Supporting information

Iron-catalyzed oxidative biaryl cross-couplings via mixed diaryl titanates: significant influence of the order of combining aryl Grignard reagents with titanate

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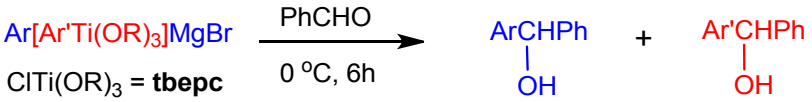
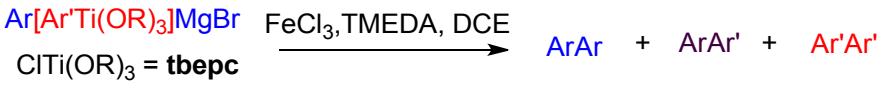
1. Specific data for the results in Fig. 1 and 2

Table S1 Comparison of the additions of the mixed diaryl titanates Ar[Ar′Ti(OR)$_3$]MgX and Ar′[ArTi(OR)$_3$]MgX to PhCHO



	Ar[Ar′Ti(OR)$_3$]MgBr	Yield(%) ArCHPh OH	Yield(%) Ar'CHPh OH
3ba	**4-MeOC$_6$H$_4$[4-MeC$_6$H$_4$Ti(OR)$_3$]MgBr**	74	20
3ab	**4-MeC$_6$H$_4$[4-MeOC$_6$H$_4$Ti(OR)$_3$]MgBr**	26	57
3ca	**4-MeOC$_6$H$_4$[4-EtOOCC$_6$H$_4$Ti(OR)$_3$]MgBr**	74	8
3ac	**4-EtOOCC$_6$H$_4$[4-MeOC$_6$H$_4$Ti(OR)$_3$]MgBr**	58	37
3ed	**4-FC$_6$H$_4$[4-MeNHCOC$_6$H$_4$Ti(OR)$_3$]MgBr**	88	5
3de	**4-MeNHCOC$_6$H$_4$[4-FC$_6$H$_4$Ti(OR)$_3$]MgBr**	37	32

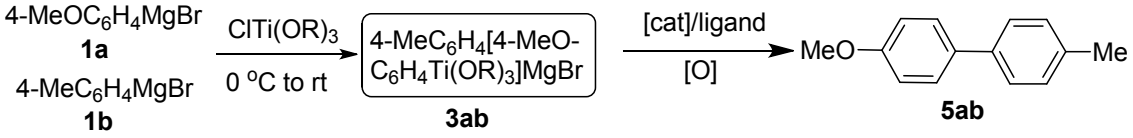
Table S2 Comparison of the iron-catalyzed oxidative couplings of the mixed diaryl titanates Ar[Ar′Ti(OR)$_3$]MgX and Ar′[ArTi(OR)$_3$]MgX



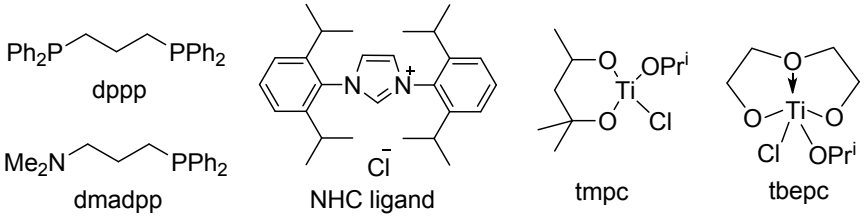
	Ar[Ar′Ti(OR)$_3$]MgBr	Yield(%) ArAr	Yield(%) ArAr’	Yield(%) Ar’Ar’
3ba	**4-MeOC$_6$H$_4$[4-MeC$_6$H$_4$Ti(OR)$_3$]MgBr**	34	55	11
3ab	**4-MeC$_6$H$_4$[4-MeOC$_6$H$_4$Ti(OR)$_3$]MgBr**	10	79	11
3ca	**4-MeOC$_6$H$_4$[4-EtOOCC$_6$H$_4$Ti(OR)$_3$]MgBr**	57	27	9
3ac	**4-EtOOCC$_6$H$_4$[4-MeOC$_6$H$_4$Ti(OR)$_3$]MgBr**	15	74	10
3ed	**4-FC$_6$H$_4$[4-MeNHCOC$_6$H$_4$Ti(OR)$_3$]MgBr**	42	44	11
3de	**4-MeNHCOC$_6$H$_4$[4-FC$_6$H$_4$Ti(OR)$_3$]MgBr**	13	84	3

2. Reaction optimization studies

2.1 Table S3. Reaction optimization for oxidative cross-coupling.[a]



entry	[cat]/ligand[b]	titanate	[O]	Time (h)	Yield (%)[c]
1	$PdCl_2$/dppp	$ClTi(OiPr)_3$	O_2	24	–
2	$NiCl_2$/dppp	$ClTi(OiPr)_3$	DCE	24	18
3	$FeCl_3$/PBu_3	$ClTi(OiPr)_3$	DCE	6	47
4	$FeCl_3$/PCy_3	$ClTi(OiPr)_3$	DCE	6	40
5	$FeCl_3$/dppp	$ClTi(OiPr)_3$	DCE	6	51
6	$FeCl_3$/dmadpp	$ClTi(OiPr)_3$	DCE	10	42
7	$FeCl_3$/NHC ligand	$ClTi(OiPr)_3$	DCE	10	52
8	$FeCl_3$/2,2'-biPy	$ClTi(OiPr)_3$	DCE	12	45
9	$FeCl_3$/tmeda	$ClTi(OiPr)_3$	DCE	8	68
10	$FeCl_3$/tmeda	$ClTi(OEt)_3$	DCE	8	64
11	$FeCl_3$/tmeda	tmpc	DCE	10	64
12	$FeCl_3$/tmeda	tbepc	DCE	10	74
13	$Fe(acac)_3$/tmeda	tbepc	DCE	18	68
14	$FeCl_3$/tmeda[d]	tbepc	DCE	10	78
15	$FeCl_3$/tmeda[d]	tbepc	Dry air[e]	24	66
16	$FeCl_3$/tmeda[d]	tbepc	O_2[e]	12	79
17	$FeCl_3$/tmeda[d,f]	tbepc	O_2[e]	12	76
18	$FeCl_3$/tmeda[d,g]	tbepc	O_2[e]	6	64



[a]The reaction was carried out on a 1 mmol scale at 0 °C. [b]Unless indicated otherwise, the catalyst metals were charged in 10 mol % with 20 mol % (monodentate), 10 mol % (bidentate) ligand or 30 mol % TMEDA.. [c]Isolated yield. [d]8 mol% $FeCl_3$ / 20 mol% TMEDA. [e]1 atm. [f]Using THF/NMP (10:1) as a solvent. [f] the reaction was carried at room temperature.

2.2 Discussion

As seen in Table S3, the Pd or Ni-catalyzed reactions gave rather low or no yields of cross-coupling products (entries 1 and 2), indicating a significant synergetic effect between iron and titanium. While the simple phosphine ligands (PBu_3, PCy_3); bidentate phosphine ligand (dppp); N-containing phosphine ligand (dmadpp), NHC ligand and 2,2'-bipy can all improve cross-coupling, $FeCl_3$/TMEDA proved to be the most effective catalyst system, which promotes the oxidative cross-coupling reactions with yields up to 68% (entries 3–9). Also, we examined the influence of different titanates (entries 9–12). The cross-coupling occurred in a highly selective way (78% yield) by using easy preparation and handling of solid tbepc (entry 12). $Fe(acac)_3$ could also promote the cross coupling almost equally well, yet with prolonged reaction time (entry 13). Lowering the loading of the catalyst to 8 mol% $FeCl_3$/20 mol% TMEDA did not affect the yield (entry 14). Bearing in mind that atmospheric oxygen or oxygen is indeed the greenest candidate oxidant, we tried to use atmospheric oxygen or oxygen as an oxidant in this reaction (entries 15 and 16). It was observed that while dry air could give an acceptable yield (66%) with a prolonged reaction time, the reaction using oxygen could proceed as well as those using DCE. We also explored the influence of solvent and temperature. The results showed that using THF/NMP instead of THF as a solvent did not improve the yield (entry 17). Rising the reaction temperature shortened the reaction time, yet the yield of cross-coupling product was reduced (entry 18).

3. General experimental details

All NMR spectra were collected using 400 MHz (100 MHz for ^{13}C spectroscopy) and all spectra recorded with tetramethylsilane as an internal standard unless otherwise noted. ESI mass spectra were recorded on TRACE MS spectrometer. High resolution mass spectra (HRMS) were obtained with a Bruker microTOF (ESI). Infrared data were acquired using an AVATAR 360 FT-IR spectrophotometer. Elemental analysis was carried out with an Elementear Vario instrument. Melting points were recorded on a TECH X-4 microscopic instrument and uncorrected.

4. General procedure for the additions of the mixed diaryl titanates to PhCHO

4.1 General remarks for the preparation of aryl Grignard reagents

All reagents and solvents used for aryl magnesium reagents and reactions were freshly dehydrated before use. The corresponding glassware was oven dried (120 ^oC) and cooled under a stream of argon gas.

Aryl Grignard reagents such as phenyl magnesium or 4-methoxyphenyl magnesium were prepared

according to standard procedure. Functionalized aryl Grignard reagents such as 2-cyanophenyl magnesium chloride or 4-(ethoxycarbonyl)phenyl magnesium chloride were prepared via iodine - magnesium exchange using *i*-PrMgCl·LiCl according to Knochel's method.[1] All the Grignard reagents were titrated before use.[2]

4.2 Typical procedure for General procedure for the additions of the mixed diaryl titanate (3ac) to PhCHO.

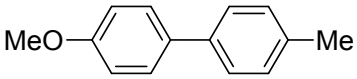
Under Ar atmosphere, a solution of 4-$MeOC_6H_4MgBr$ (2.5 mmol, 1.0 M in THF) was added dropwise to a solution of **tbepc** (615 mg, 2.5 mmol) in 10 mL THF at 0 °C and stirred for 2h at that temperature. To this mixture was added dropwise 4-(ethoxycarbonyl)phenyl magnesium chloride (2.5 mmol, 1.0 M in THF). The resulting mixture stirred at 0 °C for 0.5–1h. PhCHO (2.5 mmol, 265 mg) was added into the mixture at 0 °C and reacted at this temperature for 6 h (monitored by TLC). The reaction was quenched with saturated aqueous NH_4Cl and extacted with ethyl acetate. The organic layer was dried over Na_2SO_4 and concentrated to yield the crude compound, which was purified by column chromatography to yield the desired product **7a** (315 mg, yield 58%) and **8c** (237 mg, 37%).

5. Typical procedure for iron-catalyzed oxidative couplings of the mixed diaryl titanate (Table 1, entry 9)

Under Ar atmosphere, a solution of PhMgBr (2.5 mmol, 1.0 M in THF) was added dropwise to a solution of **tbepc** (615 mg, 2.5 mmol) in 10 mL THF at 0 °C and stirred for 2 h at that temperature. To this mixture was added dropwise 2-cyanophenyl magnesium chloride (2.5 mmol, 1.0 M in THF). The resulting mixture stirred at 0 °C for 0.5–1h. The solution of $FeCl_3$ (32.5 mg, 0.2 mmol), TMEDA (58 mg, 0.5 mmol) in THF (5 ml) was added in at one portion. The Ar atmosphere was changed into O_2 atmosphere (applied by an oxygen bag). The thus-obtained mixture was stirred at 0 °C until the completion of the reaction (monitored by TLC) (Note). The reaction was quenched with saturated aqueous Na_2CO_3 and diluted with CH_2Cl_2. After being filtered, the mixture was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and concentrated to yield the crude compound, which was purified by column chromatography to yield the desired product **5lm** (350 mg, 78% yield).

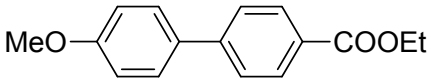
Note: The reactions of Aryl Grignard reagents bearing amide groups (Table 1, entries 10-13) were carried out at 10–15 °C.

6. Characterization data for products



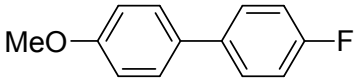
4-Methoxy-4'-methyl-1,1'-biphenyl(5ab)

The product was purified by column chromatography on silica gel with hexane to obtain a whitish solid (391 mg, 79% yield), m.p. = 180.3–181.5 °C （lit. 181–182 °C[3]). IR (cm^{-1}, KBr): 3030, 2965, 1608, 1300, 1270, 1214, 1180, 1011; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.52–7.44 (m, 4H), 7.25–7.21 (m, 2H), 6.97–6.94 (m, 2H), 3.84 (s, 3H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 158.9, 138.0, 133.8, 129.4, 128.0, 127.7, 126.6, 114.2, 55.4, 21.1.



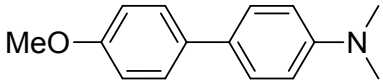
Ethyl 4'-methoxy-[1,1'-biphenyl]-4-carboxylate(5ac) [4]

The product was purified by column chromatography on silica gel with hexane to obtain a whitish solid (473 mg, 74% yield), m.p. = 103.6–104.4 °C. （lit. 105 °C）. IR (cm^{-1}, KBr): 2952, 1718, 1602, 1291, 1110, 770; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.11 (d, *J* = 6.6 Hz, 2H), 7.64 (d, *J* = 6.6 Hz, 2H), 7.60 (d, *J* = 6.9 Hz, 2H), 7.02 (d, *J* = 6.9 Hz, 2H), 4.42 (q, *J* = 5.7 Hz, 2H), 3.89 (s, 3H), 1.44 (t, *J* = 5.7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm)166.6, 159.8, 145.1, 132.5, 130.1, 128.6, 128.4, 126.4, 114.4, 60.9, 55.4, 14.4.



4-Fluoro-4'-methoxy-1,1'-biphenyl(5ad) [7]

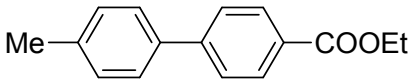
The product was purified by column chromatography on silica gel with hexane to obtain a whitish solid (404 mg, 80% yield), m.p. = 87.6–88.4 °C. （lit. 87.3–87.8 °C）. IR (cm^{-1}, KBr): 1607, 1488, 1251, 833, 760, 690; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.56-7.52 (m, 3H), 7.46 (d, *J* = 8.7 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 7.3 Hz, 1H), 6.97 (t, *J* = 8.8 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 163.3, 160.9, 159.2, 137.0, 132.8, 128.3, 128.0, 126.7, 126.6, 115.6, 115.4, 114.3, 55.3.



4'-Methoxy-N,N-dimethyl-[1,1'-biphenyl]-4-amine(5ag) [5]

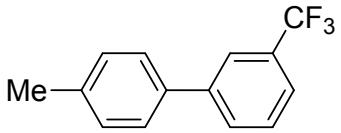
The product was purified by column chromatography on silica gel with hexane to obtain a whitish

solid (448 mg, 79% yield), m.p. = 155.6–157.4 °C. （lit. 156–157 °C）. IR （cm^{-1}, KBr): 2897, 1612, 1507, 1248, 1177, 1040, 810; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.46 (t, *J* = 9.6 Hz, 4H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 3.83 (s, 3H), 2.97 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 158.3, 149.6, 134.0, 129.3, 127.4, 127.3, 114.2, 113.1, 55.4, 40.7.



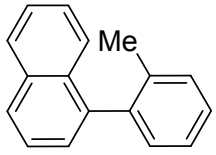
Ethyl 4'-methyl-[1,1'-biphenyl]-4-carboxylate(5bc) [6]

The product was purified by column chromatography on silica gel with hexane to obtain a whitish solid (463 mg, 77% yield), m.p. = 74.3–75.4 °C. （lit. 76–77 °C）. IR （cm^{-1}, KBr): 2879, 1705, 1604, 1273, 1111, 770; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.09 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 4.40 (q, *J* = 7.2 Hz, 2H), 2.40 (s, 3H), 1.42 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm)166.6, 145.5, 138.1, 137.2, 130.1, 129.7, 129.0, 127.1, 126.8, 60.9, 21.2, 14.4.



4'-Methyl-3-(trifluoromethyl)-1,1'-biphenyl(5bf) [3]

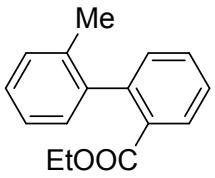
The product was purified by column chromatography on silica gel with hexane to obtain a colorless oil (496 mg, 84% yield). IR (cm^{-1}, KBr): 2955, 1610, 1335, 1126, 798; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.82 (s, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.59–7.48(m, 4H), 7.27 (d, *J* = 7.9 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 141.9, 138.0, 131.3, 131.0, 130.2, 129.7, 129.2, 127.0, 124.7 (d), 124.0(d), 123.7(q), 21.1..



1-(O-tolyl)naphthalene(5hi) [7]

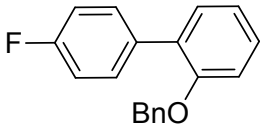
The product was purified by column chromatography on silica gel with hexane to obtain a whitish solid (392 mg, 72% yield), m.p. = 63.6–64.4 °C. （lit. 65–66°C [8]）. IR （cm^{-1}, KBr): 3049, 1590, 1504, 1485, 1392, 1122; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.97–7.91 (m, 2H), 7.60–7.52 (m,

3H), 7.43–7.41 (m, 6H), 2.09 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm)140.3, 139.8, 136.9, 133.6, 132.1, 130.4, 129.9, 128.3, 127.6, 127.5, 126.7, 126.2, 126.0, 125.8, 125.6, 125.4, 20.1.



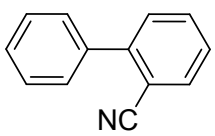
Ethyl 2'-methyl-[1,1'-biphenyl]-2-carboxylate(5ij) [9]

The product was purified by column chromatography on silica gel with hexane to obtain a colorless oil (456 mg, 76% yield). IR (cm^{-1}, KBr): 3018, 2926, 1722, 1603, 1458, 1379, 1047; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.70 (d, *J* = 7.9 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.20-7.17 (m, 5H), 6.73 (d, *J* = 7.2 Hz, 1H), 3.80 (q, *J* = 7.2 Hz, 2H), 2.38 (s, 3H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 167.6, 141.6, 141.2, 135.8, 131.8, 131.3, 131.2, 129.2, 129.0, 127.7, 126.6, 126.5, 124.7, 62.1, 19.9, 14.2.



2-(Benzyloxy)-4'-fluoro-1,1'-biphenyl(5dk)

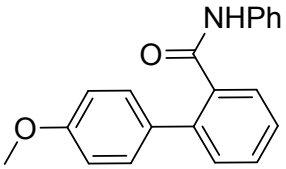
The product was purified by column chromatography on silica gel with EtOAc/petroleum ether (1:20) to obtain a whitish solid (465 mg, 67% yield), m.p. = 145.4–147.0°C. IR (cm^{-1}, KBr): 3044, 1604, 1587, 1450, 1276, 1110; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.55–7.51 (m, 2H), 7.34–7.26 (m, 7H), 7.10–7.01 (m, 4H), 5.07 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 163.0, 161.1, 155.5, 137.1, 134.4 (d, 134.46, 134.44), 131.2 (d, 131.27, 131.21), 130.9, 130.4, 128.7, 128.5, 127.7, 126.9, 121.4, 114.9, 114.7, 113.4, 70.5. Anal. Calcd for $C_{19}H_{15}FO$: C, 81.99; H, 5.43; Found: C, 81.69; H, 5.14. MS (ESI): $[M+H]^+$ (m/z 279).



[1,1'-Biphenyl]-2-carbonitrile(5lm) [10]

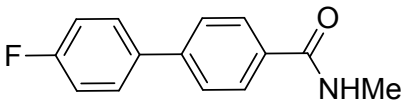
The product was purified by column chromatography on silica gel with hexane to obtain a colorless oil (350 mg, 78% yield). IR (cm^{-1}, KBr): 3046, 2225, 1599, 1480, 760; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.79 (d, *J* = 6.2 Hz, 1H), 7.67 (td, *J* = 6.2 Hz, 0.8 Hz, 1H), 7.60 (d, *J* = 5.8 Hz,

2H), 7.56–7.51 (m, 3H), 7.50–7.47 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 145.5, 138.2, 133.8, 132.9, 130.1, 128.79, 128.77, 127.6, 127.2, 118.8, 111.3.



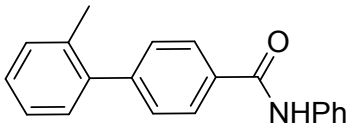
4'-Methoxy-N-phenyl-[1,1'-biphenyl]-2-carboxamide(5an) [11]

The product was purified by column chromatography on silica gel with EtOAc/petroleum ether (1:5) to obtain a whitish solid (598 mg, 79% yield), m.p. = 144.2–144.8 °C.（lit. 143–144°C）. IR (cm^{-1}, KBr): 3439, 3242, 1655, 1601, 1536, 1244, 757; ^{1}H NMR (CD_3SOCD_3, 400 MHz) δ (ppm) 10.26 (s, 1H), 7.59 (t, *J* = 6.1 Hz, 4H), 7.49 (t, *J* = 5.6 Hz, 2H), 7.43 (d, *J* = 7.0 Hz, 2H), 7.32 (t, *J* = 6.3 Hz, 2H), 7.09 (t, *J* = 5.9 Hz, 1H), 6.98 (d, *J* = 7.0 Hz, 2H), 3.78 (s, 3H); ^{13}C NMR (CD_3SOCD_3, 100 MHz) δ (ppm) 173.2, 163.9, 144.4, 144.0, 142.2, 137.5, 135.1, 134.9, 134.7, 133.8, 133.0, 131.9, 128.7, 124.9, 119.0, 60.3.



4'-Fluoro-N-methyl-[1,1'-biphenyl]-4-carboxamide(5de)

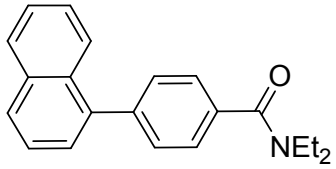
The product was purified by column chromatography on silica gel with EtOAc/petroleum ether (1:5) to obtain a whitish solid (480 mg, 84% yield), m.p. = 188.2–189.6 °C. IR (cm^{-1}, KBr): 3295, 1633, 1552, 1495, 1231, 831; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.85 (d, *J* = 6.4 Hz, 2H), 7.62–7.57 (m, 4H), 7.16 (t, *J* = 6.8 Hz, 2H), 6.27 (br s, 1H), 3.06 (d, *J* = 2.7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 167.8, 164.1, 161.6, 143.2, 136.2 (d, 136.19, 136.16), 133.3, 128.8 (d, 128.9, 128.8), 127.4–127.1 (d, 127.4, 127.1), 116.0–115.7 (d, 116.0, 115.7), 26.9. Anal. Calcd for $C_{14}H_{12}FNO$: C, 73.35; H, 5.28; N, 6.11; Found: C, 73.15; H, 5.44; N, 6.15. MS (ESI): $[M+H]^+$ (m/z 230).



2'-Methyl-N-phenyl-[1,1'-biphenyl]-4-carboxamide (5io)

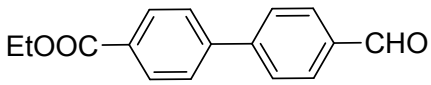
The product was purified by column chromatography on silica gel with EtOAc/petroleum ether (1:5) to obtain a whitish solid (545 mg, 76% yield), m.p. = 189.8–190.6 °C. IR (cm^{-1}, KBr): 3352,

3035, 2939, 1654, 1572, 1390, 1265, 812; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.93 (d, *J* = 7.9 Hz, 2H), 7.87 (br s, 1H), 7.67 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.30–7.22 (m, 4H), 7.17 (t, *J* = 7.5 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 165.6, 145.8, 140.7, 138.0, 135.2, 133.4, 130.5, 129.7, 129.6, 129.2, 127.9, 126.9, 126.0, 124.6, 120.2, 20.4. Anal. Calcd for $C_{20}H_{17}NO$: C, 83.59; H, 5.96; N, 4.87; Found: C, 83.45; H, 5.94; N, 5.03. MS (ESI): $[M+H]^+$ (m/z 288).



