Simple Silver Salts and Palladium Bis(N-heterocyclic carbene) Complexes As Complementary Catalysts for the Nazarov Cyclization

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SUPPORTING INFORMATION

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GENERAL EXPERIMENTAL DETAILS

All manipulations were carried out under air unless otherwise noted. Diethyl ether (Acros), toluene (Pharmco), and hexanes (Pharmco) were purified by distillation from sodium benzophenone ketyl. Dichloromethane (Pharmco) and dichloroethane (Acros) were washed with a sequence of concentrated H_2SO_4, deionized water, 5% Na_2CO_3 and deionized water, followed by pre-drying over anhydrous $CaCl_2$, and then refluxed over and distilled from P_2O_5 under nitrogen. Acetonitrile (Pharmco) was pre-dried over anhydrous $CaCl_2$ and refluxed over and distilled from CaH_2 under nitrogen. NMR solvents were purchased from Cambridge Isotopes Laboratories. DMSO-d_6 and CD_3CN-d_3 were dried over activated 4 Å molecular sieves followed by vacuum distillation at room temperature and stored in the glovebox for use. CD_2Cl_2 was dried over activated 4 Å molecular sieves and stored over P_2O_5 and then vacuum distilled at room temperature for use. Silver salts were purchased from Strem ($AgSbF_6$, 98%; $AgBF_4$, 99%; $AgPF_6$, 99%; AgOAc, 99%; AgOTf, 98%) or prepared by a literature procedure ($AgBAr^F{}_4$)[1] and stored in a nitrogen glove box in foil-wrapped containers. Compounds **1**,[2,3] **4**,[2] 1,1´-(1,2-phenylene)bis(imidazole) (**24**),[4] and 1-(bromomethyl)-2,4,6-trimethylbenzene[5] were prepared using literature procedures. All other reagents (excluding Nazarov substrates—see below) were purchased from Acros, Aldrich, or Strem and used as received.

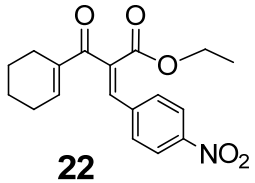
NMR spectra were recorded on Varian GEMINI 2000 (300 MHz) or Varian Unity INOVA (400 MHz) spectrometers. Reported chemical shifts are referenced to residual solvent peaks. IR spectra were acquired on a Perkin Elmer System 2000 FT-IR spectrometer, using 0.5 cm^{-1} resolution and weak apodization. HRMS were recorded on a Thermo LCQ Orbitrap XL mass spectrometer using nano-electrospray ionization. Elemental analyses were performed by Midwest Microlab, Indianapolis, Indiana.

SYNTHESIS OF NAZAROV CYCLIZATION SUBSTRATES

β-Keto esters **2**,[6] **9**,[6] and **11**[7] were synthesized by literature procedures. Known β-keto esters **7**, **13**, **16**, and **19** were prepared by a synthetic procedure reported by Togni and co-workers for **2** and **9**,[6] and their NMR spectra were compared with published data for the same compounds synthesized by different methods (**7**, **13**, and **19**;[8] **16**[9]). New β-keto ester **22** was prepared by the same general procedure, which is summarized below.

The starting acid (α-methylcinnamic acid or cyclohexenyl-1-carboxylic acid) was treated with oxalyl chloride in dichloromethane, with a few drops of dimethyl formamide added, at 0 °C for 3 h to form the corresponding acid chloride. The volatiles were evaporated, and the residue was dried under vacuum for 2 h and then dissolved in THF. Ethyl acetate was treated with lithium diisopropylamide generated in situ by reaction of *n*-butyl lithium with diisopropylamine in dry THF at -78 °C. The acid chloride solution was added to the lithium enolate solution, and the mixture was stirred for 3 h at -78 °C. Acidic workup and flash chromatography afforded the vinyl β-keto ester intermediate as a yellow oil. A Knoevenagel condensation was then used to produce the Nazarov substrate. The vinyl β-keto ester was treated with the corresponding aldehyde in the presence of catalytic amounts of acetic acid and piperidine in a Dean-Stark apparatus, using benzene as a solvent. Divinyl β-keto esters were purified by flash chromatography on silica with ethyl acetate/hexane or Et_2O/hexane mixtures as eluents.

(*Z*)-Ethyl-2-(cyclohex-1-enecarbonyl)-3-(4-nitrophenyl)acrylate (22)



22

R_f 0.62 (1:1 Et_2O/hexanes); white solid, mp 128-129 °C; yield 1.28 g, 64%. ^{1}H NMR (400 MHz, $CDCl_3$; *Z* stereochemistry assigned by NOESY): δ 8.17 (AB, *J* = 2.0 Hz, *C* = 4.4 Hz, 2H, Ar), 7.80 (s, 1H, Ar-C*H*), 7.49 (AB, *J* = 2.0 Hz, *C* = 4.4 Hz, 2H, Ar), 6.80-6.78 (m, 1H, cyclohex. C*H*), 4.29 (q, *J* = 7.2 Hz, 2H, OCH_2), 2.34-2.32 (m, 2H, cyclohex. CH_2), 2.17-2.14 (m, 2H, cyclohex. CH_2), 1.66-1.55 (m, 4H, cyclohex. CH_2), 1.29 (t, *J* = 7.2 Hz, 3H, CH_3). ^{13}C NMR (101

MHz, CD_3CN): δ 195.5 (C=O), 164.4 (O-C=O), 148.0 (Ar *para*), 145.9 (Ar), 139.5 (Ar *ipso*), 139.4 (HC=*C*), 138.3 (Ar), 135.7 (HC=*C*), 130.3 (C=*C*H), 123.8 (C=*C*H), 61.8 (O-*C*H_2), 26.3 (*C*H_2), 22.6 (*C*H_2), 21.5 (*C*H_2), 21.3 (*C*H_2), 14.0 (*C*H_3). IR (thin film, cm^{-1}): ν 1715 (s), 1657 (s), 1628 (s), 1597 (m). Anal. Calcd. for $C_{18}H_{19}NO_5$: C, 65.64; H, 5.82; N, 4.25 %. Found: C, 65.56; H, 5.84: N, 4.29 %.

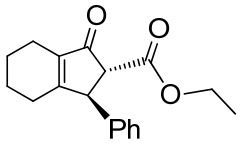
CATALYTIC NAZAROV CYCLIZATION PROCEDURE

In a nitrogen glovebox, catalyst was placed into a 4 mL reaction vial. The vial was sealed by a screw cap with a PTFE/silicon septum and then placed in an aluminum heating block on a Chemglass OptiChem heat/stir plate. A nitrogen-saturated 61 mM solution of substrate in freshly distilled CH_2Cl_2 or DCE (2 mL) was injected into the reaction vial through the septum, and stirring was commenced, with heating if applicable. Reaction progress was monitored by TLC and/or HPLC until starting material had been consumed. After aqueous $NaHCO_3$ workup, products were purified by flash chromatography on silica with ethyl acetate/hexanes or Et_2O/hexanes mixtures as eluents.

CHARACTERIZATION OF NAZAROV CYCLIZATION PRODUCTS

Characterization data of **3**,[6] **10**,[6] **12**,[6] **17**,[9] and **18**[9] have been previously reported. Copies of ^1H and ^{13}C NMR spectra of these compounds are included below as evidence of identity and purity.

Ethyl 1-oxo-3-phenyl-2,3,4,5,6,7-hexahydro-1H-indene-2-carboxylate (8)

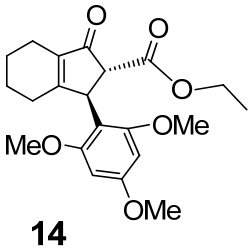


8

R_f 0.42 (3:2 Et_2O/hexanes); yellow oil. ^1H NMR (400 MHz, $CDCl_3$; assignments by comparison with **14** and **20**): δ 7.28-7.18 (m, 3H, Ar), 7.04-7.01 (m, 2H, Ar), 4.18-4.11 (m, 3H, overlapping O-CH_2 & C*H*), 3.29 (d, J = 2.8 Hz, 1H, C*H*), 2.18-1.99 (m, 4H, cyclohex. CH_2), 1.66-1.56 (m, 4H, cyclohex. CH_2), 1.21 (t, $^3J_{HH}$ = 7.2 Hz, 3H, CH_3,). ^{13}C NMR (101 MHz, $CDCl_3$; assignments

by comparison with **14** and **20**): δ 200.6 (C=O), 175.2 (O-C=O), 168.9 (C=*C*), 140.0 (C=*C*), 137.5 (Ph), 129.0 (Ph), 127.5 (Ph), 127.4 (Ph), 61.6 (O*C*H_2), 61.4 (*C*H), 52.0 (*C*H), 26.4 (*C*H_2), 21.9 (*C*H_2), 21.3 (*C*H_2), 20.3 (*C*H_2), 14.1 (*C*H_3). IR (neat, cm^{-1}): ν 1730 (s), 1670 (s), 1646 (s). HRMS (ESI, $C_{18}H_{20}O_3 + H^+$) calcd. 285.1491, found m/z 285.1479.

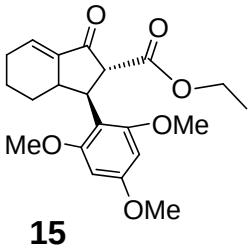
Ethyl 1-oxo-3-(2,4,6-trimethoxyphenyl)-2,3,4,5,6,7-hexahydro-1H-indene-2-carboxylate (14)



14

R_f 0.51 (3:2 Et_2O/hexanes); yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$; assignments by HMQC): δ 6.14 (d, *J* = 2.0 Hz, 1H, Ar), 6.04 (d, *J* = 2.0 Hz, 1H, Ar), 4.81 (bs, 1H, C*H*), 4.24-4.13 (m, 2H, OC*H*$_2$), 3.79 (s, 6H, OC*H*$_3$), 3.78 (s, 3H, OC*H*$_3$), 3.54 (d, *J* = 2.8 Hz, 1H, C*H*), 2.18-1.94 (m, 4H, cyclohex. C*H*$_2$), 1.71-1.56 (m, 4H, cyclohex. C*H*$_2$), 1.26 (t, *J* = 7.2 Hz, 3H, C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$; assignments by HMQC): δ 202.1 (C=O), 177.5 (C=*C*), 170.7 (O-C=O), 160.7 (Ar), 159.8 (Ar), 159.6 (Ar), 135.3 (C=*C*), 107.4 (Ar *ipso*), 91.0 (Ar), 90.9 (Ar), 61.3 (O*C*H_2), 58.7 (*C*H), 56.3 (O*C*H_3), 55.2 (O*C*H_3), 55.5 (O*C*H_3), 41.8 (*C*H), 26.5 (*C*H_2), 22.4 (*C*H_2), 21.9 (*C*H_2), 20.5 (*C*H_2), 14.5 (*C*H_3). IR (neat, cm^{-1}): ν 1733 (s), 1699 (s), 1646 (s), 1607 (s). HRMS (ESI, $C_{21}H_{26}O_6 + H^+$) calcd. 375.1808, found m/z 375.1788.

Ethyl 1-oxo-3-(2,4,6-trimethoxyphenyl)-2,3,3a,4,5,6-hexahydro-1H-indene-2-carboxylate (15)

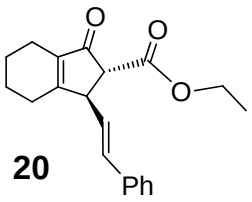


15

R_f 0.60 (3:2 Et_2O/hexanes); yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$; assignments by HMQC and DEPT): δ 6.79 (pseudo q, *J* = 3.2, 3.6 Hz, 1H, vinylic C*H*), 6.13 (s, 2H, Ar), 4.24 (d, *J* = 12 Hz,

1H, C(=O)C*H*), 4.20-4.00 (m, 2H, OCH_2), 3.92 (pseudo t, *J* = 12 Hz, 1H, C*H*), 3.80 (s, 3H, OCH_3), 3.78 (s, 6H, OCH_3), 2.97-2.91 (m, 1H, C*H*), 2.34-2.19 (m, 2H, cyclohex. CH_2), 1.88-1.80 (m, 2H, cyclohex. CH_2), 1.49-1.42 (m, 2H, cyclohex. CH_2), 1.17 (t, *J* = 7.2 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$; assignments by HMQC and DEPT): δ 199.8 (C=O), 170.0 (O-C=O), 160.1 (Ar), 159.9 (Ar), 140.9 (HC=*C*), 134.5 (C=*C*H), 107.7 (Ar *ipso*), 91.2 (Ar), 60.9 (O*C*H$_2$), 58.0 (*C*H), 56.0 (O*C*H$_3$), 55.4 (O*C*H$_3$), 40.7 (*C*H), 39.8 (*C*H$_2$), 27.4 (*C*H$_2$), 25.9 (*C*H$_2$), 21.8 (*C*H$_2$), 14.3 (*C*H$_3$). IR (neat, cm^{-1}): ν 1739 (s), 1712 (s), 1651 (s), 1608 (s). HRMS (ESI, $C_{21}H_{26}O_6$ + H^+) calcd. 375.1808, found m/z 375.1794.

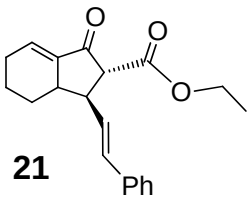
(*E*)-Ethyl 1-oxo-3-styryl-2,3,4,5,6,7-hexahydro-1H-indene-2-carboxylate (20)



20

R_f 0.41 (1:1 Et_2O/hexanes); yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$; assignments by HMQC, HMBC, and DEPT): δ 7.36-7.21 (m, 5H, Ph), 6.57 (d, *J* = 16 Hz, 1H, C=C*H*Ph), 5.93 (dd, *J* = 9.0, 16 Hz, 1H, C=C*H*), 4.25-4.17 (m, 2H, OCH_2), 3.83 (br d, *J* = 9.0 Hz, 1H, C*H*), 3.26 (d, *J* = 2.8 Hz, 1H, C*H*), 2.40-2.16 (m, 4H, cyclohex.), 1.74-1.60 (m, 4H, cyclohex.), 1.29 (t, *J* = 7.2 Hz, 3H, CH_3,). ^{13}C NMR (101 MHz, $CDCl_3$; assignments by HMQC, HMBC, and DEPT): δ 200.2 (C=O), 174.7 (C=*C*), 169.0 (O-C=O), 137.2 (C=*C*), 136.3 (Ph *ipso*), 133.5 (C=*C*H), 128.6 (Ar), 127.9 (C=*C*H), 126.3 (Ar), 61.6 (O*C*H$_2$), 58.8 (*C*H), 50.1 (*C*H), 26.7 (*C*H$_2$), 22.0 (*C*H$_2$), 21.4 (*C*H$_2$), 20.3 (*C*H$_2$), 14.2 (*C*H$_3$). IR (neat, cm^{-1}): ν 1734 (s), 1718 (s), 1653 (s), 1599 (m). HRMS (ESI, $C_{18}H_{20}O_3$ + H^+) calcd. 311.1642, found m/z 311.1632.

(*E*)-Ethyl 1-oxo-3-styryl-2,3,3a,4,5,6-hexahydro-1H-indene-2-carboxylate (21)

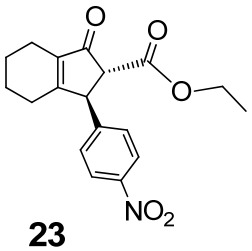


21

R_f 0.48 (1:1 Et_2O/hexanes); yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$; assignments by comparison with **15** and **20**): δ 7.37-7.20 (m, 5H, Ar), 6.83 (pseudo q, *J* = 3.0, 3.6 Hz, 1H, cyclohex. vinylic

C*H*), 6.53 (d, *J* = 16 Hz, 1H, C=C*H*Ph), 6.16 (dd, *J* = 8.0, 16 Hz, 1H, C=C*H*), 4.25-4.15 (m, 2H, OCH_2), 3.25 (d, *J* = 12 Hz, 1H, C(=O)C*H*), 2.88-2.80 (m, 1H, C*H*), 2.44-2.30 (m, 2H, cyclohex. CH_2), 2.27-2.14 (m, 2H, cyclohex. CH_2), 1.95-1.87 (m, 2H, cyclohex. CH_2), 1.25 (t, *J* = 12 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$; assignments by comparison with **15** and **20**) δ 197.8 (C=O), 169.2 (O-C=O), 139.1 (cyclohex HC=*C*), 136.8 (cyclohex H*C*=C), 136.0 (Ph *ipso*), 132.4 (C=*C*H), 128.8 (C=*C*H), 128.7 (Ph), 127.7 (Ph), 126.4 (Ph), 61.5 (O*C*H_2), 61.1 (*C*H), 49.7 (*C*H), 42.0 (*C*H), 27.0 (*C*H_2), 25.8 (*C*H_2), 21.7 (*C*H_2), 14.4 (*C*H_3). IR (neat, cm^{-1}): ν 1733 (s), 1700 (s), 1645 (s), 1600 (m). HRMS (ESI, $C_{20}H_{22}O_3$ + H^+) calcd. 311.1642, found m/z 311.1630.

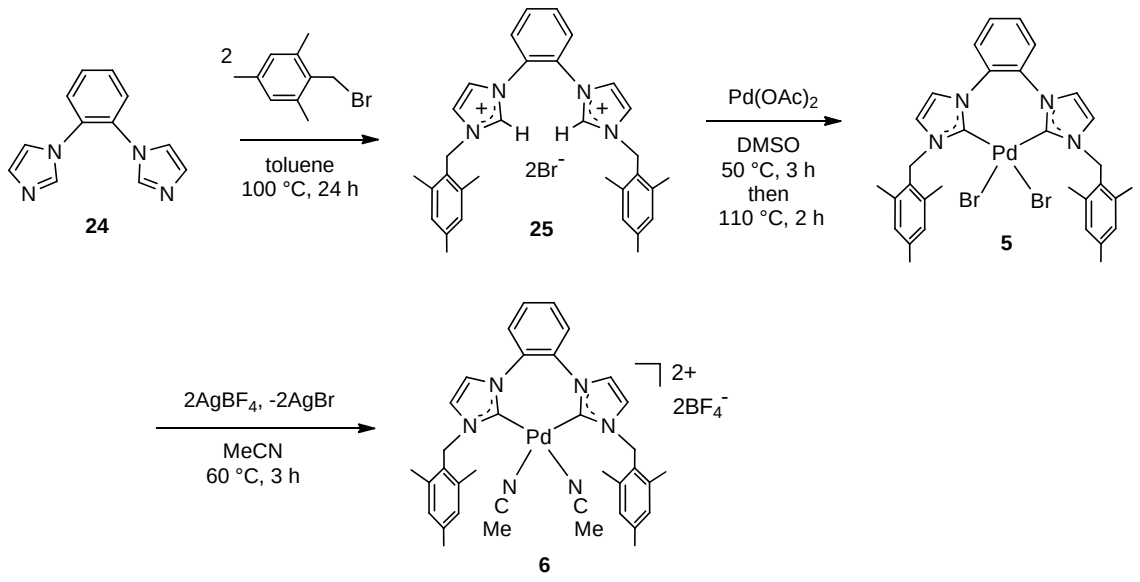
Ethyl 1-(4-nitrophenyl)-3-oxo-2,3,4,5,6,7-hexahydro-1H-indene-2-carboxylate (23)



23

R_f 0.40 (7:3 Et_2O/hexanes); white solid, mp 31-32 °C. ^{1}H NMR (400 MHz, $CDCl_3$; assignments by comparison with **14** and **20**): δ 8.19 (m, 2H, Ar), 7.27 (m, 2H, Ar), 4.37 (br s, 1H, C*H*), 4.27-4.15 (m, 2H, OCH_2), 3.29 (d, *J* = 2.8 Hz, 1H, C*H*), 2.26-1.96 (m, 4H, cyclohex. CH_2), 1.72-1.68 (m, 4H, cyclohex. CH_2), 1.27 (t, *J* = 6.9 Hz, 3H, CH_3,). ^{13}C NMR (101 MHz, $CDCl_3$; assignments by comparison with **14** and **20**): δ 199.6 (C=O), 173.3 (O-C=O), 168.3 (C=*C*), 147.8 (Ar), 147.5 (Ar), 138.9 (C=*C*), 128.7 (Ar), 124.6 (Ar), 62.2 (O*C*H_2), 61.1 (*C*H), 51.7 (*C*H), 26.6 (*C*H_2), 22.1 (*C*H_2), 21.4 (*C*H_2), 20.5 (*C*H_2), 14.3 (*C*H_3). IR (neat, cm^{-1}): ν 1734 (s), 1706 (s), 1653 (s), 1599 (m). Anal. Calcd. for $C_{18}H_{19}NO_5$: C, 65.64; H, 5.82; N, 4.25 %. Found: C, 65.56; H, 5.72: N, 4.30 %.

SYNTHESIS OF PALLADIUM BIS(NHC) COMPLEXES



24 **25** **5** **6**

Note: Despite repeat analyses on freshly prepared samples that showed no significant impurities in their ^{1}H and ^{13}C NMR spectra (see scanned spectra below), elemental analyses of compounds **25**, **5**, **6**, and **26** were consistently off for one element (low % C for **25**, **5**, and **26**; high % N for **6**). We believe that the phenylene bridge renders these compounds resistant to combustion relative to methylene-linked bis(NHC) analogues. We have found several complexes of the latter type to give acceptable analyses under identical conditions,[10,11] which included the use of a WO_3 combustion aid.

Bis(imidazolium) salt (25)

1,1′-(1,2-phenylene)bis(imidazole)[4] **24** (500 mg, 2.38 mmol) and 1-(bromomethyl)-2,4,6-trimethylbenzene[5] (558 mg, 2.62 mmol) were suspended in freshly distilled toluene (25 mL), and the mixture was heated in flask sealed with a PTFE stopcock at 100 ^{o}C for 24 hours. The precipitated solid was collected by filtration and washed with THF. The crude product was recrystallized from CH_2Cl_2 and then dried in vacuo for 12 h. Yield: 890 mg, 75 %. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.19 (s, 2H, imidazole), 7.89 (s, 4H, imidazole) 7.78 (d, J = 1.6 Hz, 2H, phen.), 7.76 (d, J = 1.6 Hz, 2H, phen.), 6.98 (s, 4H, Mes), 5.40 (s, 4H, CH_2), 2.27 (s, 6H, p-CH_3), 2.22 (s, 12H, o-CH_3). ^{13}C NMR (101.5 MHz, DMSO-d_6): 138.7 (Ar), 138.2 (Ar), 137.4 (Ar), 131.9 (Ar), 129.9 (Ar), 129.4 (Ar), 128.4 (Ar), 126.0 (Ar), 123.7 (imidazole), 122.8 (imidazole),

47.6 (N*C*H_2), 20. 6 (CH_3), 19.4 (CH_3). Anal. Calcd. for $C_{32}H_{36}Br_2N_4$: C, 60.39; H, 5.70; N, 8.80 %. Found: C, 59.17; H, 5.61; N, 8.97 %. HRMS (ESI, $[M - 2HBr]^+$) calcd. 474.2783, found m/z 474.2900.

Bis(NHC)PdBr$_2$ complex (5)

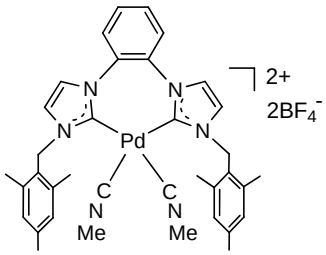
$Pd(OAc)_2$ (176 mg, 0.786 mmol) and **25** (500 mg, 0.786 mmol) were dissolved in undried DMSO (10 mL), and the solution was heated at 50 ^oC for 2 h, followed by further heating at 110 ^oC for 3 h. Addition of CH_2Cl_2 to the cooled reaction mixture afforded pale yellow crystals. The product was isolated by filtration and dried in vacuo for 12 h. Yield: 303 mg, 52 %. ^1H NMR (400 MHz, DMSO-d_6): δ 7.88-7.86 (m, 2H, phen.), 7.79-7.71 (m, 2H, phen.), 7.71 (br s, 2H, imidazole), 7.00 (s, 4H, Mes), 6.53 (s, 2H, imidazole), 6.02 (d, *J* = 14 Hz, 2H, C*H*$_2$), 5.43 (d, *J* = 14 Hz, 2H, C*H*$_2$), 2.27 (s, 6H, *p*-C*H3*), 2.23 (s, 12H, *o*-C*H*$_3$). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 162.9 (carbene), 139.6 (Ar), 139.0 (Ar), 133.3 (Ar), 130.6 (Ar), 129.9 (Ar), 127.3 (Ar), 127.1 (Ar), 122.2 (Ar), 121.3 (imidazole), 50.8 (N*C*H_2), 21.2 (*C*H_3), 20.4 (*C*H_3); traces of DMSO (41.5) and Et_2O (66.0, 15.4) visible. Anal. Calcd. for $C_{32}H_{34}Br_2N_4Pd$: C, 51.87; H, 4.63; N, 7.56 %. Found: C, 51.06; H, 4.55: N, 7.22 %.

[Bis(NHC)Pd(NCMe)$_2$][BF$_4$]$_2$ (6)

A mixture of **5** (150 mg, 0.202 mmol), $AgBF_4$ (79 mg, 0.404 mmol), and dried acetonitrile (15 mL) was placed in a sealable flask under nitrogen. The reaction mixture was heated at 60 ^oC under nitrogen for 4 h with stirring. The mixture was then filtered through celite, the solvent was removed under vacuum, and the residue was dried in vacuo for 3 h. The crude product was dissolved in acetonitrile (5 mL), the solution was filtered again through celite, the solvent was evaporated, and the residue was dried in vacuo for 3 h. This sequence was repeated a third time to ensure complete removal of AgBr. Diethyl ether was added to the acetonitrile solution obtained after the last celite filtration, affording white crystals of **6**. The product was isolated by filtration and dried in vacuo for 12 h. Yield: 139 mg, 82%. ^1H NMR (400 MHz, CD_3CN): δ 7.84-7.75(m, 4H, phen.), 7.50 (d, *J* = 2.0 Hz, imidazole), 7.06 (s, 4H, Mes), 6.65 (d, *J* = 2.0 Hz, imidazole), 5.53 (br s, 4H, C*H*$_2$), 2.32 (s, 6H, *p*-C*H*$_3$), 2.30 (s, 12H, *o*-C*H*$_3$), 2.15 (s, 6H, C*H*$_3$CN). ^{13}C NMR (101 MHz, CD_3CN): δ 148.2 (carbene), 140.8 (Ar), 139.7 (Ar), 132.3 (Ar), 131.8 (Ar), 130.6 (Ar), 128.2 (Ar), 127.0 (Ar), 125.5 (Ar), 123.5 (imidazole), 50.2 (N*C*H_2), 21.1

(CH_3), 20.0 (CH_3), 3.5(CH_3CN). Anal. Calcd. for $C_{36}H_{40}B_2F_8N_6Pd$: C, 51.67; H, 4.82; N, 10.04 %. Found: C, 51.34; H, 4.92: N, 10.89 %. HRMS (ESI, $[C_{36}H_{40}N_6Pd + H]^+$) calcd. 659.2449, found m/z 659.2980.

