Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012

Supporting Information

Transition metal-free direct C-H bond thiolations of 1,3,4-oxadiazoles and related heteroarenes

Liang-Hua Zou, Jens Reball, Jakob Mottweiler and Carsten Bolm*

RWTH Aachen University, Landoltweg 1, 52074 Aachen, Germany
Email: carsten.bolm@oc.rwth-aachen.de

CONTENTS

Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012

1. General Information

All reactions were carried out in 10 mL sealable tubes. Oxadiazoles **1a-d**, **1f-h**[1], **1i**[2], **1m**[3] and disulfides **2c-f**[4] were prepared according to the reported methods. **1j** (97%)**, 1n** (99.7%) and cesium carbonate (99% and 99.994%) were purchased from Alfa Aesar. **1k** and **1l** were bought from Sigma-Aldrich. 1,4-Dioxane and 2-(1,3,4-oxadiazol-2-yl)-phenol (97%) were purchased from Acros and Maybridge, respectively. Flash chromatography was carried out with Merck silica gel 60 (35-75 mesh). Analytical TLC was performed with aluminium sheets silica gel 60 F254 (Merck), and the products were visualized by UV detection. NMR spectra were recorded on a Varian Mercury 300 (^{1}H NMR: 300 MHz, ^{13}C NMR: 75 MHz, ^{19}F NMR: 282 MHz), Varian Inova 400 (^{1}H NMR: 400 MHz, ^{13}C NMR: 100 MHz), Varian VNMRS 600 (^{1}H NMR: 600 MHz, ^{13}C NMR: 125 MHz, ^{19}F NMR: 564 MHz) spectrometer. Chemical shifts (δ) are given in ppm relative to TMS (δ = 0 ppm) or solvent residual peaks ($CDCl_3$, δ = 7.26 ppm, DMSO, δ = 2.50 ppm) as internal standard or as external standard. Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), bd (broad doublet), bdd (broad doublet of doublet) and bm (broad multiplet). IR spectra (ATR) were recorded with a Perkin Elmer 100 FT/IR spectrometer and are reported in frequency of absorption (cm^{-1}). Melting points were determined on an electrothermal capillary melting point apparatus without correcting. Mass spectra were recorded on a Finnigan SSQ 7000 spectrometer, and elemental analyses were performed on an Elementar Vario EL instrument.

2. General procedure for the syntheses of the azoles and the disulfides

2.1. Syntheses of azoles 1a-i

Synthesis of 1,3,4-oxadiazoles 1a, 1b, 1d, 1g, 1h: The procedures were reported by Miura and co-workers.[1] Compounds **1c** and **1f** were prepared according to this method.

2-Phenyl-1,3,4-oxadiazole (1a)[1]

A 200 mL two-necked flask was charged with benzhydrazide (10 g, 73.0 mmol) and triethyl orthoformate (40 mL) and the solution was stirred vigorously at 160 °C for 4 h. The formed ethanol and residual triethyl orthoformate were distilled off under reduced pressure. The product was purified by distillation under high vacuum (about 0.2 mbar) to afford 2-phenyl-1,3,4-oxadiazole (**1a**, 9.8 g, 67.1 mmol) in 92% yield.

Syntheses of 2-aryl 1,3,4-oxadiazoles 1b-d and 1f-h

The preparation of 2-(4-methylphenyl)-1,3,4-oxadiazole (**1b**) is representative for the syntheses of these 2-aryl 1,3,4-oxadiazoles.

Step 1: A flamed-dried and argon-flushed 100 mL two-necked reaction flask, equipped with an addition funnel and an argon inlet, was charged with 4-methylbenzoic acid (4.1 g, 30.0 mmol) and K_2CO_3 (6.2 g, 45.0 mmol). Dry DMF (30 mL) and methyl iodide (2.8 mL, 45.0 mmol) were added dropwise over a period of 15 min. The mixture was stirred at room temperature for 10 h, poured into water and extracted with hexane/ethyl acetate (20:1, v/v). Under reduced pressure, the combined organic layers were evaporated. The product was purified by flash chromatography with hexane/ethyl acetate (10:1, v/v) as eluent giving methyl 4-methylbenzoate (4.5 g, 30.0 mmol) in quantitative yield.

Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012

Step 2: A 100 mL two-necked flask, equipped with a reflux condenser, was charged with methyl 4-methylbenzoate (4.5 g, 30.0 mmol), hydrazine monohydrate (7.5 g, 150.0 mmol), and EtOH (30 mL). Then, the reaction mixture was stirred at reflux for 10 h. After cooling to room temperature, the mixture was concentrated under reduced pressure. The resulting residue was filtered with hexane and dried, affording 3.6 g of the product. For the following reaction step the product was not further purified.

Step 3: A 100 mL two-necked reaction flask, equipped with a reflux condenser, was charged with the hydrazide obtained in step 2 and triethyl orthoformate (25 mL) and the solution was stirred vigorously at 140 °C for 8 h. The formed ethanol and residual triethyl orthoformate were distilled off under reduced pressure. The product was purified by flash chromatography (pentane/ethyl acetate = 8:1, v/v) furnishing 2-(4-methylphenyl)-1,3,4-oxadiazole (**1b**, 2.3 g, 14.4 mmol) in 48% yield over 2 steps.

Synthesis of 2-(2-methoxyphenyl)-1,3,4-oxadiazole (1e)

In a flame-dried and argon-flushed 50 mL two-necked reaction flask, equipped with a reflux condenser and argon inlet, methyl iodide (0.426 g, 3.0 mmol), K_2CO_3 (0.276 g, 2.0 mmol) and 2-(1,3,4-oxadiazol-2-yl)-phenol (0.162 g, 1.0 mmol) were dissolved in dry acetone (2 mL). The mixture was stirred at 85 °C (reflux) over night, cooled to room temperature, diluted with EtOAc (20 mL), and filtered. The filtrate was concentrated under reduced pressure and purified by flash chromatography (pentane/ethyl acetate = 8:1, v/v), providing 2-(2-methoxy-phenyl)-1,3,4-oxadiazole (**1e**, 0.158 g, 0.9 mmol) in 90% yield.

Synthesis of 2-(3-pyridinyl)-1,3,4-oxadiazole (1i)[2]

Step 1: A 250 mL two-necked flask, equipped with a reflux condenser, was charged with 3-pyridinecarboxylic acid (12.3 g, 100.0 mmol), ethanol (60 mL) and conc. H_2SO_4 (2 mL). The reaction mixture was stirred under refluxed for 10 hours. After cooling to room temperature, crushed ice (200 g) and sat. ammonia solution (15 mL) were added to the mixture. The solution was extracted with diethyl ether (5 x 25 mL). The combined organic layers were dried over $MgSO_4$, filtrated and concentrated under reduced pressure. The product was purified by flash chromatography (pentane: EtOAc =15:1) giving 12.5 g (83 mmol) of the product (83% yield).

Step 2: A 100 mL two-necked flask, equipped with a reflux condenser, was charged with the ester obtained in step 1 (4.53 g, 30.0 mmol), hydrazine hydrate (1.44 g, 45.0 mmol) and ethanol (30 mL). The reaction mixture was stirred under reflux over night. The excess of ethanol was removed by distillation. The product was purified by flash chromatography, providing 3.5 g (25.5 mmol) of the desired product (85% yield).

Step 3: A 100 mL two-necked reaction flask, equipped with a reflux condenser, was charged with 4.11 g (30.0 mmol) of the hydrazide obtained in step 2 and triethyl orthoformate (25 mL) and the solution was stirred vigorously at 140 °C over night. The formed ethanol and residual triethyl orthoformate were distilled off under reduced pressure. The product was purified by flash chromatography (pentane/ethyl acetate = 8:1, v/v) furnishing 2-(3-pyridinyl)-1,3,4-oxadiazole (**2i,** 4.1 g, 27.9 mmol) in 93% yield.

Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012

Synthesis of 1-phenyl-benzimidazole (1m)[3]

In a flame-dried and argon-flushed 25 mL two-necked reaction flask, equipped with a reflux condenser and argon inlet, 1-*H*-benzimidazole (0.236 mg**,** 2.0 mmol), Cs_2CO_3 (1.303 g**,** 4 mmol), and CuI (0.076 g**,** 0.4 mmol) were dissolved in DMF (4 mL). At room temperature, iodobenzene (0.612 g**,** 3.0 mmol) was added to the mixture. The reaction mixture was stirred at 130 °C for 24 h. After cooling to room temperature, the solution was diluted with EtOAc (20 mL), filtered through a pad of silica gel and washed with additional EtOAc (10 mL). The filtrate was concentrated under reduced pressure and the product purified by flash chromatography (pentane: EtOAc = 1:1) providing 0.252 mg (1.3 mmol) of the desired product **1m** in 65% yield.

2.2. Syntheses of disulfides 2c-f[4]

The preparation of bis(4-methoxyphenyl) disulfide (**2c**) is representative for the syntheses of these disulfides.

A 100 ml flask was charged with 4-methoxythiophenol (1.402 g**,** 10.0 mmol) in a 10% aq. solution of sodium hydroxide (10 mL). Potassium ferricyanide (3.3 g, 10.0 mmol in 25 mL of water) was added slowly using a syringe. After the addition was complete, the reaction was stirred at room temperature for 1 h. The mixture was extracted with EtOAc (3 x 20 mL), washed with H_2O (20 mL), dried over $MgSO_4$, filtrated and concentrated under reduced pressure. The product was purified by flash chromatography (pentane), providing 1.294 g (4.65 mmol) of product **2c** in 93% yield. Products **2d-f** were prepared according to this procedure.

3. General procedure for the thiolations of azoles 1

3.1. Thiolations with disulfides 2

The preparation of 2-phenyl-5-(4-methylphenylthio)-1,3,4-oxadiazole (**3aa**) is representative for the syntheses of the thiolated products.

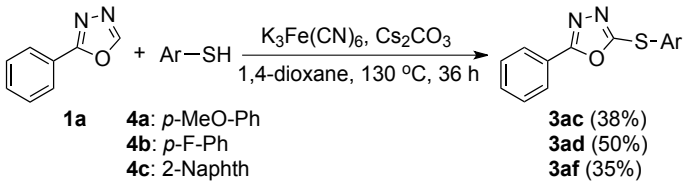
A 10 mL sealable tube equipped with a magnetic stirring bar was charged with all solid reaction components, including 2-phenyl-1,3,4-oxadiazole (**1a,** 0.073 g**,** 0.5 mmol), bis(4-methylphenyl) disulfide (**2a**, 0.308 g**,** 1.25 mmol), Cs_2CO_3 (0.325 g**,** 1.0 mmol). The aperture of the tube was then covered with a rubber septum, and purged using an argon flow for 10 minutes. After the addition of 1,4-dioxane (2 mL) via a syringe, the septum was replaced by a teflon-coated screw cap, and the reaction vessel was placed in a pre-heated oil bath at 130 ^{o}C and stirred for 18 h**.** It was cooled to room temperature and diluted with ethyl acetate (15 mL). The resulting solution was directly filtered through a filter paper and concentrated under reduced pressure. Purification by flash chromatography (at first pentane, then pentane/ethyl acetate = 8:1) gave 116.6 mg (0.435 mmol) of product **3aa** (87% yield).

In general, the identity and purity of the products were confirmed by ^{1}H and ^{13}C NMR spectroscopy, MS (EI), elemental analysis (CHN) and melting point determination.

Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012

3.2. Thiolations with thiols 4

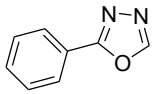
2-Phenyl-1,3,4-oxadiazole (**1a**, 0.5 mmol) was combined with aryl thiol **4c** (1.25 mmol, 2.5 equiv.), $K_3Fe(CN)_6$ (1.25 mmol, 2.5 equiv.) and Cs_2CO_3 (2 mmol, 4 equiv.) in 1,4-dioxane (2 mL), and the mixture stirred at 130 °C under argon (Scheme S1). After 36 h, the starting material **1a** was completely converted and product **3ac** was isolated in 38% yield. In an analogous manner, thio ethers **3ad** and **3af** were obtained in 50% and 35% yield, respectively.



Scheme S1.

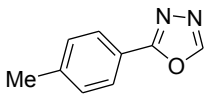
4. Analytical data of the products

2-Phenyl-1,3,4-oxadiazole (1a)



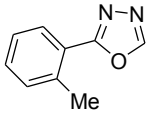
White solid, m.p. <30 °C (lit.[1] m.p. <30 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.46 (s, 1H), 8.00 (bm, 2H), 7.47-7.41 (bm, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.6, 152.7, 131.9, 129.0, 127.0, 123.4; MS *m/z* (EI): 146.1 (M^+).

2-(4-Methylphenyl)-1,3,4-oxadiazole (1b)



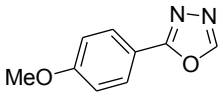
White solid, m.p. 89-90 °C (lit.[1] 84.3-86.0 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.41 (s, 1H), 8.01 (dd, J = 6.8 Hz, 2.0 Hz, 2H), 7.01 (dd, J = 6.8 Hz, 2.0 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.7, 162.5, 152.2, 128.9, 116.0, 114.6, 55.5; MS *m/z* (EI): 160.1 (M^+).

2-(2-Methylphenyl)-1,3,4-oxadiazole (1c)



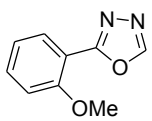
Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.49 (s, 1H), 7.93 (d, J = 7.6 Hz, 1H), 7.42 (t, J = 7.4 Hz, 1H), 7.35-7.30 (m, 2H), 2.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.9, 152.2, 138.6, 131.7, 131.4, 129.1, 126.2, 122.6, 22.0; MS *m/z* (EI): 160.1 (M^+).

2-(4-Methoxyphenyl)-1,3,4-oxadiazole (1d)



White solid, m.p. 60-61 °C (lit.[5] 62.5-63.5 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.40 (s, 1H), 7.96 (dd, J = 7.2 Hz, 2.4 Hz, 2H), 6.97 (dd, J = 6.8 Hz, 2.0 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.6, 162.4, 152.2, 128.8, 115.9, 114.5, 55.4; MS *m/z* (EI): 176.1 (M^+).

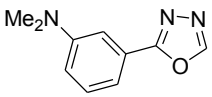
2-(2-Methoxyphenyl)-1,3,4-oxadiazole (1e)



White solid, m.p. 55-56 °C (lit.[6] 47-49 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.47 (d, 1H), 7.93-7.91 (bm, 1H), 7.49-7.48 (bm, 1H), 7.07-7.03 (bm, 2H), 3.92-394 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 163.5, 157.9, 152.5, 133.3, 130.6, 120.7, 112.6, 112.0, 56.0; MS *m/z* (EI): 176.1 (M^+).

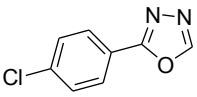
Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012

2-[3-*N*,*N*-Dimethylphenyl]-1,3,4-oxadiazole (1f)



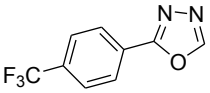
White solid, m.p. 60-61 °C (lit.[7] 61-62 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.44 (s, 1H), 7.43-7.42 (bm, 1H), 7.37-7.33 (m, 2H), 6.90-7.87 (m, 1H), 3.03 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.5, 152.4, 150.6, 129.7, 124.0, 115.7, 114.8, 110.3, 40.4; MS *m/z* (EI): 189.2 (M^+).

2-(4-Chlorophenyl)-1,3,4-oxadiazole (1g)



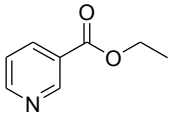
White solid, m.p. 132-133 °C (lit.[1] 133-135 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.42 (s, 1H), 7.33 (dd, J = 6.8 Hz, 2.0 Hz, 2H), 7.41 (dd, J = 6.8 Hz, 2.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.9, 152.7, 138.3, 129.5, 128.3, 121.9; MS *m/z* (EI): 180.5 (M^+).

2-(4-Trifluoromethylphenyl)-1,3,4-oxadiazole (1h)[1]



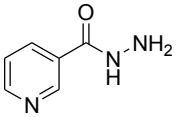
White solid, m.p. 111-113 °C (lit.[1] 112-114 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.47 (s, 1H), 8.14 (d, J = 8.1 Hz, 2H), 7.41 (d, J = 8.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 163.9, 153.1, 133.6 (q, $J_{F\text{-}C}$ = 32.7 Hz), 127.4, 126.7, 126.2 (q, $J_{F\text{-}C}$ = 3.8 Hz), 123.5 (q, $J_{F\text{-}C}$ = 272.5 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ = –63.1 (s, 3F); MS *m/z* (EI): 214.1 (M^+).

3-(Ethoxycarbonyl)-pyridine (1i-1)[8]



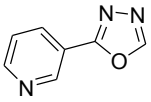
Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.20-9.19 (m, 1H), 9.74 (dd, J = 4.8 Hz, 1.6 Hz, 1H), 8.28-8.26 (m, 1H), 7.38-7.34 (m, 1H), 4.39 (q, 2H), 1.38 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.2, 153.2, 150.8, 136.9, 126.3, 123.2, 61.4, 14.2; MS *m/z* (EI): 151.1 (M^+).

3-Pyridinecarbohydrazide (1i-2)



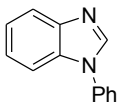
White solid, m.p. 160-162 °C (lit.[9] 161-163 °C). ^{1}H NMR (600 MHz, d_6-DMSO) δ = 8.96 (s, 1H), 8.68 (d, J = 4.8 Hz, 1H), 8.15-8.14 (m, 1H), 7.50-7.47 (m, 1H), 3.43 (bq, 3H); ^{13}C NMR (150 MHz, d_6-DMSO) δ = 164.8, 152.2, 148.5, 135.1, 129.3, 123.9; MS *m/z* (EI): 137.1 (M^+).

2-(3-Pyridinyl)-1,3,4-oxadiazole (1i)



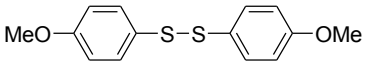
Pale yellow solid, m.p. 72-74 °C (lit.[6] 75-76 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.25 (bd, J = 0.8 Hz, 1H), 8.75-8.74 (bm, 1H), 8.55 (s, 1H), 8.36-8.33 (bm, 1H), 7.47-7.43 (bm, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.7, 153.1, 152.6, 147.9, 134.3, 123.8, 120.0; MS *m/z* (EI): 147.1 (M^+).

***N*-Phenylbenzimidazole (1m)**[3]



Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.05 (s, 1H), 7.87-7.84 (m, 1H), 7.52-7.44 (m, 3H), 7.44-7.37 (m, 3H), 7.31-7.24 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.0, 142.2, 136.3, 133.6, 130.0, 128.0, 123.9, 123.6, 122.7, 120.6, 110.4; MS *m/z* (EI): 194.2 (M^+).

4,4'-Dimethoxydiphenyl disulfide (2c)

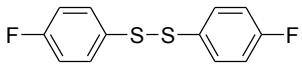


White solid, m.p. 35-36 °C (lit.[10] 34-35 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40 (dd, J = 9.2 Hz, 3.2 Hz, 4H), 6.83 (dd, J

Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012

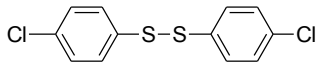
= 8.8 Hz, 2.8 Hz, 4H), 3.80 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.9, 132.7, 128.4, 114.6, 55.4; MS *m/z* (EI): 278.3 (M^+).

4,4'-Difluorodiphenyl disulfide (2d)



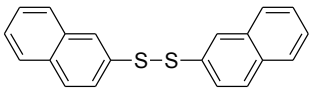
White solid, m.p. 49-51 °C (lit.[11] 50-52 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40-7.37 (m, 4H), 7.28-7.24 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.6 (d, $J_{F\text{-}C}$ = 246.7 Hz), 132.2 (d, $J_{F\text{-}C}$ = 3.3 Hz), 131.3 (d, $J_{F\text{-}C}$ = 8.0 Hz), 116.2 (d, $J_{F\text{-}C}$ = 22.1 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ = –113.4 (s, 2F) ppm; MS *m/z* (EI): 254.2 (M^+).

4,4'-Dichlorodiphenyl disulfide (2e)



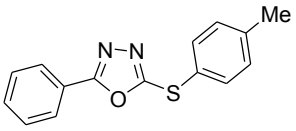
Pale yellow solid, m.p. 71-73 °C (lit.[12] 70-72 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47-7.43 (m, 4H), 7.04-6.99 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 135.1, 133.6, 129.3, 129.2; MS *m/z* (EI): 287.2 (M^+).

2,2'-Dinaphthyl disulfide (2f)



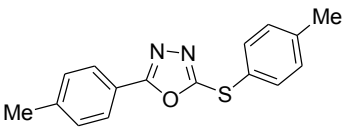
White solid, m.p. 139-141 °C (lit.[13] 138-140 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 (*J* = 1.6 Hz, 2H), 7.81-7.78 (m, 4H); 7.75-7.73 (m, 2H); 7.63 (dd, *J* = 8.8 Hz, 2.0 Hz, 2H); 7.49-7.43 (m, 4H); ^{13}C NMR (100 MHz (100 MHz, $CDCl_3$) δ = 134.2, 133.5, 132.5, 128.9, 127.7, 127.4, 126.7, 126.5, 126.2, 125.6; MS *m/z* (EI): 318.4 (M^+).

2-Phenyl-5-(4-methylphenylthio)-1,3,4-oxadiazole (3aa)



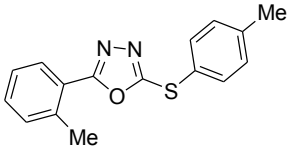
White solid, m.p. 71-72 °C (lit.[14] 68-69 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.97-7.94 (m, 2H), 7.57 (dd, *J* = 6.3 Hz, 1.8 Hz, 2H); 7.51-7.44 (m, 3H), 7.24 (d, *J* = 8.1 Hz 2H), 2.39 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 166.2, 163.4, 140.4, 134.0, 131.7, 130.5, 129.0, 126.7, 123.6, 123.2, 21.3; Anal. Calcd for $C_{15}H_{12}N_2OS$ (268.33): C, 67.14; H, 4.51; N, 10.44; found: C, 67.23; H, 4.53; N, 10.50; MS *m/z* (EI): 268.2 (M^+).

2-(4-Methylphenyl)-5-(4-methylphenylthio)-1,3,4-oxadiazole (3ba)



White solid, m.p. 71-73 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.85-7.83 (m, 2H), 7.58-7.55 (m, 2H), 7.28-7.22 (m, 4H), 2.40 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 166.4, 163.0, 142.3, 140.3, 133.9, 130.5, 129.7, 126.7, 123.4, 120.8, 21.6, 21.3; Anal. Calcd for $C_{16}H_{14}N_2OS$ (282.36): C, 68.06; H, 5.00; N, 9.92; Found: C, 67.99; H, 4.76; N, 9.88; MS *m/z* (EI): 282.2 (M^+).

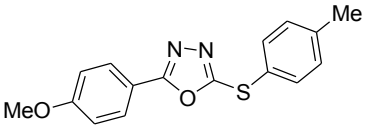
2-(2-Methylphenyl)-5-(4-methylphenylthio)-1,3,4-oxadiazole (3ca)



White solid, m.p. 51-52 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.82-7.79 (m, 1H), 7.59-7.55 (m, 2H), 7.39-7.34 (m, 1H), 7.29-7.21 (m, 4H), 2.59 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 166.3, 163.2, 140.4, 138.3, 134.2, 131.7, 131.2, 130.5, 128.8, 126.1, 123.1, 122.6, 22.0, 21.3; Anal. Calcd for $C_{16}H_{14}N_2OS$ (282.36): C, 68.06; H, 5.00; N, 9.92; Found: C, 68.00; H, 4.77; N, 9.90; MS *m/z* (EI): 282.2 (M^+).

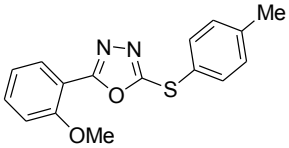
Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012

2-(4-Methoxyphenyl)-5-(4-methylphenylthio)-1,3,4-oxadiazole (3da)



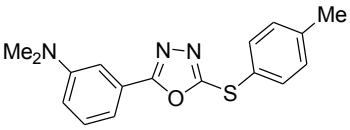
White solid, m.p. 73-74 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.88 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 7.8 Hz, 2H), 6.96 (d, J = 8.4 Hz, 2H), 3.85 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 166.3, 162.5, 162.3, 140.2, 133.8, 130.5, 128.5, 123.6, 116.1, 114.4, 55.4, 21.3; Anal. Calcd for $C_{16}H_{14}N_2O_2S$ (298.08): C, 64.41; H, 4.73; N, 9.39; Found: C, 64.53; H, 4.69; N, 9.40; IR: 3075, 2938, 2103, 1898, 1610, 1478, 1304, 1254, 1163, 1067, 1022, 955, 835, 803, 733, 697 cm^{-1}; MS *m/z* (EI): 298.1 (M^+).

2-(2-Methoxyphenyl)-5-(4-methylphenylthio)-1,3,4-oxadiazole (3ea)



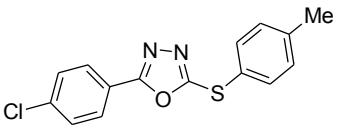
White solid, m.p. 91-93 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.83-7.80 (bdd, J = 8.1 Hz, 1.5 Hz, 1H), 7.57 (d, J = 8.1 Hz, 2H), 7.50-7.44 (m, 1H), 7.22 (d, J = 7.8 Hz, 2H), 7.02 (t, J = 7.2 Hz, 2 H), 3.89 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = = 163.0, 157.8, 140.1, 133.9, 133.1, 130.4, 130.3, 129.6, 123.6, 120.7, 112.8, 111.9, 55.9, 21.3; Anal. Calcd for $C_{16}H_{14}N_2O_2S$ (298.36): C, 64.41; H, 4.73; N, 9.39; Found: C, 64.28; H, 4.36; N, 9.29; MS *m/z* (EI): 298.1 (M^+).

2-(3-N,N-Dimethylaminophenyl)-5-(4-methylphenylthio)-1,3,4-oxadiazole (3fa)



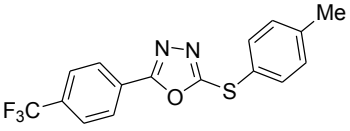
Yelllow solid, m.p. 103-104 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.57-7.55 (m, 2H), 7.32-7.28 (bm, 2H), 7.24-7.22 (bm, 3H), 6.85 (dd, J = 8.4 Hz, 2.4 Hz, 1H), 3.00 (s, 6H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.0, 163.0, 150.5, 140.2, 133.8, 130.4, 129.6, 124.1, 123.5, 115.6, 114.7, 110.0, 40.4, 21.3; Anal. Calcd for $C_{17}H_{17}N_3OS$ (311.40): C, 65.57; H, 5.50; N, 13.49; Found: C, 65.30; H, 5.43; N, 13.20; MS *m/z* (EI): 311.2 (M^+).

2-(4-Chlorophenyl)-5-(4-methylphenylthio)-1,3,4-oxadiazole (3ga)



White solid, m.p. 121-122 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.90-7.88 (m, 2H), 7.58-7.56 (m, 2H), 7.46-7.43 (m, 2H), 7.24 (d, J = 8.0 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.3, 163.8, 140.5, 138.0, 134.1, 130.6, 129.4, 128.0, 122.9, 122.0, 21.3; Anal. Calcd for $C_{15}H_{11}ClN_2OS$ (302.78): C, 59.50; H, 3.66; N, 9.25; Found: C, 59.12; H, 3.33; N, 9.11; MS *m/z* (EI): 302.1 (M^+).

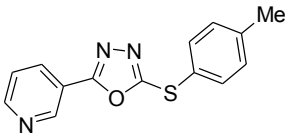
2-(4-Trifluoromethylphenyl)-5-(4-methylphenylthio)-1,3,4-oxadiazole (3ha)



White solid, m.p. 116-118 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.07 (d, J = 8.4 Hz, 2H), 7.72 (d, J = 7.8 Hz , 2H), 7.58 (d, J = 7.8 Hz, 2H), 7.25 (d, J = 7.8 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 164.9, 164.6, 140.7, 134.2, 133.3 (q, $J_{C\text{-}F}$ = 32.8 Hz), 130.6, 130.4, 127.0, 126.8, 126.3 (q, $J_{C\text{-}F}$ = 3.7 Hz), 123.5 (q, $J_{C\text{-}F}$ = 272.6 Hz), 21.3; ^{19}F NMR (282 MHz, $CDCl_3$) δ = –63.2 (s, 3F) ppm; Anal. Calcd for $C_{16}H_{11}F_3N_2OS$ (336.33): C, 57.14; H, 3.30; N, 8.33; Found: C, 57.57; H, 3.39; N, 8.18; MS *m/z* (EI): 336.2 (M^+).

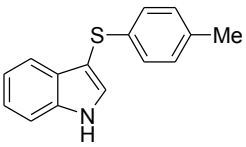
Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012

2-(3-Pyridinyl)-5-(4-methylphenylthio)-1,3,4-oxadiazole (3ia)



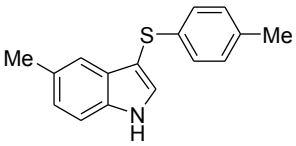
White solid, m.p. 78-79 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.13 (s, 1H), 8.72 (d, J = 4.4 Hz , 1H), 8.23 (d, J = 8.0 Hz , 1H), 7.56 (d, J = 8.0 Hz, 2H), 7.42-7.39 (m, 1H), 7.23 (d, J = 7.2 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.9, 164.6, 140.7, 134.3, 130.6, 127.0, 126.1 (2C), 126.0 (2C), 122.6, 21.3; Anal. Calcd for $C_{14}H_{11}N_3OS$ (269.32): C, 62.43; H, 4.12; N, 15.60; Found: C, 62.48; H, 3.90; N, 15.87; MS *m/z* (EI): 269.1 (M^+).

3-(4-Methylphenylthio)-indole (3ja)



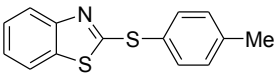
White solid, m.p. 127-129 °C (lit.[15] 125.0-126.0). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.30 (bs, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.44-7.43 (m, 1H), 7.42-7.40 (m, 1H), 7.28-7.24 (m, 1H), 7.18-7.14 (m, 1H), 7.04 (dd, J = 8.8 Hz, 2.0 Hz, 2H), 6.98 (d, J = 8.0 Hz, 2H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 136.4, 135.5, 134.7, 130.4, 129.5, 129.1, 126.2, 123.0, 120.8, 119.7, 111.5, 103.4, 20.9; Anal. Calcd for $C_{15}H_{13}NS$ (239.34): C, 75.28; H, 5.47; N, 5.85; Found: C, 75.16; H, 5.19; N, 5.72; MS *m/z* (EI): 239.2 (M^+).

3-(4-Methylphenylthio)-6-methylindole (3ka)



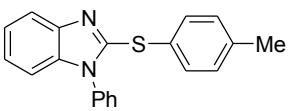
White solid, m.p. 137-138 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.23 (bs, 1H), 7.44 (s, 1H), 7.41 (s, 1H), 7.31 (d, J = 8.4 Hz, 1H), 7.10 (d, J = 8.4 Hz, 1H), 7.05 (d, J = 8.4 Hz, 2H), 7.00 (t, J = 7.8 Hz, 2H), 2.44 (s, 1H), 2.28 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 135.8, 134.8, 134.5, 130.7, 130.3, 129.5, 129.4, 126.0, 124.6, 119.2, 111.2, 102.6, 21.4, 20.9; Anal. Calcd for $C_{16}H_{15}NS$ (253.09): C, 75.85; H, 5.97; N, 5.53; Found: C, 75.71; H, 5.87; N, 5.38; MS *m/z* (EI): 253.1 (M^+).

2-(4-Methylphenylthio)-benzothiazole (3la)



White solid, m.p. 72-73 °C (lit.[16] 73-74 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.87 (d, J = 8.1 Hz, 1H), 7.63 (d, J = 8.0 Hz, 3H), 7.40 (t, J = 7.7 Hz, 1H), 7.31-7.23 (m, 3H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 170.8, 154.0, 141.2, 135.6, 130.8, 126.3, 126.1, 124.2, 121.8, 120.7, 21.5; Anal. Calcd for $C_{14}H_{11}NS_2$ (257.03): C, 65.33; H, 4.31; N, 5.44; Found: C, 65.31; H, 4.09; N, 5.36; IR: 3057, 2913, 2110, 1988, 1591, 1491, 1452, 1420, 1235, 1083, 1003, 847, 814, 755, 725, 669 cm^{-1}; MS *m/z* (EI): 256.2 (M^+).

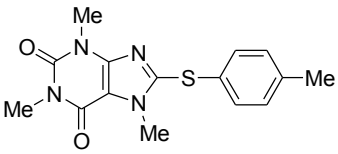
1-Phenyl-2-(4-methylphenylthio)-benzimidazole (3ma)



White solid, m.p. 122-124 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.76 (d, J = 8.4 Hz, 1H), 7.54-7.50 (m, 3H), 7.37-7.36 (m, 2H), 7.31 (d, J = 7.8 Hz, 2H), 7.27-7.25 (m, 1H), 7.20 (t, J = 7.8 Hz, 1H), 7.12-7.09 (m, 3H), 2.33 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 150.2, 143.1, 138.7, 137.3, 135.5, 133.0, 130.0, 129.5, 128.9, 127.5, 126.7, 123.1, 122.5, 119.3, 109.8, 21.2; Anal. Calcd for $C_{20}H_{16}N_2S$ (316.42): C, 75.92; H, 5.10; N, 8.85; Found: C, 75.54; H, 5.11; N, 8.68; IR: 3011, 2945, 2319, 2100, 1903, 1703, 1591, 1491, 1438, 1369, 1304, 1266, 1176, 1073, 1005, 905, 807, 750, 697 cm^{-1}; MS *m/z* (EI): 316.2 (M^+).

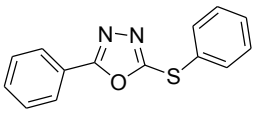
Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012

2-(4-Methylphenylthio)-caffeine (3na)



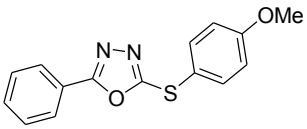
White solid, m.p. 144-146 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.28-7.26 (m, 2H), 7.14 (d, J = 7.8 Hz, 2H), 3.91-3.90 (t, 3H), 3.54 (t, 3H), 3.38 (t, 3H), 2.33 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 154.9, 151.4, 148.0, 147.2, 136.7, 131.2, 130.3, 126.8, 109.4, 33.0, 29.8, 27.9, 21.1; Anal. Calcd for $C_{15}H_{16}N_4O_2S$ (316.38): C, 56.94; H, 5.10; N, 17.71; Found: C, 56.88; H, 4.85; N, 17.75; IR: 3034, 2953, 2130, 1701, 1658, 1540, 1447, 1336, 1219, 1035, 971, 811, 744, 668 cm^{-1}; MS *m/z* (EI): 316.2 (M^+).

2-Phenyl-5-phenylthio-1,3,4-oxadiazole (3ab)



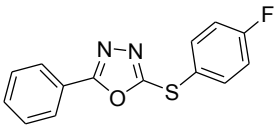
Colorless oil (lit.[14] 62.4-63.1 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.97-7.95 (m, 2H), 7.68-7.67 (m, 2H), 7.51-7.43 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 166.4, 162.9, 133.6, 131.8, 129.8, 129.7, 129.0, 127.1, 126.8, 123.5; Anal. Calcd for $C_{14}H_{10}N_2OS$ (254.05): C, 66.12; H, 3.96; N, 11.02; Found: C, 66.11; H, 3.76; N, 11.42; MS *m/z* (EI): 254.1 (M^+).

2-Phenyl-5-(4-methoxyphenylthio)-1,3,4-oxadiazole (3ac)



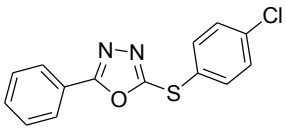
White solid, m.p. 89.4-90.4 °C (lit.[14] 85.5-86.5 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.94 (d, J = 7.7 Hz, 2H), 7.63 (d, J = 8.3 Hz, 2H), 7.50-7.45 (m, 3H), 6.96 (d, J = 8.3 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 166.1, 163.9, 161.3, 136.3, 131.7, 129.0, 126.7, 123.6, 116.7, 115.3, 55.4; Anal. Calcd for $C_{15}H_{12}N_2O_2S$ (284.06): C, 63.36; H, 4.25; N, 9.85; Found: C, 63.25; H, 4.16; N, 9.79; MS *m/z* (EI): 284.1 (M^+).

