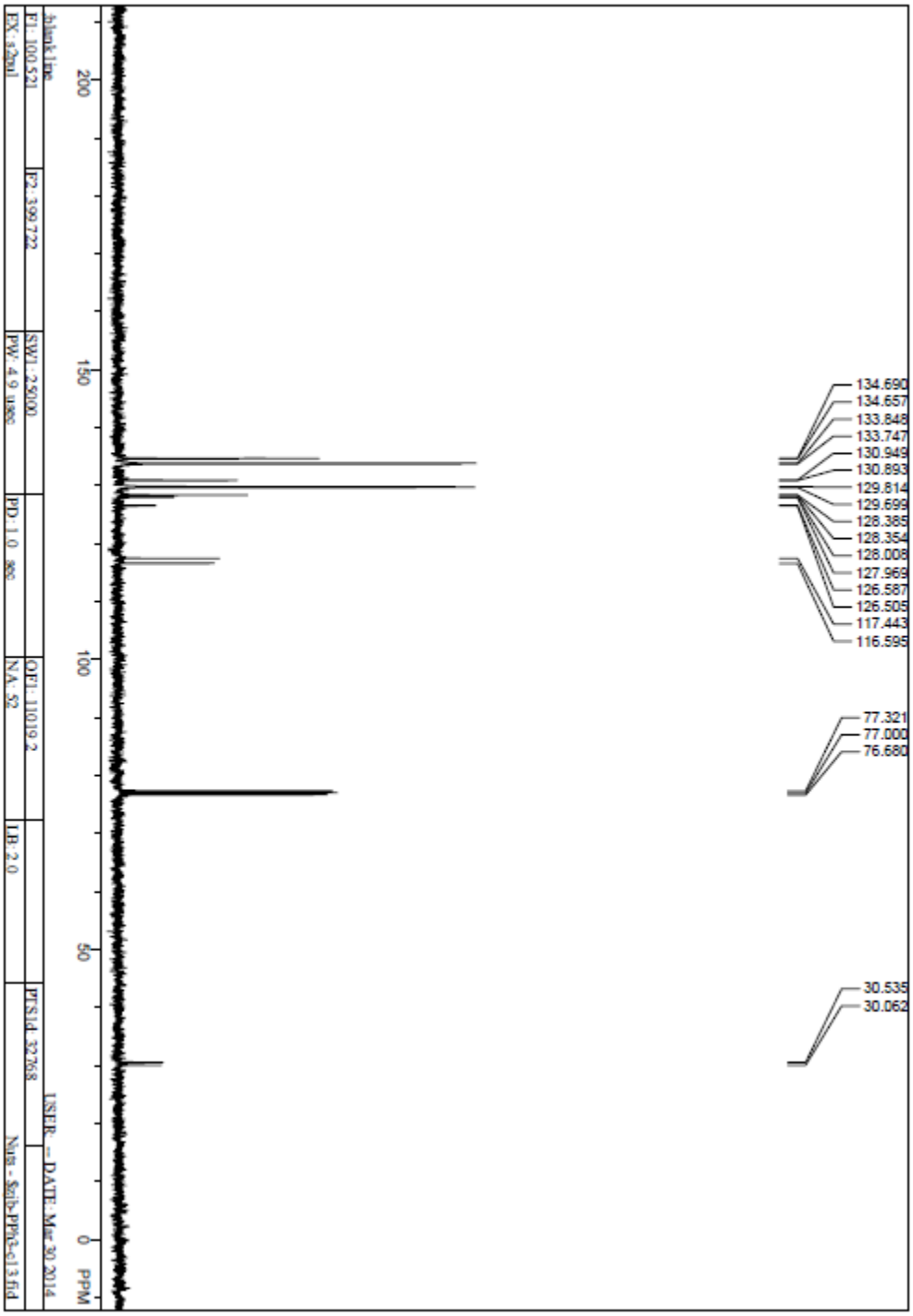


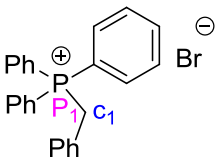
^{13}C NMR (100 M Hz in $CDCl_3$)



