Supporting Information

N-Aryl Acylureas as Intermediates in Sequential Self-Repetitive Reactions (SSRR) to Form Poly(amide-imide)s

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Experimental Section

General. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian Inova 200 MHz or 600 MHz. Chemical shifts are given in δ, the coupling constants *J* are given in Hz. The spectra were recorded in solvents such as acetone-d_6 or DMSO-d_6 at room temperature, and chemical shifts are given relative to the solvent signals. FT-IR was carried out using a Perkin Elmer spectrum one FT-IR spectrometer. HPLC was performed using a 5 μm spherical particle /100 Å pore size column (Hypersil-100 C18) an UV detection at 254 nm with MeCN/H_2O = 50/50 as an eluent at a flow rate of 0.5 ml/min. Differential scanning calorimeter (DSC) was performed on a Perkin Elmer Pyris 6 instrument at heating and cooling rates of 10 ^{o}C/min. Thermal gravimetric analysis (TGA) was performed using a Perkin Elmer Pyris 1 at a heating rate of 10 ^{o}C/min up to 850 ^{o}C under nitrogen. The number-average molecular weights (*M*n) was estimated by gel permeation chromatography (Jasco GPC, RI detector), calibrated by polystyrene standards. De-gassed N, N-dimethylformamide (DMF) was used as the eluent and performed at a flow rate of 1.0 ml min^{-1}.

Synthesis of 5a-j. Reaction of DPCDI with **2f**: Table 1, entry 8: As a typical example, phenyl isocyanate (5g, 42 mmol) and, 1, 3-Dimethyl-3-phospholene oxide (DMPO; 0.15 g) were dissolved in 50 ml of dry THF and was heated under nitrogen to 60 ^{o}C for 3 hours. Then 5-isoindolinecarboxylic acid **2f** (5.19 g, 21 mmol) synthesized from trimellitic anhydride and butylamine, was added and the reaction mixture and stirred for 3 hour at 25 ^{o}C. Product **5h** was precipitated from 1L of hexane (88%). ^{1}H-NMR (600 MHz, acetone) δ (ppm): 0.90 (t, *J* = 7.2 Hz, 3H), 1.29 (sxt, *J* = 7.2 Hz, 2H), 1.58-1.63 (m, 2H), 3.59 (t, *J* = 7.2 Hz, 2H), 7.12 (dt, *J* = 7.2, Hz, 1H), 7.25-7.37 (m, 5H), 7.45 (dd, *J* = 8.4, 0.6 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.91 (dd, *J* = 6.6, 1.8 Hz, 2H), 10.80 (bs, 1H); ^{13}C-NMR (150 MHz, acetone) δ (ppm): 13.8, 20.6, 31.1, 38.3, 120.5, 120.6, 122.7, 123.3, 124.9, 129.1, 129.7, 129.8, 130.8, 132.7, 133.8, 134.1, 138.9, 139.5, 142.9, 152.5, 167.9, 172.4. Anal. Calcd. for

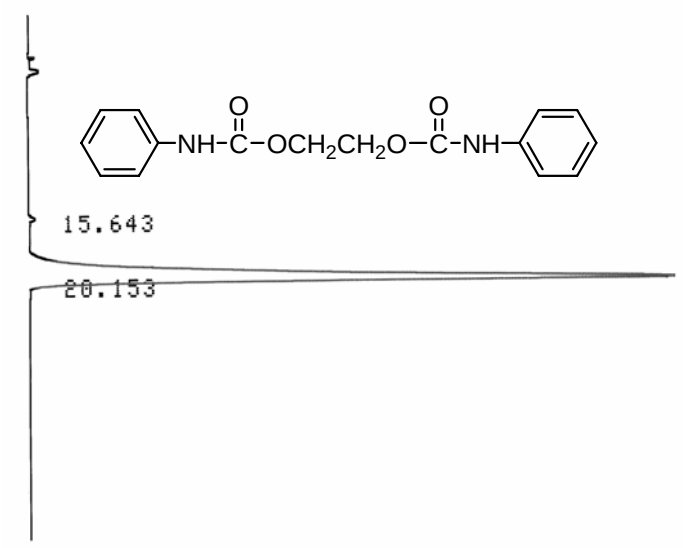
$C_{26}H_{23}N_3O_4$: N, 9.52%; C, 70.73 %; H, 5.25 %. Found: N, 9.76 %, C, 71.59 %, H, 5.65 %. mp 105.1-105.8 ^oC

Synthesis of 9. Scheme 2: 5.0 g (0.5 g, 1.3 mmol), DMPO (75 mg, 0.57 mmol) were dissolved in 30 ml of dry tetramethylene sulfone at room temperature. Methanol (42 mg, 1.3 mmol) and triethylamine (0.13 g; 1 equivalent) were added into the reaction mixture and heated to 140 ^oC for 45 minutes and 210 ^oC for 30 minutes. Then the final solution was added to 500 ml of water and a brown precipitate of amide-imide **11** formed. The precipitate was filtered and recrystallization from 25 ml of hot xylene and dried under vacuum (93%). ^{1}H-NMR (600 MHz, DMSO) δ (ppm): 7.14 (t, *J* = 7.2 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.46-7.50 (m, 3H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.82 (d, *J* = 7.8 Hz, 2H), 8.12 (d, *J* = 7.8 Hz, 1H), 8.45 (dd, *J* = 7.8, 1.8 Hz, 1H), 8.54 (s, 1H), 10.64 (s, 1H); ^{13}C-NMR (150 MHz, DMSO) δ (ppm): 120.6, 122.2, 123.6, 124.2, 127.4, 128.2, 128.7, 128.9, 131.8, 131.9, 133.9, 134.4, 138.7, 140.3, 163.6, 166.5, 166.6. Anal. Calcd. for $C_{21}H_{14}N_2O_3$: N, 8.20 %; C, 73.70 %; H, 4.10 %. Found: N, 8.21 %; C, 73.59 %; H, 4.42 %. mp 271.4-273.1 ^oC.

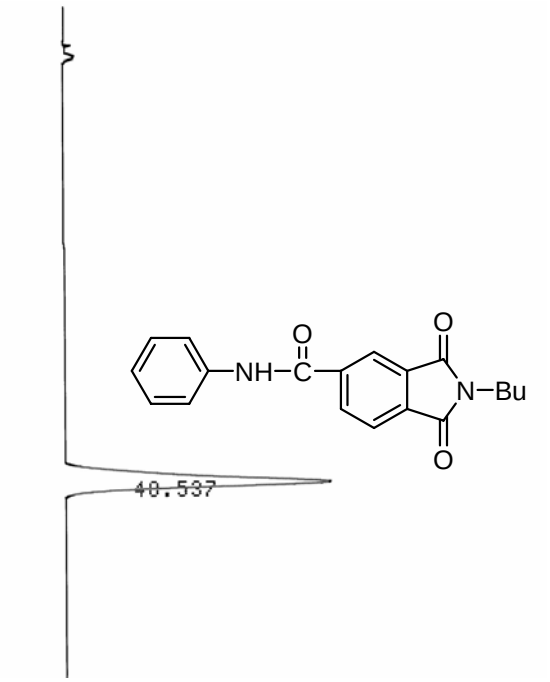
Synthesis of poly(amide-imide). Into a 250-ml, three-necked, round-bottomed flask equipped with a thermometer, a nitrogen gas inlet tube, a reflux condenser, an oil bath, and a magnetic stirrer was placed 4-4′-methylene-bis(phenylisocyanate) (MDI; 15 g; 59.9 mmol) and dissolved in 200 ml of dry N-methyl-2-pyrrolidone (NMP). The reaction mixture was heated to 90 ^oC and phenyl isocyanate (0.89 g; 7.47 mmol) was added. The mixture was stirred and maintained at 90 ^oC for a few minutes until the solution was homogeneous and then DMPO (70 mg) was added. Evolution of carbon dioxide began almost immediately. The solution was heated at 90 ^oC for 3 h and the corresponding poly(carbodiimide) was formed. When the mixture was cooled to room temperature, trimellitic anhydride (12.2 g; 63.5 mmol) was added, stirred for 1 h, and followed by adding methanol (2.04 g; 63.7 mmol) and triethylamine (6.4 g; 63.7 mmol) and stirring for 30 minutes. The reaction mixture was further heated to 202 ^oC for 1 h and poured into 2 L of water. The resulting product was filtered and dried, to yield 23.3 g

(92 %) of poly(amide-imide) (brown solid). The number-average molecular weights (*M*n) determined by gel permeation chromatography (GPC) was 20,600 g/mol.

