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Borane-Catalyzed Arylation of Aryldiazoacetates with *N*,*N*-Dialkylanilines

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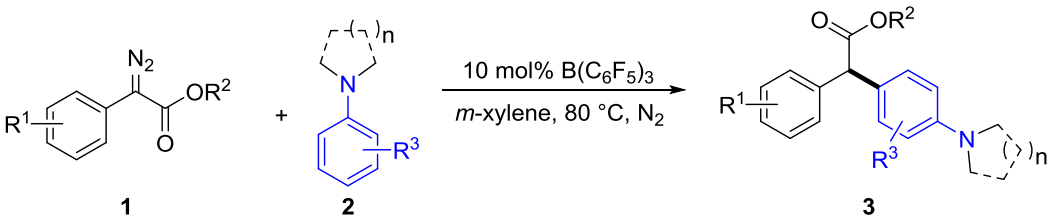
1. General Information

^{1}H and ^{13}C NMR spectra were recorded on a Bruker (400 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26), carbon (chloroform δ 77.0) or tetramethylsilane (TMS δ 0.00) was used as a reference. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), bs (broad singlet). Coupling constants were reported in Hertz (Hz). Infrared spectra were recorded on a Thermo Fisher Nicolet iS10 FTIR spectrometer, and the resulting spectra are reported in wavenumbers (cm^{-1}). All high resolution mass spectra (**HRMS**) were obtained on Agilent 1260-6224 LC-MS TOF using ESI (electrospray ionization). For thin layer chromatography (**TLC**), Merck pre-coated TLC plates (Merck 60 F254) were used, and compounds were visualized with a UV light at 254 nm. Further visualization was achieved by staining with I_2.

All reactions were carried out under nitrogen atmosphere. All commercially available reagents were used as received for the reactions without any purification. All solvents were dried on alumina columns using a solvent dispensing system. $B(C_6F_5)_3$ were purchased from TCI. Aryldiazoacetates were prepared according to the literature procedures[1, 2]. Aromatic tertiary amines were prepared according to the literature procedures[3]. Reactions were monitored by TLC on silica gel using a combination of hexane and ethyl acetate as eluents.

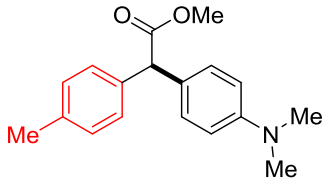
2. Typical Procedure of Borane-catalyzed Arylation reaction



To a Schlenk tube equipped with a dried stir bar was added $B(C_6F_5)_3$ (0.02 mmol), diazoester **1** (0.4 mmol), *N*,*N*-dialkylaniline **2** (0.20 mmol) and *m*-Xylene (2.0 mL) in the glovebox. The Schlenk tube was sealed with a Teflon screw cap. The reaction mixture was taken outside the glovebox and allowed to stir at 80 ℃ until the *N*,*N*-dialkylaniline **2** was completely consumed. The crude reaction mixture was concentrated under reduced pressure and directly purified by silica gel chromatography (ethyl acetate: hexanes = 1:40) to afford arylation product **3**.

3. Analytical Data of Arylation Products

methyl 2-(4-(dimethylamino)phenyl)-2-(*p*-tolyl)acetate (3a)[4]



3a

Purification by column chromatography (EtOAc/hexane, 1:40 v/v) afforded **3a**; light yellow oil, 47.5 mg, 84% yield (12h); R_f = 0.47 (1:10 EtOAc/hexanes).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 – 7.18 (m, 4H), 7.15 (d, *J* = 8.1 Hz, 2H), 6.71 (d, *J* = 8.7 Hz, 2H), 4.95 (s, 1H), 3.75 (s, 3H), 2.95 (s, 6H), 2.34 (s, 3H).

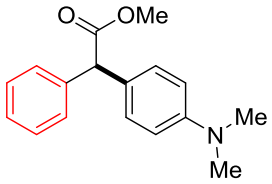
^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.82, 149.83, 136.71, 136.54, 129.32, 129.29, 128.45, 126.71, 112.73, 55.87, 52.24, 40.67, 21.12.

IR (film) ν_{max} 3089, 3019, 2985, 2948, 2914, 2849, 2797, 1743, 1613, 1513, 1344, 1275, 1187, 945, 817 cm^{-1}.

HRMS (ESI): m/z Calcd. for [$C_{18}H_{21}NO_2$, M+H]$^+$: 284.1646; Found: 284.1645.

Spectral data is consistent with those reported in reference S4.

methyl 2-(4-(dimethylamino)phenyl)-2-phenylacetate (3b)[4]



3b

Purification by column chromatography (EtOAc/hexane, 1:40 v/v) afforded **3b**; light yellow oil, 39.8 mg, 74% yield (26h); R_f = 0.4 (1:10 EtOAc/hexanes).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32-7.28 (m, 4H), 7.25 – 7.21 (m, 1H), 7.17 (d, *J* = 8.8 Hz, 2H), 6.68 (d, *J* = 8.8 Hz, 2H), 4.95 (s, 1H), 3.72 (s, 3H), 2.91 (s, 6H).

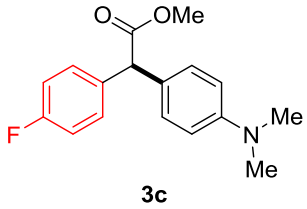
^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.66, 149.86, 139.52, 129.37, 128.58, 127.11, 126.47, 112.70, 56.23, 52.27, 40.64.

IR (film) ν_{max} 3086, 3060, 3032, 2990, 2951, 2920, 2880, 2844, 2794, 1738, 1613, 1521, 1352, 1193, 945, 809, 723, 694 cm^{-1}.

HRMS (ESI): m/z Calcd. for [$C_{17}H_{19}NO_2$, M+H]$^+$: 270.1489; Found: 270.1489.

Spectral data is consistent with those reported in reference S4.

methyl 2-(4-(dimethylamino)phenyl)-2-(4-fluorophenyl)acetate (3c)



3c

Purification by column chromatography (EtOAc/hexane, 1:40 v/v) afforded **3c**; light yellow oil, 45.3 mg, 79% yield (18h); R_f = 0.32 (1:10 EtOAc/hexanes).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.26 (m, 2H), 7.16 (d, *J* = 8.8 Hz, 2H), 7.03 – 6.96 (m, 2H), 6.70 (d, *J* = 8.8 Hz, 2H), 4.92 (s, 1H), 3.74 (s, 3H), 2.94 (s, 6H).

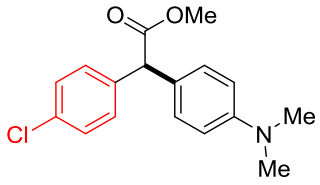
^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.57, 161.99 (d, *J* = 245.6 Hz), 149.91, 135.30 (d, *J* = 3.0 Hz), 130.19 (d, *J* = 8.0 Hz), 129.22, 126.22, 115.37 (d, *J* = 21.6 Hz), 112.71, 55.38, 52.34, 40.60.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -115.87.

IR (film) ν_{max} 3076, 3040, 2990, 2946, 2886, 2852, 2802, 1746, 1610, 1568, 1503, 1442, 1352, 817 cm^{-1}.

HRMS (ESI): m/z Calcd. for $[C_{17}H_{18}FNO_2, M+H]^+$: 288.1395; Found: 288.1394.

methyl 2-(4-chlorophenyl)-2-(4-(dimethylamino)phenyl)acetate (3d)[4]



3d

Purification by column chromatography (EtOAc/hexane, 1:40 v/v) afforded **3d**; light yellow oil, 41.8 mg, 69% yield (20h); R_f = 0.32 (1:10 EtOAc/hexanes).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.22 (m, 4H), 7.15 (d, *J* = 8.8 Hz, 2H), 6.69 (d, *J* = 8.8 Hz, 2H), 4.91 (s, 1H), 3.73 (s, 3H), 2.93 (s, 6H).

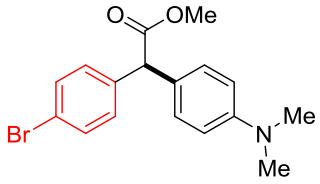
^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.34, 149.95, 138.07, 133.03, 130.01, 129.26, 128.71, 125.91, 112.73, 55.54, 52.41, 40.63.

IR (film) ν_{max} 3073, 3029, 2990, 2946, 2886, 2849, 2805, 1740, 1615, 1519, 1349, 1193, 817, 744, 551 cm^{-1}.

HRMS (ESI): m/z Calcd. for $[C_{17}H_{18}ClNO_2, M+H]^+$: 304.1099; Found: 304.1099.

Spectral data is consistent with those reported in reference S4.

methyl 2-(4-bromophenyl)-2-(4-(dimethylamino)phenyl)acetate (3e)[5]



3e

Purification by column chromatography (EtOAc/hexane, 1:40 v/v) afforded **3e**; light yellow oil, 45.1 mg, 65% yield (23h); R_f = 0.32 (1:10 EtOAc/hexanes).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 7.14 (d, *J* = 8.8 Hz, 2H), 6.68 (d, *J* = 8.8 Hz, 2H), 4.89 (s, 1H), 3.73 (s, 3H), 2.93 (s, 6H).

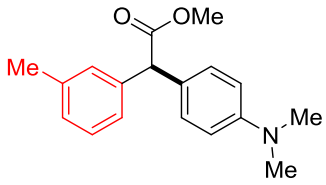
^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.26, 149.96, 138.60, 131.66, 130.39, 129.26, 125.81, 121.18, 112.73, 55.61, 52.42, 40.62.

IR (film) ν_{max} 3076, 2990, 2951, 2891, 2849, 2800, 1733, 1618, 1516, 1360, 1193, 814 cm^{-1}.

HRMS (ESI): m/z Calcd. for $[C_{17}H_{18}BrNO_2, M+H]^+$: 348.0594; Found: 348.0593.

Spectral data is consistent with those reported in reference S5.

methyl 2-(4-(dimethylamino)phenyl)-2-(m-tolyl)acetate (3f)



3f

Purification by column chromatography (EtOAc/hexane, 1:40 v/v) afforded **3f**; light yellow oil, 40.8 mg, 72% yield (16h); R_f = 0.47 (1:10 EtOAc/hexanes).

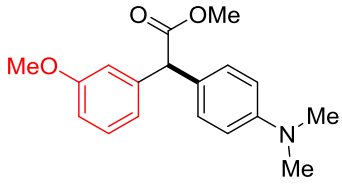
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 – 7.16 (m, 3H), 7.14 – 7.04 (m, 3H), 6.70 (d, *J* = 8.8 Hz, 2H), 4.92 (s, 1H), 3.73 (s, 3H), 2.93 (s, 6H), 2.32 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.79, 149.88, 139.40, 138.24, 129.40, 129.30, 128.51, 127.94, 126.62, 125.62, 112.76, 56.23, 52.29, 40.70, 21.60.

IR (film) ν_{max} 3097, 2990, 2953, 2917, 2800, 1735, 1612, 1523,1348, 1190, 1061, 886, 824,783, 740, 699 cm^{-1}.

HRMS (ESI): m/z Calcd. for $[C_{18}H_{21}NO_2, M+H]^+$: 284.1645; Found: 284.1646.

methyl 2-(4-(dimethylamino)phenyl)-2-(3-methoxyphenyl)acetate (3g)[4]



3g

Purification by column chromatography (EtOAc/hexane, 1:40 v/v) afforded **3g**; light yellow oil, 34.7 mg, 58% yield (28h); R_f = 0.27 (1:10 EtOAc/hexanes).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 (t, *J* = 7.9 Hz, 1H), 7.18 (d, *J* = 8.8 Hz, 2H), 6.90 (dt, *J* = 7.6, 0.8 Hz, 1H), 6.87 (t, *J* = 2.1 Hz, 1H), 6.79 (ddd, *J* = 8.3, 2.6, 0.9 Hz, 1H), 6.70 (d, *J* = 8.8 Hz, 2H), 4.92 (s, 1H), 3.77 (s, 3H), 3.73 (s, 3H), 2.93 (s, 6H).

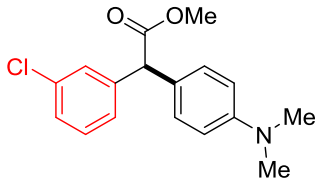
^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.56, 159.80, 149.88, 141.00, 129.57, 129.39, 126.44, 121.03, 114.54, 112.82, 112.46, 56.24, 55.31, 52.33, 40.74.

IR (film) ν_{max} 3073, 2995, 2943, 2838, 2799, 1748, 1615, 1521, 1351, 1288, 1260, 1198, 1144, 871, 819, 779, 692 cm^{-1}.

HRMS (ESI): m/z Calcd. for $[C_{18}H_{21}NO_3, M+H]^+$: 300.1594; Found: 300.1595.

Spectral data is consistent with those reported in reference S4.

methyl 2-(3-chlorophenyl)-2-(4-(dimethylamino)phenyl)acetate (3h)[4]



3h

Purification by column chromatography (EtOAc/hexane, 1:40 v/v) afforded **3h**; light yellow oil, 24.2 mg, 40% yield (24h); R_f = 0.45 (1:10 EtOAc/hexanes).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 (s, 1H), 7.24 – 7.18 (m, 3H), 7.16 (d, *J* = 8.8 Hz, 2H), 6.69 (d, *J* = 8.8 Hz, 2H), 4.90 (s, 1H), 3.73 (s, 3H), 2.93 (s, 6H).

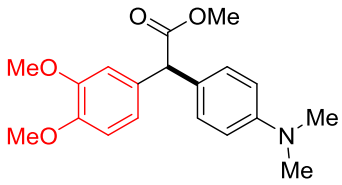
^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.15, 150.04, 141.55, 134.45, 129.81, 129.35, 128.82, 127.38, 126.86, 125.67, 112.76, 55.86, 52.47, 40.63.

IR (film) ν_{max} 3066, 2998, 2943, 2904, 2880, 2852, 2802, 1735, 1615, 1519, 1362, 1267, 878, 788, 814, 684, 619 cm^{-1}.

HRMS (ESI): m/z Calcd. for $[C_{17}H_{18}ClNO_2, M+H]^+$: 304.1099; Found: 304.1098.

Spectral data is consistent with those reported in reference S4.

methyl 2-(3,4-dimethoxyphenyl)-2-(4-(dimethylamino)phenyl)acetate (3i)



3i

Purification by column chromatography (EtOAc/hexane, 1:40 v/v) afforded **3i**; light yellow oil, 41.5 mg, 63% yield (18h); R_f = 0.2 (1:5 EtOAc/hexanes).

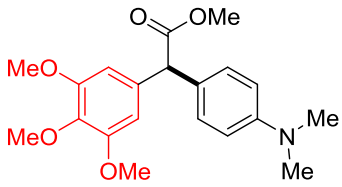
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.17 (d, *J* = 8.8 Hz, 2H), 6.87 – 6.84 (m, 2H), 6.82 – 6.79 (m, 1H), 6.70 (d, *J* = 8.8 Hz, 2H), 4.89 (s, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 3.73 (s, 3H), 2.93 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.86, 149.79, 149.00, 148.22, 131.92, 129.20, 126.81, 120.77, 112.80, 111.92, 111.14, 55.98, 55.72, 52.30, 40.73.

IR (film) ν_{max} 3076, 3000, 2948, 2839, 2801, 1740, 1614, 1501, 1358, 1259, 1196, 1134, 813 cm^{-1}.

HRMS (ESI): m/z Calcd. for [$C_{19}H_{23}NO_4$, M+H]$^+$: 330.1700; Found: 330.1696.

methyl 2-(4-(dimethylamino)phenyl)-2-(3,4,5-trimethoxyphenyl)acetate (3j)



3j

Purification by column chromatography (EtOAc/hexane, 1:5 v/v) afforded **3j**; light yellow oil, 39.5 mg, 55% yield (18h); R_f = 0.2 (1:5 EtOAc/hexanes).

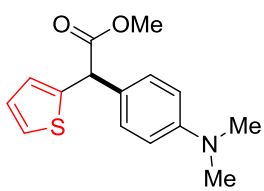
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.19 (d, *J* = 8.8 Hz, 2H), 6.70 (d, *J* = 8.8 Hz, 2H), 6.56 (s, 2H), 4.87 (s, 1H), 3.82 (s, 9H), 3.74 (s, 3H), 2.93 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.63, 153.21, 149.86, 136.96, 134.86, 129.12, 126.14, 112.61, 105.56, 60.88, 56.19, 56.12, 52.35, 40.61.

IR (film) ν_{max} 3079, 3000, 2951, 2922, 2836, 2800, 1735, 1607, 1503, 1388, 1352, 1256, 1188, 1128, 822 cm^{-1}.

HRMS (ESI): m/z Calcd. for [$C_{20}H_{25}NO_5$, M+H]$^+$: 360.1806; Found: 360.1801.

methyl 2-(4-(dimethylamino)phenyl)-2-(thiophen-2-yl)acetate (3k)



3k

Purification by column chromatography (EtOAc/hexane, 1:40 v/v) afforded **3k**; light yellow oil, 34.1 mg, 62% yield (10h); R_f = 0.46 (1:10 EtOAc/hexanes).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 – 7.23 (m, 2H),

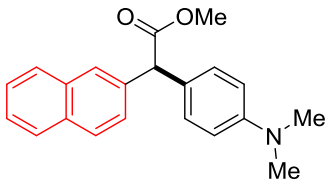
7.21 (dd, *J* = 4.9, 1.5 Hz, 1H), 6.97 – 6.93 (m, 2H), 6.69 (d, *J* = 8.9 Hz, 2H), 5.13 (s, 1H), 3.74 (s, 3H), 2.94 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.83, 150.13, 142.35, 129.02, 126.64, 126.25, 126.01, 125.08, 112.62, 52.57, 51.54, 40.62.

IR (film) ν_{max} 3100, 3071, 2987, 2951, 2888, 2849, 2802, 1740, 1615, 1521, 1435, 1357, 1196, 1060, 997, 945, 817 cm^{-1}.

HRMS (ESI): m/z Calcd. for $[C_{15}H_{17}NO_2S, M+H]^+$: 276.1053; Found: 276.1053.

methyl 2-(4-(dimethylamino)phenyl)-2-(naphthalen-2-yl)acetate (3l)[4]



3l

Purification by column chromatography (EtOAc/hexane, 1:40 v/v) afforded **3l**; light yellow oil, 38.3 mg, 60% yield (18h); R_f = 0.37 (1:10 EtOAc/hexanes).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 – 7.76 (m, 4H), 7.50 – 7.43 (m, 3H), 7.24 (d, *J* = 8.8 Hz, 2H), 6.72 (d, *J* = 8.8 Hz, 2H), 5.14 (s, 1H), 3.78 (s, 3H), 2.94 (s, 6H).

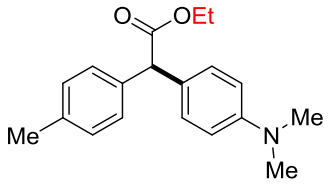
^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.69, 149.91, 136.95, 133.46, 132.58, 129.48, 128.30, 128.08, 127.68, 127.08, 126.98, 126.31, 126.18, 125.95, 112.71, 56.33, 52.38, 40.66.

IR (film) ν_{max} 3053, 3019, 2987, 2953, 2891, 2849, 2805, 1740, 1613, 1526, 1433, 1352, 1188, 1060, 1013, 947, 860, 820, 746, 710 cm^{-1}.

HRMS (ESI): m/z Calcd. for $[C_{21}H_{21}NO_2, M+H]^+$: 320.1646; Found: 320.1640.

Spectral data is consistent with those reported in reference S4.

ethyl 2-(4-(dimethylamino)phenyl)-2-(*p*-tolyl)acetate (3m)



3m

Purification by column chromatography (EtOAc/hexane, 1:40 v/v) afforded **3m**; light yellow oil, 42.8 mg, 72% yield (24h); R_f = 0.43 (1:10 EtOAc/hexanes).

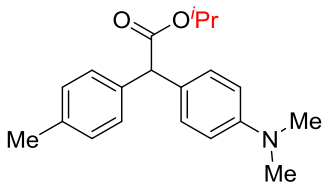
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 – 7.18 (m, 4H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.71 (d, *J* = 8.8 Hz, 2H), 4.91 (s, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.94 (s, 6H), 2.34 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.34, 149.78, 136.72, 136.63, 129.32, 129.26, 128.46, 126.94, 112.72, 61.03, 55.97, 40.69, 21.13, 14.29.

IR (film) ν_{max} 3094, 2979, 2922, 2797, 1736, 1610, 1520, 1480, 1346, 1187, 801 cm^{-1}.

HRMS (ESI): m/z Calcd. for $[C_{19}H_{23}NO_2, M+H]^+$: 298.1802; Found: 298.1807.

isopropyl 2-(4-(dimethylamino)phenyl)-2-(*p*-tolyl)acetate (3n)



3n

Purification by column chromatography (EtOAc/hexane, 1:40 v/v) afforded **3n**; light yellow oil, 41.1 mg, 66% yield (26h); R_f = 0.4 (1:10 EtOAc/hexanes).

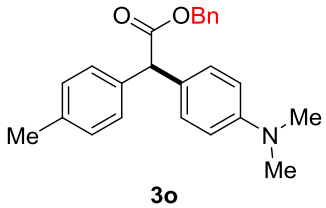
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 – 7.15 (m, 4H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.69 (d, *J* = 8.8 Hz, 2H), 5.11 – 5.03 (m, 1H), 4.85 (s, 1H), 2.93 (s, 6H), 2.32 (s, 3H), 1.23 (d, *J* = 6.2 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.85, 149.75, 136.88, 136.54, 129.33, 129.23, 128.47, 127.13, 112.72, 68.35, 56.12, 40.72, 21.84, 21.15.

IR (film) ν_{max} 3097, 3053, 3021, 2980, 2922, 2878, 2802, 1725, 1618, 1519, 1389, 1371, 1354, 1193, 825 cm^{-1}.

HRMS (ESI): m/z Calcd. for $[C_{20}H_{25}NO_2, M+H]^+$: 312.1959; Found: 312.1959.

benzyl 2-(4-(dimethylamino)phenyl)-2-(*p*-tolyl)acetate (3o)



3o

Purification by column chromatography (EtOAc/hexane, 1:40 v/v) afforded **3o**; light yellow oil, 50.3 mg, 70% yield (26h); R_f = 0.43 (1:10 EtOAc/hexanes).

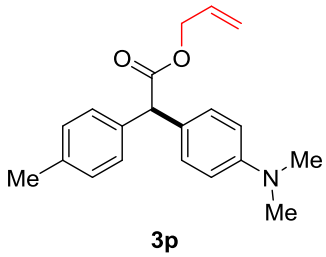
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.27 (m, 5H), 7.20 – 7.14 (m, 4H)., 7.10 (d, *J* = 7.7 Hz, 2H), 6.67 (d, *J* = 8.8 Hz, 2H), 5.17 (s, 2H), 4.96 (s, 1H), 2.92 (s, 6H), 2.31 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.19, 149.84, 136.70, 136.52, 136.06, 129.37, 129.27, 128.57, 128.49, 128.26, 128.21, 126.71, 112.71, 66.78, 55.88, 40.69, 21.14.

IR (film) ν_{max} 3086, 3060, 3032, 2951, 2914, 2873, 2797, 1730, 1610, 1513, 1456, 1373, 1277, 1184, 806, 746, 697 cm^{-1}.

HRMS (ESI): m/z Calcd. for $[C_{24}H_{25}NO_2, M+H]^+$: 360.1959; Found: 360.1953.

allyl 2-(4-(dimethylamino)phenyl)-2-(*p*-tolyl)acetate (3p)



3p

Purification by column chromatography (EtOAc/hexane, 1:40 v/v) afforded **3p**; light yellow oil, 43.3 mg, 70% yield (21h); R_f = 0.4 (1:10 EtOAc/hexanes).

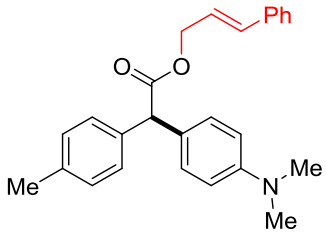
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 – 7.17 (m, 4H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.69 (d, *J* = 8.8 Hz, 2H), 5.96 – 5.85 (m, 1H), 5.29 – 5.18 (m, 2H), 4.94 (s, 1H), 4.64 (dt, *J* = 5.7, 1.4 Hz, 2H), 2.93 (s, 6H), 2.32 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.02, 149.83, 136.73, 136.55, 132.25, 129.37, 129.30, 128.49, 126.83, 118.43, 112.79, 65.67, 55.93, 40.73, 21.15.

IR (film) ν_{max} 3091, 3021, 2982, 2877, 2797, 1732, 1645, 1615, 1510, 1478, 1354, 1276, 1188, 991, 926, 849, 816 cm^{-1}.

HRMS (ESI): m/z Calcd. for $[C_{20}H_{23}NO_2, M+H]^+$: 310.1802: Found: 310.1802.

cinnamyl 2-(4-(dimethylamino)phenyl)-2-(*p*-tolyl)acetate (3q)



3q

Purification by column chromatography (EtOAc/hexane, 1:40 v/v) afforded **3q**; light yellow oil, 43.1 mg, 56% yield (21h); R_f = 0.4 (1:10 EtOAc/hexanes).

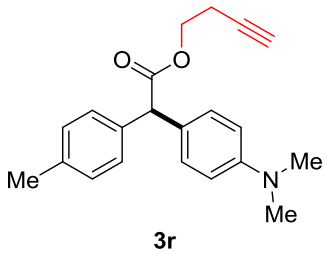
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.28 (m, 4H), 7.24 – 7.18 (m, 5H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.69 (d, *J* = 8.8 Hz, 2H), 6.55 (dt, *J* = 15.9, 1.4 Hz, 1H), 6.26 (dt, *J* = 15.9, 6.3 Hz, 1H), 4.96 (s, 1H), 4.79 (dd, *J* = 6.3, 1.4 Hz, 2H), 2.92 (s, 6H), 2.32 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.10, 149.82, 136.75, 136.52, 136.41, 134.04, 129.40, 129.32, 128.67, 128.51, 128.09, 126.79, 126.74, 123.28, 112.80, 65.49, 55.98, 40.73, 21.15.

IR (film) ν_{max} 3126, 3084, 3026, 2953, 2914, 2800, 1746, 1660, 1623, 1532, 1357, 1273, 1187, 982, 908, 886, 825, 735, 689 cm^{-1}.

HRMS (ESI): m/z Calcd. for $[C_{26}H_{27}NO_2, M+H]^+$: 386.2115; Found: 386.2114.

but-3-yn-1-yl 2-(4-(dimethylamino)phenyl)-2-(*p*-tolyl)acetate (3r)



3r

Purification by column chromatography (EtOAc/hexane, 1:40 v/v) afforded **3r**; light yellow oil, 41.7 mg, 65% yield (21h); R_f = 0.4 (1:10 EtOAc/hexanes).

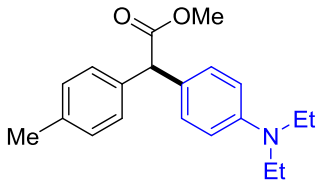
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 – 7.16 (m, 4H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.69 (d, *J* = 8.8 Hz, 2H), 4.93 (s, 1H), 4.24 (t, *J* = 7.0 Hz, 2H), 2.93 (s, 6H), 2.53 (td, *J* = 7.0, 2.7 Hz, 2H), 2.32 (s, 3H), 1.98 (t, *J* = 2.7 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.11, 149.88, 136.77, 136.42, 129.38, 129.30, 128.50, 126.60, 112.75, 80.10, 70.09, 62.71, 55.82, 40.71, 21.16, 19.03.

IR (film) ν_{max} 3291, 3089, 3021, 2956, 2922, 2852, 2802, 2121, 1739, 1615, 1516, 1443, 1352, 1185, 814, 647 cm^{-1}.

HRMS (ESI): m/z Calcd. for $[C_{21}H_{23}NO_2, M+H]^+$: 322.1802; Found: 322.1800.

methyl 2-(4-(diethylamino)phenyl)-2-(*p*-tolyl)acetate (3s)



3s

Purification by column chromatography (EtOAc/hexane, 1:40 v/v) afforded **3s**; light yellow oil, 29.9 mg, 48% yield (24h); R_f = 0.42 (1:10 EtOAc/hexanes).

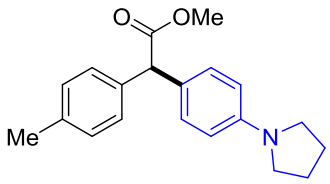
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21 (d, *J* = 8.2 Hz, 2H), 7.15 – 7.10 (m, 4H), 6.63 (d, *J* = 8.8 Hz, 2H), 4.89 (s, 1H), 3.72 (s, 3H), 3.32 (q, *J* = 7.1 Hz, 4H), 2.32 (s, 3H), 1.14 (t, *J* = 7.0 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.96, 146.93, 136.72, 136.65, 129.54, 129.31, 128.49, 111.95, 55.88, 52.26, 44.54, 21.16, 12.69.

IR (film) ν_{max} 3126, 3094, 3026, 2972, 2867, 1743, 1613, 1524, 1464, 1398, 1350, 1149, 1000, 809 cm^{-1}.

HRMS (ESI): m/z Calcd. for $[C_{20}H_{25}NO_2, M+H]^+$: 312.1959; Found: 312.1958.

methyl 2-(4-(pyrrolidin-1-yl)phenyl)-2-(*p*-tolyl)acetate (3t)



3t

Purification by column chromatography (EtOAc/hexane, 1:40 v/v) afforded **3t**; light yellow oil, 30.9 mg, 50% yield (24h); R_f = 0.46 (1:10 EtOAc/hexanes).

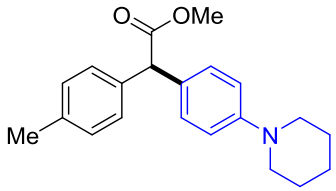
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.19 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.7 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.52 (d, *J* = 8.7 Hz, 2H), 4.91 (s, 1H), 3.72 (s, 3H), 3.31 – 3.22 (m, 4H), 2.32 (s, 3H), 2.02 – 1.95 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.98, 147.19, 136.75, 136.67, 129.46, 129.28, 128.48, 125.50, 111.79, 55.97, 52.25, 47.75, 25.60, 21.15.

IR (film) ν_{max} 3129, 3090, 3017, 2962, 2835, 1739, 1614, 1517, 1458, 1375, 1143, 1013, 807, 711 cm^{-1}.

HRMS (ESI): m/z Calcd. for $[C_{20}H_{23}NO_2, M+H]^+$: 310.1802; Found: 310.1805.

methyl 2-(4-(piperidin-1-yl)phenyl)-2-(*p*-tolyl)acetate (3u)



3u

Purification by column chromatography (EtOAc/hexane, 1:40 v/v) afforded **3u**; light yellow oil, 29.7 mg, 46% yield (24h); R_f = 0.46 (1:10 EtOAc/hexanes).

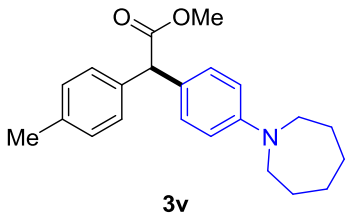
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21 – 7.14 (m, 4H), 7.11 (d, *J* = 7.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 4.91 (s, 1H), 3.72 (s, 3H), 3.16 – 3.09 (m, 4H), 2.31 (s, 3H), 1.74 – 1.63 (m, 4H), 1.59 – 1.53 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.74, 151.38, 136.85, 136.36, 129.34, 129.27, 129.18, 128.51, 116.49, 55.96, 52.32, 50.58, 25.94, 24.40, 21.17.

IR (film) ν_{max} 3128, 3094, 3026, 2940, 2846, 2800, 2753, 2706, 1738, 1613, 1509, 1454, 1386, 1281, 1190, 864, 741 cm^{-1}.

HRMS (ESI): m/z Calcd. for $[C_{21}H_{25}NO_2, M+H]^+$: 324.1959; Found: 324.1953.

methyl 2-(4-(azepan-1-yl)phenyl)-2-(*p*-tolyl)acetate (3v)



3v

Purification by column chromatography (EtOAc/hexane, 1:40 v/v) afforded **3v**; light yellow oil, 39.8 mg, 59% yield (24h); R_f = 0.46 (1:10 EtOAc/hexanes).

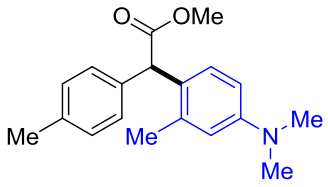
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21 (d, *J* = 8.1 Hz, 2H), 7.15 – 7.10 (m, 4H), 6.62 (d, *J* = 8.8 Hz, 2H), 4.89 (s, 1H), 3.72 (s, 3H), 3.44 – 3.38 (m, 4H), 2.32 (s, 3H), 1.76 (p, *J* = 6.5, 5.4 Hz, 4H), 1.53 (dt, *J* = 5.8, 2.7 Hz, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.00, 148.17, 136.69, 136.68, 129.46, 129.29, 128.47, 125.12, 111.19, 55.83, 52.29, 49.08, 27.92, 27.30, 21.18.

