Supporting Information

Ruthenium-Catalyzed Pyrrole Synthesis via Oxidative Annulation of Enamides and Alkynes

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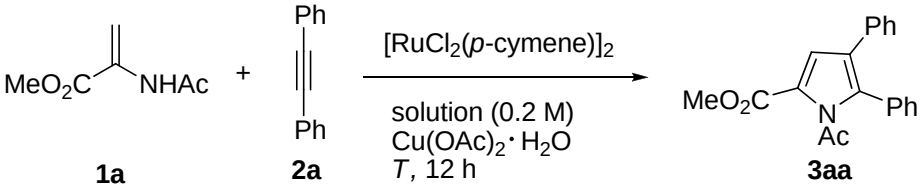
General Experimental Section:

Analytic methods. All the reactions were carried out under argon atmosphere using standard Schlenk technique. ^{1}H NMR (300 MHz or 400 MHz), ^{19}F (282 or 376 M) and ^{13}C NMR (75 MHz or 100MHz) were recorded on Bruker AV300 and AV400 NMR spectrometer with $CDCl_3$ as solvent. Chemical shifts of ^{1}H, ^{19}F, and ^{13}C NMR spectra are reported in parts per million (ppm). The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm; δ_C = 77.00 ppm). All coupling constants (*J* values) were reported in Hertz (Hz). Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), doublet of doublet of doublets (ddd), doublet of triplets (dt), triplet (t), triplet of doublets (td), quartet (q), and multiplet (m). Column chromatography was performed on silica gel 200-300 mesh. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm). IR spectra were recorded as KBr disks on a Nicolet 380 FT-IR spectrometer. EI mass spectra and HRMS were done on Thermo Finnigan TRACE DSQ and Varian 7.0 T FTICR-mass spectrometers, respectively

General preparation for chemicals. [{$RuCl_2$(*p*-cymene)}$_2$] was prepared from $RuCl_3.xH_2O$ following a literature procedure.[1] All other reagents were used is from commercial sources. Unless otherwise noted below, all other compounds have been reported in the literature or are commercially available from Alfa Aesar China (Tianjin) Chemical Co., Ltd. without any further purification. The substrates methyl 2-acetamidoacrylate (**1a**),[1] (*Z*)-N-(1-cyanoprop-1-en-2-yl)acetamide (**4**),[2] 1,2-bis(4-fluorophenyl)ethyne (**2b**),[3] 1,2-bis(4-chlorophenyl)ethyne (**2c**),[3] 1,2-bis(4-bromophenyl)ethyne (**2d**),[3] diethyl 4,4'-(ethyne-1,2-diyl)dibenzoate (**2e**),[3] 1,2-di-p-tolylethyne (**2f**),[3] 1,2-bis(4-methoxyphenyl)ethyne (**2g**)[3] were prepared according to the known procedure.

Table S1. Optimization studies for tetrasubstituted pyrroles **3**[a]

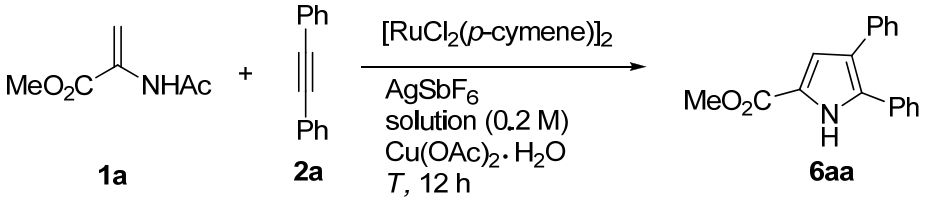


1a **2a** **3aa**

entry	catalyst loading (x mol%)	solution	oxidant loading (equiv)	*T* (^{o}C)	conversion (%)[b]
1	5.0	*t*-AmOH	2.2	110	100 (84)[c]
2	4.0	*t*-AmOH	2.2	110	91
3	3.0	*t*-AmOH	2.2	110	85
4	5.0	Dioxane	2.2	110	100 (83)[c]
5	5.0	CH_3CN	2.2	110	93
6	5.0	DCE	2.2	110	100 (88)[c]
7	5.0	H_2O	2.2	110	100 (55)[c]
8	5.0	DCE	2.2	100	100 (89)[c]
9	5.0	DCE	2.2	90	90
10	5.0	DCE	2.2	80	82
11	5.0	DCE	1.5	100	100
12	5.0	DCE	1.0	100	100
13	5.0	DCE	0.5	100	100 (90)[c]
14	0.0	DCE	0.5	100	0

[a] Reaction condition: **1a** (1.0 equiv), **2a** (1.1 equiv), [{$RuCl_2$(*p*-cymene)}$_2$] (x mol%), solution (0.2M), *T*, 12 h . [b] determined by GC. [c] isolated yields.

Table S2. Optimization studies for trisubstituted pyrroles **6**[a]

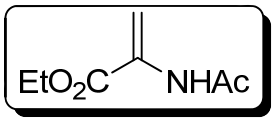


1a **2a** **6aa**

entry	additive loading (x mol%)	solution	oxidant loading (equiv)	*T* (°C)	conversion (%)[b]
1	0.0	CF_3CH_2OH	2.2	110	35
2	0.0	MeOH	2.2	110	53 (20)[c]
3	0.0	*t*-BuOH	2.2	110	20
4	20.0	CF_3CH_2OH	2.2	110	38
5	20.0	MeOH	2.2	110	60 (43)[c]
6	20.0	MeOH/t-AmOH (2:1)	2.2	100	55
7	20.0	MeOH/DCE (2:1)	2.2	100	100 (93)[c]
8	20.0	MeOH/DCE (2:1)	2.2	100	100 (89)[c]
9	20.0	MeOH/DCE (2:1)	2.0	100	100 (91)[c]
10	20.0	MeOH/DCE (2:1)	1.0	100	100 (80)[c]
11	20.0	MeOH/DCE (2:1)	0.5	100	100 (70)[c]
12	0.0	MeOH/DCE (2:1)	2.0	100	75 (40)[c]

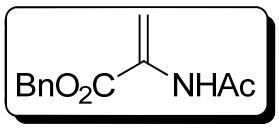
[a] Reaction condition: **1a** (0.3 mmol, 1.0 equiv), **2a** (0.33 mmol, 1.1 equiv), [{$RuCl_2$(*p*-cymene)}$_2$] (5 mol%), $AgSbF_6$ (x mmol%), solution (0.2M), *T*, 12 h . [b] determined by GC. [c] isolated yields.

Preparation and Characterization of Substrates 1b and 1c



ethyl 2-acetamidoacrylate (1b).

A round-bottom flask equipped with a Dean-Stark trap was charged successively with acetamide (1.5 g, 25.4 mmol), ethyl pyruvate (2.7 g, 22.9 mmol, 0.9 equiv), a catalytic amount of *p*-TsOH, 4-methoxyphenol (4 mg, 25.4 mmol, 0.001 equiv) and toluene (50 mL). The stirred mixture was heated under reflux for 26 h then concentrated in vacuo. The resulting yellow oil was taken up in CH_2Cl_2 (100 mL), washed with sat. $NaHCO_3$ (100 mL) and H_2O (100 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo to give ethyl 2-acetamidoacrylate. R_f = .25 (5:1, Hexanes/EtOAc); **^{1}H NMR ($CHCl_3$, 400 MHz):** δ 8.59 (1H, br s), 6.47 (1H, s), 4.40 (2H, q, *J* = 7.1 Hz), 2.28 (3H, s), 1.41 (3H, t, *J* = 7.1 Hz); **^{13}C NMR ($CHCl_3$, 100 MHz):** δ 168.8, 164.0, 131.0, 108.3, 62.1, 24.5, 14.0; **IR (cm^{-1}):** ν 3362, 2986, 1693, 1188, 731, 584.

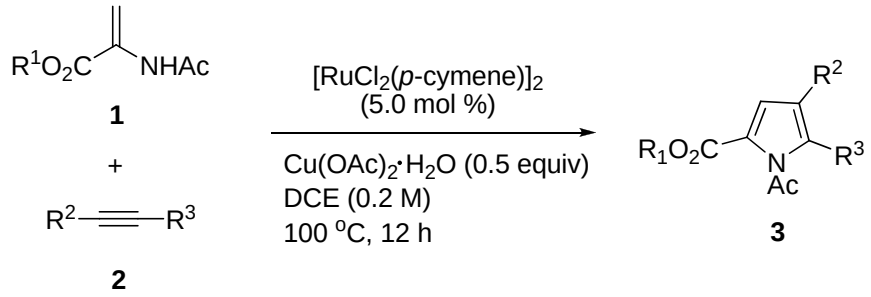


benzyl 2-acetamidoacrylate (1c).

A round-bottom flask equipped with a Dean-Stark trap was charged successively with acetamide (1.5 g, 25.4 mmol), benzyl pyruvate (4.1 g, 22.9 mmol, 0.9 equiv), a catalytic amount of *p*-TsOH, 4-methoxyphenol (4 mg, 25.4 mmol, 0.001 equiv) and toluene (50 mL). The stirred mixture was heated under reflux for 26 h then concentrated in vacuo. The resulting yellow oil was taken up in CH_2Cl_2 (100 mL), washed with sat. $NaHCO_3$ (100 mL) and H_2O (100 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo to give benzyl 2-acetamidoacrylate. R_f = .28 (5:1, Hexanes/EtOAc); **^{1}H NMR ($CHCl_3$, 400 MHz):** δ 7.73 (1H, br s), 7.38 (5H, br s), 6.62 (1H, s), 5.94 (1H, s), 5.27 (2H, s), 2.12 (3H, s); **^{13}C NMR ($CHCl_3$, 100 MHz):** δ 168.8, 164.0, 135.0, 130.9, 128.6, 128.5, 128.1, 108.9, 67.7, 24.6; **IR (cm^{-1}):** ν 3365, 1712, 1518, 1193, 742, 691.

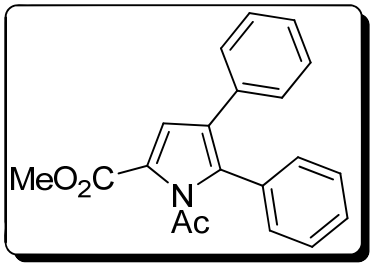
Preparation and Characterization of Products 3 and 5

General procedure A: Ruthenium catalyzed tetrasubstituted pyrroles (3) synthesis



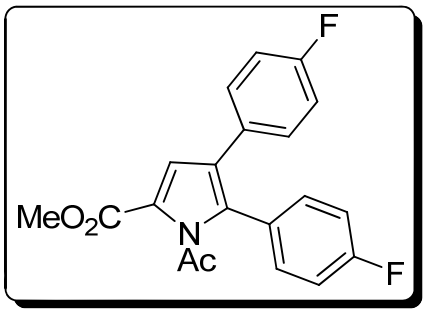
A mixture of the enamide (**1**) (0.30 mmol, 1.0 equiv.), the alkyne (**2**) (if solid) (0.33 mmol, 1.1 equiv.), $[RuCl_2(p\text{-cymene})]_2$ (9.2 mg, 0.015 mmol, 5.0 mol %) and $Cu(OAc)_2 \cdot H_2O$ (30.0 mg, 0.15 mmol, 0.5 equiv.) were weighted in a Schlenk tube equipped with a stir bar. Dry DCE (1.5 mL) was added (followed immediately by the alkyne if it is a liquid) and the mixture was stirred at 100 °C for 12 hours under Ar atmosphere. Afterwards, it was diluted with CH_2Cl_2 and transferred to a round bottom flask. Silica was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel.

Analytical data of Pyrroles 3



methyl 1-acetyl-4,5-diphenyl-1*H*-pyrrole-2-carboxylate (3aa).[4]

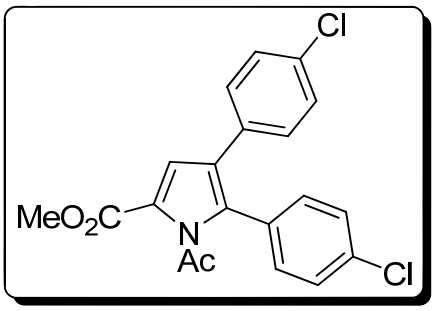
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20 to 1/15) as a clear oil in 89% yield (87 mg) from **1a** (0.30 mmol, 42.9 mg, 1.0 equiv.) following the general procedure A. R_f = .45 (10:1 Hexanes/EtOAc); **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.39-7.33 (3H, m), 7.31-7.29 (2H, m), 7.20-7.16 (4H, m), 7.14-7.12(2H, m), 3.89 (3H, s), 2.31 (H, s); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 173.8, 161.1, 134.5, 133.9, 130.6, 128.8, 128.5, 128.2, 128.0, 126.4, 124.8, 122.9, 118.3, 51.8, 28.8 (one signal missing due to overlap); **MS (EI):** Calcd for $C_{20}H_{17}NO_3$ [M^+] 319.12, Found: 319.



methyl 1-acetyl-4,5-bis(4-fluorophenyl)-1*H*-pyrrole-2-carboxylate (3ab).

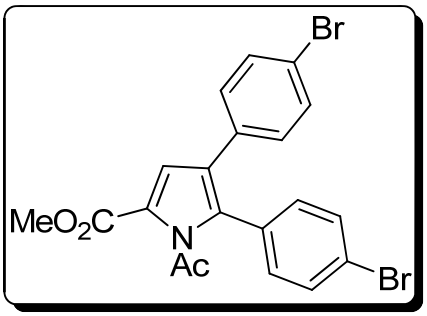
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20 to 1/15) as a white solid in 91% yield (97 mg) from **1a** (0.30 mmol, 42.9 mg, 1.0 equiv.) following the general procedure A. R_f = .40 (10:1 Hexanes/EtOAc); m.p.: 94-96 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.42-7.39 (3H, m), 7.22-7.18 (4H, m), 7.07-7.02 (2H, m), 4.03 (3H, s), 2.48 (3H, s); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 173.6, 162.9 (d, $J_{C\text{-}F}$ = 249.8 Hz), 161.6 (d, $J_{C\text{-}F}$ = 246.2 Hz), 160.9, 133.4, 132.7 (d, $J_{C\text{-}F}$ = 8.3 Hz), 129.8 (d, $J_{C\text{-}F}$ = 3.2 Hz), 129.5 (d, $J_{C\text{-}F}$ = 7.8 Hz), 126.3 (d, $J_{C\text{-}F}$ = 3.5 Hz), 124.2, 123.0, 118.2, 115.7 (d, $J_{C\text{-}F}$ = 21.7 Hz), 115.2 (d, $J_{C\text{-}F}$ = 21.5 Hz), 51.9, 28.9; **^{19}F NMR ($CDCl_3$, 376 MHz):** δ -111.34 (s), -115.59 (s); **HRMS (ESI):** Calcd for

$C_{20}H_{15}F_2NNaO_3$ $[M+Na]^+$ 378.0912, Found: 378.0910; **IR (cm^{-1}):** ν 2955, 1766, 1700, 840, 532.



methyl 1-acetyl-4,5-bis(4-chlorophenyl)-1*H*-pyrrole-2-carboxylate (3ac).

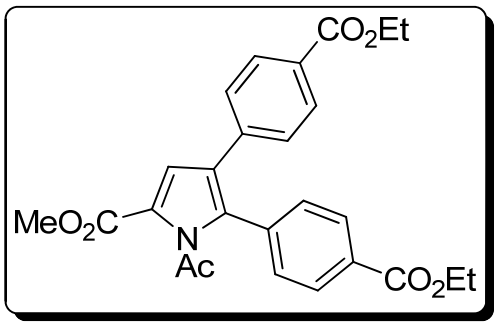
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20 to 1/15) as an off-white solid in 89% yield (104 mg) from **1a** (0.30 mmol, 42.9 mg, 1.0 equiv.) following the general procedure A. R_f = .46 (10:1 Hexanes/EtOAc); m.p.: 96-98 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.34 (2H, d, *J* = 8.4 Hz), 7.22 (2H, d, *J* = 8.5 Hz), 7.19 (2H, d, *J* = 8.5 Hz), 7.13 (1H, br s), 7.03 (2H, d, *J* = 8.5 Hz), 3.89 (3H, s), 2.35(3H, s); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 173.5, 160.9, 135.2, 133.3, 132.5, 132.1, 132.0, 129.2, 128.9, 128.64, 128.56, 124.0, 123.3, 118.1, 52.0, 28.9; **HRMS (ESI):** Calcd for $C_{20}H_{15}Cl_2NNaO_3$ $[M+Na]^+$ 410.0321, Found: 410.0322; **IR (cm^{-1}):** ν 2951, 1756, 1705, 763, 649.



methyl 1-acetyl-4,5-bis(4-bromophenyl)-1*H*-pyrrole-2-carboxylate (3ad).

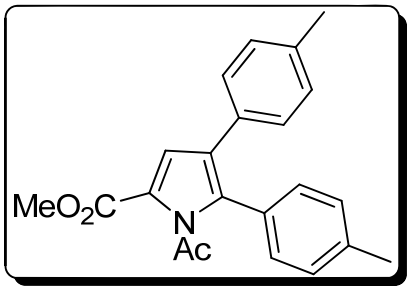
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20 to 1/15) as a clear oil in 88% yield (126 mg) from **1a** (0.30 mmol, 42.9 mg, 1.0 equiv.) following the general procedure A. R_f = .48 (10:1 Hexanes/EtOAc); **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.50 (2H, d, *J* = 8.5 Hz), 7.34 (2H, d, *J* = 8.5 Hz), 7.15 (2H, d, *J* = 8.5 Hz), 7.12 (1H, br s), 7.00 (2H, d, *J* = 8.5 Hz), 3.89 (3H, s), 2.35 (3H, s); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 173.4,

160.9, 133.3, 132.6, 132.3, 131.9, 131.5, 129.6, 129.1, 124.0, 123.6, 123.3, 120.7, 118.1, 52.0, 29.0; **HRMS (ESI):** Calcd for $C_{20}H_{15}Br_2NNaO_3$ $[M+Na]^+$ 497.9311, Found: 497.9314; **IR (cm^{-1}):** ν 2949, 1757, 1705, 761, 648.



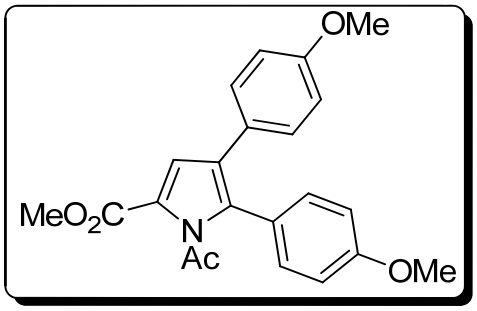
dimethyl 4,4'-(1-acetyl-5-(methoxycarbonyl)-1*H*-pyrrole-2,3-diyl)dibenzoate (3ae).

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20 to 1/15) as a a white solid in 90% yield (125 mg) from **1a** (0.30 mmol, 42.9 mg, 1.0 equiv.) following the general procedure A. R_f = .30 (10:1 Hexanes/EtOAc); m.p.: 101-104 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.04 (2H, d, *J* = 8.4 Hz), 7.87 (2H, d, *J* = 8.4 Hz), 7.36 (2H, d, *J* = 8.4 Hz), 7.21 (1H, br s), 7.15 (2H, d, *J* = 8.4 Hz), 4.39 (2H, q, *J* = 7.1 Hz), 4.34 (2H, q, *J* = 7.1 Hz), 3.90 (3H, s), 2.36 (3H, s), 1.40 (3H, t, *J* = 7.1 Hz), 1.36 (3H, t, *J* =7.1 Hz); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 173.2, 166.1, 165.7, 160.7, 138.1, 134.6, 133.8, 130.8, 130.5, 129.7, 129.5, 128.4, 127.7, 124.3, 123.6, 118.1, 61.1, 60.7, 51.9, 28.8, 14.1 (one signal missing due to overlap); **HRMS (ESI):** Calcd for $C_{26}H_{25}NNaO_7$ $[M+Na]^+$ 486.1523, Found: 486.1524; **IR (cm^{-1}):** ν 2984, 1757, 1712, 760, 705.



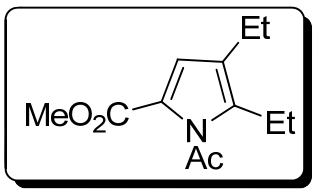
methyl 1-acetyl-4,5-di-p-tolyl-1*H*-pyrrole-2-carboxylate (3af).

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20 to 1/15) as a clear oil in 94% yield (98 mg) from **1a** (0.30 mmol, 42.9 mg, 1.0 equiv.) following the general procedure A. R_f = .49 (10:1 Hexanes/EtOAc); **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.19-7.15 (5H, m), 7.05-7.00 (5H, m), 3.87 (3H, s), 2.37 (3H, s), 2.30 (3H, s), 2.29 (3H, s); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 174.0, 161.1, 138.7, 135.9, 134.5, 131.0, 130.4, 129.2, 128.9, 127.8, 127.7, 124.6, 122.6, 118.3, 51.7, 28.8, 21.3, 21.0; **HRMS (ESI):** Calcd for $C_{22}H_{21}NNaO_3$ $[M+Na]^+$ 370.1414, Found: 370.1419; **IR (cm^{-1}):** ν 2946, 1752, 1704, 762, 731.



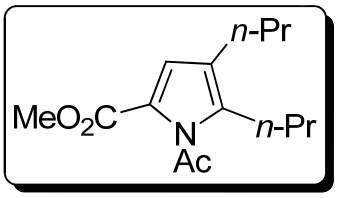
methyl 1-acetyl-4,5-bis(4-methoxyphenyl)-1*H*-pyrrole-2-carboxylate (3ag).

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/15 to 1/5) as a clear oil in 75% yield (85 mg) from **1a** (0.30 mmol, 42.9 mg, 1.0 equiv.) following the general procedure A. R_f = .25 (10:1 Hexanes/EtOAc); **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.22 (2H, d, *J* = 8.8 Hz), 7.12 (1H, br s), 7.06 (2H, d, *J* = 8.9 Hz), 6.88 (2H, d, *J* = 8.8 Hz), 6.75 (2H, d, *J* = 8.8 Hz), 3.87 (3H, s), 3.83 (3H, s), 3.76 (3H, s), 2.30 (3H, s); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 174.0, 161.0, 159.8, 158.1, 134.1, 132.0, 128.9, 126.4, 124.3, 122.7, 122.4, 118.2, 113.9, 113.6, 55.1, 55.0, 51.7, 28.8; **HRMS (ESI):** Calcd for $C_{22}H_{21}NNaO_5$ $[M+Na]^+$ 402.1312, Found: 402.1309; **IR (cm^{-1}):** ν 2955, 1753, 1705, 834, 544.



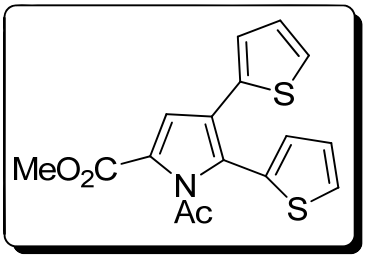
methyl 1-acetyl-4,5-diethyl-1*H*-pyrrole-2-carboxylate (3ah).

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/30 to 1/20) as a clear oil in 72% yield (48 mg) from **1a** (0.30 mmol, 42.9 mg, 1.0 equiv.) following the general procedure A. R_f = .65 (10:1 Hexanes/EtOAc); **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 6.86 (1H, br s), 3.81 (3H, s), 2.63 (2H, q, *J* = 7.6 Hz), 2.52 (3H, s), 2.39 (2H, q, *J* = 7.6 Hz), 1.16 (3H, t, *J* = 7.6 Hz), 1.13 (3H, t, *J* = 7.5 Hz); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 173.9, 161.0, 139.4, 124.4, 121.4, 121.0, 51.5, 28.4, 18.43, 18.36, 14.9, 14.7; **HRMS (ESI):** Calcd for $C_{12}H_{17}NNaO_3$ $[M+Na]^+$ 246.1101, Found: 246.1103; **IR (cm^{-1}):** ν 2969, 1742, 1483, 763, 677.



methyl 1-acetyl-4,5-dipropyl-1*H*-pyrrole-2-carboxylate (3ai).[4]

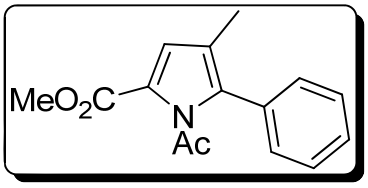
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/30 to 1/20) as a clear oil in 62% yield (47 mg) from **1a** (0.30 mmol, 42.9 mg, 1.0 equiv.) following the general procedure A. R_f = .65 (10:1 Hexanes/EtOAc); **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 6.83 (1H, br s), 3.81 (3H, s), 2.58 (2H, t, *J* = 7.7 Hz), 2.51 (3H, s), 2.32 (2H, t, *J* = 7.6 Hz), 1.60-1.47 (4H, m), 0.94 (3H, t, *J* = 7.4 Hz), 0.92 (3H, t, *J* = 7.4 Hz); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 174.0, 161.1, 138.4, 123.3, 121.5, 121.4, 51.5, 28.5, 27.4, 27.0, 23.6, 13.9 (two signals missing due to overlap); **MS (EI):** Calcd for $C_{14}H_{21}NO_3$ $[M^+]$ 251.15, Found: 251.



methyl 1-acetyl-4,5-di(thiophen-2-yl)-1*H*-pyrrole-2-carboxylate (3aj)

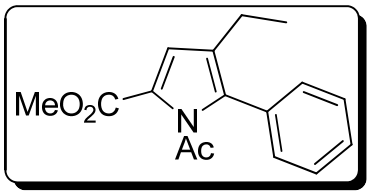
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/30 to 1/20) as a white solid in 65% yield (64 mg) from **1a** (0.30 mmol, 42.9 mg, 1.0 equiv.) following the general procedure A. R_f = .65 (10:1 Hexanes/EtOAc); m.p.: 101-103 °C;

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52 (1H, dd, *J* = 5.0, 0.8 Hz), 7.18 (1H, dd, *J* = 3.4, 0.8 Hz), 7.16 (1H, br s), 7.14-7.12 (2H, m), 6.93-6.91 (1H, m), 6.88 (1H, dd, *J* = 3.5, 0.8 Hz), 3.89 (3H, s), 2.37 (3H, s); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 172.9, 160.9, 135.6, 131.8, 129.6, 129.2, 127.4, 127.0, 125.8, 124.5, 124.1, 121.4, 117.1, 52.1, 28.4 (one signal missing due to overlap); **HRMS (ESI):** Calcd for $C_{16}H_{13}NNaO_3S_2$ $[M+Na]^+$ 354.0229, Found: 354.0231; **IR (cm^{-1}):** ν 2944, 1757, 1245, 755, 718.



methyl 1-acetyl-4-methyl-5-phenyl-1*H*-pyrrole-2-carboxylate (3ak).[4]

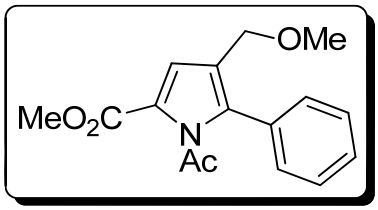
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/30 to 1/20) as a white solid in 93% yield (72 mg) from **1a** (0.30 mmol, 42.9 mg, 1.0 equiv.) following the general procedure A. R_f = .60 (10:1 Hexanes/EtOAc); **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.45-7.38 (3H, m), 7.30-7.28 (2H, m), 6.86 (1H, br s), 3.84 (3H, s), 2.27 (3H, s), 1.99 (3H, s); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 173.5, 161.1, 135.6, 131.0, 129.8, 128.40, 128.37, 122.5, 120.4, 119.5, 51.7, 28.4, 11.1; **MS (EI):** Calcd for $C_{15}H_{15}NO_3$ $[M^+]$ 257.11, Found: 257.



methyl 1-acetyl-4-ethyl-5-phenyl-1*H*-pyrrole-2-carboxylate (3al).[5]

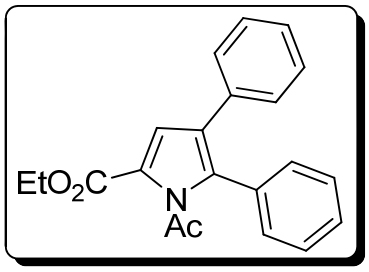
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/30 to 1/20) as a clear oil in 74% yield (60 mg) from **1a** (0.30 mmol, 42.9 mg, 1.0 equiv.) following the general procedure A. R_f = .60 (10:1 Hexanes/EtOAc); **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.43-7.39 (3H, m), 7.30-7.28 (2H, m), 6.92 (1H, br s), 3.84 (3H, s), 2.34 (2H, q, *J* = 7.6 Hz), 2.26 (3H, s), 1.11 (3H, t, *J* = 7.6 Hz); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 173.5, 161.2, 135.1, 131.0, 130.0, 128.5, 128.4, 126.4, 122.8, 118.9, 51.7, 28.5, 18.7, 15.1; **MS (EI):** Calcd

for $C_{16}H_{17}NO_3$ [M^+] 271.12, Found: 271.



methyl 1-acetyl-4-(2-methoxyethyl)-5-phenyl-1*H*-pyrrole-2-carboxylate (3am).

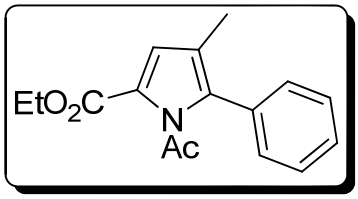
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20 to 1/10) as a clear oil in 68% yield (59 mg) from **1a** (0.30 mmol, 42.9 mg, 1.0 equiv.) following the general procedure A. R_f = .30 (10:1 Hexanes/EtOAc); **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.44-7.41 (3H, m), 7.38-7.35 (2H, m), 7.06 (1H, br s), 4.15 (2H, s), 3.85 (3H, s), 3.31 (3H, s), 2.28 (3H, s); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 173.6, 161.0, 137.0, 129.9, 128.8, 128.4, 123.0, 120.8, 119.5, 66.2, 57.7, 51.8, 28.5 (one signal missing due to overlap); **HRMS (ESI):** Calcd for $C_{16}H_{17}NNaO_4$ [M+Na]$^+$ 310.1050, Found: 310.1047; **IR (cm^{-1}):** ν 2953, 1761, 1716, 773, 702.



ethyl 1-acetyl-4,5-diphenyl-1*H*-pyrrole-2-carboxylate (3ba).

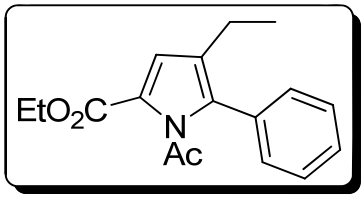
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20 to 1/15) as an off-white solid in 85% yield (85 mg) from **1b** (0.30 mmol, 47.1 mg, 1.0 equiv.) following the general procedure A. R_f = .40 (10:1 Hexanes/EtOAc); m.p.: 75-77 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.39-7.33 (3H, m), 7.32-7.29 (2H, m), 7.22-7.17 (4H, m), 7.16-7.12 (2H, m), 4.35 (2H, q, *J* = 7.1 Hz), 2.31 (3H, s), 1.38 (3H, t, *J* = 7.1 Hz); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 173.8, 160.6, 134.4, 133.9, 130.7, 130.6, 128.8, 128.5, 128.2, 128.0,

126.3, 124.7, 123.3, 118.2, 60.8, 28.9, 14.2; **HRMS (ESI):** Calcd for $C_{21}H_{19}NNaO_3$ $[M+Na]^+$ 356.1257, Found: 356.1255; **IR (cm^{-1}):** ν 2980, 1757, 1699, 761, 697.



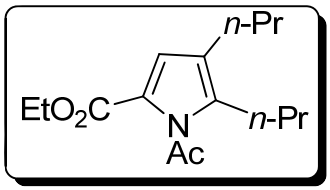
ethyl 1-acetyl-4-methyl-5-phenyl-1*H*-pyrrole-2-carboxylate (3bk).

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/30 to 1/20) as an off-white solid in 70% yield (57 mg) from **1b** (0.30 mmol, 47.1 mg, 1.0 equiv.) following the general procedure A. R_f = .60 (10:1 Hexanes/EtOAc); **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.44-7.38 (3H, m), 7.30-7.27 (2H, m), 6.86 (1H, br s), 4.30 (2H, q, *J* = 7.1 Hz), 2.27 (3H, s), 1.99 (3H, s), 1.35 (3H, t, *J* = 7.1 Hz); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 173.6, 160.8, 135.5, 131.1, 129.9, 128.41, 128.36, 123.0, 120.3, 119.5, 60.6, 28.5, 14.2, 11.1; **HRMS (ESI):** Calcd for $C_{16}H_{17}NNaO_3$ $[M+Na]^+$ 294.1101, Found: 294.1102; **IR (cm^{-1}):** ν 2981, 1750, 1705, 765, 699.



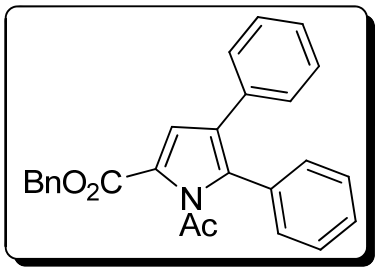
ethyl 1-acetyl-4-ethyl-5-phenyl-1*H*-pyrrole-2-carboxylate (3bl).

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/30 to 1/20) as an off-white solid in 69% yield (59 mg) from **1b** (0.30 mmol, 47.1 mg, 1.0 equiv.) following the general procedure A. R_f = .60 (10:1 Hexanes/EtOAc); **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.42-7.39 (3H, m), 7.29-7.27 (2H, m), 6.92 (1H, br s), 4.31 (2H, q, *J* = 7.1 Hz), 2.34 (2H, q, *J* = 7.6 Hz), 2.26 (3H, s), 1.36 (3H, t, *J* = 7.1 Hz), 1.11 (3H, t, *J* = 7.6 Hz); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 173.5, 160.8, 134.9, 131.1, 130.0, 128.42, 128.38, 126.4, 123.2, 118.7, 60.7, 28.5, 18.7, 15.1, 14.2; **HRMS (ESI):** Calcd for $C_{17}H_{19}NNaO_3$ $[M+Na]^+$ 308.1257, Found: 308.1255; **IR (cm^{-1}):** ν 2973, 1748, 1716, 762, 701.



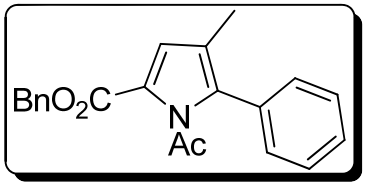
ethyl 1-acetyl-4,5-dipropyl-1*H*-pyrrole-2-carboxylate (3bi).

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/30 to 1/20) as a clear oil in 54% yield (43 mg) from **1b** (0.30 mmol, 47.1 mg, 1.0 equiv.) following the general procedure A. R_f = .61 (10:1 Hexanes/EtOAc); **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 6.83 (1H, br s), 4.27 (2H, q, *J* = 7.1 Hz), 2.58 (2H, t, *J* = 7.7 Hz), 2.51 (3H, s), 2.32 (2H, t, *J* = 7.6 Hz), 1.59-1.49 (4H, m), 1.34 (3H, t, *J* = 7.1 Hz), 0.95 (3H, t, *J* = 7.3 Hz), 0.92 (3H, t, *J* = 7.3 Hz); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 174.1, 160.7, 138.2, 123.3, 121.9, 121.2, 60.5, 28.6, 27.4, 27.0, 23.61, 23.58, 14.3, 13.9 (one signal missing due to overlap); **HRMS (ESI):** Calcd for $C_{15}H_{23}NNaO_3$ $[M+Na]^+$ 288.1570, Found: 288.1572; **IR (cm^{-1}):** ν 2962, 1761, 1716, 773, 702.



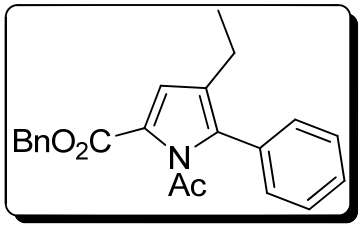
benzyl 1-acetyl-4,5-diphenyl-1*H*-pyrrole-2-carboxylate (3ca).

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20 to 1/15) as an off-white solid in 75% yield (89 mg) from **1c** (0.30 mmol, 65.8 mg, 1.0 equiv.) following the general procedure A. R_f = .50 (10:1 Hexanes/EtOAc); m.p.: 100-105 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.45-7.33 (8H, m), 7.31-7.28 (2H, m), 7.22 (1H, br s), 7.19-7.15 (3H, m), 7.13-7.11 (2H, m), 5.33 (2H, s), 2.28 (3H, s); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 173.8, 160.4, 135.8, 134.7, 133.9, 130.7, 130.6, 128.9, 128.6, 128.28, 128.25, 128.22, 128.20, 128.0, 126.4, 124,9, 122.9, 118.7, 66.5, 28.9; **HRMS (ESI):** Calcd for $C_{26}H_{21}NNaO_3$ $[M+Na]^+$ 418.1414, Found: 418.1413; **IR (cm^{-1}):** ν 2957, 1753, 1702, 748, 696.



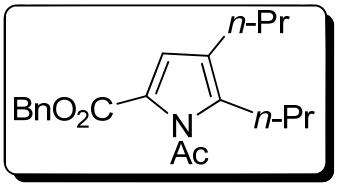
benzyl 1-acetyl-4-methyl-5-phenyl-1*H*-pyrrole-2-carboxylate (3ck).

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20 to 1/15) as a clear oil in 61% yield (61 mg) from **1c** (0.30 mmol, 65.8 mg, 1.0 equiv.) following the general procedure A. R_f = .60 (10:1 Hexanes/EtOAc); **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.43-7.33 (8H, m), 7.29-7.27 (2H, m), 6.91 (1H, br s), 5.29 (2H, s), 2.25 (3H, s), 1.98 (3H, s); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 173.5, 160.5, 135.92, 135.87, 131.0, 129.8, 128.5, 128.4, 128.2, 128.1, 122.5, 120.8, 119.6, 66.3, 28.5, 11.1 (one signal missing due to overlap); **HRMS (ESI):** Calcd for $C_{21}H_{19}NNaO_3$ $[M+Na]^+$ 356.1257, Found: 356.1259; **IR (cm^{-1}):** ν 2925, 1753, 1706, 761, 697.



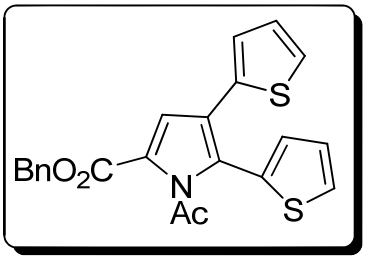
benzyl 1-acetyl-4-ethyl-5-phenyl-1*H*-pyrrole-2-carboxylate (3cl).

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20 to 1/15) as a clear oil in 84% yield (87 mg) from **1c** (0.30 mmol, 65.8 mg, 1.0 equiv.) following the general procedure A. R_f = .62 (10:1 Hexanes/EtOAc); **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.44-7.34 (8H, m), 7.29-7.27 (2H, m), 6.96 (1H, br s), 5.29 (2H, s), 2.33 (2H, q, *J* = 7.6 Hz), 2.24 (3H, s), 1.09 (3H, t, *J* = 7.6 Hz); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 173.4, 160.4, 135.9, 135.2, 130.9, 129.9, 128.5, 128.3, 128.1, 126.4, 122.7, 119.1, 66.3, 28.4, 18.6, 15.1 (two signals missing due to overlap); **HRMS (ESI):** Calcd for $C_{22}H_{21}NNaO_3$ $[M+Na]^+$ 370.1414, Found: 370.1412; **IR (cm^{-1}):** ν 2966, 1751, 1705, 758, 699.



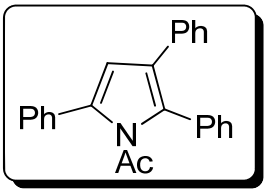
benzyl 1-acetyl-4,5-dipropyl-1*H*-pyrrole-2-carboxylate (3ci).

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20 to 1/15) as a clear oil in 54% yield (53 mg) from **1c** (0.30 mmol, 65.8 mg, 1.0 equiv.) following the general procedure A. R_f = .65 (10:1 Hexanes/EtOAc); **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.42-7.33 (5H, m), 6.87 (1H, br s), 5.26 (2H, s), 2.58 (2H, t, *J* = 7.7 Hz), 2.49 (3H, s), 2.32 (2H, t, *J* =7.7 Hz), 1.57-1.49 (4H, m), 0.95-0.90 (6H, m); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 174.0, 160.4, 138.6, 136.0, 128.5, 128.2, 128.1, 123.4, 121.6, 121.5, 66.1, 28.6, 27.4, 27.0, 23.61, 23.57, 13.9 (one signal missing due to overlap); **HRMS (ESI):** Calcd for $C_{20}H_{25}NNaO_3$ $[M+H]^+$ 350.1727, Found: 350.1726; **IR (cm^{-1}):** ν 2961, 1742, 1702, 756, 699.



benzyl 1-acetyl-4,5-di(thiophen-2-yl)-1*H*-pyrrole-2-carboxylate (3cj).

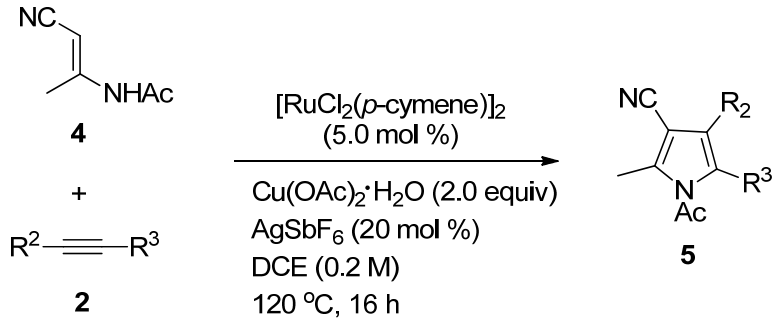
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20 to 1/15) as a white solid in 75% yield (92 mg) from **1c** (0.30 mmol, 65.8 mg, 1.0 equiv.) following the general procedure A. R_f = .65 (10:1 Hexanes/EtOAc); m.p.: 103-105 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.52 (1H, dd, *J* = 5.0, 1.0 Hz), 7.45-7.36 (5H, m), 7.19 (1H, br s), 7.17 (1H, dd, *J* = 3.5, 1.1 Hz), 7.13-7.11 (2H, m), 6.92-6.90 (1H, m), 6.88 (1H, *J* = 3.5, 1.0 Hz), 5.33 (2H, s), 2.35 (3H, s); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 172.8, 160.1, 135.50, 135.45, 131.8, 129.5, 129.2, 128.6, 128.4, 128.2, 127.4, 127.0, 125.9, 124.6, 124.5, 124.0, 121.3, 117.3, 66.7, 28.4; **HRMS (ESI):** Calcd for $C_{22}H_{17}NNaO_3S_2$ $[M+Na]^+$ 430.0542, Found: 430.0544; **IR (cm^{-1}):** ν 2954, 1762, 1248, 767, 698.



1-(2,3,5-triphenyl-1*H*-pyrrol-1-yl)ethanone (3da).[6]

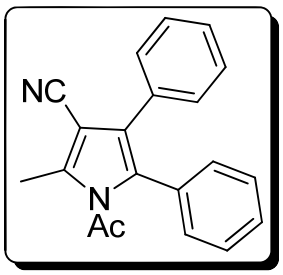
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20 to 1/15) as a white solid in 30% yield (30 mg) from **1d** (0.30 mmol, 48.9 mg, 1.0 equiv.) following the general procedure A, but adding $AgSbF_6$ (21 mg, 0.060 mmol, 20.0 mmol %) and using CH_3CN as solvent. R_f = .65 (10:1 Hexanes/EtOAc); m.p.: 123-128 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.45-7.40 (4H, m), 7.36 (6H, br s), 7.22-7.15 (5H, m), 6.54 (1H, s), 2.03 (3H, s); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 172.8, 134.80, 134.76, 133.4, 132.8, 131.0, 130.9, 128.5, 128.4, 128.37, 128.14, 128.06, 127.6, 126.2, 125.5, 113.6, 28.6 (one signal missing due to overlap); **MS (EI):** Calcd for $C_{24}H_{19}NO$ [M^+] 337.14, Found: 337.

General procedure B: Ruthenium catalyzed pentasubstituted pyrroles (5) synthesis



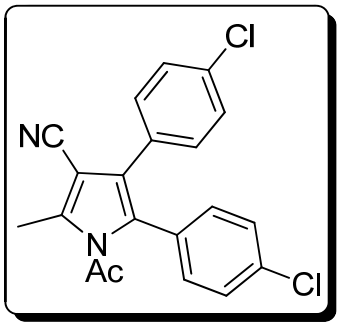
A mixture of the enamide (**4**) (0.39 mmol, 1.3 equiv.), the alkyne (**2**) (if solid) (0.30 mmol, 1.0 equiv.), $[RuCl_2(p\text{-cymene})]_2$ (9.2 mg, 0.015 mmol, 5.0 mol %), $AgSbF_6$ (21 mg, 0.060 mmol, 20.0 mmol %) and $Cu(OAc)_2 \cdot H_2O$ (120.0 mg, 0.6 mmol, 2.0 equiv.) were weighted in a Schlenk tube equipped with a stir bar. Dry DCE (1.5 mL) was added (followed immediately by the alkyne if it is a liquid) and the mixture was stirred at 120 °C for 16 hours under Ar atmosphere. Afterwards, it was diluted with CH_2Cl_2 and transferred to a round bottom flask. Silica was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel.

Analytical data of Pyrroles 5



1-acetyl-2-methyl-4,5-diphenyl-1*H*-pyrrole-3-carbonitrile (5a).[2]

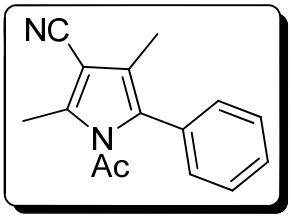
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20 to 1/10) as a white solid in 55% yield (49 mg) from **4** (0.39mmol, 48.3 mg, 1.3 equiv.) following the general procedure B. R_f = .25 (10:1 Hexanes/EtOAc); **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.39-7.36 (3H, m), 7.28-7.23 (5H, m), 7.21-7.18 (2H,m), 2.66 (3H, s), 1,97 (3H, s); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 172.2, 140.9, 131.5, 131.4, 130.2, 129.7, 129.1, 129.0, 128.9, 128.3, 127.4, 125.4, 115.6, 97.2, 28.0, 14.2; **MS (EI):** Calcd for $C_{20}H_{16}N_2O$ [M^+] 300.13, Found: 300.



1-acetyl-4,5-bis(4-chlorophenyl)-2-methyl-1*H*-pyrrole-3-carbonitrile (5c).

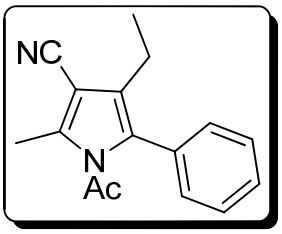
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20 to 1/10) as a white solid in 57% yield (63 mg) from **4** (0.39mmol, 48.3 mg, 1.3 equiv.) following the general procedure B. R_f = .23 (10:1 Hexanes/EtOAc); m.p.: 139-143 °C**;** **^{1}H-NMR ($CDCl_3$, 400 MHz):** δ 7.36 (2H, dd, *J* = 2.0, 6.6 Hz), 7.25 (2H, dd, *J* = 2.0, 6.5 Hz), 7.14 (2H, dd, *J* = 2.0, 6.6 Hz), 7.08 (2H, dd, *J* = 2.0, 6.6 Hz), 2.62 (3H, s), 2.00 (3H, s); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 171.7, 141.2, 135.3, 133.7, 131.3, 130.4, 129.7, 129.5, 128.8, 128.5, 124.8, 115.1, 97.2, 28.1, 14.2 (one signal missing due to overlap); **HRMS (ESI):** Calcd for

$C_{20}H_{14}Cl_2N_2NaO$ $[M+Na]^+$ 391.0375, Found: 391.0372; **IR (cm^{-1}):** ν 2925, 1749, 1577, 734, 692.



1-acetyl-2,4-dimethyl-5-phenyl-1*H*-pyrrole-3-carbonitrile (5k).

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20 to 1/10) as a white solid in 58% yield (41 mg) from **4** (0.39mmol, 48.3 mg, 1.3 equiv.) following the general procedure B. R_f = .30 (10:1 Hexanes/EtOAc); m.p.: 106-108 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.48-7.40 (3H, m), 7.27-7.24 (2H, m), 2.57 (3H, s), 2.05 (3H, s), 1.92 (3H, s); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 171.9, 140.3, 132.0, 129.9, 129.6, 129.0, 128.5, 121.3, 115.5, 98.3, 27.7, 14.4, 10.2; **HRMS (ESI):** Calcd for $C_{15}H_{14}N_2NaO$ $[M+Na]^+$ 261.0998, Found: 261.0997; **IR (cm^{-1}):** ν 2924, 1736, 1376, 762, 731.

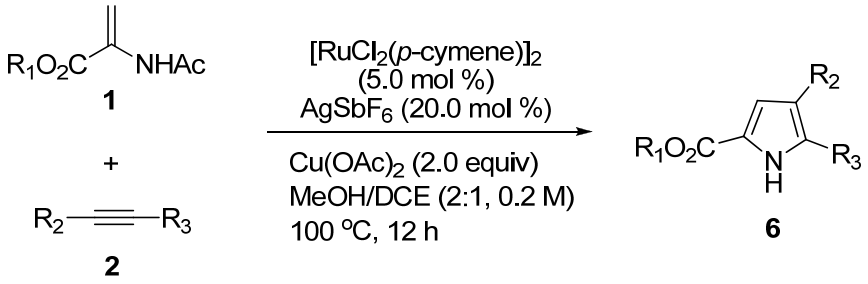


1-acetyl-4-ethyl-2-methyl-5-phenyl-1*H*-pyrrole-3-carbonitrile (5l).[2]

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20 to 1/10) as a white solid in 61% yield (46 mg) from **4** (0.39mmol, 48.3 mg, 1.3 equiv.) following the general procedure B. R_f = .30 (10:1 Hexanes/EtOAc); **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.48-7.42 (3H, m), 7.27-7.25 (2H, m), 2.58 (3H, s), 2.41 (2H, q, *J* = 7.6 Hz), 1.90 (3H, s), 1.14 (3H, t, *J* = 7.6 Hz); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 171.8, 140.8, 131.9, 129.9, 129.8, 129.4, 128.9, 128.7, 127.6, 115.5, 97.1, 27.7, 18.2, 15.0, 14.4; **MS (EI):** Calcd for $C_{16}H_{16}N_2O$ $[M^+]$ 252.13, Found: 252.

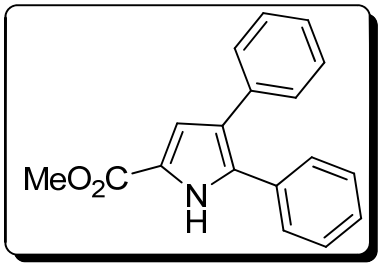
Preparation and Characterization of Products 6

General procedure C: Ruthenium catalyzed trisubstituted pyrroles (6) synthesis



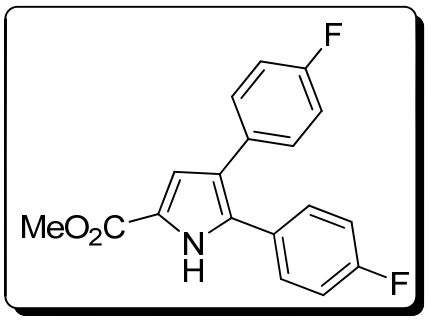
A mixture of the enamide (**1**) (0.30 mmol, 1.0 equiv.), the alkyne (**2**) (if solid) (0.33 mmol, 1.1 equiv.), $[RuCl_2(p\text{-cymene})]_2$ (9.2 mg, 0.015 mmol, 5.0 mol %), $AgSbF_6$ (0.060 mmol, 20.0 mol%) and $Cu(OAc)_2 \cdot H_2O$ (30.0 mg, 0.50 mmol, 0.5 equiv.) were weighted in a Schlenk tube equipped with a stir bar. A mixture solution of dry MeOH and DCE (MeOH/DCE, 2:1, 1.5 mL) was added (followed immediately by the alkyne if it is a liquid) and the mixture was stirred at 100 °C for 12 hours under Ar atmosphere. Afterwards, it was diluted with CH_2Cl_2 and transferred to a round bottom flask. Silica was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel.

Analytical data of trisubstituted pyrroles 6



methyl 4,5-diphenyl-1*H*-pyrrole-2-carboxylate (6aa).[5]

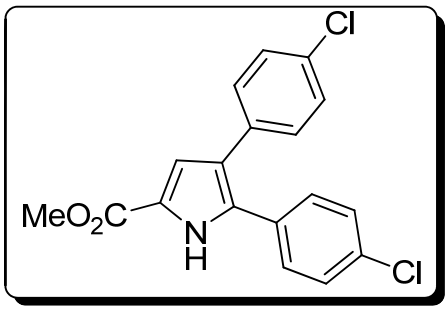
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20 to 1/15) as a white solid in 91% yield (76 mg) from **1a** (0.30mmol, 42.9 mg, 1.0 equiv.) following the general procedure C. R_f = .40 (10:1 Hexanes/EtOAc); **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 9.22 (1H, br s), 7.39-7.26 (10H, m), 7.25-7.21 (1H, m), 7.07 (1H, d, *J* = 2.7 Hz), 3.88 (3H, s); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 161.8, 135.4, 133.5, 131.9, 128.6, 128.44, 128.35, 128.0, 127.9, 126.3, 124.1, 122.0, 116.8, 51.6; **MS (EI):** Calcd for $C_{18}H_{15}NO_2$ [M^+] 277.11, Found: 277.



methyl 4,5-bis(4-fluorophenyl)-1*H*-pyrrole-2-carboxylate (6ab).

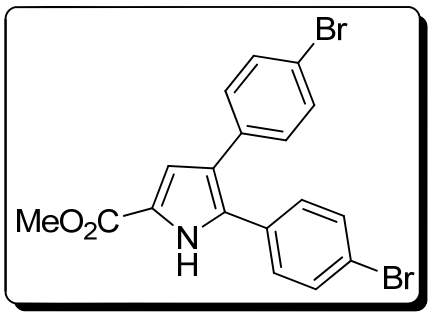
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20 to 1/15) as a clear oil in 89% yield (83 mg) from **1a** (0.30mmol, 42.9 mg, 1.0 equiv.) following the general procedure C. R_f = .39 (10:1 Hexanes/EtOAc); **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 9.13 (1H, br s), 7.33-7.30 (2H, m), 7.24-7.21 (2H, m), 7.06-7.02 (2H, m), 7.01-6.96 (3H, m), 3.88 (3H, s); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 162.5 (d, $J_{C\text{-}F}$ = 248.4 Hz), 161.9, 161.7 (d, $J_{C\text{-}F}$ = 245.6 Hz), 132.6, 131.2 (d, $J_{C\text{-}F}$ = 3.3 Hz), 130.0, 129.9 (d, $J_{C\text{-}F}$ = 1.3 Hz), 127.9 (d, $J_{C\text{-}F}$ = 3.2 Hz), 123.1, 122.1, 116.8, 115.8 (d, $J_{C\text{-}F}$ = 21.7 Hz), 115.4 (d, $J_{C\text{-}F}$ = 21.2 Hz), 51.7; **^{19}F NMR ($CDCl_3$, 376 MHz):** δ -112.93 (s), -116.12 (s); **HRMS (ESI):** Calcd for $C_{18}H_{12}F_2NO_2$

[M-H]$^-$ 312.0842, Found: 312.0843; **IR (cm^{-1}):** ν 3302, 1689, 1453, 767, 523.



methyl 4,5-bis(4-chlorophenyl)-1*H*-pyrrole-2-carboxylate (6ac).

