Supporting Information

Iron(II)-catalyzed [2+2+2] cycloaddition for pyridine ring construction

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General considerations

All reactions were carried out using Schlenk technique under an atmosphere of dry Argon. Microwave synthesis was carried out using microwave reactor (10 mL) with teflon lid under an atmosphere of dry Argon. The reactions were carried out using single-mode automatic microwave synthesizers *Synthesis System Explorer* from CEM Corporation. Solvents were purchased from Carlo Erba and degassed prior to use by freeze-pump-thaw procedure (4 times). Solvents for NMR spectroscopy were dried over molecular sieves. NMR spectra were recorded on 400 MHz and 500 MHz Brücker spectrometers. Proton (^{1}H) NMR information is given in the following format: multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; qui, quintet; sept, septet; m, multiplet), coupling constant(s) (*J*) in Hertz (Hz), number of protons. The prefix *app* is occasionally applied when the true signal multiplicity was unresolved and *br* indicates the signal in question broadened. Carbon (^{13}C) NMR spectra are reported in ppm (δ) relative to residual $CHCl_3$ (δ 77.2) unless noted otherwise, NMR information is given in the following format: Cq quaternary carbon, CH tertionary carbon, CH_2 secondary carbon, CH_3 primary carbone. HRMS analyses were performed on Q-TOF Micro WATERS by electrospray ionization (ESI) by LCMT analytical services. Infrared (IR) spectra were recorded with a Perkin Elmer 16 PC FT-IR spectrometer. Unless noted otherwise. HRMS analyses were performed by LCMT analytical services. IR was recorded on a PerkinElmer FT-IR spectrometer (Spectrum One).

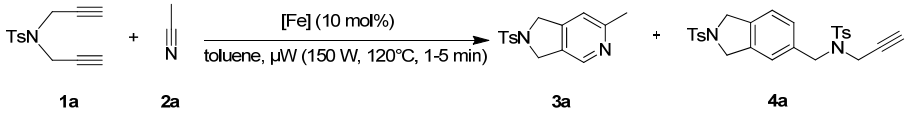
Part 1: Reaction conditions optimisation.

No reaction takes place without any catalyst when the reaction was performed in toluene under 50W microwave irradiation (entry 1, Table 1).[1] Iron(II) salts and [CpFe(naphth)][PF_6][2] were totally inactive, as well (entries 2-4, Table 1). To design the most efficient iron catalyst, we prepared several complexes and evaluated the role of each ligand: the cyclopendanienyl ancillary ligand (Cp or Cp*) and the other ligands (coordinating anion, monophosphines, diphosphines **11-12** and hemilabile bidentate ligands **5-10**). Whatever the other ligands on the iron centre, no reaction occurred with the Cp* complexes, a result in sharp contrast to the reactivity observed in ruthenium chemistry.[5] However, the pyridine **3a** was obtained in 53% conversion in the presence of the [CpFeCl] species, generated *in-situ* from [CpFe(naphth)][PF_6] and Et_3BnNCl (entry 2, Table 2), although accompanied by the intermolecular [2+2+2] cycloaddition by-product **4a**. Under conventional heating (120°C in 1/1 mixture of toluene and acetonitrile), pyridine **3a** was obtained in 53% conversion after 14h and the same selectivity **3a**/**4a** was observed (entries 2 and 3, Table 2). Based on this encouraging result, various anions were screened but none of them improved either the conversion or the chemoselectivity (Table 3). A threshold temperature of 120°C and a catalyst loading of 10 mol% appeared necessary to ensure an efficient cycloaddition reaction. Variation of the solvent revealed that none improved the yield. Then toluene was kept for this study (Table 4). Evaluation of pi-donor ligands was thus undertaken (Table 5). When one equivalent, relative to the iron complex, of monophosphine or phosphite was introduced, the expected pyridine **3a** was obtained in moderate yields (21% conversion, entry 1, Table 5) but **4a** was also detected. The electron density on the phosphine ligand seems to not alter the reactivity of the in-situ generated complex, because similar yields were obtained with electron rich and electron deficient monophosphines. Compared to monodentate phosphines, the use of the hemilabile bidentate ligand **5** improved the chemoselectivity in favour of the [2+2+2] cycloadduct **3a**. Interestingly, (P,O)-ligands led to higher chemoselectivity than (P,N)-ligands (entries 4-7 *vs.* 2-3, Table 5). The selectivity was also improved by increasing the number of chelating substituents (ligand **7** *vs.* **8**, **9**, **10**, entries 4-7, Table 5). Better results were finally obtained with phosphine **10**. In the presence of 10 mol% of [CpFe(naphth)][PF_6] and 10 mol% of **10** in toluene under microwave irradiation (120°C, 50W) after 30 min, pyridine **3a** was selectively isolated in a gratifying yield of 81%. To demonstrate further the importance of hemilabile ligand, bidentate phosphines, such as 1,2-diphenylphosphinobenzene (dppbz, **11**) and 1,3-bis(diphenylphosphino)-propane (**12**, dppp), were used but then no reaction occurred. A rapid screening of the solvent showed the same trend that the one observed with neutral complexes (Table 5). A final optimisation of microwave power showed that

[1] For a metal-free intramolecular [2+2+2] cycloaddition reaction providing pyridines, see: T. Sakai, R. L. Danheiser, *J. Am. Chem Soc.* **2010**, *132*, 13203-13205.
[2] E. P. Kündig, P. Jeger, G. Bernardelli, *Inorg. Chem. Act.*, 2004, **357**, 1909-1919.

150W gave the pyridine **3a** within a minute in 81% yield.

Table S1. Screening of iron sources.[a]

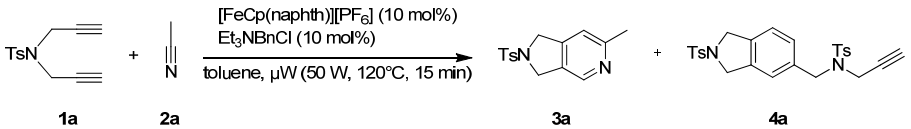


1a **2a** **3a** **4a**

Entry	[Fe] cat.	Ligand	Conv.[a] (%)	**3a**/**4a**
1	-	-	0	
2	$FeCl_2$	-	0	
3	$[Fe(BF_4)_2 \cdot 6H_2O]$	-	0	
4	$[CpFe(napth)][PF_6]$	-	0	

[a] Isolated yield in bracket. [b] diyne **1a**, acetonitrile **2a** (40 eq.), [Fe] cat. (10 mol%), toluene (0.6M), 120°C, μW 150W, 30 min.

Table S2. Influence of the catalyst and substrate loading.[a]

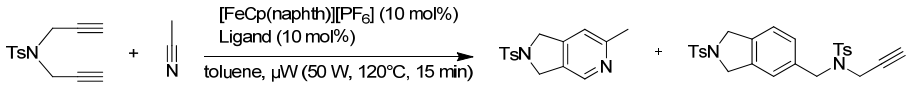


1a **2a** **3a** **4a**

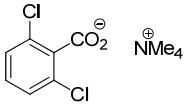
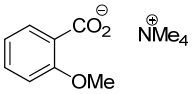
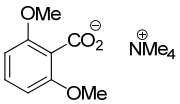
Entry	Cat. (mol%)	Et_3NBnCl (mol%)	CH_3CN **2a** (eq.)	Conv. (%)	Ratio **3a** / **4a**
1	10	10	20	32	81 / 19
2	10	10	40	53	83 / 17
3[b]	10	10	40	52	81 / 19
4	10	20	40	55	84 / 16
5	20	20	40	58	86 / 14

[a] Reaction conditions: diyne **1a** (0.25 mmol), cat. $[CpFe(naphth)][PF_6]$ (see table 1), Et_3NBnCl (10 mol%), CH_3CN **2a** (see table 1), toluene (0.4 mL, 0.6 M), μW irradiation (15 min, 50 W, 120°C). [b] thermal condition, 120°C for 14h.

Table S3. Influence of the ancillary ligand.[a]

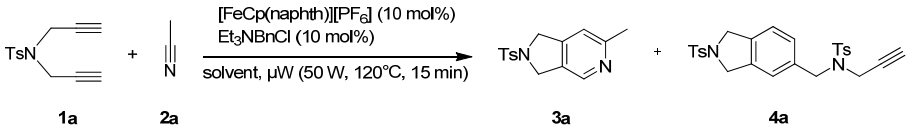


1a 2a 3a 4a

Entry	Ligand	Conv. (%)	Ratio **3a** / **4a**
1	$IN(nBu)_4$	24	57/ 43
2	$BrN(nBu)_4$	33	87 / 13
3	$ClN(nBu)_4$	57	84 / 16
4	$FN(nBu)_4$	13	100 / 0
5	Et_3BnNCl	53	83 / 17
6	$CF_3CO_2NMe_4$	33	100 / 0
7	$TsONMe_4$	17	100 / 0
8	$TfONMe_4$	18	22 / 78
9	$AcONMe_4$	13	100 / 0
10	NH_4Cl	13	23 / 77
11		27	100 / 0
12		28	100 / 0
13		9	100 / 0
14	KCN	0	0
15	Et_4NCN	34	91 / 9

[a] Reaction conditions: diyne **1a** (0.25 mmol), $[CpFe(naphth)][PF_6]$ (10 mol%), ligand (10 mol%), CH_3CN **2a** (40 eq.) toluene (0.4 mL, 0.6 M), µW irradiation (15 min, 50 W, 120°C).

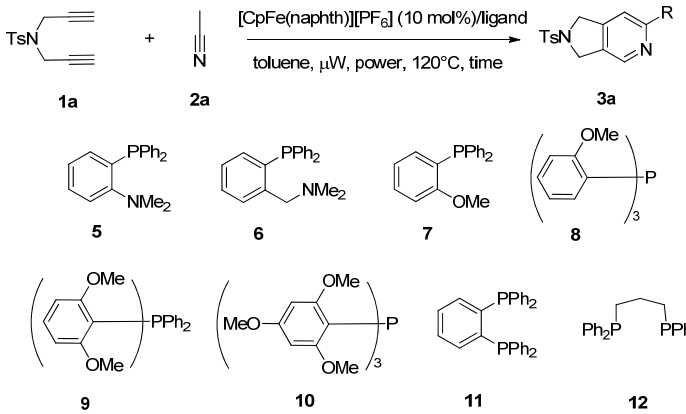
Table S4. Influence of the solvent.[a]



Entry	Solvent	Conv. (%)	Ratio **3a** / **4a**
1	1,2-dichloroethane	18	100 / 0
2	1,4-dioxane	54	80 / 20
3	toluene	53	83 / 17
4	H_2O	0	-
5	CH_3NO_2	0	-
6	DMF	33	85 / 15
7	Pentane	26	100 / 0
8	THF	36	83 / 17
9	*Iso*-propanol	23	100 / 0

[a] Reaction conditions: diyne **1a** (0.25 mmol), [CpFe(naphth)][PF_6] (10 mol%), Et_3NBnCl (10 mol%), CH_3CN **2a** (40 eq.) solvent (0.4 mL, 0.6 M), µW irradiation (15 min, 50 W, 120°C).

Table S5. Screening of phosphine ancillary ligands for the synthesis of pyridine **3a**.



Entry	[Fe] cat.	Ligand	conv[a] (%)	**3a**/**4a**
1	[CpFe(napth)][PF_6]	PPh_3	21	1/3
2	[CpFe(napth)][PF_6]	**5**	88	0,8/1
3	[CpFe(napth)][PF_6]	**6**	93	1/1
4	[CpFe(napth)][PF_6]	**7**	29	1/1
5	[CpFe(napth)][PF_6]	**8**	20	1,5/1
6	[CpFe(napth)][PF_6]	**9**	61	3/1
7	[CpFe(napth)][PF_6]	**10**	85 (81)	100/0
8	[CpFe(napth)][PF_6]	**11**	0	
9	[CpFe(napth)][PF_6]	**12**	0	

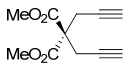
[a] Isolated yield in bracket. [b] diyne **1a**, acetonitrile **2a** (40 eq.), [Fe] cat. (10 mol%), phosphine (10 mol%), toluene (0.6M), 120°C, µW 150W, 30 min.

Part 2: Synthesis of diynes 1, phosphine ligands 5 and 9, and iron complex.

General procedure for the formation of symmetric diynes: Propargyle bromide (80% in toluene, 30 mL, 205 mmol, 3.5 eq.) was added to a solution of a malonate or sulfonamide (58.5 mmol, 1eq.) and potassium carbonate (40 g, 292.4 mmol, 5 eq.) in acetone (100 mL). The suspension was stirred at room temperature for two days. The suspension was diluted with EtOAc (100 mL) organic layer was washed with water (3x100 mL), brine (1x100 mL) and dried over $MgSO_4$. After filtration, the solvent was removed under vacuum.

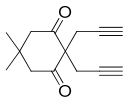
Chemical Formula: $C_{13}H_{13}NO_2S$
Exact Mass: 247,07 g.mol^{-1}

4-methyl-*N*,*N*-di(prop-2-yn-1-yl)benzenesulfonamide 1a[3]: Following the general procedure for the formation of symmetric diyne afforded **1a** as colorless solid (13 g, 52.6 mmol, 90% yield) after recrystallisation in a 6:1 solution of pentane/ethyl acetate (mp: 61 - 62 °C). R_f = 0.44 (80:20 pentane / ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.71 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 4.16 (d, *J* = 2.4 Hz, 4H), 2.42 (s, 3H), 2.15 (t, *J* = 2.4 Hz, 2H) ppm.



Chemical Formula: $C_{11}H_{12}O_4$
Exact Mass: 208,07 g.mol^{-1}

Dimethyl diprop-2-yn-1-ylpropanedioate 1b[4]: Following the general procedure for the formation of symmetric diyne afforded **1b** as colorless solid (11.5 g, 55.6 mmol, 95% yield) after recrystallisation in a 6:1 solution of pentane/ethyl acetate (mp: 86 - 87°C). ^{1}HNMR (400 MHz, $CDCl_3$) δ = 3.75 (s, 6 H), 2.98 (d, *J* = 2.6 Hz, 4 H), 2.03 (t, *J* = 2.6 Hz, 2 H) ppm.



Chemical Formula: $C_{14}H_{16}O_2$
Exact Mass: 216,12 g.mol^{-1}

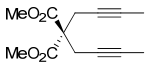
5,5-dimethyl-2,2-di(prop-2-yn-1-yl)cyclohexane-1,3-dione 1c:[5] Following the general procedure for the formation of symmetric diyne afforded **1c** as colorless solid (1.36 g, 6.3 mmol, 63% yield) after recrystallisation in a 6:1 solution of pentane/ethyl acetate (mp: 81 - 82°C). R_f = 0.68 (7:3 pentane /

[3] B. M. Trost, M. T. Rudd, *J. Am. Chem. Soc.*, 2005, **127**, 4763-4776.
[4] M. Schuster, C. Blechert, *Angew. Chem. Int. Ed.*, 1997, **36**, 2036-2056.
[5] A. S. K. Hashmi, T. Häffner, M. Rudolph, F. Rominger, *Chem. Eur. J.*, 2011, **17**, 8195-8201.

ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.66 (s, 4 H), 2.64 (d, *J* = 2.7 Hz, 4 H), 2.04 (t, *J* = 2.7 Hz, 2 H), 1.03 (s, 6 H) ppm.

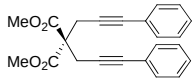
Chemical Formula: C_6H_6O
Exact Mass: 94,04 g.mol^{-1}

3-(prop-2-yn-1-yloxy)prop-1-yne 1d[6]**:** In a round bottom flask, NaOH (30g, 0.75 mol, 5 eq.) was dissolved in H_2O (4 mL) then, the TEBAC (0.6 g, 0.003 mol, 0.02 eq.), the propargylic alcohol (8.85 mL, 0.15 mol) and H_2O (20 mL) were added. The reaction mixture was stirred 10 min at room temperature and then propargyl bromide (15.75 mL, 0.15 mol) was added. The resulting mixture was stirred at 60°C for 3 hours. Organic layers were extracted with Et_2O (3x10 mL). Combined organic layers were dried over $MgSO_4$. After filtration the solvent was removed under vacuum. The resulting mixture was purified by distillation (760 mmHg) 117°C. The product was diyne **1d** was obtained as colorless oil (7.94 g, 0.084 mol, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.40 (d, *J* = 2.4 Hz, 4 H), 2.59 (t, *J* = 2.4 Hz, 2 H) ppm.



Chemical Formula: $C_{13}H_{16}O_4$
Exact Mass: 236,10 g.mol^{-1}

Dimethyl dibut-2-yn-1-ylpropanedioate 1e:[7] Following the general procedure for the formation of symmetric diyne afforded **1e** as a colorless solid (1.6 g, 6.72 mmol, 67% yield) after recrystallisation in a 6:1 solution of pentane/ethyl acetate (mp: 56 - 56°C). R_f = 0.78 (pentane / ethyl acetate 8:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.57 (s, 6 H), 2.70 (d, *J* = 2.4 Hz, 4 H), 1.58 (s, 6 H) ppm.

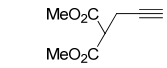


Chemical Formula: $C_{23}H_{20}O_4$
Exact Mass: 360,14 g.mol^{-1}

Dimethyl bis(3-phenylprop-2-yn-1-yl)propanedioate 1f:[8] In a flamed dried Schlenk triethylamine (5 mL, 6 eq.) and iodobenzene (1.5 mL, 13.36 mmol, 2.2 eq.) was added to a solution of diyne (6.07 mmol, 1 eq.), tetrakis-triphenylphosphine palladium (35 mg, 0.05 mmol, 0.5 mol%), copper iodide (23 mg, 0.121 mmol, 2mol%) in dried degassed THF (20 mL). the yellow solution was stirred at room temperature overnight. Ethyl acetate (100mL) was added to the reaction mixture. The organic layer was washed with a saturated solution of NH_4Cl (2x75 mL), water (2x75 mL) and then brine (1x100 mL). The organic layer was collected, dried over $MgSO_4$. After filtration, the solvent was removed

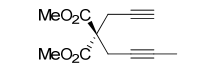
[6] R. E. Geiger, M. Lalonde, H. Stoller, K. Schleich, *Helvetica Chemica Acta* 1984, **67**, 1274-1282.
[7] R. S. Atkinson, M. J. Grimshire, *J. Chem. Soc., Perkin Trans. 1*, 1986, 1215-1224.
[8] Y. Hu, H. Yao, Y. Sun, J. Wan, X. Lin, T. Zhu, *Chem. Eur. J.*, 2010, **16**, 7635-7641.

under vacuum. The residue was purified by flash chromatography on silica gel (90:10 pentane / ethyl acetate) affording **1f** (1.1 g, 3.05 mmol, 50% yield) as a yellow oil. R_f = 0.70 (80:20 pentane / ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.41 - 7.37 (m, 4 H), 7.31 - 7.28 (m, 6 H), 3.80 (s, 6 H), 3.27 (s, 4 H) ppm.



Chemical Formula: $C_8H_{10}O_4$
Exact Mass: 170,06 g.mol^{-1}

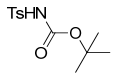
Dimethyl prop-2-yn-1-ylpropanedioate S1[9]: propargyle bromide (80% in toluene, 1.46 mL, 10 mmol) was added at room temperature to a solution of dimethyl propanedioate (3.44 mL, 30 mmol, 3 eq.) and potassium carbonate (2.8 g, 20 mmol, 4 eq.) in acetone (16 mL). The yellow suspension was stirred at room temperature for 2 days. After completion, the solvent was removed under vacuum. The residue was diluted with dichloromethane and water, aqueous layer was extracted with dichloromethane (3x50 mL), combined organic layers were dried over $MgSO_4$. After filtration, the solvent was removed under vacuum. The residue was purified by flash chromatography on silica gel (90:10 pentane / ethyl acetate) afforded **S1** as a colorless oil (1.5 g, 8.8 mmol, 88% yield). R_f = 0.27 (70:30 pentane / ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.49 (s, 6 H), 3.36 (t, *J* = 7.7 Hz, 1 H), 2.48 (dd, *J* = 2.7, 7.7 Hz, 2 H), 1.89 (t, *J* = 2.7 Hz, 1 H) ppm.



Chemical Formula: $C_{12}H_{14}O_4$
Exact Mass: 222,09 g.mol^{-1}

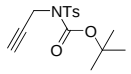
Dimethyl but-2-yn-1-yl(prop-2-yn-1-yl)propanedioate 1g:[10] 1-bromo-2-butyne (1.5 mL, 17.6 mmol, 2 eq.) was added at room temperature to a solution of a dimethyl prop-2-yn-1-ylpropanedioate (1.5 g, 8.8 mmol) with potassium carbonate (2.7 g, 19.4 mmol, 2.2 eq.) in acetone (15 mL). The yellow suspension was stirred at room temperature for two. After completion, the solvent was removed under vacuum. The residue was diluted with dichloromethane and water, aqueous layer was extracted with dichloromethane (3x50 mL), combined organic layers were dried over $MgSO_4$. After filtration, the solvent was removed under vacuum. The residue was crystallised (mp: 54 - 55°C) with a solution of pentane ethyl acetate (6:1) afforded **1g** as colourless solid (1.58 g, 7.12 mmol, 81% yield). R_f = 0.82 (70: 30 pentane / ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.72 (s, 6 H), 2.94 (d, *J* = 2.7 Hz, 2 H), 2.89 (q, *J* = 2.5 Hz, 2 H), 2.00 (t, *J* = 2.7 Hz, 1 H), 1.72 (t, *J* = 2.5 Hz, 3 H) ppm.

[9] D. Llrena, O. Buisine, C. Aubert, M. Malacria, *Tetrahedron* 1998, **54**, 9373-9392.
[10] T. Shimamoto, M. Chimori, H. Sogawa, K. Yamamoto, *J. Am. Chem. Soc.*, 2005, **127**, 16410-16411.



Chemical Formula: $C_{12}H_{17}NO_4S$
Exact Mass: 271,09 $g.mol^{-1}$

***tert*-butyl [(4-methylphenyl)sulfonyl]carbamate S2**:[11] a solution of Boc_2O (7.3 g, 33 mmol, 1.15 eq.) in dichloromethane (57 mL) was added dropwise at room temperature to a solution of *p*-toluenesulfonamide (5 g, 29 mmol), DMAP (353 mg, 2.9 mmol, 0.1 eq.) and triethylamine (4.4 mL, 32 mmol, 1.1 eq.) in dichloromethane (36 mL). The colorless reaction mixture was stirred at room temperature for 2 hour. After completion the solvent was removed under vacuum, the residue was diluted with ethyl acetate and a saturated solution of NH_4Cl. Organic layer was washed with water (3x100mL), brine (1x100mL) and then dried over $MgSO_4$. After filtration the solvent was removed under vacuum. The residue was recrystalized (mp: 117 - 118°C) with hexane afforded **S2** as a colorless solid (6.71 g, 24.8 mmol, 85% yield). R_f = 0.41 (70:30 petroleum ether / ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.97 (*br*. s, 1 H), 7.87 (d, *J* = 8.2 Hz, 2 H), 7.30 (d, *J* = 8.2 Hz, 2 H), 2.42 (s, 3 H), 1.35 (s, 9 H) ppm.



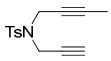
Chemical Formula: $C_{15}H_{19}NO_4S$
Exact Mass: 309,10 $g.mol^{-1}$

***tert*-butyl [(4-methylphenyl)sulfonyl]prop-2-yn-1-ylcarbamate S3**:[11] sodium hydride (60% dispersed in mineral oil, 81 mg, 2.03 mmol, 1.1 eq.) was added dropwise to a solution of *tert*-butyl [(4-methylphenyl)sulfonyl]carbamate (500 mg, 1.84 mmol) in dry THF (3 mL) at 0°C. The reaction mixture was stirred at 0°C for 30min. Propargyl bromide (80% in toluene, 1 mL, 4.4 mmol, 1.3 eq.) was added dropwise at 0°C. The reaction mixture was warmed up to room temperature overnight. After completion, water (20 mL) was added to the reaction mixture, aqueous layer was extracted with ethyl acetate (3x20 mL). Combined organic layers were washed with brine and dried over $MgSO_4$. The residue was purified by flash chromatography on silica gel (93:7 petroleum ether / ethyl acetate) afforded **S3** as a colorless solid (256 mg, 0.828 mmol, 45% yield) (mp: 96 - 97°C). R_f = 0.6 (80:20 petroleum ether / ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.83 (d, *J* = 8.2 Hz, 2 H), 7.24 (d, *J* = 8.2 Hz, 2 H), 4.55 (d, *J* = 1.5 Hz, 2 H), 2.36 (s, 3 H), 2.28 (t, *J* = 1.5 Hz, 1 H), 1.27 (s, 9 H) ppm.

Chemical Formula: $C_{10}H_{11}NO_2S$
Exact Mass: 209,05 $g.mol^{-1}$

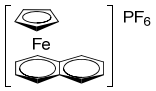
[11] Q. Wu, J. Hu, X. Ren, J. S. Zhou, *Chem. Eur. J.*, 2011, **17**, 11553-11558.

4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide S4:[12] trifluoroacetic acid (4 mL, 50 mmol, 40 eq.) was added at room temperature to a solution of *tert*-butyl [(4-methylphenyl)sulfonyl]prop-2-yn-1-ylcarbamate (380 mg, 1.23 mmol) in dichloromethane (4mL). The yellow solution was stirred at room temperature for 4 hours. Yellow solution was diluted with ethyl acetate (50mL), organic layer was washed with $NaHCO_3$ (saturated solution, 3x25mL), then water (25mL) and brine (25mL). Organic layer was collected, dried over $MgSO_4$. After filtration, the solvent was removed under. The residue was purified by flash chromatography on silica gel (20:10 cyclohexane / ethyl acetate) afforded **S4** as a colorless solid (226mg, 1.08mmol, 88% yield) (mp: 73 - 74°C). R_f = 0.33 (20:10 cyclohexane / ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.77 (d, *J* = 8.2 Hz, 2 H), 7.32 (d, *J* = 8.2 Hz, 2 H), 4.57 (*br*. s, 1 H), 3.83 (dd, *J* = 2.5, 6.0 Hz, 2 H), 2.43 (s, 3 H), 2.11 (t, *J* = 2.5 Hz, 1 H) ppm.



Chemical Formula: $C_{14}H_{15}NO_2S$
Exact Mass: 261,08 g.mol^{-1}

N-(but-2-yn-1-yl)-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide 1h:[13] 1-bromo-2-butyne (1.14 mL, 13.1 mmol, 1.5eq.) was added at room temperature to a solution of 4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide (914 mg, 4.37 mmol) and potassium carbonate (1.21 g, 8.74mmol, 2 eq.) in acetone (43 mL). The colorless solution was stirred at room temperature overnight. The reaction mixture was diluted with ethyl acetate (50mL), organic layer was washed with water (3x50 mL), brine (50 mL) and dried over $MgSO_4$. After filtration, the solvent was removed under vacuum. The crude product was purified by flash chromatography on silica gel (80:20 pentane / ethyl acetate) afforded **1h** (1.04g, 3.98 mmol, 90% yield). R_f = 0.75 (30:70 pentane/ethyl acetate) (mp: 66 - 67°C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.69 (d, *J* = 8.3 Hz, 2 H), 7.27 (d, *J* = 8.3 Hz, 2 H), 4.11 (d, *J* = 2.5 Hz, 2 H), 4.08 (d, *J* = 2.4 Hz, 2 H), 2.40 (s, 3 H), 2.13 (t, *J* = 2.5 Hz, 1 H), 1.62 (t, *J* = 2.4 Hz, 3H) ppm.

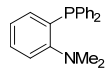


Chemical Formula: $C_{15}H_{13}F_6FeP$
Exact Mass: 394,00 g.mol^{-1}

η^6-Naphtalene) (η^5-cyclopentadienyl)- iron (II) hexafluorophosphate:[2] In a flame dried Schenk was added naphthalene (13.8 g, 108 mmol, 4 eq.), ferrocene (5 g, 27 mmol), aluminium trichloride (3.58 g, 29.7 mmol, 1.1 eq) and aluminium powder (379 mg, 14.6 mmol, 0.52 eq). The system was purged from air by vacuum. The Schlenk was placed under argon and degassed *n*-heptane (45 mL) was added at room temperature. The reaction mixture was heated at 30°C and titanium chloride (1.48 mL, 13.5 mmol, 0.5 eq) was added dropwise over 15 min. The reaction mixture was heated at 90°C for

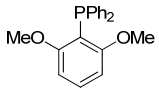
[12] A. S. K. Hashmi, J. P. Weyrauch, E. Kurpejovic, T. M. Frost, B. Michlich, W. Frey, J. W. Bats, *Chem. Eur. J.* 2006, **12**, 5806-5814.
[13] S. Apte, B. Radetich, S. Shin, T. V. RajanBabu, *Org. Lett.*, 2004, **6**, 4053-4056.

