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Supporting Information

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Benzannulated Bicycles by Three-Component Aryne Reactions**

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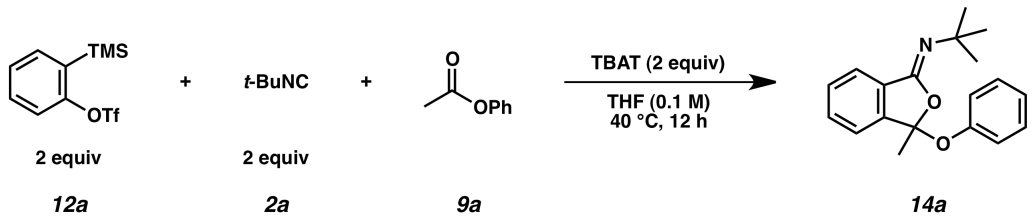
Materials and Methods

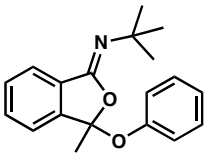
Unless stated otherwise, reactions were performed in flame-dried glassware under an argon or nitrogen atmosphere using dry, deoxygenated solvents (distilled or passed over a column of activated alumina). Commercially obtained reagents were used as received. Tetra-*n*-butylammonium difluorotriphenylsilicate (TBAT) was azeotropically dried from acetonitrile prior to use. 3-Methoxy-2-(trimethylsilyl)phenyl triflate,[1] 3,5-dimethoxy-2-(trimethylsilyl)phenyl triflate,[2] 4,5-dimethoxy-2-(trimethylsilyl)phenyl triflate,[3] 6-(trimethylsilyl)benzo[*d*][1,3]dioxol-5-yl triflate,[4] and 4,5-difluoro-2-(trimethylsilyl)phenyl triflate[5] were prepared according to literature procedures. Reaction temperatures were controlled by an IKAmag temperature modulator. Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized by UV fluorescence quenching, potassium permanganate, or ceric ammonium molybdate staining. Silia*Flash* P60 Academic Silica gel (particle size 0.040-0.063 mm) was used for flash chromatography. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova 500 (at 500 MHz and 125 MHz, respectively) and are reported relative to Me_4Si (δ 0.0). Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Data for ^{13}C NMR spectra are reported in terms of chemical shift relative to Me_4Si (δ 0.0). IR spectra were recorded on a Perkin Elmer Paragon 1000 Spectrometer and are reported in frequency of absorption (cm^{-1}). High resolution mass spectra were acquired using an Agilent 6200 Series TOF with an Agilent G1978A Multimode source in electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI) or mixed (MM) ionization mode, or obtained from the Caltech Mass Spectral Facility (EI+ or FAB+).

Representative Procedure for the Synthesis of Iminoisobenzofurans from Arynes, Isocyanides, and Phenyl Esters:



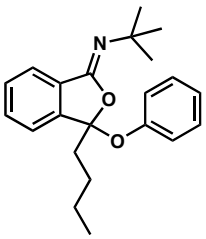
A flame-dried 50 mL round bottomed flask with a magnetic stir bar was charged with TBAT (1.70 g, 3.15 mmol, 2.0 equiv) and THF (16 mL). To this solution was added phenyl acetate (**9a**) (0.20 mL, 1.57 mmol), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**12a**) (0.765 mL, 3.15 mmol, 2.0 equiv), and *tert*-butyl isocyanide (**2a**) (0.356 mL, 3.15 mmol, 2.0 equiv) sequentially via syringe. The reaction was heated to 40 °C under argon for 12 h, at which point TLC analysis showed complete consumption of phenyl acetate. The reaction was cooled to ambient temperature and passed over a plug of silica (3 cm diam. x 5 cm length) eluting with 15:85 EtOAc/hexanes in order to remove excess TBAT from solution. The solvents were removed under reduced pressure and the crude residue was purified via flash chromatography over silica gel.

Spectroscopic Data for Iminoisobenzofurans:



Iminoisobenzofuran 14a

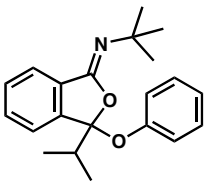
Purified by flash chromatography (SiO_2, 2:98 EtOAc/hexanes) to yield a colorless oil (83% yield). R_f = 0.46 (15:85 EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (dt, *J* = 7.6, 1.0 Hz, 1H), 7.49 (d, *J* = 1.0 Hz, 1H), 7.48 (dd, *J* = 2.0, 1.0 Hz, 1H), 7.39 (ddd, *J* = 8.3, 5.1, 3.2 Hz, 1H), 7.12 (dd, *J* = 8.3, 7.3 Hz, 2H), 6.97 (tt, *J* = 7.3, 1.2 Hz, 1H), 6.92 (dd, *J* = 8.8, 1.2 Hz, 2H), 1.97 (s, 3H), 1.43 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.8, 152.7, 143.6, 136.6, 132.9, 131.4, 130.1, 129.1, 128.3, 124.4, 123.4, 122.8, 122.3, 110.6, 54.1, 30.4, 26.3; IR (Neat Film, NaCl) 2968, 1778, 1704, 1662, 1490, 1215, 1114 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{19}H_{21}NO_2$ $[M+H]^+$: 296.1651, found 296.1650.



Iminoisobenzofuran 14b

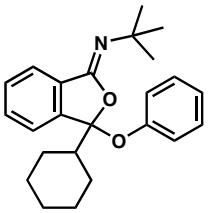
Purified by flash chromatography (SiO_2, 2:98 EtOAc/hexanes) to yield a colorless oil (79% yield). R_f = 0.43 (15:85 EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.6 Hz, 1H), 7.50–7.42 (comp m, 2H), 7.37 (dt, *J* = 7.8, 2.0 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 2H), 6.94 (t, *J* = 7.3 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 2H), 2.42 (ddd, *J* = 13.9, 12.0, 4.6 Hz, 1H), 2.20 (ddd, *J* = 13.9, 12.0, 4.6 Hz, 1H), 1.51–1.40 (m, 1H), 1.44 (s, 9H), 1.39–1.26 (m, 2H), 1.22–1.11 (m, 1H), 0.88 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.7, 153.0, 142.5, 136.6, 130.0, 129.0, 128.3, 124.3, 123.4, 122.9, 122.6, 112.8, 54.0, 39.2,

30.4, 25.7, 22.8, 14.2; IR (Neat Film, NaCl) 2963, 2871, 1706, 1592, 1491, 1214 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{22}H_{27}NO_2$ $[M+H]^+$: 338.2120, found 338.2125.



Iminoisobenzofuran 14c[6]

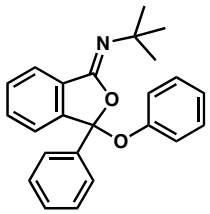
Purified by flash chromatography (SiO_2, 2:98 EtOAc/hexanes) to yield a colorless oil (72% yield). R_f = 0.54 (15:85 EtOAc/hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.61 (dt, *J* = 7.6, 1.0 Hz, 1H), 7.43 (dd, *J* = 4.4, 1.2 Hz, 1H), 7.41 (d, *J* = 5.1 Hz, 1H), 7.34 (ddd, *J* = 7.8, 6.1, 2.4 Hz, 1H), 7.03 (dd, *J* = 8.3, 7.3 Hz, 2H), 6.90 (tt, *J* = 7.3, 1.2 Hz, 1H), 6.78 (dd, *J* = 8.8, 1.2 Hz, 2H), 2.62 (septet, *J* = 6.8 Hz, 1H), 1.42 (s, 9H), 1.22 (d, *J* = 6.8 Hz, 3H), 0.87 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.9, 153.4, 141.6, 134.1, 131.2, 130.0, 129.0, 124.2, 123.3, 123.0, 122.9, 114.9, 54.0, 37.4, 30.4, 17.3, 16.8; IR (Neat Film, NaCl) 2968, 1706, 1592, 1491, 1214, 1070 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{21}H_{25}NO_2$ $[M+H]^+$: 324.1964, found 324.1959.



Iminoisobenzofuran 14d[6]

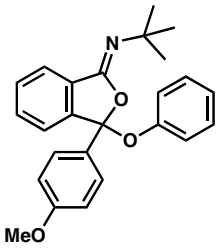
Purified by flash chromatography (SiO_2, 2:98 EtOAc/hexanes) to yield a colorless oil (75% yield). R_f = 0.46 (15:85 EtOAc/hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.6 Hz, 1H), 7.43–7.40 (comp m, 2H), 7.34 (dd, *J* = 7.8, 2.4 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 2H), 6.90 (t, *J* = 7.3 Hz, 1H), 6.78 (d, *J* = 7.6

Hz, 2H), 2.29 (td, J = 12.0, 3.2 Hz, 2H), 1.86 (br d, J = 12.9 Hz, 1H), 1.71 (br s, 1H), 1.50–1.41 (m, 1H), 1.43 (s, 9H), 1.38–1.14 (comp m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.8, 153.3, 141.7, 136.6, 134.1, 131.1, 129.9, 129.0, 128.3, 124.2, 123.3, 123.0, 122.9, 114.3, 54.0, 47.0, 30.4, 27.2, 26.8, 26.6, 26.3, 26.2; IR (Neat Film, NaCl) 2931, 1706, 1593, 1491, 1213 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{24}H_{29}NO_2$ [M+H]$^+$: 364.2271, found 364.2273.



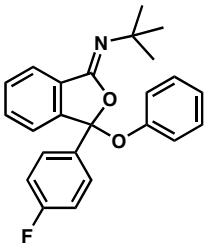
Iminoisobenzofuran 14e

Purified by flash chromatography (SiO_2, 3:97 EtOAc/hexanes) to yield a white solid (91% yield). R_f = 0.40 (15:85 EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (dt, J = 7.6, 1.0 Hz, 1H), 7.64 (dd, J = 7.1, 1.5 Hz, 2H), 7.45-7.33 (comp m, 6H), 7.13 (dd, J = 8.5, 7.3 Hz, 2H), 6.99 (dd, J = 7.6, 1.2 Hz, 2H), 6.95 (t, J = 7.3 Hz, 1H), 1.47 (s, 9H);); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.1, 152.8, 144.5, 139.8, 131.8, 131.7, 130.1, 129.2, 129.0, 128.9, 126.0, 123.6, 123.5, 123.3, 121.5, 110.4, 54.3, 30.5; IR (Neat Film, NaCl) 2968, 1709, 1590, 1491, 1213 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{24}H_{24}NO_2$ [M+H]$^+$: 358.1807, found 358.1798.



Iminoisobenzofuran 14f

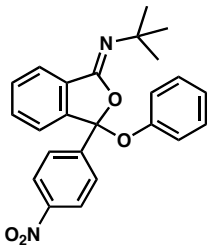
Purified by flash chromatography (SiO_2, 4:96 EtOAc/hexanes) to yield a colorless oil (64% yield). R_f = 0.30 (15:85 EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, J = 7.6 Hz, 1H), 7.55 (d, J = 8.8 Hz, 2H), 7.44 (dd, J = 7.3, 6.6 Hz, 1H), 7.41–7.36 (comp m, 2H), 7.13 (dd, J = 8.5, 7.3 Hz, 2H), 6.99 (d, J = 7.8 Hz, 2H), 6.95 (t, J = 7.3 Hz, 1H), 6.90 (d, J = 8.8 Hz, 2H), 3.80 (s, 3H), 1.47 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.1, 154.1, 152.9, 144.7, 131.9, 131.7, 131.3, 130.0, 129.1, 128.7, 127.4, 126.9, 123.6, 123.2, 121.6, 114.2, 55.5, 54.3, 30.5; IR (Neat Film, NaCl) 2967, 1708, 1661, 1513, 1490, 1254, 1213, 1173 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{25}H_{25}NO_3$ $[M+H]^+$: 388.1913, found 388.1923.



Iminoisobenzofuran 14g

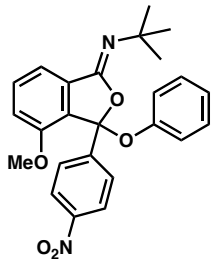
Purified by flash chromatography (SiO_2, 2:98 EtOAc/hexanes) to yield a colorless oil (86% yield). R_f = 0.43 (15:85 EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (dt, J = 7.3, 1.0 Hz, 1H), 7.61 (dd, J = 9.0, 5.1 Hz, 2H), 7.45 (td, J = 7.3, 1.2 Hz, 1H), 7.40 (dd, J = 7.3, 1.2 Hz, 1H), 7.38 (tt, J = 7.3, 1.0 Hz, 1H), 7.13 (dd, J = 8.8, 7.1 Hz, 2H), 7.07 (t, J = 8.8 Hz, 2H), 6.97 (d, J = 7.1 Hz, 2H), 6.96 (tt, J = 7.1, 1.2 Hz, 1H), 1.47 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.9, 161.9, 153.6, 152.1, 143.9, 136.4, 131.7, 131.5, 130.1, 129.9, 129.0, 128.1, 127.8 (d, J_{C-F} = 8.6 Hz), 123.6 (d, J_{C-F} = 21.9 Hz), 123.0, 121.5,

115.6 (d, J_{C-F} = 21.5 Hz), 109.9, 54.1, 30.2; ^{19}F NMR (282 MHz, $CDCl_3$) d –113.0 (app septet, J = 5.1 Hz); IR (Neat Film, NaCl) 2968, 1710, 1590, 1509, 1491, 1211, 1158 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{24}H_{22}FNO_2$ $[M+H]^+$: 376.1713, found 376.1747.



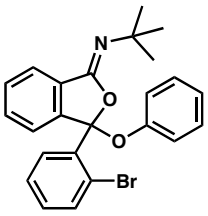
Iminoisobenzofuran 14h

Purified by flash chromatography (SiO_2, 2:98 EtOAc/hexanes) to yield a white solid (90% yield). R_f = 0.37 (15:85 EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, J = 9.0 Hz, 2H), 7.83 (d, J = 9.0 Hz, 2H), 7.76 (dt, J = 7.6, 1.0 Hz, 1H), 7.47 (td, J = 7.3, 1.2 Hz, 1H), 7.42 (td, J = 7.6, 1.2 Hz, 1H), 7.38 (d, J = 7.6 Hz, 1H), 7.15 (dd, J = 8.5, 7.3 Hz, 2H), 7.00 (tt, J = 7.3, 1.2 Hz, 1H), 6.97 (d, J = 7.6 Hz, 2H), 1.49 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.2, 151.6, 148.2, 146.6, 142.9, 135.1, 131.8, 130.5, 129.2, 127.9, 127.0, 124.1, 124.0, 123.8, 123.0, 121.6, 109.3, 54.4, 30.3; IR (Neat Film, NaCl) 2969, 1712, 1590, 1525, 1490, 1350, 1210 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{24}H_{22}N_2O_4$ $[M+H]^+$: 403.1658, found 403.1670.



Iminoisobenzofuran 14i[6]

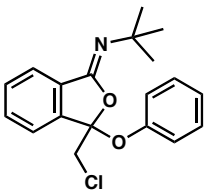
Purified by flash chromatography (SiO_2, 2:98 → 6:94 EtOAc/hexanes) to yield a pale yellow solid (96% yield). R_f = 0.10 (15:85 EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 9.0 Hz, 2H), 7.84 (d, *J* = 9.0 Hz, 2H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.28 (dd, *J* = 7.8, 0.7 Hz, 1H), 7.13 (dd, *J* = 8.5, 7.3 Hz, 2H), 7.02 (dd, *J* = 8.8, 1.2 Hz, 2H), 6.99 (ddd, *J* = 7.3, 1.2, 1.0 Hz, 1H), 6.84 (d, *J* = 8.1 Hz, 1H), 3.79 (s, 3H), 1.46 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.3, 153.2, 151.6, 147.9, 146.1, 134.4, 132.7, 129.2, 128.9, 127.8, 124.7, 123.2, 122.2, 115.4, 113.4, 109.8, 55.5, 54.2, 30.2; IR (Neat Film, NaCl) 2968, 1700, 1613, 1524, 1490, 1349, 1271, 1211, 1044 cm^{-1}; HRMS (MM: ESI–APCI) *m/z* calc'd for $C_{25}H_{24}N_2O_5$ $[M–H]^-$: 431.1612, found 431.1621.



Iminoisobenzofuran 14j

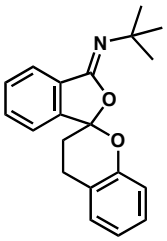
Purified by flash chromatography (SiO_2, 2:98 EtOAc/hexanes) to yield a colorless oil (77% yield). R_f = 0.40 (15:85 EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.62 (td, *J* = 7.9, 1.2 Hz, 2H), 7.46 (td, *J* = 7.9, 1.2 Hz, 1H), 7.45–7.38 (comp m, 2H), 7.25 (td, *J* = 7.6, 1.7 Hz, 1H), 7.11 (t, *J* = 7.3 Hz, 2H), 6.97 (t, *J* = 7.3 Hz, 1H), 6.90 (d, *J* = 7.6 Hz, 2H), 1.40 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.9, 152.4, 142.5, 137.2, 136.4, 135.4, 135.0, 131.2, 130.5,

130.1, 129.7, 128.8, 128.1, 127.9, 127.2, 123.9, 123.1, 123.0, 122.5, 109.5, 54.2, 30.3; IR (Neat Film, NaCl) 2968, 1711, 1589, 1490, 1429, 1289, 1209 cm^{-1}; HRMS (MM: ESI–APCI) *m/z* calc'd for $C_{24}H_{22}BrNO_2$ $[M+H]^+$: 438.0889, found 438.0881.



Iminoisobenzofuran 14k

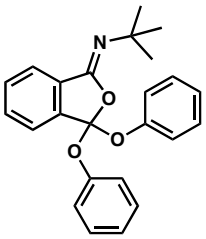
Purified by flash chromatography (SiO_2, 3:97 EtOAc/hexanes) to yield a pale yellow oil (76% yield). R_f = 0.55 (15:85 EtOAc/hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.6 Hz, 1H), 7.56 (dt, *J* = 7.6, 1.0 Hz, 1H), 7.48 (dt, *J* = 7.6, 1.0 Hz, 1H), 7.42 (dt, *J* = 7.6, 1.0 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 2H), 6.98 (tt, *J* = 7.3, 1.0 Hz, 1H), 6.90 (dd, *J* = 7.6, 1.0 Hz, 2H), 4.14 (d, *J* = 11.7 Hz, 1H), 4.07 (d, *J* = 11.7 Hz, 1H), 1.43 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.2, 151.7, 139.7, 134.1, 131.5, 130.8, 129.3, 124.9, 123.6, 123.2, 122.7, 109.6, 54.4, 47.9, 30.3; IR (Neat Film, NaCl) 2968, 1788, 1709, 1591, 1490, 1210 cm^{-1}; HRMS (MM: ESI–APCI) *m/z* calc'd for $C_{19}H_{20}ClNO_2$ $[M+H]^+$: 330.1255, found 330.1271.



Iminoisobenzofuran 14l

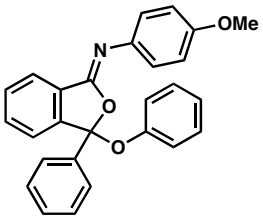
Purified by flash chromatography (SiO_2, 2:98 EtOAc/hexanes) to yield a white solid (86% yield). R_f = 0.37 (15:85 EtOAc/hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.6 Hz, 1H), 7.55 (dd, *J* = 7.3, 1.5 Hz, 1H), 7.51 (ddd, *J* = 7.3, 1.5, 1.2 Hz, 1H), 7.39 (td, *J* = 7.3, 1.2 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 1H),

7.17 (t, J = 8.1 Hz, 1H), 7.00 (td, J = 7.3, 1.2 Hz, 1H), 6.87 (dd, J = 8.1, 1.2 Hz, 1H), 3.29 (ddd, J = 13.7, 13.4, 5.6 Hz, 1H), 2.95 (ddd, J = 16.4, 5.6, 1.7 Hz, 1H), 2.43 (td, J = 13.7, 5.9 Hz, 1H), 2.19 (ddd, J = 13.4, 5.9, 2.0 Hz, 1H), 1.34 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.7, 152.7, 143.7, 136.1, 135.0, 131.4, 130.3, 129.2, 127.7, 123.6, 121.7, 121.5, 117.0, 105.9, 54.1, 30.0, 28.0, 22.0; IR (Neat Film, NaCl) 2967, 1706, 1586, 1489, 1362, 1228, 1044 cm^{-1}; HRMS (FAB+) m/z calc'd for $C_{20}H_{21}NO_2$ $[M+H]^+$: 308.1651, found 308.1661.



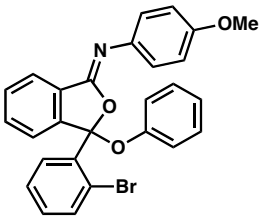
Iminoisobenzofuran 14m

Purified by flash chromatography (SiO_2, 2:98 EtOAc/hexanes) to yield a colorless oil (71% yield). R_f = 0.43 (15:85 EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (dd, J = 7.6, 1.0 Hz, 1H), 7.62 (d, J = 8.1, 1.5 Hz, 2H), 7.48 (tt, J = 7.3, 1.5 Hz, 1H), 7.43 (dd, J = 6.8, 1.2 Hz, 1H), 7.38 (td, J = 7.6, 1.0 Hz, 1H), 7.20 (dd, J = 8.5, 7.6 Hz, 2H), 7.12 (td, J = 7.6, 1.2 Hz, 1H), 7.05 (ddd, J = 7.3, 1.2, 1.0 Hz, 2H), 6.94 (dd, J = 8.5, 1.0 Hz, 2H), 6.36 (dt, J = 7.6, 1.0 Hz, 1H), 1.77 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.8, 153.6, 139.1, 138.2, 136.4, 134.2, 132.4, 132.3, 131.6, 131.1, 130.3, 130.1, 129.1, 128.1, 124.1, 123.2, 123.0, 121.9, 121.3, 113.4, 57.1, 28.4; IR (Neat Film, NaCl) 2966, 1713, 1589, 1489, 1357, 1323, 1202, 1128, 1016 cm^{-1}; HRMS (FAB+) m/z calc'd for $C_{24}H_{23}NO_3$ $[M+H]^+$: 374.1756, found 374.1763.



Iminoisobenzofuran 14n[6]

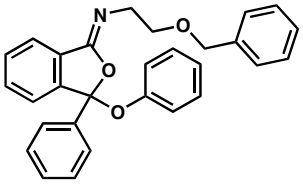
Purified by flash chromatography (SiO_2, 2:98 → 4:96 EtOAc/hexanes) to yield a white solid (68% yield). R_f = 0.35 (15:85 EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (ddd, *J* = 7.6, 1.2, 1.0 Hz, 1H), 7.65 (ddd, *J* = 8.1, 1.2 Hz, 2H), 7.50–7.45 (comp m, 3H), 7.49 (d, *J* = 9.0 Hz, 2H), 7.42–7.35 (comp m, 3H), 7.12 (dd, *J* = 8.8, 7.3 Hz, 2H), 6.98 (dd, *J* = 8.8, 1.2 Hz, 2H), 6.97 (dd, *J* = 6.1, 1.0 Hz, 1H), 6.92 (d, *J* = 9.3 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.0, 153.9, 153.6, 144.4, 138.9, 138.6, 135.0, 131.9, 131.2, 130.2, 130.1, 129.0, 129.0, 128.7, 127.9, 125.9, 125.9, 123.8, 123.5, 123.3, 121.8, 113.9, 55.4; IR (Neat Film, NaCl) 3062, 2928, 2833, 1685, 1591, 1506, 1488, 1292, 1245, 1208, 1030 cm^{-1}; HRMS (MM: ESI–APCI) *m/z* calc'd for $C_{27}H_{21}NO_3$ $[M+H]^+$: 408.1594, found 408.1608.



Iminoisobenzofuran 14o

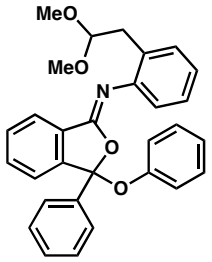
Purified by flash chromatography (SiO_2, 2:98→ 4:96 EtOAc/hexanes) to yield a white solid (62% yield). R_f = 0.37 (15:85 EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.77 (dd, *J* = 7.3, 1.0 Hz, 1H), 7.62 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.51 (td, *J* = 7.3, 1.2 Hz, 1H), 7.47 (dd, *J* = 7.3, 1.2 Hz, 1H), 7.44–7.41 (comp m, 2H), 7.43 (d, *J* = 9.0 Hz, 2H), 7.26 (ddd, *J* = 0.5, 1.7, 8.1 Hz, 1H), 7.09

(dd, J = 8.6, 7.3 Hz, 2H), 6.99 (ddd, J = 7.3, 1.2, 1.0 Hz, 1H), 6.90 (d, J = 9.0 Hz, 2H), 6.87 (dd, J = 8.6, 1.2 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.9, 154.3, 152.4, 142.7, 138.7, 136.4, 135.4, 135.0, 133.3, 131.7, 130.7, 130.4, 130.1, 129.6, 128.9, 127.9, 127.3, 125.6, 124.4, 123.2, 123.1, 123.0, 121.4, 113.9, 55.4; IR (Neat Film, NaCl) 3062, 2928, 2833, 1692, 1590, 1506, 1490, 1466, 1293, 1244, 1202, 1034 cm^{-1}; HRMS (MM: ESI–APCI) m/z calc'd for $C_{27}H_{20}BrNO_3$ $[M+H]^+$: 488.0684, found 488.0714.



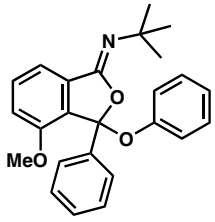
Iminoisobenzofuran 14p[6]

Purified by flash chromatography (SiO_2, 2:98→ 8:92 EtOAc/hexanes) to yield a pale yellow solid (67% yield). R_f = 0.30 (25:75 EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (dt, J = 7.8, 1.0 Hz, 1H), 7.65–7.62 (comp m, 2H), 7.46 (dd, J = 6.8, 1.0 Hz, 1H), 7.44 (dd, J = 7.6, 0.7 Hz, 1H), 7.41 (ddd, J = 7.6, 1.7, 1.0 Hz, 1H), 7.40–7.37 (comp m, 2H), 7.36–7.33 (comp m, 5H), 7.28 (tt, J = 7.3, 1.0, 1H), 7.10 (dd, J = 8.8, 7.3 Hz, 2H), 6.99 (dd, J = 7.6, 1.2 Hz, 2H), 6.94 (tt, J = 7.3, 1.2 Hz, 1H), 4.64 (s, 2H), 3.98 (dt, J = 13.7, 6.3 Hz, 1H), 3.88 (ddd, J = 13.7, 6.3, 5.4 Hz, 1H), 3.80 (ddd, J = 6.6, 6.3, 1.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.0, 153.5, 144.9, 138.9, 138.5, 135.3, 131.6, 130.3, 129.9, 128.9, 128.8, 128.5, 128.3, 127.7, 127.4, 125.8, 123.7, 123.2, 123.1, 121.8, 73.0, 70.1, 47.8; IR (Neat Film, NaCl) 3057, 2858, 1707, 1589, 1490, 1449, 1293, 1208, 1100 cm^{-1}; HRMS (FAB+) m/z calc'd for $C_{29}H_{25}NO_3$ $[M+H]^+$: 436.1907, found 436.1893.



Iminoisobenzofuran 14q[6]

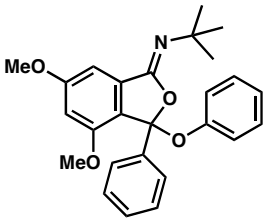
Purified by flash chromatography (SiO_2, 2:98 → 5:95 EtOAc/hexanes) to yield a yellow oil (58% yield). R_f = 0.40 (25:75 EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (dd, *J* = 7.3, 1.0 Hz, 1H), 7.74 (ddd, *J* = 7.3, 1.2, 1.0 Hz, 1H), 7.65 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.57 (ddd, *J* = 7.6, 1.5, 1.0 Hz, 1H), 7.45 (dd, *J* = 7.3, 1.5 Hz, 2H), 7.40 (ddd, *J* = 7.57, 1.5, 1.2 Hz, 2H), 7.27 (m, 1H), 7.26 (tt, *J* = 7.3, 1.5 Hz, 1H), 7.22 (dd, *J* = 7.8, 7.3 Hz, 2H), 7.12 (dd, *J* = 7.8, 1.2 Hz, 2H), 6.99 (dd, *J* = 7.8, 1.0 Hz, 1H), 6.82 (td, *J* = 7.6, 1.2 Hz, 1H), 6.62 (td, *J* = 8.1, 1.5 Hz, 1H), 5.23 (dd, *J* = 7.8, 1.2 Hz, 1H), 3.66 (t, *J* = 5.4 Hz, 1H), 3.01 (s, 6H), 2.98 (t, *J* = 5.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.6, 144.7, 142.9, 138.1, 138.0, 135.8, 135.6, 134.7, 133.5, 133.2, 131.2, 130.2, 130.1, 129.8, 128.8, 128.6, 128.5, 127.9, 127.6, 127.4, 127.3, 125.0, 124.2, 121.4, 102.9, 51.7, 31.3; IR (Neat Film, NaCl) 3067, 2935, 1617, 1597, 1429, 1303, 1121, 1068, 1048 cm^{-1}; HRMS (MM: ESI–APCI) *m/z* calc'd for $C_{30}H_{27}NO_4$ $[M+H]^+$: 466.2013, found 466.2008.



Iminoisobenzofuran 14r[6]

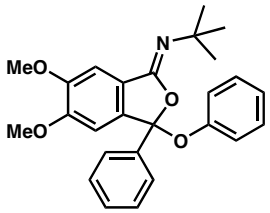
Purified by flash chromatography (SiO_2, 2:98 → 4:96 EtOAc/hexanes) to yield a white solid (75% yield). X-ray diffraction crystals were grown via slow evaporation of a solution of the white solid (20

mg) in $CDCl_3$ (0.6 mL) at ambient temperature; mp 101–104 °C. R_f = 0.30 (15:85 EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 6.6 Hz, 2H), 7.40–7.34 (comp m, 3H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.11 (dd, *J* = 8.6, 7.1 Hz, 2H), 7.06 (dd, *J* = 7.6, 1.2 Hz, 2H), 6.97 (tt, *J* = 7.3, 1.2 Hz, 1H), 6.83 (d, *J* = 8.6 Hz, 1H), 3.78 (s, 3H), 1.47 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.6, 154.0, 153.1, 139.2, 135.1, 134.6, 132.3, 130.6, 129.0, 128.7, 128.1, 126.9, 124.4, 122.4, 115.5, 113.6, 55.7, 54.3, 30.4; IR (Neat Film, NaCl) 2967, 1699, 1612, 1489, 1271, 1213, 1049 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{25}H_{25}NO_3$ $[M+H]^+$: 388.1907, found 388.1925.



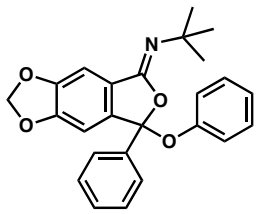
Iminoisobenzofuran 14s[6]

Purified by flash chromatography (SiO_2, 2:98 → 4:96 EtOAc/hexanes) to yield a white solid (68% yield). R_f = 0.27 (15:85 EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.36 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.35 (tt, *J* = 7.8, 1.7 Hz, 1H), 7.12 (dd, *J* = 8.3, 7.3 Hz, 2H), 7.04 (dd, *J* = 8.3, 1.2 Hz, 2H), 6.97 (tt, *J* = 7.3, 1.2 Hz, 1H), 6.72 (d, *J* = 2.0 Hz, 1H), 6.38 (d, *J* = 2.0 Hz, 1H), 3.80 (s, 3H), 3.74 (s, 3H), 1.45 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.3, 155.1, 153.8, 152.9, 139.4, 135.5, 128.7, 128.4, 128.1, 127.8, 126.5, 124.1, 123.8, 122.4, 102.7, 97.0, 55.8, 55.4, 54.0, 30.2; IR (Neat Film, NaCl) 2964, 1695, 1619, 1599, 1355, 1204, 1146, 1037 cm^{-1}; HRMS (MM: ESI–APCI) *m/z* calc'd for $C_{26}H_{27}NO_4$ $[M+H]^+$: 418.2013, found 418.2020.



Iminoisobenzofuran 14t

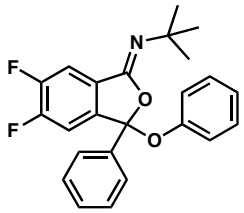
Purified by flash chromatography (SiO_2, 5:95 → 10:90 EtOAc/hexanes) to yield a white solid (85% yield). R_f = 0.23 (15:85 EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 6.8 Hz, 2H), 7.40 (dd, *J* = 7.1, 6.8 Hz, 2H), 7.35 (tt, *J* = 7.1, 1.5 Hz, 1H), 7.14 (dd, *J* = 8.5, 7.1, 2H), 7.12 (s, 1H), 7.00–6.95 (comp m, 3H), 6.77 (s, 1H), 3.92 (s, 3H), 3.88 (s, 3H), 1.45 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.8, 153.0, 152.6, 151.0, 139.8, 137.4, 129.8, 128.9, 128.7, 128.6, 128.2, 125.7, 123.5, 121.5, 104.5, 104.4, 56.3, 56.2, 54.0, 30.3; IR (Neat Film, NaCl) 2966, 1701, 1595, 1501, 1491, 1317, 1214 cm^{-1}; HRMS (MM: ESI–APCI) *m/z* calc'd for $C_{26}H_{27}NO_4$ $[M+H]^+$: 418.2013, found 418.2016.



Iminoisobenzofuran 14u

Purified by flash chromatography (SiO_2, 2:98 EtOAc/hexanes) to yield a colorless oil (76% yield). R_f = 0.30 (15:85 EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.1 Hz, 2H), 7.39 (dd, *J* = 7.6, 6.8 Hz, 2H), 7.34 (tt, *J* = 7.1, 1.0 Hz, 1H), 7.16 (dd, *J* = 8.5, 7.6 Hz, 2H), 7.06 (s, 1H), 7.00 (dd, *J* = 8.5, 1.0 Hz, 2H), 6.98 (t, *J*= 7.3 Hz, 1H), 6.74 (s, 1H), 6.02 (d, *J* = 1.2 Hz, 1H), 5.97 (d, *J* = 1.2 Hz, 1H), 1.44 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.8, 152.2, 151.2, 149.7, 139.7, 139.3, 136.0, 135.0, 129.0, 128.8, 128.7, 125.7, 123.4, 121.4, 102.8, 102.6, 102.2, 53.9, 30.3; IR (Neat Film, NaCl) 2967, 1707,

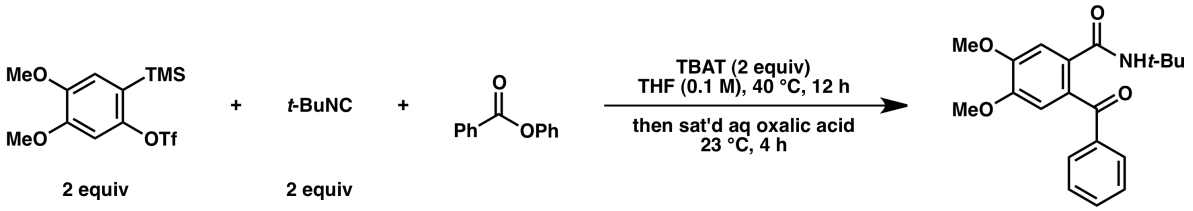
1473, 1307, 1213, 1059, 1037 cm^{-1}; HRMS (MM: ESI–APCI) *m/z* calc'd for $C_{25}H_{23}NO_4$ $[M+H]^+$: 402.1700, found 402.1684.



Iminoisobenzofuran 14v

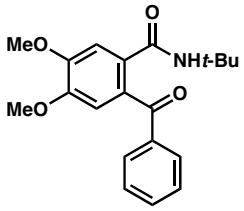
Purified by flash chromatography (SiO_2, 0:100 → 2:98 EtOAc/hexanes) to yield a pale yellow oil (62% yield). R_f = 0.50 (15:85 EtOAc/hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 6.6, 1.5 Hz, 2H), 7.48 (dd, *J* = 8.8, 7.1 Hz, 1H), 7.40 (d, *J* = 7.6 Hz, 2H), 7.39 (dd, *J* = 8.3, 6.8 Hz, 1H), 7.17 (tt, *J* = 7.6, 1.5 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 2H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.98 (dd, *J* = 7.6, 7.1 Hz, 2H), 1.45 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.0 (d, $J_{C–F}$ = 14.7 Hz), 153.5, 153.1 (d, $J_{C–F}$ = 14.3 Hz), 151.9 (d, $J_{C–F}$ = 14.3 Hz), 151.1 (d, $J_{C–F}$ = 14.3 Hz), 150.3, 140.3, 138.8, 129.2, 129.1, 128.9, 125.6, 123.8, 121.3, 111.0 (dd, $J_{C–F}$ = 19.8, 4.1 Hz), 109.4, 54.3, 30.1; ^{19}F NMR (282 MHz, $CDCl_3$) δ –130.3 (ddd, *J* = 18.9, 7.9, 7.6 Hz), –133.7 (ddd, *J* = 18.9, 7.1, 6.8 Hz); IR (Neat Film, NaCl) 2968, 1711, 1498, 1451, 1343, 1211 cm^{-1}; HRMS (MM: ESI–APCI) *m/z* calc'd for $C_{24}H_{21}F_2NO_2$ $[M–H]^-$: 392.1468, found 392.1479.

Representative Procedure for the One-Pot Synthesis and Hydrolysis of Iminoisobenzofurans:



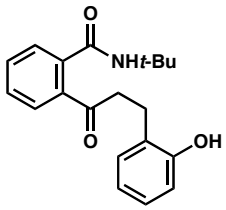
A flame-dried 15 mL long reaction tube with a magnetic stir bar was charged with TBAT (0.545 g, 1.01 mmol, 2 equiv), phenyl benzoate (**9m**) (0.100 g, 0.504 mmol), and THF (5 mL). To this solution was added silyl aryl triflate **12b** (0.362 g, 1.01 mmol, 2 equiv) and *tert*-butyl isocyanide (**2a**) (0.114 mL, 1.01 mmol, 2 equiv) sequentially via syringe. The reaction was heated to 40 °C under argon for 12 h, at which point TLC analysis showed complete consumption of phenyl benzoate (NOTE: at this point, the major component of the reaction is the iminoisobenzofuran). The reaction was cooled to ambient temperature and a saturated aqueous solution of oxalic acid (5 mL) was added via syringe. The mixture was vigorously stirred for 4 h, at which point TLC analysis showed complete comsumption of the intermediate iminoisobenzofuran. The reaction was quenched by the slow addition of a saturated aqueous solution of $NaHCO_3$ (10 mL) and stirred until bubbling ceased. The aqueous layer was extracted with EtOAc (3 x 25 mL), and the combined organic layers were washed with brine (40 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified via flash chromatography over silica gel.

Spectroscopic Data for *ortho*-Ketobenzamides:



***ortho*-Ketobenzamide 16a**

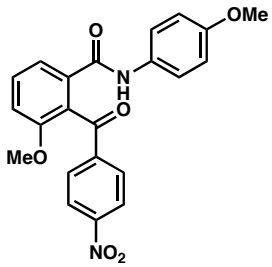
Purified by flash chromatography (SiO_2, 15:85 → 40:60 EtOAc/hexanes) to yield a white solid (81% yield). R_f = 0.37 (50:50 EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (dd, J = 8.3, 1.2 Hz, 2H), 7.57 (tt, J = 7.6, 1.2 Hz, 1H), 7.45 (dd, J = 8.1, 7.6 Hz, 2H), 7.24 (s, 1H), 6.95 (s, 1H), 5.59 (br s, 1H), 4.00 (s, 3H), 3.92 (s, 3H), 1.05 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.6, 166.7, 150.4, 150.3, 137.5, 133.5, 130.7, 129.8, 128.6, 127.8, 111.1, 110.7, 56.3, 56.2, 51.8, 28.0; IR (Neat Film, NaCl) 3318, 2965, 1654, 1648, 1596, 1502, 1449, 1348, 1293, 1273, 1215 1084 cm^{-1}; HRMS (MM: ESI–APCI) m/z calc'd for $C_{20}H_{23}NO_4$ $[M–H]^-$: 340.1554, found 340.1556.



***ortho*-Ketobenzamide 16b**

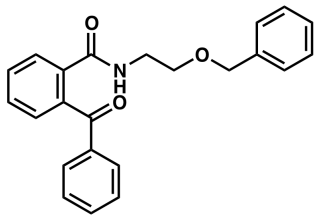
Purified by flash chromatography (SiO_2, 10:90 → 25:75 EtOAc/hexanes) to yield a white solid (75% yield). R_f = 0.10 (25:75 EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49–7.42 (comp m, 4H), 7.12–7.08 (comp m, 2H), 6.88 (dd, J = 8.5, 1.2 Hz, 1H), 6.84 (td, J = 7.3, 1.2 Hz, 1H), 5.72 (br s, 1H), 3.26 (t, J = 6.4 Hz, 2H), 3.02 (t, J = 6.4 Hz, 2H), 1.45 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.0, 168.4, 154.5, 138.5, 136.8, 131.1, 130.4, 130.2, 129.9, 127.6, 127.5, 127.3, 120.5, 117.2, 52.2, 43.2, 28.6,

24.2; IR (Neat Film, NaCl) 3315, 2970, 1681, 1644, 1593, 1532, 1456, 1366, 1230 cm^{-1}; HRMS (MM: ESI–APCI) *m/z* calc'd for $C_{20}H_{23}NO_3$ $[M–H]^-$: 324.1605, found 324.1620.



***ortho*-Ketobenzamide 16c**

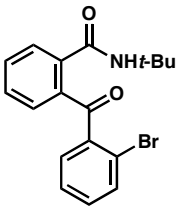
Purified by flash chromatography (SiO_2, 10:90 → 30:70 EtOAc/hexanes) to yield a yellow solid (84% yield). R_f = 0.10 (25:75 EtOAc/hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 8.51 (d, *J* = 11.7 Hz, 1H), 8.33 (d, *J* = 1.7 Hz, 1H), 7.88 (m, 1H), 7.45 (d, *J* = 9.0 Hz, 2H), 7.28 (br s, 1H), 7.04 (d, *J* = 8.9 Hz, 2H), 6.90 (d, *J* = 9.0 Hz, 2H), 6.87 (d, *J* = 9.0 Hz, 2H), 3.81 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.0, 158.8, 157.7, 156.7, 129.9, 129.5, 121.8, 121.7, 114.9, 114.2, 55.6, 55.5; IR (Neat Film, NaCl) 3270, 3127, 3062, 1684, 1603, 1512, 1412, 1301, 1247, 1032 cm^{-1}; HRMS (MM: ESI–APCI) *m/z* calc'd for $C_{22}H_{18}N_2O_6$ $[M+H]^+$: 407.1238, found 407.1233.



***ortho*-Ketobenzamide 16d**[6]

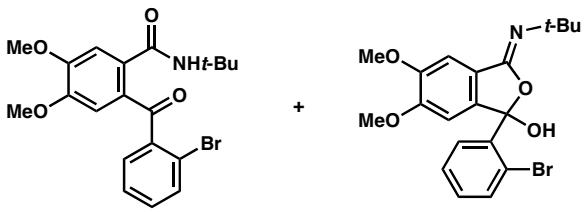
Purified by flash chromatography (SiO_2, 5:95 → 15:85 EtOAc/hexanes) to yield a white solid (59% yield). R_f = 0.27 (25:75 EtOAc/hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.48 (td, *J* = 7.3, 1.5 Hz, 1H), 7.45 (ddd, *J* = 7.3, 1.5, 0.5 Hz, 1H), 7.39 (dd, *J* = 5.1, 1.5 Hz, 1H), 7.38–

7.31 (comp m, 7H), 7.29 (dd, J = 8.1, 1.5 Hz, 2H), 6.09 (t, J = 5.4 Hz, 1H), 4.38 (s, 2H), 3.15 (t, J = 5.1 Hz, 2H), 2.97 (dt, J = 5.4, 5.1 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.1, 169.4, 143.2, 139.2, 138.0, 136.1, 135.7, 134.0, 129.8, 129.7, 129.0, 128.5, 127.8, 127.7, 127.6, 126.6, 72.9, 68.4, 39.4; IR (Neat Film, NaCl) 3284, 3067, 2860, 1634, 1631, 1536, 1427, 1300, 1107 cm^{-1}; HRMS (MM: ESI–APCI) m/z calc'd for $C_{23}H_{21}NO_3$ [M+H]$^+$: 360.1594, found 360.1588.



***ortho*-Ketobenzamide 16e**

Purified by flash chromatography (SiO_2, 20:80 → 30:70 EtOAc/hexanes) to yield a colorless oil (77% yield). R_f = 0.20 (25:75 EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (dd, J = 7.8, 1.2 Hz, 1H), 7.56–7.54 (comp m, 2H), 7.49 (dd, J = 7.6, 2.0 Hz, 1H), 7.46–7.44 (comp m, 2H), 7.38 (td, J = 7.6, 1.5 Hz, 1H), 7.34 (td, J = 7.8, 2.0 Hz, 1H), 5.74 (br s, 1H), 1.34 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.1, 167.9, 139.4, 138.7, 137.3, 133.8, 132.3, 131.8, 131.7, 130.3, 129.6, 127.9, 127.3, 120.8, 51.9, 28.5; IR (Neat Film, NaCl) 3320, 2969, 1663, 1534, 1452, 1297, 1248, 1220 cm^{-1}; HRMS (MM: ESI–APCI) m/z calc'd for $C_{18}H_{18}BrNO_2$ [M+H]$^+$: 360.0594, found 360.0594.

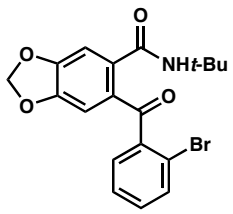


***ortho*-Ketobenzamide 16f**

Purified by flash chromatography (SiO_2, 10:90 → 30:70 EtOAc/hexanes) to yield a colorless oil (69% yield). R_f = 0.10 (25:75 EtOAc/hexanes). Product was isolated as a 2:1 mixture of inseparable ketobenzamide and cyclic imidate isomers. ^{1}H and ^{13}C NMR data are reported for individual isomers; IR and HRMS data are reported for the mixture.

***ortho*-Ketobenzamide:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.46 (dd, *J* = 7.3, 2.0 Hz, 1H), 7.40 (td, *J* = 7.6, 1.5 Hz, 1H), 7.34 (td, *J* = 7.8, 2.0 Hz, 1H), 7.08 (s, 1H), 6.96 (s, 1H), 5.70 (br s, 1H), 3.99 (s, 3H), 3.83 (s, 3H), 1.28 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.0, 167.6, 151.9, 149.4, 139.7, 135.2, 133.8, 133.1, 132.2, 131.5, 127.4, 120.7, 113.1, 111.2, 56.3, 56.2, 51.9, 28.3.

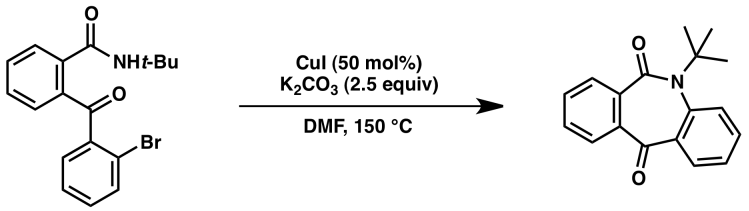
Cyclic imidate: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.50 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.43 (ddd, *J* = 8.1, 7.3, 1.2 Hz, 1H), 7.23 (s, 1H), 7.19 (ddd, *J* = 7.8, 7.3, 1.7 Hz, 1H), 6.37 (s, 1H), 3.94 (s, 3H), 3.77 (s, 3H), 2.87 (br s, 1H), 1.45 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.7, 153.0, 150.7, 140.4, 139.0, 129.9, 129.7, 129.0, 127.3, 126.0, 121.0, 104.3, 103.6, 91.8, 57.0, 56.3, 56.2, 28.8. IR (Neat Film, NaCl) 3357, 2966, 2936, 1664, 1593, 1507, 1502, 1463, 1349, 1289, 1272, 1212, 1089 cm^{-1}; HRMS (MM: ESI–APCI) *m/z* calc'd for $C_{20}H_{22}BrNO_4$ $[M+H]^+$: 420.0805, found 420.0817.



ortho-Ketobenzamide 16g

Purified by flash chromatography (SiO_2, 5:95 → 20:80 EtOAc/hexanes) to yield a white solid (64% yield). R_f = 0.10 (25:75 EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (dd, J = 7.8, 1.2 Hz, 1H), 7.47 (dd, J = 7.6, 2.0 Hz, 1H), 7.39 (td, J = 7.6, 1.2 Hz, 1H), 7.33 (td, J = 7.8, 2.0 Hz, 1H), 7.01 (s, 1H), 6.86 (s, 1H), 6.07 (s, 2H), 5.63 (br s, 1H), 1.31 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.5, 167.4, 150.5, 148.3, 139.7, 135.1, 133.6, 132.1, 131.3, 127.4, 121.4, 120.5, 110.4, 108.7, 102.3, 51.9, 28.4; IR (Neat Film, NaCl) 3317, 2969, 2907, 1654, 1650, 1607, 1503, 1482, 1453, 1367, 1285, 1259, 1226, 1035 cm^{-1}; HRMS (MM: ESI–APCI) m/z calc'd for $C_{19}H_{18}BrNO_4$ $[M+H]^+$: 404.0492, found 404.0505.

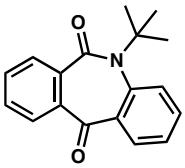
Representative Procedure for the Intramolecular Amide-Aryl Bromide Coupling:



16e ***17a***

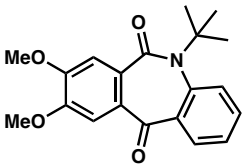
A flame-dried 1.5 dram vial containing a magnetic stir bar and sealed with a PTFE/silicone septum and screw cap was charged with copper(I) iodide (0.005 g, 0.028 mmol, 0.5 equiv) and potassium carbonate (0.019 g, 0.137 mmol, 2.5 equiv). The vial was evacuated and backfilled with argon twice. A solution of *ortho*-ketobenzamide **16e** (0.020 g, 0.056 mmol) in DMF (0.6 mL) was then added via syringe and the mixture was heated to 150 °C. The solution started as a pale yellow and became progressively brighter yellow over the course of the reaction. After 24 h, the reaction was cooled to ambient temperature and filtered through a pad of silica under EtOAc elution to remove solids. The solvents were removed under reduced pressure and the resulting yellow residue was purified via flash chromatography over silica gel.

Spectroscopic Data for Dibenzoketocaprolactams:



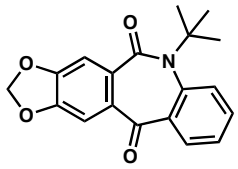
Dibenzoketocaprolactam 17a

Purified by flash chromatography (SiO_2, 5:95 → 10:90 EtOAc/hexanes) to yield a white solid (85% yield). R_f = 0.50 (25:75 EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (ddd, *J* = 7.8, 1.2, 0.7 Hz, 1H), 7.57 (ddd, *J* = 7.8, 6.4, 2.5 Hz, 1H), 7.53 (d, *J* = 1.7 Hz, 1H), 7.52 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.42–7.37 (comp m, 2H), 7.40 (dd, *J* = 6.1, 1.5 Hz, 1H), 7.31–7.27 (m, 1H), 1.52 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.7, 166.9, 142.1, 141.1, 137.3, 133.5, 132.2, 131.9, 131.8, 130.1, 127.9, 127.3, 126.0, 125.8, 60.9, 30.0; IR (Neat Film, NaCl) 2974, 1689, 1647, 1592, 1483, 1446, 1340, 1280, 1188 cm^{-1}; HRMS (MM: ESI–APCI) *m/z* calc'd for $C_{18}H_{17}NO_2$ $[M+H]^+$: 280.1332, found 280.1340.



Dibenzoketocaprolactam 17b

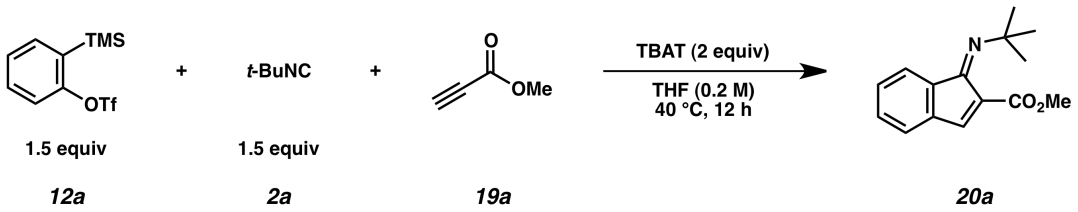
Purified by flash chromatography (SiO_2, 5:95 → 10:90 EtOAc/hexanes) to yield a pale yellow oil (61% yield). R_f = 0.30 (25:75 EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.44 (ddd, *J* = 7.6, 1.5, 0.5 Hz, 1H), 7.42 (ddd, *J* = 7.6, 1.7, 1.5 Hz, 1H), 7.39 (app td, *J* = 6.8, 1.7 Hz, 1H), 7.29 (ddd, *J* = 7.6, 6.8, 1.7 Hz, 1H), 7.08 (s, 1H), 3.97 (s, 3H), 3.96 (s, 3H), 1.52 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.4, 166.7, 151.8, 151.5, 141.6, 137.2, 134.6, 130.0, 127.6, 127.4, 127.0, 126.3, 113.9, 108.4, 60.9, 56.3, 56.2, 30.1; IR (Neat Film, NaCl) 2969, 2935, 1674, 1645, 1589, 1514, 1447, 1360, 1331, 1286, 1219, 1185, 1077 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{20}H_{21}NO_4$ $[M^{\bullet}]^+$: 339.1471, found 339.1484.



Dibenzoketocaprolactam 17c

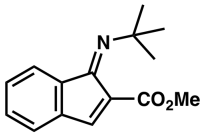
Purified by flash chromatography (SiO_2, 5:95 EtOAc/hexanes) to yield a yellow oil (73% yield). R_f = 0.40 (25:75 EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.39 (app dd, *J* = 2.7, 1.0 Hz, 2H), 7.38 (dd, *J* = 5.9, 1.5 Hz, 1H), 7.29 (t, *J* = 3.7 Hz, 1H), 7.00 (s, 1H), 6.05 (d, *J* = 9.5 Hz, 2H), 1.50 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.2, 166.1, 150.8, 150.4, 141.7, 137.1, 136.8, 129.9, 127.7, 127.1, 126.1, 111.6, 105.9, 102.4, 60.9, 30.0; IR (Neat Film, NaCl) 2973, 2909, 1679, 1645, 1608, 1593, 1483, 1448, 1373, 1332, 1282, 1187, 1037 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{19}H_{17}NO_4$ $[M+H]^+$: 324.1230, found 324.1241.

Representative Procedure for the Synthesis of Iminoindenones from Arynes, Isocyanides, and Alkynes:



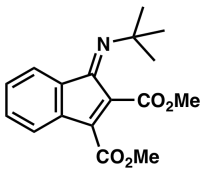
A flame-dried 15 mL round bottomed flask with a magnetic stir bar was charged with TBAT (0.607 g, 1.124 mmol, 2.0 equiv) and THF (3 mL). To this solution was added methyl propiolate (**19a**) (0.05 mL, 0.562 mmol), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**12a**) (0.204 mL, 0.843 mmol, 1.5 equiv), and *tert*-butyl isocyanide (**2a**) (0.095 mL, 0.843 mmol, 1.5 equiv) sequentially via syringe. The reaction was heated to 40 °C under argon for 12 h, at which point TLC analysis showed complete consumption of the aryne precursor (**12a**). The reaction was cooled to ambient temperature, and then adsorbed on to Celite by removal of solvent under reduced pressure. The resulting powder was loaded directly on to a chromatography column and purified via flash chromatography over silica gel.

Spectroscopic Data for Iminoindenones:



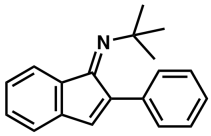
Iminoindenone 20a

Purified by flash chromatography (SiO_2, 5:95 EtOAc/hexanes) to yield a yellow solid (88% yield). R_f = 0.66 (20:80 EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (dd, J = 8.8, 2.2 Hz, 1H), 7.66 (dd, J = 8.1, 1.2 Hz, 1H), 7.46–7.36 (comp m, 3H), 3.89 (s, 3H), 1.51 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.6, 144.3, 138.0, 135.0, 130.8, 128.3, 128.1, 127.1, 88.0, 78.4, 57.8, 53.2, 29.7; IR (Neat Film, NaCl) 2969, 2245, 1723, 1590, 1526, 1466, 1436, 1390, 1362, 1334, 1281, 1256, 1208, 1158, 1128, 1114, 1082, 1058 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{15}H_{17}NO_2$ $[M^{\bullet}]^+$: 243.1259, found 243.1260.



