SUPPORTING INFORMATION FOR *CHEMICAL COMMUNICATIONS*

Acyclic Diaminocarbenes: Simple, Versatile Ligands for Cross-Coupling Reactions

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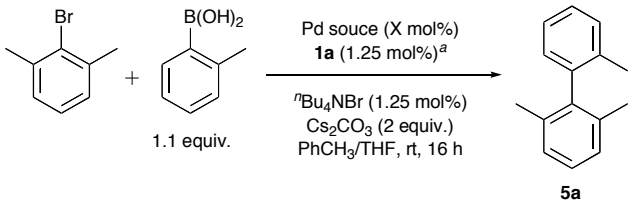
EXPERIMENTAL PROCEDURES and CHARACTERIZATION DATA

General. THF was dried and distilled over sodium/benzophenone ketal. Toluene and *N*,*N*-dimethylacetamide (DMA) were dried and distilled over calcium hydride. THF, toluene and DMA were also degassed (freeze-pump-thaw) just prior to use. Cesium carbonate was dried under vacuum (60 °C, 1 mm Hg) just prior to use. Aryl and alkenyl halides in liquid form were distilled prior to use. Methyl acrylate was distilled just prior to use. All other reagents were used as received (Aldrich, Acros, Strem). Silica gel (60 Å, 230-400 mesh) was obtained from Silicycle and used as received. All reactions were performed under an atmosphere of anhydrous nitrogen or argon. Melting points are uncorrected and were measured on a Fisher-Johns melting point apparatus. ^{1}H and ^{13}C NMR were recorded at 300 or 500 MHz and 75 or 125 MHz respectively on a Bruker Spectrospin 300 or 500 MHz spectrometer. Proton chemical shifts were internally referenced to the residual proton resonance in $CDCl_3$ (7.26). Carbon chemical shifts were internally referenced to the deuterated solvent signals in $CDCl_3$ (77.00). Infrared spectra were obtained on a Bruker VECTOR22 FT-IR spectrometer. HRMS-CI were performed on a Waters/Micromass GCT time-of-flight mass spectrometer.

All the requisite formamidinium salts were prepared as previously described by Alder *et al*., and without any modifications.[1]

Optimization Studies

Table 4. Effect of the Nature of the Palladium Source on the Suzuki-Miyaura Coupling of 2-Bromo-1,3-dimethylbenzene with 2-Methylphenylboronic acid using ADC **1a** as Ligand

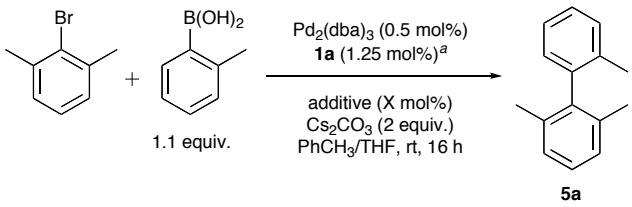


Entry	Pd source/mol%	Yield/%
1	$Pd_2(dba)_3$/0.5	89
2	$Pd(OAc)_2$/1.0	62
3	$[Pd(allyl)Cl]_2$/0.5	80
4	$PdCl_2(CH_3CN)_2$/1.0	79

[a] Prepared *in situ* via deprotonation of the corresponding formamidinium salt

Please note that we found it to be optimal if **1a** was allowed to pre-mix with the palladium catalyst before the addition of the other reagents. We suggest that this observation is due to the fact that once the ADC is bound to the metal center, the resulting catalyst species is more robust and less likely to degrade to palladium black during the course of the reaction. If **1a** was added at the same time as the other reagents, lower conversions were observed probably due to the earlier appearance of palladium black in the reaction mixture.

Table 5. Effect of Additives on the Suzuki-Miyaura Coupling of 2-Bromo-1,3-dimethylbenzene with 2-Methylphenylboronic acid using ADC **1a** as Ligand

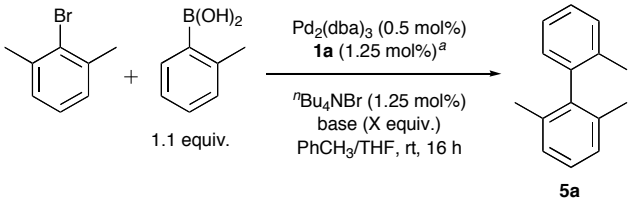


Entry	Additive	Mol%	Yield/%
1	none	-	62
2	LiBr	5	65
3	NH_4Br	5	60
4	$^{n}Bu_4NBr$	5	90
5	$^{n}Bu_4NI$	5	89
6	$^{n}Bu_4NBr$	2	90
7	$^{n}Bu_4NBr$	1	84
8	$^{n}Bu_4NBr$	1.25	89

[a] Prepared *in situ* via deprotonation of the corresponding formamidinium salt

The use of $^{n}Bu_4NBr$ is precedented in NHC catalyzed Suzuki-Miyaura couplings (see: K. Arentsen, S. Caddick, F. G. N. Cloke, A. P. Herring and P. B. Hitchcock, *Tetrahedron Lett.*, 2004, **45**, 3511). We found that the use of $^{n}Bu_4NBr$ allowed the palladium catalyst to remain homogenous and soluble for a longer period of time (*i.e.* palladium black formation was delayed until near full conversion was achieved).

Table 6. Effect of the Nature of the Base on the Suzuki-Miyaura Coupling of 2-Bromo-1,3-dimethylbenzene with 2-Methylphenylboronic acid using ADC **1a** as Ligand



Entry	Base	Equiv.	Yield/%
1	none	-	<2%
2	Cs_2CO_3	2.0	89
3	$^{i}Pr_2NEt$	2.0	<10
3	CsF	2.0	85
4	KOMe	5.0	78
5	Na_2CO_3	5.0	19
6	NaOH	2.0	<10
7	Cs_2CO_3	1.5	85
8	Cs_2CO_3	1.1	77

[a] Prepared *in situ* via deprotonation of the corresponding formamidinium salt

Please note that we tried to deprotonate the formamidinium precursor to ADC **1a** with Cs_2CO_3 in one pot but were unsuccessful (see: R. W. Alder, P. R. Allen, M. Murray and A. G. Orpen, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1121). Similar attempts with KO^{t}Bu gave lower yields. Thus, we decided to pre-form ADC **1a** via Alder's procedure using LDA, and then complex it with the palladium catalyst (see General Experimental Details for Table 1, *vide infra*).

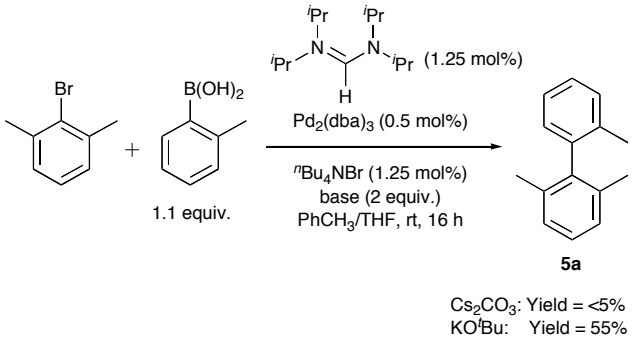
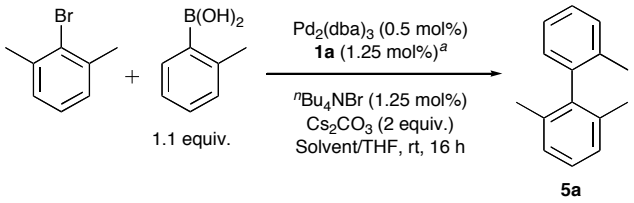


Table 7. Effect of the Solvent on the Suzuki-Miyaura Coupling of 2-Bromo-1,3-dimethylbenzene with 2-Methylphenylboronic acid using ADC **1a** as Ligand

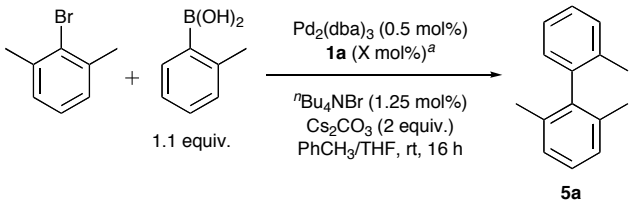


Entry	Solvent	Yield/%
1	THF	70
2	$PHCH_3$	89
3	DME	73
4	DMA	80
5	CH_2Cl_2	24
6	benzene	85

[a] Prepared *in situ* via deprotonation of the corresponding formamidinium salt

Please note that the THF in the reaction scheme is derived from the deprotonation of the corresponding formamidinium salt precursor to form ADC **1a** *in situ*, which is carried out in THF (see General Procedure for Tables 1-3, *vide infra*). The ratio of solvent:THF is *ca*. 10:1.

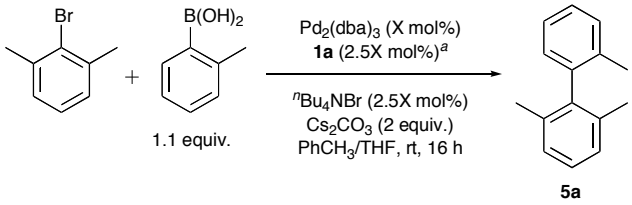
Table 8. Effect of Pd:**1a** ratio on the Suzuki-Miyaura Coupling of 2-Bromo-1,3-dimethylbenzene with 2-Methylphenylboronic acid using ADC **1a** as Ligand



Entry	**1a**/mol%	Yield/%
1	0.5	43
2	1.0	79
3	1.25	89
4	1.5	85
5	2.0	80
6	4.0	61

[a] Prepared *in situ* via deprotonation of the corresponding formamidinium salt

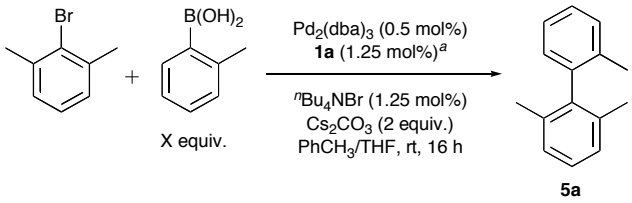
Table 9. Effect of $Pd_2(dba)_3$ loading on the Suzuki-Miyaura Coupling of 2-Bromo-1,3-dimethylbenzene with 2-Methylphenylboronic acid using ADC **1a** as Ligand



Entry	$Pd_2(dba)_3$/mol%	Yield/%
1	1.5	95
2	1.0	90
3	0.5	89
4	0.3	82
5	0.2	59
6	0.1	31

[a] Prepared *in situ* via deprotonation of the corresponding formamidinium salt

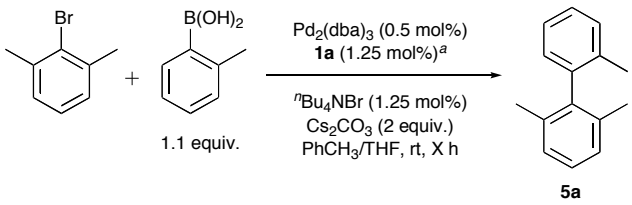
Table 10. Effect of the Stoichiometry of the Boronic Acid on the Suzuki-Miyaura Coupling of 2-Bromo-1,3-dimethylbenzene with 2-Methylphenylboronic acid using ADC **1a** as Ligand



Entry	$ArB(OH)_2$/equiv.	Yield/%
1	2.0	96
2	1.5	90
3	1.3	89
4	1.2	85
5	1.1	89
6	1.0	81

[a] Prepared *in situ* via deprotonation of the corresponding formamidinium salt

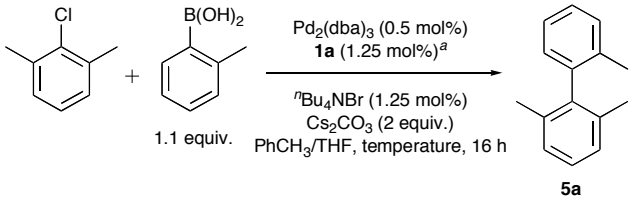
Table 11. Effect of Reaction Time on the Suzuki-Miyaura Coupling of 2-Bromo-1,3-dimethylbenzene with 2-Methylphenylboronic acid using ADC **1a** as Ligand



Entry	Time/h	Yield/%
1	1.0	47
2	6.0	70
3	12.0	84
4	16.0	89
5	24.0	88

[a] Prepared *in situ* via deprotonation of the corresponding formamidinium salt

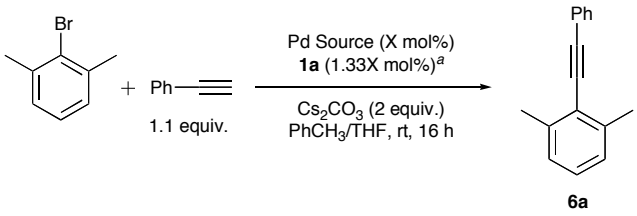
Table 12. Effect of Temperature on the Suzuki-Miyaura Coupling of 2-Chloro-1,3-dimethylbenzene with 2-Methylphenylboronic acid using ADC **1a** as Ligand



Entry	Temperature/°C	Yield/%
1	rt	22
2	30	47
3	45	81
4	60	87
5	80	95

[a] Prepared *in situ* via deprotonation of the corresponding formamidinium salt

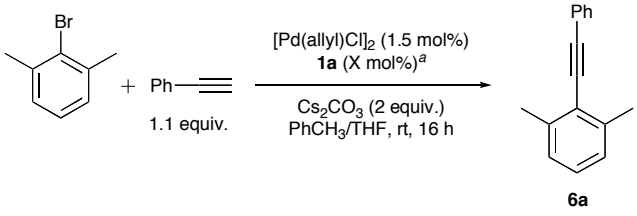
Table 13. Effect of the Palladium Source and Loading on the Room Temperature Sonogashira Coupling of Aryl Bromides using Ligand **1a**



Entry	Pd source	Mol%	Yield/%
1	$Pd_2(dba)_3$	1.5	70
2	$Pd(OAc)_2$	1.5	51
3	$[Pd(allyl)Cl]_2$	1.5	80
4	$PdCl_2(CH_3CN)_2$	1.5	71
5	$[Pd(allyl)Cl]_2$	1.0	65
6	$[Pd(allyl)Cl]_2$	0.5	49

[a] Prepared *in situ* via deprotonation of the corresponding formamidinium salt

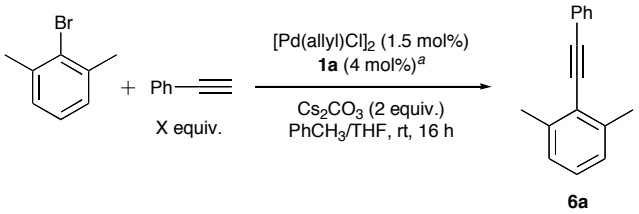
Table 14. Effect of the Ratio of $[Pd(allyl)Cl]_2$:**1a** on the Room Temperature Sonogashira Coupling of Aryl Bromides using Ligand **1a**



Entry	**1a**/mol%	Yield/%
1	1.5	49
2	3.0	73
3	4.0	80
4	5.0	81

[a] Prepared *in situ* via deprotonation of the corresponding formamidinium salt

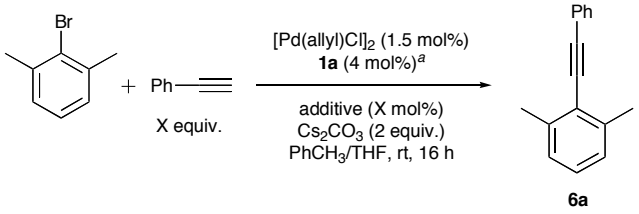
Table 15. Effect of the Stoichiometry of Alkyne on the Room Temperature Sonogashira Coupling of Aryl Bromides using Ligand **1a**



Entry	Alkyne/equiv.	Yield/%
1	2.0	84
2	1.5	80
3	1.1	81

[a] Prepared *in situ* via deprotonation of the corresponding formamidinium salt

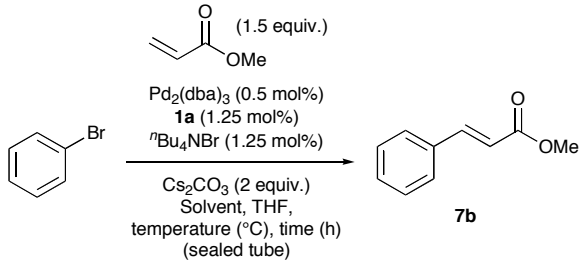
Table 16. Effect of the Additives on the Room Temperature Sonogashira Coupling of Aryl Bromides using Ligand **1a**



Entry	Additive	Mol %	Yield/%
1	none	-	80
2	$^{n}Bu_4NBr$	1.25	80
3	$^{n}Bu_4NBr$	4.0	75

[a] Prepared *in situ* via deprotonation of the corresponding formamidinium salt

Table 17. Effect of Temperature, Time and Solvent on the Heck Reaction of Aryl Bromides Using ADC **1a** as Ligands

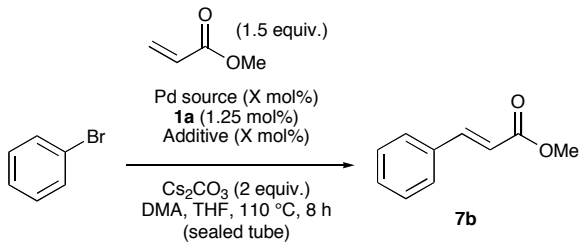


Entry	Solvent	Temperature/°C	Time/h	Yield/%
1	$PhCH_3$	110	8	39
2	DMF	110	8	73
3	DMA	110	8	78
4	DMA	110	16	80
5	DMA	90	8	62
6	DMA	50	8	17

[a] Prepared *in situ* via deprotonation of the corresponding formamidinium salt

Please note that the THF in the reaction scheme is derived from the deprotonation of the corresponding formamidinium salt precursor to form ADC **1a** *in situ*, which is carried out in THF (see General Procedure for Tables 1-3, *vide infra*). The ratio of solvent:THF is *ca.* 10:1.

Table 18. Effect of Palladium Source and Additives on the Heck Reaction of Aryl Bromides Using ADC **1a** as Ligands



Entry	Palladium Source/mol%	Additive/mol%	Yield/%
1	$Pd_2(dba)_3$/0.5	None	61
2	$Pd_2(dba)_3$/0.5	$^nBu_4NBr$/1.25	78
3	$Pd_2(dba)_3$/0.25	$^nBu_4NBr$/0.65	38
4	$Pd(OAc)_2$/1.0	None	22
5	$Pd(OAc)_2$/1.0	$^nBu_4NBr$/1.25	32
6	$[Pd(allyl)Cl]_2$/0.5	$^nBu_4NBr$/1.25	73
7	$PdCl_2(CH_3CN)_2$/1.0	$^nBu_4NBr$/1.25	61

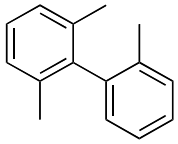
[a] Prepared *in situ* via deprotonation of the corresponding formamidinium salt

General Procedure for Suzuki Couplings of Aryl Bromides/Chlorides (Tables 1–3)

A 1.25 M solution of carbene **1a** was made as follows[2]: To a solution of diisopropylaminomethylidene(diisopropyl)ammonium tetrafluoroborate[1] (1.500 g, 5.00 mmol) in anhydrous THF (2.33 mL) cooled to –20 °C was added a freshly prepared solution of LDA (3.0 M in THF, 1.67 mL, 5.00 mmol). The reaction mixture was stirred for 30 min at –20 °C prior to the next step.

To a solution of $Pd_2(dba)_3$ (9.1 mg, 0.010 mmol) in anhydrous THF (0.25 mL) cooled to –20 °C was added carbene **1a** (1.25 M in THF, 20 μL, 0.025 mmol). The reaction mixture was stirred for 30 min at –20 °C, and another 5 min at rt. Anhydrous toluene (2.50 mL) was then added followed by cesium carbonate (1.30 g, 4.00 mmol), tetra-*n*-butylammonium bromide (8.0 mg, 0.025 mmol), aryl/alkenyl halide (2.00 mmol) and boronic acid/ester (2.20 mmol) in that particular order. *For aryl/alkenyl bromides (Table 1)*–the reaction mixture was subsequently stirred for 16 h at rt. *For aryl chlorides (Table 2)*–the reaction was subsequently stirred for 16 h at 45 °C. The reaction mixture was next diluted with EtOAc/hexanes (1:1, 30 mL), filtered and concentrated *in vacuo*. The residue was then subjected to silica gel chromatography.

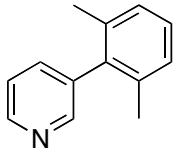
2,2',6-Trimethylbiphenyl (5a)[3]



5a

5a isolated as a clear, colorless oil: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.32 – 7.25 (3H, m), 7.22 – 7.11 (3H, m), 7.07 – 7.02 (1H, m), 2.00 (3H, s), 1.98 (6H, s); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 141.08, 140.53, 135.84, 135.60, 129.95, 128.83, 127.20, 126.98, 126.89, 126.03, 20.31, 19.37.

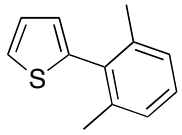
3-(2,6-Dimethylphenyl)pyridine (5b)[4]



5b

5b isolated as a clear, colorless oil: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.47 (1H, d, *J* = 3.5 Hz), 8.31 (1H, s), 7.50 (1H, dt, *J* = 7.5, 2.0 Hz), 7.35 (1H, dd, *J* = 7.5, 5.0 Hz), 7.21 (1H, dd, *J* = 8.0, 7.0 Hz), 7.13 (2H, d, *J* = 7.5 Hz), 2.02 (6H, s); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 149.55, 147.61, 137.59, 136.89, 136.14, 127.81, 127.44, 125.84, 123.36, 20.78.

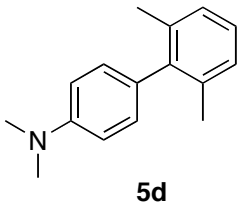
2-(2,6-Dimethylphenyl)thiophene (5c)



5c

5c isolated as a clear, colorless oil: ^{1}H NMR ($CDCl_3$, 300 MHz) 7.40 (1H, dd, J = 5.0, 1.0 Hz), 7.24 – 7.10 (4H, m), 6.85 (1H, dd, J = 3.0, 1.0 Hz), 2.18 (6H, s); ^{13}C NMR ($CDCl_3$, 125 MHz) 141.31, 138.42, 134.04, 128.04, 127.22, 127.02, 126.23, 125.26, 20.78; IR (film) 3141, 3066, 3021, 2953, 2922, 2855, 1582, 1463, 1441, 1377, 1253, 1237, 1194, 1039, 951, 848, 830, 771, 731, 695 cm^{-1}; HRMS (CI) m/z calcd. for $C_{12}H_{12}S$ (M^+) 188.0660, found 188.0654.

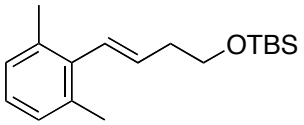
(2'6'-Dimethylbiphenyl-4-yl)dimethylamine (5d)



5d

5d isolated as a clear, colorless crystalline solid: m.p. = 75–77 °C ($CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) 7.18 – 7.11 (3H, m), 7.05 (2H, d, J = 8.5 Hz), 6.82 (2H, d, J = 8.5 Hz), 3.02 (6H, s), 2.10 (6H, s); ^{13}C NMR ($CDCl_3$, 125 MHz) 149.07, 141.99, 136.80, 129.69, 129.09, 127.14, 126.54, 112.35, 40.60, 20.99; IR (KBr) 3156, 2918, 2852, 2794, 1830, 1612, 1524, 1465, 1441, 1376, 1340, 1223, 1193, 1165, 1123, 1096, 1060, 1030, 946, 822, 767 cm^{-1}; HRMS (CI) m/z calcd. for $C_{16}H_{20}N$ (MH^+) 226.1596, found 226.1599

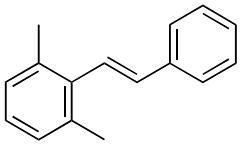
(*E*)-*tert*-Butyl[4-(2,6-dimethylphenyl)but-3-enyloxy]dimethylsilane (5e)



5e

Xa isolated as a clear, colorless oil: ^{1}H NMR ($CDCl_3$, 500 MHz) 7.03 – 7.00 (3H, m), 6.39 (1H, d, J = 16.0 Hz), 5.69 (1H, dt, J = 16.0, 7.0 Hz), 3.77 (2H, t, J = 7.0 Hz), 2.47 (2H, dq, J = 7.0, 1.0 Hz), 2.30 (6H, s), 0.92 (9H, s); ^{13}C NMR ($CDCl_3$, 125 MHz) 137.56, 135.93, 132.25, 129.19, 127.56, 126.18, 63.11, 37.14, 25.95, 20.93, 18.33, 5.28; IR (film) 3111, 2954, 2929, 2857, 1670, 1471, 1379, 1361, 1255, 1097, 1006, 971, 940, 836, 768 cm^{-1}; HRMS (CI) m/z calcd. for $C_{18}H_{31}OSi$ (MH^+) 291.2144, found 291.2137.

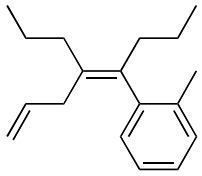
1,3-Dimethyl-2-[(*E*)-2-phenyl-1-ethenyl]benzene (5f)[5]



5f

5f isolated as a clear, colorless crystalline solid: m.p. = 33-35 °C ($CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.52 (2H, q, *J* = 7.5 Hz), 7.39 (2H, d, *J* = 7.5 Hz), 7.37 – 7.26 (1H, m), 7.13 (1H, d, *J* = 16.5 Hz), 7.12 – 7.08 (3H, m), 6.62 (1H, d, *J* = 16.5 Hz), 2.39 (6H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 137.67, 137.02, 136.31, 134.04, 128.73, 127.94, 127.64, 127.01, 126.77, 126.35, 21.13.

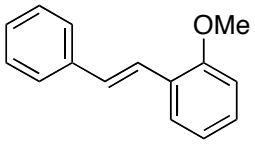
1-(1,2-Diisopropylpenta-1,4-dienyl)-2-methylbenzene (5g)



5g

5g isolated as a clear, colorless oil: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.20 – 7.09 (3H, m), 6.95 (1H, dd, *J* = 7.0, 1.5 Hz), 5.67 – 5.58 (1H, m), 4.92 – 4.83 (2H, m), 2.52 – 2.39 (3H, m), 2.31 – 2.23 (1H, m), 2.18 (3H, s), 2.12 – 2.02 (2H, m), 1.57 – 1.45 (2H, m), 1.42 – 1.23 (2H, m), 0.99 (3H, t, *J* = 7.5 Hz), 0.89 (3H, t, *J* = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 142.92, 137.14, 136.40, 135.32, 133.50, 129.74, 129.37, 126.13, 125.08, 114.95, 37.47, 35.66, 32.30, 21.85, 21.44, 19.42, 14.31 (one overlap); IR (film) ν 3120, 3059, 3014, 2959, 2871, 1677, 1635, 1485, 1455, 1378, 1119, 1092, 1042, 910, 767, 758, 733 cm^{-1}; HRMS (EI) *m*/*z* calcd. for $C_{18}H_{26}$ (M^+) 242.2035, found 242.2038.

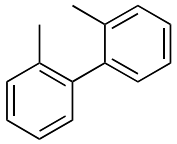
1-Methoxy-2-[(*E*)-2-phenyl-1-ethenyl]benzene (5h)[6]



5h

5h isolated as a clear, colorless oil: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.61 (1H, dd, *J* = 7.5, 1.5 Hz), 7.55 (2H, d, *J* = 7.5 Hz), 7.50 (1H, d, *J* = 16.5 Hz), 7.36 (2H, t, *J* = 7.5 Hz), 7.28 – 7.23 (2H, m), 7.13 (1H, d, *J* = 16.5 Hz), 6.98 (1H, t, *J* = 7.5 Hz), 6.91 (1H, d, *J* = 8.0 Hz), 3.90 (3H, s); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 156.91, 137.96, 129.09, 128.64, 128.56, 127.33, 126.55, 126.44, 126.40, 123.49, 120.73, 110.93, 55.51; HRMS (CI) *m*/*z* calcd. for $C_{15}H_{14}O$ (M^+) 210.1045, found 210.1054.

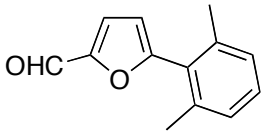
2,2'-Dimethylbiphenyl (5i)[7]



5i

5i isolated as a clear, colorless oil: ^{1}H NMR ($CDCl_3$, 500 MHz) 7.38 – 7.30 (6H, m), 7.23 – 7.20 (2H, m), 2.17 (6H, s); ^{13}C NMR ($CDCl_3$, 125 MHz) 141.55, 135.73, 129.76, 129.23, 127.11, 125.50, 19.79.

