Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

for

AsCat and FurCat: New Pd catalysts for selective room-temperature Stille cross-couplings of benzyl chlorides with organostannanes

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Detailed experimental procedures, characterisation data and ^{1}H and ^{13}C NMR spectra for compounds 5a–q, *E*-7, *Z*-7, 10a and 10b.

1. General Experimental Details

Reagents were purchased from Sigma-Aldrich, Alfa Aesar, Acros Organics or Fluorochem and used as received unless otherwise noted. Dry dichloromethane was obtained dry from a Pure Solv MD-7 solvent machine and stored under nitrogen. Dry DMF was purchased from Acros Organics (<50 ppm water) and degassed by nitrogen bubbling and sonication prior to use. Petrol refers to the fraction of petroleum ether boiling in the range 40–60 °C.

Compounds **3c**,[1] **3d**,[2] ***Z*-4e**[3] and ***E*-4e**[3] were synthesised as described in the literature. Compound **3e** was synthesised from 4-cyanobenzaldehyde by reduction[4] followed by chlorination using a modified literature procedure.[5]

^{1}H NMR and ^{13}C NMR spectra were recorded on a Jeol ECX400 or Jeol ECS400 spectrometer operating at 400 and 100 MHz respectively, or on a Bruker AV500 operating at 500 and 125 MHz respectively. ^{31}P NMR spectra were recorded on a Jeol ECX400 spectrometer at 162 MHz. TLC analysis was carried out using Merck 5554 aluminium backed silica plates. Preparatory TLC was carried out using Analtech UNIPLATE glass-backed silica plates. Flash column chromatography was performed using SiO_2/K_2CO_3 (9:1, *w*/*w*) as the stationary phase[6] with the solvent systems specified within the text. Electrospray ionisation (ESI) mass spectrometry was performed on a Bruker daltronics micrOTOF spectrometer; electron impact (EI), atmospheric pressure chemical ionisation (APCI) and liquid induction field desorption ionisation (LIFDI) were performed on a Waters GCT Premier mass spectrometer. Less than 5 ppm error was recorded for all HRMS samples. Infrared (IR) spectroscopy was performed on a PerkinElmer Spectrum Two spectrometer using an UATR attachment. Melting point analyses were performed on a Stuart SMP3 melting point apparatus, using a temperature ramp of 3 °C/minute. UV–visible spectroscopy was performed on a Jasco V-560 spectrometer, with a background taken in the appropriate solvent prior to recording spectra. Elemental analysis was carried out using an Exeter Analytical CE-440 Elemental Analyser.

2. General Procedures

General procedure 1: synthesis of complexes 1 and 2:

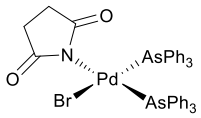
An oven-dried Schlenk tube (under N_2) was charged with a stirrer bar, the appropriate ligand (0.388 mmol), Pd_2dba_3•$CHCl_3$ (0.097 mmol) and dry CH_2Cl_2 (6 mL). The resulting solution was stirred for 10 min, before a solution of *N*-bromosuccinimide (0.193 mmol) in CH_2Cl_2 (3 mL) was added. After another 10 min the reaction mixture was poured into petroleum ether (20 mL), and additional petroleum ether (200 mL) was added. No special precautions for the exclusion of air were made during the reaction workup. The resulting precipitate was collected by filtration and dried *in vacuo*.

General procedure 2: Stille cross-coupling reactions

To a solution of the appropriate catalyst (5.84 μmol, 0.05 eq.) and benzyl halide (0.117 mmol, 1 eq.) in dry DMF (1.5 mL) under N_2 in a Schlenk tube was added the appropriate stannane (0.176 mmol, 1.5 eq.). The reaction vessel was sealed and stirred at room temperature for the required time. After this time the solution was diluted with diethyl ether (20 mL), washed with water (3 × 10 mL), dried ($MgSO_4$) and evaporated. No special precautions for the exclusion of air were made during the reaction workup. When purification was performed, it was done using flash column chromatography with a SiO_2/K_2CO_3 (9:1, *w*/*w*) stationary phase.

3. Compound Characterisation Data

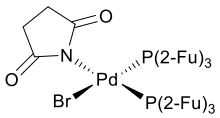
***cis*-Bromobis(triphenylarsine)(*N*-succinimide)palladium(II) (1)**



Prepared using general procedure 1 (L = $AsPh_3$), affording the *title compound* as a light brown powder (179.5 mg, 52%).

M.P. 108–112 °C (dec.); IR (ATR)/cm^{-1} 1715w, 1637s, 1482w, 1436m, 1349m, 1235m, 1078w, 999w, 736s, 691s, 482s, 468w; ^{1}H NMR (400 MHz, $CDCl_3$, *cis*:*trans* = *ca*. 4:1) 7.75 (dd, *J* = 7.9, 1.7 Hz), 7.59–7.54 (m), 7.46–7.33 (m), 7.33–7.19 (m), 7.20–7.12 (m), 2.37–2.29 (m, 2H, *cis*), 1.63–1.56 (m, 2H, *cis*), 1.29 (s, 4H, *trans*); UV–Vis (CH_2Cl_2, nm) λ_{max} 288 (ε = 18040 mol dm^{-3} cm^{-1}); MS (LIFDI$^+$) *m*/*z* 896.88 ([M]$^+$); Elemental anal.: C: 52.21, H: 3.76, N: 1.49, $C_{40}H_{34}As_2BrNO_2Pd$•$0.24C_4H_4O_2NBr$ requires C: 52.45, H: 3.76, N: 1.83 (this ratio has been corroborated by ^{1}H NMR spectroscopy).

***cis*-Bromobis(tri(2-furyl)phosphine)(*N*-succinimide)palladium(II) (2)**

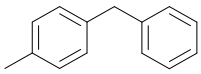


Prepared using general procedure 1 (L = $P(2\text{-Fu})_3$), affording the *title compound* as a light brown powder (123.7 mg, 85%).

M.P. 90–93 °C (dec.); IR (ATR)/cm^{-1} 1712w, 1633m, 1455w, 1350w, 1235m, 1215m, 1125m, 1010s, 752s, 590m, 535s, 503s; ^{1}H NMR (400 MHz, CD_2Cl_2, *cis*:*trans* = *ca*. 9:1) 7.76–7.74 (m, 6H, *trans*), 7.65 (td, *J* = 1.9, 0.7 Hz, 3H, *cis*), 7.51 (td, *J* = 1.8, 0.7 Hz, 3H, *cis*), 7.30 (dd, *J* = 3.6, 1.0 Hz, 6H, *trans*), 7.12 (ddd, *J* = 3.5, 2.5, 0.7, 3H, *cis*), 7.03–6.99 (m, 3H, *cis*), 6.57 (ddd,

J = 3.6, 1.9, 1.0 Hz, 6H, *trans*), 6.47 (dt, *J* = 3.4, 1.6 Hz, 3H, *cis*), 6.42 (dt, *J* = 3.4, 1.6 Hz, 3H, *cis*), 2.42–2.34 (m, 2H, *cis*), 2.17–2.09 (m, 2H, *cis*), 1.92 (s, 4H, *trans*); ^{31}P NMR (162 MHz, CD_2Cl_2) −25.7 (d, *J* = 13.5 Hz, *cis*), −26.6 (d, *J* = 13.5 Hz, *cis*), −32.0 (s, *trans*); UV–Vis (CH_2Cl_2, nm) λ_{max} 296 (ε = 14720 mol dm^{-3} cm^{-1}); MS (LIFDI$^+$) *m*/*z* 748.91 ([M]$^+$); Elemental anal.: C: 44.56, H: 2.97, N: 1.70; $C_{28}H_{22}BrNO_8P_2Pd$ requires C: 44.91, H: 2.96, N: 1.87.

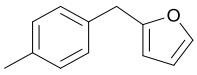
1-Benzyl-4-methylbenzene[7] (5a)



Title compound was synthesised using general procedure 2, isolated after flash chromatography (petrol) as a colourless oil (18.8 mg, 88%).

R_f: 0.56 (ether/petrol, 1:99, *v*/*v*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.26 (m, 2H), 7.22–7.17 (m, 3H), 7.10 (s, 4H), 3.95 (s, 2H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.6, 138.2, 135.7, 129.3, 129.0, 128.9, 128.6, 126.1, 41.7, 21.2; MS (EI$^+$) *m*/*z* (rel. %) 182 ([M]$^+$, 75), 167 ([M−Me]$^+$, 100).

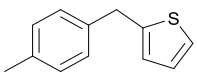
2-[(4-Methylphenyl)methyl]furan[8] (5b)



Title compound was synthesised using general procedure 2, isolated after flash chromatography (petrol) as a colourless oil (16.7 mg, 83%).

R_f: 0.70 (ether/petrol, 1:9, *v*/*v*); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.30 (m, 1H), 7.13 (s, 4H), 6.33–6.26 (m, 1H), 6.00 (d, *J* = 2.6 Hz, 1H), 3.94 (s, 2H), 2.34 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.0, 141.6, 136.1, 135.2, 129.3, 128.7, 110.3, 106.2, 34.2, 21.2; MS (EI$^+$) *m*/*z* (rel. %) 172 ([M]$^+$, 100), 157 ([M−Me]$^+$, 75); HRMS (EI$^+$) 172.0888 [M]$^+$, $C_{12}H_{12}O$ requires 172.0888.

2-[(4-Methylphenyl)methyl]thiophene[8] (5c)

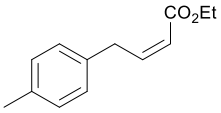


Title compound was synthesised using general procedure 2, isolated after flash chromatography (petrol) as a colourless oil (21.3 mg, 97%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18–7.10 (m, 5H), 6.98–6.87 (m, 1H), 6.80 (d, *J* = 2.6 Hz, 1H), 4.12 (s, 2H), 2.34 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.6, 137.5, 136.1, 129.4, 128.6,

126.9, 125.1, 124.0, 35.8, 21.2; MS (EI$^+$) *m*/*z* (rel. %) 188 ([M]$^+$, 100), 187 ([M−H]$^+$, 50), 173 ([M−Me]$^+$, 75); HRMS (EI$^+$) 188.0655 [M]$^+$, $C_{12}H_{12}S$ requires 188.0660.

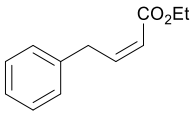
Ethyl (2*Z*)-4-(4-methylphenyl)but-2-enoate (5e)



Title compound was synthesised using general procedure 2, isolated after flash chromatography (diethyl ether/petrol, 5:95, *v*/*v*) as a colourless oil (19.9 mg, 83%).

R_f: 0.26 (ether/petrol, 1:19, *v*/*v*); IR (thin film)/cm^{-1} 2981m, 1717s, 1643m, 1514m, 1410m, 1387w, 1298w, 1192s, 1162s, 1096w, 1040m, 925w, 807m, 504w, 476w; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (s, 4H), 6.33 (dt, *J* = 11.4, 7.6 Hz, 1H), 5.83 (dt, *J* = 11.4, 1.7 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.98 (dd, *J* = 7.6, 1.7 Hz, 2H), 2.32 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.6, 148.4, 136.6, 136.0, 129.4, 128.6, 119.9, 60.1, 34.9, 21.2, 14.4; MS (ESI$^+$) *m*/*z* (rel. %) 227 ([M+Na]$^+$, 100), 205 ([M+Na]$^+$, 15); HRMS (ESI$^+$) 227.1034 [M+Na]$^+$, $C_{13}H_{16}NaO_2$ requires 227.1043.

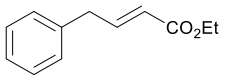
Ethyl (2*Z*)-4-phenylbut-2-enoate[9] (*Z*-7)



Title compound was synthesised using general procedure 2, isolated after flash chromatography (diethyl ether/petrol, 1:9, *v*/*v*) as a colourless oil (20.2 mg, 91%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.27 (m, 2H), 7.25–7.19 (m, 3H), 6.35 (dt, *J* = 11.4, 7.6 Hz, 1H), 5.35 (dt, *J* = 11.4, 1.8 Hz, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 4.03 (dd, *J* = 7.6, 1.8 Hz, 2H), 1.31 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 148.1, 139.6, 128.8 (2 × CH, overlapping), 126.5, 120.1, 60.2, 35.3, 14.4; MS (ESI$^+$) *m*/*z* (rel. %) 213 ([M+Na]$^+$, 100), 191 ([M+H]$^+$, 60); HRMS (ESI$^+$) 213.0880 [M+Na]$^+$, $C_{12}H_{14}NaO_2$ requires 213.0886.

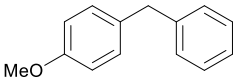
Ethyl (2*E*)-4-phenylbut-2-enoate[9] (*E*-7)



Title compound was synthesised using general procedure 2, isolated after flash chromatography (diethyl ether/petrol, 1:9, *v*/*v*) as a colourless oil (19.8 mg, 89%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.29 (m, 2H), 7.27–7.21 (m, 1H), 7.18 (ddt, *J* = 7.4, 1.3, 0.6 Hz, 2H), 7.10 (dt, *J* = 15.6, 6.8 Hz, 1H), 5.81 (dt, *J* = 15.6, 1.7 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.52 (dd, *J* = 6.8, 1.7 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 147.4, 137.9, 129.0, 126.8, 122.5, 60.4, 38.6, 14.4; MS (ESI$^+$) *m*/*z* (rel. %) 213 ([M+Na]$^+$, 100), 191 ([M+H]$^+$, 50); HRMS (ESI$^+$) 213.0883 [M+Na]$^+$, $C_{12}H_{14}NaO_2$ requires 213.0886.

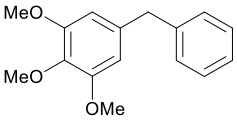
1-Benzyl-4-methoxybenzene[10] (5f)



Title compound was synthesised using general procedure 2, isolated after flash chromatography (petrol) as a colourless oil (21.3 mg, 92%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.26 (m, 2H), 7.23–7.15 (m, 3H), 7.13–7.09 (m, 2H), 6.86–6.81 (m, 2H), 3.93 (s, 2H), 3.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1, 141.7, 133.4, 130.0, 129.0, 128.6, 126.1, 114.0, 55.4, 41.2; MS (EI$^+$) *m*/*z* (rel. %) 198 ([M]$^+$, 100), 197 ([M−H]$^+$, 45), 167 ([M−OMe]$^+$, 40), 121 ([M−Ph]$^+$, 25); HRMS (EI$^+$) 198.1053 [M]$^+$, $C_{14}H_{14}O$ requires 198.1045.

5-Benzyl-1,2,3-trimethoxybenzene (5g)

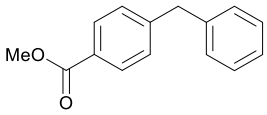


Title compound was synthesised using general procedure 2, isolated after flash chromatography (diethyl ether/petrol, 2:98, *v*/*v*) as a colourless oil (25.1 mg, 83%).

R_f: 0.24 (ether/petrol, 3:7, *v*/*v*); IR (thin film)/cm^{-1} 2936m, 2837w, 1589m, 1505m, 1495m, 1452m, 1420m, 1329m, 1236s, 1183w, 1124s, 1009m, 970w, 844w, 782w, 702m, 593w; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.25 (m, 2H), 7.27–7.16 (m, 3H), 6.40 (s, 2H), 3.93 (s, 2H), 3.82 (s, 3H), 3.81 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.3, 141.0, 136.9, 128.9, 128.6,

126.3, 106.1, 61.0, 56.2, 42.4; MS (ESI$^+$) *m*/*z* (rel. %) 281 ([M+Na]$^+$, 100), 259 ([M+H]$^+$, 60); HRMS (ESI$^+$) 259.1320 [M+H]$^+$, $C_{16}H_{19}O_3$ requires 259.1329.

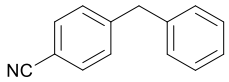
Methyl 4-benzylbenzoate[7] (5h)



Title compound was synthesised using general procedure 2, isolated after flash chromatography (diethyl ether/petrol, 3:97 → 5:95, *v*/*v*) as a colourless oil (17.8 mg, 67%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.33–7.20 (m, 3H), 7.22–7.13 (m, 2H), 4.03 (s, 2H), 3.90 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 146.7, 140.3, 130.0, 129.1, 128.7, 128.2, 126.5, 52.2, 42.1; MS (ESI$^+$) *m*/*z* (rel. %) 249 ([M+Na]$^+$, 100), 227 ([M+Na]$^+$, 15); HRMS (ESI$^+$) 249.0882 [M+Na]$^+$, $C_{15}H_{14}NaO_2$ requires 249.0886.

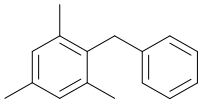
4-Benzylbenzonitrile[11] (5i)



Title compound was synthesised using general procedure 2 (with a reaction temperature of 40 °C), isolated after flash chromatography (diethyl ether/petrol, 2:98 → 5:95, *v*/*v*) as a colourless oil (21.3 mg, 94%).

R_f: 0.36 (ether/petrol, 1:9, *v*/*v*); IR (thin film)/cm^{-1} 3029w, 2922w, 2227s, 1603m, 1495m, 1454m, 1414m, 1261w, 1177w, 1074w, 1021m, 915w, 855m, 797s, 761s, 725s, 698s, 593s, 543s, 494m; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63–7.52 (m, 2H), 7.36–7.19 (m, 5H), 7.18–7.09 (m, 2H), 4.03 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.9, 139.5, 132.5, 129.8, 129.1, 128.9, 126.8, 119.1, 110.2, 42.1; MS (APCI$^+$) *m*/*z* (rel. %) 206 ([M+H]$^+$, 100); HRMS (APCI$^+$) 194.0957 [M+H]$^+$, $C_{14}H_{12}N$ requires 194.0964.

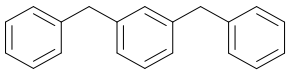
2-Benzyl-1,3,5-trimethylbenzene[12] (5j)



Title compound was synthesised using general procedure 2, isolated after flash chromatography (petrol) and preparatory thin layer chromatography (*n*-pentane) as a colourless oil (17.8 mg, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.17 (m, 2H), 7.20–7.10 (m, 1H), 7.06–6.97 (m, 2H), 6.89 (s, 2H), 4.02 (s, 2H), 2.30 (s, 3H), 2.21 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.2, 137.2, 135.8, 133.9, 129.0, 128.5, 128.0, 125.8, 34.8, 21.1, 20.3; MS (EI$^+$) *m*/*z* (rel. %) 210 ([M]$^+$, 75), 195 ([M−Me]$^+$, 100), 180 ([M−2Me]$^+$, 25), 165 ([M−3Me]$^+$, 20); HRMS (EI$^+$) 210.1413 [M]$^+$, $C_{16}H_{18}$ requires 210.1409.

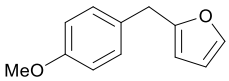
1,3-Dibenzylbenzene[13] (5k)



Title compound was synthesised using general procedure 2, isolated after flash chromatography (petrol) as a colourless oil (24.0 mg, 79%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.26 (m, 4H), 7.23–7.16 (m, 7H), 7.06 (t, *J* = 1.8 Hz, 1H), 7.02 (dd, *J* = 7.6, 1.8 Hz, 2H), 3.95 (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 141.3, 129.8, 129.1, 128.7, 128.6, 126.9, 126.2, 42.0; MS (EI$^+$) *m*/*z* (rel. %) 258 ([M]$^+$, 75), 167 ([M−CH_2Ph]$^+$, 100); HRMS (EI$^+$) 258.1416 [M]$^+$, $C_{20}H_{18}$ requires 258.1409.

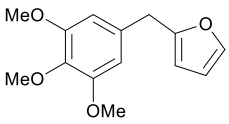
2-[(4-Methoxyphenyl)methyl]furan[14] (5l)



Title compound was synthesised using general procedure 2, isolated after flash chromatography (diethyl ether/petrol, 1:99, *v*/*v*) as a colourless oil (19.6 mg, 89%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 1.9, 0.9 Hz, 1H), 7.16 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.29 (dd, *J* = 3.2, 1.9 Hz, 1H), 5.98 (dd, *J* = 3.2, 0.9 Hz, 1H), 3.92 (s, 2H), 3.80 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.4, 155.2, 141.5, 130.3, 129.8, 114.1, 110.3, 106.1, 55.4, 33.8; MS (EI$^+$) *m*/*z* (rel. %) 188 ([M]$^+$, 100), 173 ([M−Me]$^+$, 10), 157 ([M−MeO]$^+$, 20); HRMS (EI$^+$) 188.0840 [M]$^+$, $C_{12}H_{12}O_2$ requires 188.0837.

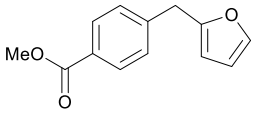
2-[(3,4,5-Trimethoxyphenyl)methyl]furan (5m)



Title compound was synthesised using general procedure 2, isolated after flash chromatography (diethyl ether/petrol, 1:9, *v*/*v*) as a colourless oil (22.3 mg, 77%).

R_f: 0.22 (ether/petrol, 3:7, *v*/*v*); IR (thin film)/cm^{-1} 2938w, 2838w, 1590m, 1505m, 1457m, 1421m, 1334m, 1236s, 1183w, 1122s, 1008s, 970w, 806w, 729m, 650w, 660w, 528w; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 1.9, 0.9 Hz, 1H), 6.45 (s, 2H), 6.31 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.05 (dd, *J* = 3.2, 0.9 Hz, 1H), 3.91 (s, 2H), 3.83 (s, 6H), 3.82 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.5, 153.4, 141.7, 136.7, 133.9, 110.4, 106.5, 105.8, 61.0, 56.2, 34.9; MS (ESI$^+$) *m*/*z* (rel. %) 271 ([M+Na]$^+$, 100), 249 ([M+H]$^+$, 55); HRMS (ESI$^+$) 271.0948 [M+Na]$^+$, $C_{14}H_{16}NaO_4$ requires 271.0941.

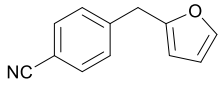
Methyl 4-(furan-2-ylmethyl)benzoate (5n)



Title compound was synthesised using general procedure 2, isolated after flash chromatography (diethyl ether/petrol, 3:97 → 5:95, *v*/*v*) as a colourless oil (18.8 mg, 74%).

R_f: 0.16 (ether/petrol, 1:19, *v*/*v*); IR (thin film)/cm^{-1} 2952w, 1718s, 1612m, 1506w, 1435m, 1417m, 1277s, 1178m, 1150w, 1105s, 1020m, 1011m, 939w, 794w, 727s, 600m, 491w; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.2 Hz, 2H), 7.35–7.32 (m, 1H), 7.30 (d, *J* = 8.2 Hz, 2H), 6.31–6.29 (m, 1H), 6.03 (d, *J* = 2.7 Hz, 1H), 4.02 (s, 2H), 3.90 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.1, 153.6, 143.6, 141.9, 130.0, 128.8, 128.6, 110.5, 106.8, 52.2, 34.6; MS (ESI$^+$) *m*/*z* (rel. %) 239 ([M+Na]$^+$, 100), 217 ([M+Na]$^+$, 30); HRMS (ESI$^+$) 239.0678 [M+Na]$^+$, $C_{13}H_{12}NaO_3$ requires 239.0679.

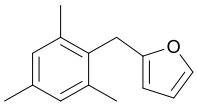
4-(Furan-2-ylmethyl)benzonitrile (5o)



Title compound was synthesised using general procedure 2 (with a reaction temperature of 40 °C), isolated after flash chromatography (diethyl ether/petrol, 2:98 → 4:96, *v*/*v*) as a colourless oil (18.6 mg, 87%).

R_f: 0.38 (ether/petrol, 1:9, *v*/*v*); IR (thin film)/cm^{-1} 2922w, 2229s, 1980w, 1715m, 1608s, 1505s, 1417m, 1150m, 1011s, 939m, 852m, 811s, 736s, 599m, 550s; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.57 (m, 2H), 7.34–7.30 (m, 3H), 6.31 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.06 (dq, *J* = 3.2, 0.9 Hz, 1H), 4.03 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.7, 143.9, 142.2, 132.5, 129.6, 119.0, 110.6, 110.5, 107.2, 34.6; MS (ESI$^+$) *m*/*z* (rel. %) 206 ([M+Na]$^+$, 100); HRMS (ESI$^+$) 206.0583 [M+Na]$^+$, $C_{12}H_9NNaO$ requires 206.0576.

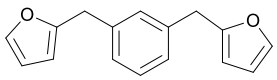
2-[(2,4,6-Trimethylphenyl)methyl]furan (5p)



Title compound was synthesised using general procedure 2, isolated after flash chromatography (petrol) as a colourless oil (19.5 mg, 83%).

R_f: 0.31 (petrol); IR (thin film)/cm^{-1} 2920m, 1614m, 1593m, 1506m, 1485m, 1446m, 1377w, 1168m, 1135w, 1074m, 1007s, 934w, 885w, 852m, 789m, 727s, 679w, 599m, 557w; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.28 (m, 1H), 6.87 (s, 2H), 6.23 (dd, *J* = 3.2, 1.9 Hz, 1H), 5.76 (dd, *J* = 3.2, 1.1 Hz, 1H), 3.94 (s, 2H), 2.30 (s, 6H), 2.28 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.2, 141.2, 137.0, 136.1, 131.6, 129.0, 110.2, 105.5, 28.4, 21.0, 20.0; MS (EI$^+$) *m*/*z* (rel. %) 200 ([M]$^+$, 100), 185 ([M−Me]$^+$, 75), 144 (50), 132 ([M−Fu−H]$^+$, 85); HRMS (EI$^+$) 200.1202 [M]$^+$, $C_{14}H_{16}O$ requires 200.1201.