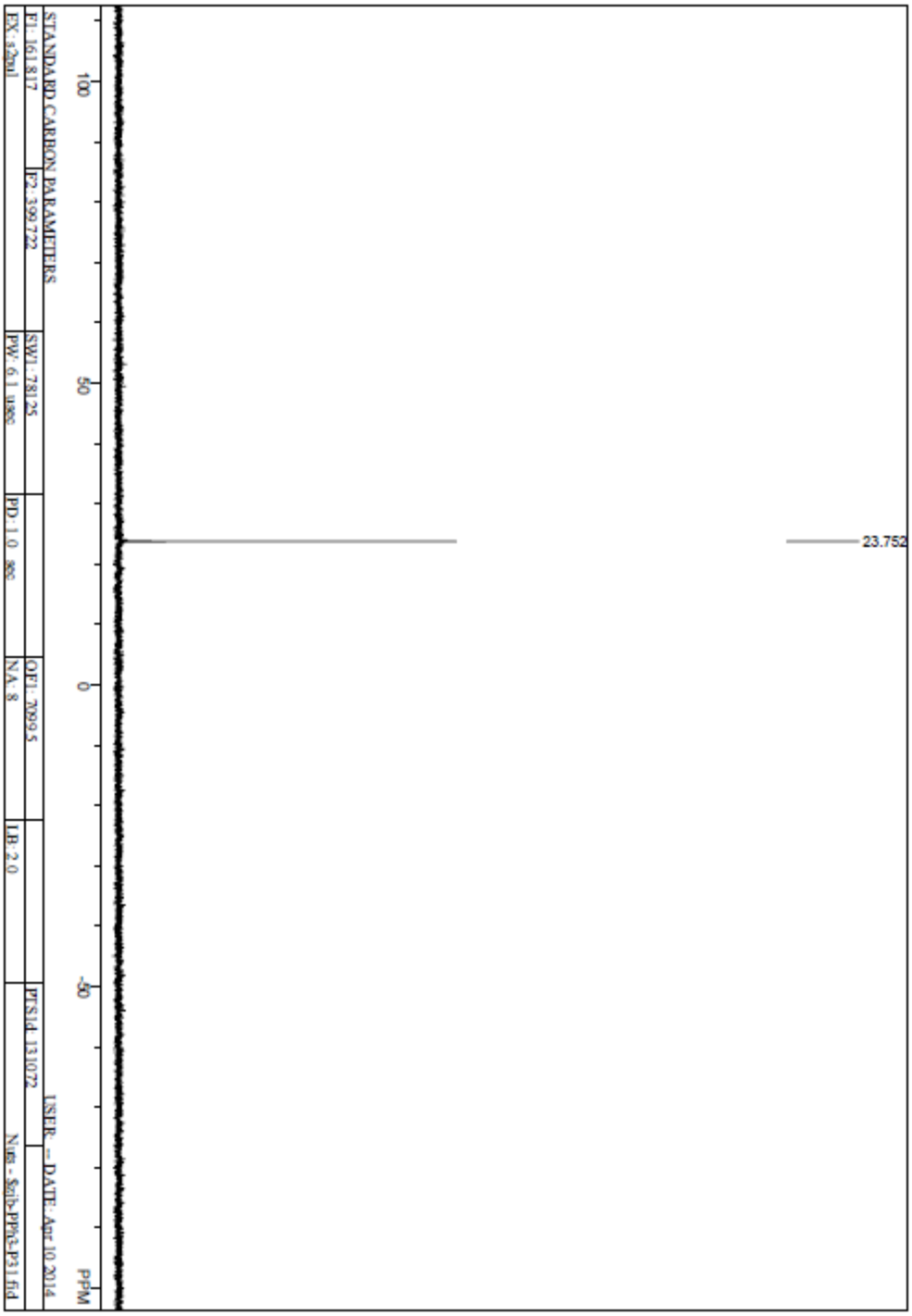


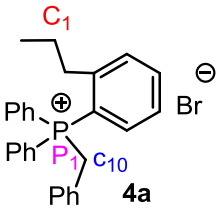
4-PPh$_3$ ^{13}C NMR (100 M Hz in $CDCl_3$)