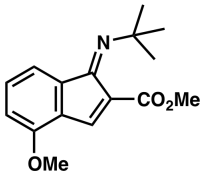
Iminoindenone 20b

Purified by flash chromatography (SiO_2, 10:90 EtOAc/hexanes) to yield a white solid (83% yield). R_f = 0.38 (30:70 EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, J = 7.6, 1H), 7.35 (d, J = 6.5 Hz, 1H), 7.24 (dd, J = 7.6, 4.0 Hz, 1H), 7.13 (dd, J = 13.5, 7.0 Hz, 1H), 3.52 (s, 3H), 3.27 (s, 3H) 1.14 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.1, 150.9, 141.2, 135.0, 131.9, 130.9, 130.1, 127.9, 123.6, 122.4, 101.2, 80.2, 54.5, 53.1, 30.1; IR (Neat Film, NaCl) 2969, 2245, 1723, 1590, 1526, 1466, 1436, 1390, 1362, 1334, 1281, 1256, 1208, 1158, 1128, 1114, 1082, 1058 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{17}H_{19}NO_4$ $[M^{\bullet}]^+$: 301.1314, found 301.1315.



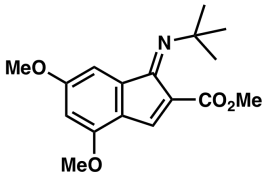
Iminoindenone 20c

Purified by flash chromatography (SiO_2, 5:95 CH_2Cl_2/hexanes) to yield a pale yellow oil (51% yield). R_f = 0.60 (5:95 EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, J = 2.4 Hz, 1H), 8.08 (d, J = 3.7, 1.2 Hz, 1H), 7.61–7.58 (comp m, 2H), 7.46–7.38 (comp m, 6H), 1.56 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.1, 147.0, 139.5, 136.9, 131.6, 130.0, 129.6, 128.6, 128.1, 127.2, 122.0, 98.9, 84.1, 57.0, 29.5; IR (Neat Film, NaCl) 2968, 1778, 1704, 1662, 1490, 1215, 1114 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{19}H_{19}N$ $[M+H]^+$: 262.1590, found 262.1592.



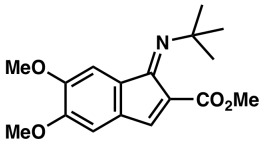
Iminoindenone 20d

Purified by flash chromatography (SiO_2, 15:85 EtOAc/hexanes) to yield a yellow oil (66% yield). R_f = 0.41 (30:70 EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, J = 8.0 Hz, 1H), 7.54 (s, 1H), 7.4 (app t, J = 8.0 Hz, 1H), 6.98 (d, J = 8.0 Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 1.50 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.6, 153.6, 144.1, 139.4, 129.3, 120.0, 116.7, 111.8, 87.9, 78.6, 57.8, 55.4, 53.1, 29.6; IR (Neat Film, NaCl) 2969, 215, 1720, 1602, 1576, 1486, 1466, 1433, 1362, 1275, 1252, 1206, 1175, 1043 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{16}H_{19}NO_3$ $[M+H]^+$: 274.1438, found 274.1454.



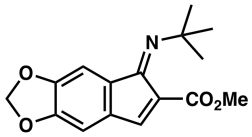
Iminoindenone 20e

Purified by flash chromatography (SiO_2, 10:90 EtOAc/hexanes) to yield a white solid (79% yield). R_f = 0.41 (15:85 EtOAc/Hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (dd, J = 2.2, 1.2 Hz, 2H), 6.54 (dt, J = 2.2, 1.2 Hz, 1H), 3.87 (s, 3H), 3.84 (s, 6H), 1.47 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.7, 153.5, 144.1, 140.1, 135.0, 130.1, 127.9, 105.2, 102.9, 87.9, 78.3, 57.8, 55.5, 53.1, 29.6; IR (Neat Film, NaCl) 2968, 2839, 2216, 1720, 1606, 1580, 1458, 1428, 1390, 1361, 1328, 1299, 1259, 1207, 1156, 1118, 1066, 1052 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{17}H_{21}NO_4$ $[M+H]^+$: 304.1543, found 304.1560.



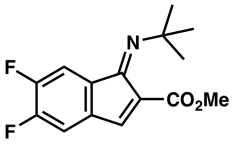
Iminoindenone 20f

Purified by flash chromatography (SiO_2, 15:85 EtOAc/hexanes) to yield a colorless oil (54% yield). R_f = 0.22 (15:85 EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, J = 2.1 Hz, 1H), 7.55 (dd, J = 8.4, 2.1 Hz, 1H), 6.87 (d, J = 8.4 Hz, 1H), 3.94 (s, 3H), 3.92 (s, 3H), 3.88 (s, 3H), 1.49 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.6, 151.4, 148.9, 143.6, 131.2, 121.2, 110.2, 108.8, 87.8, 78.4, 57.4, 56.0, 55.9, 53.1, 29.7; IR (Neat Film, NaCl) 2966, 2215, 1719, 1599, 1570, 1511, 1464, 1436, 1418, 1362, 1267, 1206, 1169, 1146, 1080, 1026 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{17}H_{21}NO_4$ $[M+H]^+$: 304.1543, found 304.1552.



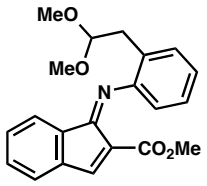
Iminoindenone 20g

Purified by flash chromatography (SiO_2, 10:90 EtOAc/hexanes) to yield a white solid (56% yield). R_f = 0.46 (15:85 EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.51 (d, J = 8.3 Hz, 1H), 6.82 (d, J = 8.3 Hz, 1H), 6.00 (s, 2H), 3.88 (s, 3H), 1.48 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.6, 149.9, 148.0, 143.3, 132.9, 122.6, 107.7, 106.7, 101.5, 87.7, 78.3, 57.4, 53.1, 29.7; IR (Neat Film, NaCl) 2697, 2217, 1718, 1576, 1504, 1488, 1444, 1362, 1275, 1257, 1207, 1117, 1039 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{16}H_{17}NO_4$ [M+H]$^+$: 288.1230, found 288.1227.



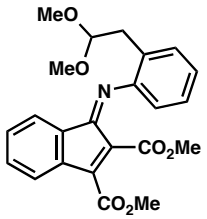
Iminoindenone 20h

Purified by flash chromatography (SiO_2, 2:98 EtOAc/hexanes) to yield a colorless oil (80% yield). R_f = 0.46 (15:85 EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (dq, J = 8.0, 2.2 Hz, 1H), 7.73 (d, J = 2.2 Hz, 1H), 7.19 (q, J = 8.0 Hz, 1H), 3.90 (s, 3H), 1.48 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.3, 142.0, 136.3, 128.3, 123.7, 117.0, 116.9, 116.0, 115.8, 88.24, 58.0, 53.3, 29.6; IR (Neat Film, NaCl) 2968, 1778, 1704, 1662, 1490, 1215, 1114 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{15}H_{15}F_2NO_2$ [M+H]$^+$: 280.1144, found 280.1162.



Iminoindenone 20i

Purified by flash chromatography (SiO_2, 15:85 EtOAc/hexanes) to yield yellow oil (66% yield). R_f = 0.39 (15:85 EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, J = 8.8 Hz, 2H), 7.56–7.50 (comp m, 3H), 7.35 (d, J = 7.2 Hz, 1H), 7.28 (app t, J = 7.8 Hz, 1H), 7.19 (app t, J = 7.2 Hz, 1H), 7.02 (d, J = 7.2 Hz, 1H), 4.53 (t, J = 5.9 Hz, 1H), 3.79 (s, 3H), 3.29 (s, 6H), 2.97 (d, J = 5.9 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.0, 149.0, 147.0, 136.0, 131.8, 130.9, 129.2, 128.6, 128.0, 127.0, 126.0, 118.7, 104.8, 85.6, 77.7, 53.7, 53.1, 35.9; IR (Neat Film, NaCl) 2924, 2852, 2360, 2117, 1716, 1590, 1566, 1482, 1448, 1433, 1362, 1316, 1285, 1245, 1214, 1186, 1119, 1063, 1047, 1000 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{21}H_{21}NO_4$ $[M^{\bullet}]^+$: 351.1471, found 351.1457.



Iminoindenone 20j

Purified by flash chromatography (SiO_2, 15:85 EtOAc/hexanes) to yield an orange solid (91% yield). R_f = 0.57 (20:80 EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, J = 6.5 Hz, 1H), 7.68–7.61 (comp m, 3H), 7.31 (d, J = 7.5 Hz, 1H), 7.26 (app t, J = 6.5 Hz, 2H) 7.11 (app t, J = 6.9 Hz, 1H), 4.62 (t, J = 5.0, 1H), 3.79 (s, 3H), 3.59 (s, 3H), 3.31(s, 6H), 3.04 (d, J = 7.1 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.6, 153.0, 152.9, 144.1, 142.2, 132.9, 131.4, 130.8, 130.6, 130.4, 126.9, 124.6, 123.9, 122.7, 122.0, 104.8, 53.8, 53.7, 53.5, 53.1, 35.9, 30.9; IR (Neat Film, NaCl) 2939, 2832, 1722, 1598,

1489, 1435, 1337, 1281, 1258, 1088, 1060 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{23}H_{23}NO_6$ $[M+H]^+$: 410.1604, found 410.1624.

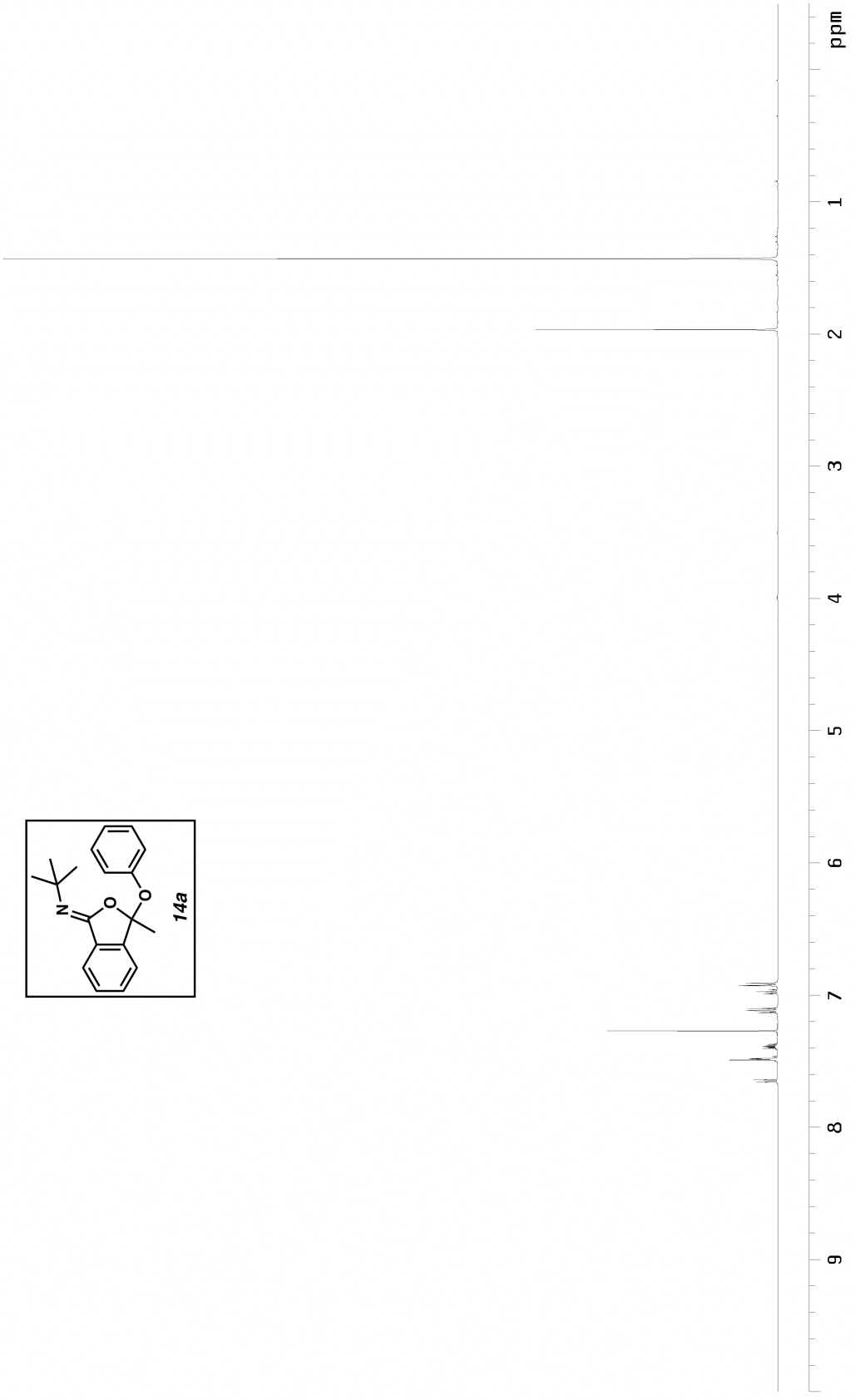


Figure 1.1 ^{1}H NMR (500 MHz, $CDCl_3$) of iminoisobenzofuran **14a**.

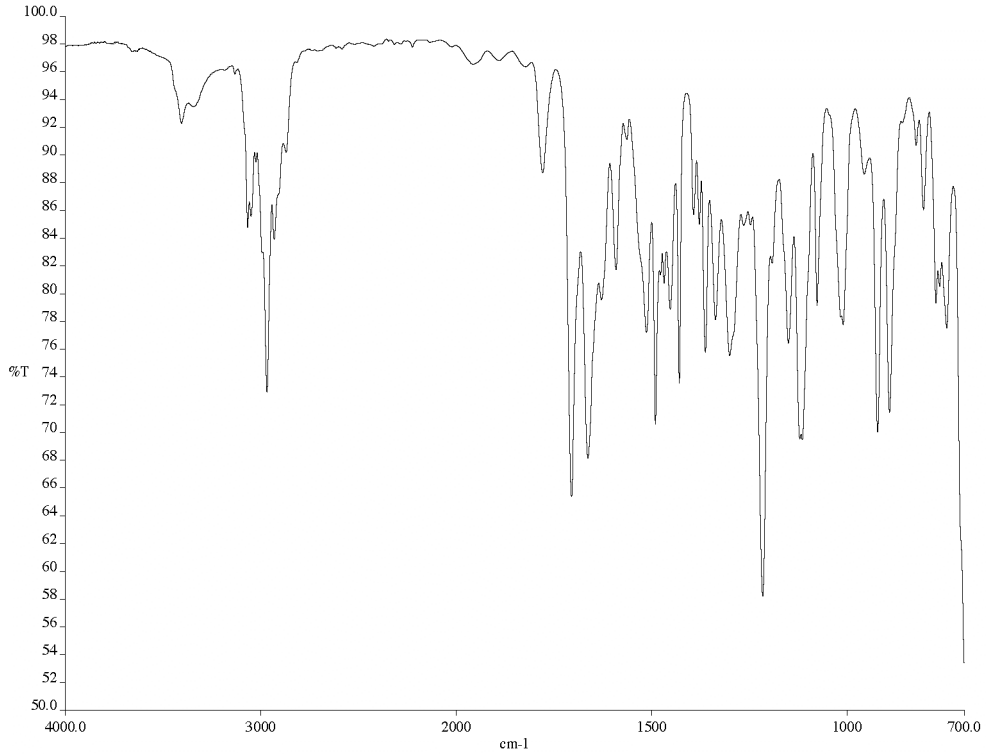


Figure 1.2 Infrared spectrum (thin film/NaCl) of iminoisobenzofuran **14a**.

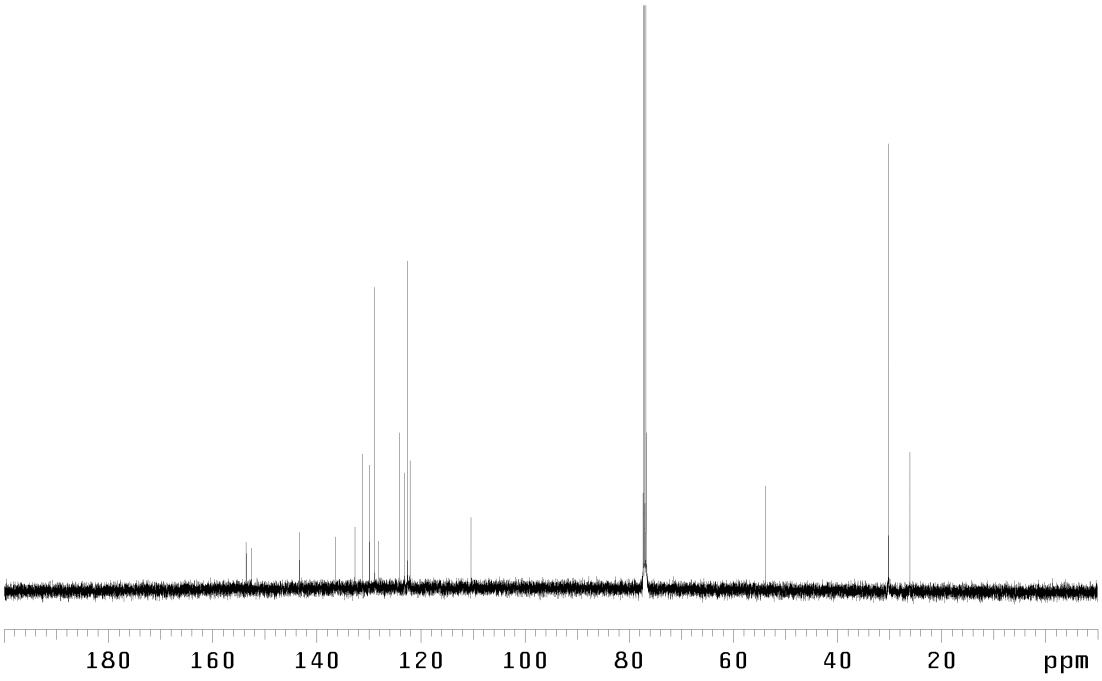


Figure 1.3 ^{13}C NMR (125 MHz, $CDCl_3$) of iminoisobenzofuran **14a**.

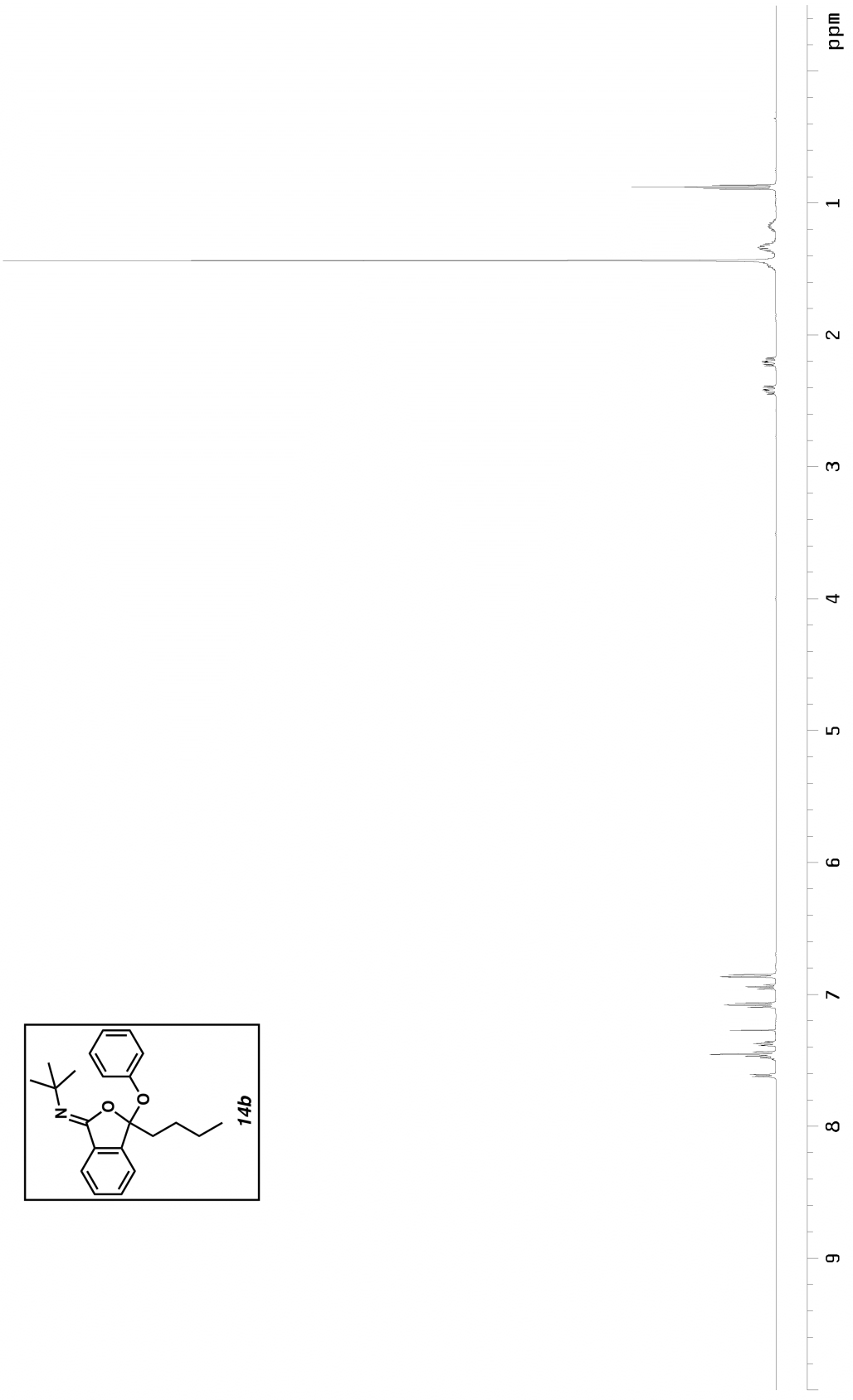


Figure 2.1 ^{1}H NMR (500 MHz, $CDCl_3$) of iminoisobenzofuran **14b**.

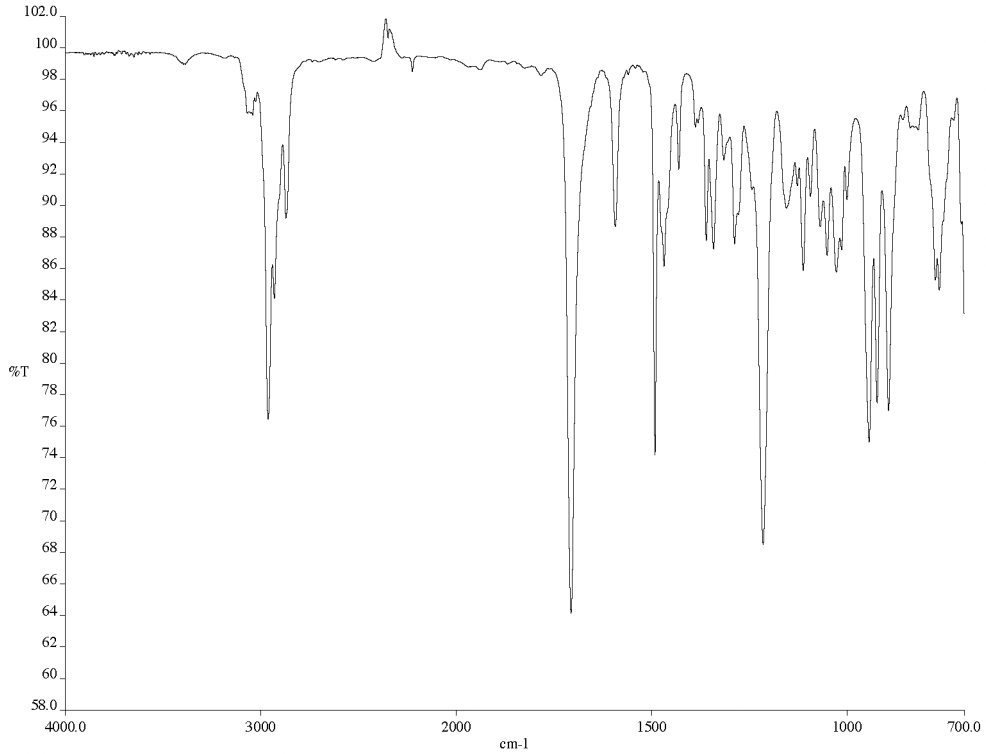


Figure 2.2 Infrared spectrum (thin film/NaCl) of iminoisobenzofuran **14b**.

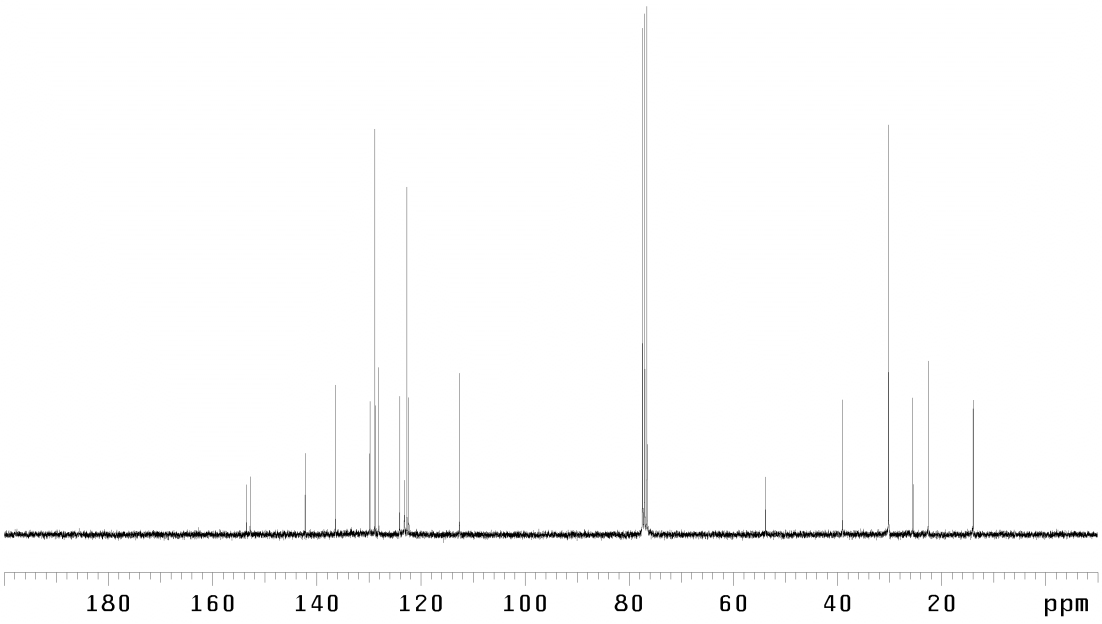


Figure 2.3 ^{13}C NMR (125 MHz, $CDCl_3$) of iminoisobenzofuran **14b**.

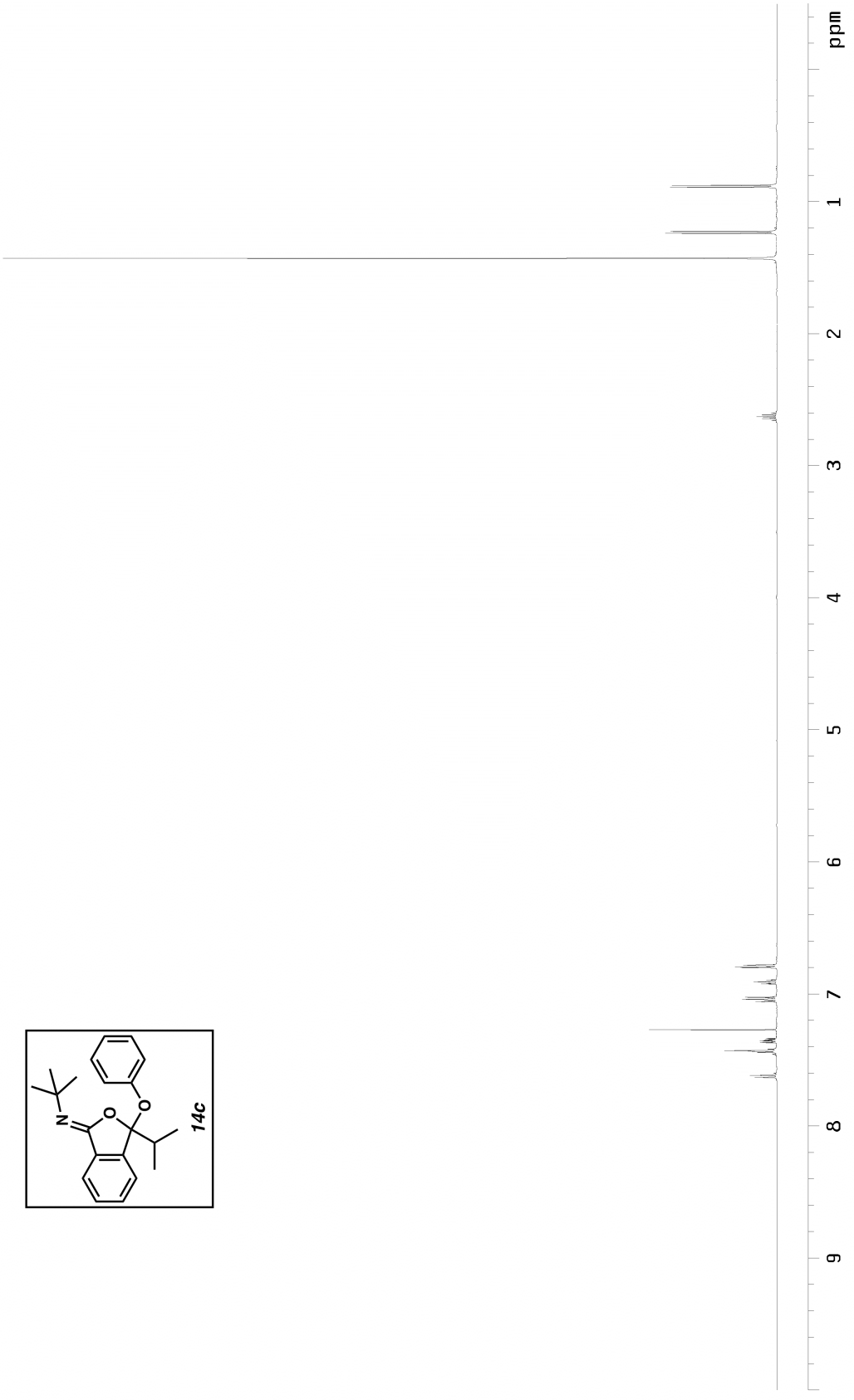


Figure 3.1 ^{1}H NMR (500 MHz, $CDCl_3$) of iminoisobenzofuran **14c**.

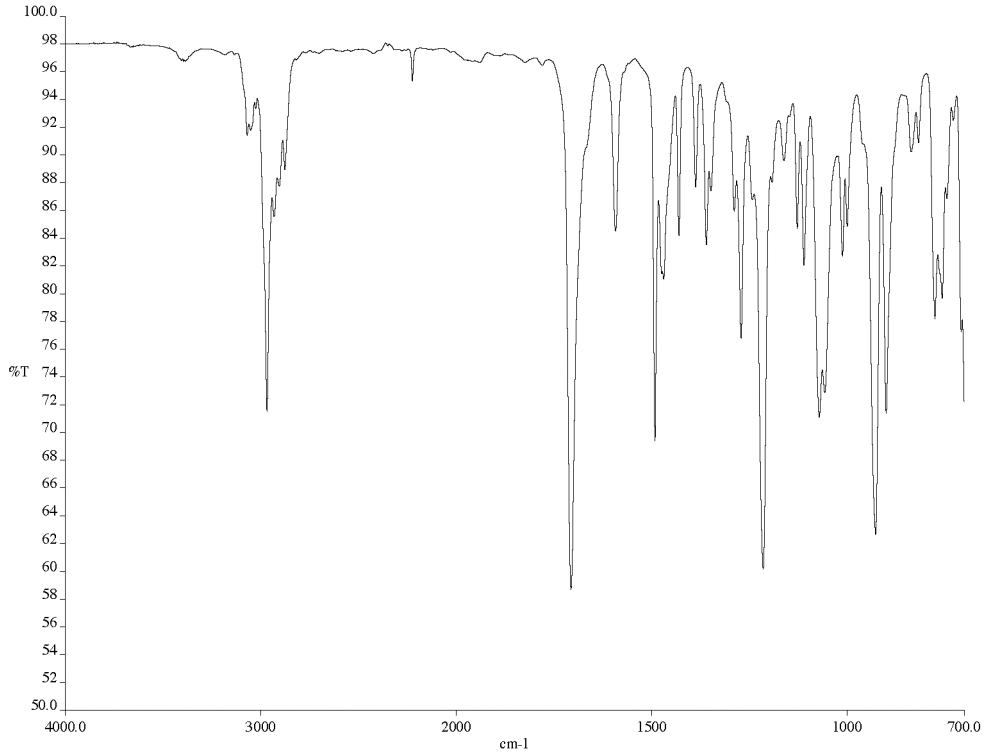


Figure 3.2 Infrared spectrum (thin film/NaCl) of iminoisobenzofuran **14c**.

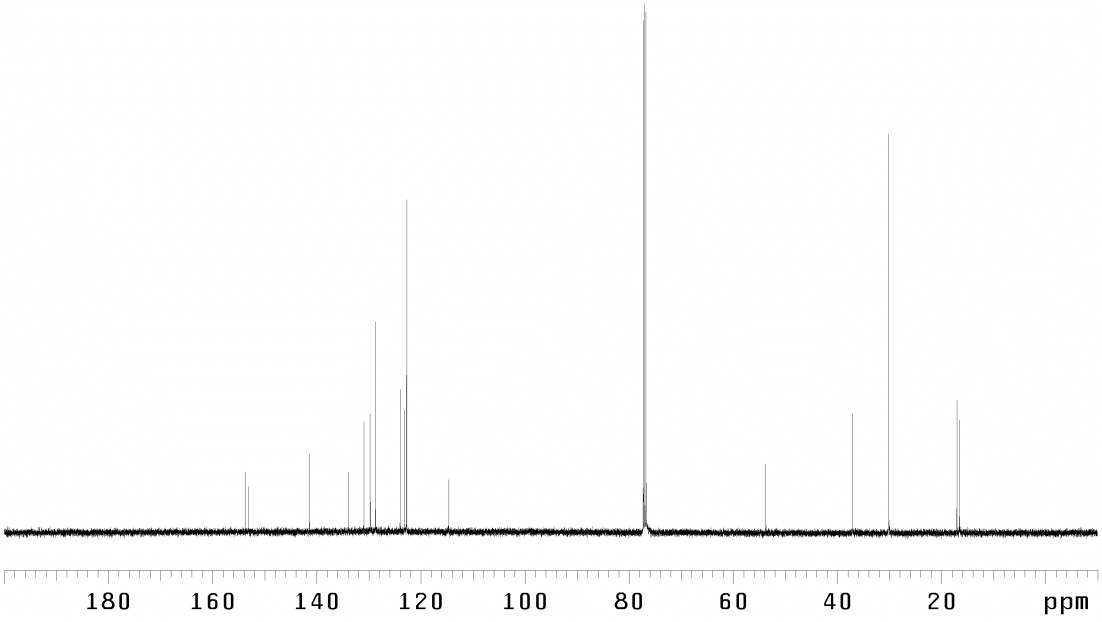


Figure 3.3 ^{13}C NMR (125 MHz, $CDCl_3$) of iminoisobenzofuran **14c**.

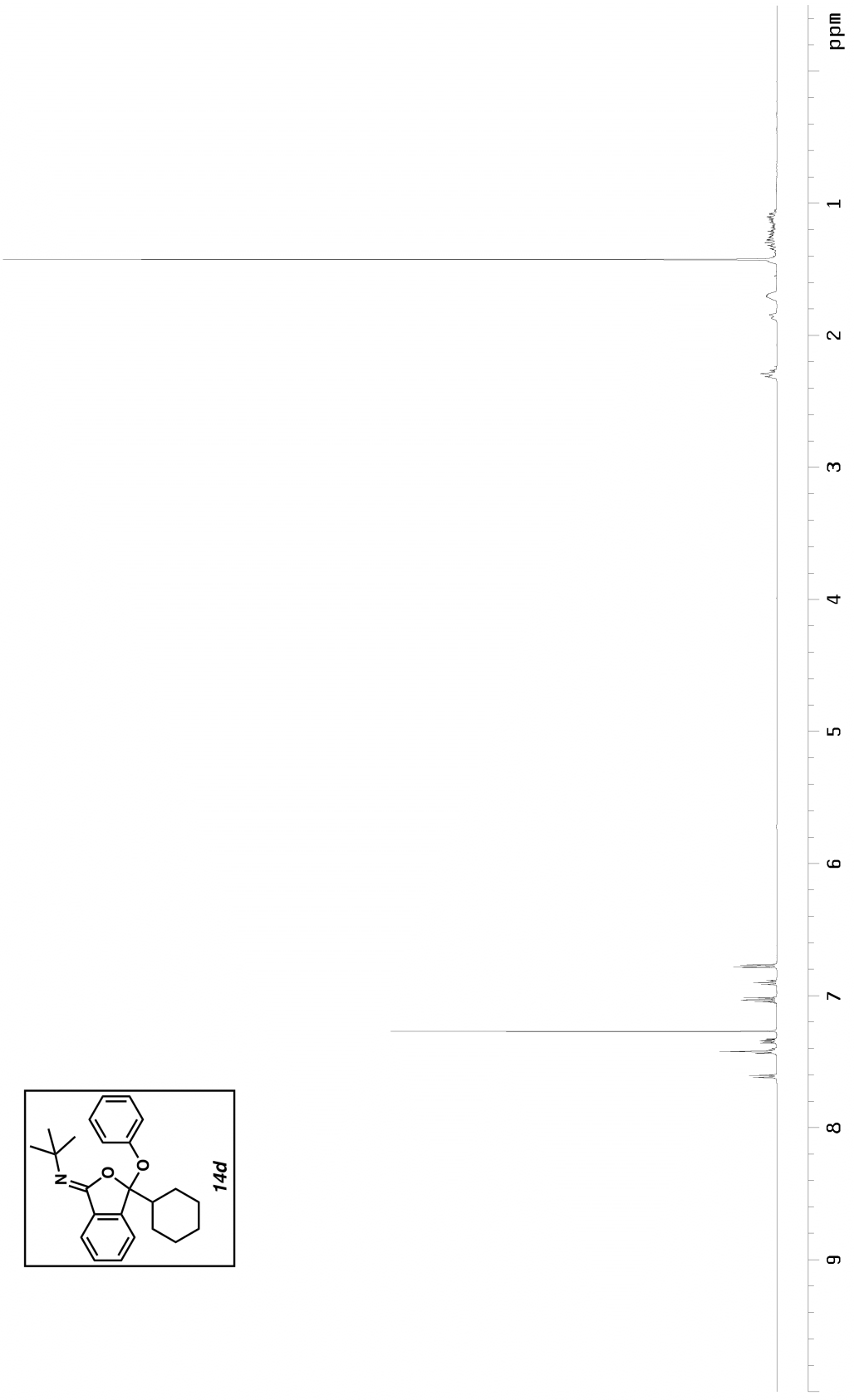


Figure 4.1 ^{1}H NMR (500 MHz, $CDCl_3$) of iminoisobenzofuran **14d**.

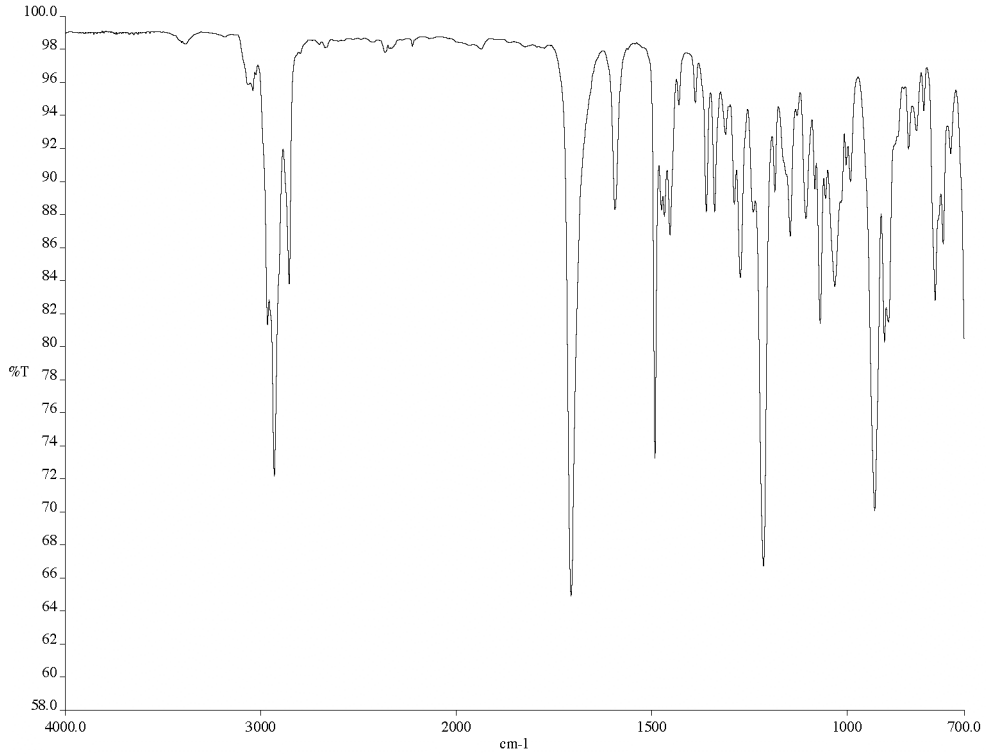


Figure 4.2 Infrared spectrum (thin film/NaCl) of iminoisobenzofuran **14d**.

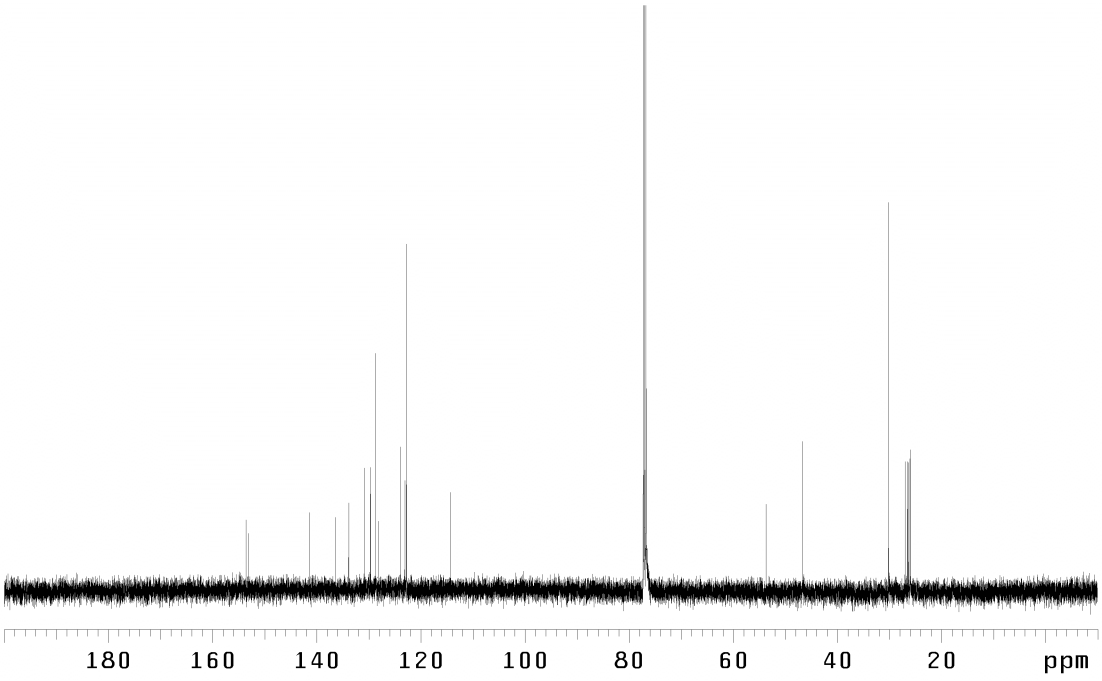


Figure 4.3 ^{13}C NMR (125 MHz, $CDCl_3$) of iminoisobenzofuran **14d**.

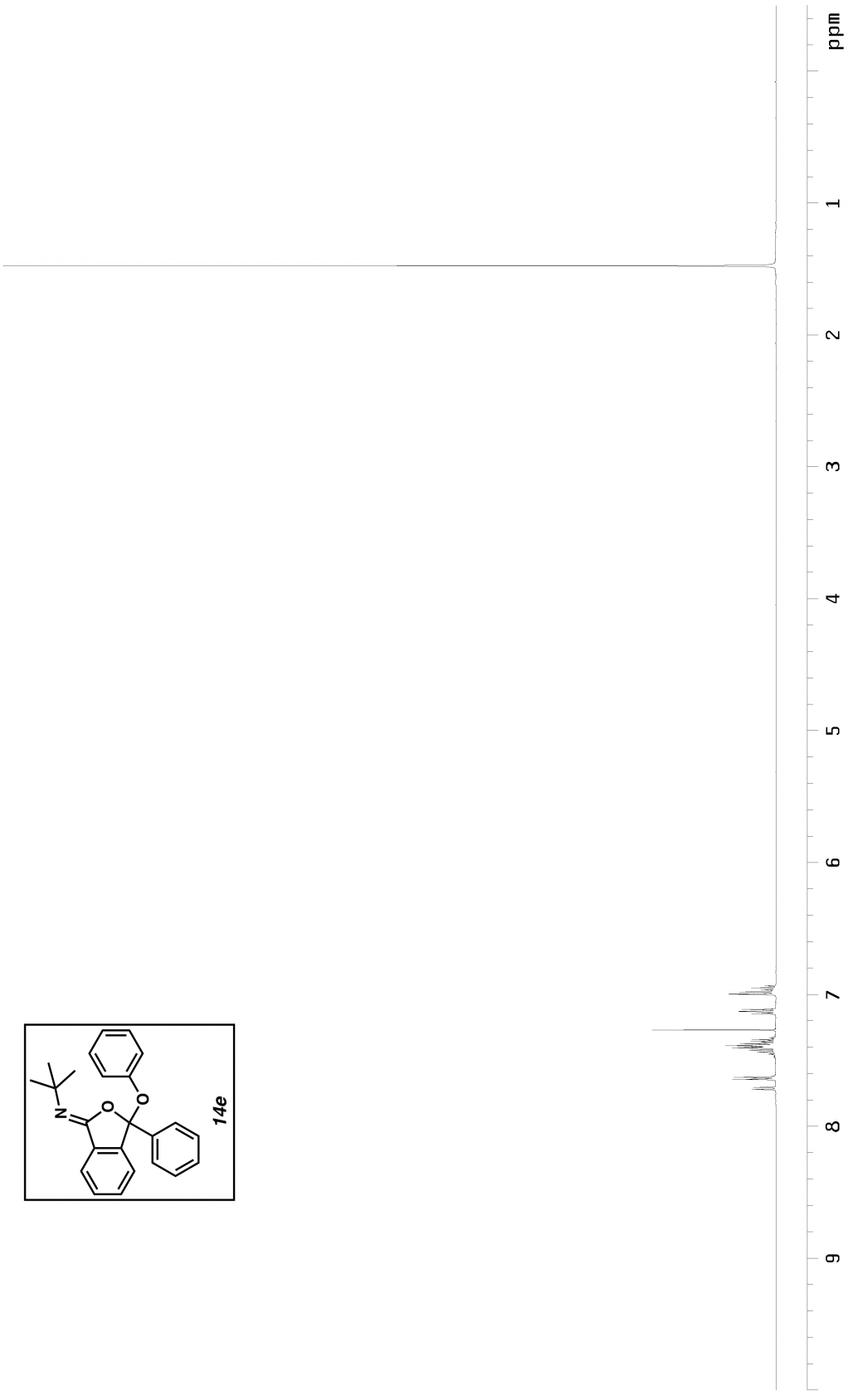


Figure 5.1 ^{1}H NMR (500 MHz, $CDCl_3$) of iminoisobenzofuran **14e**.

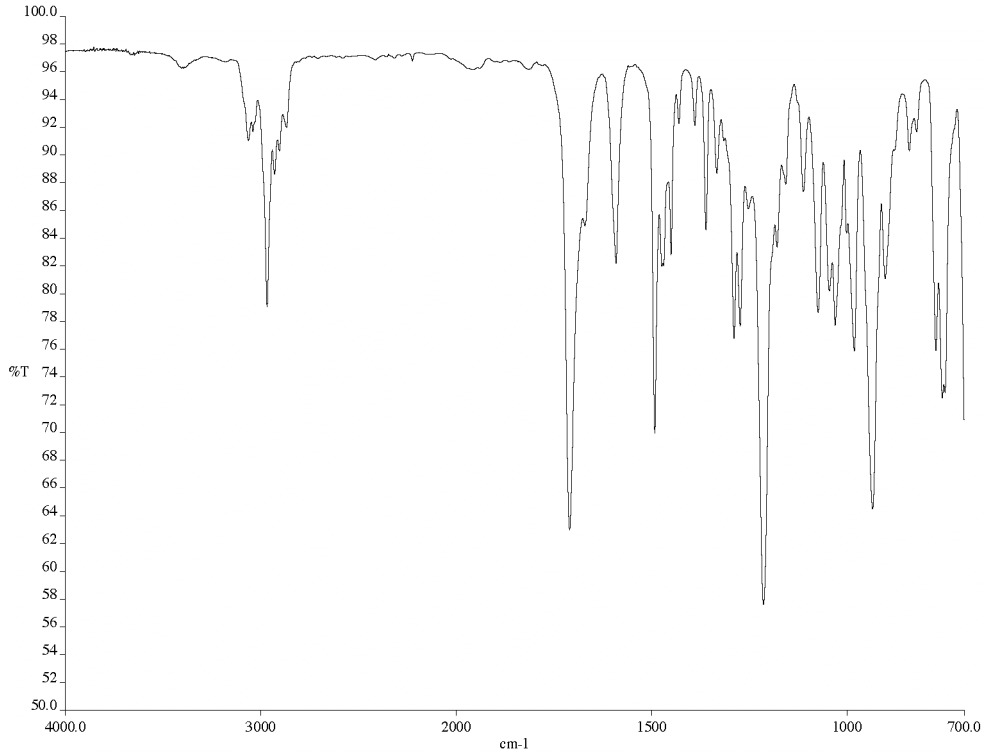


Figure 5.2 Infrared spectrum (thin film/NaCl) of iminoisobenzofuran **14e**.

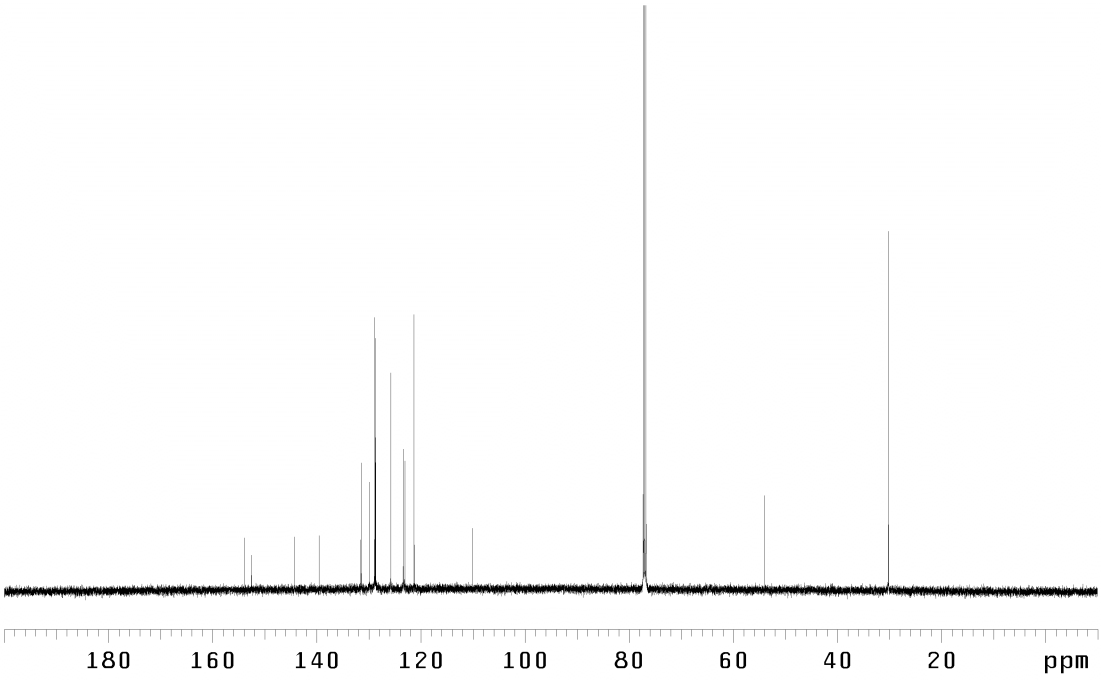


Figure 5.3 ^{13}C NMR (125 MHz, $CDCl_3$) of iminoisobenzofuran **14e**.

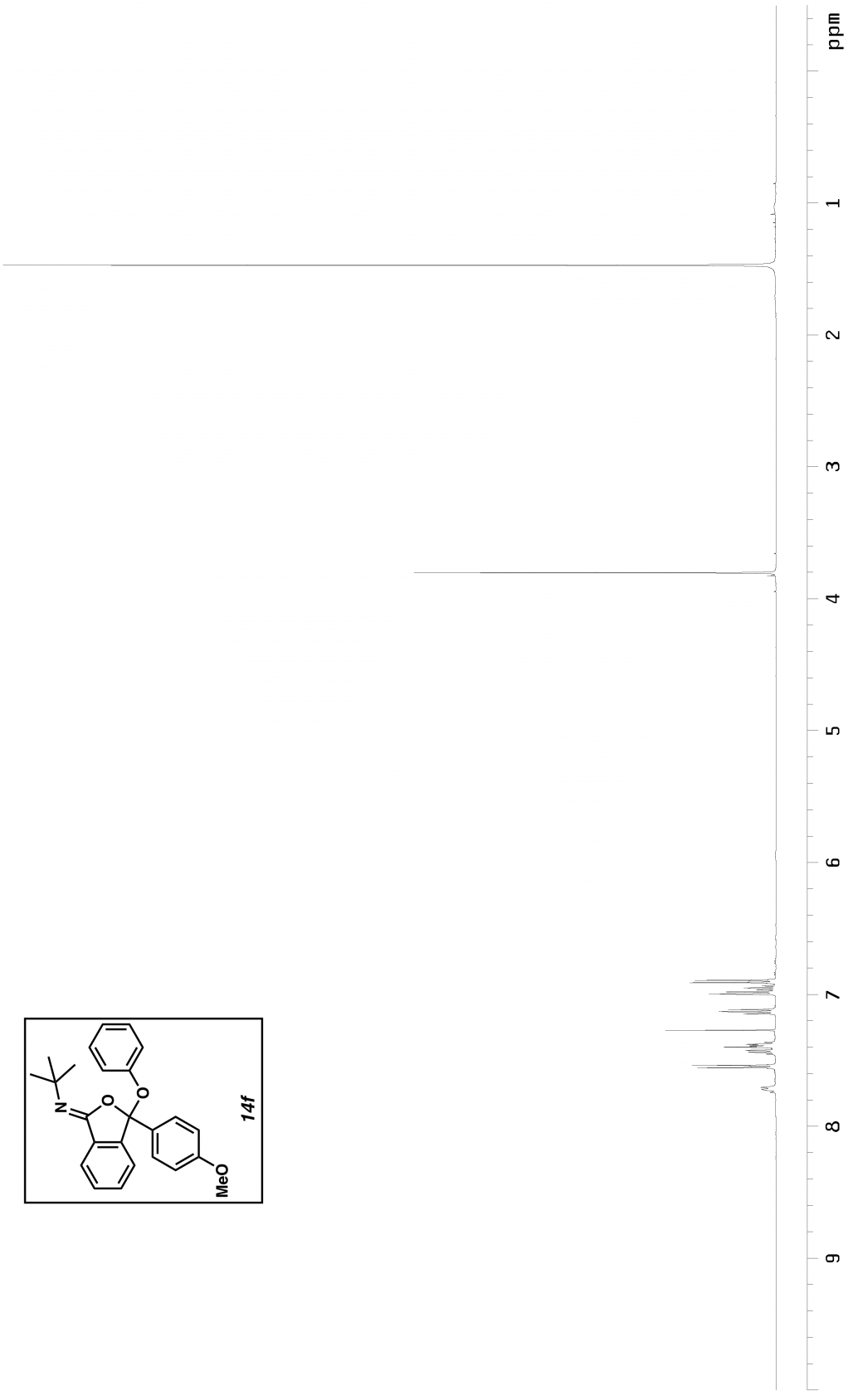


Figure 6.1 ^{1}H NMR (500 MHz, $CDCl_3$) of iminoisobenzofuran **14f**.