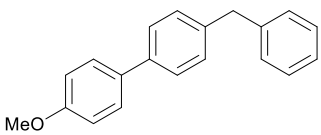
1,3-Di(furan-2-ylmethyl)benzene (5q)



Title compound was synthesised using general procedure 2, isolated after flash chromatography (diethyl ether/petrol, 1:99 → 2:98, *v*/*v*) as a colourless oil (24.8 mg, 89%).

R_f: 0.15 (petrol); IR (thin film)/cm^{-1} 2908w, 1592m, 1506m, 1446m, 1250w, 1449m, 1073m, 1009s, 939m, 884m, 798m, 719s, 599s; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 1.9, 0.9 Hz, 2H), 7.25–7.21 (m, 1H), 7.12–7.07 (m, 3H), 6.29 (dd, *J* = 3.2, 1.9 Hz, 2H), 5.99 (dd, *J* = 3.2, 0.9 Hz, 2H), 3.95 (s, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.6, 141.6, 138.5, 129.3, 128.8, 127.0, 110.4, 106.4, 34.5; MS (EI$^+$) *m*/*z* (rel. %) 238 ([M]$^+$, 100), 157 ([M−CH_2Fu]$^+$, 80); HRMS (EI$^+$) 238.0994 [M]$^+$, $C_{16}H_{14}O_2$ requires 238.0994.

1-Benzyl-4-(4-methoxyphenyl)benzene[15] (10a)

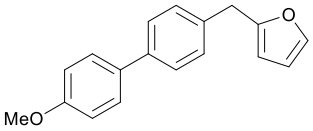


Reaction between 4-bromobenzyl chloride (1 eq.) and tributylphenylstannane (1.1 eq.) was conducted according to general procedure 2. At the end of the reaction time (24 h), 4-methoxybenzeneboronic acid (26.7 mg, 0.176 mmol) was added, followed by 2 M aq. Na_2CO_3 (1 mL) and the reaction heated to 60 °C for 20 h with vigorous stirring. After this time the work-

up was conducted according to general procedure 2 and purification by flash chromatography (diethyl ether/petrol, 1:199, *v*/*v*) and preparatory thin layer chromatography (diethyl ether/petrol, 1:9, *v*/*v*) afforded the *title compound* as a white solid (23.3 mg, 73%).

M.P. 93–95 °C (lit.[15] 100–101 °C); R_f: 0.24 (ether/petrol, 1:19, *v*/*v*); IR (thin film)/cm^{-1} 3027w, 2912w, 2838w, 1606m, 1582w, 1528w, 1498s, 1454m, 1402w, 1279m, 1250s, 1211m, 1179m, 1074w, 1037s, 1015m, 907s, 828s, 793s, 730s, 698s, 668m, 598m, 554w, 544w, 498m; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.9 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.33–7.27 (m, 2H), 7.26–7.20 (m, 5H), 6.96 (d, *J* = 8.9 Hz, 2H), 4.01 (s, 2H), 3.84 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.2, 141.2, 139.7, 138.8, 133.7, 129.4, 129.1, 128.6, 128.1, 126.9, 126.3, 114.3, 55.5, 41.7; MS (EI$^+$) *m*/*z* (rel. %) 274 ([M]$^+$, 100), 259 ([M−Me]$^+$, 15), 243 ([M−OMe]$^+$, 10), 197 ([M−Ph]$^+$, 10); HRMS (EI$^+$) 274.1348 [M]$^+$, $C_{20}H_{18}O$ requires 274.1358.

2-([4-(4-Methoxyphenyl)phenyl]methyl)furan (10b)



Reaction between 4-bromobenzyl chloride (1 eq.) and 2-(tributylstannyl)furan (1.1 eq.) was conducted according to general procedure 2. At the end of the reaction time (3 h), 4-methoxybenzeneboronic acid (26.7 mg, 0.176 mmol) was added, followed by 2 M aq. Na_2CO_3 (1 mL) and the reaction heated to 60 °C for 19 h with vigorous stirring. After this time the work-up was conducted according to general procedure 2 and purification by flash chromatography (diethyl ether/petrol, 1:99 → 2:98, *v*/*v*) afforded the *title compound* as a white solid (22.5 mg, 73%).

M.P. 93–94 °C; R_f: 0.25 (ether/petrol, 1:19, *v*/*v*); IR (thin film)/cm^{-1} 2962w, 2837w, 1607m, 1500s, 1291m, 1274m, 1254s, 1182m, 1150w, 1037s, 1011s, 937w, 908w, 816s, 759s, 733s, 601w, 505w; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.9 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.35 (dd, *J* = 1.9, 0.8 Hz, 1H), 7.28 (d, *J* = 8.1 Hz, 2H), 6.97 (d, *J* = 8.9 Hz, 2H), 6.31 (dd, *J* = 3.0, 1.9 Hz, 1H), 6.05 (dd, *J* = 3.0, 0.8 Hz, 1H), 4.00 (s, 2H), 3.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 154.7, 141.7, 139.2, 136.7, 133.6, 129.2, 128.2, 127.0, 114.3, 110.4, 106.4, 55.5, 34.2; MS (EI$^+$) *m*/*z* (rel. %) 264 ([M]$^+$, 100), 249 ([M−Me]$^+$, 10); HRMS (EI$^+$) 264.1147 [M]$^+$, $C_{18}H_{16}O_2$ requires 264.1150.

4. UV–Visible Spectroscopy data

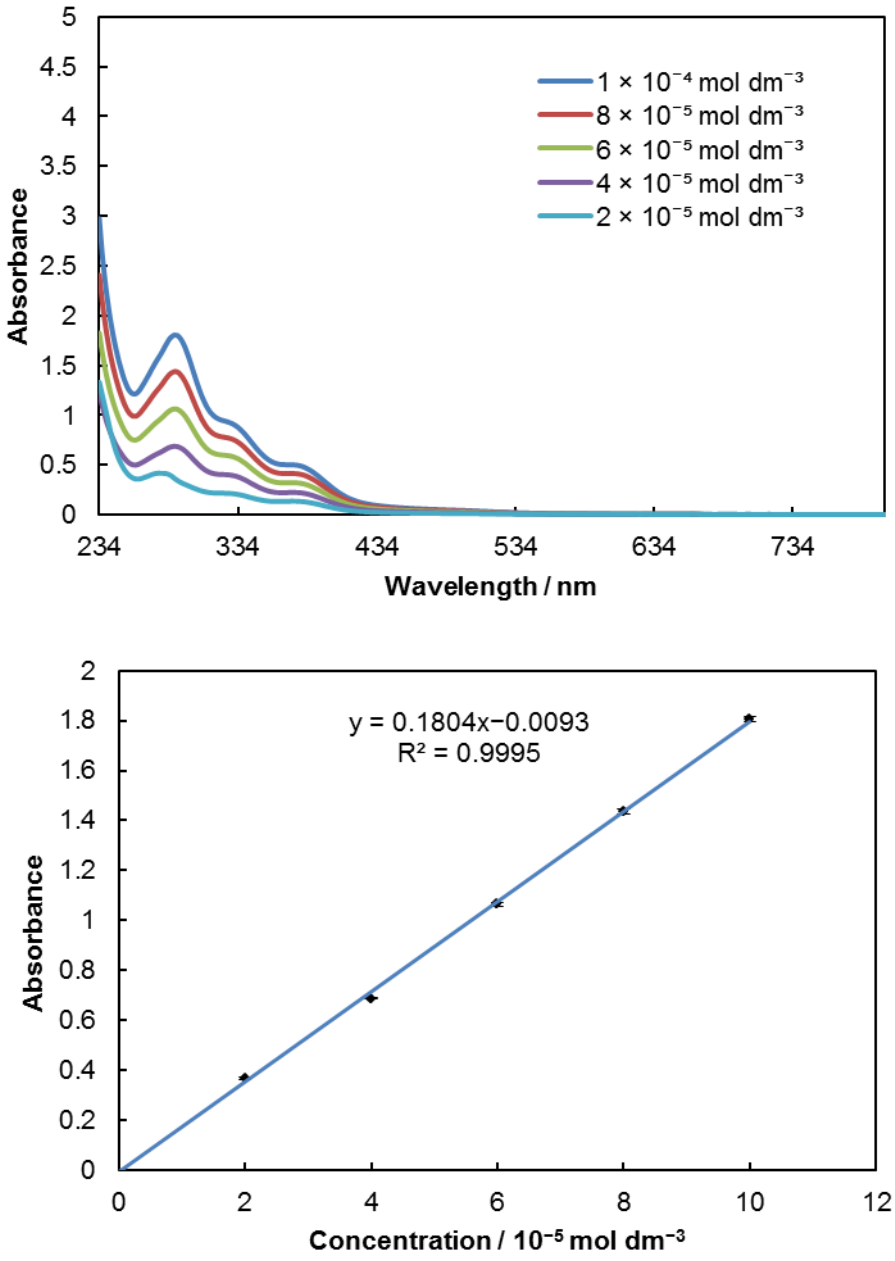


Figure S1 UV–visible spectroscopy data for compound **1**.

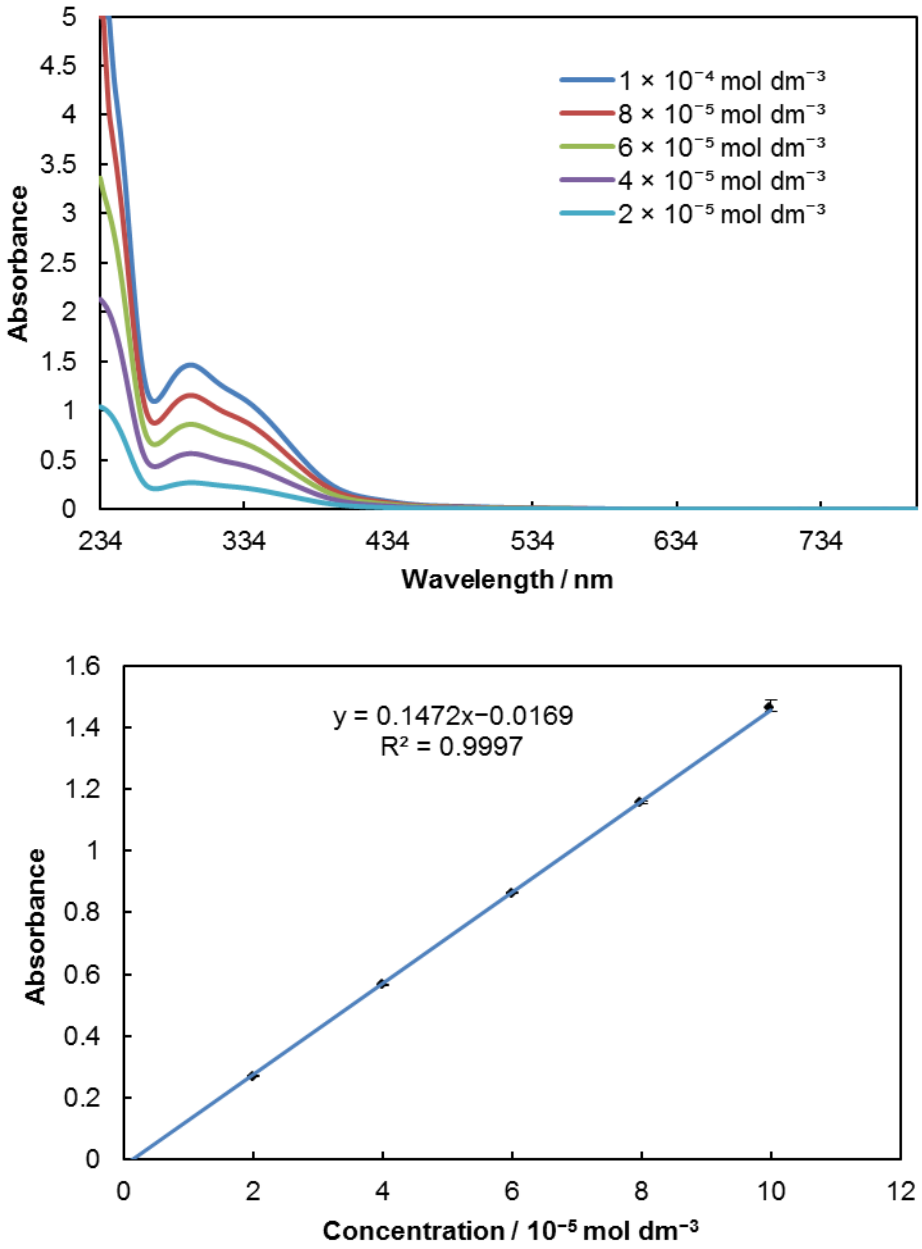


Figure S2 UV–visible spectroscopy data for compound **2**.

5. X-Ray Crystallography Data

Table S1 Crystal data and structure refinement for ijsf1401.

CCDC Number	CCDC 1036905
Identification code	ijsf1401
Empirical formula	$C_{40}H_{34}As_2BrNO_2Pd$
Formula weight	896.83
Temperature/K	110.05(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	12.2363(2)
b/Å	15.6103(3)
c/Å	19.0632(3)
α/°	90
β/°	105.4121(17)
γ/°	90
Volume/Å^3	3510.35(11)
Z	4
ρ_{calc}mg/mm^3	1.697
m/mm^{-1}	3.574
F(000)	1776.0
Crystal size/mm^3	0.2713 × 0.1255 × 0.0375
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection	5.664 to 60°
Index ranges	−17 ≤ h ≤ 13, −19 ≤ k ≤ 21, −26 ≤ l ≤ 25
Reflections collected	18231
Independent reflections	10230 [R_{int} = 0.0319, R_{sigma} = 0.0582]
Data/restraints/parameters	10230/0/424
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0405, wR_2 = 0.0798
Final R indexes [all data]	R_1 = 0.0699, wR_2 = 0.0933
Largest diff. peak/hole / e Å^{-3}	0.91/−0.99