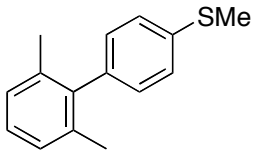
5-(2,6-Dimethylphenyl)furan-2-carbaldehyde (5j)



5j

5j isolated as a clear, colorless crystalline solid: m.p. = 143-145 °C ($CHCl_3$) ^{1}H NMR ($CDCl_3$, 500 MHz) 9.67 (1H, s), 7.36 (1H, d, *J* = 3.5 Hz), 7.24 (1H, t, *J* = 7.5 Hz), 7.11 (2H, d, *J* = 7.5 Hz), 6.52 (1H, *J* = 3.5 Hz), 2.12 (6H, s); ^{13}C NMR ($CDCl_3$, 125 MHz) 177.56, 158.90, 152.29, 138.23, 129.64, 129.22, 127.70, 121.96, 112.49, 20.43; IR (KBr) 3102, 2965, 2847, 1666, 1640, 1526, 1468, 1384, 1278, 1231, 1172, 1023, 964, 922, 812, 771 cm^{-1}; HRMS (CI) *m/z* calcd. for $C_{13}H_{12}O_2$ (M^+) 200.0837, found 200.0836.

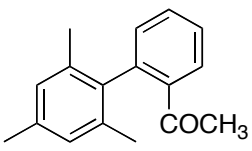
2,6-Dimethyl-4'-methylsulfanylbiphenyl (5k)



5k

5k isolated as a white solid: m.p. = 48-50 °C ($CHCl_3$) ^{1}H NMR ($CDCl_3$, 300 MHz) 7.41 – 7.33 (2H, m), 7.24 – 7.09 (5H, m), 2.57 (3H, s), 2.09 (6H, s) ;^{13}C NMR ($CDCl_3$, 75 MHz) 141.14, 137.77, 136.47, 136.12, 129.50, 127.26, 127.03, 126.49, 20.81, 15.73; IR (KBr) 3115, 3056, 2917, 2853, 1870, 1675, 1464, 1438, 1388, 1183, 1164, 1109, 1090, 964, 822, 77, 753 cm^{-1}; HRMS (CI) *m/z* calcd. for $C_{15}H_{16}S$ (M^+) 228.0973, found 228.0975.

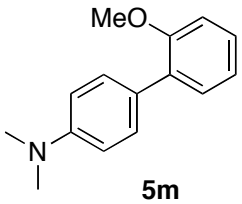
1-(2',4',6'-Trimethylbiphenyl-3-yl)ethanone (5l)



5l

5l isolated as a clear, colorless oil: ^{1}H NMR ($CDCl_3$, 500 MHz) 7.94 (1H, dt, *J* = 8.0, 1.0 Hz), 7.75 (1H, t, *J* = 1.5 Hz), 7.52 (1H, t, *J* = 8.0 Hz), 7.36 (1H, dt, *J* = 7.5, 1.5 Hz), 6.96 (2H, s), 2.61 (3H, s), 2.34 (3H, s), 1.99 (6H, s); ^{13}C NMR ($CDCl_3$, 125 MHz) 198.20, 145.51, 137.85, 137.32, 137.05, 135.78, 134.14, 129.33, 128.73, 128.19, 126.53, 26.70, 20.99, 20.72; IR (film) 3120, 3040, 2919, 1686, 1613, 1599, 1579, 1474, 1433, 1356, 1286, 1230, 1034, 851, 799, 704 cm^{-1} HRMS (CI) *m/z* calcd. for $C_{17}H_{18}O$ (M^+) 238.1358, found 238.1361.

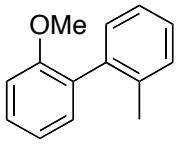
(2'-Methoxybiphenyl-4-yl)dimethylamine (5m)



5m

5m isolated as a yellow solid: m.p. = 45-46 °C ($CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) 7.45 (2H, dd, *J* = 9.0, 2.0 Hz), 7.32 (1H, dd, *J* = 7.5, 2.0 Hz), 7.26 (1H, dt, *J* = 8.5, 1.5 Hz), 7.04 – 6.94 (2H, m), 6.80 (2H, d, *J* = 8.5 Hz), 3.82 (3H, s), 2.99 (6H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) 156.44, 149.51, 130.75, 130.42, 130.13, 127.51, 126.62, 120.72, 112.17, 111.05, 55.46, 40.61; IR (KBr) 3062, 2932, 2833, 1678, 1613. 1526, 1489, 1462, 1353, 1297, 1261, 1239, 1198, 1166, 1120, 1057, 1029, 947, 819, 803, 752 cm^{-1}; HRMS (CI) *m/z* calcd. for $C_{15}H_{17}NO$ (M^+) 227.1310, found 227.1313.

2-Methoxy-2'-methylbiphenyl (5n)[8]



5n

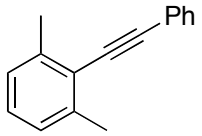
5n isolated as a clear, colorless crystalline solid: m.p. = 42-44 °C ($CHCl_3$) ^{1}H NMR ($CDCl_3$, 500 MHz) 7.34 – 7.26 (6H, m), 7.01 (2H, d, *J* = 8.0 Hz), 3.89 (3H, s), 2.33 (3H, s); ^{13}C NMR ($CDCl_3$, 125 MHz) 158.48, 141.52, 135.44, 134.33, 130.27, 130.22, 129.88, 126.95, 125.74, 113.45, 55.22, 20.53 (two overlap).

General Procedure for Sonogashira Couplings of Aryl Bromides (Table 4)

A 1.25 M solution of carbene **1a** was made as follows[1]: To a solution of diisopropylaminomethylidene(diisopropyl)ammonium tetrafluoroborate[2] (1.500 g, 5.00 mmol) in anhydrous THF (2.33 mL) cooled to –20 °C was added a freshly prepared solution of LDA (3.0 M in THF, 1.67 mL, 5.00 mmol). The reaction mixture was stirred for 30 min at –20 °C prior to the next step.

To a solution of $[Pd(allyl)Cl]_2$ (5.5 mg, 0.015 mmol) in anhydrous THF (0.25 mL) cooled to –20 °C was added carbene **1a** (1.25 M in THF, 32 μL, 0.04 mmol). The reaction mixture was stirred for 30 min at –20 °C, and then for 5 min at rt. Anhydrous toluene (1.00 mL) was then added followed by cesium carbonate (652 mg, 2.00 mmol), aryl bromide (1.00 mmol) and acetylene (1.10 mmol) in that particular order. The reaction mixture was subsequently stirred for 16 h at rt. The mixture was then diluted with Et_2O (20 mL), filtered through celite, and the filtrate concentrated *in vacuo*. The resulting residue was purified by silica gel chromatography.

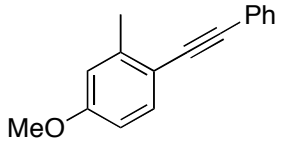
2,6-Dimethyl-1-(phenylethynyl)benzene (6a)[9]



6a

6a isolated as a clear, colorless oil: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.61 – 7.55 (2H, m), 7.43 – 7.34 (3H, m), 7.20 – 7.08 (3H, m), 2.56 (6H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 140.23, 131.37, 128.34, 128.07, 127.45, 126.67, 123.79, 122.92, 97.80, 87.10, 21.11.

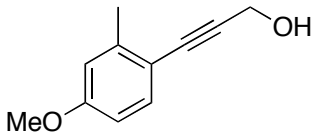
3-Methyl-4-(phenylethynyl)anisole (6b)[10]



6b

6b isolated as a white solid: m.p. = 78-79 °C ($CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.56 (2H, d, *J* = 8.0 Hz), 7.47 (1H, d, *J* = 8.5 Hz), 7.42 – 7.32 (3H, m), 6.81 (1H, d, *J* = 2.5 Hz), 6.75 (1H, dd, *J* = 8.5, 2.5 Hz), 3.83 (3H, s), 2.54 (3H, s); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 159.50, 141.94, 133.11, 131.29, 128.27, 127.80, 123.80, 115.23, 115.06, 111.19, 91.89, 88.34, 55.17, 20.99.

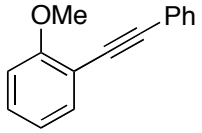
3-(4-Methoxy-2-methylphenyl)prop-2-yn-1-ol (6c)



6c

6c isolated as a clear, colorless oil: ^{1}H NMR ($CDCl_3$, 500 MHz) 7.33 (1H, d, J = 8.5 Hz), 6.73 (1H, d, J = 2.0 Hz), 6.67 (1H, dd, J = 8.5, 2.5 Hz), 4.52 (2H, s), 3.79 (3H, s), 2.41 (3H, s), 1.71 (1H, br s); ^{13}C NMR ($CDCl_3$, 125 MHz) 159.66, 142.09, 133.45, 115.04, 114.59, 111.21, 89.56, 84.59, 55.20, 51.81, 20.90; IR (film) 3424, 2213, 1643, 1497, 1234, 1163, 1120, 1039 cm^{-1}; HRMS (CI) m/z calcd. for $C_{11}H_{12}O_2$ (M^+) 176.0837, found 176.0837.

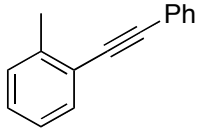
2-(Phenylethynyl)anisole (6d)[11]



6d

6d isolated as a clear, colorless oil: ^{1}H NMR ($CDCl_3$, 500 MHz) 7.62 (2H, dd, J = 8.0, 1.5 Hz), 7.56 (1H, dd, J = 7.5, 1.5 Hz), 7.41–7.31 (4H, m), 6.98 (1H, t, J = 7.5 Hz), 6.93 (1H, d, J = 8.5 Hz), 3.94 (3H, s); ^{13}C NMR ($CDCl_3$, 125 MHz) 159.81, 133.47, 131.56, 129.70, 128.17, 128.03, 123.45, 120.38, 112.28, 110.57, 93.34, 85.67, 55.69.

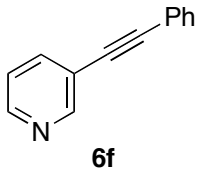
2-(Phenylethynyl)toluene (6e)[12]



6e

6e isolated as a clear, colorless oil: ^{1}H NMR ($CDCl_3$, 300 MHz) 7.60 – 7.50 (3H, m), 7.41 – 7.33 (3H, m), 7.26 – 7.16 (3H, m), 2.54 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) 140.15, 131.80, 131.48, 129.43, 128.32, 128.28, 128.14, 125.55, 123.50, 122.98, 93.31, 88.30, 20.73.

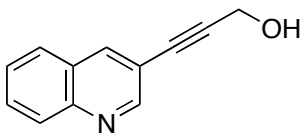
3-(Phenylethynyl)pyridine (6f)[9]



6f

6f isolated as a white solid: m.p. = 48-50 °C ($CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) 8.77 (1H, d, J = 1.0 Hz), 8.53 (1H, dd, J = 4.5, 1.0 Hz), 7.79 (1H, dt, J = 8.0, 2.0 Hz), 7.57 – 7.52 (2H, m), 7.38 – 7.33 (3H, m), 7.28 (1H, dd, J = 8.0, 5.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) 152.10, 148.42, 138.30, 131.56, 128.69, 128.33, 122.92, 122.36, 120.32, 92.53, 85.83.

3-Quinolin-3-ylprop-2-yn-1-ol (6g)[13]



6g

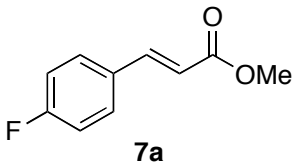
6g isolated as a white solid: m.p. = 121-123 °C ($CHCl_3$); 1H NMR (CD_3OD, 500 MHz) 8.78 (1H, d, *J* = 1.5 Hz), 8.33 (1H, s), 7.98 (1H, d, *J* = 8.5 Hz), 7.85 (1H, d, *J* = 8.0 Hz), 7.74 (1H, dt, *J* = 8.0, 1.5 Hz), 7.59 (1H, t, *J* = 8.0 Hz), 4.76 (2H, s) (OH not detected); ^{13}C NMR (CD_3OD, 75 MHz) 152.75, 147.36, 140.34, 131.77, 129.15, 129.04, 128.81, 128.75, 118.57, 92.85, 82.15, 51.17.

General Procedure for Heck Couplings of Aryl Bromides (Equation 1)

A 1.25 M solution of carbene **1a** was made as follows[1]: To a solution of diisopropylaminomethylidene(diisopropyl)ammonium tetrafluoroborate[2] (1.500 g, 5.00 mmol) in anhydrous THF (2.33 mL) cooled to –20 °C was added a freshly prepared solution of LDA (3.0 M in THF, 1.67 mL, 5.00 mmol). The reaction mixture was stirred for 30 min at –20 °C prior to the next step.

A solution of $Pd_2(dba)_3$ (9.1 mg, 0.010 mmol) in anhydrous THF (0.25 mL) in a sealed tube equipped with a septa was cooled to –20 °C. To this solution was added carbene **1a** (1.25 M in THF, 20 L, 0.025 mmol). The reaction mixture was stirred for 30 min at –20 °C, and another 5 min at rt. Anhydrous *N*,*N*-dimethylacetamide (2.50 mL) was then added followed by cesium carbonate (1.30 g, 4.00 mmol), tetra-*n*-butylammonium bromide (8.1 mg, 0.025 mmol), aryl bromide (2.00 mmol) and methyl acrylate (270 L, 3.00 mmol) in that particular order. The septa was then removed and the tube sealed. The sealed tube was subsequently heated at 110 °C for 8 h. After cooling to room temperature, the contents of the tube were diluted with Et_2O (25 mL) and washed with H_2O (25 mL). The organic phase was dried (Na_2SO_4), filtered and concentrated *in vacuo* to afford a yellow oil. The desired cross-coupled product was isolated by silica gel chromatography.

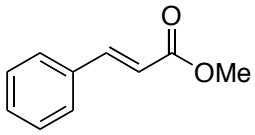
Methyl *trans*-4-Fluorocinnamate (7a)[14]



7a

7a isolated as a clear, colorless crystalline solids: m.p. = 48-49 °C ($CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz) 7.61 (1H, d, *J* = 16.0 Hz), 7.49 – 7.39 (2H, m), 7.07 – 6.95 (2H, m), 6.32 (1H, d, *J* = 16.0 Hz), 3.75 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) 166.24 (d, *J* = 126 Hz), 162.08, 143.34, 130.48, 129.79 (d, *J* = 8.5 Hz), 117.40, 115.86 (d, *J* = 22 Hz), 51.51.

Methyl *trans*-Cinnamate (7b)[15]



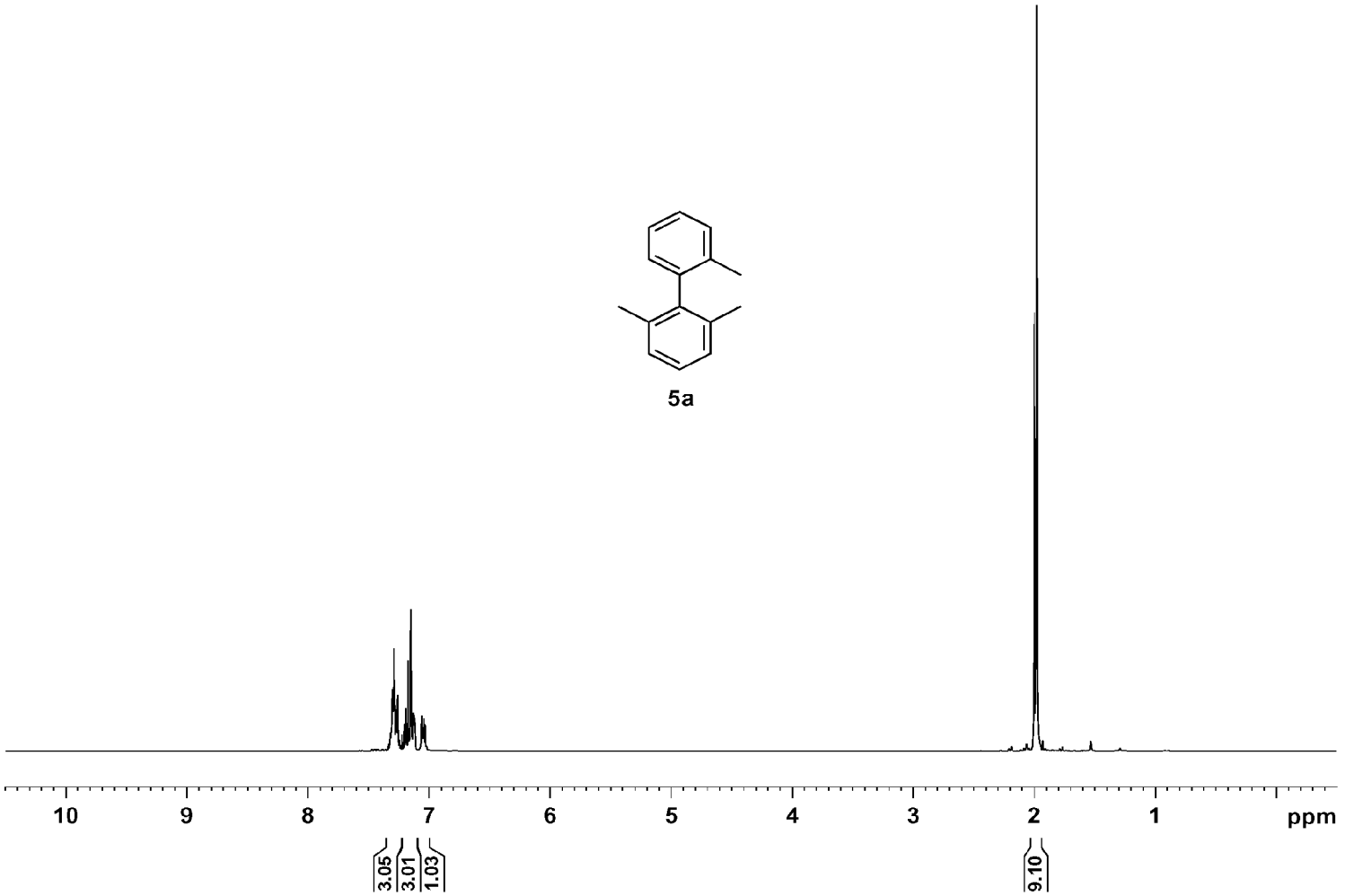
7b

7b isolated as a clear, colorless crystalline solid: m.p. = 37-38 °C ($CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz) 7.68 (1H, d, *J* = 16.0 Hz), 7.52 – 7.44 (2H, m), 7.39 – 7.30 (3H, m), 6.43 (1H, d, *J* = 16.0 Hz), 3.78 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) 167.33, 144.79, 134.32, 130.22, 128.82, 128.00, 117.74, 51.60.

References:

1) R. W. Alder, M. E. Blake, S. Bufali, C. P. Butts, A. G. Orpen, J. Schütz and S. J. Williams, *J. Chem. Soc. Perkin Trans. 1*, 2001, 1586.
2) R. W. Alder, P. R. Allen, M. Murray and A. G. Orpen, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1121.
3) G. Altenhoff, R. Goddard, C. W. Lehmann and F. Glorius, *J. Am. Chem. Soc.*, 2004, **126**, 15195.
4) A. O. Aliprantis and J. W. Canary, *J. Am. Chem. Soc.*, 1994, **116**, 6985.
5) V. K. Aggarwal. J. R. Fulton, C. G. Sheldon and J. de Vicente, *J. Am. Chem. Soc.*, 2003, **125**, 6034.
6) J. P. Stambuli, S. R. Stauffer, K. H. Shaughnessy and J. F. Hartwig, *J. Am. Chem. Soc.*, 2001, **123**, 2677.
7) O. Navarro, R. A. Kelly, III, and S. P. Nolan, *J. Am. Chem. Soc.*, 2003, **125**, 16194.
8) T. E. Barder, S. D. Walker, J. R. Martinelli and S. L. Buchwald, *J. Am. Chem. Soc.*, 2005, **127**, 4685.
9) A. Soheili, J. Albaneze-Walker, J. A. Murry, P. G. Dormer and D. L. Hughes, *Org. Lett.*, 2003, **5**, 4191.
10) R. B. DeVasher, L. R. Moore and K. H. Shaughnessy, *J. Org. Chem.*, 2004, **69**, 7919.
11) Y. Ma, C. Song, W. Jiang, Q. Wu, Y. Wang, X. Liu, and M. B. Andrus, *Org. Lett.*, 2003, **5**, 3317.
12) T. Hundertmark, A. F. Littke, S. L. Buchwald and G. C. Fu, *Org. Lett.*, 2000, **2**, 1729.
13) S. A. Glase, H. C. Akunne, T. G. Heffner, J. C. Jaen, R. G. MacKenzie, L. T. Meltzer, T. A. Pugsley, S. J. Smith and L. D. Wise, *J. Med. Chem.*, 1996, **39**, 3179.
14) L. Djakovitch and K. Koehler, *J. Am. Chem. Soc.*, 2001, **123**, 5990.
15) D. Yang, Y.-C. Chen and N.-Y. Zhu, *Org. Lett.*, 2004, **6**, 1577.