IR (film) ν_{max} 3133, 3094, 3021, 2946, 2846, 1746, 1610, 1521, 1385, 1269, 1200, 1098, 806, 713 cm^{-1}.

HRMS (ESI): m/z Calcd. for $[C_{22}H_{27}NO_2, M+H]^+$: 338.2115; Found: 338.2116.

methyl 2-(4-(dimethylamino)-2-methylphenyl)-2-(*p*-tolyl)acetate (3w)



3w

Purification by column chromatography (EtOAc/hexane, 1:40 v/v) afforded **3w**; light yellow oil, 41.6 mg, 70% yield (16h); R_f = 0.43 (1:10 EtOAc/hexanes).

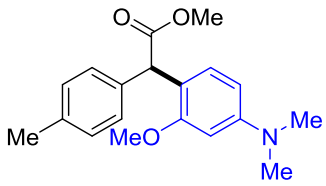
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.13 – 7.08 (m, 5H), 6.60 – 6.55 (m, 2H), 5.11 (s, 1H), 3.73 (s, 3H), 2.93 (s, 6H), 2.32 (s, 3H), 2.26 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.10, 149.80, 137.08, 136.67, 135.84, 129.28, 128.93, 128.80, 125.38, 114.87, 110.51, 52.67, 52.29, 40.70, 21.17, 20.44.

IR (film) ν_{max} 3125, 3086, 3023, 2943, 2797, 1742, 1604, 1515, 1375, 1355, 1191, 840 cm^{-1}.

HRMS (ESI): m/z Calcd. for $[C_{19}H_{23}NO_2, M+H]^+$: 298.1802; Found: 298.1802.

methyl 2-(4-(dimethylamino)-2-methoxyphenyl)-2-(*p*-tolyl)acetate (3x)



3x

Purification by column chromatography (EtOAc/hexane, 1:40 v/v) afforded **3x**; light yellow oil, 38.2 mg, 61% yield (18h); R_f = 0.43 (1:10 EtOAc/hexanes).

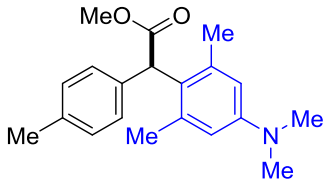
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.88 (d, *J* = 8.1 Hz, 1H), 6.28 – 6.19 (m, 2H), 5.19 (s, 1H), 3.82 (s, 3H), 3.71 (s, 3H), 2.94 (s, 6H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.37, 157.70, 151.31, 136.65, 135.55, 129.56, 129.30, 128.94, 116.19, 104.62, 96.04, 55.51, 52.23, 49.87, 40.82, 21.22.

IR (film) ν_{max} 3089, 2998, 2951, 2917, 2834, 2802, 1741, 1619, 1515, 1361, 1238, ,1155, 1110, 811 cm^{-1}.

HRMS (ESI): m/z Calcd. for $[C_{19}H_{23}NO_2, M+H]^+$: 314.1751; Found: 314.1756.

methyl 2-(4-(dimethylamino)-2,6-dimethylphenyl)-2-(*p*-tolyl)acetate (3y)



3y

Purification by column chromatography (EtOAc/hexane, 1:40 v/v) afforded **3y**; light yellow oil, 42.3 mg, 68% yield (16h); R_f = 0.43 (1:10 EtOAc/hexanes).

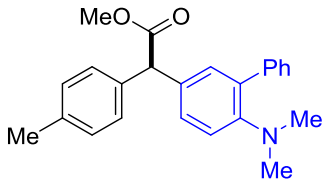
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.09 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.47 (s, 2H), 5.29 (s, 1H), 3.73 (s, 3H), 2.95 (s, 6H), 2.32 (s, 3H), 2.18 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.58, 149.45, 138.37, 136.24, 134.55, 128.93, 128.73, 123.91, 113.23, 52.29, 50.22, 40.56, 21.53, 21.14.

IR (film) ν_{max} 3092, 3050, 3021, 2951, 2925, 2891, 2854, 2805, 1733, 1602, 1506, 1365, 1169, 830 cm^{-1}.

HRMS (ESI): m/z Calcd. for $[C_{20}H_{25}NO_2, M+H]^+$: 312.1959; Found: 312.1951.

methyl 2-(4-(dimethylamino)-2-phenylphenyl)-2-(*p*-tolyl)acetate (3z)



3z

The reaction was performed in DCM at 60 ℃. Purification by column chromatography (EtOAc/hexane, 1:40 v/v) afforded **3z**; light yellow oil, 16 mg, 22% yield (48h); R_f = 0.64 (1:10 EtOAc/hexanes).

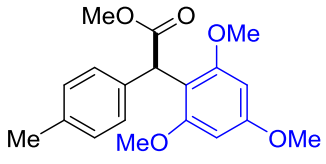
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 7.3 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.25 – 7.20 (m, 3H), 7.19 (d, *J* = 2.4 Hz, 1H), 7.15 (d, *J* = 2.3 Hz, 1H), 7.12 (d, *J* = 7.8 Hz, 2H), 6.96 (d, *J* = 8.3 Hz, 1H), 4.95 (s, 1H), 3.73 (s, 3H), 2.51 (s, 6H), 2.31 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.58, 150.43, 141.89, 136.97, 136.09, 134.03, 132.06, 131.64, 129.44, 128.80, 128.50, 128.43, 128.03, 126.67, 117.75, 56.12, 52.41, 43.42, 21.18.

IR (film) ν_{max} 3050, 3021, 2948, 2867, 2831, 2776, 1738, 1602, 1506, 1380, 1323, 1256, 1193, 945, 820, 773, 741, 700 cm^{-1}.

HRMS (ESI): m/z Calcd. for [$C_{24}H_{25}NO_2$, M+H]$^+$: 360.1958; Found: 360.1951.

methyl 2-(*p*-tolyl)-2-(2,4,6-trimethoxyphenyl)acetate (5)



5

The reaction was performed in DCM at 60 ℃. Purification by column chromatography (EtOAc/hexane, 1:10 v/v) afforded **3ab**; light yellow oil, 42.9 mg, 65% yield (40h); R_f = 0.26 (1:5 EtOAc/hexanes).

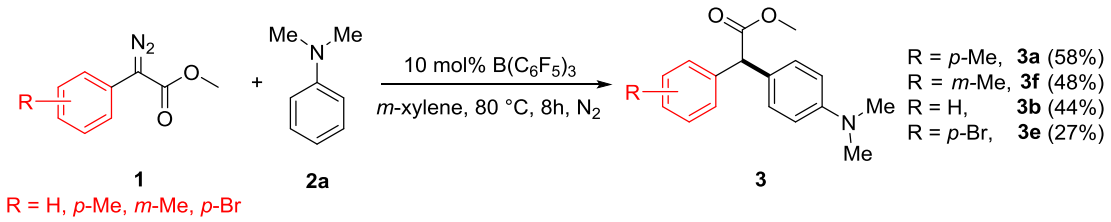
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 6.16 (s, 2H), 5.29 (s, 1H), 3.81 (s, 3H), 3.79 (s, 6H), 3.69 (s, 3H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.46, 160.52, 158.29, 136.20, 136.02, 129.25, 128.82, 109.88, 91.12, 55.87, 55.43, 52.06, 45.47, 21.21.

IR (film) ν_{max} 3094, 3003, 2943, 2836, 1746, 1602, 1503, 1376, 1276, 1200, 1112, 822 cm^{-1}.

HRMS (ESI): m/z Calcd. for [$C_{19}H_{22}O_5$, M+H]$^+$: 331.1540; Found: 331.1537.

4. Hammett Studies



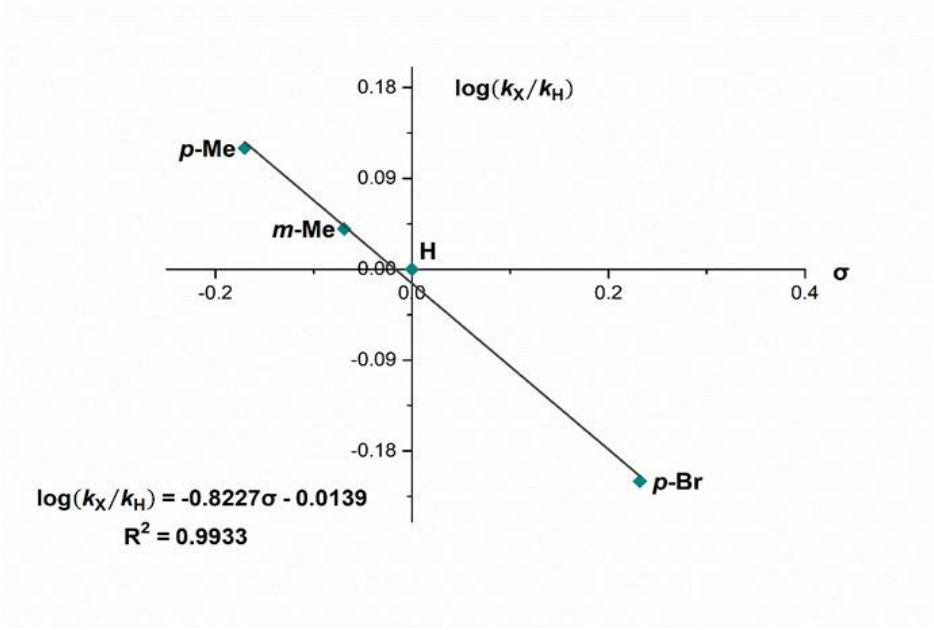


Figure S1. $\log(k_X/k_H)$ *vs* σ is employed to determine the ρ value

Experimental procedure: In four different 10 mL Schlenk tubes, *N*, *N*-dimethylaniline **2a** (0.1 mmol, 1.0 equiv.) and $B(C_6F_5)_3$ (0.01 mmol, 10 mol %) were dissolved in 0.5 mL *m*-xylene in the glovebox. Next, 0.5 mL *m*-xylene solution of diazoacetate **1a**, **1f**, **1b** and **1e** (0.2 mmol, 2 equiv.) was added in the four different Schlenk tubes, respectively. The Schlenk tubes were sealed with Teflon screw caps. The reaction mixtures were taken outside the glovebox and allowed to stir at 80 ℃ for 8 hours. The crude reaction mixture was concentrated under reduced pressure and directly purified by silica gel chromatography to afford products **3a**, **3f**, **3b** and **3e** in 58%, 48%, 44%, and 27% yields, respectively. The ratio of the reaction rate was

determined from the ratio of the yields of the corresponding product to draw the Hammett plot (Figure S1).

Substrates **1** with electron-donating groups on the aryl-ring reacted at faster rates, which possibly providing enhanced stabilization for the resulting enol cation intermediates.

5. References

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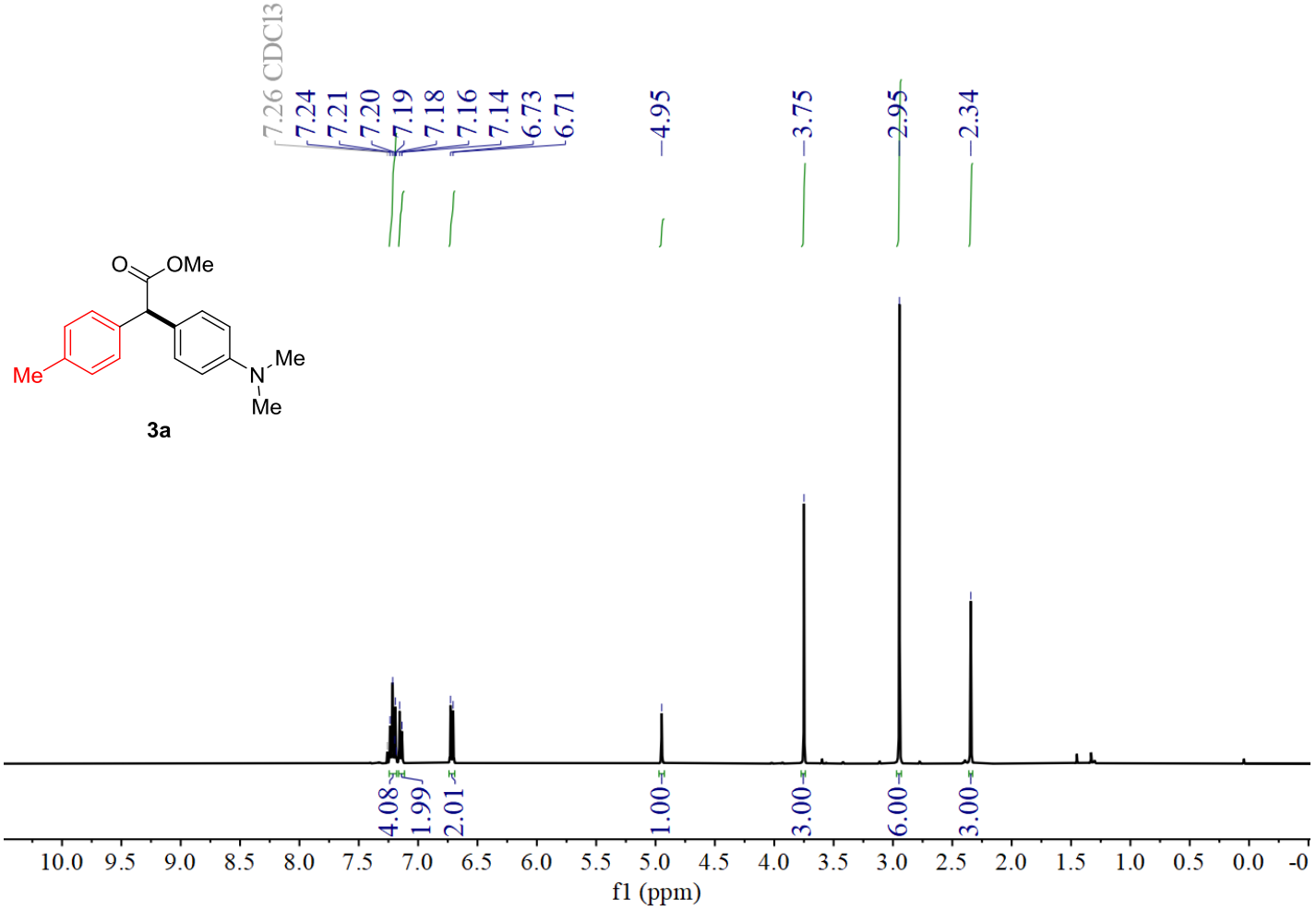
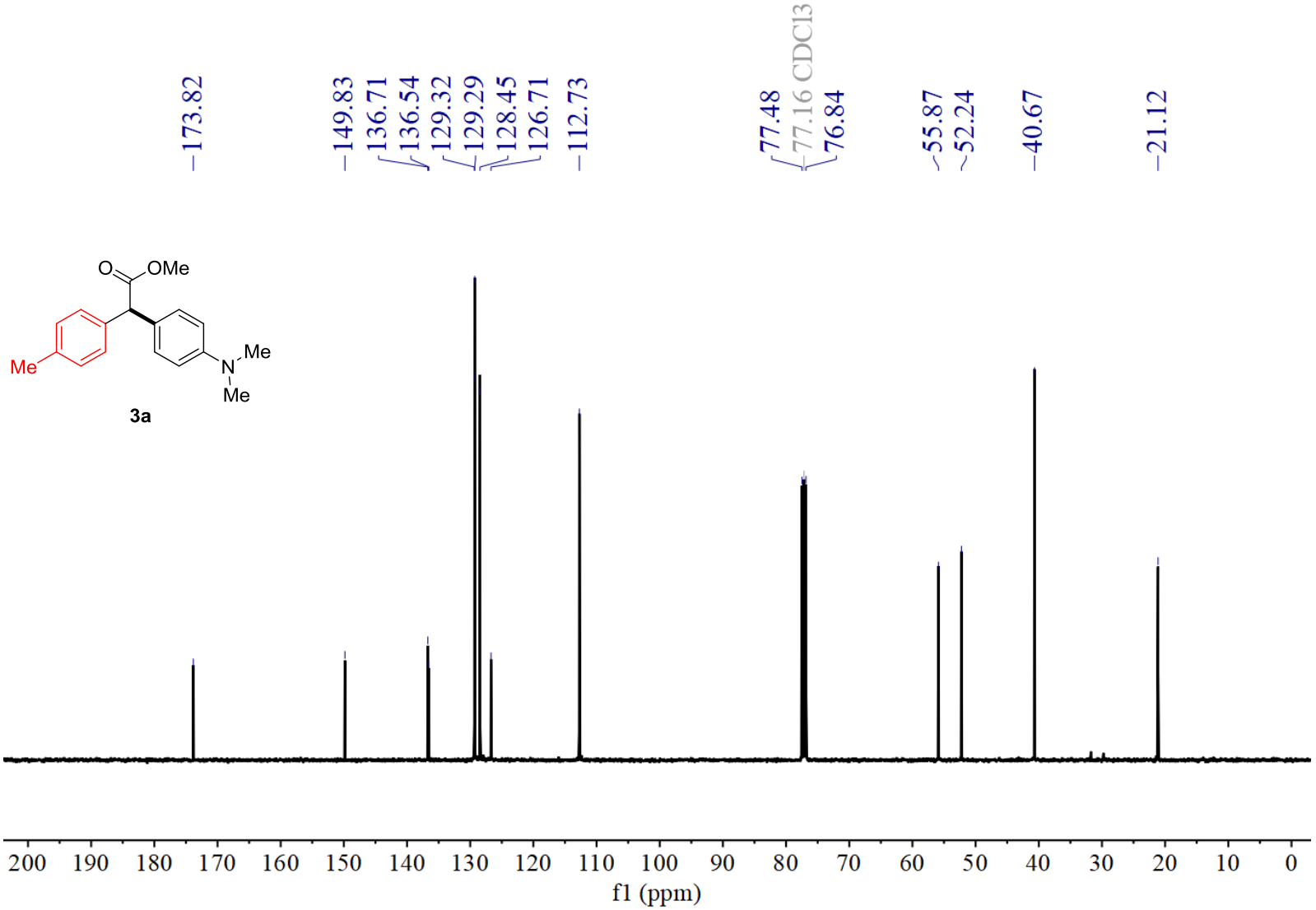
(2) R. D. C. Gallo, P. B. Momo, D. P. Day and A. C. B. Burtoloso, *Org. Lett.*, 2020, **22**, 2339-2343.
(3) B. Xu, M. L. Li, X. D. Zuo, S. F. Zhu and Q. L. Zhou, *J. Am. Chem. Soc.*, 2015, **137**, 8700-8703.
(4) J. Yang, Y. Cai, S. Zhu and Q. Zhou, *Org. Biomol. Chem.*, 2016, **14**, 5516-5519.
(5) H. M. L. Davies and Q. Jin, *Org. Lett.*, 2004, **6**, 1769-1772.