6. References

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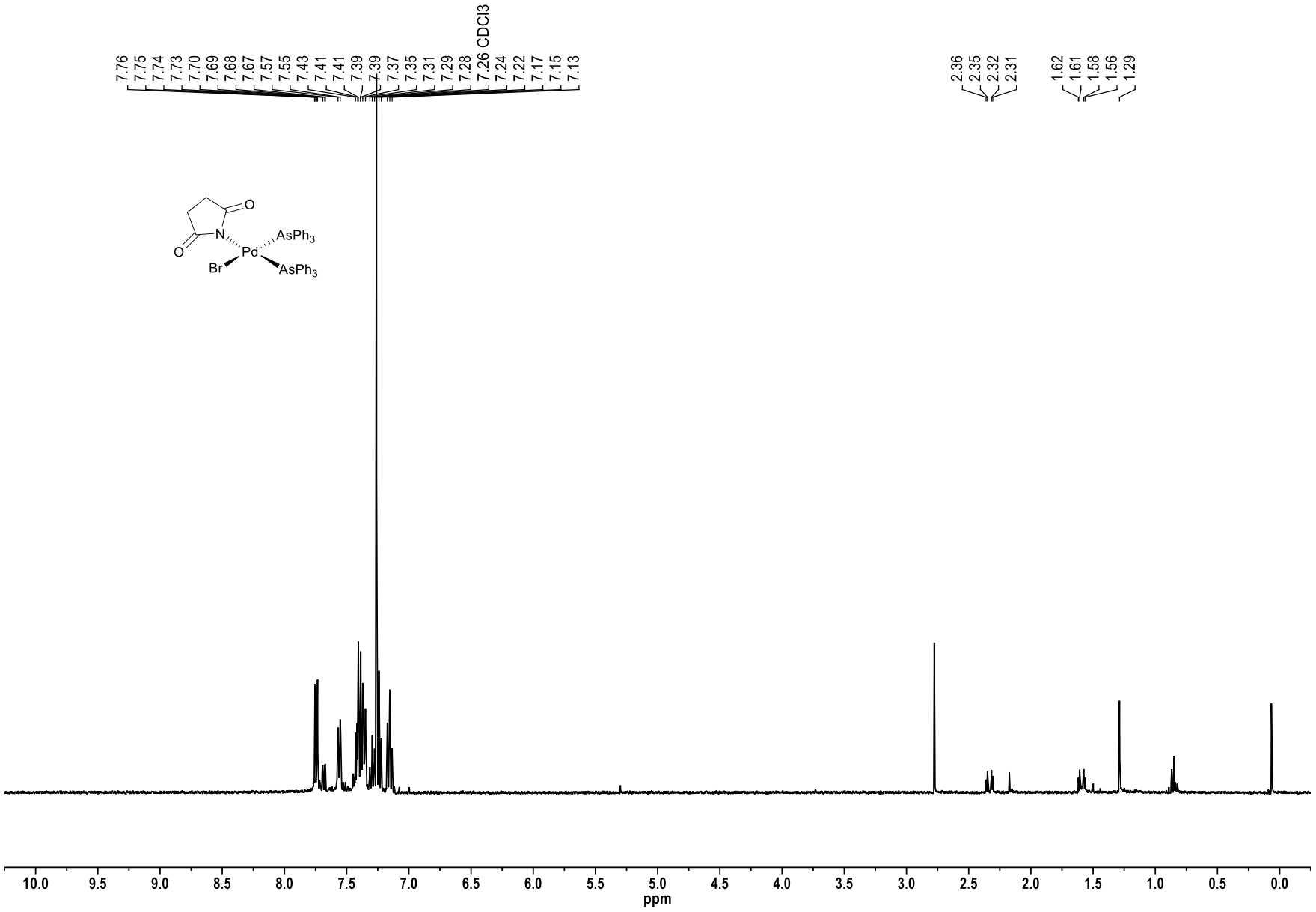
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2.31
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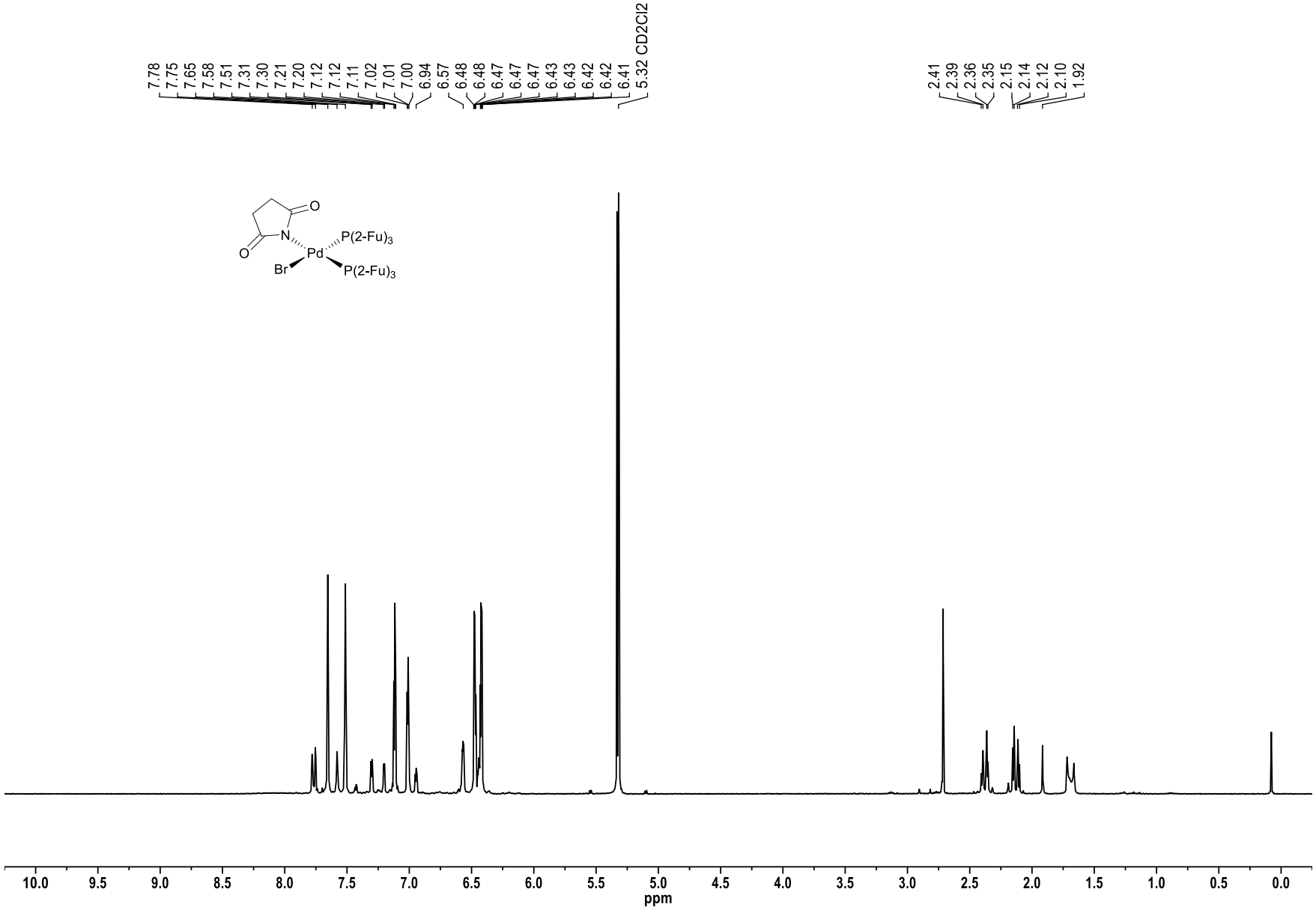
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2.12
2.10
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O
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N
Pd
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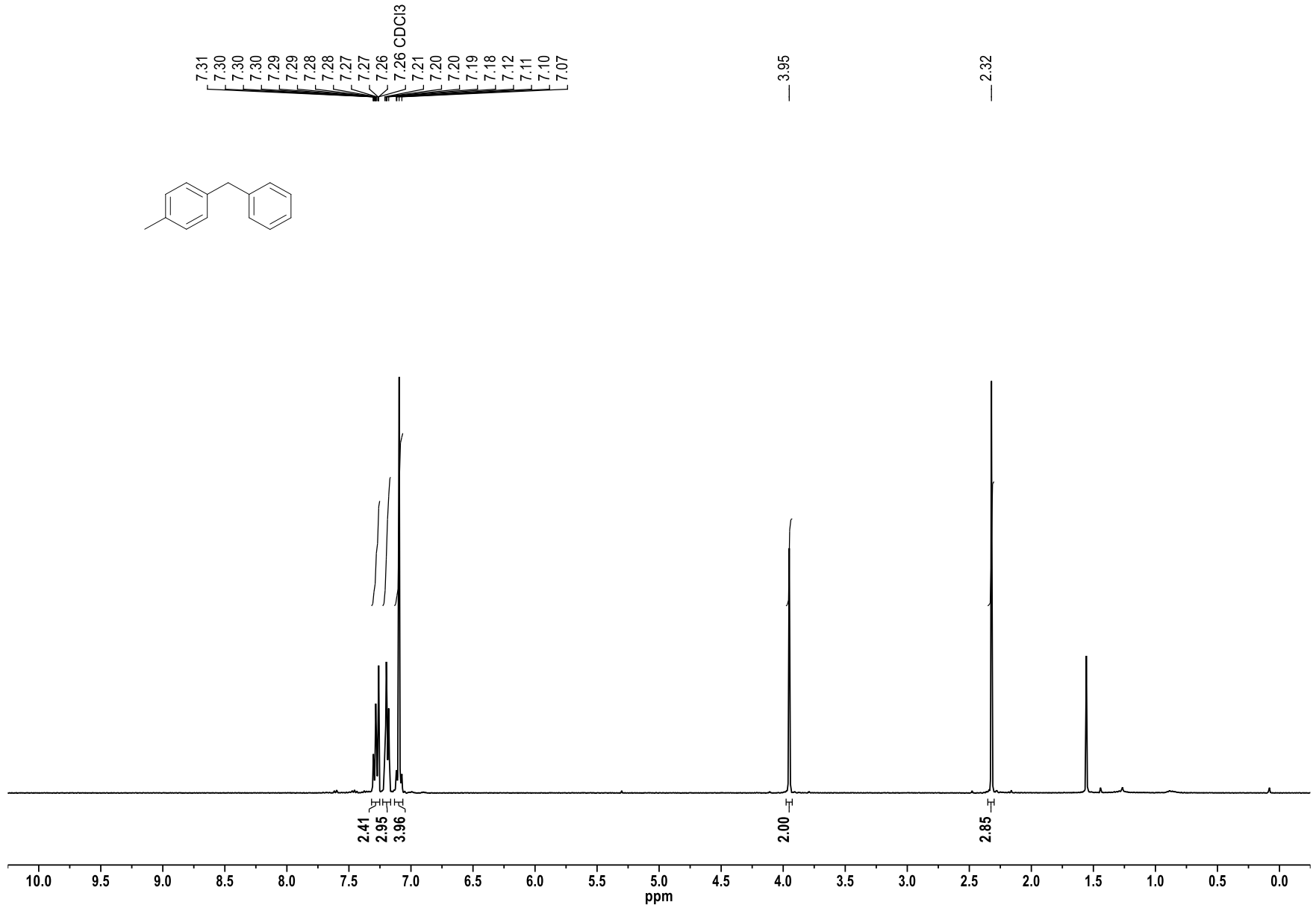
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7.12
7.11
7.10
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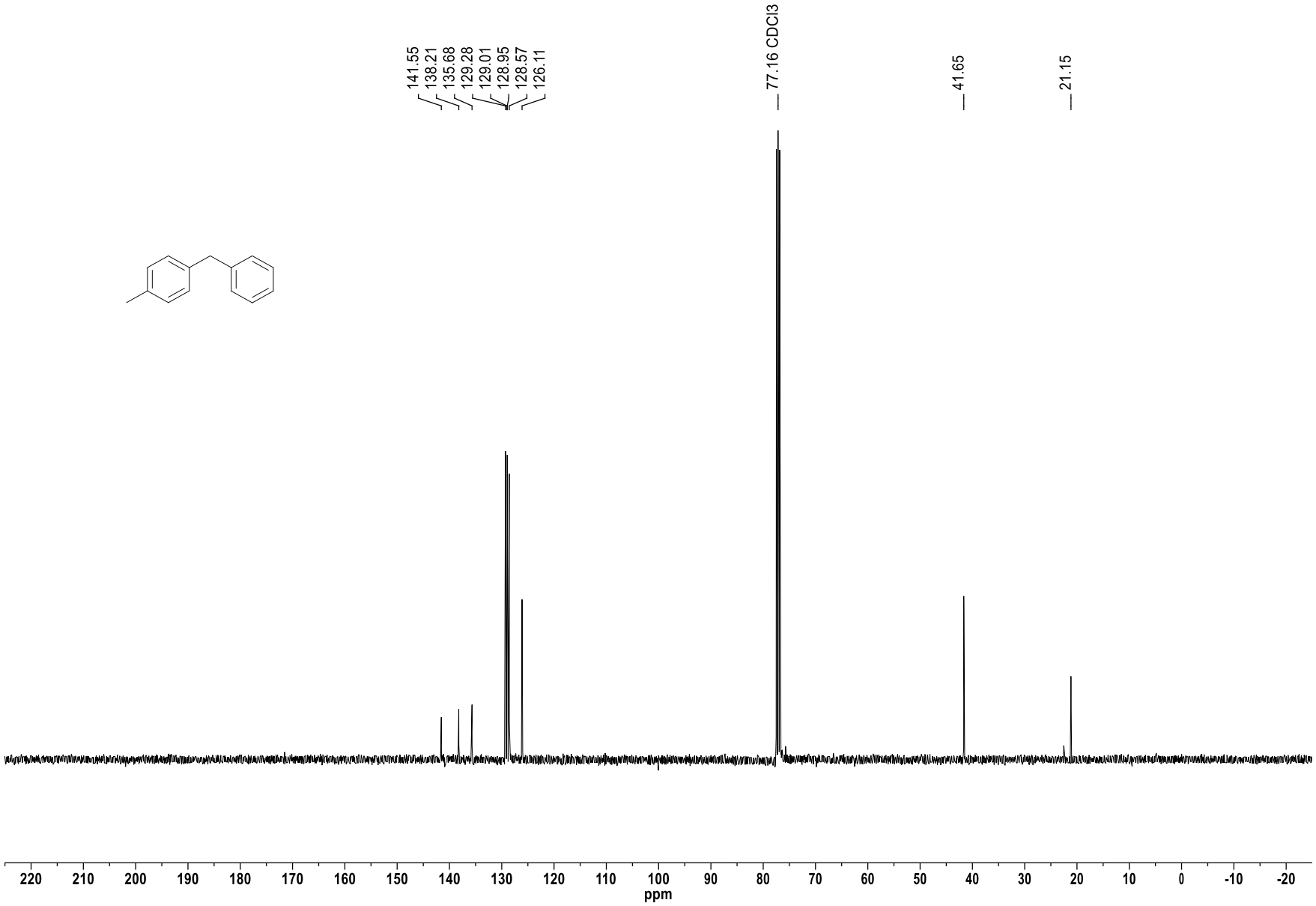
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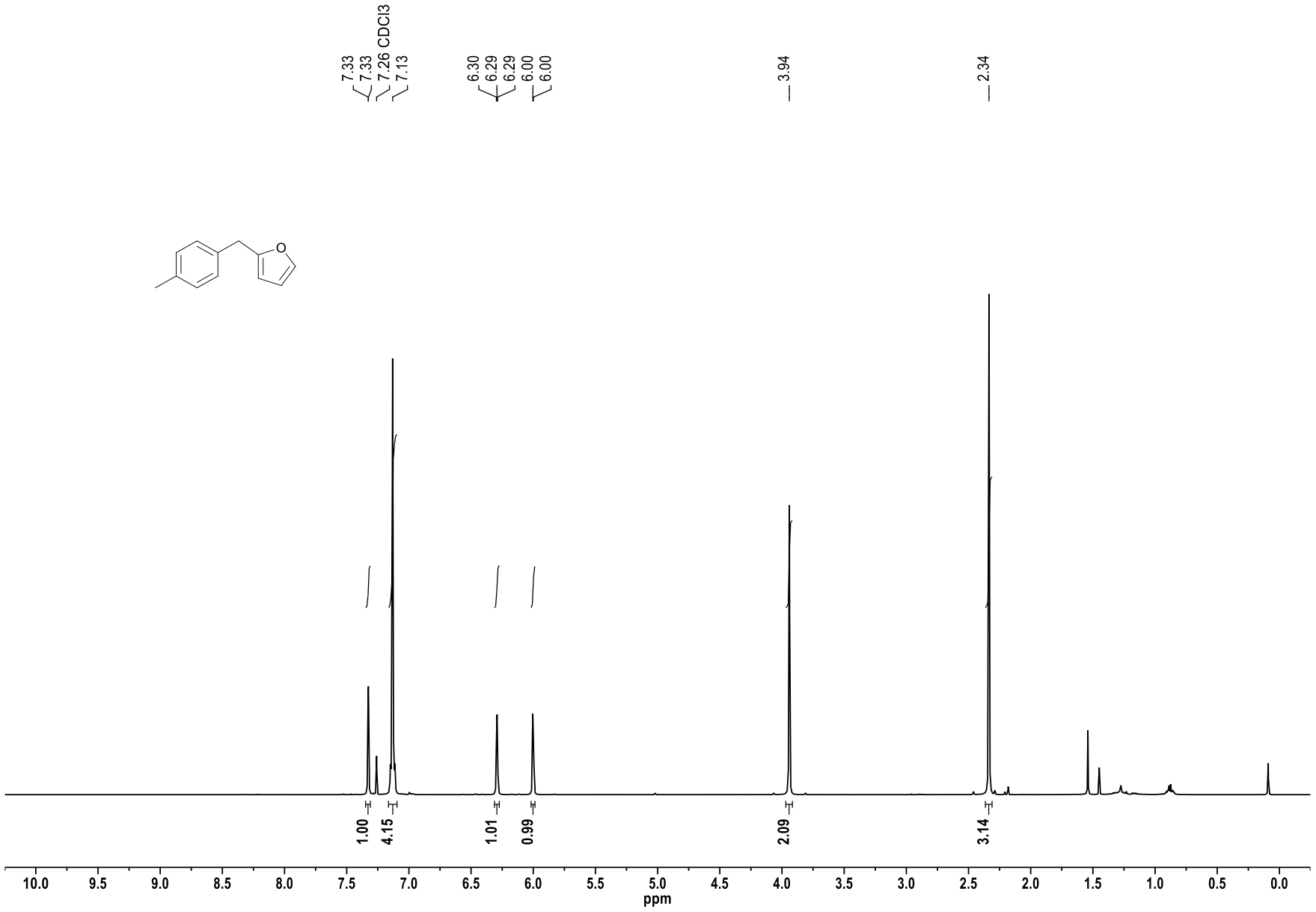
ppm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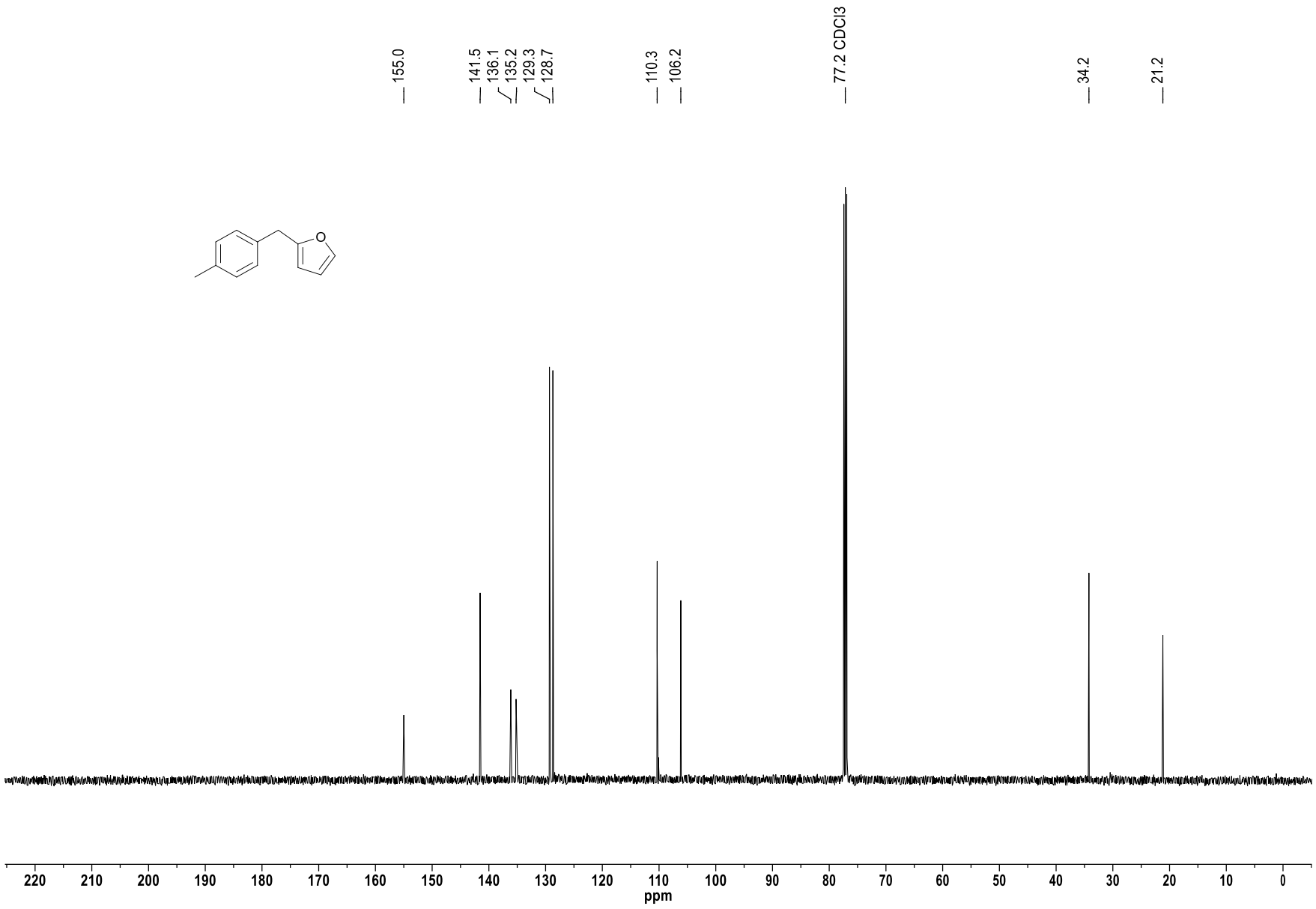
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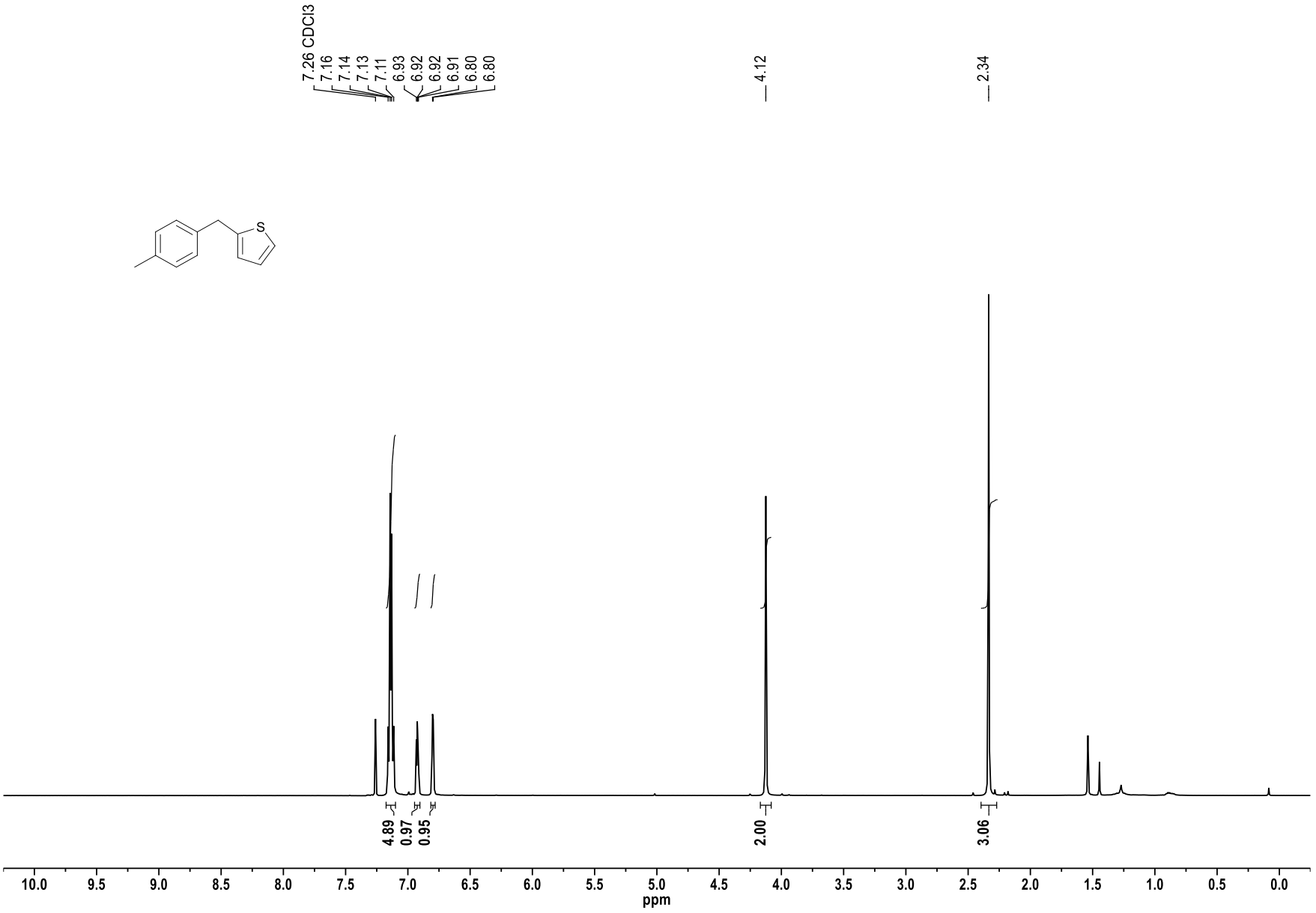
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S
4.89
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0.95
2.00
3.06
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8.0
7.5
7.0
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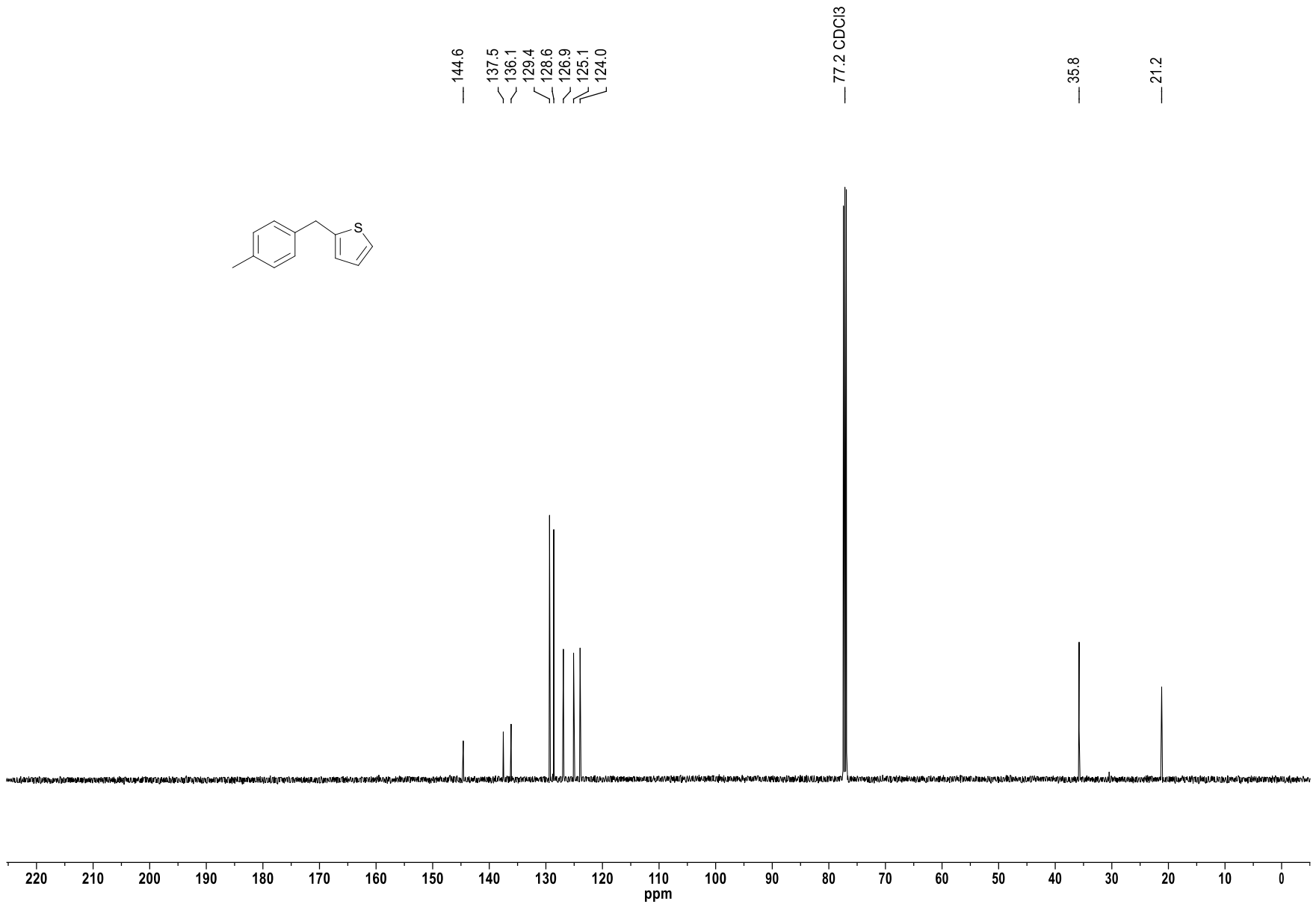
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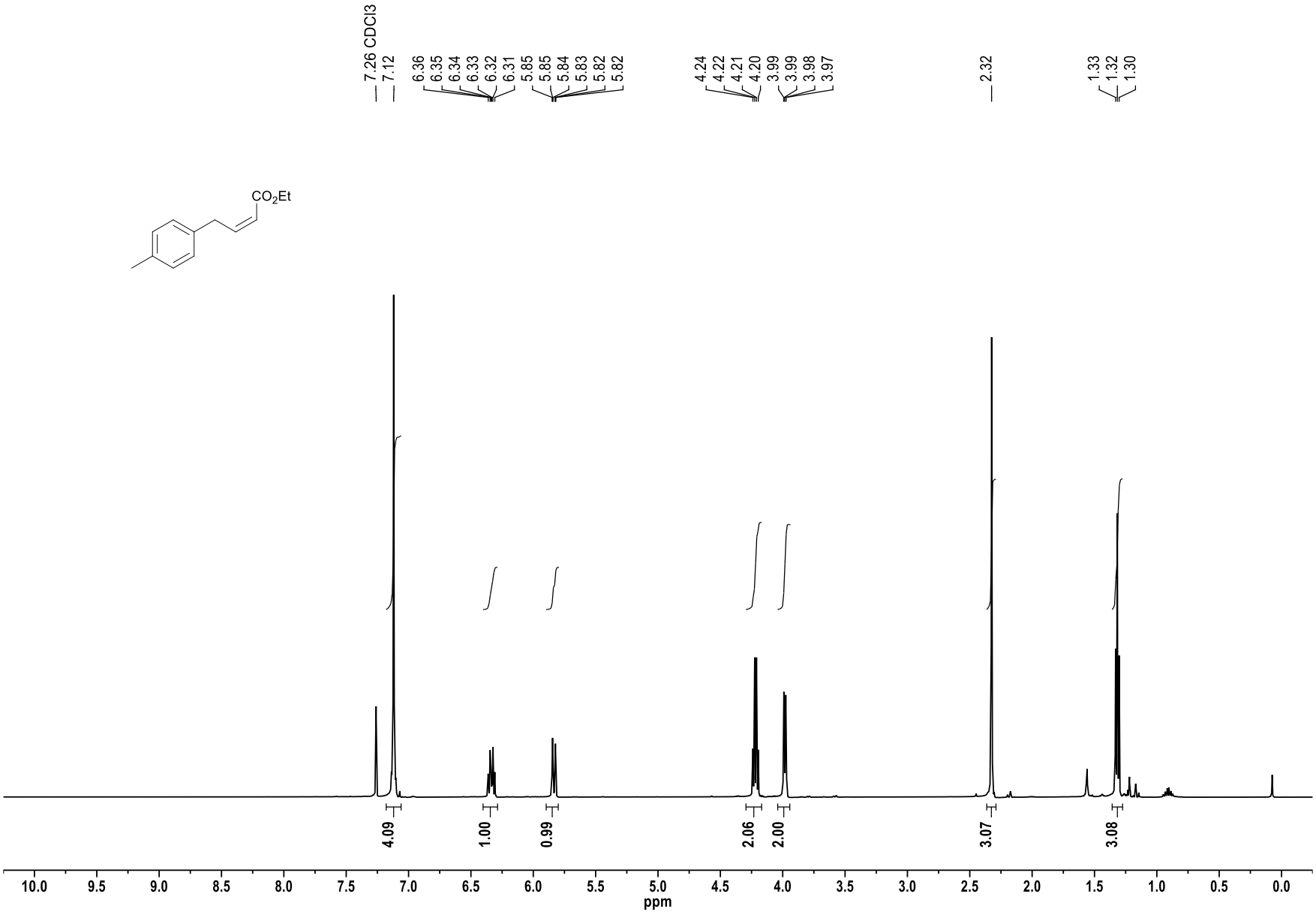
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5.83
5.82
5.82
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4.22
4.21
4.20
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3.99
3.98
3.97
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1.33
1.32
1.30
CO2Et
4.09
1.00
0.99
2.06
2.00
3.07
3.08
10.0
9.5
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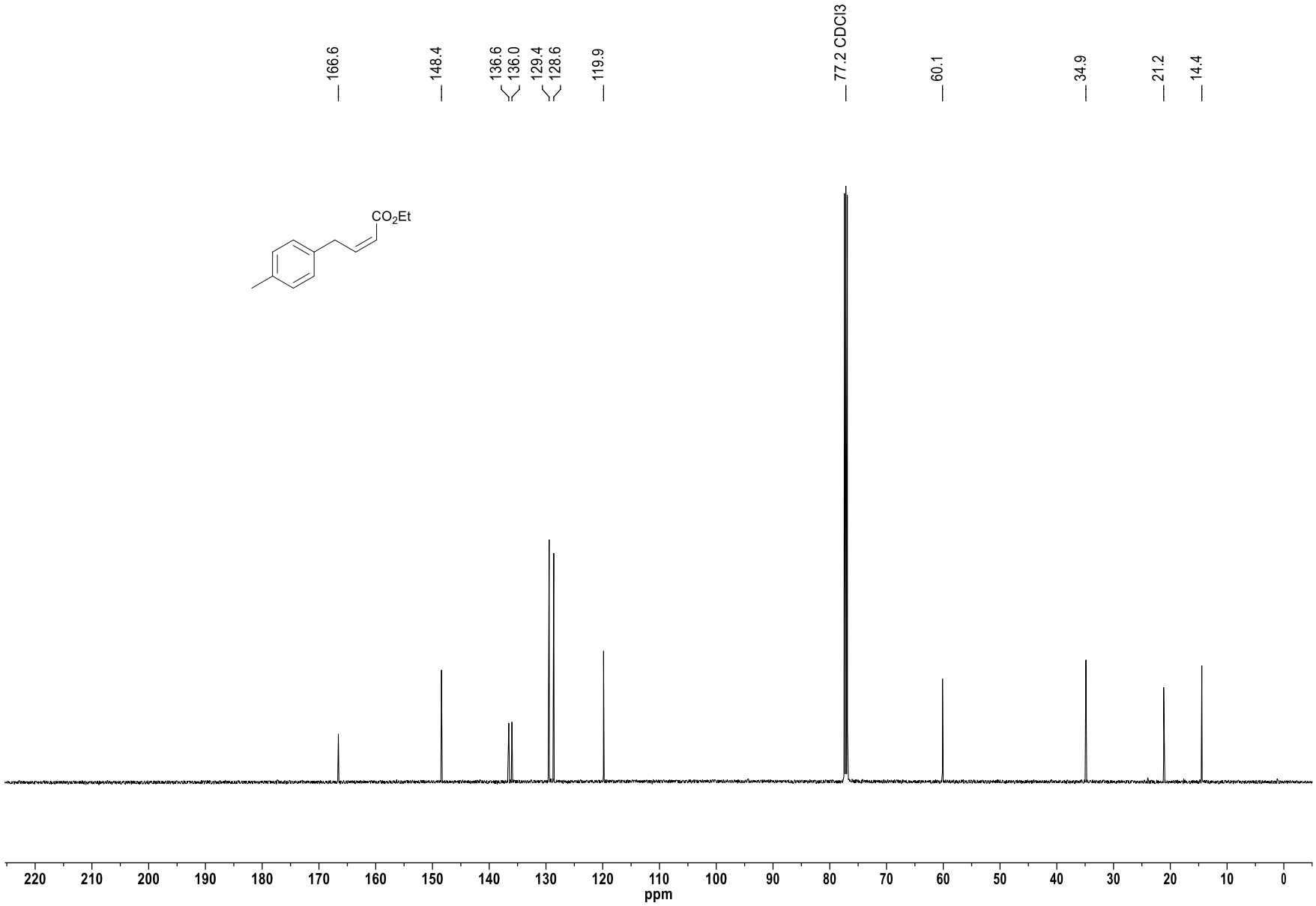
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77.2 CDCl3
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34.9