3 hours (the Schenk was equipped with a reflux condenser). Aflter cooling to 0°C, the black reaction mixture was treated with a degassed hydrochloride solution (10 mL conc. HCl in 45 mL of water) followed by a solution of hydrogen peroxide (0.8 mL, 30% aq. solution). The red reaction mixture was stirred at 50°C for 45 min, and then the aqueous phase was separated, filtered and treated with an aqueous degassed solution of potassium hexafluorophosphate solution (4.97 g, 27 mmol, 1 eq, in 45 mL of water). After cooling to 0°C, the orange precipitate was filtered and dried under vacuum afforded (4.22 g, 10.74 mmol, 40% yield) (mp 156 - 157°C). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.07-8.04 (m, 2 H), 7.83-7.80 (m, 2 H), 7.35 (dd, *J* = 2.7, 4.6 Hz, 2 H), 6.46 (dd, *J* = 2.7, 4.6 Hz, 2 H), 4.64 (s, 5 H) ppm.



Chemical Formula: $C_{20}H_{20}NP$
Exact Mass: 305,13 g.mol^{-1}

Ligand 5: To a solution of 2-bromo-(N,N-dimethyaniline) (2.06 g, 10.3 mmol) in degassed THF (17 mL) at -78°C was added *n*-BuLi (2.5 M in hexane, 4.4 mL, 10.86 mmol, 1.05 eq.). The reaction mixture was stirred at -78°C for 30 minutes, then, at 0°C for 15 minutes. The PPh_2Cl (1.93 mL, 10.86 mmol, 1.05 eq.) was added at -78°C. The resulting reaction mixture was stirred at 0°C overnight, then worked up by filtration on a pad of Celite®. The residue was purified by flash chromatography on silica gel (90:10 cyclohexane / ethyl acetate) affording **5** (2.3 g, 7.54 mmol, 73% yield) as a white solid (mp 120 – 121°C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36 - 7.27 (m, 10 H), 7.23 (ddd, *J* = 1.0, 4.7, 8.0 Hz, 1 H), 7.04 - 6.99 (dddd, *J* = 0.5, 1.3, 7.3, 7.7, 1 H), 6.85 - 6.81 (dddd, *J* = 0.4, 1.6, 3.8, 7.6 Hz, 1 H), 2.63 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.3 (d, *J* = 19.5 Hz, Cq), 138.4 (d, *J* = 11.9 Hz, Cq), 134.6 (d, *J* = 9.2 Hz, Cq), 134.5 (CH), 134.0 (d, *J* = 20.1 HZ, CH), 130.0 (CH), 128.54 (2xCH), 128.4 (d, *J* = 5.1 Hz, 4xCH), 124.6 (CH), 120.7 (d, *J* = 2.6 Hz, CH), 45.7 (2xCH_3) ppm. ^{31}P NMR (162 MHz, $CDCl_3$) δ = -14.2 ppm.



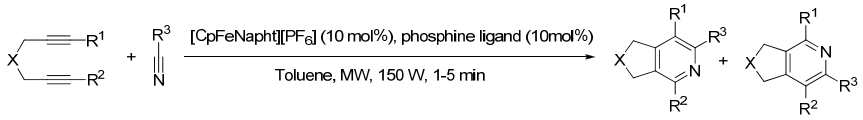
Chemical Formula: $C_{20}H_{19}O_2P$
Exact Mass: 322,11

Ligand 9:[14] To a solution of 1,3-dimethoxybenzene (1.3 mL, 10 mmol, 1 eq.) in dried and degassed diethyl ether (10 mL), TMEDA (0.01 eq.) and *n*-BuLi (2.5M in hexane, 1.05 eq.) were successively slowly added at 0°C under argon. The reaction mixture was stirred at 0°C for 1h30 under argon. Then, the reaction mixture was slowly warmed to room temperature. Ph_2PCl (1.9 mL, 10.5 mmol, 1.05 eq.) was added dropwise at -50°C. The reaction was stirred for 2 h, at -50°C, then overnight at room

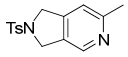
[14] McEwen,W.E. et al., *J. Am. Chem. Soc*., **1978,** 100, 7304 – 7311.

temperature. The reaction mixture was diluted in diethyl ether and water. Aqueous layer was extracted with diethylether and the combined organic layers were dried over $MgSO_4$. After filtration, the solvent was removed under vacuum. The residue was purified by flash chromatography on silica gel (60:40 pentane/ethyl acetate) to afford compound **9** (0.488 g, 1.49 mmol, 15%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40-7.35 (m, 5H), 7.30-7.25 (m, 6H overlapped with residual $CHCl_3$), 6.55 (dd, *J* = 2.4, 8.4 Hz, 2H), 3.54 (s, 6H) ppm. ^{31}P {decoupled H} NMR (162 MHz, $CDCl_3$) δ = -25.2 ppm.

Part 3: General procedure and description of pyridines 3.

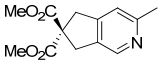


General procedure for iron catalyzed [2+2+2] cycloaddition reaction: In a flamed microwave reactor was added diyne (0.5 mmol.) in presence of iron catalyst (20 mg, 0.05 mmol, 10 mol%) and tris(2,4,6-trimethoxyphenyl)phosphine (27 mg, 0.05 mmol, 10 mol%). The system was purged with argon. Dry and degassed toluene was added to the solid (840 µL) followed by the degassed nitrile (5 or 40 eq. depending of the boiling point of the nitrile). The reactor vessel was irradiated with microwave (150 W) for 5 min. The solvent was removed under vacuum. The residue was directly purified by flash chromatography on silica gel.



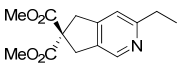
Chemical Formula: $C_{15}H_{16}N_2O_2S$
Exact Mass: 288,09 g.mol^{-1}

Compound 3a:[15] Following the general procedure for the iron catalyzed [2+2+2] cycloaddition reaction compound **3a** (103 mg, 0.36 mmol, 72%) was obtained after flash chromatography on silica gel (70:30 ethyl acetate / pentane) as a colorless solid (mp: 170 - 171°C). R_f = 0.16 (70:30 ethyl acetate / pentane). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.30 (s, 1 H), 7.72 (d, *J* = 8.3 Hz, 2 H), 7.29 (d, *J* = 8.3 Hz, 2 H), 6.97 (s, 1 H), 4.60 (s, 2 H), 4.56 (s, 2 H), 2.51 (s, 3 H), 2.40 (s, 3 H) ppm.



Chemical Formula: $C_{13}H_{15}NO_4$
Exact Mass: 249,10 g.mol^{-1}

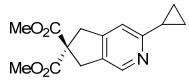
Compound 3b:[16] Following the general procedure for the iron catalyzed [2+2+2] cycloaddition reaction compound **3b** (121 mg, 0.48 mmol, 97% yield) was obtained after flash chromatography on silica gel (30:70 pentane / ethyl acetate) as a colorless solid (mp: 95 - 96°C). R_f = 0.25 (30:70 pentane / ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.29 (s, 1 H), 6.99 (s, 1 H), 3.72 (s, 6 H), 3.54 (s, 2 H), 3.51 (s, 2 H), 2.47 (s, 3 H) ppm.



Chemical Formula: $C_{14}H_{17}NO_4$
Exact Mass: 263,12 g.mol^{-1}

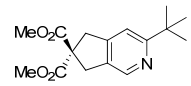
[15] C. Wang, X. Li, F. Wu, B. Wan, *Angew. Chem. Int. Ed.*, 2011, **50**, 7162-7166.
[16] K. Tanaka, N. Suzuki, G. Nishida, *Eur. J. Chem. Org.*, 2006, 3917-3922.

Compound 3c:[17] Following the general procedure for the iron catalyzed [2+2+2] cycloaddition reaction compound **3c** (121 mg, 0.48 mmol, 97% yield) was obtained after flash chromatography on silica gel (30:70 pentane / ethyl acetate) as a colorless solid (mp: 95 - 96°C). R_f = 0.25 (3:7 pentane / ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.27 (s, 1 H), 6.96 (s, 1 H), 3.67 (s, 6 H), 3.51 (s, 2 H), 3.49 (s, 2 H), 2.70 (q, *J* = 7.6 Hz, 2 H), 1.20 (t, *J* = 7.6 Hz, 3 H) ppm.



Chemical Formula: $C_{15}H_{17}NO_4$
Exact Mass: 275,12 g.mol^{-1}

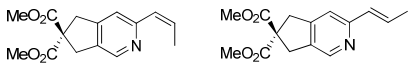
Compound 3d: Following the general procedure for the iron catalyzed [2+2+2] cycloaddition reaction compound **3d** (133 mg, 0.483 mmol, 96% yield) was obtained after flash chromatography on silica gel (80:20 pentane / ethyl acetate) as a colorless oil. R_f = 0.17 (80:20 pentane / ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.21 (d, *J* = 0.7 Hz, 1 H), 6.94 (s, 1 H), 3.70 (s, 6 H), 3.51 (s, 2 H), 3.49 (s, 2 H), 1.97 - 1.91 (m, 1 H), 0.91 - 0.88 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.6 (2xCq), 161.4 (Cq), 149.6 (Cq), 144.7 (CH), 132.8 (Cq), 116.9 (CH), 60.2 (Cq), 53.1 (2xCH_3), 40.2 (CH_2), 38.0 (CH_2), 17.1 (CH), 9.6 (2xCH_2) ppm. IR (neat) λ = 2989, 2954, 2870, 1731, 1611, 1433, 1271, 1199, 1158, 1051, 940, 814 cm^{-1}. MS [ESI (+)] m/z (%) 176 ([MH]$^+$, 100%). Mass calcd for $C_{15}H_{18}NO_4$ (MH)$^+$ 276.1236; found 276.1240.



Chemical Formula: $C_{16}H_{21}NO_4$
Exact Mass: 291,15 g.mol^{-1}

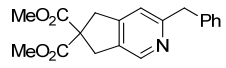
Compound 3e: Following the general procedure for the iron catalyzed [2+2+2] cycloaddition reaction compound **3e** (94 mg, 0.32 mmol, 64% yield) was obtained after flash chromatography on silica gel (80:20 pentane / ethyl acetate) as a colorless solid (mp: 73 - 74°C). R_f = 0.37 (80:20 pentane / ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.34 (d, *J* = 0.8 Hz, 1 H), 7.16 (s, 1 H), 3.71 (s, 6 H), 3.55 (s, 2 H), 3.54 (s, 2 H), 1.31 - 1.28 (m, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.7 (2xCq), 167.9 (Cq), 149.7 (Cq), 144.1 (CH), 132.9 (Cq), 114.9 (CH), 60.1 (Cq), 53.1 (2xCH_3), 40.5 (CH_2), 38.0 (CH_2), 37.3 (Cq), 30.3 (3xCH_3) ppm. IR (neat) λ = 2955, 1728, 1604, 1434, 1280, 1265, 1199, 1157, 1068, 1052, 885 cm^{-1}. MS [ESI (+)] m/z (%) 292 ([M+H]$^+$, 100%). Mass calcd for $C_{16}H_{22}NO_4$ [M+H]$^+$ 292.549; found 292.1557.

[17] B. M. Trost, A. C. Gutierrez, *Org. Lett.*, 2007, **9**, 1473-1476.



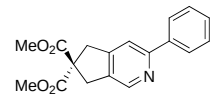
Chemical Formula: $C_{15}H_{17}NO_4$
Exact Mass: 275,12 g.mol^{-1}

Compound 3f: Following the general procedure for the iron catalyzed [2+2+2] cycloaddition reaction compound **3f** (56 mg, 0.203 mmol, 41% yield) was obtained after flash chromatography on silica gel (80:20 pentane / ethyl acetate) as a colorless oil. R_f = 0.16 (80:20 pentane / ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$) δ = ***Z***: 8.42 (*br*. s, 1 H), 7.12 (s, 1 H), 6.49 - 6.40 (m, 1 H), 5.94 (dd, *J* = 7.2, 11.8 Hz, 1 H), 3.74 (s, 6 H), 3.60 – 3.58 (m, 4 H), 2.03 (dd, *J* = 1.8, 7.2 Hz, 3 H) ppm. ***E***: 8.33 (s, 1 H), 7.11 (s, 1 H), 6.69 - 6.58 (m, 1 H), 6.49 - 6.40 (m, 1 H), 3.73 (s, 6 H), 3.59 – 3.55 (m, 4 H), 1.89 (dd, *J* = 1.6, 6.7 Hz, 3 H) ppm. ^{13}C NMR (101 MHz , $CDCl_3$) δ = ***Z***: 171.6 (Cq), 155.4 (Cq), 150 (Cq), 144.9 (CH), 134.0 (Cq), 131.2 (CH), 130.3 (CH), 129.6 (CH), 119.6 (CH), 60.2 (Cq), 53.2 (2xCH_3), 40.4 (CH_2), 38.2 (CH_2), 18.4 (CH_3) ppm. ***E*** (partial): 171.6 (Cq), 155.0 (Cq), 149 (Cq), 144.9 (CH), 133.6 (Cq), 130.7 (CH), 116.5 (CH), 60.2 (Cq), 53.2 (2xCH_3), 40.3 (CH_2), 38.2 (CH_2), 15.1 (CH_3) ppm. IR (neat) λ = 2955, 1731, 1606, 1433, 1269, 1159, 1068, 966, 884 cm^{-1}. MS [ESI (+)] m/z (%) 277 (15), 276 ([M+H]$^+$, 100%). Mass calcd for $C_{15}H_{18}NO_4$ [M+H]$^+$ 276.1236; found 276.1227.



Chemical Formula: $C_{19}H_{19}NO_4$
Exact Mass: 325,13

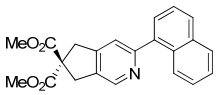
Compound 3g: Following the general procedure for the iron catalyzed [2+2+2] cycloaddition reaction compound **3g** (152 mg, 0.47 mmol, 93% yield) was obtained after flash chromatography on silica gel (40:60 pentane / ethyl acetate) as brownish solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.38 (s, 1H), 7.20-7.32 (m, 5H), 6.96 (s, 1H), 4.12 (s, 2H), 3.75 (s, 6H), 3.58 (s, 2H), 3.52 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.6 (2xCq), 159.5 (CH_2), 150.3 (CH_2), 144.9 (CH), 139.6 (CH_2), 133.7 (CH_2), 129.1 2xCH), 128.6 (2xCH), 126.4 (CH), 118.9 (CH), 60.1 (CH_2), 53.2 (2xCH_3), 44.5 (CH_2), 40.3 (CH_2), 38.0 (CH_2) ppm. Mass Calcd for $C_{19}H_{19}NO_4$ [M+H]$^+$ 326.1402 ; found 326.1392.



Chemical Formula: $C_{18}H_{17}NO_4$
Exact Mass: 311,12 g.mol^{-1}

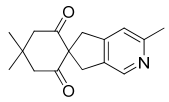
Compound 3h:[16] Following the general procedure for the iron catalyzed [2+2+2] cycloaddition reaction compound **3h** (133 mg, 0.43 mmol, 86% yield) was obtained after flash chromatography on silica gel (80:20 pentane / ethyl acetate) as a colorless solid (mp: 115 - 116°C). R_f = 0.2 (80:20 pentane

/ ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.50 (d, *J* = 0.8 Hz, 1 H), 7.91 (dd, *J* = 1.3, 8.3 Hz, 2 H), 7.55 (s, 1 H), 7.46 - 7.33 (m, 3 H), 3.74 (s, 6 H), 3.64 (s, 2 H), 3.62 (s, 2 H) ppm.



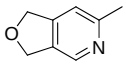
Chemical Formula: $C_{22}H_{19}NO_4$
Exact Mass: 361,13 g.mol^{-1}

Compound 3i: Following the general procedure for the iron catalyzed [2+2+2] cycloaddition reaction compound **3i** (65 mg, 0.180 mmol, 36% yield) was obtained after flash chromatography on silica gel (80:20 pentane / ethyl acetate) as a yellow oil. R_f = 0.11 (80:20 pentane / ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.64 (s, 1 H), 8.09 - 8.04 (m, 1 H), 7.90 (d, *J* = 7.3 Hz, 2 H), 7.58 - 7.45 (m, 4 H), 7.44 (s, 1 H), 3.81 (s, 6 H), 3.75 (s, 2 H), 3.71 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.6 (2xCq), 157.9 (Cq), 150.2 (Cq), 145.2 (CH), 138.6 (Cq), 134.6 (Cq), 134.0 (Cq), 131.3 (Cq), 128.8 (CH), 128.4 (CH), 127.4 (CH), 126.5 (CH), 125.9 (CH), 125.7 (CH), 125.3 (CH), 120.9 (CH), 60.2 (Cq), 53.3 (2xCH_3), 40.5 (CH_2), 38.3 (CH_2) ppm. IR (neat) λ = 2988, 2870, 1731, 1604, 1433, 1377, 1261, 1199, 1159, 1069, 802, 778 cm^{-1}. MS [ESI (+)] m/z (%) 362 ($[M+H]^+$, 100%)? 304 (5), 276 (10). Mass calcd for $C_{22}H_{20}NO_4$ $[M+H]^+$ 362.1392; found 362.1375.



Chemical Formula: $C_{16}H_{19}NO_2$
Exact Mass: 257,14 g.mol^{-1}

Compound 3j:[18] Following the general procedure for the iron catalyzed [2+2+2] cycloaddition reaction compound **3j** (103 mg, 0.4 mmol, 80% yield) was obtained after flash chromatography on silica gel (30:70 pentane / ethyl acetate) as a colorless solid (mp: 144 - 145°C). R_f = 0.13 (30:70 pentane / ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.21 (s, 1 H), 6.97 (s, 1 H), 3.39 (s, 2 H), 3.35 (s, 2 H), 2.74 (d, *J* = 14.2 Hz, 2 H), 2.56 (d, *J* = 14.2 Hz, 2 H), 2.45 (s, 3 H), 1.05 (s, 3 H), 0.91 (s, 3 H) ppm.

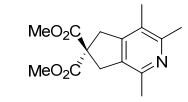


Chemical Formula: C_8H_9NO
Molecular Weight: 135,1632

Compound 3k: Following the general procedure for the iron catalyzed [2+2+2] cycloaddition reaction compound **3k** (23 mg, 0.17 mmol, 34% yield) was obtained after flash chromatography on silica gel (3:7 pentane / ethyl acetate) as a colorless oil. R_f = 0.1 (30:70 pentane / ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.39 (s, 1 H), 7.05 (s, 1 H), 5.09 (s, 2 H), 5.03 (s, 2 H), 2.55 (s, 3 H) ppm. ^{13}C NMR

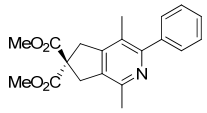
[18] K. Kase, A. Goswami, K. Ohtaki, E. Tanabe, N. Saino, S. Okamoto, *Org. Lett.*, 2007, **9**, 931-934.

(100 MHz, $CDCl_3$) δ = 157.1 (Cq), 149.6 (Cq), 142.0 (CH), 132.5 (Cq), 116.0 (CH), 72.9 (CH_2), 71.7 (CH_2), 24.4 (CH_3) ppm. IR (neat) λ = 3033, 3009, 1921, 2861, 1615, 1395, 1302, 1042, 897, 834 cm^{-1}. MS [ESI (+)] m/z (%) 136 ($[MH]^+$, 100%). Mass calcd for $C_8H_{10}NO$ $(MH)^+$ 136.0762; found 136.0758.



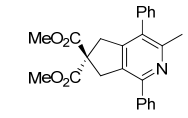
Chemical Formula: $C_{15}H_{19}NO_4$
Exact Mass: 277,13

Compound 3o:[14,17] Following the general procedure for the iron catalyzed [2+2+2] cycloaddition reaction compound **3o** (92 mg, 0.33 mmol, 66% yield) was obtained after flash chromatography on silica gel (60:40 pentane / ethyl acetate) as a colorless solid (mp: 122 - 123°C). R_f = 0.31 (60:40 pentane / ethyl acetate). ^1H NMR (400 MHz, $CDCl_3$) δ = 3.75 (s, 6 H), 3.52 (s, 4 H), 2.42 (s, 3 H), 2.38 (s, 3 H), 2.14 (s, 3 H) ppm.



Chemical Formula: $C_{20}H_{21}NO_4$
Exact Mass: 339,15

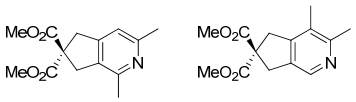
Compound 3p:[14,17] Following the general procedure for the iron catalyzed [2+2+2] cycloaddition reaction compound **3p** (62 mg, 0.183 mmol, 36% yield) was obtained after flash chromatography on silica gel (80:20 pentane / ethyl acetate) as a yellow oil. R_f = 0.21 (80:20 pentane / ethyl acetate). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.47 - 7.32 (m, 5 H), 3.79 (s, 6 H), 3.63 (s, 2 H), 3.60 (s, 2 H), 2.48 (s, 3 H), 2.19 (s, 3 H) ppm.



Chemical Formula: $C_{25}H_{23}NO_4$
Exact Mass: 401,16

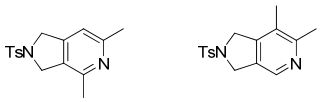
Compound 3q: following the general procedure for the iron catalyzed [2+2+2] cycloaddition reaction compound **3q** (51 mg, 0.13 mmol, 26% yield) was obtained after flash chromatography on silica gel (90:10 pentane / ethyl acetate) as a yellow oil. R_f = 0.18 (90:10 pentane / ethyl acetate). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.79 (dd, *J* = 1.3, 8.3 Hz, 2 H), 7.53 - 7.45 (m, 4 H), 7.44 - 7.36 (m, 2 H), 7.33 - 7.28 (m, 2 H), 3.83 (s, 2 H), 3.71 (s, 6 H), 3.39 (s, 2 H), 2.43 (s, 3 H) ppm. ^{13}C NMR (100 MHz , $CDCl_3$) δ = 171.7 (2xCq), 155.0 (Cq), 152.3 (Cq), 139.7 (Cq), 138.0 (Cq), 132.3 (Cq), 131.7 (Cq), 130.6 (Cq), 129.0 (2xCH), 128.8 (2xCH), 128.6 (2xCH), 128.5 (2xCH), 127.7 (2xCH), 60.3 (Cq), 53.2 ($2xCH_3$), 40.5 (CH_2), 40.2 (CH_2), 23.1 (CH_3) ppm. IR (neat) λ =1953, 2870, 1732, 1433, 1261, 1200, 1072, 760,

700 cm^{-1}. MS [ESI (+)] m/z (%) 402 ($[M+H]^+$, 100%). Mass calcd for $C_{25}H_{24}NO_4$ $[M+H]^+$ 402.1705; found 402.1718.



Chemical Formula: $C_{14}H_{17}NO_4$
Exact Mass: 263,12

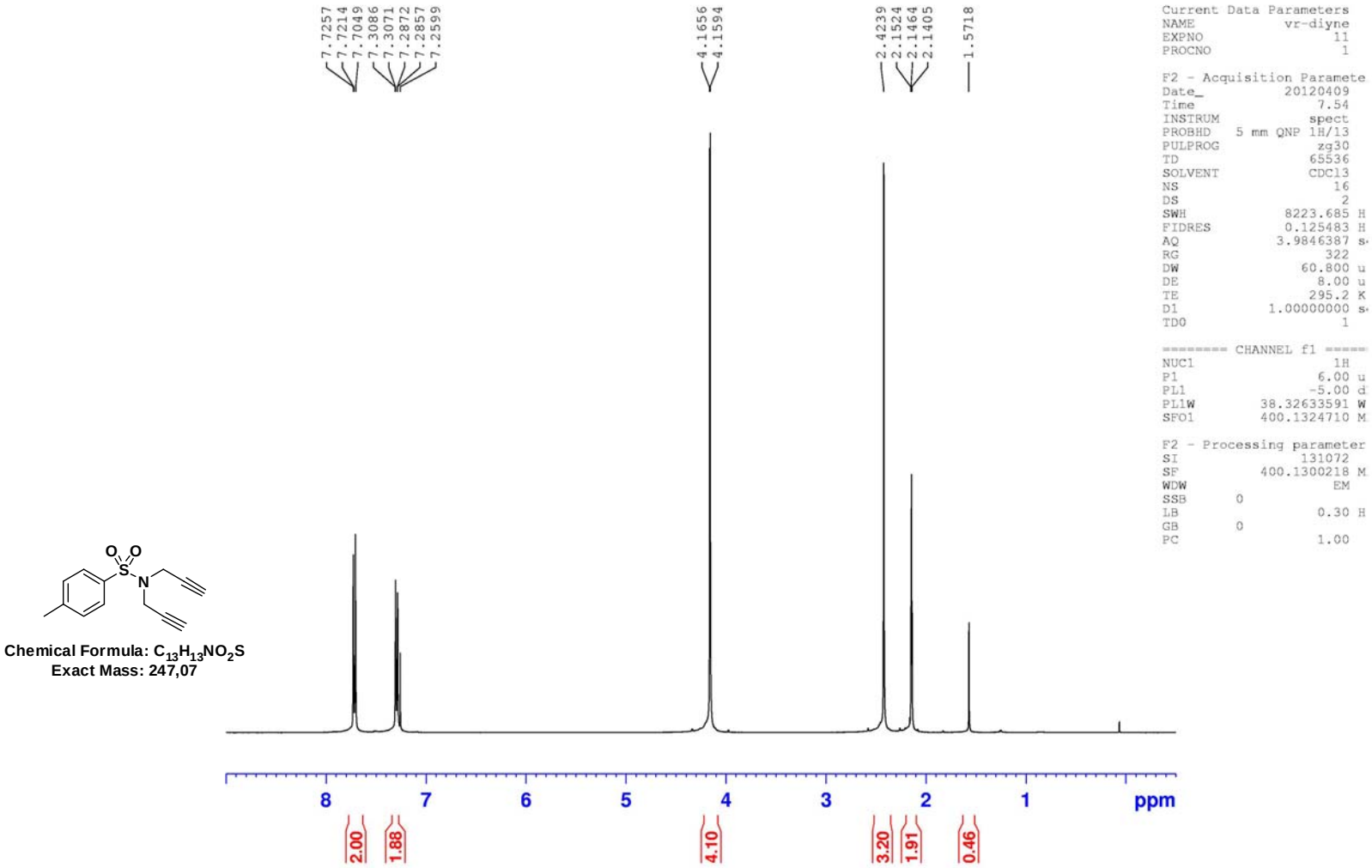
Compound 3r and 3s:[14] Following the general procedure for the iron catalyzed [2+2+2] cycloaddition reaction compounds a 1:6 ratio of **3r**/**3s** (116 mg, 0.44 mmol, 89% yield) were obtained after flash chromatography on silica gel (20:80 pentane / ethyl acetate) as a colorless oil. R_f = 0.16 (30:70 pentane / ethyl acetate). **3r** ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.83 (s, 1 H), 3.73 (s, 6 H), 3.52 (s, 2 H), 3.49 (s, 2 H), 2.44 (s, 3 H), 2.41 (s, 3 H) ppm. **3s** (partial): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.12 (s, 1H), 2.42, (s, 3H) ppm.