^{1}H and ^{13}C NMR Spectra of All Products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8
7
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5
4
3
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1
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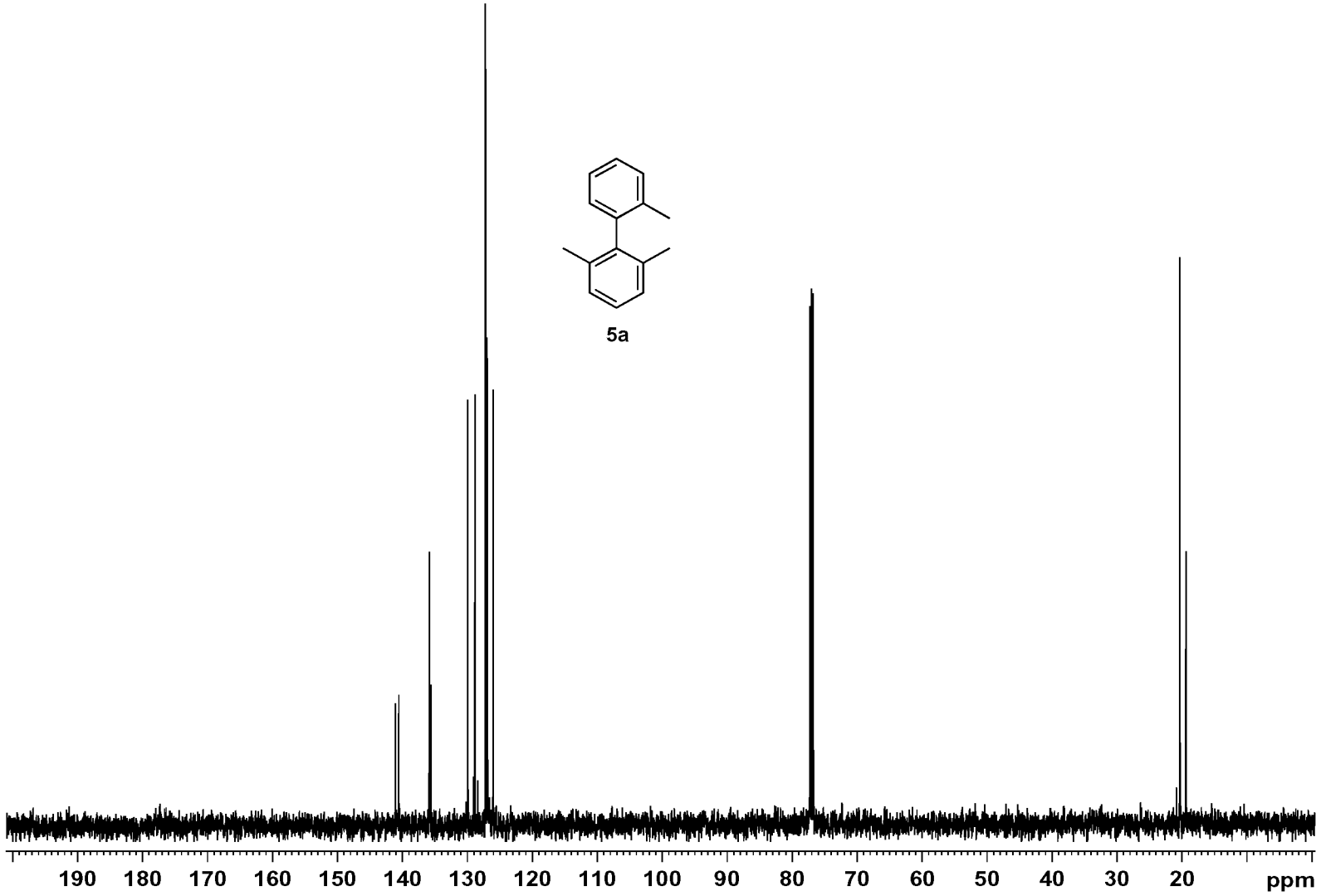
1.03
9.10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20
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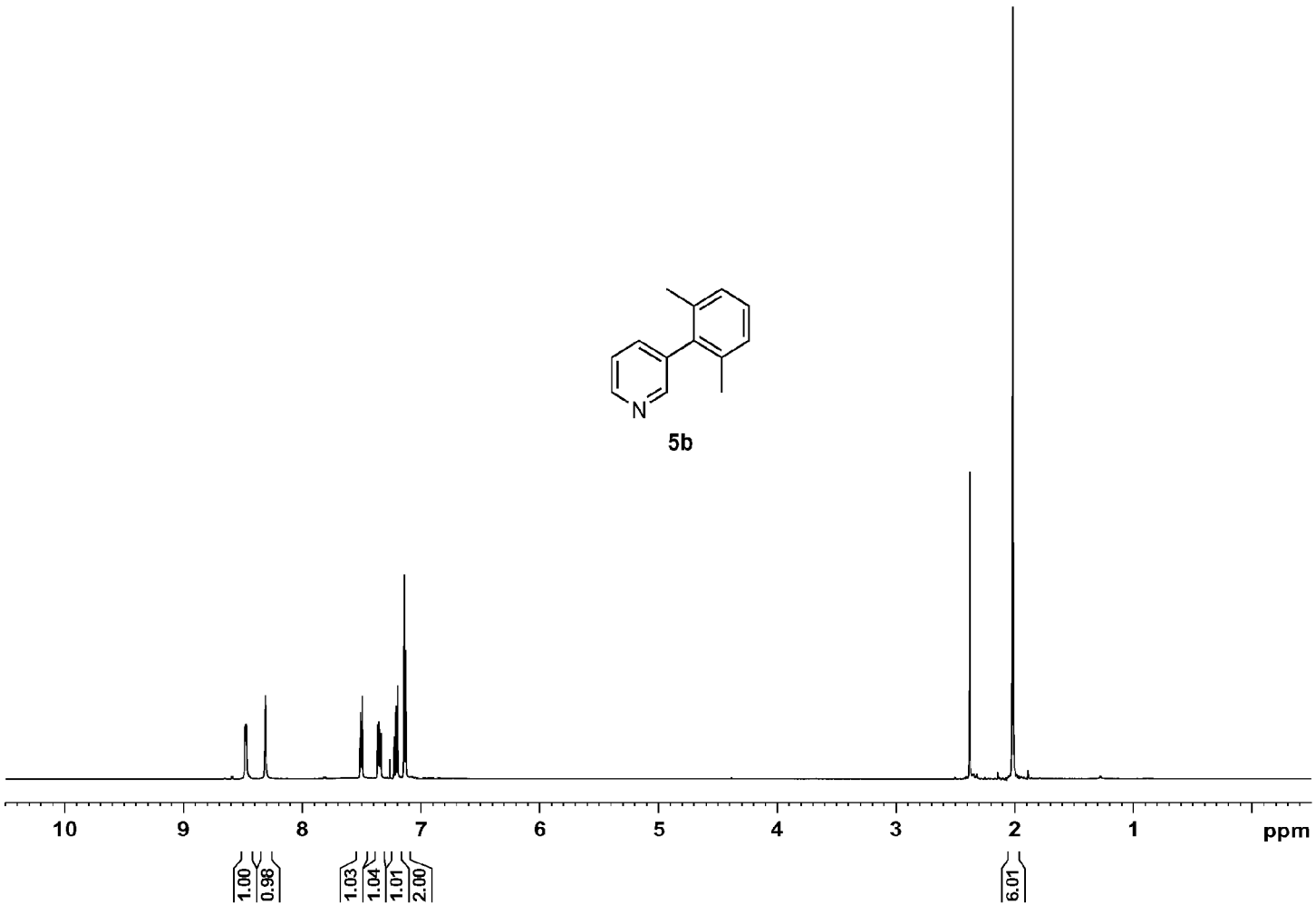
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1
ppm
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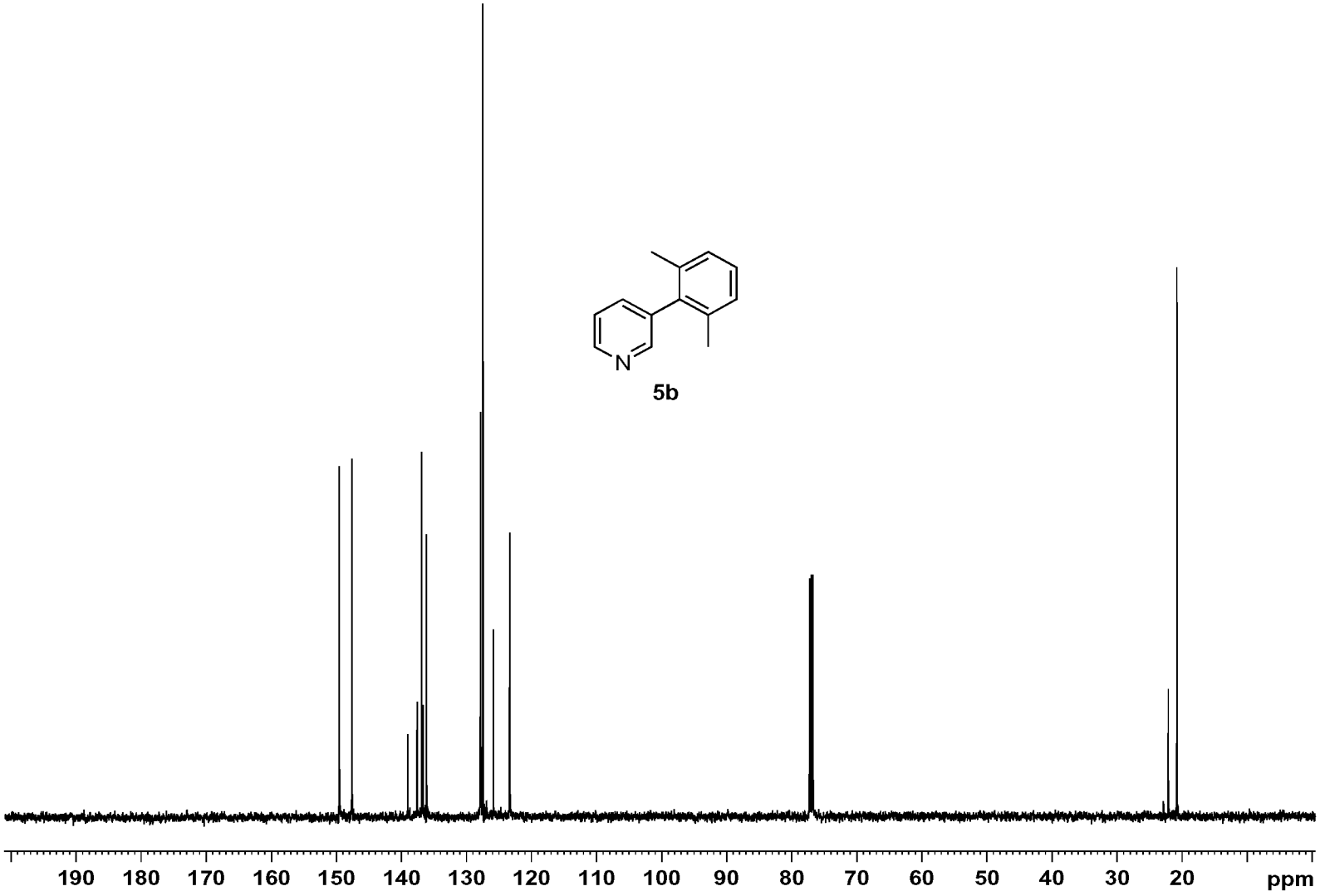
0.98
1.03
1.04
1.01
2.00
6.01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110
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90
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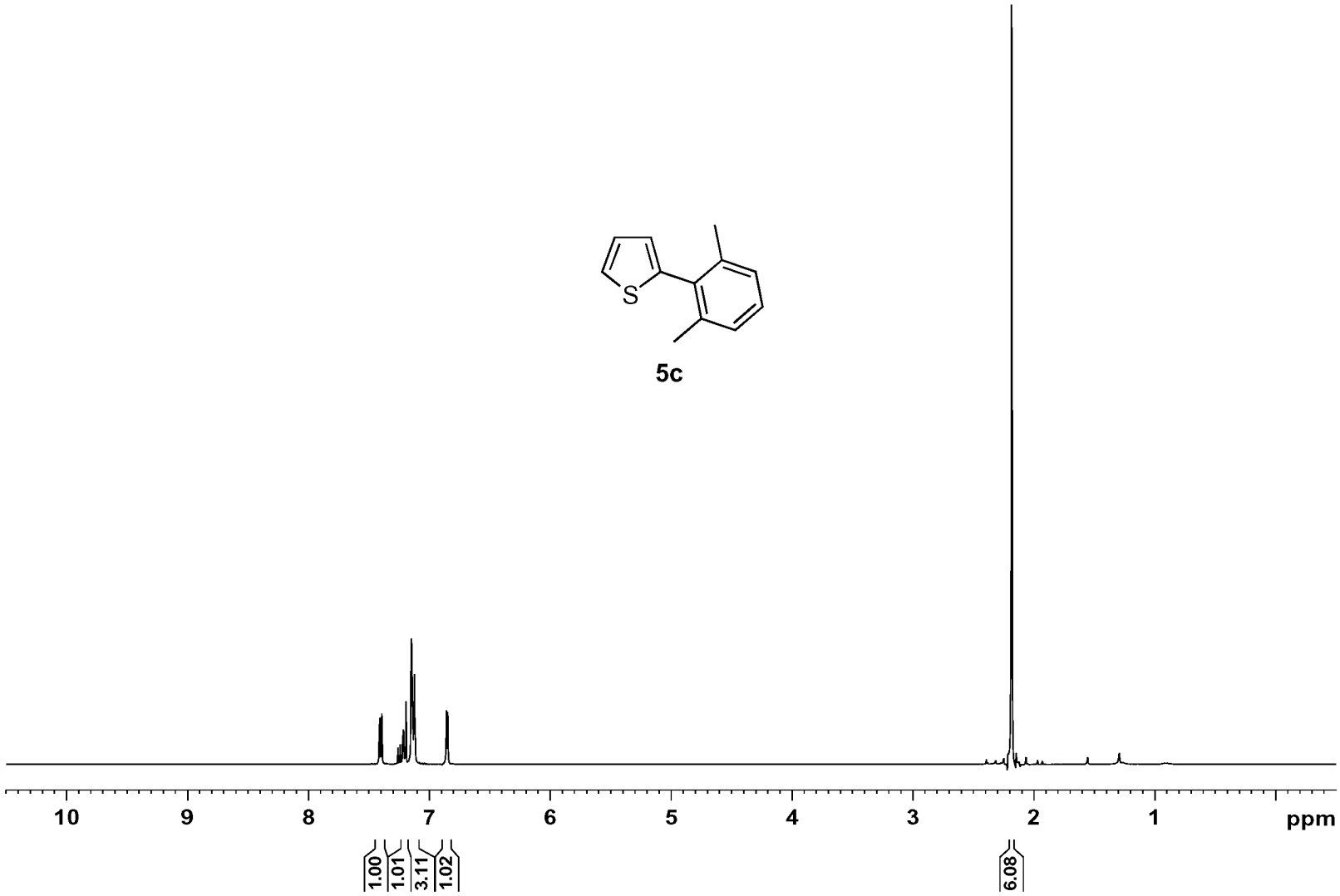
50
40
30
20
ppm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4
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ppm
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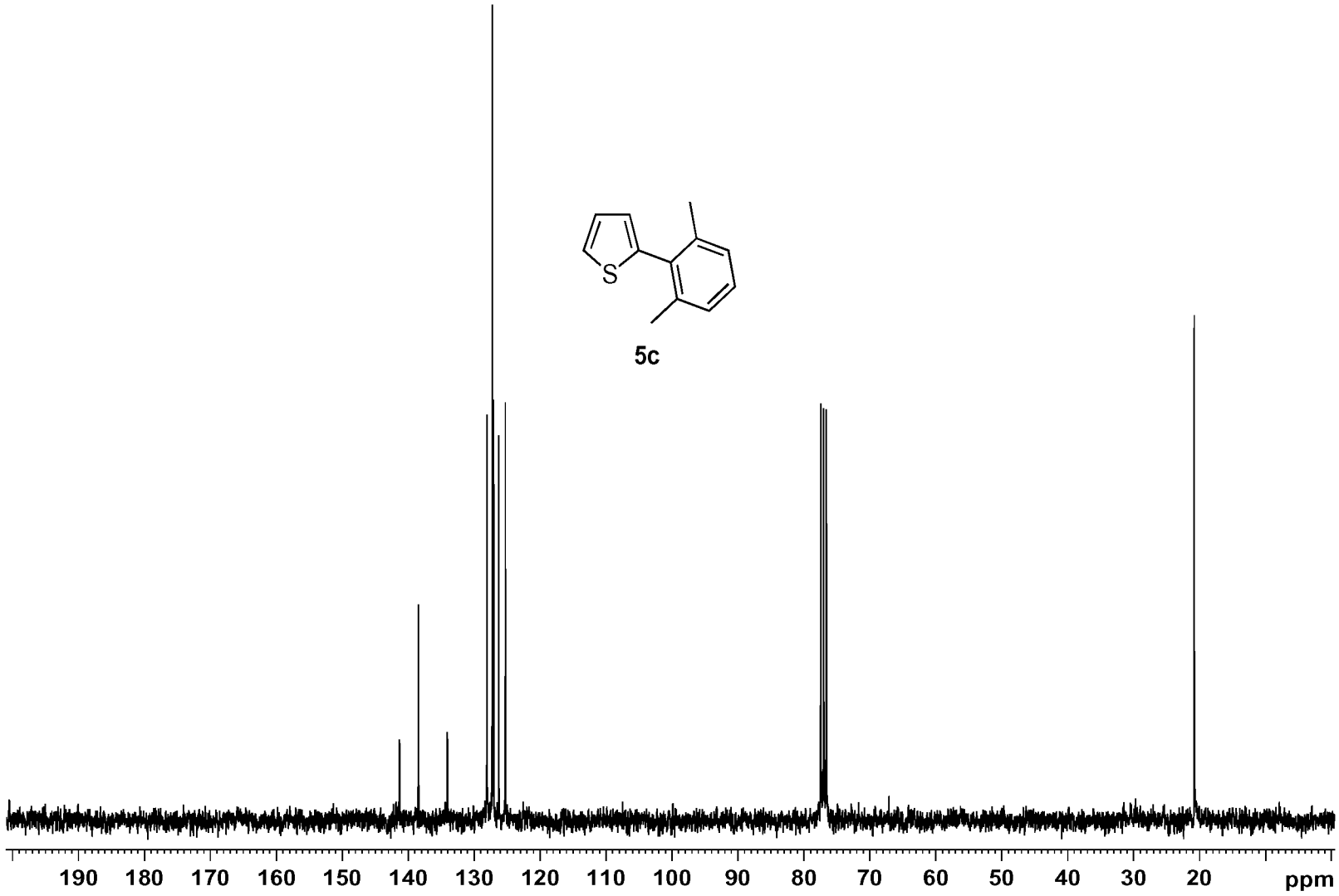
1.01
3.11
1.02
6.08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100
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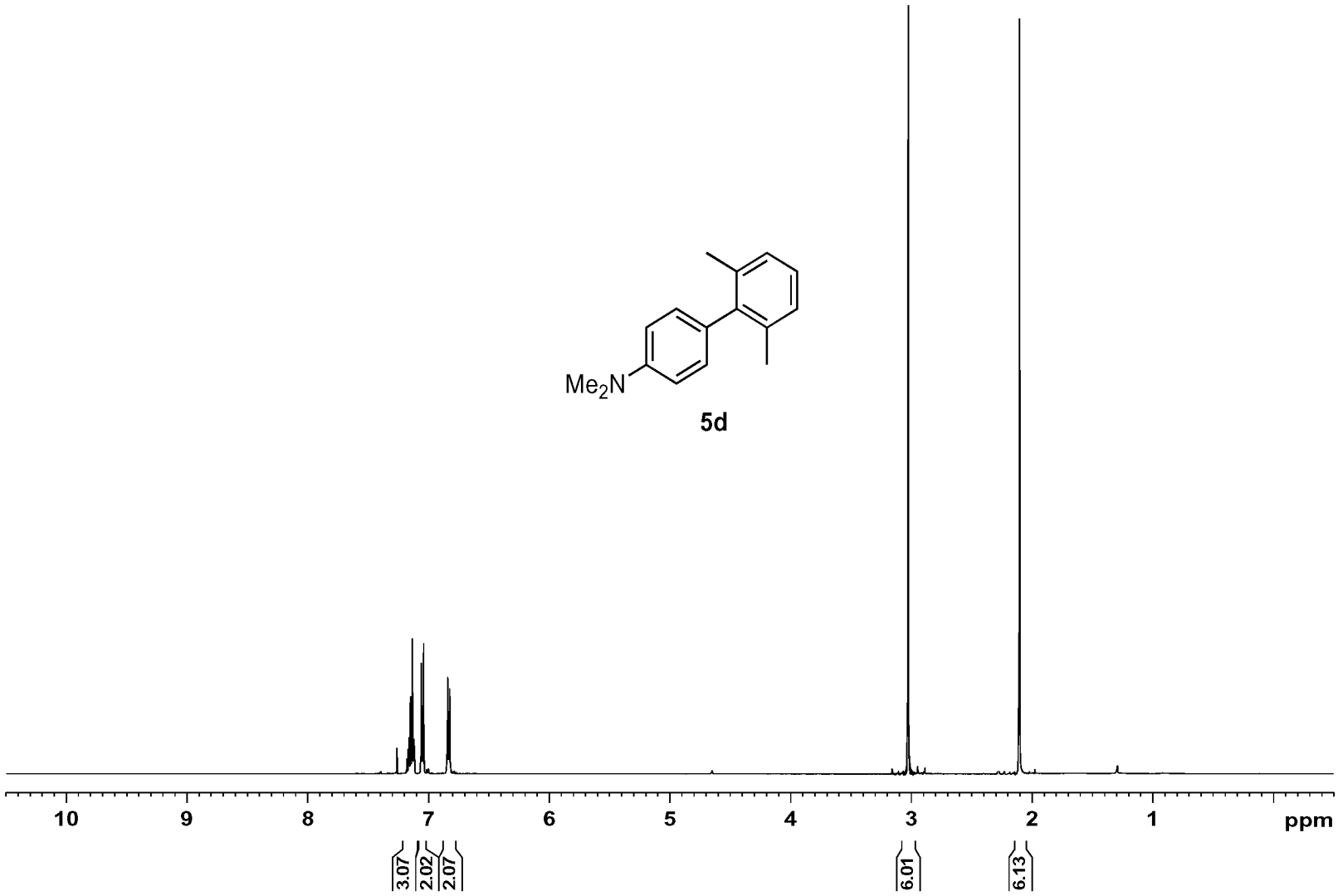
50
40
30
20
ppm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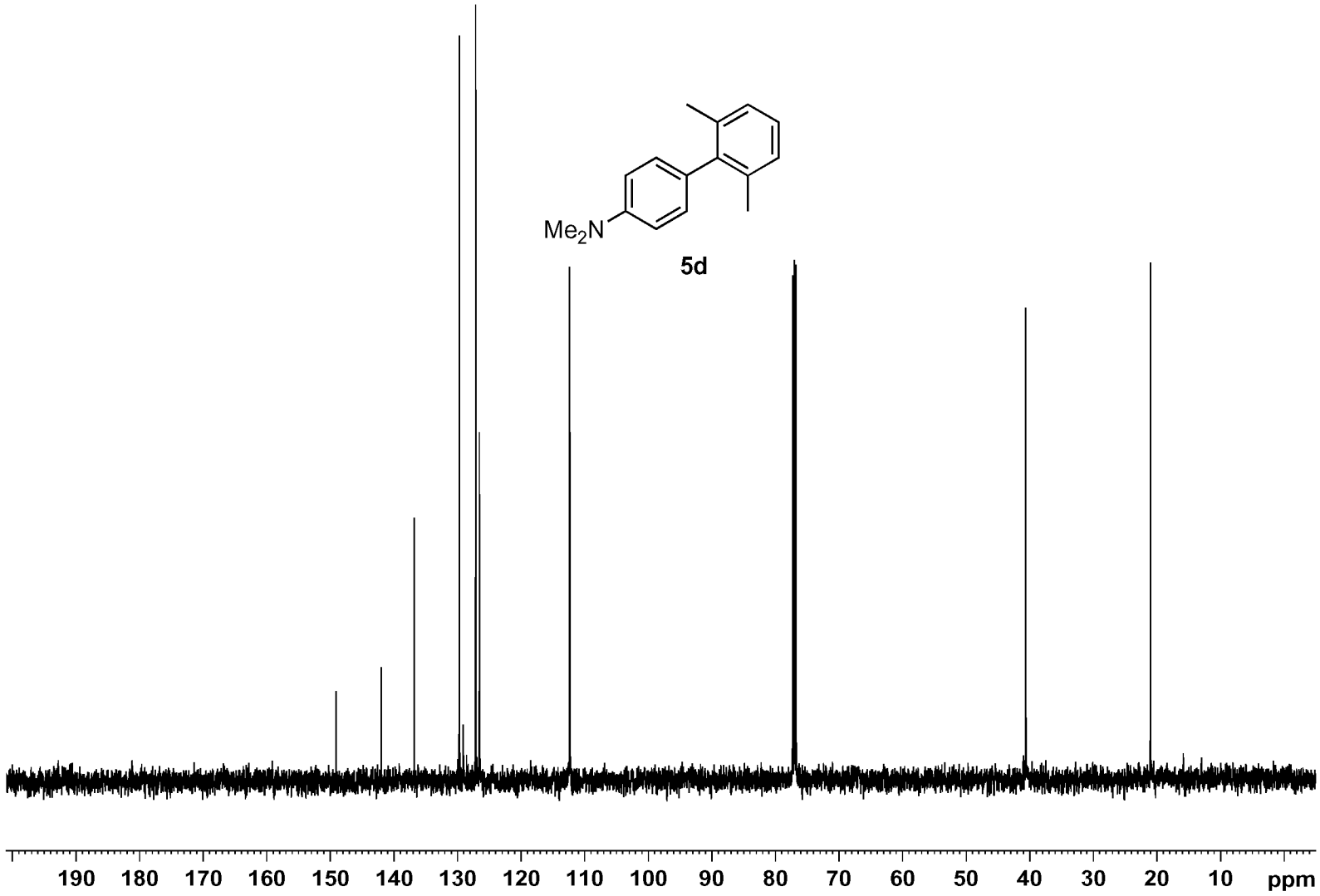
2.07
6.01
6.13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5d
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180
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100
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80
70
60
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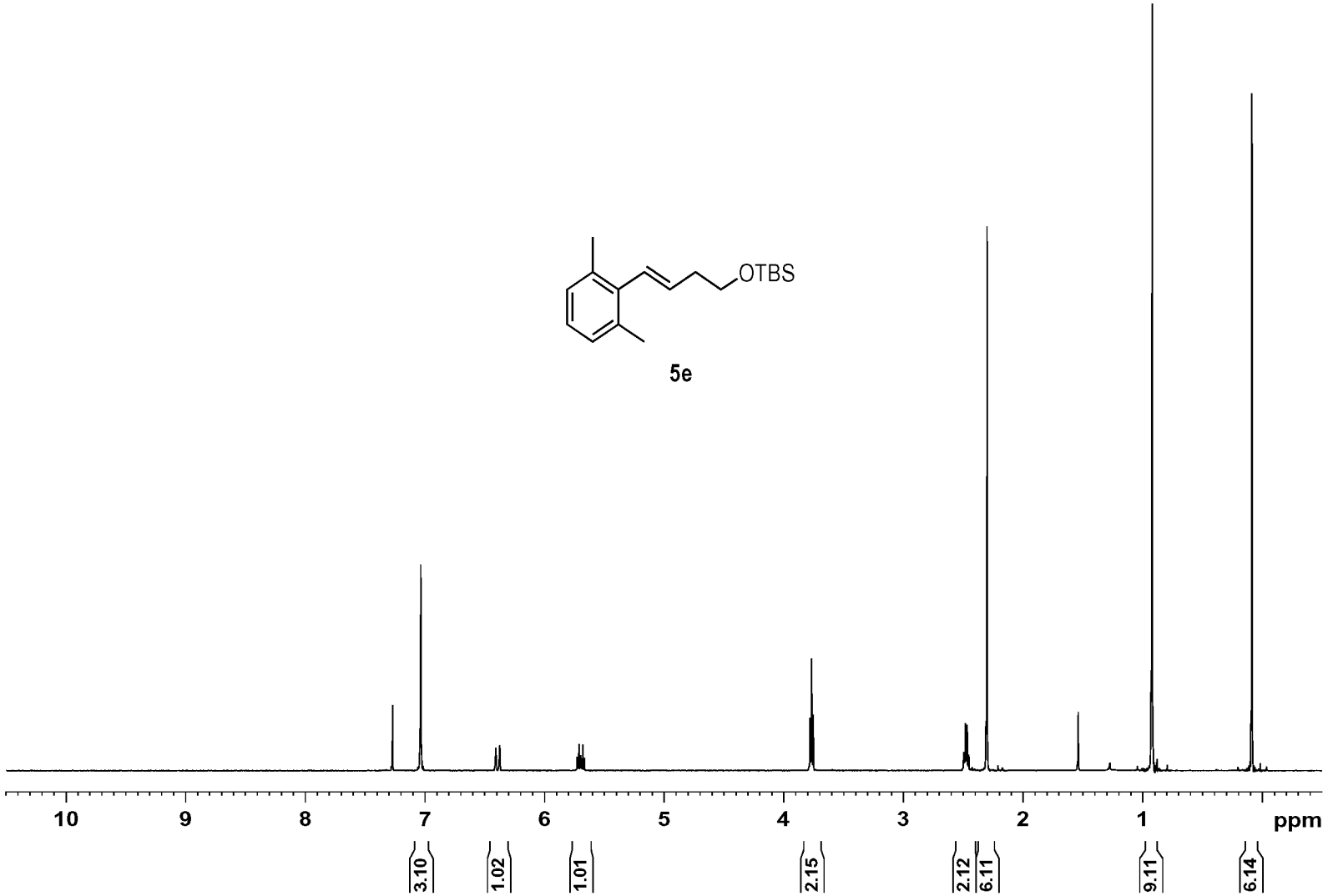
40
30
20
10
ppm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9
8
7
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ppm
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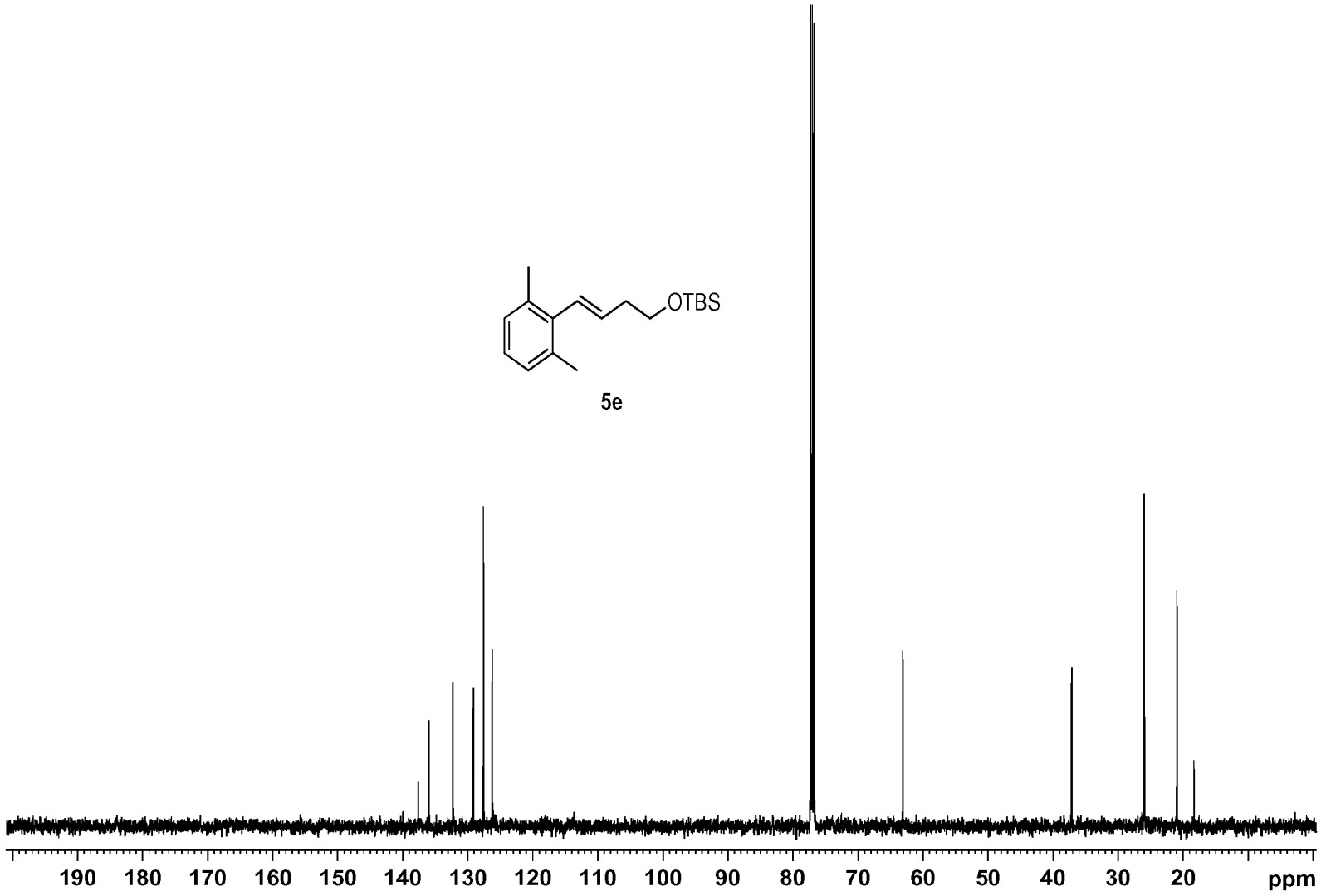
1.02
1.01
2.15
2.12
6.11
9.11
6.14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160
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140
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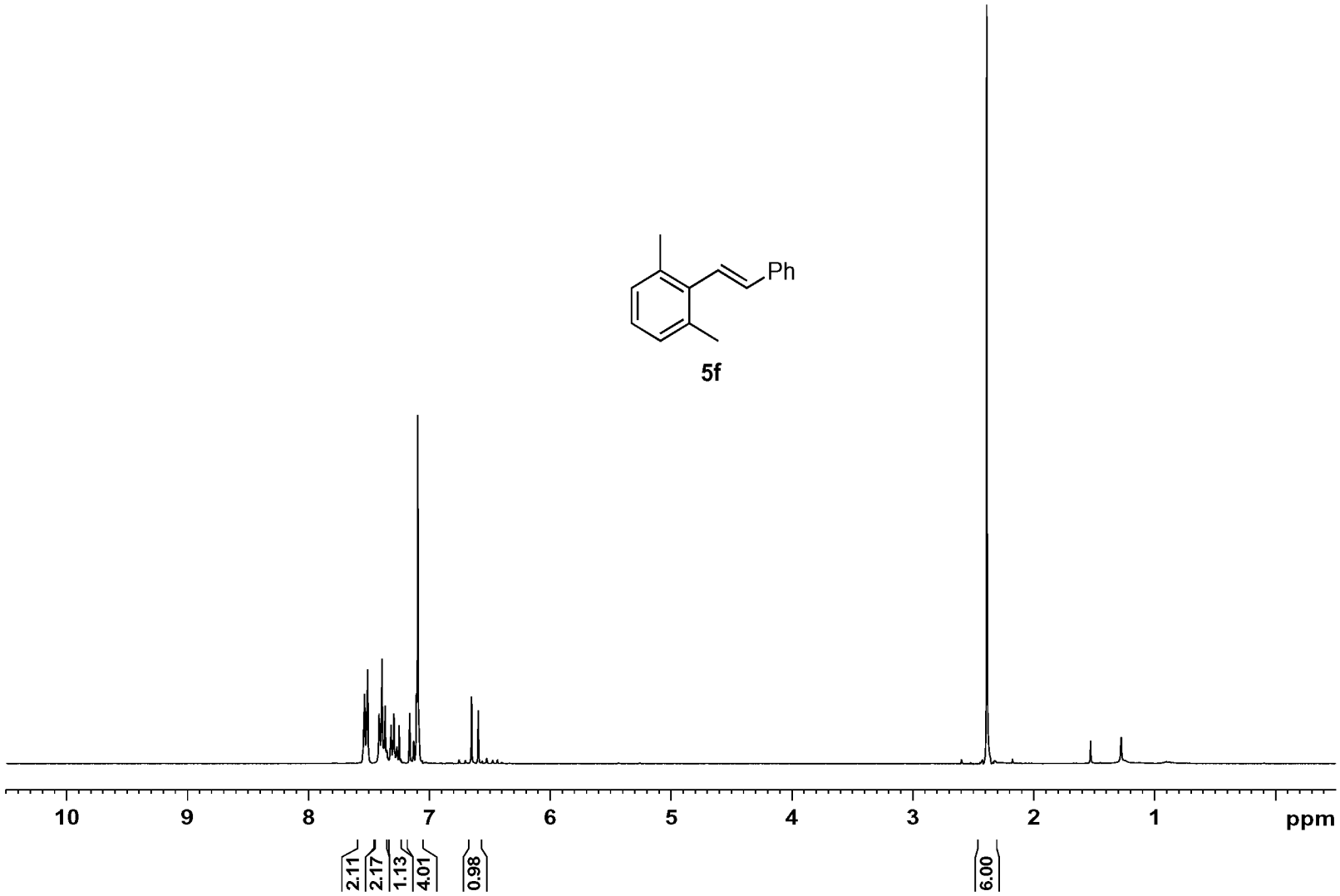
120
110
100
90
80
70
60
50
40
30
20
ppm


