Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Electronic Supplementary Information

for

Oxidative C(sp^3)–H amidation of tertiary arylamines with nitriles

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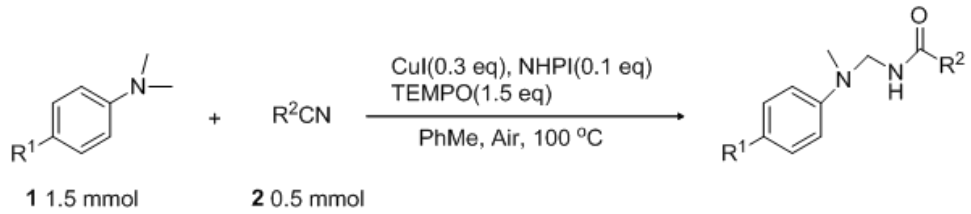
General:

All reactions were carried out under air. Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured on Bruker AVⅢ 400M spectrometers with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the ^{1}H spectrum as 0.00 ppm and $CDCl_3$ resonance in the ^{13}C spectrum as 77.26 ppm. All coupling constants (*J* values) were reported in Hertz (Hz). Chemical shifts of common trace ^{1}H NMR impurities (ppm): H_2O: 1.56, $CHCl_3$: 7.26. Column chromatography was performed on silica gel 300-400 mesh. The unknown products were further characterized by HRMS (FT-ICR-MS) and electrospray ionization source in positive-ion mode.

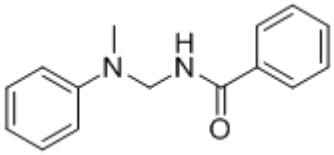
Experimental Procedure for the Synthesis of N-((methyl(phenyl)amino)methyl)benzamide



1 (1.5 mmol, 3 equiv), **2** (0.5 mmol, 1 equiv), CuI (0.15 mmol, 30 mol%), NHPI (0.05 mmol, 30 mol%), TEMPO (0.75 mmol, 1.5 eq) and toluene (2.0 mL) were placed in a round bottom flask at room temperature. The reaction mixture was heated with stirring at 80 °C in the air for 16 hours. Upon completion, the reaction mixture was concentrated under vacuum. The residue was purified by silica gel column chromatography using a hexane/AcOEt (10:1-2:1, v/v) as the eluent to give the corresponding products.

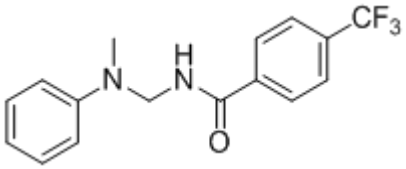
Spectral Data for Products

N-((methyl(phenyl)amino)methyl)benzamide (**3a**)



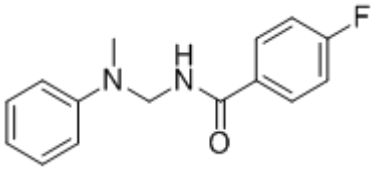
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.64 (d, J = 7.8 Hz, 2H), 7.39 (t, J = 7.1 Hz, 1H), 7.31 (t, J = 7.4 Hz, 2H), 7.21 – 7.17 (m, 2H), 6.79 – 6.72 (m, 3H), 6.55 (s, 1H), 5.03 (d, J = 5.5 Hz, 2H), 2.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 168.1 (s), 148.0 (s), 134.3 (s), 131.8 (s), 129.6 (s), 128.7 (s), 127.1 (s), 118.4 (s), 113.4 (s), 58.3 (s), 38.1 (s). HRMS Calcd for $C_{15}H_{16}N_2NaO^+$ $[M+Na]^+$ 263.1155, found 263.1155.

N-((methyl(phenyl)amino)methyl)-4-(trifluoromethyl)benzamide (**3b**)



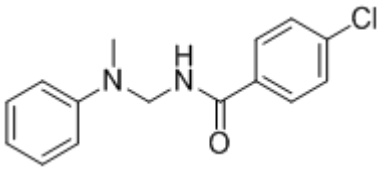
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.83 (d, J = 9.1 Hz, 2H), 7.64 (t, J = 9.0 Hz, 2H), 7.33 – 7.29 (m, 2H), 6.93 – 6.84 (m, 4H), 5.13 (d, J = 5.5 Hz, 2H), 3.10 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.9 (s), 147.9 (s), 137.5 (s), 133.4 (m, $J_{C\text{-}F}$ = 31.4 Hz), 129.6 (s), 127.6 (s), 125.6 (m, $J_{C\text{-}F}$ = 3.7 Hz), 123.7 (m, $J_{C\text{-}F}$ = 272.7 Hz), 118.5 (s), 113.4 (s), 58.5 (s), 38.1 (s). HRMS Calcd for $C_{16}H_{15}F_3N_2NaO^+$ $[M+Na]^+$ 331.1029, found 331.1031.

4-Fluoro-N-((methyl(phenyl)amino)methyl)benzamide (**3c**)



White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.74 – 7.71 (m, 2H), 7.28 – 7.25 (m, 2H), 7.06 – 7.03 (m, 2H), 6.86 – 6.80 (m, 3H), 6.65 (s, 1H), 5.08 (d, J = 5.6 Hz, 2H), 3.05 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.0 (s), 164.9 (d, $J_{C\text{-}F}$ = 252.3 Hz), 147.9 (s), 130.4 (d, $J_{C\text{-}F}$ = 3.5 Hz), 129.6 (s), 129.5 (m, $J_{C\text{-}F}$ = 8.9 Hz), 118.4 (s), 115.7 (m, $J_{C\text{-}F}$ = 272.7 Hz), 113.3 (s), 58.4 (s), 38.1 (s). HRMS Calcd for $C_{15}H_{15}FN_2NaO^+$ $[M+Na]^+$ 281.1061, found 281.1059.

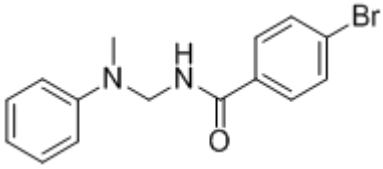
4-Chloro-N-((methyl(phenyl)amino)methyl)benzamide (**3d**)



White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.65 – 7.62 (m, 2H), 7.34 – 7.31 (m, 2H), 7.27

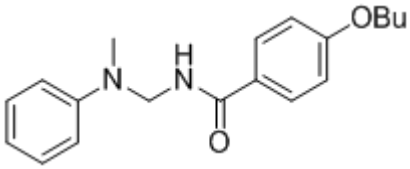
– 7.24 (m, 2H), 6.85 – 6.77 (m, 4H), 5.06 (d, *J* = 5.5 Hz, 2H), 3.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.1 (s), 147.9 (s), 138.0 (s), 132.5 (s), 129.6 (s), 128.9 (s), 128.6 (s), 118.4 (s), 113.3 (s), 58.3 (s), 38.1 (s). HRMS Calcd for $C_{15}H_{15}ClN_2NaO^+$ $[M+Na]^+$ 297.0765, found 297.0758.

4-Bromo-N-((methyl(phenyl)amino)methyl)benzamide (**3e**)



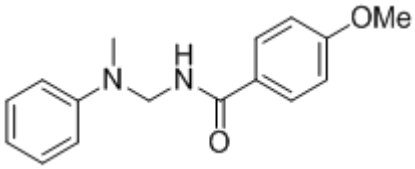
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.59 – 7.56 (m, 2H), 7.53 – 7.51 (m, 2H), 7.29 – 7.25 (m, 2H), 6.86 – 6.81 (m, 3H), 6.59 (s, 1H), 5.09 (d, *J* = 5.6 Hz, 2H), 3.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.1 (s), 147.9 (s), 133.0 (s), 131.99 (s), 131.93 (s), 129.7 (s), 126.5 (s), 118.5 (s), 113.4 (s), 58.4 (s), 38.2 (s). HRMS Calcd for $C_{15}H_{15}BrN_2NaO^+$ $[M+Na]^+$ 341.0260, found 341.0257.

4-Butoxy-N-((methyl(phenyl)amino)methyl)benzamide (**3f**)



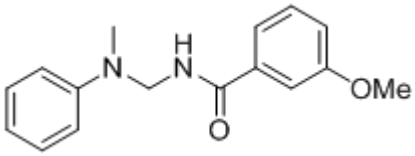
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.67 (d, *J* = 8.1 Hz, 2H), 7.25 (t, *J* = 7.4 Hz, 2H), 6.85 – 6.71 (m, 6H), 5.05 (d, *J* = 5.4 Hz, 2H), 3.94 (t, *J* = 6.5 Hz, 2H), 3.02 (s, 3H), 1.77 – 1.72 (m, 2H), 1.51 – 1.43 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.6 (s), 162.0 (s), 148.1 (s), 129.5 (s), 128.9 (s), 126.1 (s), 118.1 (s), 114.3 (s), 113.3 (s), 67.9 (s), 58.2 (s), 38.0 (s), 31.2 (s), 19.2 (s), 13.8 (s). HRMS Calcd for $C_{19}H_{24}N_2NaO^+$ $[M+Na]^+$ 335.1730, found 335.1726.

4-Methoxy-N-((methyl(phenyl)amino)methyl)benzamide (**3g**)



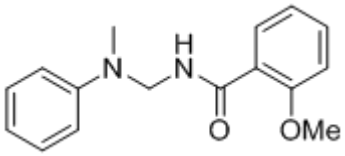
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.71 – 7.67 (m, 2H), 7.29 – 7.25 (m, 2H), 6.89 – 6.79 (m, 5H), 6.54 (s, 1H), 5.09 (d, *J* = 5.6 Hz, 2H), 3.81 (s, 3H), 3.05 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.5 (s), 162.4 (s), 148.1 (s), 129.6 (s), 128.9 (s), 126.4 (s), 118.3 (s), 113.9 (s), 113.3 (s), 58.2 (s), 55.5 (s), 38.1 (s). HRMS Calcd for $C_{16}H_{18}N_2NaO^+$ $[M+Na]^+$ 293.1260, found 293.1253.

3-Methoxy-N-((methyl(phenyl)amino)methyl)benzamide (**3h**)



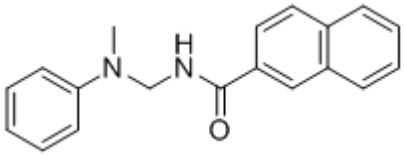
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.32 (s, 1H), 7.26 – 7.21 (m, 4H), 7.00 – 6.98 (m, 1H), 6.85 – 6.78 (m, 4H), 5.06 (d, *J* = 5.5 Hz, 2H), 3.09 (s, 3H), 3.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.9 (s), 159.8 (s), 148.0 (s), 135.7 (s), 129.6 (s), 129.5 (s), 118.8 (s), 118.2 (s), 117.9 (s), 113.3 (s), 112.5 (s), 58.3 (s), 55.4 (s), 38.0 (s). HRMS Calcd for $C_{16}H_{18}N_2NaO^+$ $[M+Na]^+$ 293.1260, found 293.1255.

2-Methoxy-N-((methyl(phenyl)amino)methyl)benzamide (**3i**)



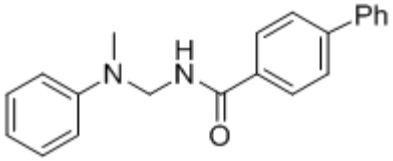
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.32 (s, 1H), 8.20 – 8.18 (m, 1H), 7.44 – 7.40 (m, 1H), 7.31 – 7.26 (m, 2H), 7.08 – 7.05 (m, 1H), 6.92 – 6.87 (m, 3H), 6.83 – 6.80 (m, 1H), 5.13 (d, *J* = 5.6 Hz, 2H), 3.76 (s, 3H), 3.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.8 (s), 157.6 (s), 148.4 (s), 133.1 (s), 132.3 (s), 129.4 (s), 121.42 (s), 121.40 (s), 118.2 (s), 113.6 (s), 111.5 (s), 57.9 (s), 56.0 (s), 38.2 (s). HRMS Calcd for $C_{16}H_{18}N_2NaO^+$ $[M+Na]^+$ 293.1260, found 293.1263.

N-((methyl(phenyl)amino)methyl)-2-naphthamide (**3j**)



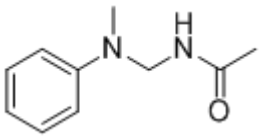
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.27 - 8.25 (m, 1H), 7.91 - 7.85 (m, 2H), 7.54 - 7.51 (m, 3H), 7.42 - 7.38 (m, 1H), 7.33 - 7.29 (m, 2H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.86 (t, *J* = 7.7 Hz, 1H), 6.59 (s, 1H), 5.18 (d, *J* = 5.7 Hz, 2H), 3.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 170.1 (s), 147.9 (s), 134.2 (s), 133.7 (s), 130.8 (s), 130.1 (s), 129.6 (s), 128.4 (s), 127.2 (s), 126.5 (s), 125.4 (s), 125.0 (s), 124.7 (s), 118.5 (s), 113.6 (s), 58.0 (s), 38.2 (s). HRMS Calcd for $C_{19}H_{18}N_2NaO^+$ $[M+Na]^+$ 313.1311, found 313.1301.