(a)



(b)



(c)

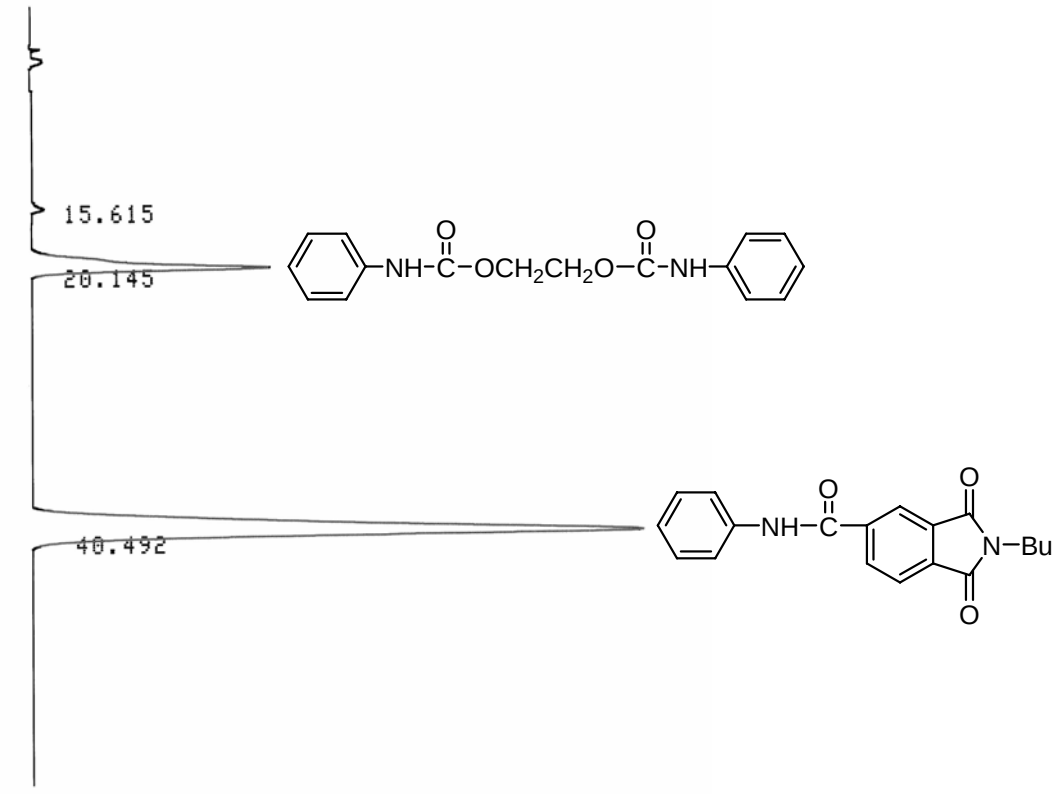
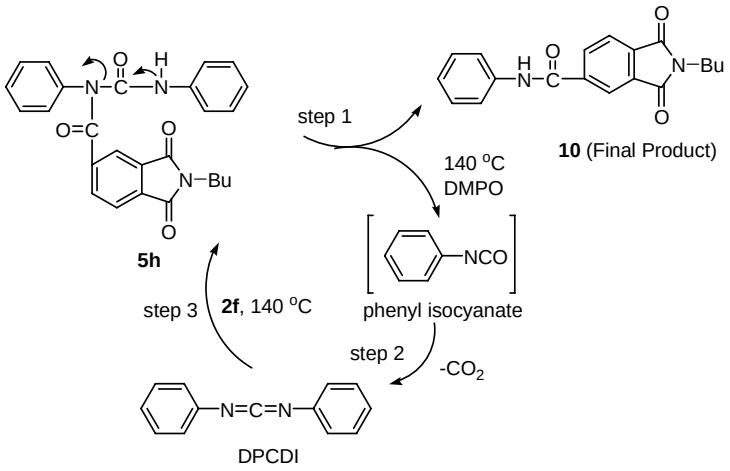


Figure S1. HPLC Analysis (a) bisurethane (obtained from phenyl isocyanate and ethylene glycol); (b) amide-imide (obtained from 5h and 2f); (c) bisurethane and amide-imide (obtained from 5h and ethylene glycol).



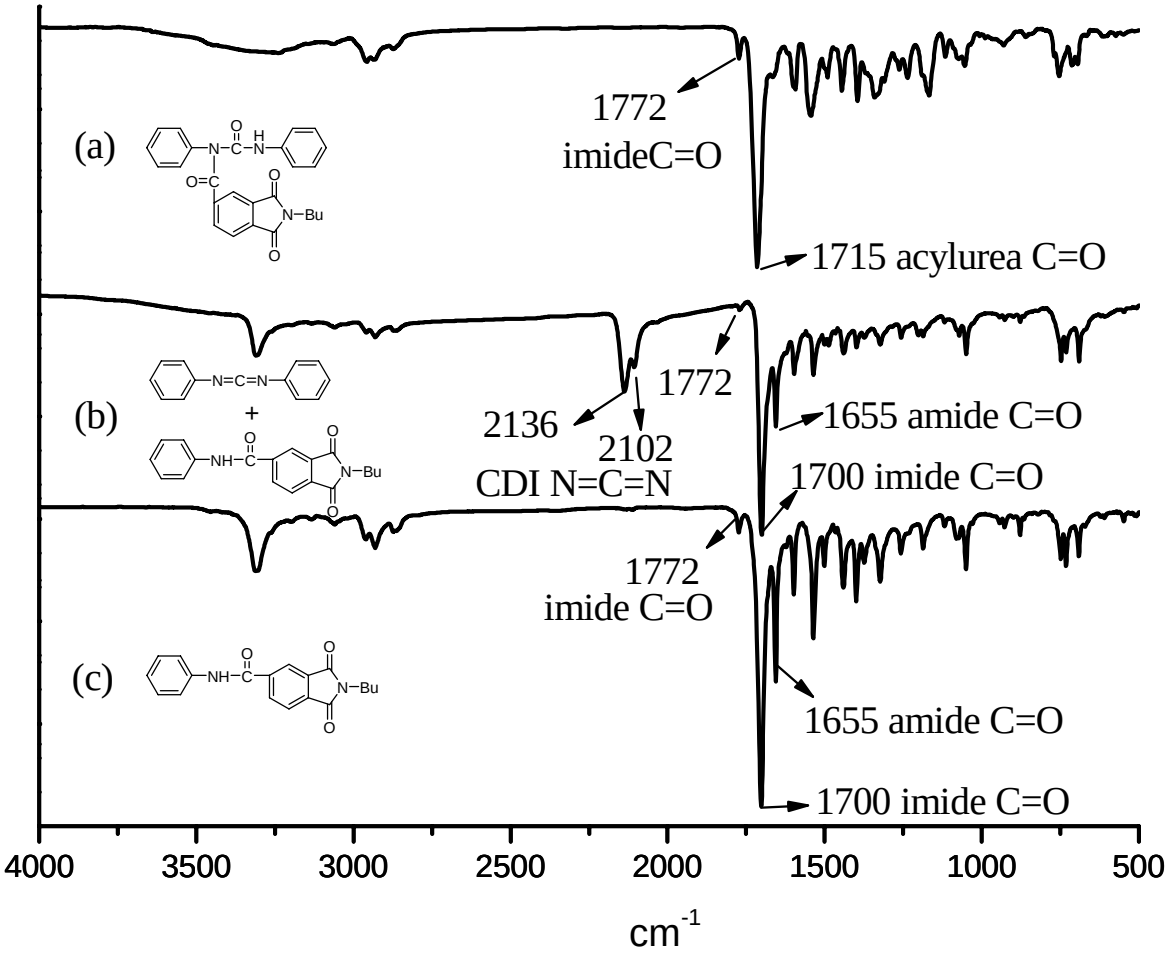


Figure S2. FT-IR spectra for sequential self-repetitive reaction of the N-acylurea **5h**: (a) starting N-acylurea **5h**; (b) thermolysis at 140 °C for 10 min; (c) in situ addition of carboxylic acids during N-acylurea thermolysis.