Ph
5f
10
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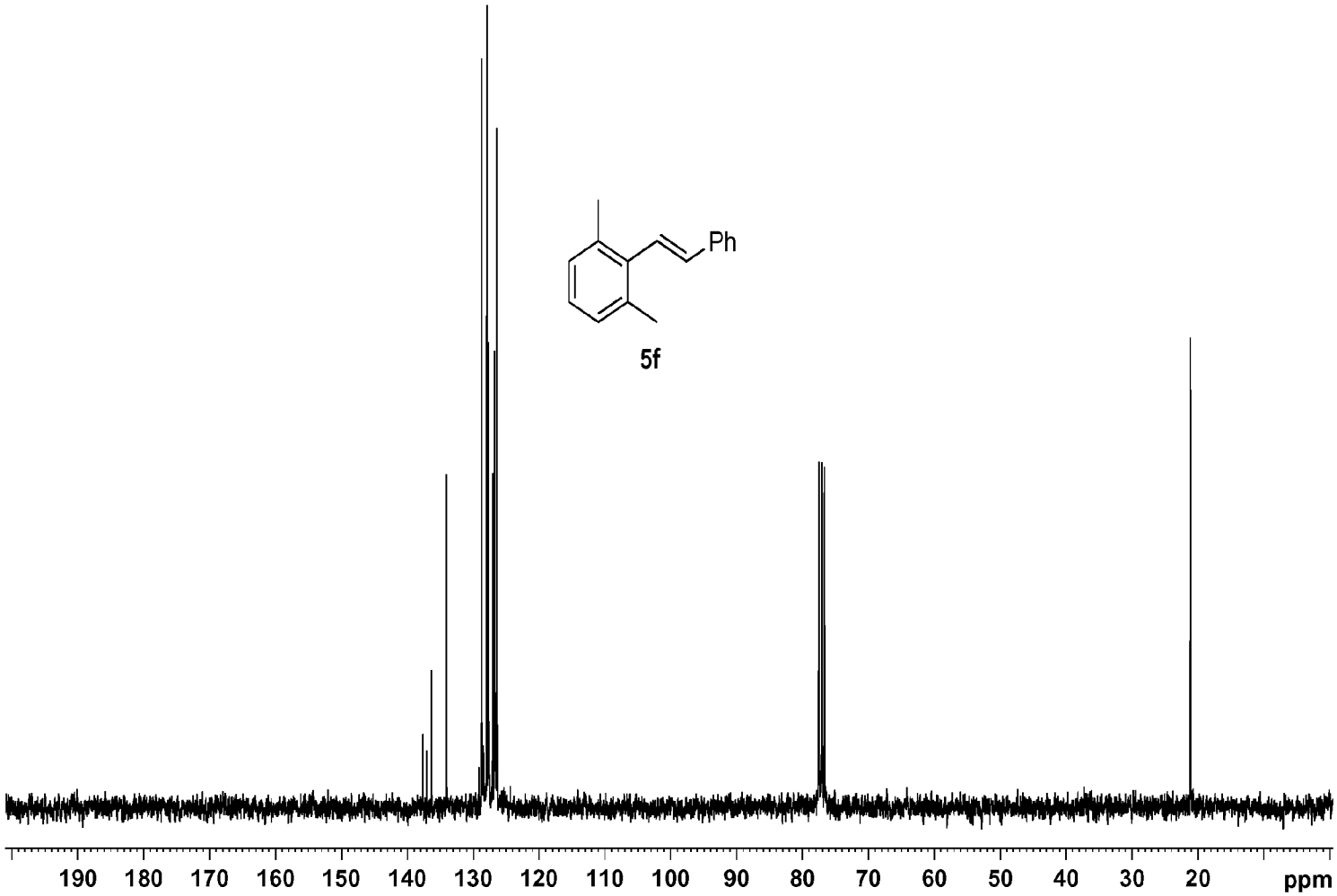
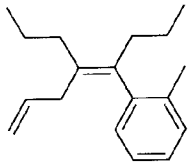
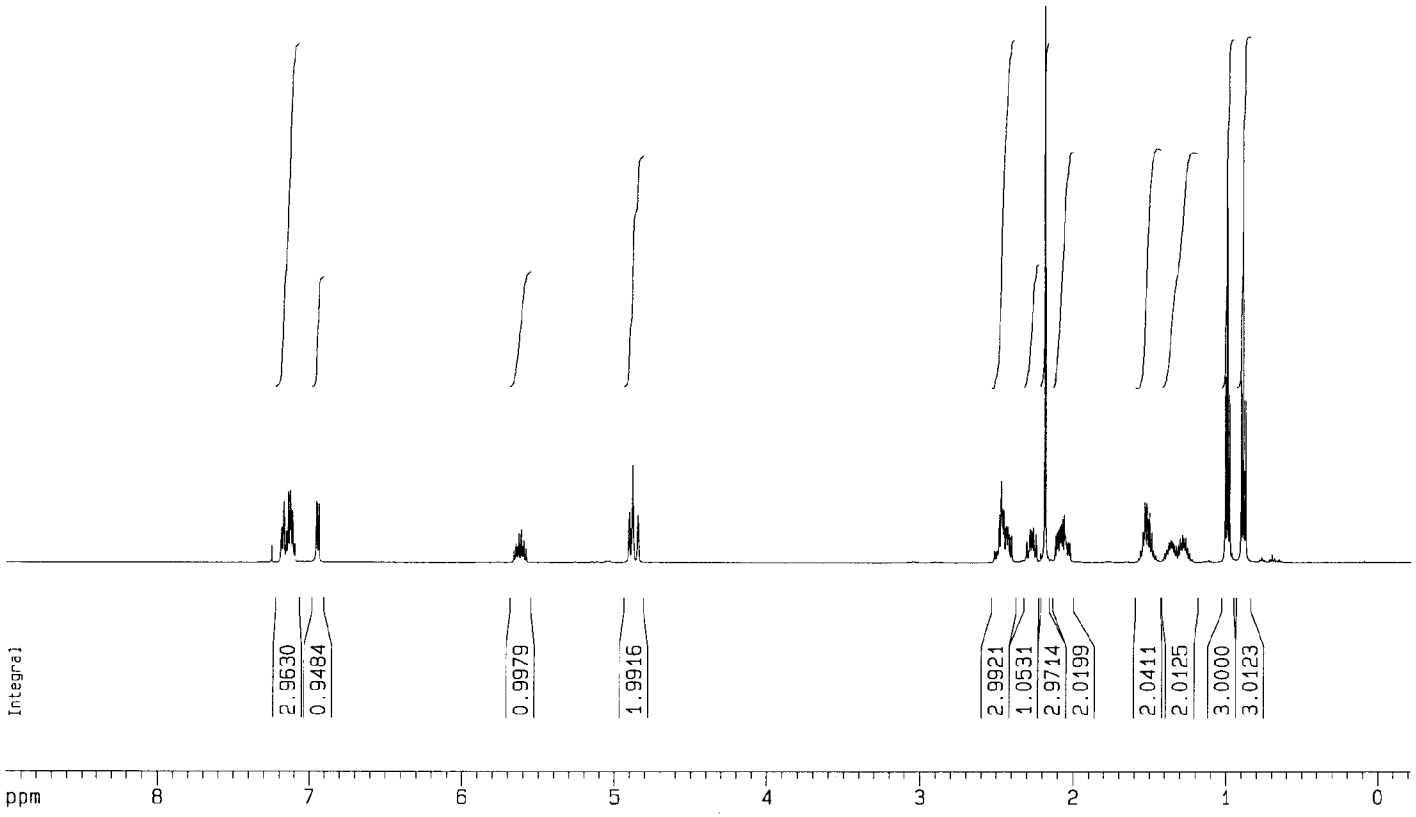
8
7
6
5
4
3
2
1
ppm
2.11
2.17
1.13
4.01
0.98
6.00


Ph
5f
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm



5g



F2 - Acquisition Parameters

Date_	20040520
Time	16.17
INSTRUM	spect
PROBHD	5 mm QNP 1H
PULPROG	zg
TD	32768
SOLVENT	CDCl3
NS	4
DS	0
SWH	5208.333 Hz
FIDRES	0.158946 Hz
AQ	3.1457779 sec
RG	32
DW	96.000 usec
DE	4.50 usec
TE	300.0 K
D1	2.00000000 sec

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

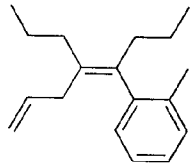
NUC1	1H
P1	10.00 usec
PL1	0.00 dB
SFO1	500.1320118 MHz

F2 - Processing parameters

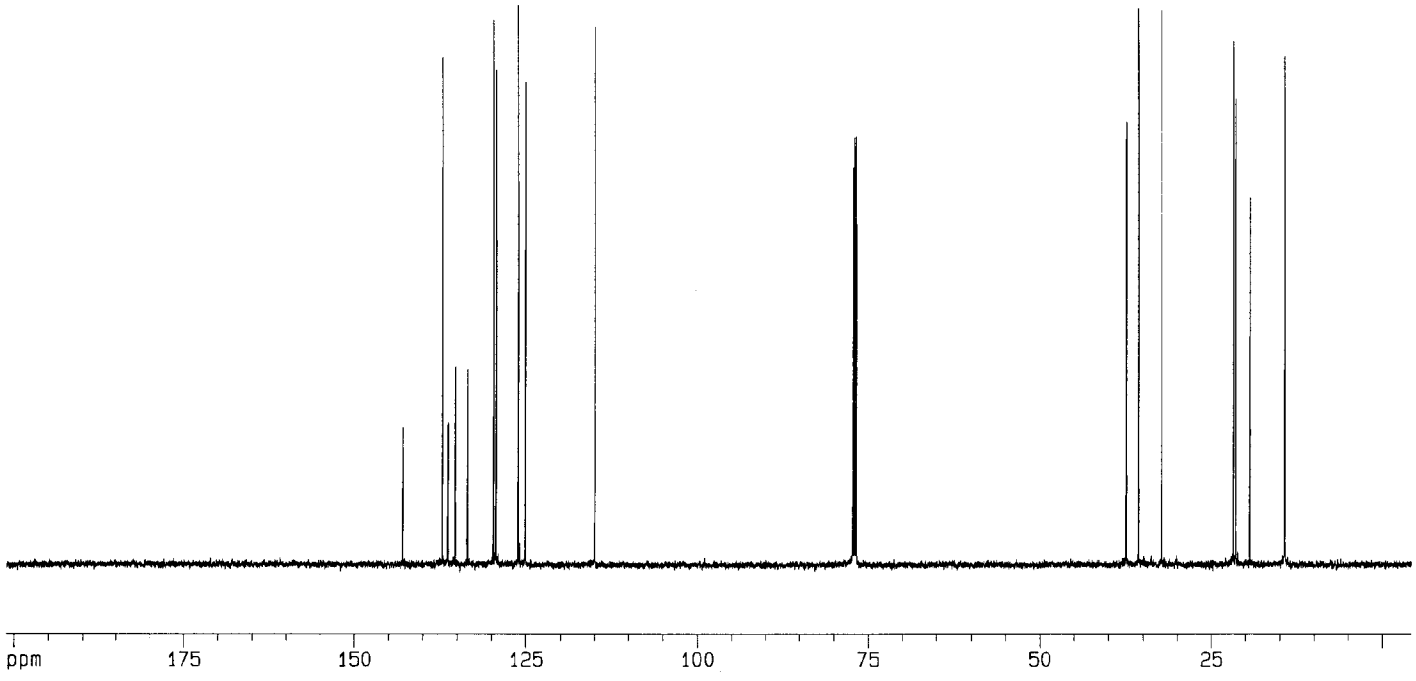
SI	16384
SF	500.1300181 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	9.000 ppm
F1	4501.08 Hz
F2P	-0.214 ppm
F2	-107.03 Hz
PPMCM	0.46069 ppm/cm
HZCM	230.40584 Hz/cm



5g



F2 - Acquisition Parameters

Date_	20040520
Time	16.35
INSTRUM	spect
PROBHD	5 mm QNP 1H
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TD	238090
SOLVENT	Aceton
NS	136
DS	0
SWH	39682.539 Hz
FIDRES	0.166670 Hz
AQ	2.9999840 sec
RG	2048
DW	12.600 usec
DE	7.50 usec
TE	300.0 K
D1	4.00000000 sec
d11	0.03000000 sec

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

NUC1	13C
P1	8.20 usec
PL1	0.00 dB
SFO1	125.7736214 MHz

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

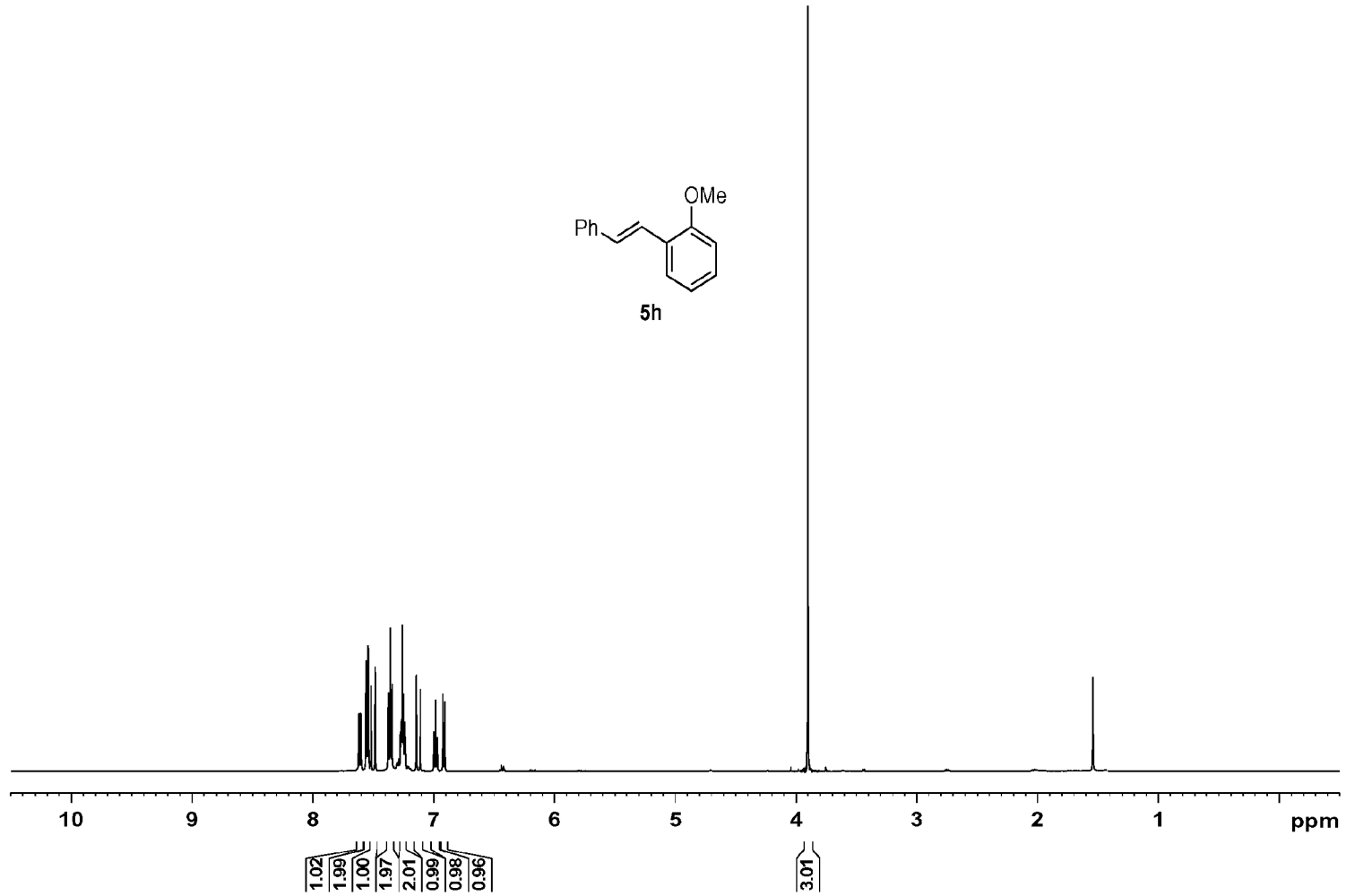
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	120.00 dB
PL12	19.00 dB
SFO2	500.1338000 MHz

F2 - Processing parameters

SI	32768
SF	125.7577946 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
F1P	201.122 ppm
F1	25292.62 Hz
F2P	-4.160 ppm
F2	-523.16 Hz
PPMCM	10.26409 ppm/cm
HZCM	1290.78894 Hz/cm


OMe
Ph
5h
10
9
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7
6
5
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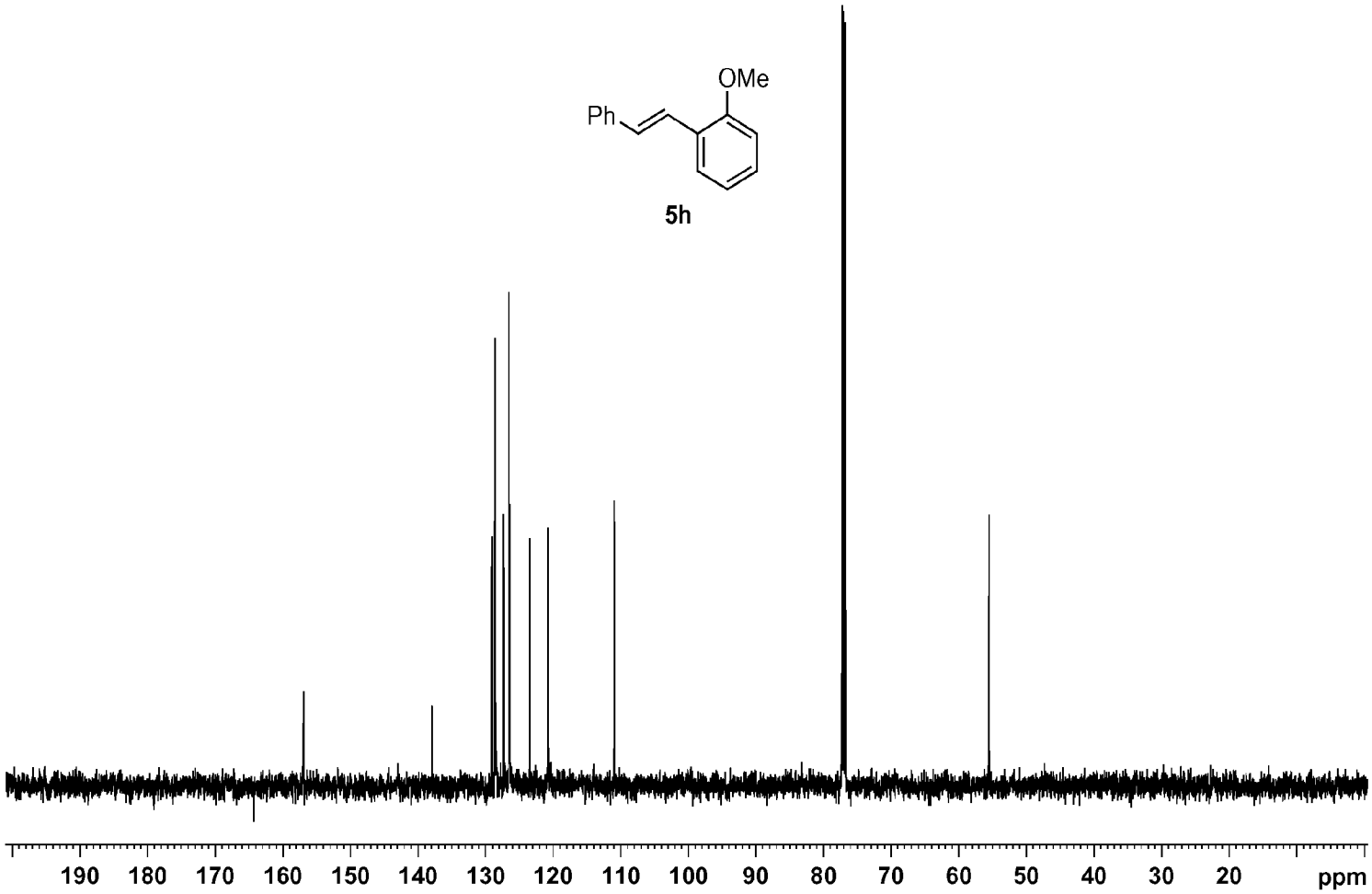
3.01


OMe
Ph
5h
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80
70
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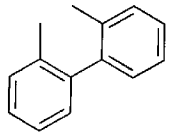
50
40
30
20
ppm



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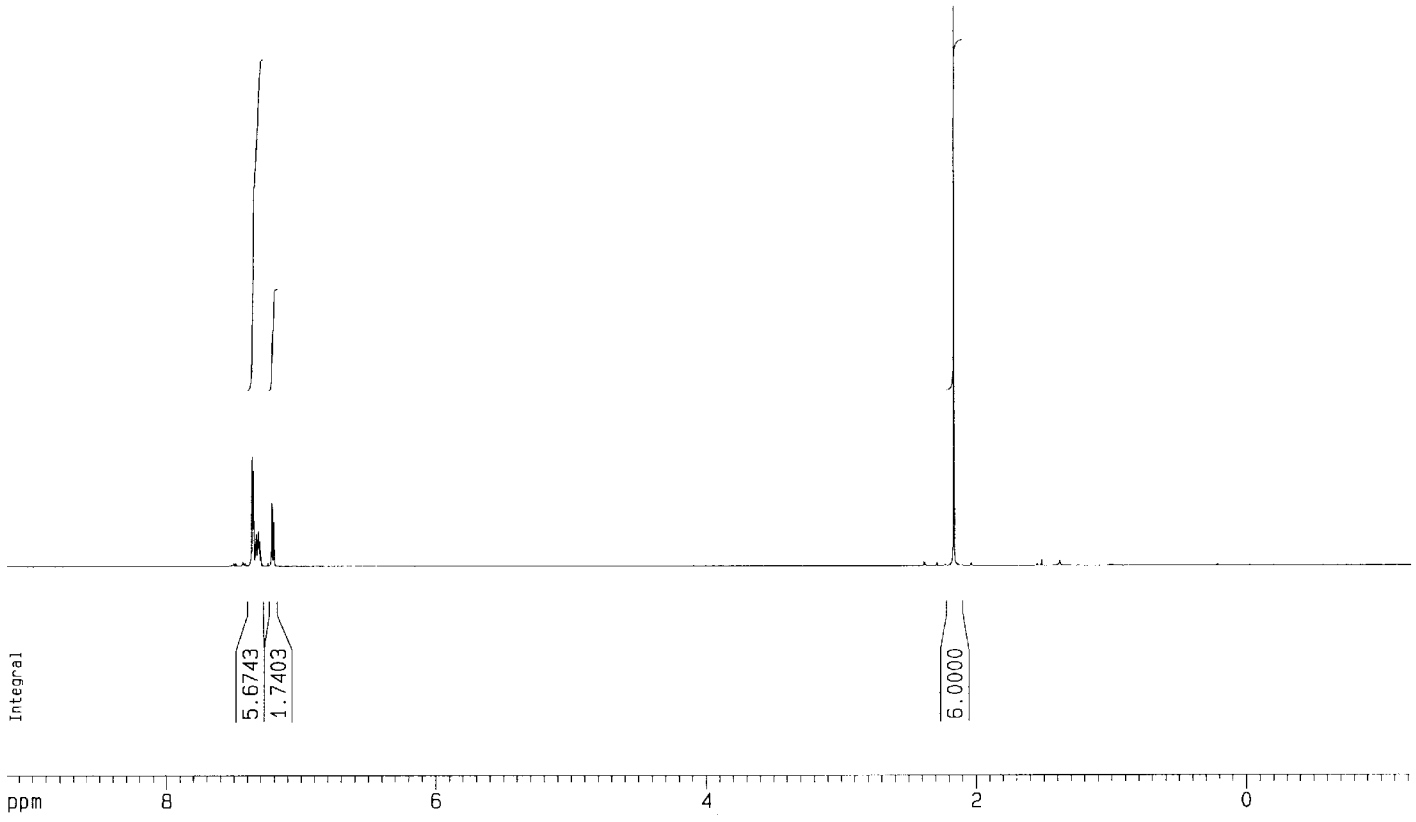


F2 - Acquisition Parameters

Date_	20040517
Time	15.59
INSTRUM	spect
PROBHD	5 mm QNP 1H
PULPROG	zg
TD	32768
SOLVENT	CDCl3
NS	4
DS	0
SWH	5208.333 Hz
FIDRES	0.158946 Hz
AQ	3.1457779 sec
RG	16
DW	96.000 usec
DE	4.50 usec
TE	300.0 K
D1	2.00000000 sec

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

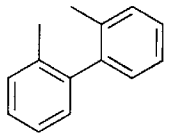
NUC1	1H
P1	10.00 usec
PL1	0.00 dB
SFO1	500.1320118 MHz

F2 - Processing parameters

SI	16384
SF	500.1300181 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	9.193 ppm
F1	4597.89 Hz
F2P	-1.221 ppm
F2	-610.44 Hz
PPMCM	0.52070 ppm/cm
HZCM	260.41666 Hz/cm