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14.4
CO2Et
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200
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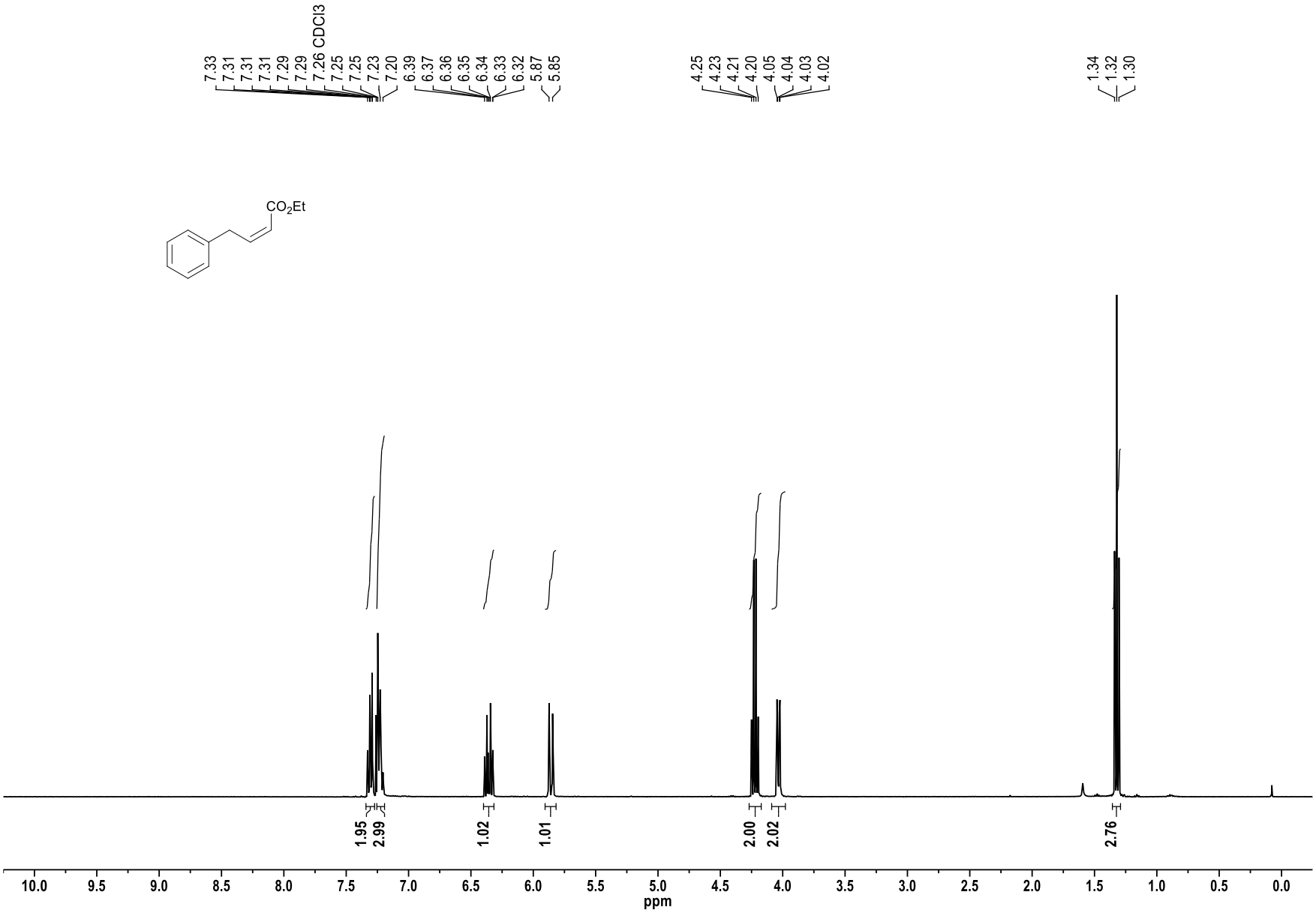
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6.35
6.34
6.33
6.32
5.87
5.85
4.25
4.23
4.21
4.20
4.05
4.04
4.03
4.02
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1.32
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CO2Et
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2.76
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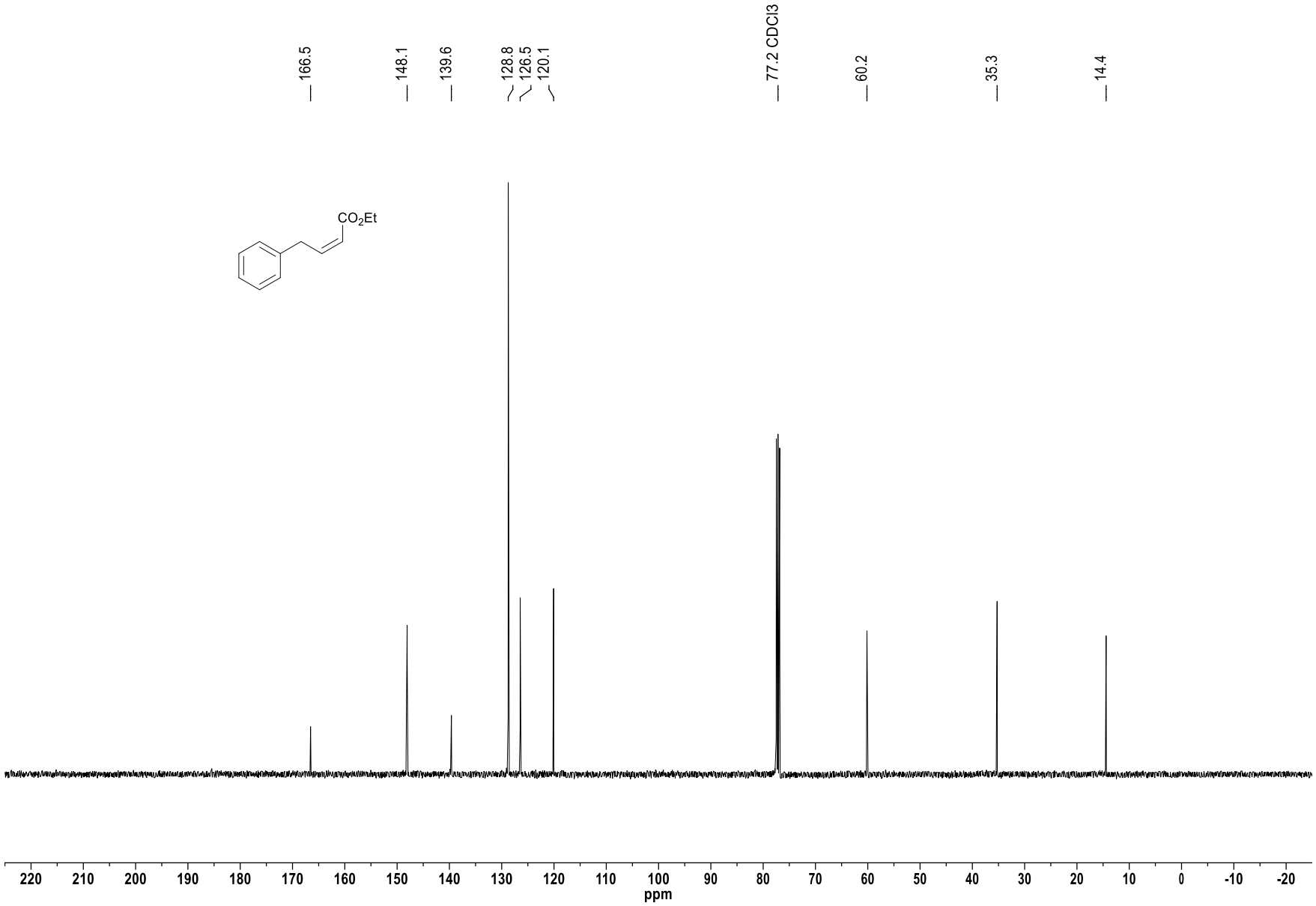
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CO2Et
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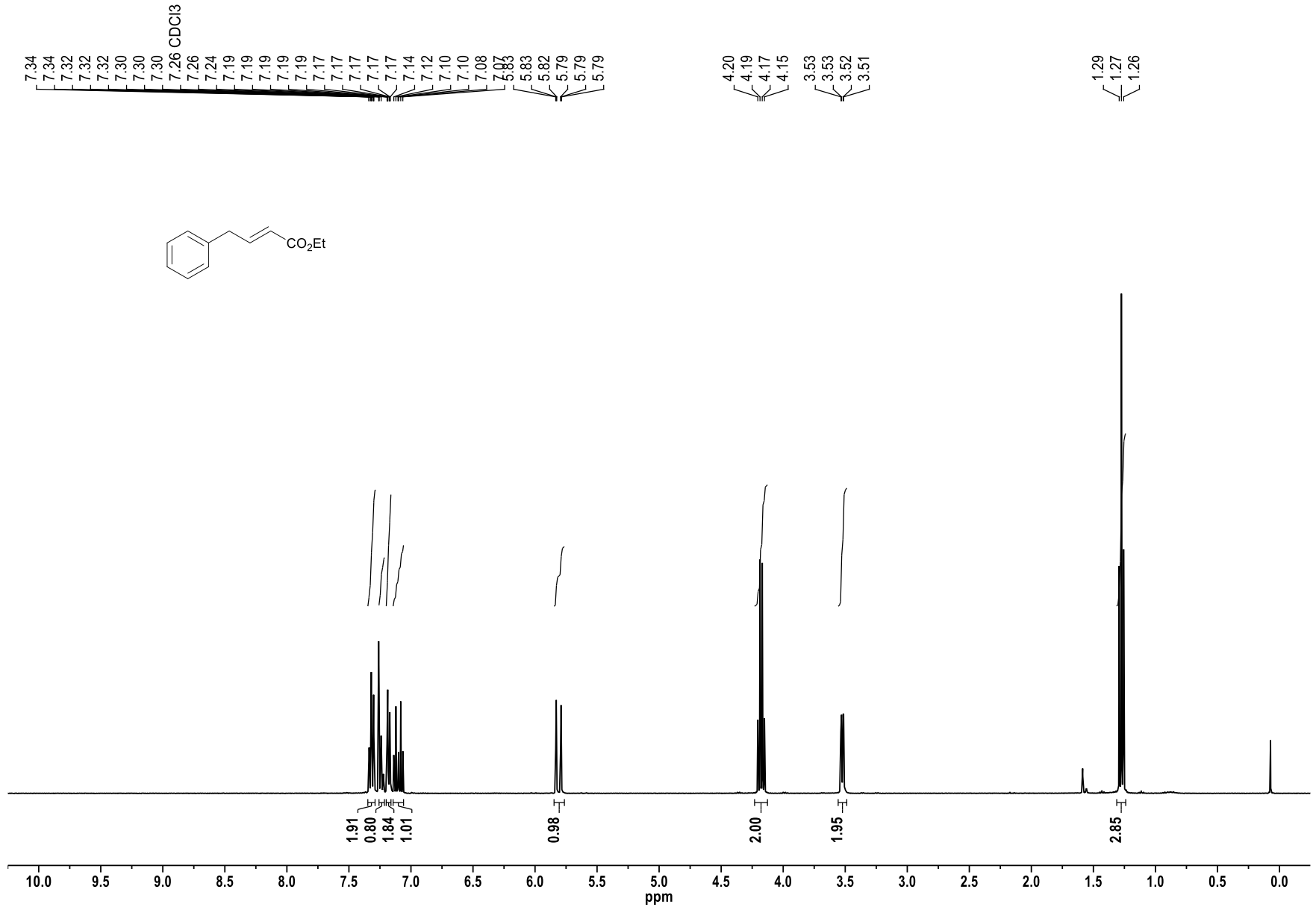
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7.19
7.19
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7.14
7.12
7.10
7.10
7.08
7.07
5.83
5.83
5.82
5.79
5.79
5.79
4.20
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4.17
4.15
3.53
3.53
3.52
3.51
1.29
1.27
1.26
CO2Et
1.91
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1.84
1.01
0.98
2.00
1.95
2.85
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9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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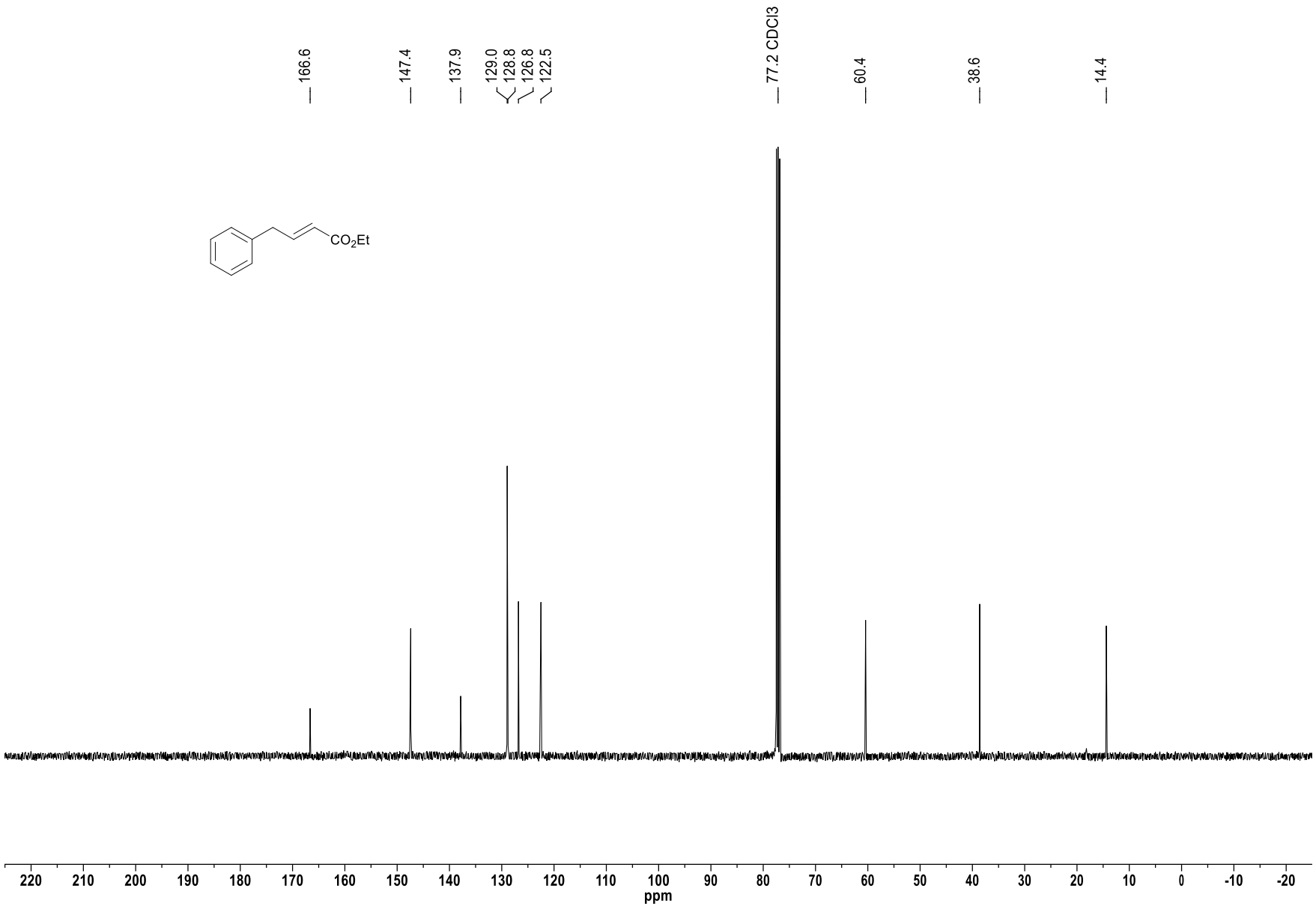
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126.8
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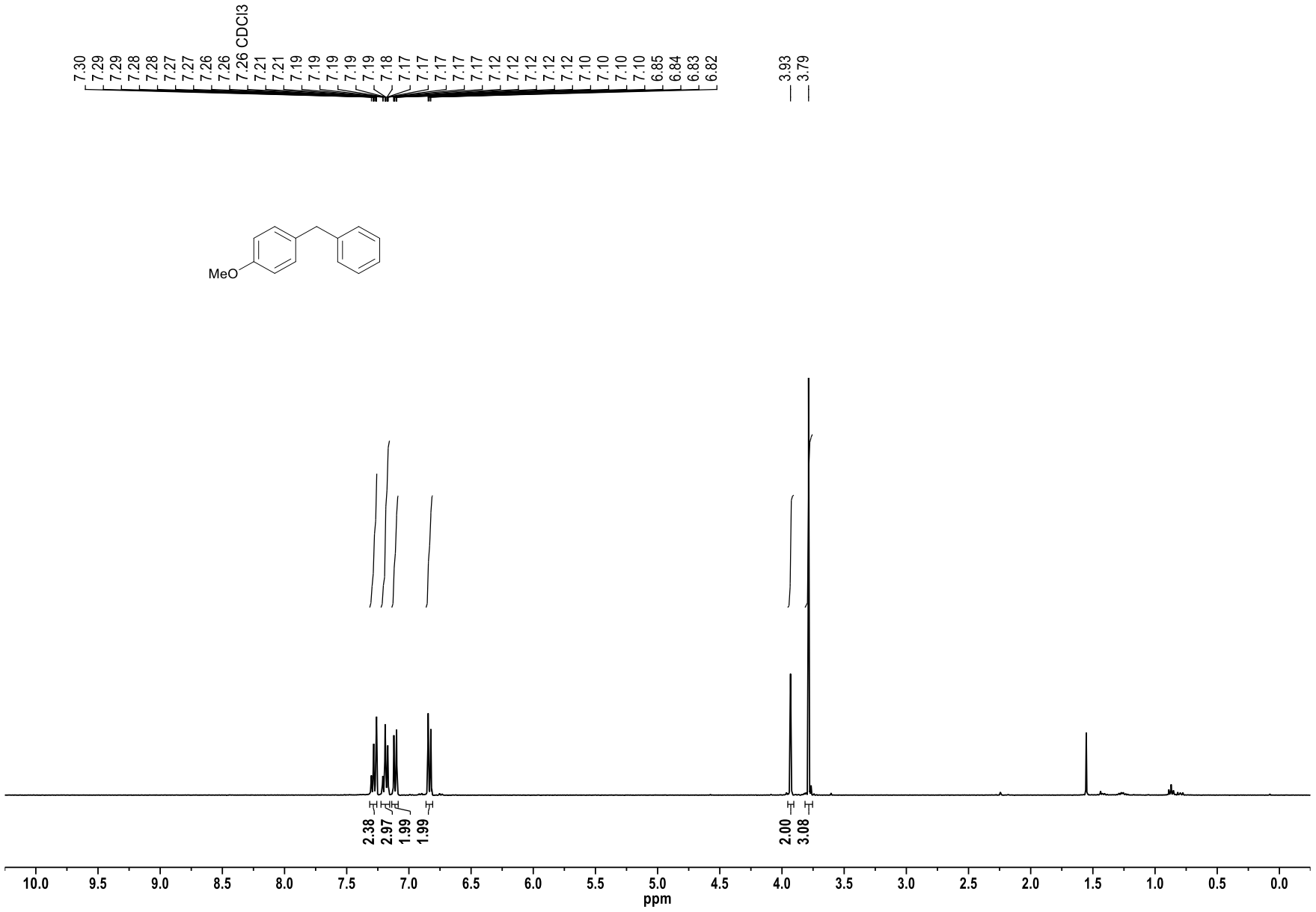
CO2Et
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
ppm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7.12
7.12
7.12
7.10
7.10
7.10
7.10
6.85
6.84
6.83
6.82
3.93
3.79
MeO
2.38
2.97
1.99
1.99
2.00
3.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.0
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3.0
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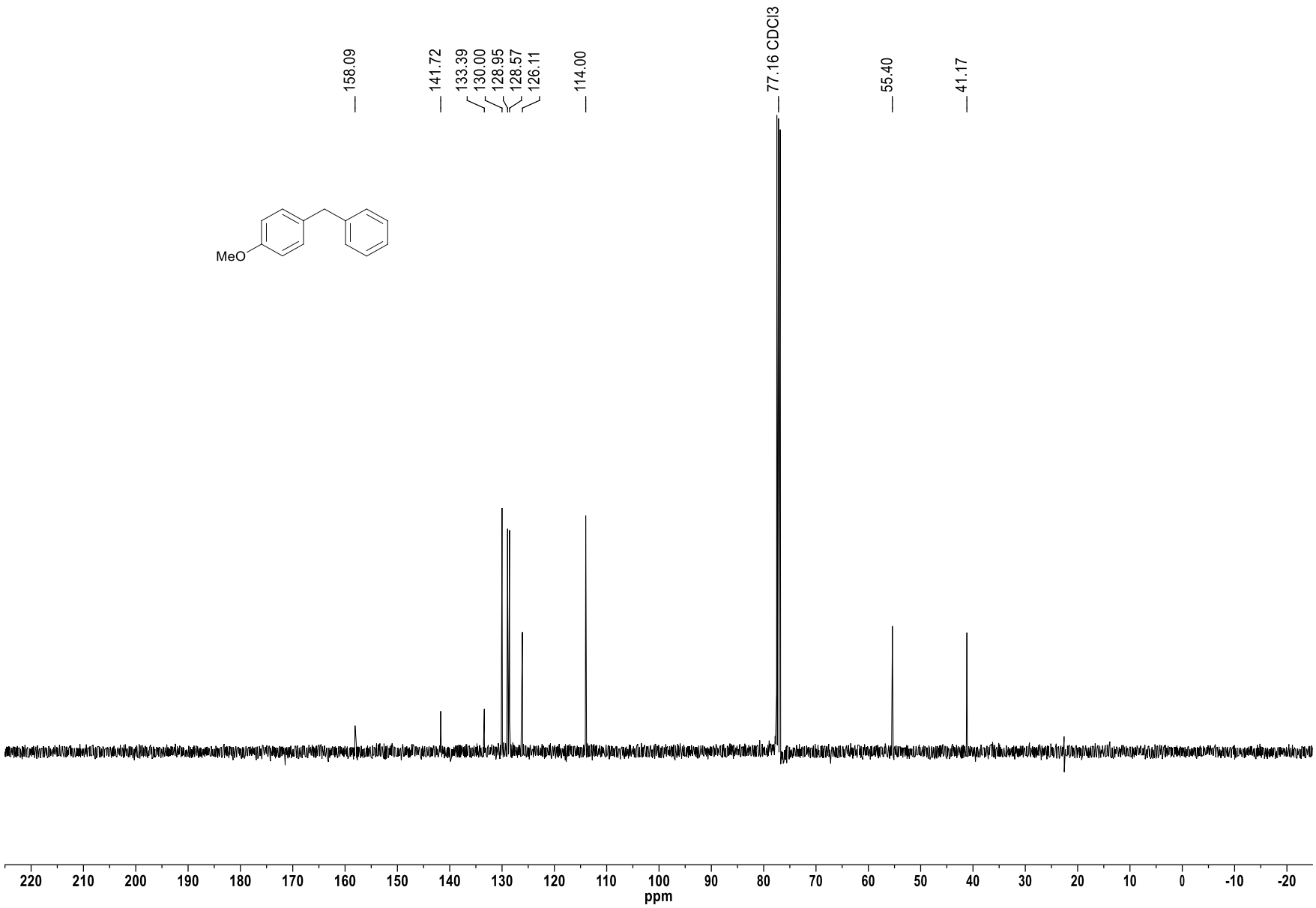
