Electronic Supplementary Information

Copper-Catalyzed Electrophilic Amination Using *N*-Methoxyamines

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A. Complete lists of references

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B. Experimental Procedures

General Details

DME was distilled from Na/benzophenone, degassed using the freeze-pump-thaw technique (3x), dried over activated 3Å molecular sieves, and stored in a glove box. DMF was distilled from $CaSO_4$, and dried over 3Å molecular sieves. CH_2Cl_2 and EtOH were dried over activated 3Å molecular sieves. THF (dehydrated, stabilizer free) was purchased from KANTO CHEMICAL CO., INC. Triphenylboroxin was purchased from WAKO PURE CHEMICAL INDUSTRIES, LTD. Tris(4-fluorophenyl)boroxin was purchased from TOKYO CHEMICAL INDUSTRY, CO., LTD. Other triarylboroxins were prepared according to the reported procedure.[1] Other commercial reagents were used without further purification.

Reactions were performed in oven-dried glassware fitted with rubber septa under an argon atmosphere. Thin-layer chromatography was performed on Merck TLC silica gel 60 F_{254}, which were visualized by exposure to UV (254 nm) or stained by submersion in aquatic cerium-ammonium molybdate, ethanolic ninhydrin or ethanolic phosphomolybdic acid solution followed by heating on a hot plate. Flash column chromatography was performed on silica gel (Silica Gel 60 N; 63–210 or 40–50 mesh, KANTO CHEMICAL CO., INC.). Preparative layer chromatography was performed on Merck PLC silica gel 60 F_{254}. ^{1}H NMR spectra were recorded at 500 MHz with JEOL ECA-500 spectrometer or 400 MHz with JEOL ECS-400 spectrometer. ^{13}C NMR spectra at 125 MHz with JEOL ECA-500 spectrometer or 100 MHz with JEOL ECS-400 spectrometer. Chemical shifts are reported in ppm with reference to solvent signals [^{1}H NMR: $CDCl_3$ (7.26); ^{13}C NMR: $CDCl_3$ (77.16),]. Signal patterns are indicated as brs, broad peak; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Infrared spectra were recorded using a BRUKER ALPHA FT-IR spectrometer. Mass spectra (ESI-TOF) were measured with a Waters, LCT Premier XE. Melting points were measured with a Mitamura-Riken microhot stage.

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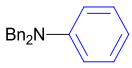
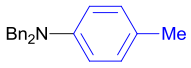


9a

[General procedure A]

***N,N*-dibenzylaniline (9a)**

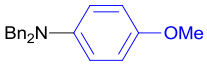
In a glove box, triphenylboroxin (90.4 mg, 290 μmol, 1.1 equiv) and $[Cu(OTf)_2]\cdot C_6H_6$ (13.3 mg, 26.4 μmol, 10 mol %) were added to a solution of *N,N*-dibenzyl-*O*-methylhydroxyamine **12**[2] (52 μL, 260 μmol) and DME (660 μL, 0.4 M). The flask was then removed from the glove box, and heated to 85 °C. After stirring at 85 °C for 24 h, the solution was cooled to room temperature, quenched with saturated aqueous $NaHCO_3$ (3 mL), and extracted with EtOAc (3x 15 mL). The combined organic extracts were washed with brine (3 x 1 mL), dried over Na_2SO_4, and concentrated. The residue was purified by silica gel chromatography (EtOAc/hexane 1:1) to give 50.4 mg of *N,N*-dibenzylaniline **9a** (70%), along with 7.3 mg of *N,N*-dibenzylaniline **13** (14%): a colorless oil; IR (film) 3060, 3027, 2912, 2862, 1598, 1505, 1451, 1358, 1229, 747, 729, 694 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.36 (t, *J* = 7.2 Hz, 4H), 7.26–7.24 (m, 6H), 7.17 (dd, *J* = 8.0, 7.2 Hz, 2H), 6.74 (d, *J* = 8.0 Hz, 2H), 6.70 (t, *J* = 7.2 Hz, 1H), 4.66 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.3 (C), 138.7 (C), 129.3 (CH), 128.8 (CH), 127.0 (CH), 126.8 (CH), 116.8 (CH), 112.6 (CH), 54.3 (CH_2); HRMS (ESI), calcd for $C_{20}H_{20}N^+$ $(M+H)^+$, 274.1596, found 274.1593.



9b

***N,N*-dibenzyl-4-methylaniline (9b)**

Following the general procedure A with tri-4-tolylboroxin (103 mg, 290 μmol), *N,N*-dibenzyl-*O*-methylhydroxyamine **12** (52 μL, 260 μmol) was converted to 56.6 mg of *N,N*-dibenzylaniline **9b** (75%): a yellow oil; IR (film) 3028, 2920, 2861, 1619, 1527, 1452, 1360, 1235, 802, 735, 697 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.31 (t, *J* = 6.6 Hz, 4H), 7.26–7.24 (m, 6H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.65 (d, *J* = 8.0 Hz, 2H), 4.62 (s, 4H), 2.24 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.2 (C), 139.0 (C), 129.9 (CH), 128.7 (CH), 126.94 (CH), 126.85 (CH), 126.0 (C), 112.8 (CH), 54.5 (CH_2), 20.3 (CH_3); HRMS (ESI), calcd for $C_{21}H_{22}N^+$ $(M+H)^+$ 288.1752, found 288.1752.



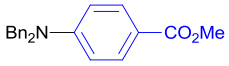
9c

***N,N*-dibenzyl-4-methoxyaniline (9c)**

Following the general procedure A with tris(4-methoxyphenyl)boroxin (117 mg, 290 μmol), *N,N*-dibenzyl-*O*-methylhydroxy amine **12** (52 μL, 260 μmol) was converted to 41.0 mg of *N,N*-dibenzylaniline **9c** (51%): a

[2] P.-P. Kung, R. Bharadwaj, A. S. Fraser, D. R. Cook, A. M. Kawasaki, P. D. Cook, *J. Org. Chem*. **1998**, *63*, 1846–1852.

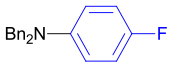
colorless oil; IR (film) 3027, 2930, 2905, 2831, 1513, 1452, 1241, 1029, 813, 736, 696 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.5 Hz, 4H), 7.26–7.22 (m, 6H), 6.76 (d, *J* = 9.2 Hz, 2H), 6.70 (d, *J* = 9.2 Hz, 2H), 4.56 (s, 4H), 3.73 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.8 (C), 144.0 (C), 139.1 (C), 128.7 (CH), 127.1 (CH), 127.0 (CH), 114.9 (CH), 114.7 (CH), 55.9 (CH_3), 55.3 (CH_2); HRMS (ESI), calcd for $C_{21}H_{22}NO^+$ $(M+H)^+$ 304.1701, found 304.1697.



9d

methyl 4-(dibenzylamino)benzoate (9d)

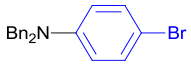
Following the general procedure A with tris(4-(methoxycarbonyl)phenyl)boroxin (197 mg, 396 μmol, 1.5 equiv), *N*,*N*-dibenzyl-*O*-methylhydroxyamine **12** (52 μL, 260 μmol) was converted to 67.2 mg of *N*,*N*-dibenzylaniline **9d** (77%): a colorless oil; IR (film) 3029, 2947, 1706, 1605, 1523, 1285, 1186, 1110, 769, 731, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.7 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 4H), 7.27 (t, *J* = 7.6 Hz, 2H), 7.21 (d, *J* = 7.6 Hz, 4H), 6.71 (d, *J* = 8.7 Hz, 2H), 4.71 (s, 4H), 3.83 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.4 (C), 152.7 (C), 137.5 (C), 131.6 (CH), 129.0 (CH), 127.4 (CH), 126.6 (CH), 118.1 (C), 111.4 (CH), 54.1 (CH_2), 51.6 (CH_3); HRMS (ESI), calcd for $C_{22}H_{22}NO_2^+$ $(M+H)^+$ 332.1651, found 332.1654.



9e

***N*,*N*-dibenzyl-4-fluoroaniline (9e)**

Following the general procedure A with tris(4-fluorophenyl)boroxin (106 mg, 290 μmol), *N*,*N*-dibenzyl-*O*-methylhydroxyamine **12** (52 μL, 260 μmol) was converted to 48.0 mg of *N*,*N*-dibenzylaniline **9e** (64%): a colorless oil; IR (film) 3061, 3029, 2912, 2859, 1516, 1452, 1361, 1228, 813, 737, 696 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.5 Hz, 4H), 7.29–7.25 (m, 6H), 6.88 (t, *J* = 9.0 Hz, 2H), 6.68–6.64 (m, 2H), 4.62 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.6 (C, *J* = 234.3 Hz), 145.8 (C), 138.6 (C), 128.8 (CH), 127.1 (CH), 126.8 (CH), 115.7 (CH, *J* = 22.1 Hz), 113.9 (CH, *J* = 7.8 Hz), 55.2 (CH_2); HRMS (ESI), calcd for $C_{20}H_{19}NF^+$ $(M+H)^+$ 292.1502, found 292.1494.

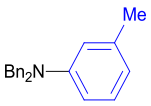


9f

***N*,*N*-dibenzyl-4-bromoaniline (9f)**

Following the general procedure A with tris(4-bromophenyl)boroxin (147 mg, 290 μmol), *N*,*N*-dibenzyl-*O*-methylhydroxyamine **12** (52 μL, 260 μmol) was converted to 45.5 mg of *N*,*N*-dibenzylaniline **9f** (51%): white crystals, mp 121.1–121.5 °C; IR (film) 3061, 3028, 3002, 2918, 2865, 1592, 1496, 1452, 1359, 1233, 807, 730, 696 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.5, Hz, 4H), 7.27–7.21 (m, 8H), 6.59 (d, *J* = 8.9, Hz, 2H),

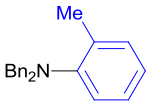
4.63 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ148.2 (C), 138.1 (C), 132.0 (CH), 128.9 (CH), 127.2 (CH), 126.7 (CH), 114.3 (CH), 108.8 (C), 54.6 (CH_2); HRMS (ESI), calcd for $C_{20}H_{19}NBr^+$ $(M+H)^+$ 352.0701, found 352.0964.



9g

***N*,*N*-dibenzyl-3-methylaniline (9g)**

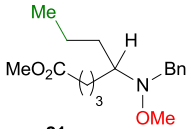
Following the general procedure A with tri-3-tolylboroxin (140 mg, 396 μmol, 1.5 equiv), *N*,*N*-dibenzyl-*O*-methylhydroxyamine **12** (52 μL, 260 μmol) was converted to 46.0 mg of *N*,*N*-dibenzylaniline **9g** (61%): a colorless oil; IR (film) 3061, 3028, 2916, 2860, 1602, 1580, 1495, 1451, 1360, 1181, 960, 766, 733, 695 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (t, *J* = 8.0 Hz, 4H), 7.26–7.25 (m, 6H), 7.07 (t, *J* = 8.0 Hz, 1H), 6.60 (s, 1H), 6.56 (t, *J* = 8.0 Hz, 2H), 4.64 (s, 4H), 2.25 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.5 (C), 139.1 (C), 138.9 (C), 129.2 (CH), 128.7 (CH), 127.0 (CH), 126.9 (CH), 117.9 (CH), 113.2 (CH), 109.8 (CH), 54.1 (CH_2), 22.1 (CH_3), ; HRMS (ESI), calcd for $C_{21}H_{21}N^+$ $(M+H)^+$ 288.1152, found 288.1744.



9h

***N*,*N*-dibenzyl-2-methylaniline (9h)**

Following the general procedure A with tri-2-tolylboroxin (140 mg, 396 μmol, 1.5 equiv), *N*,*N*-dibenzyl-*O*-methylhydroxyamine **12** (52 μL, 260 μmol) was converted to 34.4 mg of *N*,*N*-dibenzylaniline **9h** (45%): a colorless oil; IR (film) 3084, 3062, 3027, 2925, 2841, 2814, 1598, 1493, 1453, 1361, 1186, 1105, 1029, 766, 745, 722, 697 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29–7.25 (m, 8H), 7.24–7.17 (m, 3H), 7.05 (td, *J* = 7.1, 1.5 Hz, 1H), 6.96 (td, *J* = 7.1, 1.2 Hz, 2H), 4.07 (s, 4H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.0 (C), 138.7 (C) , 134.0 (C), 131.2 (CH), 128.8 (CH), 128.3 (CH), 127.0 (CH), 126.2 (CH), 123.6 (CH), 122.6 (CH), 57.0 (CH_2), 18.7 (CH_3); HRMS (ESI), calcd for $C_{21}H_{22}N^+$ $(M+H)^+$ 288.1752. found 288.1750.



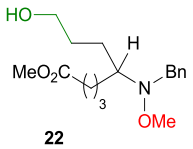
21

Methyl 5-(benzyl(methoxy)amino)octanoate (21)

A flask containing *N*-methoxyamine **20**[3] (173 mg, 595 μmol), palladium on carbon (10 wt%, 17.3 mg) and

[3] Shirokane, T. Wada, M. Yoritate, R. Minamikawa, N. Takayama, T. Sato, N. Chida, *Angew. Chem. Int. Ed.* **2014**, *53*, 512–516.

EtOH (5.9 mL) was fitted with a balloon of hydrogen gas. The reaction vessel was evacuated and backfilled with hydrogen. The mixture was stirred under hydrogen atmosphere at room temperature for 22 h, filtered through Celite, washed with EtOAc and concentrated. The residue was purified by silica gel column chromatography (EtOAc/hexane 1:10 to 1:3) to give 154 mg of octanoate **21** (88%): a colorless oil; IR (film) 2955, 2935, 2872, 1741, 1455, 1436, 1169, 1045, 732, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.32–7.29 (m, 2H), 7.26–7.23 (m, 1H), 3.82 (d, *J* = 13.2 Hz, 1H),), 3.79 (d, *J* = 13.2 Hz, 1H), 3.68 (s, 3H), 3.25 (s, 3H), 2.66 (tt, *J* = 6.3, 6.3 Hz, 1H), 2.31 (t, *J* = 7.5 Hz, 2H), 1.84–1.60 (m, 4H), 1.45–1.33 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.3 (C), 139.0 (C), 129.5 (CH), 128.2 (CH), 127.0 (CH), 63.5 (CH), 61.4 (CH_3), 57.2 (CH_2), 51.6 (CH_3), 34.3 (CH_2), 32.1 (CH_2), 29.7 (CH_2), 22.6 (CH_2), 20.3 (CH_2), 14.4 (CH_3); HRMS (ESI), calcd for $C_{17}H_{28}NO_3^+$ $(M+H)^+$ 294.2069, found 294.2059.

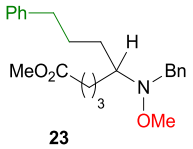


22

Methyl 5-(benzyl(methoxy)amino)-8-hydroxyoctanoate (22)

2,3-Dimethyl-2-butene (160 μL, 1.3 mmol) was added to borane THF complex (0.85 M in THF, 1.5 mL, 1.3 mmol) at –10 °C. After maintaining for 10 min, the solution was warmed to 0 °C, and maintained at 0 °C for 1 h to give a THF solution of thexylborane.