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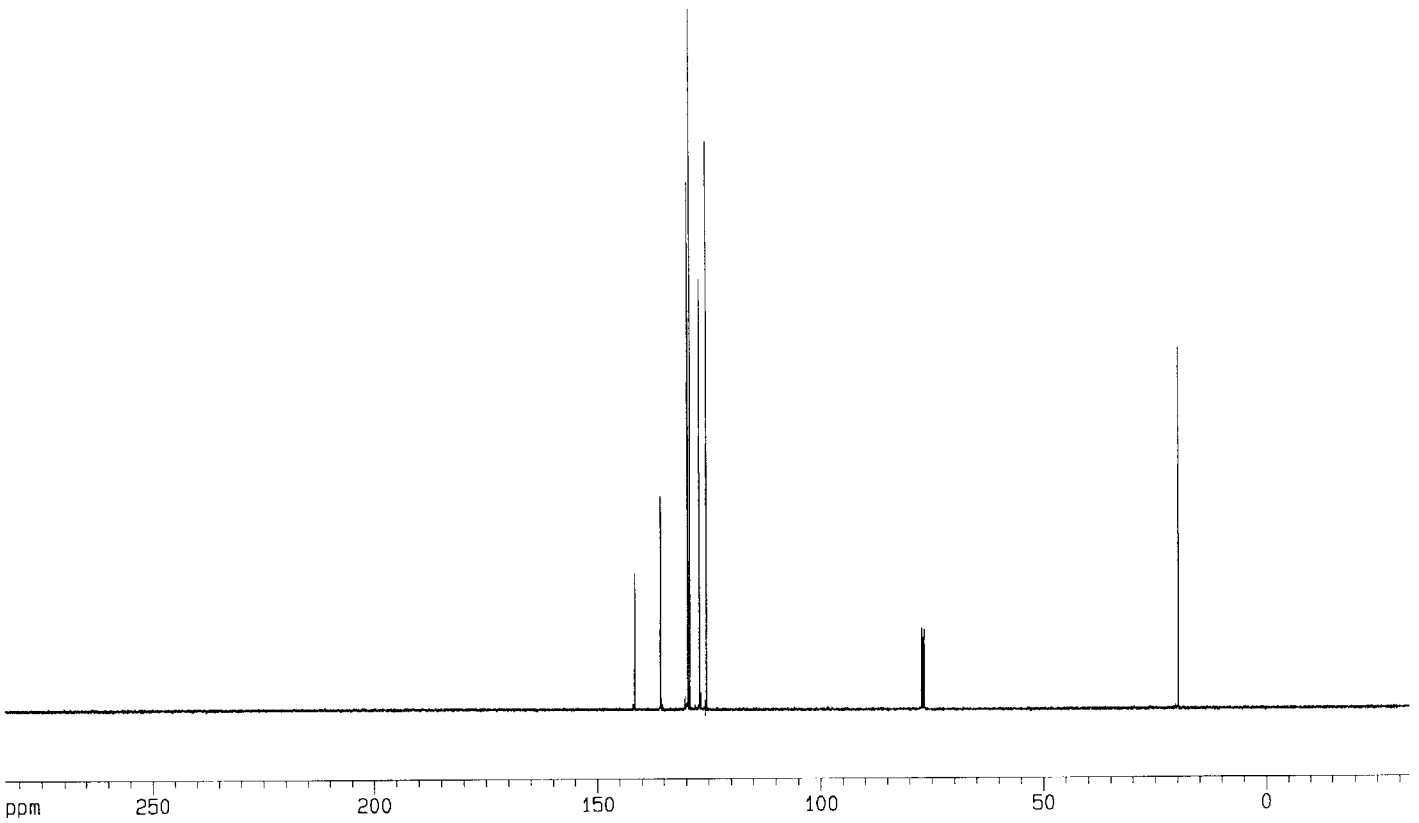

F2 - Acquisition Parameters

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Time	16.06
INSTRUM	spect
PROBHD	5 mm QNP 1H
PULPROG	zgdc
TD	238090
SOLVENT	Aceton
NS	24
DS	0
SWH	39682.539 Hz
FIDRES	0.166670 Hz
AQ	2.9999840 sec
RG	4096
DW	12.600 usec
DE	7.50 usec
TE	300.0 K
D1	4.00000000 sec
d11	0.03000000 sec

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

NUC1	13C
P1	8.20 usec
PL1	0.00 dB
SFO1	125.7736214 MHz

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

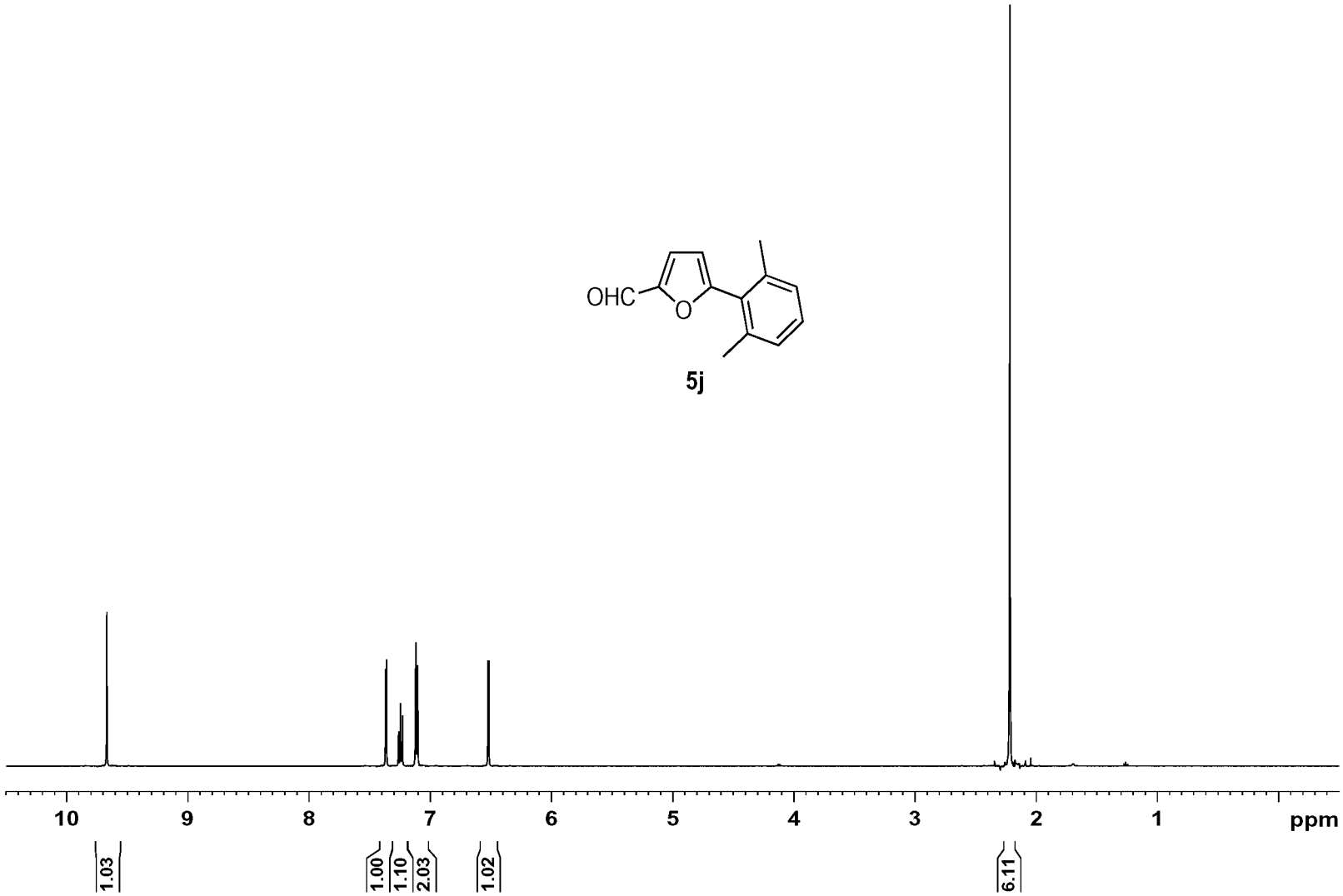
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	120.00 dB
PL12	19.00 dB
SFO2	500.1338000 MHz

F2 - Processing parameters

SI	32768
SF	125.7578116 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
F1P	283.491 ppm
F1	35651.14 Hz
F2P	-32.057 ppm
F2	-4031.40 Hz
PPMCM	15.77737 ppm/cm
HZCM	1984.12708 Hz/cm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O
5j
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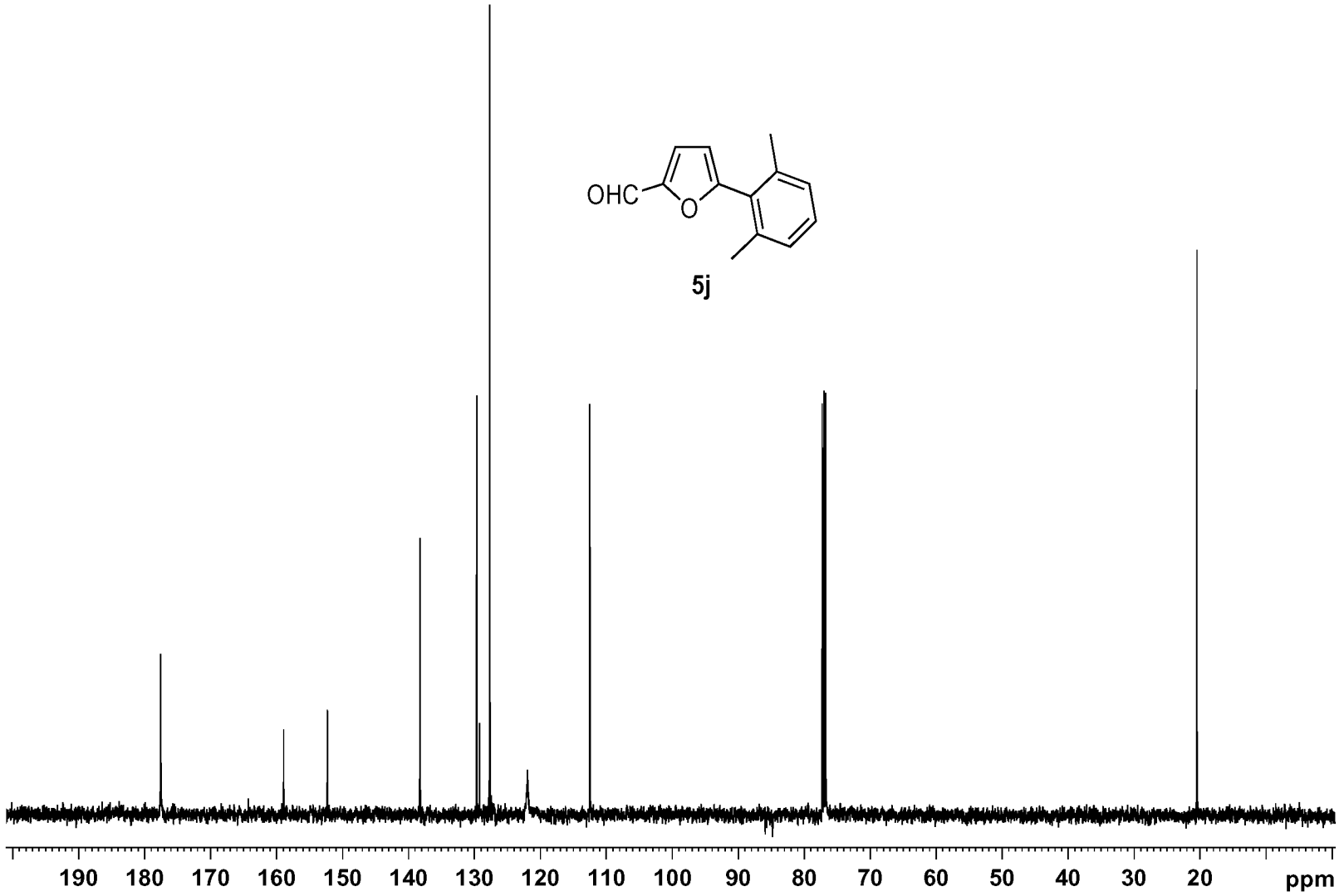
8
7
6
5
4
3
2
1
ppm
1.03
1.00
1.10
2.03
1.02
6.11


OHC
O
5j
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150
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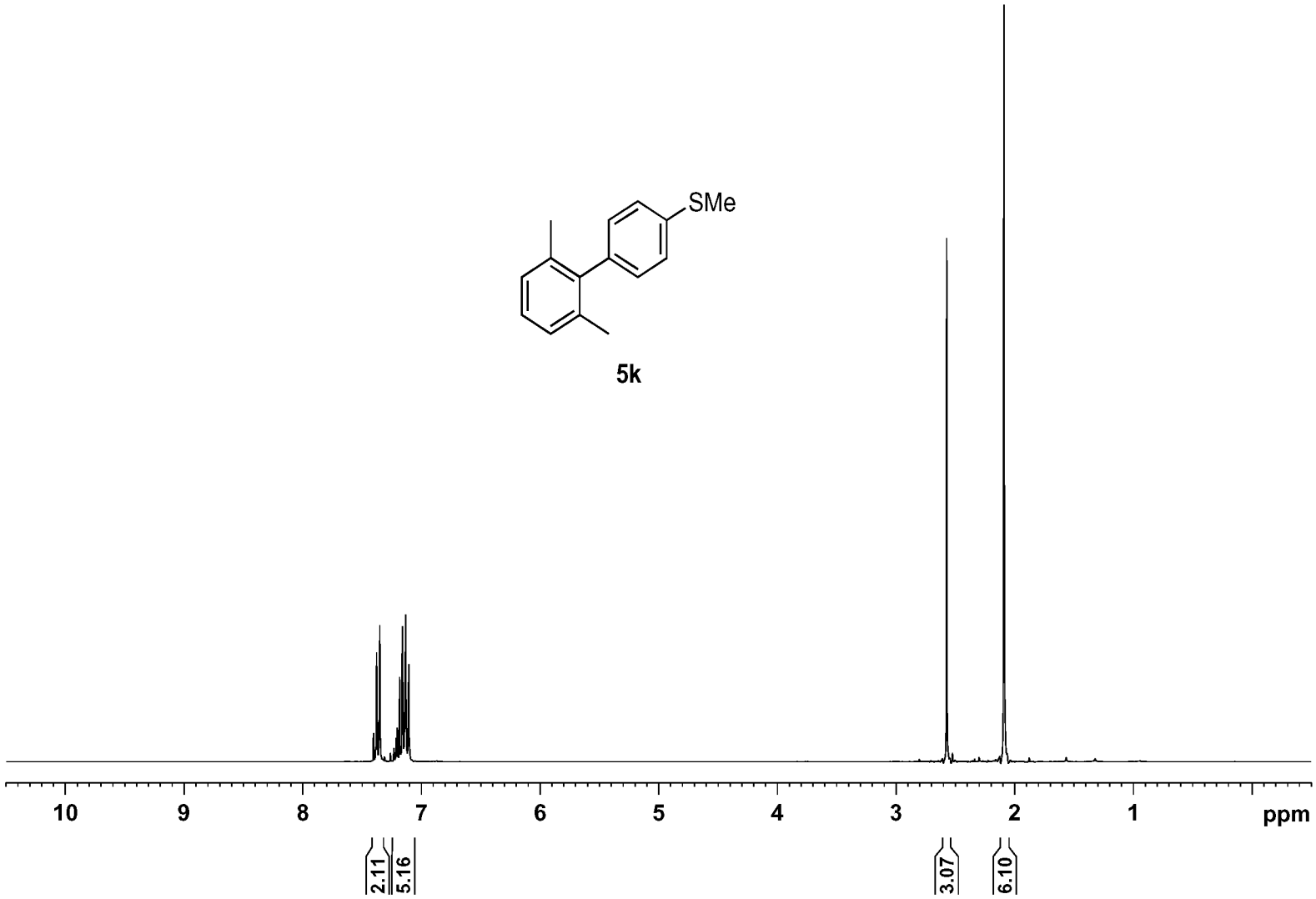
130
120
110
100
90
80
70
60
50
40
30
20
ppm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6
5
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1
ppm
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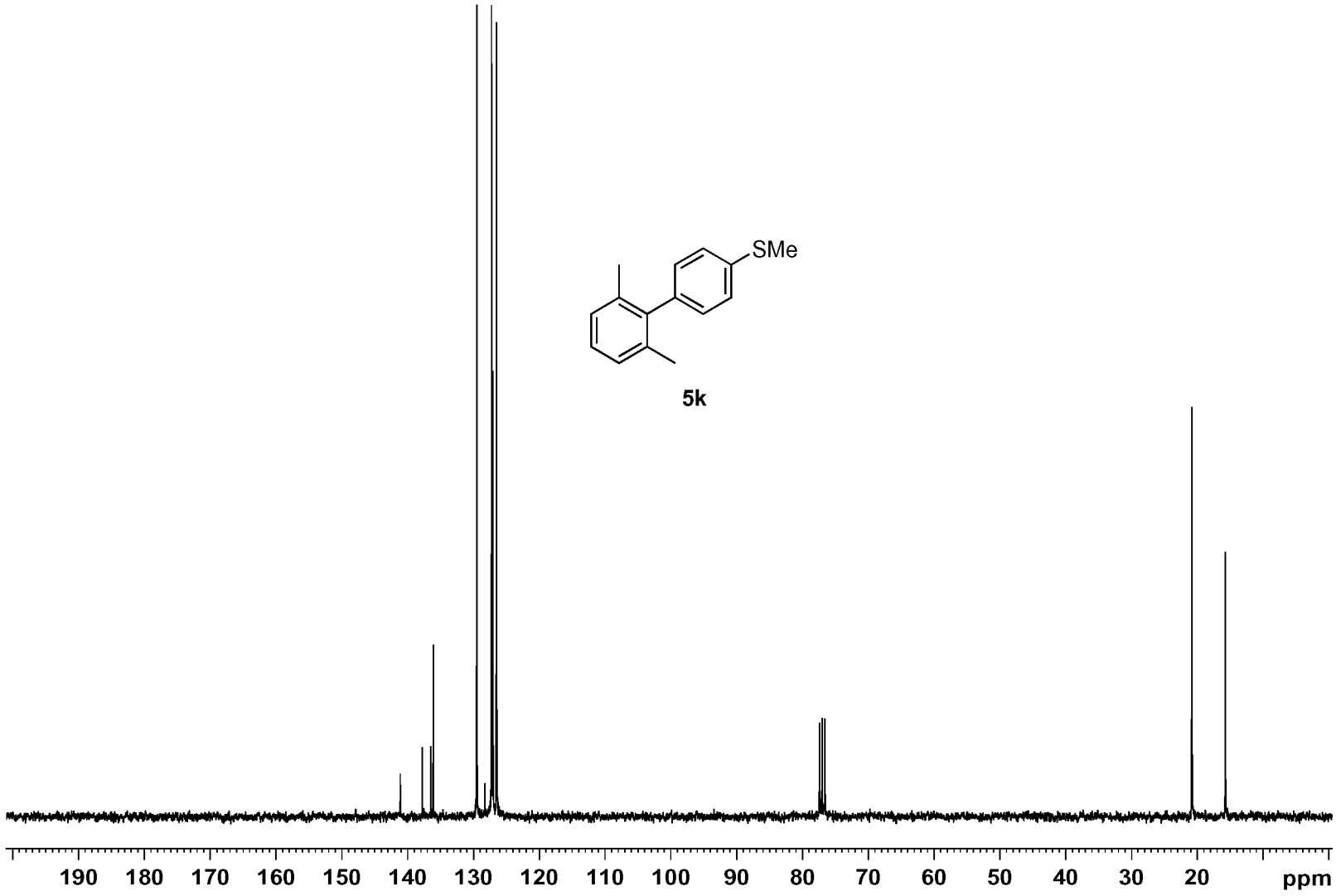
6.10


SMe
5k
190
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170
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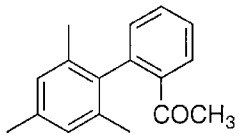
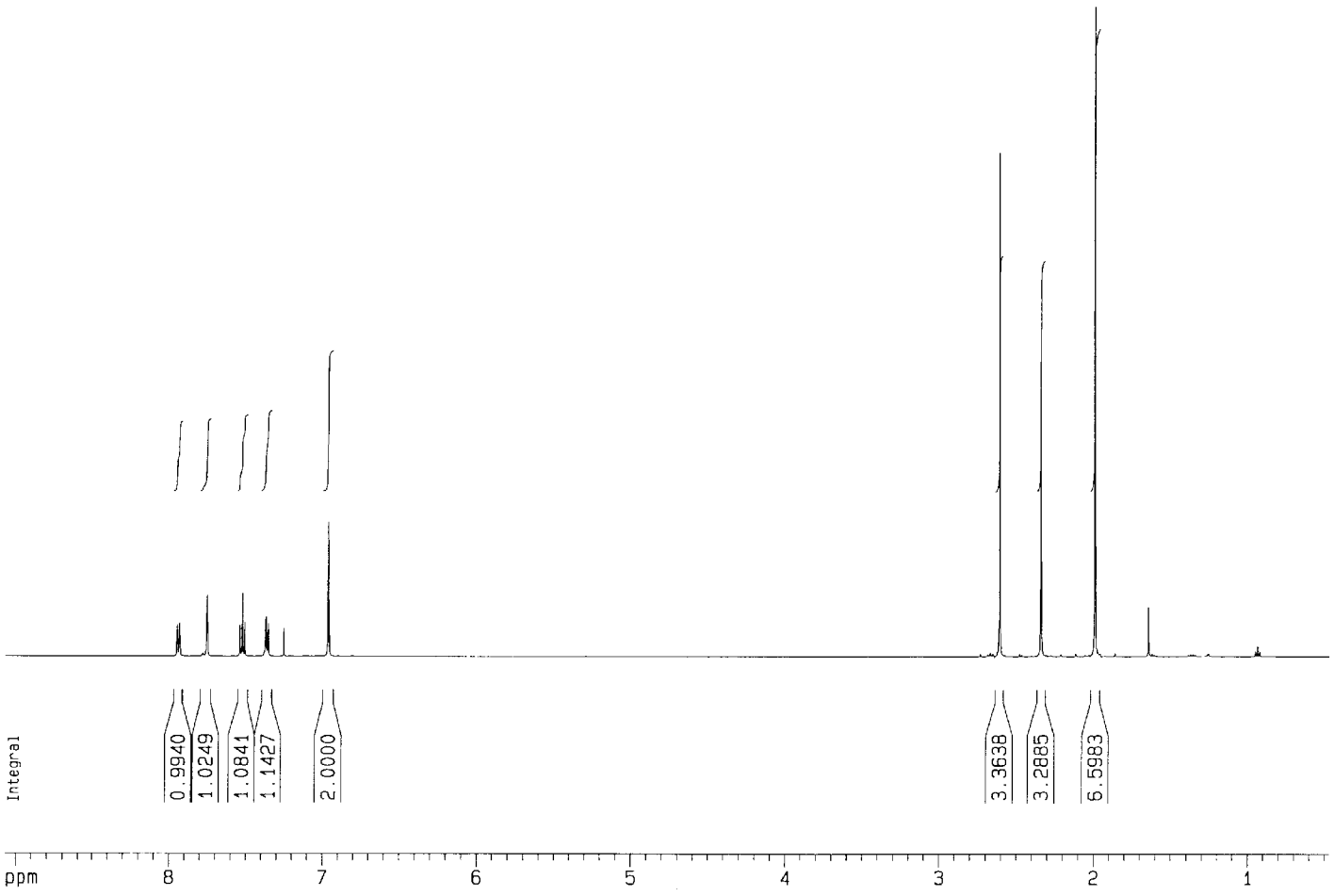
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm



5l



F2 - Acquisition Parameters

Date_	20040524
Time	18.00
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PROBHD	5 mm GNP 1H
PULPROG	zg
TD	32768
SOLVENT	CDCl3
NS	4
DS	0
SWH	5208.333 Hz
FIDRES	0.158946 Hz
AQ	3.1457779 sec
RG	64
DW	96.000 usec
DE	4.50 usec
TE	300.0 K
D1	2.00000000 sec

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

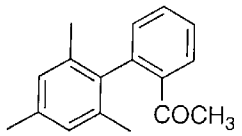
NUC1	1H
P1	10.00 usec
PL1	0.00 dB
SFO1	500.1320118 MHz

F2 - Processing parameters

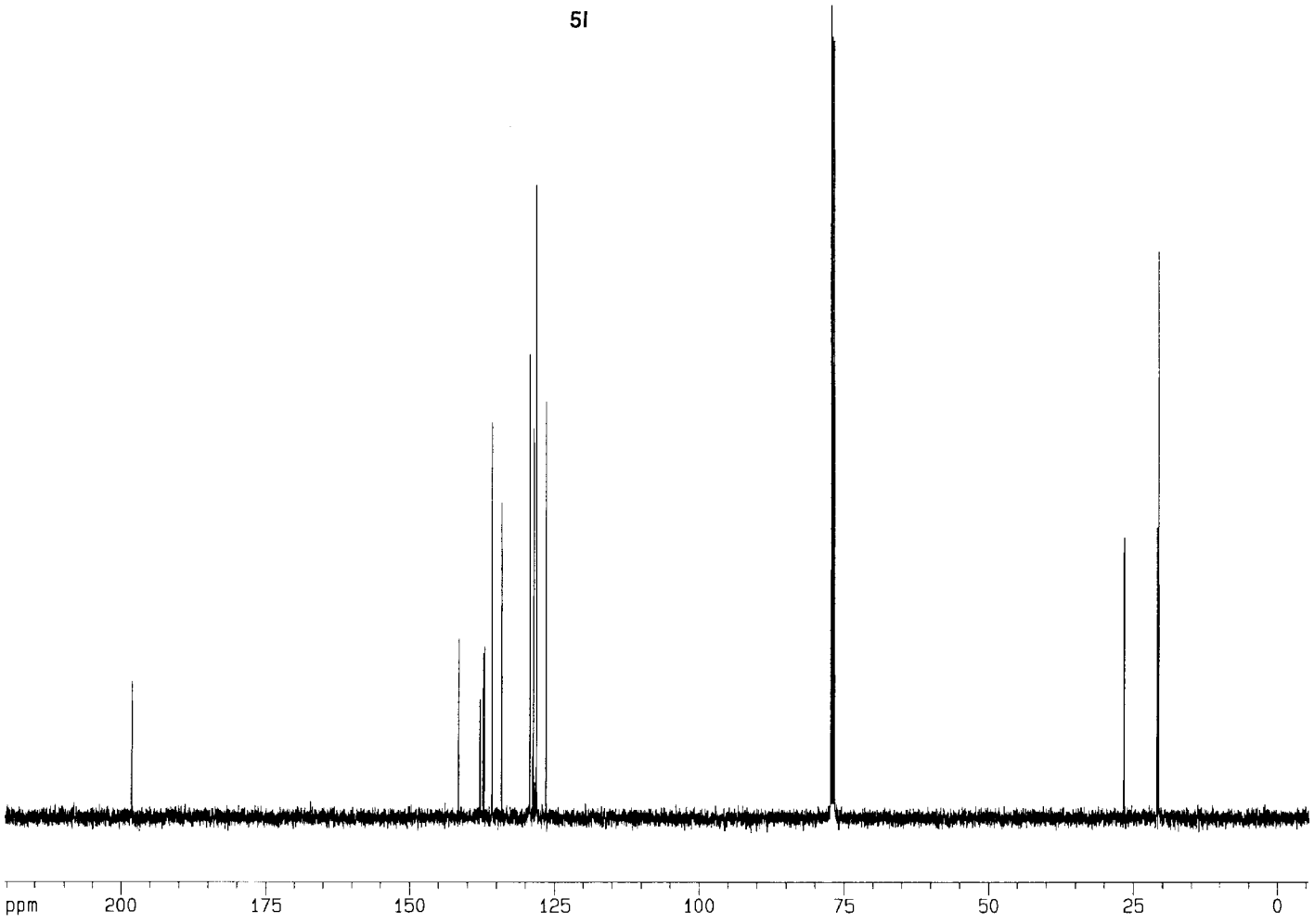
SI	16384
SF	500.1300181 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	9.070 ppm
F1	4536.09 Hz
F2P	0.471 ppm
F2	235.46 Hz
PPMCM	0.42995 ppm/cm
HZCM	215.03154 Hz/cm



5l



F2 - Acquisition Parameters

Date_	20040524
Time	18.15
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PROBHD	5 mm QNP 1H
PULPROG	zgdc
TD	238090
SOLVENT	Aceton
NS	60
DS	0
SWH	39682.539 Hz
FIDRES	0.166670 Hz
AQ	2.9999840 sec
RG	2048
DW	12.600 usec
DE	7.50 usec
TE	300.0 K
D1	4.00000000 sec
d11	0.03000000 sec