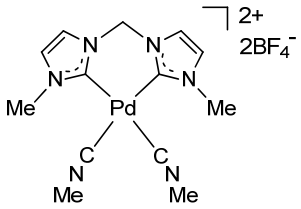
Bis(methylisocyanide) adduct of 6 for $\Delta\nu^{MeNC}$ determination (26)



26

Methyl isocyanide (17 μL, 0.30 mmol) was added to a stirred solution of **5** (90 mg, 0.12 mmol) in acetonitrile (10 mL), and the mixture was stirred for 1 h. $AgBF_4$ (47 mg, 0.24 mmol) was then added, and the mixture was stirred for an additional 2 h. The mixture was filtered through celite, solvent was evaporated, and the residue was dried in vacuo for 12 h. The crude product was dissolved in dichloromethane (5 mL), the solution was filtered through celite, the solvent was evaporated, and the residue was dried in vacuo for 12 h. This sequence was repeated two more times to ensure complete removal of AgBr. Diethyl ether was added to the dichloromethane solution obtained after the last celite filtration, affording **26** as white crystals. The product was isolated by filtration and dried in vacuo for 12 h. Yield: 84 mg, 93%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.96 (d, J = 2.0 Hz, 2H, imidazole), 7.82 (s, 4H, phen.), 7.05 (s, 4H, Mes), 6.97 (d, J = 2.0 Hz, imidazole), 5.41 (AB, J = 15 Hz, C = 19 Hz, 4H, CH_2), 3.63 (s, 6H, CH_3NC), 2.29 (s, 6H, *p*-CH_3), 2.27 (s, 12H, *o*-CH_3). ^{13}C NMR (101 MHz, DMSO-d_6): δ 155.3 (carbene), 138.7 (Ar), 138.1 (Ar), 131.1 (Ar), 130.8 (Ar), 129.5 (Ar), 127.5 (Ar), 126.5 (Ar), 125.5 (imidazole), 123.4 (CH_3NC), 122.9 (imidazole), 49.2 (NCH_2), 30.4 (CH_3NC), 20.7 (CH_3), 19.4 (CH_3). IR (Nujol, cm^{-1}): ν 2279 (m), 2271 (m). Anal. Calcd. for $C_{36}H_{40}B_2F_8N_6Pd\cdot0.5CH_2Cl_2$ (solvent content by ^{1}H NMR): C, 50.88; H, 4.80; N, 9.76 %. Found: C, 49.33; H, 5.08: N, 9.45 %.

Bis(methylisocyanide) adduct of 4 for $\Delta\nu^{MeNC}$ determination (27)



27

Methyl isocyanide (16 μL, 0.28 mmol) was added to a stirred solution of methylene-bridged bis(NHC)$PdBr_2$ complex **1**[2,3] (50 mg, 0.11 mmol) in acetonitrile (10 mL), and the mixture was stirred for 1 h. $AgBF_4$ (44 mg, 0.23 mmol) was then added, and the reaction mixture was stirred for 2 h. The mixture was filtered through celite, the solvent was evaporated, and the solid was dried in vacuo for 12 h. The crude product was dissolved in acetonitrile (5 mL), the solution was filtered through celite, the solvent was evaporated, and the solid was dried in vacuo for 12 h. This sequence was repeated a third time to ensure complete removal of AgBr. Diethyl ether was added to the dichloromethane solution obtained after the last celite filtration, affording **27** as white crystals. The product was isolated by filtration and dried in vacuo for 12 h. Yield: 48 mg, 80 %. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.75 (d, J = 1.8 Hz, 2H, imidazole), 7.58 (d, J = 1.8 Hz, 2H, imidazole), 6.35 (br s, 2H, CH_2), 3.86 (s, 6H, CNCH_3), 3.72 (s, 6H, imid.NCH_3). ^{13}C NMR (101 MHz, CD_3CN): δ 155.6 (carbene), 124.1 (imidazole), 124.0 (CNCH_3), 123.0 (imidazole), 62.4 (NCH_2), 38.2 (imid. NCH_3), 30.4 (CNCH_3). IR (Nujol, cm^{-1}): ν 2269 (m). Anal. Calcd. for $C_{13}H_{18}B_2F_8N_6Pd\cdot0.22CH_2Cl_2$ (solvent content by ^{1}H NMR): C, 28.51; H, 3.34; N, 15.09 %. Found: C, 28.26; H, 3.15: N, 14.71 %.

REFERENCES

(1) Miller, K. J.; Kitagawa, T. T.; Abu-Omar, M. M. *Organometallics* **2001**, *20*, 4403-4412.

(2) Gardiner, M. G.; Herrmann, W. A.; Reisinger, C.-P.; Schwarz, J.; Spiegler, M. *J. Organomet. Chem.* **1999**, *572*, 239-247.

(3) Herdtweck, E.; Muehlhofer, M.; Strassner, T. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2003**, *E59*, m970-m971.

(4) So, Y.-H. *Macromolecules* **1992**, *25*, 516-520.

(5) van der Made, A. W.; van der Made, R. H. *J. Org. Chem.* **1993**, *58*, 1262-1263.

(6) Walz, I.; Bertogg, A.; Togni, A. *Eur. J. Org. Chem.* **2007**, 2650-2658.

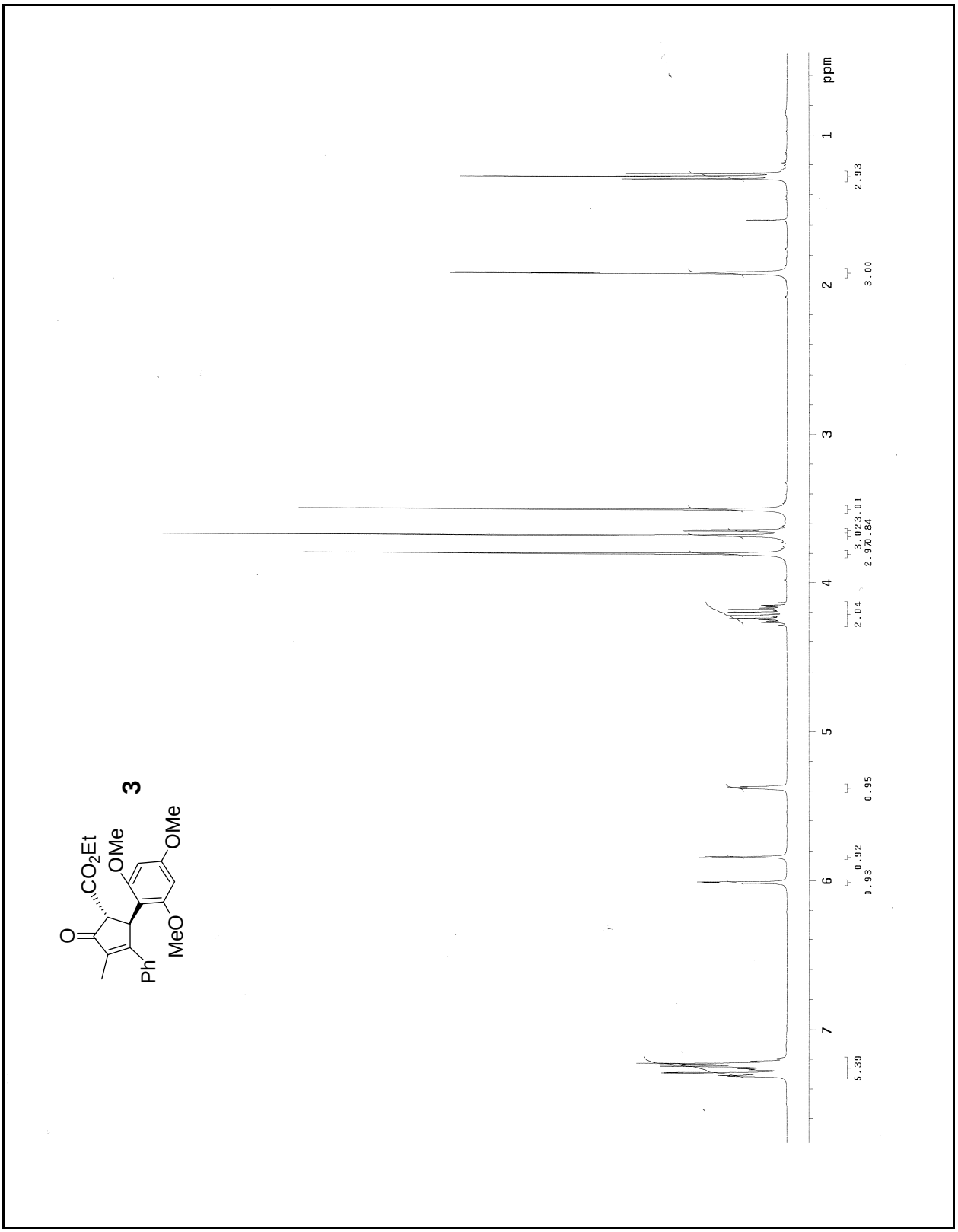
(7) Aggarwal, V. K.; Belfield, A. J. *Org. Lett.* **2003**, *5*, 5075-5078.

(8) Canterbury, D. P.; Herrick, I. R.; Um, J.; Houk, K. N.; Frontier, A. J. *Tetrahedron* **2009**, *65*, 3165-3179.

(9) Murugan, K.; Srimurugan, S.; Chen, C. *Chem. Commun.* **2010**, *46*, 1127-1129. ***Note***: Compounds **16-18** were incorrectly depicted as the phenyl derivative in the text of this reference (compounds **12**, **12a**, and **12b**; Table 2, entry 9), but the experimental procedures and scanned NMR spectral data in the Supporting Information confirm that they are in fact the *p*-methoxyphenyl compounds.

(10) Wanniarachchi, Y. A.; Khan, M. A.; Slaughter, L. M. *Organometallics* **2004**, *23*, 5881-5884.

(11) Subramanium, S. S.; Slaughter, L. M. *Dalton Trans.* **2009**, 6930-6933.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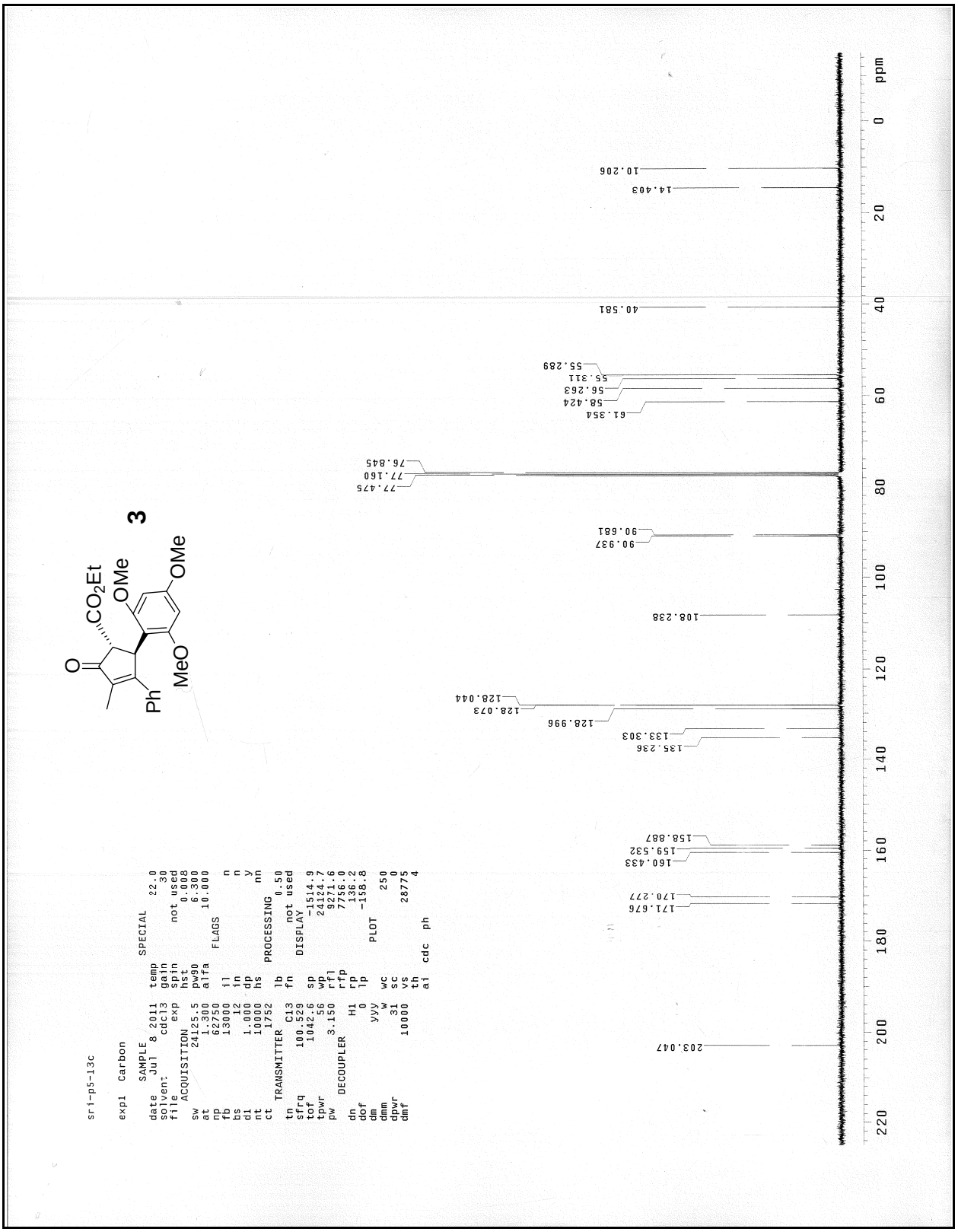
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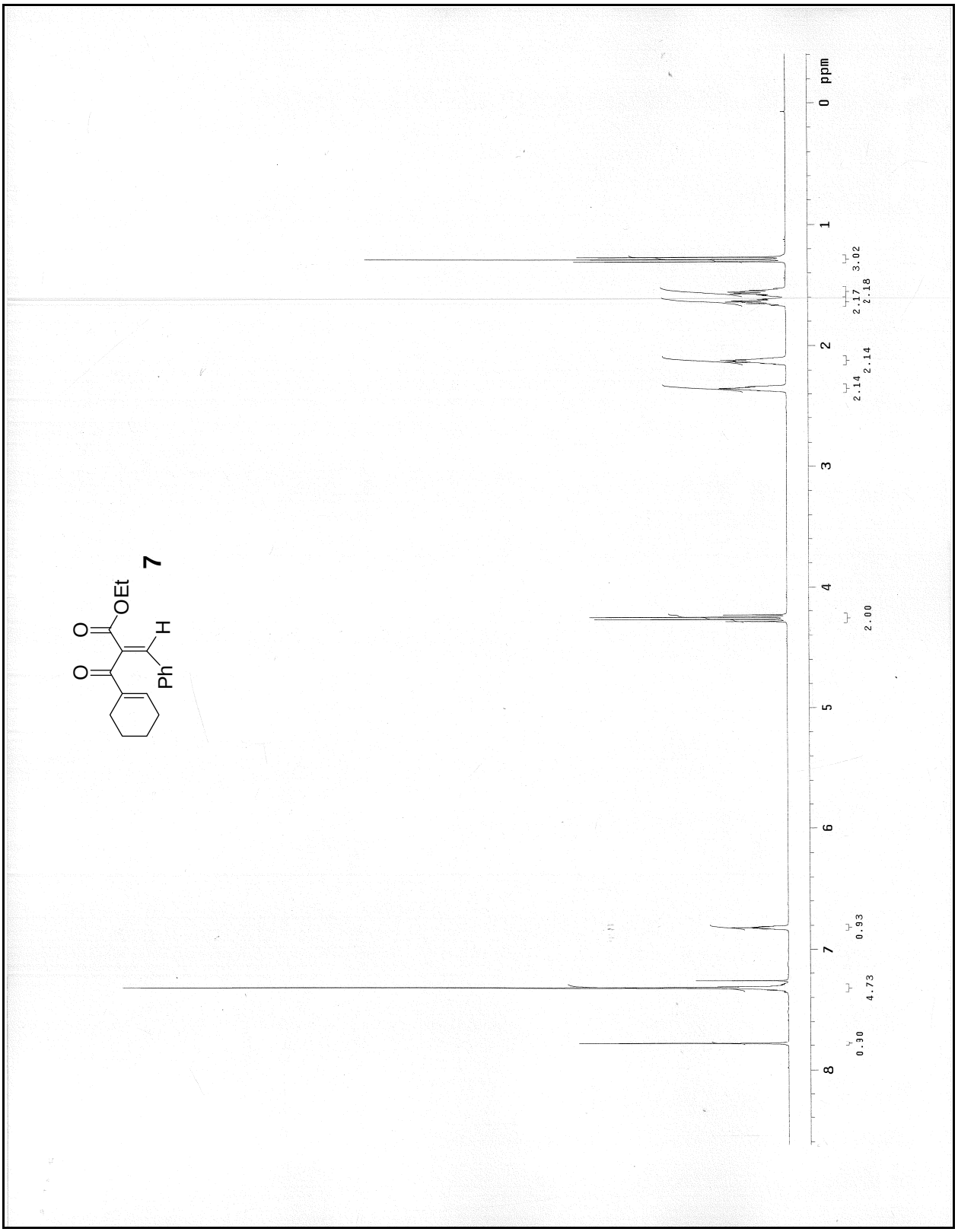
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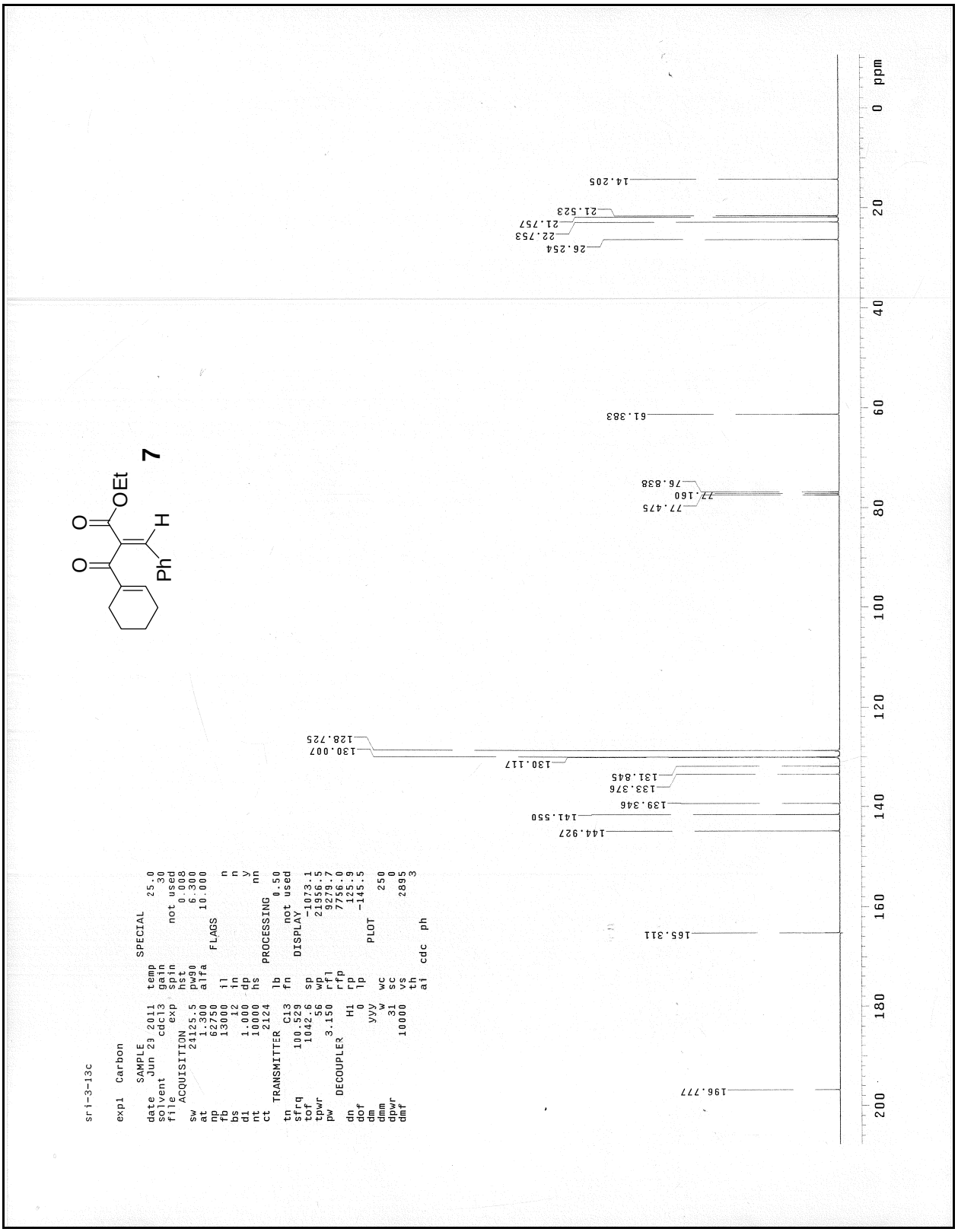
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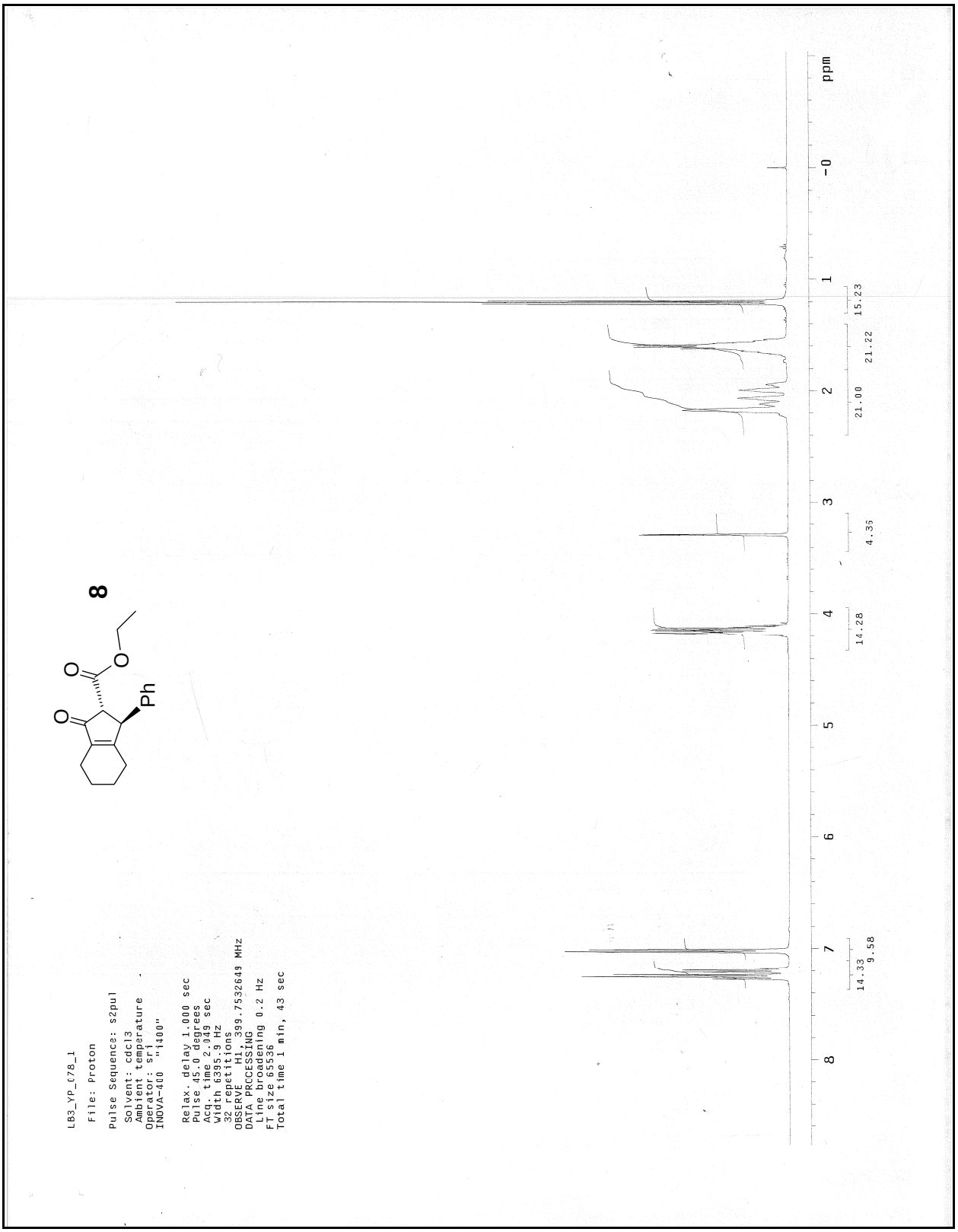
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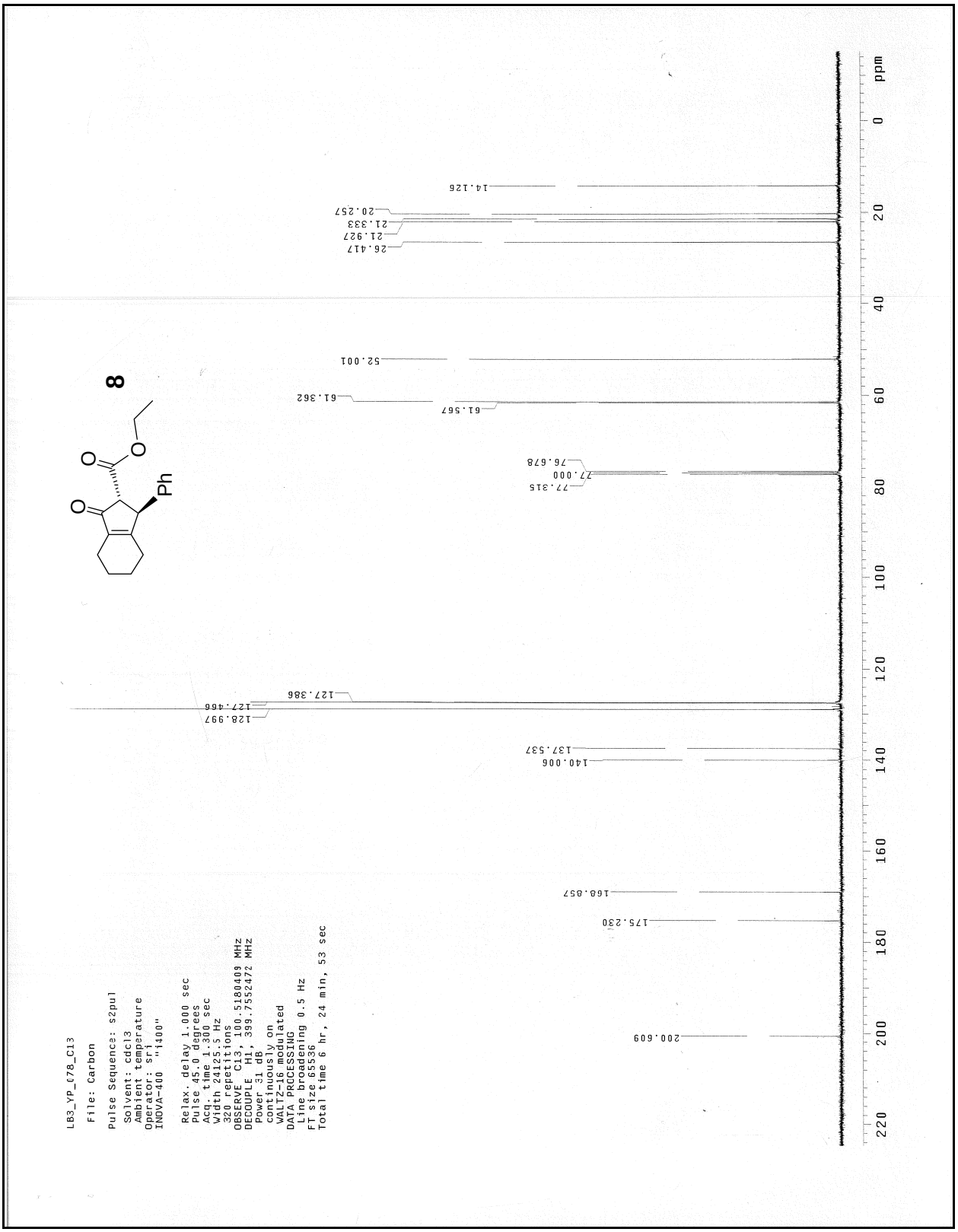
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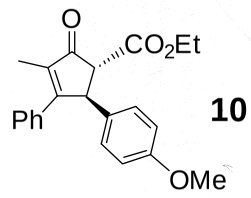