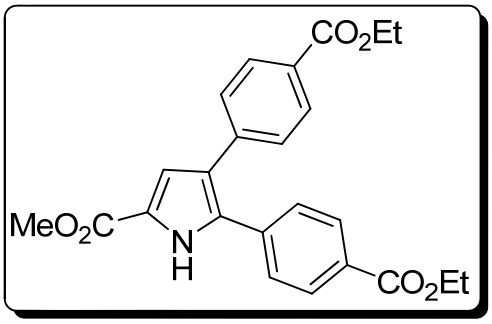
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20 to 1/15) as a clear oil in 80% yield (78 mg) from **1a** (0.30mmol, 42.9 mg, 1.0 equiv.) following the general procedure C. R_f = .40 (10:1 Hexanes/EtOAc); **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 9.09 (1H, br s), 7.34-7.32 (2H, m), 7.29-7.27 (2H, m), 7.27-7.25 (2H, m), 7.21-7.19 (2H, m), 7.01 (1H, d, *J* = 2.7 Hz), 3.89 (3H, s); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 161.9, 134.0, 133.6, 132.5, 132.3, 130.0, 129.6, 129.4, 128.9, 128.6, 123.2, 122.4, 116.8, 51.7; **HRMS (ESI):** Calcd for $C_{18}H_{12}Cl_2NO_2$ [M-H]$^-$ 344.0251, Found: 344.0250; **IR (cm^{-1}):** ν 3302, 2981, 1757, 1699, 761.



methyl 4,5-bis(4-bromophenyl)-1*H*-pyrrole-2-carboxylate (6ad).

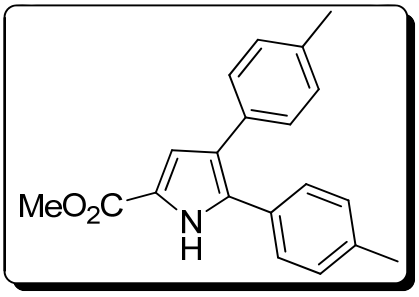
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20 to 1/15) as a white solid in 77% yield (100 mg) from **1a** (0.30mmol, 42.9 mg, 1.0 equiv.) following the general procedure C. R_f = .42 (10:1 Hexanes/EtOAc); m.p.: 222-224 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 9.11 (1H, br s), 7.48 (2H, d, *J* = 8.5 Hz), 7.41 (2H, d, *J* = 8.4 Hz), 7.21 (2H, d, *J* = 8.5 Hz), 7.14 (2H, d, *J* = 8.4 Hz), 7.01 (1H, d, *J* = 2.7 Hz), 3.89 (3H,

s); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 161.7, 134.0, 132.3, 132.0, 131.7, 130.4, 130.0, 129.5, 123.2, 122.6, 122.3, 120.5, 116.7, 51.8; **HRMS (ESI):** Calcd for $C_{18}H_{12}Br_2NO_2$ $[M-H]^-$ 431.9240, Found: 431.9242; **IR (cm^{-1}):** ν 3299, 2948, 1757, 1699, 761.



diethyl 4,4'-(5-(methoxycarbonyl)-1*H*-pyrrole-2,3-diyl)dibenzoate (6ae).

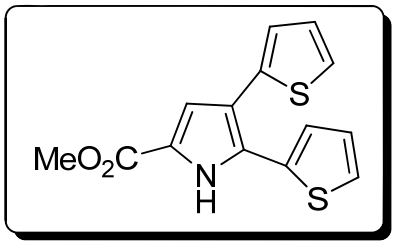
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20 to 1/15) as a white solid in 98% yield (124 mg) from **1a** (0.30mmol, 42.9 mg, 1.0 equiv.) following the general procedure C. R_f = .35 (10:1 Hexanes/EtOAc); m.p.: 161-163 °C ; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 9.37 (1H, br s), 8.01 (2H, d, *J* = 8.4 Hz), 7.96 (2H, d, *J* = 8.4 Hz), 7.42 (2H, d, *J* = 8.4 Hz), 7.35 (2H, d, *J* = 8.4 Hz), 7.09 (1H, d, *J* = 2.6 Hz), 4.41-4.35 (4H, m), 3.89 (3H, s), 1.40 (3H, t, *J* = 7.1 Hz), 1.39 (3H, t, *J* = 7.1 Hz); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 166.4, 166.0, 161.7, 139.7, 135.7, 132.9, 129.81, 129.78, 129.73, 128.4, 128.2, 127.9, 124.1, 123.1, 116.9, 61.0, 60.8, 51.8, 14.23, 14.21; **HRMS (ESI):** Calcd for $C_{24}H_{22}NO_6$ $[M-H]^-$ 420.1453, Found: 420.1454; **IR (cm^{-1}):** ν 3288, 2981, 1757, 1699, 761.



methyl 4,5-di-p-tolyl-1*H*-pyrrole-2-carboxylate (6af).

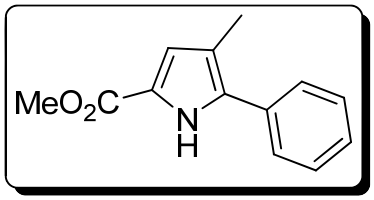
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20 to 1/15) as a white solid in 72% yield (65 mg) from **1a** (0.30mmol, 42.9 mg, 1.0

equiv.) following the general procedure C. R_f = .40 (10:1 Hexanes/EtOAc); m.p.: 185-187 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 9.02 (1H, br s), 7.26 (2H, d, *J* = 8.1 Hz), 7.20 (2H, d, *J* = 8.1 Hz), 7.14 (2H, d, *J* = 7.9 Hz), 7.09 (2H, d, *J* = 8.0 Hz), 7.03 (1H, d, *J* = 2.7 Hz), 3.88 (3H, s), 2.36 (3H, s), 2.34 (3H, s); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 161.9, 137.7, 135.8, 133.6, 132.5, 129.2, 129.0, 128.3, 127.8, 123.7, 121.6, 116.8, 51.5, 21.2, 21.1; **HRMS (ESI):** Calcd for $C_{20}H_{19}NNaO_2$ $[M+Na]^+$ 328.1308, Found: 328.1311; **IR (cm^{-1}):** ν 3317, 3020, 2059, 1691, 765.



methyl 4-ethyl-5-phenyl-1*H*-pyrrole-2-carboxylate (6aj).

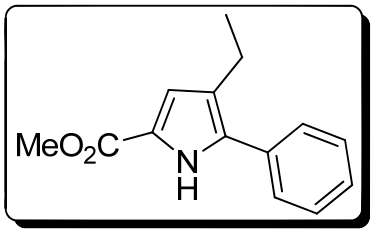
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20 to 1/15) as a off-white solid in 41% yield (36 mg) from **1a** (0.30mmol, 42.9 mg, 1.0 equiv.) following the general procedure C. R_f = .45 (10:1 Hexanes/EtOAc); m.p.: 113-115 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 9.18 (1H, br s), 7.33 (1H. d, *J* = 5.1 Hz), 7.23 (1H, dd, *J* = 5.0, 0.8 Hz), 7.20 (1H, d, *J* = 3.6, 0.6 Hz), 7.06-6.99 (4H, m), 3.88 (3H, s); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 161.4, 136.4, 132.4, 127.5, 127.3, 127.1, 127.0, 126.4, 125.6, 124.7, 122.1, 118.0, 116.9, 51.7; **HRMS (ESI):** Calcd for $C_{14}H_{11}NNaO_2S_2$ $[M+Na]^+$ 312.0123, Found: 312.0121; **IR (cm^{-1}):** ν 3285, 2924, 1684, 770, 704.



methyl 4-methyl-5-phenyl-1*H*-pyrrole-2-carboxylate (6ak).[4]

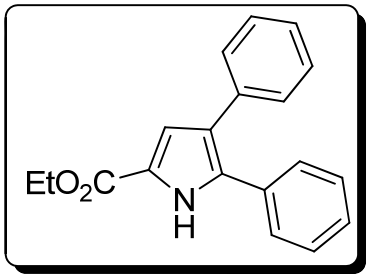
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20 to 1/15) as a clear oil in 87% yield (56 mg) from **1a** (0.30mmol, 42.9 mg, 1.0 equiv.) following the general procedure C. R_f = .44 (10:1 Hexanes/EtOAc); **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.97 (1H, br s), 7.49-7.42 (4H, m), 7.35-7.31 (1H, m), 6.81 (1H, d, *J* = 2.6 Hz),

3.86 (3H, s), 2.26 (3H, s); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 161.8, 133.9, 132.2, 128.7, 127.3, 127.0, 121.0, 118.3, 118.2, 51.4, 12.4; **MS (EI):** Calcd for $C_{13}H_{13}NO_2$ [M^+] 215.09, Found: 215.



methyl 4-ethyl-5-phenyl-1*H*-pyrrole-2-carboxylate (6al).[5]

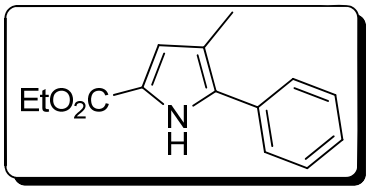
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20 to 1/15) as a clear oil in 66% yield (45 mg) from **1a** (0.30mmol, 42.9 mg, 1.0 equiv.) following the general procedure C. R_f = .45 (10:1 Hexanes/EtOAc); **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.94 (1H, br s), 7.47-7.42 (4H, m), 7.36-7.32 (1H, m), 6.89 (1H, d, *J* = 2.7 Hz), 3.86 (3H, s), 2.64 (2H, q, *J* = 7.5 Hz), 1.23 (3H, t, *J* = 7.6 Hz); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 161.8, 133.4, 132.3, 128.7, 127.5, 127.3, 125.3, 121.3, 116.1, 51.4, 19.5, 15.1; **MS (EI):** Calcd for $C_{14}H_{15}NO_2$ [M^+] 229.27, Found: 229.



ethyl 4,5-diphenyl-1*H*-pyrrole-2-carboxylate (6ba).[7]

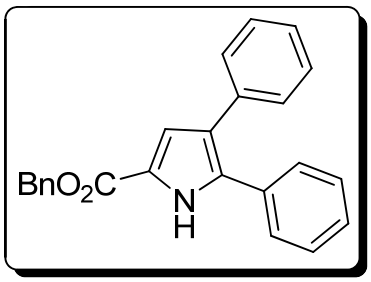
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20 to 1/15) as a white solid in 94% yield (82 mg) from **1b** (0.30mmol, 47.1 mg, 1.0 equiv.) following the general procedure C. R_f = .40 (10:1 Hexanes/EtOAc); m.p.: 140-142 °C**;** **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 9.20 (1H, br s), 7.39-7.37 (2H, m), 7.35-7.28 (7H, m), 7.24-7.21 (1H, m), 7.07 (1H, d, *J* = 2.7 Hz), 4.34 (2H, q, *J* = 7.1 Hz), 1.38 (3H, t, *J* = 7.1 Hz); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 161.5, 135.4, 133.5, 131.9, 128.6, 128.4, 128.3, 128.1, 127.8, 126.2,

124.0, 122.4, 116.7, 60.5, 14.4; **MS (EI):** Calcd for $C_{19}H_{17}NO_2$ [M^+] 291.13, Found: 291.



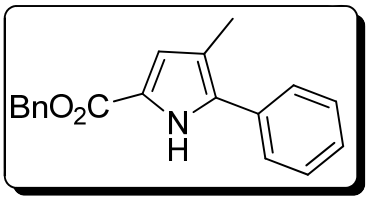
ethyl 4-methyl-5-phenyl-1*H*-pyrrole-2-carboxylate (6bk).[8]

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20 to 1/15) as a white solid in 85% yield (58 mg) from **1b** (0.30mmol, 47.1 mg, 1.0 equiv.) following the general procedure C. R_f = .45 (10:1 Hexanes/EtOAc); m.p.: 104-106 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 9.00 (1H, br s), 7.49-7.42 (4H, m), 7.35-7.31 (1H, m), 6.81 (1H, d, *J* = 2.5 Hz), 4.32 (2H, q, *J* = 7.1 Hz), 2.26 (3H, s), 1.36 (3H, t, *J* = 7.1 Hz); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 161.5, 133.8, 132.3, 128.6, 127.2, 127.1, 121.4, 118.2, 118.0, 60.2, 14.4, 12.4; **MS (EI):** Calcd for $C_{14}H_{15}NO_2$ [M^+] 229.11, Found: 229.



benzyl 4,5-diphenyl-1*H*-pyrrole-2-carboxylate (6ca).

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20 to 1/15) as a white solid in 92% yield (97 mg) from **1c** (0.30mmol, 58.8 mg, 1.0 equiv.) following the general procedure C. R_f = .40 (10:1 Hexanes/EtOAc); m.p.: 171-173 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 9.27 (1H, br s), 7.45-7.36 (7H, m), 7.35-7.28 (7H, m), 7.24-7.21 (1H, m), 7.13 (1H, d, *J* = 2.7 Hz), 5.33 (2H, s), ; **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 161.2, 136.0, 135.3, 133.8, 131.9, 128.6, 128.5, 128.4, 128.3, 128.2, 128.08, 128.06, 127.9, 126.3, 124.1, 122.0, 117.2, 66.1; **HRMS (ESI):** Calcd for $C_{24}H_{19}NNaO_2$ [M+Na]$^+$ 376.1308, Found: 376.1305; **IR (cm^{-1}):** ν 3294, 2953, 1681, 1454, 764.

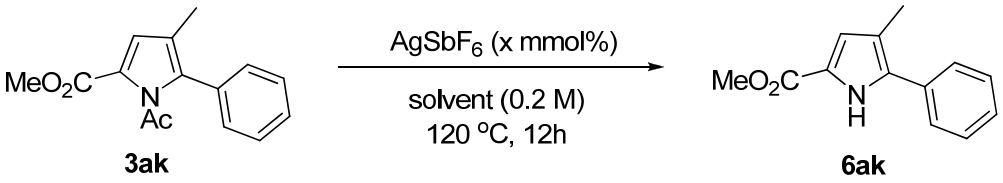


benzyl 4-methyl-5-phenyl-1*H*-pyrrole-2-carboxylate (6ck).

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20 to 1/15) as a white solid in 67% yield (58 mg) from **1c** (0.30mmol, 58.8 mg, 1.0 equiv.) following the general procedure C. R_f = .47 (10:1 Hexanes/EtOAc); m.p.: 141-143 °C**;** **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.96 (1H, br s), 7.49-7.31 (10H, m), 6.86 (1H, d, *J* = 2.6 Hz), 5.32 (2H, s), 2.25 (3H, s); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 161.1, 136.2, 134.1, 132.2, 128.7, 128.5, 128.11, 128.05, 127.4, 127.0, 121.0, 118.5, 118.4, 65.9, 12.4; **HRMS (ESI):** Calcd for $C_{19}H_{17}NNaO_2$ $[M+Na]^+$ 314.1152, Found: 314.1152; **IR (cm^{-1}):** ν 3309, 2951, 1690, 1462, 766.

Mechanistic Experiments

Transformation of pyrroles 3 to decarboxylated pyrroles 6



3ak **6ak**

entry	$AgSbF_6$ (x mmol%)	solvent	yield (%)
1	0.0	MeOH/DCE (2:1)	55
2	20.0	DCE	34
3	20.0	MeOH/DCE (2:1)	98

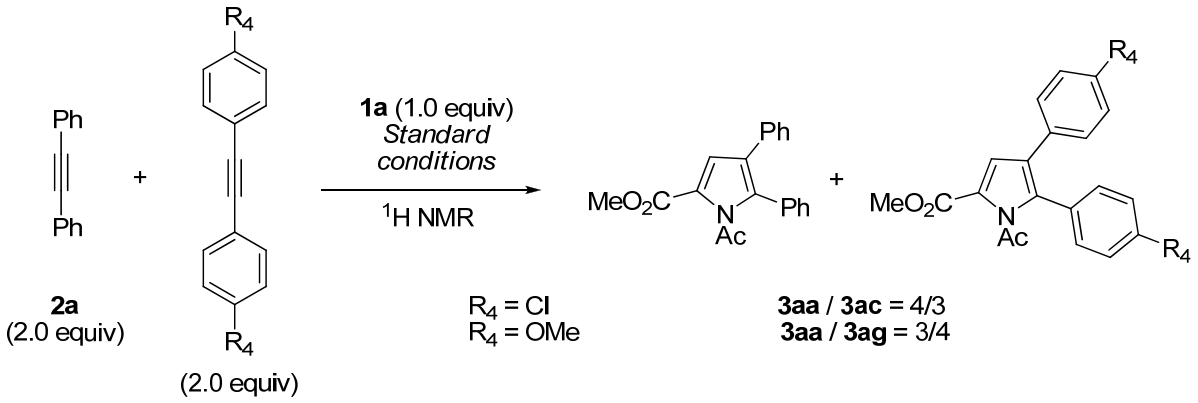
The pyrrole (**3ak**) (0.20 mmol, 1.0 equiv.) and $AgSbF_6$ (14.0 mg, 0.04 mmol, 20 mmol %) were weighted in a Schlenk tube equipped with a stir bar. A mixture solution of dry MeOH and DCE (MeOH/DCE, 2:1, 1.0 mL) was added and the mixture was stirred at 100 °C for 12 hours under Ar atmosphere, which afforded the **6ak** with 98 % yield by column chromatography.

When reaction was operated under the same reaction condition without $AgSbF_6$ only afforded **6ak** in 55 % yield.

When reaction was operated in DCE afforded **6ak** in 34 % yield.

These experiments suggest that both $AgSbF_6$ and MeOH play key factors during pyrrole decarboxylation.

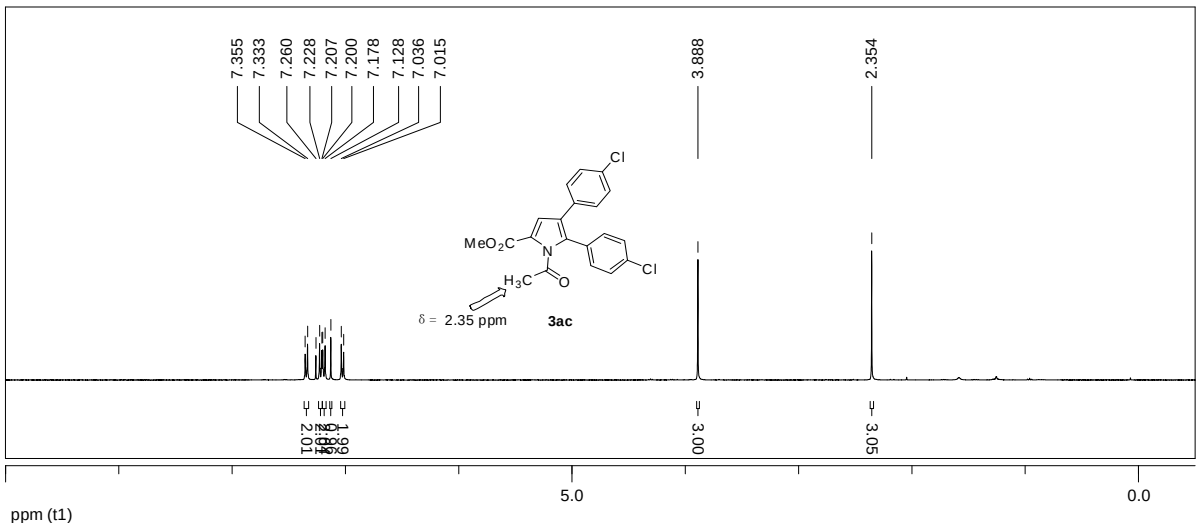
Competition Experiments: with electronically different Alkynes



A mixture of the enamide (**1a**) (28.7 mg, 0.20 mmol, 1.0 equiv.), diphenyl acetylene (**2a**) (71.2 mg, 0.40 mmol, 2.0 equiv.), another alkyne (0.40 mmol, 2.0 equiv.), $[RuCl_2(p\text{-cymene})]_2$ (6.1 mg, 0.010 mmol, 5.0 mol %) and $Cu(OAc)_2 \cdot H_2O$ (20.0 mg, 0.10 mmol, 0.5 equiv.) were weighted in a Schlenk tube equipped with a stir bar. Dry DCE (1.5 mL) was added and the mixture was stirred at 100 °C for 12 hours under Ar atmosphere. Afterwards, it was diluted with CH_2Cl_2 and filtered through a short pad of silica. The solid was washed with CH_2Cl_2, the combined filtrates were concentrated under reduced pressure. The mixture was dissolved in $CDCl_3$ carefully and measured ^1H NMR.

A) Using bis-(4-chlorophenyl)-ethyne (2c) as another alkyne:

Bis-(4-chlorophenyl)-ethyne (**2c**) was added (98.8 mg, 0.4 mmol, 2.0 equiv.) (Figure 1).



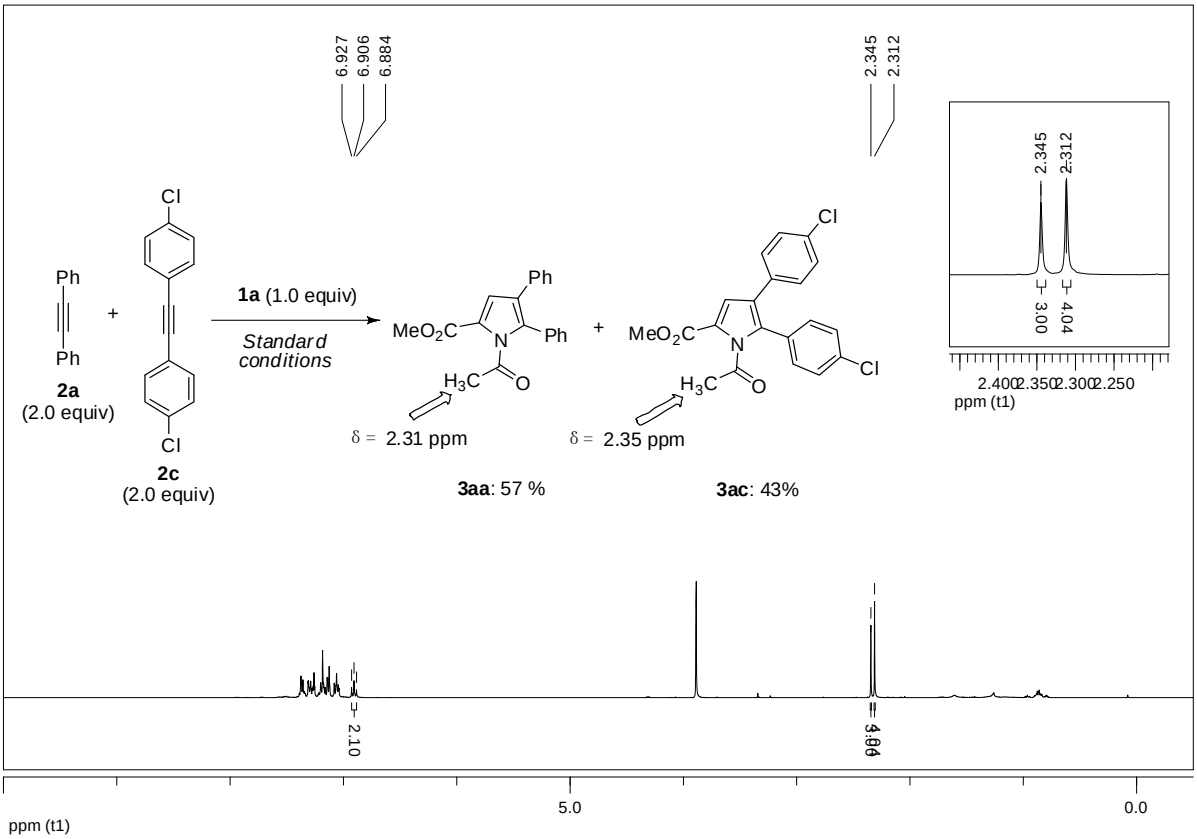
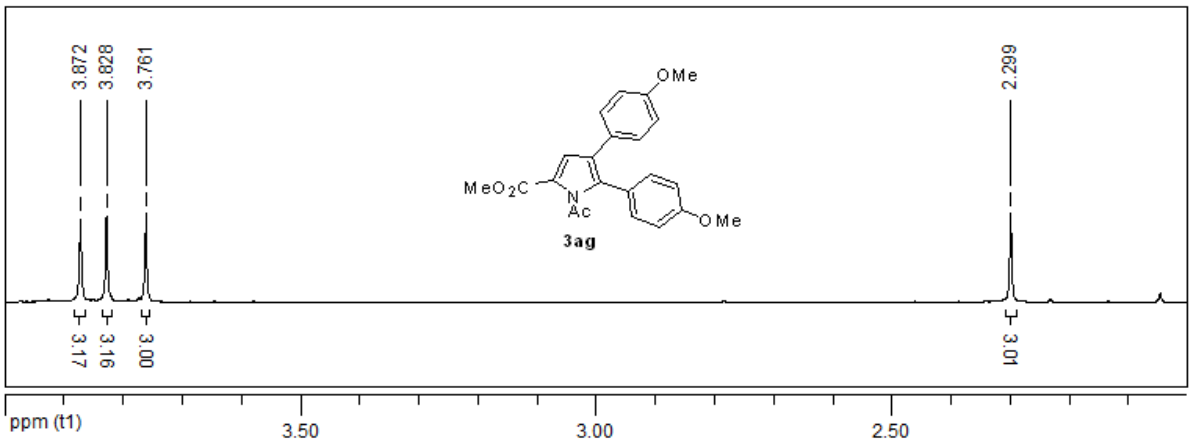


Figure 1: Competition reaction between **2a** and **2b** keeping limiting amount of **1a**

B) Using bis-(4-methoxyphenyl)-ethyne (2g) as another alkyne:

Bis-(4-methoxyphenyl)-ethyne (**2g**) was added (95.2 mg, 0.4 mmol, 2.0 equiv.) (Figure 2).



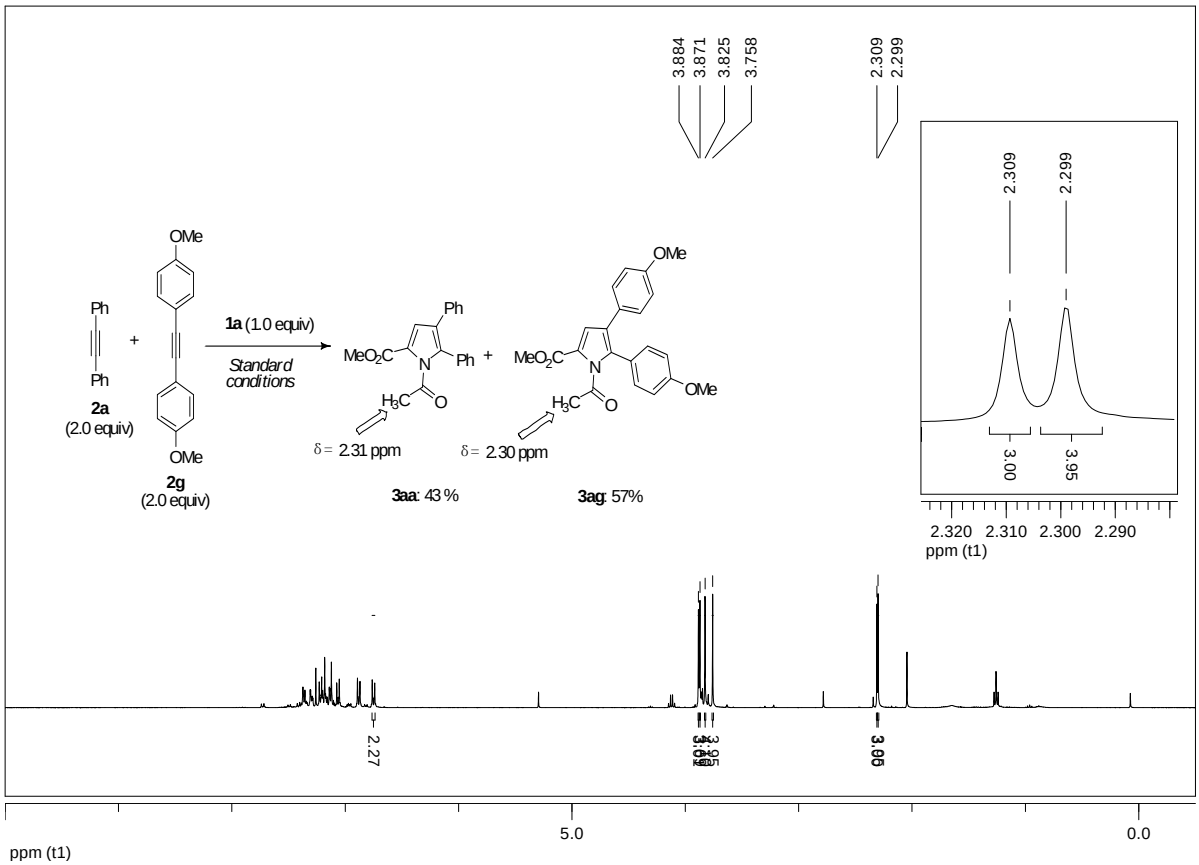


Figure 2: Competition reaction between **2a** and **2g** keeping limiting amount of **1a**

Reaction with and without oxidant:

A) General Procedure D (reaction without $Cu(OAc)_2 \cdot H_2O$)

A mixture of methyl 2-acetamidoacrylate (**1a**) (42.9 mg, 0.30 mmol, 1.0 equiv.), diphenyl acetylene (**2a**) (58.8 mg, 0.33 mmol, 1.1 equiv.), NaOAc, and $[RuCl_2(p\text{-cymene})]_2$ were weighted in a Schlenk tube equipped with a stir bar. Dry DCE (1.5 mL) was added and the mixture was stirred at 100 °C for 12 hours under Ar atmosphere. Afterwards, it was diluted with CH_2Cl_2 and transferred to a round bottom flask, then was concentrated under reduced pressure. The mixture was dissolved in $CDCl_3$ carefully and measured ^1H NMR.

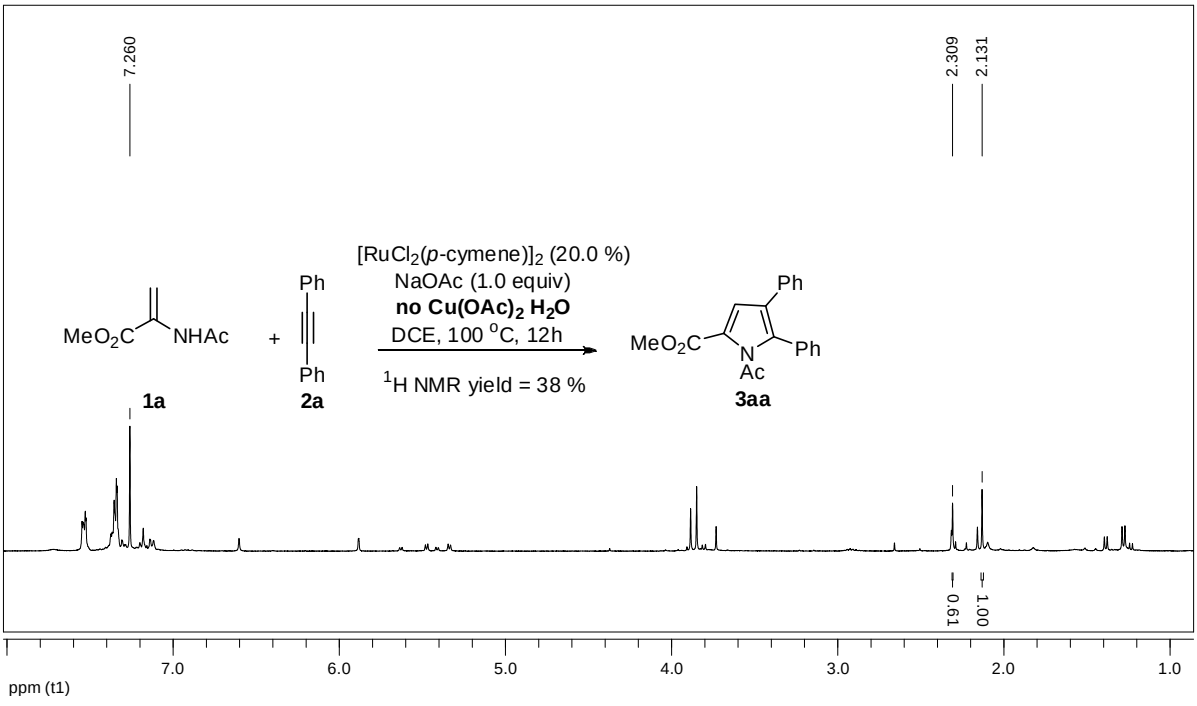
B) General Procedure E: for reaction with $Cu(OAc)_2 \cdot H_2O$

A mixture of methyl 2-acetamidoacrylate (**1a**) (42.9 mg, 0.30 mmol, 1.0 equiv.), diphenyl acetylene (**2a**) (58.8 mg, 0.33 mmol, 1.1 equiv.), NaOAc, and $[RuCl_2(p\text{-cymene})]_2$ were weighted in a Schlenk tube equipped with a stir bar. Dry DCE (1.5 mL) was added and

the mixture was stirred at 100 °C under Ar atmosphere. After 12 hours the solution was cooled to approx. 80 °C and $Cu(OAc)_2 \cdot H_2O$ (30mg, 0.15 mmol, 0.5 equiv.) was added under a stream of argon. The solution was again dipped into a preheated oil bath at 100 °C and stirred. After 10 hours, the reaction mixture was diluted with CH_2Cl_2 and transferred to a round bottom flask, then was concentrated under reduced pressure. The mixture was dissolved in $CDCl_3$ carefully and measured ^{1}H NMR.

I) Using 20 % [$RuCl_2$(*p*-cymene)]$_2$:

By following general procedure D, using NaOAc (24.6 mg, 0.3 mmol, 1.0 equiv) and [$RuCl_2$(*p*-cymene)]$_2$ (36.8 mg, 0.060 mmol, 20.0 mol %), we have observed 38% ^{1}H NMR yield. But the same set up using 0.5 equiv. of $Cu(OAc)_2 \cdot H_2O$ (by following general procedure E) we have observed 100 % ^{1}H NMR yield (Figure 3).



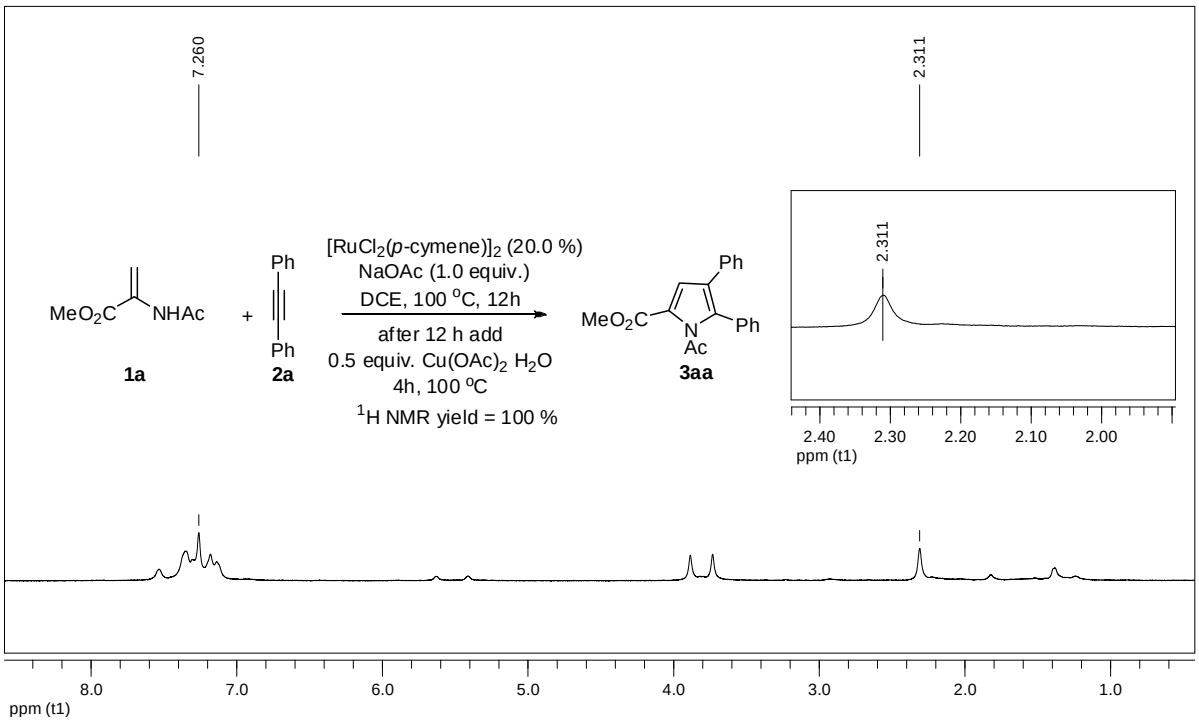
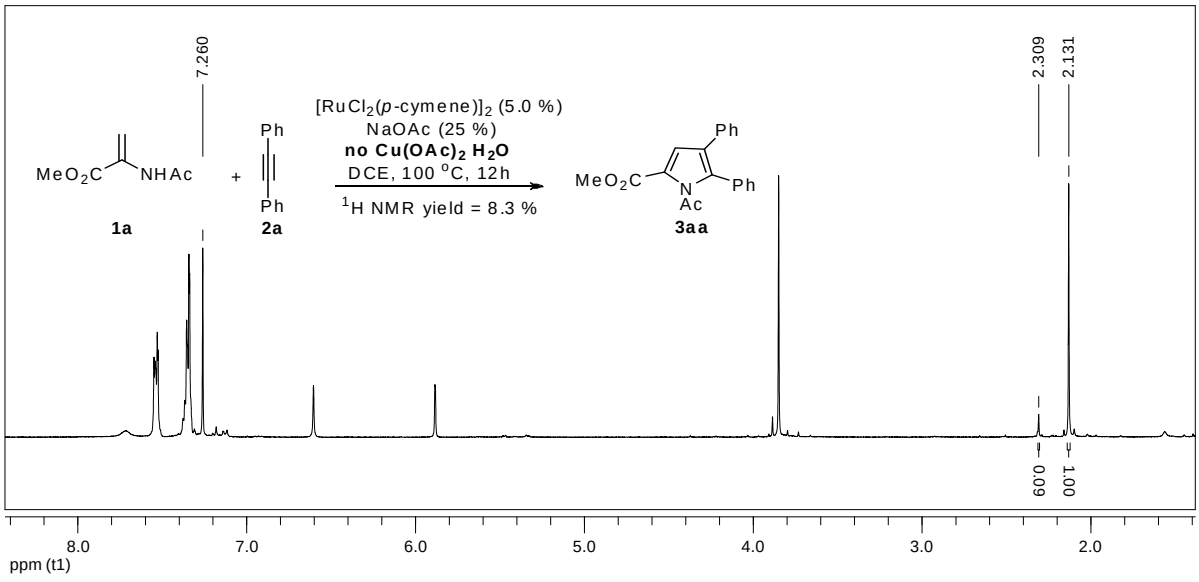


Figure 3: ^{1}H NMR spectra of crude reaction mixture comparison with SM (**1a**) and product (**3aa**)

II) Using 5.0 mol% [RuCl$_2$(*p*-cymene)]$_2$:

By following general procedure D, using NaOAc (6.2 mg, 0.075 mmol, 20 mmol %) and [RuCl$_2$(*p*-cymene)]$_2$ (9.1 mg, 0.015 mmol, 5.0 mol %), we have observed 8% ^{1}H NMR yield. But the same set up using 0.5 equiv. of Cu(OAc)$_2$·H$_2$O (by following general procedure E) we have observed 100% ^{1}H NMR yield (Figure 4).



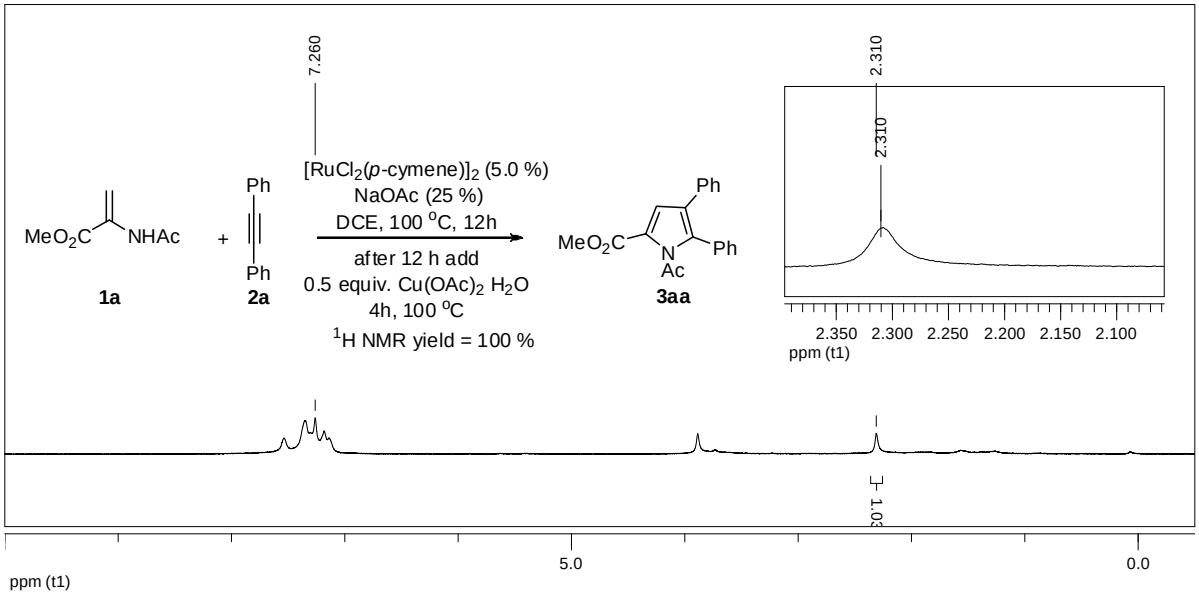


Figure 4: ^{1}H NMR spectra of crude reaction mixture comparison with SM (**1a**) and product (**3aa**)

These two experiments suggest that $Cu(OAc)_2 \cdot H_2O$ does not play any role to form the product. $Cu(OAc)_2$ just acts as reoxidant for Ru(I) to achieve turn over in catalytic cycle (Figure 5).

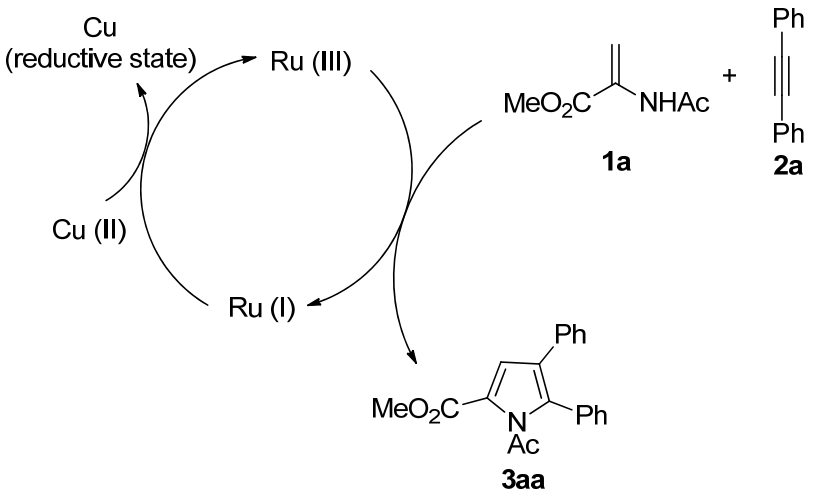


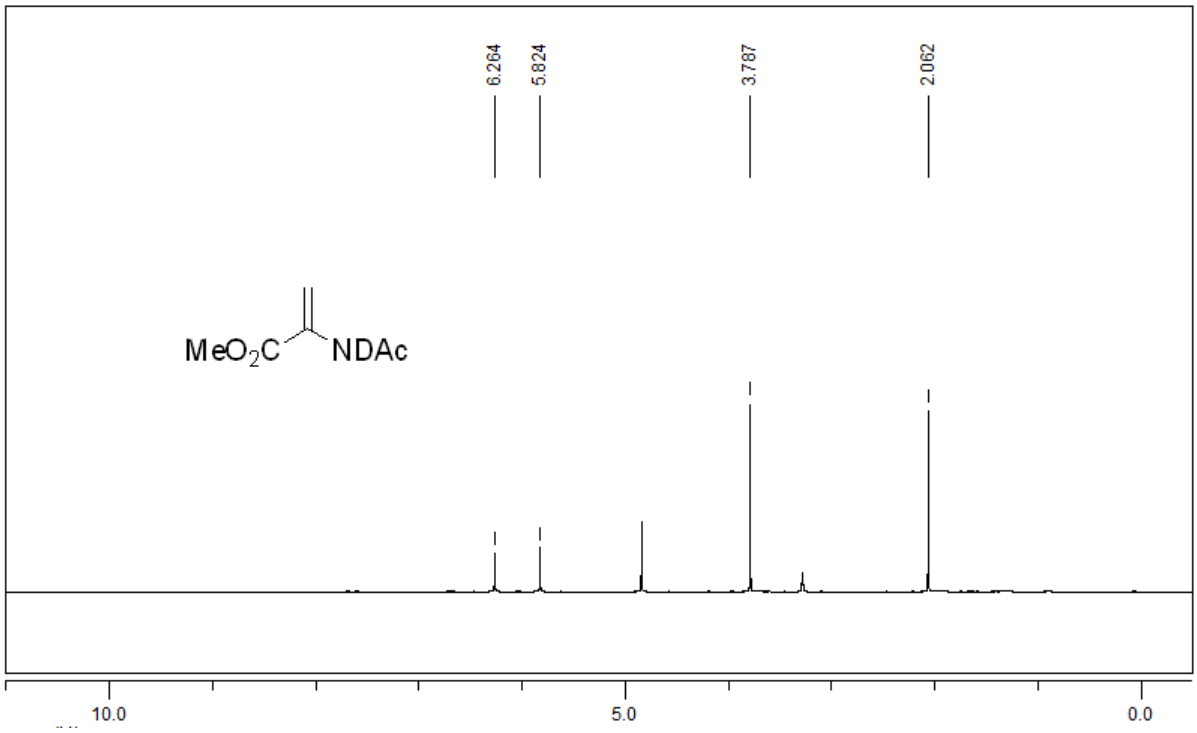
Figure 5: Role of Cu(II)-salt

Deuterium Experiments :

I) Deuteration Experiments without Ru ctatlyst

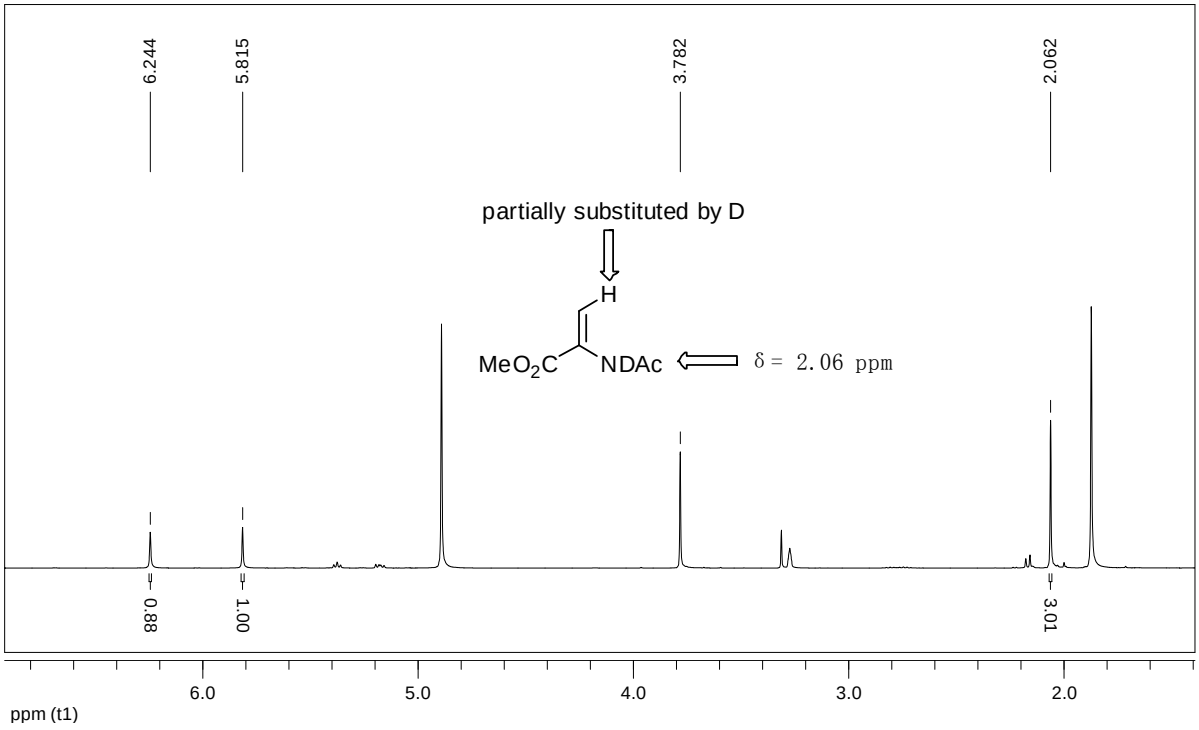
Enamine (**1a**) (22.8 mg, 0.1591 mmol) was submitted to 1 ml dry CD_3OD. The solution was

then stirred at 70 °C for 12 hours. The crude mixture was transferred to the NMR tube under argon atmosphere. ^{1}H NMR (300 MHz, CD_3OD): δ = 6.26 (1H, s, CH_{olefin}), 5.82 (1H, s, CH_{olefin}), 3.79 (3H, s, OCH_3), 2.06 (3H, s, Ac). Note: the NH signal is absent due to deuteration.