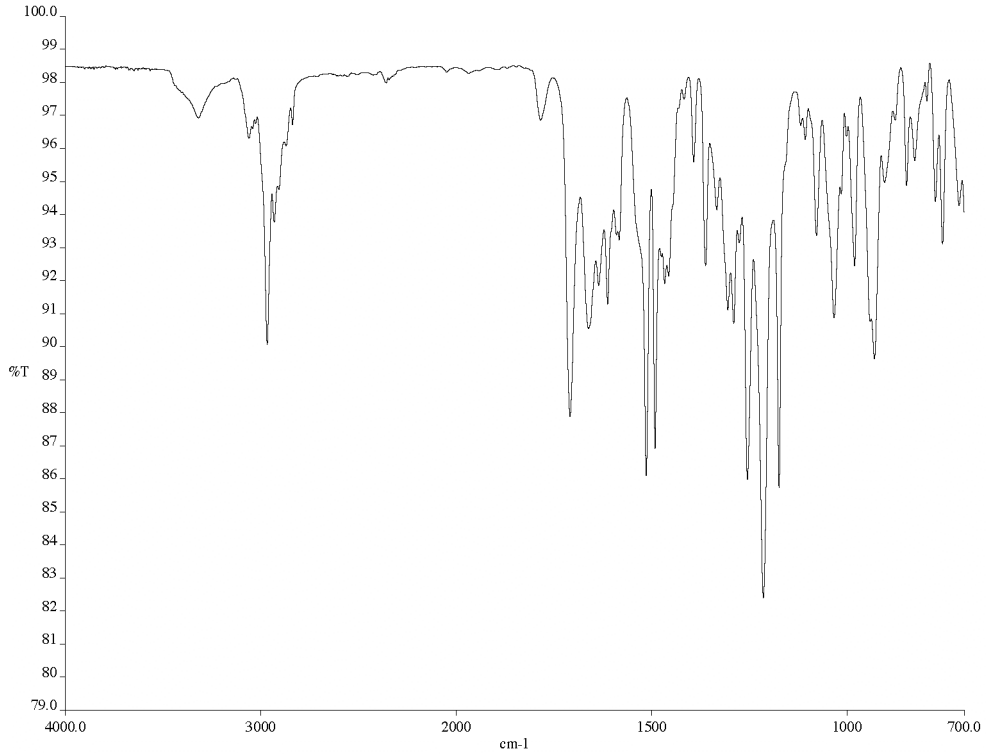


Figure 6.2 Infrared spectrum (thin film/NaCl) of iminoisobenzofuran **14f**.

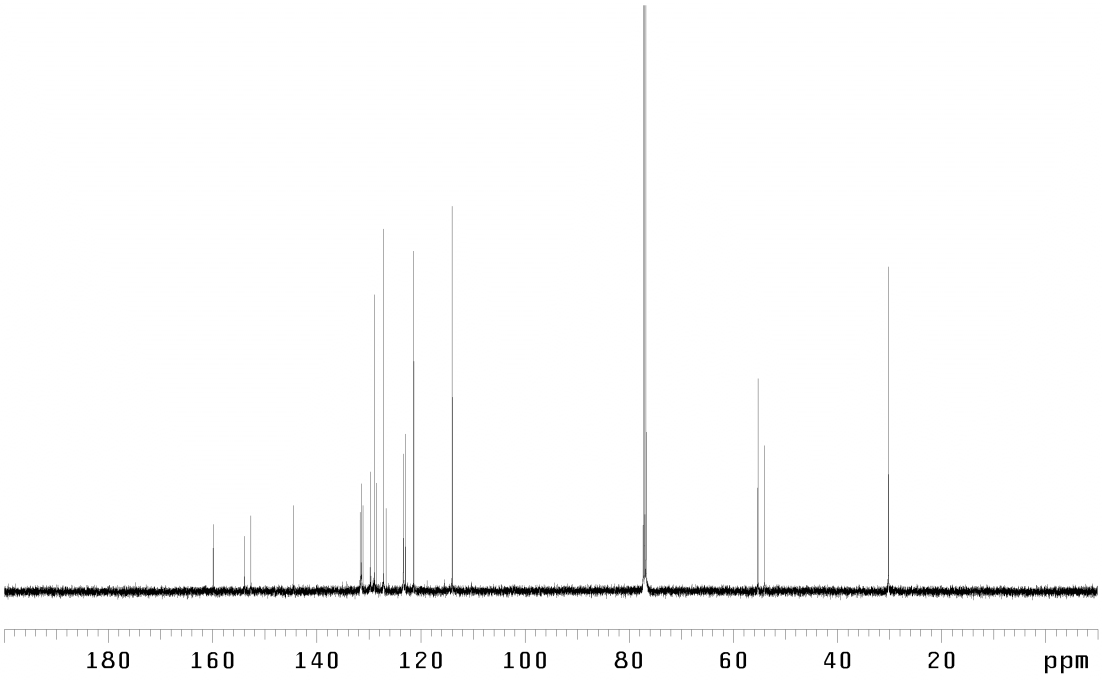


Figure 6.3 ^{13}C NMR (125 MHz, $CDCl_3$) of iminoisobenzofuran **14f**.

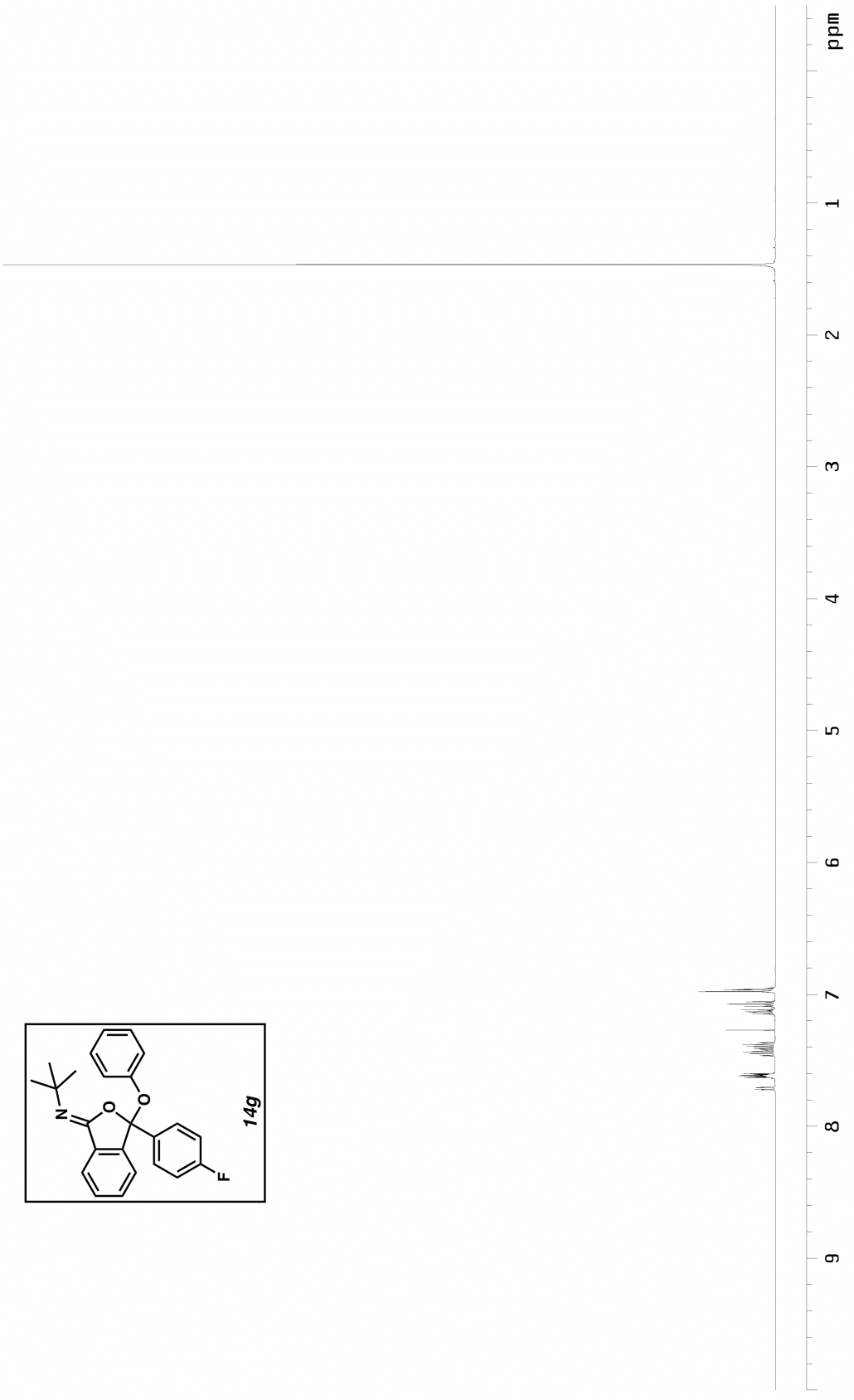


Figure 7.1 ^{1}H NMR (500 MHz, $CDCl_3$) of phenoxy iminoisobenzofuran **14g**.

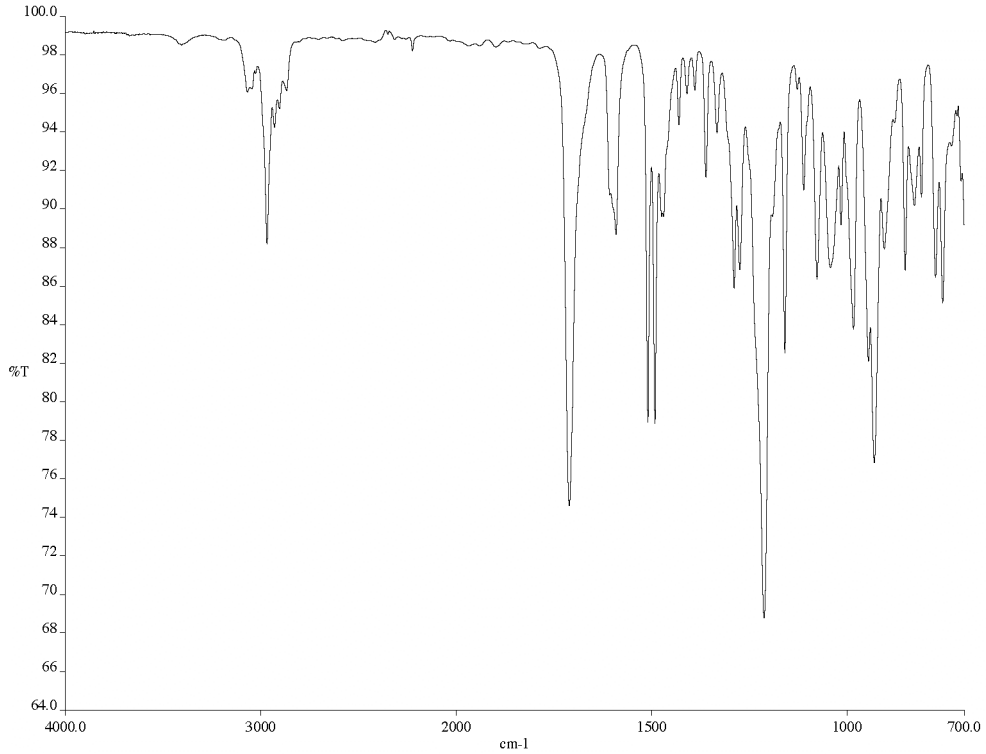


Figure 7.2 Infrared spectrum (thin film/NaCl) of iminoisobenzofuran **14g**.

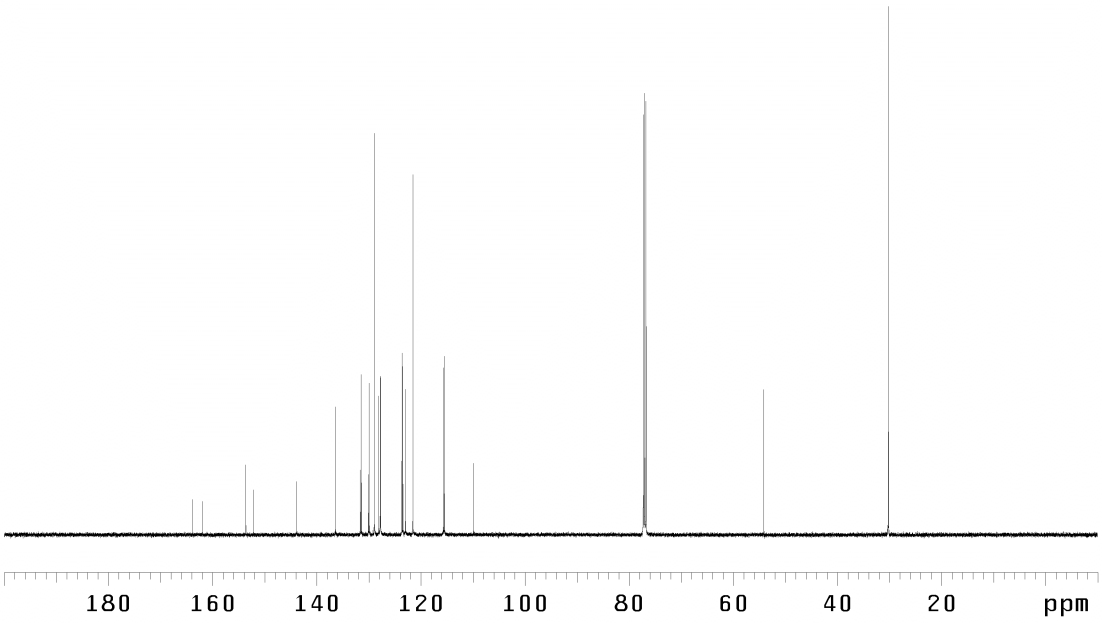


Figure 7.3 ^{13}C NMR (125 MHz, $CDCl_3$) of iminoisobenzofuran **14g**.

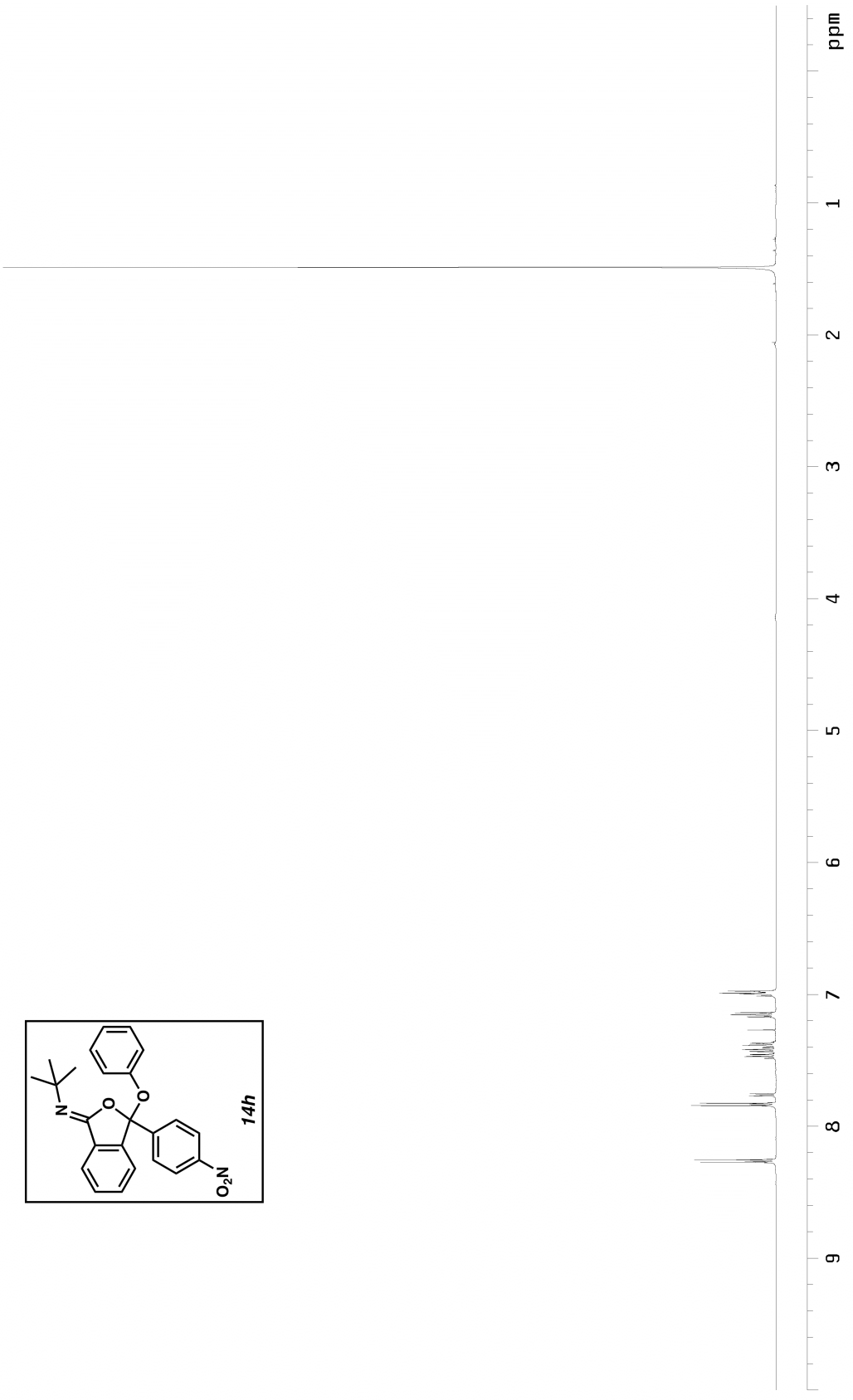


Figure 8.1 ^{1}H NMR (500 MHz, $CDCl_3$) of iminoisobenzofuran **14h**.

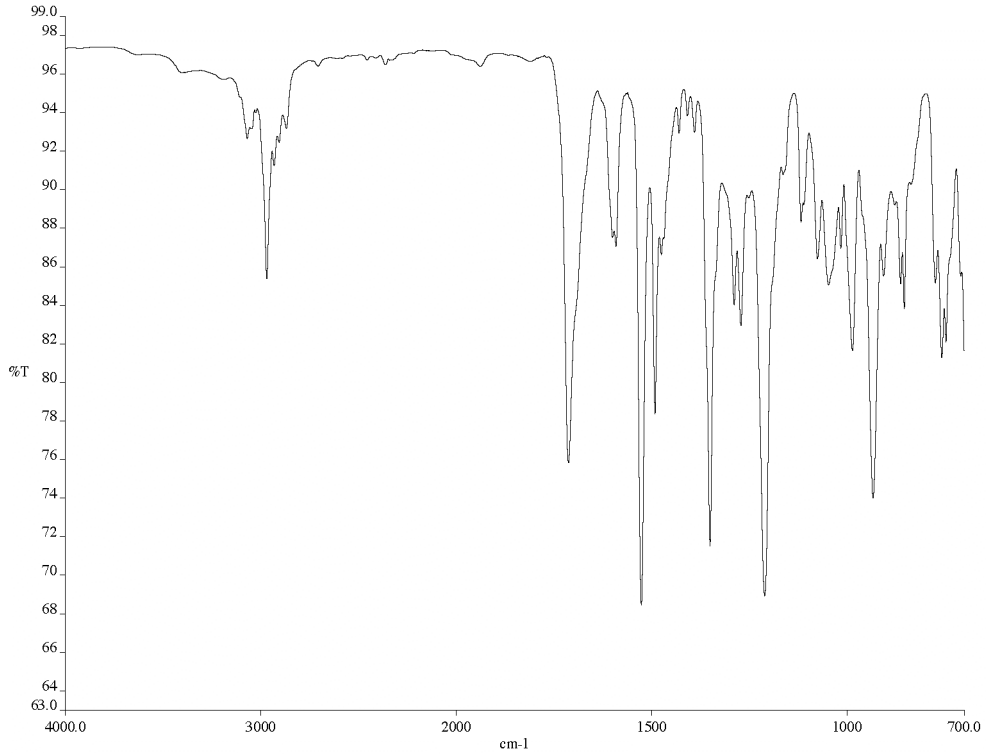


Figure 8.2 Infrared spectrum (thin film/NaCl) of iminoisobenzofuran **14h**.

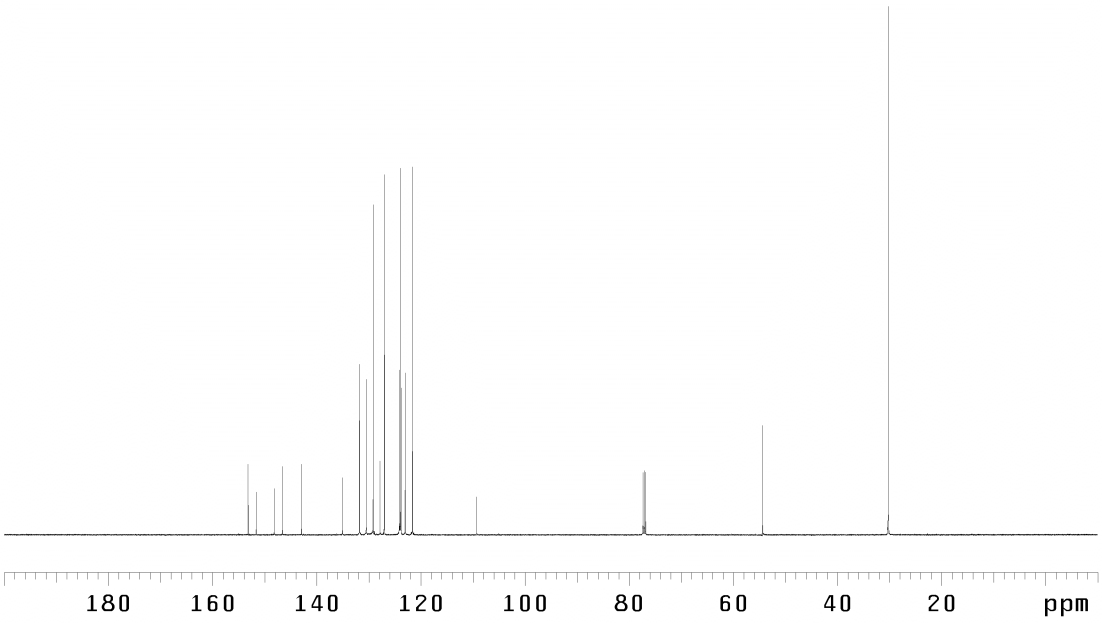


Figure 8.3 ^{13}C NMR (125 MHz, $CDCl_3$) of iminoisobenzofuran **14h**.

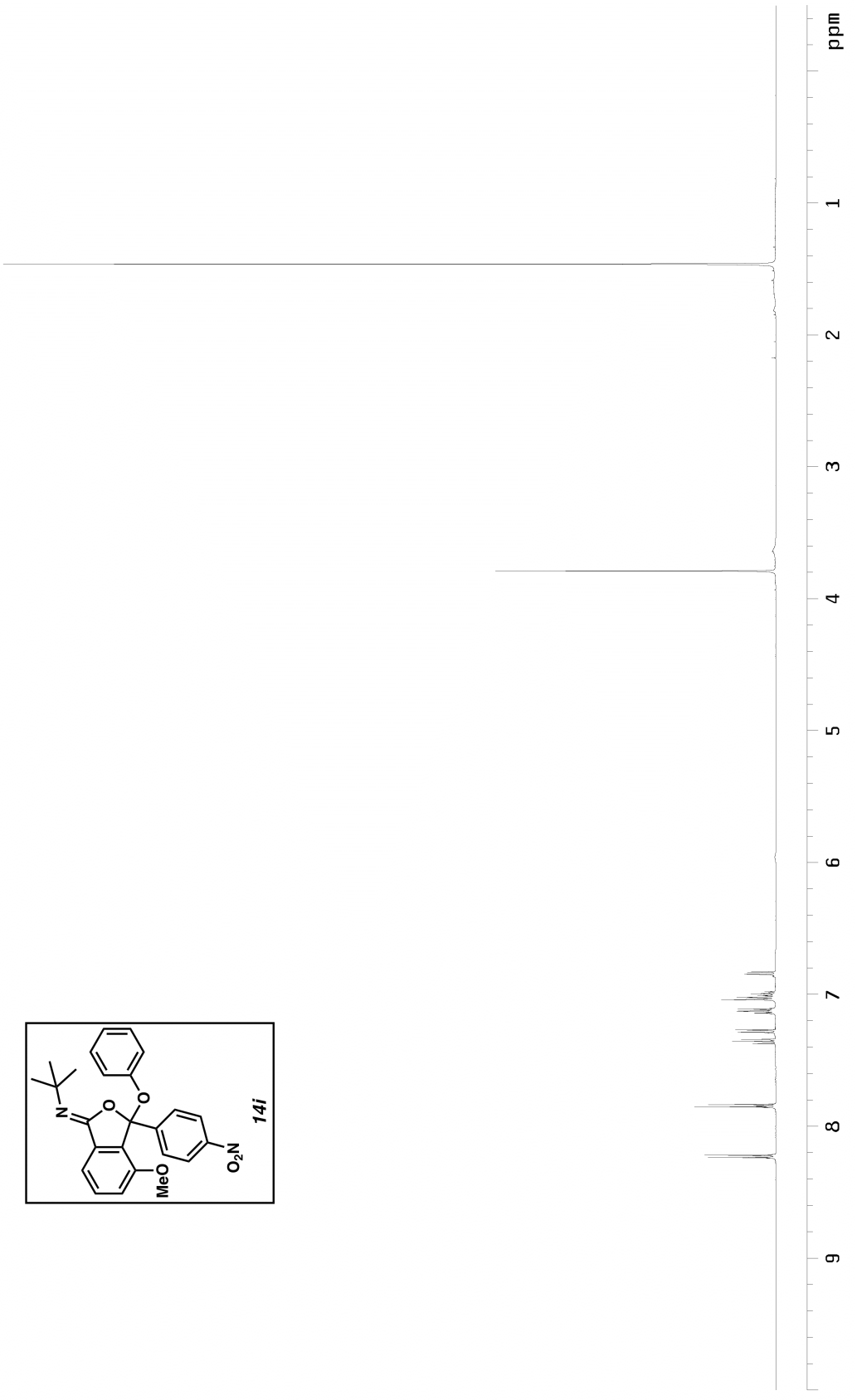


Figure 9.1 ^{1}H NMR (500 MHz, $CDCl_3$) of iminoisobenzofuran **14i**.

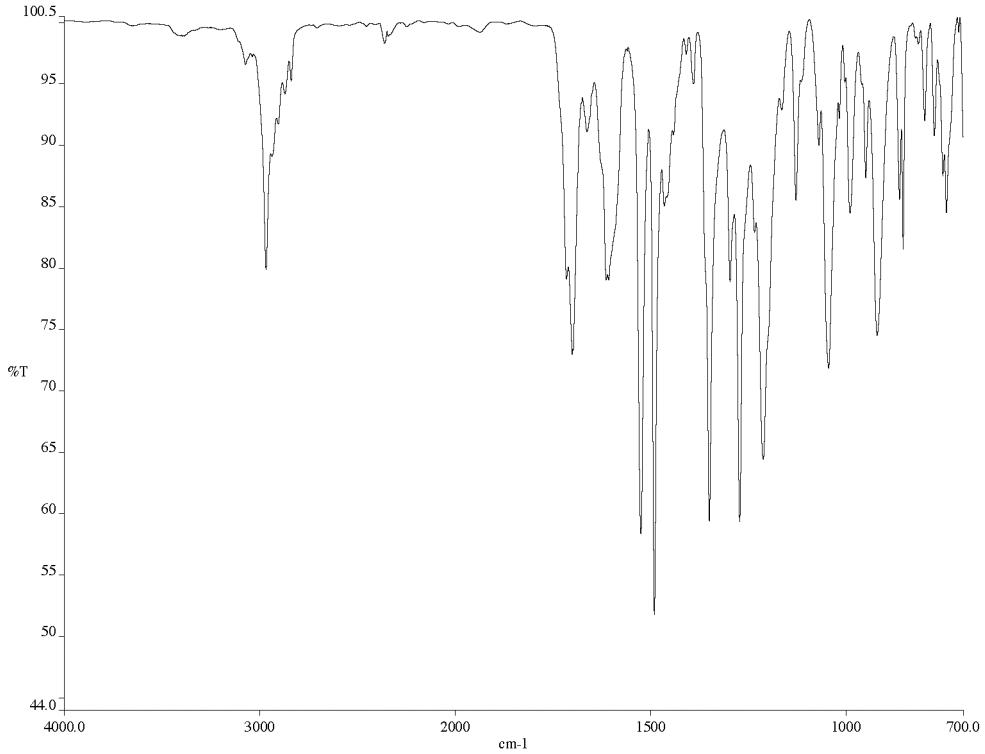


Figure 9.2 Infrared spectrum (thin film/NaCl) of iminoisobenzofuran **14i**.

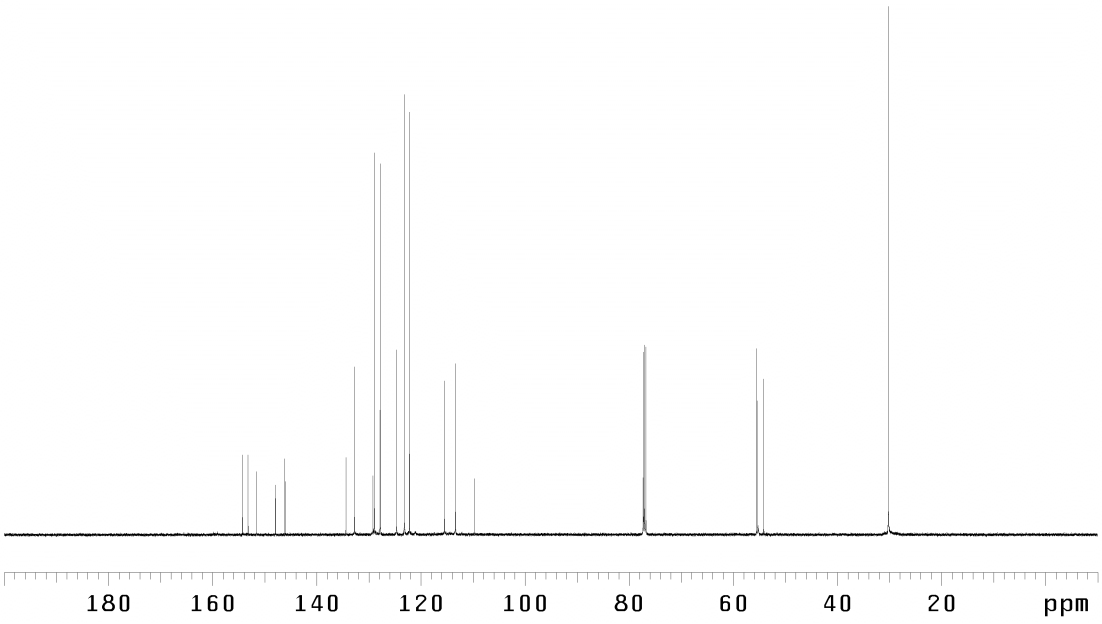


Figure 9.3 ^{13}C NMR (125 MHz, $CDCl_3$) of iminoisobenzofuran **14i**.

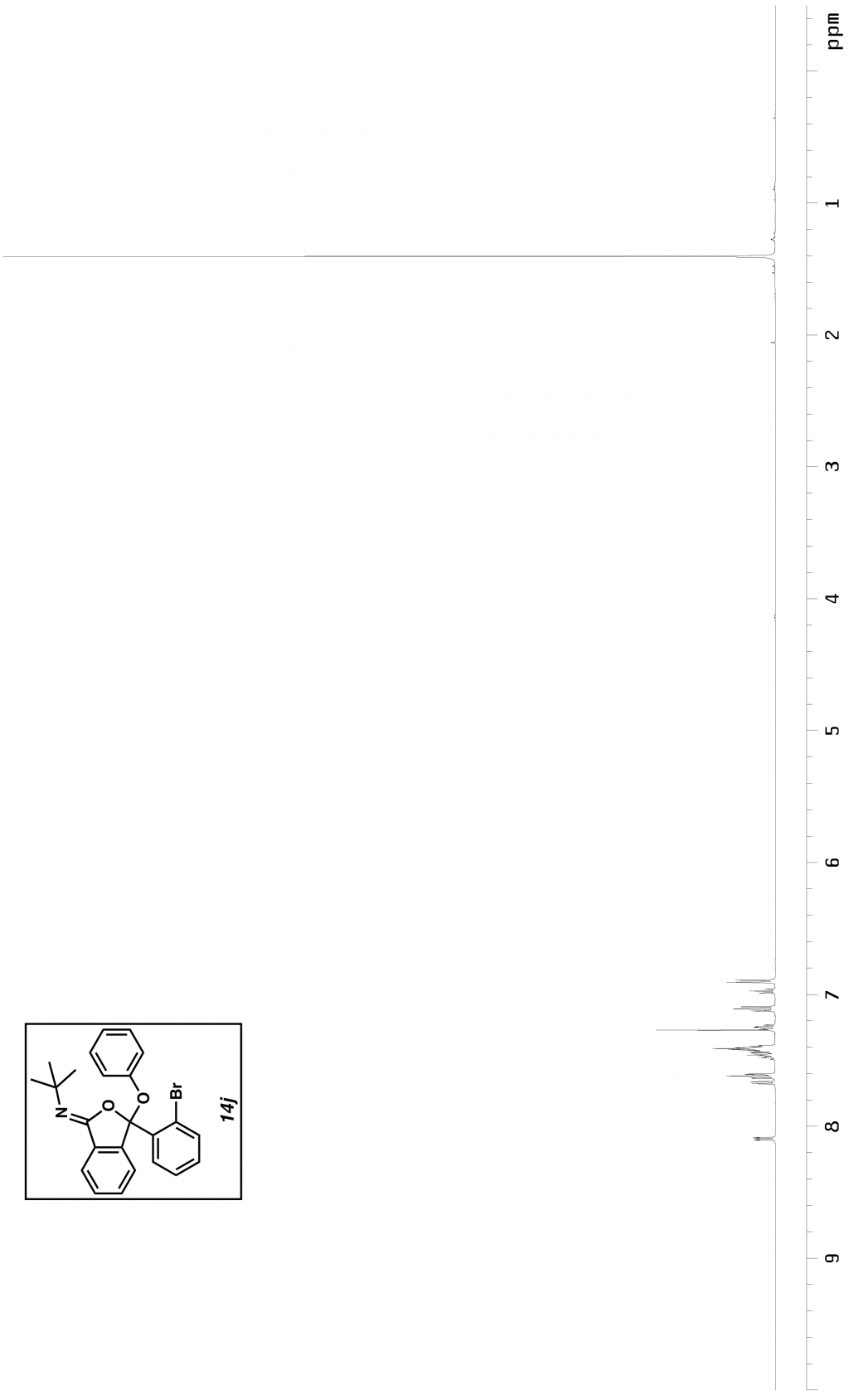


Figure 10.1 ^{1}H NMR (500 MHz, $CDCl_3$) of iminoisobenzofuran **14j**.

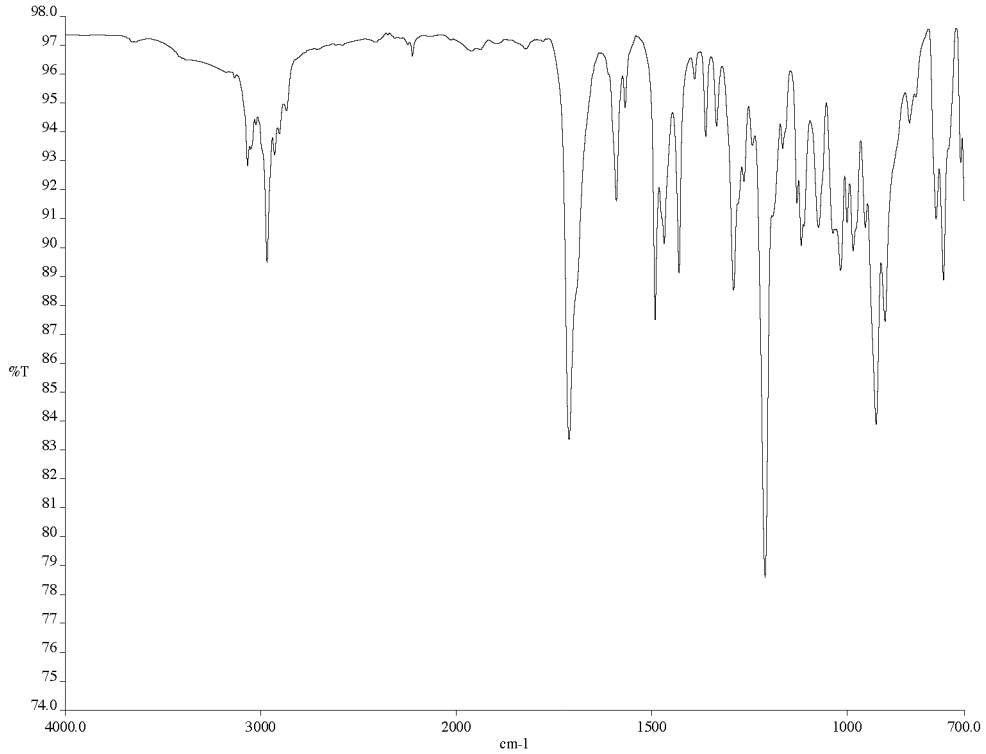


Figure 10.2 Infrared spectrum (thin film/NaCl) of iminoisobenzofuran **14j**.

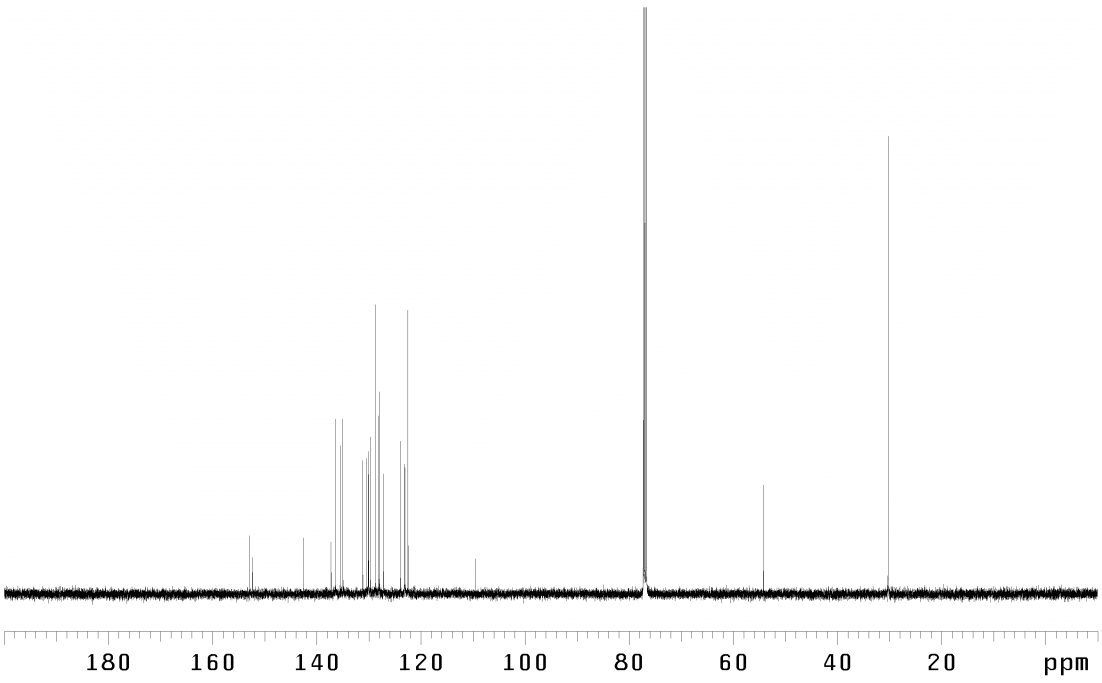


Figure 10.3 ^{13}C NMR (125 MHz, $CDCl_3$) of iminoisobenzofuran **14j**.

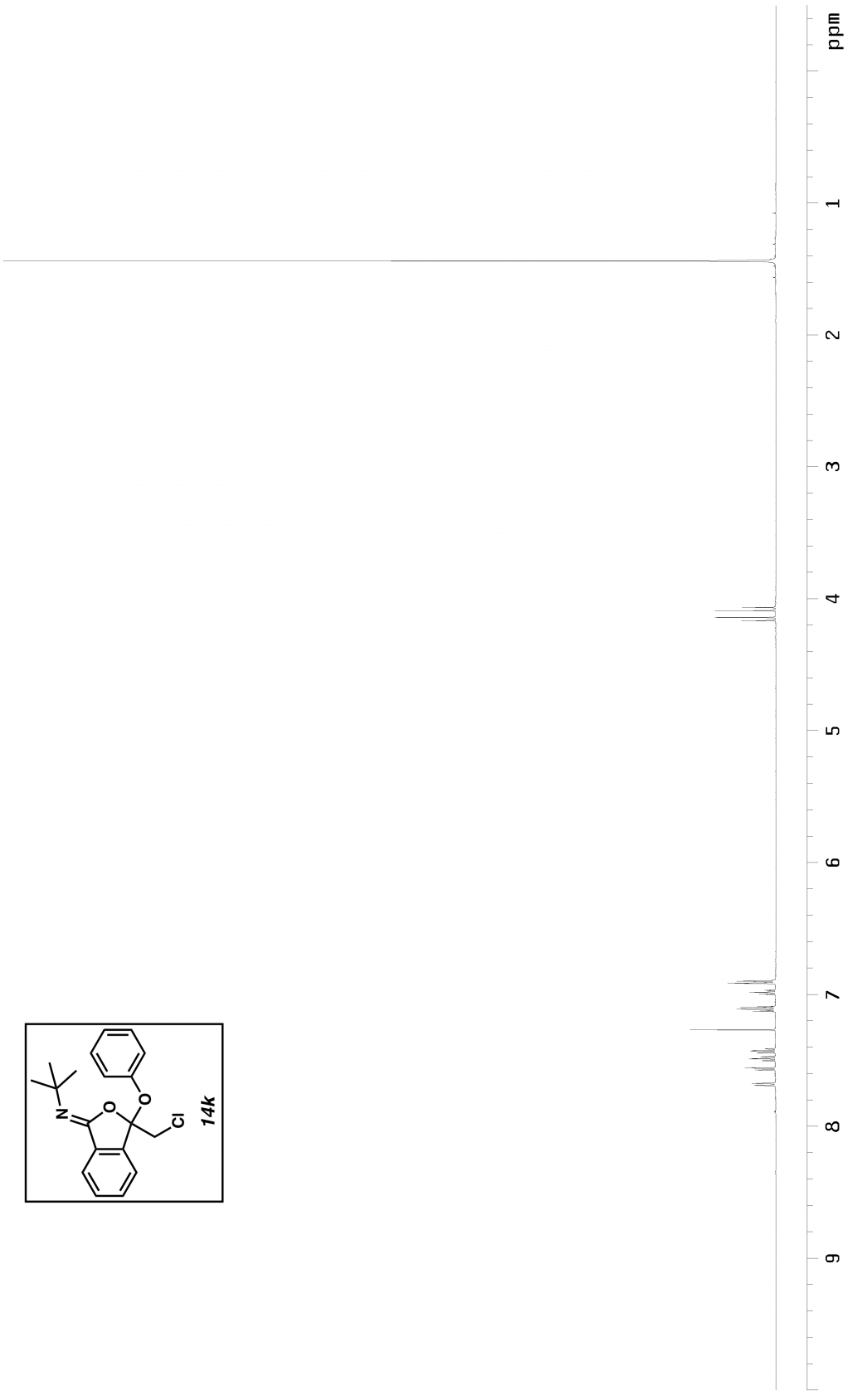


Figure 11.1 ^{1}H NMR (500 MHz, $CDCl_3$) of iminoisobenzofuran **14k**.

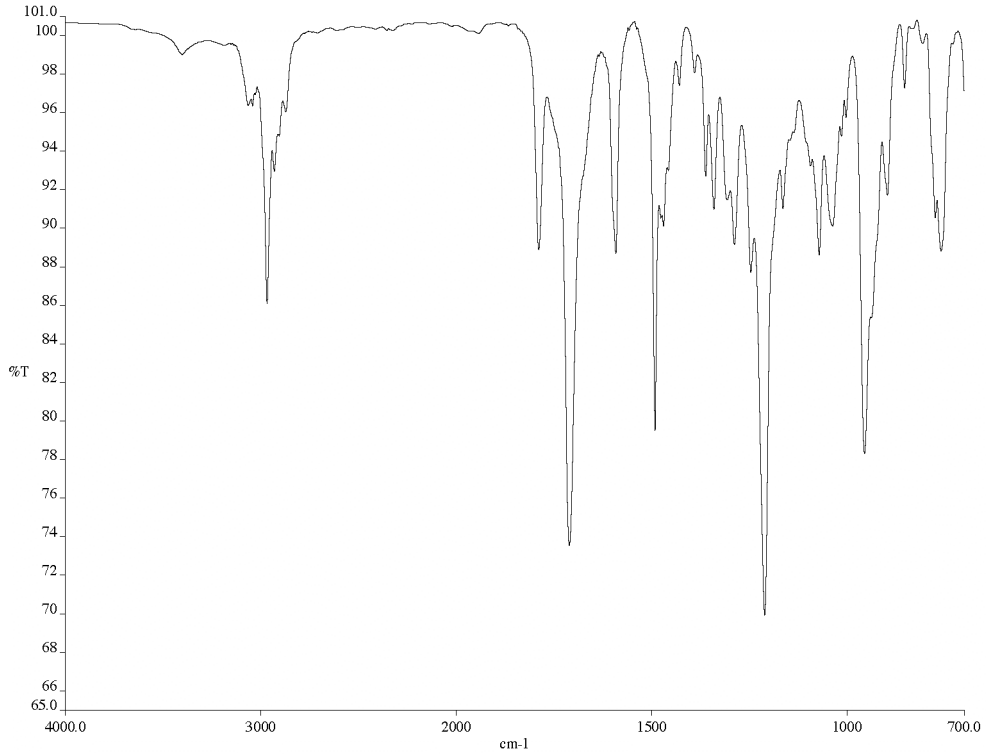


Figure 11.2 Infrared spectrum (thin film/NaCl) of iminoisobenzofuran **14k**.

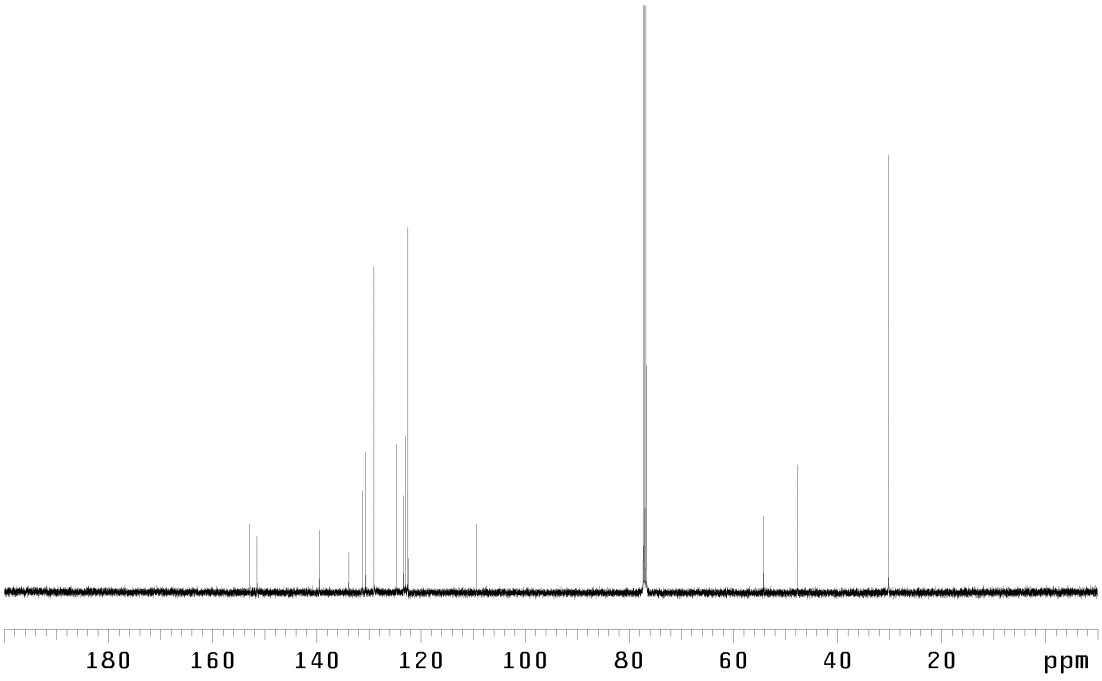


Figure 11.3 ^{13}C NMR (125 MHz, $CDCl_3$) of iminoisobenzofuran **14k**.

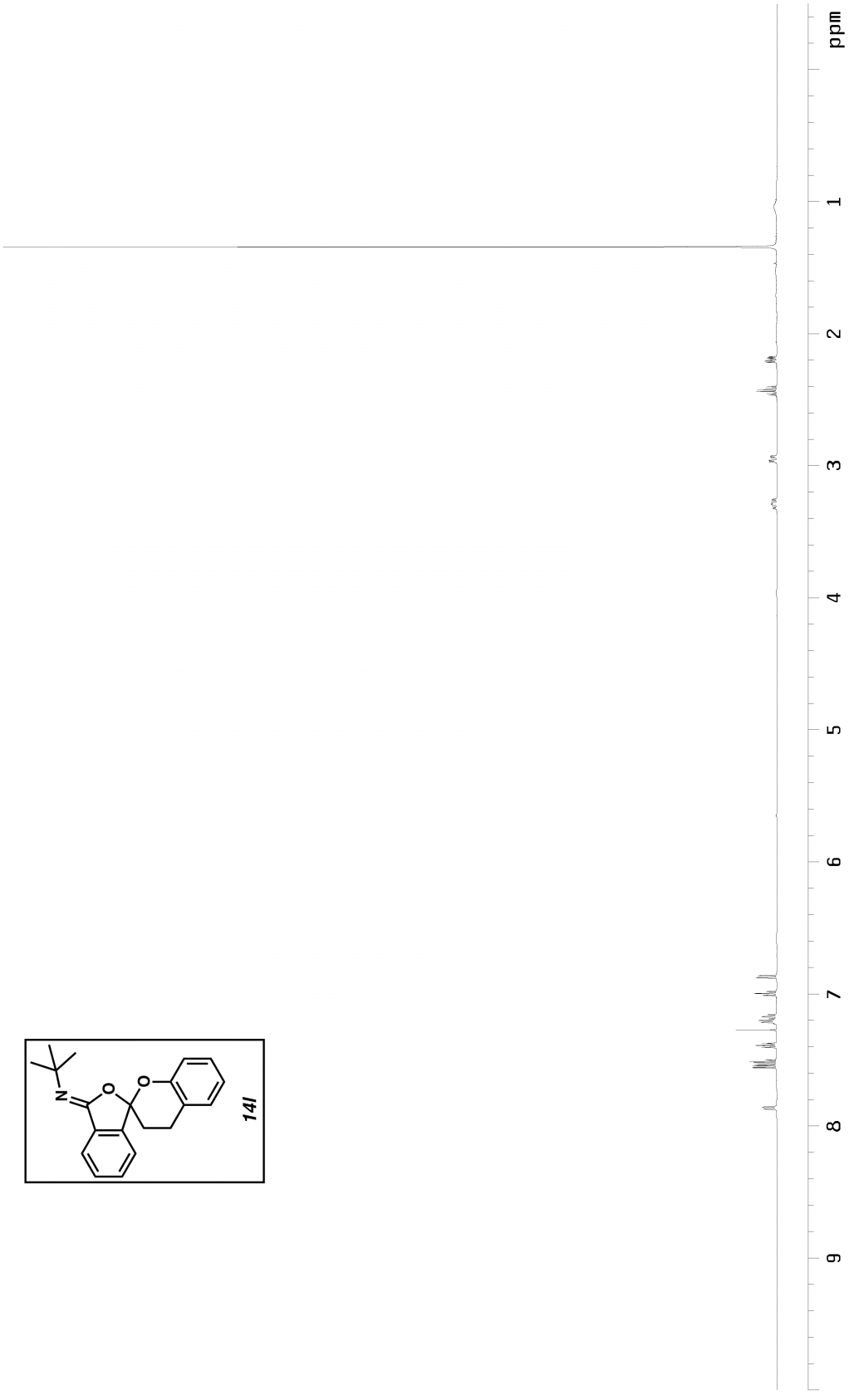


Figure 12.1 ^{1}H NMR (500 MHz, $CDCl_3$) of iminoisobenzofuran **14l**.

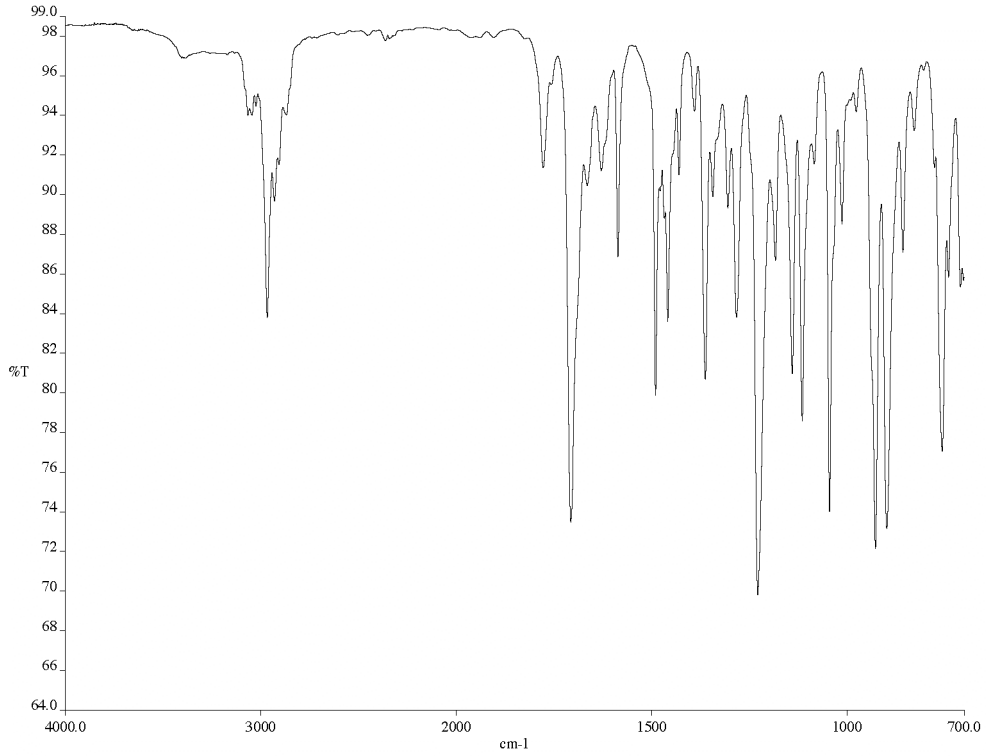


Figure 12.2 Infrared spectrum (thin film/NaCl) of iminoisobenzofuran **14l**.

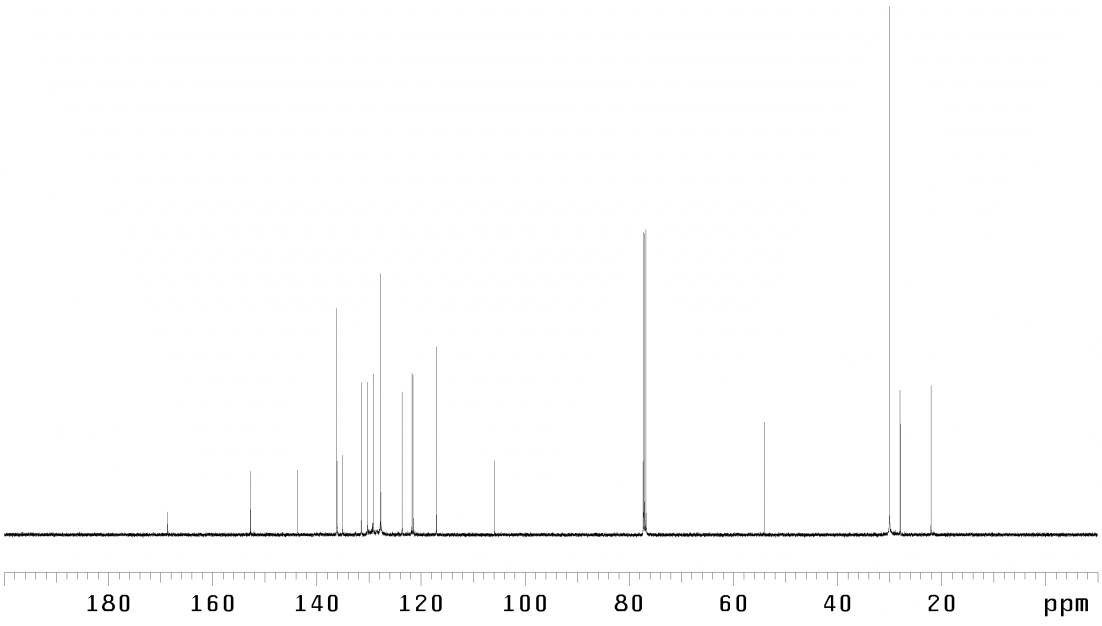


Figure 12.3 ^{13}C NMR (125 MHz, $CDCl_3$) of iminoisobenzofuran **14l**.