N-((methyl(phenyl)amino)methyl)-[1,1'-biphenyl]-4-carboxamide (**3k**)



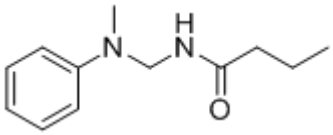
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.82 - 7.80 (m, 2H), 7.64 - 7.58 (m, 4H), 7.47 - 7.38 (m, 3H), 7.32 - 7.26 (m, 2H), 6.90 - 6.83 (m, 3H), 6.63 (s, 1H), 5.16 (d, *J* = 5.6 Hz, 2H), 3.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.8 (s), 148.1 (s), 144.7 (s), 140.1 (s), 132.9 (s), 129.7 (s), 129.0 (s), 128.2 (s), 127.7 (s), 126.4 (s), 125.3 (s), 118.4 (s), 113.4 (s), 58.4 (s), 38.1 (s). HRMS Calcd for $C_{21}H_{20}N_2NaO^+$ $[M+Na]^+$ 339.1468, found 339.1458.

N-((methyl(phenyl)amino)methyl)acetamide (**3l**)



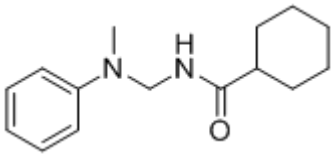
Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.28 (d, *J* = 7.4 Hz, 2H), 6.82 (t, *J* = 4.5 Hz, 3H), 6.20 (s, 1H), 4.90 (d, *J* = 5.7 Hz, 2H), 3.01 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 170.7 (s), 148.0 (s), 129.5 (s), 118.2 (s), 113.2 (s), 57.5 (s), 37.9 (s), 23.3 (s). HRMS Calcd for $C_{10}H_{14}N_2NaO^+$ $[M+Na]^+$ 201.0998, found 201.0996.

N-((methyl (phenyl)amino)methyl)butyramide (**3m**)



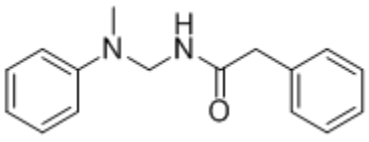
Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.29 (t, *J* = 7.7 Hz, 2H), 6.84 - 6.81 (m, 3H), 6.06 (s, 1H), 4.92 (d, *J* = 5.7 Hz, 2H), 3.01 (s, 3H), 2.15 (t, *J* = 8.9 Hz, 2H), 1.71 - 1.62 (m, 2H), 0.94 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 170.7 (s), 148.0 (s), 129.5 (s), 118.2 (s), 113.2 (s), 57.5 (s), 37.9 (s), 23.3 (s). HRMS Calcd for $C_{12}H_{18}N_2NaO^+$ $[M+Na]^+$ 229.1311, found 229.1311.

N-((methyl(phenyl)amino)methyl)cyclohexanecarboxamide (**3n**)



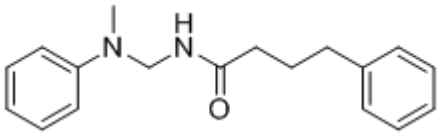
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.29 (t, *J* = 7.7 Hz, 2H), 6.82 (t, *J* = 4.9 Hz, 3H), 5.97 (s, 1H), 4.92 (d, *J* = 5.6 Hz, 2H), 3.00 (s, 3H), 2.09 - 2.03 (m, 1H), 1.84 - 1.68 (m, 5H), 1.49 - 1.41 (m, 2H), 1.28 - 1.22 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 176.7 (s), 148.0 (s), 129.5 (s), 118.1 (s), 113.3 (s), 57.4 (s), 45.7 (s), 37.8 (s), 29.7 (s), 25.74 (s), 25.71 (s). HRMS Calcd for $C_{15}H_{22}N_2NaO^+$ $[M+Na]^+$ 269.1624, found 269.1619.

N-((methyl (phenyl)amino)methyl)-2-phenylacetamide (**3o**)



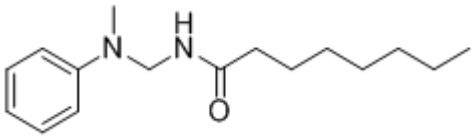
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.27 - 7.14 (m, 7H), 6.77 - 6.71 (m, 3H), 6.26 (s, 1H), 4.78 (d, *J* = 5.7 Hz, 2H), 3.45 (s, 2H), 2.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 171.6 (s), 147.9 (s), 134.8 (s), 129.3 (s), 129.2 (s), 128.8 (s), 127.2 (s), 118.2 (s), 113.3 (s), 57.7 (s), 43.5 (s), 37.8 (s). HRMS Calcd for $C_{16}H_{18}N_2NaO^+$ $[M+Na]^+$ 277.1311, found 277.1307.

N-((methyl(phenyl)amino)methyl)-4-phenylbutanamide (**3p**)



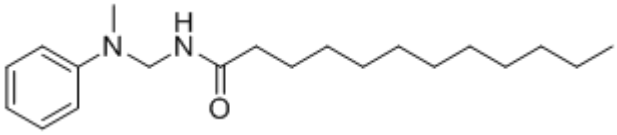
Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.33 - 7.27 (m, 4H), 7.23 - 7.15 (m, 3H), 6.87 - 6.83 (m, 3H), 6.04 (s, 1H), 4.93 (d, *J* = 5.8 Hz, 2H), 3.06 (s, 3H), 2.66 (t, *J* = 7.4 Hz, 2H), 2.18 (t, *J* = 7.2 Hz, 2H), 2.03 - 1.95 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 173.3 (s), 147.9 (s), 141.4 (s), 129.5 (s), 128.5 (s), 128.4 (s), 126.0 (s), 118.2 (s), 113.3 (s), 57.4 (s), 38.0 (s), 35.8 (s), 35.1 (s), 27.0 (s). HRMS Calcd for $C_{18}H_{22}N_2NaO^+$ $[M+Na]^+$ 305.1624, found 305.1621.

N-((methyl(phenyl)amino)methyl)octanamide (**3q**)



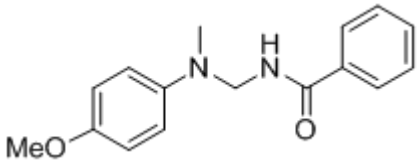
Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.31 - 7.27 (m, 2H), 6.84 - 6.81 (m, 3H), 5.91 (s, 1H), 4.94 (d, *J* = 5.7 Hz, 2H), 3.02 (s, 3H), 2.26 - 2.15 (m, 2H), 1.67 - 1.60 (m, 2H), 1.33 - 1.28 (m, 8H), 0.89 (t, *J* = 5.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 173.8 (s), 148.1 (s), 129.65 (s), 118.3 (s), 113.4 (s), 57.5 (s), 38.0 (s), 36.9 (s), 31.8 (s), 29.3 (s), 29.1 (s), 25.7 (s), 22.7 (s), 14.2 (s). HRMS Calcd for $C_{16}H_{26}N_2NaO^+$ $[M+Na]^+$ 285.1937, found 285.1934.

N- ((methyl(phenyl)amino)methyl)dodecanamide (**3r**)



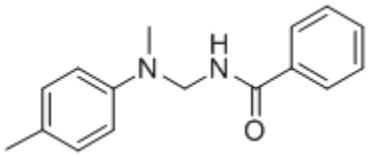
Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.31 - 7.26 (m, 2H), 6.85 - 6.82 (m, 3H), 5.91 (s, 1H), 4.94 (d, *J* = 5.8 Hz, 2H), 3.02 (s, 3H), 2.17 (t, *J* = 7.4 Hz, 2H), 1.64 - 1.59 (m, 2H), 1.27 (s, 16H), 0.91 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 173.8 (s), 148.0 (s), 129.6 (s), 118.3 (s), 113.4 (s), 57.4 (s), 38.0 (s), 36.9 (s), 32.0 (s), 29.7 (s), 29.5 (s), 29.4 (s), 25.7 (s), 22.8 (s), 14.3 (s). HRMS Calcd for $C_{20}H_{34}N_2NaO^+$ $[M+Na]^+$ 341.2563, found 341.2554.

N-(((4-methoxyphenyl)(methyl)amino)methyl)benzamide (**3s**)



White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.72 - 7.70 (m, 2H), 7.50 - 7.46 (m, 1H), 7.41 - 7.37 (m, 2H), 6.86 (s, 4H), 6.57 (s, 1H), 5.04 (d, *J* = 5.6 Hz, 2H), 3.76 (s, 3H), 2.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 168.0 (s), 153.1 (s), 142.5 (s), 134.4 (s), 131.8 (s), 128.7 (s), 127.1 (s), 115.9 (s), 115.1 (s), 59.4 (s), 55.8 (s), 38.4 (s). HRMS Calcd for $C_{16}H_{19}N_2O_2^+$ $[M+H]^+$ 271.1441, found 271.1436.

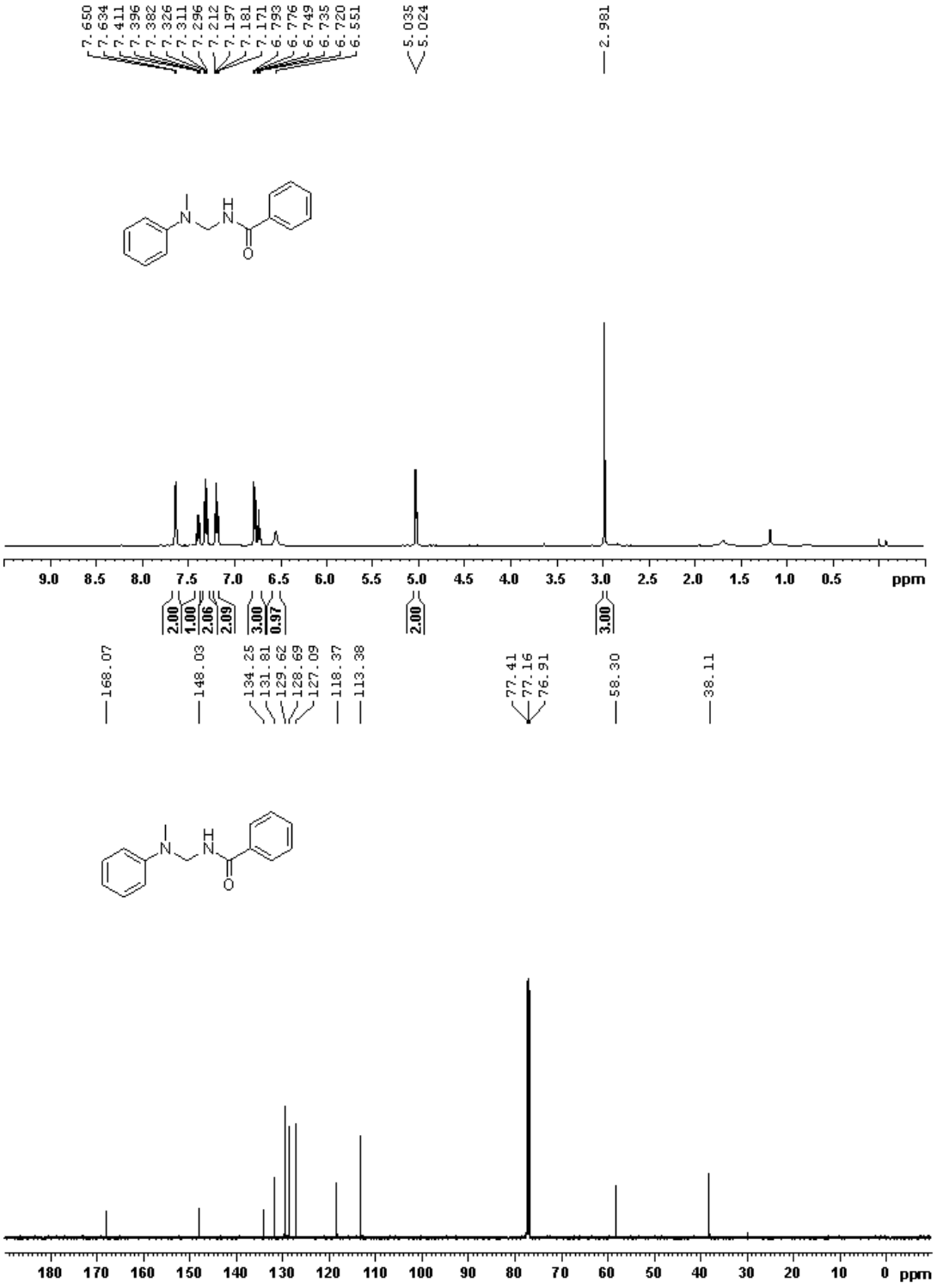
N-((methyl(p-tolyl)amino)methyl)benzamide (**3t**)