Chemical Formula: $C_{16}H_{18}N_2O_2S$
Exact Mass: 302,11

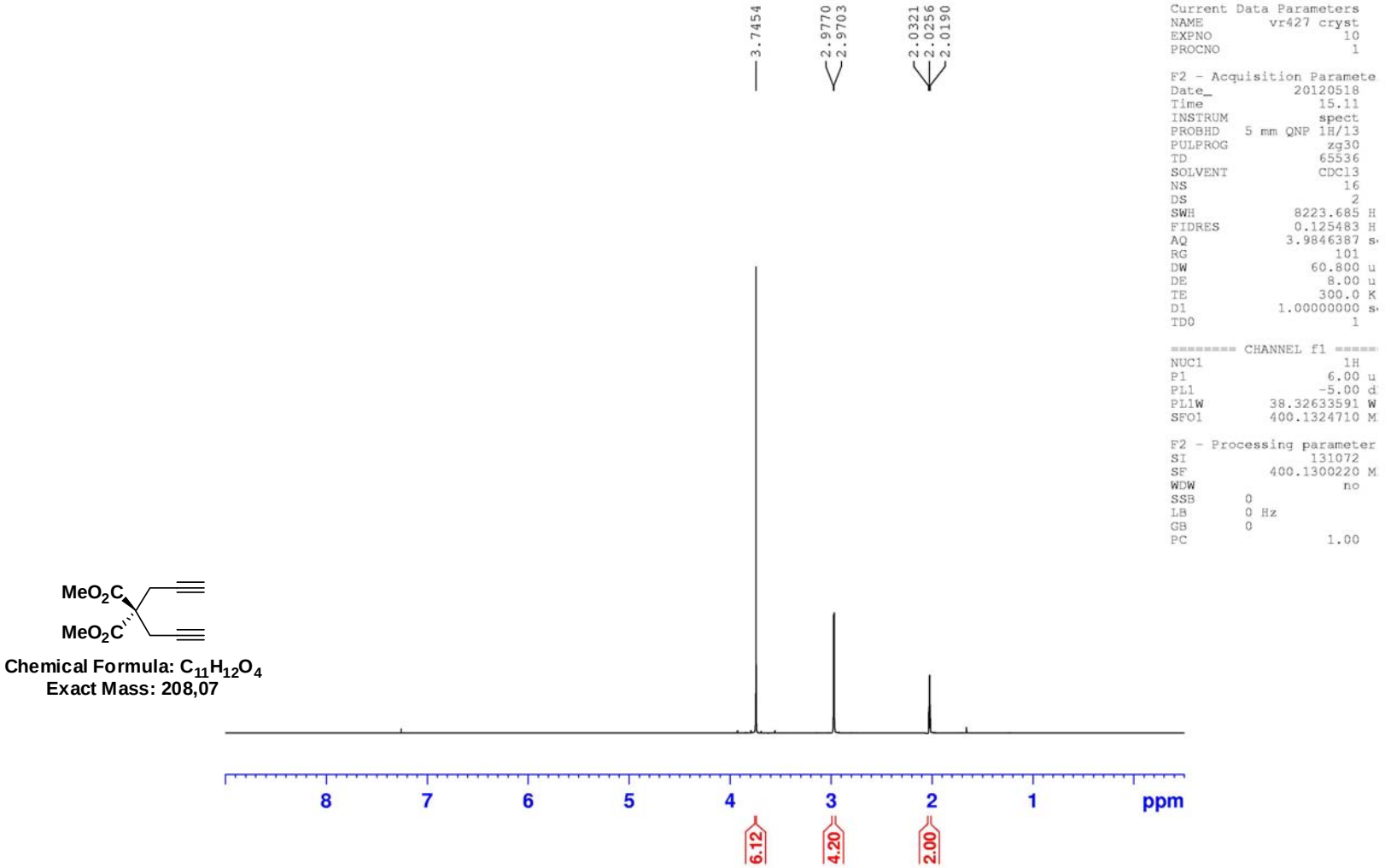
Compound 3t and 3u: Following the general procedure for the iron catalyzed [2+2+2] cycloaddition reaction compounds a 1:25 ratio of **3t**/**3u** (74 mg, 0.25 mmol, 50% yield) were obtained after flash chromatography on silica gel (20:80 pentane / ethyl acetate) as a colorless solid. R_f = 0.32 (20:80 pentane / ethyl acetate). **3t** ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.76 (d, *J* = 8.3 Hz, 2 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 6.81 (s, 1 H), 4.57 - 4.51 (m, 4 H), 2.46 (s, 3 H), 2.40 (s, 3 H), 2.37 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.3 (Cq), 151.9 (Cq), 145.8 (Cq), 143.9 (Cq), 133.5 (Cq), 129.9 (2xCH), 127.7 (Cq), 127.4 (2xCH), 114.7 (CH), 53.5 (CH_2), 51.9 (CH_2), 24.2 (CH_3), 21.8 (CH_3), 21.4 (CH_3) ppm. **3u** (partial) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.12 (s, 1H), 4.59 (*br.* s, 2H), 2.52 (*br.* s, 2H), 2.42 (s, 3H), 2.11 (s 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.1, 144.8, 140.3, 52.9 (CH_2), 52.3 (CH_2), 22.4 (CH_3), 15.3 (CH_3), 14.1 (CH_3) ppm. IR (neat) λ = 2959, 2920, 2857, 1617, 1465, 1337, 1154, 1098, 1070, 839, 810, 669 cm^{-1}. MS [ESI (+)] m/z (%) 302 ($[M+H]^+$, 100%),Mass calcd for $C_{16}H_{19}N_2O_2S$ $[M+H]^+$ 302.1182; found 302.1179.

Spectrum of **1a** (^{1}H NMR, $CDCl_3$, 400 MHz)

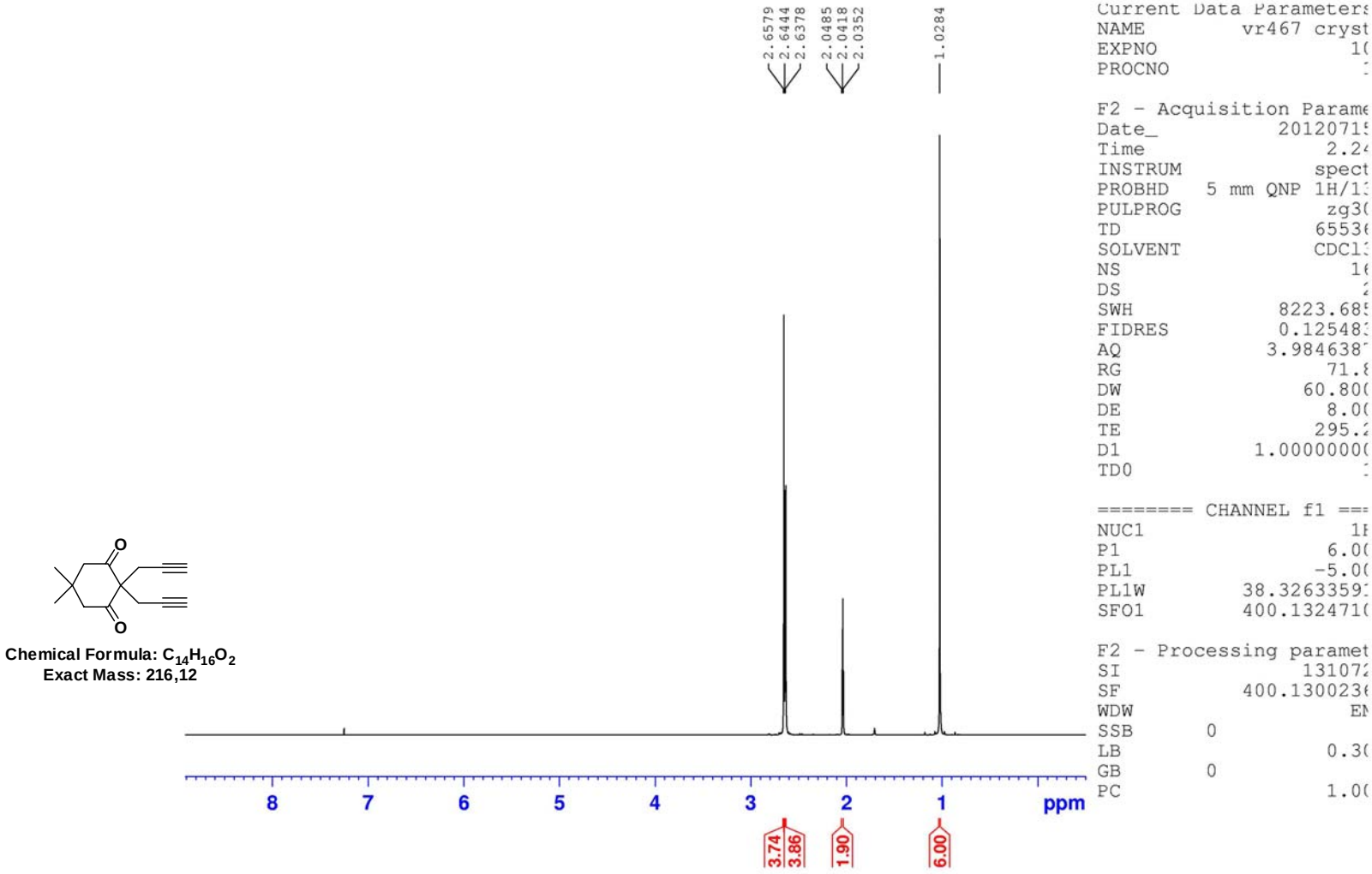


Chemical Formula: $C_{13}H_{13}NO_2S$
Exact Mass: 247,07

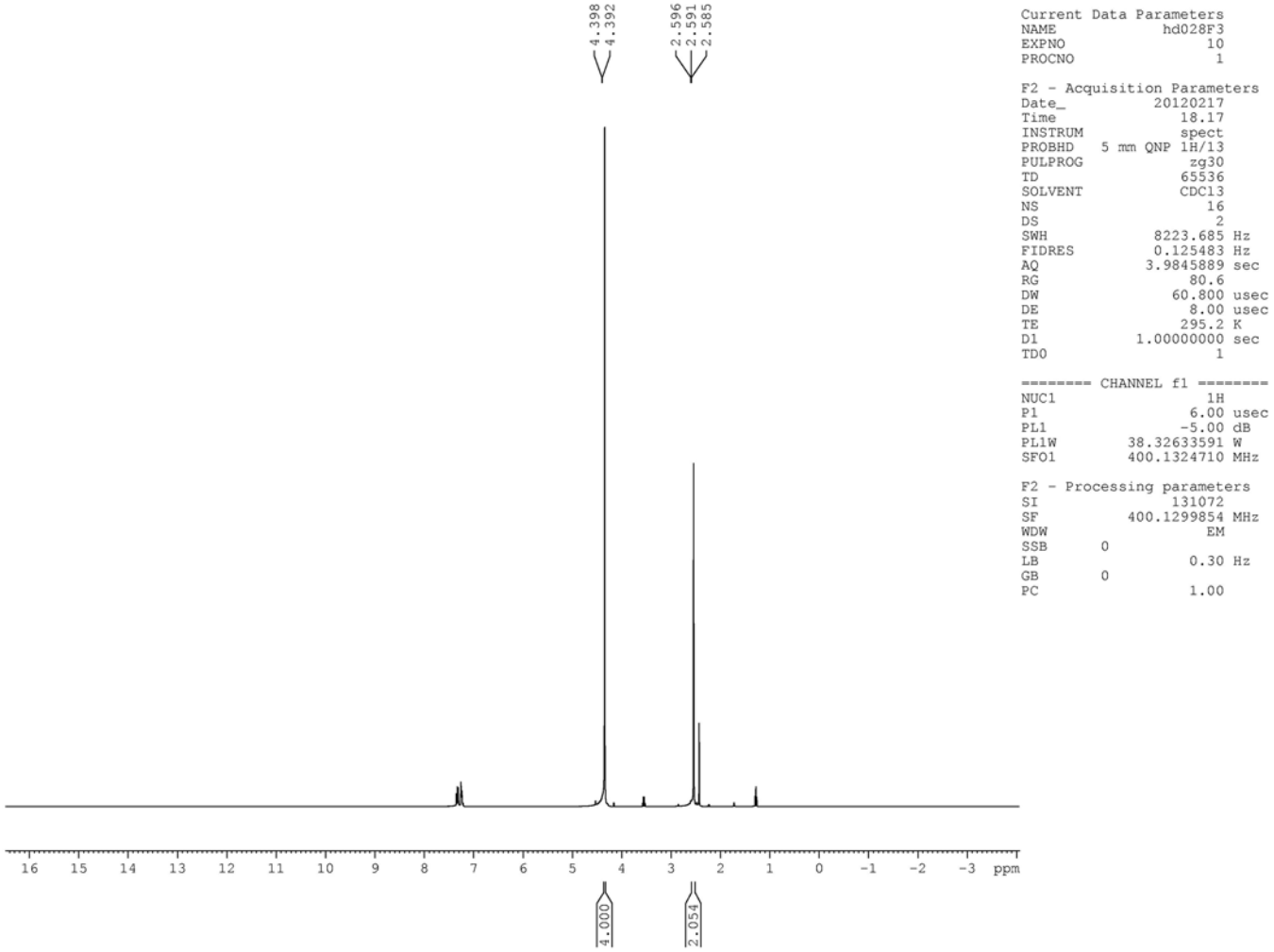
Spectrum of **1b** (^{1}H NMR, $CDCl_3$, 400 MHz)



Spectrum of **1c** (^{1}H NMR, $CDCl_3$, 400 MHz)



Spectrum of **1d** (^{1}H NMR, $CDCl_3$, 400 MHz)

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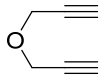
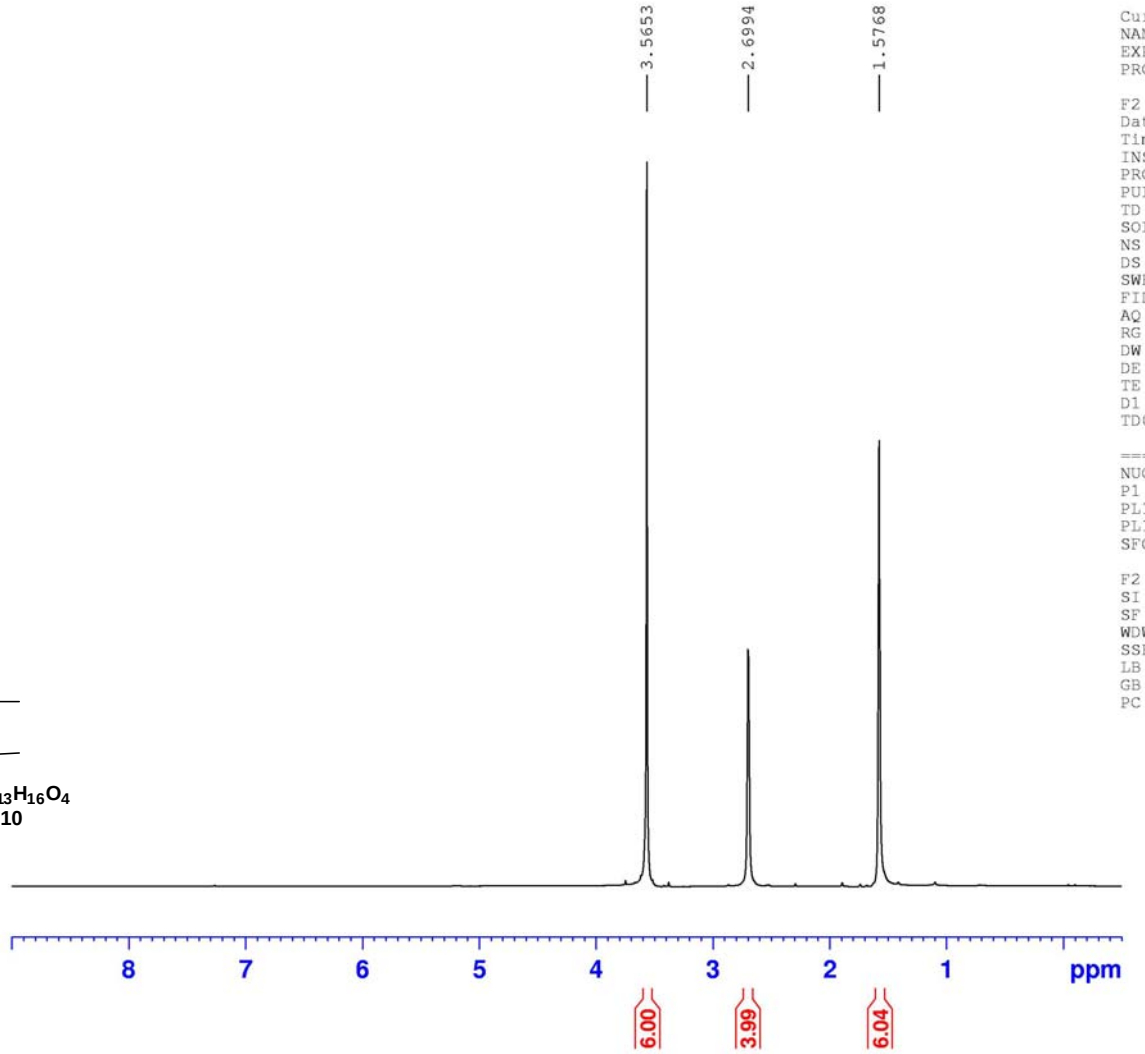


Chemical Formula: C_6H_6O
Exact Mass: 94,04 g.mol^{-1}

Spectrum of **1e** (^{1}H NMR, $CDCl_3$, 400 MHz)

Chemical Formula: $C_{13}H_{16}O_4$
Exact Mass: 236,10

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FIDRES                0.125483 Hz
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TE                      295.2 K
D1                    1.00000000 sec
TD0                          1

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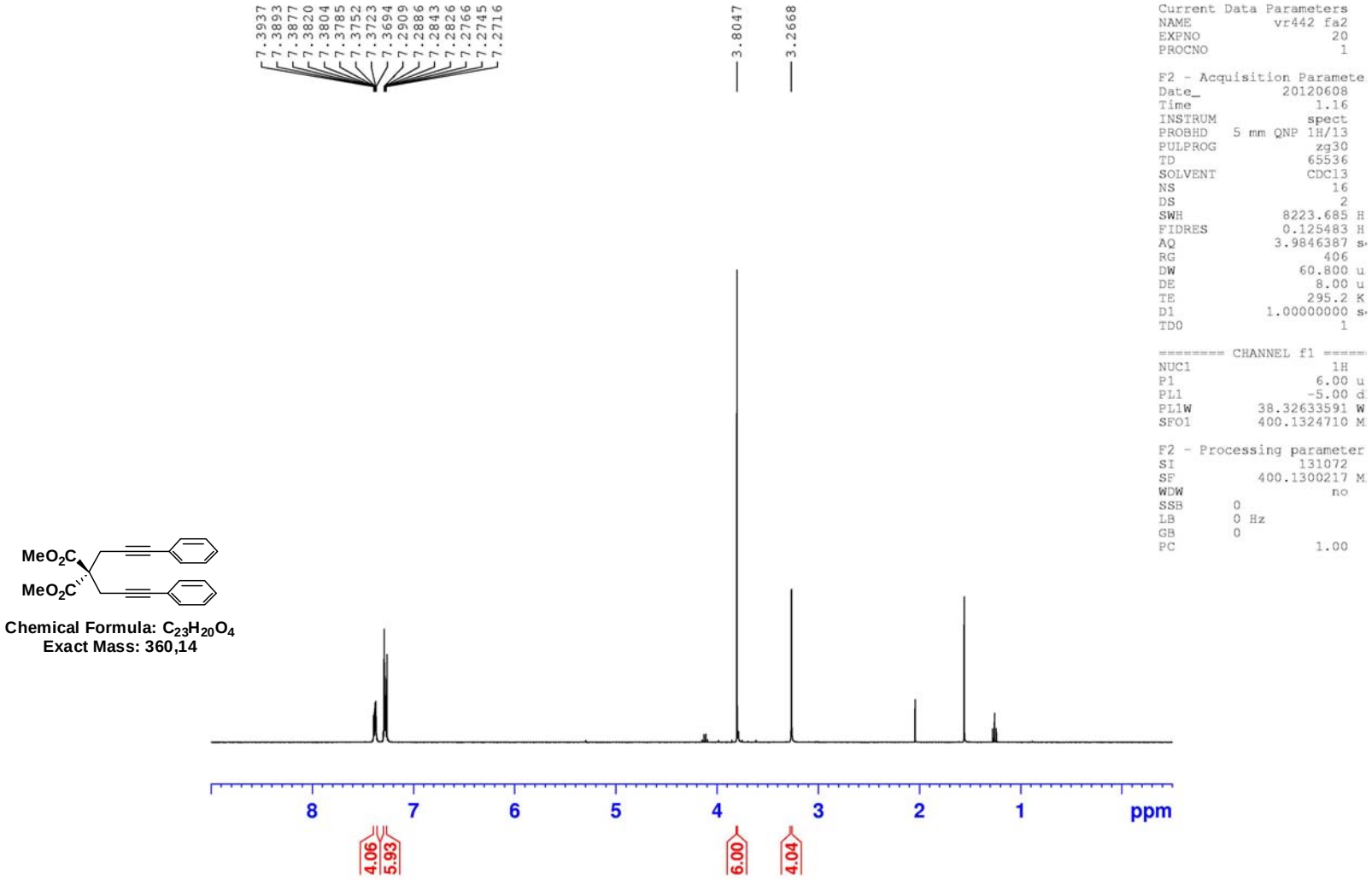
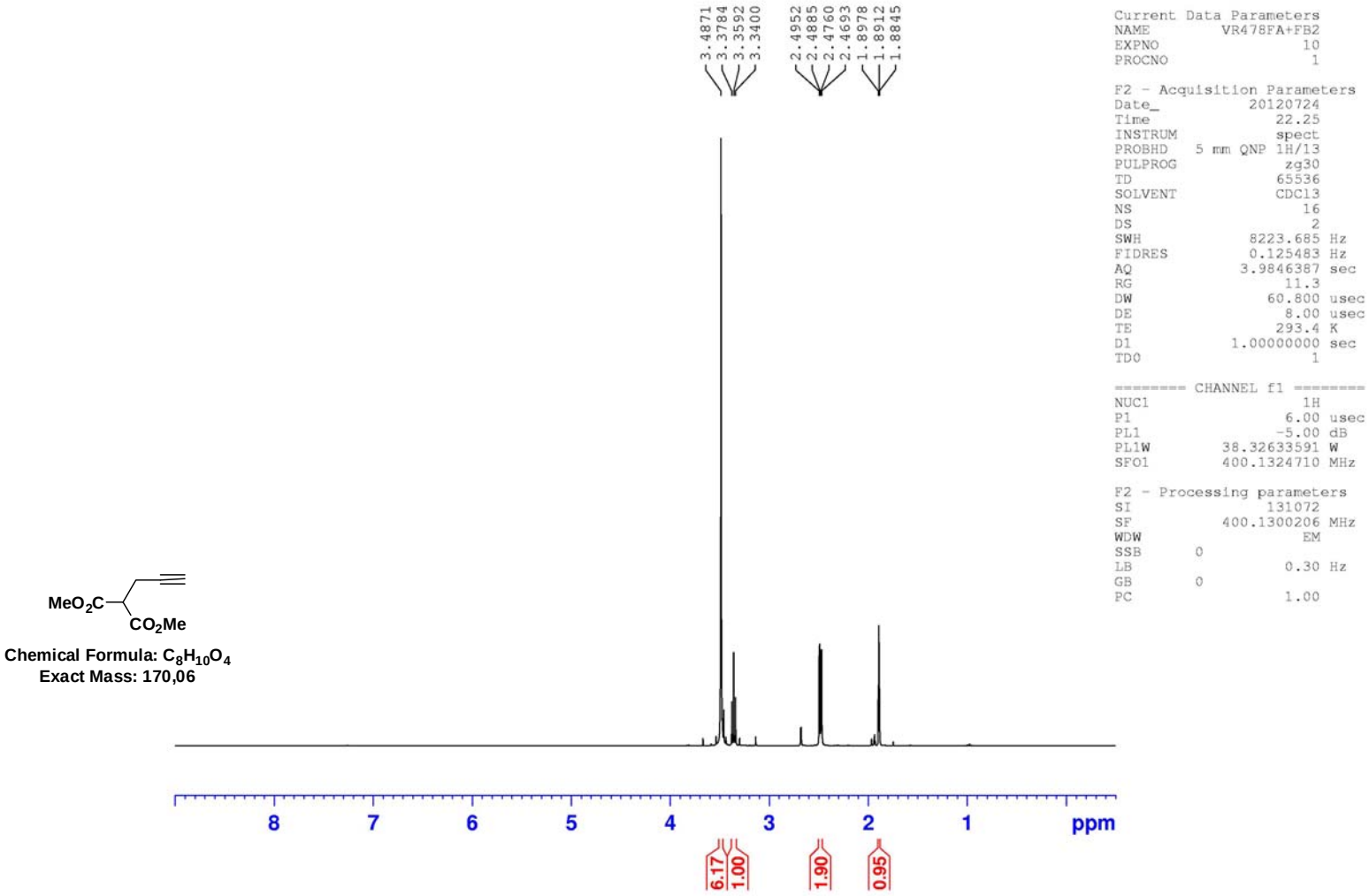
Spectrum of **1f** (^{1}H NMR, $CDCl_3$, 400 MHz)



Spectrum of **S1** (^{1}H NMR, $CDCl_3$, 400 MHz)

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TE                293.4 K
D1           1.00000000 sec
TD0                    1

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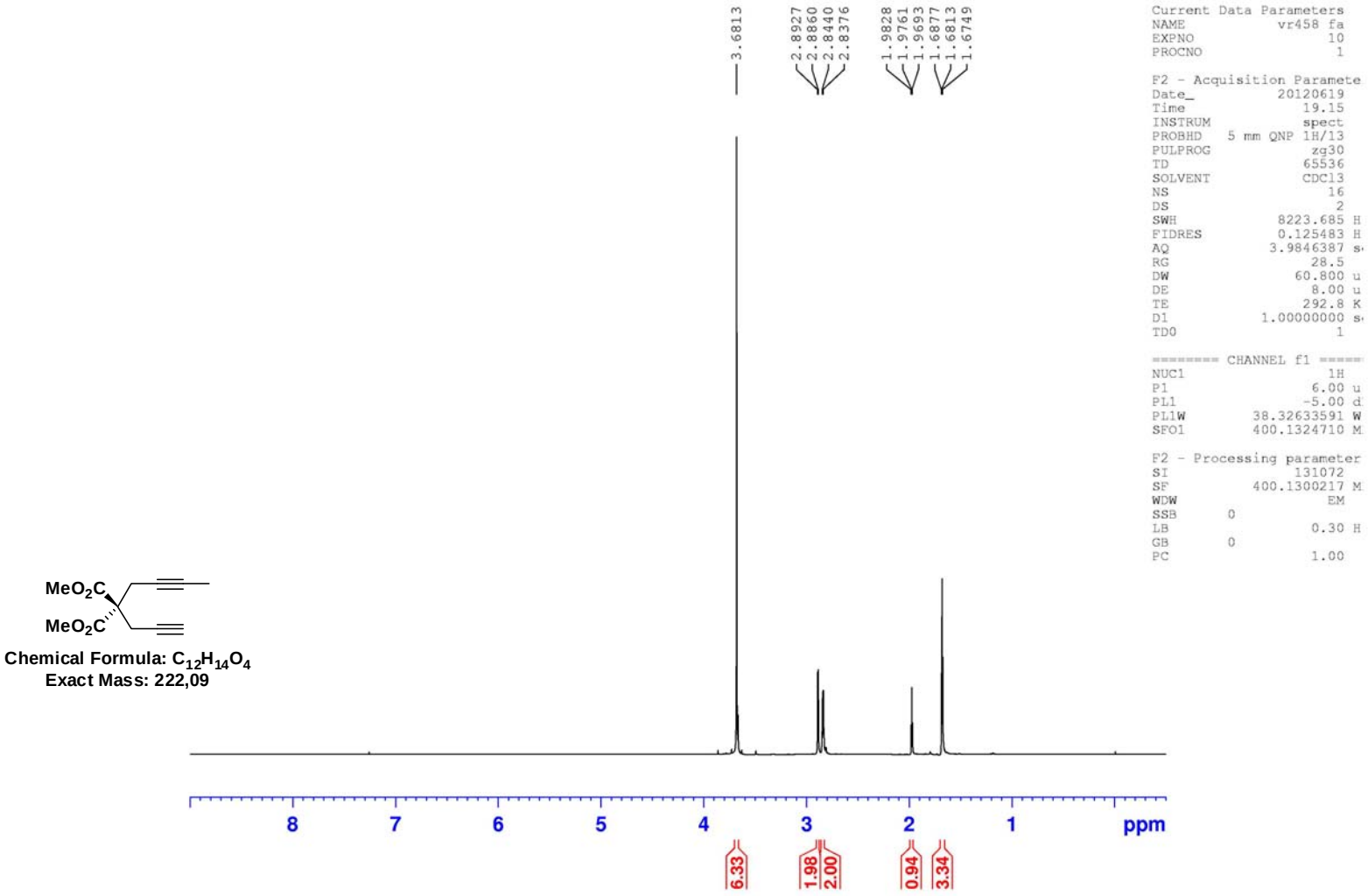
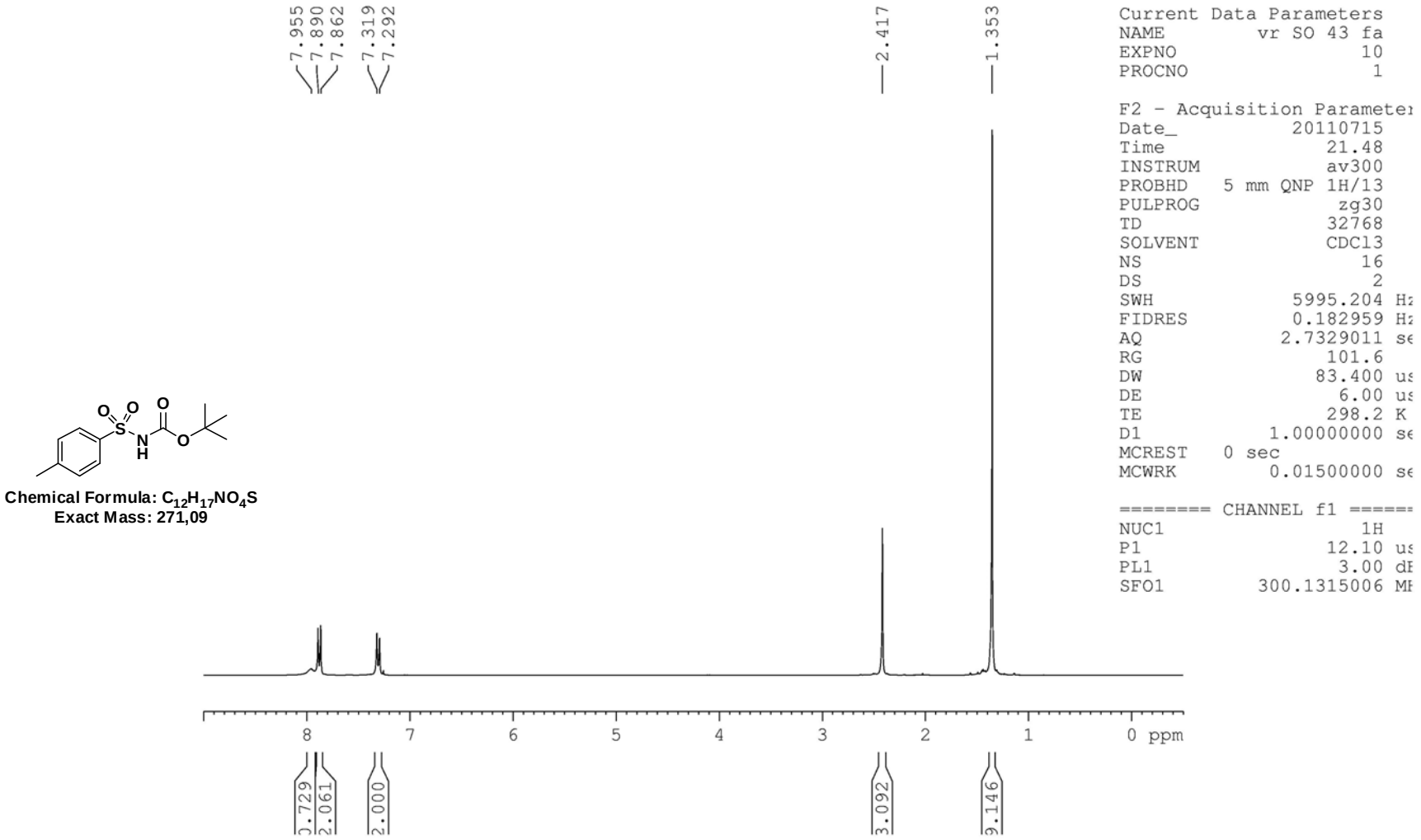
Spectrum of **1g** (^{1}H NMR, $CDCl_3$, 400 MHz)