2-Phenyl-5-(4-fluorophenylthio)-1,3,4-oxadiazole (3ad)



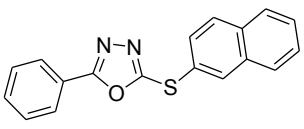
White solid, m.p. 96.0-97.1 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.95 (d, J = 7.5 Hz, 2H), 7.71-7.68 (m, 2H), 7.53–7.51 (m, 1H), 7.47 (t, J = 7.2 Hz, 2H), 7.14 (t, J = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 166.3, 164.7, 163.0 (d, $J_{F\text{-}C}$ = 9.6 Hz), 136.4 (d, $J_{F\text{-}C}$ = 8.7 Hz), 131.8, 129.0 (d, $J_{F\text{-}C}$ = 13.1 Hz), 126.7, 123.5, 121.9 (d, $J_{F\text{-}C}$ = 3.2 Hz), 117.1 (d, $J_{F\text{-}C}$ = 22.4 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ = -109.8 (m, 1F); Anal. Calcd for $C_{14}H_9FN_2OS$ (272.04): C, 61.75; H, 3.33; N, 10.29; Found: C, 61.90; H, 3.13; N, 10.26; MS *m/z* (EI): 272.1 (M^+).

2-Phenyl-5-(4-chlorophenylthio)-1,3,4-oxadiazole (3ae)



White solid, m.p. 97.5-98.6 °C (lit.[14] 95-95.5 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.97 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.53-7.51 (m, 1H), 7.49-7.47 (m, 2H), 7.42-7.40 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 166.5, 162.4, 136.4, 134.9, 131.9, 130.0, 129.0, 126.8, 125.4, 123.4; Anal. Calcd for $C_{14}H_9ClN_2OS$ (288.01): C, 58.23; H, 3.14; N, 9.70; Found: C, 58.31; H, 2.92; N, 9.72; MS *m/z* (EI): 288.1 (M^+).

2-Phenyl-5-(2-naphthylthio)-1,3,4-oxadiazole (3af)

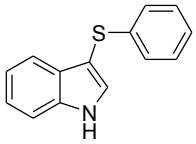


White solid, m.p. 114.3-115.6 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.21 (s, 1H), 7.96 (d, J = 7.8 Hz, 2H), 7.89 (d, J = 9.0 Hz, 1H), 7.86 (t, J = 9.6 Hz, 2H), 7.68 (d, J = 8.4 Hz, 1H), 7.58-7.54 (m, 2H), 7.51-7.49 (m, 1H), 7.46 (t, J = 7.8 Hz, 2H); ^{13}C NMR (150 MHz,

Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012

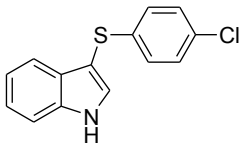
$CDCl_3$) δ = 166.4, 162.9, 133.6, 133.5, 133.4, 131.8, 129.7, 129.6, 129.0, 127.9, 127.8, 127.5, 127.0, 126.8, 124.2, 123.5; Anal. Calcd for $C_{18}H_{12}N_2OS$ (304.07): C, 71.03; H, 3.97; N, 9.20; Found: C, 71.15; H, 3.83; N, 9.23; MS m/z (EI): 304.1 (M^+).

3-Phenylthioindole (3jb)



White solid, m.p. 152.6-153.5 °C (lit.[17] 152-154 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.36 (bs, 1H), 7.64 (d, J = 8.7 Hz, 1H), 7.48 (d, J = 2.6 Hz, 1H), 7.45-7.43 (m, 1H), 7.31-7.26 (m, 1H), 7.20-7.11 (m, 5H), 7.09-7.05 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 137.8, 136.5, 130.7, 130.6, 128.8, 128.7, 127.1, 123.2, 121.1, 119.5, 111.7, 102.5; Anal. Calcd for $C_{14}H_{11}NS$ (225.31): C, 74.63; H, 4.92; N, 6.22; Found: C, 74.57; H, 4.74; N, 6.12; MS m/z (EI): 225.1 (M^+).

3-(4-Chlorophenylthio)-indole (3je)



White solid, m.p. 135.2-136.3 °C (lit.[15] 134.0-135.1 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.39 (bs, 1H), 7.59 (d, J = 7.8 Hz, 1H), 7.48 (d, J = 2.4 Hz, 1H), 7.45 (t, J = 8.4 Hz, 1H), 7.29 (t, J = 7.2 Hz, 1H), 7.19 (t, J = 7.2 Hz, 1H), 7.12 (dd, J = 8.4 Hz, 1.2 Hz, 2H), 7.04-7.03 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 137.8, 136.5, 130.7, 130.6, 128.8, 128.7, 127.1, 123.2, 121.1, 119.5, 111.7, 102.5; Anal. Calcd for $C_{14}H_{10}ClNS$ (259.02): C, 64.73; H, 3.88; N, 5.39; Found: C, 64.70; H, 3.72; N, 5.30; MS m/z (EI): 259.1 (M^+).

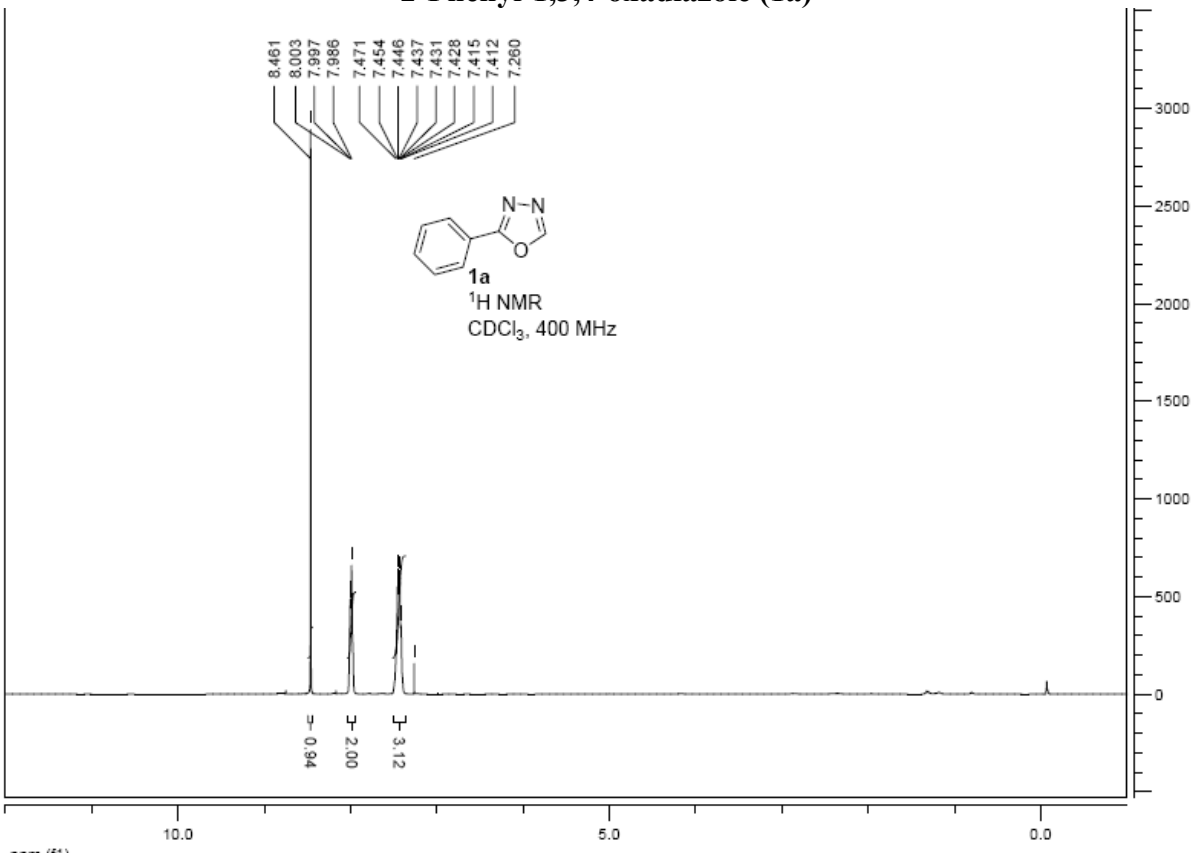
4. References

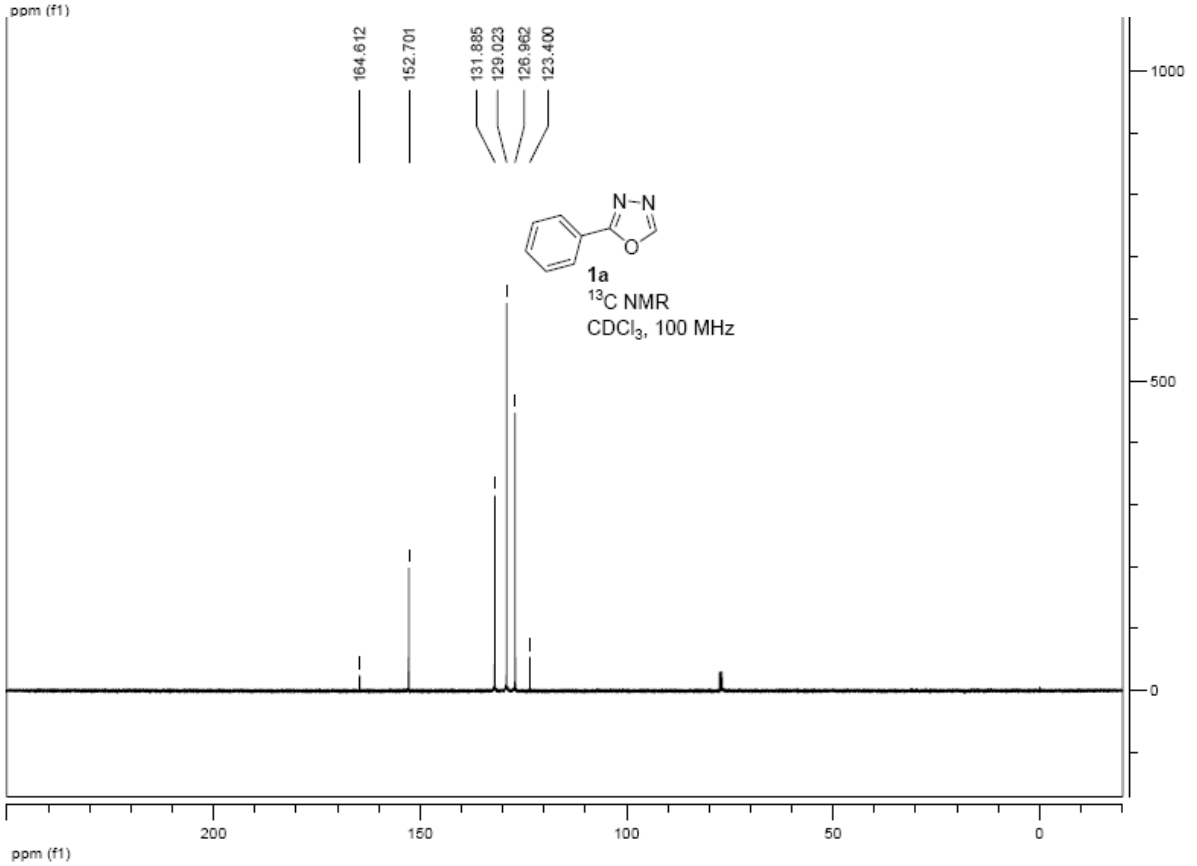
1 T. Kawano, K. Hirano, T. Satoh and M. Miura, *J. Am. Chem. Soc*., 2010, **132**, 6900.
2 (a) K. Ohmoto, T. Yamamoto, M. Okuma, T. Horiuchi, H. Imanishi, Y. Odagaki, K. Kawabata, T. Sekioka, Y. Hirota, S. Matsuoka, H. Nakai and M. Toda, *J. Med. Chem*., 2001, **44**, 1268. (b) D. K. Mehta, R. Das and K. Dua, *Int. J. Chem. Sci*., 2009, **7**, 225.
3 T. Mino, Y. Harada, H. Shindo, M. Sakamoto and T. Fujita, *Synlett*, 2008, **19**, 614.
4 D. Giles, M. S. Prakash and K.V. Ramseshu, *E-J. Chem*., 2007, **4**, 428.
5 T. Mukai, K. Hirano, T. Satoh and M. Miura, *J. Org. Chem*., 2009, **74**, 6410.
6 C. Ainsworth, *J. Am. Chem. Soc*., 1955, **77**, 1148.
7 J. Maillard and M. Vincent, *Bull. Soc. Chim. Fr.*, 1966, 376.
8 M. C. Kloetzel and F. L. Chubb, *J. Am. Chem. Soc*., 1957, **79**, 4226.
9 F. A. Adekunle, J. A. O. Woods, O. O. E. Onawumi and O. A. Odunola, *Asian J. Chem*., 2010, **22**, 5543.
10 M. Oba, K. Tanaka, K. Nishiyama and W. Ando, *J. Org. Chem.*, 2011, **76**, 4173.
11 D. R. Dreyer, H.-P. Jia, A. D. Todd, J. X. Geng and C. W. Bielawski, *Org. Bio. Chem*. 2011, **9**, 7292.
12 J. L. Garcia Ruano, A. Parra and J. Aleman, *Green Chem*., 2008, **10**, 706.
13 L. H. Wang and D. L. J. Clive, *Org. Lett.*, 2011, **13**, 1734.
14 L.-F. Niu, Y. Cai, C. Liang, X.-P. Hui and P.-F. Xu, *Tetrahedron*, 2011, **67**, 2878.
15 F. Li, R.-Y. Tang, P.-Z. Zhong and J.-H. Li, *Synthesis*, 2009, **41**, 4183.
16 A. Mieko, F. Toriyama and M. Yamaguchi, *Tetrahedron Lett*., 2011, **52**, 2344.
17 C. C. Silveira, S. R. Mendes, L. Wolf and G. M. Martins, *Tetrahedron Lett.*, 2010, **51**, 2014.

Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012

5. NMR spectra

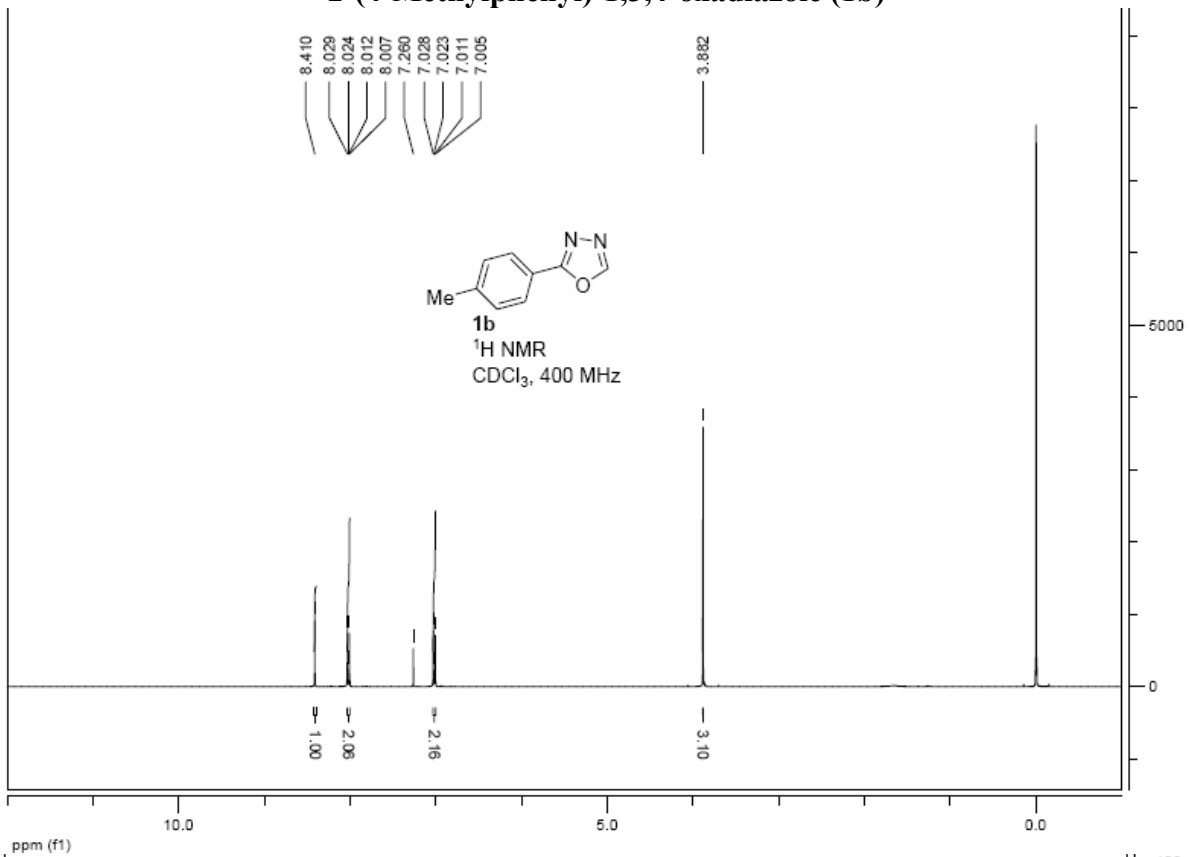
2-Phenyl-1,3,4-oxadiazole (1a)

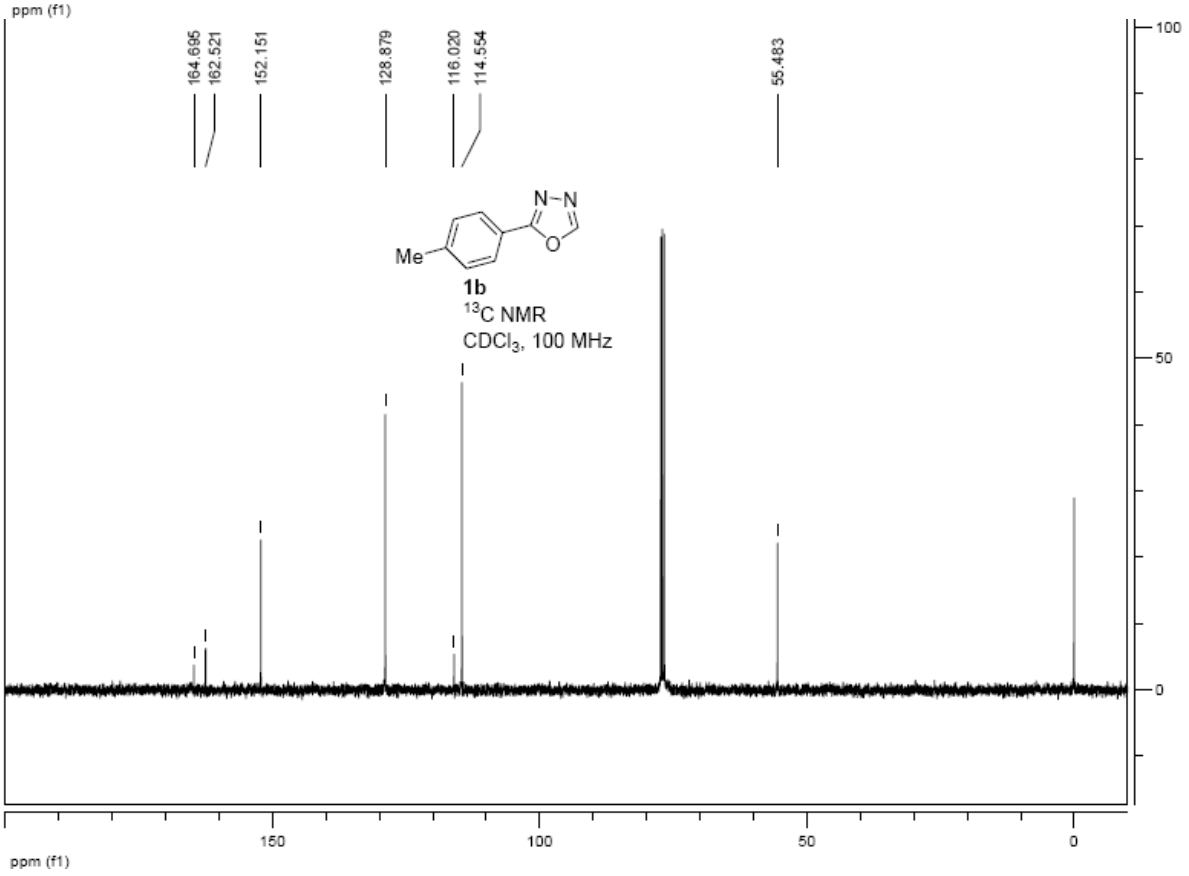




Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012

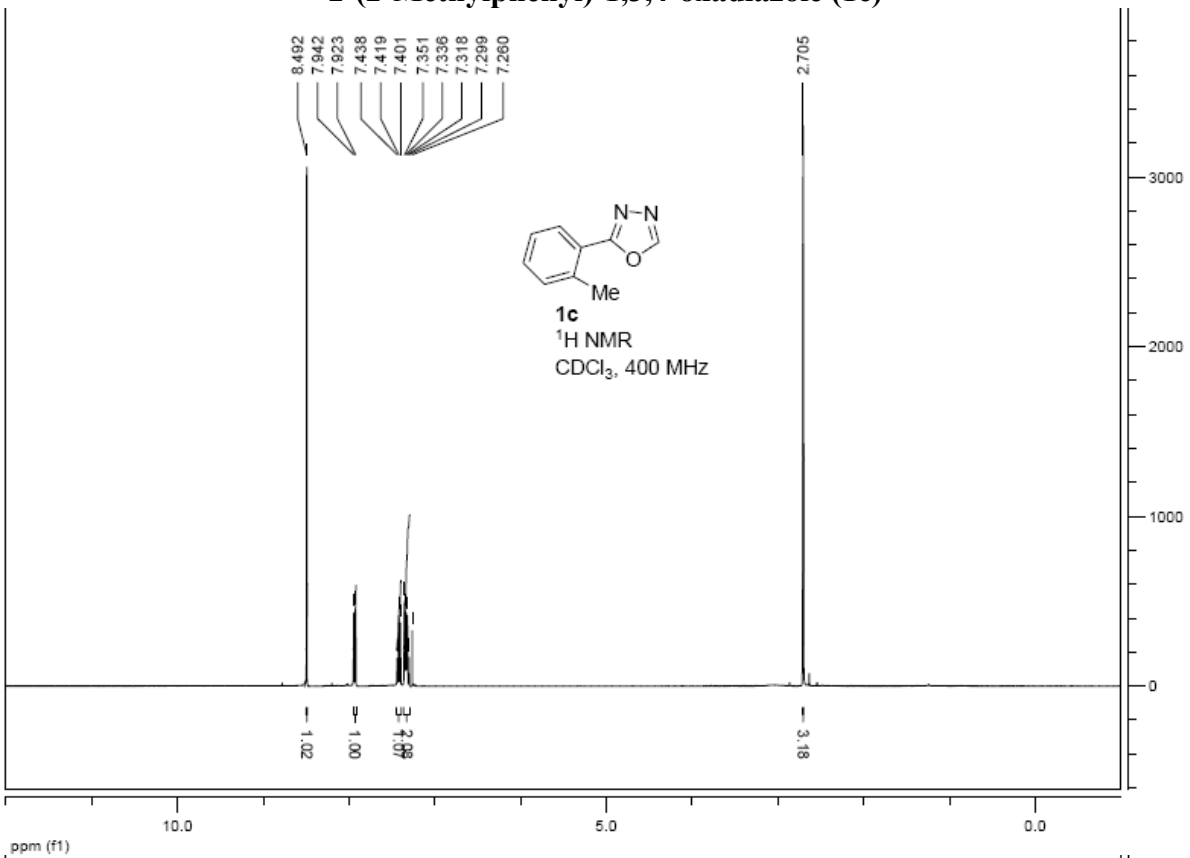
2-(4-Methylphenyl)-1,3,4-oxadiazole (1b)

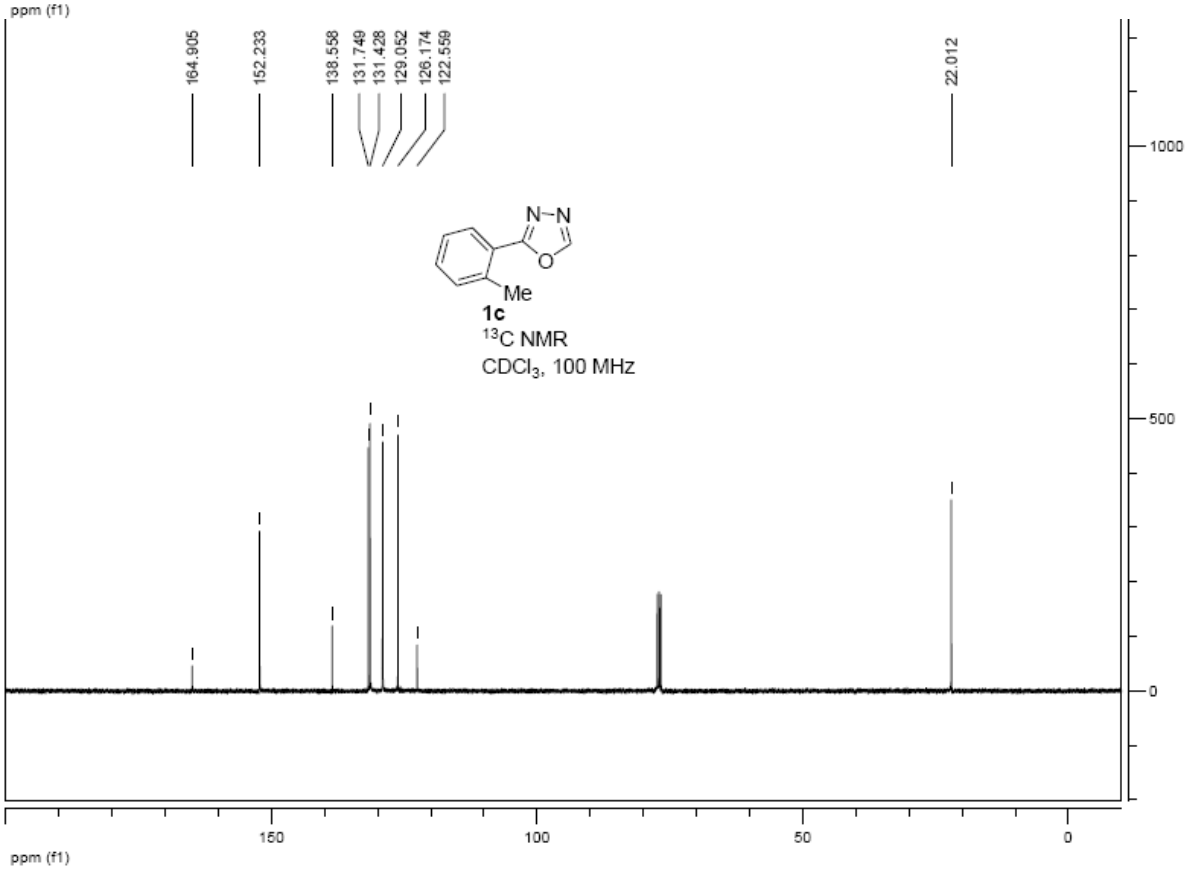




Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012

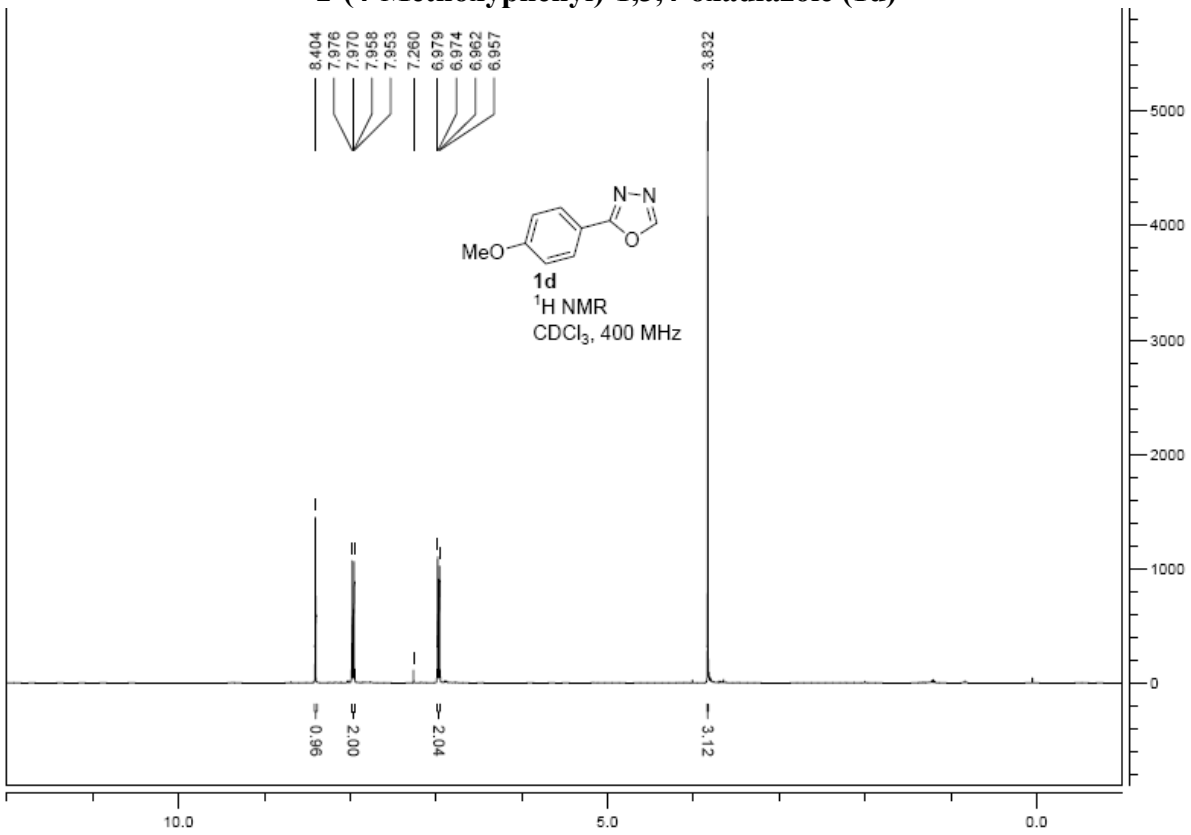
2-(2-Methylphenyl)-1,3,4-oxadiazole (1c)

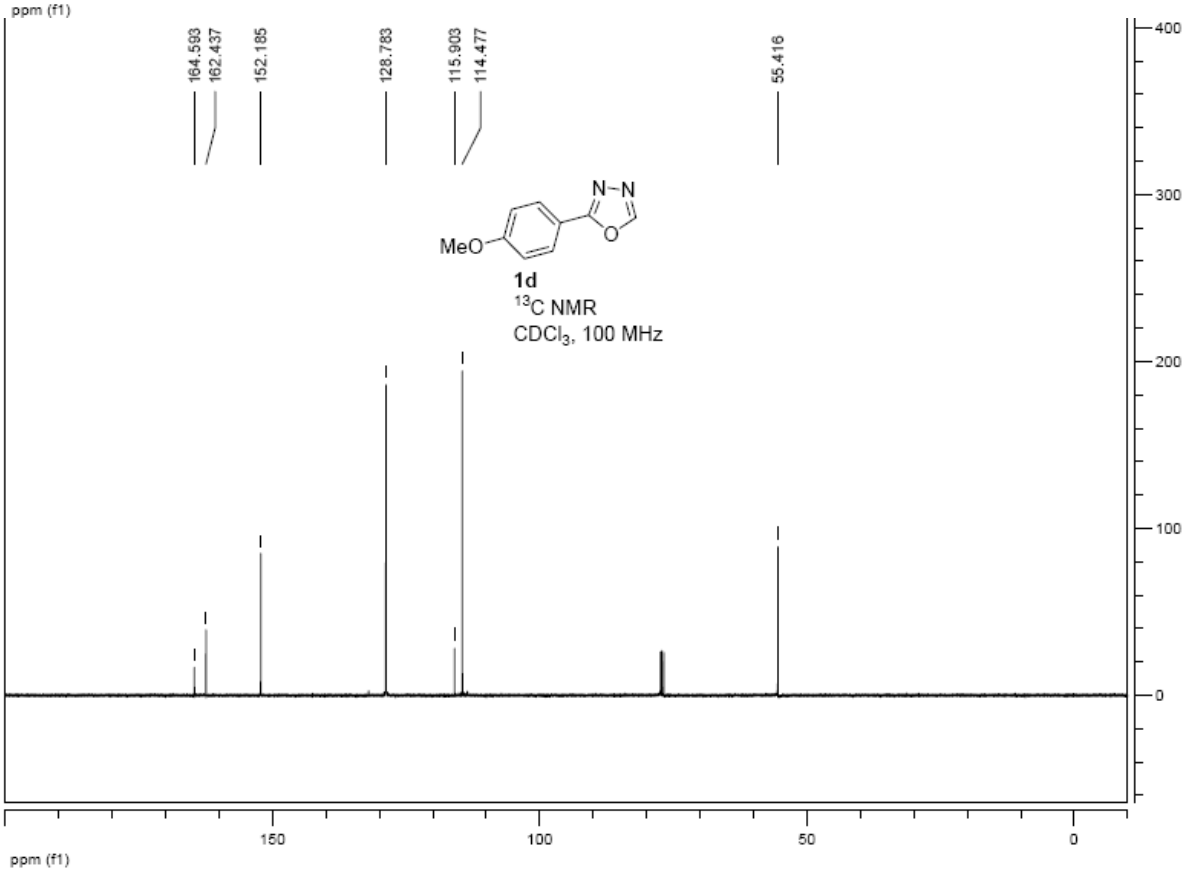




Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012

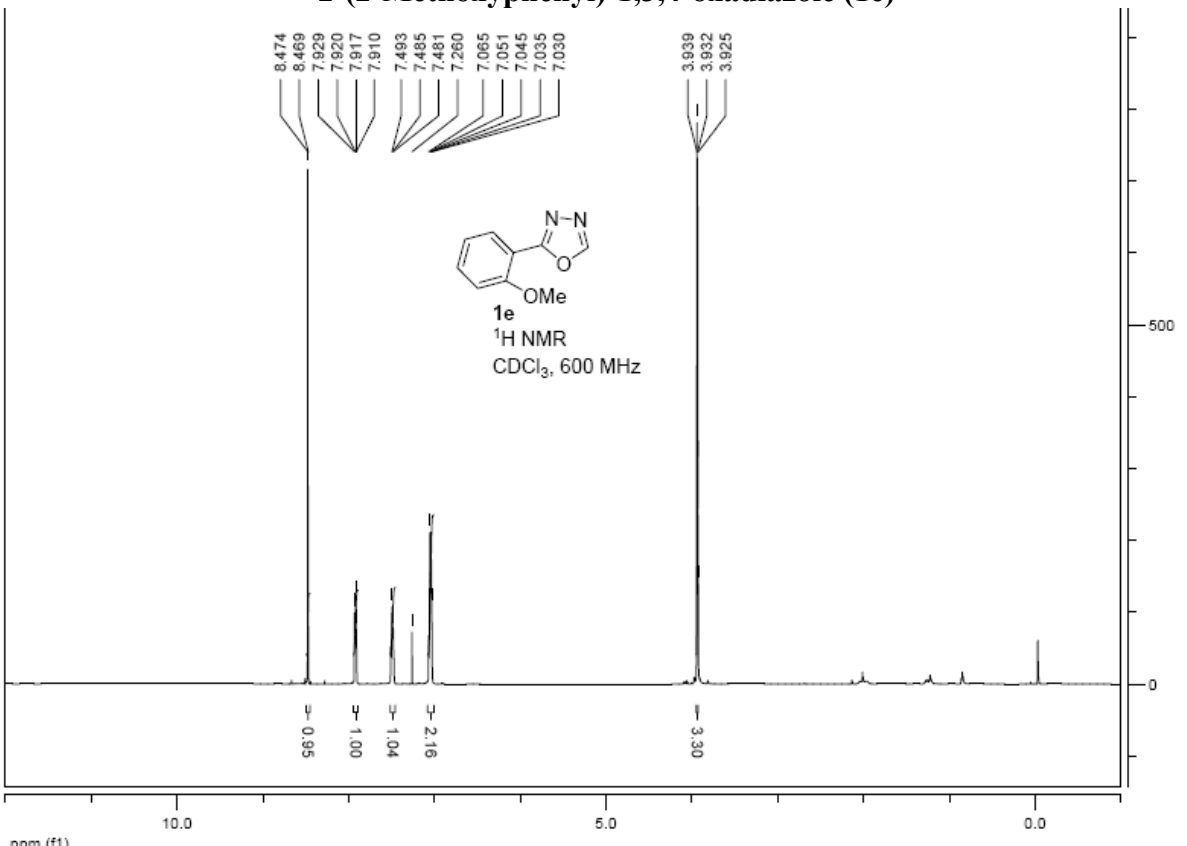
2-(4-Methoxyphenyl)-1,3,4-oxadiazole (1d)

