

Supplementary Experimental Information

Efficient Palladium/1, 10-Phenanthroline Catalyzed Reductive Carbonylation of Mono- and Dinitroarenes to Urethanes in Phosphonium Salt Ionic Liquids

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I. General remarks

Unless otherwise noted, all the materials were purchased from commercial suppliers and employed as received. Methanol was freshly distilled by standard procedure prior to use. All ^1H and ^{13}C NMR spectra were recorded at room temperature on a Bruker 400MHz spectrometer. Chemical shifts are reported in ppm with the solvent resonance as the internal standard (CDCl_3 7.24 ppm for proton, and 77.0 ppm for carbon magnetic resonance spectroscopy or DMSO 2.50 ppm for proton, and 39.5 ppm for carbon magnetic resonance spectroscopy). Data are reported as follows: chemical shift, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, br=broad, m=multiplet), coupling constants (Hz). Mass spectra were obtained on a VG7070E mass spectrometer. All Ionic Liquids used were obtained from Cytec Canada Inc., Niagara Falls, Ontario. Ionic liquids were degassed under high vacuum at 100 °C for at least one hour immediately prior to use.

II. General procedure for the reductive carbonylation of mononitroarenes

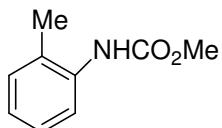
A mixture of the mononitroarene (2.0 mmol), PdCl_2 (0.02 mmol), 1, 10-phenanthroline (0.04 mmol), MeOH (30 mmol), and PSIL110 [trihexyl(tetradecyl)phosphonium hexafluorophosphate] (2.0 g) was added to the autoclave with magnetic stirring. The autoclave was closed, purged three times with carbon monoxide, and then pressurized with 200 *psi* of carbon monoxide at room temperature and the autoclave was immersed in an oil bath preheated at 135 °C for 24 h. Excess CO was discharged at room temperature. The reaction mixture was purified by flash chromatography on silica gel with the eluent hexane / EtOAc (v/v: 10:1) to give the corresponding monourethanes in 79-96% yields.

III. General procedure for the reductive carbonylation of dinitroarenes

A mixture of dinitroarene (2.0 mmol), PdCl_2 (0.1 or 0.04 mmol), 1, 10-phenanthroline (0.2 or 0.08 mmol), MeOH (60 mmol) and PSIL110 (2.0 g) was added to the autoclave. The autoclave was closed and purged three times with CO, then pressurized with 200 *psi* of CO and the autoclave was immersed in an oil bath preheated

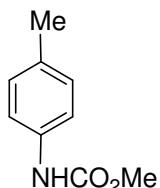
at 135 °C for 24 hrs. The reaction mixture was purified by flash chromatography on silica gel (gradient from hexane/CHCl₃ 1:1 to pure CHCl₃) to give the corresponding diurethanes, but contaminated with trace of PSIL110. Pure products were obtained after washing with toluene (70-86%).

IV. Characterization data for mono- and diurethanes



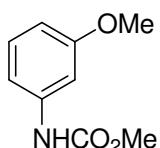
Methyl *o*-tolylurethane, **2**

¹H NMR (400MHz, CDCl₃): δ 7.74 (br s, 1H), 7.21-7.13 (m, 2H), 7.04-7.00 (m, 1H), 6.48 (br s, 1H), 3.76 (s, 3H), 2.23 (s, 3H); ¹³C NMR (100MHz, CDCl₃): δ 154.4, 135.7, 130.3, 126.7, 124.2, 52.3, 17.5; HRMS (EI) m/z calcd for C₉H₁₁NO₂ (M⁺) 165.0790, found 165.0768.



Methyl *p*-tolylurethane, **4**

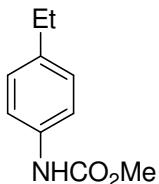
¹H NMR (400MHz, CDCl₃): δ 7.28 (d, 2H, *J* = 8.0 Hz), 7.08 (d, 2H, *J* = 8.0 Hz), 7.06 (br s, 1H), 3.75 (s, 3H), 2.29 (s, 3H); ¹³C NMR (100MHz, CDCl₃): δ 154.3, 135.2, 132.7, 129.3, 118.8, 52.0, 20.5; HRMS (EI) m/z calcd for C₉H₁₁NO₂ (M⁺) 165.0790, found 165.0802.



Methyl 3-methoxyphenylurethane, **6**

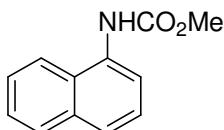
¹H NMR (400MHz, CDCl₃): δ 7.22-7.14(m, 3H), 6.91 (dd, 1H, *J* = 8.0 and 1.2 Hz),

6.62-6.59 (m, 1H), 3.75 (s, 3H), 3.74 (s, 3H); ^{13}C NMR (100MHz, CDCl_3): δ 160.0, 154.1, 139.1, 129.5, 110.9, 108.9, 104.4, 55.0, 52.1; HRMS (EI) m/z calcd for $\text{C}_9\text{H}_{11}\text{NO}_3$ (M^+) 181.0739, found 181.0732.



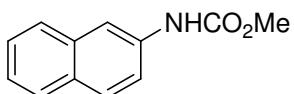
Methyl 4-ethylphenylurethane, **8**

^1H NMR (400MHz, CDCl_3): δ 7.28 (d, 2H, $J = 8.0$ Hz), 7.11 (d, 2H, $J = 8.4$ Hz), 6.79 (br s, 1H), 3.75 (s, 3H), 2.59 (t, 2H, $J = 7.6$ Hz); ^{13}C NMR (100MHz, CDCl_3): δ 154.2, 139.4, 135.4, 128.2, 118.9, 52.2, 28.1, 15.6; HRMS (EI) m/z calcd for $\text{C}_{10}\text{H}_{13}\text{NO}_2$ (M^+) 179.0946, found 179.0954.



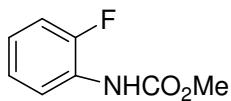
Methyl naphthalen-1-ylurethane, **10**

^1H NMR (400MHz, CDCl_3): δ 7.86-7.83 (m, 3H), 7.65 (d, 1H, $J = 8.0$ Hz), 7.49-7.42 (m, 3H), 7.10 (br s, 1H), 3.80 (s, 3H); ^{13}C NMR (100MHz, CDCl_3): δ 155.0, 134.0, 132.4, 128.6, 126.1, 125.9, 125.6, 125.1, 120.5, 52.5; HRMS (EI) m/z calcd for $\text{C}_{12}\text{H}_{11}\text{NO}_2$ (M^+) 201.0790, found 201.0784.



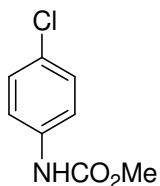
Methyl naphthalen-2-ylurethane, **12**

^1H NMR (100MHz, CDCl_3): δ 7.99 (br s, 1H), 7.77-7.72 (m, 3H), 7.46-7.36 (m, 3H), 7.16 (br s, 1H), 3.80 (s, 3H); ^{13}C NMR (100MHz, CDCl_3): δ 154.2, 135.3, 133.8, 130.1, 128.7, 127.4, 127.3, 126.4, 124.5, 119.2, 114.9, 52.3; HRMS (EI) m/z calcd for $\text{C}_{12}\text{H}_{11}\text{NO}_2$ (M^+) 201.0790, found 201.0791.



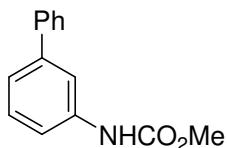
Methyl 2-fluorophenylurethane, **14**

^1H NMR (400MHz, CDCl_3): δ 88.07 (br s, 1H), 7.11-6.94 (m, 4H), 3.77 (s, 3H); ^{13}C NMR (100MHz, CDCl_3): δ 153.7, 152.1 (d, $J = 241.1$ Hz), 126.3 (d, $J = 10.1$ Hz), 124.4 (d, $J = 3.7$ Hz), 123.3 (d, $J = 7.4$ Hz), 120.2, 114.7 (d, $J = 19.0$ Hz), 52.3; HRMS (EI) m/z calcd for $\text{C}_8\text{H}_8\text{FNO}_2$ (M^+) 169.0539, found 169.0543.



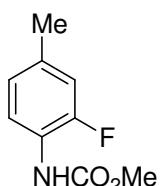
Methyl 4-chlorophenylurethane, **16**

^1H NMR (40MHz, CDCl_3): δ 7.30 (d, 1H, $J = 8.4$ Hz), 7.20 (dd, 2H, $J = 6.8$ and 2.0 Hz), 3.72 (s, 3H); ^{13}C NMR (100MHz, CDCl_3): δ 153.9, 136.4, 129.0, 128.4, 119.9, 52.4; HRMS (EI) m/z calcd for $\text{C}_8\text{H}_8\text{ClNO}_2$ (M^+) 185.0244, found 185.0260.



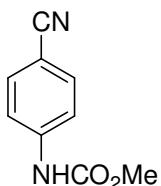
Methyl biphenyl-3-ylurethane, **18**

^1H NMR (400MHz, CDCl_3): δ 7.66 (br s, 1H), 7.59(d, 1H, $J = 1.2$ Hz), 7.58 (s, 1H), 7.44-7.29 (m, 6H), 6.99 (br s, 1H), 3.78(S, 3H); ^{13}C NMR (100MHz, CDCl_3): δ 154.1, 142.0, 140.6, 138.3, 129.3, 128.6, 127.4, 127.0, 122.2, 117.5, 52.2; HRMS (EI) m/z calcd for $\text{C}_{14}\text{H}_{13}\text{NO}_2$ (M^+) 227.0946, found 227.0952.



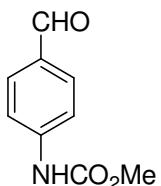
Methyl 2-fluoro-4-methylphenylurethane, **20**

¹H NMR (400MHz, CDCl₃): δ 7.86 (br s, 1H), 7.11-6.94 (m, 4H), 3.77 (s, 3H); ¹³C NMR (100MHz, CDCl₃): 153.8, δ152.1 (d, *J* = 240.7 Hz), 133.7 (d, *J* = 2.5 Hz), 124.7 (d, *J* = 3.2 Hz), 123.4 (d, *J* = 10.4 Hz), 120.3, 115.2 (d, *J* = 18.7 Hz), 52.2, 20.5; HRMS (EI) m/z calcd for C₉H₁₀FNO₂ (M⁺) 183.0696, found 183.0709.



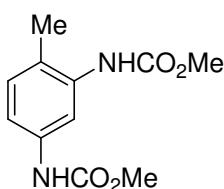
Methyl 4-cyanophenylurethane, **22**

¹H NMR (400MHz, CDCl₃): δ 7.61-7.57 (m, 2H), 7.52 (dd, 2H, *J* = 6.8 and 2.0 Hz), 6.97 (br s, 1H), 3.80 (s, 3H); ¹³C NMR (100MHz, CDCl₃): δ 153.3, 142.1, 133.3, 118.9, 118.2, 106.2, 52.7; HRMS (EI) m/z calcd for C₉H₈N₂O₂ (M⁺) 176.0586, found 176.0581.



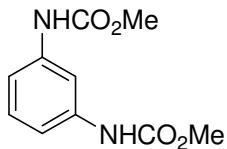
Methyl 4-formylphenylurethane, **24**

¹H NMR (400MHz, CDCl₃): δ 9.89 (s, 1H), 7.82 (d, 2H, *J* = 8.4 Hz), 7.55 (d, 2H, *J* = 8.4 Hz), 6.98(br s, 1H), 3.79 (s, 3H); ¹³C NMR (100MHz, CDCl₃): δ 190.9, 153.4, 143.6, 131.7, 131.3, 118.0, 52.7; HRMS (EI) m/z: calcd for C₁₂H₉NO₃ (M⁺) 179.0582, found 179.0596.



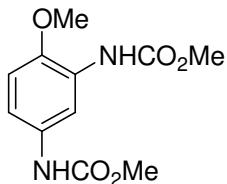
Dimethyl 4-methyl-1, 3-phenylenediurethane, **26**

¹H NMR (400MHz, DMSO): δ 9.51 (s, 1H), 8.77 (s, 1H), 7.47 (s, 1H), 7.15 (d, 1H, *J* = 1.6 Hz), 7.13 (d, 1H, *J* = 1.6 Hz), 3.612 (s, 3H), 3.608 (s, 3H), 2.09 (s, 3H); ¹³C NMR (100MHz, DMSO): δ 155.2, 154.4, 137.7, 136.9, 130.7, 126.0, 115.5, 115.3, 52.1, 52.0, 17.5; HRMS (EI) m/z: calcd for C₁₁H₁₄N₂O₄ (M⁺) 238.0954, found 238.0957.



Dimethyl 1,3-phenylenediurethane, **28**

¹H NMR (400MHz, DMSO): δ 9.56 (s, 1H), 7.62 (s, 1H), 7.14-7.10 (m, 1H), 7.06-7.03 (m, 2H), 3.61 (s, 6H); ¹³C NMR (100MHz, DMSO): δ 154.4, 140.0, 129.3, 113.1, 109.1, 52.0; HRMS (EI) m/z: calcd for C₁₀H₁₂N₂O₄ (M⁺) 224.0797, found 224.0810.



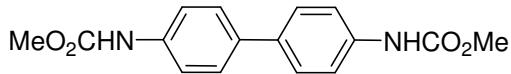
Dimethyl 4-methoxy-1,3-phenylenediurethane, **30**

¹H NMR (400MHz, DMSO): δ 9.39 (s, 1H), 8.35 (s, 1H), 7.73 (s, 1H), 7.12 (d, 1H, *J* = 8.0 Hz), 6.89 (d, 1H, *J* = 8.8 Hz), 3.71 (s, 3H), 3.602 (s, 3H), 3.597 (s, 3H); ¹³C NMR (100MHz, DMSO): δ 154.62, 154.58, 146.3, 132.5, 127.5, 114.8, 113.7, 111.9, 56.4, 52.2, 51.9; HRMS (EI) m/z: calcd for C₁₁H₁₄N₂O₅ (M⁺) 254.0903, found 254.0878.