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

NUC1	13C
P1	8.20 usec
PL1	0.00 dB
SFO1	125.7736214 MHz

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

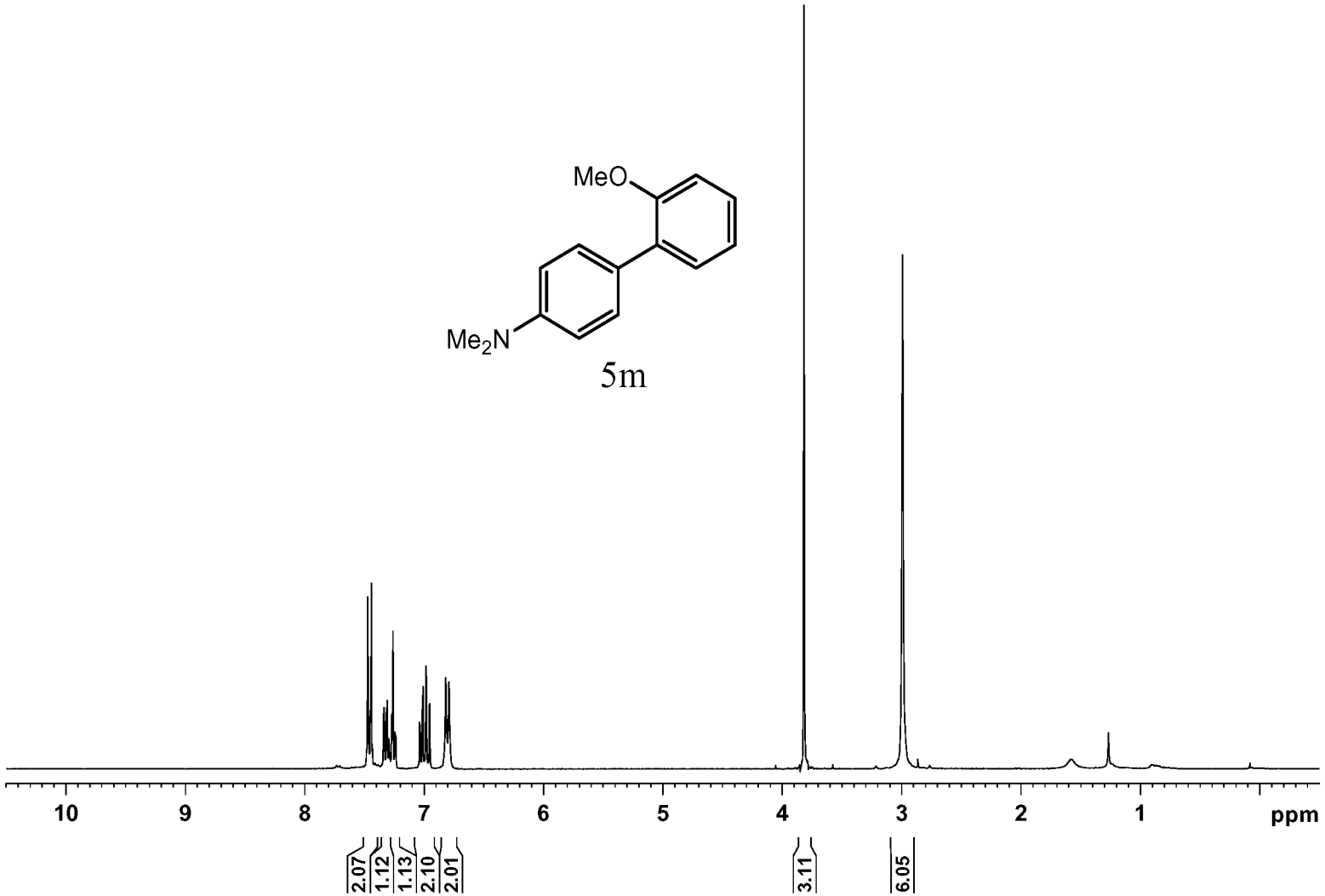
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	120.00 dB
PL12	19.00 dB
SFO2	500.1338000 MHz

F2 - Processing parameters

SI	32768
SF	125.7577970 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
F1P	220.262 ppm
F1	27699.67 Hz
F2P	-5.352 ppm
F2	-673.11 Hz
PPMCM	11.28072 ppm/cm
HZCM	1418.63867 Hz/cm


MeO
Me2N
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2
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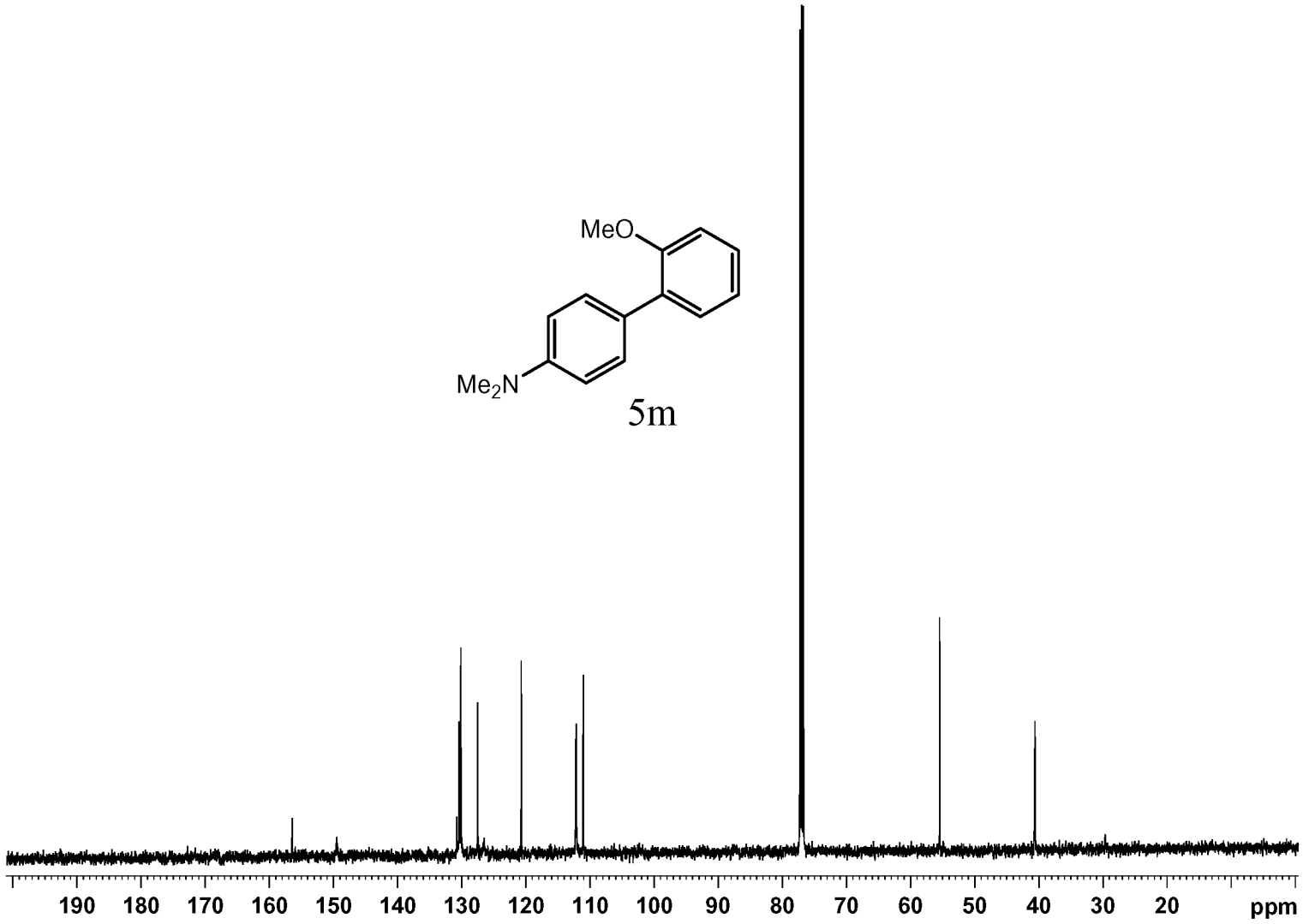
1.13
2.10
2.01
3.11
6.05


MeO
Me2N
5m
190
180
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150
140
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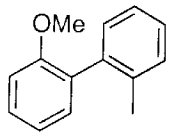
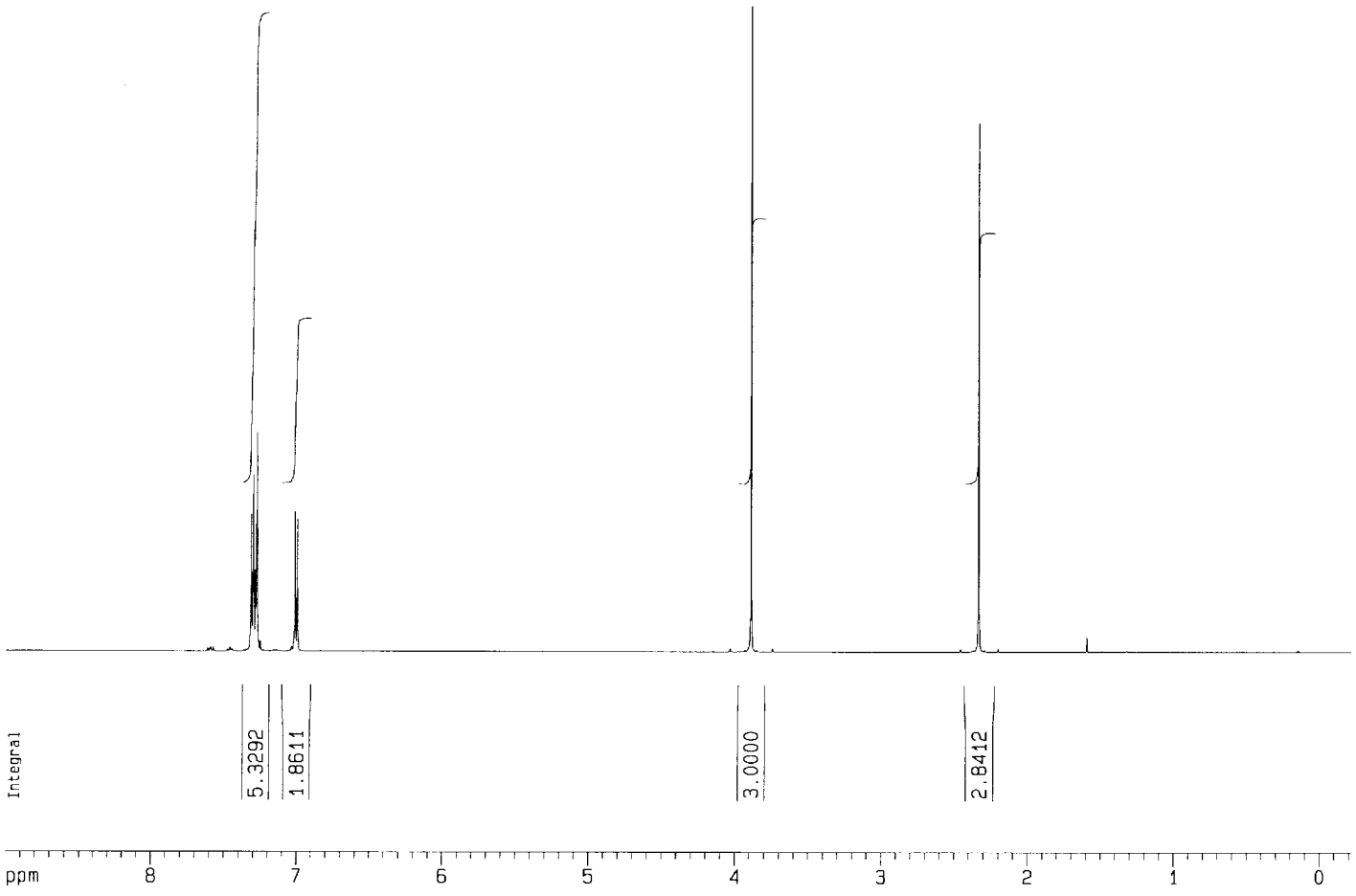
120
110
100
90
80
70
60
50
40
30
20
ppm



5n



F2 - Acquisition Parameters

Date_	20040518
Time	19.32
INSTRUM	spect
PROBHD	5 mm QNP 1H
PULPROG	zg
TD	32768
SOLVENT	CDCl3
NS	4
DS	0
SWH	5208.333 Hz
FIDRES	0.158946 Hz
AQ	3.1457779 sec
RG	32
DW	96.000 usec
DE	4.50 usec
TE	300.0 K
D1	2.00000000 sec

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

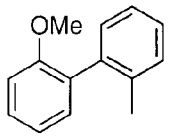
NUC1	1H
P1	10.00 usec
PL1	0.00 dB
SFO1	500.1320118 MHz

F2 - Processing parameters

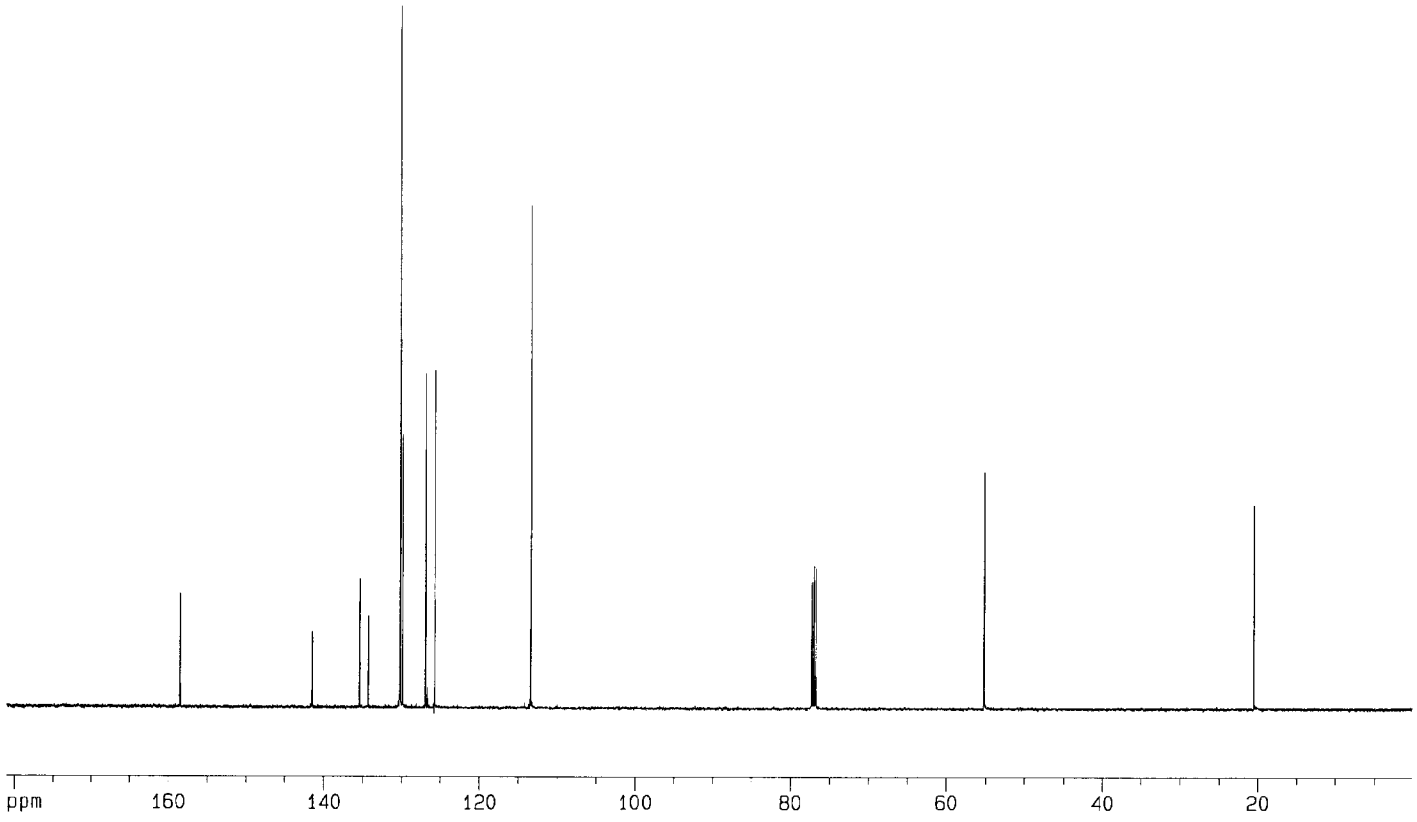
SI	16384
SF	500.1300181 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	9.000 ppm
F1	4501.08 Hz
F2P	-0.214 ppm
F2	-107.03 Hz
PPMCM	0.46069 ppm/cm
HZCM	230.40584 Hz/cm



5n

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Current Data Parameters
NAME          haploindole
EXPNO                 624
PROCNO                  1

F2 - Acquisition Parameters
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Time               19.40
INSTRUM            spect
PROBHD     5 mm QNP  1H
PULPROG            zgdc
TD               238090
SOLVENT          Aceton
NS                   60
DS                    0
SWH           39682.539 Hz
FIDRES        0.166670 Hz
AQ            2.9999840 sec
RG                 2048
DW               12.600 usec
DE                7.50 usec
TE               300.0 K
D1            4.00000000 sec
d11           0.03000000 sec

============ CHANNEL f1 ==========
NUC1                13C
P1                 8.20 usec
PL1                0.00 dB
SF01         125.7736214 MHz

============ CHANNEL f2 ==========
CPDPRG2         waltz16
NUC2                1H
PCPD2             90.00 usec
PL2              120.00 dB
PL12              19.00 dB
SF02         500.1338000 MHz

F2 - Processing parameters
SI                 32768
SF           125.7578019 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
F1P               180.927 ppm
F1              22753.04 Hz
F2P                0.151 ppm
F2                18.95 Hz
PPMCM             9.03884 ppm/cm
HZCM           1136.70471 Hz/cm
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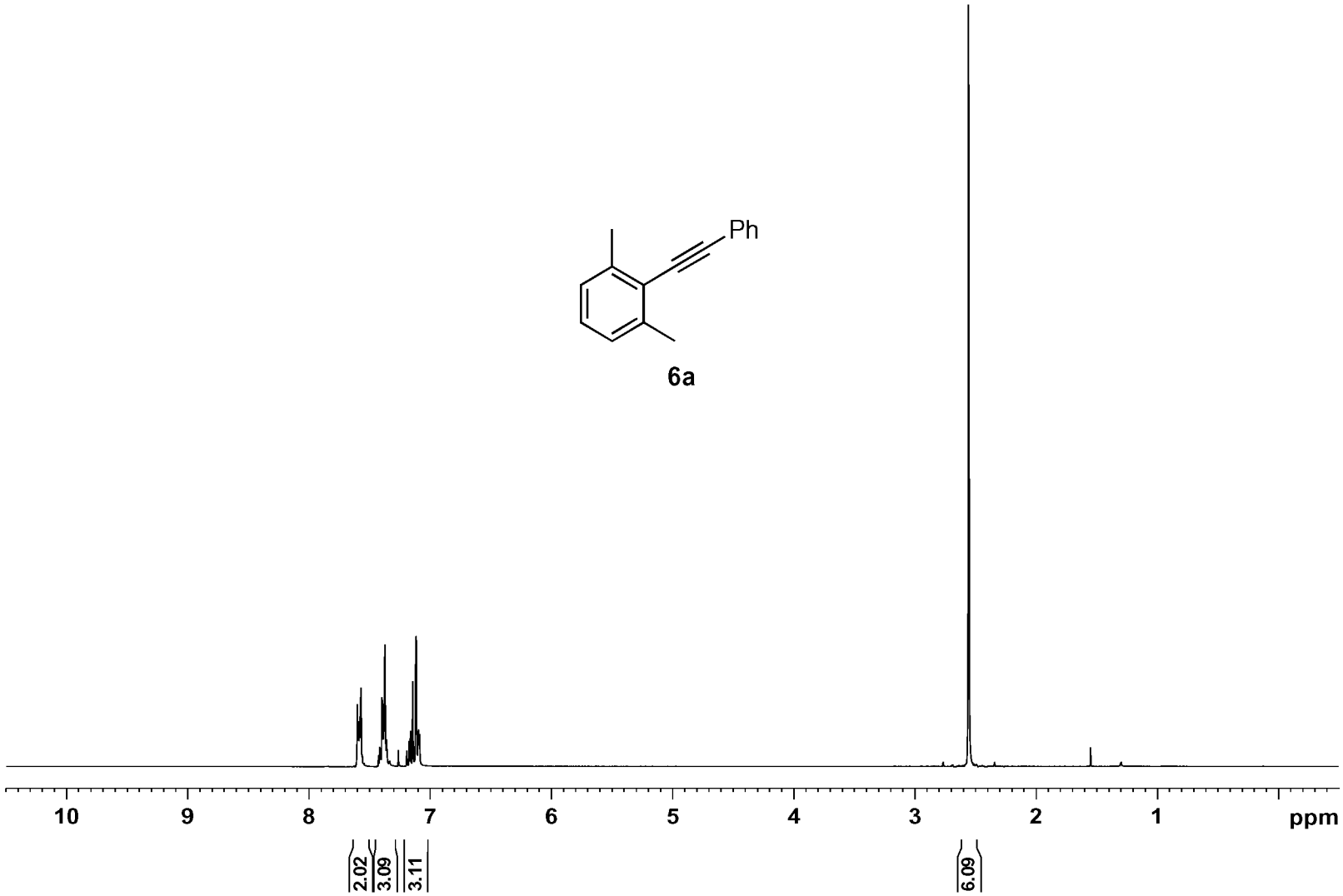
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9
8
7
6
5
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3
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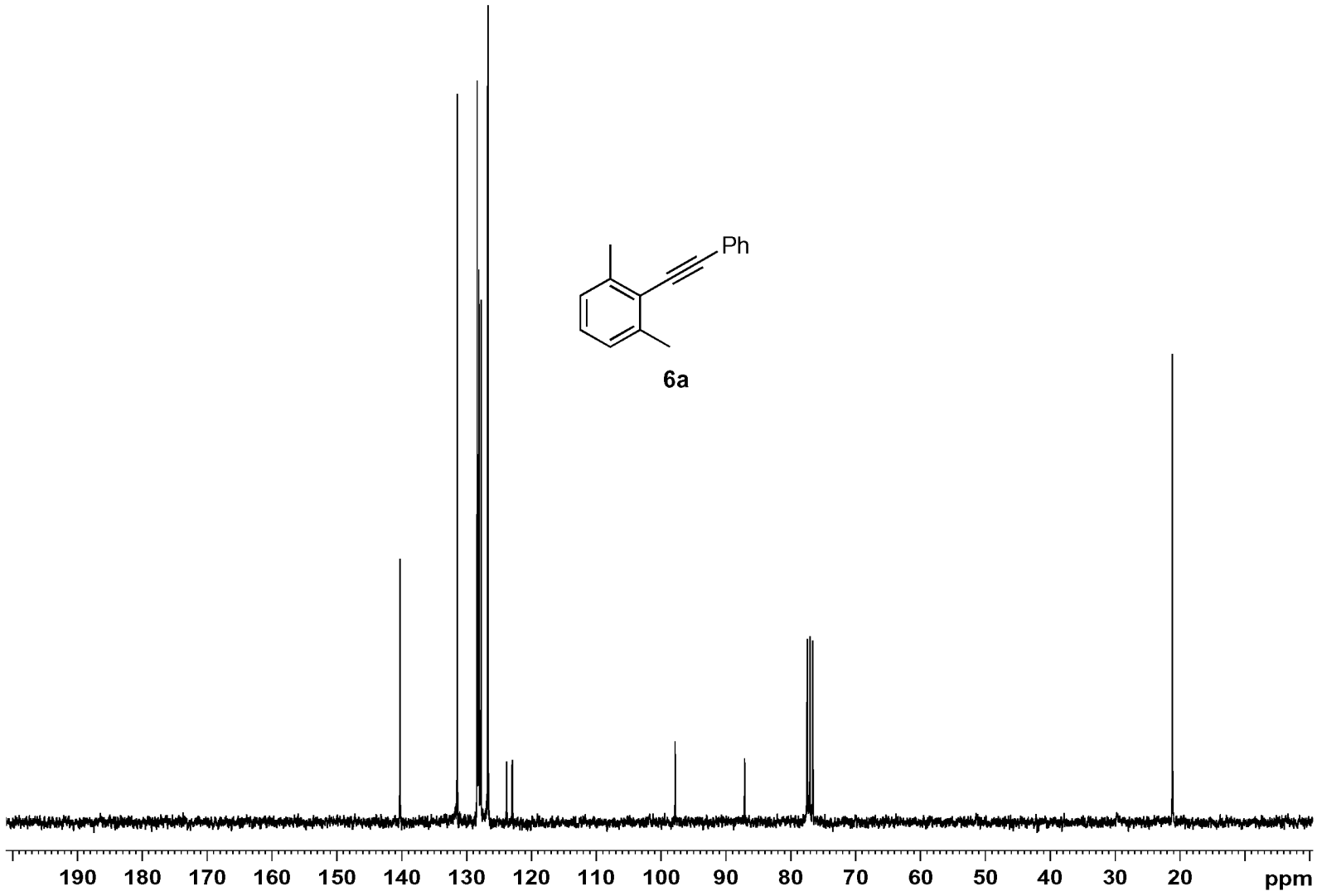
ppm
2.02
3.09
3.11
6.09