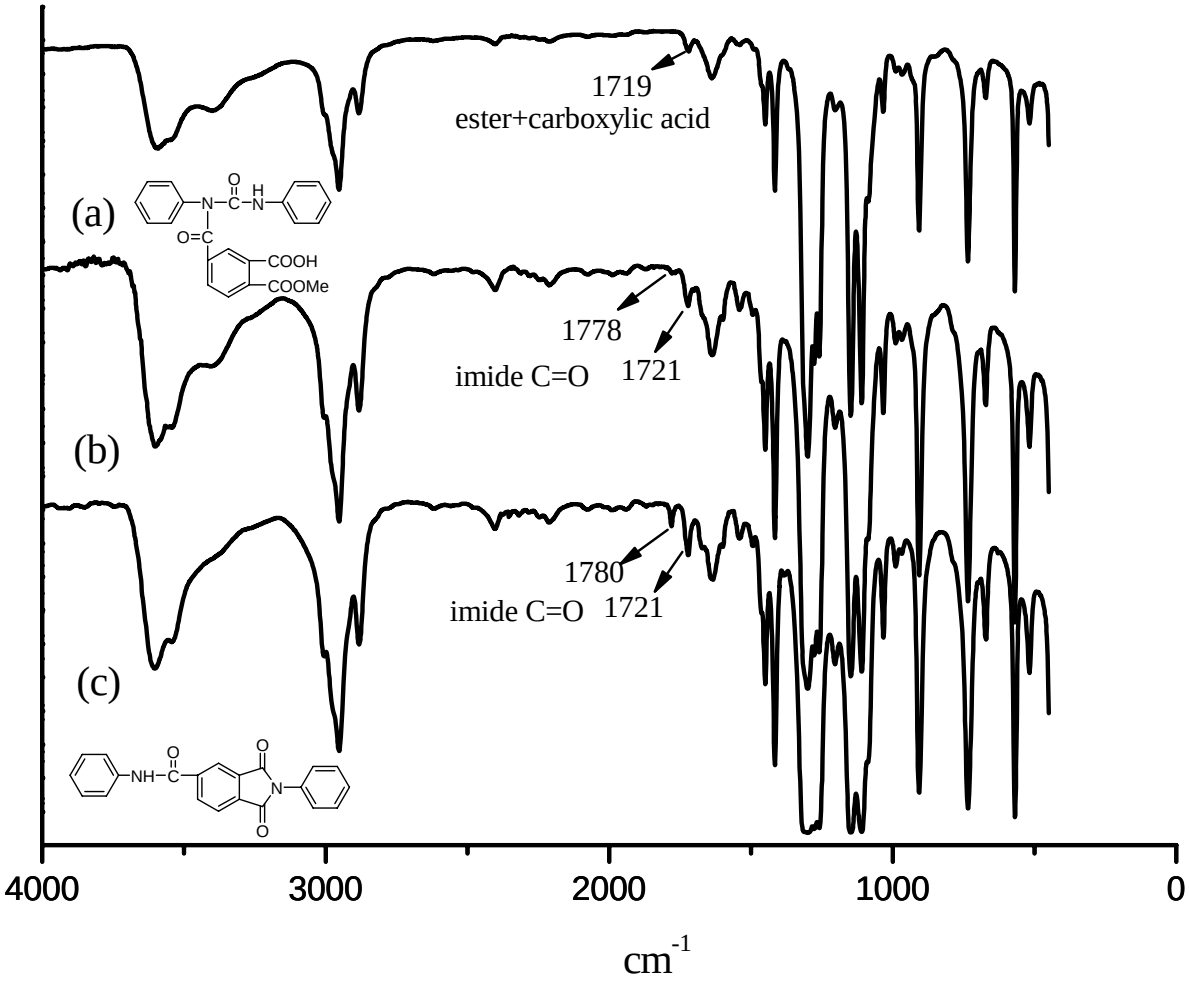


Figure S3. FT-IR Analysis (a) N-acylurea **6**; (b) thermolysis at 140 ^{o}C for 45 min; (c) thermolysis at 210 ^{o}C for 30 min.