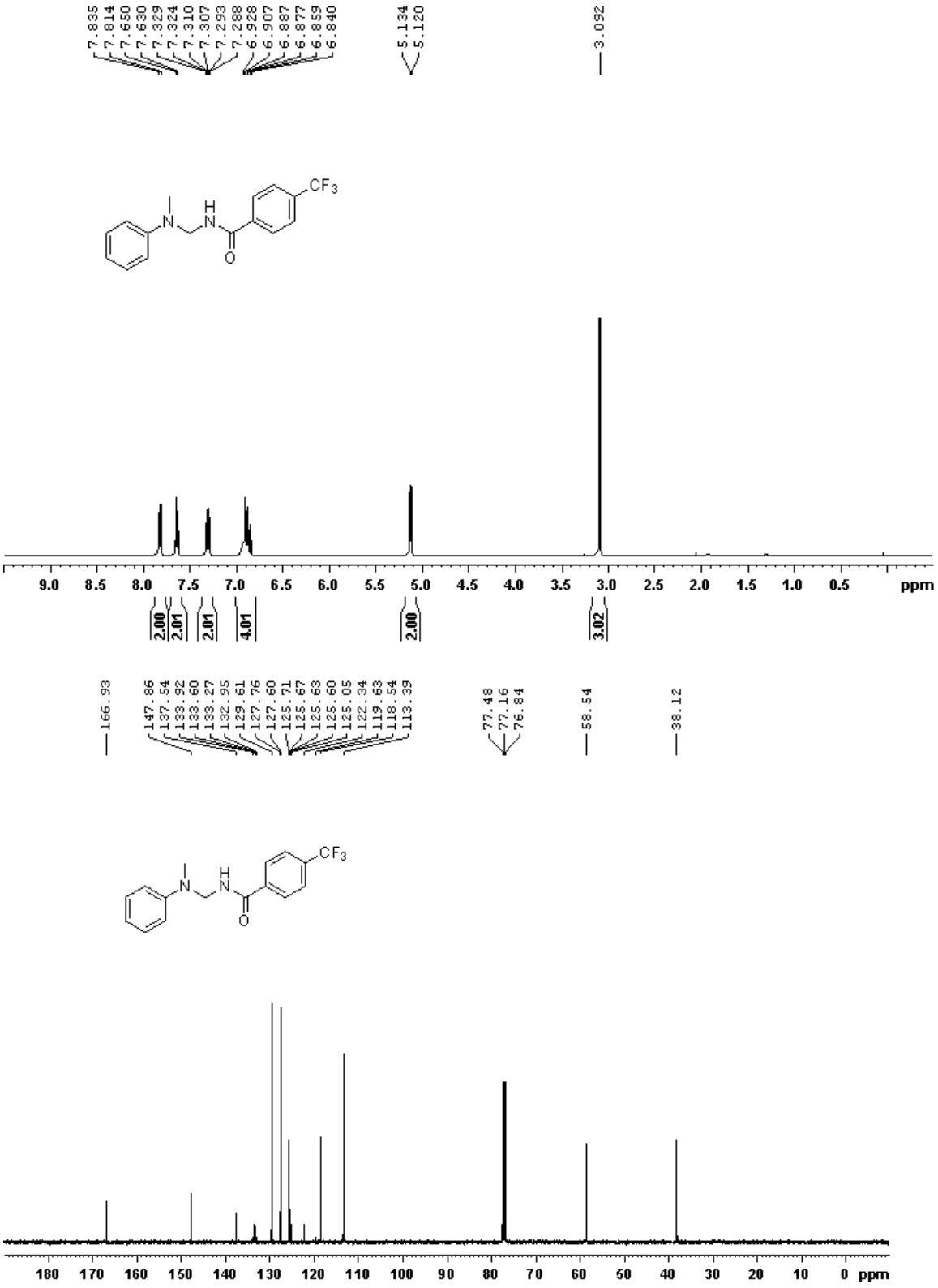
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.72 (d, *J* = 7.3 Hz, 2H), 7.50 - 7.38 (m, 3H), 7.09 (d, *J* = 8.3 Hz, 2H), 6.80 (d, *J* = 8.9 Hz, 2H), 6.56 (s, 1H), 5.09 (d, *J* = 5.5 Hz, 2H), 3.03 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 168.1 (s), 145.9 (s), 134.4 (s), 131.8 (s), 130.1 (s), 128.7 (s), 127.9 (s), 127.1 (s), 113.9 (s), 58.7 (s), 38.2 (s), 20.4 (s). HRMS Calcd for $C_{16}H_{18}N_2NaO^+$ $[M+Na]^+$ 277.1311, found 277.1305.

^{1}H NMR and ^{13}C NMR Spectra for All Compounds

3a



3b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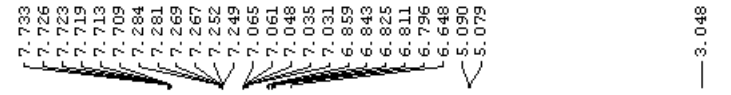
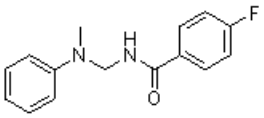
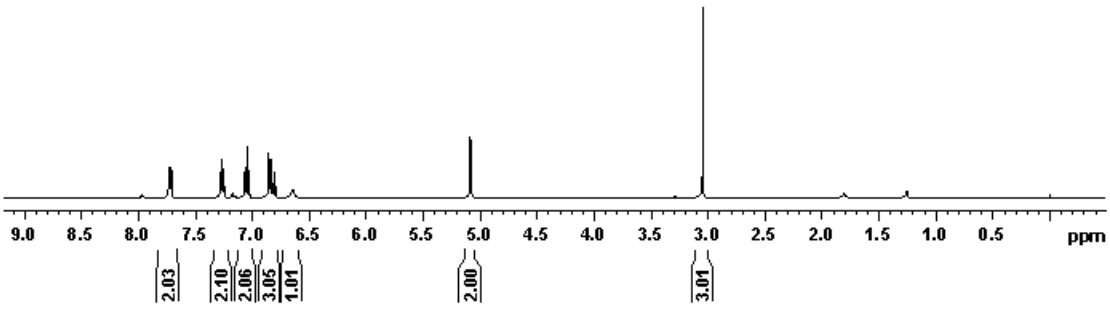
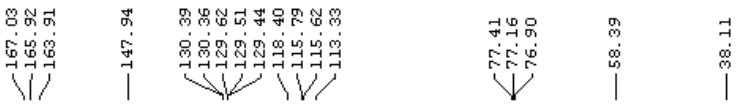
7.814
7.650
7.630
7.329
7.324
7.310
7.307
7.293
7.288
6.928
6.907
6.887
6.877
6.859
6.840
5.134
5.120
3.092
CF3
N
H
N
O
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
2.01
2.01
4.01
2.00
3.02
166.93
147.86
137.54
133.92
133.60
133.27
132.95
129.61
127.76
127.60
125.71
125.67
125.63
125.60
125.05
122.34
119.63
118.54
113.39
77.48
77.16
76.84
58.54
38.12
CF3
N
H
N
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

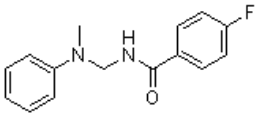
3c

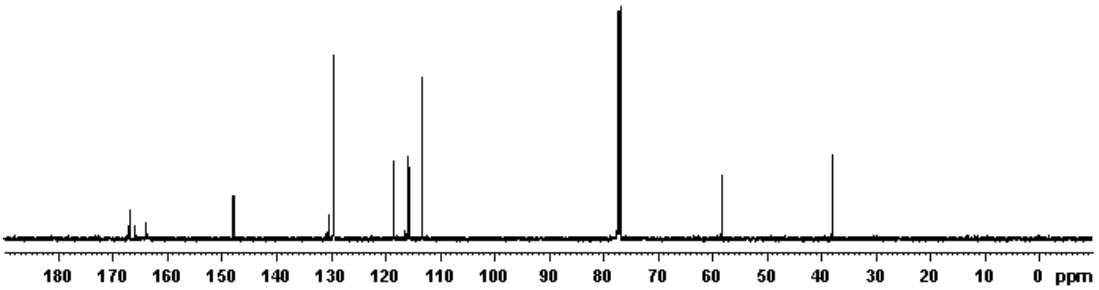

7.733
7.726
7.723
7.719
7.713
7.709
7.284
7.281
7.269
7.267
7.252
7.249
7.065
7.061
7.048
7.035
7.031
6.859
6.843
6.825
6.811
6.796
6.648
5.090
5.079
3.048


F
N
H
N
O

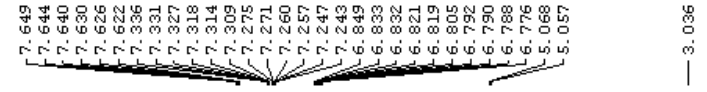

9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.03
2.10
2.06
3.05
1.01
2.00
3.01

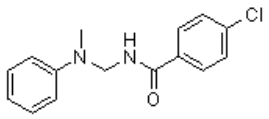

167.03
165.92
163.91
147.94
130.39
130.36
129.62
129.51
129.44
118.40
115.79
115.62
113.33
77.41
77.16
76.90
58.39
38.11

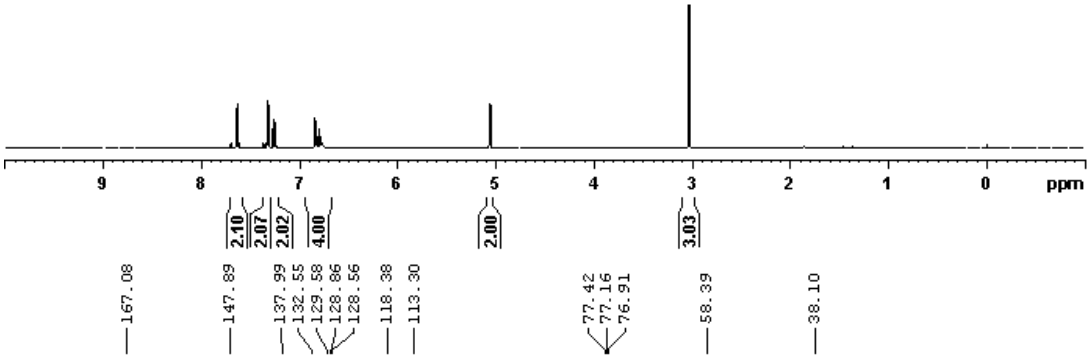

F
N
H
N
O

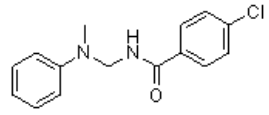

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

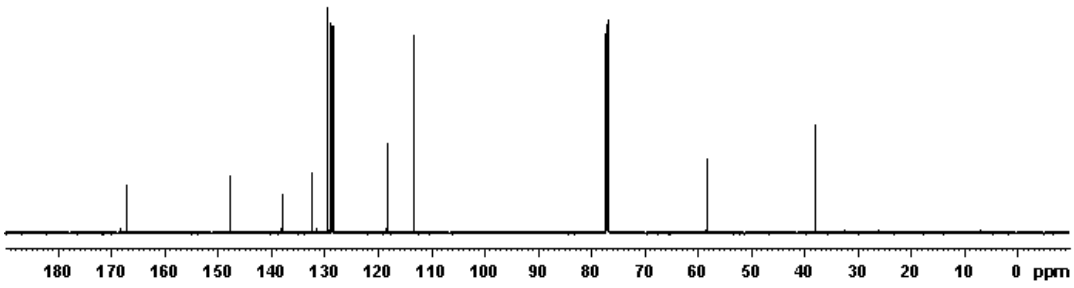
3d


7.649
7.644
7.640
7.630
7.626
7.622
7.336
7.331
7.327
7.318
7.314
7.309
7.275
7.271
7.260
7.257
7.247
7.243
6.849
6.833
6.832
6.821
6.819
6.805
6.792
6.790
6.788
6.776
5.068
5.057
3.036