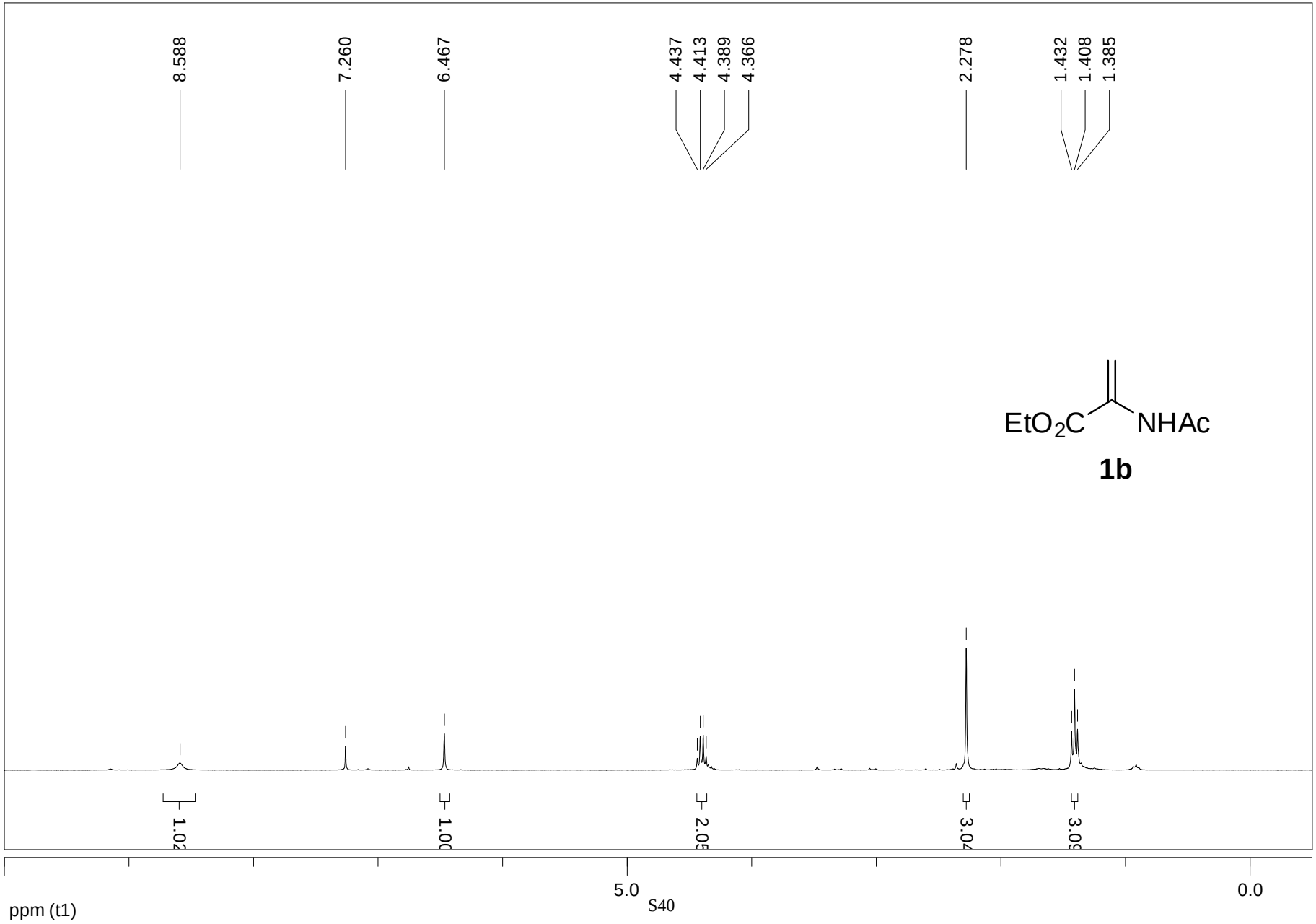


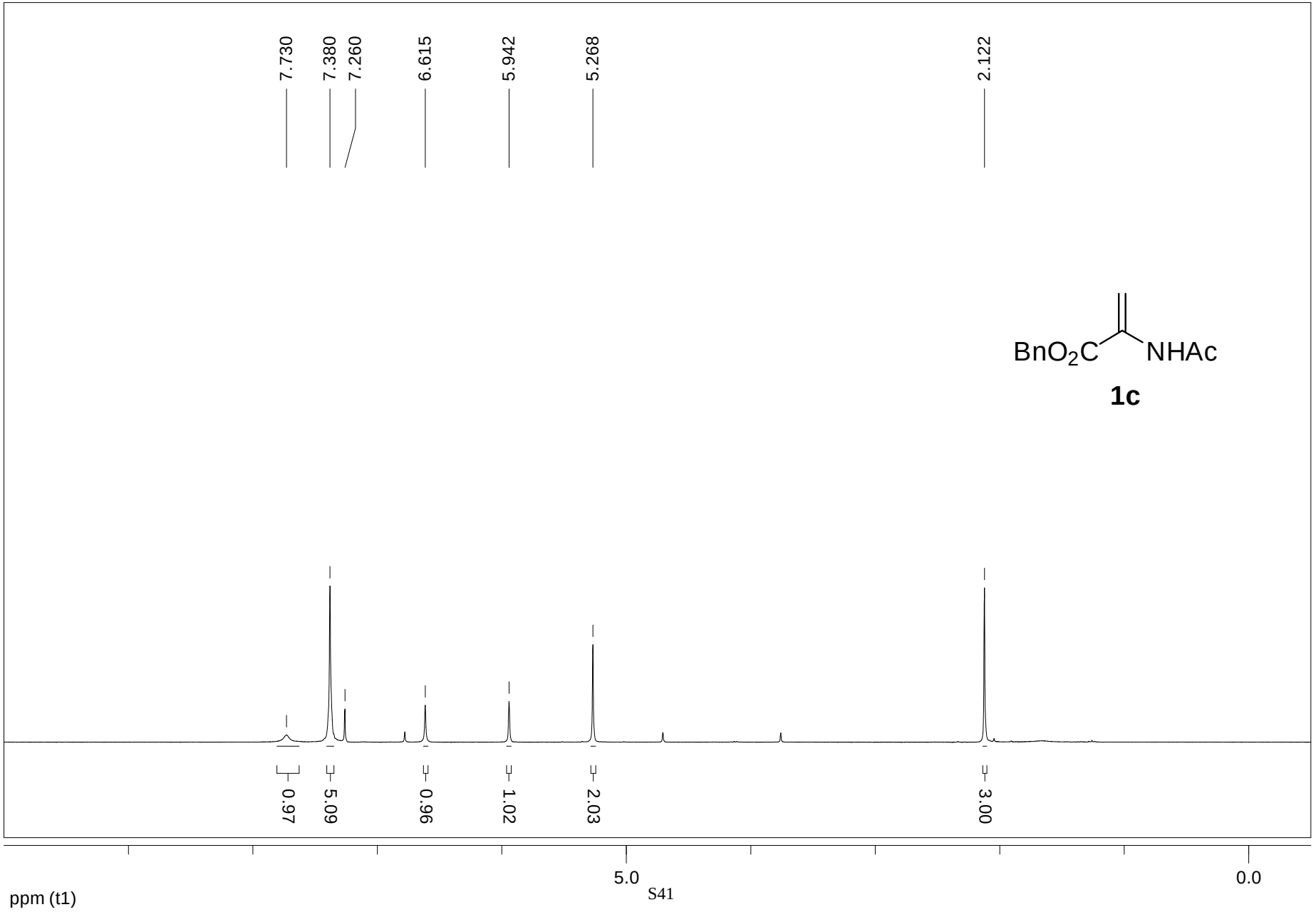
II) Deuteration Experiments with Ru catalyst:

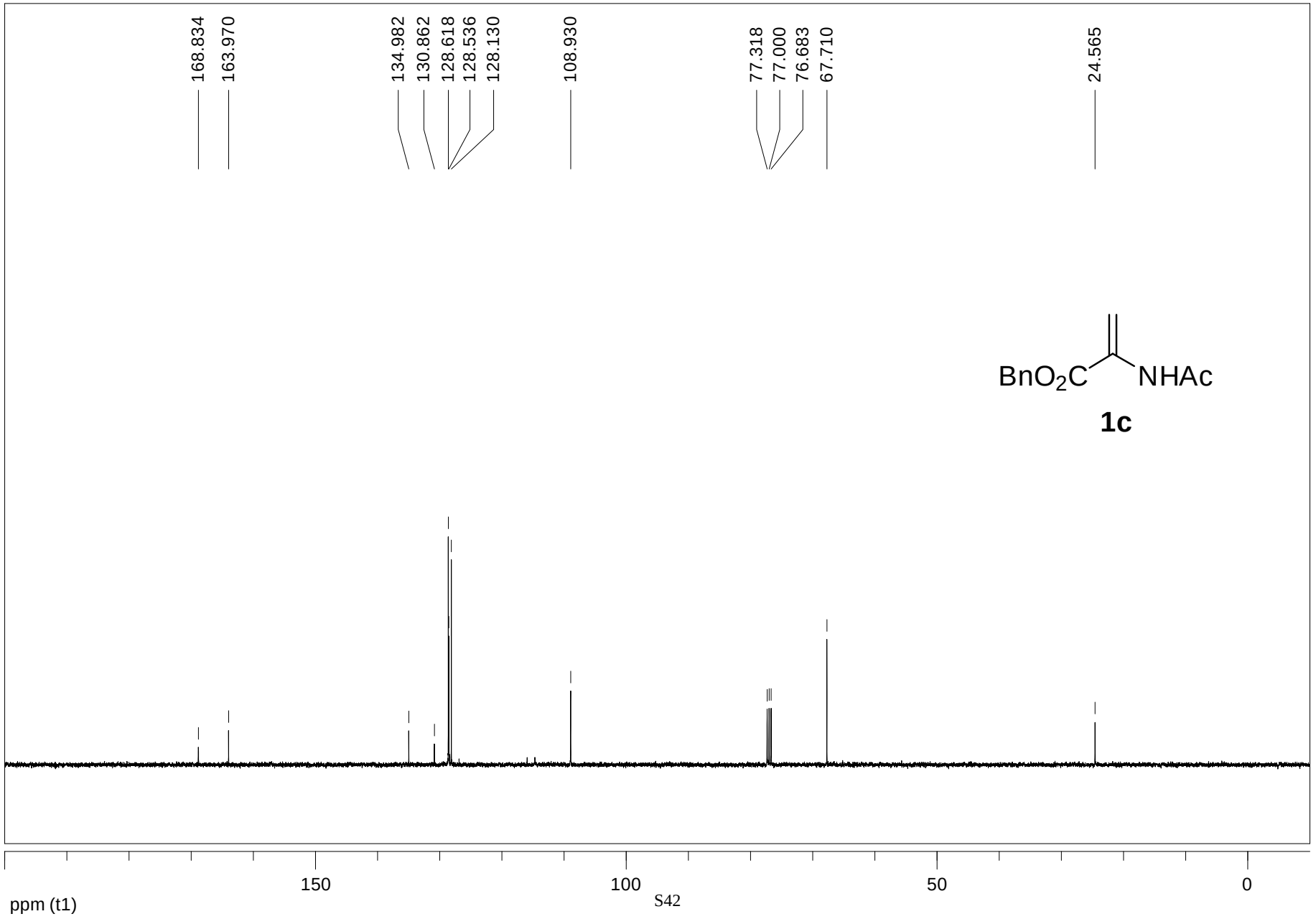
Enamine (**1a**) (22.8 mg, 0.16 mmol, 1.0 equiv.), $[RuCl_2(p\text{-cymene})]_2$ (9.8 mg, 0.008 mmol, 5.0 mol %) and NaOAc (13.1 mg, 0.16 mmol, 1.0 equiv.) were weighted in a Schlenk tube equipped with a stir bar and dry CD_3OD (1.0 mL) was then added. The solution was then stirred at 70 °C for 12 hours. The crude mixture was transferred to the NMR tube under argon atmosphere. ***We found 12% deuterium incorporation at the CH_{olefin}*** (see below). ***This experiment suggests that under the reaction conditions C–H insertion is probably irreversible.***

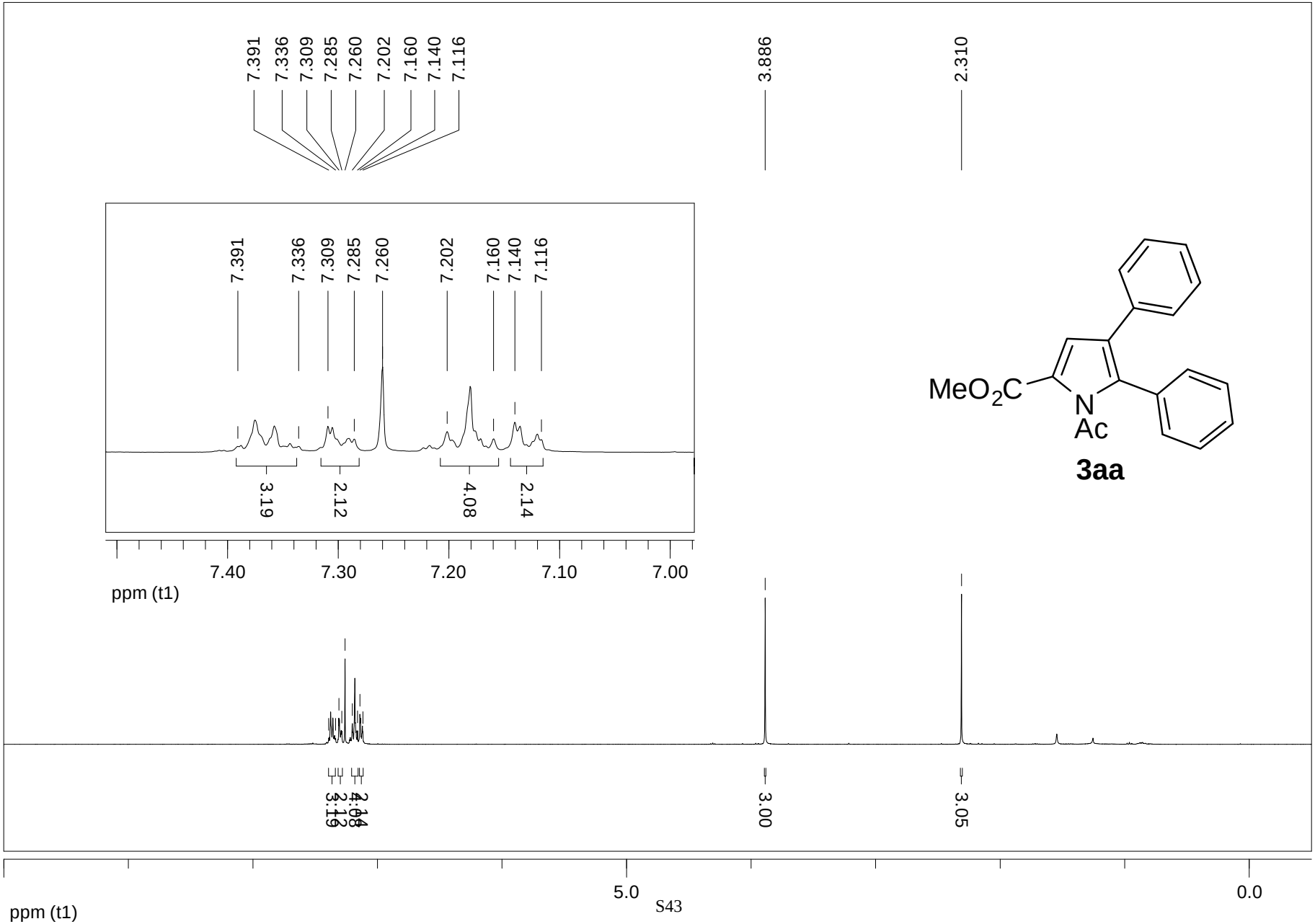

6.244
5.815
3.782
2.062
partially substituted by D
H
MeO2C
NDAc
δ = 2.06 ppm
0.88
1.00
3.01
6.0
5.0
4.0
3.0
2.0
ppm (t1)

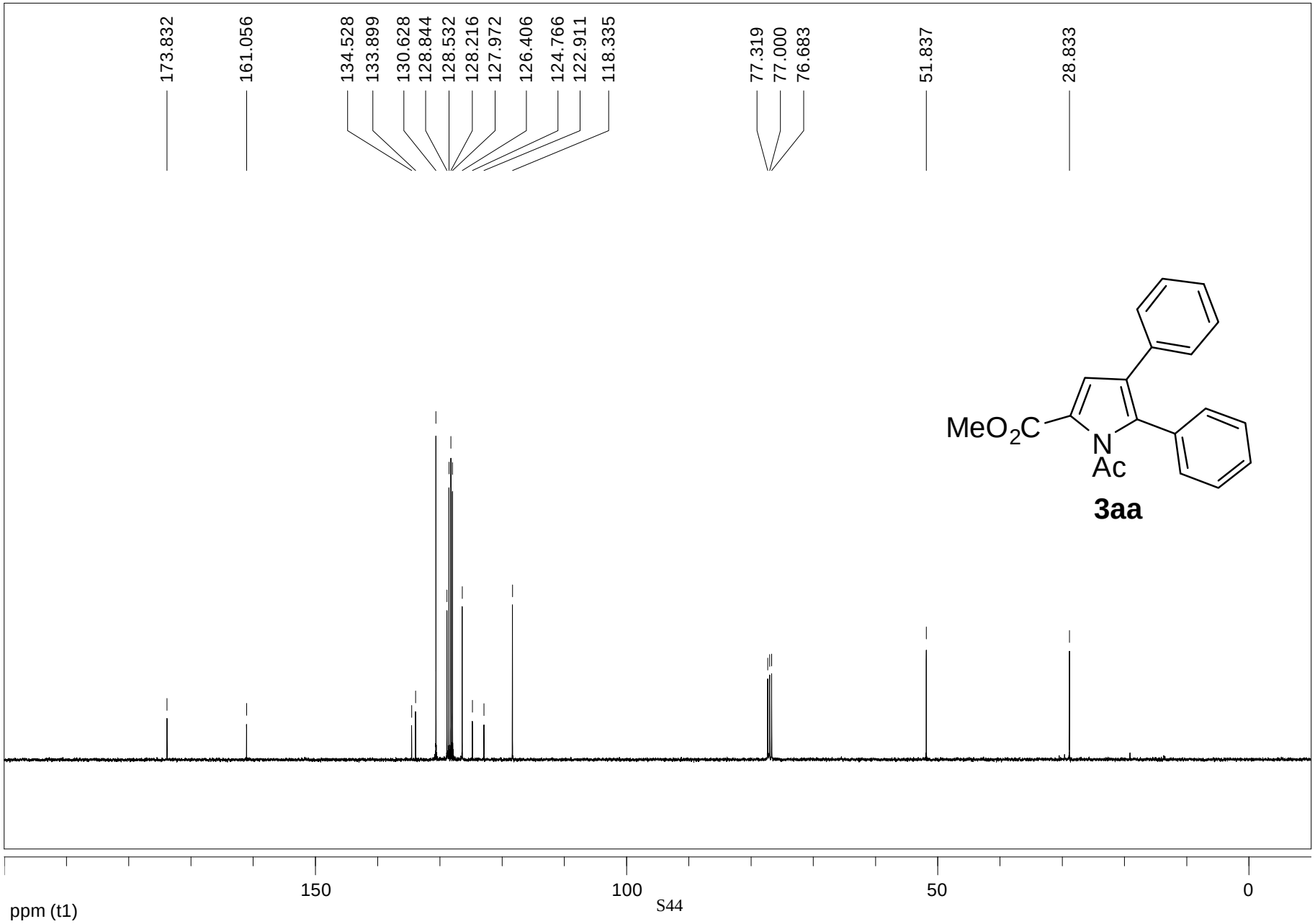
Spectral Copies of ^{1}H, ^{13}C NMR and ^{19}F of Compounds Obtained in this Study

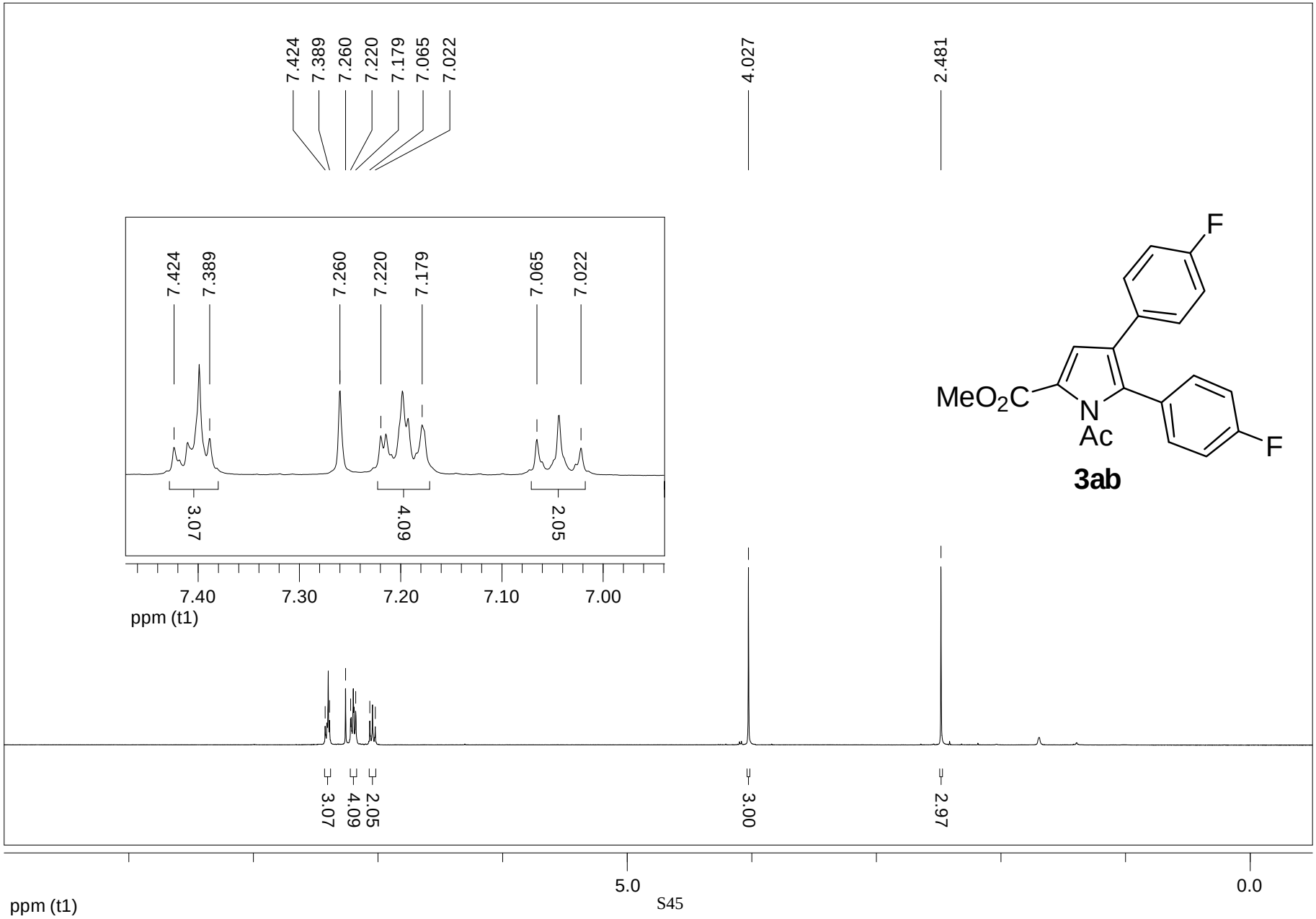

8.588
7.260
6.467
4.437
4.413
4.389
4.366
2.278
1.432
1.408
1.385
EtO2C
NHAc
1b
1.02
1.00
2.05
3.07
3.05
5.0
0.0
ppm (t1)


7.730
7.380
7.260
6.615
5.942
5.268
2.122
BnO2C
NHAc
1c
0.97
5.09
0.96
1.02
2.03
3.00
5.0
0.0
ppm (t1)


168.834
163.970
134.982
130.862
128.618
128.536
128.130
108.930
77.318
77.000
76.683
67.710
24.565
BnO2C
NHAc
1c
150
100
50
0
ppm (t1)


7.391
7.336
7.309
7.285
7.260
7.202
7.160
7.140
7.116
3.886
2.310
3.19
2.12
4.08
2.14
7.40
7.30
7.20
7.10
7.00
ppm (t1)
MeO2C
N
Ac
3aa
3.00
3.05
5.0
0.0
ppm (t1)


173.832
161.056
134.528
133.899
130.628
128.844
128.532
128.216
127.972
126.406
124.766
122.911
118.335
77.319
77.000
76.683
51.837
28.833
MeO2C
N
Ac
3aa
150
100
50
0
ppm (t1)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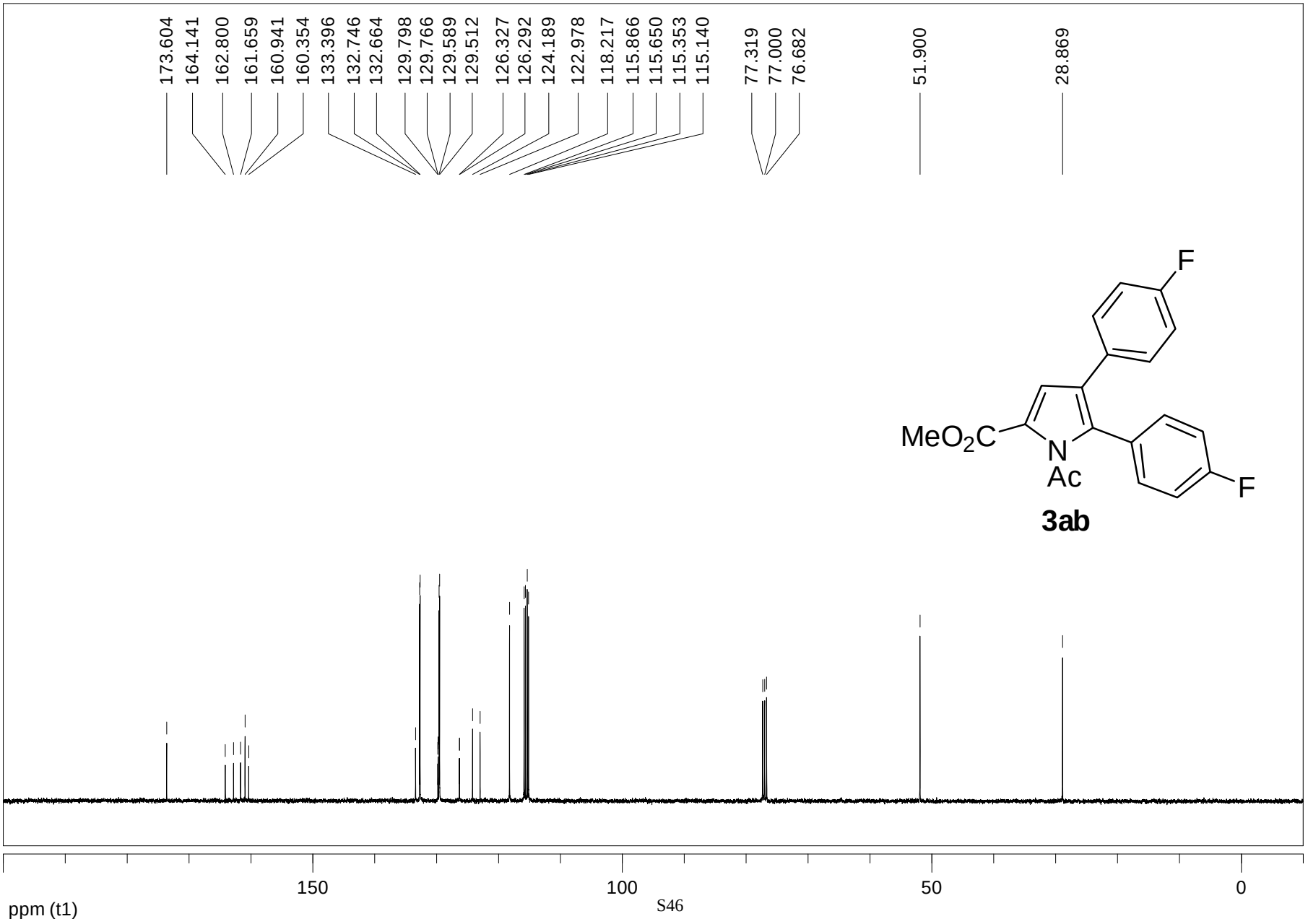
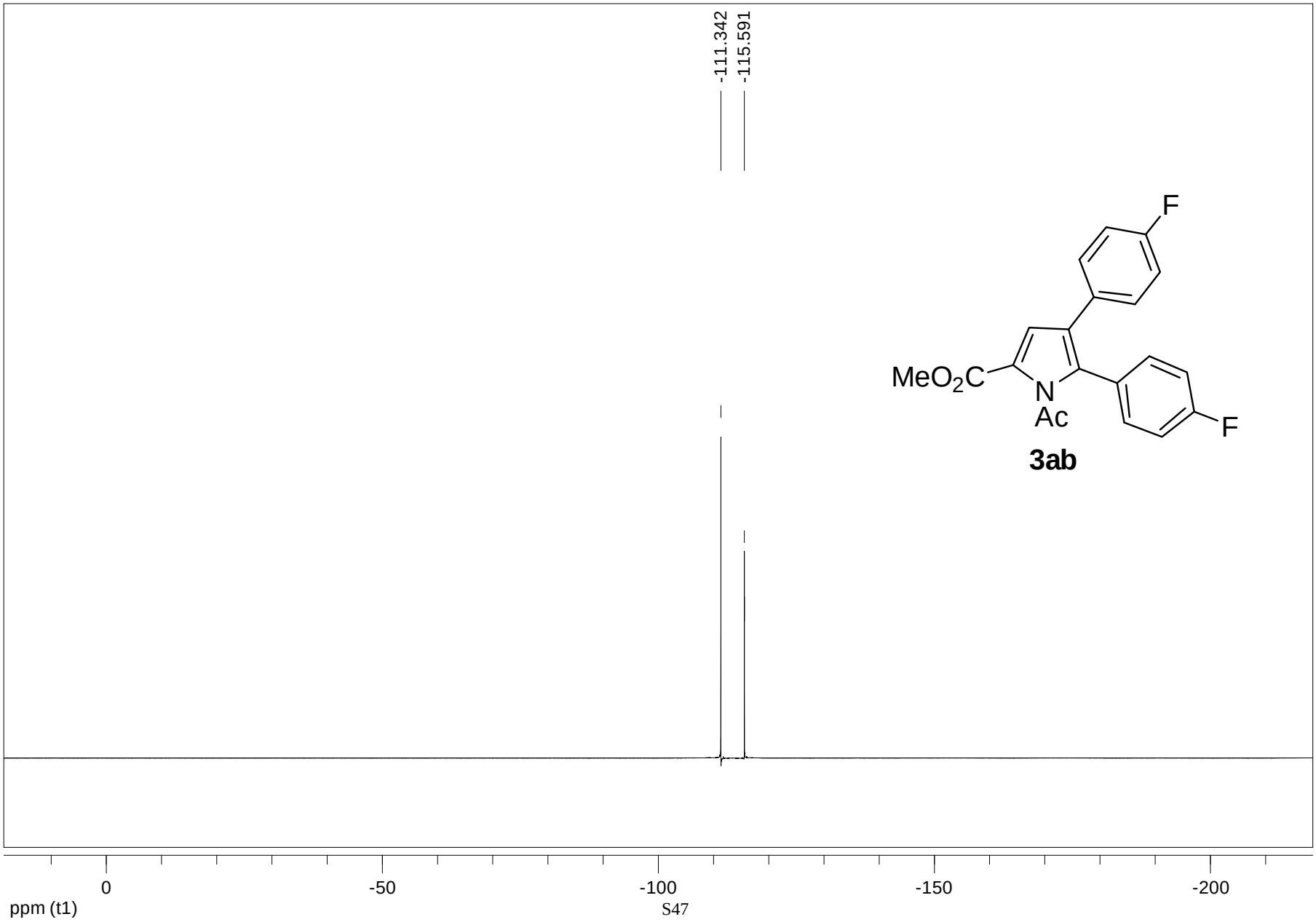
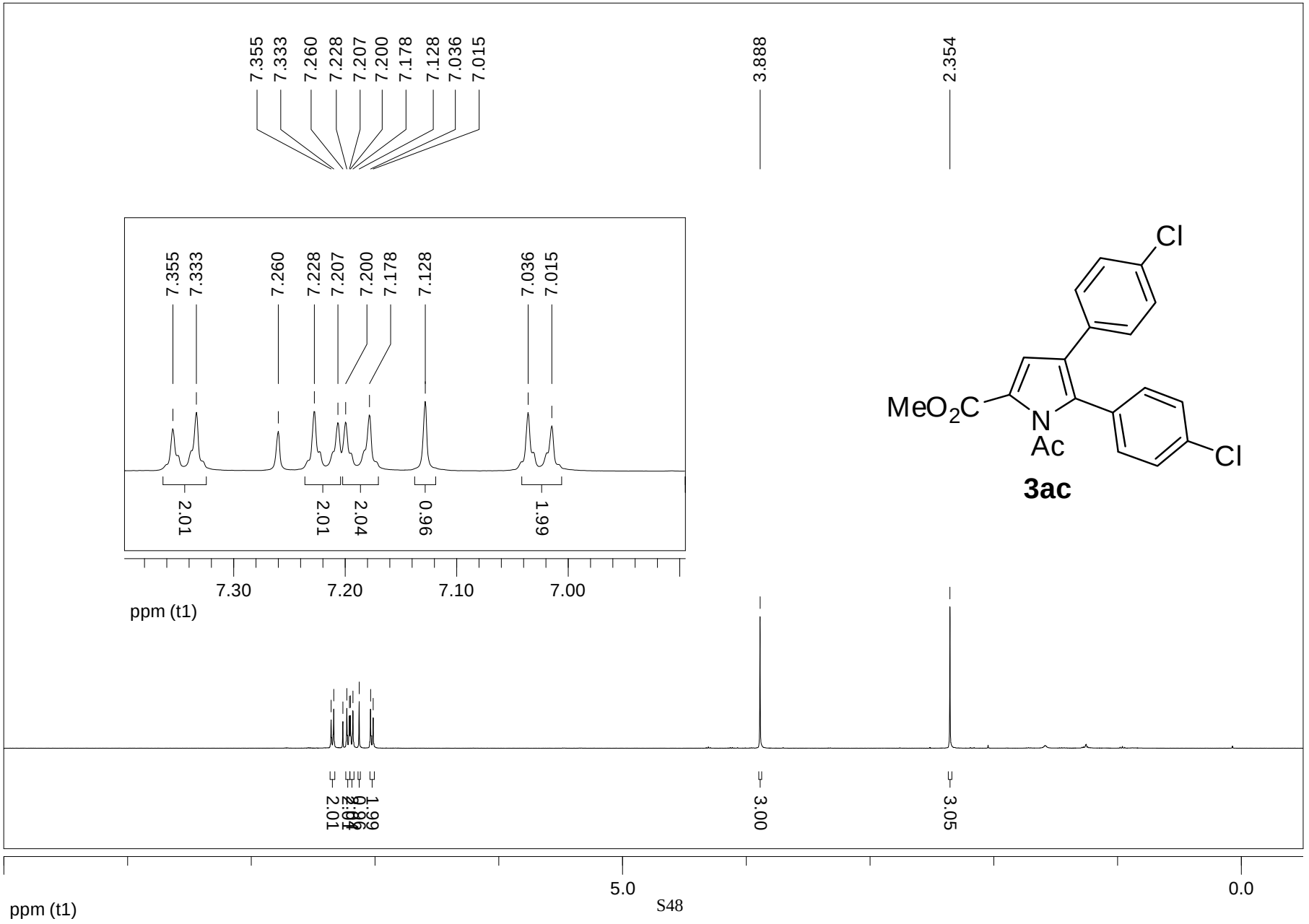
7.389
7.260
7.220
7.179
7.065
7.022
4.027
2.481
3.07
4.09
2.05
7.40
7.30
7.20
7.10
7.00
ppm (t1)
F
MeO2C
N
Ac
F
3ab
3.07
4.09
2.05
3.00
2.97
5.0
0.0
ppm (t1)


173.604
164.141
162.800
161.659
160.941
160.354
133.396
132.746
132.664
129.798
129.766
129.589
129.512
126.327
126.292
124.189
122.978
118.217
115.866
115.650
115.353
115.140
77.319
77.000
76.682
51.900
28.869
F
MeO2C
N
Ac
F
3ab
150
100
50
0
ppm (t1)


-111.342
-115.591
F
MeO2C
N
Ac
F
3ab
0
-50
-100
-150
-200
ppm (t1)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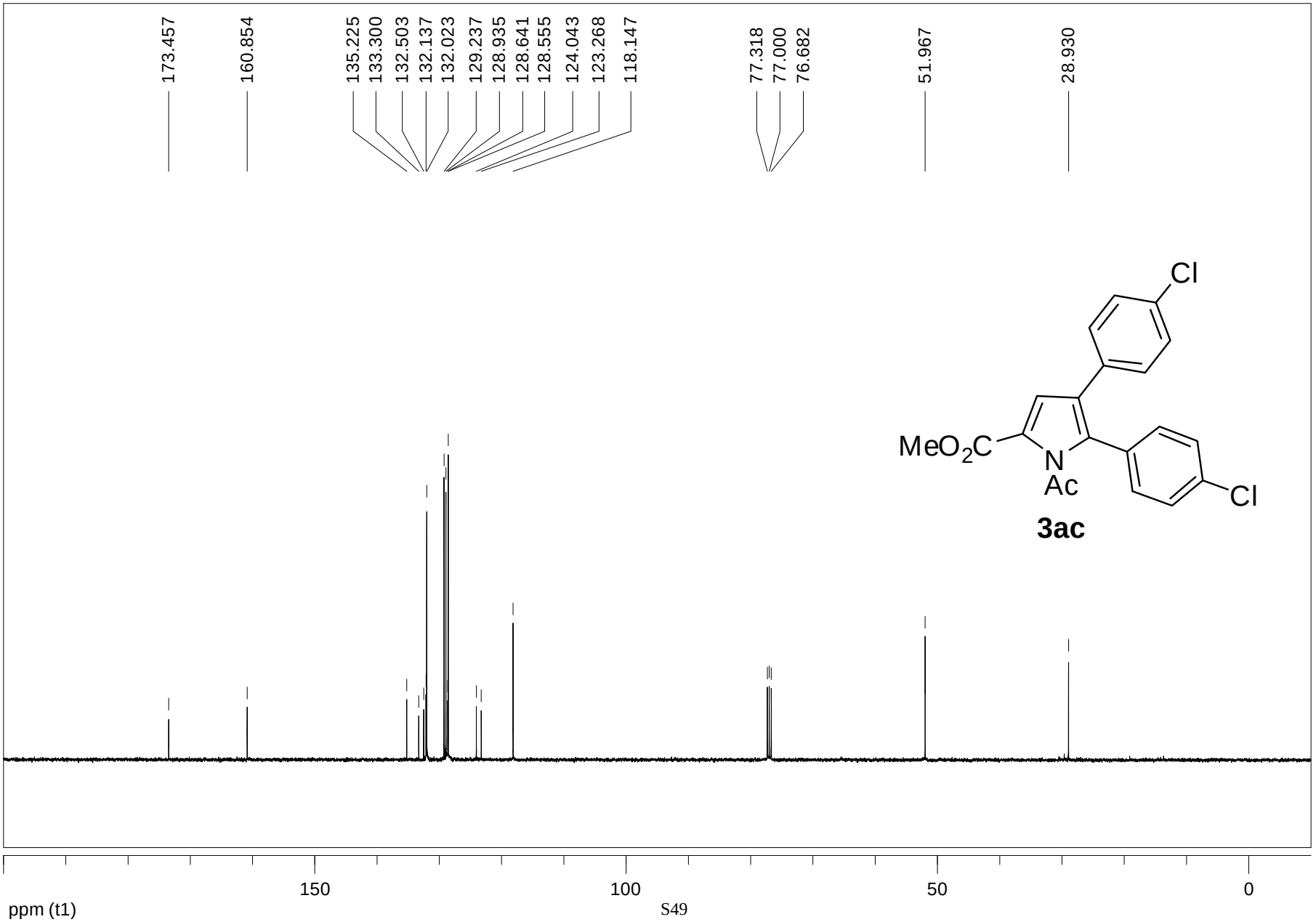
7.333
7.260
7.228
7.207
7.200
7.178
7.128
7.036
7.015
3.888
2.354
2.01
2.01
2.04
0.96
1.99
7.30
7.20
7.10
7.00
ppm (t1)
Cl
MeO2C
N
Ac
Cl
3ac
2.01
1.99
3.00
3.05
5.0
0.0
ppm (t1)


173.457
160.854
135.225
133.300
132.503
132.137
132.023
129.237
128.935
128.641
128.555
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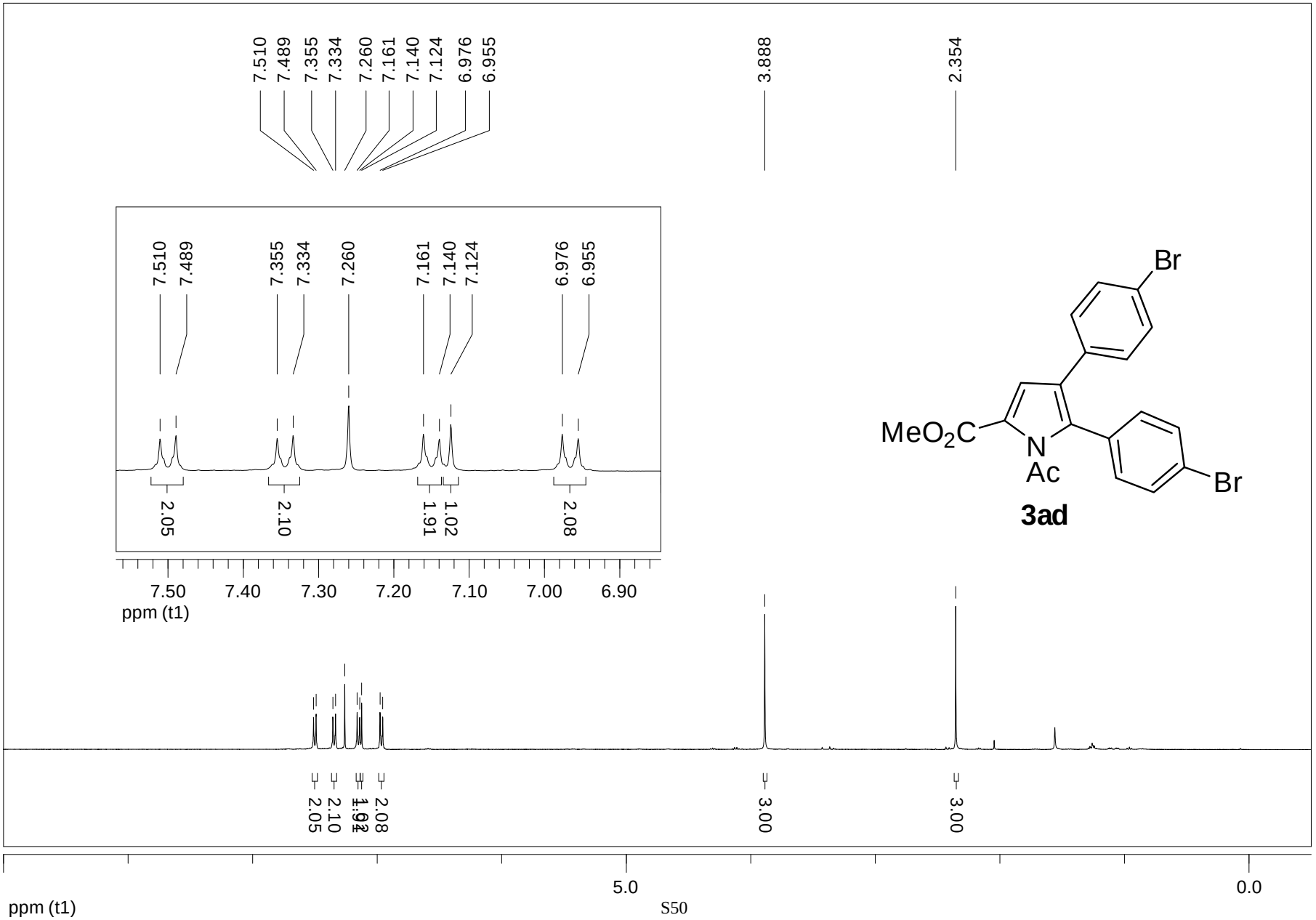
123.268
118.147
77.318
77.000
76.682
51.967
28.930
Cl
MeO2C
N
Ac
Cl
3ac
150
100
50
0
ppm (t1)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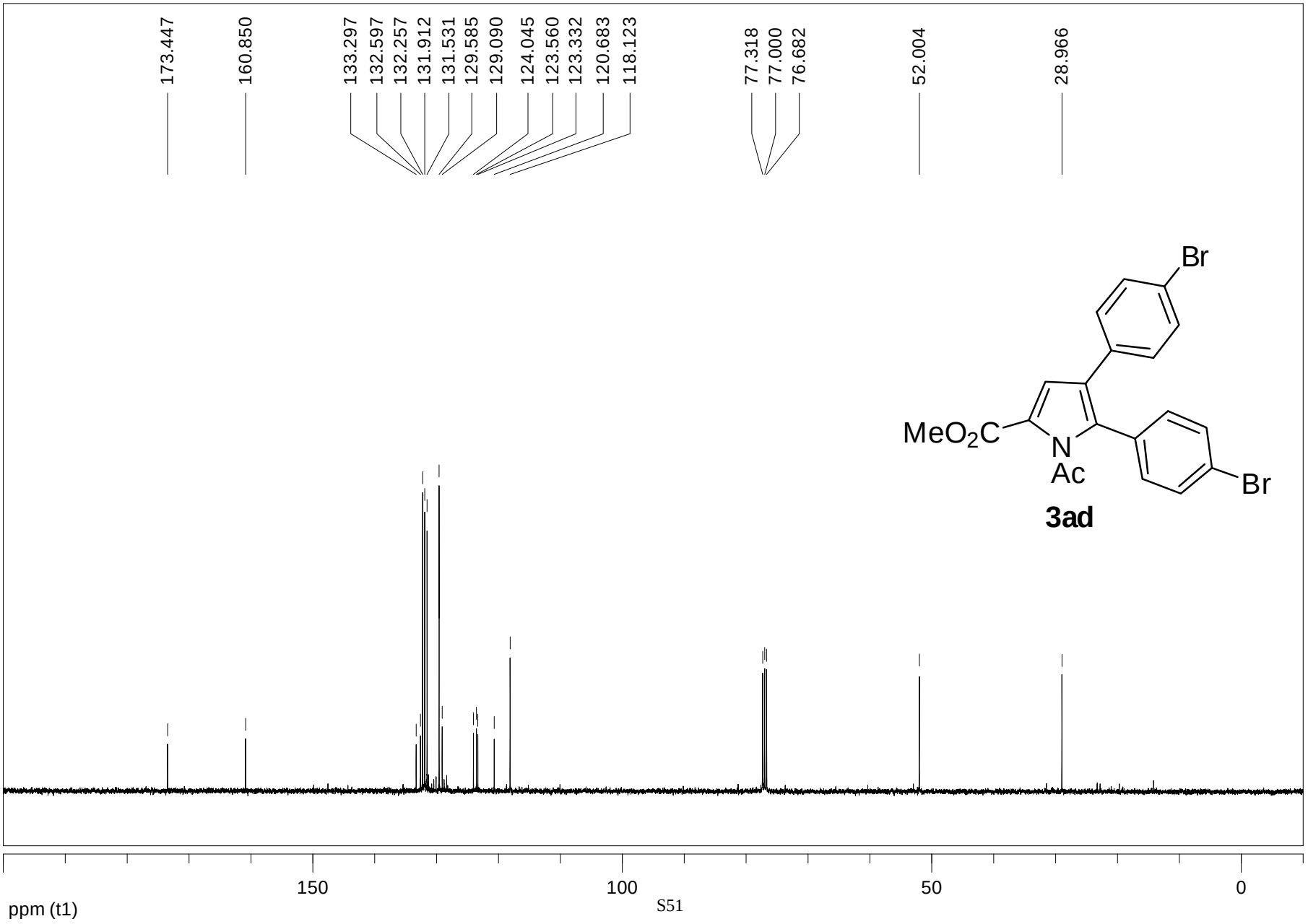
7.334
7.260
7.161
7.140
7.124
6.976
6.955
3.888
2.354
2.05
2.10
1.91
1.02
2.08
7.50
7.40
7.30
7.20
7.10
7.00
6.90
ppm (t1)
Br
MeO2C
N
Ac
Br
3ad
3.00
3.00
5.0
0.0
ppm (t1)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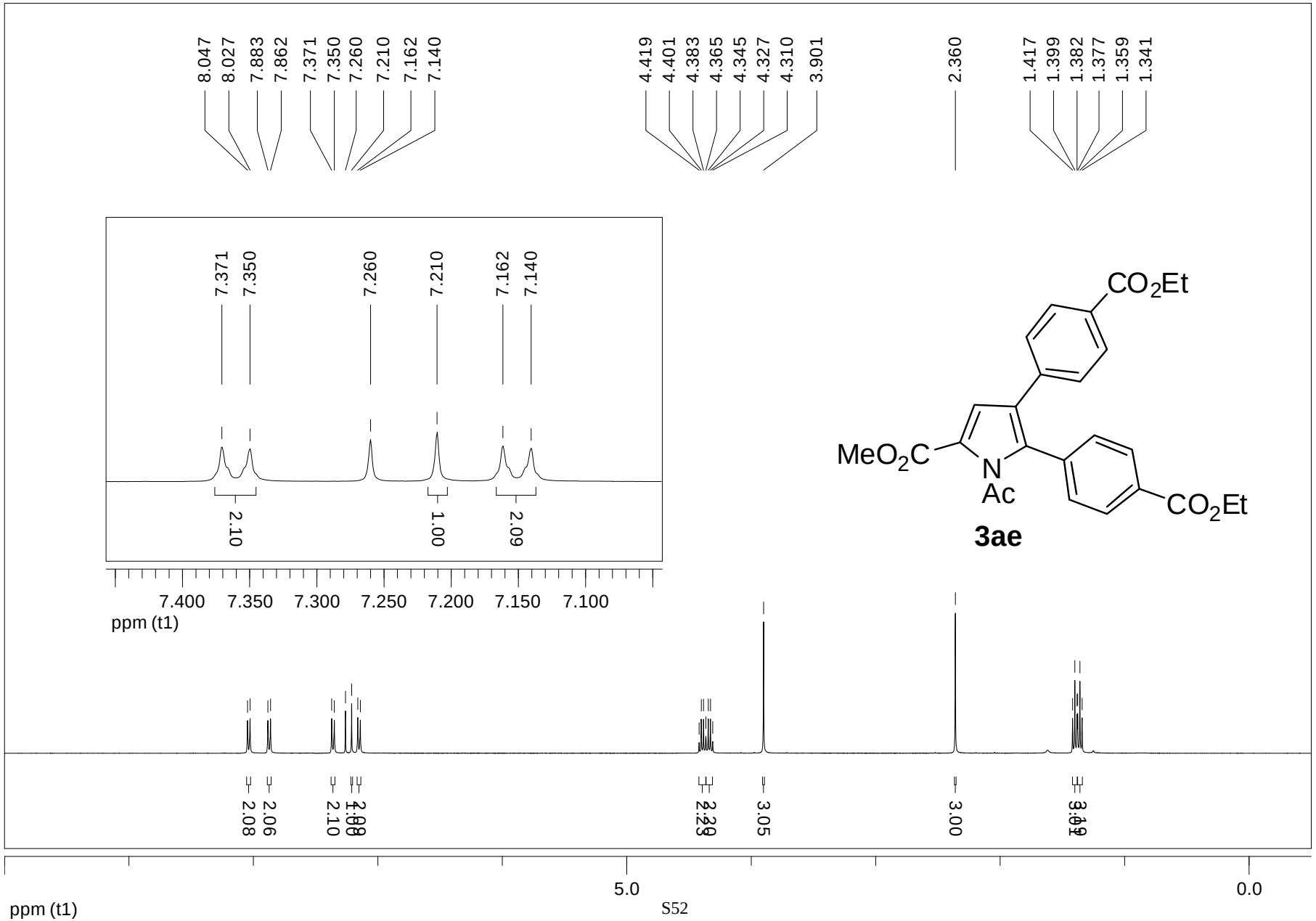
133.297
132.597
132.257
131.912
131.531
129.585
129.090
124.045
123.560
123.332
120.683
118.123
77.318
77.000
76.682
52.004
28.966
Br
MeO2C
N
Ac
Br
3ad
150
100
50
0
ppm (t1)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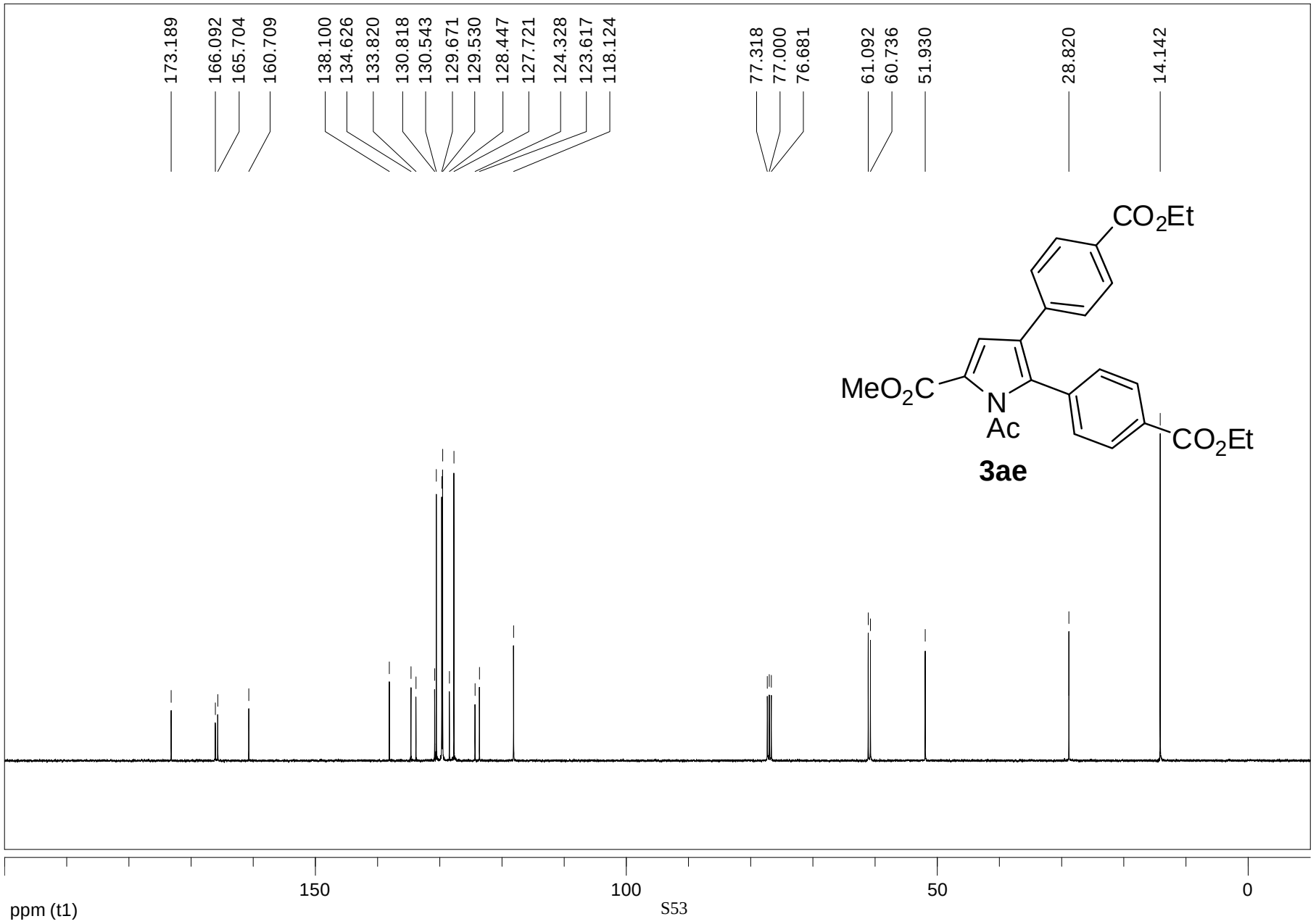
8.027
7.883
7.862
7.371
7.350
7.260
7.210
7.162
7.140
4.419
4.401
4.383
4.365
4.345
4.327
4.310
3.901
2.360
1.417
1.399
1.382
1.377
1.359
1.341
2.10
1.00
2.09
7.400
7.350
7.300
7.250
7.200
7.150
7.100
ppm (t1)
CO2Et
MeO2C
N
Ac
CO2Et
3ae
2.08
2.06
2.10
4.00
2.23
3.05
3.00
3.01
5.0
0.0
ppm (t1)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134.626
133.820
130.818
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129.671
129.530
128.447
127.721
124.328
123.617
118.124
77.318
77.000
76.681
61.092
60.736
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14.142
CO2Et
MeO2C
N
Ac
CO2Et
3ae
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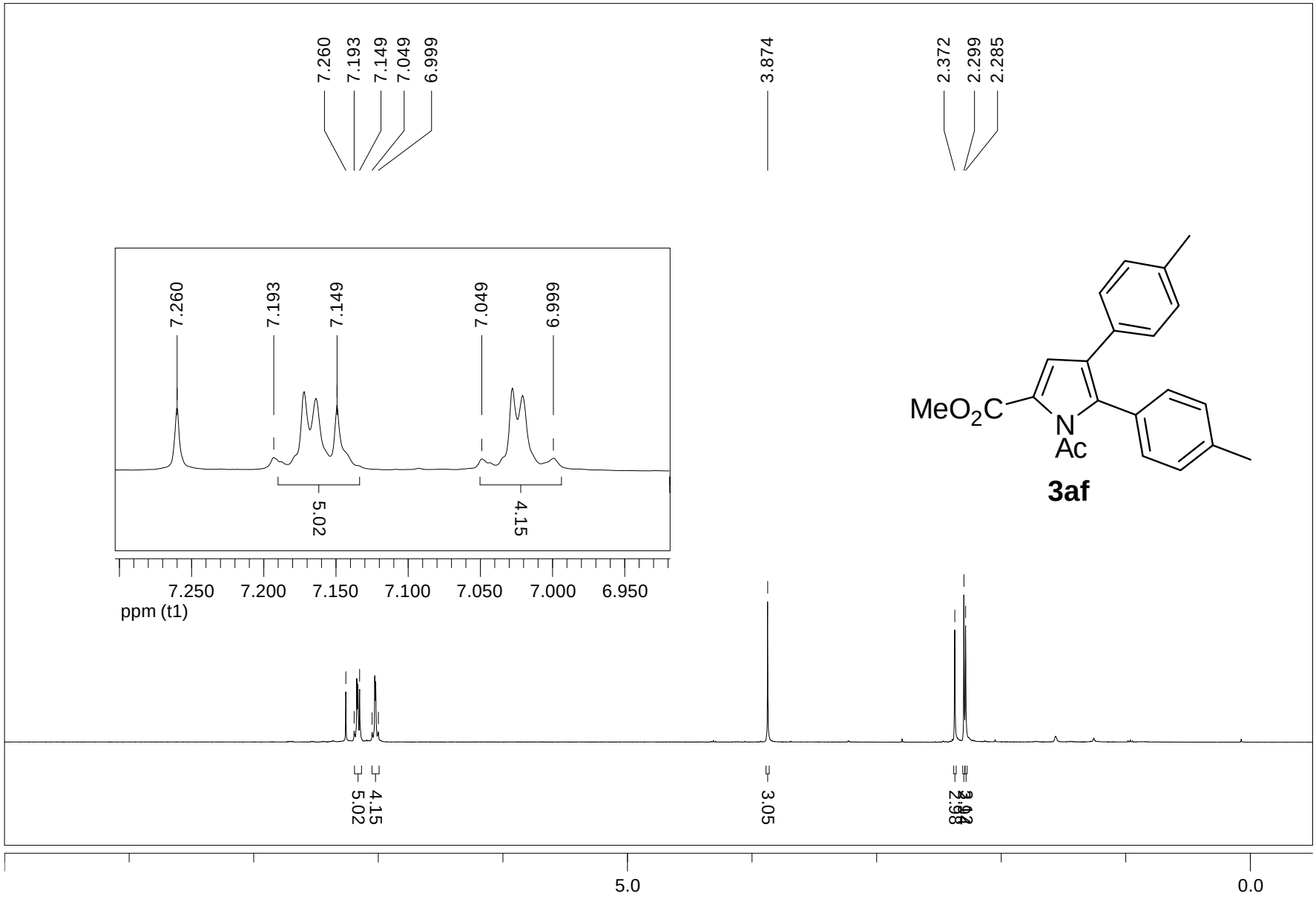
100
50
0
ppm (t1)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7.149
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3.874
2.372
2.299
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7.260
7.193
7.149
7.049
6.999
5.02
4.15
7.250
7.200
7.150
7.100
7.050
7.000
6.950
ppm (t1)
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N
Ac
3af
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4.15
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2.68
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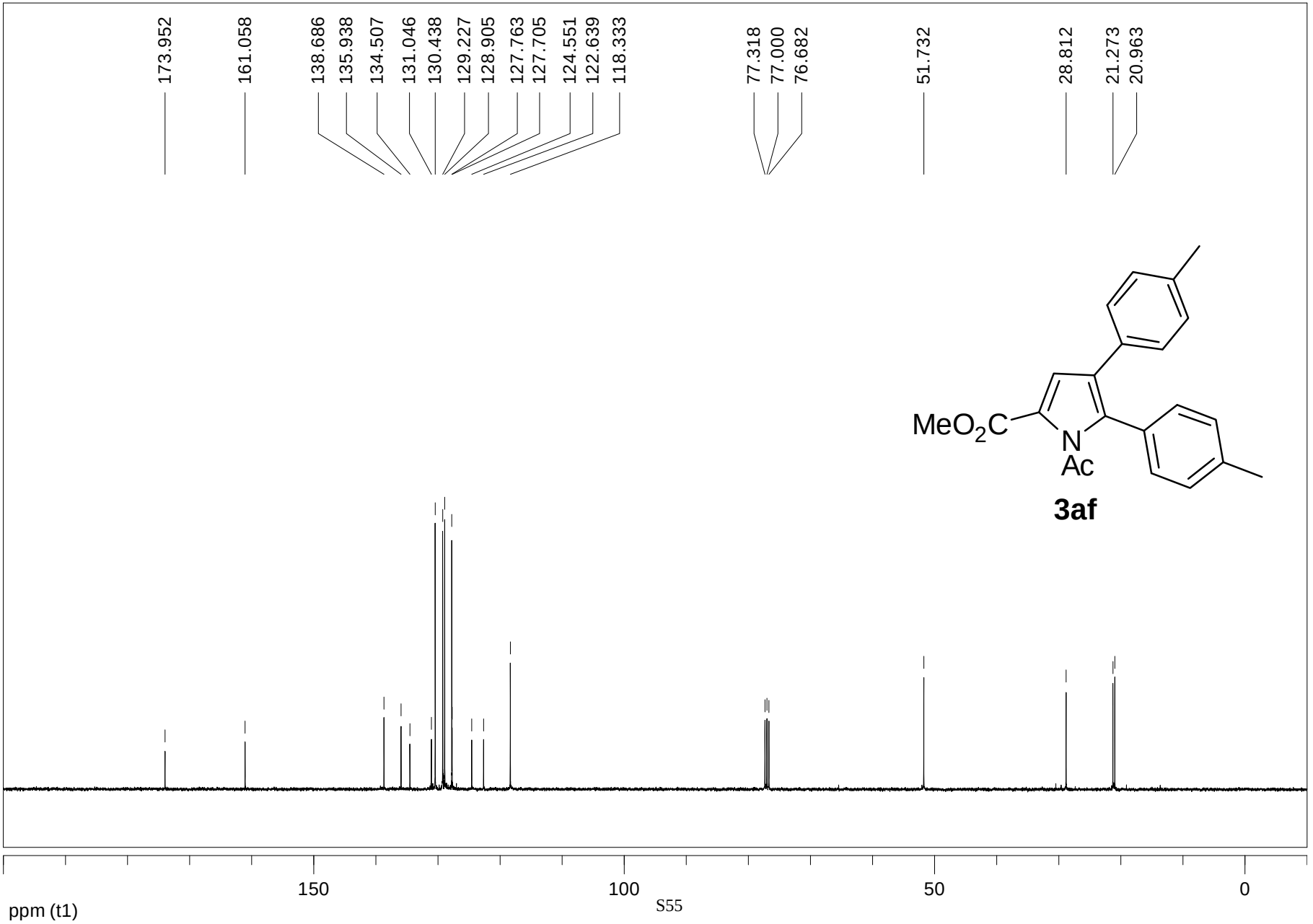
ppm (t1)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135.938
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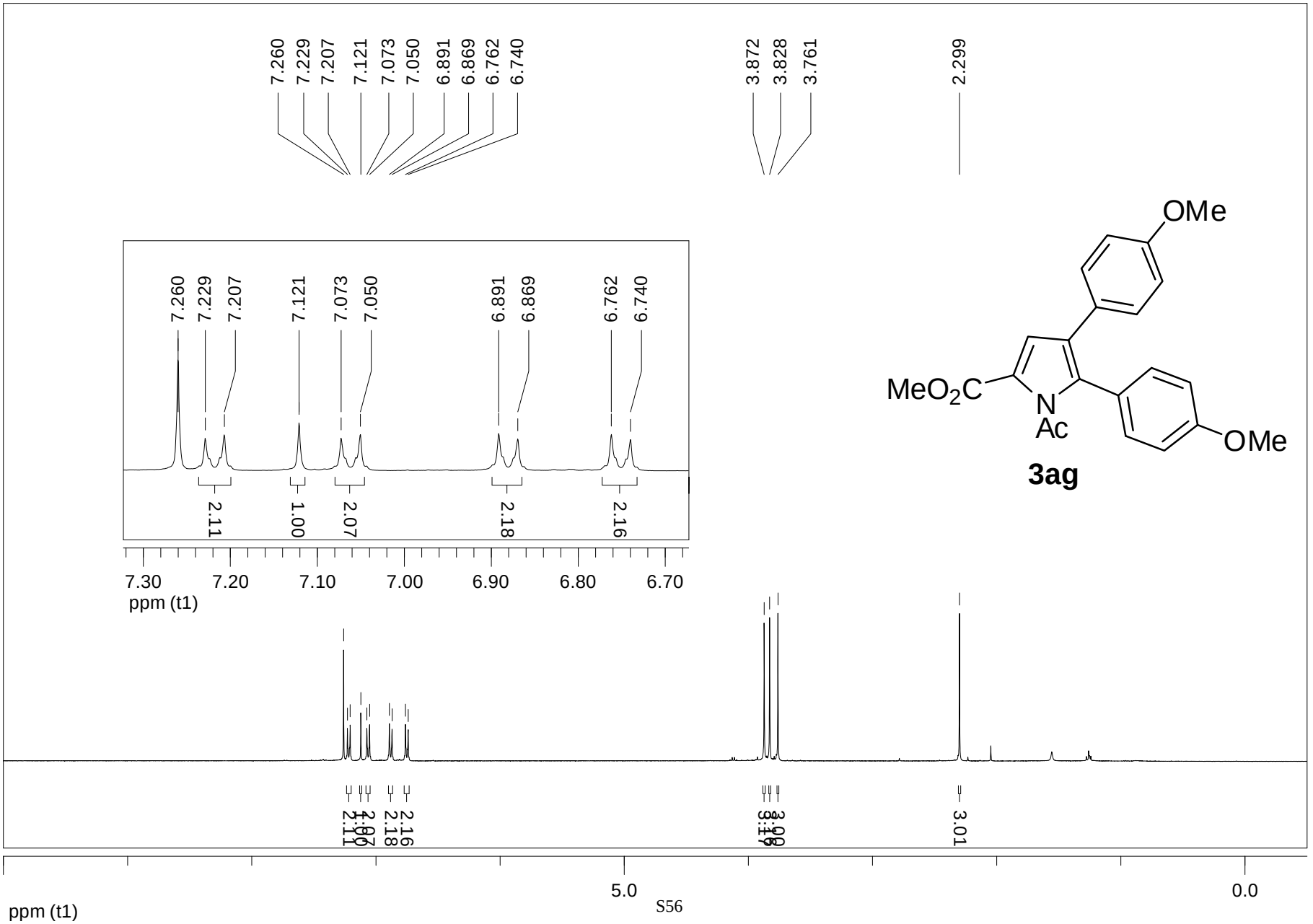
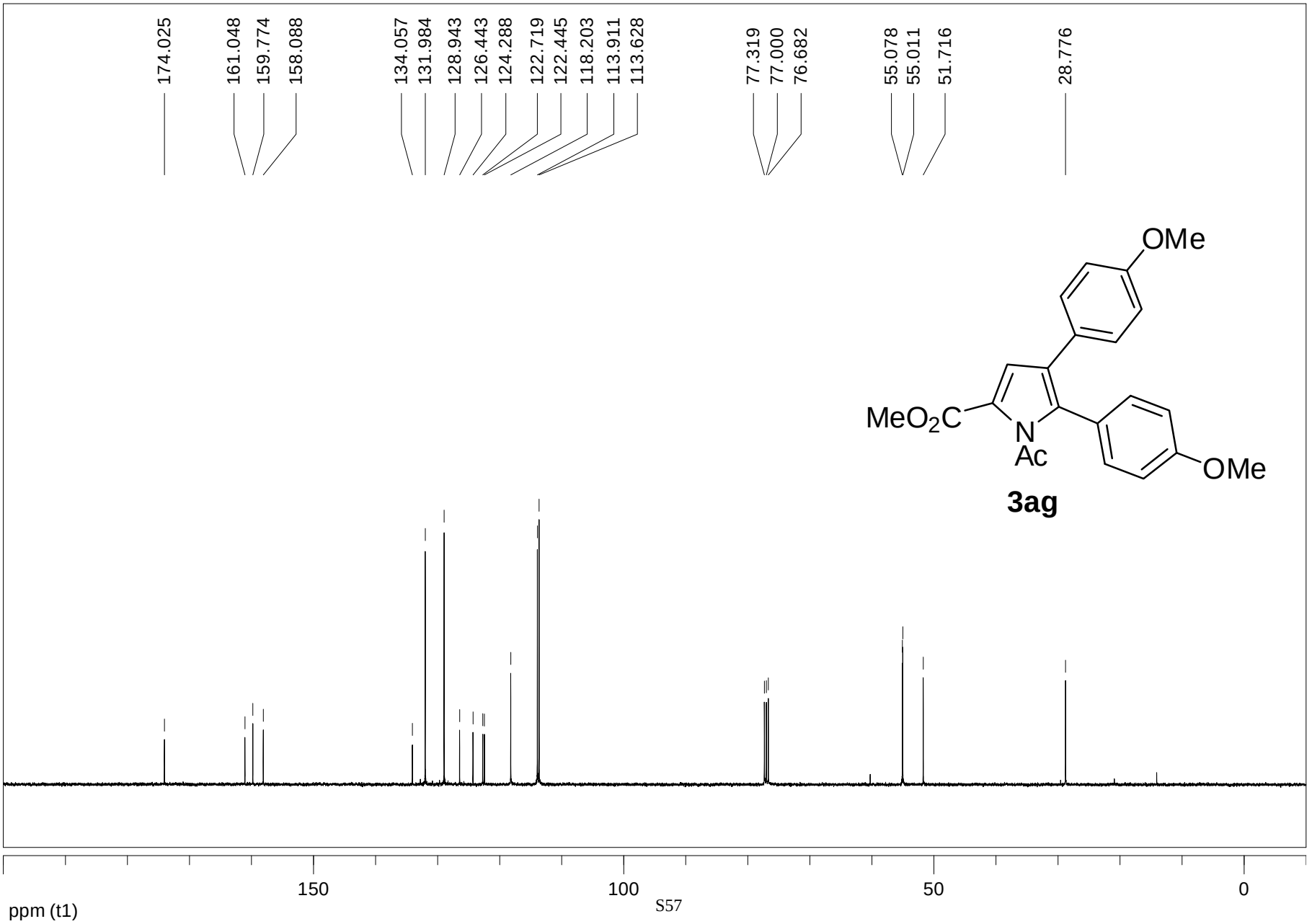
131.046
130.438
129.227
128.905
127.763
127.705
124.551
122.639
118.333
77.318
77.000
76.682
51.732
28.812
21.273
20.963
MeO2C
N
Ac
3af
150
100
50
0
ppm (t1)