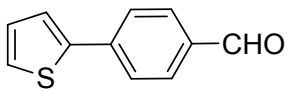
N,N-diethyl-4-(naphthalen-1-yl)benzamide (5hp)

The product was purified by column chromatography on silica gel with EtOAc/petroleum ether (1:5) to obtain a yellow solid (598 mg, 79% yield), m.p. = 92.4–94.2 °C. IR (cm^{-1}, KBr): 3057, 2972, 1634, 1427, 1286, 781; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.92–7.87 (m, 3H), 7.55–7.49 (m, 6H), 7.47–7.41 (m, 2H), 3.50 (b, 4H), 1.25 (b, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 171.2, 141.7, 139.5, 136.1, 133.8, 131.4, 130.1, 128.3, 128.0, 127.0, 126.4, 126.2, 125.9, 125.8, 125.4, 43.5, 39.4, 14.4, 13.1. Anal. Calcd for $C_{21}H_{21}NO$: C, 83.13; H, 6.98; N, 4.62; Found: C, 83.15; H, 6.54; N, 5.04. MS (ESI): $[M+H]^+$ (m/z 304).



Ethyl 4'-formyl-[1,1'-biphenyl]-4-carboxylate (5cq)

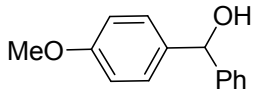
The product was purified by column chromatography on silica gel with hexane to obtain a whitish solid (457 mg, 72% yield), m.p. = 62.6–64.4 °C. IR (cm^{-1}, KBr): 2936, 1702, 1606, 1276, 1187, 1104, 771; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 10.11 (s, 1H), 8.14 (d, *J* = 8.4, 3H), 7.92–7.88 (m, 2H), 7.71–7.68 (m, 2H), 7.65 (t, *J* = 7.7 Hz, 1H), 4.42 (q, *J* = 7.2, 2H), 1.43 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 192.0, 166.3, 143.9, 141.1, 137.1, 133.1, 130.3, 129.7, 128.2, 127.1, 61.1, 14.4.



4-(Thiophen-2-yl)benzaldehyde(5rq) [12]

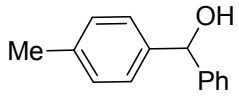
The product was purified by column chromatography on silica gel with hexane to obtain a whitish

solid (448 mg, 79% yield), m.p. = 69.1–69.4 °C.（lit. 69.0–69.5 °C）. IR (cm^{-1}, KBr): 3011, 1701, 1604, 1276, 792; ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 10.03 (s, 1H), 7.91 (d, *J* = 8.3, 2H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.49 (dd, *J* = 3.6 Hz, 0.9 Hz, 1 H), 7.43–7.42 (m, 1H), 7.16 (dd, *J* = 5.0 Hz, 3.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm) 191.5, 142.7, 140.1, 135.1, 130.5, 128.5, 127.0, 126.1, 125.1.



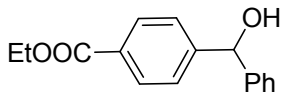
(4-Methoxyphenyl)(phenyl)methanol (7a) [13]

The product was purified by column chromatography on silica gel with EtOAc/petroleum ether (1:10) to obtain a whitish solid. m.p. = 93.5–94.5 °C （lit. 95 °C[14]). IR (cm^{-1}, KBr): 3556, 1606, 1461, 1180, 1028, 845; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.34–7.28 (m, 4H), 7.24 (d, *J* = 8.4 Hz, 3H), 6.83 (d, *J* = 8.8 Hz, 2H), 5.73 (s, 1H), 3.75 (s, 3H), 2.45 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 159.1, 144.1, 136.3, 128.4, 128.0, 127.3, 126.5, 113.9, 75.8, 55.3.



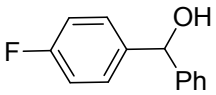
Phenyl(p-tolyl)methanol(8b) [15]

The product was purified by column chromatography on silica gel with EtOAc/petroleum ether (1:10) to obtain a whitish solid. m.p. = 53.5–54.5 °C （lit. 53.4–54.0 °C). IR (cm^{-1}, KBr): 3373, 1559, 1472, 1380, 1171, 1020, 856, 779; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.47 (d, *J* = 7.3 Hz, 1H), 7.29–7.26 (m, 4H), 7.24–7.15 (m, 3H), 7.10 (d, *J* = 7.2 Hz, 1H), 5.91 (s, 1H), 2.35 (br s, 1H), 2.20 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 138.2, 136.8, 130.7, 125.8, 123.8, 122.9, 122.8, 122.4, 121.6, 121.4, 68.6, 14.7.



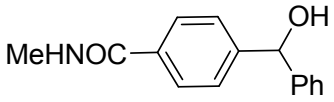
Ethyl 4-(hydroxy(phenyl)methyl)benzoate(8c)

The product was purified by column chromatography on silica gel with EtOAc/petroleum ether (1:10) to obtain a colorless oil. IR (cm^{-1}, KBr): 3475, 3010, 1715, 1640, 1253, 1180, 1080, 787, 694; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.98 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.35–7.26 (m, 5H), 5.85 (s, 1H), 4.34 (q, *J* = 7.2 Hz, 2H), 2.69 (br s, 1H), 1.37 (t, *J* = 7.2 Hz, 3H),; ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 166.6, 148.7, 143.2, 129.8, 129.5, 128.7, 127.9, 126.7, 126.3, 75.9, 61.0, 14.3.



(4-Fluorophenyl)(phenyl)methanol(7d)[13]

The product was purified by column chromatography on silica gel with EtOAc/petroleum ether (1:10) to obtain colorless oil. IR (cm^{-1}, KBr): 3330, 1601, 1487, 1173, 1100, 1012, 922, 823, 774; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.30–7.19 (m, 7H), 6.95 (t, *J* = 8.7 Hz, 2H), 5.71 (s, 1H), 2.49 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 158.4–156.5 (d), 138.9, 134.8 (d, 134.82, 134.80), 123.9, 123.5(d, 123.58, 123.51), 123.0, 121.8, 110.65–110.48(d), 70.9,



4-(Hydroxy(phenyl)methyl)-N-methylbenzamide(8e)

The product was purified by column chromatography on silica gel with EtOAc/petroleum ether (1:2) to obtain a whitish solid, m.p. = 107.1–108.5 °C. IR (cm^{-1}, KBr): 3450, 2956, 1641, 1552, 1400, 1325, 1296, 852 ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm)7.59 (d, *J* = 8.2 Hz, 2H), 7.34–7.23 (m, 7H), 6.59 (d, *J* = 4.6 Hz, 1H), 5.78 (s, 1H), 3.85 (br s, 1H), 2.88 (d, *J* = 4.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 168.3, 147.5, 143.6, 133.4, 128.5, 127.7, 127.0, 126.63, 126.56, 75.6, 26.8. Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.81; Found: C, 74.59; H, 6.34; N, 5.82. MS (ESI): $[M+H]^+$ (m/z 242).

7. Reference.

[1] A. Krasovskiy, P. Knochel, *Angew. Chem. Int. Ed.*, **2004**, *43*, 3333.

[2] A. Krasovskiy, P. Knochel, *Synthesis*, **2006**, *5*, 890.

[3] L. Ackermann. A. Althammer, *Org. Lett.*, **2006**, *8*(16), 3457.

[4] M. Amatore, C. Gosmini, *Angew. Chem. Int. Ed.* **2008**, *47*(11), 2089.

[5] S. E. Denmark, R. C. Smith, W. T. Chang, J. M. Muhuhi, *J. Am. Chem. Soc.*, **2009**, *131*(8), 3104.

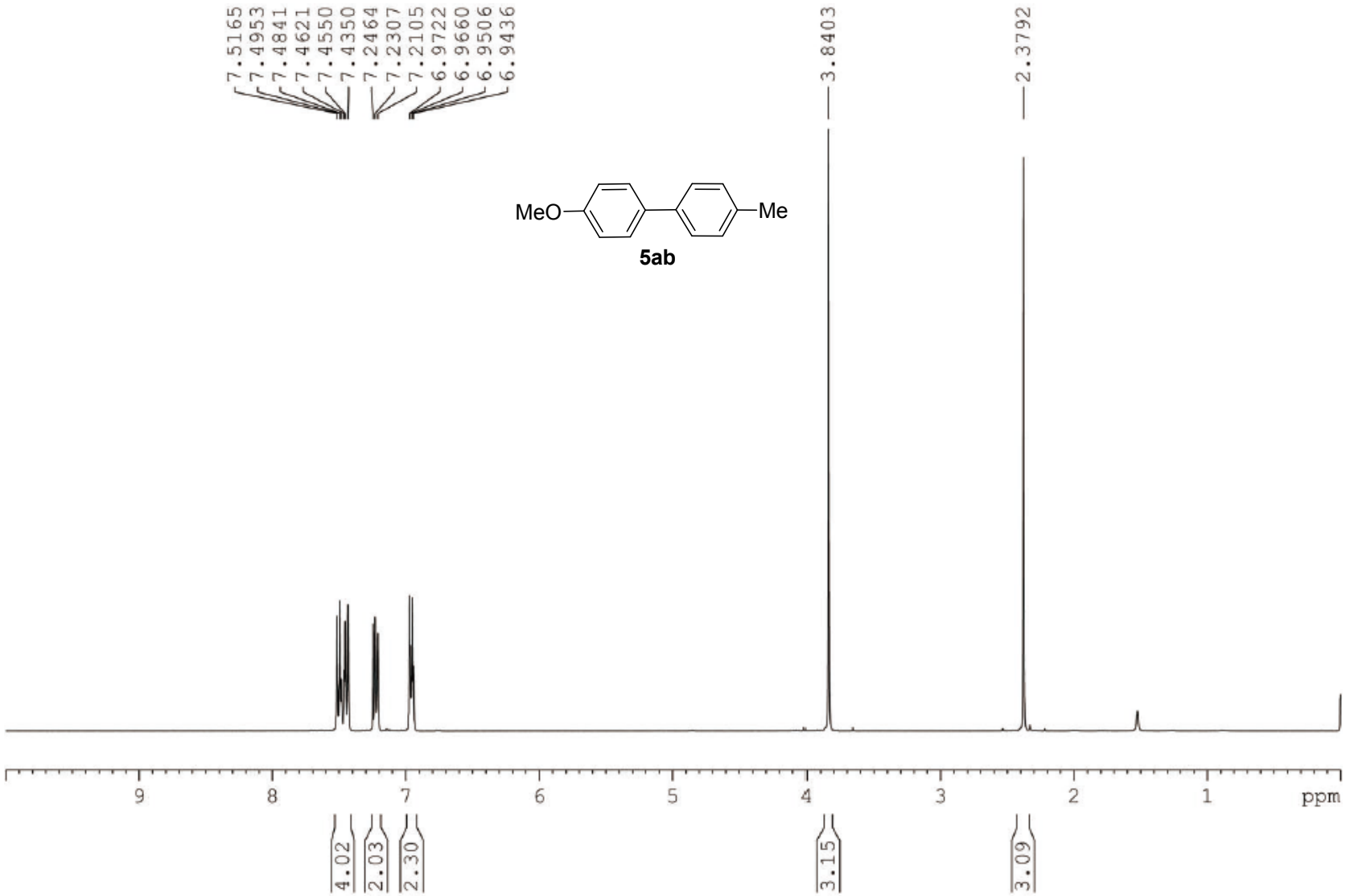
[6] L. G. Xie, Z. X. Wang, *Chem. Eur. J.*, **2010**, *16*(34), 10332.

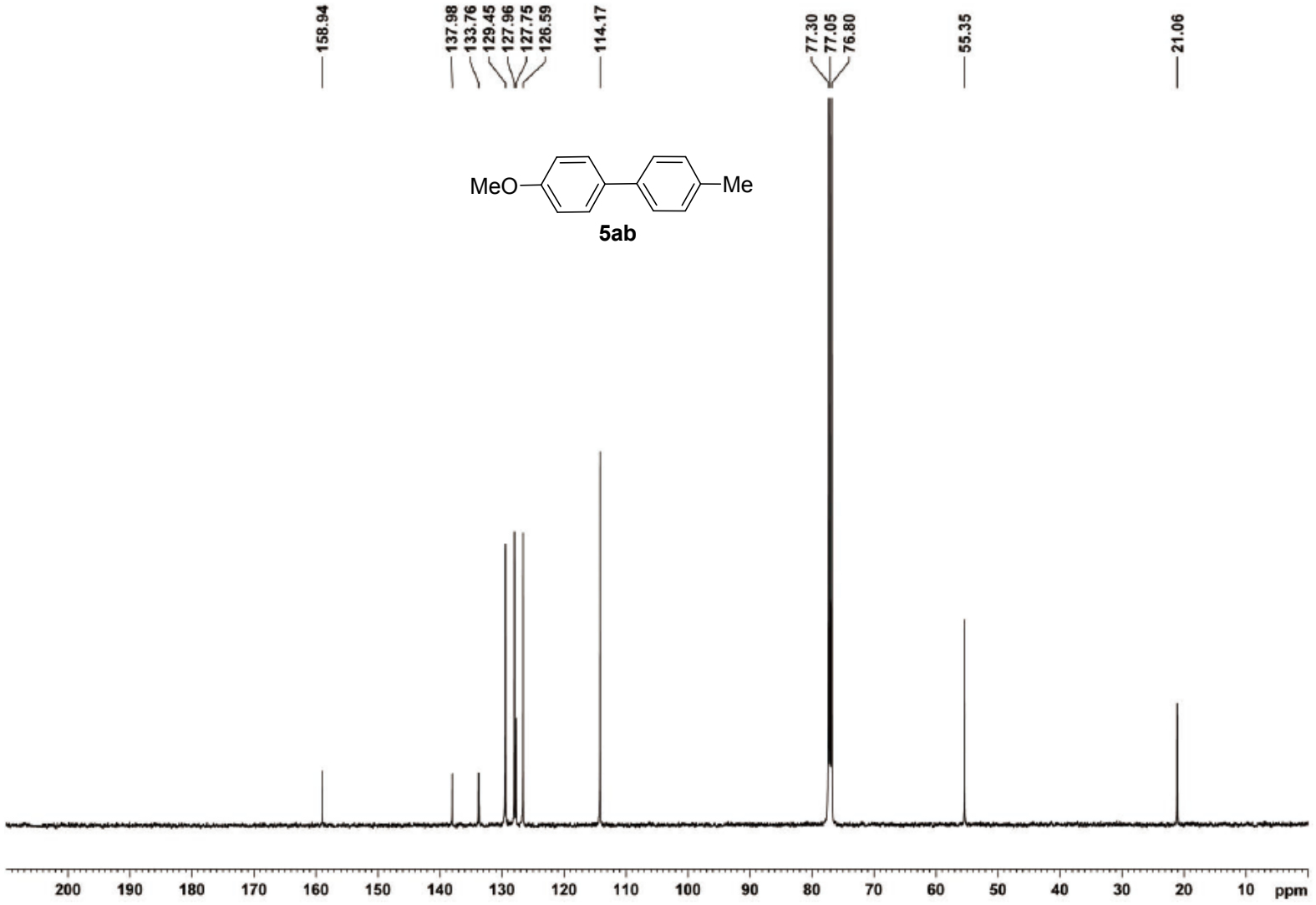
[7] R. J. Madhushaw, J. Reniguntala, C-Y. Lo, C-W Hwang, M-D. Su, H-C. Shen, S. Pal, I. R. Shaikh, R-S. Liu, *J. Am. Chem. Soc.*, **2004**, *126*(47), 15560.

[8] C. J. O'Brien, E. A. B. Kantchev, C. Valente, N. Hadei, C. Niloufar, G. A. Chass, A. Lough, A. C. Hopkinson, M. G. Organ, *Chem. Eur. J.*, **2006**, *12*(18), 4743.

[9] P. Maël, L. Stephane, D. Georges, P. Cyril, M, Francis, L. Vincent, *Tetrahedron. Lett*., **2005**, *46*, 8385.