6. NMR Spectra of products

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126.71
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77.48
77.16 CDCl3
76.84
55.87
52.24
40.67
21.12
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Me
N
Me
Me
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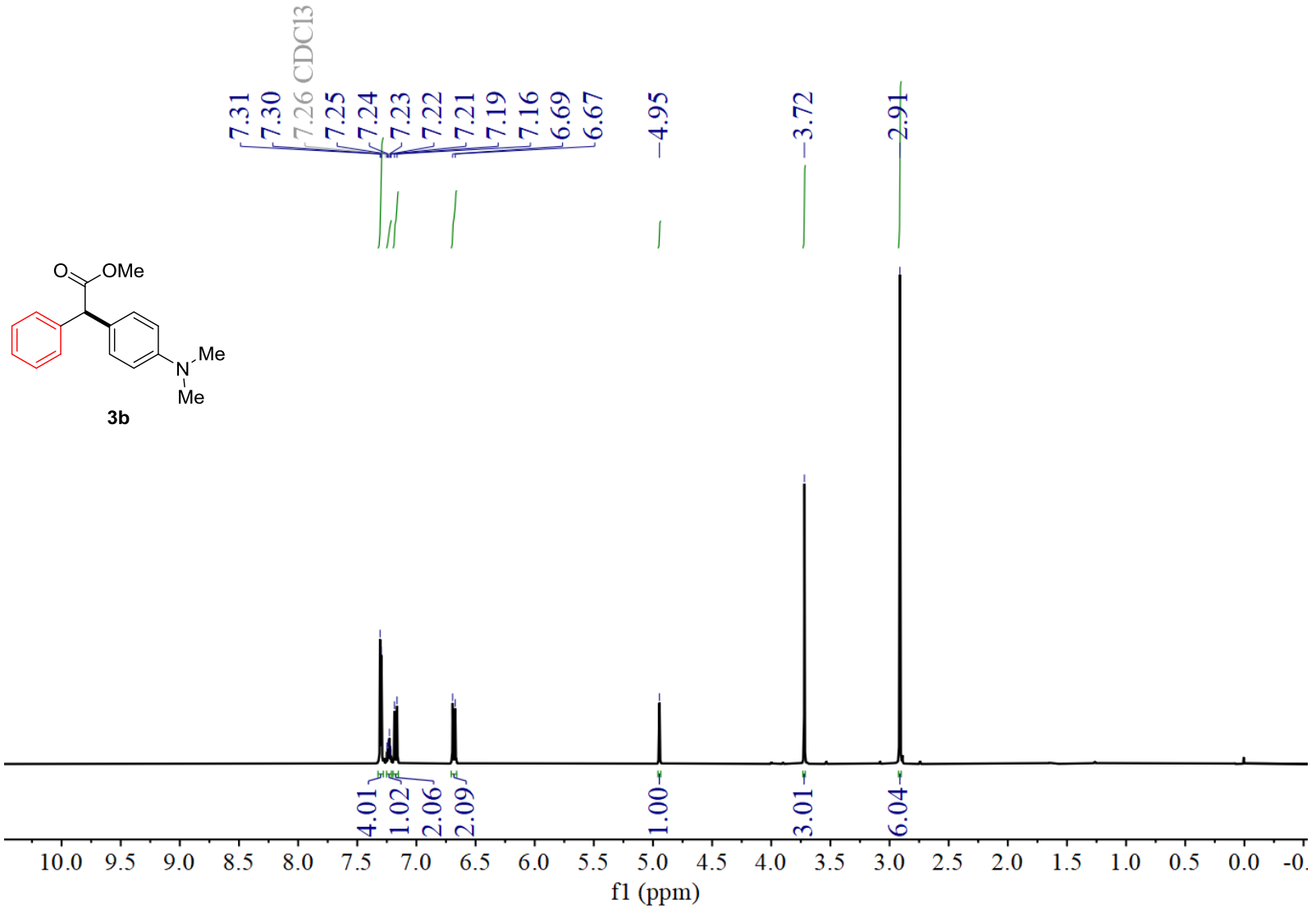
f1 (ppm)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7.19
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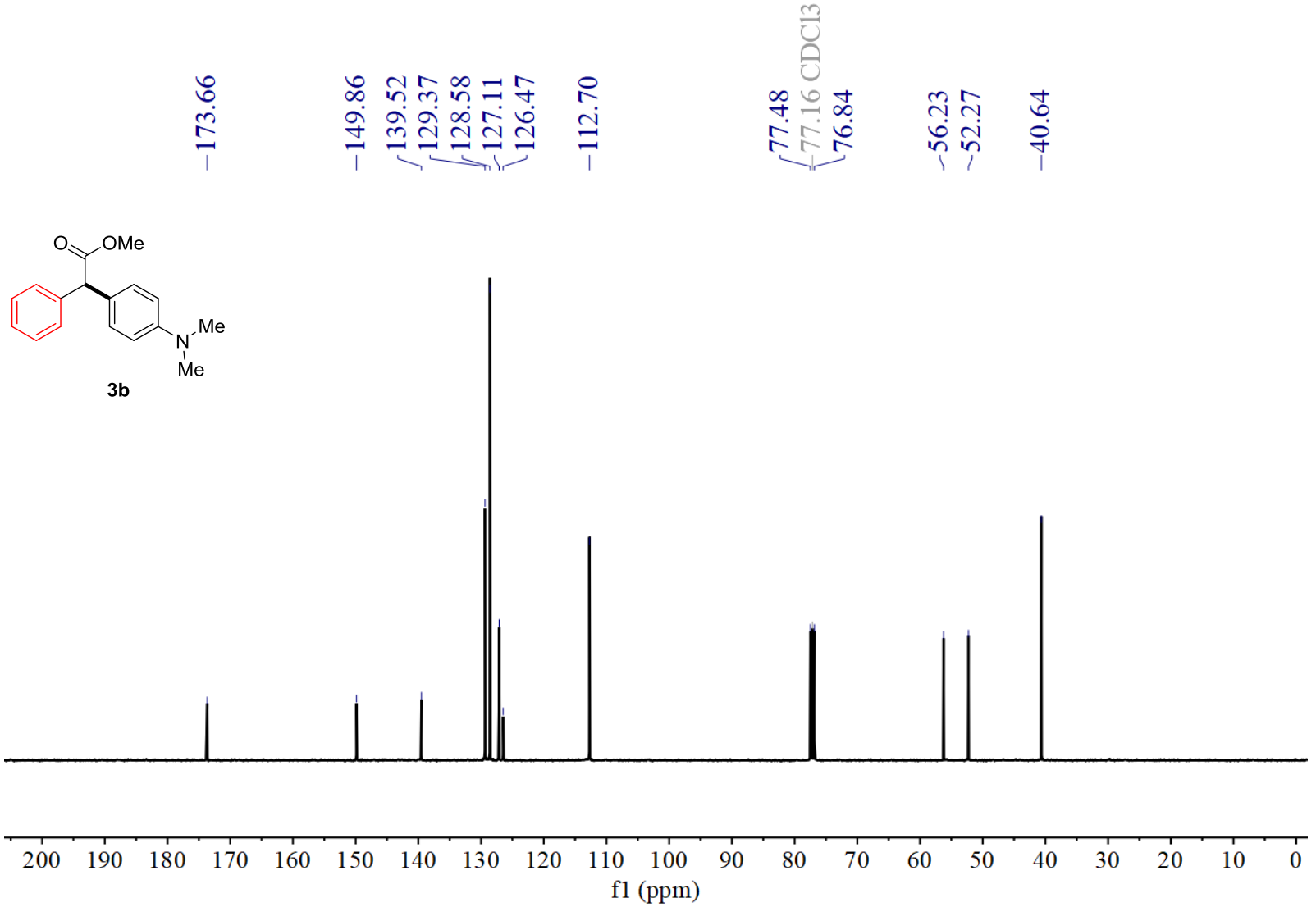
6.67
4.95
3.72
2.91
O
OMe
N
Me
Me
3b
4.01
1.02
2.06
2.09
1.00
3.01
6.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)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Me
Me
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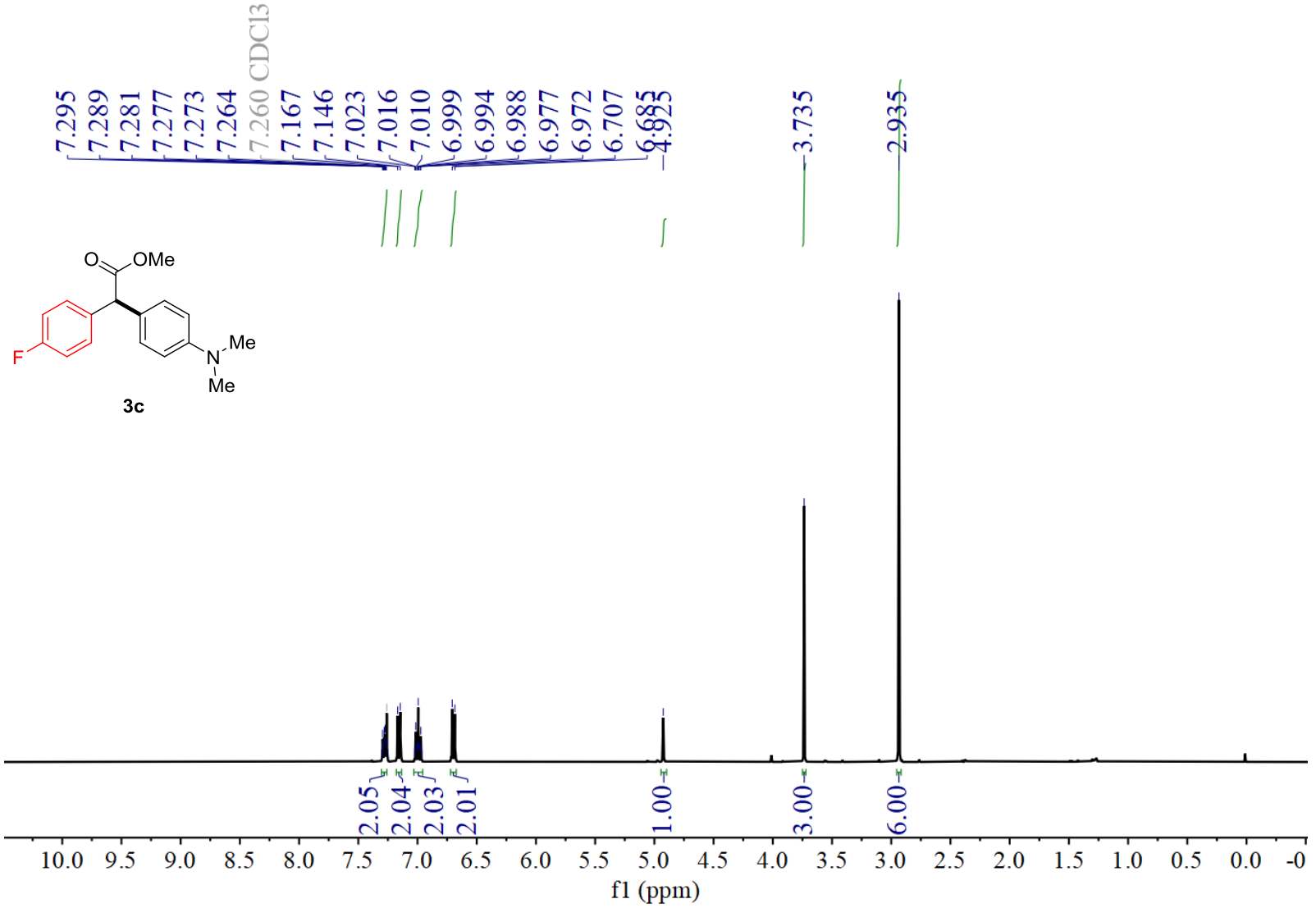
f1 (ppm)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6.994
6.988
6.977
6.972
6.707
6.685
4.925
3.735
2.935
O
OMe
F
N
Me
Me
3c
2.05
2.04
2.03
2.01
1.00
3.00
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
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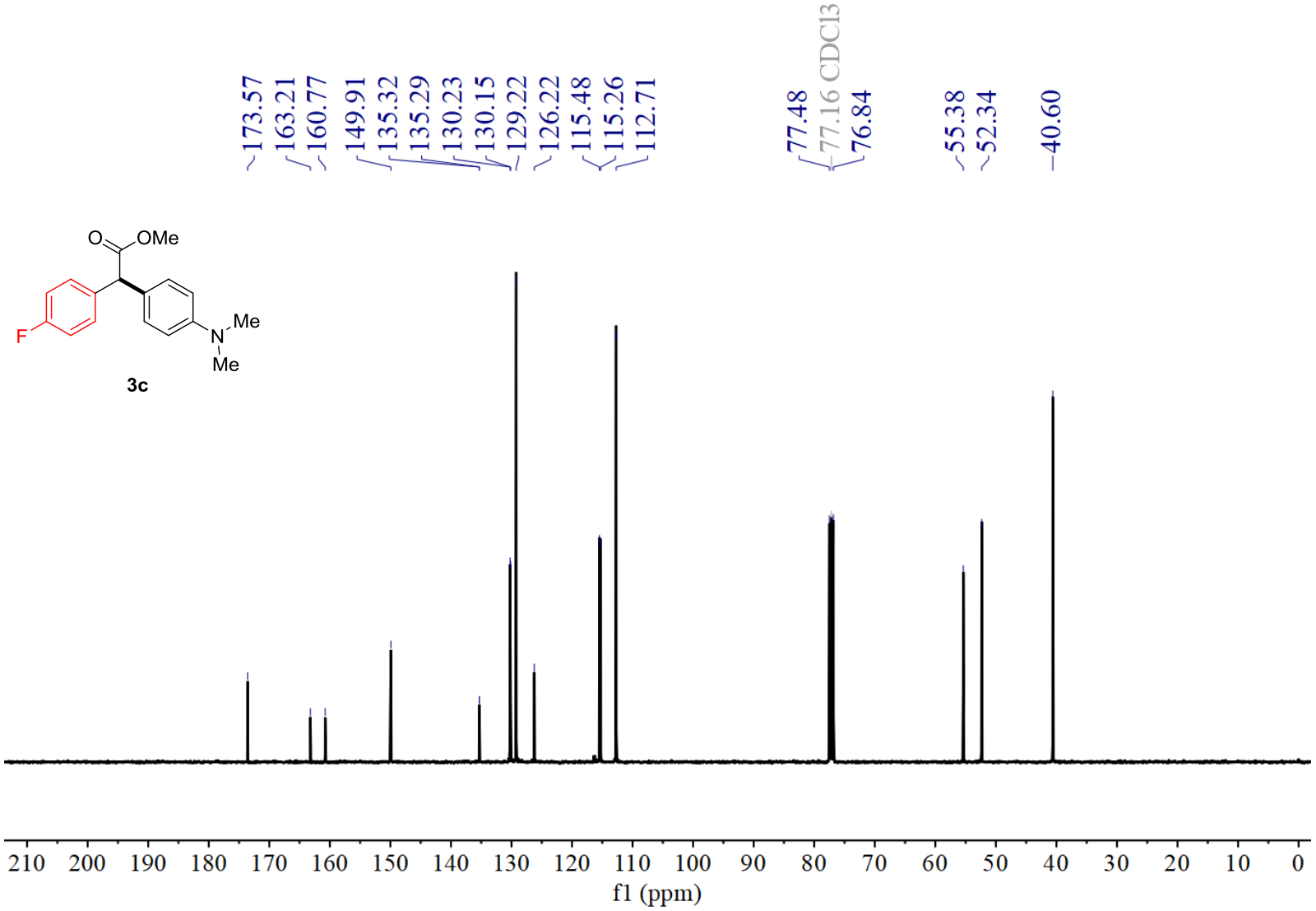
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130.15
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115.26
112.71
77.48
77.16 CDCl3
76.84
55.38
52.34
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F
N
Me
Me
3c
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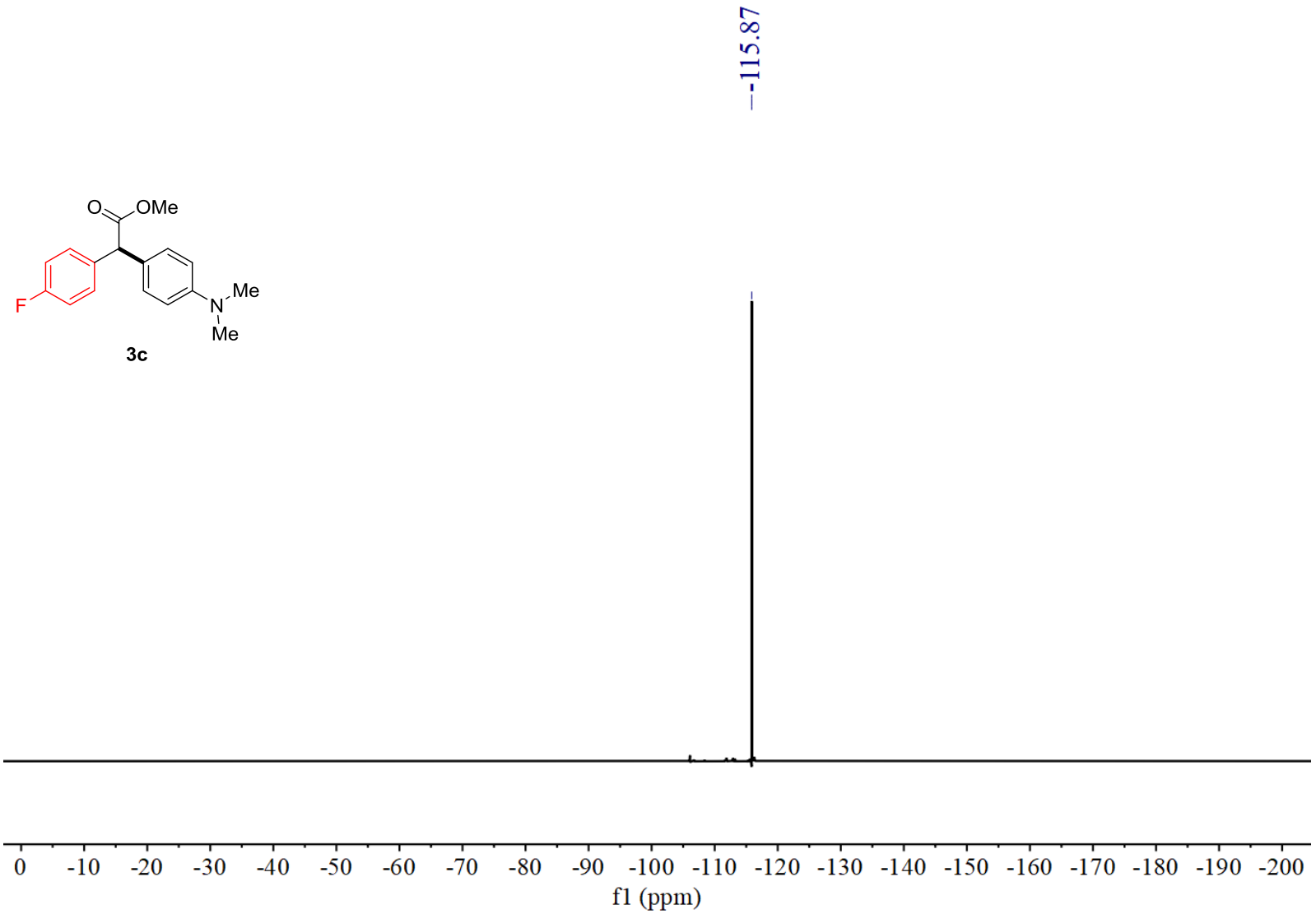
f1 (ppm)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Me
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0
-10
-20
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-40
-50
-60
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-120
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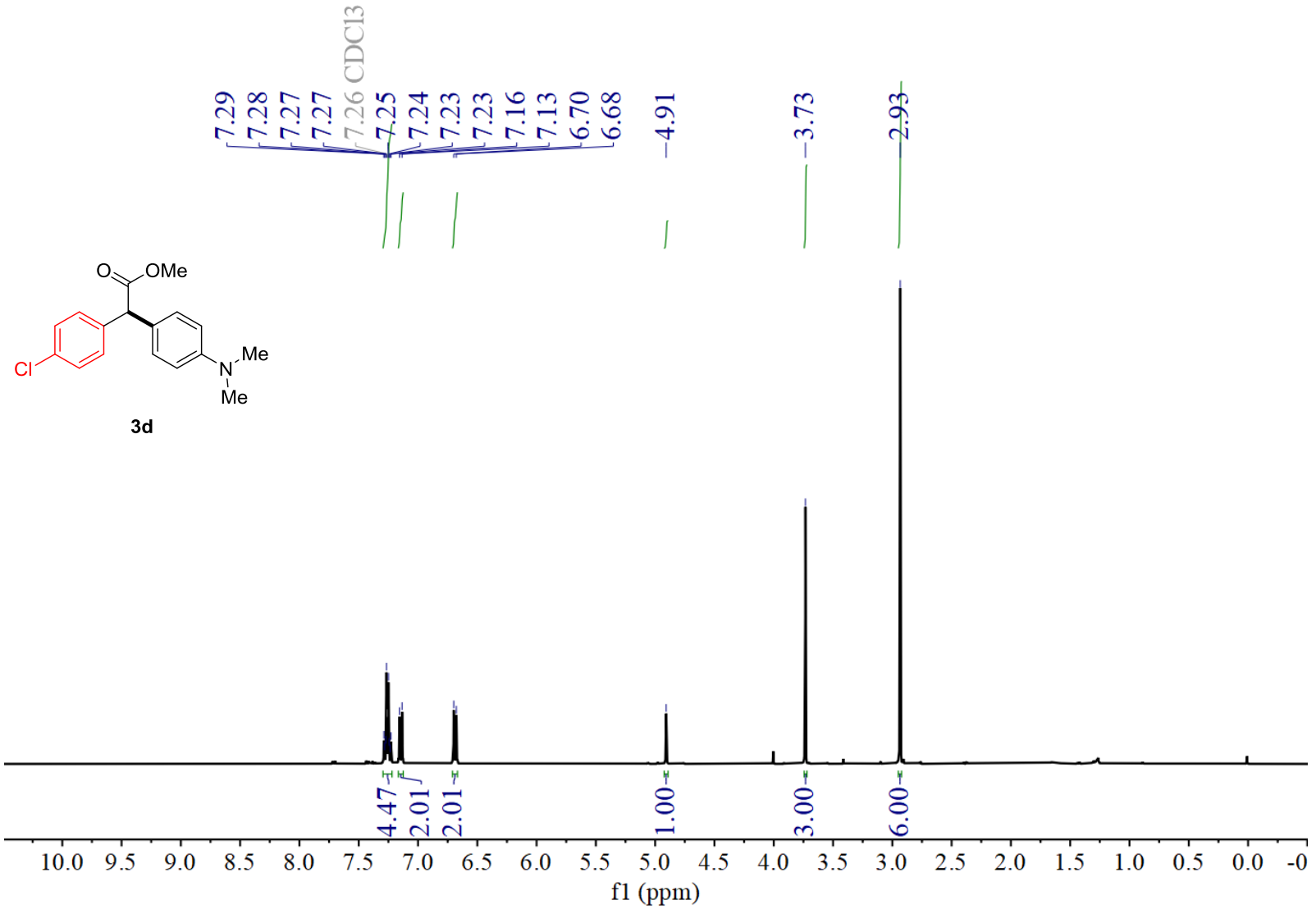
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)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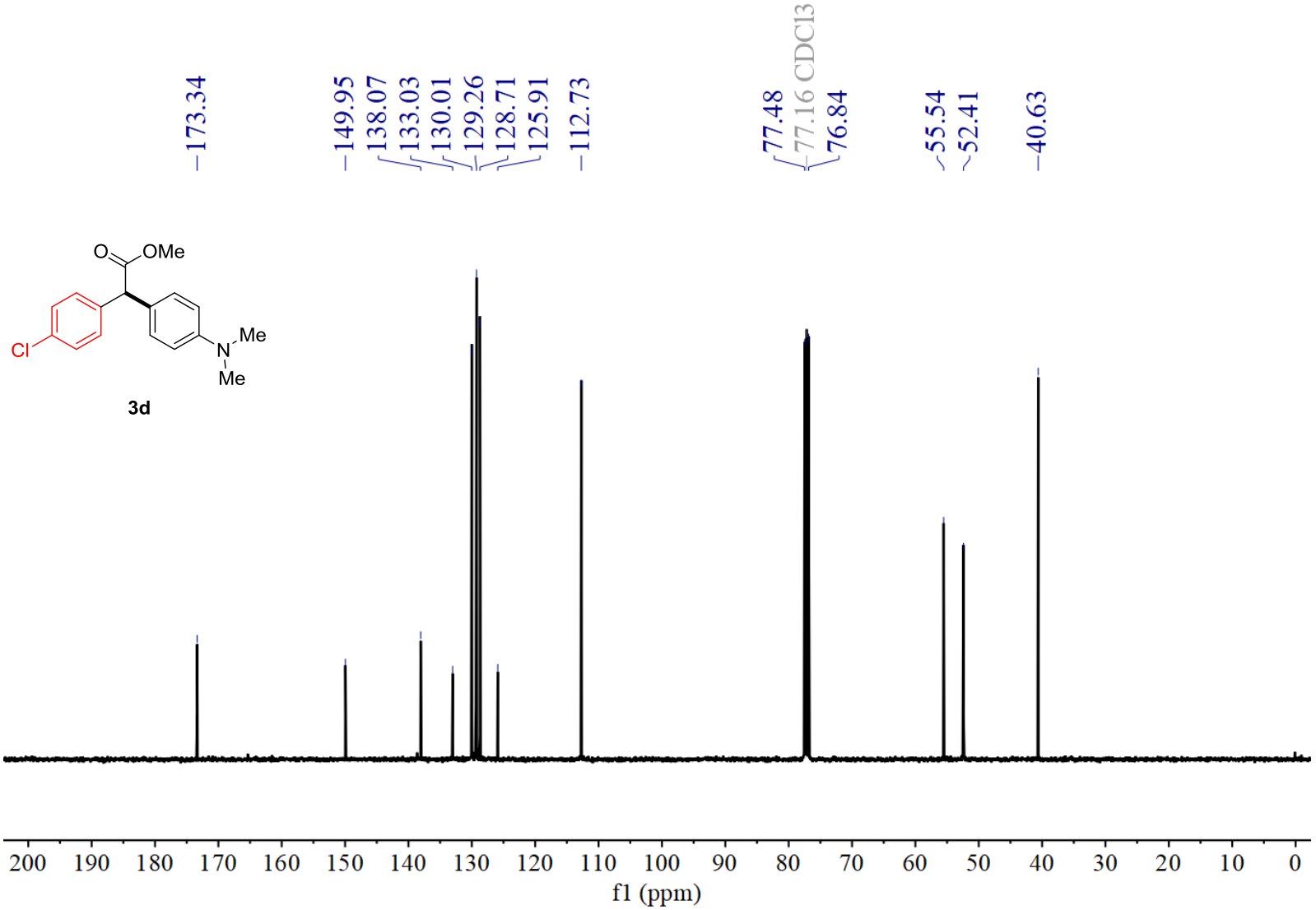
7.13
6.70
6.68
4.91
3.73
2.93
O
OMe
Cl
N
Me
Me
3d
4.47
2.01
2.01
1.00
3.00
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)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125.91
112.73
77.48
77.16 CDCl3
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55.54
52.41
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Cl
N
Me
Me
3d
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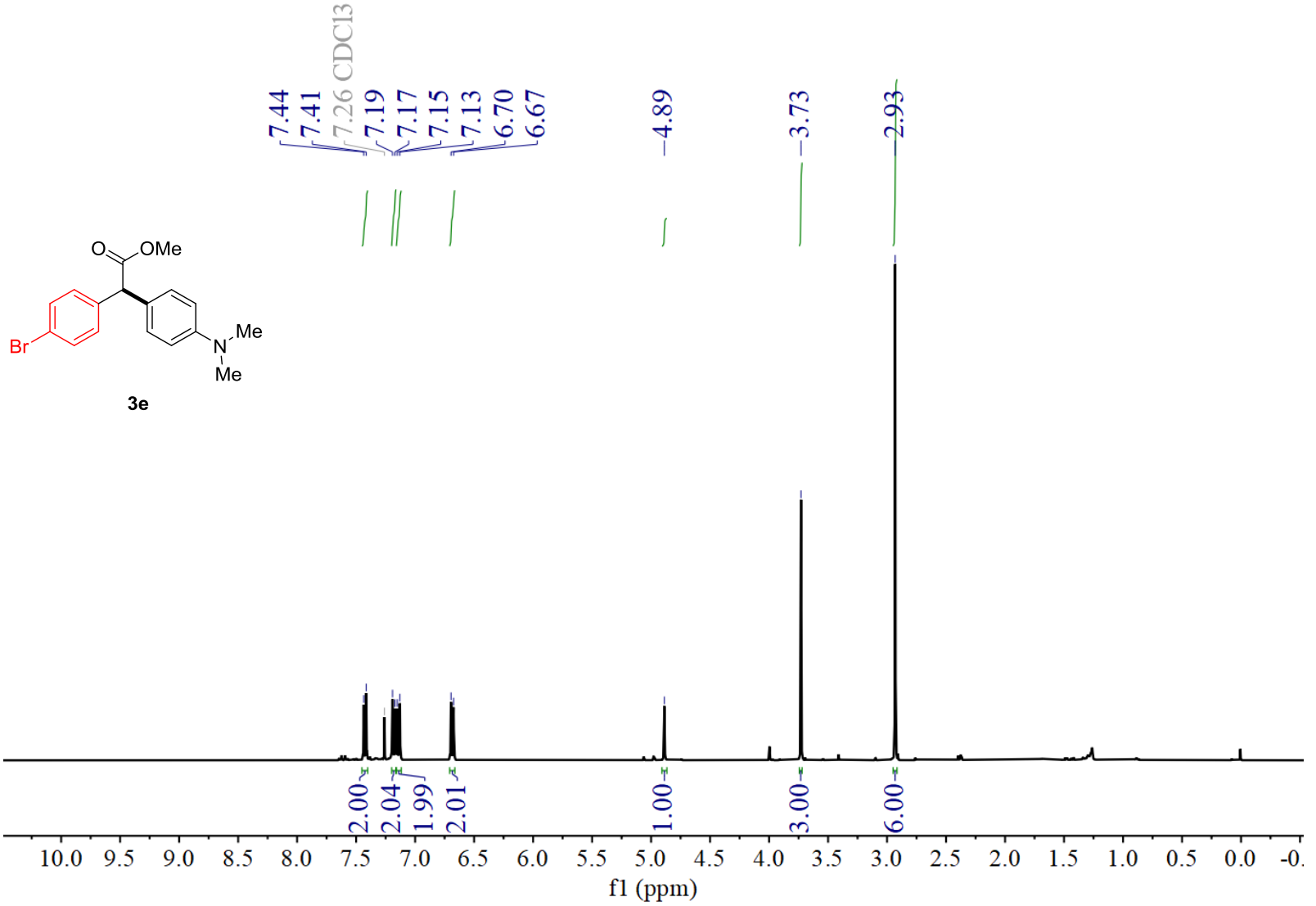
f1 (ppm)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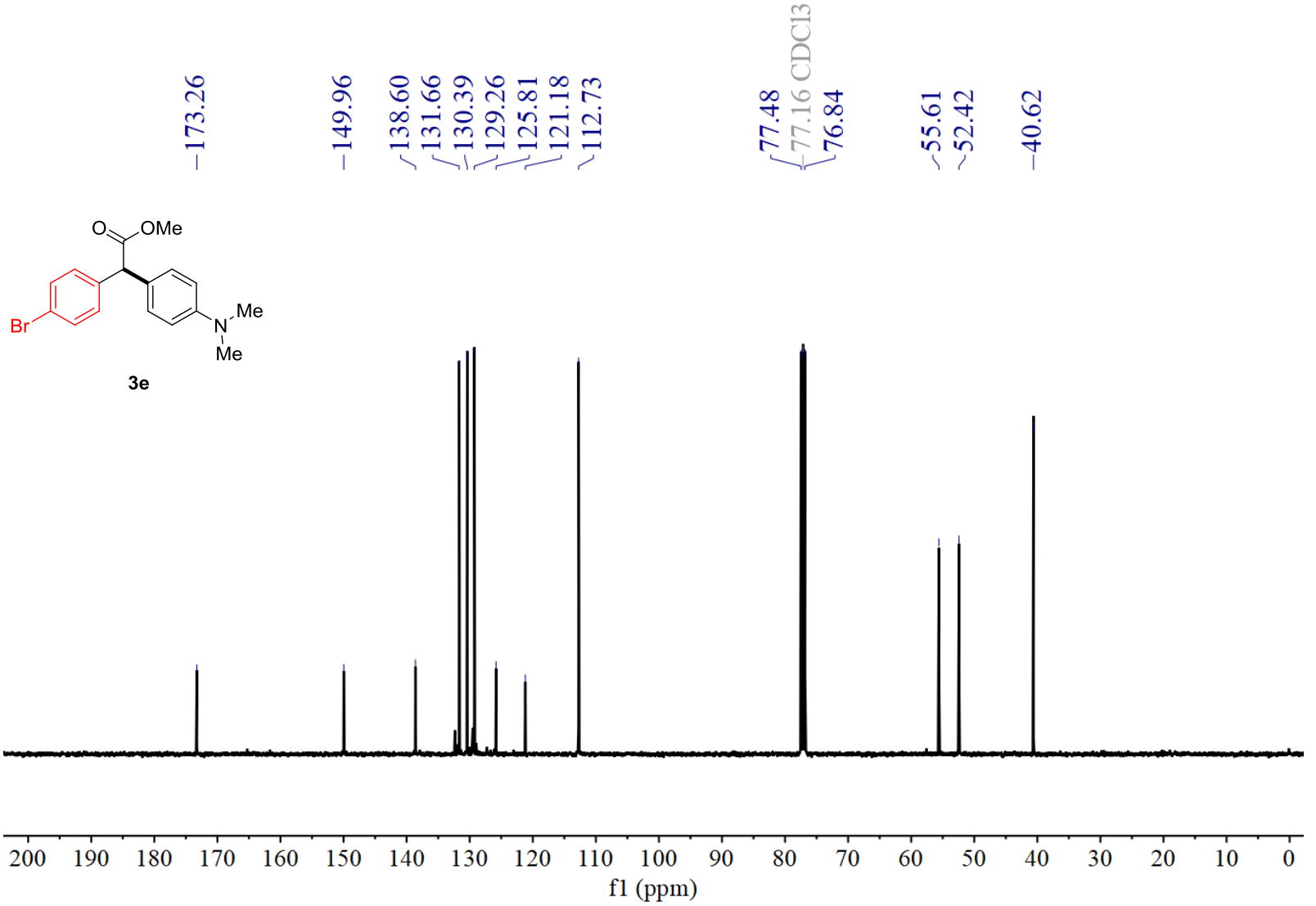
7.17
7.15
7.13
6.70
6.67
4.89
3.73
2.93
O
OMe
Br
N
Me
Me
3e
2.00
2.04
1.99
2.01
1.00
3.00
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)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77.48
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55.61
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40.62
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Br
N
Me
Me
3e
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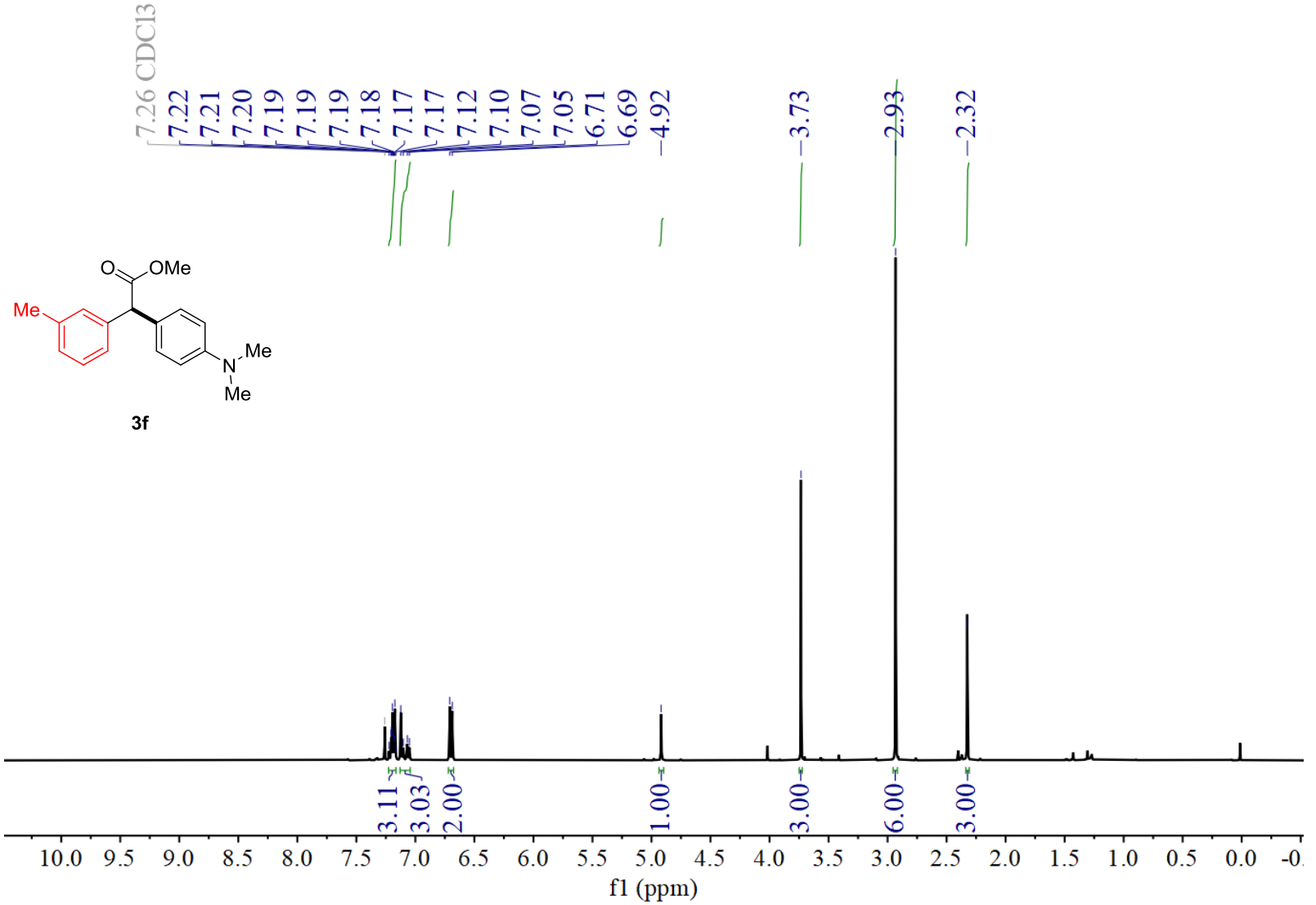
f1 (ppm)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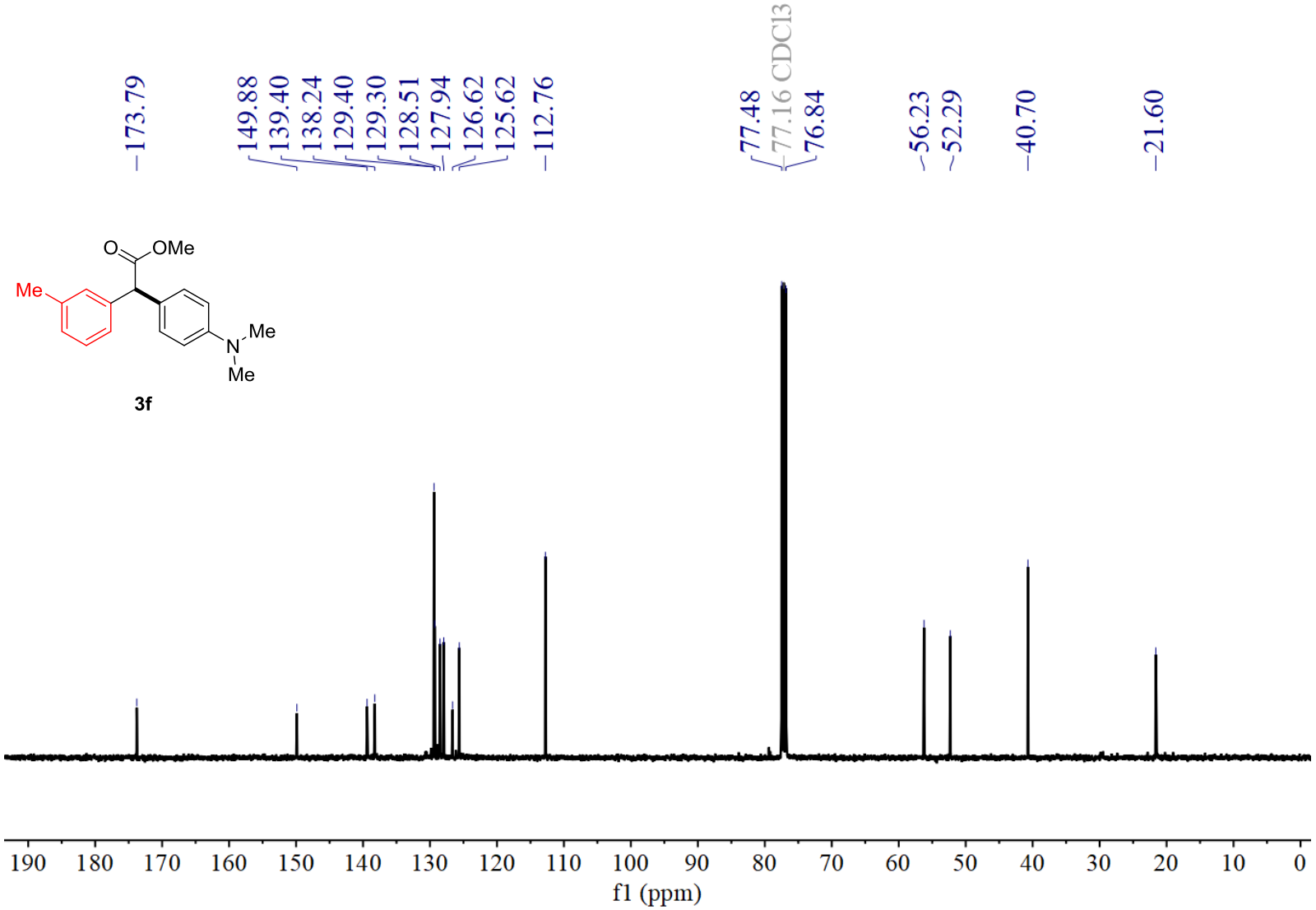
7.18
7.17
7.17
7.12
7.10
7.07
7.05
6.71
6.69
4.92
3.73
2.93
2.32
O
OMe
Me
N
Me
Me
3f
3.11
3.03
2.00
1.00
3.00
6.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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125.62
112.76
77.48
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76.84
56.23
52.29
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OMe
Me
N
Me
Me
3f
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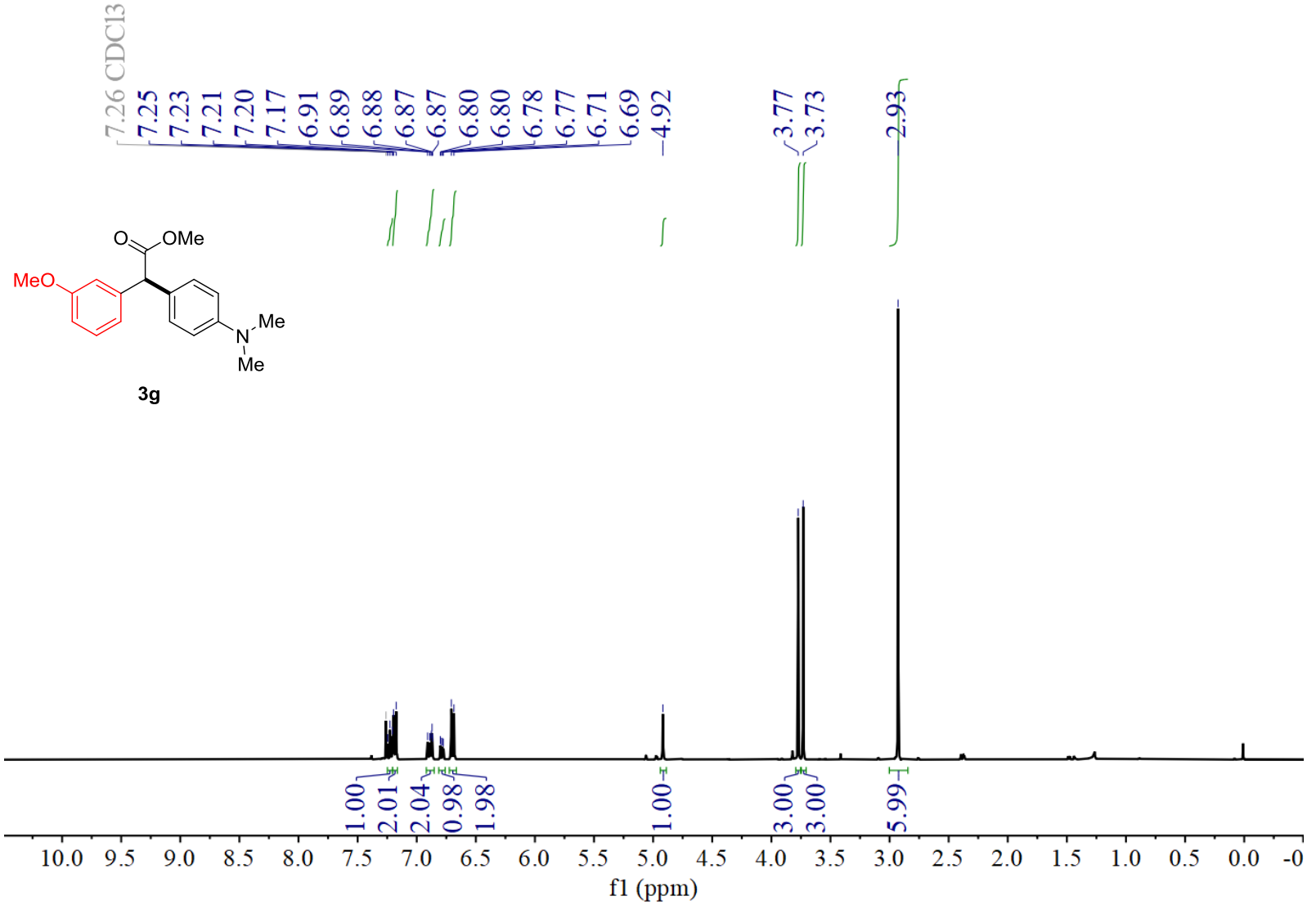
f1 (ppm)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6.87
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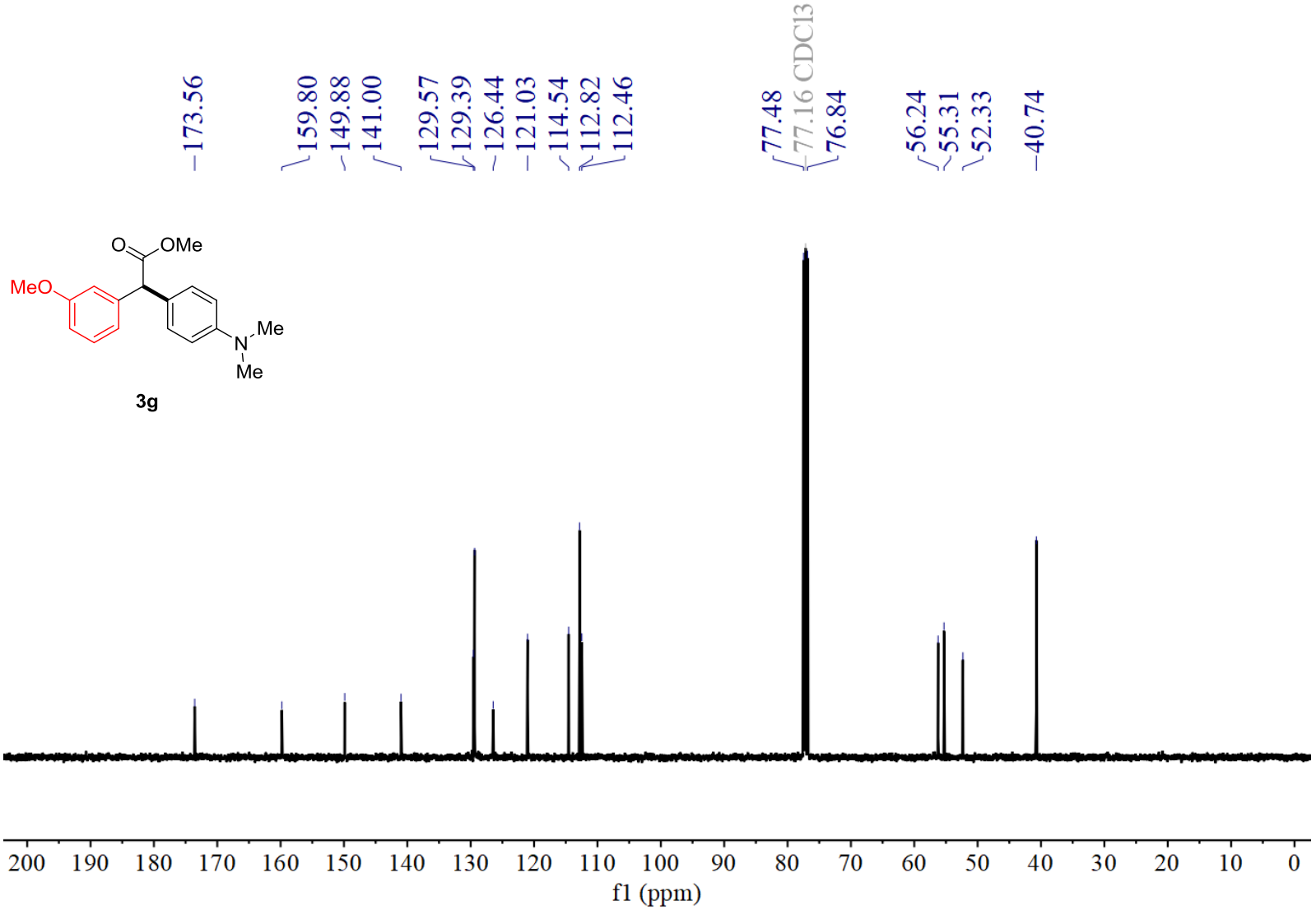
6.80
6.80
6.78
6.77
6.71
6.69
4.92
3.77
3.73
2.93
O
OMe
MeO
N
Me
Me
1.00
2.01
2.04
0.98
1.98
1.00
3.00
3.00
5.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