The resulting solution of thexylborane was added to a solution of *N*-methoxyamine **20** (317 mg, 1.09 mmol) and THF (5.5 mL) at 0 °C. After stirring for 40 min, the solution was quenched with H_2O (5.5 mL) and sodium perborate tetrahydrate (2.02 g, 13.1 mmol) at 0 °C. The resulting mixture was allowed to warm to room temperature, stirred for 1 h, and extracted with EtOAc (2x 20 mL). The combined organic extracts were washed with brine (2x 6 mL), dried over Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography (EtOAc/hexane 1:2) to give 296 mg of hydroxyoctanoate **22** (88%): a colorless oil; IR (film) 3412, 2944, 1737, 1454, 1437, 1364, 1197, 1173, 1043, 733, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40–7.24 (m, 5H), 3.86 (d, *J* = 13.0 Hz, 1H), 3.79 (d, *J* = 13.0 Hz, 1H), 3.68 (s, 3H), 3.65–3.64 (m, 2H), 3.25 (s, 3H), 2.72–2.68 (m, 1H), 2.55–2.48 (m, 1H), 2.34 (t, *J* = 7.2 Hz, 2H), 1.80–1.56 (m, 8H), 1.45–1.39 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.2 (C), 138.1 (C), 129.7 (CH), 128.3 (CH), 127.3 (CH), 64.1 (CH), 63.0 (CH_2), 61.3 (CH_3), 57.3 (CH_2), 51.6 (CH_3), 34.2 (CH_2), 30.6 (CH_2), 29.1 (CH_2), 27.3 (CH_2), 22.6 (CH_2); HRMS (ESI), calcd for $C_{17}H_{28}NO_4^+$ $(M+H)^+$ 310.2018, found 310.2010.

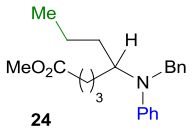


23

Methyl 5-(benzyl(methoxy)amino)-8-phenyloctanoate (23)

9-Borabicyclo[3.3.1]nonane (0.5 M solution in THF, 10 mL, 5.0 mmol) was added to a solution of *N*-

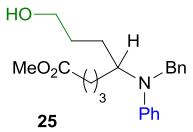
methoxyamine **20** (751 mg, 2.58 mmol) and THF (26 mL) at 0 °C. The solution was allowed to warm to room temperature, maintained for 4 h at room temperature, and quenched with H_2O (460 μL, 26 mmol). Phenyl iodide (570 μL, 5.2 mmol) was added to the solution, which was then degassed using the freeze-pump-thaw technique (3x). Meanwhile, DMF (52 mL) was degassed using the freeze-pump-thaw technique (3x), and added via cannula to a mixture of Cs_2CO_3 (1.51 g, 4.64 mmol), $AsPPh_3$ (79.0 mg, 258 mmol, 10 mol %) and $PdCl_2(dppf)\cdot CH_2Cl_2$ (105 mg, 129 μmol, 5 mol %) at room temperature. The solution of the organoborane was added via cannula to the mixture of the catalyst, and stirred for 9 h at room temperature. The mixture was quenched with H_2O (30 mL) at room temperature, and extracted with EtOAc (3x 100 mL). The combined organic extracts were washed with brine (3x 10 mL), dried over Na_2SO_4 and concentrated. The residue was purified by silica gel column chromatography (EtOAc/hexane 1:40 to 1:30) to give 772 mg of phenyloctanoate **23** (81%): a colorless oil; IR (film) 2940, 1738, 1453, 1436, 1171, 1044, 732, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.36–7.23 (m, 7H), 7.19–7.17 (m, 3H), 3.78 (s, 2H), 3.67 (s, 3H), 3.24 (s, 3H), 2.67 (tt, *J* = 6.0, 6.0 Hz, 1H), 2.62–2.58 (m, 2H), 2.30 (t, *J* = 7.5 Hz, 2H), 1.78–1.63 (m, 6H), 1.47–1.36 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.2 (C), 142.7 (C), 138.8 (C), 129.5 (CH), 128.6 (CH), 128.4 (CH), 128.2 (CH), 127.1 (CH), 125.8 (CH), 63.5 (CH), 61.4 (CH_3), 57.2 (CH_2), 51.6 (CH_3), 36.2 (CH_2), 34.3 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.0 (CH_2), 22.6 (CH_2); HRMS (ESI), calcd for $C_{23}H_{32}NO_3^+$ $(M+H)^+$ 370.2382, found 370.2379.



24

Methyl 5-(benzyl(phenyl)amino)octanoate (24)

Following the general procedure A, octanoate **21** (77.2 mg, 264 μmol) was converted to 71.5 mg of aniline **24** (80%): a colorless oil; IR (film) 2955, 2870, 1737, 1598, 1502, 1168, 748, 694 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.28–7.25 (m, 4H), 7.20–7.17 (m, 1H), 7.14–7.11 (dd, *J* = 8.0, 7.2 Hz, 2H), 6.74 (d, *J* = 7.5 Hz, 2H), 6.65 (tt, *J* = 7.5, 0.9 Hz, 1H), 4.39 (s, 2H), 3.92 (td, *J* = 7.7, 5.7 Hz, 1H), 3.63 (s, 3H), 2.25 (t, *J* = 7.2 Hz, 2H), 1.75–1.45 (m, 6H), 1.45–1.32 (m, 2H), 0.87 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.0 (C), 150.0 (C), 140.0 (C), 129.1 (CH), 128.5 (CH), 126.8 (CH), 126.5 (CH), 116.9 (CH), 114.5 (CH), 59.2 (CH) , 51.6 (CH_3), 48.0 (CH_2), 35.8 (CH_2), 34.1 (CH_2), 33.0 (CH_2), 22.8 (CH_2), 20.6 (CH_2), 14.3 (CH_3); HRMS (ESI), calcd for $C_{22}H_{30}NO_2^+$ $(M+H)^+$ 340.2277, found 340.2278.

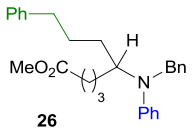


25

Methyl 5-(benzyl(phenyl)amino)-8-hydroxyoctanoate (25)

Following the general procedure A using DME (260 μL, 1.0 M), hydroxyoctanoate **22** (81.7 mg, 264 μmol) was converted to 66.6 mg of aniline **25** (71%): a colorless oil; IR (film) 3402, 2947, 2863, 1735, 1597, 1502, 1196, 1173, 749, 695 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.28–7.24 (m, 4H), 7.20–7.17 (m, 1H), 7.14 (dd, *J* = 8.0, 7.2 Hz, 2H), 6.76 (d, *J* = 8.3 Hz, 2H), 6.67 (tt, *J* = 7.2, 0.9 Hz, 1H), 4.41 (s, 2H), 3.97–3.92 (m, 1H), 3.63 (s,

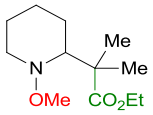
3H), 3.57 (t, *J* = 5.4 Hz, 2H), 2.25 (t, *J* = 7.1 Hz, 2H), 1.75–1.54 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.0 (C), 150.0 (C), 139.8 (C), 129.1 (CH), 128.5 (CH), 126.8 (CH), 126.6 (CH), 117.1 (CH), 114.6 (CH), 62.9 (CH_2), 59.4 (CH), 51.6 (CH_3), 48.0 (CH_2), 34.1 (CH_2), 33.0 (CH_2), 30.5 (CH_2), 29.7 (CH_2), 22.8 (CH_2); HRMS (ESI), calcd for $C_{22}H_{30}NO_3^+$ $(M+H)^+$ 356.2226, found 356.2222.



26

Methyl 5-(benzyl(phenyl)amino)-8-phenyloctanoate (26)

Following the general procedure A using $[Cu(OTf)]_2 \cdot C_6H_6$ (39.9 mg, 79.2 μmol, 30 mol %) and DME (260 μL, 1.0 M), phenyloctanoate **23** (97.6 mg, 264 μmol) was converted to 68.3 mg of aniline **26** (62%): a colorless oil; IR (film) 3025, 2946, 2857, 1737, 1598, 1502, 1196, 1173, 748, 696 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28–7.15 (m, 8H), 7.13 (dd, *J* = 8.9, 7.2 Hz, 2H), 7.06 (d, *J* = 7.1 Hz, 2H), 6.73 (d, *J* = 8.2 Hz, 2H), 6.66 (tt, *J* = 7.2, 0.9 Hz, 1H), 4.36 (s, 2H), 3.97–3.90 (m, 1H), 3.63 (s, 3H), 2.58–2.47 (m, 2H), 2.24 (t, *J* = 7.2 Hz, 2H), 1.74–1.50 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.0 (C), 150.1 (C), 142.3 (C), 139.9 (C), 129.1 (CH), 128.51 (CH), 128.49 (CH), 128.41 (CH), 126.8 (CH), 126.5 (CH), 125.9 (CH), 117.0 (CH), 114.6 (CH), 59.4 (CH), 51.6 (CH_3), 47.9 (CH_2), 36.0 (CH_2), 34.1 (CH_2), 33.14 (CH_2), 33.08 (CH_2), 29.2 (CH_2), 22.8 (CH_2); HRMS (ESI), calcd for $C_{28}H_{34}NO_2^+$ $(M+H)^+$ 416.2590, found 416.2591.



28

Ethyl 2-(1-methoxypiperidin-2-yl)-2-methylpropanoate (28)

Red-Al® (3.6 M in toluene, 340 μL, 1.2 mmol) was added to a solution of Cp_2ZrCl_2 (725 mg, 2.48 μmol) and THF (9.3 mL) at room temperature. A white suspension was formed during addition. After stirring for 2 h, the suspension was added to a solution of *N*-methoxylactam **27**[4] (200 mg, 1.55 mmol) and CH_2Cl_2 (19 mL) at room temperature. After stirring for 10 min, ((1-Ethoxy-2-methylprop-1-en-1-yl)oxy)trimethylsilane[5] (650 μL, 3.1 mmol) and $BF_3 \cdot Et_2O$ (310 μL, 2.5 mmol) were subsequently added to the resulting yellow solution at room temperature. This solution was maintained for 1 h, and quenched with saturated aqueous $NaHCO_3$ (12 mL). The resulting mixture was extracted with EtOAc (2x 40 mL). The combined organic extracts were washed with brine (2x 6 mL), dried over Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography (EtOAc/hexane 1:20) to give 286 mg of *N*-methoxypiperidin **28** (81%): a colorless oil; IR (film) 2940, 2859, 1731, 1142, 1044 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.11–4.02 (m, 2H), 3.41–3.38 (m, 1H), 3.36 (s, 3H), 2.90 (d, *J* = 8.9 Hz, 1H), 2.34 (t, *J* = 11.0 Hz, 1H), 1.80–1.45 (m, 4H), 1.29–1.19 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.18 (s, 3H), 1.07 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.4 (C), 71.9 (CH), 60.0 (CH_2), 58.6 (CH_3), 55.9

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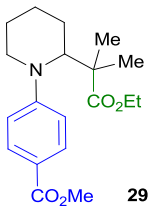
[4] K. Griesbaum, X. Liu, Y. Dong, *Tetrahedron* **1997**, *53*, 5463–5470.
[5] E. Juaristi, J. S. Cruz-SBnchez. *J. Org. Chem.* **1988**, *53*, 3334–3338.

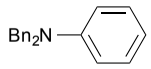
(CH_2), 44.0 (C), 25.7 (CH_2), 25.2 (CH_3), 24.3 (CH_2), 17.9 (CH_3), 14.3 (CH_3); HRMS (ESI), calcd for $C_{12}H_{24}NO_3^+$ $(M+H)^+$ 230.1756, found 230.1750.



29

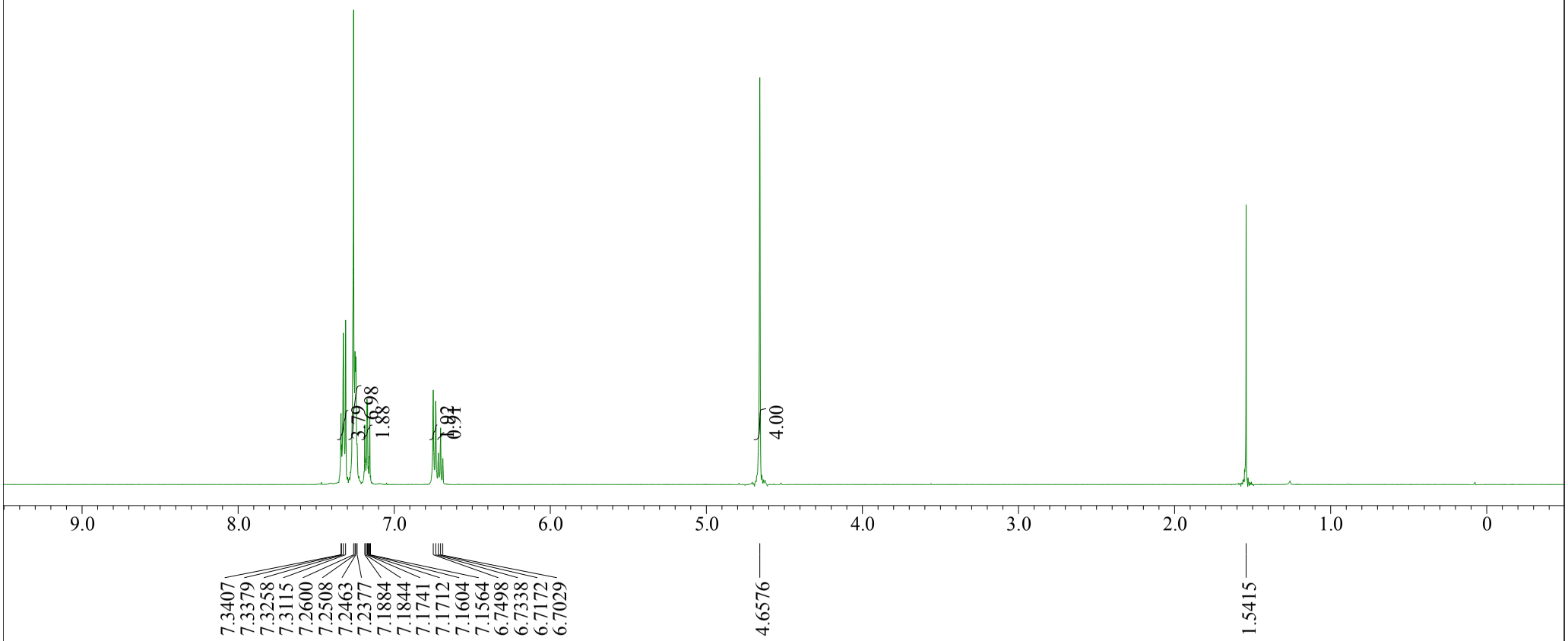
Methyl 4-(2-(1-ethoxy-2-methyl-1-oxopropan-2-yl)piperidin-1-yl)benzoate (29)

Following the general procedure A using tris(4-(methoxycarbonyl)phenyl)boroxin (197 mg, 396 μmol, 1.5 equiv) and $[Cu(OTf)]_2 \cdot C_6H_6$ (19.9 mg, 39.6 μmol, 15 mol %), *N*-methoxypiperidin **28** (59 μL, 264 μmol) was converted to 61.3 mg of aniline **29** (70%): a colorless oil; IR (film) 2948, 1711, 1603, 1517, 1284, 1259, 1188, 1113, 770 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 9.2 Hz, 2H), 6.87 (d, *J* = 9.2 Hz, 2H), 4.16 (t, *J* = 6.6 Hz, 1H), 4.11–4.00 (m, 2H), 3.85 (s, 3H), 3.73 (dd, *J* = 14.7, 6.0 Hz, 1H), 3.27 (ddd, *J* = 14.7, 12.2, 4.8 Hz, 1H), 1.82–1.48 (m, 56H), 1.31 (s, 3H), 1.27 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ177.0 (C), 167.3 (C), 155.0 (C), 131.3 (CH), 117.8 (C), 112.7 (CH), 61.9 (CH), 60.9 (CH_2), 51.6 (CH_3), 48.7 (C), 41.8 (CH_2), 24.5 (CH_3), 23.1 (CH_2), 22.8 (CH_3), 21.5 (CH_2), 19.0 (CH_2), 14.2 (CH_3); HRMS (ESI), calcd for $C_{19}H_{28}NO_4^+$ $(M+H)^+$ 334.2018, found 334.2018.