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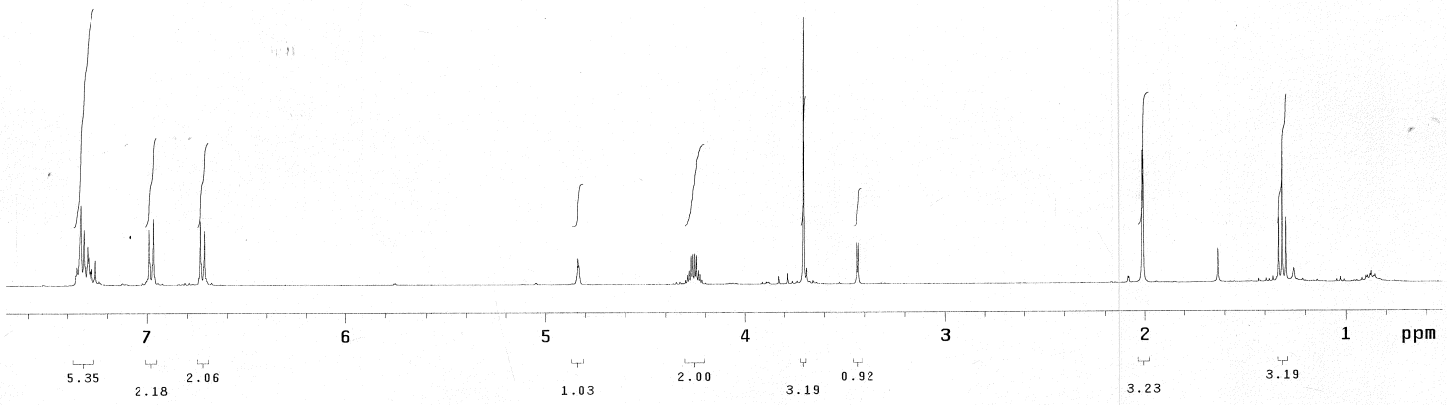