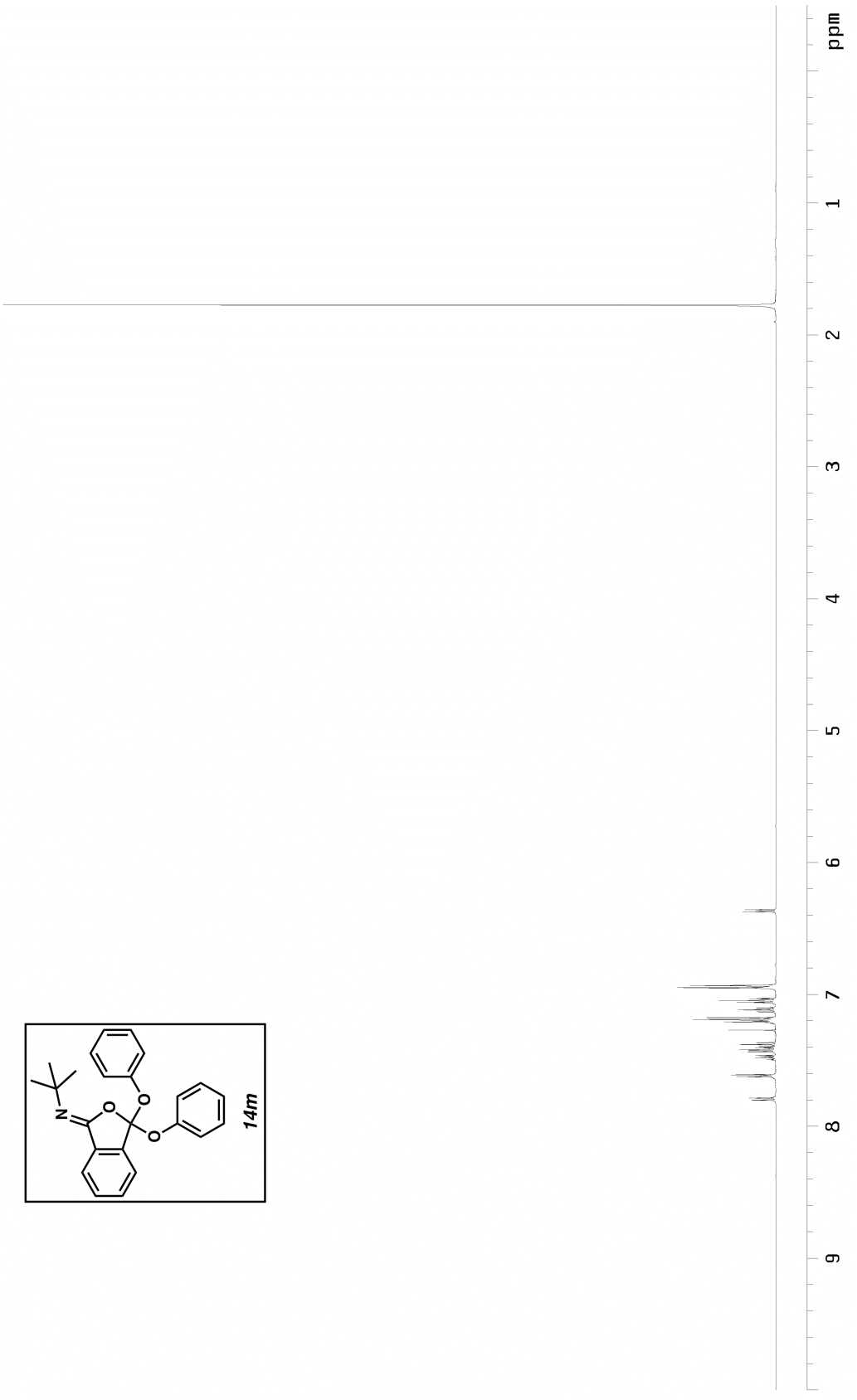


Figure 13.1 ^{1}H NMR (500 MHz, $CDCl_3$) of iminoisobenzofuran **14m**.

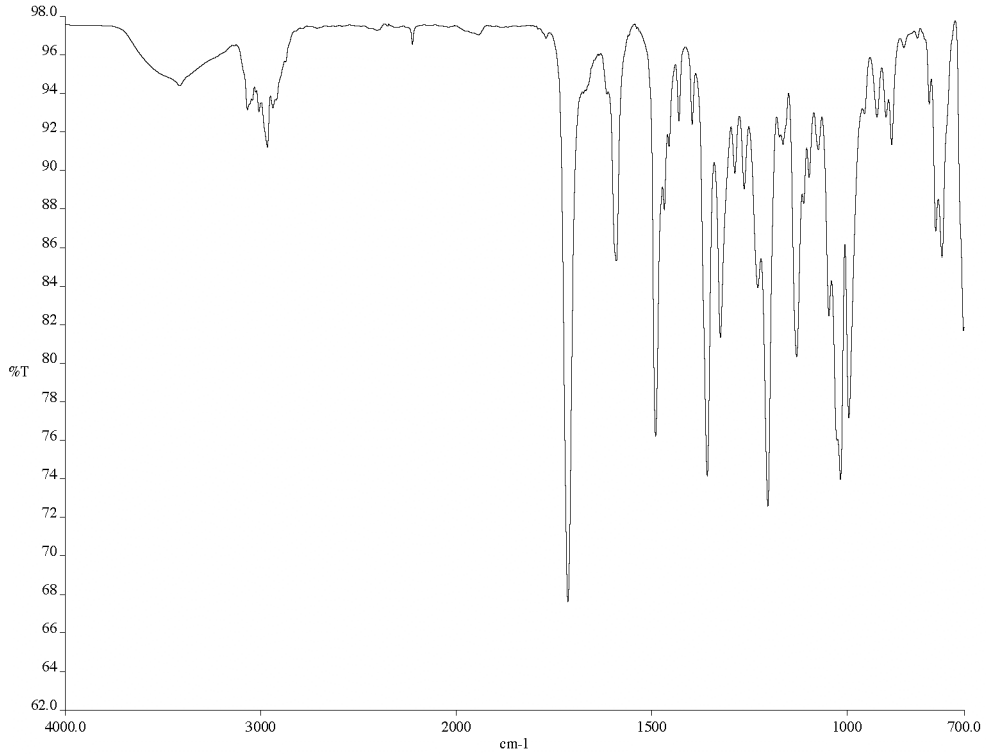


Figure 13.2 Infrared spectrum (thin film/NaCl) of iminoisobenzofuran **14m**.

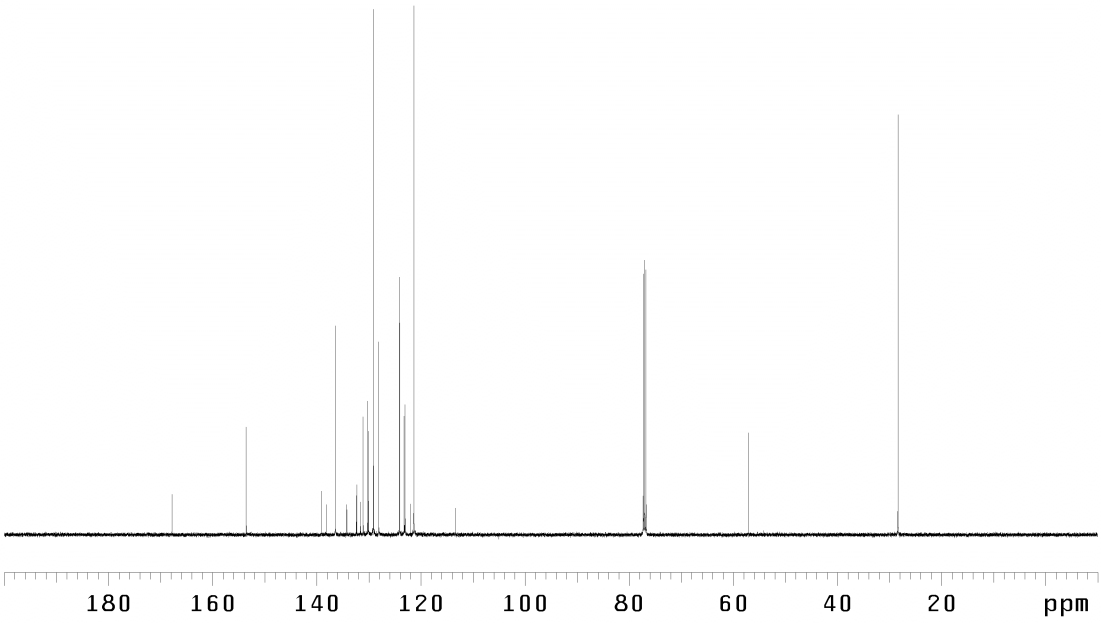


Figure 13.3 ^{13}C NMR (125 MHz, $CDCl_3$) of iminoisobenzofuran **14m**.

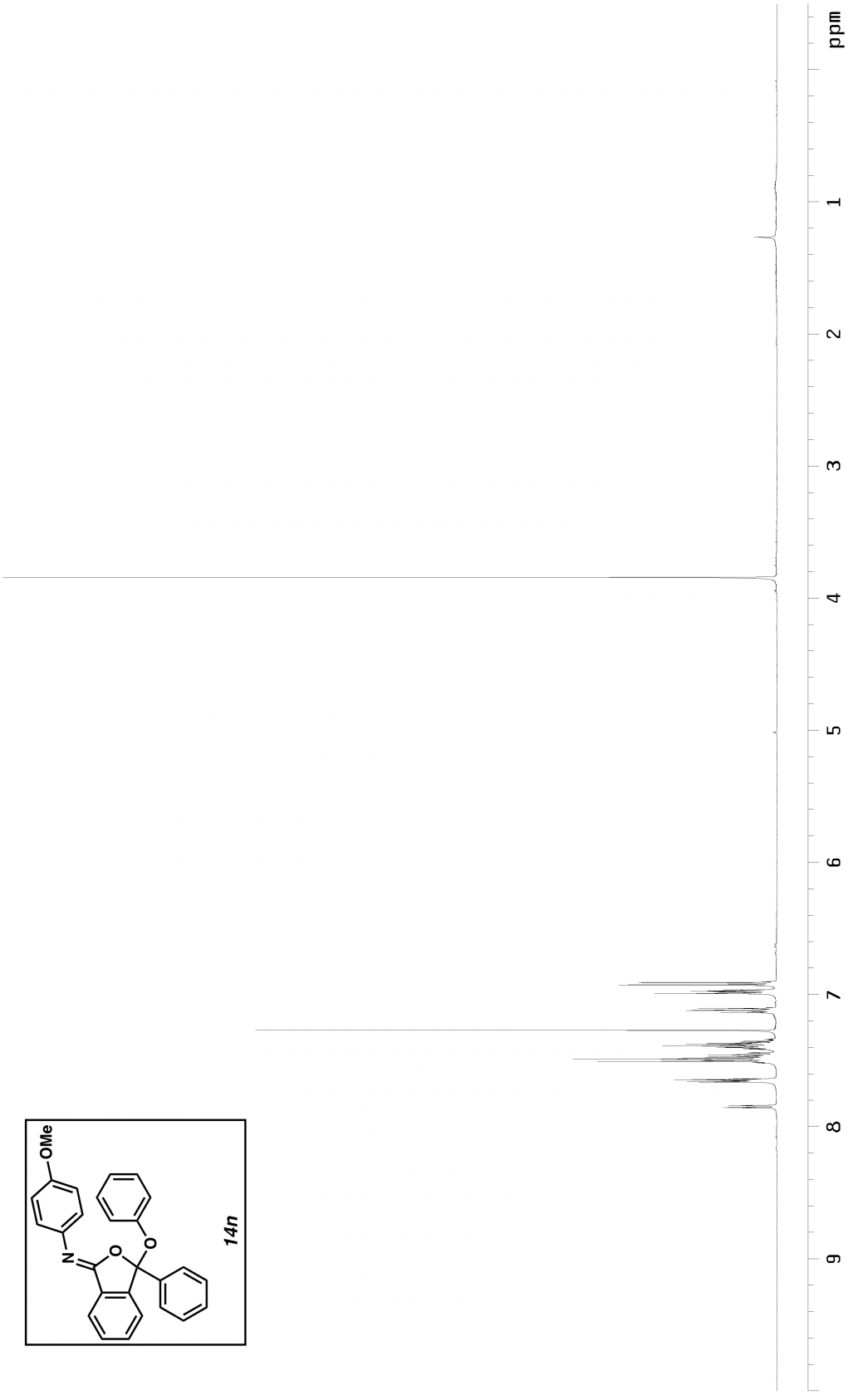


Figure 14.1 ^{1}H NMR (500 MHz, $CDCl_3$) of iminoisobenzofuran **14n**.

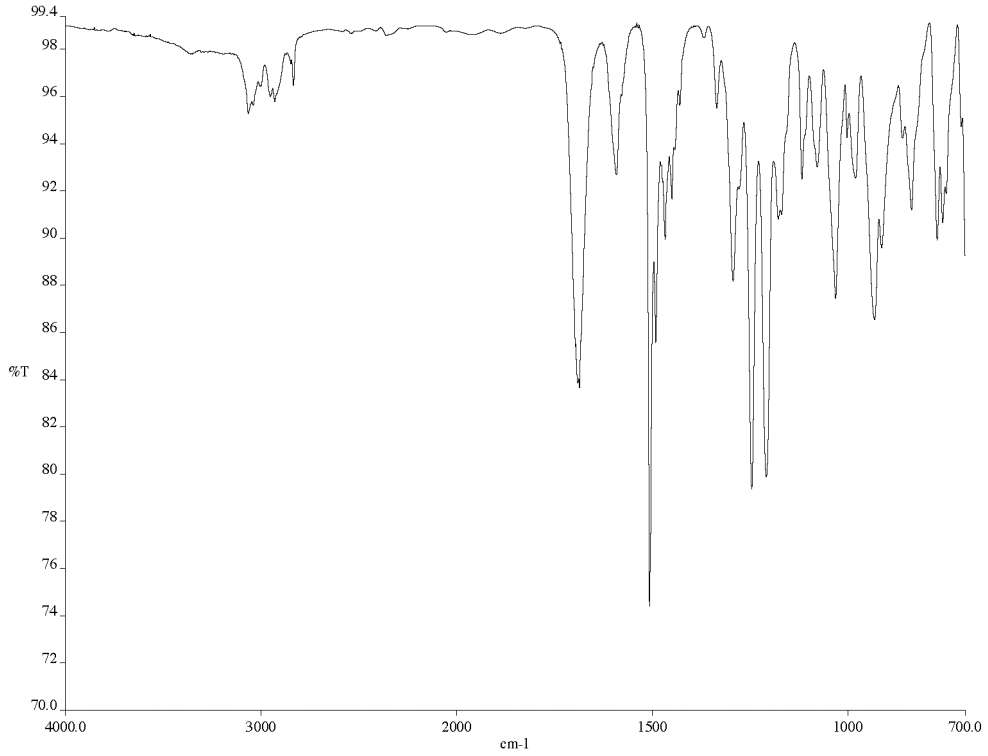


Figure 14.2 Infrared spectrum (thin film/NaCl) of iminoisobenzofuran **14n**.

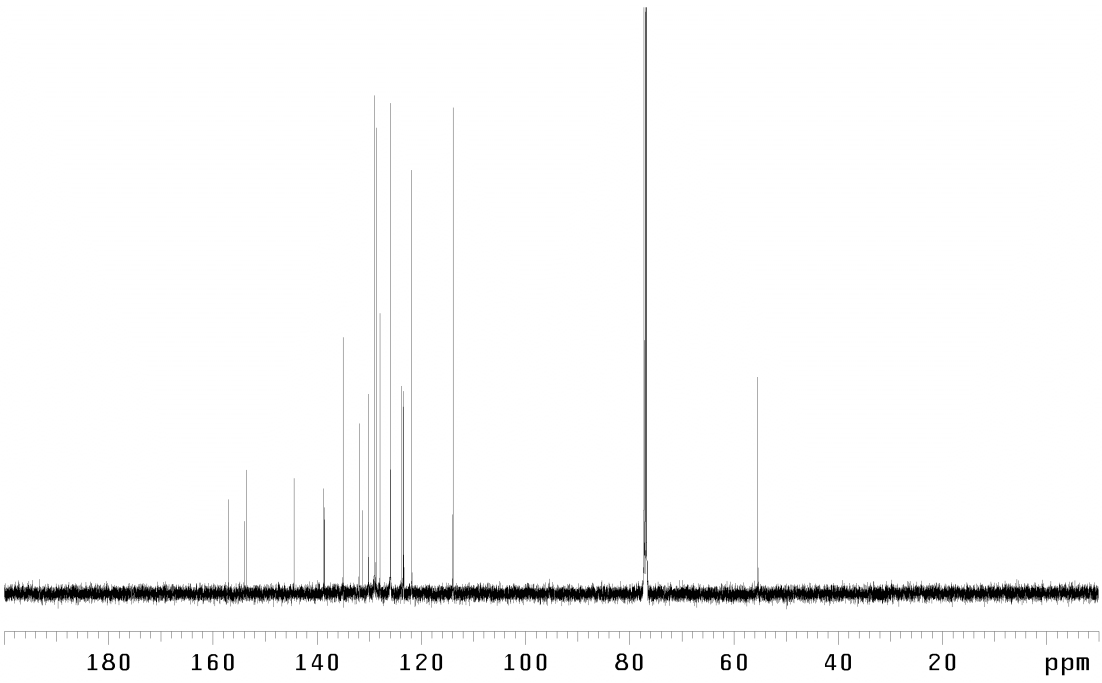


Figure 14.3 ^{13}C NMR (125 MHz, $CDCl_3$) of iminoisobenzofuran **14n**.

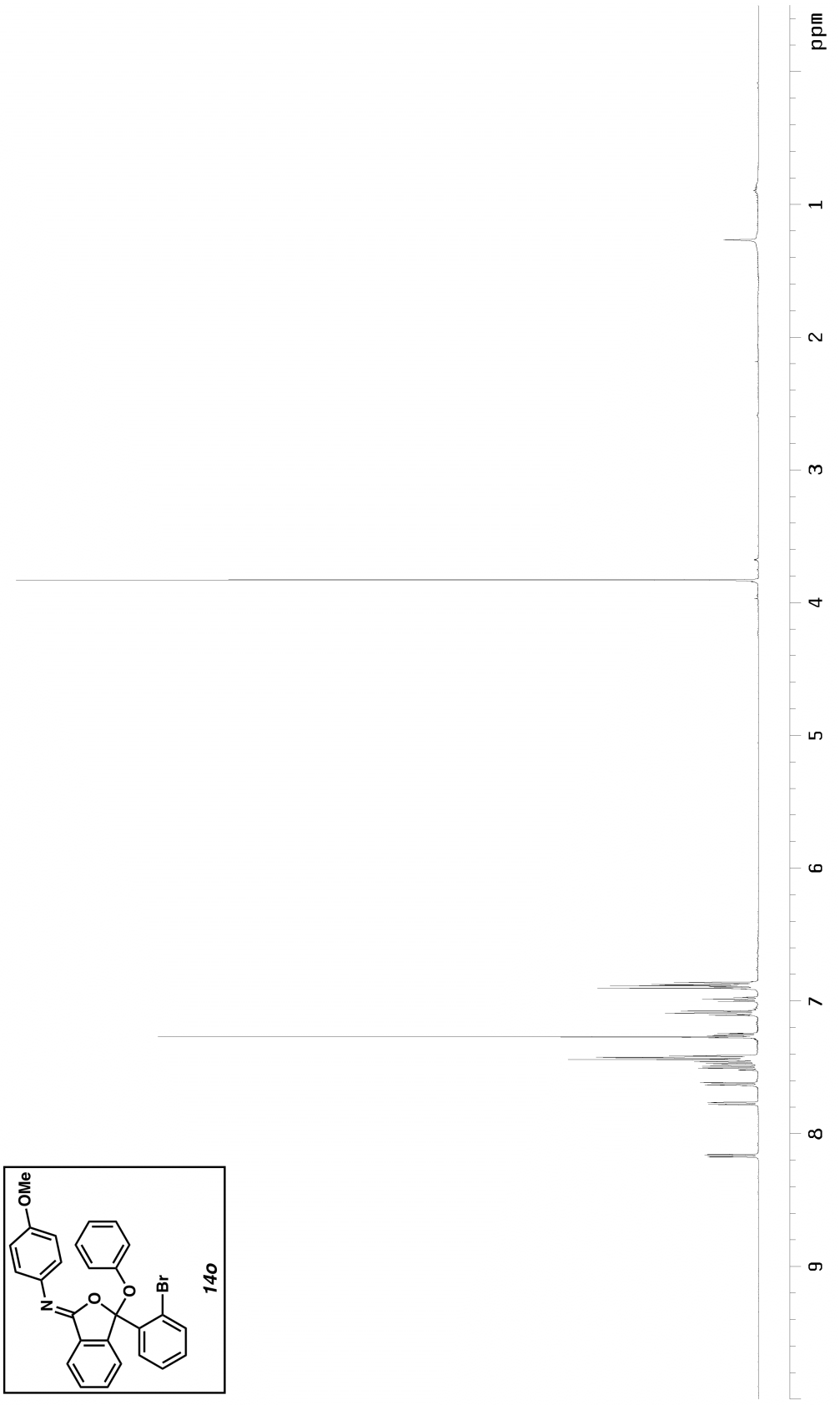


Figure 15.1 ^{1}H NMR (500 MHz, $CDCl_3$) of iminoisobenzofuran **14o**.

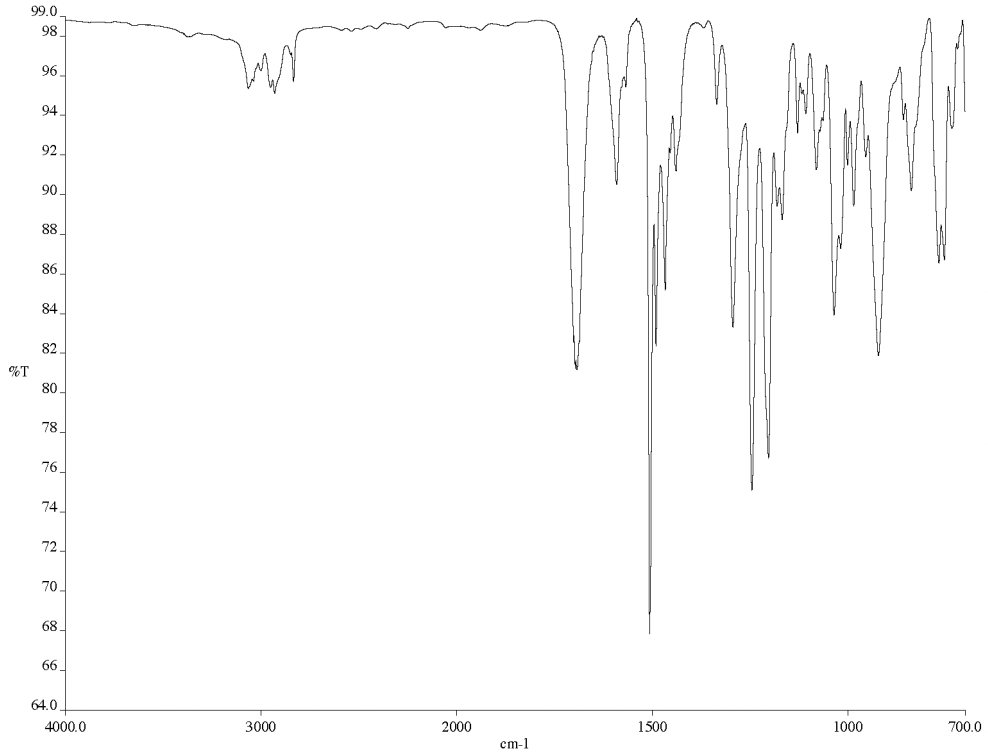


Figure 15.2 Infrared spectrum (thin film/NaCl) of iminoisobenzofuran **14o**.

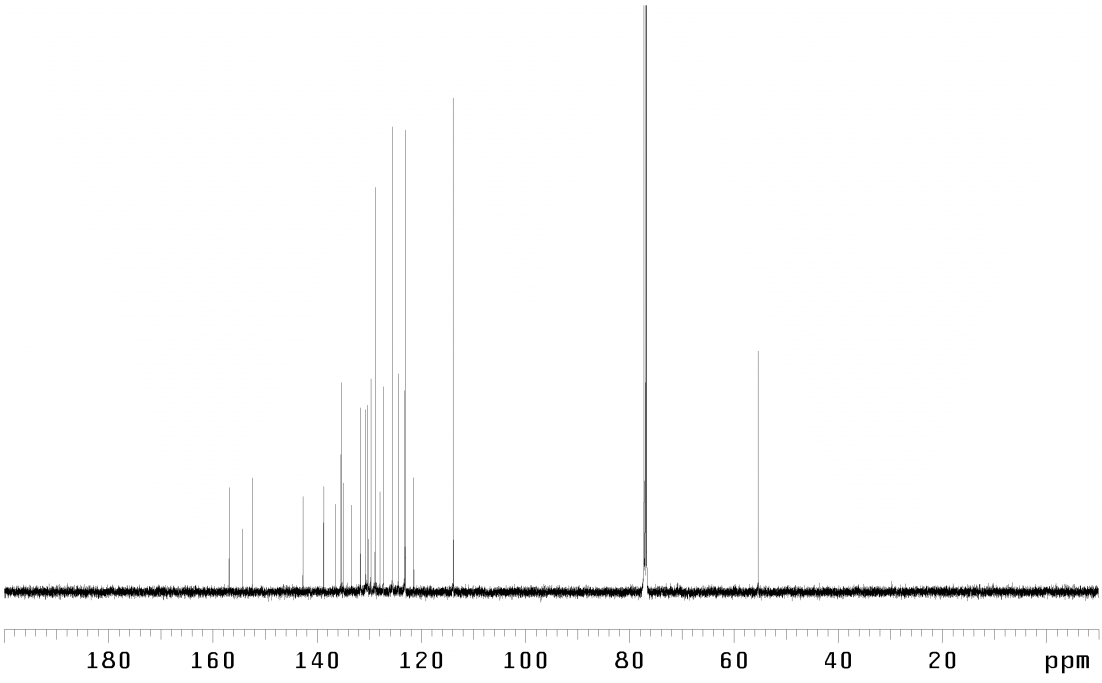


Figure 15.3 ^{13}C NMR (125 MHz, $CDCl_3$) of iminoisobenzofuran **14o**.

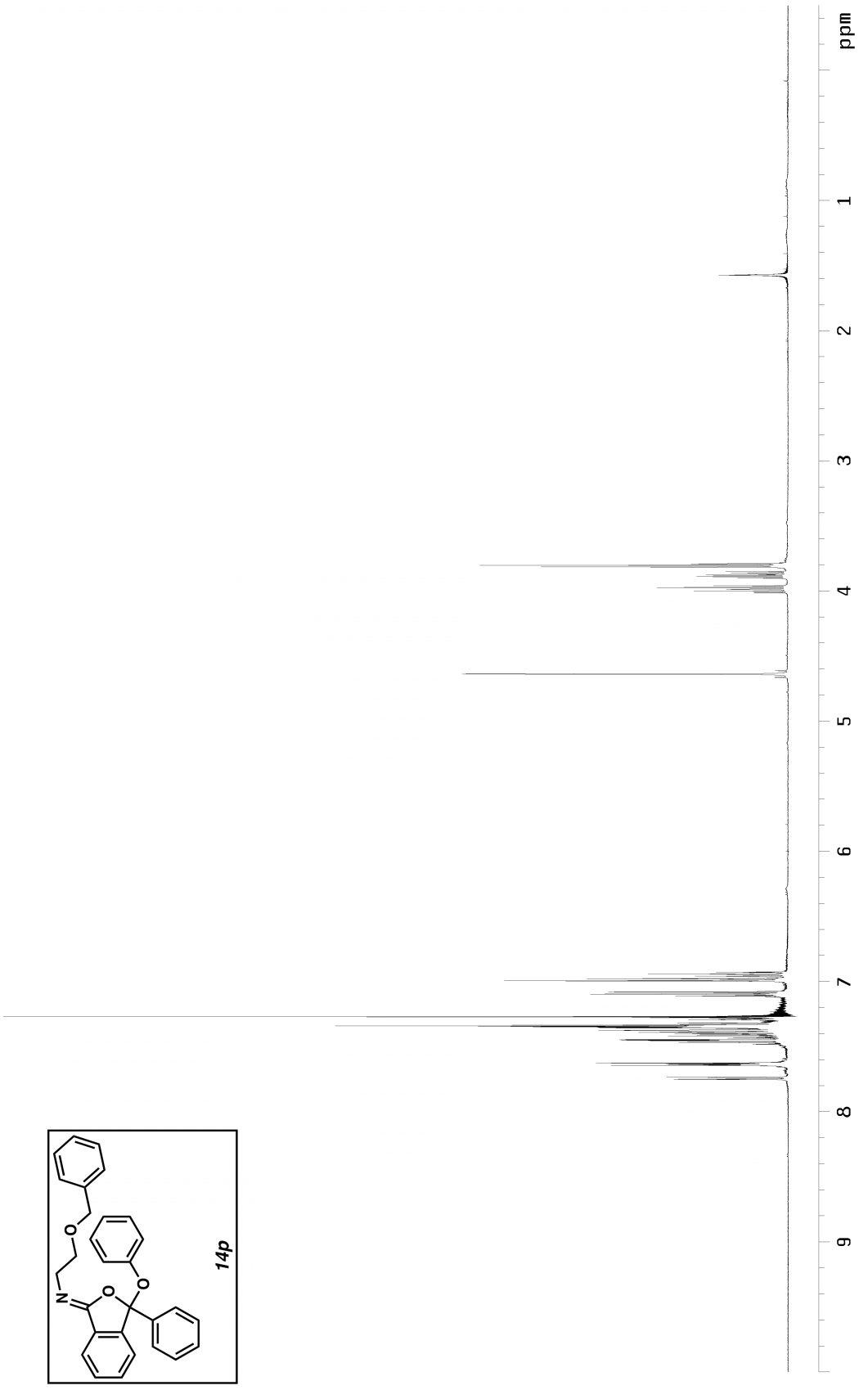


Figure 16.1 ^{1}H NMR (500 MHz, $CDCl_3$) of iminoisobenzofuran **14p**.

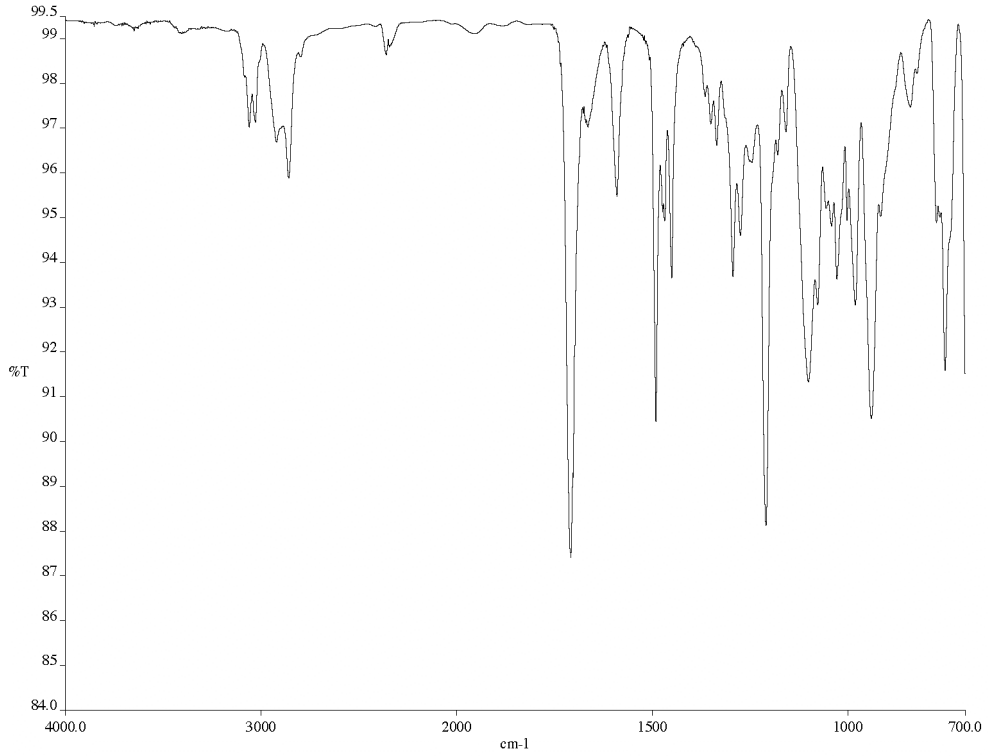


Figure 16.2 Infrared spectrum (thin film/NaCl) of iminoisobenzofuran **16p**.

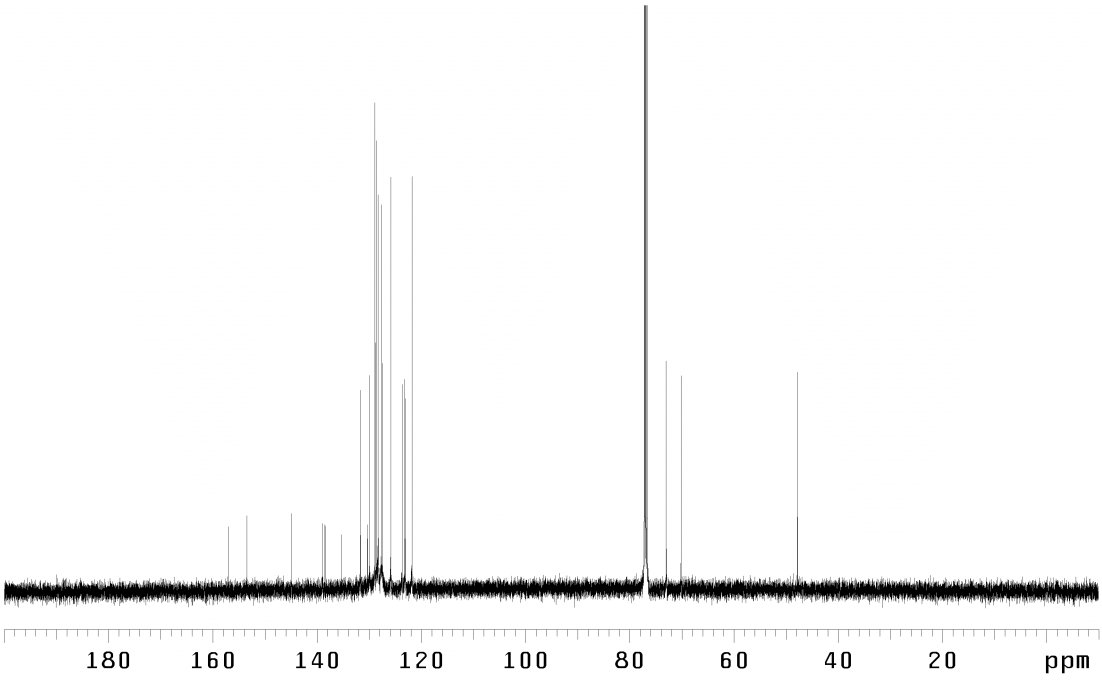


Figure 16.3 ^{13}C NMR (125 MHz, $CDCl_3$) of iminoisobenzofuran **16p**.

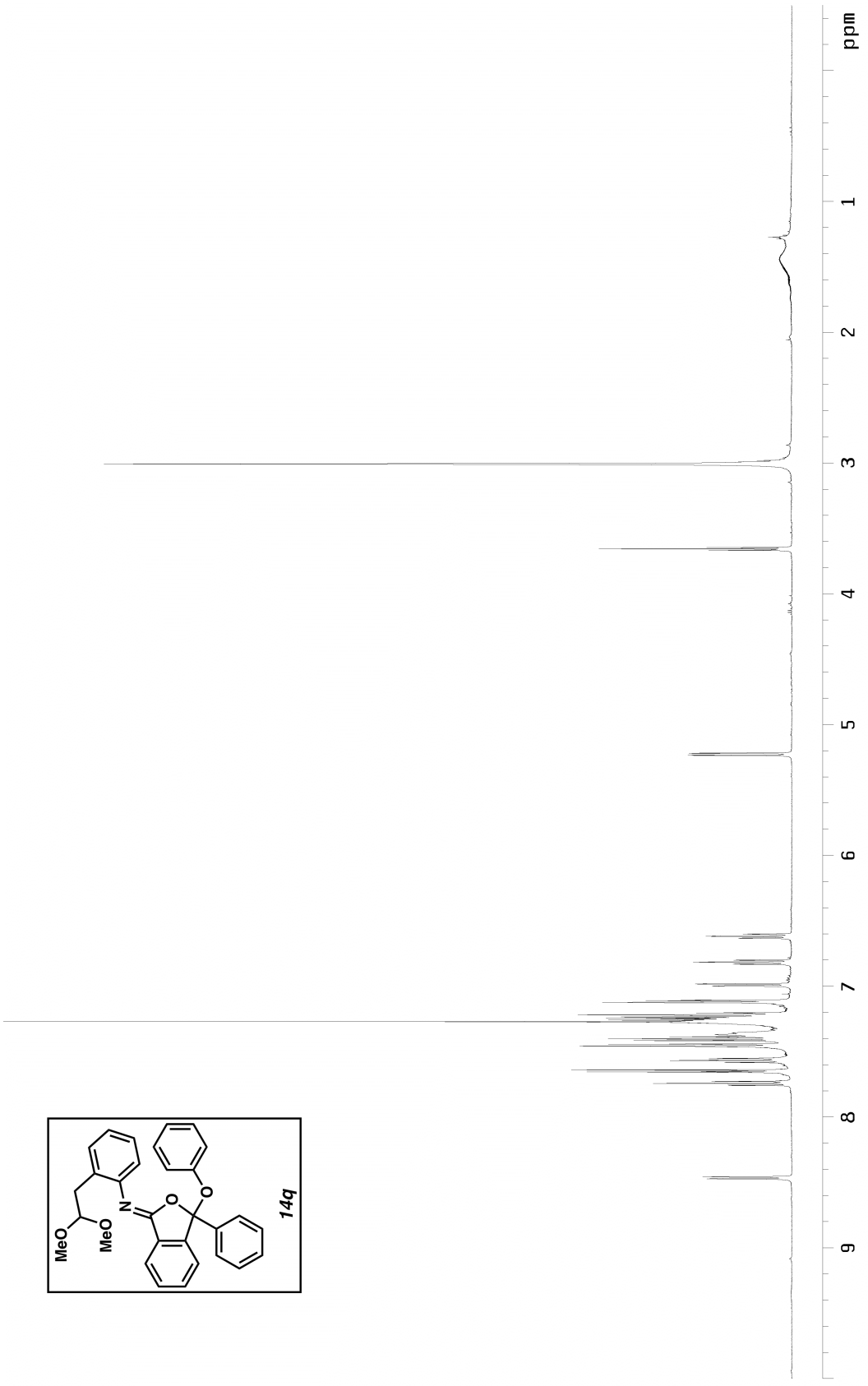


Figure 17.1 ^{1}H NMR (500 MHz, $CDCl_3$) of iminoisobenzofuran **14q**.

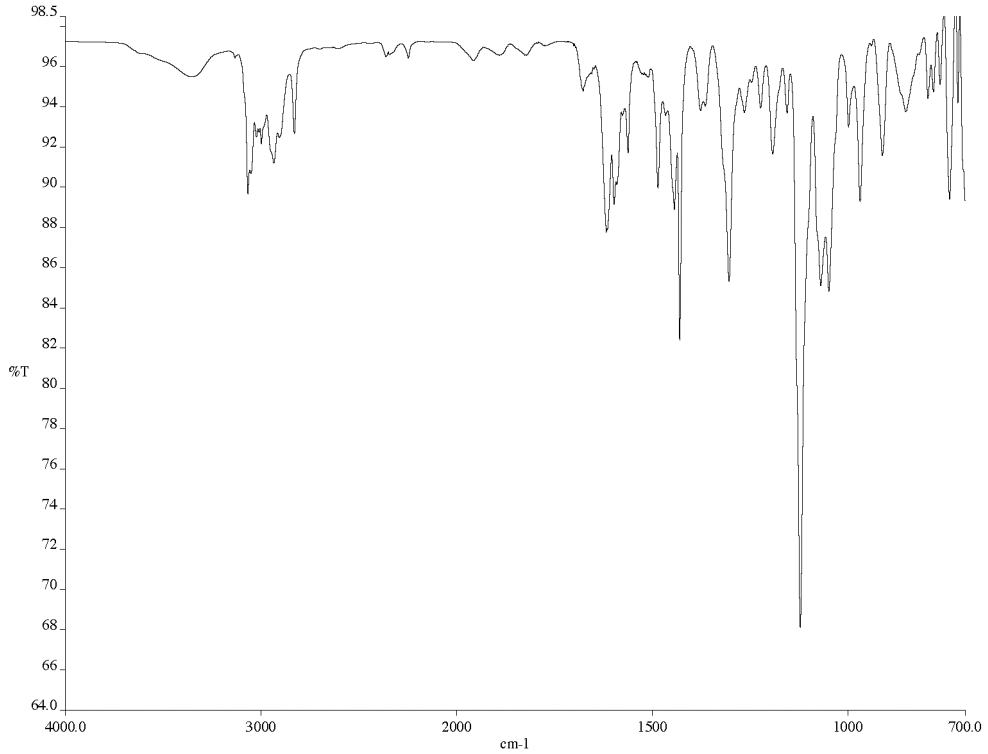


Figure 17.2 Infrared spectrum (thin film/NaCl) of iminoisobenzofuran **14q**.

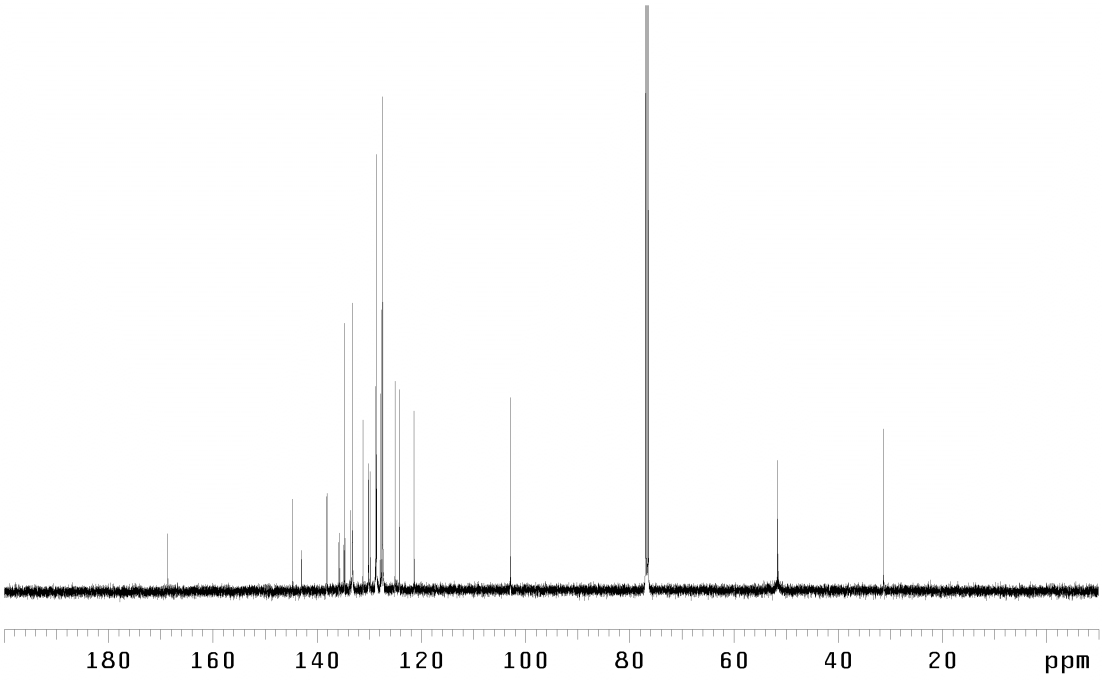


Figure 17.3 ^{13}C NMR (125 MHz, $CDCl_3$) of iminoisobenzofuran **14q**.

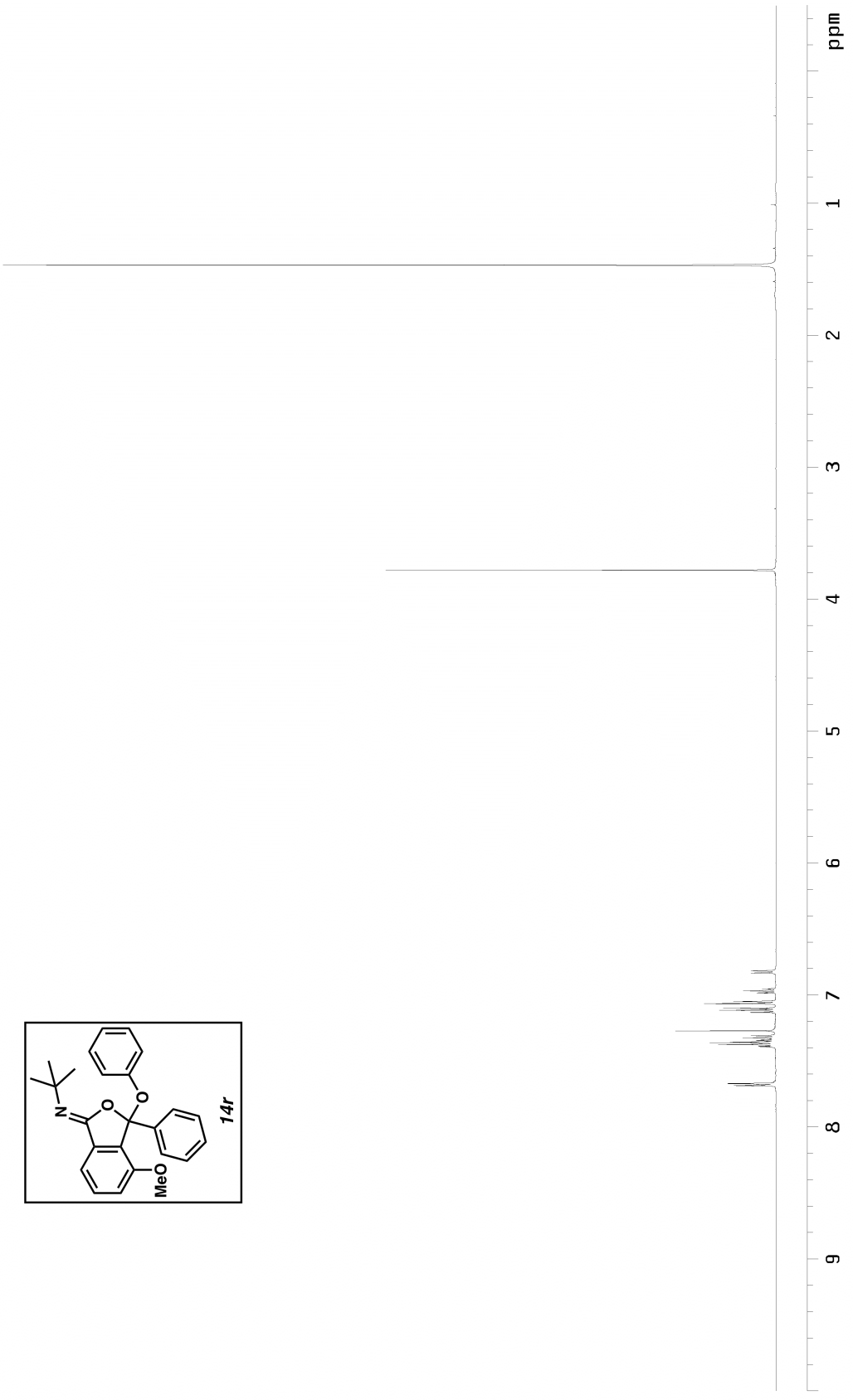


Figure 18.1 ^{1}H NMR (500 MHz, $CDCl_3$) of iminoisobenzofuran **14r**.

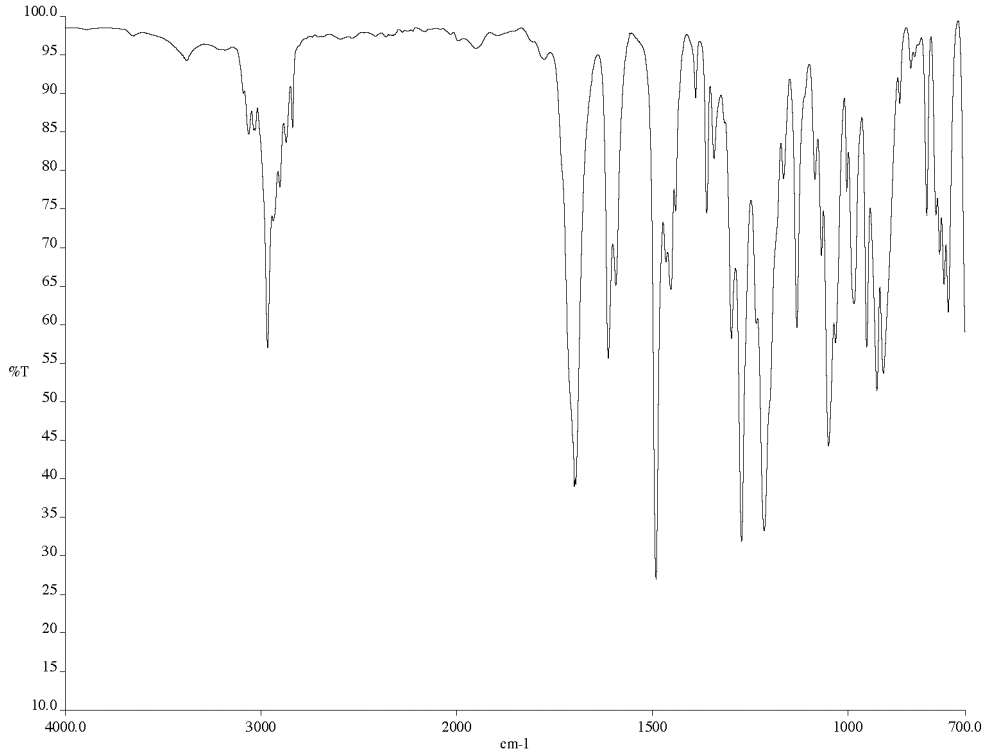


Figure 18.2 Infrared spectrum (thin film/NaCl) of iminoisobenzofuran **14r**.

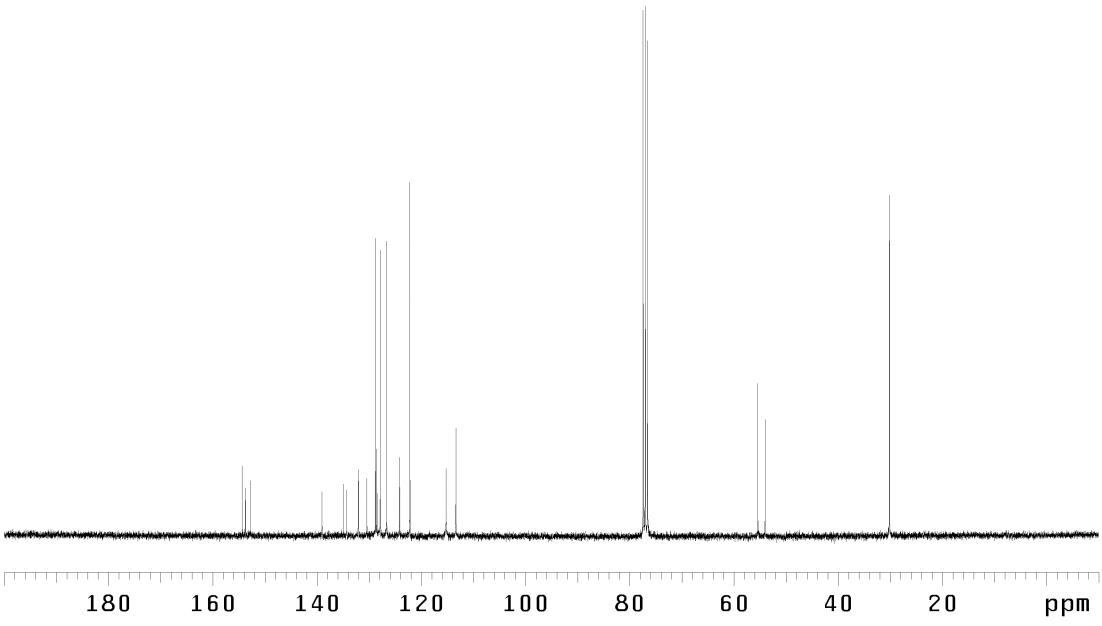


Figure 18.3 ^{13}C NMR (125 MHz, $CDCl_3$) of iminoisobenzofuran **14r**.

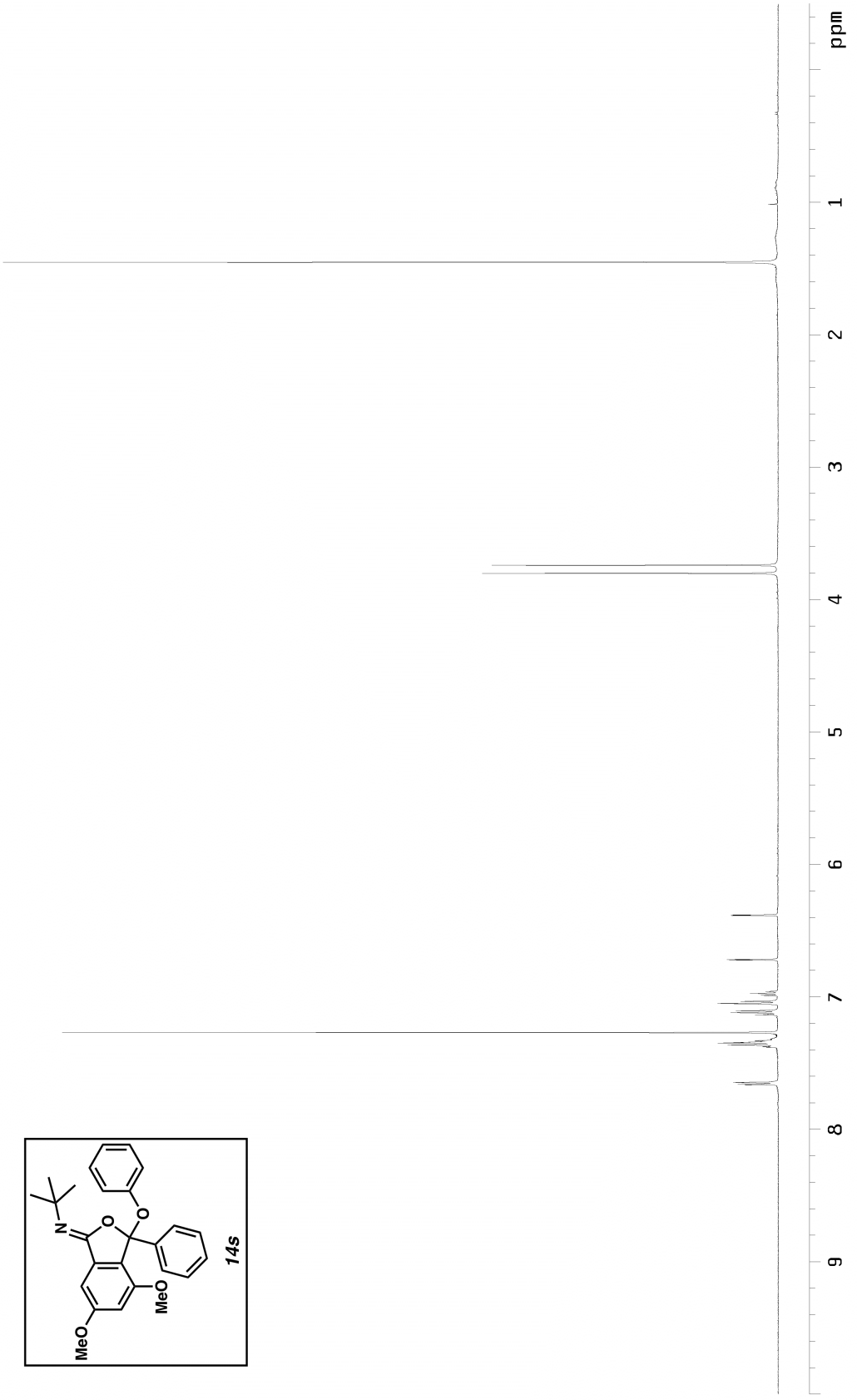


Figure 19.1 ^{1}H NMR (500 MHz, $CDCl_3$) of iminoisobenzofuran **14s**.

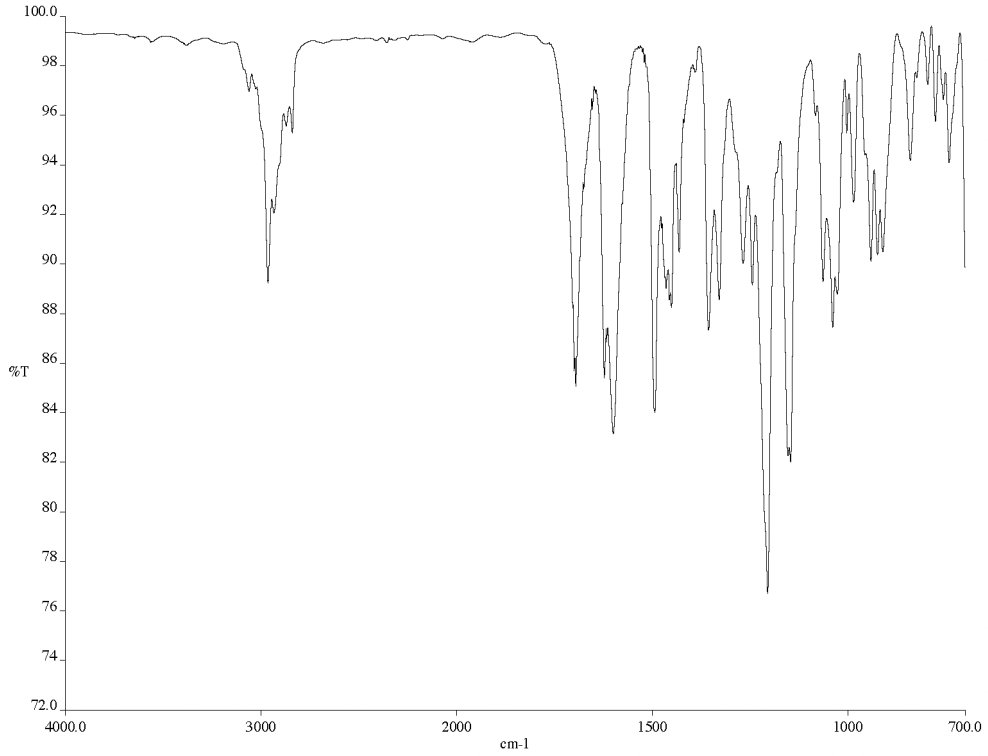


Figure 19.2 Infrared spectrum (thin film/NaCl) of iminoisobenzofuran **14s**.

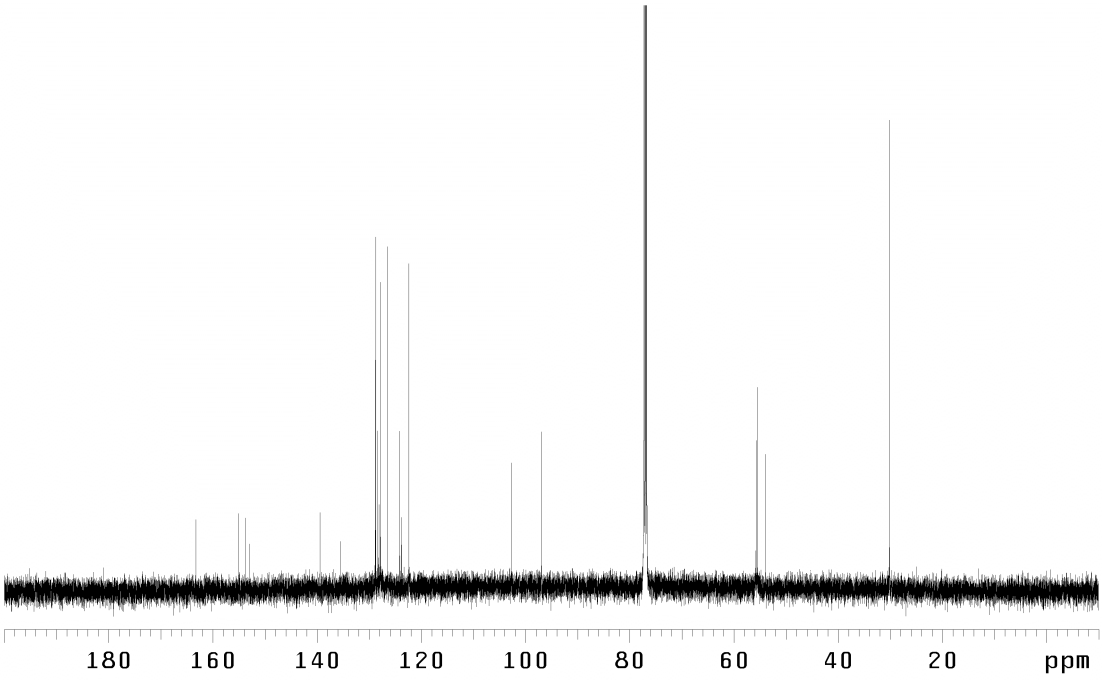


Figure 19.3 ^{13}C NMR (125 MHz, $CDCl_3$) of iminoisobenzofuran **14s**.

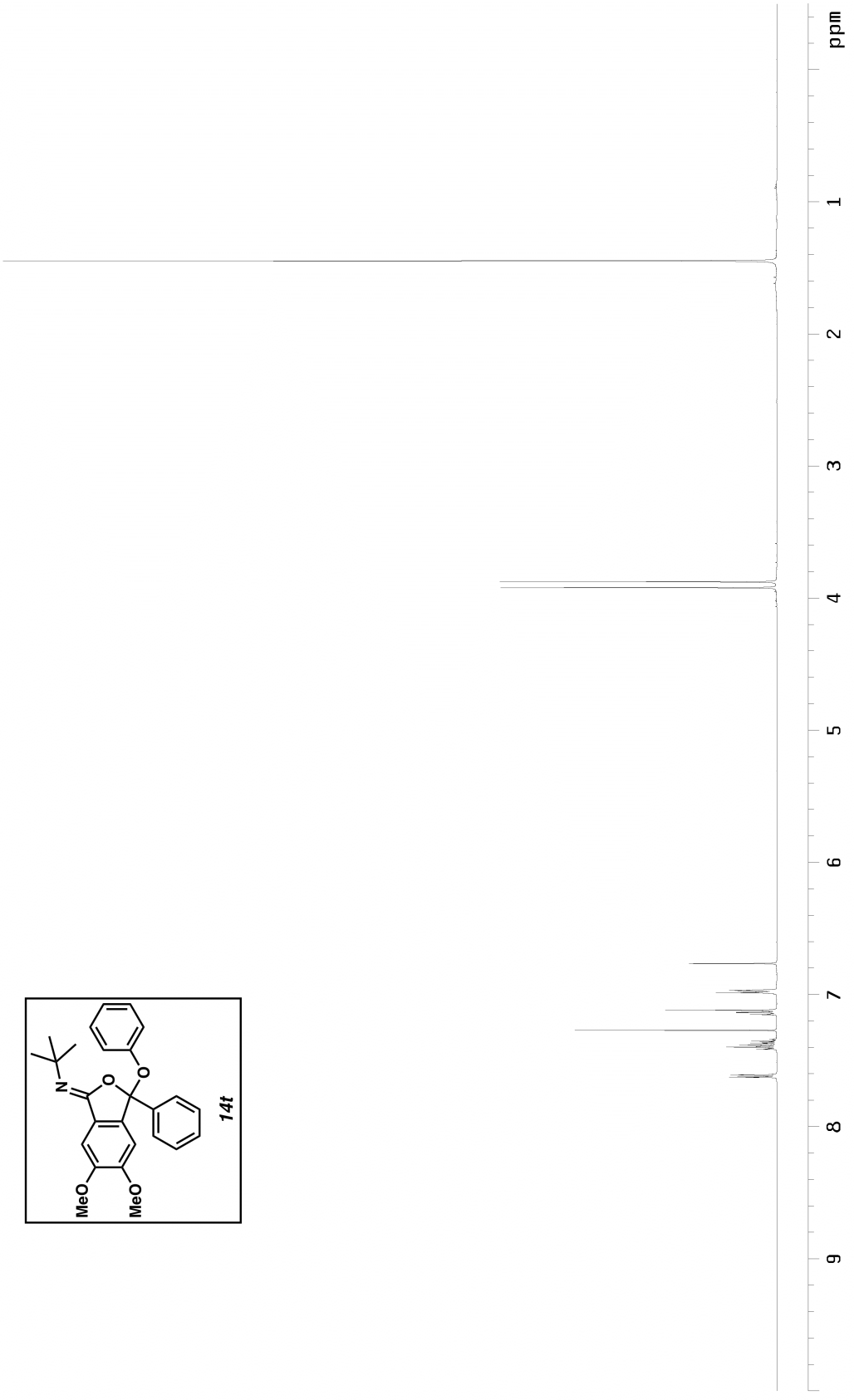


Figure 20.1 ^{1}H NMR (500 MHz, $CDCl_3$) of iminoisobenzofuran **14t**.

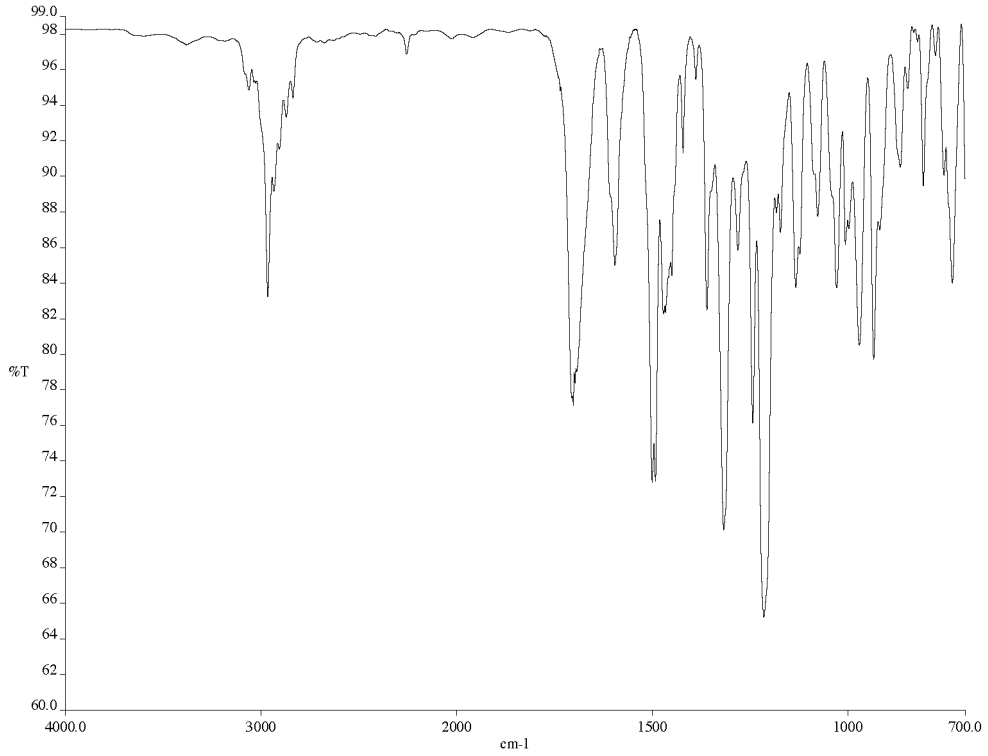


Figure 20.2 Infrared spectrum (thin film/NaCl) of iminoisobenzofuran **14t**.

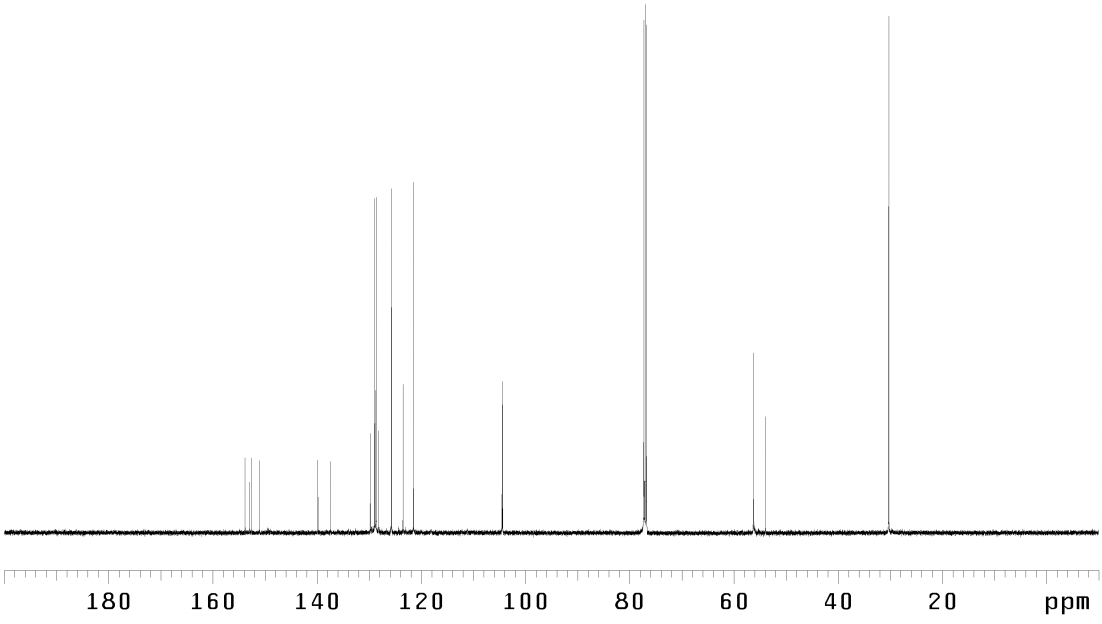


Figure 20.3 ^{13}C NMR (125 MHz, $CDCl_3$) of iminoisobenzofuran **14t**.

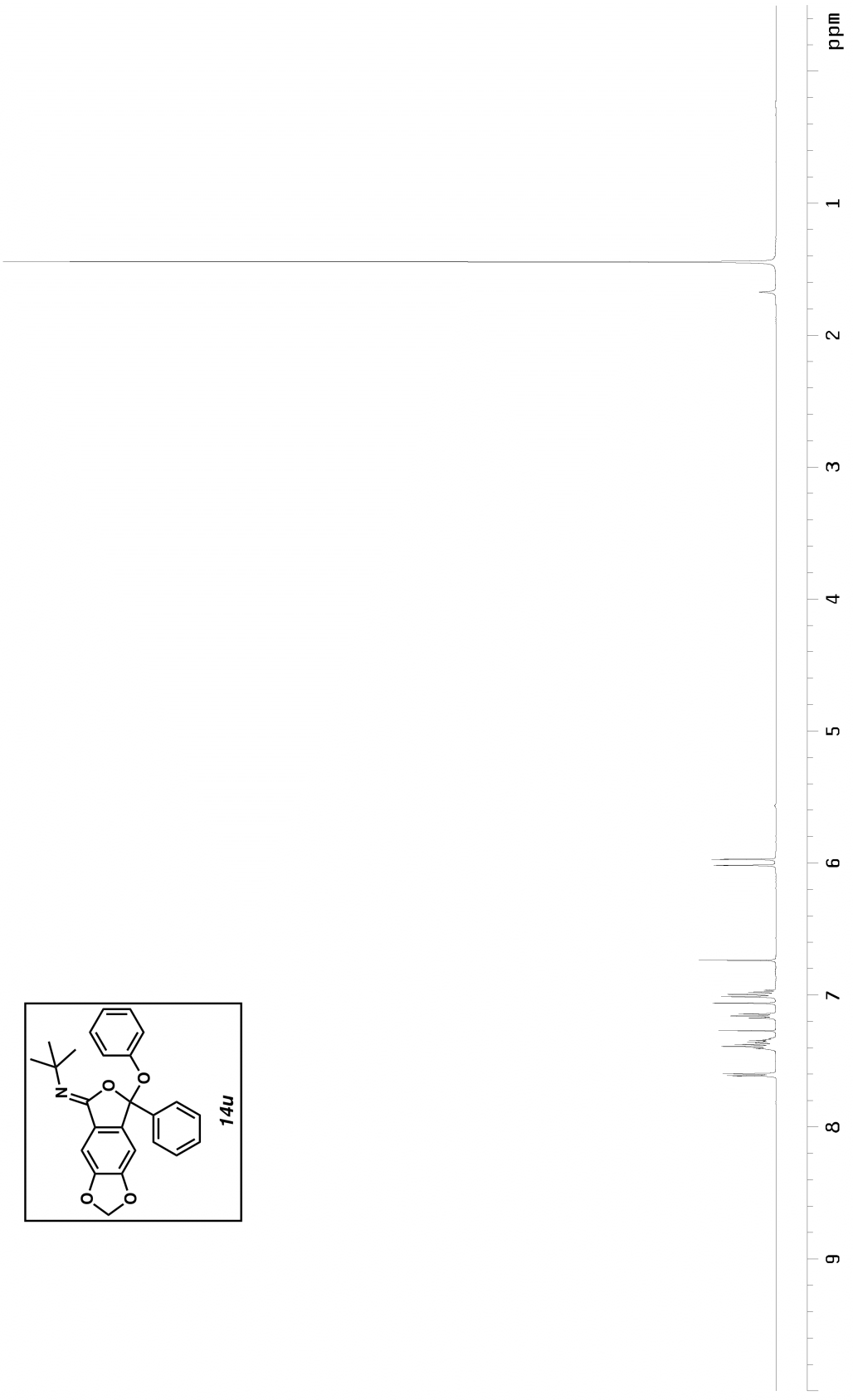


Figure 21.1 ^{1}H NMR (500 MHz, $CDCl_3$) of iminoisobenzofuran **14u**.

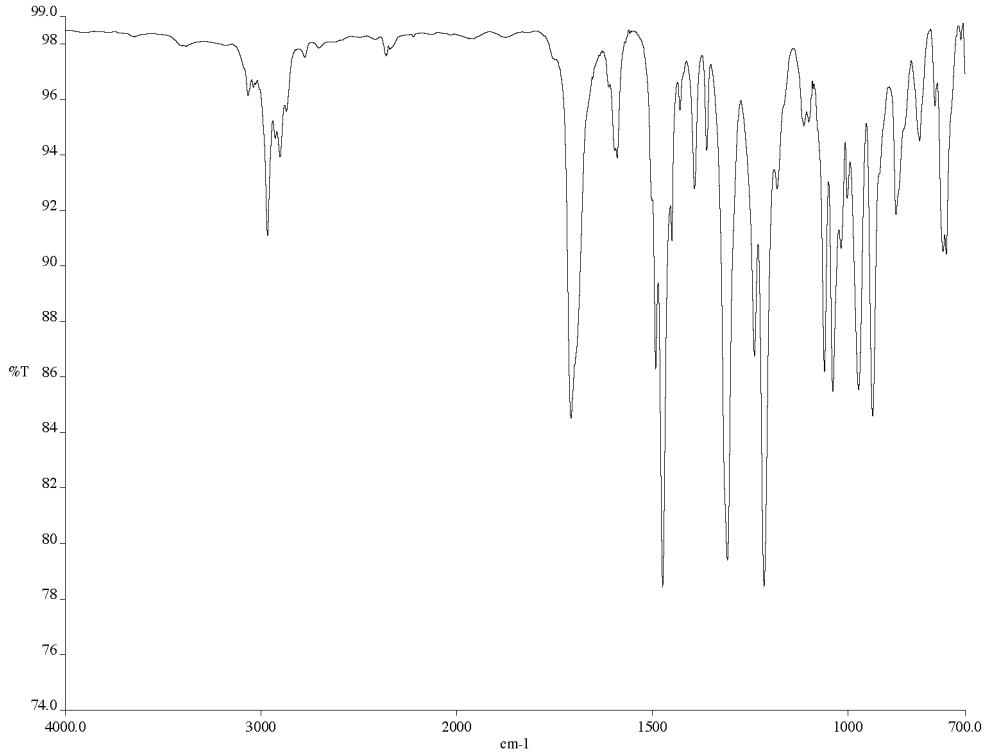


Figure 21.2 Infrared spectrum (thin film/NaCl) of iminoisobenzofuran **14u**.

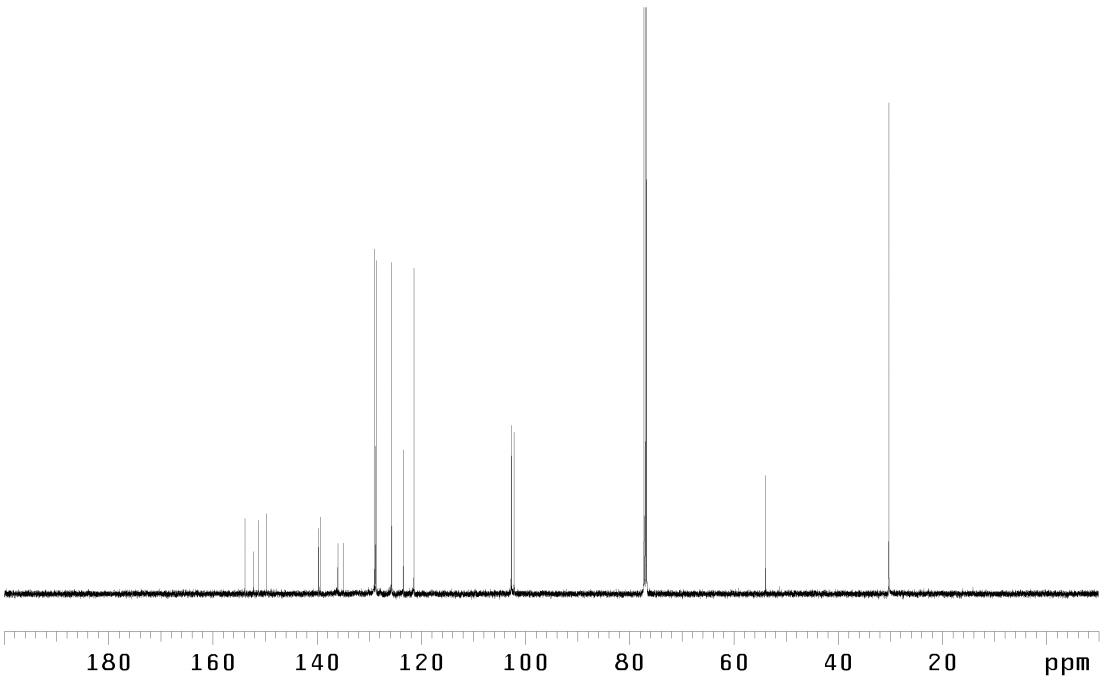


Figure 21.3 ^{13}C NMR (125 MHz, $CDCl_3$) of iminoisobenzofuran **14u**.

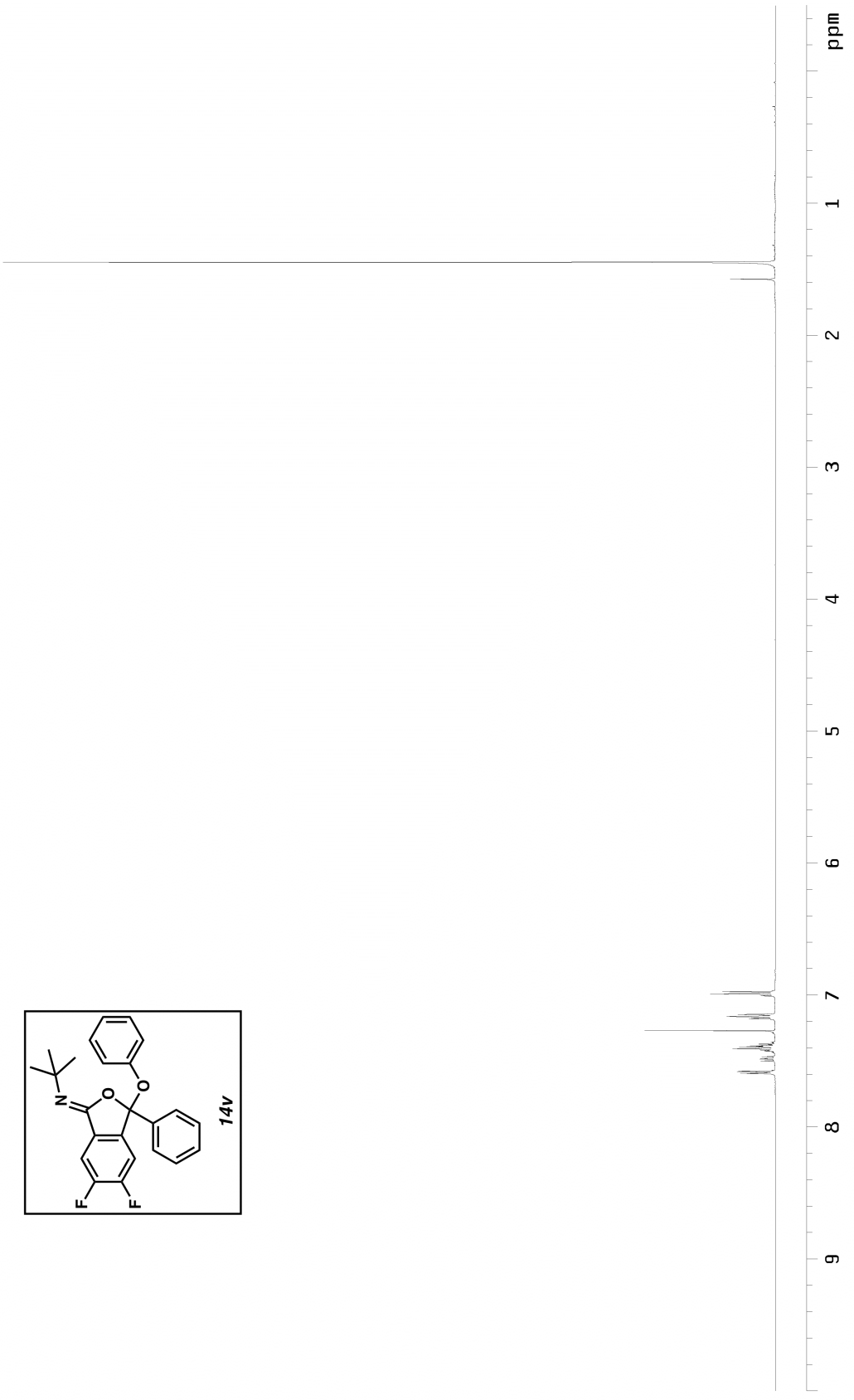


Figure 22.1 ^{1}H NMR (500 MHz, $CDCl_3$) of iminoisobenzofuran **14v**.

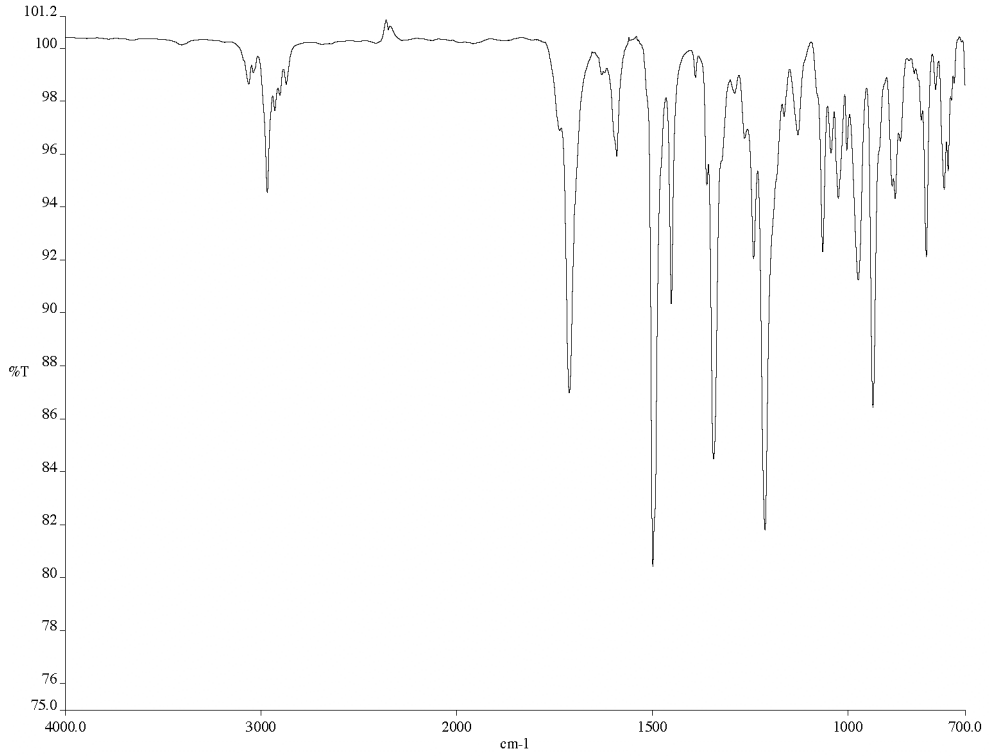


Figure 22.2 Infrared spectrum (thin film/NaCl) of iminoisobenzofuran **14v**.

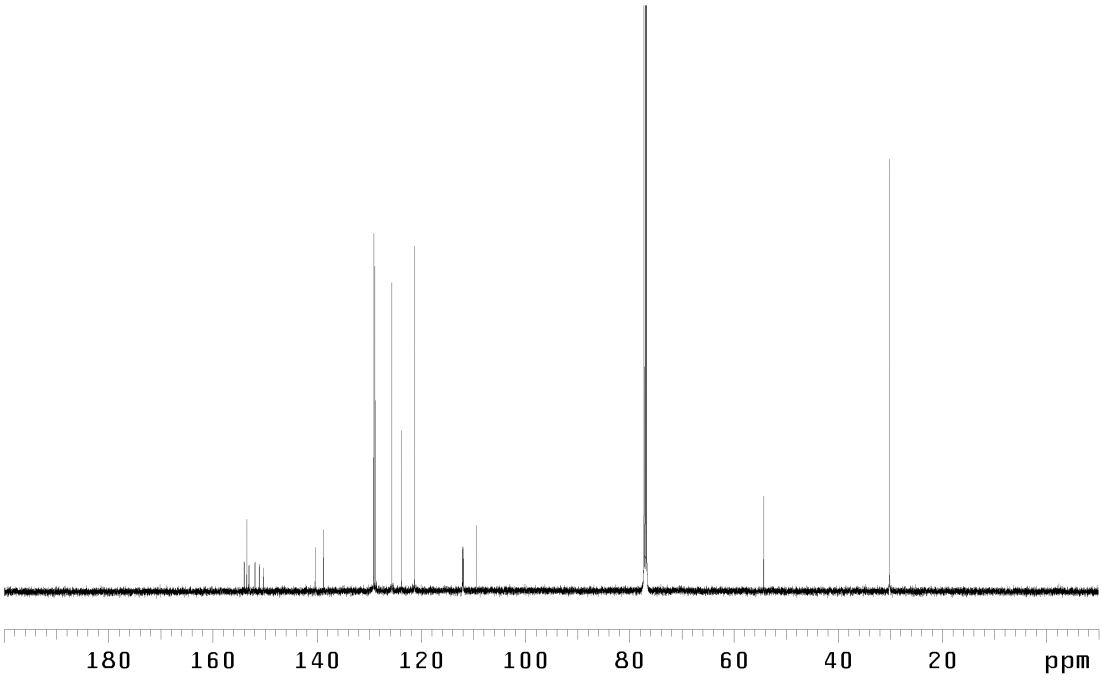


Figure 22.3 ^{13}C NMR (125 MHz, $CDCl_3$) of iminoisobenzofuran **14v**.

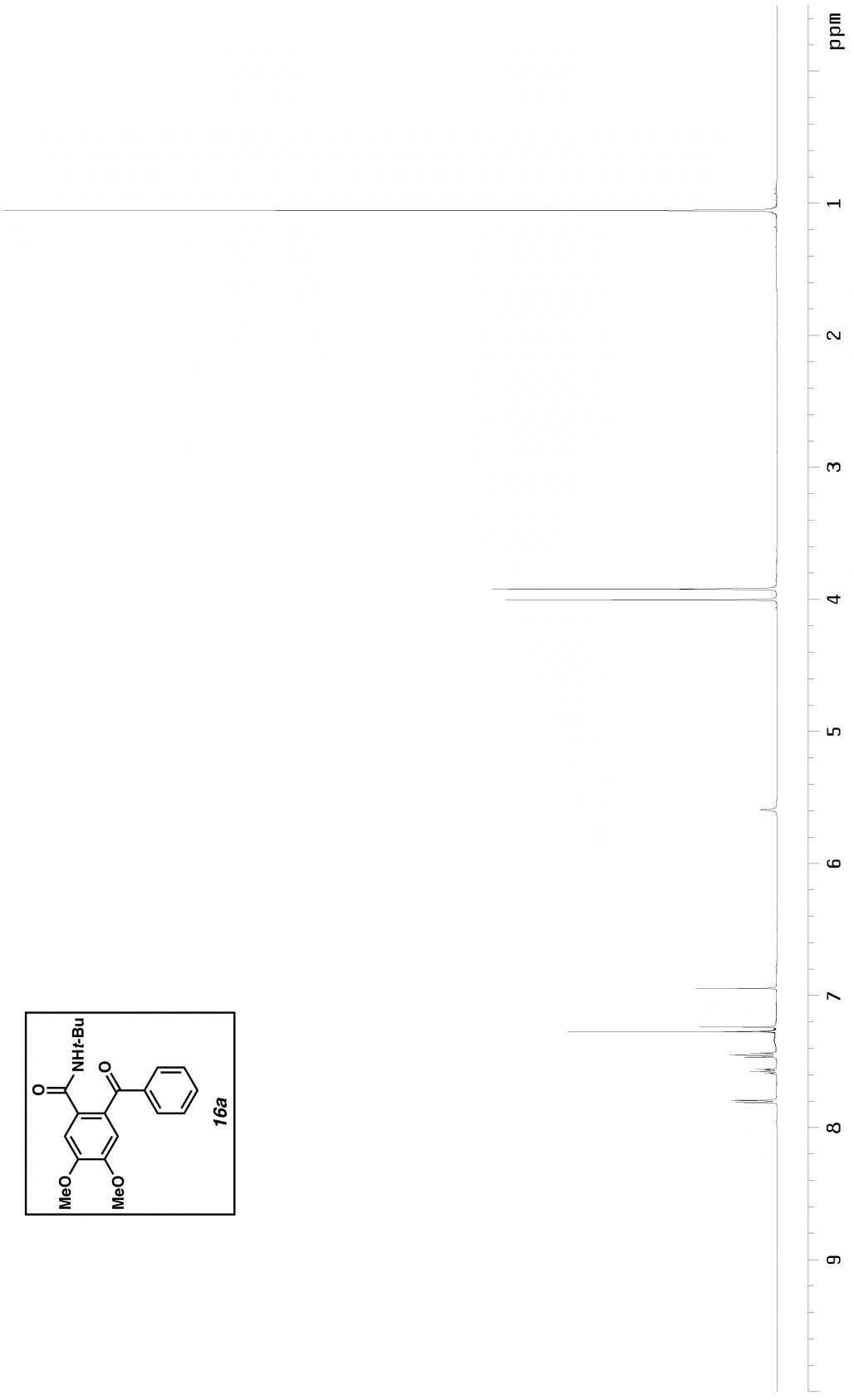


Figure 23.1 ^{1}H NMR (500 MHz, $CDCl_3$) of *ortho*-ketobenzamide **16a**.

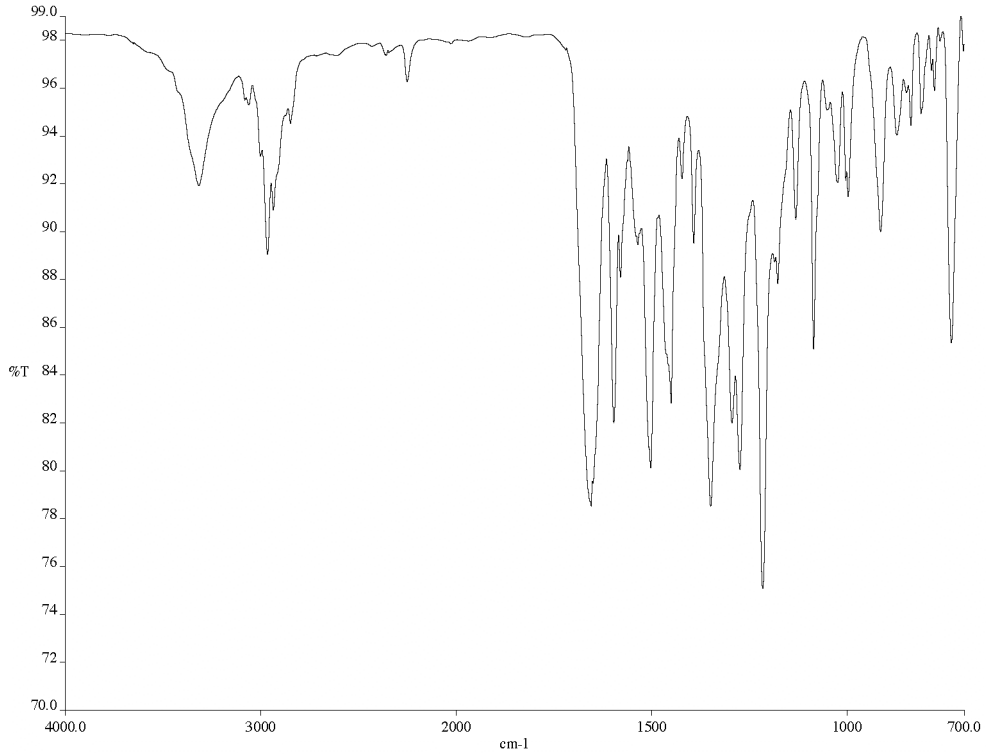


Figure 23.2 Infrared spectrum (thin film/NaCl) of *ortho*-ketobenzamide **16a**.

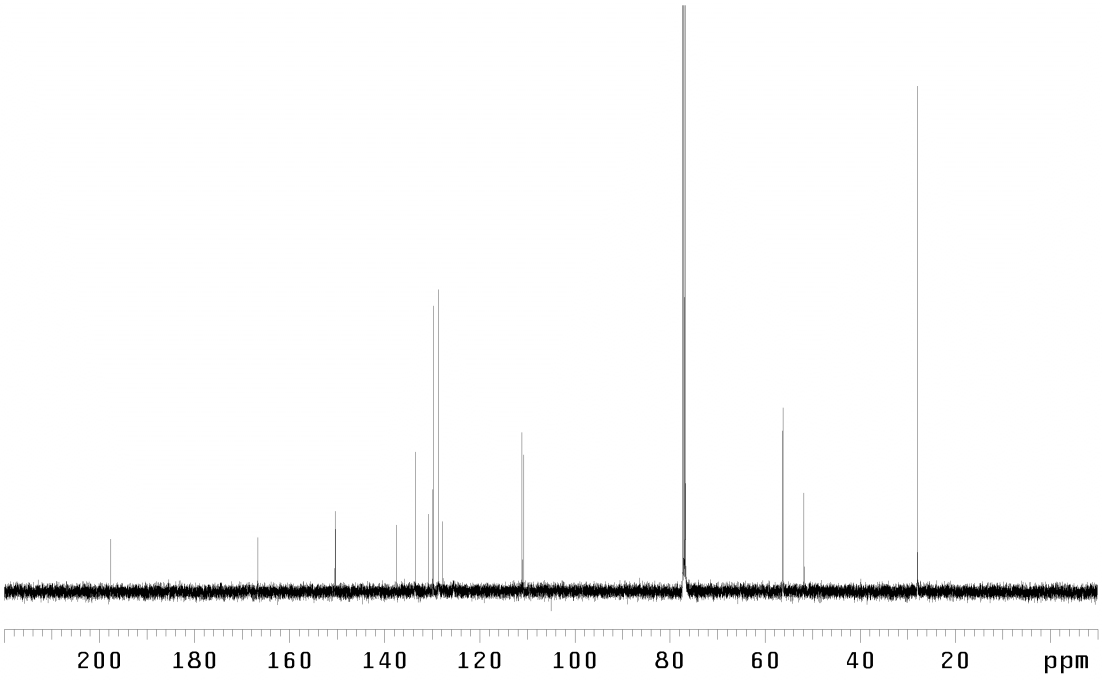


Figure 23.3 ^{13}C NMR (125 MHz, $CDCl_3$) of *ortho*-ketobenzamide **16a**.

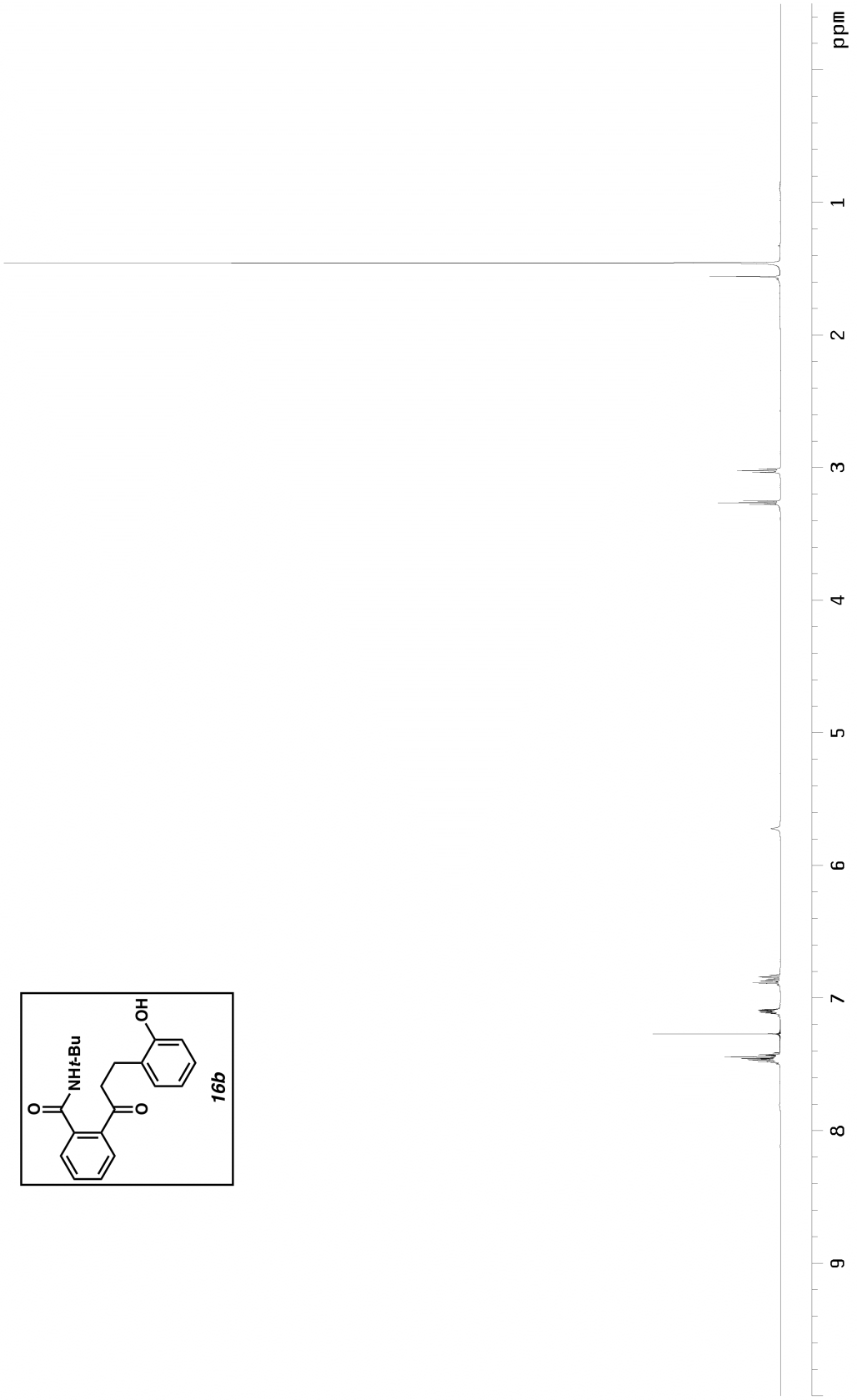


Figure 24.1 ^{1}H NMR (500 MHz, $CDCl_3$) of *ortho*-ketobenzamide **16b**.

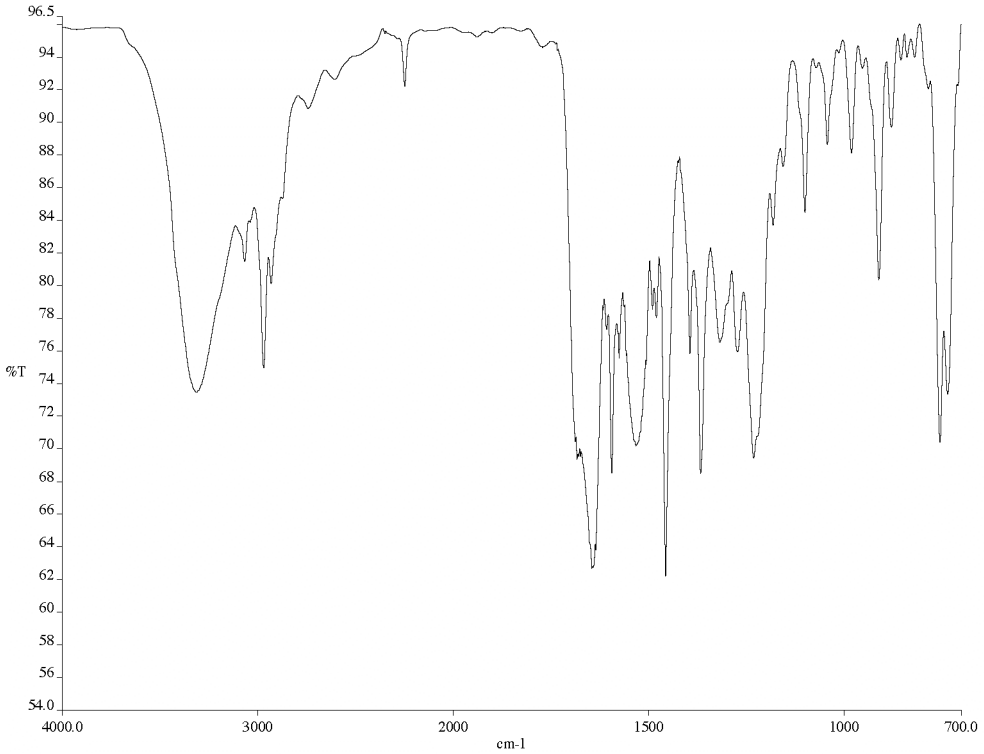


Figure 24.2 Infrared spectrum (thin film/NaCl) of *ortho*-ketobenzamide **16b**.

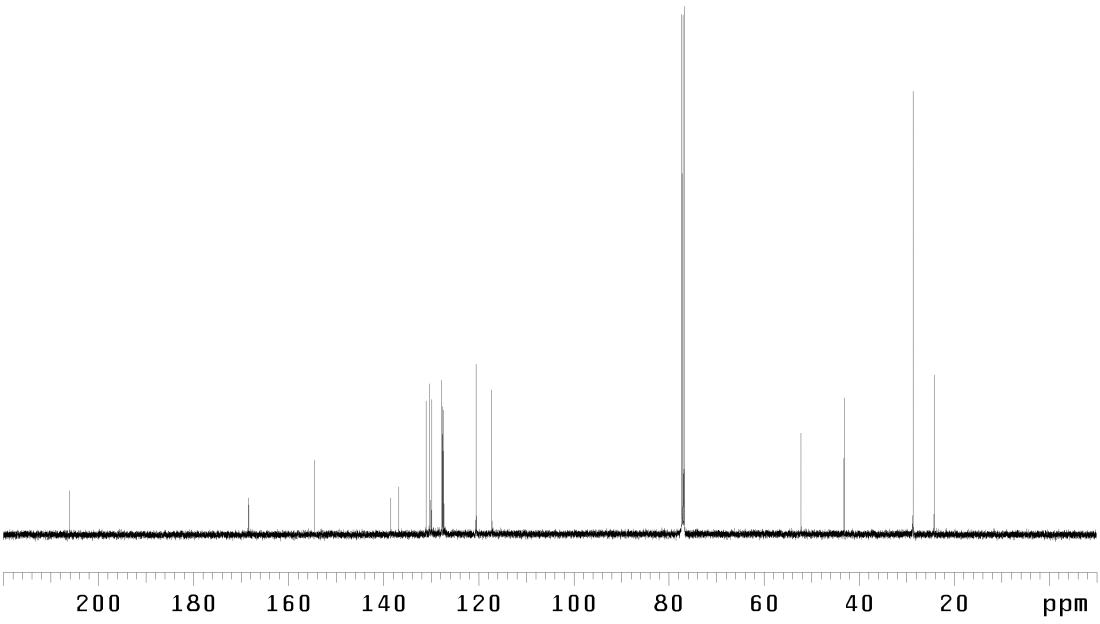


Figure 24.3 ^{13}C NMR (125 MHz, $CDCl_3$) of *ortho*-ketobenzamide **16b**.

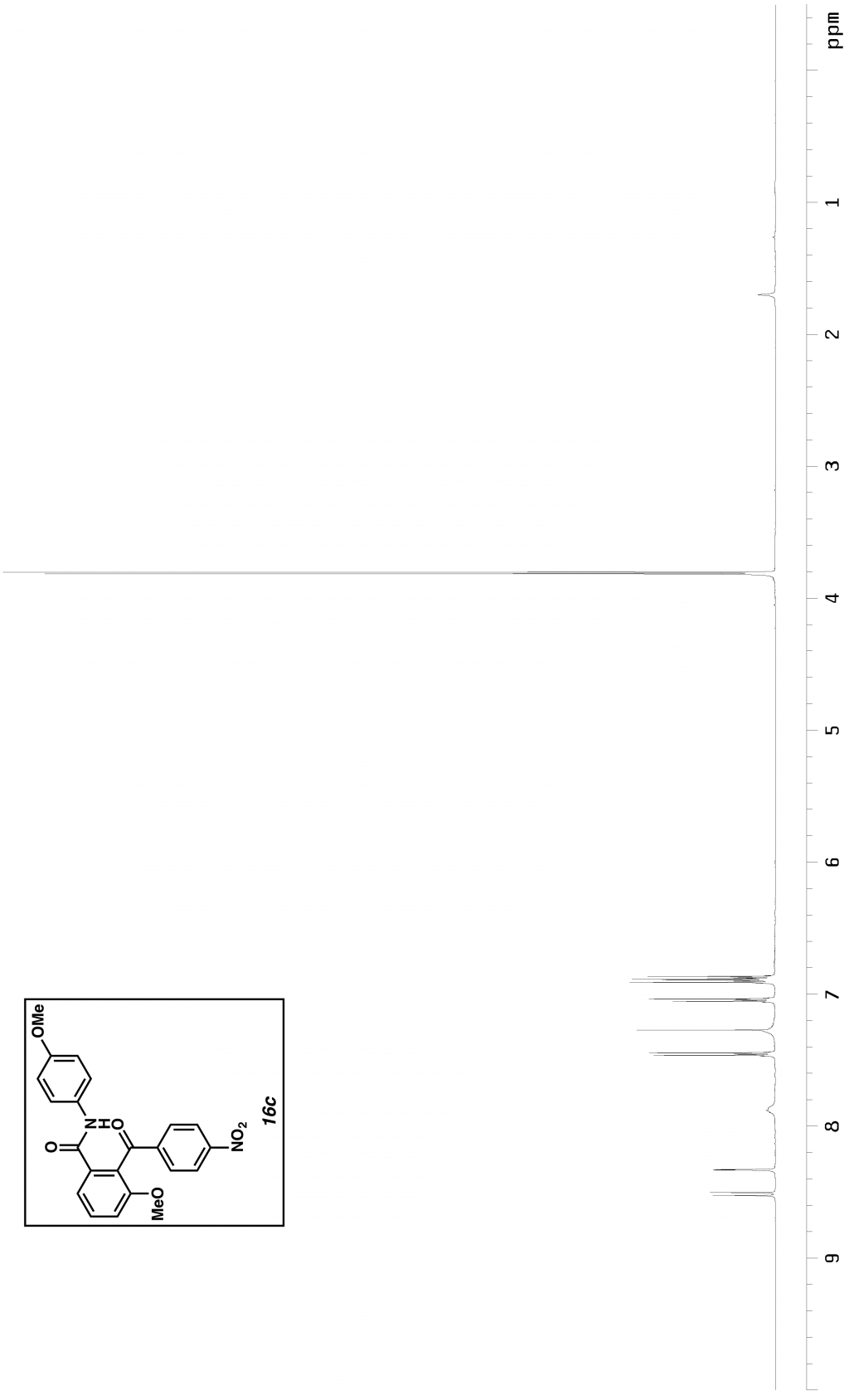


Figure 25.1 ^{1}H NMR (500 MHz, $CDCl_3$) of *ortho*-ketobenzamide **16c**.

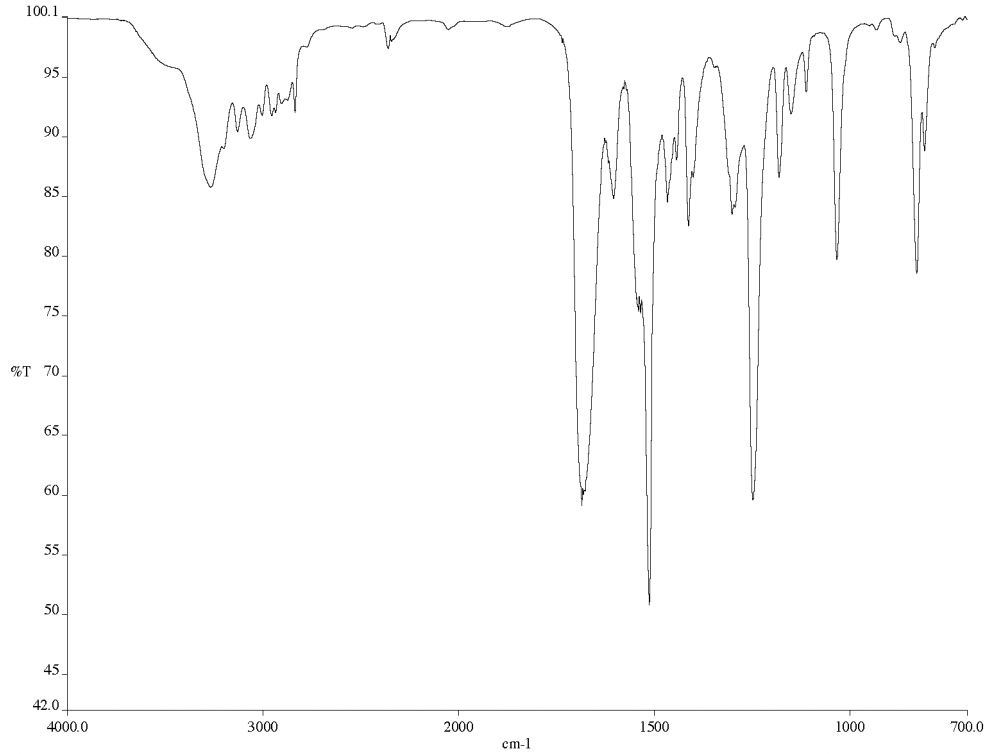


Figure 25.2 Infrared spectrum (thin film/NaCl) of *ortho*-ketobenzamide **16c**.

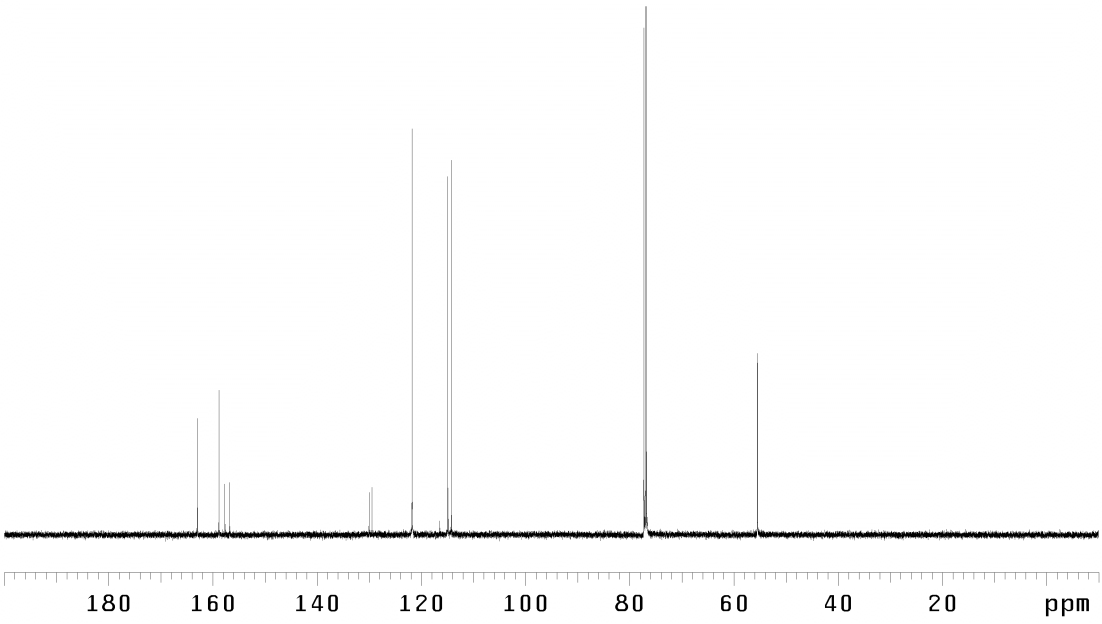


Figure 25.3 ^{13}C NMR (125 MHz, $CDCl_3$) of *ortho*-ketobenzamide **16c**.

