

Supporting Information

Synthesis of 4-Substituted-Pyridine-2,6-dicarboxylic Acid Derivatives from Pyruvates and Aldehydes in One Pot

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1. General

For thin layer chromatography (TLC), Merck Silica gel 60 F254 aluminum sheets were used. Flash column chromatography was performed using Merck silica gel 60 (230-400 mesh). ¹H NMR and ¹³C NMR were recorded on a Bruker Avance 400. Proton chemical shifts are reported in ppm downfield from tetramethylsilane or from the residual solvent as internal standard in CDCl₃ (δ 7.26 ppm) and in CD₃OD (δ 3.31 ppm). Carbon chemical shifts were internally referenced to the deuterated solvent signals in CDCl₃ (δ 77.0 ppm) and in CD₃OD (δ 49.0 ppm). High-resolution mass spectra were recorded on a Thermo Scientific LTQ Orbitrap ESI ion trap mass spectrometer.

2. Synthesis of 4-Substituted Pyridine-2,6-Dicarboxylic Acid Esters 1

Procedure for the Synthesis of Dihydropyran Derivative 2a (Table 1, entry 7)

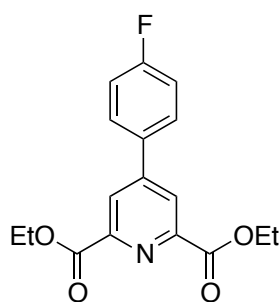
To a solution of 4-nitrobenzaldehyde (75.5 mg, 0.50 mmol) and ethyl pyruvate (166.7 μ L, 1.50 mmol) in CH₃CN (0.50 mL), acetic acid (28.6 μ L, 0.50 mmol) and pyrrolidine (16.5 μ L, 0.20 mmol) were added at room temperature (25 °C). The mixture was stirred at the same temperature for 24 h. The mixture was poured into saturated NH₄Cl solution (4 mL) and extracted with EtOAc (15 mL x 3). Organic layers were combined, dried over Na₂SO₄, filtered, concentrated, and purified by flash column chromatography (hexane/EtOAc = 7:3) to afford **2a**¹ (111.4 mg, 61%).

General Procedure for the Synthesis of 4-Substituted Pyridine-2,6-Dicarboxylic Acid Esters 1 from Aldehyde and Pyruvate in One Pot (Table 3)

To a solution of aldehyde (1.0 mmol) and ethyl pyruvate (3.0 mmol) in CH₃CN (1.0 mL), acetic acid (1.0 mmol) and pyrrolidine (0.4 mmol) were added at room temperature (25 °C) and the mixture was stirred at the same temperature. After 30 h, NH₄OAc (3.0 mmol) and acetic acid (1.0 mmol) was added to the mixture and the resulting mixture was stirred at the same temperature for 24 h. The mixture was poured into saturated aqueous NaHCO₃ solution (5.0 mL) and extracted with EtOAc (30 mL x 3). Organic layers were combined, dried over Na₂SO₄, filtered, concentrated, and purified by flash column chromatography (hexane/EtOAc) to afford **1**.

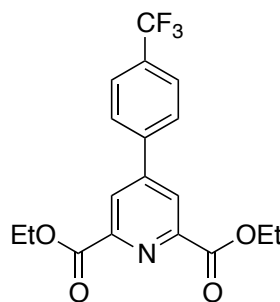
Compounds **1a**, **1b**, **1c**, **1i**, and **1k** were previously reported.¹

Diethyl 4-(4-fluorophenyl) pyridine-2, 6-dicarboxylate (**1d**)



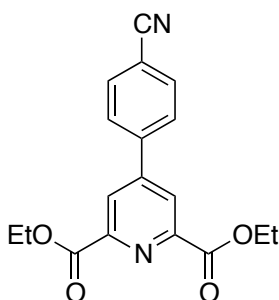
Flash column chromatography (hexane/EtOAc = 7:3); colorless solid. ¹H NMR (400 MHz, CDCl₃): δ 8.46 (s, 2H), 7.75 (dd, J = 8.8 Hz, 5.2 Hz, 2H), 7.23 (t, J = 8.8 Hz, 2H) 4.52 (q, J = 7.2 Hz, 4H), 1.48 (t, J = 7.2 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 164.8, 164.0 (d, $J_{C,F}$ = 249 Hz), 149.9, 149.4, 132.5 (d, $J_{C,F}$ = 3 Hz), 129.1 (d, $J_{C,F}$ = 9 Hz), 125.3, 116.5 (d, $J_{C,F}$ = 22 Hz), 62.5, 14.3. ESI-HRMS: calcd for C₁₇H₁₇NO₄F ([M+H]⁺) 318.1136, found 318.1138.

Diethyl 4-(4-(trifluoromethyl)phenyl)pyridine-2,6-dicarboxylate (**1e**)



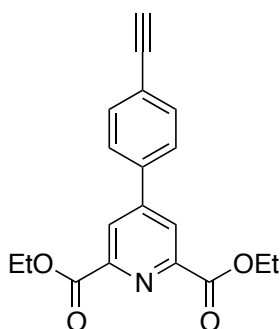
Flash column chromatography (hexane/EtOAc = 7:3); colorless solid. ¹H NMR (400 MHz, CDCl₃): δ 8.49 (s, 2H), 7.85 (d, J = 8.2 Hz, 2H), 7.79 (d, J = 8.2 Hz, 2H), 4.52 (q, J = 7.2 Hz, 4H), 1.46 (t, J = 7.2 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 164.6, 149.6, 149.5, 140.0, 132.0 (q, $J_{C,F}$ = 33 Hz), 127.6, 126.3 (q, $J_{C,F}$ = 4 Hz), 125.6, 123.7 (q, $J_{C,F}$ = 271 Hz), 62.5, 14.2. ESI-HRMS: calcd for C₁₈H₁₇NO₄F₃ ([M+H]⁺) 368.1104, found 368.1090.

Diethyl 4-(4-cyanophenyl)pyridine-2,6-dicarboxylate (1f)



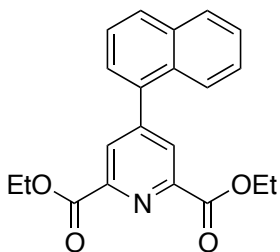
Flash column chromatography (hexane/EtOAc = 7:3); pale yellow solid. ^1H NMR (400 MHz, CDCl_3): δ 8.49 (s, 2H), 7.87-7.83 (m, 4H), 4.53 (q, $J = 7.2$ Hz, 4H), 1.48 (t, $J = 7.2$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 164.4, 149.7, 148.9, 140.8, 133.1, 127.9, 125.4, 118.0, 113.8, 62.6, 14.2. ESI-HRMS: calcd for $\text{C}_{18}\text{H}_{17}\text{N}_2\text{O}_4$ ($[\text{M}+\text{H}]^+$) 325.1183, found 325.1186.

Diethyl 4-(4-ethynylphenyl)pyridine-2,6-dicarboxylate (1g)



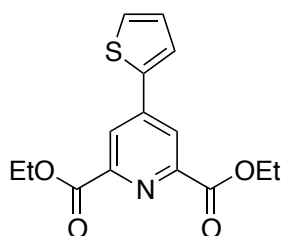
Flash column chromatography (hexane/EtOAc = 4:1); colorless solid. ^1H NMR (400 MHz, CDCl_3): δ 8.49 (s, 2H), 7.73 (d, $J = 8.6$ Hz, 2H), 7.65 (d, $J = 8.6$ Hz, 2H), 4.52 (q, $J = 7.2$ Hz, 4H), 3.22 (s, 1H), 1.48 (t, $J = 7.2$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 164.7, 149.9, 149.4, 136.6, 133.0, 127.1, 125.3, 124.0, 82.7, 79.4, 62.5, 14.2. ESI-HRMS: calcd for $\text{C}_{19}\text{H}_{18}\text{NO}_4$ ($[\text{M}+\text{H}]^+$) 324.1230, found 324.1234.

Diethyl 4-(naphthalen-1-yl)pyridine-2,6-dicarboxylate (1h)



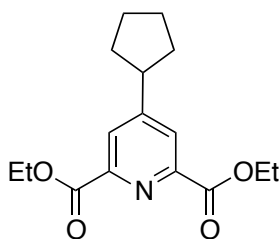
Flash column chromatography (hexane/EtOAc = 4:1); pale yellow gum. ^1H NMR (400 MHz, CDCl_3): δ 8.42 (s, 2H), 7.98-7.94 (m, 2H), 7.73 (dd, $J = 8.0$ Hz, 0.4 Hz, 1H), 7.60-7.46 (m, 4H), 4.52 (q, $J = 7.2$ Hz, 4H), 1.47 (t, $J = 7.2$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 164.7, 151.4, 148.9, 135.6, 133.7, 130.4, 129.7, 128.9, 128.7, 127.3, 127.2, 126.4, 125.3, 124.5, 62.4, 14.2. ESI-HRMS: calcd for $\text{C}_{21}\text{H}_{20}\text{NO}_4$ ($[\text{M}+\text{H}]^+$) 350.1387, found 350.1388.

Diethyl 4-(thiophen-2-yl)pyridine-2,6-dicarboxylate (1j)



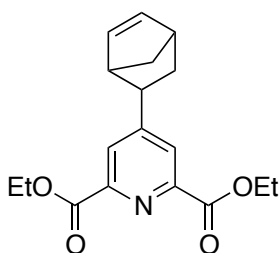
Flash column chromatography (hexane/EtOAc = 7:3); colorless solid. ^1H NMR (400 MHz, CDCl_3): δ 8.42 (s, 2H), 7.68 (dd, $J = 3.6$ Hz, 1.2 Hz, 1H), 7.50 (dd, $J = 5.0$ Hz, 1.2 Hz, 1H), 7.18 (dd, $J = 5.0$ Hz, 3.6 Hz, 1H), 4.51 (q, $J = 7.2$ Hz, 4H), 1.48 (t, $J = 7.2$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 164.7, 149.3, 144.0, 139.4, 128.8, 128.7, 126.8, 123.5, 62.4, 14.2. ESI-HRMS: calcd for $\text{C}_{15}\text{H}_{16}\text{NO}_4\text{S}$ ($[\text{M}+\text{H}]^+$) 306.0795, found 306.0797.

Diethyl 4-cyclopentylpyridine-2,6-dicarboxylate (**1l**)



Flash column chromatography (hexane/EtOAc = 4:1); colorless solid. ^1H NMR (400 MHz, CDCl_3): δ 8.13 (s, 2H), 4.47 (q, $J = 7.2$ Hz, 4H), 3.17-3.08 (m, 1H), 2.19-2.12 (m, 2H), 1.92-1.81 (m, 2H), 1.81-1.59 (m, 4H), 1.45 (t, $J = 7.2$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 165.0, 158.6, 148.5, 126.7, 62.2, 45.2, 34.0, 25.5, 14.2. ESI-HRMS: calcd for $\text{C}_{16}\text{H}_{22}\text{NO}_4$ ($[\text{M}+\text{H}]^+$) 292.1543, found 292.1545

Diethyl 4-bicyclo[2.2.1]hept-5-en-2-ylpyridine-2,6-dicarboxylate (**1m**)



Compound **1m** was synthesized using 5-norbornene-2-carboxaldehyde (isomers mixture). Flash column chromatography (hexane/EtOAc = 4:1); dr = 1: 0.4; colorless solid. ^1H NMR (400 MHz, CDCl_3): δ 8.16 (d, $J = 0.8$ Hz, 2H x 0.4/1.4), 8.02 (d, $J = 0.4$ Hz, 2H x 1.0/1.4), 6.33 (dd, $J = 5.6$ Hz, 3.2 Hz, 1H x 1.0/1.4), 6.26 (dd, $J = 5.6$ Hz, 3.2 Hz, 1H x 0.4/1.4), 6.22 (dd, $J = 5.6$ Hz, 2.8 Hz, 1H x 0.4/1.4), 5.72 (dd, $J = 5.6$ Hz, 2.8 Hz, 1H x 1.0/1.4), 4.48 (q, $J = 7.2$ Hz, 4H x 0.4/1.4), 4.46 (q, $J = 7.2$ Hz, 4H x 1.0/1.4), 3.50 (dt, $J = 9.6$ Hz, 4.0 Hz, 1H x 1.0/1.4), 3.20-3.16 (m, 1H x 1.0/1.4), 3.06-3.00 (m, 1H x 1.0/1.4 + 2H x 0.4/1.4), 2.81 (dd, $J = 8.4$ Hz, 5.2 Hz, 1H x 0.4/1.4), 2.26 (ddd, $J = 11.6$ Hz, 9.6 Hz, 4.0 Hz, 1H x 1.0/1.4), 1.80-1.37 (m, 3H x 1.0/1.4 + 4H x 0.4/1.4), 1.45 (t, $J = 7.2$ Hz, 6H x 0.4/1.4), 1.44 (t, $J = 7.2$ Hz, 6H x 1.0/1.4). ^{13}C NMR (100 MHz, CDCl_3): δ 165.13, 165.10, 158.5, 157.3, 148.6, 148.1, 138.4, 138.0, 136.7, 131.9, 127.6, 127.1, 62.3, 62.2, 50.3, 48.5, 47.8, 45.8, 43.7, 43.5, 43.2, 42.5, 33.6, 32.5, 14.2. ESI-HRMS: calcd for $\text{C}_{18}\text{H}_{22}\text{NO}_4$ ($[\text{M}+\text{H}]^+$) 316.1543, found 316.1548.

Diethyl 4-(dimethoxymethyl)pyridine-2,6-dicarboxylate (**1n**)¹

During the synthesis of **1n** (Rf 0.33, hexane/EtOAc = 7:3), formation of diethyl 4-(dimethoxymethyl)-1,4-dihydropyridine-2,6-dicarboxylate (Rf 0.67, hexane/EtOAc = 7:3) was observed. The dihydropyridine derivative was easily air-oxidized by usual handling under air. When the dihydropyridine derivative was isolated by flash column chromatography and concentrated, the fractions were completely converted to **1n** after 1 day.

A 5 mmol-Scale Reaction to Afford **1g**

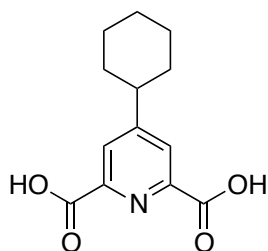
To a solution of 4-ethynylbenzaldehyde (650.7 mg, 5.00 mmol) and ethyl pyruvate (1.66 mL, 15.0 mmol) in CH_3CN (5.0 mL), acetic acid (286 μL , 5.00 mmol) and pyrrolidine (164.5 μL , 2.00 mmol) were added at room temperature (25 $^\circ\text{C}$) and the mixture was stirred at the same temperature. After 30 h, NH_4OAc (1.16 g, 15.0 mmol) and acetic acid (286 μL , 5.00 mmol) were added to the mixture and the resulting mixture was stirred at the same temperature for 24 h. The mixture was poured into saturated aqueous NaHCO_3 solution and extracted with EtOAc (100 mL x 3). Organic layers were combined, dried over Na_2SO_4 , filtered, concentrated, and purified by flash column chromatography (hexane/EtOAc = 4:1) to give **1g** (726.7 mg, 45%).

3. Transformation of **1** to 4-Substituted Pyridine-2,6-Dicarboxylic Acids **3**

General Procedure for the Hydrolysis of **1** to Afford **3** (Scheme 3)

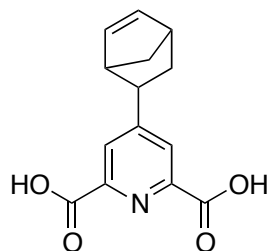
A mixture of compound **1** (0.5 mmol) and 3 M KOH solution in EtOH (6.25 mL) was refluxed for 2 h under nitrogen.² After being cooled to room temperature, EtOH was partly evaporated under vacuum. The mixture was diluted with water and washed with CH₂Cl₂ (10 mL x 2). The aqueous phase was adjusted to be pH 2.0-2.5 with aqueous HCl solution and concentrated under vacuum until solid was started to generate. The mixture was stored at 5 °C for 14 h and generated solid was collected by filtration to give **3**.