3g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76.84
56.24
55.31
52.33
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Me
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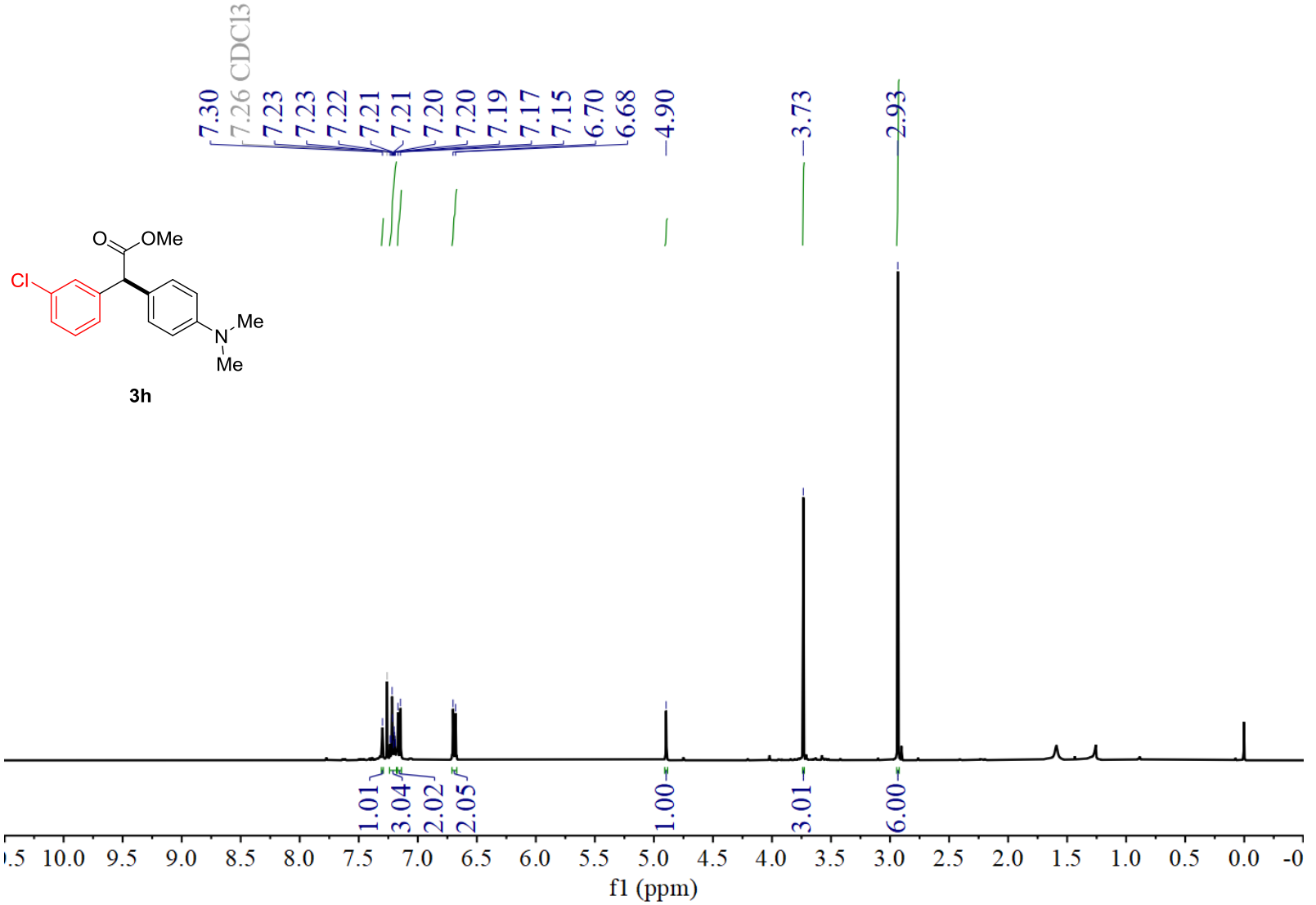
f1 (ppm)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7.20
7.20
7.19
7.17
7.15
6.70
6.68
4.90
3.73
2.93
O
OMe
Cl
N
Me
Me
3h
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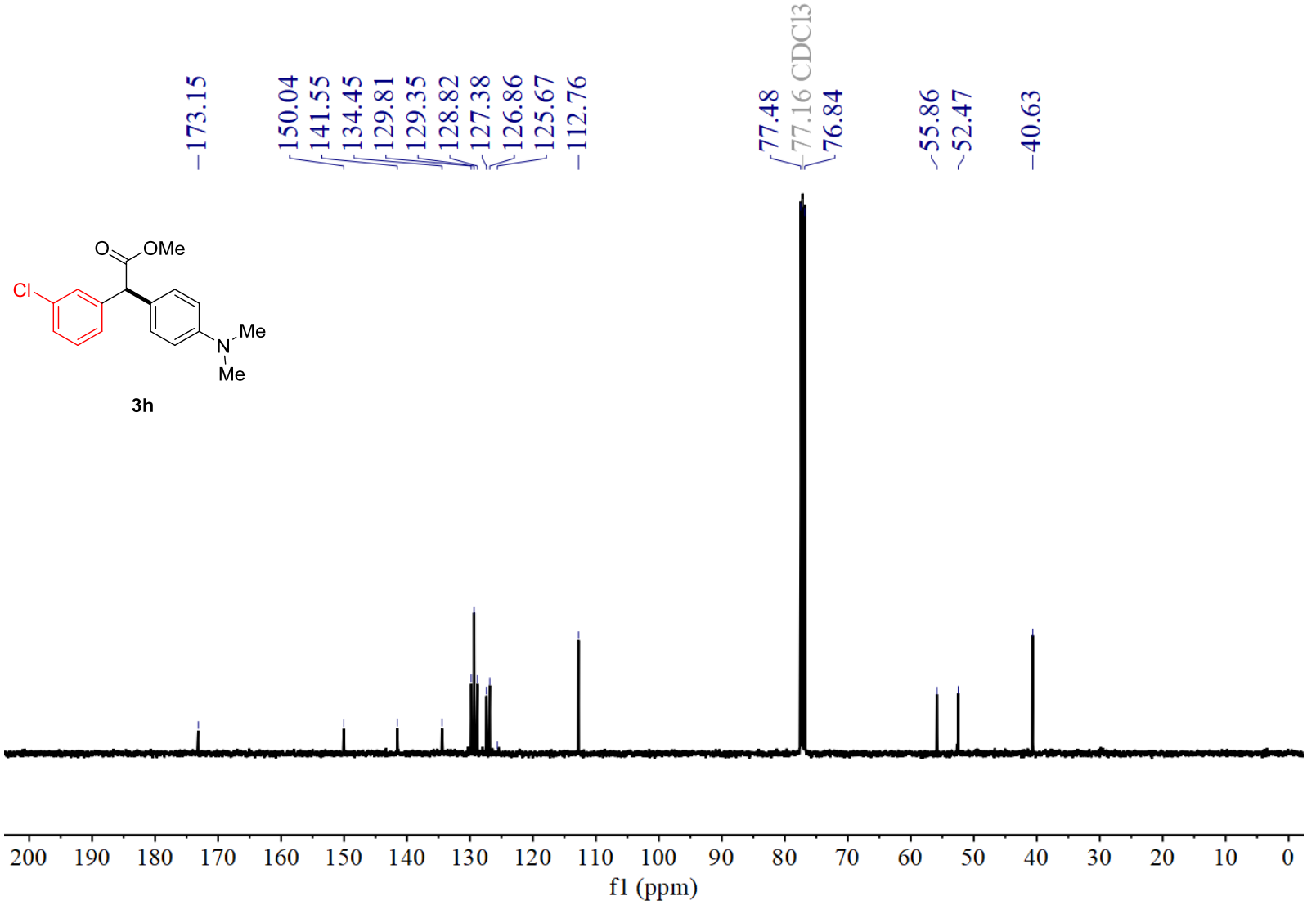
3.04
2.02
2.05
1.00
3.01
6.00
f1 (ppm)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77.48
77.16 CDCl3
76.84
55.86
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Cl
N
Me
Me
3h
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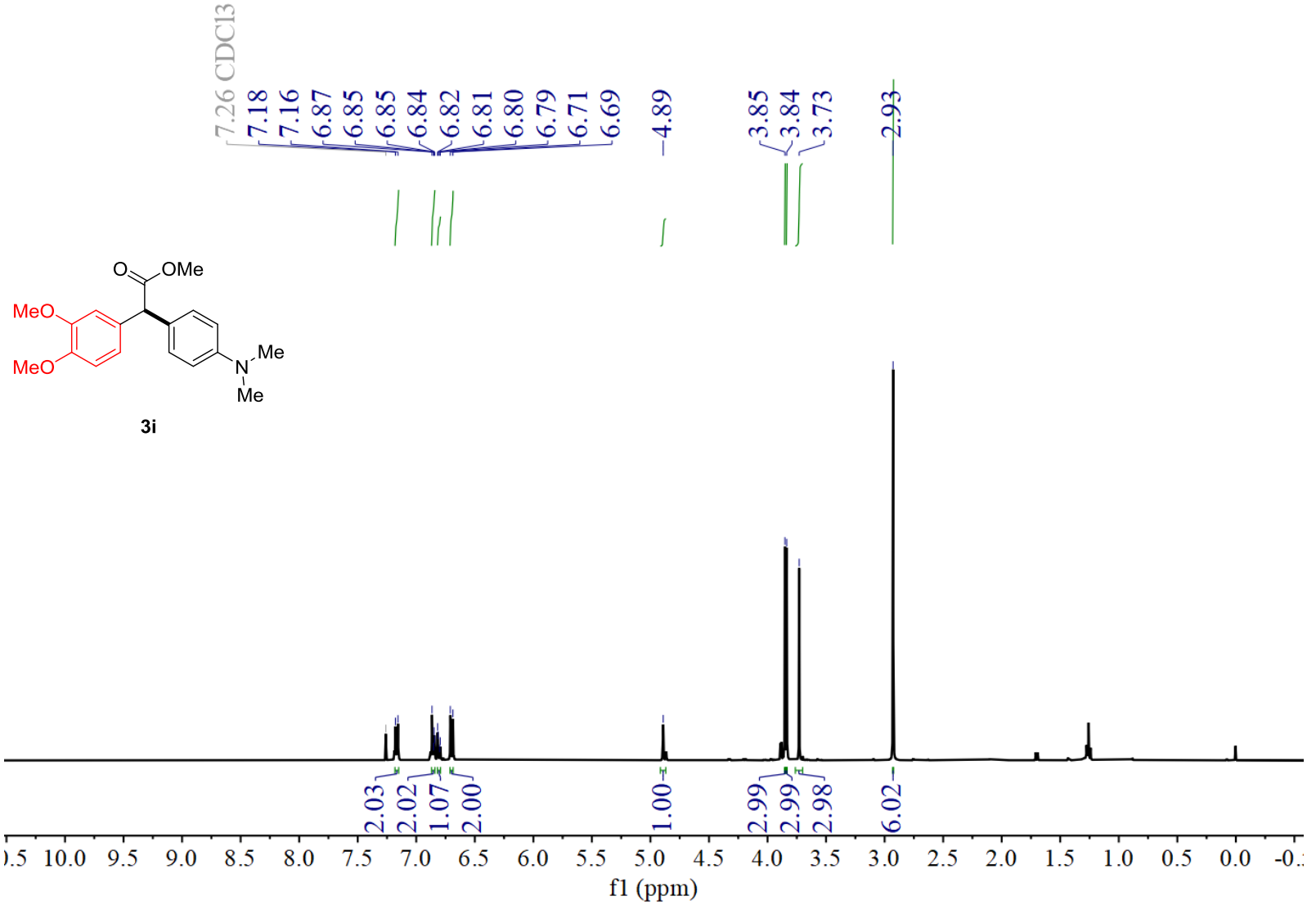
f1 (ppm)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6.69
4.89
3.85
3.84
3.73
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OMe
MeO
MeO
N
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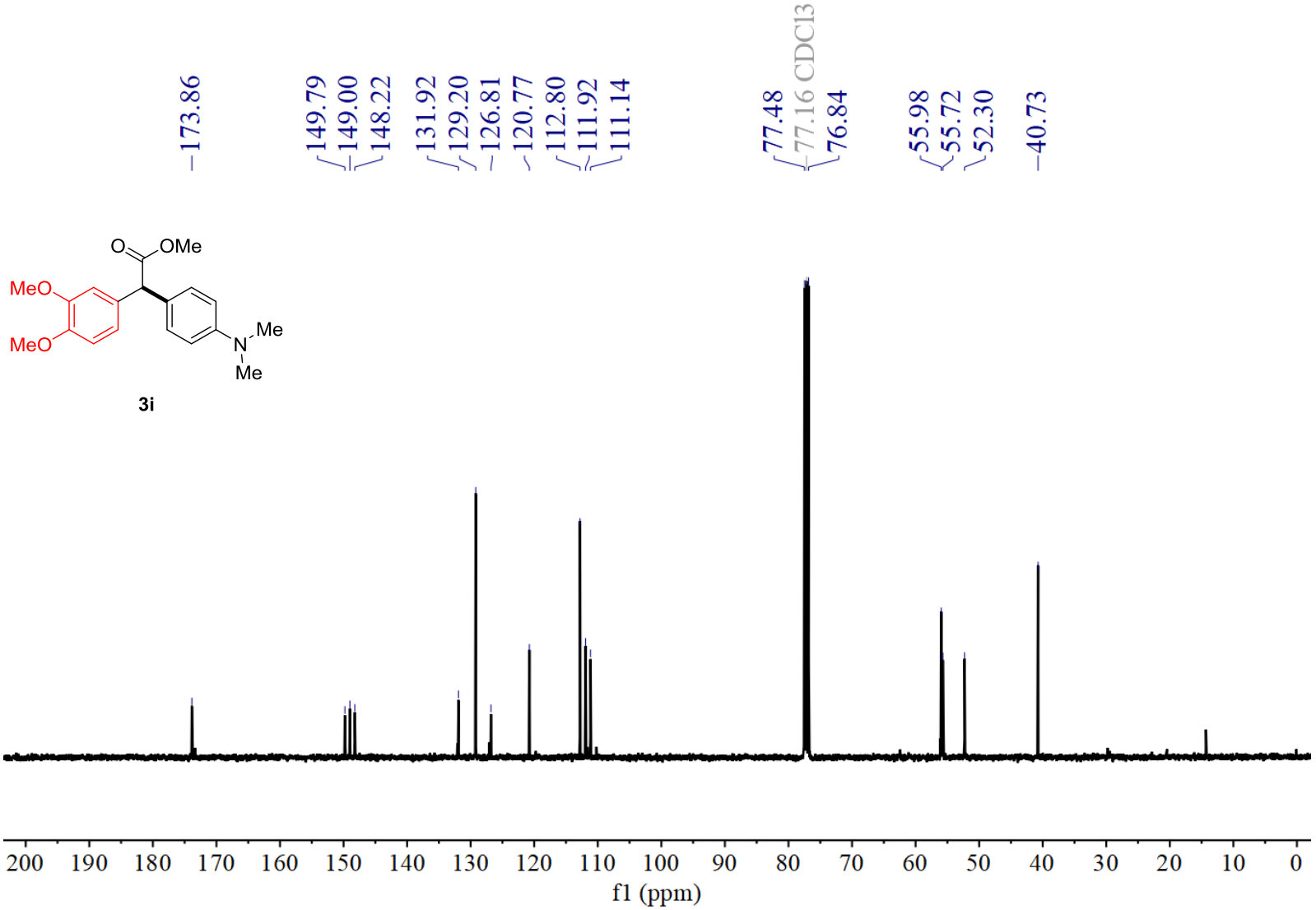
6.02
f1 (ppm)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77.16 CDCl3
76.84
55.98
55.72
52.30
40.73
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MeO
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Me
3i
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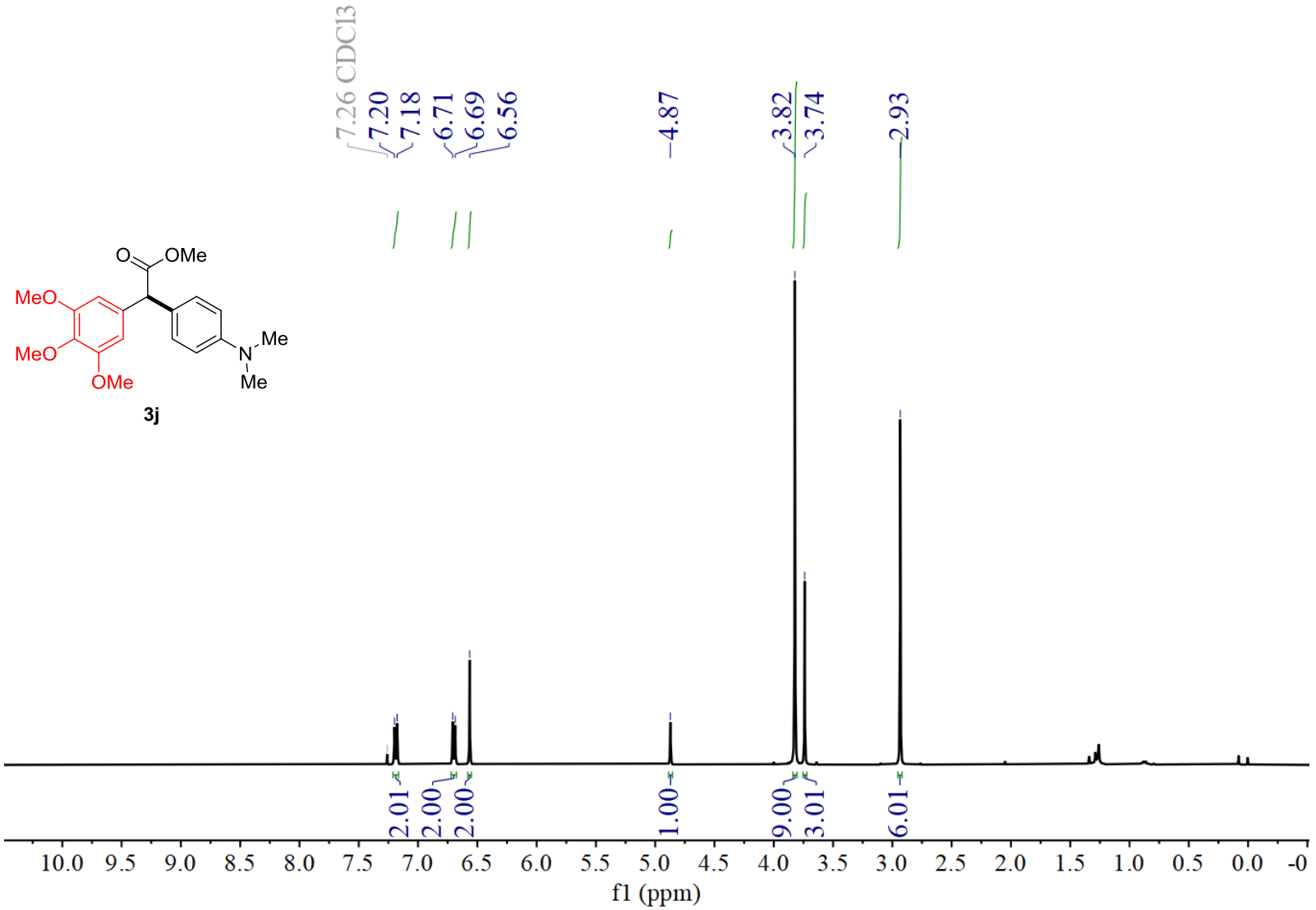
f1 (ppm)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2.93
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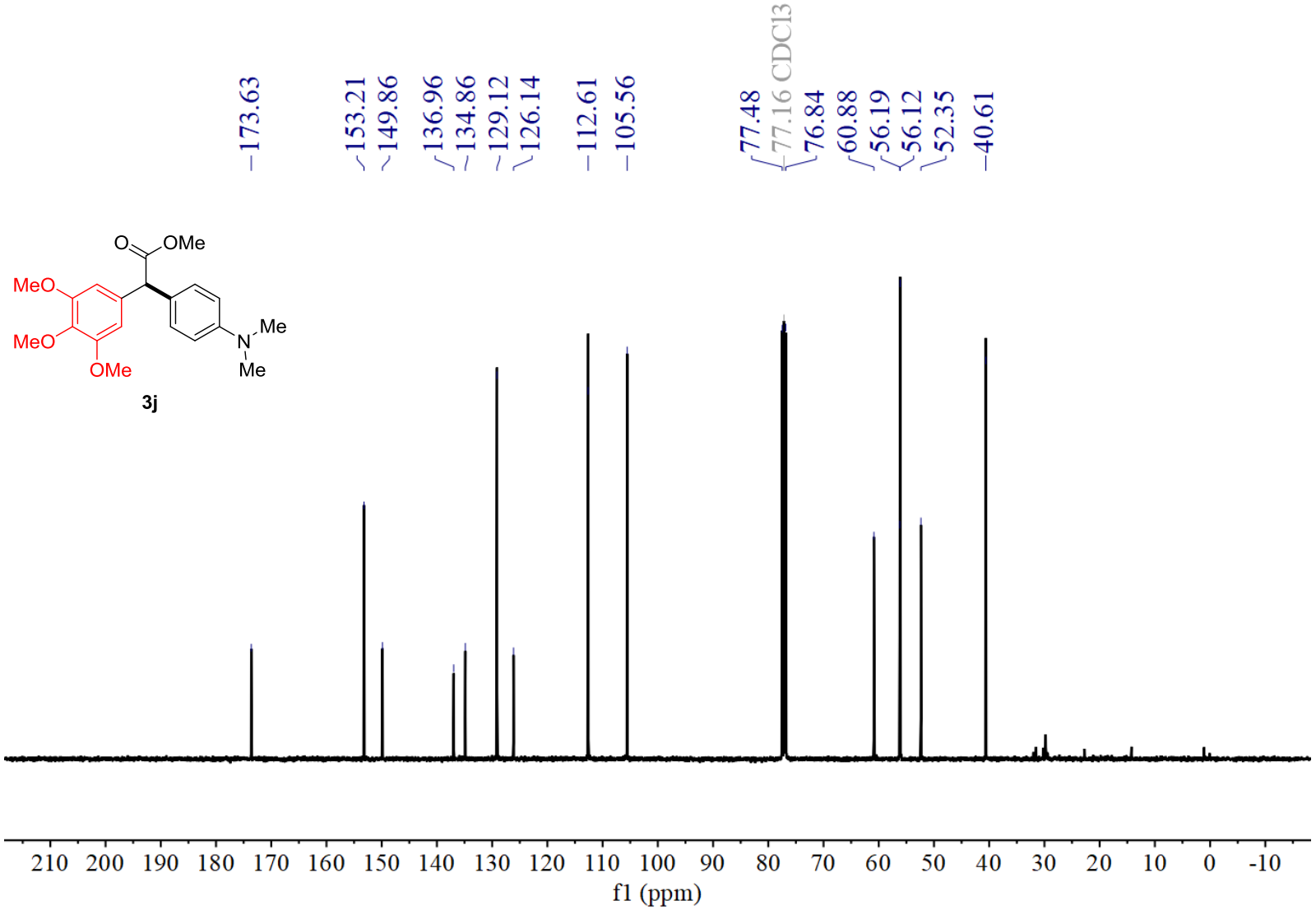
MeO
MeO
OMe
N
Me
Me
3j
2.01
2.00
2.00
1.00
9.00
3.01
6.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)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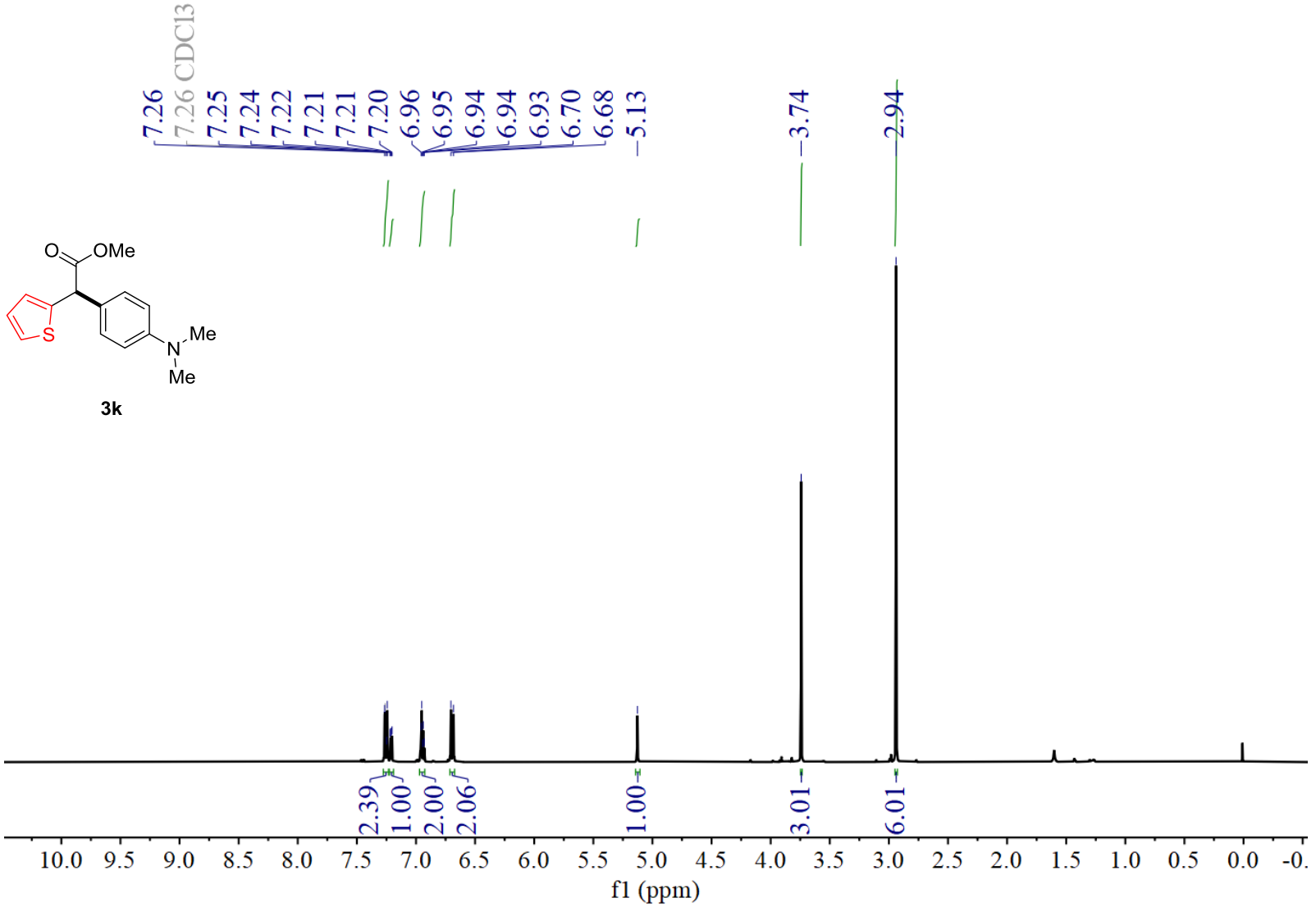
77.48
77.16 CDCl3
76.84
60.88
56.19
56.12
52.35
40.61
O
OMe
MeO
MeO
OMe
N
Me
Me
3j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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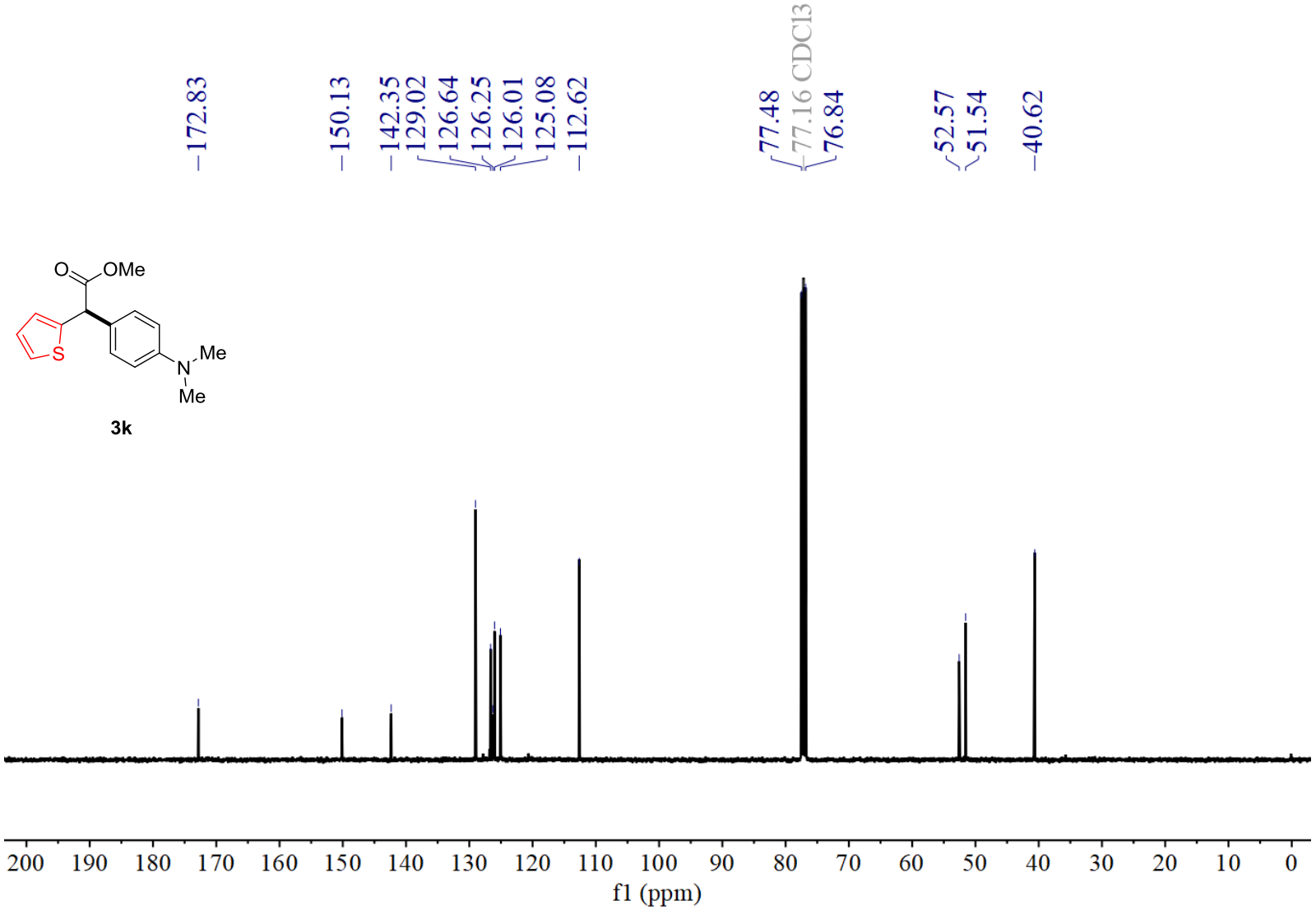
6.96
6.95
6.94
6.94
6.93
6.70
6.68
5.13
3.74
2.94
O
OMe
S
N
Me
Me
3k
2.39
1.00
2.00
2.06
1.00
3.01
6.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)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129.02
126.64
126.25
126.01
125.08
112.62
77.48
77.16 CDCl3
76.84
52.57
51.54
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S
N
Me
Me
3k
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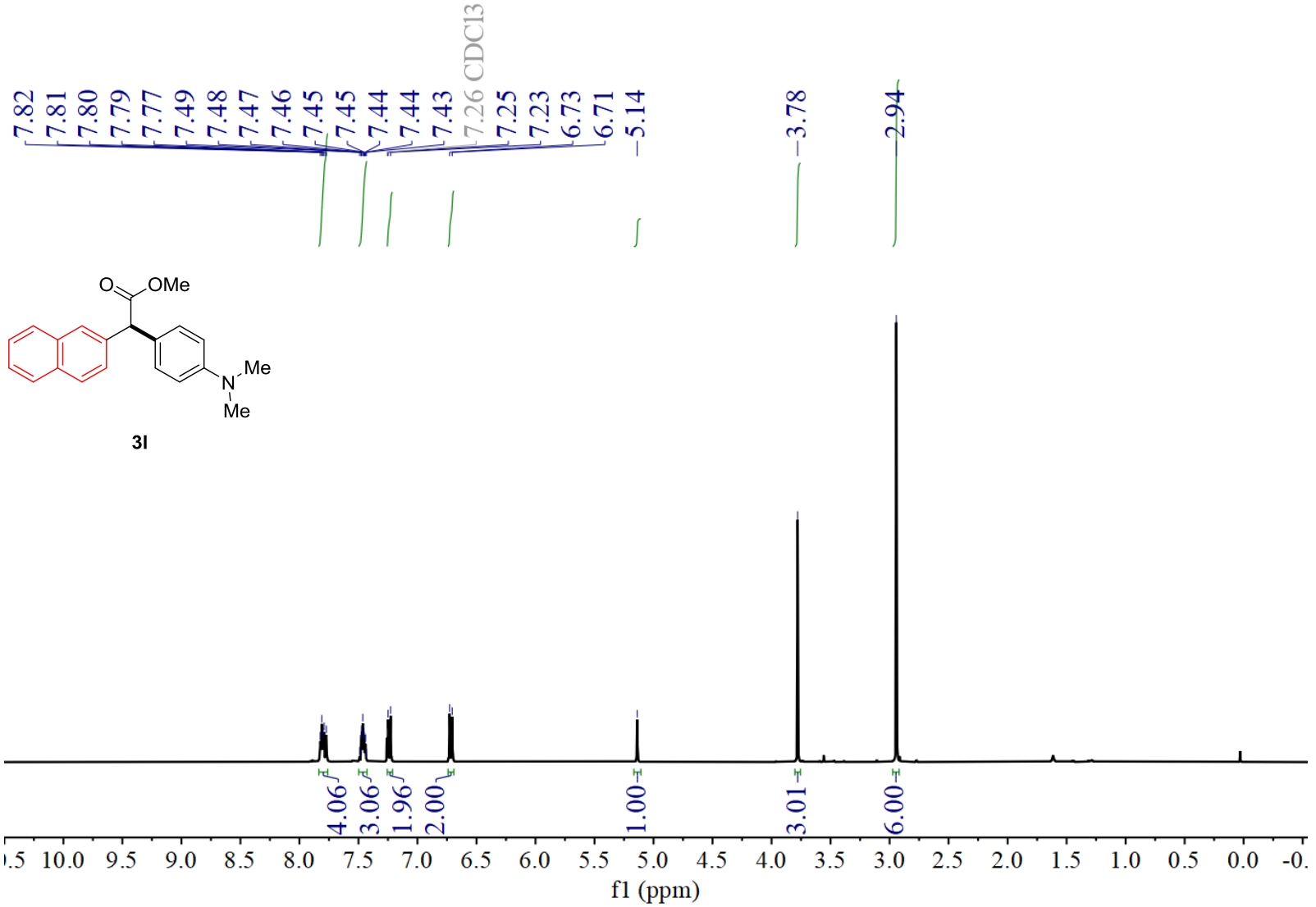
f1 (ppm)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7.43
7.26 CDC13
7.25
7.23
6.73
6.71
5.14
3.78
2.94
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1.96
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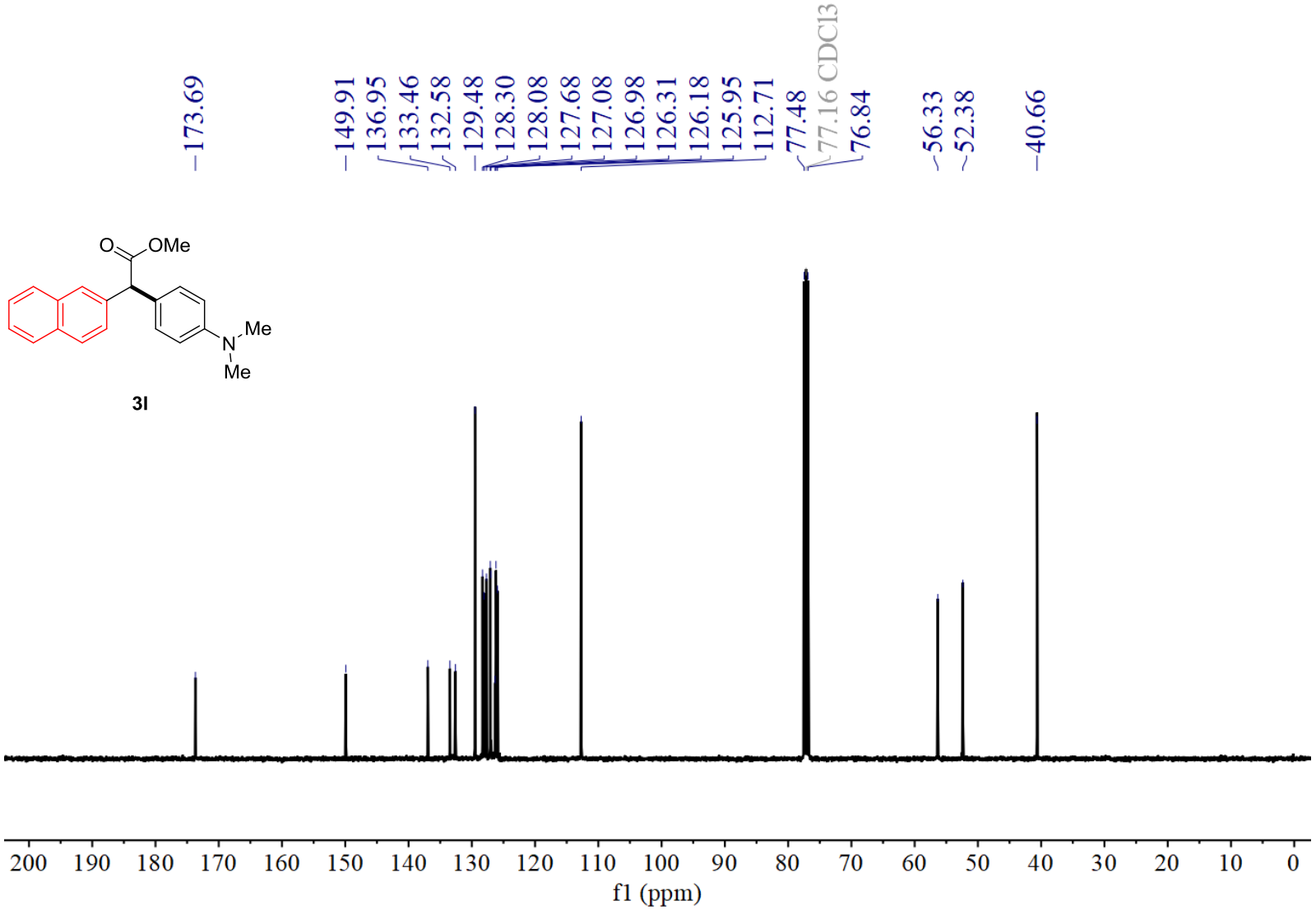
6.00
f1 (ppm)