ppm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77.16 CDCl3
55.40
41.17
MeO
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210
200
190
180
170
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100
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40
30
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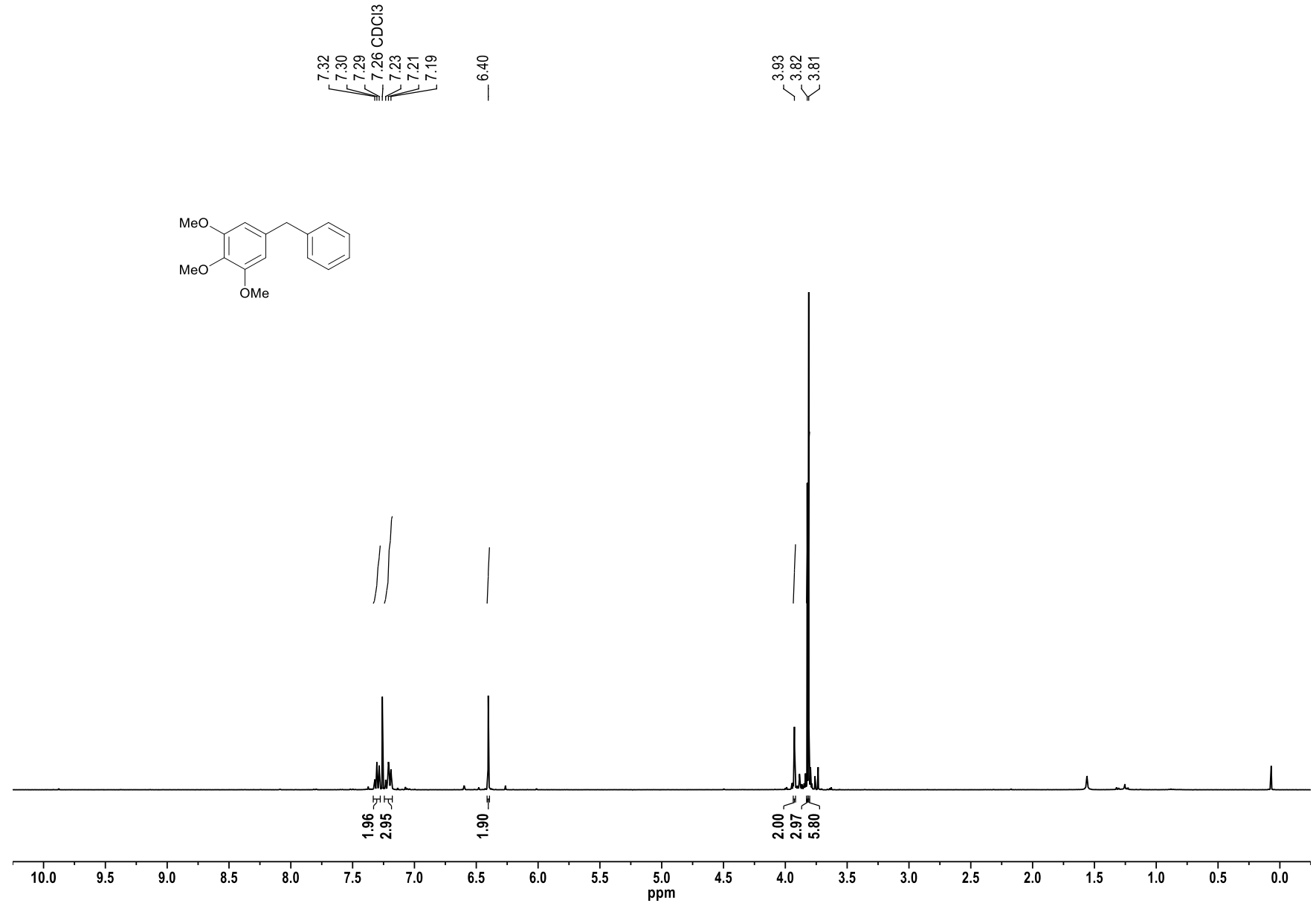
ppm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7.29
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7.23
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7.19
6.40
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3.82
3.81
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MeO
OMe
1.96
2.95
1.90
2.00
2.97
5.80
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9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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0.5
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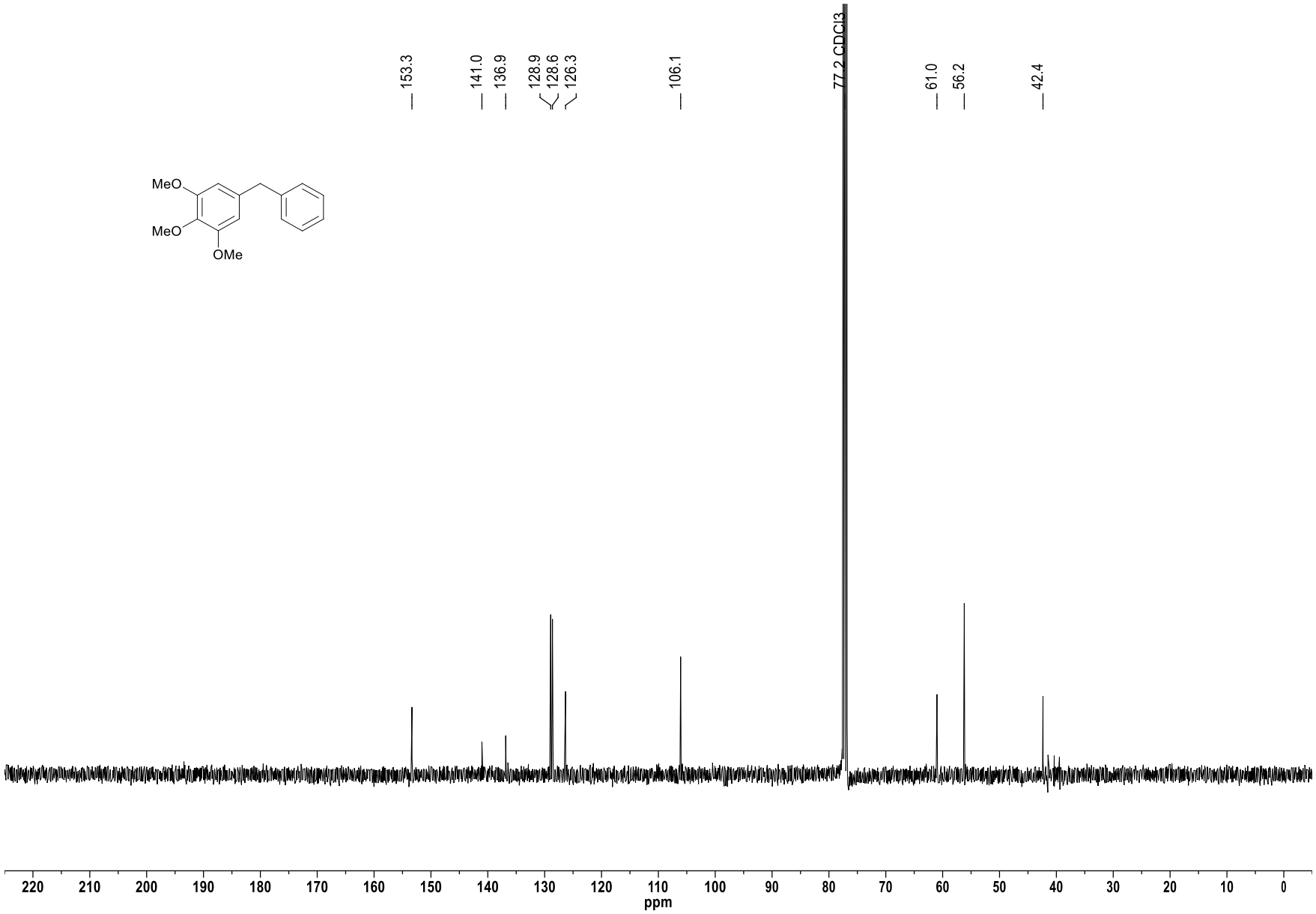
ppm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61.0
56.2
42.4
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MeO
OMe
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210
200
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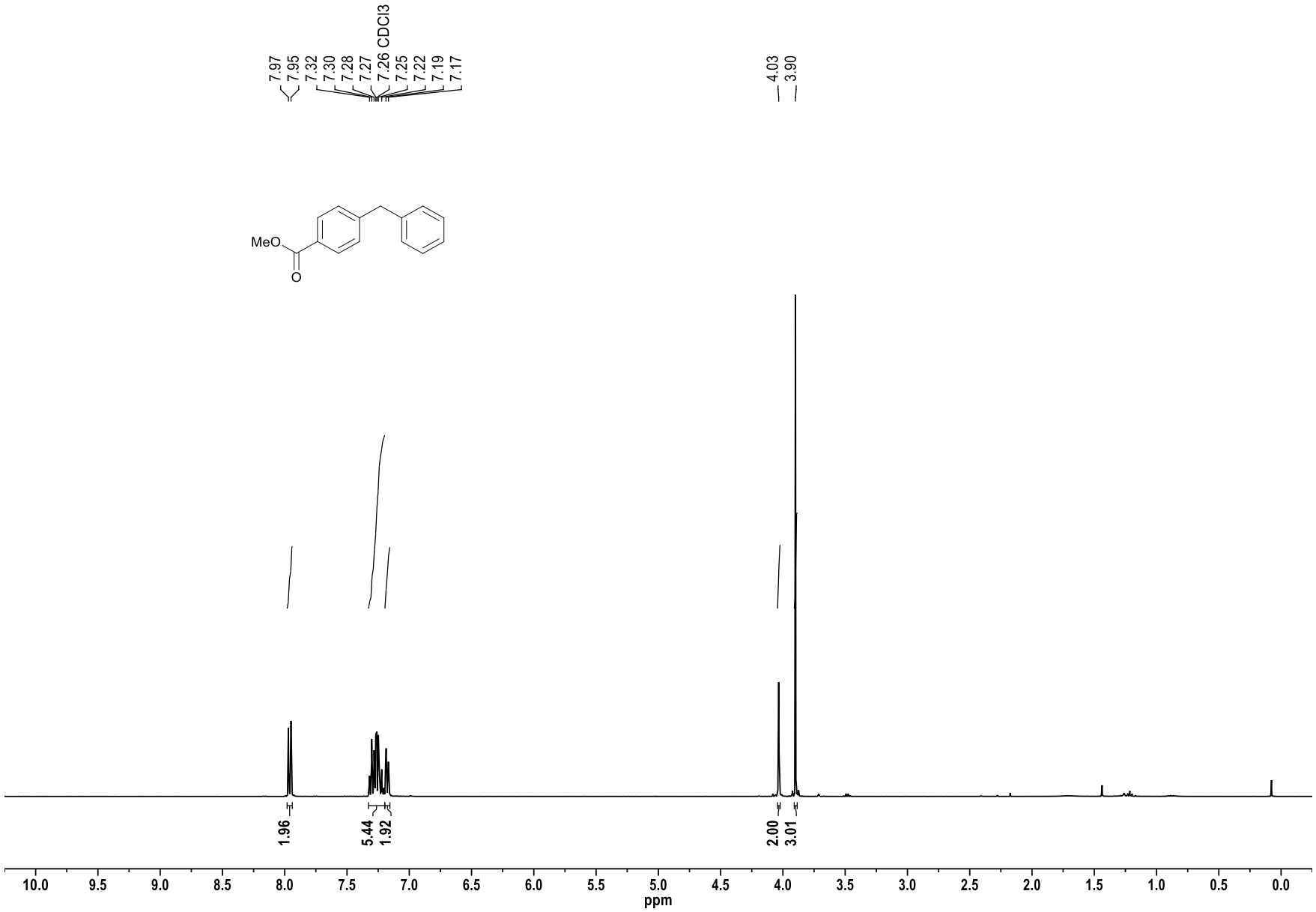
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7.22
7.19
7.17
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8.0
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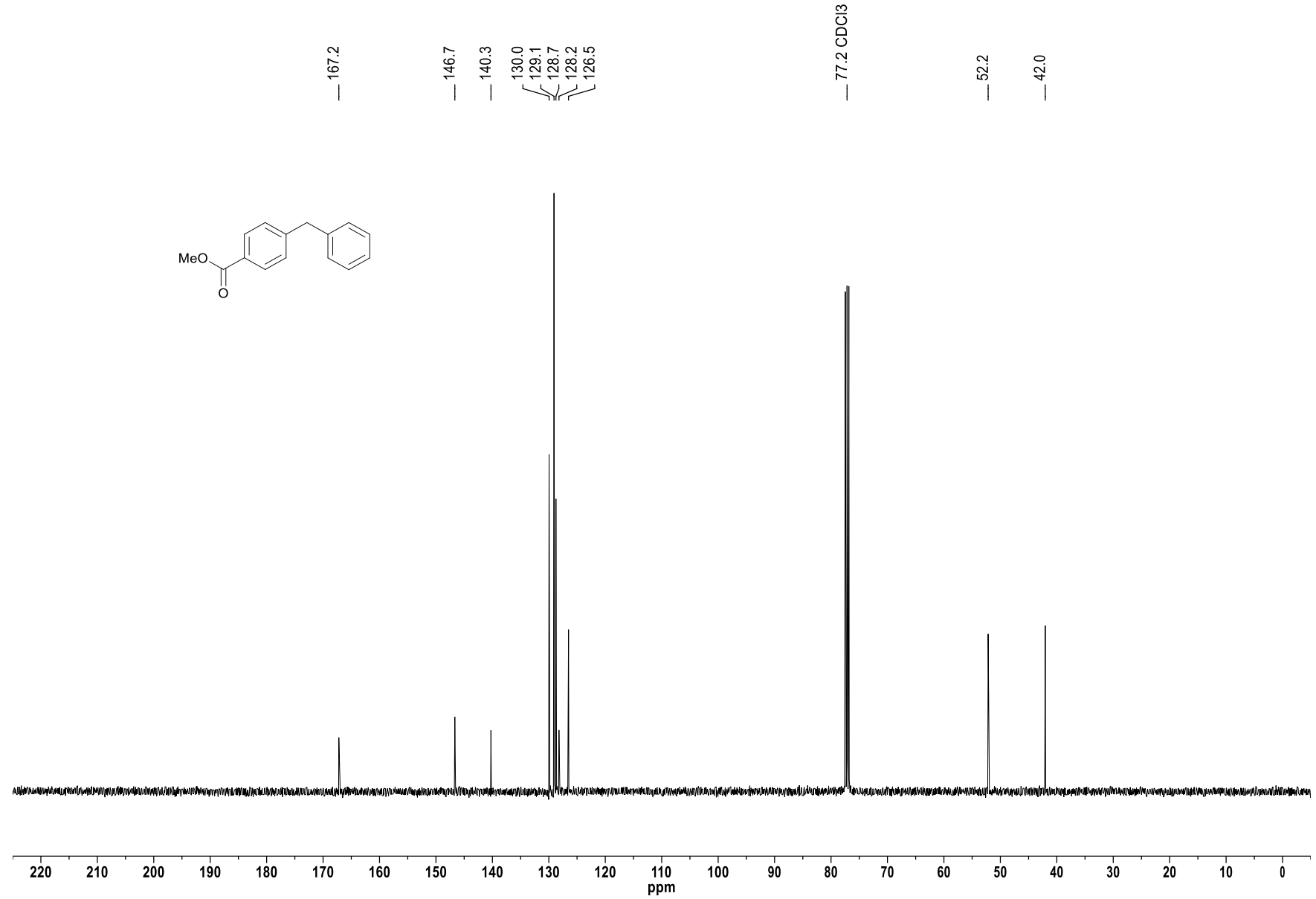
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126.5
77.2 CDCl3
52.2
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210
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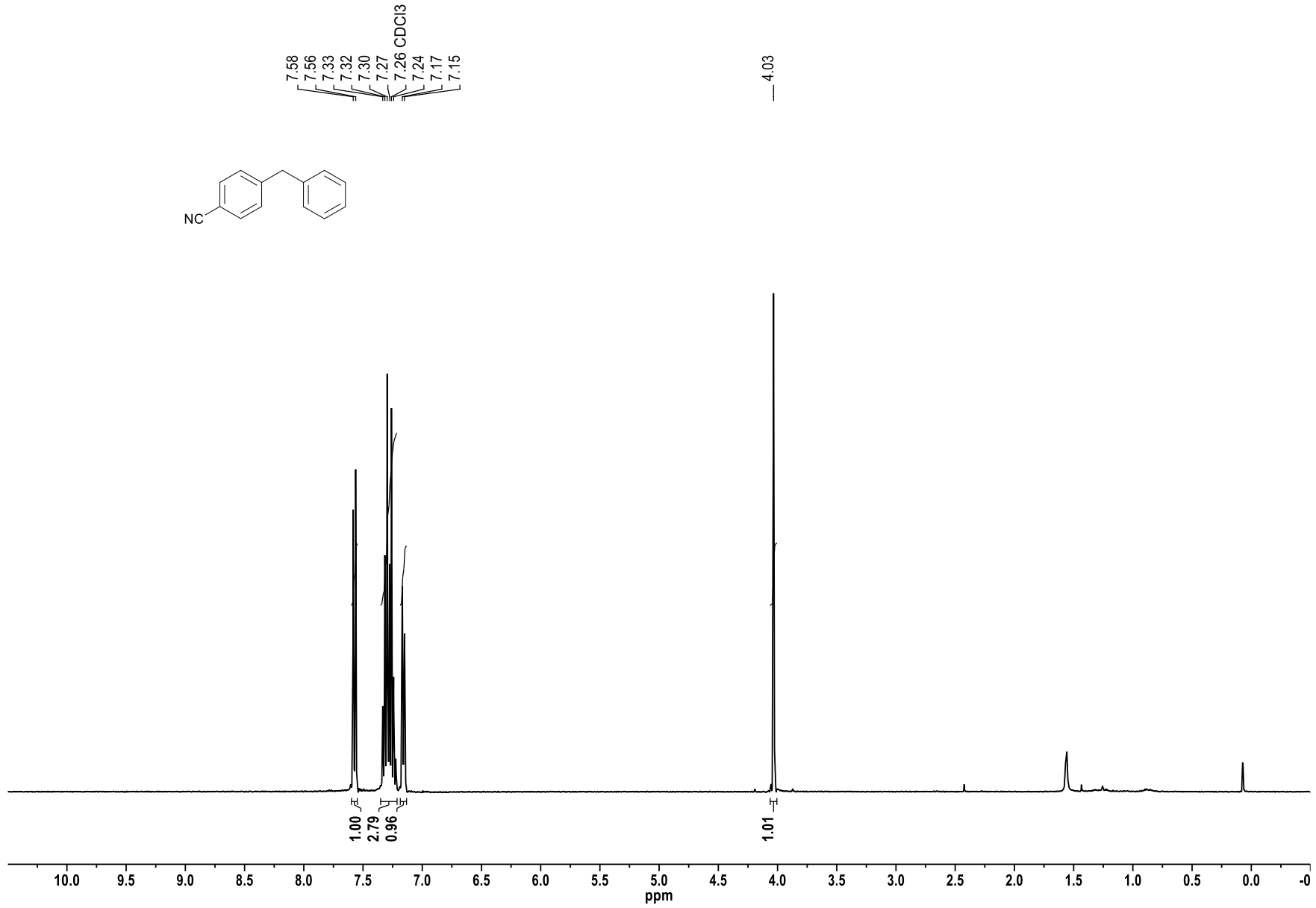
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7.15
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9.0
8.5
8.0
7.5
7.0
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6.0
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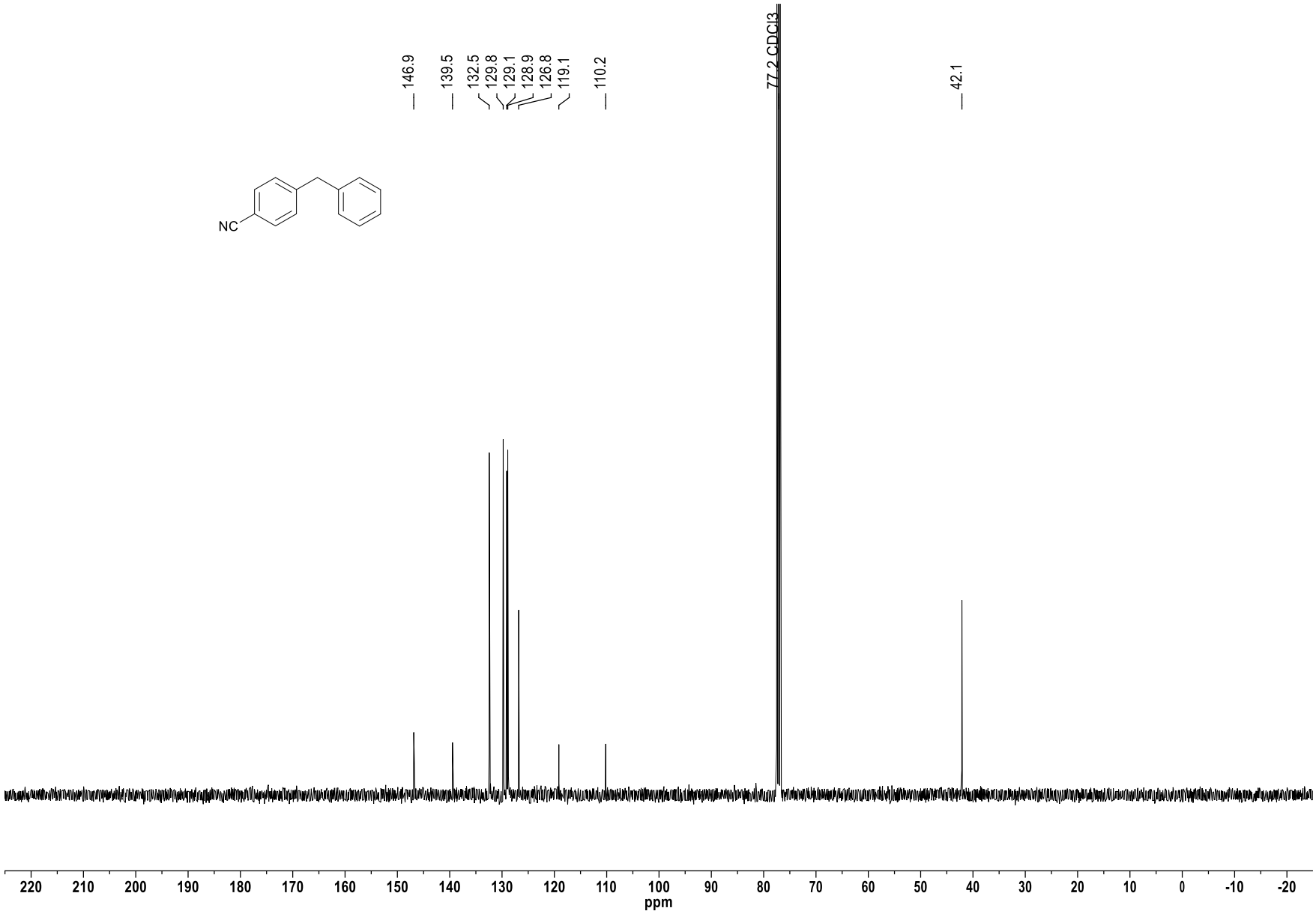
