

ELECTRONIC SUPPLEMENTARY INFORMATION

Palladium-catalyzed synthesis of 2-amino ketones from propargylic carbonates and secondary amines

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GENERAL INFORMATIONS

Reagents and methods: All the starting materials, catalysts, bases, solvents and eluents are commercially available and were used as purchased, without further purification. ^1H NMR (400.13 MHz), ^{13}C NMR (100.6 MHz) and ^{19}F spectra (376.5 MHz) were recorded with a Bruker Avance 400 spectrometer. Infrared spectra were recorded on a Jasco FT/IR-430 spectrophotometer. Melting points were determined with a Büchi B-545 apparatus and are uncorrected.

TYPICAL PROCEDURE FOR THE PREPARATION OF ETHYL PROPARGYL CARBONATES

Ethyl propargyl carbonates were prepared via Sonogashira cross-coupling of aryl iodides with propargyl alcohols. The isolated cross-coupling products were treated with ethyl chlorocarbonate to give the propargylic esters in 70-98% overall yield.

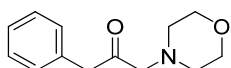
Typical procedure for the preparation of 3-*m*-tolylprop-2-yn-1-ol: A flask equipped with a magnetic stirring bar was charged with $\text{PdCl}_2(\text{PPh}_3)_2$ (0.017 mmol, 12.0 mg) and CuI (0.017 mmol, 3.2 mg) dissolved in diisopropylamine (1.8 ml) and *N,N*-dimethylformamide (0.9 ml). The resultant solution was stirred under Nitrogen at room temperature for 10 minutes before adding 3-iodotoluene (1.7 mmol, 372.8 mg) in *N*-ethyl-*N*-diisopropylamine (1.2 ml) and 2-propyn-1-ol (2.05 mmol, 115.0 mg, 119.4 μl). The reaction mixture was stirred for 3 hours at room temperature. After this time, the reaction mixture was diluted with Et_2O and washed with HCl 2N, with a saturated NH_4Cl solution and with brine. The organic layer was dried over Na_2SO_4 , filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel, eluting with a 73/27 (v/v) *n*-hexane/AcOEt mixture to obtain 211.0 mg (85% yield) of 3-*m*-tolylprop-2-yn-1-ol.

Typical procedure for the preparation of ethyl 3-*m*-tolylprop-2-ynyl carbonate: A flask equipped with a magnetic stirring bar was charged with 3-*m*-tolylprop-2-yn-1-ol (1.44 mmol, 210.5 mg) solved in CH_2Cl_2 (3 ml) and 4-(*N,N*-dimethylamino)pyridine (2.16 mmol, 263.9 mg). The resultant solution was stirred at -30°C for 10 minutes before adding ethyl chloroformate (1.73 mmol, 186.8 mg, 164.6 μl). The reaction mixture was stirred for 30 minutes at -30°C and then for an hour at 0°C . After this time, the reaction mixture was diluted with Et_2O and washed with HCl 2N and with brine. The organic layer was dried over Na_2SO_4 , filtered and concentrated under reduced pressure to obtain 308 mg (98% yield) of 3-*m*-tolylprop-2-ynyl carbonate.

TYPICAL PROCEDURE FOR THE PREPARATION OF 1-AMINO-3-ARYLPROPAN-2-ONES 3a - 3p

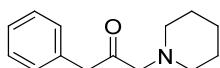
A Carousel Tube Reaction (Radley Discovery) was charged with Pd_2dba_3 (8.0 mg, 0.0087 mmol), dppf (9.7 mg, 0.0175 mmol) and anhydrous THF (1 ml). The solution was stirred under Nitrogen at room temperature for 10 minutes before adding ethyl 3-phenylprop-2-ynyl carbonate (71.4 mg, 0.350 mmol) dissolved in THF (1 ml) and morpholine (91.4 mg, 1.05 mmol, 91.5 μl). The reaction mixture was warmed at 80°C and stirred for 3 hours. After cooling, the volatile materials were evaporated at reduced pressure and the residue was purified by chromatography on neutral aluminum oxide (Brockmann 1) [*n*-hexane/EtOAc 85/15 (v/v)] to afford 58.2 mg (76% yield) of the following compound:

3a



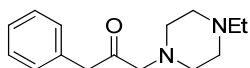
Oil; IR (neat) 3060, 3028, 2960, 2922, 2856, 1714, 1452, 1385 cm^{-1} ; ^1H NMR (400 MHz) (CDCl_3) δ 7.36-7.24 (m, 5 H), 3.76-3.74 (m, 6 H), 3.23 (s, 2 H), 2.47-2.46 (m, 4 H); ^{13}C NMR (100.6 MHz) (CDCl_3) δ 205.8, 134.0, 129.4, 128.8, 127.1, 67.0, 66.8, 53.7, 47.8; Anal. Calcd. for $\text{C}_{13}\text{H}_{17}\text{NO}_2$: C, 71.21; H, 7.81; N, 6.39; Found: C, 71.13; H, 7.83; N, 6.36.

3b



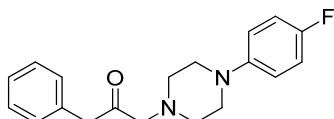
Oil; IR (Neat) 3060, 3028, 2935, 2854, 2804, 1714, 1597, 1574, 1454, 1385 cm^{-1} ; ^1H NMR (400 MHz) (CDCl_3) δ 7.35-7.32 (m, 2 H), 7.28-7.25 (m, 3 H), 3.78 (s, 2 H), 3.17 (s, 2 H), 2.40-2.39 (m, 4 H), 1.66-1.61 (m, 4 H), 1.46-1.45 (m, 2 H); ^{13}C NMR (100.6 MHz) (CDCl_3) δ 207.0, 134.3, 129.4, 128.6, 126.9, 67.7, 54.7, 47.5, 25.8, 23.8; Anal. Calcd. for $\text{C}_{14}\text{H}_{19}\text{NO}$: C, 77.38; H, 8.81; N, 6.45; Found: C, 77.44; H, 8.78; N, 6.47.

3c



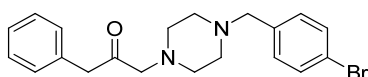
Oil; IR (Neat) 3060, 3028, 2970, 2933, 2812, 1720, 1454, 1385 cm^{-1} ; ^1H NMR (400 MHz) (CDCl_3) δ 7.32-7.21 (m, 5 H), 3.73 (s, 2 H), 3.20 (s, 2 H), 2.50 (m, 8 H), 2.42 (q, $J = 7.2$ Hz, 2 H), 1.07 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (100.6 MHz) (CDCl_3) δ 206.2, 134.1, 129.4, 128.7, 127.0, 66.8, 53.4, 52.6, 52.3, 47.7, 12.0; Anal. Calcd. for $\text{C}_{15}\text{H}_{22}\text{N}_2\text{O}$: C, 73.13; H, 9.00; N, 11.37; Found: C, 73.35; H, 9.02; N, 11.36.

3d



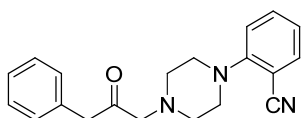
Oil; IR (Neat) 3060, 3030, 2931, 2821, 1722, 1510, 1454, 1385, 1232 cm^{-1} ; ^1H NMR (400 MHz) (CDCl_3) δ 7.37-7.26 (m, 5 H), 7.00-6.96 (m, 2 H), 6.90-6.87 (m, 2 H), 3.79 (s, 2 H), 3.30 (s, 2 H), 3.18-3.16 (m, 4 H), 2.65-2.63 (m, 4 H); ^{13}C NMR (100.6 MHz) (CDCl_3) δ 205.9, 157.2 (d, $J_{\text{CF}} = 237.4$ Hz), 147.9 (d, $J_{\text{CF}} = 2.1$ Hz), 134.0, 129.4, 128.7, 127.1, 117.9 (d, $J_{\text{CF}} = 7.6$ Hz), 115.5 (d, $J_{\text{CF}} = 21.9$ Hz), 66.6, 53.3, 50.0, 47.8; ^{19}F NMR {H} (376.5 MHz) (CDCl_3) δ -124.3; Anal. Calcd. for $\text{C}_{19}\text{H}_{21}\text{FN}_2\text{O}$: C, 73.05; H, 6.78; N, 8.97; Found: C, 73.06; H, 6.77; N, 8.95.

3e



Oil; IR (Neat) 3060, 3028, 2935, 2812, 1720, 1487, 1454, 1011 cm^{-1} ; ^1H NMR (400 MHz) (CDCl_3) δ 7.44 (d, $J = 8.1$ Hz, 2 H), 7.34-7.31 (m, 2 H), 7.28-7.19 (m, 5 H), 3.75 (s, 2 H), 3.46 (s, 2 H), 3.22 (s, 2 H), 2.49 (bs, 8 H); ^{13}C NMR (100.6 MHz) (CDCl_3) δ 206.2, 137.3, 134.1, 131.4, 130.8, 129.5, 128.7, 127.1, 120.9, 66.8, 62.2, 53.4, 52.9, 47.7; Anal. Calcd. for $\text{C}_{20}\text{H}_{23}\text{BrN}_2\text{O}$: C, 62.02; H, 5.99; N, 7.23; Found: C, 62.15; H, 6.01; N, 7.25.

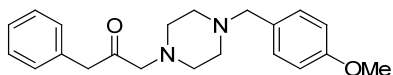
3f



Oil; IR (Neat) 3062, 3030, 2916, 2825, 2220, 1716, 1595, 1489, 1448, 1383, 1230 cm^{-1} ; ^1H NMR (400 MHz) (CDCl_3) δ 7.56 (d, $J = 7.9$ Hz, 1 H), 7.49 (t, $J = 7.8$ Hz, 1 H), 7.36-7.25 (m, 5 H), 7.03-7.00 (m, 2 H), 3.77 (s, 2 H), 3.33 (s, 2 H), 3.28-3.26 (m, 4 H), 2.70-2.67 (m, 4 H); ^{13}C NMR (100.6 MHz) (CDCl_3) δ 205.6, 155.6,

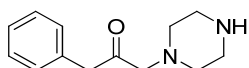
134.3, 133.9, 133.8, 129.4, 128.8, 127.1, 121.9, 118.7, 118.4, 106.1, 66.5, 53.3, 51.3, 47.8; Anal. Calcd. for $C_{20}H_{21}N_3O$: C, 75.21; H, 6.63; N, 13.16; Found: C, 75.26; H, 6.64; N, 13.13.

3g



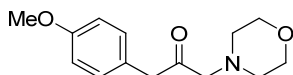
Oil; IR (Neat) 3060, 3030, 2933, 2810, 1720, 1612, 1512, 1454, 1246 cm^{-1} ; 1H NMR (400 MHz) ($CDCl_3$) δ 7.35-7.23 (m, 7 H), 6.87 (d, $J = 8.3$ Hz, 2 H), 3.81 (s, 3 H), 3.75 (s, 2 H), 3.47 (s, 2 H), 3.21 (s, 2 H), 2.50 (bs, 8 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$) δ 206.3, 158.8, 134.2, 130.4, 130.1, 129.5, 128.7, 127.0, 113.6, 66.8, 62.4, 55.3, 53.4, 52.8, 47.7; Anal. Calcd. for $C_{21}H_{26}N_2O_2$: C, 74.52; H, 7.74; N, 8.28 Found: C, 74.42; H, 7.71; N, 8.29.

3h



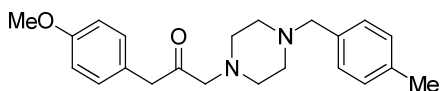
Oil; IR (Neat) 3060, 3028, 2815, 1716, 1496, 1455, 1270, 1008, 732, 701 cm^{-1} ; 1H NMR (400 MHz) ($CDCl_3$) δ 7.33-7.22(m, 5 H), 3.75 (s, 2 H), 3.17 (s, 2 H), 2.90 (bs, 4 H), 2.41 (bs, 4 H), 2.04 (bs, 1 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$) δ 206.3, 134.1, 129.4, 128.6, 127.0, 67.3, 54.5, 47.6, 45.8; Anal. Calcd. for C, 71.53; H, 8.31; N, 12.83; Found: C, 71.43; H, 8.30; N, 12.81;

3i



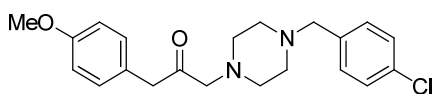
Oil; IR (Neat) 2918, 2852, 1722, 1610, 1512, 1454, 1248, 1117 cm^{-1} ; 1H NMR (400 MHz) ($CDCl_3$) δ 7.16 (d, $J = 8.4$ Hz, 2 H), 6.87 (d, $J = 8.5$ Hz, 2 H), 3.80 (s, 3 H), 3.75-3.73 (m, 4 H), 3.68 (s, 2 H), 3.21 (s, 2 H), 2.47-2.45 (m, 4 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$) δ 206.1, 158.7, 130.4, 125.9, 114.2, 66.80, 66.77, 55.2, 53.6, 46.9; Anal. Calcd. for $C_{14}H_{19}NO_3$: C, 67.45; H, 7.68; N, 5.62; Found: C, 67.57; H, 7.70; N, 5.64.

3j



Wax; IR (KBr) 2933, 2810, 1716, 1510, 1246 cm^{-1} ; 1H NMR (400 MHz) ($CDCl_3$) δ 7.21 (d, $J = 7.7$ Hz, 2 H), 7.17-7.13 (m, 4 H), 6.87 (d, $J = 8.4$ Hz, 2 H), 3.81 (s, 3 H), 3.68 (s, 2 H), 3.51 (s, 2 H), 3.20 (s, 2 H), 2.52-2.50 (m, 8 H), 2.35 (s, 3 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$) δ 206.6, 158.7, 136.7, 134.7, 130.4, 129.3, 128.9, 126.2, 114.2, 66.6, 62.7, 55.3, 53.3, 52.8, 46.8, 21.1; Anal. Calcd. for $C_{22}H_{28}N_2O_2$: C, 74.97; H, 8.01; N, 7.95; Found: C, 74.81; H, 7.99; N, 7.93.

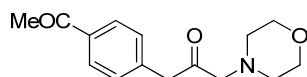
3k



Oil; IR (Neat) 2935, 2812, 1720, 1610, 1512, 1456, 1248 cm^{-1} ; 1H NMR (400 MHz) ($CDCl_3$) δ 7.30-7.25 (m, 4 H), 7.15 (d, $J = 8.3$ Hz, 2 H), 6.86 (d, $J = 8.4$ Hz, 2 H), 3.80 (s, 3 H), 3.68 (s, 2 H), 3.49 (s, 2 H), 3.21 (s, 2 H), 2.50 (bs, 8 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$) δ 206.5, 158.7, 136.7, 132.8, 130.4, 128.4, 126.1, 114.2,

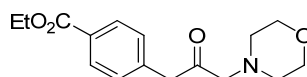
66.6, 62.2, 55.3, 53.3, 52.9, 46.8; Anal. Calcd. for $C_{21}H_{25}ClN_2O_2$: C, 67.64; H, 6.76; N, 7.51; Found: C, 67.73; H, 6.77; N, 7.53;

3l



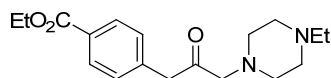
Oil; IR (Neat) 2922, 2856, 1724, 1680, 1606, 1452, 1385, 1269, 1115 cm^{-1} ; 1H NMR (400 MHz) ($CDCl_3$) δ 7.91 (d, $J = 8.0$ Hz, 2 H), 7.32 (d, $J = 8.0$ Hz, 2 H), 3.83 (s, 2 H), 3.73-3.71 (m, 4 H), 3.21 (s, 2 H), 2.58 (s, 3 H), 2.47-2.44 (m, 4 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$) δ 204.9, 197.5, 139.3, 136.0, 129.7, 128.7, 67.4, 66.7, 53.7, 47.3, 26.5; Anal. Calcd. for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33; N, 5.36; Found: C, 68.85; H, 7.33; N, 5.34;

3m



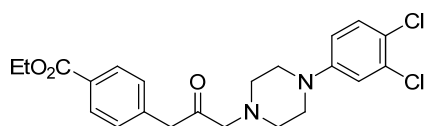
Oil; IR (Neat) 2978, 2925, 2856, 1712, 1610, 1448, 1385, 1275 cm^{-1} ; 1H NMR (400 MHz) ($CDCl_3$) δ 7.99 (d, $J = 8.1$ Hz, 2 H), 7.29 (d, $J = 8.0$ Hz, 2 H), 4.35 (q, $J = 7.1$ Hz, 2 H), 3.80 (s, 2 H), 3.72-3.70 (m, 4 H), 3.19 (s, 2 H), 2.45-2.42 (m, 4 H), 1.37 (t, $J = 7.1$ Hz, 3 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$) δ 205.0, 166.3, 139.0, 129.9, 129.5, 129.4, 67.3, 66.8, 61.0, 53.7, 47.5, 14.3; Anal. Calcd. for $C_{16}H_{21}NO_4$: C, 65.96; H, 7.27; N, 4.81; Found: C, 65.59; H, 7.30; N, 4.83.

3n



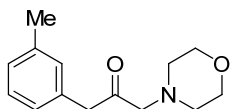
Oil; IR (Neat) 2974, 2931, 2816, 1716, 1452, 1385, 1277, 1105 cm^{-1} ; 1H NMR (400 MHz) ($CDCl_3$) δ 7.96 (d, $J = 8.1$ Hz, 2 H), 7.27 (d, $J = 8.1$ Hz, 2 H), 4.33 (q, $J = 7.1$ Hz, 2 H), 3.83 (s, 2 H), 3.22 (s, 2 H), 2.54 (bs, 8 H), 2.46 (q, $J = 7.2$ Hz, 2 H), 1.40 (t, $J = 7.1$ Hz, 3 H), 1.11 (t, $J = 7.1$ Hz, 3 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$) δ 205.5, 166.3, 139.2, 129.8, 129.5, 129.3, 67.1, 60.9, 53.4, 52.5, 52.2, 47.3, 14.3, 11.9; Anal. Calcd. for $C_{18}H_{26}N_2O_3$: C, 67.90; H, 8.23; N, 8.80; Found: C, 67.81; H, 8.21; N, 8.78;

3o



Oil; IR (Neat) 2979, 2933, 2827, 1714, 1593, 1483, 1452, 1385, 1277 cm^{-1} ; 1H NMR (400 MHz) ($CDCl_3$) δ 8.01 (d, $J = 8.2$ Hz, 2 H), 7.31 (d, $J = 8.1$ Hz, 2 H), 7.25 (d, $J = 8.9$ Hz, 1 H), 6.93 (d, $J = 2.7$ Hz, 1 H), 6.71 (dd, $J^1 = 8.9$ Hz, $J^2 = 2.7$ Hz, 1 H), 4.37 (q, $J = 7.1$ Hz, 2 H), 3.84 (s, 2 H), 3.28 (s, 2 H), 3.21-3.19 (m, 4 H), 2.62-2.59 (m, 4 H), 1.40 (t, $J = 7.1$ Hz, 3 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$) δ 205.0, 166.3, 150.5, 139.0, 132.8, 130.5, 129.9, 129.5, 122.3, 117.3, 115.4, 66.8, 61.0, 53.0, 48.5, 47.5, 14.4; Anal. Calcd. for $C_{22}H_{24}Cl_2N_2O_3$: C, 60.70; H, 5.56; N, 6.43; Found: C, 60.81; H, 5.57; N, 6.45.

3p

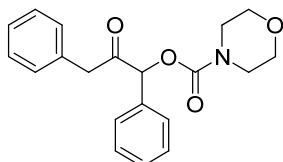


Oil; IR (Neat) 2958, 2920, 2854, 2812, 1720, 1606, 1452, 1385, 1117 cm^{-1} ; ^1H NMR (400 MHz) (CDCl_3) δ 7.22 (t, $J = 7.5$ Hz, 1 H), 7.10-7.03 (m, 3 H), 3.75-3.73 (m, 4 H), 3.71 (s, 2 H), 3.22 (s, 2 H), 2.47-2.45 (m, 4 H), 2.35 (s, 3 H); ^{13}C NMR (100.6 MHz) (CDCl_3) δ 205.9, 138.4, 133.9, 130.2, 128.7, 127.9, 126.4, 66.9, 66.8, 53.7, 47.8, 21.4; Anal. Calcd. for $\text{C}_{14}\text{H}_{19}\text{NO}_2$: C, 72.07; H, 8.21; N, 6.00; Found: C, 72.19; H, 8.24; N, 5.98.