3l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127.08
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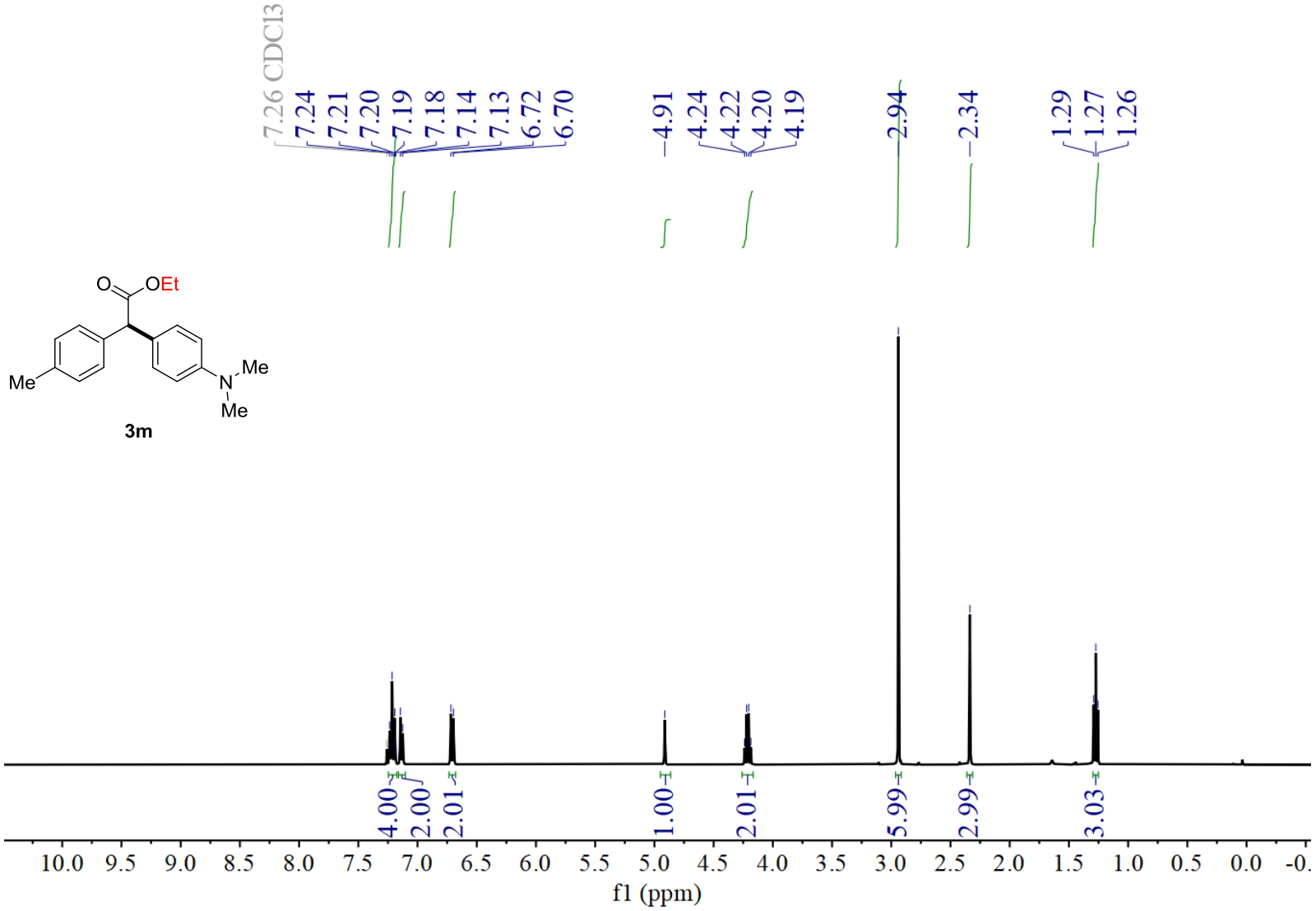
126.31
126.18
125.95
112.71
77.48
77.16 CDCl3
76.84
56.33
52.38
40.66
O
OMe
N
Me
Me
3l
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.13
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6.70
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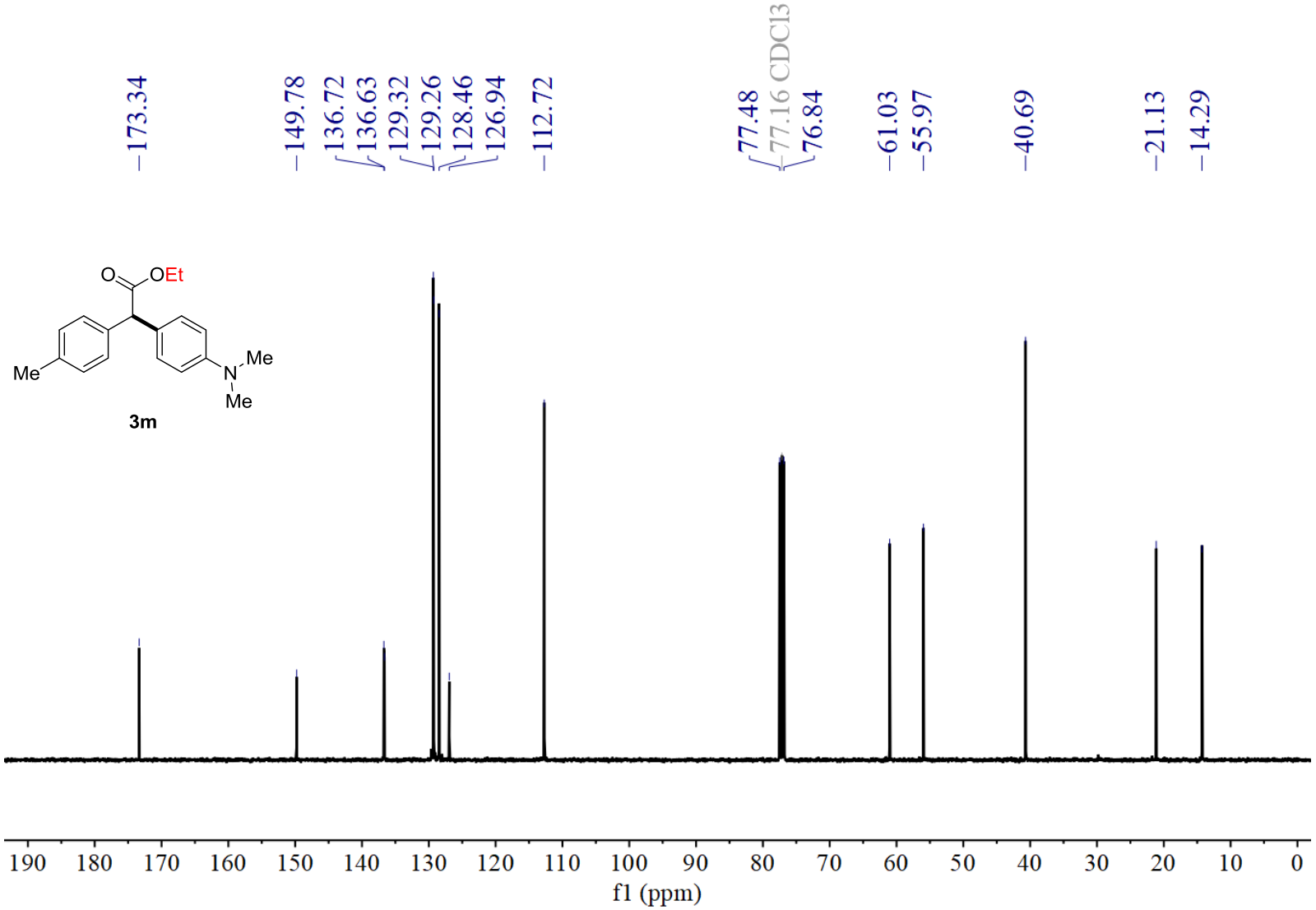
4.24
4.22
4.20
4.19
2.94
2.34
1.29
1.27
1.26
O
OEt
Me
N
Me
Me
3m
4.00
2.00
2.01
1.00
2.01
5.99
2.99
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)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136.72
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129.26
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126.94
112.72
77.48
77.16 CDCl3
76.84
61.03
55.97
40.69
21.13
14.29
O
OEt
Me
N
Me
Me
3m
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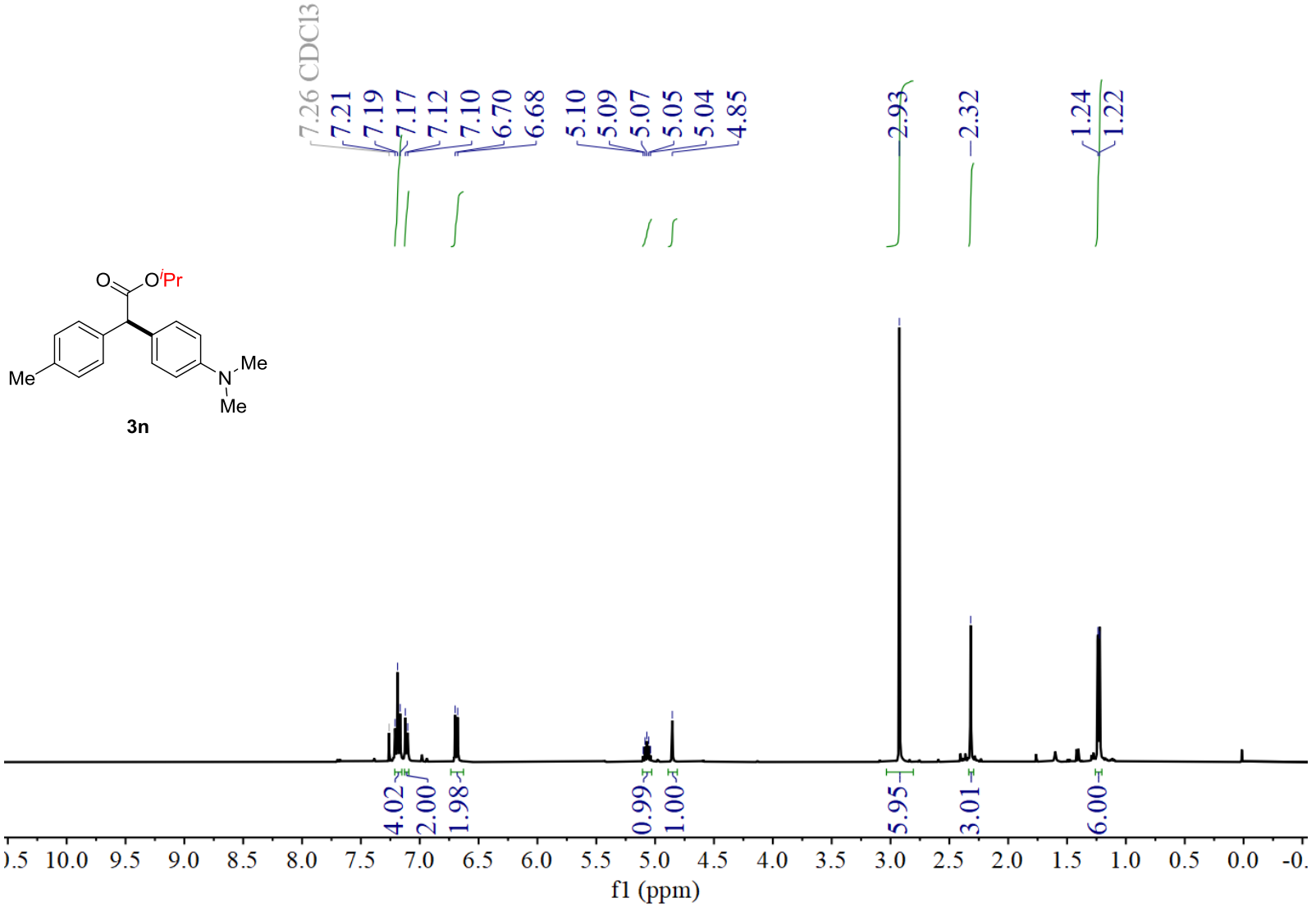
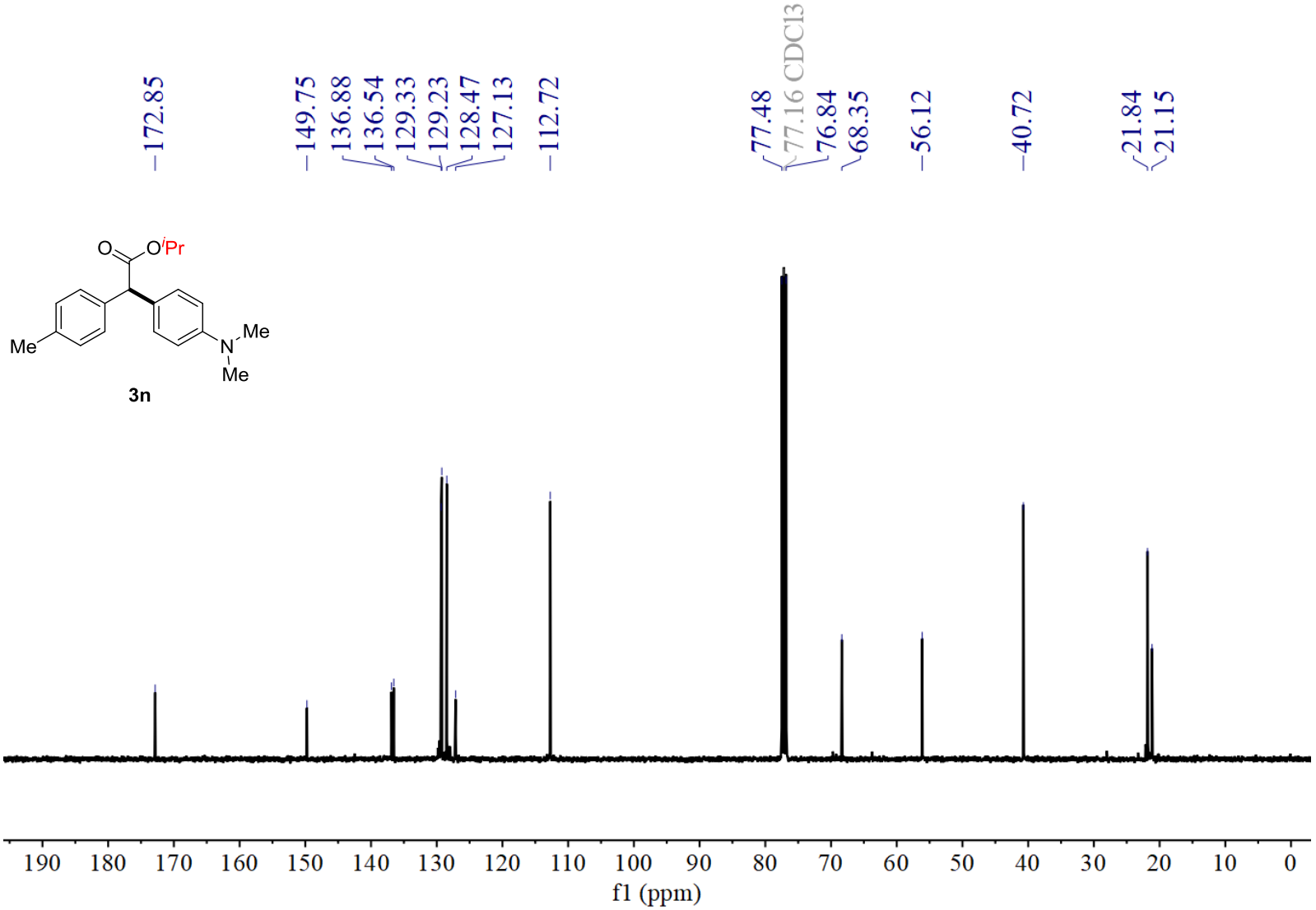
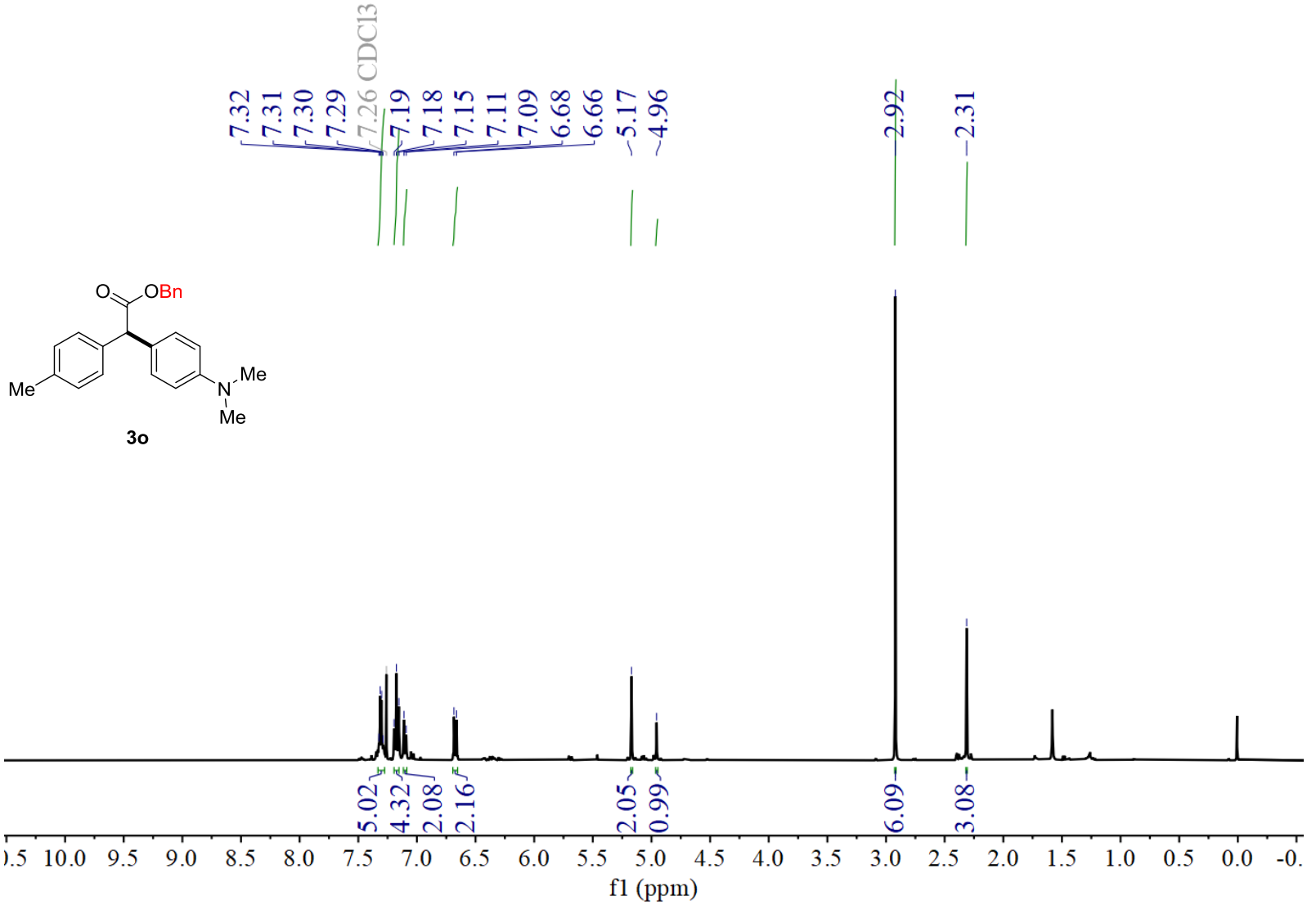
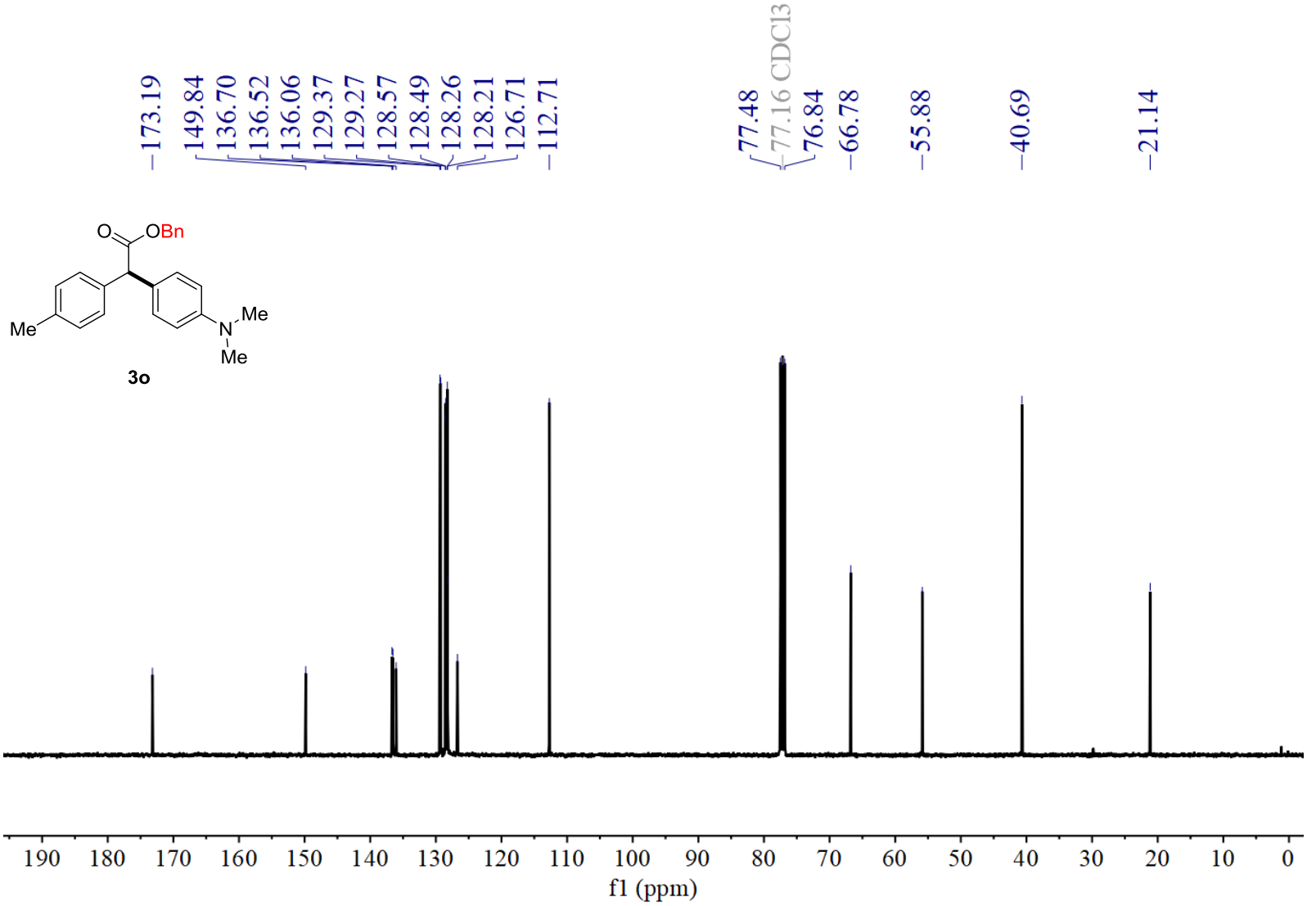
f1 (ppm)