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77.2 CDCl3
42.1
NC
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200
190
180
170
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100
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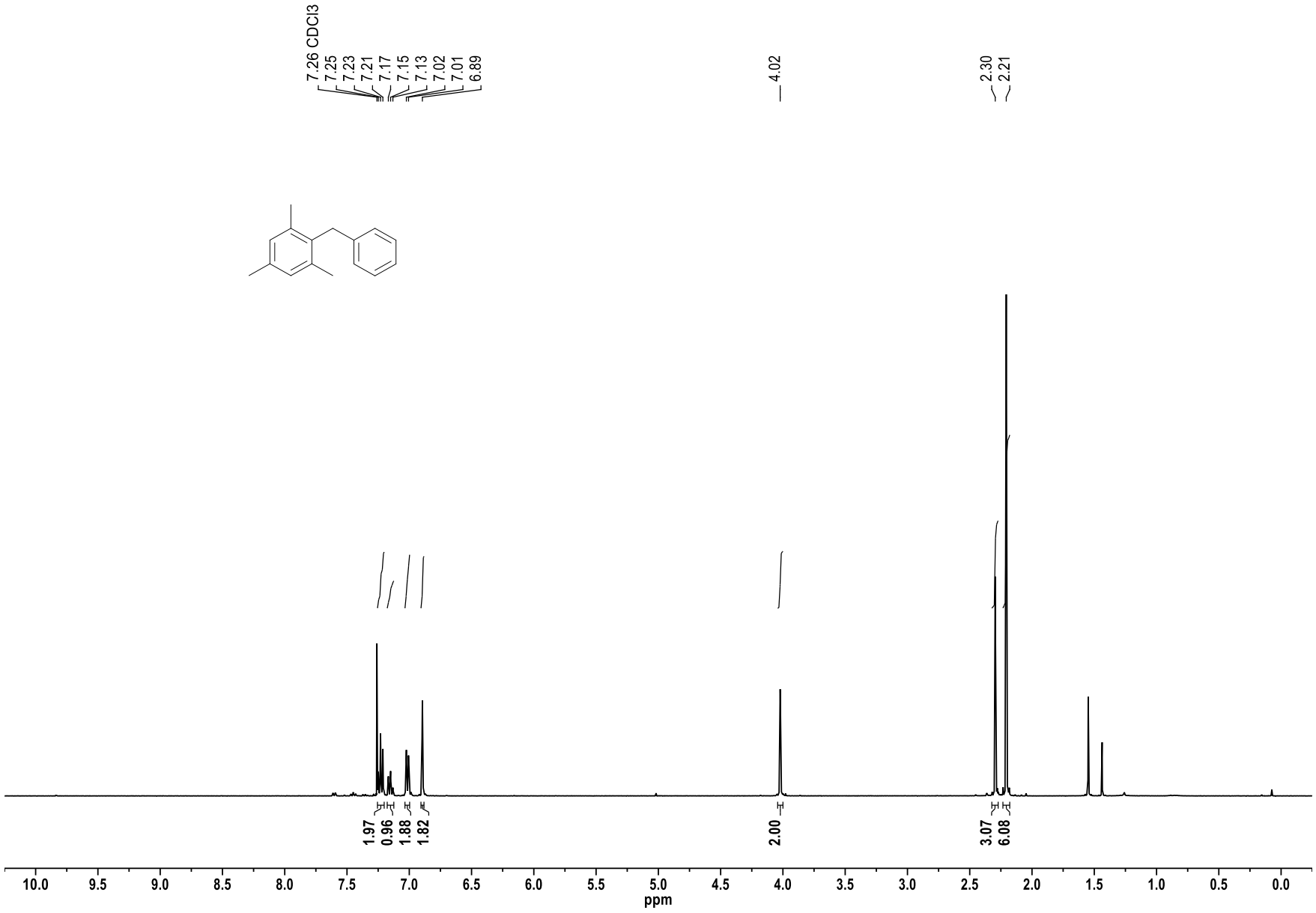
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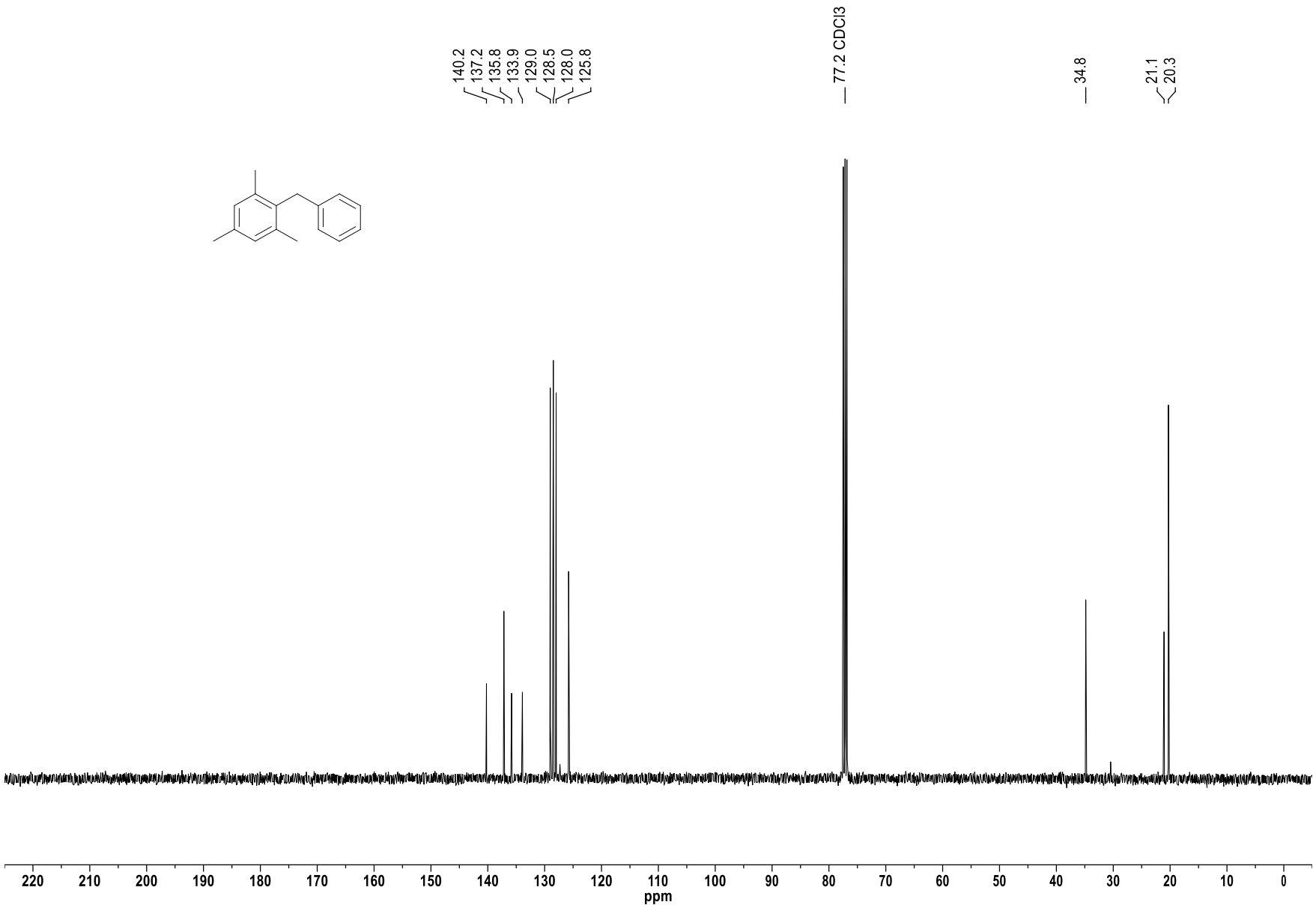
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77.2 CDCl3
34.8
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200
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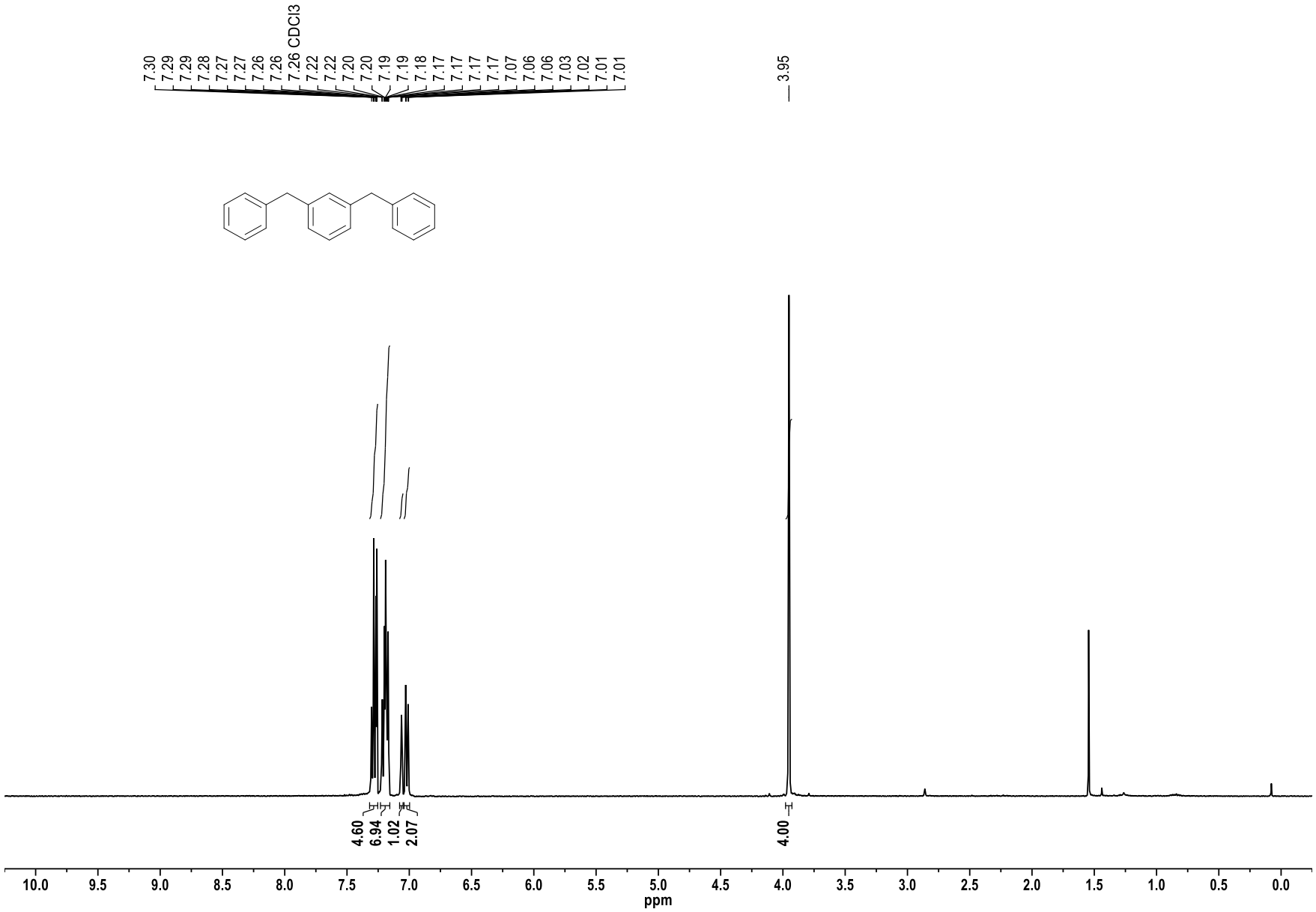
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7.07
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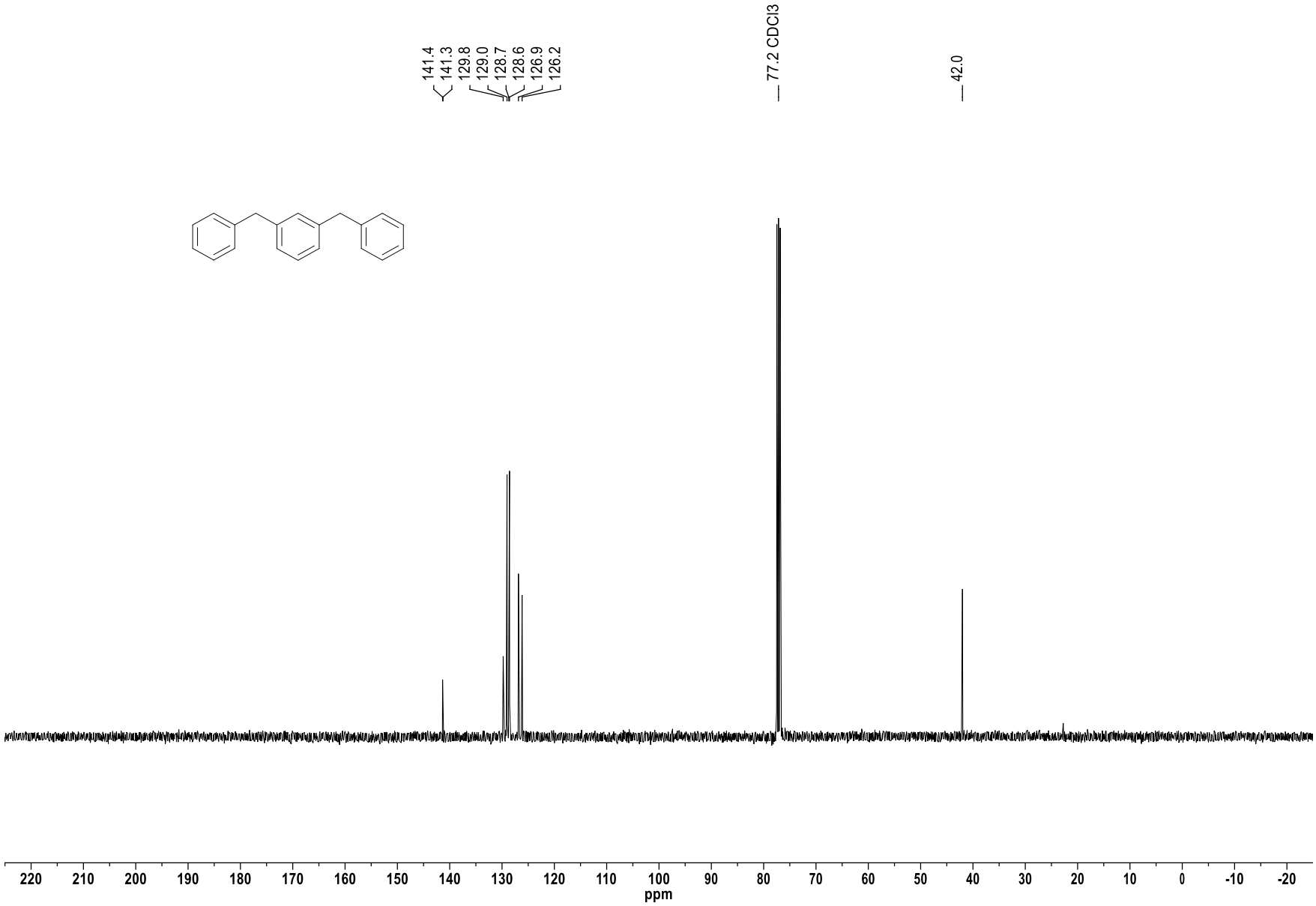
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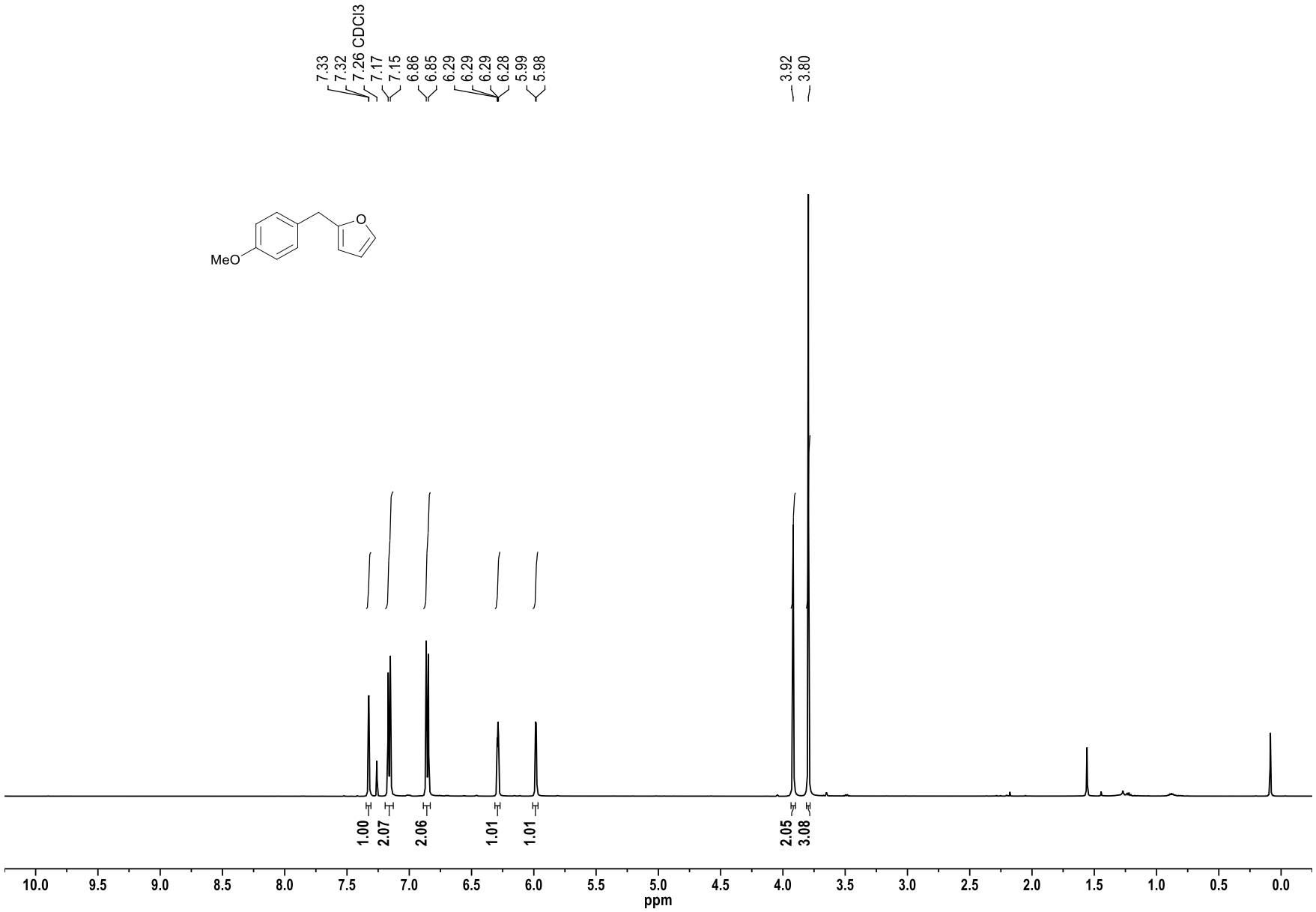
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2.05
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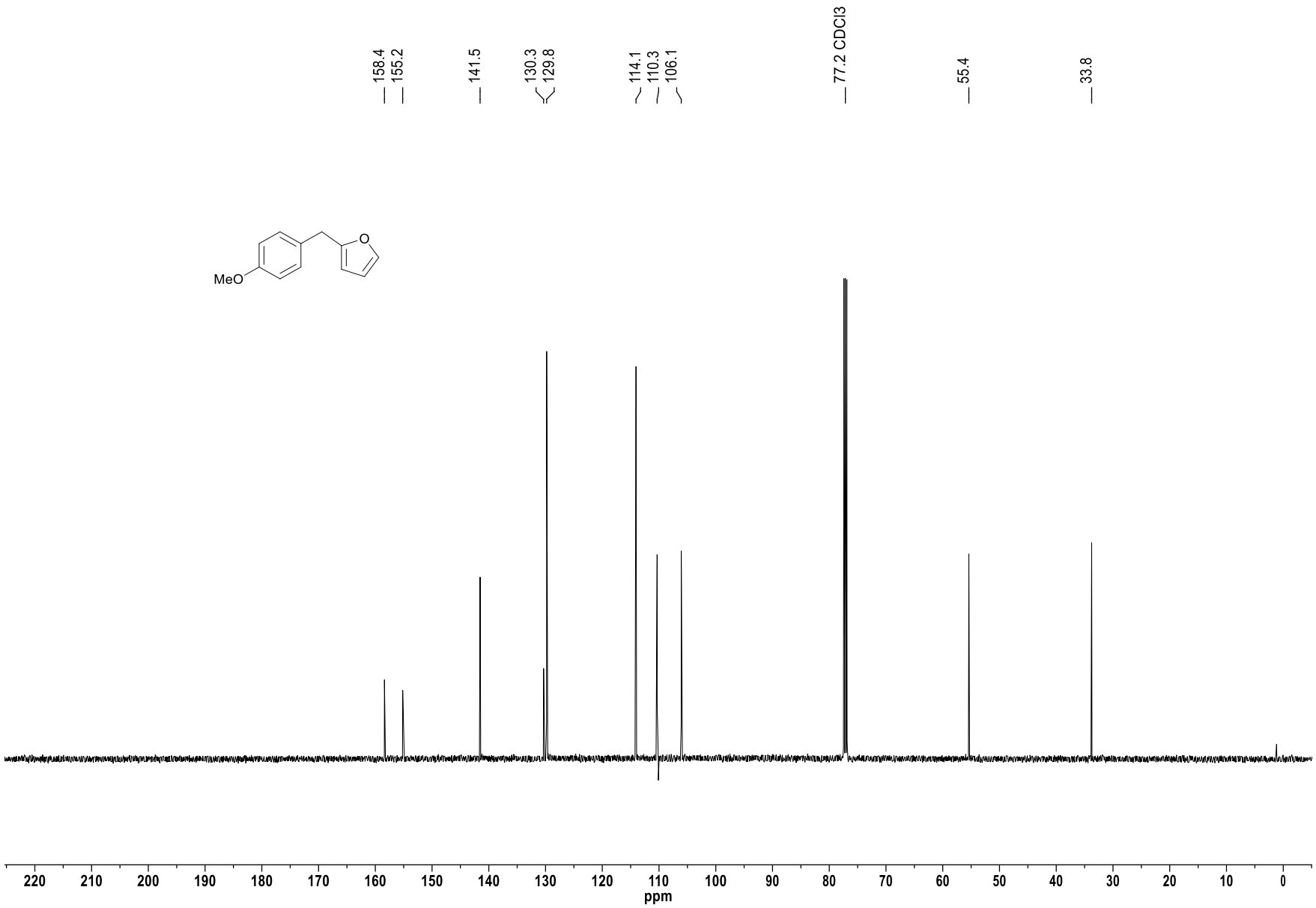
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106.1
77.2 CDCl3
55.4
33.8
MeO
O
220
210
200
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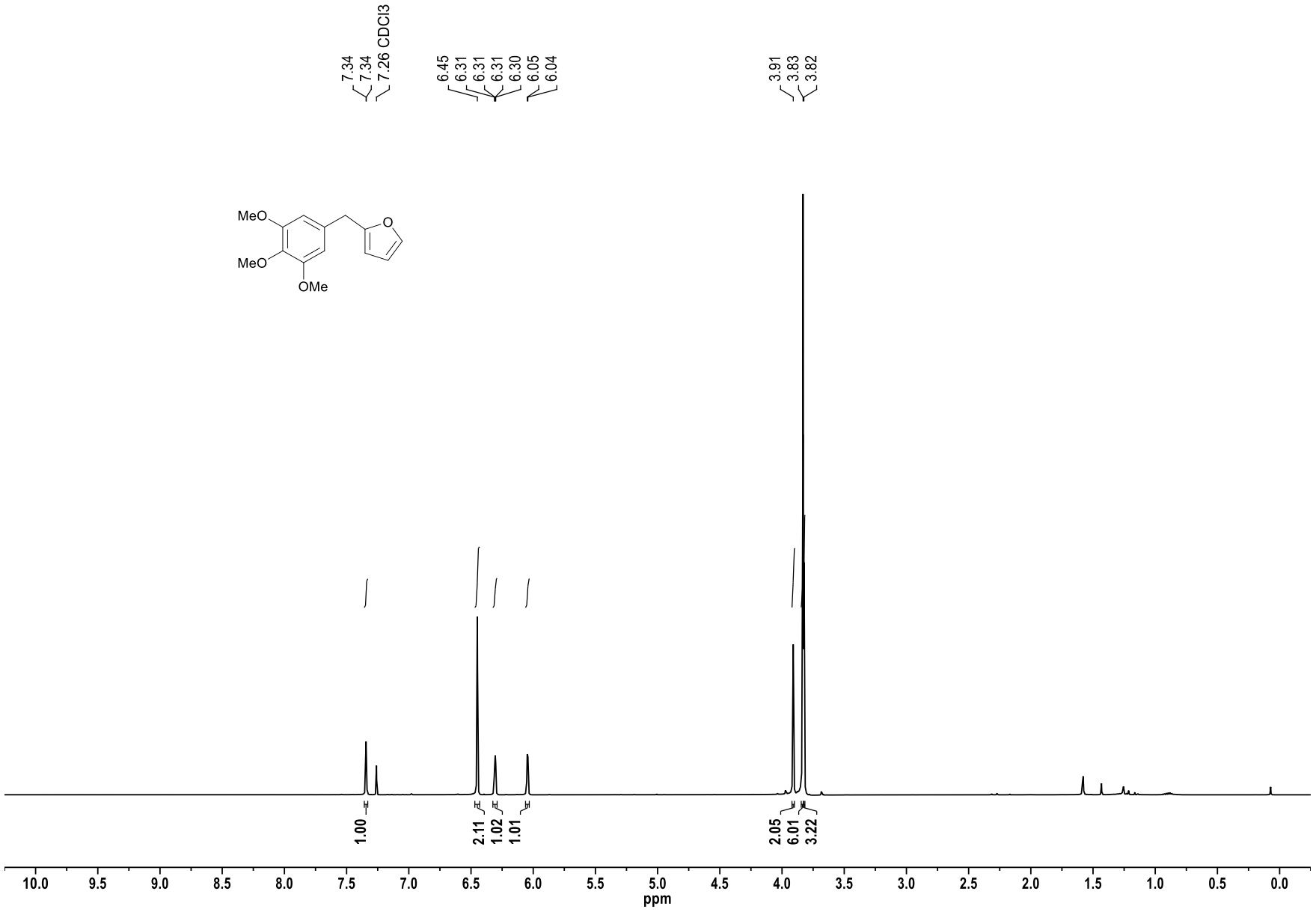
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6.04
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3.83
3.82
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MeO
OMe
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2.11
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1.01
2.05
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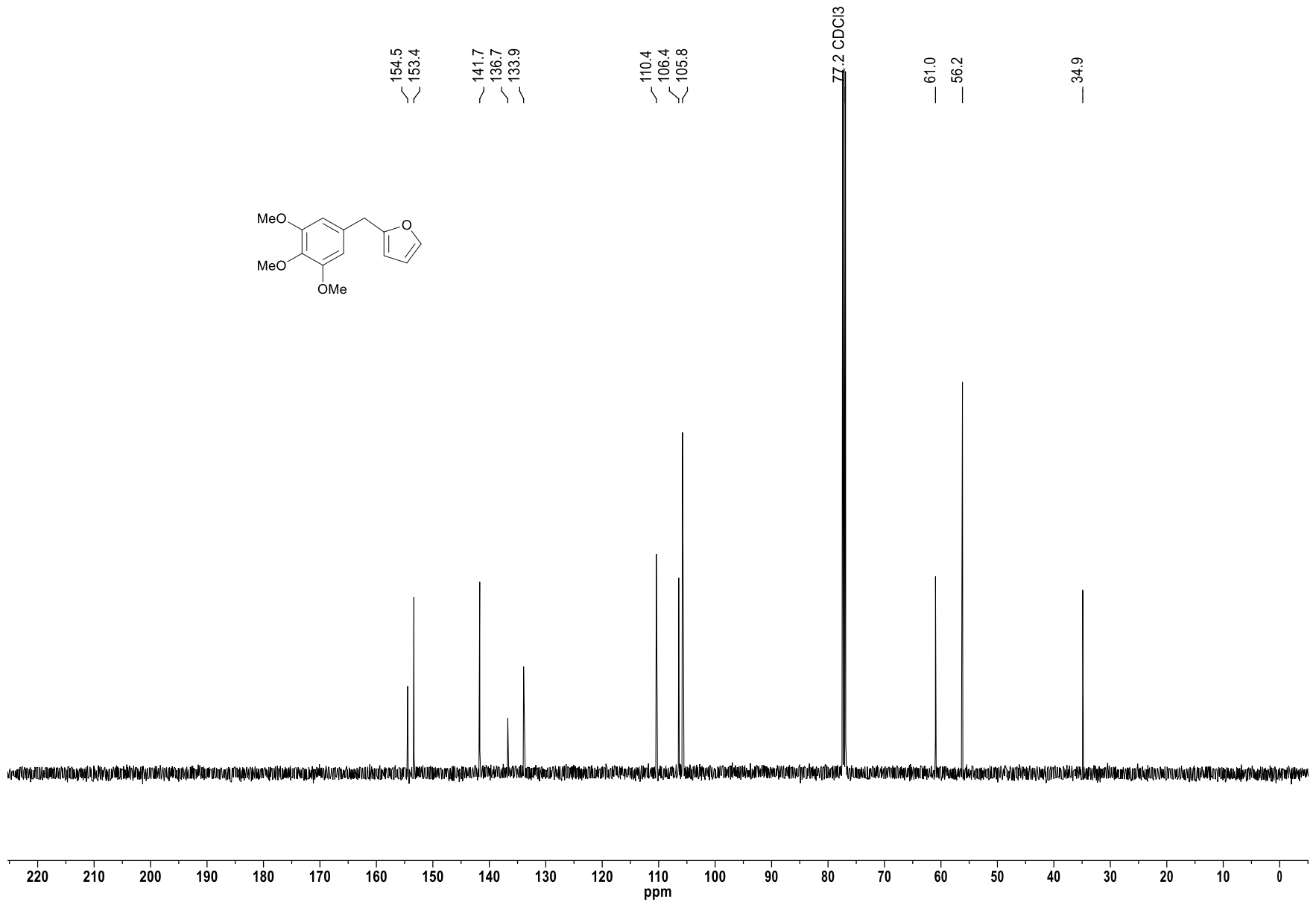
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MeO
MeO
OMe
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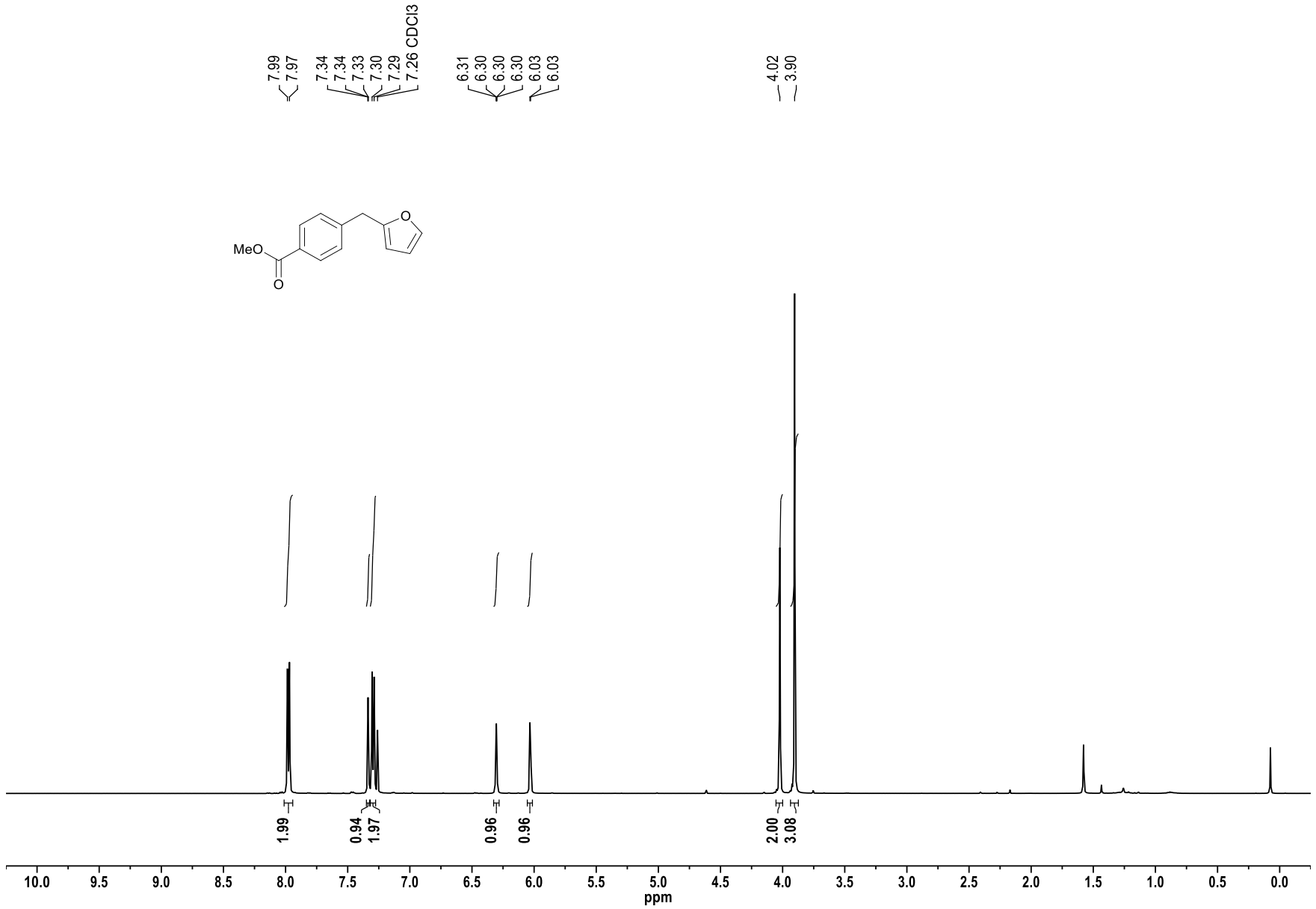
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6.03
6.03
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O