TYPICAL PROCEDURE FOR THE PREPARATION OF 2-OXO-1,3-DIPHENYLPROPYLAMINO-4-CARBOXYLATES 7a, 7q – 7t

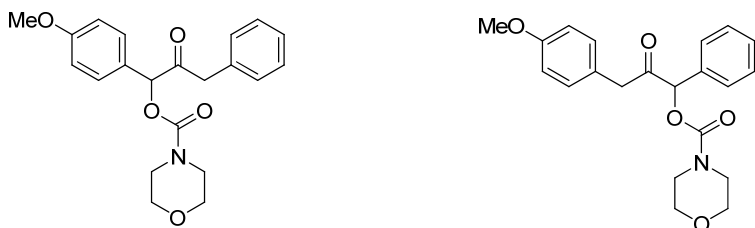
A Carousel Tube Reaction (Radley Discovery) was charged with Pd₂dba₃ (7.8 mg, 0.0085 mmol), dppf (9.4 mg, 0.0170 mmol) and anhydrous THF (1 ml). The resultant solution was stirred under Nitrogen at room temperature for 10 minutes before adding 1,3-diphenylprop-2-ynyl ethyl carbonate (95.0 mg, 0.34 mmol) dissolved in THF (1 ml) and morpholine (88.7 mg, 1.02 mmol, 88.8 μl). The reaction mixture was warmed at 80°C and stirred for 1 hours. After cooling, the volatile materials were evaporated at reduced pressure and the residue was purified by chromatography on silica gel eluting with a 70/30 (v/v) n-hexane/AcOEt mixture to afford 76.7 mg (77% yield) of the following compound:

7a



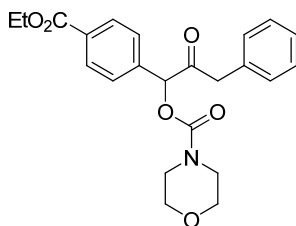
Mp: 132-134 °C; IR (KBr) 3066, 2974, 2904, 2860, 1732, 1714, 1431, 1234, 1117 cm⁻¹; ¹H NMR (400 MHz) (CDCl₃) δ 7.41-7.23 (m, 8 H) 7.05-7.03 (m, 2 H), 6.09 (s, 1 H), 3.75-3.53 (m, 10 H); ¹³C NMR (100.6 MHz) (CDCl₃) δ 202.2, 154.3, 133.3, 133.0, 129.7, 129.4, 129.1, 128.5, 128.4, 127.1, 81.0, 66.5, 45.7, 44.6, 44.1; Anal. Calcd. for C₂₀H₂₁NO₄: C, 70.78; H, 6.24; N, 4.13; Found: C, 70.89; H, 6.26; N, 4.11.

7q + 7q'



Mixture; ¹H NMR (400 MHz) (CDCl₃) δ 7.41-7.39 (m, 2 H), 7.30-7.21 (m, 3 H), 7.06-7.04 (m, 1 H), 6.96-6.92 (m, 2 H), 6.81 (m, 1 H), 6.08 (s, 0.25 H, PhCH₂CO, 7q'), 6.04 (s, 0.75 H, *p*-CH₃OPhCH₂CO, 7q), 3.83 (s, 2.25 H, *p*-CH₃OPhCH₂CO, 7q), 3.77 (s, 0.75 H, *p*-CH₃OPhCH₂, 7q'), 3.73-3.43 (m, 10 H); ¹³C NMR (100.6 MHz) (CDCl₃) δ (some chemical shifts are isochronous) 202.6 (*p*-MeOPhCH₂CO, 7q'), 202.4 (PhCH₂CO, 7q), 160.4, 158.7, 154.5, 154.4, 133.3, 133.1, 130.7, 129.9, 129.7, 129.4, 129.0, 128.5, 128.4, 127.0, 125.1, 125.0, 114.5, 114.0, 80.9 (PhCH₂CO, 7q'), 80.5 (*p*-MeOPhCH₂CO, 7q), 66.5, 55.4, 55.2, 45.7, 44.8, 44.6, 44.0;

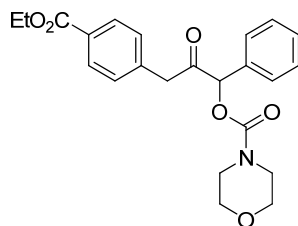
7r



Oil; IR (Neat) 2924, 2858, 1712, 1612, 1456, 1433, 1277, 1238, 1111 cm⁻¹; ¹H NMR (400 MHz) (CDCl₃) δ 8.07 (d, *J* = 8.1 Hz, 2 H), 7.43 (d, *J* = 8.0 Hz, 2 H), 7.28-7.26 (m, 3 H), 7.05-7.03 (m, 2 H), 6.12 (s, 1 H), 4.42 (q, *J* = 7.0 Hz, 2 H), 3.76 (s, 2 H), 3.71-3.47 (m, 8 H), 1.43 (t, *J* = 7.0 Hz, 3 H); ¹³C NMR (100.6 MHz) (CDCl₃) δ 201.8, 166.0, 154.1, 138.0, 132.6, 131.4, 130.2, 129.6, 128.6, 128.1, 127.2, 80.4, 66.4 (bs), 61.3,

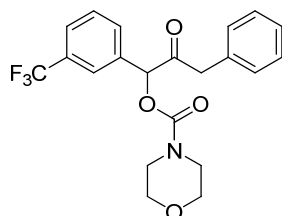
45.9, 44.6, 44.1, 14.3; Anal. Calcd. for C₂₃H₂₅NO₆: C, 67.14; H, 6.12; N, 3.40; Found: C, 67.20; H, 6.14; N, 3.42.

7r'



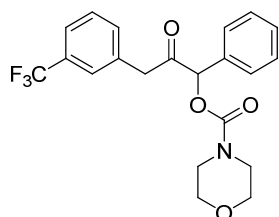
Oil; IR (Neat) 2978, 2925, 2858, 1712, 1612, 1429, 1277, 1238, 1107 cm⁻¹; ¹H NMR (400 MHz) (DMSO-d₆) (350 K) δ 7.84 (d, *J* = 7.6 Hz, 2 H), 7.47-7.42 (m, 5 H), 7.18 (d, *J* = 7.6 Hz, 2 H), 6.14 (s, 1 H), 4.33 (q, *J* = 6.8 Hz, 2 H), 4.00 (d, *J* = 16.4 Hz, 1 H), 3.88 (d, *J* = 16.4 Hz, 1 H), 3.63-3.61 (m, 4 H), 3.48-3.47 (m, 4 H), 1.34 (t, *J* = 6.8 Hz, 3 H); ¹³C NMR (100.6 MHz) (DMSO-d₆) (350 K) δ 202.4, 166.1, 154.2, 139.7, 134.3, 130.3, 129.4, 129.35, 129.28, 129.1, 128.2, 81.2, 66.3, 61.0, 44.8, 44.6, 14.5; Anal. Calcd. for C₂₃H₂₅NO₆: C, 67.14; H, 6.12; N, 3.40; Found: C, 67.20; H, 6.16; N, 3.39.

7s



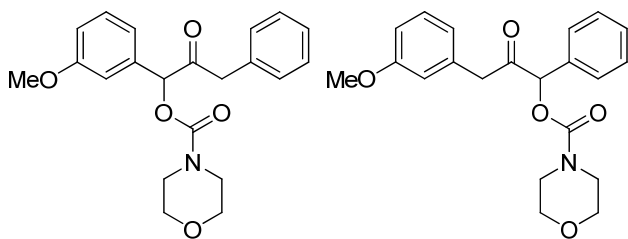
Oil; IR (Neat) 2924, 2858, 1712, 1433, 1331, 1238, 1124 cm⁻¹; ¹H NMR (400 MHz) (CDCl₃) δ 7.66-7.64 (m, 1 H), 7.54-7.49 (m, 3 H), 7.28-7.23 (m, 3H), 7.05-7.04 (m, 2 H), 6.12 (s, 1 H), 3.78 (s, 2 H), 3.72-3.53 (m, 8 H); ¹³C NMR (100.6 MHz) (CDCl₃) δ (323 K) δ 201.9, 154.0, 134.6, 132.5, 131.5, 131.4 (q, *J*_{CF} = 32.6 Hz), 129.6, 129.5, 128.6, 127.3, 126.1 (q, *J*_{CF} = 3.6 Hz), 125.0 (q, *J*_{CF} = 3.8 Hz), 123.7 (q, *J*_{CF} = 271.5 Hz), 80.0, 66.5, 46.3, 44.6, 44.1; ¹⁹F NMR {H} (376.5 MHz) (CDCl₃) δ -62.7; Anal. Calcd. for C₂₁H₂₀F₃NO₄: C, 61.91; H, 4.95; N, 3.44; Found: C, 61.82; H, 4.93; N, 3.47.

7s'



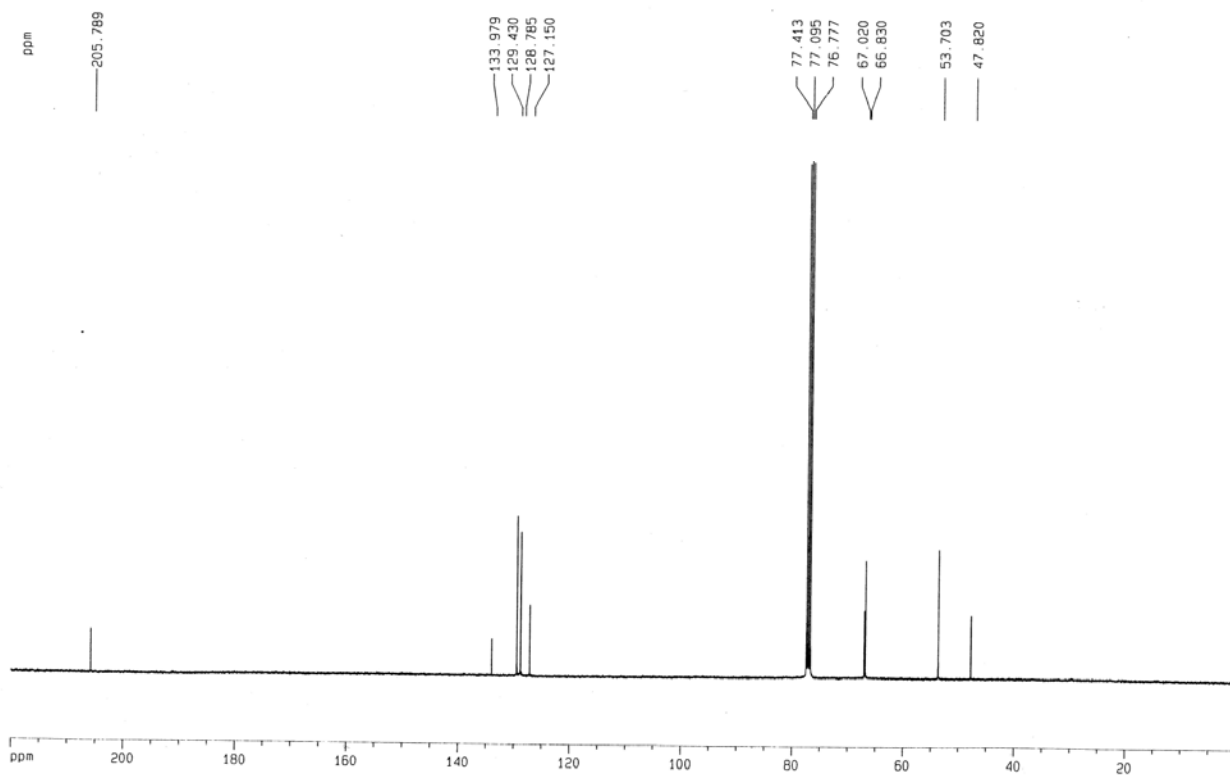
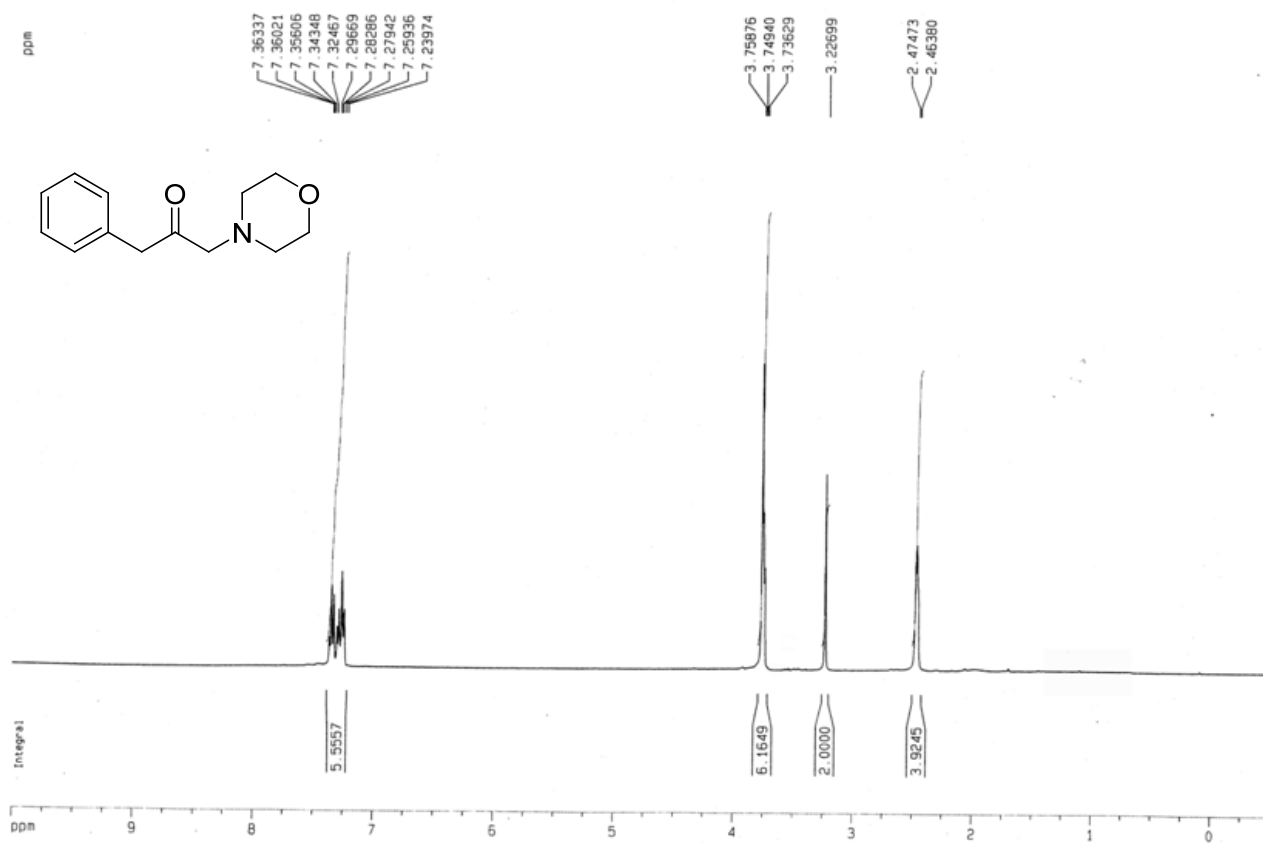
Mp: 97-99 °C; IR (KBr) 2862, 1728, 1705, 1433, 1336, 1117 cm⁻¹; ¹H NMR (400 MHz) (CDCl₃) δ 7.49 (d, *J* = 7.6 Hz, 1 H), 7.44-7.37 (m, 6 H), 7.24 (d, *J* = 7.9 Hz, 1 H), 7.21 (s, 1 H), 6.07 (s, 1 H), 3.81-3.48 (m, 10 H); ¹³C NMR (100.6 MHz) (DMSO-d₆) (350 K) δ 202.6, 154.2, 135.8, 134.2, 134.1, 129.7, 129.5, 129.4, 129.3, 128.3, 126.5 (q, *J*_{CF} = 4.0 Hz), 124.7 (q, *J*_{CF} = 271.4 Hz), 123.7 (q, *J*_{CF} = 3.8 Hz), 81.3, 66.3, 44.6, 44.4; ¹⁹F NMR {H} (376.5 MHz) (CDCl₃) δ -62.6; Anal. Calcd. for C₂₁H₂₀F₃NO₄: C, 61.91; H, 4.95; N, 3.44; Found: C, 61.82; H, 4.93; N, 3.42.

7t + 7t'