7.26 CDCl3
7.21
7.19
7.17
7.12
7.10
6.70
6.68
5.10
5.09
5.07
5.05
5.04
4.85
2.93
2.32
1.24
1.22
O
O^{i}Pr
Me
N
Me
Me
3n
4.02
2.00
1.98
0.99
1.00
5.95
3.01
6.00
f1 (ppm)


172.85
149.75
136.88
136.54
129.33
129.23
128.47
127.13
112.72
77.48
77.16 CDCl3
76.84
68.35
56.12
40.72
21.84
21.15
O
O^{i}Pr
Me
N
Me
Me
3n
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.32
7.31
7.30
7.29
7.26 CDCl3
7.19
7.18
7.15
7.11
7.09
6.68
6.66
5.17
4.96
2.92
2.31
O
OBn
Me
N
Me
Me
3o
5.02
4.32
2.08
2.16
2.05
0.99
6.09
3.08
f1 (ppm)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129.27
128.57
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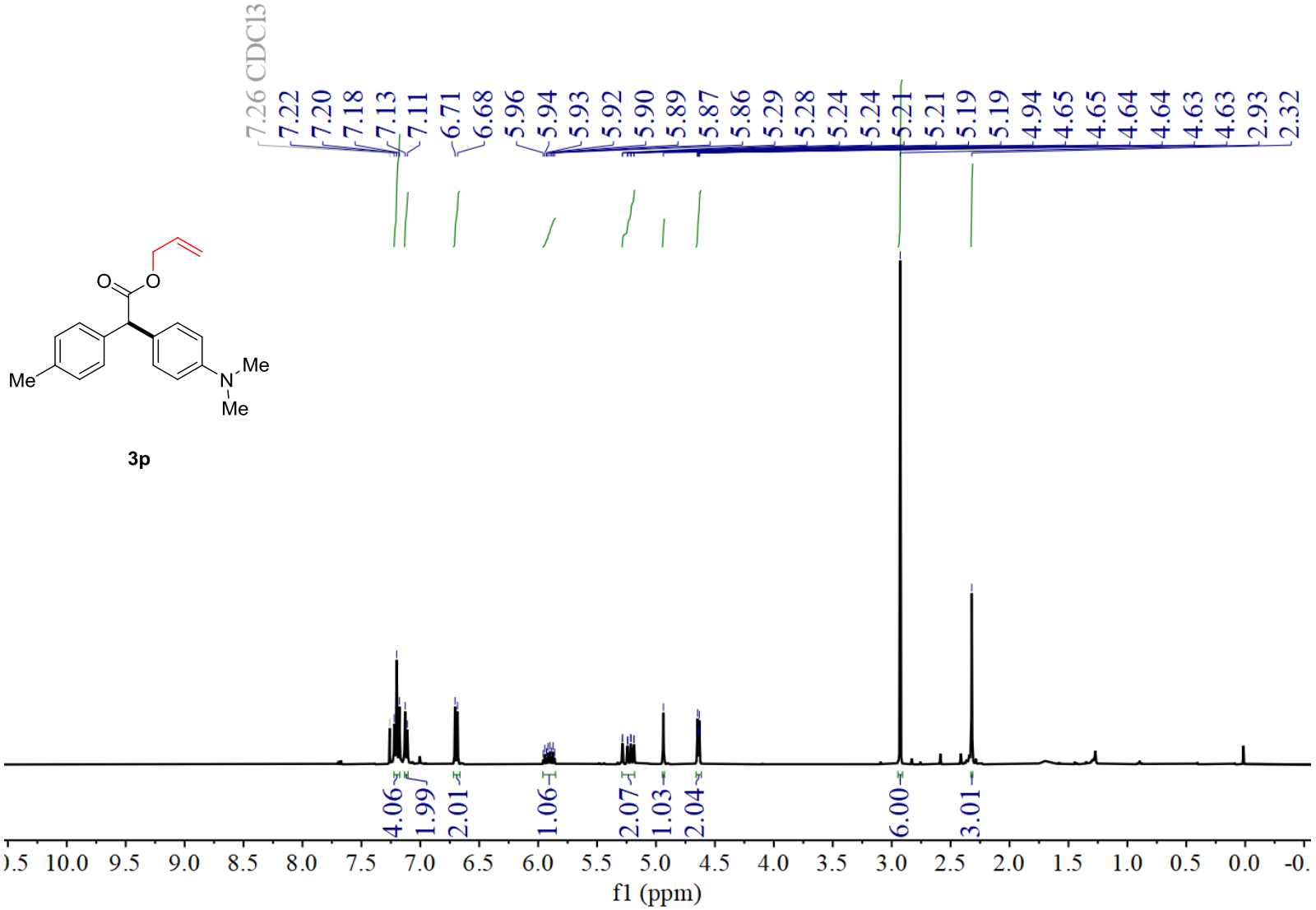
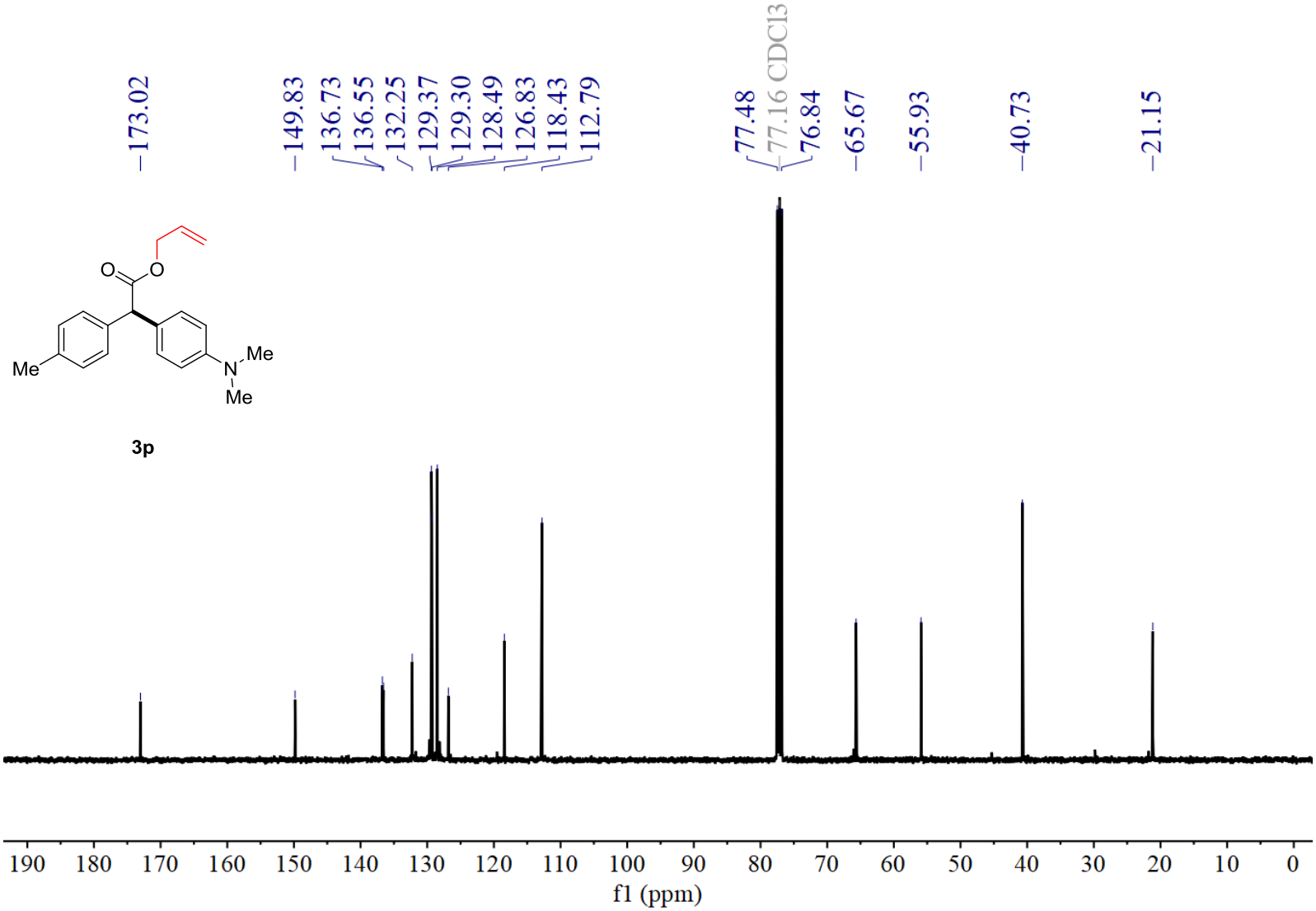
128.26
128.21
126.71
112.71
77.48
77.16 CDCl3
76.84
66.78
55.88
40.69
21.14
O
OBn
Me
N
Me
Me
3o
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.26 CDCl3
7.22
7.20
7.18
7.13
7.11
6.71
6.68
5.96
5.94
5.93
5.92
5.90
5.89
5.87
5.86
5.29
5.28
5.24
5.24
5.21
5.21
5.19
5.19
4.94
4.65
4.65
4.64
4.64
4.63
4.63
2.93
2.32
O
O
Me
N
Me
Me
4.06
1.99
2.01
1.06
2.07
1.03
2.04
6.00
3.01
f1 (ppm)

3p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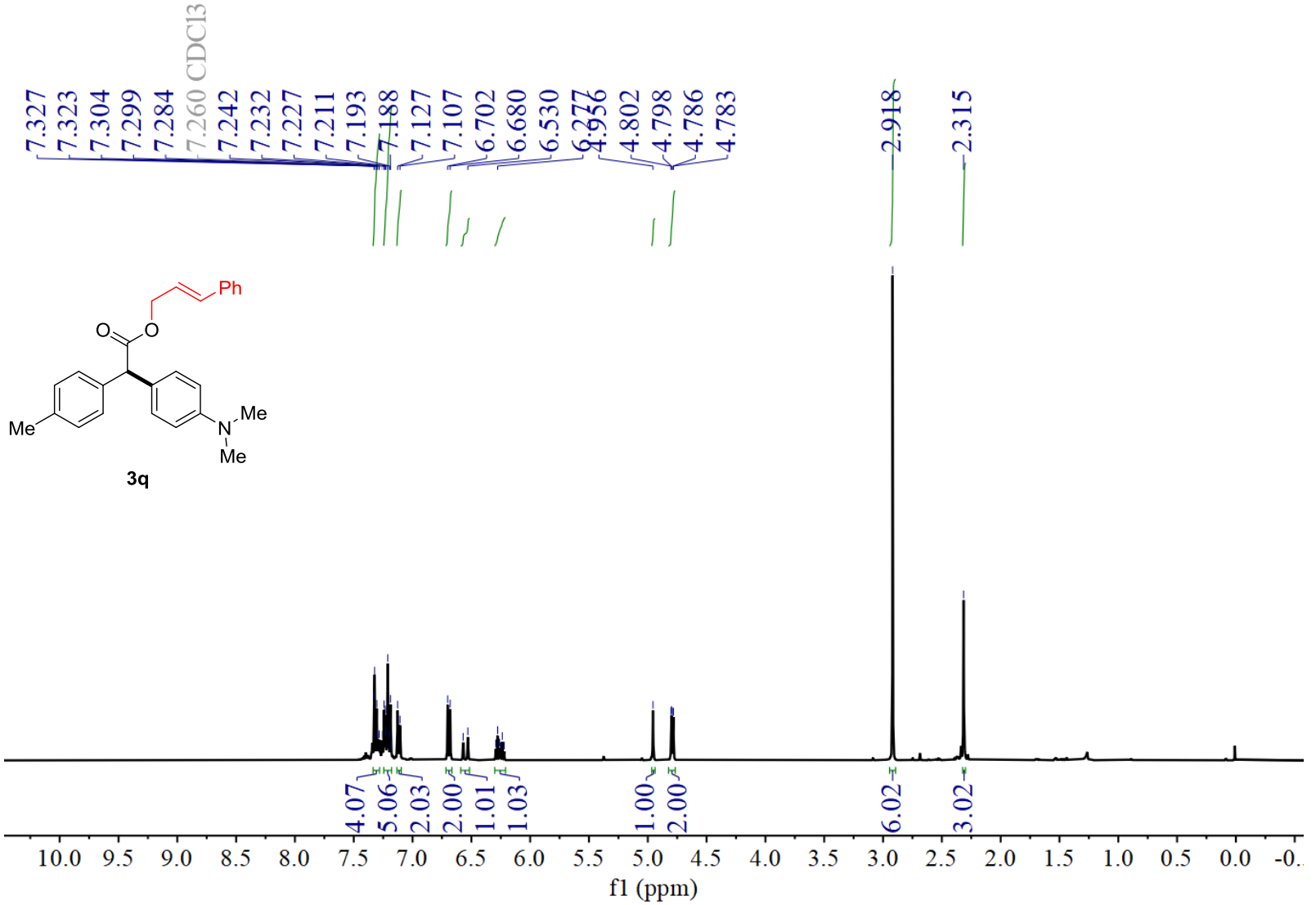
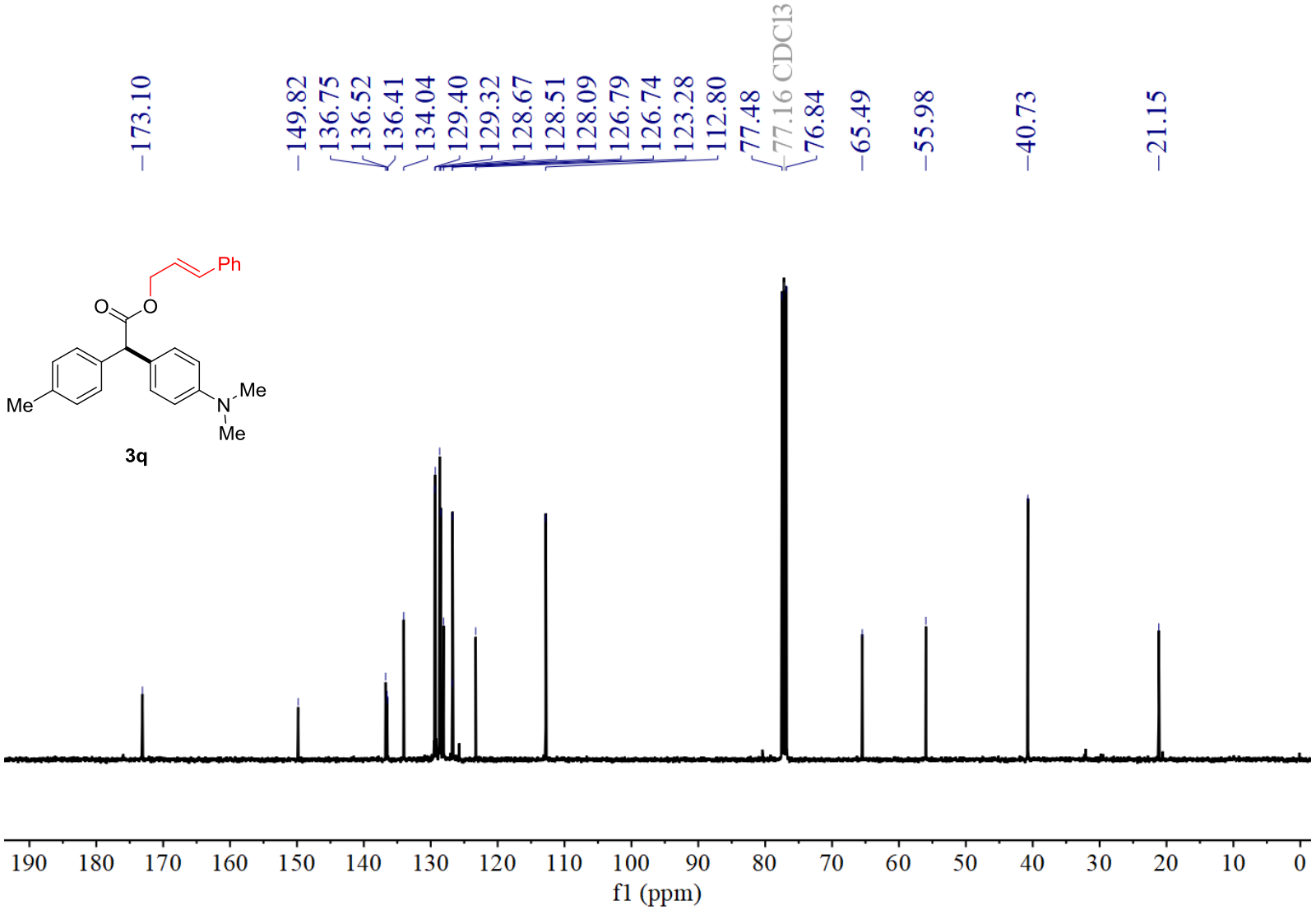
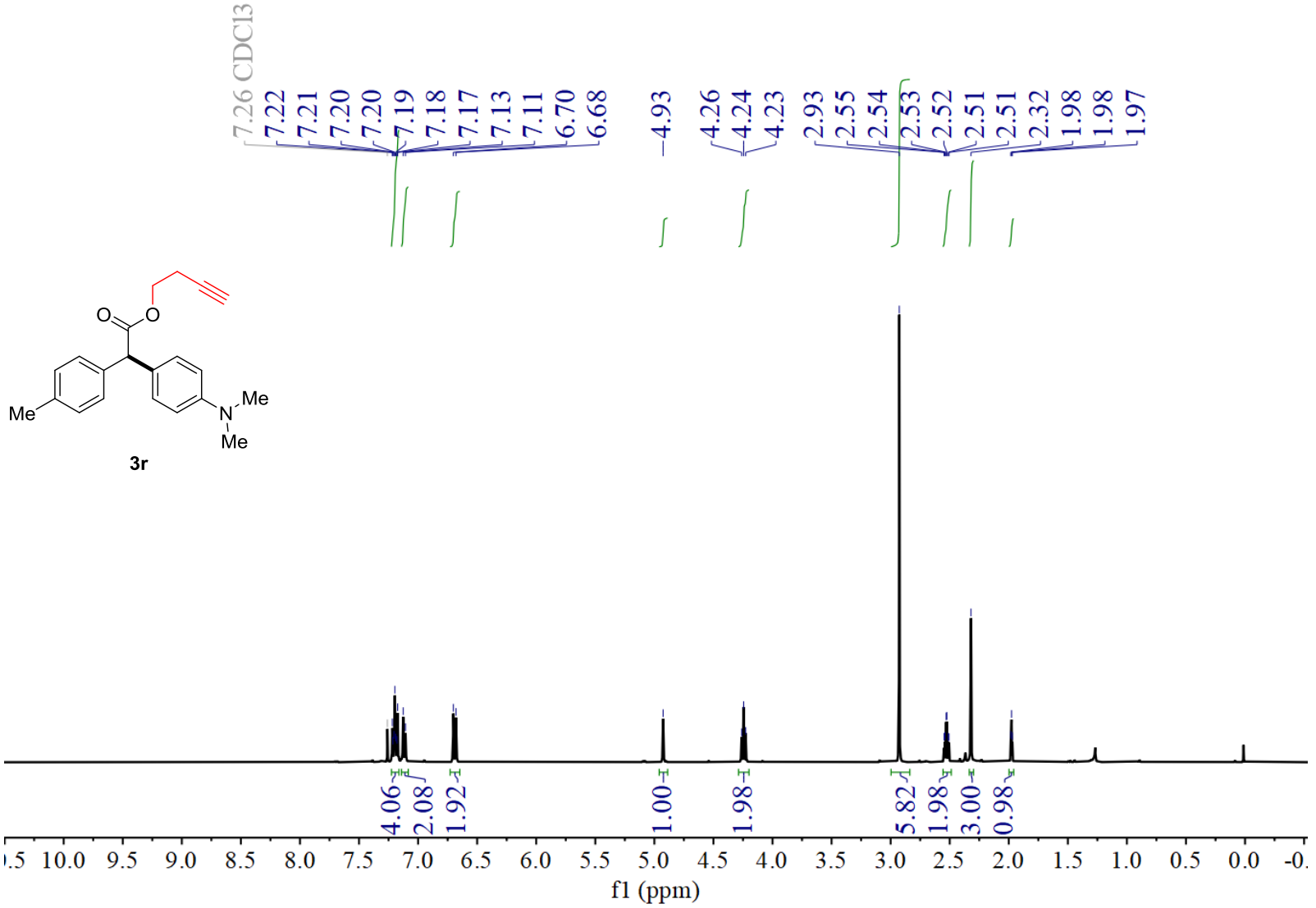
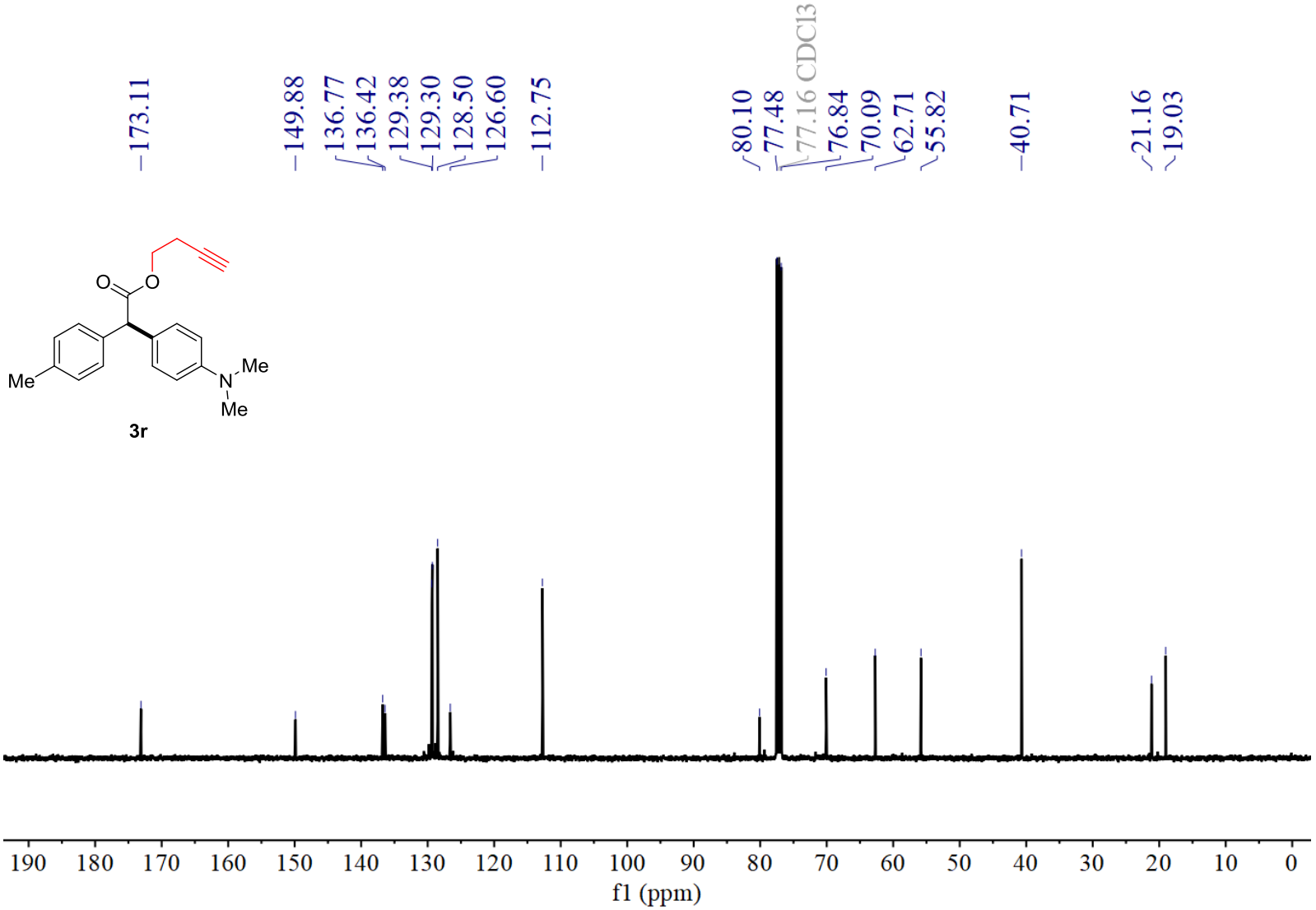
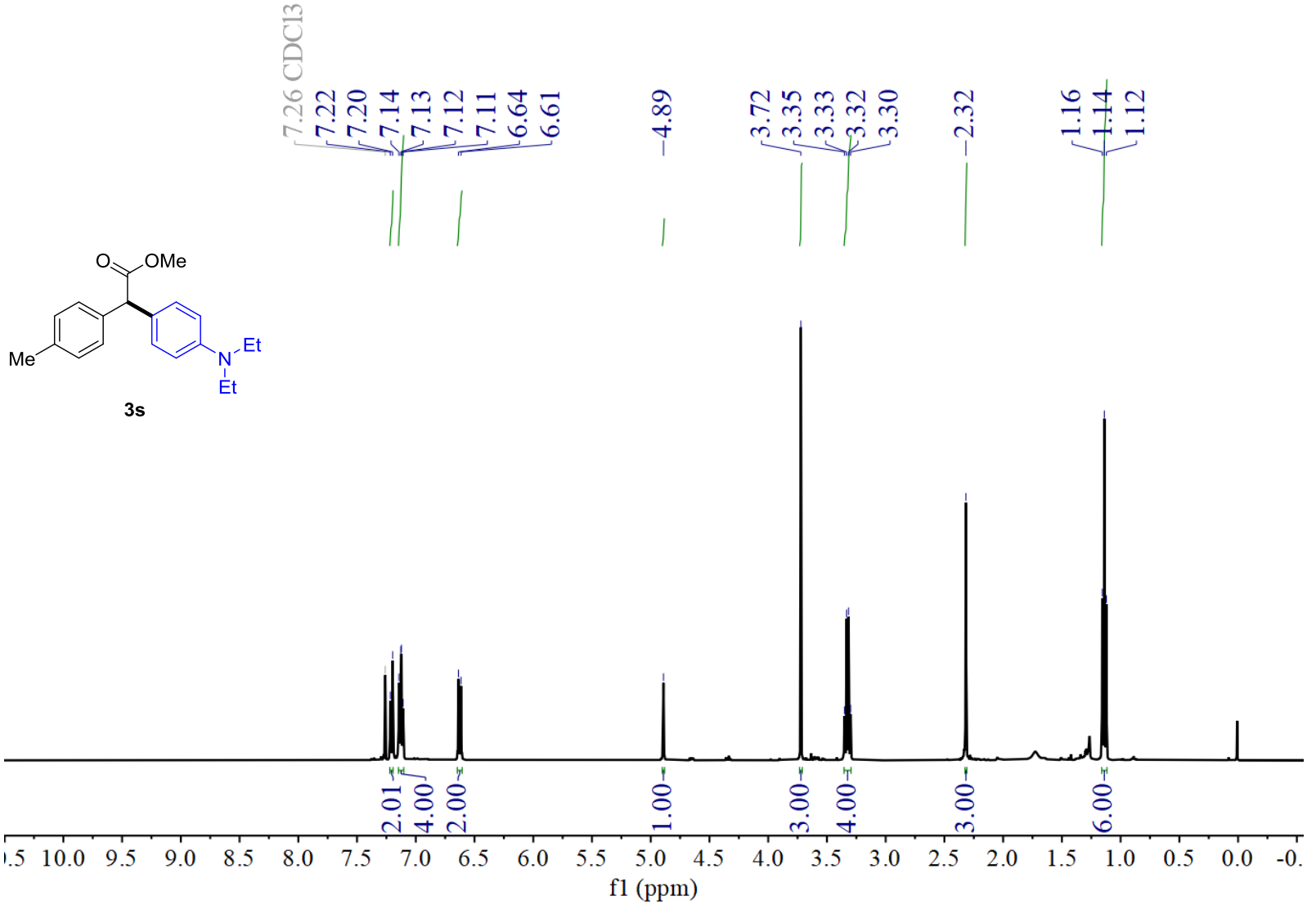
149.83
136.73
136.55
132.25
129.37
129.30
128.49
126.83
118.43
112.79
77.48
77.16 CDCl3
76.84
65.67
55.93
40.73
21.15
O
O
Me
N
Me
Me
3p
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

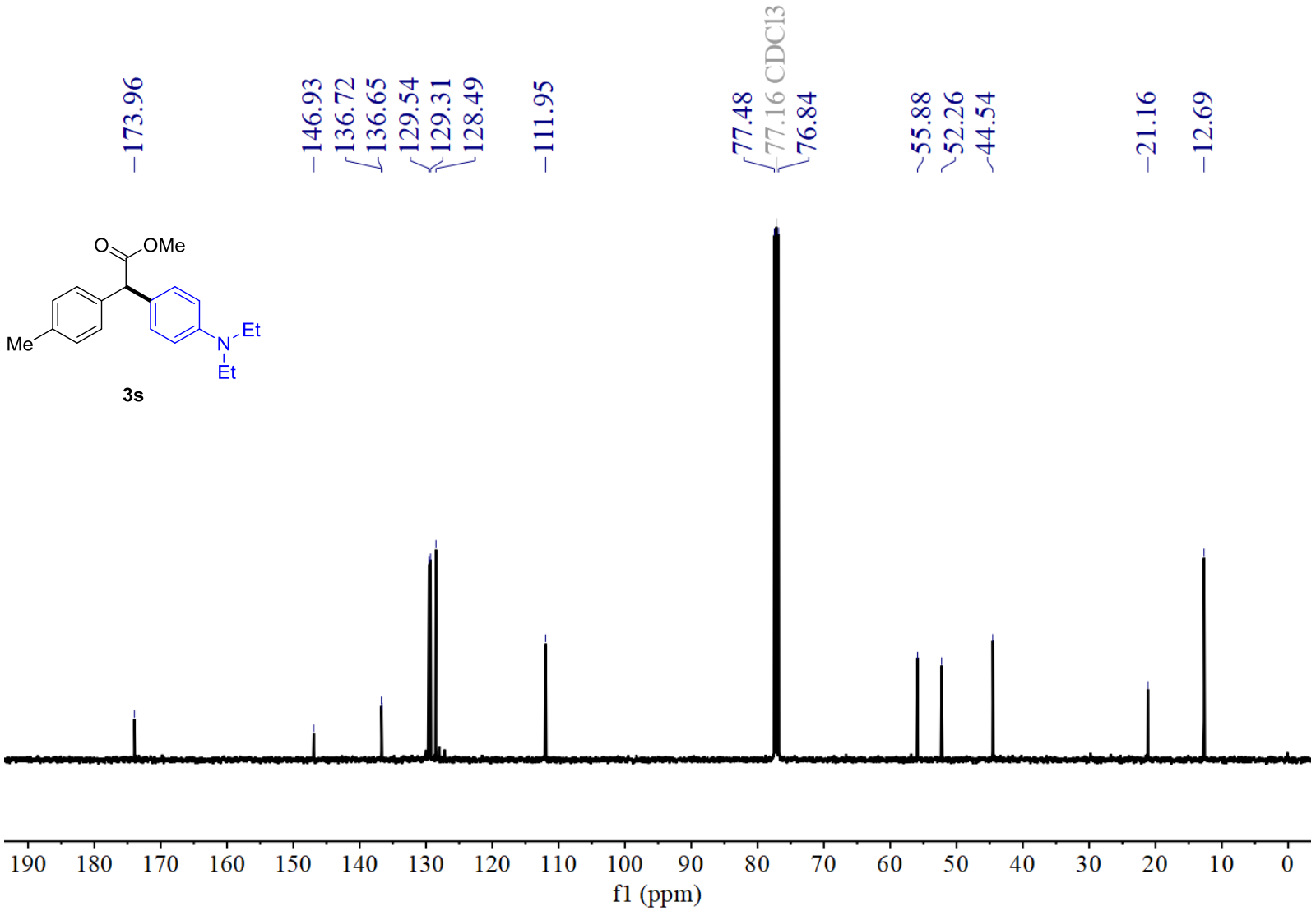

7.327
7.323
7.304
7.299
7.284
7.260 CDCl3
7.242
7.232
7.227
7.211
7.193
7.188
7.127
7.107
6.702
6.680
6.530
6.277
4.956
4.802
4.798
4.786
4.783
2.918
2.315
Ph
O
O
Me
N
Me
Me
3q
4.07
5.06
2.03
2.00
1.01
1.03
1.00
2.00
6.02
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