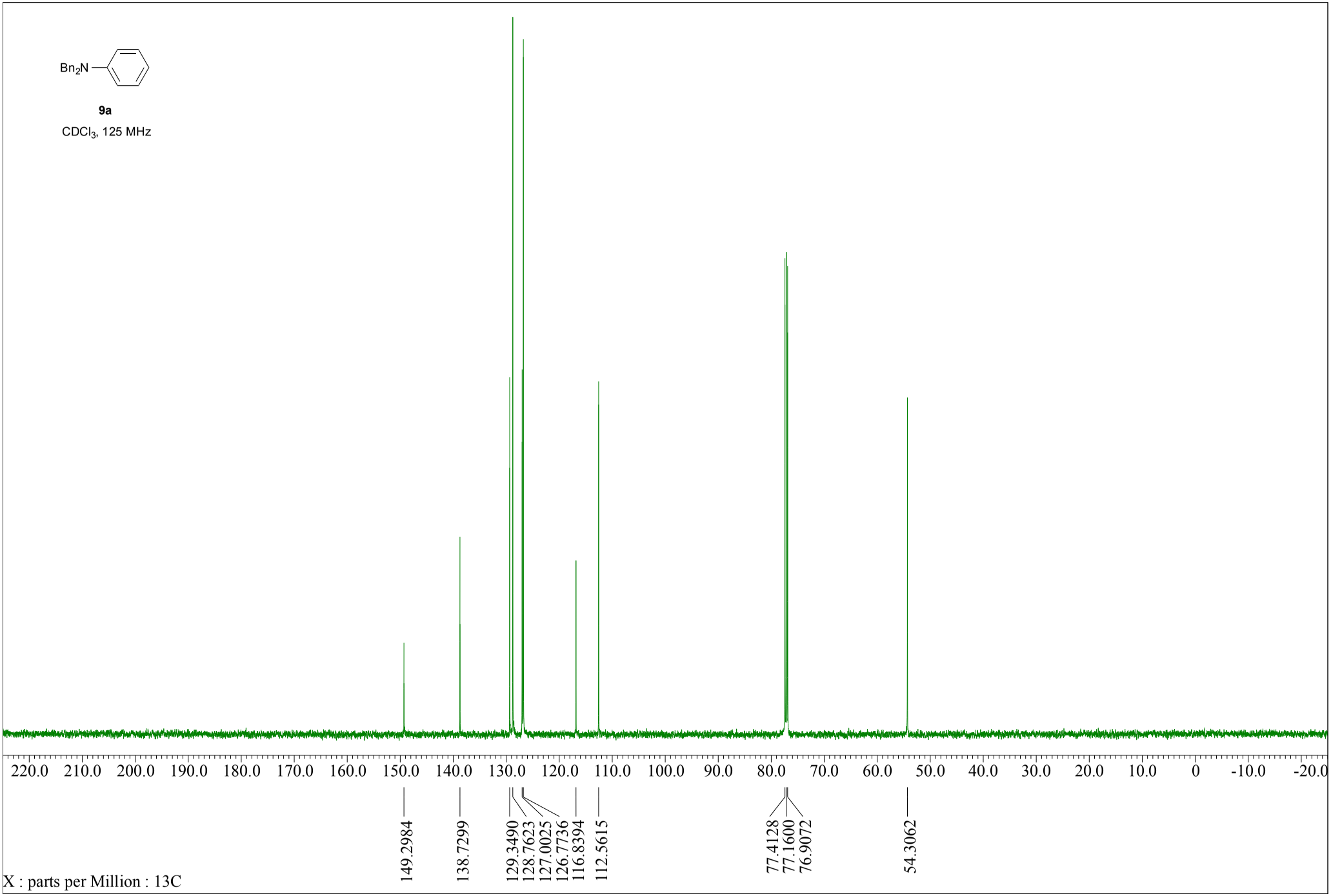


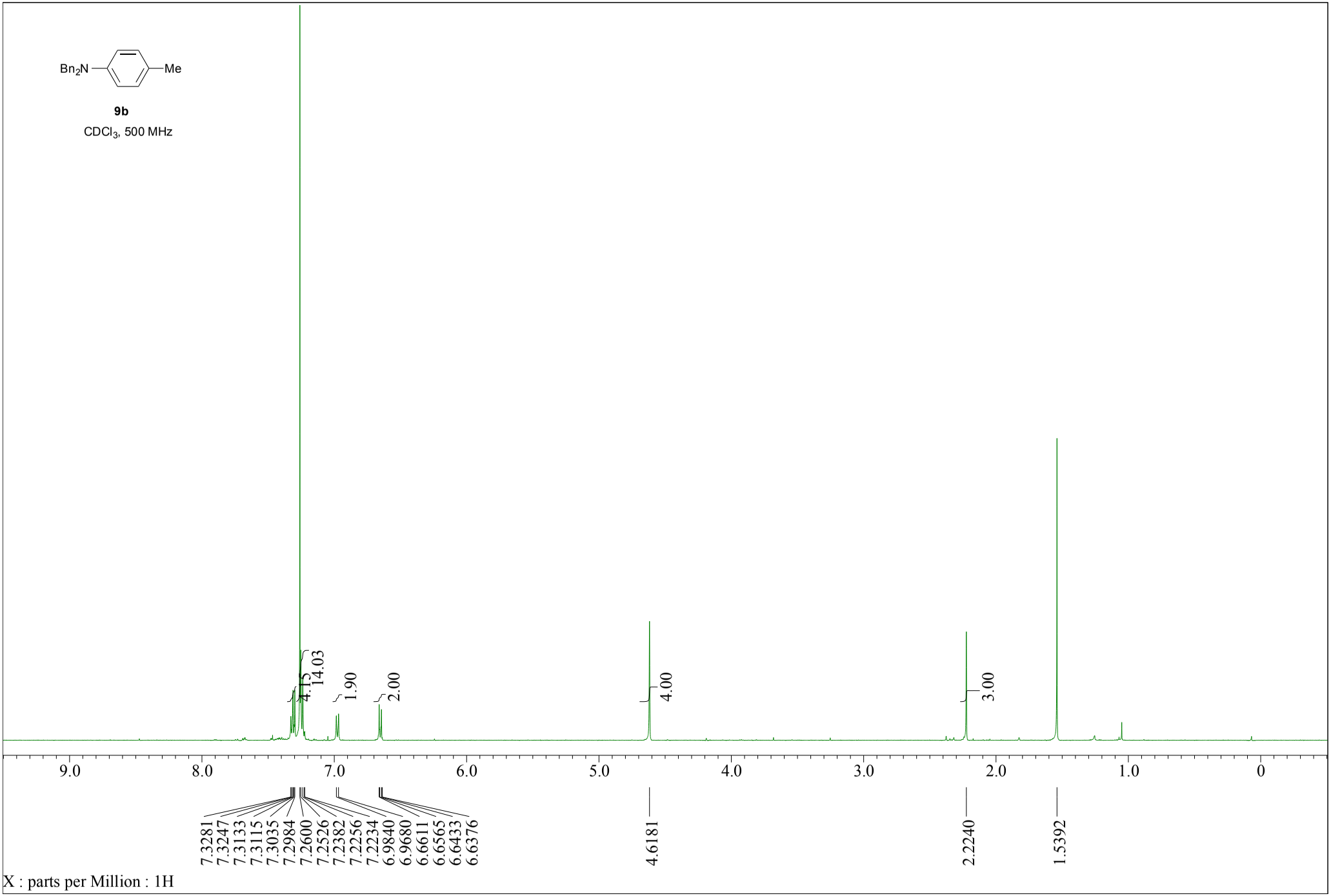
9a

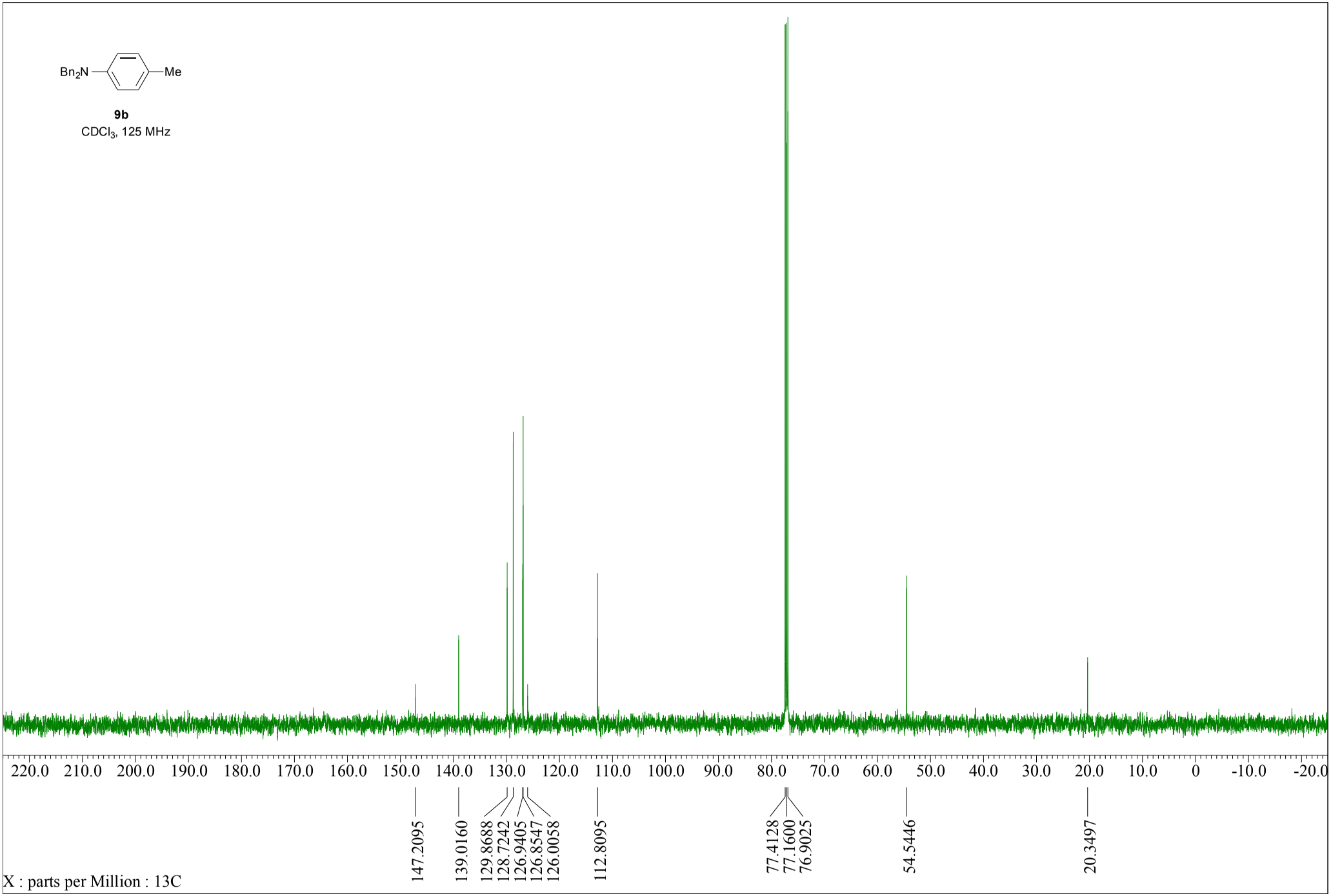
$CDCl_3$, 500 MHz

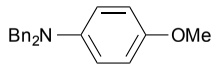


X : parts per Million : 1H


Bn2N
9a
CDCl3, 125 MHz
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
149.2984
138.7299
129.3490
128.7623
127.0025
126.7736
116.8394
112.5615
77.4128
77.1600
76.9072
54.3062
X : parts per Million : 13C

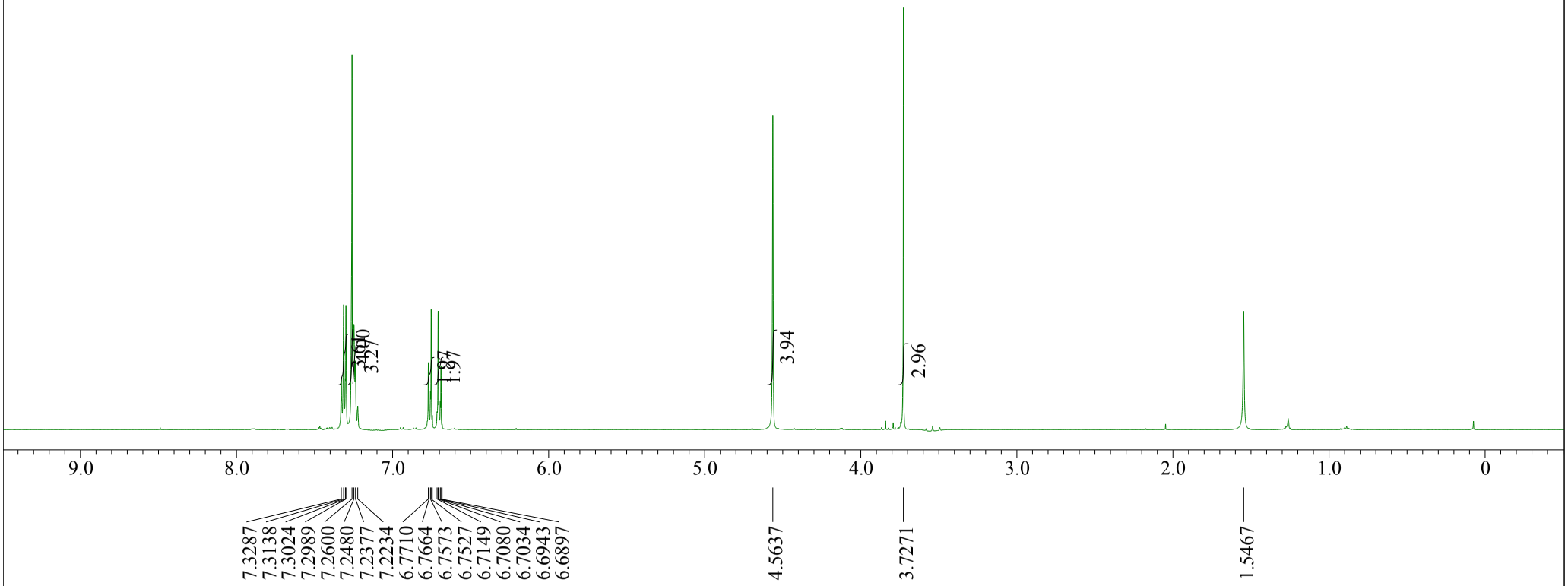

Bn2N
Me
9b
CDCl3, 500 MHz
14.03
4.15
1.90
2.00
4.00
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.3281
7.3247
7.3133
7.3115
7.3035
7.2984
7.2600
7.2526
7.2382
7.2256
7.2234
6.9840
6.9680
6.6611
6.6565
6.6433
6.6376
4.6181
2.2240
1.5392
X : parts per Million : 1H


Bn2N
Me
9b
CDCl3, 125 MHz
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
147.2095
139.0160
129.8688
128.7242
126.9405
126.8547
126.0058
112.8095
77.4128
77.1600
76.9025
54.5446
20.3497
X : parts per Million : 13C

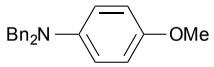


9c

$CDCl_3$, 500 MHz



X : parts per Million : 1H



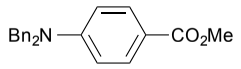
9c

$CDCl_3$, 125 MHz

220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0

143.9712
139.1448
128.6860
127.0598
126.9548
114.8793
114.6790
77.4128
77.1600
76.9072
55.8657
55.2934