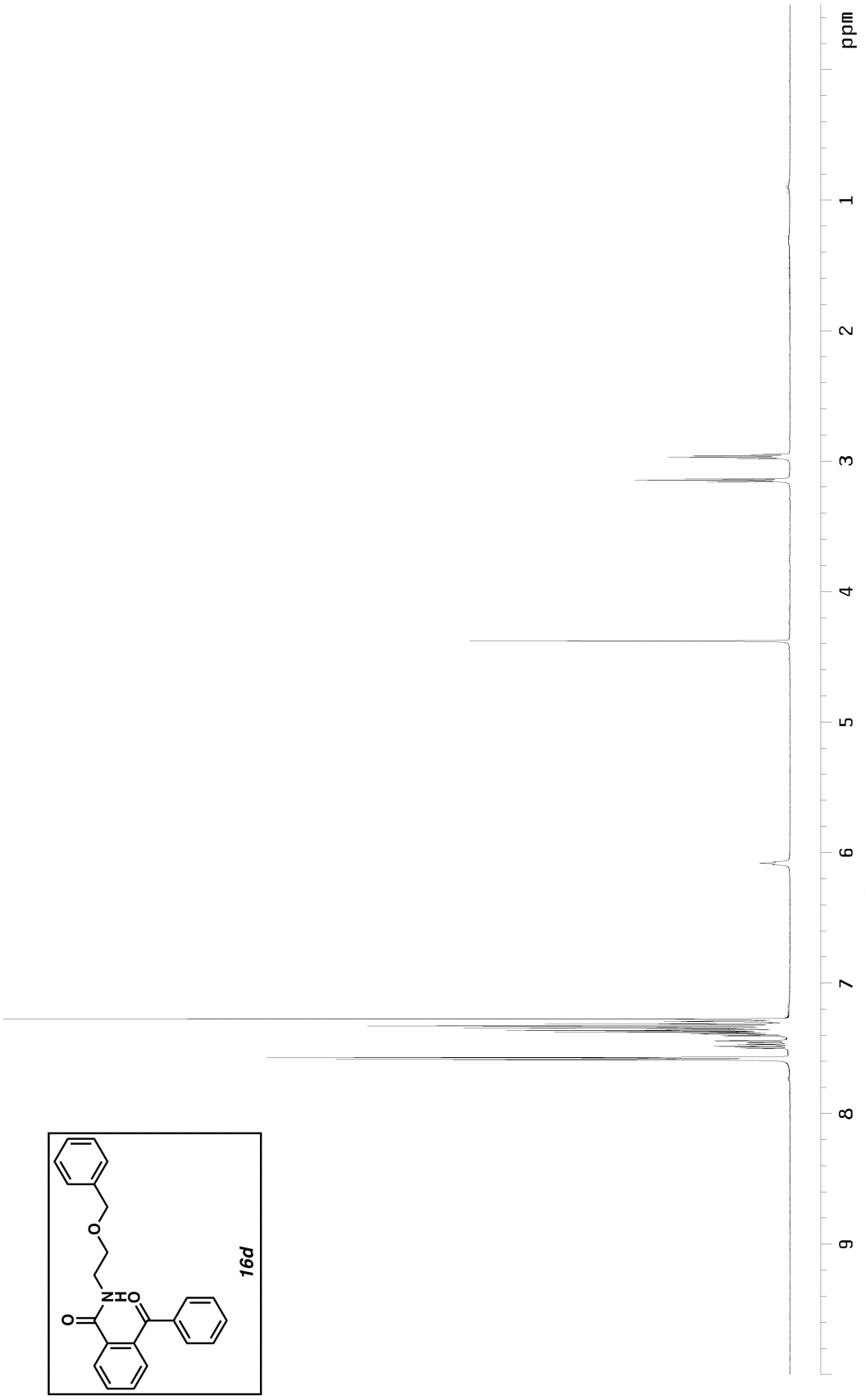


Figure 26.1 ^{1}H NMR (500 MHz, $CDCl_3$) of *ortho*-ketobenzamide **16d**.

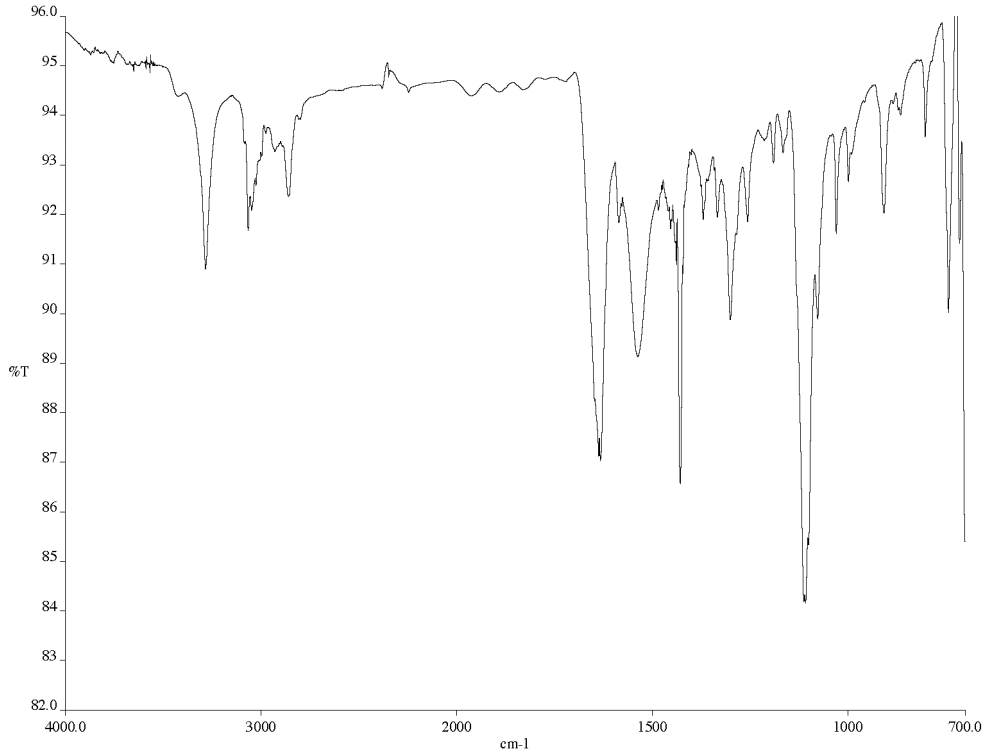


Figure 26.2 Infrared spectrum (thin film/NaCl) of *ortho*-ketobenzamide **16d**.

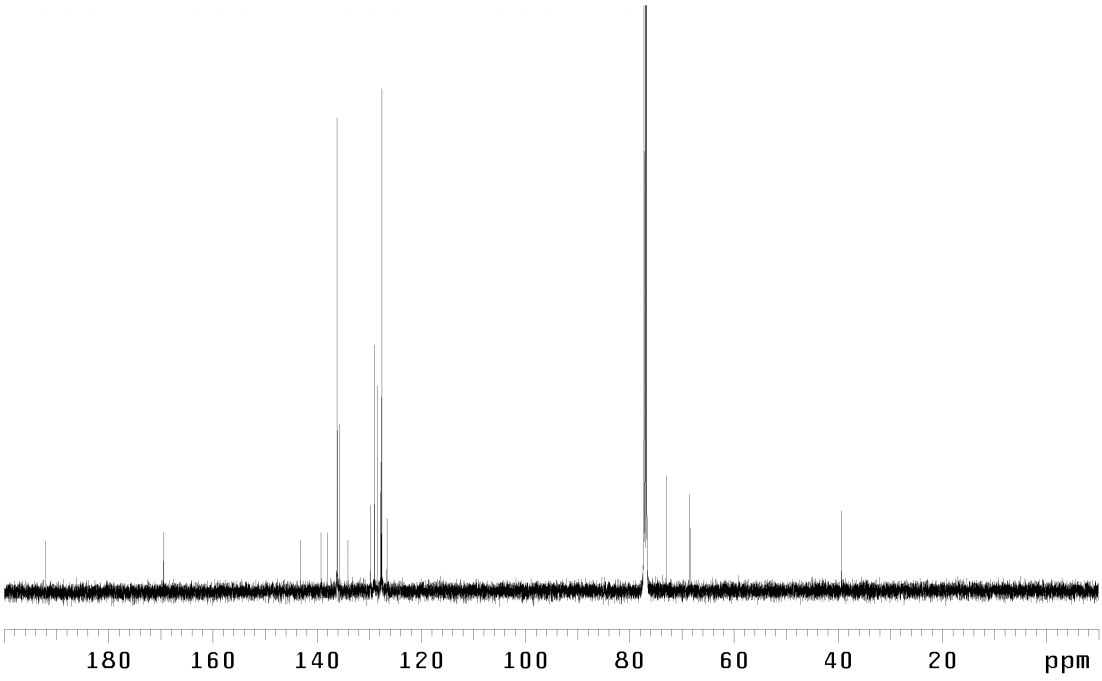


Figure 26.3 ^{13}C NMR (125 MHz, $CDCl_3$) of *ortho*-ketobenzamide **16d**.

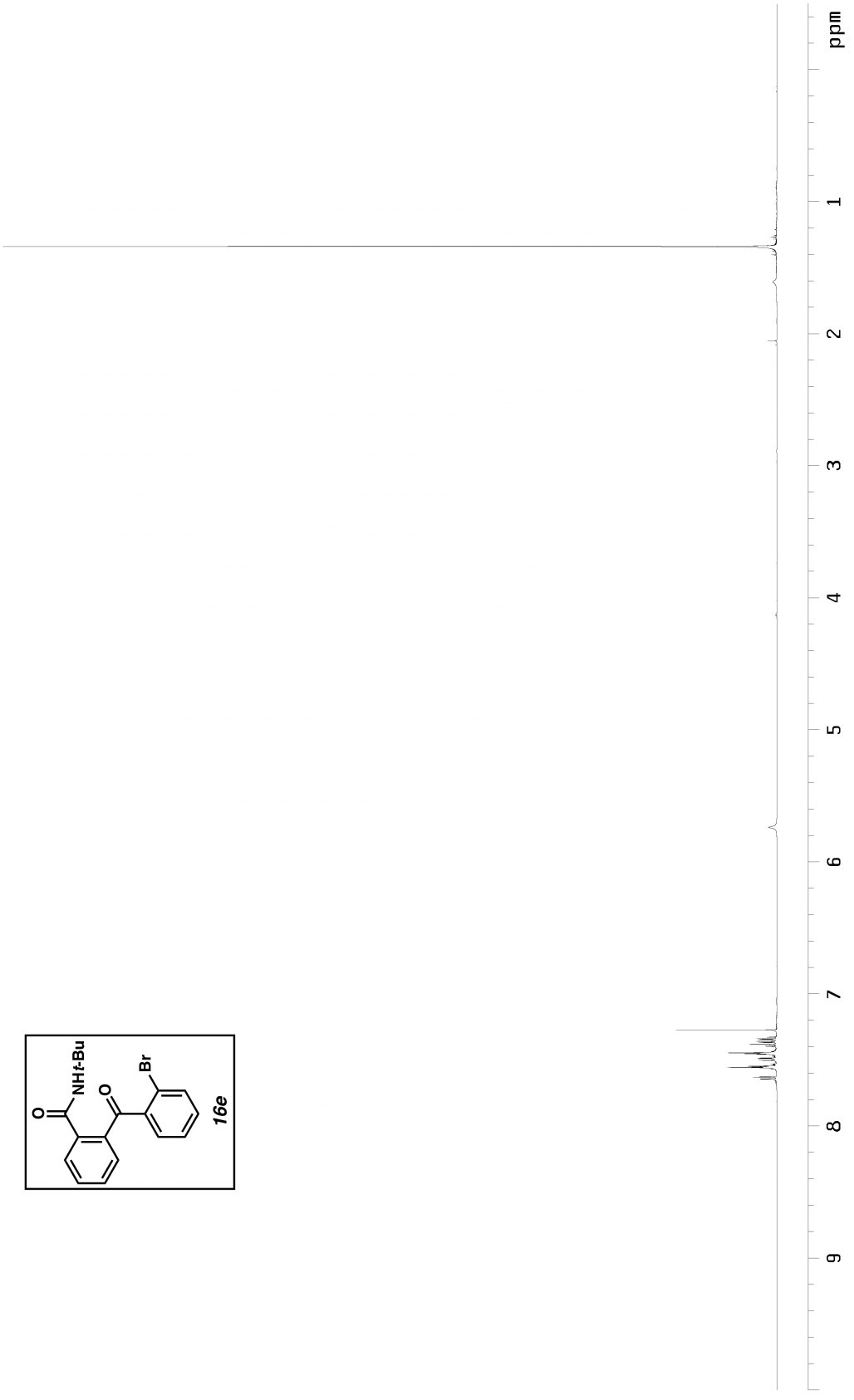


Figure 27.1 ^{1}H NMR (500 MHz, $CDCl_3$) of *ortho*-ketobenzamide **16e**.

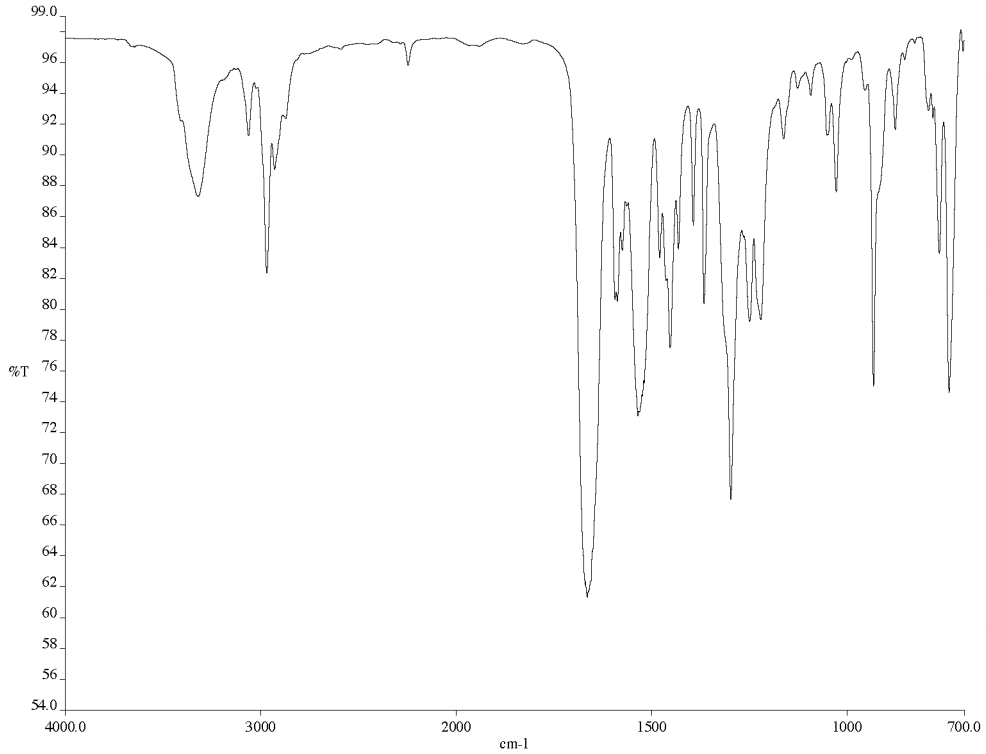


Figure 27.2 Infrared spectrum (thin film/NaCl) of *ortho*-ketobenzamide **16e**.

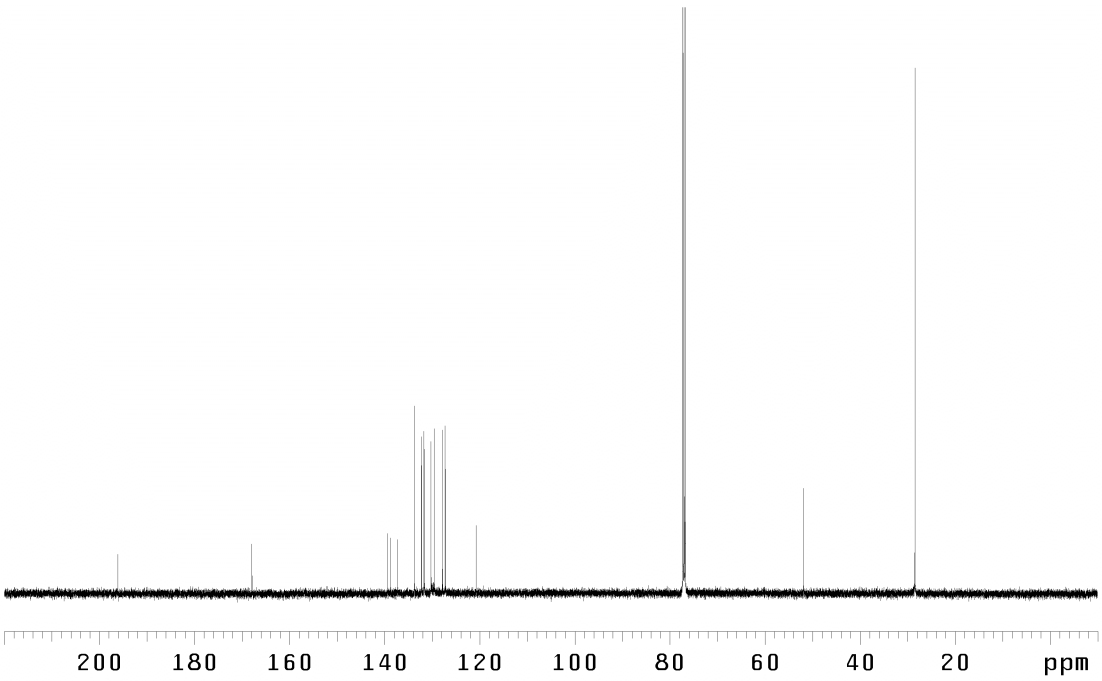


Figure 27.3 ^{13}C NMR (125 MHz, $CDCl_3$) of *ortho*-ketobenzamide **16e**.

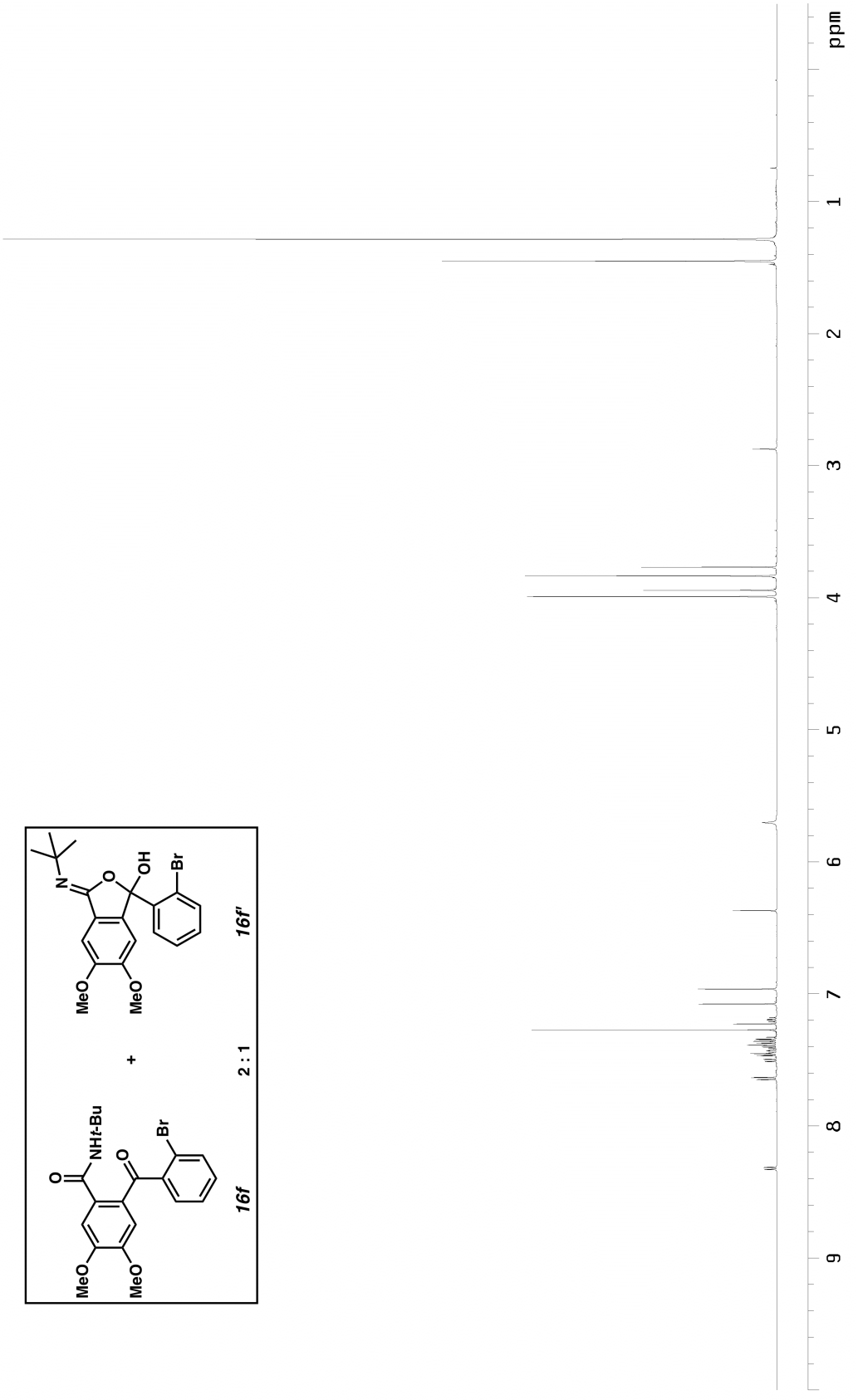


Figure 28.1 ^{1}H NMR (500 MHz, $CDCl_3$) of 2:1 mixture of *ortho*-ketobenzamide **16f** and cyclic imidate **16f'**.

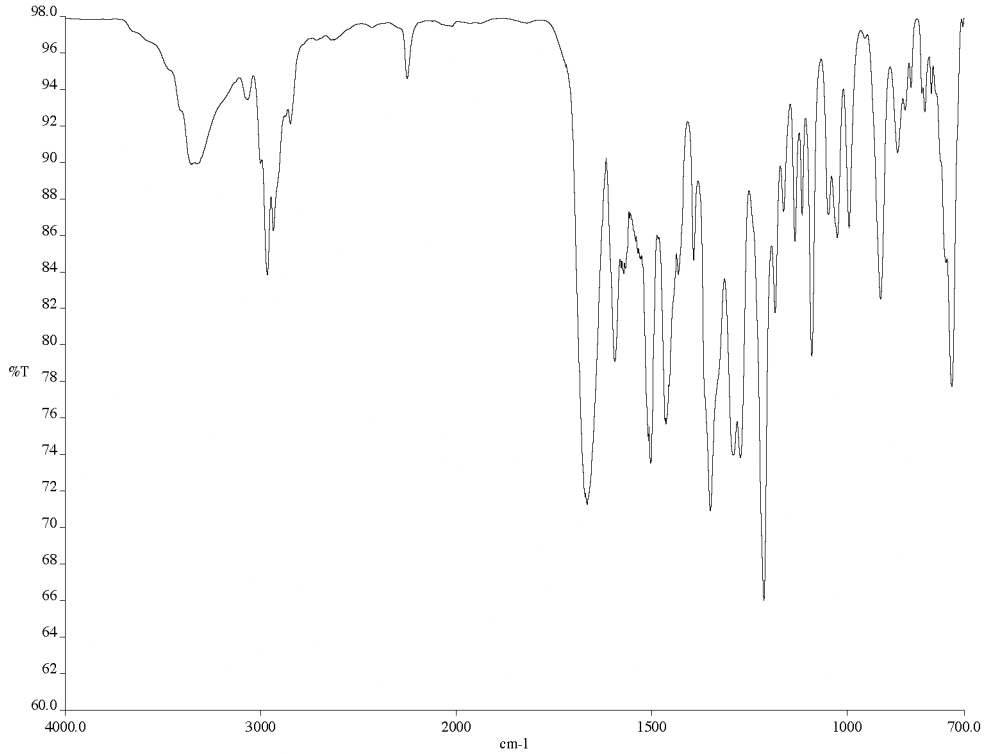


Figure 28.2 Infrared spectrum (thin film/NaCl) of 2:1 mixture of *ortho*-ketobenzamide **16f** and cyclic imidate **16f'**.

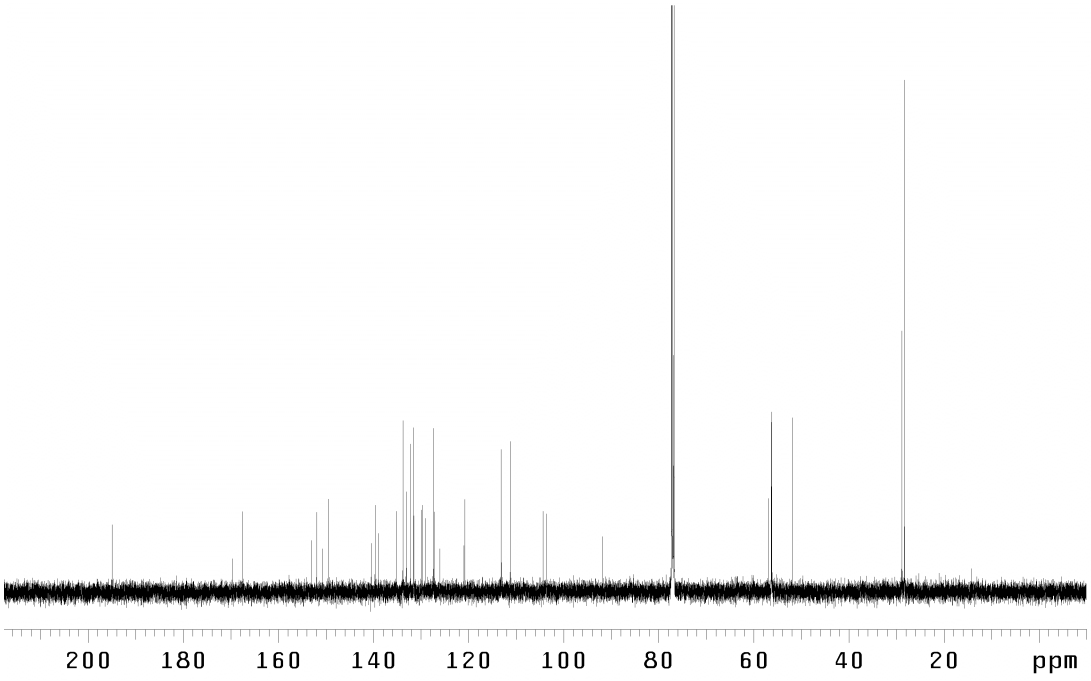


Figure 28.3 ^{13}C NMR (125 MHz, $CDCl_3$) of 2:1 mixture of *ortho*-ketobenzamide **16f** and cyclic imidate **16f'**.

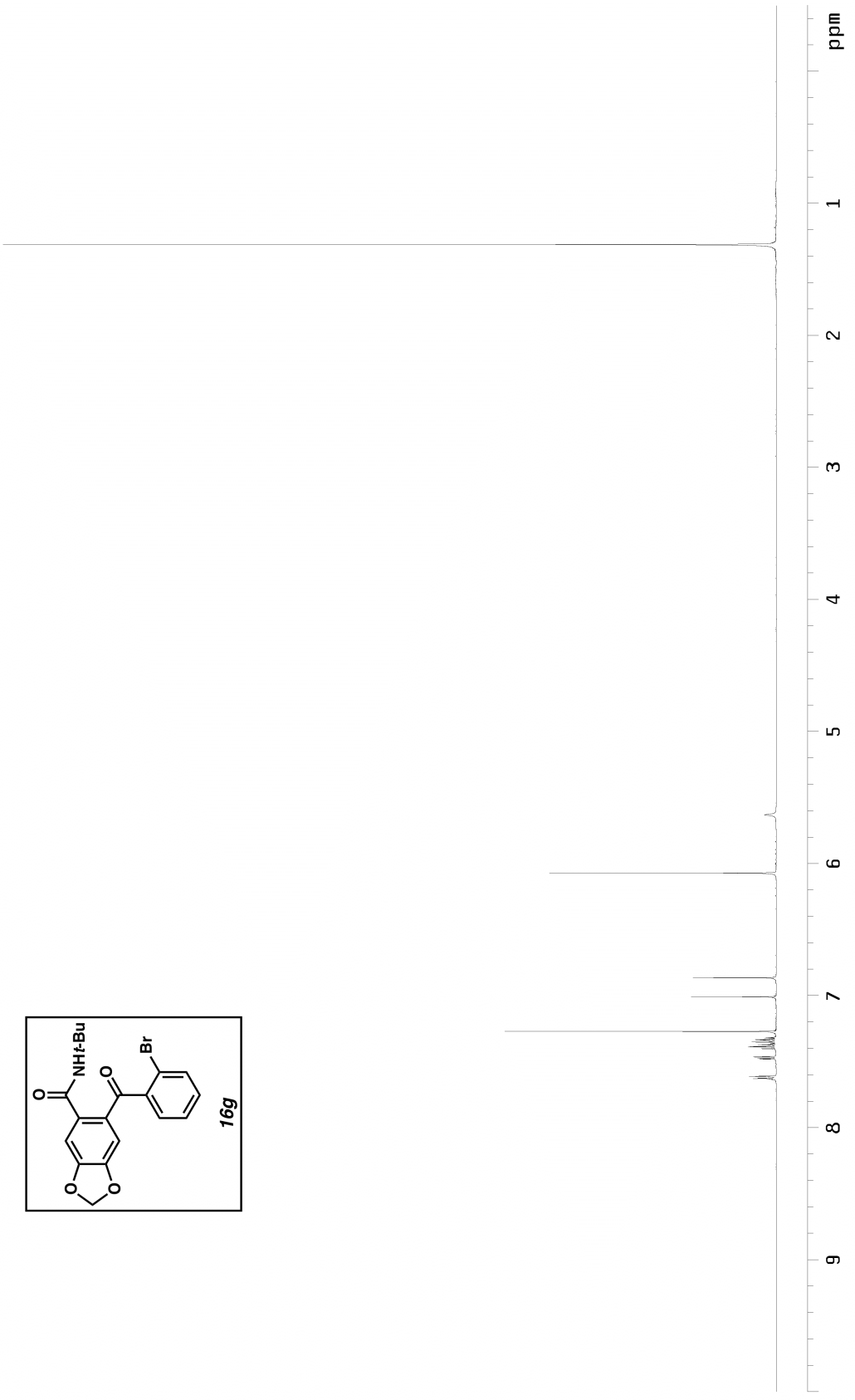


Figure 29.1 ^{1}H NMR (500 MHz, $CDCl_3$) of *ortho*-ketobenzamide **16g**.

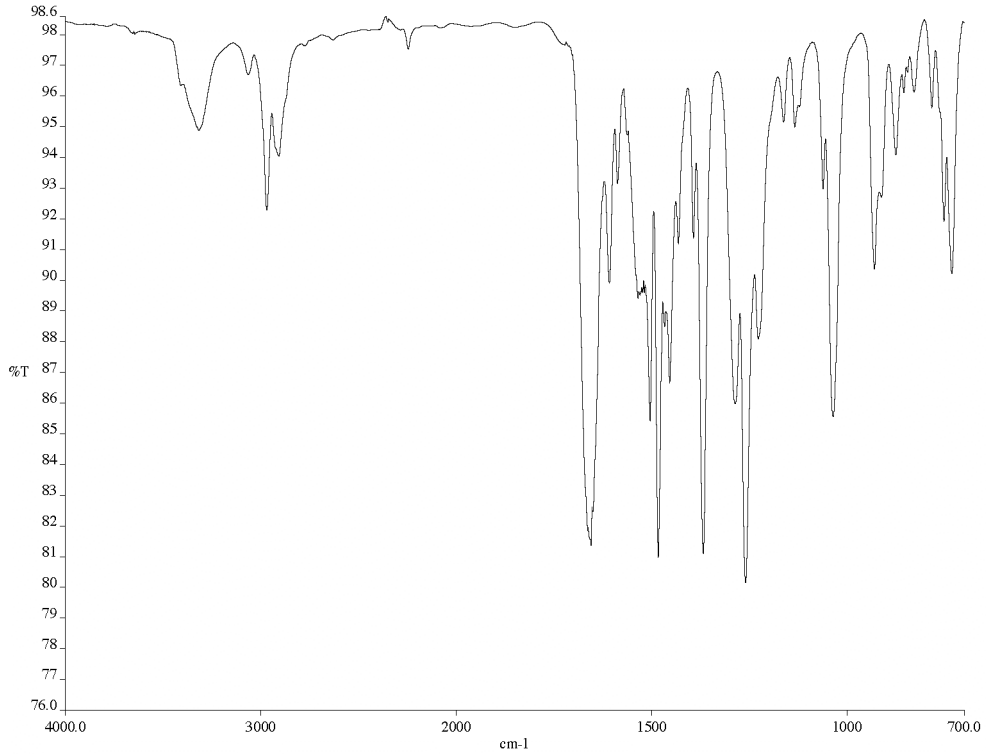


Figure 29.2 Infrared spectrum (thin film/NaCl) of *ortho*-ketobenzamide **16g**.

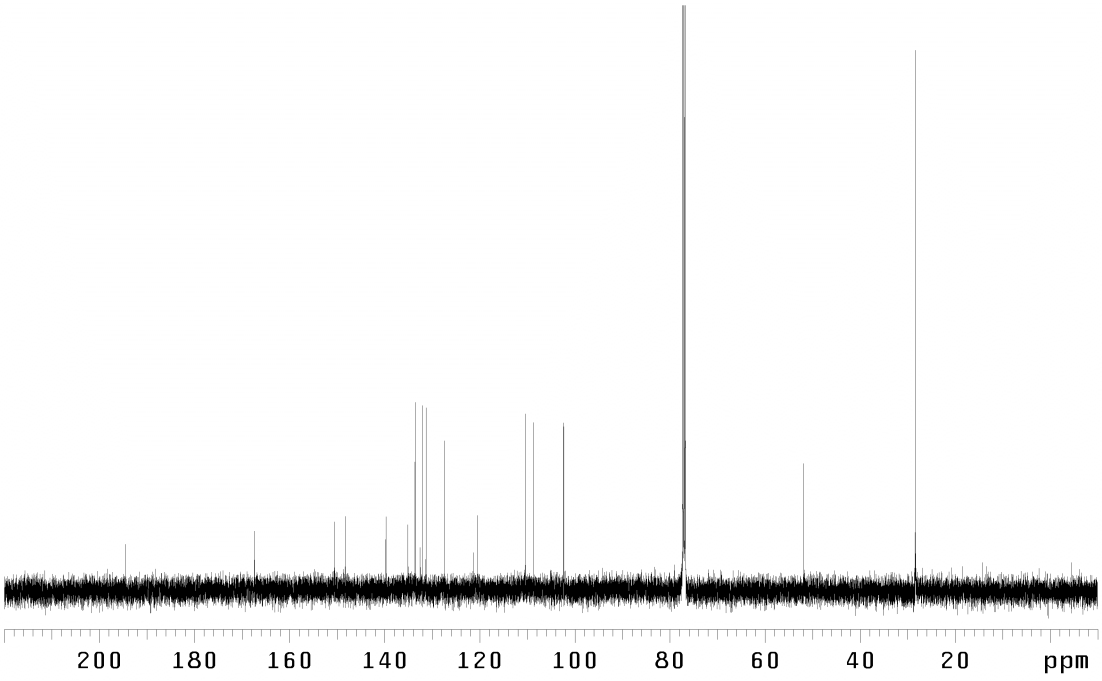


Figure 29.3 ^{13}C NMR (125 MHz, $CDCl_3$) of *ortho*-ketobenzamide **16g**.

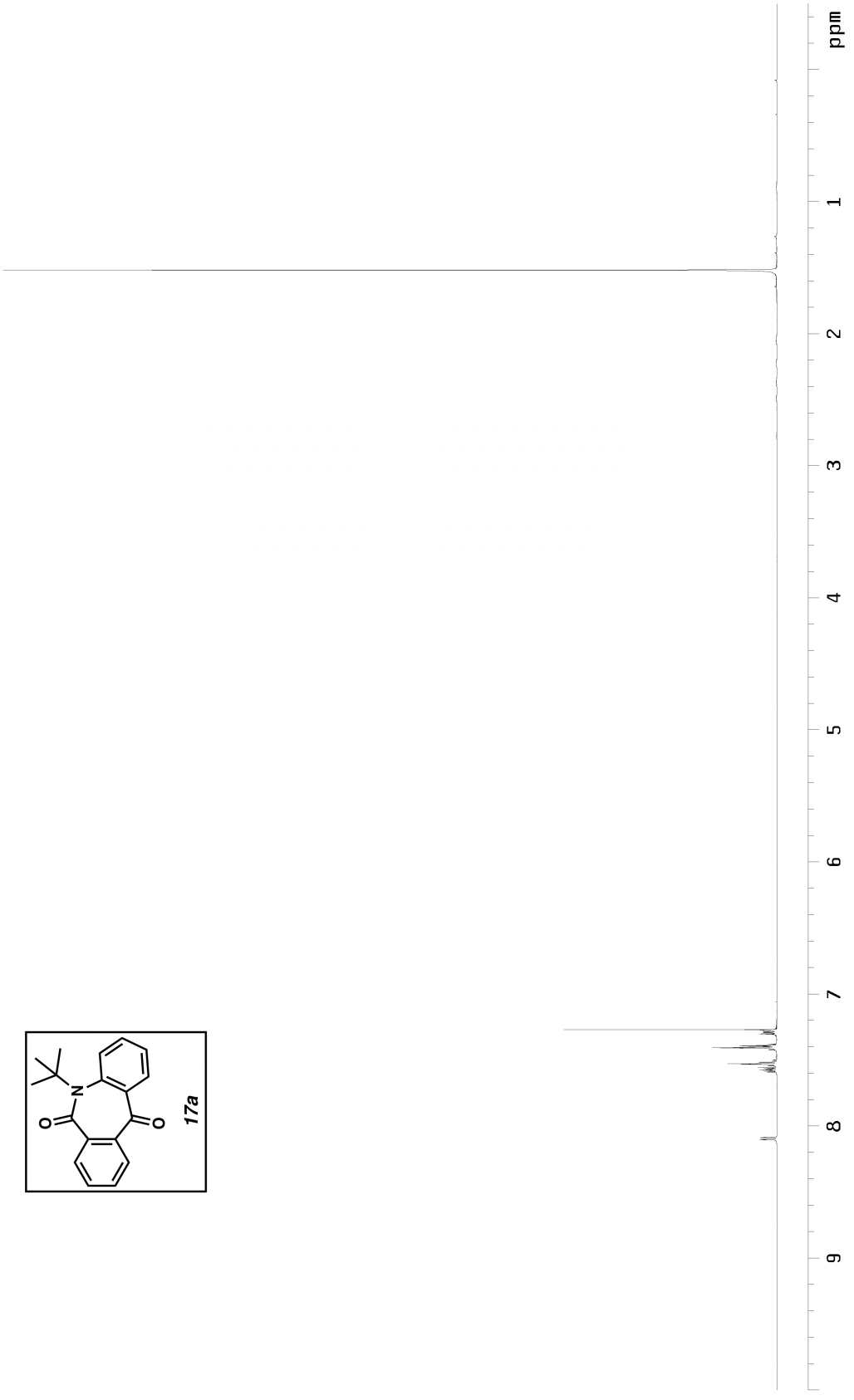


Figure 30.1 ^{1}H NMR (500 MHz, $CDCl_3$) of dibenzoketocaprolactam **17a**.

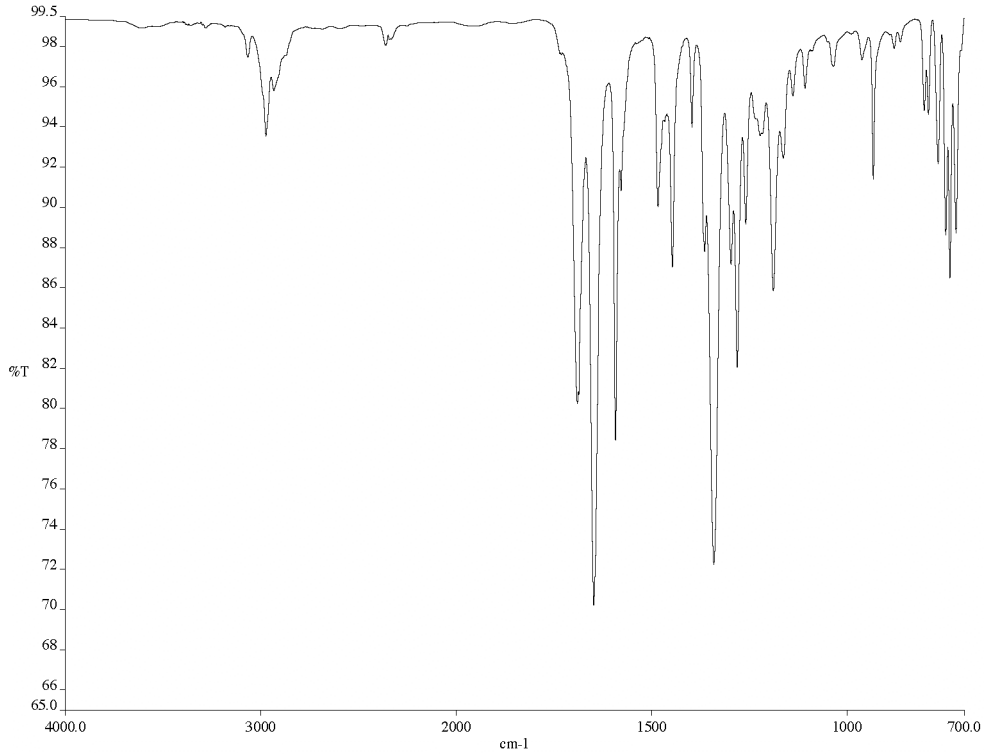


Figure 30.2 Infrared spectrum (thin film/NaCl) of dibenzoketocaprolactam **17a**.

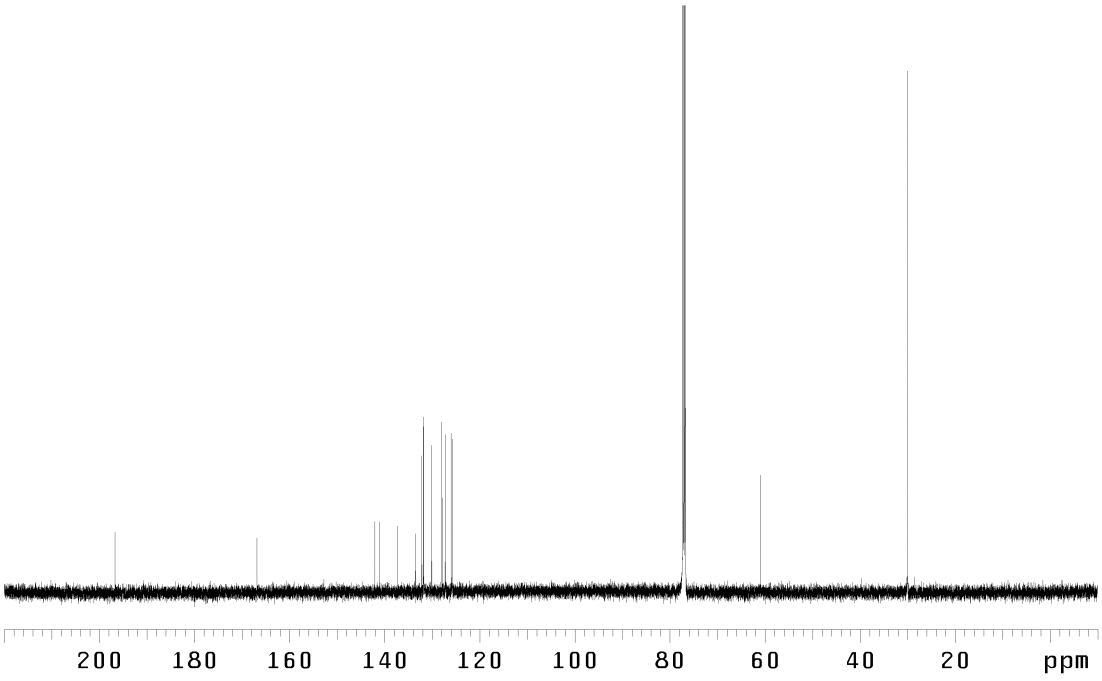


Figure 30.3 ^{13}C NMR (125 MHz, $CDCl_3$) of dibenzoketocaprolactam **17a**.

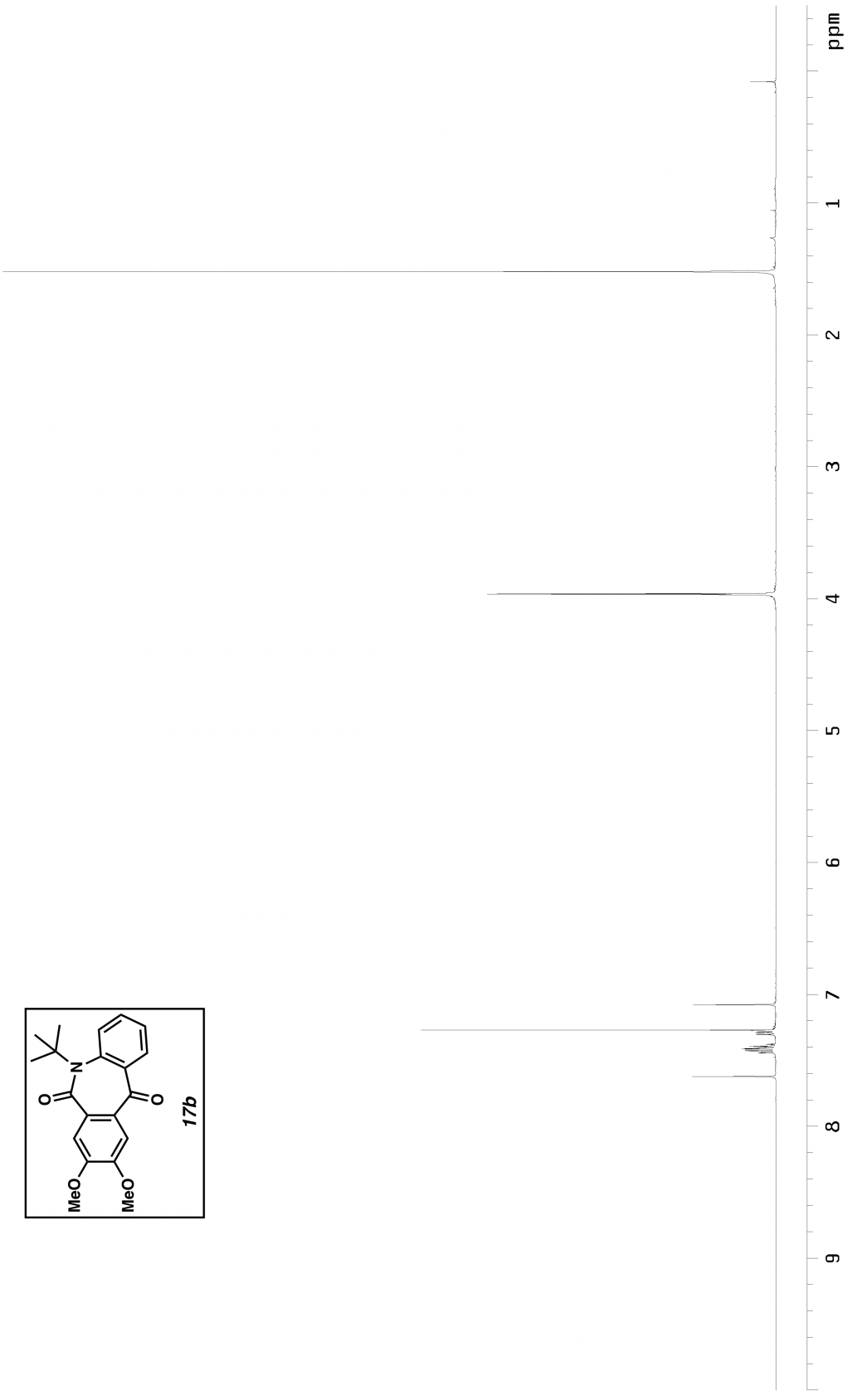


Figure 31.1 ^{1}H NMR (500 MHz, $CDCl_3$) of dibenzoketocaprolactam **17b**.

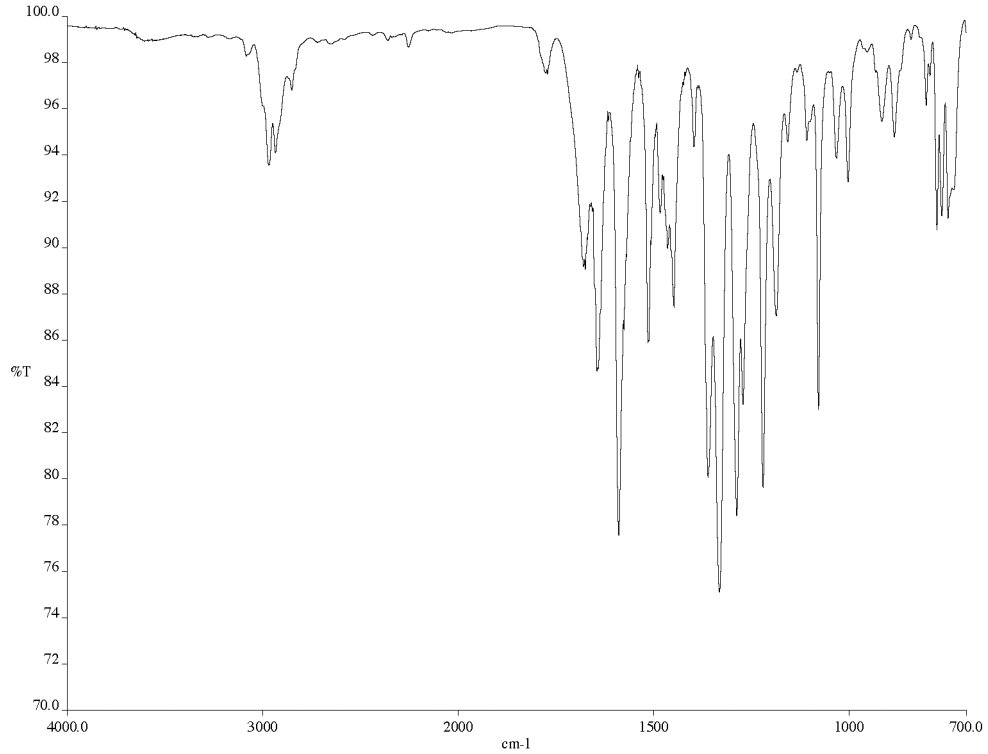


Figure 31.2 Infrared spectrum (thin film/NaCl) of dibenzoketocaprolactam **17b**.

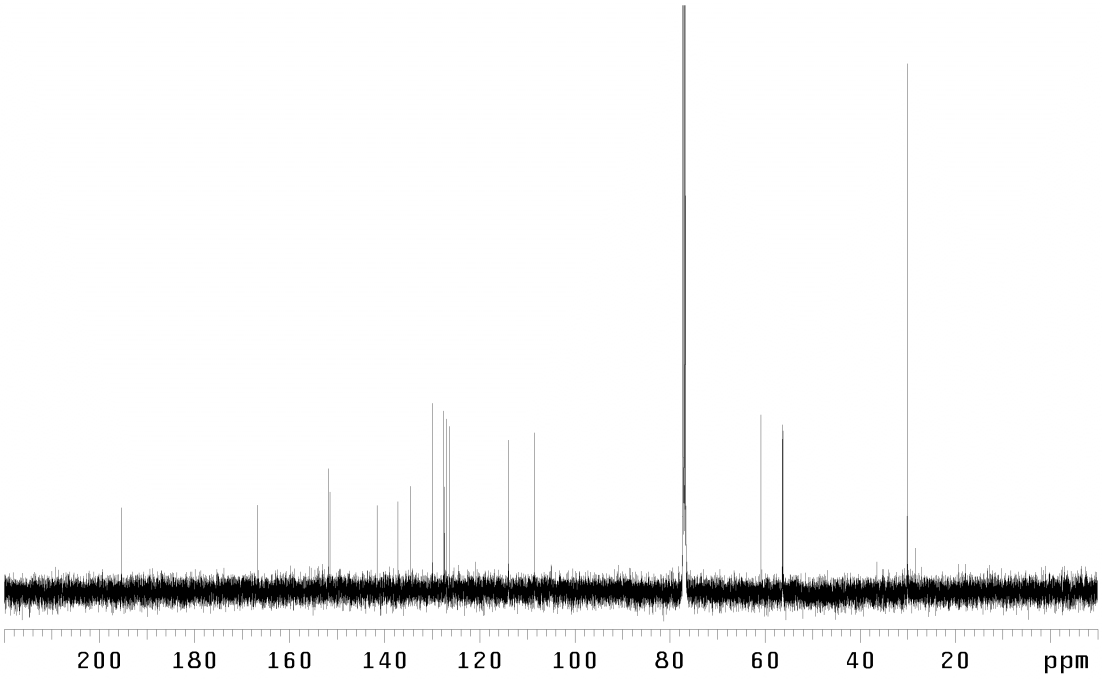


Figure 31.3 ^{13}C NMR (125 MHz, $CDCl_3$) of dibenzoketocaprolactam **17b**.

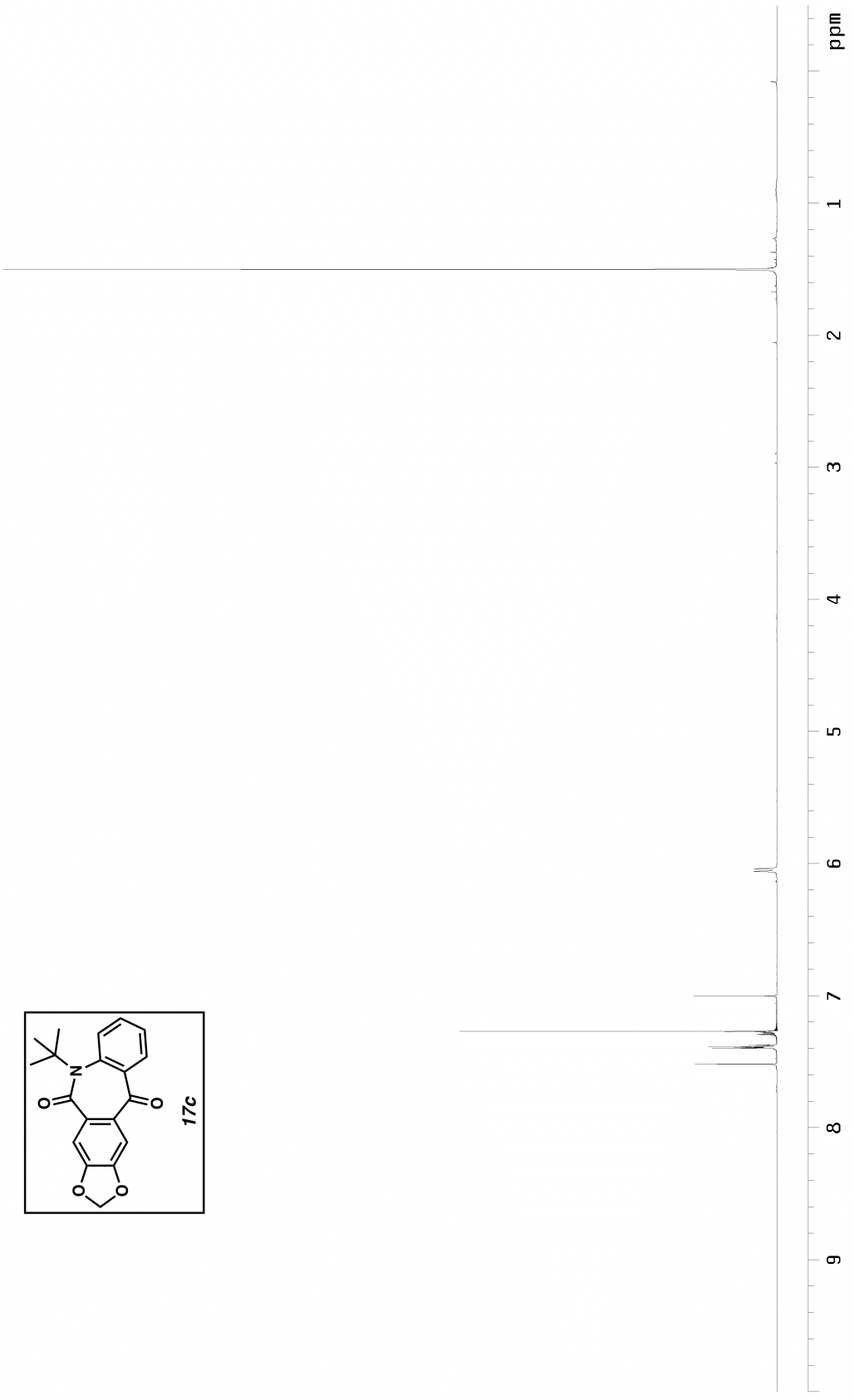


Figure 32.1 ^{1}H NMR (500 MHz, $CDCl_3$) of dibenzoketocaprolactam **17c**.