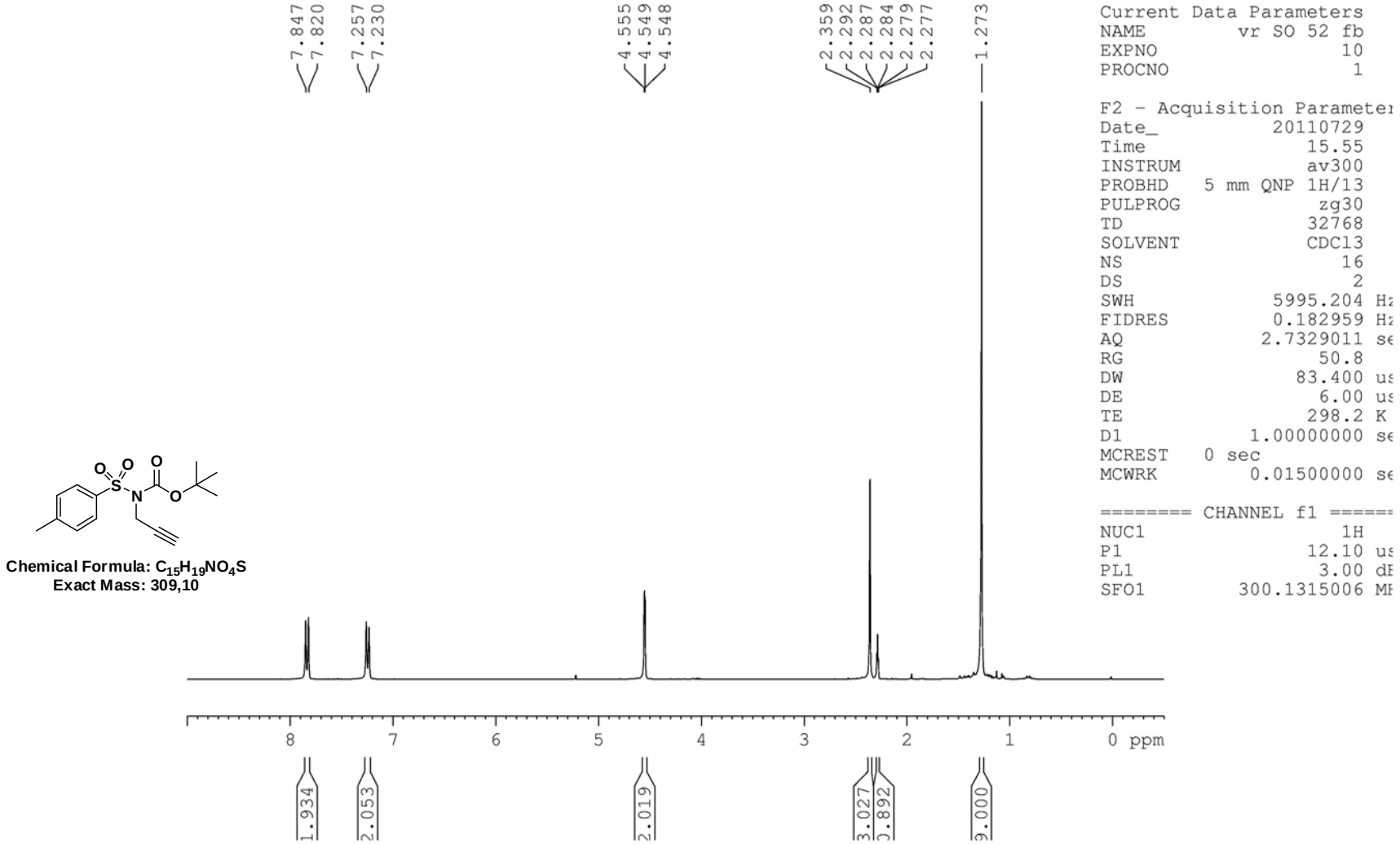


Spectrum of **S2** (^{1}H NMR, $CDCl_3$, 400 MHz)



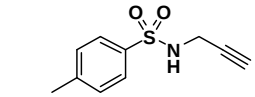
Chemical Formula: $C_{12}H_{17}NO_4S$
Exact Mass: 271,09

Spectrum of **S3** (^{1}H NMR, $CDCl_3$, 400 MHz)

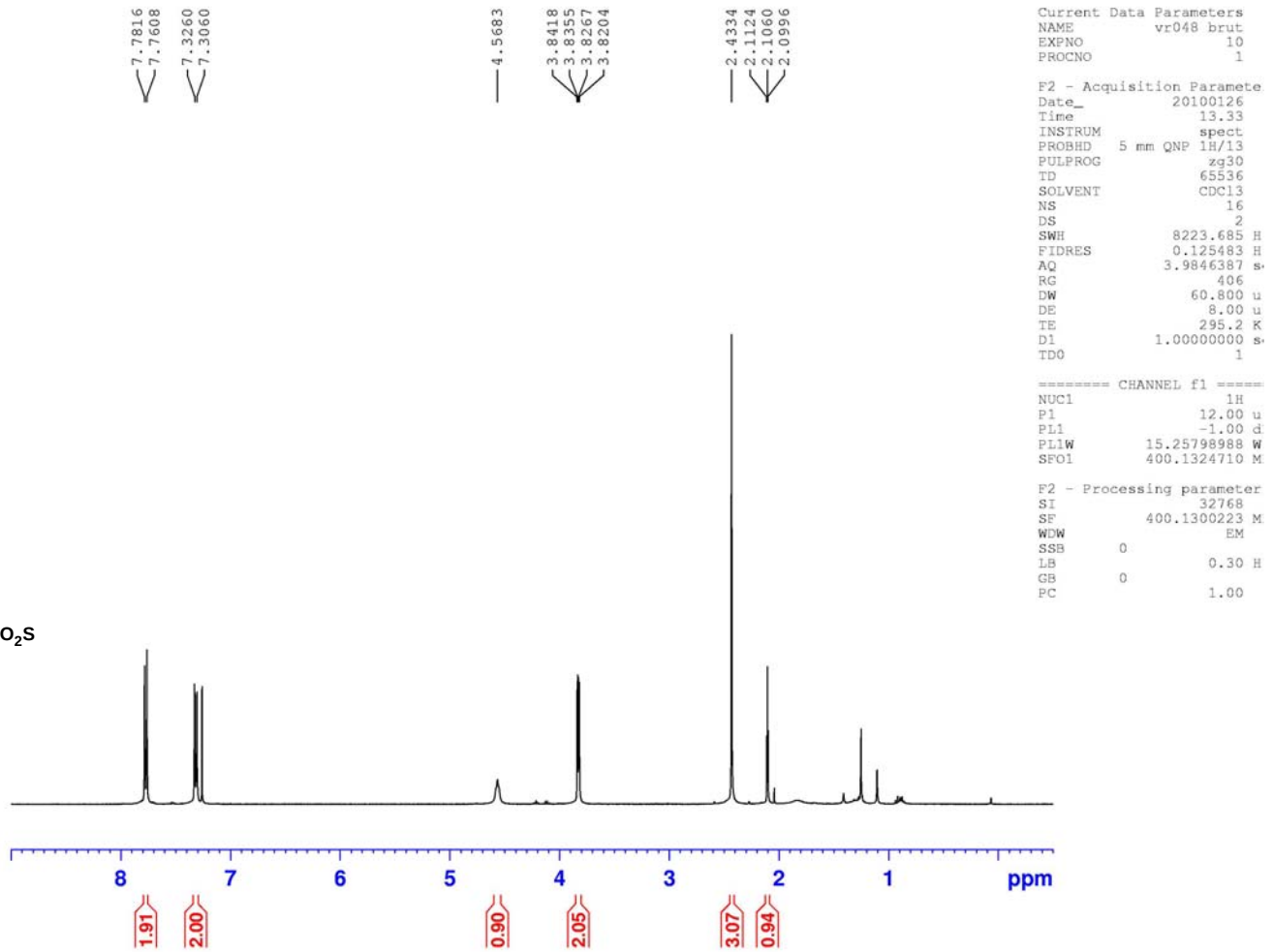


Chemical Formula: $C_{15}H_{19}NO_4S$
Exact Mass: 309,10

Spectrum of **S4** (^{1}H NMR, $CDCl_3$, 400 MHz)



Chemical Formula: $C_{10}H_{11}NO_2S$
Exact Mass: 209,05

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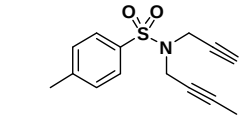
RG                         406
DW                      60.800 u
DE                       8.00 u
TE                      295.2 K
D1                 1.00000000 s
TD0                          1

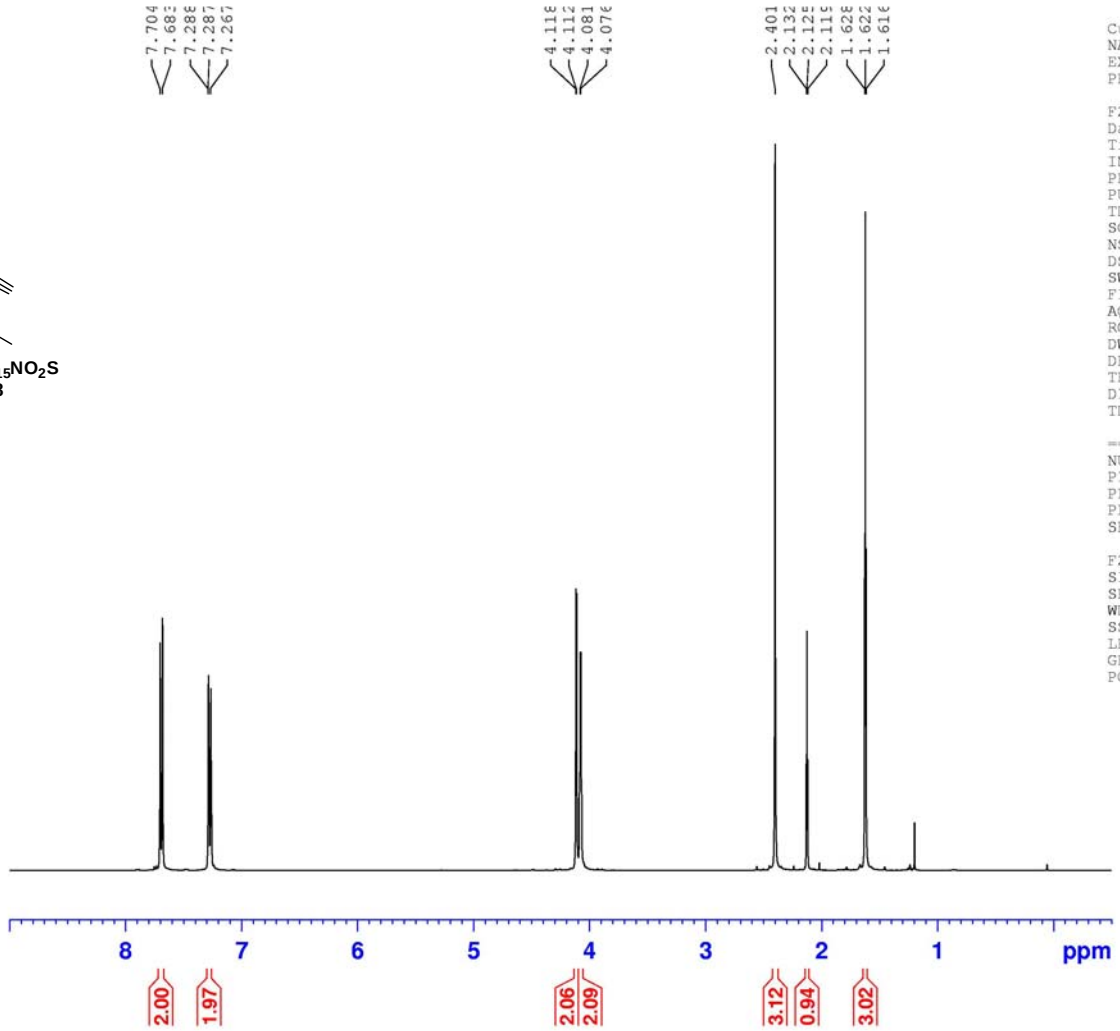
======== CHANNEL f1 ======
NUC1                        1H
P1                       12.00 u
PL1                      -1.00 d
PL1W              15.25798988 W
SFO1             400.1324710 M

F2 - Processing parameter
SI                       32768
SF                400.1300223 M
WDW                         EM
SSB          0
LB                       0.30 H
GB           0
PC                       1.00
```

Spectrum of **1h** (^{1}H NMR, $CDCl_3$, 400 MHz



Chemical Formula: $C_{14}H_{15}NO_2S$
Exact Mass: 261,08



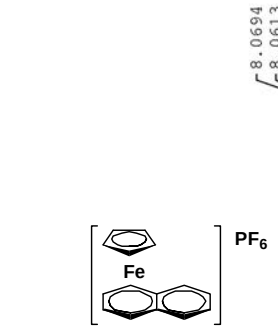

```
Current Data Parameters
NAME        vr342+343 fa
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120221
Time                2.07
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            8223.685 Hz
FIDRES        0.125483 Hz
AQ            3.9846387 sec
RG                 80.6
DW               60.800 usec
DE                8.00 usec
TE               295.2 K
D1          1.00000000 sec
TD0                    1

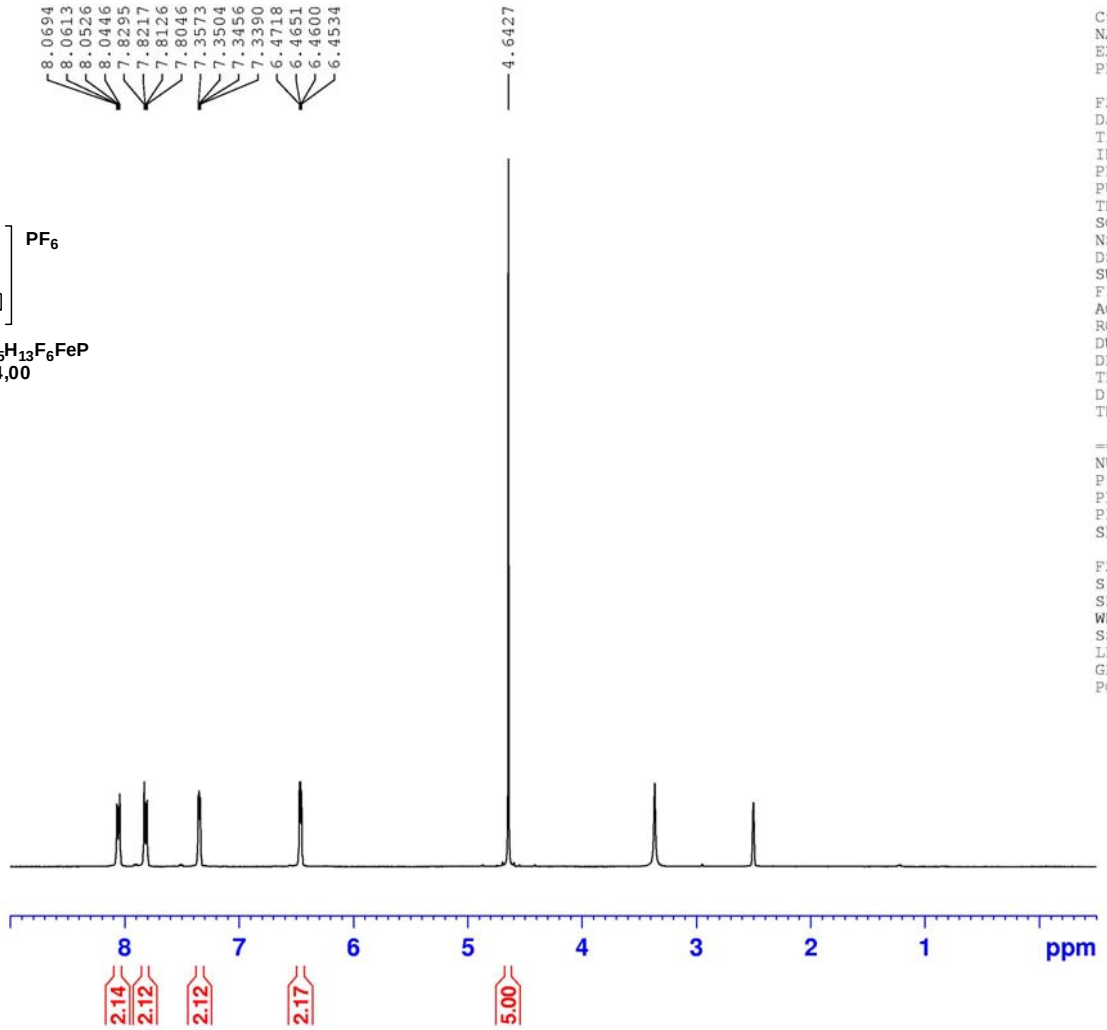
======== CHANNEL f1 ========
NUC1                  1H
P1                 6.00 usec
PL1               -5.00 dB
PL1W       38.32633591 W
SFO1       400.1324710 MHz

F2 - Processing parameters
SI                131072
SF          400.1300217 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

Spectrum of **[CpFe(napht)][PF_6]** (^{1}H NMR, DMSO, 400 MHz)



Chemical Formula: $C_{15}H_{13}F_6FeP$
Exact Mass: 394,00



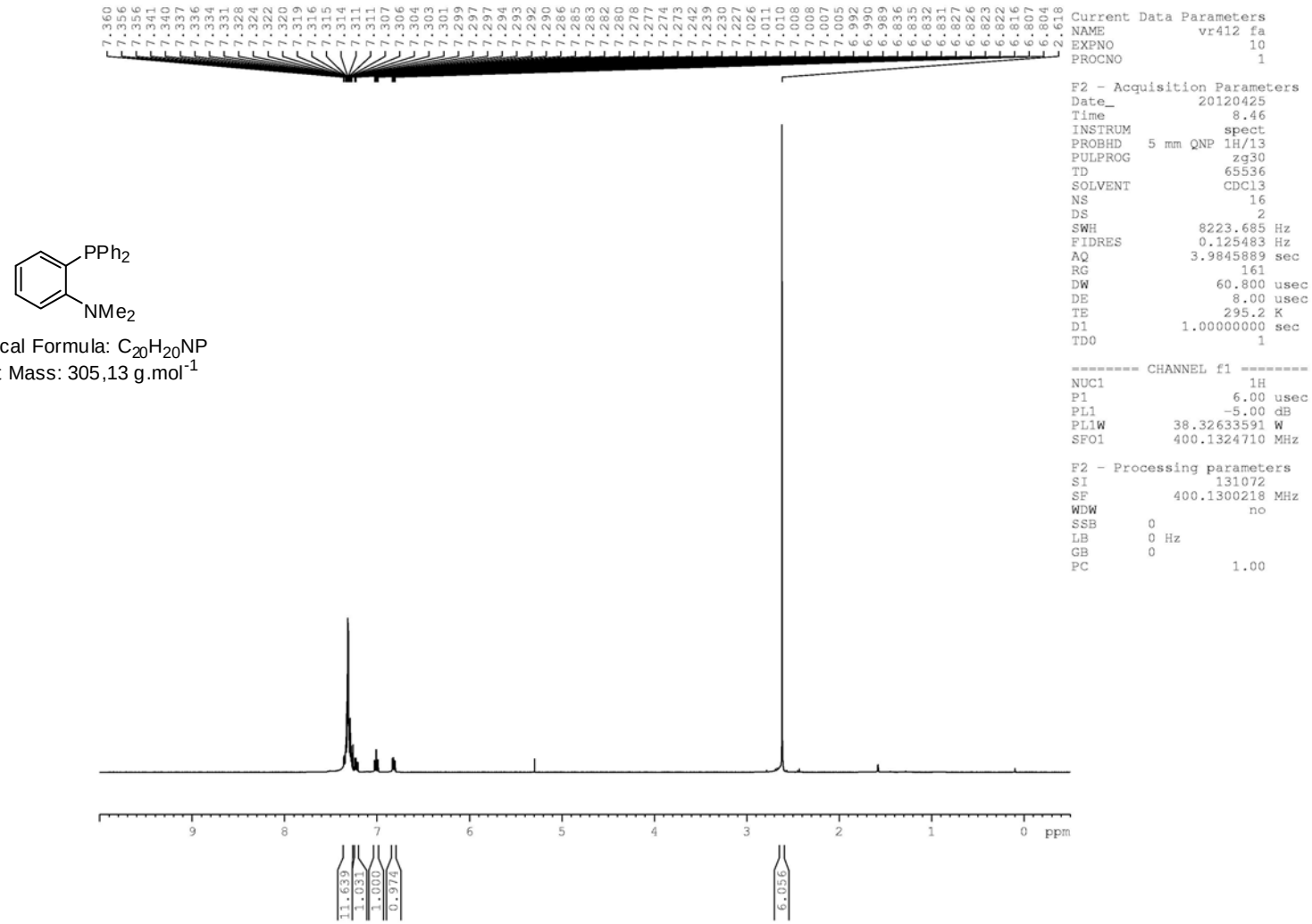

```
Current Data Parameters
NAME                  vr461
EXPNO                    10
PROCNO                    1

F2 - Acquisition Parameters
Date_              20120627
Time                  19.24
INSTRUM               spect
PROBHD   5 mm QNP 1H/13
PULPROG                zg30
TD                    65536
SOLVENT                DMSO
NS                       16
DS                        2
SWH                8223.685 Hz
FIDRES            0.125483 Hz
AQ                3.9846387 sec
RG                      322
DW                   60.800 usec
DE                    8.00 usec
TE                   294.9 K
D1                1.00000000 sec
TD0                       1

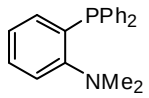
======== CHANNEL f1 ========
NUC1                     1H
P1                    6.00 usec
PL1                  -5.00 dB
PL1W           38.32633591 W
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                   131072
SF             400.1300029 MHz
WDW                      EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
```

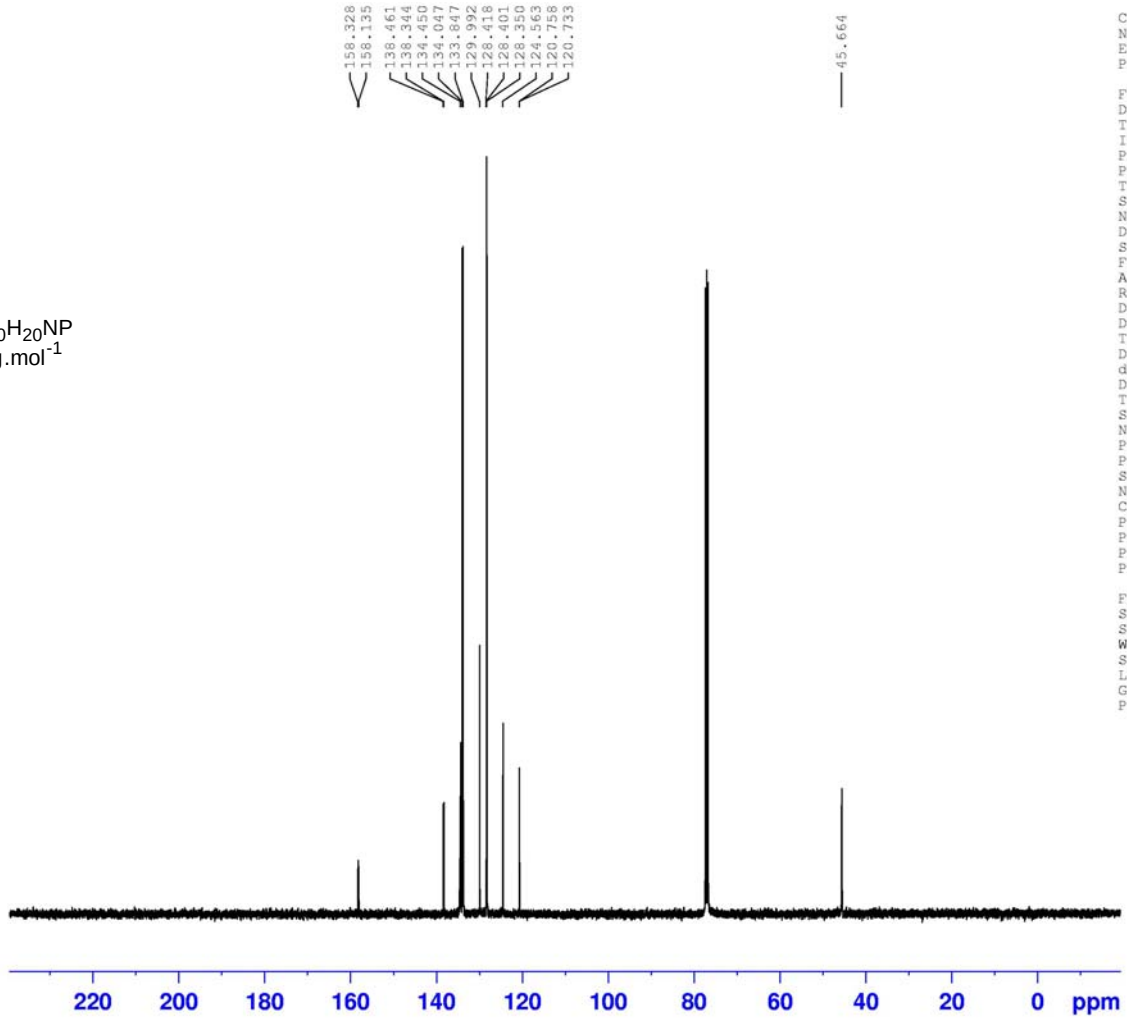
Spectrum of **5** (^{1}H NMR, $CDCl_3$, 400 MHz)



Spectrum of **5** (^{13}C NMR, $CDCl_3$, 100 MHz)