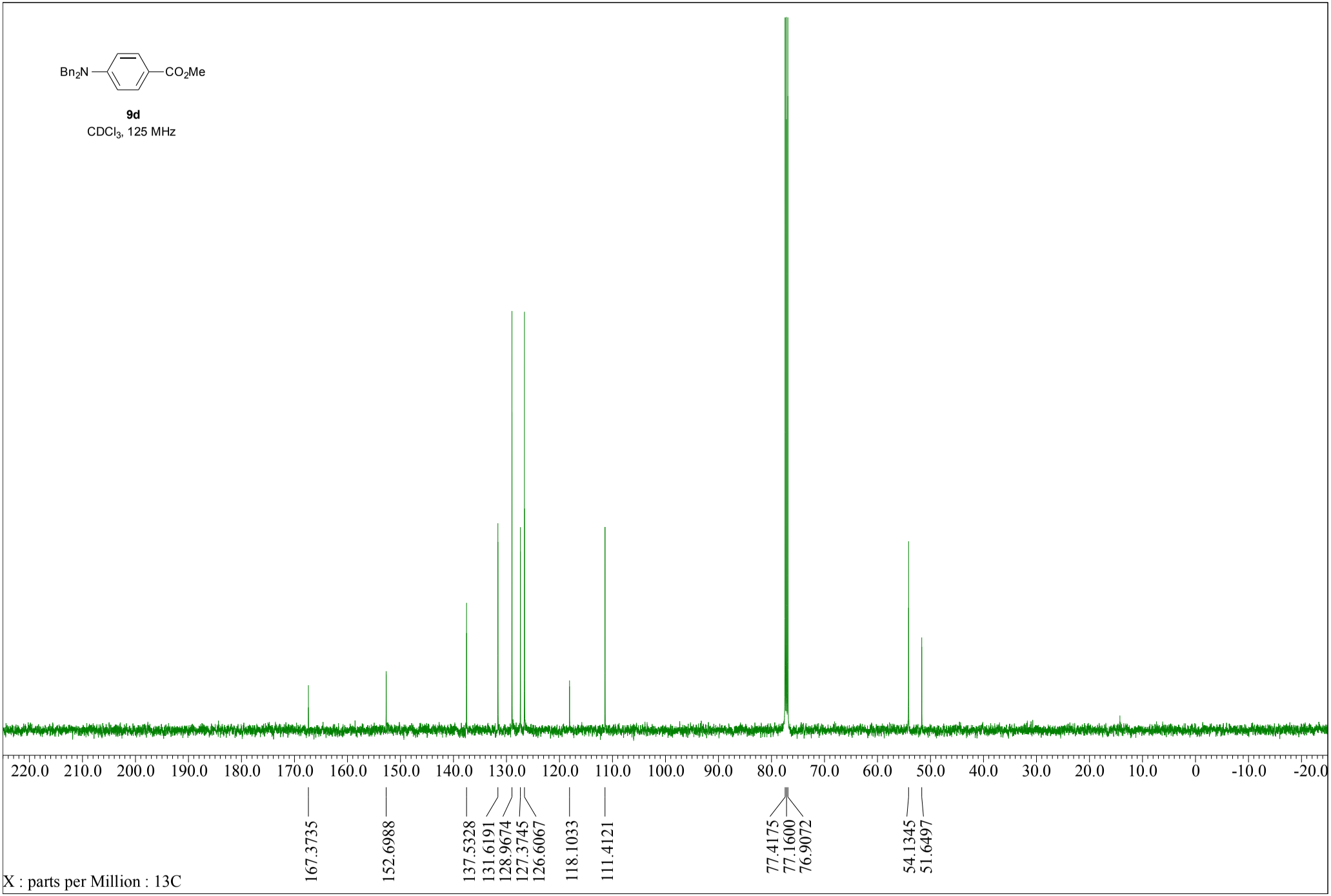
X : parts per Million : 13C

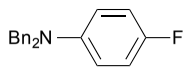


9d

$CDCl_3$, 400 MHz

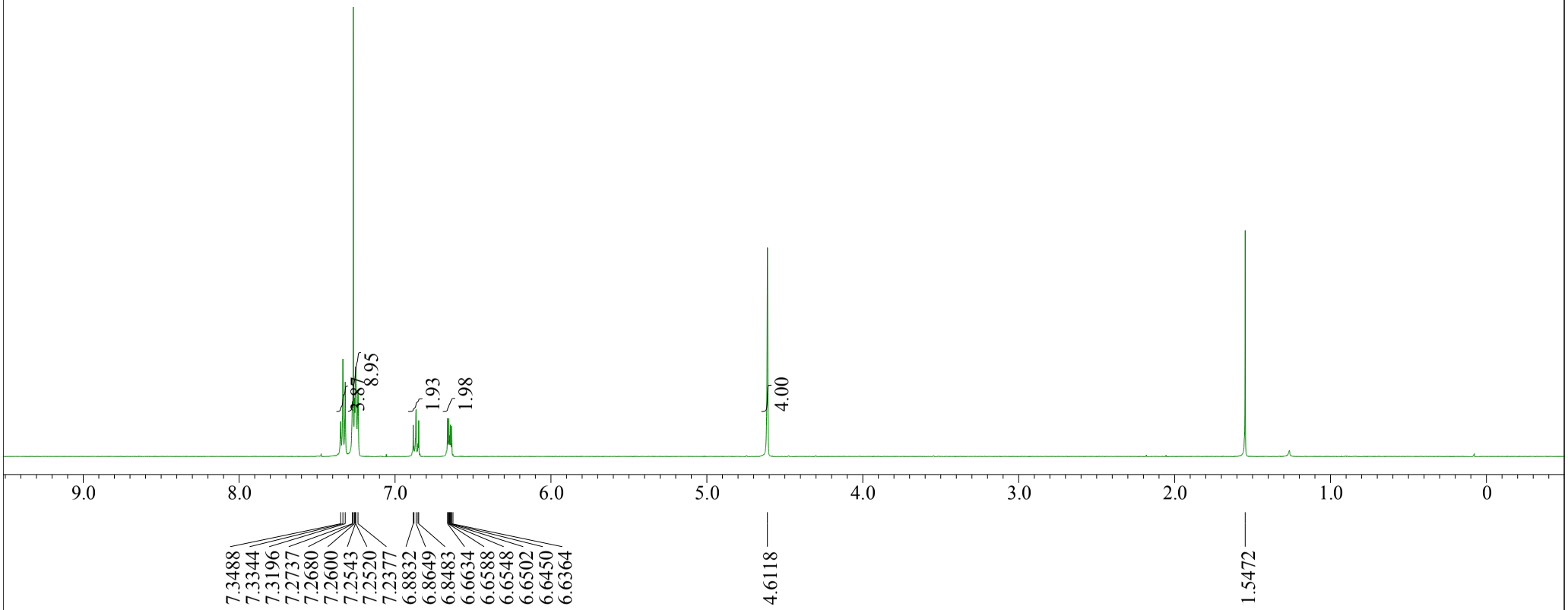
X : parts per Million : 1H


Bn2N
CO2Me
9d
CDCl3, 125 MHz
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
167.3735
152.6988
137.5328
131.6191
128.9674
127.3745
126.6067
118.1033
111.4121
77.4175
77.1600
76.9072
54.1345
51.6497
X : parts per Million : 13C

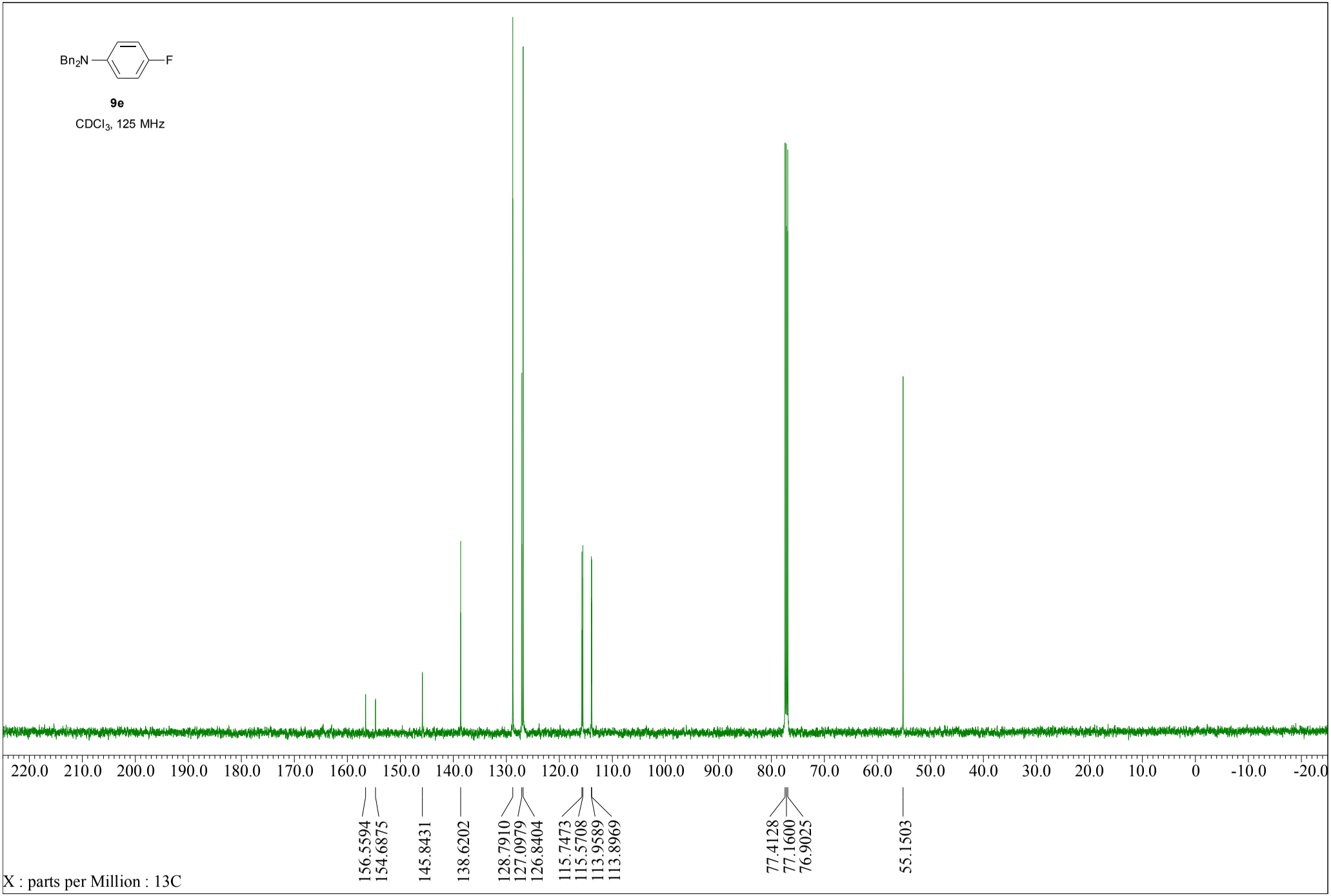


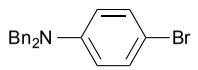
9e

$CDCl_3$, 500 MHz



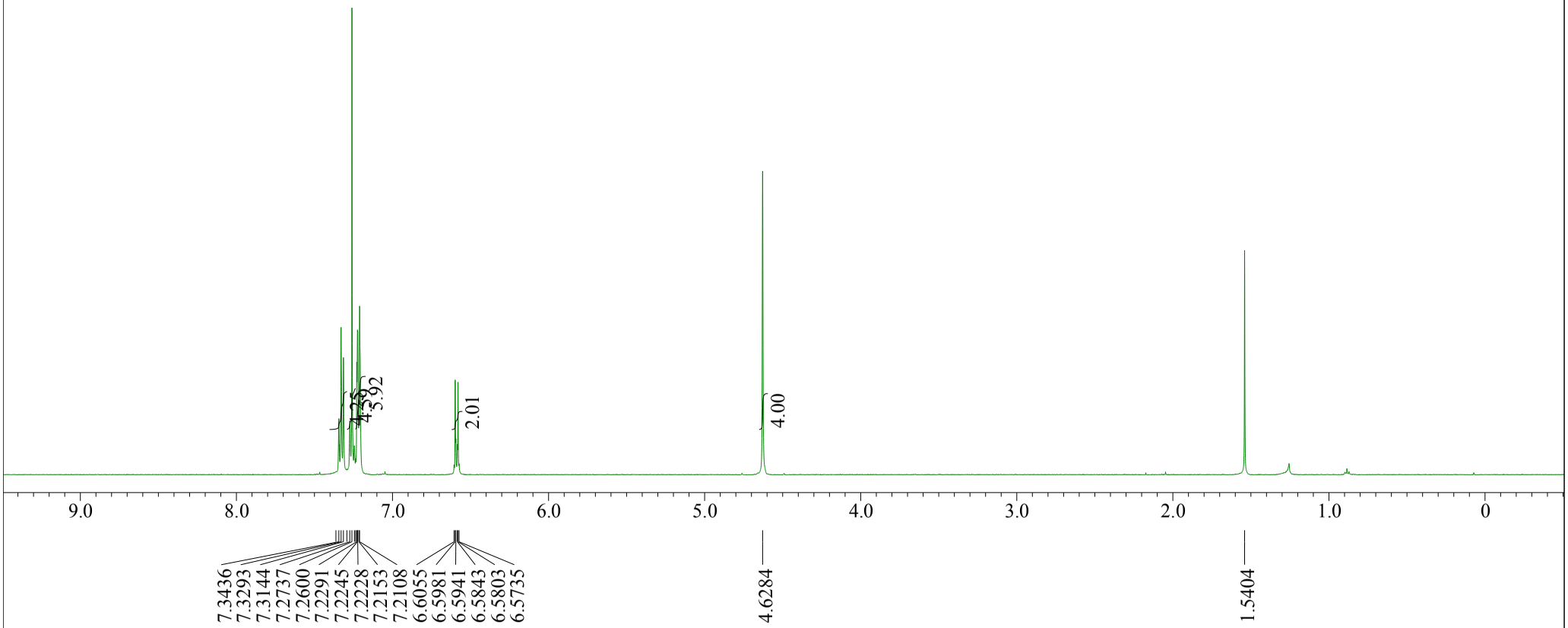
X : parts per Million : 1H


Bn2N
F
9e
CDCl3, 125 MHz
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
156.5594
154.6875
145.8431
138.6202
128.7910
127.0979
126.8404
115.7473
115.5708
113.9589
113.8969
77.4128
77.1600
76.9025
55.1503
X : parts per Million : 13C