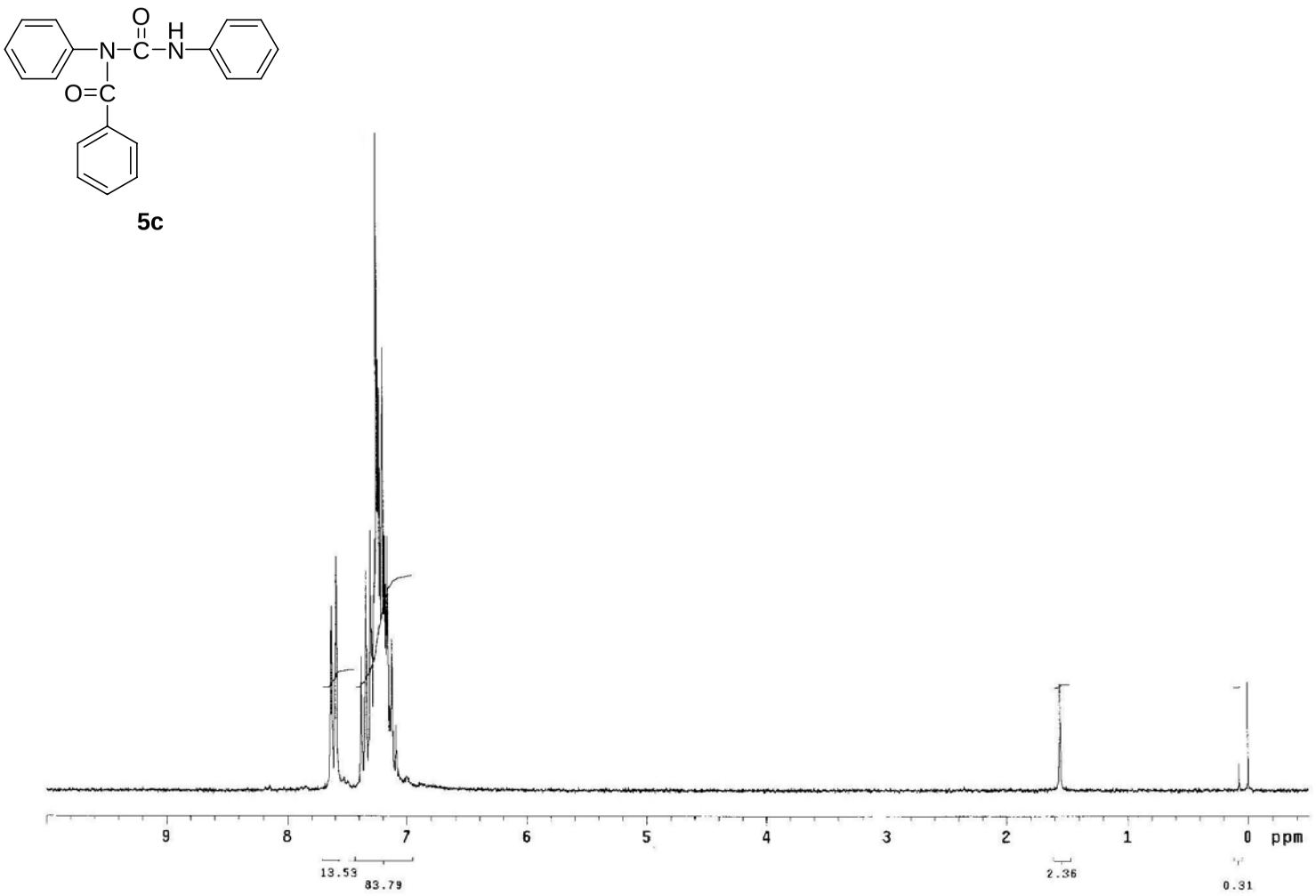


Figure S4. ^{1}H NMR (200 MHz) of **5c**

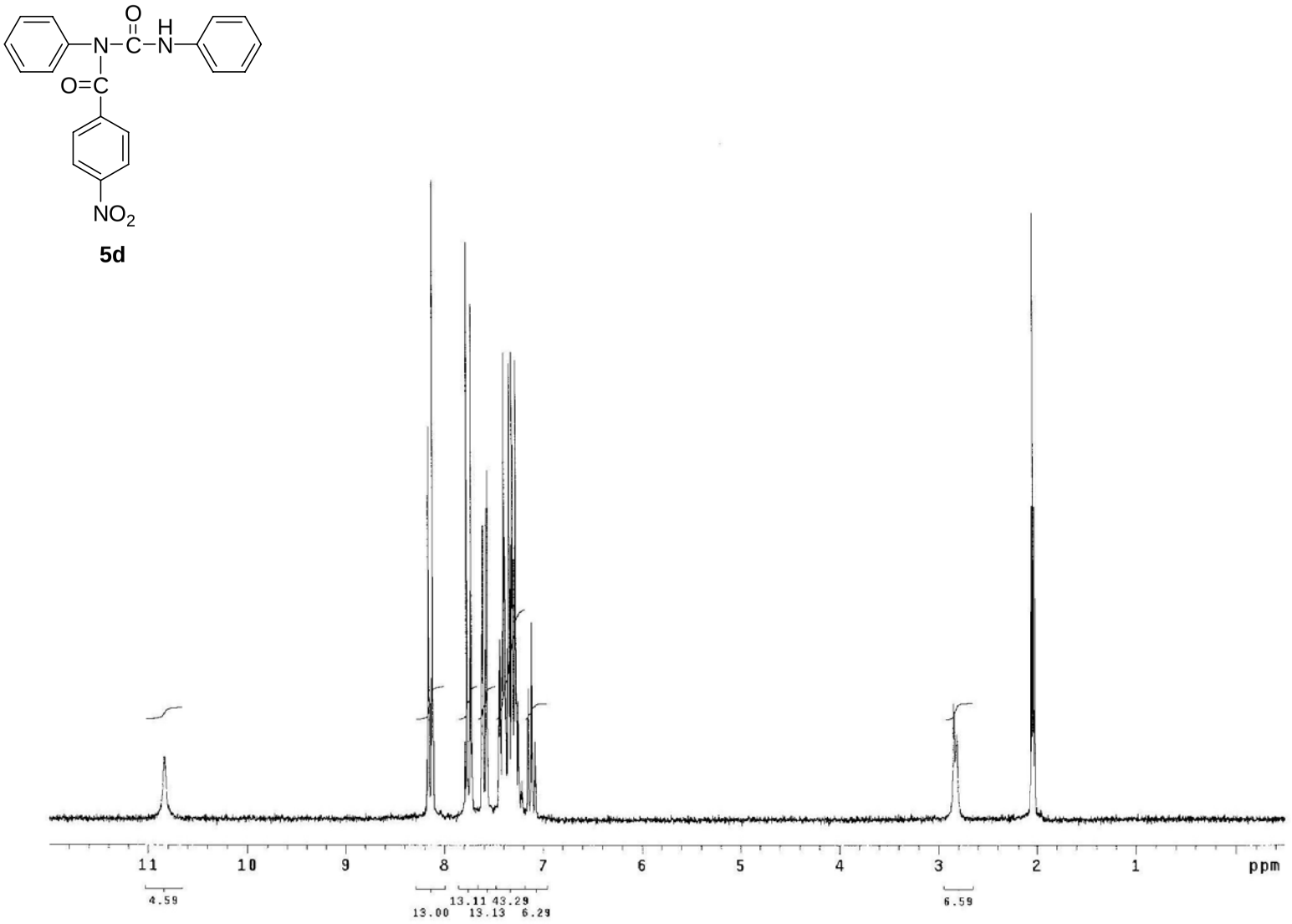
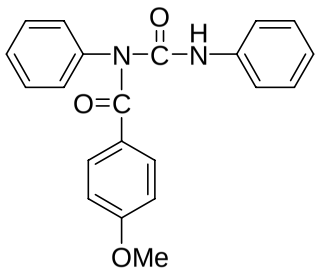


Figure S5. ^{1}H NMR (200 MHz) of **5d**



5e

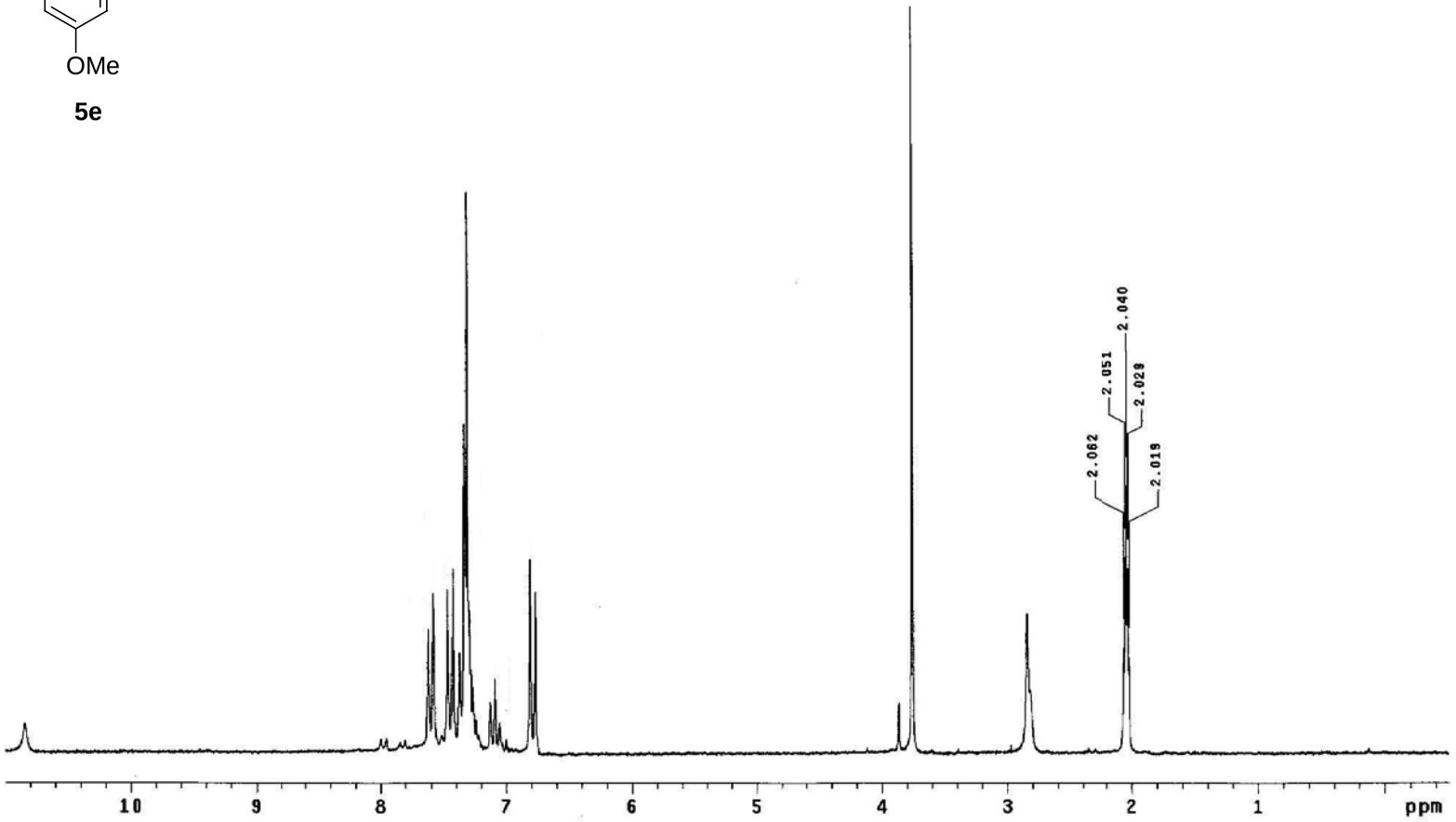
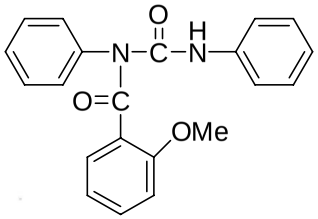