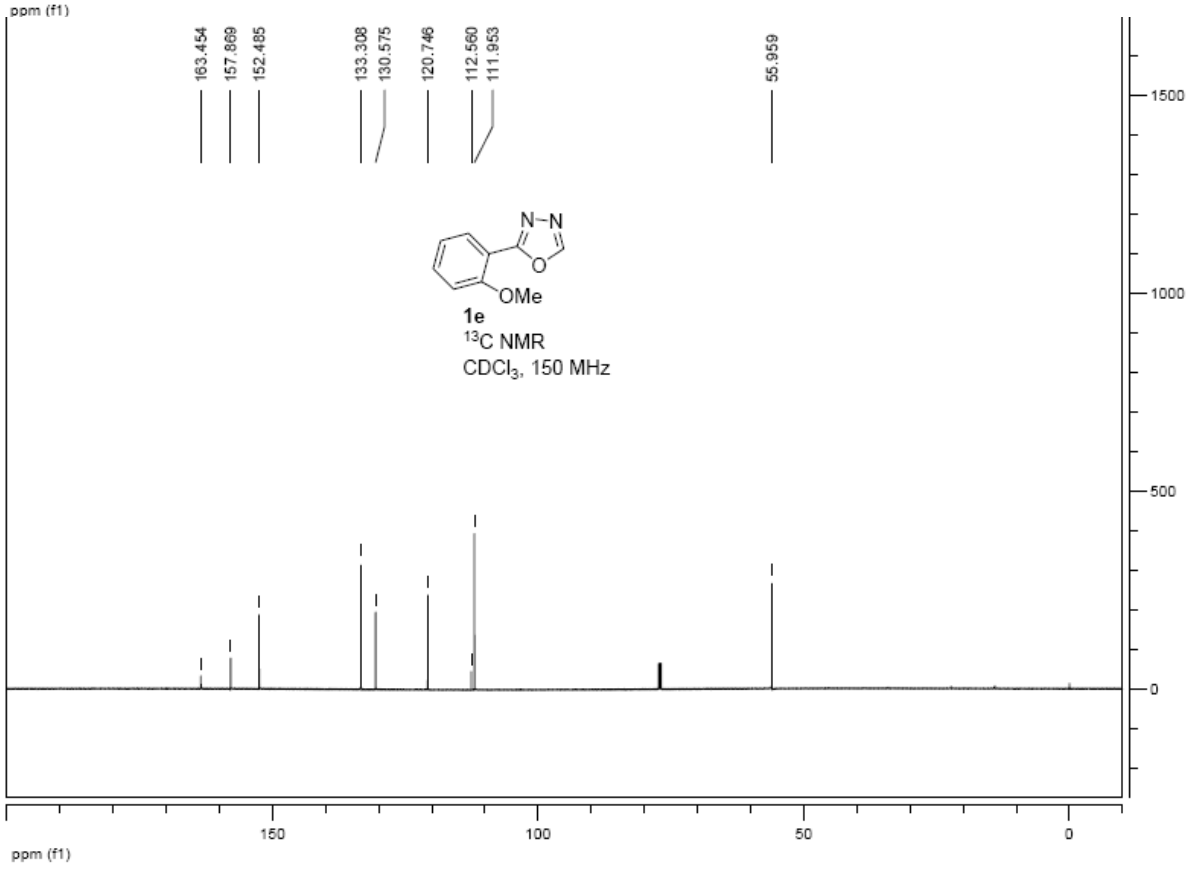




Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012

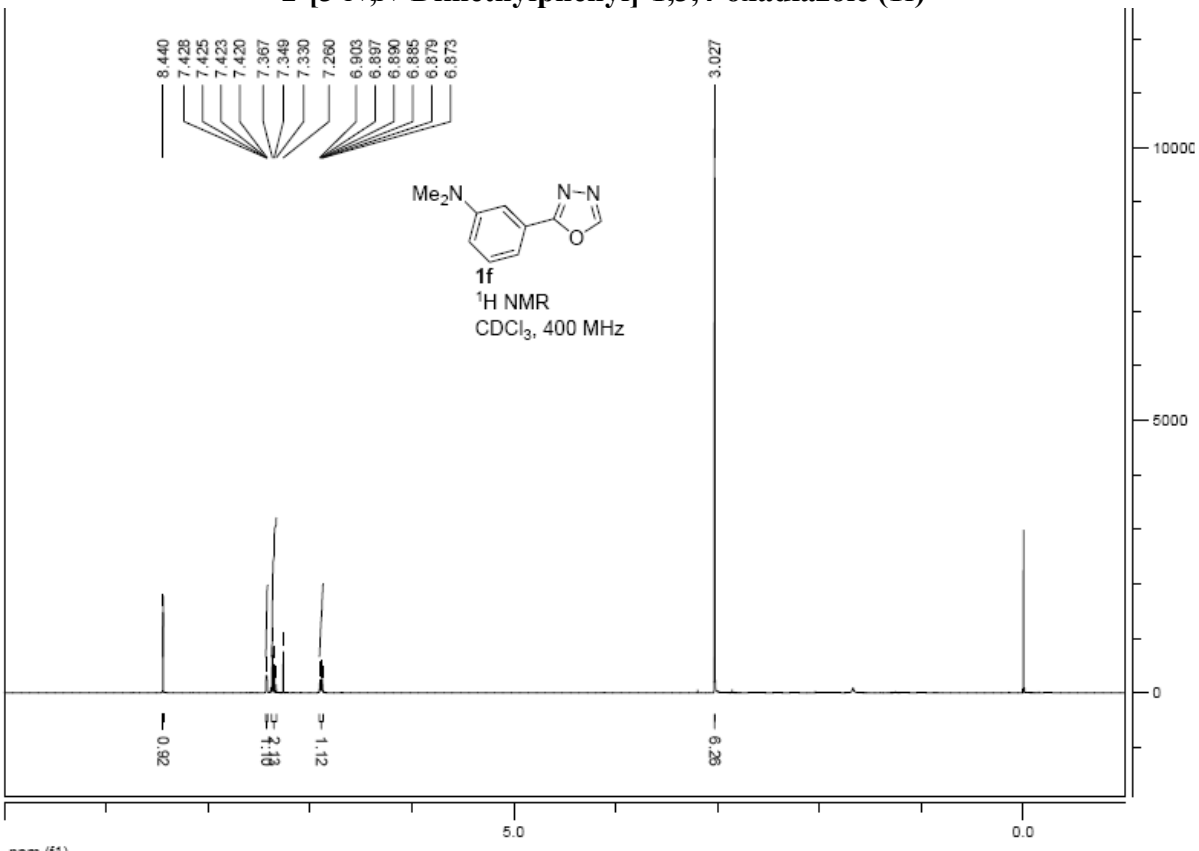
2-(2-Methoxyphenyl)-1,3,4-oxadiazole (1e)

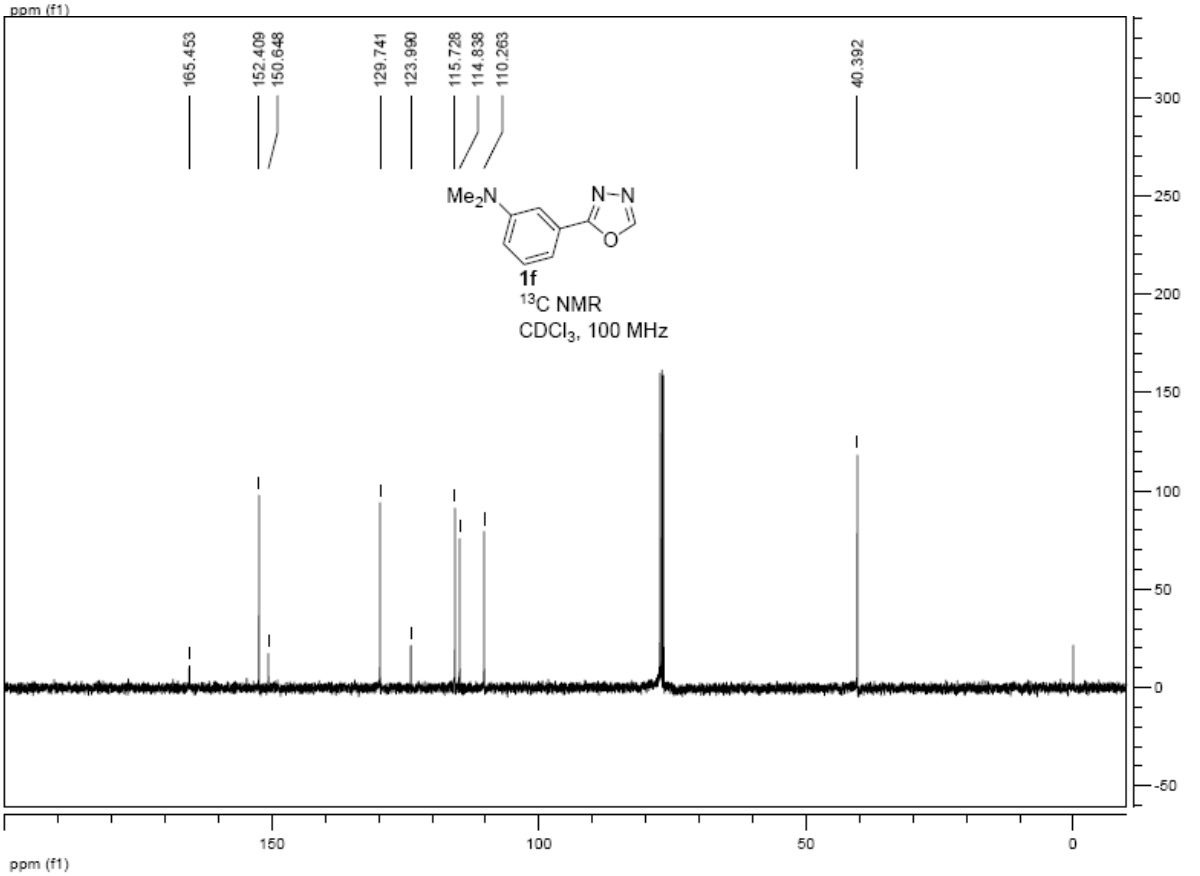




Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012

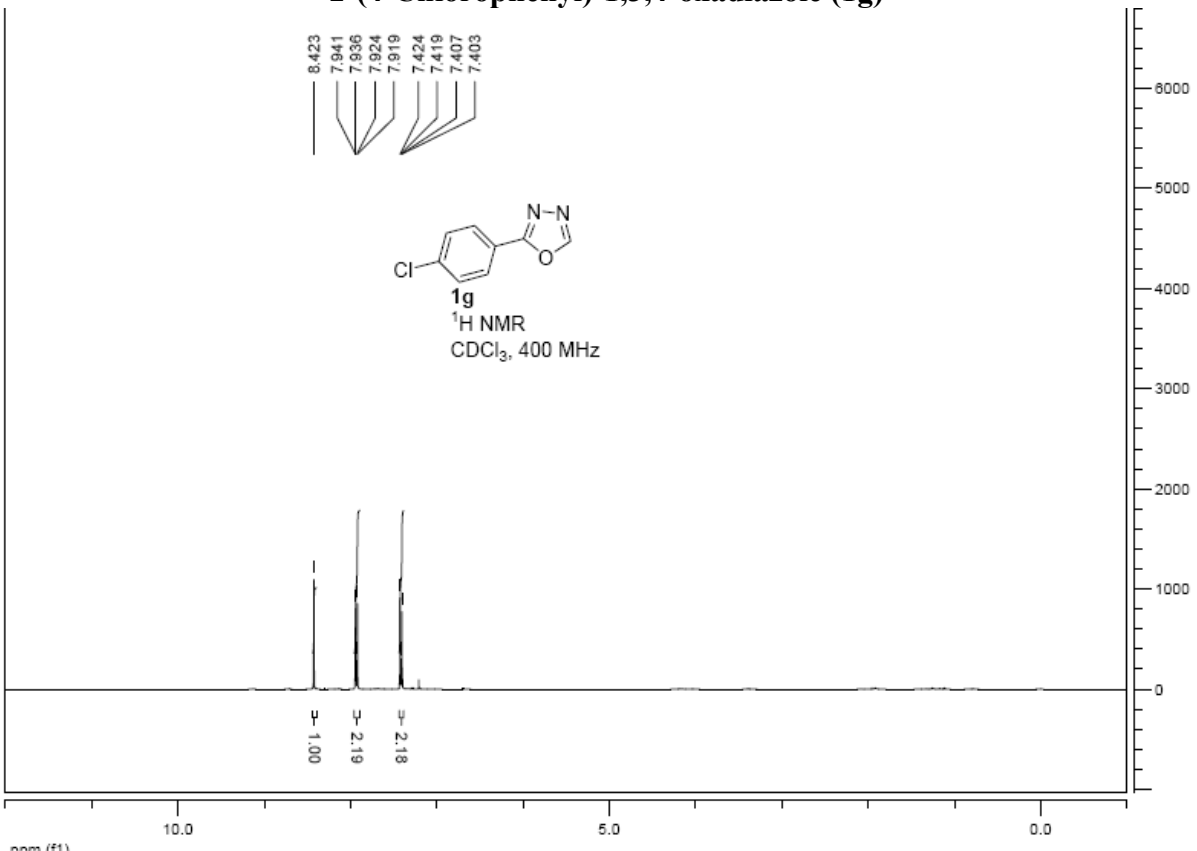
2-[3-*N*,*N*-Dimethylphenyl]-1,3,4-oxadiazole (1f)

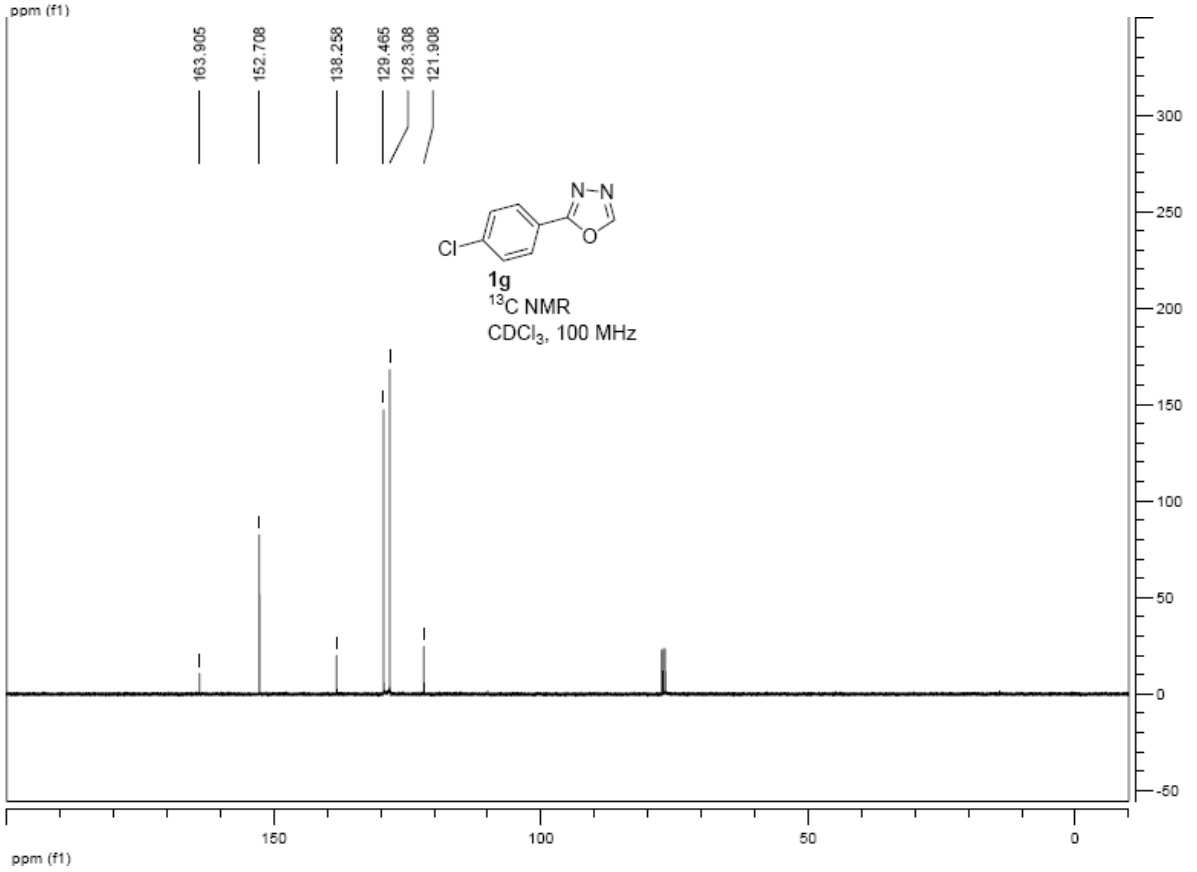




Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012

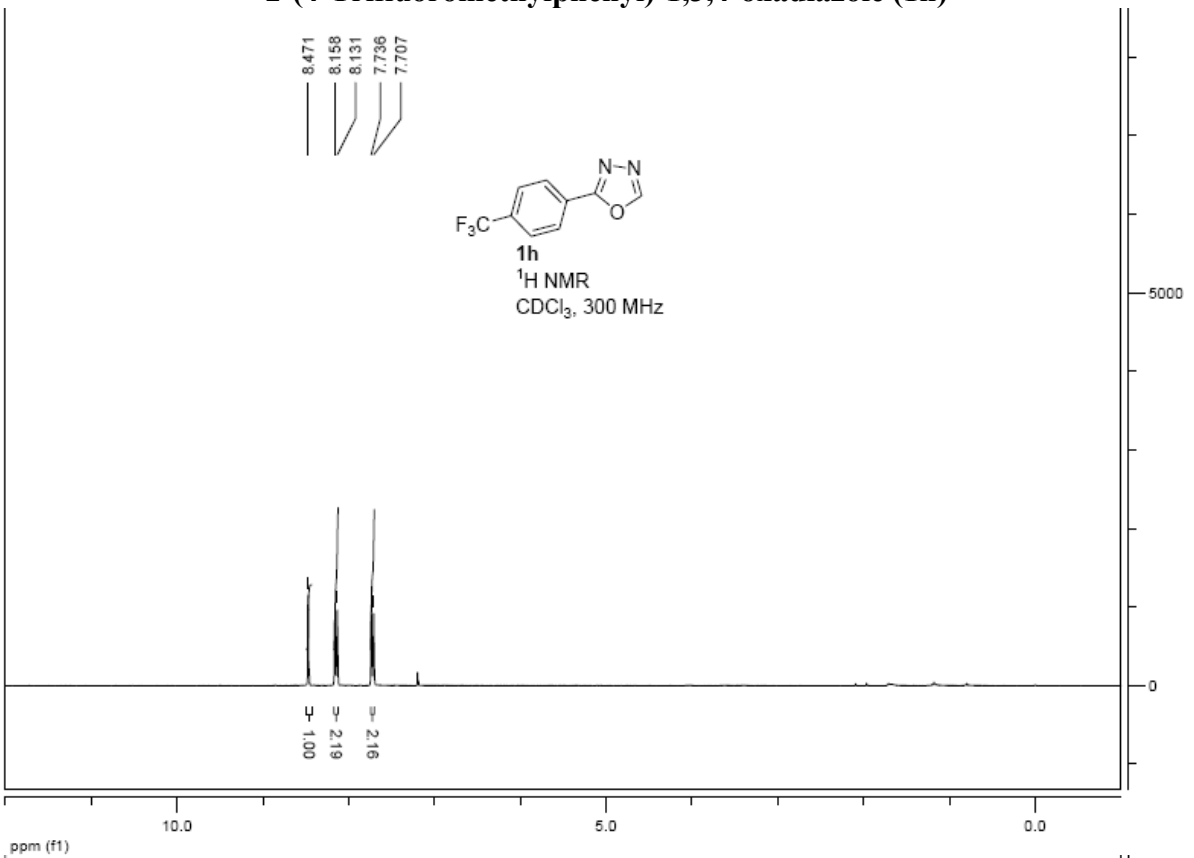
2-(4-Chlorophenyl)-1,3,4-oxadiazole (1g)

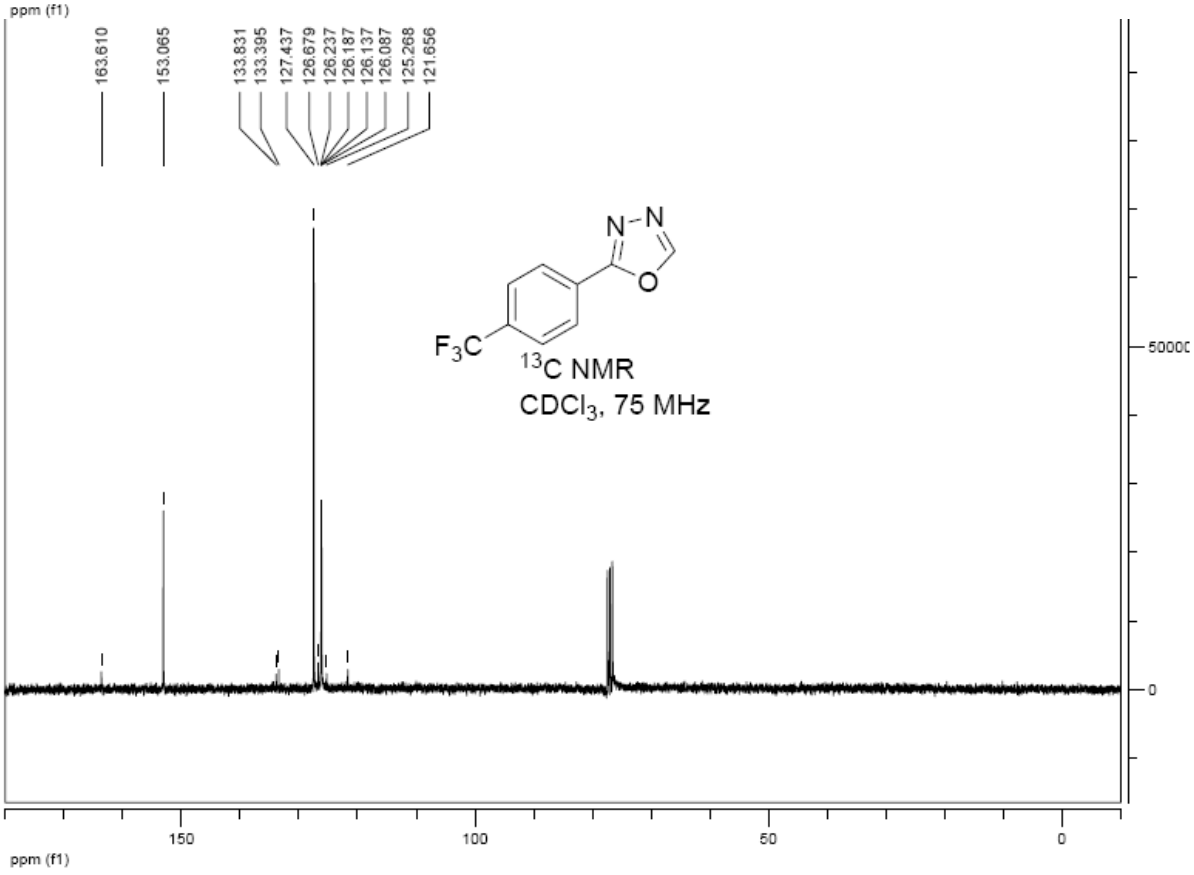




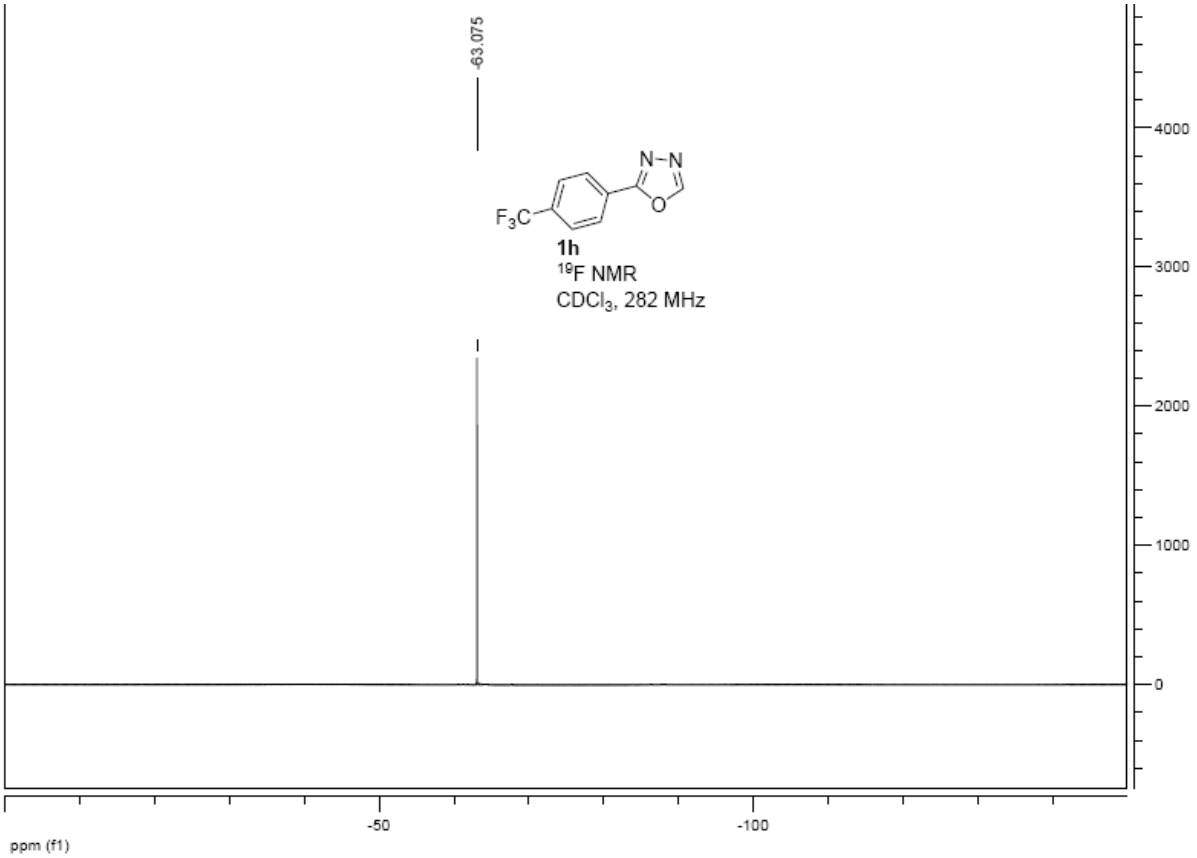
Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012

2-(4-Trifluoromethylphenyl)-1,3,4-oxadiazole (1h)

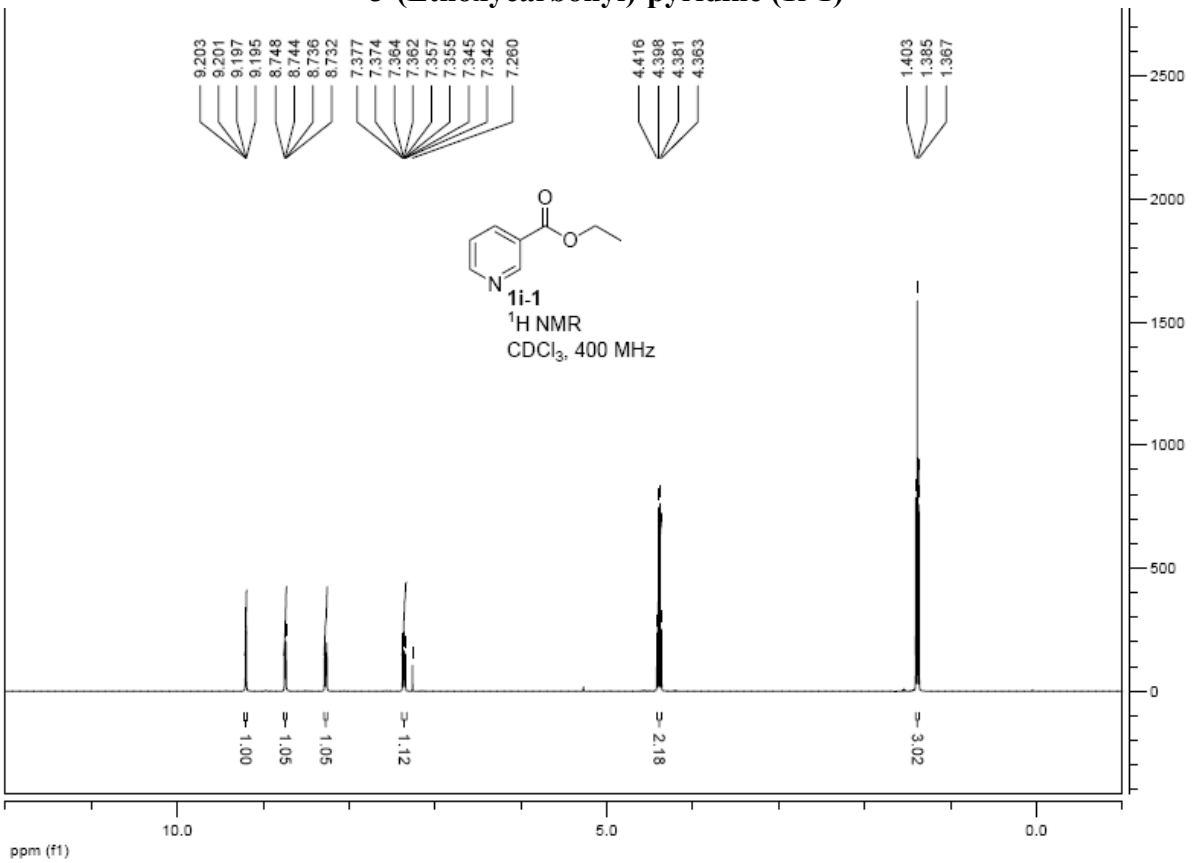




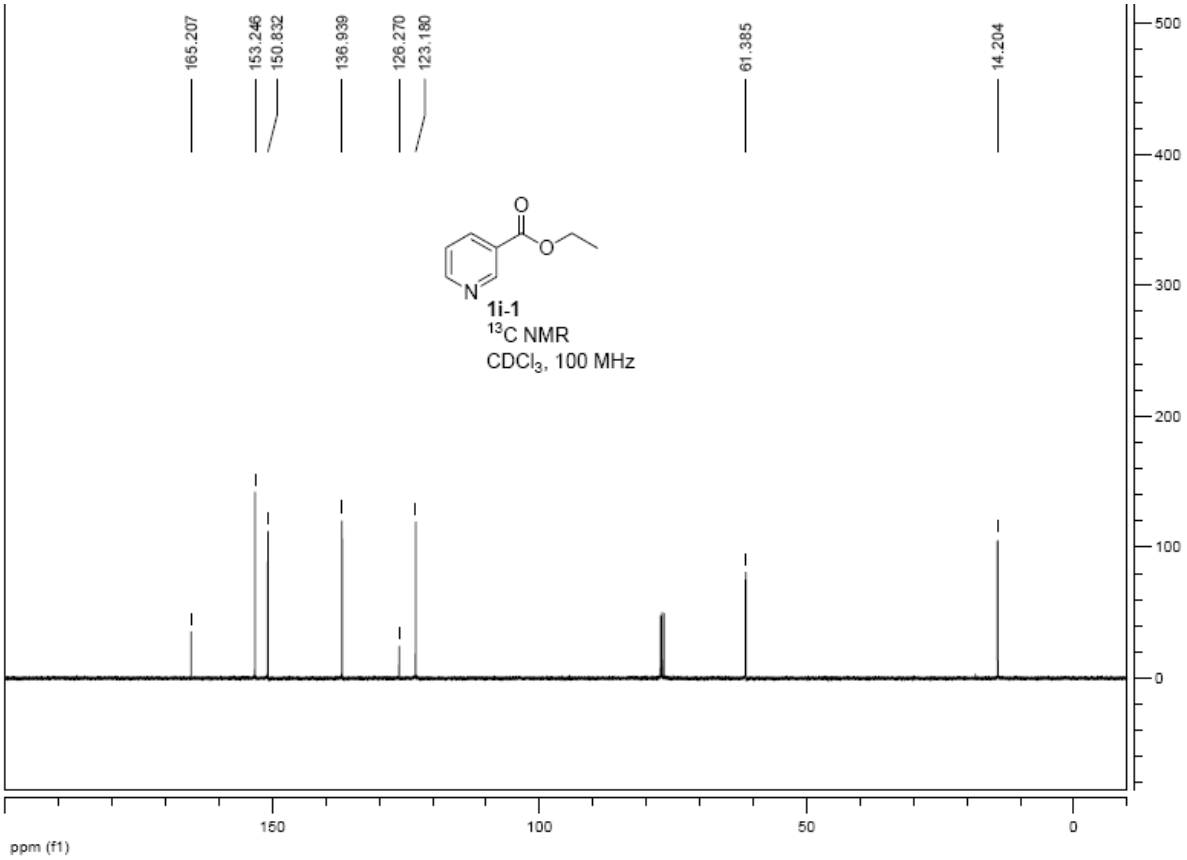
Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012



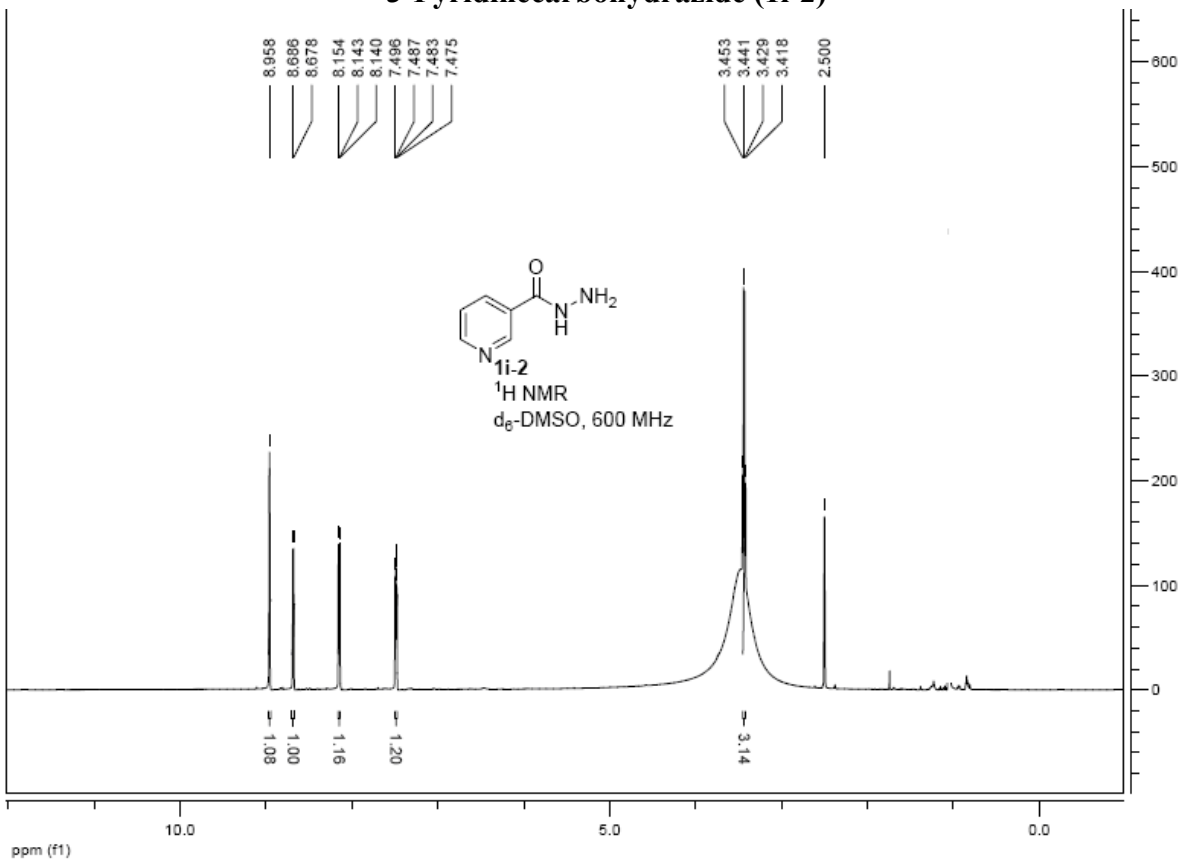
3-(Ethoxycarbonyl)-pyridine (1i-1)