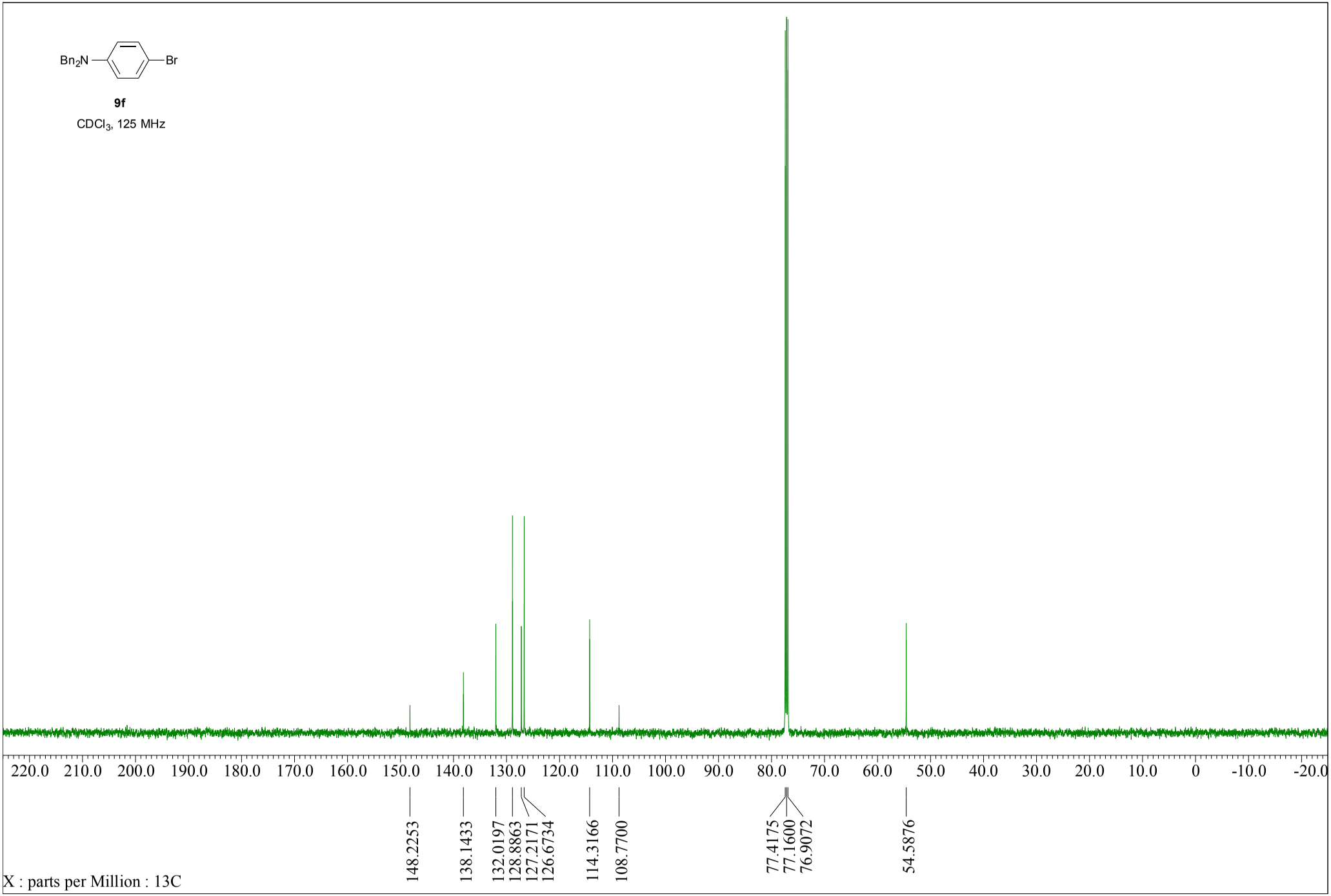


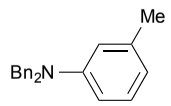
9f

$CDCl_3$, 500 MHz



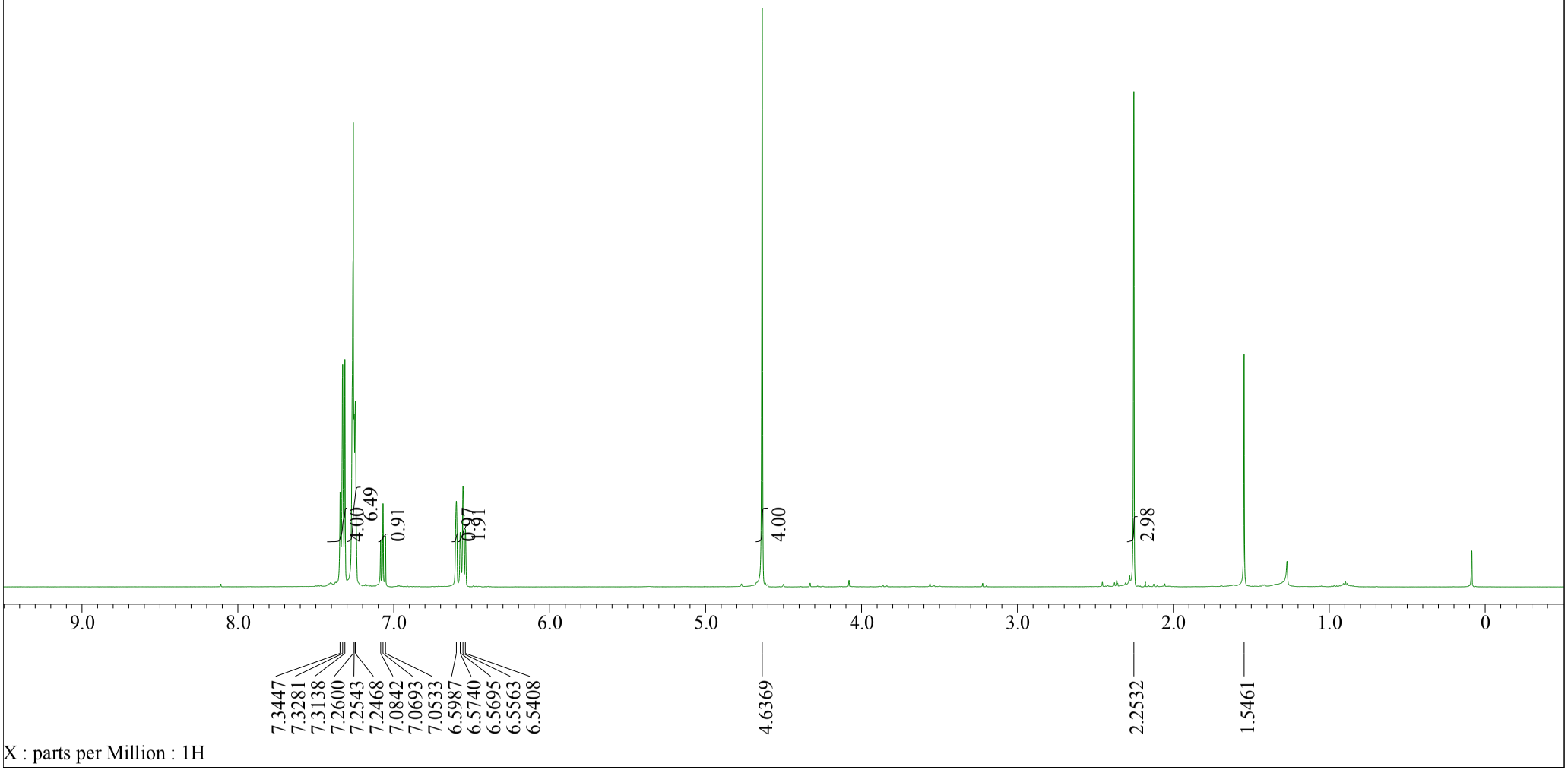
X : parts per Million : 1H


Bn2N
Br
9f
CDCl3, 125 MHz
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
148.2253
138.1433
132.0197
128.8863
127.2171
126.6734
114.3166
108.7700
77.4175
77.1600
76.9072
54.5876
X : parts per Million : 13C

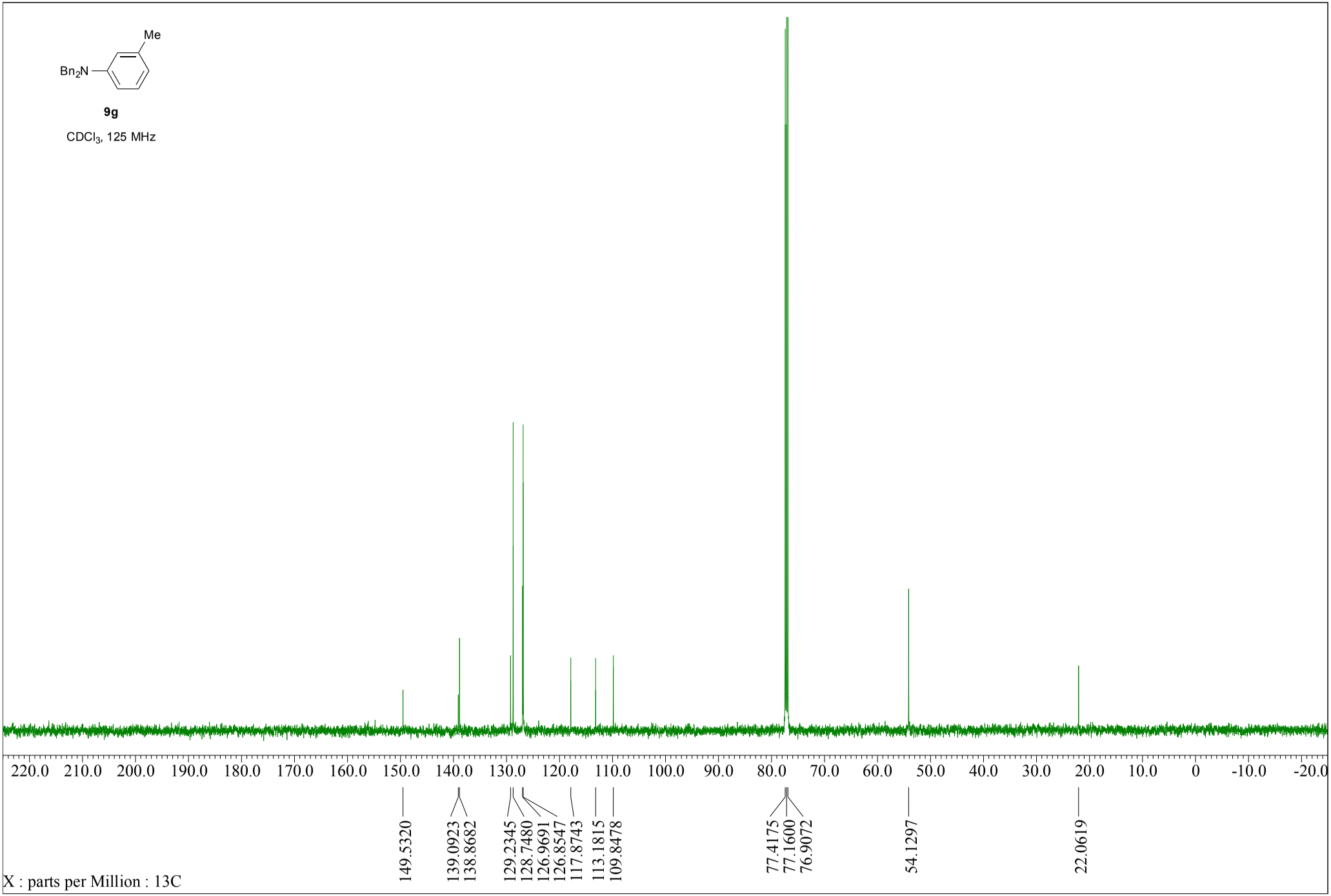


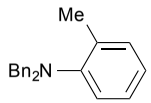
9g

$CDCl_3$, 500 MHz



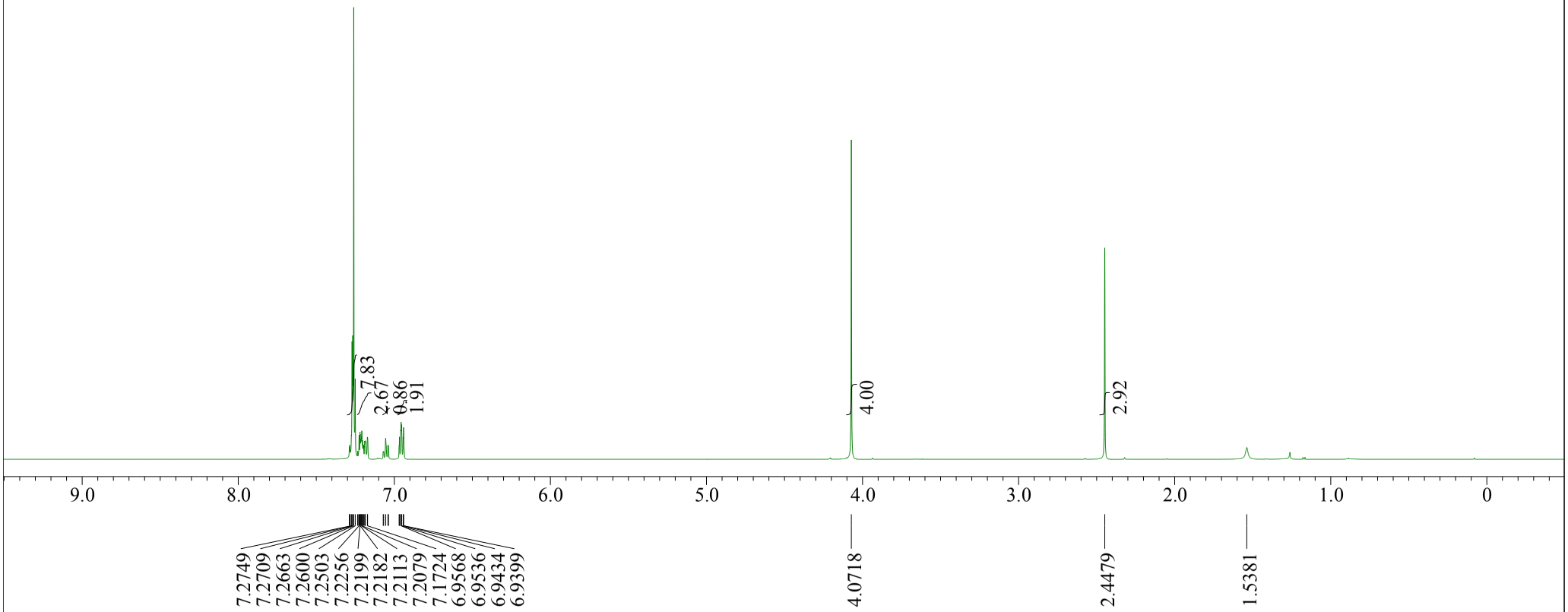
X : parts per Million : 1H


Me
Bn2N
9g
CDCl3, 125 MHz
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
149.5320
139.0923
138.8682
129.2345
128.7480
126.9691
126.8547
117.8743
113.1815
109.8478
77.4175
77.1600
76.9072
54.1297
22.0619
X : parts per Million : 13C