8. ^{1}H and ^{13}C NMR spectra for products

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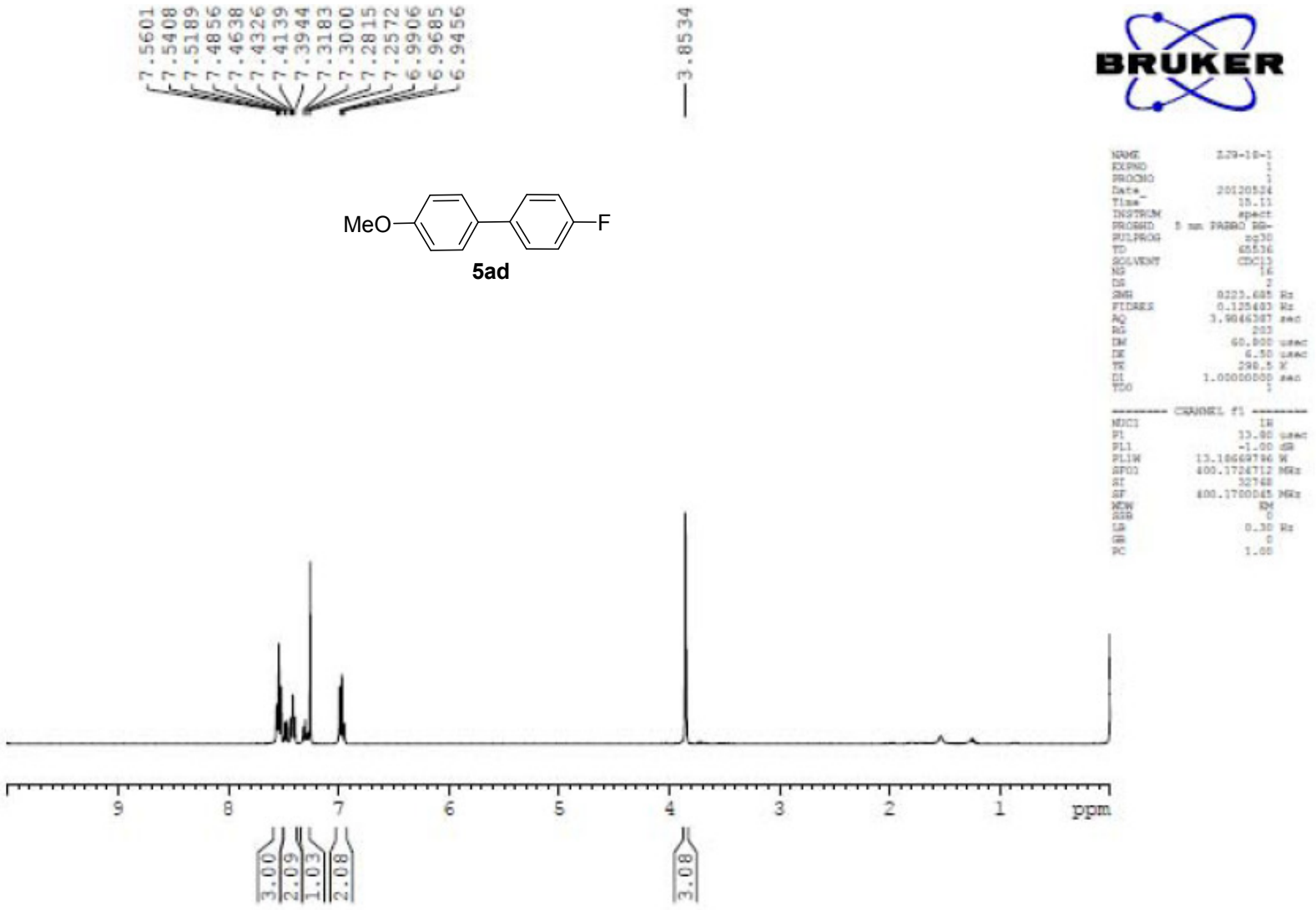
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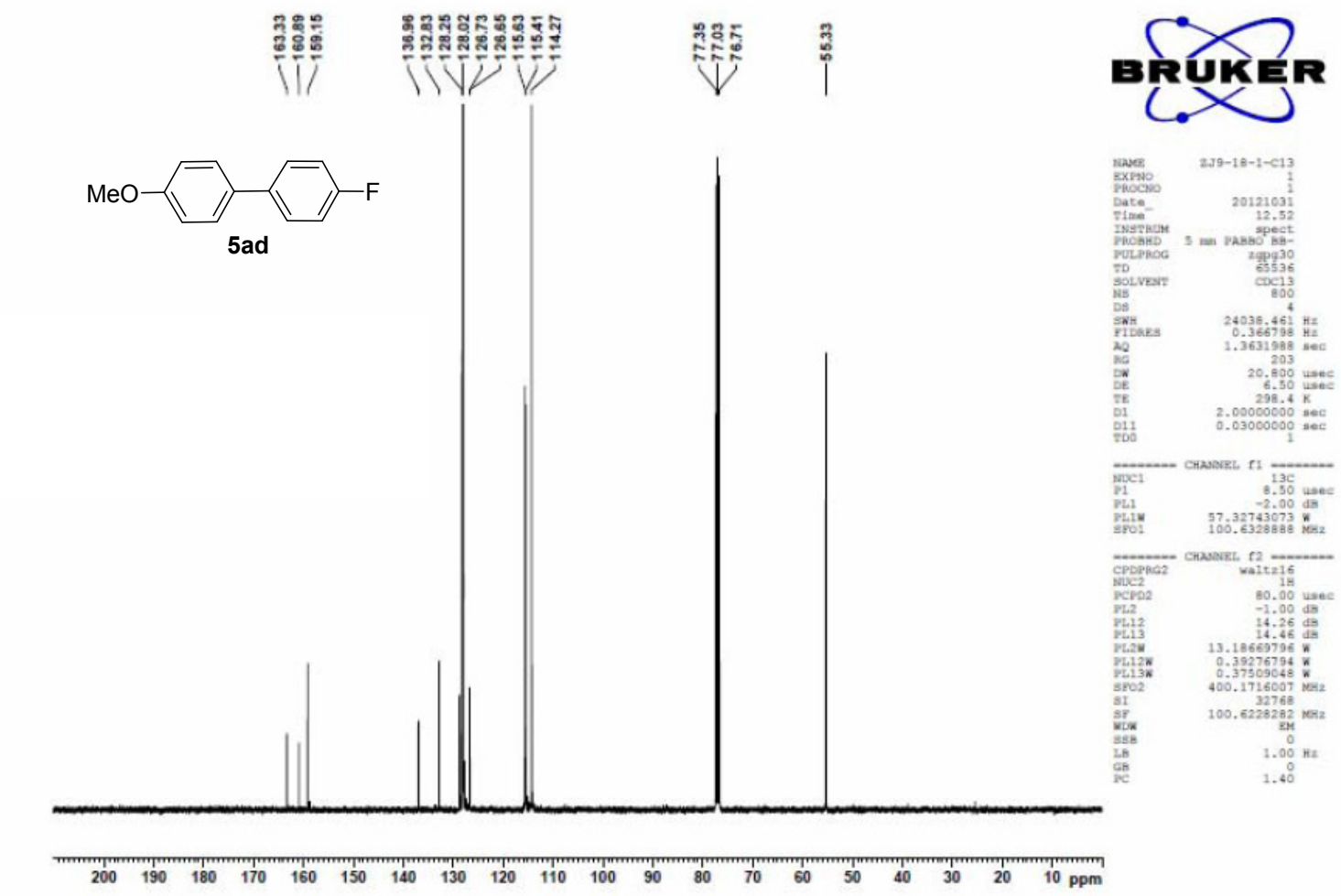
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F
5ad
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PL12 14.26 dB
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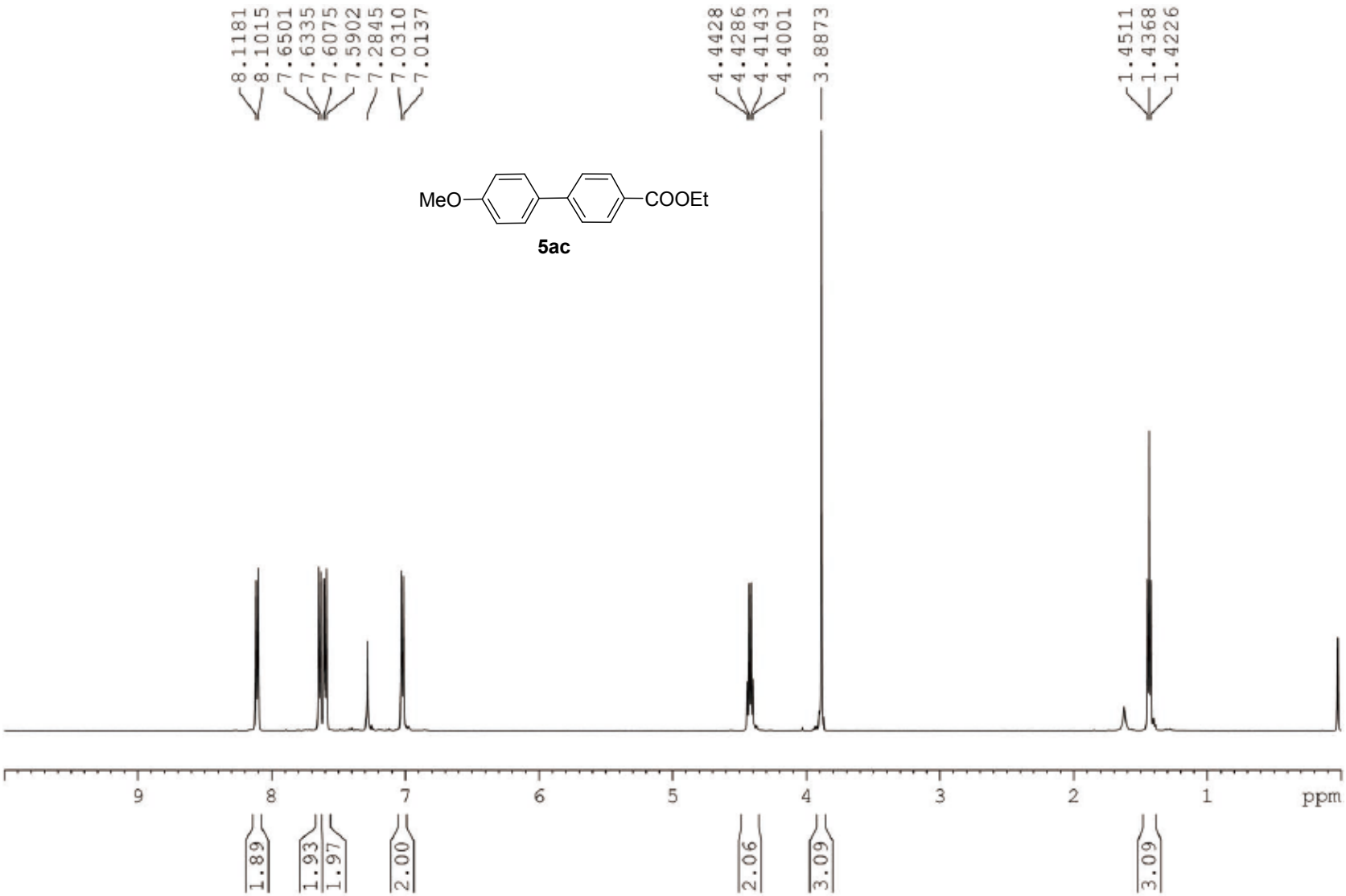
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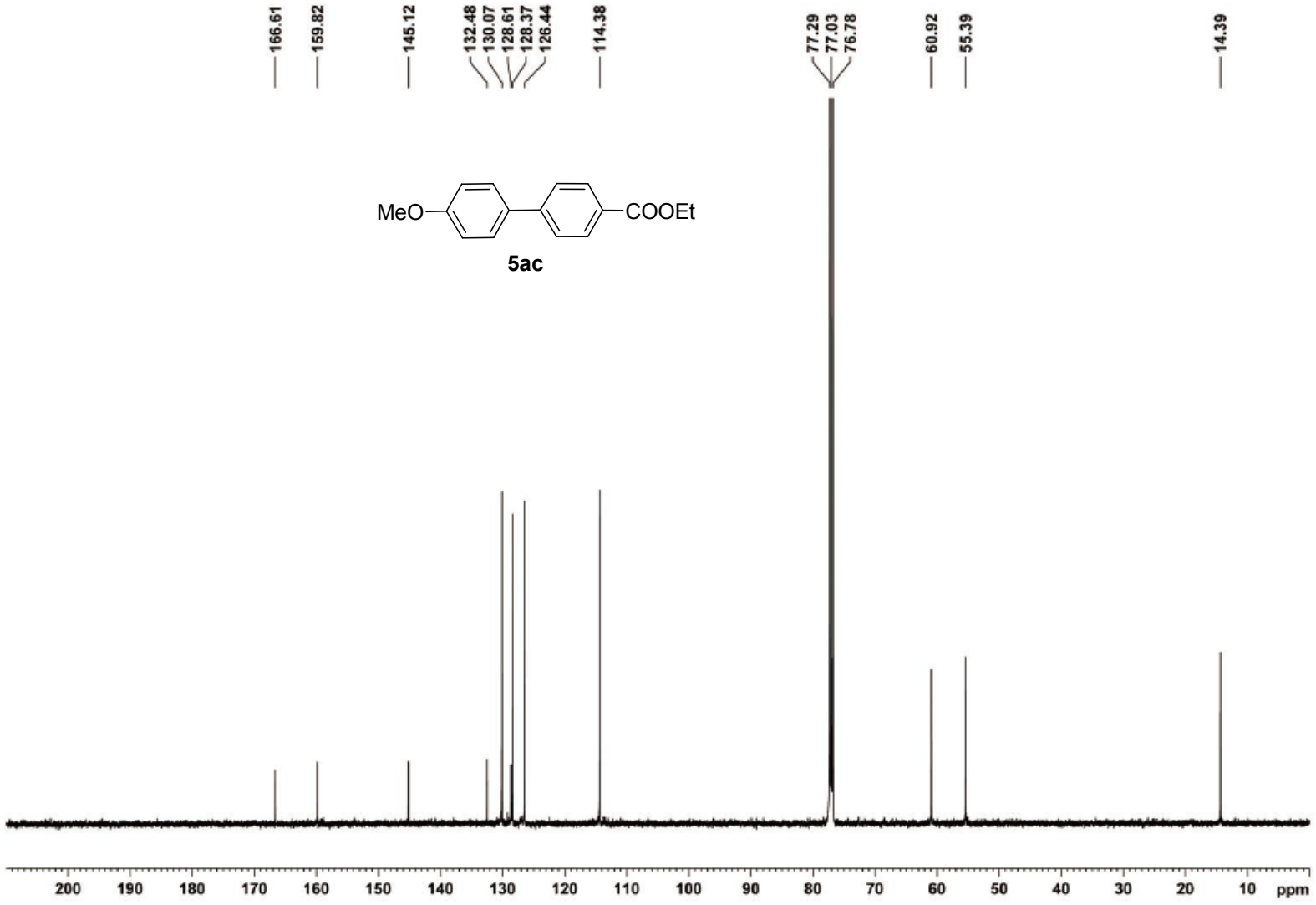
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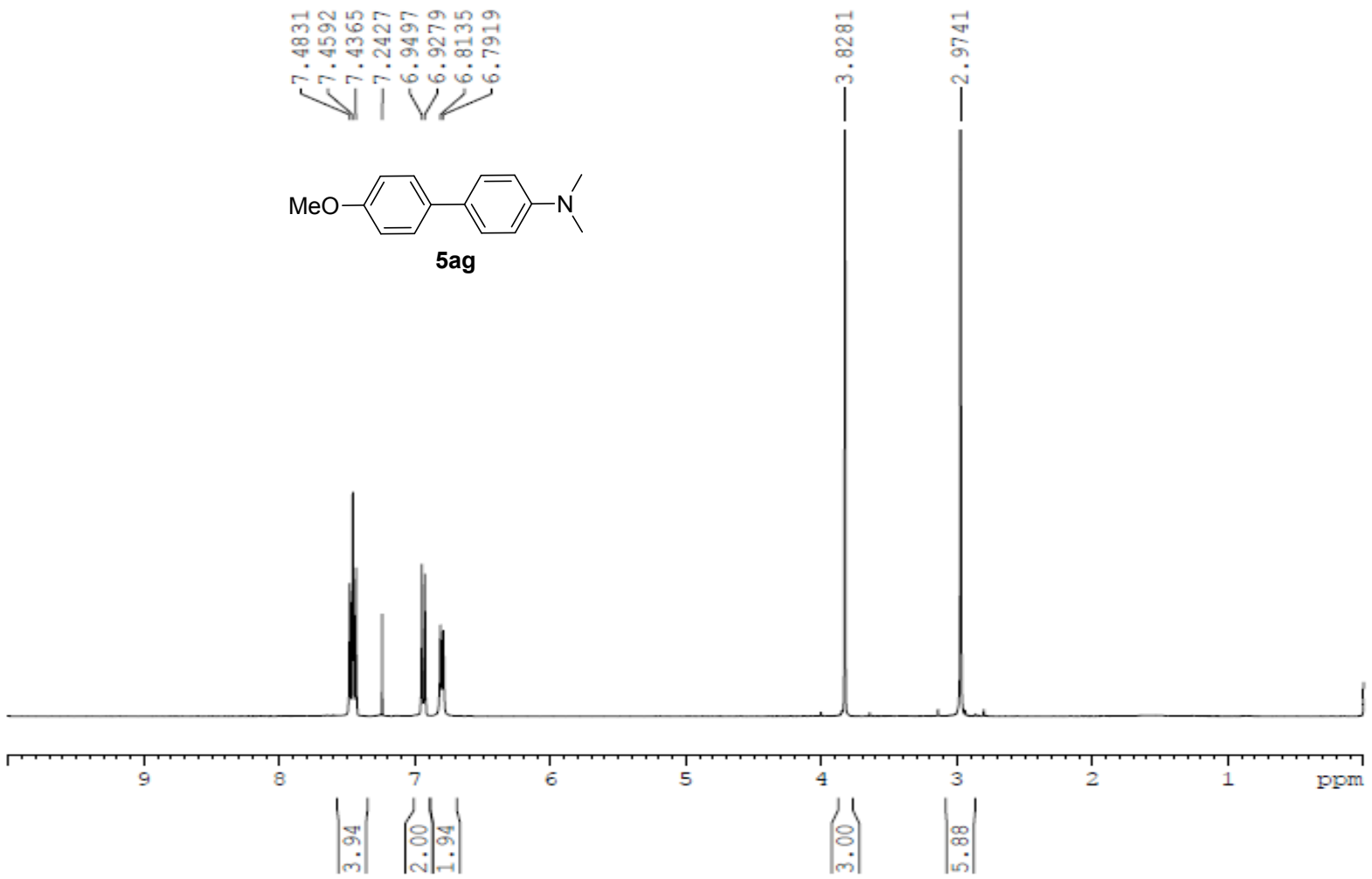
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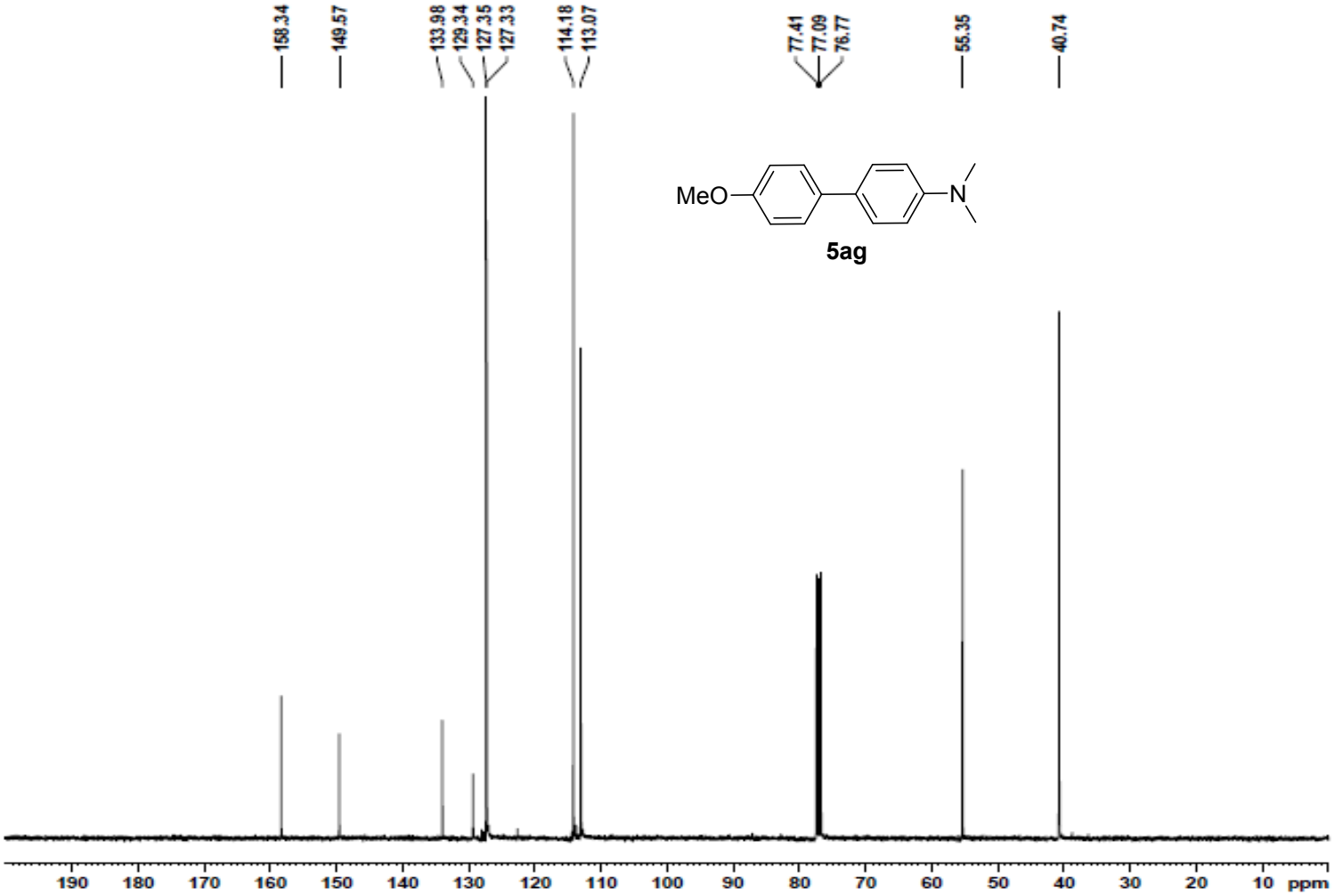
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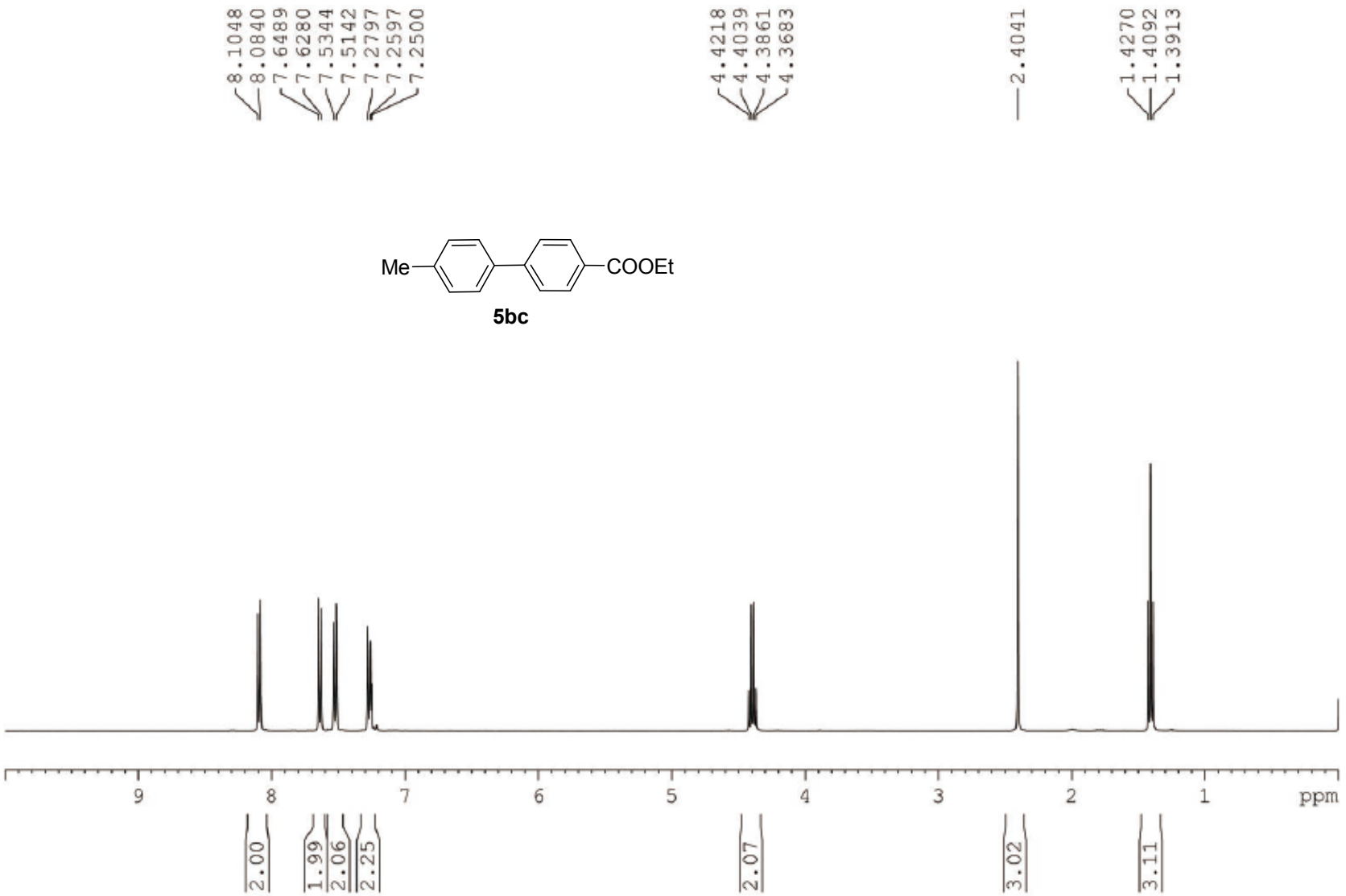
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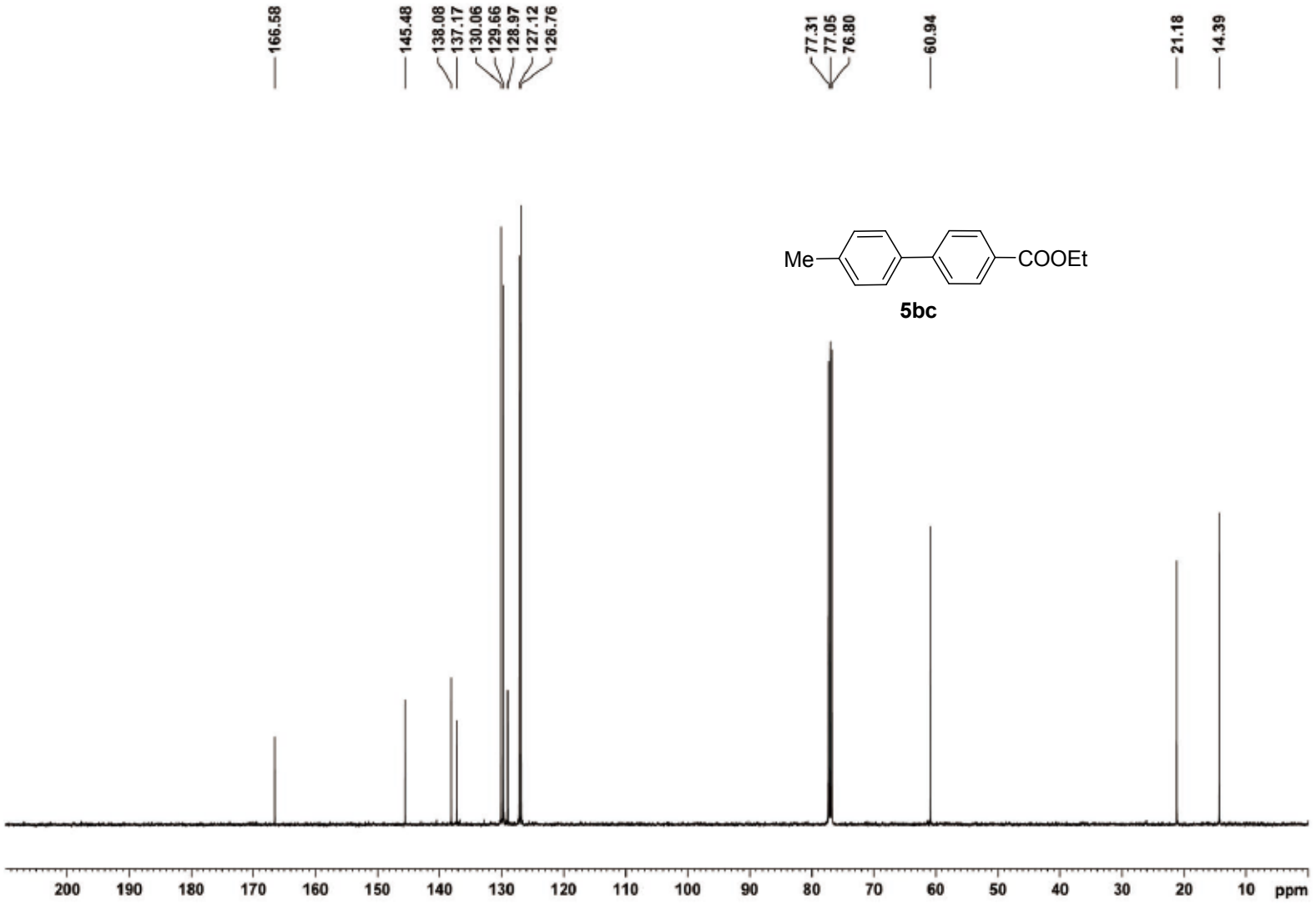
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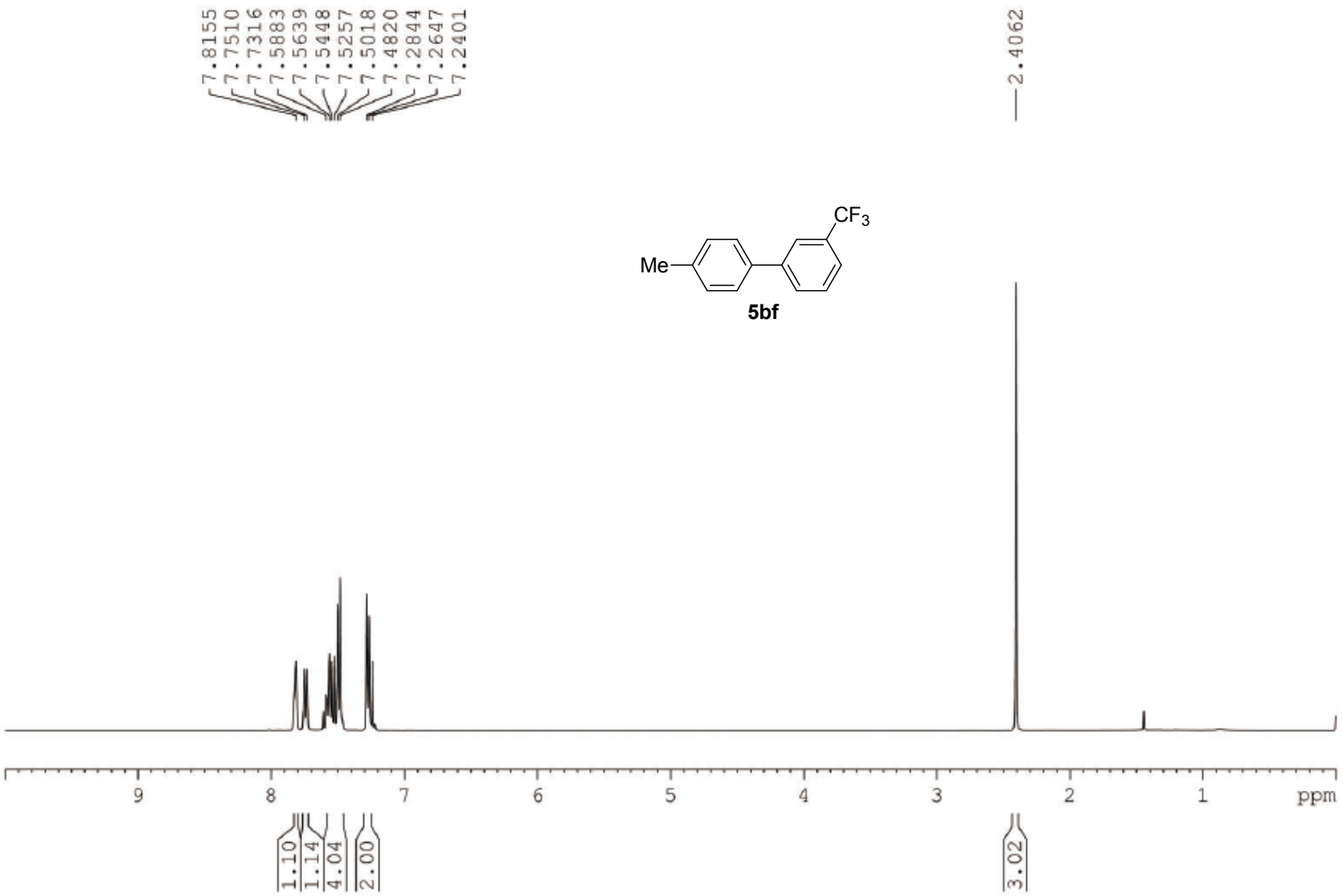
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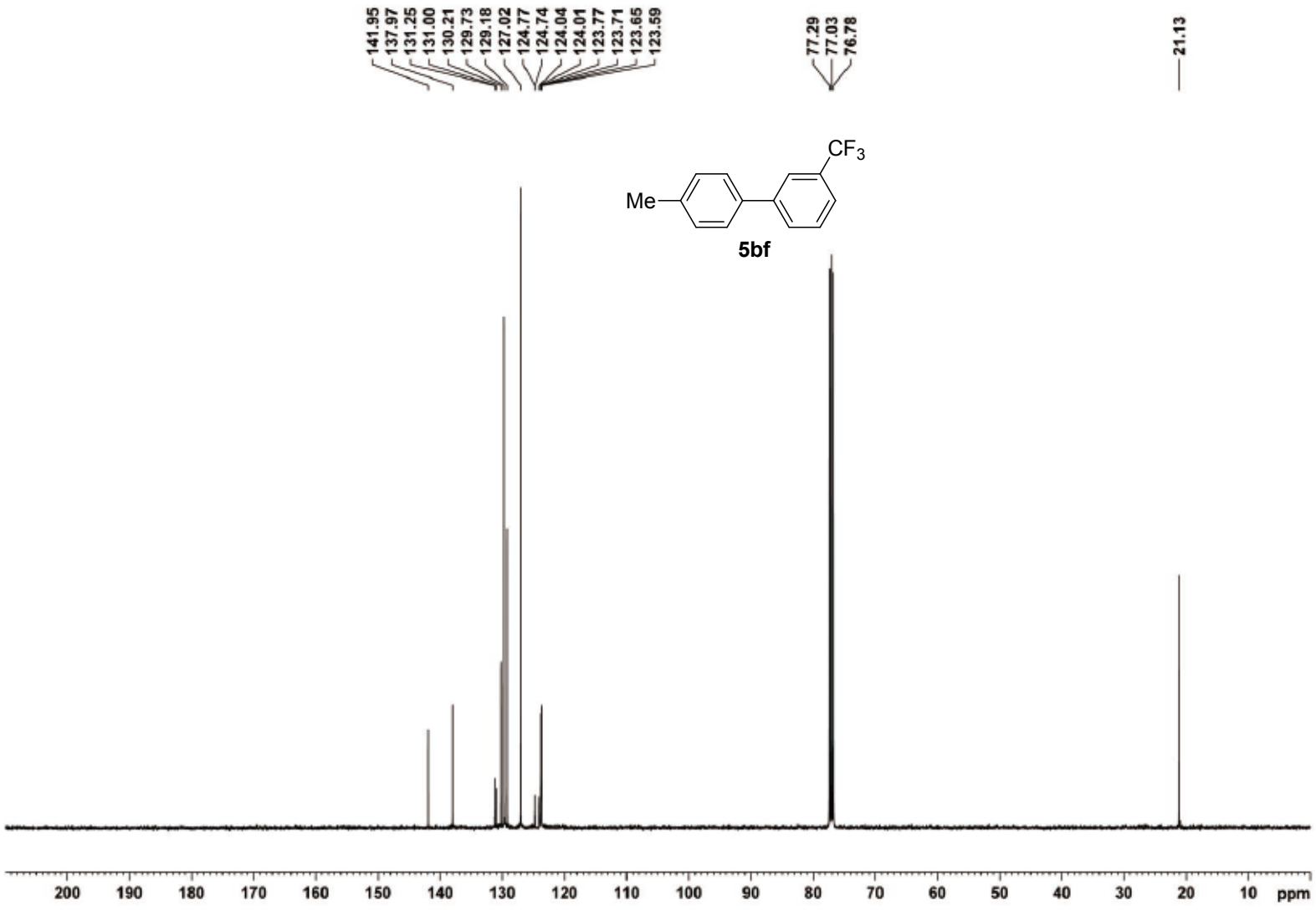
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129.73
129.18
127.02
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124.74
124.04
124.01
123.77
123.71
123.65
123.59
77.29
77.03
76.78
21.13
CF3
Me
5bf
200
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150
140
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110
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70
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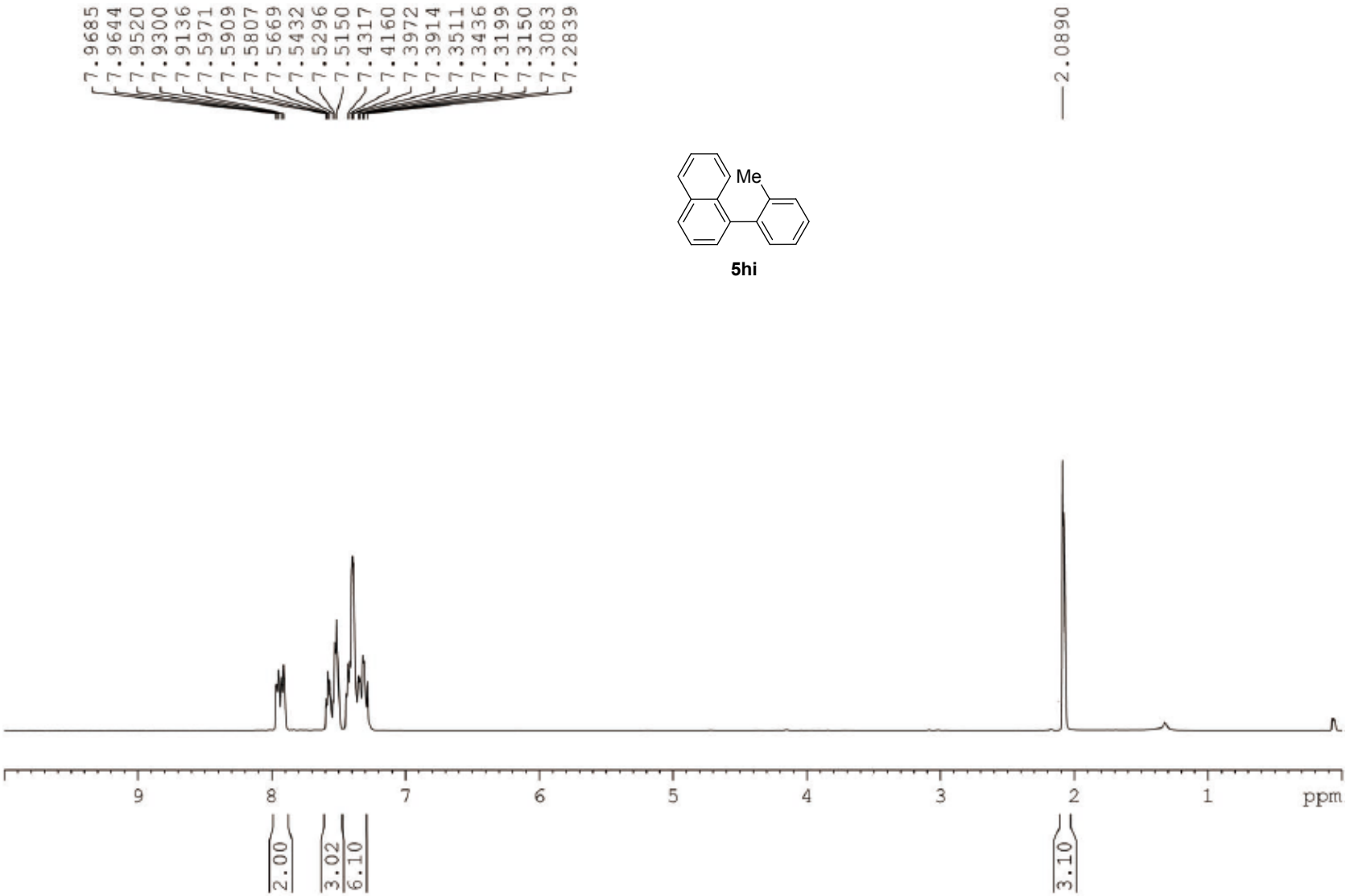
30
20
10
ppm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7.5432
7.5296
7.5150
7.4317
7.4160
7.3972
7.3914
7.3511
7.3436
7.3199
7.3150
7.3083
7.2839
2.0890
Me
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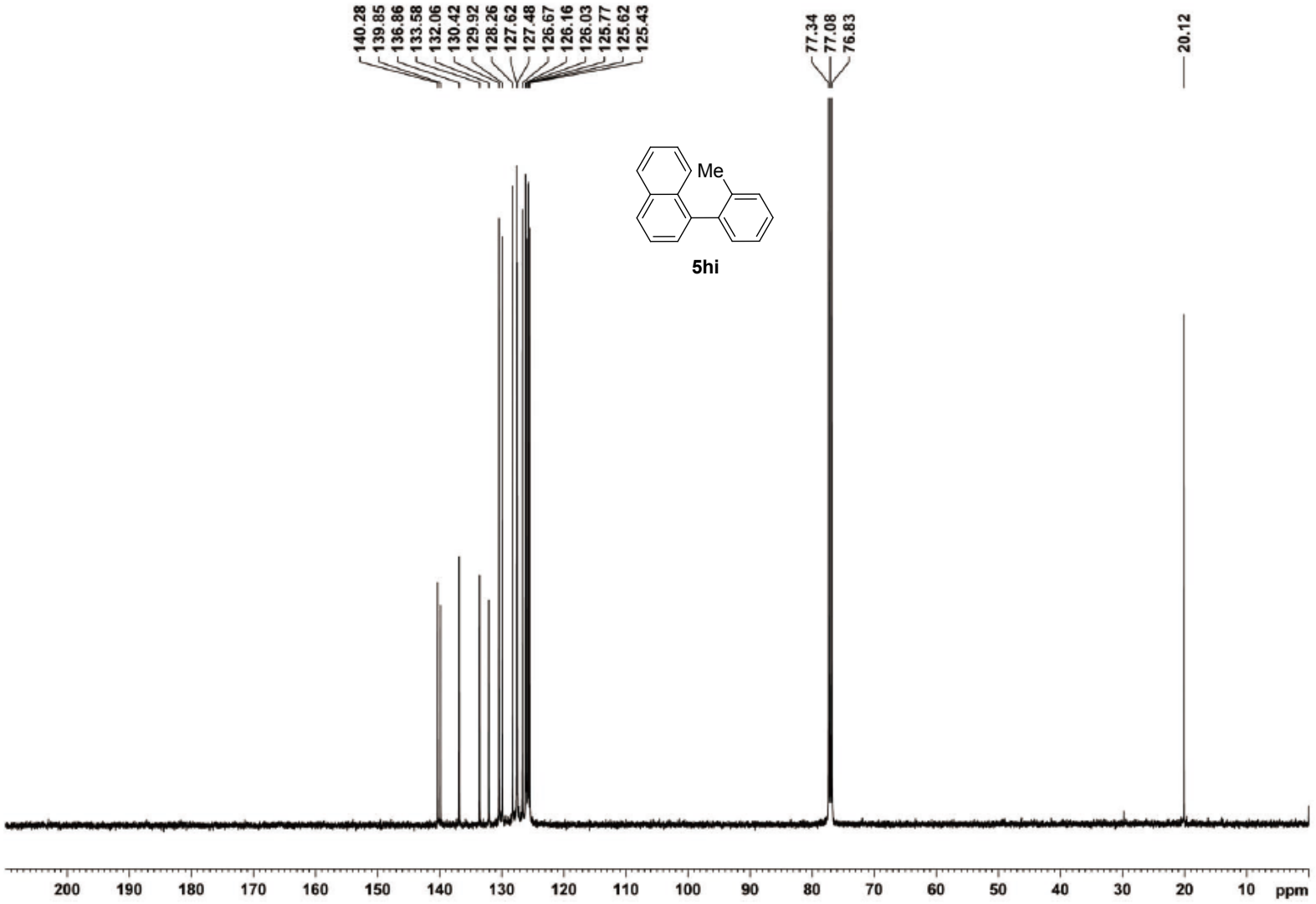
7
6
5
4
3
2
1
ppm
2.00
3.02
6.10
3.10