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2.0
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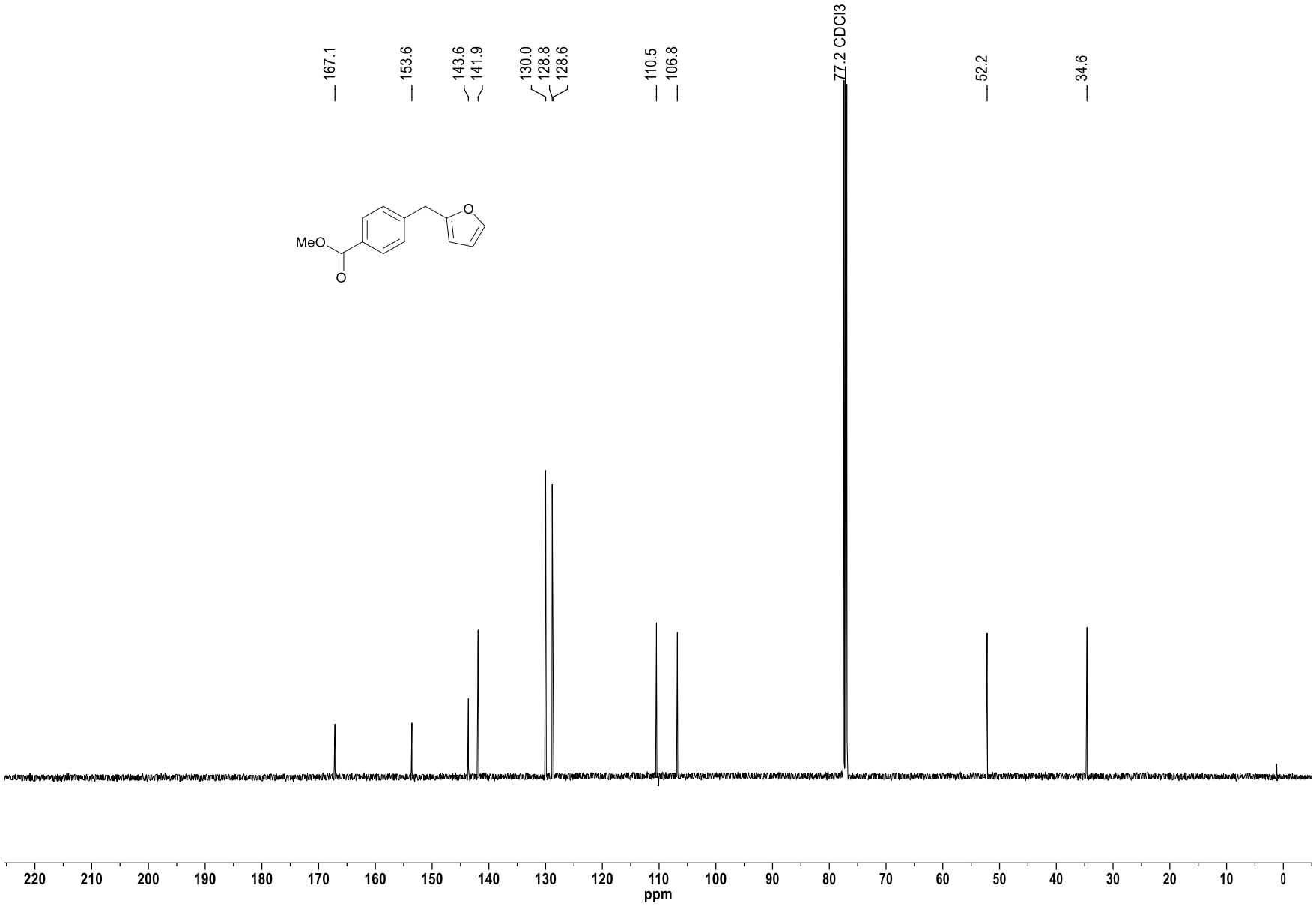
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O
O
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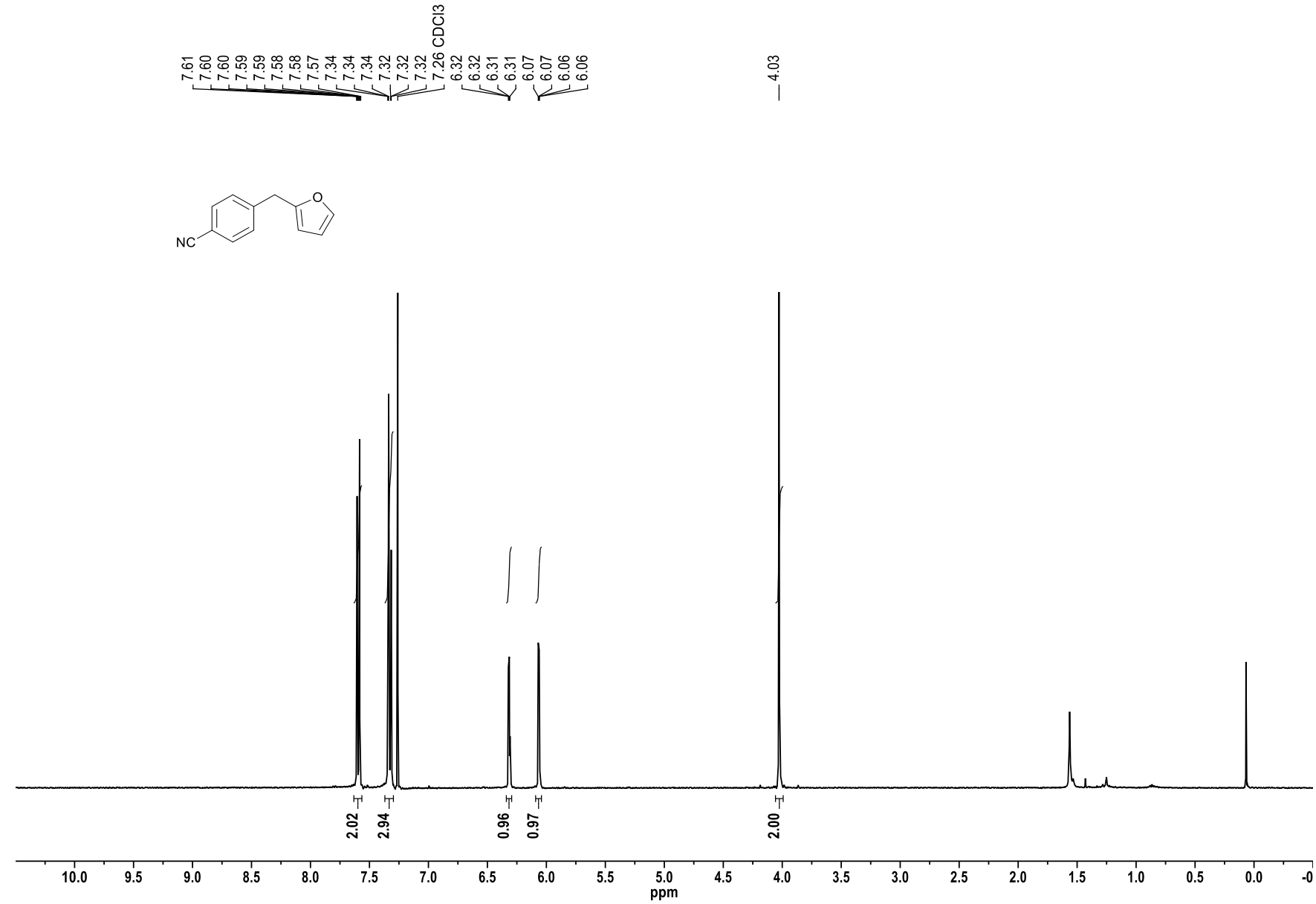
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7.32
7.26 CDCl3
6.32
6.32
6.31
6.31
6.07
6.07
6.06
6.06
4.03
NC
O
2.02
2.94
0.96
0.97
2.00
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9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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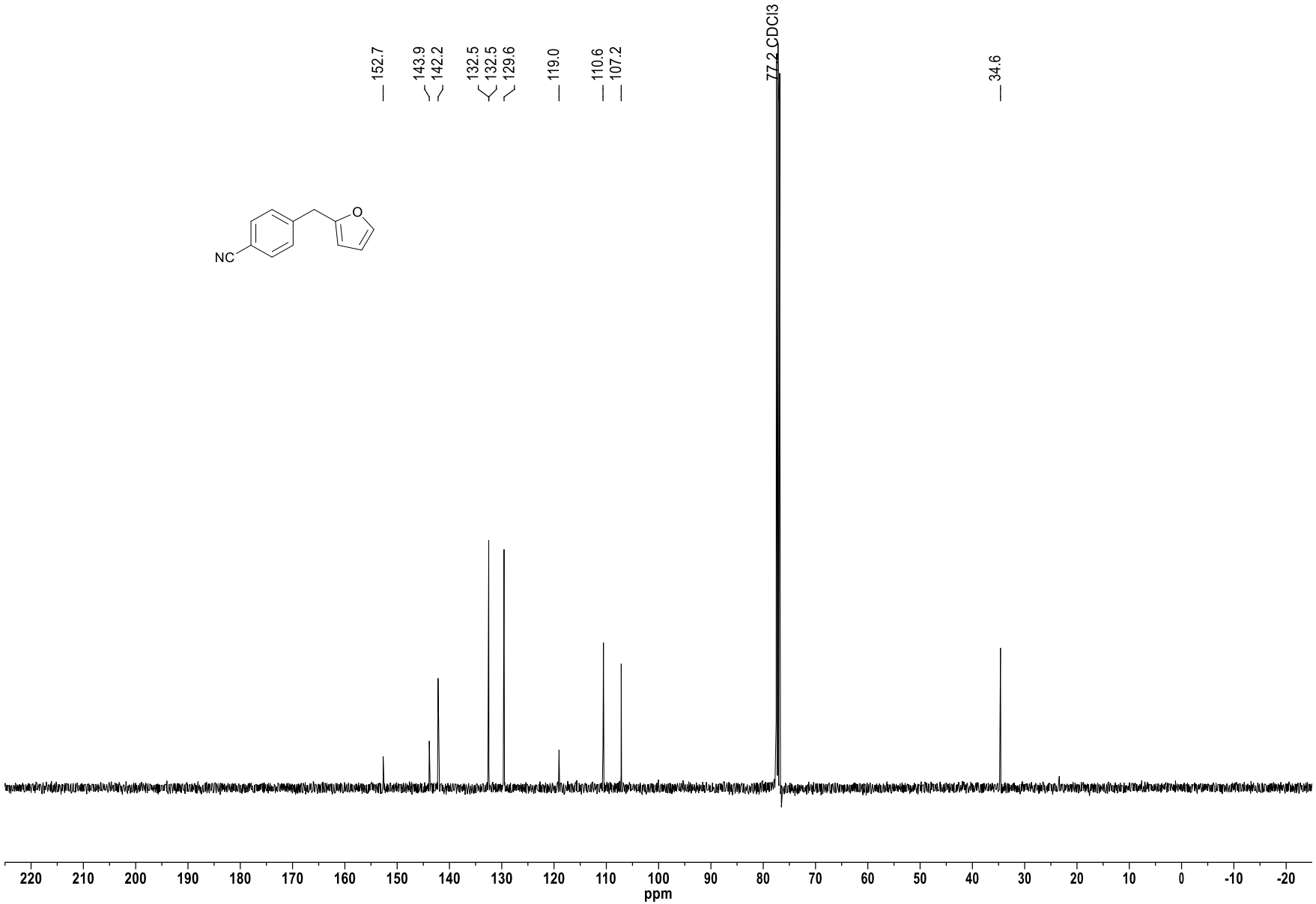
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34.6
NC
O
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210
200
190
180
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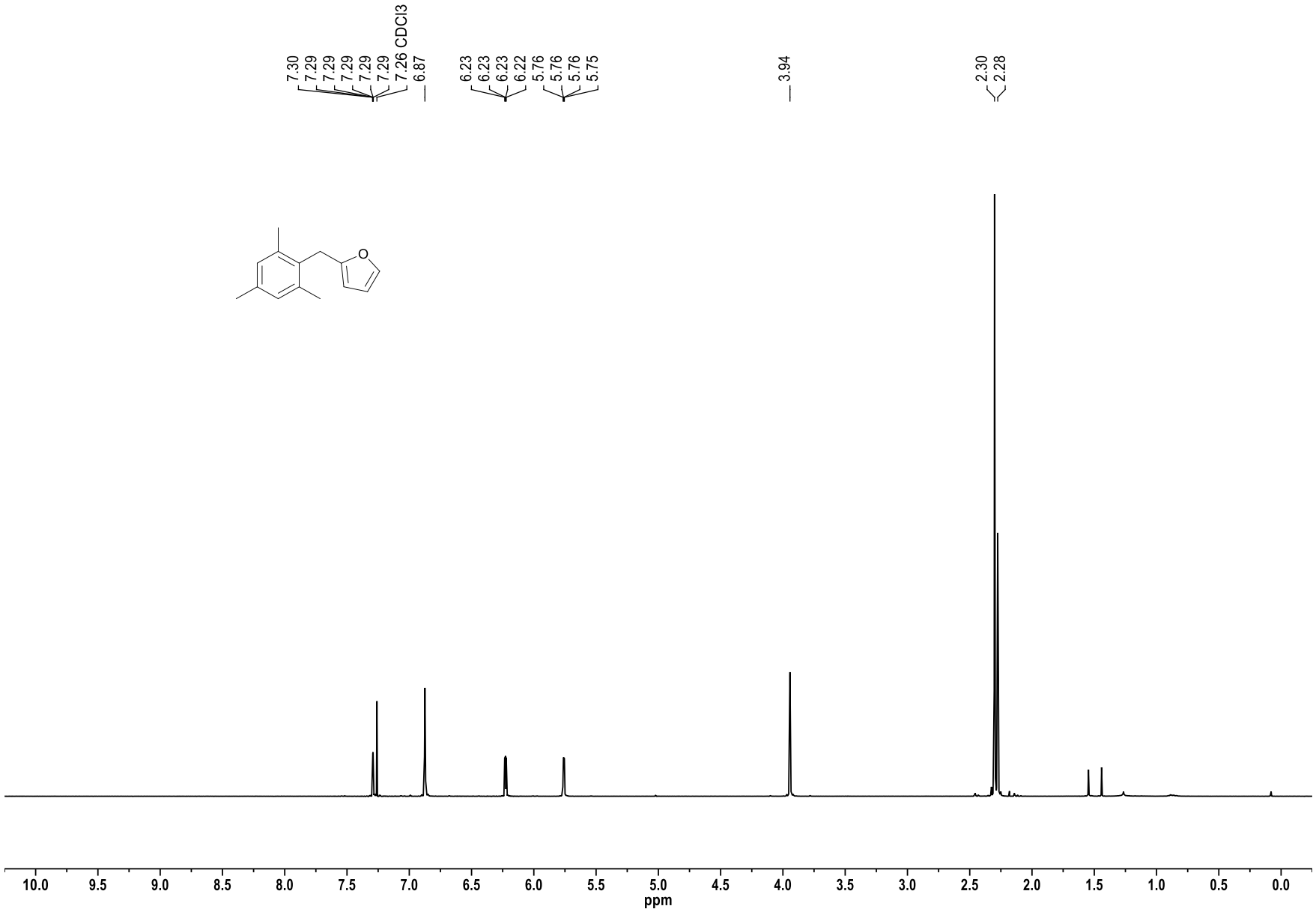
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6.23
6.22
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5.76
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5.75
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9.0
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7.0
6.5
6.0
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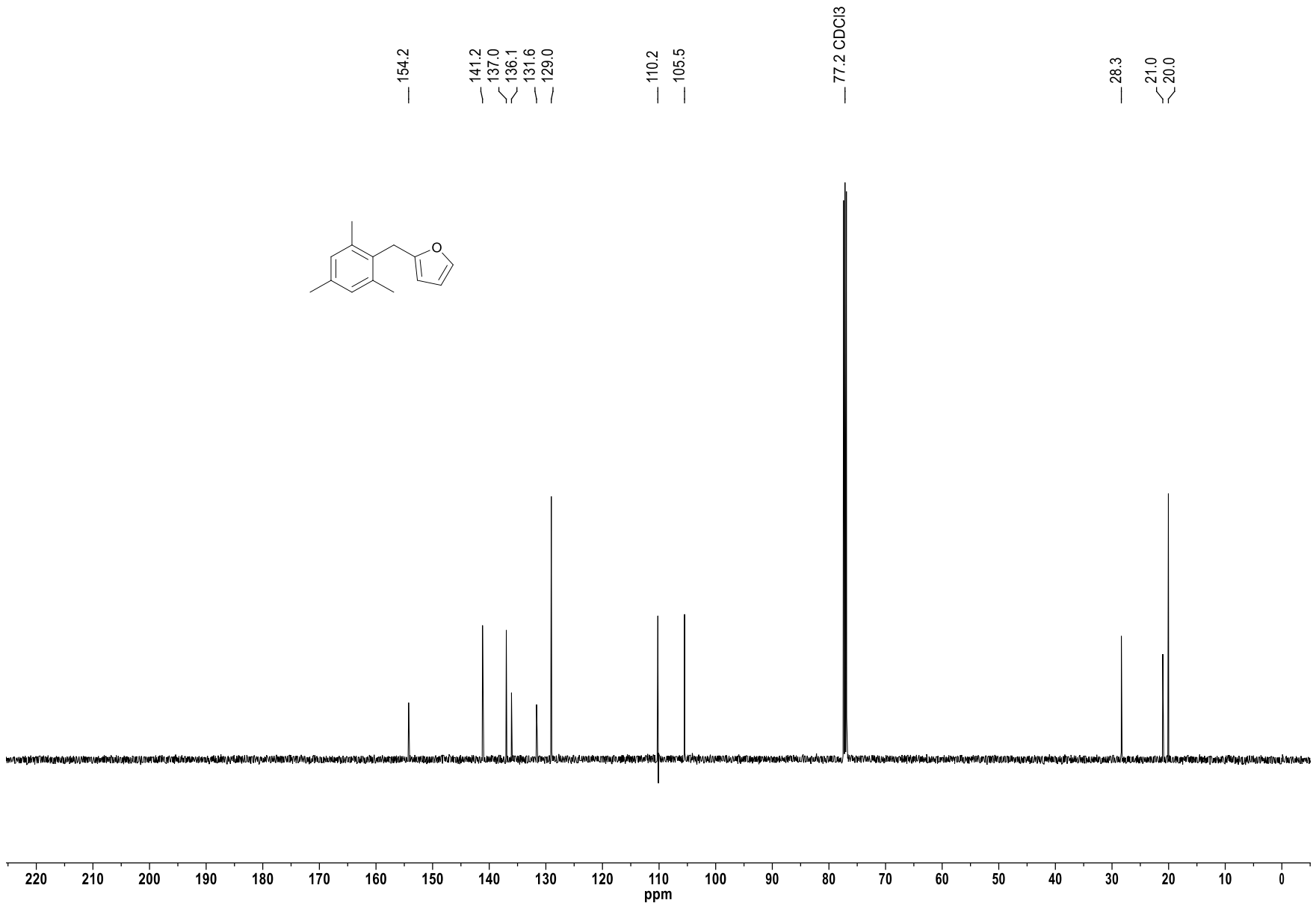
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131.6
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O
220
210
200
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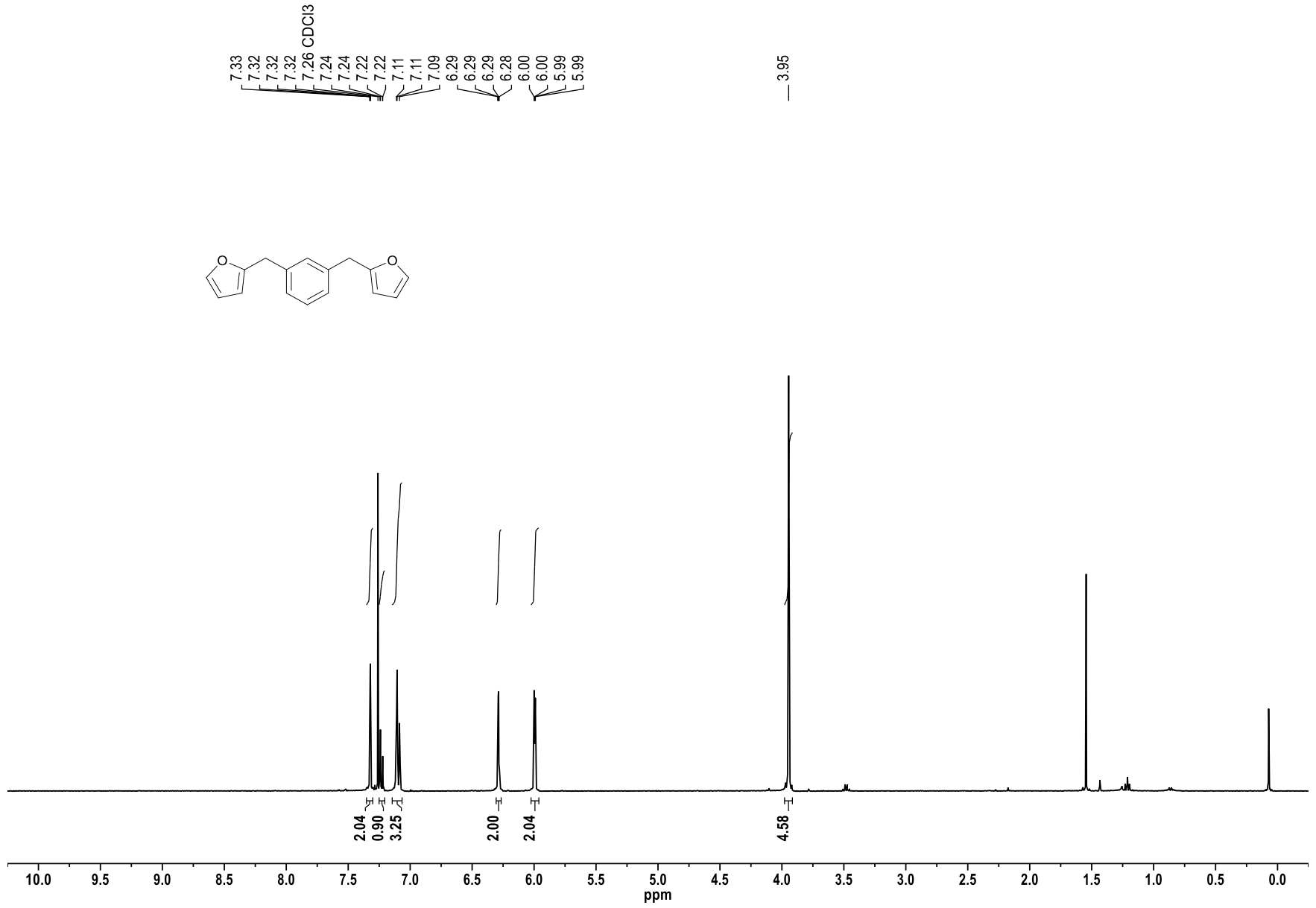
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6.29
6.29
6.28
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6.00
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5.99
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O
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0.90
3.25
2.00
2.04
4.58
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9.0
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8.0