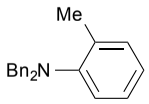


9h

$CDCl_3$, 500 MHz



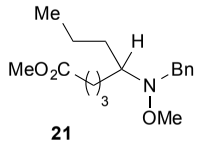
X : parts per Million : 1H



9h

$CDCl_3$, 125 MHz

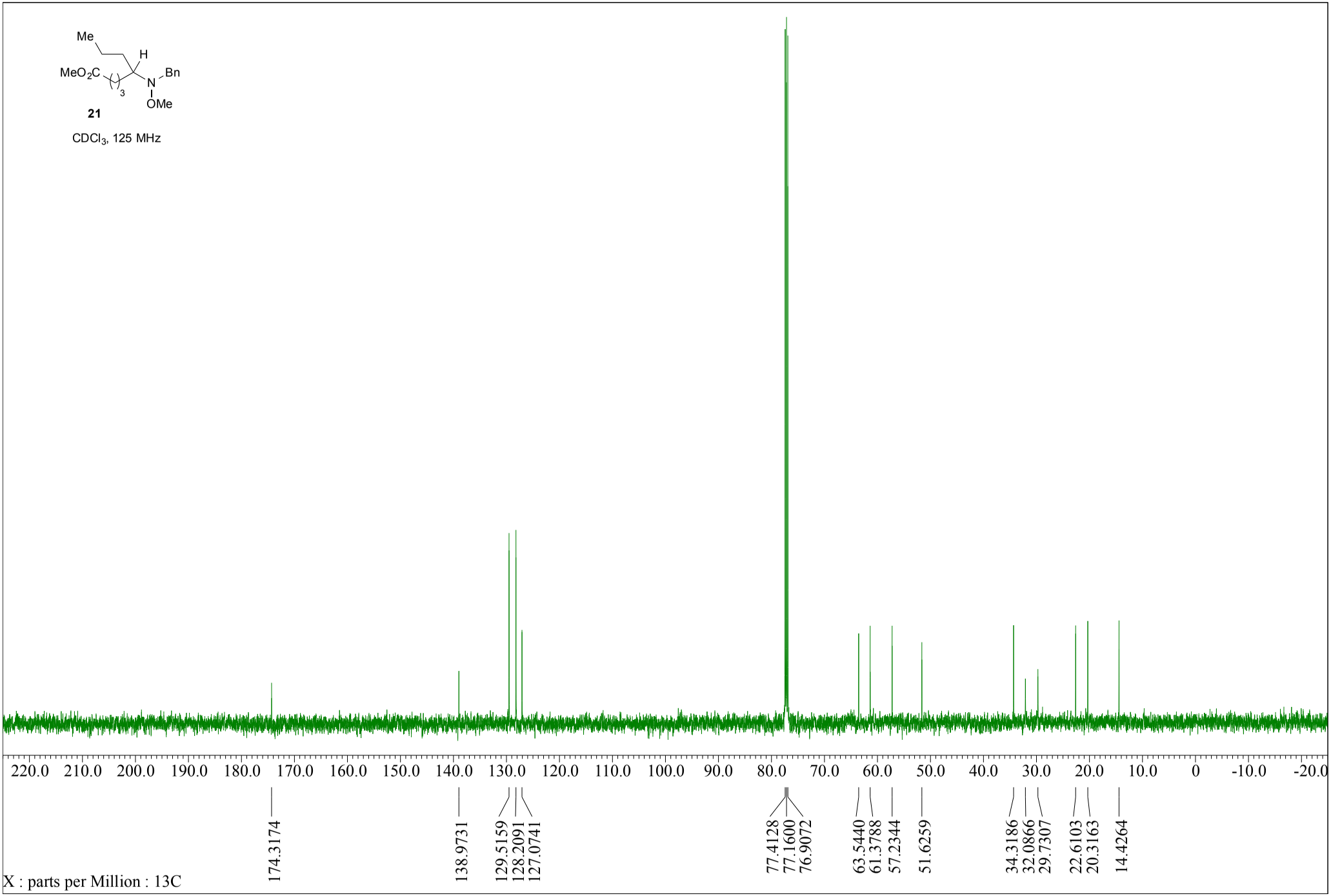
X : parts per Million : 13C

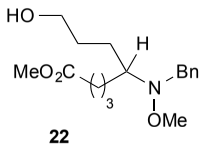


21

$CDCl_3$, 500 MHz

X : parts per Million : 1H

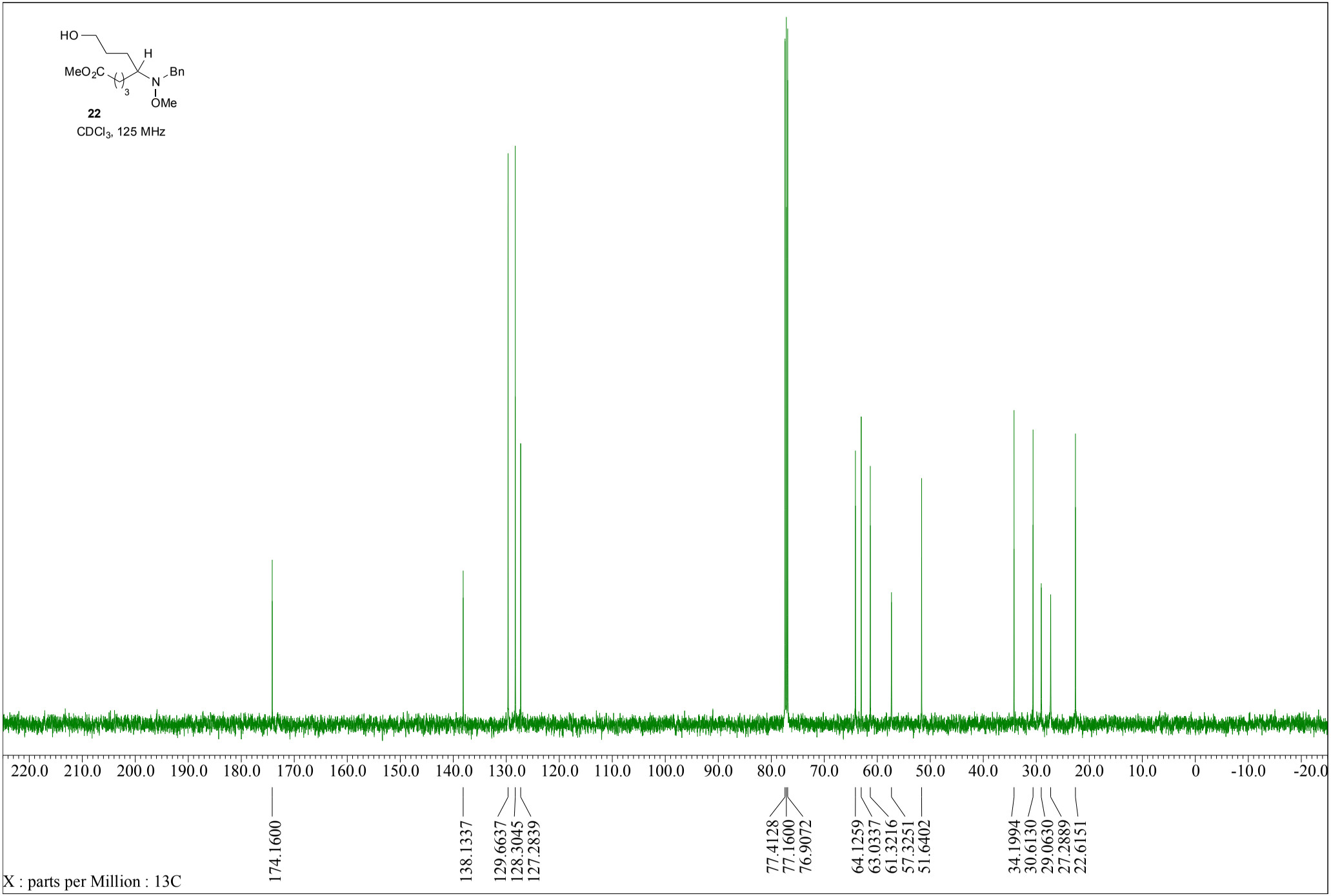

Me
H
MeO2C
3
N
Bn
OMe
21
CDCl3, 125 MHz
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
174.3174
138.9731
129.5159
128.2091
127.0741
77.4128
77.1600
76.9072
63.5440
61.3788
57.2344
51.6259
34.3186
32.0866
29.7307
22.6103
20.3163
14.4264
X : parts per Million : 13C

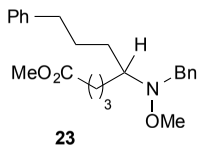


22

$CDCl_3$, 400 MHz

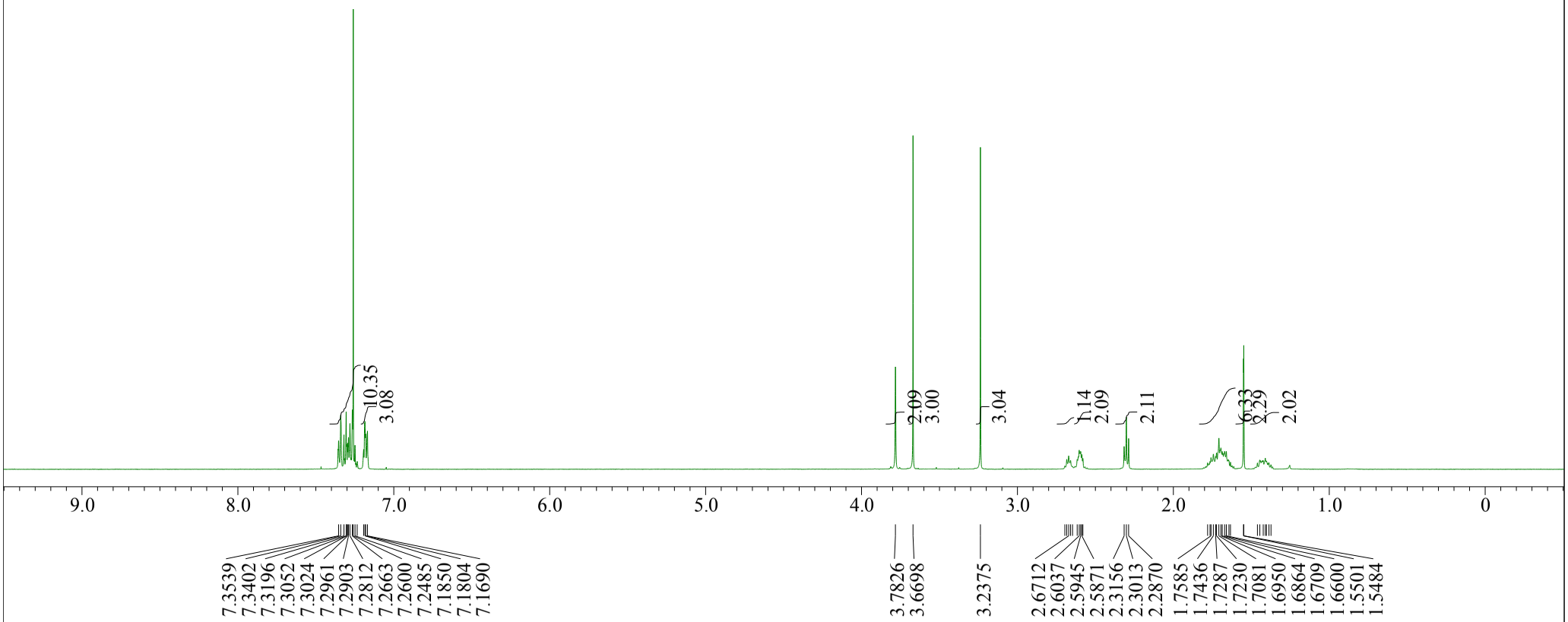
X : parts per Million : 1H


HO
H
MeO2C
3
N
Bn
OMe
22
CDCl3, 125 MHz
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
174.1600
138.1337
129.6637
128.3045
127.2839
77.4128
77.1600
76.9072
64.1259
63.0337
61.3216
57.3251
51.6402
34.1994
30.6130
29.0630
27.2889
22.6151
X : parts per Million : 13C

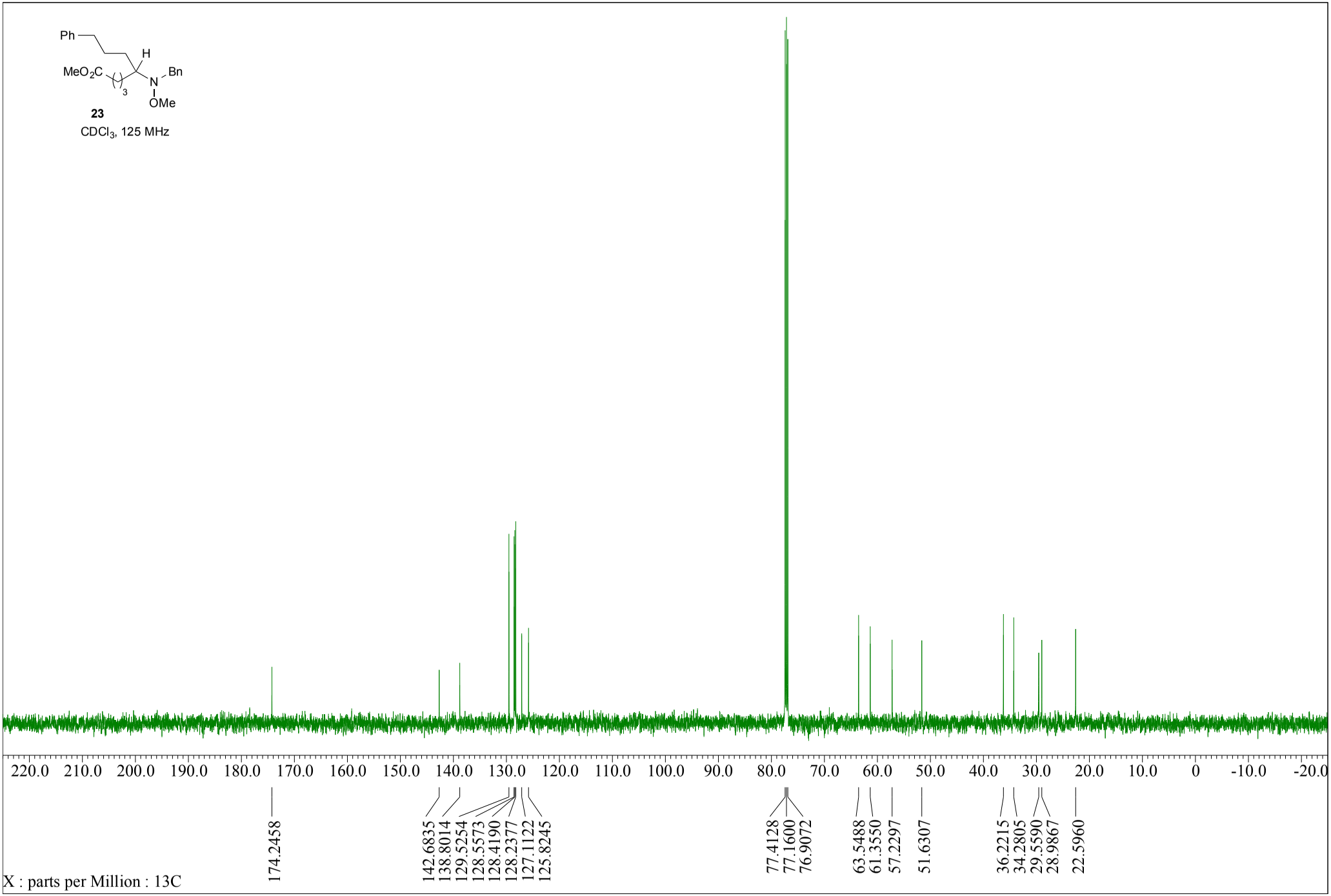


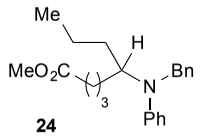
23

$CDCl_3$, 500 MHz



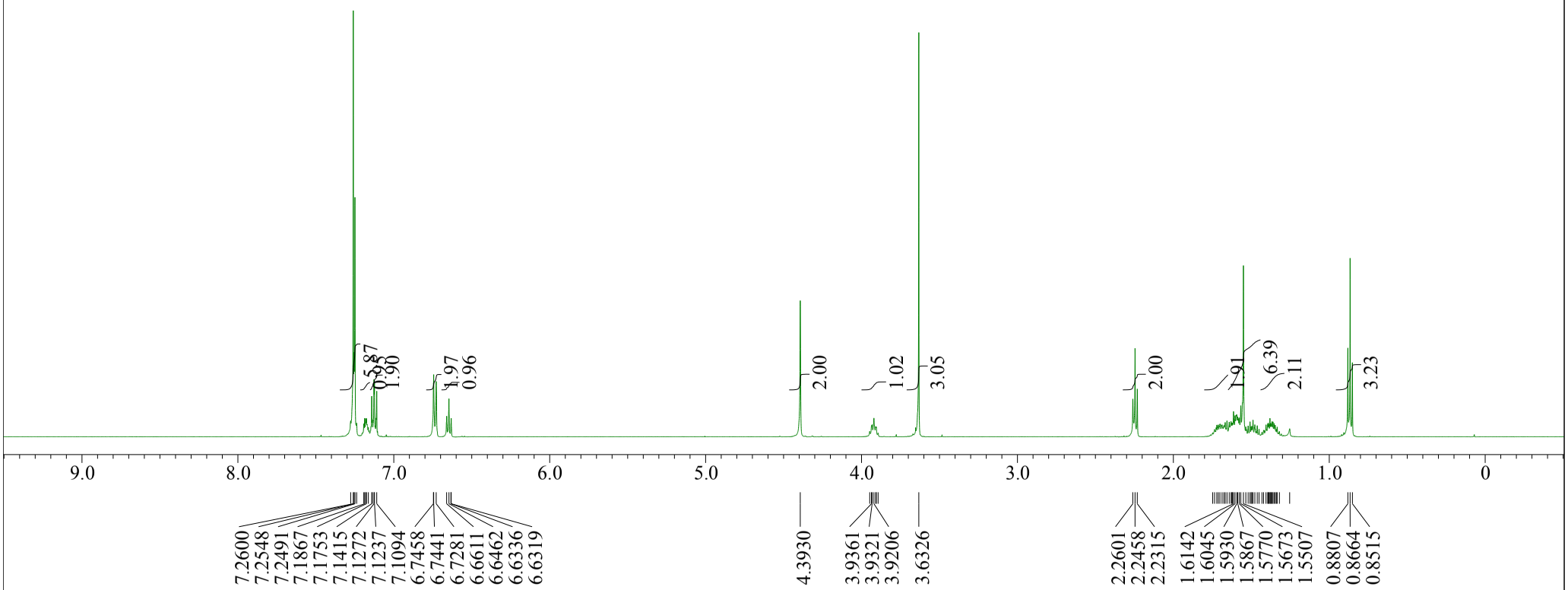
X : parts per Million : 1H


Ph
H
MeO2C
3
N
Bn
OMe
23
CDCl3, 125 MHz
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
174.2458
142.6835
138.8014
129.5254
128.5573
128.4190
128.2377
127.1122
125.8245
77.4128
77.1600
76.9072
63.5488
61.3550
57.2297
51.6307
36.2215
34.2805
29.5590
28.9867
22.5960
X : parts per Million : 13C