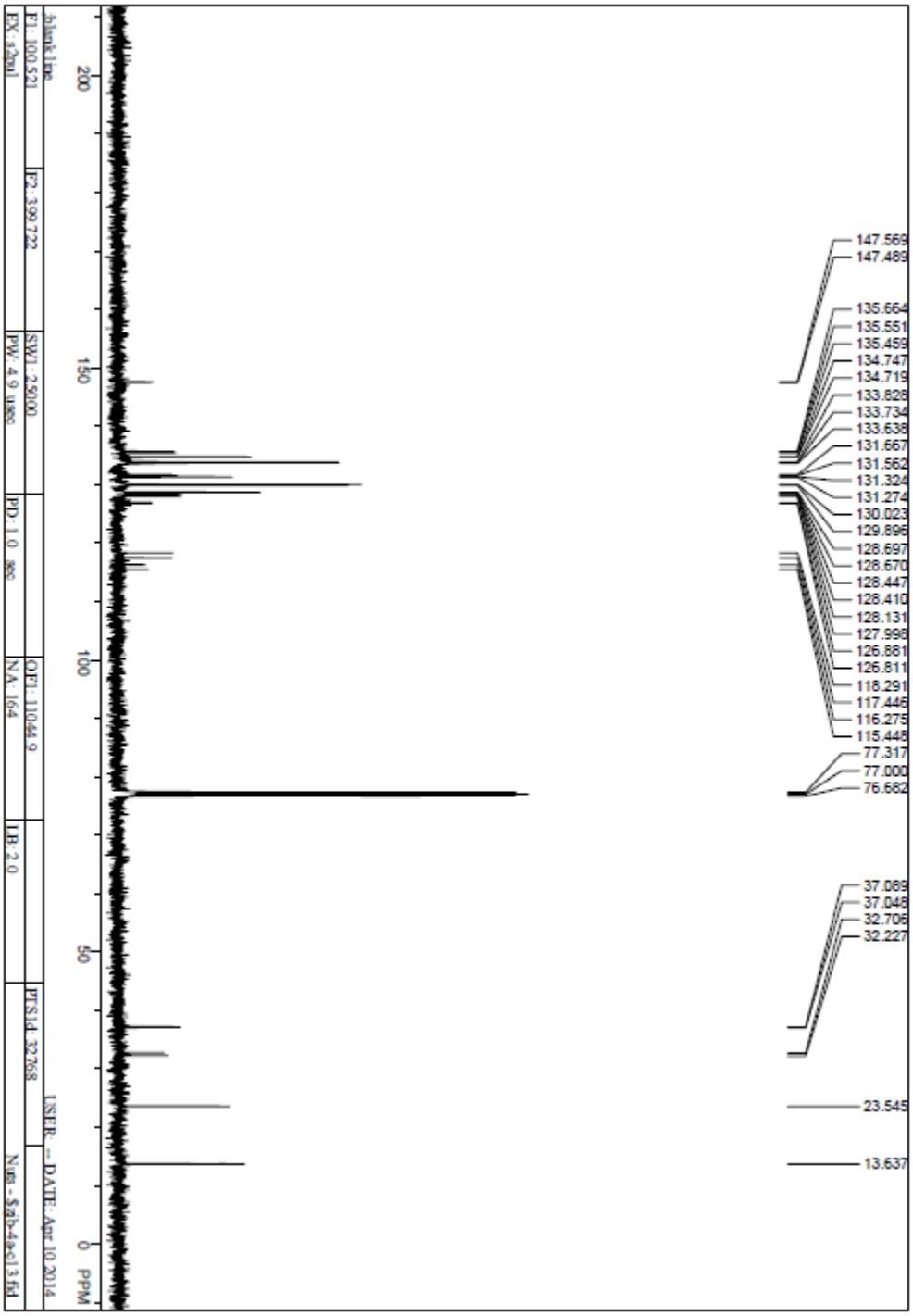


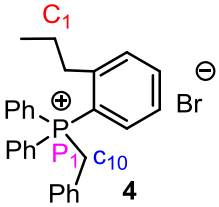
4-PPh$_3$ ^{31}P NMR (162 M Hz in $CDCl_3$)