7.260
7.229
7.207
7.121
7.073
7.050
6.891
6.869
6.762
6.740
3.872
3.828
3.761
2.299
OMe
MeO2C
N
Ac
OMe
3ag
2.11
1.00
2.07
2.18
2.16
7.30
7.20
7.10
7.00
6.90
6.80
6.70
ppm (t1)
3.01
5.0
0.0
ppm (t1)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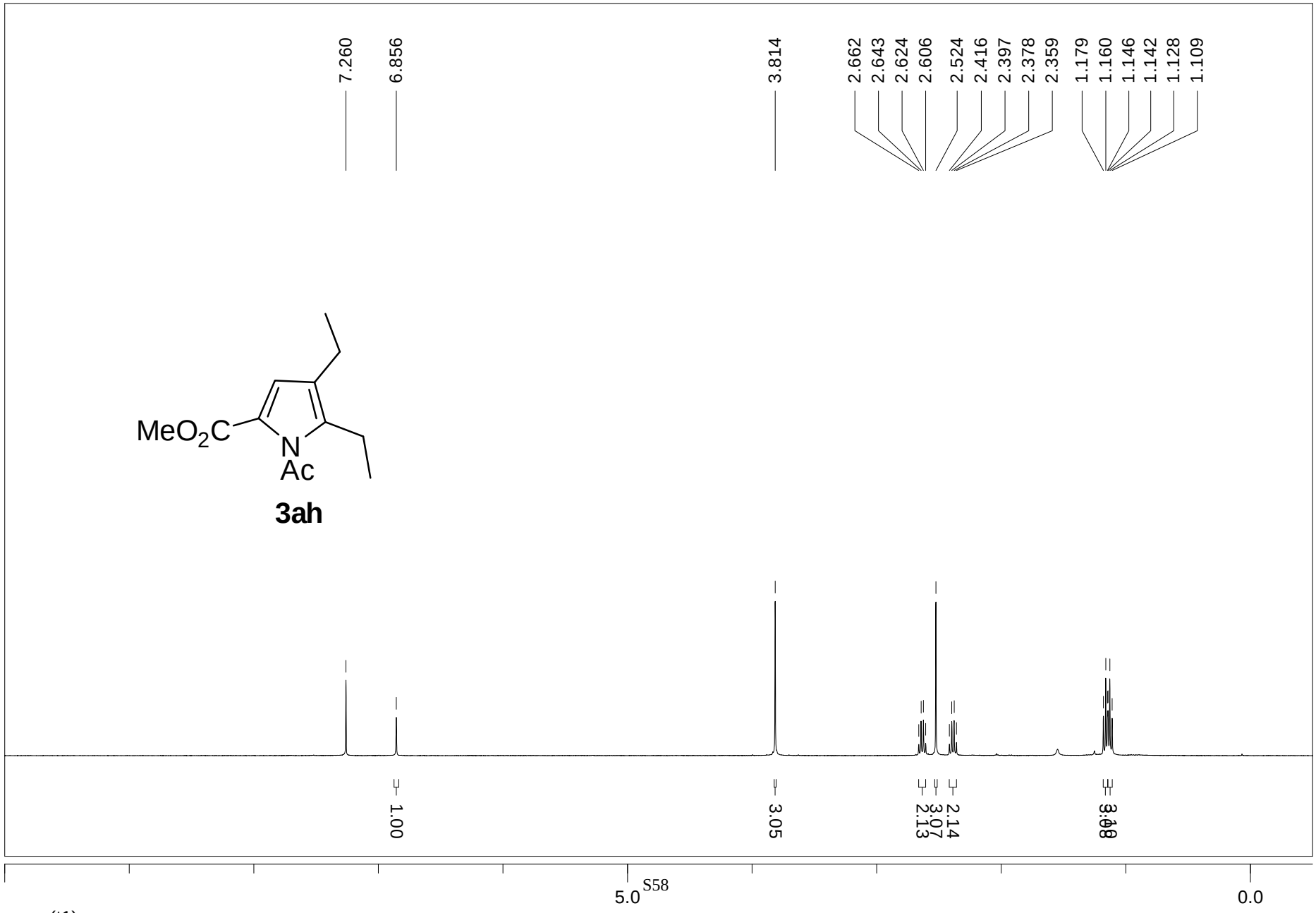
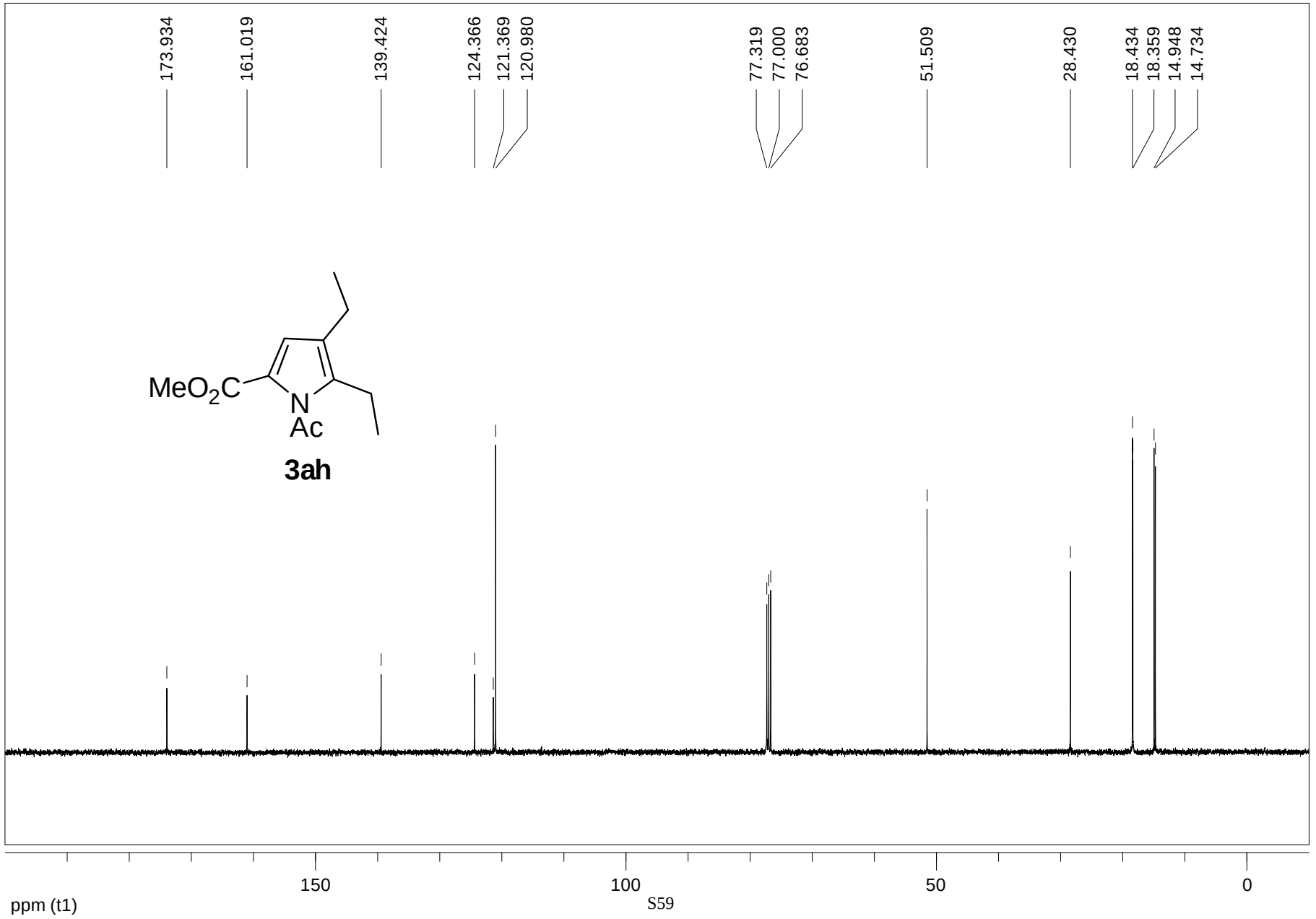
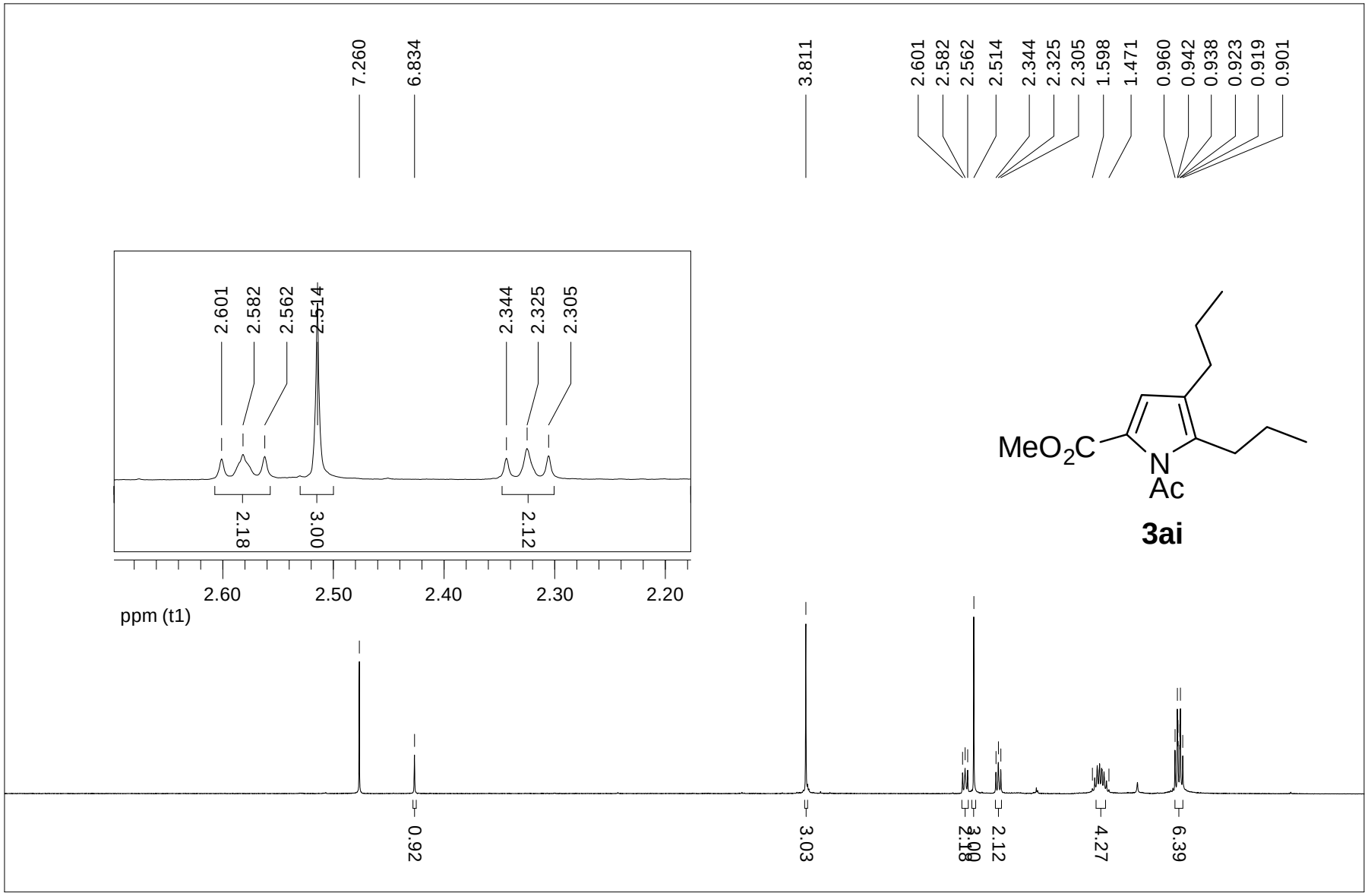
158.088
134.057
131.984
128.943
126.443
124.288
122.719
122.445
118.203
113.911
113.628
77.319
77.000
76.682
55.078
55.011
51.716
28.776
OMe
MeO2C
N
Ac
OMe
3ag
150
100
50
0
ppm (t1)


7.260
6.856
3.814
2.662
2.643
2.624
2.606
2.524
2.416
2.397
2.378
2.359
1.179
1.160
1.146
1.142
1.128
1.109
MeO2C
N
Ac
3ah
1.00
3.05
2.13
3.07
2.14
5.0
0.0
ppm (t1)


173.934
161.019
139.424
124.366
121.369
120.980
77.319
77.000
76.683
51.509
28.430
18.434
18.359
14.948
14.734
MeO2C
N
Ac
3ah
150
100
50
0
ppm (t1)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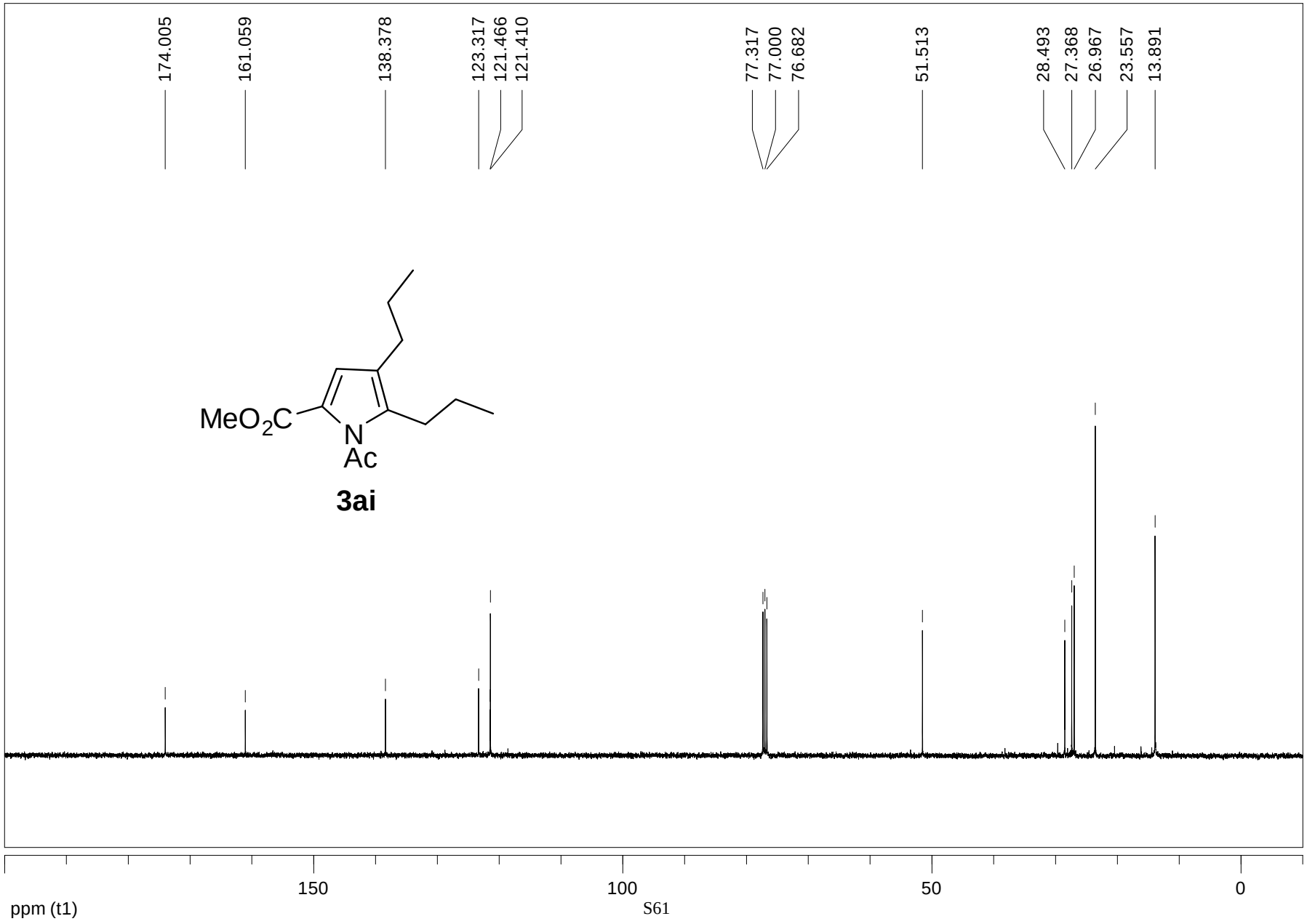
6.834
3.811
2.601
2.582
2.562
2.514
2.344
2.325
2.305
1.598
1.471
0.960
0.942
0.938
0.923
0.919
0.901
2.18
3.00
2.12
2.60
2.50
2.40
2.30
2.20
ppm (t1)
MeO2C
N
Ac
3ai
0.92
3.03
2.18
3.00
2.12
4.27
6.39
5.0
0.0
ppm (t1)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138.378
123.317
121.466
121.410
77.317
77.000
76.682
51.513
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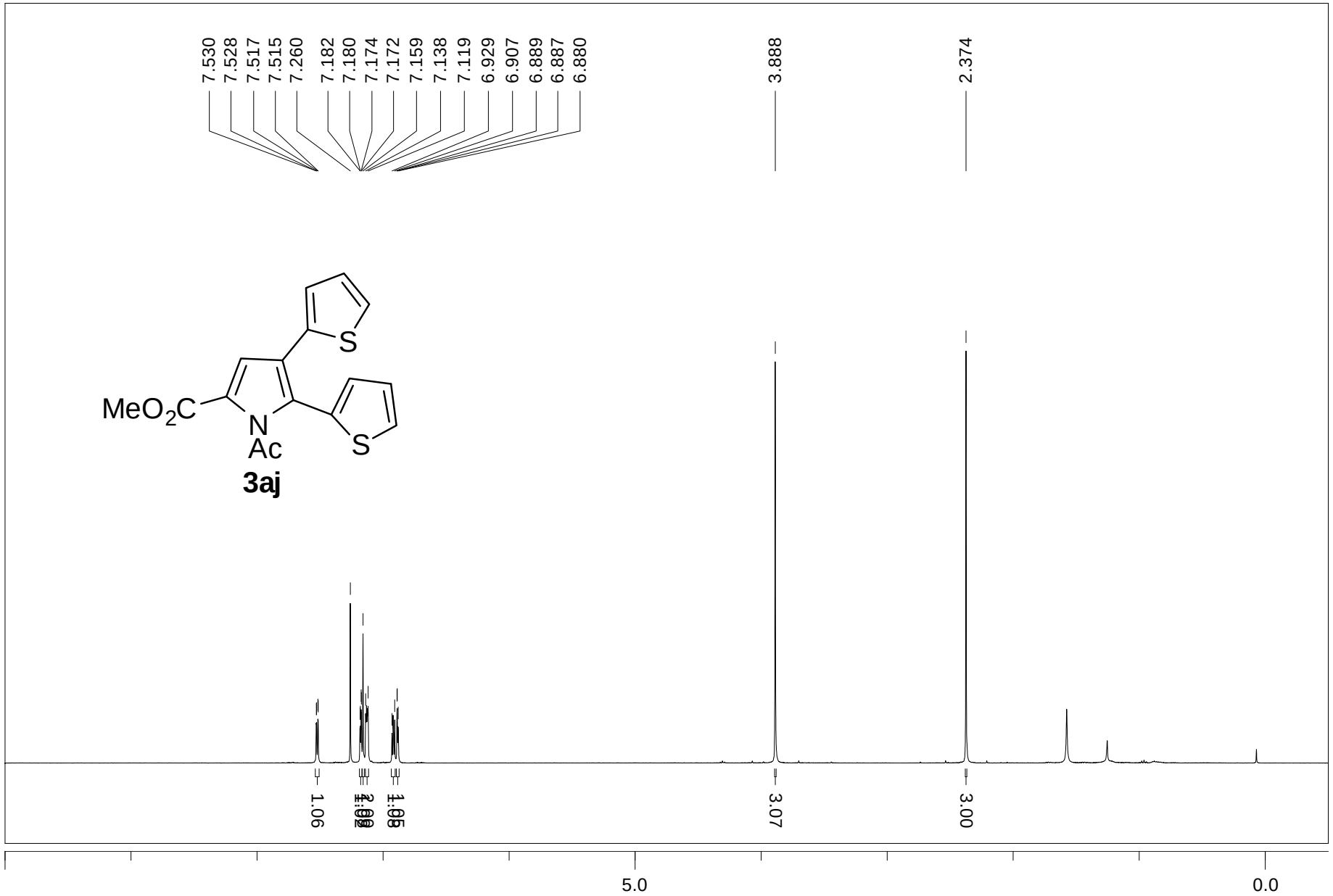
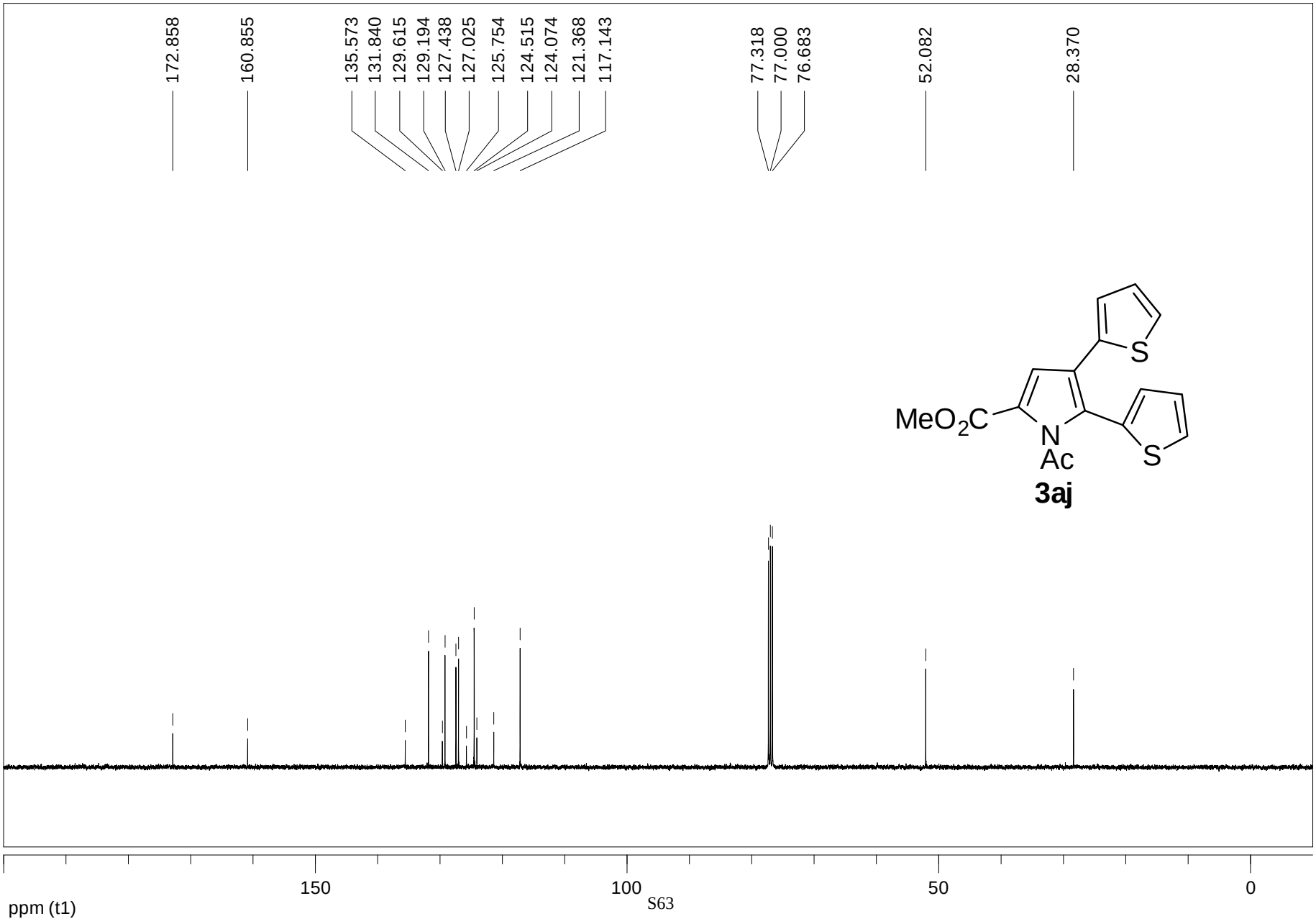
26.967
23.557
13.891
MeO2C
N
Ac
3ai
150
100
50
0
ppm (t1)


7.530
7.528
7.517
7.515
7.260
7.182
7.180
7.174
7.172
7.159
7.138
7.119
6.929
6.907
6.889
6.887
6.880
3.888
2.374
MeO2C
N
Ac
S
S
3aj
1.06
3.07
3.00
5.0
0.0
ppm (t1)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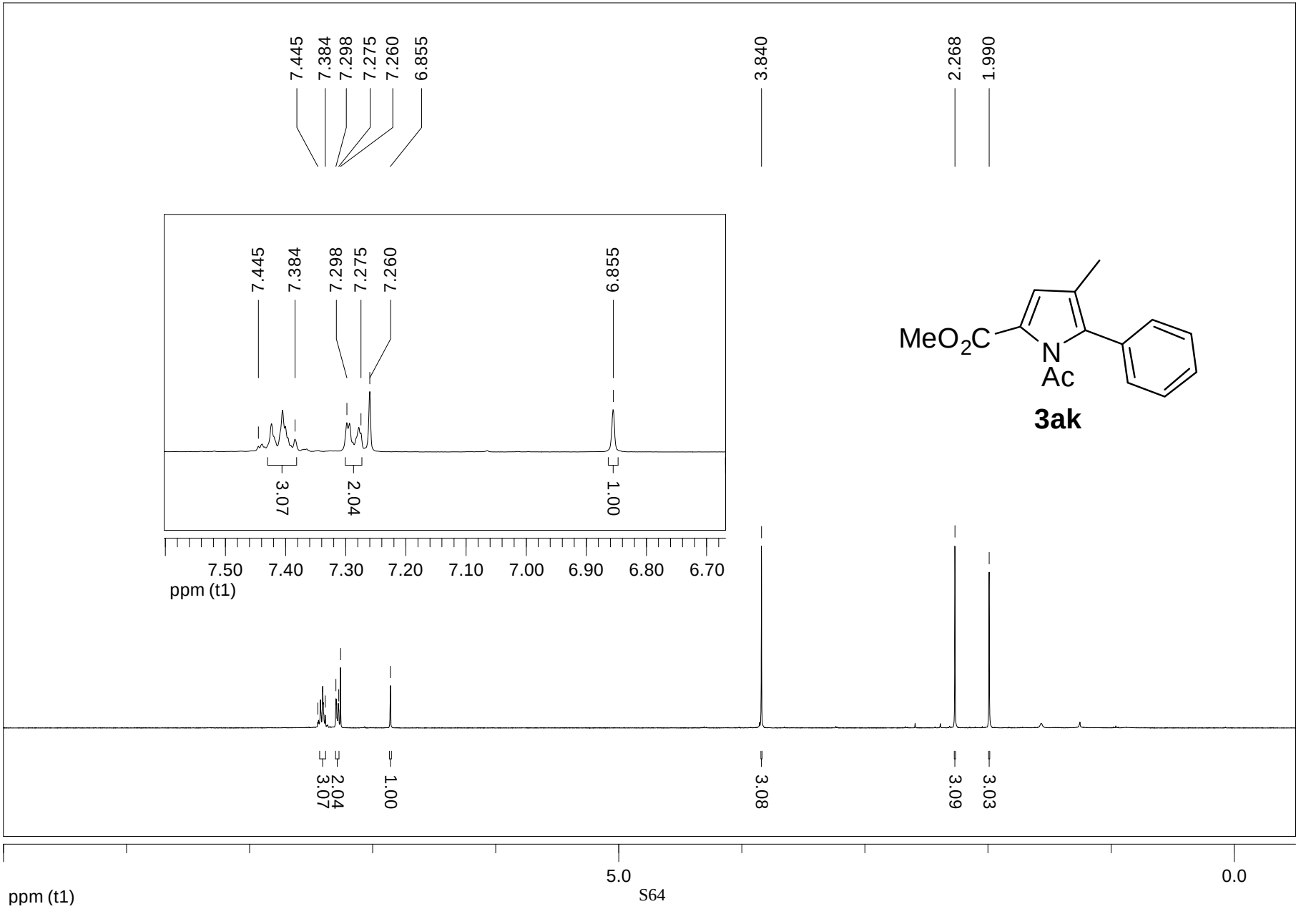
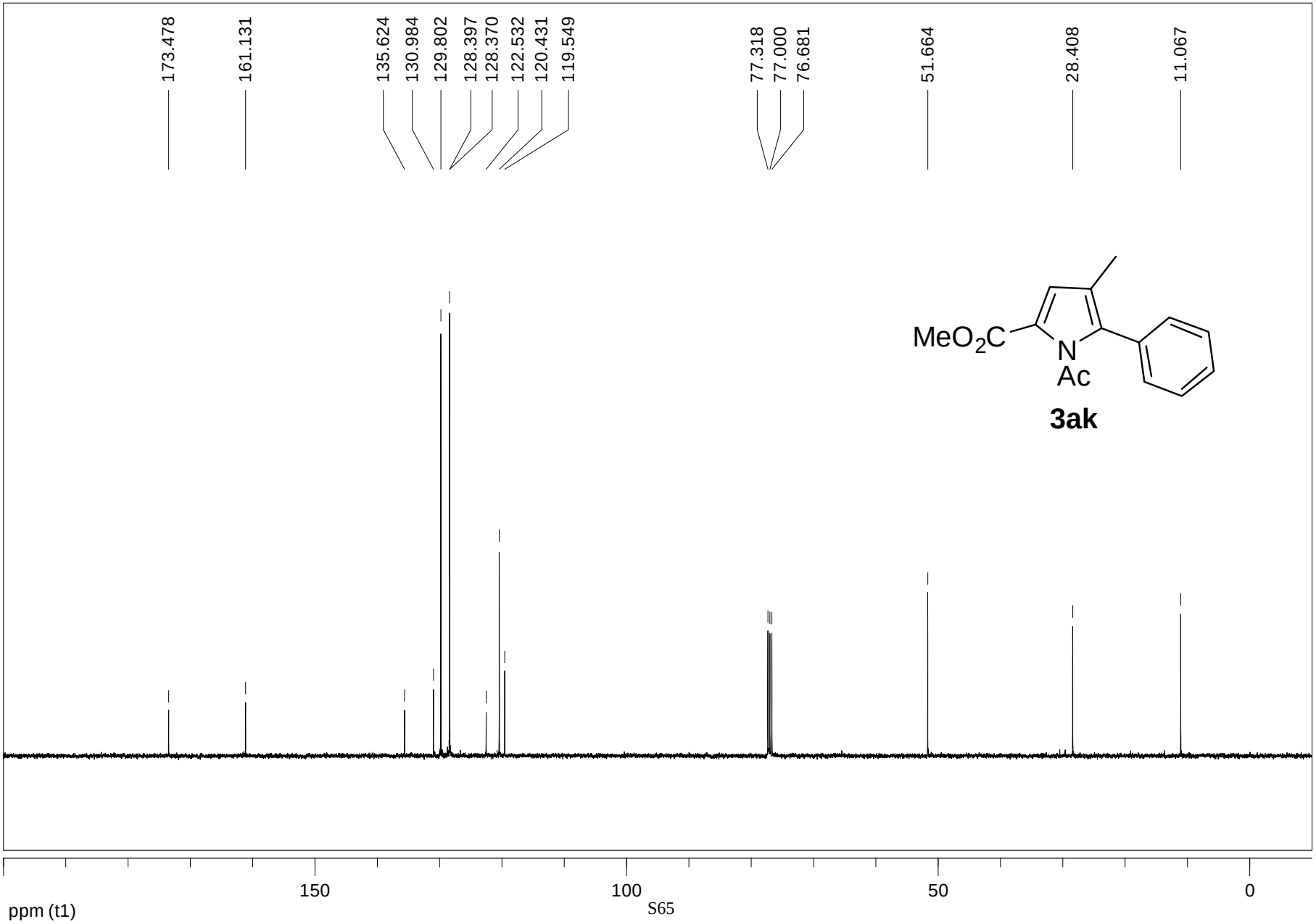
129.194
127.438
127.025
125.754
124.515
124.074
121.368
117.143
77.318
77.000
76.683
52.082
28.370
MeO2C
N
Ac
S
S
3aj
150
100
50
0
ppm (t1)


7.445
7.384
7.298
7.275
7.260
6.855
3.840
2.268
1.990
3.07
2.04
1.00
7.50
7.40
7.30
7.20
7.10
7.00
6.90
6.80
6.70
ppm (t1)
MeO2C
N
Ac
3ak
3.08
3.09
3.03
5.0
0.0
ppm (t1)


173.478
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135.624
130.984
129.802
128.397
128.370
122.532
120.431
119.549
77.318
77.000
76.681
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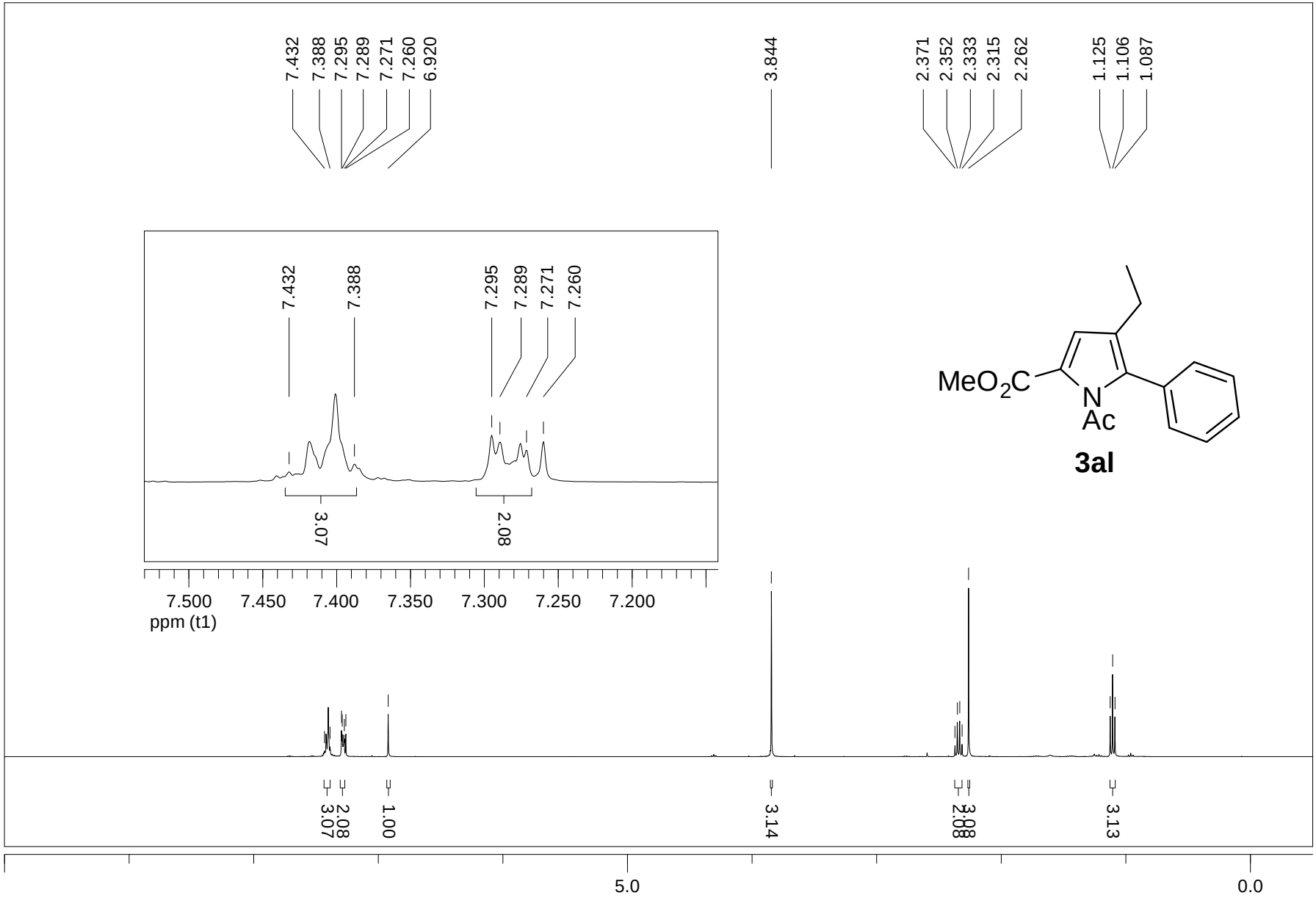
11.067
MeO2C
N
Ac
3ak
150
100
50
0
ppm (t1)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6.920
3.844
2.371
2.352
2.333
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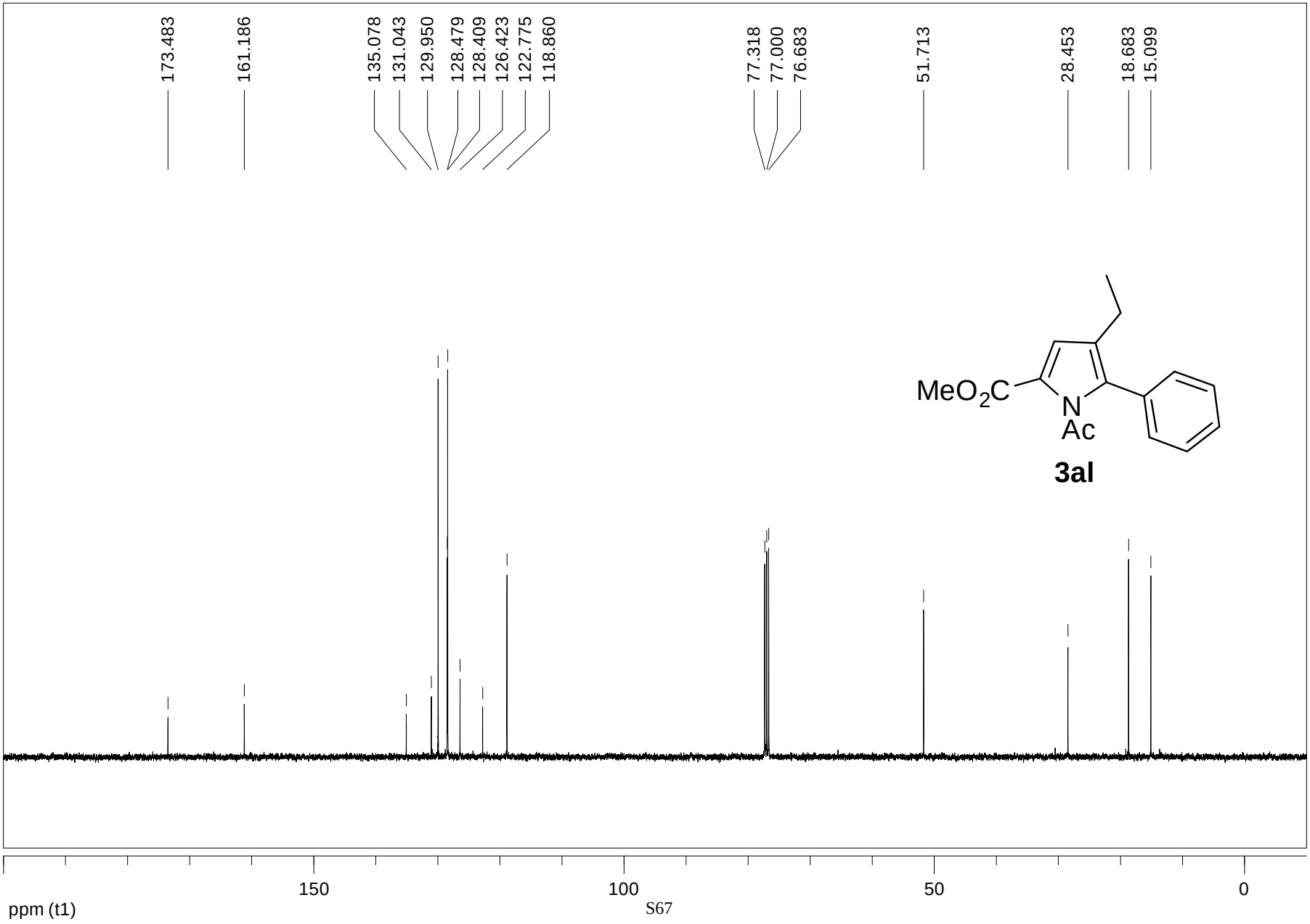
2.262
1.125
1.106
1.087
3.07
2.08
7.500
7.450
7.400
7.350
7.300
7.250
7.200
ppm (t1)
MeO2C
N
Ac
3al
3.07
2.08
1.00
3.14
2.08
3.13
5.0
0.0
ppm (t1)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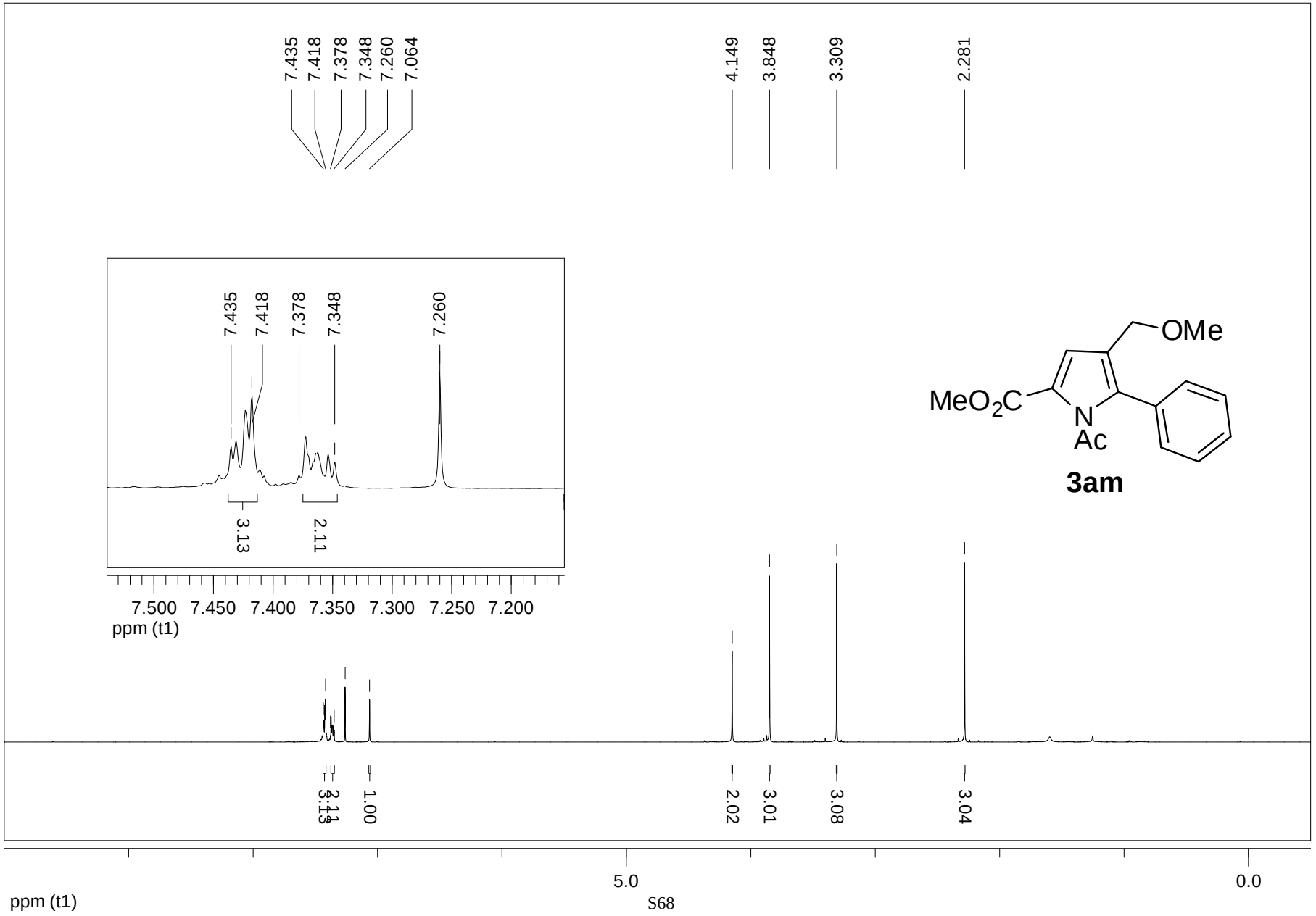
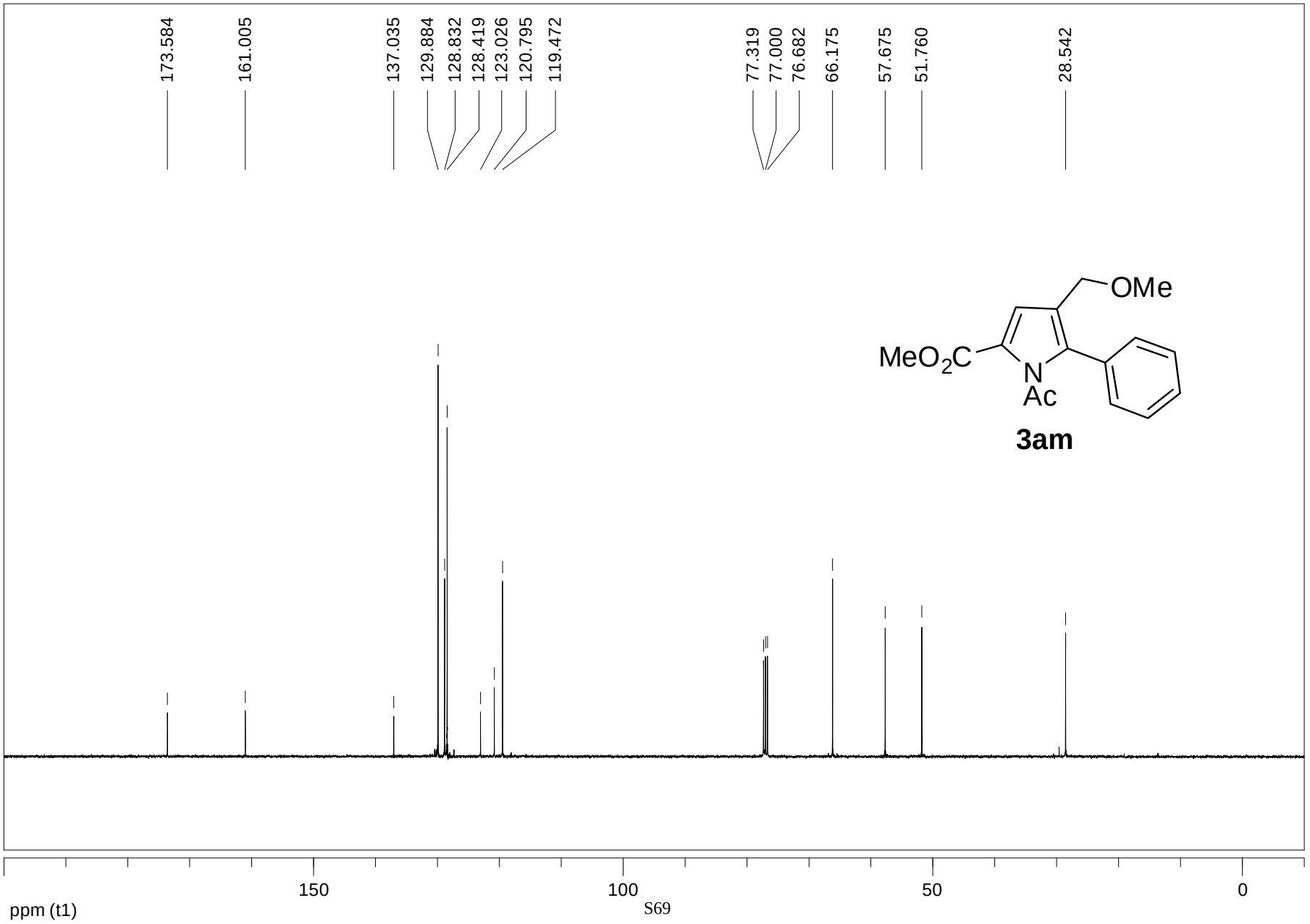
128.479
128.409
126.423
122.775
118.860
77.318
77.000
76.683
51.713
28.453
18.683
15.099
MeO2C
N
Ac
3al
150
100
50
0
ppm (t1)