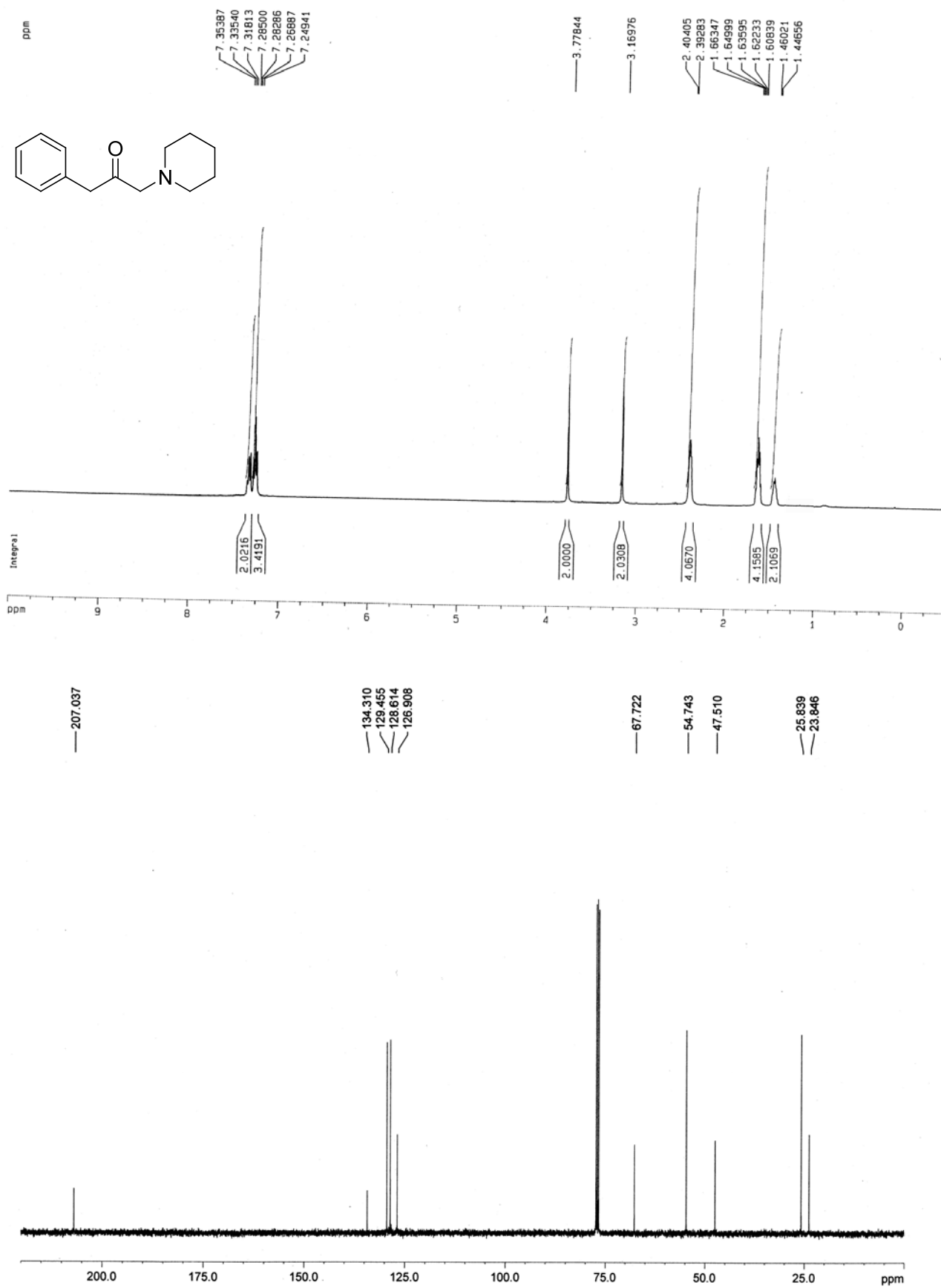


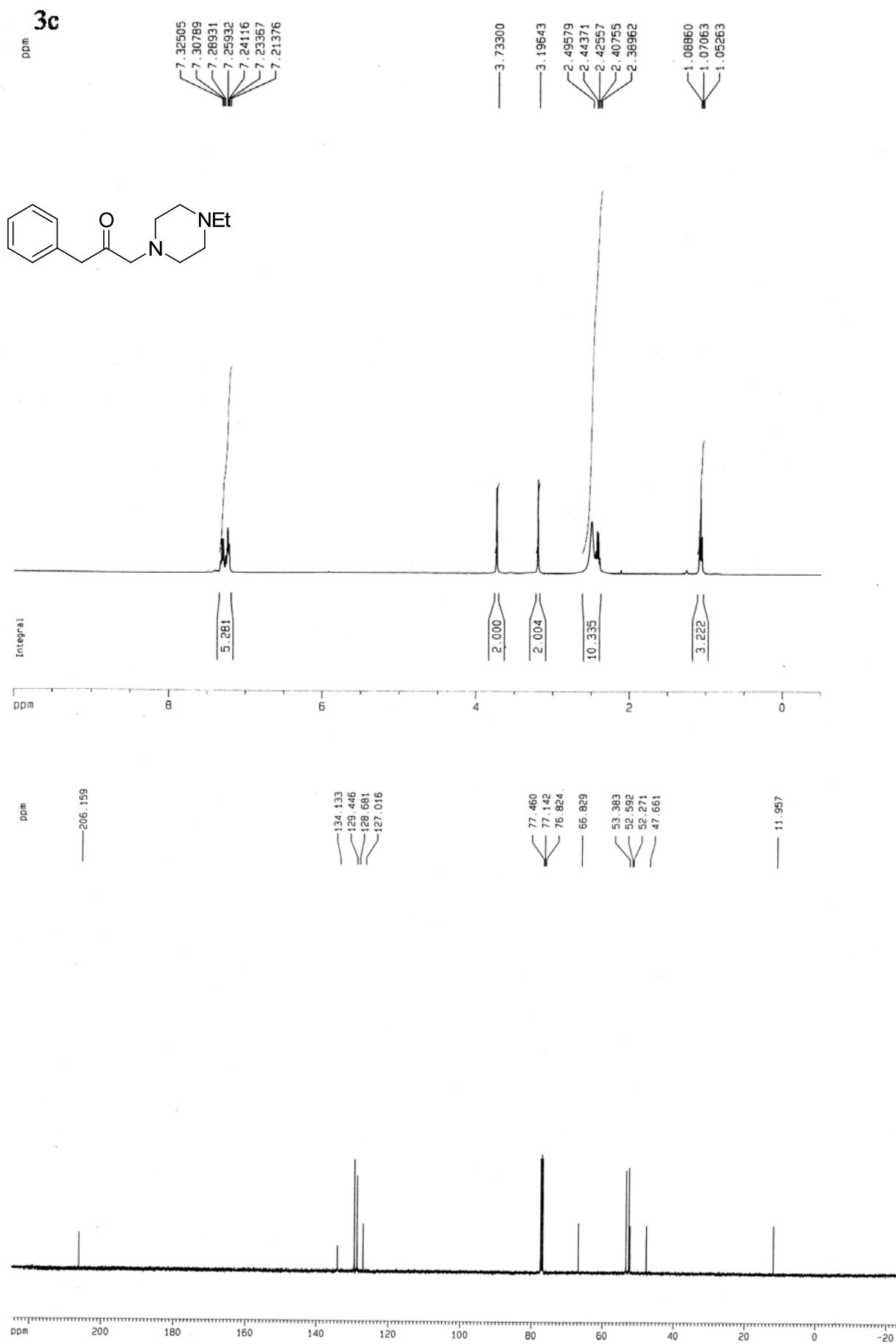
Mixture; ^1H NMR (400 MHz) (CDCl_3) δ 7.40-7.16 (m, 5 H), 7.06-7.05 (m, 1 H), 6.99-6.97 (m, 1 H), 6.88 (s, 0.43 H), 6.79-6.77 (m, 0.56 H), 6.64-6.62 (m, 0.56 H), 6.56 (s, 0.57 H), 6.08 (s, 0.57 H, PhCHOCO , 7t'), 6.06 (s, 0.43 H, *m*- MeOPhCHOCO , 7t), 3.80 (s, 1.3 H, *m*- $\text{CH}_3\text{OPhCHOCO}$, 7t), 3.74-3.51 (m, 11.7 H); ^{13}C NMR (100.6 MHz) (CDCl_3) (some chemical shifts are isochronous) δ 202.13 (*m*- $\text{MeOPhCH}_2\text{CO}$, 7t'), 202.11 (PhCH_2CO , 7t), 160.01, 159.64, 154.33, 154.30, 134.7, 134.4, 133.3, 133.1, 130.1, 129.7, 129.5, 129.4, 129.1, 128.5, 128.4, 127.1, 122.0, 120.7, 115.09, 114.95, 113.8, 112.8, 81.0 (PhCHOCO , 7t'), 80.9 (*m*- MeOPhCHOCO , 7t), 66.5, 55.3, 55.1, 45.7, 45.6, 44.6, 44.1.

3a

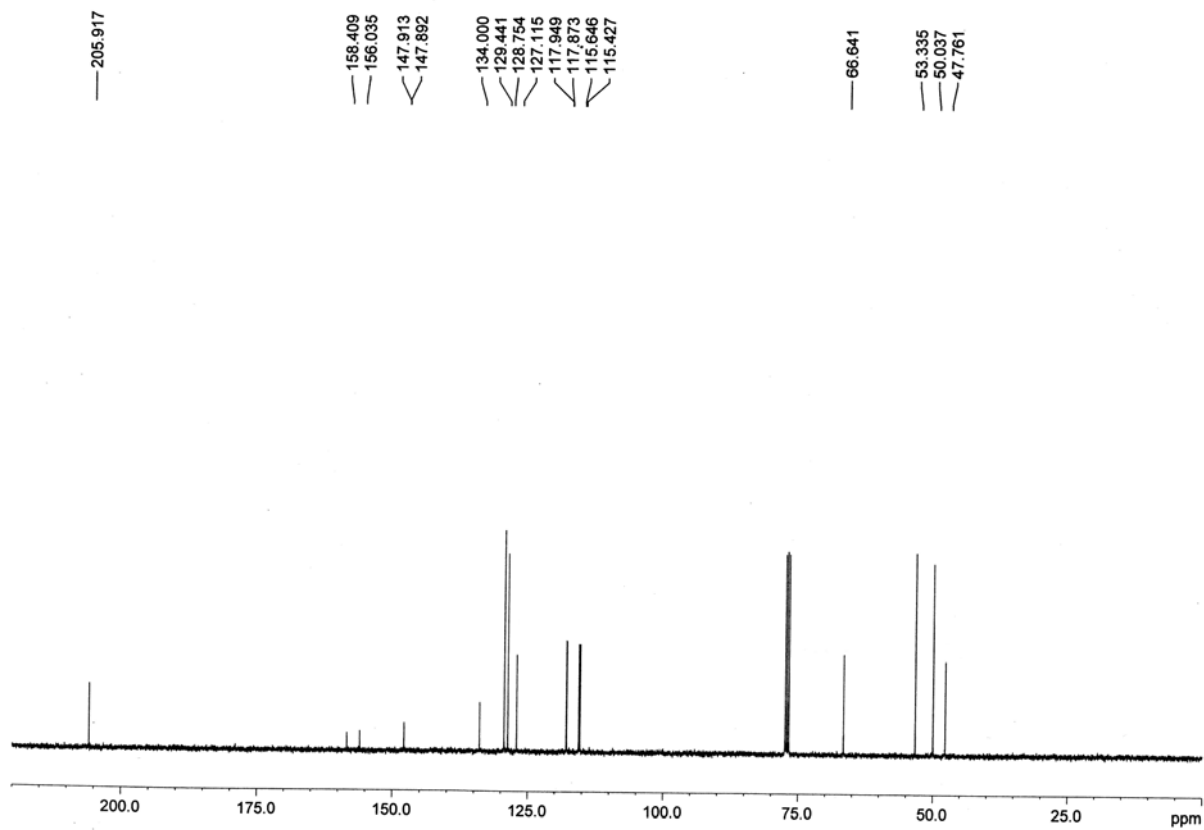
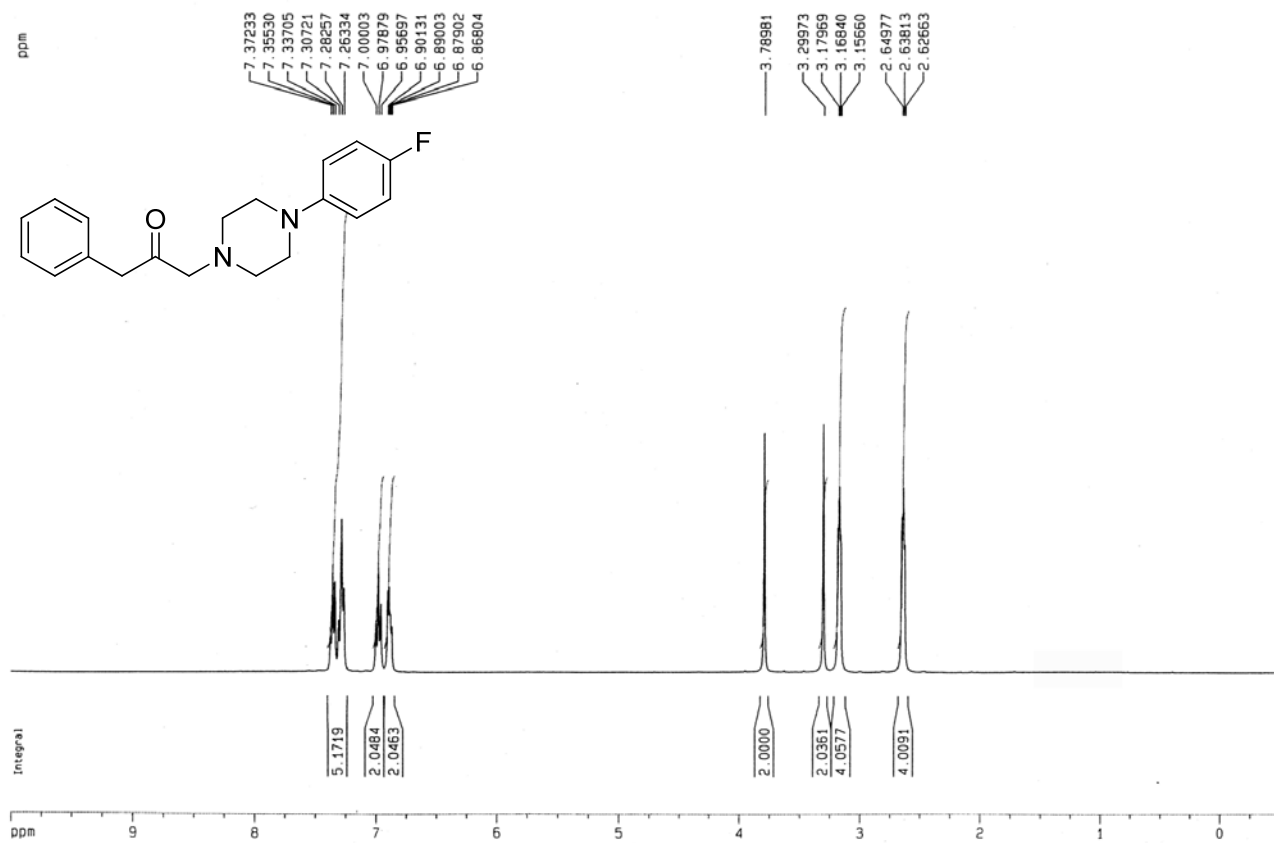


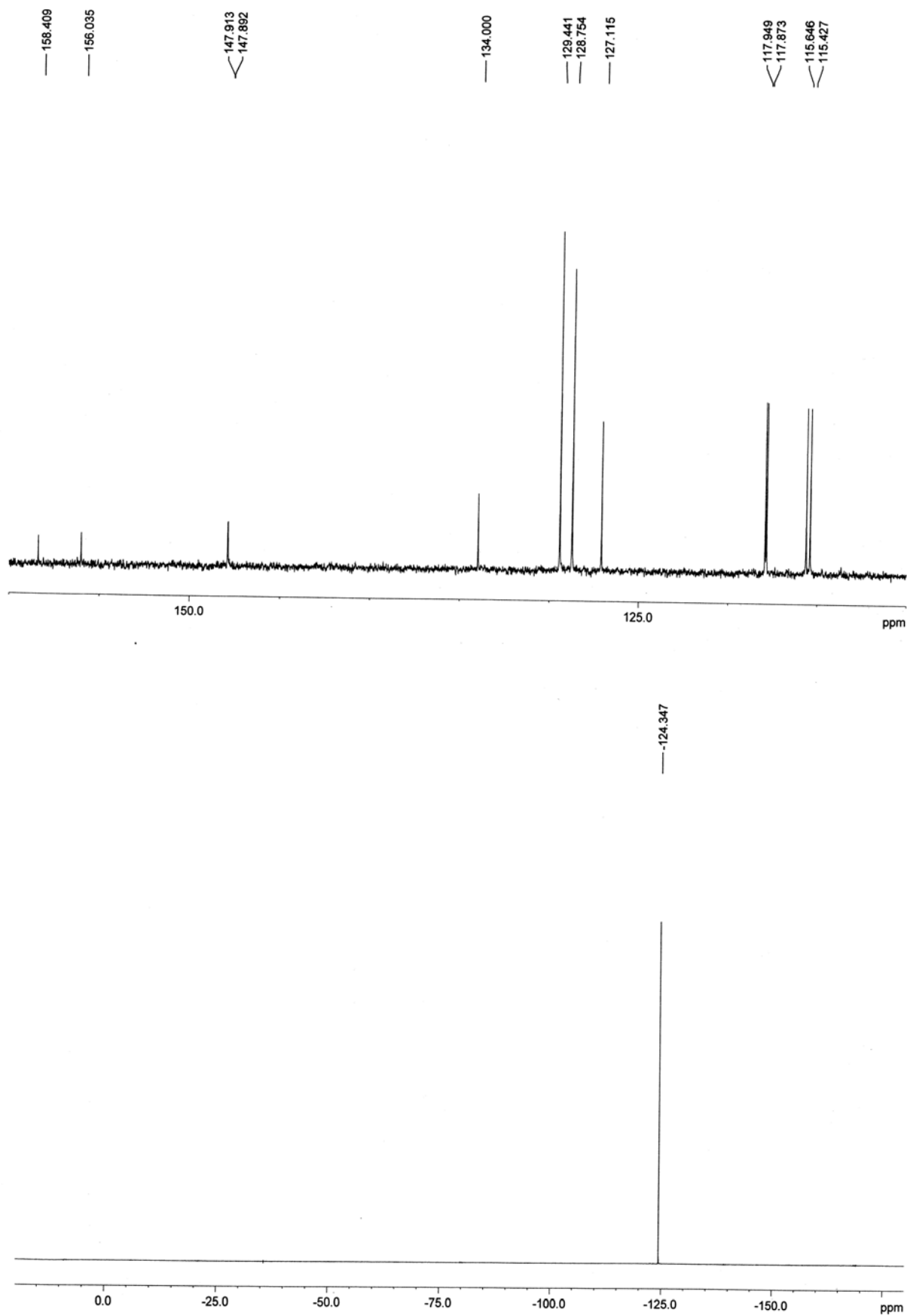
3b

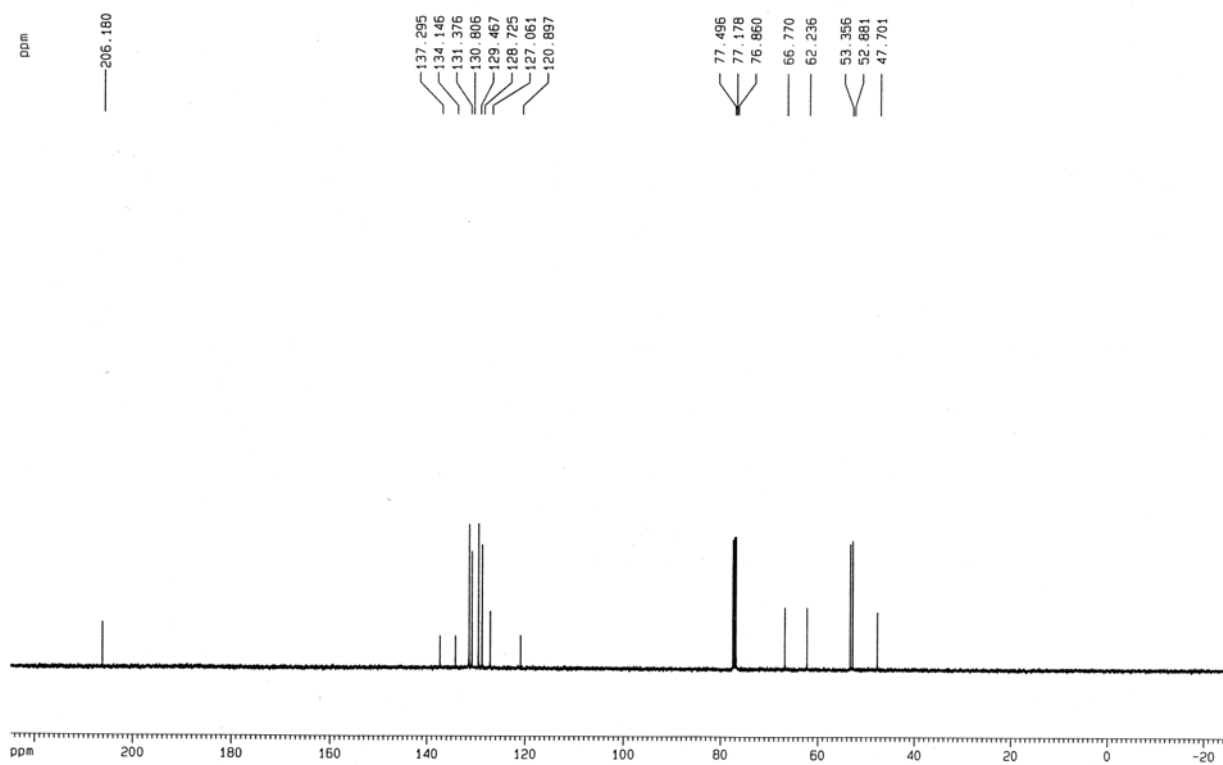
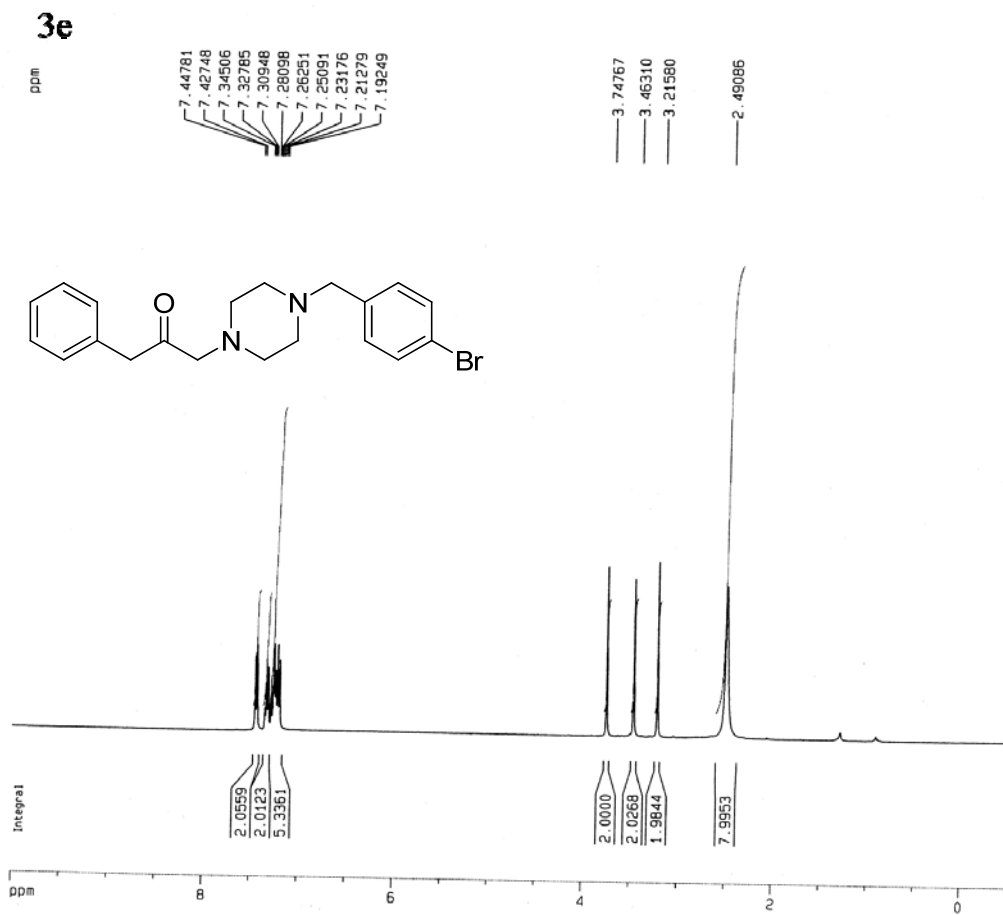




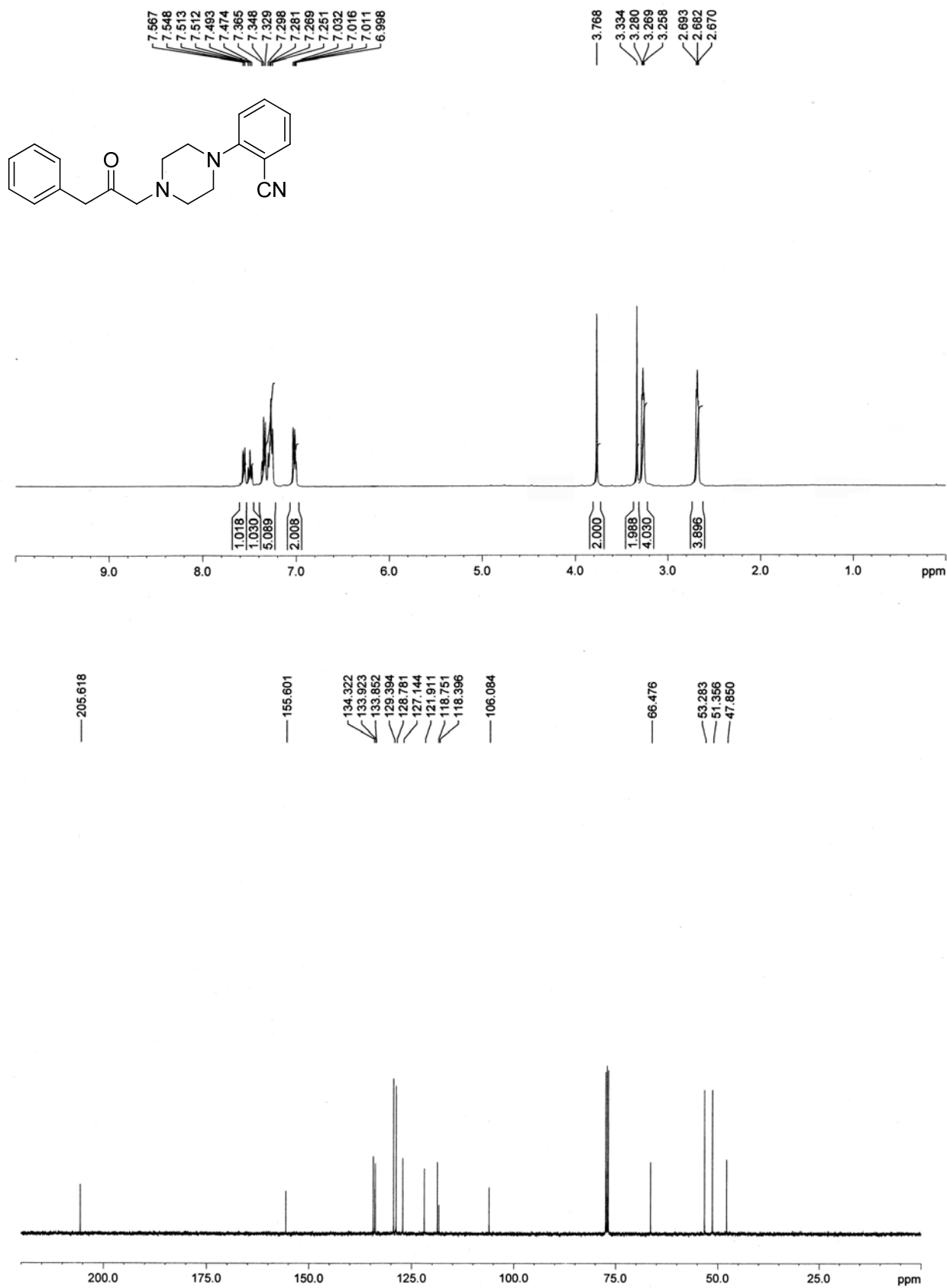
3d



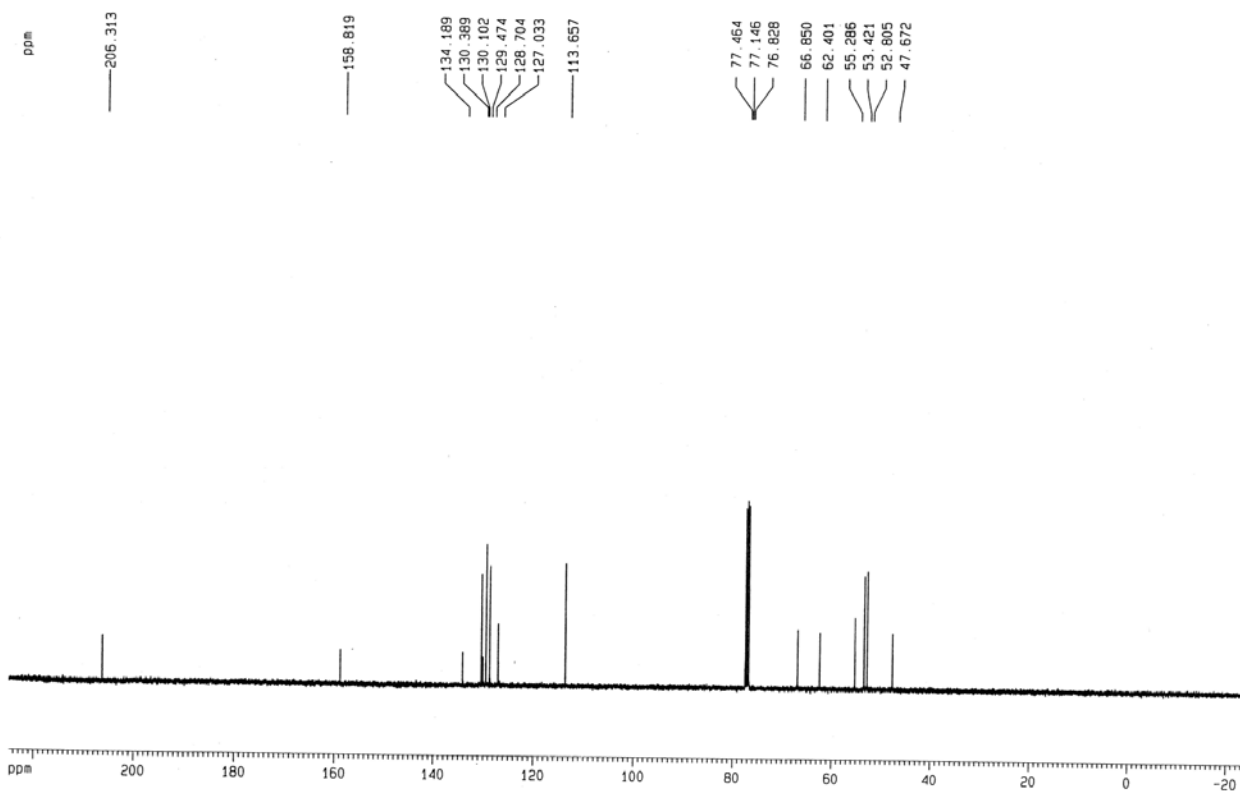
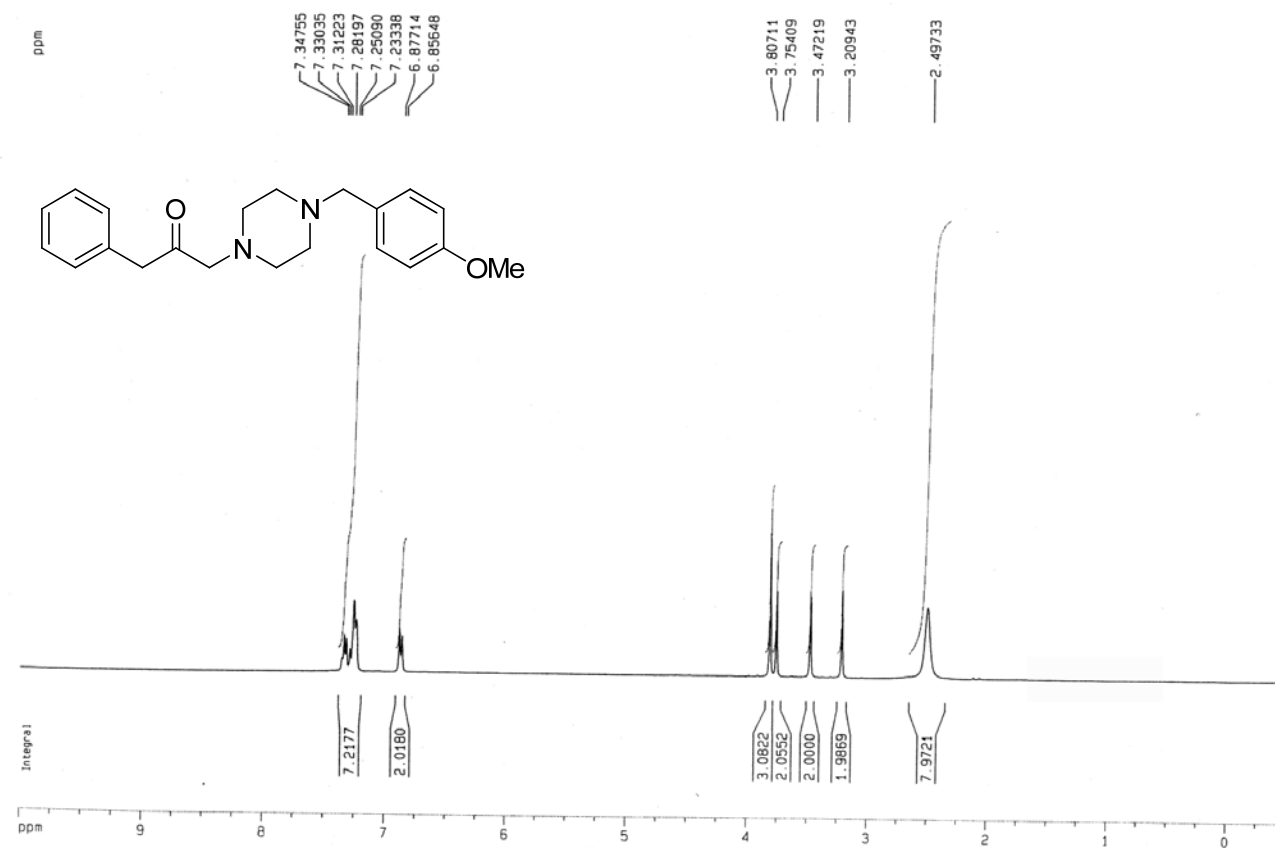




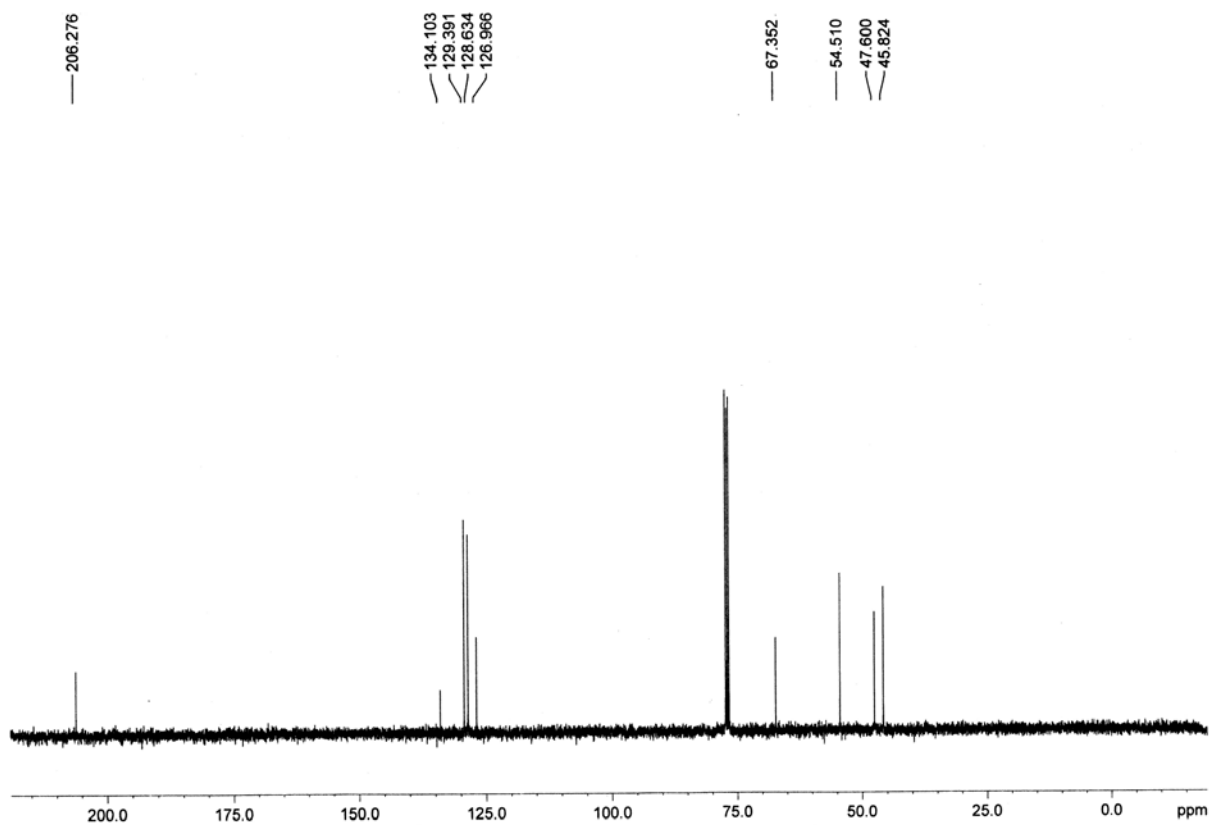
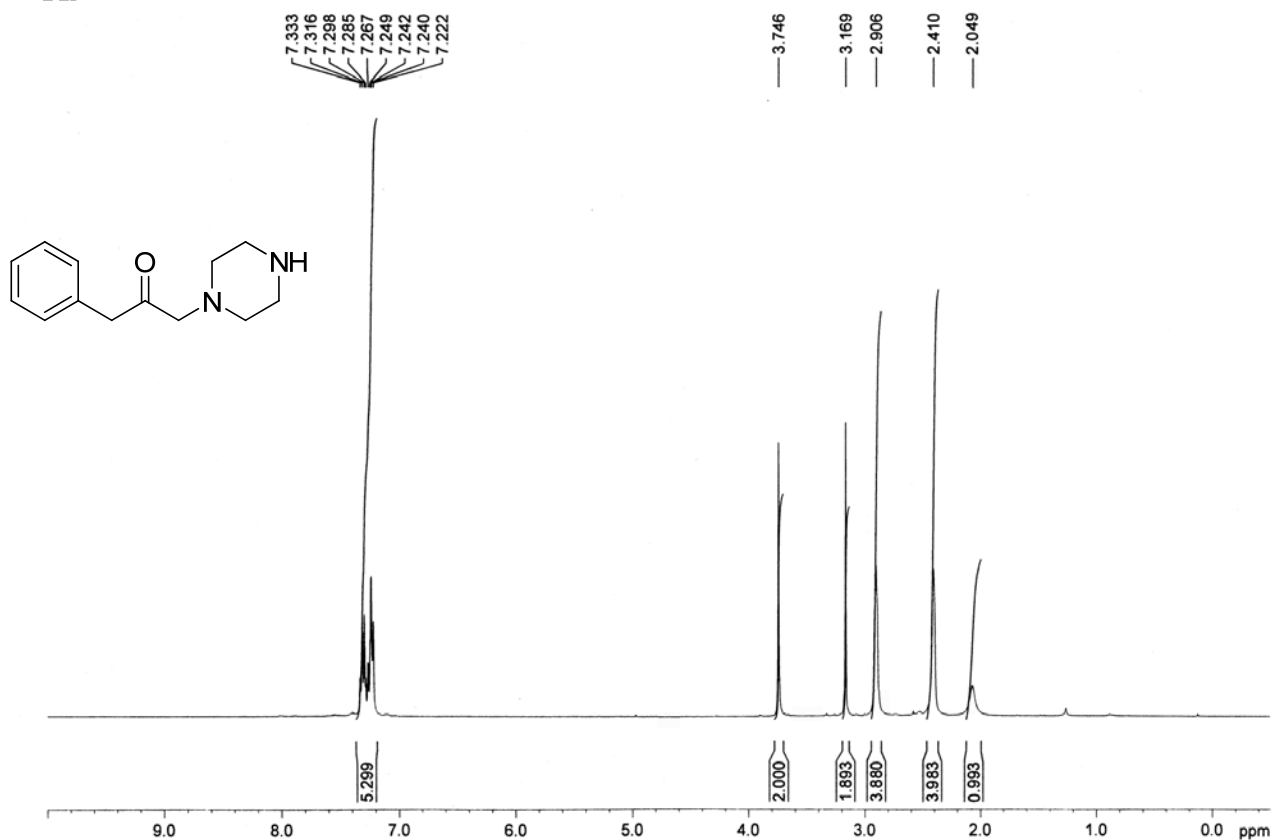
3f



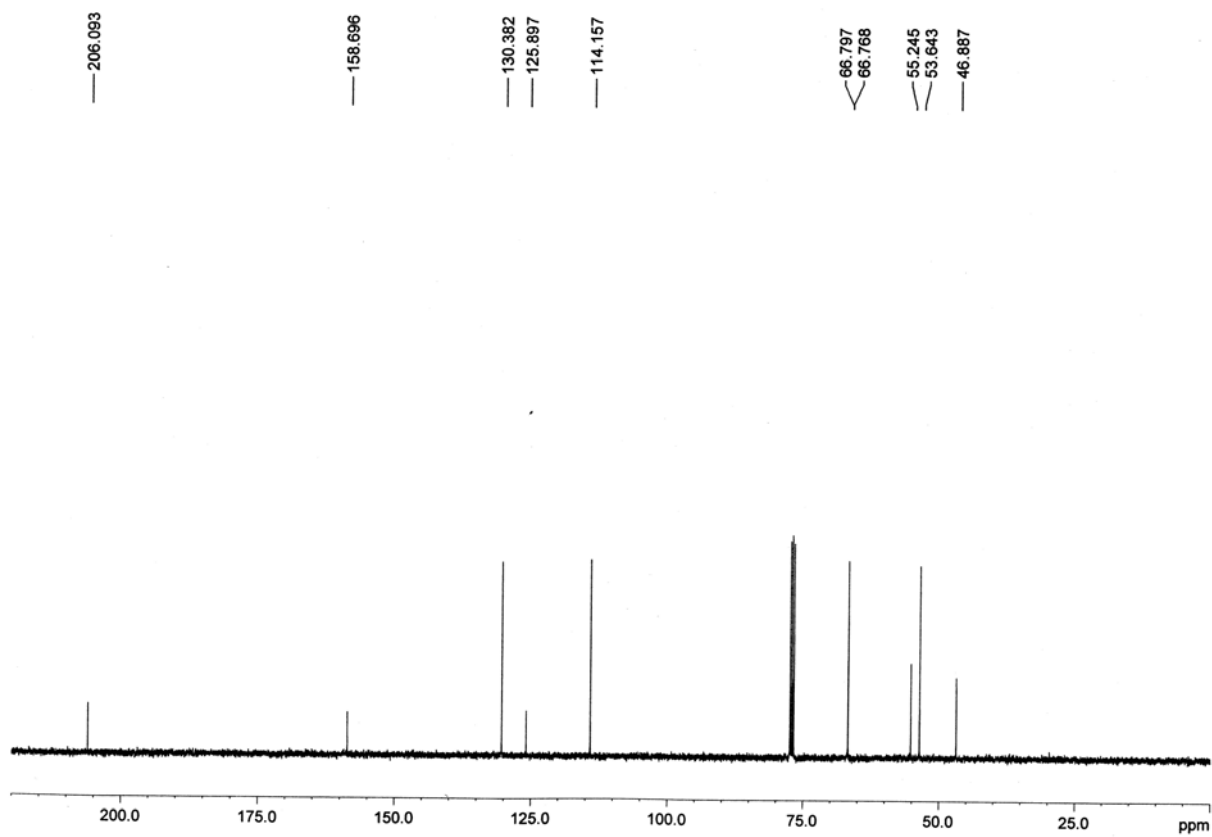
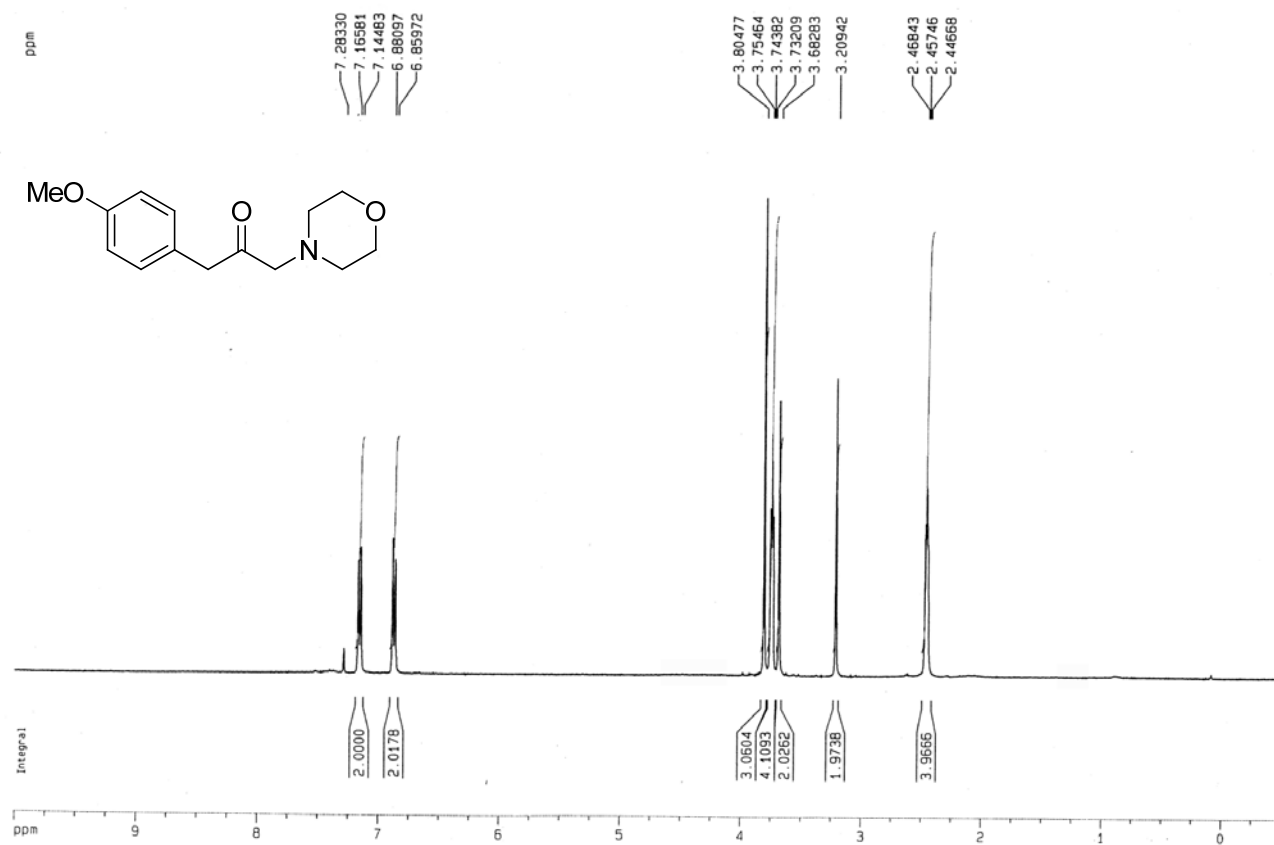
3g



