Supporting Information

Synthesis of Functionalized Pyrazoles via Vanadium-Catalyzed *C-N* Dehydrogenative Cross-Coupling and Fluorescence Switch-On Sensing of BSA Protein

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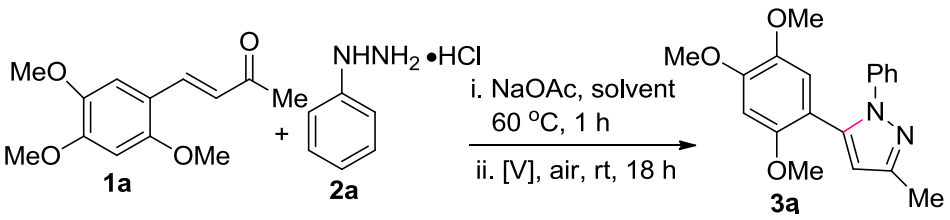
1. General information. Aryl amines and V_2O_5 (98%) of Aldrich, $VOSO_4$ (97%) and $VO(acac)_2$ (99%) of Otto and $SnCl_2 \cdot 2H_2O$ (97%) of Merck were used as received. Aryl hydrazines,[1a] *α,β*-unsaturated ketones[1b-c] and their corresponding hydrazones[1d] were prepared according to literature procedure. Analytical TLC was performed on Merck silica gel G/GF 254 plates for progress of the reaction. NMR (^1H and ^{13}C) spectra were recorded on DRX-400 Varian spectrometer, Bruker Avance III 600, and Bruker Ultrashield^{TM} 300 using $CDCl_3$ as a solvent and Me_4Si as an internal standard. Chemical shifts (δ) are reported in ppm for all ^1H NMR and ^{13}CNMR spectra and other data are reported as follows: s = singlet, d = doublet, m = multiplet and *J* = spin-spin coupling constant (Hz). Melting points were determined with a Büchi B-540 apparatus and are uncorrected. Perkin Elmer IR spectrometer was used for recording FT-IR spectra. Mass spectra were recorded on a Q-Tof ESI-MS instrument (model HAB 273). Single crystal X-ray data were collected using Bruker SMART APEX-II CCD diffractometer, which is equipped with 1.75 kW sealed-tube Mo-Kα irradiation (λ = 0.71073 Å) at 298(2) K. The crystal structure was solved by direct method using *SHELXL-97* (Göttingen, Germany) and refined with full-matrix least squares on F^2 using SHELXL-97.

2.1. General procedure for the synthesis of pyrazoles 3a-p. *α,β*-Unsaturated ketones **1a-p** (1 mmol) and aryl hydrazines **2a** (1.2 mmol) were stirred with NaOAc (2.9 mmol) in toluene: H_2O (1:1, 3 mL) at 60 ^oC for 1 h under air. The reaction mixture was cooled at room temperature and then treated with $VOSO_4$ (5 mol %). The resultant reaction mixture was stirred at room temperature under air. The progress of the reaction was monitored by TLC. After completion, toluene layer was separated and the aqueous solution was extracted with EtOAc (3 x 5 mL). The combined organic solution was washed with brine (1 x 10 mL) and water (1 x 10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using hexane and ethyl acetate as eluent.

2.2. **General procedure for the synthesis of pyrazoles 3q-z.** *α,β*-Unsaturated ketones **1** (1 mmol), and aryl hydrazines **2b-f** (1.2 mmol) were stirred in toluene (1.5 mL) at 60 ^oC for 1 h under air. The reaction mixture was cooled at room temperature and then treated with solution of $VOSO_4$ (5 mol %) in H_2O (1.5 mL). The resultant reaction mixture was stirred at room temperature under air. The progress of the reaction was monitored by TLC. The work up and purification of the pyrazoles were performed as described in 2.1.

Table 1. Optimization of the Reaction Conditions[a]



entry	[V] (mol %)	solvent	yield (%)[b,c]
1	$VOSO_4$ (20)	H_2O-toluene (1:1)	70
2	$VO(acac)_2$ (20)	H_2O-toluene (1:1)	55
3	V_2O_5 (20)	H_2O-toluene (1:1)	54
4	$VOSO_4$ (10)	H_2O-toluene (1:1)	72
5	$VOSO_4$ (5)	H_2O-toluene (1:1)	73
6	$VOSO_4$ (5)	H_2O-toluene (1:1)	trace[d]
7	-	H_2O-toluene (1:1)	n.o.

[a]Reaction Conditions: **1a** (1.0 mmol), **2a** (1.2 mmol), NaOAc (2.9 mmol), toluene : H_2O (1:1, 3 mL), 60 °C, 1 h; [V], rt, 18 h, air. [b]Isolated yield. [c]Accompanied ~10% unreacted **1a** and **2a**. [d]N_2 used. n. o = not observed.

3. Crystal Data and Structure Refinement for 3a at 298(2) K

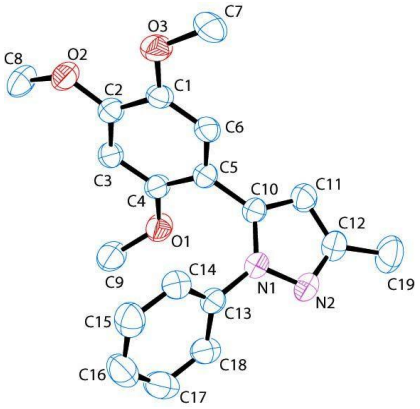
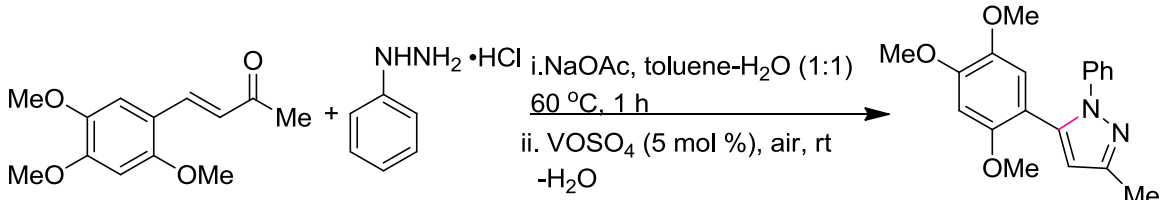


Figure1. ORTEP diagram of 3-Methyl-1-phenyl-5-(2,4,5-trimethoxyphenyl)-1*H*-pyrazole **3a** with 50% ellipsoid. H-Atoms are omitted for clarity (CCDC 949193).

Identification code	**3a**
Empirical formula	$C_{19}H_{20}N_2O_3$
Formula weight	324.37
Temperature	298(2)
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21/c
	Loop xyz
	'x, y, z'
	'-x, y+1/2, -z+1/2'
	'-x, -y, -z'
	'x, -y-1/2, z-1/2'
Unit cell dimensions	*a* = 12.4342(7)Å α(°) = 90.00
	b = 16.3750(11)Å β(°) = 106.914(4)
	c = 8.6369(5)Å γ(°) = 90.00
Volume	1682.49(18) $Å^3$
Z	4
Density (calculated)	1.281Mg/m^3
Absorption coefficient	0.087mm^{-1}
F(000)	688.0
Crystal size	0.24 x 0.22 x 0.21 mm
Theta range for data collection	2.49 to 25.40 °
Index ranges	-16<=h<=16, -22<=k<=22, -11<=l<=11
Reflections collected	4492
Independent reflections	3982 [R (int) = 0.0499]
Completeness to theta = 29.07°	99.7 %
Absorption correction	Multi-scan
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4492/ 0 /221
Goodness-of-fit on F^2	1.042
Final R indices [I>2sigma (I)]	*R1* = 0.0563, *wR2* = 0.1581
R indices (all data)	*R1* = 0.0906, *wR2* = 0.1899

4. Scheme S1. Gram Scale Synthesis

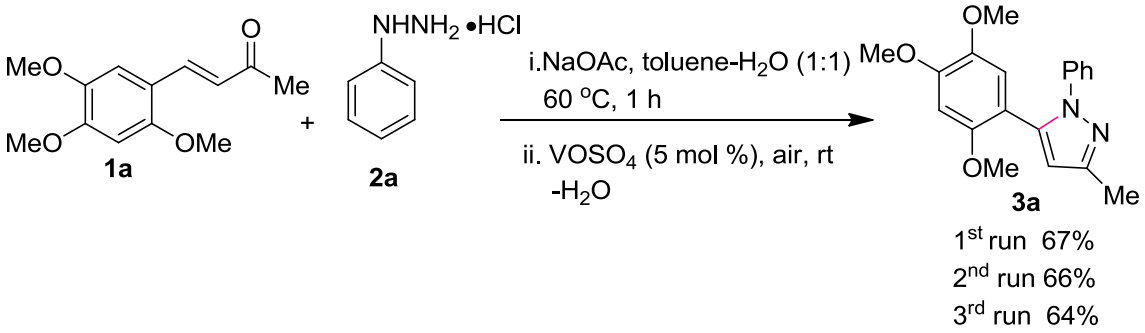


1a 4.23 mmol, 1g

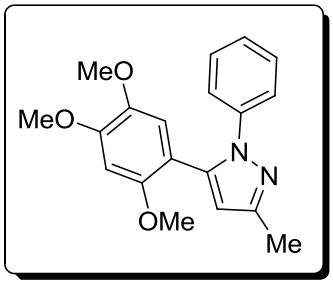
2a 5.07 mmol, 731 mg

3a 892 mg, 65%

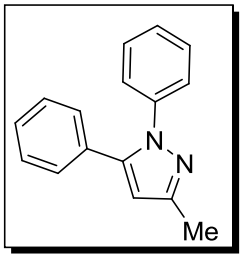
5. Scheme S2. Recyclability Experiments



6. **Characterization data**

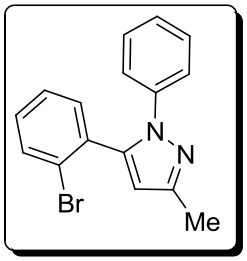


3-Methyl-1-phenyl-5-(2,4,5-trimethoxyphenyl)-1*H*-pyrazole 3a. *α,β*-Unsaturated ketone **1a** (236 mg, 1 mmol), phenylhydrazine hydrochloride **2a** (172 mg, 1.2 mmol) and NaOAc (237 mg, 2.9 mmol) were stirred at 60 °C for 1 h in toluene: H_2O (1:1, 3 mL) under air. The reaction mixture was then cooled to room temperature, treated with $VOSO_4$ (8 mg, 5 mol %) and stirred for 17 h under air. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.44; purification (1:9 ethyl acetate/hexane); white solid. Yield 73% (236 mg); mp 142-143 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28-7.19 (m, 5H), 6.73 (s, 1H), 6.42 (s, 1H), 6.27 (s, 1H), 3.89 (s, 3H), 3.73 (s, 3H), 3.37 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 150.2, 149.1, 142.9, 141.1, 140.1, 128.5, 126.5, 123.7, 114.4, 111.3, 108.4, 97.6, 56.4, 56.0, 55.8, 13.7; FT-IR (KBr) 2999, 2961, 2935, 2837, 1613, 1596, 1502, 1474, 1454, 1438, 1383, 1361, 1277, 1260, 1213, 1192, 1140, 1020, 856, 809, 762, 692 cm^{-1}; HRMS (APCI) *m/z* $[M+H]^+$ calcd for $C_{19}H_{20}N_2O_3$: 325.1547, found: 325.1551.

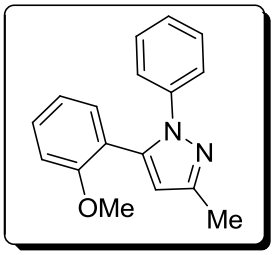


3-Methyl-1,5-diphenyl-1*H*-pyrazole 3b.[2] (E)-4-Phenylbut-3-en-2-one **1b** (146 mg, 1 mmol), phenylhydrazine hydrochloride **2a** (172 mg, 1.2 mmol) and NaOAc (237 mg, 2.9 mmol) were stirred at 60 °C for 1 h in toluene: H_2O (1:1, 3 mL) under air. The reaction mixture was then cooled to room

temperature, treated with $VOSO_4$ (8 mg, 5 mol %) and stirred for 17 h under air. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.41; purification (1:19 ethyl acetate/hexane); yellow liquid. Yield 48% (112 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.20 (m, 10H), 6.31 (s, 1H), 2.39 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.6, 143.8, 140.3, 130.8, 128.9, 128.7, 128.5, 128.2, 127.2, 125.2, 107.8, 13.7; FT-IR (neat) 3060, 2925, 1950, 1669, 1596, 1553, 1504, 1455, 1439, 1417, 1377, 1364, 1195, 1072, 1013, 969, 695 cm^{-1}; HRMS (APCI) *m/z* $[M+H]^+$ calcd for $C_{16}H_{14}N_2$: 235.1230, found: 235.1232.

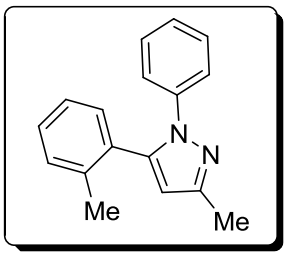


5-(2-Bromophenyl)-3-methyl-1-phenyl-1*H*-pyrazole 3c. *(E)*-4-(2-Bromophenyl)but-3-en-2-one **1c** (223 mg, 1 mmol), phenylhydrazine hydrochloride **2a** (172 mg, 1.2 mmol) and NaOAc (237 mg, 2.9 mmol) were stirred at 60 ^{o}C for 1 h in toluene: H_2O (1:1, 3 mL) under air. The reaction mixture was the cooled to room temperature, treated with $VOSO_4$ (8 mg, 5 mol %) and stirred for 20 h under air. Analytical TLC on silica gel, 1:6 ethyl acetate/hexane R_f = 0.63; purification (1:19 ethyl acetate/hexane); yellow solid. Yield 45% (140 mg); mp 73-74 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.4 Hz, 1H), 7.27-7.19 (m, 8H), 6.30 (s, 1H), 2.42 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.3, 142.0, 140.2, 133.3, 132.9, 132.3, 130.3, 128.9, 127.4, 126.9, 124.2, 124.1, 109.4, 13.8; FT-IR (KBr) 3052, 2961, 2924, 2859, 1598, 1548, 1502, 1430, 1362, 1377, 1261, 1194, 1098, 1026, 970, 783, 756, 689 cm^{-1}; HRMS (APCI) *m/z* $[M+H]^+$ calcd for $C_{16}H_{13}BrN_2$: 313.0335, found: 313.0335.

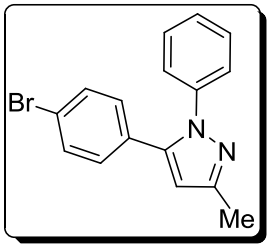


5-(2-Methoxyphenyl)-3-methyl-1-phenyl-1*H*-pyrazole 3d. *(E)*-4-(2-Methoxyphenyl)but-3-en-2-one **1d** (176 mg, 1 mmol), phenylhydrazine hydrochloride **2a** (172 mg, 1.2 mmol) and NaOAc (237 mg, 2.9 mmol) at 60 ^{o}C for 1 h in toluene: H_2O (1:1, 3 mL) under air. The reaction mixture was then cooled to room temperature, treated with $VOSO_4$ (8 mg, 5 mol %) and stirred 18 h under air. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.53; purification (1:19 ethyl acetate/hexane); yellow liquid. Yield 66% (174 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.2 Hz, 1H), 7.27-7.23 (m, 5H), 7.18-7.16 (m,

1H), 6.96 (t, *J* = 7.8 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 6.27 (s, 1H), 3.37 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.6, 149.3, 141.3, 140.5, 131.3, 130.4, 128.6, 126.6, 123.6, 120.8, 120.5, 111.4, 108.8, 55.1, 13.8; FT-IR (neat) 3052, 2927, 2854, 2837, 1739, 1667, 1600, 1581, 1552, 1504, 1494, 1463, 1377, 1363, 1296, 1264, 1248, 1116, 1026, 970, 757 cm^{-1}; HRMS (APCI) *m/z* $[M+H]^+$ calcd for $C_{17}H_{16}N_2O$: 265.1335, found: 265.1336.

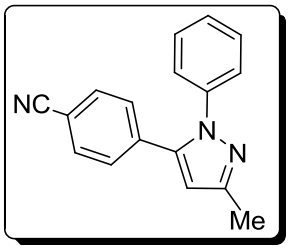


3-Methyl-1-phenyl-5-*o*-tolyl-1*H*-pyrazole 3e.[3] *(E)*-4-(2-Methylphenyl)but-3-en-2-one **1e** (160 mg, 1 mmol), phenylhydrazine hydrochloride **2a** (172 mg, 1.2 mmol) and NaOAc (237 mg, 2.9 mmol) were stirred at 60 °C for 1 h in toluene: H_2O (1:1, 3 mL) under air. The reaction mixture was cooled to room temperature, treated with $VOSO_4$ (8 mg, 5 mol %) and stirred for 18 h under air. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.73; purification (1:19 ethyl acetate/hexane); yellow liquid. Yield 53% (131 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22-7.15 (m, 9H), 6.19 (s, 1H), 2.40 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.4, 143.1, 140.5, 137.2, 131.3, 130.7, 130.5, 128.99, 128.90, 126.6, 125.9, 123.6, 108.9, 20.1, 13.8; FT-IR (neat) 3060, 2924, 2859, 1670, 1598, 1552, 1502, 1458, 1416, 1362, 1259, 1175, 1072, 1027, 968, 907, 762, 725 cm^{-1}; HRMS (APCI) *m/z* $[M+H]^+$ calcd for $C_{17}H_{16}N_2$: 249.1386, found: 249.1386.

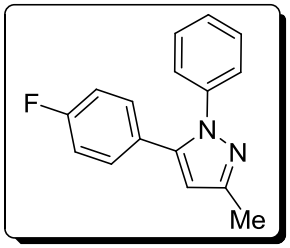


5-(4-Bromophenyl)-3-methyl-1-phenyl-1*H*-pyrazole 3f.[4] *(E)*-4-(4-Bromophenyl)but-3-en-2-one **1f** (225 mg, 1 mmol), phenylhydrazine hydrochloride **2a** (172 mg, 1.2 mmol) and NaOAc (237 mg, 2.9 mmol) were stirred at 60 °C for 1 h in toluene: H_2O (1:1, 3 mL) under air. The reaction mixture was then cooled to room temperature, treated with $VOSO_4$ (8 mg, 5 mol %) and stirred for 17 h under air. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.58; purification (1:19 ethyl acetate/hexane); yellow solid. Yield 41% (128 mg); mp 74-75 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.8 Hz, 2H), 7.33 (t, *J* =

7.2 Hz, 2H), 7.30 (d, *J* = 6.6 Hz, 1H), 7.26-7.24 (m, 2H), 7.08 (d, *J* = 7.8 Hz, 2H), 6.31 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.8, 142.6, 140.0, 132.4, 131.8, 130.3, 129.2, 127.5, 125.3, 122.5, 108.3, 13.7; FT-IR (KBr) 2925, 1625, 1503, 1487, 1260, 1072, 1010, 968, 811, 767, 693 cm^{-1}; HRMS (APCI) *m/z* $[M+H]^+$ calcd for $C_{16}H_{13}BrN_2$: 313.0335, found: 313.0335.

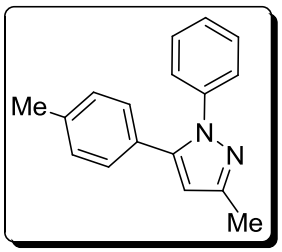


4-(3-Methyl-1-phenyl-1*H*-pyrazol-5-yl)benzonitrile 3g.[4] *(E)*-4-(4-Cyanophenyl)but-3-en-2-one **1g** (171 mg, 1 mmol), phenylhydrazine hydrochloride **2a** (172 mg, 1.2 mmol) and NaOAc (237 mg, 2.9 mmol) were stirred at 60 °C for 1 h in toluene: H_2O (1:1, 3 mL) under air. The reaction mixture was then cooled to room temperature, treated with $VOSO_4$ (8 mg, 5 mol %) and stirred for 24 h under air. Analytical TLC on silica gel, 1:6 ethyl acetate/hexane R_f = 0.55; purification (1:19 ethyl acetate/hexane); yellow liquid. Yield 38% (98 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.8 Hz, 2H), 7.35-7.29 (m, 5H), 7.24 (d, *J* = 7.2 Hz, 2H), 6.39 (s, 1H), 2.39 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.0, 141.8, 139.7, 135.2, 132.4, 129.4, 129.1, 128.0, 125.4, 118.6, 111.8, 108.8, 13.6; FT-IR (neat) 3061, 2661, 2625, 2854, 2227, 1717, 1679, 1597, 1562, 1459, 1429, 1363, 1504, 1260, 1177, 1073, 1014, 970, 844, 799, 763, 695 cm^{-1}; HRMS (APCI) *m/z* $[M+H]^+$ calcd for $C_{17}H_{13}N_3$: 260.1182, found: 260.1182.

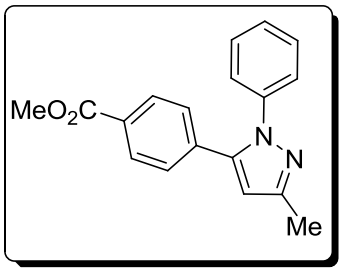


5-(4-Fluorophenyl)-3-methyl-1-phenyl-1*H*-pyrazole 3h.[1c] *(E)*-4-(4-Fluorophenyl)but-3-en-2-one **1h** (164 mg, 1 mmol), phenylhydrazine hydrochloride **2a** (172 mg, 1.2 mmol) and NaOAc (237 mg, 2.9 mmol) were stirred at 60 °C for 1 h in toluene: H_2O (1:1, 3 mL) under air. The reaction mixture was then cooled to room temperature, $VOSO_4$ (8 mg, 5 mol %) and stirred for 24 h under air. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.53; purification (1:19 ethyl acetate/hexane); yellow liquid. Yield 39% (98 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.8 Hz, 2H), 7.28-7.24 (m, 3H), 7.19-7.17 (m, 2H), 6.98 (t, *J* = 8.4 Hz, 2H), 6.28 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.5 (J_{C-F} = 246

Hz), 149.6, 142.8, 140.1, 130.6 ($J_{C\text{-}F}$ = 7.5 Hz), 129.1, 127.4, 127.0, 125.3, 115.7 ($J_{C\text{-}F}$ = 21.0 Hz), 107.9, 13.7; FT-IR (neat) 2924, 2850, 2351, 2073, 1636, 1508, 1427, 1383, 1362, 1225, 1158, 1014, 969, 838, 693 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{16}H_{13}FN_2$: 253.1136, found: 253.1137.

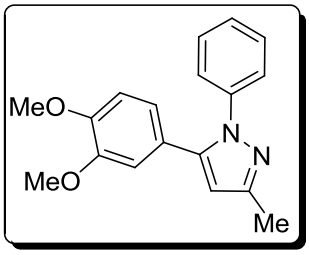


3-Methyl-1-phenyl-5-*p*-tolyl-1*H*-pyrazole 3i.[4] *(E)*-4-(4-Methylphenyl)but-3-en-2-one **1i** (160 mg, 1 mmol), phenylhydrazine hydrochloride **2a** (172 mg, 1.2 mmol) and NaOAc (237 mg, 2.9 mmol) were stirred at 60 ^oC for 1 h in toluene: H_2O (1:1, 3 mL) under air. The reaction mixture was then cooled to room temperature, treated with $VOSO_4$ (8 mg, 5 mol %) and 19 h under air. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.56; purification (1:19 ethyl acetate/hexane); yellow liquid. Yield 62% (153 mg); ^1H NMR (600 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.2 Hz, 2H), 7.27 (d, *J* = 7.2 Hz, 2H), 7.11-7.08 (m, 5H), 6.27 (s, 1H), 2.37 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.6, 143.9, 140.4, 138.2, 129.3, 129.0, 128.7, 128.0, 127.2, 125.3, 107.7, 21.4, 13.8; FT-IR (neat) 3001, 2957, 2925, 2856, 2836, 1666, 1604, 1517, 1462, 1443, 1377, 1366, 1298, 1249, 1181, 1105, 1033, 971, 833 cm^{-1}; HRMS (APCI) *m/z* $[M+H]^+$ calcd for $C_{17}H_{16}N_2$: 249.1386, found: 249.1388.

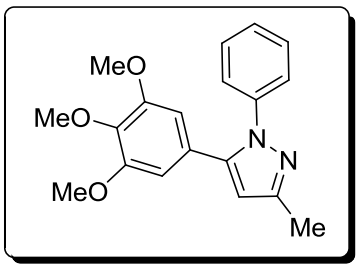


Methyl 4-(3-methyl-1-phenyl-1*H*-pyrazol-5-yl)benzoate 3j. *(E)*-Methyl 4-(3-oxobut-1-en-1-yl)benzoate **1j** (204 mg, 1 mmol), phenylhydrazine hydrochloride **2a** (172 mg, 1.2 mmol) and NaOAc (237 mg, 2.9 mmol) were stirred at 60 ^oC for 1 h in toluene: H_2O (1:1, 3 mL) under air. The reaction mixture was cooled to room temperature, treated with $VOSO_4$ (8 mg, 5 mol %) and stirred for 19 h under air. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.60; purification (1:19 ethyl acetate/hexane); yellow liquid. Yield 66% (192 mg); ^1H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 6.6 Hz, 2H), 7.30-7.24 (m, 5H), 6.38 (s, 1H), 3.90 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.8, 149.9, 142.7, 140.0, 135.2, 129.8, 129.6, 129.2, 128.6, 127.6, 125.4, 108.5, 52.4,

13.7; FT-IR (neat) 3061, 2951, 2845, 1722, 1611, 1596, 1570, 1509, 1500, 1459, 1434, 1364, 1311, 1278, 1181, 1112, 1018, 970, 860, 827, 771, 695 cm^{-1}; HRMS (APCI) *m/z* $[M+H]^+$ calcd for $C_{18}H_{16}N_2O_2$: 293.1285, found: 293.1285.

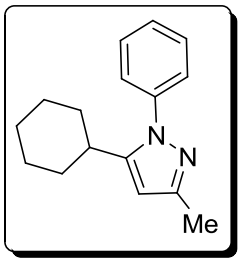


5-(3,4-Dimethoxyphenyl)-3-methyl-1-phenyl-1*H*-pyrazole 3k.[4] (*E*)-4-(3,4-Dimethoxyphenyl)but-3-en-2-one **1k** (206 mg, 1 mmol), phenylhydrazine hydrochloride **2a** (172 mg, 1.2 mmol) and NaOAc (237 mg, 2.9 mmol) were stirred at 60 °C for 1 h in toluene: H_2O (1:1, 3 mL) under air. The reaction mixture was cooled to room temperature, treated with $VOSO_4$ (8 mg, 5 mol %) and stirred for 19 h under air. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.47; purification (1:9 ethyl acetate/hexane); yellow liquid. Yield 59% (173 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33-7.28 (m, 5H), 6.84 (d, *J* = 8.4 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.63 (s, 1H), 6.28 (s, 1H), 3.87 (s, 3H), 3.62 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.5, 149.1, 148.7, 143.8, 140.4, 129.0, 127.3, 125.5, 123.5, 121.4, 112.0, 111.1, 107.2, 56.0, 55.8, 13.7; FT-IR (neat) 3062, 2999, 2932, 2835, 1597, 1553, 1513, 1500, 1463, 1436, 1362, 1254, 1235, 1164, 1136, 1073, 1026, 860, 807, 764, 696 cm^{-1}; HRMS (APCI) *m/z* $[M+H]^+$ calcd for $C_{18}H_{18}N_2O_2$: 295.1441, found: 295.1445.

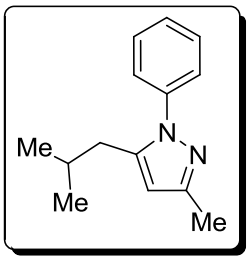


3-Methyl-1-phenyl-5-(3,4,5-trimethoxyphenyl)-1*H*-pyrazole 3l. (*E*)-4-(3,4,5-Trimethoxyphenyl)but-3-en-2-one **1l** (236 mg, 1 mmol), phenylhydrazine hydrochloride **2a** (172 mg, 1.2 mmol) and NaOAc (237 mg, 2.9 mmol) were stirred at 60 °C for 1 h in toluene: H_2O (1:1, 3 mL) under air. The reaction mixture was cooled to room temperature, treated with $VOSO_4$ (8 mg, 5 mol %) and stirred for 17 h under air. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.52; purification (1:15 ethyl acetate/hexane); yellow liquid. Yield 68% (220 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35-7.33 (m, 2H), 7.30-7.28 (m, 3H), 6.39 (s, 2H), 6.31 (s, 1H), 3.84 (s, 3H), 3.64 (s, 6H), 2.38 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.2, 149.6, 143.8, 140.4, 138.1, 129.0, 127.4, 126.1, 125.6, 107.3, 106.1, 61.1, 56.5, 56.1, 13.7; FT-IR (neat)

2935, 2834, 1691, 1585, 1551, 1500, 1462, 1426, 1362, 1322, 1239, 1126, 1007, 722, 696 cm^{-1}; HRMS (APCI) *m/z* $[M+H]^+$ calcd for $C_{19}H_{20}N_2O_3$: 325.1547 $[M+H]^+$, found: 325.1547.

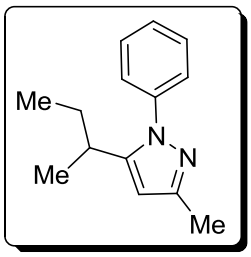


5-Cyclohexyl-3-methyl-1-phenyl-1*H*-pyrazole 3m.[4] (*E*)-4-Cyclohexylbut-3-en-2-one **1m** (152 mg, 1 mmol), phenylhydrazine hydrochloride **2a** (172 mg, 1.2 mmol) and NaOAc (237 mg, 2.9 mmol) were stirred at 60 °C for 1 h in toluene: H_2O (1:1, 3 mL) under air. The reaction mixture was cooled to room temperature, treated with $VOSO_4$ (8 mg, 5 mol %) and stirred for 17 h under air. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.54; purification (1:19 ethyl acetate/hexane); yellow liquid. Yield 62% (148 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44-7.43 (m, 4H), 7.34-7.32 (m, 1H), 6.01 (s, 1H), 2.69-2.65 (m, 1H), 2.31 (s, 3H), 2.01-1.99 (m, 2H), 1.82-1.80 (m, 2H), 1.73-1.70 (m, 1H), 1.47-1.35 (m, 5H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.8, 140.2, 139.1, 129.1, 127.3, 124.9, 104.2, 37.8, 33.5, 26.6, 26.3, 12.7; FT-IR (neat) 2925, 2851, 1727, 1599, 1553, 1504, 1447, 1380, 1261, 1072, 1016, 758, 695 cm^{-1}; HRMS (APCI) *m/z* $[M+H]^+$ calcd for $C_{16}H_{20}N_2$: 241.1699, found: 241.1699.

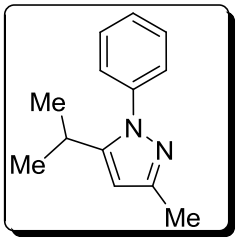


5-Isobutyl-3-methyl-1-phenyl-1*H*-pyrazole 3n.[4] (*E*)-4-Isobutylbut-3-en-2-one **1n** (126 mg, 1 mmol), phenylhydrazine hydrochloride **2a** (172 mg, 1.2 mmol) and NaOAc (237 mg, 2.9 mmol) were stirred at 60 °C for 1 h in toluene: H_2O (1:1, 3 mL) under air. The reaction mixture was cooled to room temperature, treated with $VOSO_4$ (8 mg, 5 mol %) and stirred stirred for 19 h under air. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.62; purification (1:19 ethyl acetate/hexane); yellow liquid. Yield 54% (115 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44-7.43 (m, 4H), 7.34-7.33 (m, 1H), 5.99 (s, 1H), 2.51 (d, *J* = 7.2 Hz, 2H), 2.31 (s, 3H), 1.97-1.93 (m, 1H), 0.97 (s, 3H), 0.96 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.0, 140.2, 139.2, 129.1, 127.3, 124.9, 106.7, 37.6, 29.1, 22.7, 12.7; FT-IR (neat) 3064, 2955, 2926,

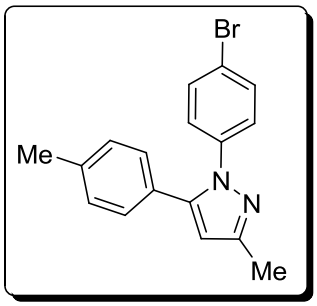
2868, 1730, 1599, 1554, 1503, 1461, 1381, 1261, 1168, 1133, 1018, 759 cm^{-1}; HRMS (APCI) *m/z* $[M+H]^+$ calcd for $C_{14}H_{18}N_2$: 215.1543, found: 215.1542.



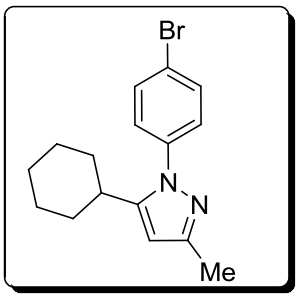
5-Sec-butyl-3-methyl-1-phenyl-1*H*-pyrazole 3o. (*E*)-4-Secbutylbut-3-en-2-one **1o** (126 mg, 1 mmol), phenylhydrazine hydrochloride **2a** (172 mg, 1.2 mmol) and NaOAc (237 mg, 2.9 mmol) were stirred at 60 ^oC for 1 h in toluene: H_2O (1:1, 3 mL) under air. The reaction mixture was cooled to room temperature, treated with $VOSO_4$ (8 mg, 5 mol %) and stirred for 19 h under air. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.41; purification (1:19 ethyl acetate/hexane); yellow liquid. Yield 58% (124 mg); ^1H NMR (600 MHz, $CDCl_3$) δ 7.46-7.43 (m, 2H), 7.39-7.36 (m, 3H), 5.98 (s, 1H), 2.76-2.72 (m, 1H), 2.31 (s, 3H), 1.58-1.54 (m, 1H), 1.50-1.47 (m, 1H), 1.17 (d, *J* = 7.2 Hz, 3H), 0.78 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.5, 149.1, 140.2, 129.2, 128.0, 126.4, 103.0, 32.4, 30.5, 21.1, 13.8, 12.0; FT-IR (neat) 3064, 2964, 2929, 2874, 1720, 1598, 1546, 1503, 1455, 1381, 1262, 1104, 1072, 1020, 767 cm^{-1}; HRMS (APCI) *m/z* $[M+H]^+$ calcd for $C_{14}H_{18}N_2$: 215.1543, found: 215.1543.



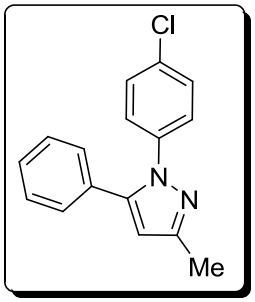
5-Isopropyl-3-methyl-1-phenyl-1*H*-pyrazole 3p.[4] (*E*)-4-Isopropylbut-3-en-2-one **1p** (112 mg, 1 mmol), phenylhydrazine hydrochloride **2a** (172 mg, 1.2 mmol) and NaOAc (237 mg, 2.9 mmol) were stirred at 60 ^oC for 1 h in toluene: H_2O (1:1, 3 mL) under air. The reaction mixture was cooled to room temperature, treated with $VOSO_4$ (8 mg, 5 mol %) and stirred for 18 h under air. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.59; purification (1:19 ethyl acetate/hexane); yellow liquid. Yield 64% (128 mg); ^1H NMR (600 MHz, $CDCl_3$) δ 7.44-7.43 (m, 4H), 7.33-7.32 (m, 1H), 6.03 (s, 1H), 3.04-2.99 (m, 1H), 2.31 (s, 3H), 1.29 (s, 3H), 1.28 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.7, 140.2, 139.2, 129.1, 127.3, 125.0, 103.9, 28.0, 23.1, 12.7; FT-IR (neat) 3064, 2962, 2928, 2869, 1725, 1599, 1552, 1504, 1457, 1380, 1300, 1130, 1071, 1016, 766 cm^{-1}; HRMS (APCI) *m/z* $[M+H]^+$ calcd for $C_{13}H_{16}N_2$: 201.1386, found: 201.1386.



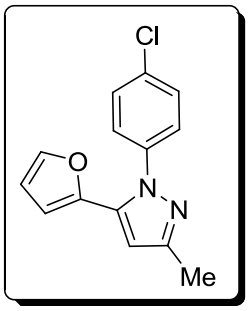
1-(4-Bromophenyl)-3-methyl-5-*p*-tolyl-1*H*-pyrazole 3q. *(E)*-4-(4-Methylphenyl)but-3-en-2-one **1i** (160 mg, 1 mmol) and (4-bromophenyl)hydrazine **2b** (224 mg, 1.2 mmol) were stirred 60 ^{o}C for 1 h in toluene (1.5 mL) at under air. The reaction mixture was cooled to room temperature, treated with $VOSO_4$ (8 mg, 5 mol %) in H_2O (1.5 mL) and stirred for 20 h under air. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.65; purification (1:19 ethyl acetate/hexane); yellow solid. Yield 74% (241 mg); mp 75-77 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.2 Hz, 2H), 7.16-7.08 (m, 6H), 6.27 (s, 1H), 2.36-2.35 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.5, 143.5, 138.9, 138.0, 131.6, 129.0, 128.3, 127.2, 126.1, 120.2, 107.8, 21.0, 13.3; FT-IR (KBr) 2922, 1634, 1509, 1491, 1400, 1359, 1261, 1097, 1070, 1012, 967, 827, 797 cm^{-1}; HRMS (APCI) *m/z* $[M+H]^+$ calcd for $C_{17}H_{15}BrN_2$: 327.0491, found: 327.0492.



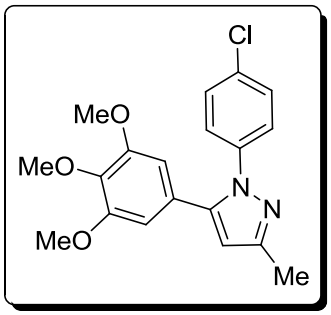
1-(4-Bromophenyl)-5-cyclohexyl-3-methyl-1*H*-pyrazole 3r. (*E*)-4-Cyclohexylbut-3-en-2-one **1m** (152 mg, 1 mmol) and (4-bromophenyl)hydrazine **2b** (224 mg, 1.2 mmol) were stirred at 60 ^{o}C for 1 h in toluene (1.5 mL) under air. The reaction mixture was cooled to room temperature, treated with $VOSO_4$ (8 mg, 5 mol %) in H_2O (1.5 mL) and stirred for 19 h under air. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.57; purification (1:19 ethyl acetate/hexane); yellow liquid. Yield 61% (193 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.7 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 5.99 (s, 1H), 2.61-2.54 (m, 1H), 2.28 (s, 3H), 1.84-1.68 (m, 5H), 1.36-1.28 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.1, 149.2, 139.0, 132.1, 127.0, 121.2, 103.6, 35.1, 33.4, 26.2, 25.7, 13.5; FT-IR (neat) 2927, 2852, 1590, 1546, 1493, 1447, 1382, 1363, 1260, 1069, 1013, 989, 830 cm^{-1}; HRMS (APCI) *m/z* $[M+H]^+$ calcd for $C_{16}H_{19}BrN_2$: 319.0804, found: 319.0805.