7.435
7.418
7.378
7.348
7.260
7.064
4.149
3.848
3.309
2.281
OMe
MeO2C
N
Ac
3am
3.13
2.11
7.500 7.450 7.400 7.350 7.300 7.250 7.200
ppm (t1)
1.00
2.02
3.01
3.08
3.04
5.0
0.0
ppm (t1)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77.319
77.000
76.682
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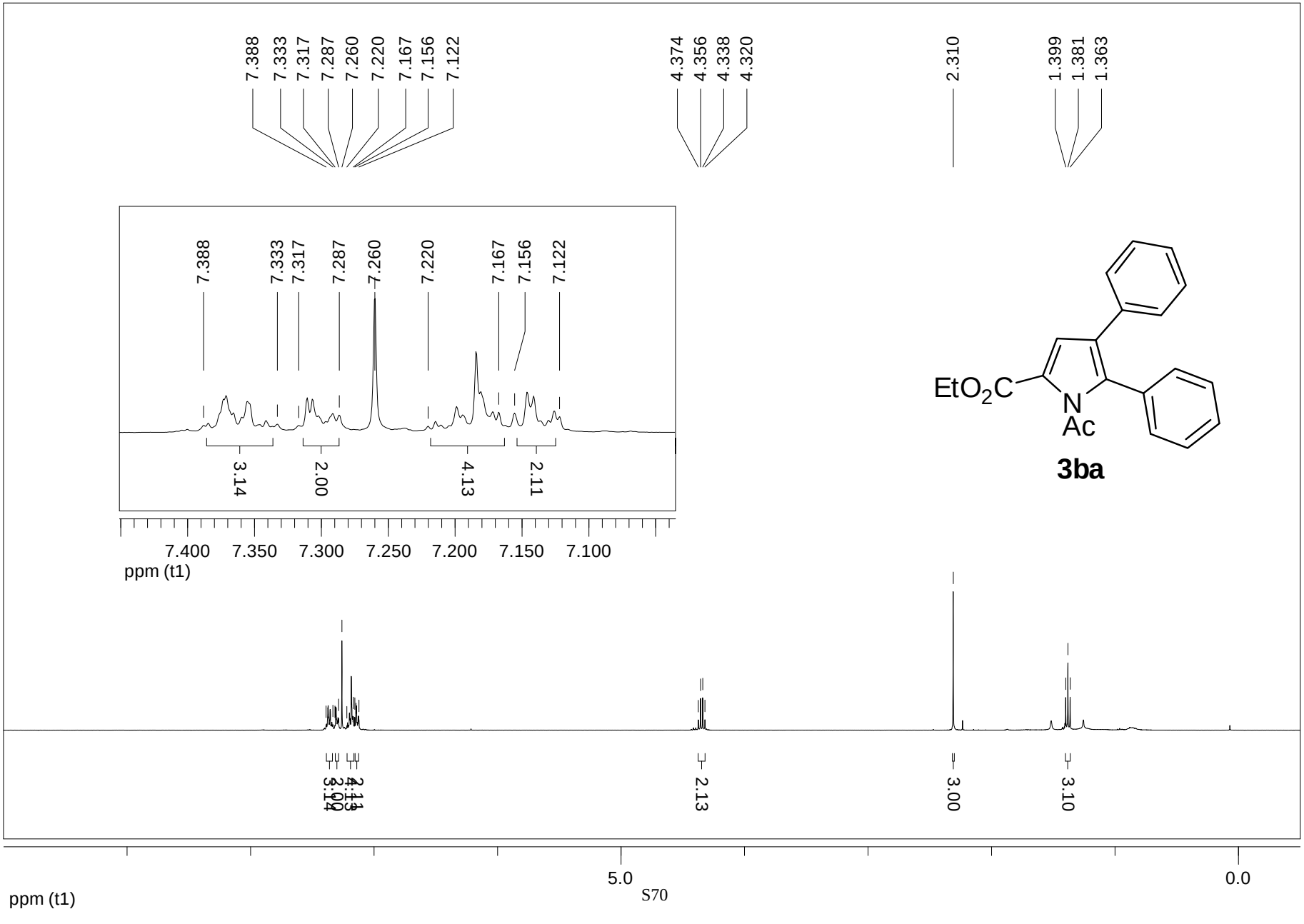
51.760
28.542
OMe
MeO2C
N
Ac
3am
150
100
50
0
ppm (t1)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7.156
7.122
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4.356
4.338
4.320
2.310
1.399
1.381
1.363
3.14
2.00
4.13
2.11
7.400
7.350
7.300
7.250
7.200
7.150
7.100
ppm (t1)
EtO2C
N
Ac
3ba
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3.10
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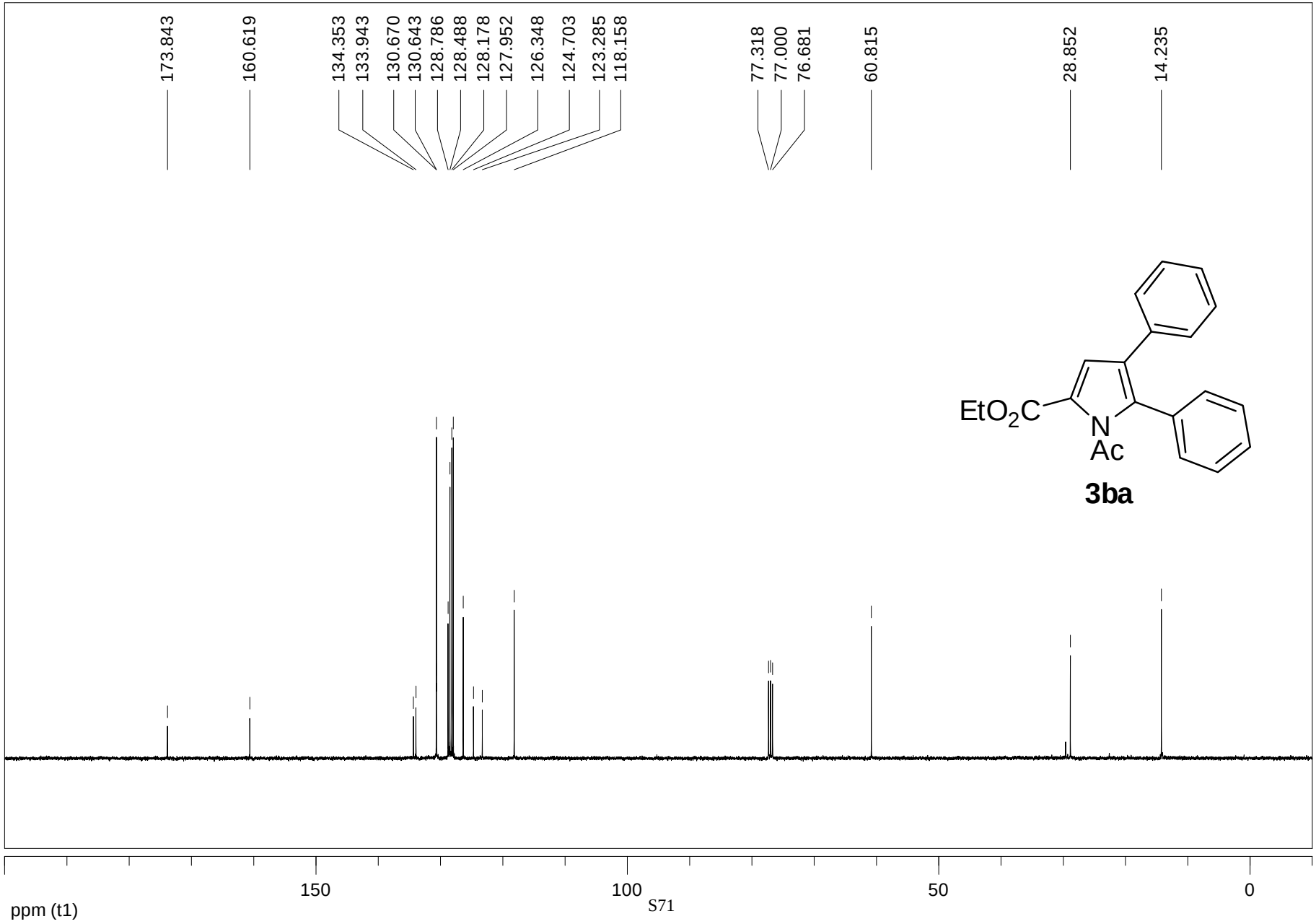
ppm (t1)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124.703
123.285
118.158
77.318
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28.852
14.235
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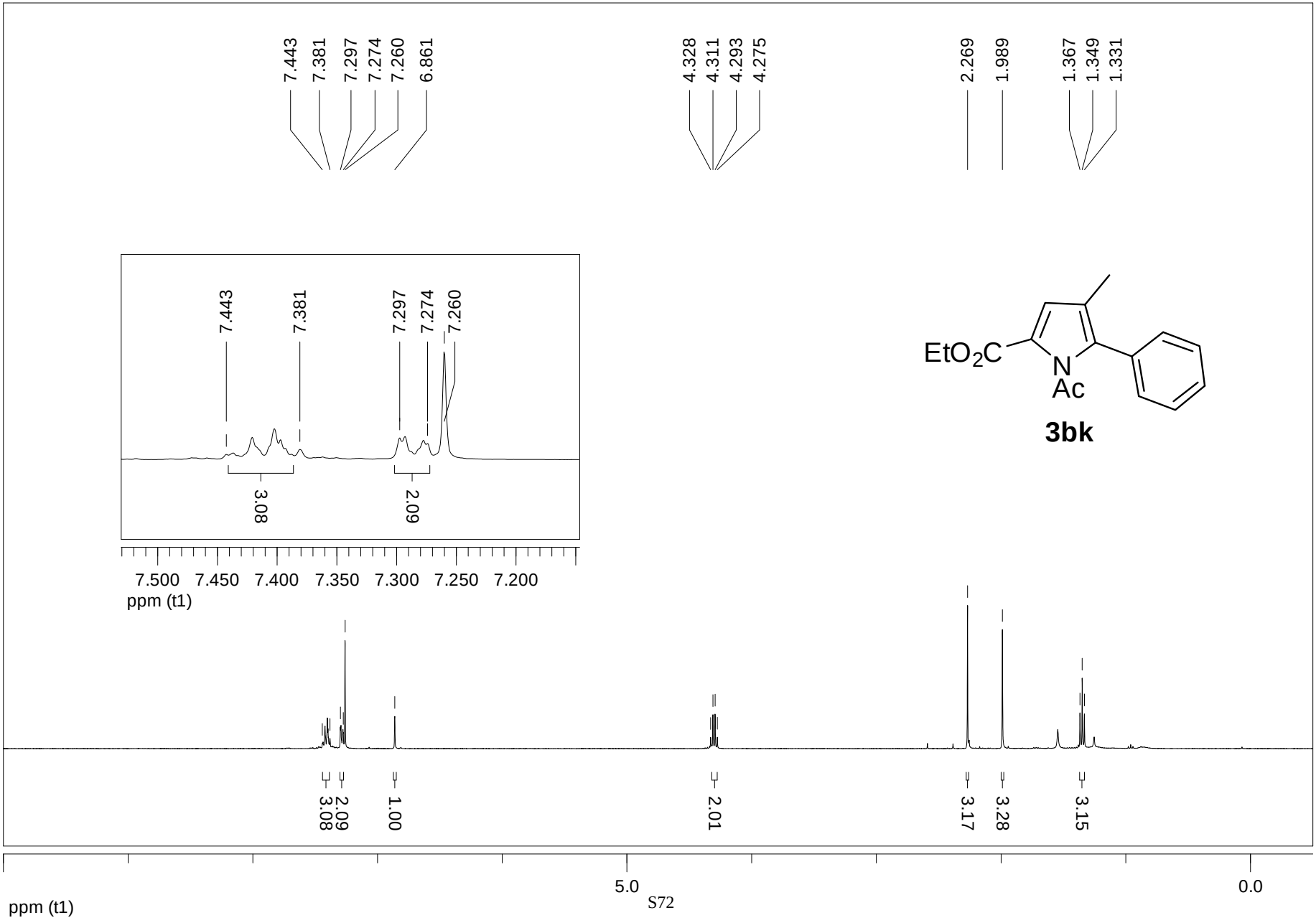
N
Ac
3ba
150
100
50
0
ppm (t1)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4.311
4.293
4.275
2.269
1.989
1.367
1.349
1.331
7.443
7.381
7.297
7.274
7.260
3.08
2.09
7.500 7.450 7.400 7.350 7.300 7.250 7.200
ppm (t1)
EtO2C
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Ac
3bk
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2.09
1.00
2.01
3.17
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3.15
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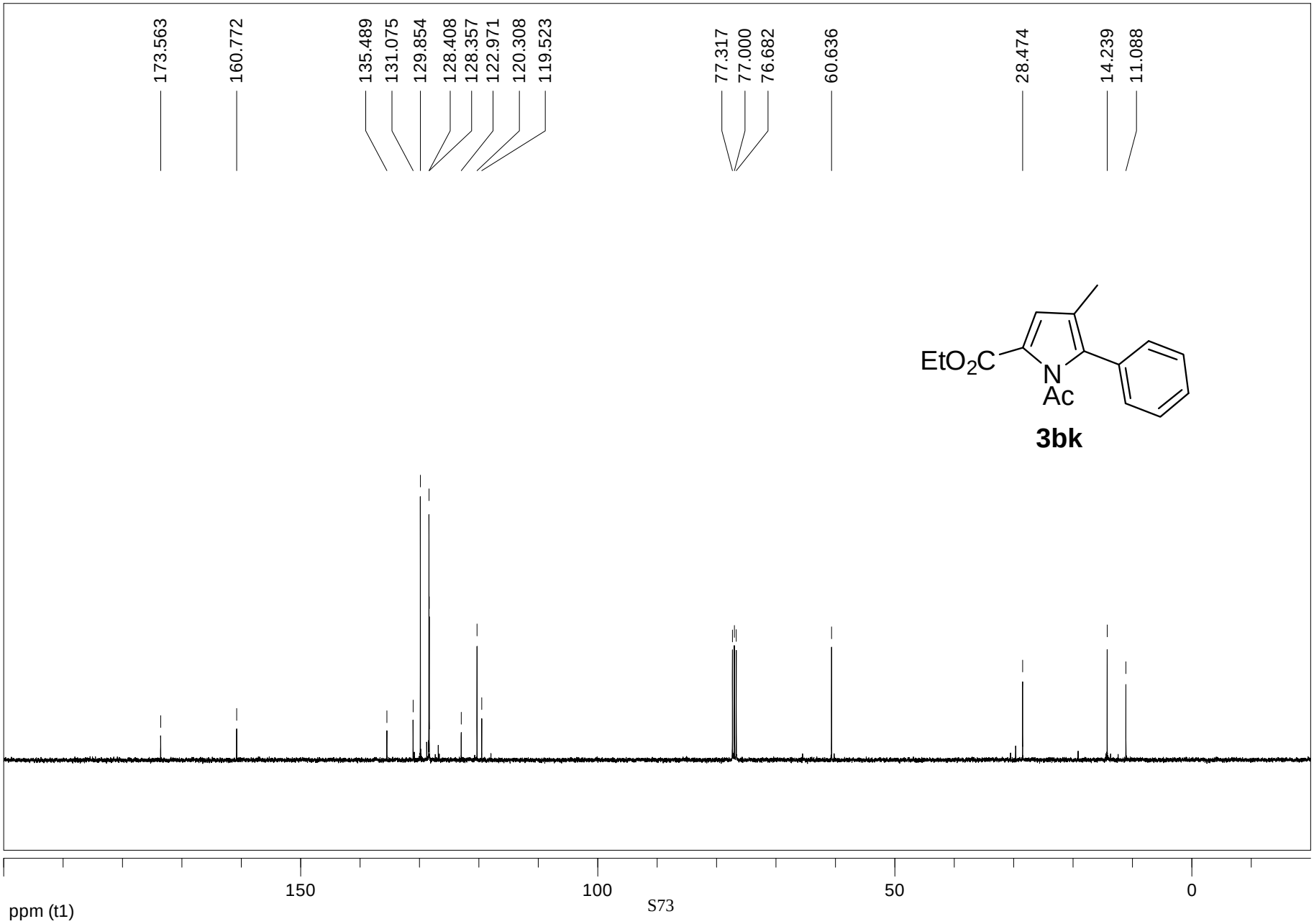
ppm (t1)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77.317
77.000
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14.239
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Ac
3bk
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50
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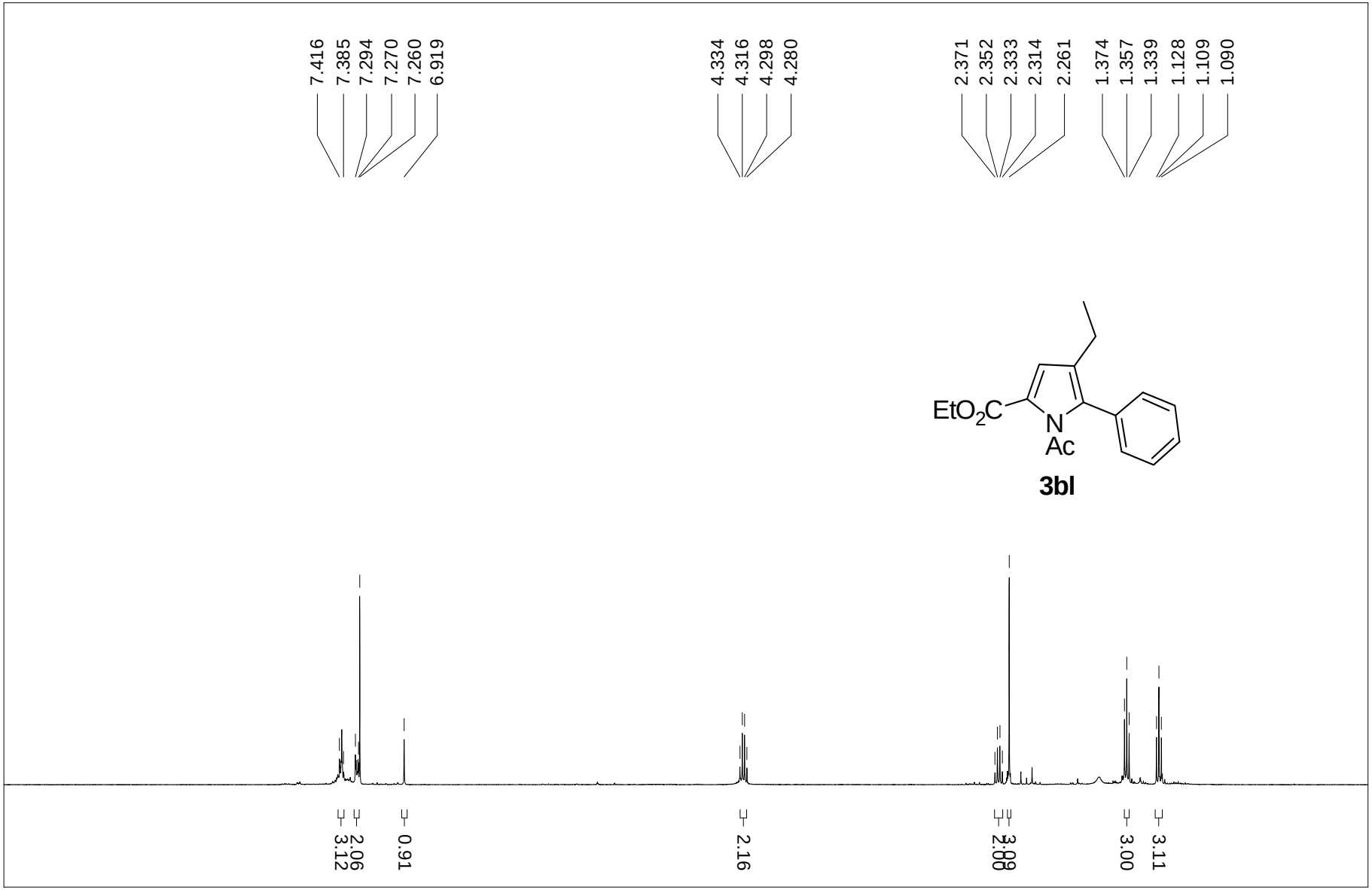
ppm (t1)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2.352
2.333
2.314
2.261
1.374
1.357
1.339
1.128
1.109
1.090
EtO2C
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Ac
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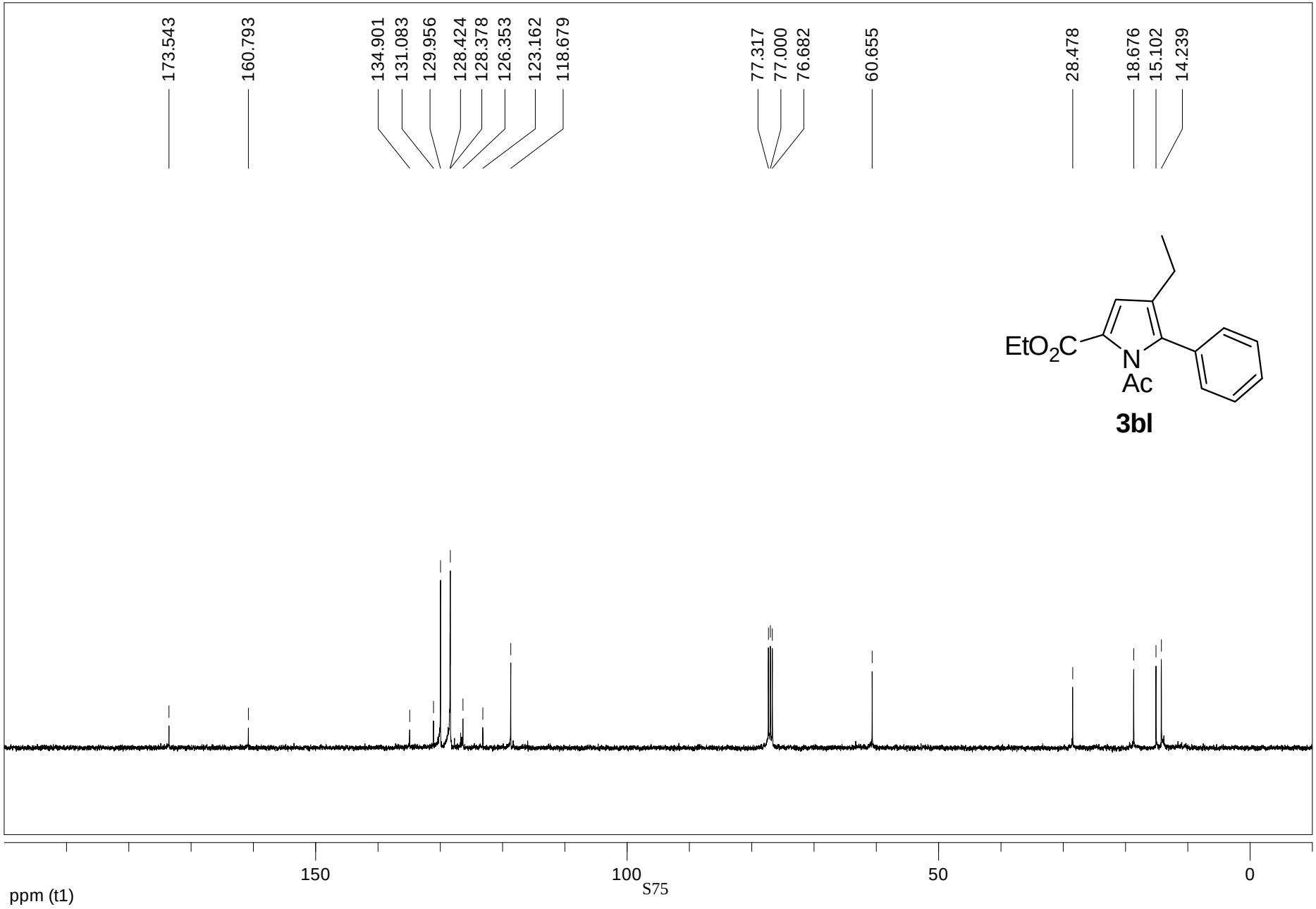
ppm (t1)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126.353
123.162
118.679
77.317
77.000
76.682
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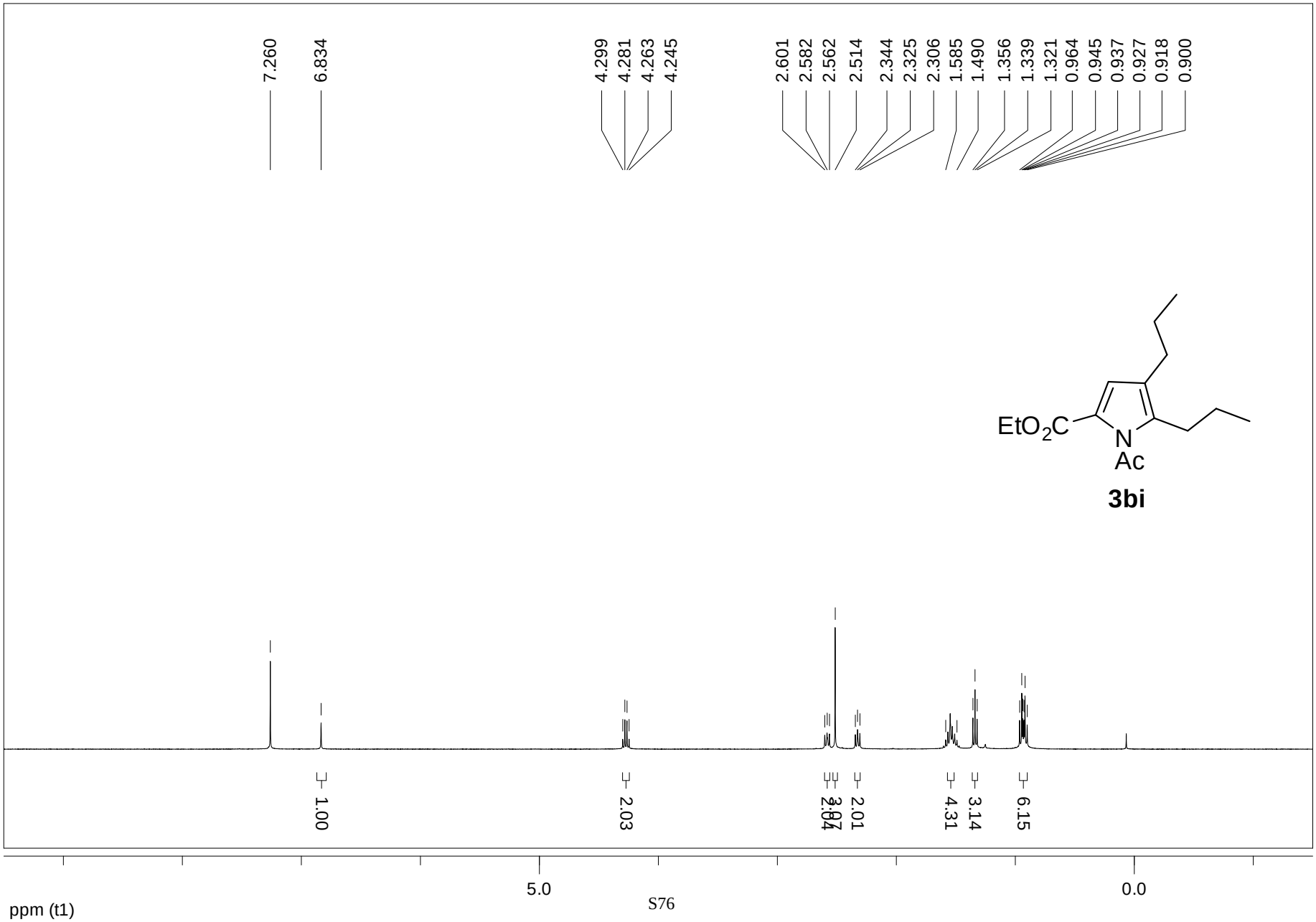
18.676
15.102
14.239
EtO2C
N
Ac
3bl
150
100
50
0
ppm (t1)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4.299
4.281
4.263
4.245
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2.582
2.562
2.514
2.344
2.325
2.306
1.585
1.490
1.356
1.339
1.321
0.964
0.945
0.937
0.927
0.918
0.900
EtO2C
N
Ac
3bi
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2.03
3.07
2.01
4.31
3.14
6.15
5.0
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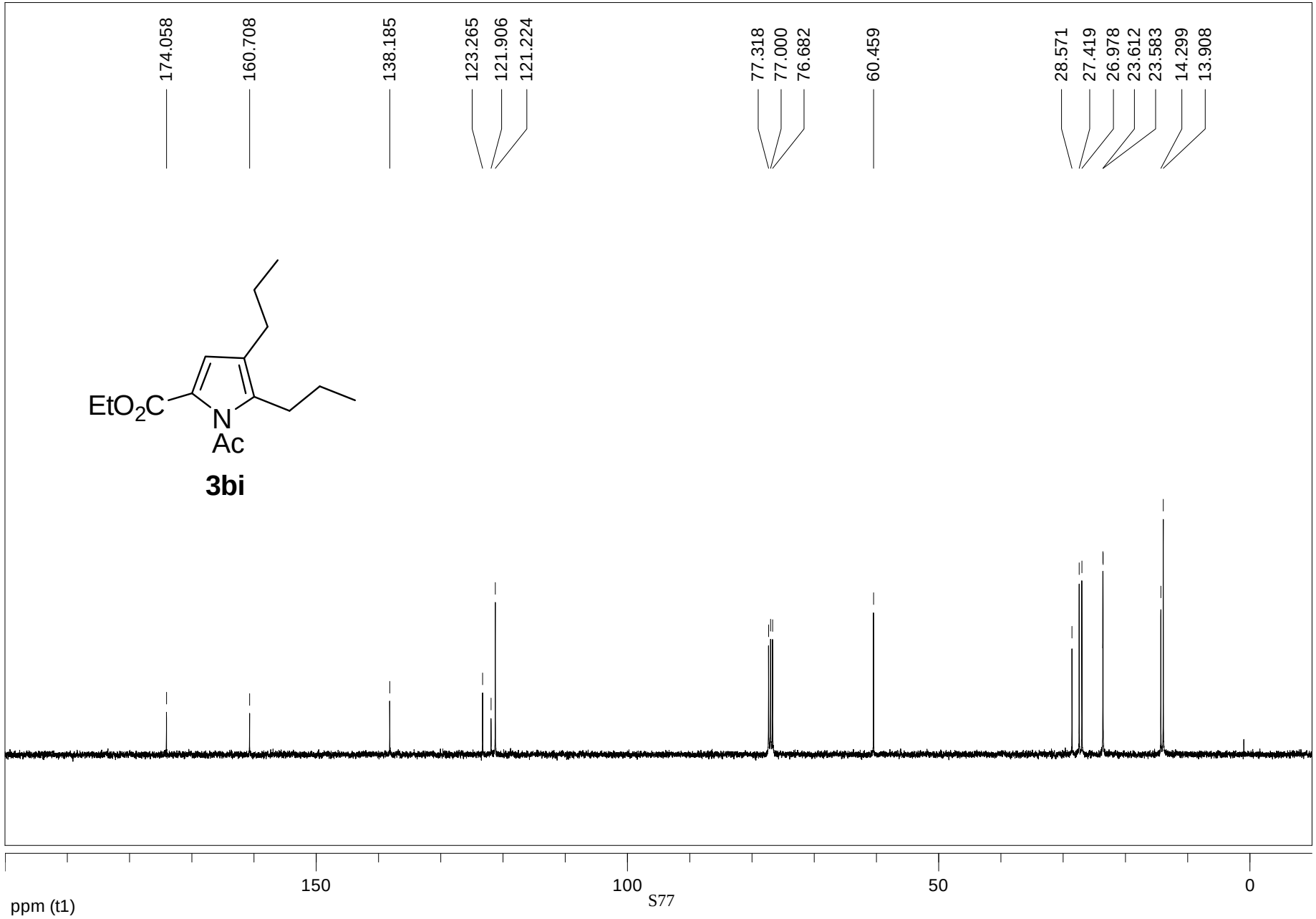
ppm (t1)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160.708
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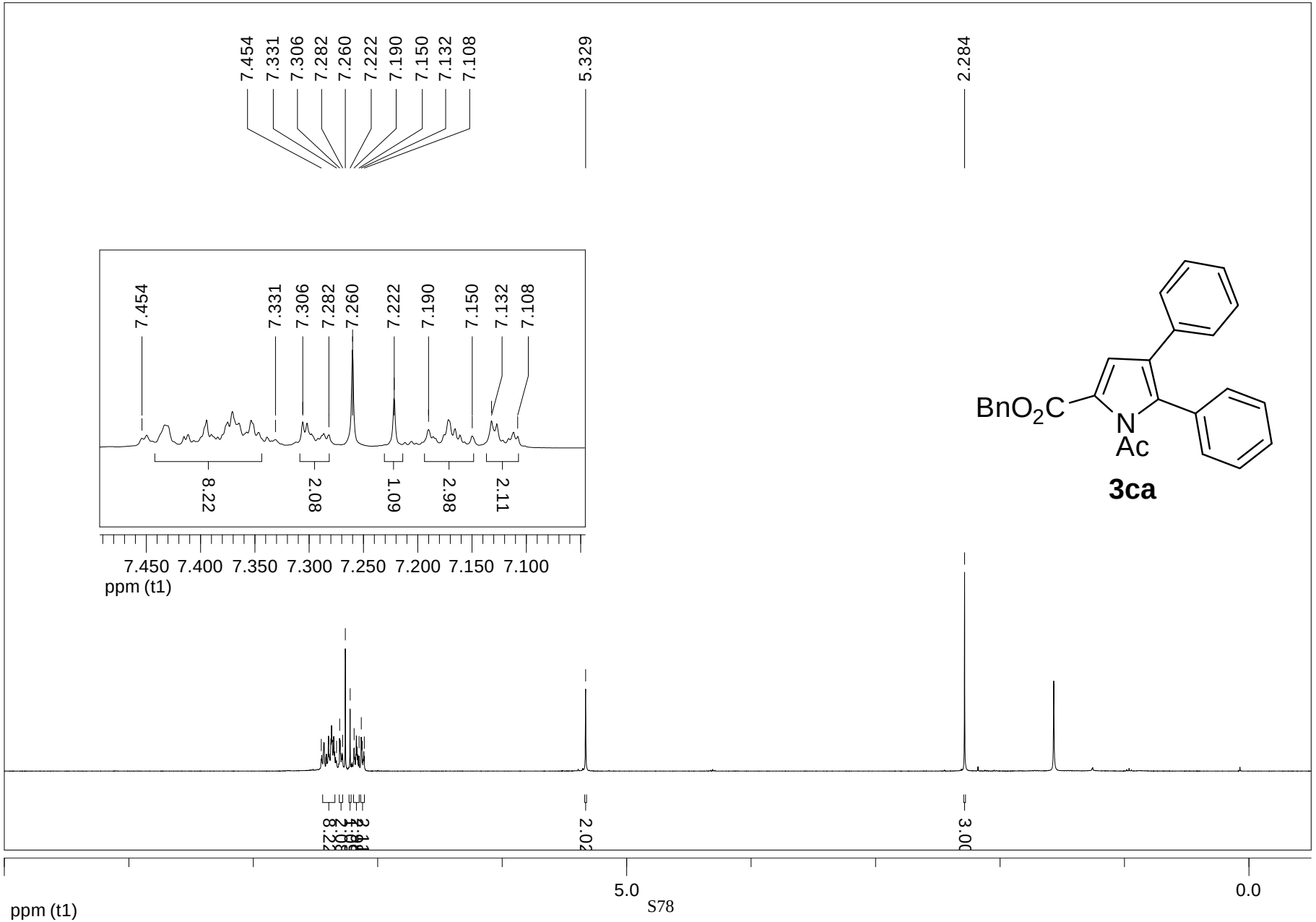
123.265
121.906
121.224
77.318
77.000
76.682
60.459
28.571
27.419
26.978
23.612
23.583
14.299
13.908
EtO2C
N
Ac
3bi
150
100
50
0
ppm (t1)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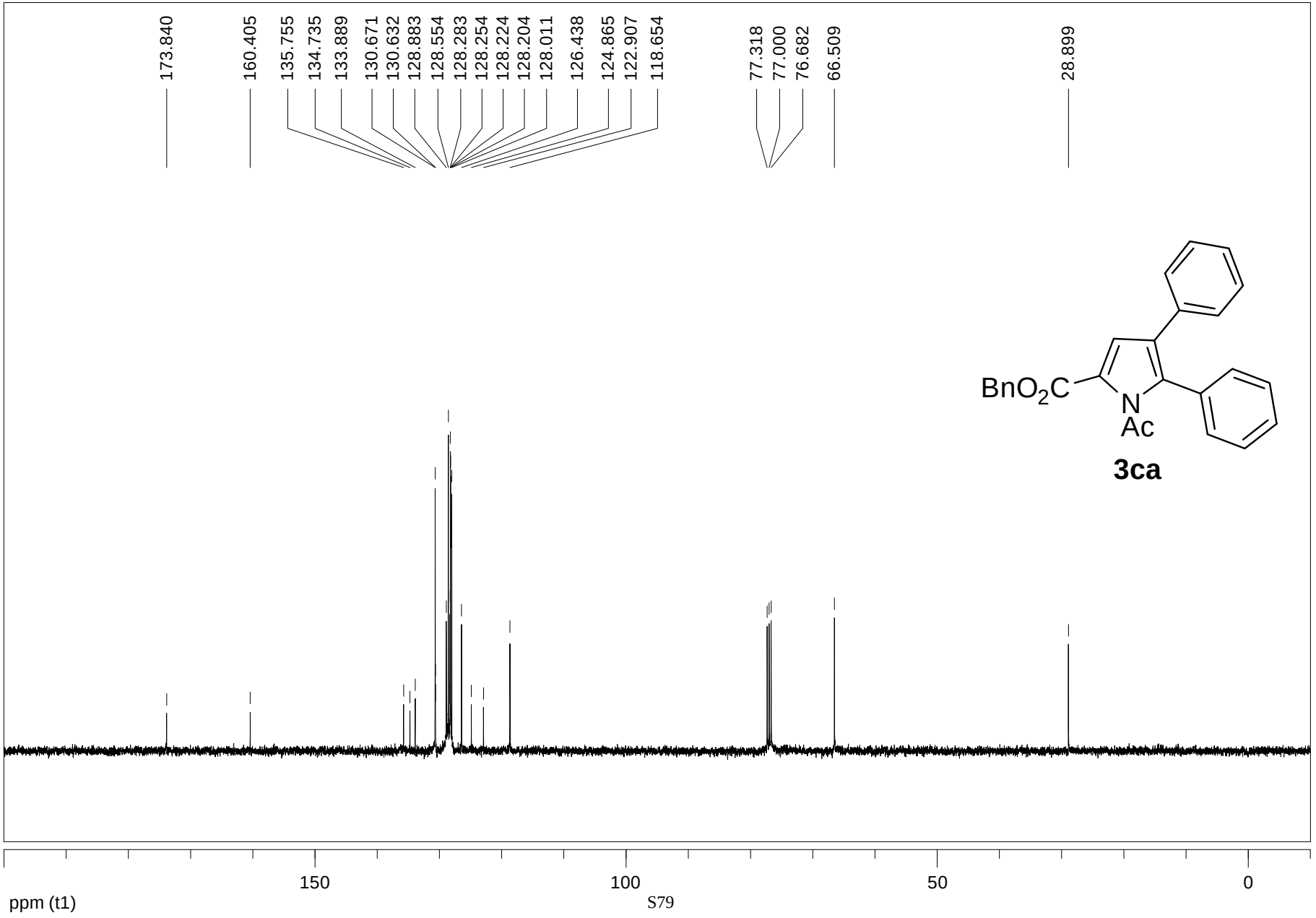
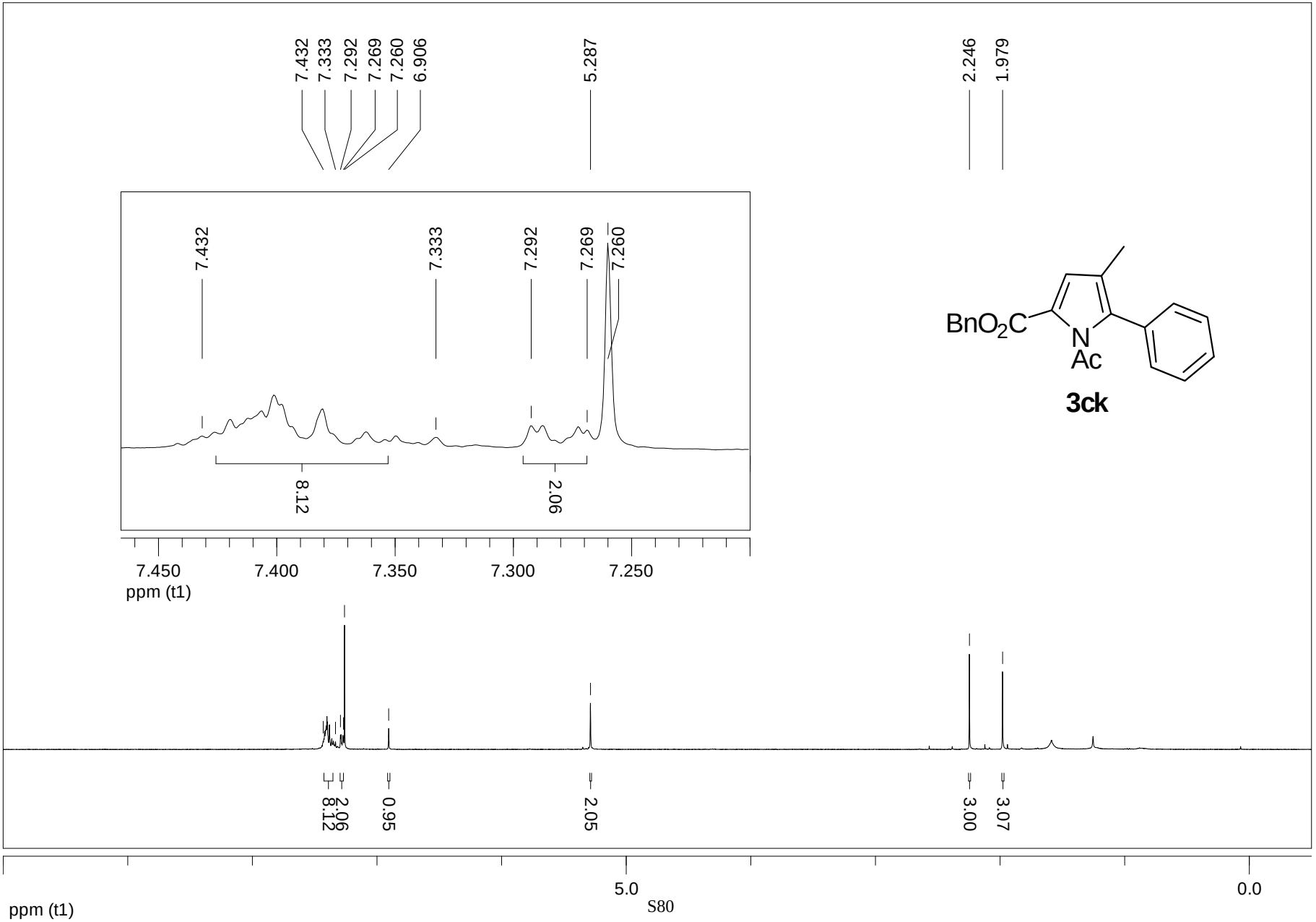
7.108
5.329
2.284
8.22
2.08
1.09
2.98
2.11
7.450 7.400 7.350 7.300 7.250 7.200 7.150 7.100
ppm (t1)
BnO2C
N
Ac
3ca
2.02
3.00
5.0
0.0
ppm (t1)


173.840
160.405
135.755
134.735
133.889
130.671
130.632
128.883
128.554
128.283
128.254
128.224
128.204
128.011
126.438
124.865
122.907
118.654
77.318
77.000
76.682
66.509
28.899
BnO2C
N
Ac
3ca
150
100
50
0
ppm (t1)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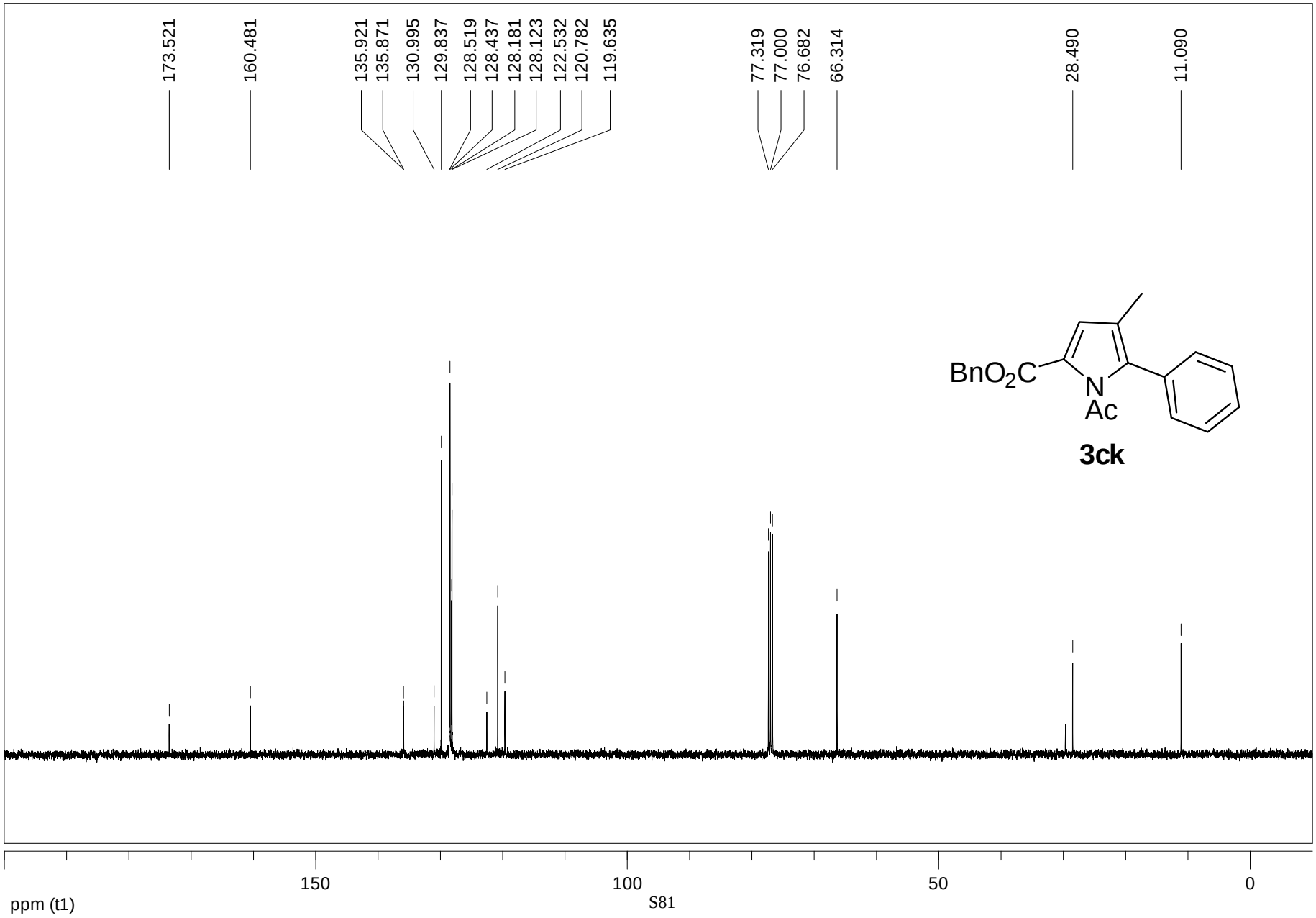
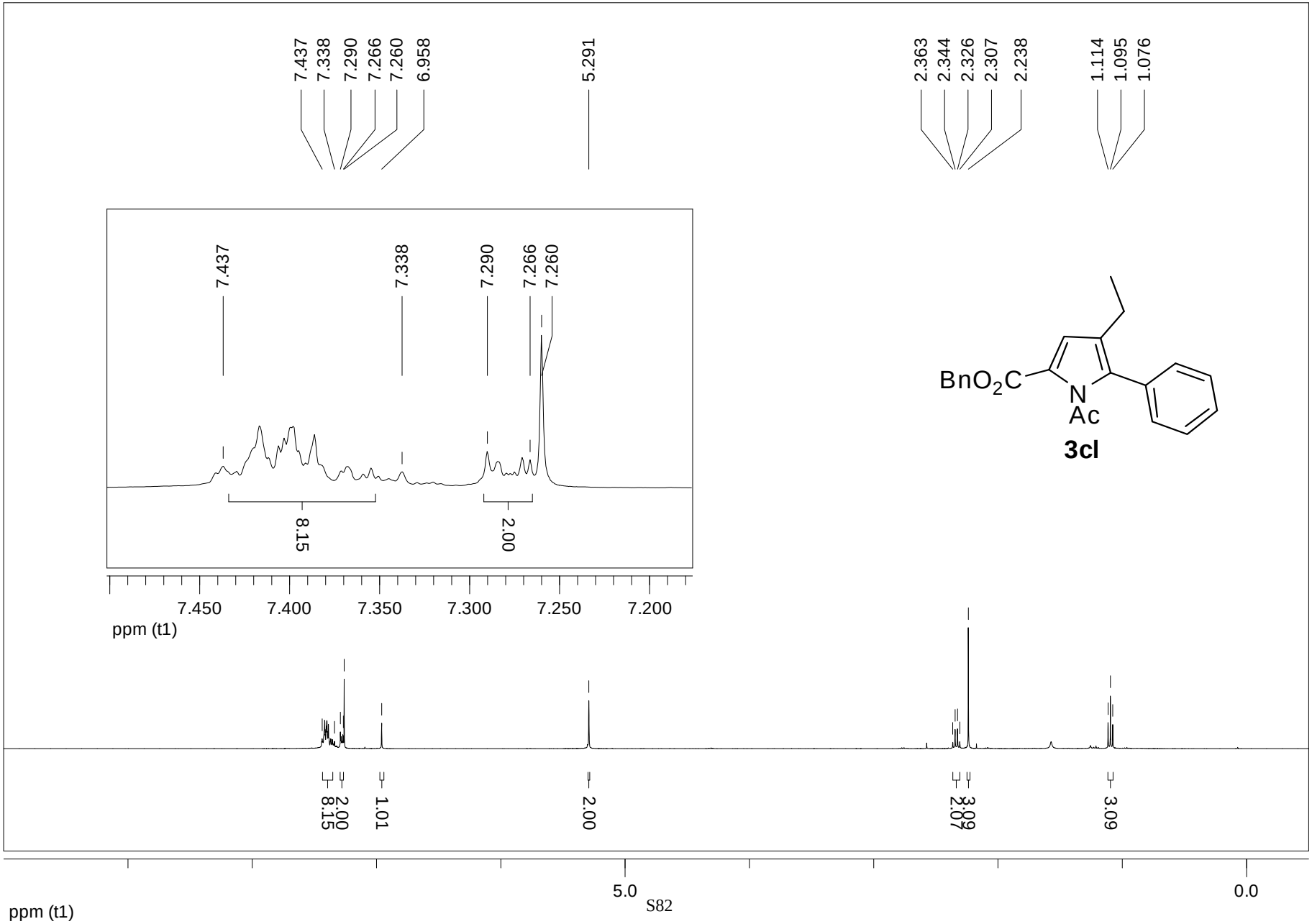
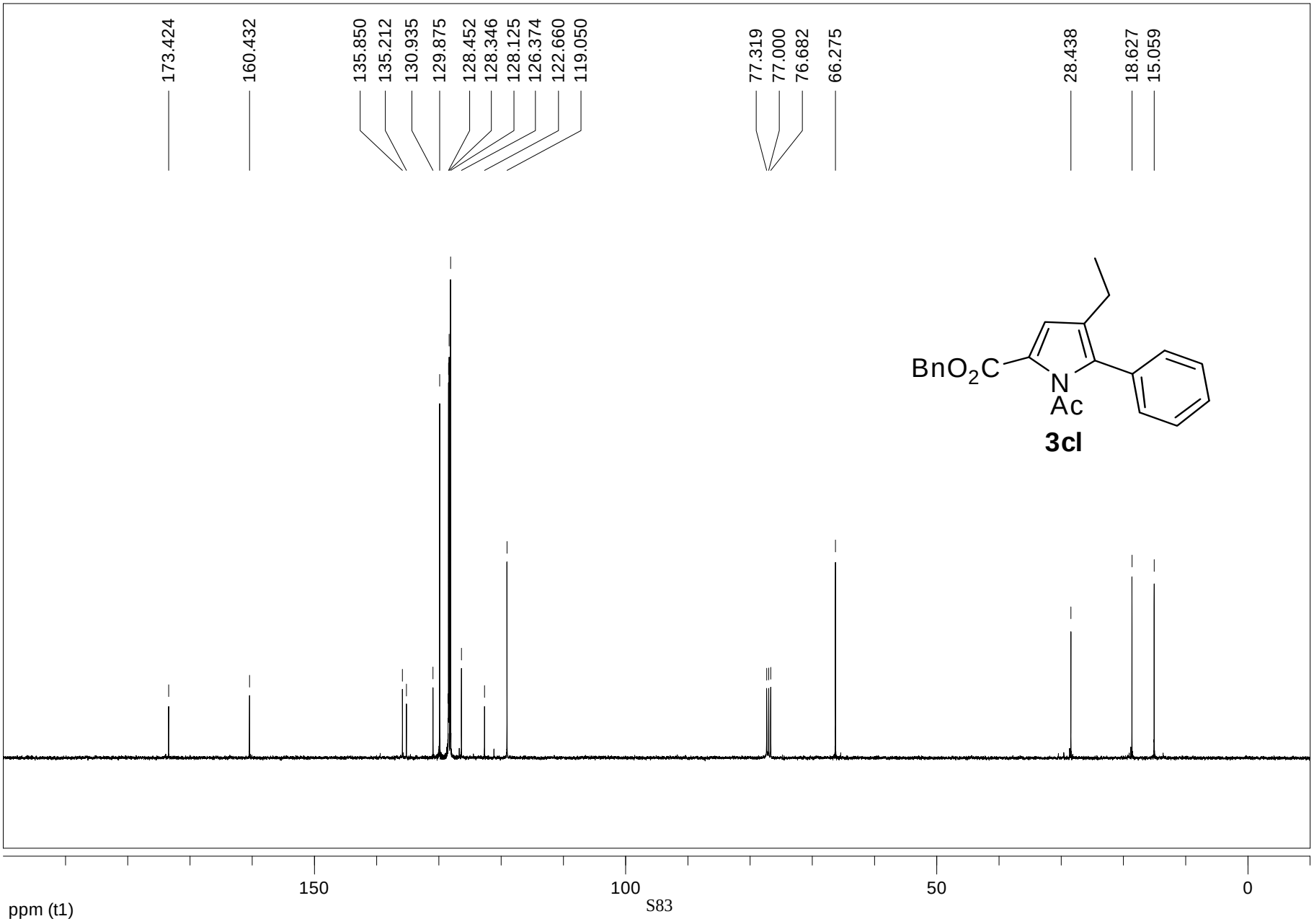
7.333
7.292
7.269
7.260
6.906
5.287
2.246
1.979
7.432
7.333
7.292
7.269
7.260
8.12
2.06
7.450
7.400
7.350
7.300
7.250
ppm (t1)
BnO2C
N
Ac
3ck
8.12
2.06
0.95
2.05
3.00
3.07
5.0
0.0
ppm (t1)