Figure S6. ^{1}H NMR (200 MHz) of **5e**



5f

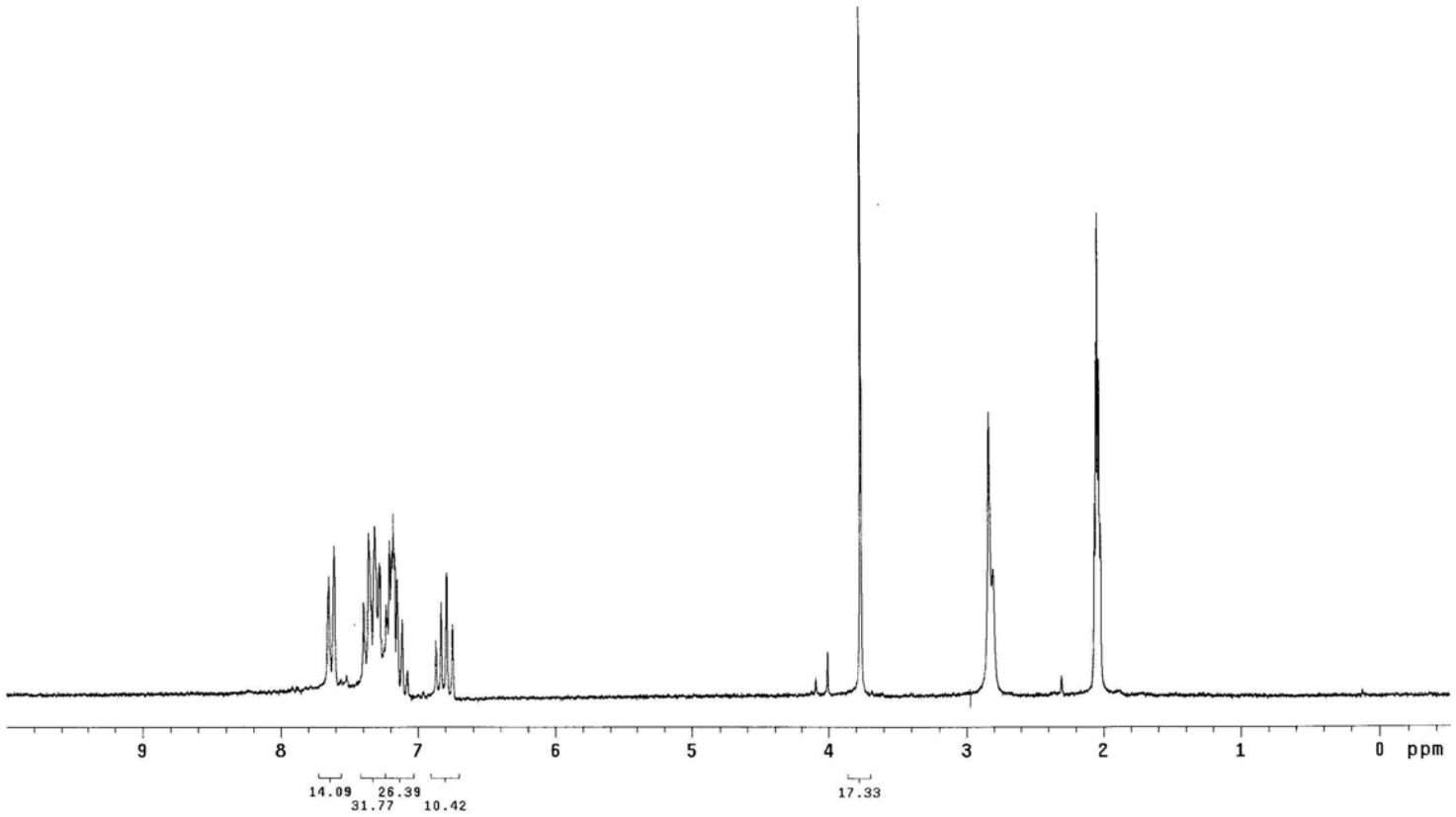


Figure S7. ^{1}H NMR (200 MHz) of **5f**

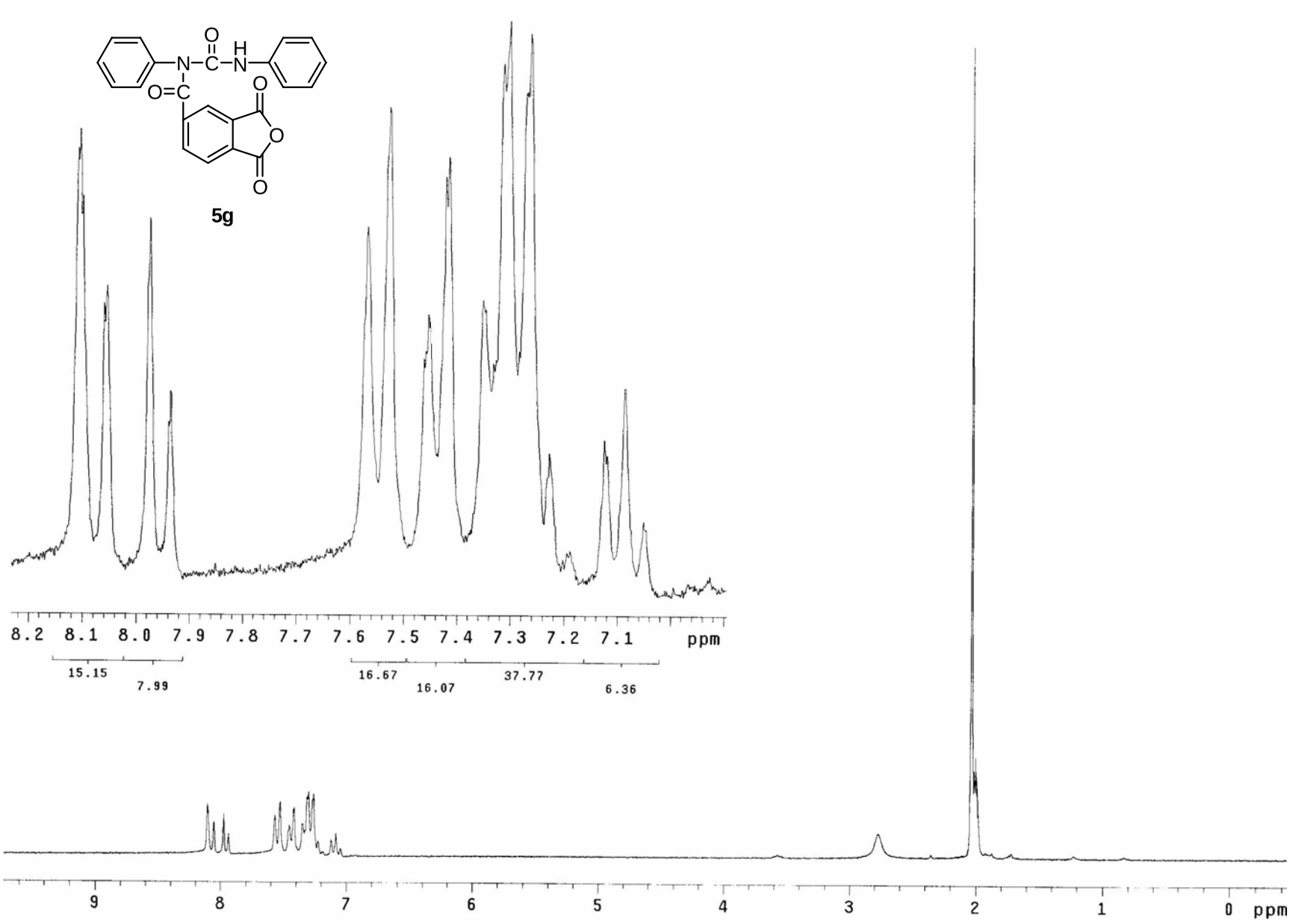


Figure S8. ^{1}H NMR (200 MHz) of **5g**

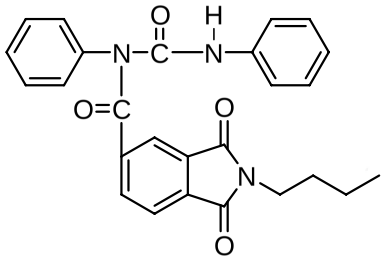


Figure S9. ^{1}H NMR (600 MHz) of **5h**