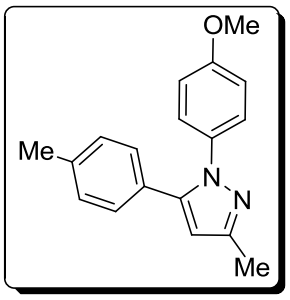
1-(4-Chlorophenyl)-3-methyl-5-phenyl-1*H*-pyrazole 3s.[5] (*E*)-4-Phenylbut-3-en-2-one **1b** (146 mg, 1 mmol) and (4-chlorophenyl)hydrazine **2c** (170 mg, 1.2 mmol) were stirred at 60 ^{o}C for 1 h in toluene (1.5 mL) under air. The reaction mixture was cooled to room temperature, treated with $VOSO_4$ (8 mg, 5 mol %) in H_2O (1.5 mL) and stirred stirred for 16 hunder air. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.64; purification (1:19 ethyl acetate/hexane); yellow liquid. Yield 71% (190 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7. 31 (s, 4H), 7.28-7.26 (m, 3H), 7.21 (d, *J* = 7.8 Hz, 2H), 6.30 (s, 1H), 2.37 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.0, 143.9, 138.8, 132.8, 130.6, 129.1, 128.8, 128.7, 128.4, 126.2, 108.3, 13.7; FT-IR (neat) 3060, 2925, 2860, 1892, 1596, 1551, 1493, 1453, 1405, 1377, 1364, 1311, 1267, 1192, 1093, 1015, 968, 831, 757, 697 cm^{-1}; HRMS (APCI) *m/z* $[M+H]^+$ calcd for $C_{16}H_{13}ClN_2$: 269.0840, found: 269.0840.



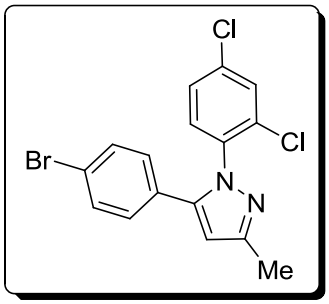
1-(4-Chlorophenyl)-5-(furan-2-yl)-3-methyl-1*H*-pyrazole 3t.[4] *(E)*-4-(furan-2-yl)but-3-en-2-one **1q** (136 mg, 1 mmol) and (4-chlorophenyl)hydrazine **2c** (170 mg, 1.2 mmol) were stirred at 60 ^{o}C for 1 h in toluene (1.5 mL) under air. The reaction mixture was cooled to room temperature, treated with $VOSO_4$ (8 mg, 5 mol %) in H_2O (1.5 mL) and stirred for 19 h under air. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.73; purification (1:19 ethyl acetate/hexane); yellow liquid. Yield 60% (154 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.4 Hz, 3H), 7.33 (d, *J* = 8.4 Hz, 2H), 6.44 (s, 1H), 6.35 (s, 1H), 6.06 (s, 1H), 2.35 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.0, 144.5, 142.8, 139.0, 135.0, 131.1, 129.3, 126.9, 111.4, 109.2, 106.8, 13.6; FT-IR (neat) 3106, 2961, 2925, 2853, 1726, 1596, 1529, 1502, 1403, 1383, 1261, 1093, 1016, 984, 895, 833, 800, 742 cm^{-1}; HRMS (APCI) *m/z* $[M+H]^+$ calcd for $C_{14}H_{11}ClN_2O$: 259.0633, found: 259.0636.



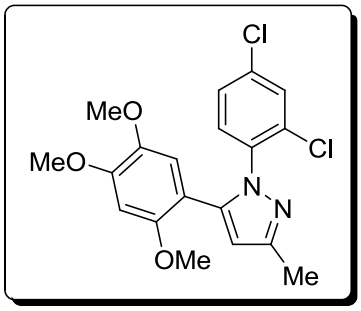
1-(4-Chlorophenyl)-3-methyl-5-(3,4,5-trimethoxyphenyl)-1*H*-pyrazole 3u. (*E*)-4-(3,4,5-Trimethoxyphenyl)but-3-en-2-one **1l** (236 mg, 1 mmol) and (4-chlorophenyl)hydrazine **2c** (170 mg, 1.2 mmol) were stirred at 60 ^{o}C for 1 h in toluene (1.5 mL) under air. The reaction mixture was cooled to room temperature, treated with $VOSO_4$ (8 mg, 5 mol %) in H_2O (1.5 mL) and stirred for 18 h under air. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.69; purification (1:9 ethyl acetate/hexane); yellow solid. Yield 48% (171 mg); mp 159-160 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (d, *J* = 9.0 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.76 (s, 1H), 6.42 (s, 1H), 6.24 (s, 1H), 3.90 (s, 3H), 3.78 (s, 3H), 3.38 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.7, 150.3, 149.5, 142.8, 140.2, 139.5, 131.8, 128.5, 124.5, 108.6, 97.2, 56.3, 55.9, 55.6, 13.6; FT-IR (KBr) 2959, 2927, 2850, 1666, 1611, 1498, 1465, 1437, 1407, 1384, 1362, 1261, 1219, 1208, 1142, 1092, 1032, 808 cm^{-1}; HRMS (APCI) *m/z* $[M+H]^+$ calcd for $C_{19}H_{19}ClN_2O_3$: 359.1162, found: 359.1162.



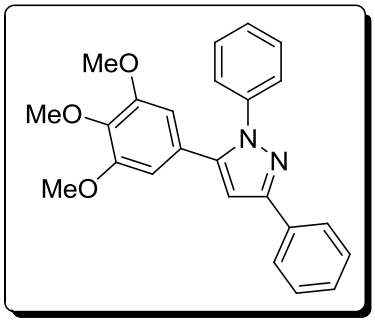
1-(4-Methoxyphenyl)-3-methyl-5-*p*-tolyl-1*H*-pyrazole 3v.[4] *(E)*-4-(4-Methylphenyl)but-3-en-2-one **1i** (160 mg, 1 mmol) and (4-methoxyphenyl)hydrazine **2d** (165 mg, 1.2 mmol) were stirred at 60 ^{o}C for 1 h in toluene (1.5 mL) under air. The reaction mixture was cooled to room temperature, treated with $VOSO_4$ (8 mg, 5 mol %) in H_2O (1.5 mL) and stirred for 17 h under air. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.48; purification (1:19 ethyl acetate/hexane); yellow liquid. Yield 68% (189 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.4 Hz, 2H), 7.08 (s, 4H), 6.84 (d, *J* = 9.0 Hz, 2H), 6.25 (s, 1H), 3.80 (s, 3H), 2.36 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.7, 149.1, 143.9, 138.0, 133.7, 129.2, 128.6, 128.0, 126.8, 114.1, 107.0, 55.6, 21.4, 13.7; FT-IR (neat) 2993, 2924, 2855, 1678, 1607, 1516, 1462, 1443, 1366, 1298, 1249, 1180, 1106, 1032, 971, 833 cm^{-1}; HRMS (APCI) *m/z* $[M+H]^+$ calcd for $C_{18}H_{18}N_2O$: 279.1492, found: 279.1494.



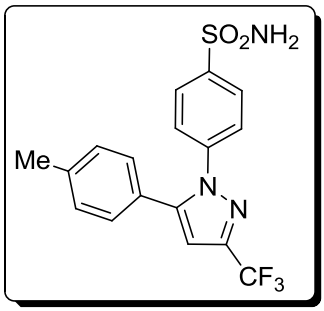
5-(4-Bromophenyl)-1-(2,4-dichlorophenyl)-3-methyl-1*H*-pyrazole 3w. *(E)*-4-(4-Bromophenyl)but-3-en-2-one **1f** (225 mg, 1 mmol) and (3,4-dichlorophenyl)hydrazine **2e** (210 mg, 1.2 mmol) were stirred at 60 ^{o}C for 1 h in toluene (1.5 mL) under air. The reaction mixture was cooled to room temperature, treated with $VOSO_4$ (8 mg, 5 mol %) in H_2O (1.5 mL) and stirred for 16 h under air. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.74; purification (1:19 ethyl acetate/hexane); yellow solid. Yield 58% (219 mg); mp 66-67 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.34 (s, 1H), 2.37 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.6, 144.8, 136.8, 135.6, 133.2, 131.9, 130.8, 130.4, 129.4, 129.1, 128.1, 122.8, 106.8, 13.8; FT-IR (KBr) 2924, 2850, 1622, 1562, 1499, 1484, 1427, 1390, 1362, 1194, 1073, 1010, 967, 812 cm^{-1}; HRMS (APCI) *m/z* $[M+H]^+$ calcd for $C_{16}H_{11}BrCl_2N_2$: 380.9555, found: 380.9556.



1-(2,4-Dichlorophenyl)-3-methyl-5-(2,4,5-trimethoxyphenyl)-1*H*-pyrazole 3x. Ketone **1a** (236 mg, 1 mmol) and (3,4-dichlorophenyl)hydrazine **2e** (210 mg, 1.2 mmol) were stirred at 60 ^{o}C for 1 h in toluene (1.5 mL) under air. The reaction mixture was cooled to room temperature, treated with $VOSO_4$ (8 mg, 5 mol %) in H_2O (1.5 mL) and stirred for 20 h under air. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.41; purification (1:9 ethyl acetate/hexane); yellow solid; Yield 63% (246 mg); mp 62-63 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (s, 1H), 7.12 (s, 2H), 6.59 (s, 1H), 6.31 (s, 1H), 6.21 (s, 1H), 3.78 (s, 3H), 3.62 (s, 3H), 3.48 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.9, 150.3, 149.9, 142.7, 142.2, 137.4, 134.3, 132.8, 130.2, 129.9, 127.1, 114.3, 110.3, 107.6, 97.1, 56.4, 56.0, 55.8, 13.7; FT-IR (KBr) 2998, 2924, 2852, 1614, 1511, 1497, 1464, 1436, 1382, 1266, 1223, 1209, 1151, 1083, 1032, 816 cm^{-1}; HRMS (APCI) *m/z* $[M+H]^+$ calcd for $C_{19}H_{18}Cl_2N_2O_3$: 393.0767, found: 393.0770.



1,3-Diphenyl-5-(3,4,5-trimethoxyphenyl)-1*H*-pyrazole 3y. *(E)*-1-phenyl-3-(3,4,5-trimethoxyphenyl)-prop-2-en-1-one **1r** (298 mg, 1 mmol), phenylhydrazine hydrochloride **2a** (172 mg, 1.2 mmol) and NaOAc were stirred at 60 ^{o}C for 1 h (237 mg, 2.9 mmol) in toluene: H_2O (1:1, 3 mL) under air. The reaction mixture was cooled to room temperature, treated with $VOSO_4$ (8 mg, 5 mol %) and stirred for 17 h under air. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.39; purification (1:9 ethyl acetate/hexane); yellow solid. Yield 72% (277 mg); mp 107-108 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.8 Hz, 2H), 7.73-7.71 (m, 1H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.51 (t, *J* = 7.2 Hz, 2H), 7.41-7.36 (m, 2H), 7.32 (s, 1H), 7.28-7.27 (m, 1H), 7.14 (s, 1H), 6.86 (s, 2H), 3.92 (s, 6H), 3.90 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.7, 145.2, 140.7, 138.5, 132.9, 130.5, 128.8, 128.6, 127.7, 125.5, 121.7, 105.9, 103.3, 61.2, 56.4; FT-IR (KBr) 2925, 2845, 1660, 1600, 1577, 1503, 1461, 1419, 1319, 1279, 1248, 1215, 1127, 1018, 983, 832, 782, 703, 603 cm^{-1}; HRMS (APCI) *m/z* $[M+H]^+$ calcd for $C_{24}H_{22}N_2O_3$: 387.1703, found: 387.1704.



4-(5-*p*-Tolyl-3-(trifluoromethyl)-1H-pyrazol-1-yl)benzenesulfonamide 3z. *(E)*-1,1,1-trifluoro-4-(p-tolyl)but-3-en-2-one **1s** (214 mg, 1 mmol) and 4-aminobenzenesulfonohydrazide **2f** (224 mg, 1.2 mmol) were stirred at 60 ^{o}C for 1 h in toluene (1.5 mL) under air. The reaction mixture was cooled to room temperature, treated with $VOSO_4$ (8 mg, 5 mol %) in H_2O (1.5 mL) and stirred for 17 h under air. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.41; purification (1:9 ethyl acetate/hexane); yellow liquid. Yield 45% (171 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91(d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 6.74 (s, 1H), 4.88 (s, 2H), 2.38 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ145.4, 144.3 (q, J_{C-F} = 39.0 Hz, C), 142.8, 141.4, 140.0, 130.0, 128.9, 127.7, 126.5, 125.9, 122.9 (q, J_{C-F} = 267.0 Hz, C), 106.6, 21.5; FT-IR (neat) 3448, 2961, 2922, 2854,

1746, 1636, 1497, 1468, 1386, 1333, 1272, 1235, 1162, 1129, 1096 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{17}H_{14}F_3N_3O_2S$: 382.0832, found: 382.0836.

7. Study of Photophysical Properties of the Fluorophoric Compounds

7.1 UV-visible and Fluorescence Measurements

All UV-visible spectra of the compound (10 μM) was measured in different solvents of varying dielectric constant by UV-visible spectrophotometer using 1 cm path length cell at 298 K. Fluorescence spectra of the compounds (10 μM) were measured in different solvents of varying dielectric constant by fluorescence spectrophotometer at 298 K using 1 cm path length cell. All the sample solutions were prepared just before doing the experiment.

$$\Phi_S = \Phi_R \frac{Fl_S^{Area}}{Fl_R^{Area}} \frac{Abs_R}{Abs_S} \frac{n_S^2}{n_R^2}$$

The fluorescence quantum yields (Φ_s) were determined using quinine sulphate as a reference with the known Φ_r (0.54) in 0.1 molar solutions in sulphuric acid. The above equation was used to calculate the quantum yield.

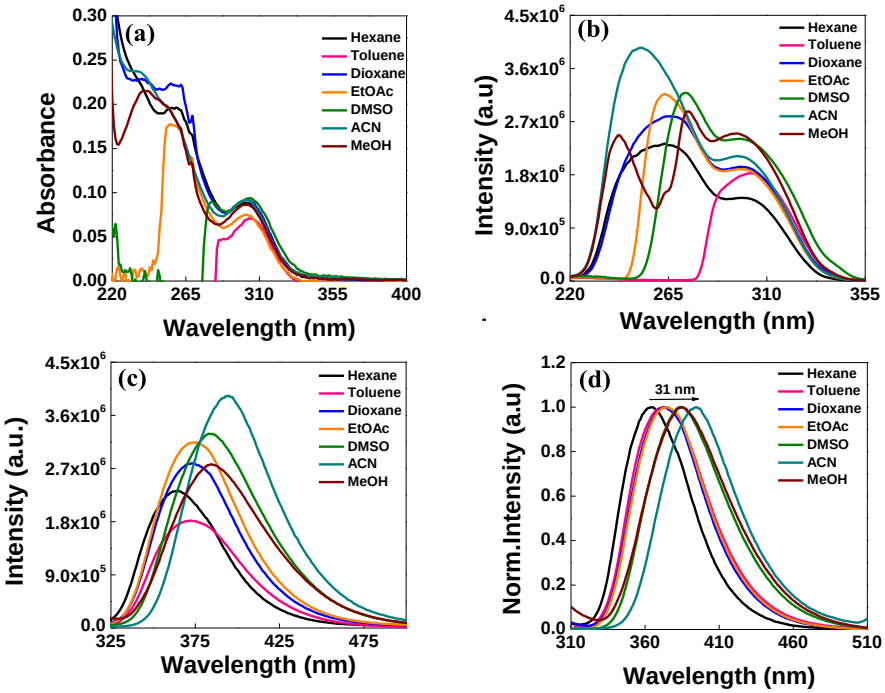


Figure 2. UV-Visible (a), excitation (b), fluorescence emission spectra (c), and normalized fluorescence emission spectra (d) of **3a** in different solvents [10 μM, r.t.; $\lambda_{ex} = \lambda_{max} \approx$ 300-305 nm in each solvent].

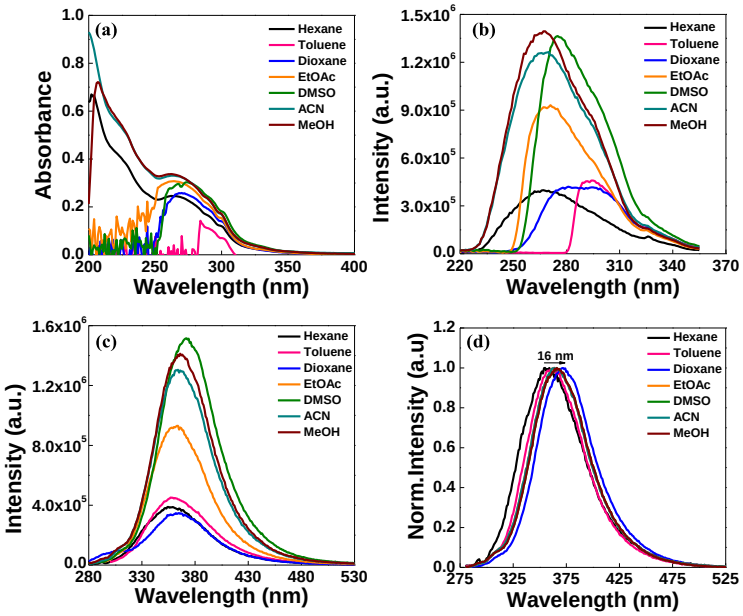


Figure 3. UV-Visible (a), excitation (b), fluorescence emission spectra (c), and normalized fluorescence emission spectra (d) of **3k** in different solvents [10 µM, r.t.; $\lambda_{ex} = \lambda_{max} \approx$ 263-272 nm in each solvent].

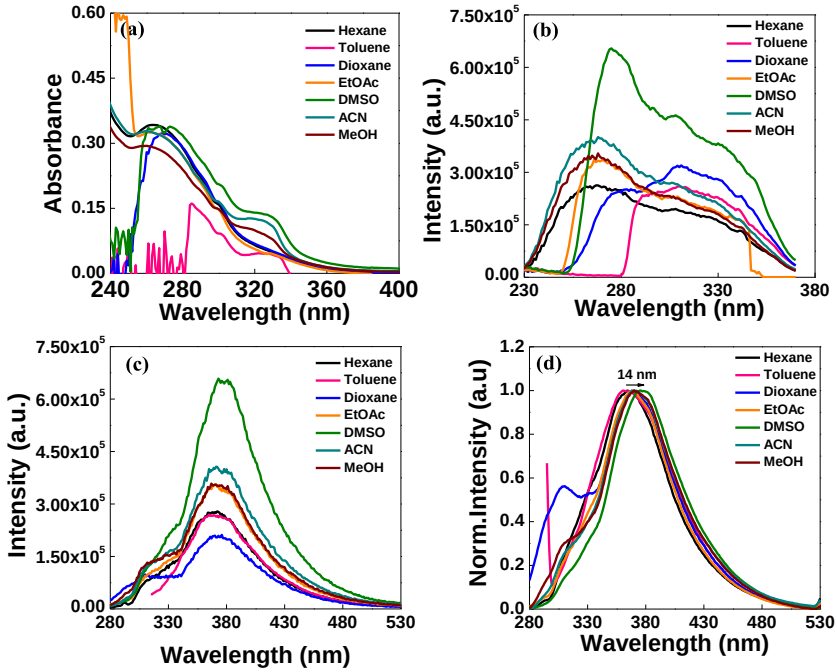


Figure 4. UV-Visible (a), excitation (b), fluorescence emission spectra (c), and normalized fluorescence emission spectra (d) of **3l** in different solvents [10 µM, r.t.; $\lambda_{ex} = \lambda_{max} \approx$ 260-270 nm in each solvent].

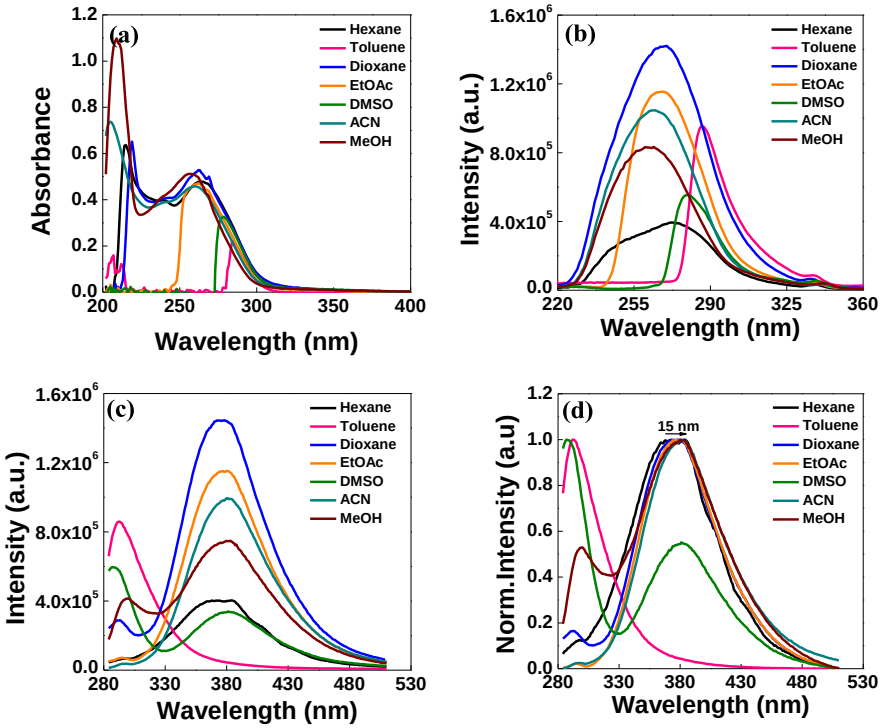


Figure 5. UV-Visible (a), excitation (b), fluorescence emission spectra (c), and normalized fluorescence emission spectra (d) of **3q** in different solvents [10 µM, r.t.; $\lambda_{ex} = \lambda_{max} \approx$ 262-265 nm in each solvent].

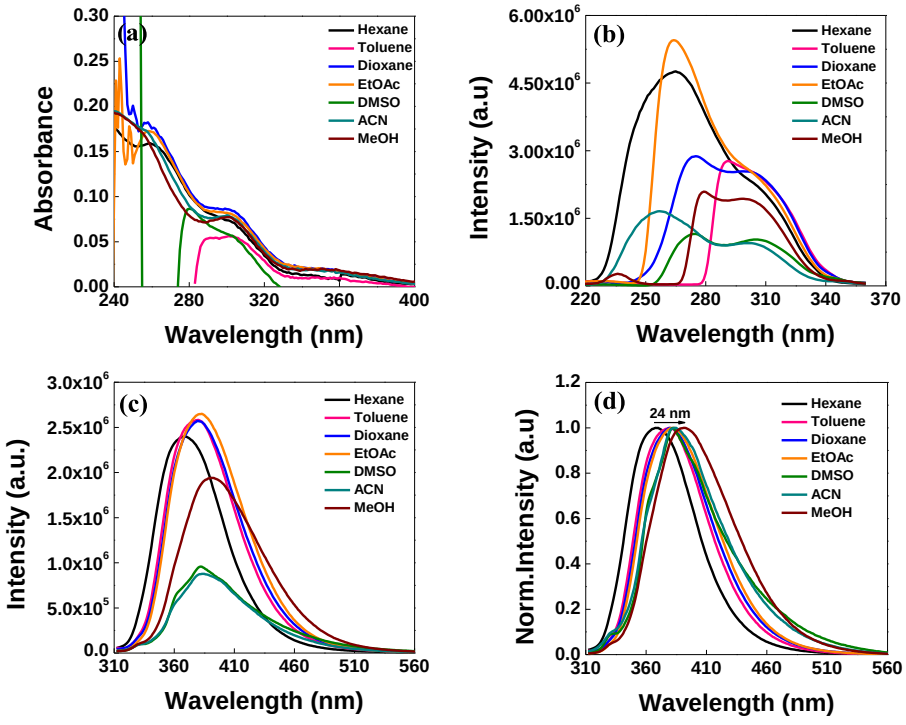


Figure 6. UV-Visible (a), excitation (b), fluorescence emission spectra (c), and normalized fluorescence emission spectra (d) of **3u** in different solvents [10 µM, r.t.; $\lambda_{ex} = \lambda_{max} \approx$ 300-305 nm in each solvent].

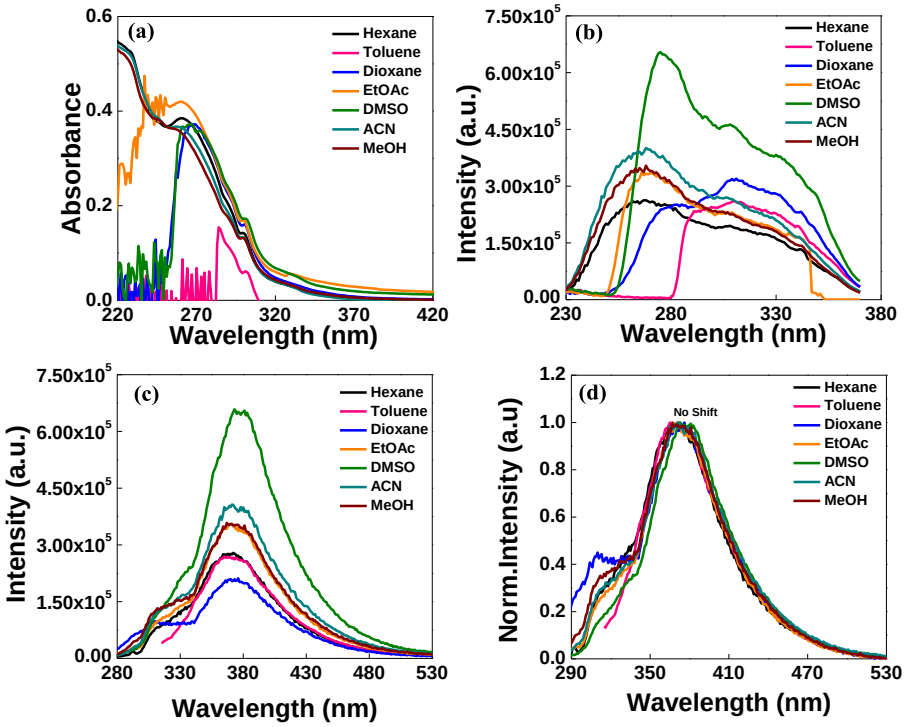


Figure 7. UV-Visible (a), excitation (b), fluorescence emission spectra (c), and normalized fluorescence emission spectra (d) of **3v** in different solvents [10 µM, r.t.; $\lambda_{ex} = \lambda_{max} \approx$ 258-268 nm in each solvent].

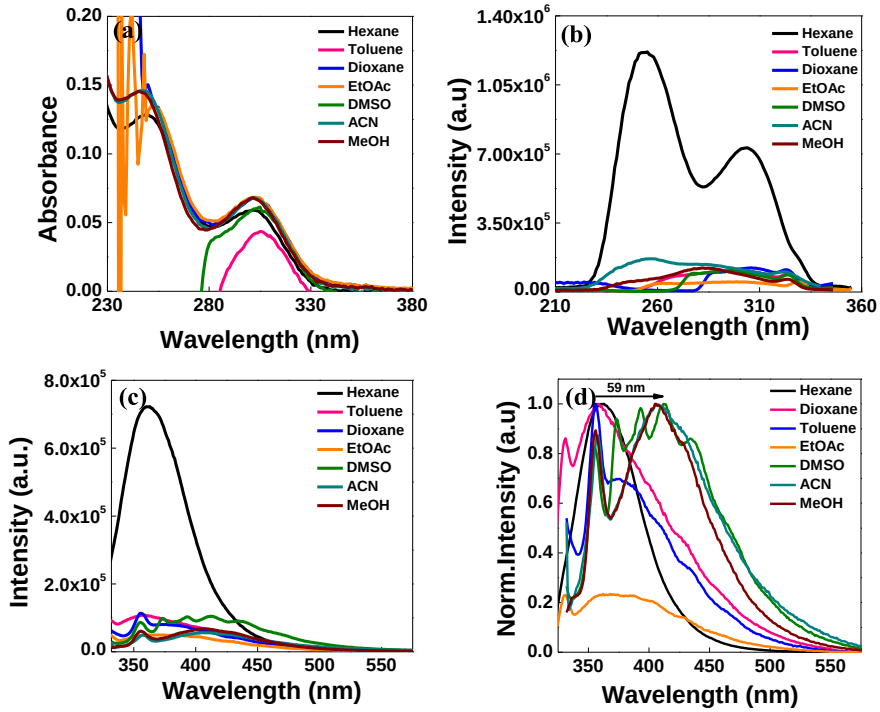


Figure 8. UV-Visible (a), excitation (b), fluorescence emission spectra (c), and normalized fluorescence emission spectra (d) of **3x** in different solvents [10 µM, r.t.; $\lambda_{ex} = \lambda_{max} \approx$ 300-305 nm in each solvent].

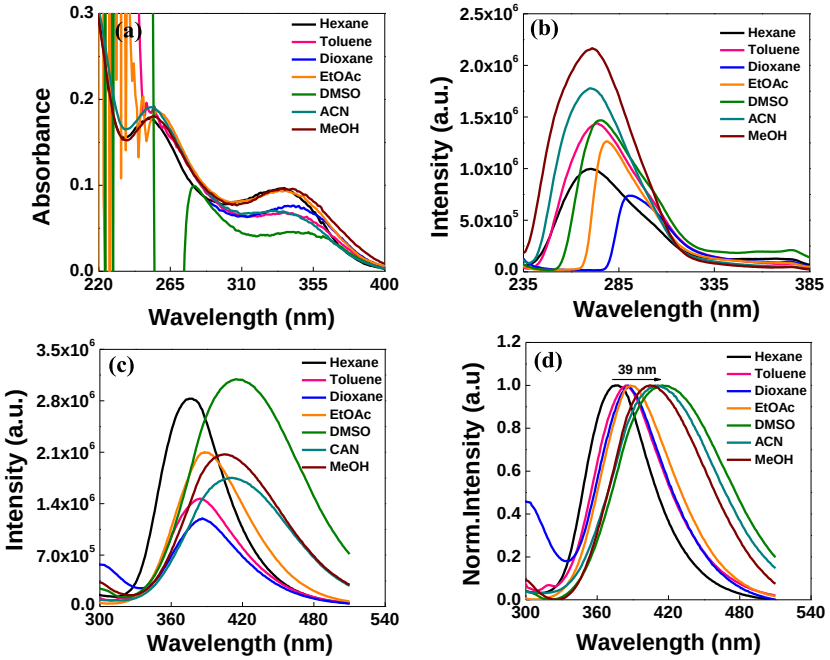


Figure 9. UV-Visible (a), excitation (b), fluorescence emission spectra (c), and normalized fluorescence emission spectra (d) of **3y** in different solvents [10 µM, r.t.; $\lambda_{ex} = \lambda_{max} \approx$ 251-256 nm in each solvent].

7.2. Photophysical Summary of Synthesized Compounds

Table 1. Summary table of photophysical properties of **3a**

Entry	Solvents	Δf	UV-Vis & Fluorescence		
			λ_{max}^{abs} (nm)	λ_{max}^{fl} (nm)	Φ_f
3a	Hexane	0.001	257, 302	363	0.105
	Toluene	0.013	305	372	0.106
	Dioxane	0.021	258, 303	373	0.132
	EtOAc	0.201	256, 302	374	0.183
	DMSO	0.265	281, 303	384	0.162
	ACN	0.307	235, 302	394	0.184
	MeOH	0.309	240, 301	384	0.158

Table 2. Summary table of photophysical properties of **3k**

Entry	Solvents	Δf	UV-Vis & Fluorescence	
			λ_{max}^{abs} (nm)	λ_{max}^{fl} (nm)
3k	Hexane	0.001	203, 264	357
	Toluene	0.013	283	358
	Dioxane	0.021	269	364
	EtOAc	0.201	263	363
	DMSO	0.265	272	373
	ACN	0.307	263	366
	MeOH	0.309	207, 264	366

Table 3. Summary table of photophysical properties of **3l**

Entry	Solvents	Δf	UV-Vis & Fluorescence	
			λ_{max}^{abs} (nm)	λ_{max}^{fl} (nm)
3l	Hexane	0.001	263,	363
	Toluene	0.013	285, 328	363
	Dioxane	0.021	269	370
	EtOAc	0.201	262	368
	DMSO	0.265	267, 327	377
	ACN	0.307	261, 325	371
	MeOH	0.309	260, 324	374

Table 4. Summary table of photophysical properties of **3q**

Entry	Solvents	Δf	UV-Vis & Fluorescence	
			λ_{max}^{abs} (nm)	λ_{max}^{fl} (nm)
3s	Hexane	0.001	214, 264	367
	Toluene	0.013	284	293
	Dioxane	0.021	219, 262	374
	EtOAc	0.201	262	377
	DMSO	0.265	278	290, 379
	ACN	0.307	205, 259	380
	MeOH	0.309	208, 257	297, 382

Table 5. Summary table of photophysical properties of **3u**

Entry	Solvents	Δf	UV-Vis & Fluorescence	
			λ_{max}^{abs} (nm)	λ_{max}^{fl} (nm)
3w	Hexane	0.001	258, 300	367
	Toluene	0.013	303	380
	Dioxane	0.021	257, 301	380
	EtOAc	0.201	259, 301	383
	DMSO	0.265	302	382
	ACN	0.307	256, 300	382
	MeOH	0.309	254, 302	391

Table 6. Summary table of photophysical properties of **3v**

Entry	Solvents	Δf	UV-Vis & Fluorescence	
			λ_{max}^{abs} (nm)	λ_{max}^{fl} (nm)
3t	Hexane	0.001	260, 299	372
	Toluene	0.013	284, 301	372
	Dioxane	0.021	268, 301	372
	EtOAc	0.201	260, 300	373
	DMSO	0.265	265, 301	373
	ACN	0.307	259, 299	375
	MeOH	0.309	258, 299	373

Table 7. Summary table of photophysical properties of **3x**

Entry	Solvents	Δf	UV-Vis & Fluorescence	
			λ_{max}^{abs} (nm)	λ_{max}^{fl} (nm)
3v	Hexane	0.001	249,301	361
	Toluene	0.013	305	358
	Dioxane	0.021	249, 303	355, 382
	EtOAc	0.201	253, 302	366
	DMSO	0.265	303	355, 375, 355
	ACN	0.307	247, 301	358, 407
	MeOH	0.309	245, 301	355, 407

Table 8. Summary table of photophysical properties of **3y**

Entry	Solvents	Δf	UV-Vis & Fluorescence		
			λ_{max}^{abs} (nm)	λ_{max}^{fl} (nm)	Φ_f
3y	Hexane	0.001	251, 335	376	0.007
	Toluene	0.013	253, 339	384	0.011
	Dioxane	0.021	339	385	0.009
	EtOAc	0.201	256, 334	388	0.007
	DMSO	0.265	280,344	415	0.017
	ACN	0.307	252, 330	409	0.008
	MeOH	0.309	254, 338	404	0.006

8. Studies on the Interaction of two Fluorophores with BSA protein

8.1. General experimental Section

8.1.1. Materials:

BSA, Na_2HPO_4 and $NaH_2PO_4.H_2O$ (for preparation of phosphate buffer) were purchased from Merck, India and used without further purification. Water was obtained from a Milli-Q purification system. All experiments were performed with freshly prepared solutions.

8.1.2. Preparation of BSA Solution

To prepare the BSA solution Milli-Q water was used. A 1000 μM of stock BSA solution was prepared by dissolving 0.198 gm of BSA in 3 mL Milli-Q water.

8.1.3. General experimental for studying the interaction with BSA:

All the spectral measurements were carried out at room temperature. To study the interaction of compound with BSA, an aqueous solution of compound (30 μM in 1mL solution) was titrated with different concentrations of BSA (ranging from 0, 7.5, 15, 22.5, 30, 37.5, 45, 60, 75, 90 μM). The total volume of the final solution for each sample was 1 mL. As the fluorophores are not soluble in water, 2-3% DMF is used to solubilize them. The presence of 2-3% DMF does not induce structural changes to biomolecules. Each sample solution was mixed well before spectral measurements.

8.1.4. Photophysical Study

UV-Visible Study

The UV-Visible absorbance measurements were performed using Shimadzu UV-2550 UV-Visible spectrophotometer with a cell of 1 cm path length at 298 K. All the UV-Visible studies were carried out in 0.1 mM phosphate buffer of pH 7.0 at 298 K. A 3 % DMF was used to solubilize the probe. The measurements were taken in absorbance mode and the absorbance values of the sample solutions were measured in the wavelength regime of 200-600 nm. All the experiments were carried out with freshly prepared sample solutions.

8.1.5. Fluorescence Study

All fluorescence and steady state anisotropy experiments were performed using a Fluoromax 4 spectrophotometer with a cell of 1 cm path length at 298 K. All the fluorescence studies were carried out in 0.1 mM phosphate buffer of pH 7.0 at 298 K. A 3 % DMF was used to solubilize the probe. Steady state anisotropy of the solutions was measured using Fluoromax 4 spectrophotometer.

Study of UV-Visible and fluorescence properties of 3a in presence BSA

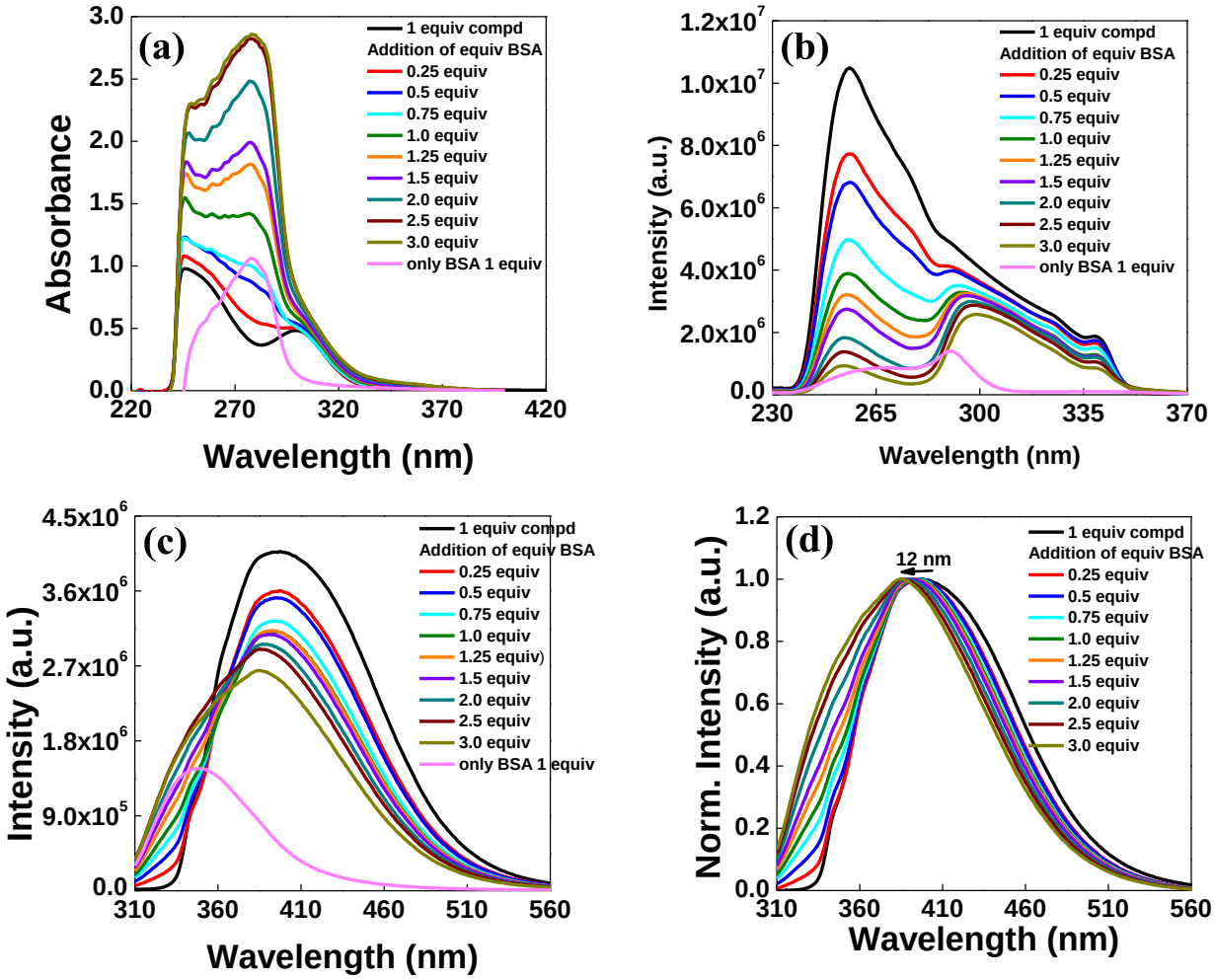


Figure 10. UV-Visible (a), excitation (b), fluorescence emission spectra (c), and normalized fluorescence emission spectra (d) of **3a** in presence of increasing BSA concentration at 298K. **3a**= 30 μM and [BSA] = 0, 7.5, 15, 22.5, 30, 37.5, 45, 60, 75, 90 μM. [$\lambda_{ex} = \lambda_{max} \approx 300$nm].