Chemical Formula: $C_{20}H_{20}NP$
Exact Mass: 305,13 g.mol^{-1}

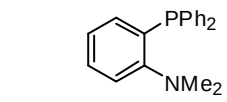



```
Current Data Parameters
NAME                  vr412 fa
EXPNO                      20
PROCNO                      1

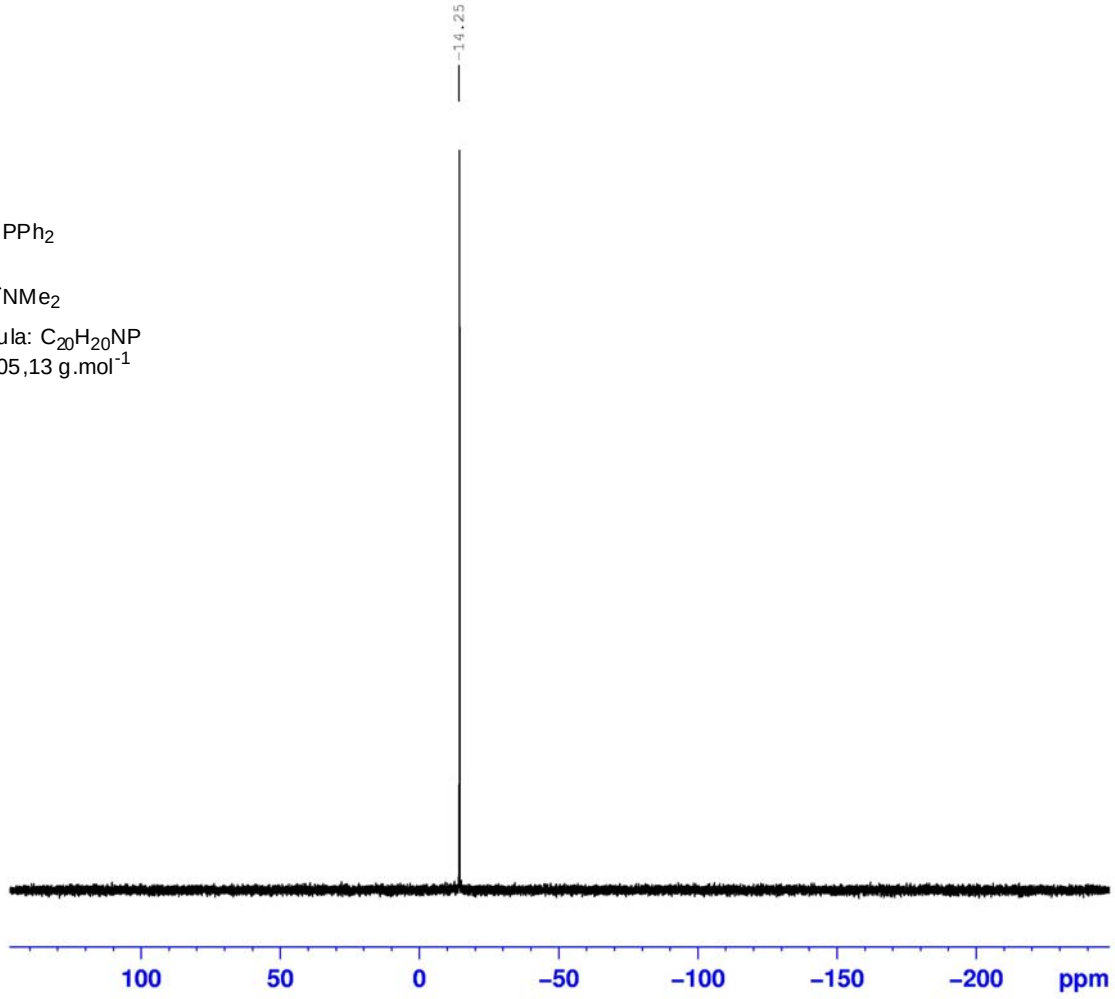
F2 - Acquisition Parameter
Date_                20120425
Time                    20.48
INSTRUM                 spect
PROBHD    5 mm QNP 1H/13
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                       1024
DS                          2
SWH                 26041.666 Hz
FIDRES                0.397364 Hz
AQ                    1.2582912 se
RG                       2050
DW                     19.200 us
DE                       8.00 us
TE                     295.2 K
D1                  1.50000000 se
d11                 0.03000000 se
DELTA               1.39999998 se
TD0                         1
SFO1               100.6238364 MH
NUC1                       13C
P1                        9.50 us
PLW1               -1.00000000 W
SFO2               400.1316005 MH
NUC2                       1H
CPDPRG[2                waltz16
PCPD2                   100.00 us
PLW2               -1.00000000 W
PLW12              -1.00000000 W
PLW13              -1.00000000 W

F2 - Processing parameters
SI                       131072
SF                 100.6127625 MH
WDW                        EM
SSB                 0
LB                        1.00 Hz
GB                  0
PC                        1.40
```

Spectrum of **5** (^{31}P NMR, $CDCl_3$, 400 MHz)



Chemical Formula: $C_{20}H_{20}NP$
Exact Mass: 305,13 g.mol^{-1}



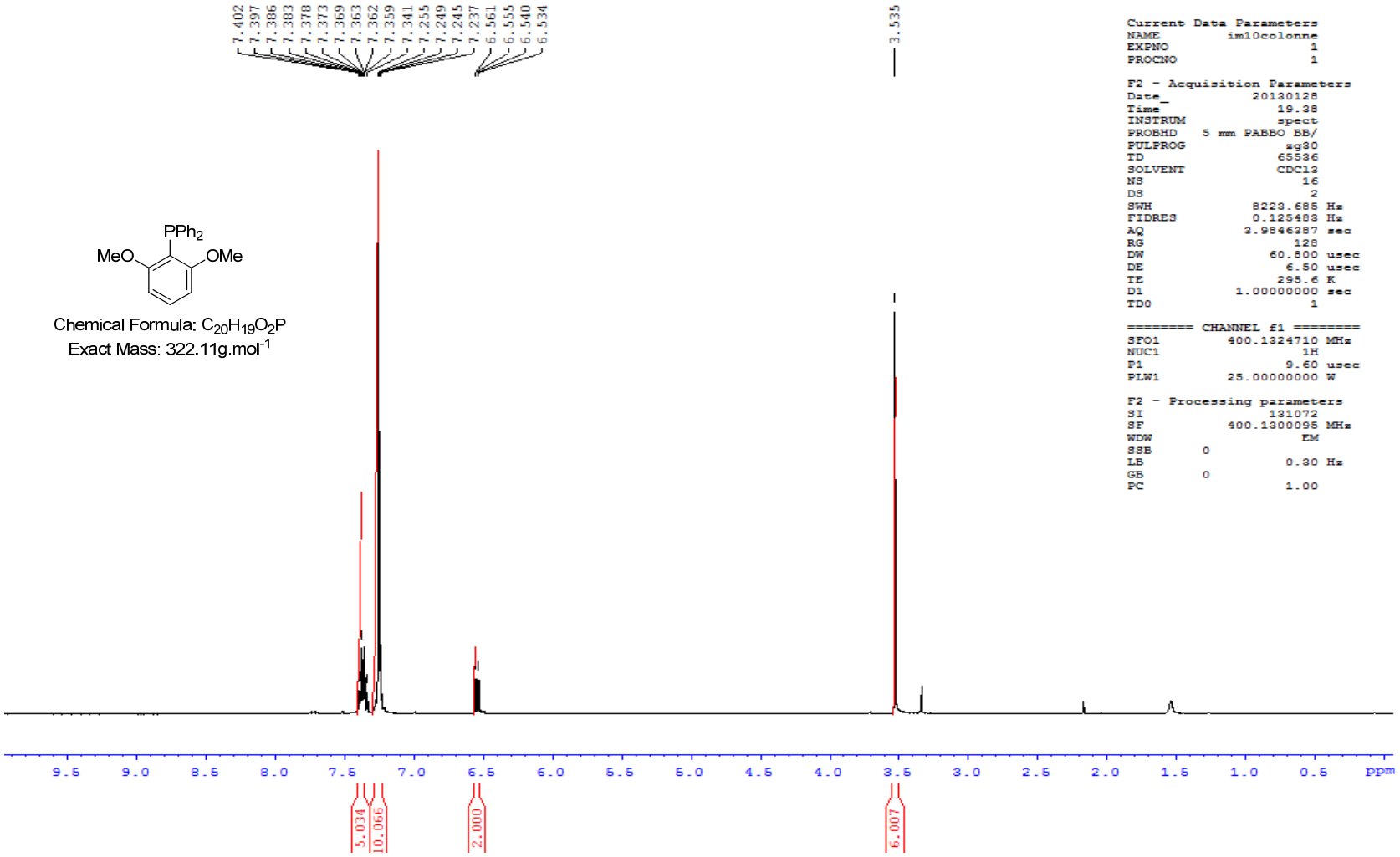

```
Current Data Parameters
NAME                 vr412 fa
EXPNO                      11
PROCNO                      1

F2 - Acquisition Parameters
Date_                20120425
Time                     8.49
INSTRUM                 spect
PROBHD   5 mm QNP 1H/13
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                        64
DS                         4
SWH                64102.563 Hz
FIDRES             0.978127 Hz
AQ                 0.5111808 sec
RG                      2050
DW                     7.800 usec
DE                     8.00 usec
TE                     295.2 K
D1                2.00000000 sec
TD0                        1

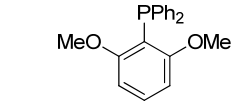
======== CHANNEL f1 ========
NUC1                     31P
P1                     8.60 usec
PL1       0 dB
PL1W            25.06862640 W
SFO1           161.9674942 MHz

F2 - Processing parameters
SI                     32768
SF               161.9755930 MHz
WDW                       EM
SSB       0
LB                     1.00 Hz
GB        0
PC                     1.40
```

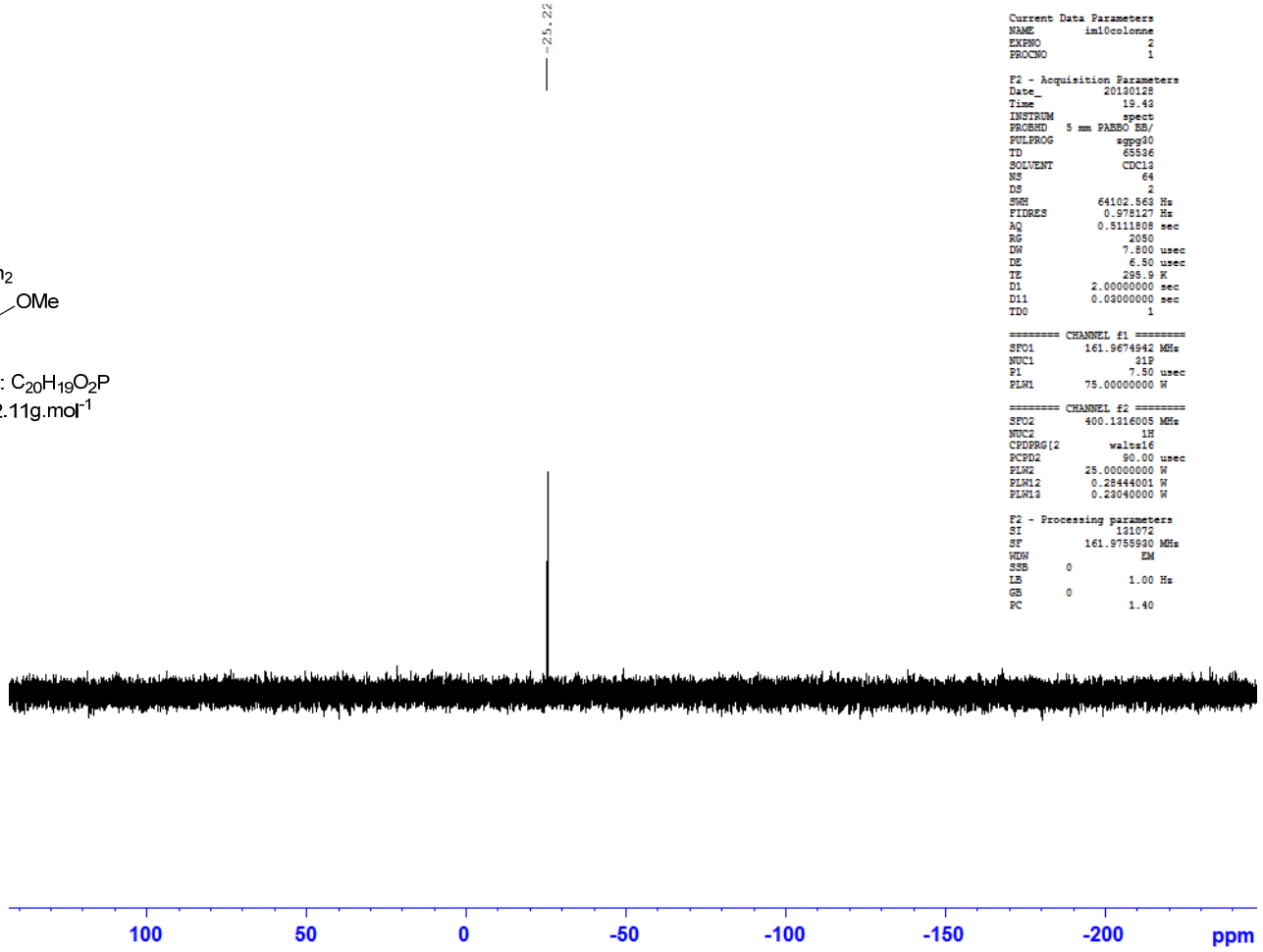
Spectrum of **5** (^{1}H NMR, $CDCl_3$, 400 MHz)



Spectrum of **9** (^{31}P NMR, $CDCl_3$, 400 MHz)



Chemical Formula: $C_{20}H_{19}O_2P$
Exact Mass: 322.11g.mol^{-1}




```
Current Data Parameters
NAME          iml0colonne
EXPNO                   2
PROCNO                  1

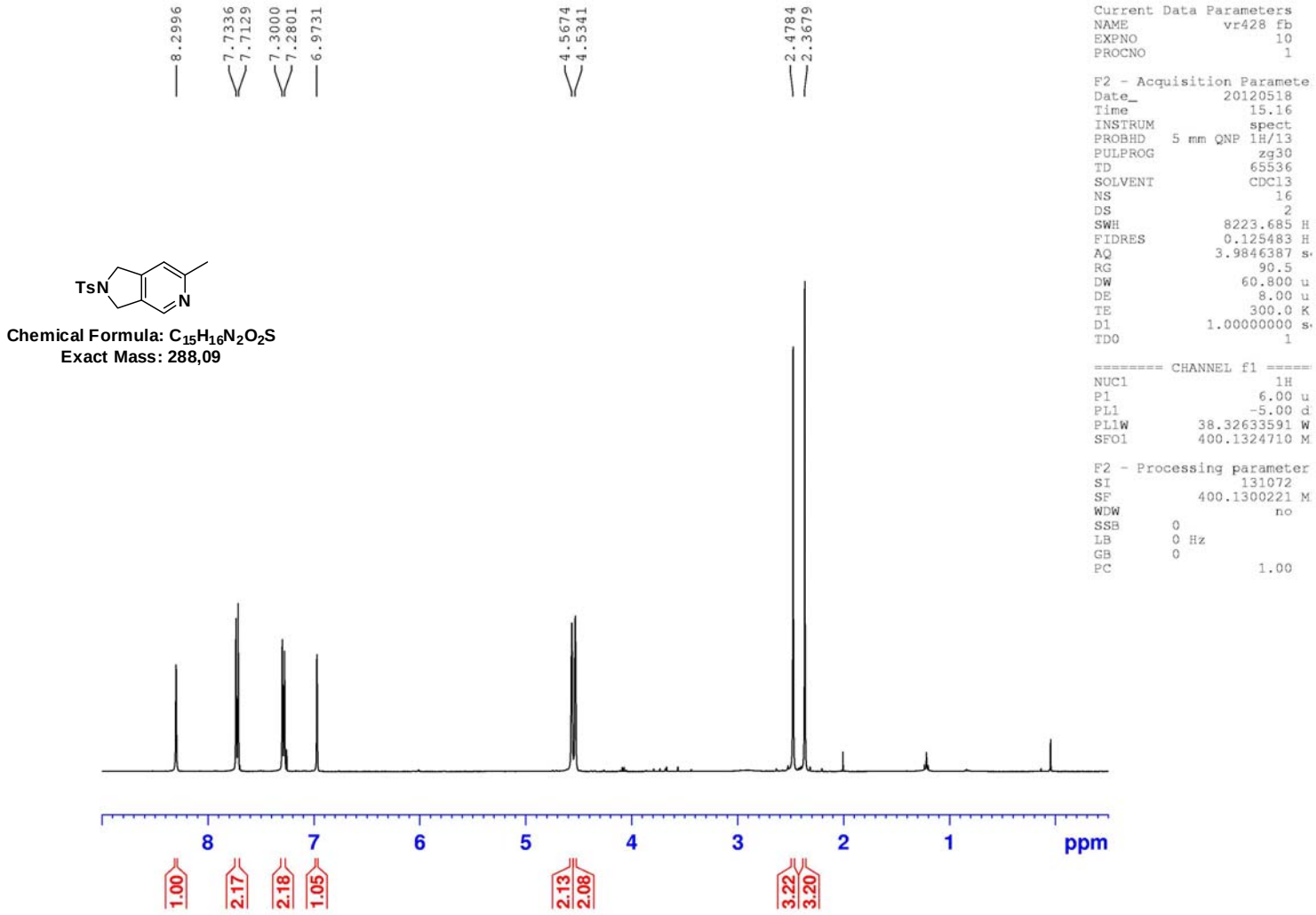
F2 - Acquisition Parameters
Date_            20130128
Time                19.43
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG          wgpg30
TD                65536
SOLVENT           CDCl3
NS                   64
DS                    2
SWH           64102.563 Hz
FIDRES         0.978127 Hz
AQ             0.5111808 sec
RG                 2050
DW               7.800 usec
DE               6.50 usec
TE               295.9 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         161.9674942 MHz
NUC1                31P
P1                 7.50 usec
PLW1         75.00000000 W

======== CHANNEL f2 ========
SFO2         400.1316005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2         25.00000000 W
PLW12         0.28444001 W
PLW13         0.23040000 W

F2 - Processing parameters
SI                 131072
SF           161.9755930 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

Spectrum of **3a** (^{1}H NMR, $CDCl_3$, 400 MHz)



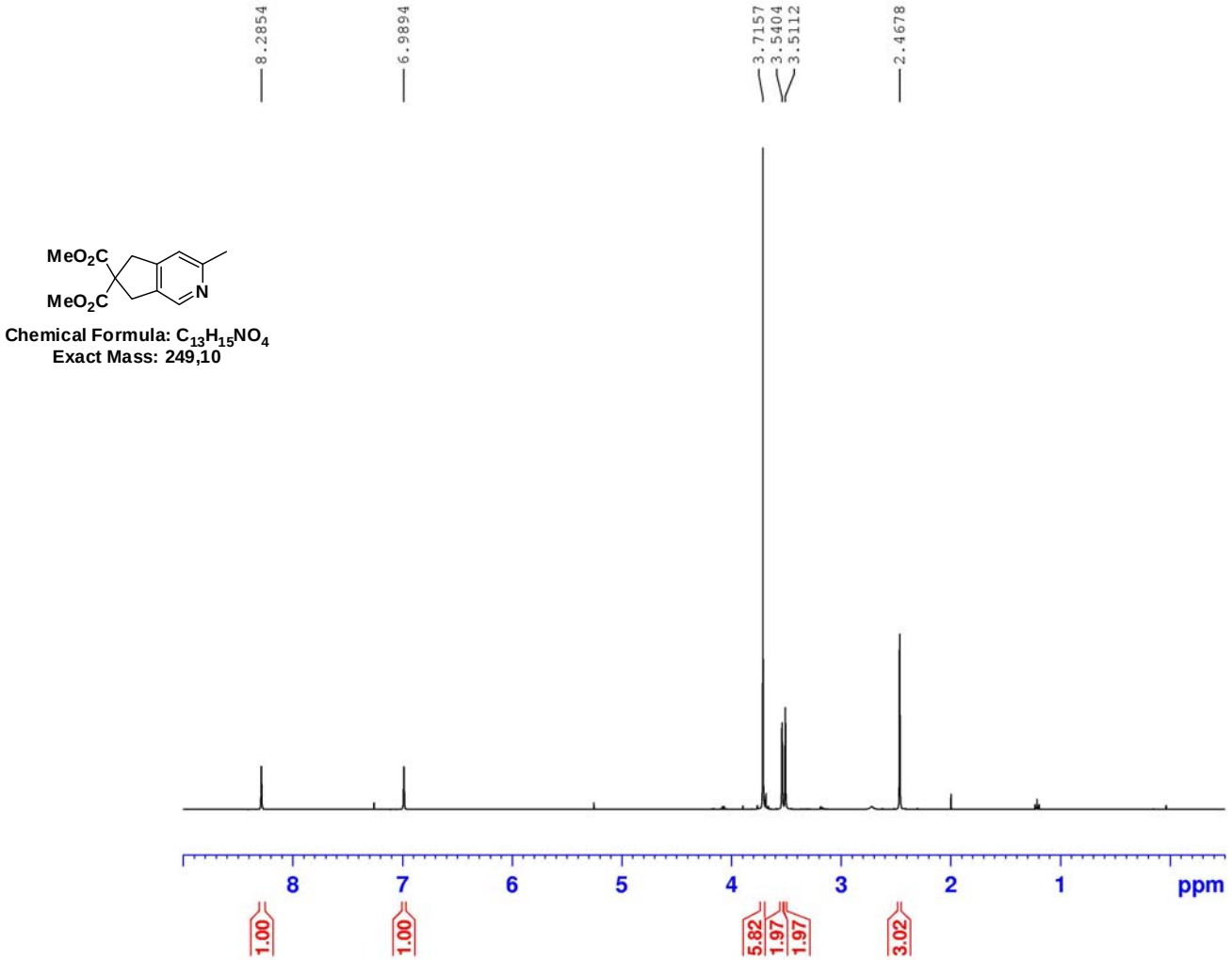

```
Current Data Parameters
NAME                  vr428 fb
EXPNO                      10
PROCNO                      1

F2 - Acquisition Paramete
Date_                20120518
Time                    15.16
INSTRUM                 spect
PROBHD    5 mm QNP 1H/13
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                 8223.685 H
FIDRES              0.125483 H
AQ                  3.9846387 s
RG                       90.5
DW                     60.800 u
DE                      8.00 u
TE                     300.0 K
D1                 1.00000000 s
TD0                        1

======== CHANNEL f1 =====
NUC1                       1H
P1                      6.00 u
PL1                    -5.00 d
PL1W               38.32633591 W
SFO1               400.1324710 M

F2 - Processing parameter
SI                        131072
SF                 400.1300221 M
WDW                           no
SSB          0
LB           0 Hz
GB           0
PC                         1.00
```

Spectrum of **3b** (^{1}H NMR, $CDCl_3$, 400 MHz)



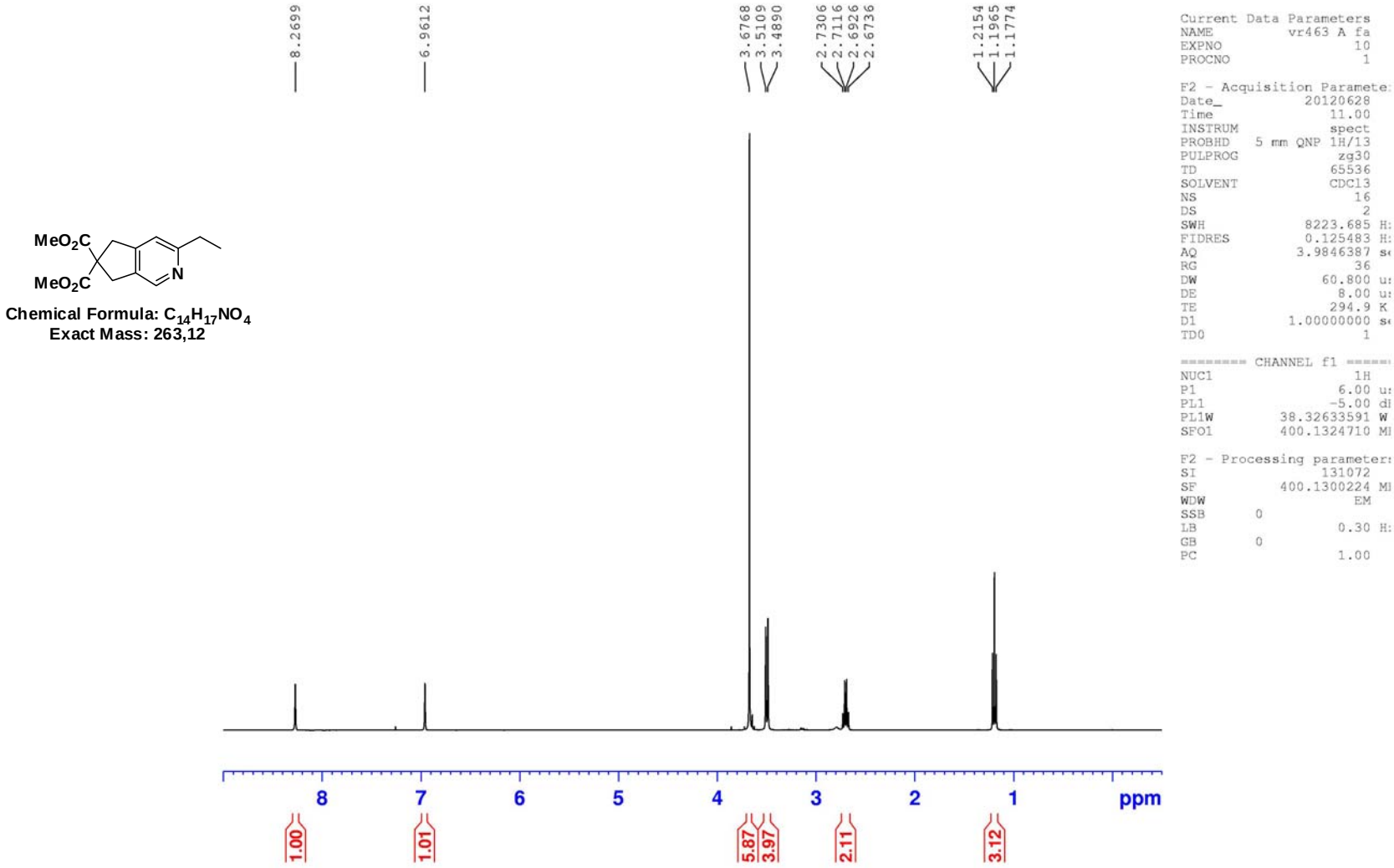

```
Current Data Parameters
NAME                  vr446 fa
EXPNO                       10
PROCNO                       1

F2 - Acquisition Paramete:
Date_                 20120601
Time                      9.00
INSTRUM                  spect
PROBHD    5 mm QNP 1H/13
PULPROG                   zg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                   8223.685 H:
FIDRES                0.125483 H:
AQ                    3.9846387 s
RG                         90.5
DW                       60.800 u:
DE                        8.00 u:
TE                       295.2 K
D1                 1.00000000 s
TD0                          1

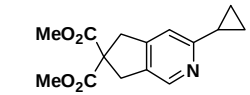
======== CHANNEL f1 ======:
NUC1                        1H
P1                       6.00 u:
PL1                     -5.00 dB
PL1W              38.32633591 W
SFO1              400.1324710 MH

F2 - Processing parameter:
SI                      131072
SF                400.1300209 MH
WDW                         EM
SSB          0
LB                       0.30 H:
GB           0
PC                       1.00
```

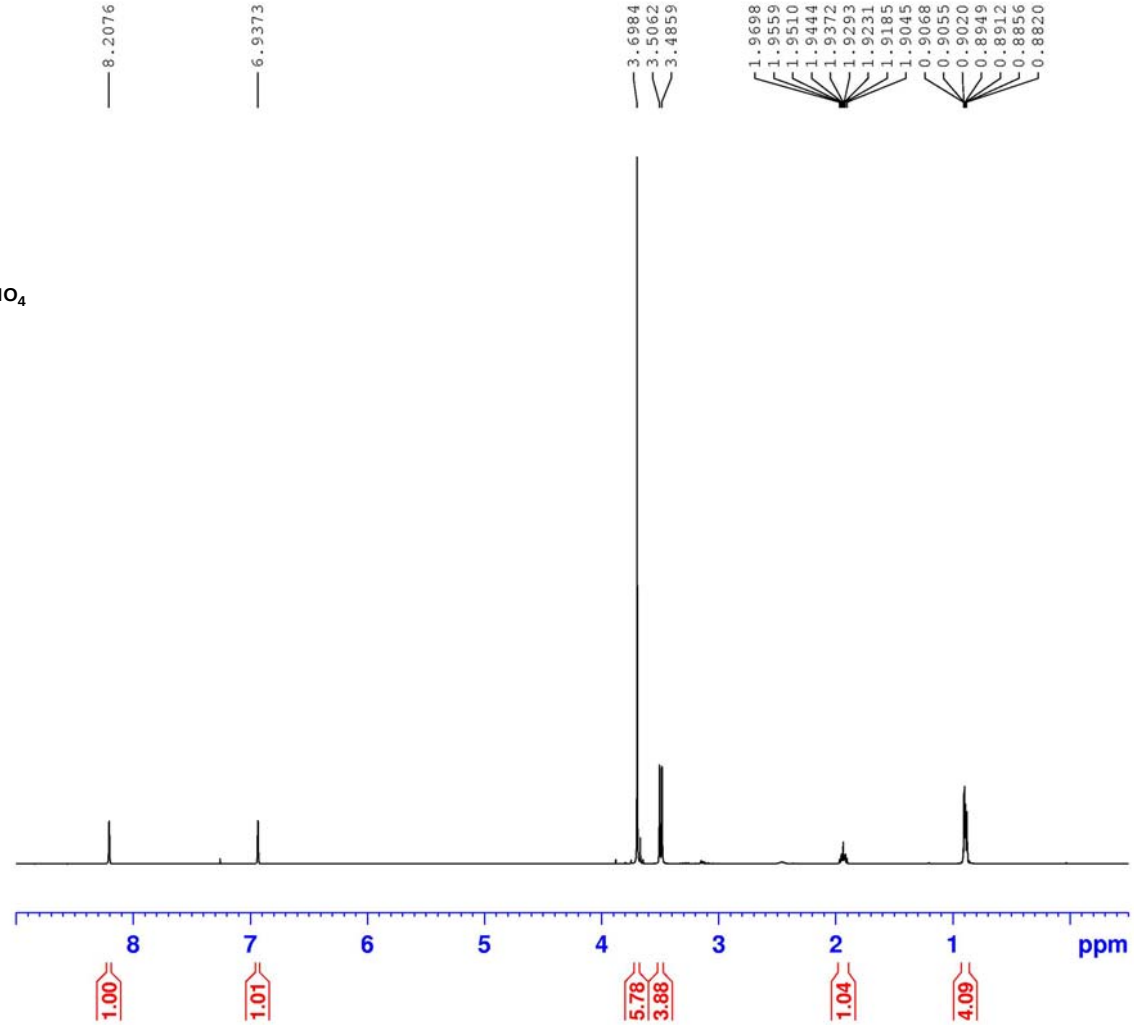
Spectrum of **3c** (^{1}H NMR, $CDCl_3$, 400 MHz)



Spectrum of **3d** (^{1}H NMR, $CDCl_3$, 400 MHz)



Chemical Formula: $C_{15}H_{17}NO_4$
Exact Mass: 275,12



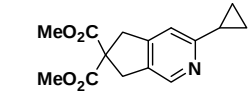