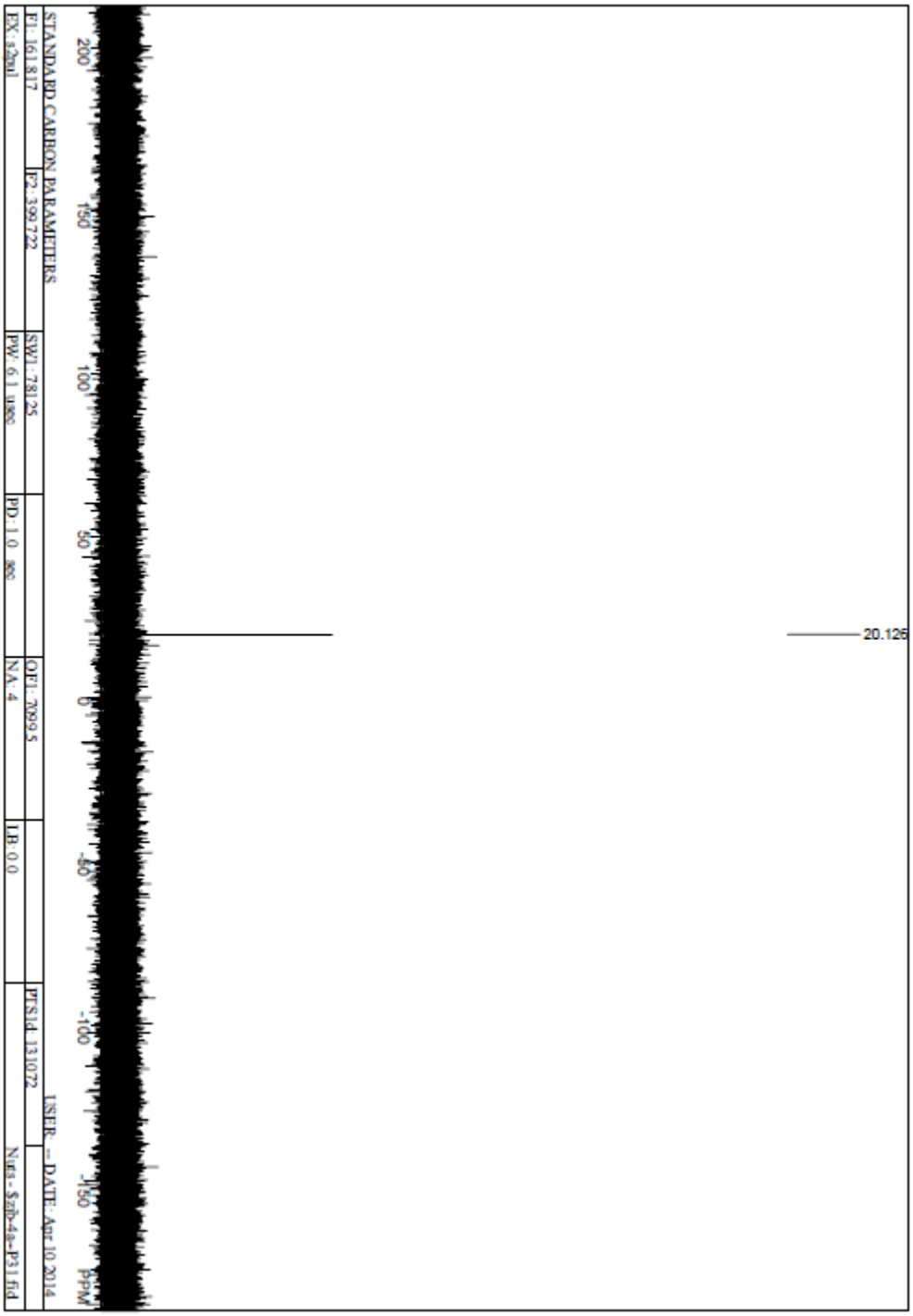
^{13}C NMR (100 M Hz in $CDCl_3$)