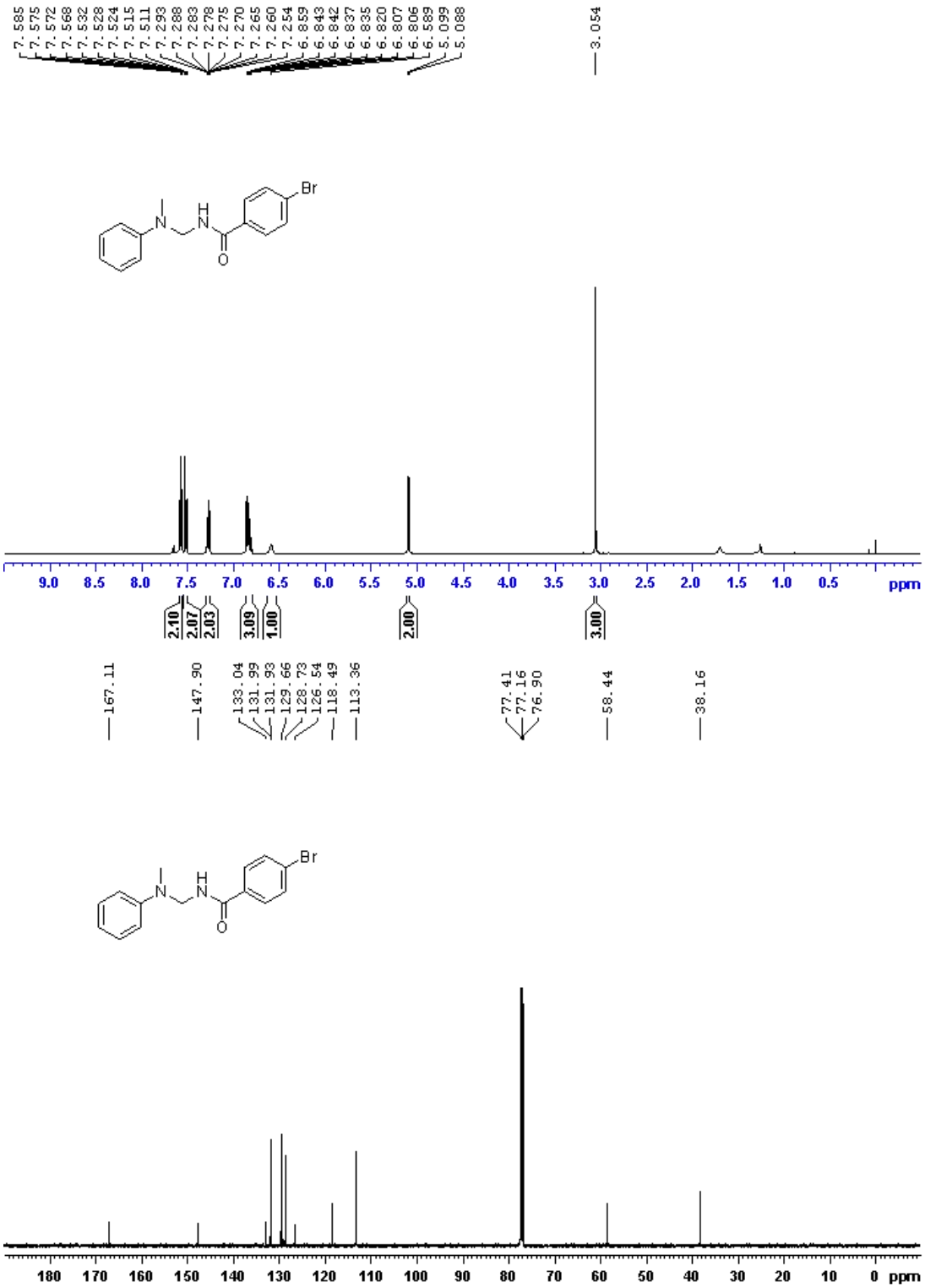

Cl
N
H
N
O


9
8
7
6
5
4
3
2
1
0
ppm
2.10
2.07
2.02
4.00
2.00
3.03
167.08
147.89
137.99
132.55
129.58
128.86
128.56
118.38
113.30
77.42
77.16
76.91
58.39
38.10

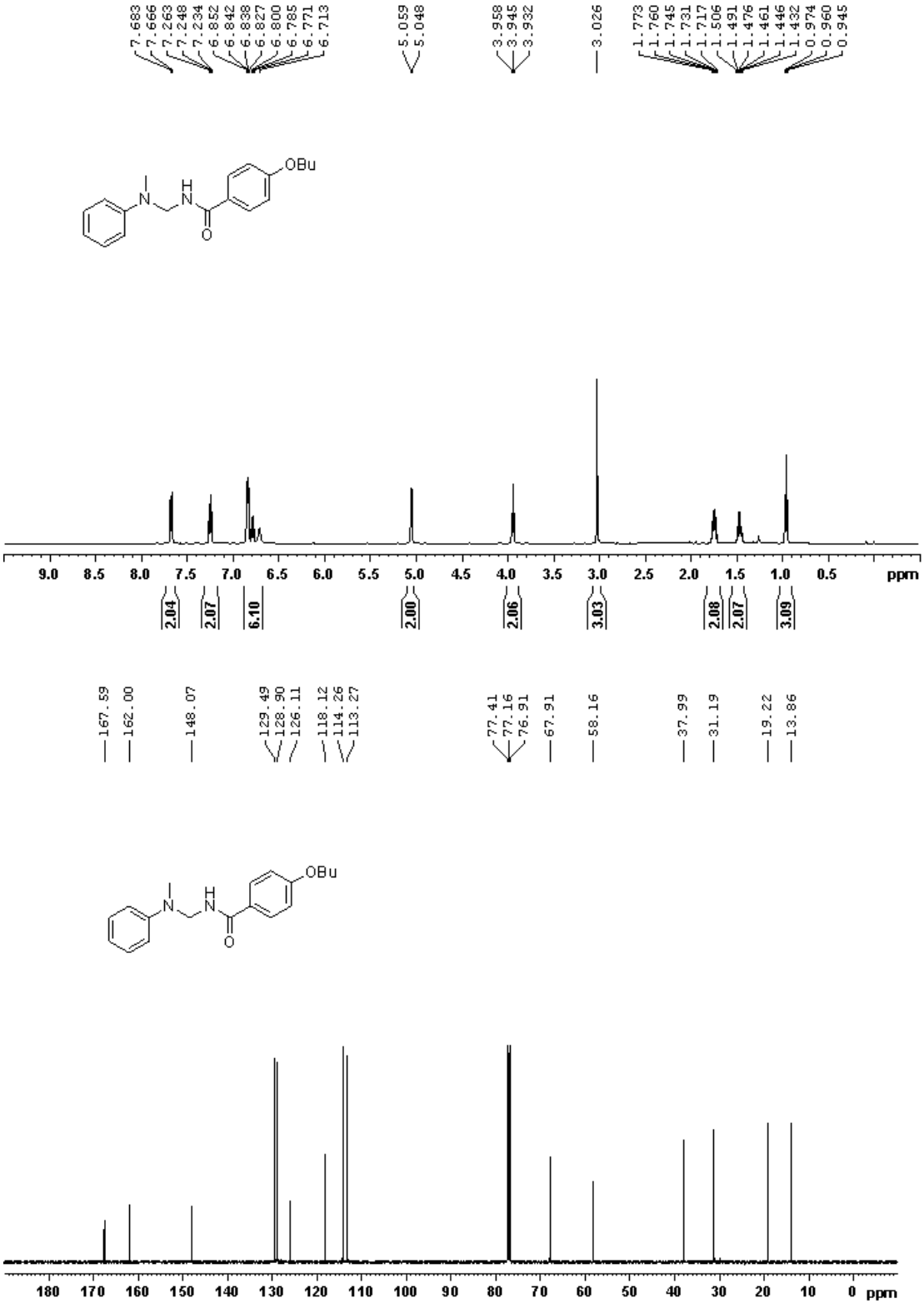

Cl
N
H
N
O


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

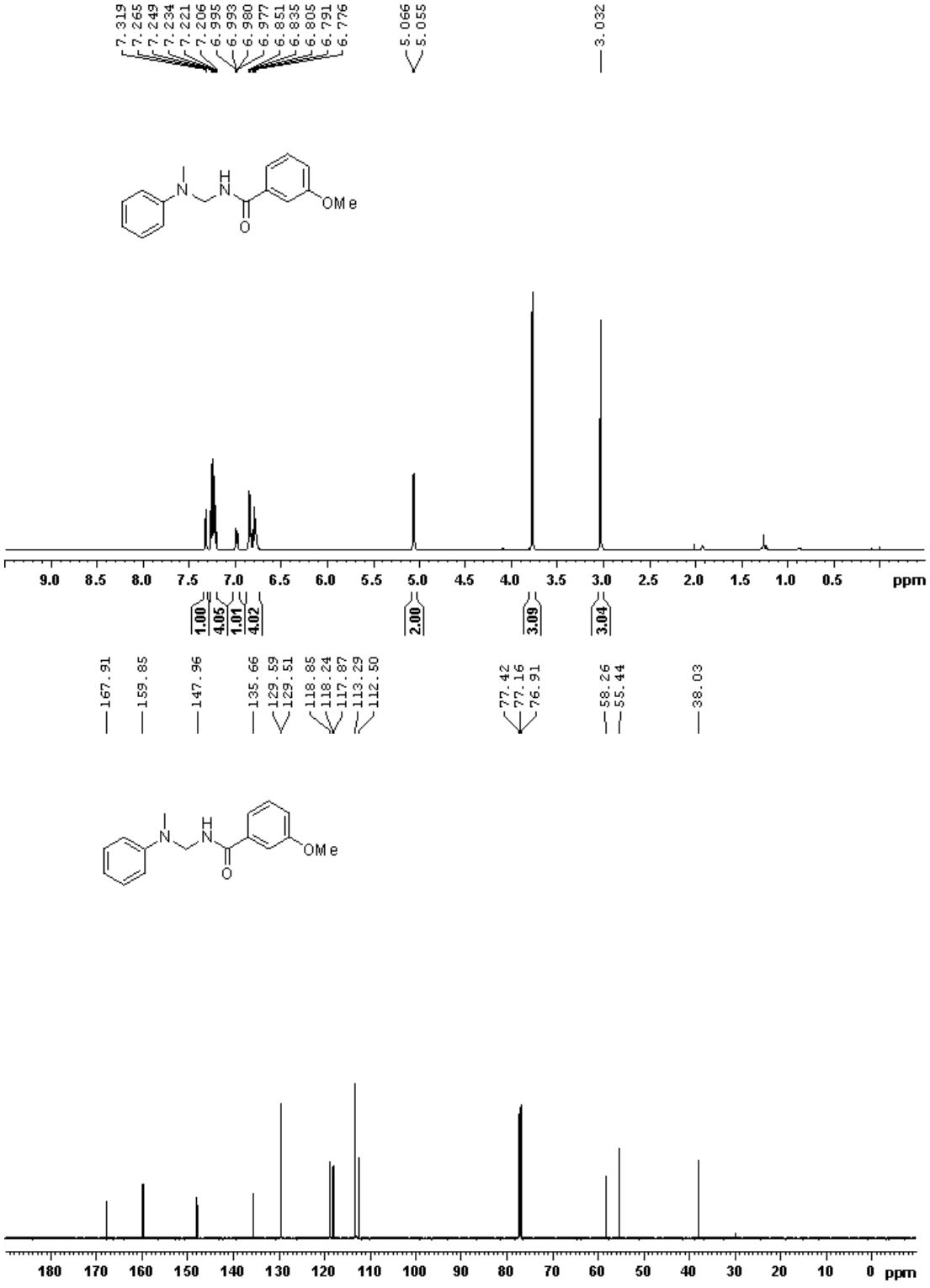
3e


7.585
7.575
7.572
7.568
7.532
7.528
7.524
7.515
7.511
7.293
7.288
7.283
7.278
7.275
7.270
7.265
7.260
7.254
6.859
6.843
6.842
6.837
6.835
6.820
6.807
6.806
6.589
5.099
5.088
3.054
Br
N
H
N
O
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 ppm
2.10
2.07
2.03
3.09
1.00
2.00
3.00
167.11
147.90
133.04
131.99
131.93
129.66
128.73
126.54
118.49
113.36
77.41
77.16
76.90
58.44
38.16
Br
N
H
N
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