5hi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136.86
133.58
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130.42
129.92
128.26
127.62
127.48
126.67
126.16
126.03
125.77
125.62
125.43
77.34
77.08
76.83
20.12
Me
5hi
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190
180
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150
140
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110
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70
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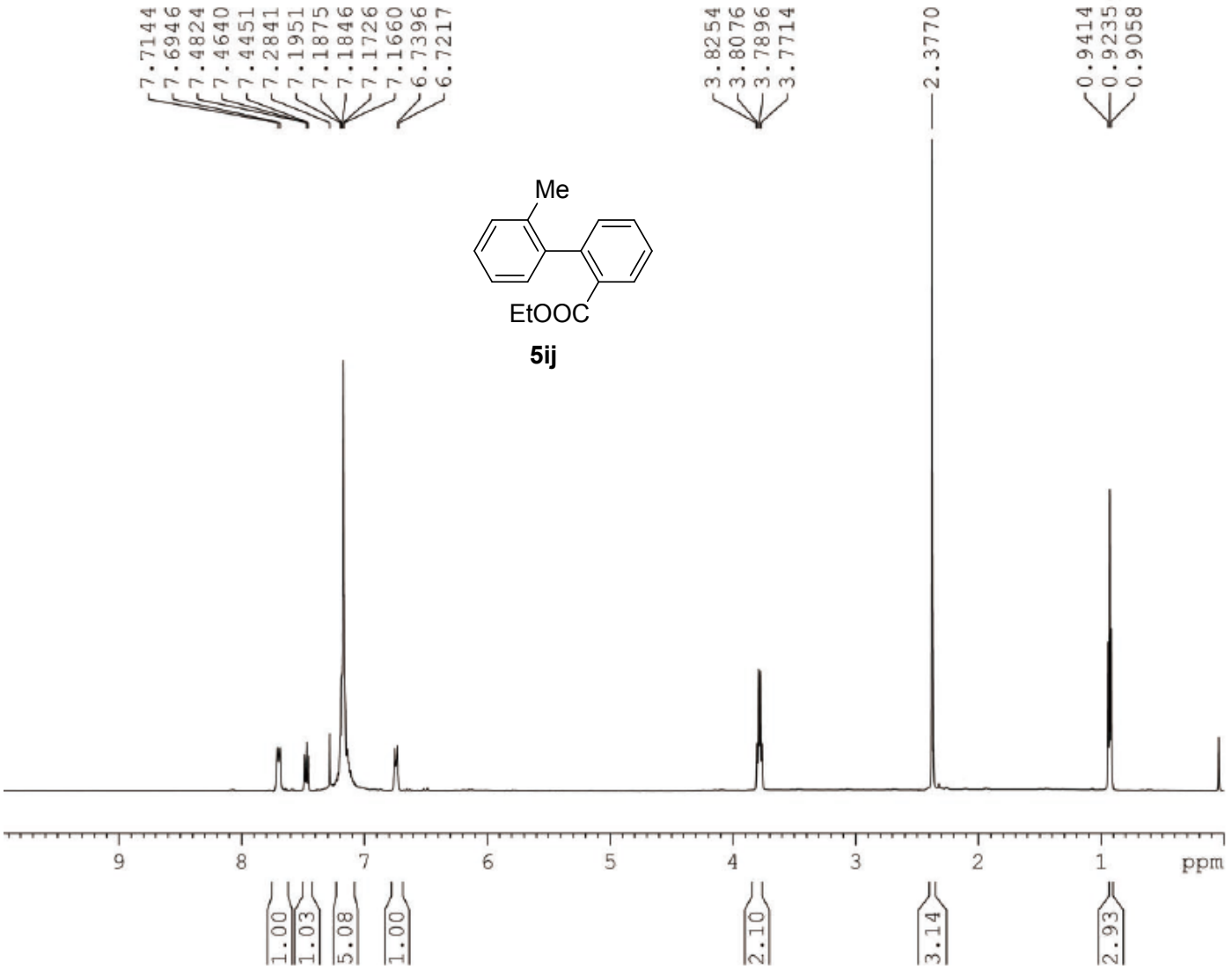
30
20
10
ppm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7.4451
7.2841
7.1951
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7.1846
7.1726
7.1660
6.7396
6.7217
3.8254
3.8076
3.7896
3.7714
2.3770
0.9414
0.9235
0.9058
Me
EtOOC
5ij
9
8
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5
4
3
2
1
ppm
1.00
1.03
5.08
1.00
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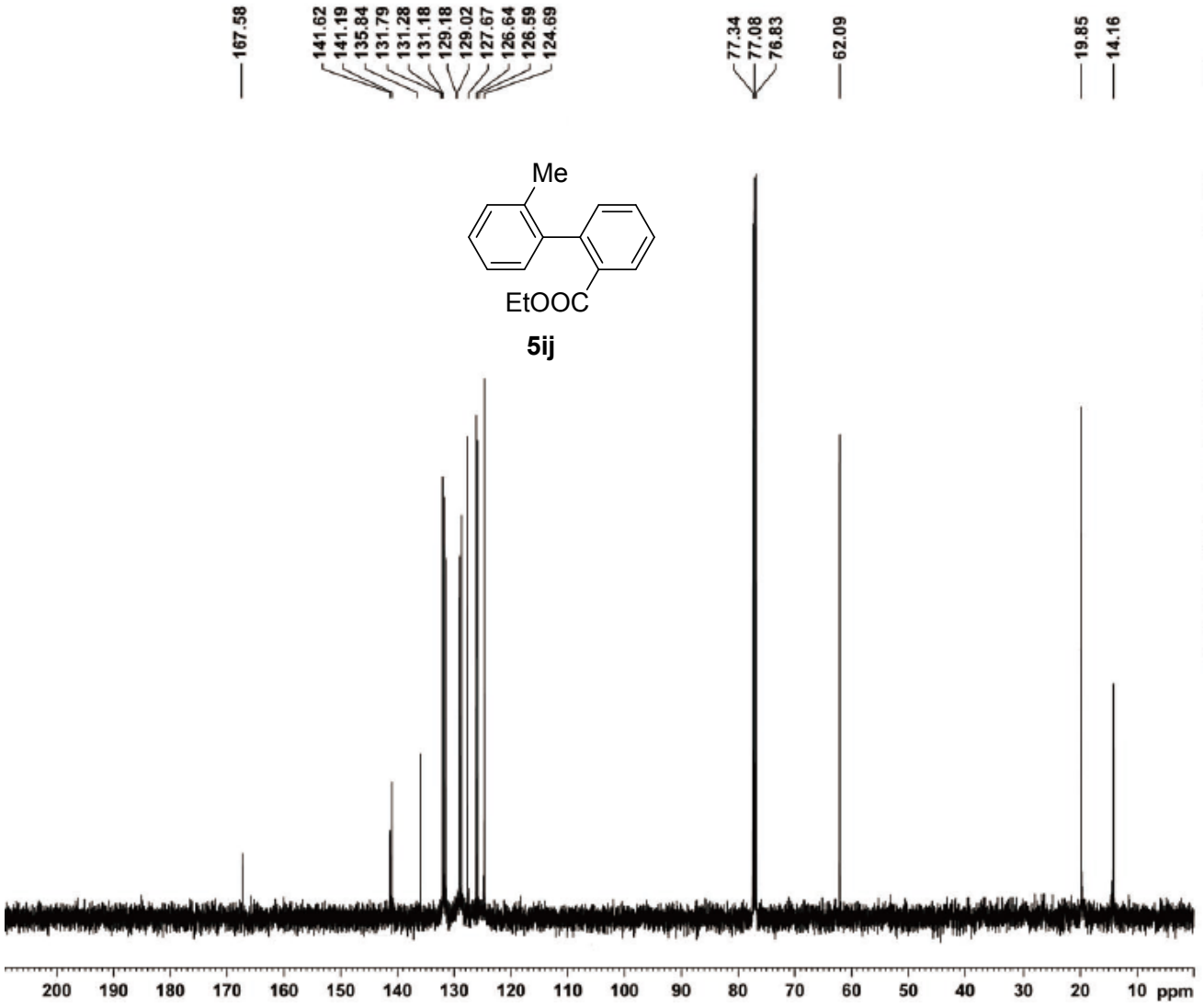
3.14
2.93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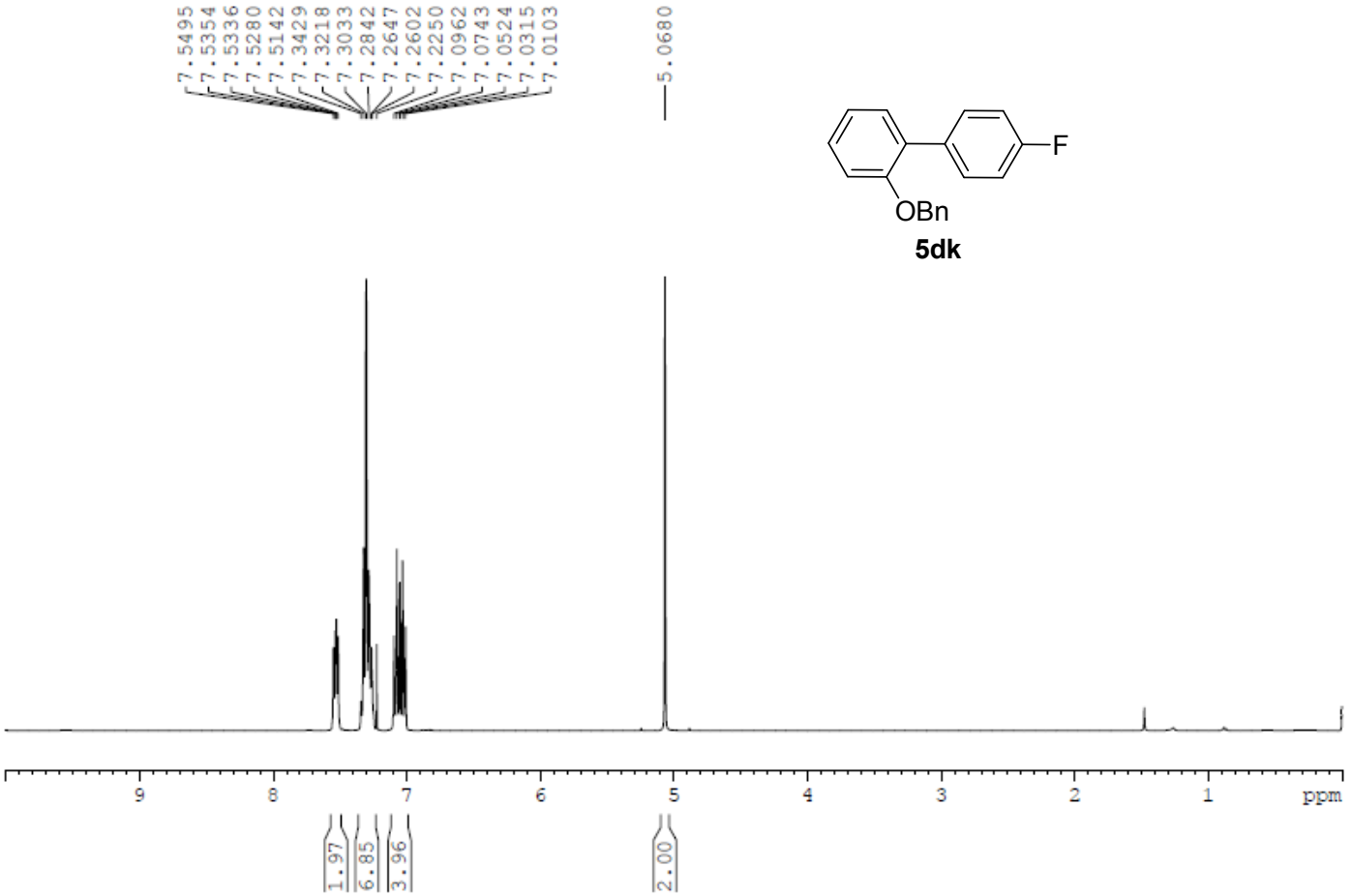
135.84
131.79
131.28
131.18
129.18
129.02
127.67
126.64
126.59
124.69
77.34
77.08
76.83
62.09
19.85
14.16
Me
EtOOC
5ij
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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7.5336
7.5280
7.5142
7.3429
7.3218
7.3033
7.2842
7.2647
7.2602
7.2250
7.0962
7.0743
7.0524
7.0315
7.0103
5.0680
F
OBn
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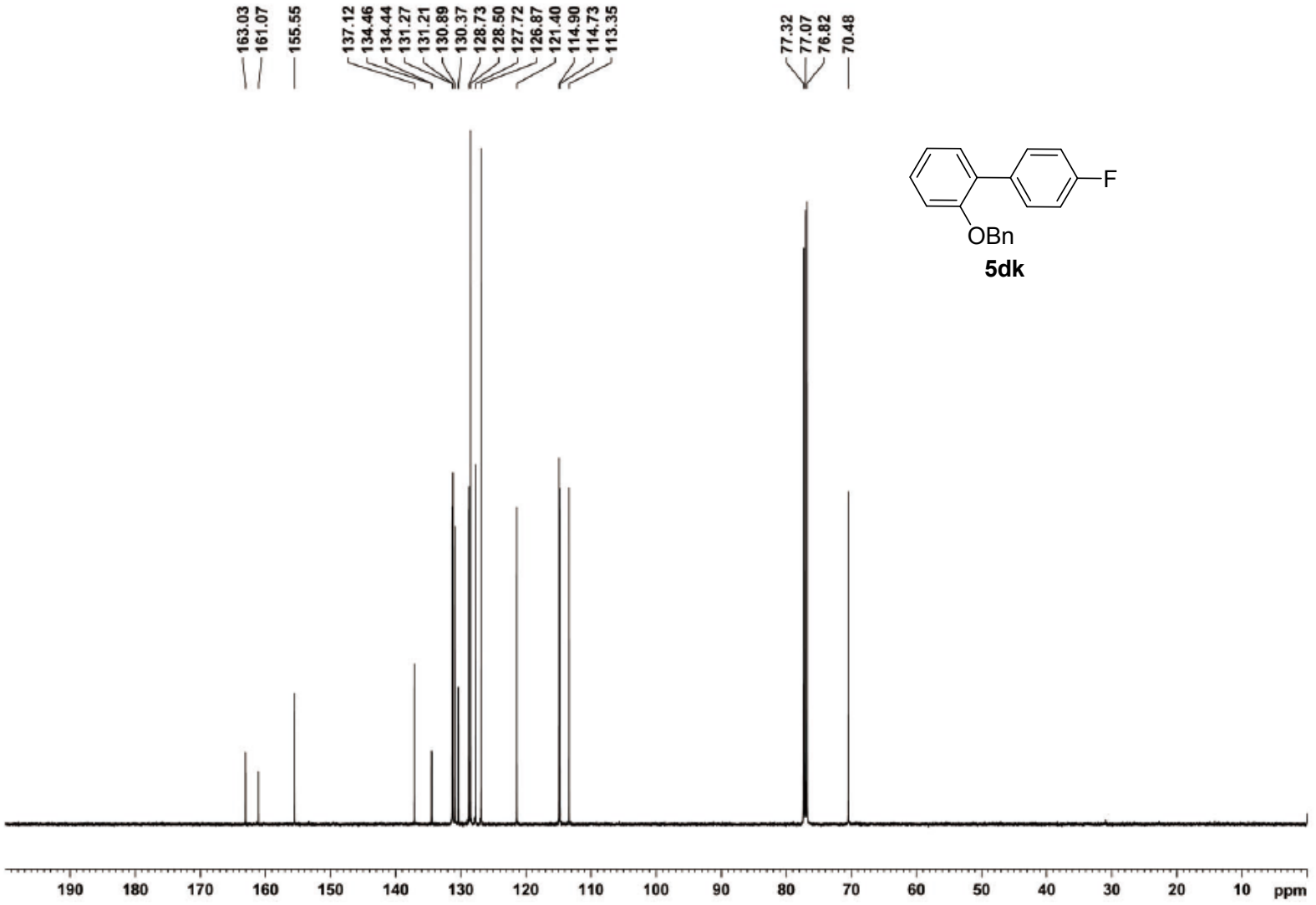
8
7
6
5
4
3
2
1
ppm
1.97
6.85
3.96
2.00