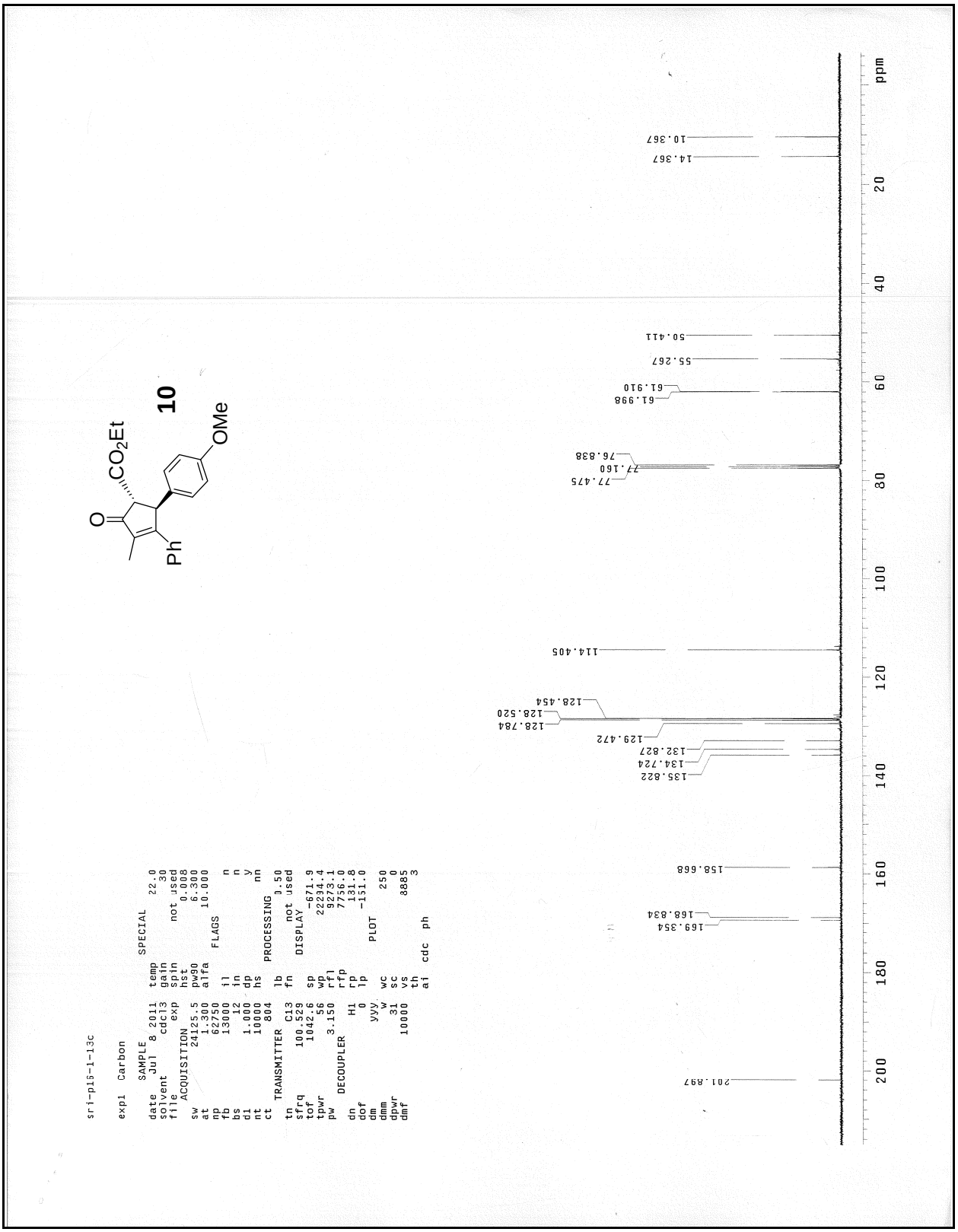
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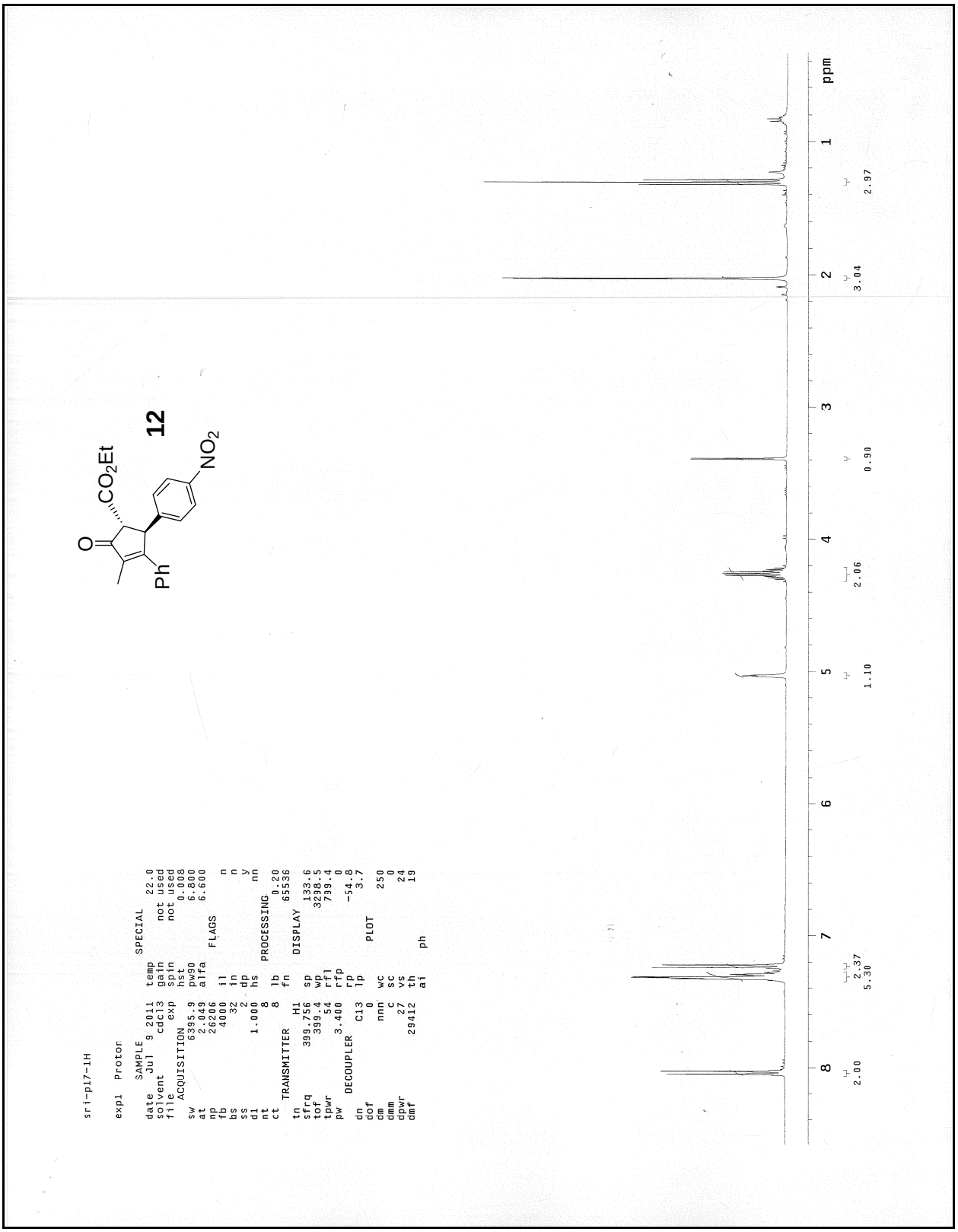
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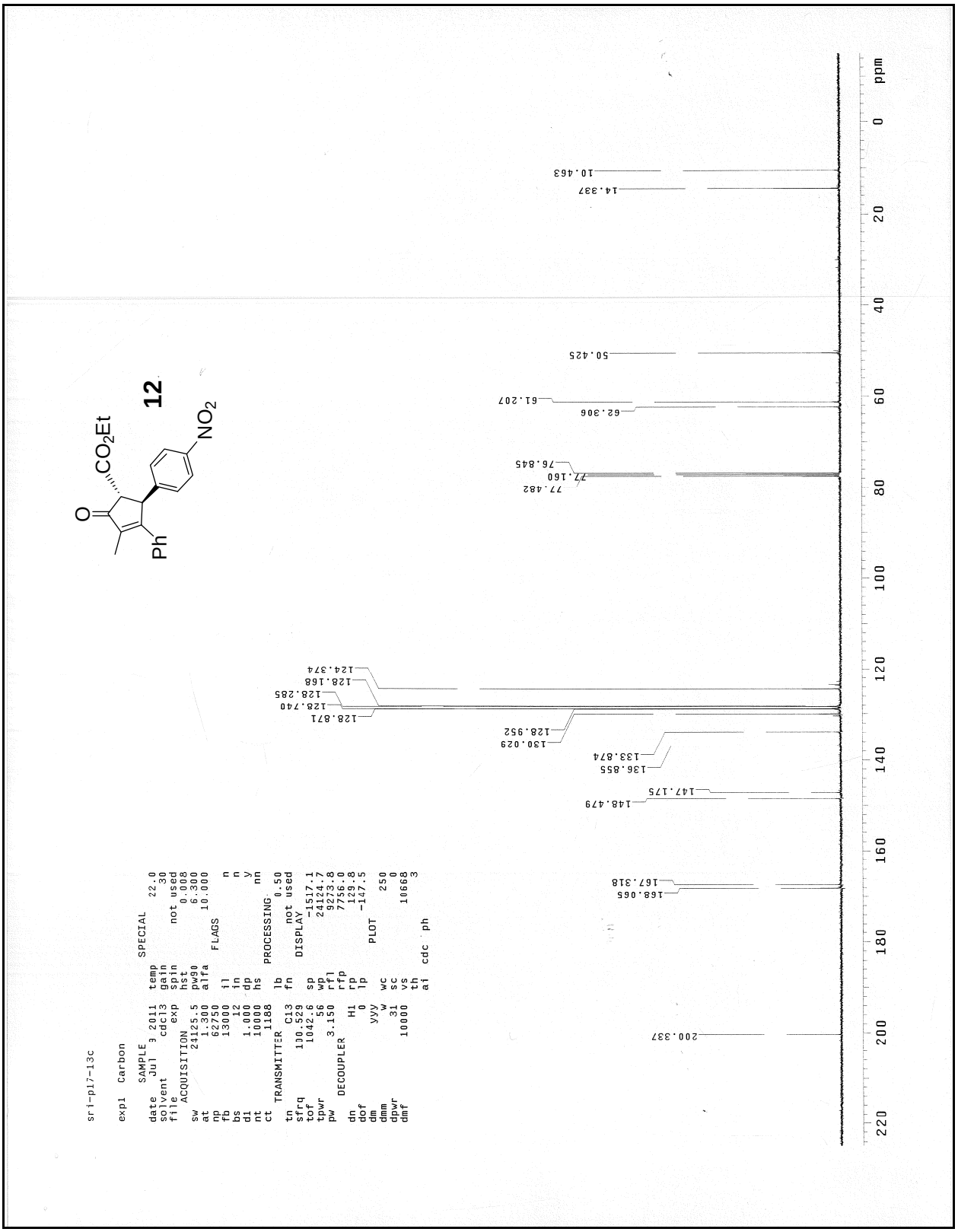
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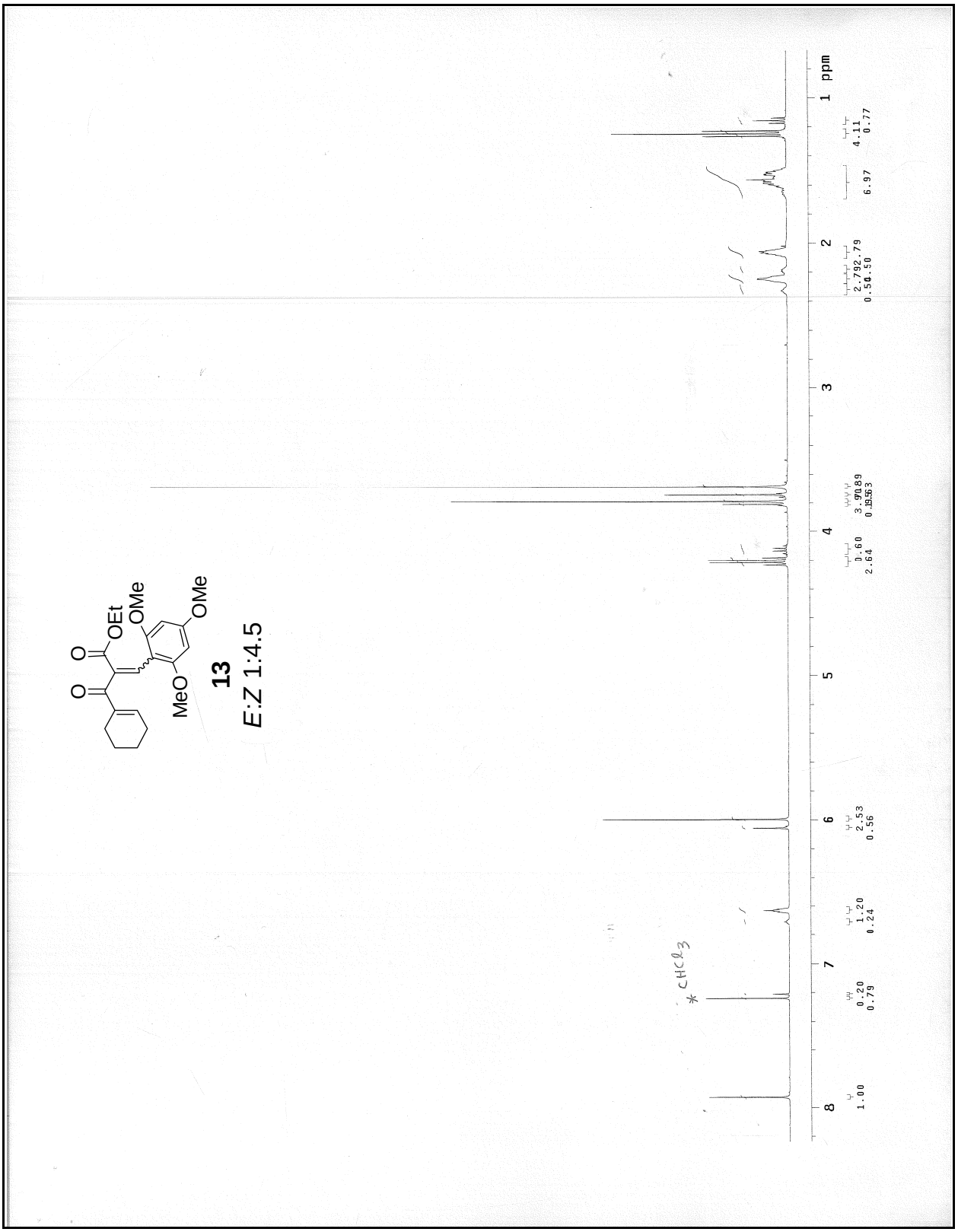
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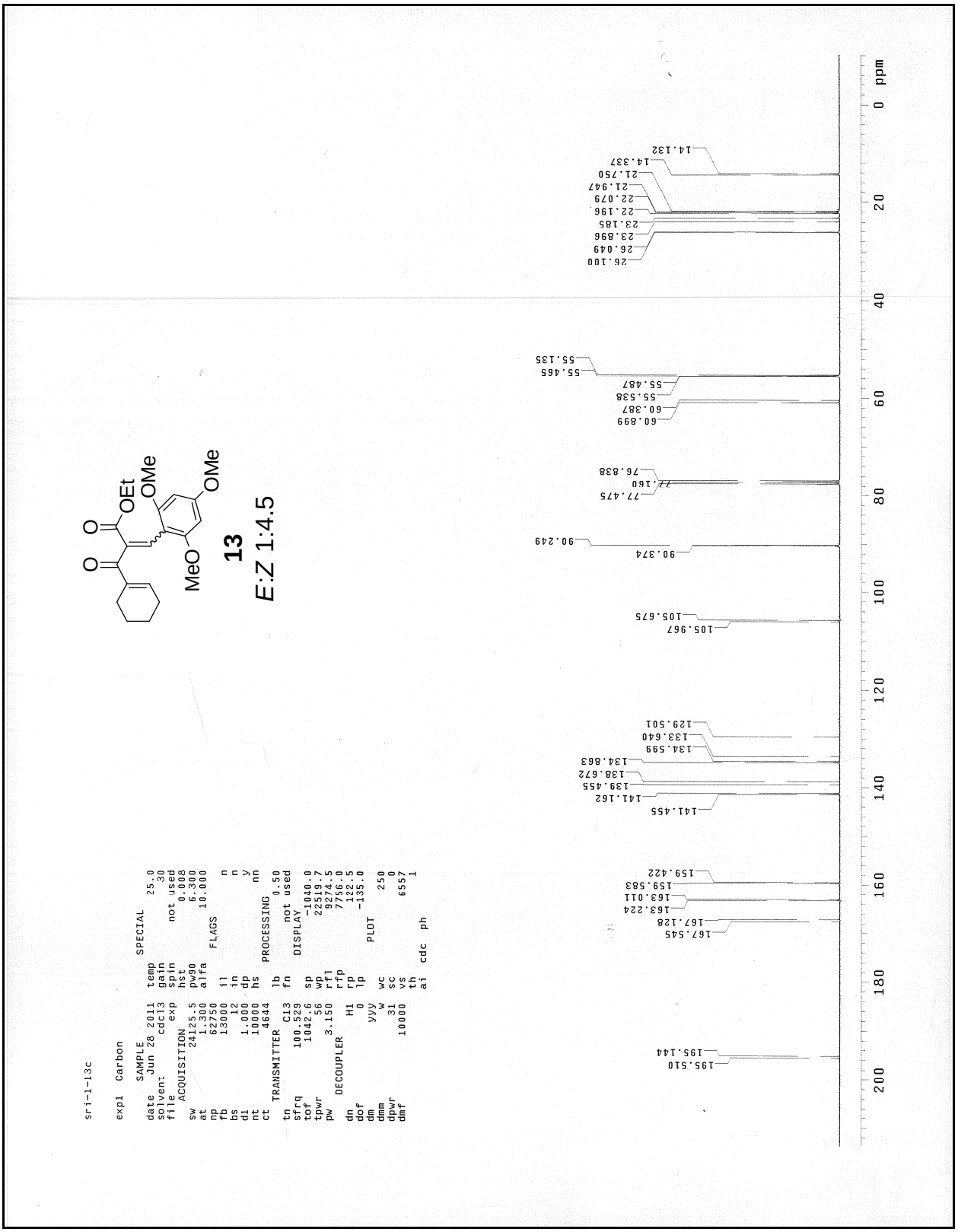
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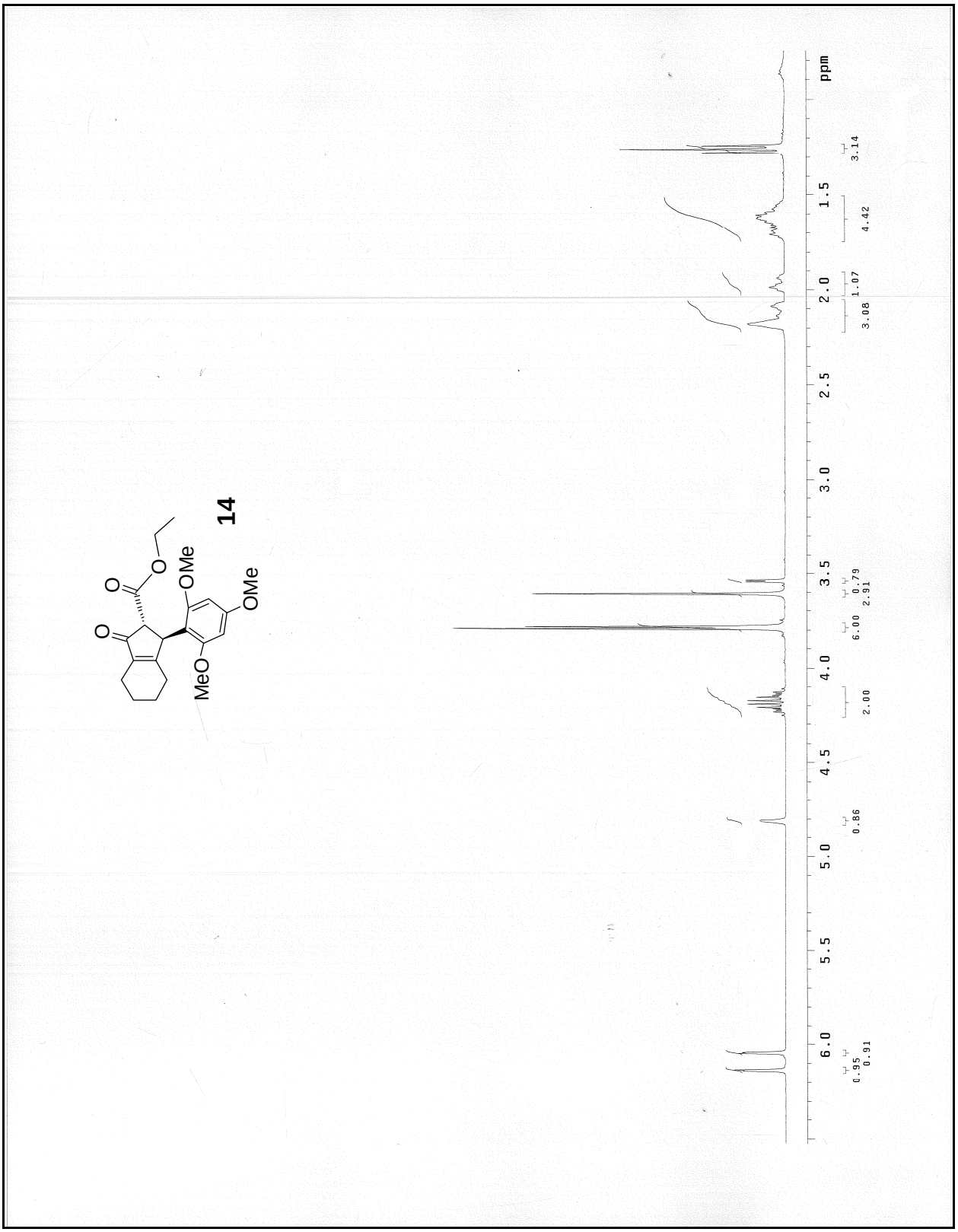
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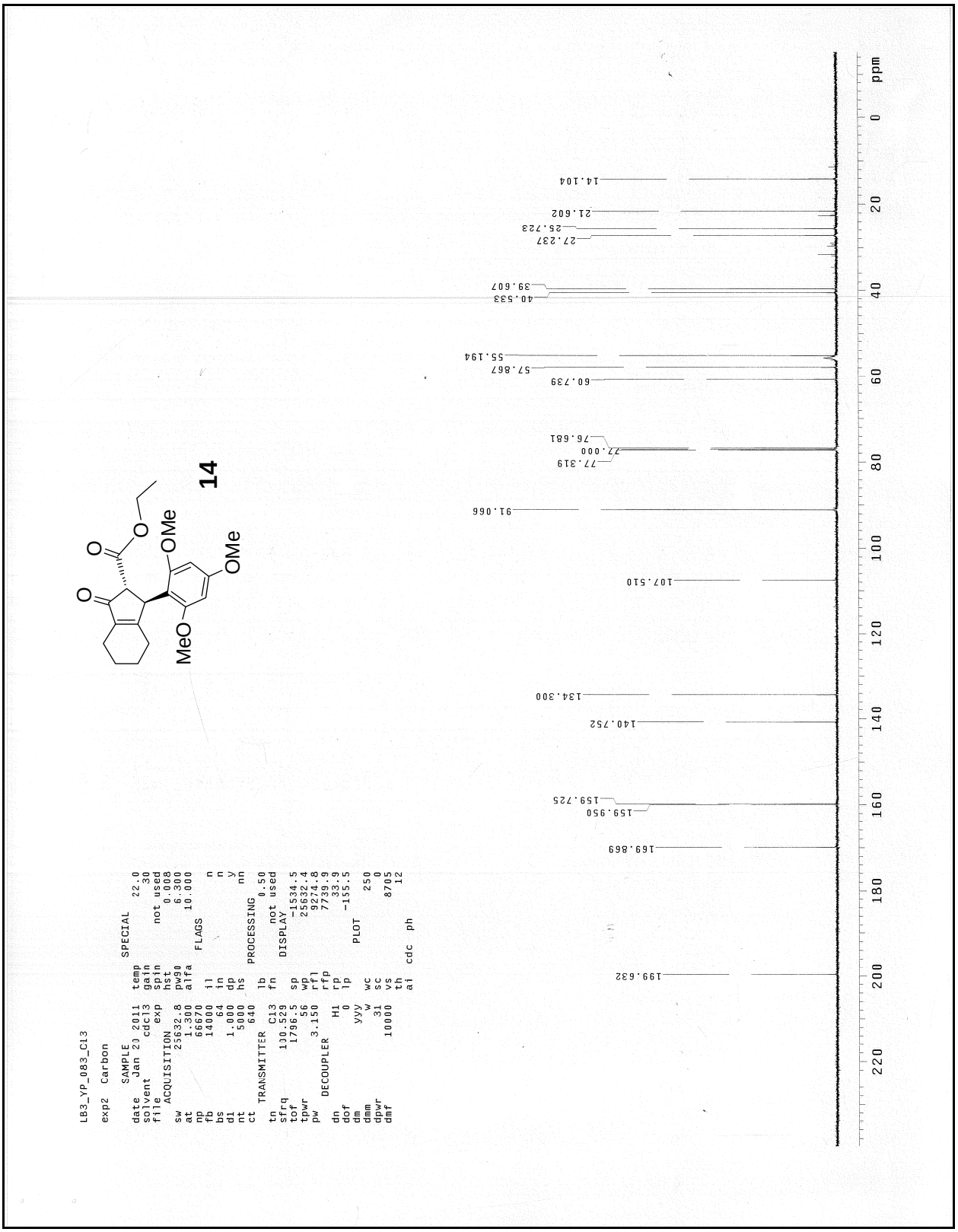
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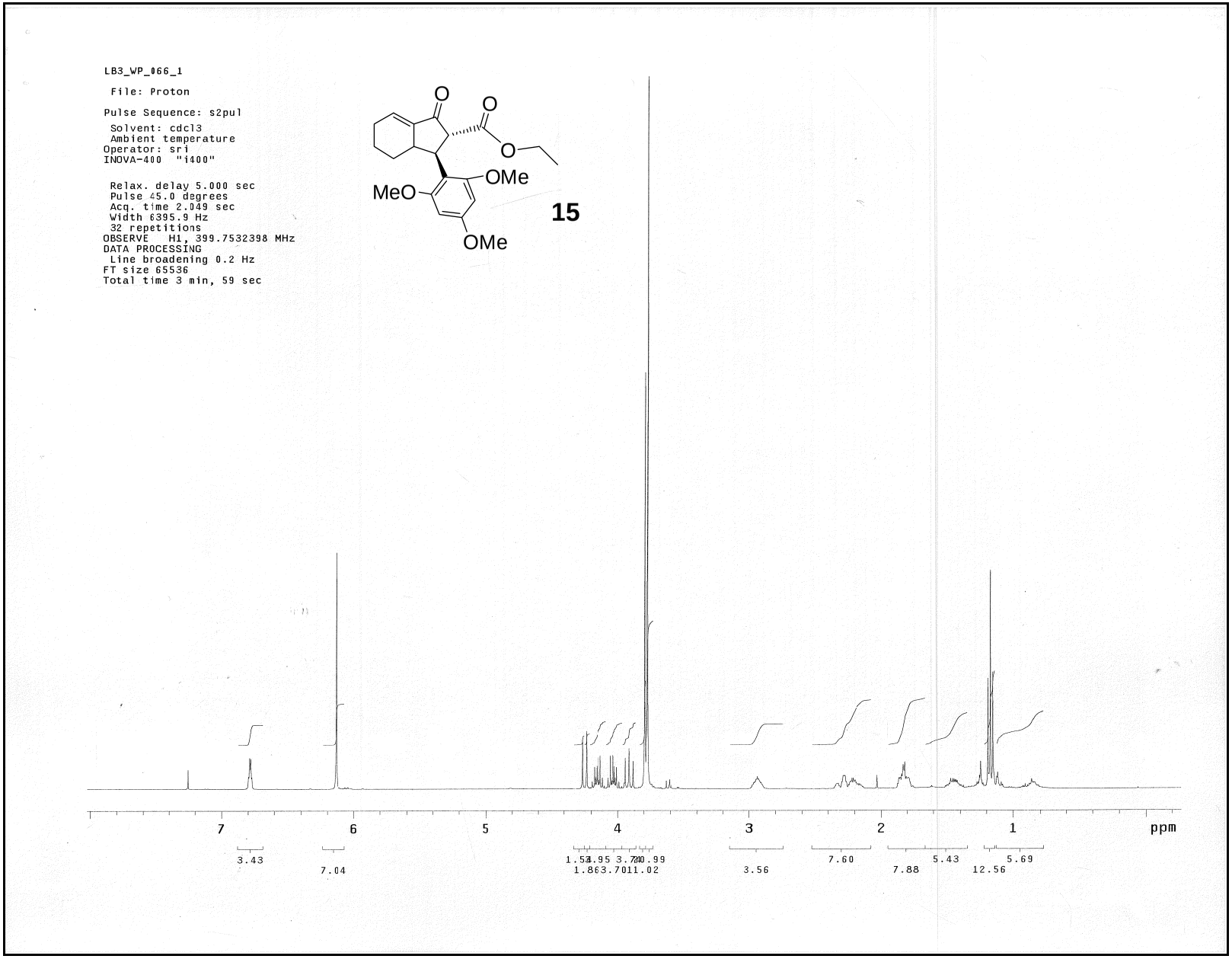
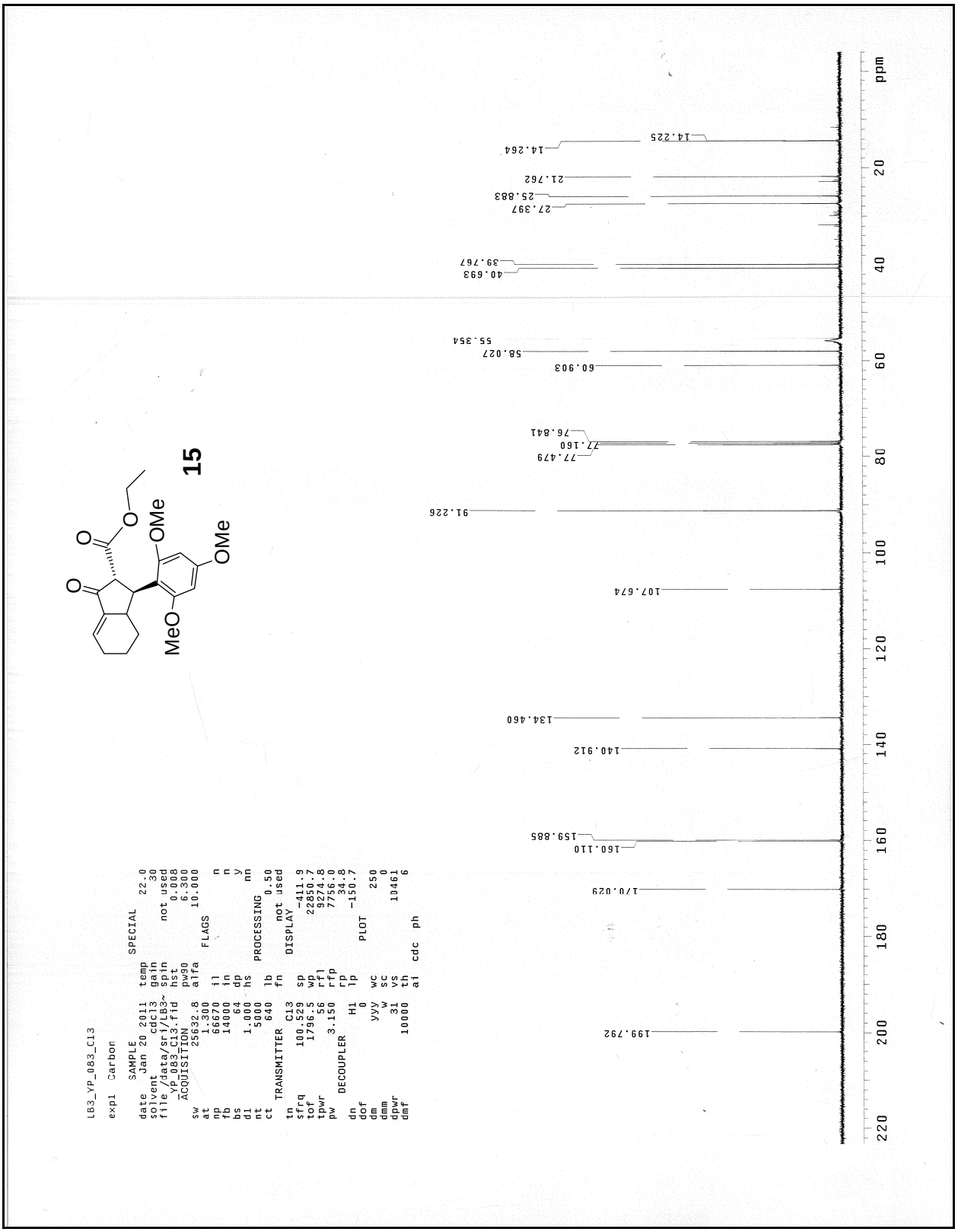
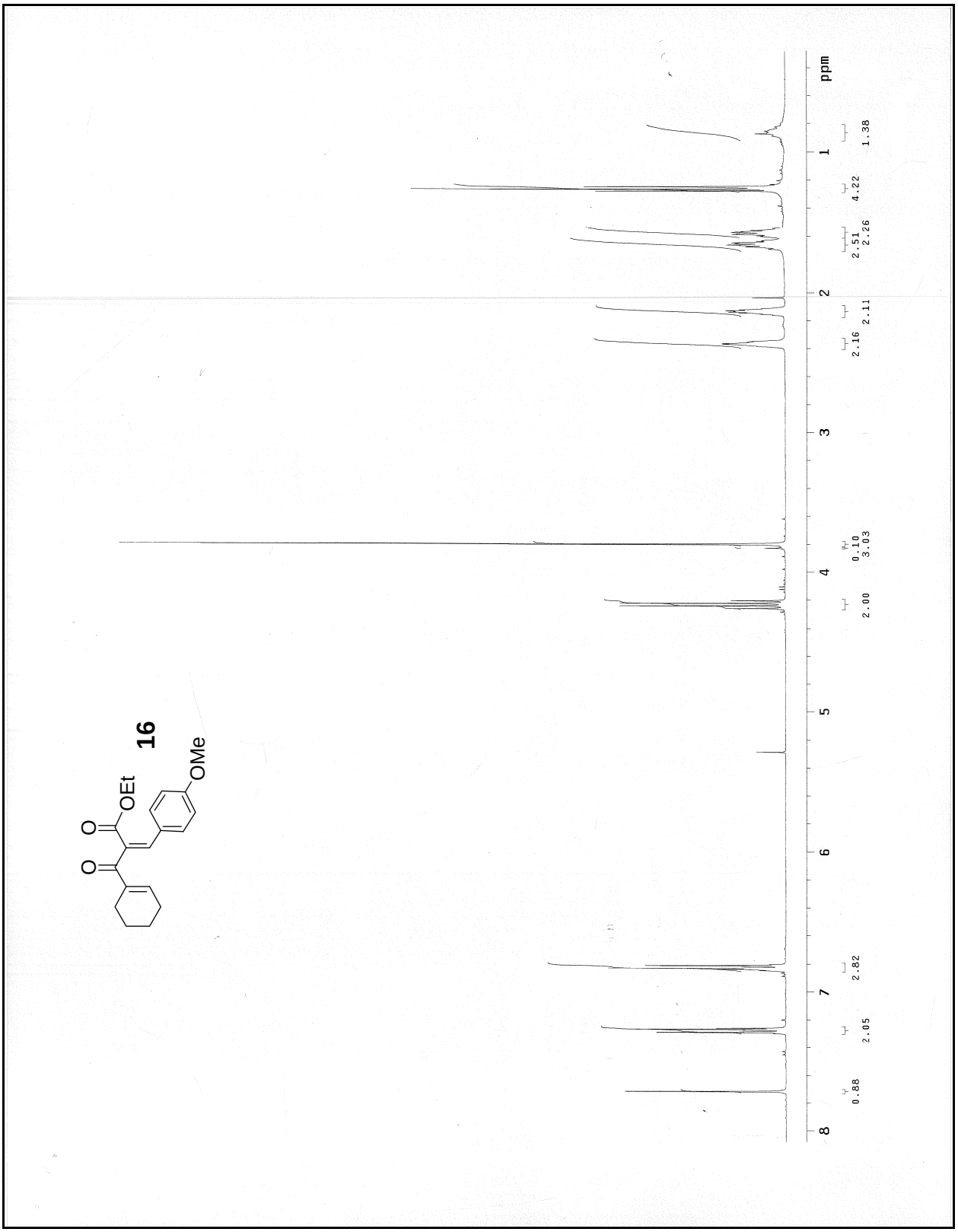
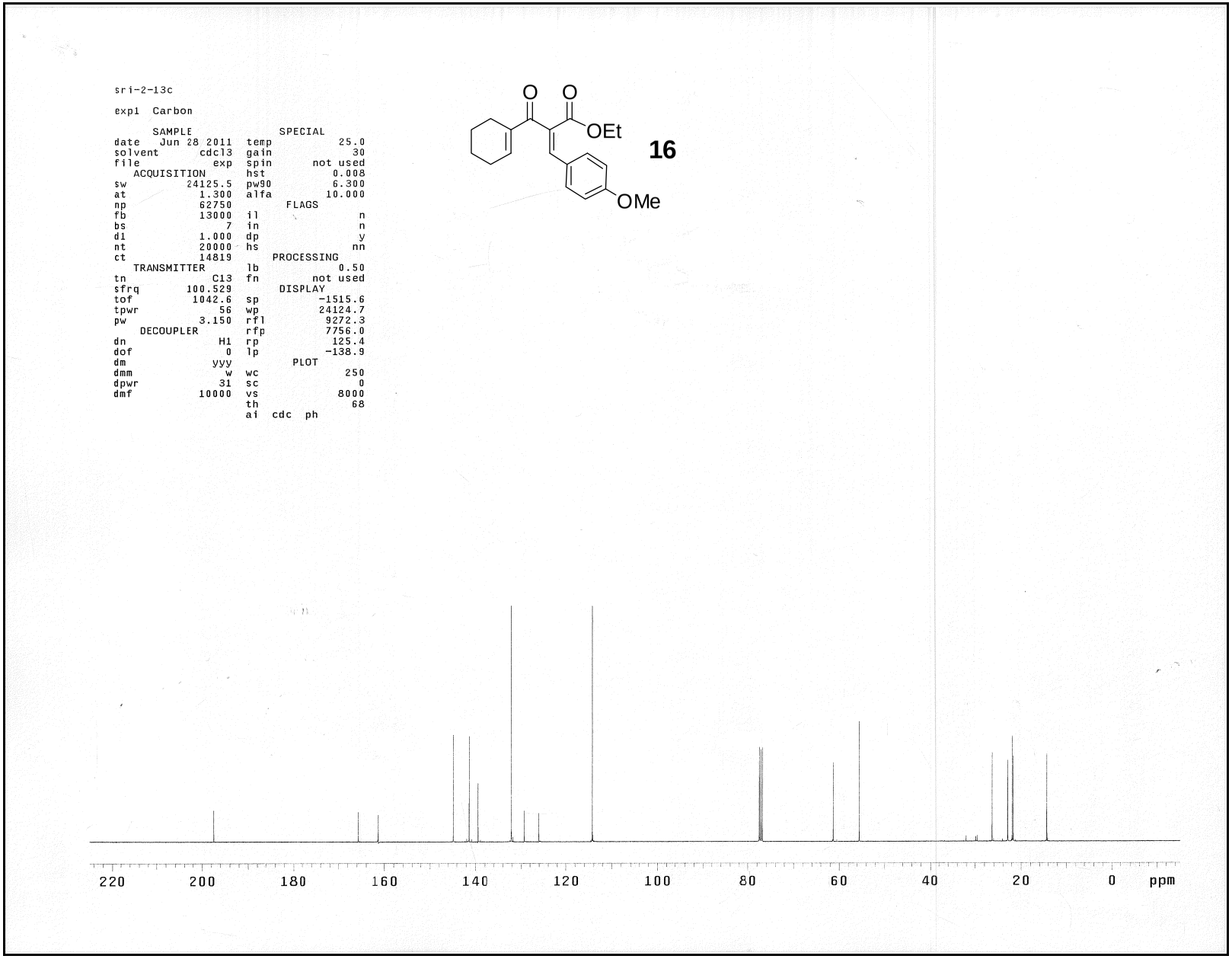
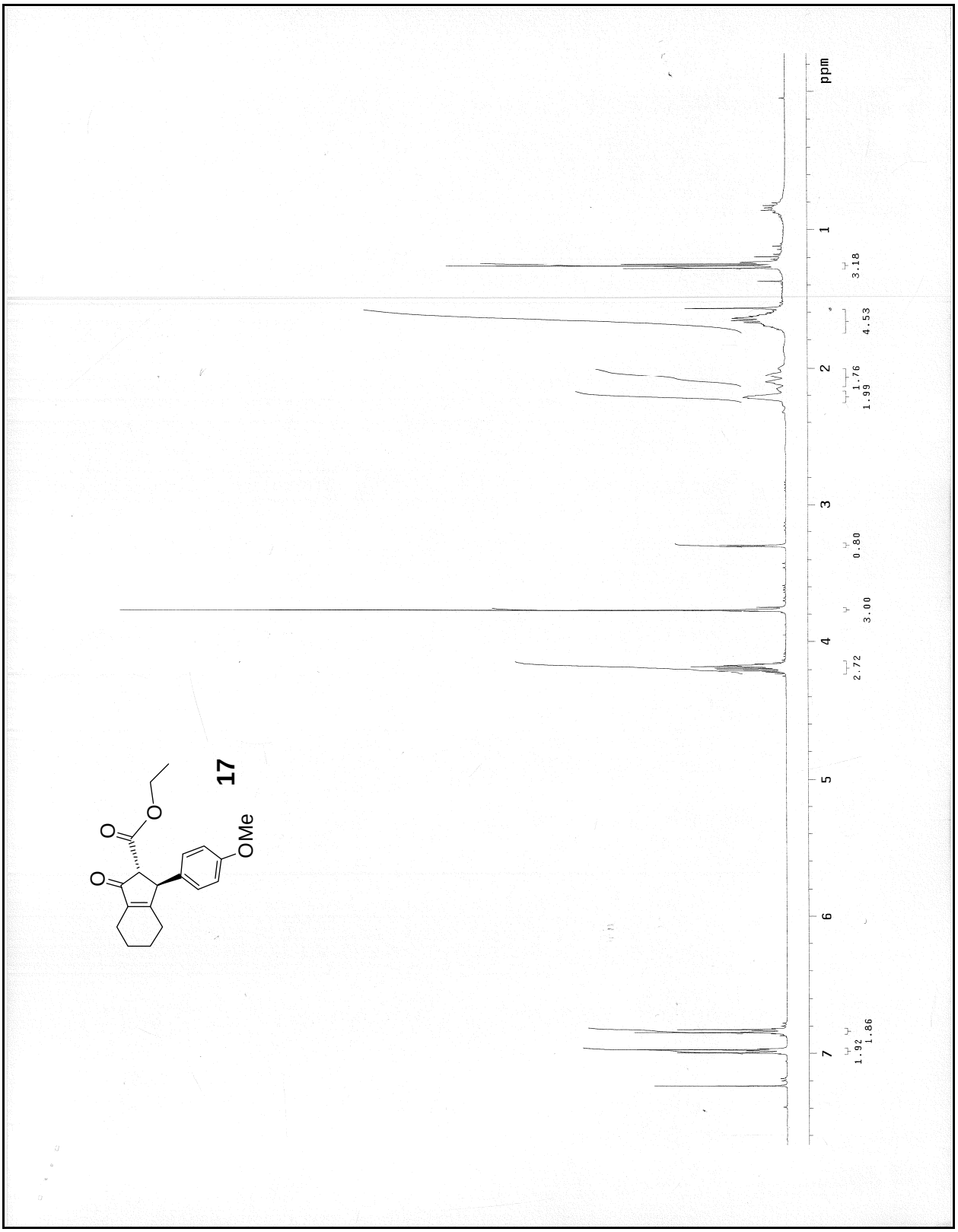
91.066
77.319
77.000
76.681
60.739
57.867
55.194
40.533
39.607
27.237
25.723
21.602
14.104
220
200
180
160
140
120
100
80
60
40
20
0
ppm