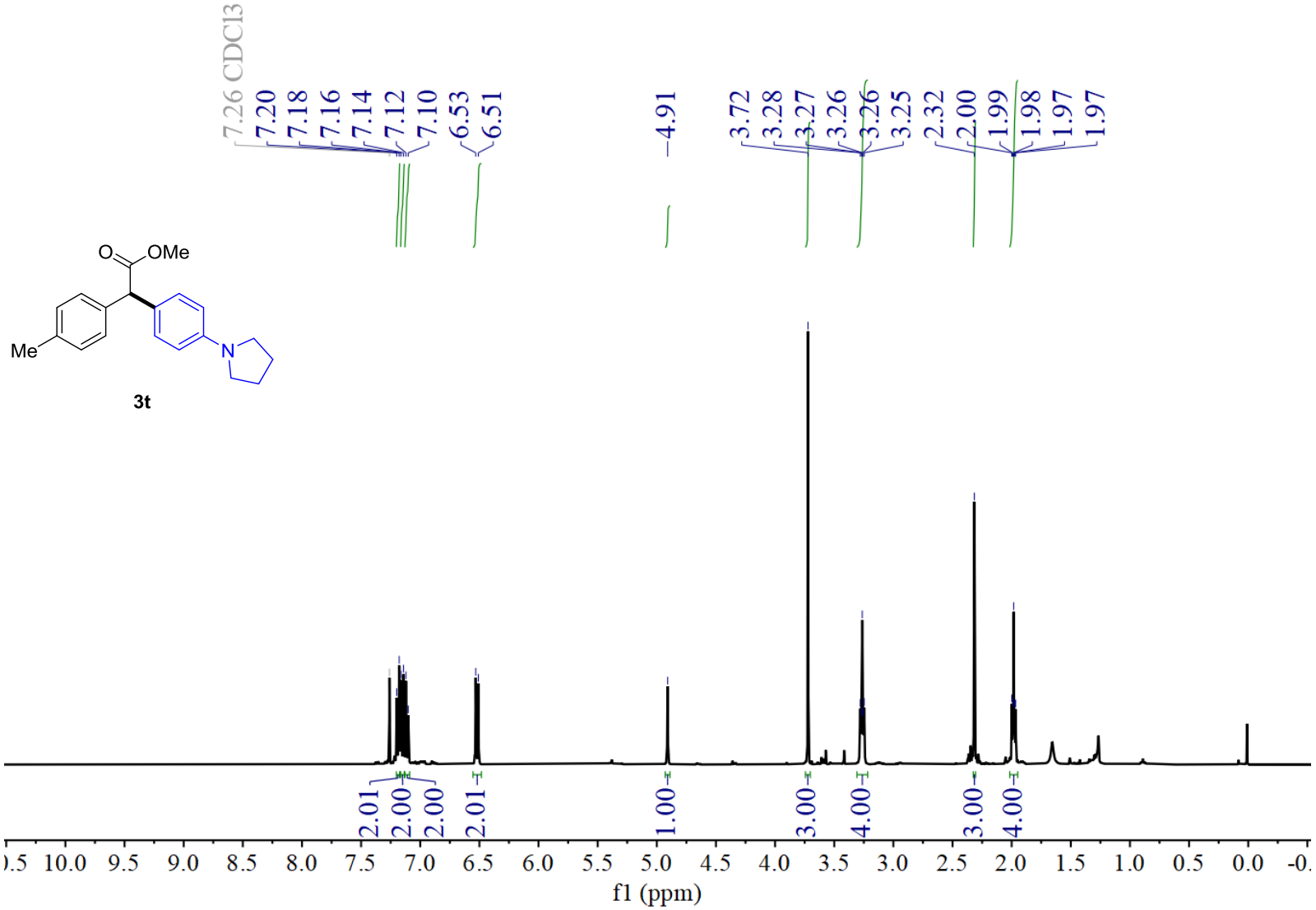

173.10
149.82
136.75
136.52
136.41
134.04
129.40
129.32
128.67
128.51
128.09
126.79
126.74
123.28
112.80
77.48
77.16 CDCl3
76.84
65.49
55.98
40.73
21.15
Ph
O
O
Me
N
Me
Me
3q
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

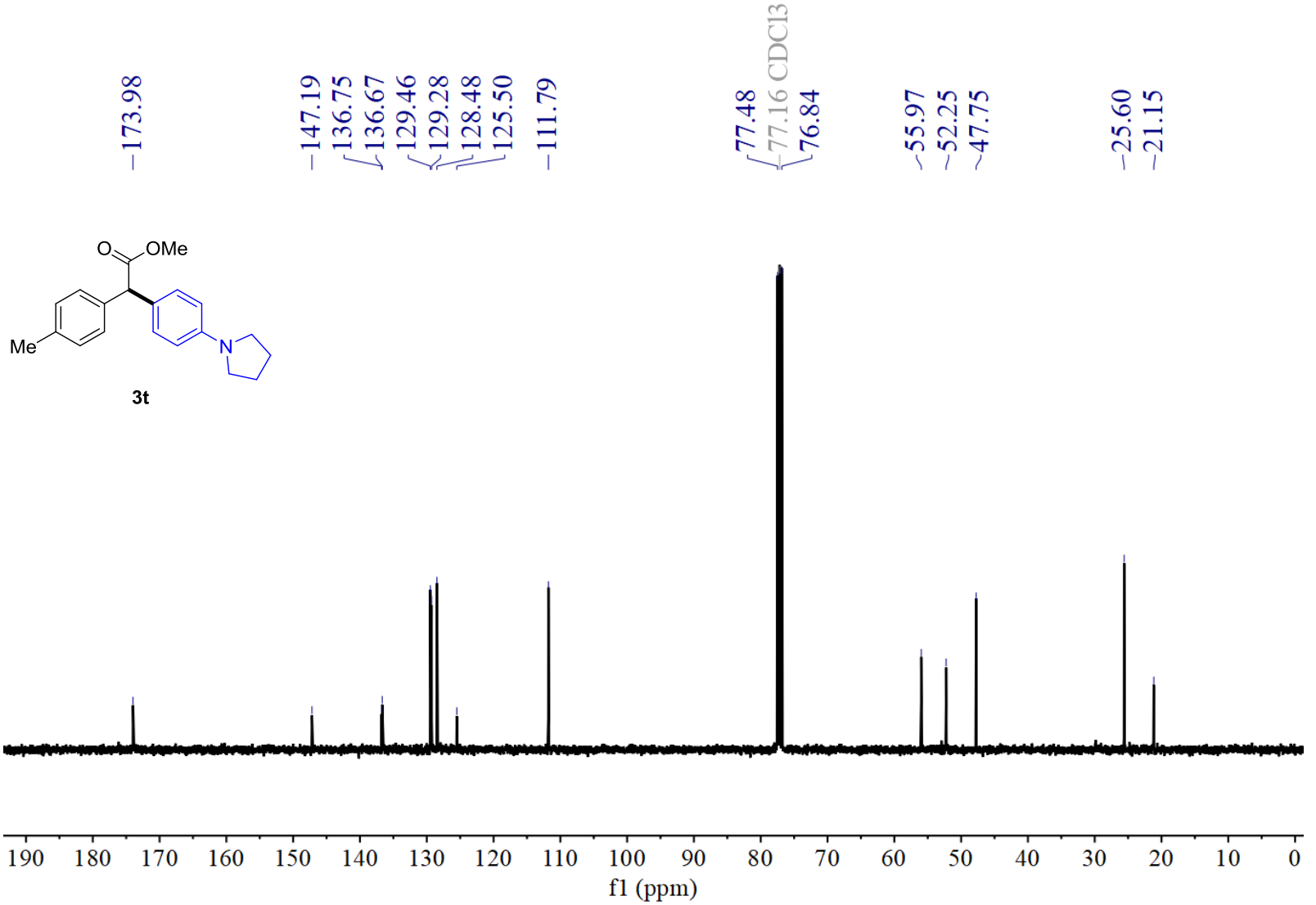

7.26 CDCl3
7.22
7.21
7.20
7.20
7.19
7.18
7.17
7.13
7.11
6.70
6.68
4.93
4.26
4.24
4.23
2.93
2.55
2.54
2.53
2.52
2.51
2.51
2.32
1.98
1.98
1.97
O
O
Me
N
Me
Me
3r
4.06
2.08
1.92
1.00
1.98
5.82
1.98
3.00
0.98
f1 (ppm)


173.11
149.88
136.77
136.42
129.38
129.30
128.50
126.60
112.75
80.10
77.48
77.16 CDCl3
76.84
70.09
62.71
55.82
40.71
21.16
19.03
O
O
Me
N
Me
Me
3r
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.26 CDCl3
7.22
7.20
7.14
7.13
7.12
7.11
6.64
6.61
4.89
3.72
3.35
3.33
3.32
3.30
2.32
1.16
1.14
1.12
O
OMe
Me
N
Et
Et
3s
2.01
4.00
2.00
1.00
3.00
4.00
3.00
6.00
f1 (ppm)