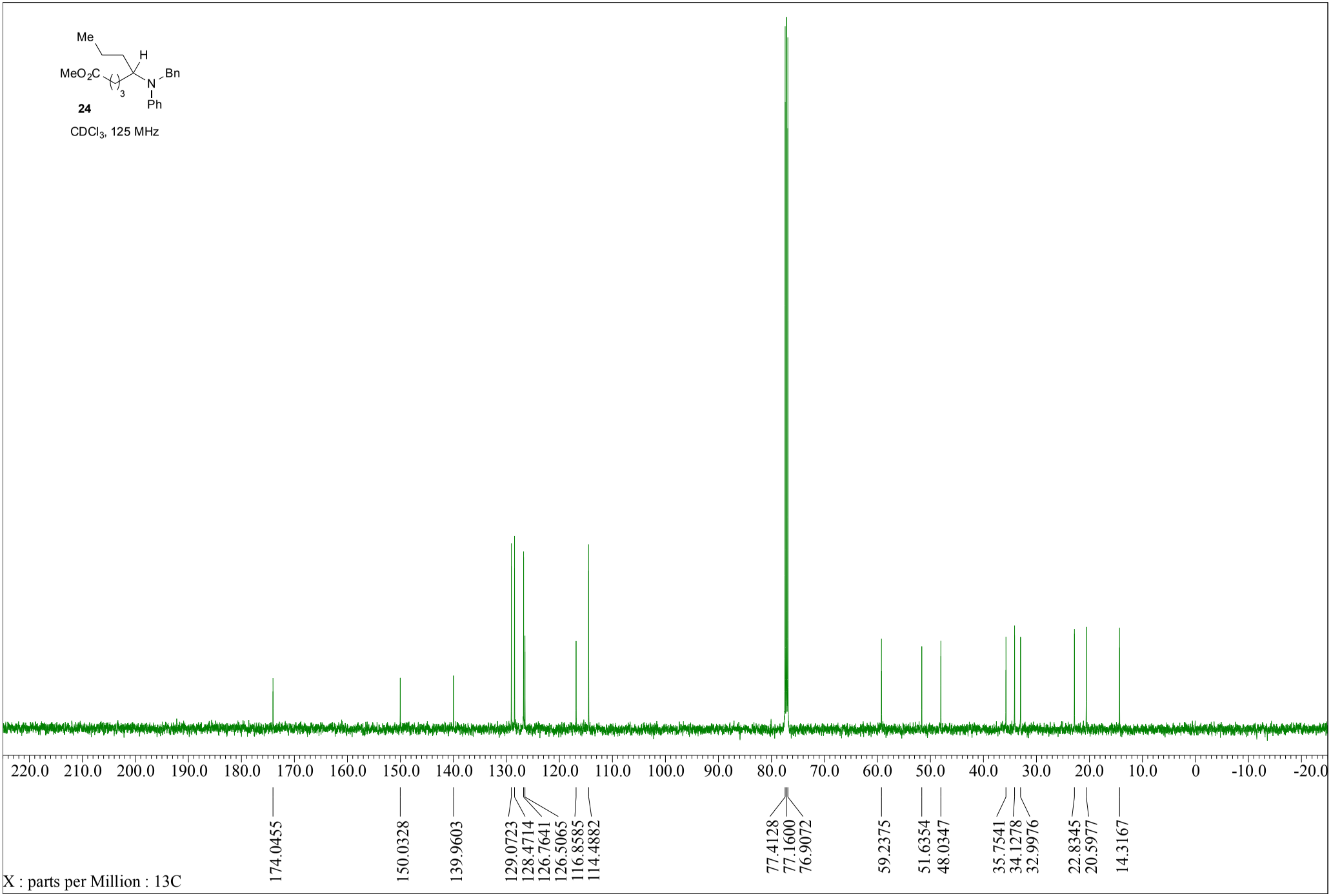


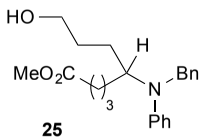
24

$CDCl_3$, 500 MHz



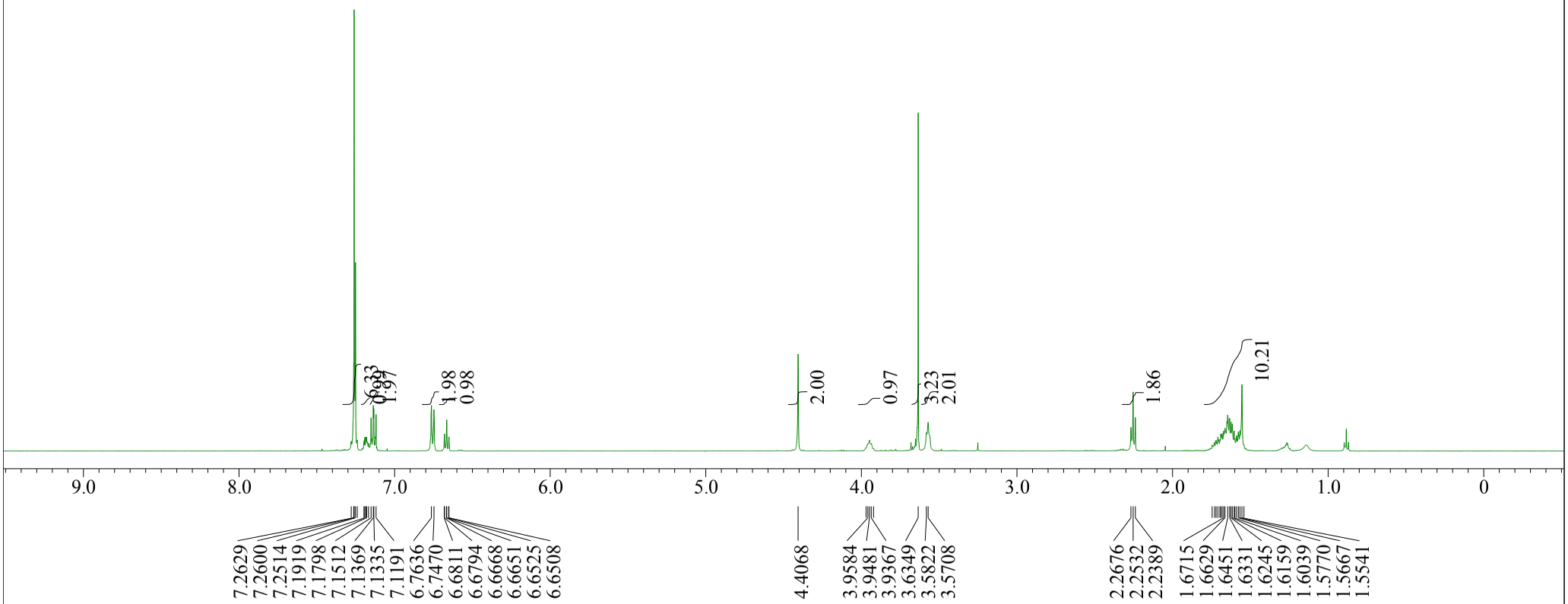
X : parts per Million : 1H


Me
H
MeO2C
3
N
Bn
Ph
24
CDCl3, 125 MHz
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
174.0455
150.0328
139.9603
129.0723
128.4714
126.7641
126.5065
116.8585
114.4882
77.4128
77.1600
76.9072
59.2375
51.6354
48.0347
35.7541
34.1278
32.9976
22.8345
20.5977
14.3167
X : parts per Million : 13C

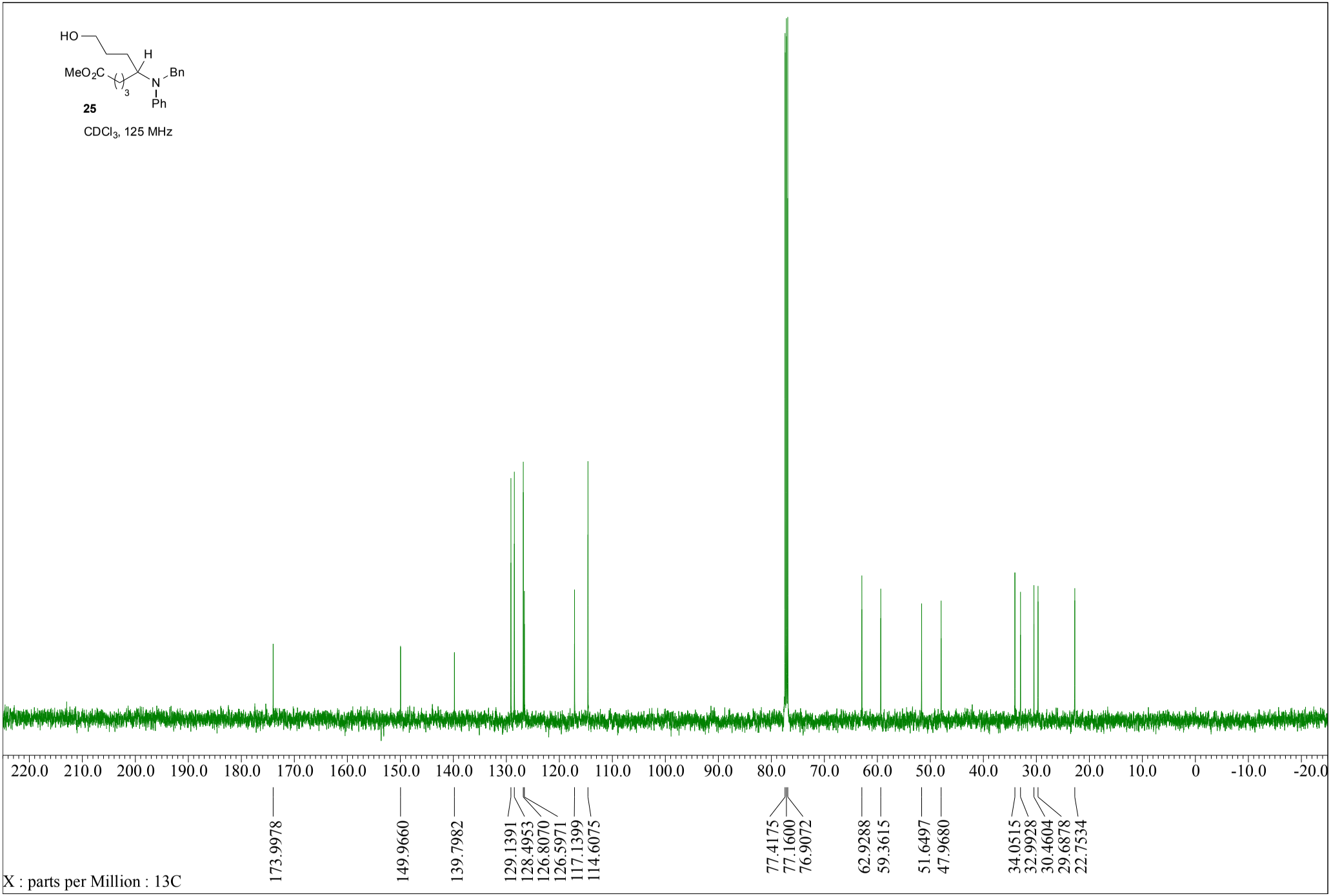


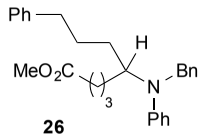
25

$CDCl_3$, 500 MHz



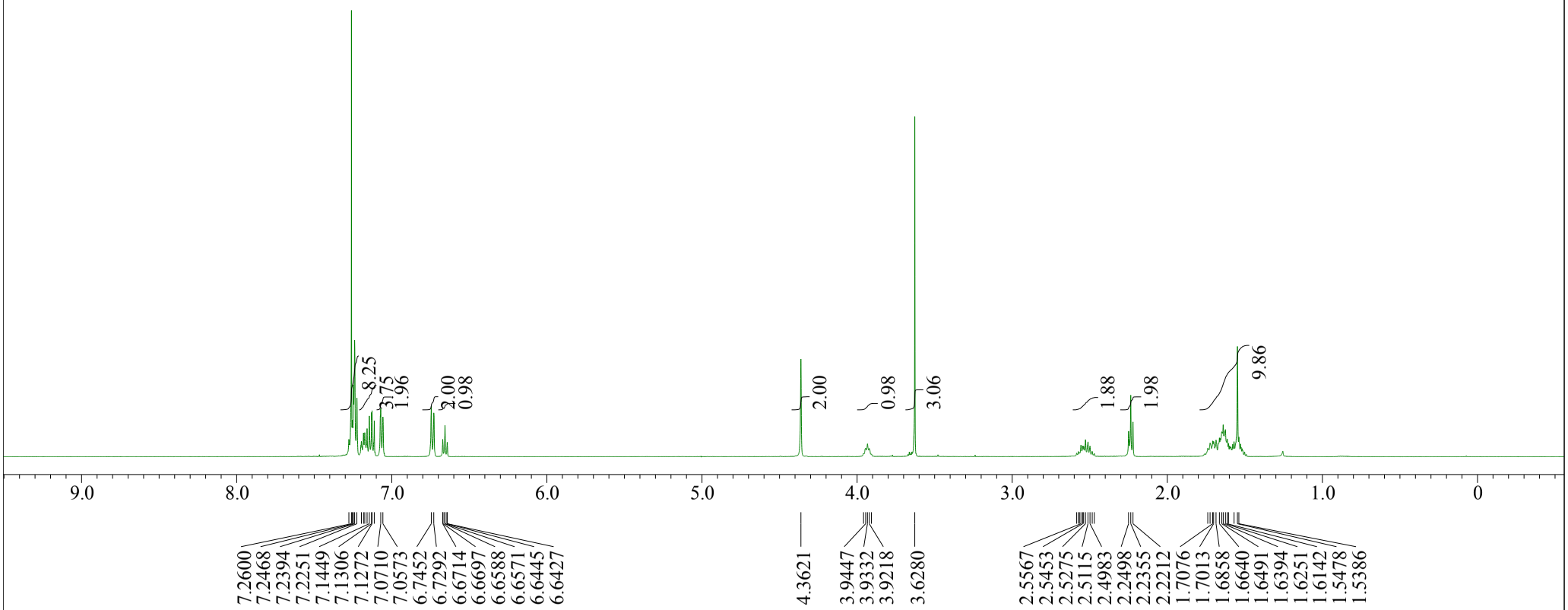
X : parts per Million : 1H


HO
H
MeO2C
3
N
Bn
Ph
25
CDCl3, 125 MHz
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
173.9978
149.9660
139.7982
129.1391
128.4953
126.8070
126.5971
117.1399
114.6075
77.4175
77.1600
76.9072
62.9288
59.3615
51.6497
47.9680
34.0515
32.9928
30.4604
29.6878
22.7534
X : parts per Million : 13C