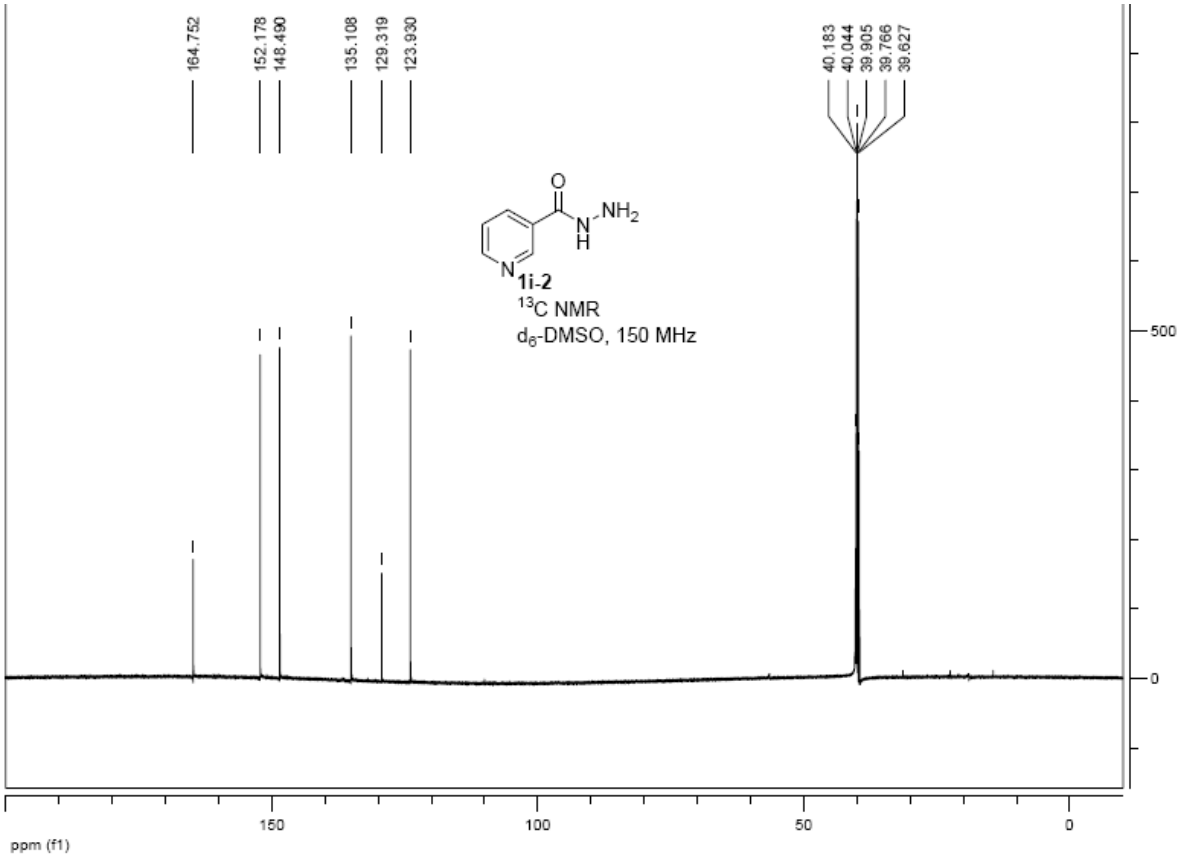
Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012



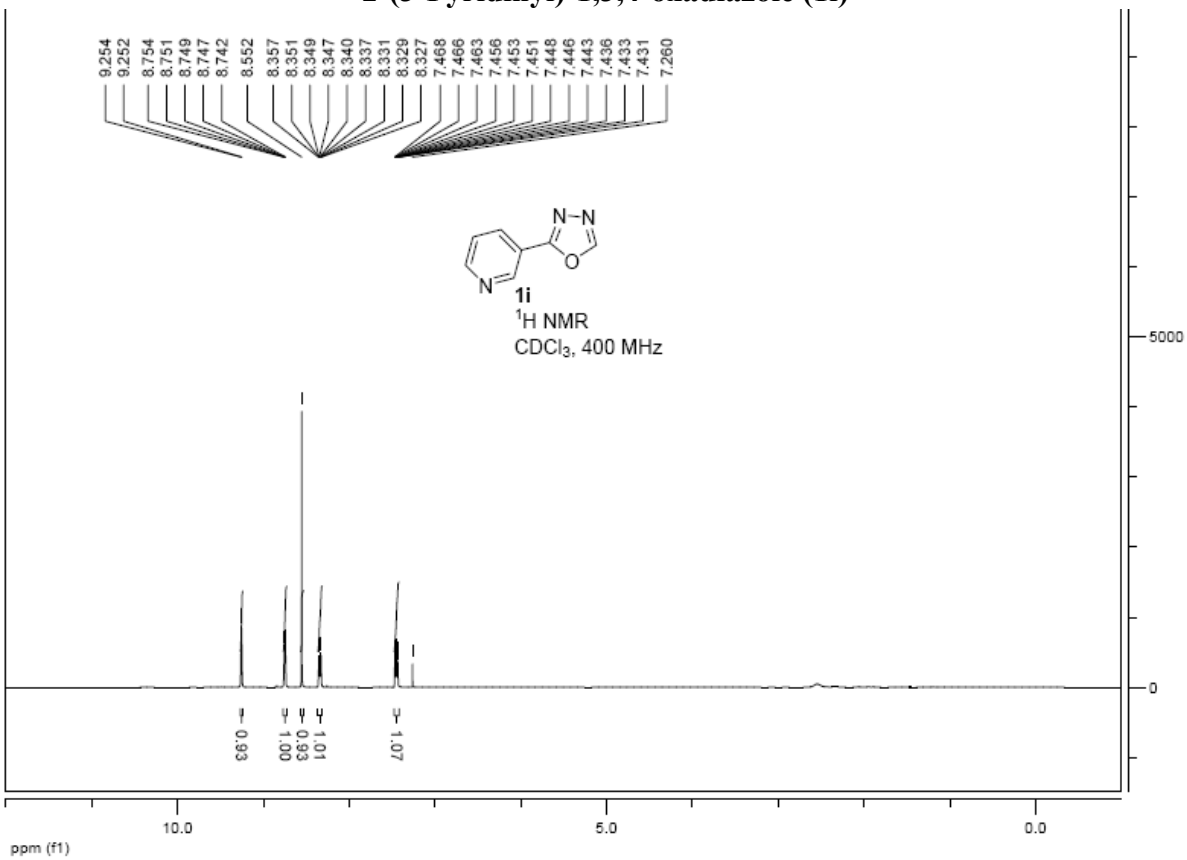
3-Pyridinecarbohydrazide (1i-2)



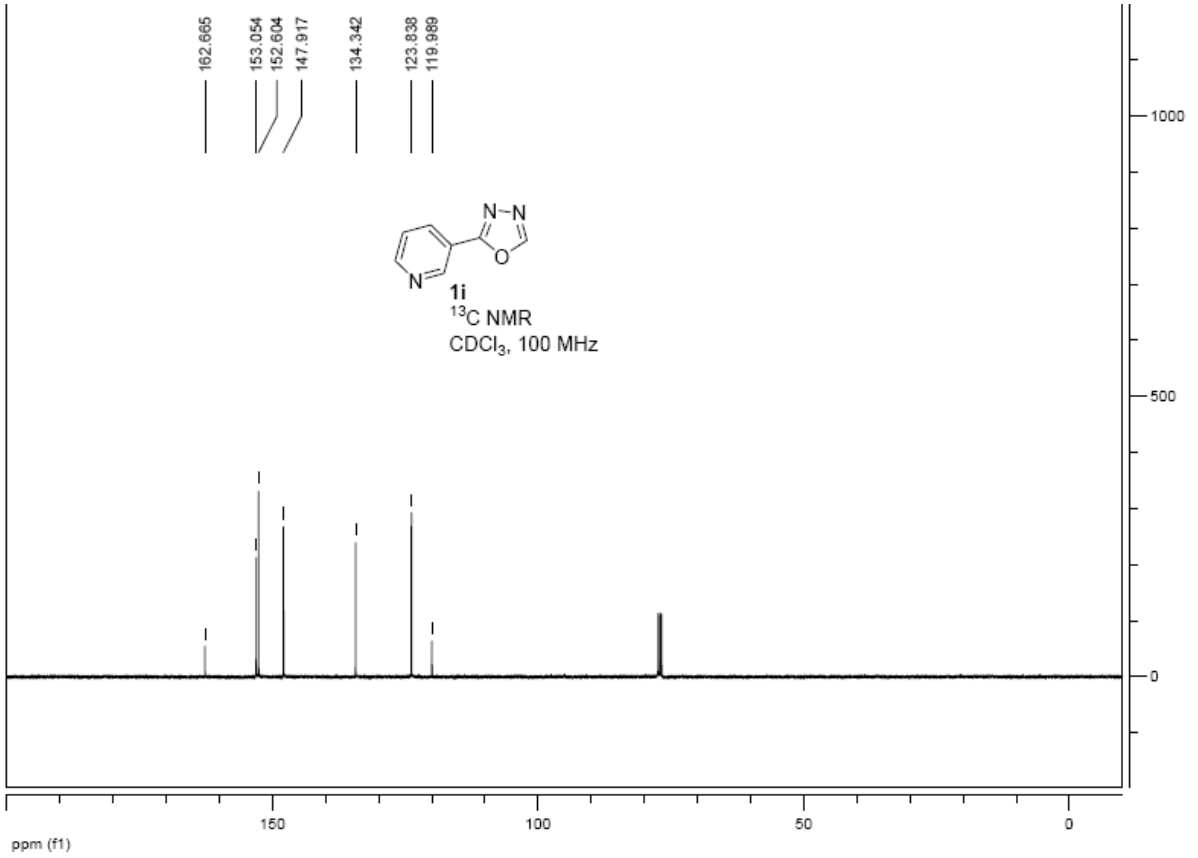
Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012



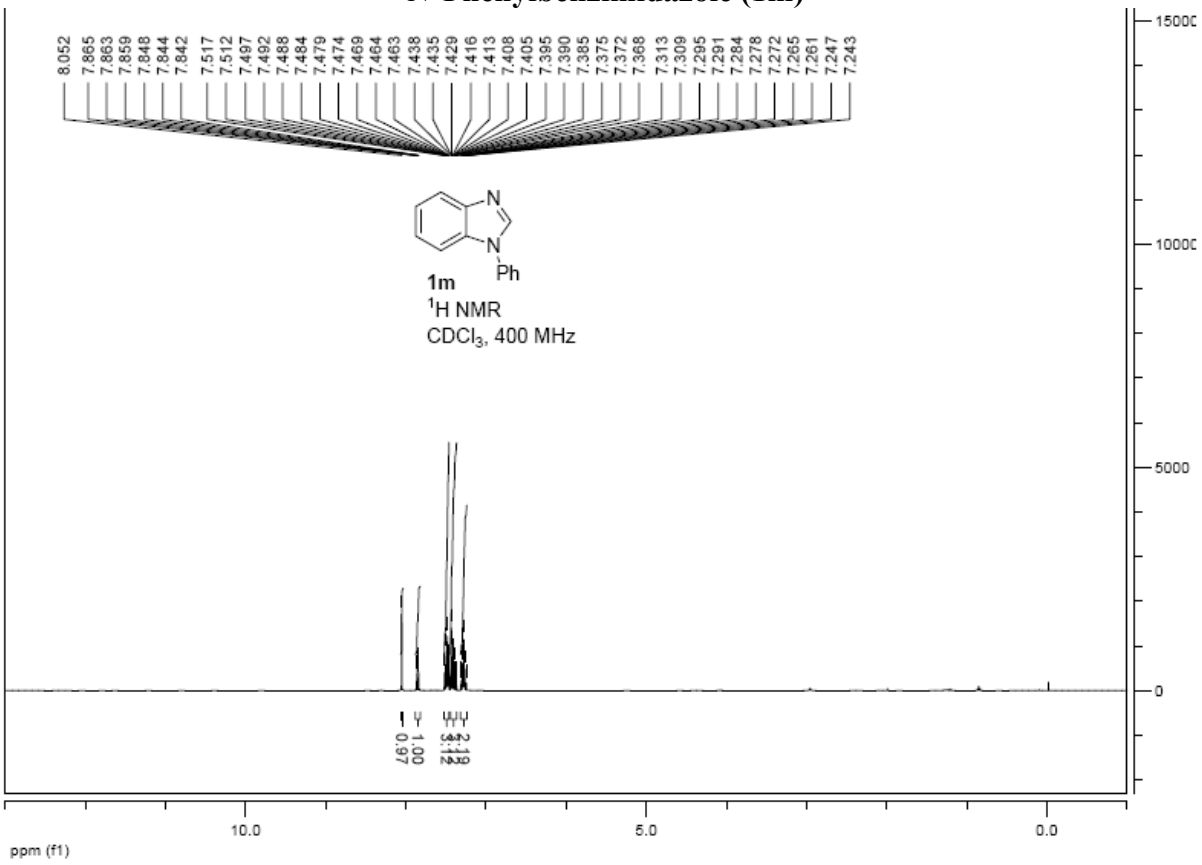
2-(3-Pyridinyl)-1,3,4-oxadiazole (1i)



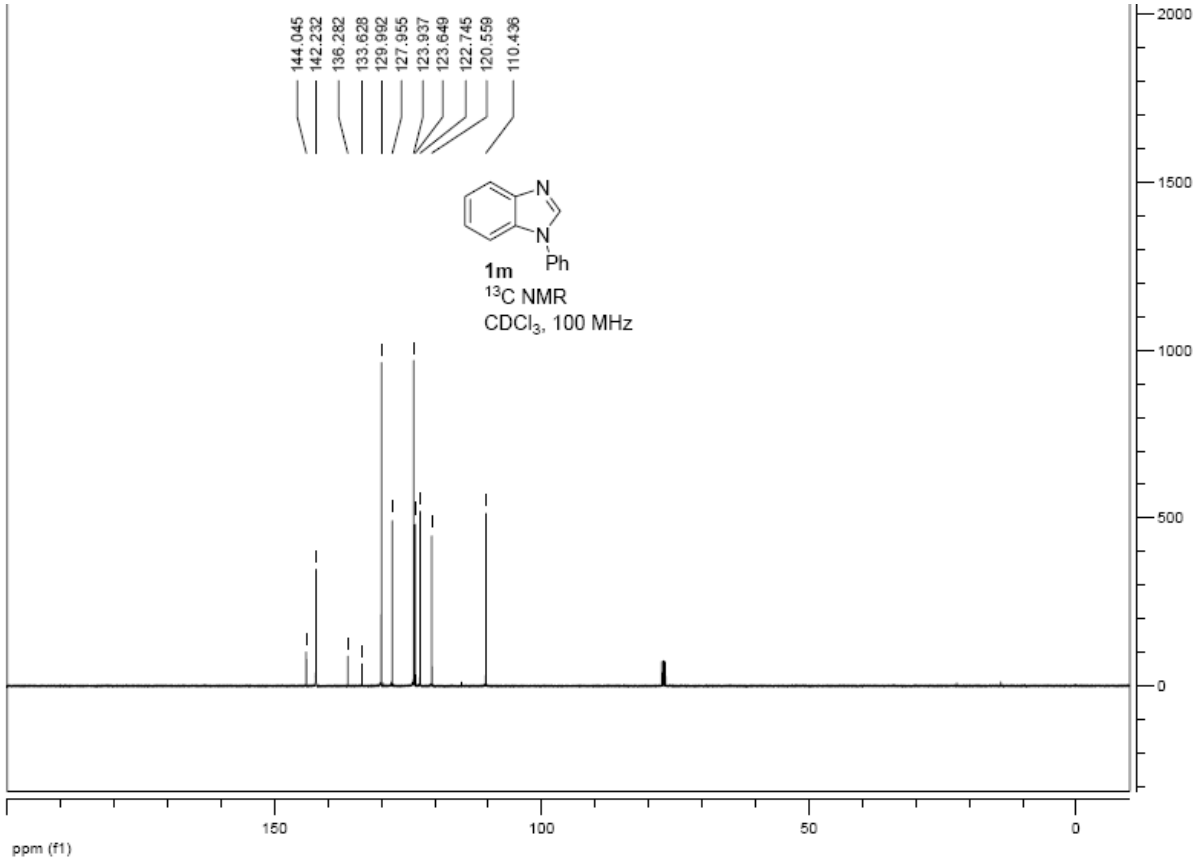
Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012



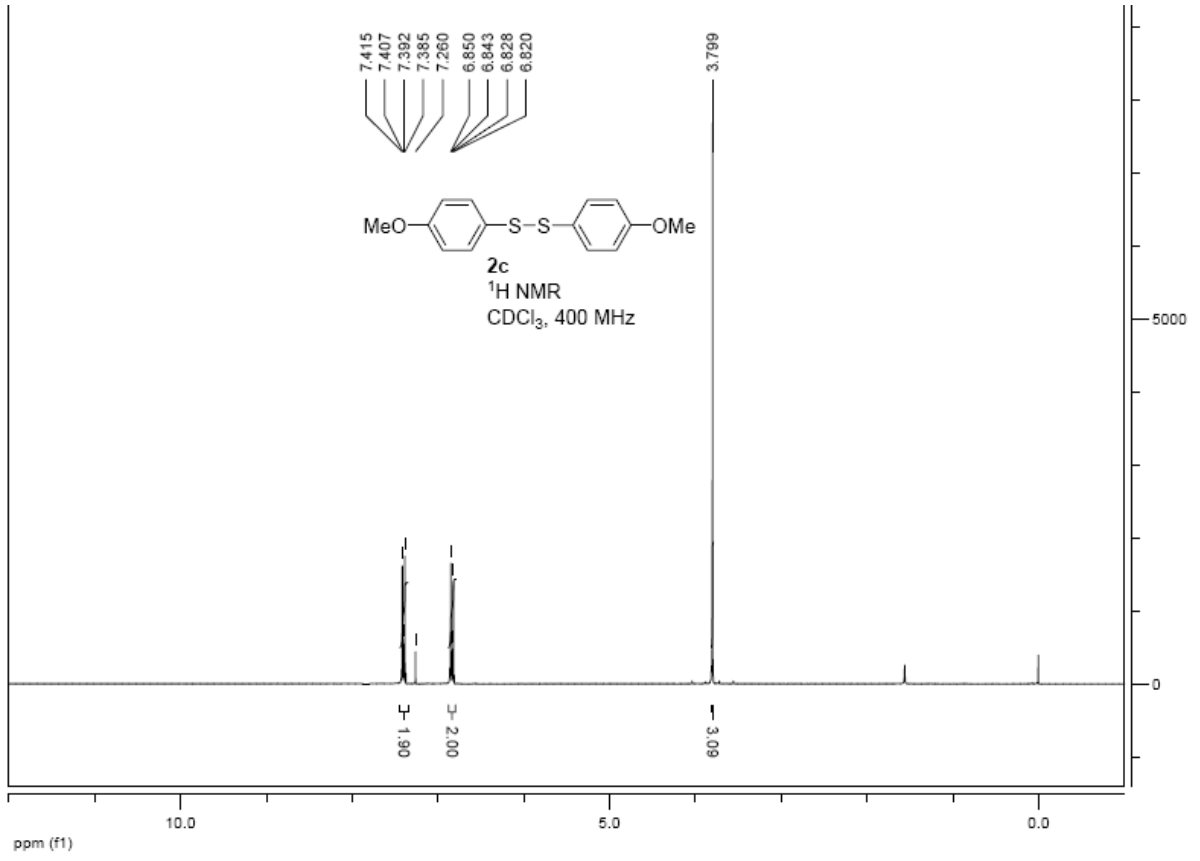
_N_-Phenylbenzimidazole (1m)



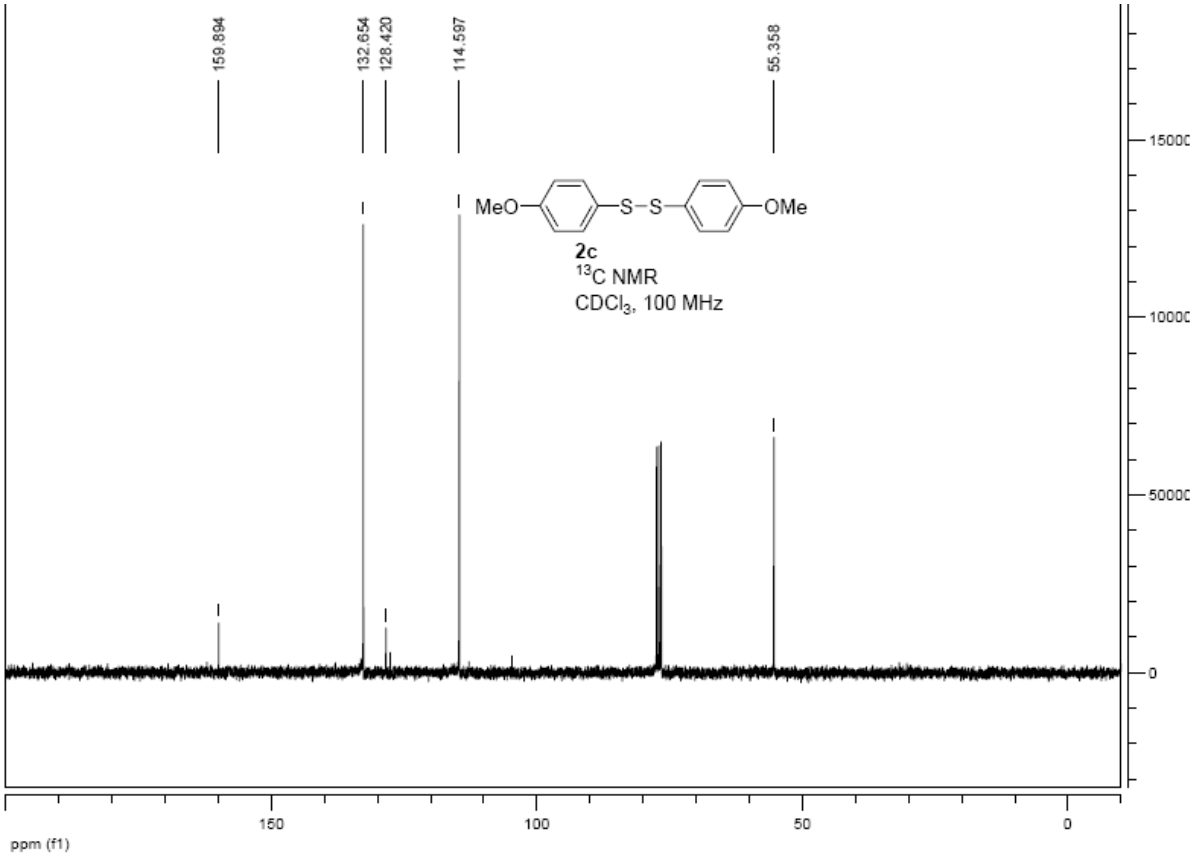
Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012



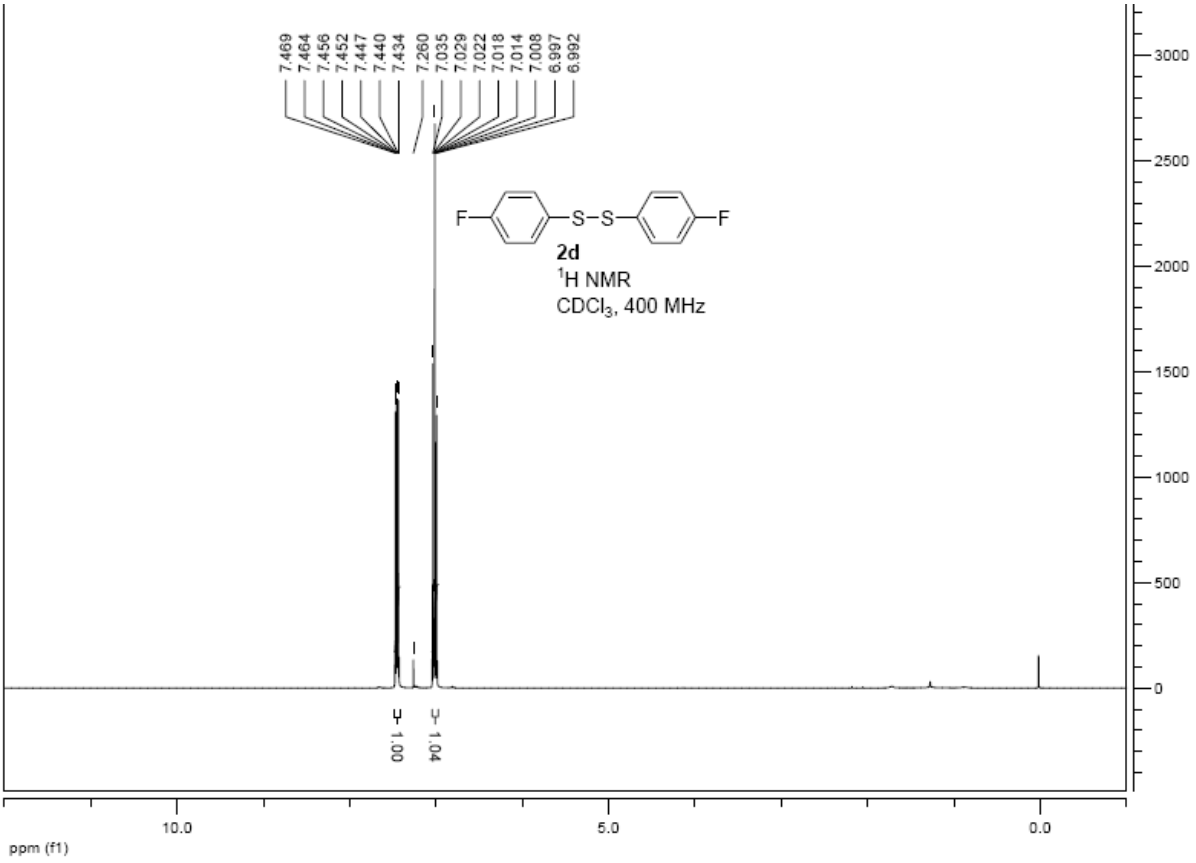
4,4'-Dimethoxydiphenyl disulfide (2c)



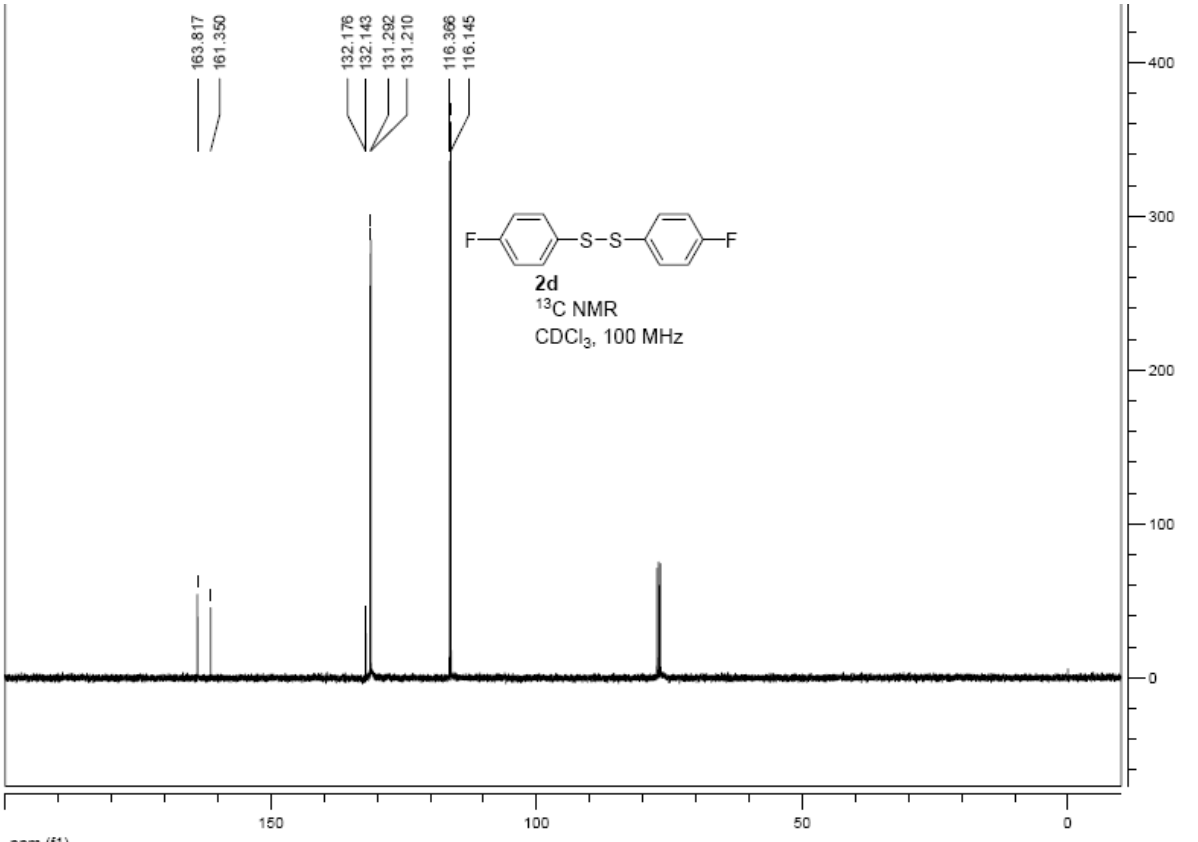
Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012

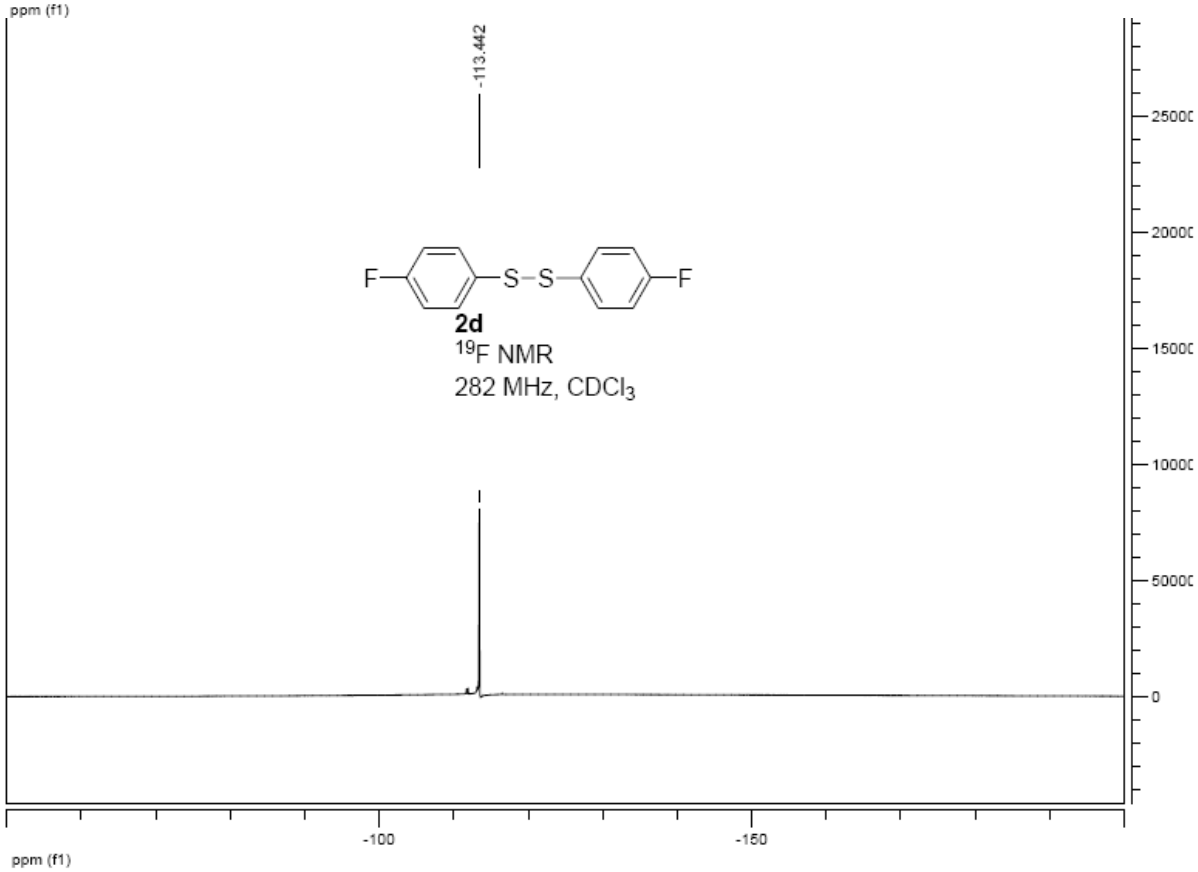


4,4'-Difluorodiphenyl disulfide (2d)



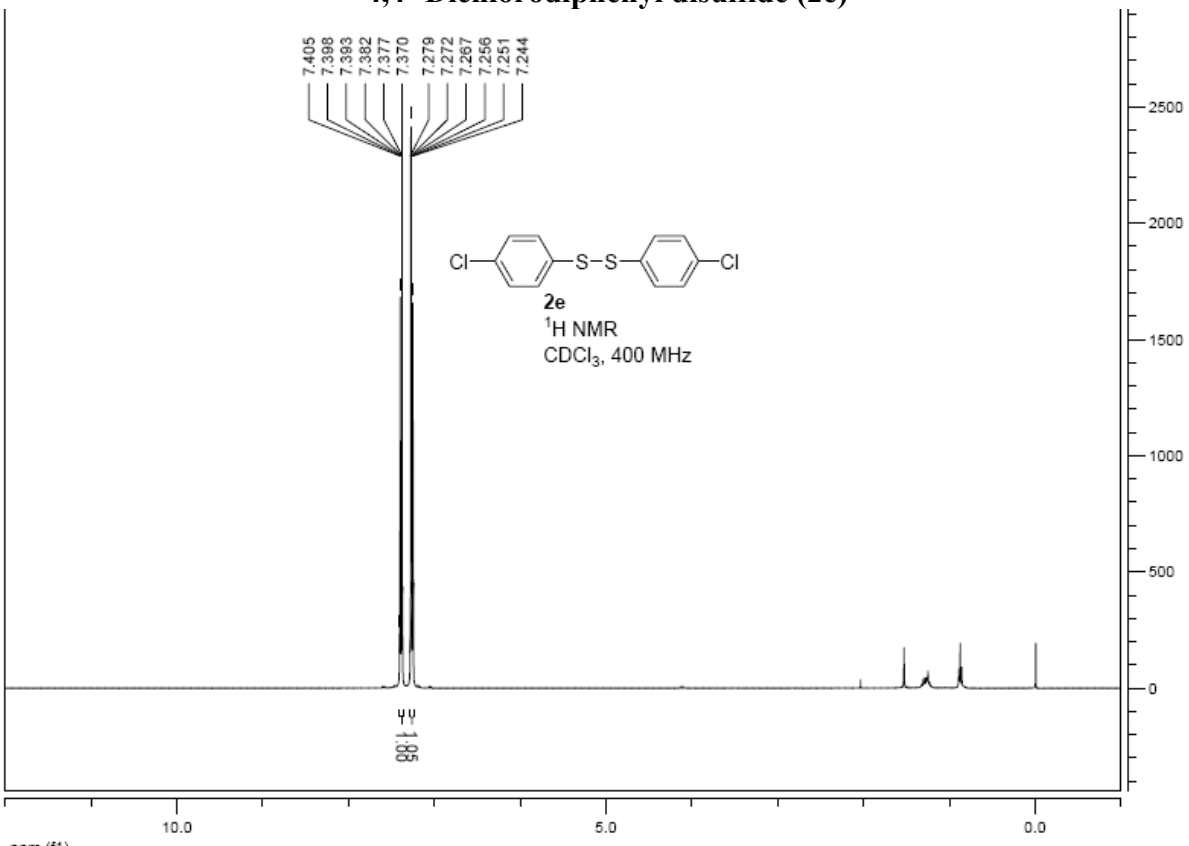
Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012