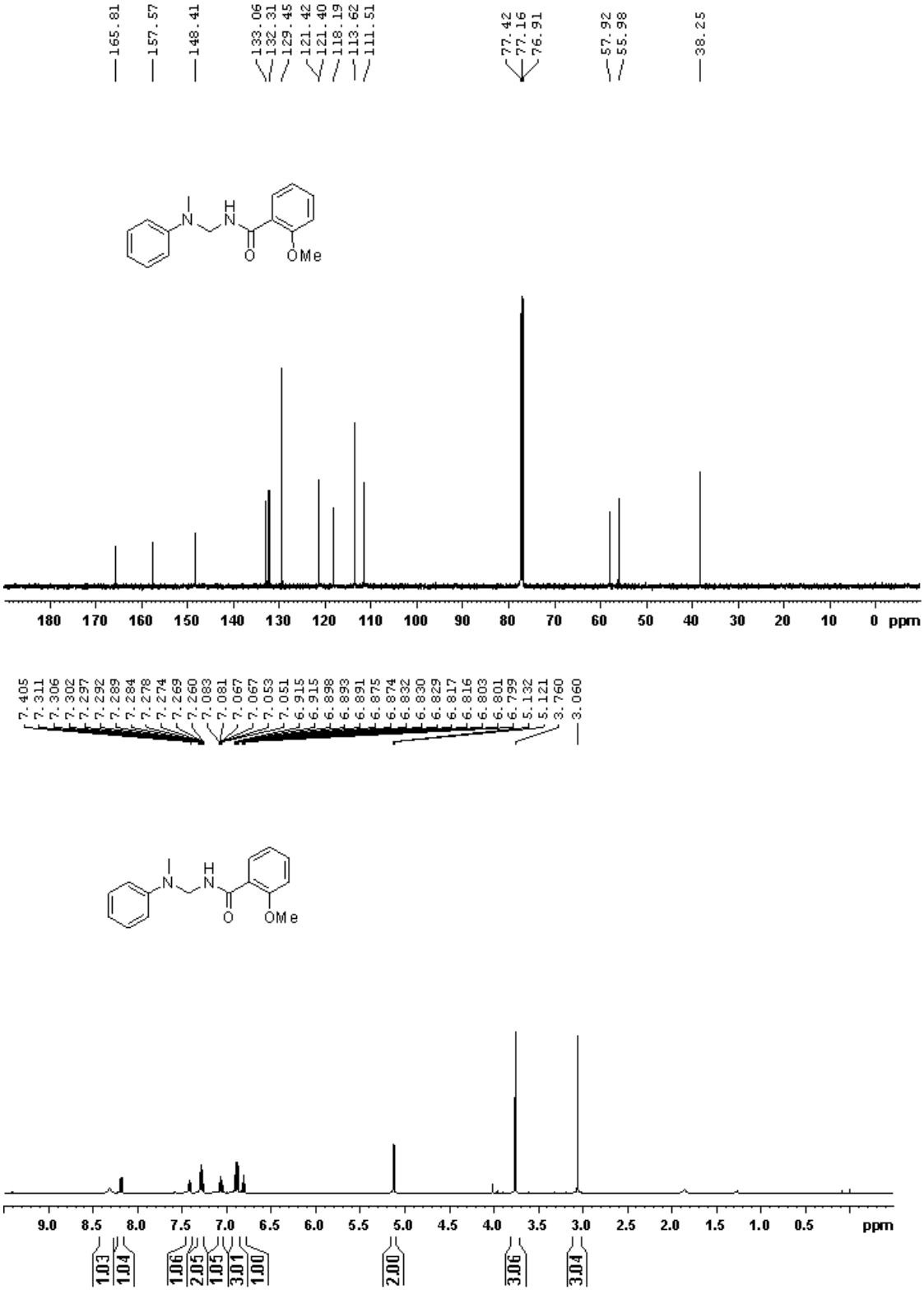
3f


7.683
7.666
7.263
7.248
7.234
6.852
6.842
6.838
6.827
6.800
6.785
6.771
6.713
5.059
5.048
3.958
3.945
3.932
3.026
1.773
1.760
1.745
1.731
1.717
1.506
1.491
1.476
1.461
1.446
1.432
0.974
0.960
0.945
OBu
ppm
2.04
2.07
6.10
2.00
2.06
3.03
2.08
2.07
3.09
167.59
162.00
148.07
129.49
128.90
126.11
118.12
114.26
113.27
77.41
77.16
76.91
67.91
58.16
37.99
31.19
19.22
13.86

3h

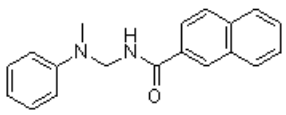

7.319
7.265
7.249
7.234
7.221
7.206
6.995
6.993
6.980
6.977
6.851
6.835
6.805
6.791
6.776
5.066
5.055
3.032
OMe
ppm
1.00
4.05
1.01
4.02
2.00
3.09
3.04
167.91
159.85
147.96
135.66
129.59
129.51
118.85
118.24
117.87
113.29
112.50
77.42
77.16
76.91
58.26
55.44
38.03

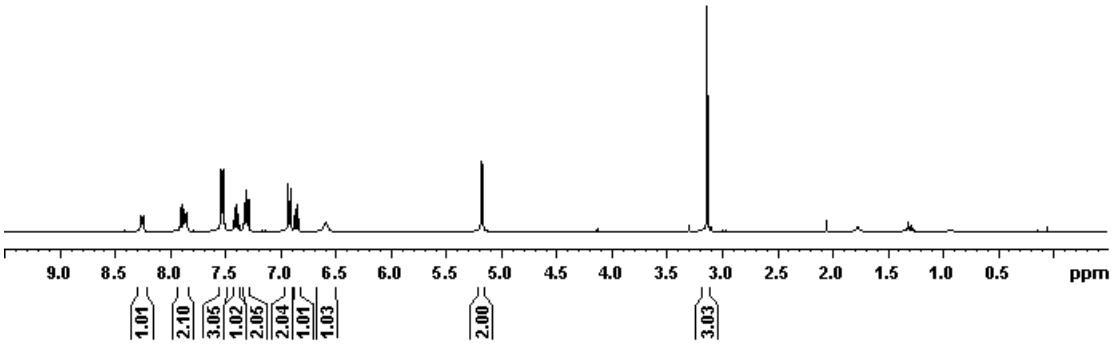
3i

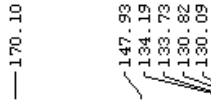

165.81
157.57
148.41
133.06
132.31
129.45
121.42
121.40
118.19
113.62
111.51
77.42
77.16
76.91
57.92
55.98
38.25
OMe
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
7.405
7.311
7.306
7.302
7.297
7.292
7.289
7.284
7.278
7.274
7.269
7.260
7.083
7.081
7.067
7.053
7.051
6.915
6.898
6.893
6.891
6.875
6.874
6.832
6.830
6.829
6.817
6.816
6.803
6.801
6.799
5.132
5.121
3.760
3.060
OMe
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 ppm
1.03
1.04
1.06
2.05
1.05
3.01
1.00
2.00
3.06
3.04

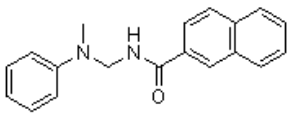
3j

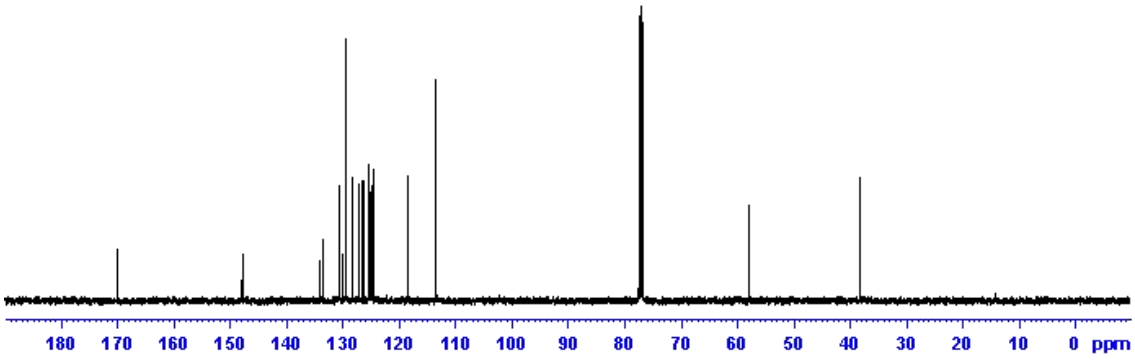

7.890
7.878
7.870
7.863
7.854
7.542
7.533
7.526
7.518
7.509
7.422
7.404
7.402
7.384
7.333
7.329
7.315
7.312
7.293
7.286
6.934
6.913
6.876
6.858
6.839
6.595
5.187
5.172
3.138



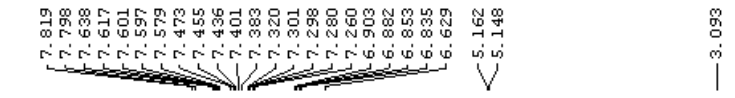

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.01
2.10
3.05
1.02
2.05
2.04
1.01
1.03
2.00
3.03

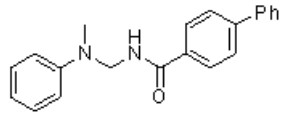

170.10
147.93
134.19
133.73
130.82
130.09
129.56
128.39
127.24
126.51
125.37
125.03
124.71
118.47
113.58
77.48
77.16
76.84
58.04
38.21

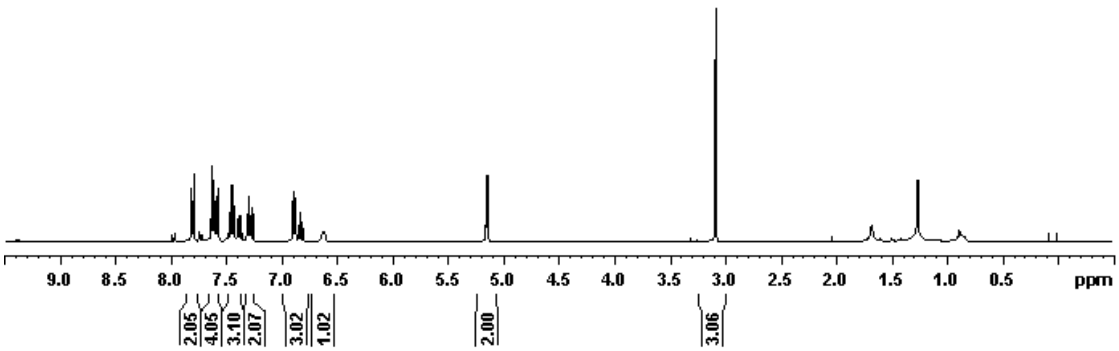



180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

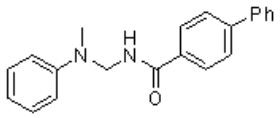
3k

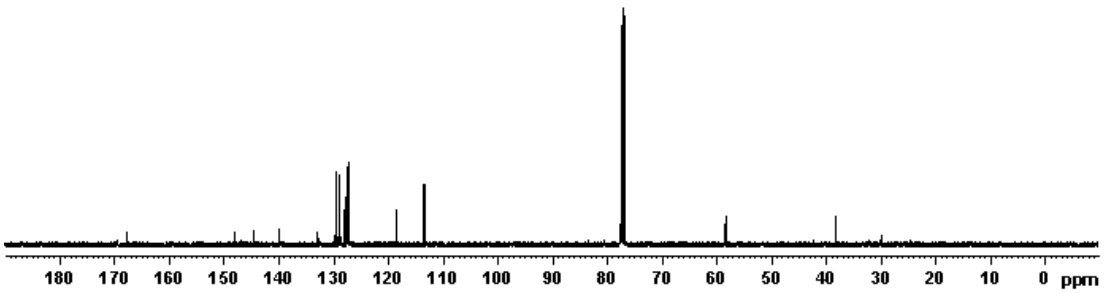

7.819
7.798
7.638
7.617
7.601
7.597
7.579
7.473
7.455
7.436
7.401
7.383
7.320
7.301
7.298
7.280
7.260
6.903
6.882
6.853
6.835
6.629
5.162
5.148
3.093


Ph
N
H
N
O

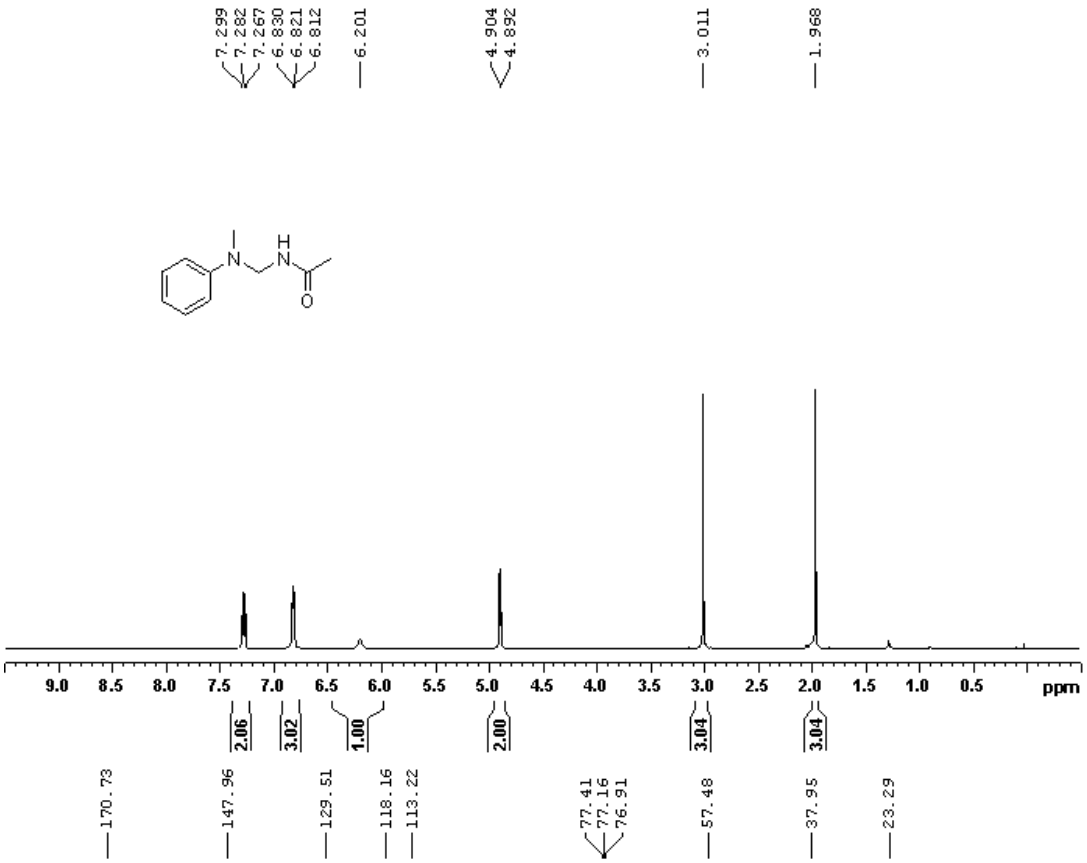

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.05
4.05
3.10
2.07
3.02
1.02
2.00
3.06