```
Current Data Parameters
NAME                  vr464 A fa
EXPNO                        10
PROCNO                        1

F2 - Acquisition Parameter
Date_                  20120704
Time                       9.00
INSTRUM                   spect
PROBHD    5 mm QNP 1H/13
PULPROG                    zg30
TD                        65536
SOLVENT                   CDCl3
NS                           16
DS                            2
SWH                    8223.685 H
FIDRES                 0.125483 H
AQ                     3.9846387 s
RG                           36
DW                        60.800 u
DE                         8.00 u
TE                        294.5 K
D1                  1.00000000 s
TD0                           1

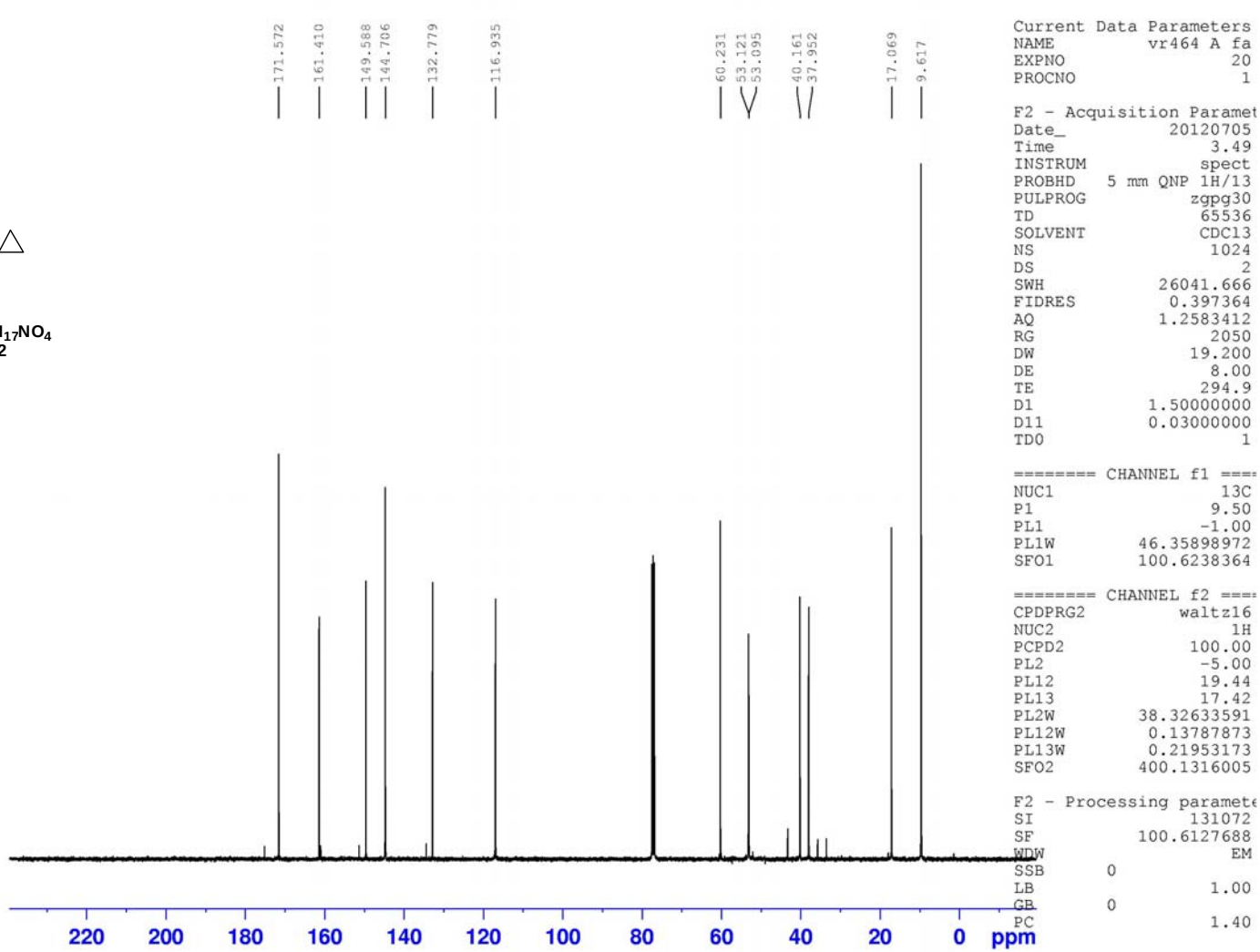
======== CHANNEL f1 ======
NUC1                         1H
P1                         6.00 u
PL1                       -5.00 d
PL1W                38.32633591 W
SFO1                400.1324710 M

F2 - Processing parameter
SI                       131072
SF                  400.1300221 M
WDW                          no
SSB          0
LB           0 Hz
GB           0
PC                         1.00
```

Spectrum of **3d** (^{13}C NMR, $CDCl_3$, 100 MHz)



Chemical Formula: $C_{15}H_{17}NO_4$
Exact Mass: 275,12




```
Current Data Parameters
NAME          vr464 A fa
EXPNO                 20
PROCNO                 1

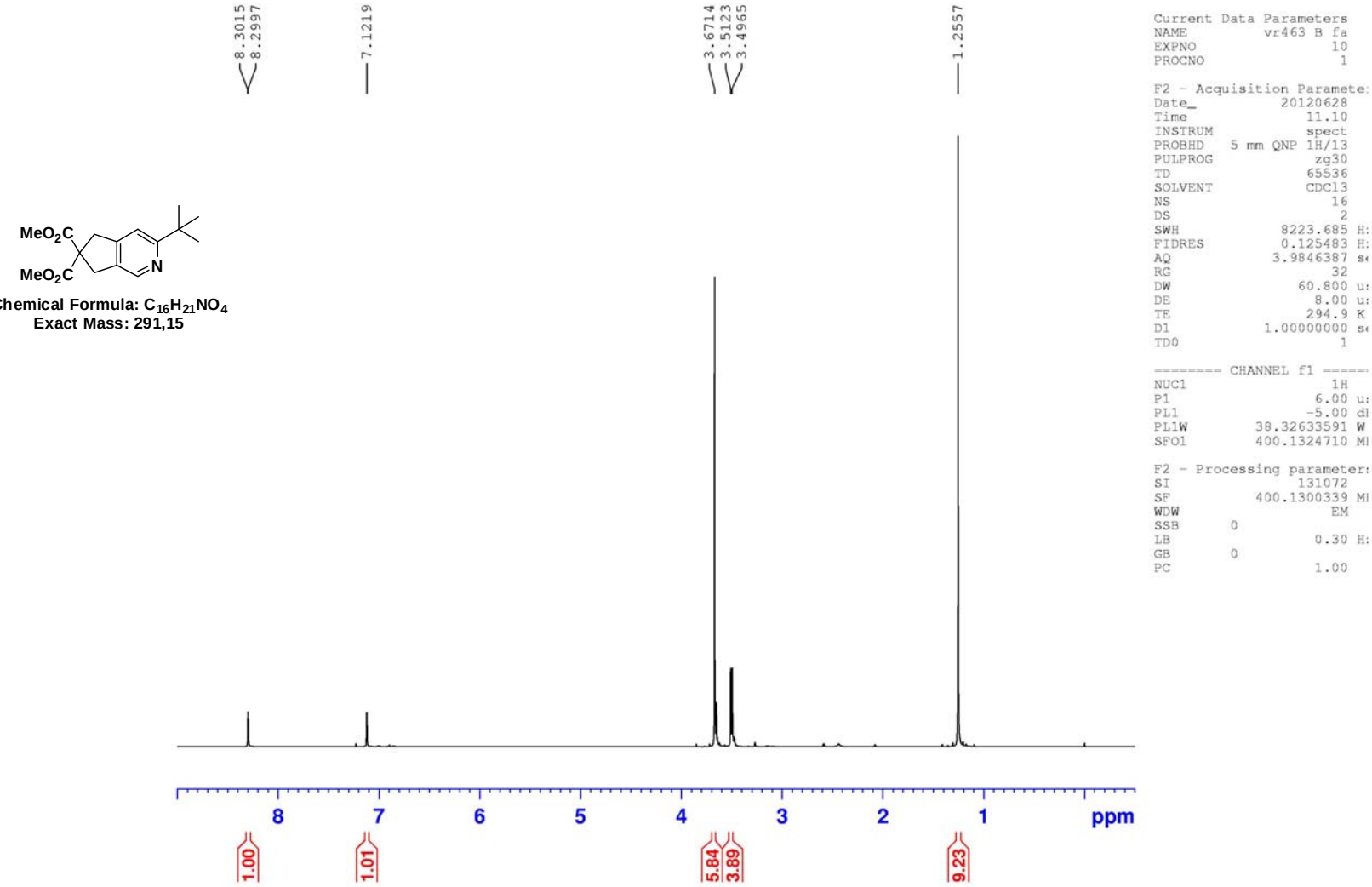
F2 - Acquisition Paramet
Date_           20120705
Time                3.49
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG          zgpg30
TD                65536
SOLVENT           CDC13
NS                 1024
DS                    2
SWH           26041.666
FIDRES         0.397364
AQ            1.2583412
RG                 2050
DW                19.200
DE                 8.00
TE                294.9
D1           1.50000000
D11          0.03000000
TD0                    1

======== CHANNEL f1 ====
NUC1                13C
P1                 9.50
PL1               -1.00
PL1W       46.35898972
SFO1       100.6238364

======== CHANNEL f2 ====
CPDPRG2         waltz16
NUC2                1H
PCPD2           100.00
PL2              -5.00
PL12             19.44
PL13             17.42
PL2W       38.32633591
PL12W       0.13787873
PL13W       0.21953173
SFO2       400.1316005

F2 - Processing paramete
SI                131072
SF          100.6127688
WDW                 EM
SSB       0
LB                 1.00
GB        0
PC                 1.40
```

Spectrum of **3e** (^{1}H NMR, $CDCl_3$, 400 MHz)



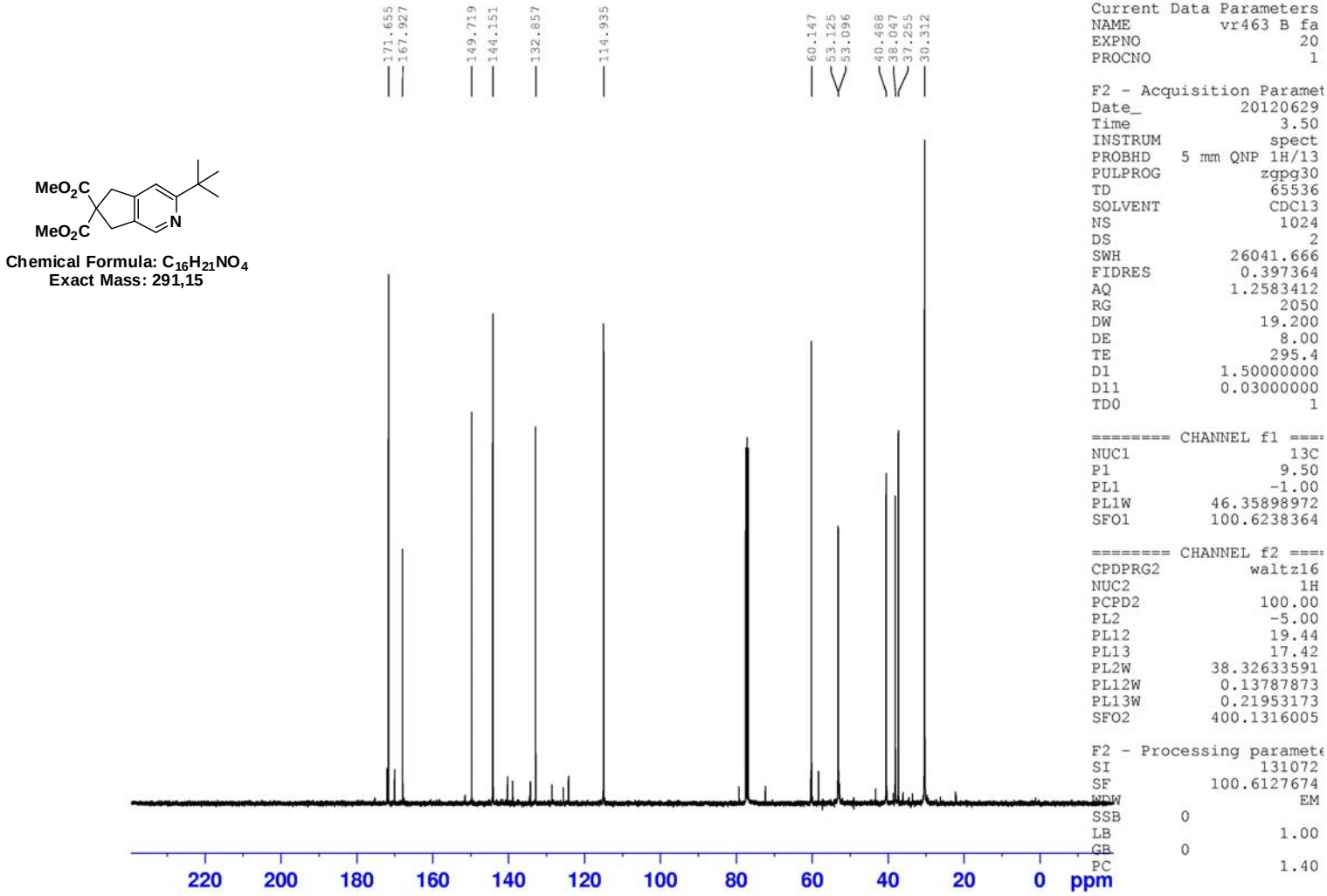

```
Current Data Parameters
NAME          vr463 B fa
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameter
Date_           20120628
Time               11.10
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8223.685 H
FIDRES          0.125483 H
AQ              3.9846387 s
RG                    32
DW                60.800 u
DE                 8.00 u
TE                294.9 K
D1           1.00000000 s
TD0                    1

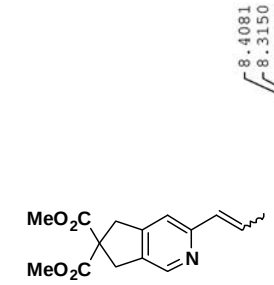
======== CHANNEL f1 =====
NUC1                  1H
P1                 6.00 u
PL1               -5.00 d
PL1W        38.32633591 W
SFO1        400.1324710 M

F2 - Processing parameter
SI                131072
SF          400.1300339 M
WDW                 EM
SSB       0
LB                0.30 H
GB        0
PC                1.00
```

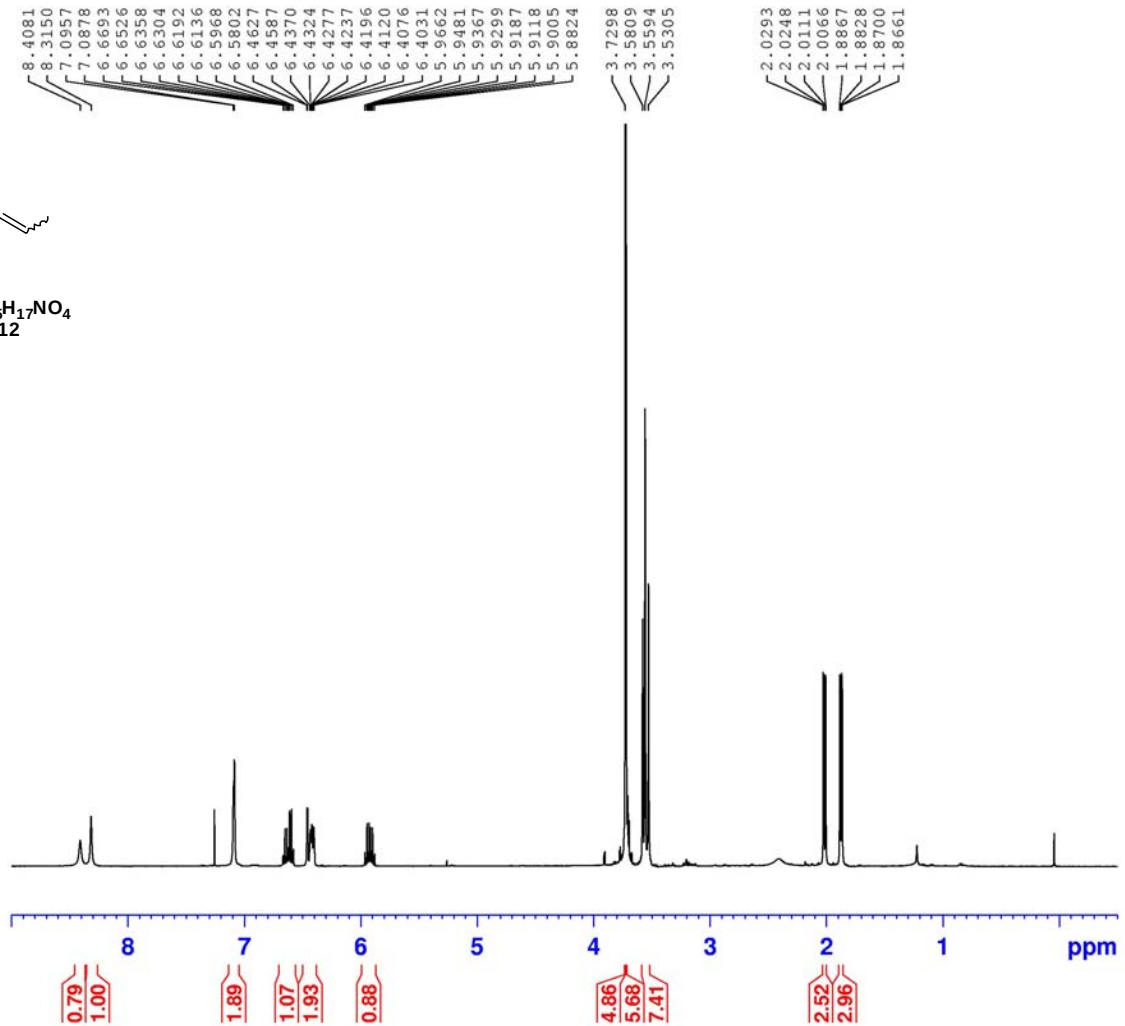
Spectrum of **3e** (^{13}C NMR, $CDCl_3$, 100 MHz)



Spectrum of **3f** (^{1}H NMR, $CDCl_3$, 400 MHz)



Chemical Formula: $C_{15}H_{17}NO_4$
Exact Mass: 275,12



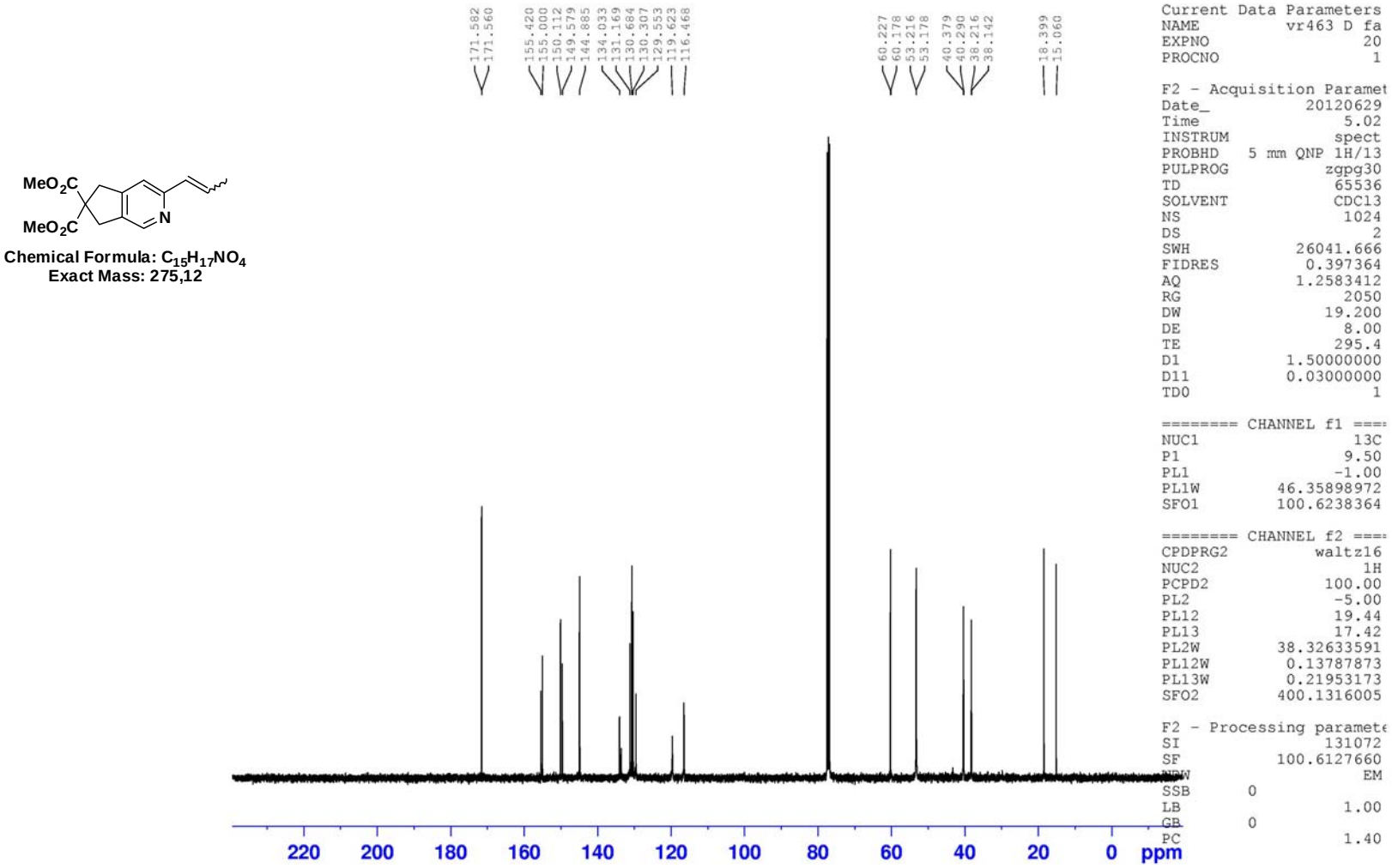

```
Current Data Parameters
NAME                 vr463 D fa
EXPNO                        10
PROCNO                        1

F2 - Acquisition Parameter
Date_                  20120628
Time                      11.15
INSTRUM                   spect
PROBHD    5 mm QNP 1H/13
PULPROG                   zg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                   8223.685 H
FIDRES                0.125483 H
AQ                    3.9846387 s
RG                         80.6
DW                       60.800 u
DE                        8.00 u
TE                       294.9 K
D1                  1.00000000 s
TD0                          1

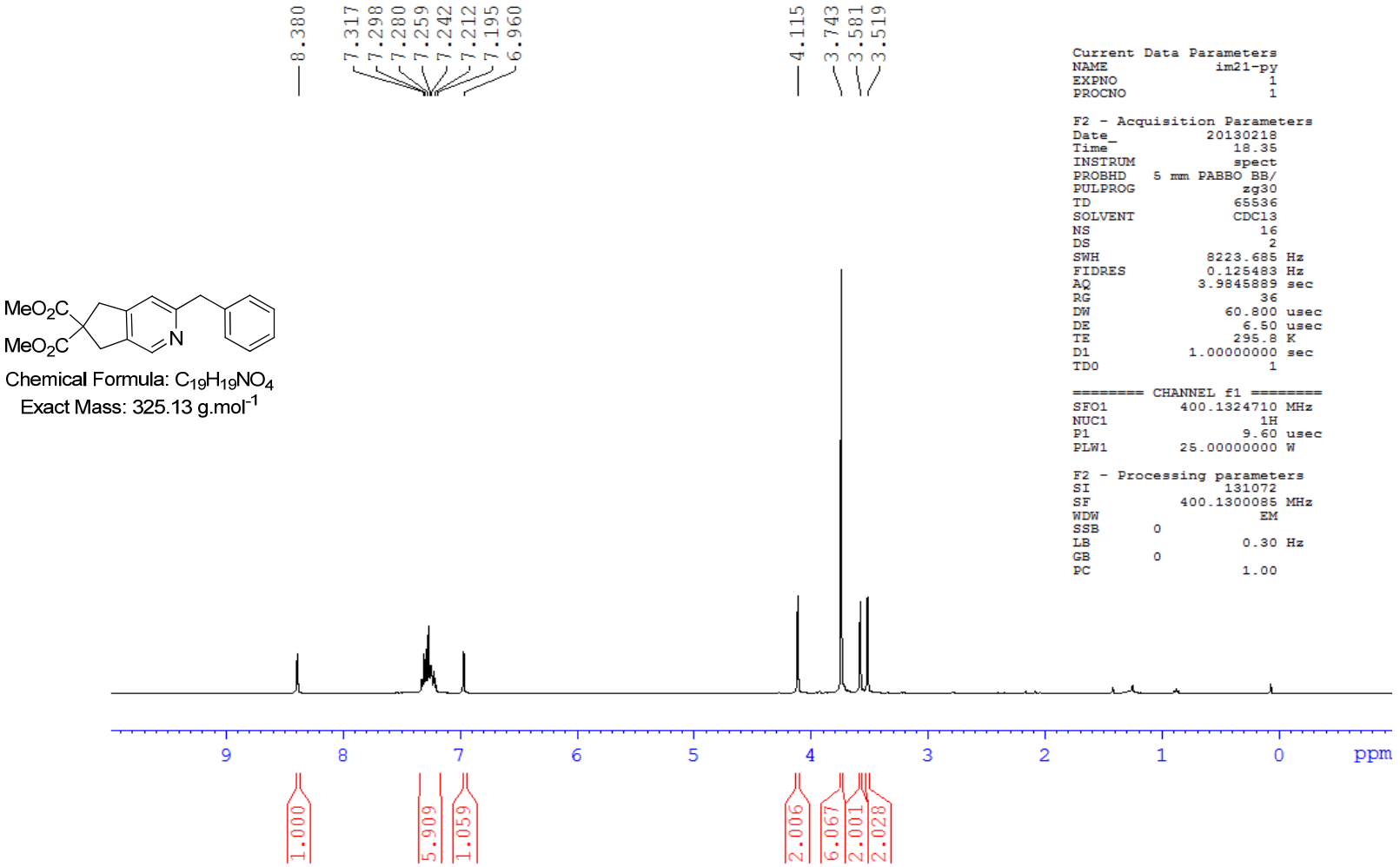
======== CHANNEL f1 ========
NUC1                        1H
P1                        6.00 u
PL1                      -5.00 d
PL1W               38.32633591 W
SFO1               400.1324710 M