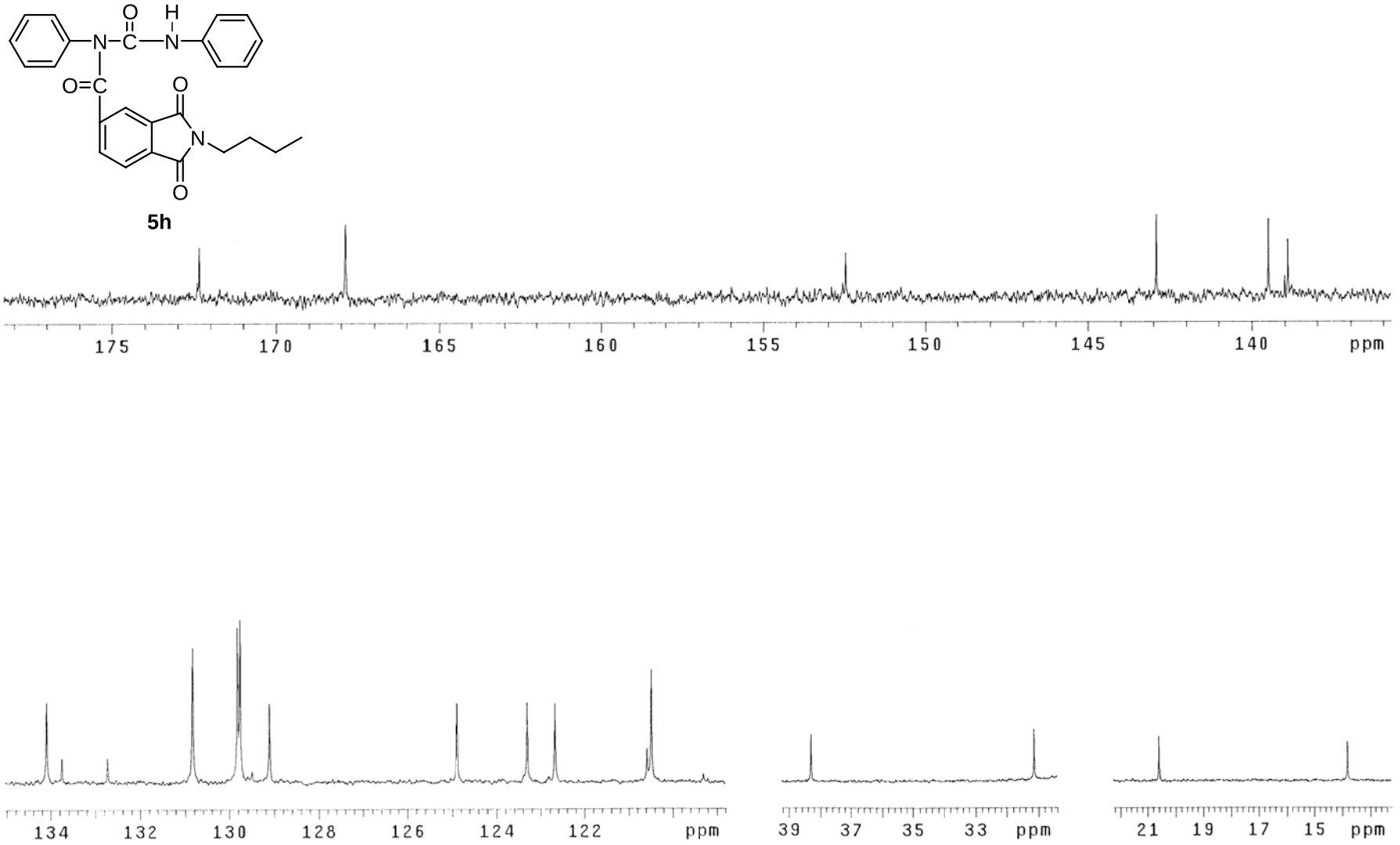
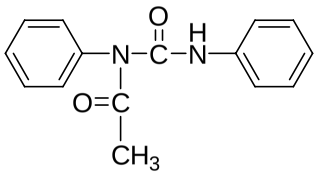


Figure S10. ^{13}C NMR (600 MHz) of **5h**



5i

Figure S11. ^{1}H NMR (200 MHz) of **5i**

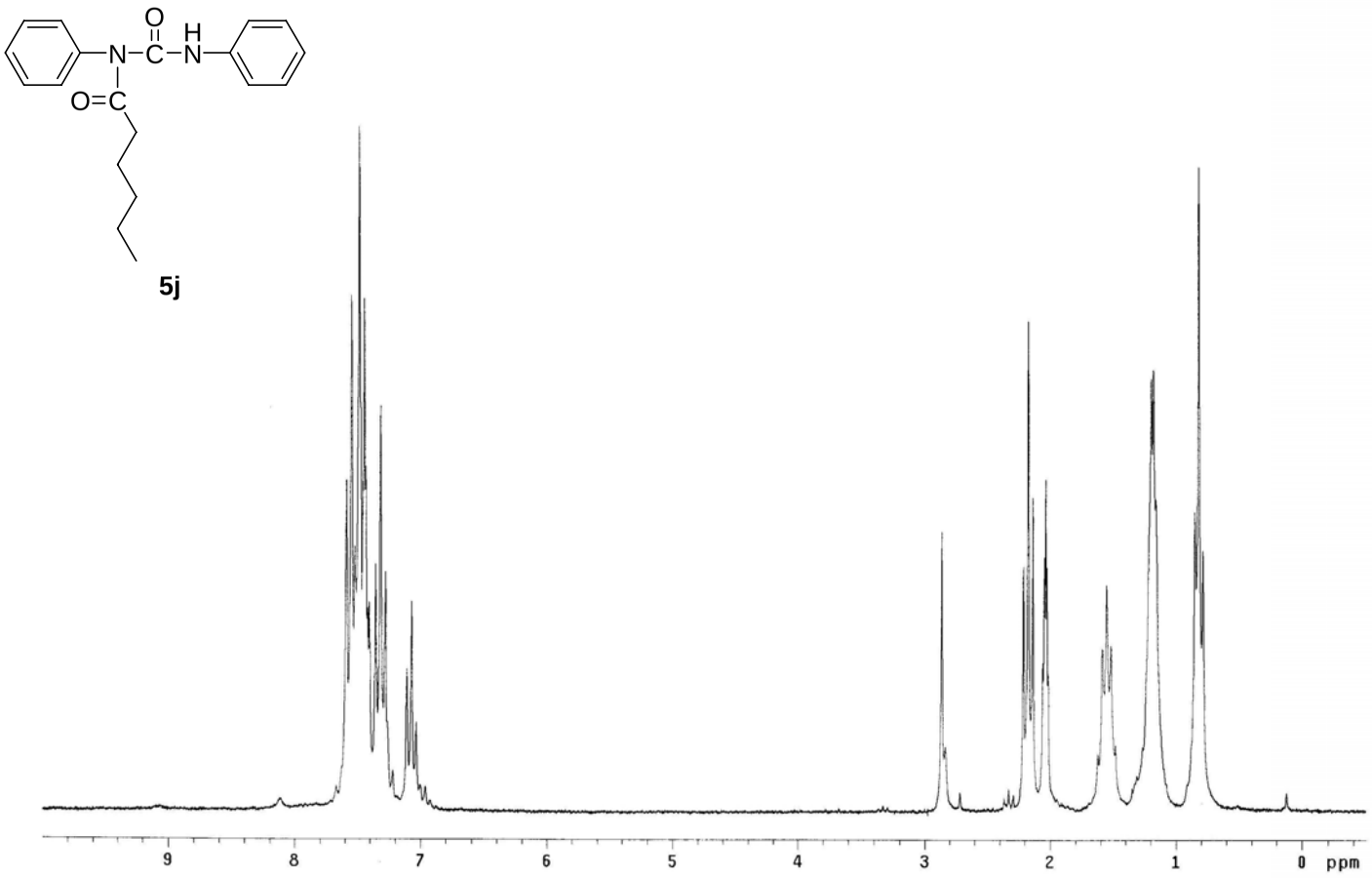
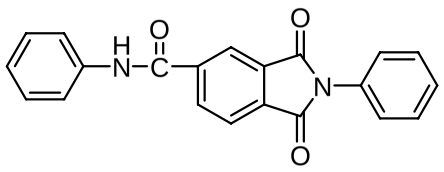
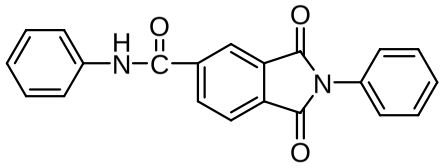