4-Cyclohexylpyridine-2,6-dicarboxylic acid (**3k**)



Colorless solid. ¹H NMR (400 MHz, CD₃OD): δ 8.18 (s, 2H), 2.83-2.74 (m, 1H), 1.98-1.86 (m, 4H), 1.83-1.76 (m, 1H), 1.60-1.43 (m, 4H), 1.41-1.28 (m, 1H). ¹³C NMR (100 MHz, CD₃OD): δ 167.9, 162.8, 149.6, 126.9, 45.3, 34.5, 27.5, 26.9. ESI-HRMS: calcd for C₁₃H₁₆NO₄ ([M+H]⁺) 250.1074, found 250.1075.

4-Bicyclo[2.2.1]hept-5-en-2-yl)pyridine-2,6-dicarboxylic acid (**3m**)



Colorless solid, dr = 1: 0.4. ¹H NMR (400 MHz, CD₃OD) δ 8.25 (s, 2H x 0.4/1.4), 8.11 (s, 2H x 1.0/1.4), 6.36 (dd, *J* = 5.6 Hz, 3.2 Hz, 1H x 1.0/1.4), 6.31 (dd, *J* = 5.6 Hz, 3.2 Hz, 1H x 0.4/1.4), 6.24 (dd, *J* = 5.6 Hz, 2.8 Hz, 1H x 0.4/1.4), 5.74 (dd, *J* = 5.6 Hz, 2.8 Hz, 1H x 1.0/1.4), 3.62 (dt, *J* = 9.2 Hz, 4.0 Hz, 1H x 1.0/1.4), 3.21-3.17 (m, 1H x 1.0/1.4), 3.06-3.00 (m, 1H x 1.0/1.4 + 2H x 0.4/1.4), 2.89 (t, *J* = 7.0 Hz, 1H x 0.4/1.4), 2.32 (ddd, *J* = 12.0 Hz, 9.2 Hz, 4.0 Hz, 1H x 1.0/1.4), 1.80-1.76 (m, 2H x 0.4/1.4) 1.60-1.48 (m, 2H), 1.40 (ddd, *J* = 12.0 Hz, 4.4 Hz, 2.0 Hz, 1H x 1.0/1.4). ¹³C NMR (100 MHz, CD₃OD): δ 167.5, 167.4, 161.4, 160.3, 148.8, 148.2, 139.6, 138.9, 137.9, 132.9, 128.6, 128.1, 51.3, 49.9, 46.6, 44.8, 44.6, 43.8, 34.7, 33.4. ESI-HRMS: calcd for C₁₄H₁₄NO₄ ([M+H]⁺) 260.0917, found 260.0924.

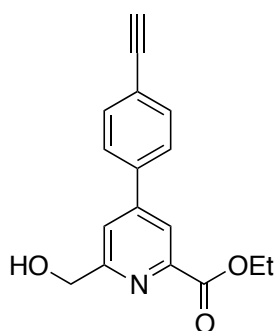
4. Transformation of **1g** to **4** and **5**

Transformation of **1g** to **4**

To a solution of **1g** (210.2 mg, 0.65 mmol) in EtOH (4.0 mL), NaBH₄ (29.5 mg, 0.78 mmol) was added at 0 °C and the mixture was stirred at the same temperature for 2 h.³ The mixture was neutralized with 1 N HCl, and concentrated under vacuum. The residue was partitioned between saturated aqueous NaHCO₃ and CH₂Cl₂. The aqueous layer was further extracted with CH₂Cl₂. Organic layers were combined, washed with water and brine, dried over Na₂SO₄, concentrated, and purified by flash column chromatography (hexane/EtOAc = 2:3) to give **4** (110.0 mg, 60%) as colorless solid. Starting material **1g** (60.0 mg, 29%) was

recovered.

Ethyl 4-(4-ethynylphenyl)-6-(hydroxymethyl)pyridine-2-carboxylate (**4**)

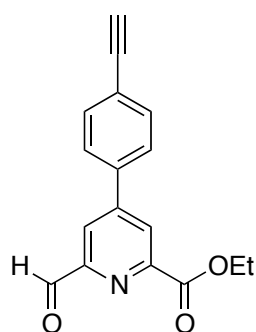


^1H NMR (400 MHz, CDCl_3): δ 8.22 (d, $J = 1.6$ Hz, 1H), 7.72 (d, $J = 1.6$ Hz, 1H), 7.66 (d, $J = 8.6$ Hz, 2H), 7.61 (d, $J = 8.6$ Hz, 2H), 4.92 (s, 2H), 4.49 (q, $J = 7.2$ Hz, 2H), 3.20 (s, 1H), 1.45 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 165.1, 161.0, 149.4, 148.2, 137.5, 132.9, 127.0, 123.6, 121.7, 121.3, 82.9, 79.1, 64.7, 62.1, 14.3. ESI-HRMS: calcd for $\text{C}_{17}\text{H}_{16}\text{NO}_3$ ($[\text{M}+\text{H}]^+$) 282.1125, found 282.1127.

Transformation of **4** to **5**

A mixture of **4** (76.9 mg, 0.27 mmol) and MnO_2 (235.0 mg, 2.70 mmol) in CH_2Cl_2 (1.0 mL) was stirred under nitrogen at room temperature (25 °C) for 15 h. The mixture was filtered through celite and washed with CH_2Cl_2 . The filtrate was concentrated and purified by flash column chromatography (hexane/EtOAc = 4:1) to give **5** (49.0 mg, 65%) as colorless solid.

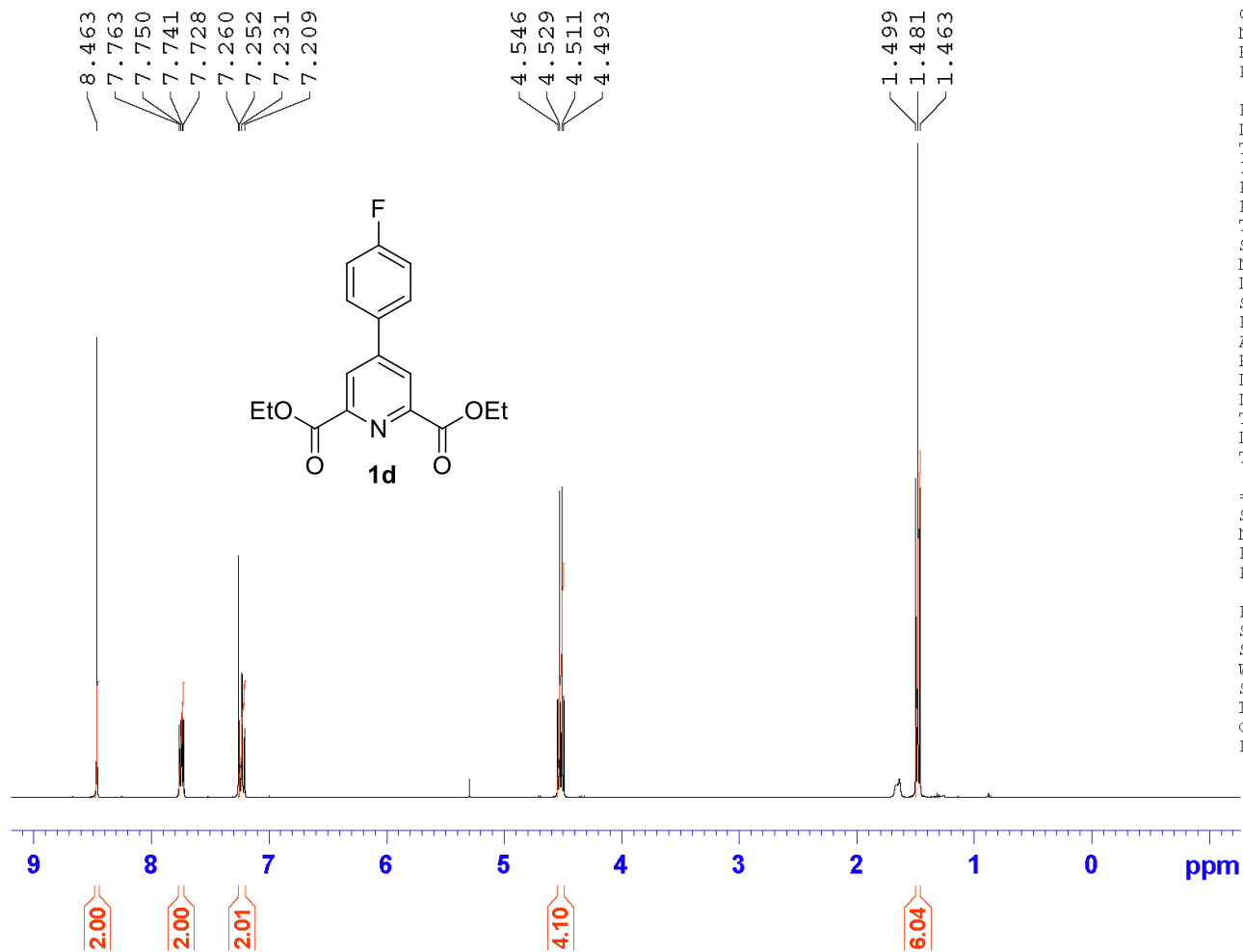
Ethyl 4-(4-ethynylphenyl)-6-formylpyridine-2-carboxylate (**5**)



^1H NMR (400 MHz, CDCl_3): δ 10.24 (s, 1H), 8.54 (d, $J = 1.8$ Hz, 1H), 8.33 (d, $J = 1.8$ Hz, 1H), 7.72 (d, $J = 8.4$ Hz, 2H), 7.65 (d, $J = 8.4$ Hz, 2H), 4.56 (q, $J = 7.2$ Hz, 2H), 3.22 (s, 1H), 1.49 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 192.7, 164.4, 153.5, 150.1, 149.7, 136.4, 133.1, 127.1, 126.4, 124.3, 121.5, 82.7, 79.5, 62.5, 14.3. ESI-HRMS: calcd for $\text{C}_{17}\text{H}_{14}\text{NO}_3$ ($[\text{M}+\text{H}]^+$) 280.0968, found 280.0973.

5. References

1. P. V. Chouthaiwale, F. Tanaka, *Chem. Commun.* 2014, **50**, 14881-14884.
2. N. Ouali, B. Bocquet, S. Rigault, P.-Y. Morgantini, J. Weber, C. Piguet, *Inorg. Chem.* 2002, **41**, 1436-1445.
3. A. Suga, T. Sugiyama, M. Otsuka, M. Ohno, Y. Sugiura, K. Maeda, *Tetrahedron* 1991, **47**, 1191-1204.

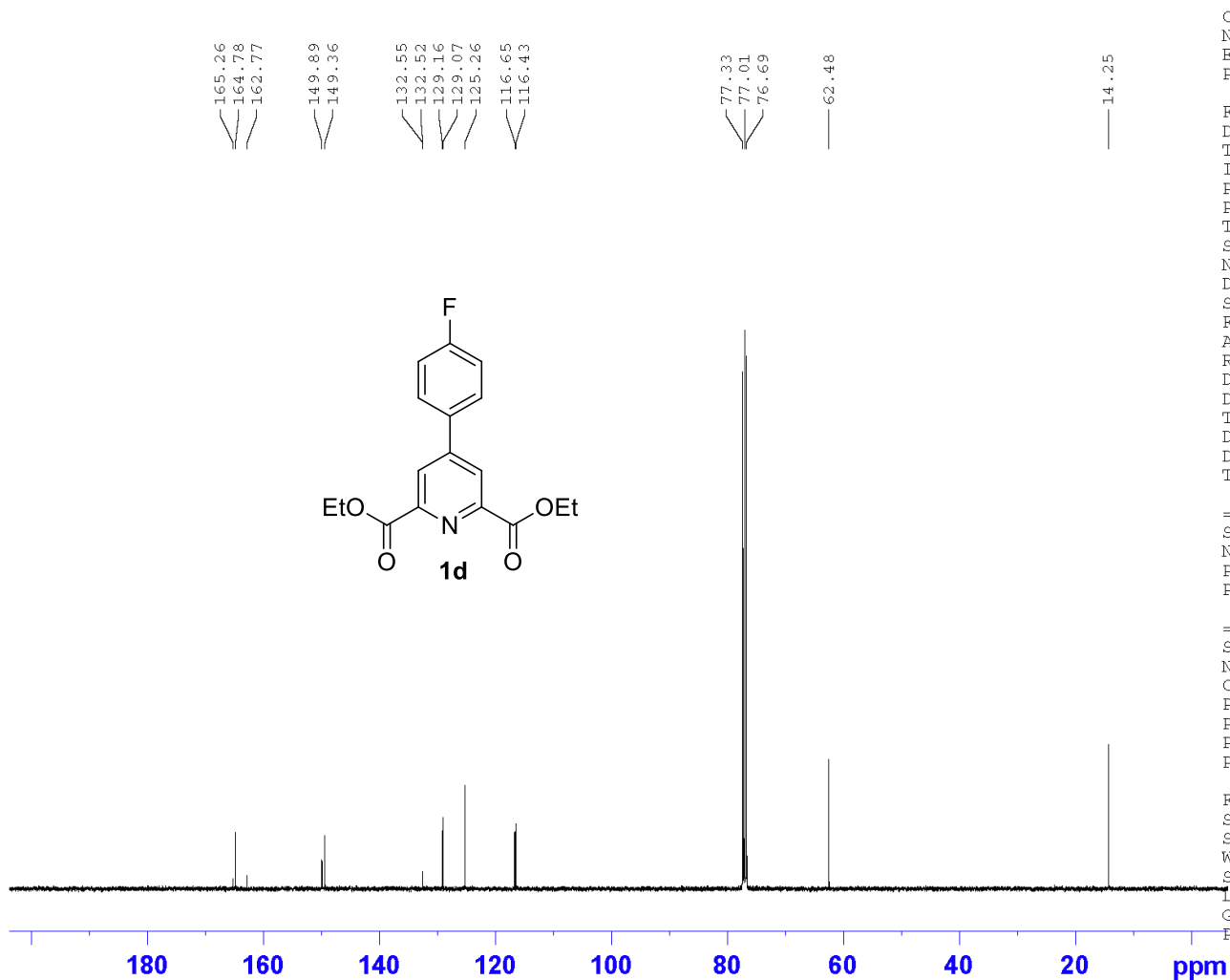
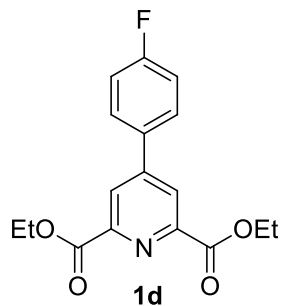