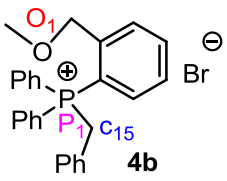




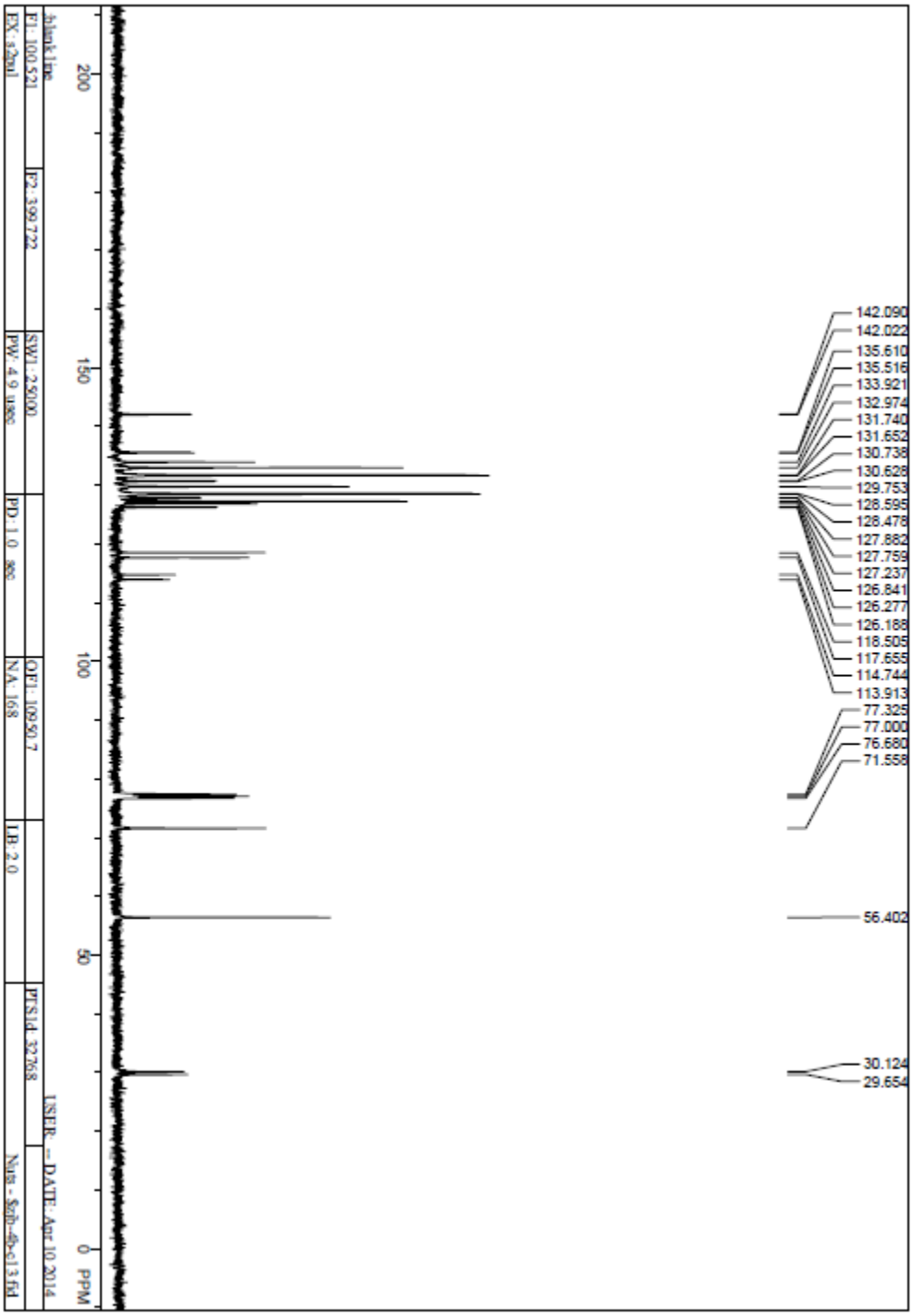
4a

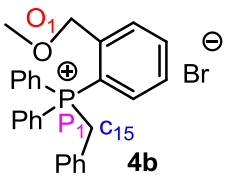
^{31}P NMR (162 M Hz in $CDCl_3$)