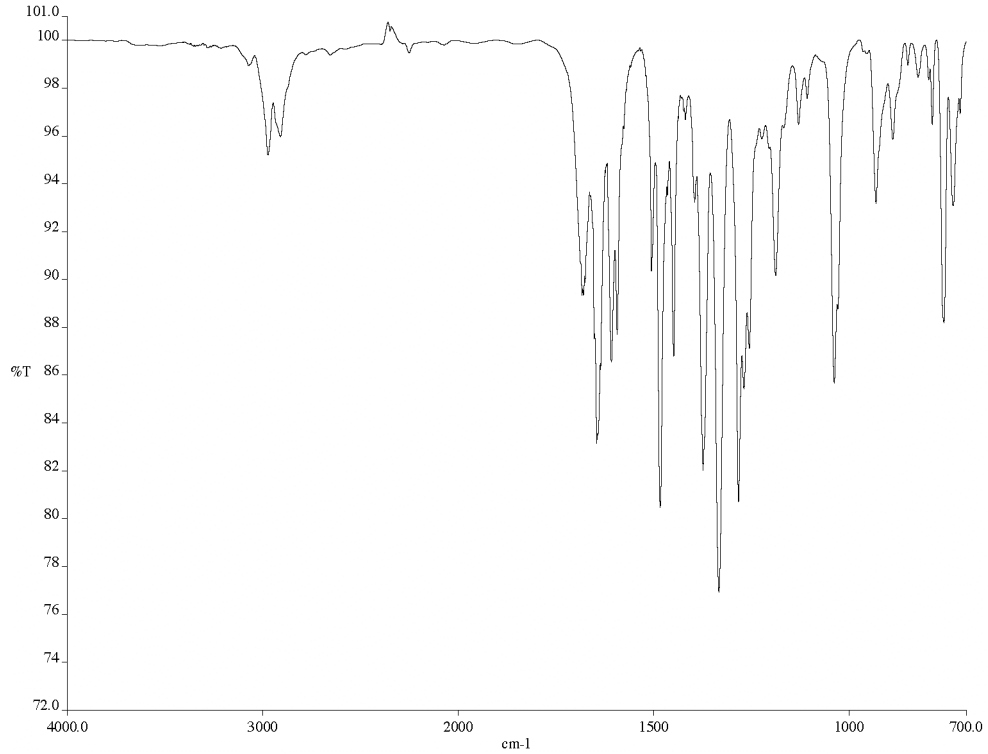


Figure 32.2 Infrared spectrum (thin film/NaCl) of dibenzoketocaprolactam **17c**.

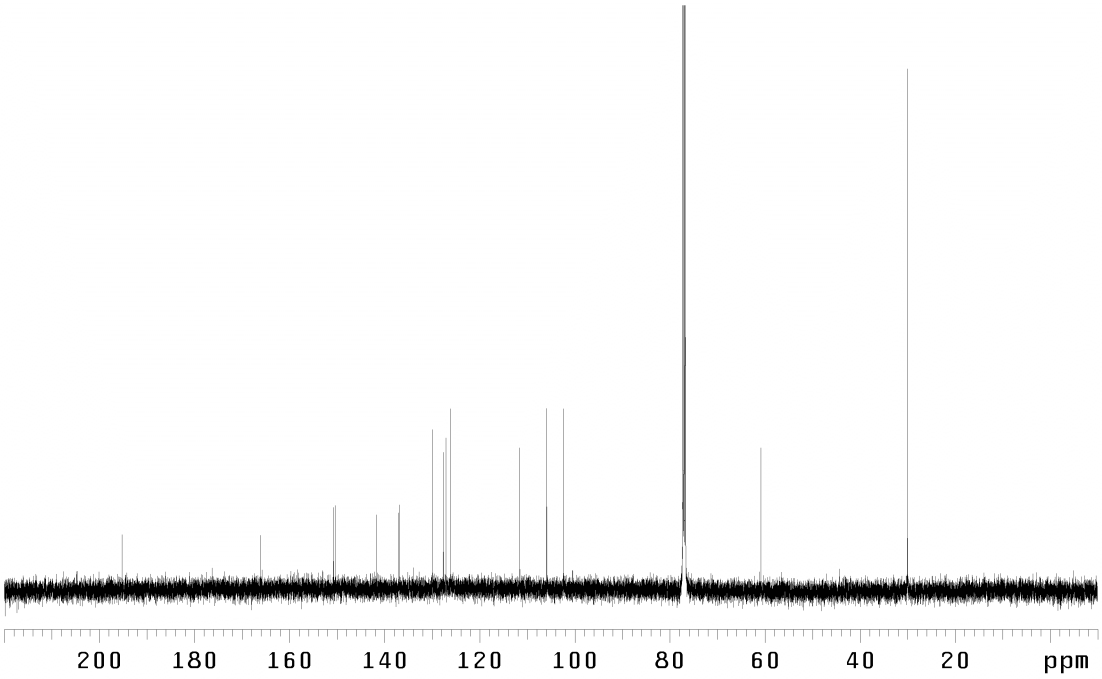


Figure 32.3 ^{13}C NMR (125 MHz, $CDCl_3$) of dibenzoketocaprolactam **17c**.

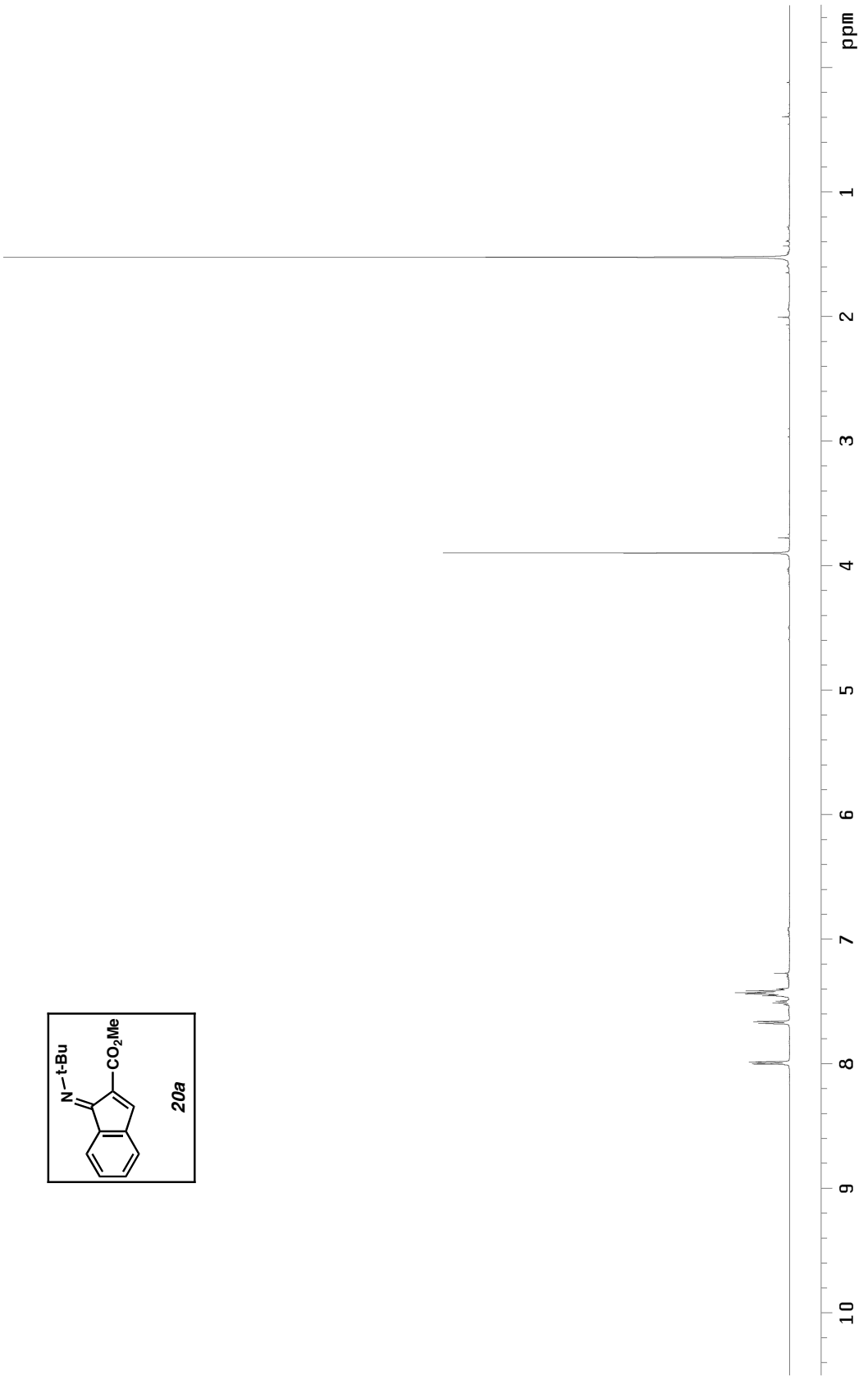


Figure 33.1 ^{1}H NMR (500 MHz, $CDCl_3$) of compound **20a**.

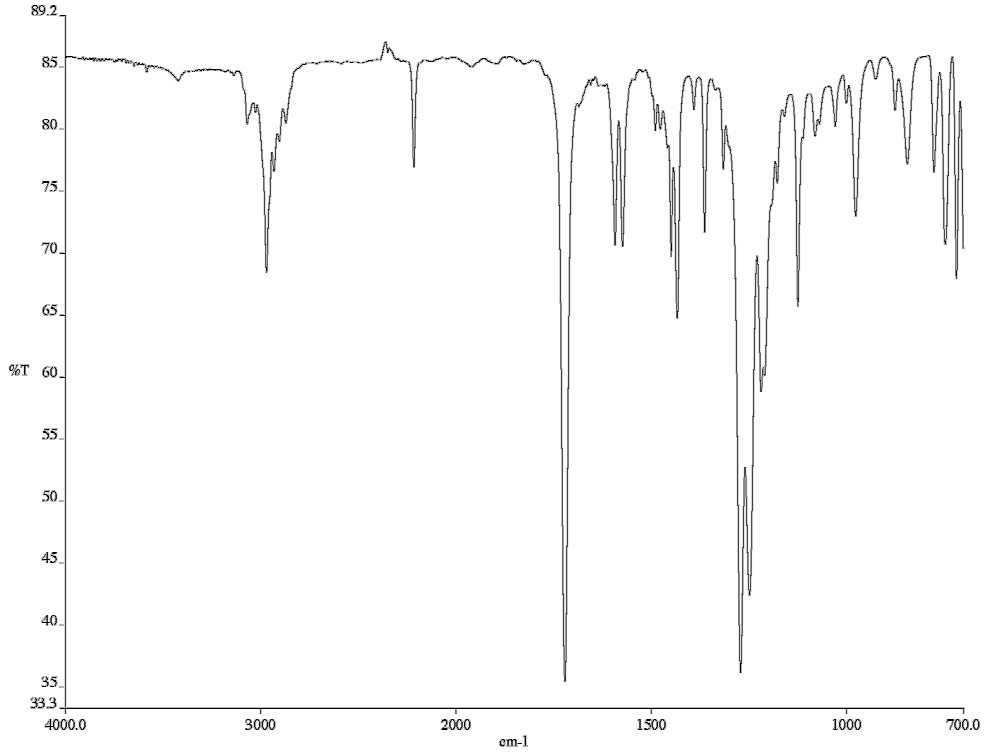


Figure 33.2 Infrared spectrum (thin film/NaCl) of compound **20a**.

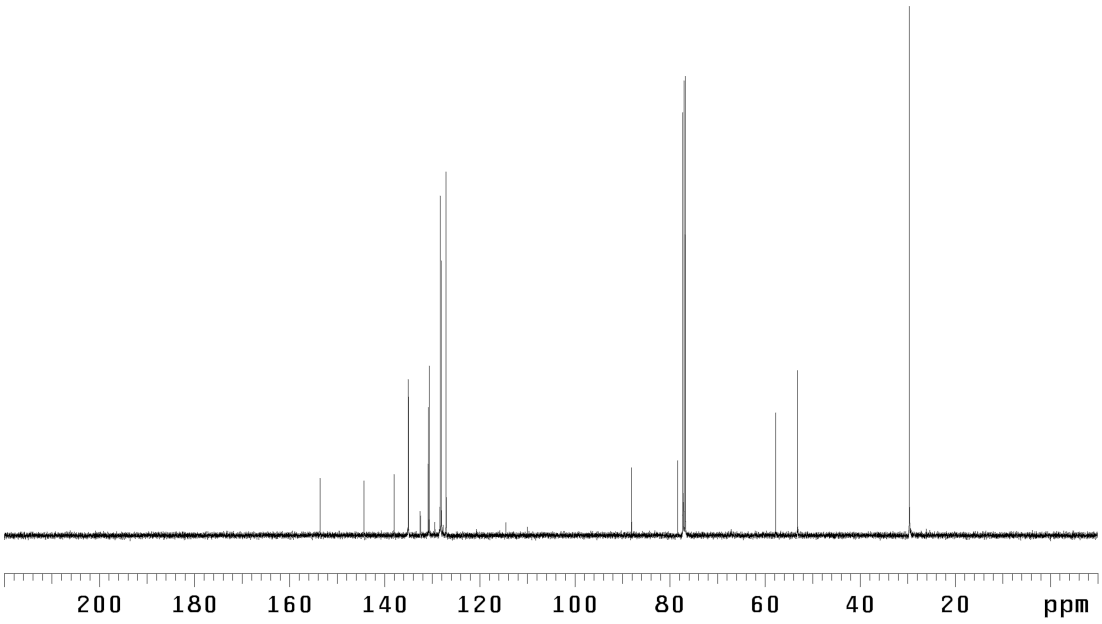


Figure 33.3 ^{13}C NMR (125 MHz, $CDCl_3$) of compound **20a**.

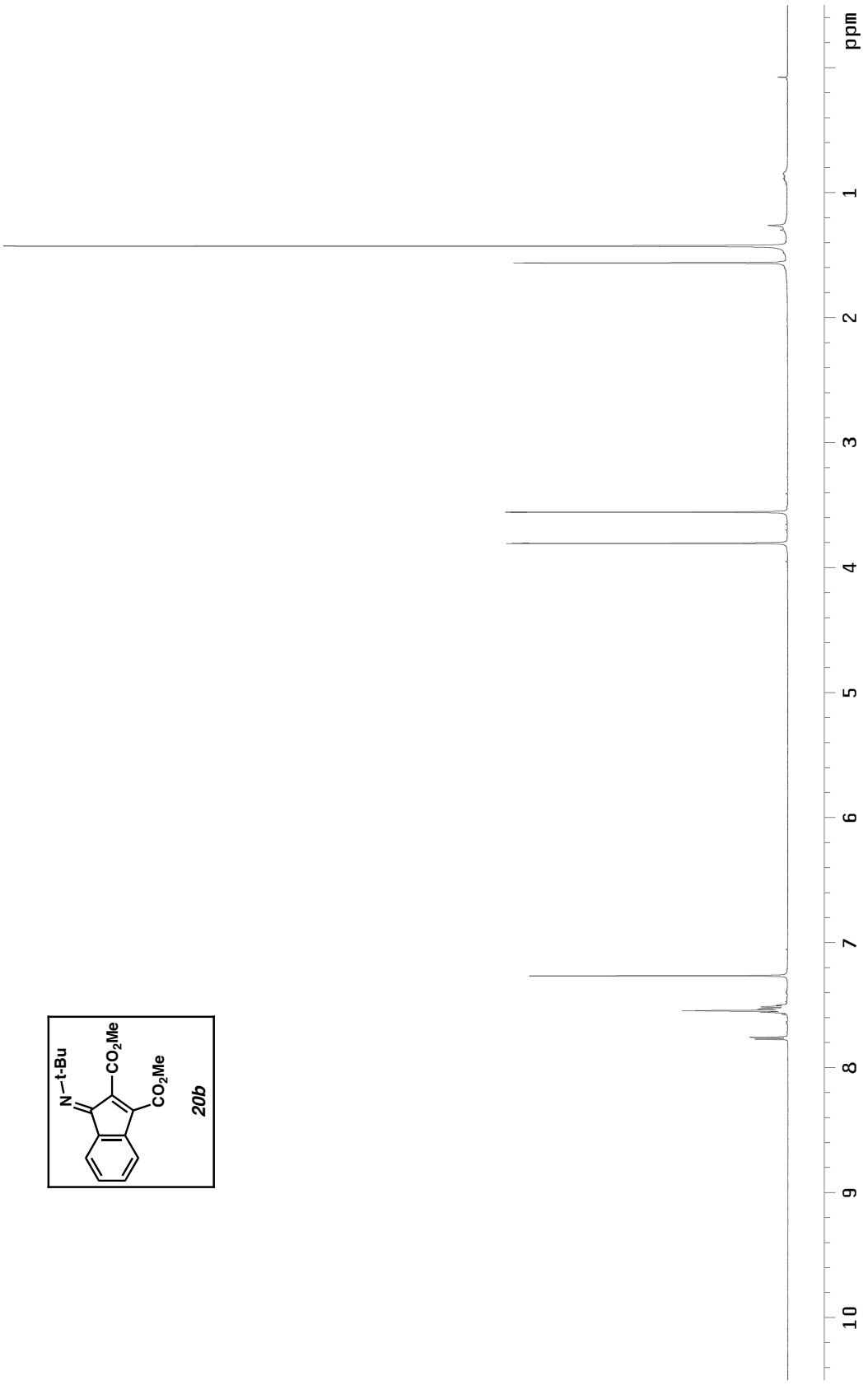


Figure 34.1 ^{1}H NMR (500 MHz, $CDCl_3$) of compound **20b**.

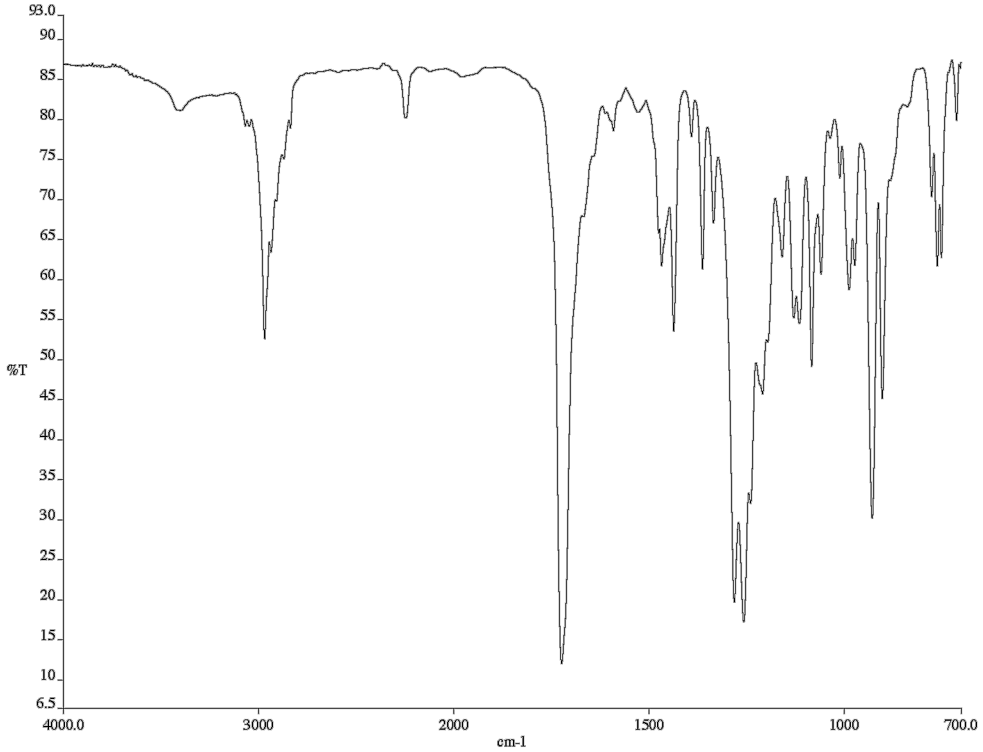


Figure 34.2 Infrared spectrum (thin film/NaCl) of compound **20b**.

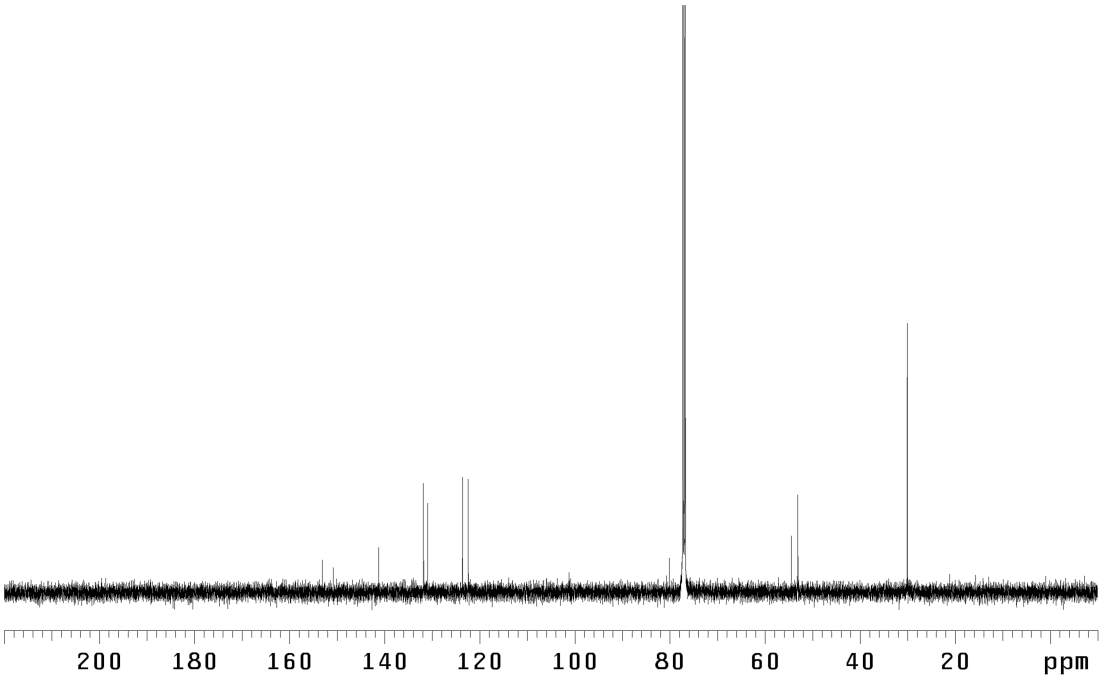


Figure 34.3 ^{13}C NMR (125 MHz, $CDCl_3$) of compound **20b**.

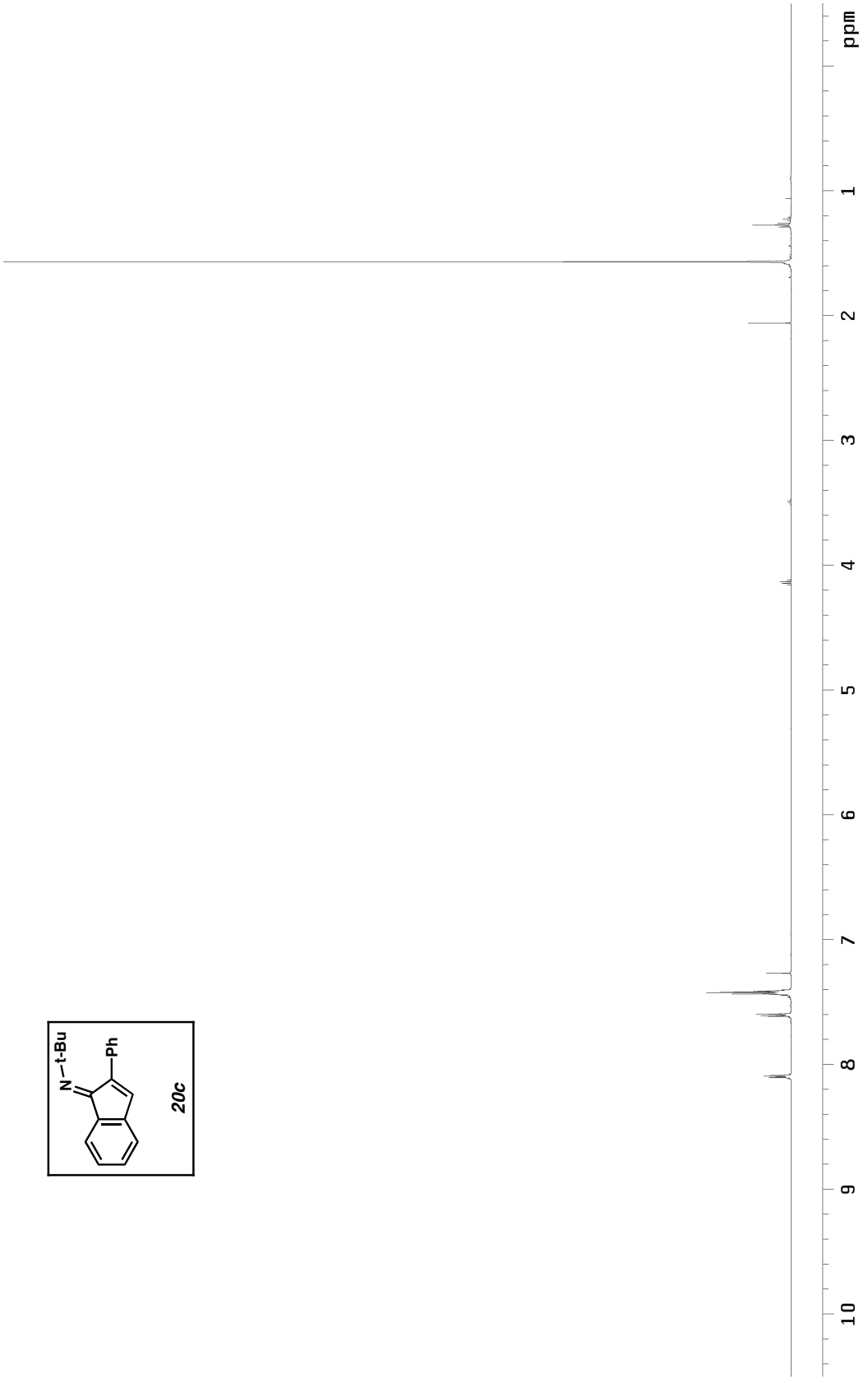


Figure 35.1 ^{1}H NMR (500 MHz, $CDCl_3$) of compound **20c**.

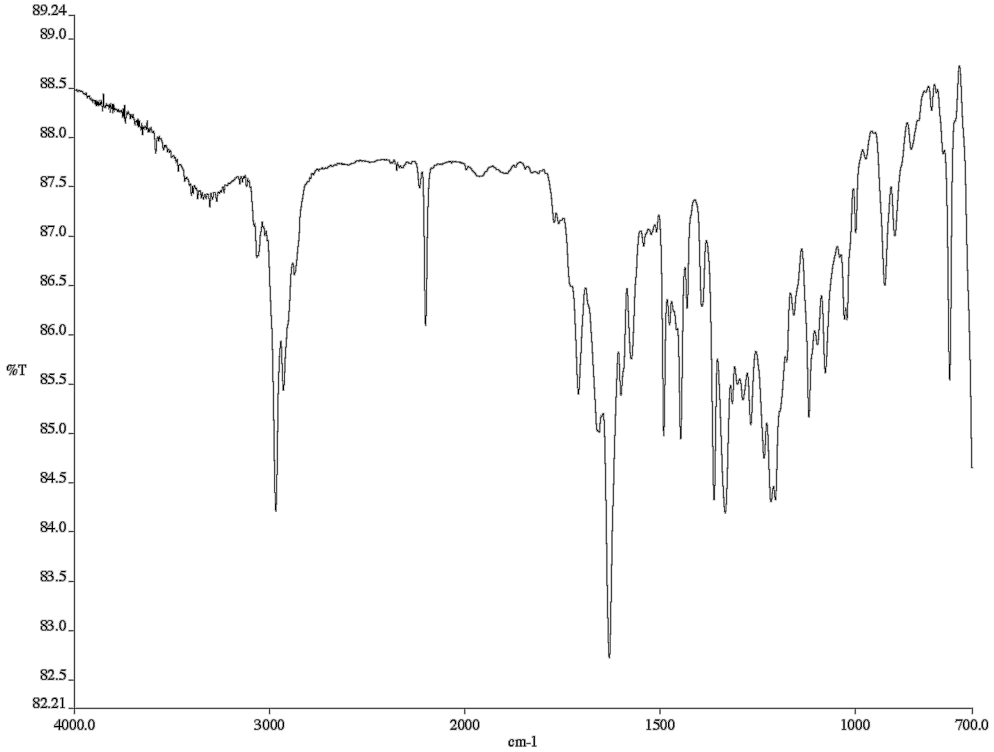


Figure 35.2 Infrared spectrum (thin film/NaCl) of compound **20c**.

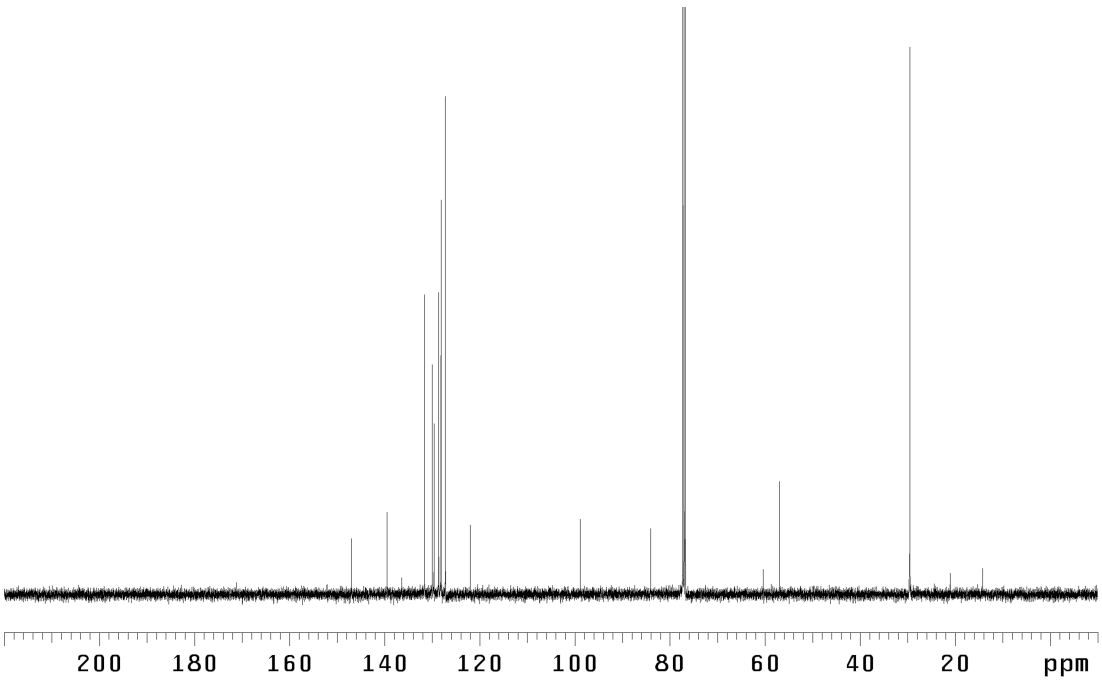


Figure 35.3 ^{13}C NMR (125 MHz, $CDCl_3$) of compound **20c**.

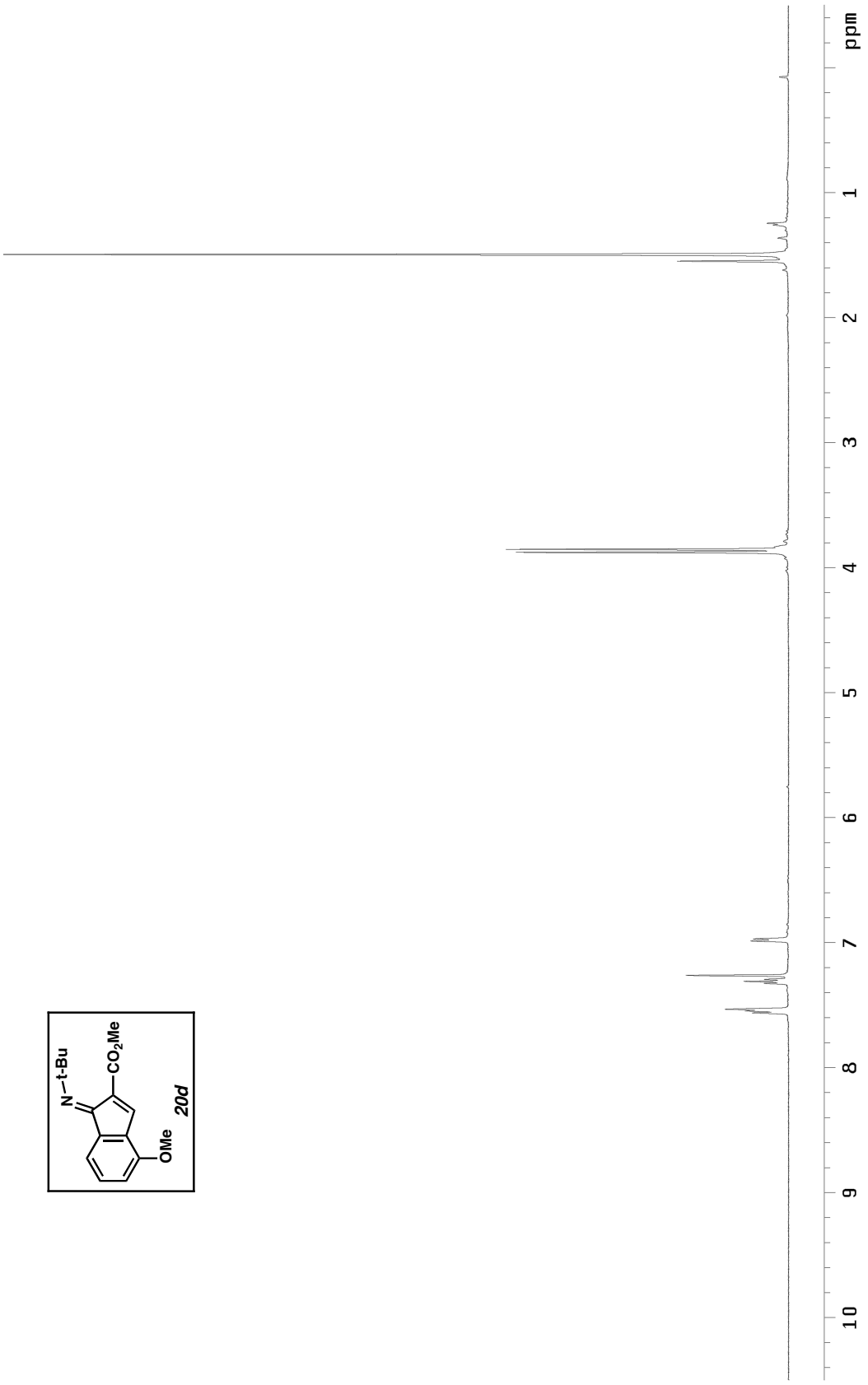


Figure 36.1 ^{1}H NMR (500 MHz, $CDCl_3$) of compound **20d**.

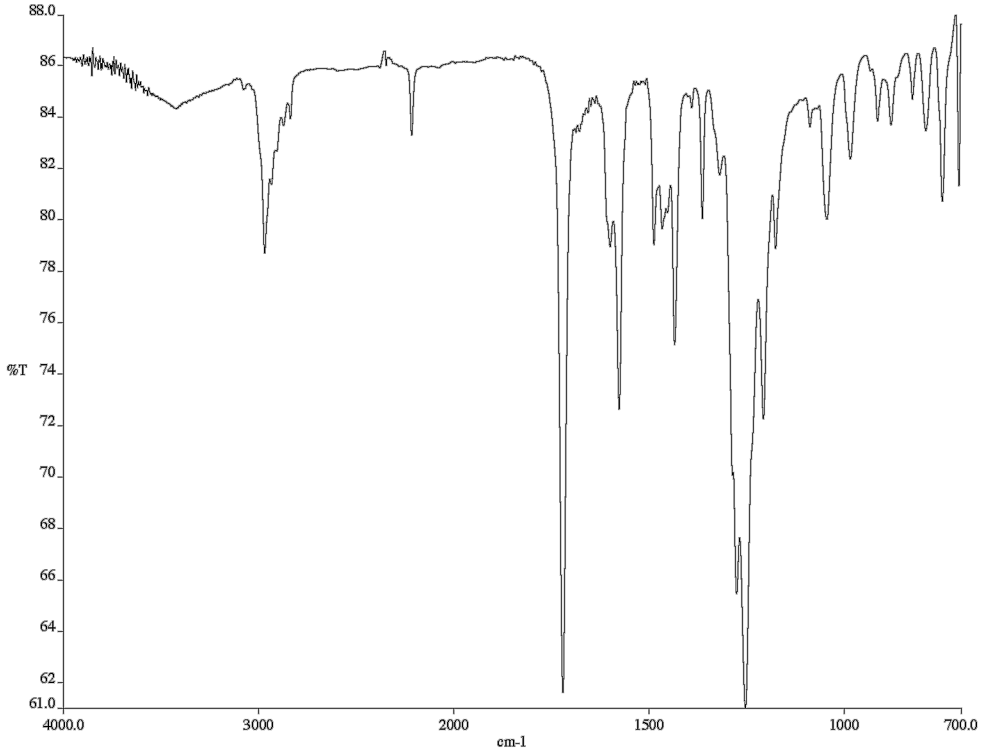


Figure 36.2 Infrared spectrum (thin film/NaCl) of compound **20d**.

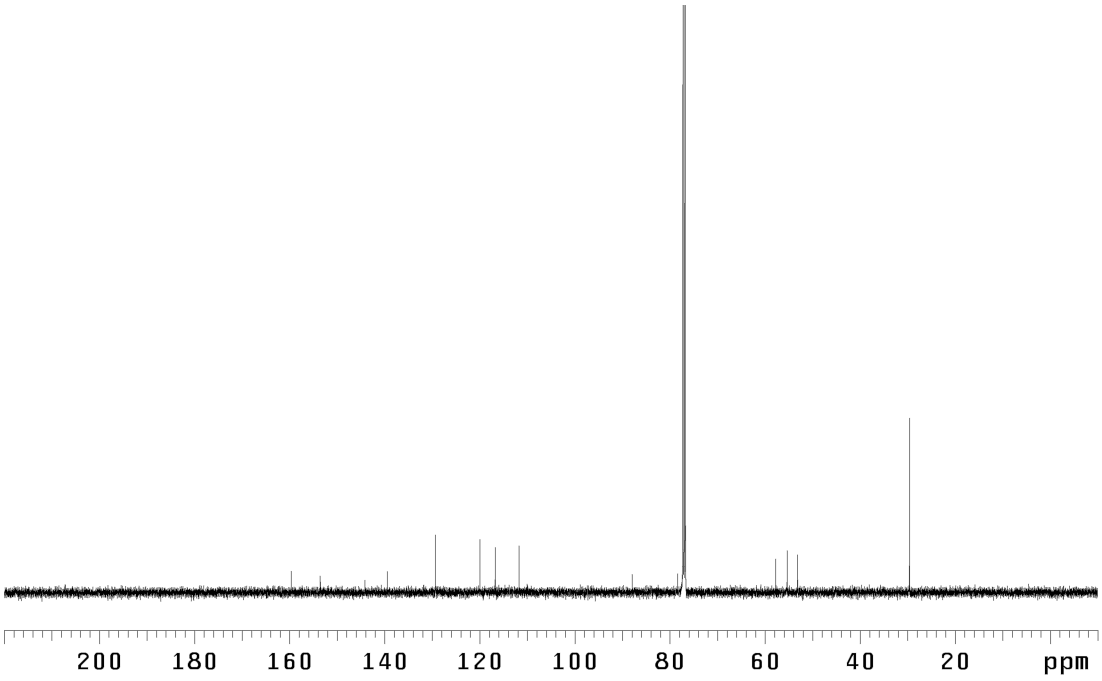


Figure 36.3 ^{13}C NMR (125 MHz, $CDCl_3$) of compound **20d**.

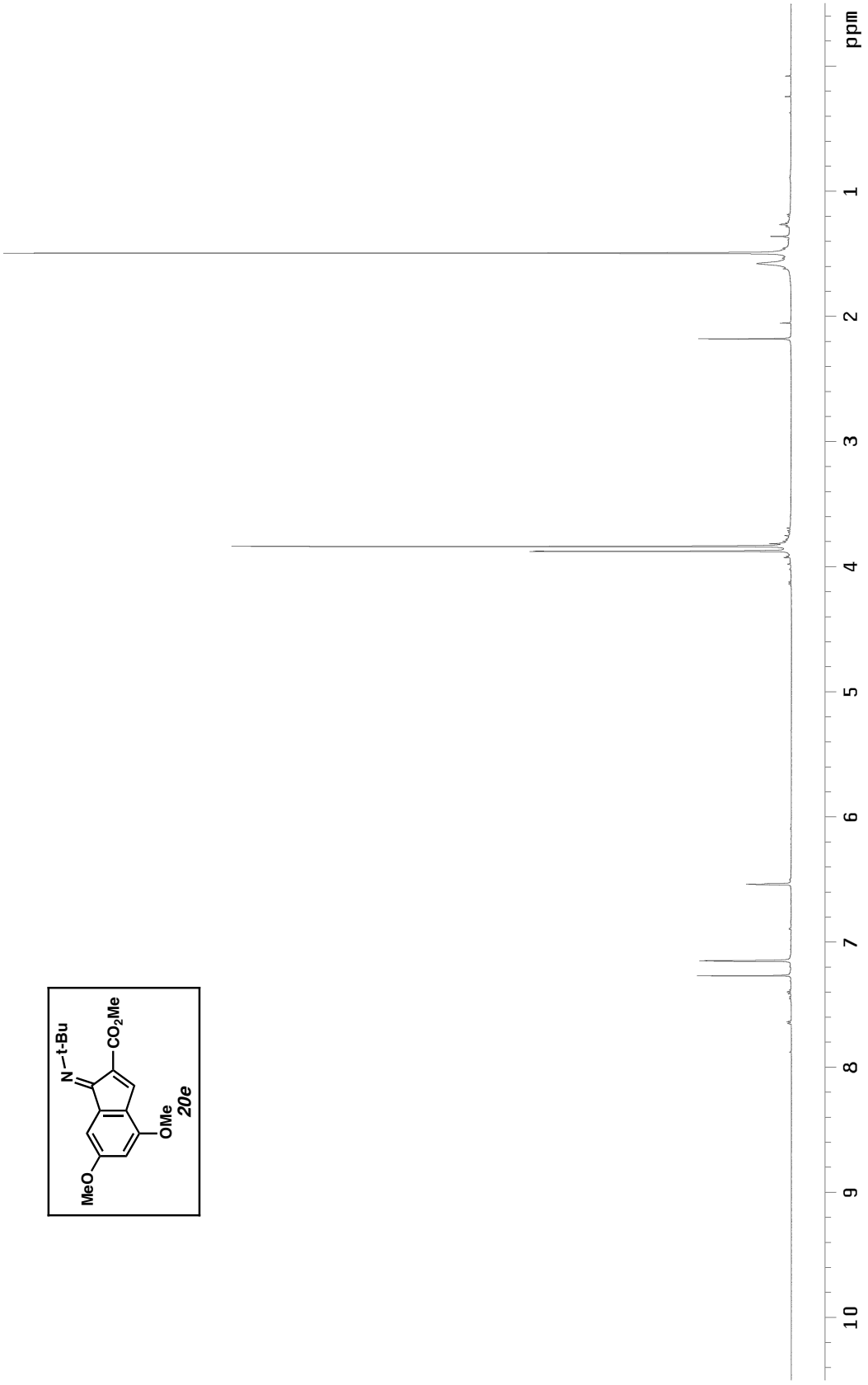


Figure 37.1 ^{1}H NMR (500 MHz, $CDCl_3$) of compound **20e**.

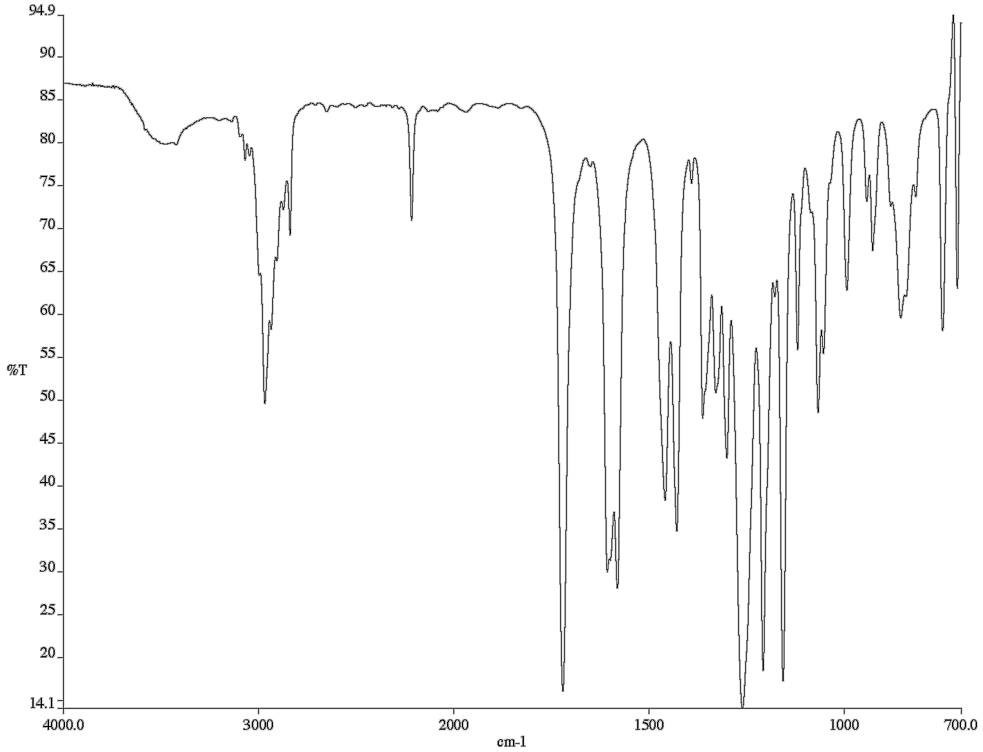


Figure 37.2 Infrared spectrum (thin film/NaCl) of compound **20e**.

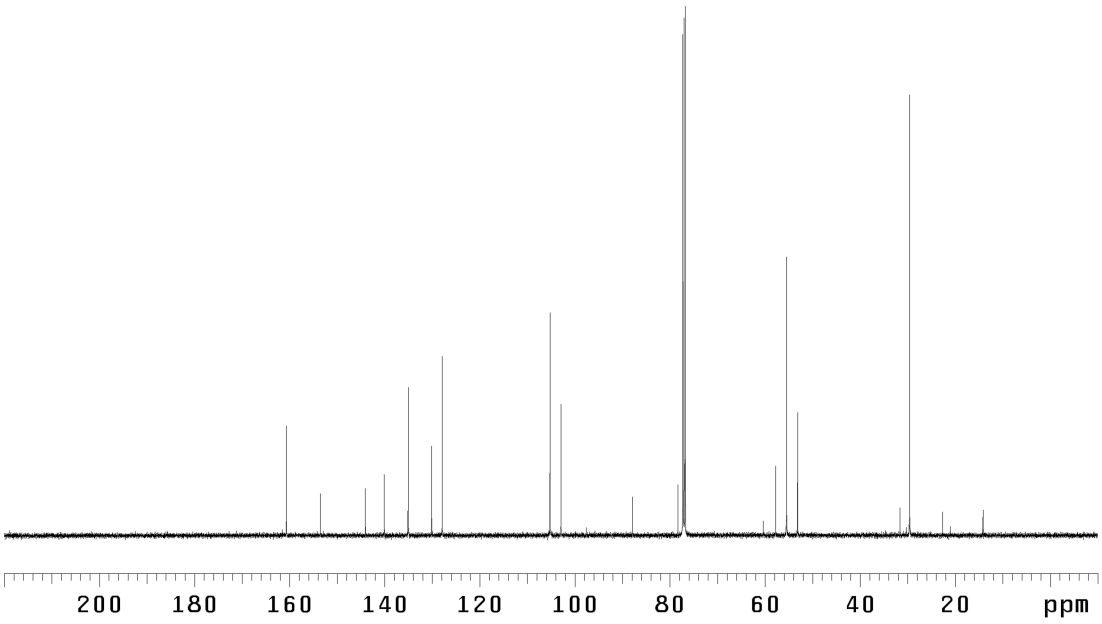


Figure 37.3 ^{13}C NMR (125 MHz, $CDCl_3$) of compound **20e**.

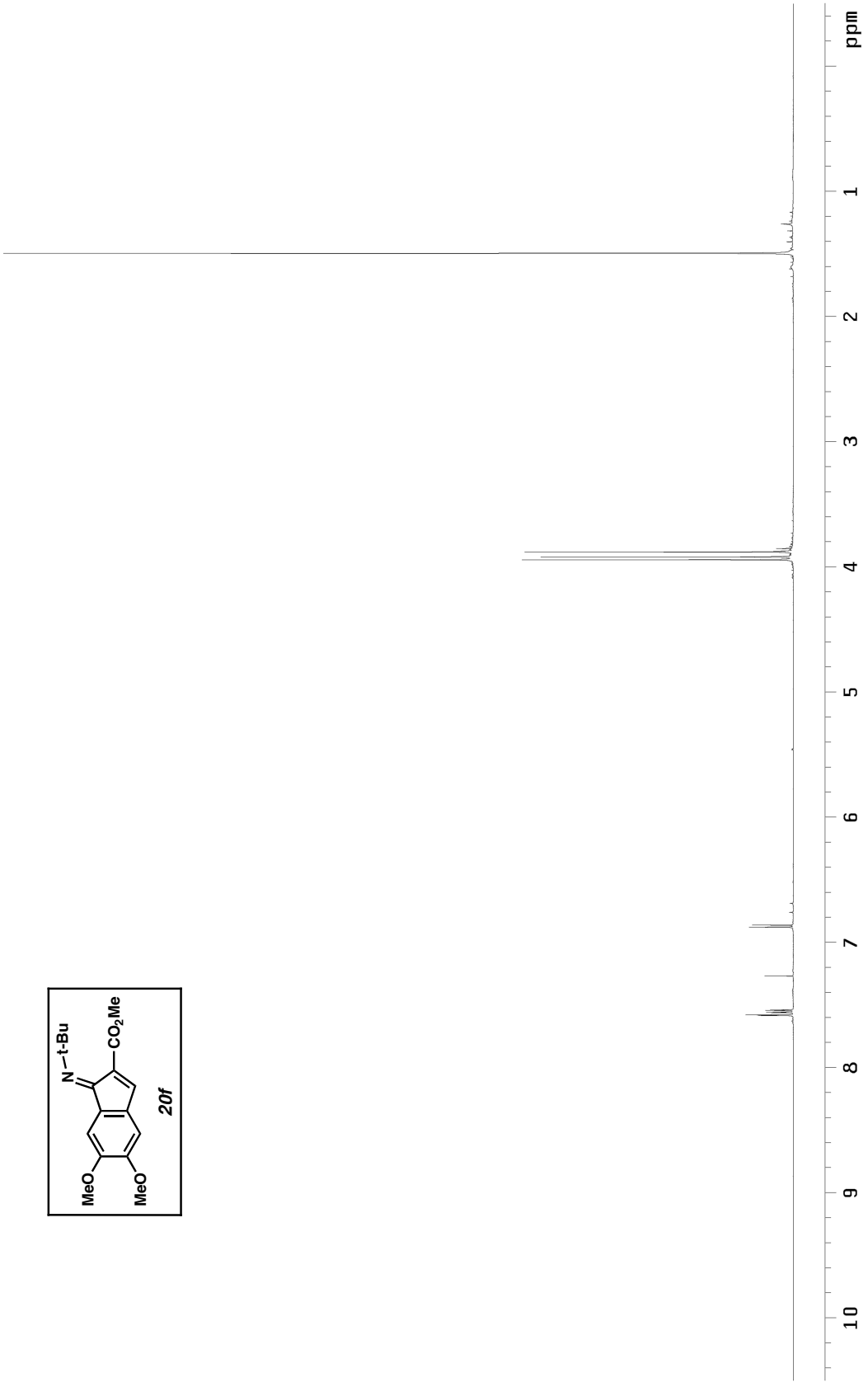


Figure 38.1 ^{1}H NMR (500 MHz, $CDCl_3$) of compound **20f**.

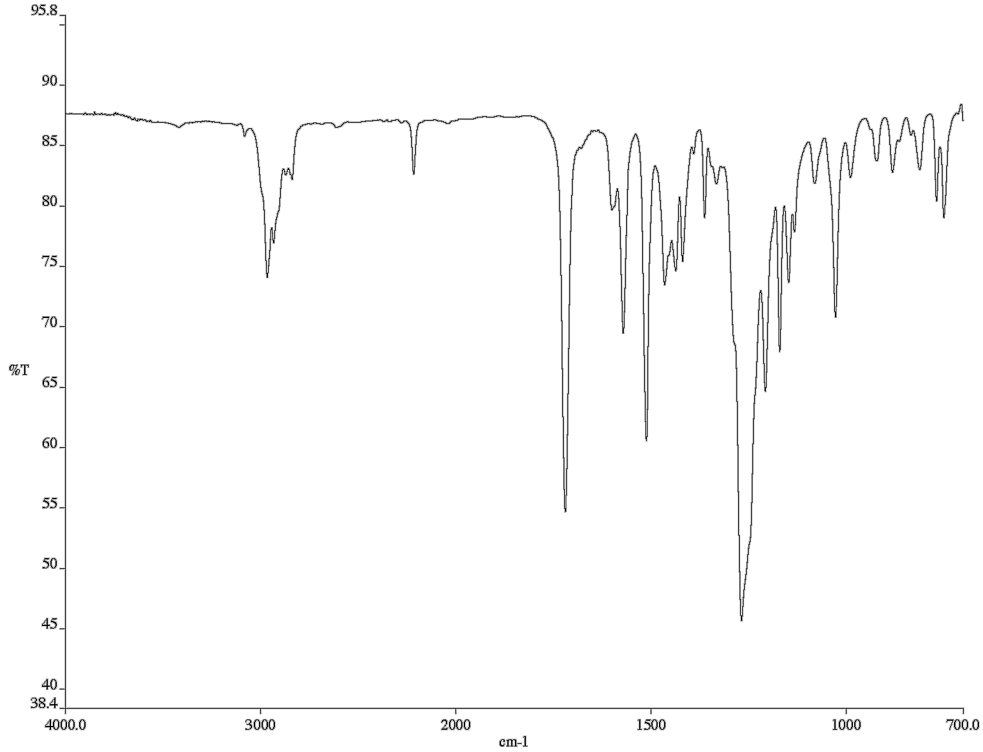


Figure 38.2 Infrared spectrum (thin film/NaCl) of compound **20f**.

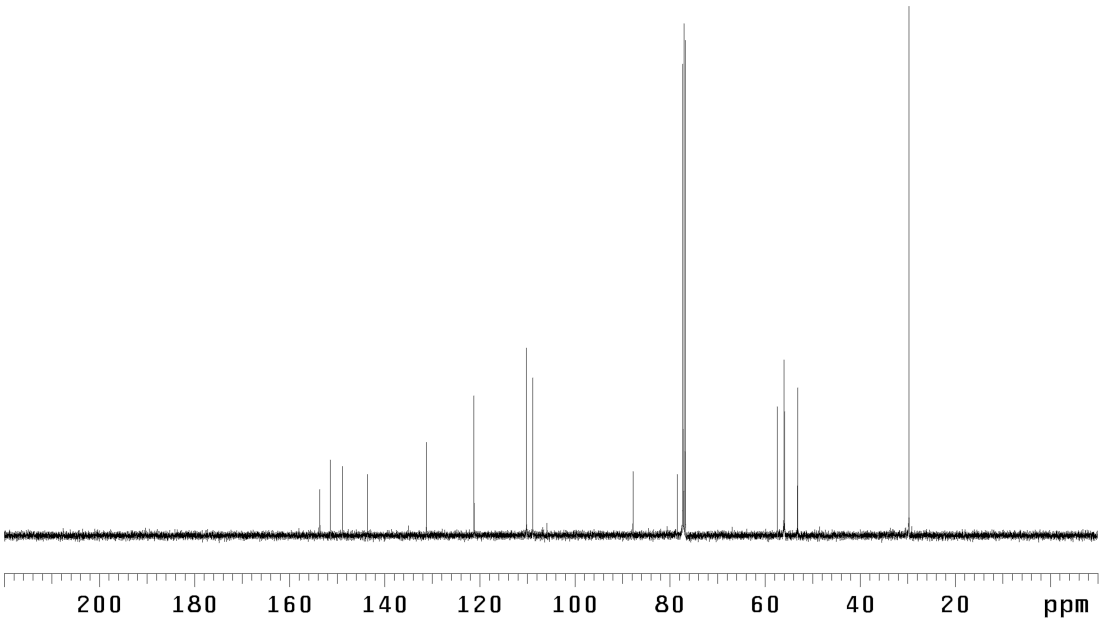


Figure 38.3 ^{13}C NMR (125 MHz, $CDCl_3$) of compound **20f**.

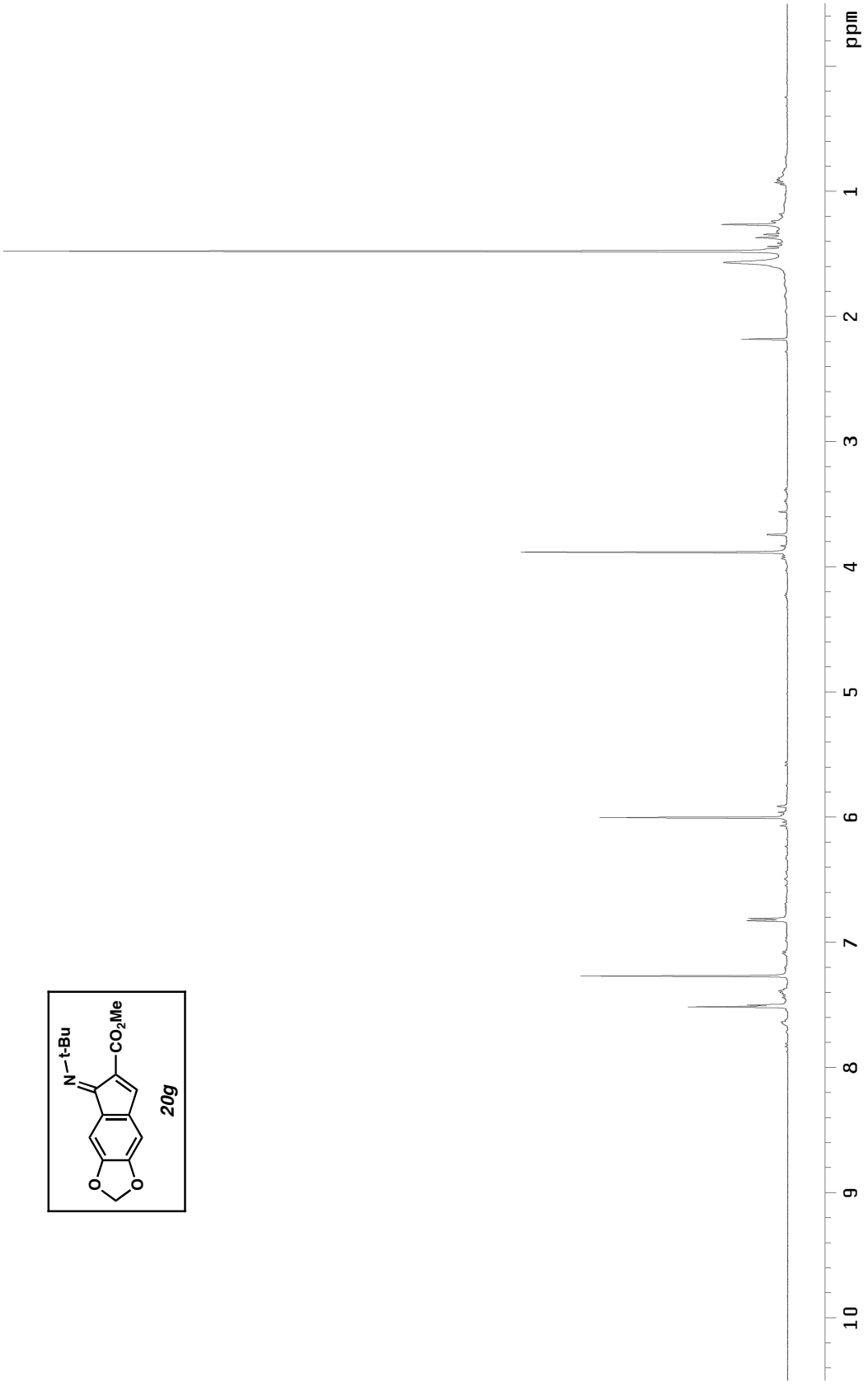


Figure 39.1 ^{1}H NMR (500 MHz, $CDCl_3$) of compound **20g**.

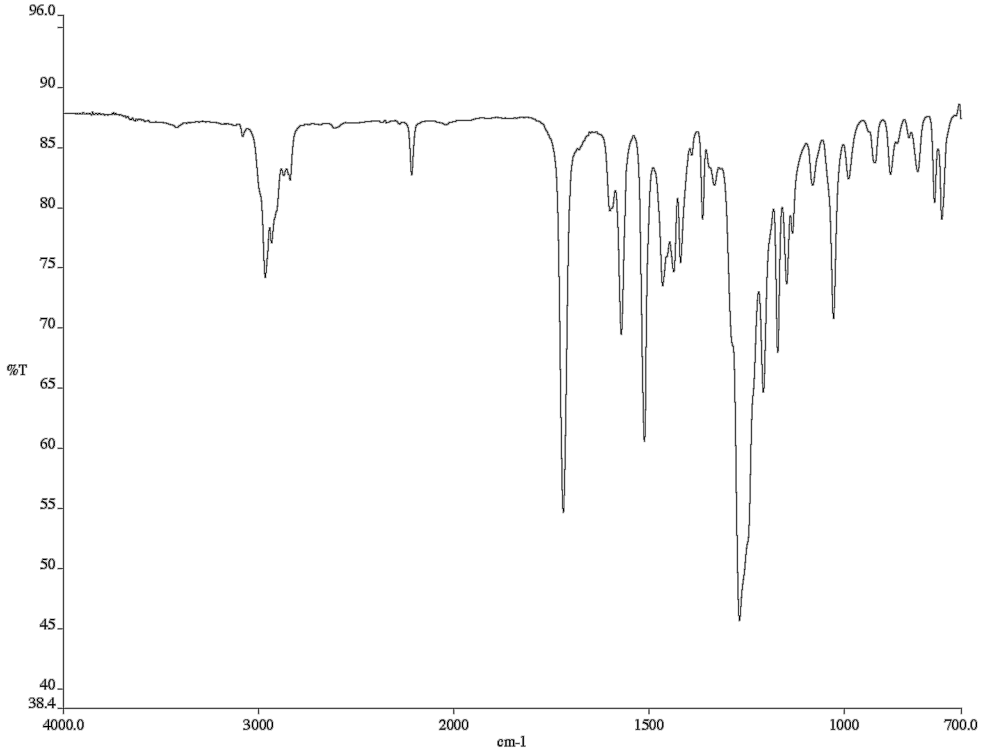


Figure 39.2 Infrared spectrum (thin film/NaCl) of compound **20g**.

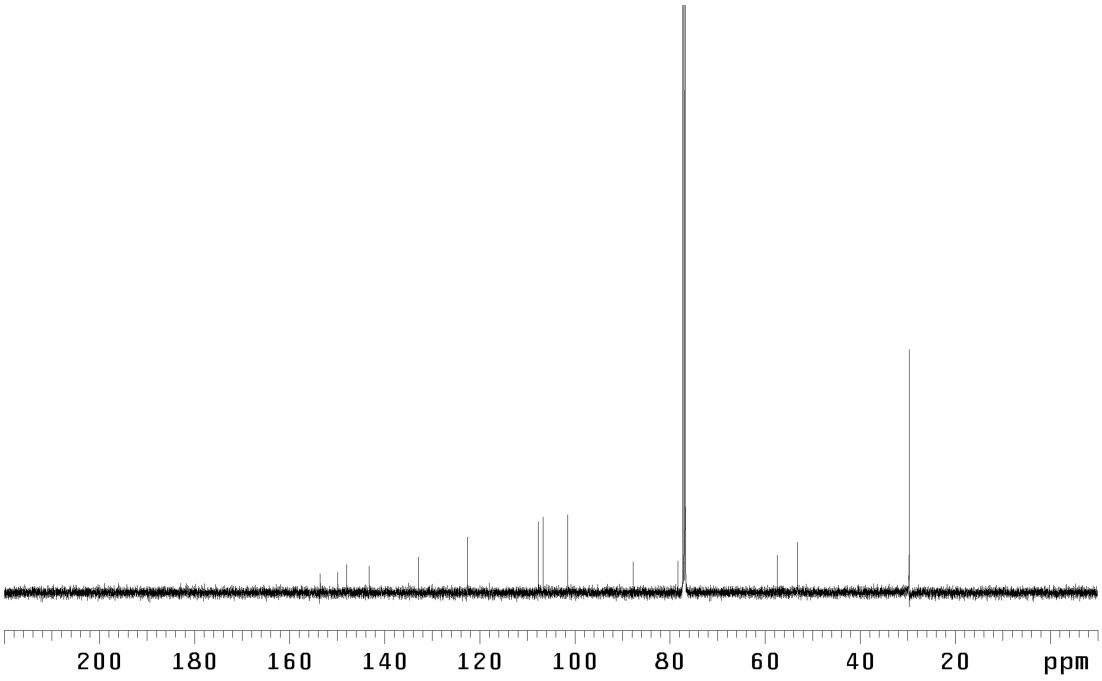


Figure 39.3 ^{13}C NMR (125 MHz, $CDCl_3$) of compound **20g**.

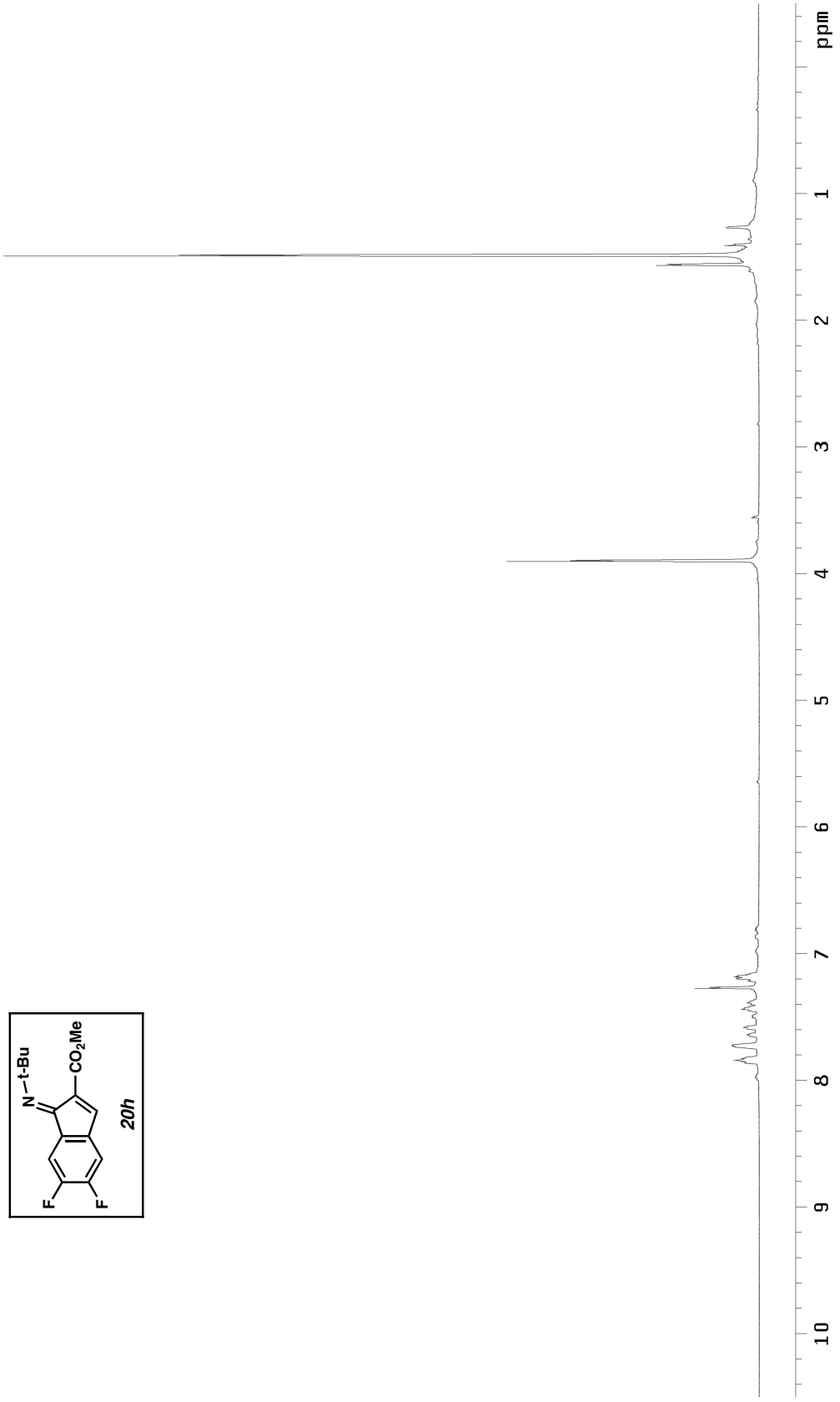


Figure 40.1 ^{1}H NMR (500 MHz, $CDCl_3$) of compound **20h**.

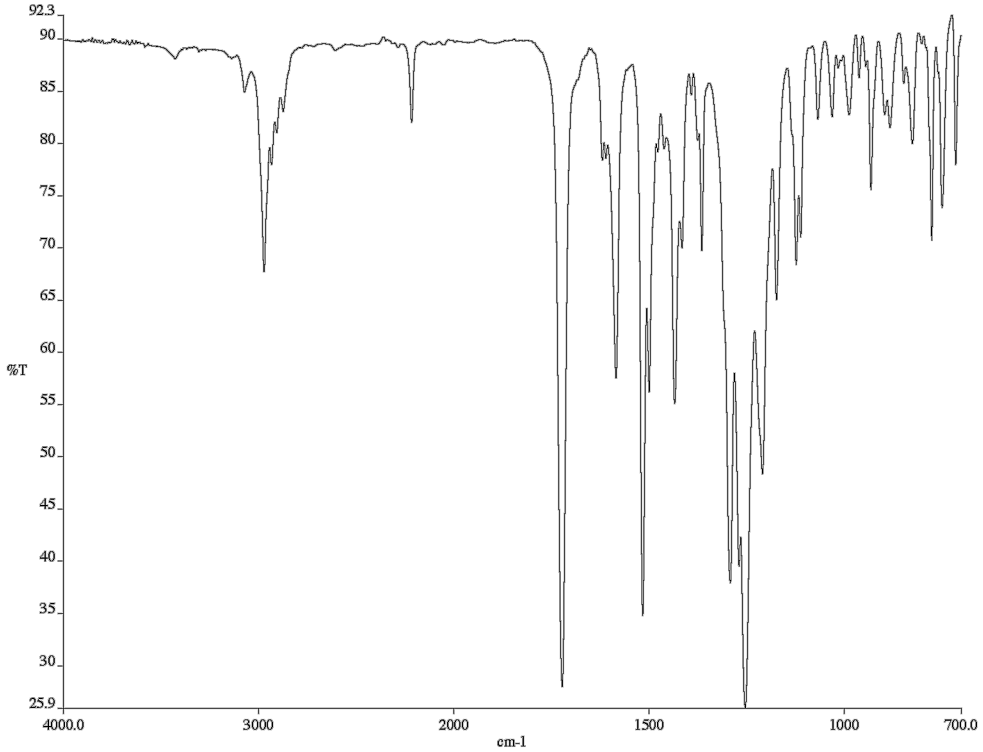


Figure 40.2 Infrared spectrum (thin film/NaCl) of compound **20h**.

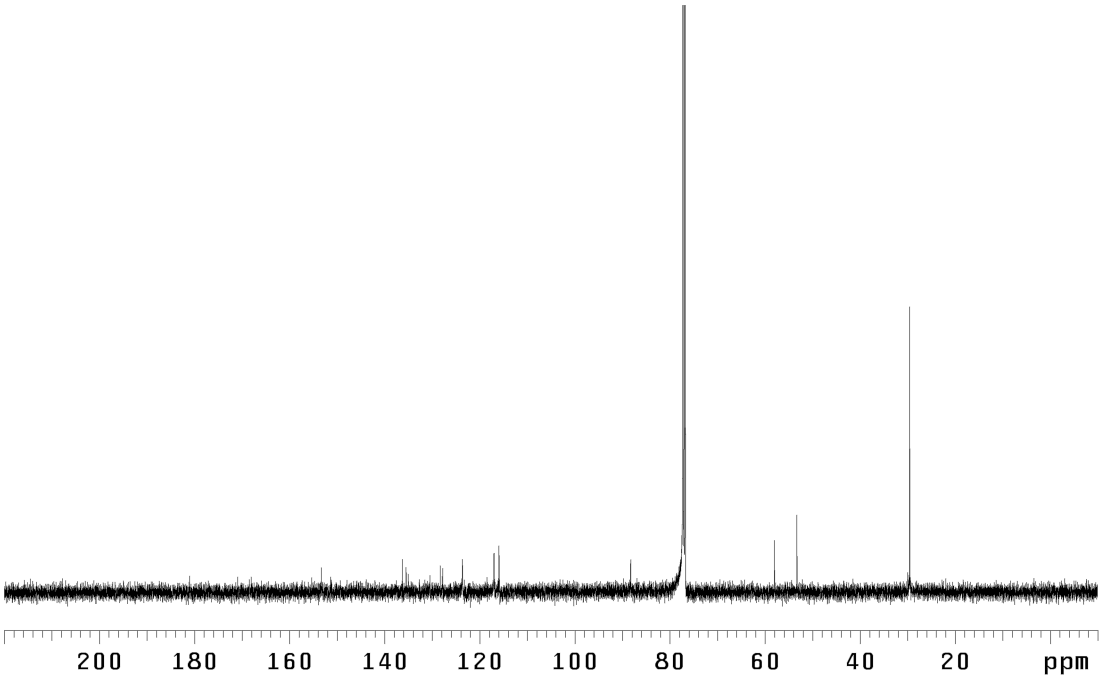


Figure 40.3 ^{13}C NMR (125 MHz, $CDCl_3$) of compound **20h**.

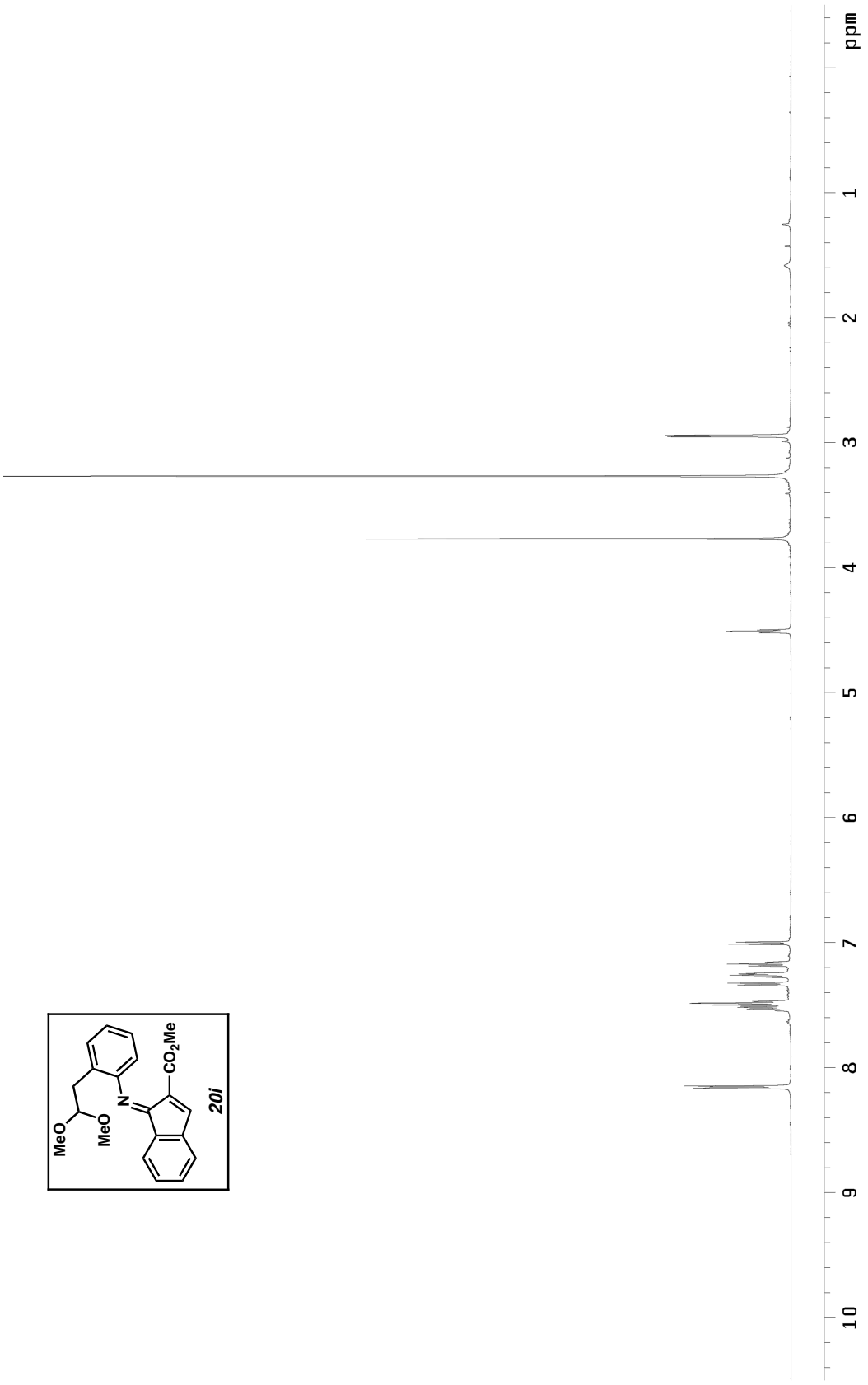


Figure 41.1 ^{1}H NMR (500 MHz, $CDCl_3$) of compound **20i**.

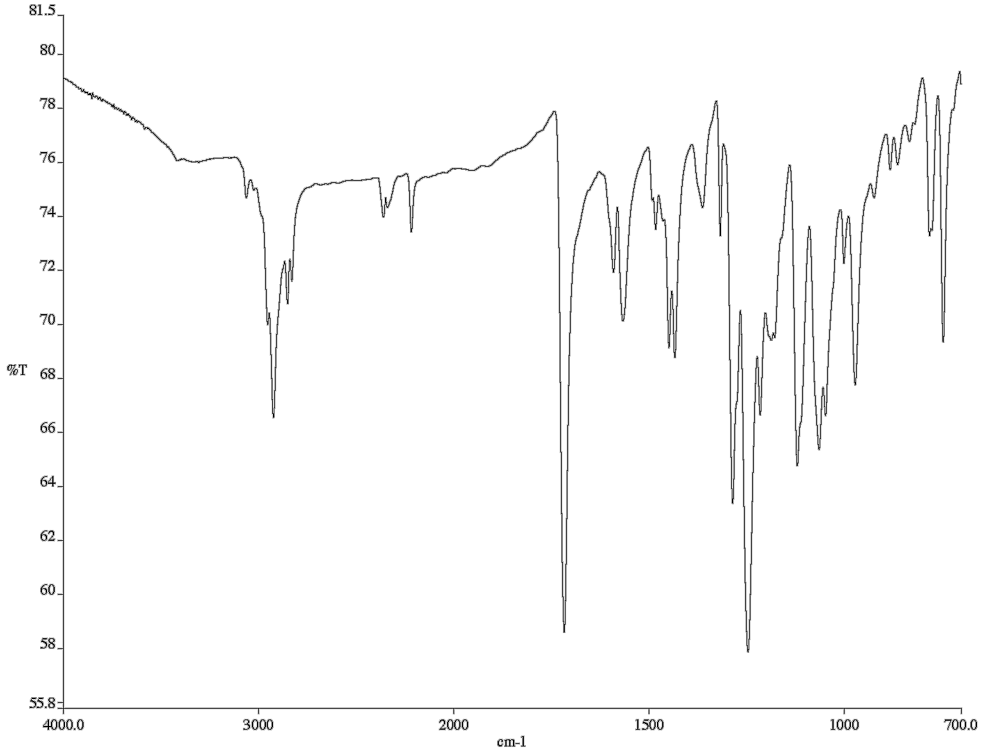


Figure 41.2 Infrared spectrum (thin film/NaCl) of compound **20i**.

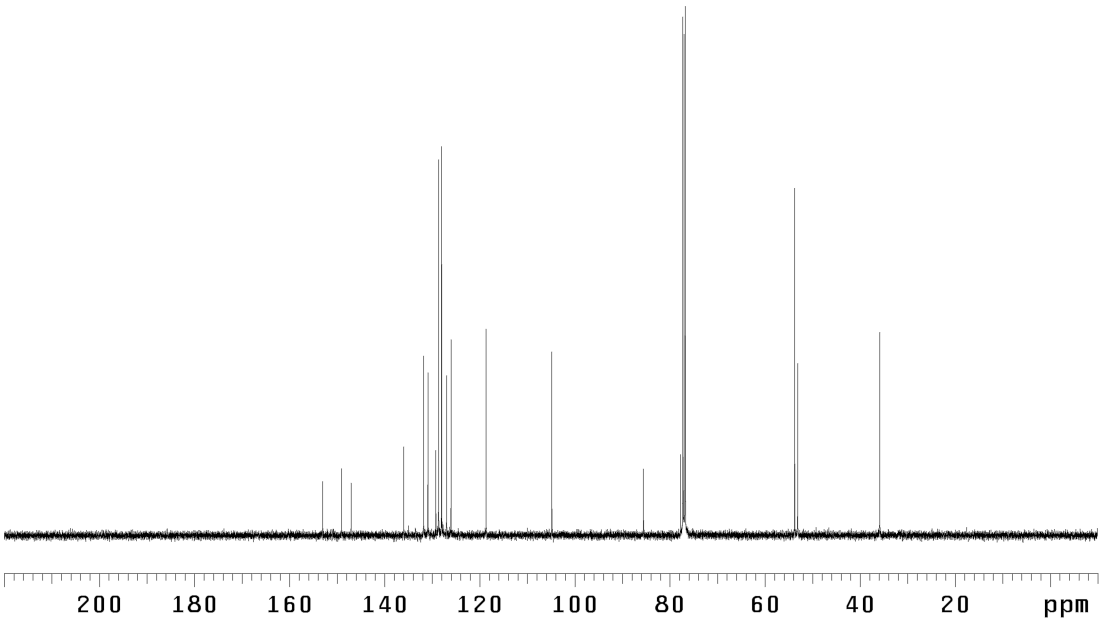


Figure 41.3 ^{13}C NMR (125 MHz, $CDCl_3$) of compound **20i**.

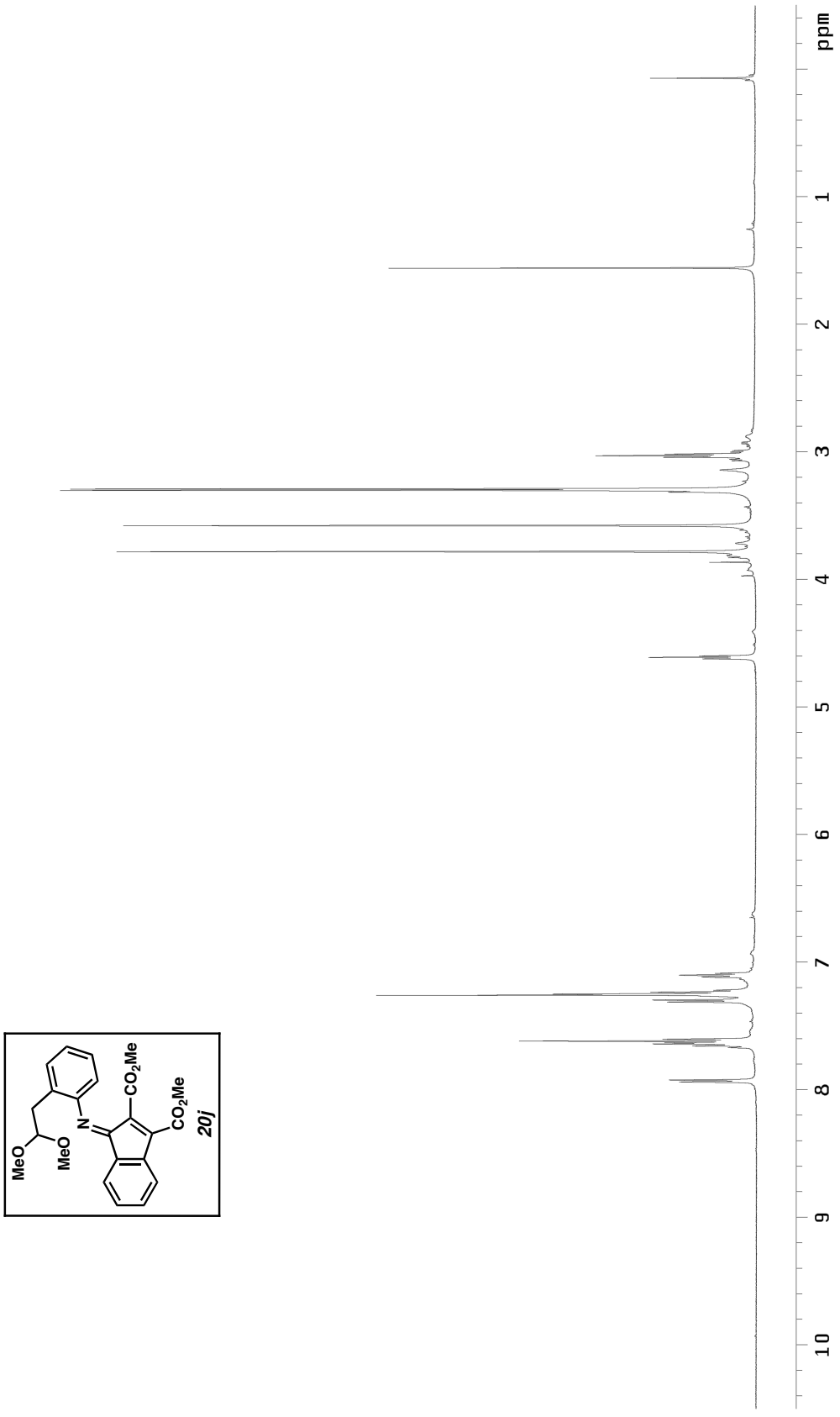


Figure 42.1 ^{1}H NMR (500 MHz, $CDCl_3$) of compound **20j**.

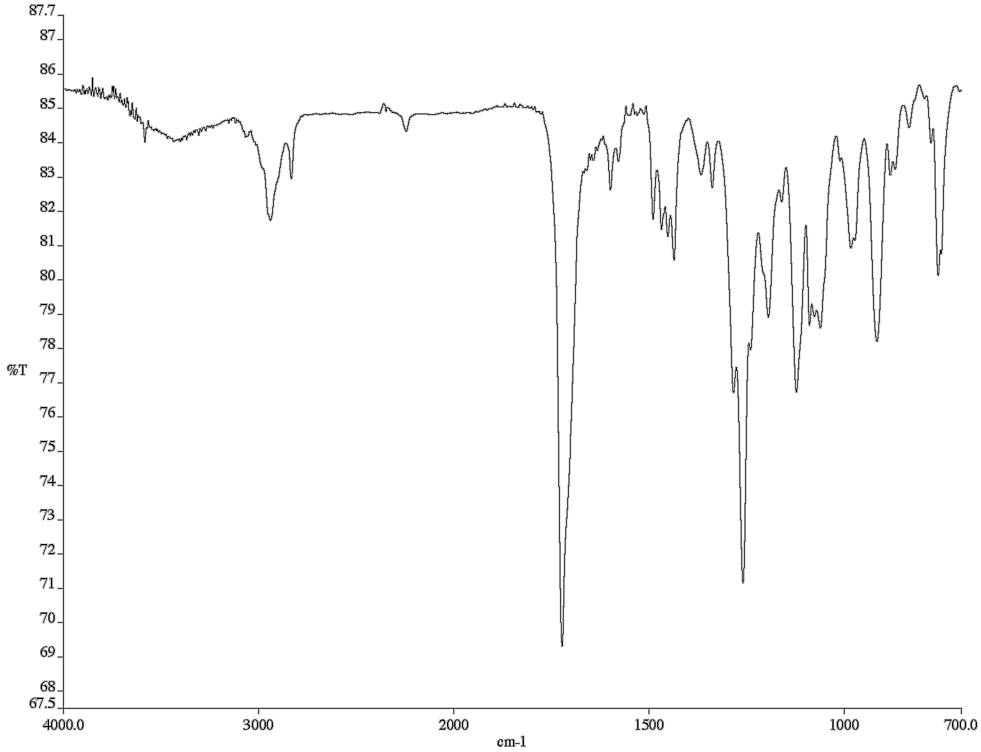


Figure 42.2 Infrared spectrum (thin film/NaCl) of compound **20j**.

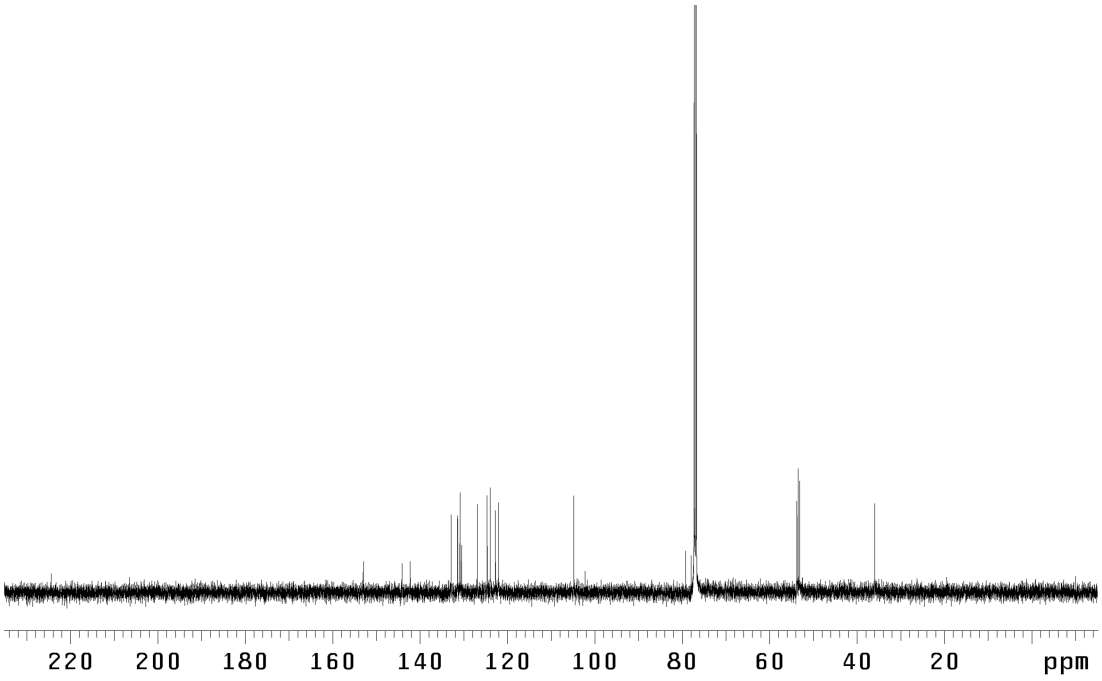


Figure 42.3 ^{13}C NMR (125 MHz, $CDCl_3$) of compound **20j**.

Figure S.1. ORTEP drawing of iminoisobenzofuran **14r** (shown with 50% probability ellipsoids).

NOTE: Crystallographic data have been deposited in the Cambridge Database (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK, and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 739396.

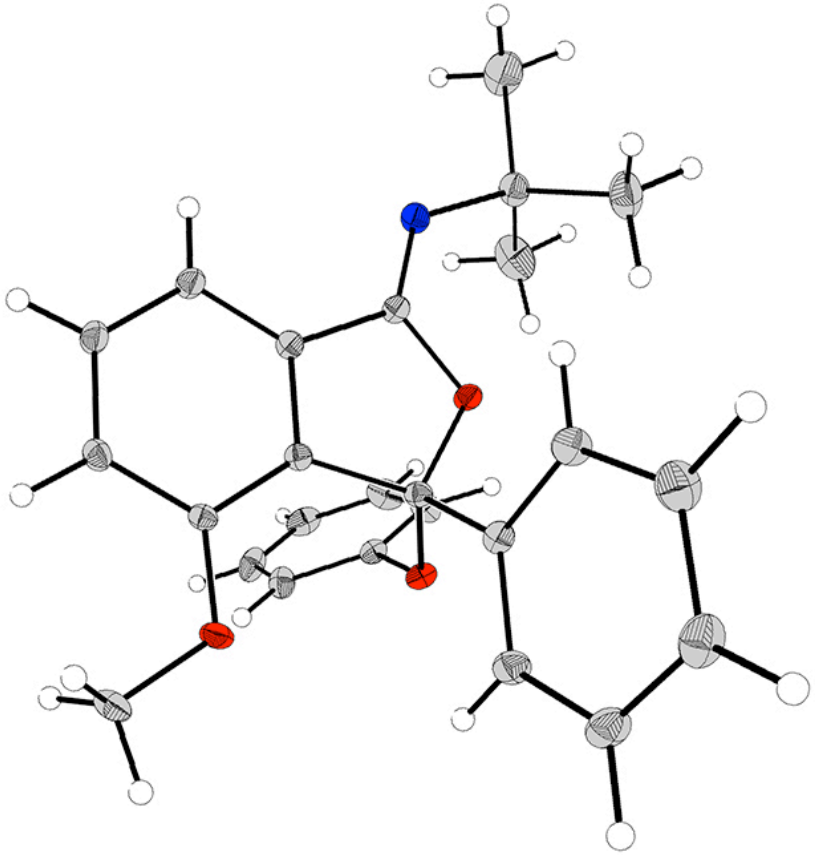
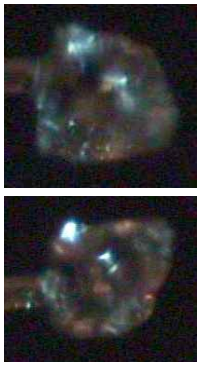


Table S.1. Crystal data and structure refinement for iminoisobenzofuran **14r** (CCDC 739396).

Empirical formula	$C_{25}H_{25}NO_3$
Formula weight	387.46
Crystallization Solvent	$CDCl_3$
Crystal Habit	Block
Crystal size	0.31 x 0.27 x 0.25 mm^3
Crystal color	Colorless



Data Collection

Type of diffractometer	Bruker KAPPA APEX II	
Wavelength	0.71073 Å MoKα	
Data Collection Temperature	100(2) K	
θ range for 9578 reflections used in lattice determination	2.48 to 38.91°	
Unit cell dimensions	a = 8.4862(3) Å b = 9.8342(3) Å c = 13.1013(4) Å	α= 77.791(2)° β= 77.424(2)° γ = 80.138(2)°
Volume	1033.97(6) $Å^3$	
Z	2	
Crystal system	Triclinic	
Space group	P-1	
Density (calculated)	1.245 Mg/m^3	
F(000)	412	
Data collection program	Bruker APEX2 v2.1-0	
θ range for data collection	2.14 to 39.22°	
Completeness to θ = 39.22°	95.3 %	
Index ranges	$-14 \le h \le 14, -15 \le k \le 17, -22 \le l \le 23$	
Data collection scan type	ω scans; 18 settings	
Data reduction program	Bruker SAINT-Plus v7.34A	
Reflections collected	51220	
Independent reflections	11606 [R_{int}= 0.0801]	
Absorption coefficient	0.081 mm^{-1}	
Absorption correction	None	
Max. and min. transmission	0.9800 and 0.9752	

Table S.1. (cont.)

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 2008)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	SHELXL-97 (Sheldrick, 2008)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	11606 / 0 / 362
Treatment of hydrogen atoms	Unrestrained
Goodness-of-fit on F^2	1.891
Final R indices [I>2σ(I), 8945 reflections]	R1 = 0.0431, *w*R2 = 0.1014
R indices (all data)	R1 = 0.0581, *w*R2 = 0.1036
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.001
Average shift/error	0.000
Largest diff. peak and hole	0.648 and -0.292 e.Å^{-3}

Special Refinement Details

Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Figure S.2. Iminoisobenzofuran **14r**.

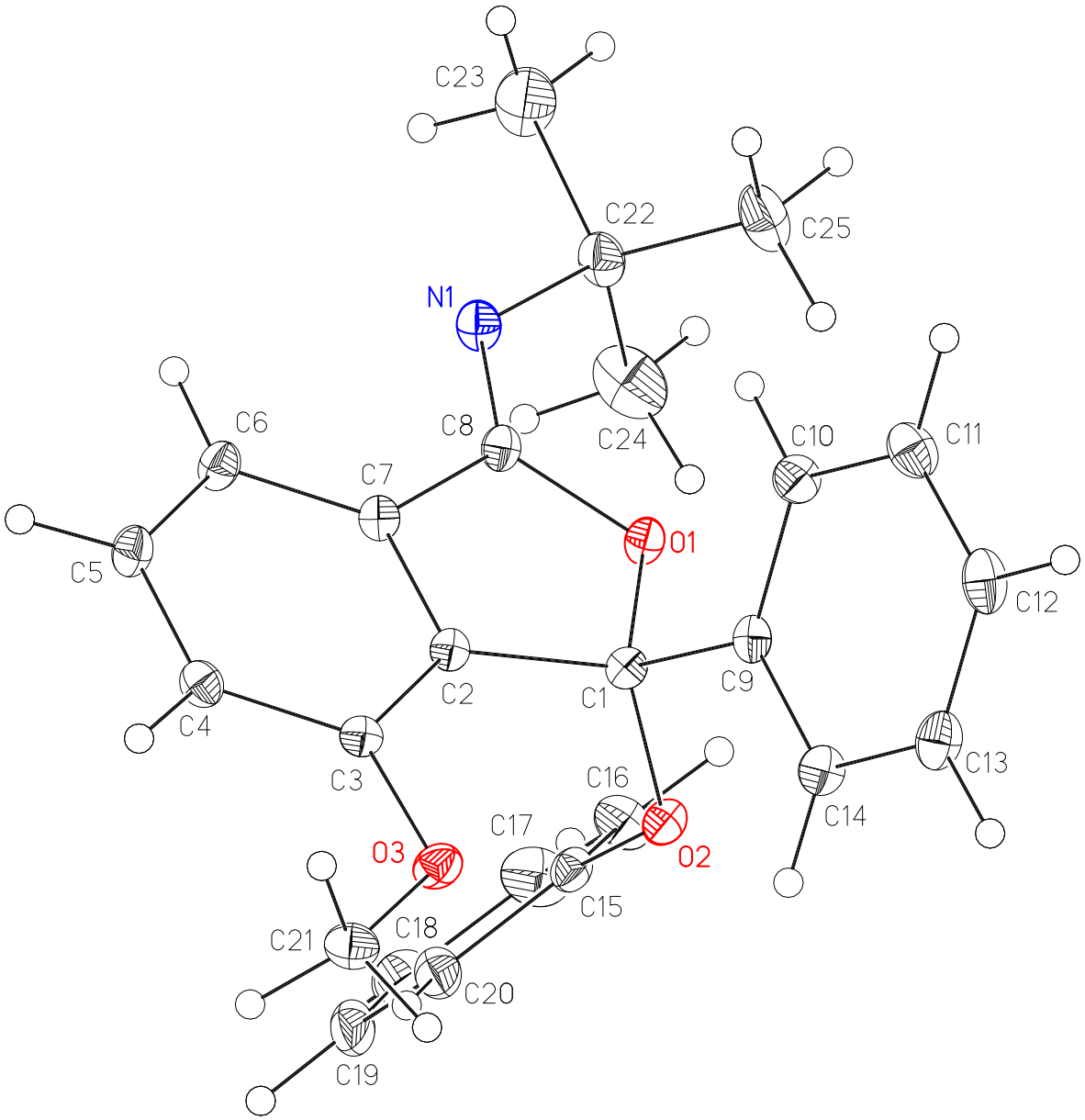


Table S.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **14r** (CCDC 739396). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
O(1)	3472(1)	9014(1)	1779(1)	12(1)
O(2)	5165(1)	9139(1)	2930(1)	12(1)
O(3)	2639(1)	9400(1)	5108(1)	15(1)
N(1)	1898(1)	7586(1)	1261(1)	14(1)
C(1)	3544(1)	9449(1)	2754(1)	11(1)
C(2)	2329(1)	8643(1)	3583(1)	11(1)
C(3)	1846(1)	8646(1)	4671(1)	11(1)
C(4)	591(1)	7865(1)	5232(1)	13(1)
C(5)	-124(1)	7092(1)	4714(1)	14(1)
C(6)	360(1)	7080(1)	3636(1)	14(1)
C(7)	1594(1)	7881(1)	3088(1)	11(1)
C(8)	2302(1)	8109(1)	1950(1)	11(1)
C(9)	3117(1)	11036(1)	2619(1)	11(1)
C(10)	1992(1)	11714(1)	1985(1)	15(1)
C(11)	1592(1)	13170(1)	1848(1)	18(1)
C(12)	2320(1)	13954(1)	2340(1)	18(1)
C(13)	3425(1)	13278(1)	2980(1)	17(1)
C(14)	3820(1)	11817(1)	3134(1)	14(1)
C(15)	5864(1)	7735(1)	3005(1)	12(1)
C(16)	6663(1)	7253(1)	2082(1)	19(1)
C(17)	7442(1)	5878(1)	2155(1)	24(1)
C(18)	7425(1)	5014(1)	3138(1)	23(1)
C(19)	6657(1)	5516(1)	4060(1)	22(1)
C(20)	5858(1)	6889(1)	3996(1)	17(1)
C(21)	2051(1)	9494(1)	6203(1)	16(1)
C(22)	2651(1)	7806(1)	125(1)	17(1)
C(23)	1637(1)	7108(1)	-400(1)	32(1)
C(24)	4405(1)	7088(1)	-15(1)	30(1)
C(25)	2593(1)	9360(1)	-384(1)	25(1)

Table S.3. Bond lengths [Å] and angles [°] for **14r** (CCDC 739396).

O(1)-C(8)	1.3962(7)	C(24)-H(24A)	0.954(13)
O(1)-C(1)	1.4473(8)	C(24)-H(24B)	0.999(13)
O(2)-C(15)	1.3989(7)	C(24)-H(24C)	1.014(14)
O(2)-C(1)	1.4153(8)	C(25)-H(25A)	0.970(12)
O(3)-C(3)	1.3597(7)	C(25)-H(25B)	1.003(12)
O(3)-C(21)	1.4299(8)	C(25)-H(25C)	1.002(11)
N(1)-C(8)	1.2599(8)		
N(1)-C(22)	1.4726(9)	C(8)-O(1)-C(1)	111.20(5)
C(1)-C(2)	1.5160(8)	C(15)-O(2)-C(1)	116.66(4)
C(1)-C(9)	1.5218(8)	C(3)-O(3)-C(21)	117.04(5)
C(2)-C(7)	1.3826(8)	C(8)-N(1)-C(22)	124.50(5)
C(2)-C(3)	1.3961(9)	O(2)-C(1)-O(1)	109.11(4)
C(3)-C(4)	1.4012(8)	O(2)-C(1)-C(2)	114.67(5)
C(4)-C(5)	1.4006(9)	O(1)-C(1)-C(2)	103.49(4)
C(4)-H(4)	0.975(10)	O(2)-C(1)-C(9)	106.51(4)
C(5)-C(6)	1.3843(9)	O(1)-C(1)-C(9)	108.83(5)
C(5)-H(5)	0.975(9)	C(2)-C(1)-C(9)	114.05(5)
C(6)-C(7)	1.3956(8)	C(7)-C(2)-C(3)	120.56(5)
C(6)-H(6)	0.972(10)	C(7)-C(2)-C(1)	109.08(5)
C(7)-C(8)	1.4655(9)	C(3)-C(2)-C(1)	130.25(5)
C(9)-C(10)	1.3914(9)	O(3)-C(3)-C(2)	117.35(5)
C(9)-C(14)	1.3970(9)	O(3)-C(3)-C(4)	125.00(6)
C(10)-C(11)	1.3961(9)	C(2)-C(3)-C(4)	117.65(5)
C(10)-H(10)	0.987(10)	C(3)-C(4)-C(5)	120.70(6)
C(11)-C(12)	1.3930(10)	C(3)-C(4)-H(4)	120.1(5)
C(11)-H(11)	0.977(11)	C(5)-C(4)-H(4)	119.2(5)
C(12)-C(13)	1.3849(11)	C(6)-C(5)-C(4)	121.75(6)
C(12)-H(12)	0.963(10)	C(6)-C(5)-H(5)	121.2(6)
C(13)-C(14)	1.3996(9)	C(4)-C(5)-H(5)	117.0(6)
C(13)-H(13)	0.995(11)	C(5)-C(6)-C(7)	116.73(6)
C(14)-H(14)	0.970(10)	C(5)-C(6)-H(6)	122.9(6)
C(15)-C(16)	1.3861(9)	C(7)-C(6)-H(6)	120.4(6)
C(15)-C(20)	1.3851(10)	C(2)-C(7)-C(6)	122.60(6)
C(16)-C(17)	1.3929(9)	C(2)-C(7)-C(8)	108.60(5)
C(16)-H(16)	0.990(11)	C(6)-C(7)-C(8)	128.78(6)
C(17)-C(18)	1.3846(12)	N(1)-C(8)-O(1)	127.00(6)
C(17)-H(17)	0.947(12)	N(1)-C(8)-C(7)	125.45(5)
C(18)-C(19)	1.3877(12)	O(1)-C(8)-C(7)	107.54(5)
C(18)-H(18)	0.973(10)	C(10)-C(9)-C(14)	119.65(5)
C(19)-C(20)	1.3978(10)	C(10)-C(9)-C(1)	119.45(5)
C(19)-H(19)	0.958(13)	C(14)-C(9)-C(1)	120.90(6)
C(20)-H(20)	0.966(12)	C(9)-C(10)-C(11)	120.24(6)
C(21)-H(21A)	0.970(10)	C(9)-C(10)-H(10)	119.6(6)
C(21)-H(21B)	0.958(9)	C(11)-C(10)-H(10)	120.2(6)
C(21)-H(21C)	1.026(11)	C(12)-C(11)-C(10)	120.19(7)
C(22)-C(24)	1.5246(11)	C(12)-C(11)-H(11)	120.4(5)
C(22)-C(25)	1.5293(10)	C(10)-C(11)-H(11)	119.4(5)
C(22)-C(23)	1.5306(11)	C(13)-C(12)-C(11)	119.57(6)
C(23)-H(23A)	1.033(13)	C(13)-C(12)-H(12)	120.3(7)
C(23)-H(23B)	1.006(13)	C(11)-C(12)-H(12)	120.1(7)
C(23)-H(23C)	1.005(14)	C(12)-C(13)-C(14)	120.65(6)

C(12)-C(13)-H(13)	121.6(7)	H(21A)-C(21)-H(21C)	108.9(8)
C(14)-C(13)-H(13)	117.7(7)	H(21B)-C(21)-H(21C)	111.6(9)
C(9)-C(14)-C(13)	119.68(6)	N(1)-C(22)-C(24)	109.65(6)
C(9)-C(14)-H(14)	120.0(5)	N(1)-C(22)-C(25)	112.64(5)
C(13)-C(14)-H(14)	120.3(5)	C(24)-C(22)-C(25)	110.30(7)
C(16)-C(15)-C(20)	121.38(6)	N(1)-C(22)-C(23)	105.06(6)
C(16)-C(15)-O(2)	118.70(6)	C(24)-C(22)-C(23)	110.07(7)
C(20)-C(15)-O(2)	119.72(6)	C(25)-C(22)-C(23)	108.99(7)
C(15)-C(16)-C(17)	119.13(7)	C(22)-C(23)-H(23A)	108.6(8)
C(15)-C(16)-H(16)	119.3(6)	C(22)-C(23)-H(23B)	110.6(6)
C(17)-C(16)-H(16)	121.6(6)	H(23A)-C(23)-H(23B)	107.1(10)
C(18)-C(17)-C(16)	120.15(7)	C(22)-C(23)-H(23C)	110.4(7)
C(18)-C(17)-H(17)	120.4(8)	H(23A)-C(23)-H(23C)	111.0(10)
C(16)-C(17)-H(17)	119.5(8)	H(23B)-C(23)-H(23C)	109.0(12)
C(17)-C(18)-C(19)	120.31(6)	C(22)-C(24)-H(24A)	110.2(8)
C(17)-C(18)-H(18)	120.8(7)	C(22)-C(24)-H(24B)	109.7(7)
C(19)-C(18)-H(18)	118.7(7)	H(24A)-C(24)-H(24B)	106.2(10)
C(18)-C(19)-C(20)	120.02(7)	C(22)-C(24)-H(24C)	112.6(8)
C(18)-C(19)-H(19)	120.1(6)	H(24A)-C(24)-H(24C)	107.6(12)
C(20)-C(19)-H(19)	119.8(6)	H(24B)-C(24)-H(24C)	110.2(10)
C(15)-C(20)-C(19)	118.98(7)	C(22)-C(25)-H(25A)	110.6(7)
C(15)-C(20)-H(20)	119.2(7)	C(22)-C(25)-H(25B)	110.6(6)
C(19)-C(20)-H(20)	121.8(7)	H(25A)-C(25)-H(25B)	108.2(10)
O(3)-C(21)-H(21A)	111.1(7)	C(22)-C(25)-H(25C)	113.0(7)
O(3)-C(21)-H(21B)	105.3(6)	H(25A)-C(25)-H(25C)	106.5(9)
H(21A)-C(21)-H(21B)	109.5(8)	H(25B)-C(25)-H(25C)	107.8(9)
O(3)-C(21)-H(21C)	110.6(6)		

Table S.4. Anisotropic displacement parameters ($Å^2$ x 10^4) for **14r** (CCDC 739396). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	130(2)	128(2)	105(2)	-46(1)	-1(2)	-40(1)
O(2)	100(2)	105(2)	174(2)	-44(2)	-28(2)	-3(1)
O(3)	151(2)	196(2)	119(2)	-70(2)	-24(2)	-45(2)
N(1)	172(2)	145(2)	104(2)	-52(2)	-10(2)	-32(2)
C(1)	102(2)	120(2)	104(2)	-37(2)	-15(2)	-13(2)
C(2)	103(2)	109(2)	105(2)	-35(2)	-12(2)	-7(2)
C(3)	111(2)	121(2)	107(2)	-40(2)	-24(2)	-2(2)
C(4)	134(2)	148(2)	104(3)	-33(2)	-7(2)	-13(2)
C(5)	145(3)	164(2)	126(3)	-38(2)	8(2)	-50(2)
C(6)	146(3)	146(2)	132(3)	-53(2)	-1(2)	-49(2)
C(7)	115(2)	115(2)	105(2)	-42(2)	-3(2)	-12(2)
C(8)	117(2)	106(2)	113(2)	-39(2)	-7(2)	-16(2)
C(9)	113(2)	106(2)	115(3)	-32(2)	1(2)	-11(2)
C(10)	155(3)	133(2)	161(3)	-36(2)	-36(2)	-1(2)
C(11)	187(3)	143(3)	177(3)	-22(2)	-32(2)	25(2)
C(12)	212(3)	113(2)	178(3)	-39(2)	21(2)	-4(2)
C(13)	200(3)	129(2)	186(3)	-67(2)	-2(2)	-34(2)
C(14)	153(3)	135(2)	153(3)	-50(2)	-22(2)	-17(2)
C(15)	106(2)	109(2)	159(3)	-30(2)	-27(2)	-12(2)
C(16)	221(3)	163(3)	166(3)	-53(2)	-46(2)	37(2)
C(17)	273(4)	185(3)	275(4)	-113(3)	-93(3)	76(2)
C(18)	206(3)	129(3)	371(5)	-42(3)	-111(3)	10(2)
C(19)	155(3)	186(3)	280(4)	64(3)	-56(3)	-24(2)
C(20)	130(3)	184(3)	174(3)	6(2)	-20(2)	-10(2)
C(21)	174(3)	201(3)	120(3)	-72(2)	-38(2)	-9(2)
C(22)	229(3)	178(3)	103(3)	-51(2)	-11(2)	-49(2)
C(23)	500(6)	392(5)	148(4)	-90(3)	-54(4)	-231(4)
C(24)	295(4)	383(4)	175(4)	-97(3)	29(3)	71(3)
C(25)	369(4)	209(3)	143(3)	-3(2)	-26(3)	-58(3)

Table S.5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **14r** (CCDC 739396)

	x	y	z	U_{iso}
H(4)	195(11)	7865(9)	5989(8)	16(2)
H(5)	-949(11)	6529(9)	5152(8)	19(2)
H(6)	-126(12)	6554(10)	3263(9)	24(2)
H(10)	1514(12)	11163(10)	1610(9)	24(2)
H(11)	817(12)	13634(10)	1389(9)	22(2)
H(12)	2027(12)	14956(10)	2256(9)	24(2)
H(13)	3978(13)	13807(11)	3336(9)	28(3)
H(14)	4579(11)	11346(9)	3594(8)	15(2)
H(16)	6670(12)	7893(10)	1388(9)	24(2)
H(17)	7961(15)	5535(12)	1525(11)	40(3)
H(18)	8013(13)	4068(11)	3201(9)	31(3)
H(19)	6660(14)	4920(11)	4740(10)	34(3)
H(20)	5290(14)	7260(11)	4623(10)	35(3)
H(21A)	899(12)	9846(10)	6330(9)	22(2)
H(21B)	2656(12)	10148(10)	6345(8)	20(2)
H(21C)	2231(12)	8528(10)	6677(9)	24(2)
H(23A)	1742(16)	6048(13)	-88(12)	51(4)
H(23B)	2069(15)	7207(12)	-1187(11)	38(3)
H(23C)	467(18)	7546(13)	-279(12)	58(4)
H(24A)	5072(16)	7598(13)	224(12)	51(4)
H(24B)	4858(14)	7095(11)	-786(10)	37(3)
H(24C)	4511(17)	6092(14)	400(12)	55(4)
H(25A)	1484(14)	9829(11)	-271(10)	37(3)
H(25B)	3018(13)	9472(10)	-1169(10)	28(3)
H(25C)	3247(13)	9878(11)	-80(10)	31(3)

Notes & References

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