8.1.6. Summary Table of Fluorescence of 3a with BSA.

Table 9. Summary table of photophysical properties of the **3a** with interaction with BSA

BSA : 3a	UV-Vis & Fluorescence	
	λ_{max}^{abs} (nm)	λ_{max}^{fl} (nm)
1:0	300	397
1 : 0.25	300	395
1 : 0.5	300	394
1 : 0.75	300	392
1 : 1	279, 300	391
1 : 1.25	278	391
1 : 1.5	278	389
1 : 2	277	387
1 : 2.5	277	385
1 : 3	277	385
0:1	277	346

8.1.7. Stern Volmer plot

In the simplest case of quenching of fluorescence, Stern-Volmer equation, was used

$$I_0/I = 1 + K_{SV}[Q]$$

Where I_0 and I are the fluorescence intensities observed in the absence and presence, of the quencher respectively, and K_{SV} is the Stern-Volmer quenching constant

Thus, the plot of I_0/ I versus [BSA] yields a straight line with a slope equal to K_{SV}. Here K_{SV}=0.00488

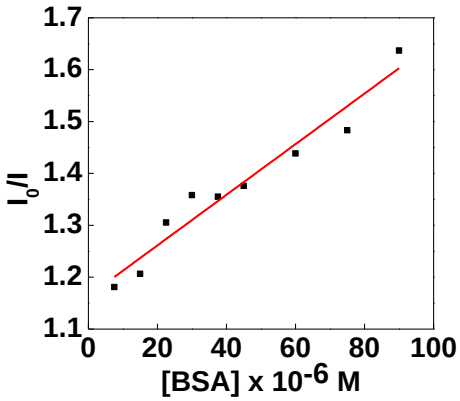


Figure 11: Stern-Volmer plot of **3a** fluorophore in presence of increasing BSA concentration. [**3a**] = 30 µM and [BSA] = 0, 7.5, 15, 22.5, 30, 37.5, 45, 60.

8.1.8. Absorption Job's Plot from UV-Visible Study

To quantify the stoichiometry between fluorophore (**3a**) and the BSA protein, the absorption measurement was carried out for Job's plot. For this purpose, an equal concentration of probe (**3a**) and BSA protein solutions was prepared separately in Phosphate buffer. Then, the fluorophore and the BSA protein were mixed in different fraction of volume maintaining the total volume of mixture 1 mL. All the solutions were mixed well and kept for some time in room temperature. Then the absorbance spectra of the solutions of different composition of fluorophore and BSA protein were recorded. To calculate the Probe-BSA protein complexation ratio, [Probe-BSA protein] *vs*. *Xprobe* were plotted, where [Probe -BSA protein]= Δ*A*/*A0* x [*probe*], {ΔA = (A-A0)}; and *Xprobe* is the mole fraction of probe, {*Xprobe* = [probe]/([*probe*] + [*BSA*])}. The Job's plot (**Figure 12**) showed the point of maximum at the mole fraction of ~0.50 of the probe, which clearly indicated a 1:1 stoichiometry of the probe to BSA in the complex.

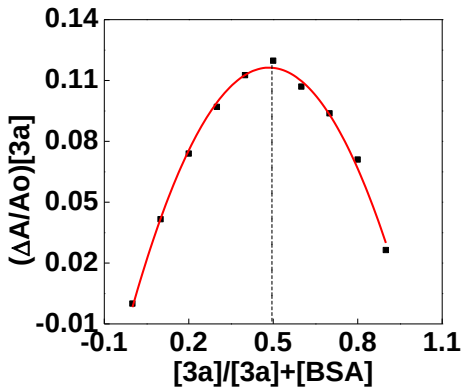


Figure 12: Job's plot of probe, **3a** in presence of BSA protein indicates a 1:1 stoichiometry of the probe to BSA in the complex.

8.1.9. Study of Fluorescence Anisotropy

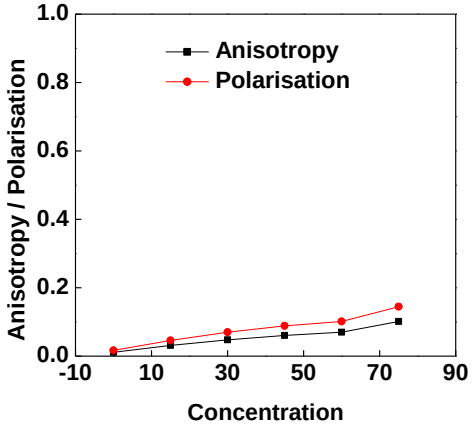


Figure 13: Fluoroscene anisotropy and polarization change of fluorophore in presence of various concentration of BSA. [fluorophore(**3a**)] = 30 µM and [BSA] =0, 15, 30, 45, 60 and 75 µM.

8.1.10. Study of UV-Visible and fluorescence properties of 3y in presence of BSA

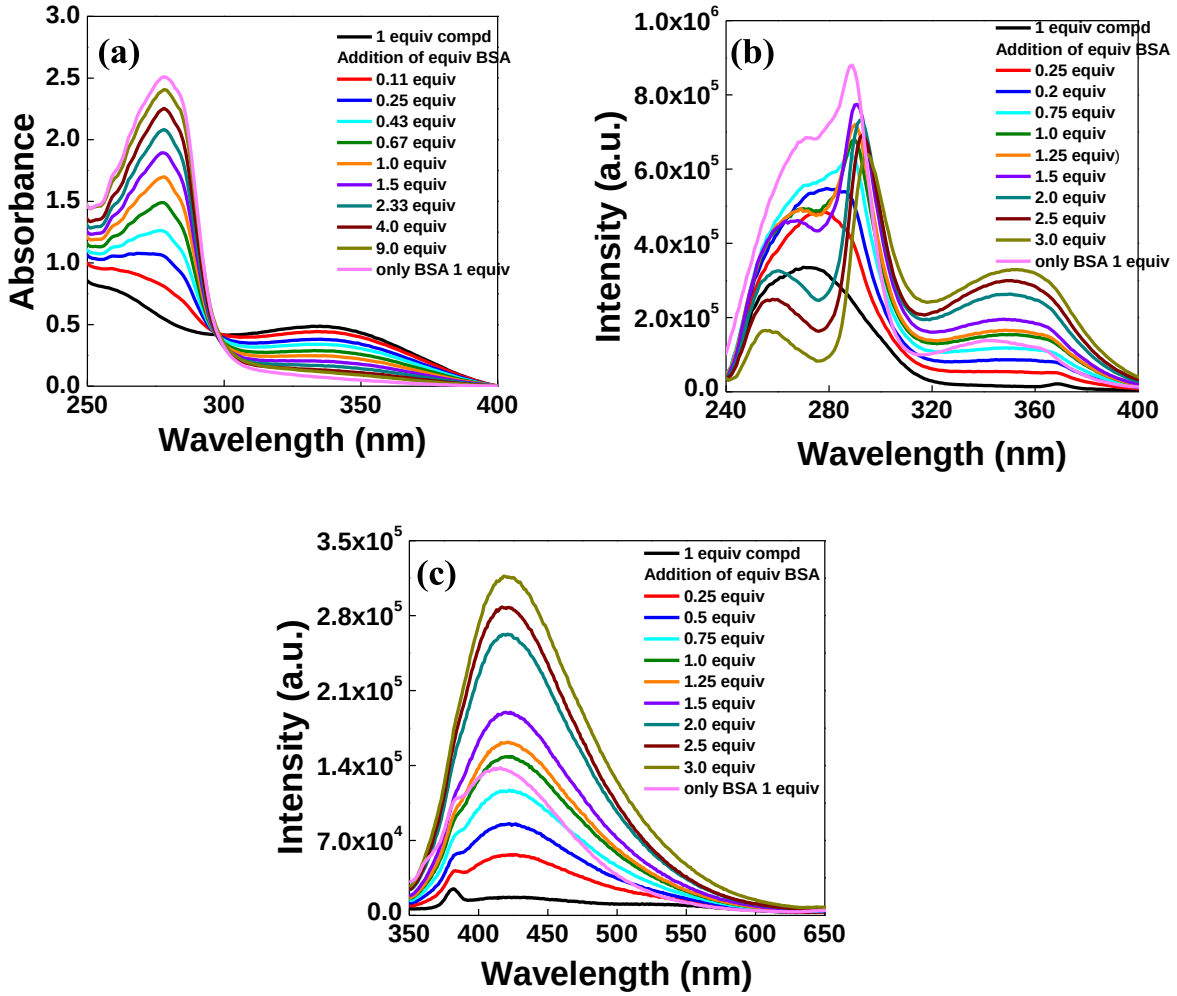


Figure 14. UV-Visible (a), excitation (b), and fluorescence emission spectra (c) of **3y** in presence of increasing BSA concentration at 298K. **3y**= 30 μM and [BSA] = 0, 7.5, 15, 22.5, 30, 37.5, 45, 60, 75, 90 μM.

8.1.11. Summary table of fluorescence 3y with BSA.

Table 10. Summary table of photophysical properties of the **3y** with interaction with BSA

BSA : 3y	UV-Vis & Fluorescence	
	λ_{max}^{abs} (nm)	λ_{max}^{fl} (nm)
1:0	335	381, 420
1 : 0.25	335	381, 420
1 : 0.5	275, 335	381, 420
1 : 0.75	277, 335	381, 420
1 : 1	277, 335	381, 420
1 : 1.25	277, 335	420
1 : 1.5	277, 335	421
1 : 2	277	421
1 : 2.5	278	421
1 : 3	278	421
0 : 1	278	412

8.1.12. Benesi-Hildebrand plot

The association constant (K) of the fluorophore (**3y**) with BSA was determined by a Benesi-Hildebrand plot. From the slope of the $1/(I - I_0)$ *vs.*$1/[BSA]$ plot binding constant K was determined and its value is 1.64×10^4 M^{-1}.

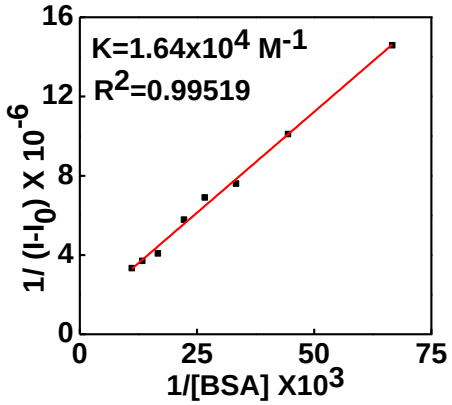


Figure 15: Benesi- Hildebrand plot of **3y** in presence of increasing BSA concentration. [**3y**] = 30 µM and [BSA] = 0, 7.5, 15, 22.5, 30, 37.5, 45, 60.

8.1.13. Absorption Job's Plot from UV-Visible Study

Absorption measurement was carried out for Job's plot to quantify the stoichiometry between fluorophore (**3y**) and the BSA protein. The Job's plot (**Figure 16**) showed the point of maximum at the mole fraction of ~0.50 of the probe, which clearly indicated a 1:1 stoichiometry of the probe to BSA in the complex.

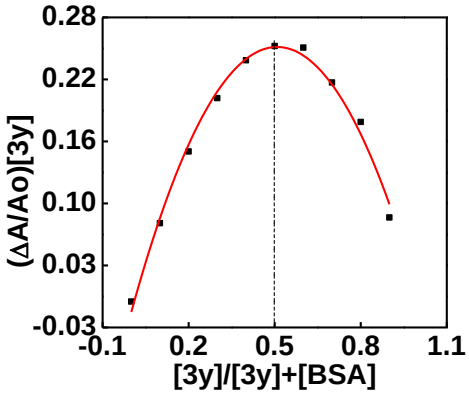


Figure 16: Absorption Job's plot of probe, **3y** in presence of BSA protein indicates a 1:1 stoichiometry of the probe to BSA in the complex.

8.1.14. Study of Fluorescence Anisotropy

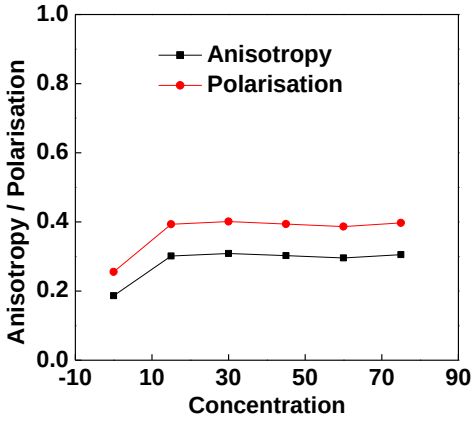


Figure 17: Fluoroscene anisotropy and polarization change of fluorophore in presence and absence of various concentration of BSA. [fluorophore(**3y**)] = 30 µM and [BSA] =0, 15, 30, 45, 60 and 75 µM.

8.1.15. Study of Circular Dichroism Spectroscopy

Circular dichroism spectra were recorded using a CD spectropolarimeter with a cell path length of 10 nm at 25 ^{o}C. All the samples were prepared in spectroscopic grade methanol solvent with 60 µM concentration.

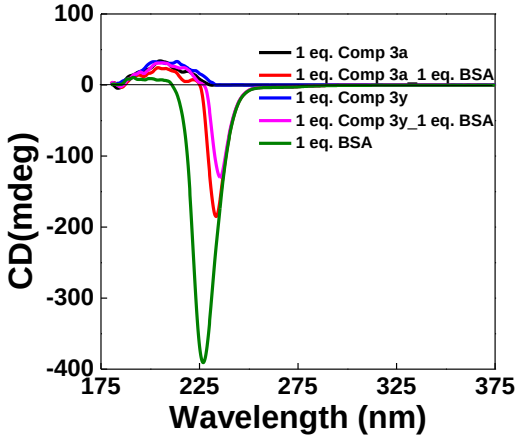
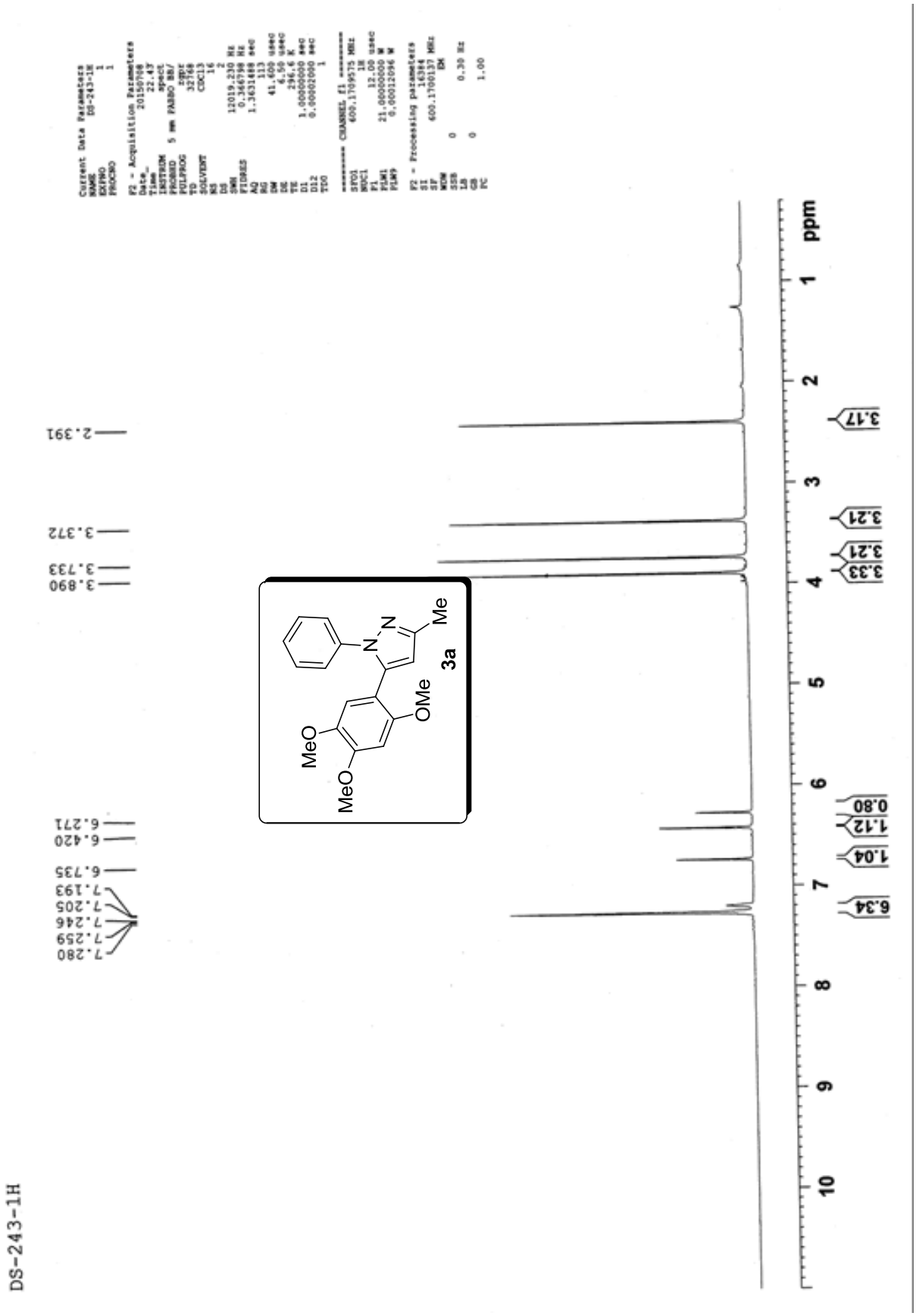


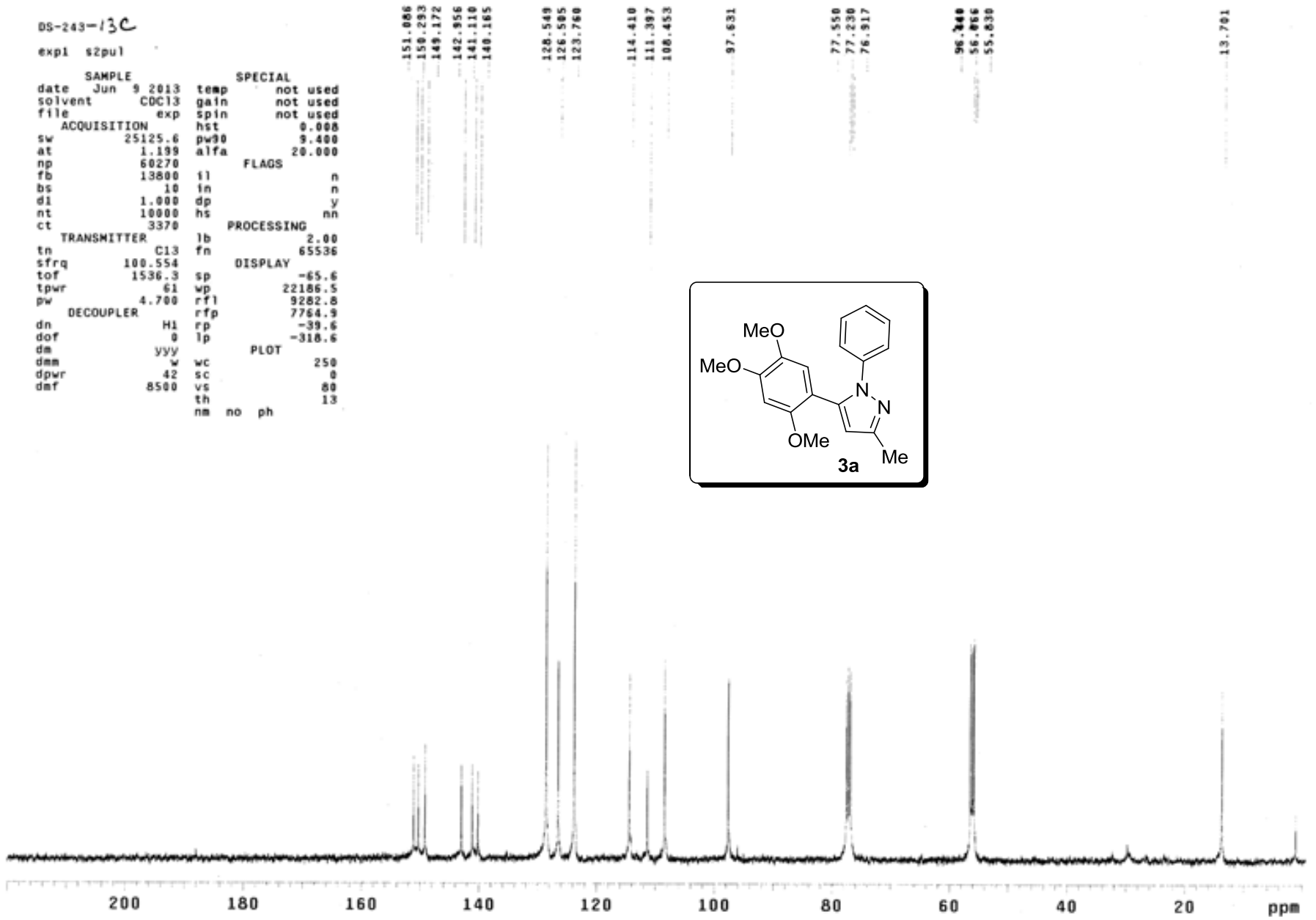
Figure 18. CD spectra of BSA in absence and in presence of synthesized compounds, **3a** and **3y**, respectively (60 µM concentration of each).

References

1. (a) Furniss, B. S.; Hannaford, A. J.; Smith, P. W. G.; Tatchell, A. R. In *Vogel's Textbook of Practical Organic Chemistry*, 5th Ed., Pearson Education Pte. Ltd., Delhi, **2004**. (b) Cao, L.; Ding, J.; Gao, M.; Wang, Z.; Li, J.; Wu, A. *Org. Lett*. **2009**, *11*, 3810. (c) Hu, J.; Chen, S.; Sun, Y.; Yang, J.; Rao, Y. *Org. Lett*. **2012**, *14*, 5030. (d) Guru, M. M.; Ali, M. A.; Punniyamurthy, T. *J. Org. Chem*. **2011**, *76*, 5295.
2. Kim, B. R.; Sung, G. H.; Ryu, K. E.; Lee, S.-G.; Yoon, H. J.; Shin, D.-S.; Yoon, Y.-J. *Chem. Commun.* **2015**, *51*, 9201.
3. Dvorak, C. A.; Rudolph, D. A.; Ma, S.; Carruthers, N. I. *J. Org. Chem*. **2005**, *70*, 4188.
4. Sar, D.; Paul, R.; Sengoden, M.; Punniyamurthy, T. *Asian J. Org. Chem*. **2014**, *3*, 638.
5. Liang, D.; Zhu, Q. *Asian J. Org. Chem*. **2015**, *4*, 42.

9. ^{1}H and ^{13}C NMR Spectra

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pw 4.700
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spin not used
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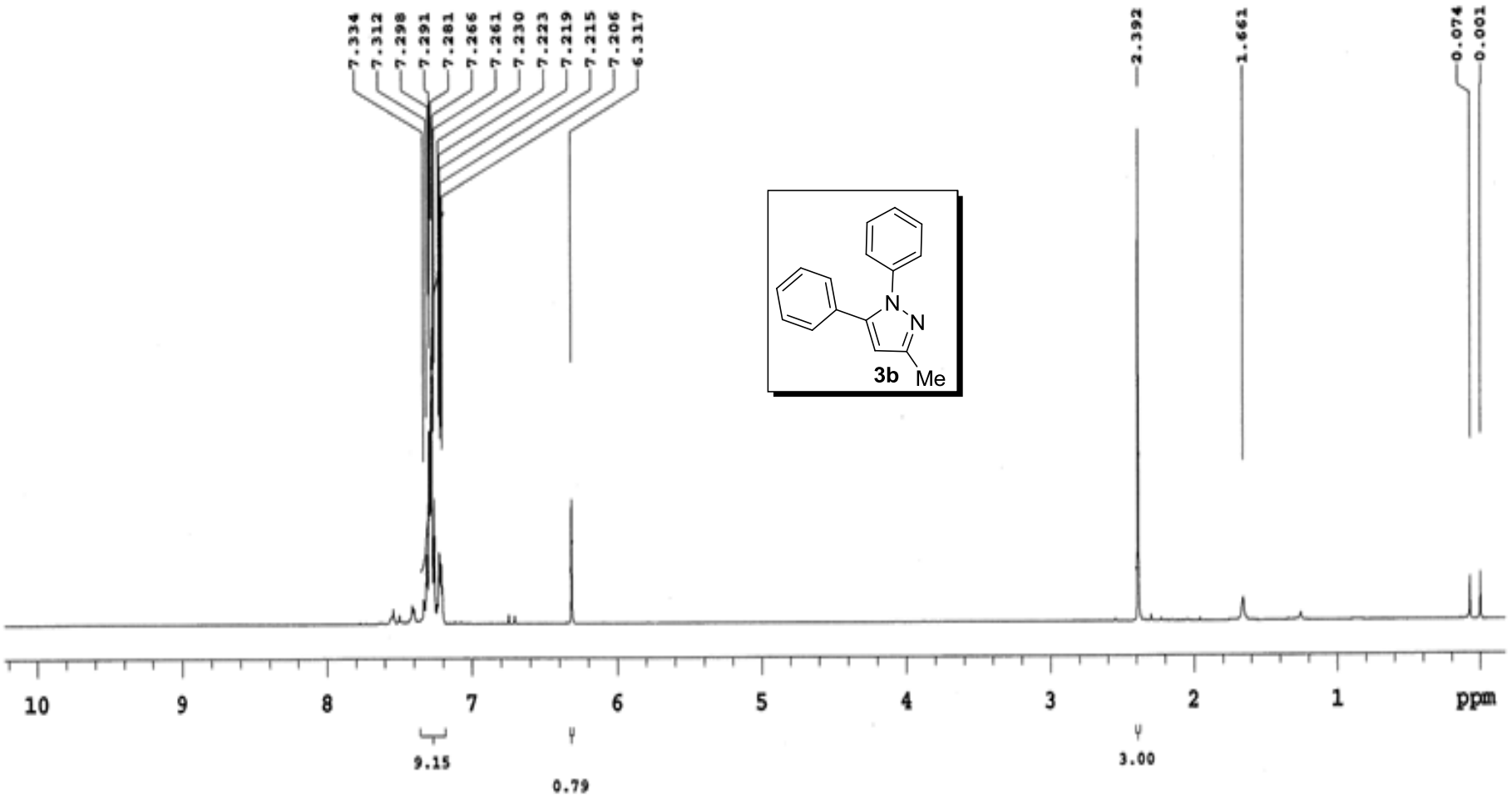

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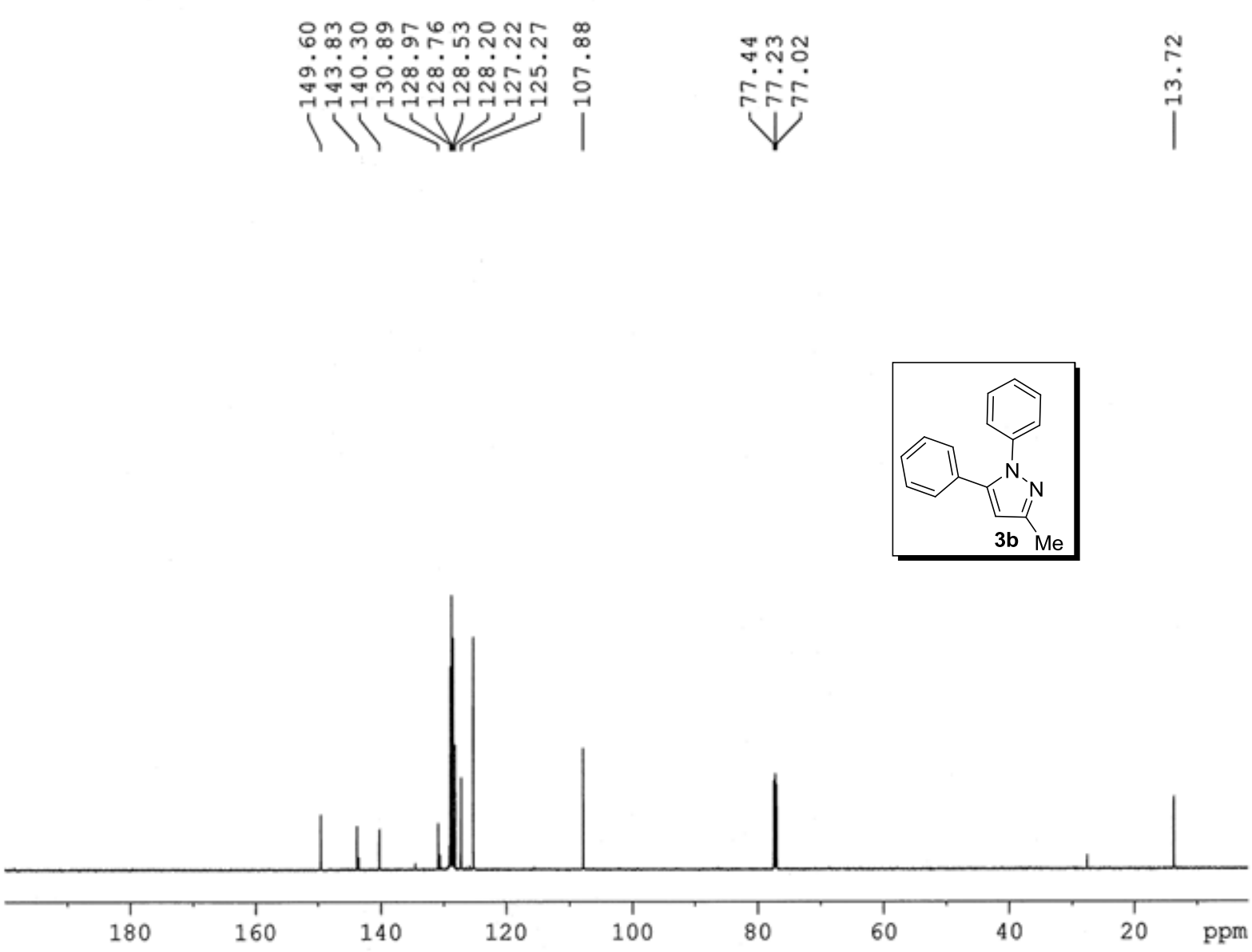
DS_359_ 13C



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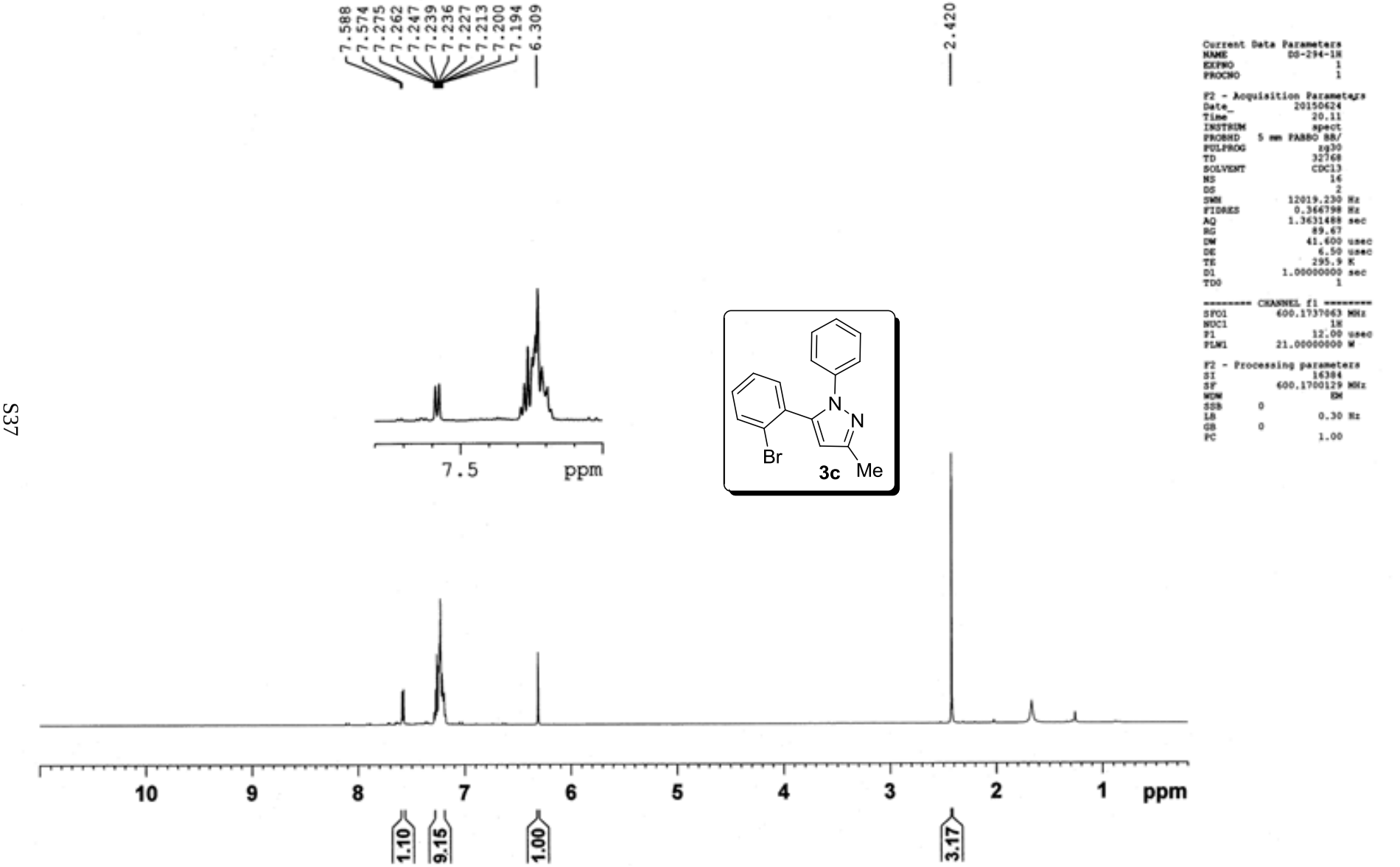


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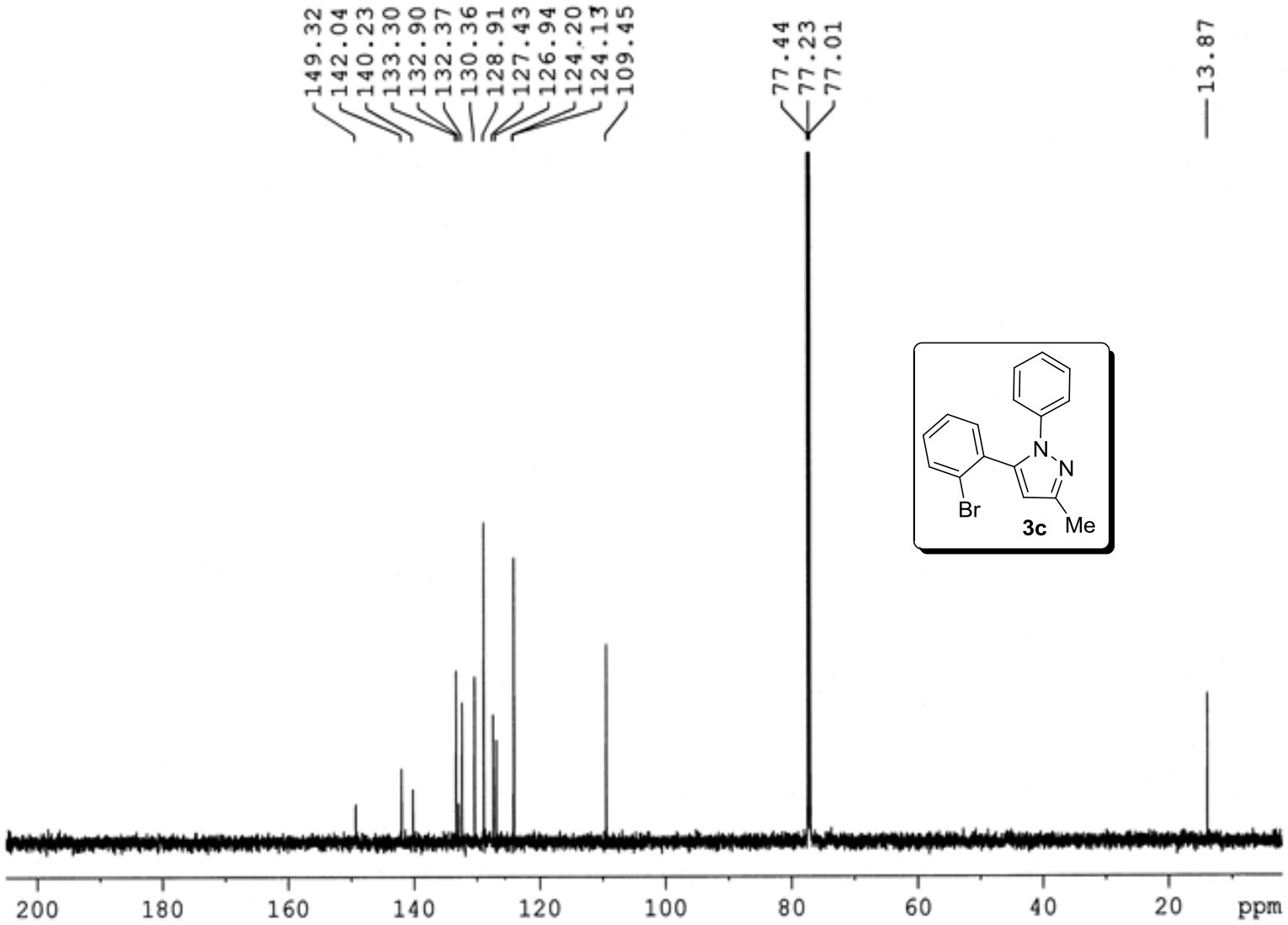