5dk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161.07
155.55
137.12
134.46
134.44
131.27
131.21
130.89
130.37
128.73
128.50
127.72
126.87
121.40
114.90
114.73
113.35
77.32
77.07
76.82
70.48
F
OBn
5dk
190
180
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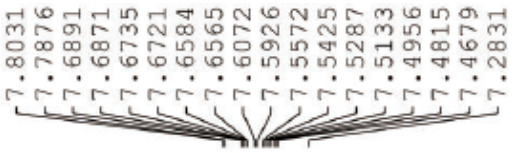
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.6584
7.6565
7.6072
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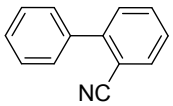
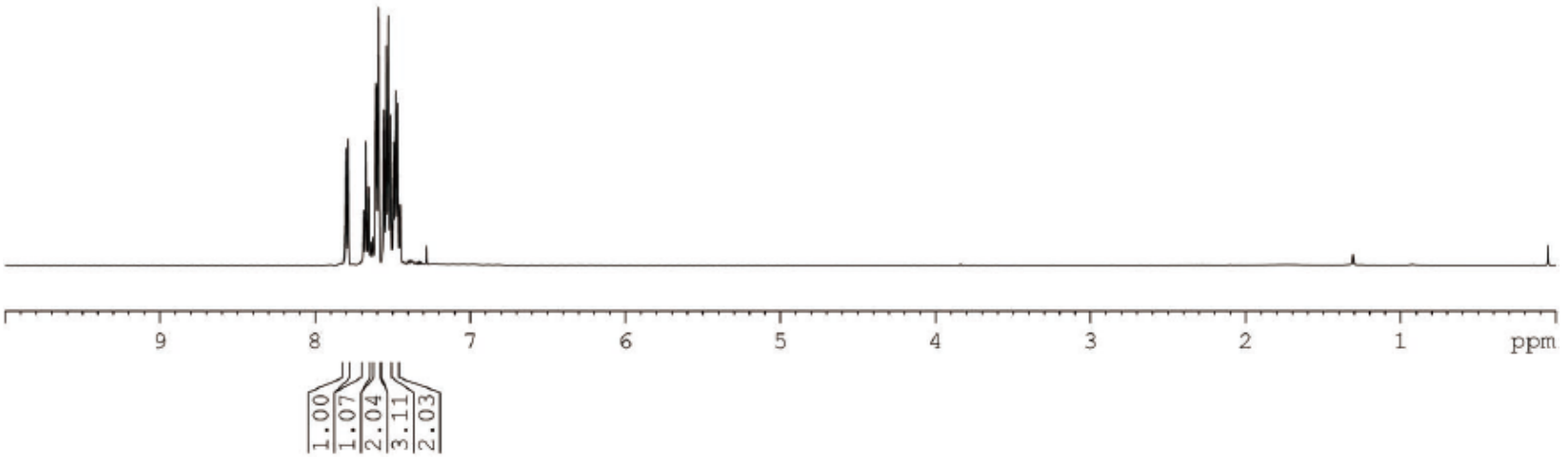
7.5572
7.5425
7.5287
7.5133
7.4956
7.4815
7.4679
7.2831


NC

5lm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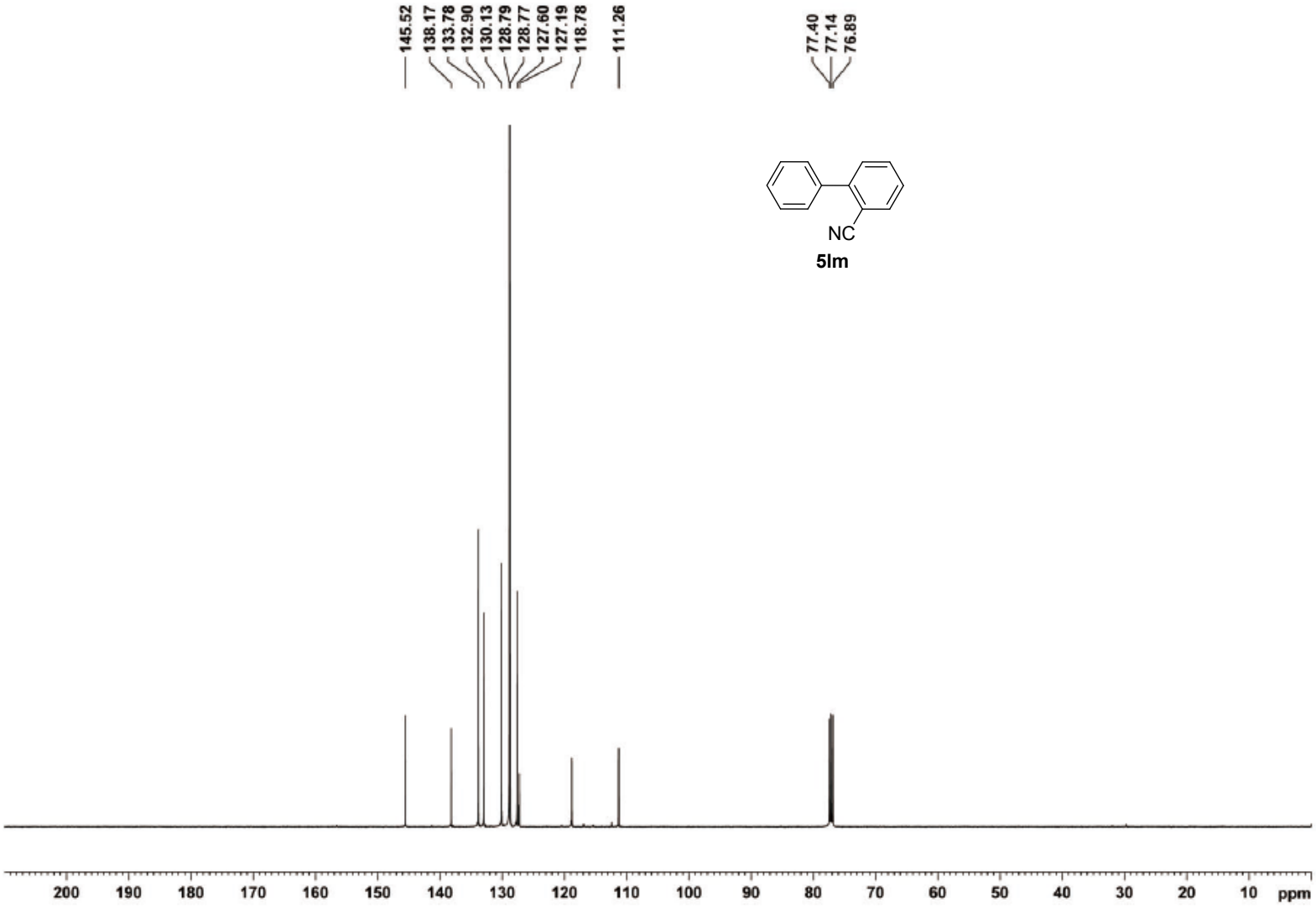
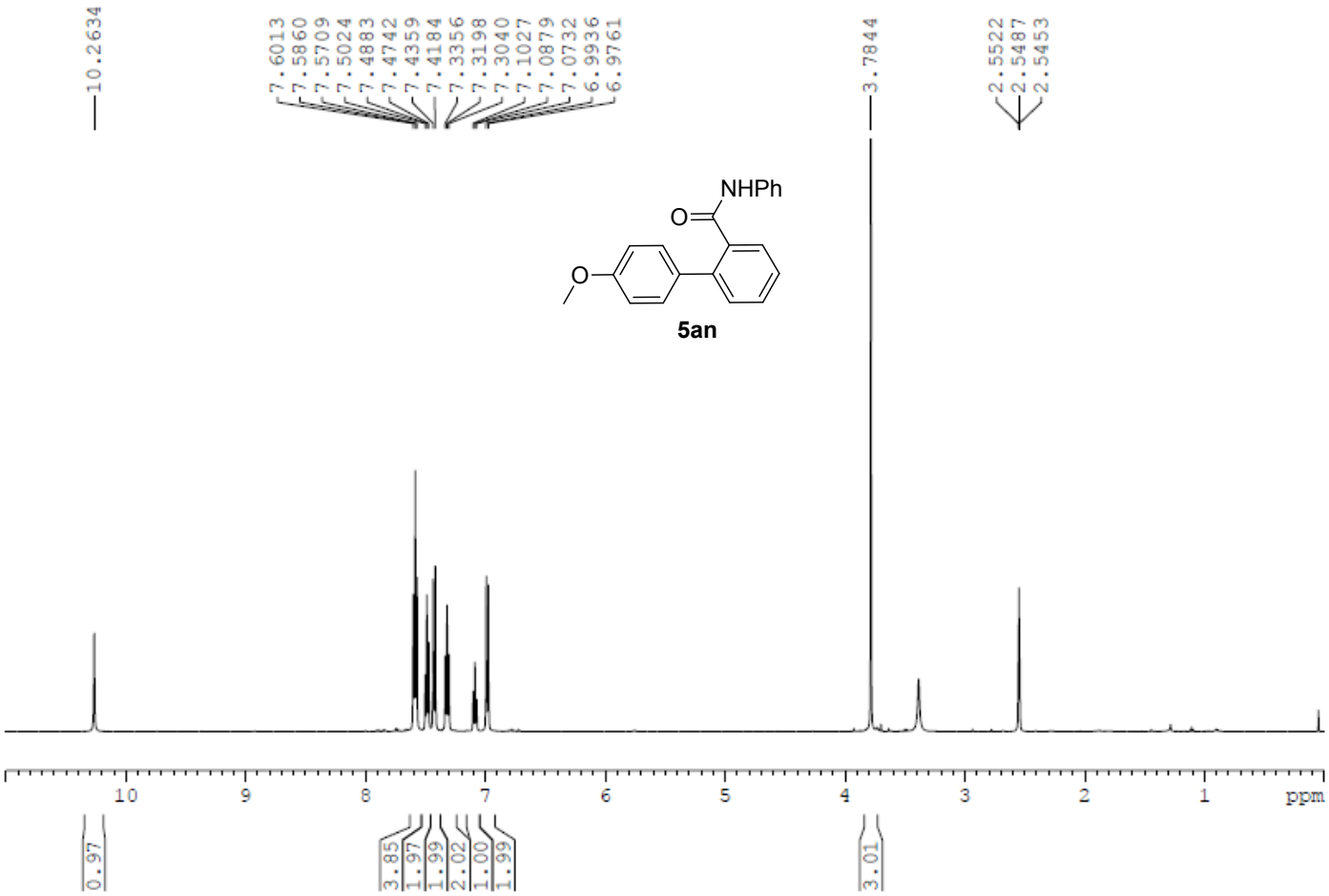
8
7
6
5
4
3
2
1
ppm
1.00
1.07
2.04
3.11
2.03


145.52
138.17
133.78
132.90
130.13
128.79
128.77
127.60
127.19
118.78
111.26
77.40
77.14
76.89
NC
5lm
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.6013
7.5860
7.5709
7.5024
7.4883
7.4742
7.4359
7.4184
7.3356
7.3198
7.3040
7.1027
7.0879
7.0732
6.9936
6.9761
3.7844
2.5522
2.5487
2.5453
NHPh
O
O
5an
10
9
8
7
6
5
4
3
2
1
ppm
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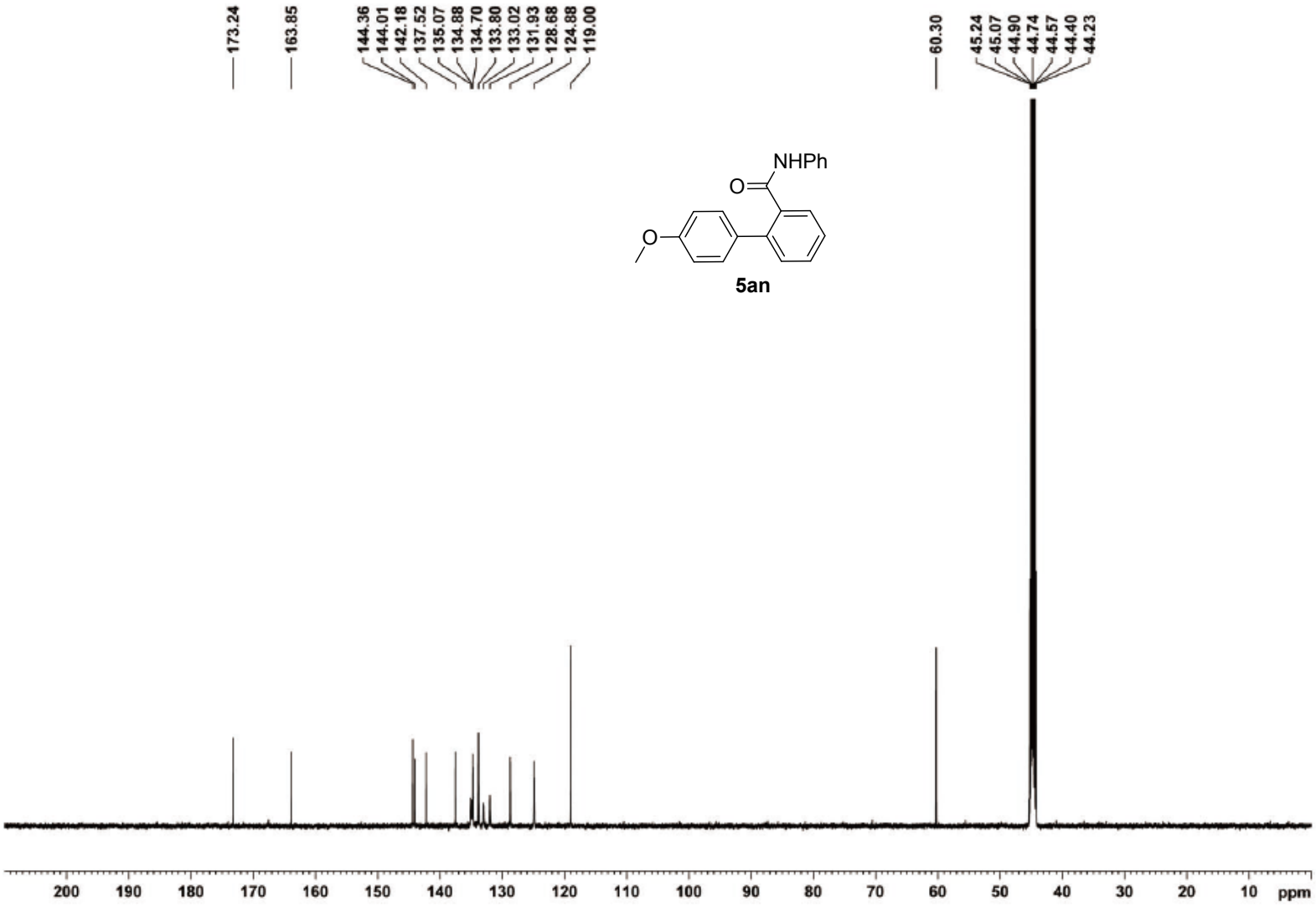
3.85
1.97
1.99
2.02
1.00
1.99
3.01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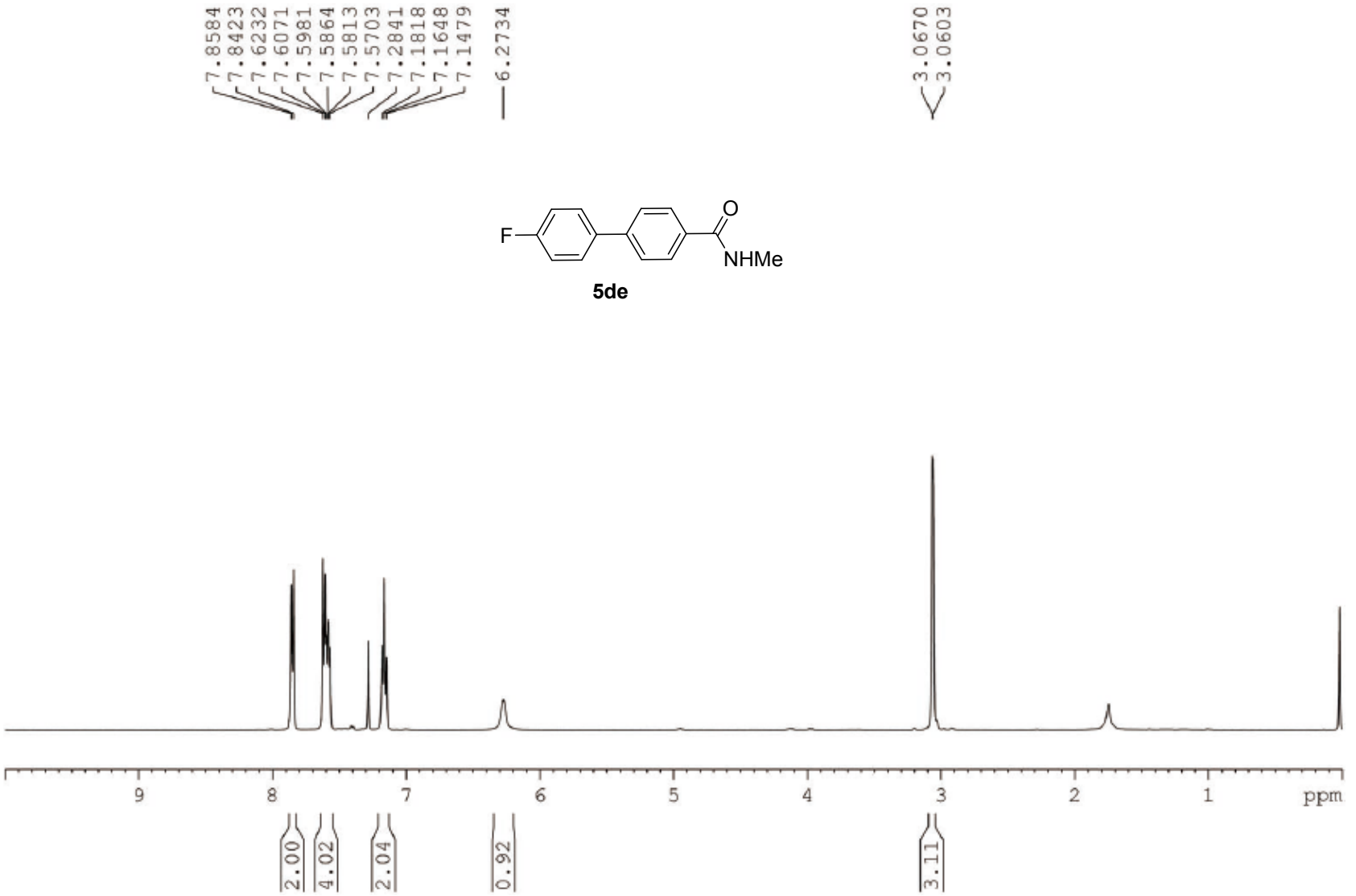
163.85
144.36
144.01
142.18
137.52
135.07
134.88
134.70
133.80
133.02
131.93
128.68
124.88
119.00
60.30
45.24
45.07
44.90
44.74
44.57
44.40
44.23
NHPh
O
O
5an
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.6232
7.6071
7.5981
7.5864
7.5813
7.5703
7.2841
7.1818
7.1648
7.1479
6.2734
3.0670
3.0603
F
O
NHMe
9
8
7
6
5
4
3
2
1
ppm
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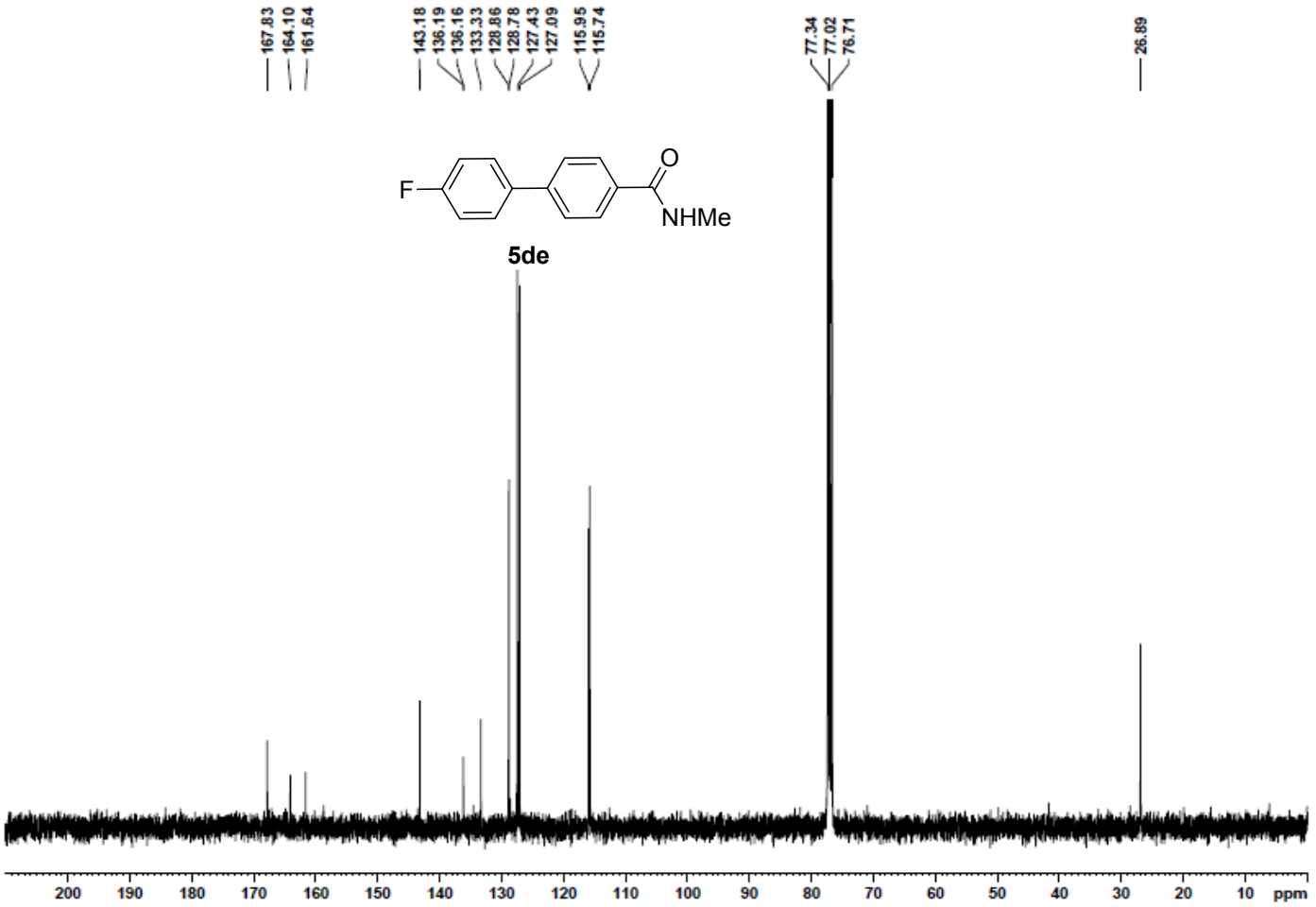
4.02
2.04
0.92
3.11