F2 - Processing parameter
SI                       131072
SF                 400.1300222 M
WDW                         no
SSB          0
LB           0 Hz
GB           0
PC                        1.00
```

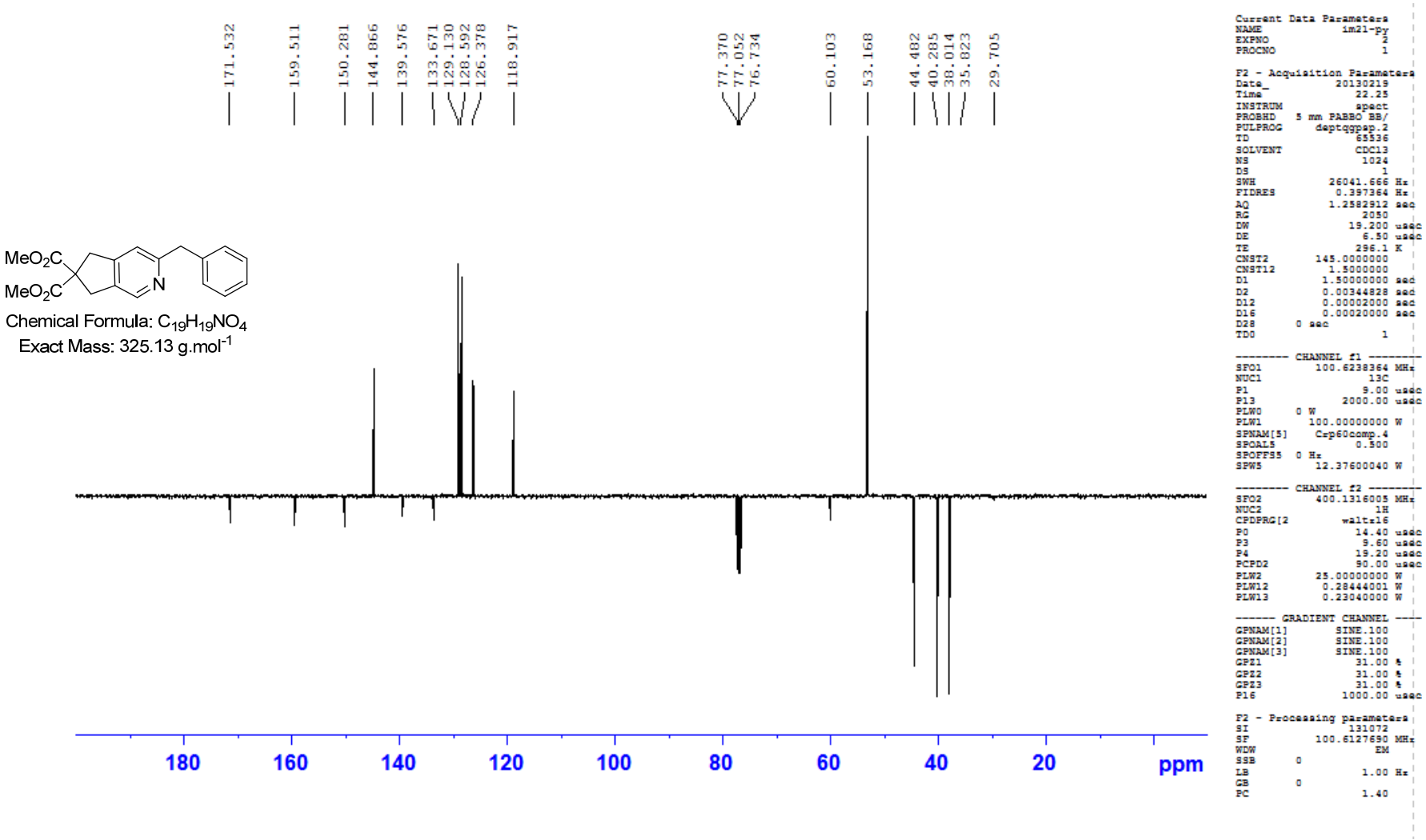
Spectrum of **3f** (^{13}C NMR, $CDCl_3$, 100 MHz)



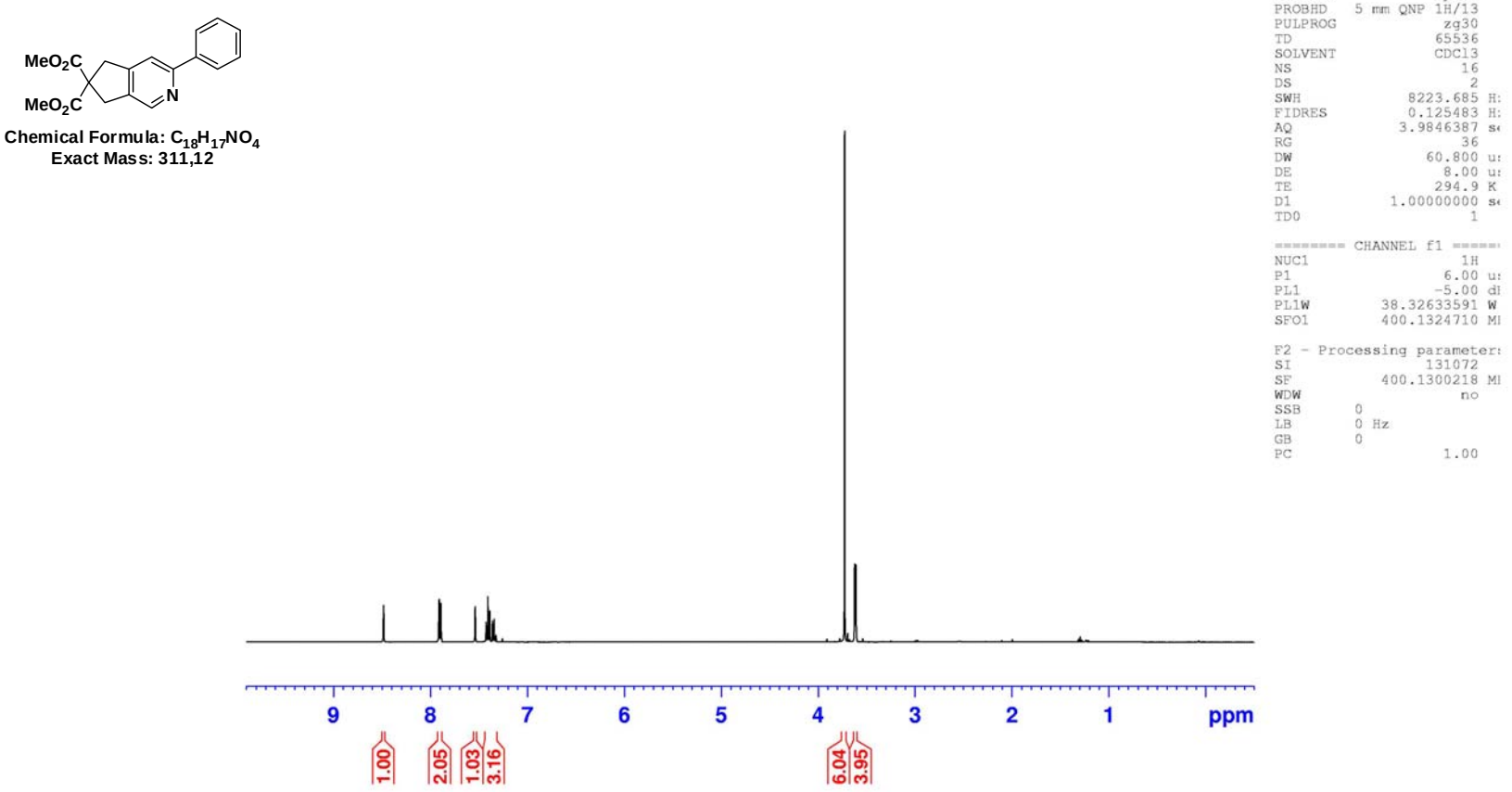
Spectrum of **3g** (^{1}H NMR, $CDCl_3$, 400 MHz)



Spectrum of **3g** (DEPT Q, $CDCl_3$, 100 MHz)



Spectrum of **3h** (^{1}H NMR, $CDCl_3$, 400 MHz)



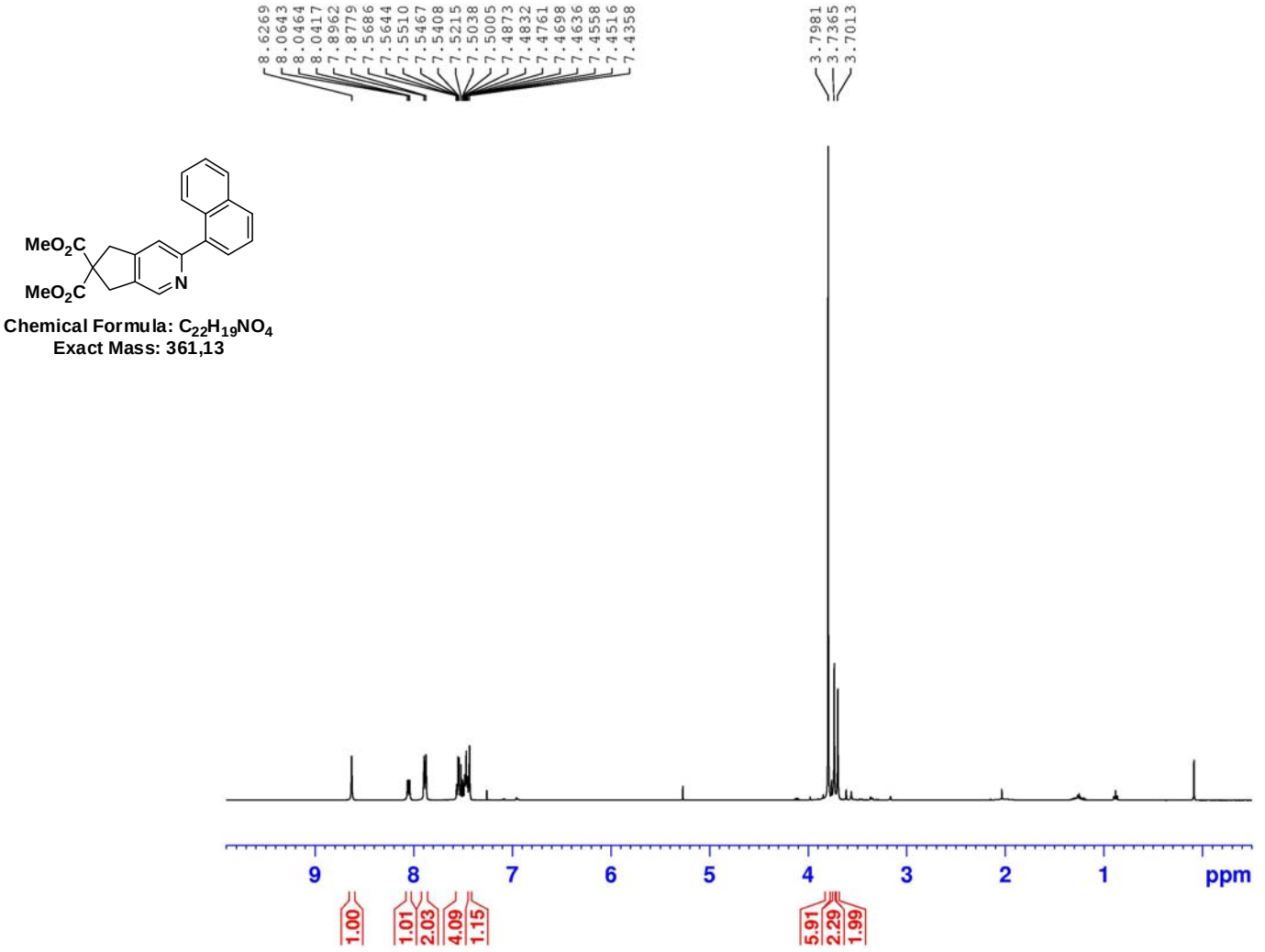

```
Current Data Parameters
NAME                 vr462 B fb
EXPNO                        10
PROCNO                        1

F2 - Acquisition Parameter
Date_                  20120628
Time                      10.55
INSTRUM                   spect
PROBHD    5 mm QNP 1H/13
PULPROG                    zg30
TD                        65536
SOLVENT                   CDCl3
NS                           16
DS                            2
SWH                    8223.685 H
FIDRES                 0.125483 H
AQ                     3.9846387 s
RG                           36
DW                        60.800 u
DE                         8.00 u
TE                        294.9 K
D1                  1.00000000 s
TD0                           1

======== CHANNEL f1 ========
NUC1                         1H
P1                         6.00 u
PL1                       -5.00 d
PL1W                38.32633591 W
SFO1                400.1324710 M

F2 - Processing parameter
SI                       131072
SF                  400.1300218 M
WDW                         no
SSB                  0
LB                   0 Hz
GB                   0
PC                        1.00
```

Spectrum of **3i** (^{1}H NMR, $CDCl_3$, 400 MHz)



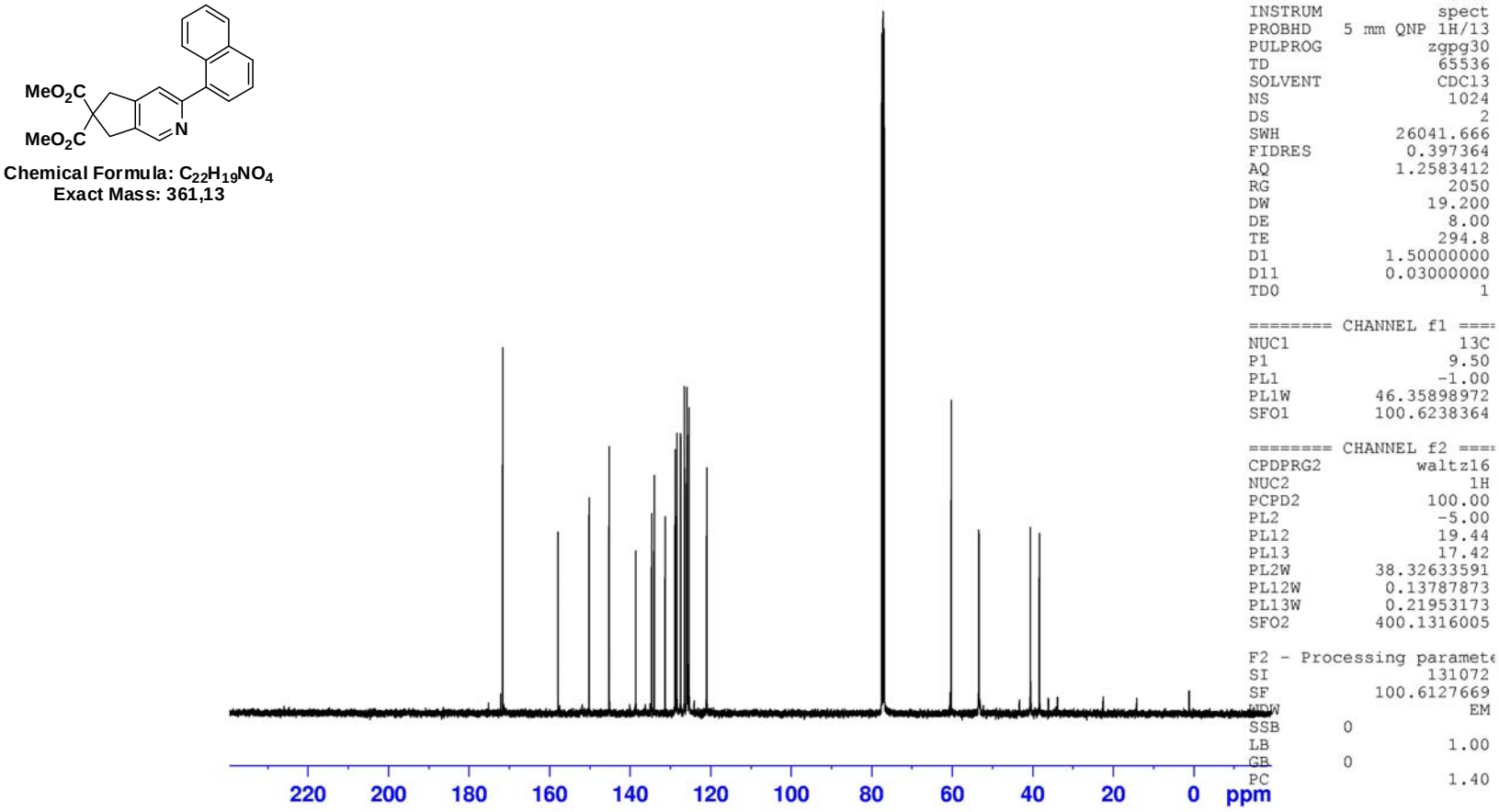

```
Current Data Parameters
NAME                  vr464 B fc
EXPNO                         10
PROCNO                         1

F2 - Acquisition Parameter
Date_                   20120704
Time                        9.05
INSTRUM                    spect
PROBHD    5 mm QNP 1H/13
PULPROG                     zg30
TD                         65536
SOLVENT                    CDCl3
NS                            16
DS                             2
SWH                     8223.685 H
FIDRES                  0.125483 H
AQ                      3.9846387 s
RG                           90.5
DW                         60.800 u
DE                          8.00 u
TE                         294.4 K
D1                    1.00000000 s
TD0                            1

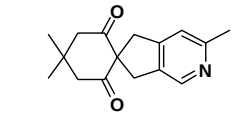
======== CHANNEL f1 ======
NUC1                          1H
P1                         6.00 u
PL1                       -5.00 d
PL1W                38.32633591 W
SFO1                400.1324710 M

F2 - Processing parameter
SI                        131072
SF                  400.1300214 M
WDW                           EM
SSB          0
LB                         0.30 H
GB           0
PC                         1.00
```

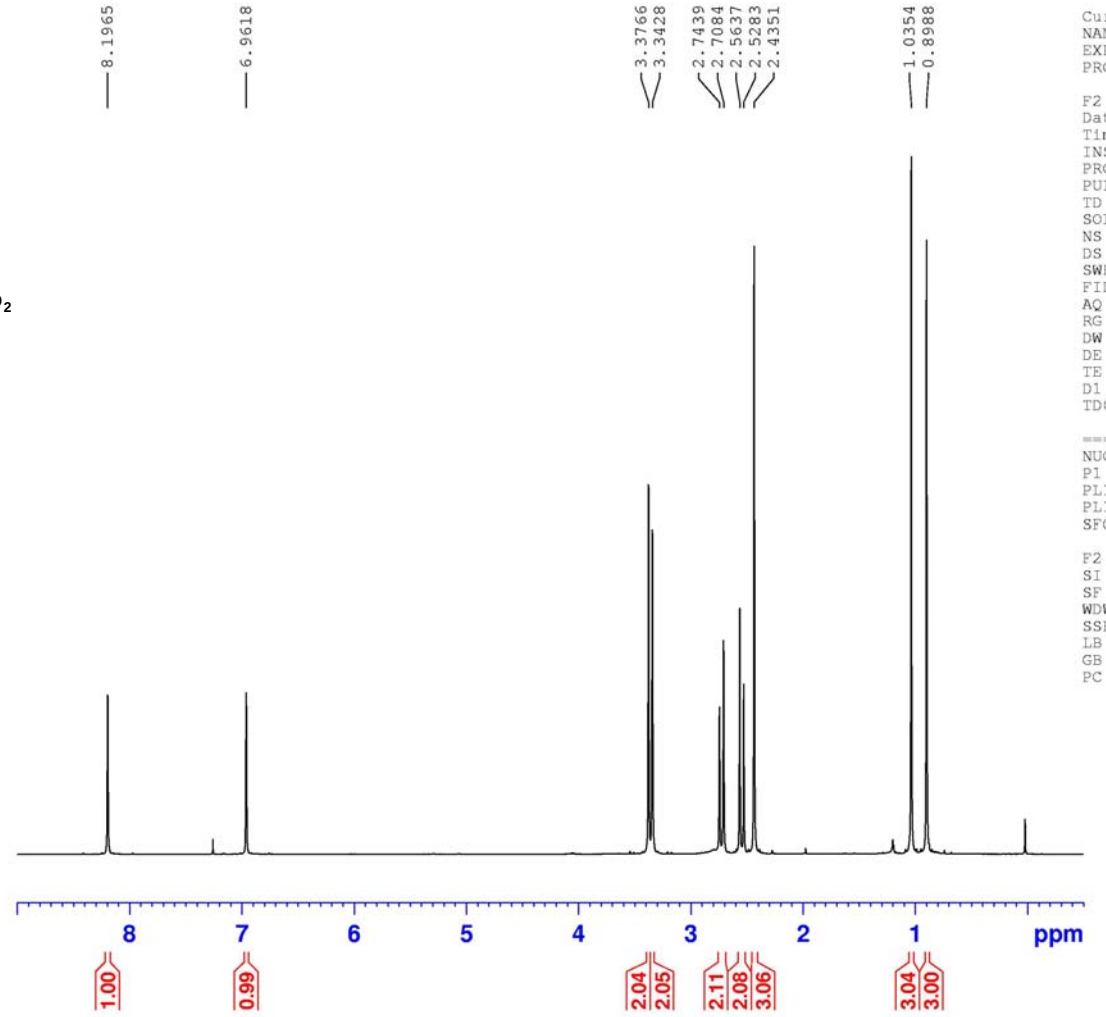
Spectrum of **3i** (^{13}C NMR, $CDCl_3$, 100 MHz)



Spectrum of **3j** (^{1}H NMR, $CDCl_3$, 400 MHz)



Chemical Formula: $C_{16}H_{19}NO_2$
Exact Mass: 257,14



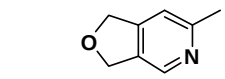

```
Current Data Parameters
NAME          vr471 A fb
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120711
Time                9.19
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ              3.9846387 sec
RG                  40.3
DW                60.800 usec
DE                 8.00 usec
TE                295.2 K
D1           1.00000000 sec
TD0                    1

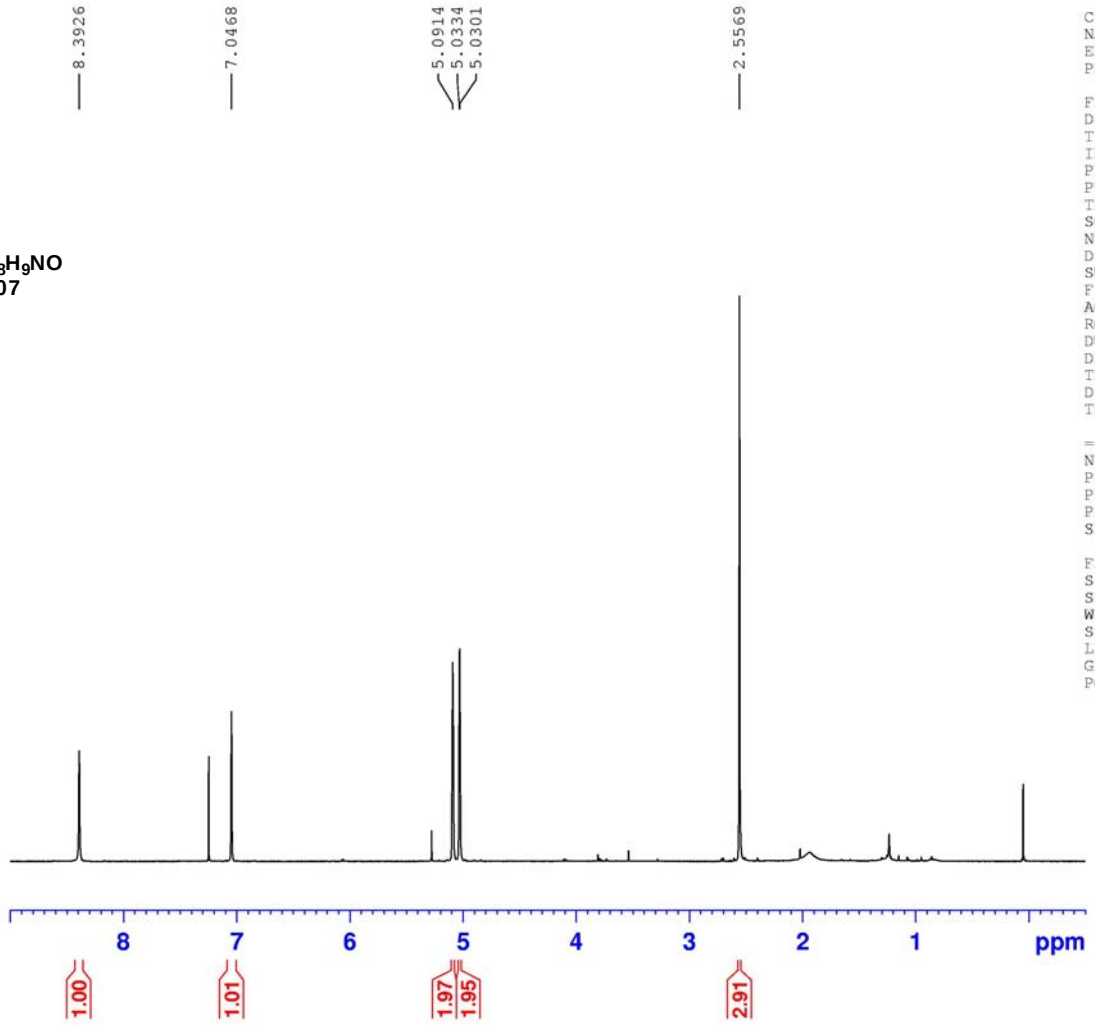
======== CHANNEL f1 ========
NUC1                  1H
P1                 6.00 usec
PL1               -5.00 dB
PL1W        38.32633591 W
SFO1       400.1324710 MHz

F2 - Processing parameters
SI                131072
SF           400.1300223 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

Spectrum of **3j** (^{1}H NMR, $CDCl_3$, 400 MHz)



Chemical Formula: C_8H_9NO
Exact Mass: 135,07



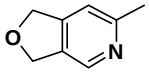

```
Current Data Parameters
NAME          vr475 A fb
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120713
Time                9.44
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ              3.9846387 sec
RG                   406
DW                60.800 usec
DE                 8.00 usec
TE                295.2 K
D1            1.00000000 sec
TD0                    1

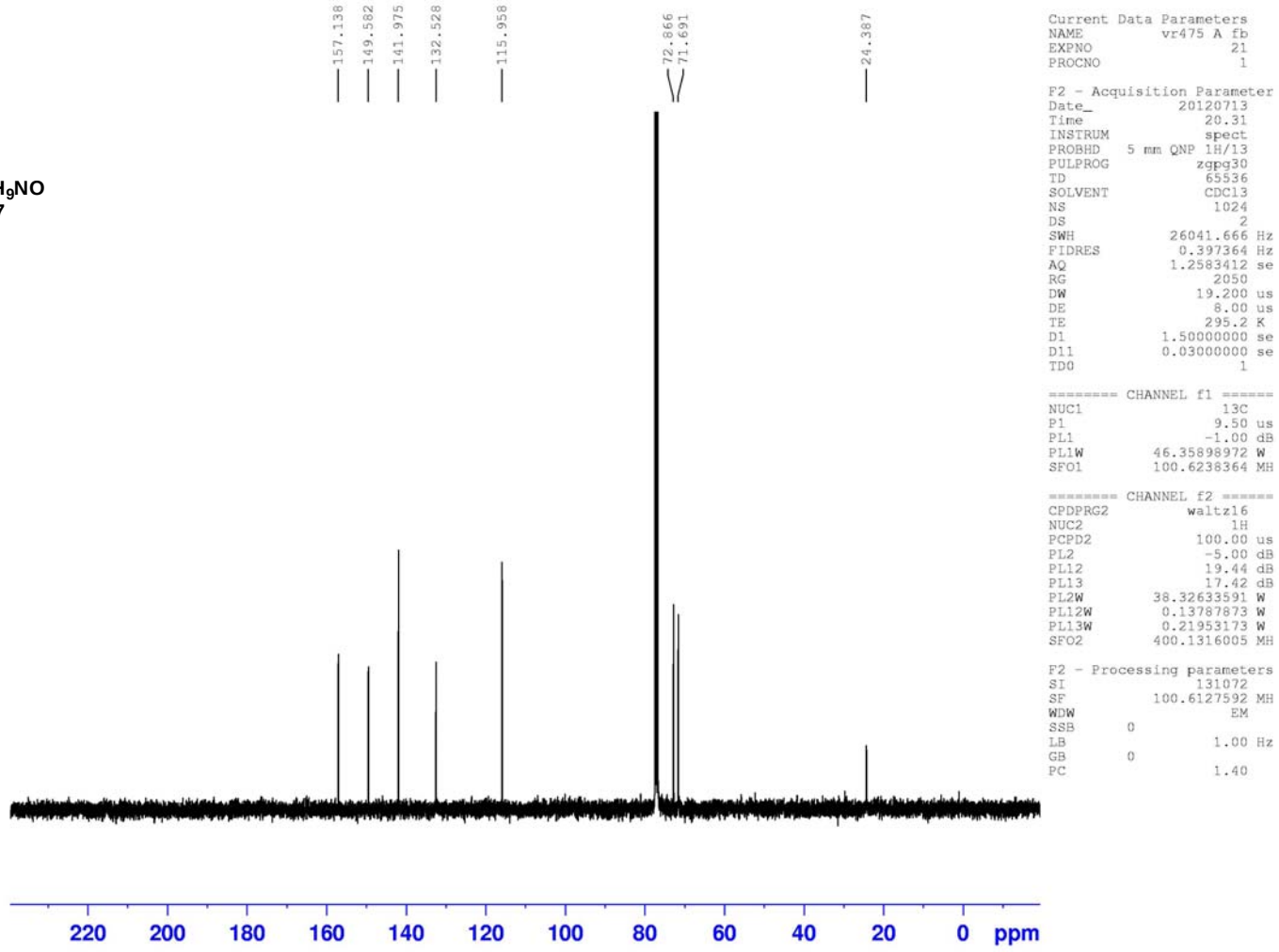
======== CHANNEL f1 ========
NUC1                  1H
P1                  6.00 usec
PL1                -5.00 dB
PL1W         38.32633591 W
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                131072
SF          400.1300266 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

Spectrum of **3k** (^{13}C NMR, $CDCl_3$, 100 MHz)



Chemical Formula: C_8H_9NO
Exact Mass: 135,07




```
Current Data Parameters
NAME          vr475 A fb
EXPNO                 21
PROCNO                 1

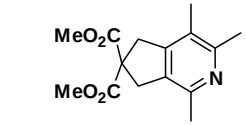
F2 - Acquisition Parameter
Date_           20120713
Time              20.31
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    2
SWH           26041.666 Hz
FIDRES        0.397364 Hz
AQ            1.2583412 se
RG                 2050
DW               19.200 us
DE                8.00 us
TE               295.2 K
D1           1.50000000 se
D11          0.03000000 se
TD0                    1

======== CHANNEL f1 ======
NUC1                13C
P1                9.50 us
PL1              -1.00 dB
PL1W       46.35898972 W
SFO1      100.6238364 MH