Ph
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110
100
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70
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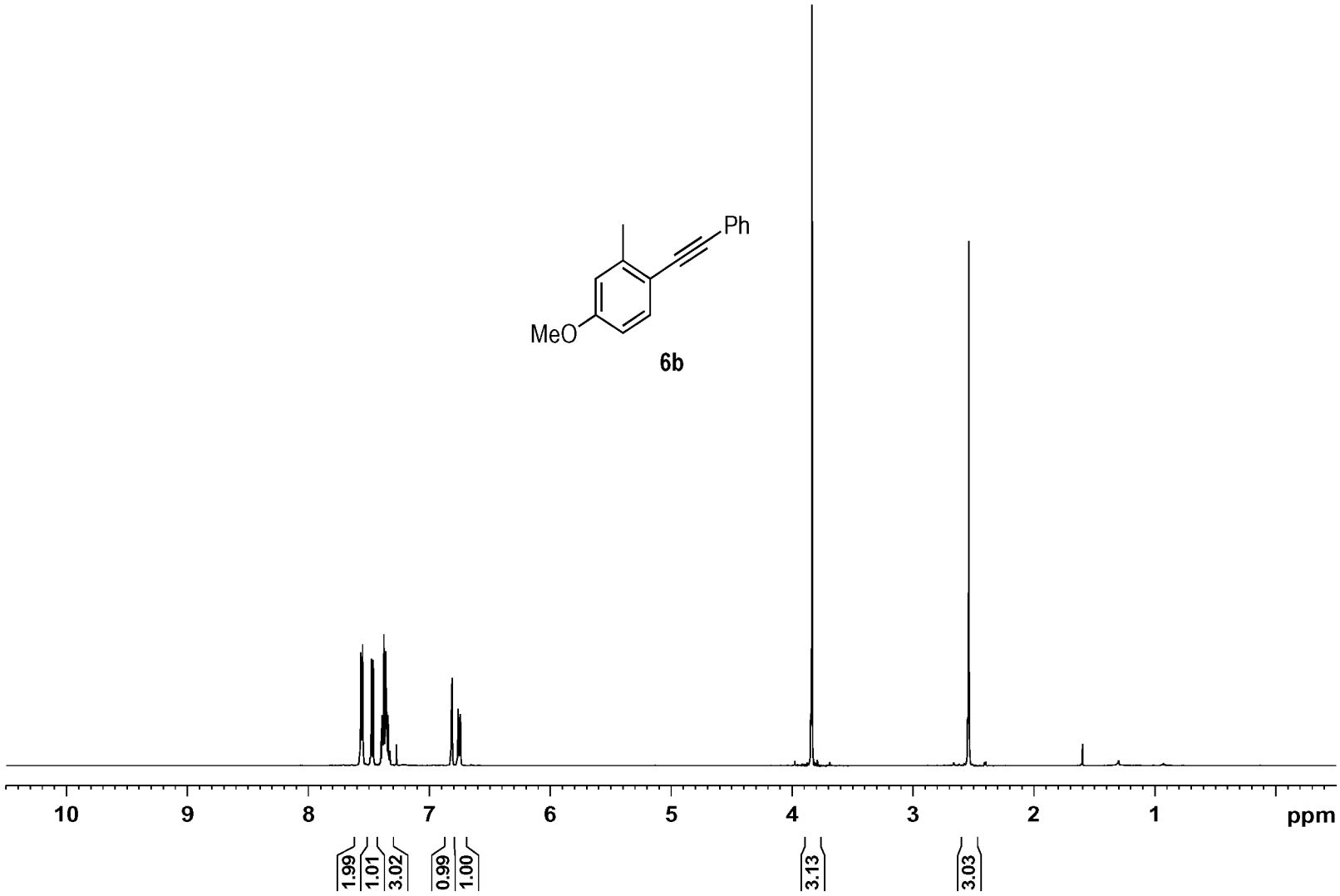
50
40
30
20
ppm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6
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2
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ppm
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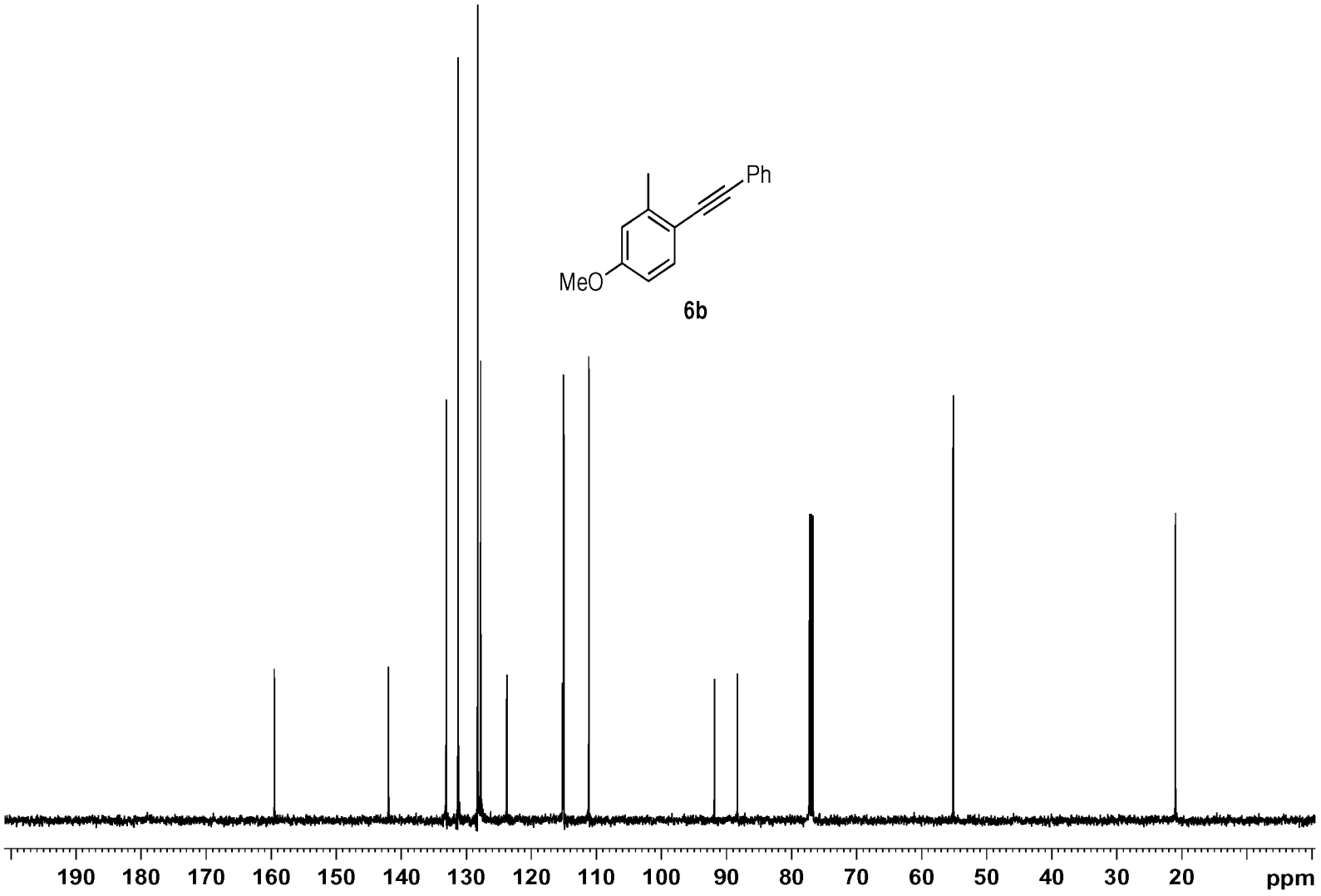
1.01
3.02
0.99
1.00
3.13
3.03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6b
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120
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100
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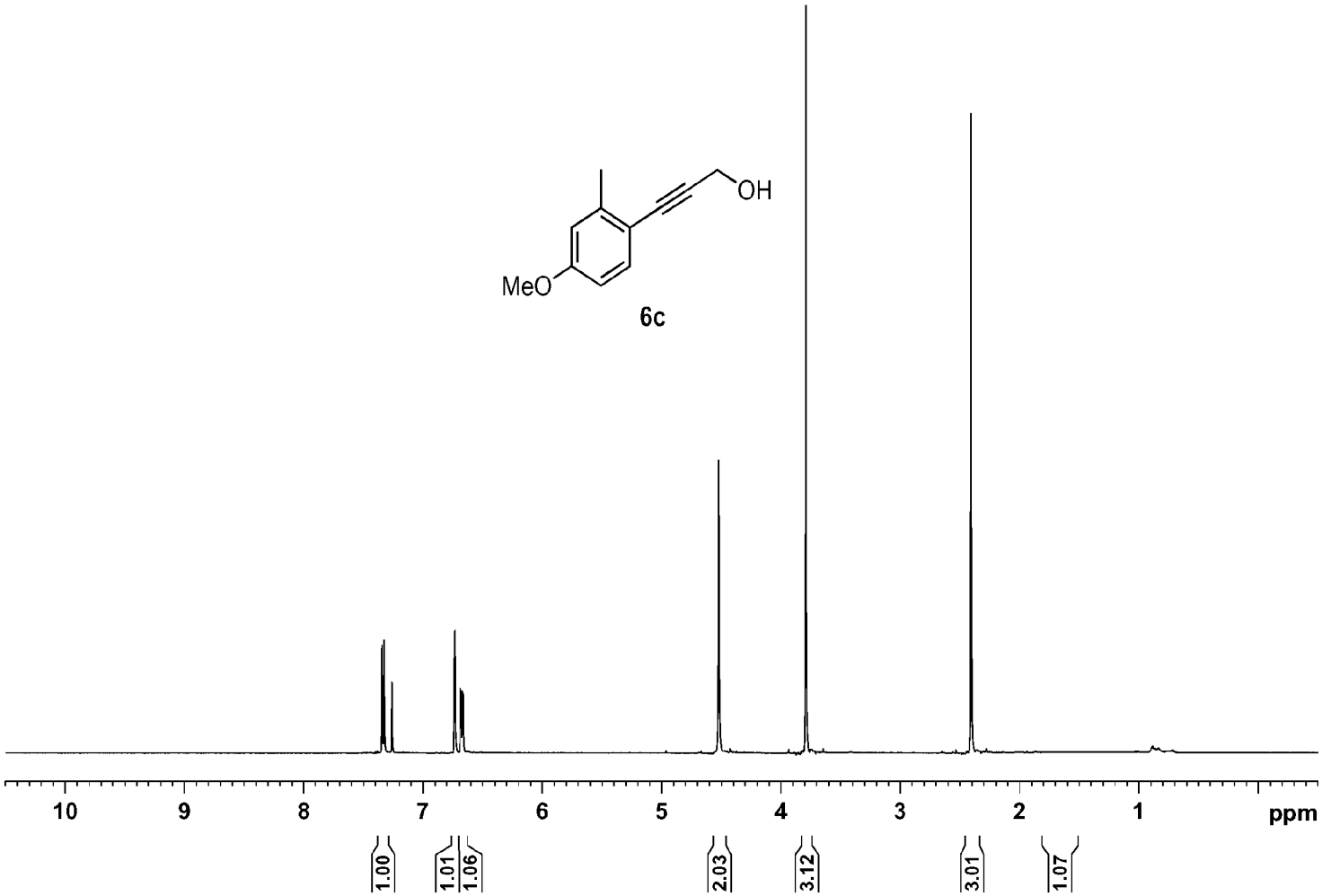
70
60
50
40
30
20
ppm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MeO
6c
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6
5
4
3
2
1
ppm
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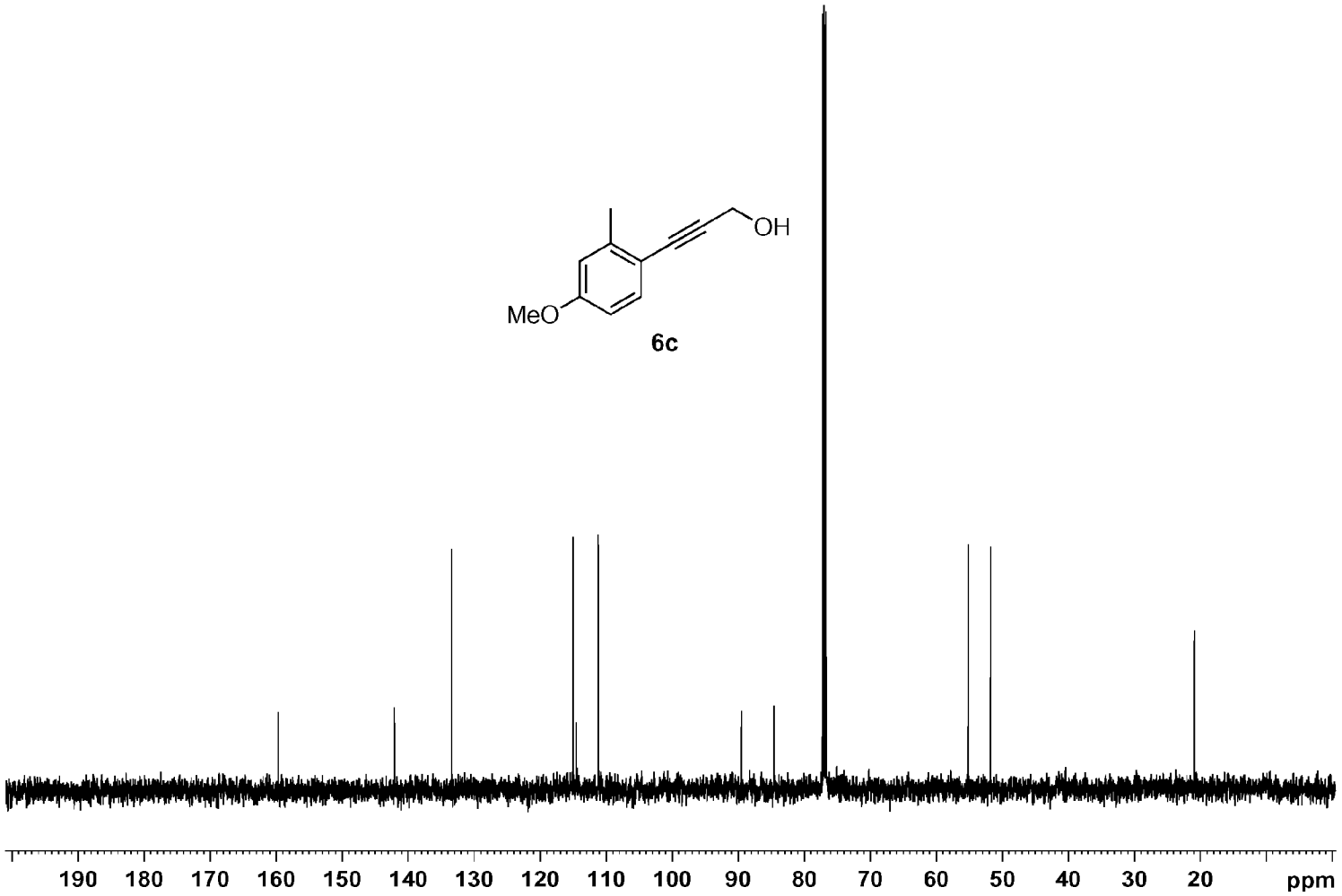
1.01
1.06
2.03
3.12
3.01
1.07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MeO
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170
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150
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110
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90
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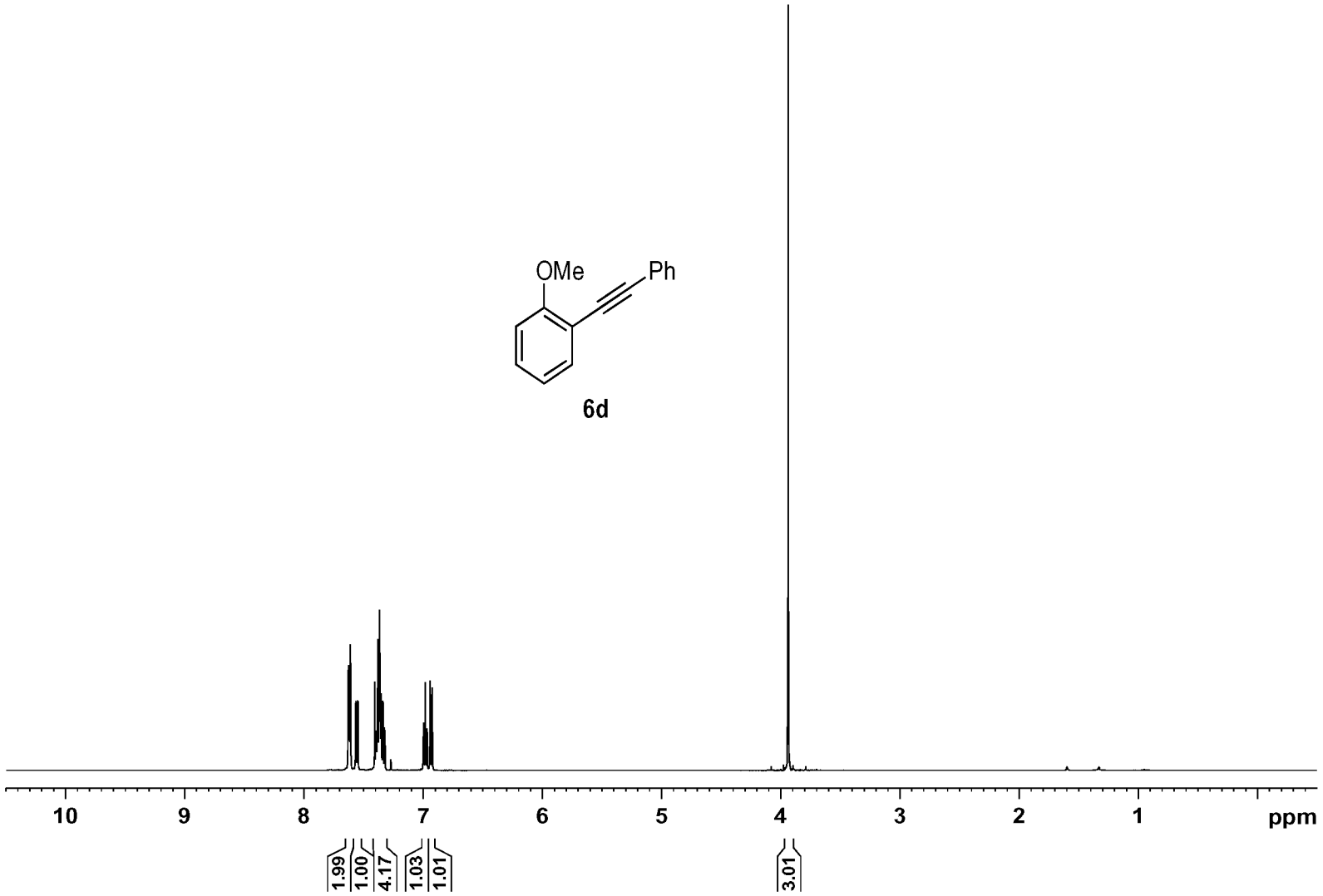
70
60
50
40
30
20
ppm

6c


OMe
Ph
6d
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7
6
5
4
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2
1
ppm
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1.00
4.17
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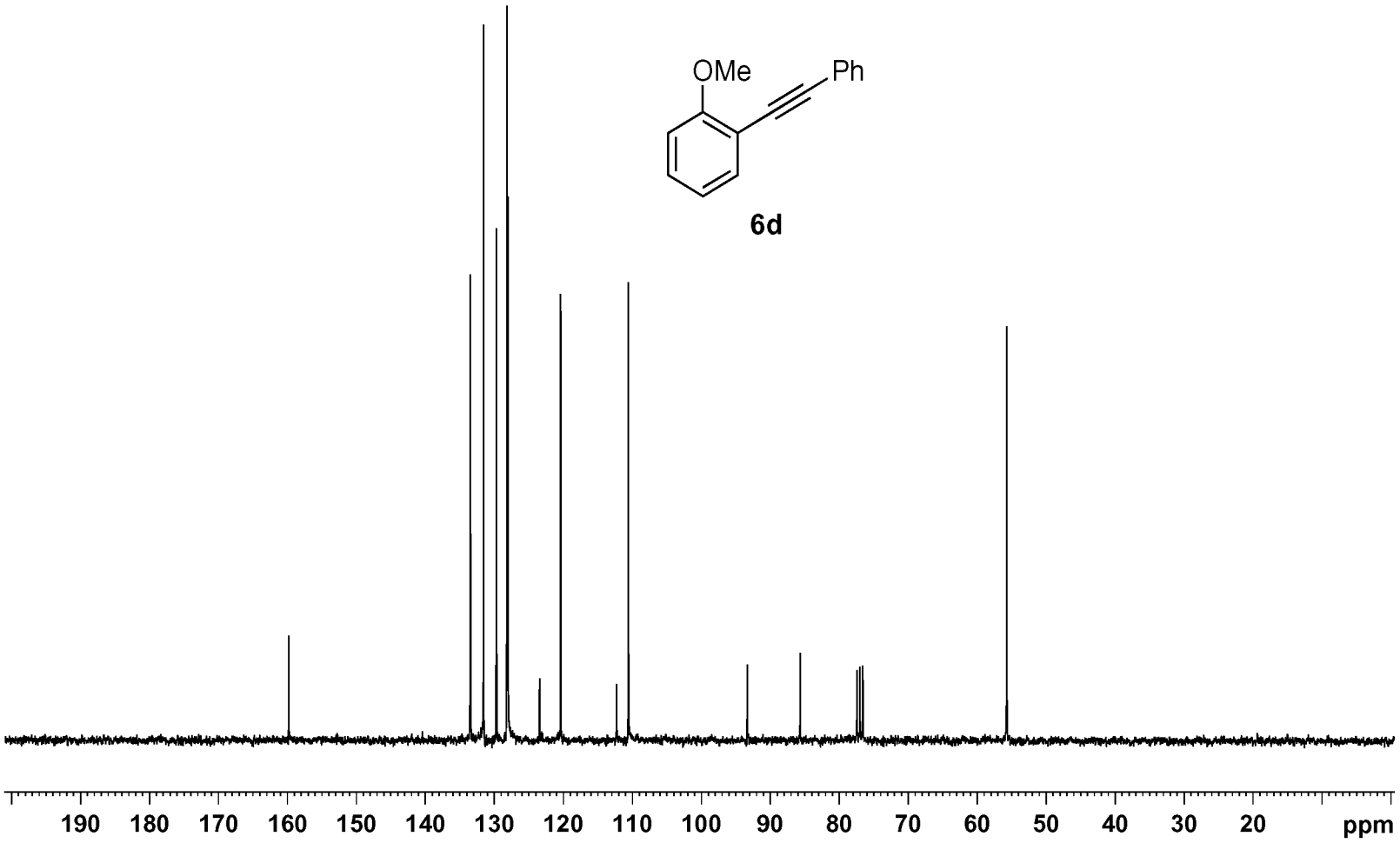
1.01
3.01


OMe
Ph
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150
140
130
120
110
100
90
80
70
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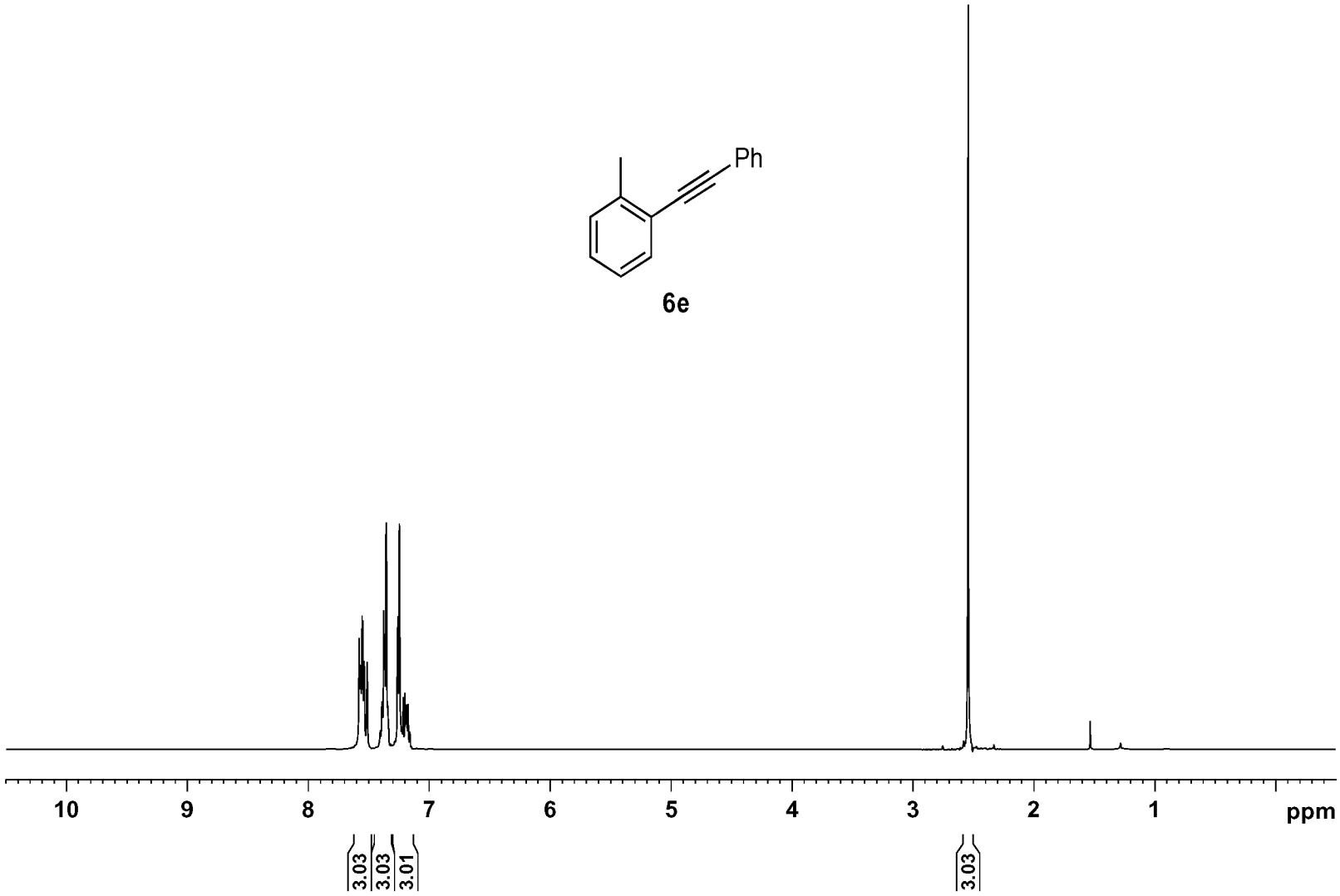
50
40
30
20
ppm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7
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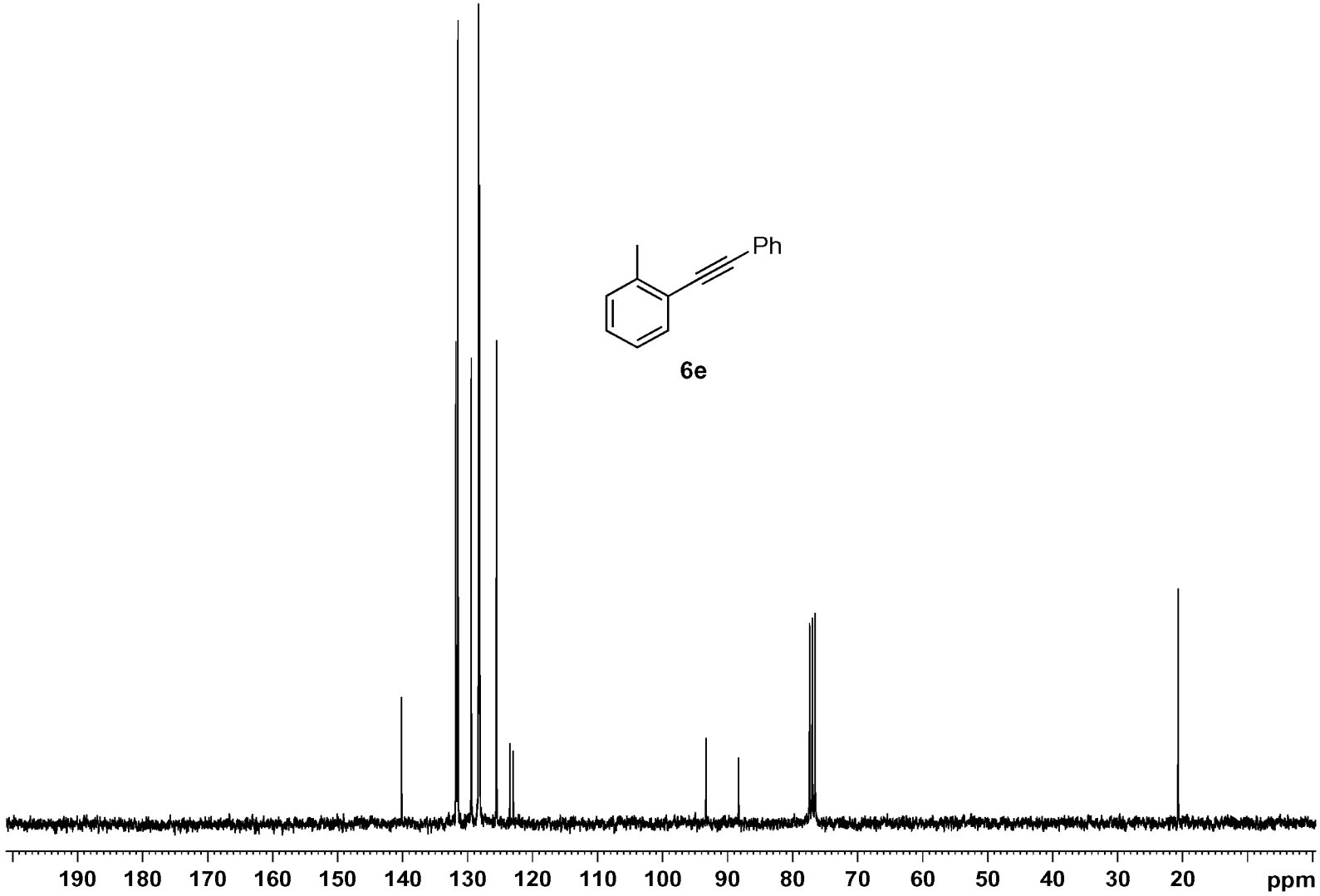
5
4
3
2
1
ppm
3.03
3.03
3.01
3.03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160
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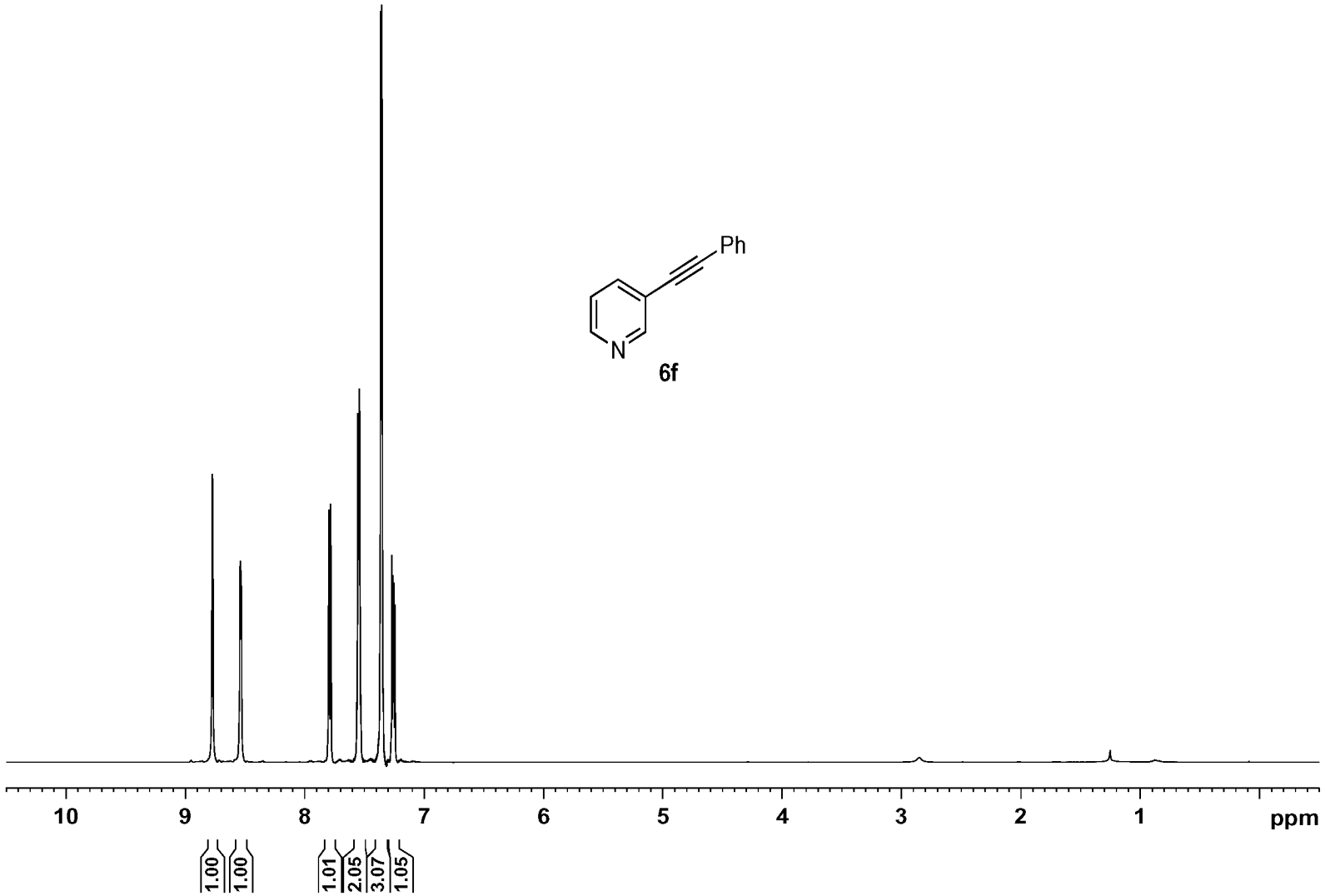
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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6f
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7
6
5
4
3
2
1
ppm
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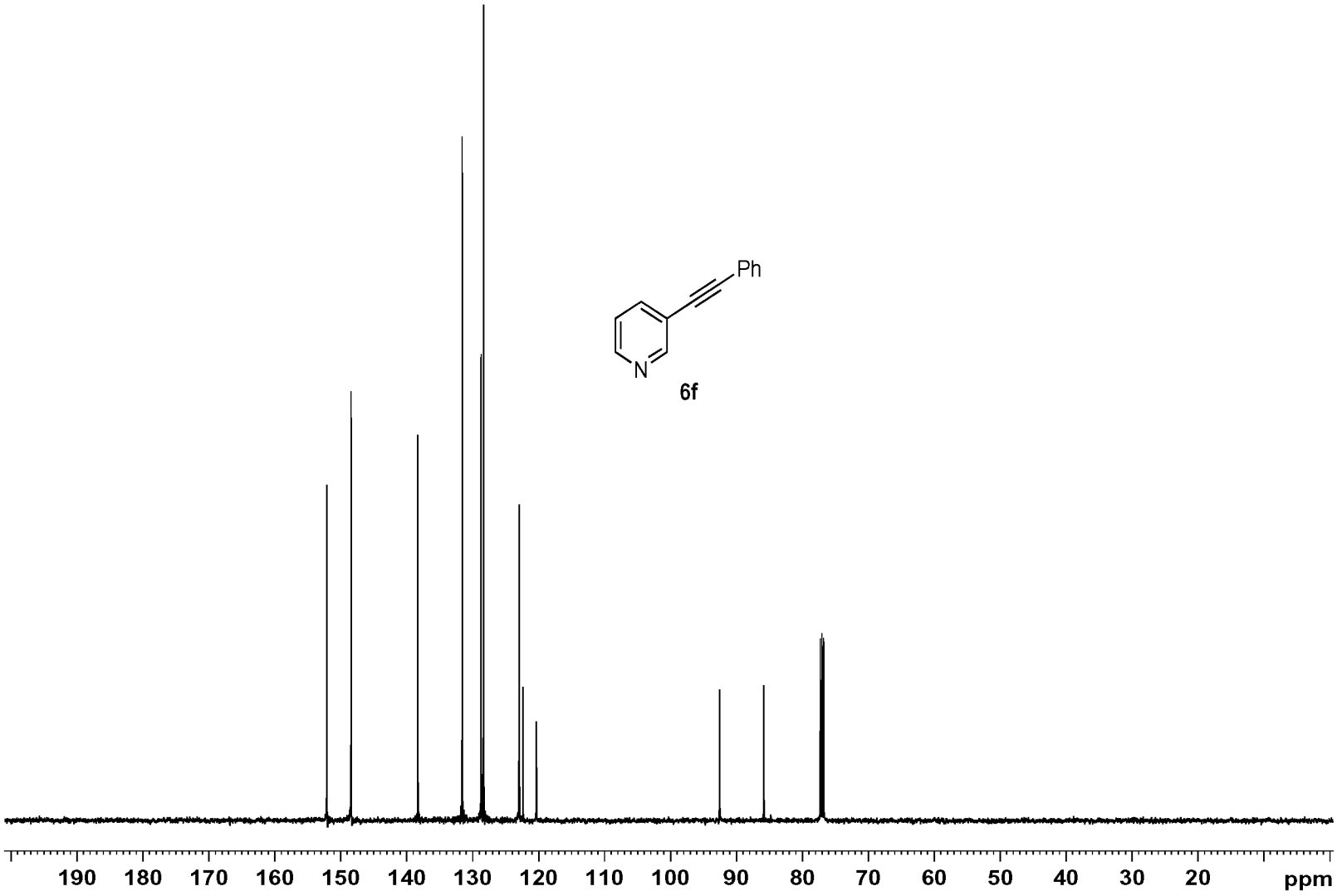
1.00
1.01
2.05
3.07
1.05