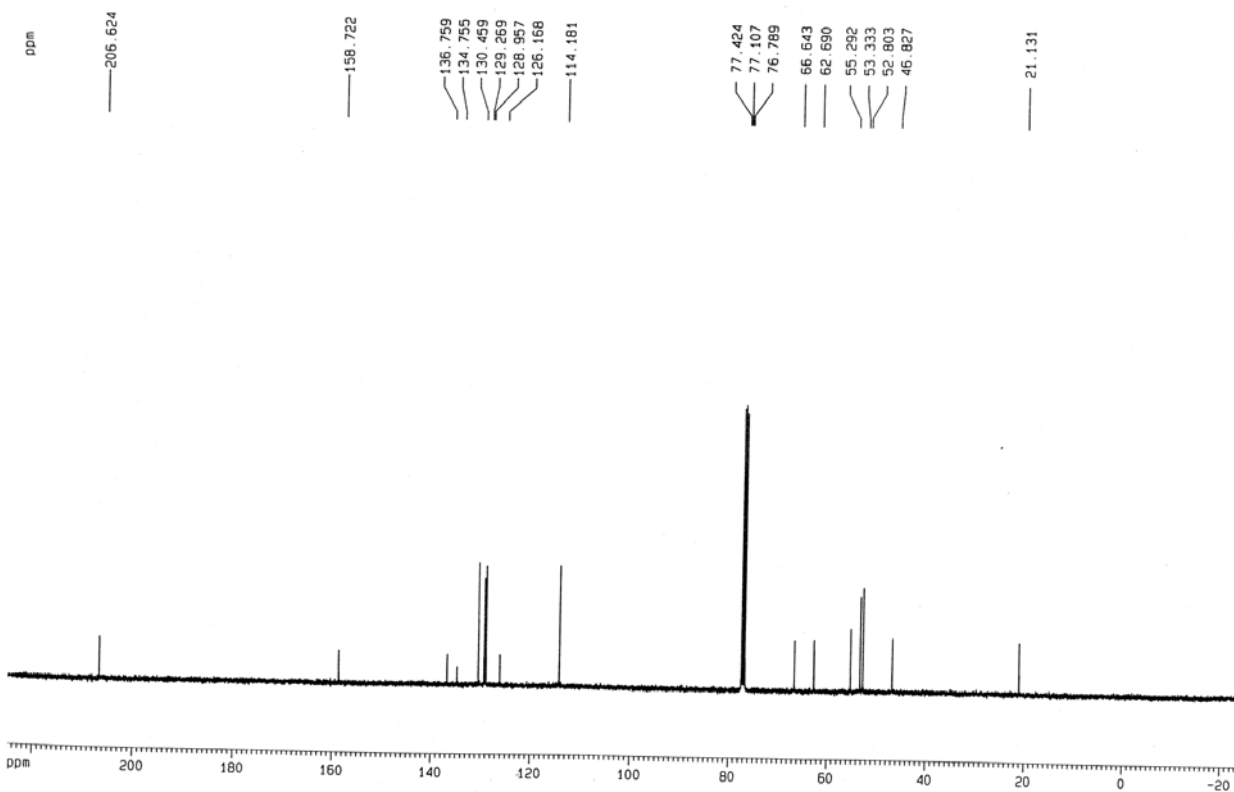
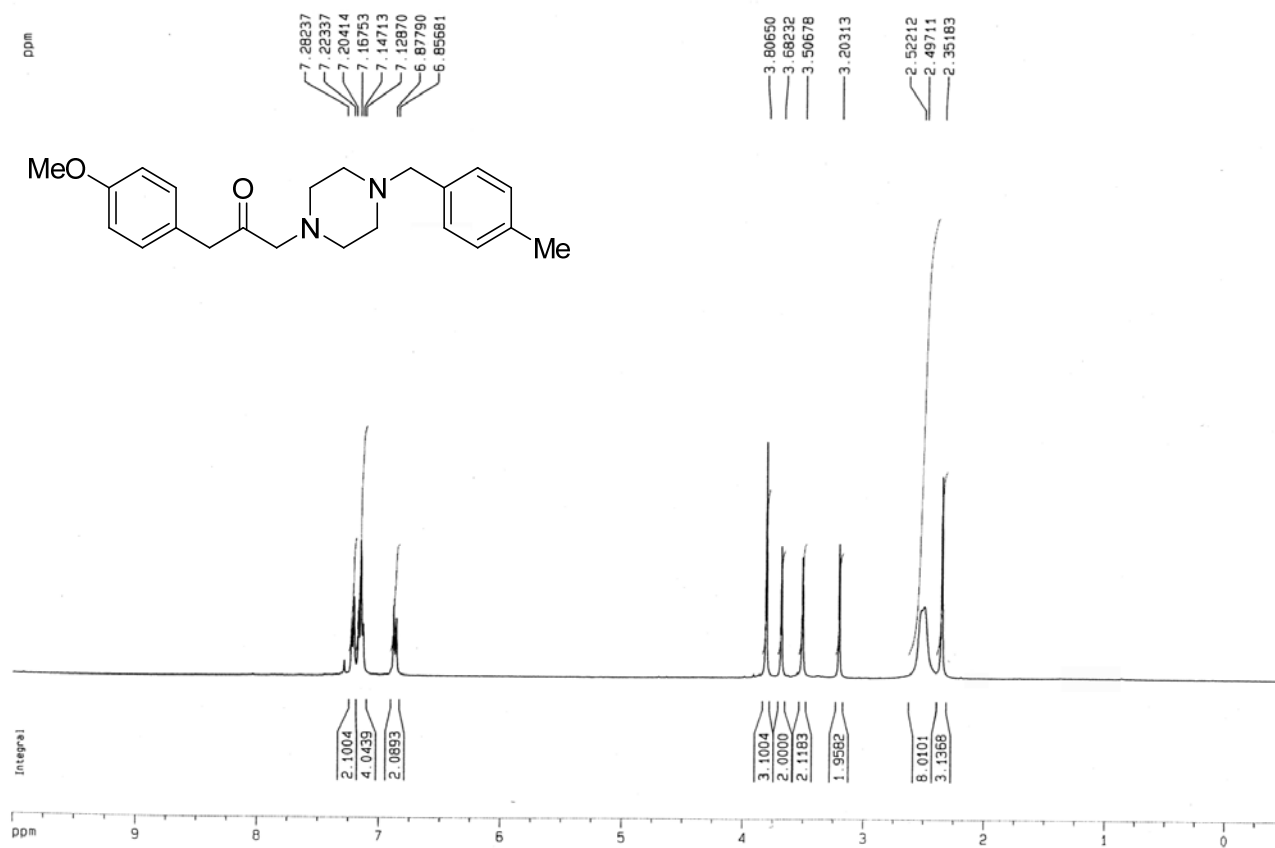
3h



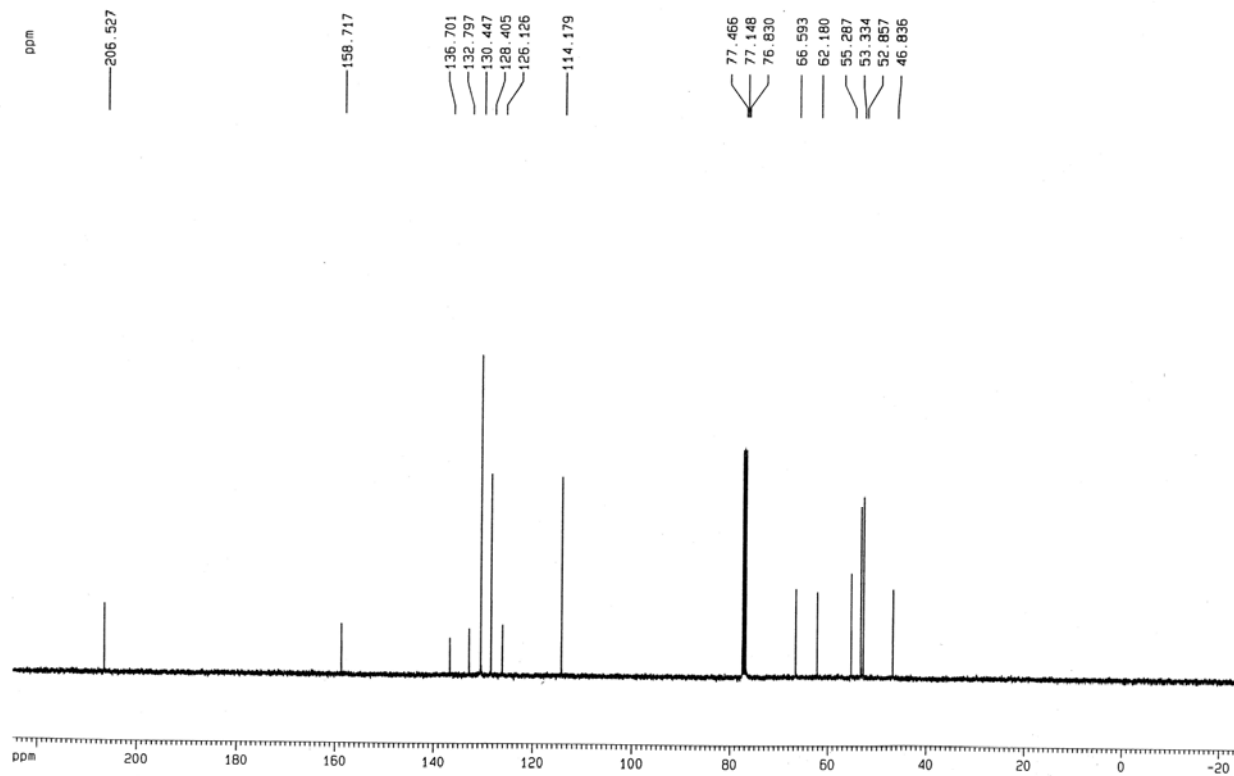
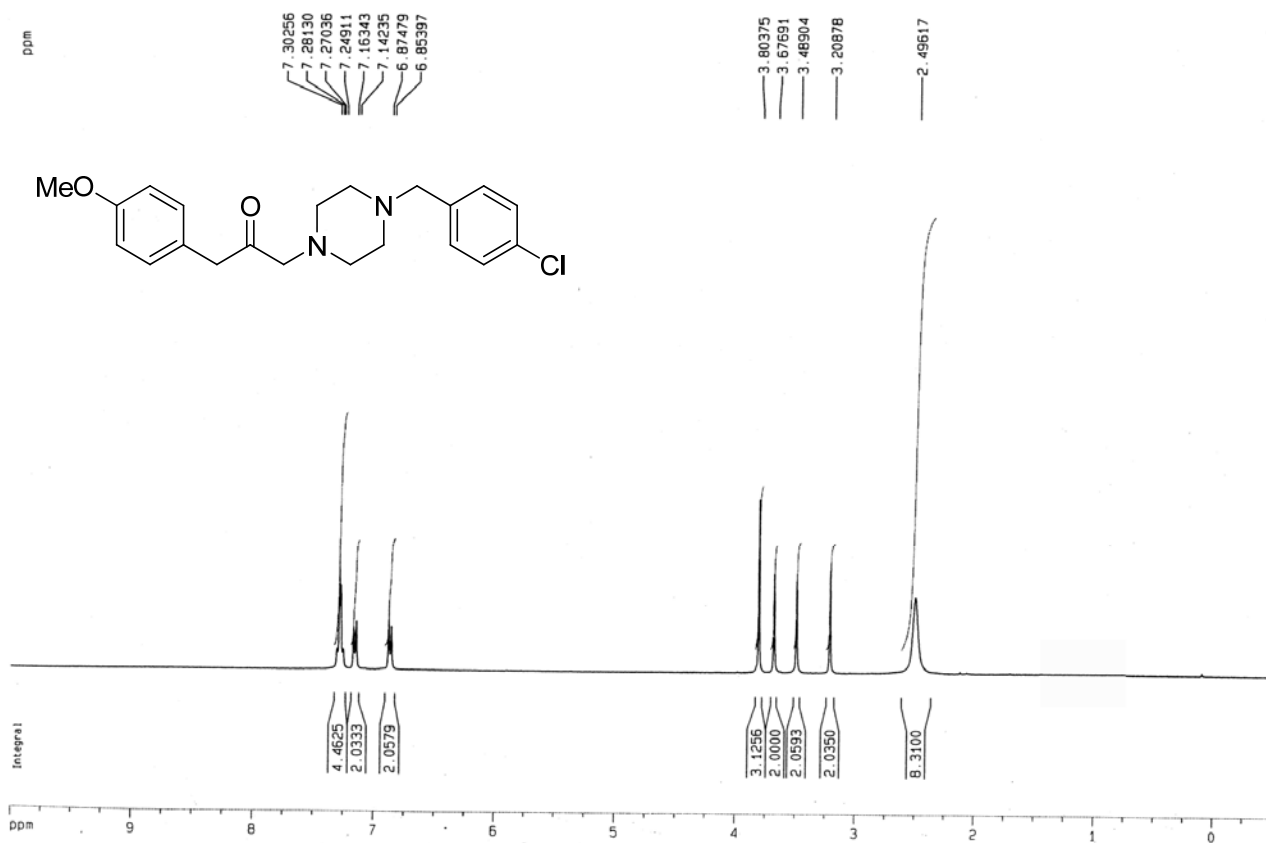
3i



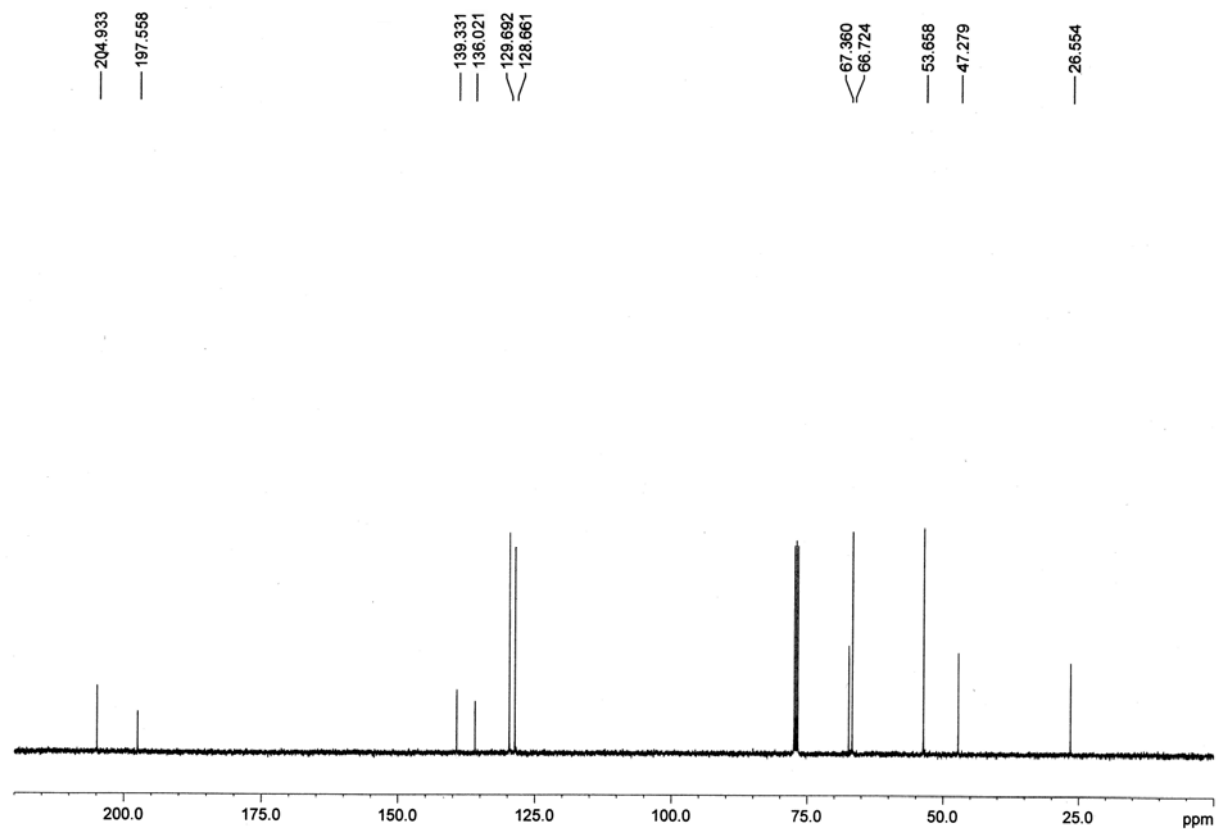
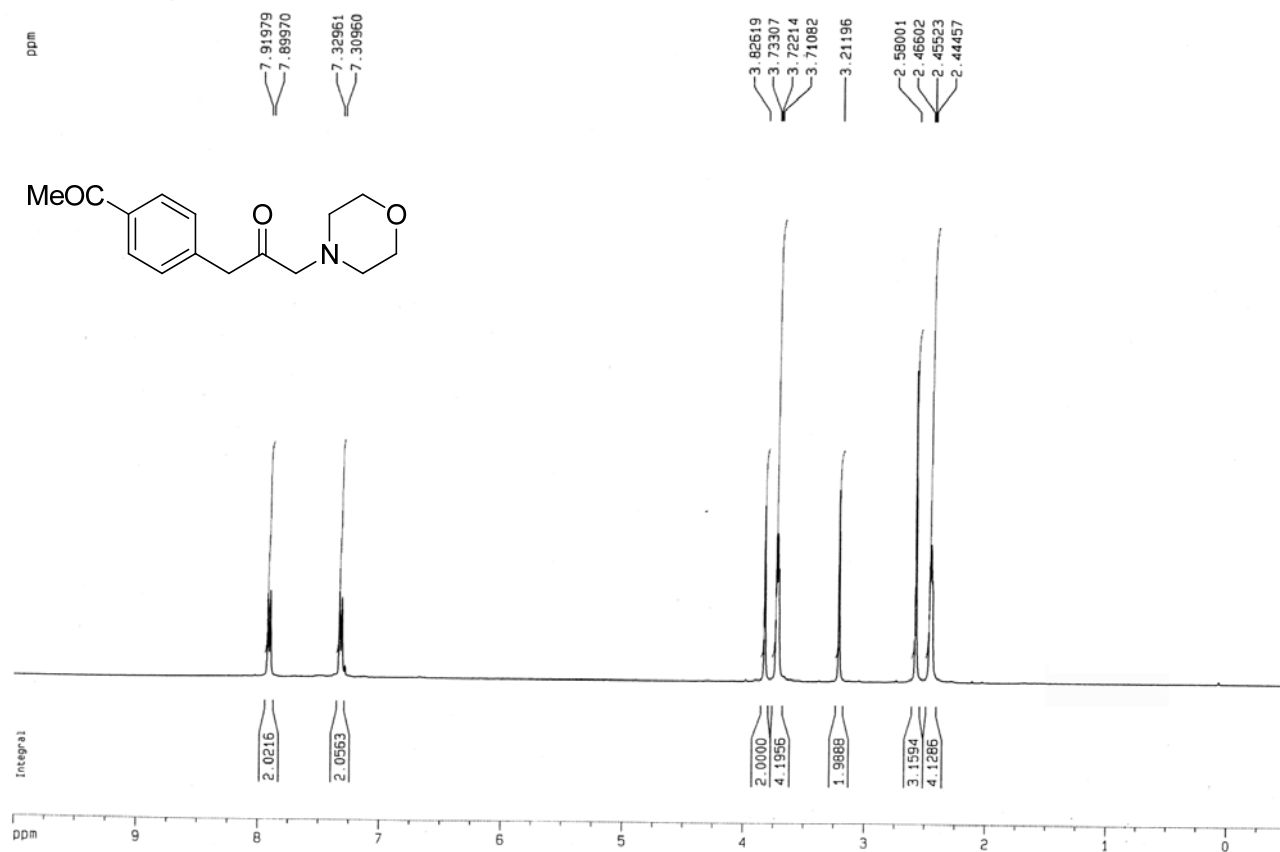
3j



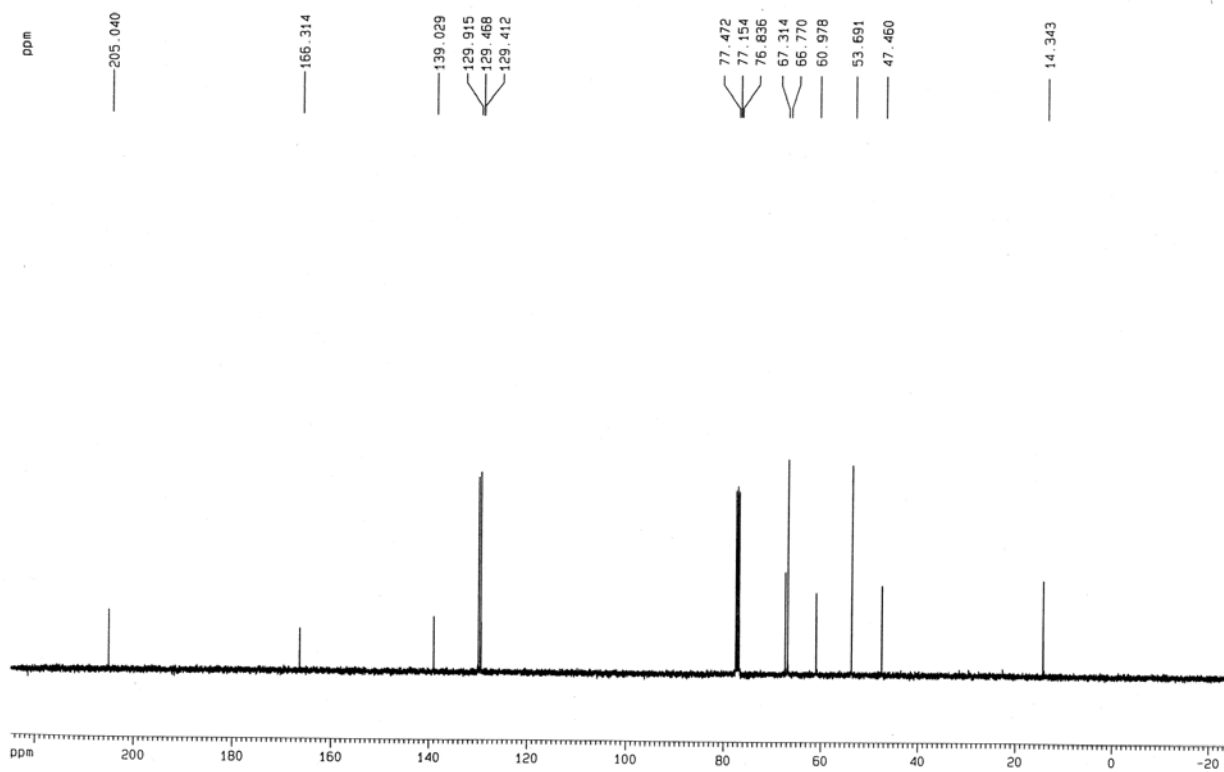
3k



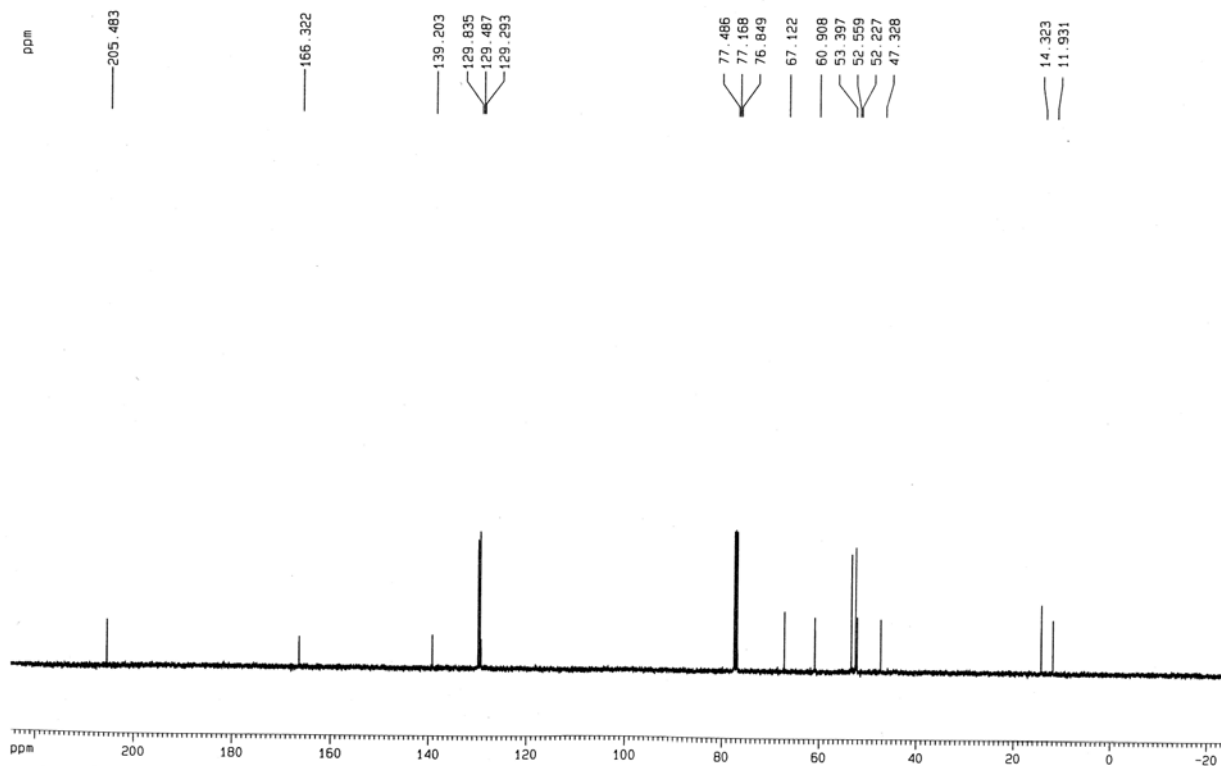
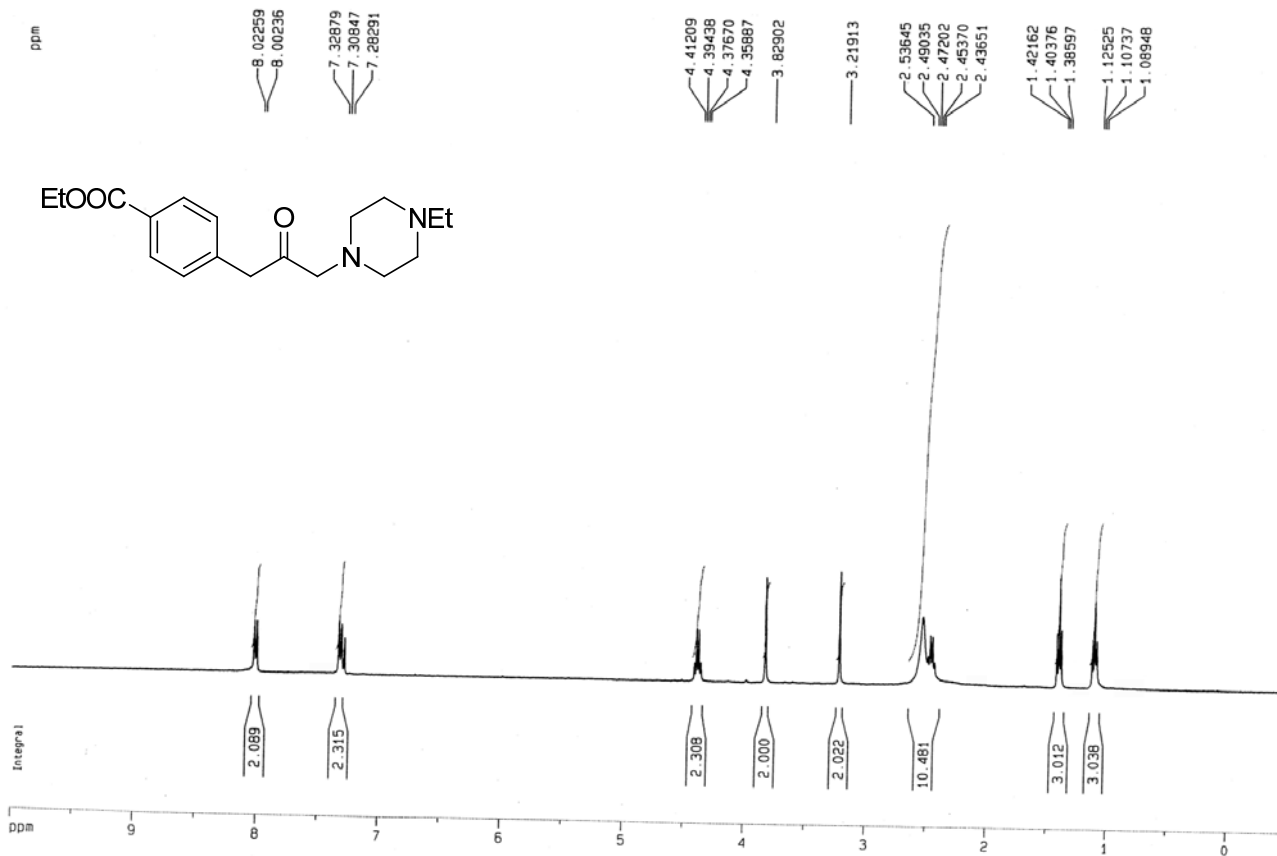
31



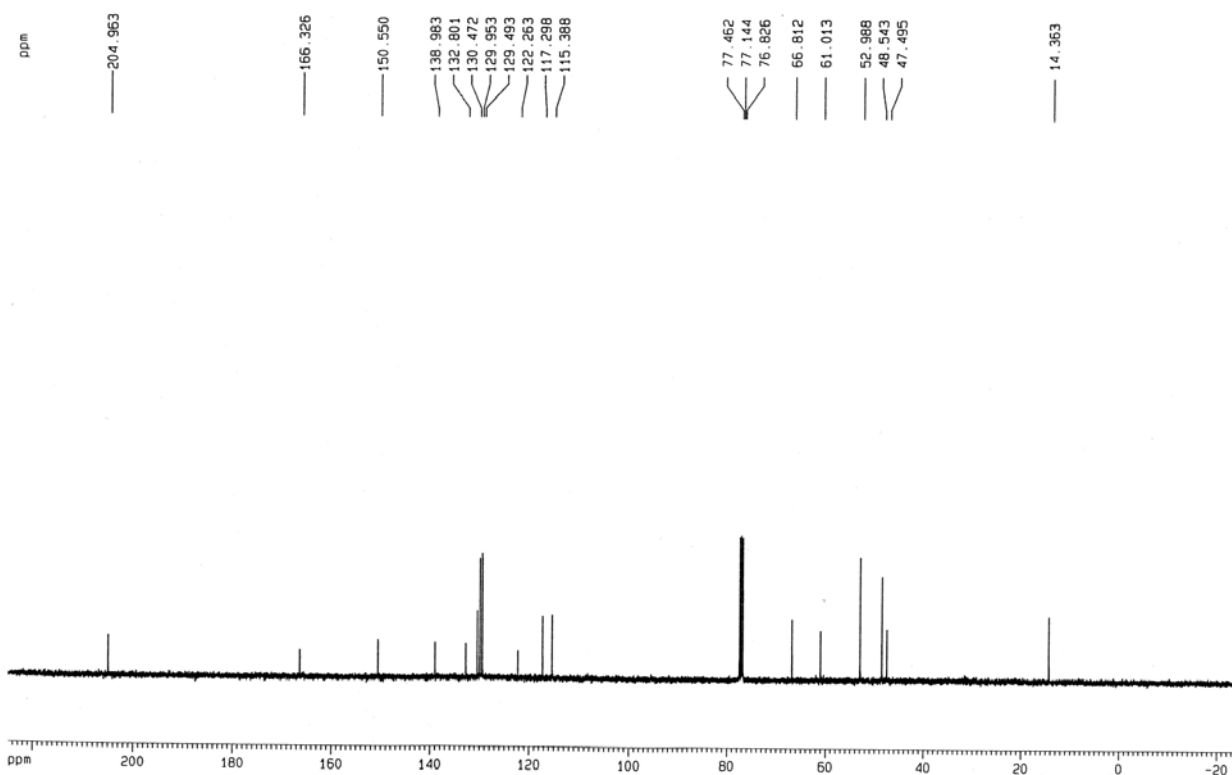
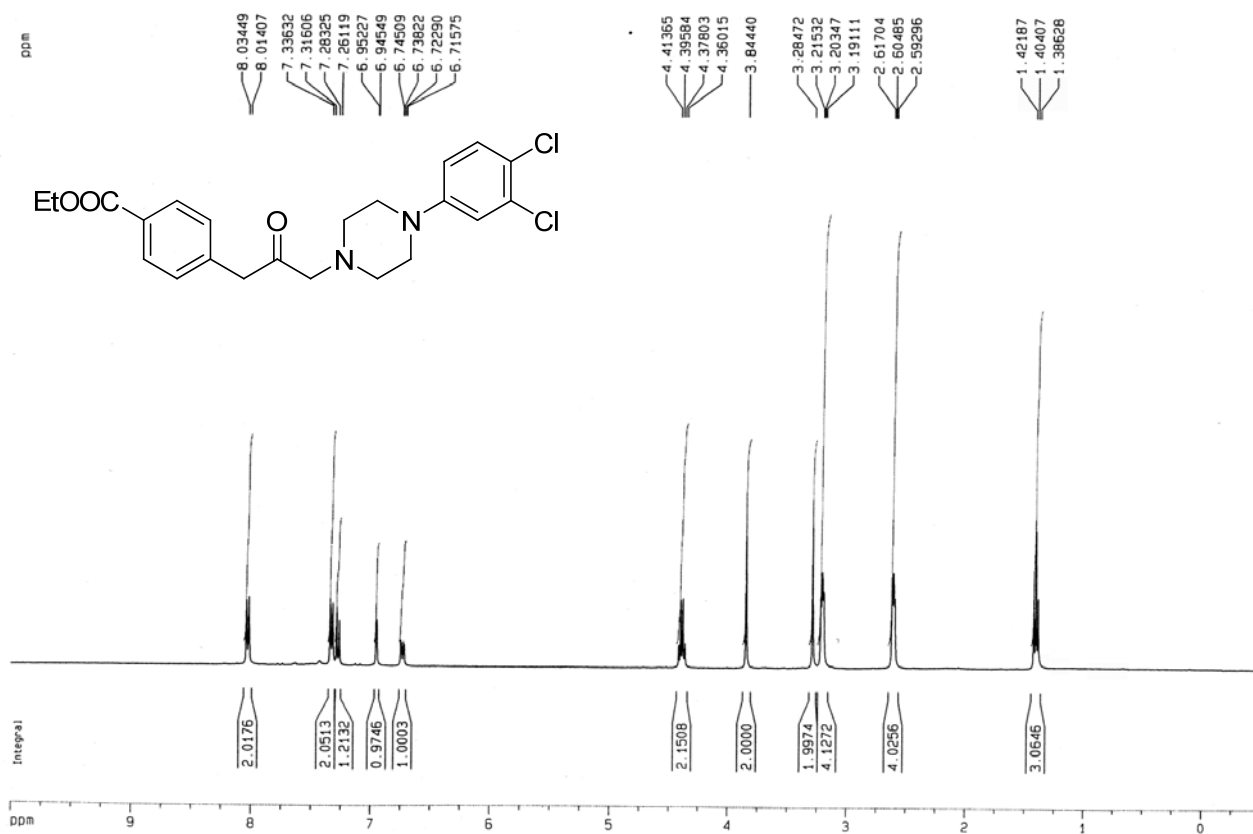
3m



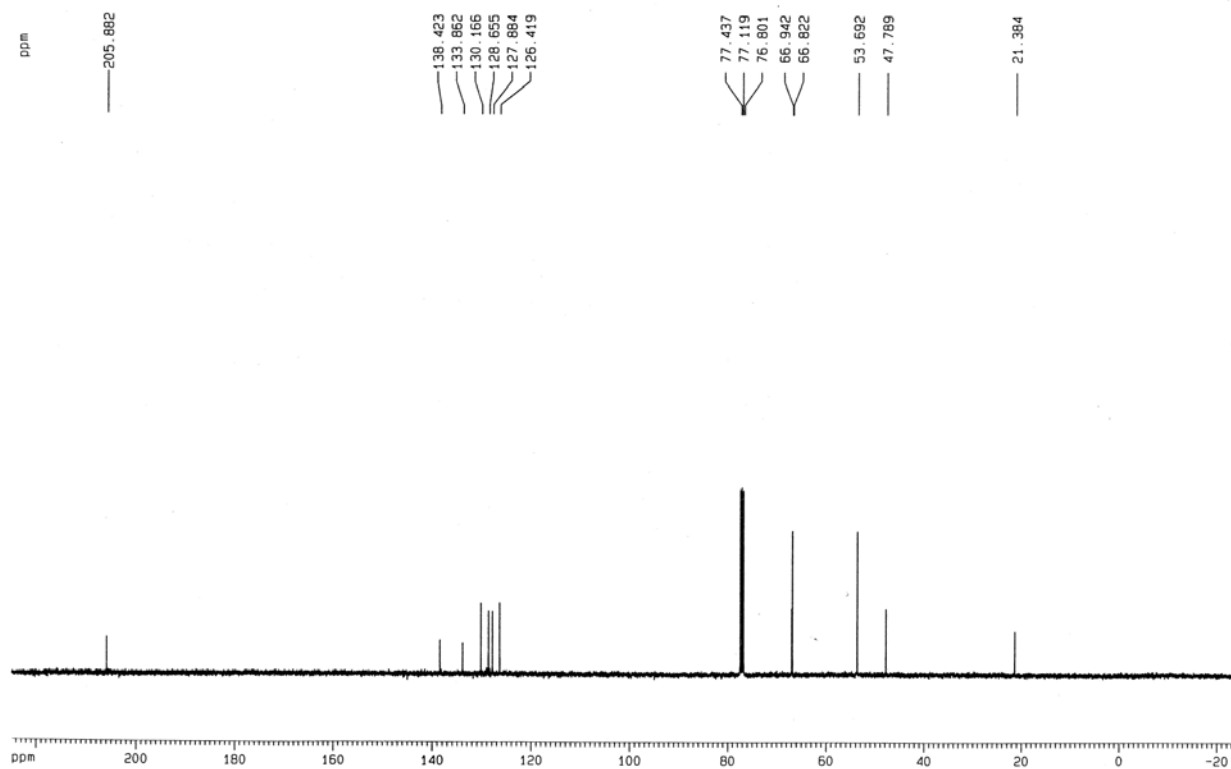
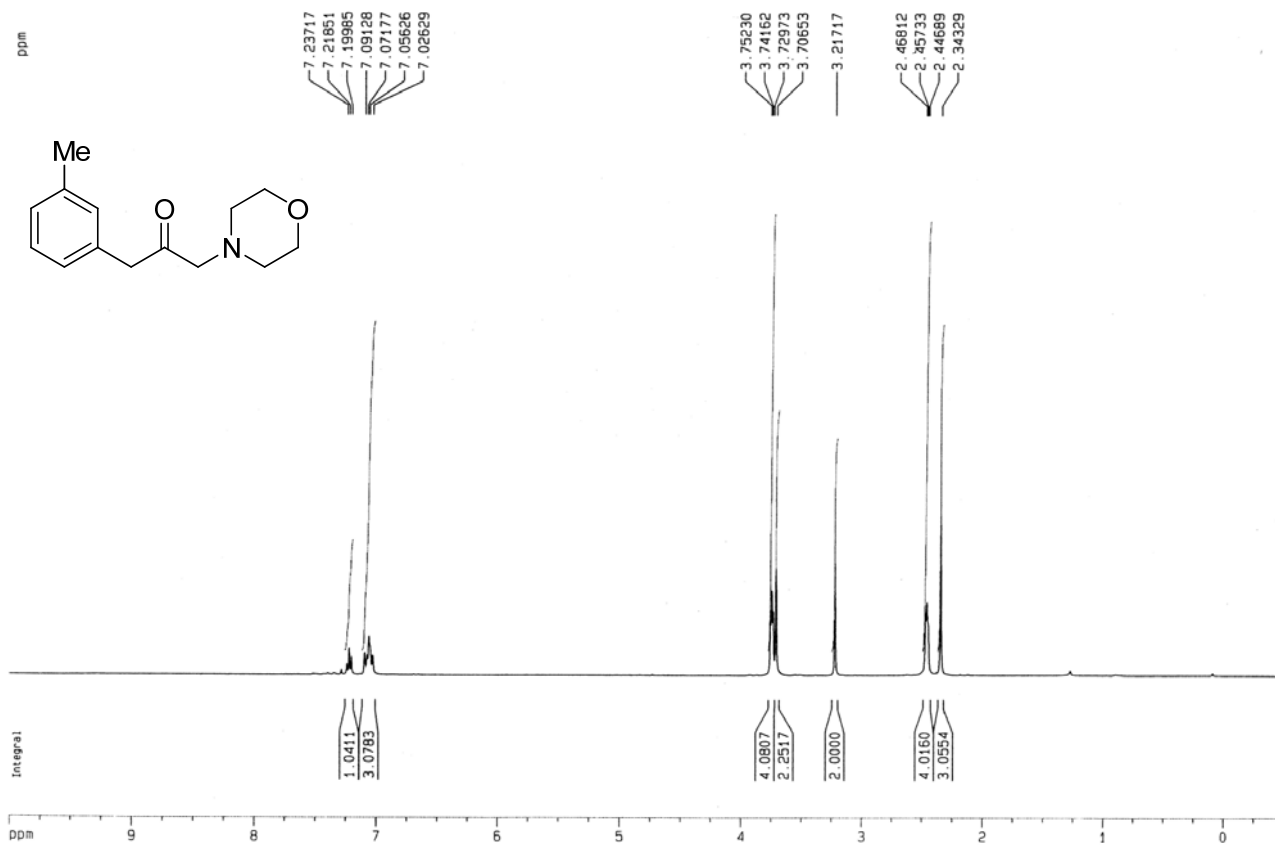
3n



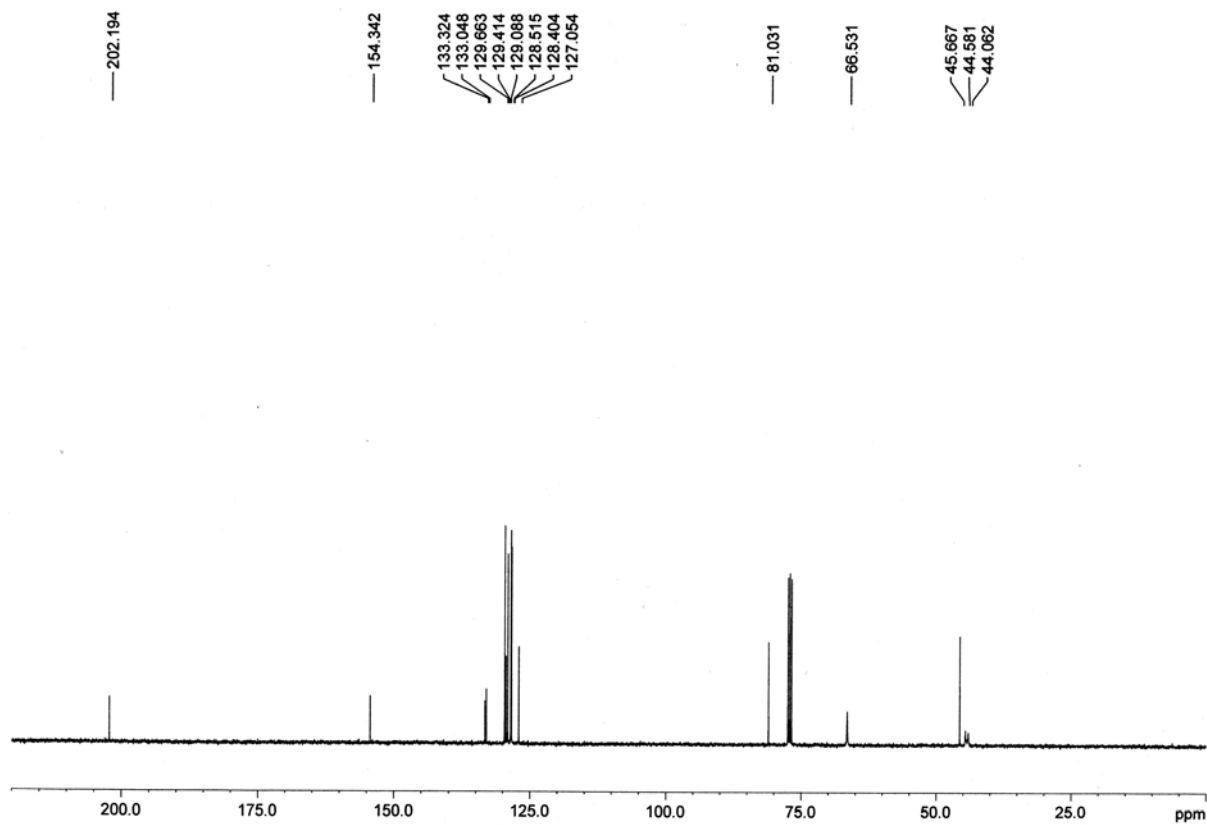
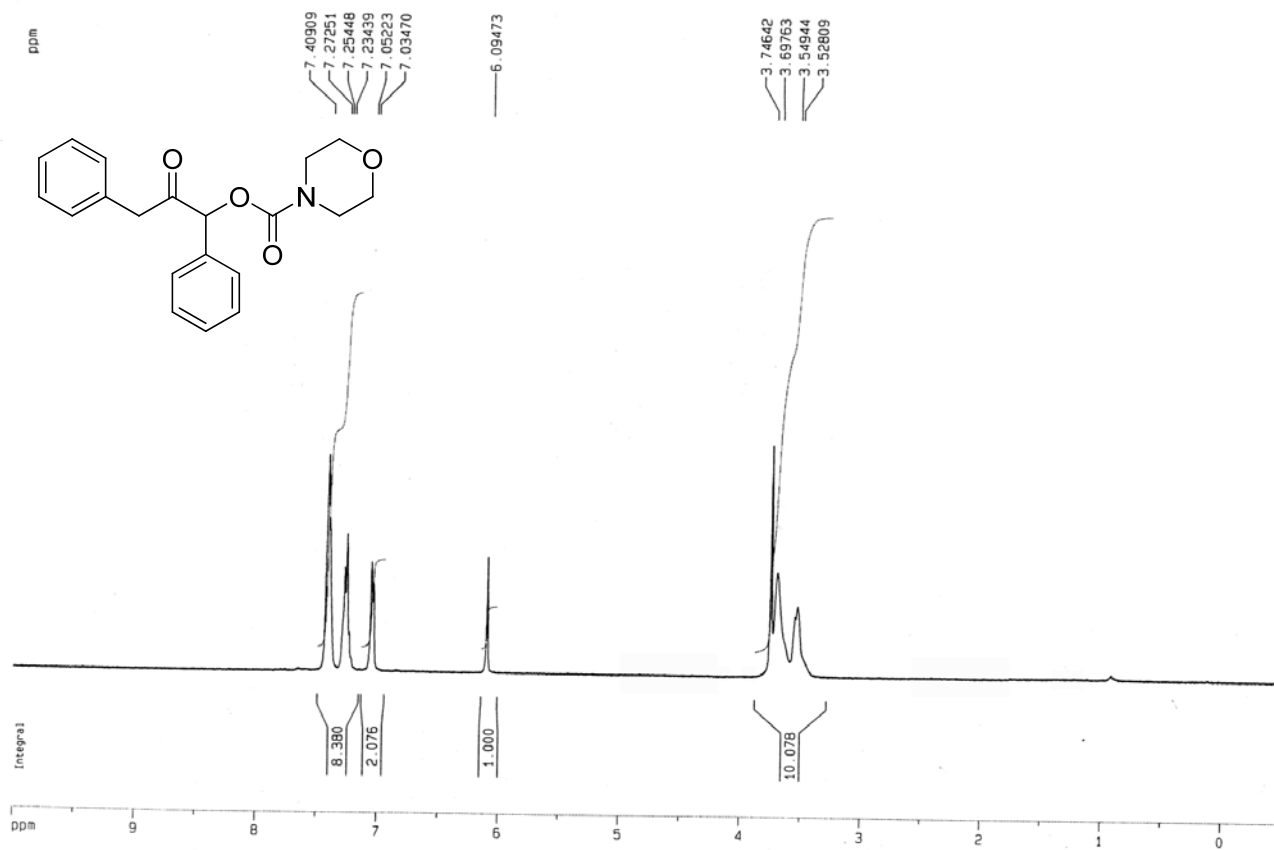
30



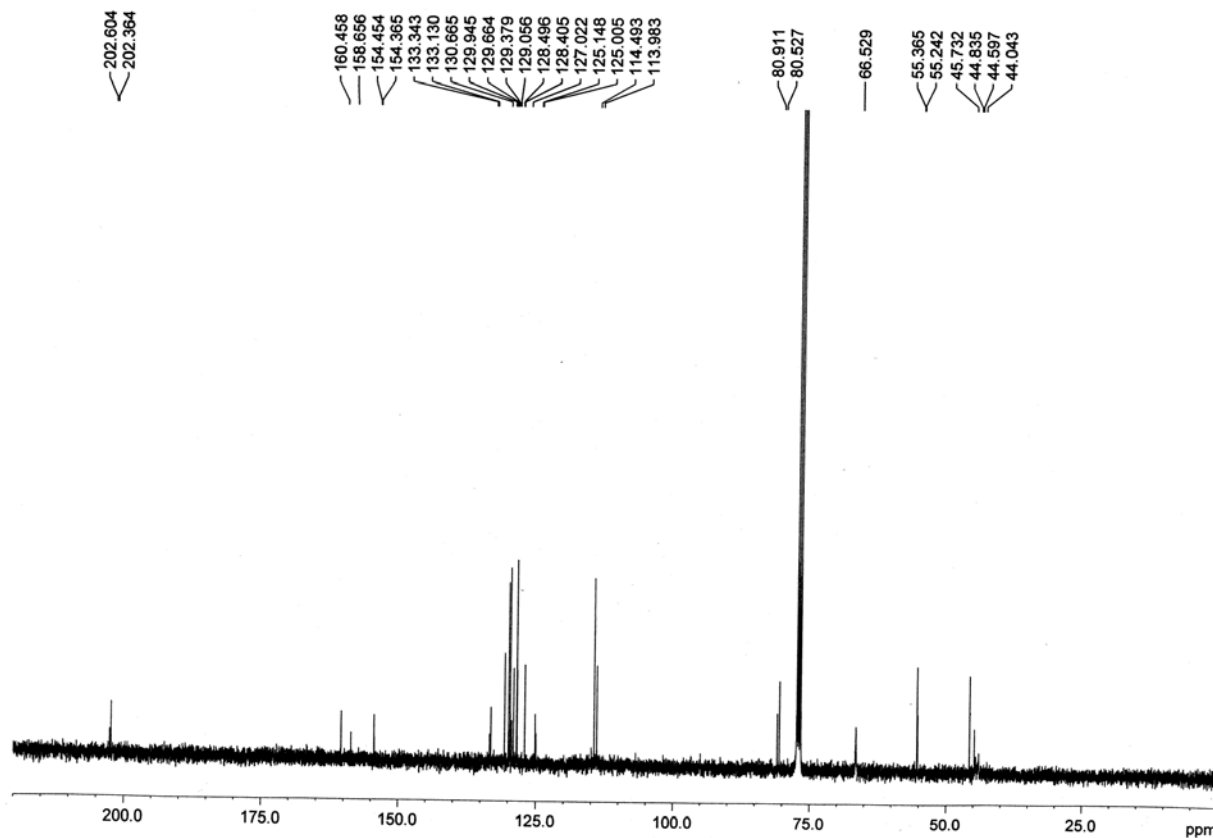
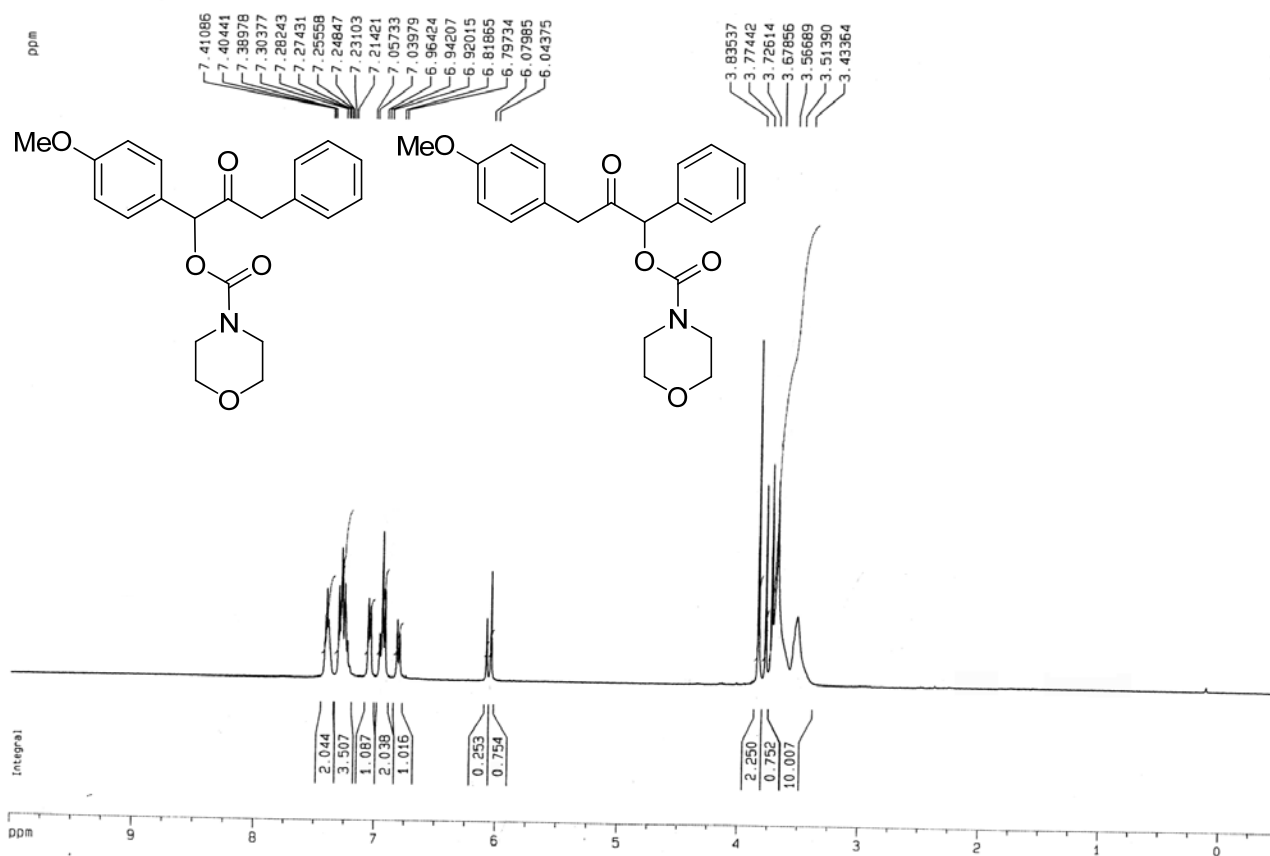
3p



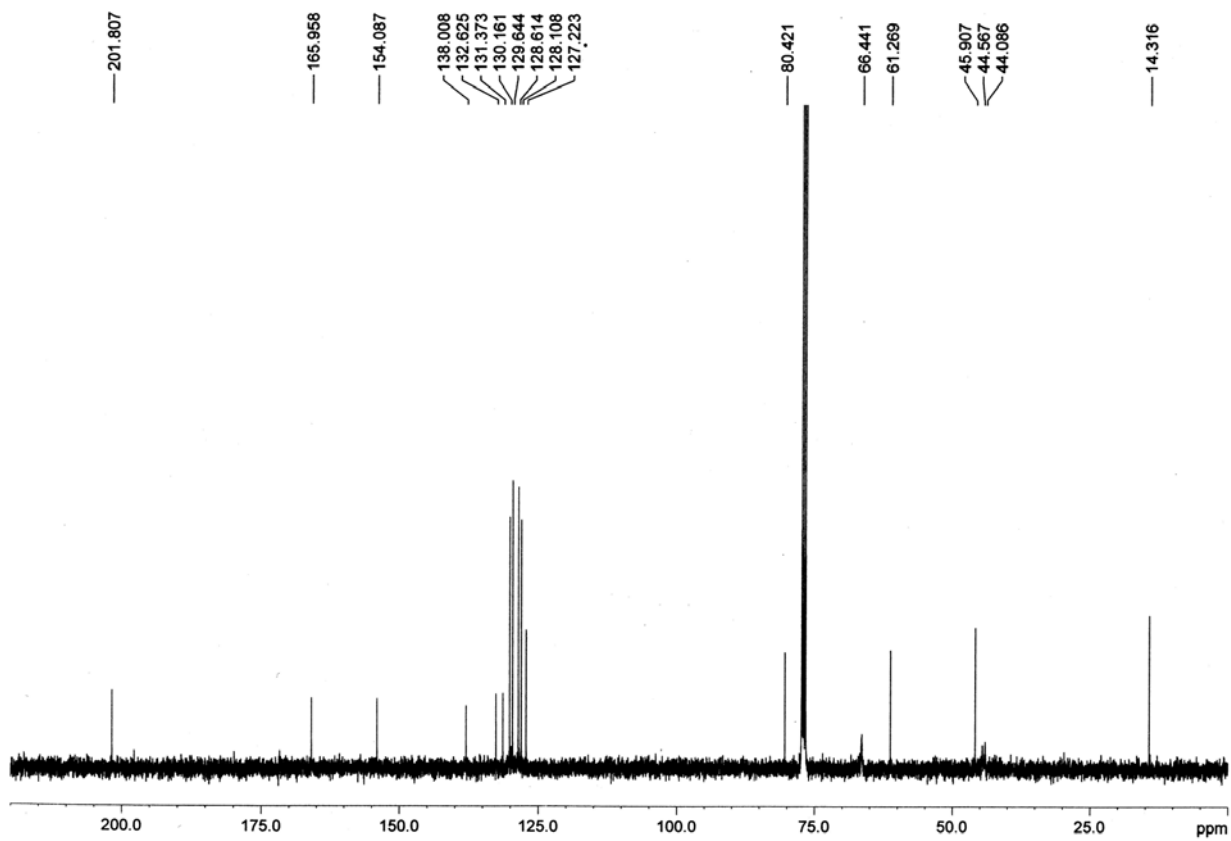
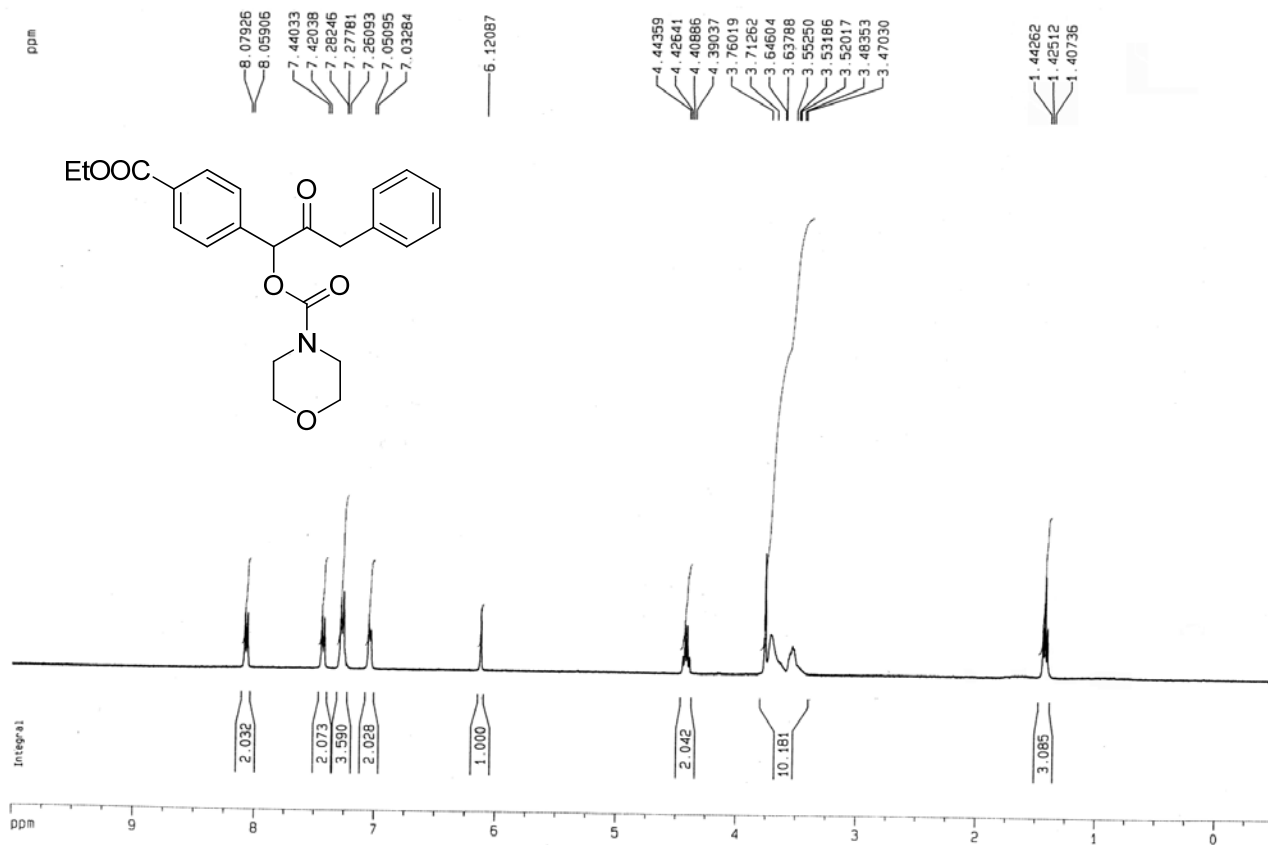
7a



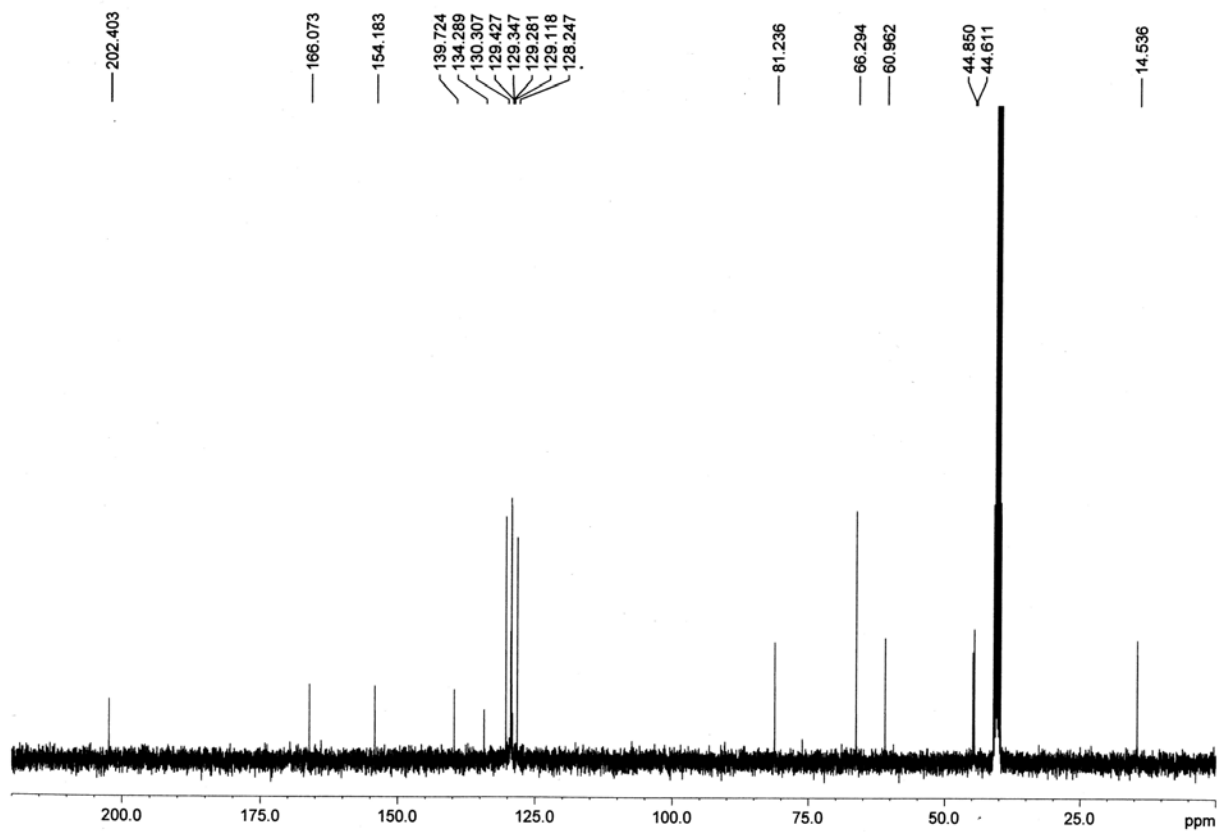
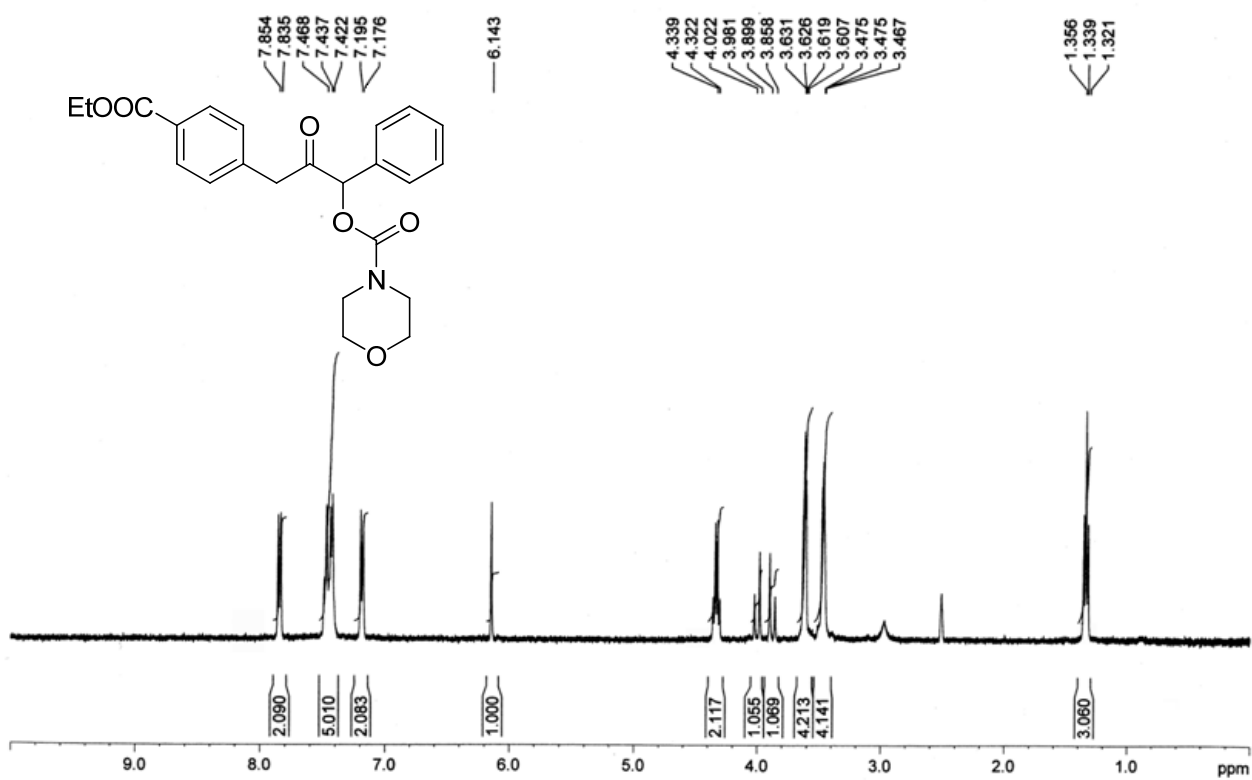
7q + 7q'



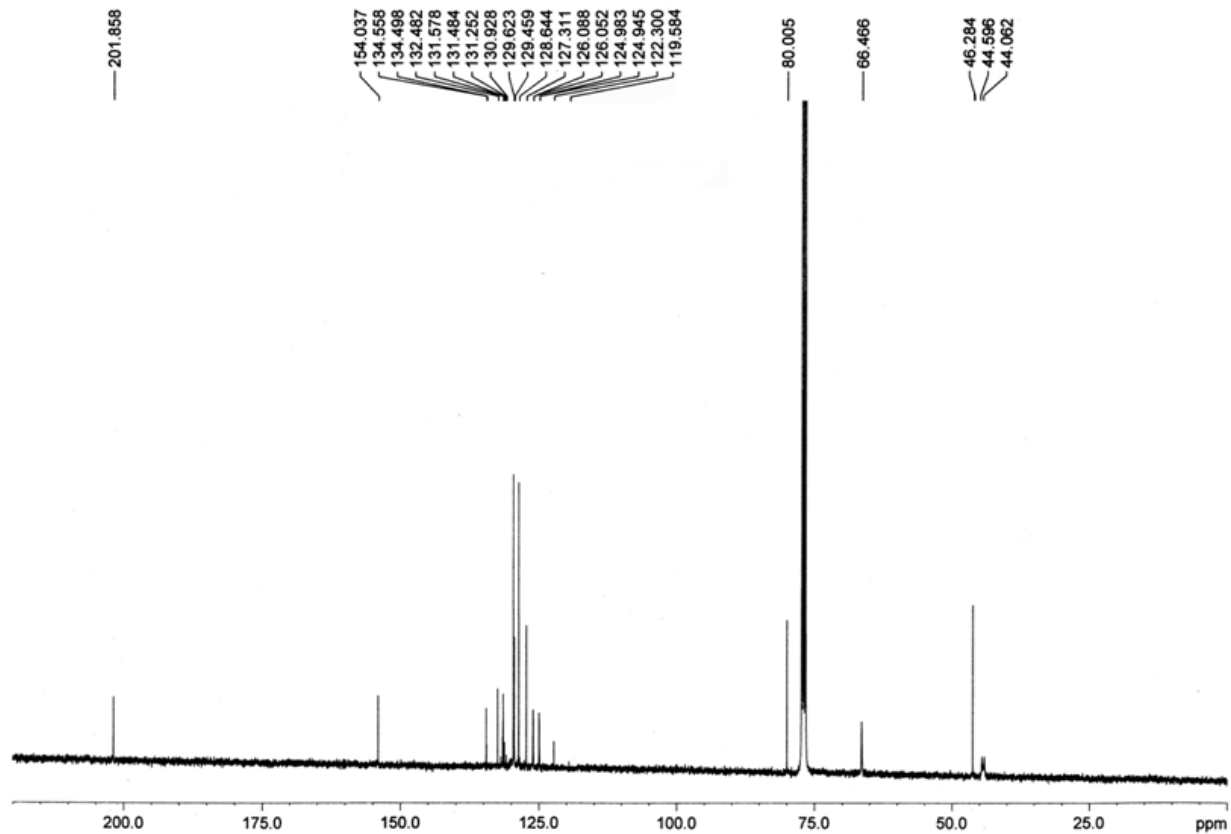
7r

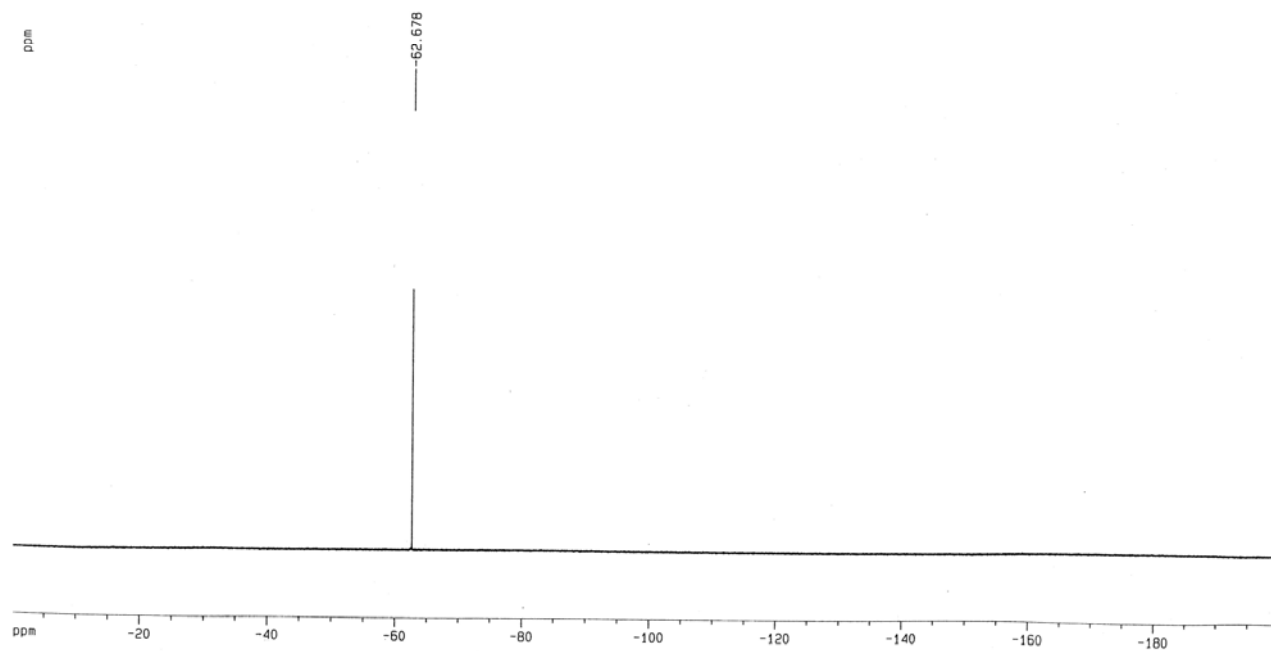


7r'

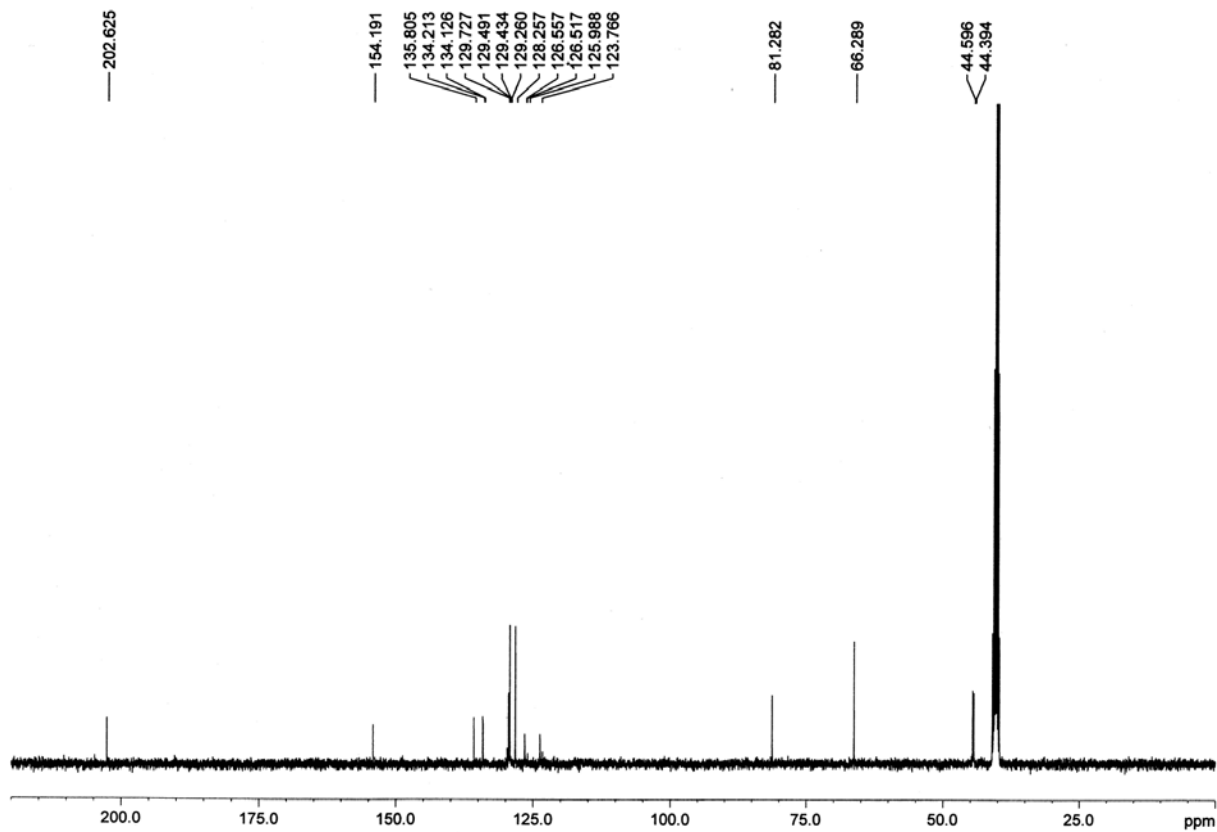
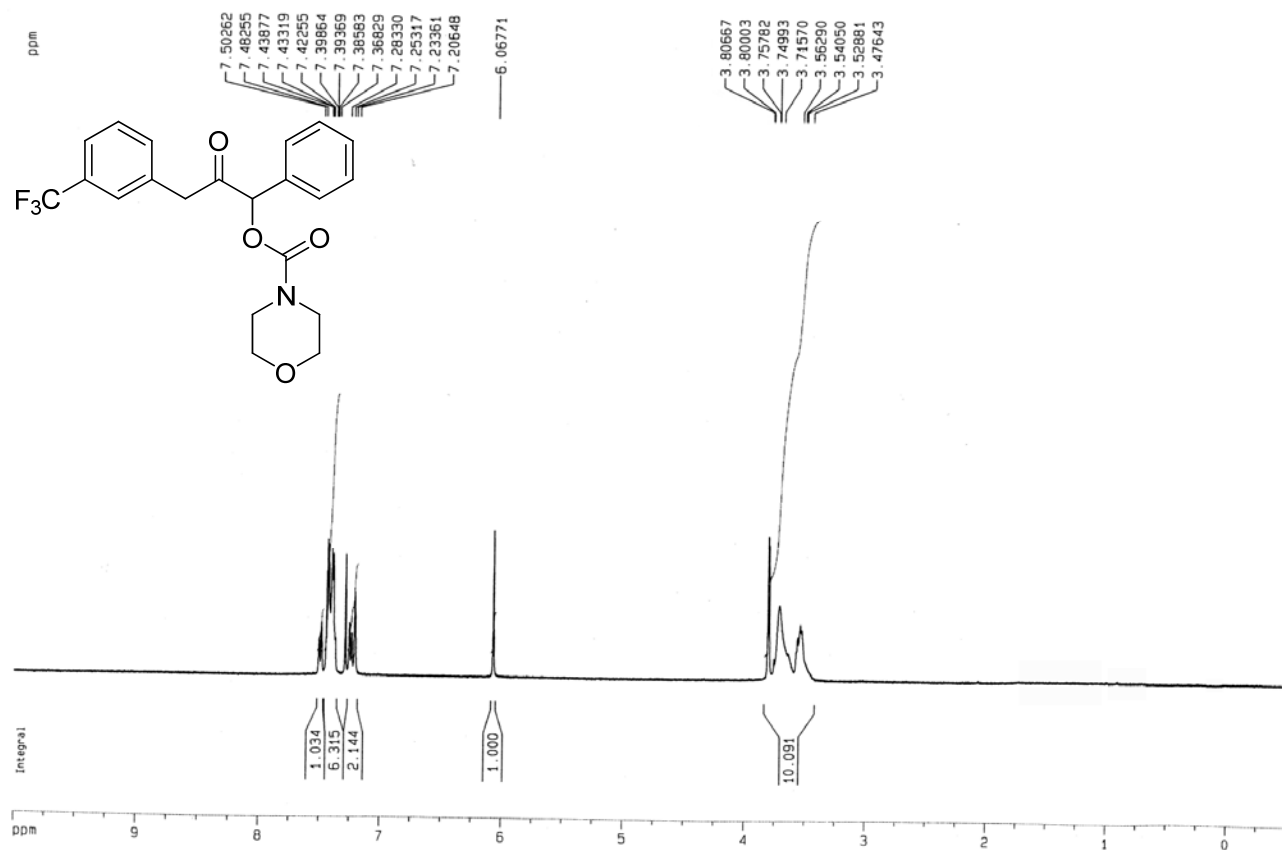


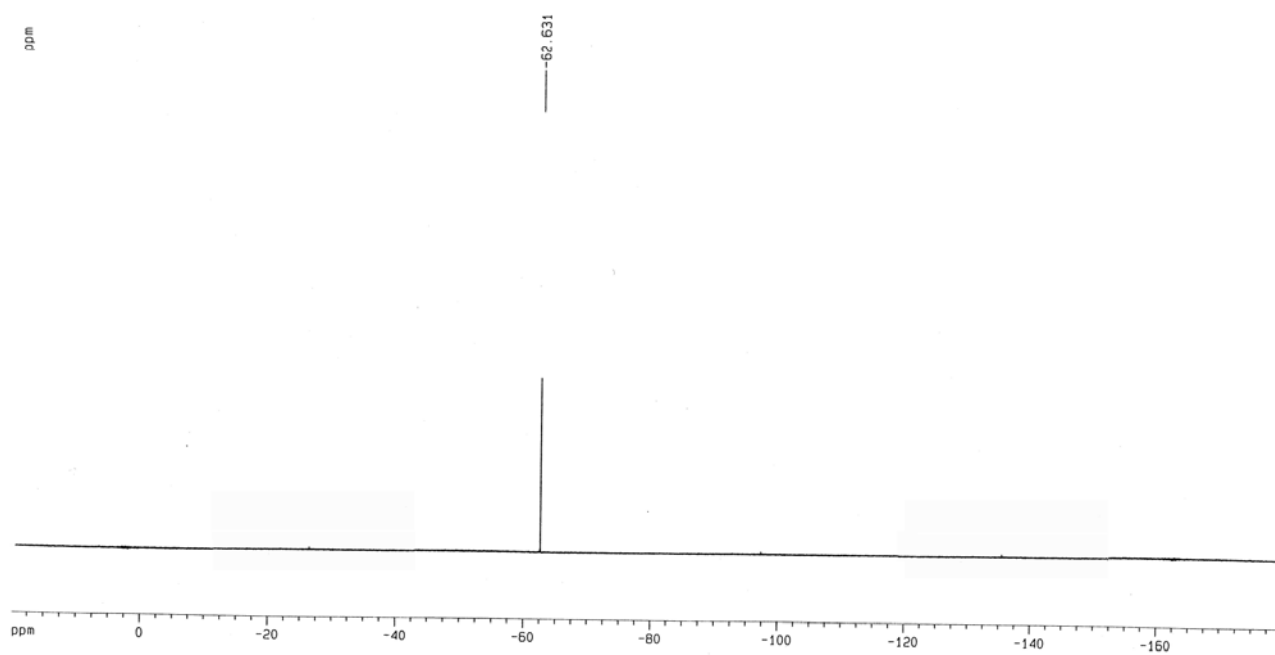
7s





7s'





7t + 7t'