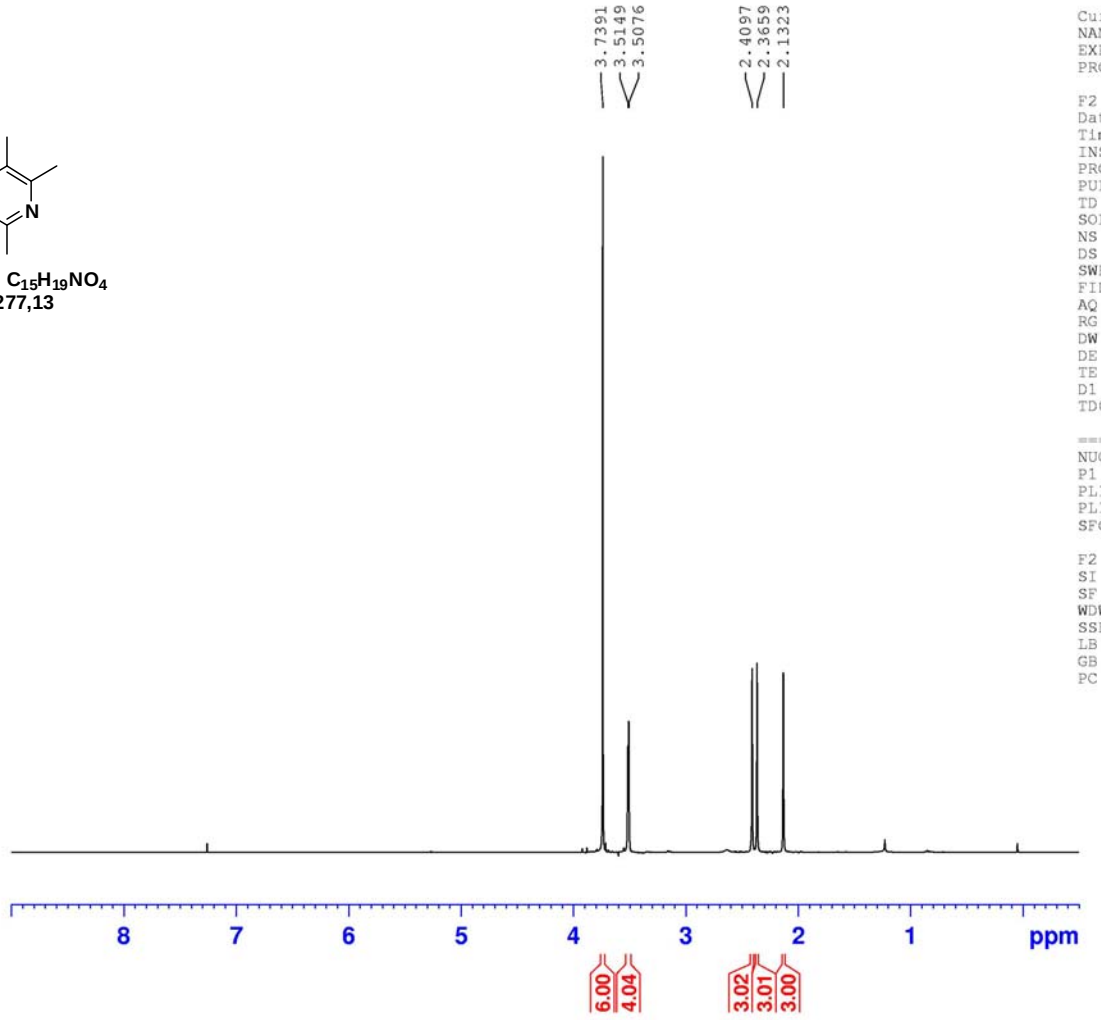
======== CHANNEL f2 ======
CPDPRG2         waltz16
NUC2                1H
PCPD2           100.00 us
PL2              -5.00 dB
PL12             19.44 dB
PL13             17.42 dB
PL2W       38.32633591 W
PL12W       0.13787873 W
PL13W       0.21953173 W
SFO2      400.1316005 MH

F2 - Processing parameters
SI                131072
SF          100.6127592 MH
WDW                 EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

Spectrum of **3o** (^{1}H NMR, $CDCl_3$, 400 MHz)



Chemical Formula: $C_{15}H_{19}NO_4$
Exact Mass: 277,13



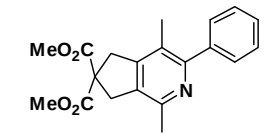

```
Current Data Parameters
NAME                  vr470 A fb
EXPNO                         10
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20120710
Time                       10.23
INSTRUM                    spect
PROBHD    5 mm QNP 1H/13
PULPROG                    zg30
TD                        65536
SOLVENT                   CDCl3
NS                           16
DS                            2
SWH                    8223.685 Hz
FIDRES                 0.125483 Hz
AQ                     3.9846387 sec
RG                          90.5
DW                        60.800 usec
DE                         8.00 usec
TE                        295.2 K
D1                     1.00000000 sec
TD0                            1

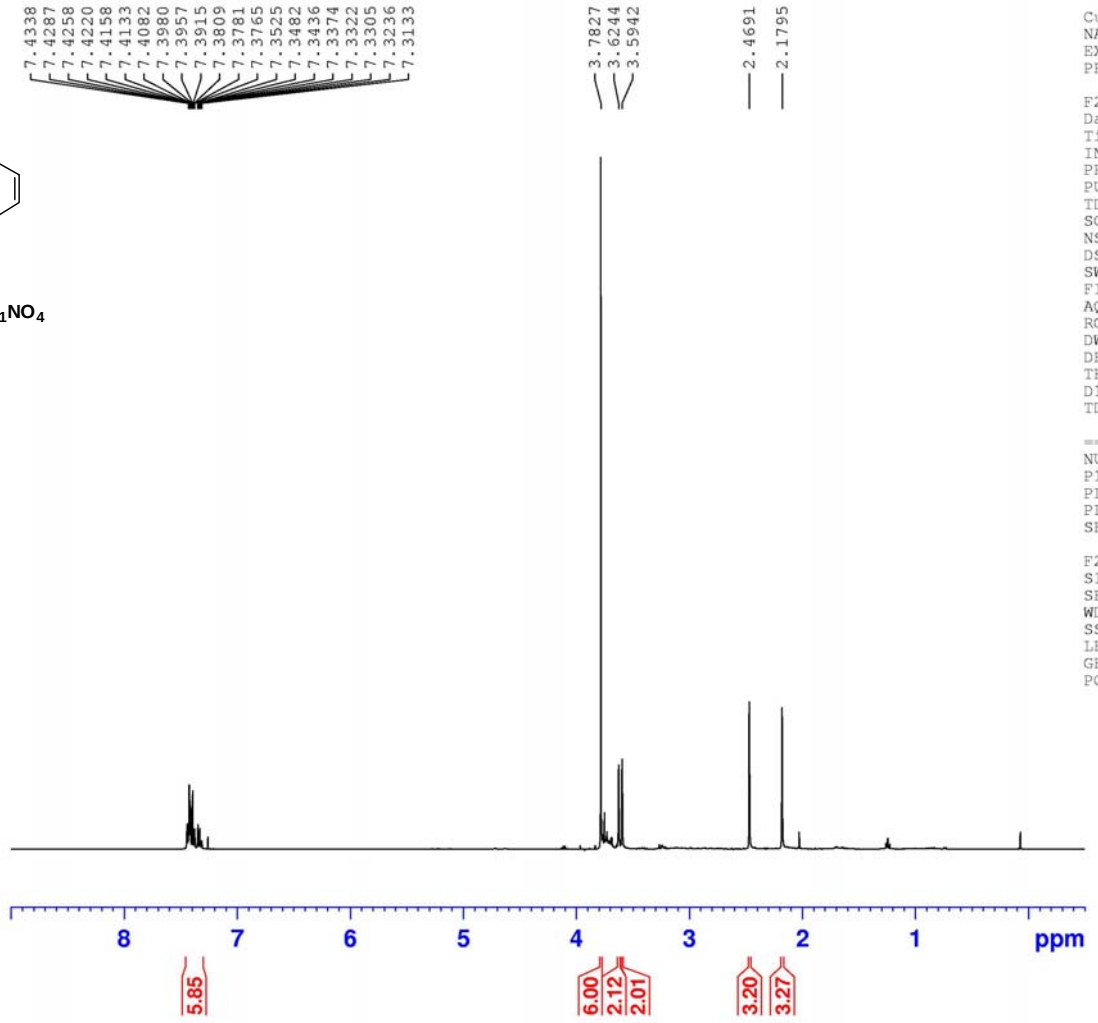
======== CHANNEL f1 ========
NUC1                          1H
P1                         6.00 usec
PL1                       -5.00 dB
PL1W                38.32633591 W
SFO1                400.1324710 MHz

F2 - Processing parameters
SI                        131072
SF                  400.1300214 MHz
WDW                           EM
SSB                0
LB                         0.30 Hz
GB                 0
PC                         1.00
```

Spectrum of **3p** (^{1}H NMR, $CDCl_3$, 400 MHz)



Chemical Formula: $C_{20}H_{21}NO_4$
Exact Mass: 339,15



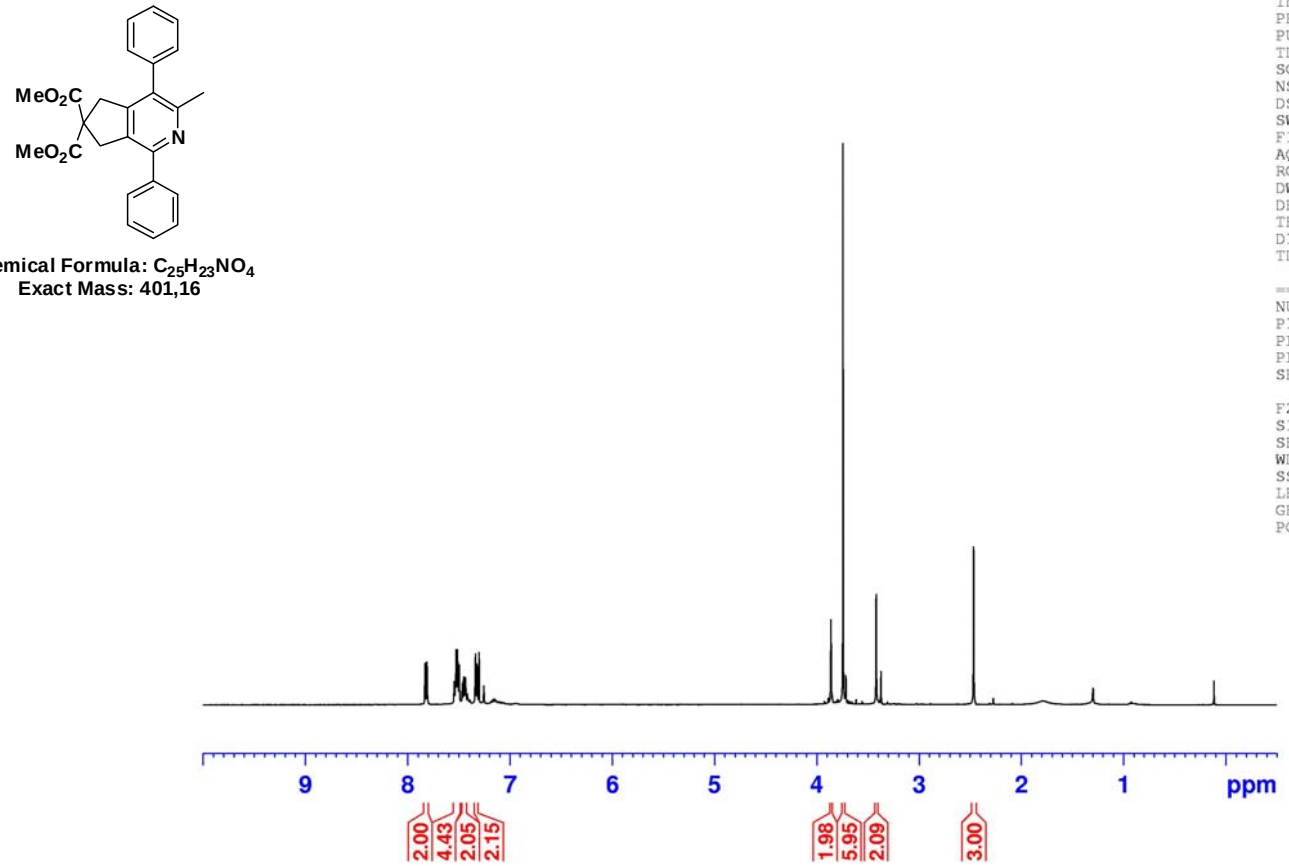

```
Current Data Parameters
NAME          vr470 B fb
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120710
Time               10.28
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8223.685 Hz
FIDRES        0.125483 Hz
AQ            3.9846387 sec
RG                 50.8
DW               60.800 usec
DE                8.00 usec
TE               295.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 6.00 usec
PL1               -5.00 dB
PL1W        38.32633591 W
SFO1       400.1324710 MHz

F2 - Processing parameters
SI                131072
SF         400.1300215 MHz
WDW                   no
SSB       0
LB        0 Hz
GB        0
PC                 1.00
```

Spectrum of **3q** (^{1}H NMR, $CDCl_3$, 400 MHz)



Chemical Formula: $C_{25}H_{23}NO_4$
Exact Mass: 401,16

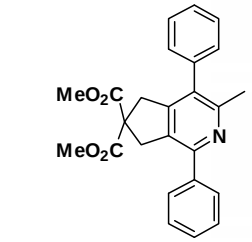
```
Current Data Parameters
NAME                  vr474
EXPNO                    10
PROCNO                    1

F2 - Acquisition Parameters
Date_              20120804
Time                   2.47
INSTRUM               spect
PROBHD    5 mm QNP 1H/13
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8223.685 Hz
FIDRES             0.125483 Hz
AQ                 3.9846387 sec
RG                       287
DW                  60.800 usec
DE                   8.00 usec
TE                   293.3 K
D1                1.00000000 sec
TD0                       1

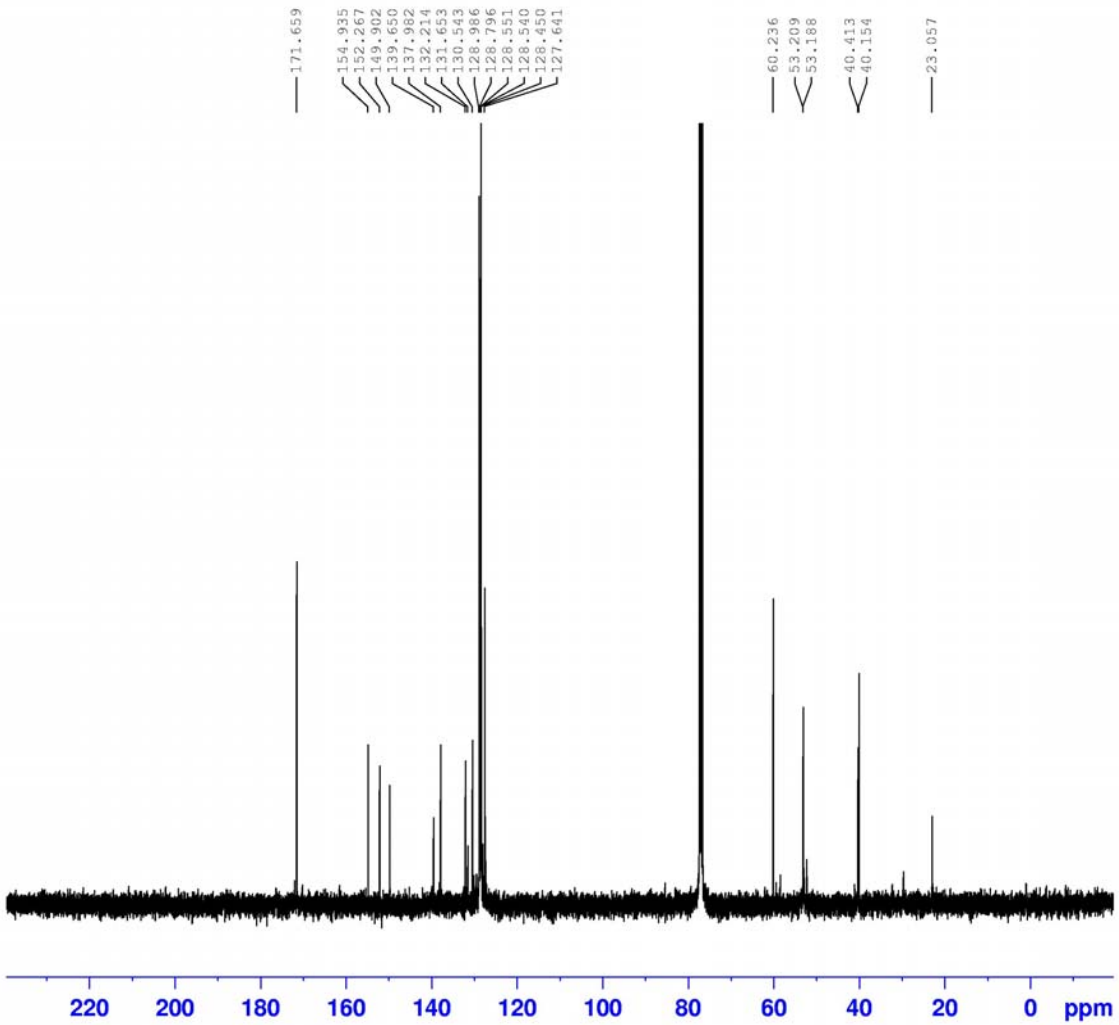
======== CHANNEL f1 ========
NUC1                     1H
P1                   6.00 usec
PL1                  -5.00 dB
PL1W           38.32633591 W
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                     131072
SF             400.1300052 MHz
WDW                      EM
SSB          0
LB                    0.30 Hz
GB           0
PC                    1.00
```

Spectrum of **3q** (^{13}C NMR, $CDCl_3$, 100 MHz)



Chemical Formula: $C_{25}H_{23}NO_4$
Exact Mass: 401,16




```
Current Data Parameters
NAME                  vr474
EXPNO                    11
PROCNO                    1

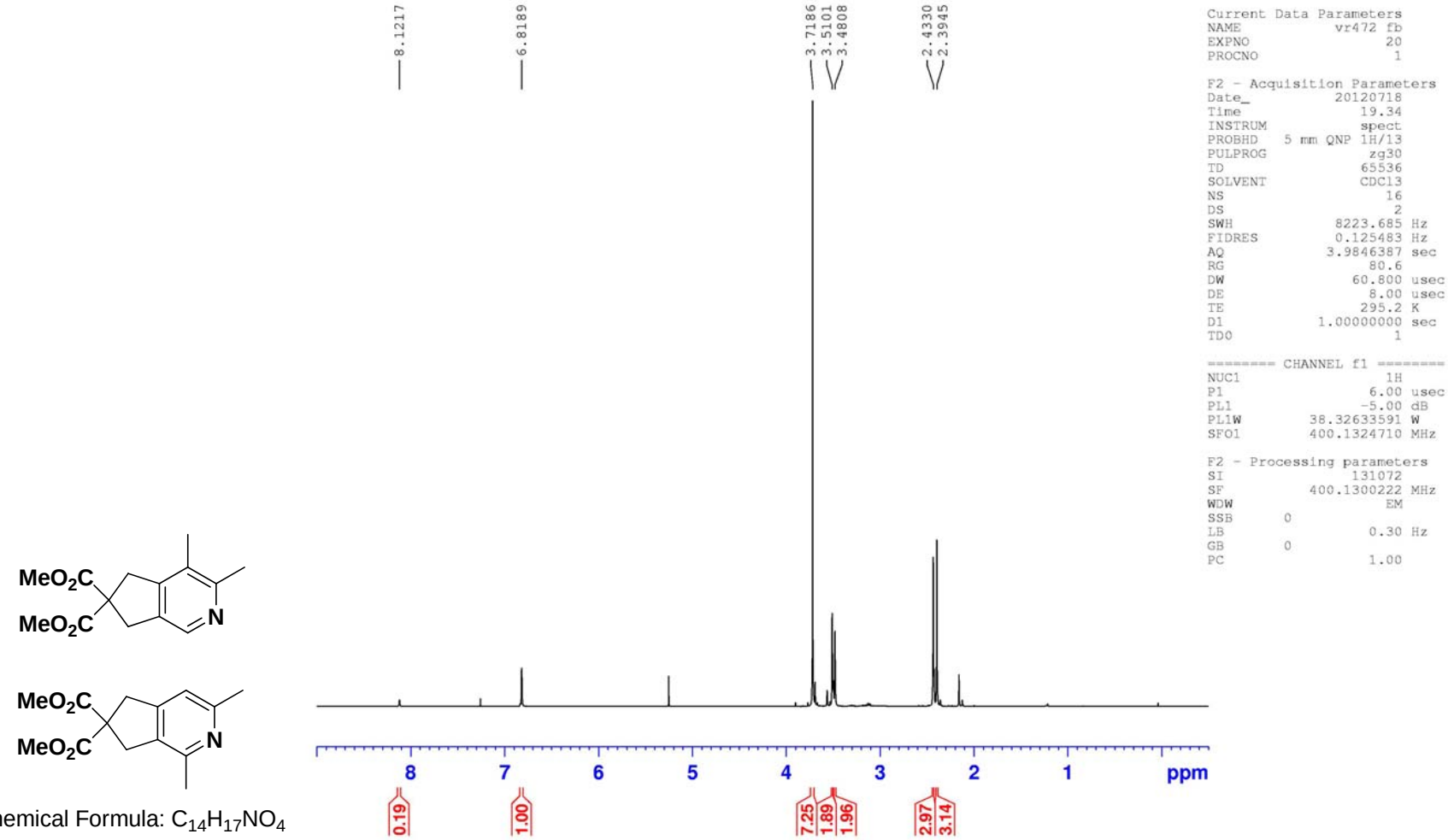
F2 - Acquisition Parameter
Date_              20120804
Time                   4.23
INSTRUM               spect
PROBHD   5 mm QNP 1H/13
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     2048
DS                        2
SWH             26041.666 Hz
FIDRES           0.397364 Hz
AQ               1.2583412 se
RG                     2050
DW                19.200 us
DE                 8.00 us
TE                 293.6 K
D1            1.50000000 se
D11           0.03000000 se
TD0                       1

======== CHANNEL f1 ======
NUC1                   13C
P1                  9.50 us
PL1                -1.00 dB
PL1W         46.35898972 W
SFO1        100.6238364 MH

======== CHANNEL f2 ======
CPDPRG2            waltz16
NUC2                   1H
PCPD2             100.00 us
PL2                -5.00 dB
PL12               19.44 dB
PL13               17.42 dB
PL2W         38.32633591 W
PL12W         0.13787873 W
PL13W         0.21953173 W
SFO2        400.1316005 MH

F2 - Processing parameters
SI                   131072
SF            100.6127641 MH
WDW                    EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
```

Spectrum of **3r+3s** (^{1}H NMR, $CDCl_3$, 400 MHz)




```
Current Data Parameters
NAME                  vr472 fb
EXPNO                       20
PROCNO                       1

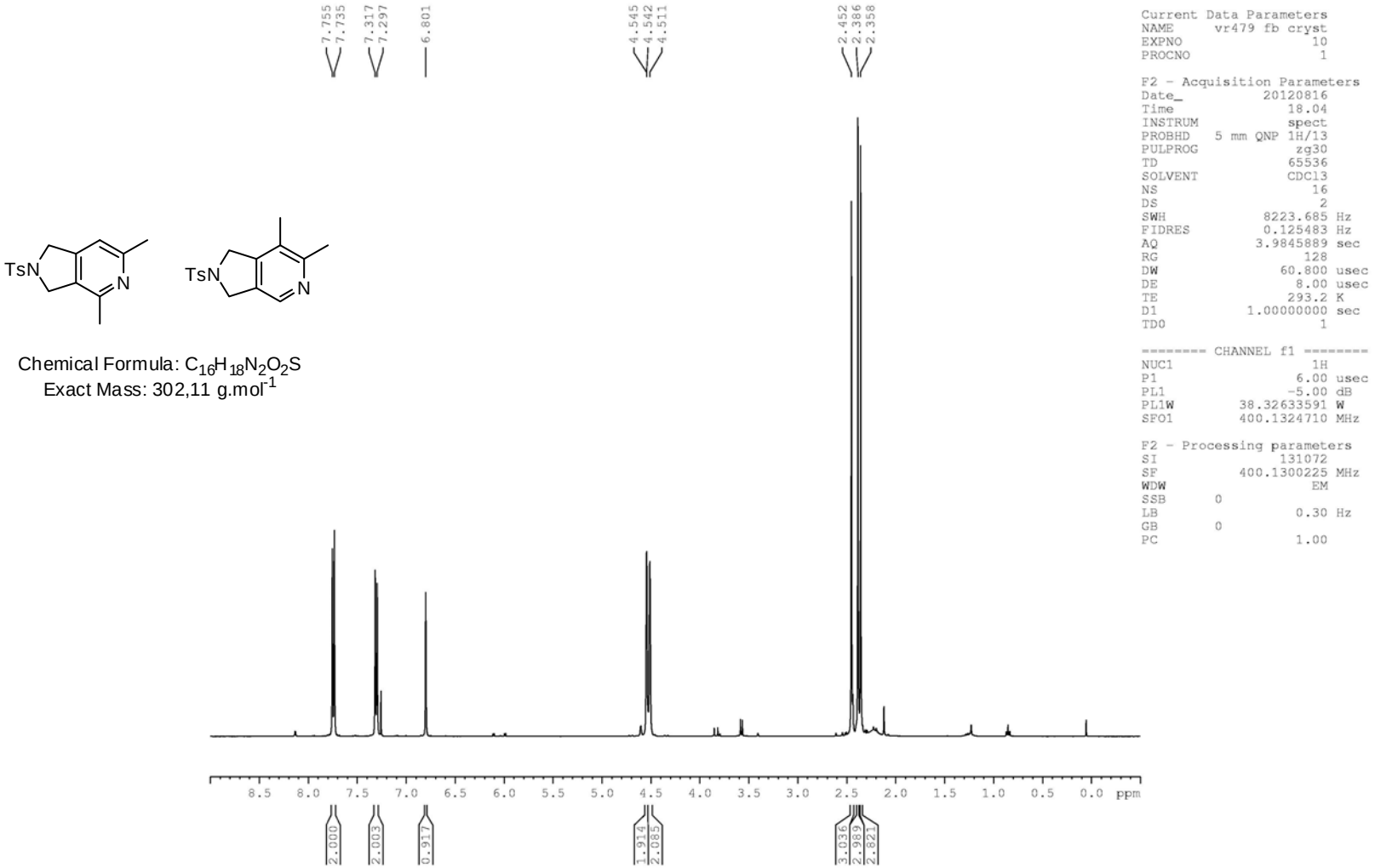
F2 - Acquisition Parameters
Date_                 20120718
Time                     19.34
INSTRUM                  spect
PROBHD    5 mm QNP 1H/13
PULPROG                  zg30
TD                      65536
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                   8223.685 Hz
FIDRES                0.125483 Hz
AQ                    3.9846387 sec
RG                         80.6
DW                       60.800 usec
DE                        8.00 usec
TE                       295.2 K
D1                 1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                        1H
P1                       6.00 usec
PL1                     -5.00 dB
PL1W              38.32633591 W
SFO1              400.1324710 MHz

F2 - Processing parameters
SI                      131072
SF                400.1300222 MHz
WDW                         EM
SSB          0
LB                       0.30 Hz
GB           0
PC                       1.00
```


Chemical Formula: $C_{14}H_{17}NO_4$
Exact Mass: 263,1158

Spectrum of **3t+3u** (^{1}H NMR, $CDCl_3$, 400 MHz)



Chemical Formula: $C_{16}H_{18}N_2O_2S$
Exact Mass: 302,11 g.mol^{-1}

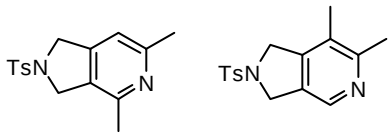
```
Current Data Parameters
NAME      vr479 fb cryst
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120816
Time               18.04
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH           8223.685 Hz
FIDRES        0.125483 Hz
AQ            3.9845889 sec
RG                  128
DW               60.800 usec
DE                8.00 usec
TE               293.2 K
D1            1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                  1H
P1                 6.00 usec
PL1               -5.00 dB
PL1W        38.32633591 W
SFO1       400.1324710 MHz

F2 - Processing parameters
SI                131072
SF         400.1300225 MHz
WDW                  EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

Spectrum of **3t+3u** (^{13}C NMR, $CDCl_3$, 100 MHz)



Chemical Formula: $C_{16}H_{18}N_2O_2S$
Exact Mass: 302,11 g.mol^{-1}


```
Current Data Parameters
NAME      vr479 fb cryst
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameter
Date_           20120816
Time               19.41
INSTRUM             spect
PROBHD   5 mm QNP 1H/13
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 2048
DS                    2
SWH           26041.666 Hz
FIDRES         0.397364 Hz
AQ             1.2582912 se
RG                 2050
DW                19.200 us
DE                 8.00 us
TE                293.7 K
D1           1.50000000 se
d11          0.03000000 se
DELTA        1.39999998 se
TD0                   1
SFO1        100.6238364 MH
NUC1                13C
P1                 9.50 us
PLW1        -1.00000000 W
SFO2        400.1316005 MH
NUC2                1H
CPDPRG[2         waltz16
PCPD2             100.00 us
PLW2        -1.00000000 W
PLW12       -1.00000000 W
PLW13       -1.00000000 W

F2 - Processing parameters
SI                131072
SF          100.6127631 MH
WDW                 EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```