Figure S12. ^{1}H NMR (200 MHz) of **5j**



9

Figure S13. ^{1}H NMR (600 MHz) of **9**



9

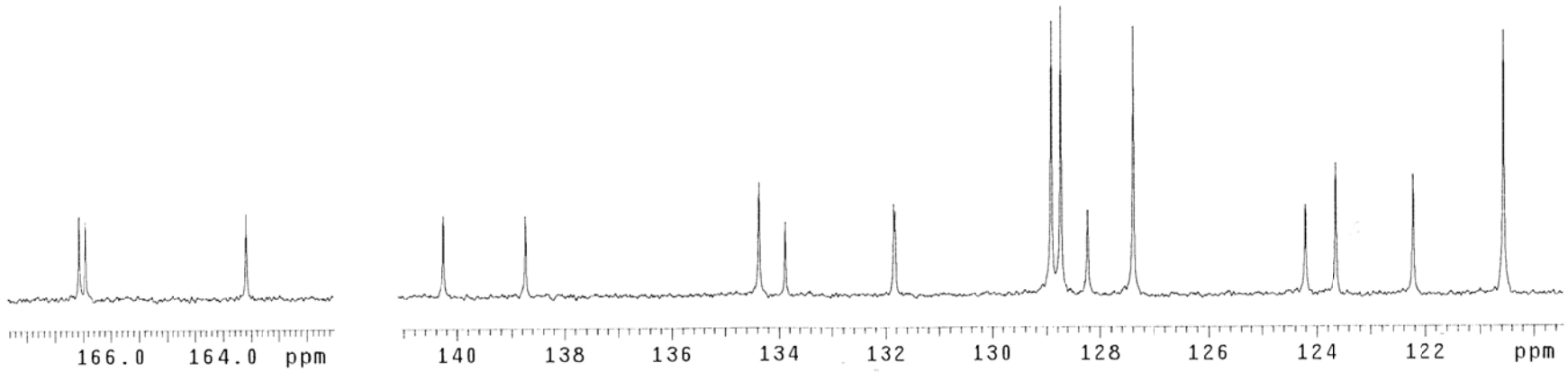
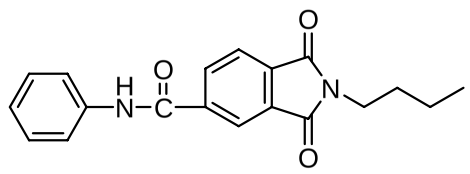


Figure S14. ^{13}C NMR (600 MHz) of **9**



10

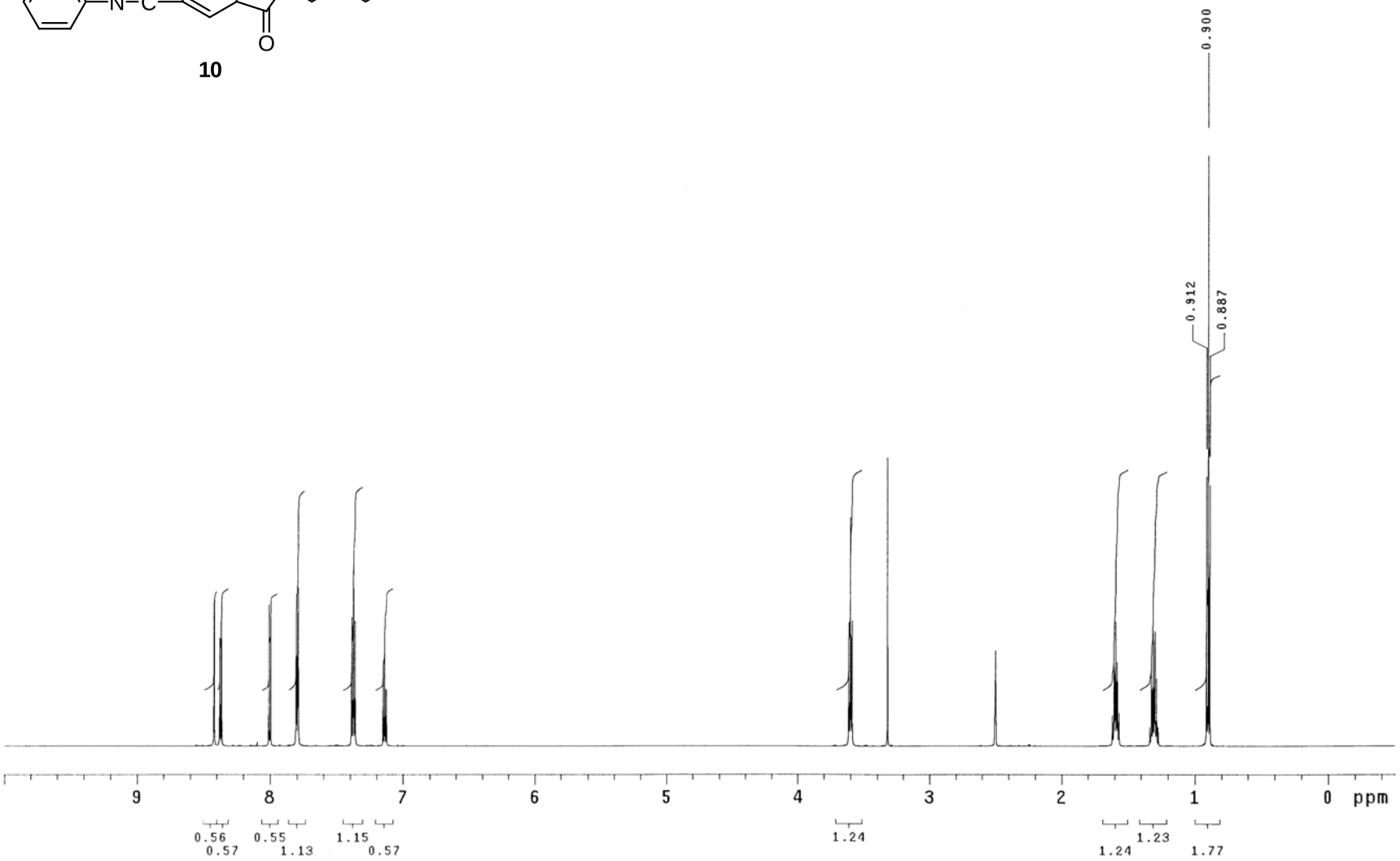
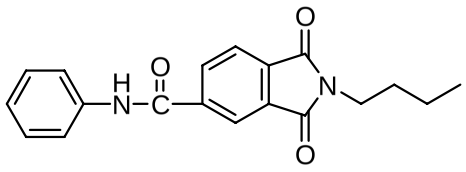
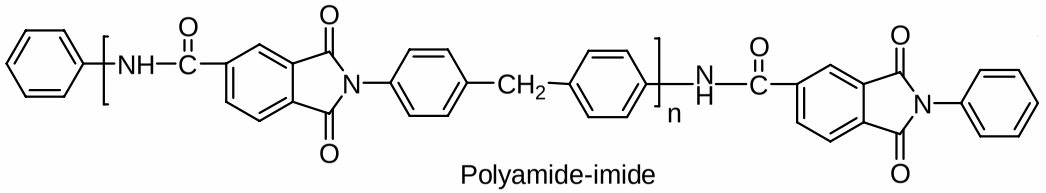


Figure S15. ^{1}H NMR (600 MHz) of **10**



10

Figure S16. ^{13}C NMR (600 MHz) of **10**



Polyamide-imide

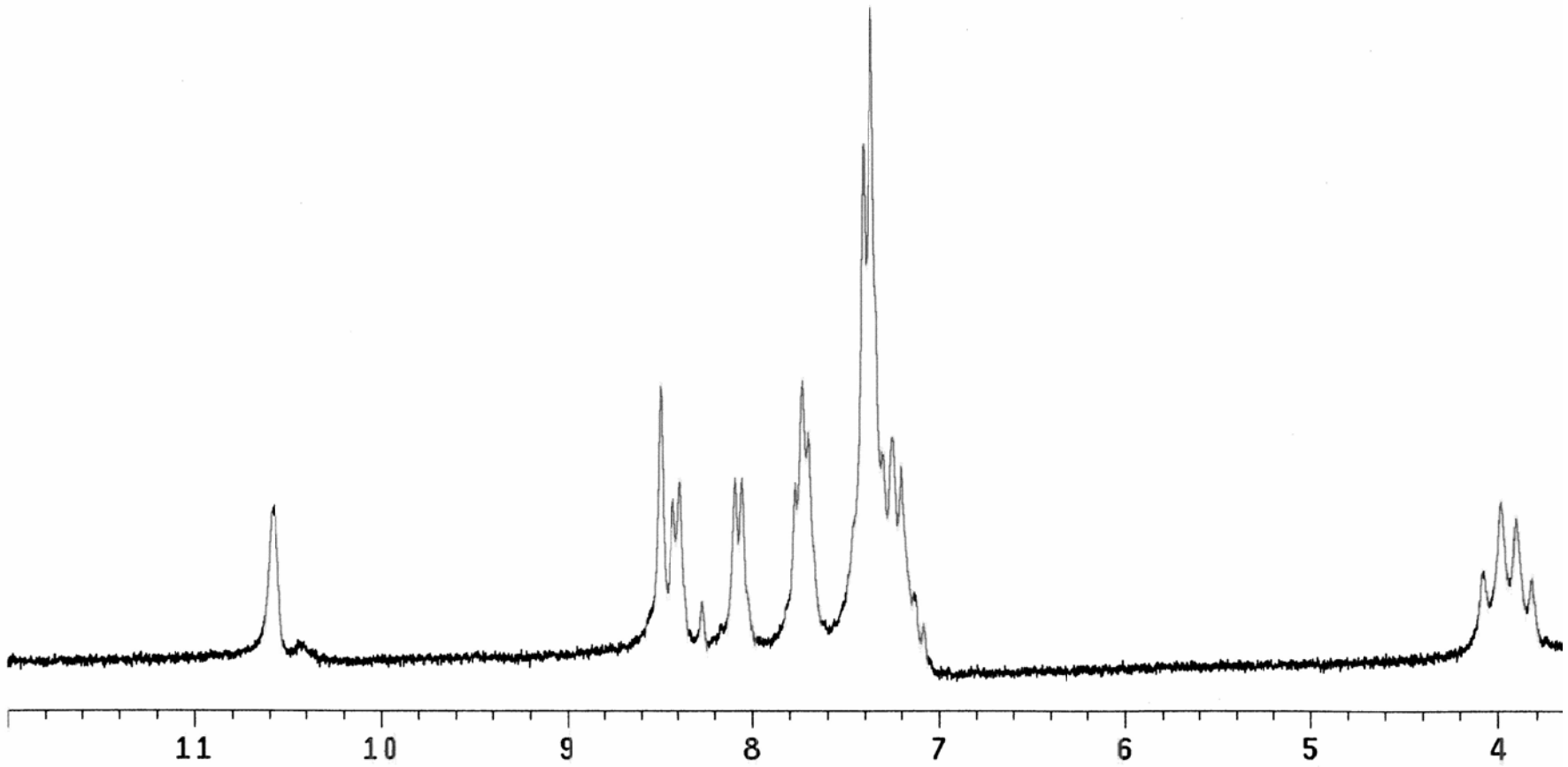


Figure S17. ^{1}H NMR (200 MHz) of **poly(amide-imide)**

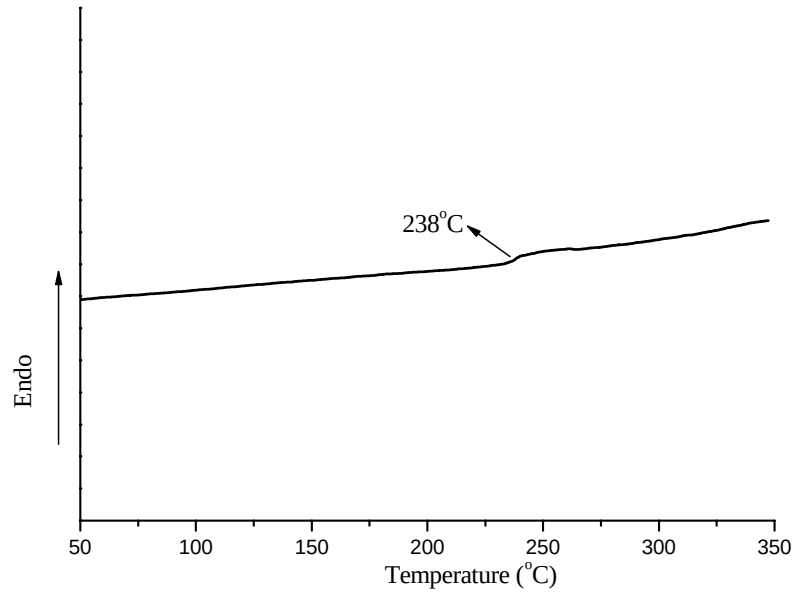


Figure S18. DSC Analysis of Polyamide-imide (T_g at 238 °C; heating rate: 10 °C/min).

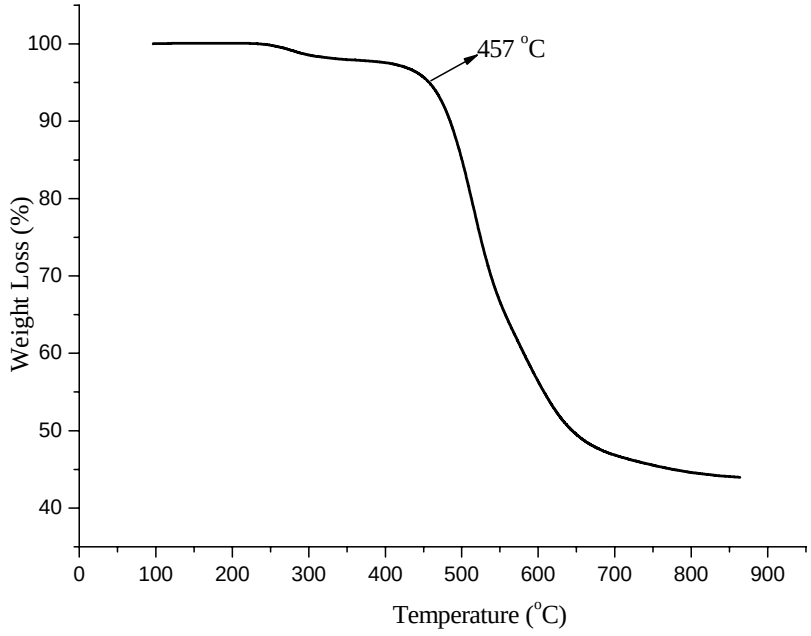


Figure S19. TGA Analysis of Polyamide-imide (T_d at 457 °C under nitrogen at 5% weight losses).