5de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161.64
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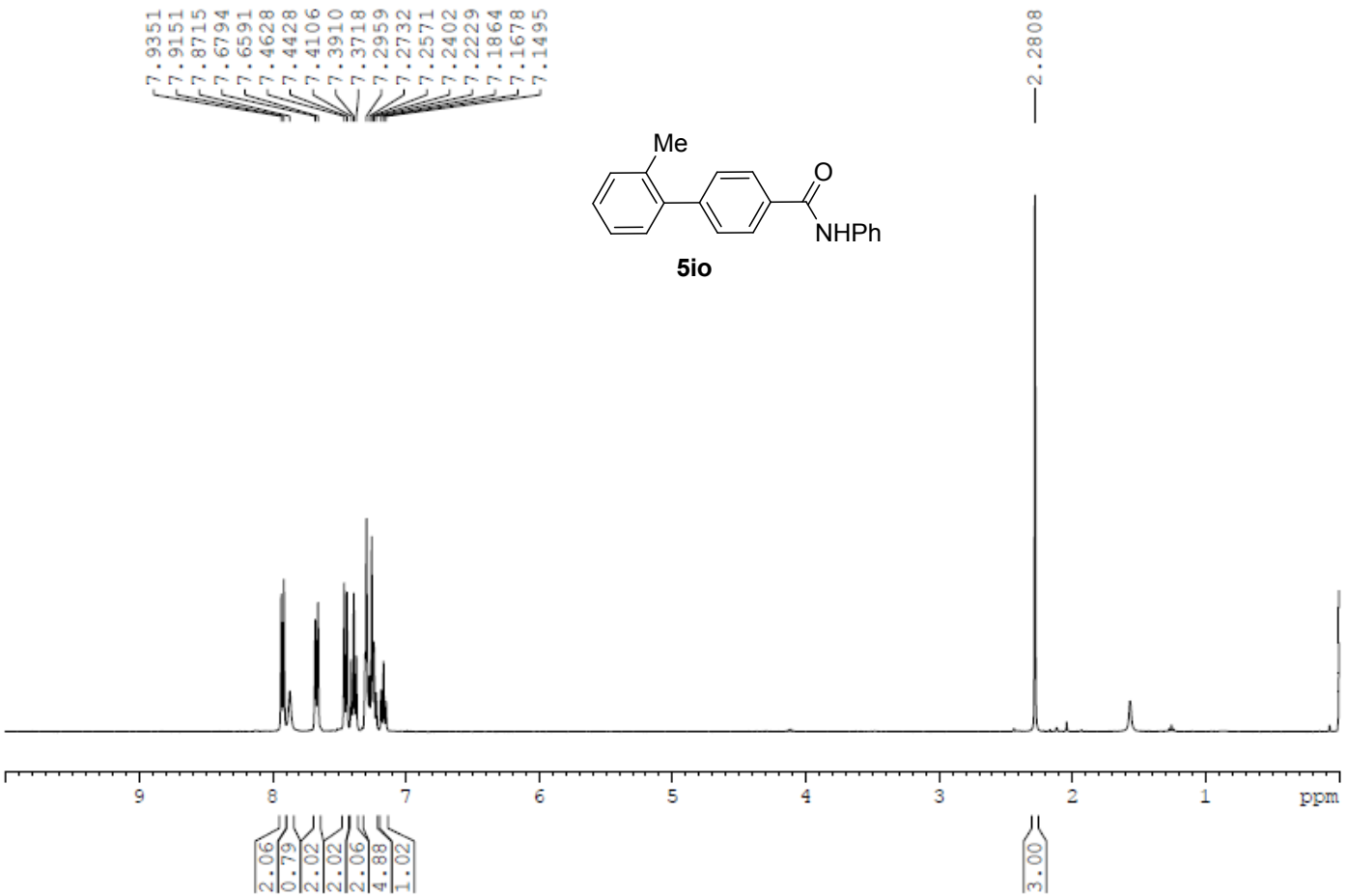
136.19
136.16
133.33
128.86
128.78
127.43
127.09
115.95
115.74
77.34
77.02
76.71
26.89
F
O
NHMe
5de
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.8715
7.6794
7.6591
7.4628
7.4428
7.4106
7.3910
7.3718
7.2959
7.2732
7.2571
7.2402
7.2229
7.1864
7.1678
7.1495
2.2808
Me
O
NHPh
9
8
7
6
5
4
3
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ppm
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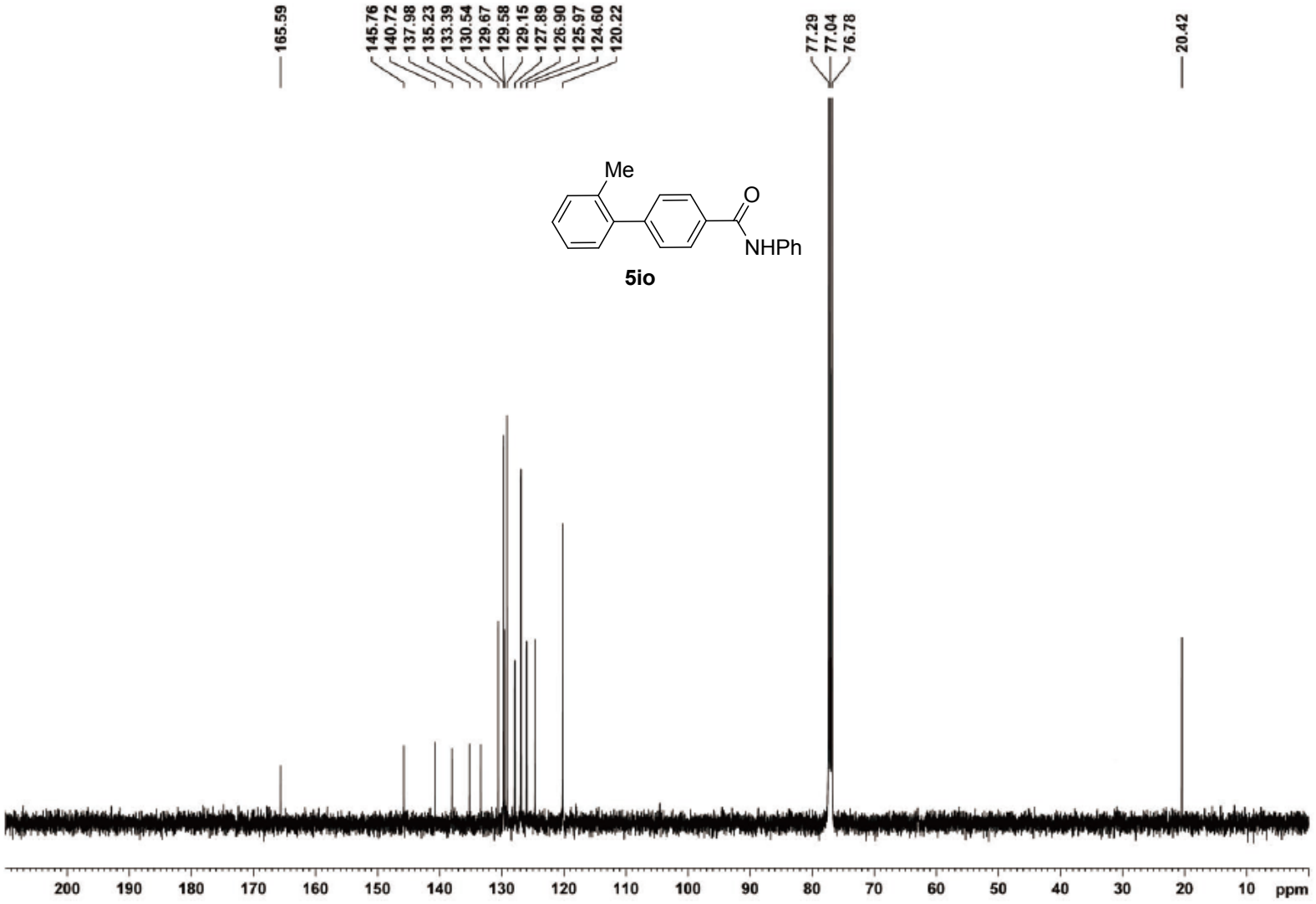
2.02
2.02
2.06
4.88
1.02
3.00

5io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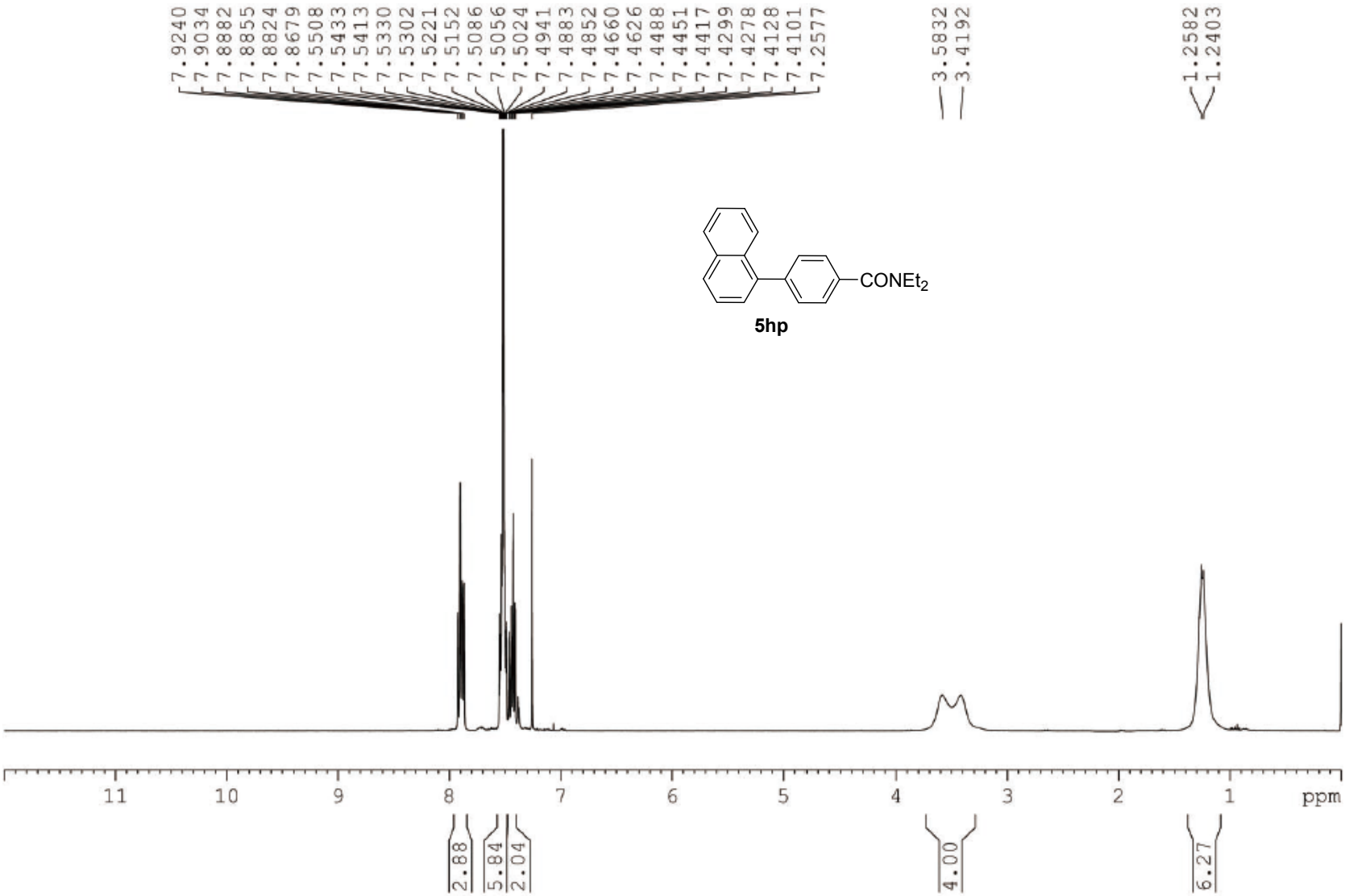
135.23
133.39
130.54
129.67
129.58
129.15
127.89
126.90
125.97
124.60
120.22
77.29
77.04
76.78
20.42
Me
O
NHPh
5io
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.8824
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7.5508
7.5433
7.5413
7.5330
7.5302
7.5221
7.5152
7.5086
7.5056
7.5024
7.4941
7.4883
7.4852
7.4660
7.4626
7.4488
7.4451
7.4417
7.4299
7.4278
7.4128
7.4101
7.2577
3.5832
3.4192
1.2582
1.2403
CONEt2
5hp
11
10
9
8
7
6
5
4
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2
1
ppm
2.88
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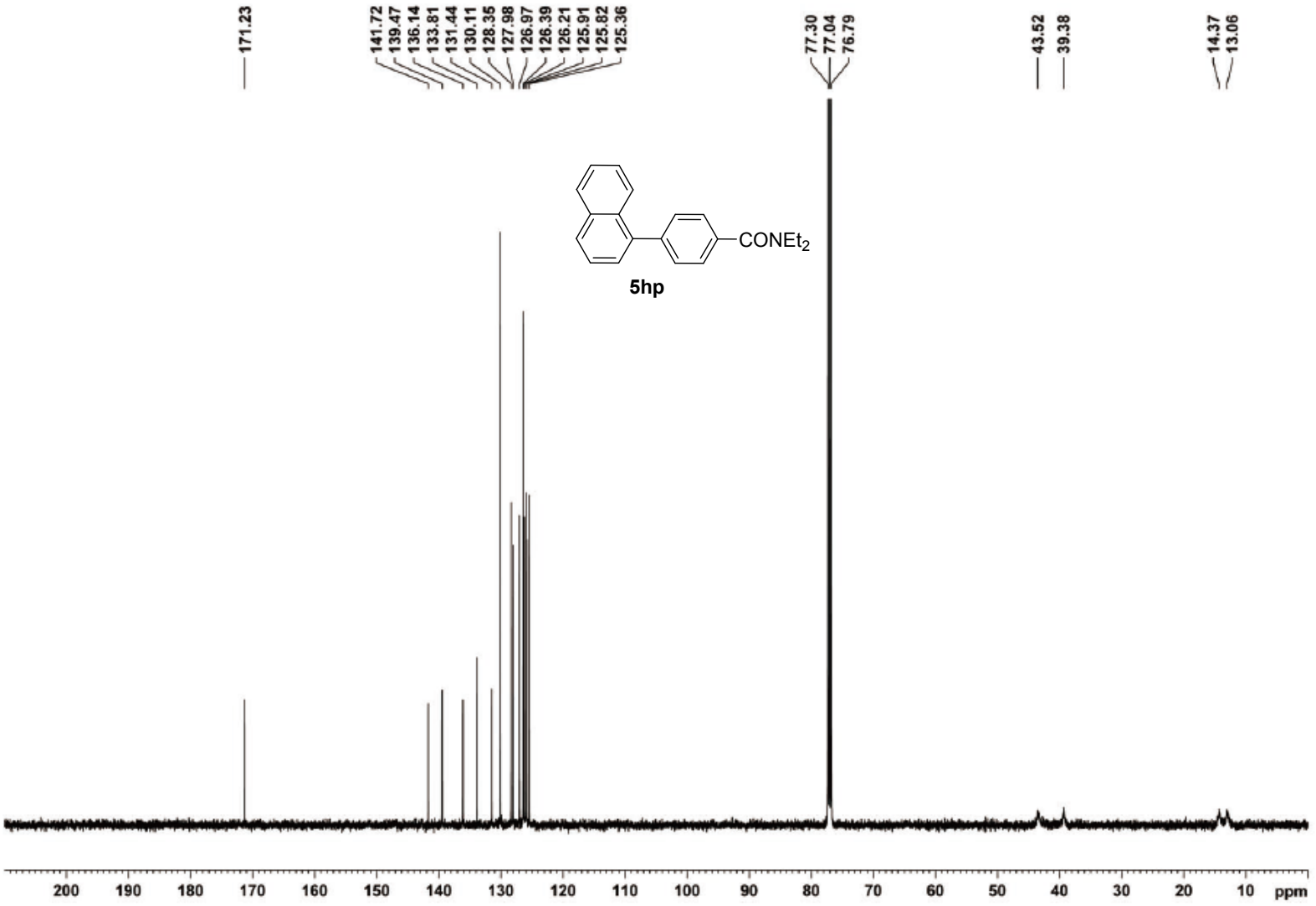
4.00
6.27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131.44
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128.35
127.98
126.97
126.39
126.21
125.91
125.82
125.36
77.30
77.04
76.79
43.52
39.38
14.37
13.06
CONEt2
5hp
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


10.1051
8.1595
8.1384
7.9197
7.9171
7.9137
7.9056
7.9011
7.8982
7.8949
7.8862
7.8819
7.7085
7.7037
7.6917
7.6874
7.6825
7.6653
7.6461
7.6270
7.2601
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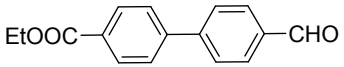
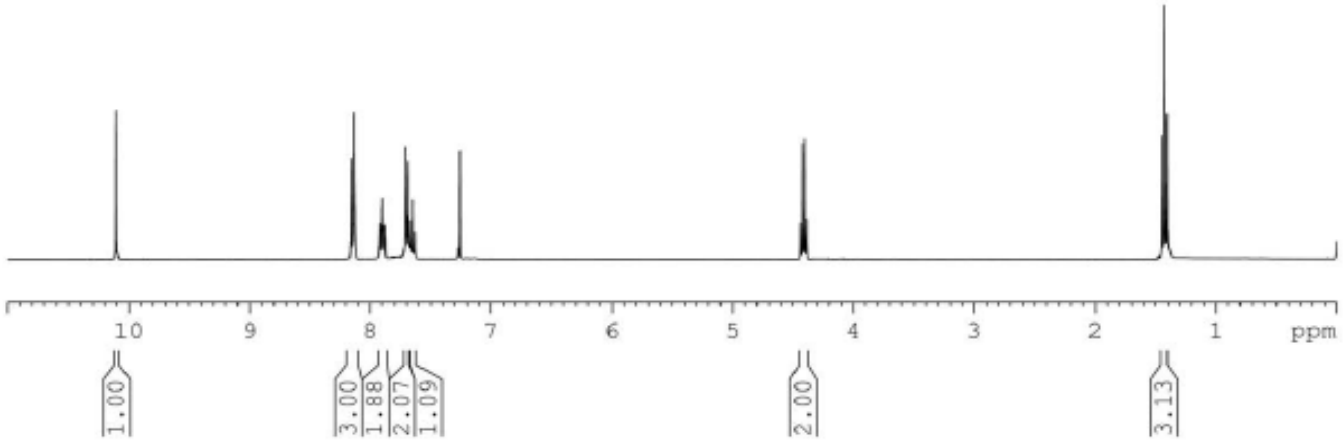
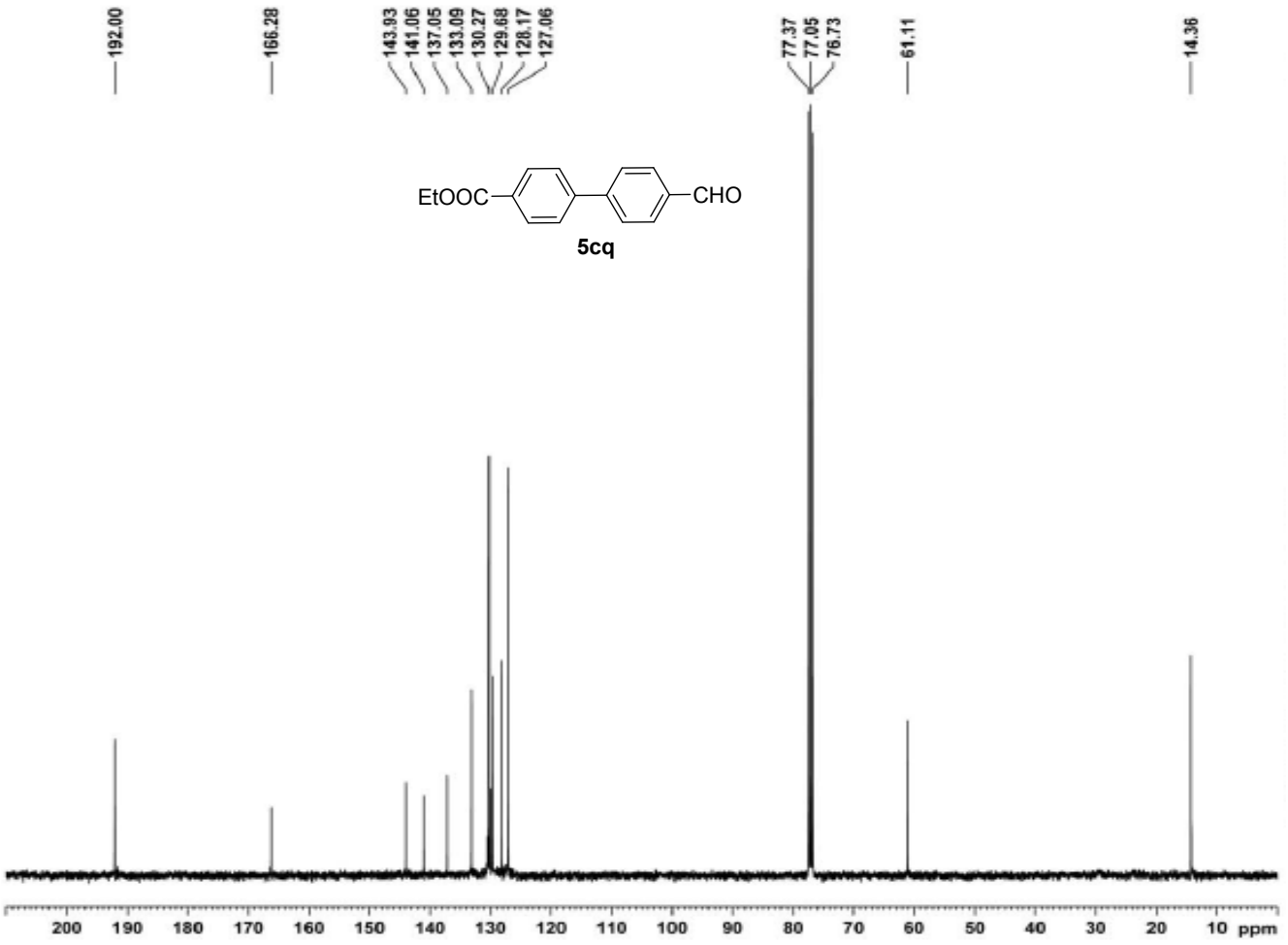
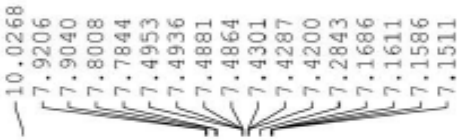
4.4244
4.4066
4.3888
1.4428
1.4250
1.4071