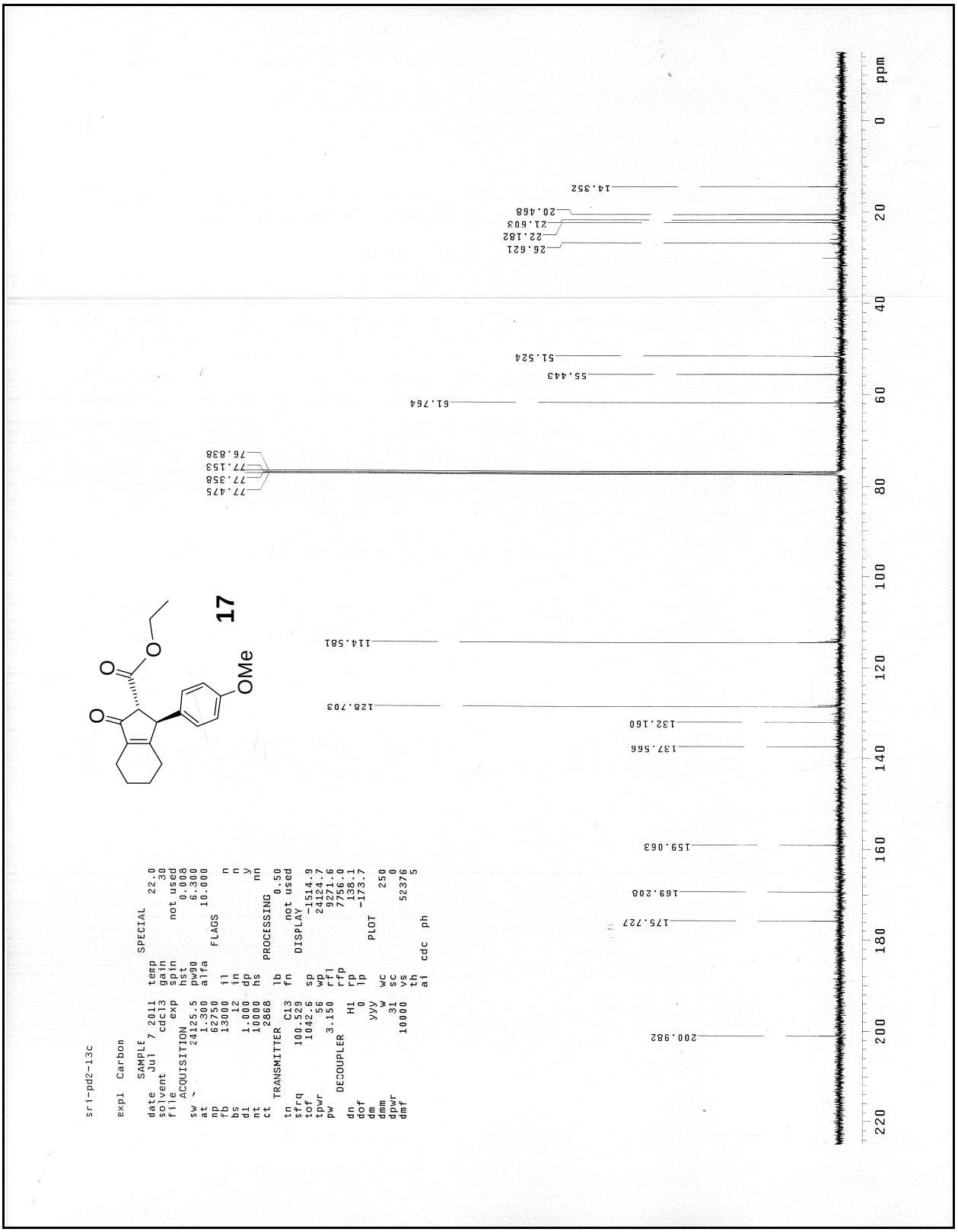

LB3_WP_066_1
File: Proton
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: sri
INOVA-400 "i400"
Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 6395.9 Hz
32 repetitions
OBSERVE H1, 399.7532398 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 3 min, 59 sec
O
O
O
OMe
MeO
OMe
15
7
6
5
4
3
2
1
ppm
3.43
7.04
1.53
1.86
3.95
3.70
3.70
11.02
0.99
3.56
7.60
7.88
5.43
12.56
5.69

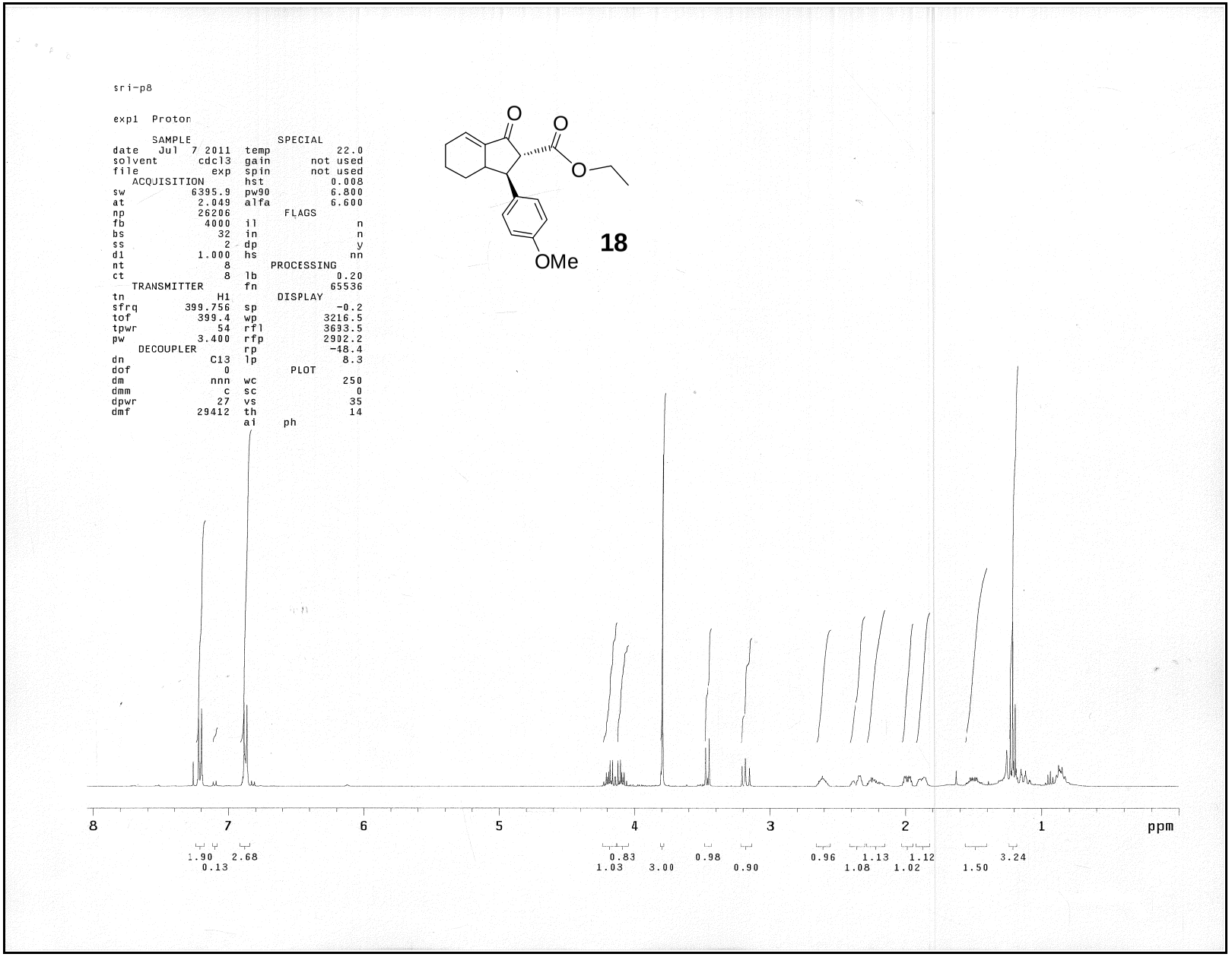

LB3_YP_083_C13
expl Carbon
SAMPLE
date Jan 20 2011
solvent cdcl3
file /data/sri/LB3~
yp_083_C13.fid
ACQUISITION
sw 25632.8
at 1.300
np 66670
fb 14000
bs 64
d1 1.000
nt 5000
ct 640
TRANSMITTER
sfrq 100.529
tof 1796.5
tpwr 56
pw 3.150
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 31
dmf 10000
SPECIAL
temp 22.0
gain
spin not used
hst 0.008
pw90 6.300
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 0.50
fn not used
C13
DISPLAY
sp -411.9
wp 22850.7
rfl 9274.8
rfp 7756.0
rp 34.8
lp -150.7
PLOT
wc 250
sc 0
vs 10461
th 6
cdc ph
ai
15
O
O
OMe
OMe
MeO
199.792
170.029
160.110
159.885
140.912
134.460
107.674
91.226
77.479
77.160
76.841
60.903
58.027
55.354
40.693
39.767
27.397
25.883
21.762
14.264
14.225
220
200
180
160
140
120
100
80
60
40
20
ppm

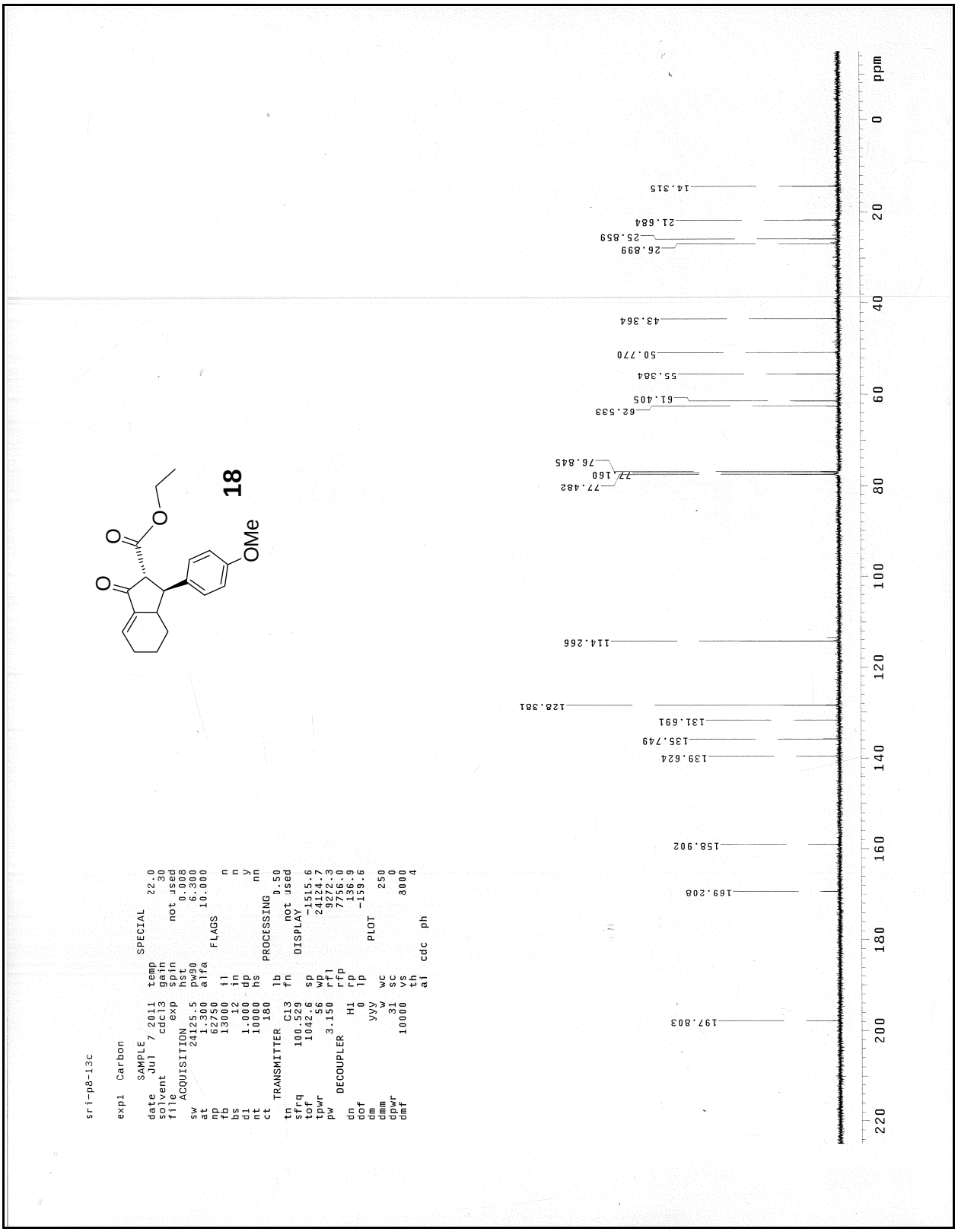

16
OEt
OMe
O
O
ppm
1
2
3
4
5
6
7
8
1.38
4.22
2.26
2.51
2.11
2.16
3.03
0.10
2.00
2.82
2.05
0.88

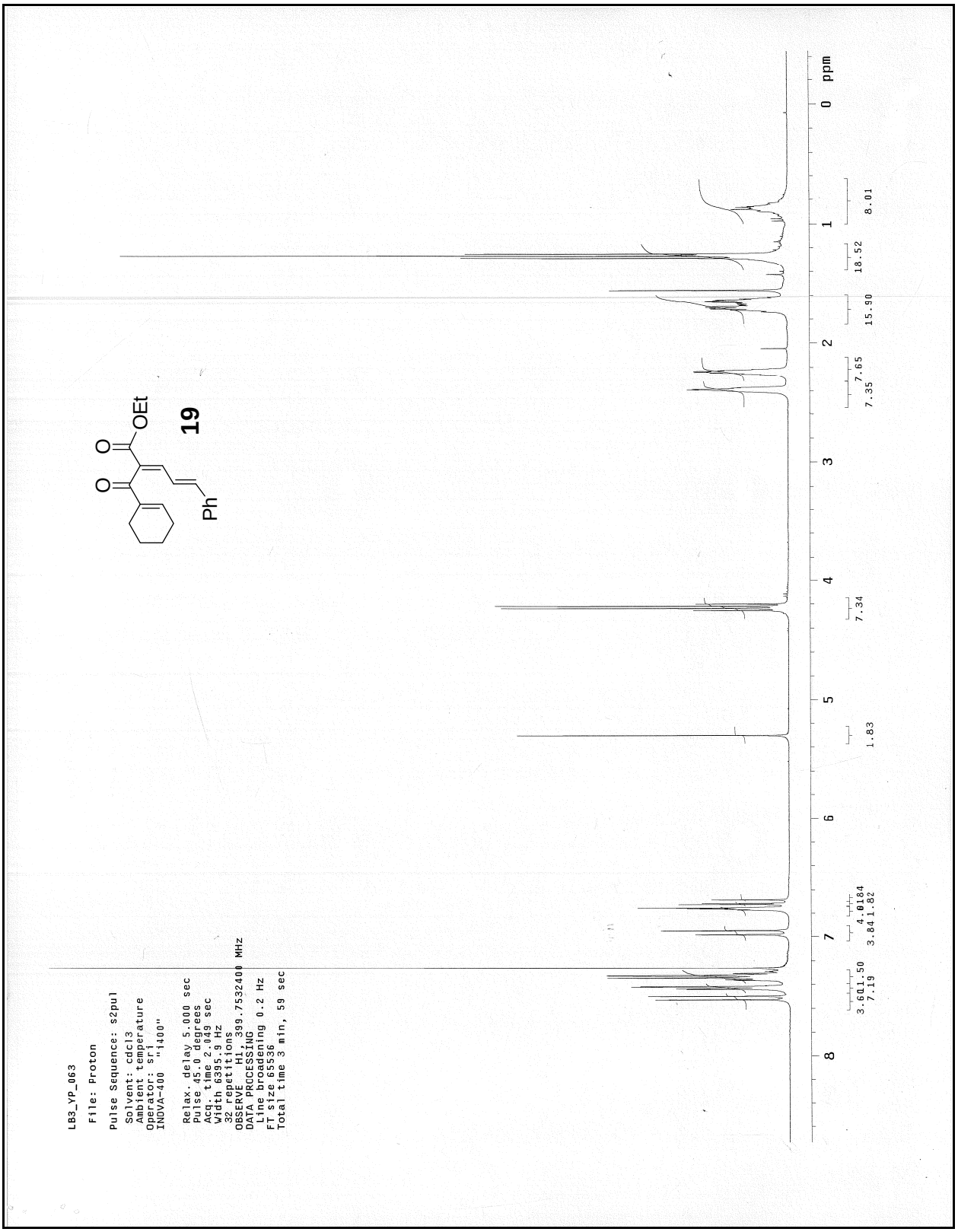

sri-2-13c
exp1 Carbon
SAMPLE
date Jun 28 2011
solvent cdcl3
file exp
ACQUISITION
sw 24125.5
at 1.300
np 62750
fb 13000
bs 7
d1 1.000
nt 20000
ct 14819
TRANSMITTER
tn C13
sfrq 100.529
tof 1042.6
tpwr 56
pw 3.150
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 31
dmf 10000
SPECIAL
temp 25.0
gain 30
spin not used
hst 0.008
pw90 6.300
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 0.50
fn not used
DISPLAY
sp -1515.6
wp 24124.7
rfl 9272.3
rfp 7756.0
rp 125.4
lp -138.9
PLOT
wc 250
sc 0
vs 8000
th 68
ai cdc ph
O
O
OEt
OMe
16
220
200
180
160
140
120
100
80
60
40
20
0
ppm

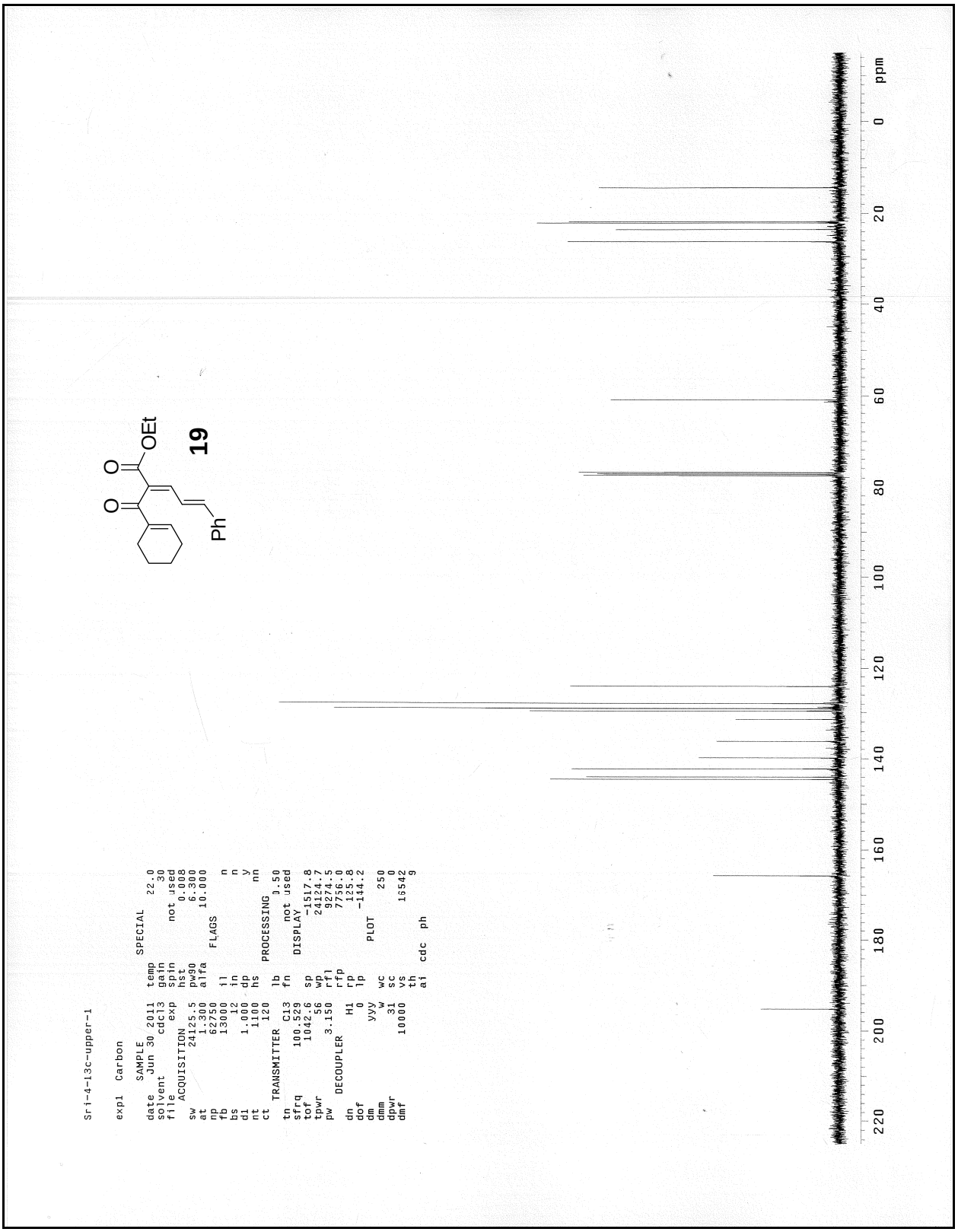

17
OMe
O
O
O
ppm
1
2
3
4
5
6
7
3.18
4.53
1.76
1.99
0.80
3.00
2.72
1.92
1.86

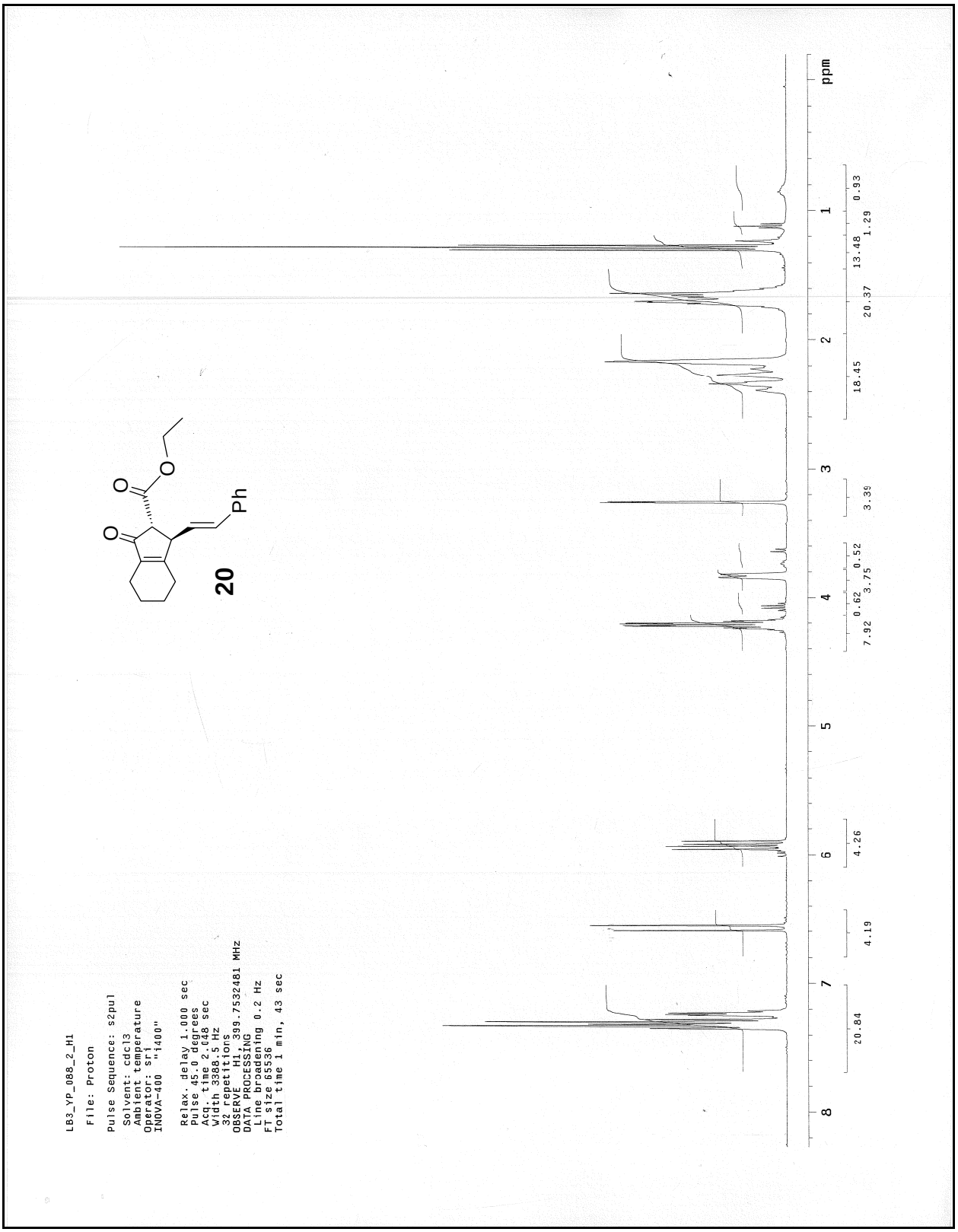

sri-pd2-13c
expl Carbon
SAMPLE
date Jul 7 2011
solvent cdcl3
file exp
ACQUISITION
sw
at
np
fb
bs
d1
nt
ct
TRANSMITTER
tn C13
sfrq 100.529
tof 1042.6
tpwr 56
pw 3.150
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 31
dmf 10000
SPECIAL
temp 22.0
gain 30
spin
hst not used
pw90 0.008
alfa 6.300
FLAGS 10.000
il n
in n
dp y
hs nn
PROCESSING
lb 0.50
fn not used
DISPLAY
sp -1514.9
wp 24124.7
rfl 9271.6
rfp 7756.0
rp 138.1
lp -173.7
PLOT
wc 250
sc 0
vs 52376
th 5
ai cdc ph
17
OMe
O
O
O
77.475
77.358
77.153
76.838
61.764
55.443
51.524
26.621
22.182
21.603
20.468
14.352
114.581
128.703
132.160
137.566
159.063
169.208
175.727
200.982
ppm