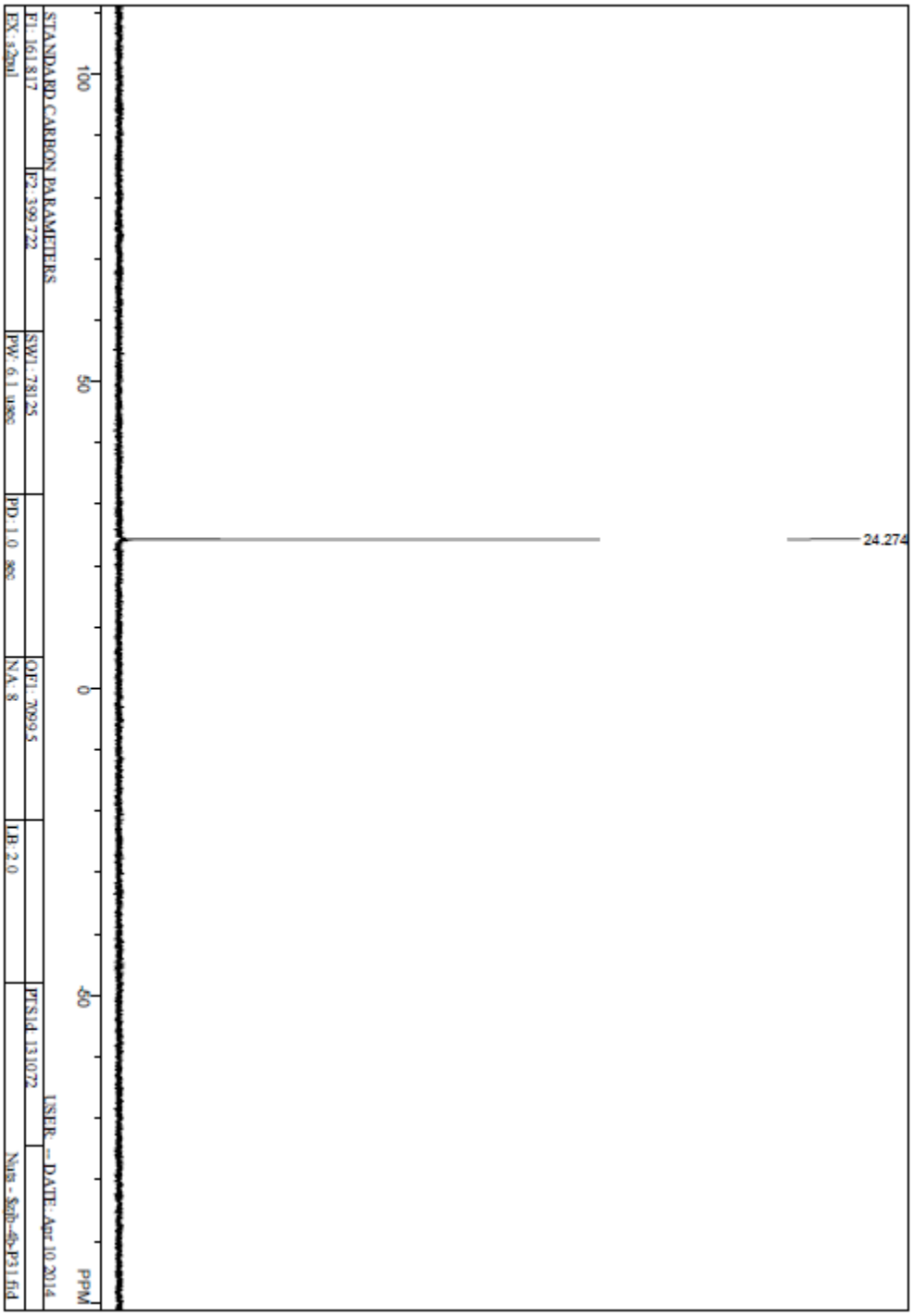
^{13}C NMR (100 M Hz in $CDCl_3$)