EtOOC
CHO

5cq


10
9
8
7
6
5
4
3
2
1
ppm
1.00
3.00
1.88
2.07
1.09
2.00
3.13


192.00
166.28
143.93
141.06
137.05
133.09
130.27
129.68
128.17
127.06
77.37
77.05
76.73
61.11
14.36
EtOOC
CHO
5cq
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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7.9206
7.9040
7.8008
7.7844
7.4953
7.4936
7.4881
7.4864
7.4301
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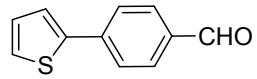
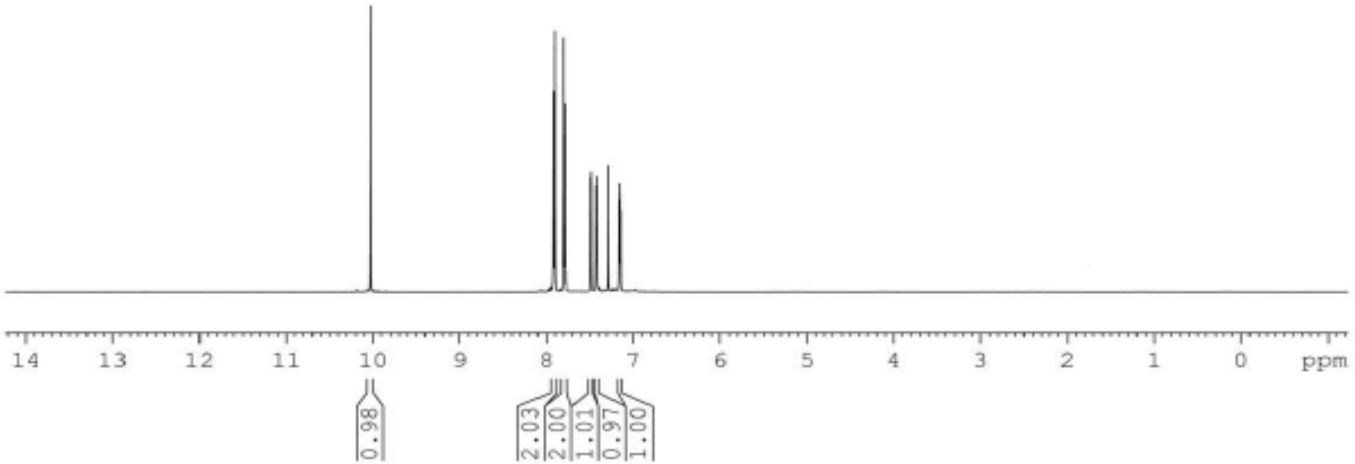
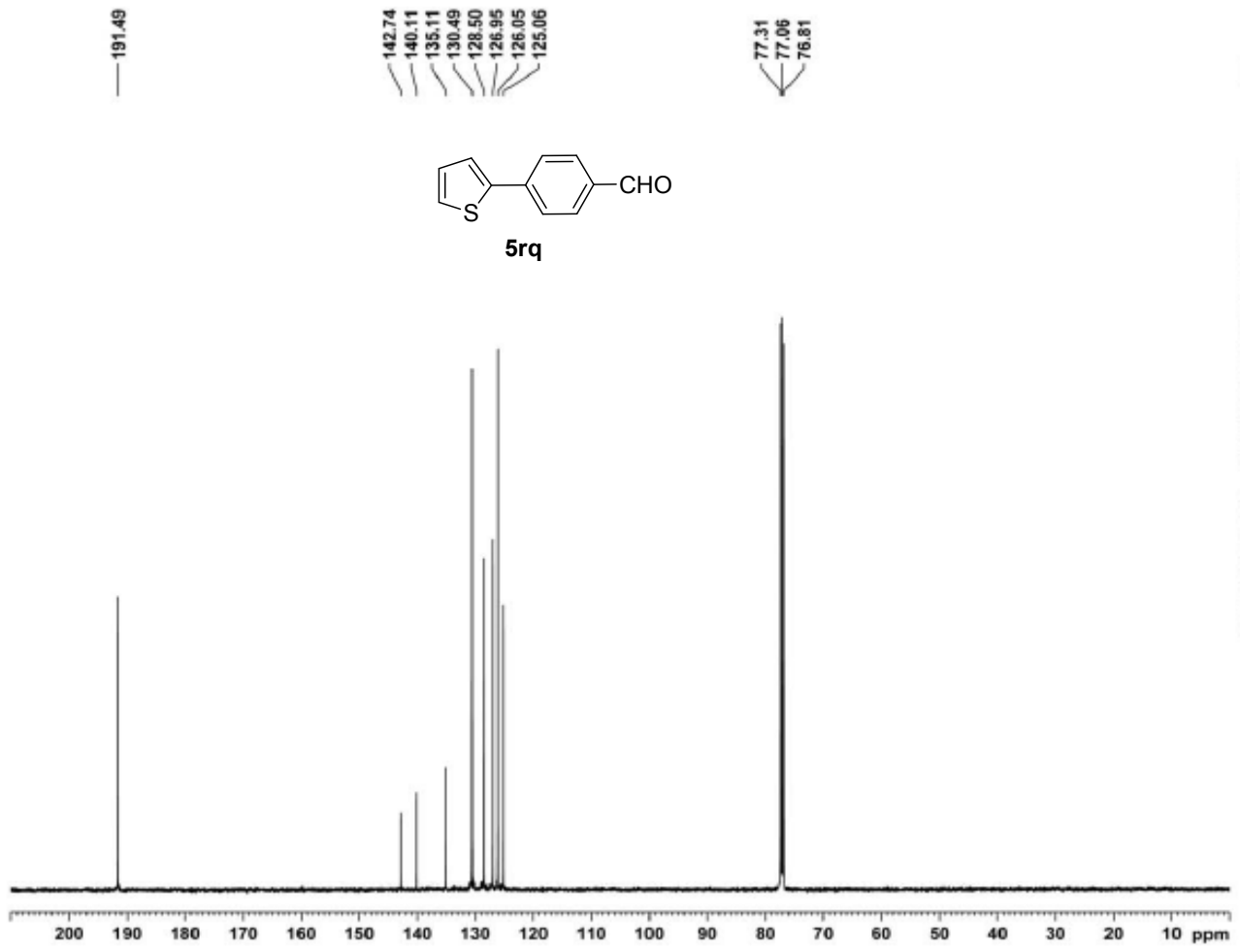
7.2843
7.1686
7.1611
7.1586
7.1511


S
CHO

5rq


14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.98
2.03
2.00
1.01
0.97
1.00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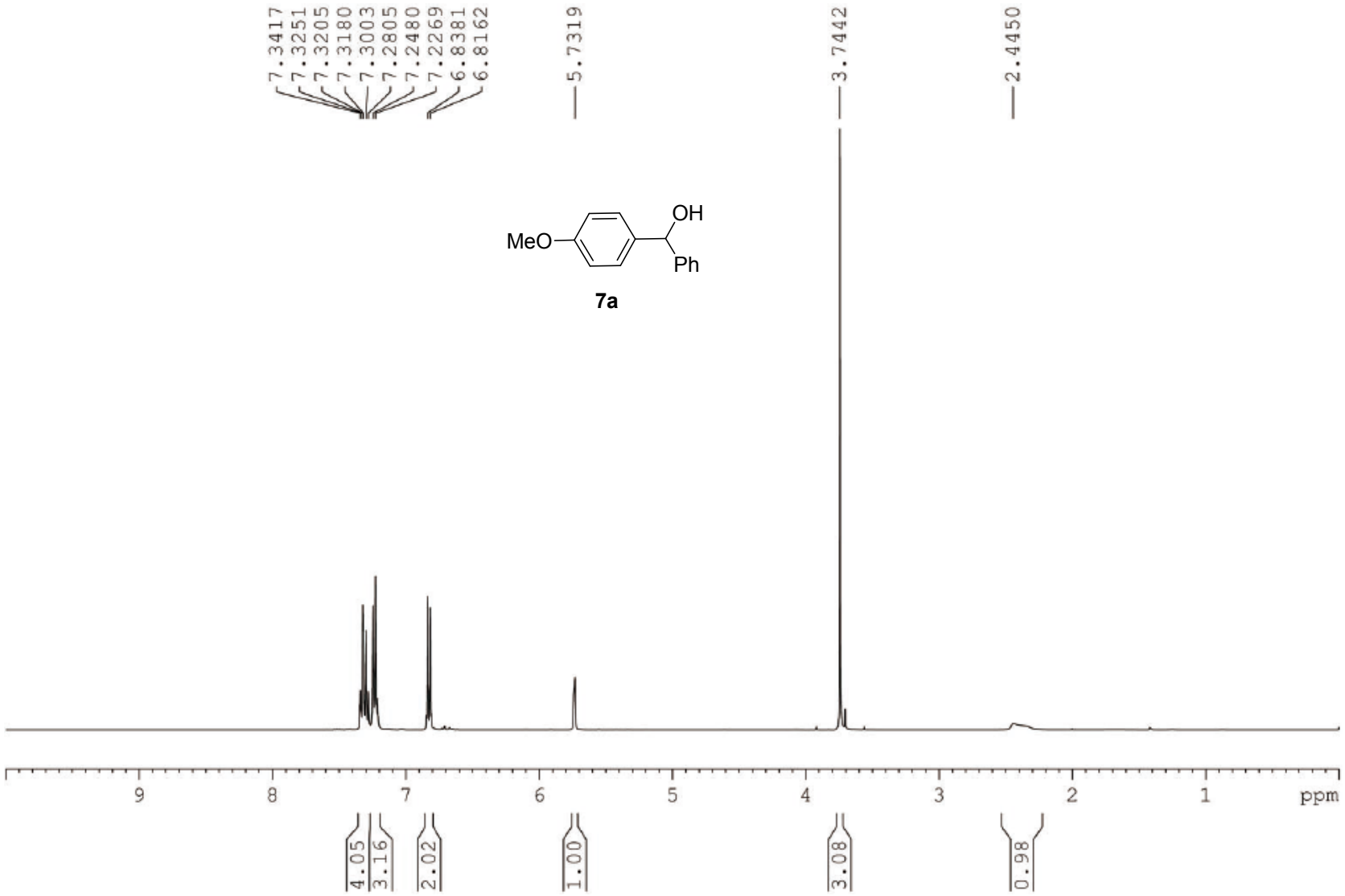
142.74
140.11
135.11
130.49
128.50
126.95
126.05
125.06
77.31
77.06
76.81
S
CHO
5rq
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.3417
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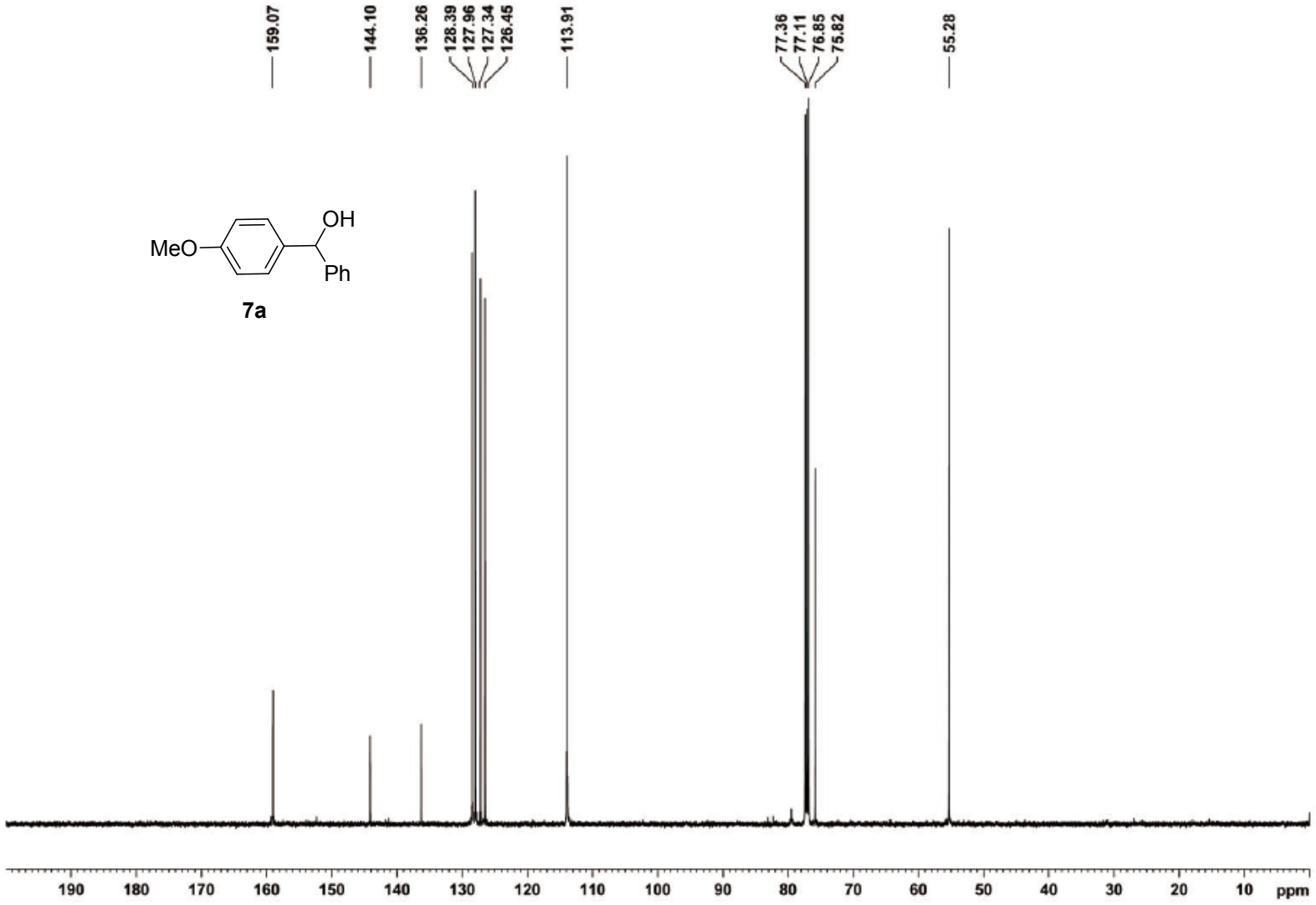
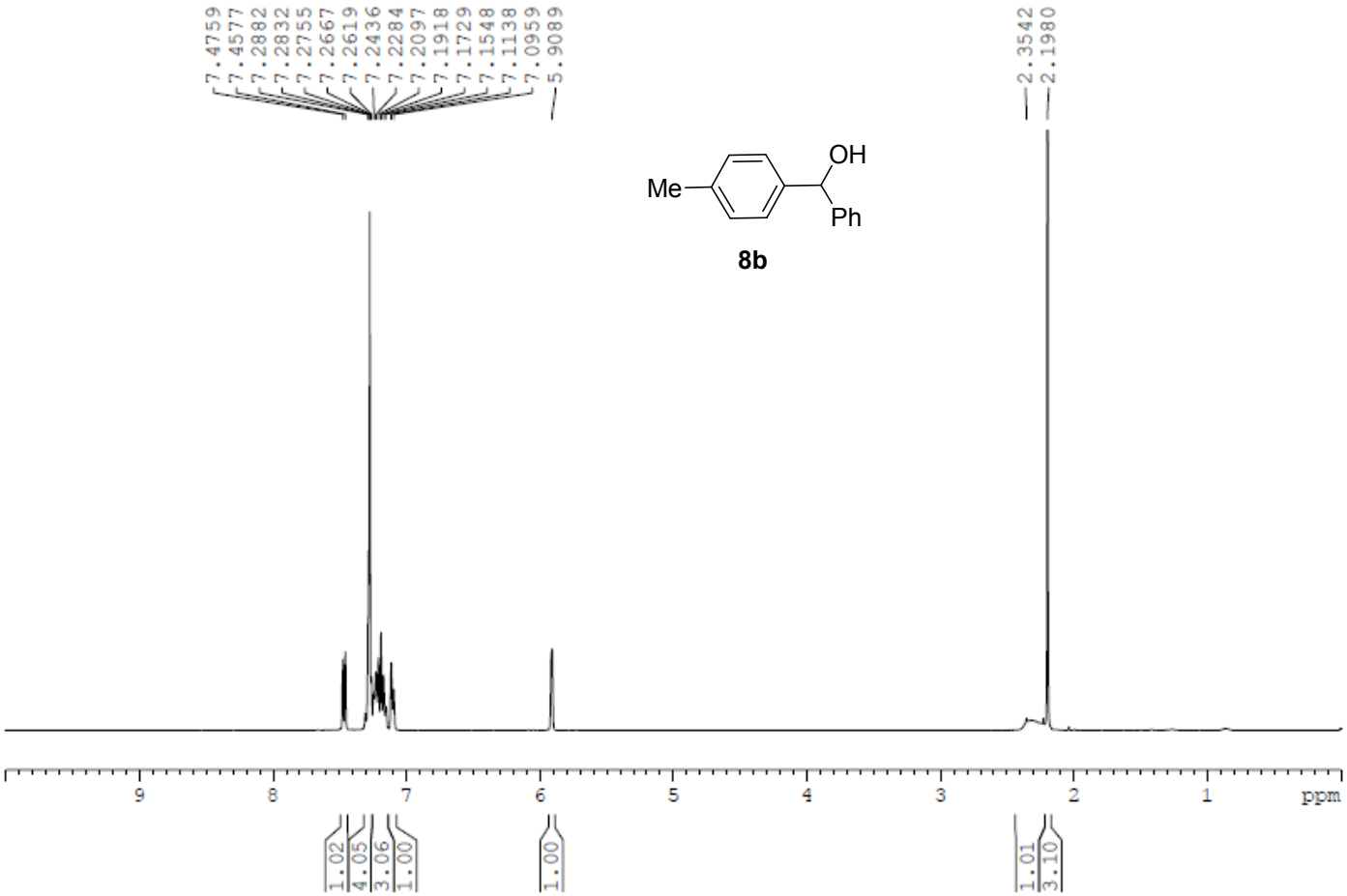
7.3205
7.3180
7.3003
7.2805
7.2480
7.2269
6.8381
6.8162
5.7319
3.7442
2.4450
MeO
OH
Ph
7a
9
8
7
6
5
4
3
2
1
ppm
4.05
3.16
2.02
1.00
3.08
0.98


159.07
144.10
136.26
128.39
127.96
127.34
126.45
113.91
77.36
77.11
76.85
75.82
55.28
OH
MeO
Ph
7a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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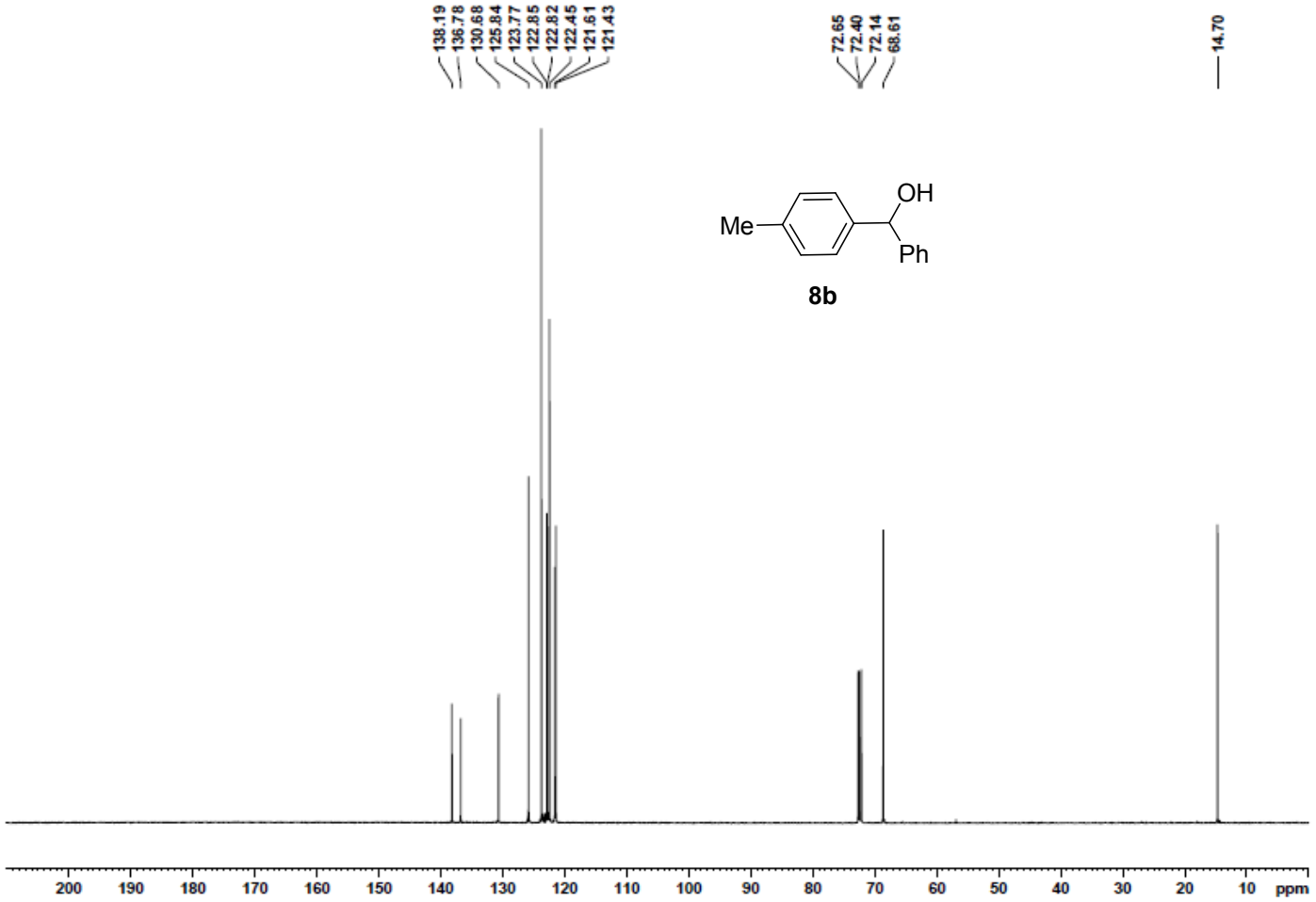
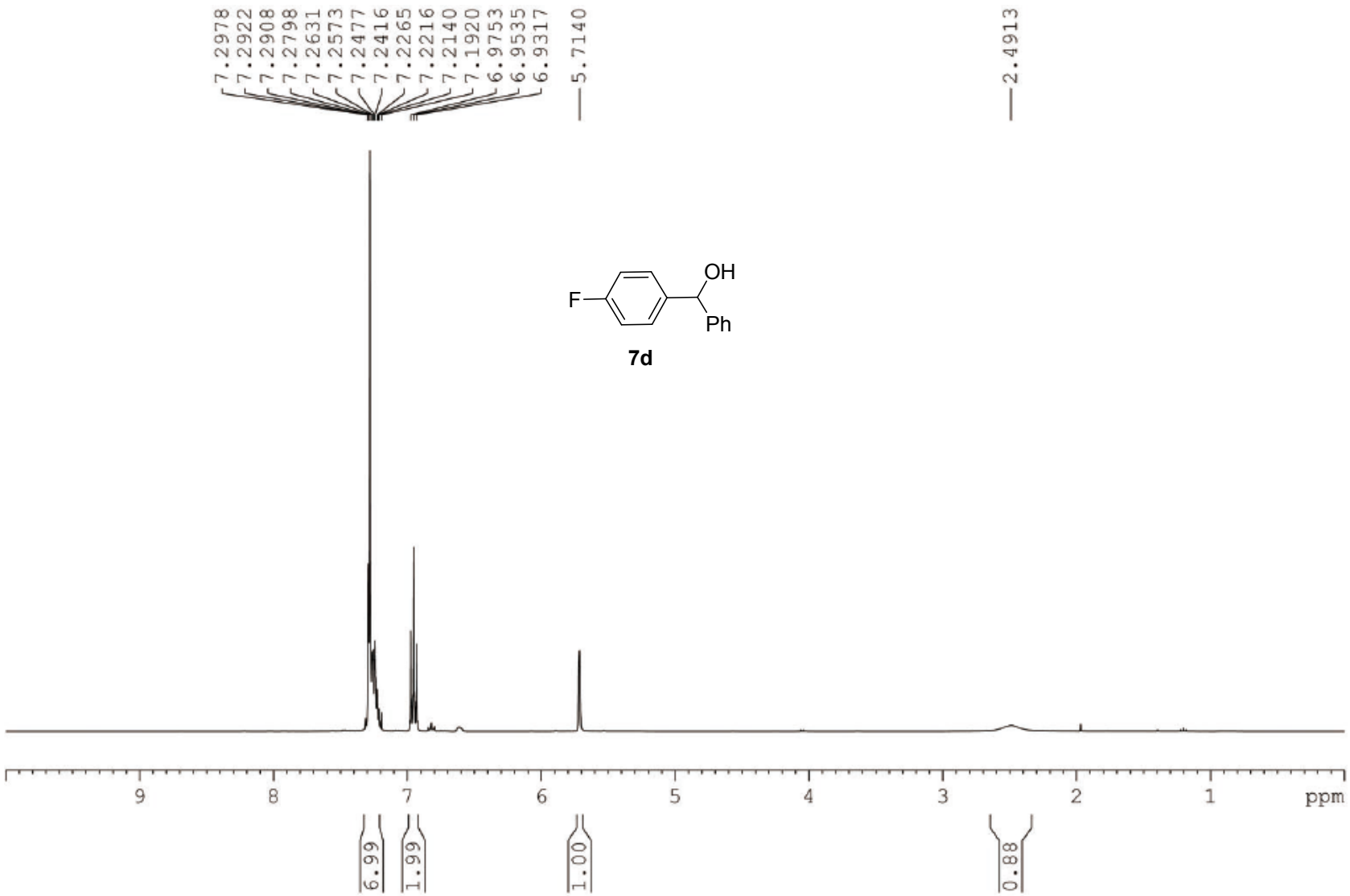
7.2882
7.2832
7.2755
7.2667
7.2619
7.2436
7.2284
7.2097
7.1918
7.1729
7.1548
7.1138
7.0959
5.9089
2.3542
2.1980
OH
Me
Ph
8b
9
8
7
6
5
4
3
2
1
ppm
1.02
4.05
3.06
1.00
1.00
1.01
3.10