Ph
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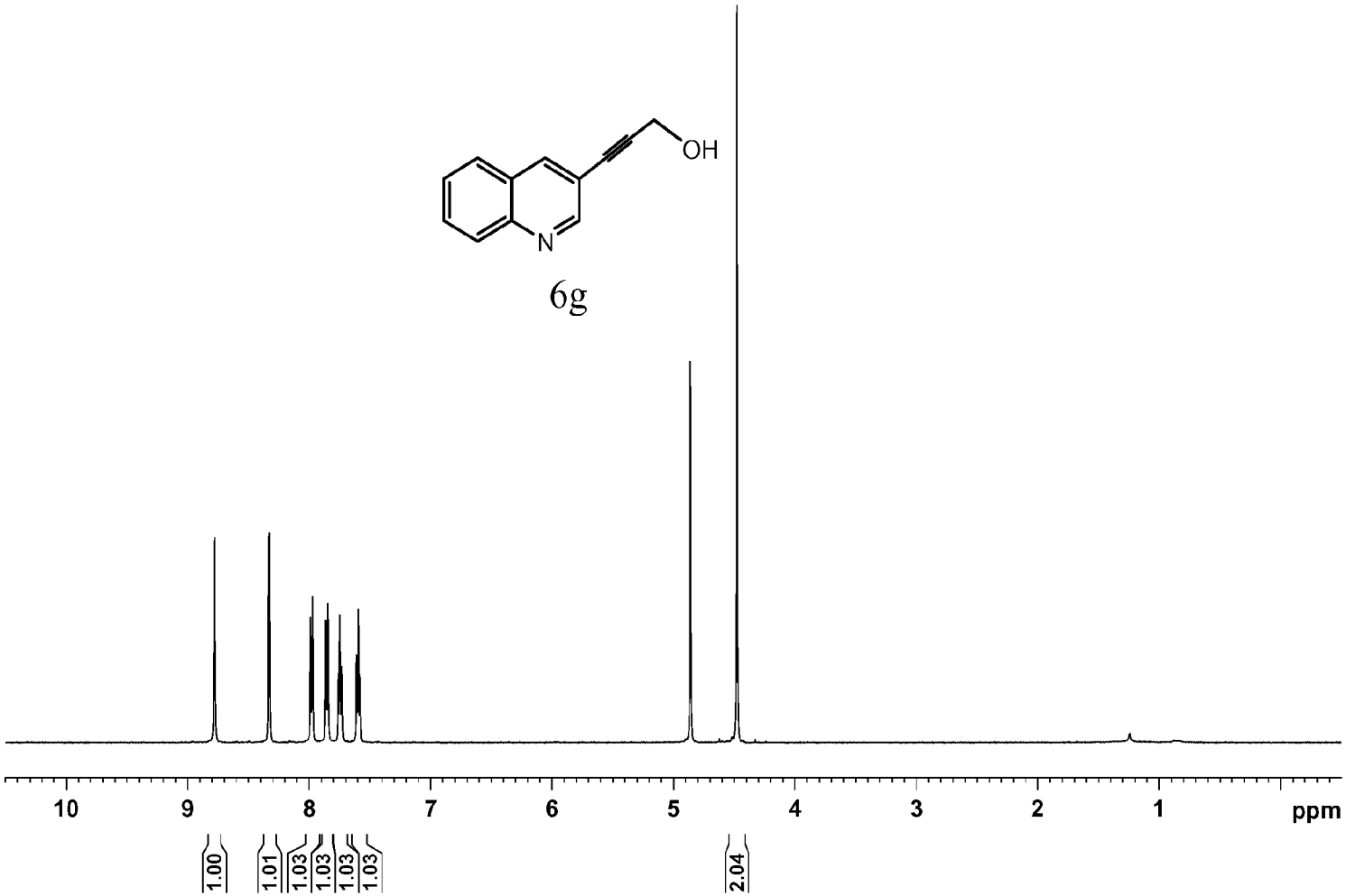
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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6g
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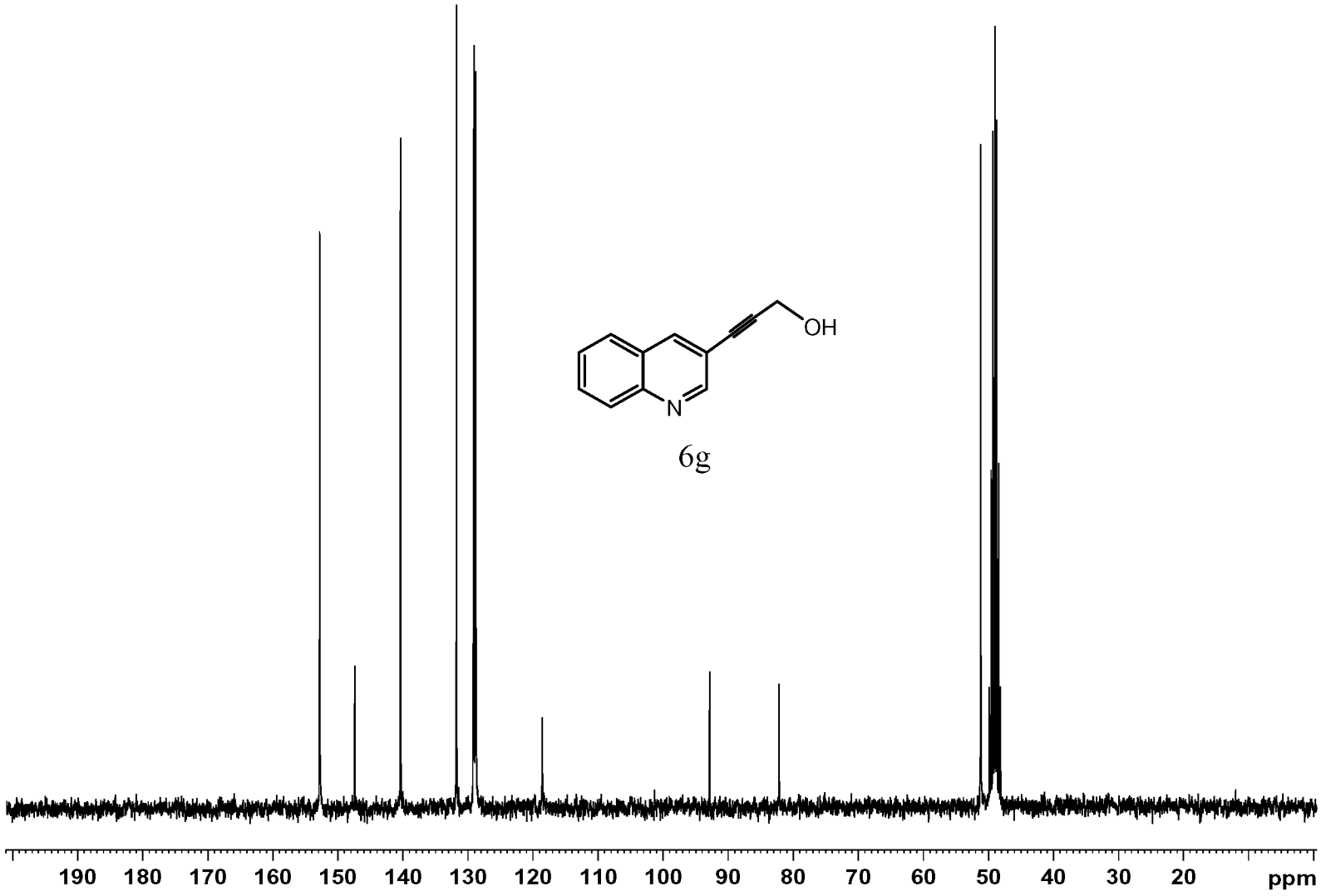
3
2
1
ppm
1.00
1.01
1.03
1.03
1.03
1.03
2.04


OH
N
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70
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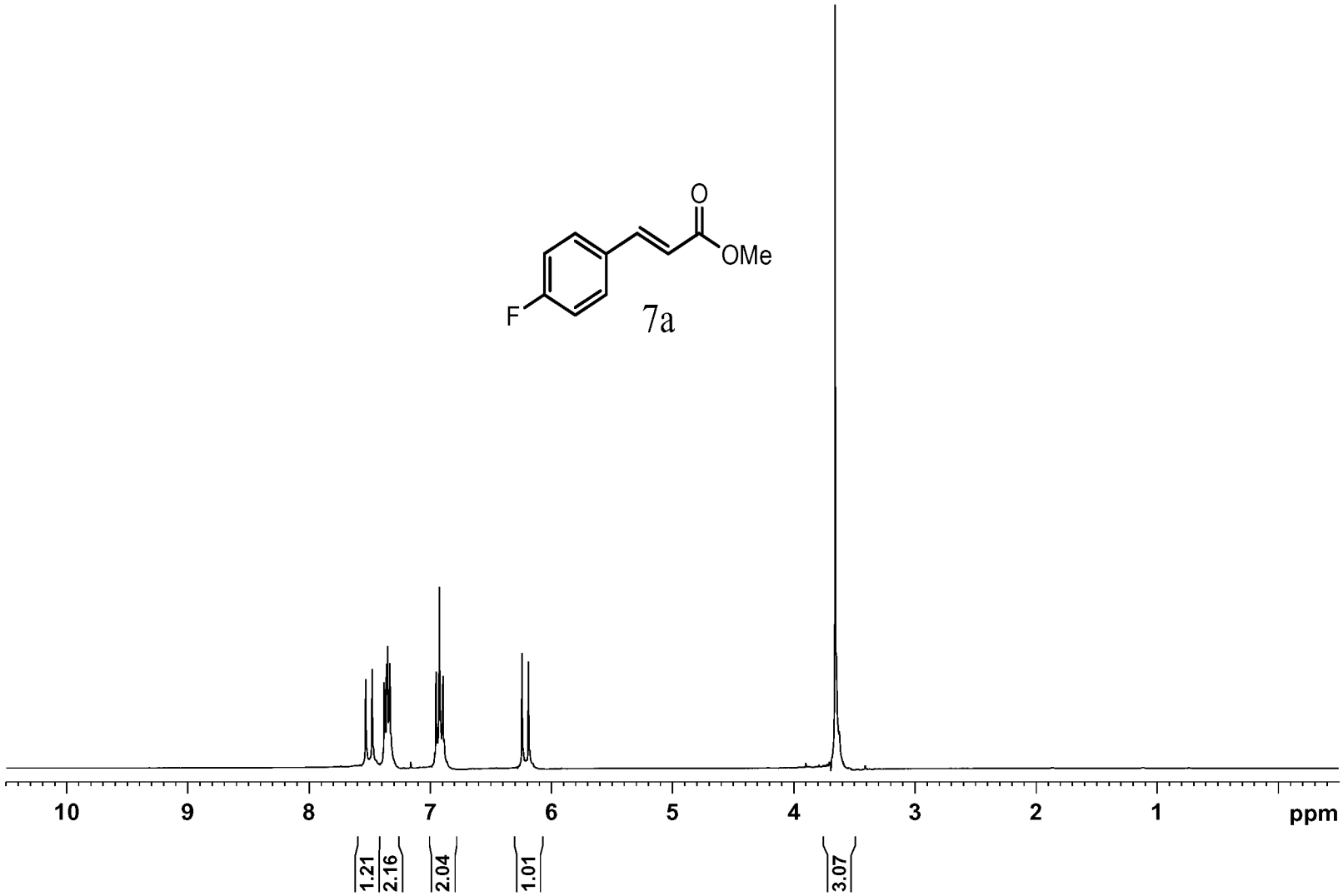
50
40
30
20
ppm

6g


O
OMe
F
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6
5
4
3
2
1
ppm
1.21
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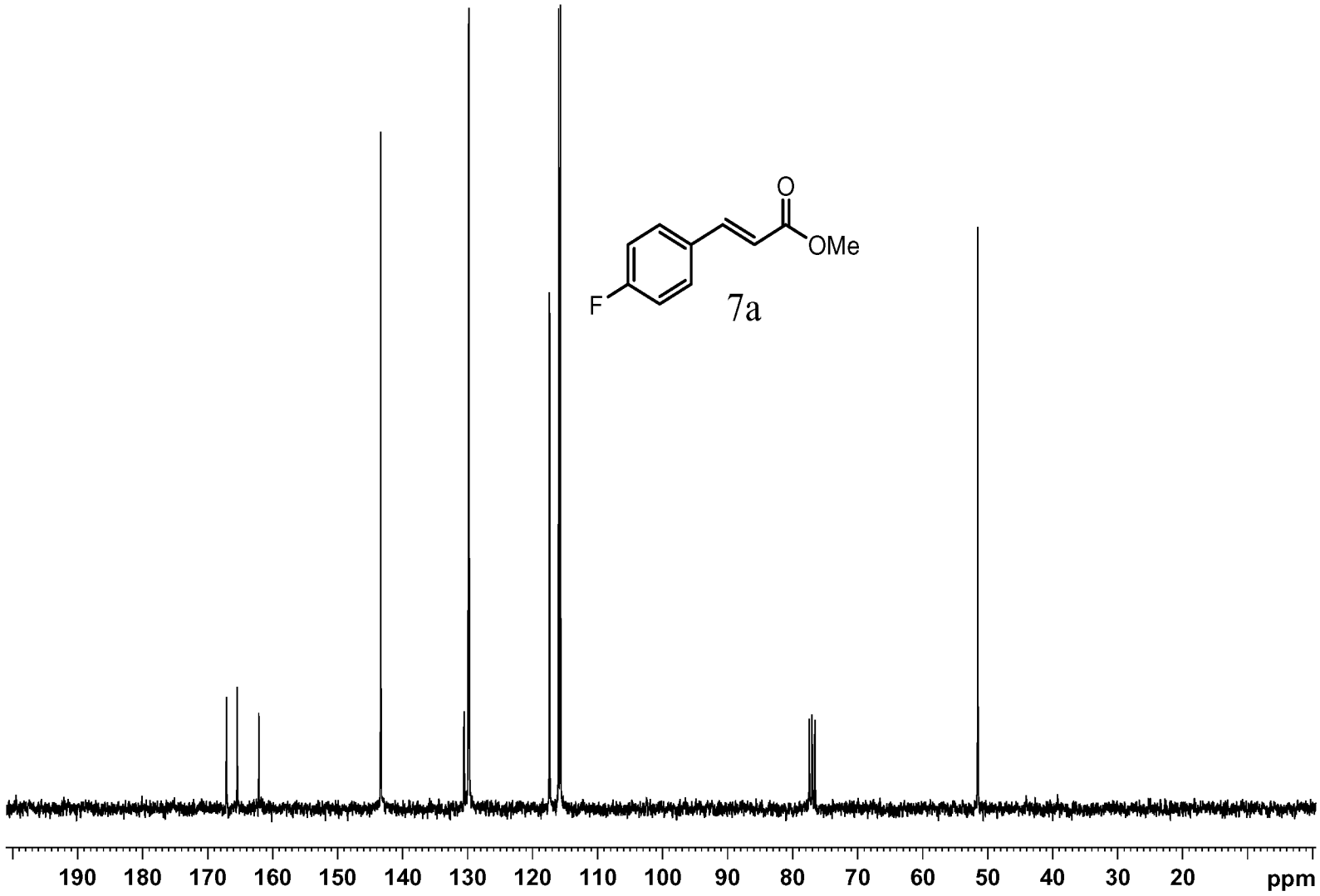
1.01
3.07


O
OMe
F
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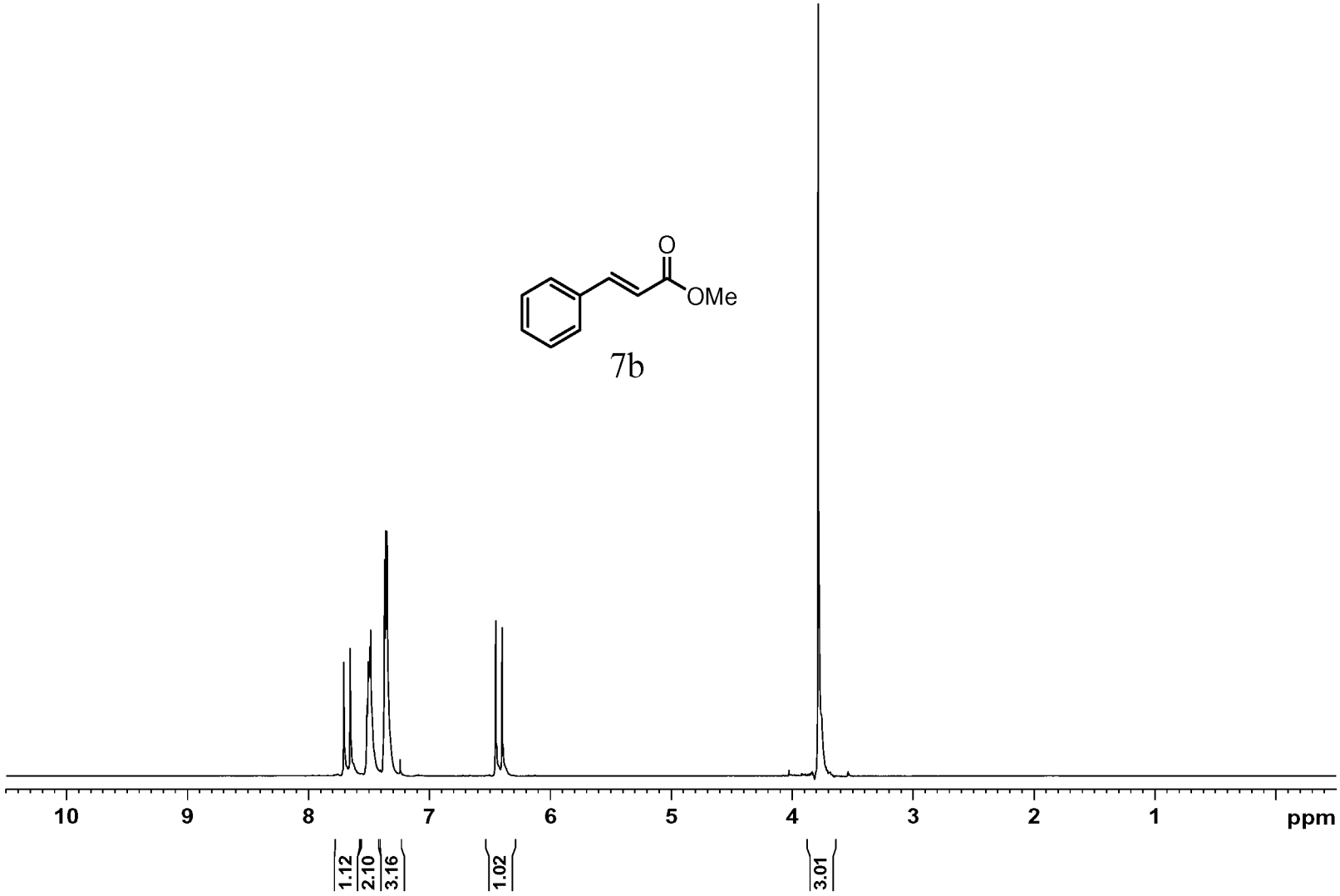
30
20
ppm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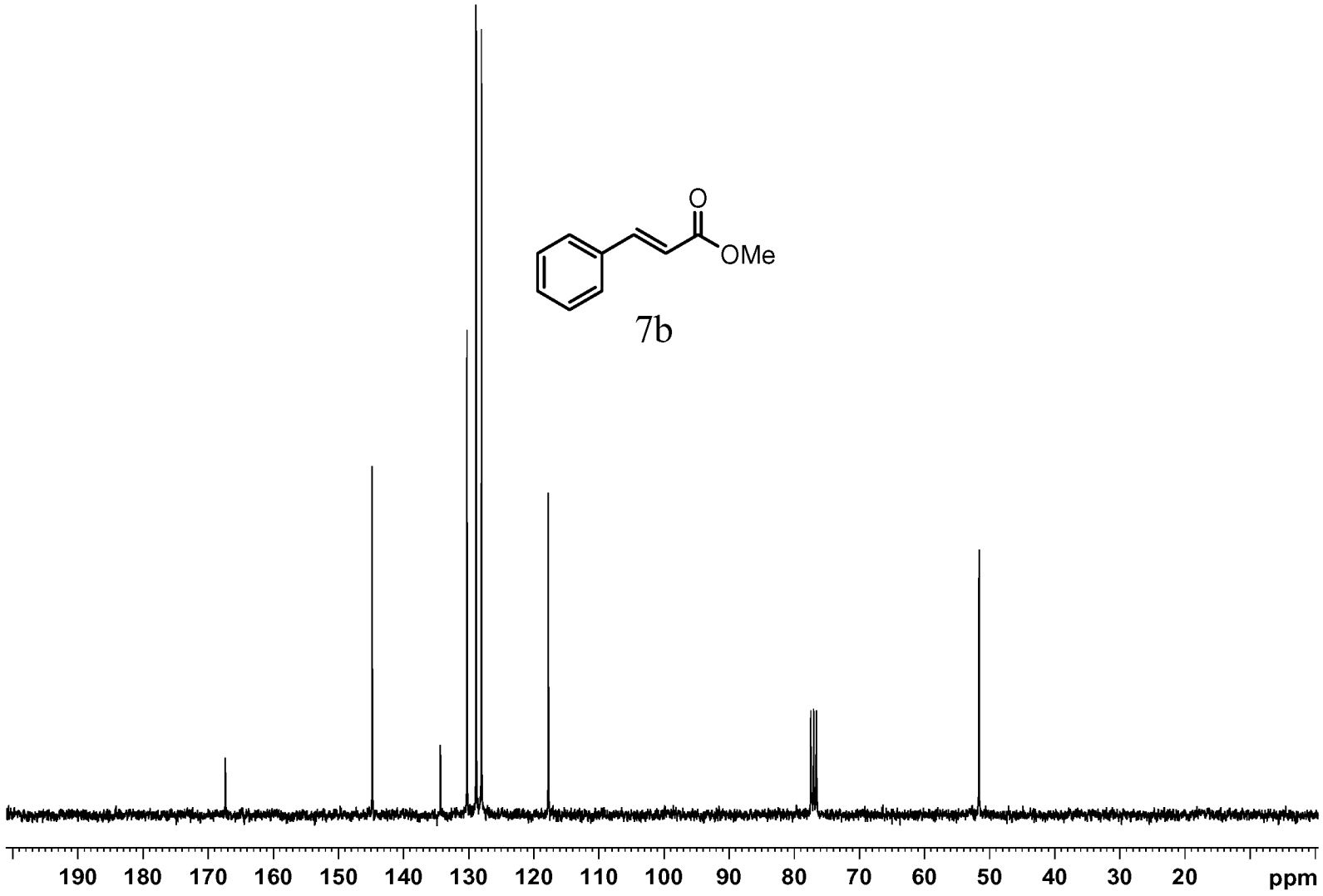
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7b
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150
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30
20
ppm