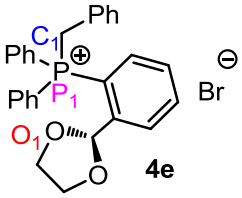




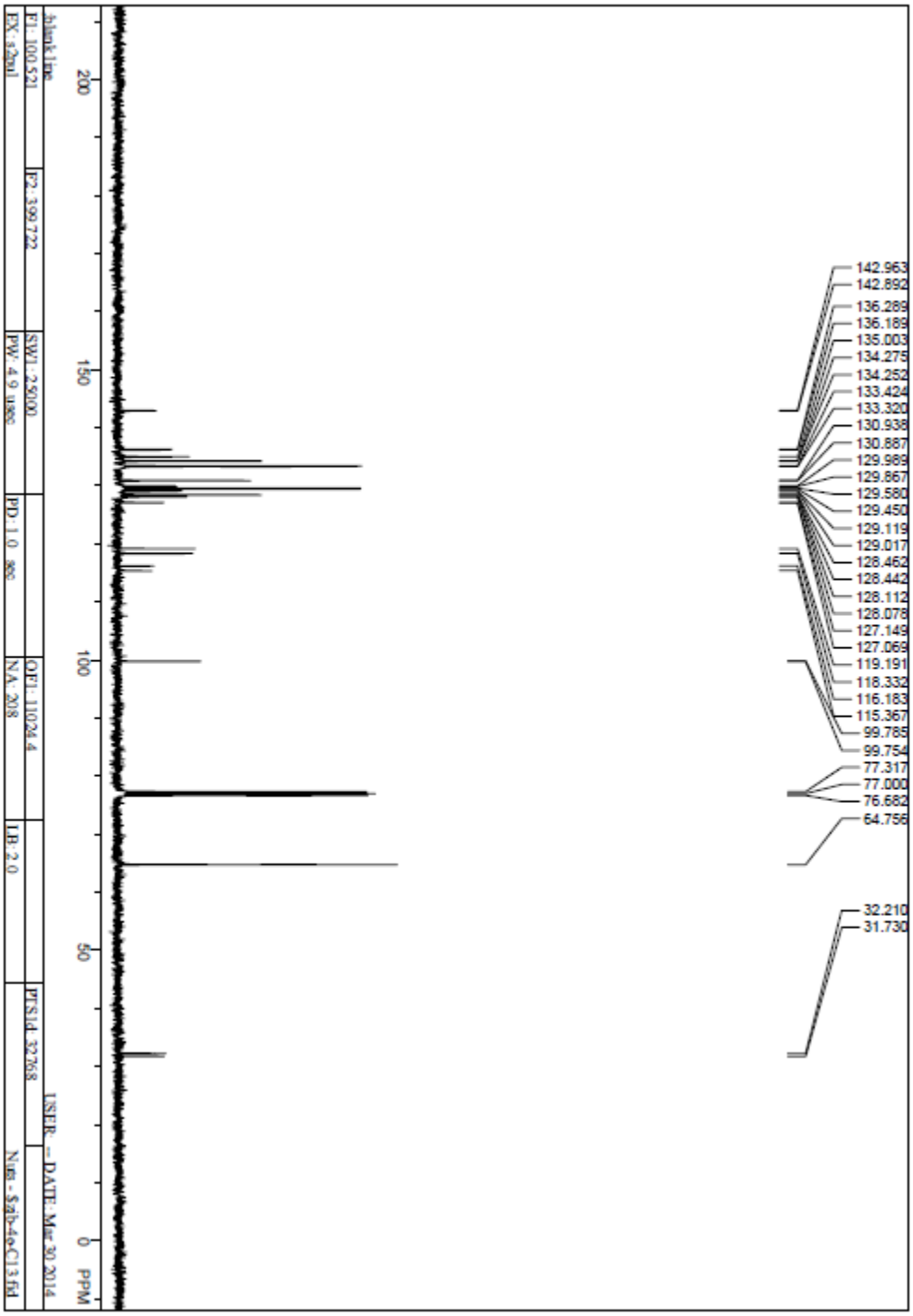
4b

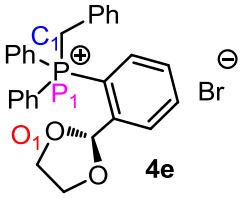
^{31}P NMR (162 M Hz in $CDCl_3$)