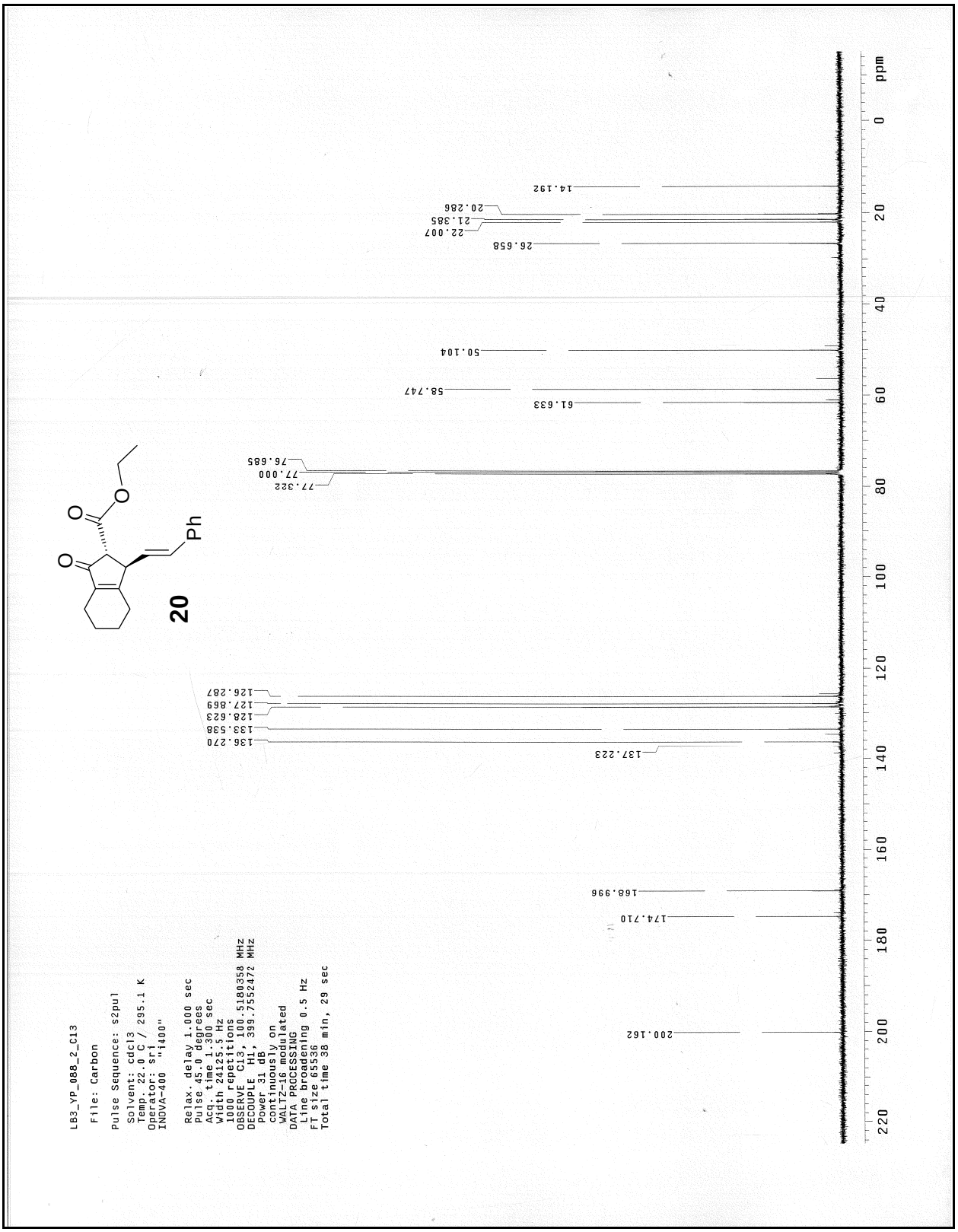

sri-p8
exp1 Proton
SAMPLE
date Jul 7 2011
solvent cdcl3
file exp
ACQUISITION
sw 6395.9
at 2.049
np 26206
fb 4000
bs 32
ss 2
d1 1.000
nt 8
ct 8
TRANSMITTER
tn H1
sfrq 399.756
tof 399.4
tpwr 54
pw 3.400
DECOUPLER
dn C13
dof 0
dm nnn
dmm c
dpwr 27
dmf 29412
SPECIAL
temp 22.0
gain not used
spin not used
hst 0.008
pw90 6.800
alfa 6.600
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 0.20
fn 65536
DISPLAY
sp -0.2
wp 3216.5
rfl 3693.5
rfp 2902.2
rp -48.4
lp 8.3
PLOT
wc 250
sc 0
vs 35
th 14
ai ph
OMe
18
8
7
6
5
4
3
2
1
ppm
1.90
0.13
2.68
0.83
1.03
3.00
0.98
0.90
0.96
1.08
1.13
1.02
1.12
1.50
3.24

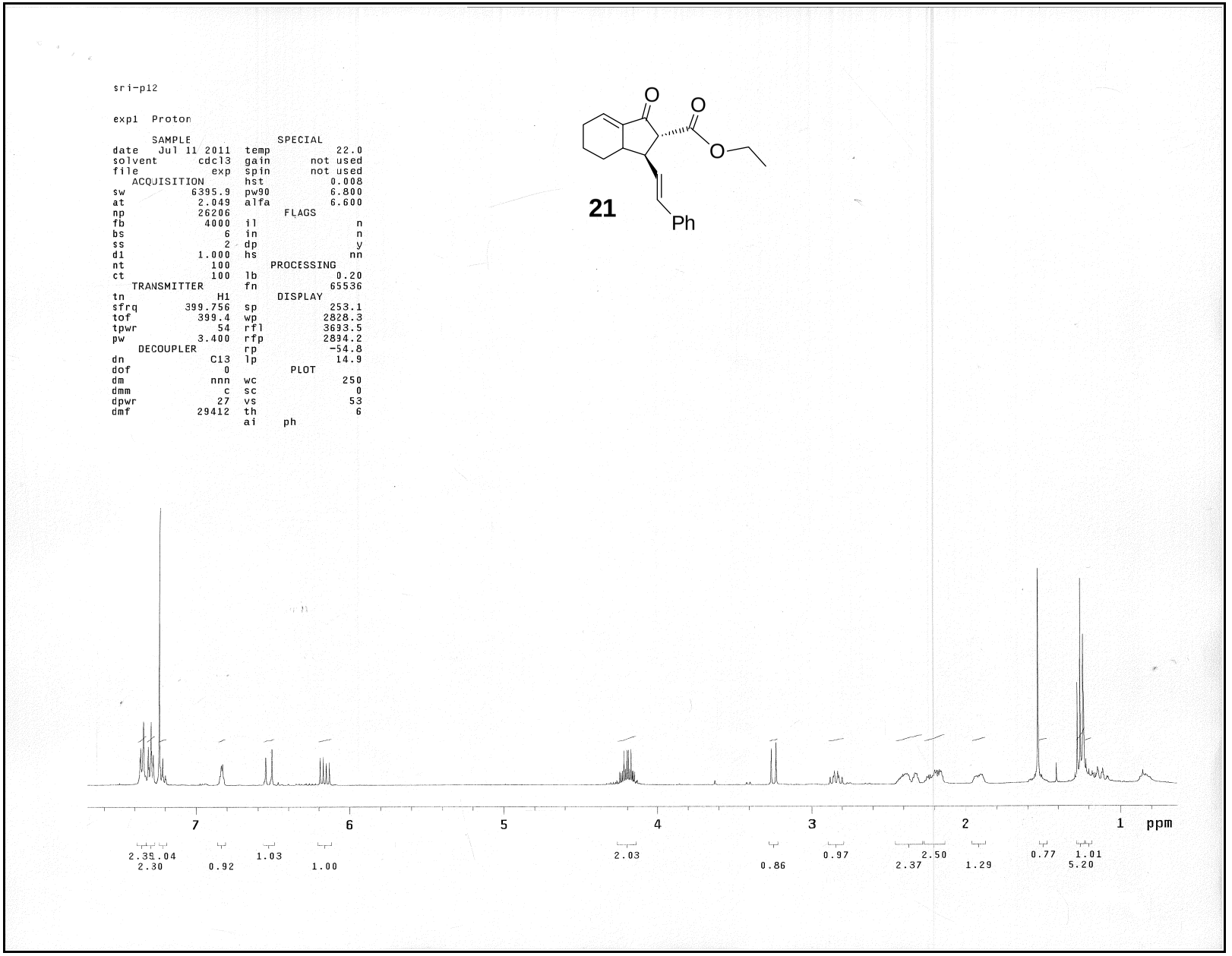

sri-pB-13c
expl Carbon
SAMPLE
date Jul 7 2011
solvent cdcl3
file exp
ACQUISITION
sw 24125.5
at 1.300
np 62750
fb 13000
bs 12
d1 1.000
nt 10000
ct 180
TRANSMITTER
tn C13
sfrq 100.529
tof 1042.6
tpwr 56
pw 3.150
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 31
dmf 10000
SPECIAL
temp 22.0
gain 30
spin not used
hst 0.008
pw90 6.300
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 0.50
fn not used
DISPLAY
sp -1515.6
wp 24124.7
rfl 9272.3
rfp 7756.0
rp 136.9
lp -159.6
PLOT
wc 250
sc 0
vs 3000
th 4
ai cdc ph
18
OMe
O
O
O
197.803
158.902
169.208
139.624
135.749
131.691
128.381
114.266
77.482
77.160
76.845
62.533
61.405
55.384
50.770
43.364
26.899
25.859
21.684
14.315
220
200
180
160
140
120
100
80
60
40
20
0
ppm

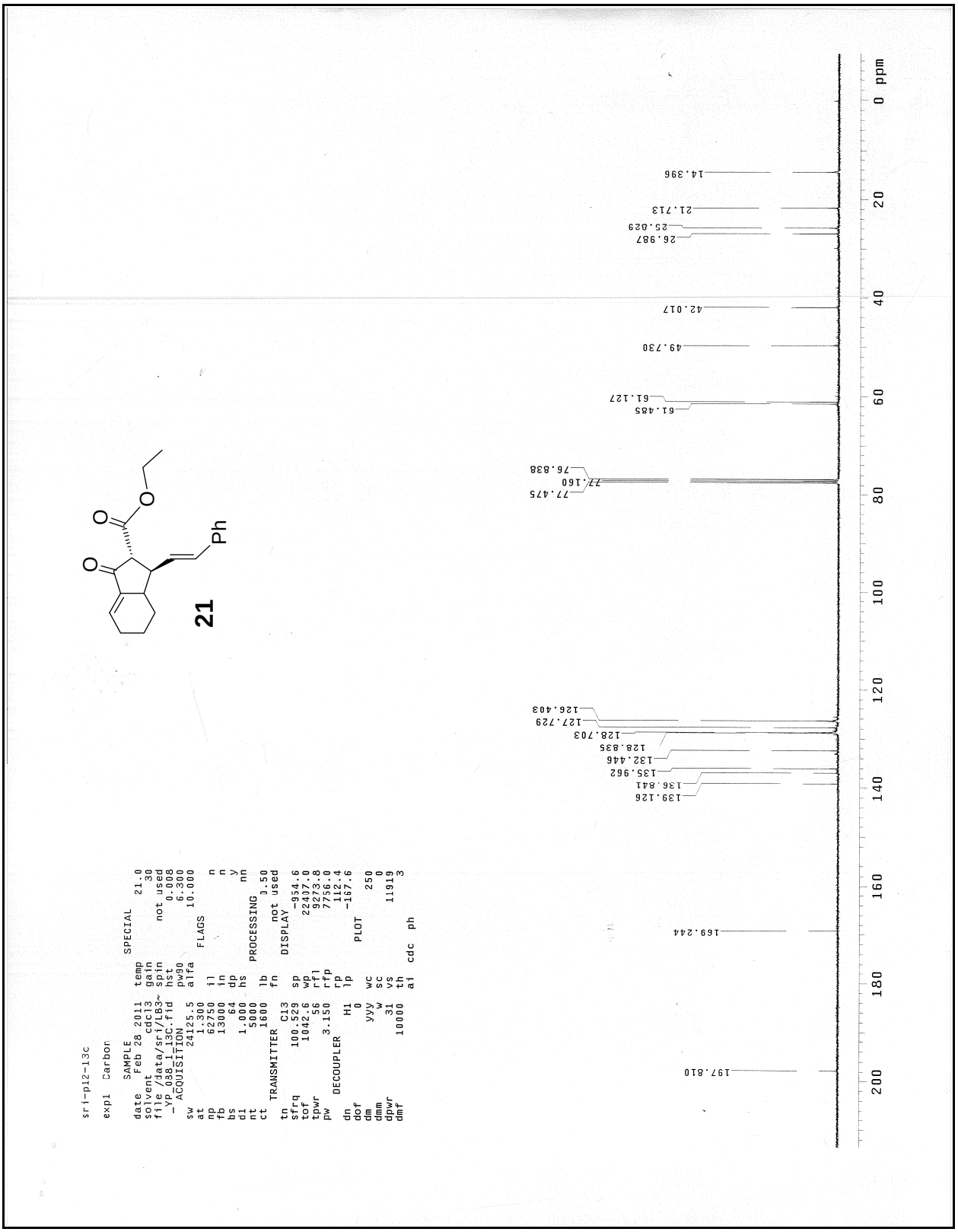

LB3_YP_063
File: Proton
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: sri
INOVA-400 "i400"
Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 8095.9 Hz
32 repetitions
OBSERVE H1, 399.7532400 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT Size 65536
Total time 3 min, 59 sec
OEt
O
O
Ph
19
ppm
0
1
2
3
4
5
6
7
8
7.65
7.35
15.90
18.52
8.01
7.34
1.83
4.0184
3.601.50
7.19
3.84 1.82

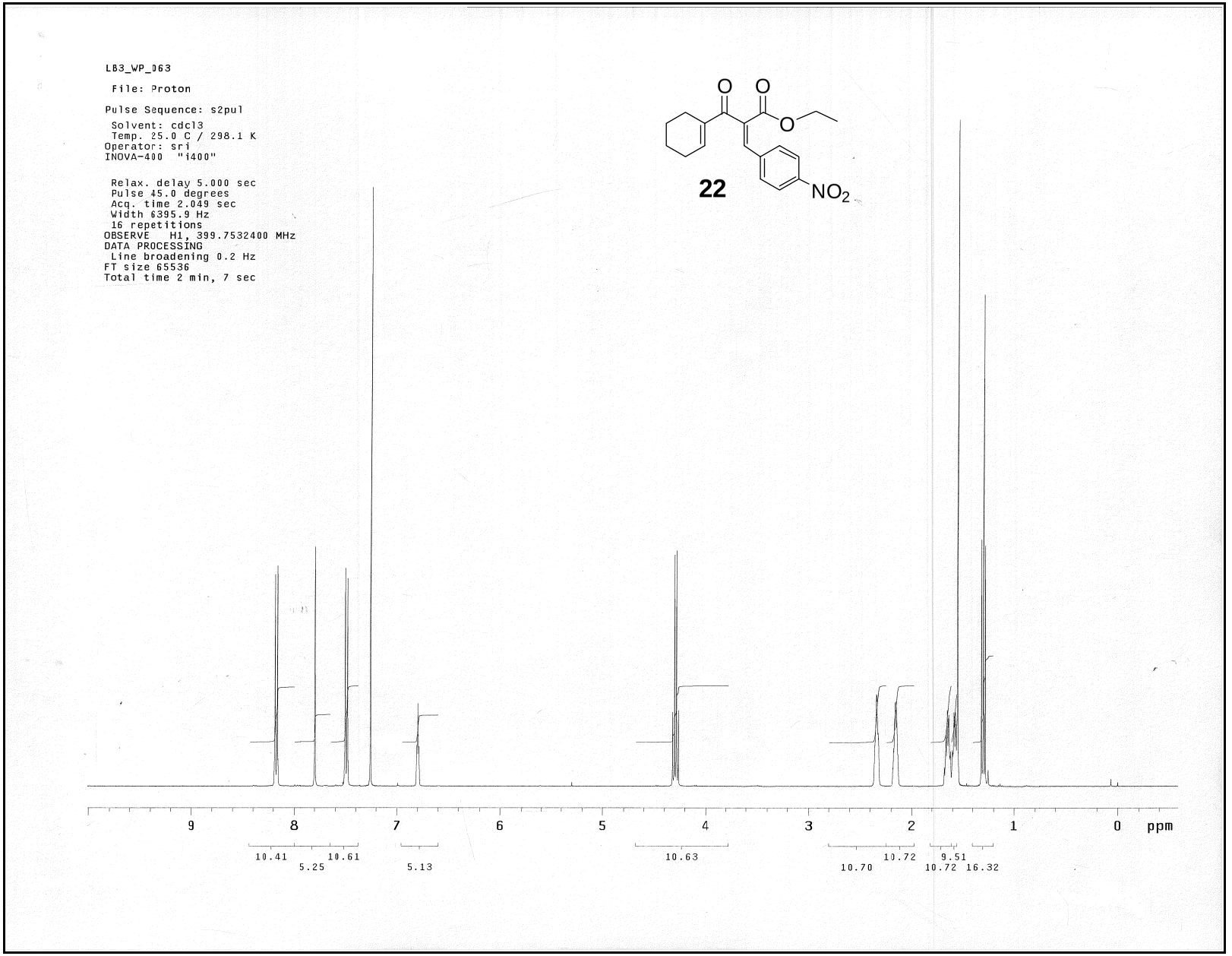

Sri-4-13c-upper-1
expl Carbon
SAMPLE
date Jun 30 2011
solvent cdcl3
file exp
ACQUISITION
sw 24125.5
at 1.300
np 62750
fb 13000
bs 12
d1 1.000
nt 1100
ct 120
TRANSMITTER
tn C13
sfrq 100.529
tof 1042.6
tpwr 56
pw 3.150
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 31
dmf 10000
SPECIAL
temp 22.0
gain 30
spin not used
hst 0.008
pw90 6.300
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 0.50
fn not used
DISPLAY
sp -1517.8
wp 24124.7
rfl 9274.5
rfp 7756.0
rp 125.8
lp -144.2
PLOT
wc 250
sc 0
vs 16542
th 9
ai cdc ph
O
O
OEt
Ph
19
220
200
180
160
140
120
100
80
60
40
20
0
ppm

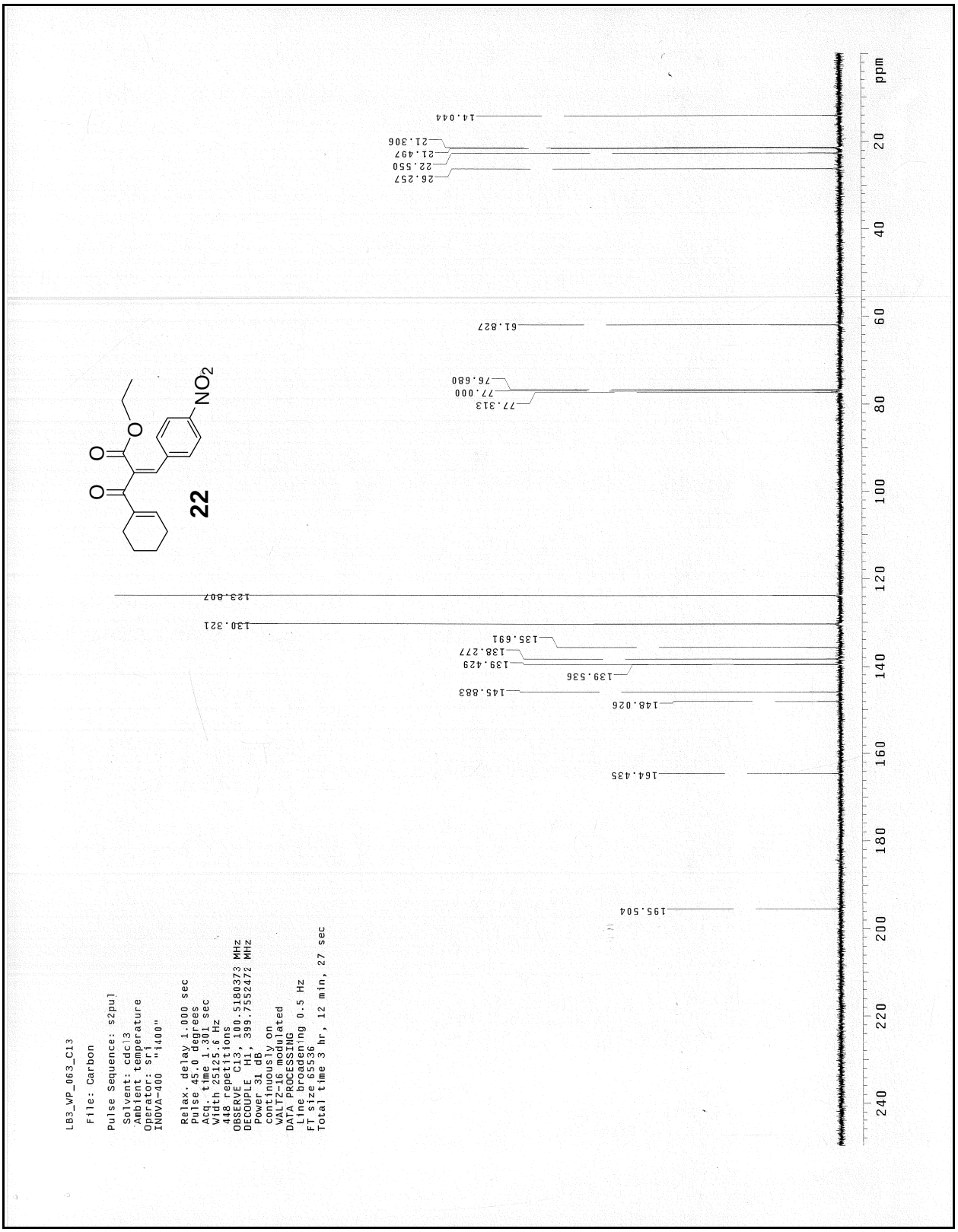

LB3_YP_088_2_H1
File: Proton
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: sri
INOVA-400 "i400"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.048 sec
Width 3388.5 Hz
32 repetitions
OBSERVE H1, 399.7532481 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 43 sec
O
O
O
Ph
20
ppm
20.84
4.19
4.26
7.92
0.62
3.75
0.52
3.39
18.45
20.37
13.48
1.29
0.93

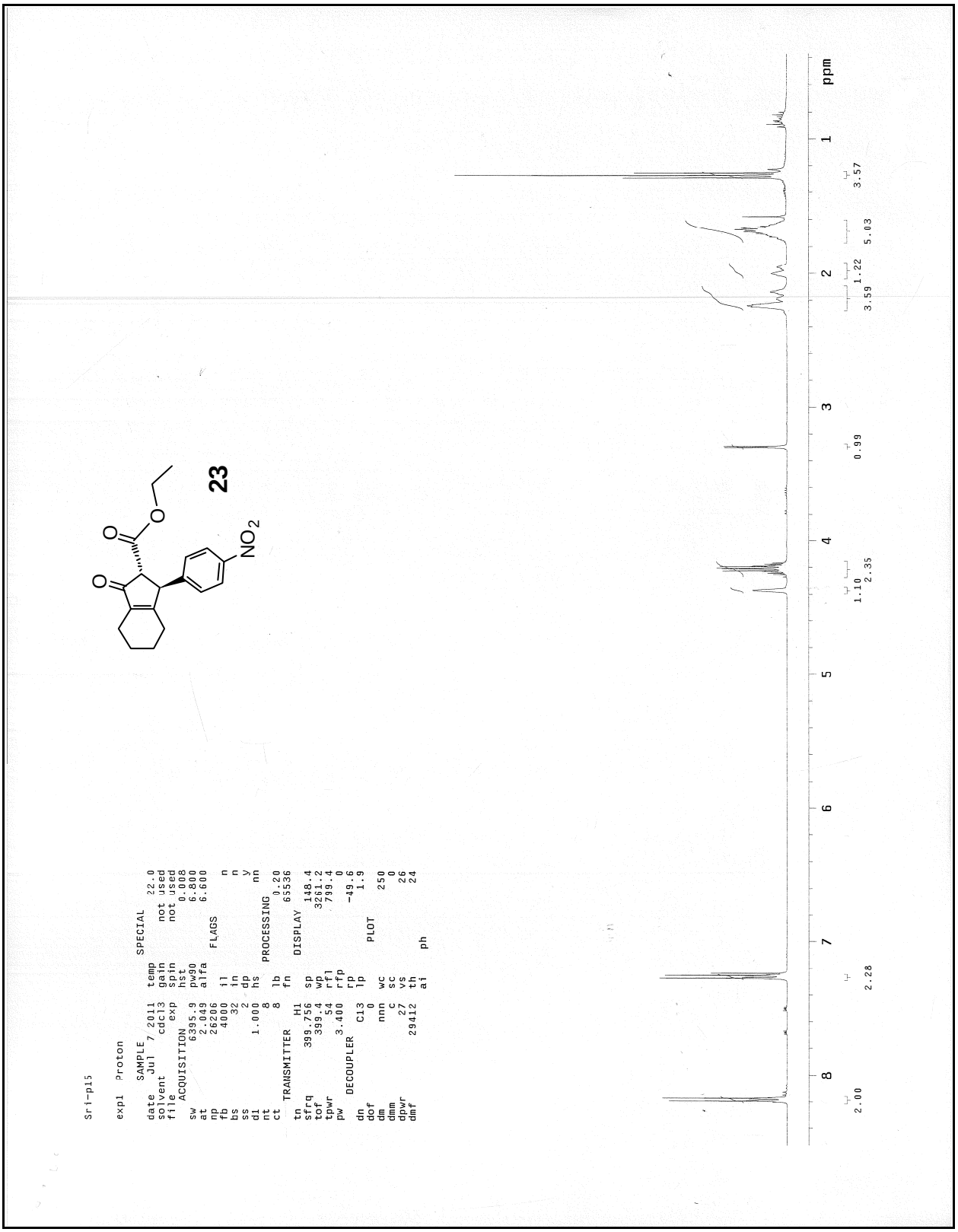

LB3_YP_088_2_C13
File: Carbon
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 22.0 C / 295.1 K
Operator: sri
INOVA-400 "i400"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24125.5 Hz
1000 repetitions
OBSERVE C13, 100.5180358 MHz
DECOUPLE H1, 399.7532472 MHz
Power 31 dB
continuously on
WALTZ16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 38 min, 29 sec
20
Ph
O
O
O
200.162
174.710
168.996
137.223
136.270
133.538
128.623
127.869
126.287
77.322
77.000
76.685
61.633
58.747
50.104
26.658
22.007
21.385
20.286
14.192
ppm