173.521
160.481
135.921
135.871
130.995
129.837
128.519
128.437
128.181
128.123
122.532
120.782
119.635
77.319
77.000
76.682
66.314
28.490
11.090
BnO2C
N
Ac
3ck
150
100
50
0
ppm (t1)


7.437
7.338
7.290
7.266
7.260
6.958
5.291
2.363
2.344
2.326
2.307
2.238
1.114
1.095
1.076
7.437
7.338
7.290
7.266
7.260
8.15
2.00
7.450
7.400
7.350
7.300
7.250
7.200
ppm (t1)
BnO2C
N
Ac
3cl
8.15
2.00
1.01
2.00
2.07
3.09
3.09
5.0
0.0
ppm (t1)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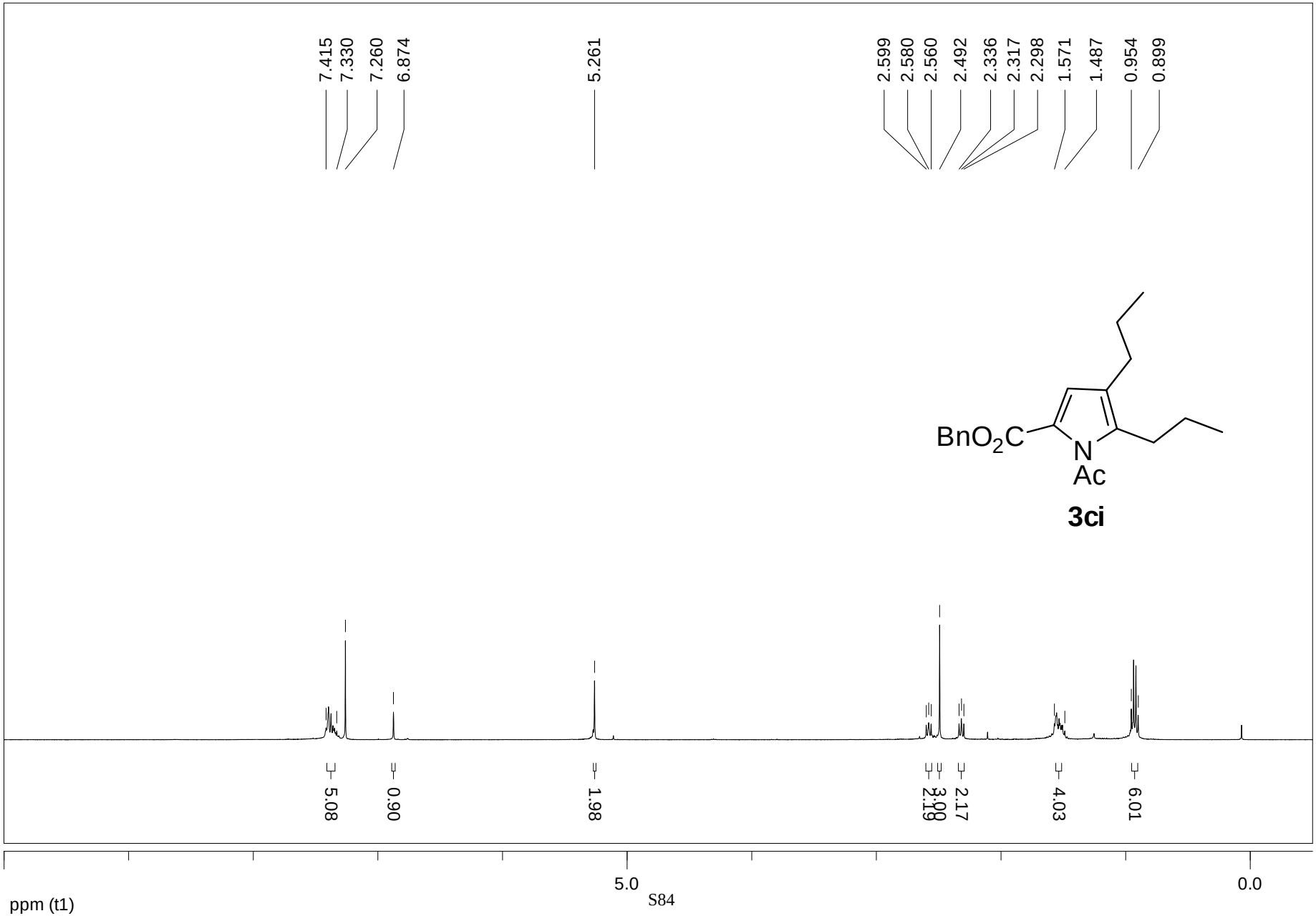
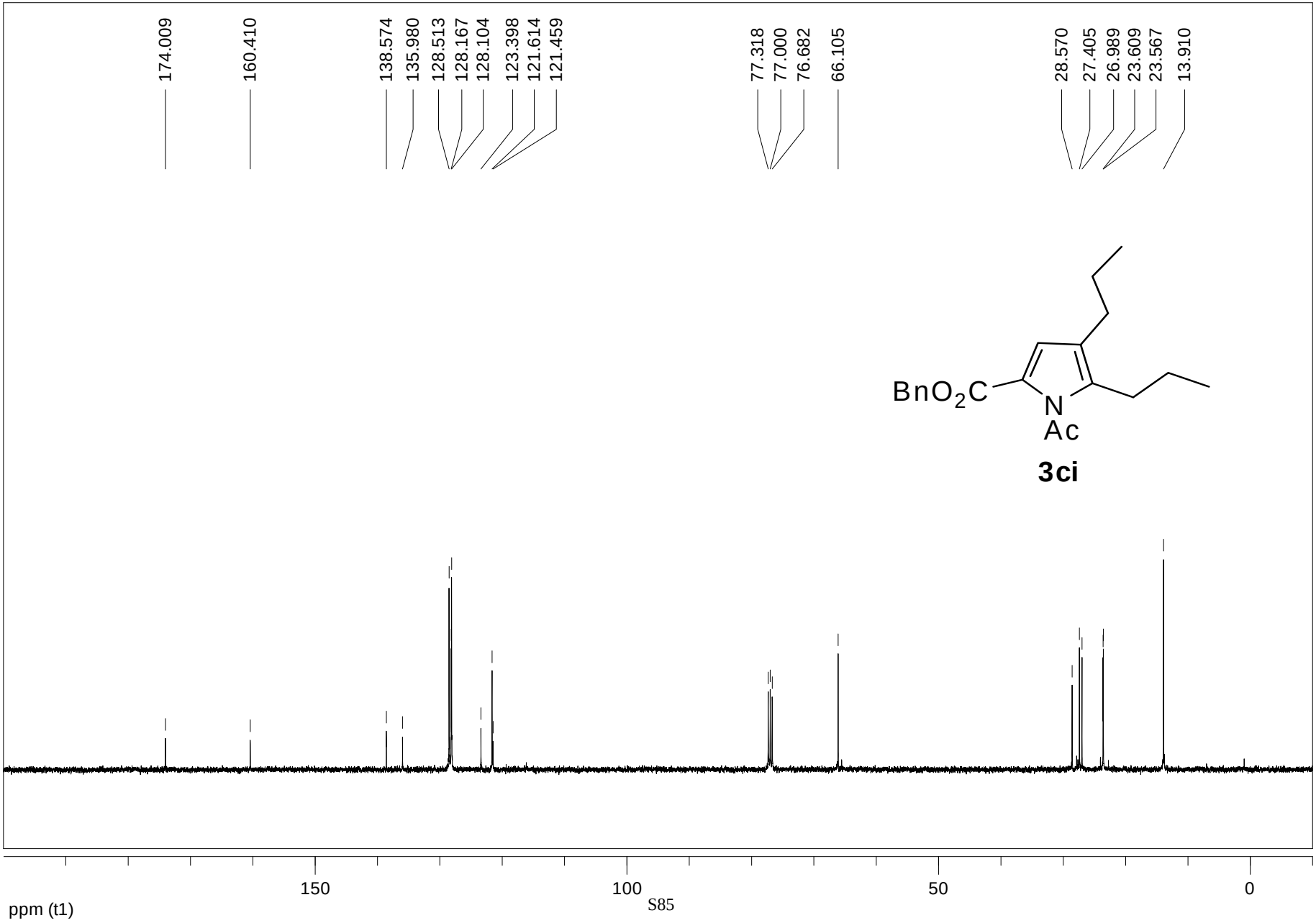
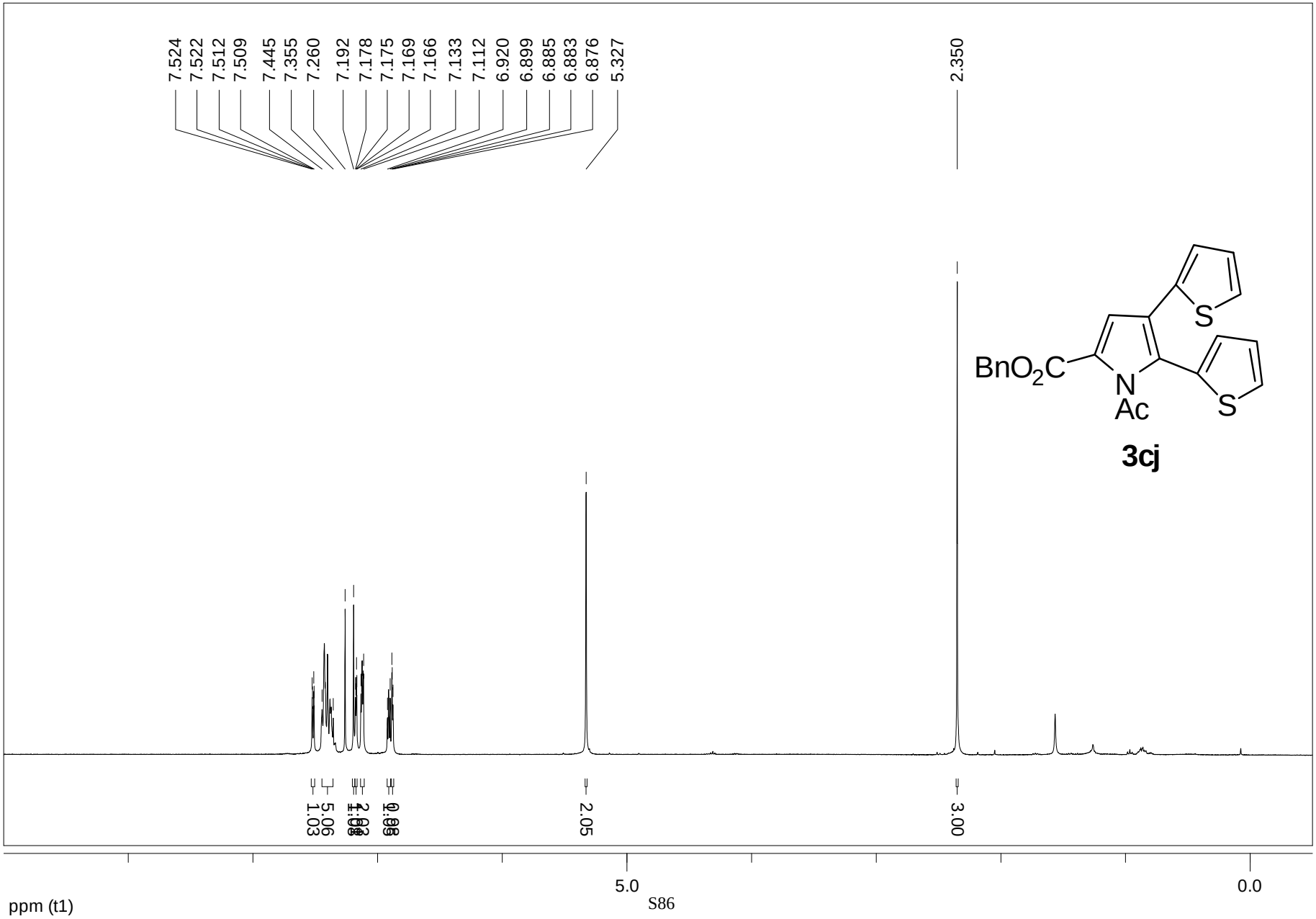
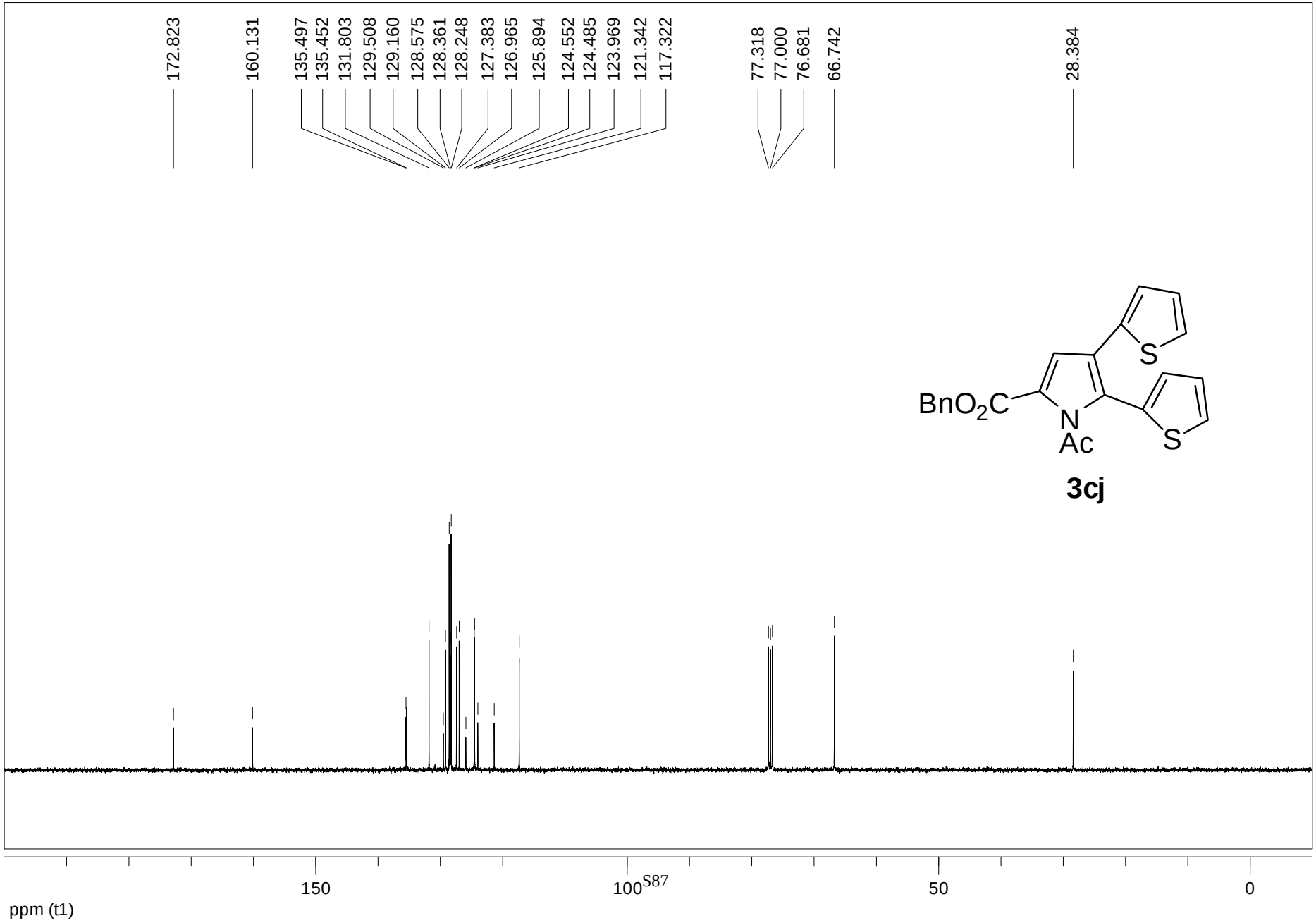
135.212
130.935
129.875
128.452
128.346
128.125
126.374
122.660
119.050
77.319
77.000
76.682
66.275
28.438
18.627
15.059
BnO2C
N
Ac
3cl
150
100
50
0
ppm (t1)


7.415
7.330
7.260
6.874
5.261
2.599
2.580
2.560
2.492
2.336
2.317
2.298
1.571
1.487
0.954
0.899
BnO2C
N
Ac
3ci
5.08
0.90
1.98
3.08
2.17
4.03
6.01
5.0
0.0
ppm (t1)


174.009
160.410
138.574
135.980
128.513
128.167
128.104
123.398
121.614
121.459
77.318
77.000
76.682
66.105
28.570
27.405
26.989
23.609
23.567
13.910
BnO2C
N
Ac
3ci
150
100
50
0
ppm (t1)


7.524
7.522
7.512
7.509
7.445
7.355
7.260
7.192
7.178
7.175
7.169
7.166
7.133
7.112
6.920
6.899
6.885
6.883
6.876
5.327
2.350
BnO2C
N
Ac
S
S
3cj
1.03
5.09
2.05
3.00
5.0
0.0
ppm (t1)


172.823
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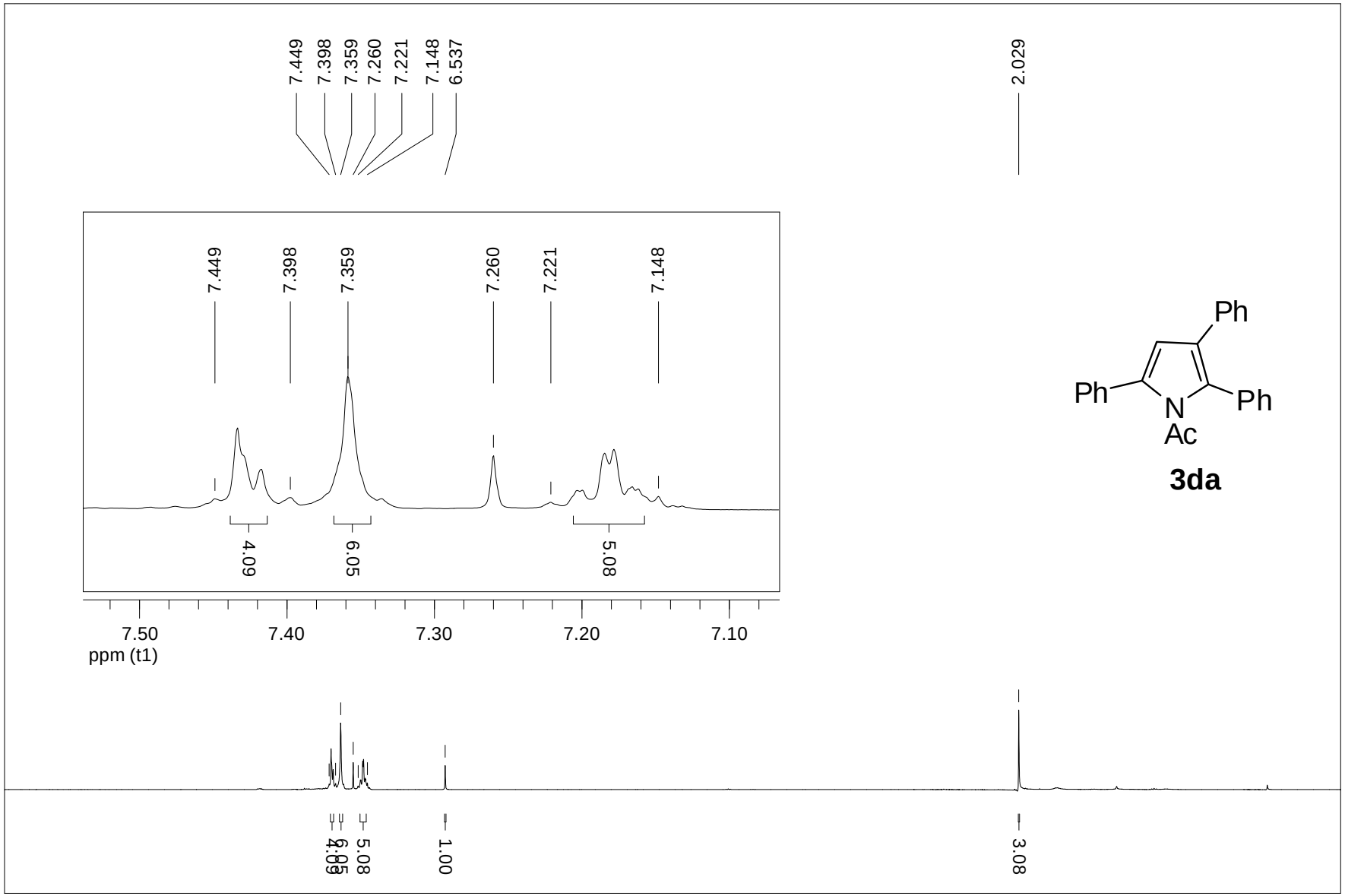
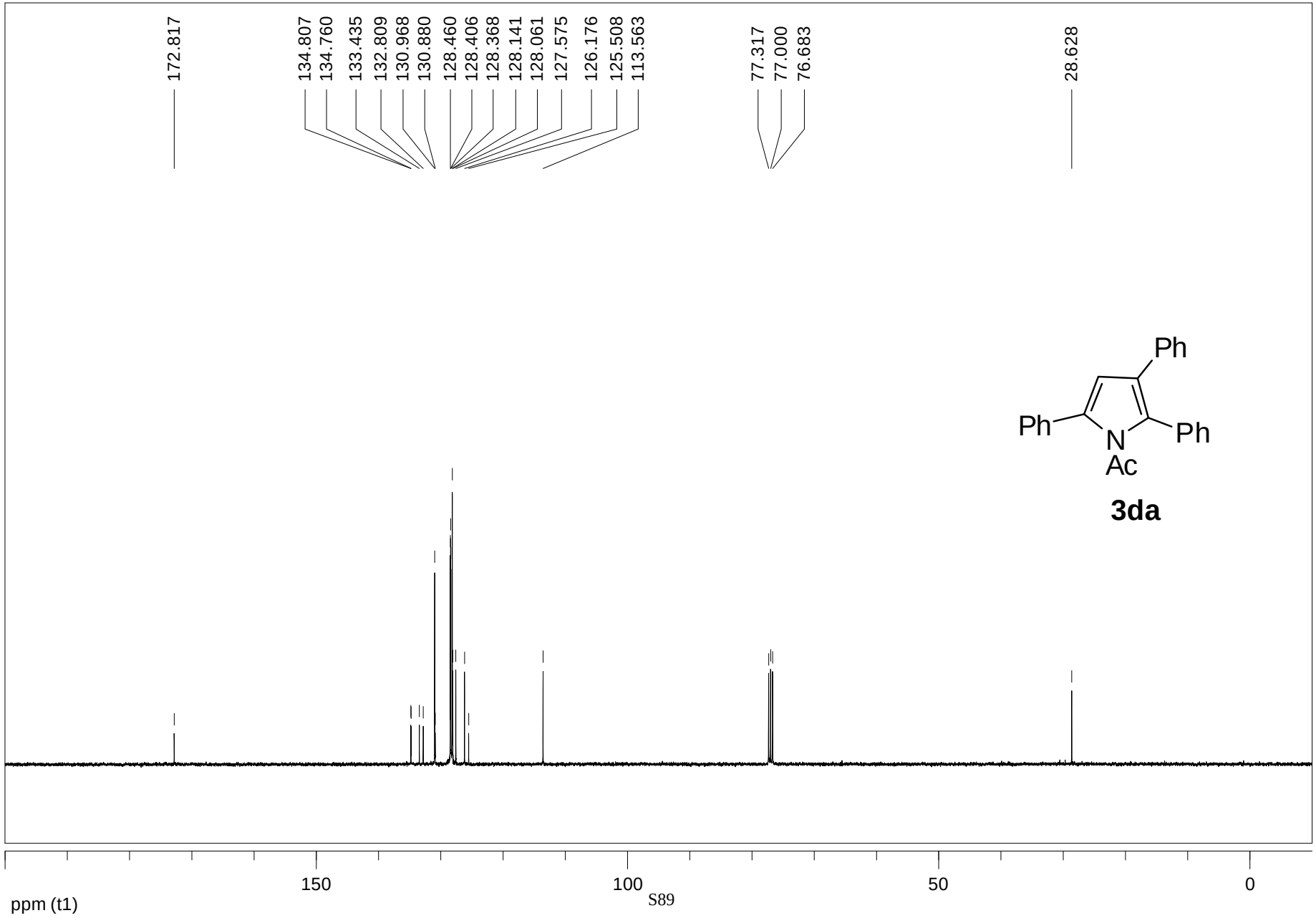
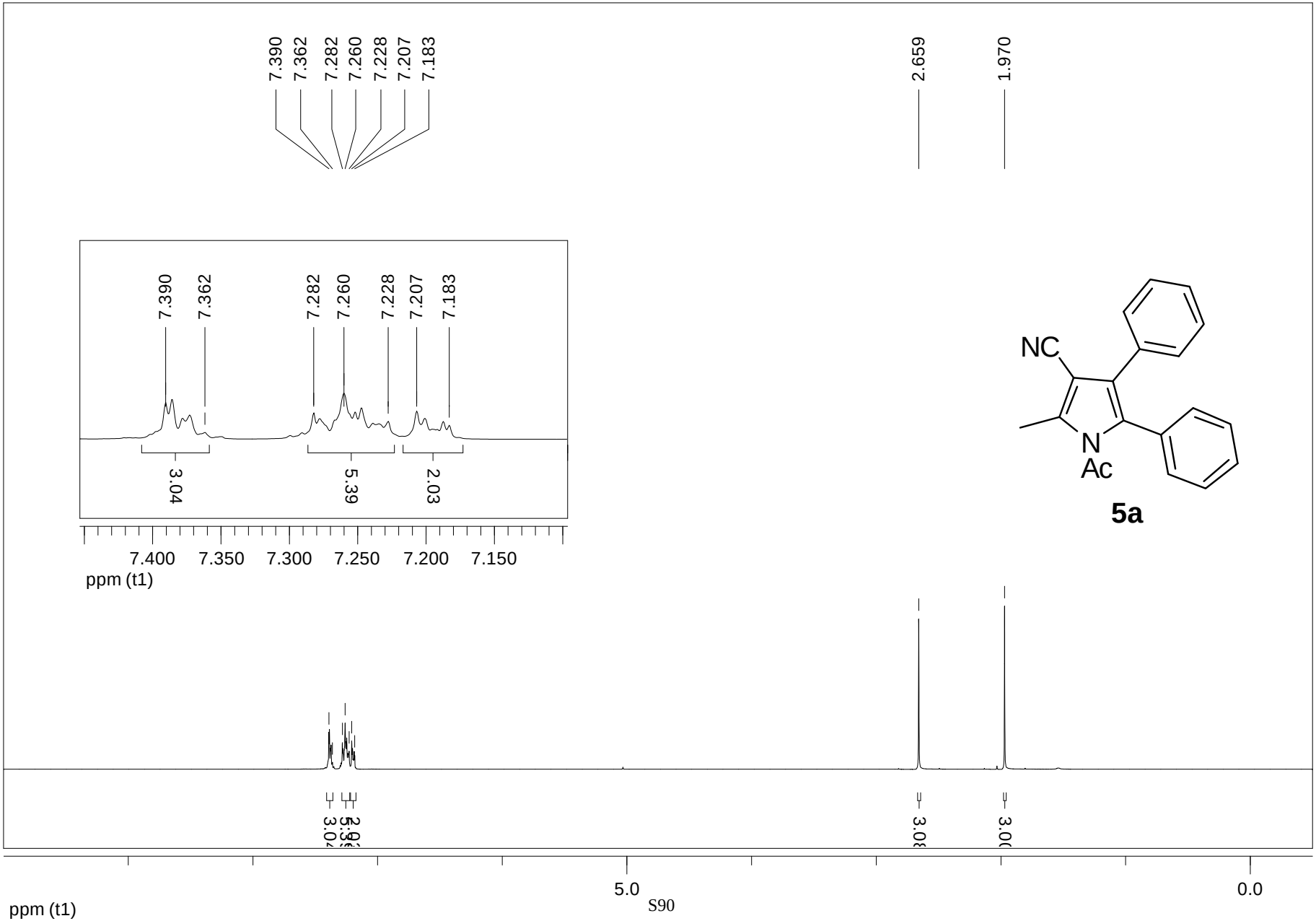
135.497
135.452
131.803
129.508
129.160
128.575
128.361
128.248
127.383
126.965
125.894
124.552
124.485
123.969
121.342
117.322
77.318
77.000
76.681
66.742
28.384
BnO2C
N
Ac
S
S
3cj
150
100
50
0
ppm (t1)

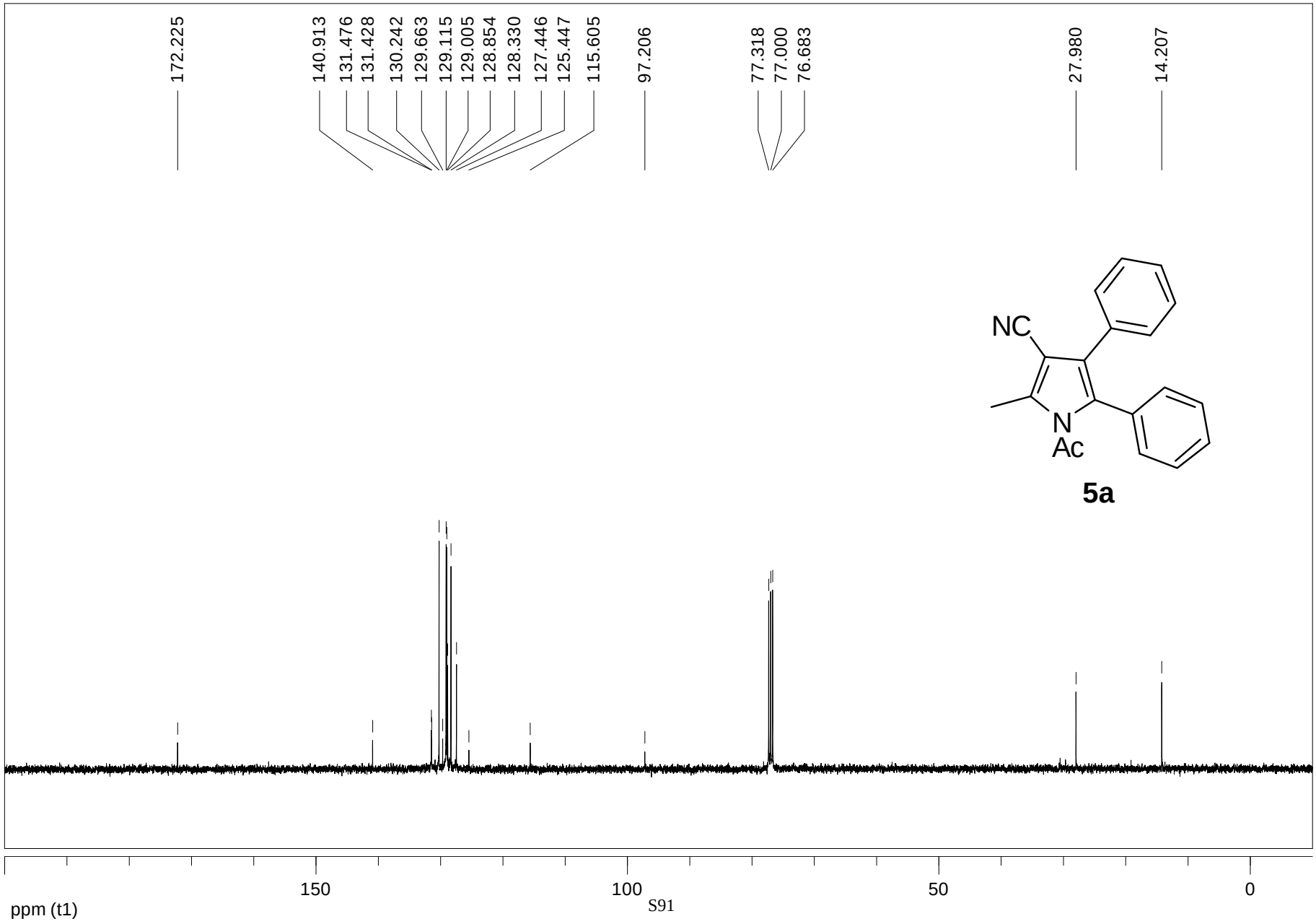

7.449
7.398
7.359
7.260
7.221
7.148
6.537
2.029
4.09
6.05
5.08
1.00
3.08
7.50
7.40
7.30
7.20
7.10
ppm (t1)
5.0
0.0
ppm (t1)

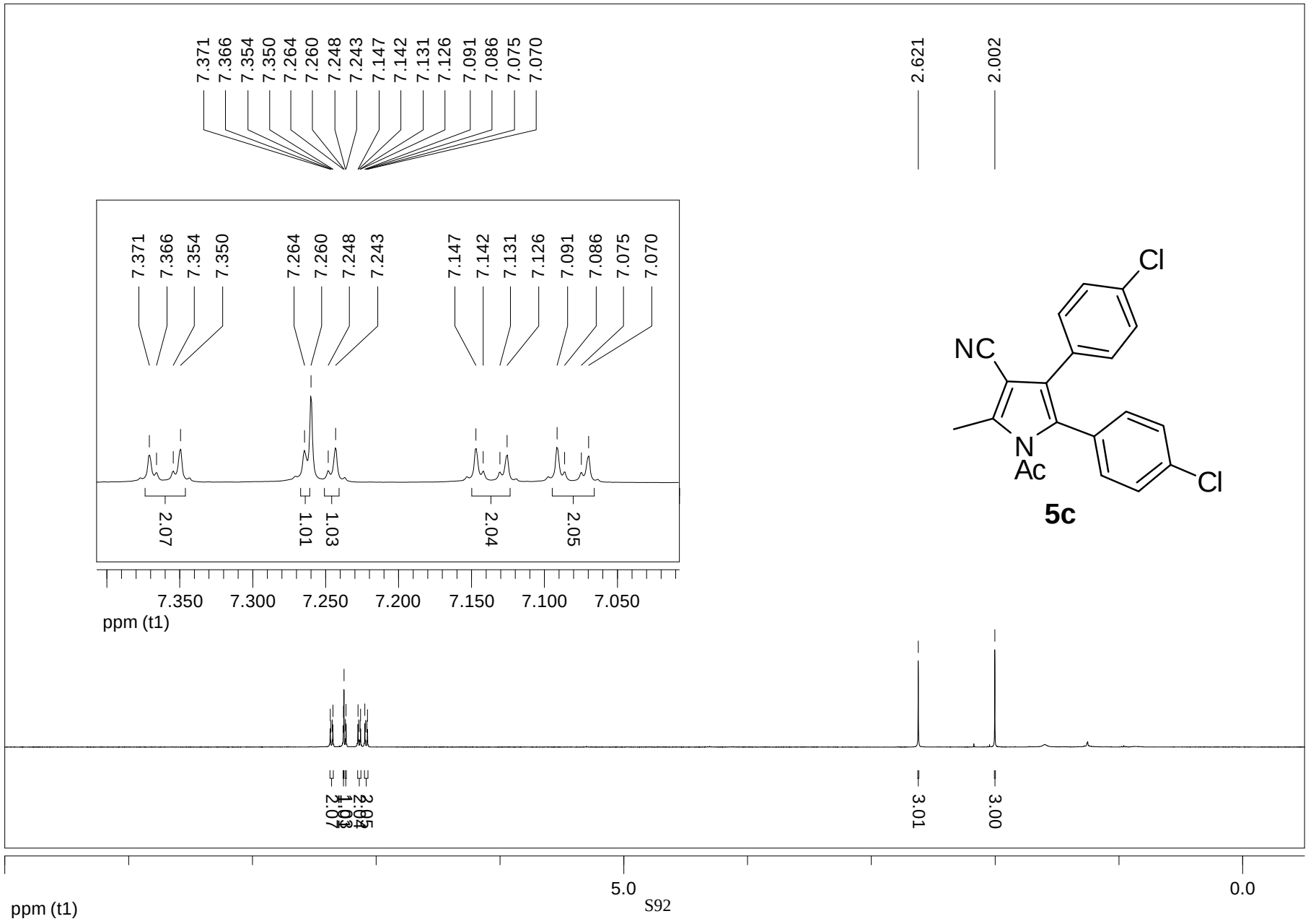
Ph
Ph
Ph
N
Ac

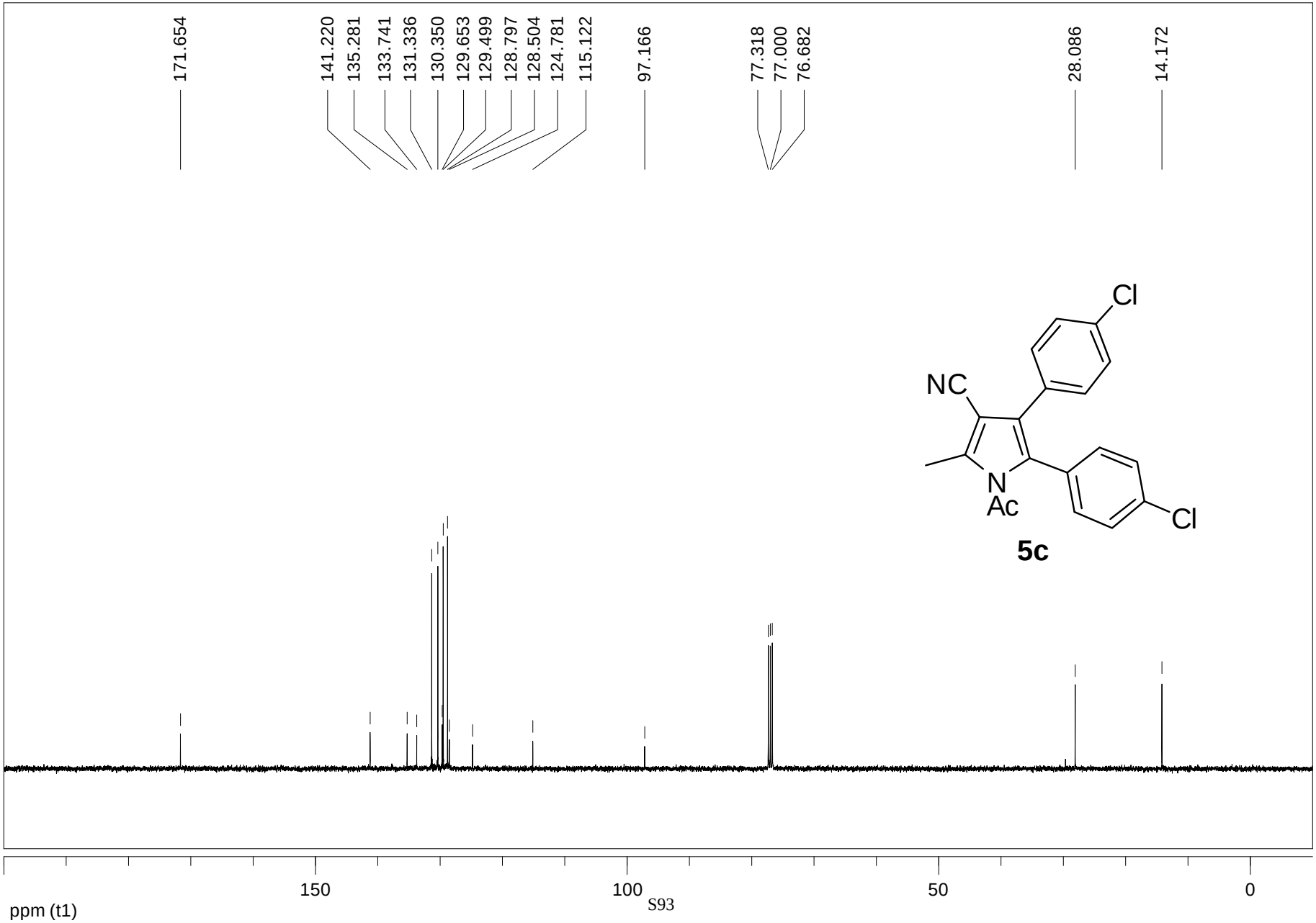
3da

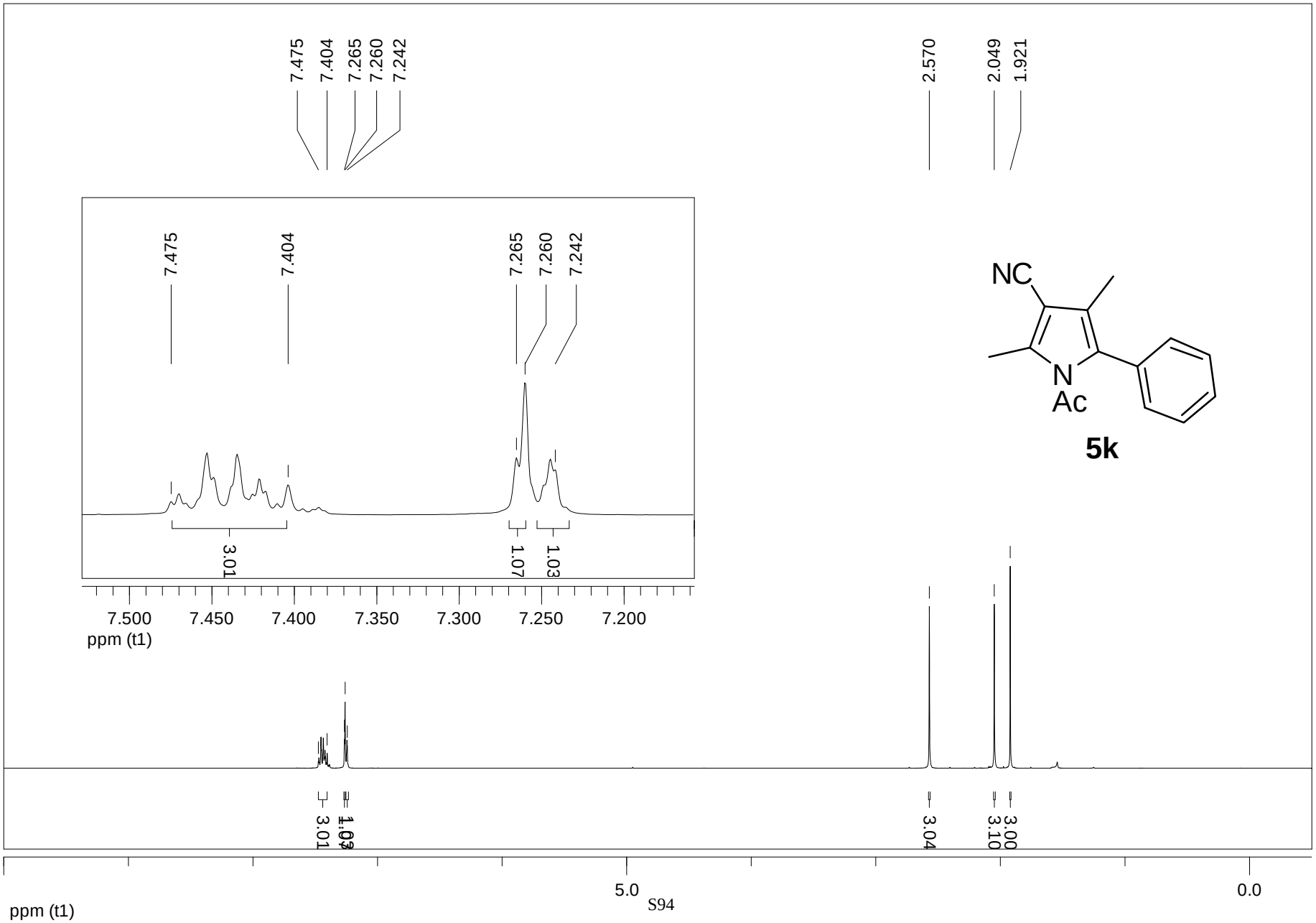

172.817
134.807
134.760
133.435
132.809
130.968
130.880
128.460
128.406
128.368
128.141
128.061
127.575
126.176
125.508
113.563
77.317
77.000
76.683
28.628
Ph
Ph
Ph
N
Ac
3da
150
100
50
0
ppm (t1)

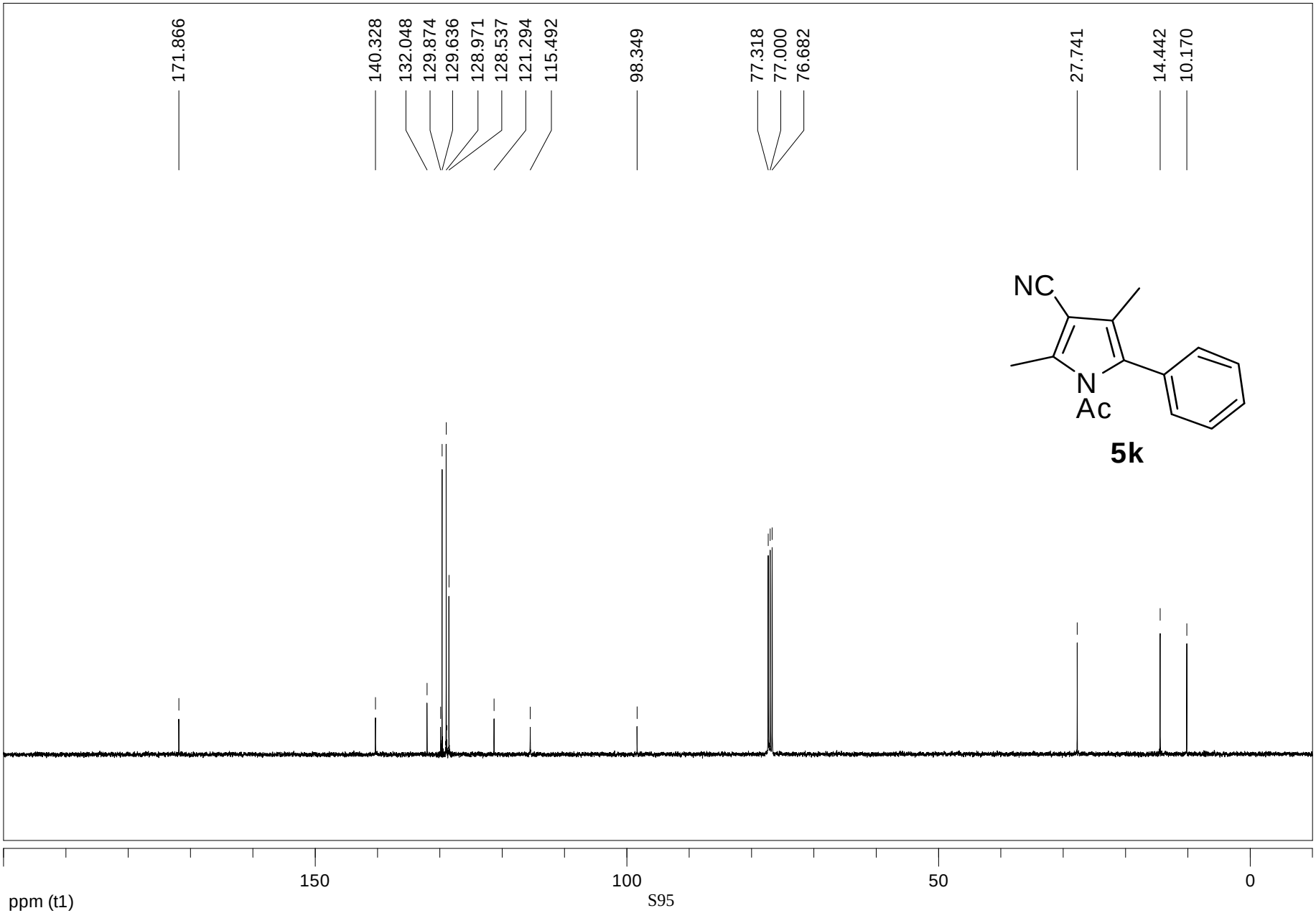

7.390
7.362
7.282
7.260
7.228
7.207
7.183
2.659
1.970
7.390
7.362
7.282
7.260
7.228
7.207
7.183
3.04
5.39
2.03
7.400
7.350
7.300
7.250
7.200
7.150
ppm (t1)
NC
N
Ac
5a
3.07
3.08
3.00
5.0
0.0
ppm (t1)


172.225
140.913
131.476
131.428
130.242
129.663
129.115
129.005
128.854
128.330
127.446
125.447
115.605
97.206
77.318
77.000
76.683
27.980
14.207
NC
N
Ac
5a
150
100
50
0
ppm (t1)


7.371
7.366
7.354
7.350
7.264
7.260
7.248
7.243
7.147
7.142
7.131
7.126
7.091
7.086
7.075
7.070
2.621
2.002
2.07
1.01
1.03
2.04
2.05
7.350
7.300
7.250
7.200
7.150
7.100
7.050
ppm (t1)
3.01
3.00
5.0
0.0
ppm (t1)
Cl
NC
N
Ac
Cl
5c


171.654
141.220
135.281
133.741
131.336
130.350
129.653
129.499
128.797
128.504
124.781
115.122
97.166
77.318
77.000
76.682
28.086
14.172
Cl
NC
N
Ac
Cl
5c
150
100
50
0
ppm (t1)