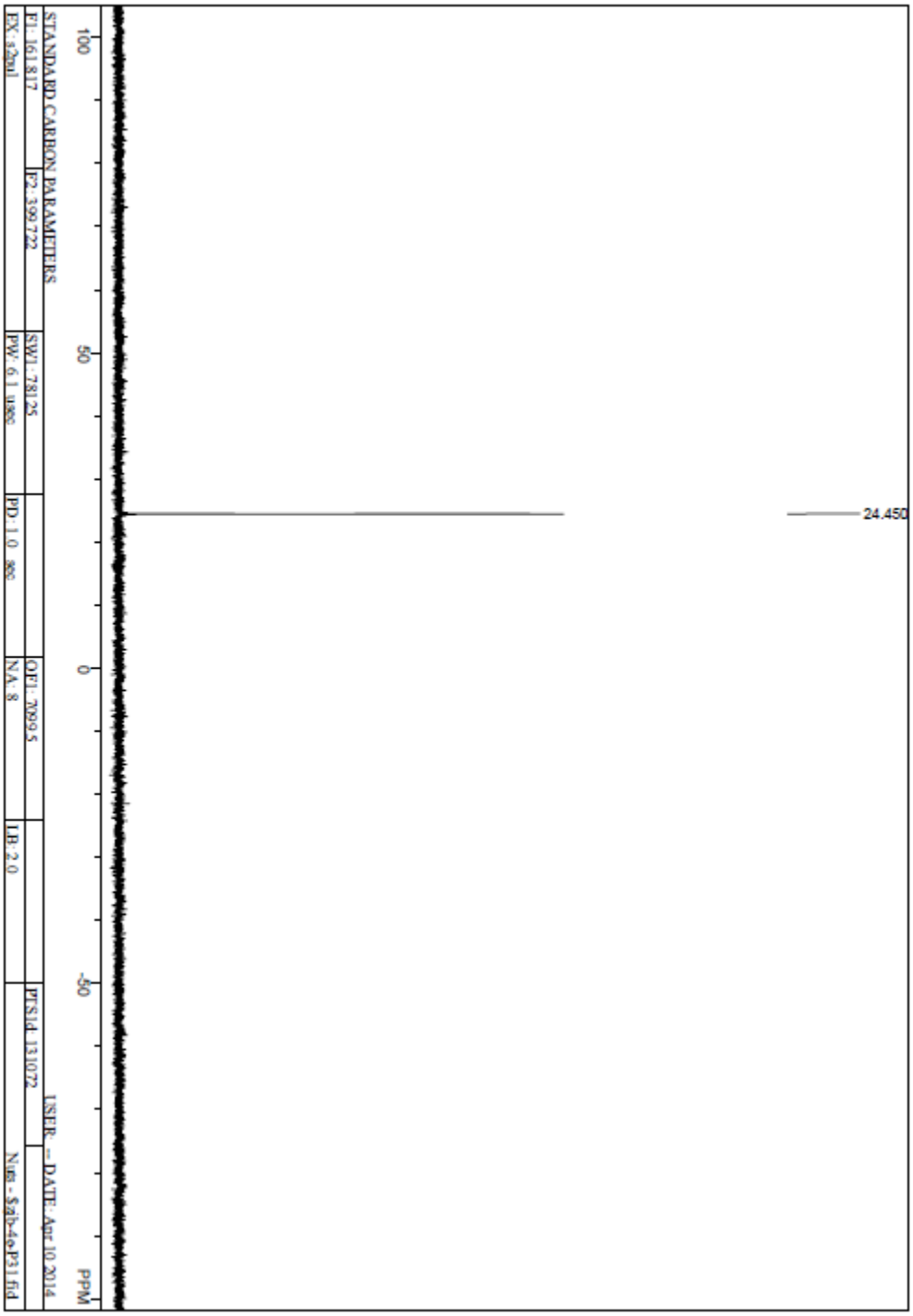




^{13}C NMR (100 M Hz in $CDCl_3$)





4e

^{31}P NMR (162 M Hz in $CDCl_3$)