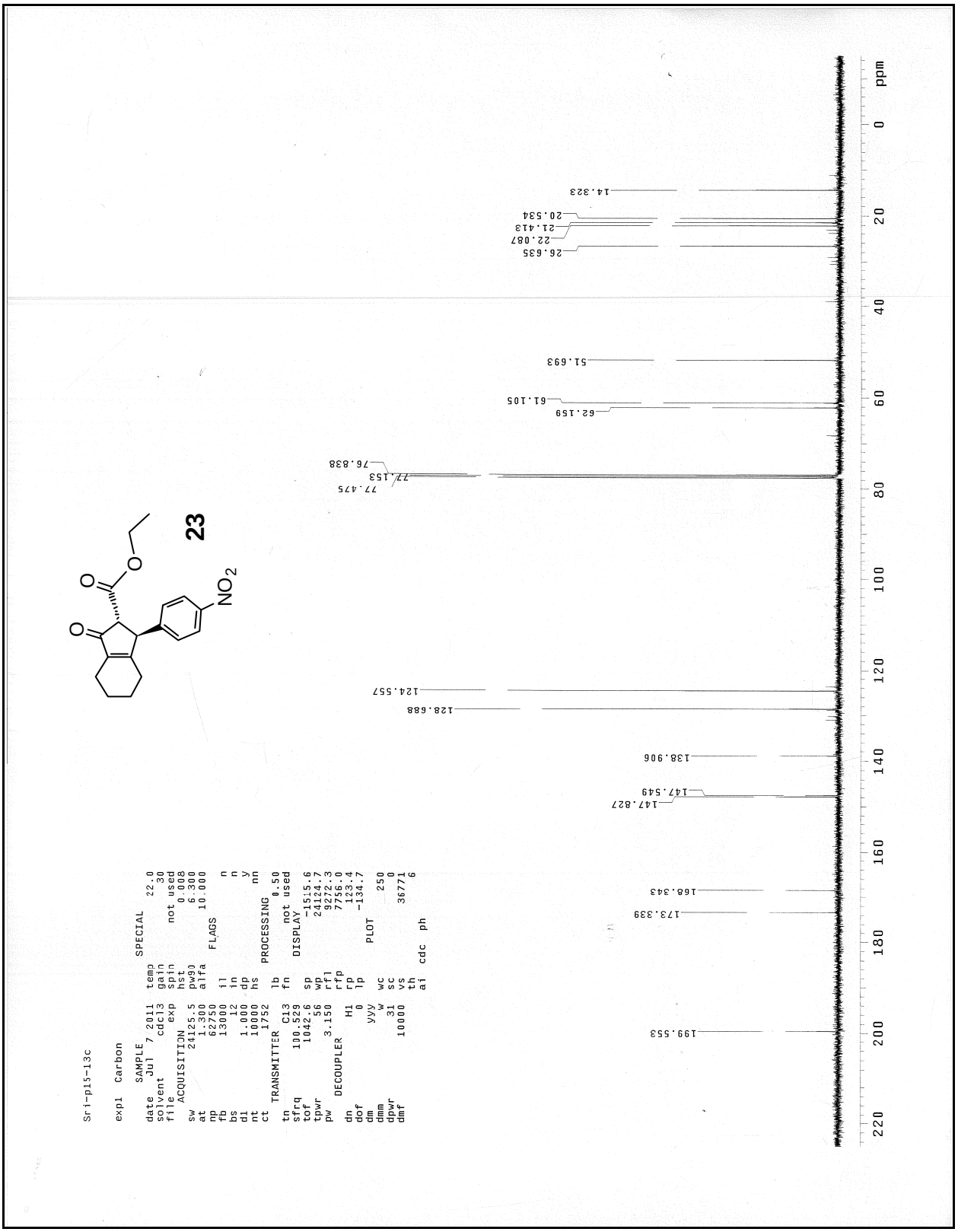

sri-p12
exp1 Proton
SAMPLE
date Jul 11 2011
solvent cdcl3
file exp
ACQUISITION
sw 6395.9
at 2.049
np 26206
fb 4000
bs 6
ss 2
d1 1.000
nt 100
ct 100
TRANSMITTER
tn H1
sfrq 399.756
tof 399.4
tpwr 54
pw 3.400
DECOUPLER
dn C13
dof 0
dm nnn
dmm c
dpwr 27
dmf 29412
SPECIAL
temp 22.0
gain not used
spin not used
hst 0.008
pw90 6.800
alfa 6.600
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 0.20
fn 65536
DISPLAY
sp 253.1
wp 2828.3
rfl 3693.5
rfp 2894.2
rp -54.8
lp 14.9
PLOT
wc 250
sc 0
vs 53
th 6
ai ph
O
O
O
21
Ph
7
6
5
4
3
2
1
ppm
2.35
2.30
1.04
0.92
1.03
1.00
2.03
0.86
0.97
2.37
2.50
1.29
0.77
5.20
1.01

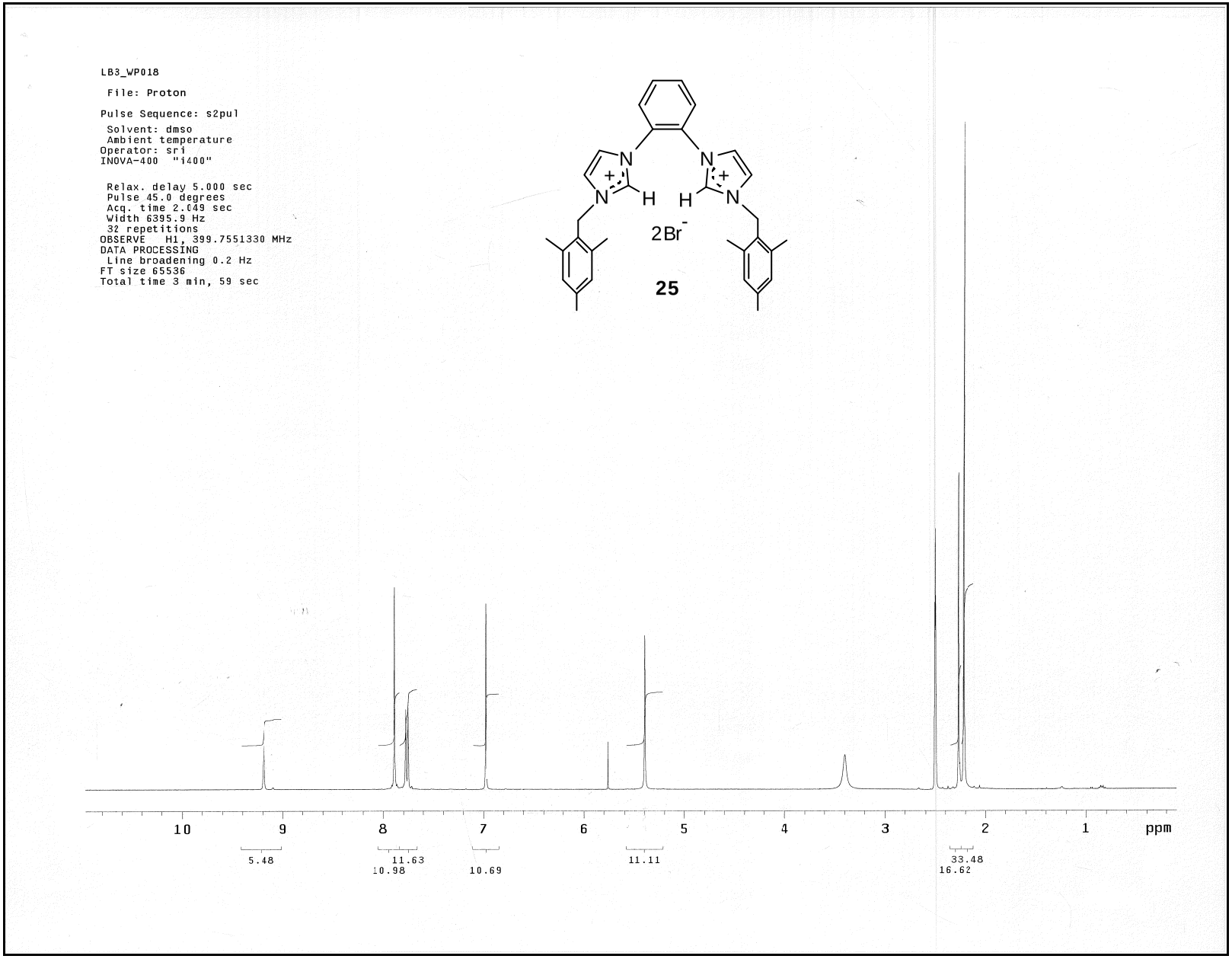

sri-pi2-13c
exp1 Carbon
SAMPLE SPECIAL
date Feb 28 2011 temp 21.0
solvent cdcl3 gain 30
file /data/sri/LB3~ spin not used
_YP_038_1_13C.fid hst 0.008
ACQUISITION pw90 6.300
sw 24125.5 alfa 10.000
at 1.300 FLAGS
np 62750 il n
fb 13000 in n
bs 64 dp y
d1 1.000 hs nn
nt 5000
ct 1600 lb PROCESSING 3.50
TRANSMITTER C13 fn DISPLAY not used
tn -954.6
sfrq 100.529 sp
tof 1042.6 wp 22407.0
tpwr 56 rfl 9273.8
pw 3.150 rfp 7756.0
DECOUPLER H1 rp 112.4
dn lp -167.6
dof 0 PLOT
dm yyy wc 250
dmm w sc 0
dpwr 31 vs 11919
dmf 10000 th 3
al cdc ph
O
O
O
Ph
21
197.810
169.244
139.126
136.841
135.962
132.446
128.835
128.703
127.729
126.403
77.475
77.160
76.838
61.485
61.127
49.730
42.017
26.987
25.629
21.713
14.396
200
180
160
140
120
100
80
60
40
20
0 ppm

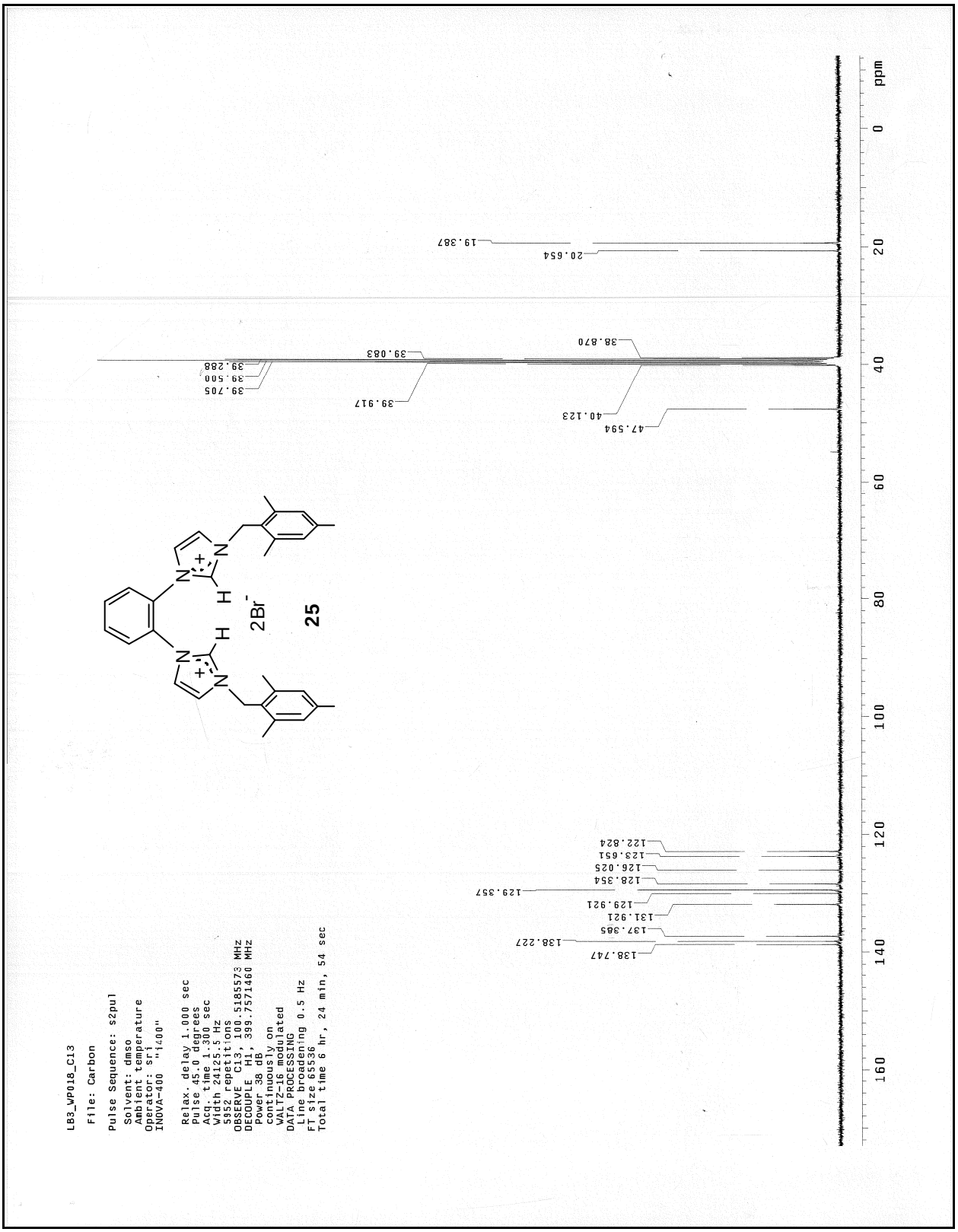

LB3_WP_063
File: Proton
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: sri
INOVA-400 "i400"
Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 6395.9 Hz
16 repetitions
OBSERVE H1, 399.7532400 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 2 min, 7 sec
O
O
O
22
NO2
9
8
7
6
5
4
3
2
1
0
ppm
10.41
10.61
5.25
5.13
10.63
10.72
10.70
9.51
10.72
16.32

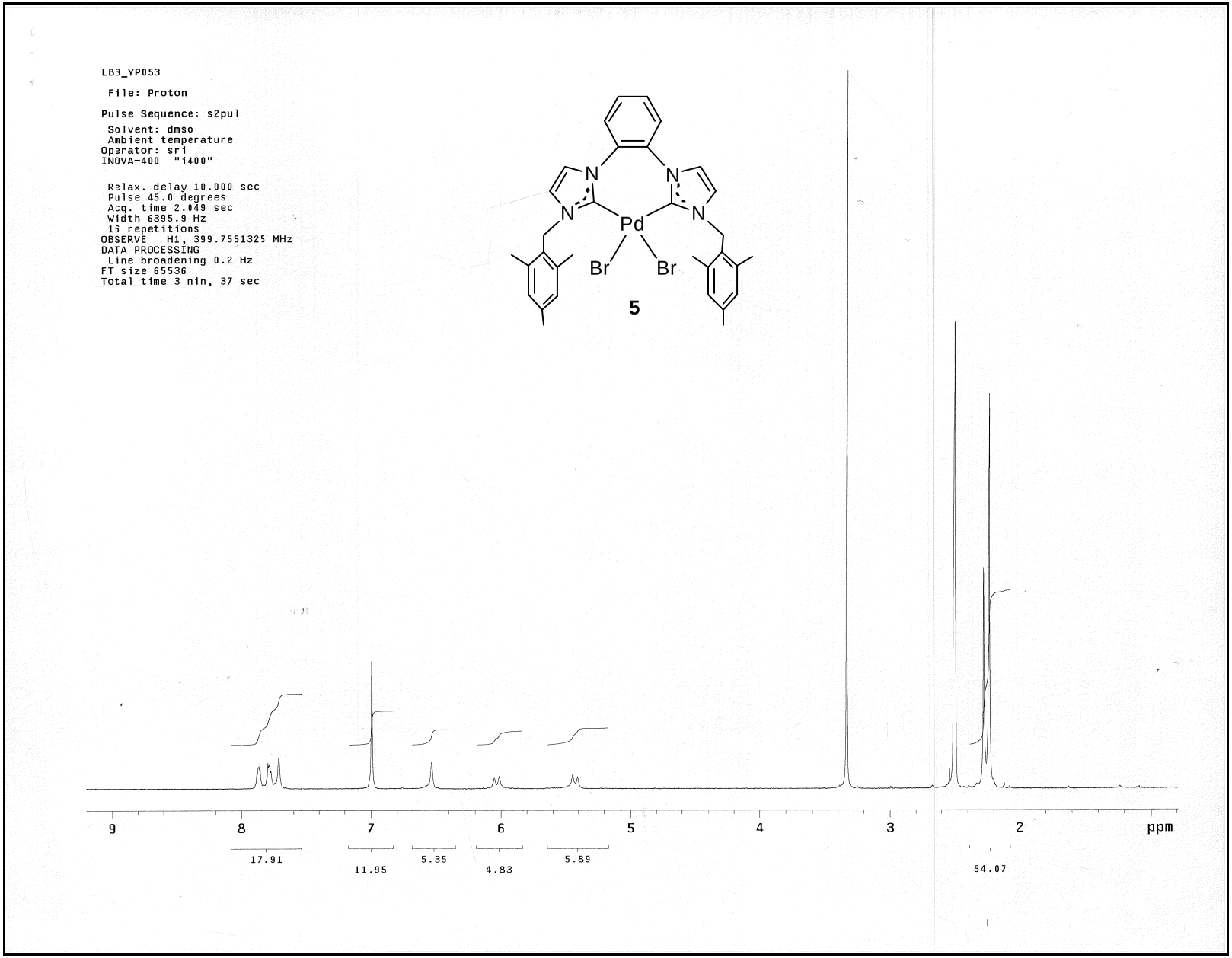

LB3_WP_063_C13
File: Carbon
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: sri
INOVA-400 "i400"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.301 sec
Width 25125.6 Hz
448 repetitions
OBSERVE C13, 100.5180373 MHz
DECOUPLE H1, 399.7552472 MHz
Power 31 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 3 hr, 12 min, 27 sec
195.504
164.435
148.026
145.883
139.536
139.429
138.277
135.691
130.321
123.807
77.313
77.000
76.680
61.827
26.257
22.550
21.497
21.306
14.044
ppm
O
O
O
O
NO2
22

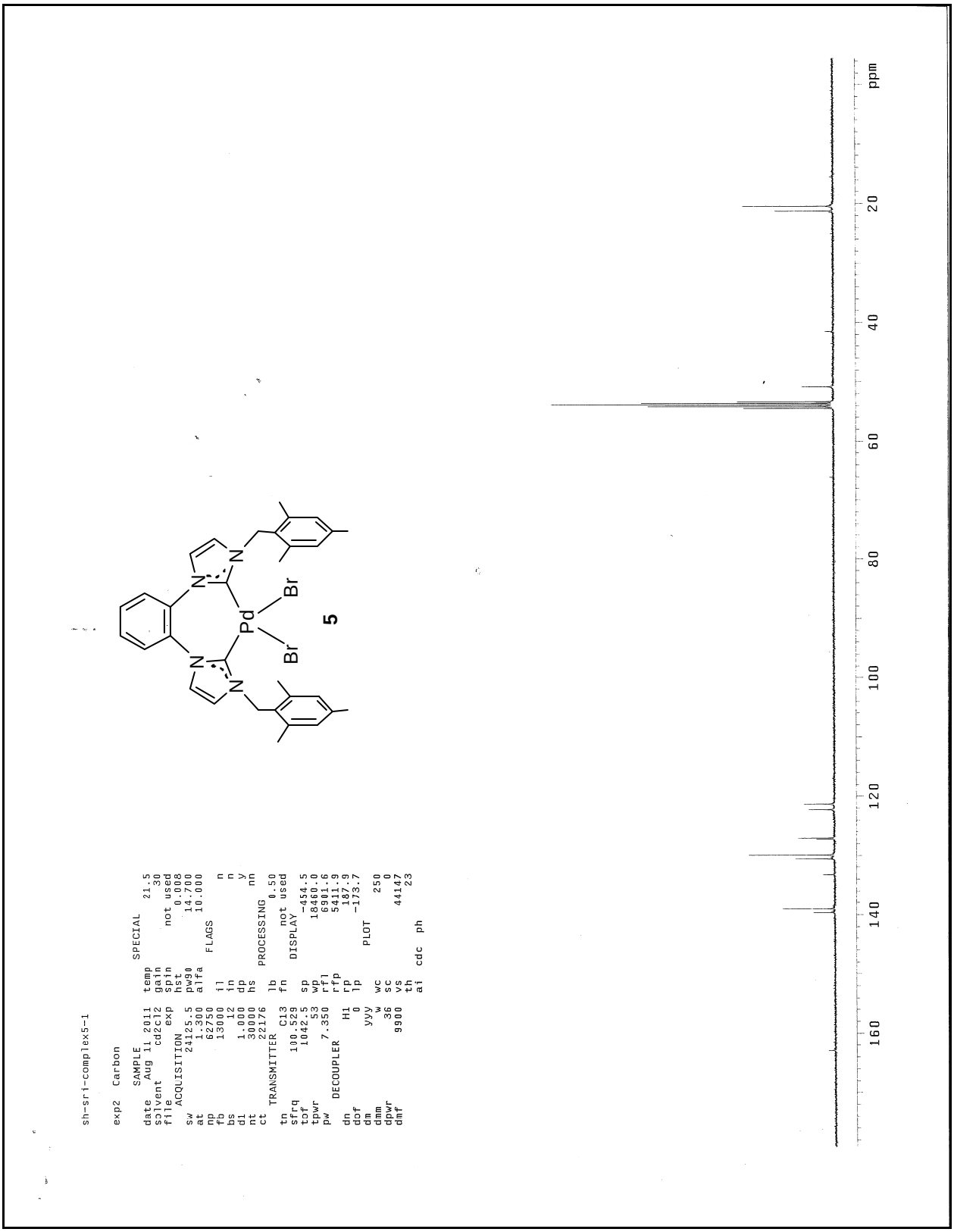

Sri-p15
exp1 Proton
SAMPLE
date Jul 7 2011
solvent cdcl3
file exp
ACQUISITION
sw 6395.9
at 2.049
np 26206
fb 4000
bs 32
ss 2
d1 1.000
nt 8
ct 8
TRANSMITTER
tn H1
sfrq 399.756
tof 399.4
tpwr 54
pw 3.400
DECOUPLER
dn C13
dof 0
dm nnn
dmm c
dpwr 27
dmf 29412
temp 22.0
gain not used
spin not used
hst 0.008
pw90 6.800
alfa 6.600
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 0.20
fn 65536
DISPLAY
sp 148.4
wp 3261.2
rfl 799.4
rfp 0
rp -49.6
lp 1.9
PLOT
wc 250
sc 0
vs 26
th 24
ai ph
23
O
O
O
NO2
8
7
6
5
4
3
2
1
ppm
2.00
2.28
1.10
2.35
0.99
3.59
1.22
5.03
3.57

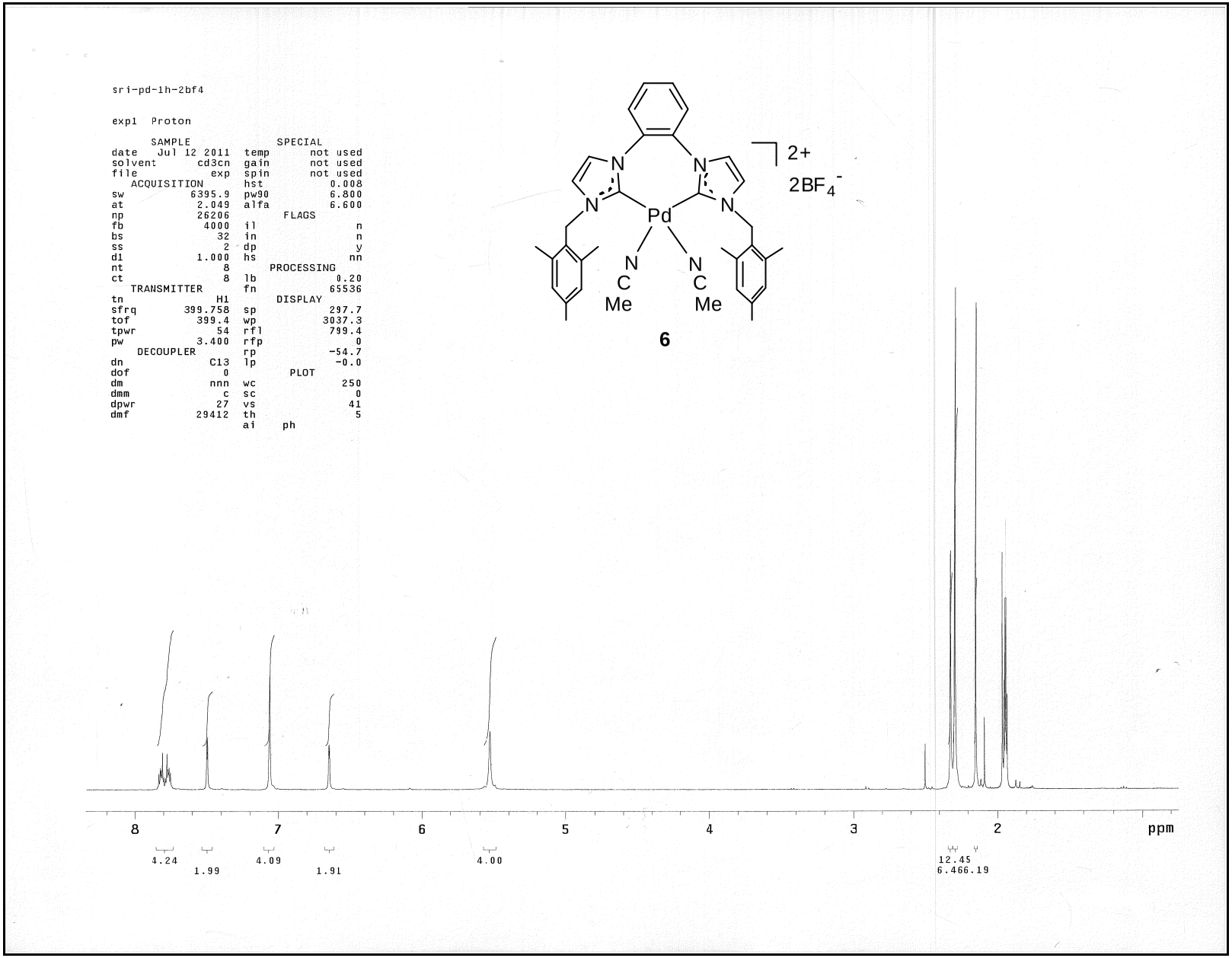

Sri-p15-13c
exp1 Carbon
SAMPLE
date Jul 7 2011
solvent cdcl3
file exp
ACQUISITION
sw 24125.5
at 1.300
np 62750
fb 13000
bs 12
d1 1.000
nt 10000
ct 1752
TRANSMITTER
tn C13
sfrq 100.529
tof 1042.6
tpwr 56
pw 3.150
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 31
dmf 10000
SPECIAL
temp 22.0
gain 30
spin not used
hst 0.008
pw90 6.300
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 0.50
fn not used
DISPLAY
sp -1515.6
wp 24124.7
rf1 9272.3
rfp 7756.0
rp -123.4
lp -134.7
PLOT
wc 250
sc 0
vs 36771
th 6
ai cdc ph
23
O
O
O
NO2
199.553
173.339
168.343
147.827
147.549
138.906
128.688
124.557
77.475
77.153
76.838
62.159
61.105
51.693
26.635
22.087
21.413
20.534
14.323
ppm
220
200
180
160
140
120
100
80
60
40
20
0