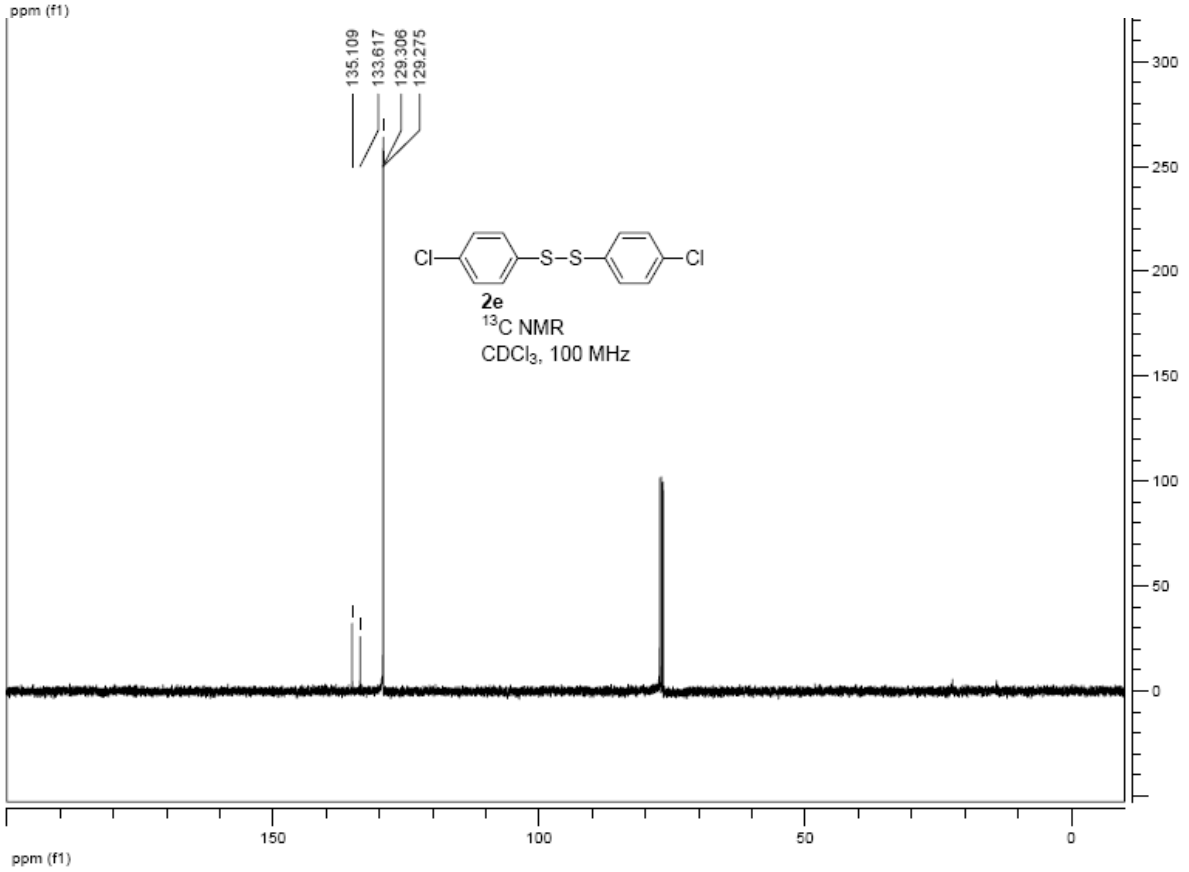




Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012

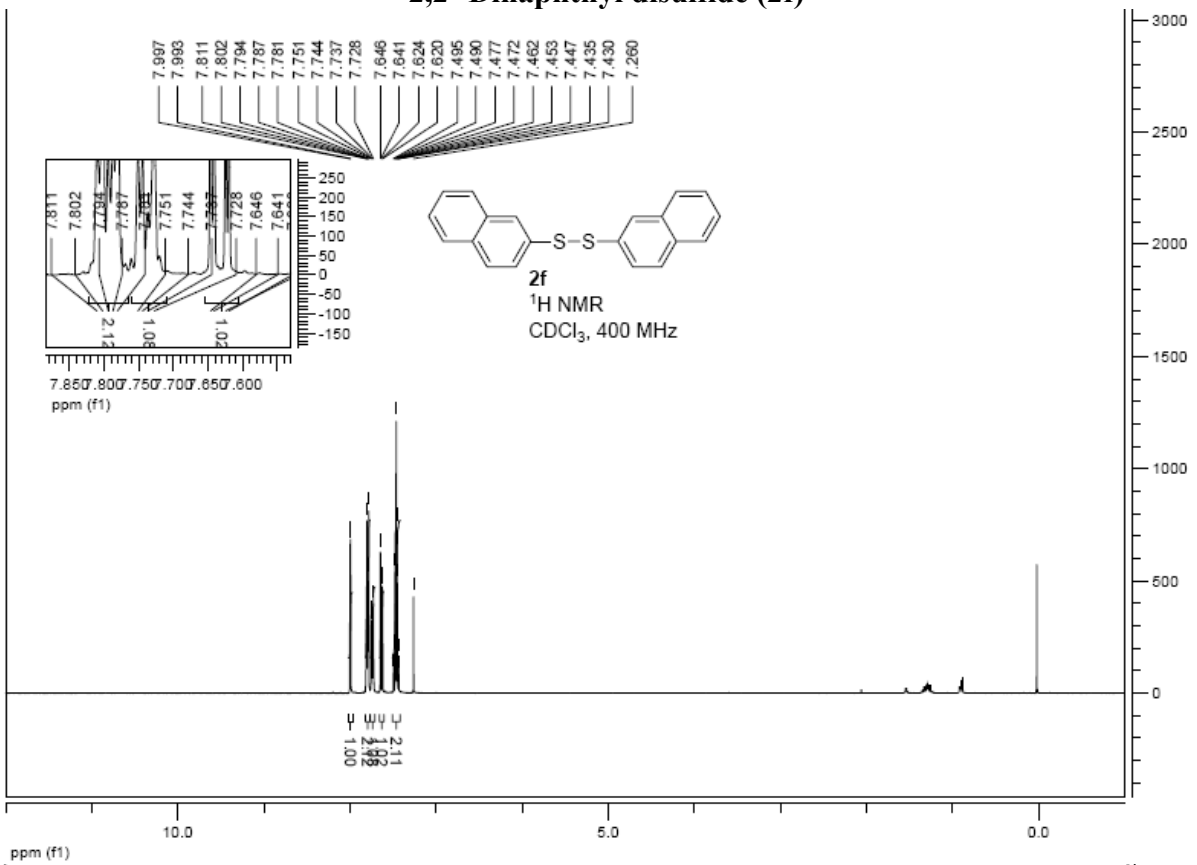
4,4'-Dichlorodiphenyl disulfide (2e)

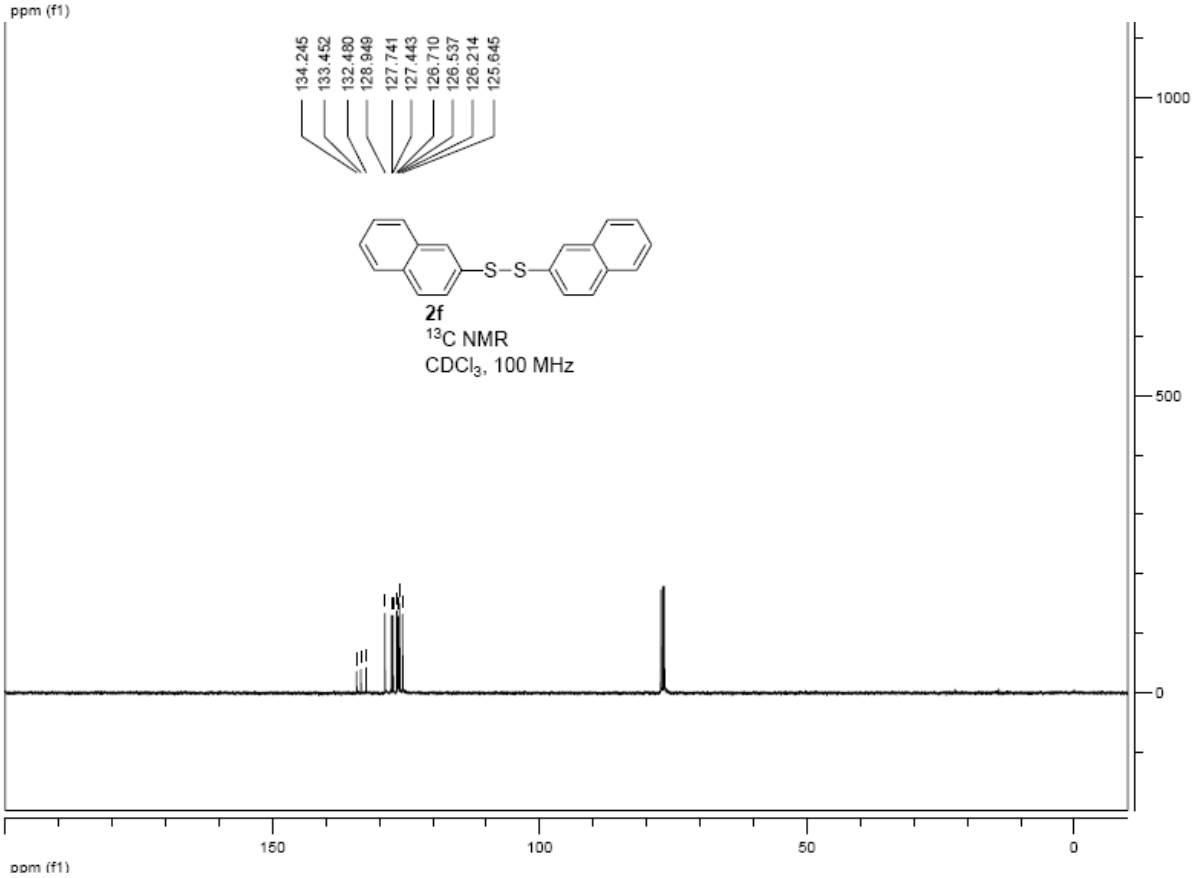




Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012

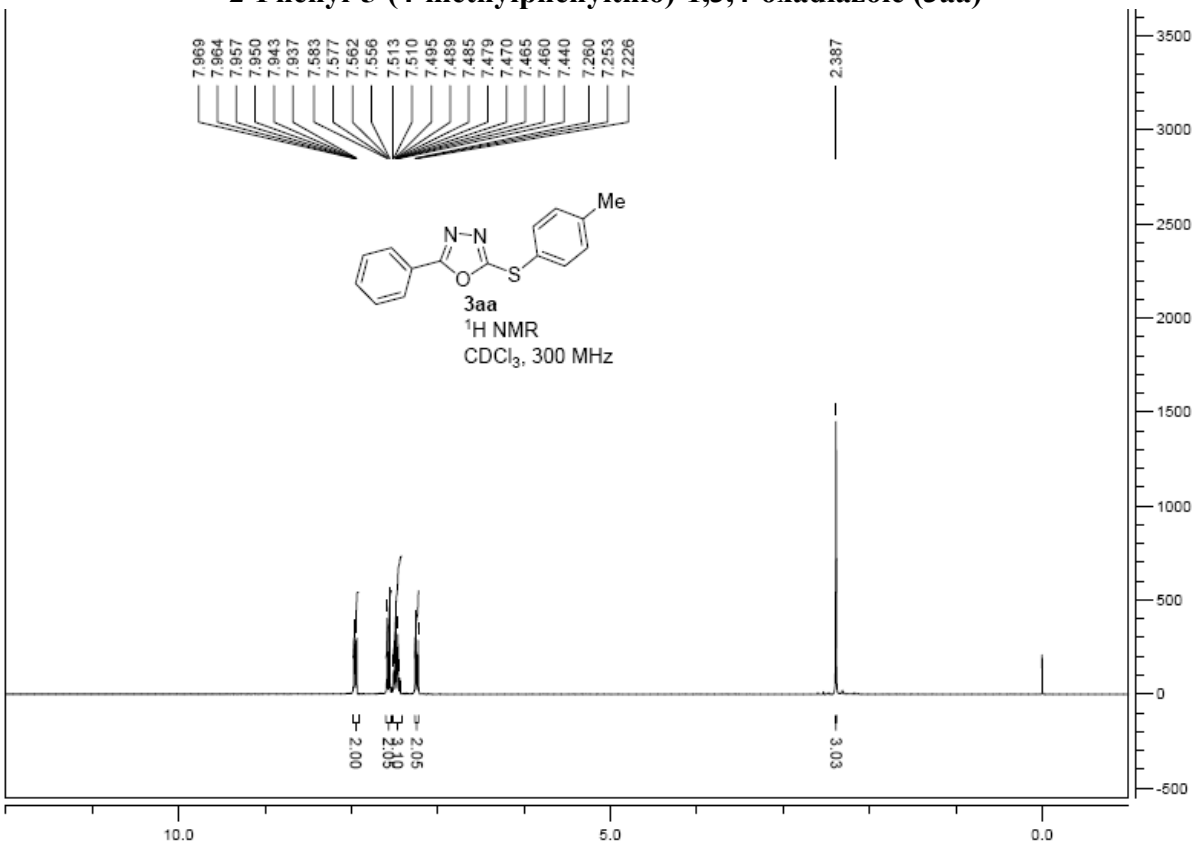
2,2'-Dinaphthyl disulfide (2f)

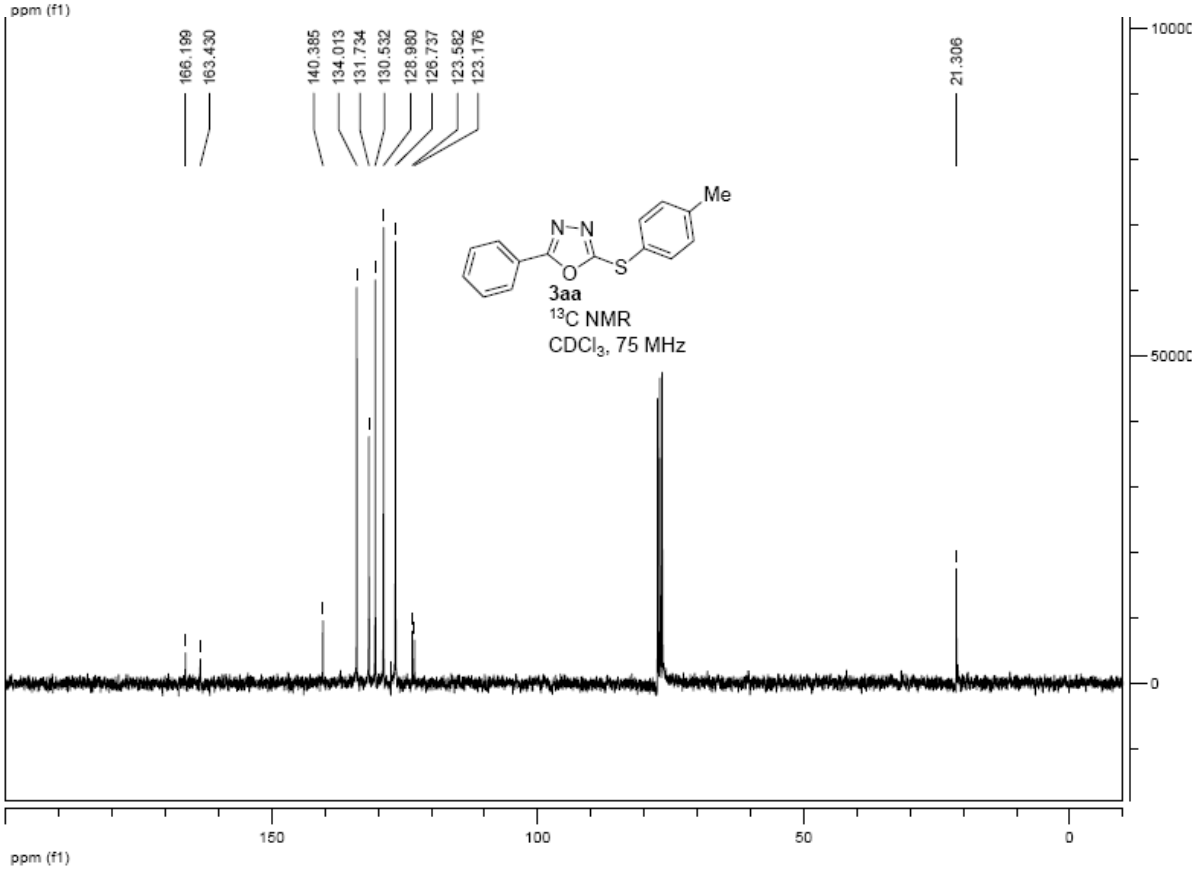




Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012

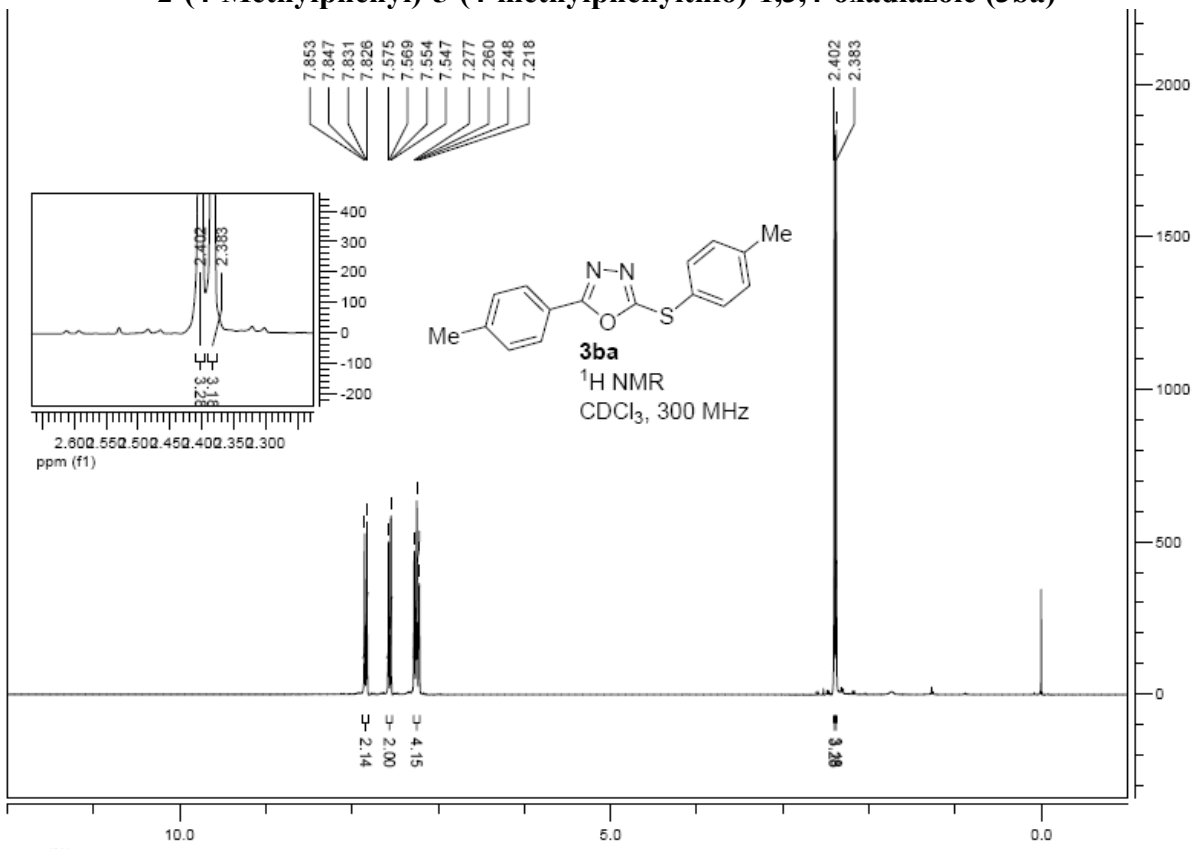
2-Phenyl-5-(4-methylphenylthio)-1,3,4-oxadiazole (3aa)

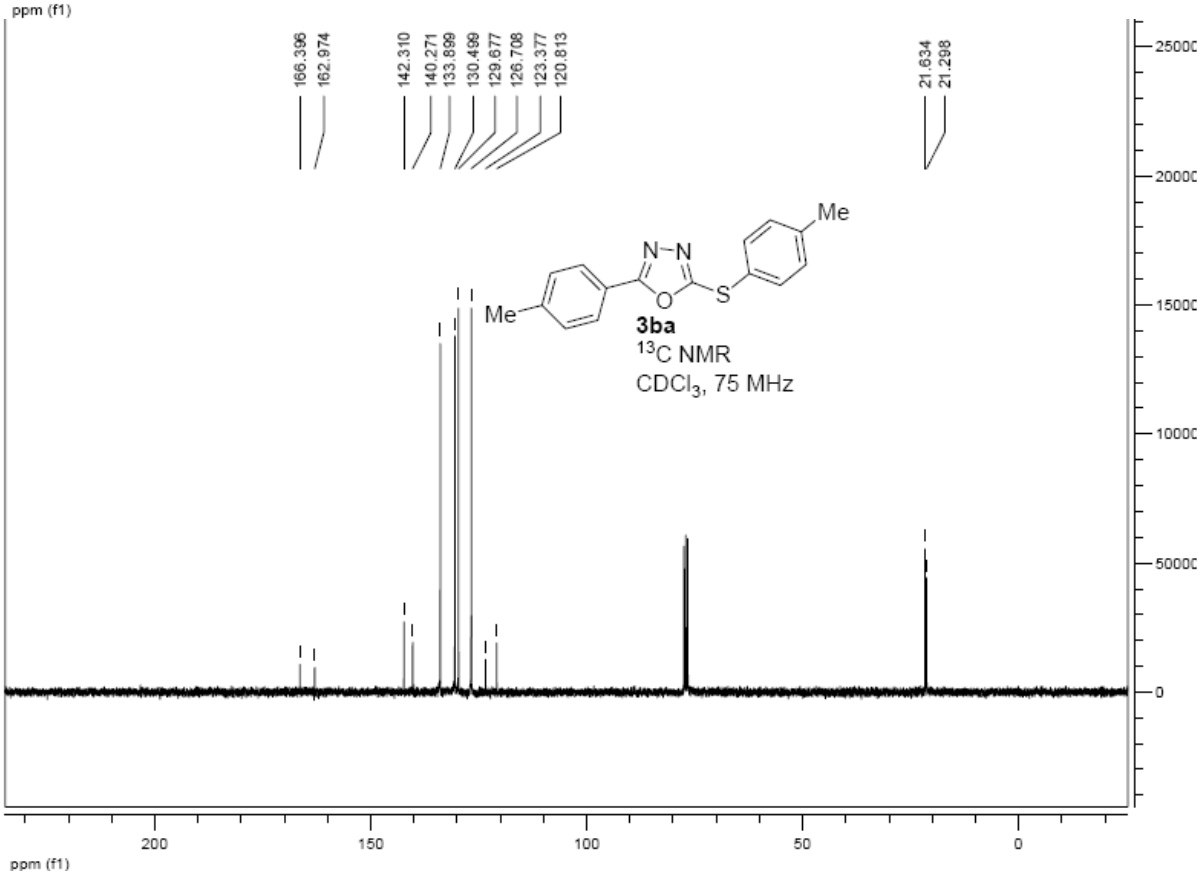




Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012

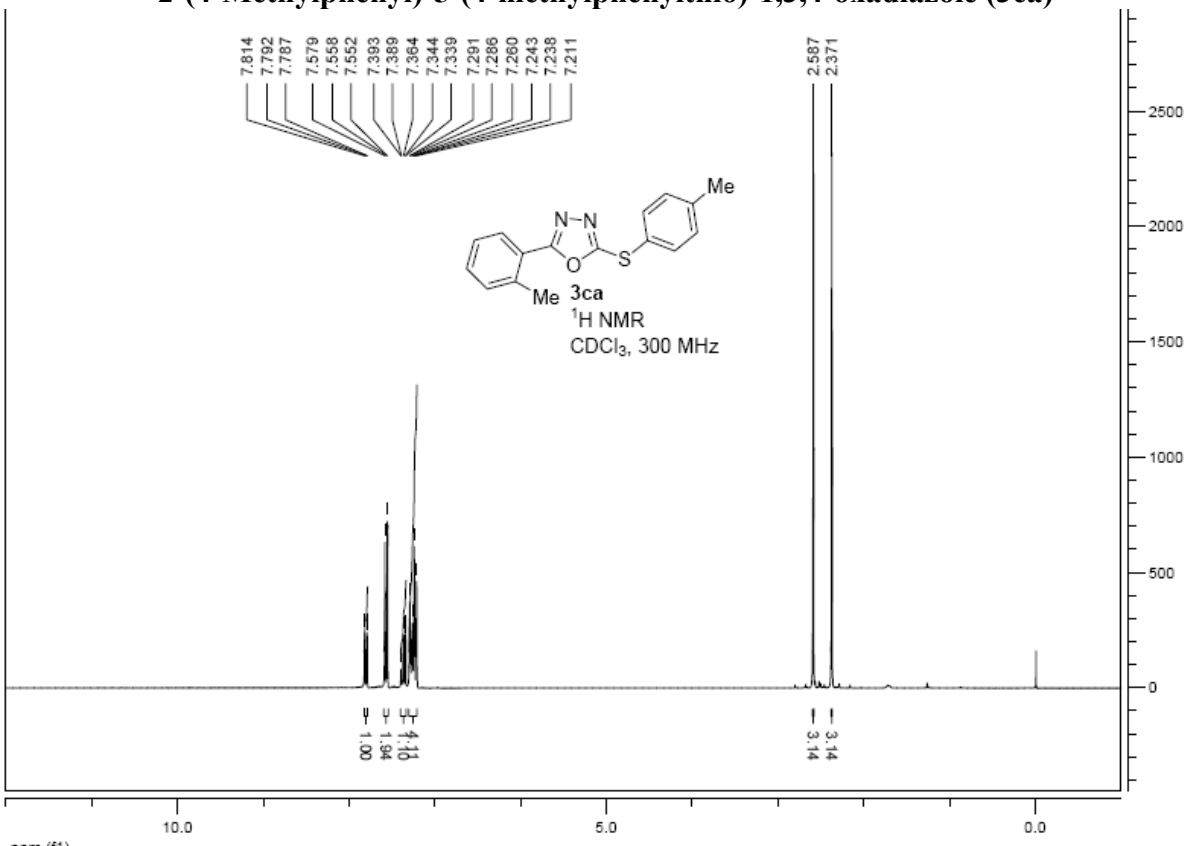
2-(4-Methylphenyl)-5-(4-methylphenylthio)-1,3,4-oxadiazole (3ba)

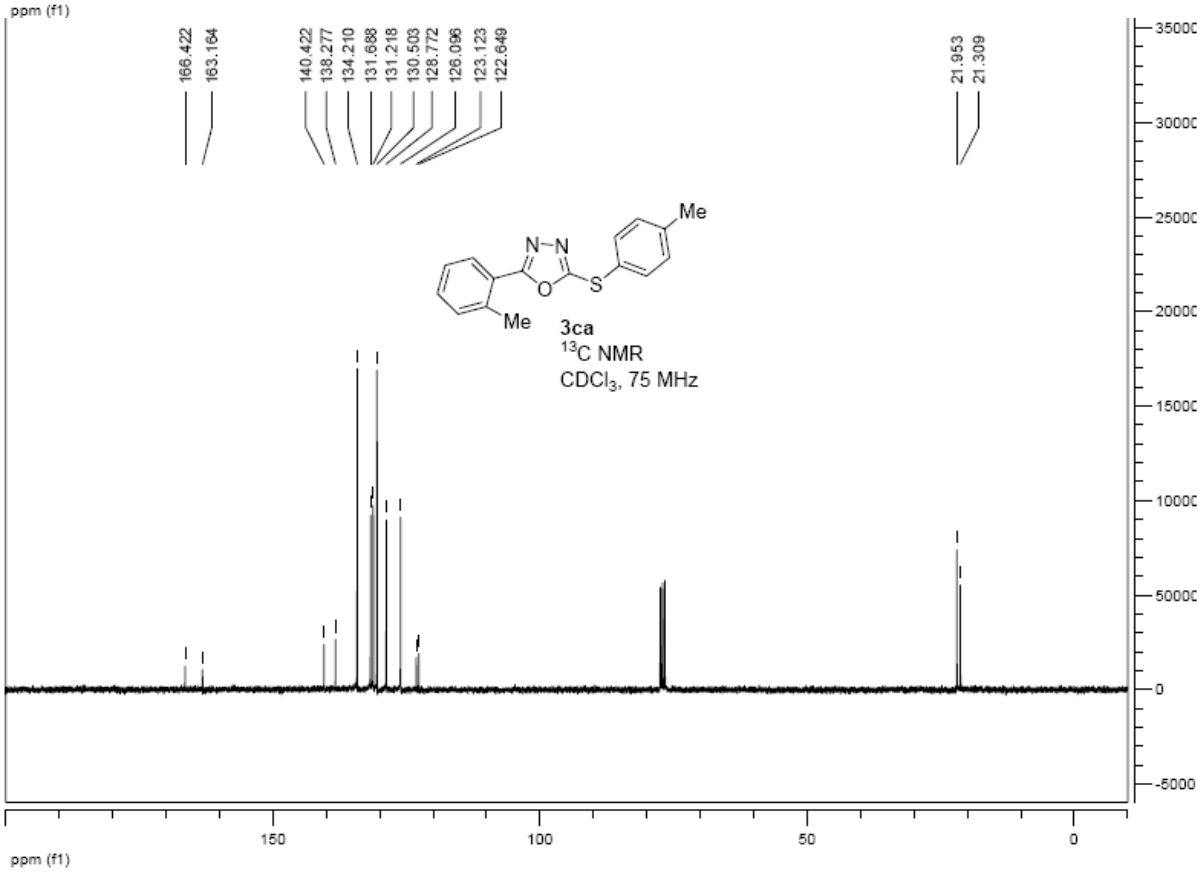




Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012

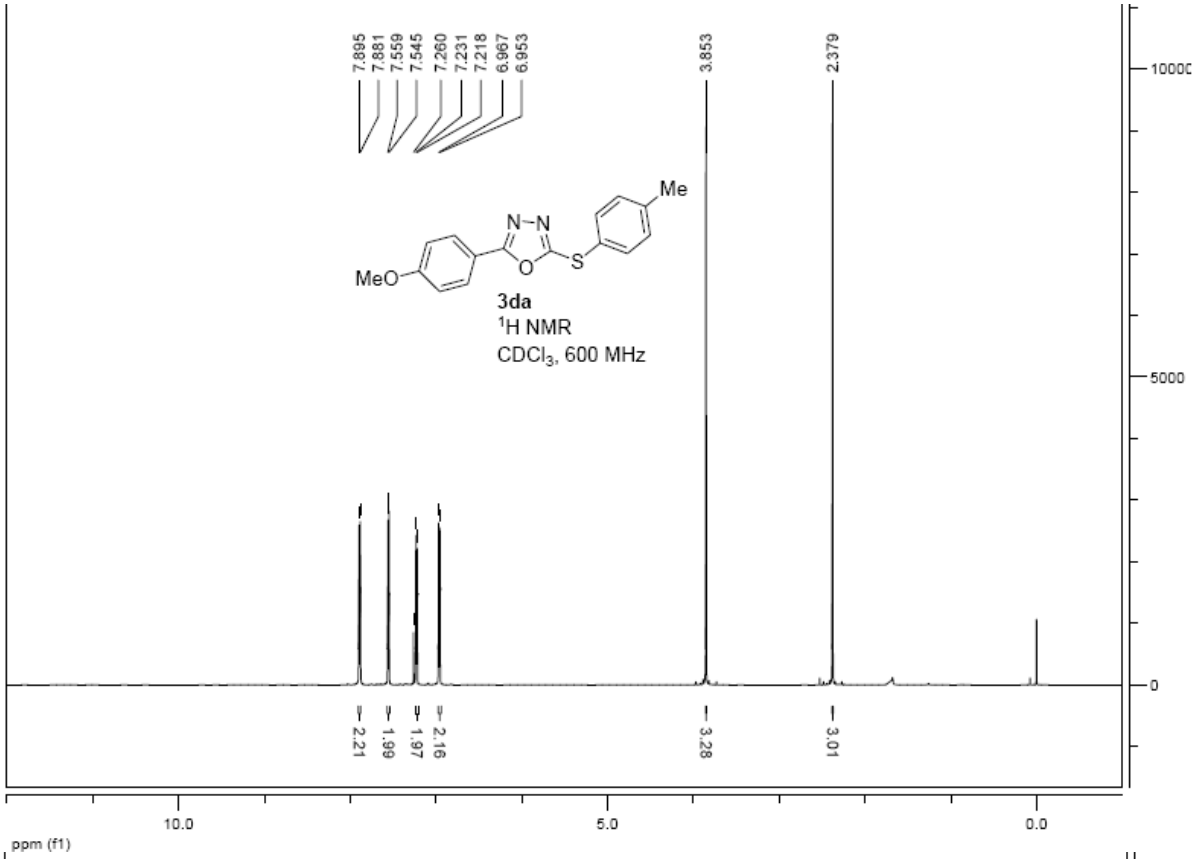
2-(4-Methylphenyl)-5-(4-methylphenylthio)-1,3,4-oxadiazole (3ca)