7.475
7.404
7.265
7.260
7.242
2.570
2.049
1.921
NC
N
Ac
5k
3.01
1.07
1.03
7.500
7.450
7.400
7.350
7.300
7.250
7.200
ppm (t1)
3.01
1.00
3.04
3.10
3.00
5.0
0.0
ppm (t1)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140.328
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129.636
128.971
128.537
121.294
115.492
98.349
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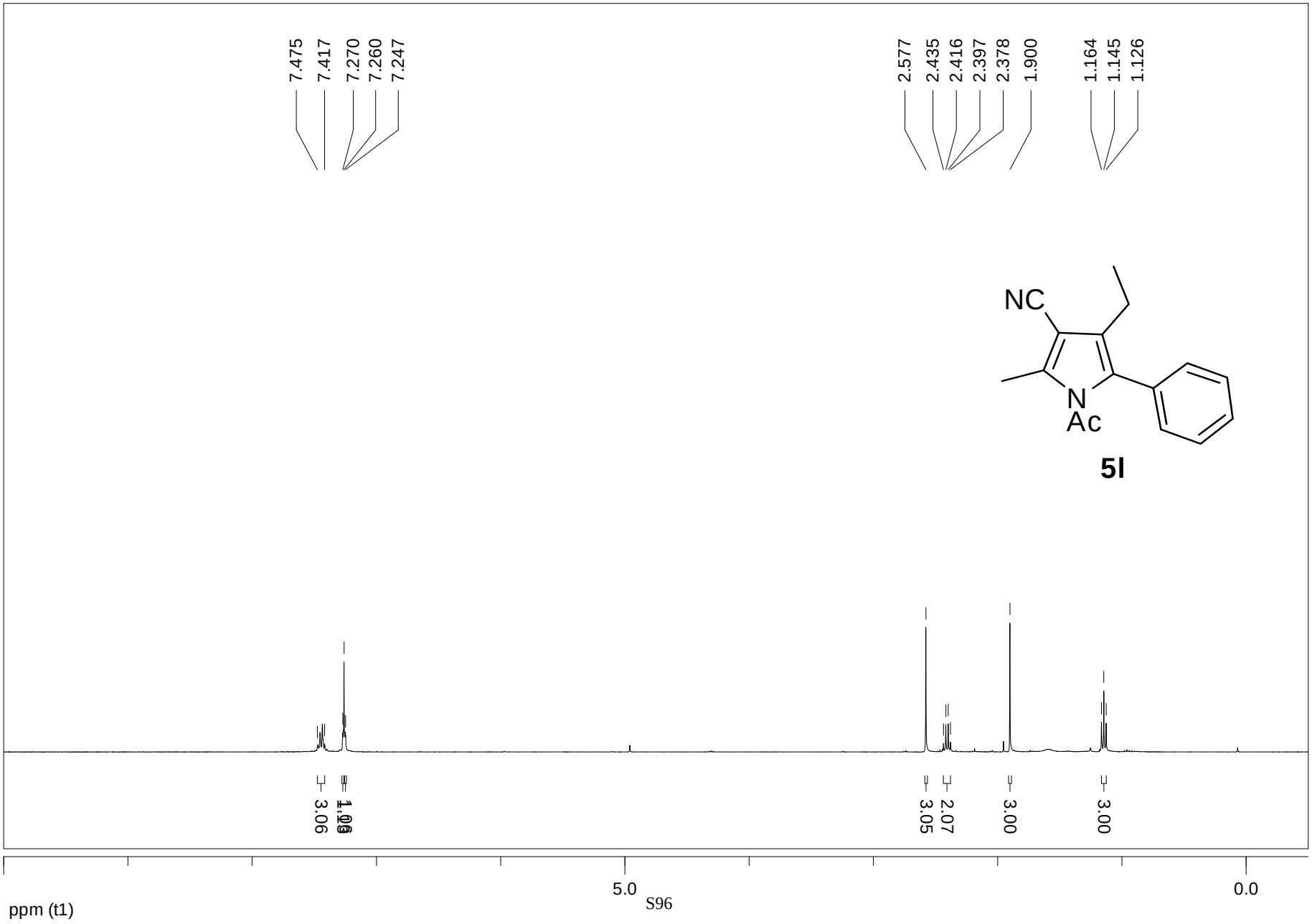
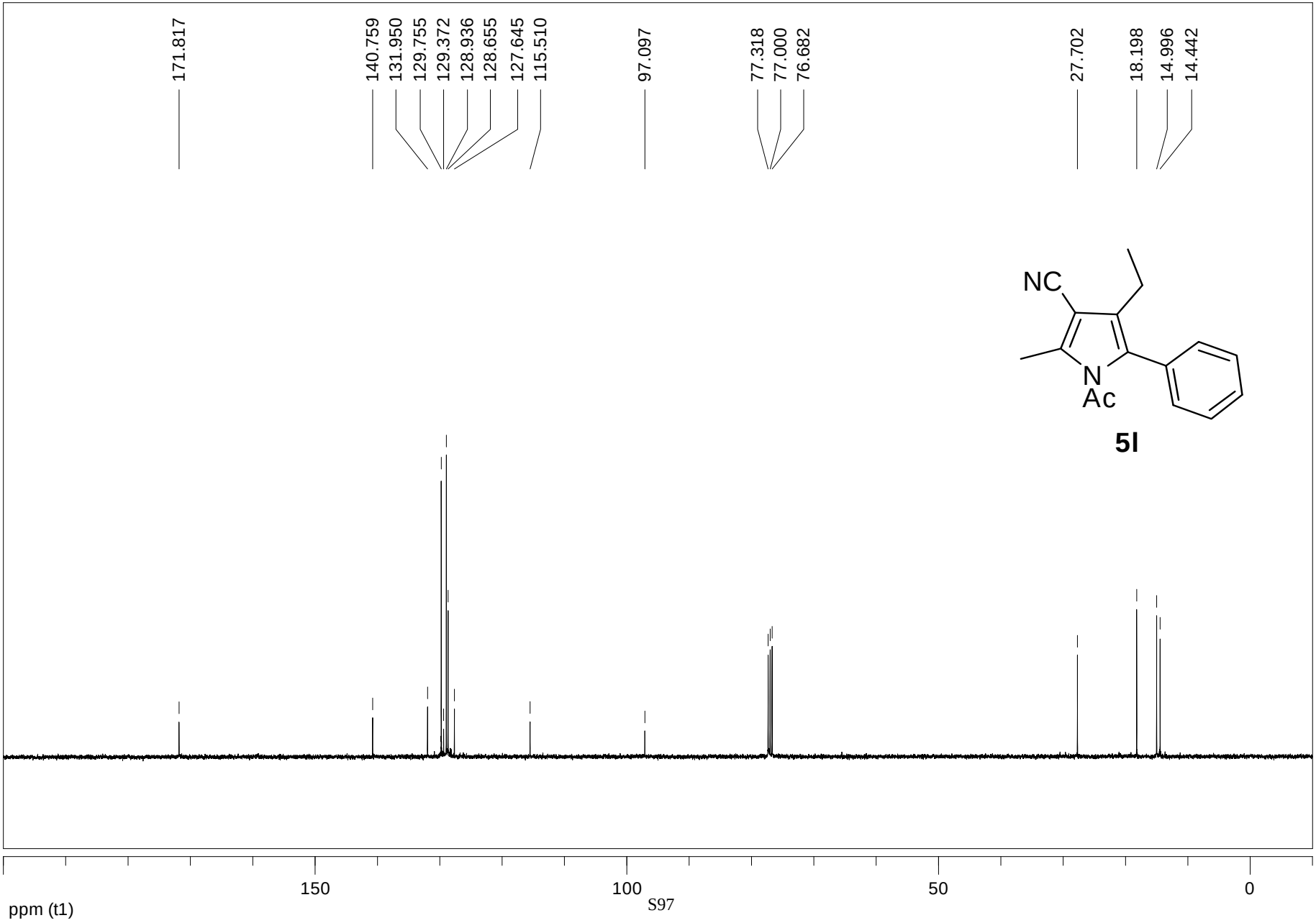
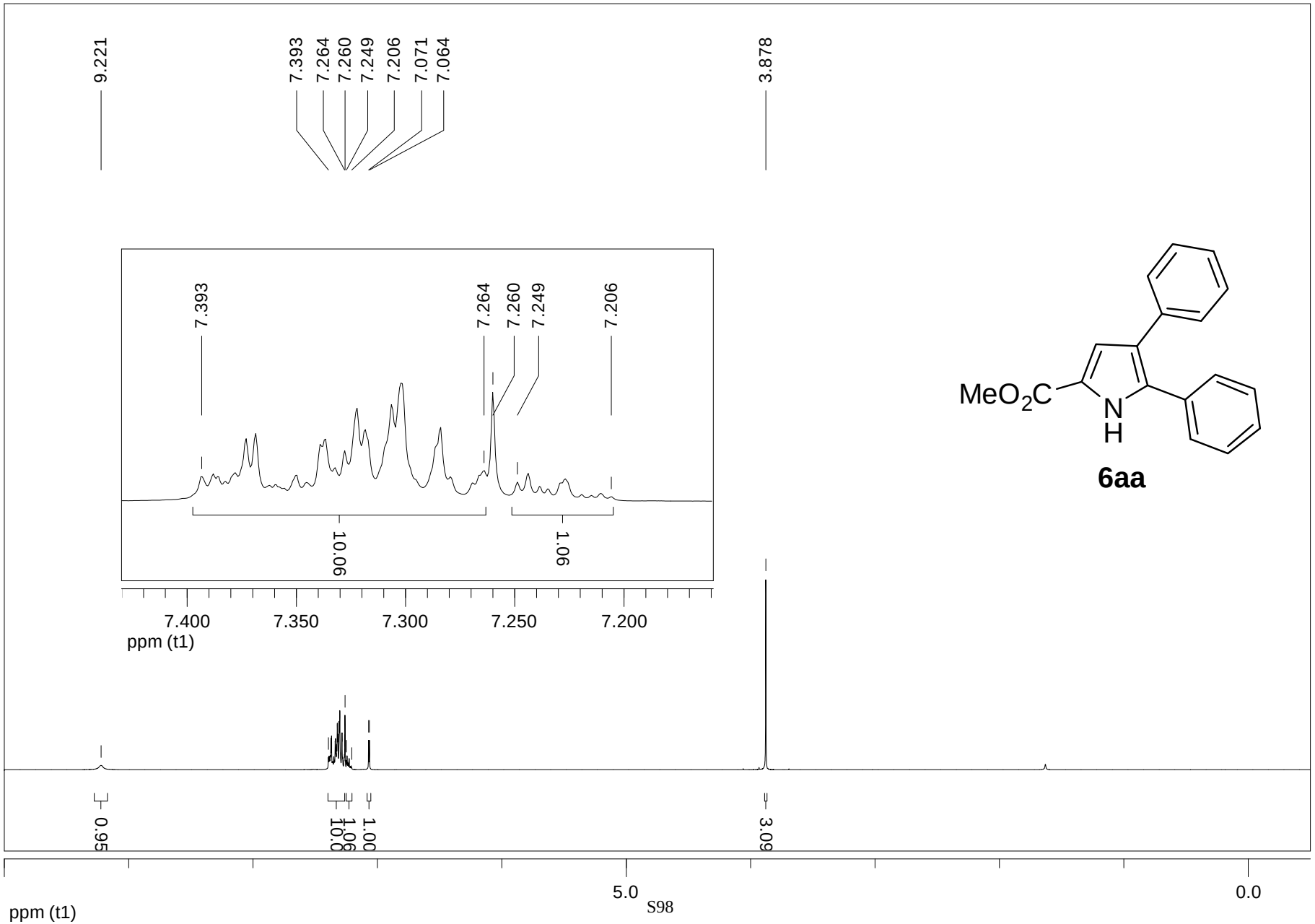
77.000
76.682
27.741
14.442
10.170
NC
N
Ac
5k
150
100
50
0
ppm (t1)


7.475
7.417
7.270
7.260
7.247
2.577
2.435
2.416
2.397
2.378
1.900
1.164
1.145
1.126
NC
N
Ac
5l
3.06
3.05
2.07
3.00
3.00
5.0
0.0
ppm (t1)


171.817
140.759
131.950
129.755
129.372
128.936
128.655
127.645
115.510
97.097
77.318
77.000
76.682
27.702
18.198
14.996
14.442
NC
N
Ac
5l
150
100
50
0
ppm (t1)


9.221
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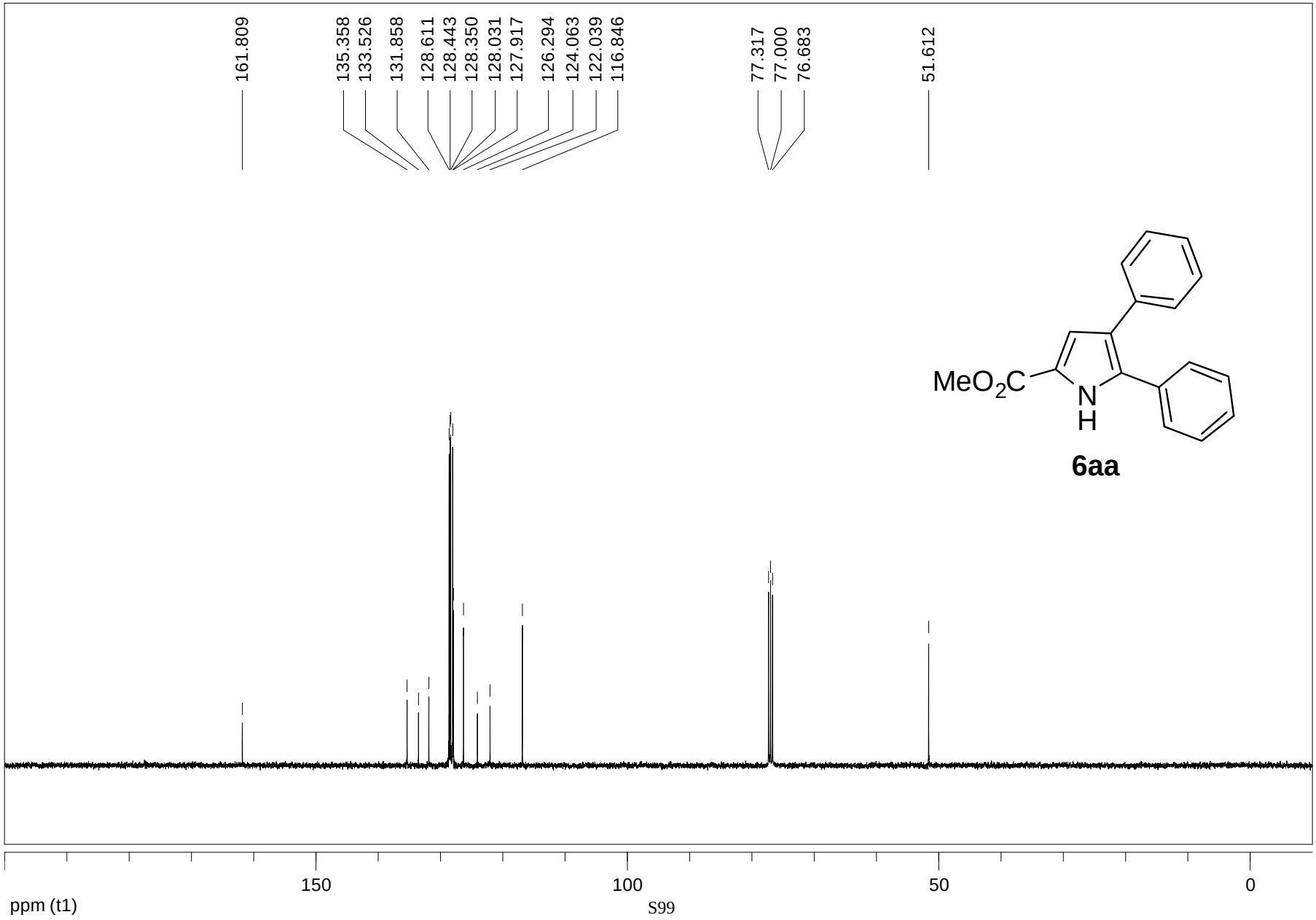
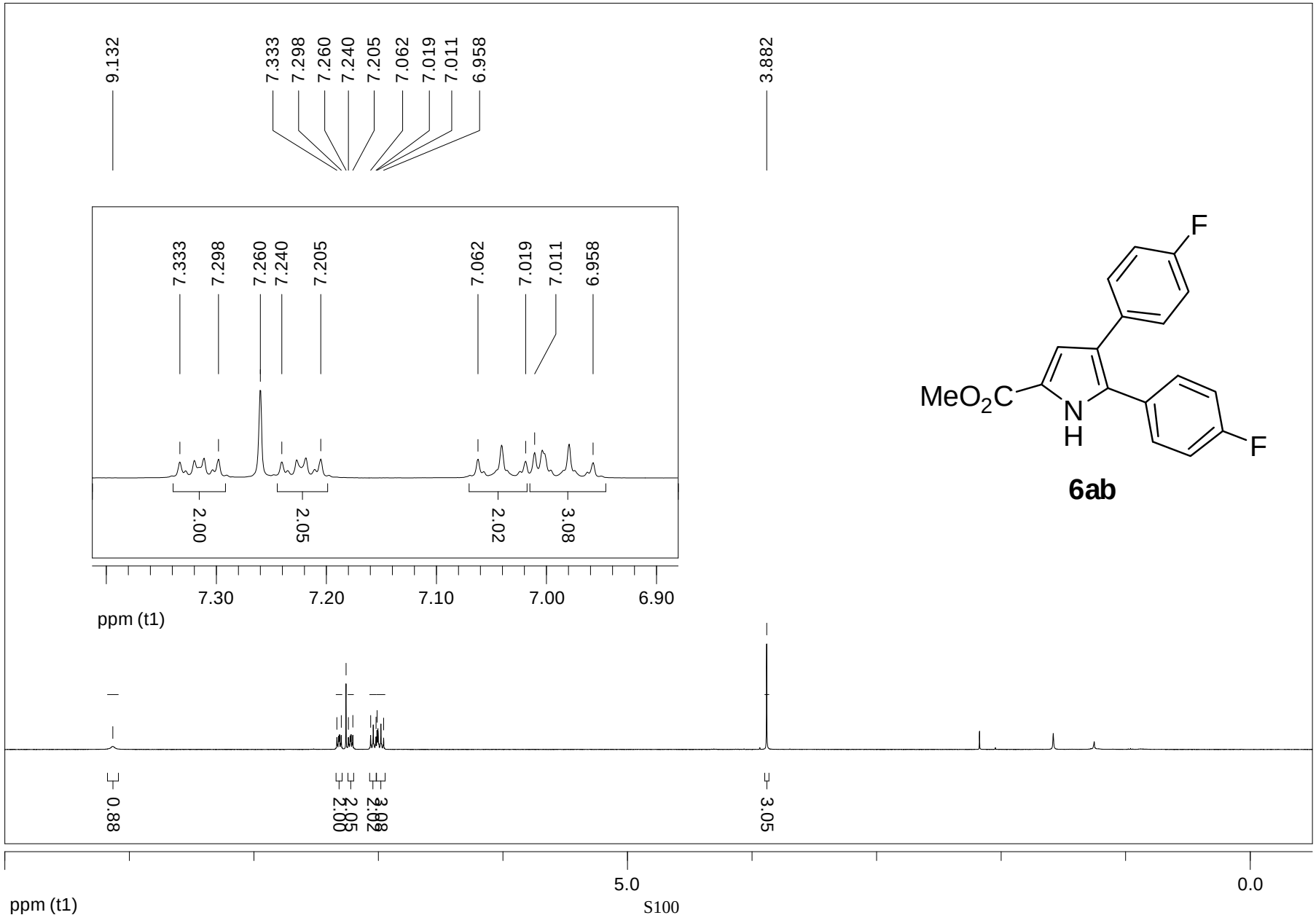
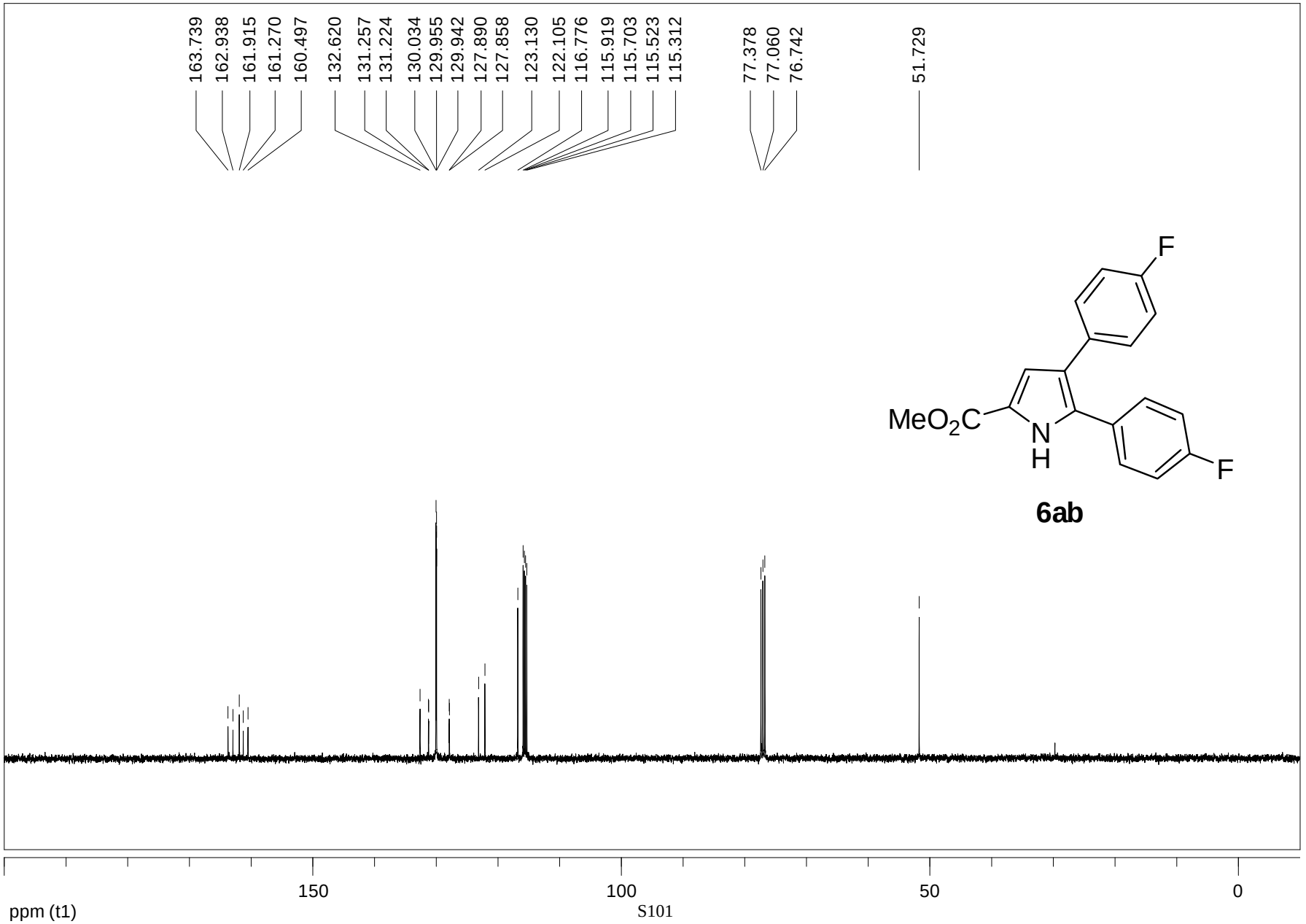
7.264
7.260
7.249
7.206
7.071
7.064
3.878
7.393
7.264
7.260
7.249
7.206
10.06
1.06
7.400
7.350
7.300
7.250
7.200
ppm (t1)
MeO2C
N
H
6aa
0.95
10.06
1.06
1.00
3.09
5.0
0.0
ppm (t1)


161.809
135.358
133.526
131.858
128.611
128.443
128.350
128.031
127.917
126.294
124.063
122.039
116.846
77.317
77.000
76.683
51.612
MeO2C
N
H
6aa
150
100
50
0
ppm (t1)


9.132
7.333
7.298
7.260
7.240
7.205
7.062
7.019
7.011
6.958
3.882
2.00
2.05
2.02
3.08
7.30
7.20
7.10
7.00
6.90
ppm (t1)
0.88
2.00
2.05
2.02
3.08
3.05
5.0
0.0
ppm (t1)
F
MeO2C
N
H
F
6ab


163.739
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161.915
161.270
160.497
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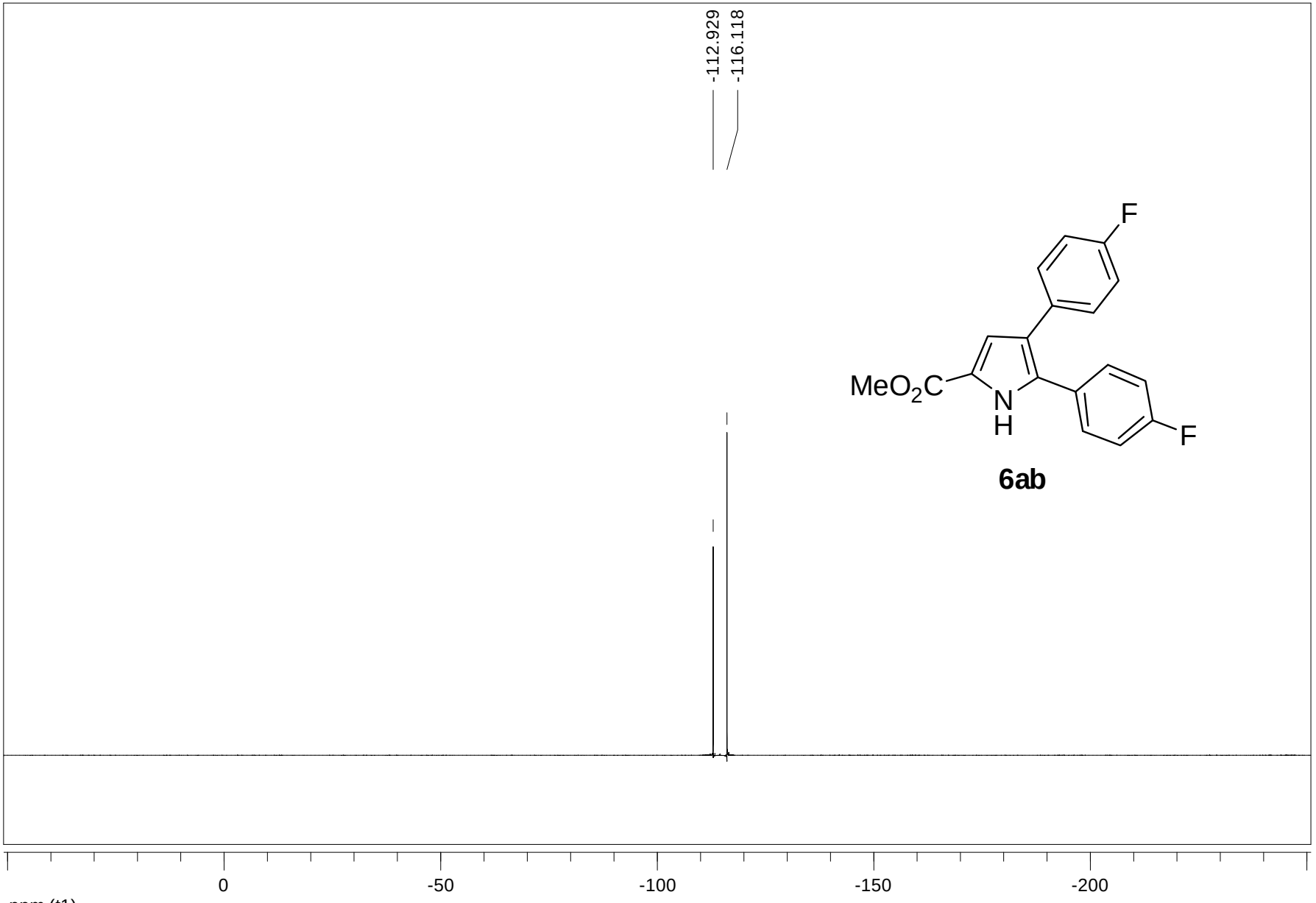
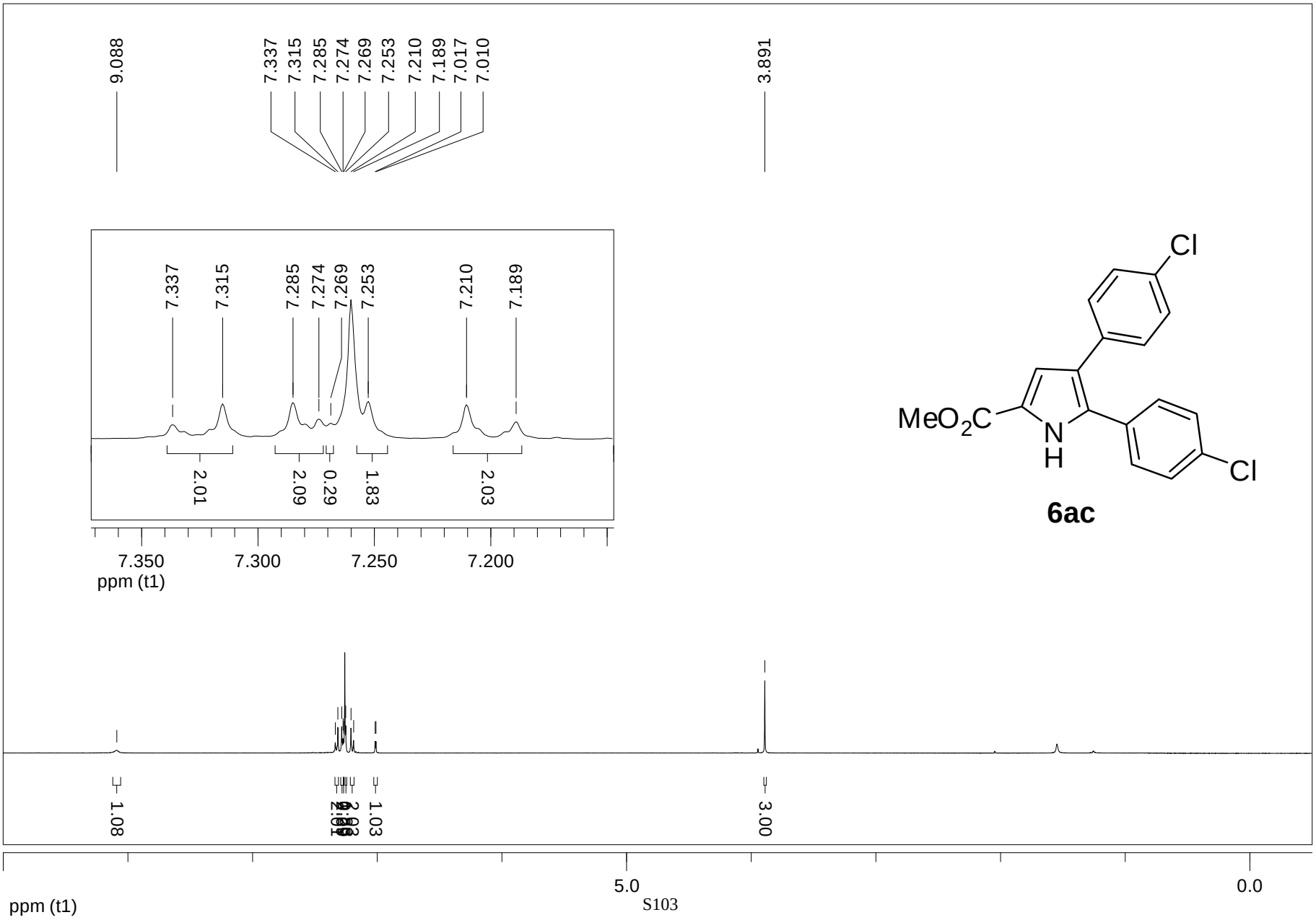
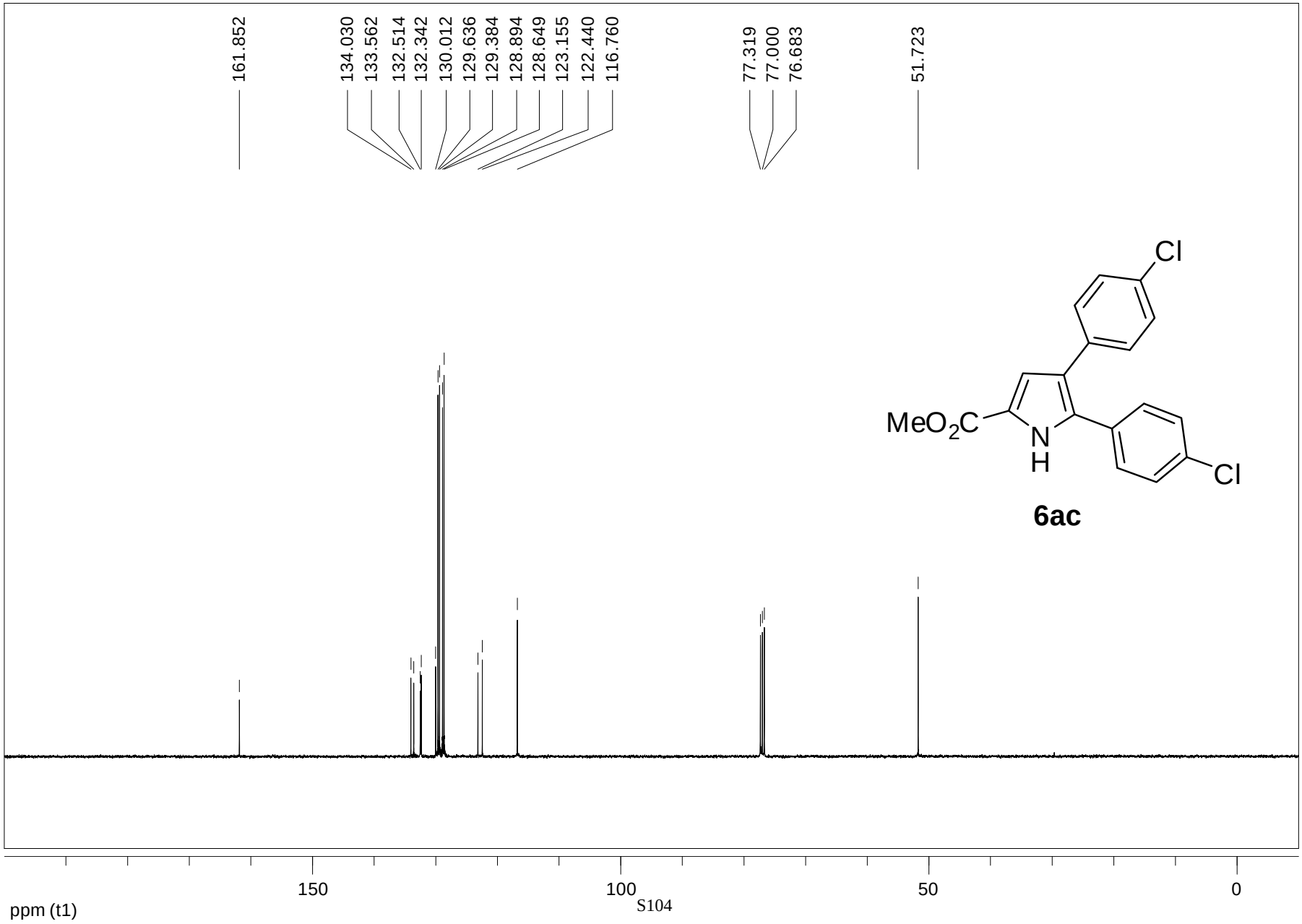
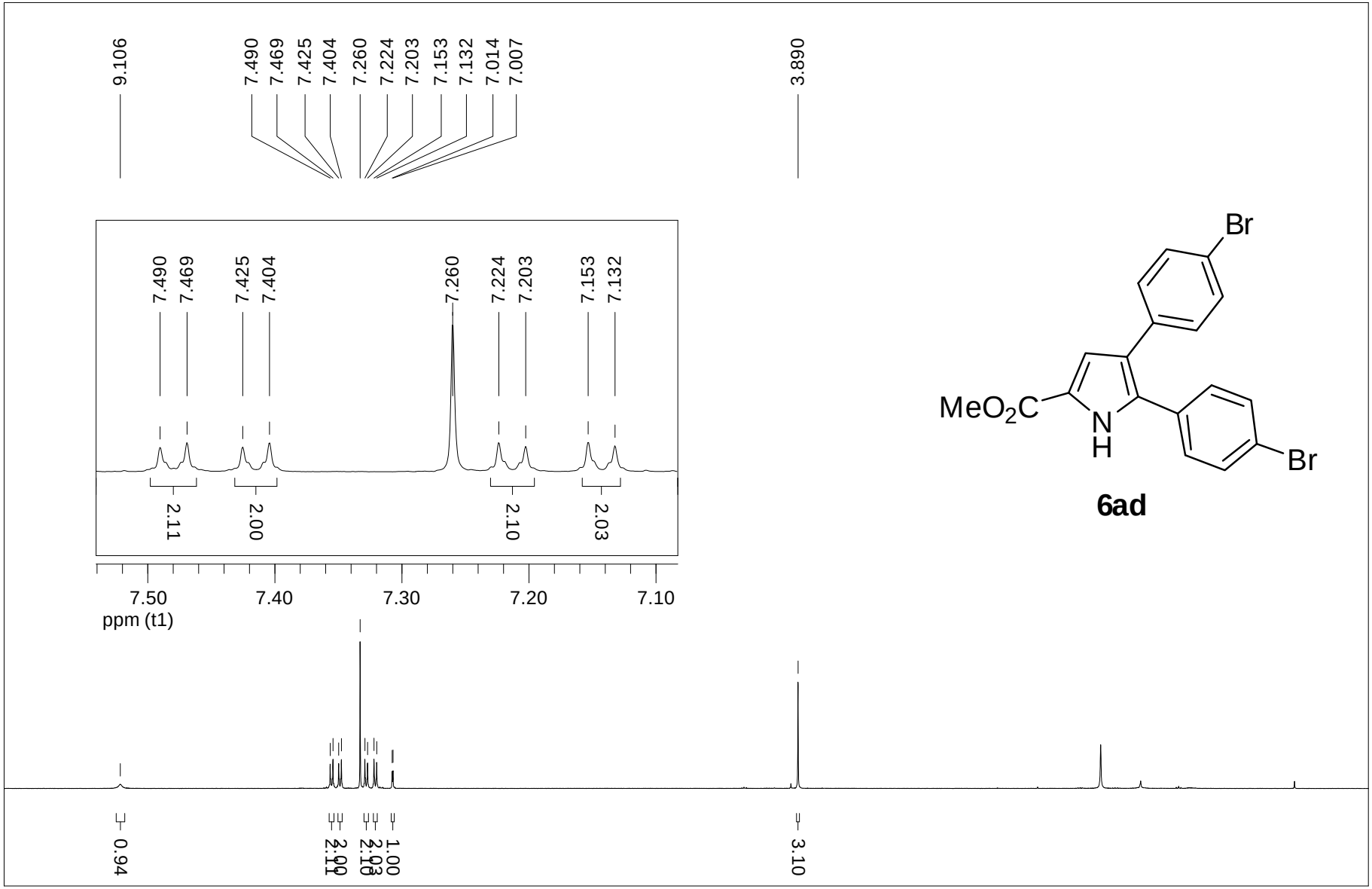
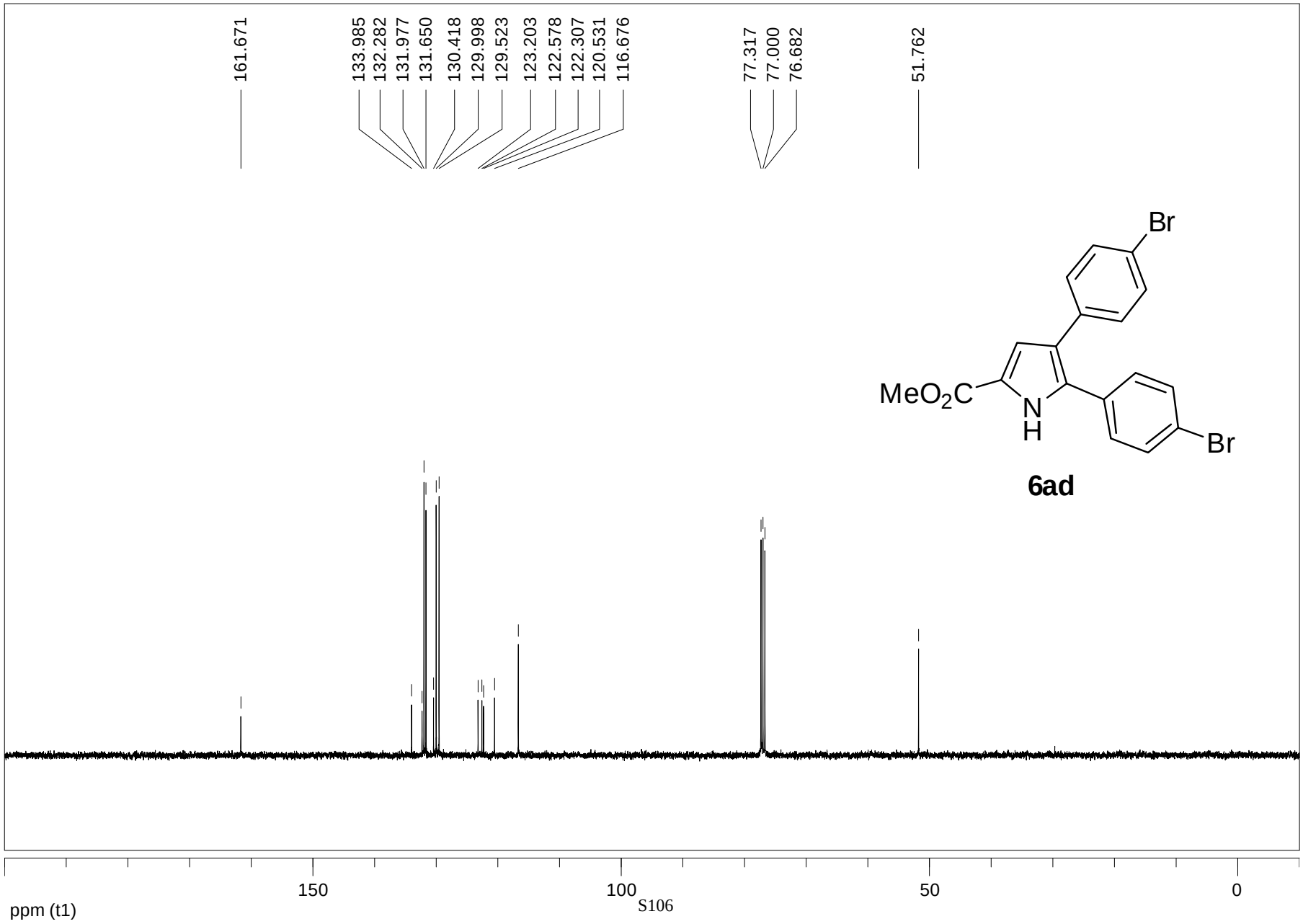
131.257
131.224
130.034
129.955
129.942
127.890
127.858
123.130
122.105
116.776
115.919
115.703
115.523
115.312
77.378
77.060
76.742
51.729
F
MeO2C
N
H
F
6ab
150
100
50
0
ppm (t1)


-112.929
-116.118
F
MeO2C
N
H
F
6ab
0
-50
-100
-150
-200
ppm (t1)


9.088
7.337
7.315
7.285
7.274
7.269
7.253
7.210
7.189
7.017
7.010
3.891
7.337
7.315
7.285
7.274
7.269
7.253
7.210
7.189
2.01
2.09
0.29
1.83
2.03
7.350
7.300
7.250
7.200
ppm (t1)
Cl
MeO2C
N
H
Cl
6ac
1.08
1.03
3.00
5.0
0.0
ppm (t1)


161.852
134.030
133.562
132.514
132.342
130.012
129.636
129.384
128.894
128.649
123.155
122.440
116.760
77.319
77.000
76.683
51.723
Cl
MeO2C
N
H
Cl
6ac
150
100
50
0
ppm (t1)


9.106
7.490
7.469
7.425
7.404
7.260
7.224
7.203
7.153
7.132
7.014
7.007
3.890
2.11
2.00
2.10
2.03
7.50
7.40
7.30
7.20
7.10
ppm (t1)
0.94
2.11
2.00
2.10
2.03
1.00
3.10
5.0
0.0
ppm (t1)
Br
MeO2C
N
H
Br
6ad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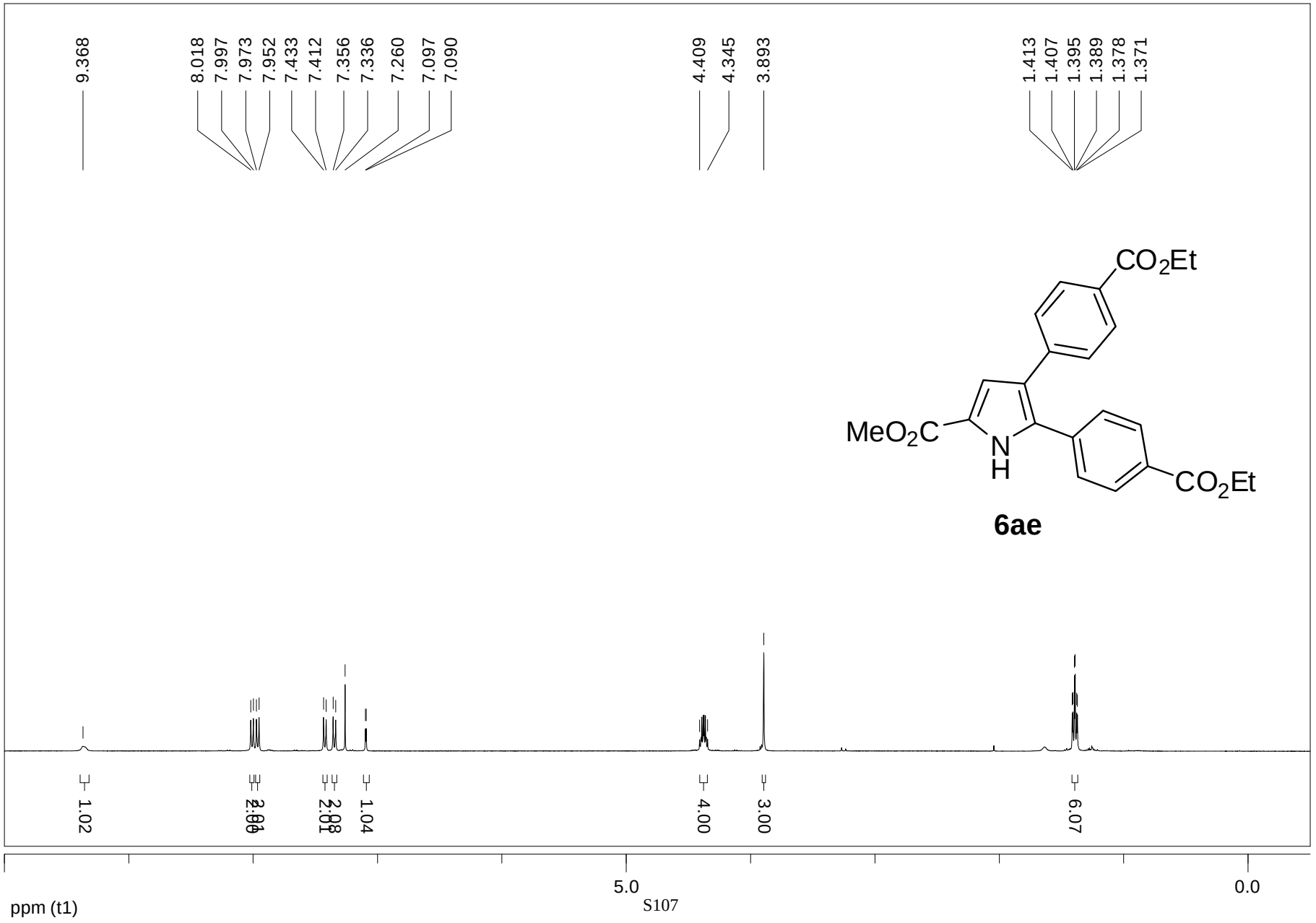
129.998
129.523
123.203
122.578
122.307
120.531
116.676
77.317
77.000
76.682
51.762
Br
MeO2C
N
H
Br
6ad
150
100
50
0
ppm (t1)


9.368
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7.973
7.952
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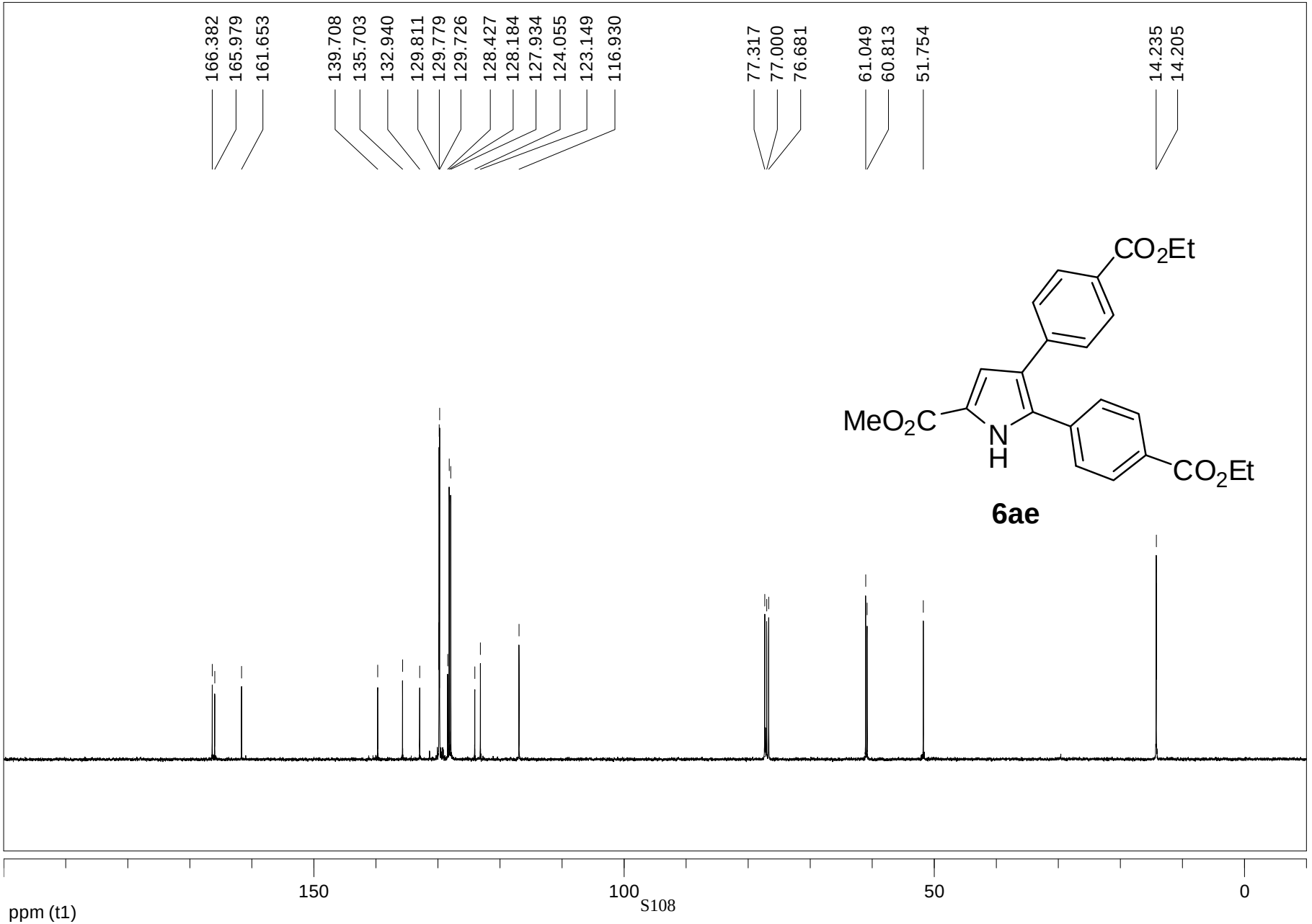
7.356
7.336
7.260
7.097
7.090
4.409
4.345
3.893
1.413
1.407
1.395
1.389
1.378
1.371
CO2Et
MeO2C
N
H
CO2Et
6ae
1.02
2.00
2.00
2.08
2.01
1.04
4.00
3.00
6.07
5.0
0.0
ppm (t1)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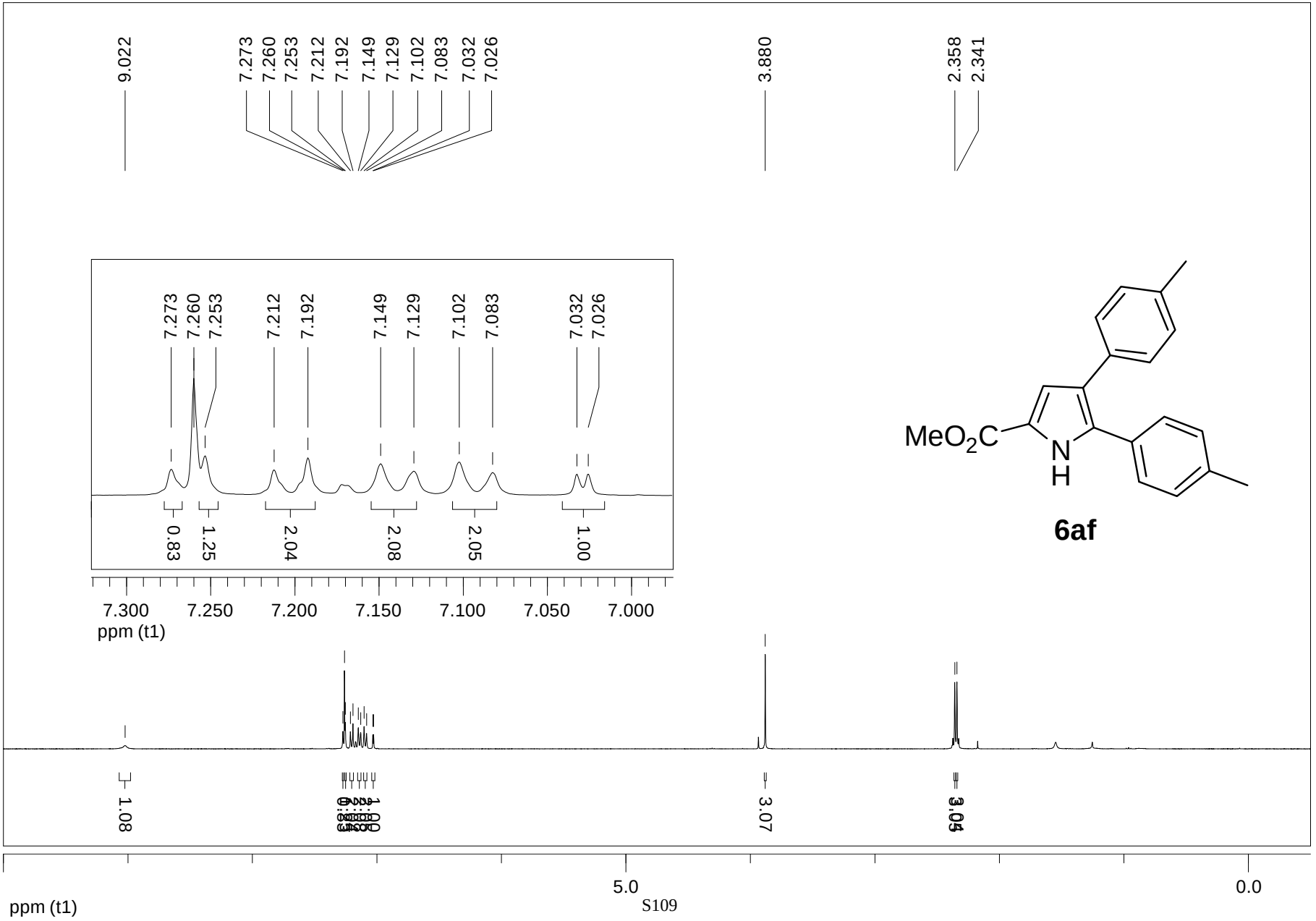
165.979
161.653
139.708
135.703
132.940
129.811
129.779
129.726
128.427
128.184
127.934
124.055
123.149
116.930
77.317
77.000
76.681
61.049
60.813
51.754
14.235
14.205
CO2Et
MeO2C
N
H
CO2Et
6ae
150
100
50
0
ppm (t1)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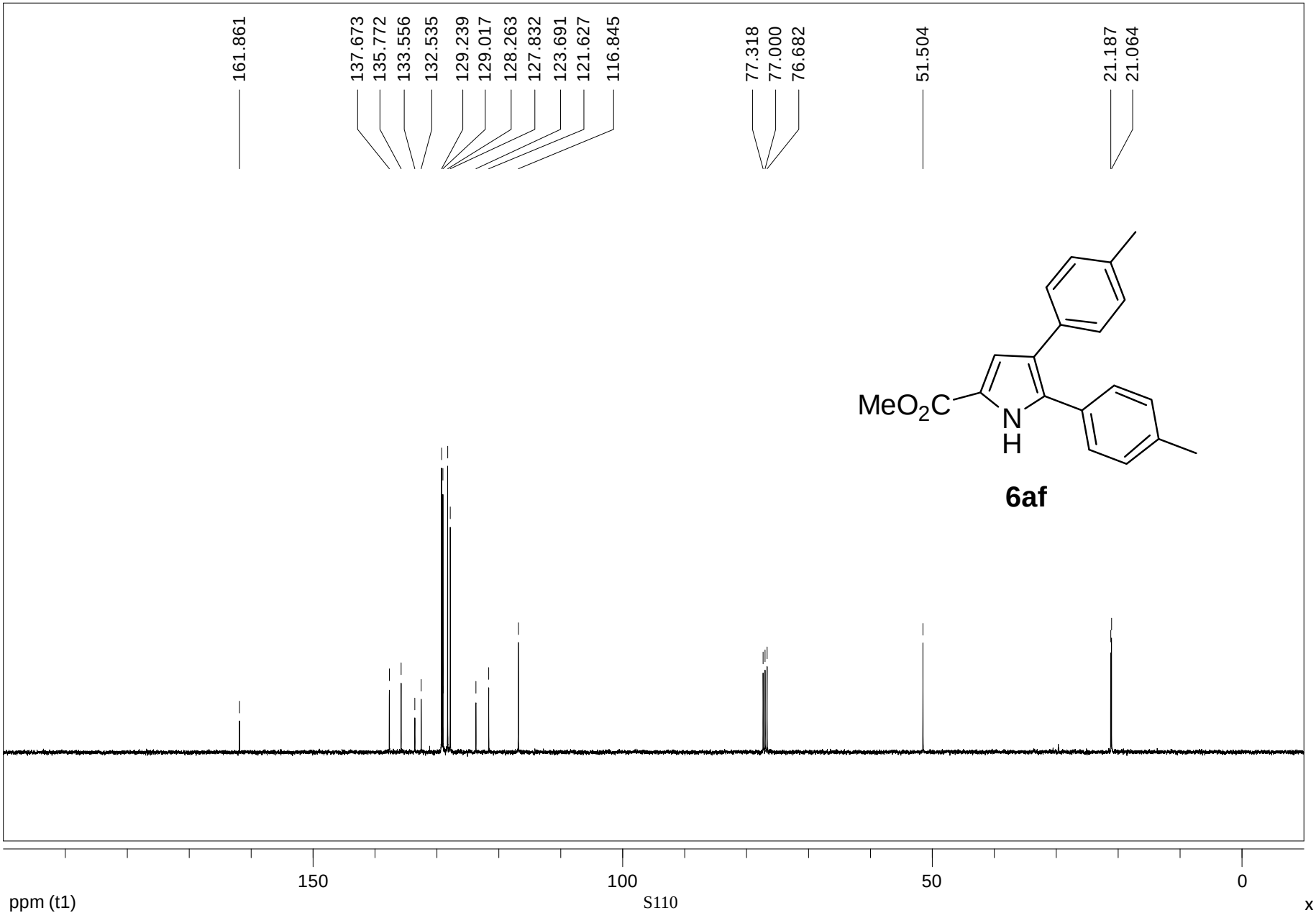
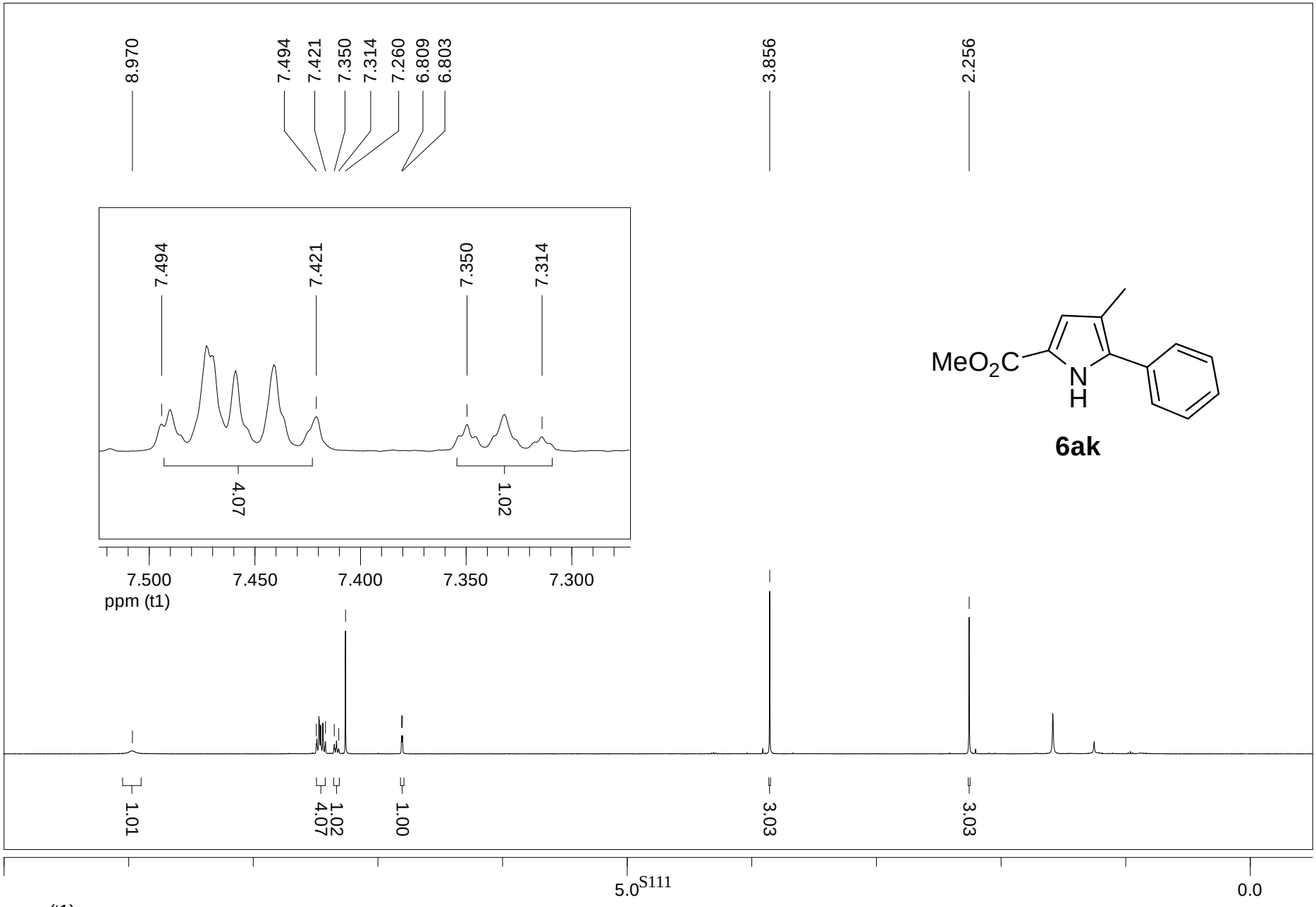
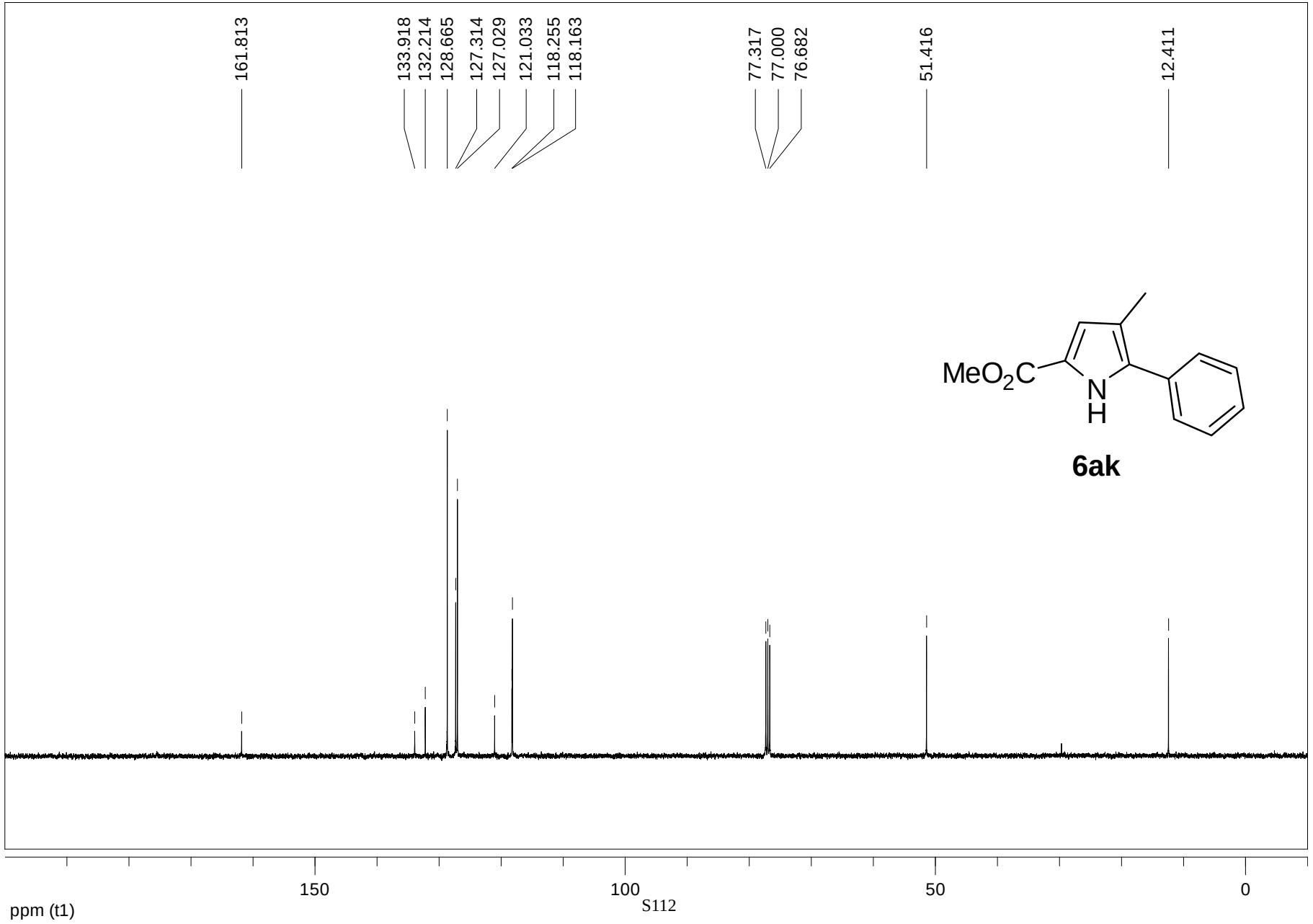
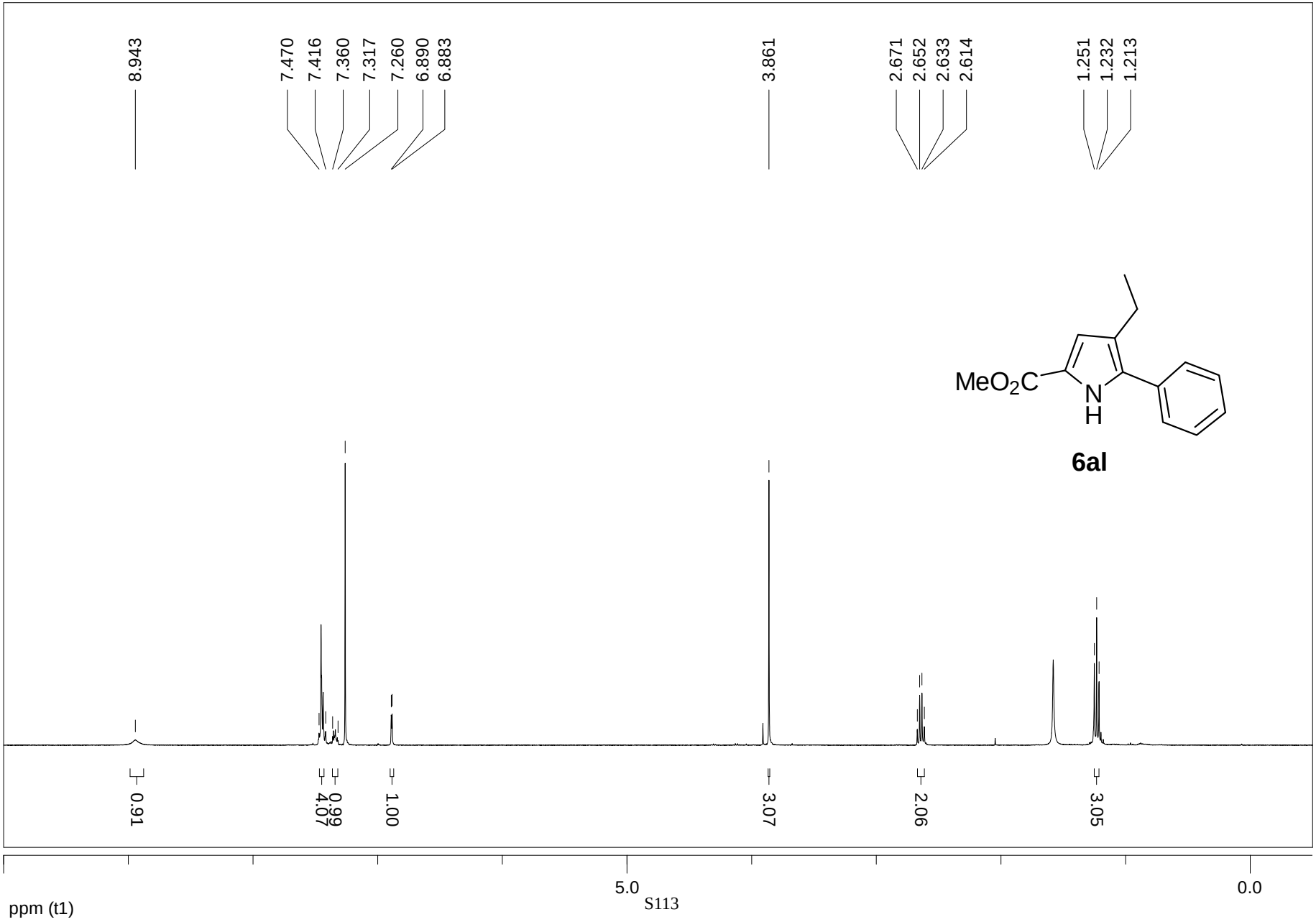
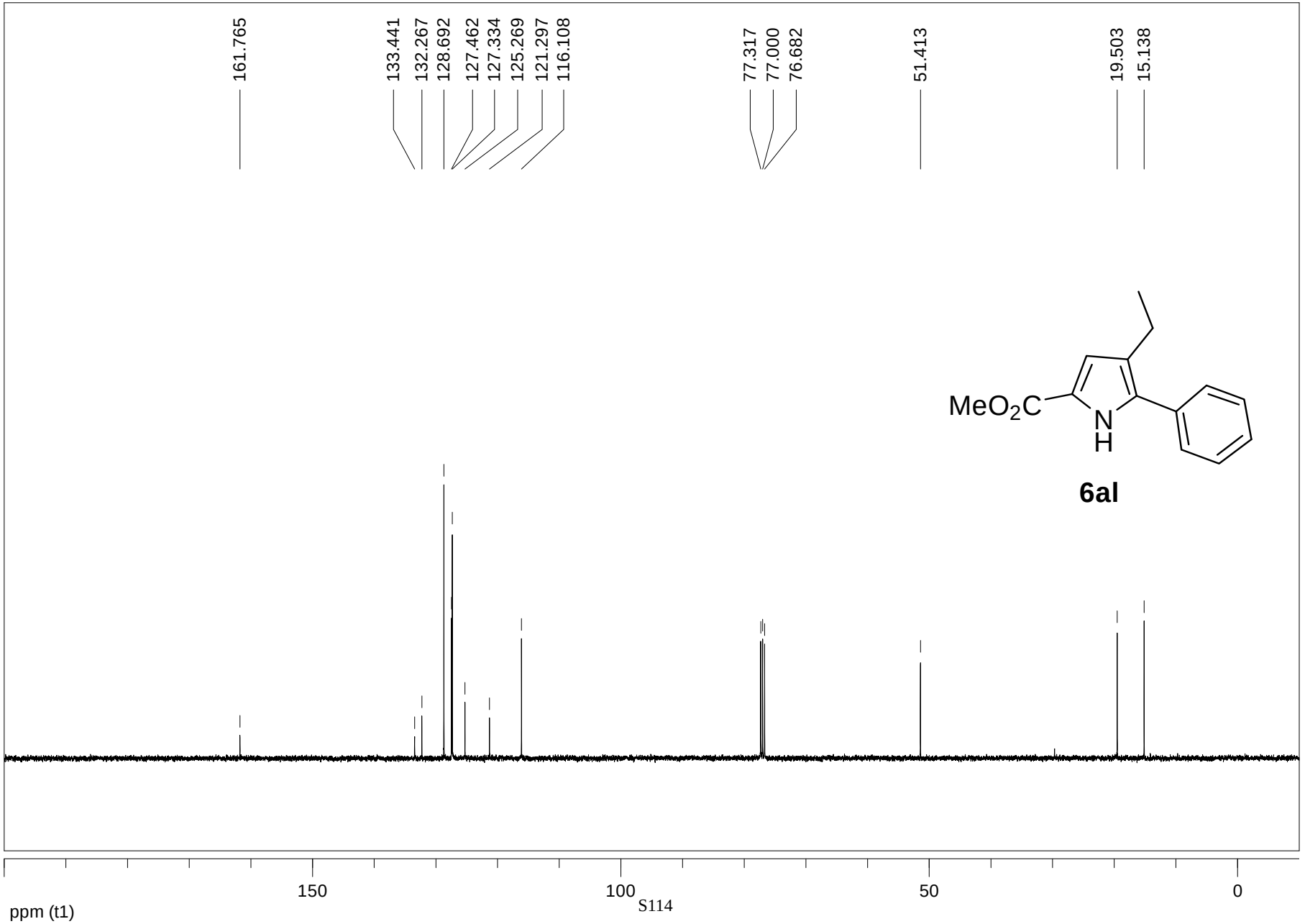
7.273
7.260
7.253
7.212
7.192
7.149
7.129
7.102
7.083
7.032
7.026
3.880
2.358
2.341
0.83
1.25
2.04
2.08
2.05
1.00
7.300
7.250
7.200
7.150
7.100
7.050
7.000
ppm (t1)
MeO2C
N
H
6af
1.08
3.07
5.0
0.0
ppm (t1)

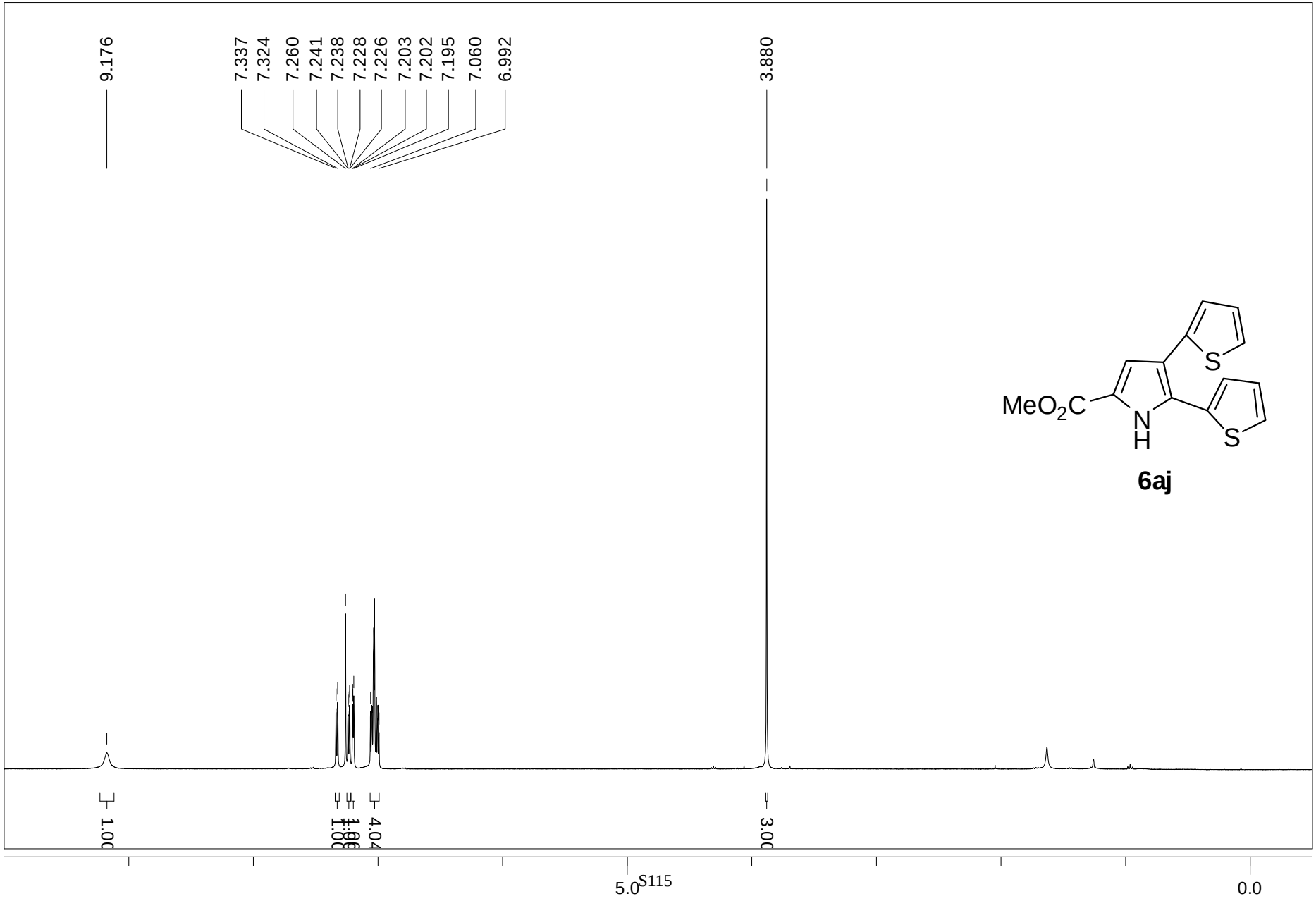

161.861
137.673
135.772
133.556
132.535
129.239
129.017
128.263
127.832
123.691
121.627
116.845
77.318
77.000
76.682
51.504
21.187
21.064
MeO2C
N
H
6af
150
100
50
0
ppm (t1)
x

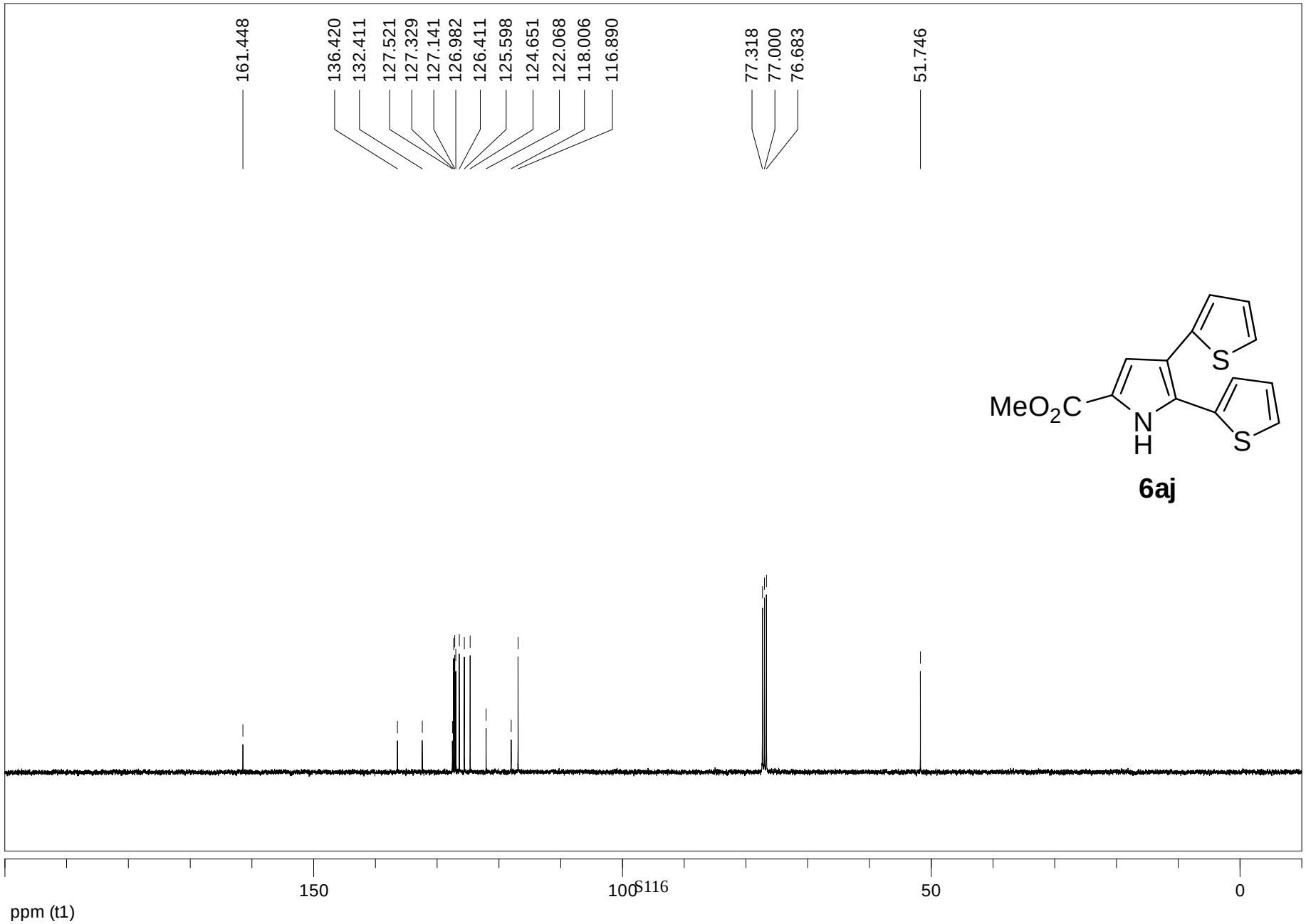

8.970
7.494
7.421
7.350
7.314
7.260
6.809
6.803
3.856
2.256
7.494
7.421
7.350
7.314
4.07
1.02
7.500
7.450
7.400
7.350
7.300
ppm (t1)
MeO2C
N
H
6ak
1.01
4.07
1.02
1.00
3.03
3.03
5.0
0.0
ppm (t1)

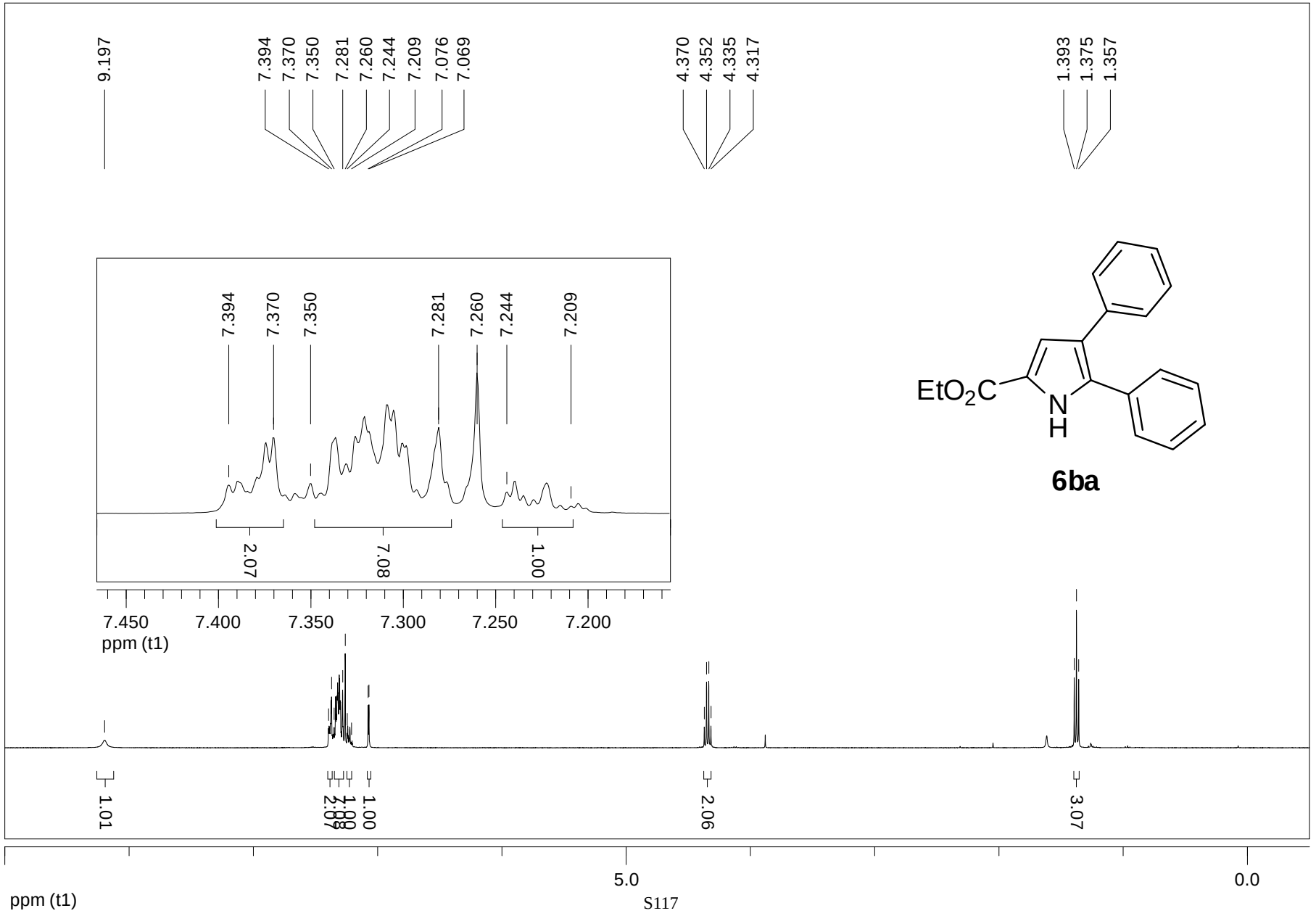

161.813
133.918
132.214
128.665
127.314
127.029
121.033
118.255
118.163
77.317
77.000
76.682
51.416
12.411
MeO2C
N
H
6ak
150
100
50
0
ppm (t1)

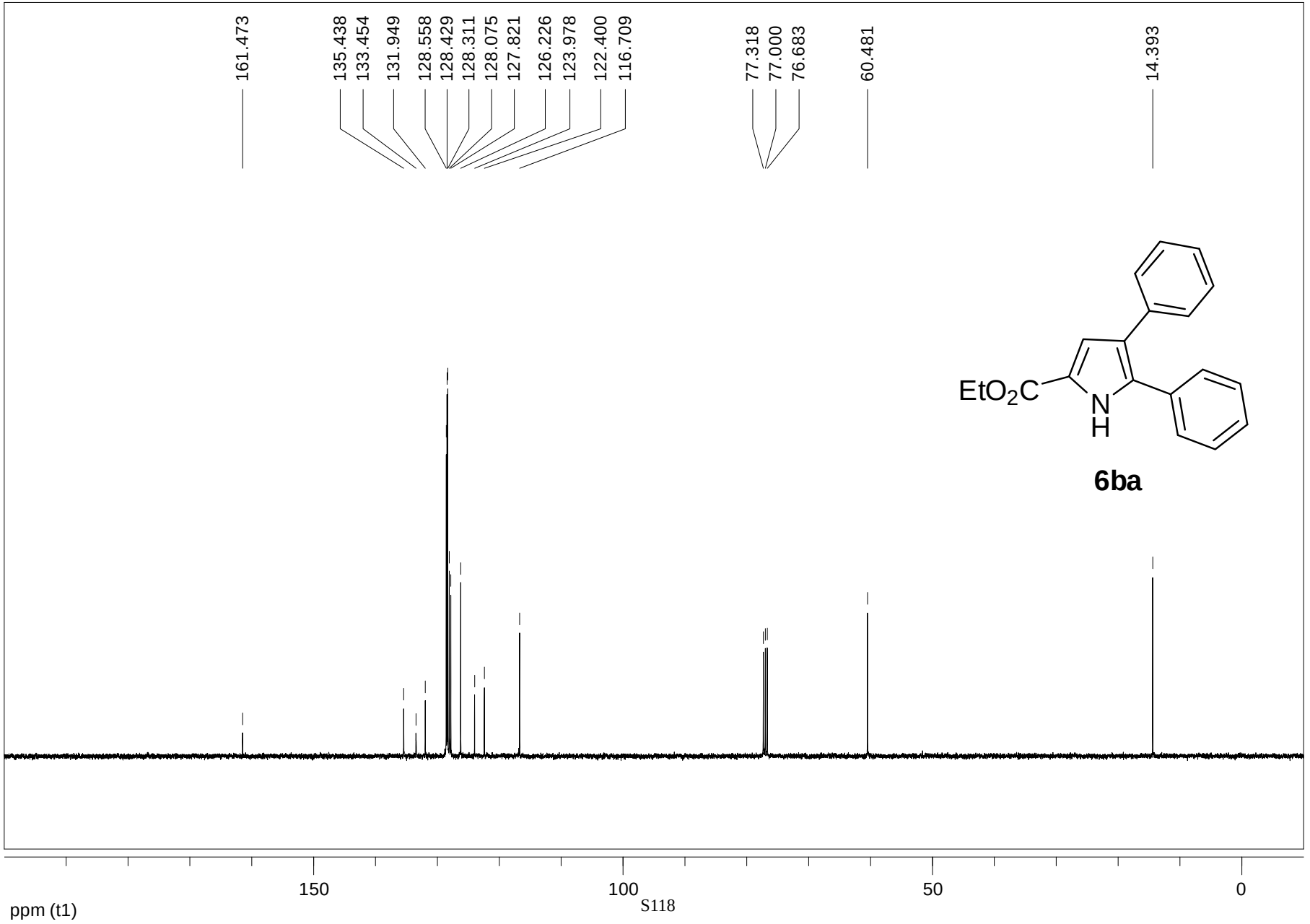

8.943
7.470
7.416
7.360
7.317
7.260
6.890
6.883
3.861
2.671
2.652
2.633
2.614
1.251
1.232
1.213
MeO2C
N
H
6al
0.91
4.07
0.99
1.00
3.07
2.06
3.05
5.0
0.0
ppm (t1)

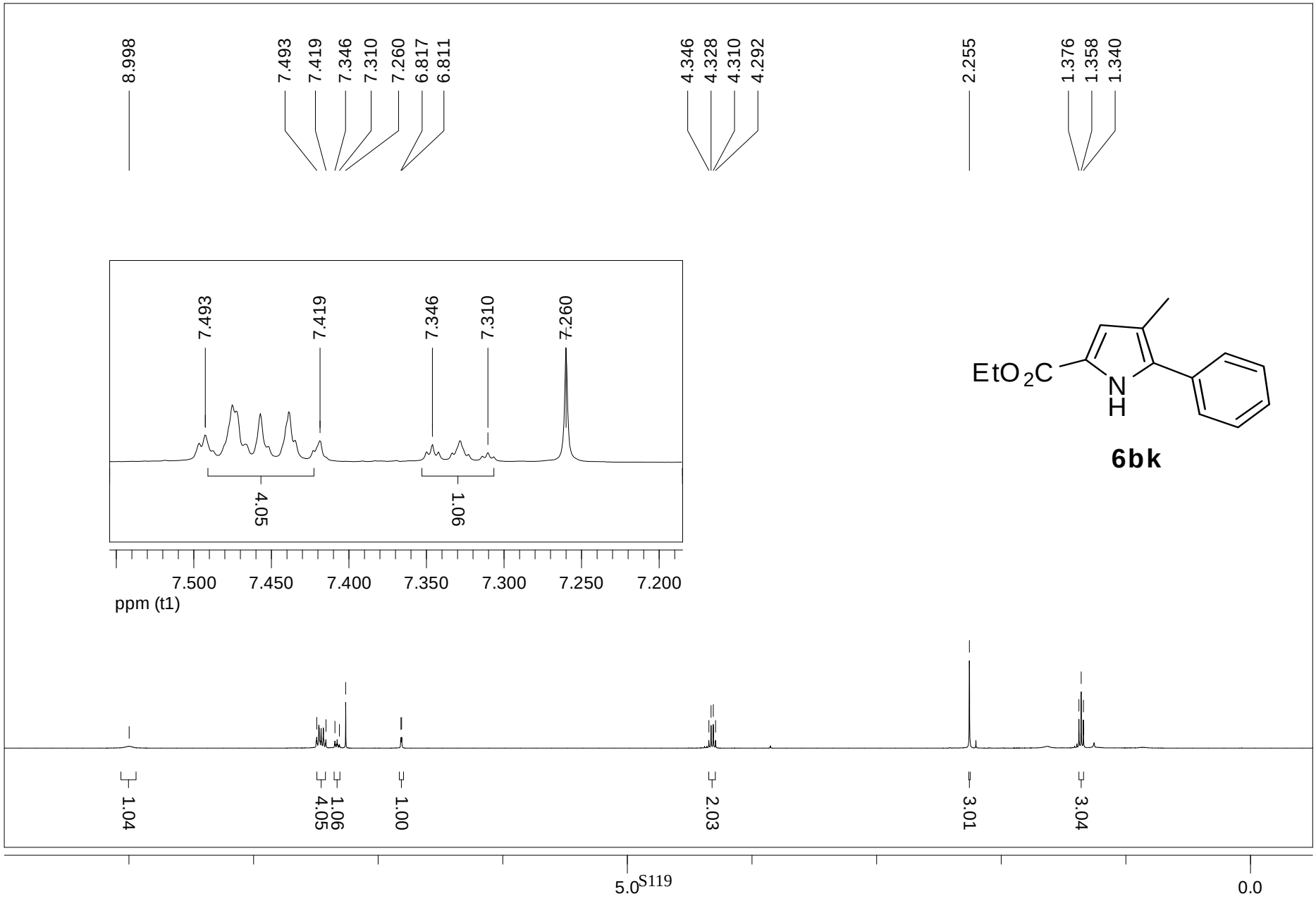

161.765
133.441
132.267
128.692
127.462
127.334
125.269
121.297
116.108
77.317
77.000
76.682
51.413
19.503
15.138
MeO2C
N
H
6al
150
100
50
0
ppm (t1)

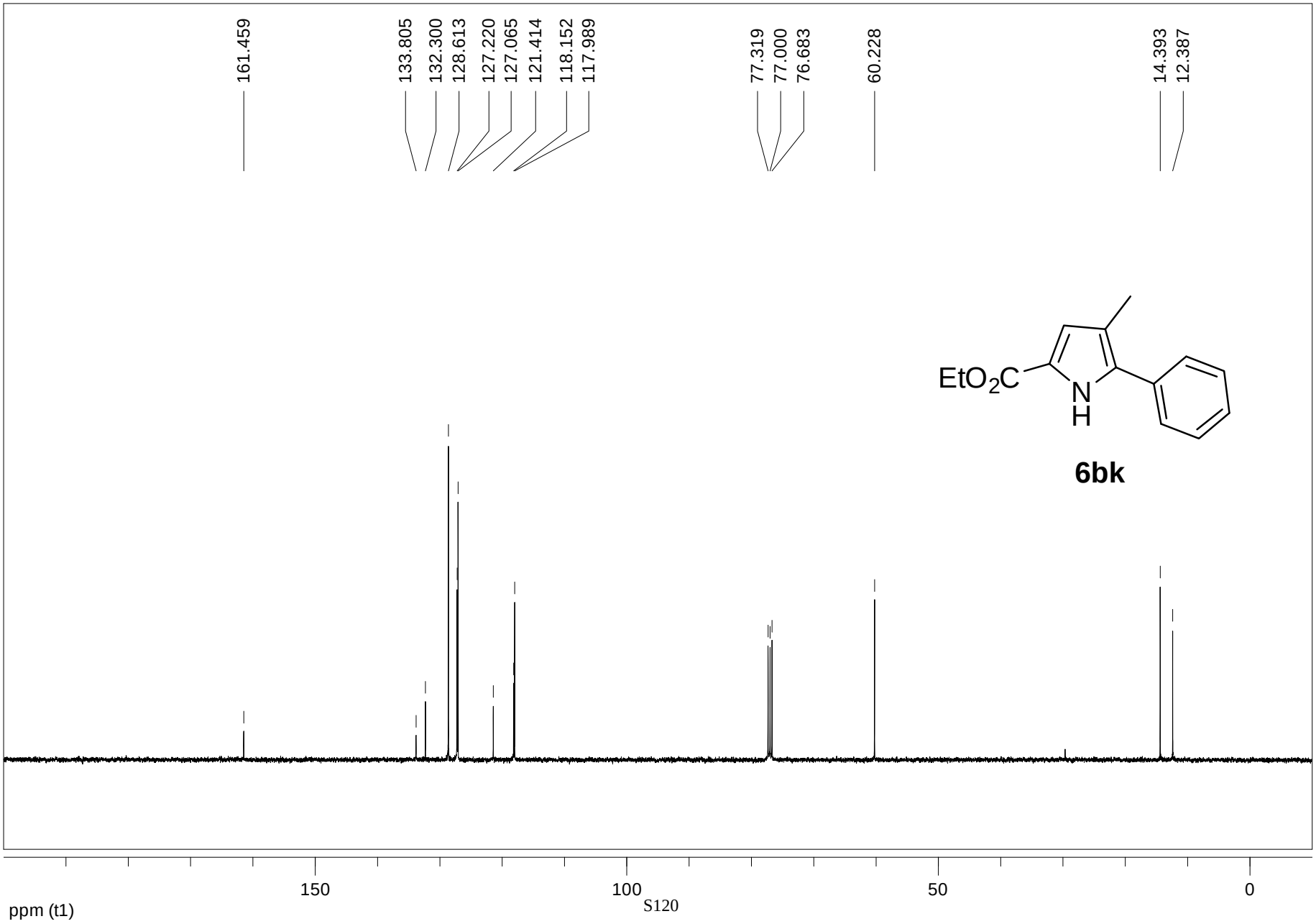

9.176
7.337
7.324
7.260
7.241
7.238
7.228
7.226
7.203
7.202
7.195
7.060
6.992
3.880
MeO2C
N
H
S
S
6aj
1.00
4.04
3.00
5.0
0.0
ppm (t1)

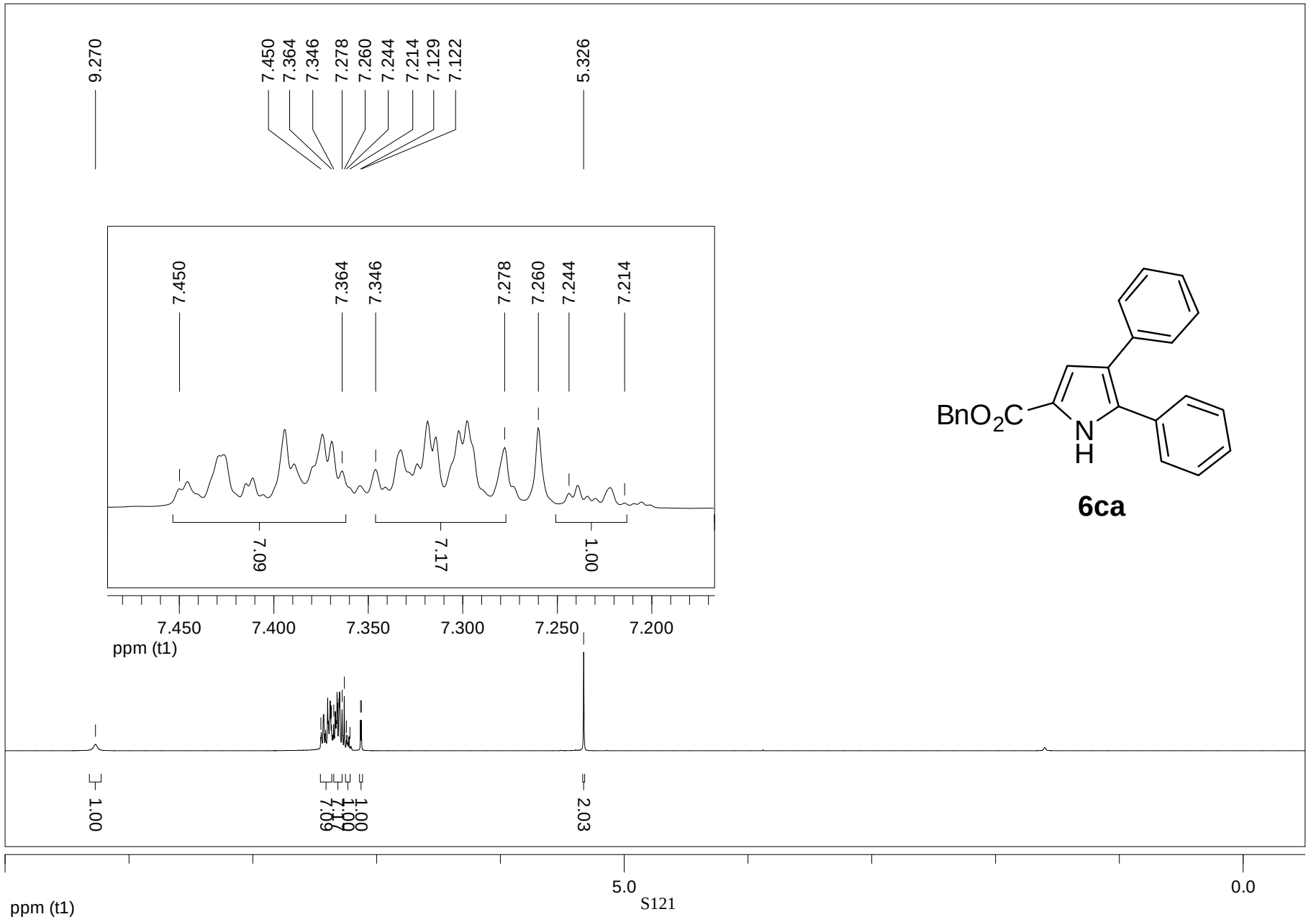

161.448
136.420
132.411
127.521
127.329
127.141
126.982
126.411
125.598
124.651
122.068
118.006
116.890
77.318
77.000
76.683
51.746
MeO2C
N
H
S
S
6aj
150
100
50
0
ppm (t1)

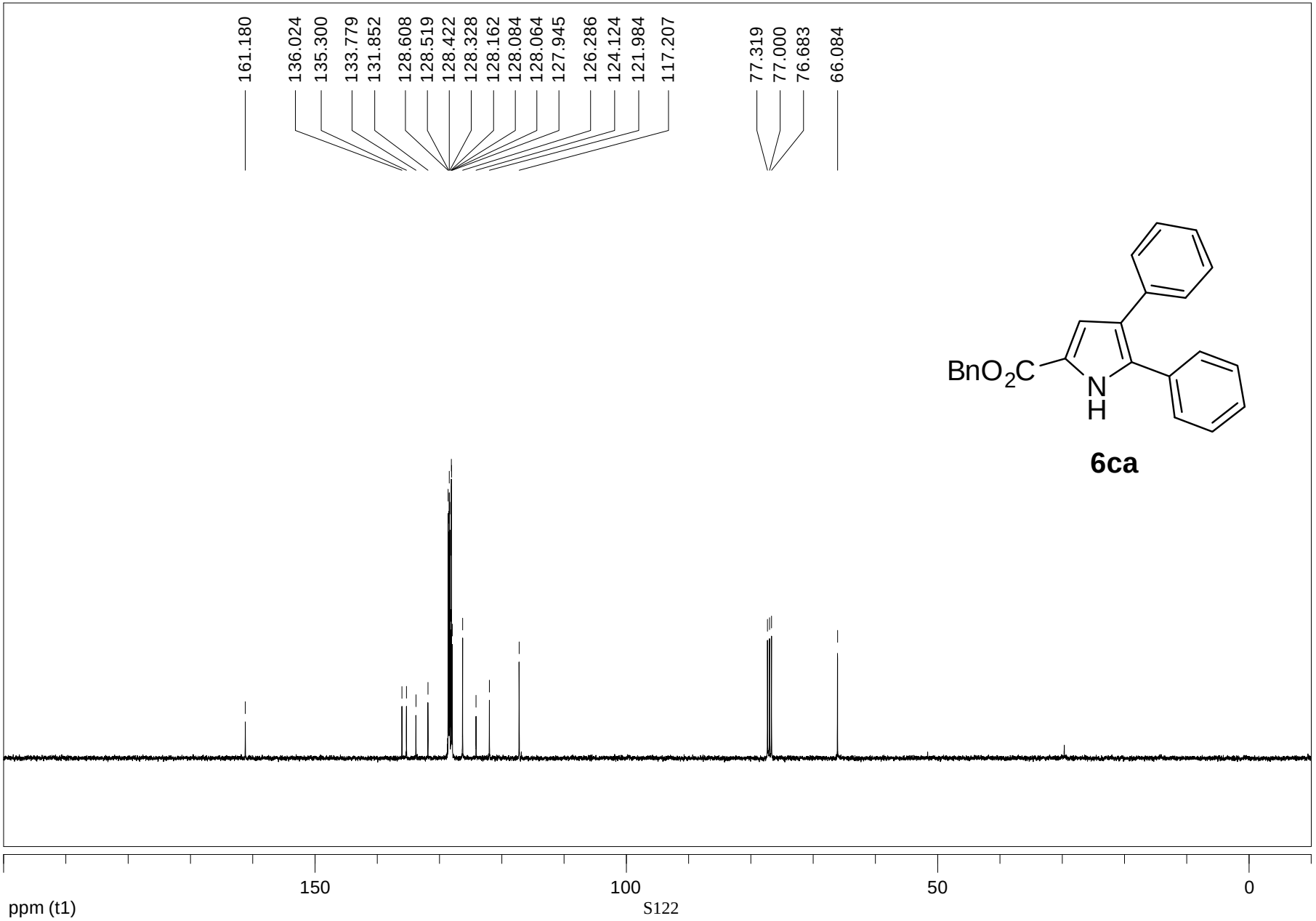

9.197
7.394
7.370
7.350
7.281
7.260
7.244
7.209
7.076
7.069
4.370
4.352
4.335
4.317
1.393
1.375
1.357
EtO2C
N
H
6ba
2.07
7.08
1.00
7.450
7.400
7.350
7.300
7.250
7.200
ppm (t1)
1.01
2.09
1.00
2.06
3.07
5.0
0.0
ppm (t1)

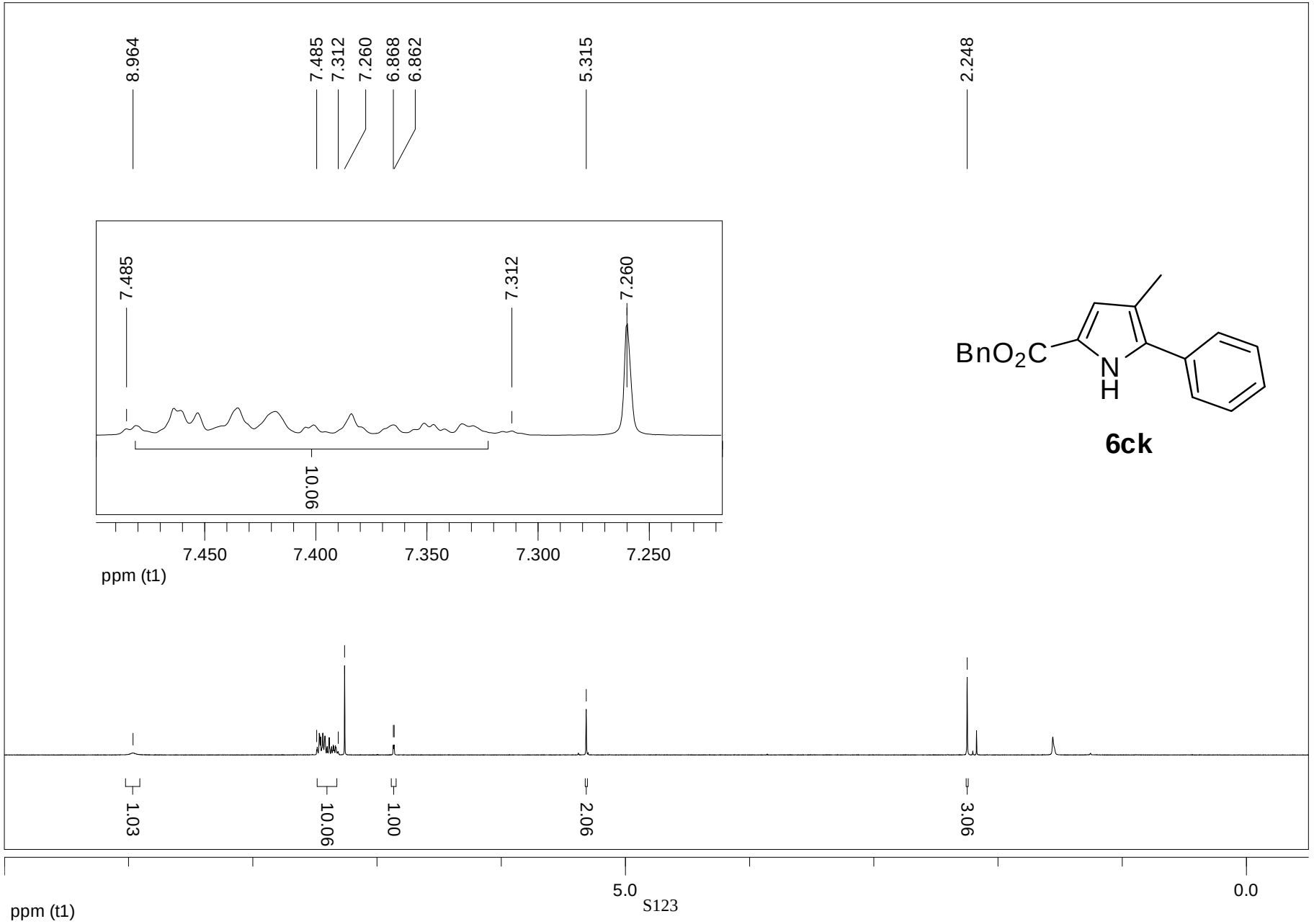

161.473
135.438
133.454
131.949
128.558
128.429
128.311
128.075
127.821
126.226
123.978
122.400
116.709
77.318
77.000
76.683
60.481
14.393
EtO2C
N
H
6ba
150
100
50
0
ppm (t1)

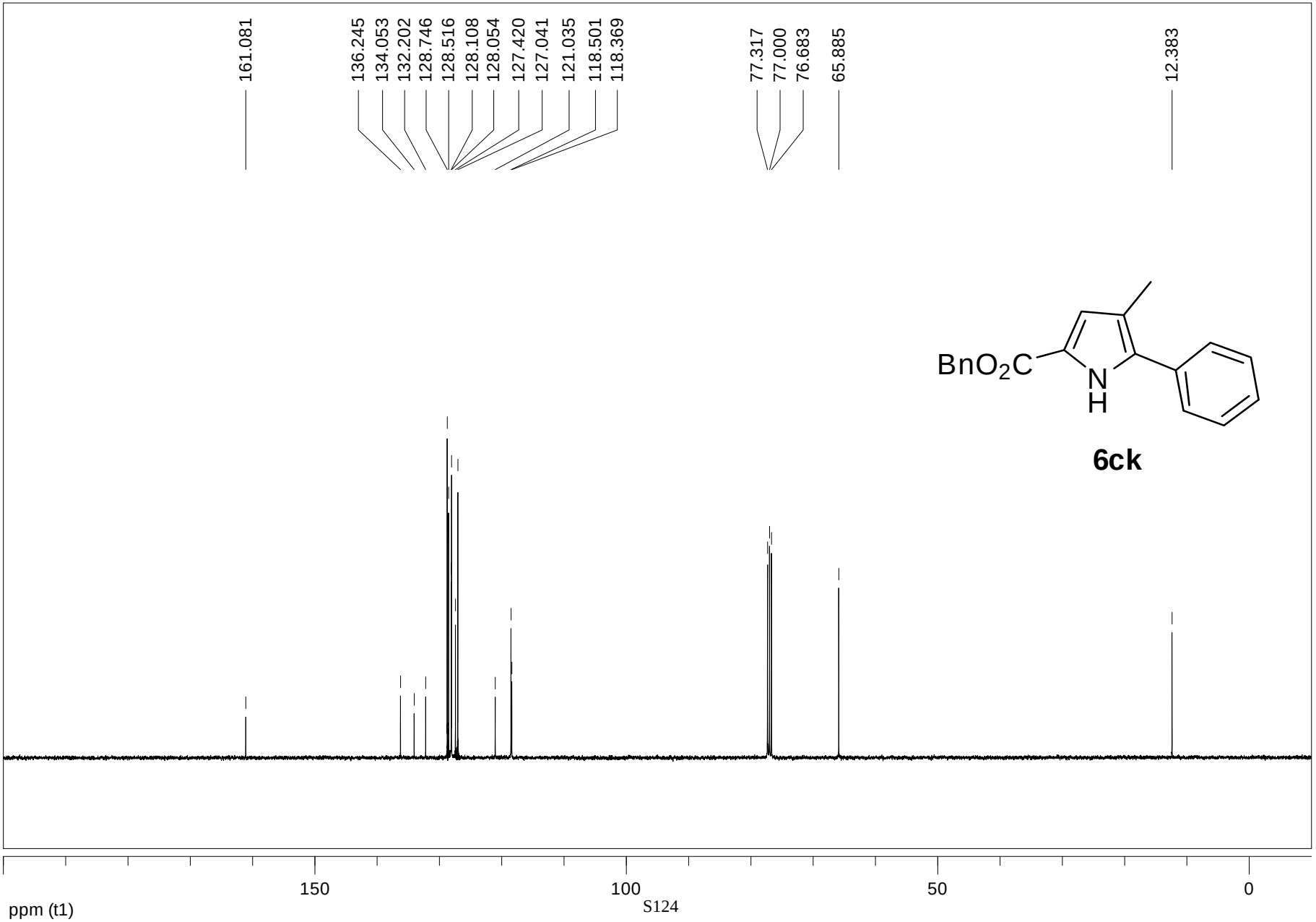

8.998
7.493
7.419
7.346
7.310
7.260
6.817
6.811
4.346
4.328
4.310
4.292
2.255
1.376
1.358
1.340
7.493
7.419
7.346
7.310
7.260
4.05
1.06
7.500
7.450
7.400
7.350
7.300
7.250
7.200
ppm (t1)
EtO2C
N
H
6bk
1.04
4.05
1.06
1.00
2.03
3.01
3.04
5.0
0.0
ppm (t1)


161.459
133.805
132.300
128.613
127.220
127.065
121.414
118.152
117.989
77.319
77.000
76.683
60.228
14.393
12.387
EtO2C
N
H
6bk
150
100
50
0
ppm (t1)


9.270
7.450
7.364
7.346
7.278
7.260
7.244
7.214
7.129
7.122
5.326
7.450
7.364
7.346
7.278
7.260
7.244
7.214
7.09
7.17
1.00
7.450
7.400
7.350
7.300
7.250
7.200
ppm (t1)
BnO2C
N
H
6ca
1.00
7.09
1.00
2.03
5.0
0.0
ppm (t1)


161.180
136.024
135.300
133.779
131.852
128.608
128.519
128.422
128.328
128.162
128.084
128.064
127.945
126.286
124.124
121.984
117.207
77.319
77.000
76.683
66.084
BnO2C
N
H
6ca
150
100
50
0
ppm (t1)


8.964
7.485
7.312
7.260
6.868
6.862
5.315
2.248
7.485
7.312
7.260
10.06
7.450
7.400
7.350
7.300
7.250
ppm (t1)
BnO2C
N
H
6ck
1.03
10.06
1.00
2.06
3.06
5.0
0.0
ppm (t1)


161.081
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134.053
132.202
128.746
128.516
128.108
128.054
127.420
127.041
121.035
118.501
118.369
77.317
77.000
76.683
65.885
12.383
BnO2C
N
H
6ck
150
100
50
0
ppm (t1)

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