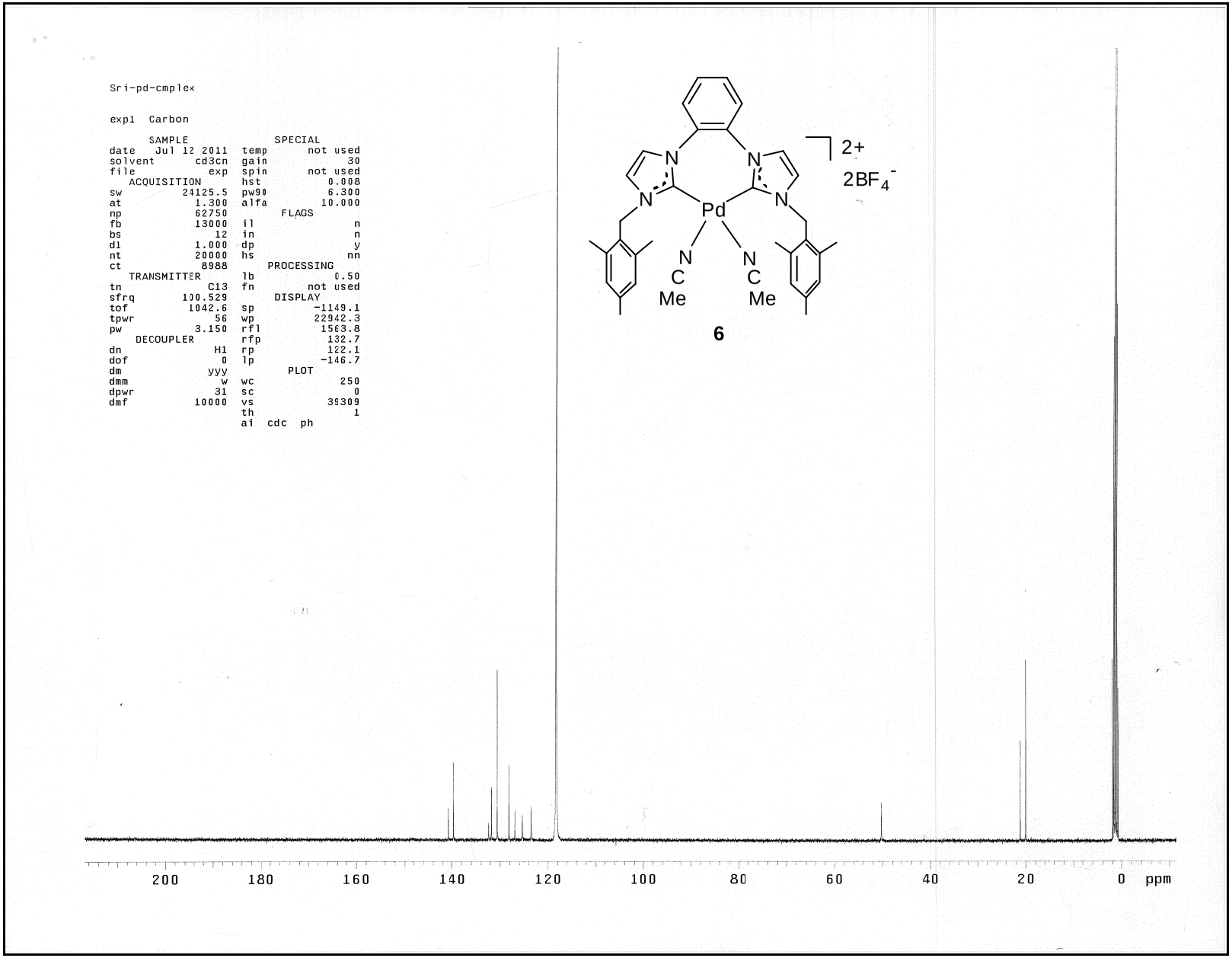

LB3_WP018
File: Proton
Pulse Sequence: s2pul
Solvent: dmso
Ambient temperature
Operator: sri
INOVA-400 "i400"
Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 6395.9 Hz
32 repetitions
OBSERVE H1, 399.7551330 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 3 min, 59 sec
2Br-
25
10
9
8
7
6
5
4
3
2
1
ppm
5.48
11.63
10.98
10.69
11.11
33.48
16.62

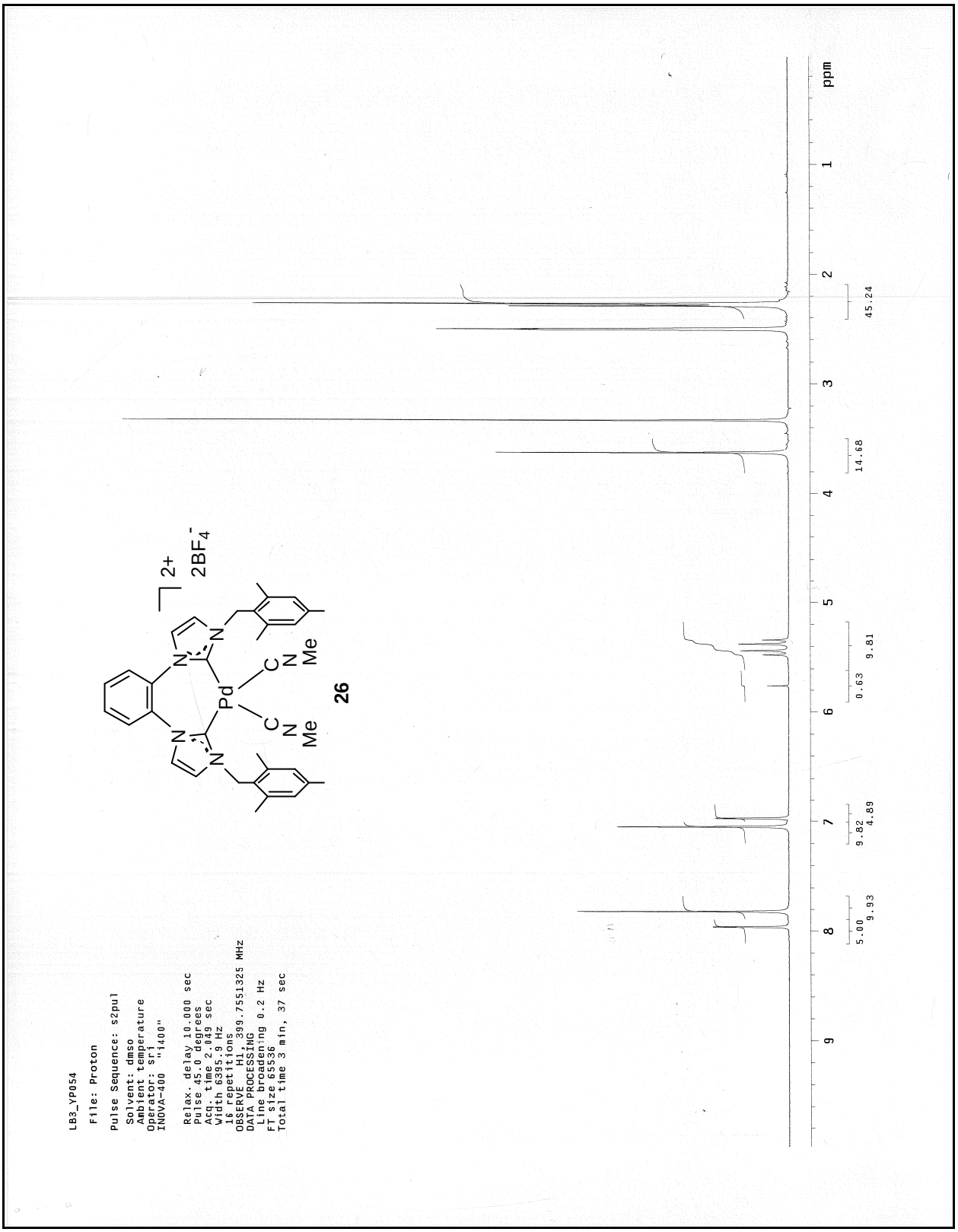

LB3_WP018_C13
File: Carbon
Pulse Sequence: s2pul
Solvent: dmso
Ambient temperature
Operator: sri
INOVA-400 "i400"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24125.5 Hz
5952 repetitions
OBSERVE C13, 100.5185573 MHz
DECOUPLE H1, 399.7571460 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 6 hr, 24 min, 54 sec
2Br-
25
19.387
20.654
38.870
39.083
39.288
39.500
39.705
39.917
40.123
47.594
122.824
123.651
126.025
128.354
129.357
129.921
131.921
137.385
138.227
138.747
ppm

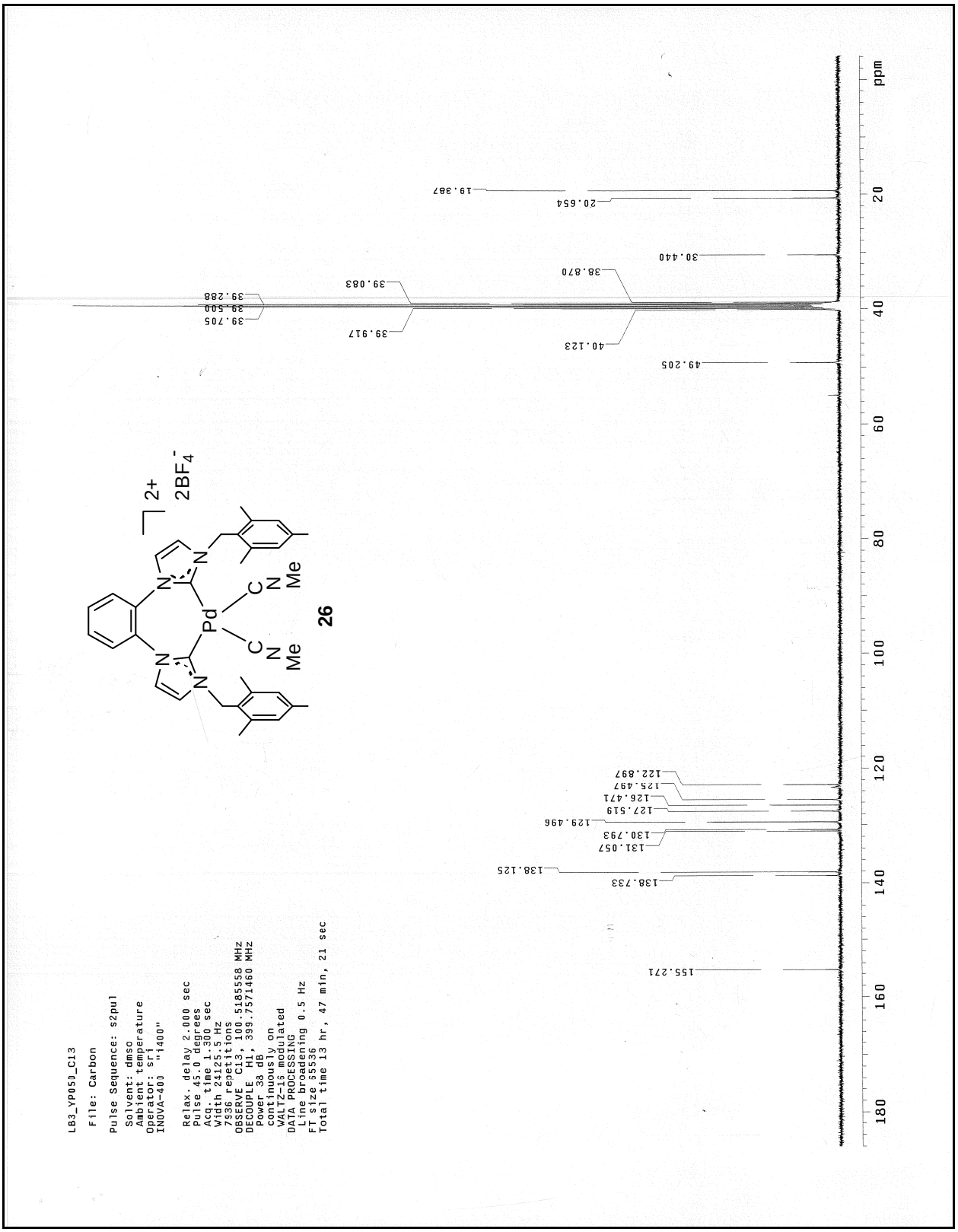

LB3_YP053
File: Proton
Pulse Sequence: s2pul
Solvent: dmso
Ambient temperature
Operator: sri
INOVA-400 "i400"
Relax. delay 10.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 6395.9 Hz
16 repetitions
OBSERVE H1, 399.7551325 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 3 min, 37 sec
N
N
N
N
Pd
Br
Br
5
9
8
7
6
5
4
3
2
ppm
17.91
11.95
5.35
4.83
5.89
54.07

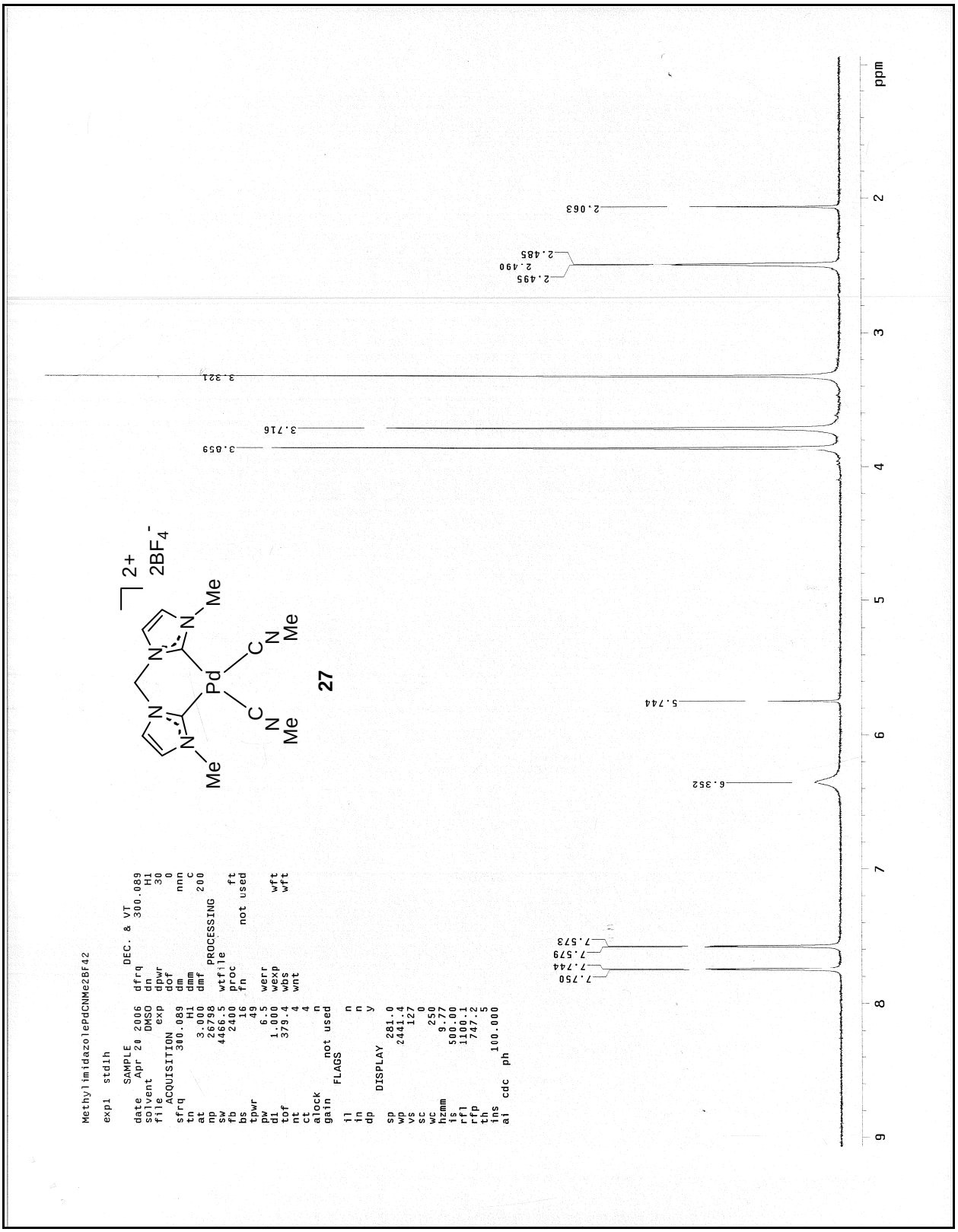

sh-sri-complex5-1
exp2 Carbon
SAMPLE SPECIAL 21.5
date Aug 11 2011 temp 30
solvent cd2cl2 gain not used
file exp spin 0.008
ACQUISITION hst 14.700
sw 24125.5 pw90 10.000
at 1.300 alfa
np 62750 FLAGS
fb 13000 il n
bs 12 in n
d1 1.000 dp y
nt 30000 hs nn
ct 22176 PROCESSING 0.50
TRANSMITTER lb not used
tn C13 fn DISPLAY
sfrq 100.529 sp -454.5
tof 1042.5 wp 18460.0
tpwr 53 rf1 6901.6
pw 7.350 rfp 5411.9
DECOUPLER rf1 187.9
dn H1 rp -173.7
dof 0 lp
dm yyy PLOT
dmm w wc 250
dpwr 36 sc 0
dmf 9900 vs 44147
th 23
ai cdc ph
Br
Pd
Br
N
N
N
N
5
160
140
120
100
80
60
40
20
ppm

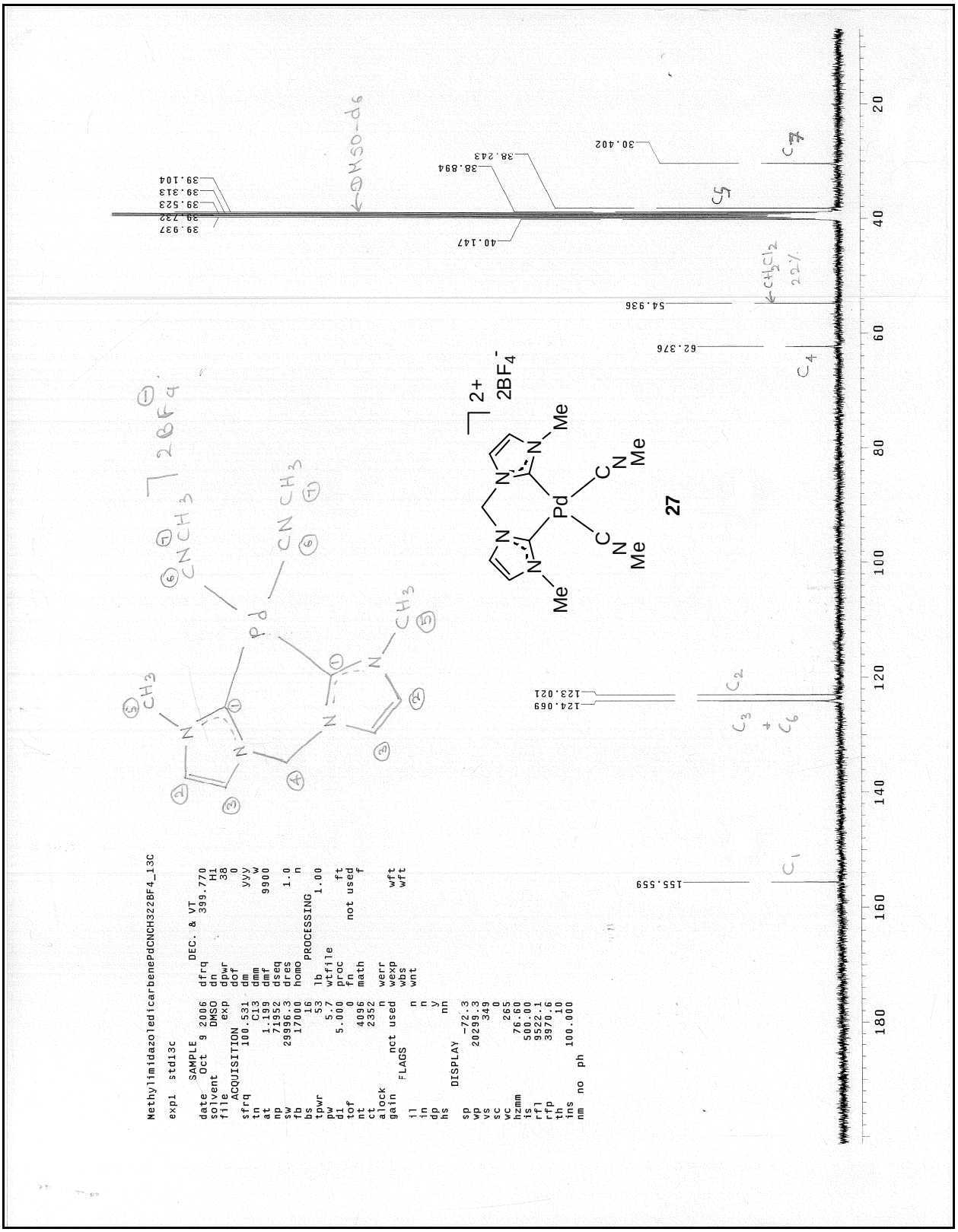

sri-pd-1h-2bf4
exp1 Proton
SAMPLE
date Jul 12 2011
solvent cd3cn
file exp
ACQUISITION
sw 6395.9
at 2.049
np 26206
fb 4000
bs 32
ss 2
d1 1.000
nt 8
ct 8
TRANSMITTER
tn H1
sfrq 399.758
tof 399.4
tpwr 54
pw 3.400
DECOUPLER
dn C13
dof 0
dm nnn
dmm c
dpwr 27
dmf 29412
SPECIAL
temp not used
gain not used
spin not used
hst 0.008
pw90 6.800
alfa 6.600
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 0.20
fn 65536
DISPLAY
sp 297.7
wp 3037.3
rfl 799.4
rfp 0
rp -54.7
lp -0.0
PLOT
wc 250
sc 0
vs 41
th 5
ai ph
N
N
N
N
Pd
N
C
Me
N
C
Me
2+
2BF4-
6
8
7
6
5
4
3
2
ppm
4.24
1.99
4.09
1.91
4.00
12.45
6.466.19


Sri-pd-cmplex
exp1 Carbon
SAMPLE
date Jul 12 2011
solvent cd3cn
file exp
ACQUISITION
sw 24125.5
at 1.300
np 62750
fb 13000
bs 12
d1 1.000
nt 20000
ct 8988
TRANSMITTER
tn C13
sfrq 100.529
tof 1042.6
tpwr 56
pw 3.150
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 31
dmf 10000
SPECIAL
temp not used
gain 30
spin not used
hst 0.008
pw90 6.300
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 0.50
fn not used
DISPLAY
sp -1149.1
wp 22942.3
rfl 1563.8
rfp 132.7
rp 122.1
lp -146.7
PLOT
wc 250
sc 0
vs 39309
th 1
ai cdc ph
N
N
N
N
Pd
N
C
Me
N
C
Me
2+
2BF4-
6
200
180
160
140
120
100
80
60
40
20
0
ppm


LB3_YP054
File: Proton
Pulse Sequence: s2pul
Solvent: dmso
Ambient temperature
Operator: sr1
INOVA-400 "i400"
Relax. delay 10.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 8335.9 Hz
16 repetitions
OBSERVE H1, 399.7551325 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 3 min, 37 sec
2+
2BF4-
Pd
C
N
Me
26
ppm
5.00
9.93
9.82
4.89
0.63
9.81
14.68
45.24


LB3_YP05D_C13
File: Carbon
Pulse Sequence: s2pul
Solvent: dmso
Ambient temperature
Operator: sri
INOVA-400 "i400"
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 1.430 sec
Width 24125.5 Hz
7436 repetitions
OBSERVE C13, 100.5185558 MHz
DECOUPLE H1, 399.7571460 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 13 hr, 47 min, 21 sec
2+
2BF4-
Pd
C
N
Me
26
ppm
19.387
20.654
30.440
38.870
39.083
39.288
39.500
39.705
39.917
40.123
49.205
122.897
125.497
126.471
127.519
129.496
130.793
131.057
138.125
138.733
155.271


Methylimidazole PdCNMe2BF42
exp1 stdih
SAMPLE DEC. & VT
date Apr 20 2006 dfrq 300.089
solvent DMSO dn H1
file exp dpwr 30
ACQUISITION dof 0
sfrq 300.089 dm nnn
tn H1 dmm c
at 3.000 dmf 200
np 26798 PROCESSING
sw 4466.5 wtfile ft
fb 2400 proc ft
bs 16 fn not used
tpwr 49
pw 6.5 werr wft
d1 1.000 wexp wft
tof 379.4 wbs
nt 4 wnt
ct 4
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp 281.0
wp 2441.4
vs 127
sc 0
wc 250
hzmm 8.77
is 500.00
rfl 1100.1
rfp 747.2
th 5
ins 100.000
al cdc ph
2+
2BF4-
Me
N
Pd
C
N
Me
27
7.750
7.744
7.579
7.573
6.352
5.744
3.859
3.716
3.321
2.495
2.490
2.485
2.063
9
8
7
6
5
4
3
2
ppm


Methylimidazoledicarbene PdCNCH322BF4_13C
exp1 std13c
SAMPLE
date Oct 9 2006
solvent DMSO
file exp
ACQUISITION
sfrq 100.531
tn C13
at 1.199
np 71952
sw 29996.3
fb 17000
bs 16
tpwr 53
pw 5.7
d1 5.000
tof 0
nt 4096
ct 2352
alock n
gain nct used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -72.3
wp 20293.3
vs 349
sc 0
wc 265
hzmm 76.60
is 500.00
rfl 9522.1
rfp 3970.6
th 10
ins 100.000
nm no ph
DEC. & VT
dfrq 399.770
dn H1
dpwr 38
dof 0
dm yyy
dmm w
dmf 9900
dseq
dres 1.0
homo n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp wft
wbs wft
wnt
PROCESSING
2BF4
CNCH3
Pd
CH3
27
2BF4-
2+
Me
N
C
DMSO-d6
CH2Cl2
155.559
124.069
123.021
62.376
54.936
40.147
39.937
39.732
39.523
39.313
39.104
38.894
38.243
30.402
C1
C2
C3 + C6
C4
C5
C7
20
40
60
80
100
120
140
160
180