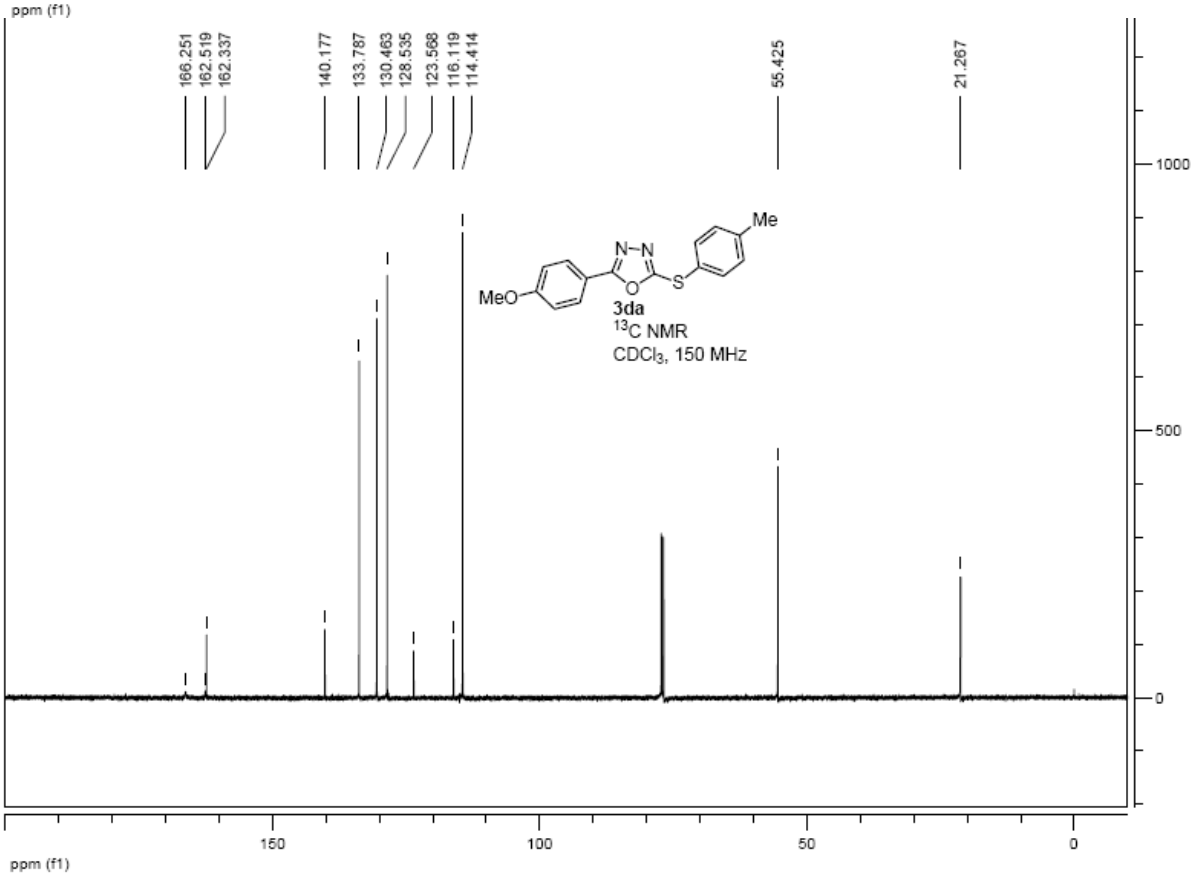




Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012

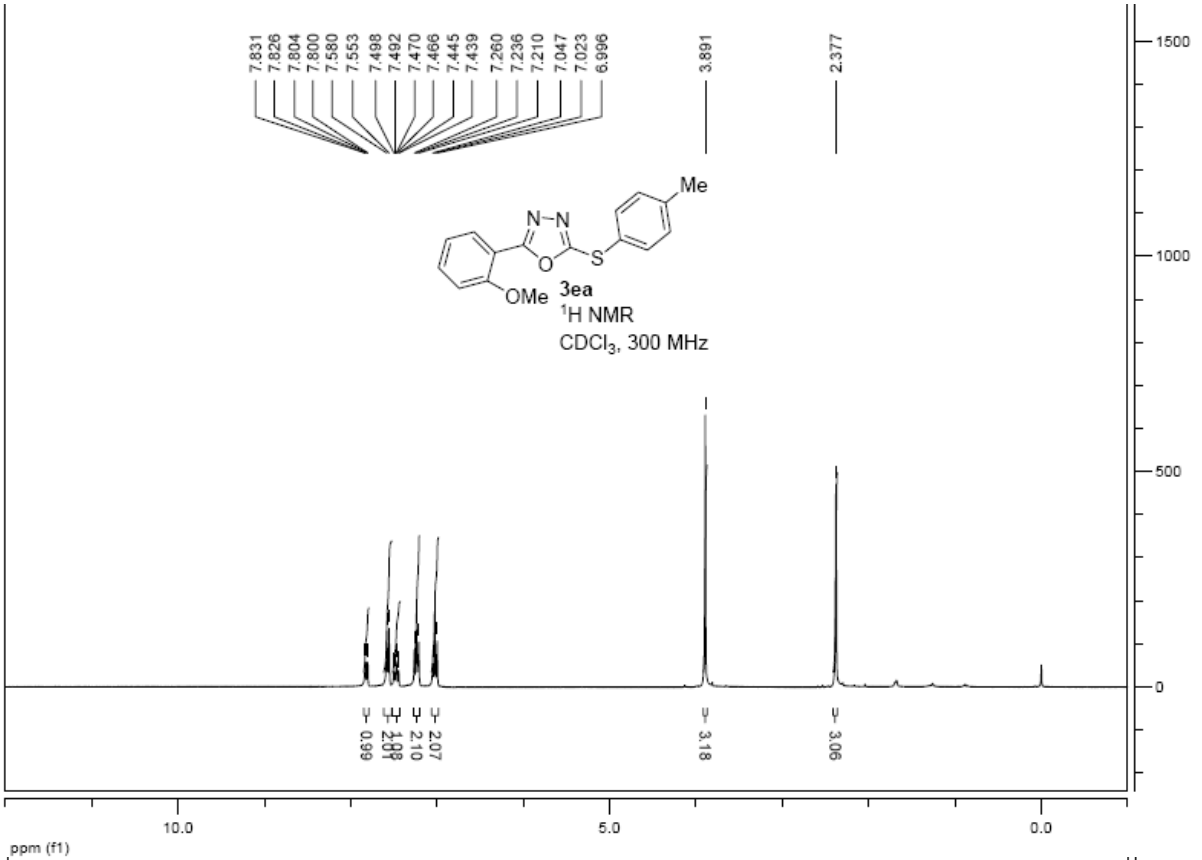
2-(4-Methoxyphenyl)-5-(4-methylphenylthio)-1,3,4-oxadiazole (3da)

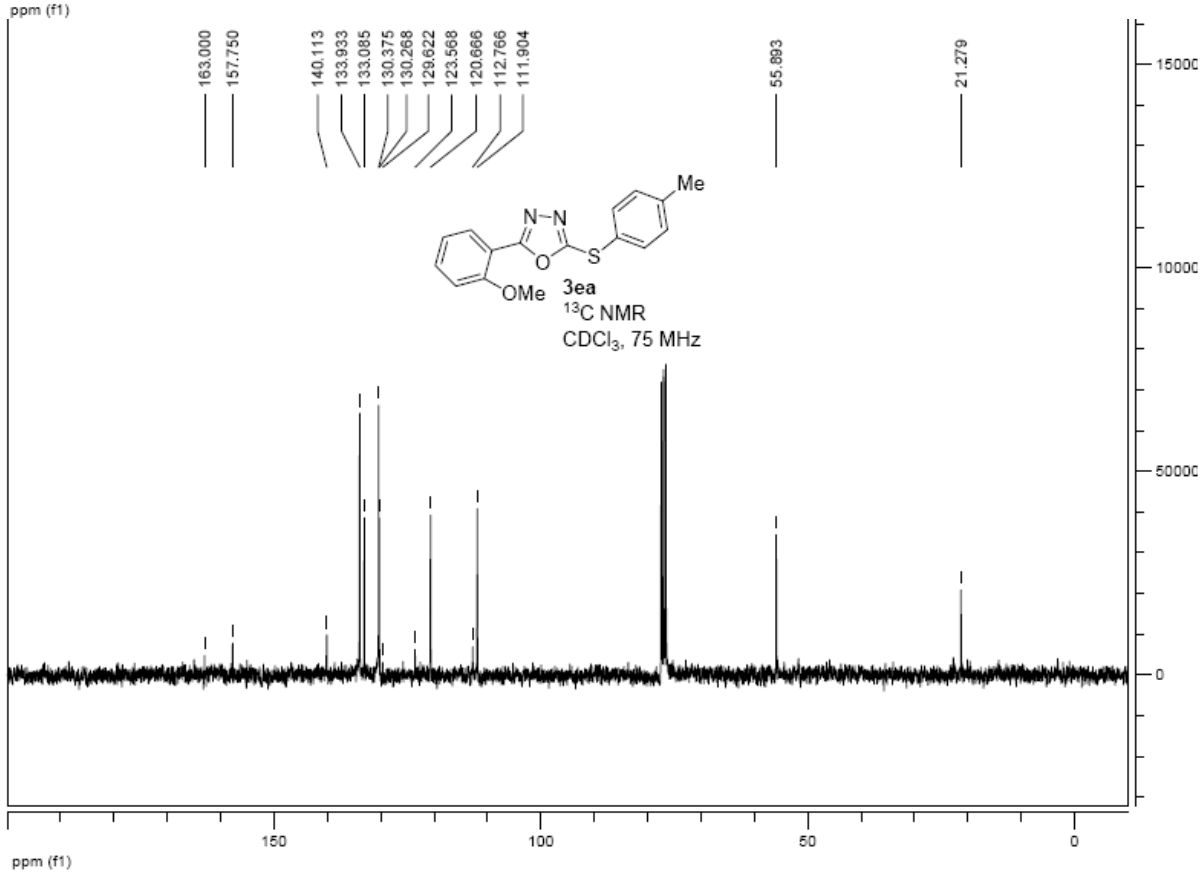




Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012

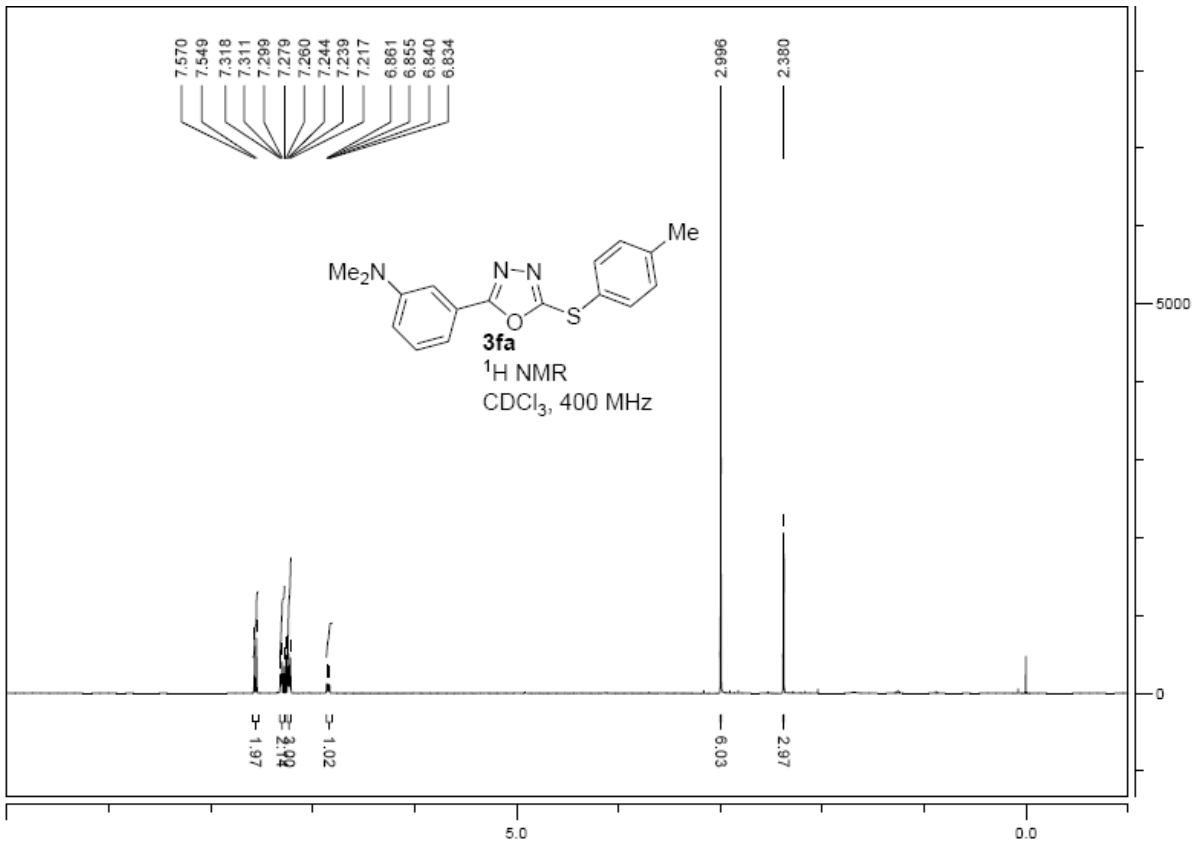
2-(2-Methoxyphenyl)-5-(4-methylphenylthio)-1,3,4-oxadiazole (3ea)

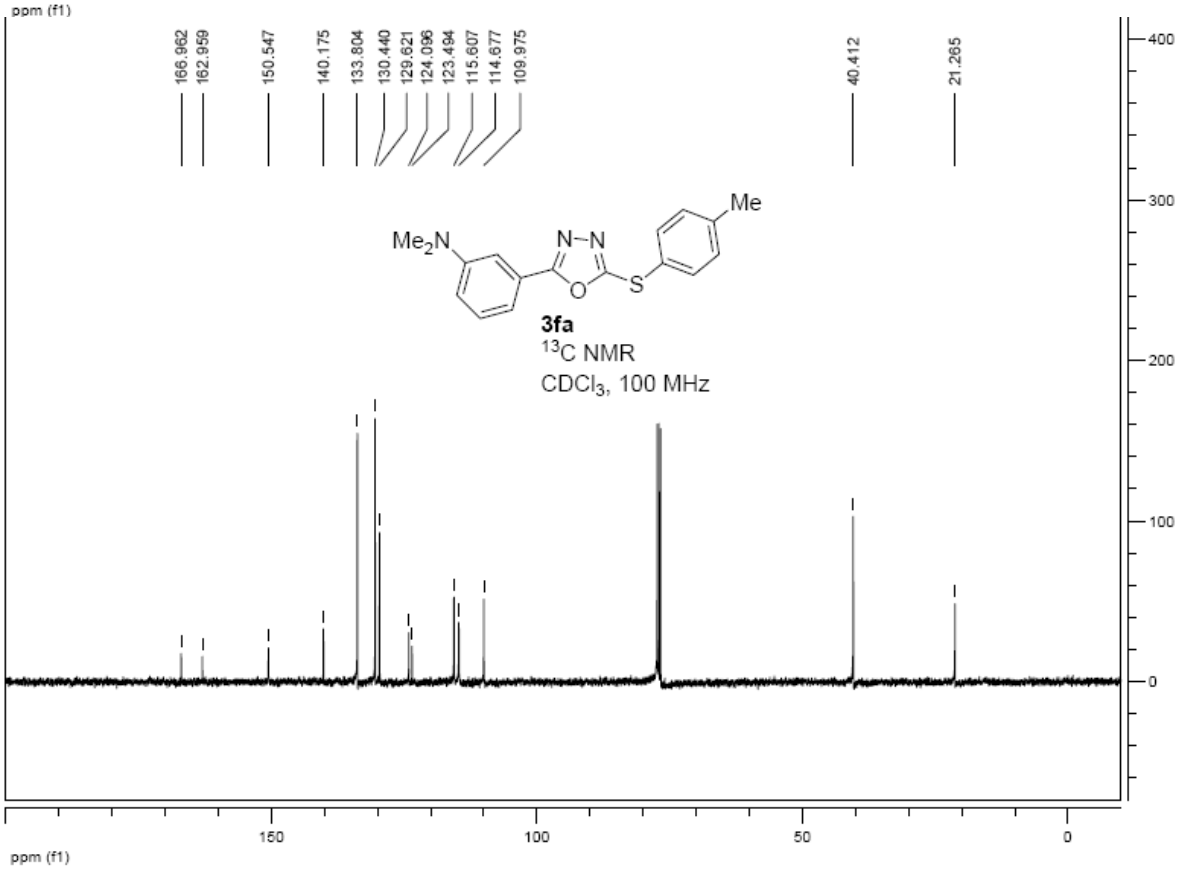




Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012

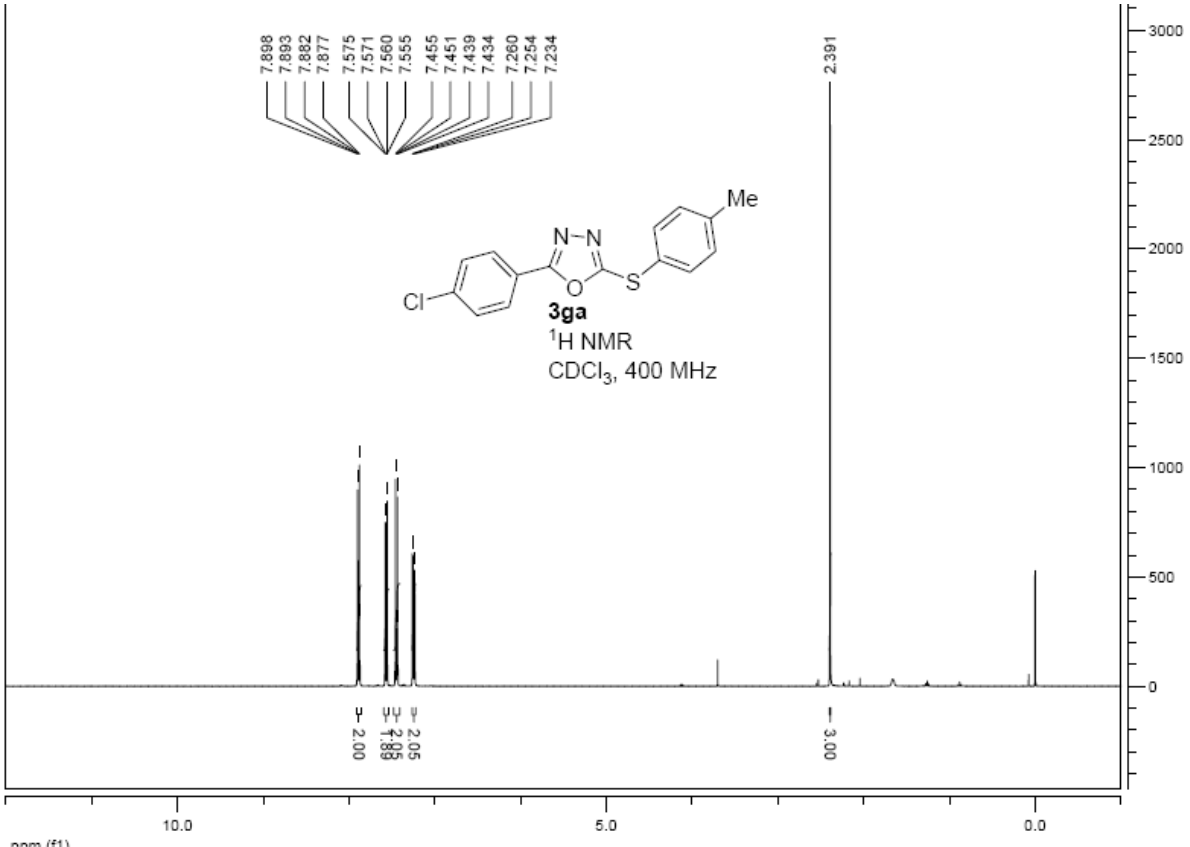
2-(3-N,N-Dimethylaminophenyl)-5-(4-methylphenylthio)-1,3,4-oxadiazole (3fa)

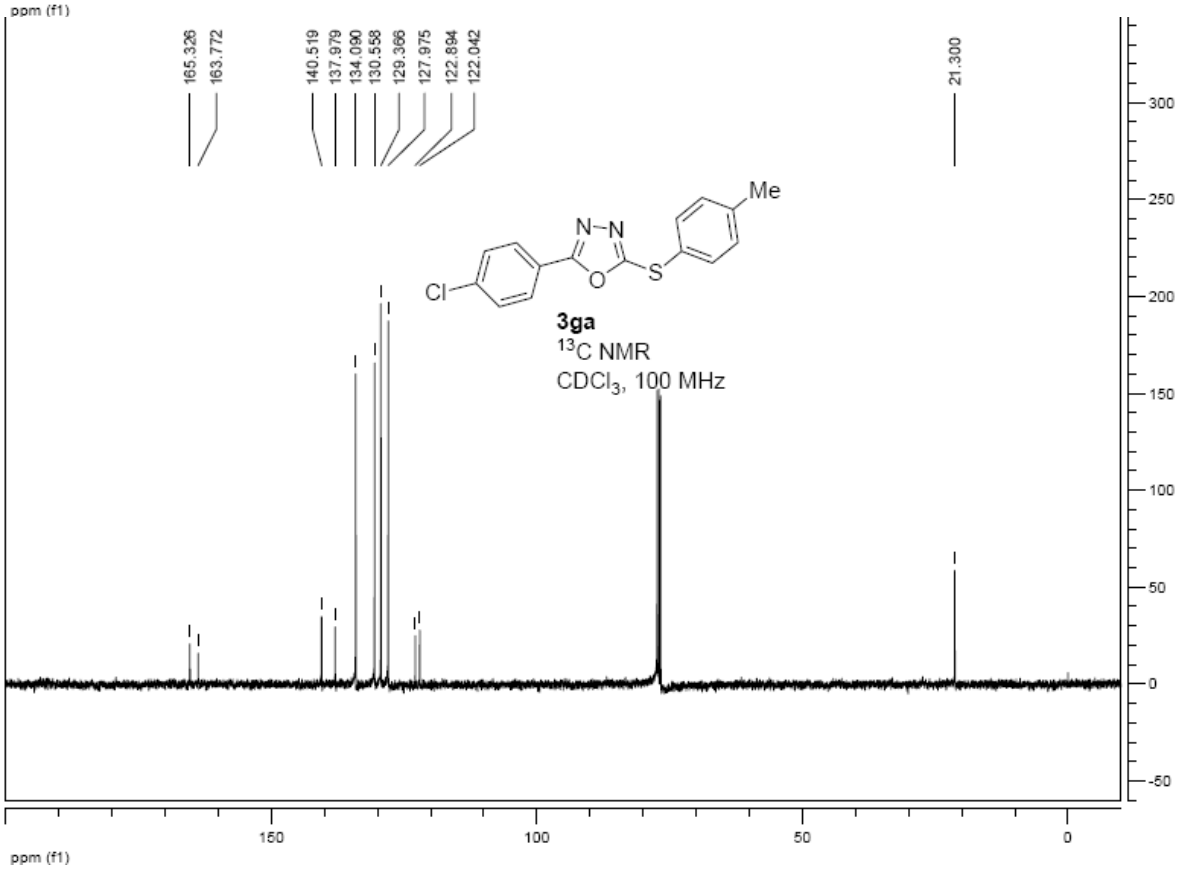




Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012

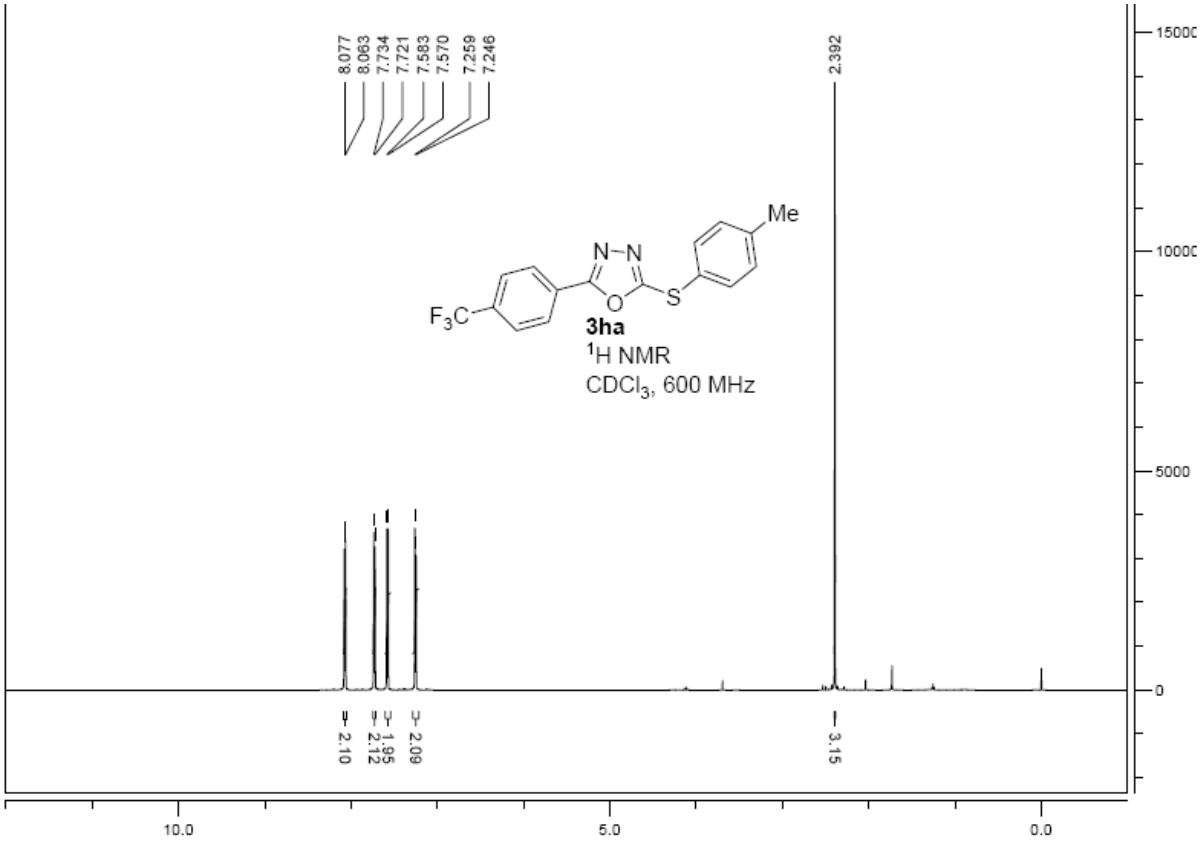
2-(4-Chlorophenyl)-5-(4-methylphenylthio)-1,3,4-oxadiazole (3ga)

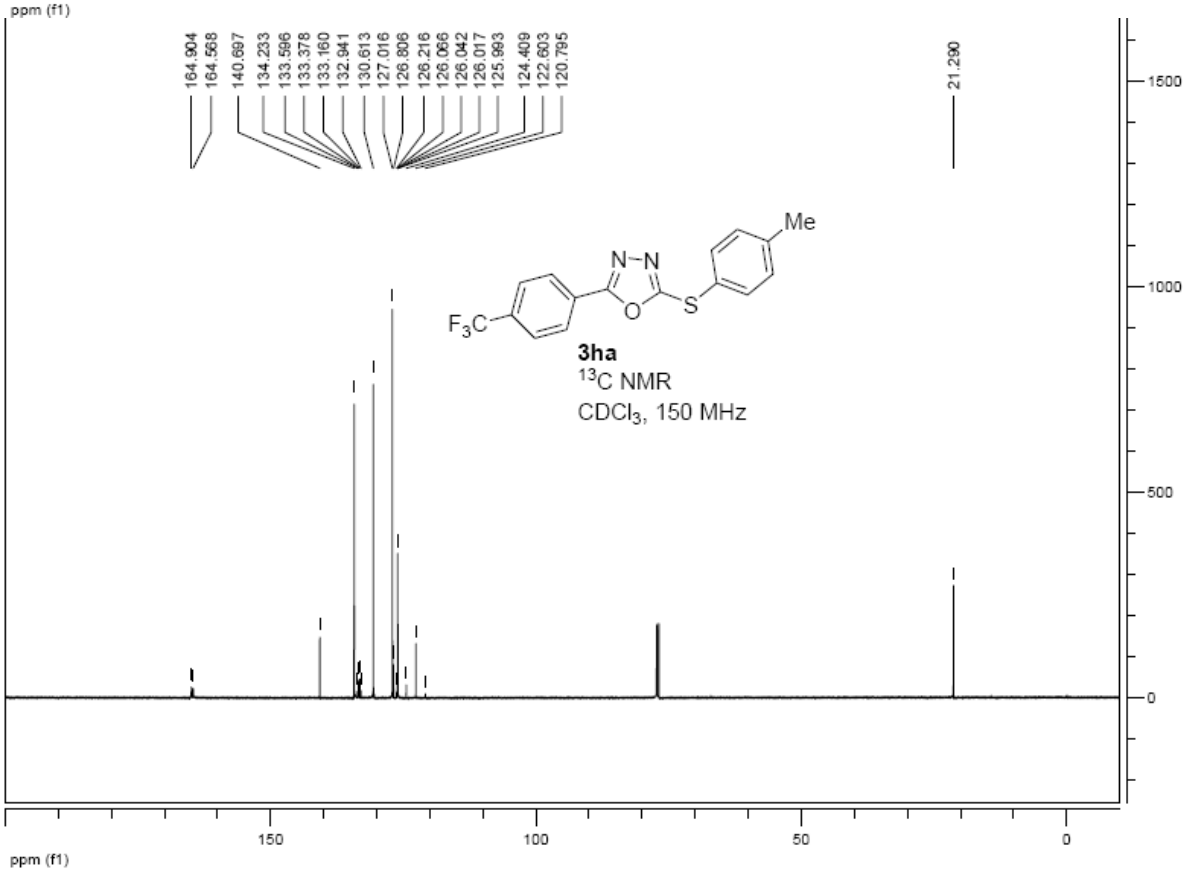




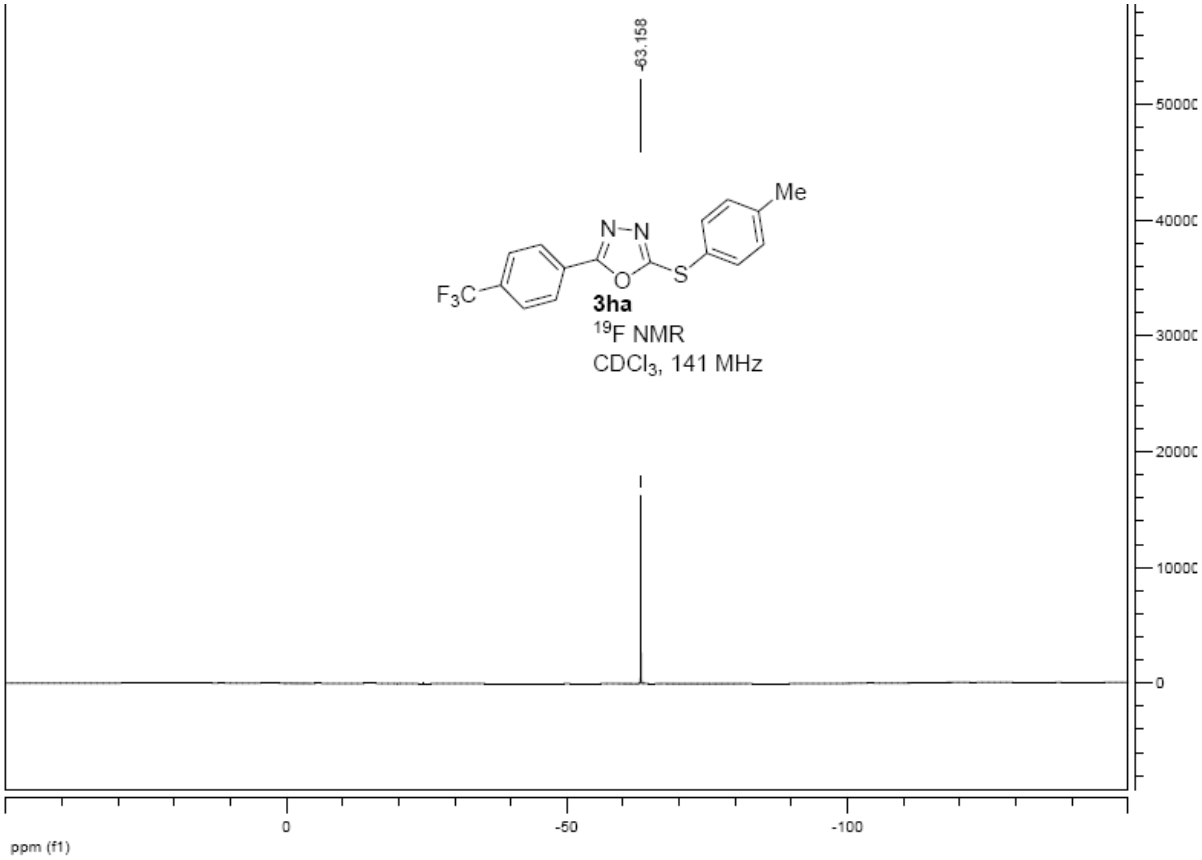
Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012

2-(4-Trifluoromethylphenyl)-5-(4-methylphenylthio)-1,3,4-oxadiazole (3ha)

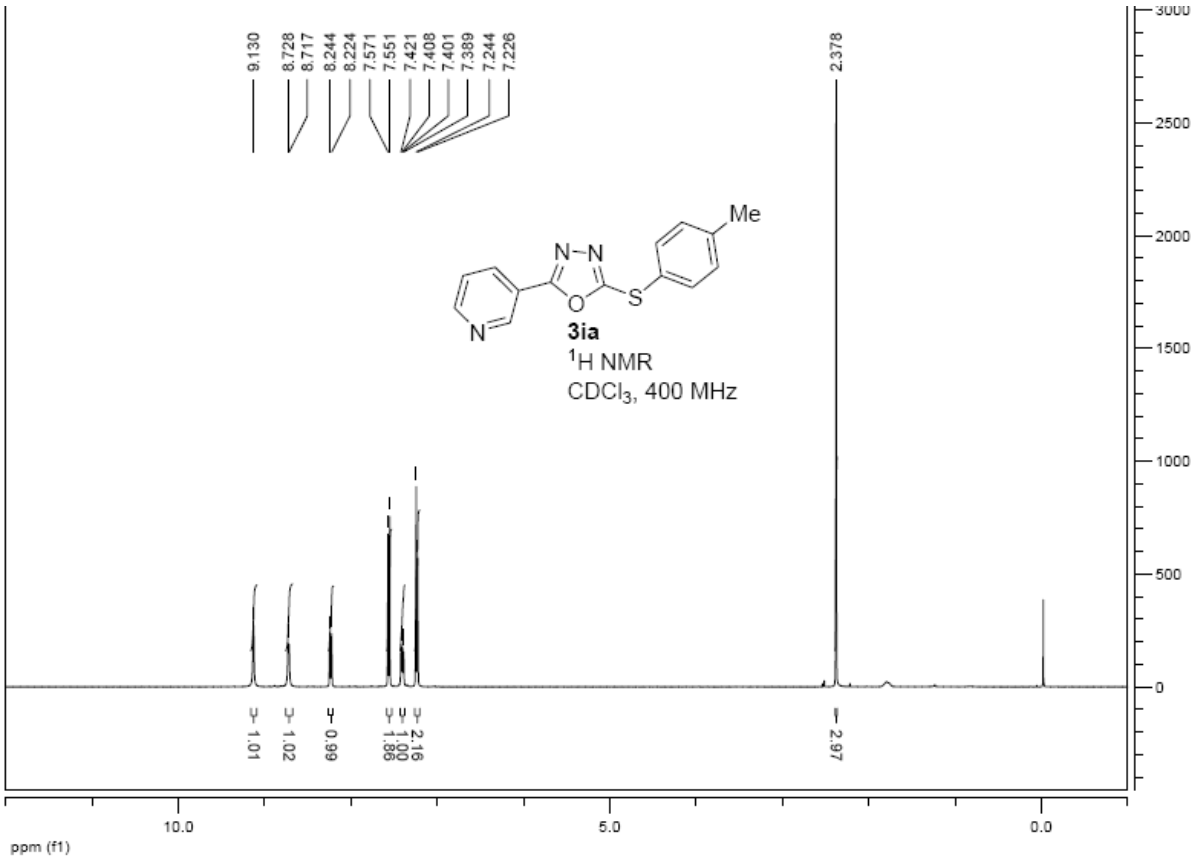




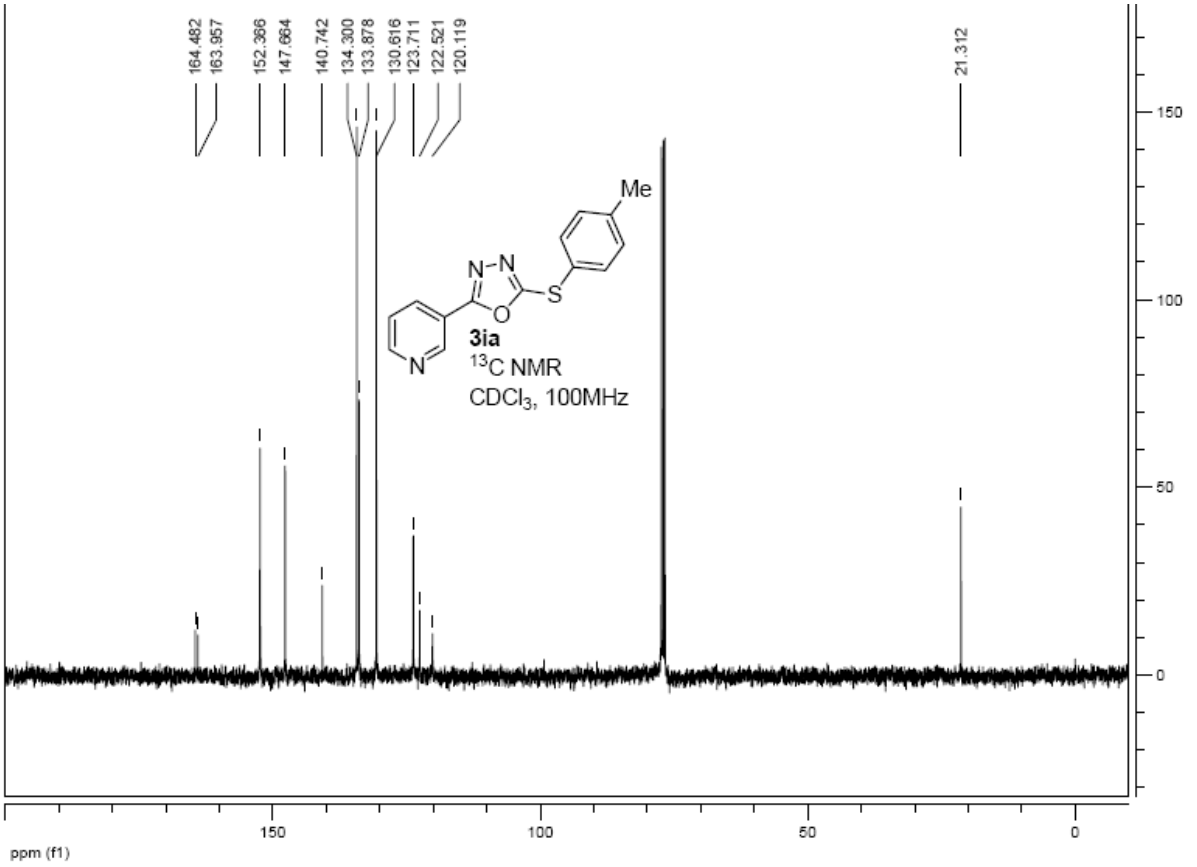
Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012