138.19
136.78
130.68
125.84
123.77
122.85
122.82
122.45
121.61
121.43
72.65
72.40
72.14
68.61
14.70
OH
Me
Ph
8b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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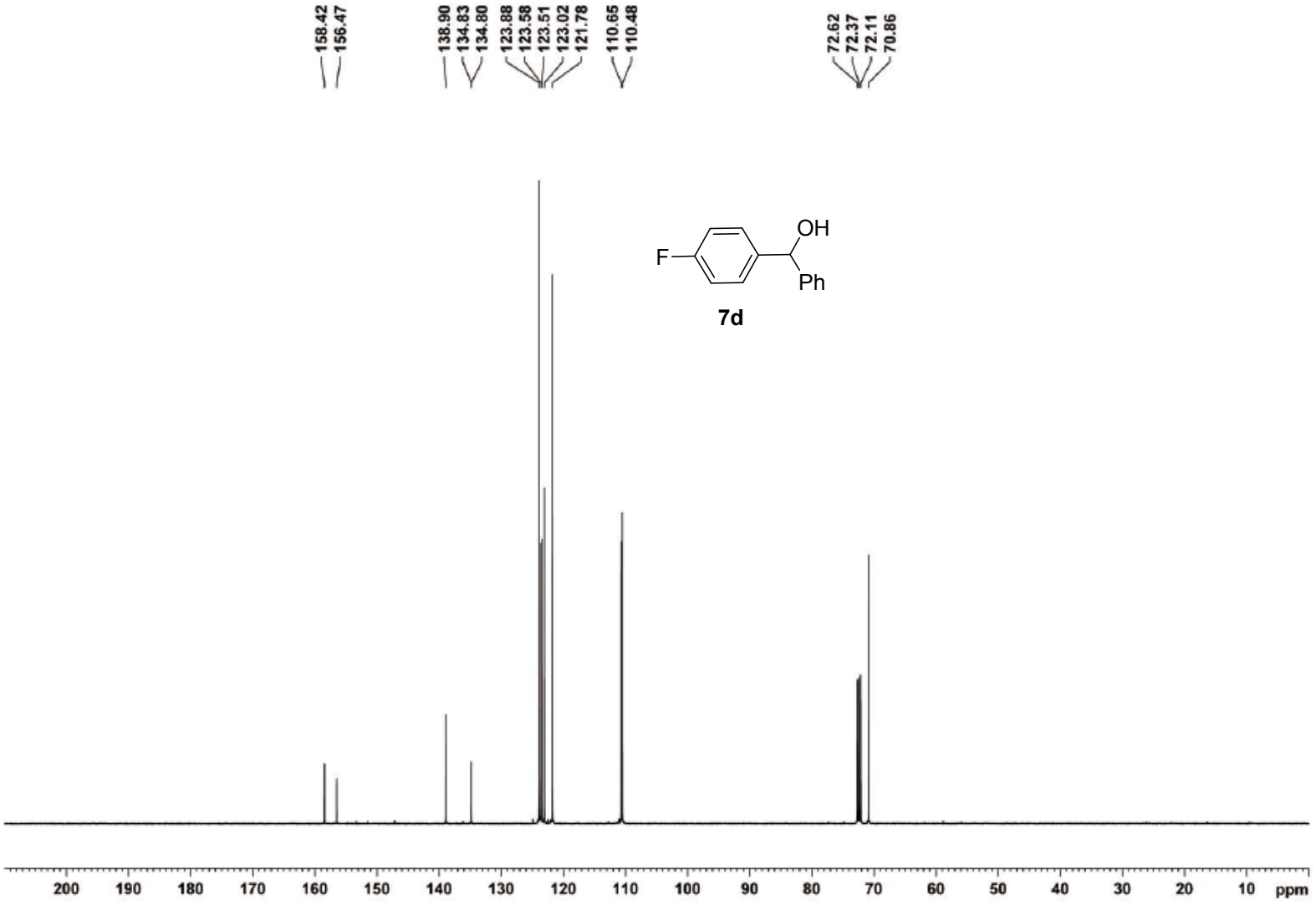
7.2922
7.2908
7.2798
7.2631
7.2573
7.2477
7.2416
7.2265
7.2216
7.2140
7.1920
6.9753
6.9535
6.9317
5.7140
2.4913
OH
F
Ph
7d
9
8
7
6
5
4
3
2
1
ppm
6.99
1.99
1.00
0.88


158.42
156.47
138.90
134.83
134.80
123.88
123.58
123.51
123.02
121.78
110.65
110.48
72.62
72.37
72.11
70.86
OH
F
Ph
7d
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.9941
7.9732
7.4542
7.4338
7.3509
7.3400
7.3340
7.3268
7.3201
7.2847
7.2779
7.2631
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4.3495
4.3316
4.3139
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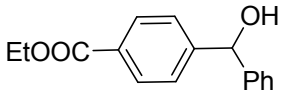
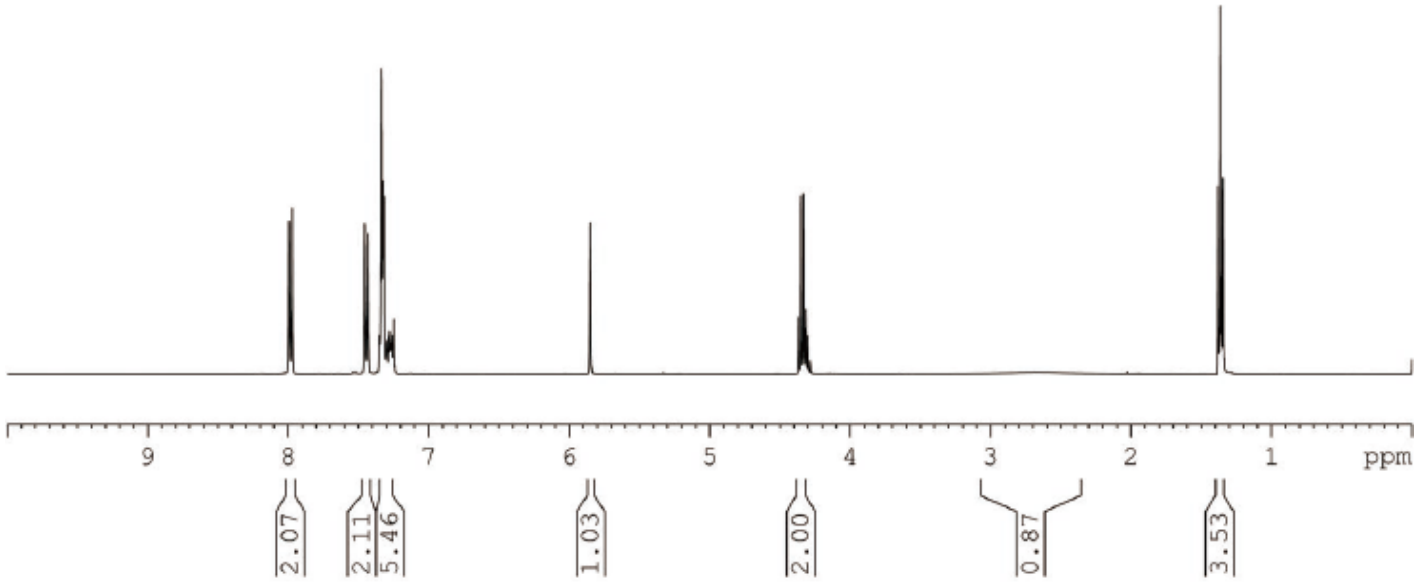
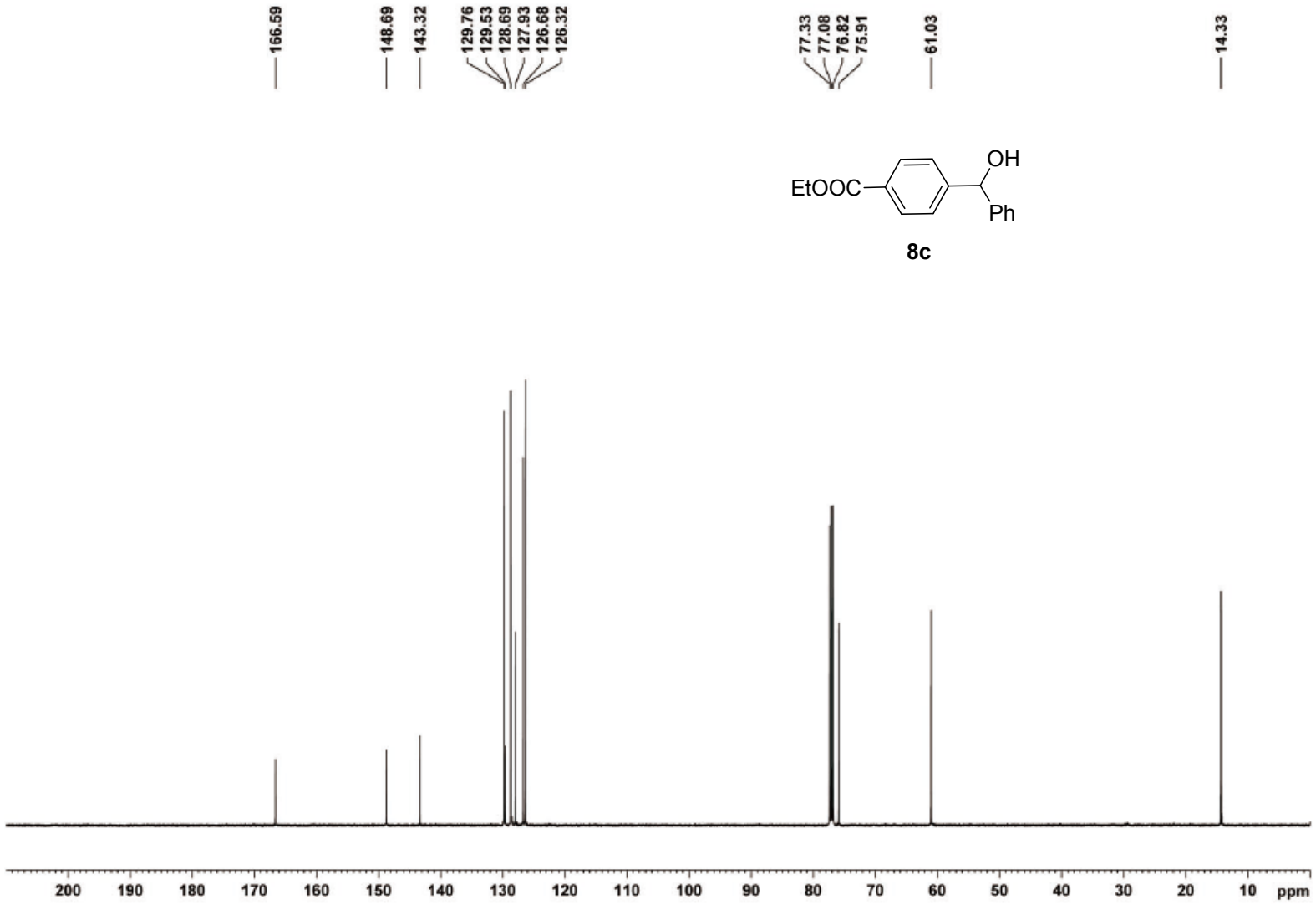
1.3653
1.3475


EtOOC
OH
Ph

8c


9
8
7
6
5
4
3
2
1
ppm
2.07
2.11
5.46
1.03
2.00
0.87
3.53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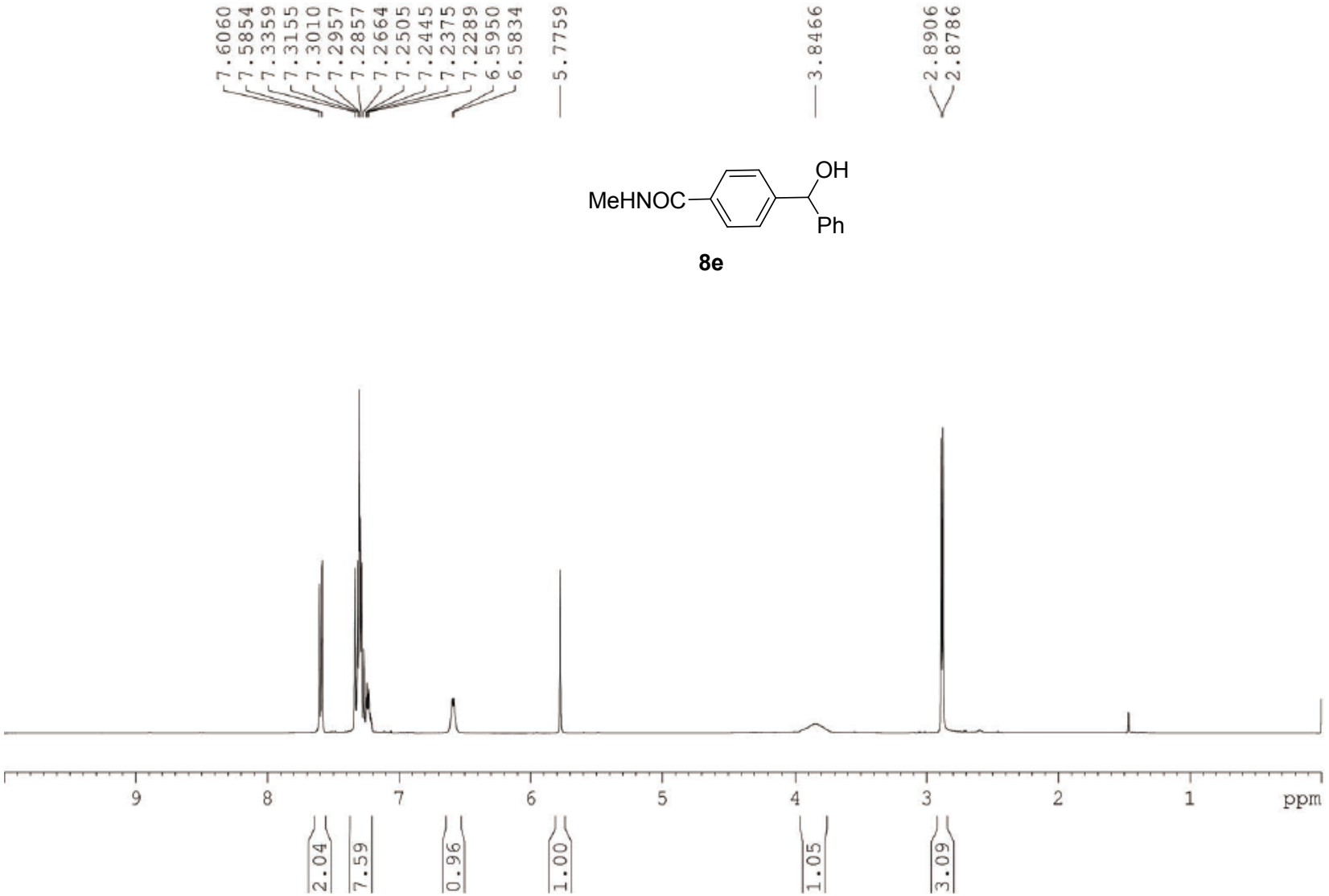
148.69
143.32
129.76
129.53
128.69
127.93
126.68
126.32
77.33
77.08
76.82
75.91
61.03
14.33
EtOOC
OH
Ph
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

8c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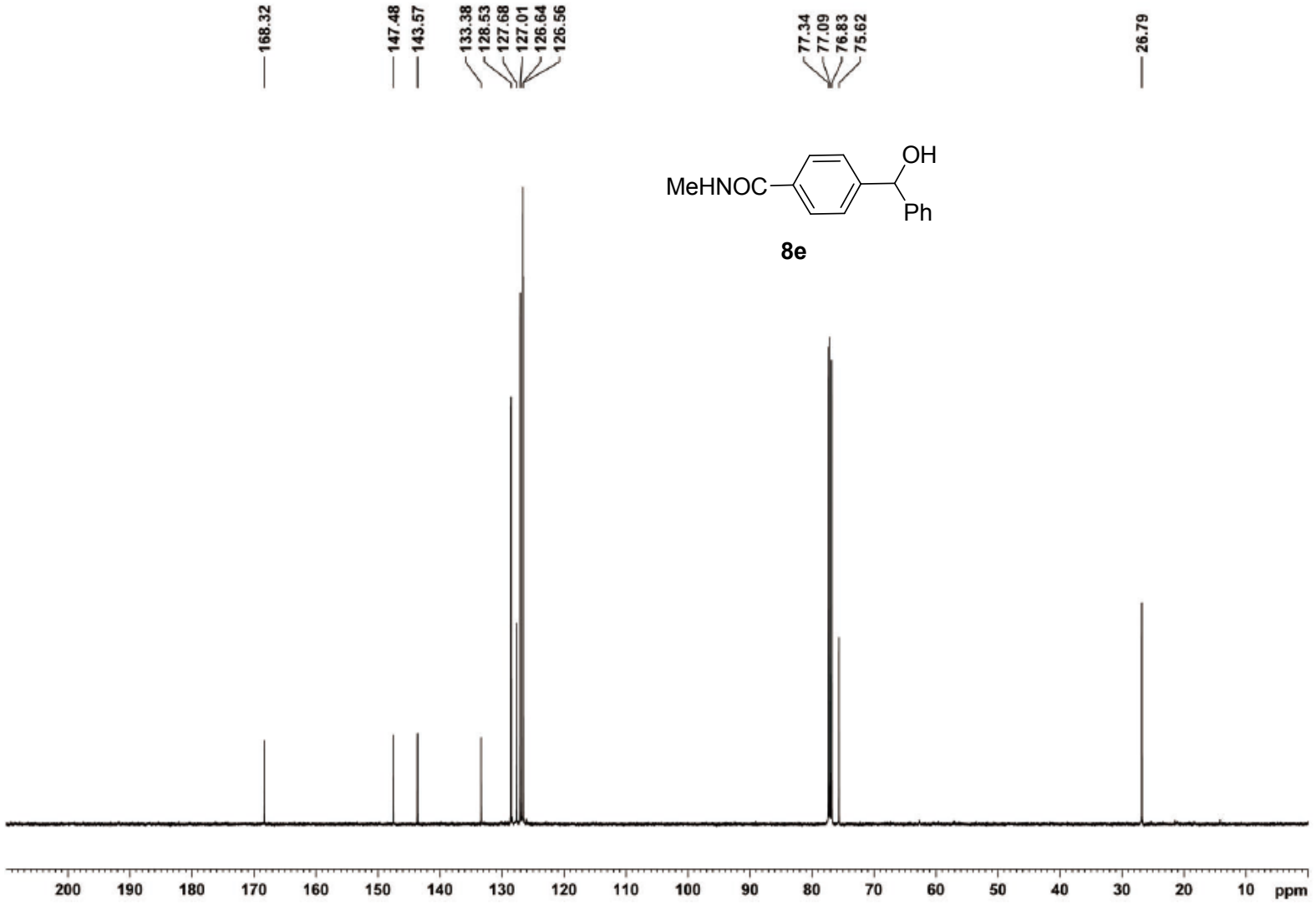
7.5854
7.3359
7.3155
7.3010
7.2957
7.2857
7.2664
7.2505
7.2445
7.2375
7.2289
6.5950
6.5834
5.7759
3.8466
2.8906
2.8786
MeHNOC
OH
Ph
9
8
7
6
5
4
3
2
1
ppm
2.04
7.59
0.96
1.00
1.05
3.09

8e


168.32
147.48
143.57
133.38
128.53
127.68
127.01
126.64
126.56
77.34
77.09
76.83
75.62
26.79
MeHNOC
OH
Ph
8e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

[10] Q.Yang, S. M. Ma, J. X. Li, F. S. Xiao, H. Xiong, *Chem. Commun.*, **2006**, *23*, 2495.

[11] S. E. Havlik, J. M. Simmons, V. J. Winton, J. B. Johnson, *J. Org. Chem*., **2011**, *76*(9), 3588.

[12] S. P. G. Costa, R. M. F. Batista, M. M. Maria, *Eur. J. Org. Chem*., **2006,** *17*, 3938.

[13] H. Li, Y. Xu, E. Shi, W. Wei, X-Q. Suo, X-B. Wan, *Chem. Commun.,* **2011**, *47*(27), 7880.

[14] M. Kuriyama, N. Ishiyama, R. Shimazawa, O. Onomura, *Tetrahedron*., **2010**, *66*, 6814.

[15] V. J. Shin, T. Yamamoto, T. Ohta, Y. Itoer, C. J. Verbanic, *J. Am. Chem. Soc.*, **1957**, *79*, 369.