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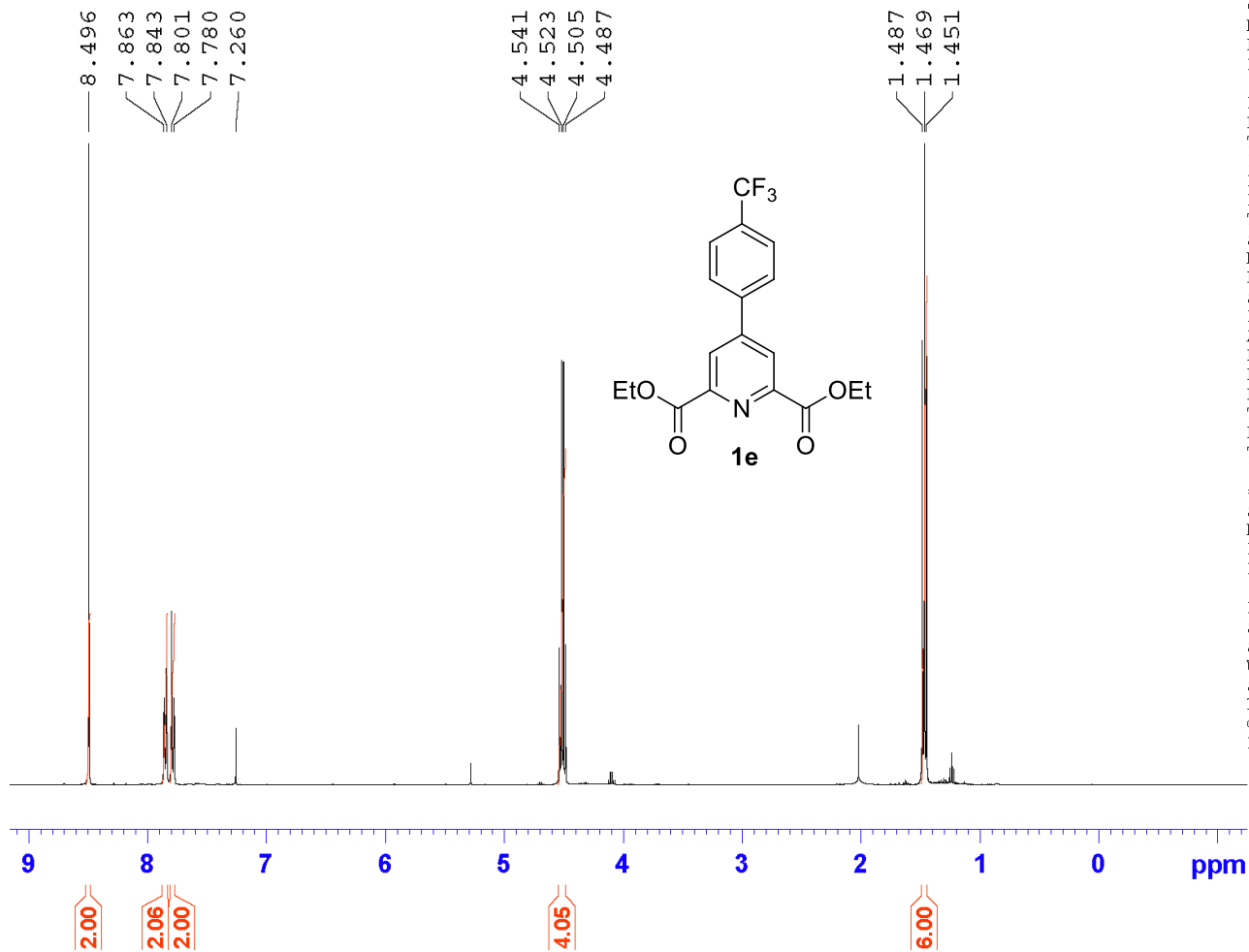
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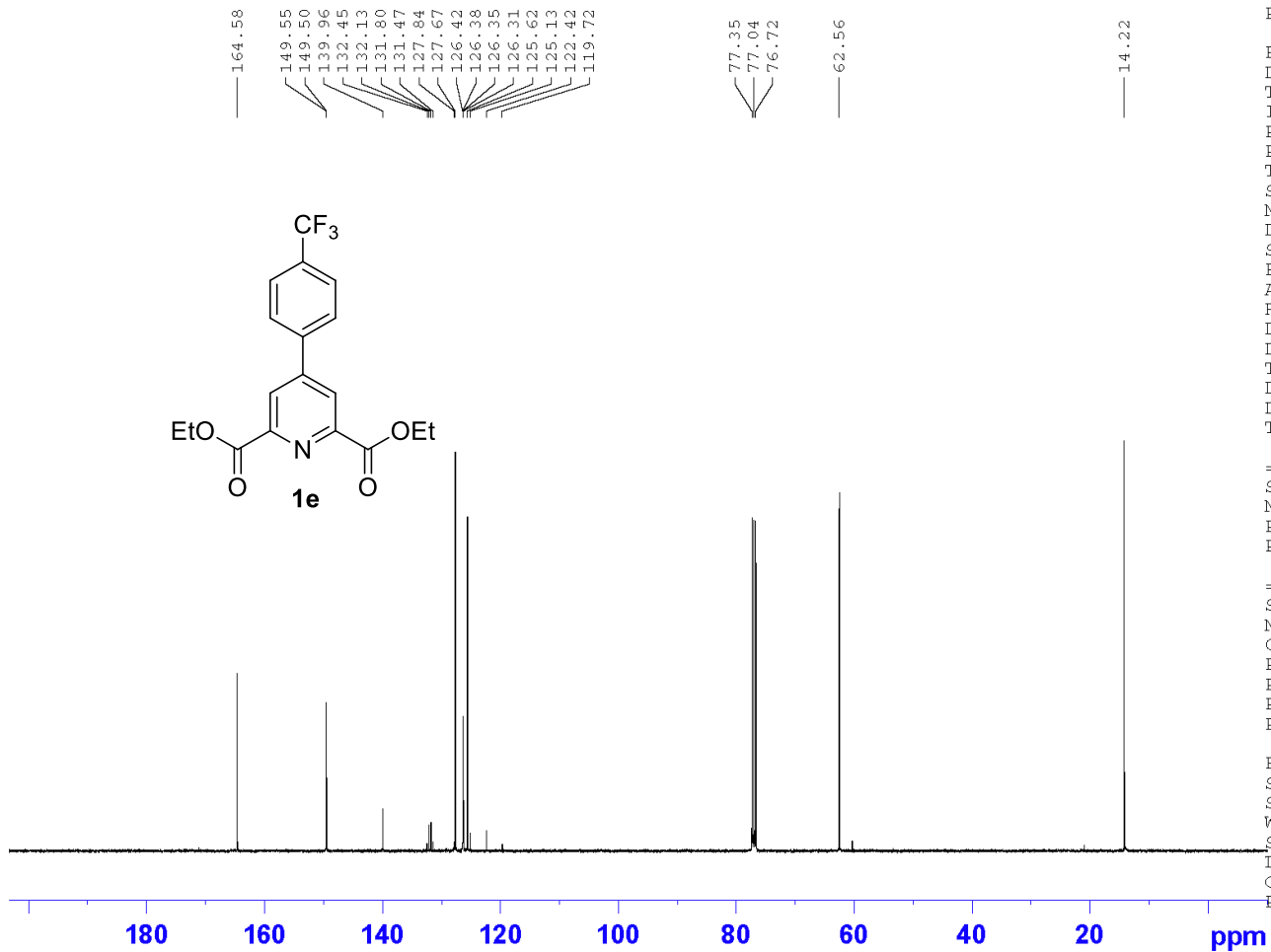
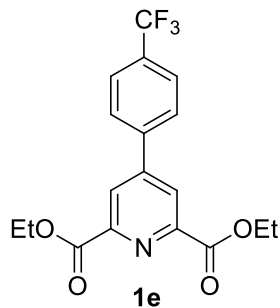


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 NAME Jul27-2016
 EXPNO 30
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20160727
 Time_ 18.40
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 8012.820 Hz
 FIDRES 0.122266 Hz
 AQ 4.0894465 sec
 RG 31.13
 DW 62.400 usec
 DE 6.50 usec
 TE 298.9 K
 D1 1.00000000 sec
 TD0 1

==== CHANNEL f1 =====
 SFO1 400.1324710 MHz
 NUC1 1H
 P1 15.00 usec
 PLW1 8.00000000 W

F2 - Processing parameters
 SI 65536
 SF 400.1300094 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



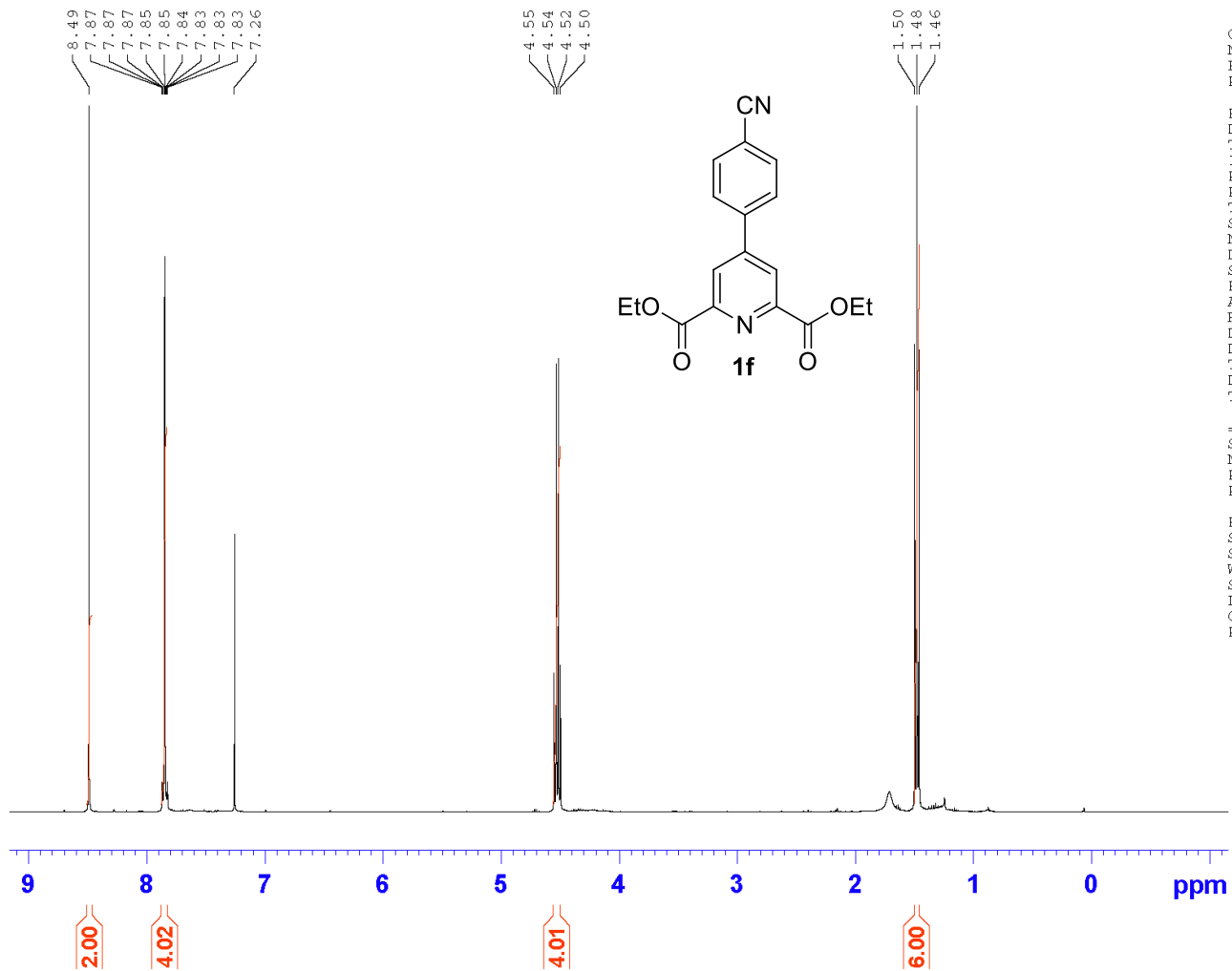
Current Data Parameters
 NAME Jul27-2016
 EXPNO 40
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20160727
 Time_ 20.10
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 1500
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631488 sec
 RG 195.88
 DW 20.800 usec
 DE 6.50 usec
 TE 299.8 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1

==== CHANNEL f1 =====
 SFO1 100.6228293 MHz
 NUC1 13C
 P1 10.00 usec
 PLW1 70.00000000 W

==== CHANNEL f2 =====
 SFO2 400.1316005 MHz
 NUC2 1H
 CPDPRG[2] waltz16
 PCPD2 80.00 usec
 PLW2 8.00000000 W
 PLW12 0.28125000 W
 PLW13 0.28125000 W

F2 - Processing parameters
 SI 32768
 SF 100.6127690 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

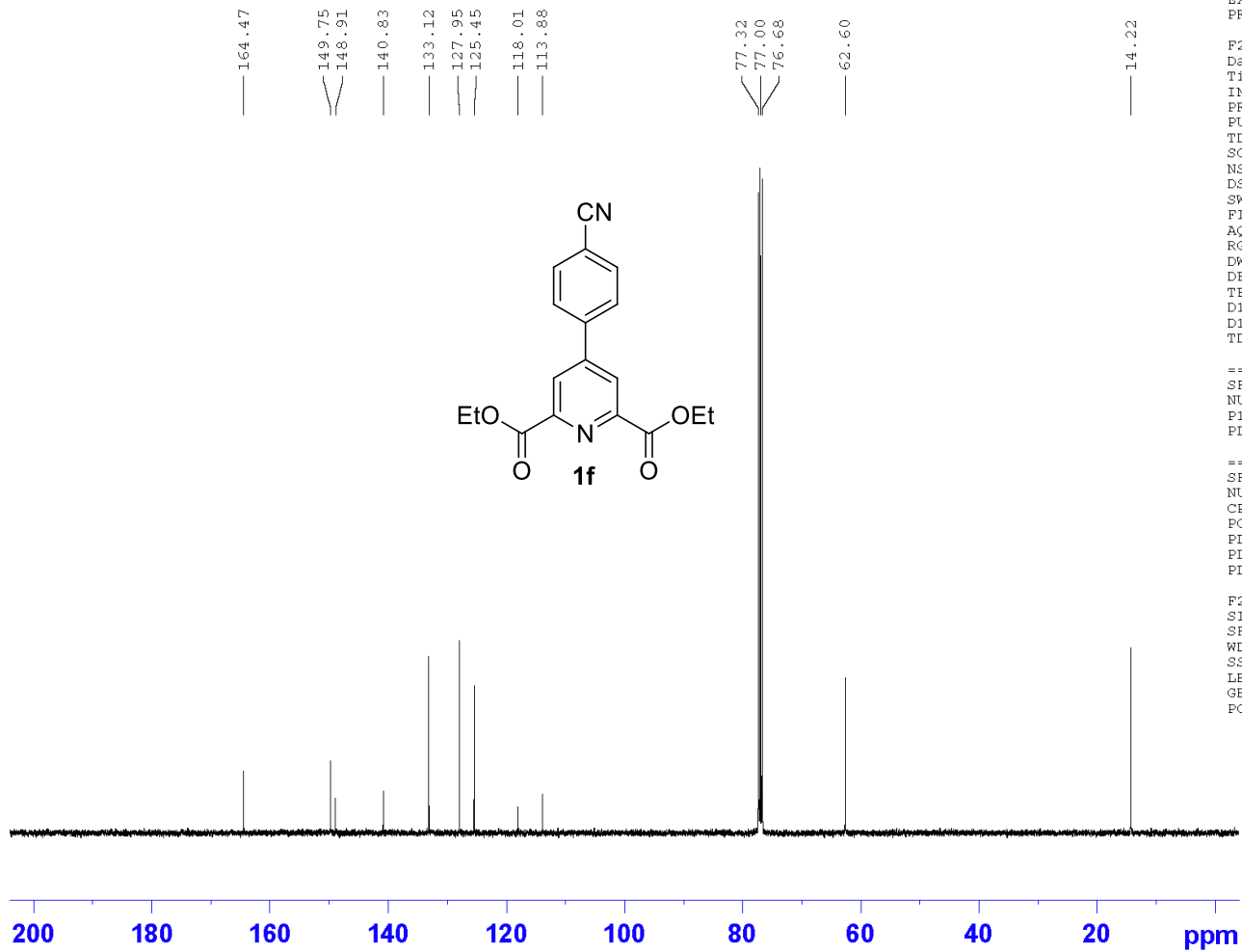


Current Data Parameters
 NAME FT-SL19-1H400crystalCDCl3
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20151214
 Time 22.06
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 8012.820 Hz
 FIDRES 0.122266 Hz
 AQ 4.0894465 sec
 RG 71.01
 DW 62.400 usec
 DE 6.50 usec
 TE 299.4 K
 D1 1.00000000 sec
 TD0 1

==== CHANNEL f1 =====
 SF01 400.1324710 MHz
 NUC1 1H
 P1 15.00 usec
 PLW1 8.00000000 W

F2 - Processing parameters
 SI 65536
 SF 400.1300095 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



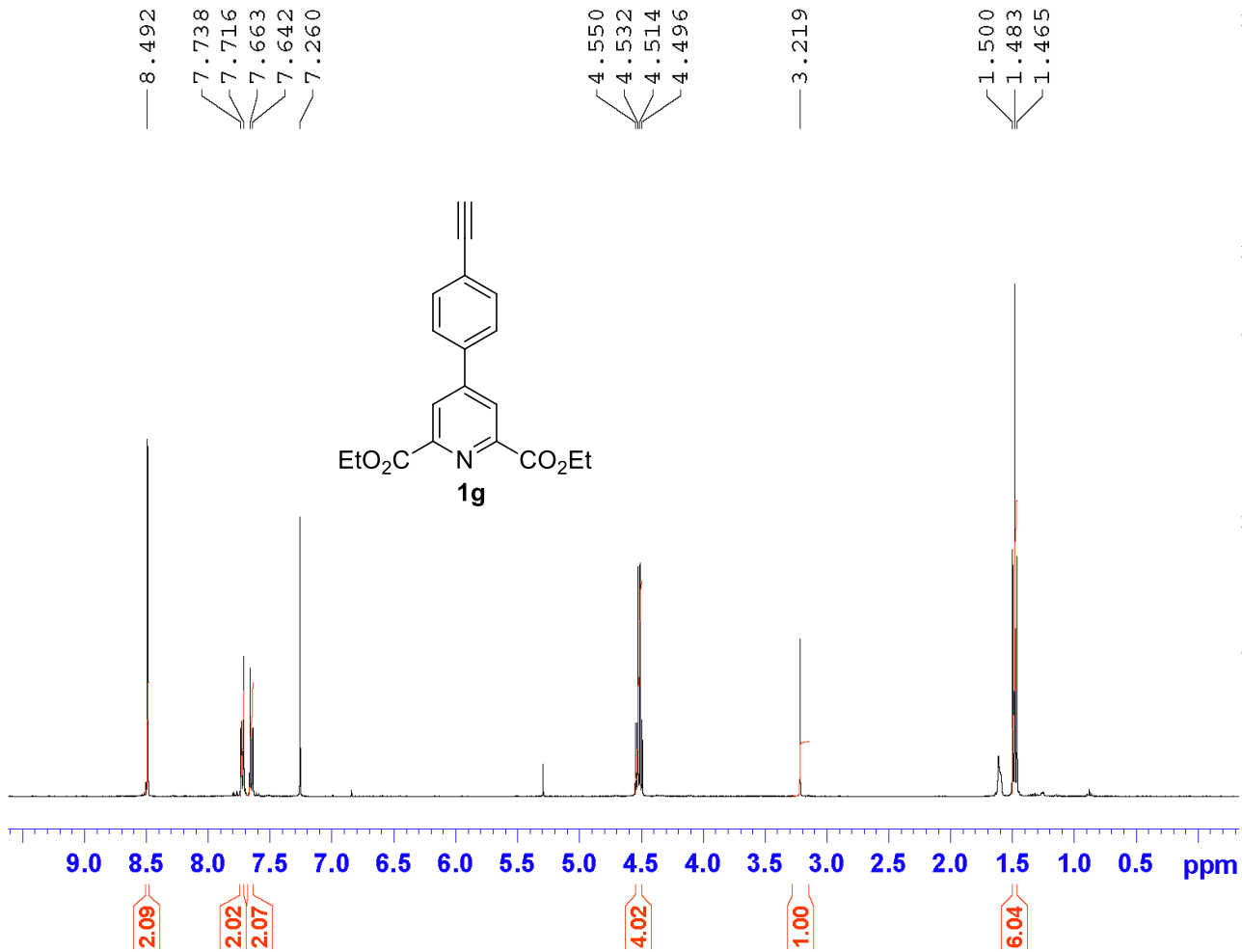
Current Data Parameters
 NAME FT-SL19-13C400crystalCDC13
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20151214
 Time_ 23:06
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDC13
 NS 1024
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631488 sec
 RG 195.88
 DW 20.800 usec
 DE 6.50 usec
 TE 300.8 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TDO 1

===== CHANNEL f1 =====
 SFO1 100.6228293 MHz
 NUC1 13C
 P1 10.00 usec
 PLW1 70.00000000 W

===== CHANNEL f2 =====
 SFO2 400.1316005 MHz
 NUC2 1H
 CPDPRG[2] waltz16
 PCPD2 80.00 usec
 PLW2 8.00000000 W
 PLW12 0.28125000 W
 PLW13 0.28125000 W

F2 - Processing parameters
 SI 32768
 SF 100.6127686 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

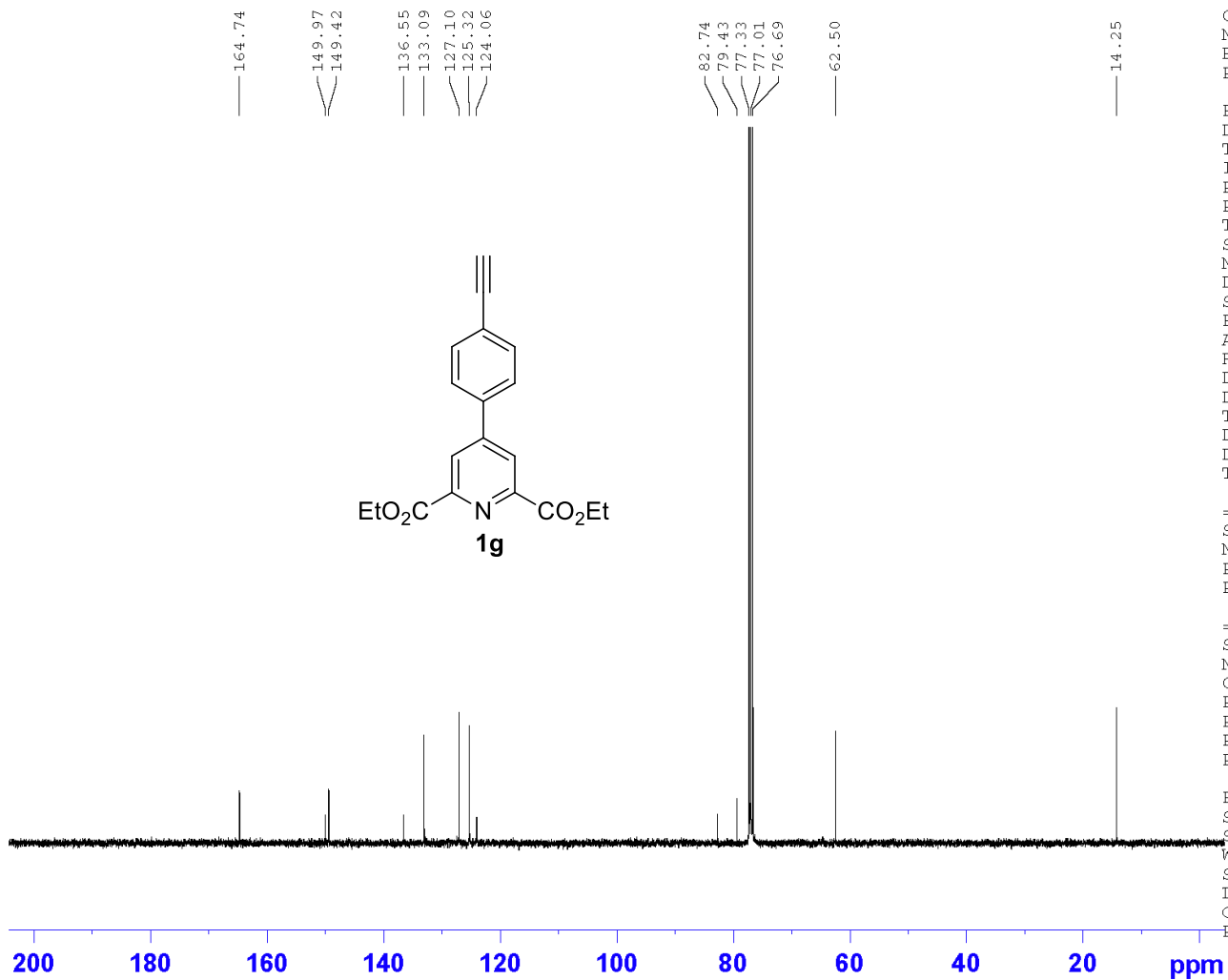


Current Data Parameters
 NAME Aug04-2016
 EXPNO 30
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20160804
 Time_ 12.36
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 8012.820 Hz
 FIDRES 0.122266 Hz
 AQ 4.0894465 sec
 RG 88.94
 DW 62.400 usec
 DE 6.50 usec
 TE 299.3 K
 D1 1.00000000 sec
 TD0 1

==== CHANNEL f1 =====
 SFO1 400.1324710 MHz
 NUC1 1H
 P1 15.00 usec
 PLW1 8.00000000 W

F2 - Processing parameters
 SI 65536
 SF 400.1300095 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



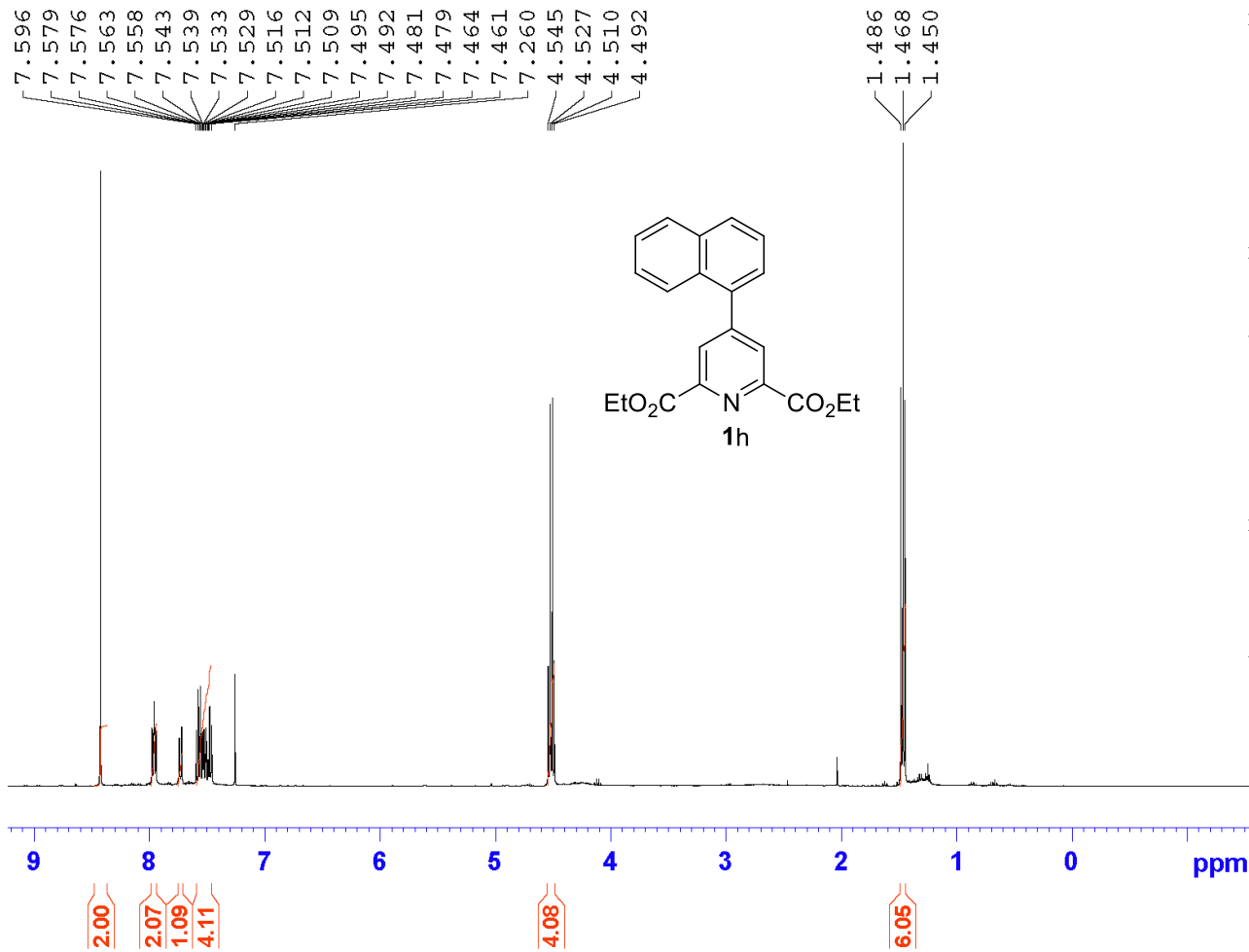
Current Data Parameters
 NAME Aug04-2016
 EXPNO 40
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20160804
 Time_ 13.42
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 1100
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631488 sec
 RG 195.88
 DW 20.800 usec
 DE 6.50 usec
 TE 300.0 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1

==== CHANNEL f1 =====
 SFO1 100.6228293 MHz
 NUC1 13C
 P1 10.00 usec
 PLW1 70.00000000 W

==== CHANNEL f2 =====
 SFO2 400.1316005 MHz
 NUC2 1H
 CPDPRG[2] waltz16
 PCPD2 80.00 usec
 PLW2 8.00000000 W
 PLW12 0.28125000 W
 PLW13 0.28125000 W

F2 - Processing parameters
 SI 32768
 SF 100.6127690 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

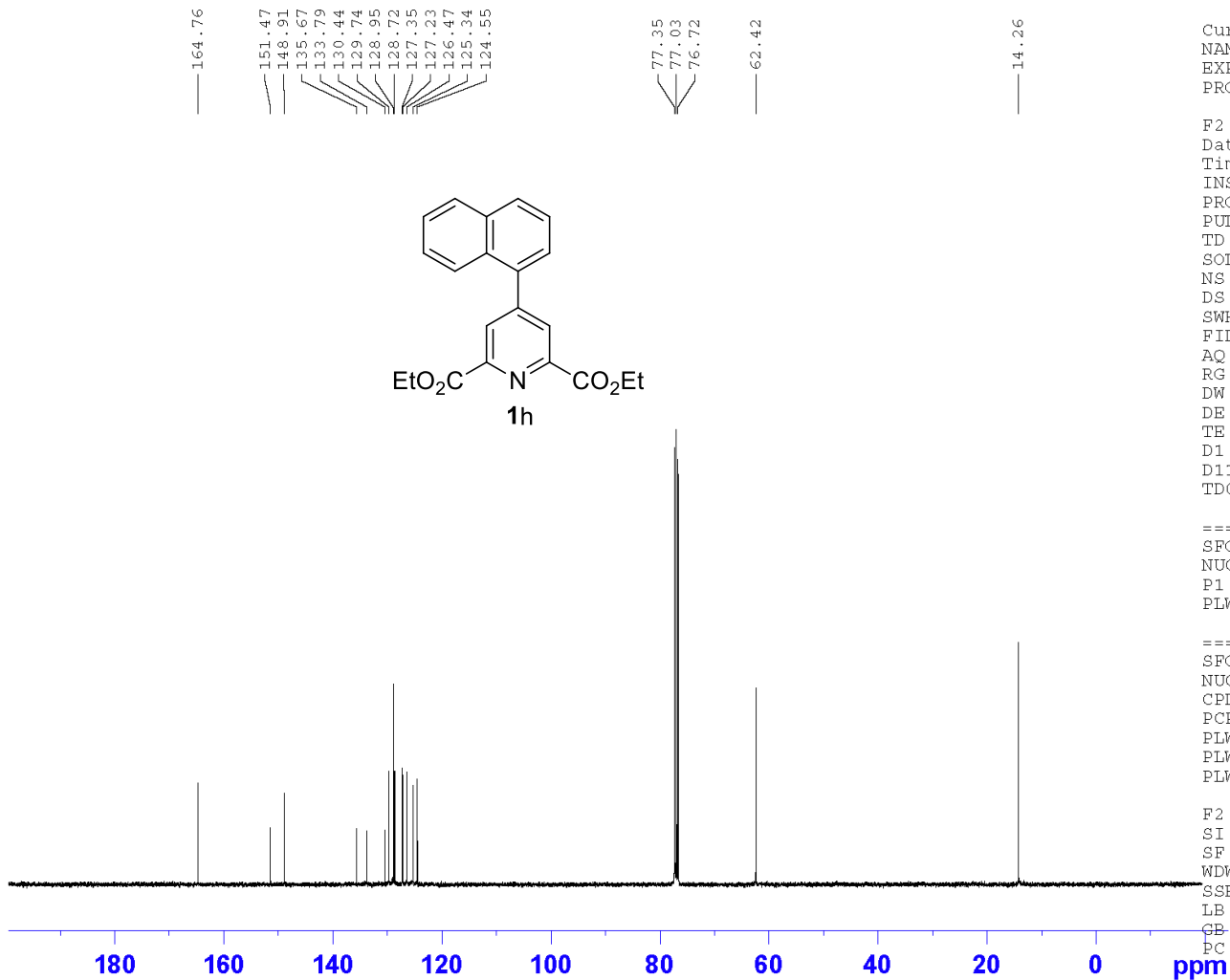


Current Data Parameters
 NAME Jul28-2016
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20160728
 Time_ 11.14
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 8012.820 Hz
 FIDRES 0.122266 Hz
 AQ 4.0894465 sec
 RG 49.09
 DW 62.400 usec
 DE 6.50 usec
 TE 299.0 K
 D1 1.00000000 sec
 TD0 1

==== CHANNEL f1 =====
 SFO1 400.1324710 MHz
 NUC1 1H
 P1 15.00 usec
 PLW1 8.00000000 W

F2 - Processing parameters
 SI 65536
 SF 400.1300094 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



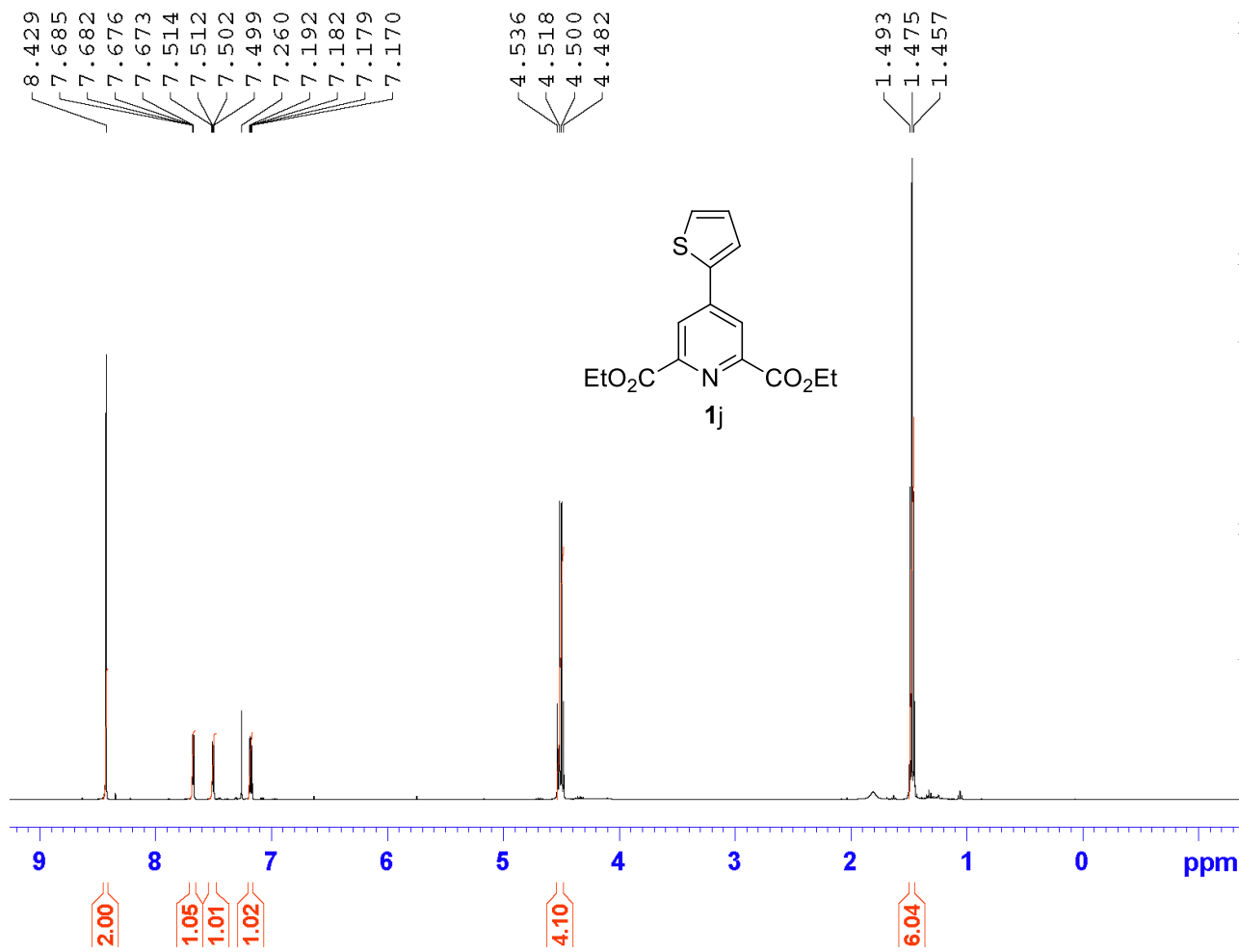
Current Data Parameters
 NAME Jul26-2016
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20160726
 Time_ 19.42
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 1024
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631488 sec
 RG 195.88
 DW 20.800 usec
 DE 6.50 usec
 TE 299.7 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1

==== CHANNEL f1 =====
 SFO1 100.6228293 MHz
 NUC1 13C
 P1 10.00 usec
 PLW1 70.00000000 W

==== CHANNEL f2 =====
 SFO2 400.1316005 MHz
 NUC2 1H
 CPDPRG[2] waltz16
 PCPD2 80.00 usec
 PLW2 8.00000000 W
 PLW12 0.28125000 W
 PLW13 0.28125000 W

F2 - Processing parameters
 SI 32768
 SF 100.6127690 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

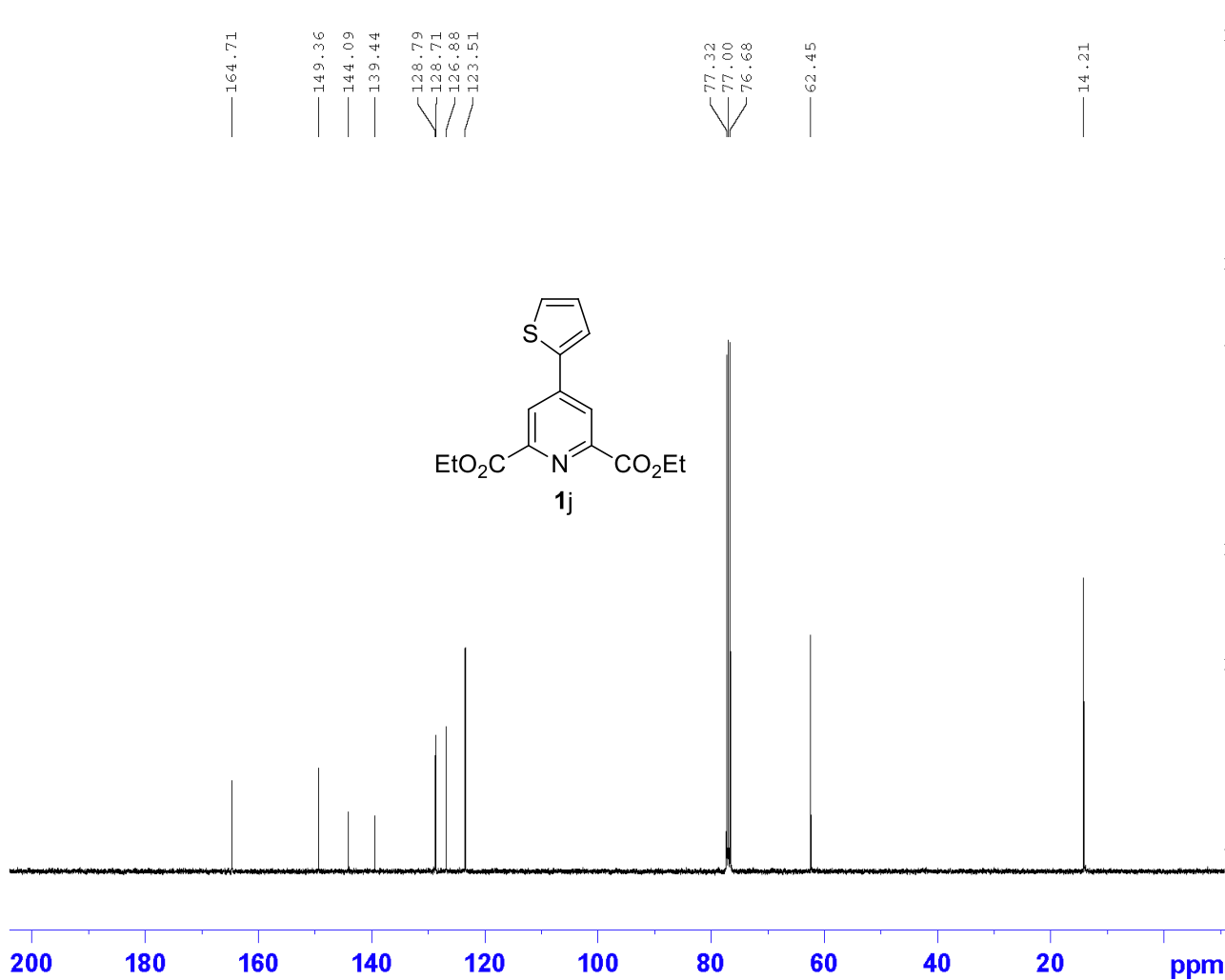


Current Data Parameters
 NAME Jul08-2016
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20160708
 Time_ 13.32
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 8012.820 Hz
 FIDRES 0.122266 Hz
 AQ 4.0894465 sec
 RG 62.88
 DW 62.400 usec
 DE 6.50 usec
 TE 299.4 K
 D1 1.00000000 sec
 TD0 1

==== CHANNEL f1 =====
 SFO1 400.1324710 MHz
 NUC1 1H
 P1 15.00 usec
 PLW1 8.00000000 W

F2 - Processing parameters
 SI 65536
 SF 400.1300094 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



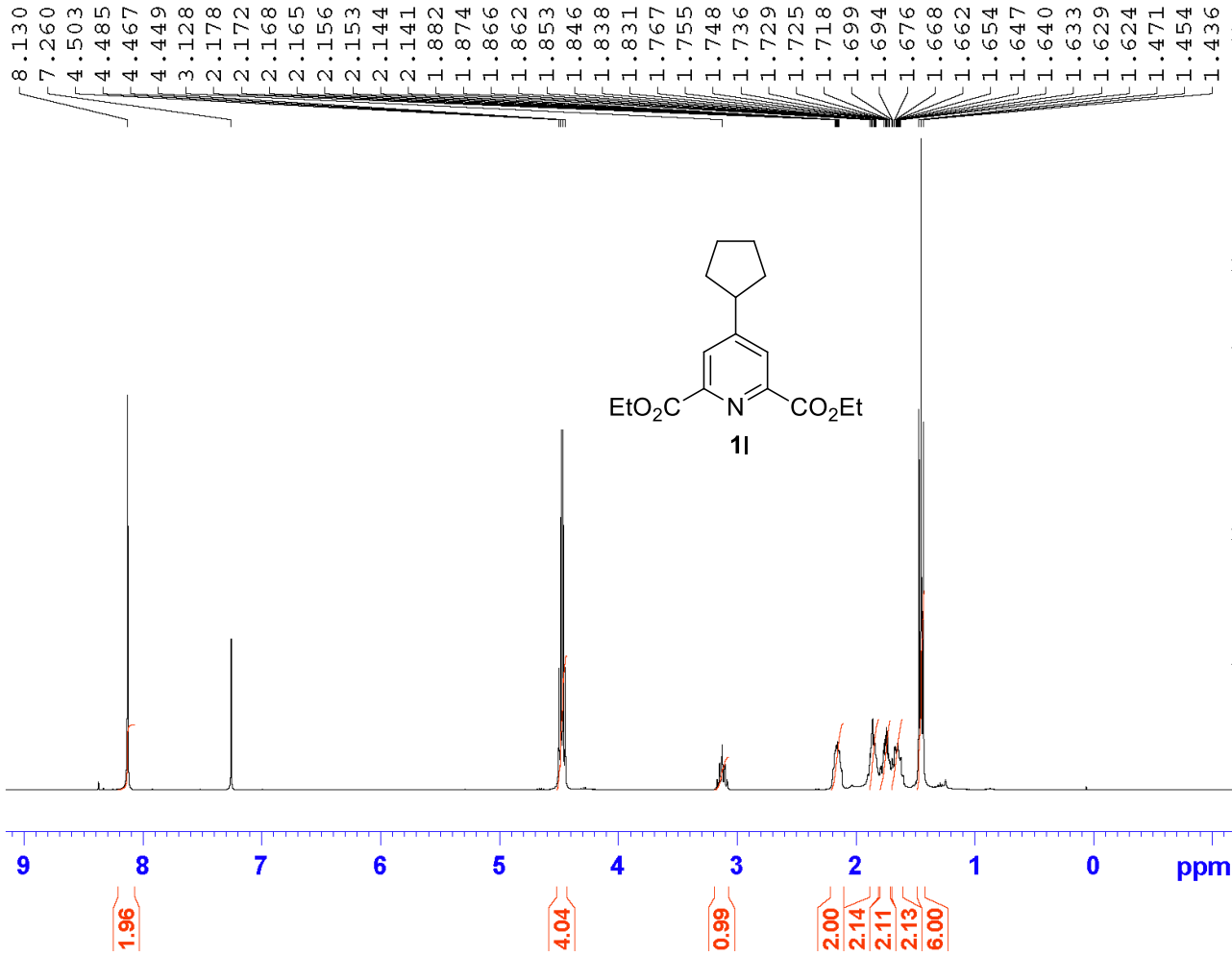
Current Data Parameters
 NAME Jul08-2016
 EXPNO 20
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20160708
 Time_ 14.34
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDC13
 NS 1024
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631488 sec
 RG 195.88
 DW 20.800 usec
 DE 6.50 usec
 TE 300.4 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1

==== CHANNEL f1 =====
 SFO1 100.6228293 MHz
 NUC1 13C
 P1 10.00 usec
 PLW1 70.00000000 W

==== CHANNEL f2 =====
 SFO2 400.1316005 MHz
 NUC2 1H
 CPDPRG[2] waltz16
 PCPD2 80.00 usec
 PLW2 8.00000000 W
 PLW12 0.28125000 W
 PLW13 0.28125000 W

F2 - Processing parameters
 SI 32768
 SF 100.6127717 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40



8.130
7.260
4.503
4.485
4.467
4.449
3.128
2.178
2.172
2.168
2.165
2.156
2.153
2.144
2.141
1.882
1.874
1.866
1.862
1.853
1.846
1.838
1.831
1.767
1.755
1.748
1.736
1.729
1.725
1.718
1.699
1.694
1.676
1.668
1.662
1.654
1.647
1.640
1.633
1.629
1.624
1.471
1.454
1.436

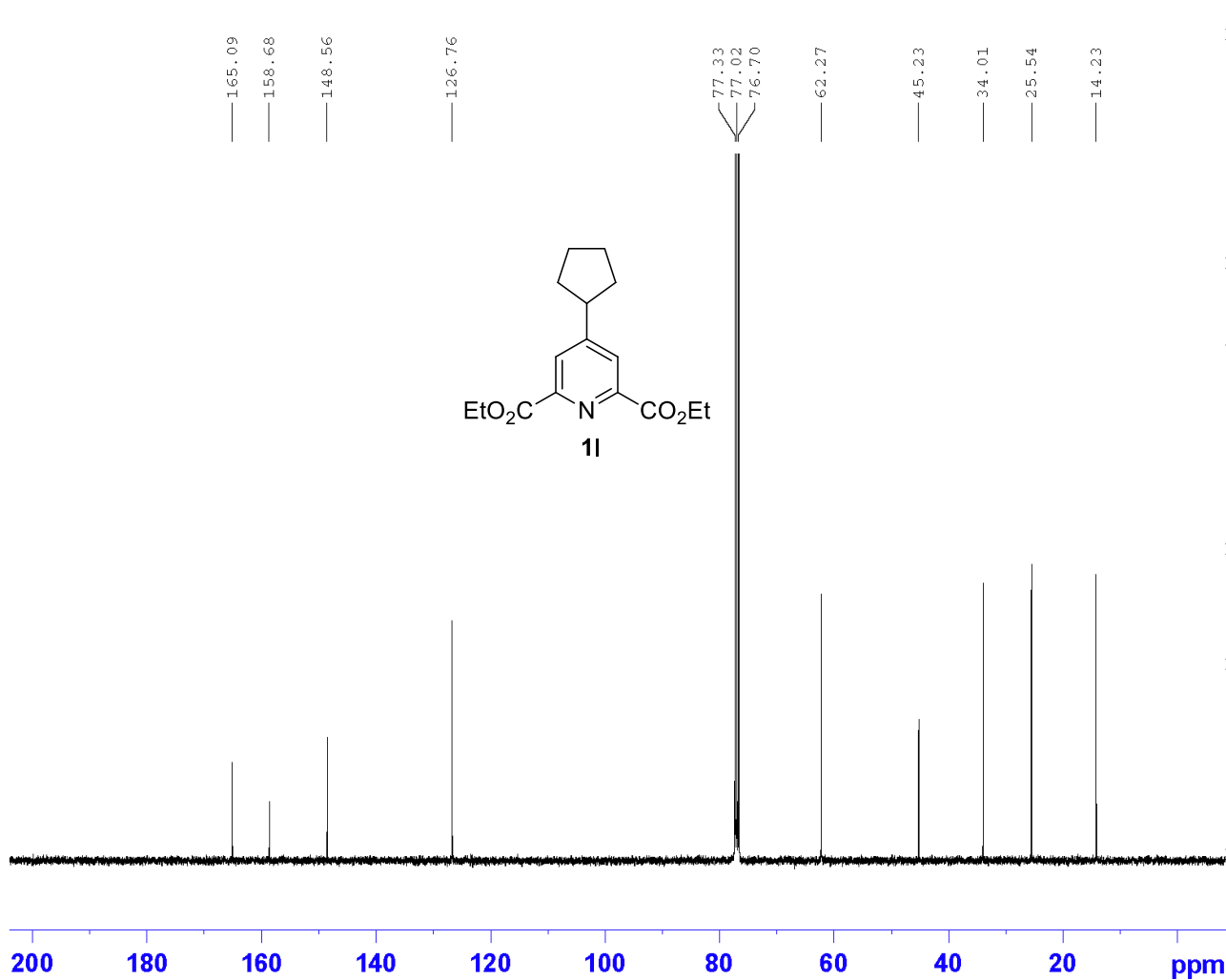
```

Current Data Parameters
NAME          Jul07-2016
EXPNO         20
PROCNO        1

F2 - Acquisition Parameters
Date_         20160707
Time_         18.41
INSTRUM       spect
PROBHD        5 mm PABBO BB/
PULPROG       zg30
TD            65536
SOLVENT       CDCl3
NS            16
DS            2
SWH           8012.820 Hz
FIDRES        0.122266 Hz
AQ            4.0894465 sec
RG            62.88
DW            62.400 usec
DE            6.50 usec
TE            299.3 K
D1            1.00000000 sec
TD0           1

===== CHANNEL f1 =====
SFO1          400.1324710 MHz
NUC1           1H
P1            15.00 usec
PLW1          8.00000000 W

F2 - Processing parameters
SI            65536
SF            400.1300093 MHz
WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            1.00
  
```



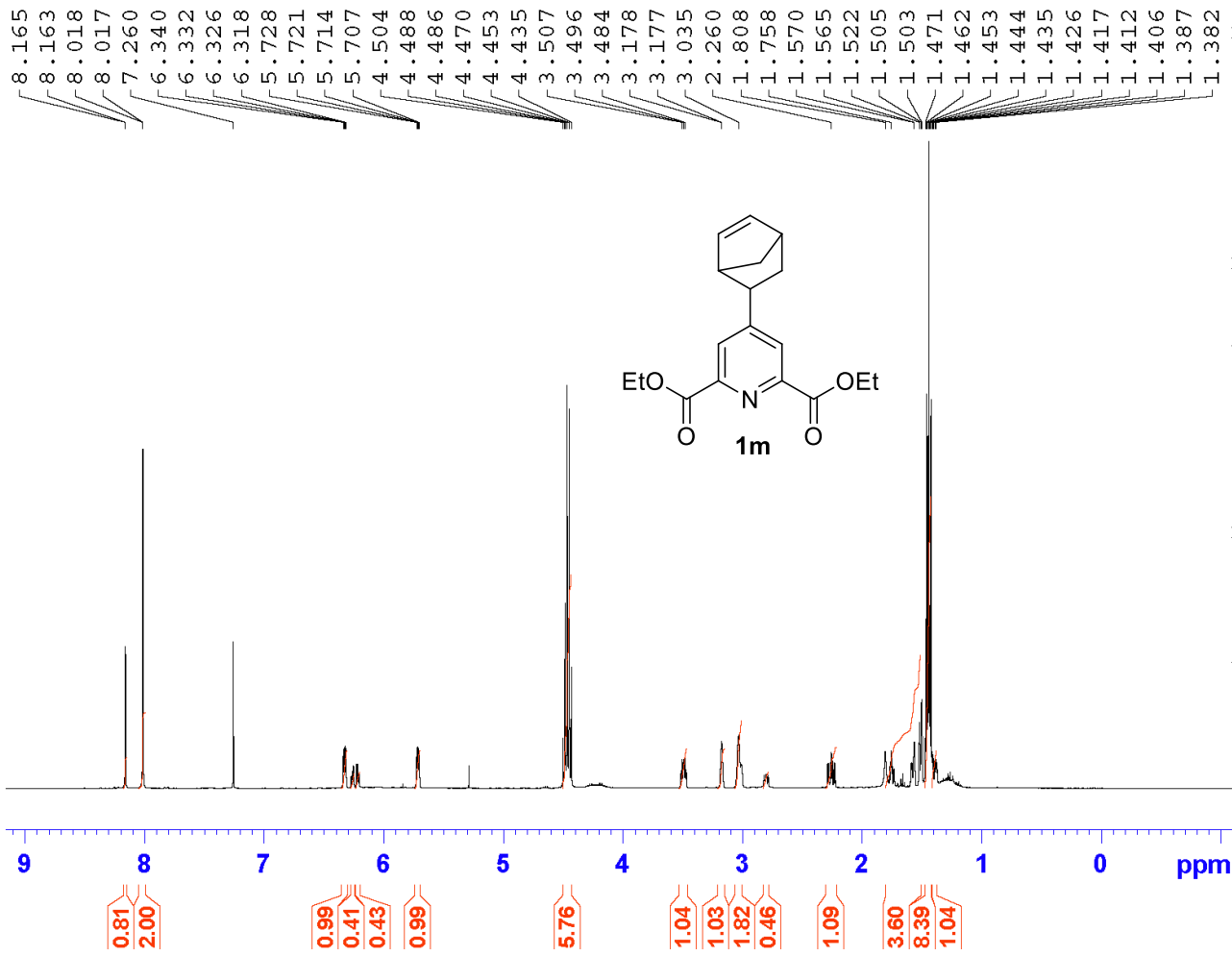
Current Data Parameters
 NAME Jul07-2016
 EXPNO 30
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20160707
 Time_ 19.49
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 1024
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631488 sec
 RG 195.88
 DW 20.800 usec
 DE 6.50 usec
 TE 300.1 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1

==== CHANNEL f1 =====
 SFO1 100.6228293 MHz
 NUC1 13C
 P1 10.00 usec
 PLW1 70.00000000 W

==== CHANNEL f2 =====
 SFO2 400.1316005 MHz
 NUC2 1H
 CPDPRG[2] waltz16
 PCPD2 80.00 usec
 PLW2 8.00000000 W
 PLW12 0.28125000 W
 PLW13 0.28125000 W

F2 - Processing parameters
 SI 32768
 SF 100.6127690 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40



```

Current Data Parameters
NAME          Jul06-2016
EXPNO        10
PROCNO       1

F2 - Acquisition Parameters
Date_        20160706
Time_        18.29
INSTRUM      spect
PROBHD       5 mm PABBO BB/
PULPROG      zg30
TD           65536
SOLVENT      CDCl3
NS           16
DS           2
SWH          8012.820 Hz
FIDRES       0.122266 Hz
AQ           4.0894465 sec
RG           31.13
DW           62.400 usec
DE           6.50 usec
TE           299.1 K
D1           1.00000000 sec
TD0          1

===== CHANNEL f1 =====
SF01         400.1324710 MHz
NUC1         1H
P1           15.00 usec
PLW1         8.00000000 W

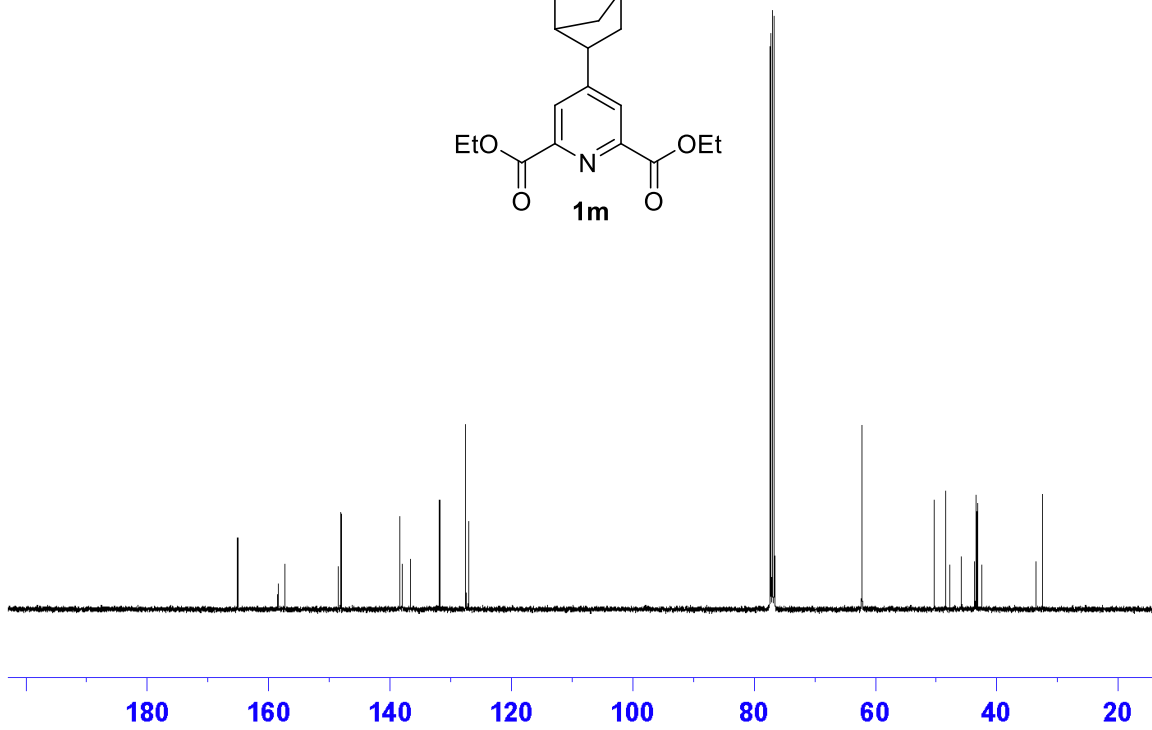
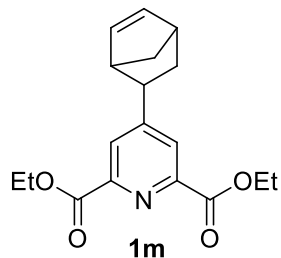
F2 - Processing parameters
SI           65536
SF           400.1300094 MHz
WDW          EM
SSB          0
LB           0.30 Hz
GB           0
PC           1.00
  
```

165.13
165.10
158.50
157.37
148.58
148.10
138.40
137.99
136.67
131.89
127.58
127.12

77.34
77.03
76.71

62.30
62.23
50.33
48.48
47.79
45.84
43.71
43.48
43.23
42.48
33.61
32.51

14.22



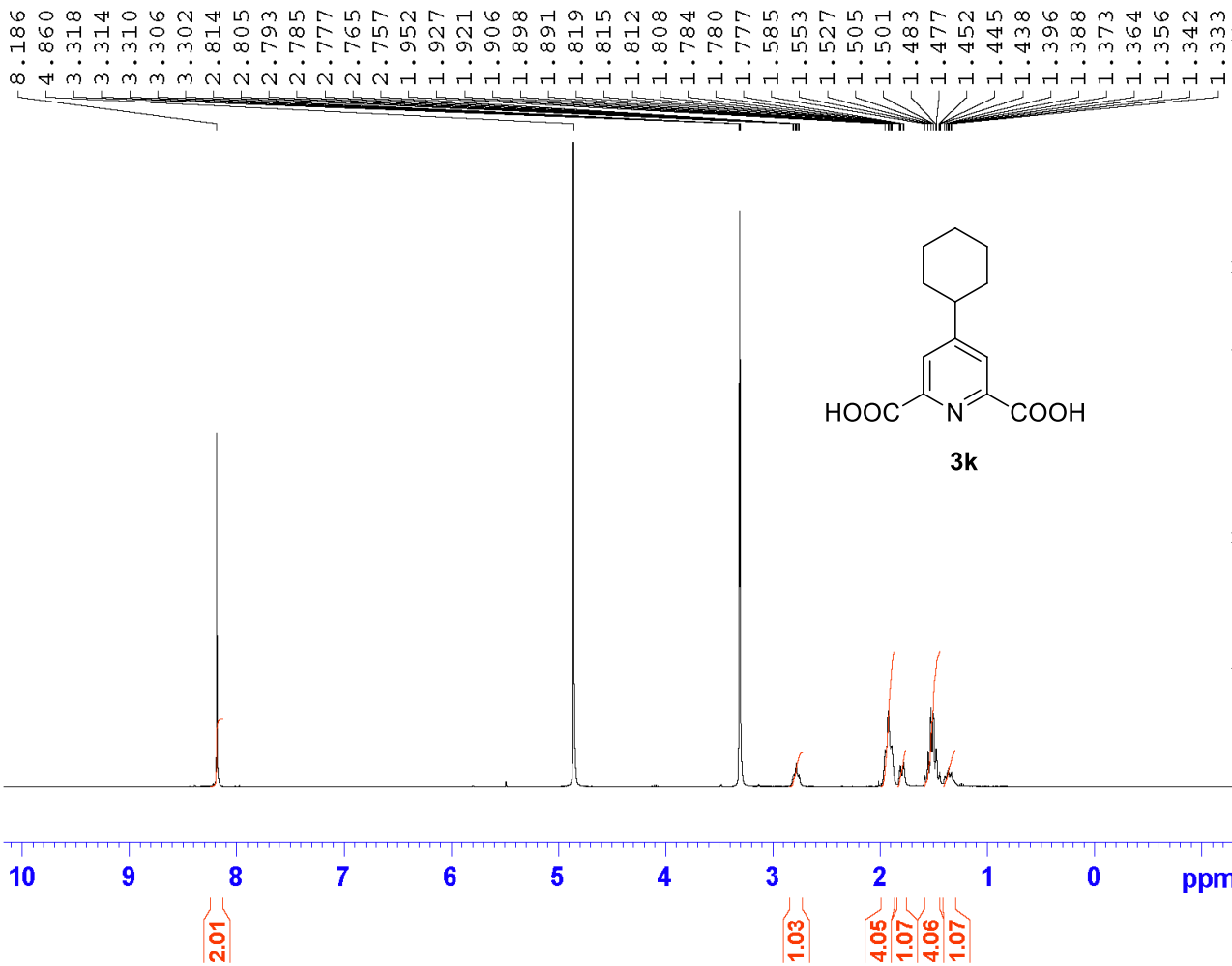
Current Data Parameters
NAME Jul06-2016
EXPNO 20
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160706
Time_ 19.31
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 195.88
DW 20.800 usec
DE 6.50 usec
TE 300.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

==== CHANNEL f1 =====
SFO1 100.6228293 MHz
NUC1 13C
P1 10.00 usec
PLW1 70.00000000 W

==== CHANNEL f2 =====
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2] waltz16
PCPD2 80.00 usec
PLW2 8.00000000 W
PLW12 0.28125000 W
PLW13 0.28125000 W

F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

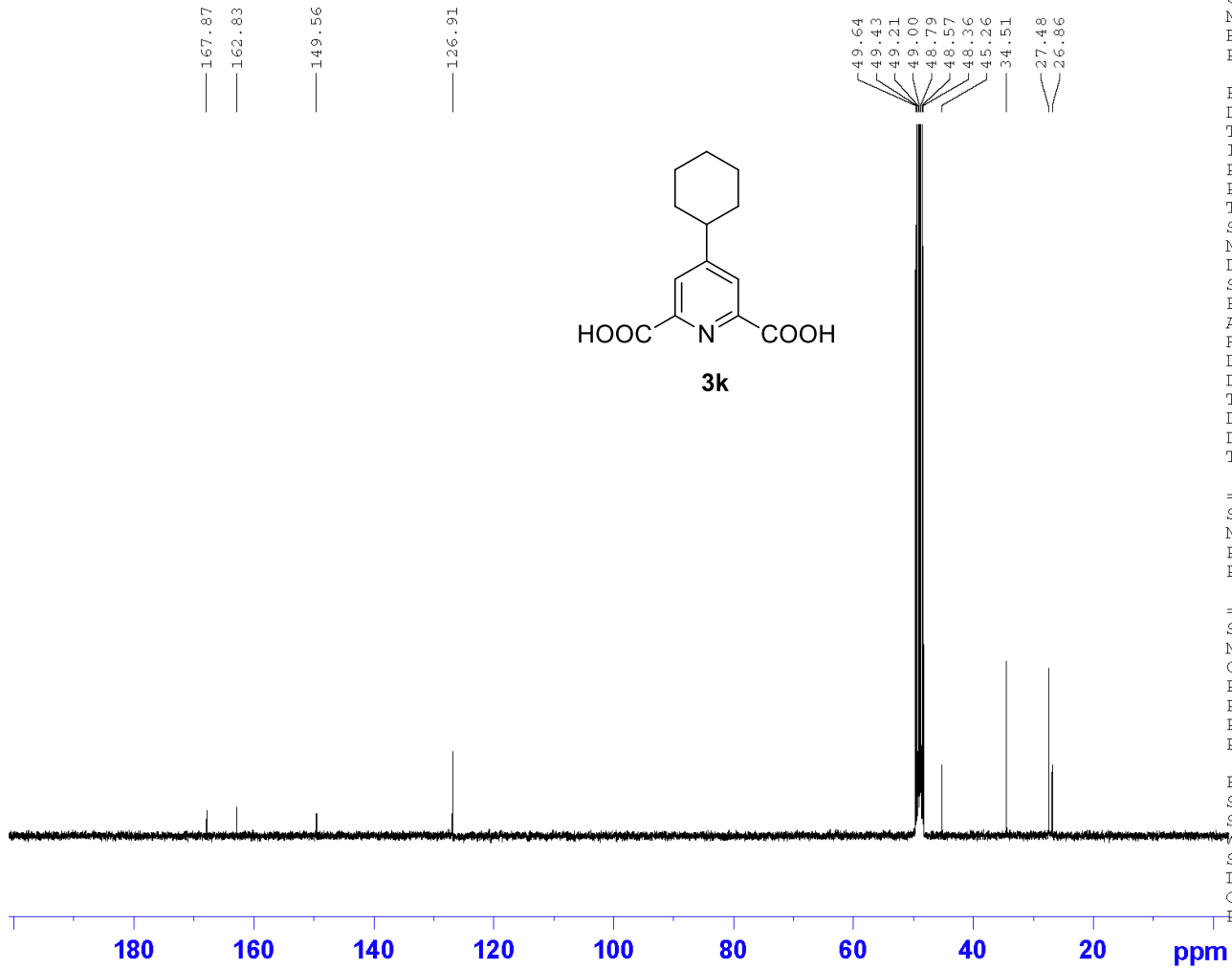


Current Data Parameters
 NAME Oct16-2014
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20141016
 Time_ 12.03
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zg30
 TD 65536
 SOLVENT MeOD
 NS 16
 DS 2
 SWH 8012.820 Hz
 FIDRES 0.122266 Hz
 AQ 4.0894465 sec
 RG 77.81
 DW 62.400 usec
 DE 6.50 usec
 TE 298.5 K
 D1 1.00000000 sec
 TD0 1

==== CHANNEL f1 =====
 SFO1 400.1324710 MHz
 NUC1 1H
 P1 15.00 usec
 PLW1 8.00000000 W

F2 - Processing parameters
 SI 65536
 SF 400.1300077 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



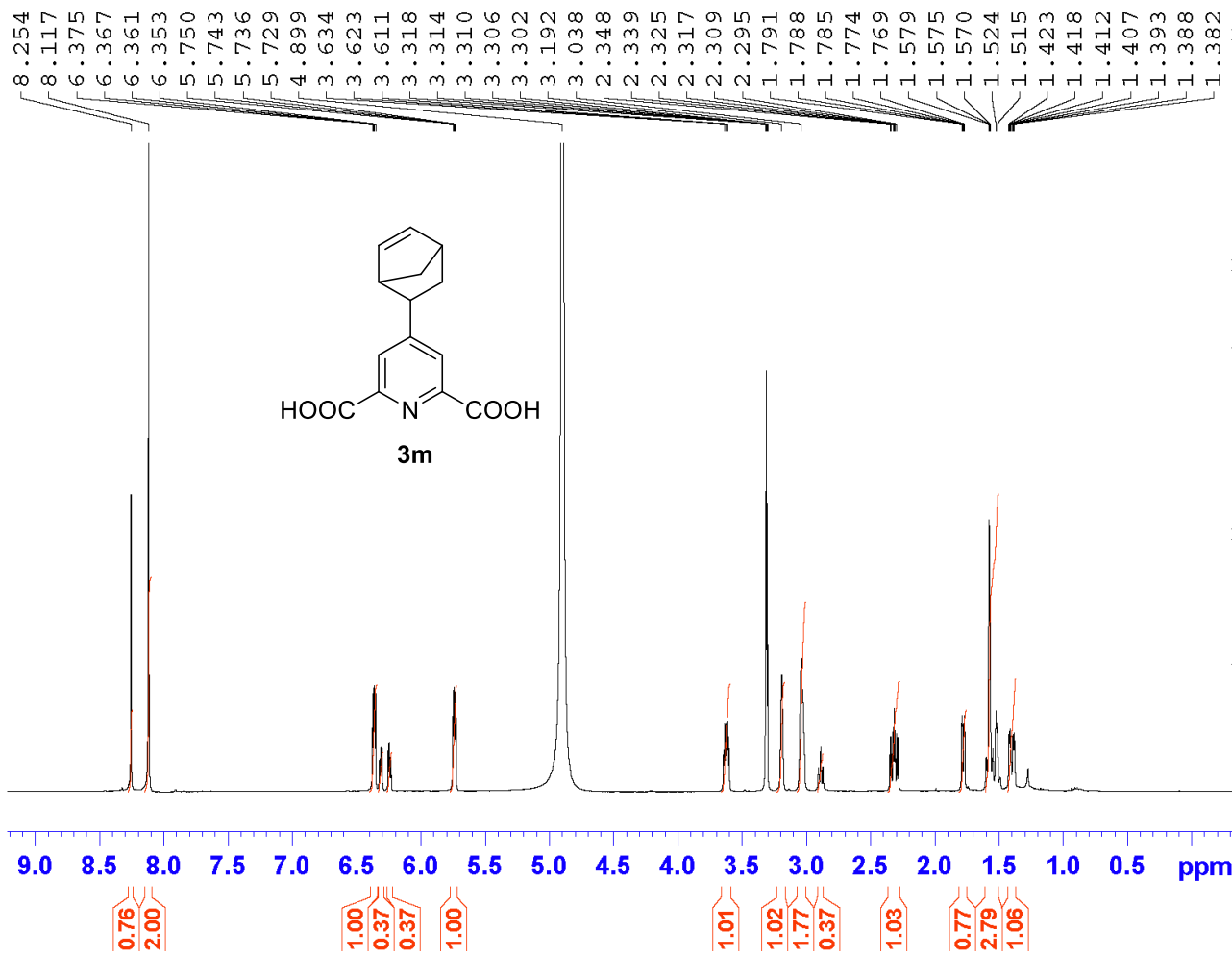
Current Data Parameters
 NAME Oct27-2014
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20141028
 Time_ 1.57
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT MeOD
 NS 2000
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631488 sec
 RG 195.88
 DW 20.800 usec
 DE 6.50 usec
 TE 299.2 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1

==== CHANNEL f1 =====
 SFO1 100.6228293 MHz
 NUC1 13C
 P1 10.00 usec
 PLW1 70.00000000 W

==== CHANNEL f2 =====
 SFO2 400.1316005 MHz
 NUC2 1H
 CPDPRG[2] waltz16
 PCPD2 80.00 usec
 PLW2 8.00000000 W
 PLW12 0.28125000 W
 PLW13 0.28125000 W

F2 - Processing parameters
 SI 32768
 SF 100.6126268 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40



```

Current Data Parameters
NAME          Jul08-2016
EXPNO         40
PROCNO        1

F2 - Acquisition Parameters
Date_         20160708
Time          14.57
INSTRUM       spect
PROBHD        5 mm PABBO BB/
PULPROG       zg30
TD            65536
SOLVENT       MeOD
NS            16
DS            2
SWH           8012.820 Hz
FIDRES        0.122266 Hz
AQ            4.0894465 sec
RG            31.13
DW            62.400 usec
DE            6.50 usec
TE            299.5 K
D1            1.00000000 sec
TD0           1

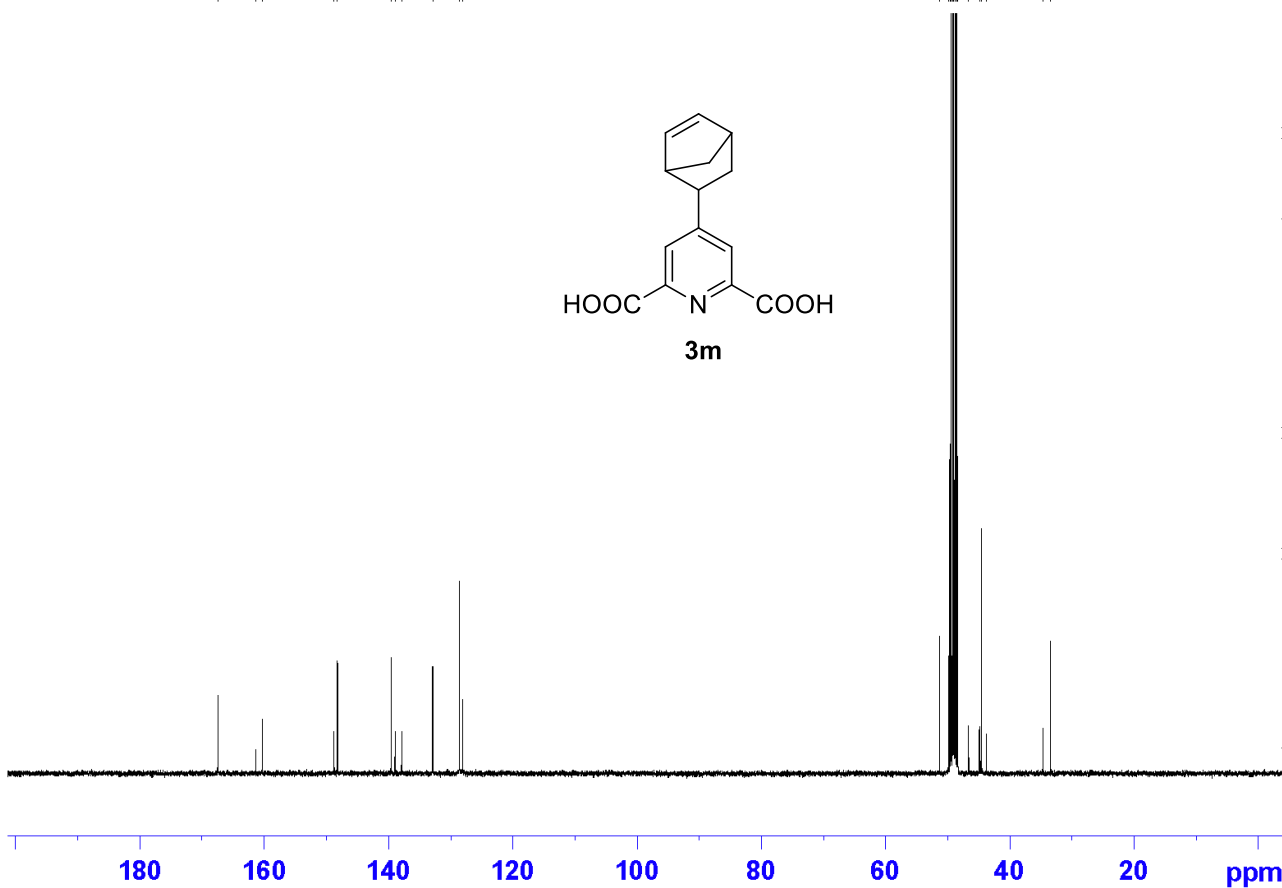
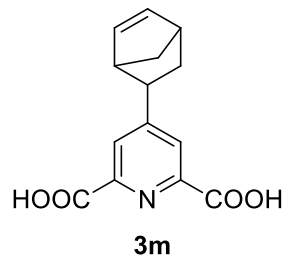
===== CHANNEL f1 =====
SFO1          400.1324710 MHz
NUC1          1H
P1            15.00 usec
PLW1          8.00000000 W

F2 - Processing parameters
SI            65536
SF            400.1300076 MHz
WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            1.00
  
```

167.46
167.43
161.39
160.32

148.75
148.20
139.58
138.94
137.88
132.88
128.60
128.09

51.30
49.86
49.64
49.43
49.21
49.00
48.79
48.58
48.36
46.61
44.87
44.59
43.79
34.68
33.43



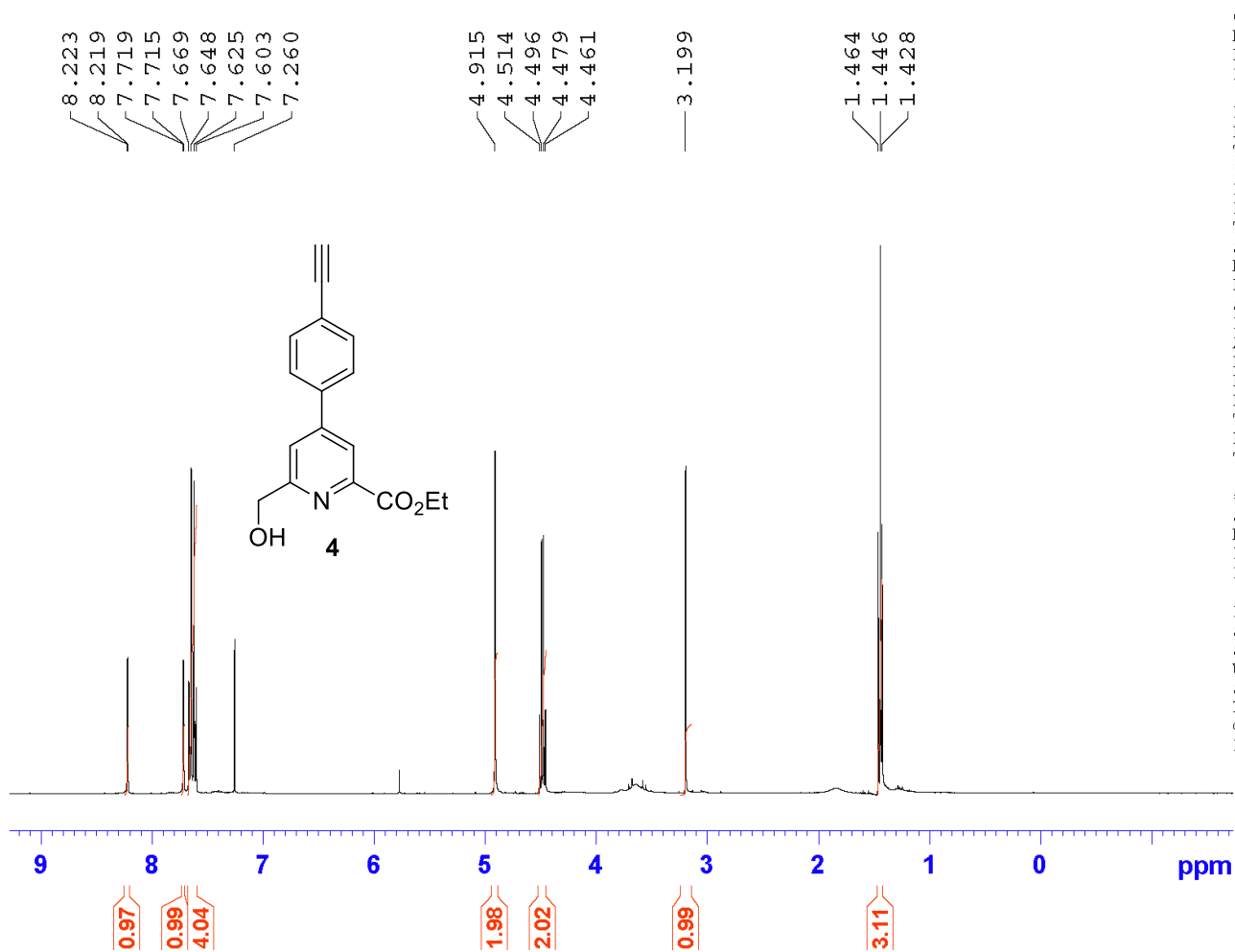
Current Data Parameters
NAME Jul08-2016
EXPNO 50
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160708
Time_ 16.01
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT MeOD
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 195.88
DW 20.800 usec
DE 6.50 usec
TE 300.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

==== CHANNEL f1 =====
SFO1 100.6228293 MHz
NUC1 13C
P1 10.00 usec
PLW1 70.00000000 W

==== CHANNEL f2 =====
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2] waltz16
PCPD2 80.00 usec
PLW2 8.00000000 W
PLW12 0.28125000 W
PLW13 0.28125000 W

F2 - Processing parameters
SI 32768
SF 100.6126297 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

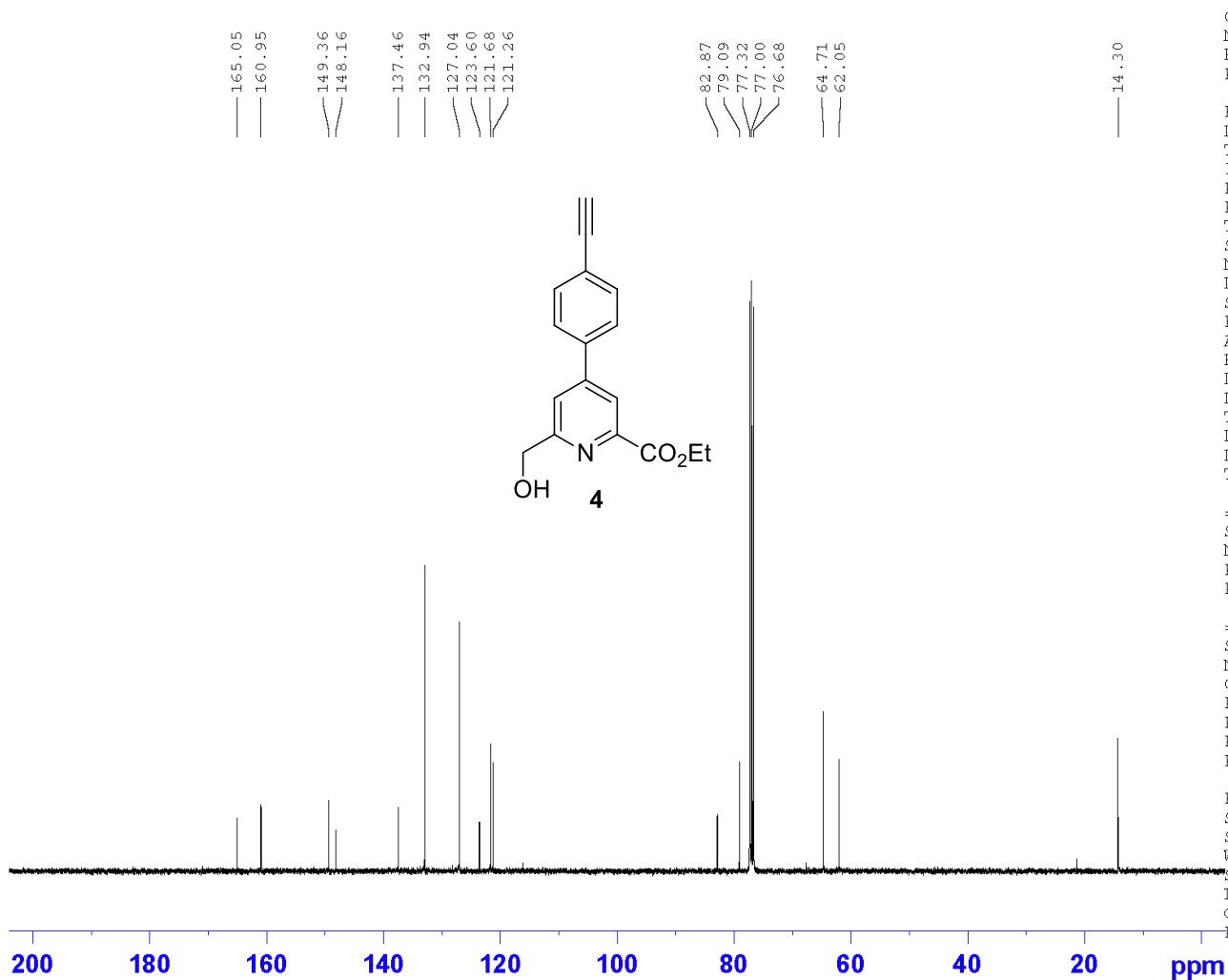


Current Data Parameters
 NAME Feb22-2016
 EXPNO 20
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20160222
 Time_ 16.35
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 8012.820 Hz
 FIDRES 0.122266 Hz
 AQ 4.0894465 sec
 RG 54.59
 DW 62.400 usec
 DE 6.50 usec
 TE 300.0 K
 D1 1.00000000 sec
 TD0 1

==== CHANNEL f1 =====
 SFO1 400.1324710 MHz
 NUC1 1H
 P1 15.00 usec
 PLW1 8.00000000 W

F2 - Processing parameters
 SI 65536
 SF 400.1300095 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



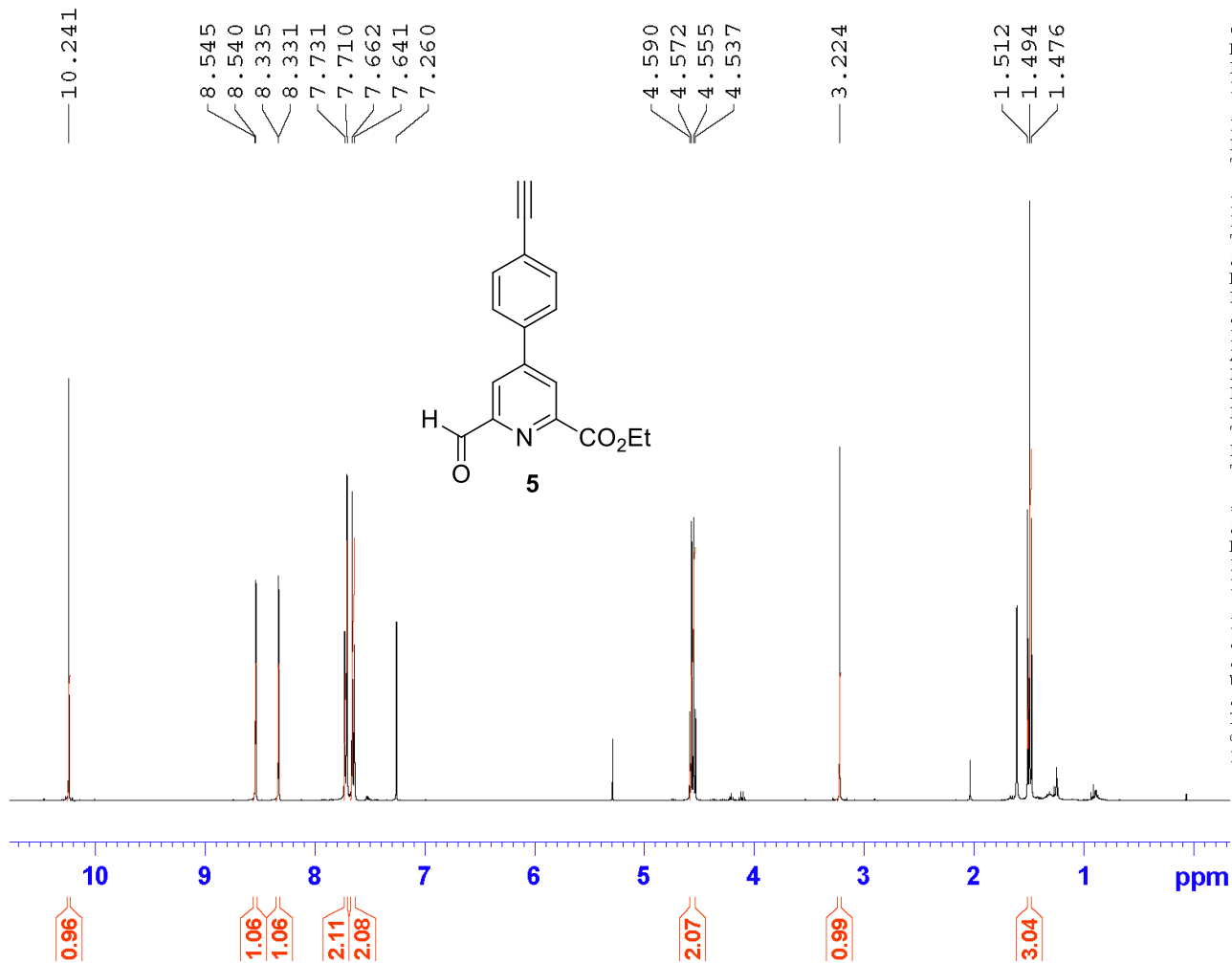
Current Data Parameters
 NAME Feb22-2016
 EXPNO 30
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20160222
 Time_ 17.36
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 1024
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631488 sec
 RG 195.88
 DW 20.800 usec
 DE 6.50 usec
 TE 301.8 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1

==== CHANNEL f1 =====
 SFO1 100.6228293 MHz
 NUC1 13C
 P1 10.00 usec
 PLW1 70.00000000 W

==== CHANNEL f2 =====
 SFO2 400.1316005 MHz
 NUC2 1H
 CPDPRG[2] waltz16
 PCPD2 80.00 usec
 PLW2 8.00000000 W
 PLW12 0.28125000 W
 PLW13 0.28125000 W

F2 - Processing parameters
 SI 32768
 SF 100.6127690 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

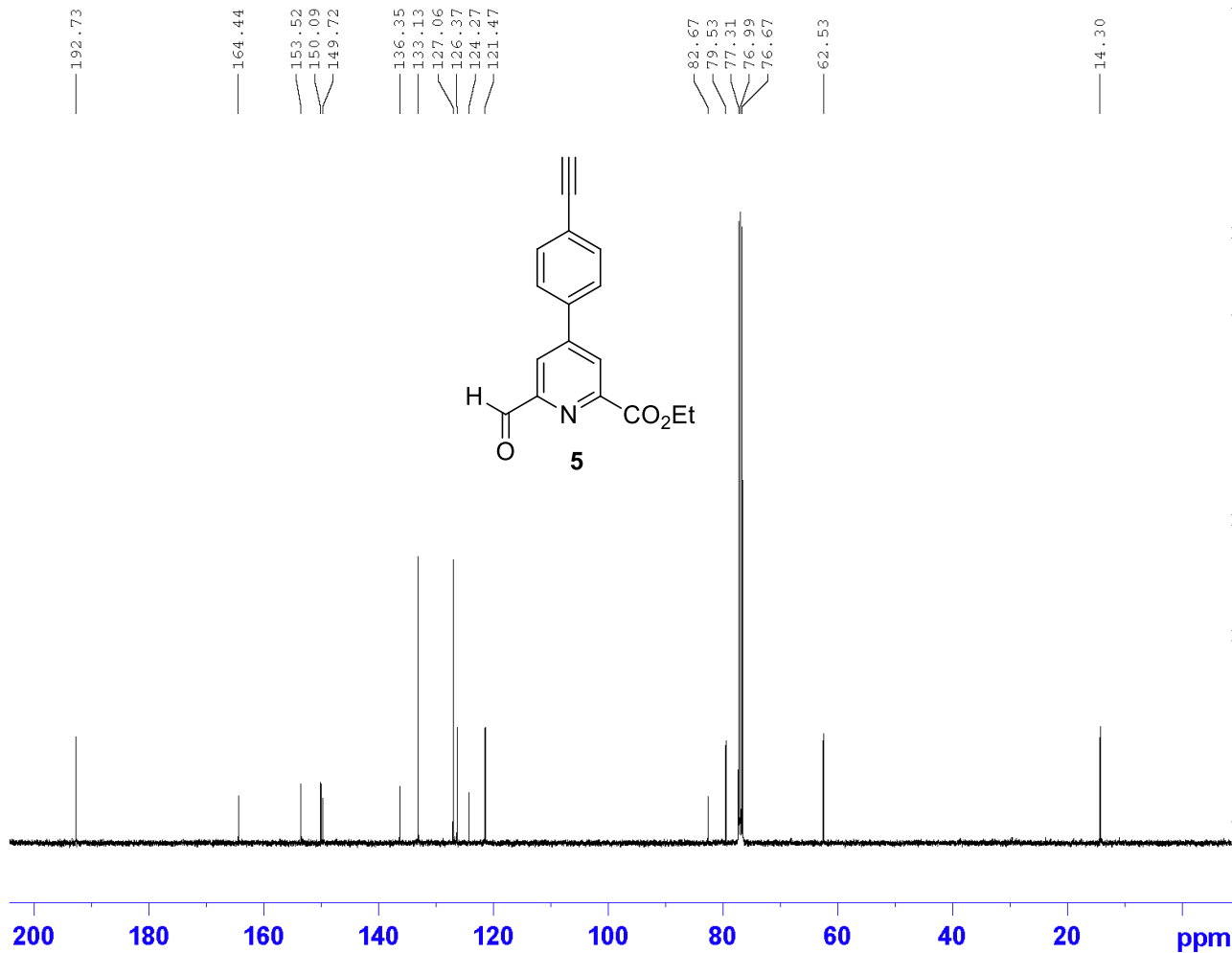


Current Data Parameters
 NAME Feb19-2016
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20160219
 Time_ 17.35
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 8012.820 Hz
 FIDRES 0.122266 Hz
 AQ 4.0894465 sec
 RG 62.88
 DW 62.400 usec
 DE 6.50 usec
 TE 300.3 K
 D1 1.00000000 sec
 TD0 1

==== CHANNEL f1 =====
 SFO1 400.1324710 MHz
 NUC1 1H
 P1 15.00 usec
 PLW1 8.00000000 W

F2 - Processing parameters
 SI 65536
 SF 400.1300094 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



Current Data Parameters
 NAME Feb19-2016
 EXPNO 20
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20160219
 Time 18.38
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 1030
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631488 sec
 RG 195.88
 DW 20.800 usec
 DE 6.50 usec
 TE 301.9 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1

==== CHANNEL f1 =====
 SFO1 100.6228293 MHz
 NUC1 13C
 P1 10.00 usec
 PLW1 70.00000000 W

==== CHANNEL f2 =====
 SFO2 400.1316005 MHz
 NUC2 1H
 CPDPRG[2] waltz16
 PCPD2 80.00 usec
 PLW2 8.00000000 W
 PLW12 0.28125000 W
 PLW13 0.28125000 W

F2 - Processing parameters
 SI 32768
 SF 100.6127690 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40