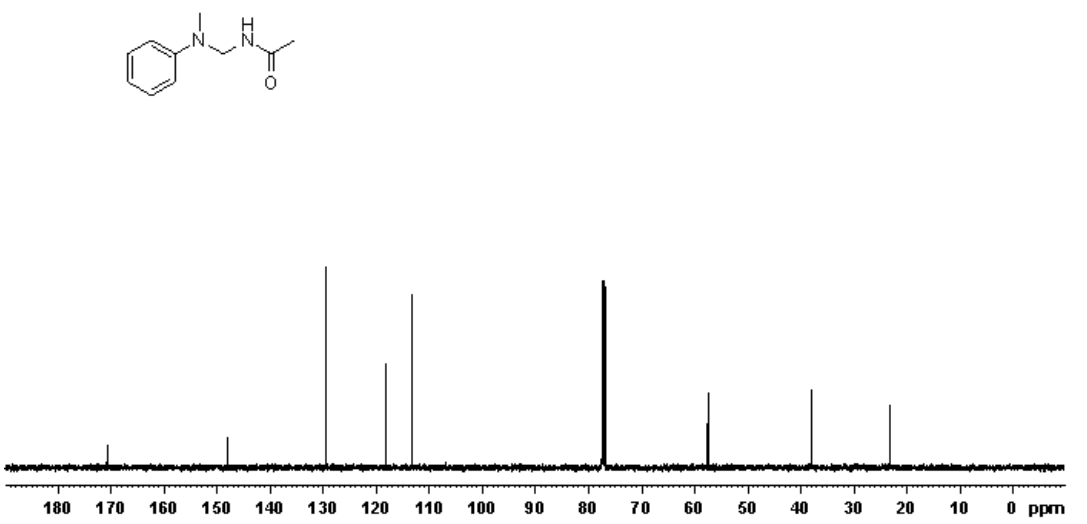

167.76
148.08
144.69
140.07
132.89
129.66
129.04
128.16
127.65
127.37
127.32
118.44
113.44
77.48
77.16
76.84
58.39
38.15


Ph
N
H
N
O

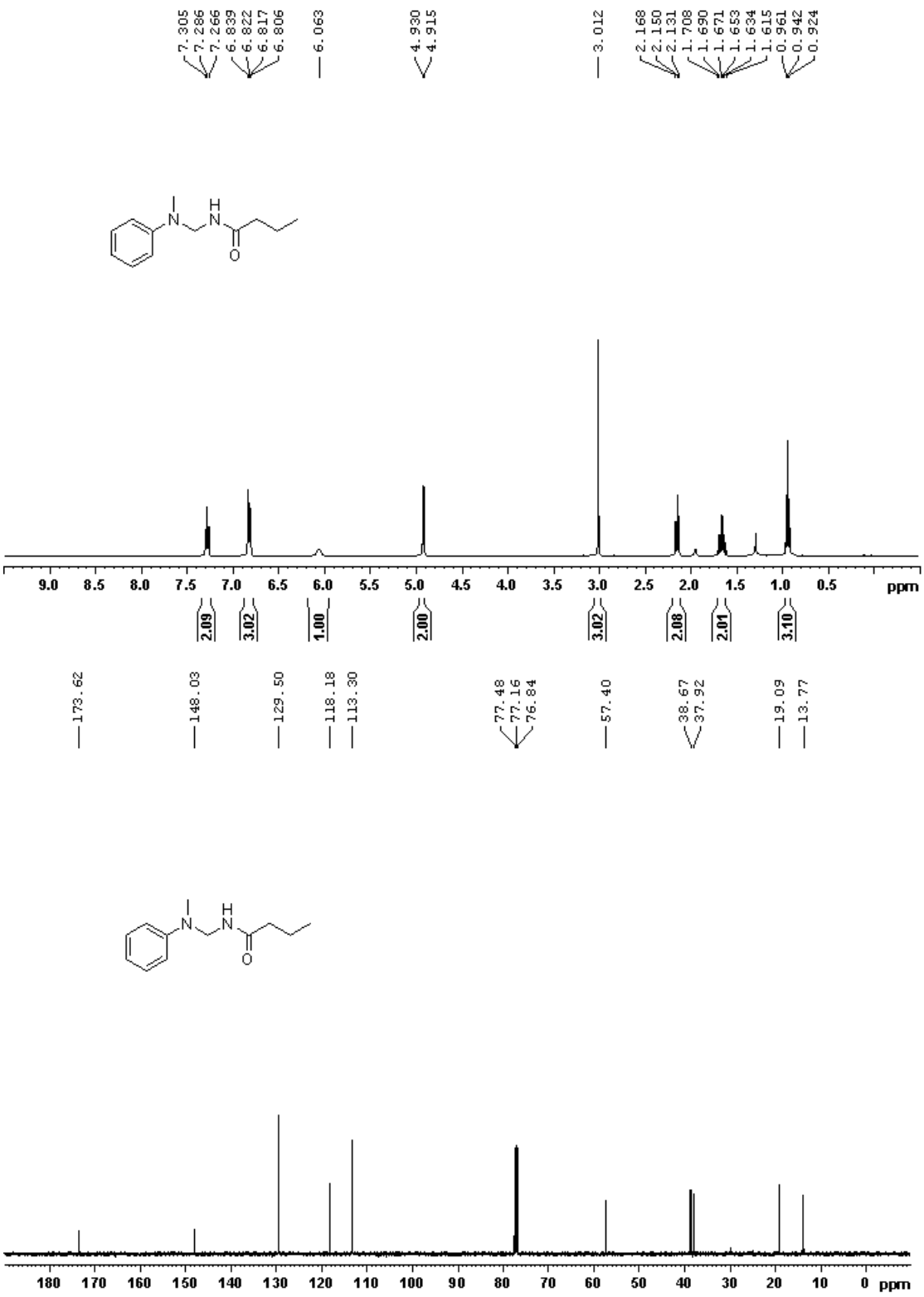

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

3l

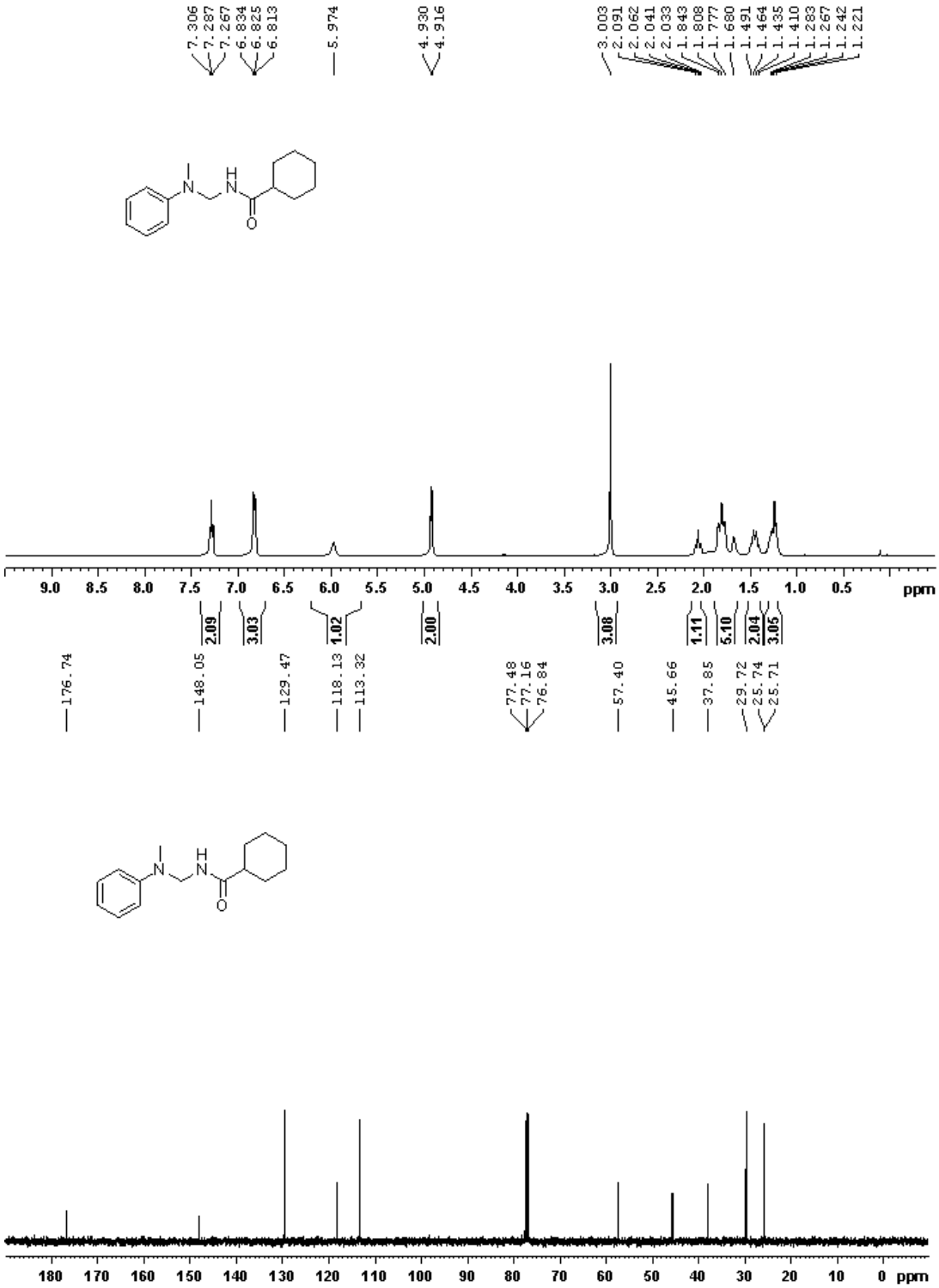

7.299
7.282
7.267
6.830
6.821
6.812
6.201
4.904
4.892
3.011
1.968
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.06
3.02
1.00
2.00
3.04
3.04


170.73
147.96
129.51
118.16
113.22
77.41
77.16
76.91
57.48
37.95
23.29
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

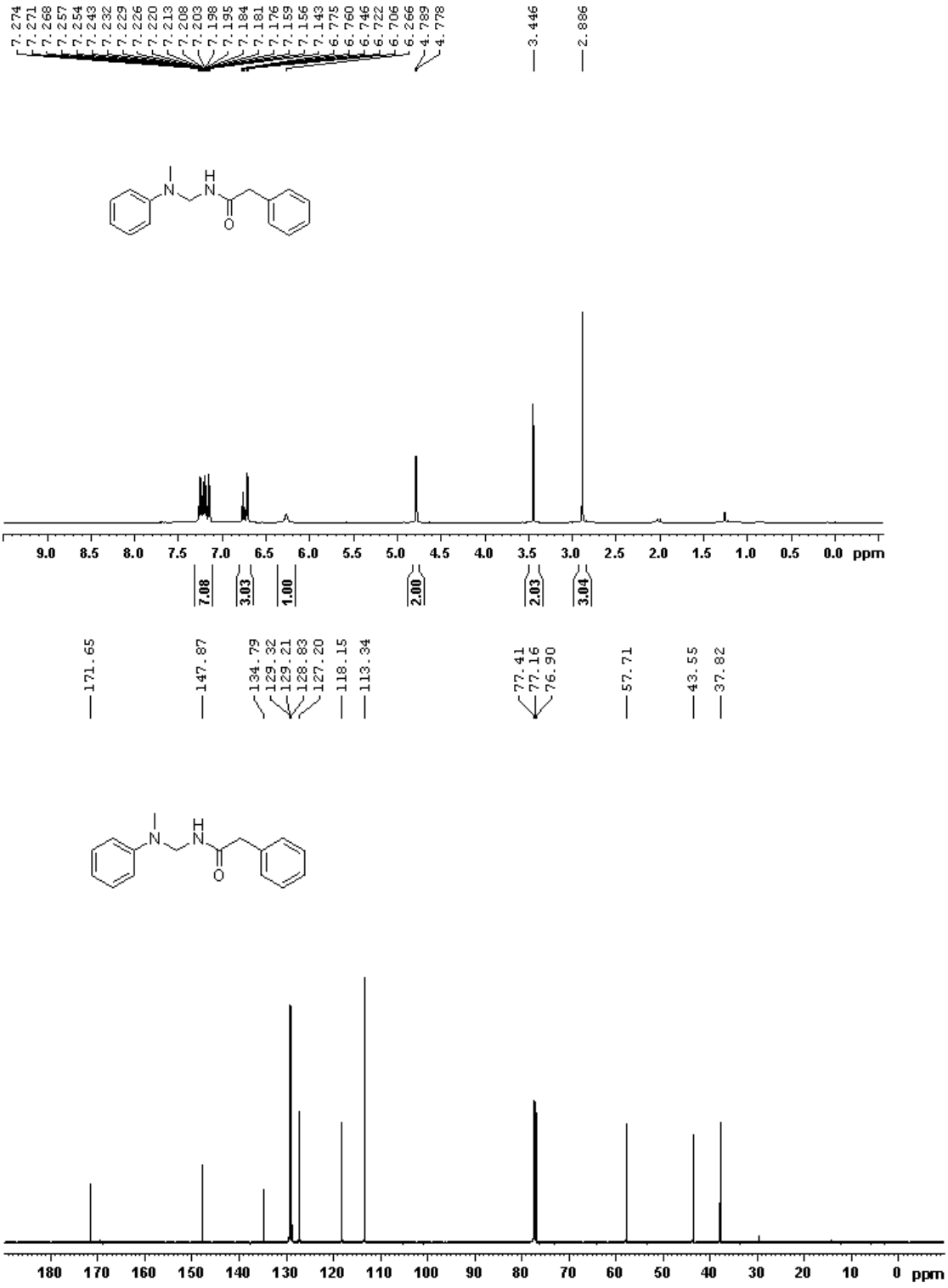
3m


7.305
7.286
7.266
6.839
6.822
6.817
6.806
6.063
4.930
4.915
3.012
2.168
2.150
2.131
1.708
1.690
1.671
1.653
1.634
1.615
0.961
0.942
0.924
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 ppm
2.09
3.02
1.00
2.00
3.02
2.08
2.01
3.10
173.62
148.03
129.50
118.18
113.30
77.48
77.16
76.84
57.40
38.67
37.92
19.09
13.77
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

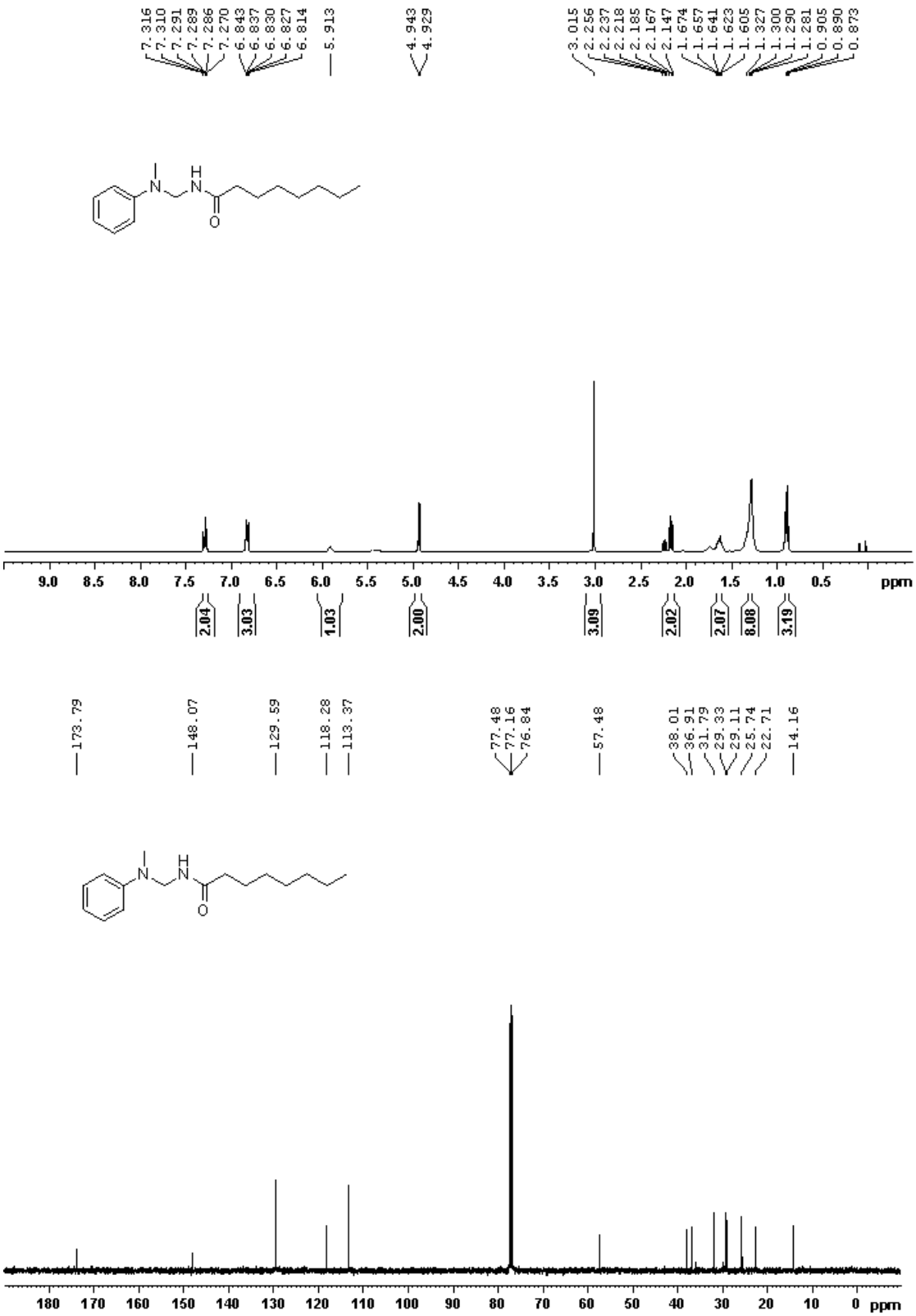
3n


7.306
7.287
7.267
6.834
6.825
6.813
5.974
4.930
4.916
3.003
2.091
2.062
2.041
2.033
1.843
1.808
1.777
1.680
1.491
1.464
1.435
1.410
1.283
1.267
1.242
1.221
ppm
2.09
3.03
1.02
2.00
3.08
1.11
5.10
2.04
3.05
176.74
148.05
129.47
118.13
113.32
77.48
77.16
76.84
57.40
45.66
37.85
29.72
25.74
25.71
ppm

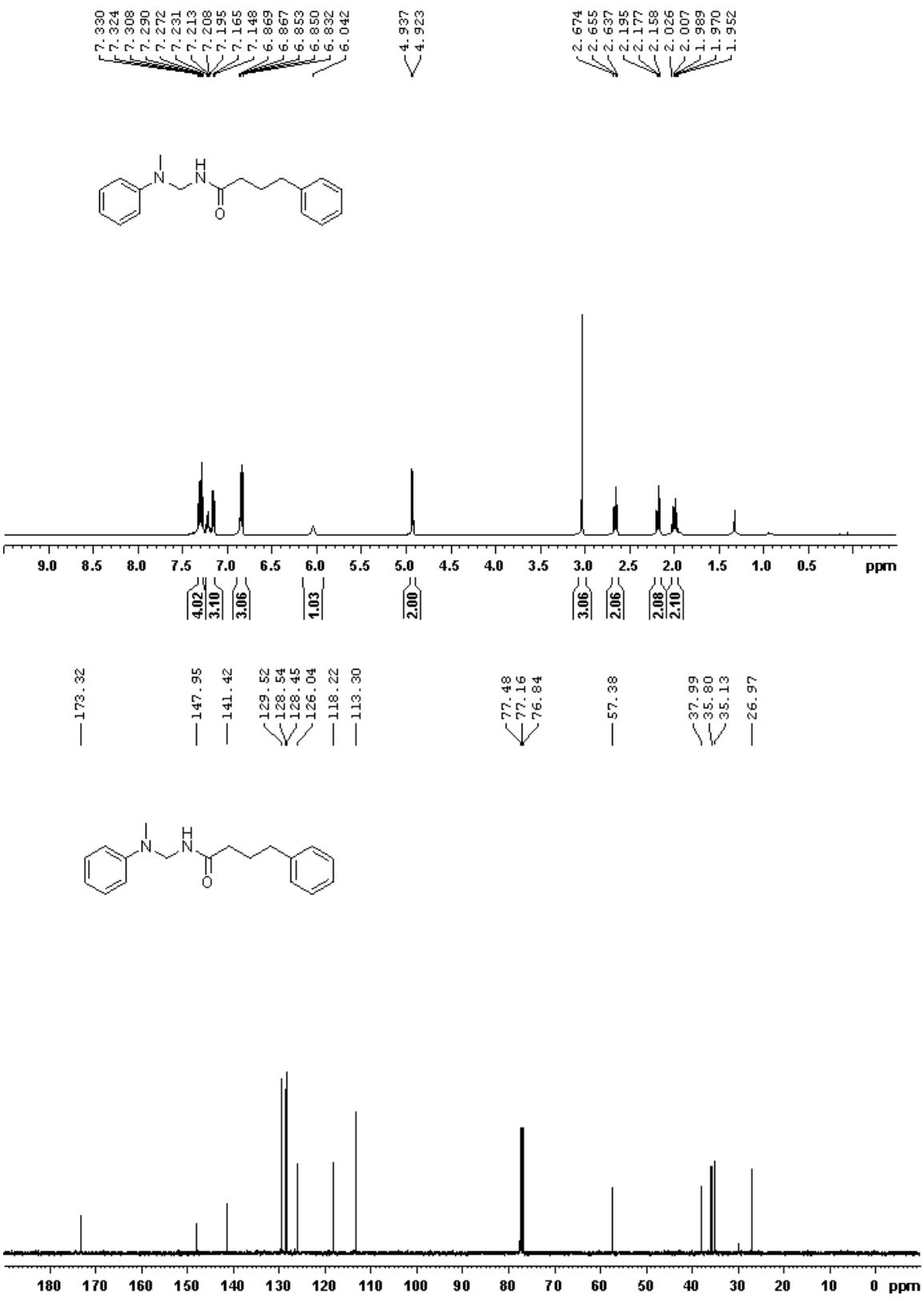
3o


7.274
7.271
7.268
7.257
7.254
7.243
7.232
7.229
7.226
7.220
7.213
7.208
7.203
7.198
7.195
7.184
7.181
7.176
7.159
7.156
7.143
6.775
6.760
6.746
6.722
6.706
6.266
4.789
4.778
3.446
2.886
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 ppm
7.08
3.03
1.00
2.00
2.03
3.04
171.65
147.87
134.79
129.32
129.21
128.83
127.20
118.15
113.34
77.41
77.16
76.90
57.71
43.55
37.82
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

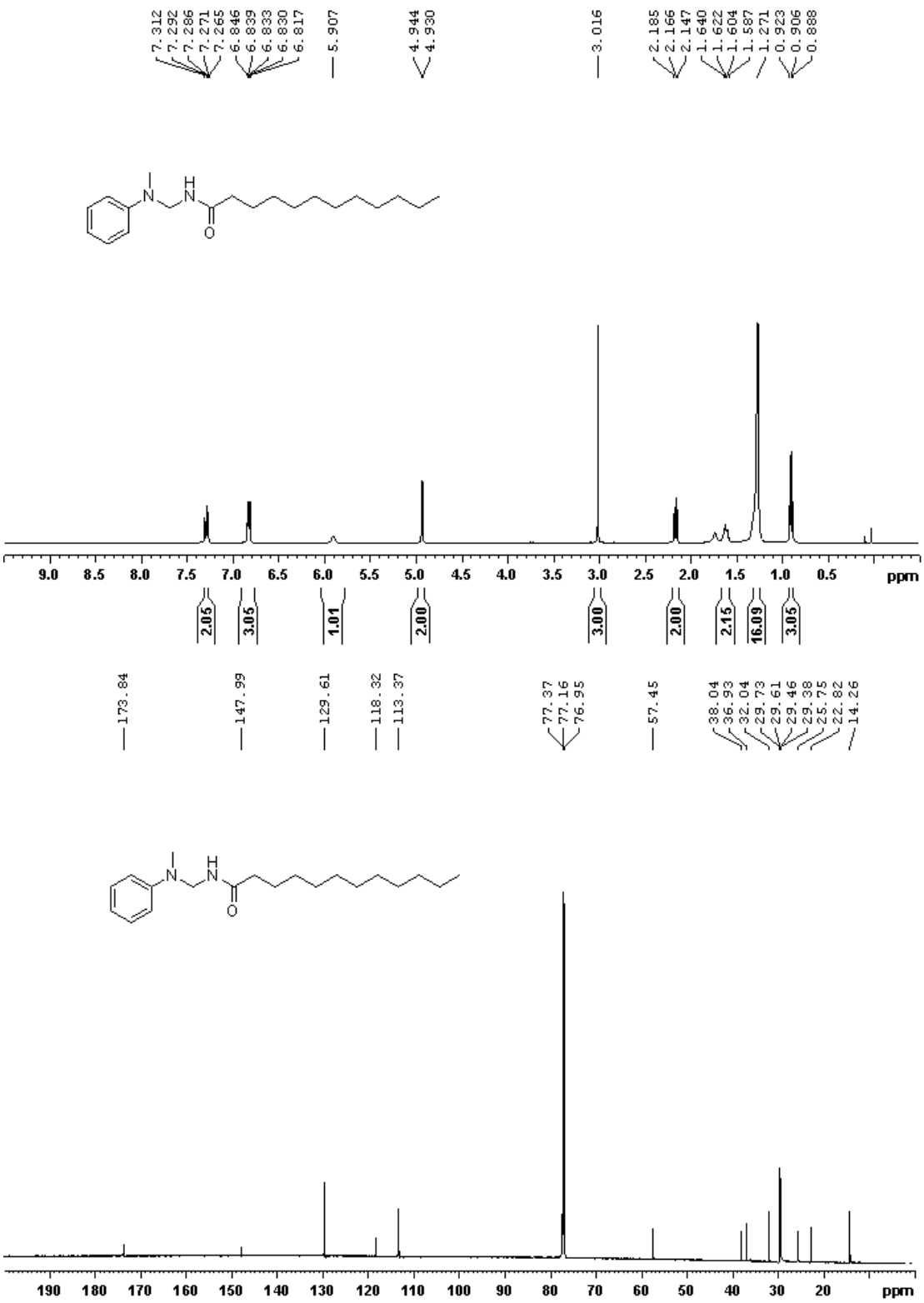
3q


7.316
7.310
7.291
7.289
7.286
7.270
6.843
6.837
6.830
6.827
6.814
5.913
4.943
4.929
3.015
2.256
2.237
2.218
2.185
2.167
2.147
1.674
1.657
1.641
1.623
1.605
1.327
1.300
1.290
1.281
0.905
0.890
0.873
ppm
2.04
3.03
1.03
2.00
3.09
2.02
2.07
8.08
3.19
173.79
148.07
129.59
118.28
113.37
77.48
77.16
76.84
57.48
38.01
36.91
31.79
29.33
29.11
25.74
22.71
14.16
ppm

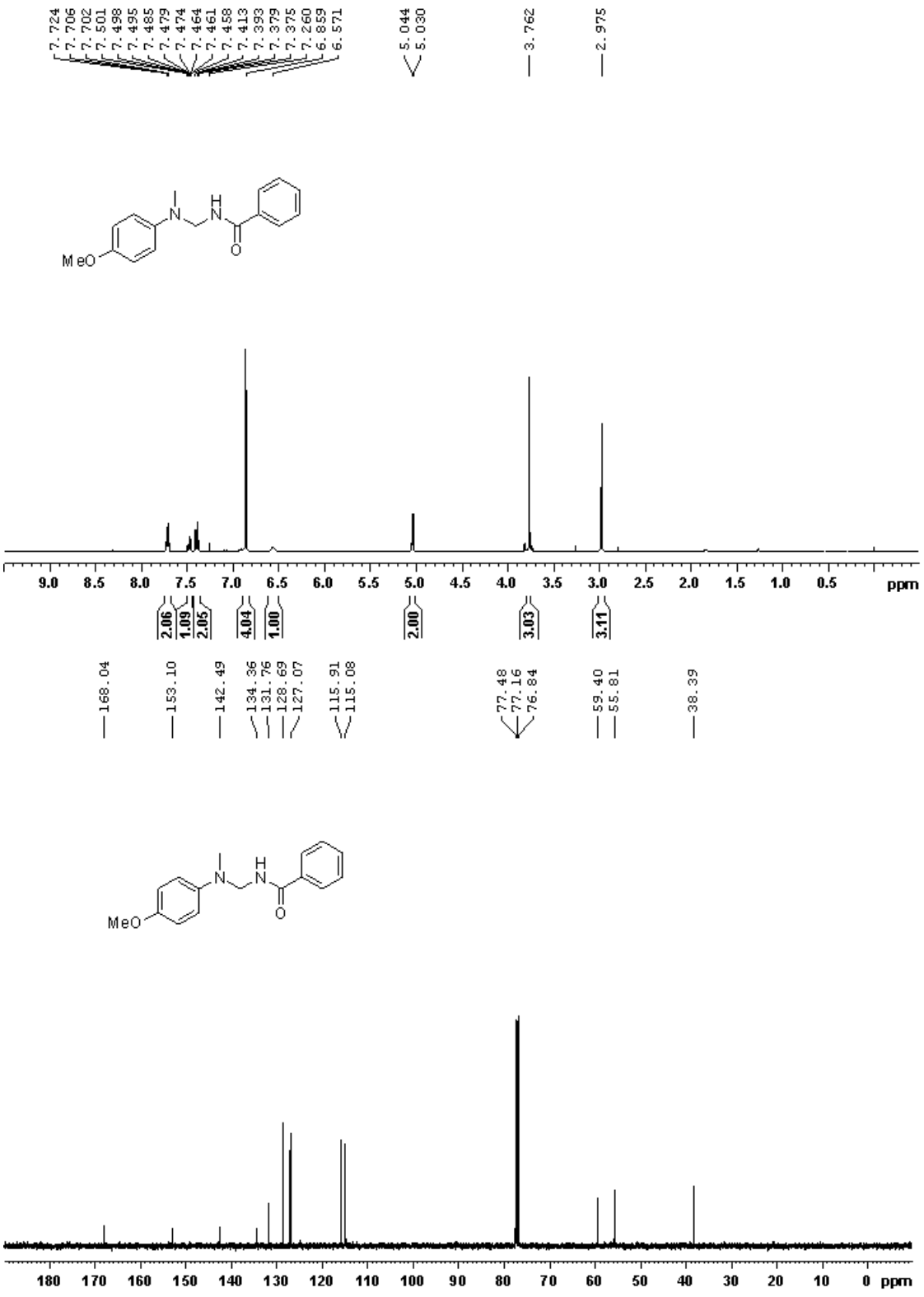
3p


7.330
7.324
7.308
7.290
7.272
7.231
7.213
7.208
7.195
7.165
7.148
6.869
6.867
6.853
6.850
6.832
6.042
4.937
4.923
2.674
2.655
2.637
2.195
2.177
2.158
2.026
2.007
1.989
1.970
1.952
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 ppm
4.02
3.10
3.06
1.03
2.00
3.06
2.06
2.08
2.10
173.32
147.95
141.42
129.52
128.54
128.45
126.04
118.22
113.30
77.48
77.16
76.84
57.38
37.99
35.80
35.13
26.97
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

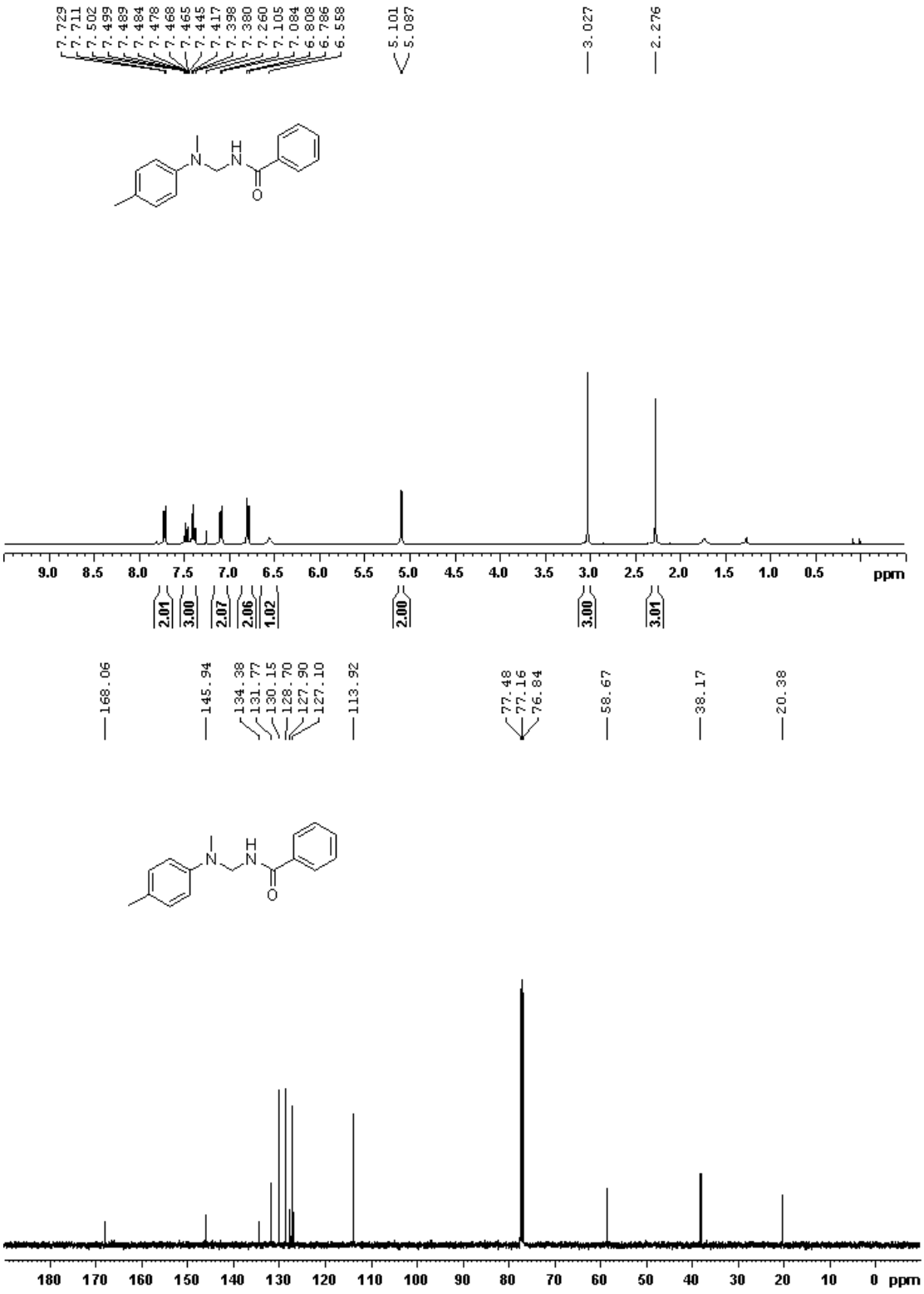
3r


7.312
7.292
7.286
7.271
7.265
6.846
6.839
6.833
6.830
6.817
5.907
4.944
4.930
3.016
2.185
2.166
2.147
1.640
1.622
1.604
1.587
1.271
0.923
0.906
0.888
ppm
2.05
3.05
1.01
2.00
3.00
2.00
2.15
16.09
3.05
173.84
147.99
129.61
118.32
113.37
77.37
77.16
76.95
57.45
38.04
36.93
32.04
29.73
29.61
29.46
29.38
25.75
22.82
14.26
ppm

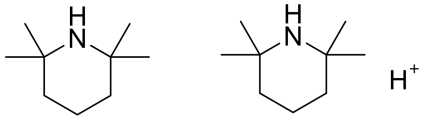
3s


7.724
7.706
7.702
7.501
7.498
7.495
7.485
7.479
7.474
7.464
7.461
7.458
7.413
7.393
7.379
7.375
7.260
6.859
6.571
5.044
5.030
3.762
2.975
MeO
ppm
2.06
1.09
2.05
4.04
1.00
2.00
3.03
3.11
168.04
153.10
142.49
134.36
131.76
128.69
127.07
115.91
115.08
77.48
77.16
76.84
59.40
55.81
38.39

3t


7.729
7.711
7.502
7.499
7.489
7.484
7.478
7.468
7.465
7.445
7.417
7.398
7.380
7.260
7.105
7.084
6.808
6.786
6.558
5.101
5.087
3.027
2.276
2.01
3.00
2.07
2.06
1.02
2.00
3.00
3.01
ppm
168.06
145.94
134.38
131.77
130.15
128.70
127.90
127.10
113.92
77.48
77.16
76.84
58.67
38.17
20.38
ppm

The *in situ* generation of 2,2,6,6-tetramethylpiperidine (TEMP, HRMS Calcd for $C_9H_{20}N^+$, $[M+H]^+$ 142.1590, found 142.1593) was proved using the HRMS (FT-ICR-MS) technique.



TEMP M+H$^+$

Chemical Formula: $C_9H_{20}N^+$

Exact Mass: 142.1590