7.5
7.0
6.5
6.0
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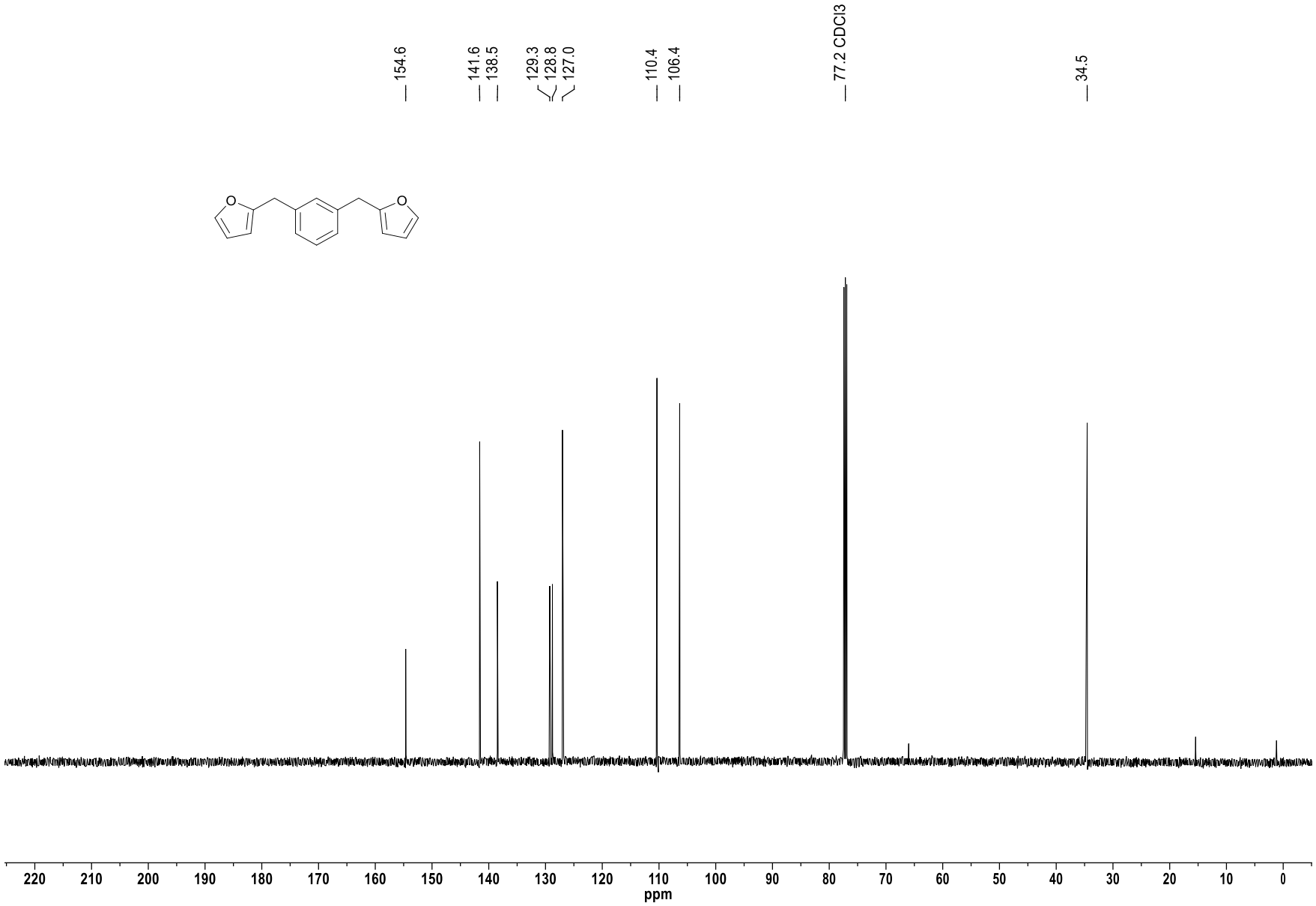
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110.4
106.4
77.2 CDCl3
34.5
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210
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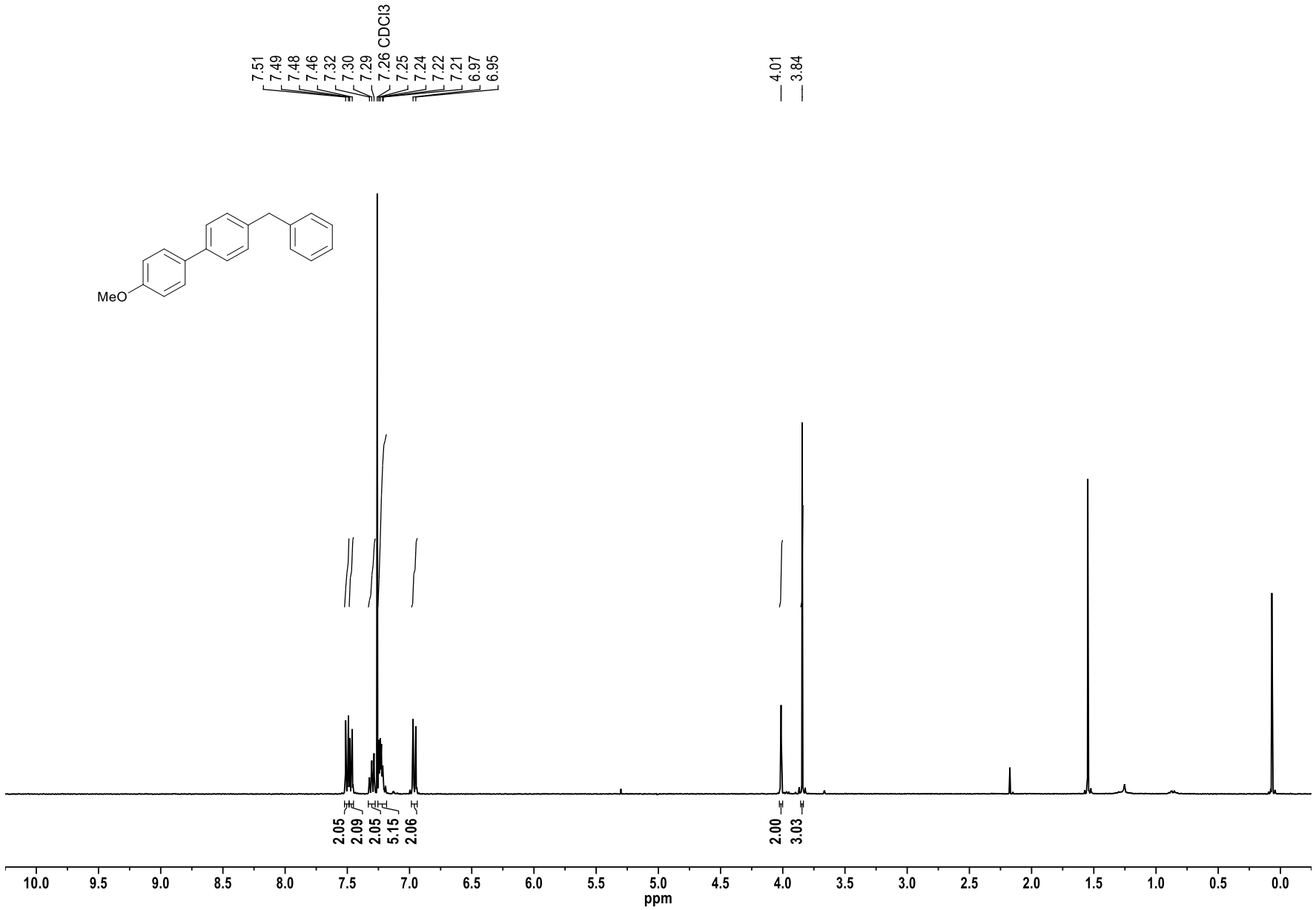
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7.24
7.22
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6.97
6.95
4.01
3.84
MeO
2.05
2.09
2.05
5.15
2.06
2.00
3.03
10.0
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9.0
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8.0
7.5
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6.0
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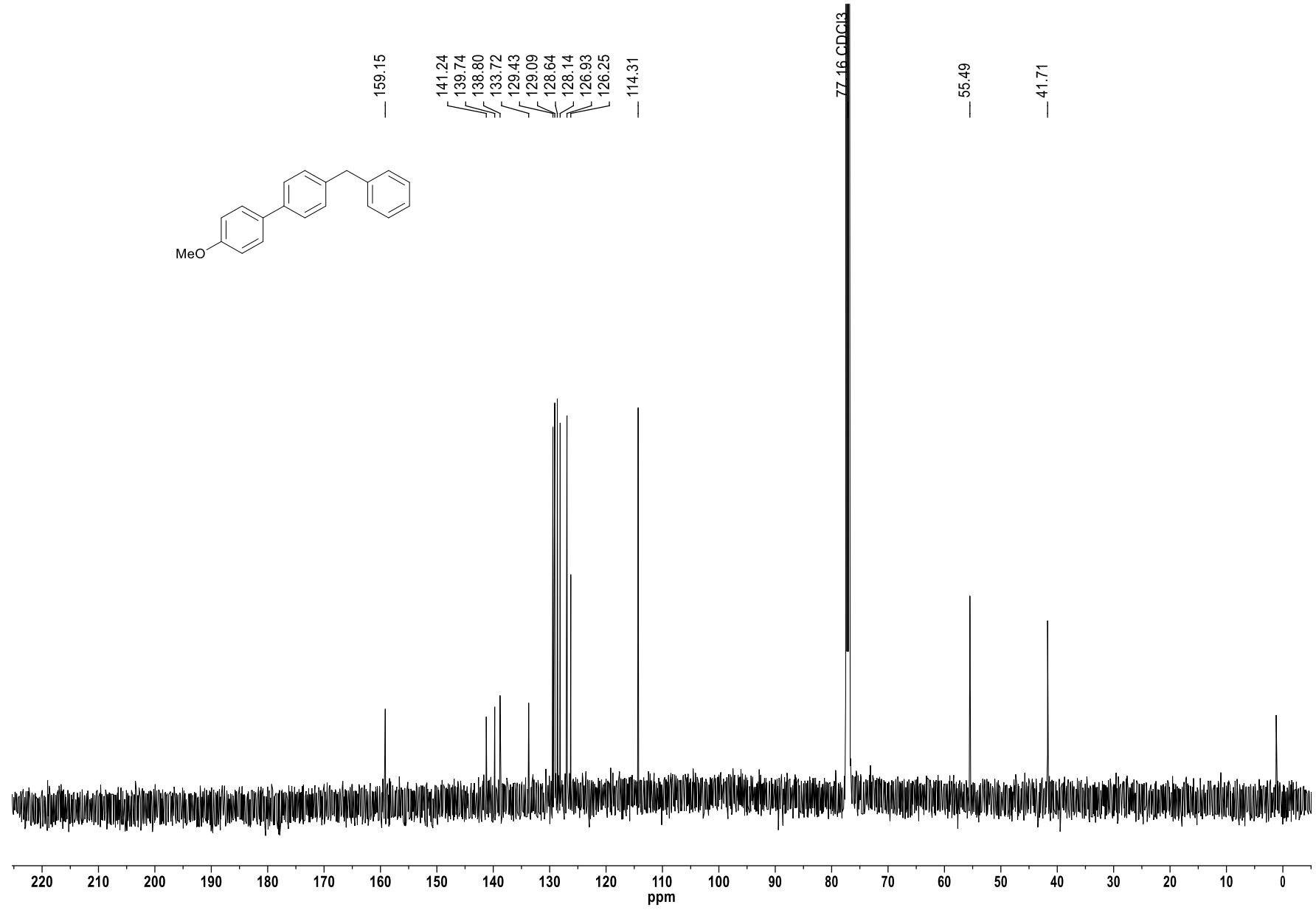
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126.93
126.25
114.31
77.16 CDCl3
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41.71
MeO
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200
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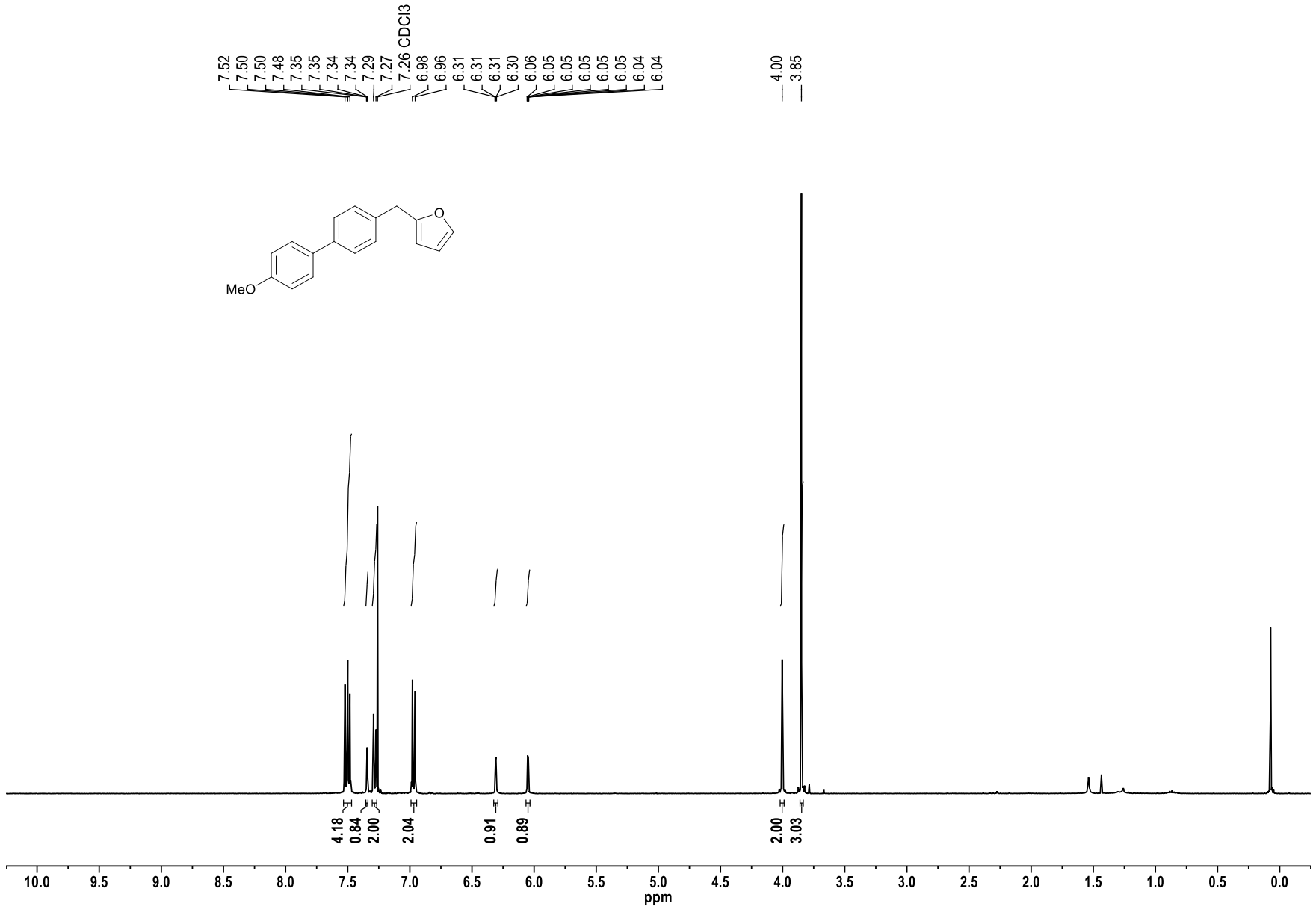
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7.34
7.29
7.27
7.26 CDCl3
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6.96
6.31
6.31
6.31
6.30
6.06
6.05
6.05
6.05
6.05
6.04
6.04
4.00
3.85
MeO
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4.18
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2.04
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0.89
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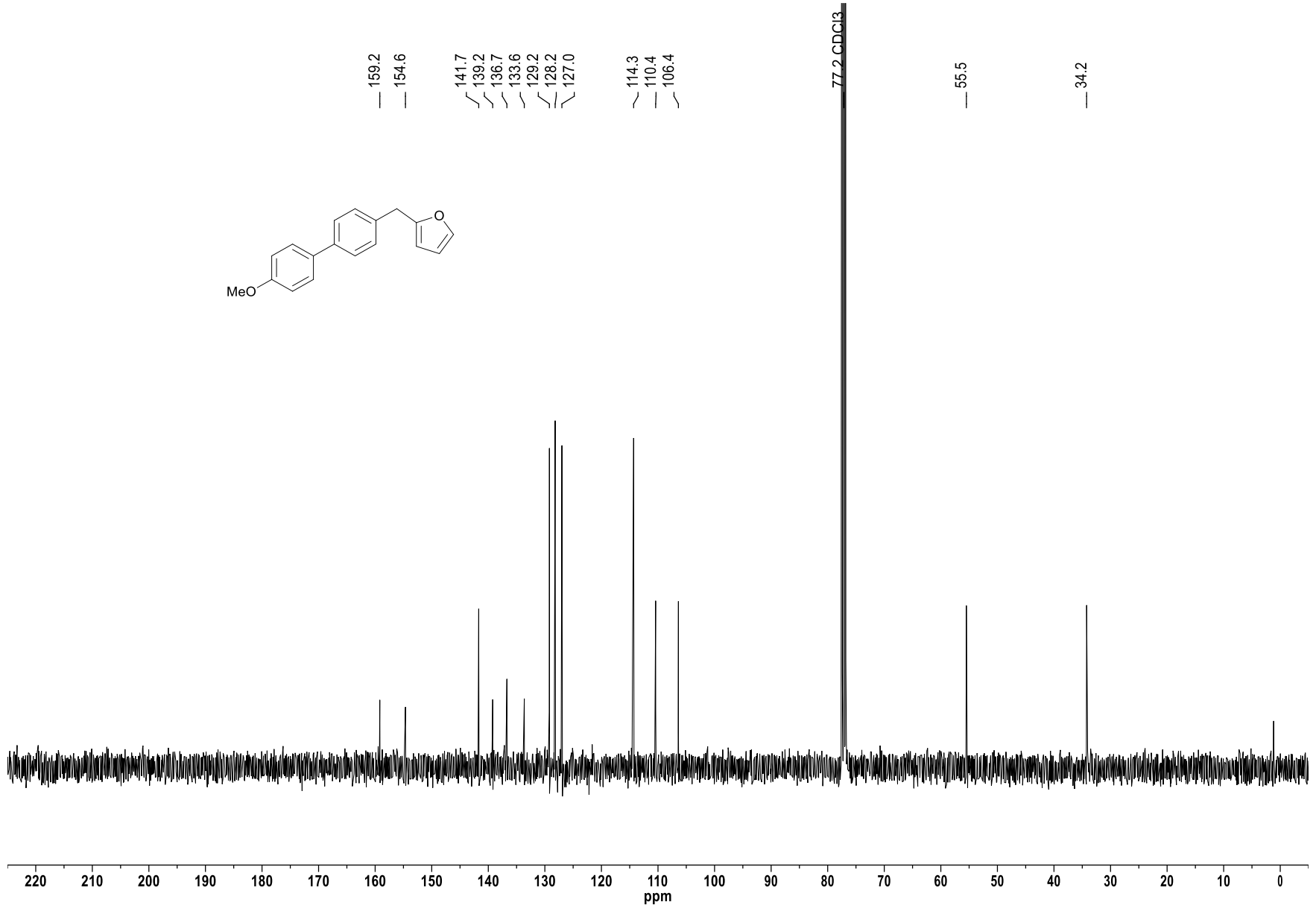
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133.6
129.2
128.2
127.0
114.3
110.4
106.4
77.2 CDCl3
55.5
34.2
MeO
O
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210
200
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180
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160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm