One-pot synthesis of 3-arylaminomaleimides from terminal alkynes and isocyanates

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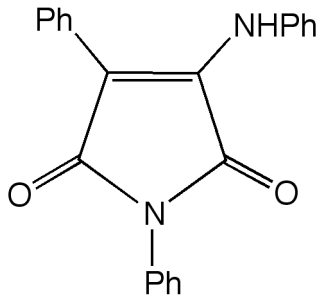
Supplementary Material for deposition

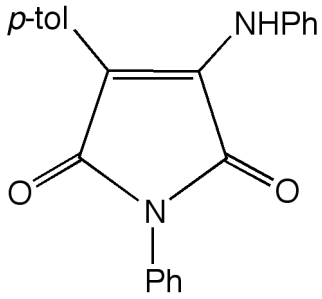
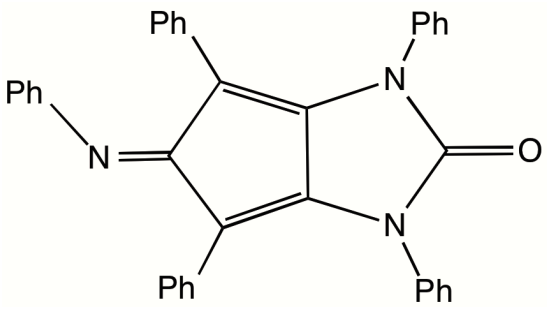
Characterisation data for all compounds

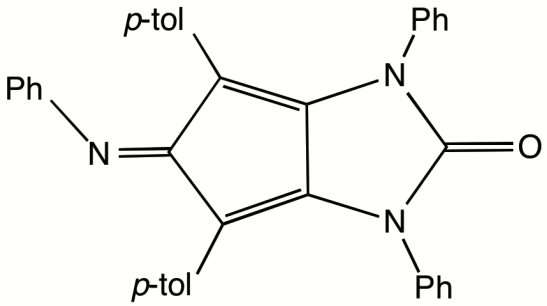
References given for compounds are to papers containing NMR data where available, or if not, to papers reporting their preparation. New compounds were characterised by ^{1}H and ^{13}C NMR spectra, mass spectrum, elemental analysis and/or HRMS. Known compounds for which NMR data are available were characterised by ^{1}H and ^{13}C NMR spectra and mass spectrum. Compounds for which no published NMR data are available were also characterised by elemental analysis and/or HRMS. Representative ^{1}H and ^{13}C NMR spectra for the compounds are also included.

The ^{1}H (250 MHz or 400 MHz) and ^{13}C NMR (62.8 MHz or 100 MHz) spectra were obtained in $CDCl_3$ solution on Bruker Avance AV250 or AV400 machines with automated sample-changers. Chemical shifts are given on the δ scale relative to $SiMe_4$. The $^{13}C\{^{1}H\}$ NMR spectra were routinely recorded using an attached proton test technique (JMOD pulse sequence). Mass spectra were recorded on a VG AutoSpec instrument operating in electron impact mode. Solid state IR spectra were recorded either as KBr disks or neat with a diamond ATR device over the range 4000-400 cm^{-1}, and solution spectra in CH_2Cl_2 solution over the range 2200-1550 cm^{-1}, on a Perkin Elmer Spectrum Two instrument.

Table S1

4a		^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 4.3 Hz, 5 H), 7.40 (m, 1 H), 7.22-7.00 (m, 8 H), 6.72 (d, *J* = 7.5 Hz, 2 H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 170.8, 167.5 (CO), 136.2, 136.2, 131.9, 129.2 (3 C_{ipso} + CNHPh), 129.8, 129.1, 128.3, 127.5, 127.3, 125.9, 124.7, 121.7 (m, Ph), 102.5 (CPh). IR (CH_2Cl_2): 1769m, 1710vs, 1652s, 1597m cm^{-1}. IR (KBr): 3305s, 1759m, 1700s, 1644s, 1597s, 1529s, 1494s, 1452m, 1442m, 1393s, 1361m, 1227m, 1124m, 1099m, 1028m, 953m, 911m, 766s cm^{-1}. UV-vis (EtOH, λ_{max} in nm, ε in $M^{-1}cm^{-1}$): 251 (ε 28450), 294sh (ε 7600), 408 (ε 6310). MS: *m/z* 340 (M^+), 220, 193. HRMS: Found: 340.1192 (M^+); calcd. for $C_{22}H_{16}N_2O_2$: 340.1206. Analysis Found: C, 77.39; H, 4.74; N, 8.19. Calcd. for $C_{22}H_{16}N_2O_2$: C, 77.69; H, 4.74; N, 8.24%. M.p. 201-203 °C (Lit. 202-203 °C) Reference 1, 2

4b		^{1}H NMR (400 MHz, $CDCl_3$): d 7.52-6.97 (m, Ph + tol), 6.72 (d, *J* = 7.7 Hz, 2 H), 2.31 (s, 3 H, Me). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 170.9, 167.6 (CO), 137.6, 136.3, 135.5, 131.9 (3 C_{ipso} + CNHPh), 129.7, 129.0, 128.3, 128.0, 127.7, 127.5, 126.2, 125.9, 124.5, 121.6 (m, aryl), 126.2 (CMe), 103.0 (Ctol), 21.4 (Me). IR(CH_2Cl_2): 1767w, 1710vs, 1652s, 1597m cm^{-1}. IR(ATR): 3309s, 3039w, 1756m, 1695s, 1642s, 1595s, 1530s, 1495s, 1450m, 1388s, 1358s, 1229m, 1108m, 954m, 912m, 752s cm^{-1}. MS: *m/z* 354 (M^+), 234, 206 HRMS: Found: 354.1372 (M^+); Calcd. For $C_{23}H_{18}N_2O_2$: 354.1363. Analysis Found: C, 77.67; H, 5.12; N, 7.81. Calcd. For $C_{23}H_{18}N_2O_2$: C, 78.00; H, 5.12; N, 7.91%. M.p. 242-244 °C.
5a		^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-6.45 (m, 25 H, Ph). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 166.2 (C=N), 155.4 (C=O), 149.3 (C_{ipso} of NPh), 133.6, 133.0, 131.9, 130.5, 130.9, 129.5, 128.6, 128.4, 127.6, 127.5, 127.4, 127.1, 126.7, 126.5, 126.2, 125.9. 125.3, 123.3, 120.6 (m, Ph).

		IR(CH_2Cl_2): 1755 cm^{-1}. IR(ATR): 1757s, 1640m, 1609m, 1585m, 1494m, 1407s, 1255m, 1189m, 1115m, 1069m, 856m, 760s, 748m cm^{-1}. MS: *m/z* 515 (M^+). HRMS: Found: 515.1996 (M^+); Calcd. for $C_{36}H_{25}N_3O$: 515.1992. Analysis Found: C, 84.45; H, 4.45; N, 8.07. Calcd. for : C, 83.93; H, 4.89; N, 8.16%. M.p. 254-255 °C.
5b		^1H NMR (400 MHz, $CDCl_3$): δ 7.26-6.59 (m, 19 H, Ph + tol), 6.36, 6.32 (both br s, 2H, Ph), 2.28, 2.06 (both s, 3H, Me). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 166.6 (C=N), 155.5 (C=O), 149.4 (C_{ipso} of NPh), 136.3, 136.1, 133.8, 133.2, 130.9, 129.5, 128.6, 128.4, 127.6, 127.5, 127.4, 127.1, 126.7, 126.5, 126.2, 125.9, 125.3, 123.3, 120.6 (m, Ph + tol), 21.3, 21.0 (Me) IR (CH_2Cl_2): 1754 cm^{-1}. IR(ATR): 1754s, 1648m, 1617m, 1604s, 1592s, 1512m, 1493m, 1483m, 1402s, 1250m, 1185m, 1069m, 984m, 813m, 785m, 751s cm^{-1}. MS: *m/z* 544 $(M+H)^+$. HRMS: Found: 544.2388 $(M+H)^+$; Calcd. for $C_{38}H_{30}N_3O$: 544.2383. Analysis Found: C, 83.58; H, 5.45; N, 7.63. Calcd. for $C_{38}H_{29}N_3O$: C, 83.86; H, 5.37; N,

		7.72%. M.p. 260-262 °C.

References for Table S1.

1. Compound **4a** is mentioned in a patent: Coghlan, M.P.; Fenwick, A.E.; Haigh, D.; Holder, J.C.; Ife, R.J.; Reith, A.D.; Smith, D.G.; Ward, R.W. WO 2000021927 A2 20000420.
2. Bird, C. W. *J. Chem. Soc.* **1965**, 5762.

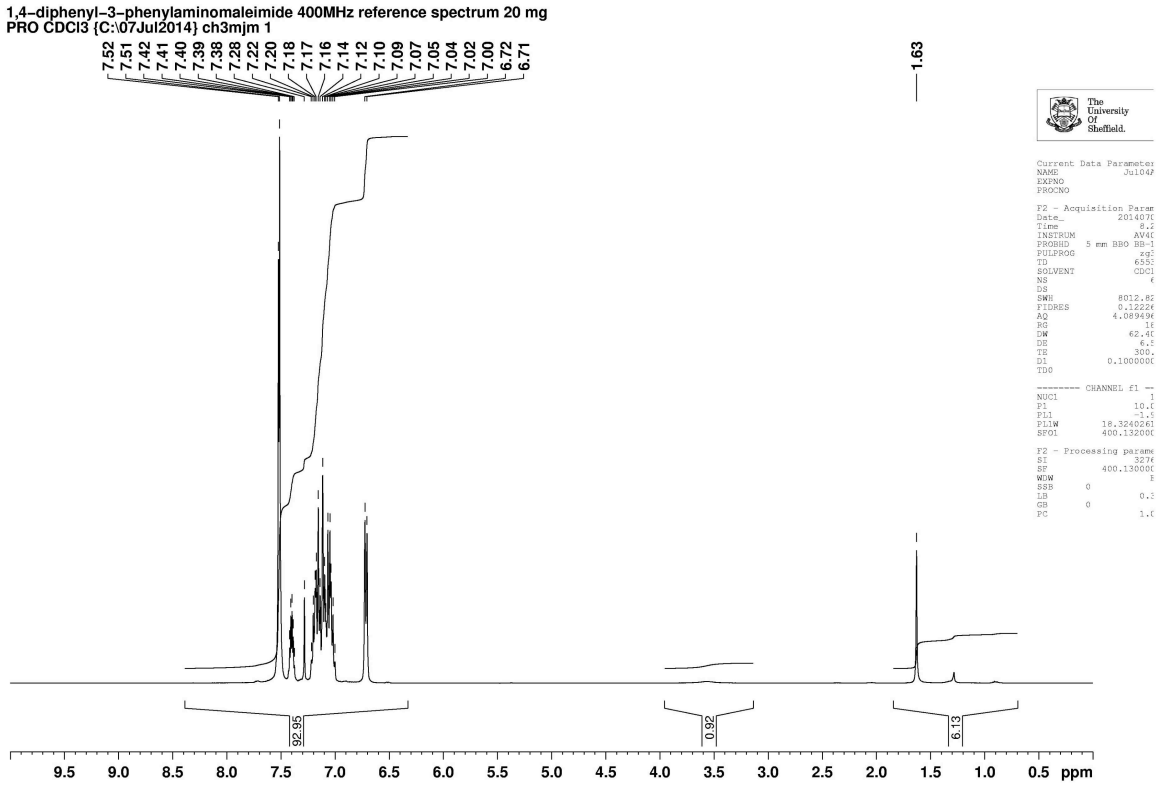


Figure S1 ^{1}H NMR spectrum of compound **4a** in $CDCl_3$. The peaks at δ 7.28 ($CHCl_3$) and 1.63 (H_2O) are impurities.

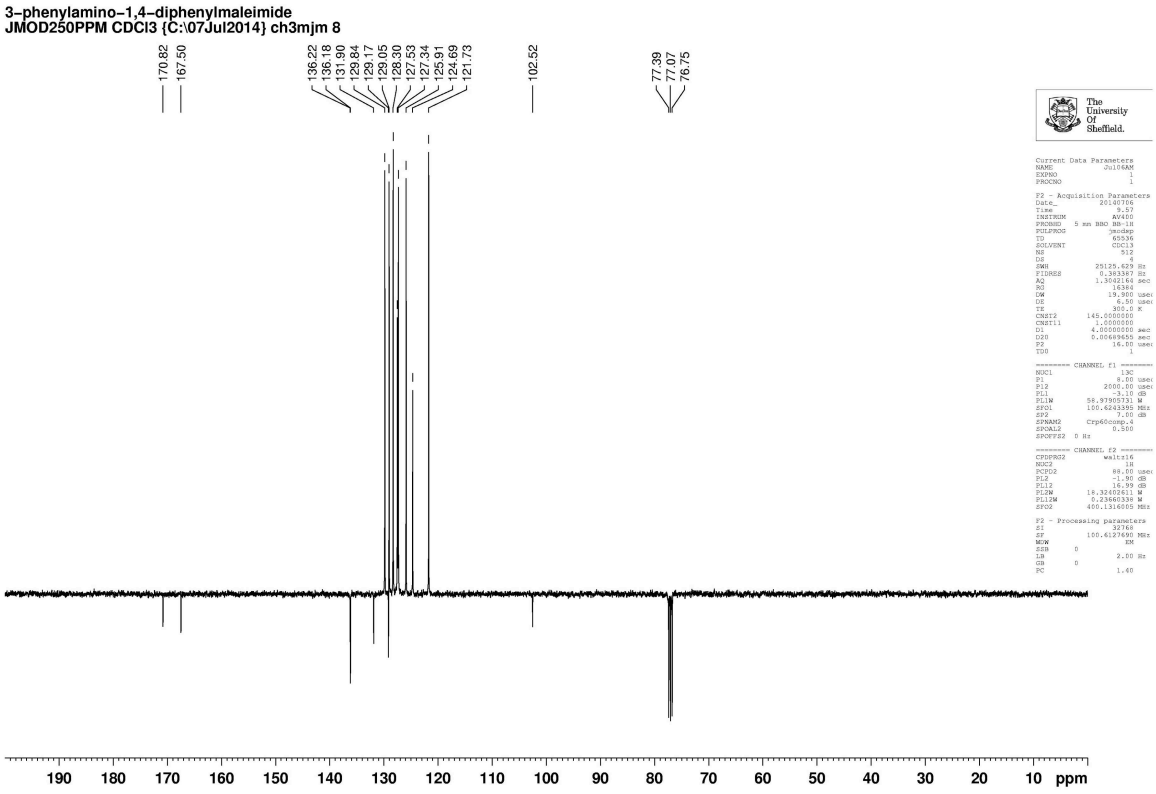


Figure S2. ^{13}C NMR spectrum of compound **4a** in $CDCl_3$.

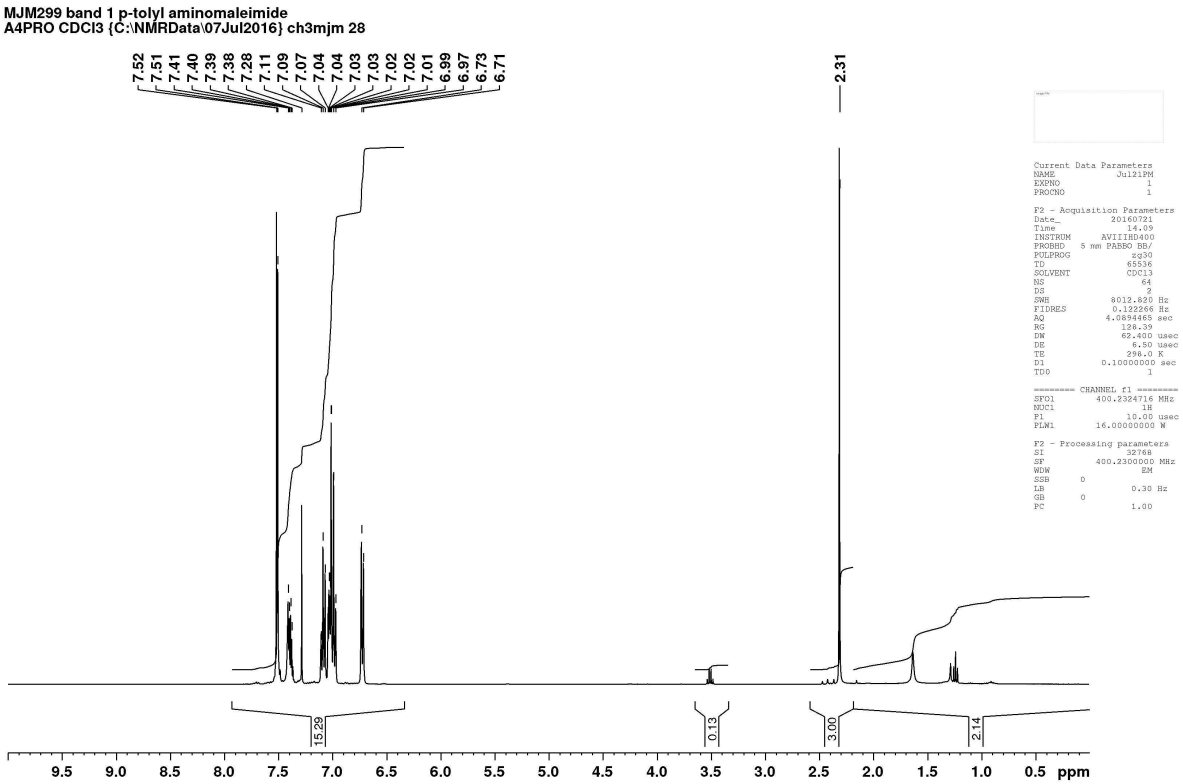


Figure S3. ^{1}H NMR spectrum of compound **4b** in $CDCl_3$.

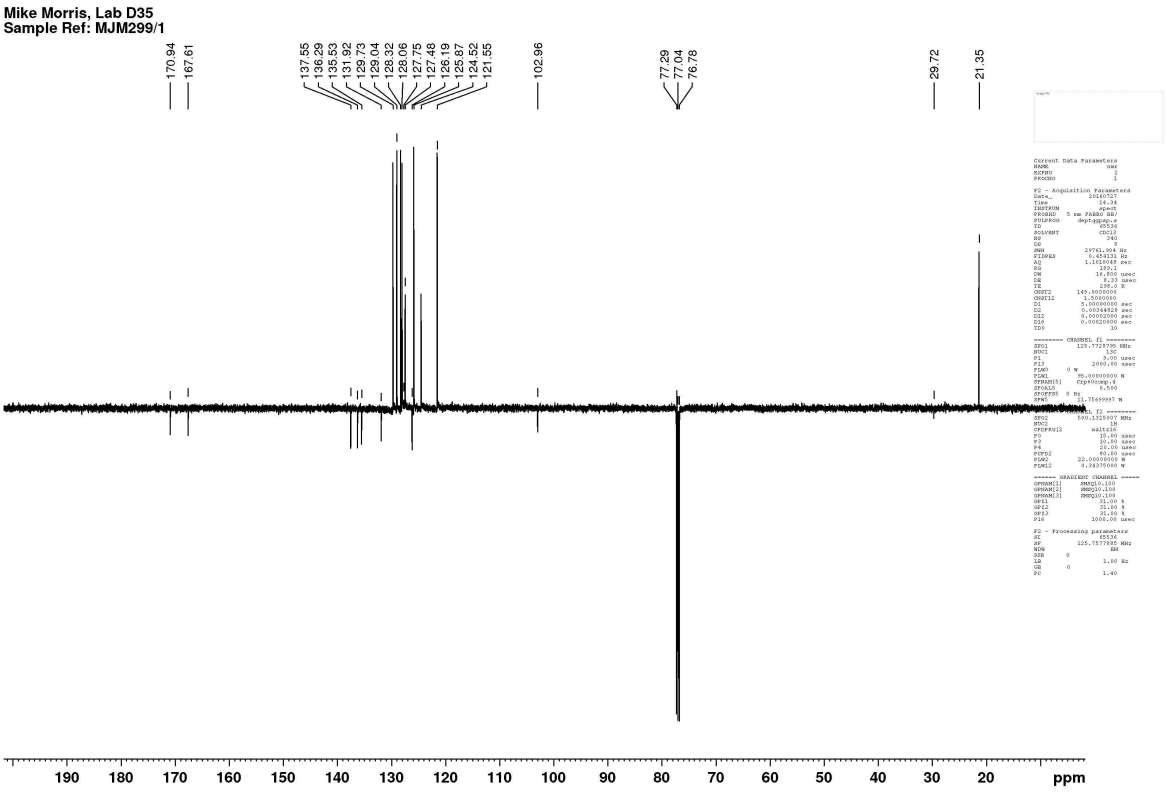


Figure S4. ^{13}C NMR spectrum of compound **4b** in $CDCl_3$.

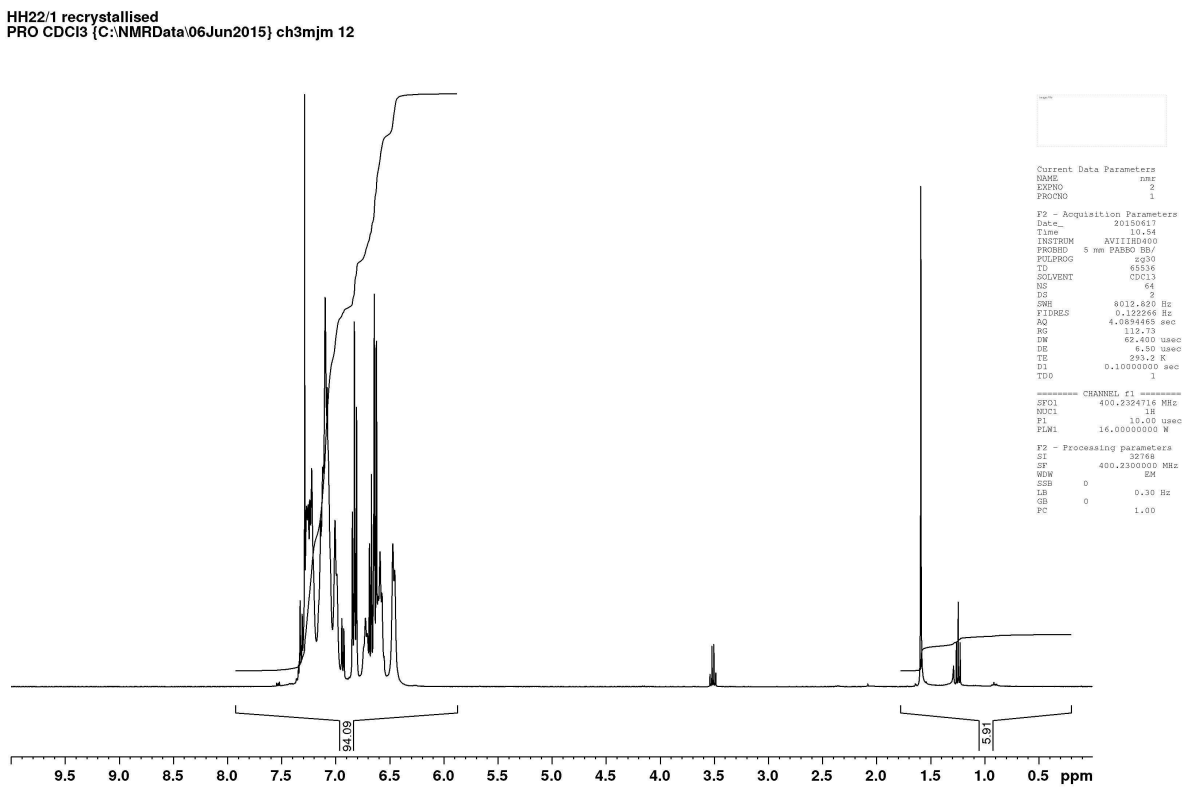


Figure S5. ^{1}H NMR spectrum of compound **5a** in $CDCl_3$.

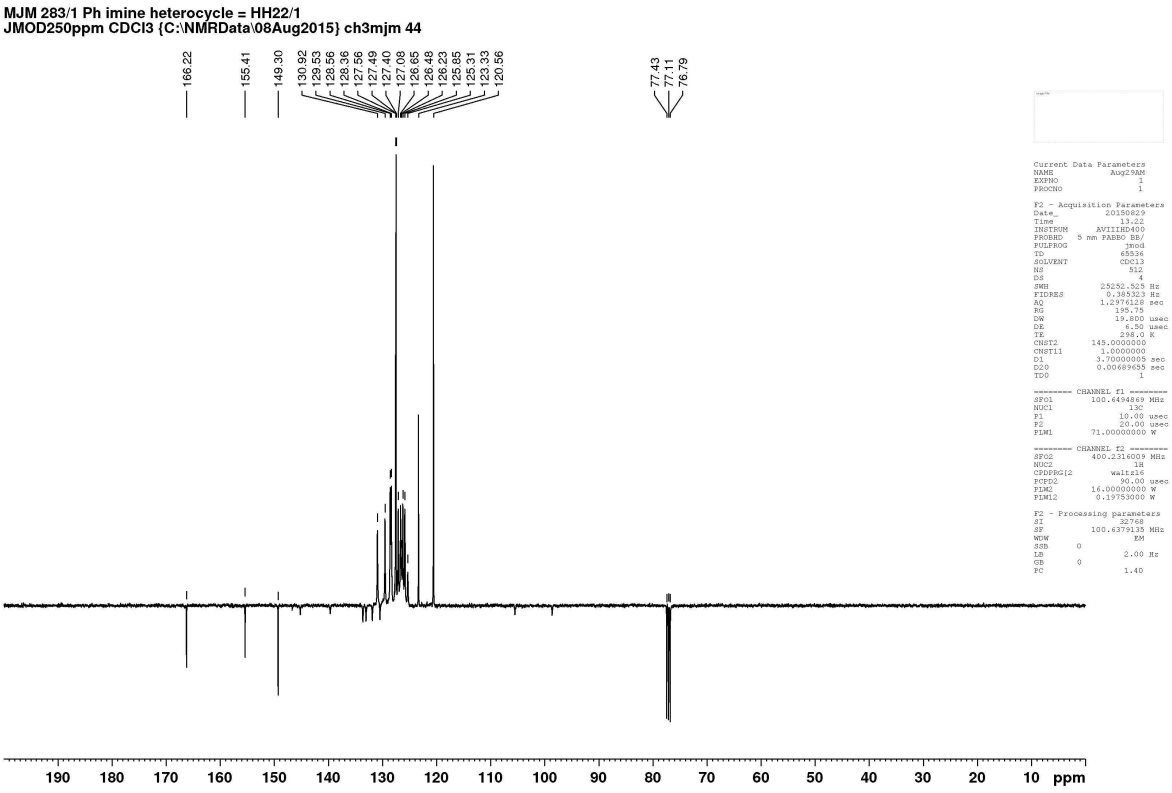


Figure S6. ^{13}C NMR spectrum of compound **5a** in $CDCl_3$.

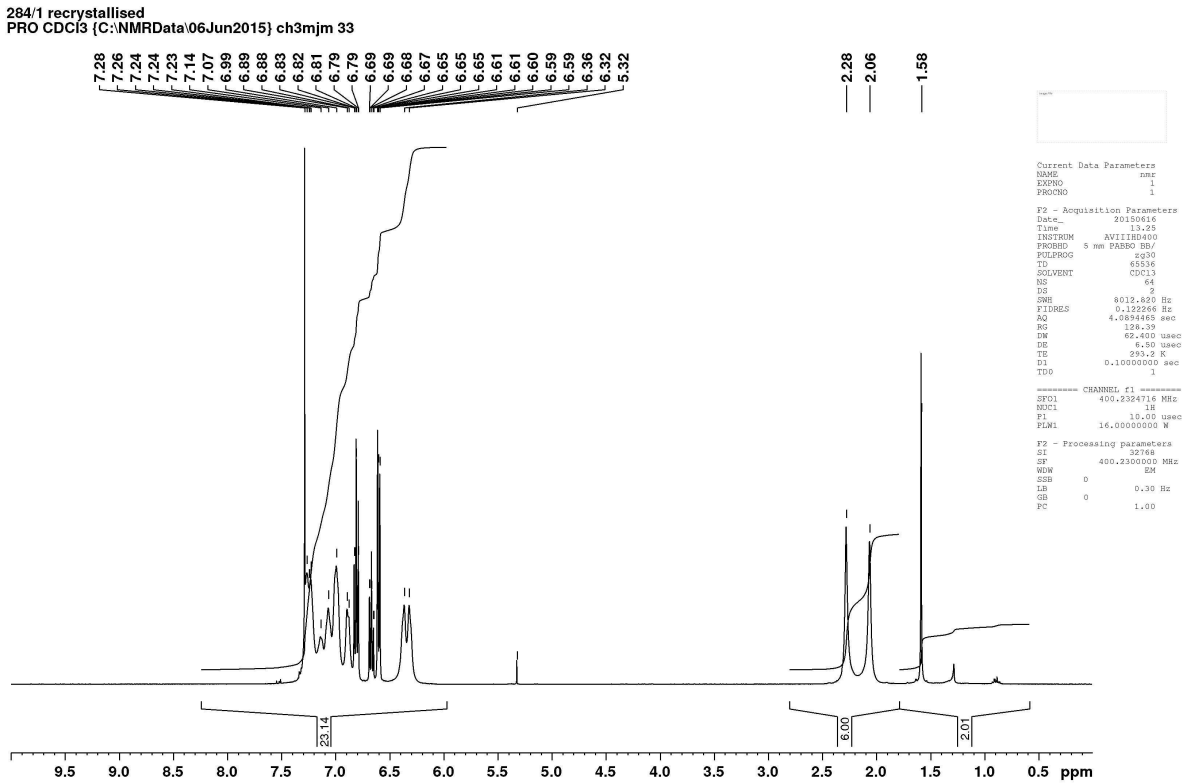


Figure S7. ^{1}H NMR spectrum of compound **5b** in $CDCl_3$.

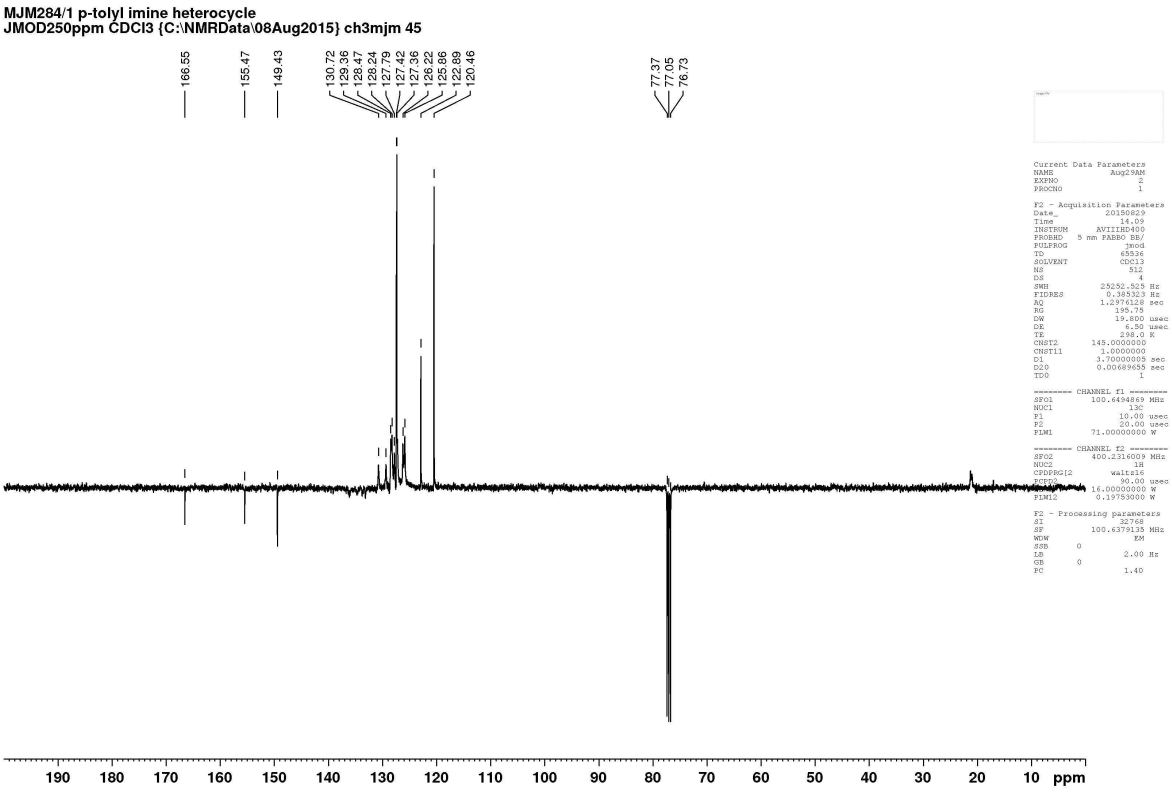


Figure S8. ^{13}C NMR spectrum of compound **5b** in $CDCl_3$.

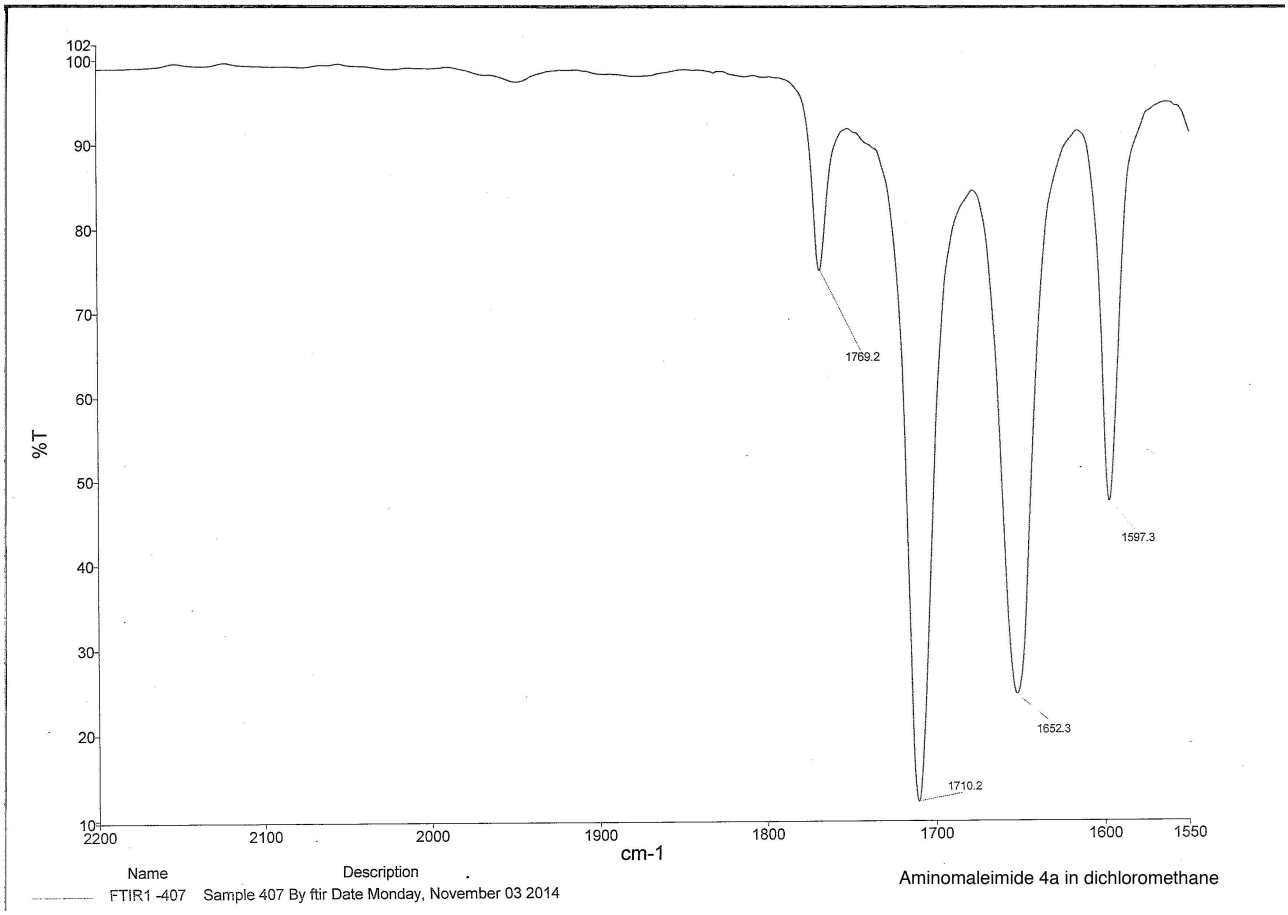


Figure S9. IR spectrum of aminomaleimide **4a** in dichloromethane solution.

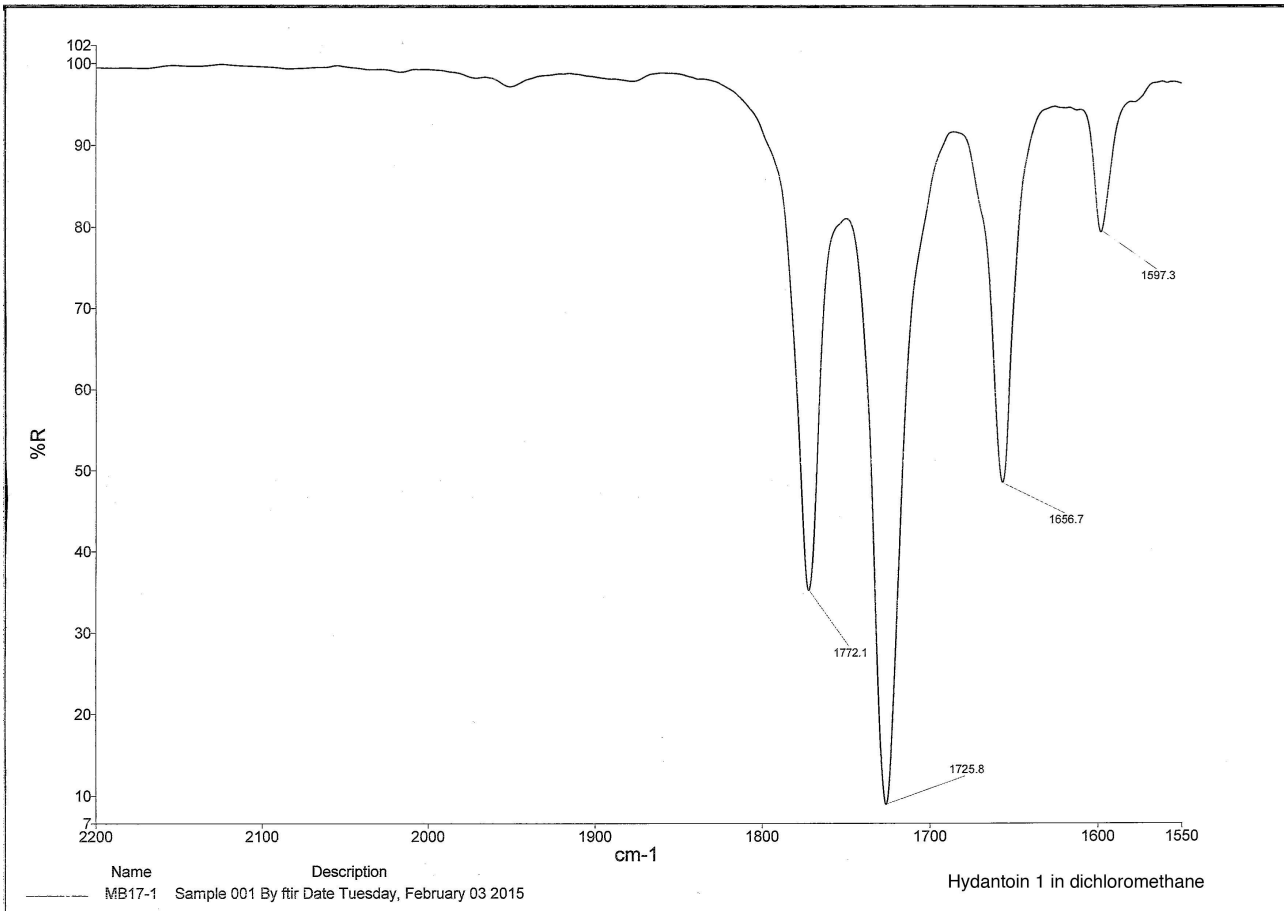


Figure S10. IR spectrum of hydantoin **1** in dichloromethane solution.