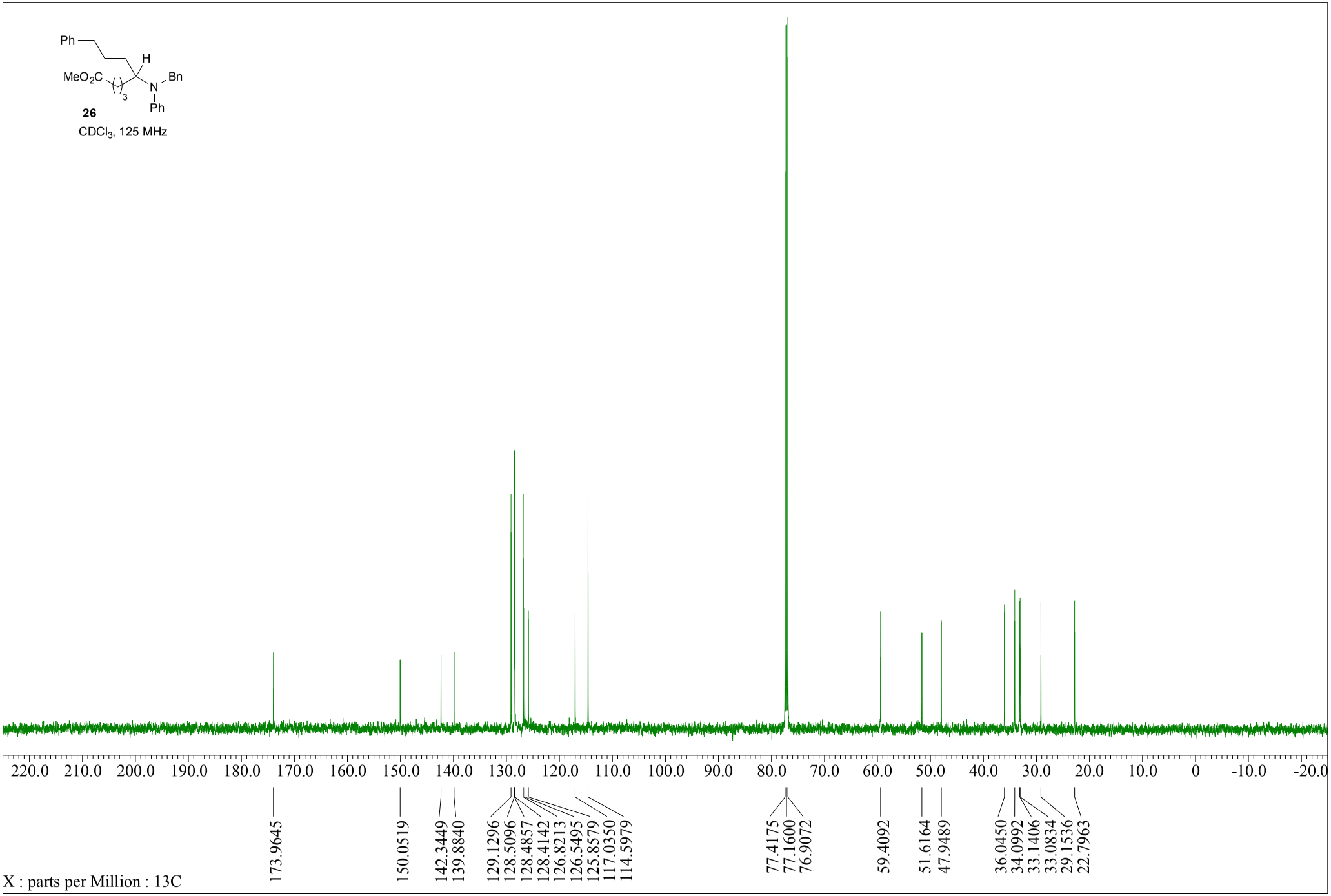


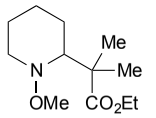
26

$CDCl_3$, 500 MHz



X : parts per Million : 1H

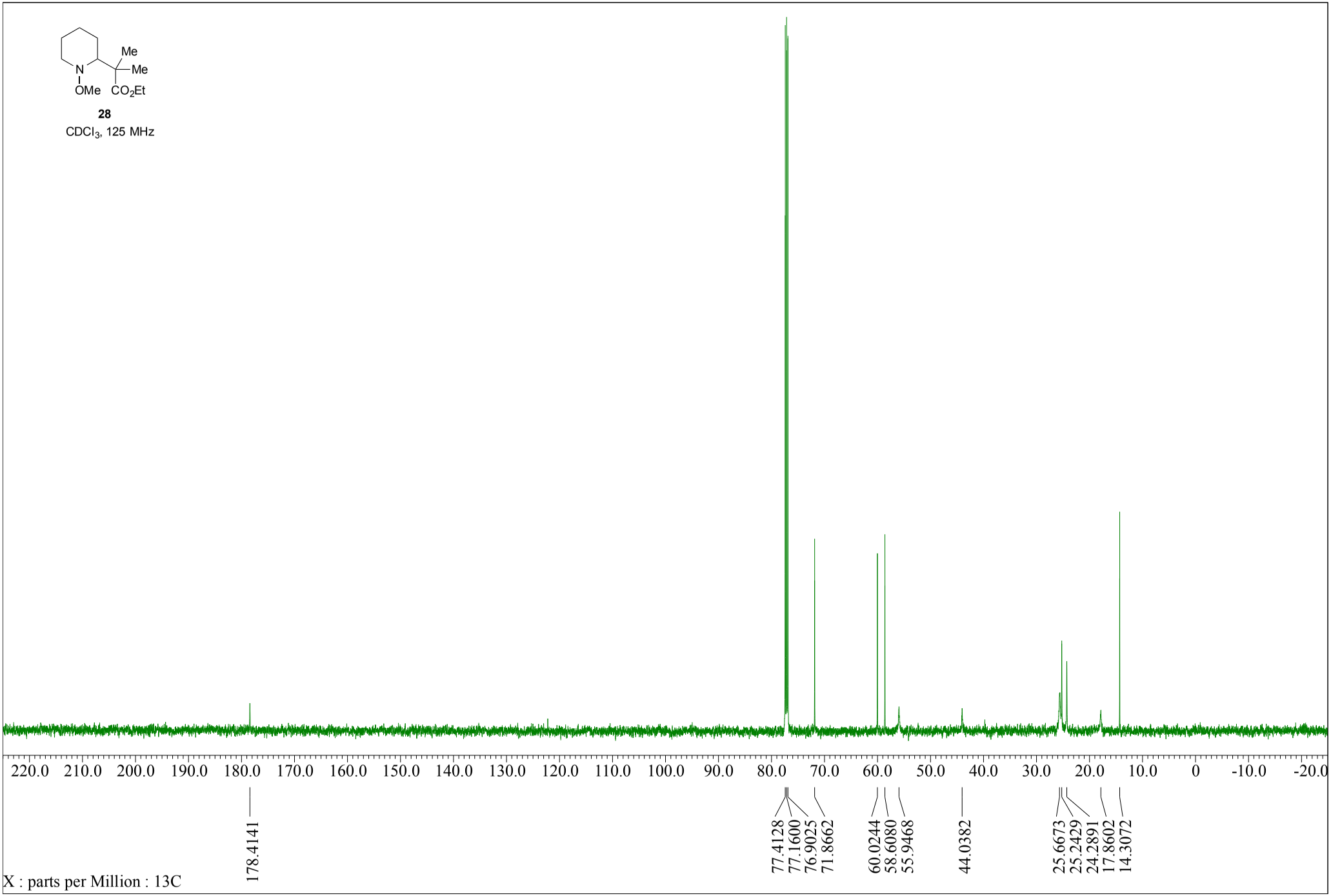

Ph
H
MeO2C
3
N
Bn
Ph
26
CDCl3, 125 MHz
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
173.9645
150.0519
142.3449
139.8840
129.1296
128.5096
128.4857
128.4142
126.8213
126.5495
125.8579
117.0350
114.5979
77.4175
77.1600
76.9072
59.4092
51.6164
47.9489
36.0450
34.0992
33.1406
33.0834
29.1536
22.7963
X : parts per Million : 13C

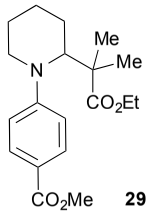


28

$CDCl_3$, 400 MHz

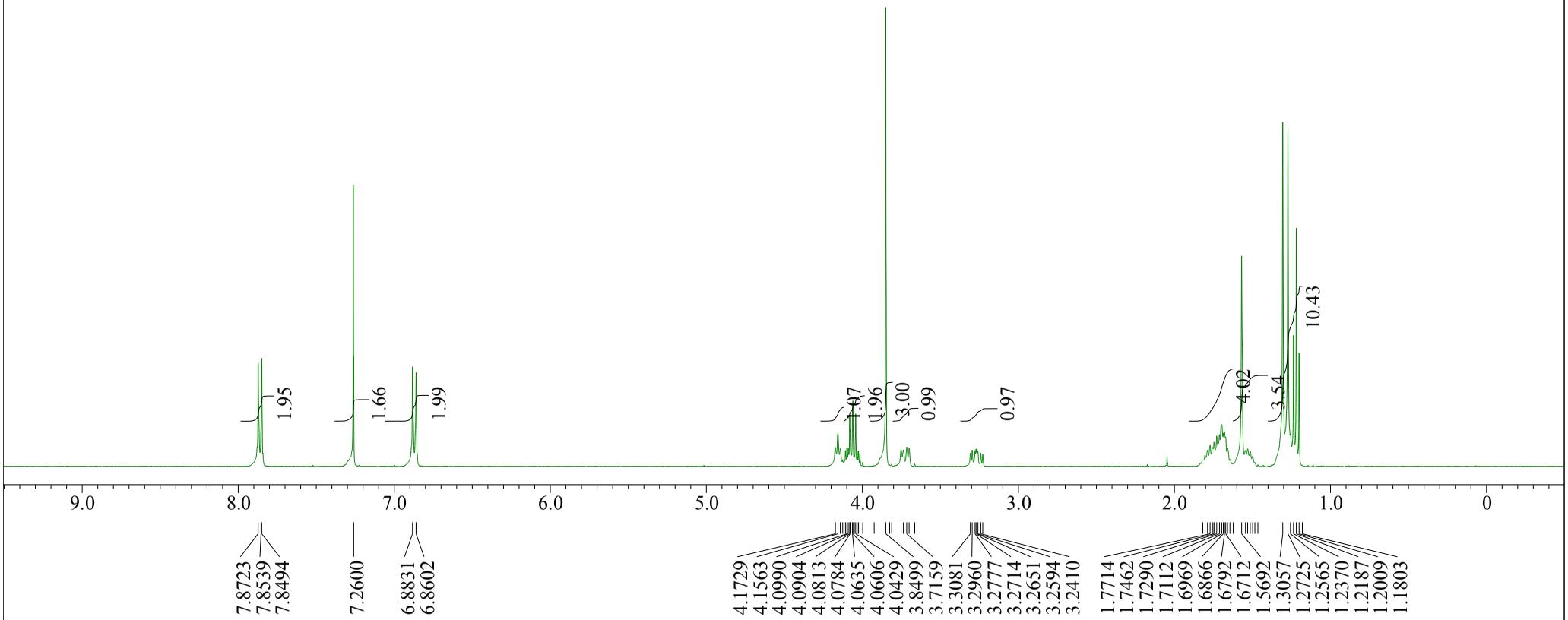
X : parts per Million : 1H


Me
N
Me
OMe
CO2Et
28
CDCl3, 125 MHz
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
178.4141
77.4128
77.1600
76.9025
71.8662
60.0244
58.6080
55.9468
44.0382
25.6673
25.2429
24.2891
17.8602
14.3072
X : parts per Million : 13C

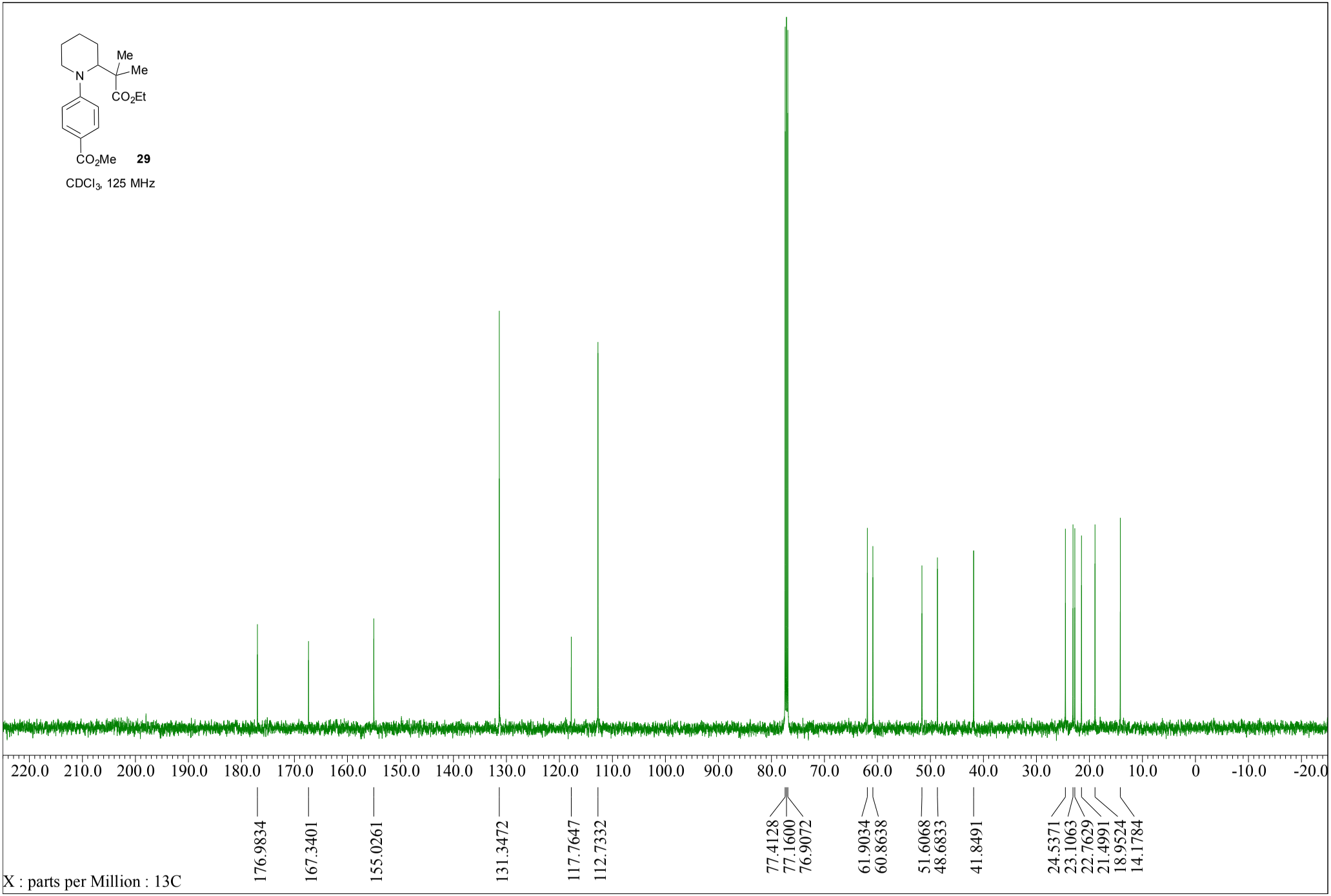


29

$CDCl_3$, 400 MHz



X : parts per Million : 1H


Me
Me
N
CO2Et
CO2Me
29
CDCl3, 125 MHz
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
176.9834
167.3401
155.0261
131.3472
117.7647
112.7332
77.4128
77.1600
76.9072
61.9034
60.8638
51.6068
48.6833
41.8491
24.5371
23.1063
22.7629
21.4991
18.9524
14.1784
X : parts per Million : 13C