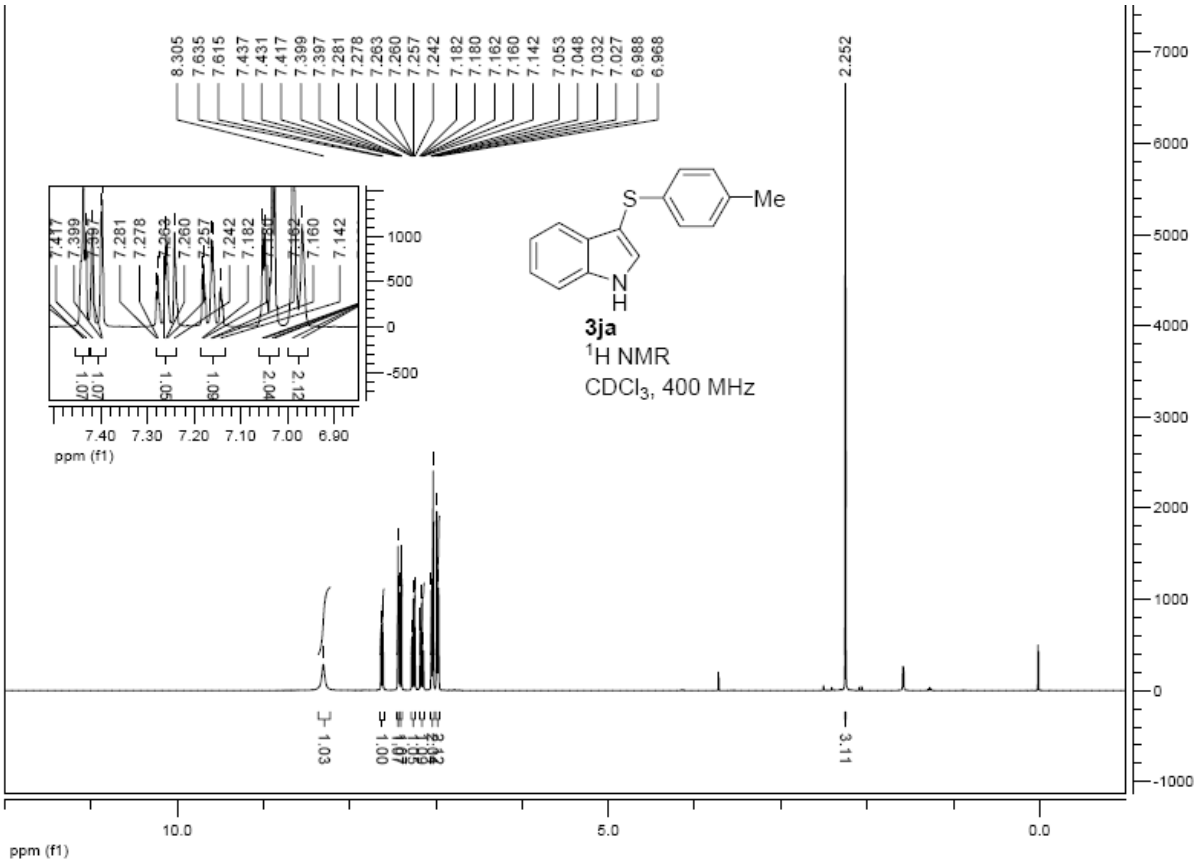
2-(3-Pyridinyl)-5-(4-methylphenylthio)-1,3,4-oxadiazole (3ia)



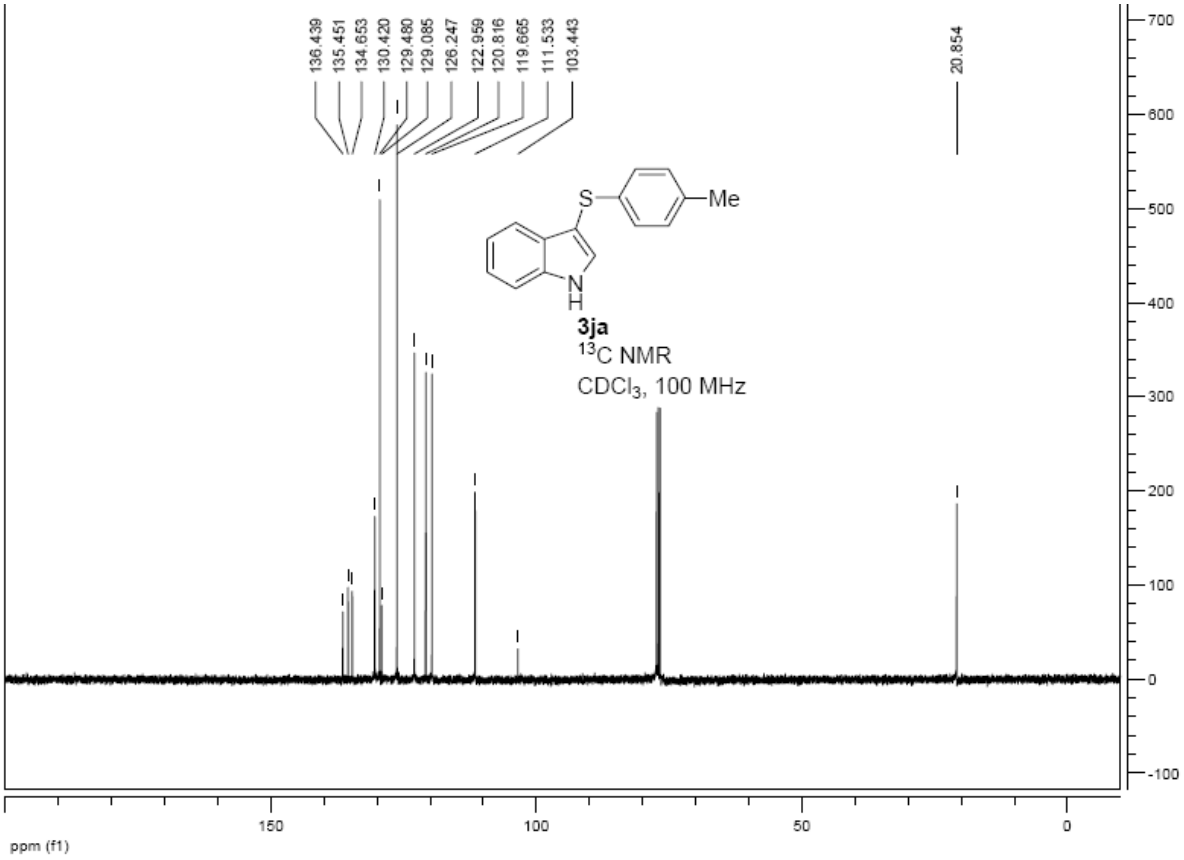
Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012



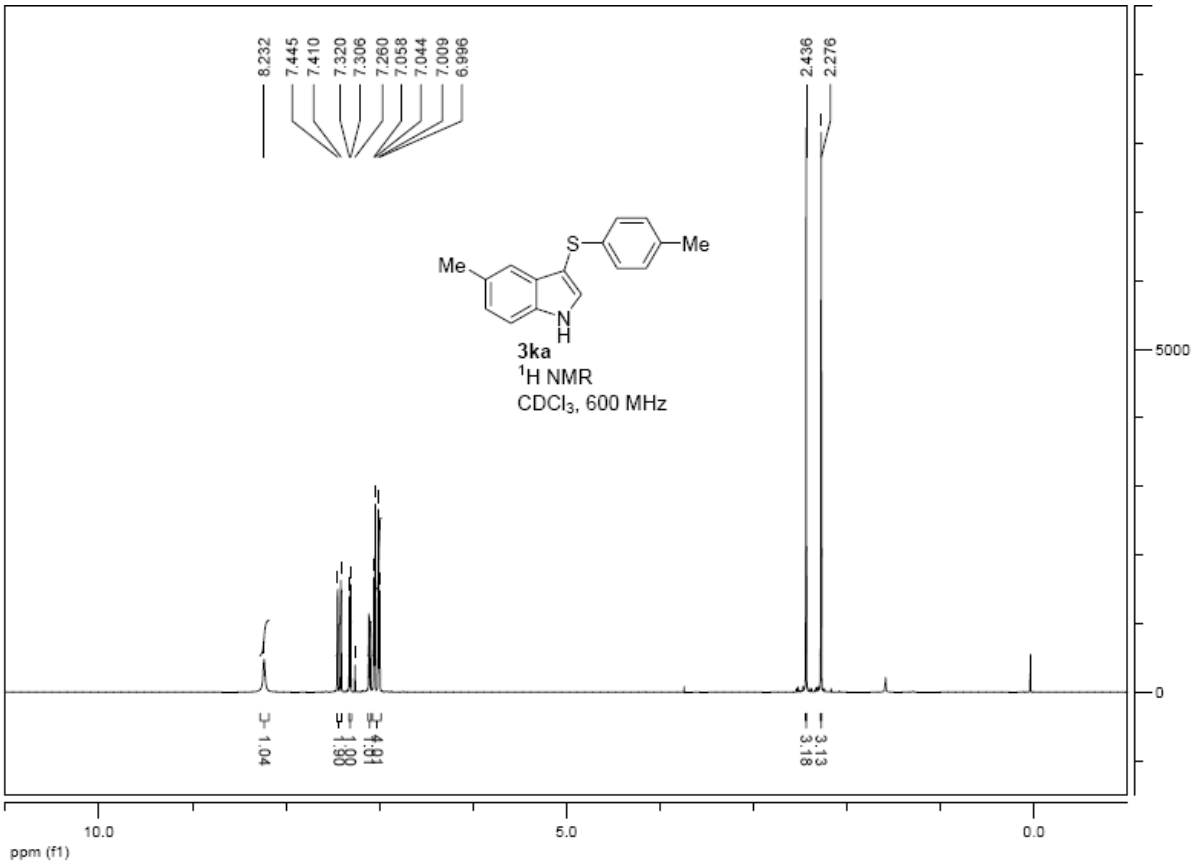
3-(4-Methylphenylthio)-indole (3ja)



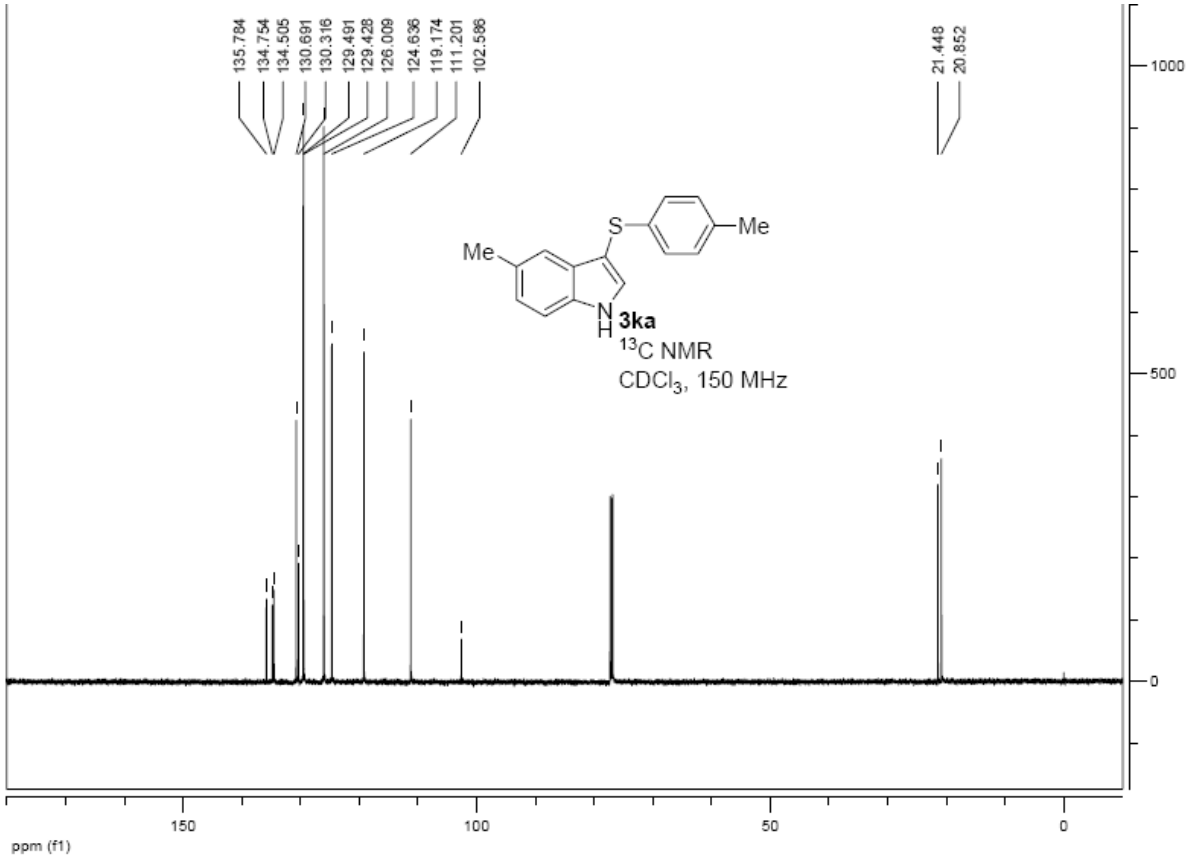
Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012



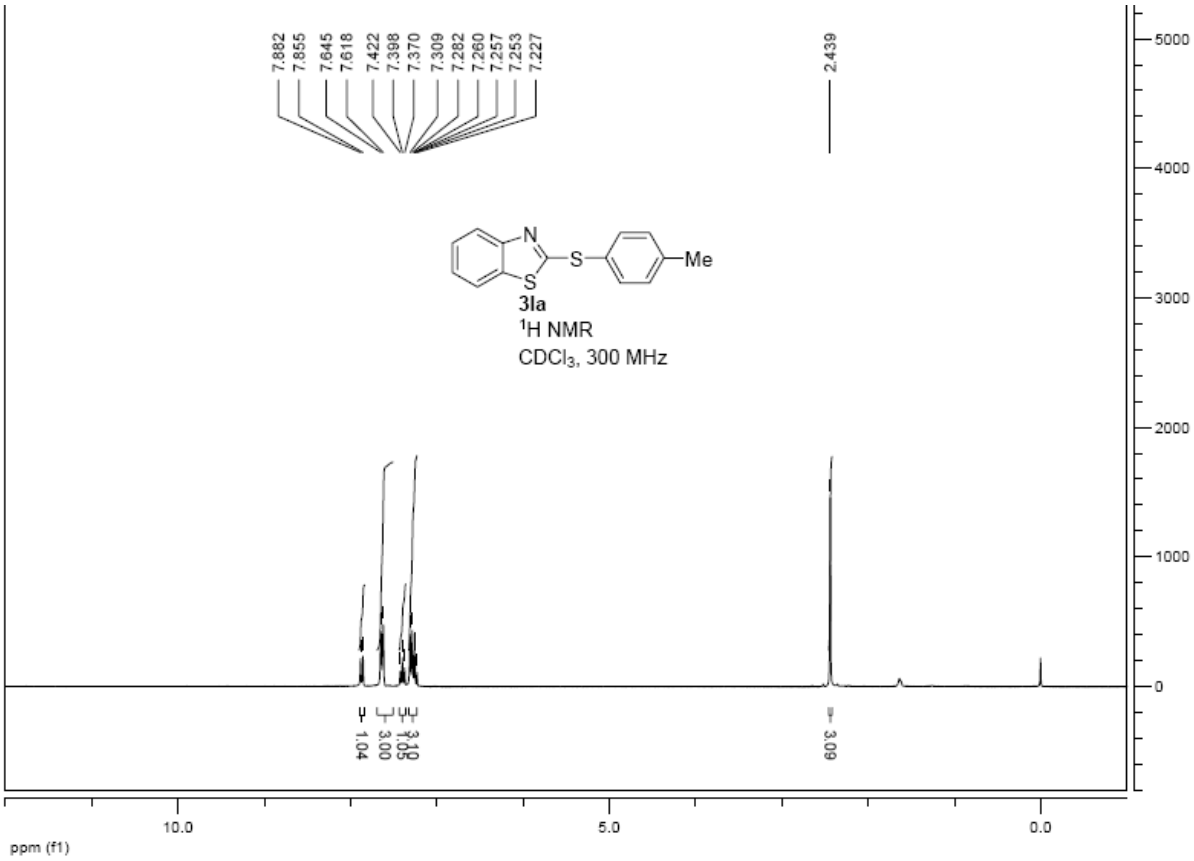
3-(4-Methylphenylthio)-6-methylindole (3ka)



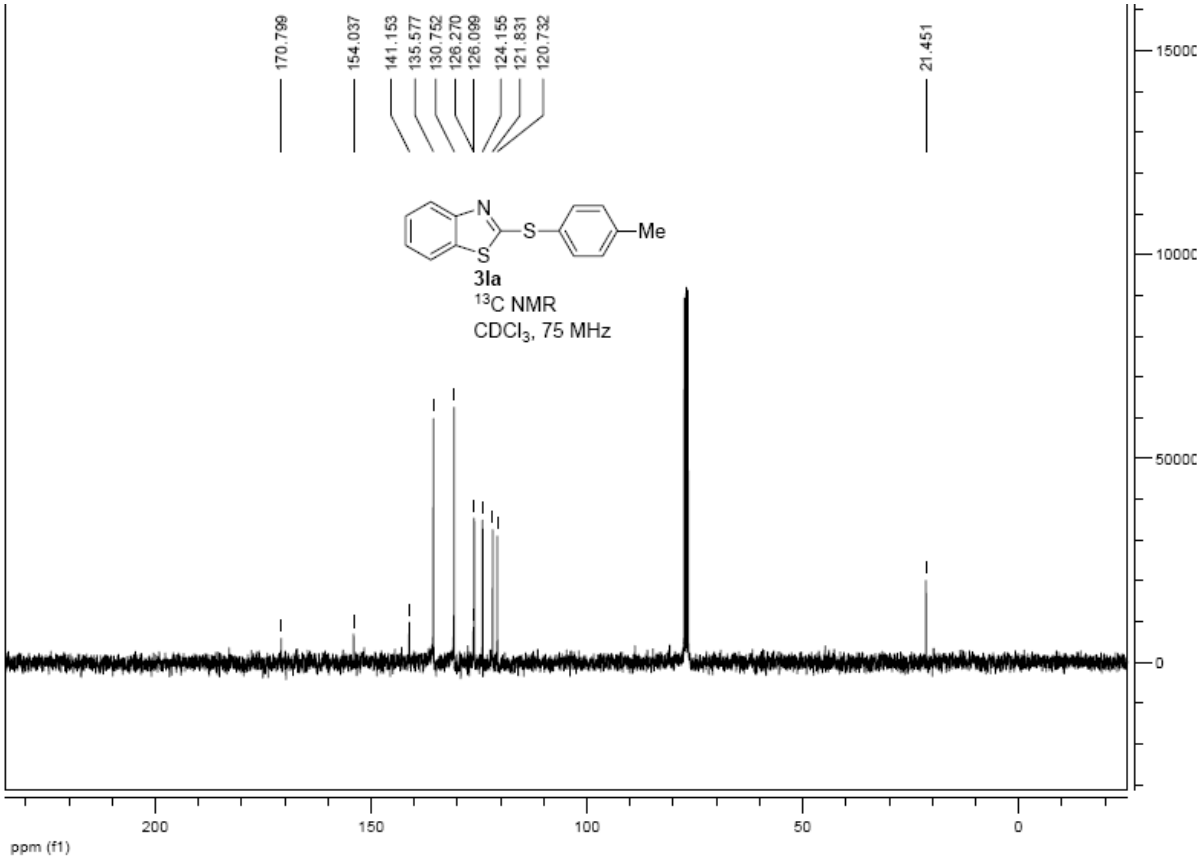
Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012



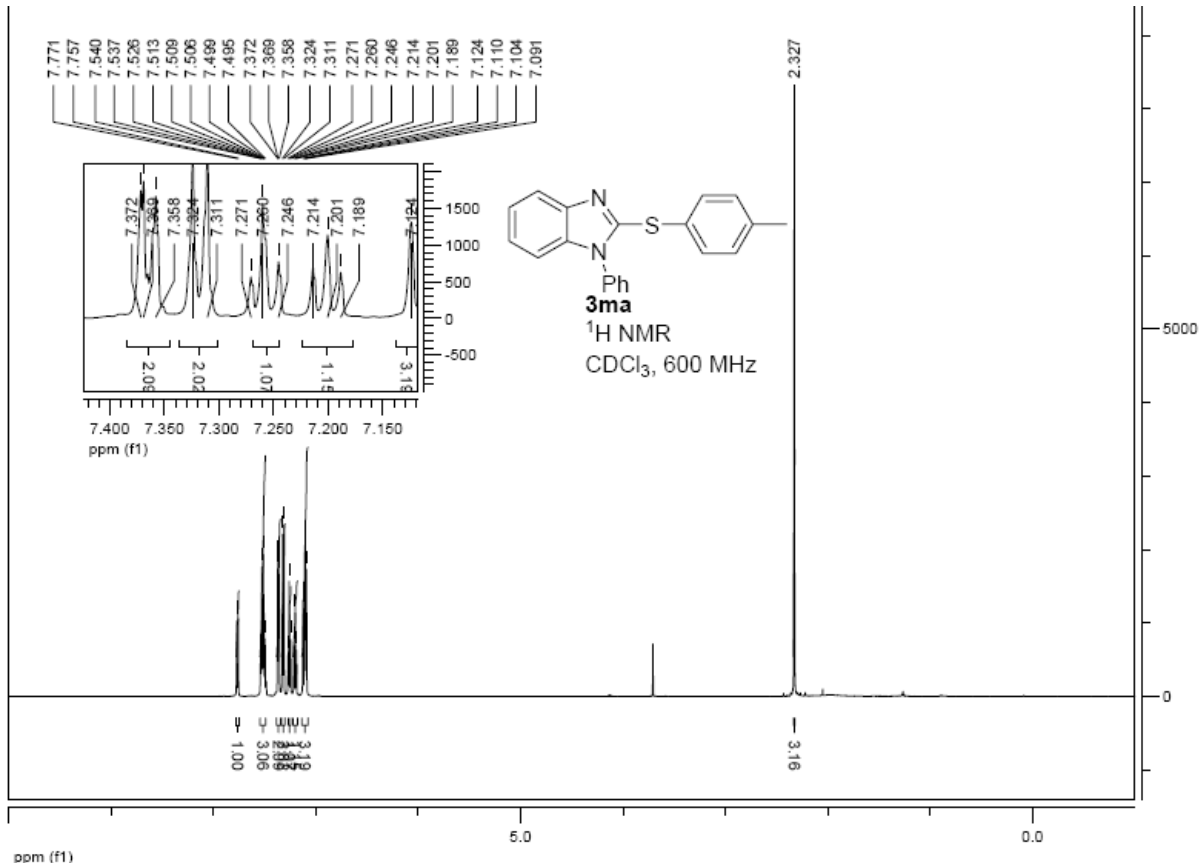
2-(4-Methylphenylthio)-benzothiazole (3la)



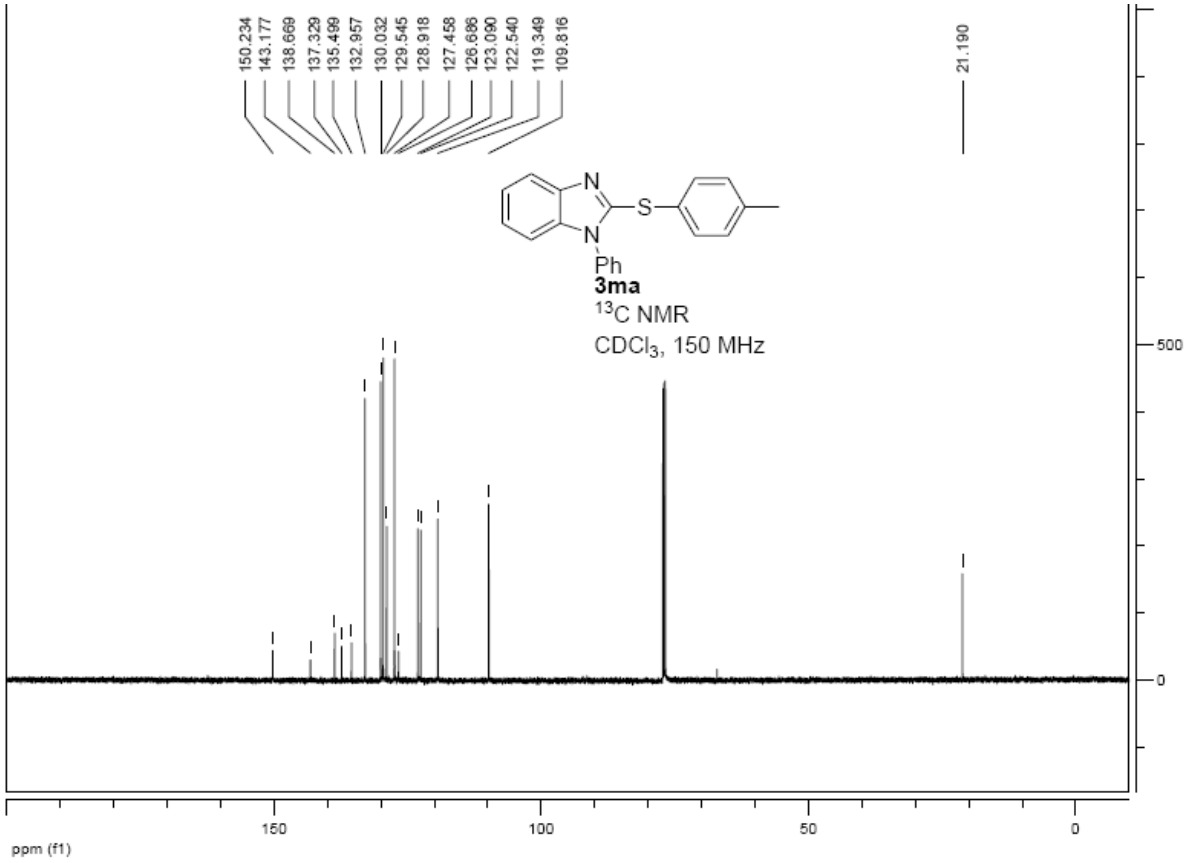
Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012



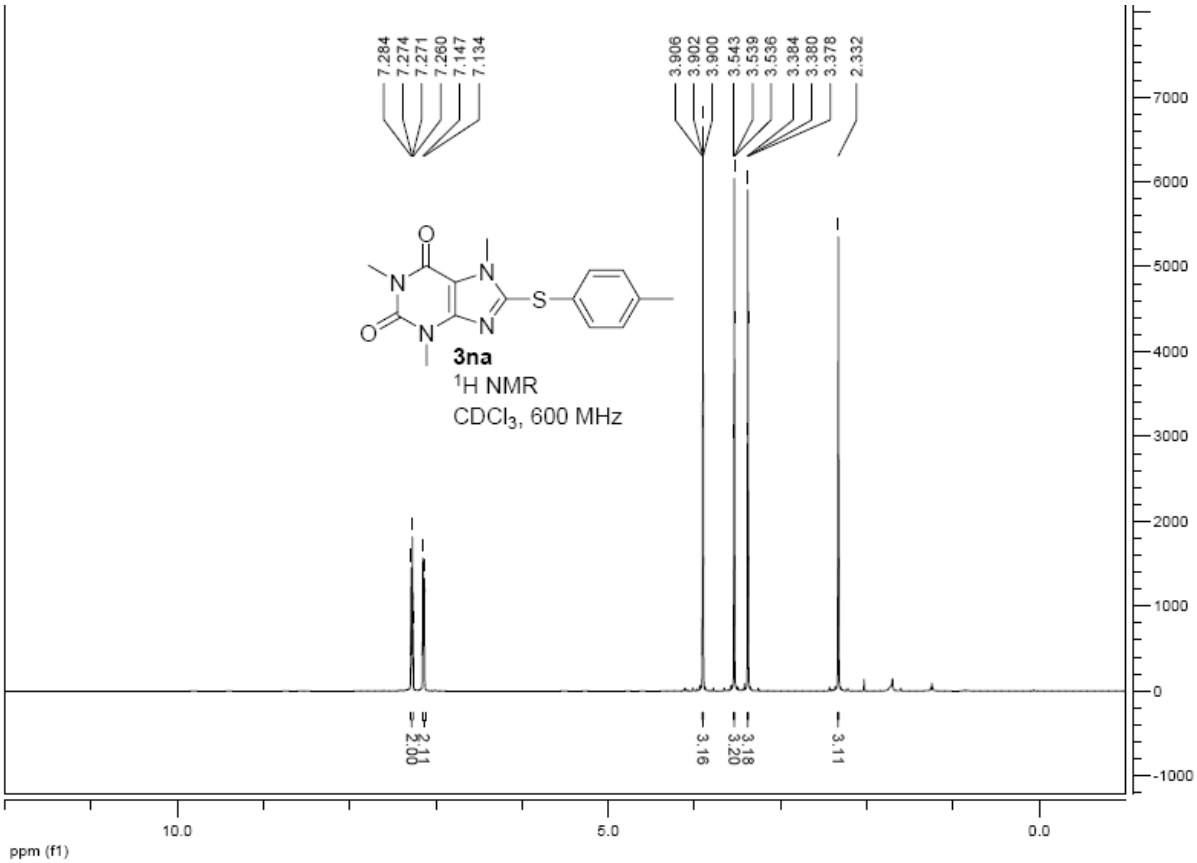
1-Phenyl-2-(4-methylphenylthio)-benzimidazole (3ma)



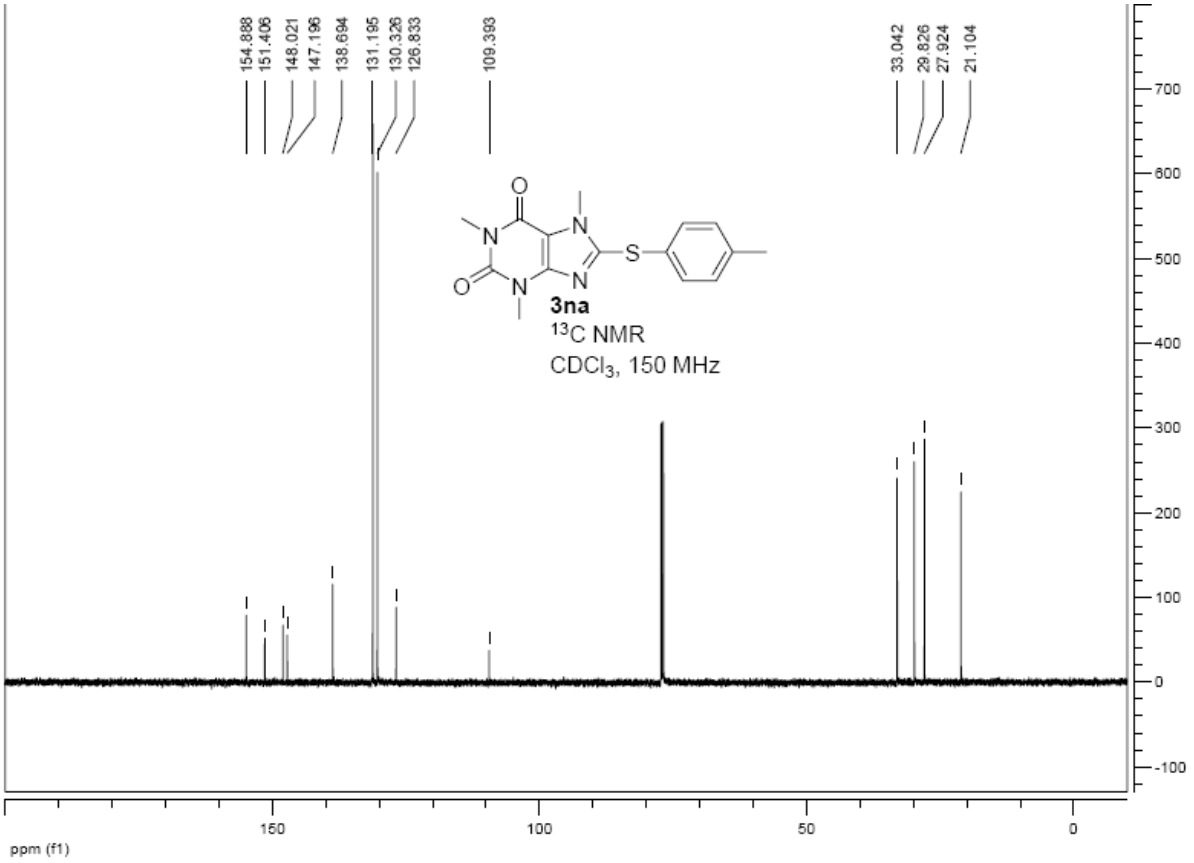
Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012



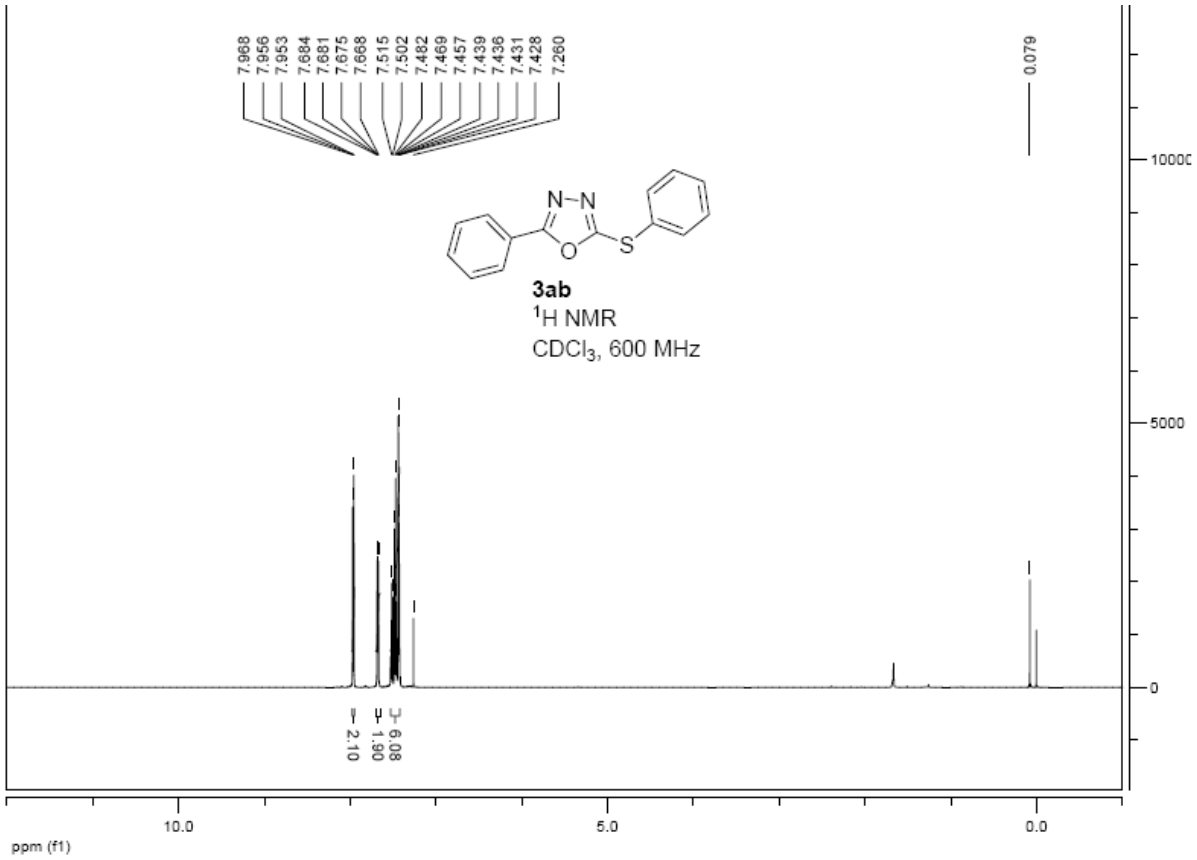
2-(4-Methylphenylthio)-caffeine (3na)