173.96
146.93
136.72
136.65
129.54
129.31
128.49
111.95
77.48
77.16 CDCl3
76.84
55.88
52.26
44.54
21.16
12.69
O
OMe
Me
N
Et
Et
3s
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.26 CDCl3
7.20
7.18
7.16
7.14
7.12
7.10
6.53
6.51
4.91
3.72
3.28
3.27
3.26
3.26
3.25
2.32
2.00
1.99
1.98
1.97
1.97
O
OMe
Me
N
3t
2.01
2.00
2.00
2.01
1.00
3.00
4.00
3.00
4.00
f1 (ppm)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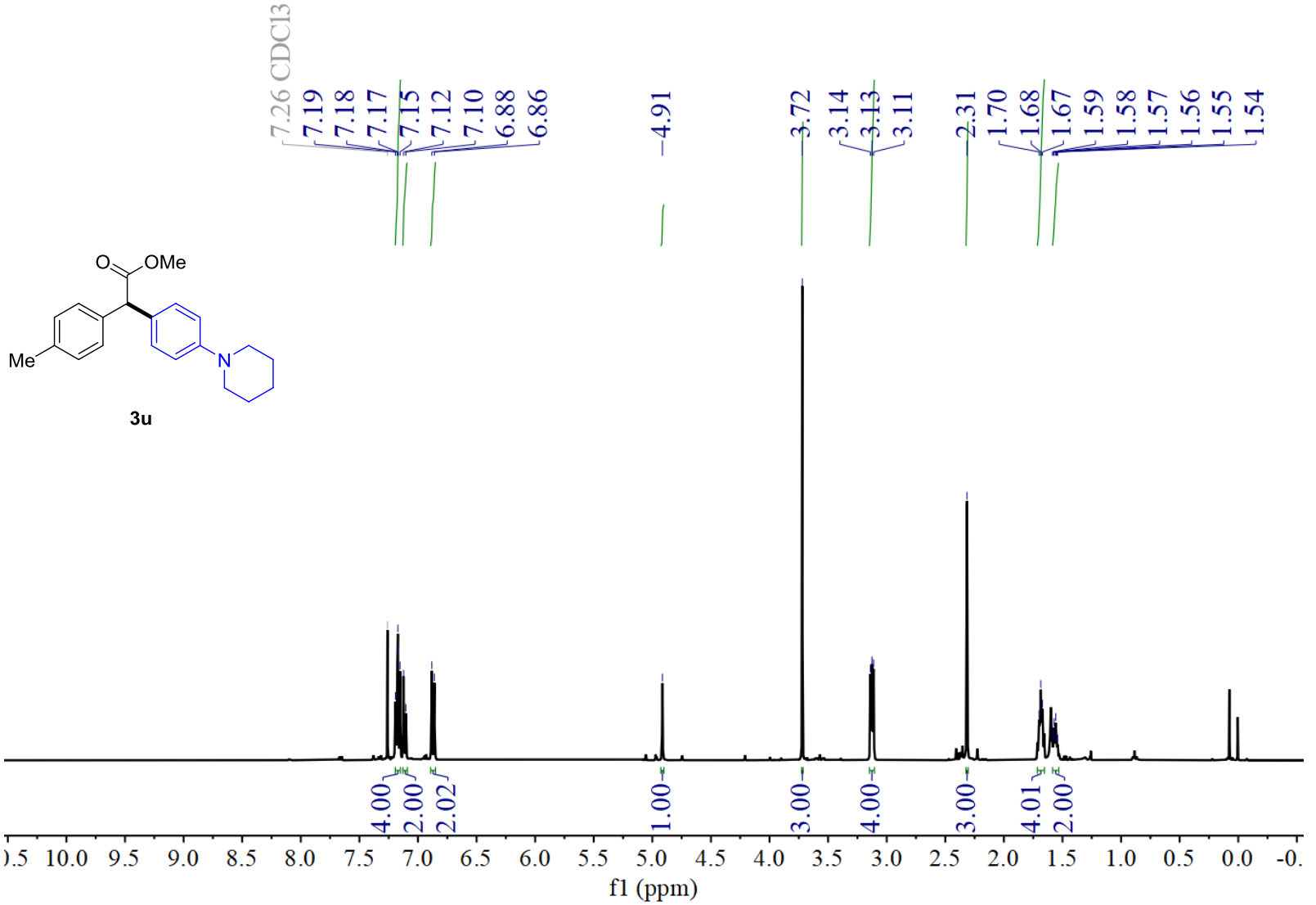
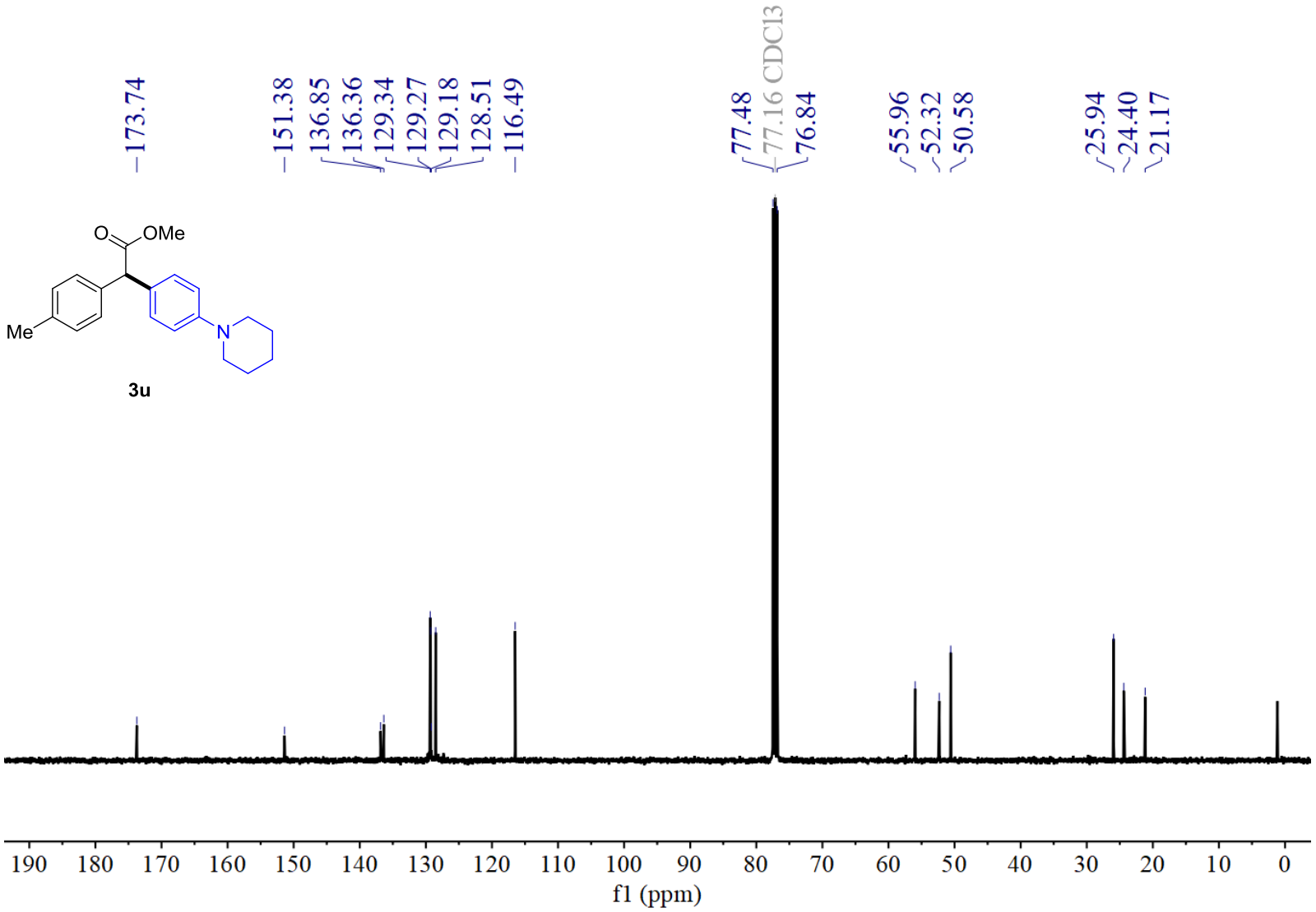
136.75
136.67
129.46
129.28
128.48
125.50
111.79
77.48
77.16 CDCl3
76.84
55.97
52.25
47.75
25.60
21.15
O
OMe
Me
N
3t
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.26 CDCl3
7.19
7.18
7.17
7.15
7.12
7.10
6.88
6.86
4.91
3.72
3.14
3.13
3.11
2.31
1.70
1.68
1.67
1.59
1.58
1.57
1.56
1.55
1.54
O
OMe
Me
N
3u
4.00
2.00
2.02
1.00
3.00
4.00
3.00
4.01
2.00
f1 (ppm)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136.36
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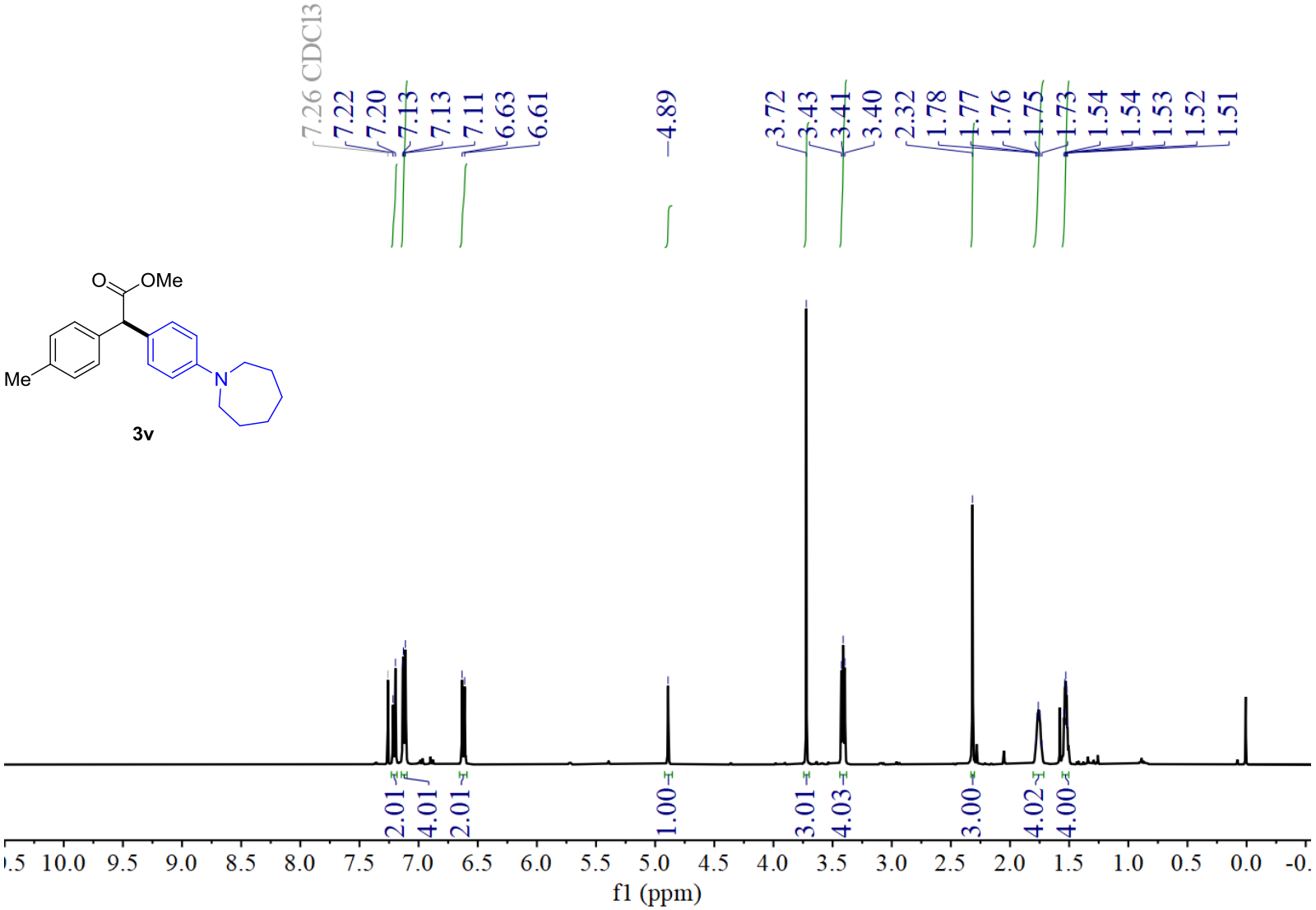
129.27
129.18
128.51
116.49
77.48
77.16 CDCl3
76.84
55.96
52.32
50.58
25.94
24.40
21.17
O
OMe
Me
N
3u
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.26 CDCl3
7.22
7.20
7.13
7.13
7.11
6.63
6.61
4.89
3.72
3.43
3.41
3.40
2.32
1.78
1.77
1.76
1.75
1.73
1.54
1.54
1.53
1.52
1.51
O
OMe
Me
N
3v
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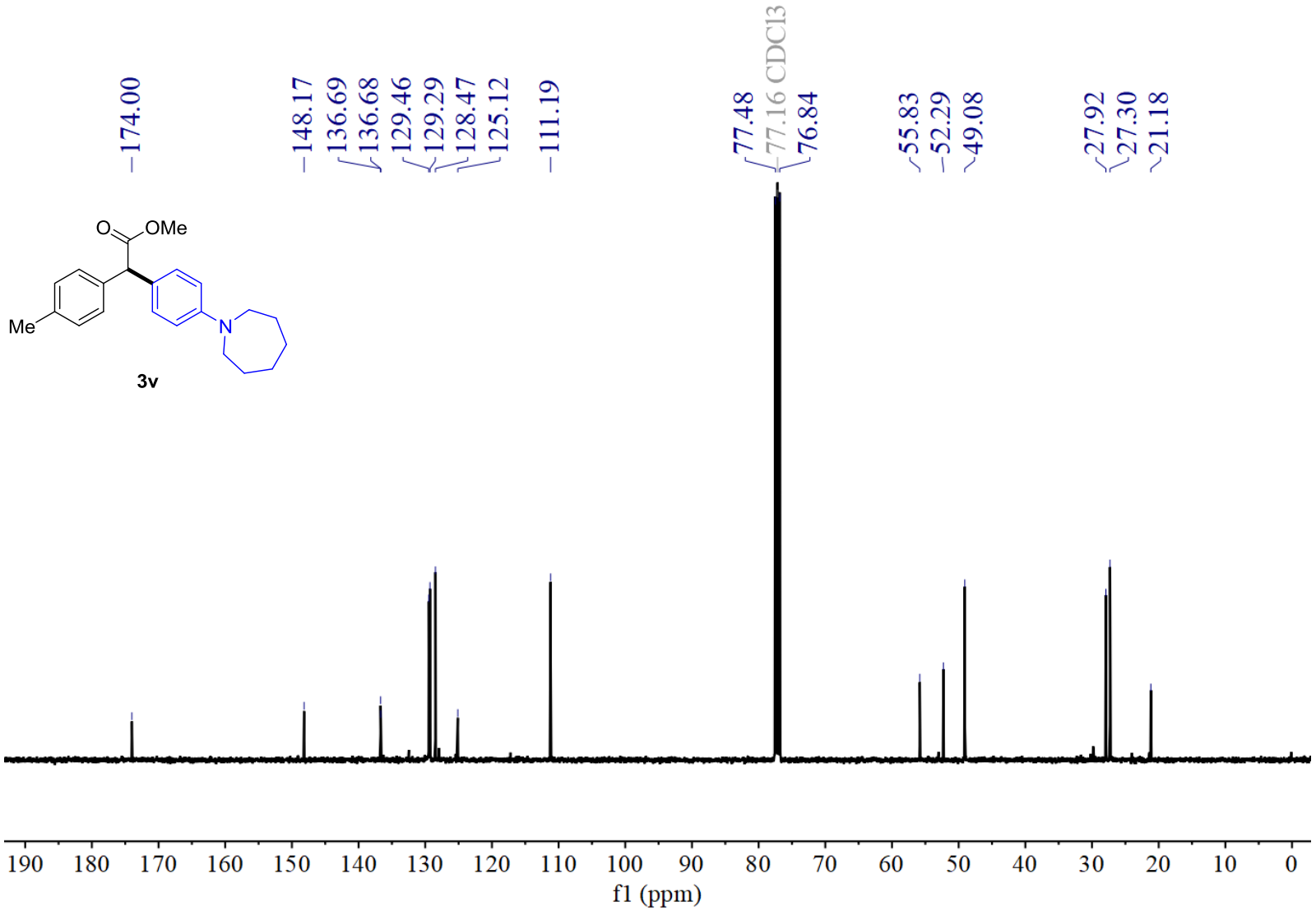
4.01
2.01
1.00
3.01
4.03
3.00
4.02
4.00
f1 (ppm)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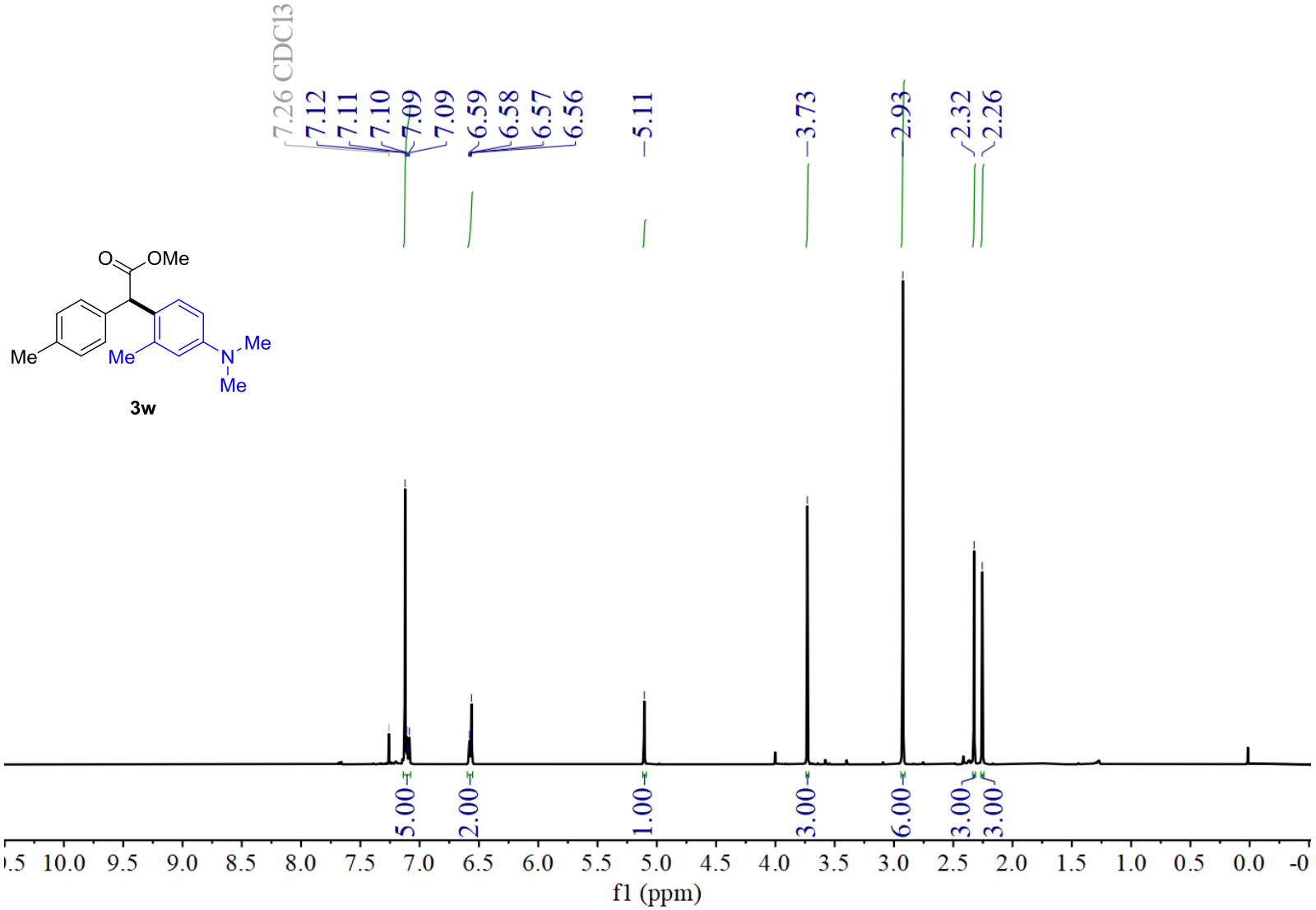
136.68
129.46
129.29
128.47
125.12
111.19
77.48
77.16 CDCl3
76.84
55.83
52.29
49.08
27.92
27.30
21.18
O
OMe
Me
N
3v
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.26 CDCl3
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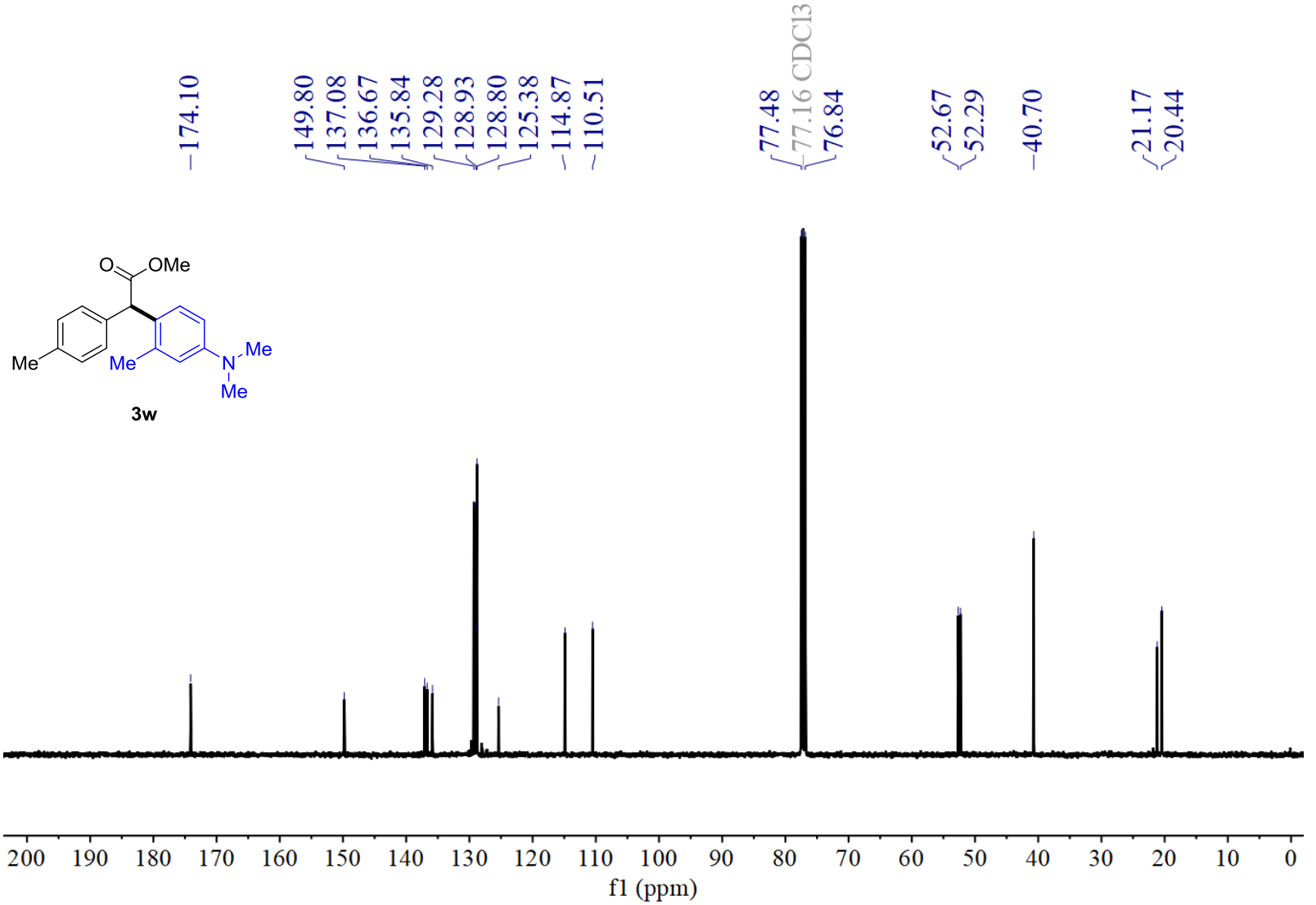
7.11
7.10
7.09
7.09
6.59
6.58
6.57
6.56
5.11
3.73
2.93
2.32
2.26
O
OMe
Me
Me
N
Me
Me
3w
5.00
2.00
1.00
3.00
6.00
3.00
3.00
f1 (ppm)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136.67
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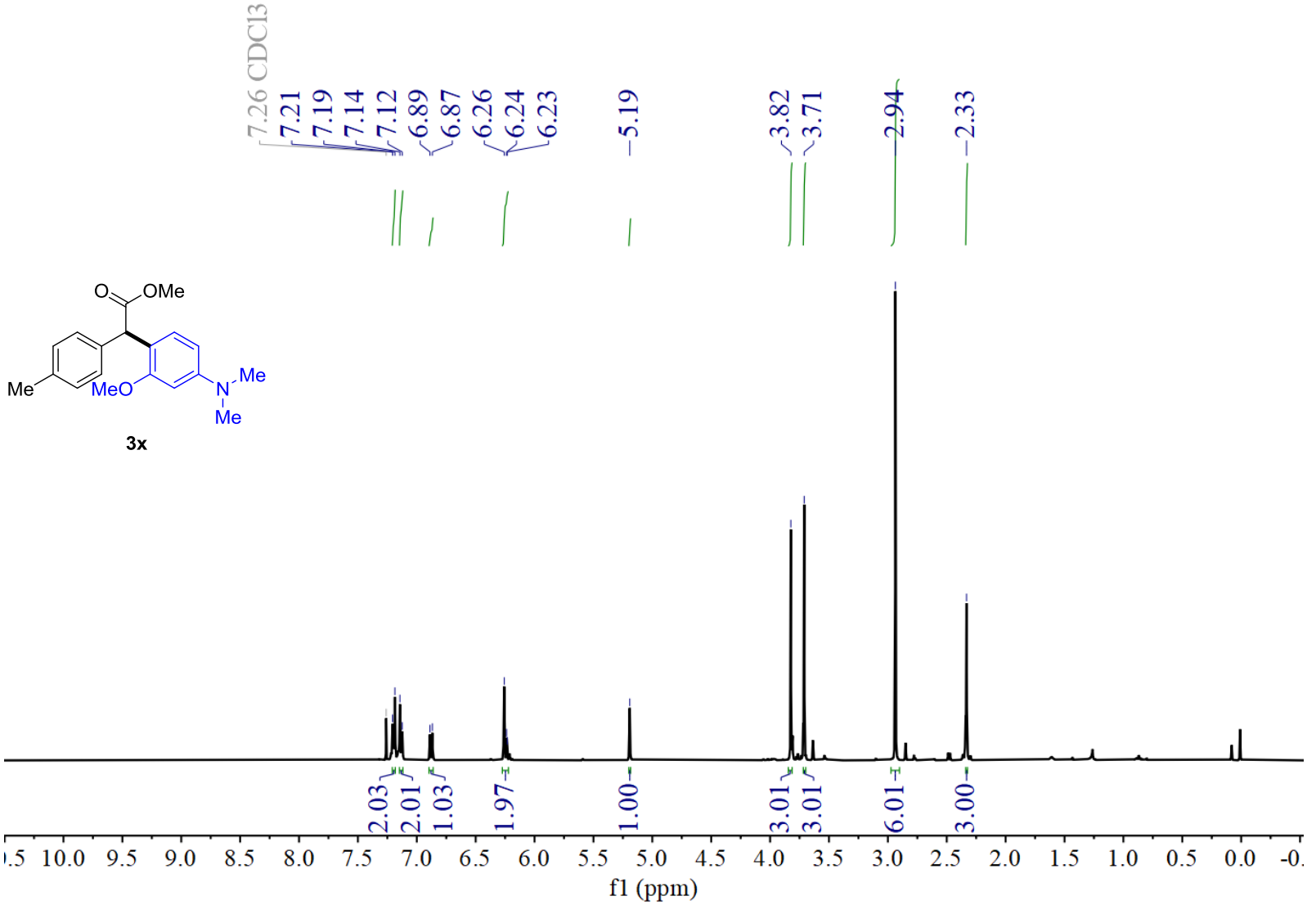
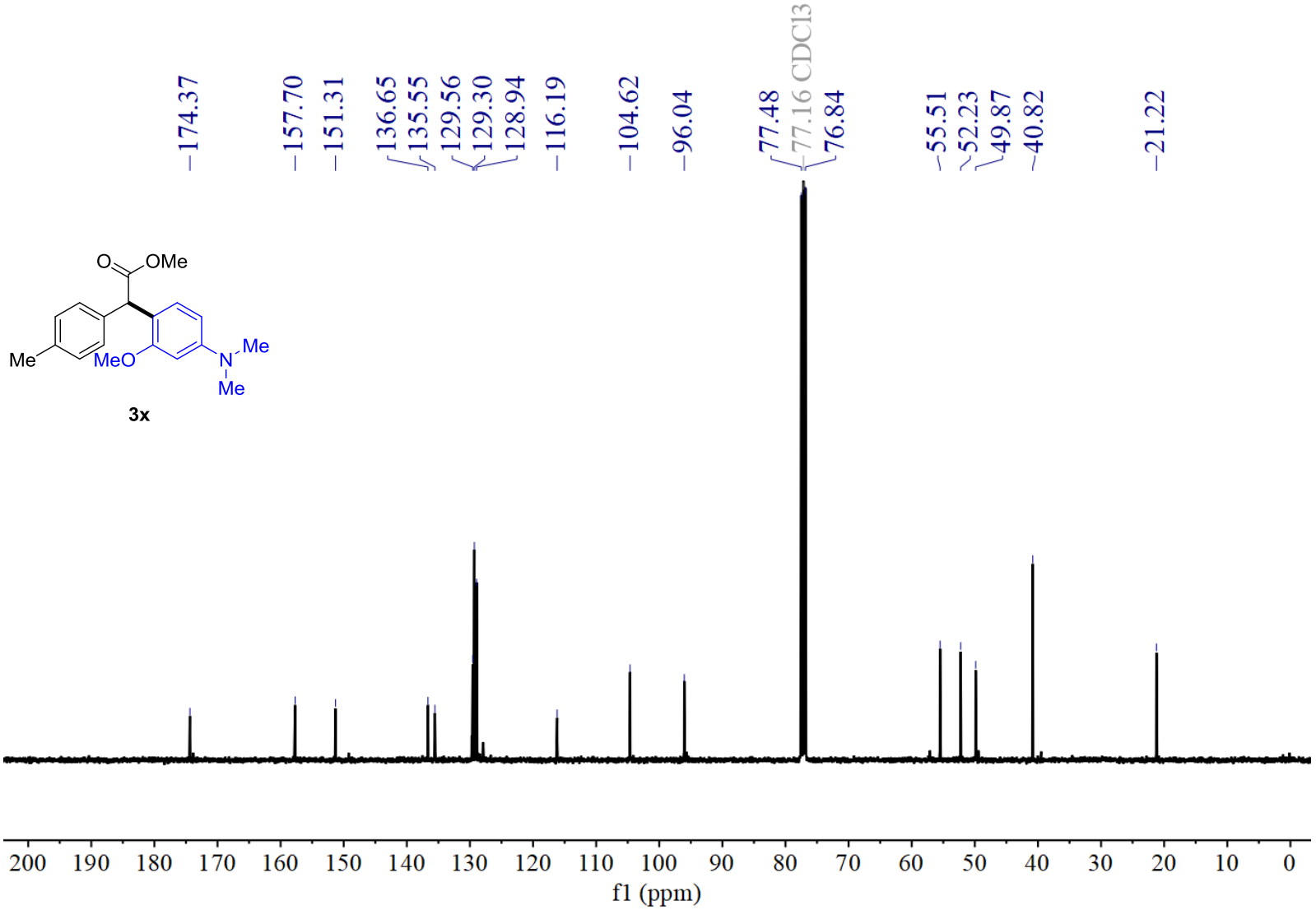
129.28
128.93
128.80
125.38
114.87
110.51
77.48
77.16 CDCl3
76.84
52.67
52.29
40.70
21.17
20.44
O
OMe
Me
Me
N
Me
Me
3w
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.26 CDCl3
7.21
7.19
7.14
7.12
6.89
6.87
6.26
6.24
6.23
5.19
3.82
3.71
2.94
2.33
O
OMe
Me
MeO
N
Me
Me
3x
2.03
2.01
1.03
1.97
1.00
3.01
3.01
6.01
3.00
f1 (ppm)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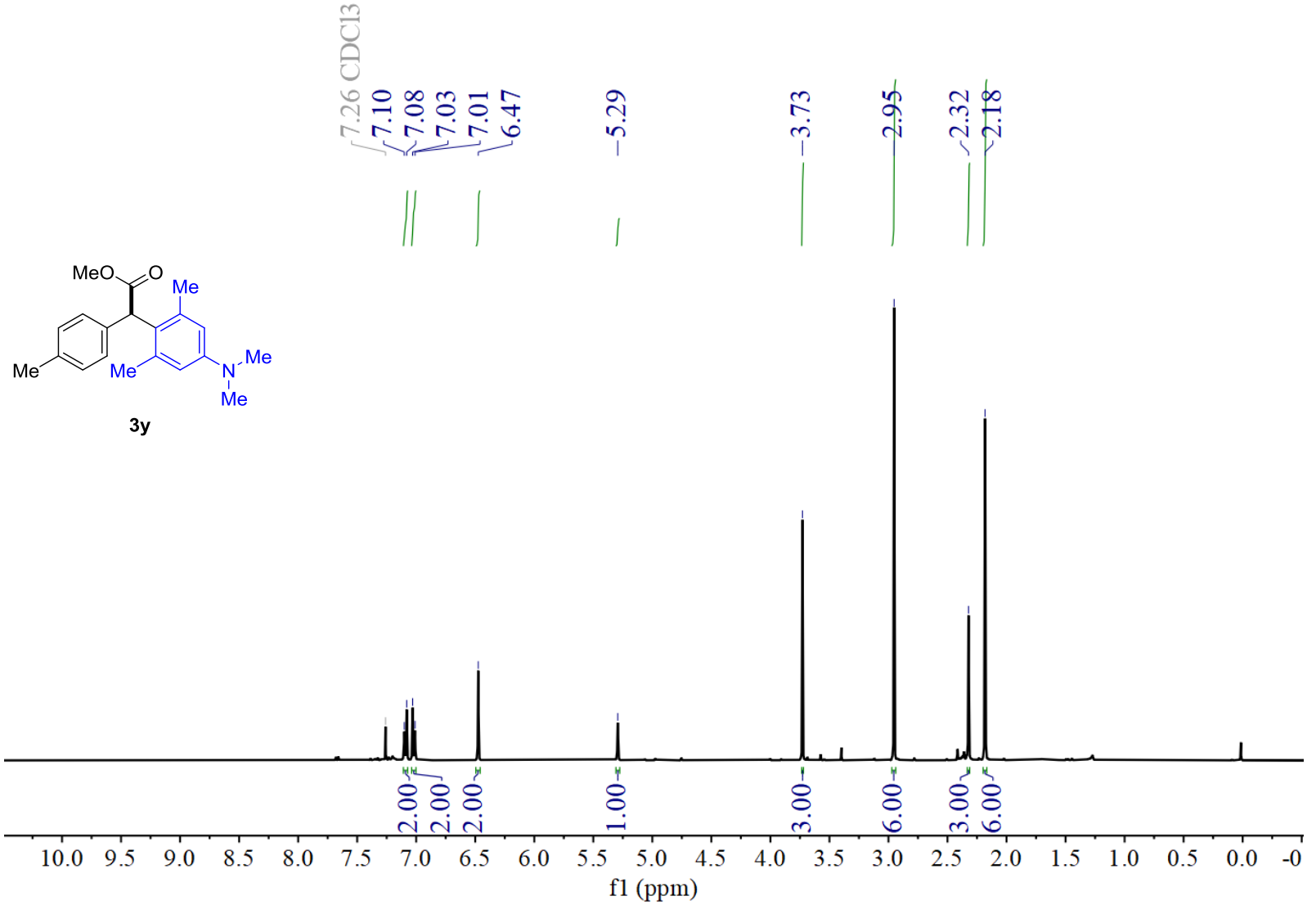
136.65
135.55
129.56
129.30
128.94
116.19
104.62
96.04
77.48
77.16 CDCl3
76.84
55.51
52.23
49.87
40.82
21.22
O
OMe
Me
MeO
N
Me
Me
3x
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.26 CDCl3
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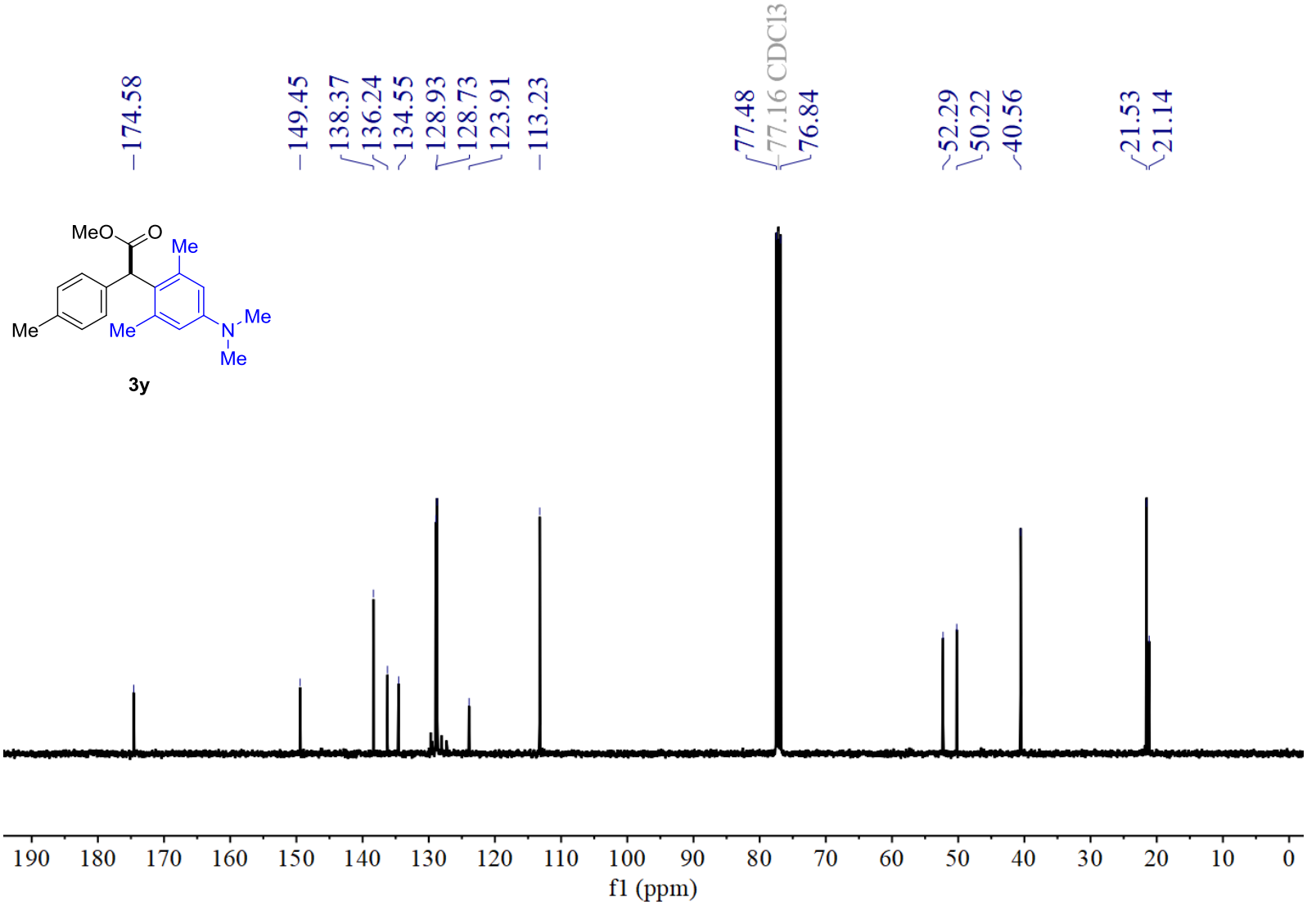
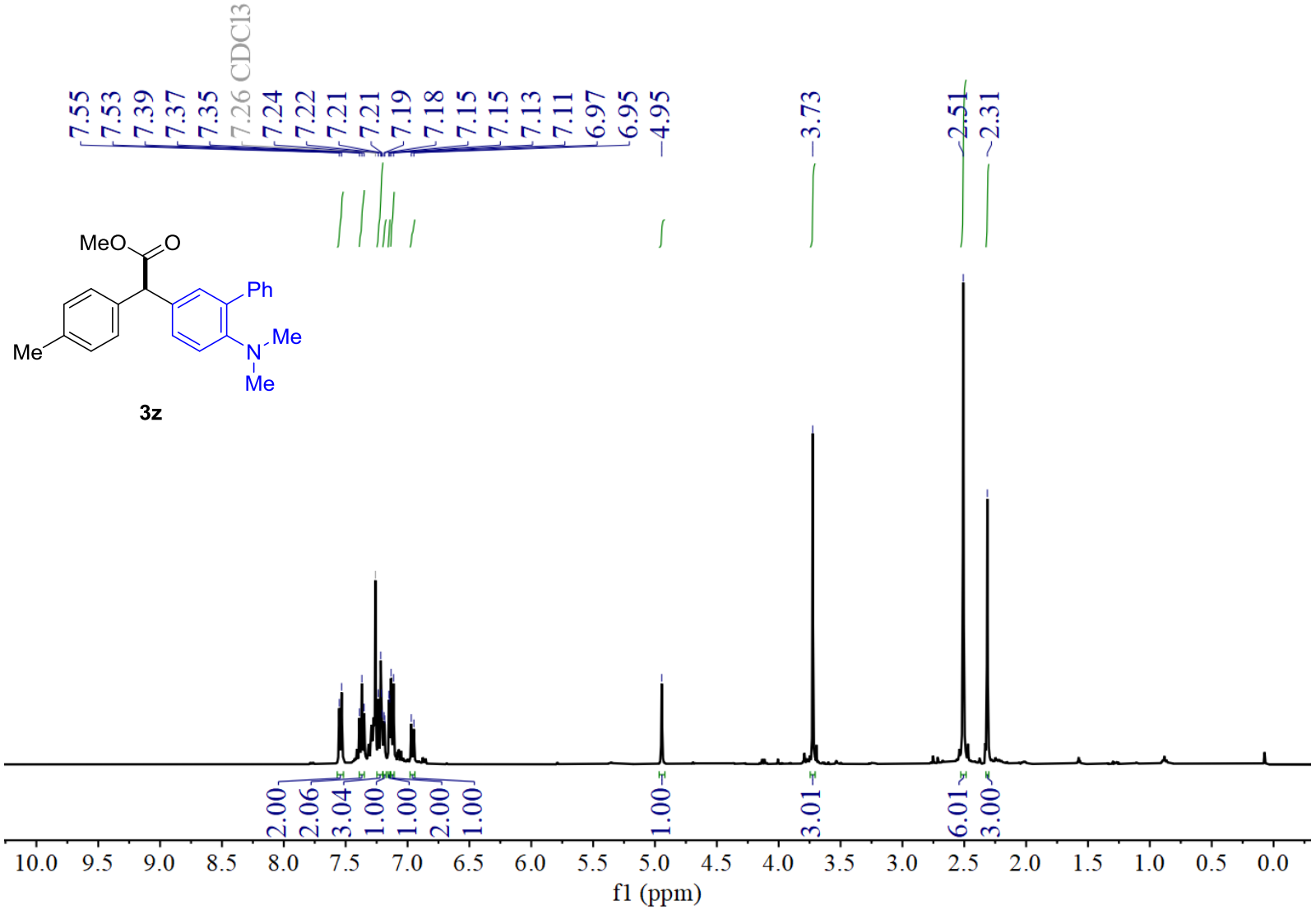
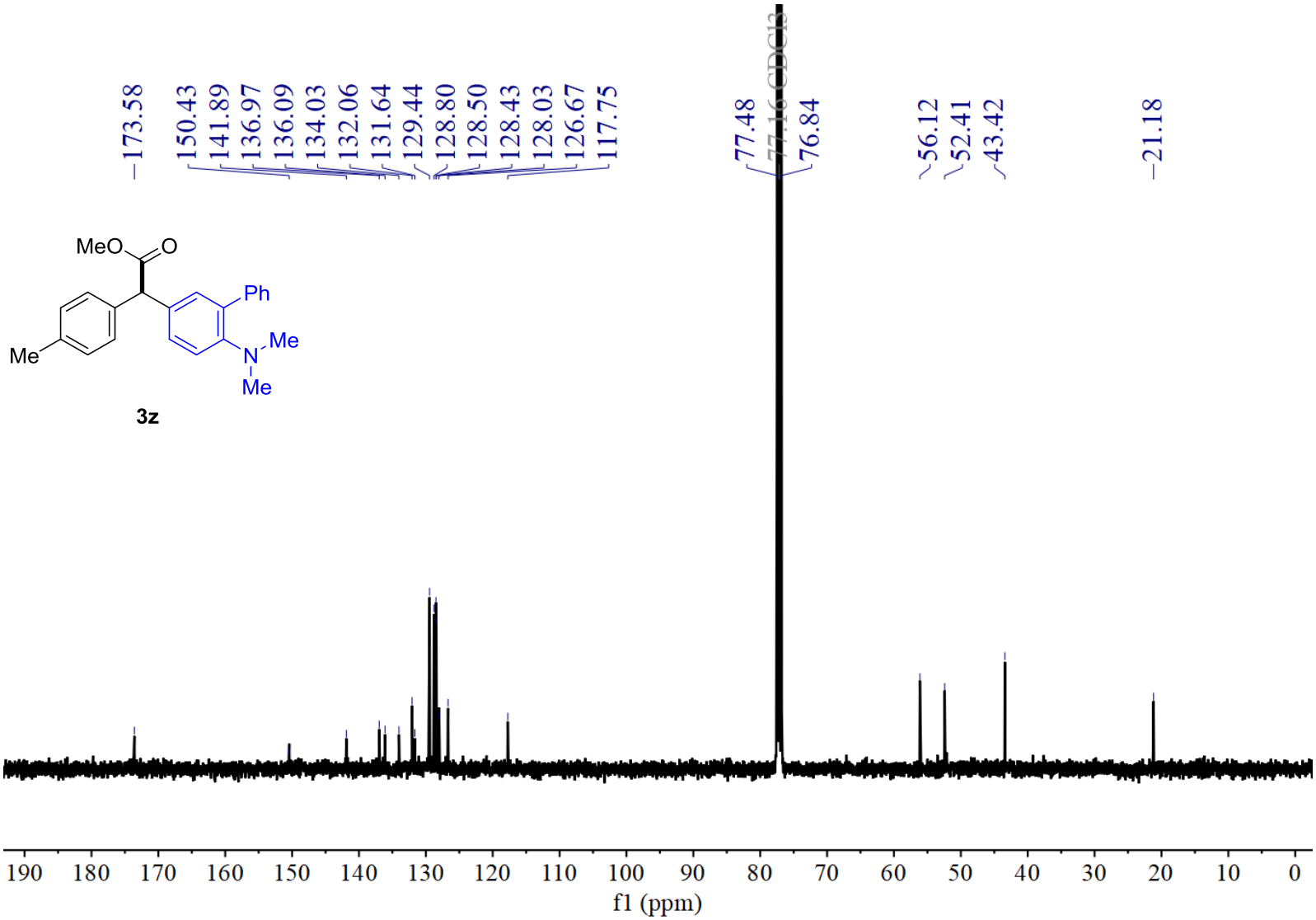
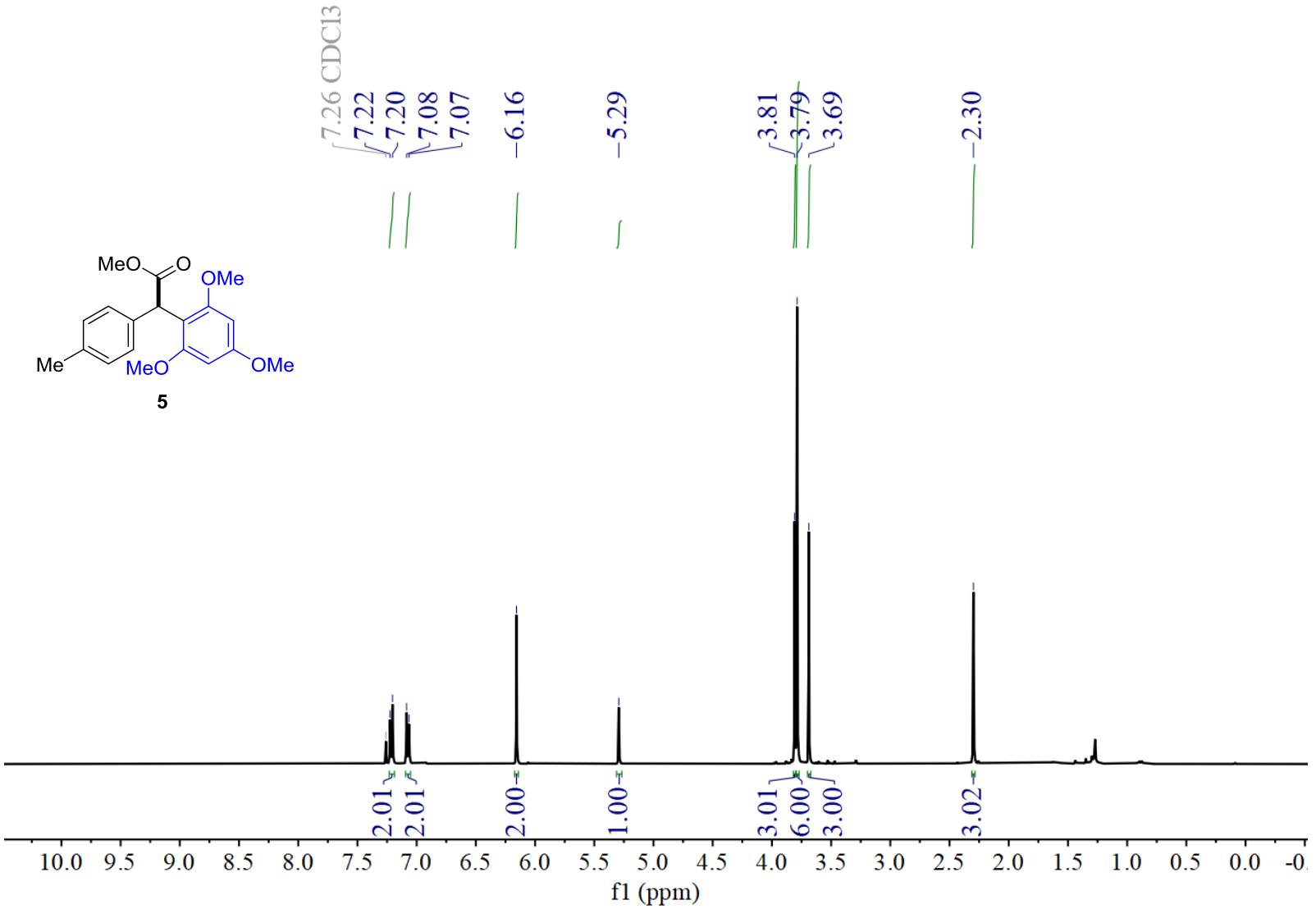
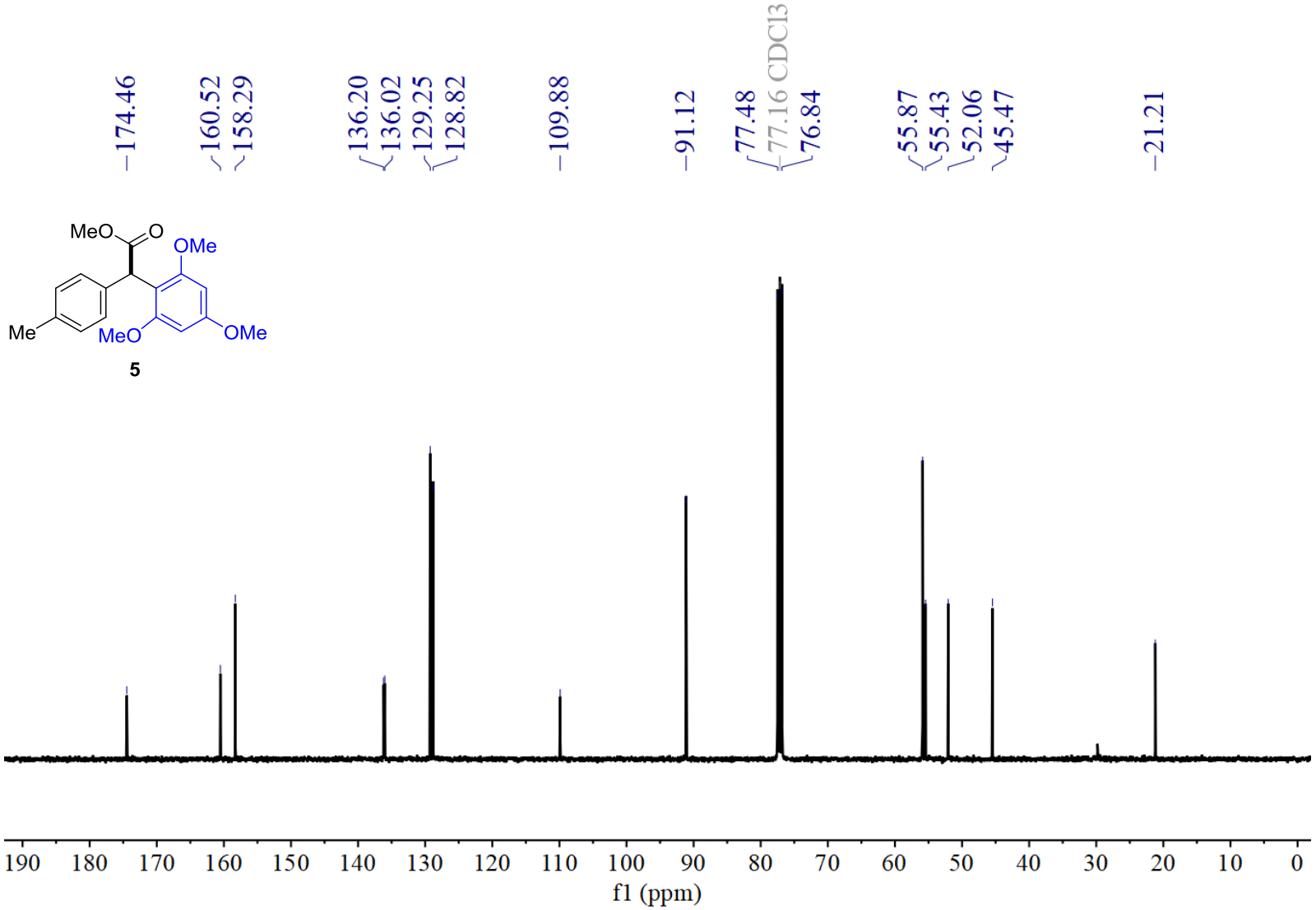
7.08
7.03
7.01
6.47
5.29
3.73
2.95
2.32
2.18
MeO
O
Me
Me
Me
N
Me
Me
3y
2.00
2.00
2.00
1.00
3.00
6.00
3.00
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)


174.58
149.45
138.37
136.24
134.55
128.93
128.73
123.91
113.23
77.48
77.16 CDCl3
76.84
52.29
50.22
40.56
21.53
21.14
MeO
O
Me
Me
Me
N
Me
Me
3y
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.55
7.53
7.39
7.37
7.35
7.26 CDCl3
7.24
7.22
7.21
7.21
7.19
7.18
7.15
7.15
7.13
7.11
6.97
6.95
4.95
3.73
2.51
2.31
MeO
O
Ph
Me
N
Me
Me
3z
2.00
2.06
3.04
1.00
1.00
2.00
1.00
1.00
3.01
6.01
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


173.58
150.43
141.89
136.97
136.09
134.03
132.06
131.64
129.44
128.80
128.50
128.43
128.03
126.67
117.75
77.48
77.16
76.84
56.12
52.41
43.42
21.18
MeO
O
Ph
Me
N
Me
Me
3z
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.26 CDCl3
7.22
7.20
7.08
7.07
6.16
5.29
3.81
3.79
3.69
2.30
MeO
O
OMe
Me
MeO
OMe
5
2.01
2.01
2.00
1.00
3.01
6.00
3.00
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


174.46
160.52
158.29
136.20
136.02
129.25
128.82
109.88
91.12
77.48
77.16 CDCl3
76.84
55.87
55.43
52.06
45.47
21.21
MeO
O
OMe
Me
MeO
OMe
5
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)