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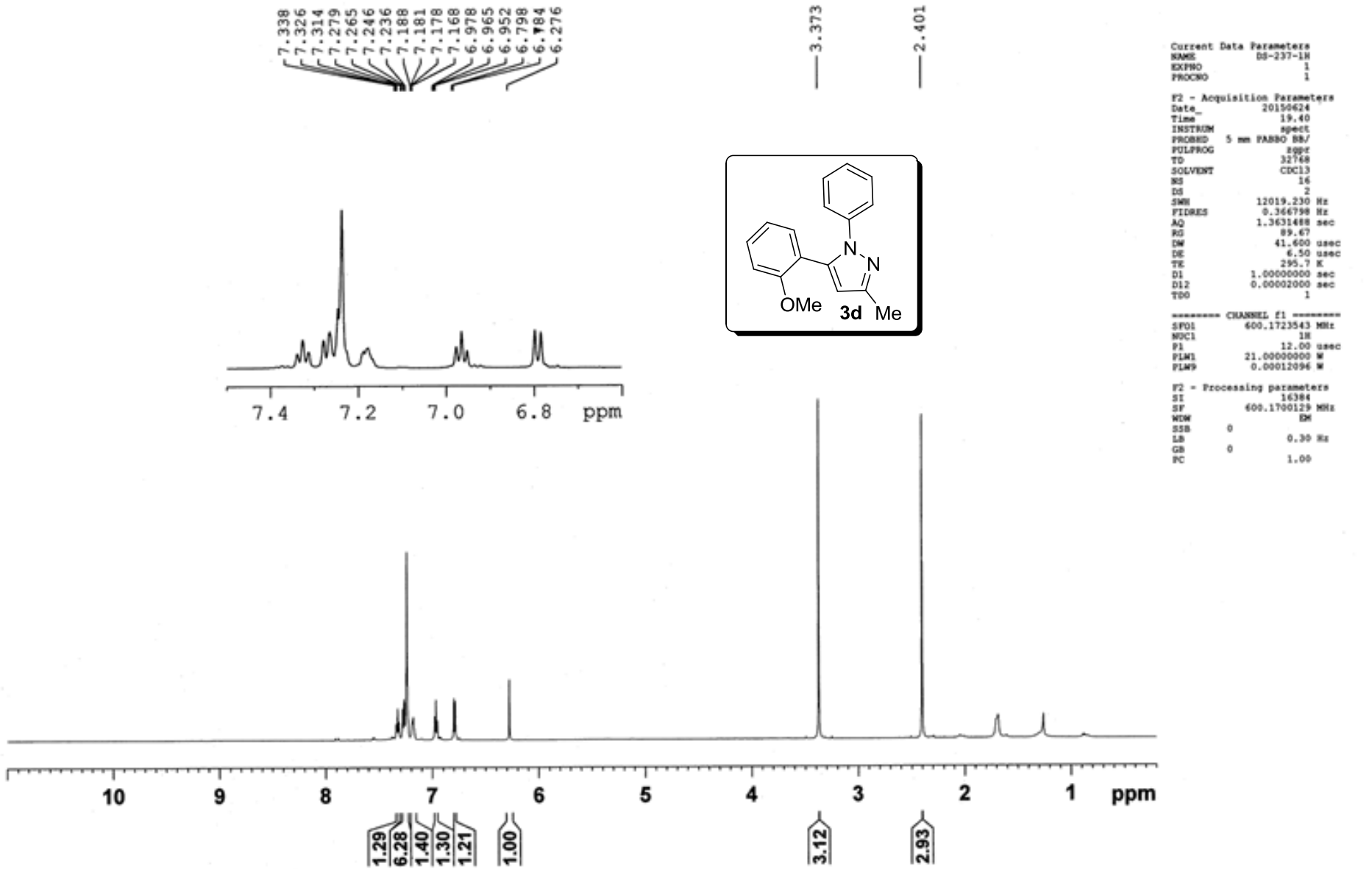


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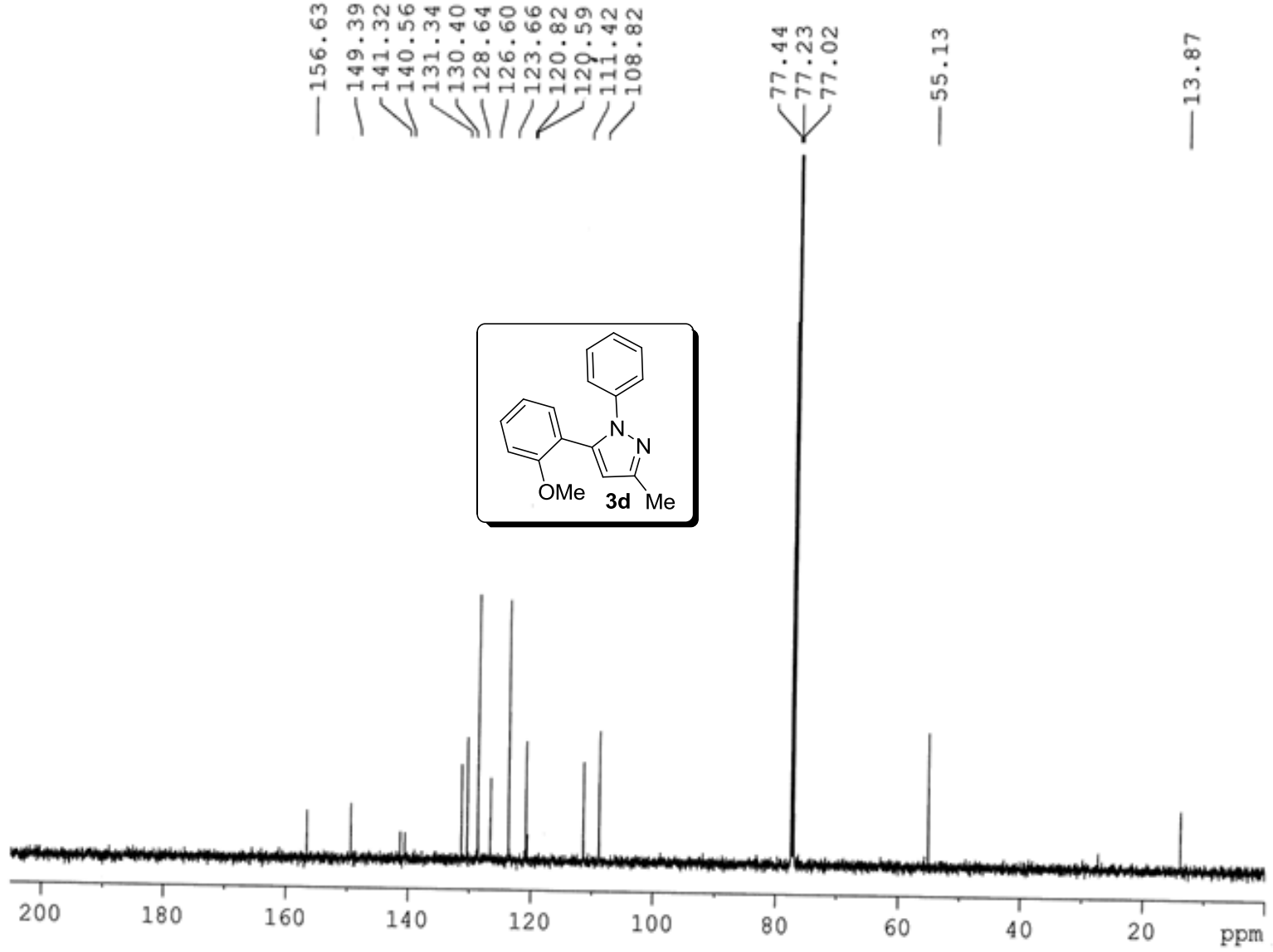

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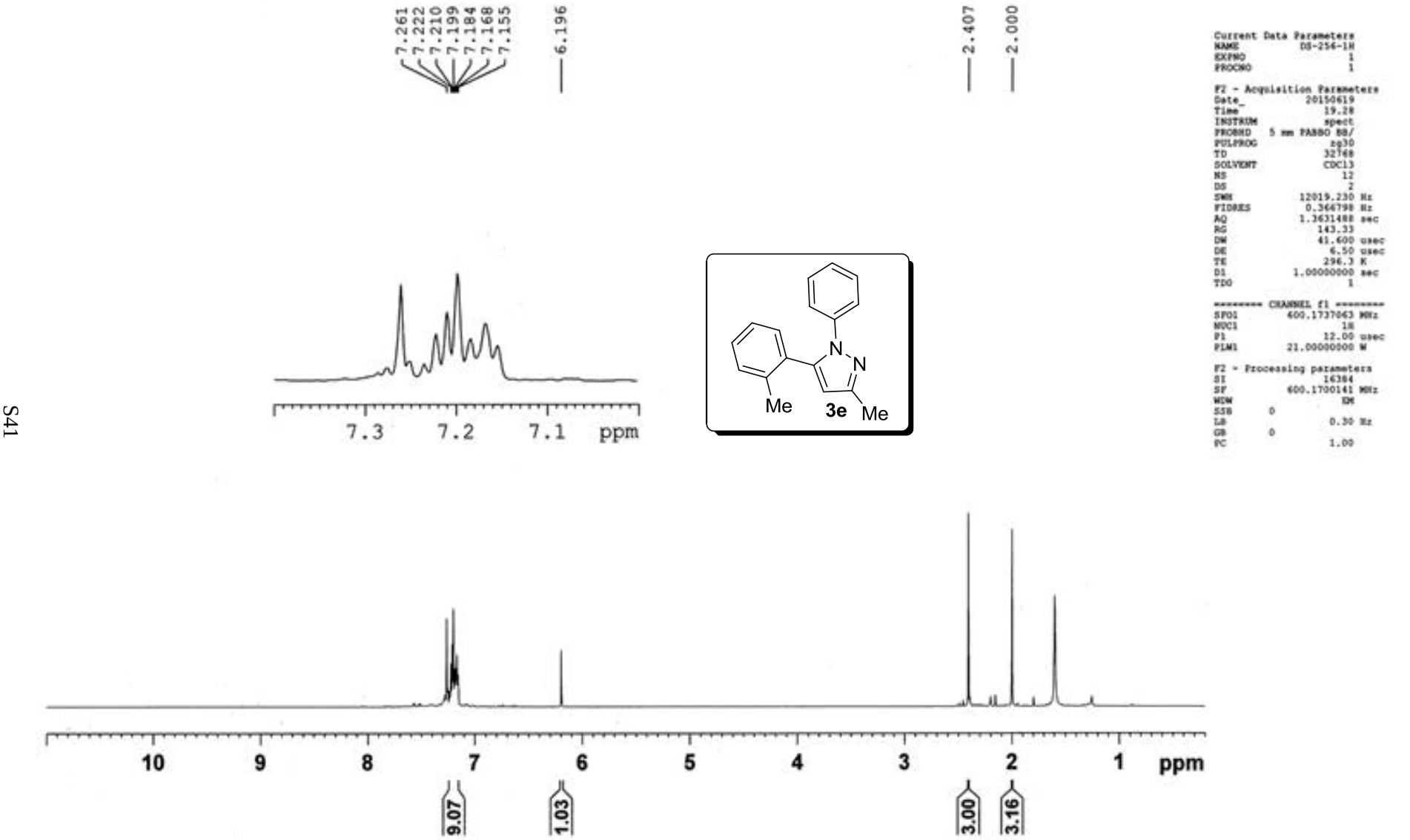
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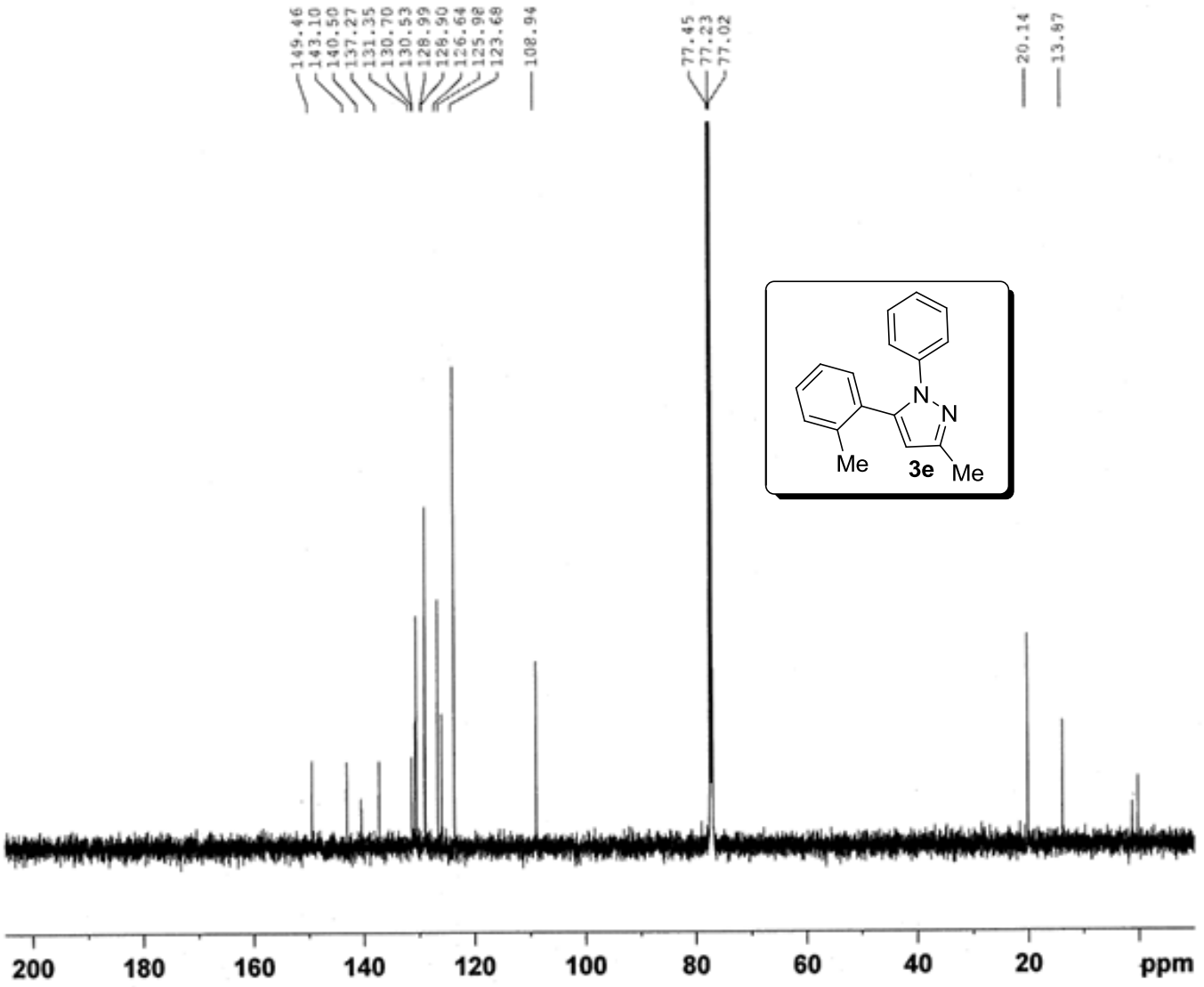

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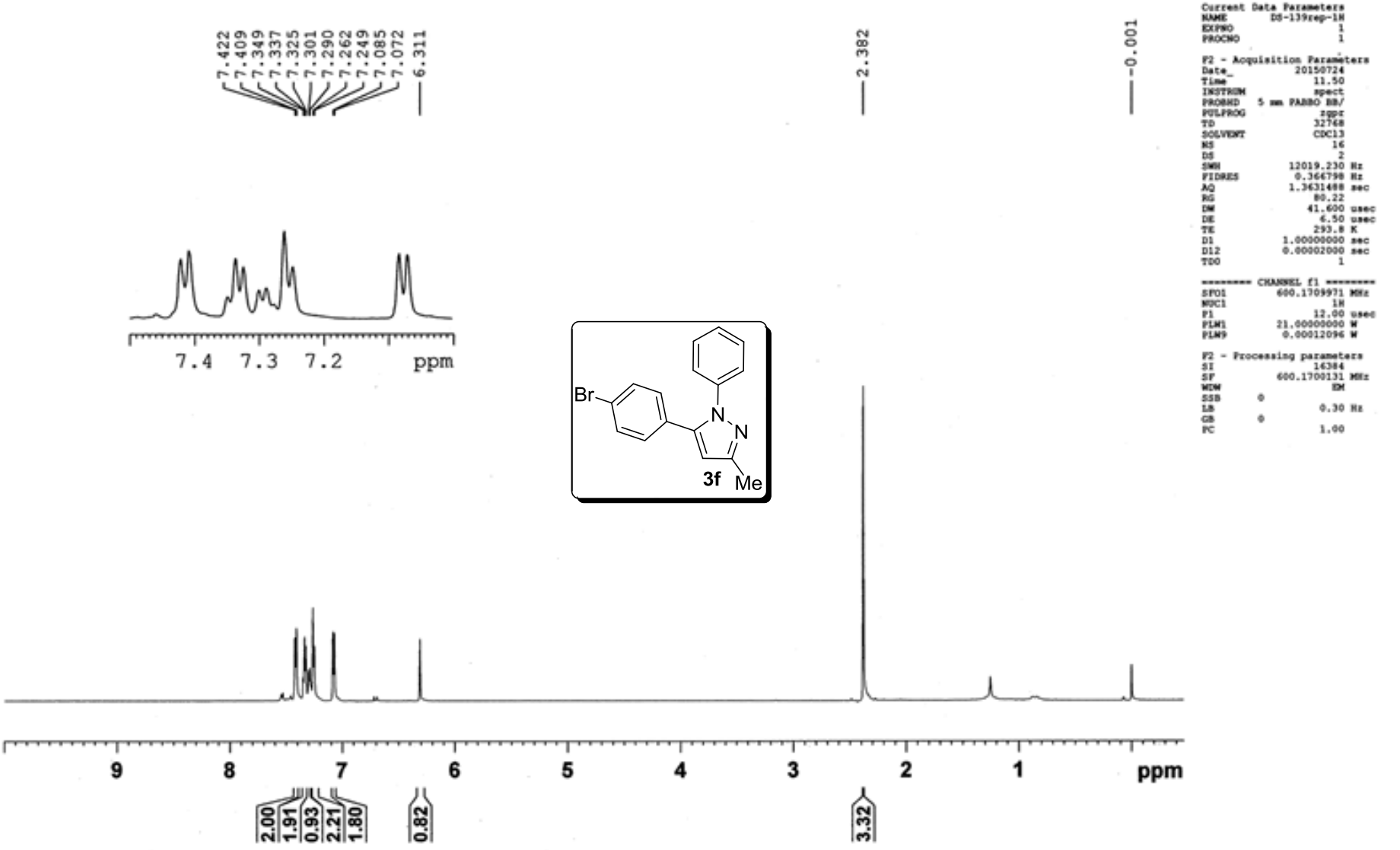
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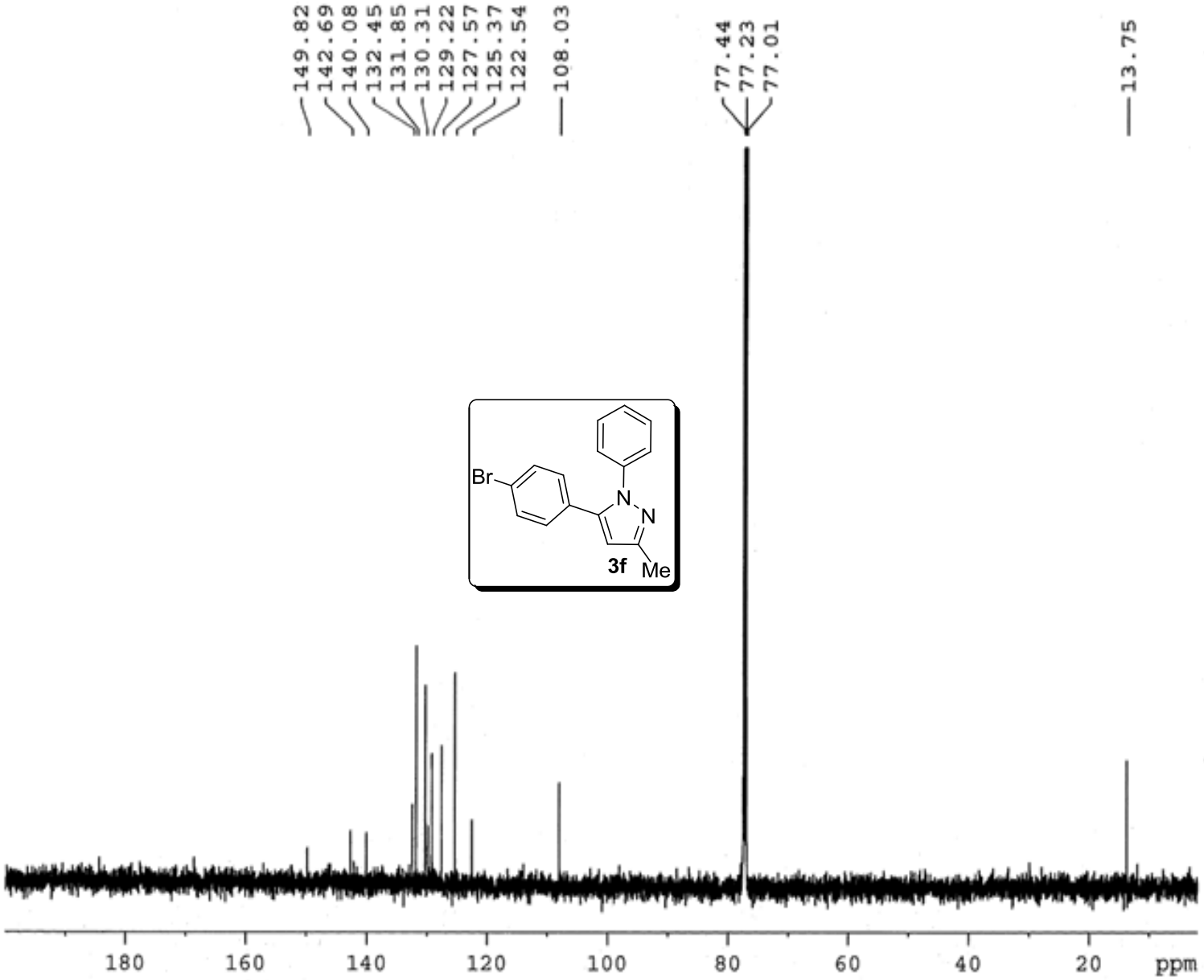


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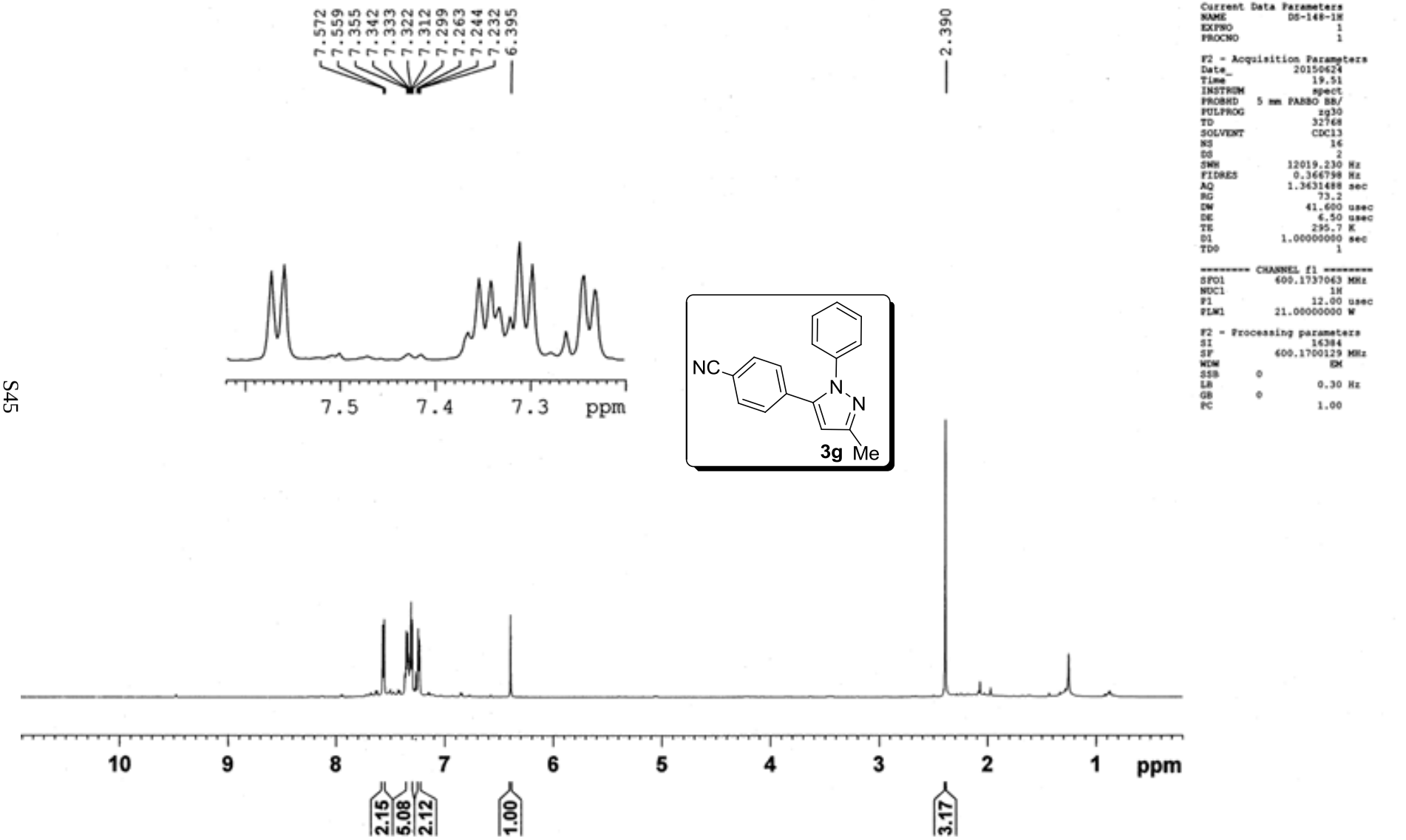
PLW1        95.00000000 W

======== CHANNEL f2 ========
SFO2        600.1724007 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             70.00 usec
PLW2        21.00000000 W
PLW12        0.61714000 W
PLW13        0.30239999 W

F2 - Processing parameters
SI                 16384
SF          150.9128365 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

DS-148-1H



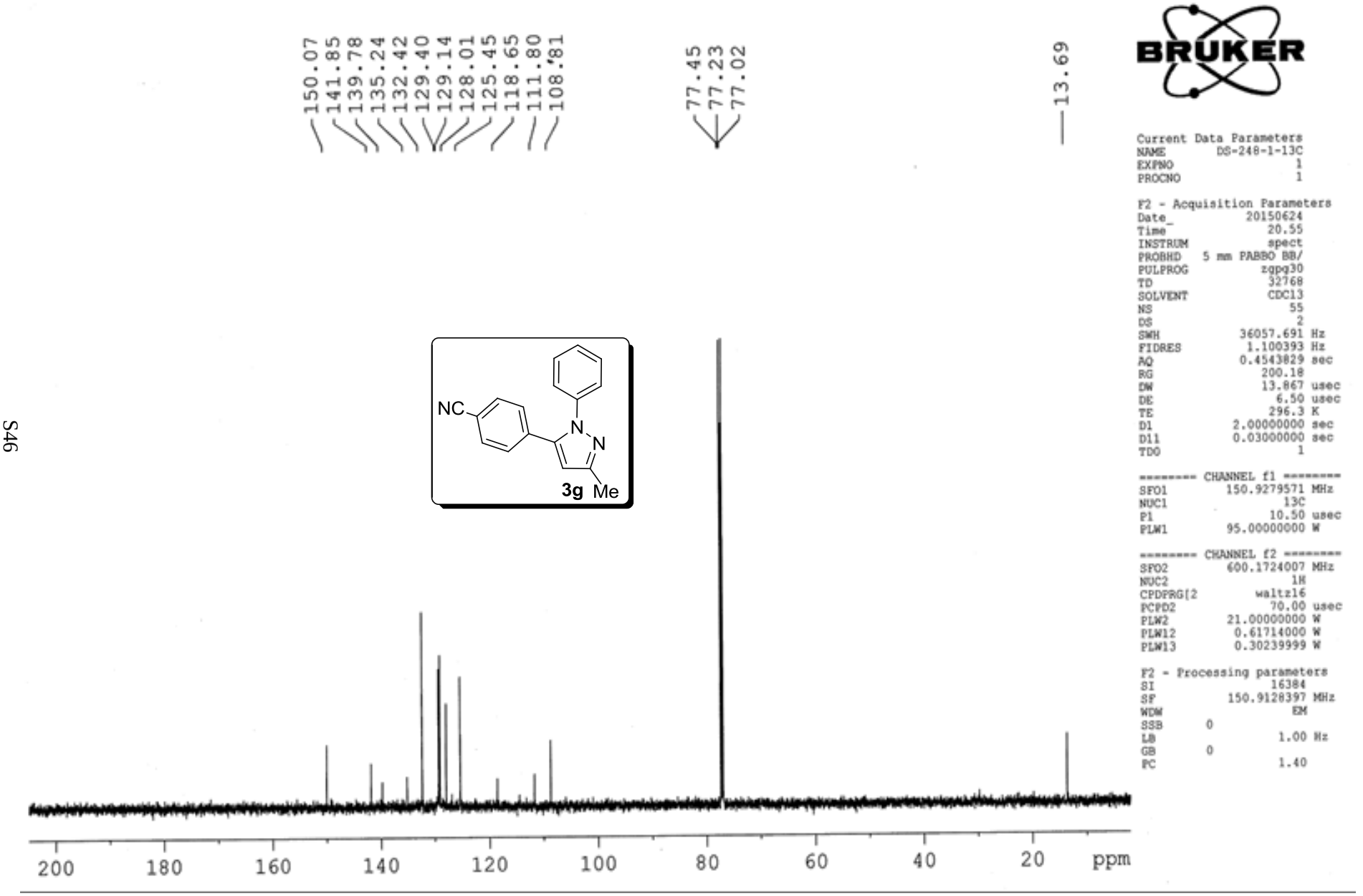

```
Current Data Parameters
NAME                  DS-148-1H
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_              20150624
Time                   19.51
INSTRUM                spect
PROBHD    5 mm PABBO BB/
PULPROG                zg30
TD                    32768
SOLVENT                CDCl3
NS                        16
DS                         2
SWH               12019.230 Hz
FIDRES             0.366798 Hz
AQ                 1.3631488 sec
RG                      73.2
DW                    41.600 usec
DE                     6.50 usec
TE                    295.7 K
D1                 1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1          600.1737063 MHz
NUC1                      1H
P1                     12.00 usec
PLW1          21.00000000 W

F2 - Processing parameters
SI                     16384
SF            600.1700129 MHz
WDW                       EM
SSB                    0
LB                     0.30 Hz
GB                     0
PC                     1.00
```

DS-248-1-13C



BRUKER

Current Data Parameters
NAME DS-248-1-13C
EXPNO 1
PROCNO 1

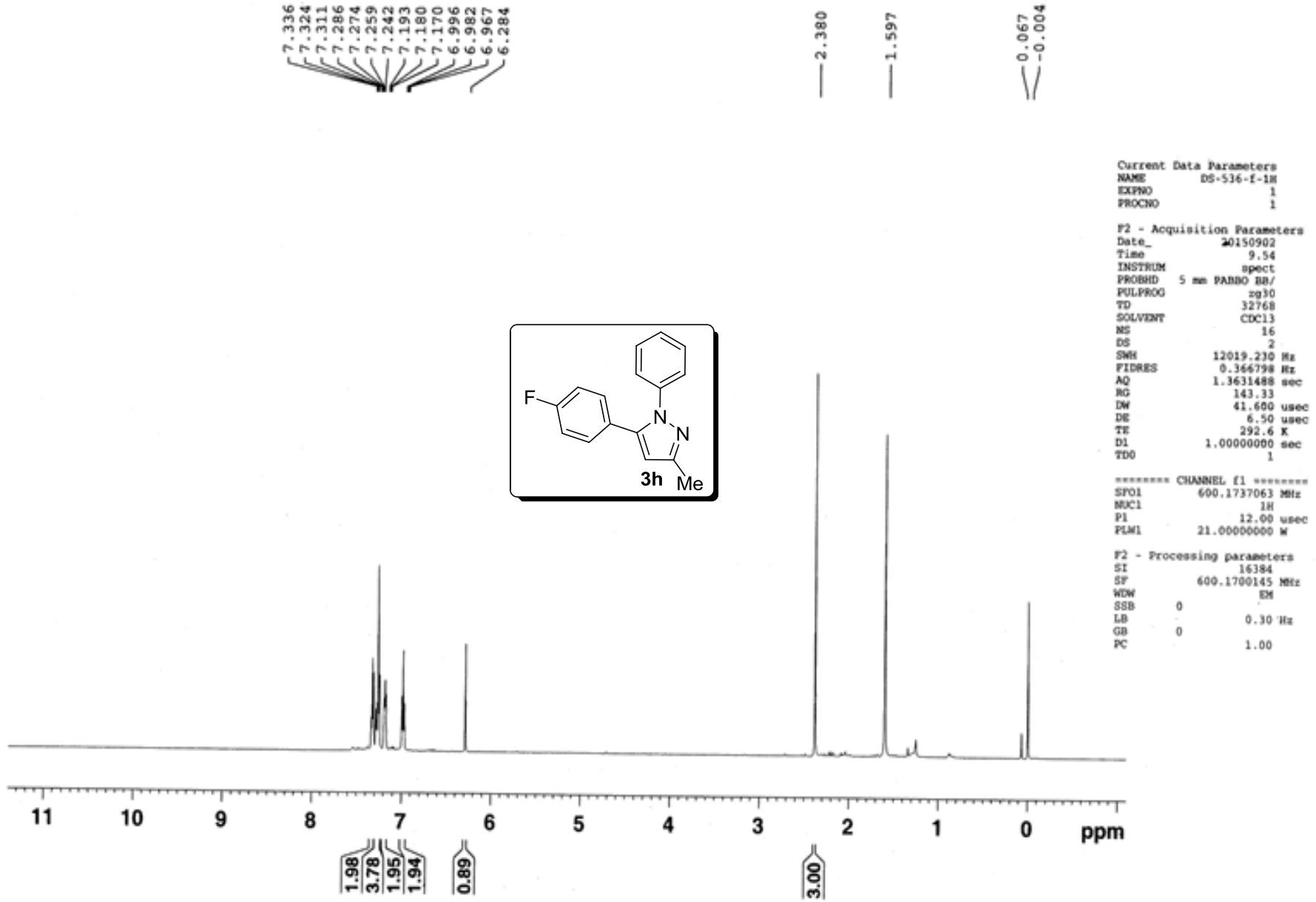
F2 - Acquisition Parameters
Date_ 20150624
Time 20.55
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 55
DS 2
SWH 36057.691 Hz
FIDRES 1.100393 Hz
AQ 0.4543829 sec
RG 200.18
DW 13.867 usec
DE 6.50 usec
TE 296.3 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 150.9279571 MHz
NUC1 13C
P1 10.50 usec
PLW1 95.00000000 W

======== CHANNEL f2 ========
SFO2 600.1724007 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 70.00 usec
PLW2 21.00000000 W
PLW12 0.61714000 W
PLW13 0.30239999 W

F2 - Processing parameters
SI 16384
SF 150.9128397 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

DS-536-f-1H



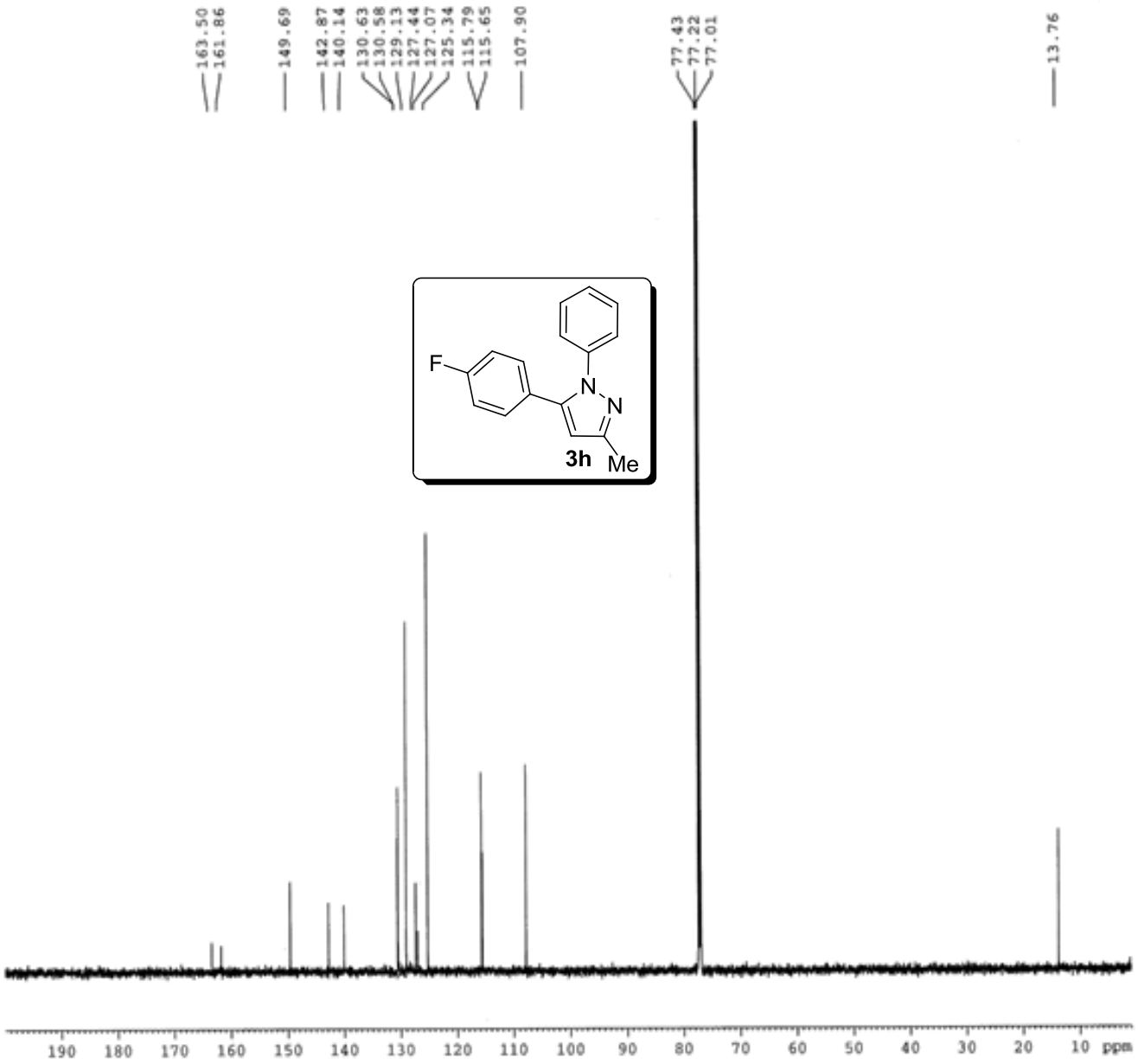
Current Data Parameters
NAME DS-536-f-1H
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150902
Time 9.54
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 12019.230 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 143.33
DW 41.600 usec
DE 6.50 usec
TE 292.6 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 600.1737063 MHz
NUC1 1H
P1 12.00 usec
PLW1 21.00000000 W

F2 - Processing parameters
SI 16384
SF 600.1700145 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

DS-536_13C



BRUKER

```
Current Data Parameters
NAME                  DS-536_13C
EXPNO                          1
PROCNO                         1

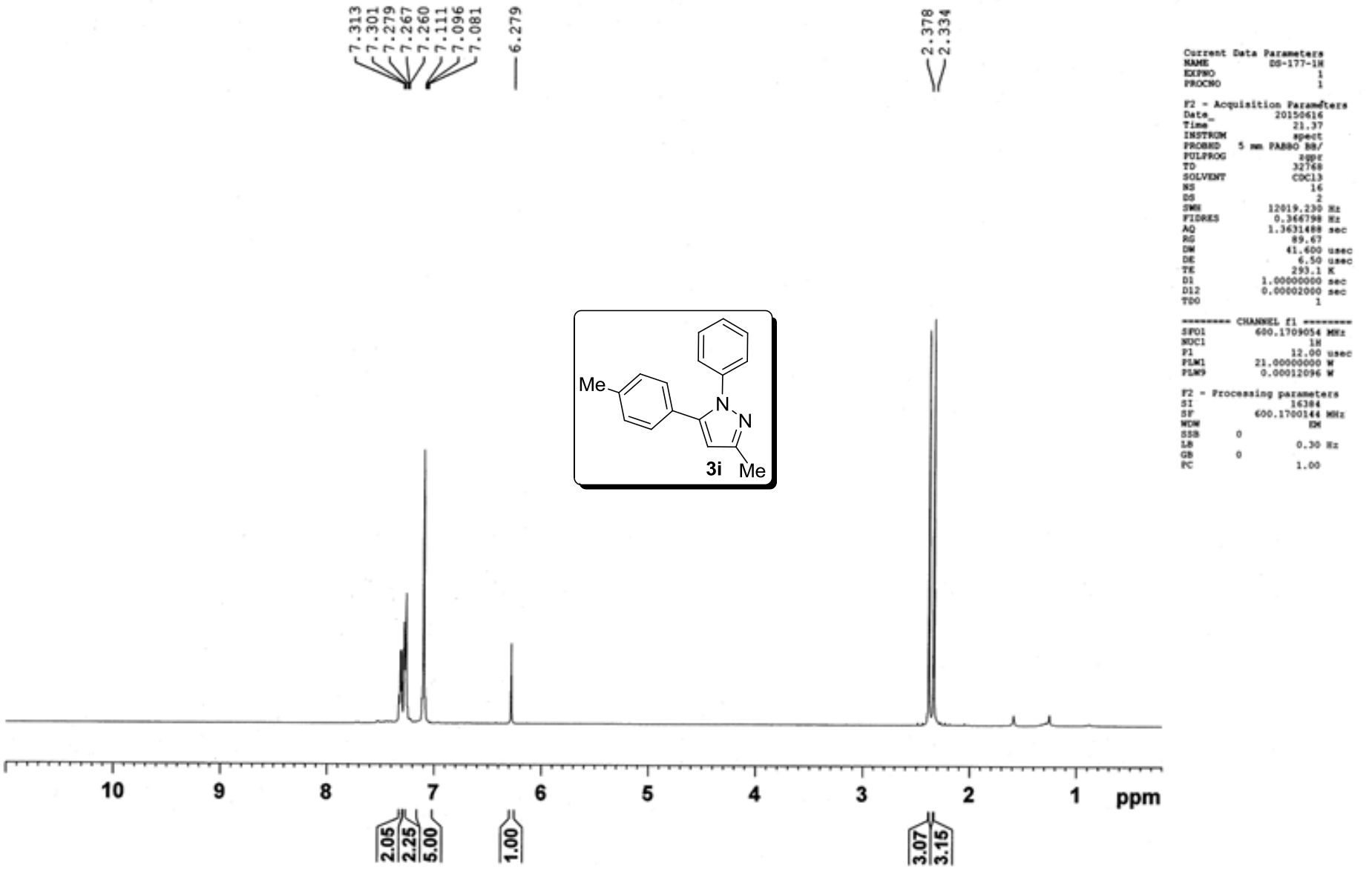
F2 - Acquisition Parameters
Date_                   20150901
Time                       13.41
INSTRUM                    spect
PROBHD   5 mm PABBO BB/
PULPROG                   zgpg30
TD                         32768
SOLVENT                    CDCl3
NS                           548
DS                             2
SWH                    42613.637 Hz
FIDRES                  1.300465 Hz
AQ                     0.3844779 sec
RG                         65.24
DW                        11.733 usec
DE                          6.50 usec
TE                         293.6 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                            1

======== CHANNEL f1 ========
SFO1                150.9279571 MHz
NUC1                        13C
P1                        10.50 usec
PLW1                95.00000000 W

======== CHANNEL f2 ========
SFO2                600.1724007 MHz
NUC2                        1H
CPDPRG[2                waltz16
PCPD2                     70.00 usec
PLW2                21.00000000 W
PLW12                0.61714000 W
PLW13                0.30239999 W

F2 - Processing parameters
SI                         16384
SF                  150.9128378 MHz
WDW                           EM
SSB                0
LB                         1.00 Hz
GB                 0
PC                         1.40
```

DS-177-1H



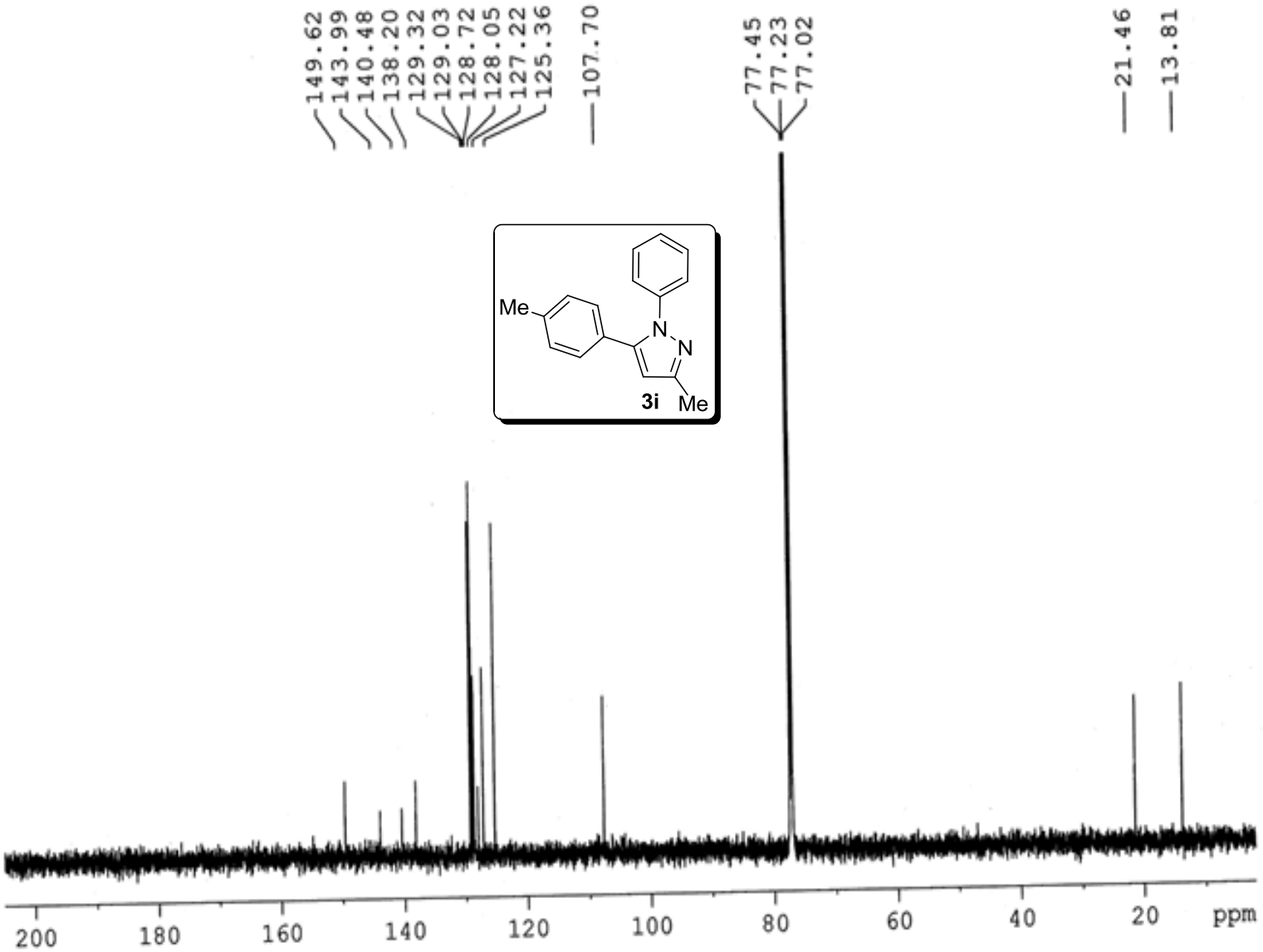

```
Current Data Parameters
NAME                  DS-177-1H
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_              20150616
Time                      21.37
INSTRUM                   spect
PROBHD    5 mm PABBO BB/
PULPROG                   zgpr
TD                       32768
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                12019.230 Hz
FIDRES              0.366798 Hz
AQ                  1.3631488 sec
RG                      89.67
DW                     41.600 usec
DE                      6.50 usec
TE                     293.1 K
D1                  1.00000000 sec
D12                 0.00002000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1               600.1709054 MHz
NDC1                        1H
P1                       12.00 usec
PLW1               21.00000000 W
PLW9                0.00012096 W

F2 - Processing parameters
SI                       16384
SF                 600.1700144 MHz
WDW                         EM
SSB          0
LB                        0.30 Hz
GB           0
PC                        1.00
```

DS-177-13C



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Current Data Parameters
NAME DS-177-13C
EXPNO 1
PROCNO 1

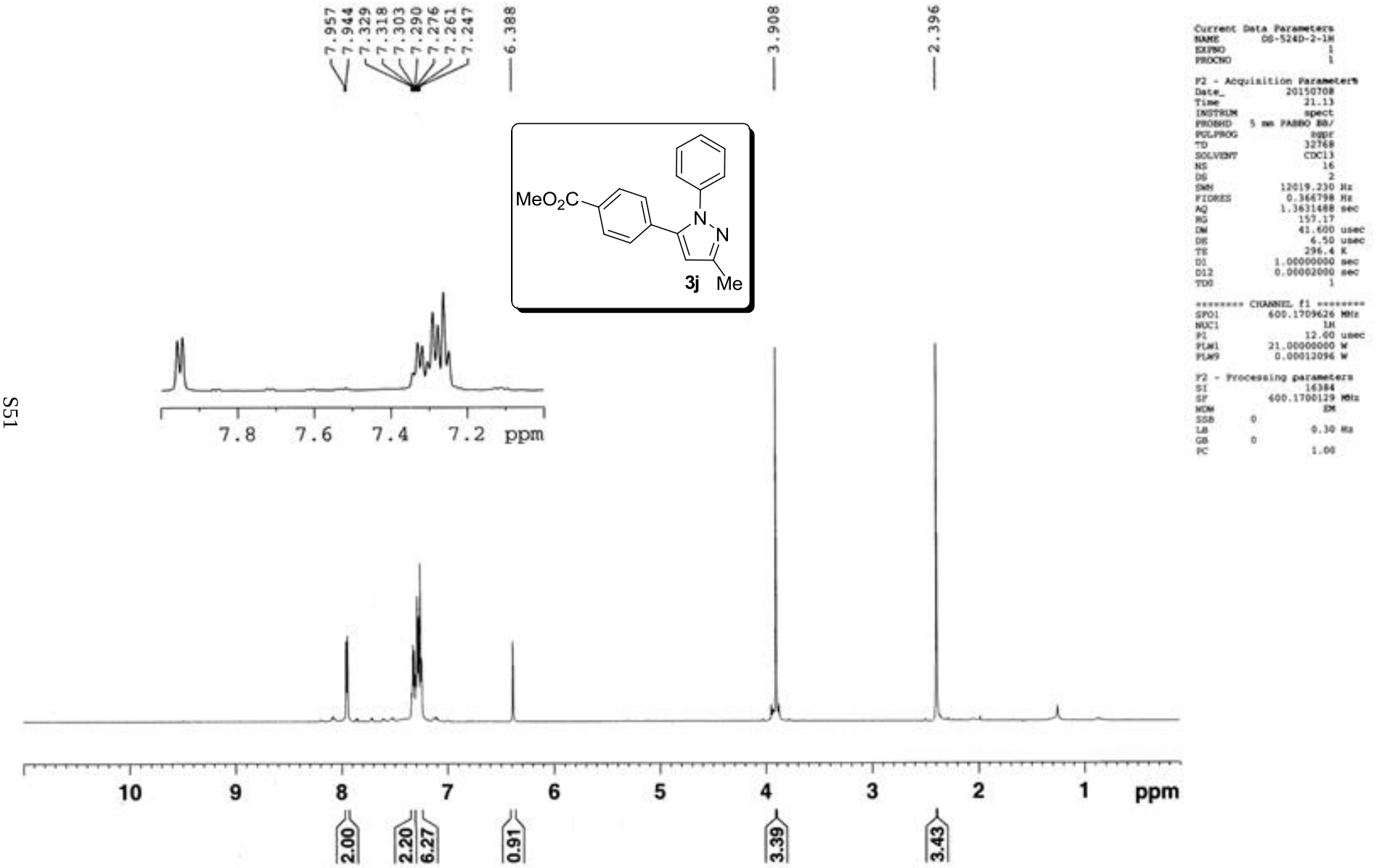
F2 - Acquisition Parameters
Date_ 20150616
Time 22.41
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 1203
DS 2
SWH 36057.691 Hz
FIDRES 1.100393 Hz
AQ 0.4543829 sec
RG 65.24
DW 13.867 usec
DE 6.50 usec
TE 293.8 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 150.9279571 MHz
NUC1 13C
P1 10.50 usec
PLW1 95.00000000 W

======== CHANNEL f2 ========
SFO2 600.1724007 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 70.00 usec
PLW2 21.00000000 W
PLW12 0.61714000 W
PLW13 0.30239999 W

F2 - Processing parameters
SI 16384
SF 150.9128347 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

DS-524D-2-1H



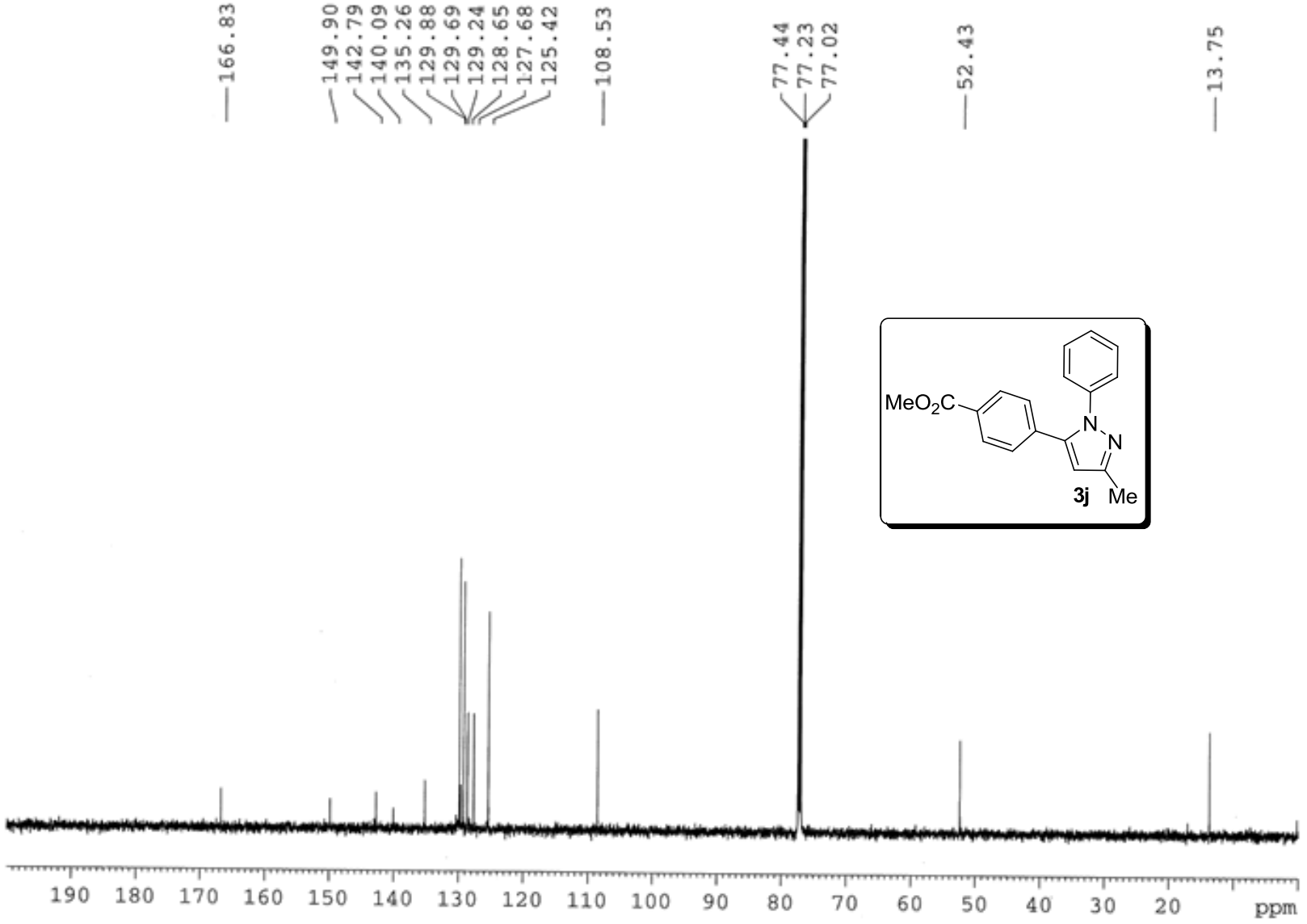

```
Current Data Parameters
NAME          DS-524D-2-1H
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_              20150708
Time                 21.13
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG              zgpr
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH             12019.230 Hz
FIDRES          0.366798 Hz
AQ              1.3631488 sec
RG                 157.17
DW                41.600 usec
DE                 6.50 usec
TE                296.4 K
D1              1.00000000 sec
D12             0.00002000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1           600.1709626 MHz
NUC1                   1H
P1                  12.00 usec
PLW1           21.00000000 W
PLW9            0.00012096 W

F2 - Processing parameters
SI                  16384
SF             600.1700129 MHz
WDW                    EM
SSB          0
LB                  0.30 Hz
GB           0
PC                  1.00
```

DS-524D-1-13C



BRUKER

Current Data Parameters
NAME DS-524D-1-13C
EXPNO 1
PROCNO 1

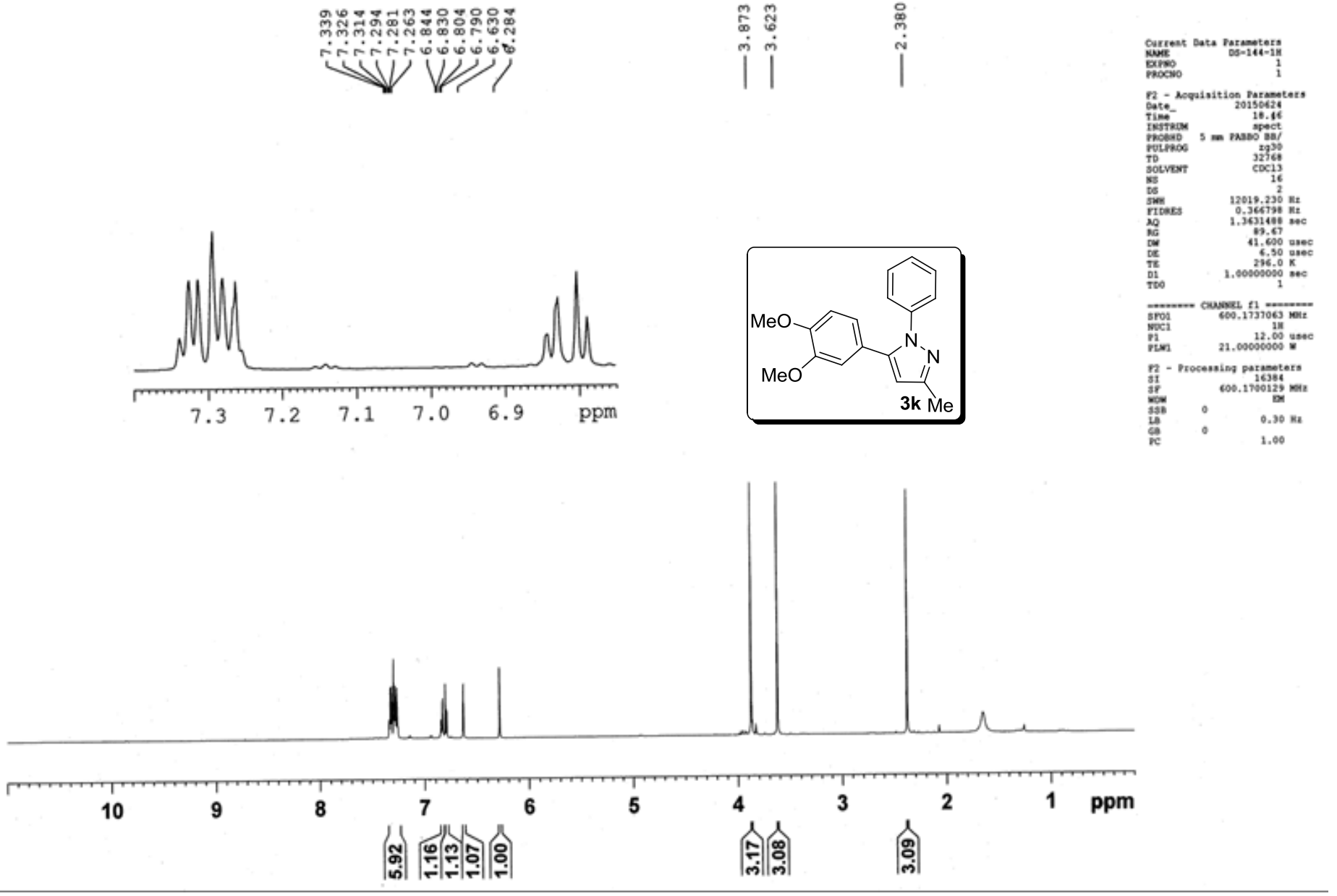
F2 - Acquisition Parameters
Date_ 20150825
Time 21.27
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 421
DS 2
SWH 42613.637 Hz
FIDRES 1.300465 Hz
AQ 0.3844779 sec
RG 65.24
DW 11.733 usec
DE 6.50 usec
TE 293.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 150.9279571 MHz
NUC1 13C
P1 10.50 usec
PLW1 95.00000000 W

======== CHANNEL f2 ========
SFO2 600.1724007 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 70.00 usec
PLW2 21.00000000 W
PLW12 0.61714000 W
PLW13 0.30239999 W

F2 - Processing parameters
SI 16384
SF 150.9128365 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

DS-144-1H



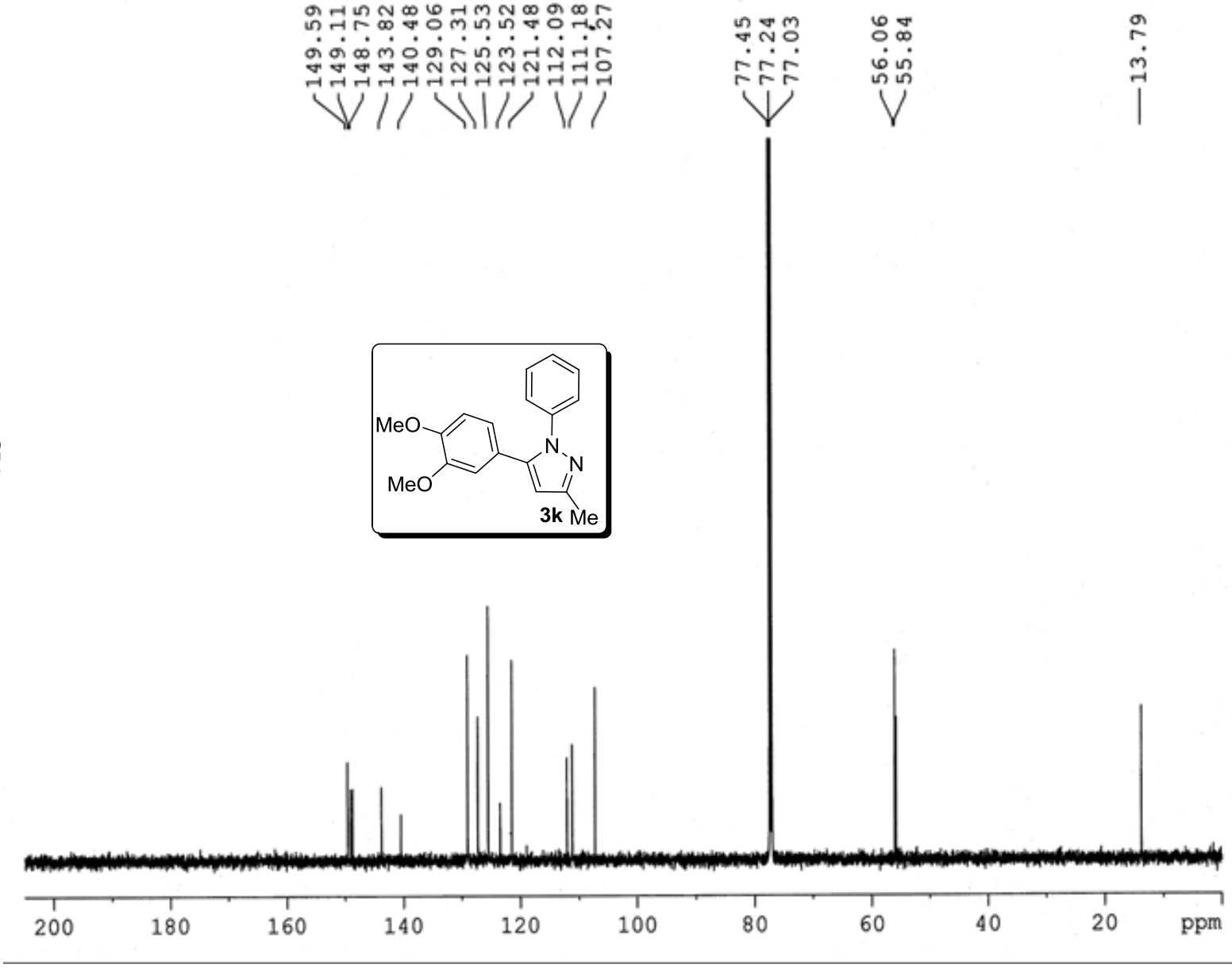
Current Data Parameters
NAME DS-144-1H
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150624
Time 18.46
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 12019.230 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 89.67
DW 41.600 usec
DE 6.50 usec
TE 296.0 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 600.1737063 MHz
NUC1 1H
P1 12.00 usec
PLW1 21.00000000 W

F2 - Processing parameters
SI 16384
SF 600.1700129 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

DS-144-13C



BRUKER

```
Current Data Parameters
NAME                  DS-144-13C
EXPNO                          1
PROCNO                         1

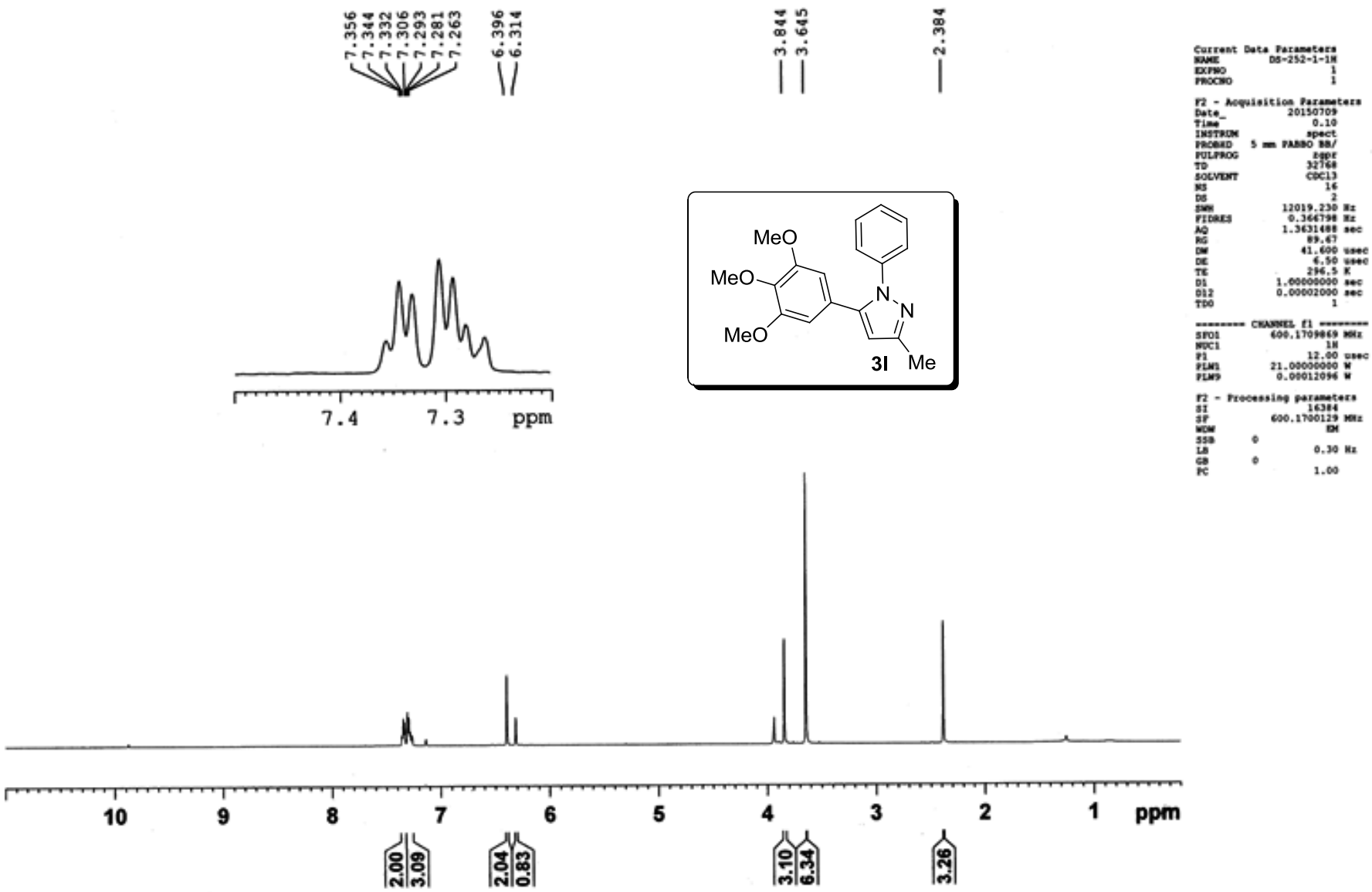
F2 - Acquisition Parameters
Date_                   20150624
Time                       18.48
INSTRUM                    spect
PROBHD     5 mm PABBO BB/
PULPROG                   zgpg30
TD                         32768
SOLVENT                    CDCl3
NS                           394
DS                             2
SWH                    36057.691 Hz
FIDRES                 1.100393 Hz
AQ                     0.4543829 sec
RG                         65.24
DW                        13.867 usec
DE                          6.50 usec
TE                         296.3 K
D1                     2.00000000 sec
D11                    0.03000000 sec
TD0                            1

======== CHANNEL f1 ========
SFO1                 150.9279571 MHz
NUC1                         13C
P1                         10.50 usec
PLW1                95.00000000 W

======== CHANNEL f2 ========
SFO2                 600.1724007 MHz
NUC2                         1H
CPDPRG[2                waltz16
PCPD2                      70.00 usec
PLW2                21.00000000 W
PLW12                0.61714000 W
PLW13                0.30239999 W

F2 - Processing parameters
SI                         16384
SF                   150.9128346 MHz
WDW                           EM
SSB                0
LB                          1.00 Hz
GB                 0
PC                          1.40
```

DS-252-1-1H

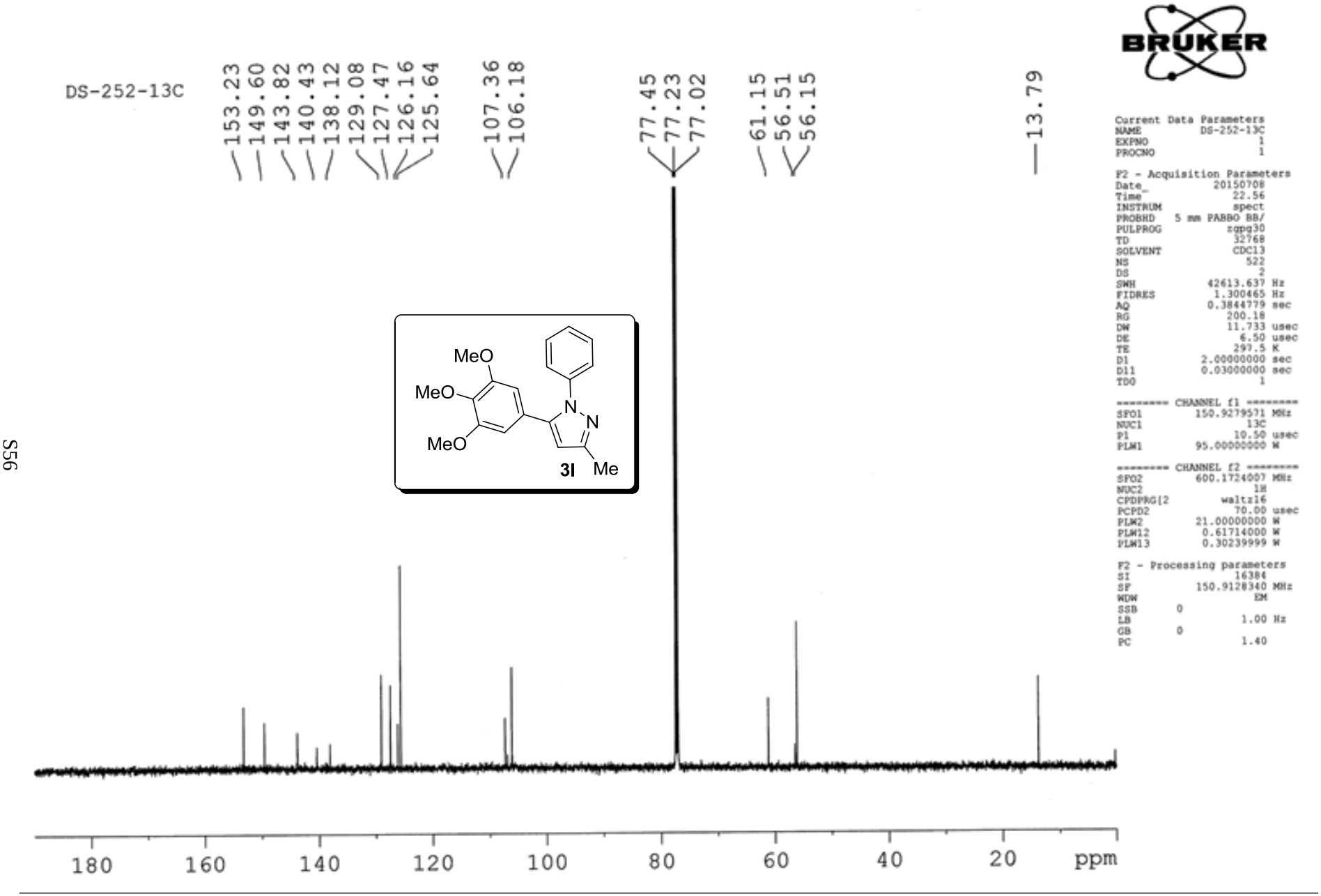



```
Current Data Parameters
NAME            DS-252-1-1H
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20150709
Time                   0.10
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG               zgpr
TD                   32768
SOLVENT              CDCl3
NS                      16
DS                       2
SWH             12019.230 Hz
FIDRES              0.366798 Hz
AQ                1.3631488 sec
RG                    89.67
DW                   41.600 usec
DE                    6.50 usec
TE                  296.5 K
D1                1.00000000 sec
D12               0.00002000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1            600.1709869 MHz
NUC1                     1H
P1                    12.00 usec
PLW1             21.00000000 W
PLW9              0.00012096 W

F2 - Processing parameters
SI                       16384
SF              600.1700129 MHz
WDW                        EM
SSB                   0
LB                    0.30 Hz
GB                    0
PC                    1.00
```



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```
Current Data Parameters
NAME                 DS-252-13C
EXPNO                         1
PROCNO                        1

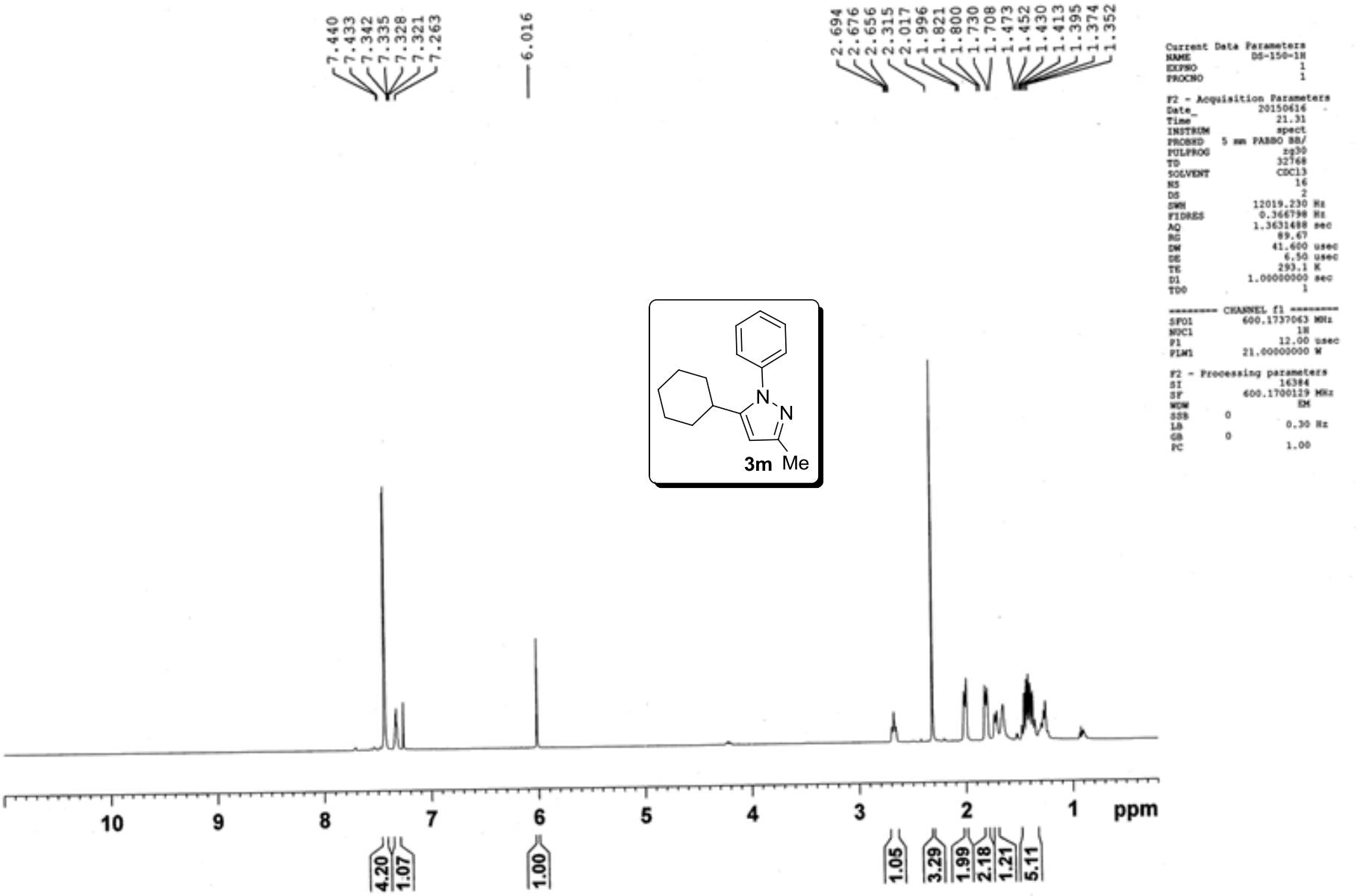
F2 - Acquisition Parameters
Date_               20150708
Time                   22.56
INSTRUM                spect
PROBHD    5 mm PABBO BB/
PULPROG              zgpg30
TD                    32768
SOLVENT               CDCl3
NS                      522
DS                        2
SWH                42613.637 Hz
FIDRES             1.300465 Hz
AQ                 0.3844779 sec
RG                    200.18
DW                    11.733 usec
DE                      6.50 usec
TE                     299.5 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                           1

======== CHANNEL f1 ========
SFO1               150.9279571 MHz
NUC1                       13C
P1                       10.50 usec
PLW1               95.00000000 W

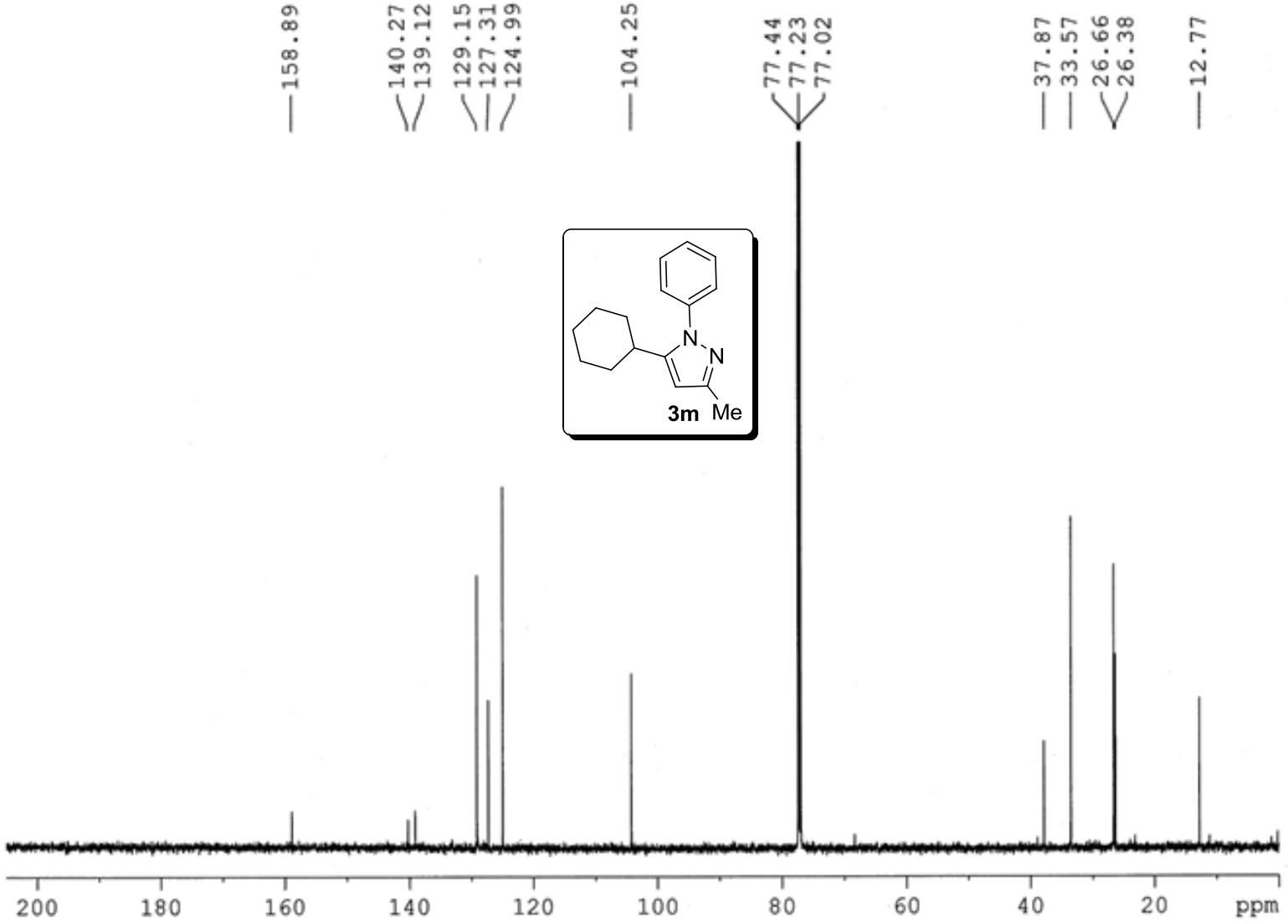
======== CHANNEL f2 ========
SFO2               600.1724007 MHz
NUC2                       1H
CPDPRG[2                waltz16
PCPD2                    70.00 usec
PLW2               21.00000000 W
PLW12               0.61714000 W
PLW13               0.30239999 W

F2 - Processing parameters
SI                        16384
SF                 150.9128340 MHz
WDW                          EM
SSB                   0
LB                        1.00 Hz
GB                    0
PC                        1.40
```

DS-150-1H


7.440
7.433
7.342
7.335
7.328
7.321
7.263
6.016
2.694
2.676
2.656
2.315
2.017
1.996
1.821
1.800
1.730
1.708
1.473
1.452
1.430
1.413
1.395
1.374
1.352
Current Data Parameters
NAME DS-150-1H
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20150616
Time 21.31
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 12019.230 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 89.67
DW 41.600 usec
DE 6.50 usec
TE 293.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 600.1737063 MHz
NUC1 1H
P1 12.00 usec
PLW1 21.00000000 W
F2 - Processing parameters
SI 16384
SF 600.1700129 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
N
N
3m Me
10
9
8
7
6
5
4
3
2
1
ppm
4.20
1.07
1.00
1.05
3.29
1.99
2.18
1.21
5.11

DS-150-13C



BRUKER

Current Data Parameters
NAME DS-150-13C
EXPNO 1
PROCNO 1

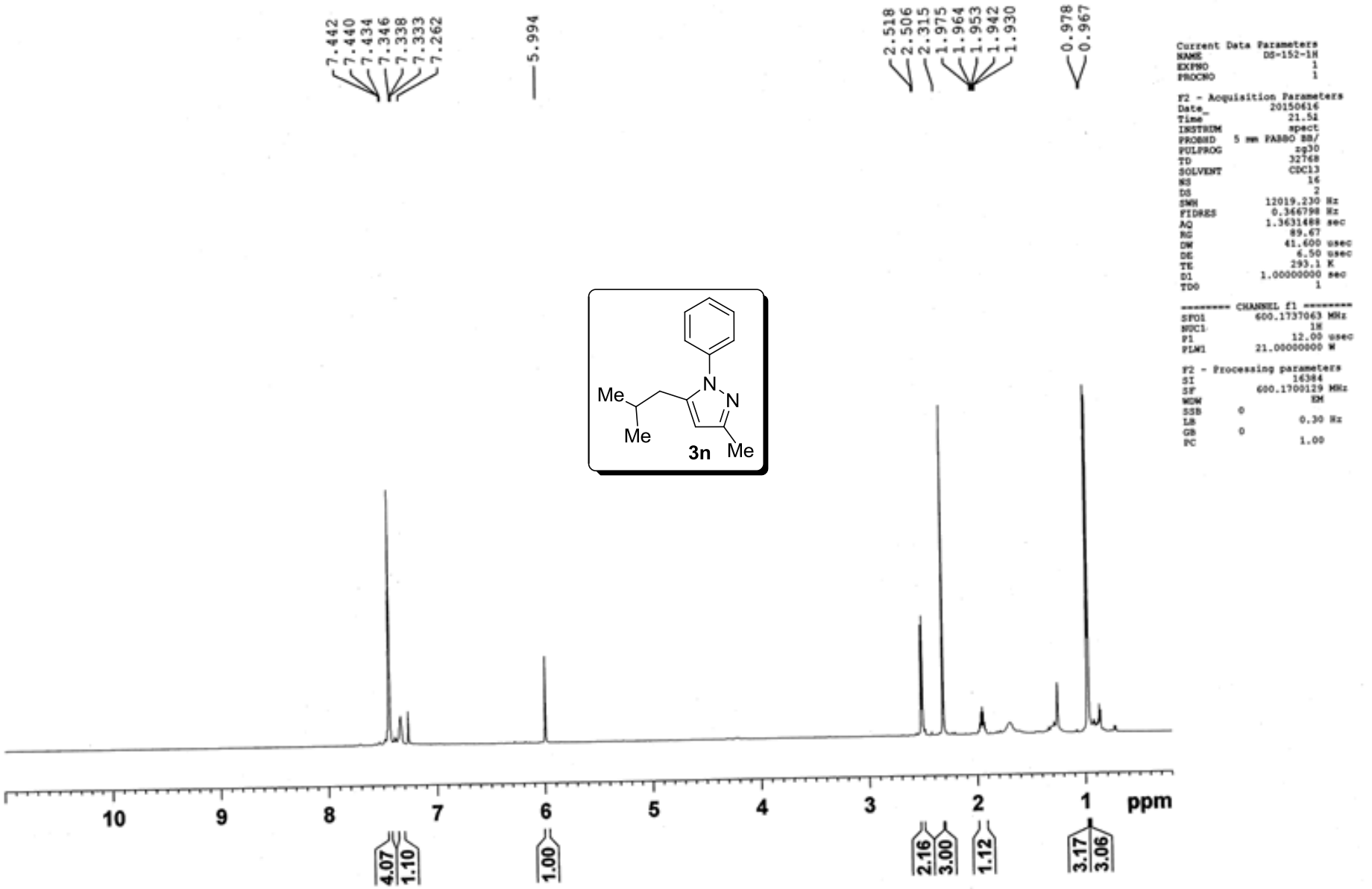
F2 - Acquisition Parameters
Date_ 20150616
Time 22.10
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 515
DS 2
SWH 36057.691 Hz
FIDRES 1.100393 Hz
AQ 0.4543829 sec
RG 65.24
DW 13.867 usec
DE 6.50 usec
TE 294.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 150.9279571 MHz
NUC1 13C
P1 10.50 usec
PLW1 95.00000000 W

======== CHANNEL f2 ========
SFO2 600.1724007 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 70.00 usec
PLW2 21.00000000 W
PLW12 0.61714000 W
PLW13 0.30239999 W

F2 - Processing parameters
SI 16384
SF 150.9128367 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

DS-152-1H



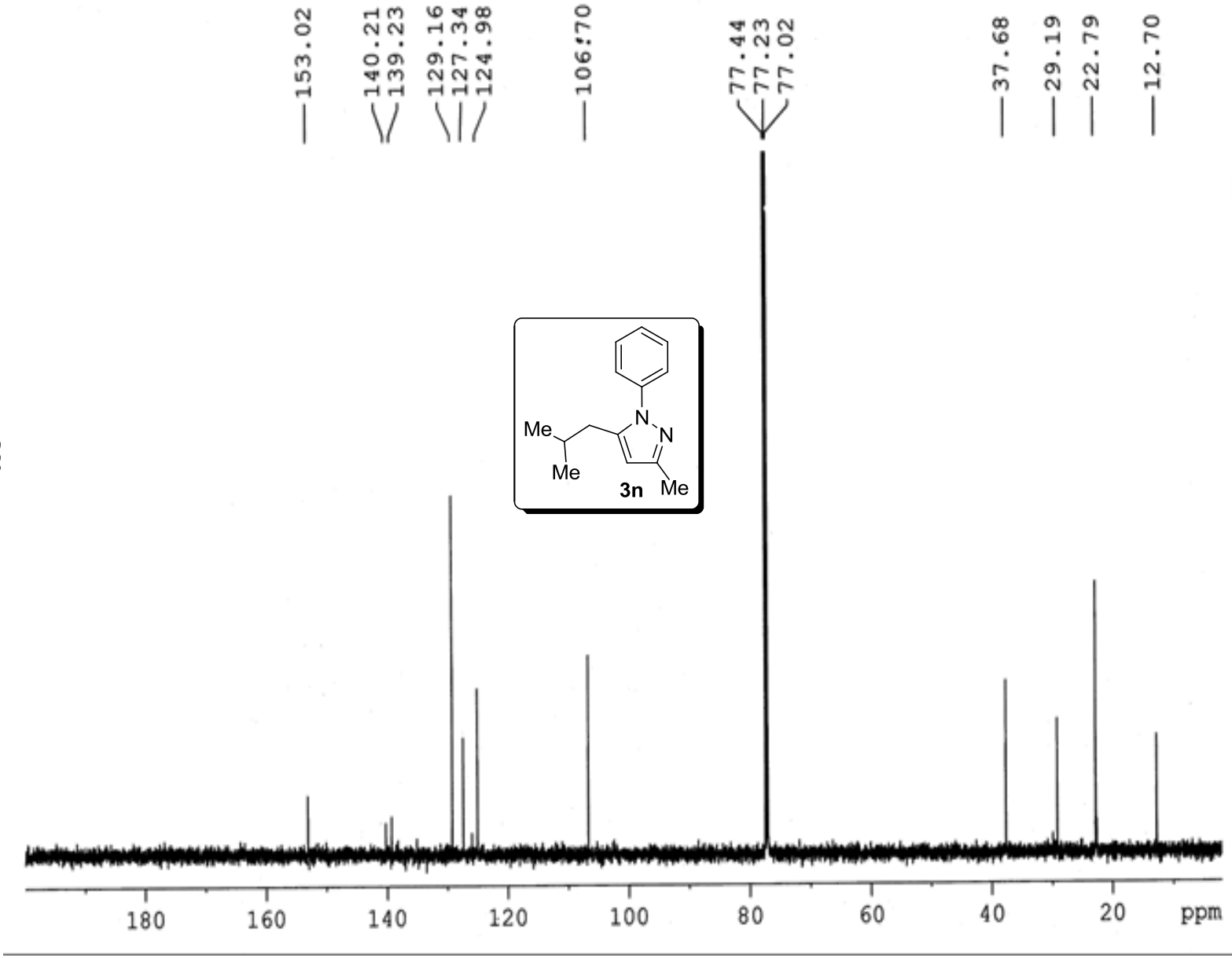

```
Current Data Parameters
NAME                  DS-152-1H
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_               20150616
Time                      21.51
INSTRUM                   spect
PROBHD   5 mm PABBO BB/
PULPROG                   zg30
TD                       32768
SOLVENT                  CDCl3
NS                           16
DS                            2
SWH                 12019.230 Hz
FIDRES               0.366798 Hz
AQ                   1.3631488 sec
RG                       89.67
DW                     41.600 usec
DE                      6.50 usec
TE                     293.1 K
D1                  1.00000000 sec
TD0                           1

======== CHANNEL f1 ========
SFO1               600.1737063 MHz
NUC1                       1H
P1                      12.00 usec
PLW1               21.00000000 W

F2 - Processing parameters
SI                        16384
SF                 600.1700129 MHz
WDW                          EM
SSB                   0
LB                      0.30 Hz
GB                    0
PC                      1.00
```

DS-152-13C



BRUKER

Current Data Parameters
NAME DS-152-13C
EXPNO 1
PROCNO 1

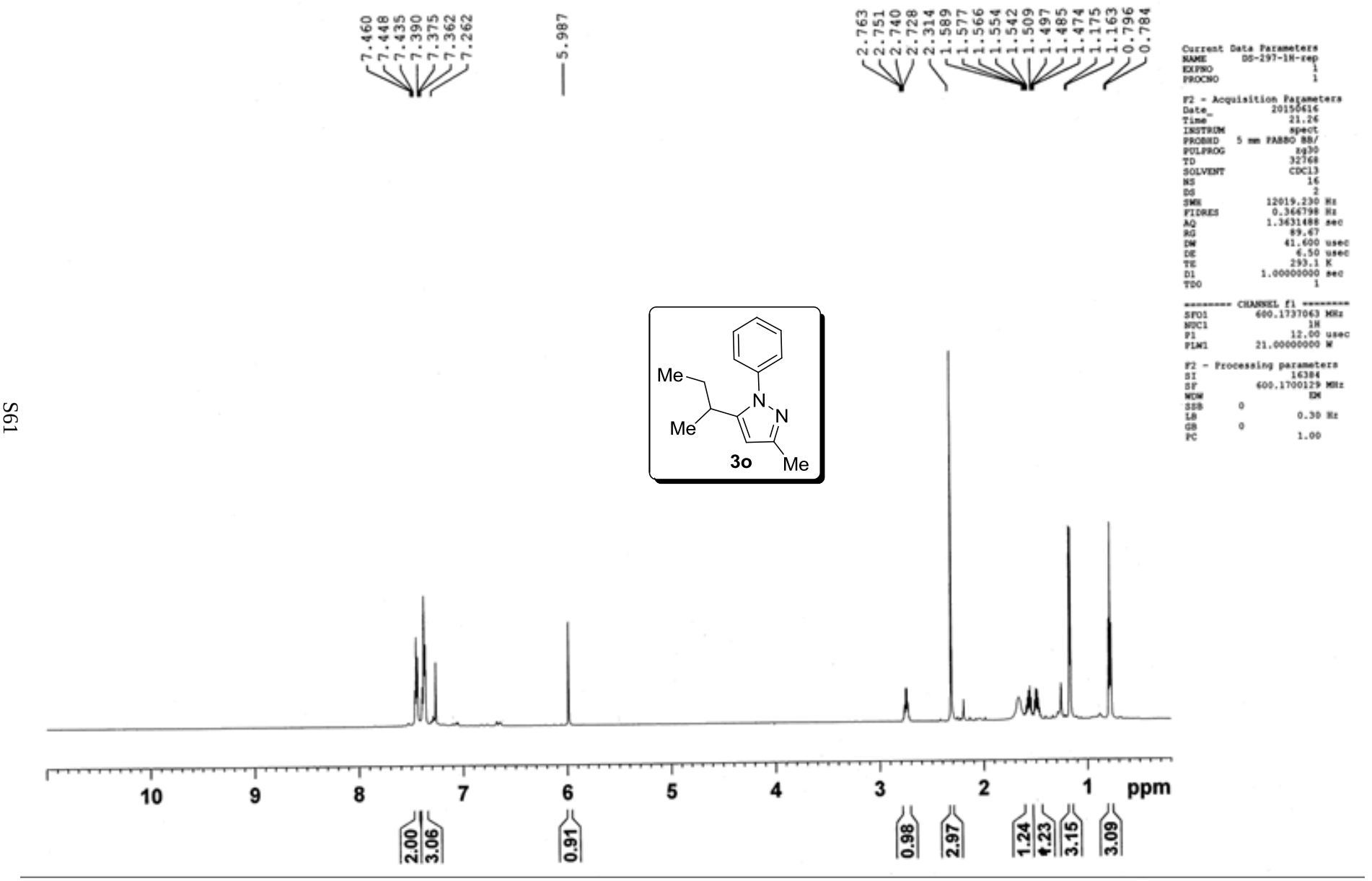
F2 - Acquisition Parameters
Date_ 20150617
Time 0.03
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 128
DS 2
SWH 36057.691 Hz
FIDRES 1.100393 Hz
AQ 0.4543829 sec
RG 200.18
DW 13.867 usec
DE 6.50 usec
TE 293.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 150.9279571 MHz
NUC1 13C
P1 10.50 usec
PLW1 95.00000000 W

======== CHANNEL f2 ========
SFO2 600.1724007 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 70.00 usec
PLW2 21.00000000 W
PLW12 0.61714000 W
PLW13 0.30239999 W

F2 - Processing parameters
SI 16384
SF 150.9128369 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

DS-297-1H-rep



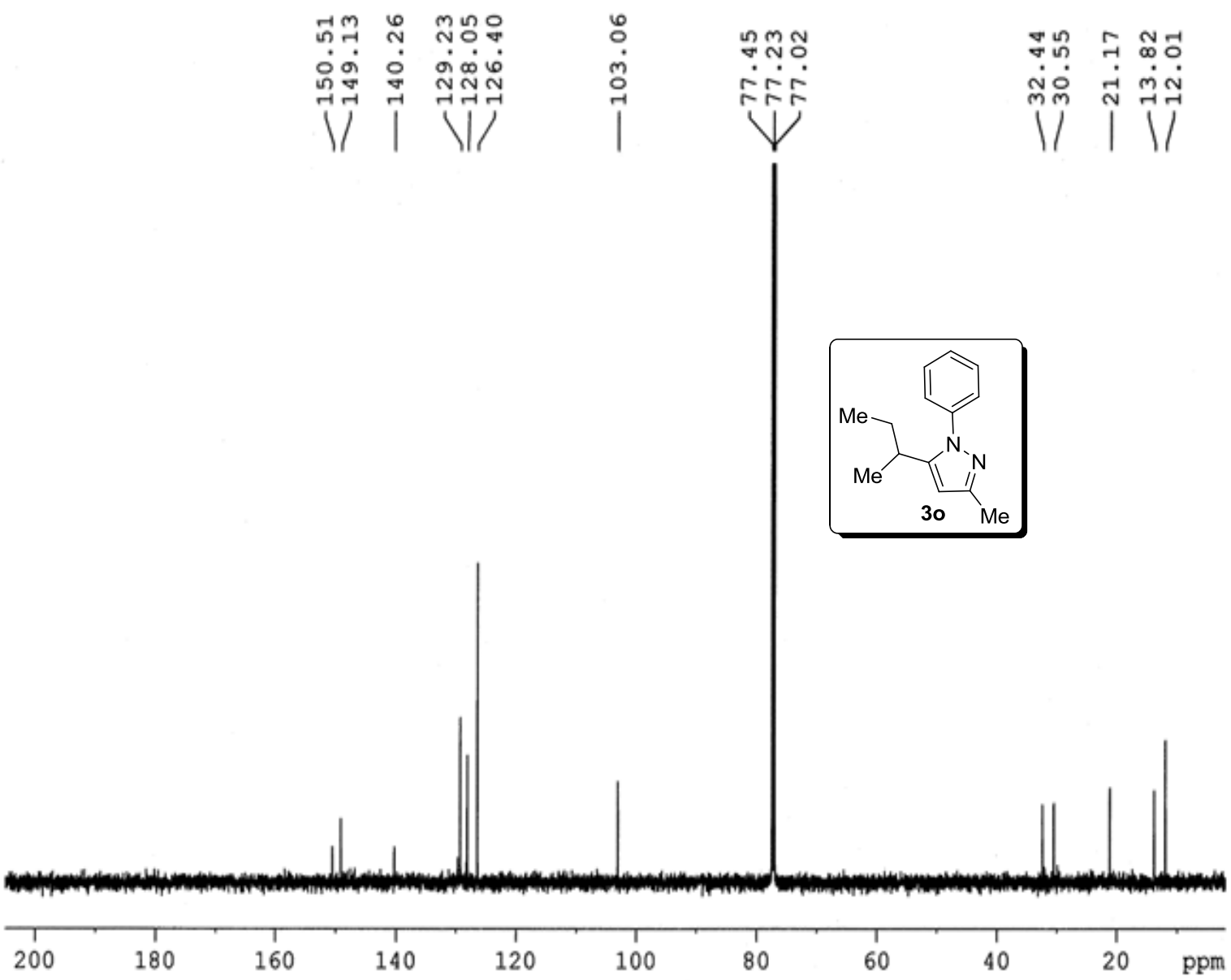
Current Data Parameters
NAME DS-297-1H-rep
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150416
Time 21.26
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 12019.230 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 89.47
DW 41.600 usec
DE 6.50 usec
TE 293.1 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 600.1737063 MHz
NUC1 1H
P1 12.00 usec
PLW1 21.00000000 W

F2 - Processing parameters
SI 16384
SF 600.1700129 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

DS-297-13C




```
Current Data Parameters
NAME            DS-297-13C
EXPNO                    1
PROCNO                   1

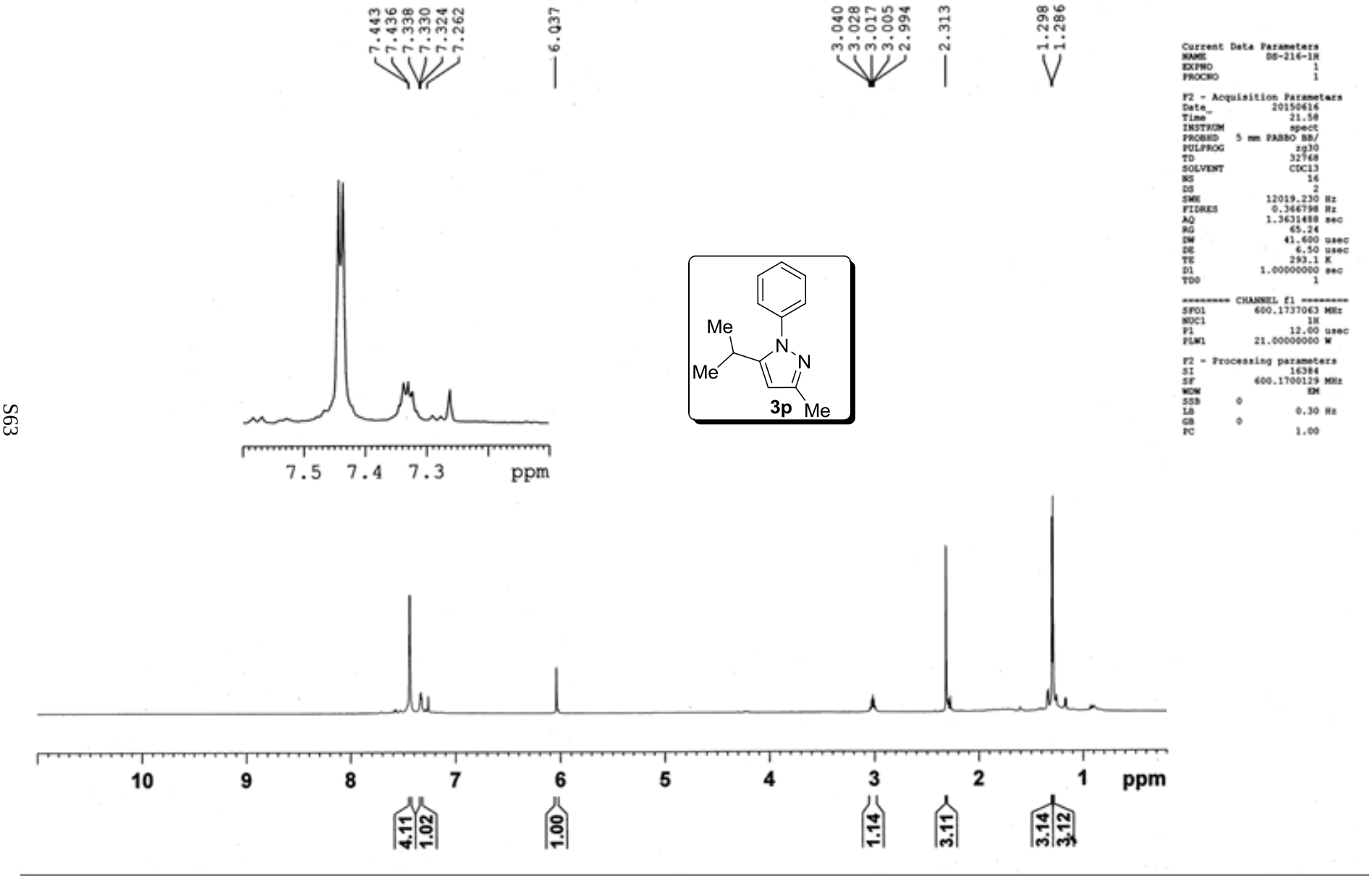
F2 - Acquisition Parameters
Date_             20150708
Time                 23.19
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                 32768
SOLVENT              CDCl3
NS                     210
DS                       2
SWH              42613.637 Hz
FIDRES            1.300465 Hz
AQ                0.3844779 sec
RG                    65.24
DW                 11.733 usec
DE                    6.50 usec
TE                   297.4 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1          150.9279571 MHz
NUC1                    13C
P1                   10.50 usec
PLW1          95.00000000 W

======== CHANNEL f2 ========
SFO2          600.1724007 MHz
NUC2                    1H
CPDPRG[2             waltz16
PCPD2                70.00 usec
PLW2          21.00000000 W
PLW12          0.61714000 W
PLW13          0.30239999 W

F2 - Processing parameters
SI                      16384
SF            150.9128341 MHz
WDW                        EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```

DS-216-1H



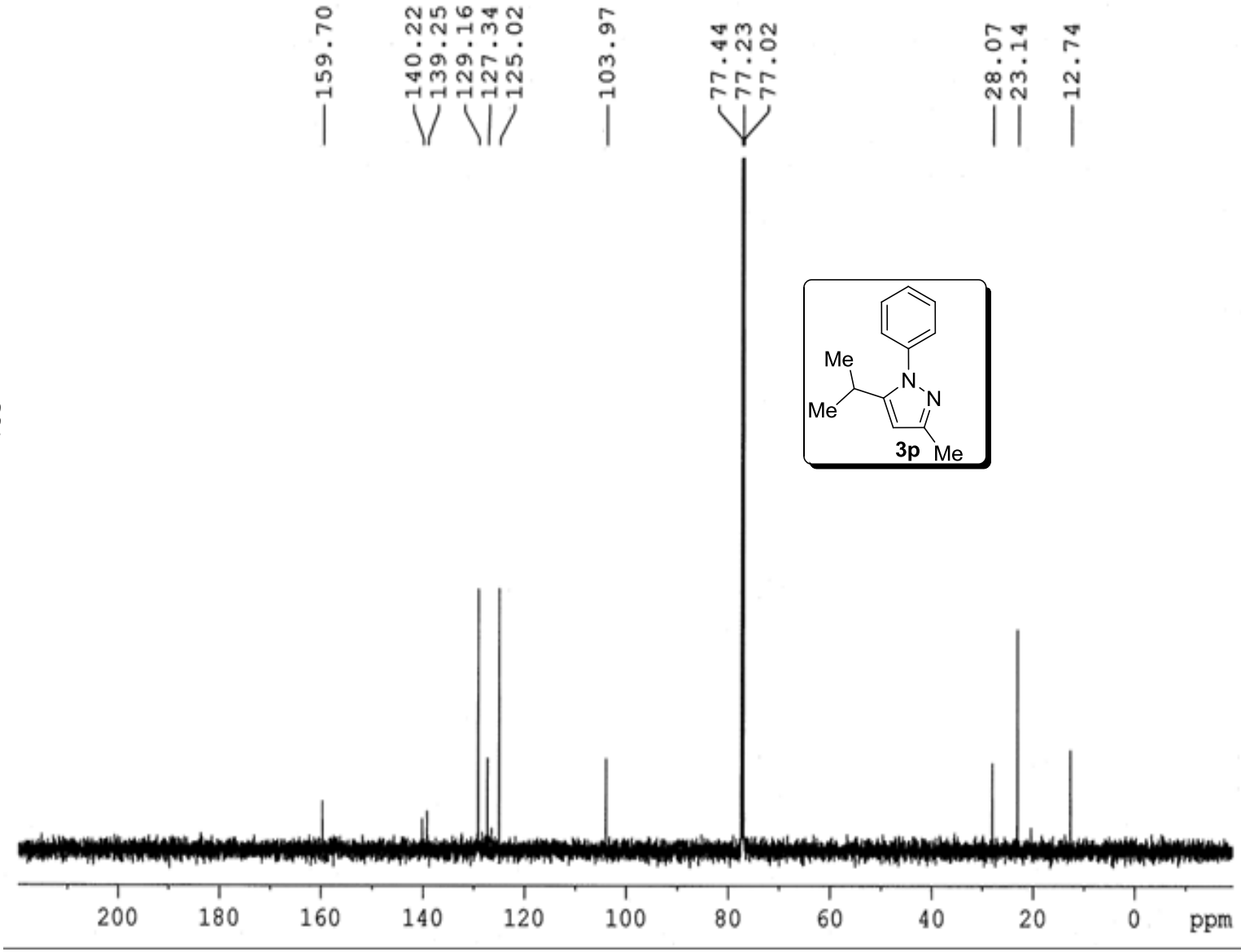
Current Data Parameters
NAME DS-216-1H
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150616
Time_ 21.58
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 12019.230 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 65.24
DW 41.600 usec
DE 6.50 usec
TE 293.1 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 600.1737063 MHz
NUC1 1H
P1 12.00 usec
PLW1 21.00000000 W

F2 - Processing parameters
SI 16384
SF 600.1700129 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

DS-177-13C-



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Current Data Parameters
NAME DS-177-13C-
EXPNO 1
PROCNO 1

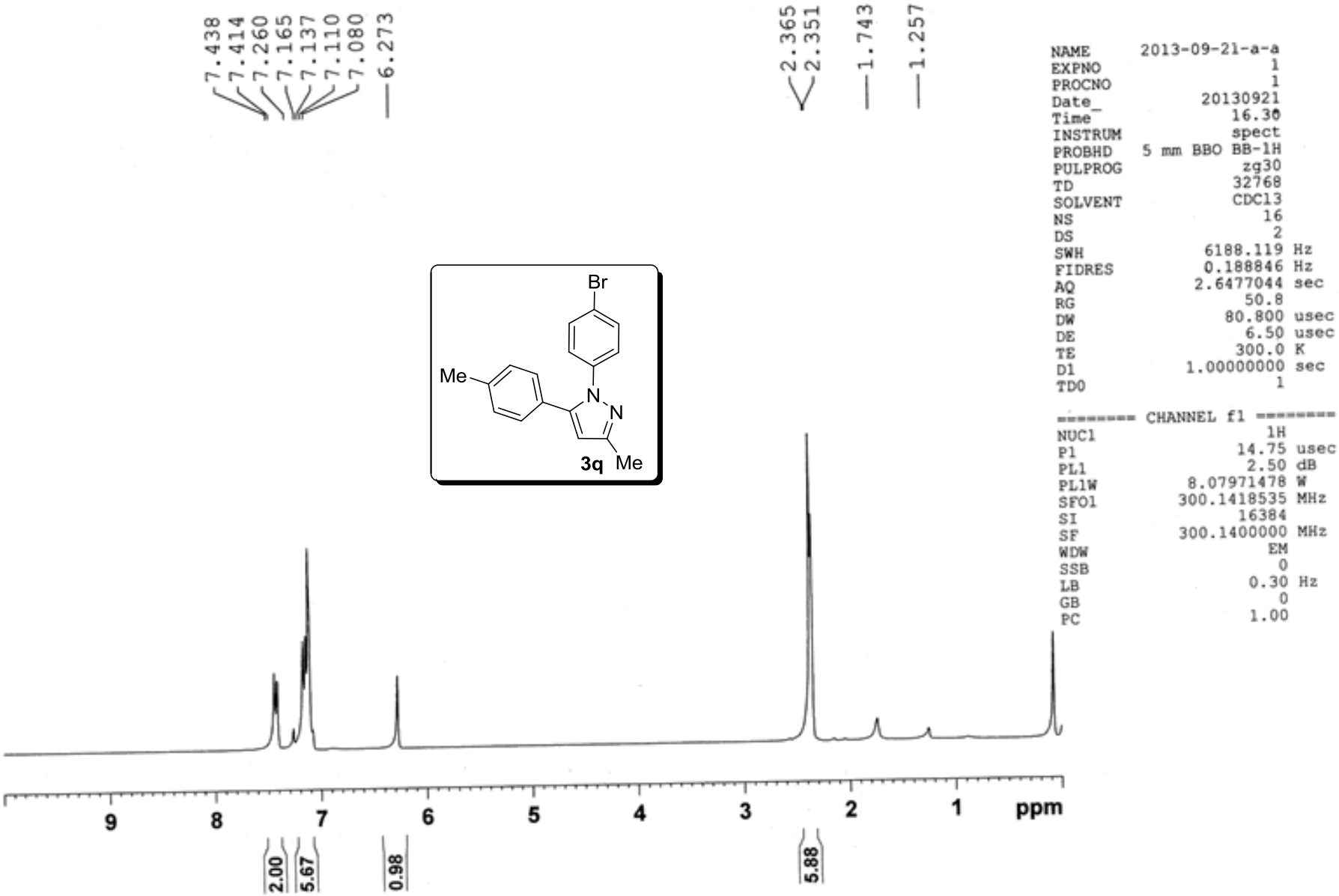
F2 - Acquisition Parameters
Date_ 20150616
Time 23.42
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 36057.691 Hz
FIDRES 1.100393 Hz
AQ 0.4543829 sec
RG 65.24
DW 13.867 usec
DE 6.50 usec
TE 294.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 150.9279571 MHz
NUC1 13C
P1 10.50 usec
PLW1 95.00000000 W

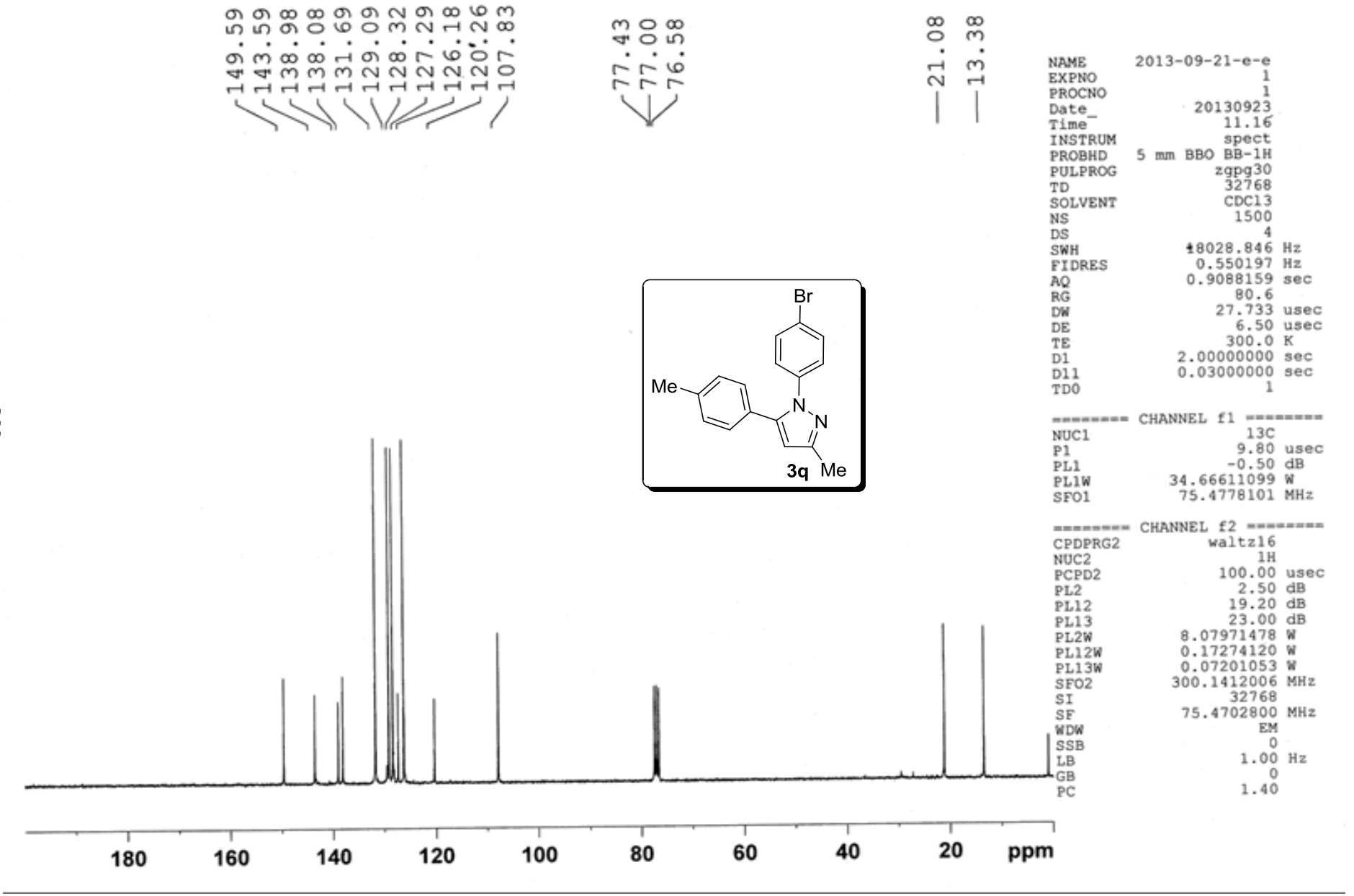
======== CHANNEL f2 ========
SFO2 600.1724007 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 70.00 usec
PLW2 21.00000000 W
PLW12 0.61714000 W
PLW13 0.30239999 W

F2 - Processing parameters
SI 16384
SF 150.9128391 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

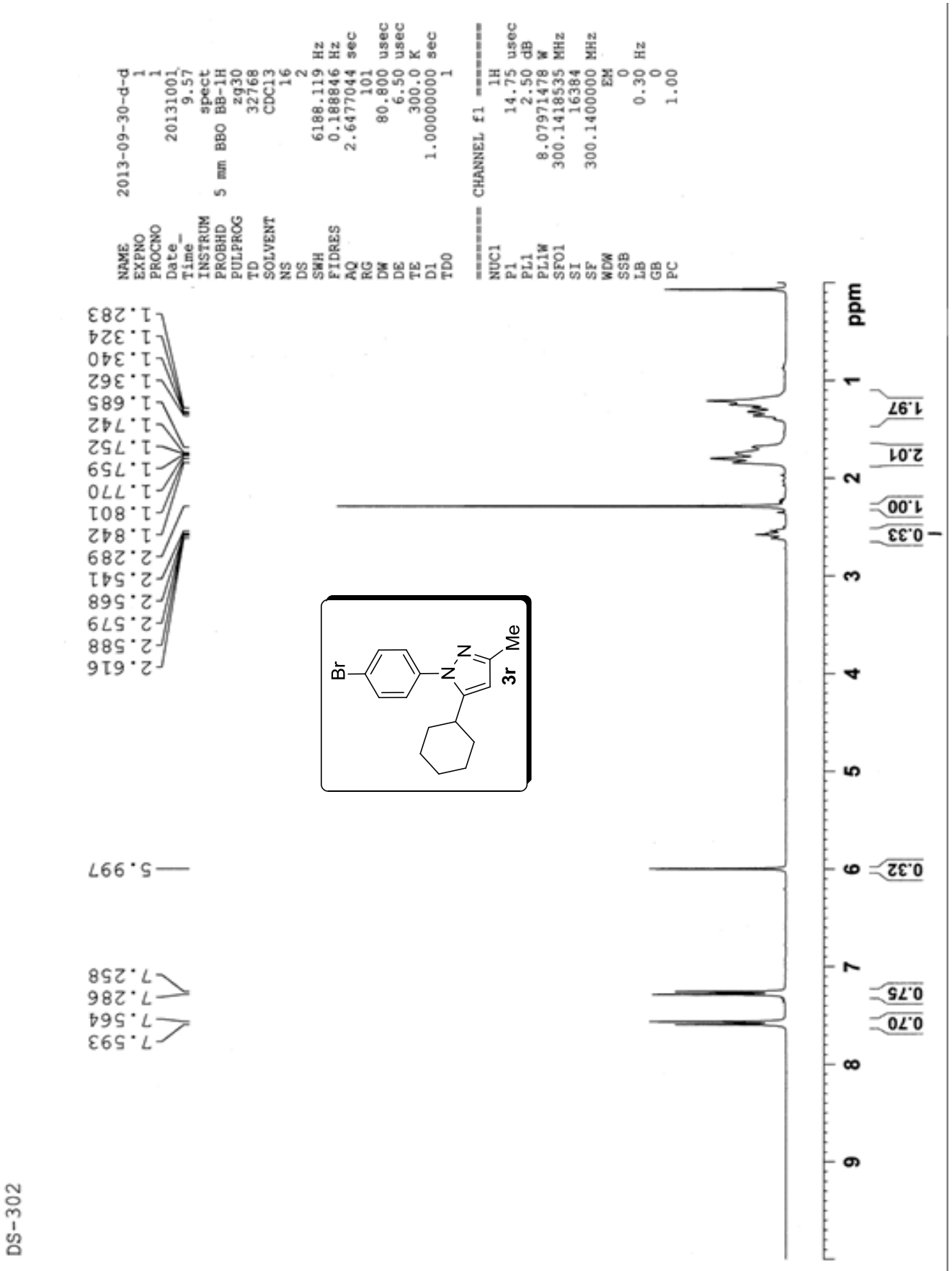
DS-300


7.438
7.414
7.260
7.165
7.137
7.110
7.080
6.273
2.365
2.351
1.743
1.257
Br
Me
N
N
Me
3q
NAME 2013-09-21-a-a
EXPNO 1
PROCNO 1
Date_ 20130921
Time 16.30
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6477044 sec
RG 50.8
DW 80.800 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.75 usec
PL1 2.50 dB
PL1W 8.07971478 W
SFO1 300.1418535 MHz
SI 16384
SF 300.1400000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
ppm
2.00
5.67
0.98
5.88

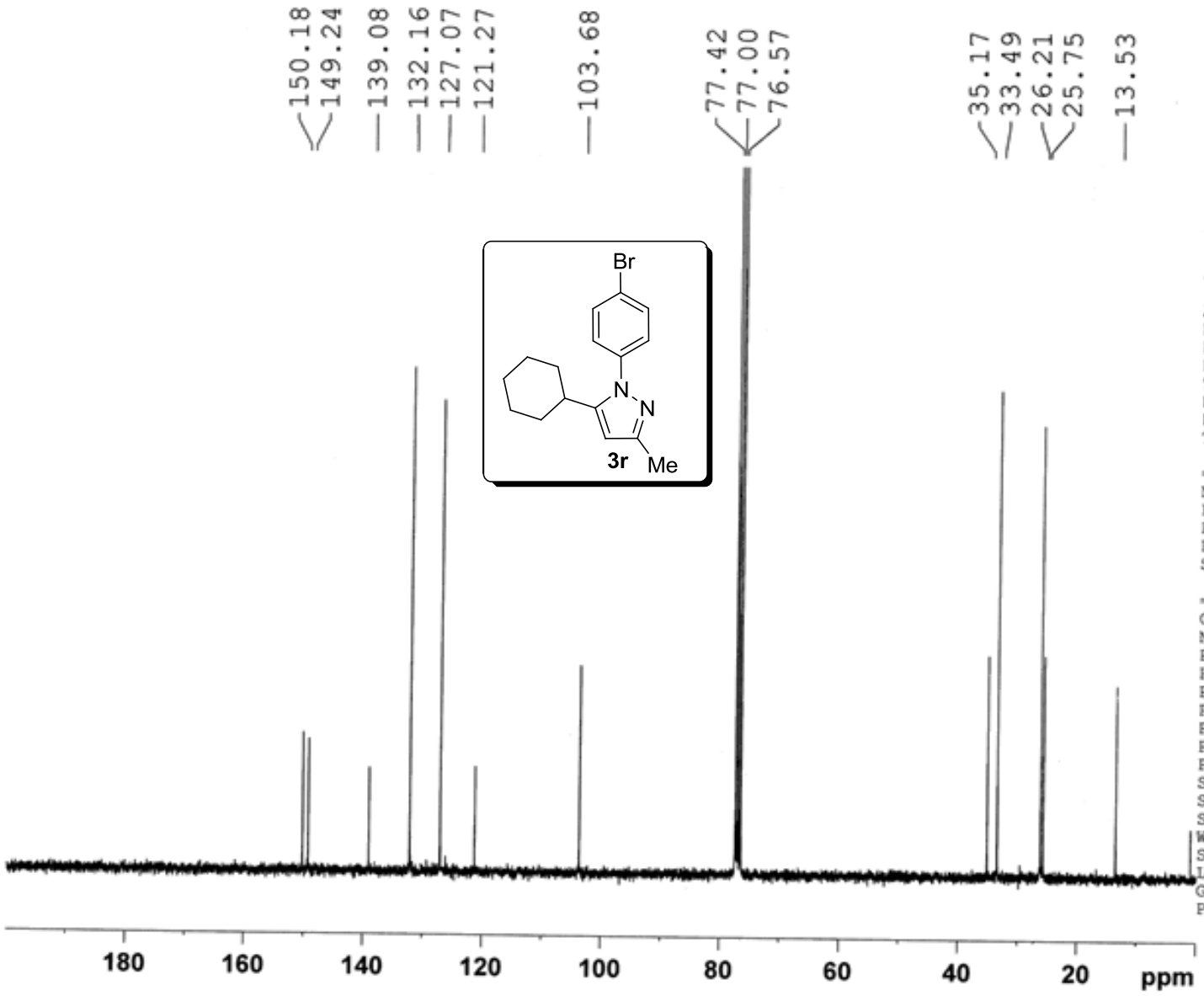
DS-300



NAME	2013-09-21-e-e
EXPNO	1
PROCNO	1
Date_	20130923
Time	11.16
INSTRUM	spect
PROBHD	5 mm BBO BB-1H
PULPROG	zgpg30
TD	32768
SOLVENT	CDCl3
NS	1500
DS	4
SWH	18028.846 Hz
FIDRES	0.550197 Hz
AQ	0.9088159 sec
RG	80.6
DW	27.733 usec
DE	6.50 usec
TE	300.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.80 usec
PL1	-0.50 dB
PL1W	34.66611099 W
SFO1	75.4778101 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	100.00 usec
PL2	2.50 dB
PL12	19.20 dB
PL13	23.00 dB
PL2W	8.07971478 W
PL12W	0.17274120 W
PL13W	0.07201053 W
SFO2	300.1412006 MHz
SI	32768
SF	75.4702800 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

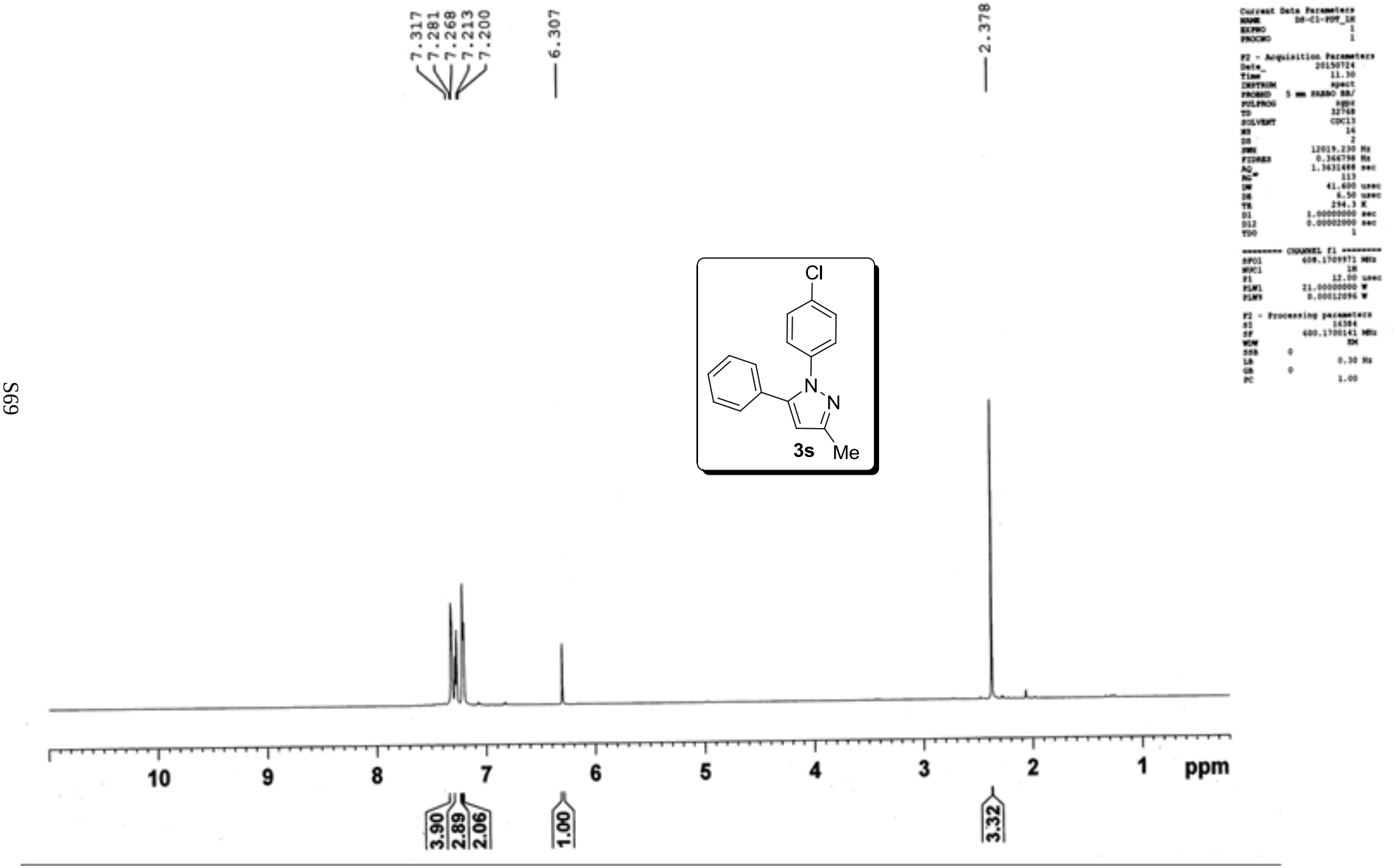

DS-302
NAME 2013-09-30-d-d
EXPNO 1
PROCNO 1
Date_ 20131001
Time 9.57
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6477044 sec
RG 101
DW 80.800 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.75 usec
PL1 2.50 dB
PL1W 8.07971478 W
SFO1 300.1418535 MHz
SI 16384
SF 300.1400000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Br
N
N
Me
3r
ppm
1.97
2.01
1.00
0.33
0.32
0.75
0.70

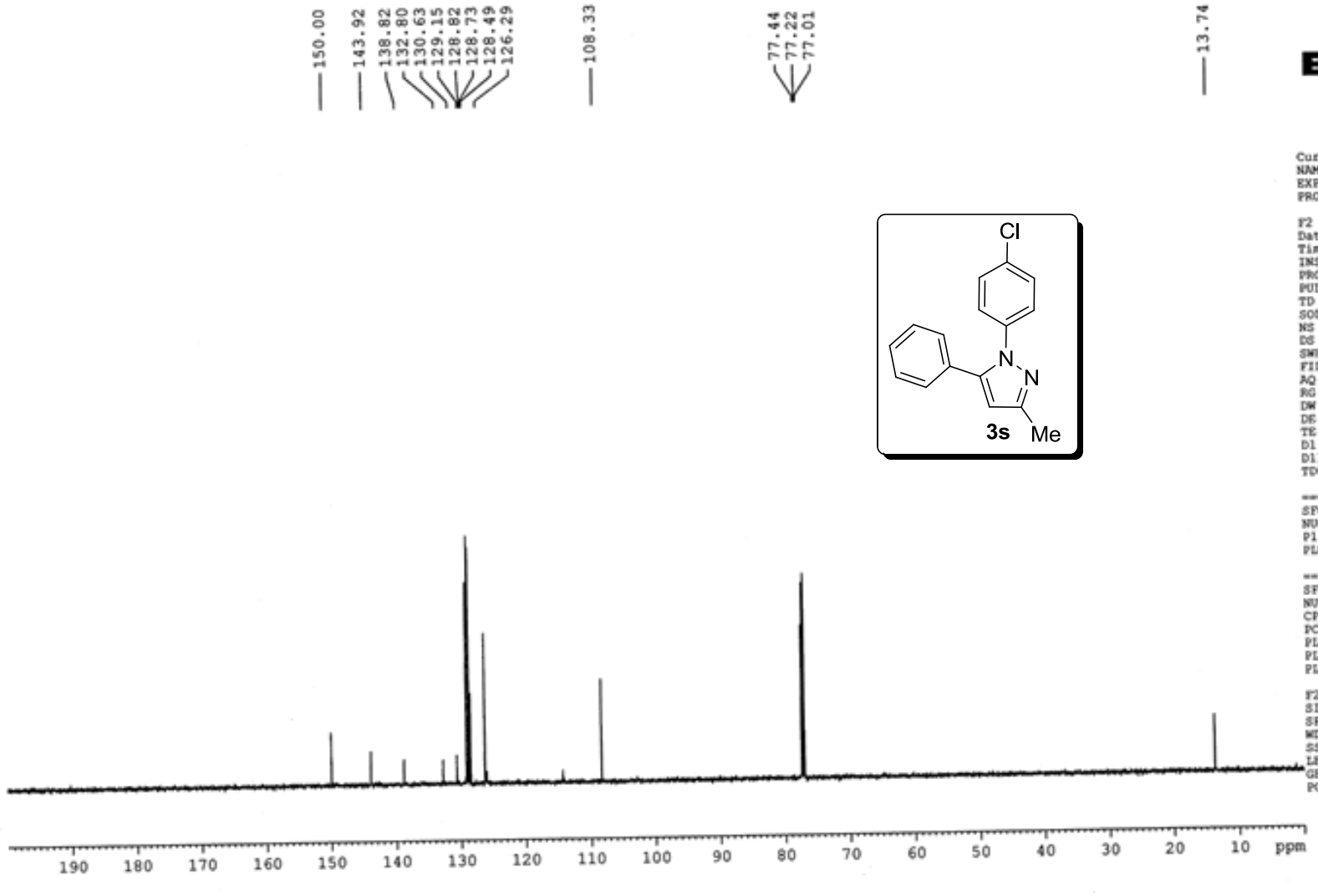
DS-302



NAME	2013-09-30-dd
EXPNO	1
PROCNO	1
Date_	20131001
Time	11.12
INSTRUM	spect
PROBhD	5 mm BBO BB-1H
PULPROG	zgpg30
TD	32768
SOLVENT	CDCl3
NS	1500
DS	4
SWH	18028.846 Hz
FIDRES	0.550197 Hz
AQ	0.9088159 sec
RG	80.6
DW	27.733 usec
DE	6.50 usec
TE	300.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	13C
P1	9.80 usec
PL1	-0.50 dB
PL1W	34.66611099 W
SFO1	75.4778101 MHz
========	CHANNEL f2 ========
CPDPRG2	waltz16
NUC2	1H
PCPD2	100.00 usec
PL2	2.50 dB
PL12	19.20 dB
PL13	23.00 dB
PL2W	8.07971478 W
PL12W	0.17274120 W
PL13W	0.07201053 W
SFO2	300.1412006 MHz
SI	32768
SF	75.4702671 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

DS-Cl-PDT_1H


7.317
7.281
7.268
7.213
7.200
6.307
2.378
Cl
N
N
Me
3s
10
9
8
7
6
5
4
3
2
1
ppm
3.90
2.89
2.06
1.00
3.32



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Current Data Parameters
NAME DS-2R-13C
EXPNO 1
PROCNO 1

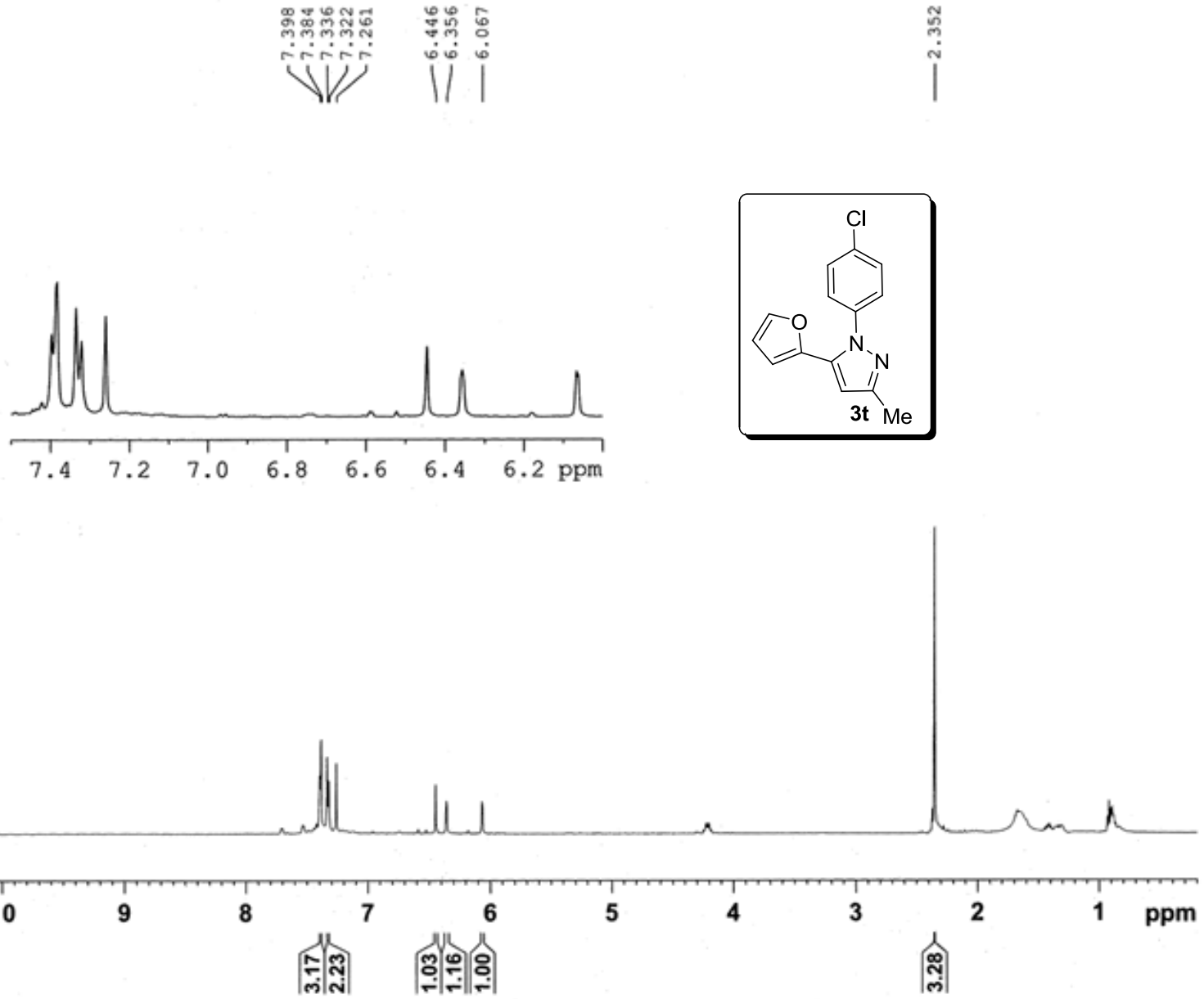
F2 - Acquisition Parameters
Date_ 20150727
Time 9.10
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 47
DS 2
SWH 42613.637 Hz
FIDRES 1.300465 Hz
AQ 0.3844779 sec
RG 200.18
DW 11.733 usec
DE 6.50 usec
TE 294.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 150.9279571 MHz
NUC1 13C
P1 10.50 usec
PLW1 95.00000000 W

======== CHANNEL f2 ========
SFO2 600.1724007 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 70.00 usec
PLW2 21.00000000 W
PLW12 0.61714000 W
PLW13 0.30239999 W

F2 - Processing parameters
SI 16384
SF 150.9128432 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

FU-CL-1H



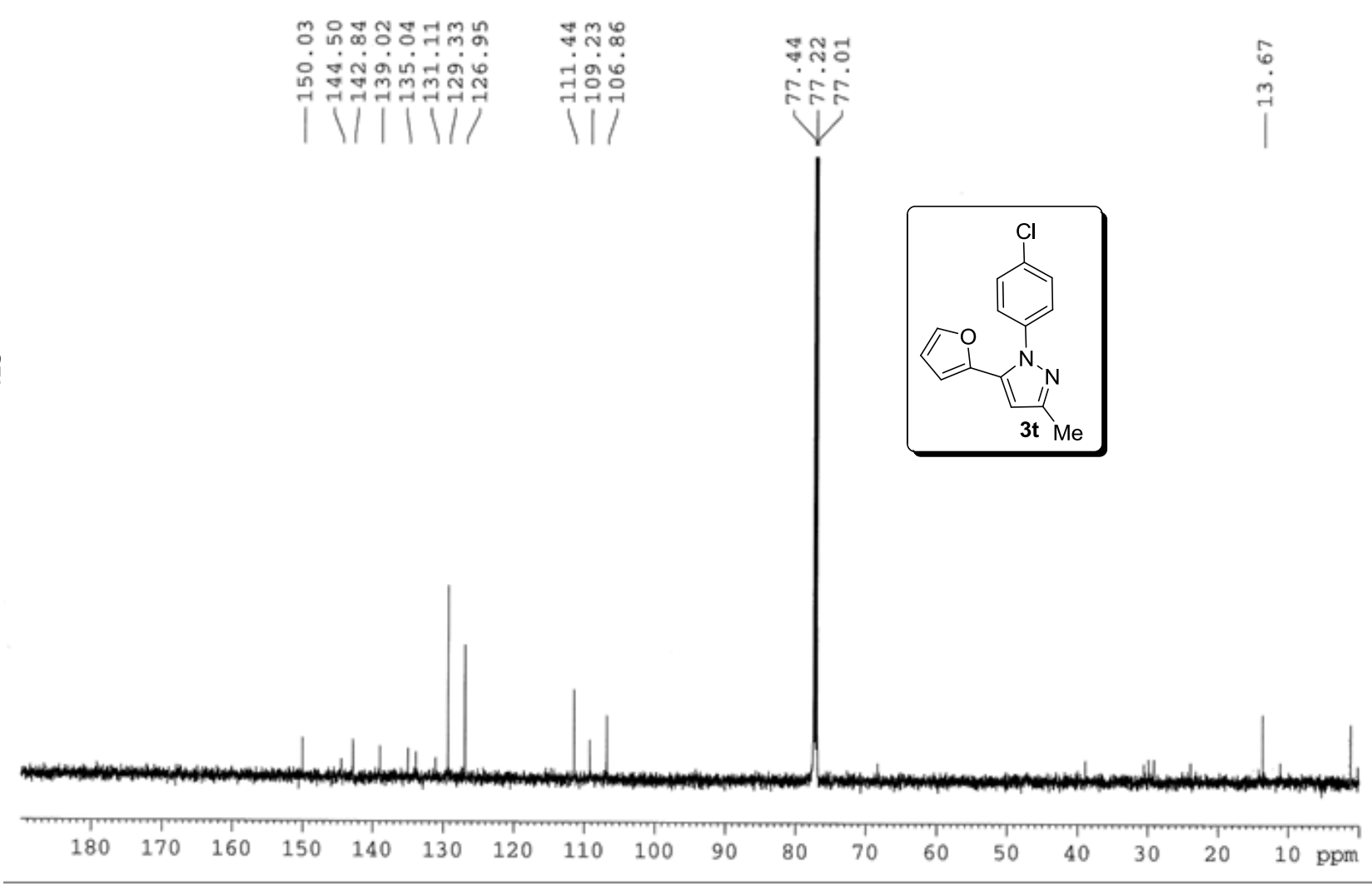
Current Data Parameters
NAME DS-FU-CL-1H
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150825
Time 22.31
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpr
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 12019.230 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 143.33
DW 41.600 usec
DE 6.50 usec
TE 293.5 K
D1 1.00000000 sec
D12 0.00002000 sec
TD0 1

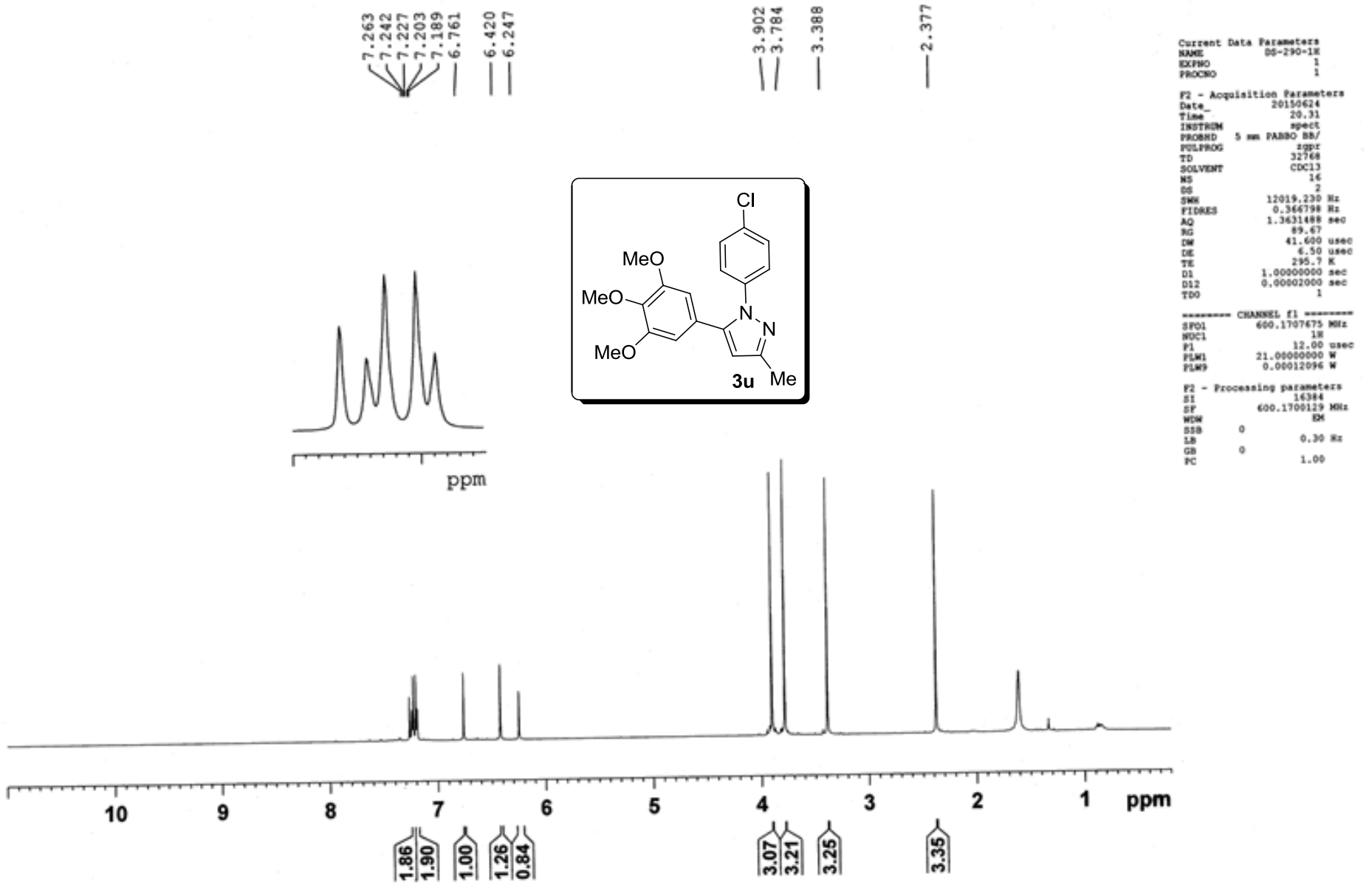
======== CHANNEL f1 ========
SFO1 600.1707660 MHz
NUC1 1H
P1 12.00 usec
PLW1 21.00000000 W
PLW9 0.00012096 W

F2 - Processing parameters
SI 16384
SF 600.1700139 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

DS-FU-CL-13C


150.03
144.50
142.84
139.02
135.04
131.11
129.33
126.95
111.44
109.23
106.86
77.44
77.22
77.01
13.67
Cl
O
N
N
3t
Me
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

DS-290-1H



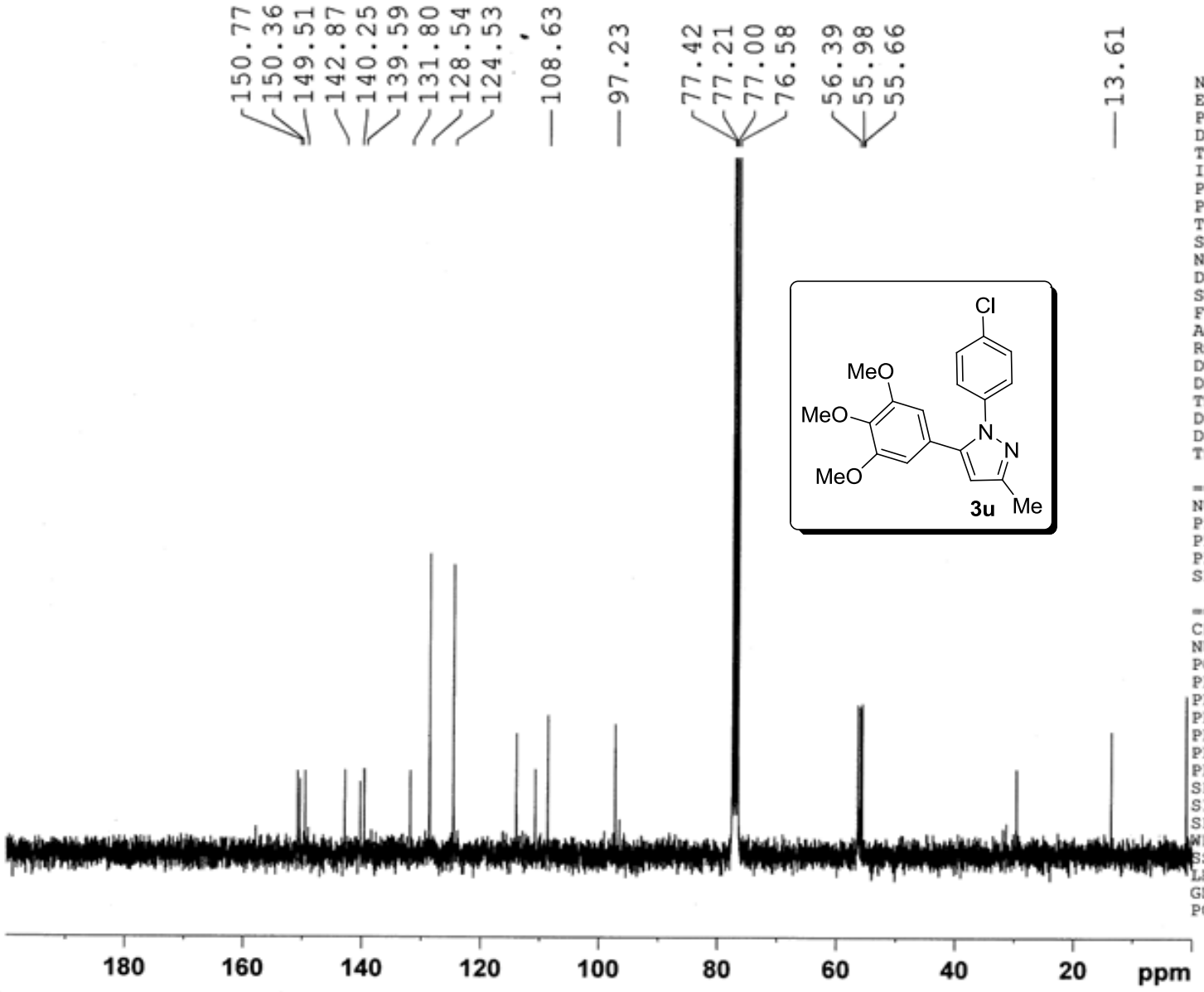
Current Data Parameters
NAME DS-290-1H
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150624
Time 20.31
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpr
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 12019.230 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 89.67
DW 41.600 usec
DE 6.50 usec
TE 295.7 K
D1 1.00000000 sec
D12 0.00002000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 600.1707675 MHz
NUC1 1H
P1 12.00 usec
PLW1 21.00000000 W
PLW9 0.00012096 W

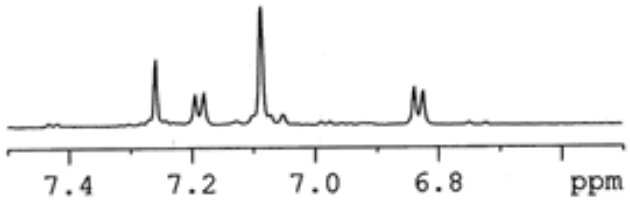
F2 - Processing parameters
SI 16384
SF 600.1700129 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

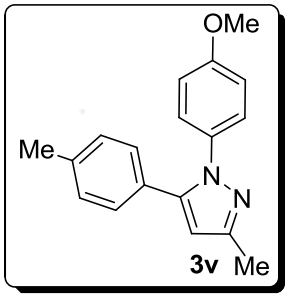
DS-290



NAME	2013-09-18-bb
EXPNO	1
PROCNO	1
Date_	20130918
Time	21.07
INSTRUM	spect
PROBHD	5 mm BBO BB-1H
PULPROG	zgpg30
TD	32768
SOLVENT	CDCl3
NS	1500
DS	4
SWH	18028.846 Hz
FIDRES	0.550197 Hz
AQ	0.9088159 sec
RG	80.6
DW	27.733 usec
DE	6.50 usec
TE	300.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	13C
P1	9.80 usec
PL1	-0.50 dB
PL1W	34.66611099 W
SFO1	75.4778101 MHz
========	CHANNEL f2 ========
CPDPRG2	waltz16
NUC2	1H
PCPD2	100.00 usec
PL2	2.50 dB
PL12	19.20 dB
PL13	23.00 dB
PL2W	8.07971478 W
PL12W	0.17274120 W
PL13W	0.07201053 W
SFO2	300.1412006 MHz
SI	32768
SF	75.4702659 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

DS-178-2_1H



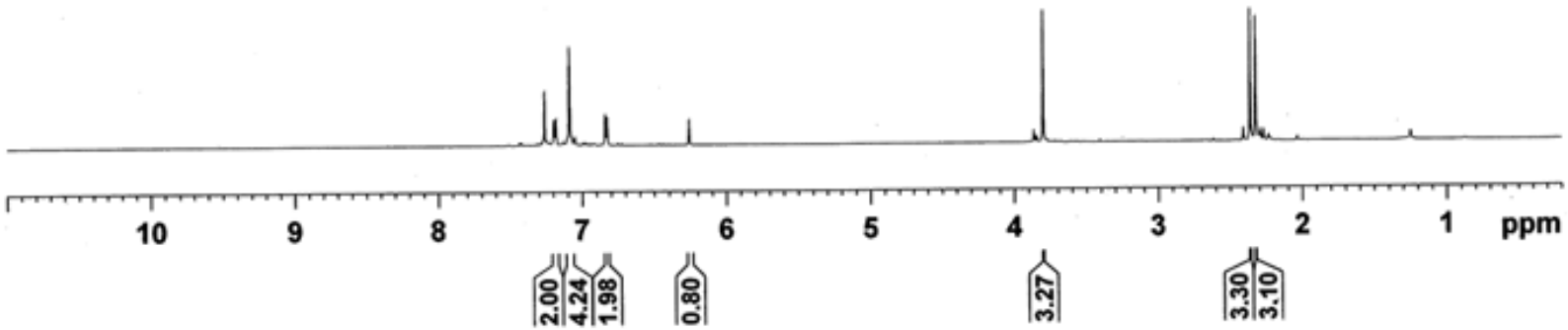



```
Current Data Parameters
NAME                  DS-178-2_1H
EXPNO                           1
PROCNO                          1

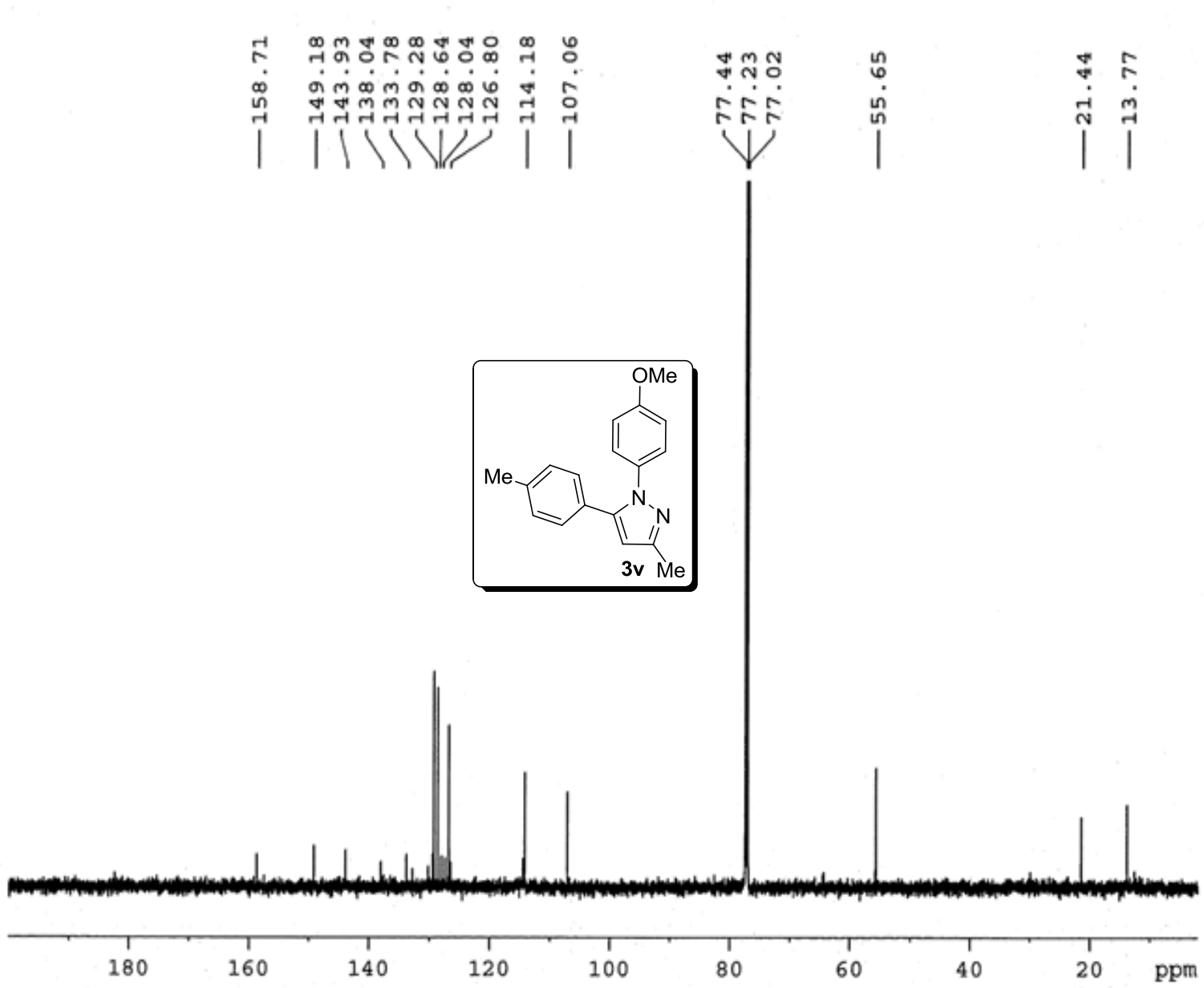
F2 - Acquisition Parameters
Date_                    20150716
Time                        13.49
INSTRUM                     spect
PROBHD    5 mm PABBO BB/
PULPROG                     zgpr
TD                         32768
SOLVENT                    CDCl3
NS                            12
DS                             2
SWH                    12019.230 Hz
FIDRES                  0.366798 Hz
AQ                      1.3631488 sec
RG                         157.17
DW                         41.600 usec
DE                          6.50 usec
TE                         291.8 K
D1                     1.00000000 sec
D12                    0.00002000 sec
TD0                            1

======== CHANNEL f1 ========
SFO1                 600.1709663 MHz
NUC1                         1H
P1                         12.00 usec
PLW1                  21.00000000 W
PLW9                   0.00012096 W

F2 - Processing parameters
SI                         16384
SF                   600.1700149 MHz
WDW                           EM
SSB                    0
LB                          0.30 Hz
GB                     0
PC                          1.00
```



DS-178-1-13C



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```
Current Data Parameters
NAME        DS-178-1-13C
EXPNO                  1
PROCNO                 1

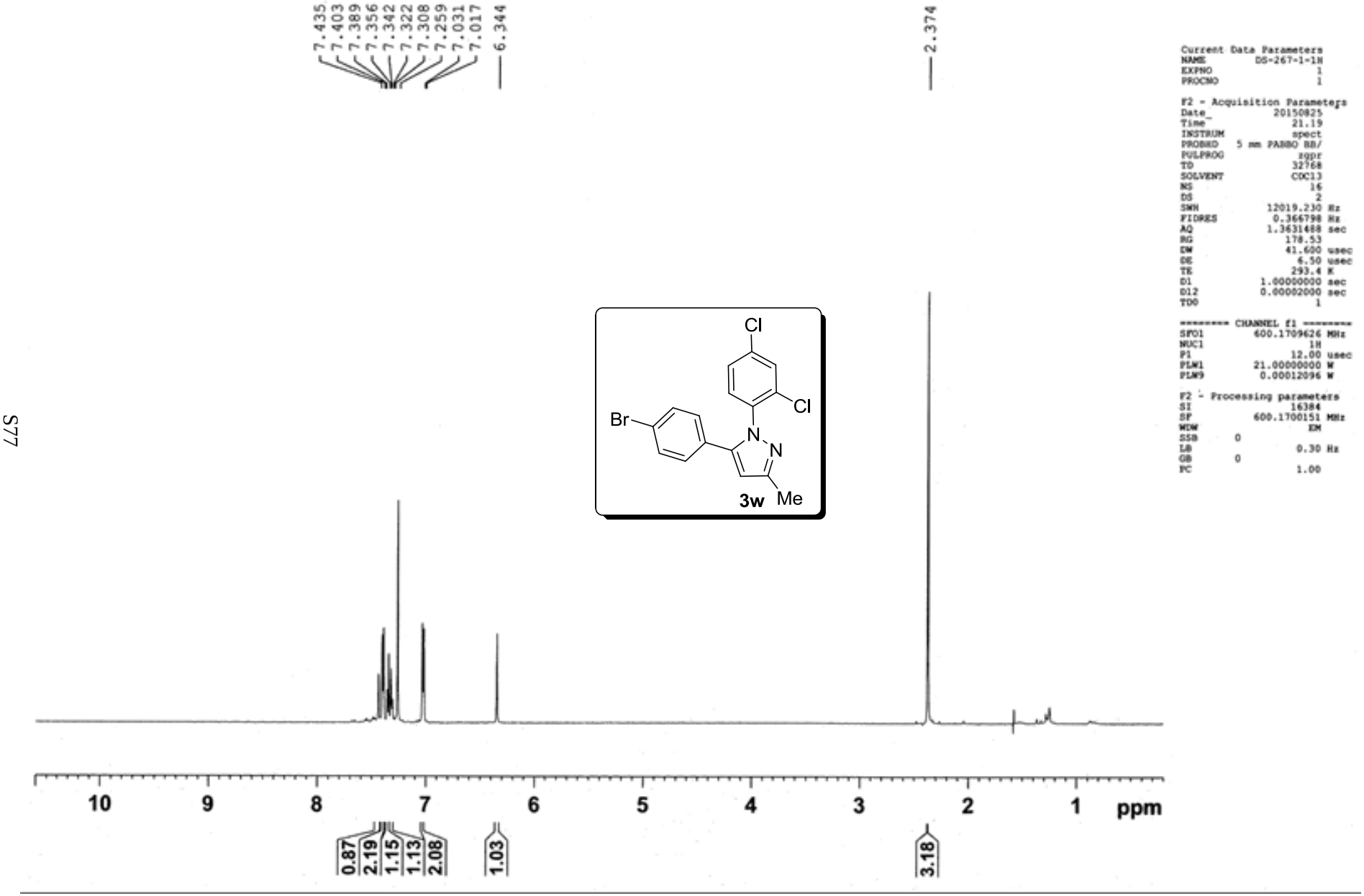
F2 - Acquisition Parameters
Date_           20150825
Time              21.48
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                32768
SOLVENT           CDCl3
NS                  279
DS                    2
SWH           42613.637 Hz
FIDRES         1.300465 Hz
AQ             0.3844779 sec
RG                200.18
DW                11.733 usec
DE                 6.50 usec
TE                293.9 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        150.9279571 MHz
NUC1                13C
P1                10.50 usec
PLW1        95.00000000 W

======== CHANNEL f2 ========
SFO2        600.1724007 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             70.00 usec
PLW2        21.00000000 W
PLW12        0.61714000 W
PLW13        0.30239999 W

F2 - Processing parameters
SI                 16384
SF          150.9128365 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

167-1-1H



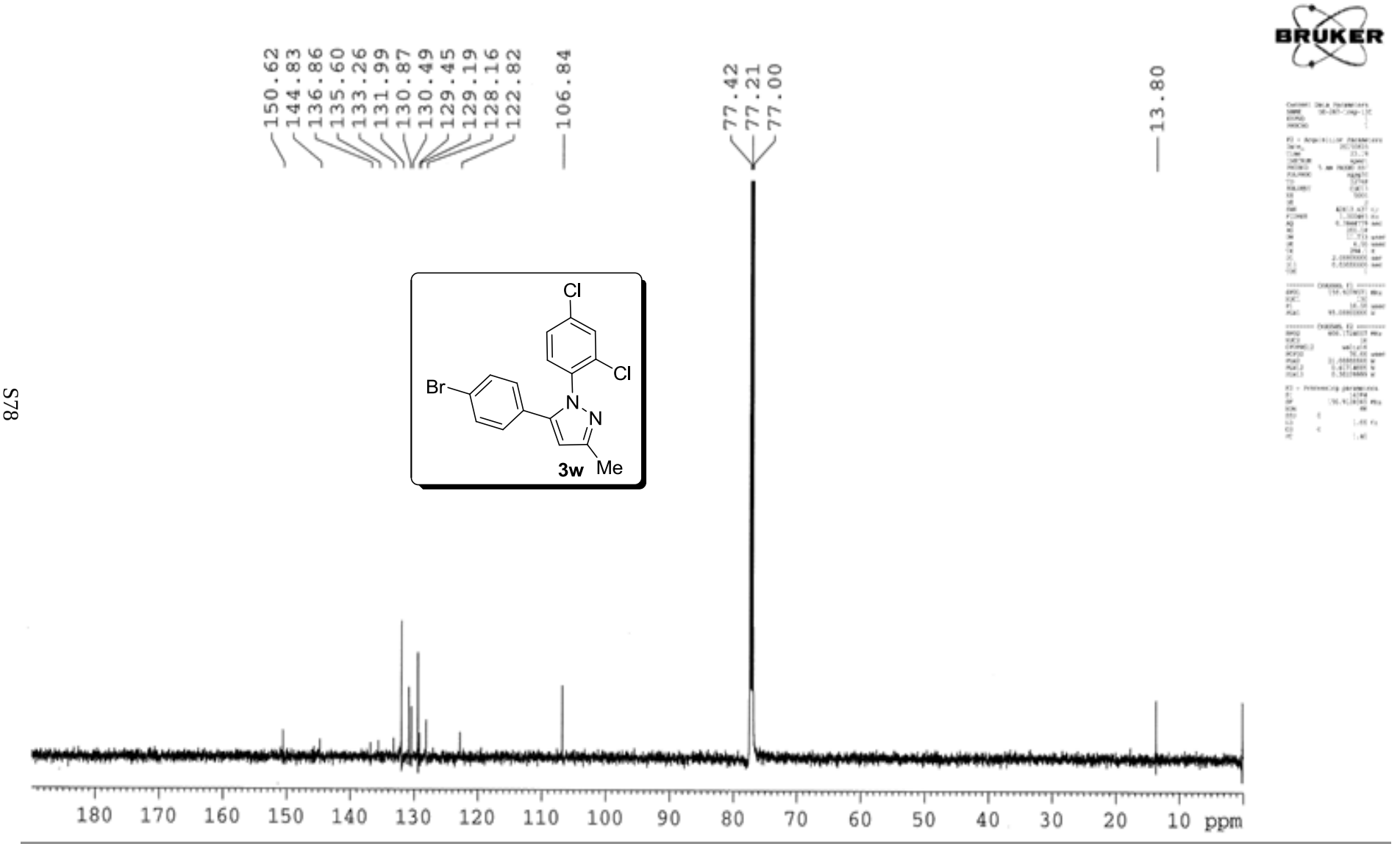

```
Current Data Parameters
NAME                  DS-267-1-1H
EXPNO                           1
PROCNO                          1

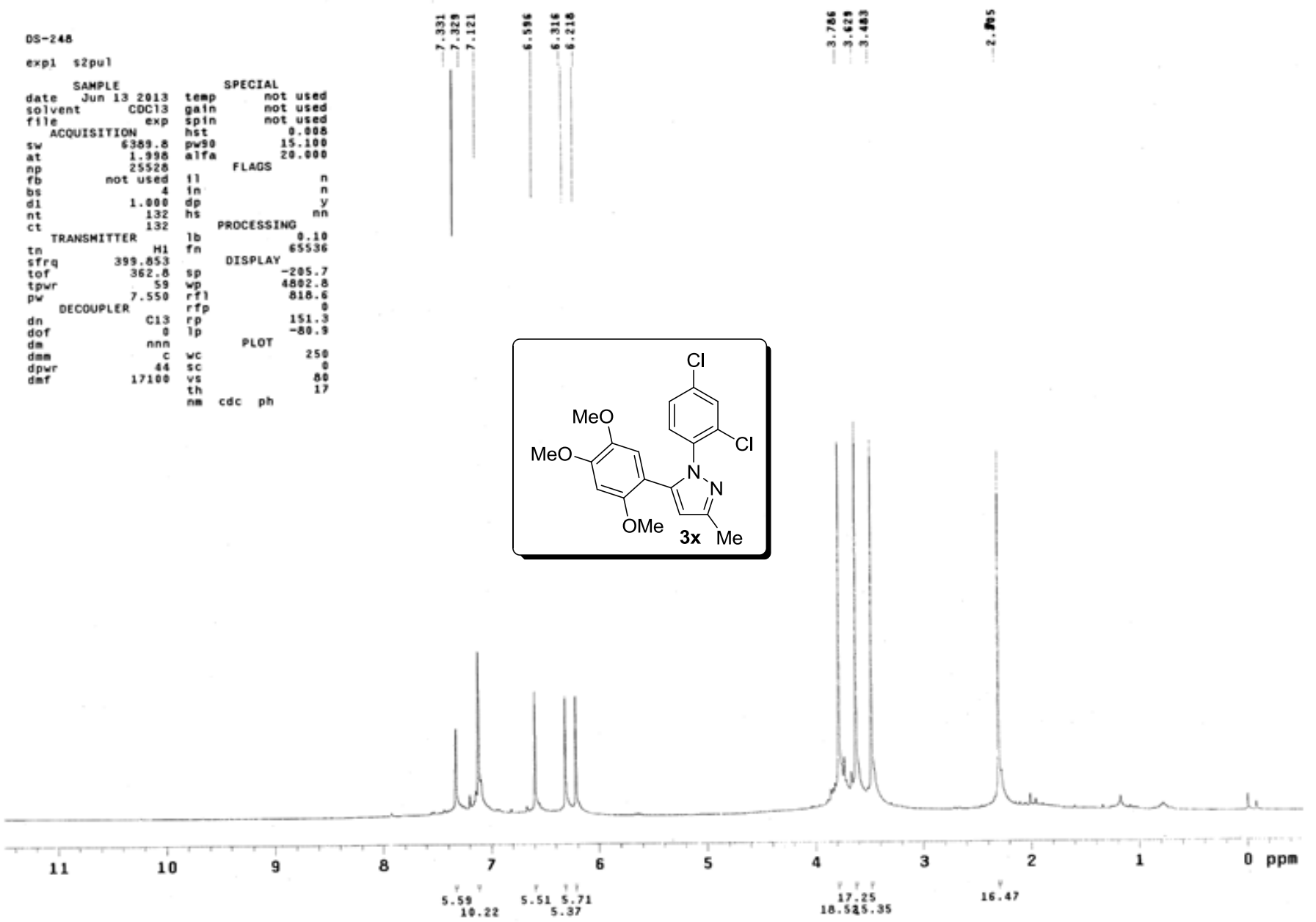
F2 - Acquisition Parameters
Date_                    20150825
Time                        21.19
INSTRUM                     spect
PROBHD    5 mm PABBO BB/
PULPROG                     zgpr
TD                         32768
SOLVENT                    CDCl3
NS                             16
DS                              2
SWH                    12019.230 Hz
FIDRES                 0.366798 Hz
AQ                     1.3631488 sec
RG                        178.53
DW                        41.600 usec
DE                         6.50 usec
TE                        293.4 K
D1                     1.00000000 sec
D12                    0.00002000 sec
TD0                             1

======== CHANNEL f1 ========
SFO1                 600.1709626 MHz
NUC1                         1H
P1                          12.00 usec
PLW1                21.00000000 W
PLW9                 0.00012096 W

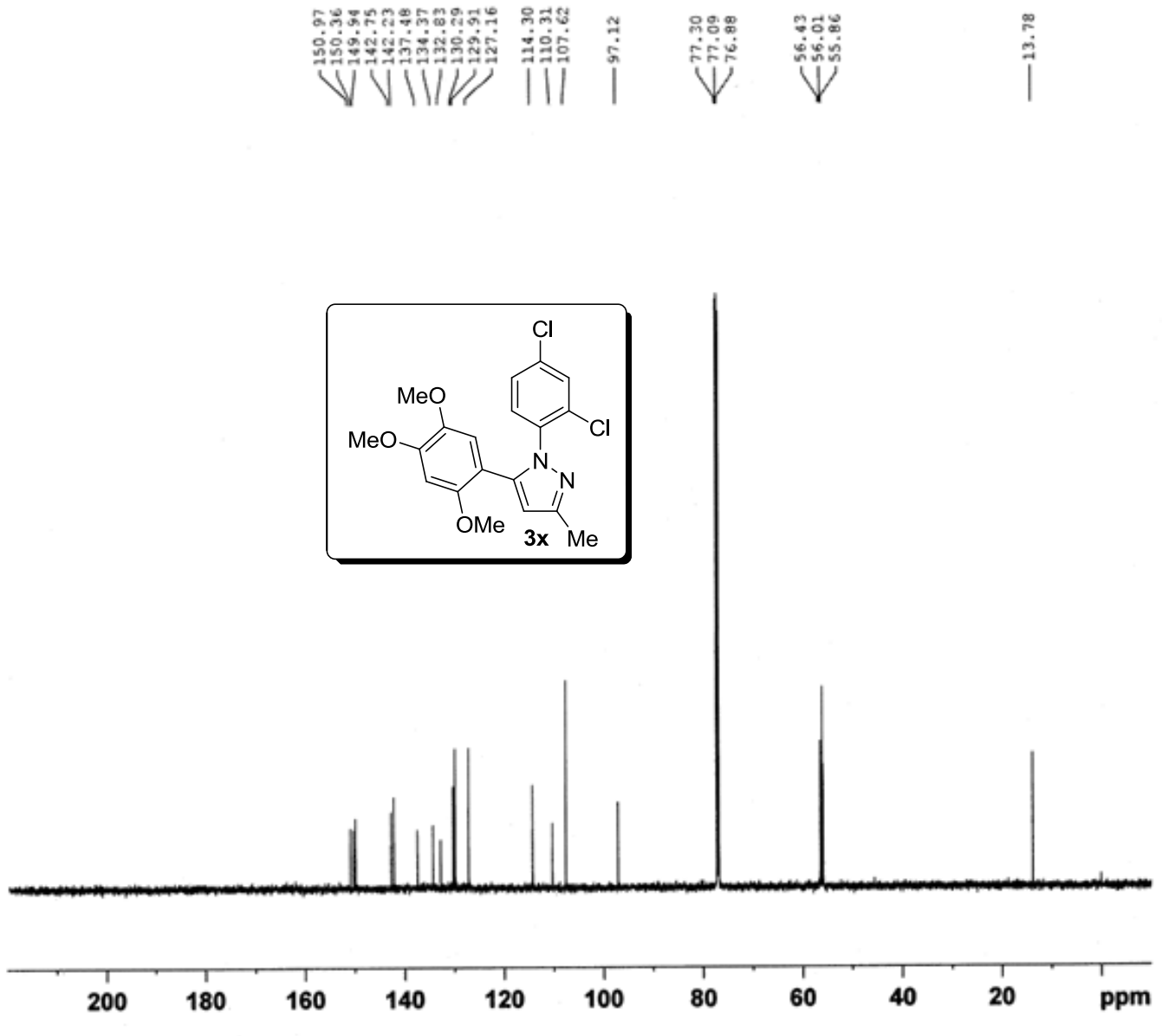
F2 - Processing parameters
SI                          16384
SF                   600.1700151 MHz
WDW                            EM
SSB          0
LB                           0.30 Hz
GB           0
PC                           1.00
```

DS-267-1rep-13C




DS-248
expl s2pul
SAMPLE
date Jun 13 2013
solvent CDCl3
file exp
ACQUISITION
sw 6389.8
at 1.998
np 25528
fb not used
bs 4
d1 1.000
nt 132
ct 132
TRANSMITTER
tn H1
sfrq 399.853
tof 362.8
tpwr 59
pw 7.550
DECOUPLER
dn C13
dof 0
dm nnn
dmm c
dpwr 44
dmf 17100
SPECIAL
temp not used
gain not used
spin not used
hst 0.008
pw90 15.100
alfa 20.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 0.10
fn 65536
DISPLAY
sp -205.7
wp 4802.8
rfl 818.6
rfp 0
rp 151.3
lp -80.9
PLOT
wc 250
sc 0
vs 80
th 17
nm cdc ph
7.331
7.329
7.121
6.596
6.316
6.218
3.786
3.629
3.483
2.305
Cl
Cl
MeO
MeO
OMe
N
N
3x
Me
11
10
9
8
7
6
5
4
3
2
1
0 ppm
5.59
10.22
5.51
5.71
5.37
17.25
18.52
15.35
16.47

BS-248-13C



Current Data Parameters

NAME	BS-248-13C
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20131211
Time	13.16
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zgpg30
TD	32768
SOLVENT	CDCl3
NS	319
DS	2
SWH	36057.691 Hz
FIDRES	1.100393 Hz
AQ	0.4543829 sec
RG	65.24
DW	13.867 usec
DE	6.50 usec
TE	298.8 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1

======== CHANNEL f1 ========

SFO1	150.9279571 MHz
NUC1	13C
P1	10.50 usec
PLW1	95.00000000 W

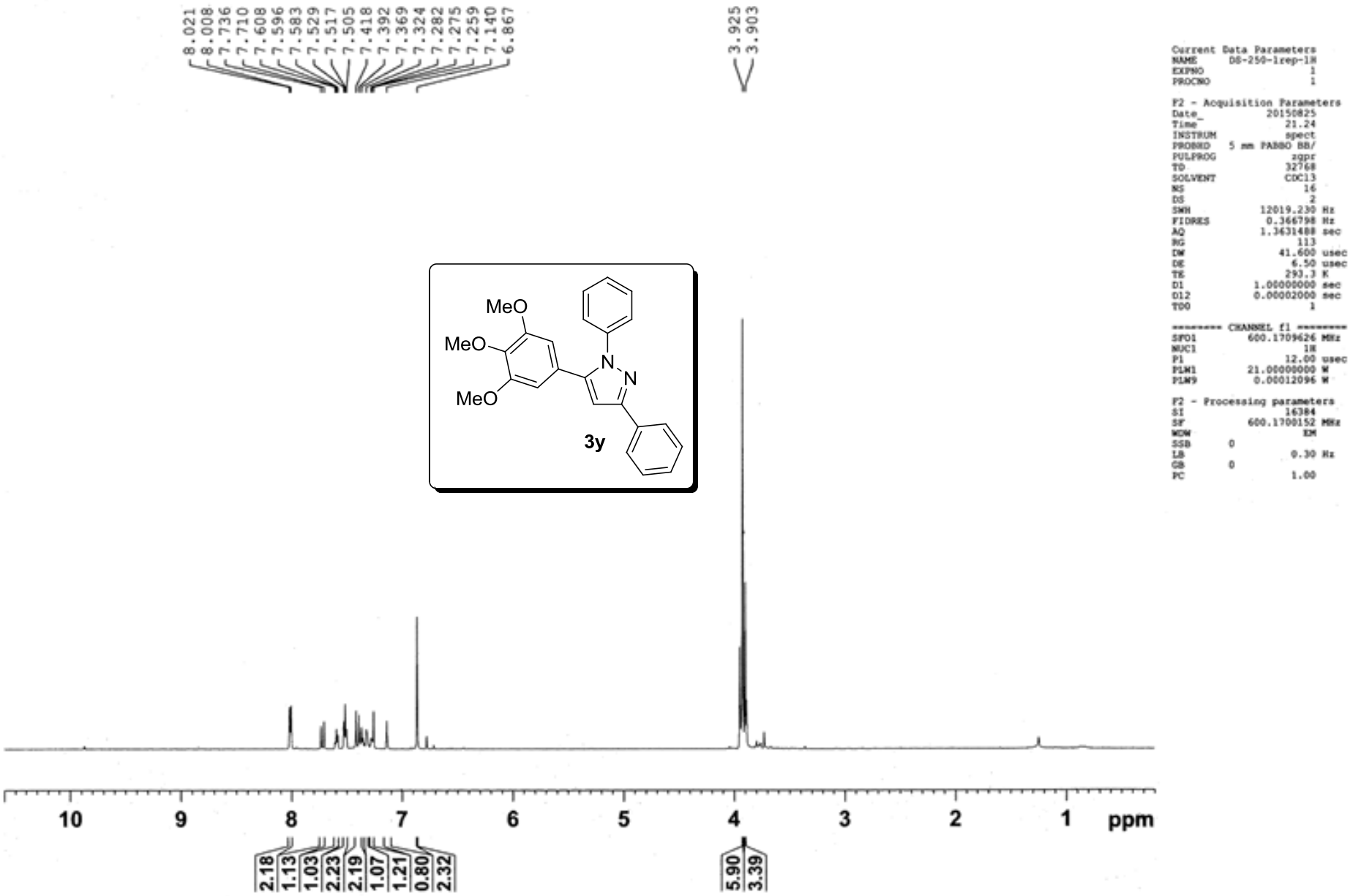
======== CHANNEL f2 ========

SFO2	600.1724007 MHz
NUC2	1H
CPDPRG[2	waltz16
PCPD2	70.00 usec
PLW2	21.00000000 W
PLW12	0.61714000 W
PLW13	0.30239999 W

F2 - Processing parameters

SI	16384
SF	150.9128587 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

I50-1rep-1H



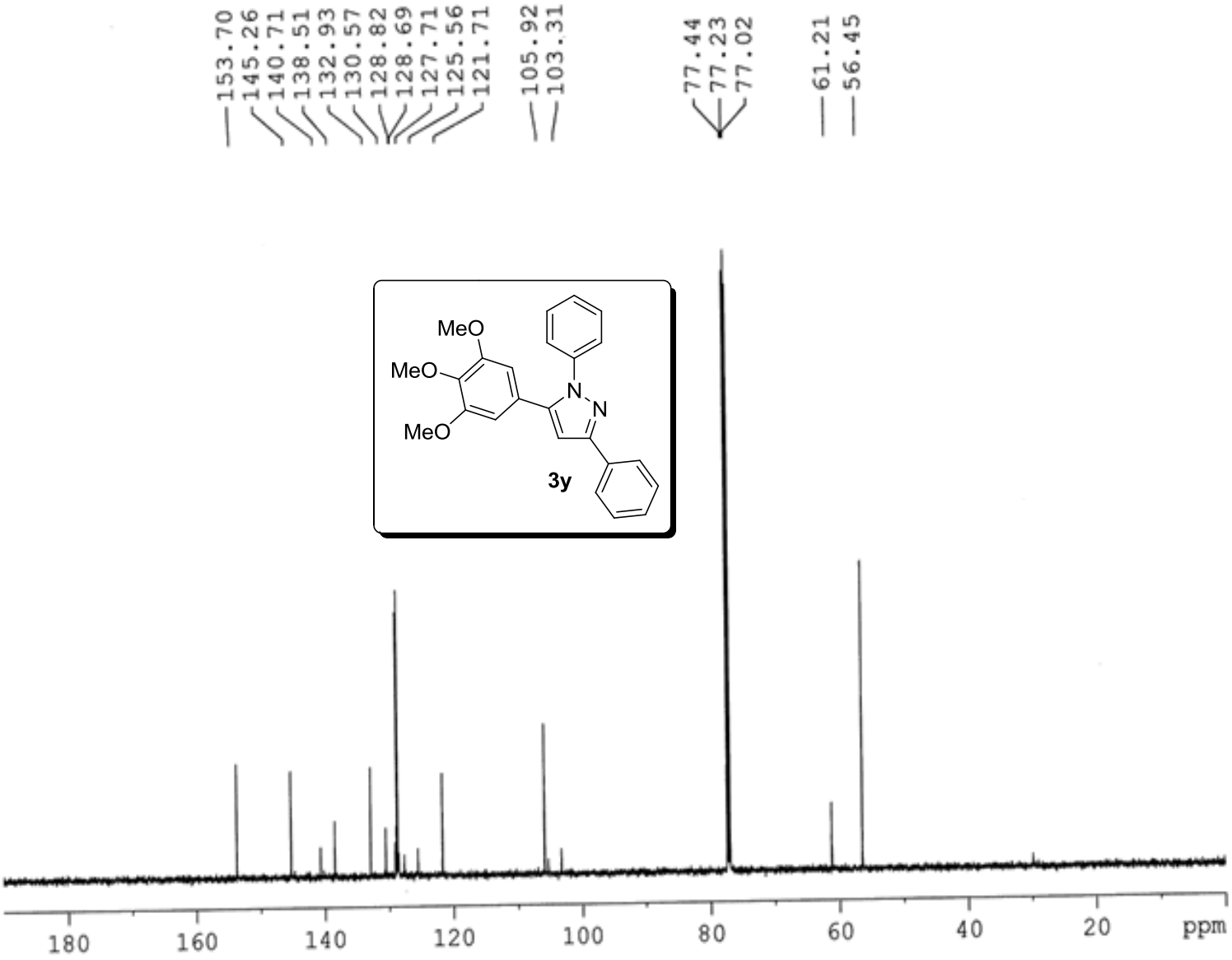

```
Current Data Parameters
NAME        DS-250-1rep-1H
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20150825
Time                 21.24
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG              zgpr
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              12019.230 Hz
FIDRES           0.366798 Hz
AQ               1.3631488 sec
RG                    113
DW                 41.600 usec
DE                  6.50 usec
TE                 293.3 K
D1               1.00000000 sec
D12              0.00002000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1            600.1709626 MHz
NUC1                    1H
P1                   12.00 usec
PLW1           21.00000000 W
PLW9            0.00012096 W

F2 - Processing parameters
SI                      16384
SF              600.1700152 MHz
WDW                     EM
SSB          0
LB                    0.30 Hz
GB           0
PC                    1.00
```

DS-250-13C



BRUKER

```
Current Data Parameters
NAME                  DS-250-13C
EXPNO                          1
PROCNO                         1

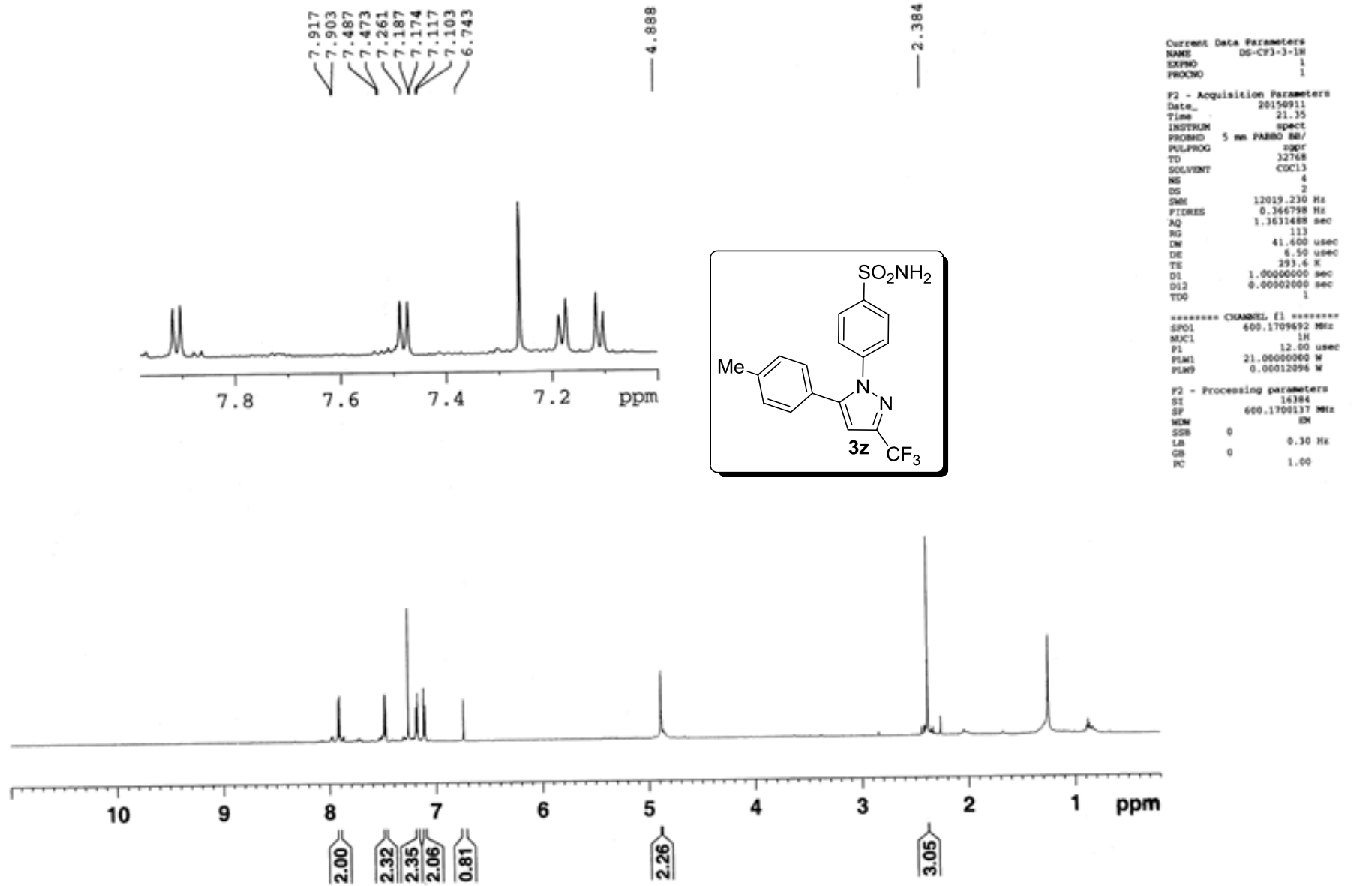
F2 - Acquisition Parameters
Date_                   20131211
Time                       17.08
INSTRUM                    spect
PROBHD     5 mm PABBO BB/
PULPROG                  zgpg30
TD                        32768
SOLVENT                   CDCl3
NS                          552
DS                            2
SWH                 36057.691 Hz
FIDRES              1.100393 Hz
AQ                  0.4543829 sec
RG                         65.24
DW                     13.867 usec
DE                      6.50 usec
TE                      298.8 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                           1

======== CHANNEL f1 ========
SFO1              150.9279571 MHz
NUC1                        13C
P1                     10.50 usec
PLW1             95.00000000 W

======== CHANNEL f2 ========
SFO2              600.1724007 MHz
NUC2                        1H
CPDPRG[2                waltz16
PCPD2                  70.00 usec
PLW2             21.00000000 W
PLW12             0.61714000 W
PLW13             0.30239999 W

F2 - Processing parameters
SI                         16384
SF                150.9128374 MHz
WDW                           EM
SSB                0
LB                      1.00 Hz
GB                 0
PC                         1.40
```

DS-CF3-3-1H



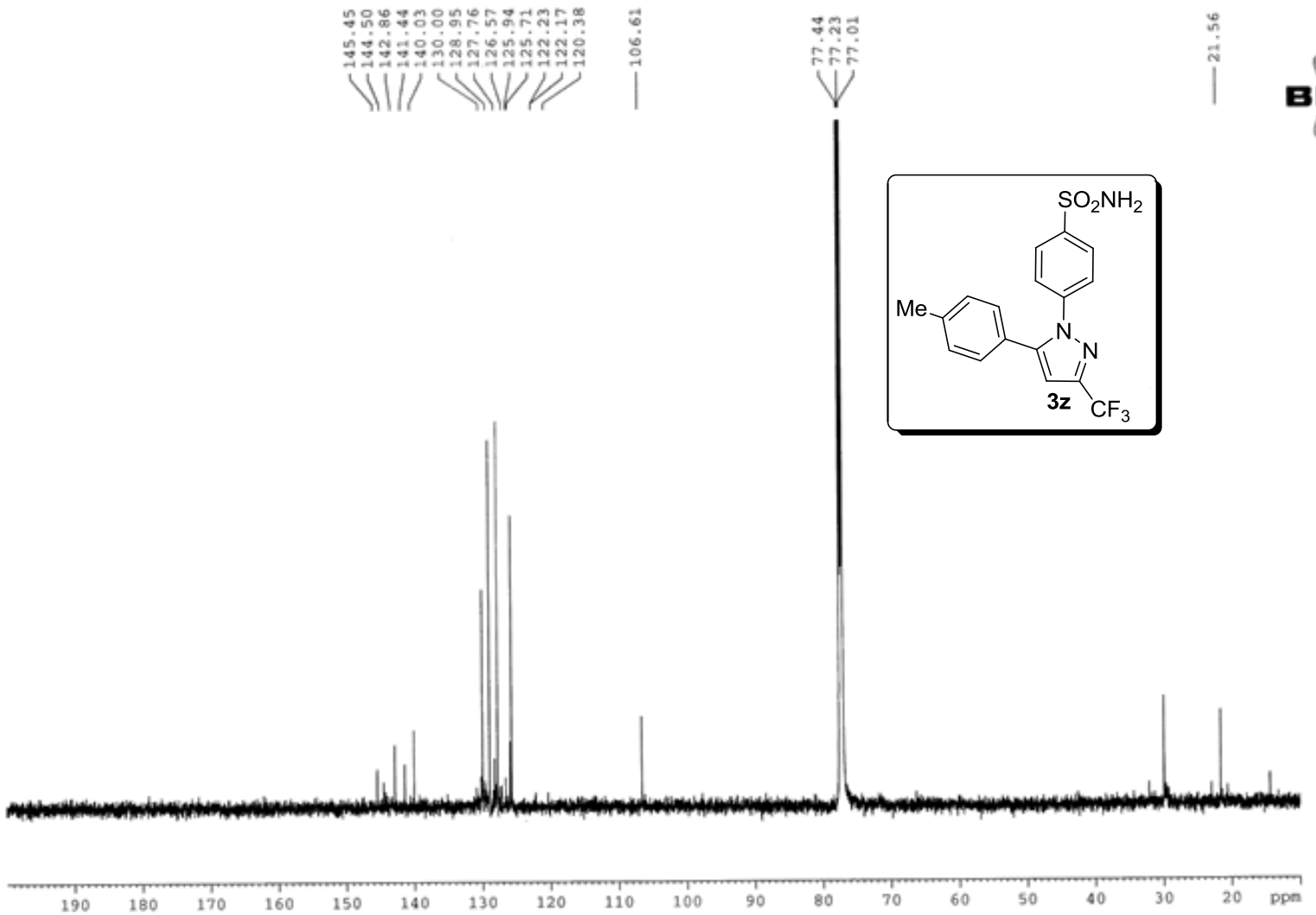
Current Data Parameters
NAME DS-CF3-3-1H
EXPNO 1
PROCNO 1

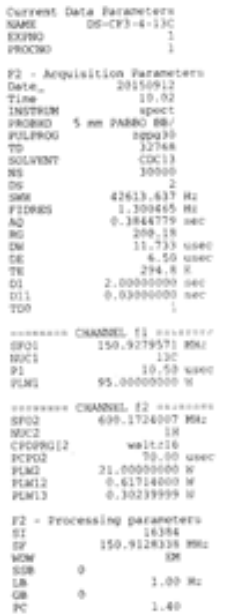
F2 - Acquisition Parameters
Date_ 20150911
Time 21.35
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpr
TD 32768
SOLVENT CDCl3
NS 4
DS 2
SWH 12019.230 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 113
DW 41.600 usec
DE 6.50 usec
TE 293.6 K
D1 1.00000000 sec
D12 0.00002000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 600.1709692 MHz
NUC1 1H
P1 12.00 usec
PLW1 21.00000000 W
PLW9 0.00112096 W

F2 - Processing parameters
SI 16384
SF 600.1700137 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

DS-CF3-4-13C





```
Current Data Parameters
NAME          DS-CF3-4-13C
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_              20150912
Time                  10.02
INSTRUM                spect
PROBHD   5 mm PABBO BB/
PULPROG             zgpg30
TD                   32768
SOLVENT              CDCl3
NS                   30000
DS                       2
SWH              42613.637 Hz
FIDRES            1.300465 Hz
AQ                0.3844779 sec
RG                   208.18
DW                  11.733 usec
DE                   6.50 usec
TE                  294.8 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1          150.9279571 MHz
NUC1                    13C
P1                    10.50 usec
PLW1          95.00000000 W

======== CHANNEL f2 ========
SFO2          600.1724007 MHz
NUC2                    1H
CPDPRG[2            waltz16
PCPD2                 70.00 usec
PLW2          21.00000000 W
PLW12          0.61714000 W
PLW13          0.30239999 W

F2 - Processing parameters
SI                     16384
SF            150.9128338 MHz
WDW                       EM
SSB          0
LB                    1.00 Hz
GB           0
PC                    1.40
```