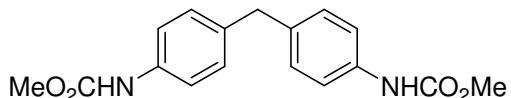
Dimethyl 1,4-phenylenediurethane, **32**

¹H NMR (400MHz, DMSO): δ 9.49 (s, 2H), 7.34 (s, 4H), 3.64 (s, 6H); ¹³C NMR (100MHz, DMSO): δ 154.5, 134.4, 119.3, 52.0; HRMS (EI) m/z: calcd for C₁₀H₁₂N₂O₄ (M⁺) 224.0797, found 224.0827.



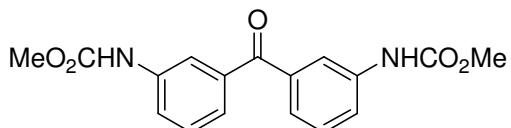
Dimethyl biphenyl-4, 4'-diyldiurethane, 34

¹H NMR (400MHz, DMSO): δ 9.67 (s, 2H), 7.54-7.47 (m, 8H), 3.64 (s, 6H); ¹³C NMR (100MHz, DMSO): δ 154.4, 138.6, 134.3, 126.9, 119.0, 52.1; HRMS (EI) m/z: calcd for C₁₆H₁₆N₂O₄ (M⁺) 300.11110, found 300.1121.



Dimethyl 4, 4'-methylenebis (4, 1-phenylene)diurethane, 36

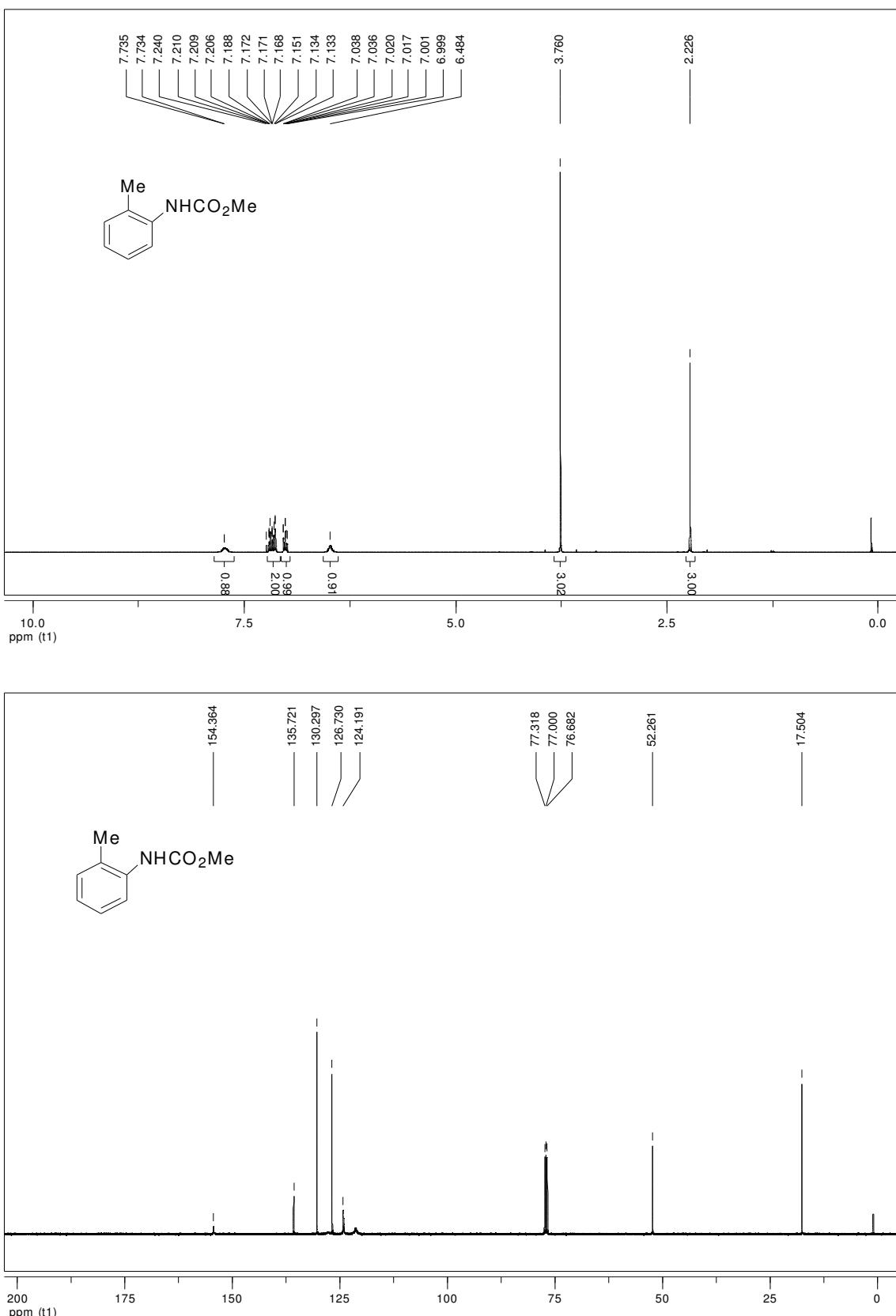
¹H NMR (400MHz, DMSO): δ 9.51 (s, 2H), 7.23 (d, 4H, J = 8.0 Hz), 7.07 (d, 4H, J = 8.8 Hz), 3.75 (s, 2H), 3.61 (s, 6H); ¹³C NMR (100MHz, DMSO): δ 154.5, 137.5, 136.0, 129.3, 118.9, 52.0; HRMS (EI) m/z: calcd for C₁₇H₁₈N₂O₄ (M⁺) 314.1267, found 314.1269.



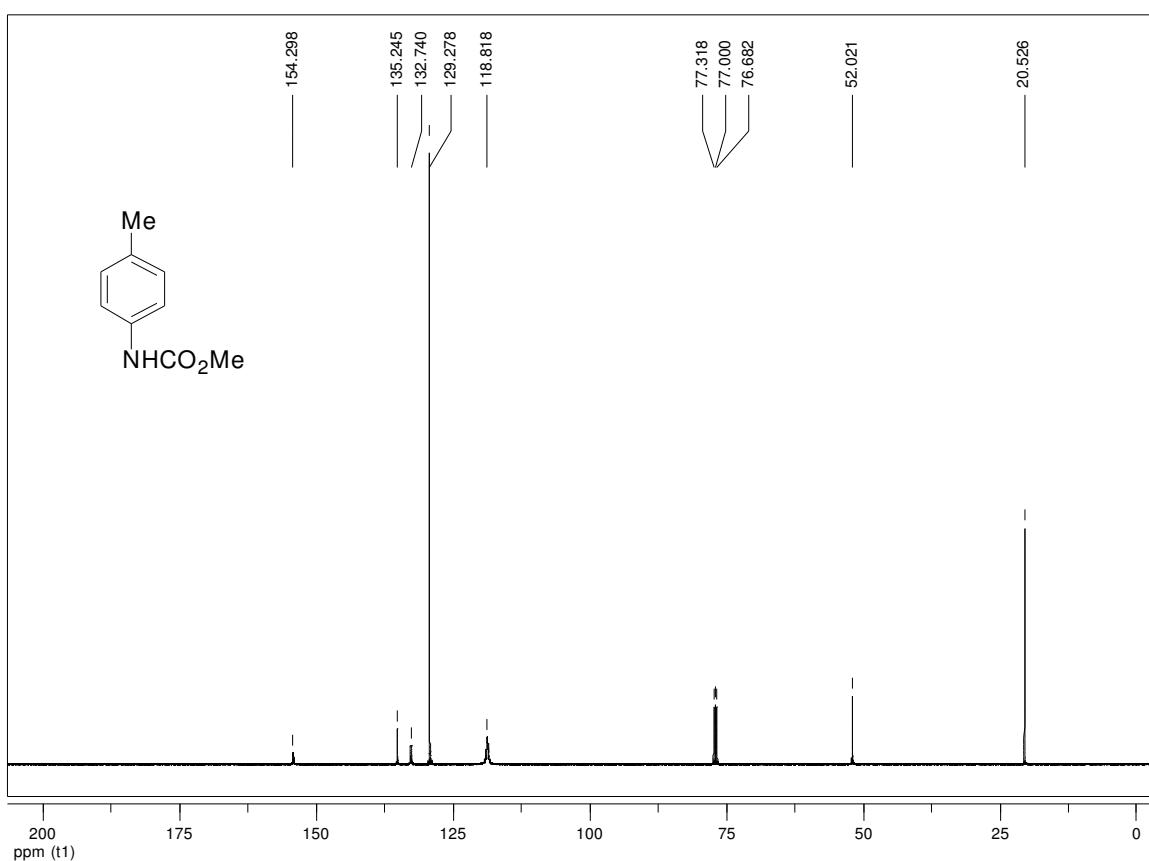
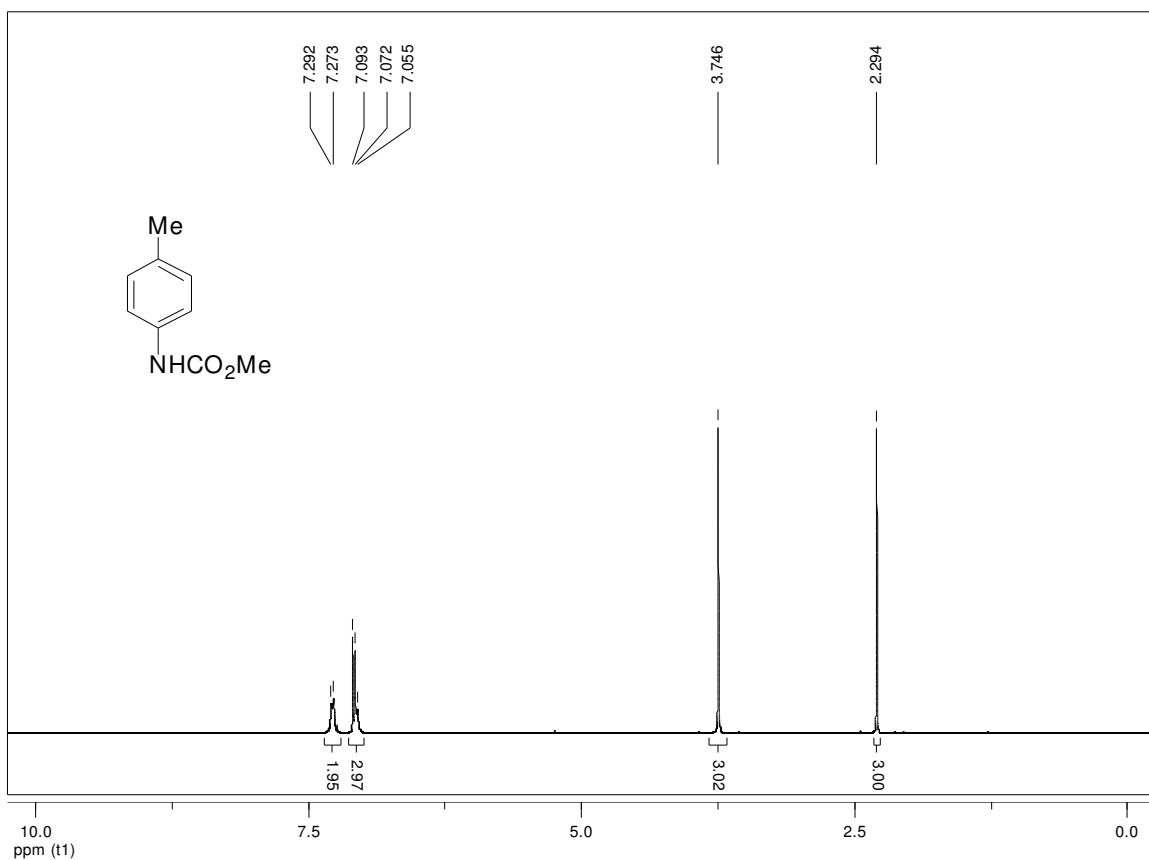
Dimethyl 3, 3'-carbonylbis (3, 1-phenylene)diurethane, 38

¹H NMR (400MHz, DMSO): δ 9.85 (s, 1H), 7.85 (s, 2H), 7.72 (d, 2H, J = 8.0 Hz), 7.43 (t, 2H, J = 8.0 Hz), 7.30 (d, 2H, J = 7.6 Hz), 3.64 (s, 6H); ¹³C NMR (100MHz, DMSO): δ 196.0, 154.5, 139.9, 138.0, 129.5, 124.2, 122.6, 119.4, 52.3; HRMS (EI) m/z: calcd for C₁₇H₁₆N₂O₅ (M⁺) 328.1059, found 328.1049.

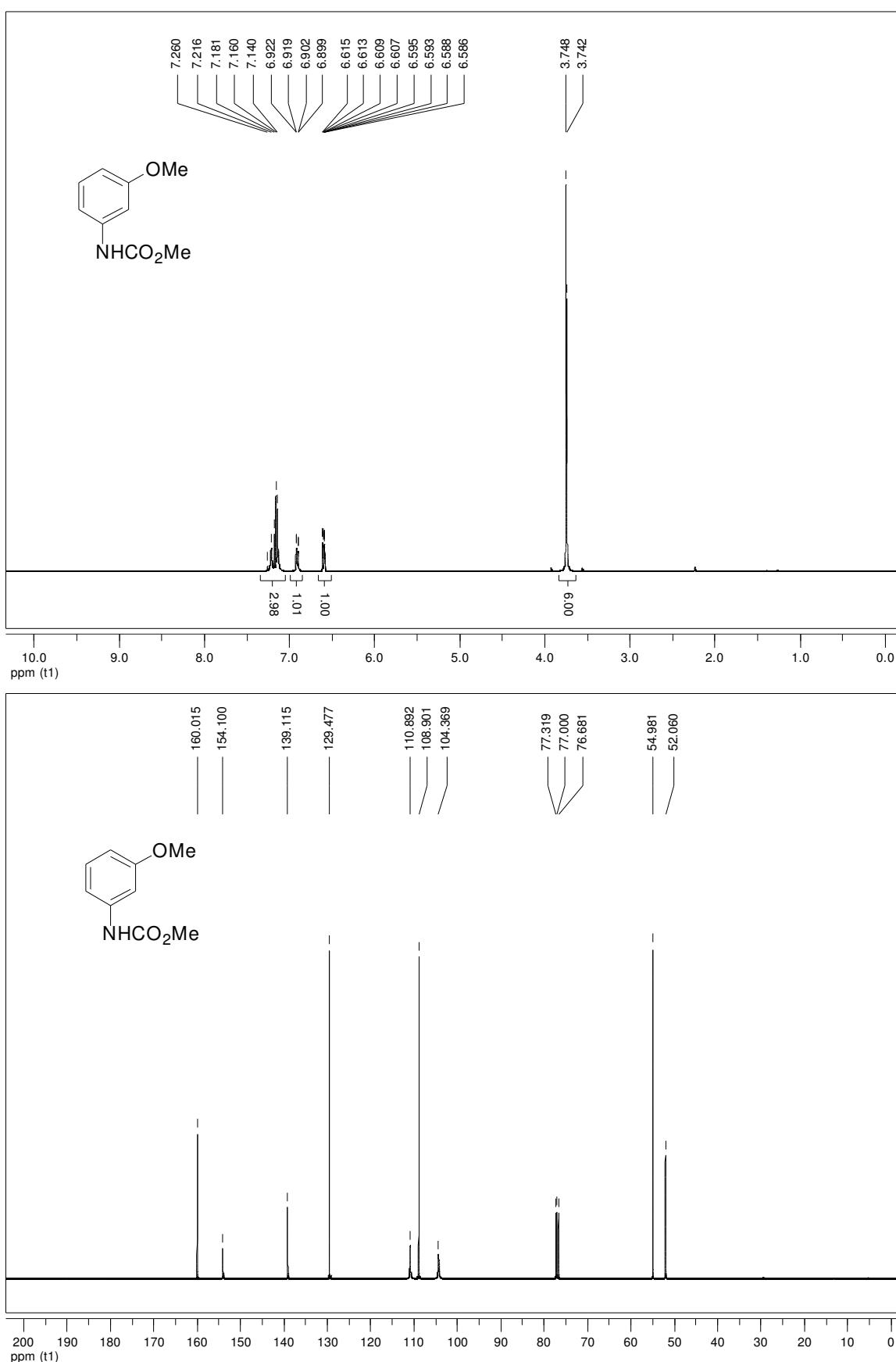
V. ^1H NMR and ^{13}C NMR spectra for mono- and diurethanes



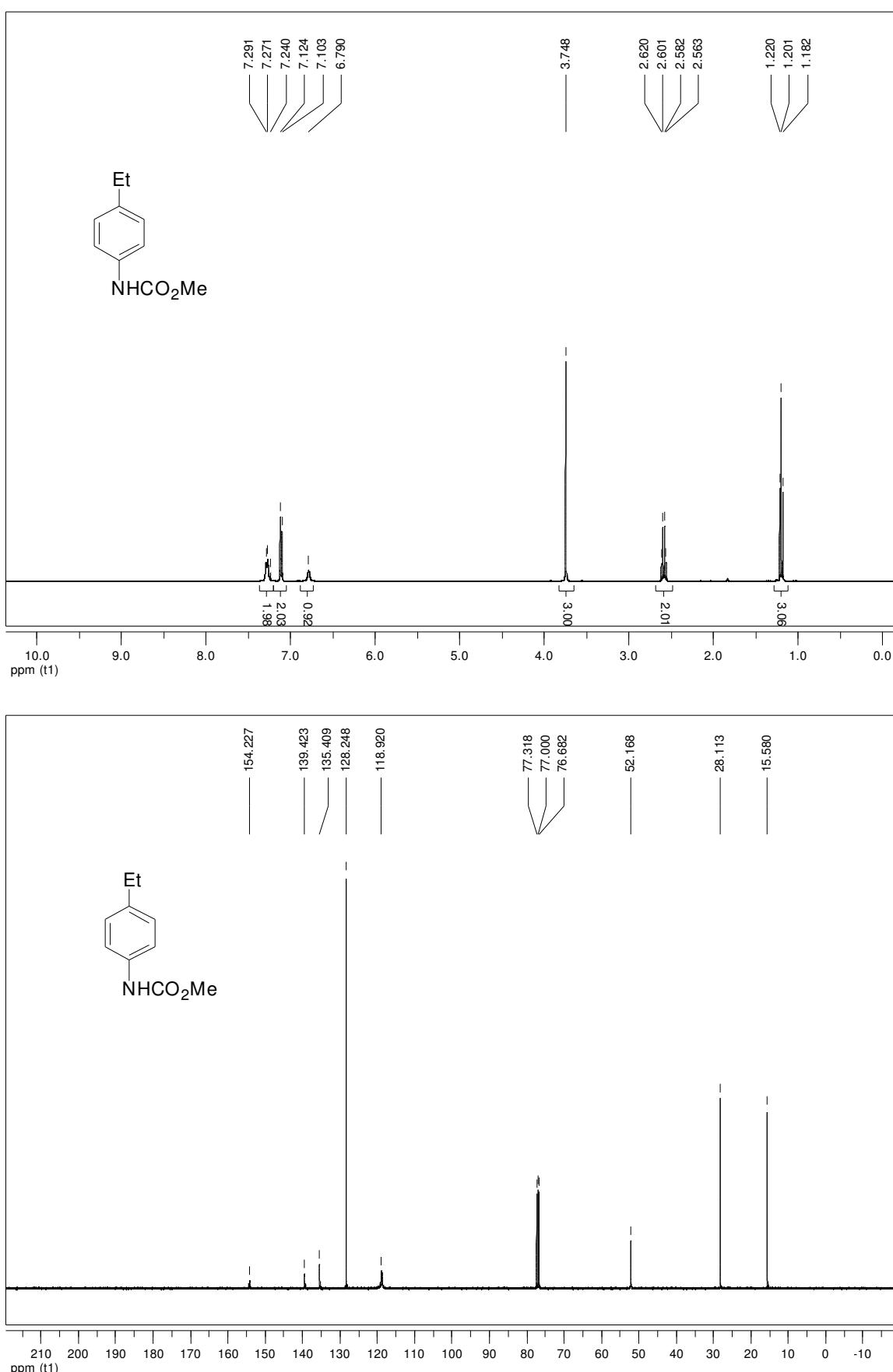
^1H NMR and ^{13}C NMR spectra of product 2



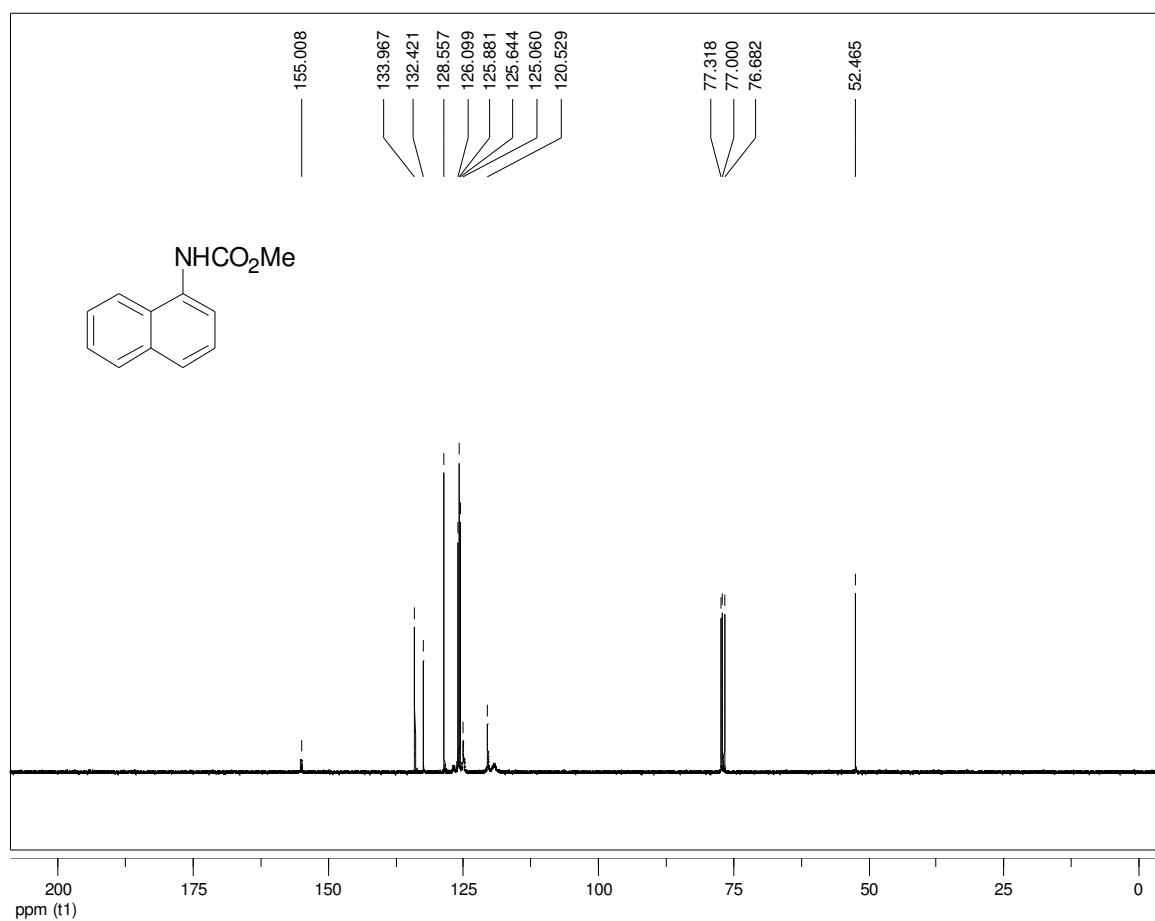
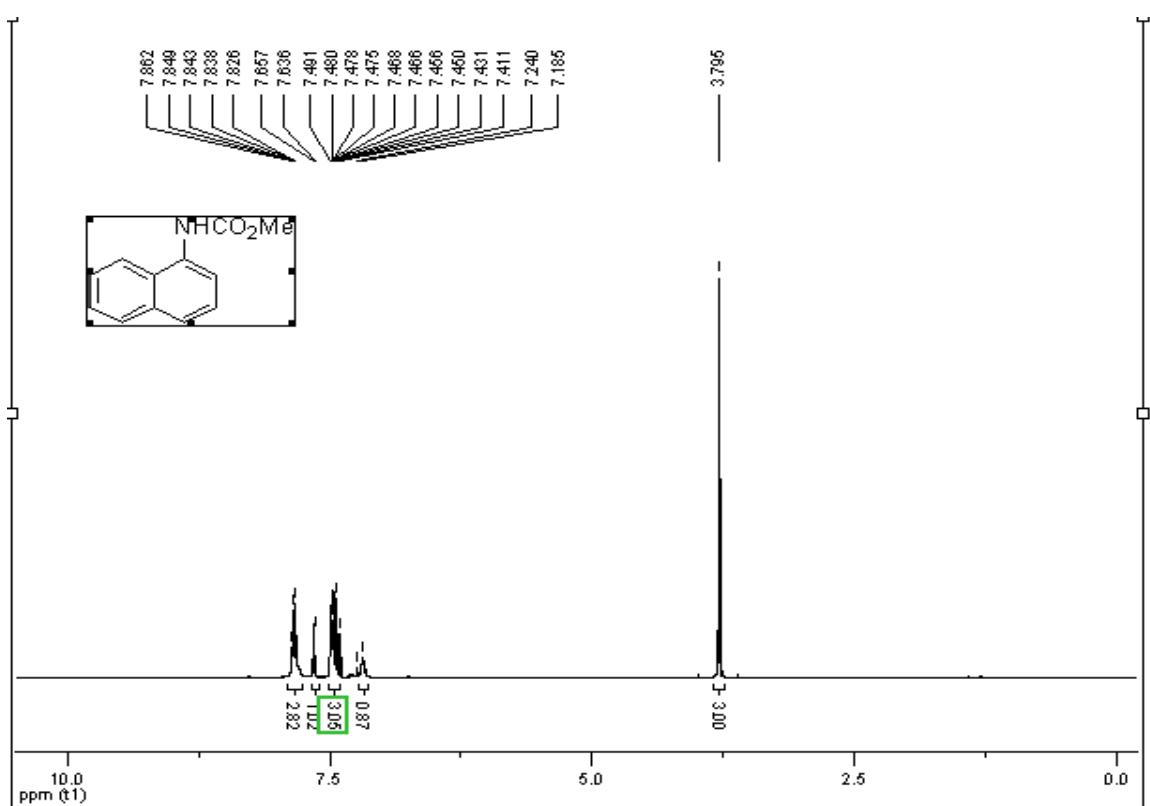
¹H NMR and ¹³C NMR spectra of product 4



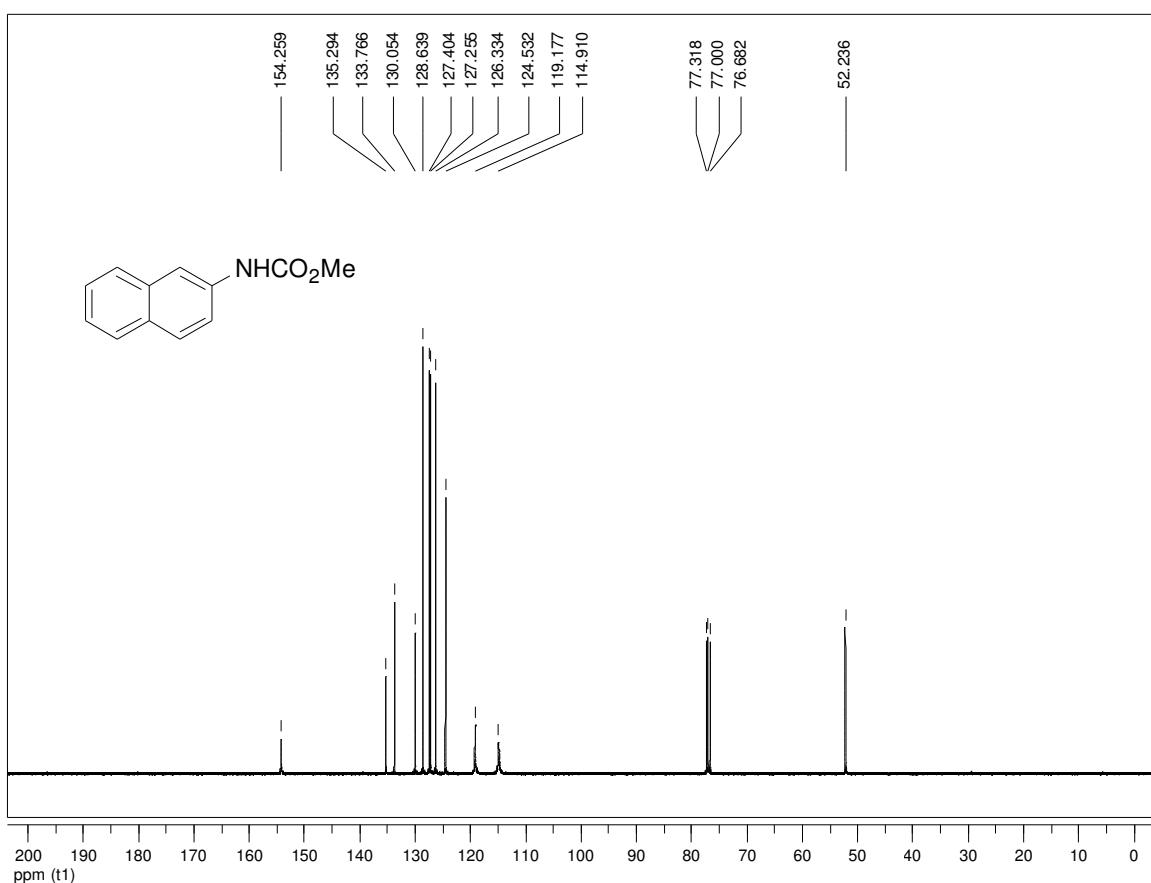
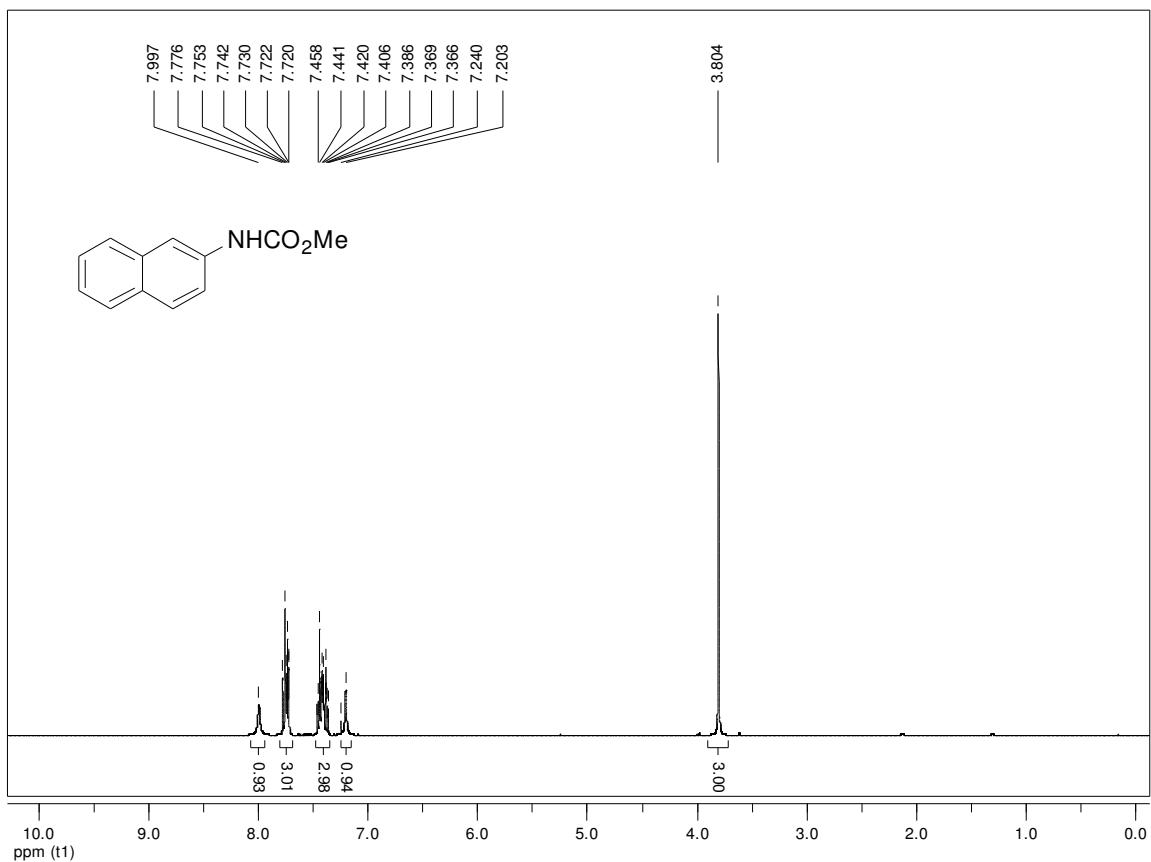
^1H NMR and ^{13}C NMR spectra of product **6**



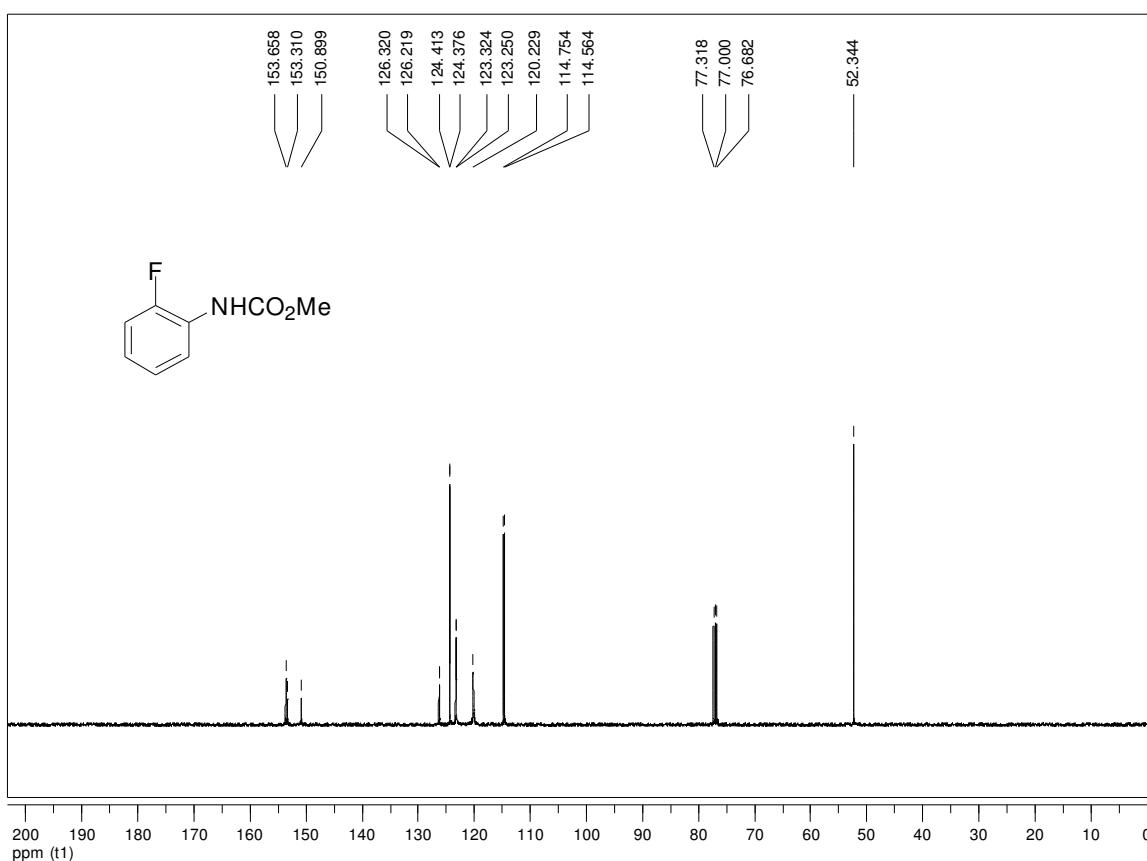
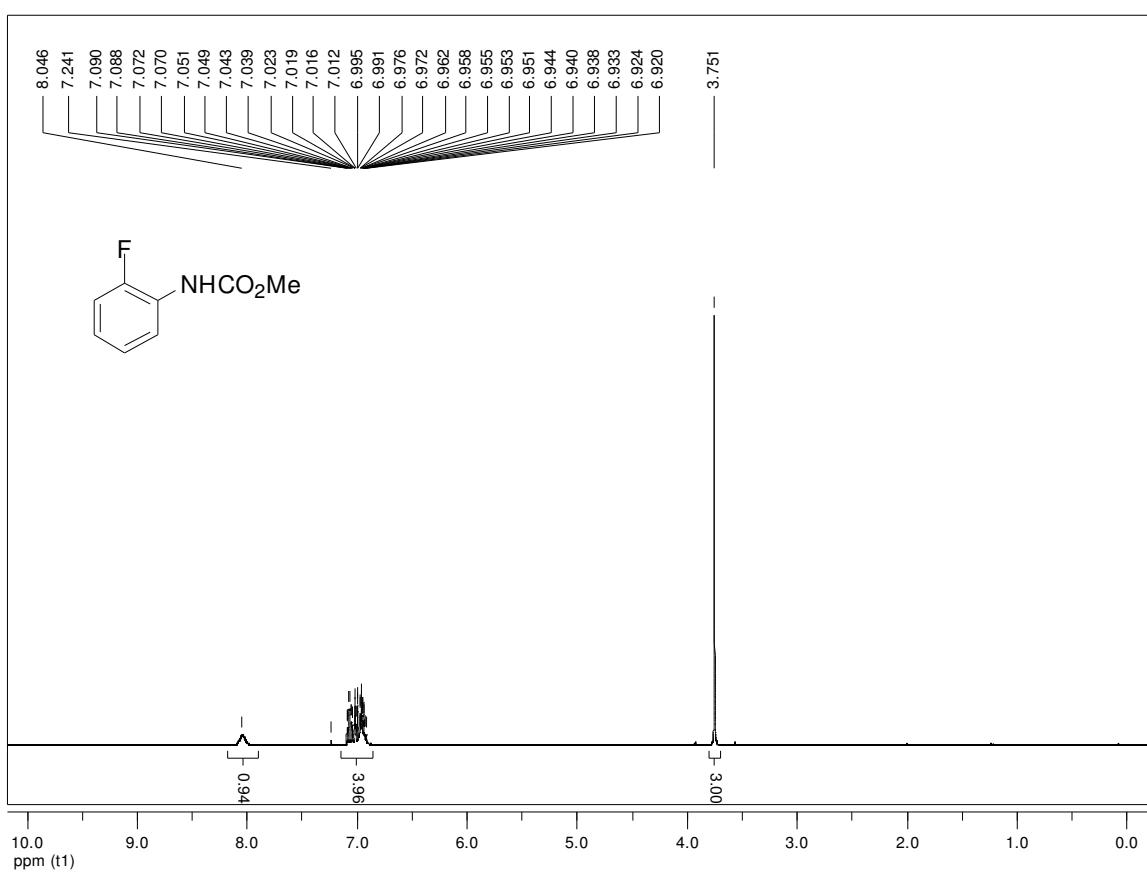
¹H NMR and ¹³C NMR spectra of product **8**



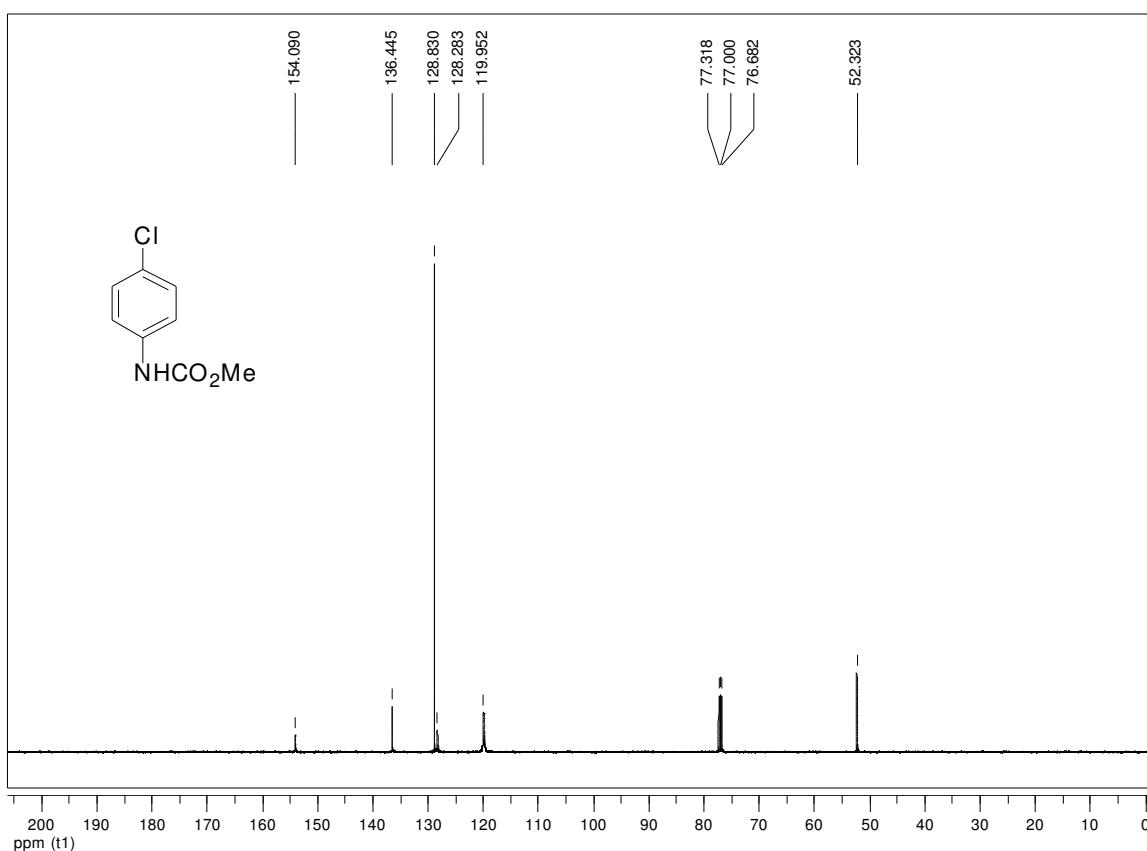
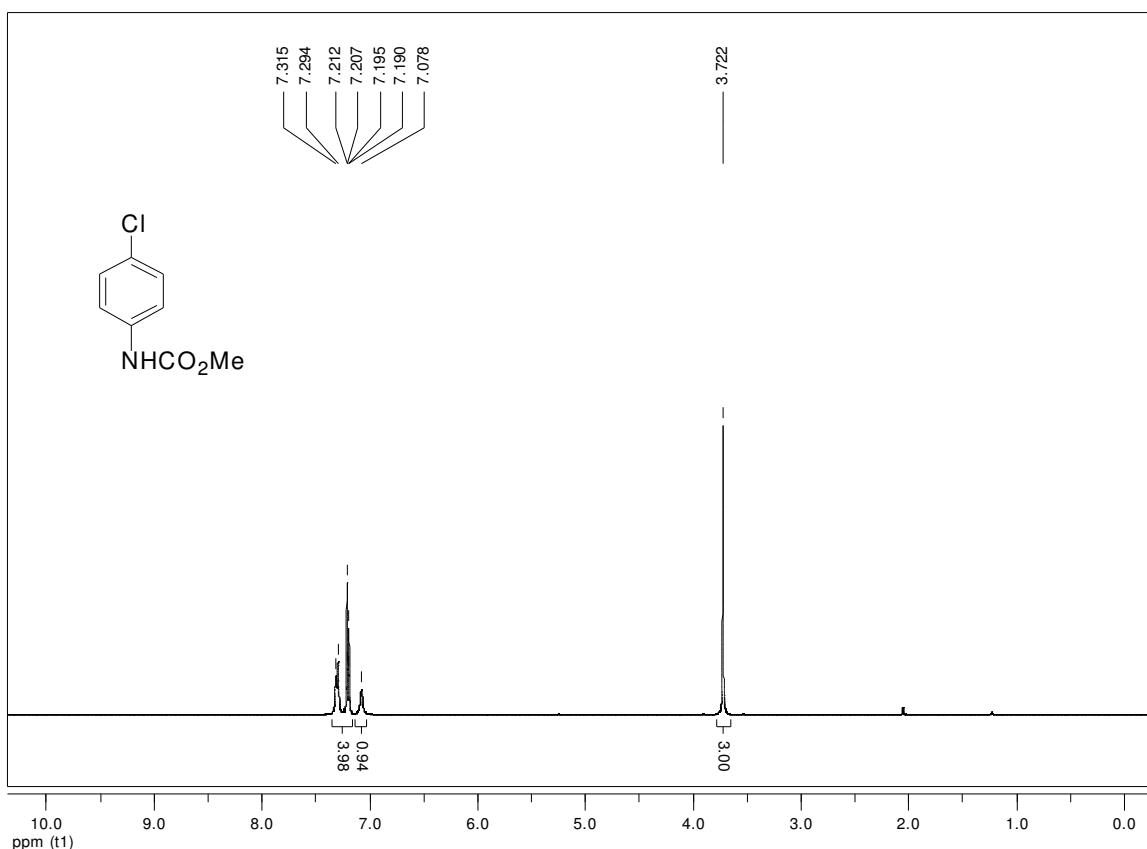
¹H NMR and ¹³C NMR spectra of product **10**



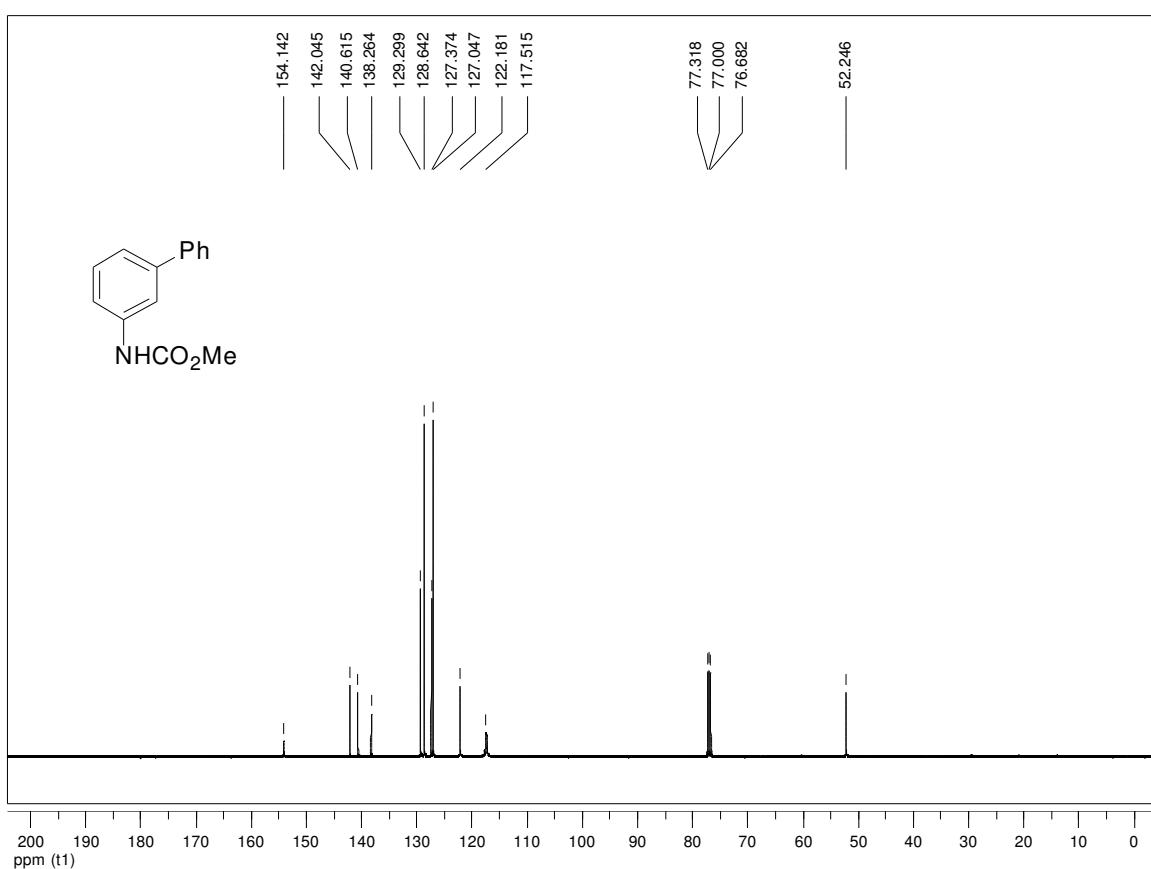
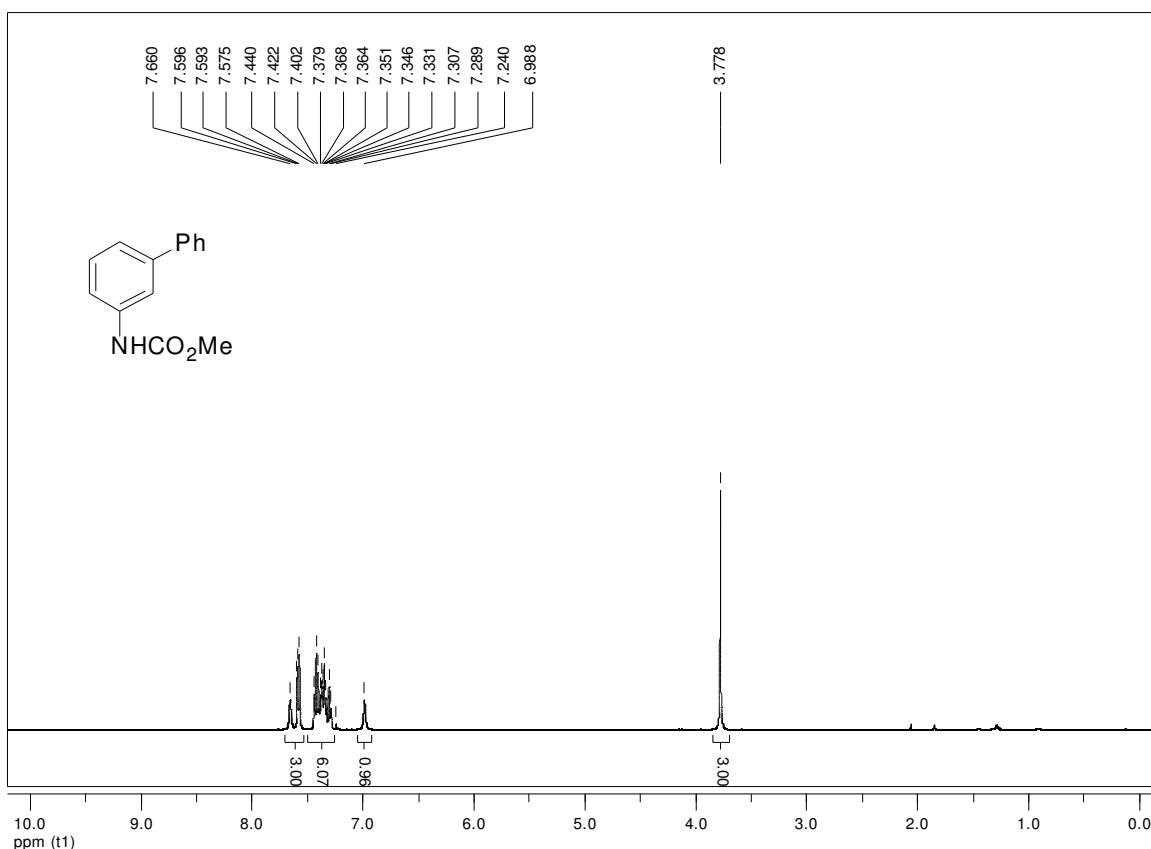
¹H NMR and ¹³C NMR spectra of product **12**



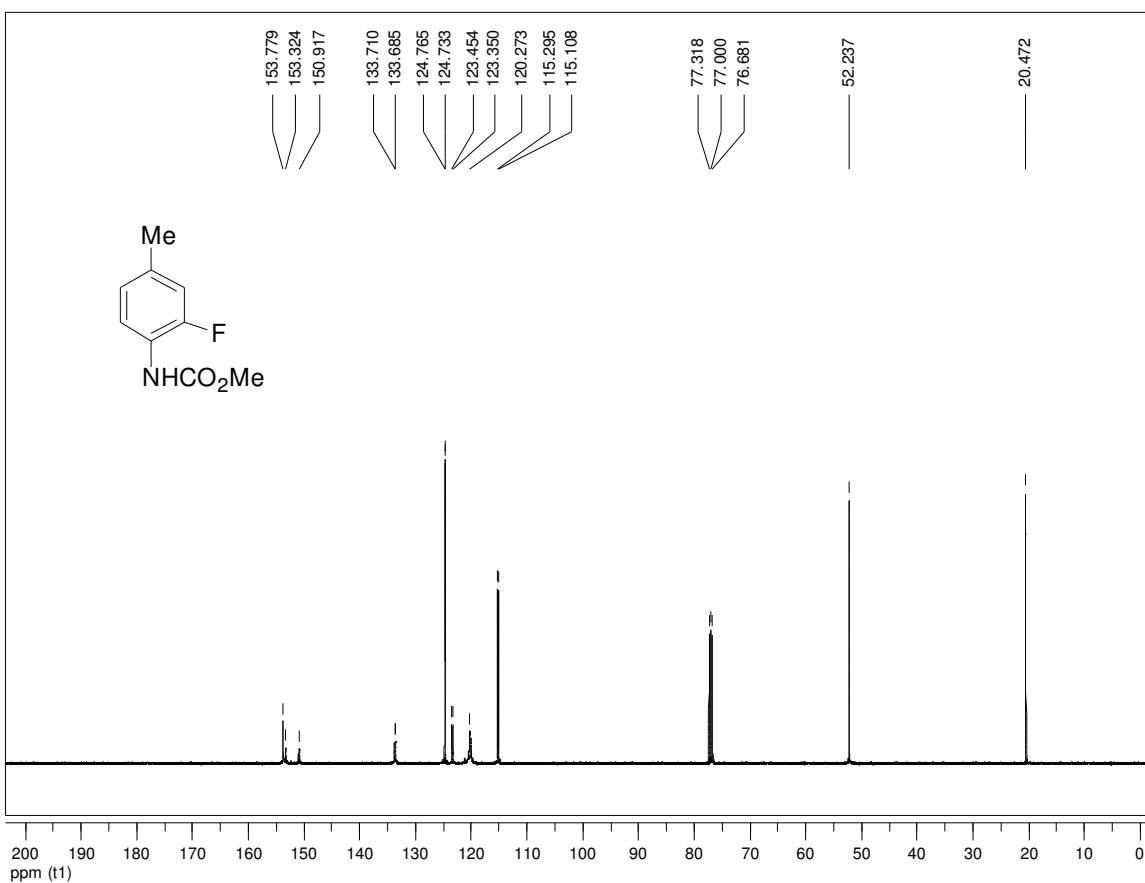
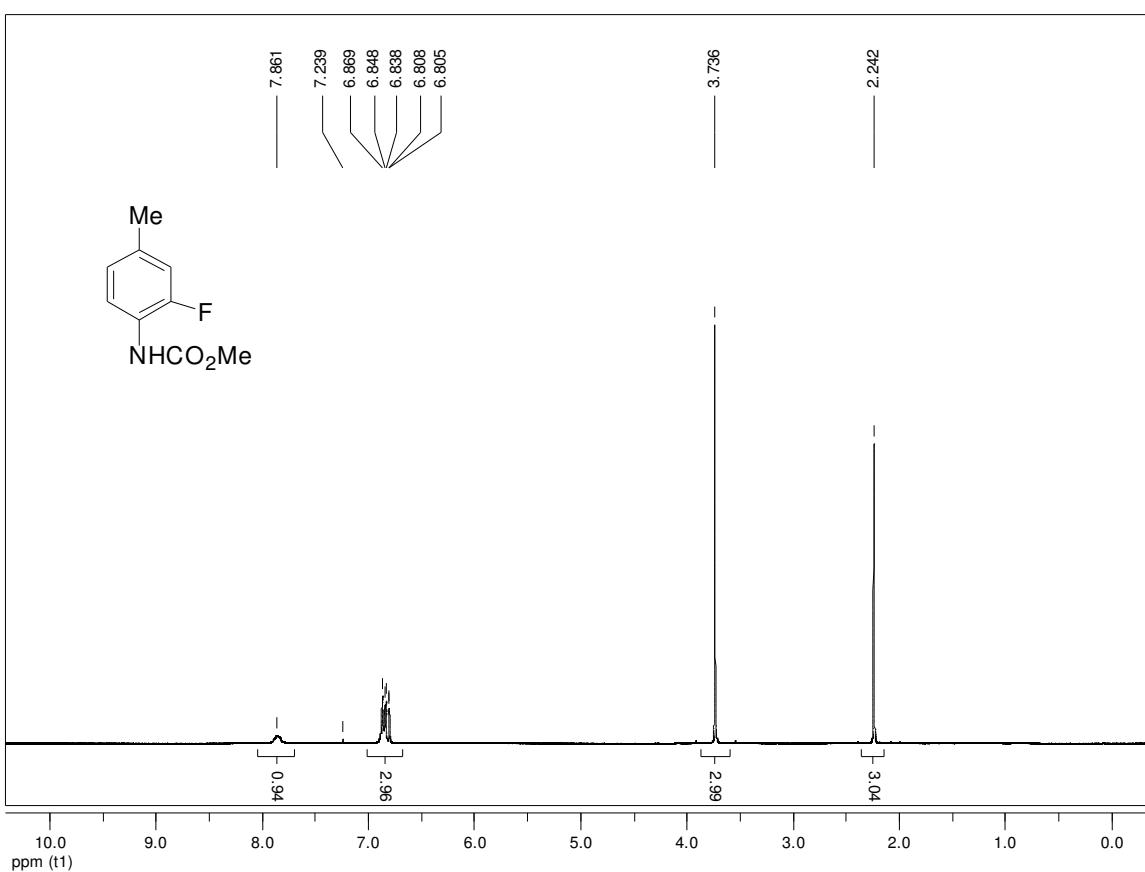
^1H NMR and ^{13}C NMR spectra of product **14**



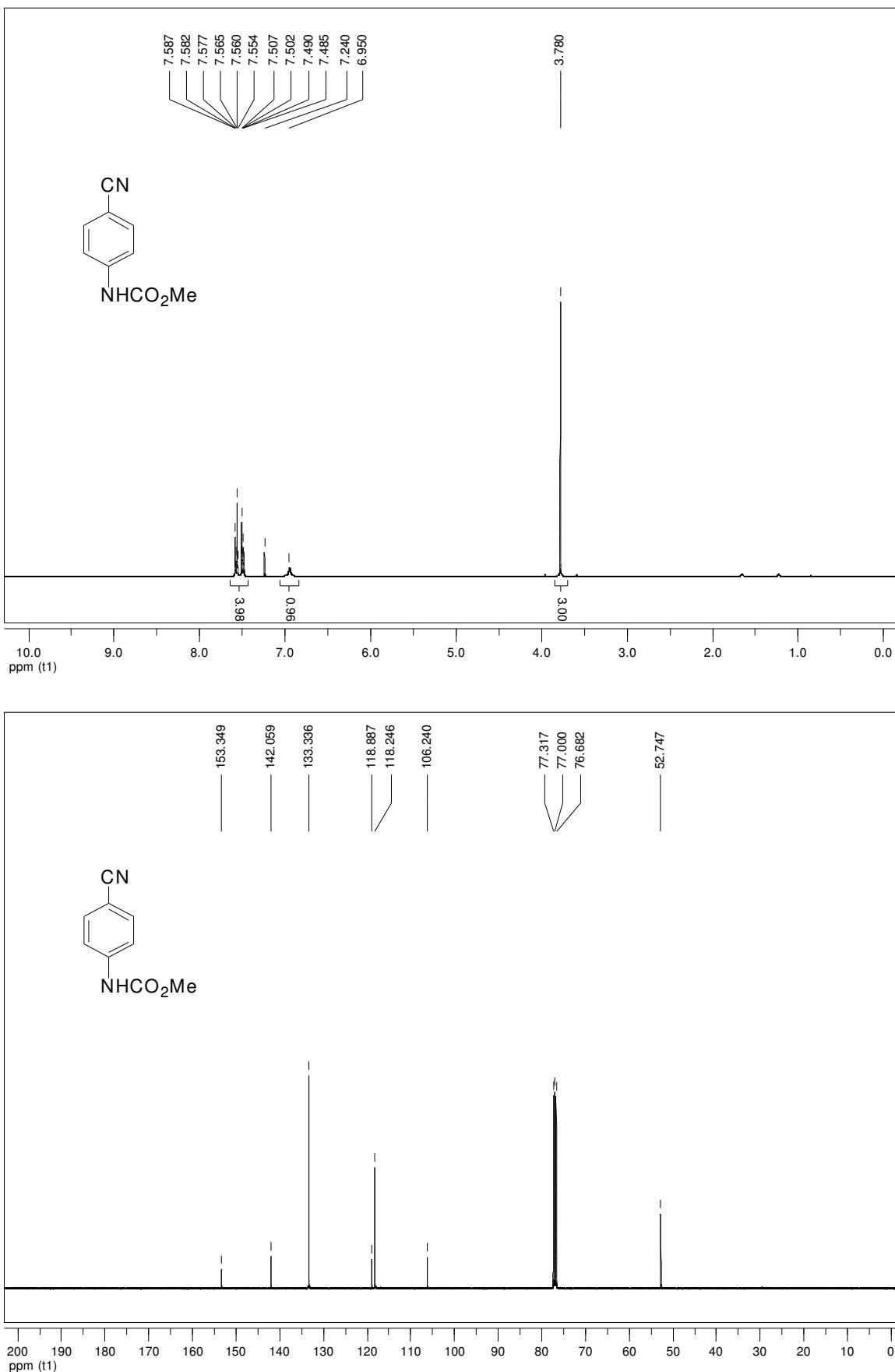
¹H NMR and ¹³C NMR spectra of product **16**



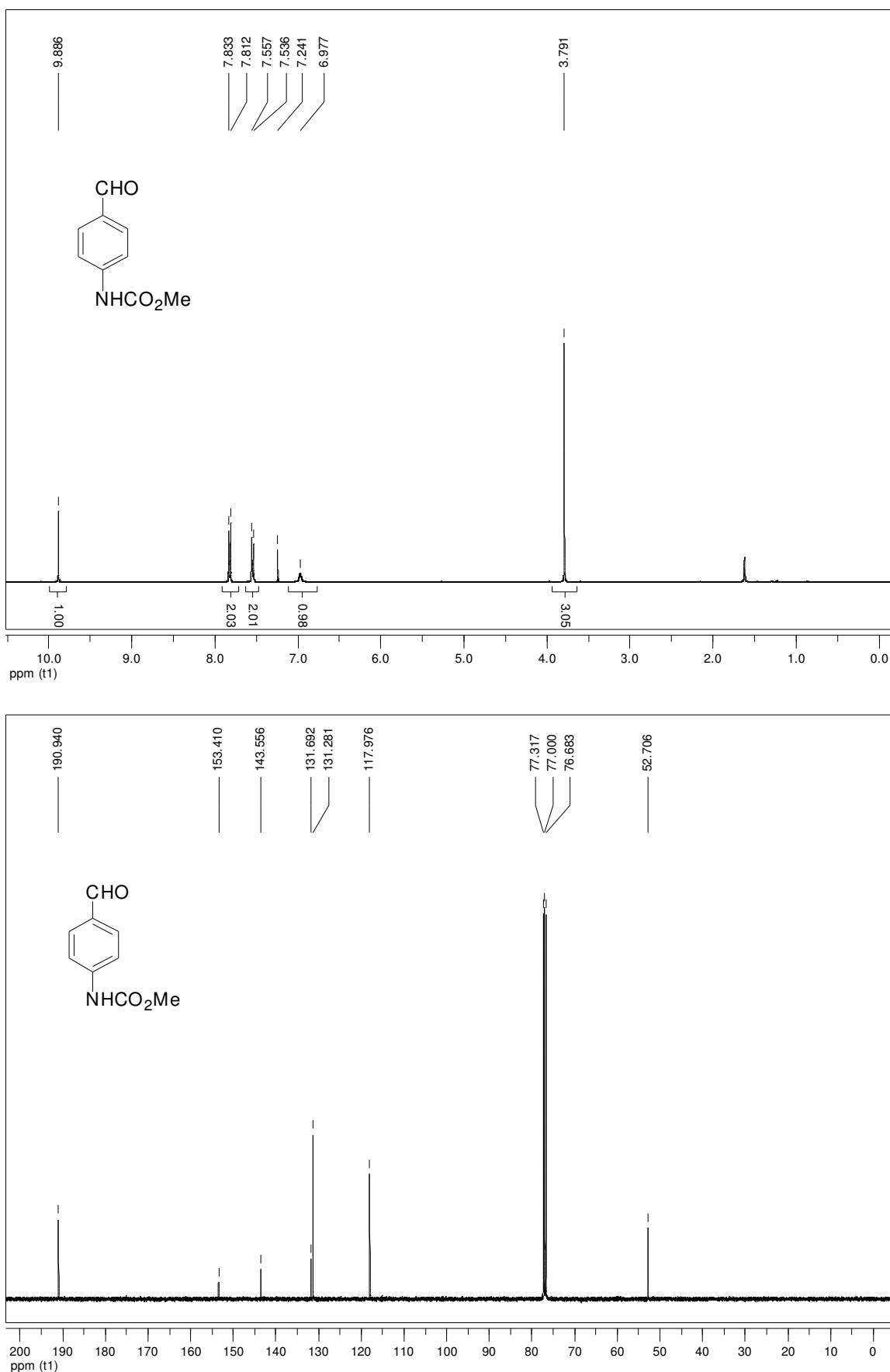
¹H NMR and ¹³C NMR spectra of product **18**



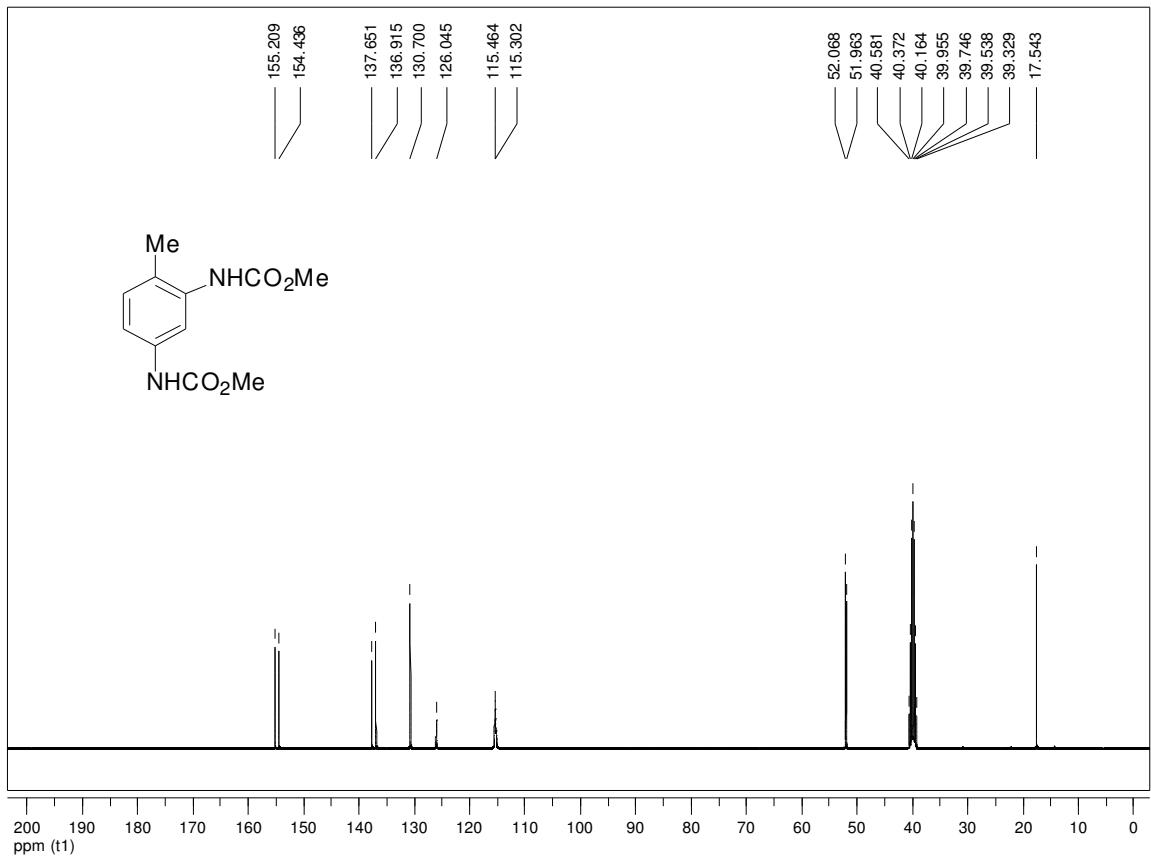
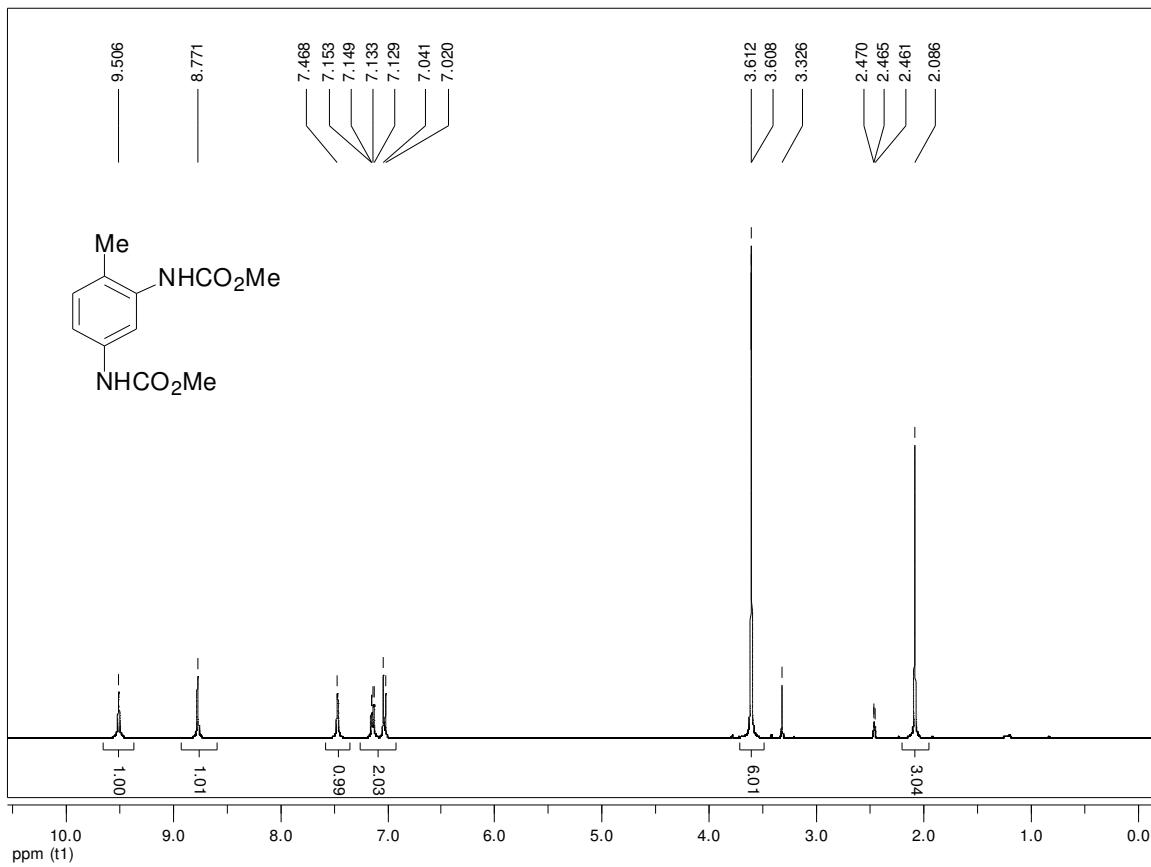
¹H NMR and ¹³C NMR spectra of product **20**



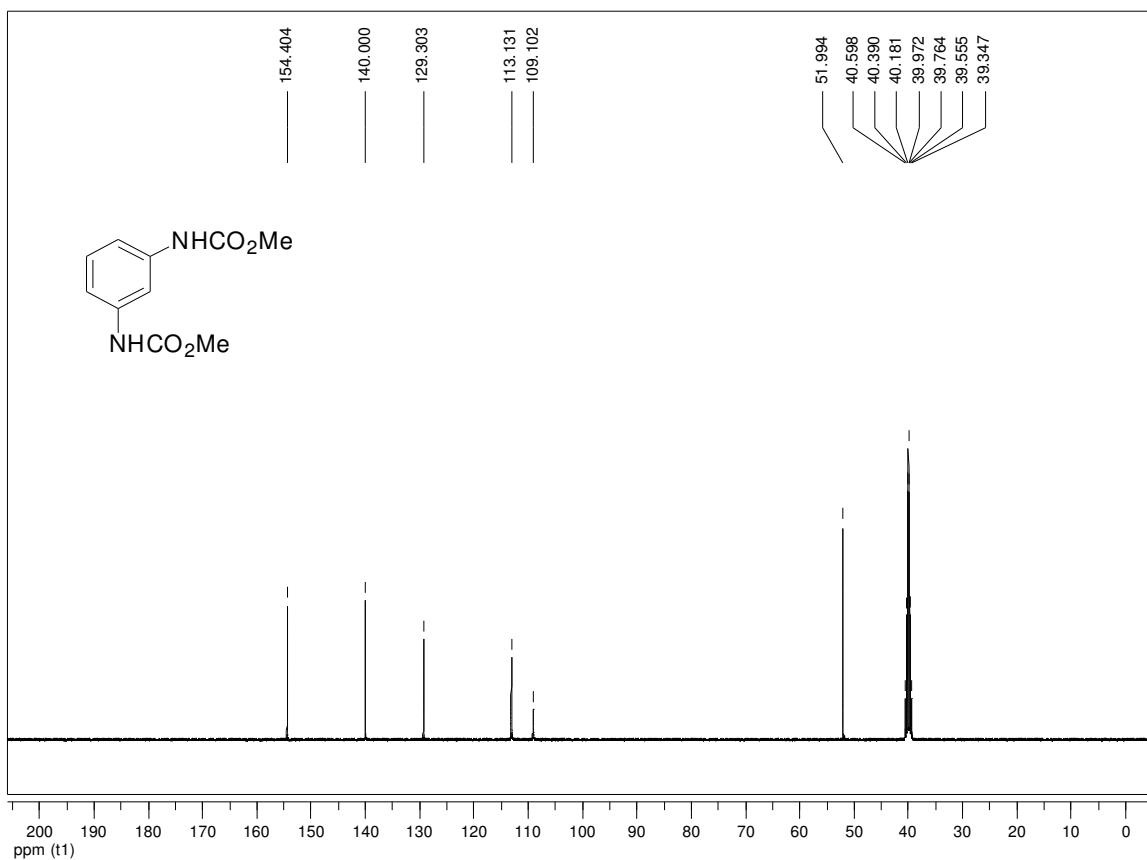
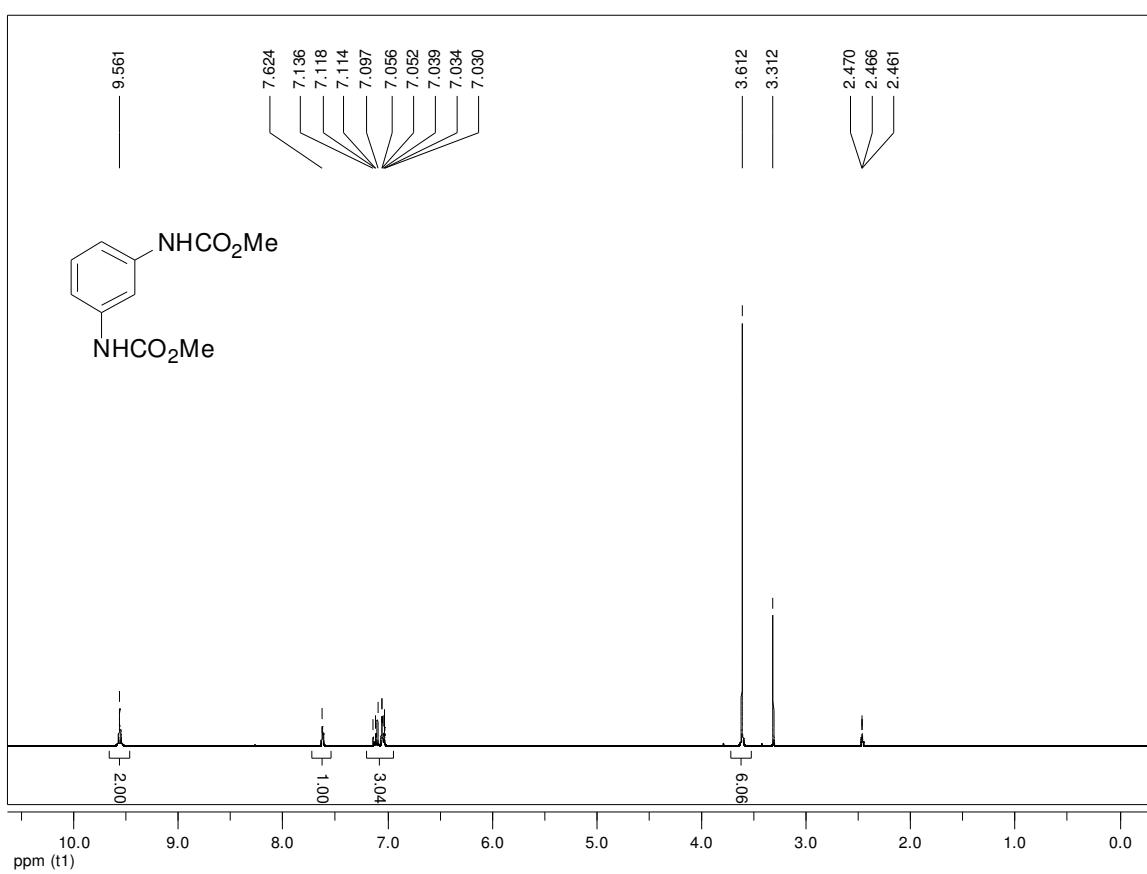
^1H NMR and ^{13}C NMR spectra of product **22**



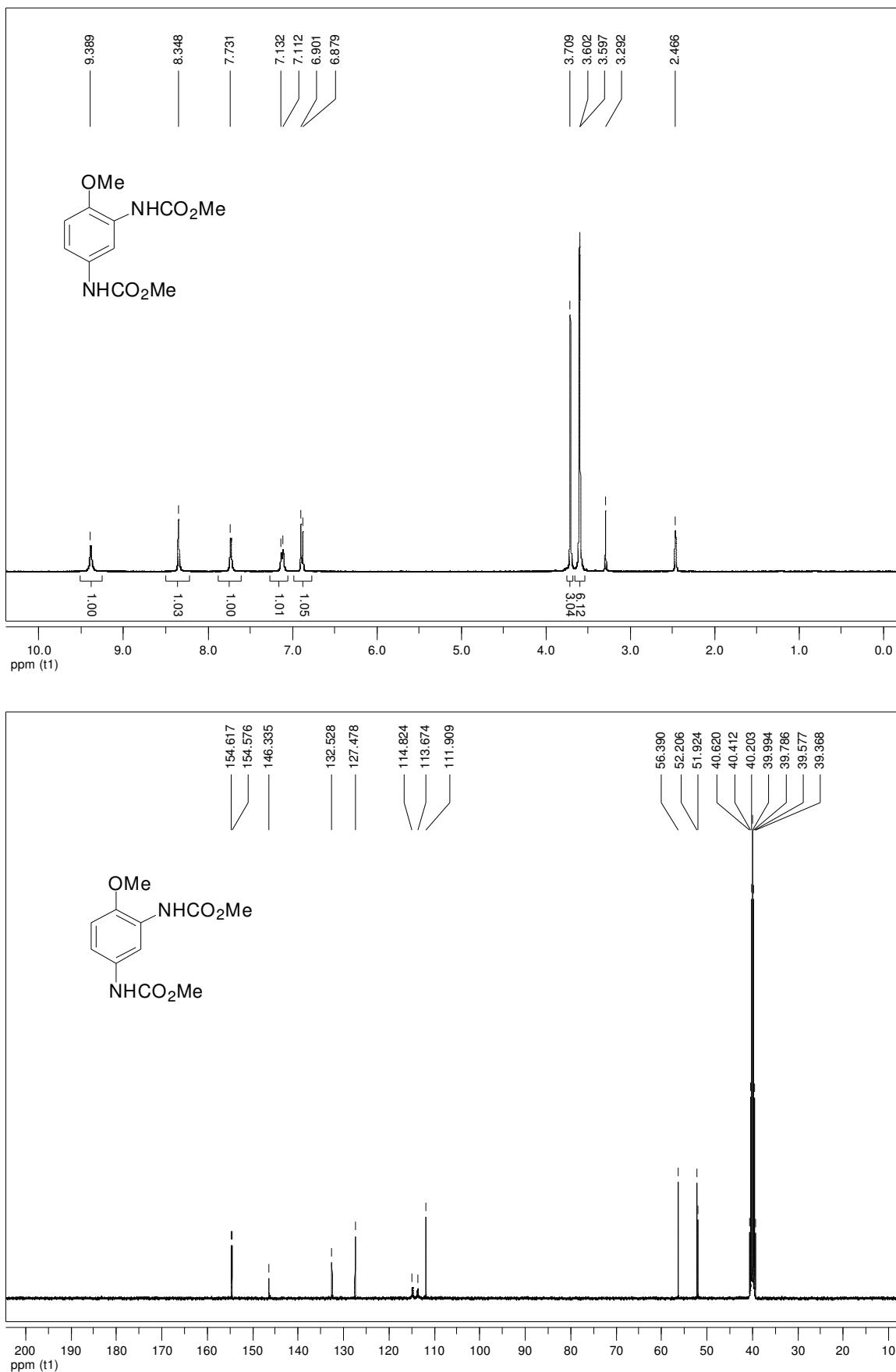
¹H NMR and ¹³C NMR spectra of product **24**



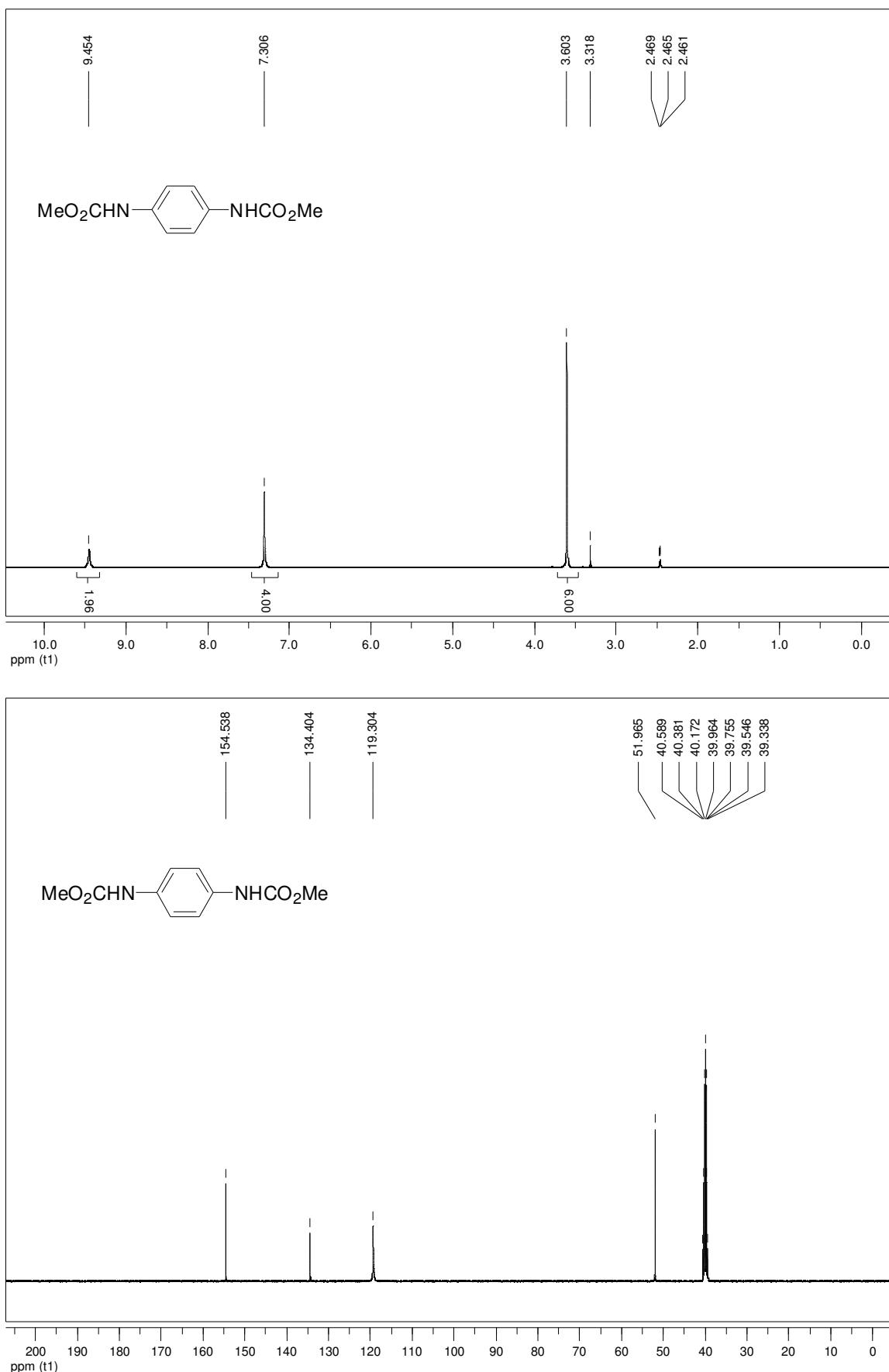
^1H NMR and ^{13}C NMR spectra of product **26**



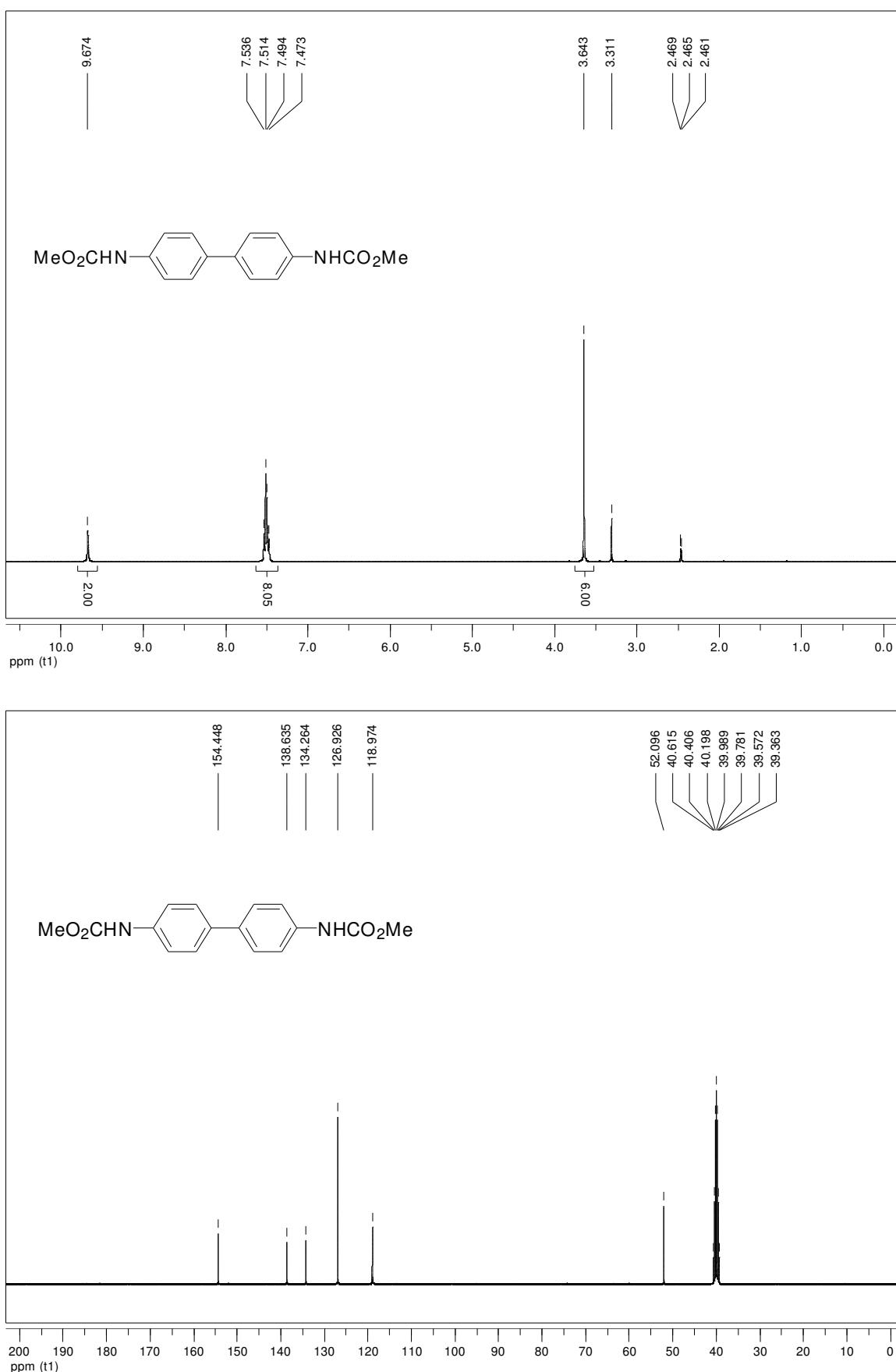
^1H NMR and ^{13}C NMR spectra of product **28**



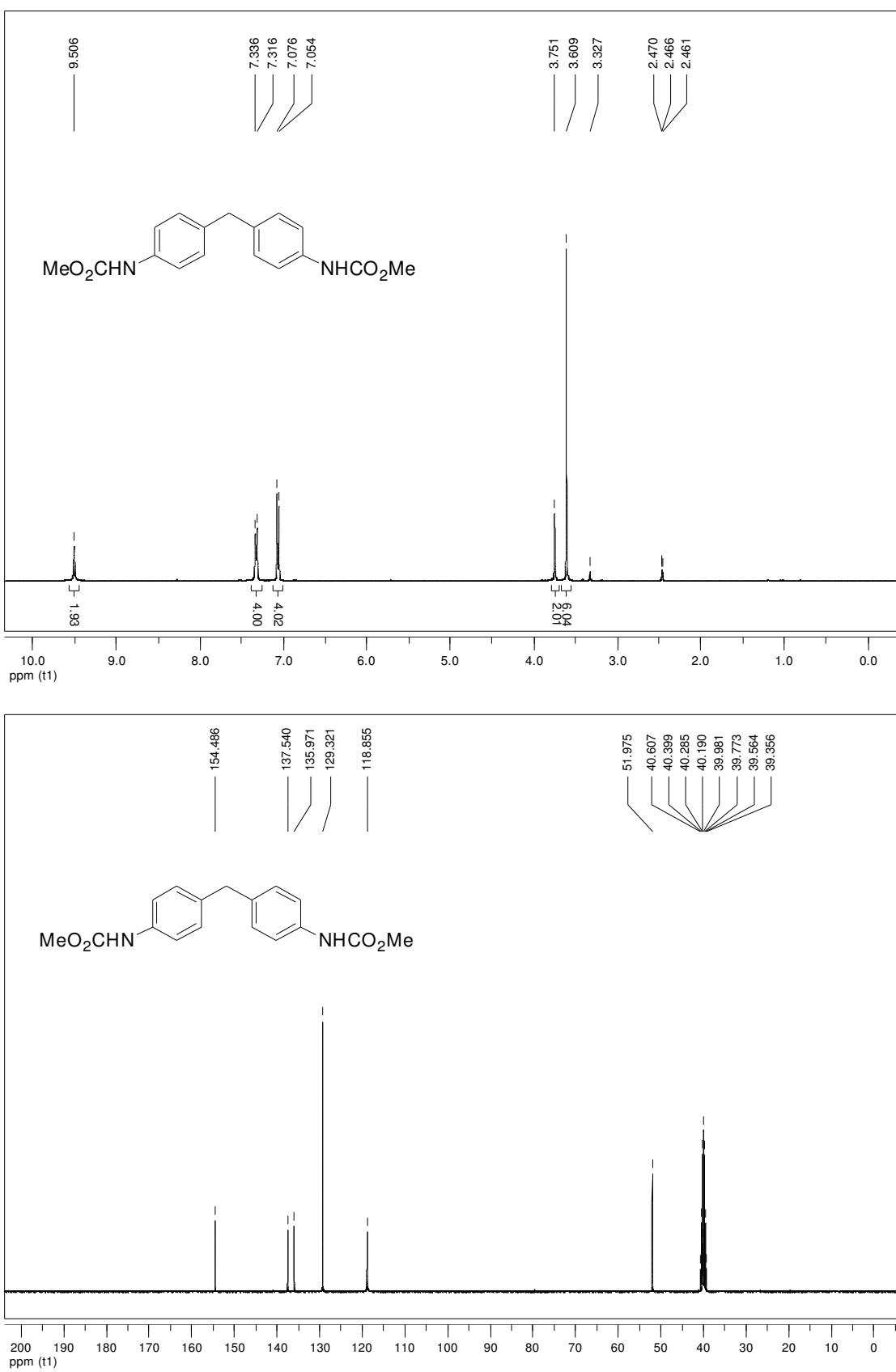
¹H NMR and ¹³C NMR spectra of product **30**



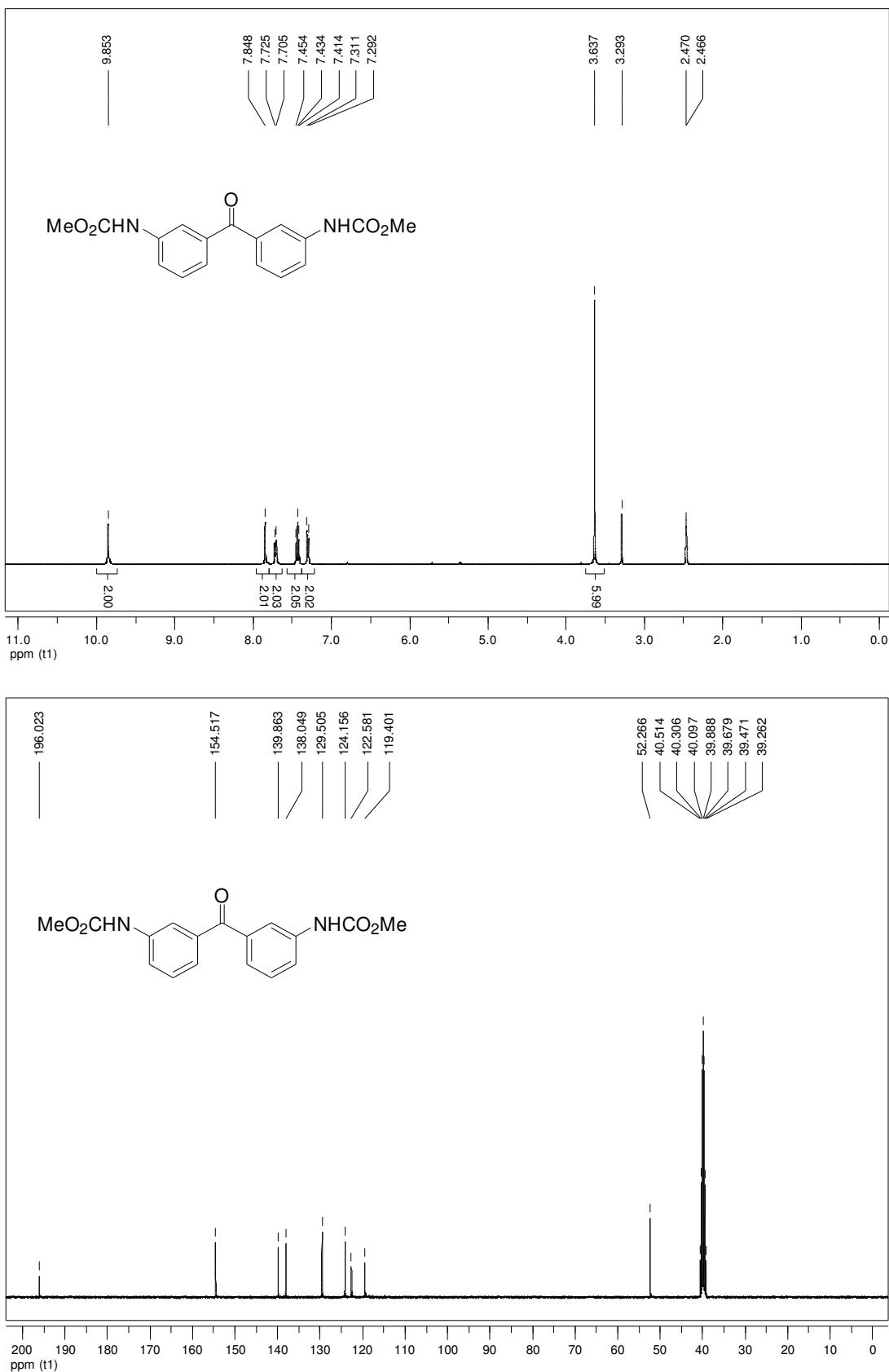
^1H NMR and ^{13}C NMR spectra of product **32**



^1H NMR and ^{13}C NMR spectra of product **34**



¹H NMR and ¹³C NMR spectra of product **36**



¹H NMR and ¹³C NMR spectra of product **38**