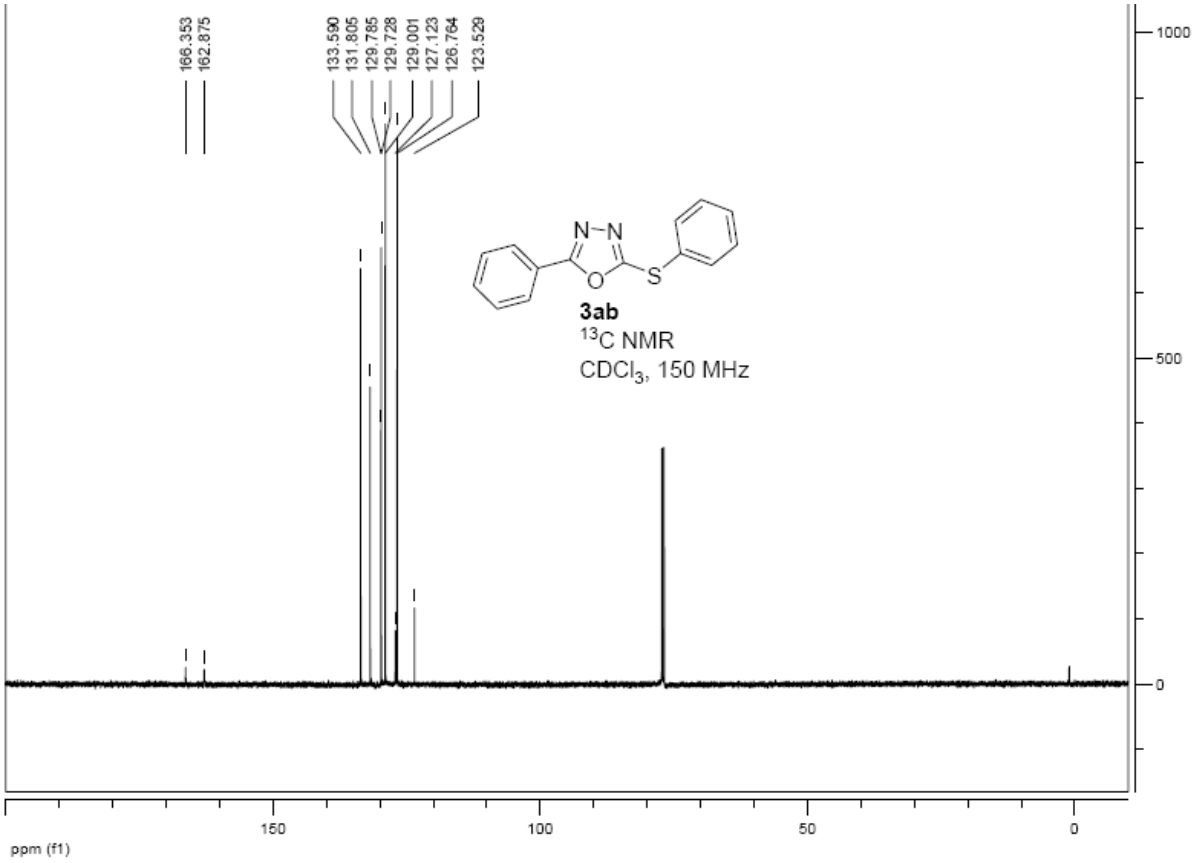
Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012



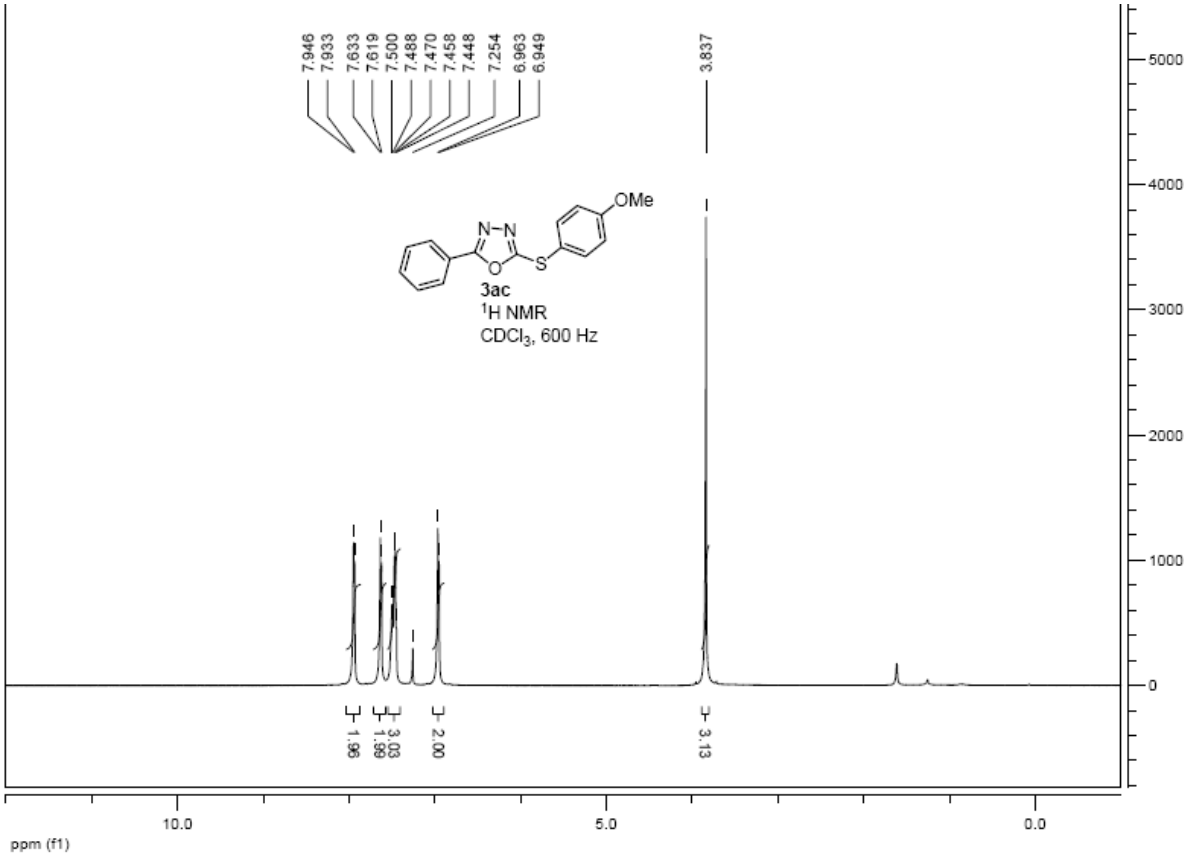
2-Phenyl-5-phenylthio-1,3,4-oxadiazole (3ab)



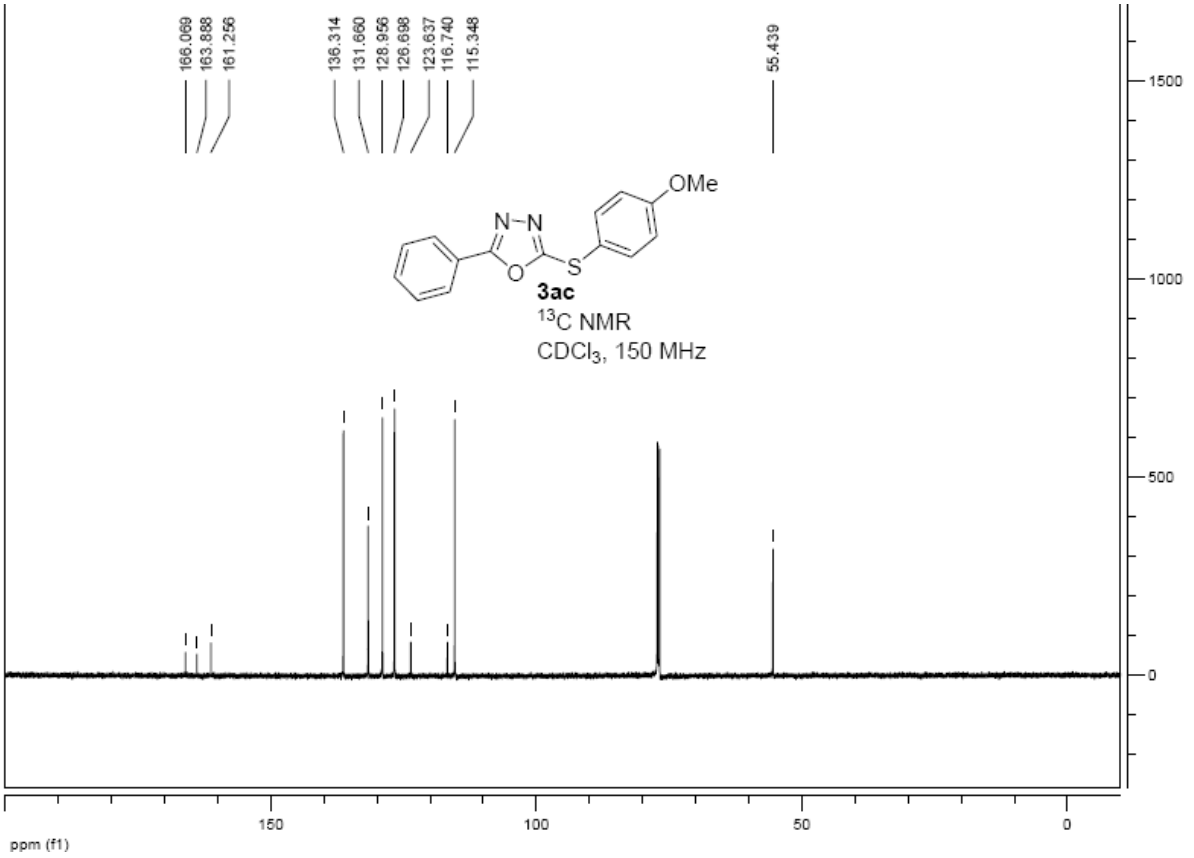
Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012



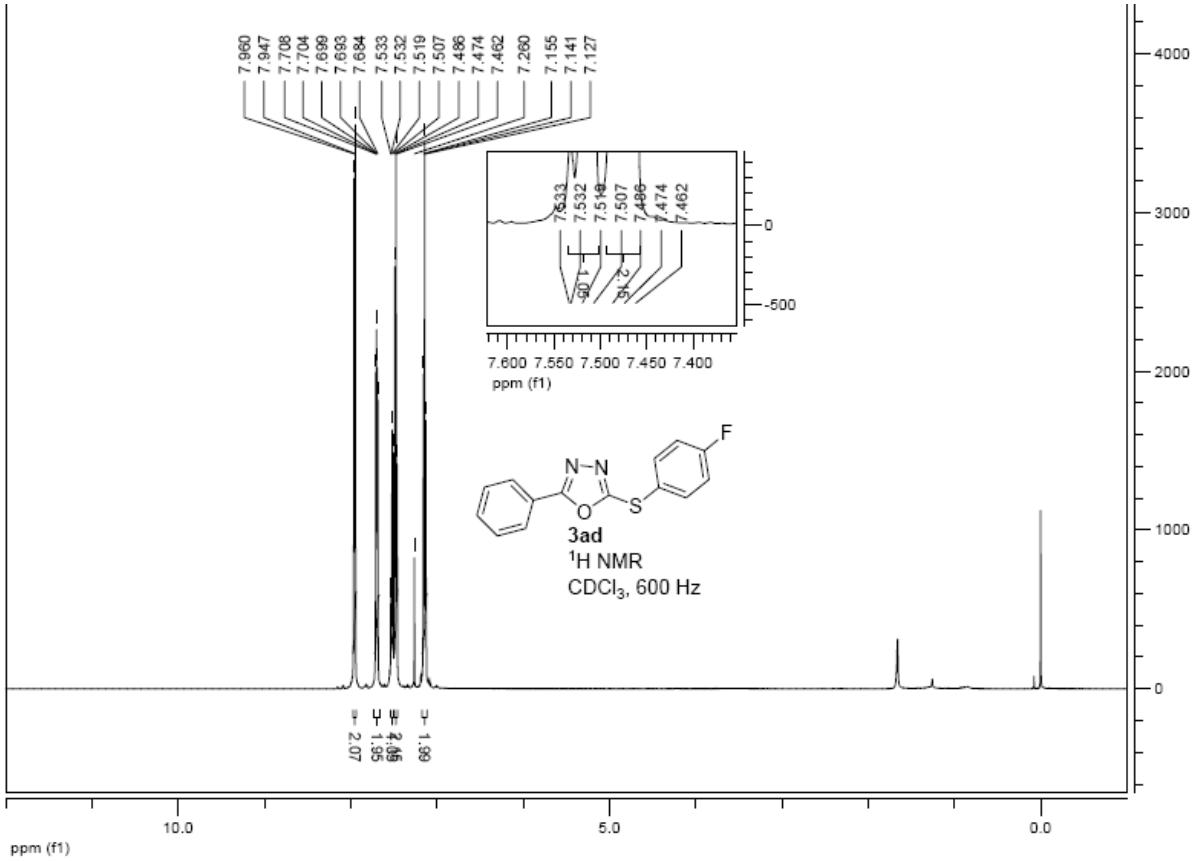
2-Phenyl-5-(4-methoxyphenylthio)-1,3,4-oxadiazole (3ac)



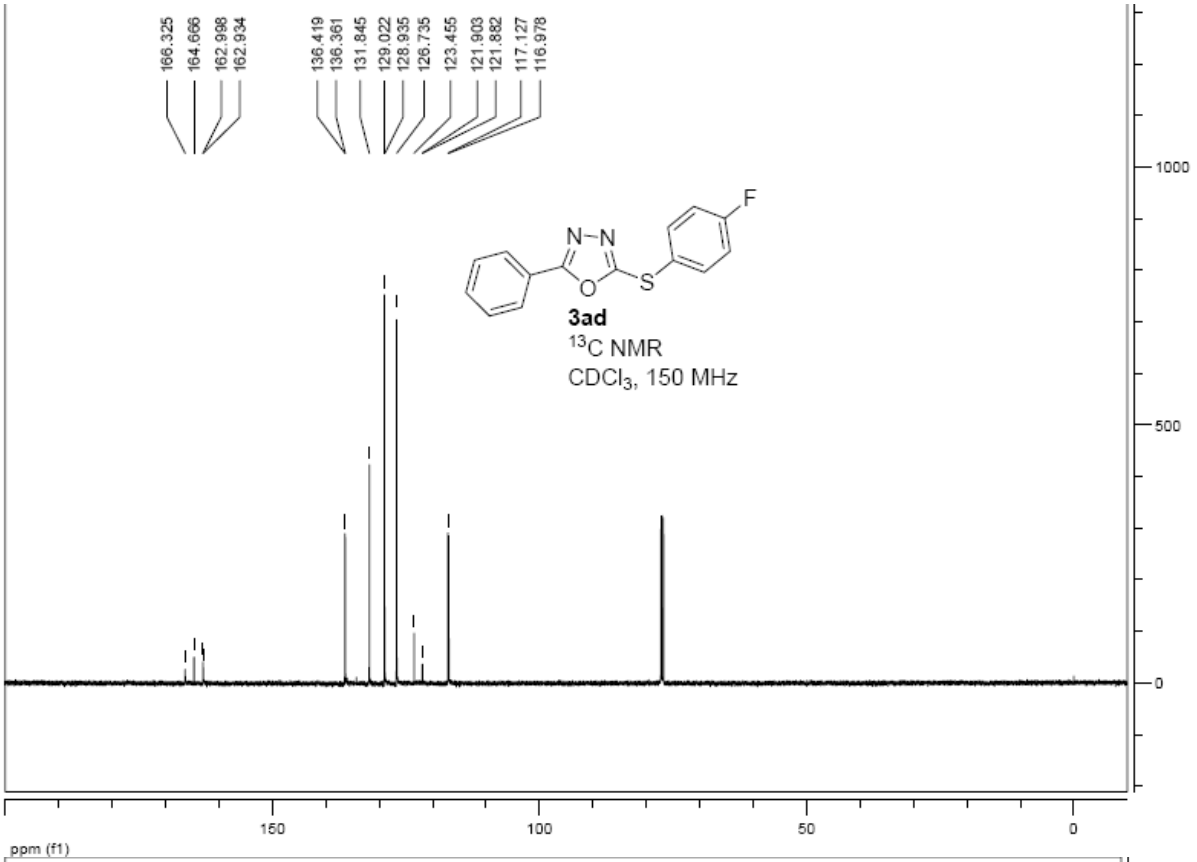
Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012

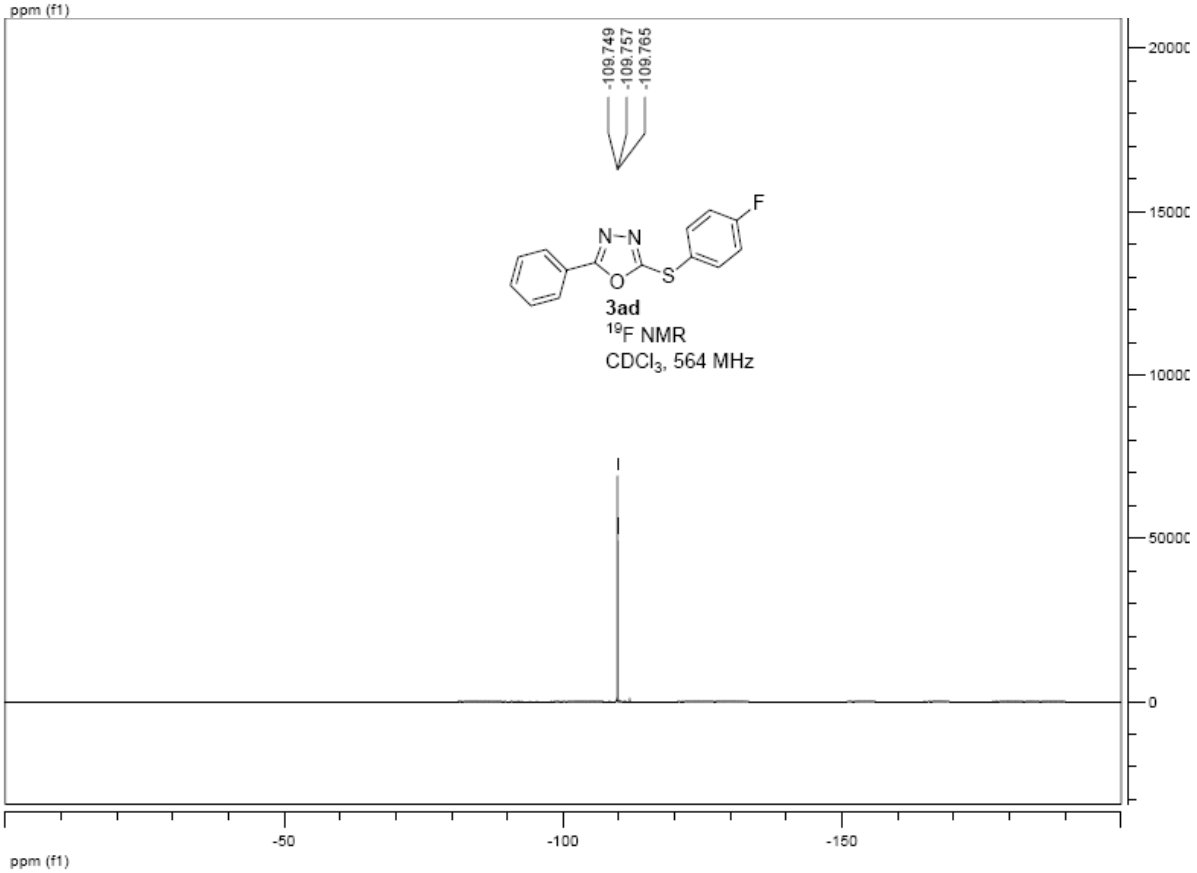


2-Phenyl-5-(4-fluorophenylthio)-1,3,4-oxadiazole (3ad)



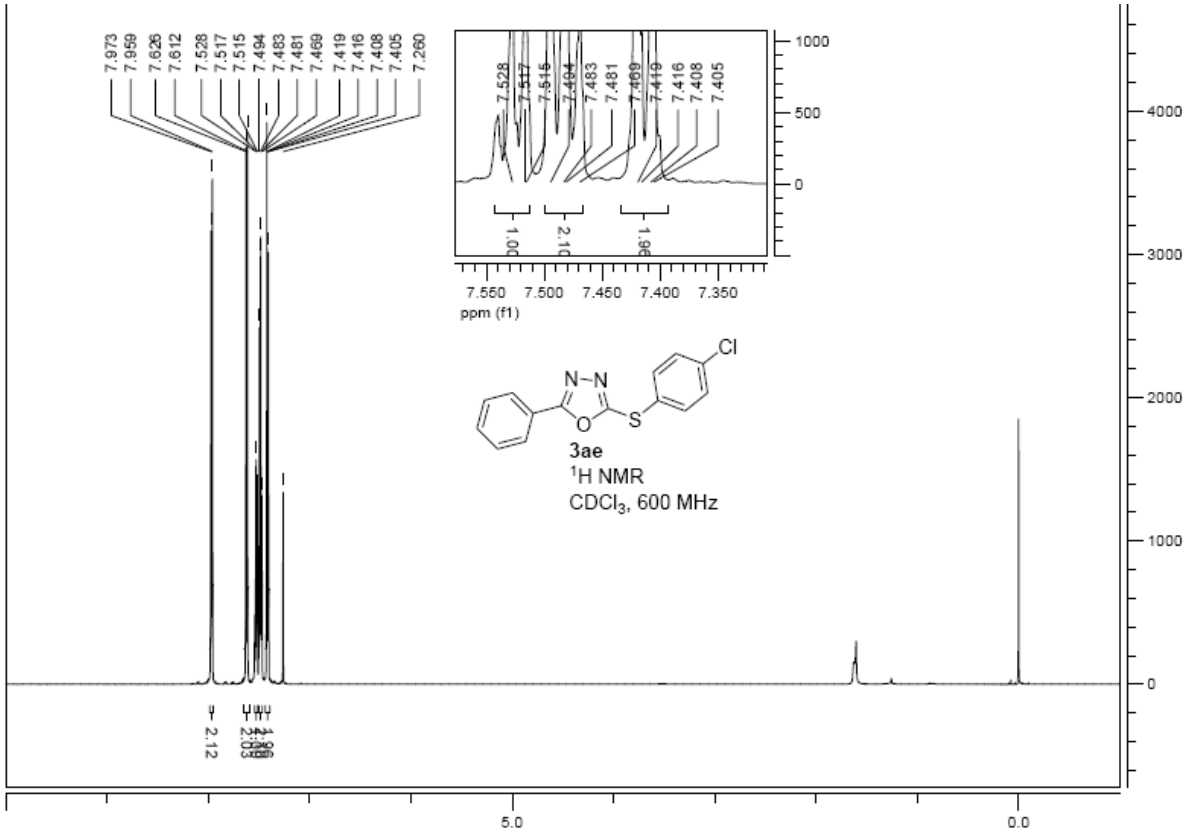
Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012

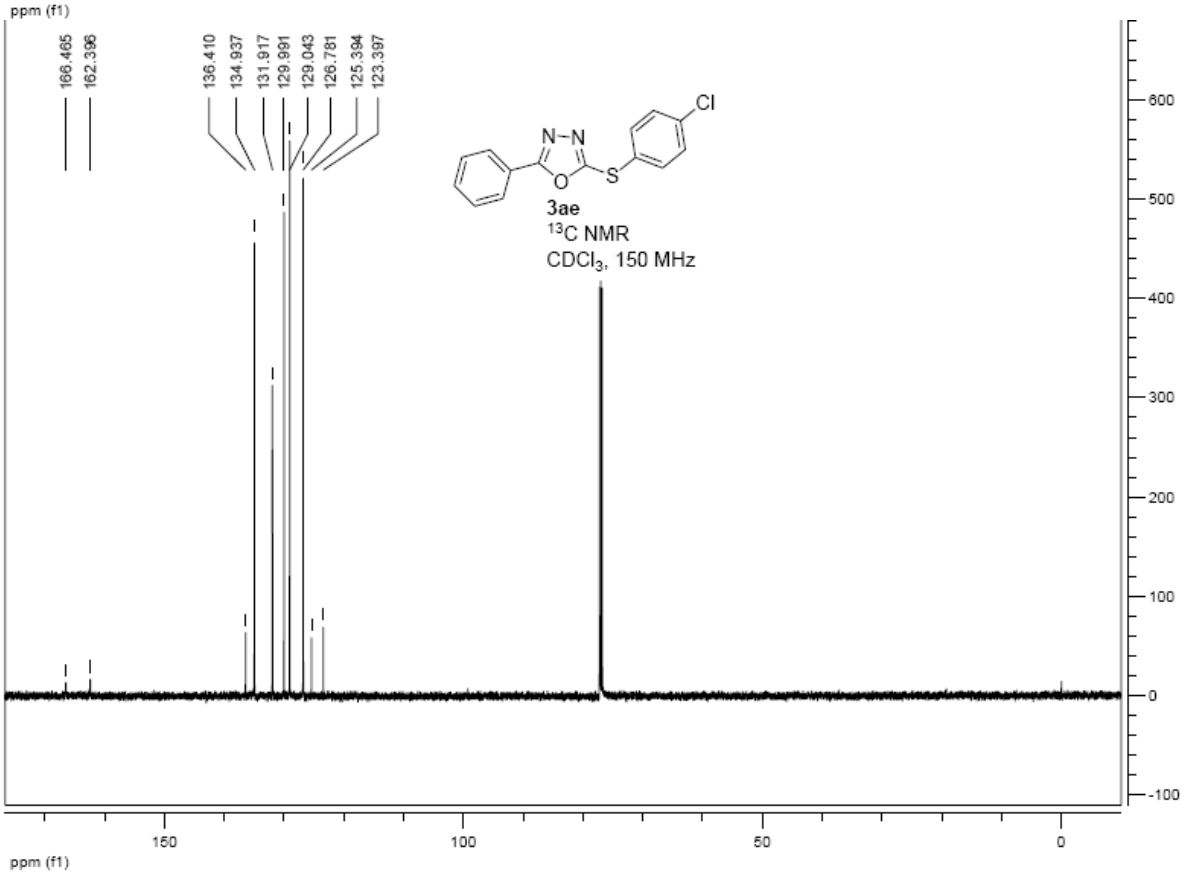




Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012

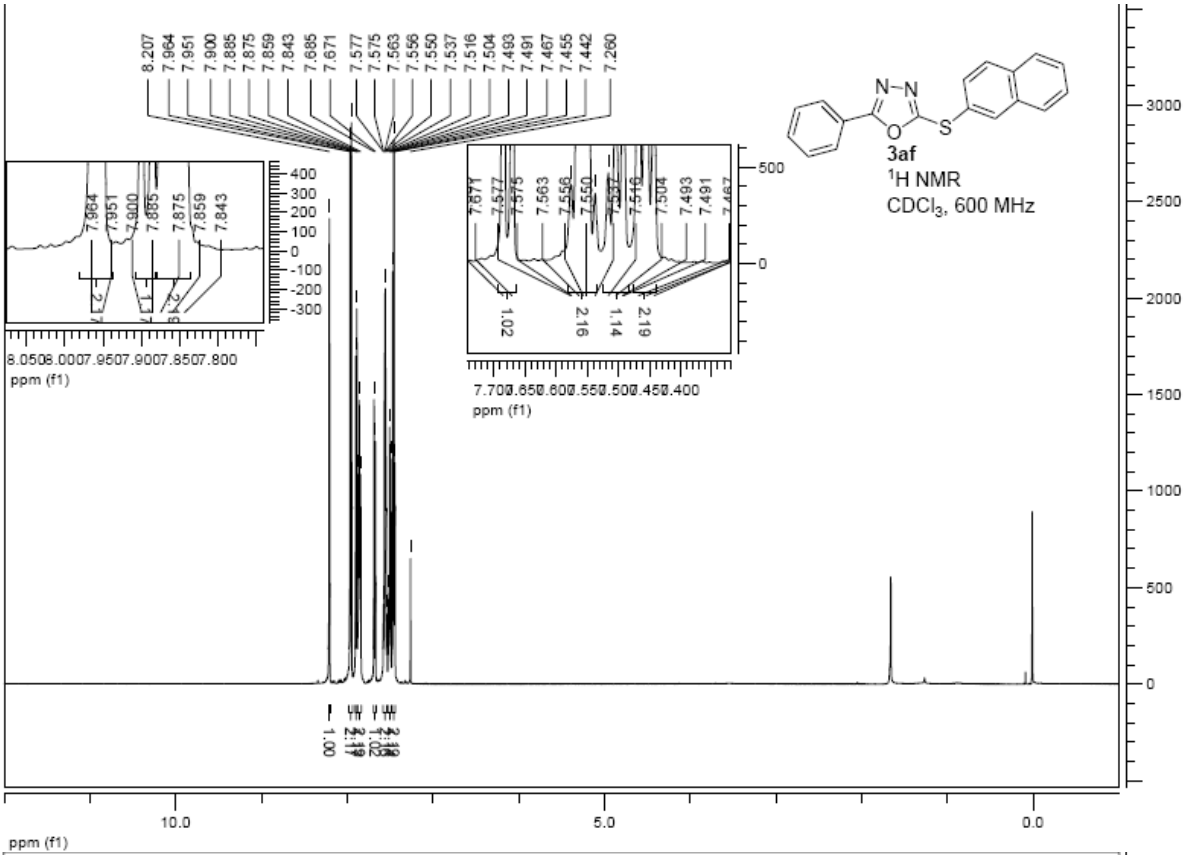
2-Phenyl-5-(4-chlorophenylthio)-1,3,4-oxadiazole (3ae)

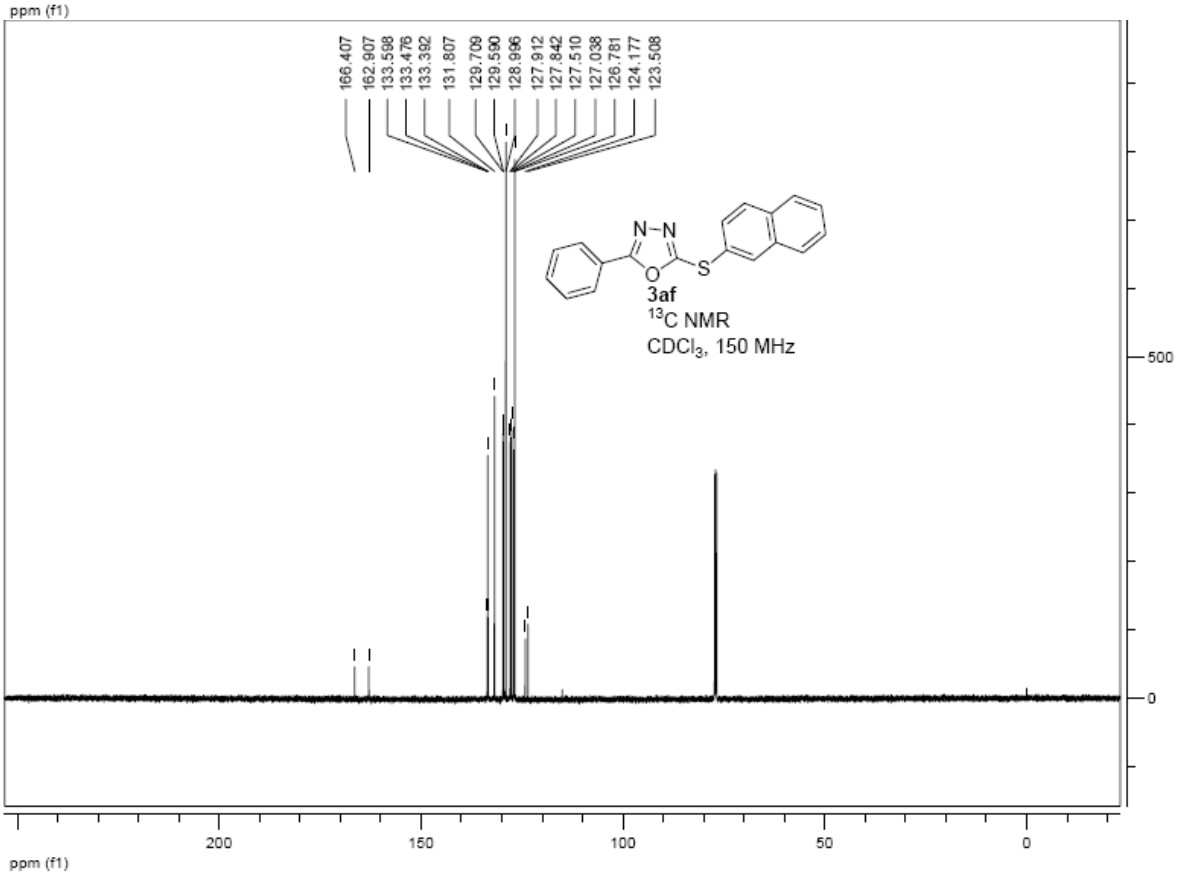




Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012

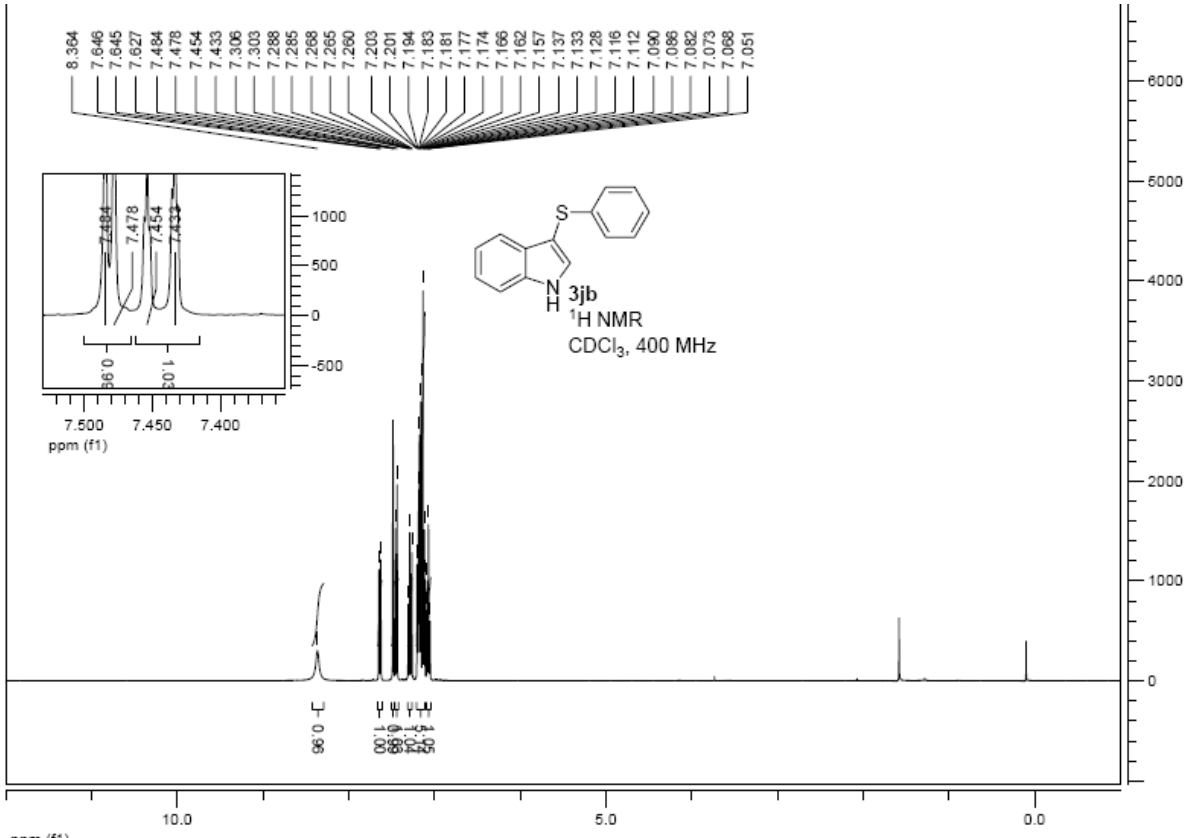
2-Phenyl-5-(2-naphthylthio)-1,3,4-oxadiazole (3af)

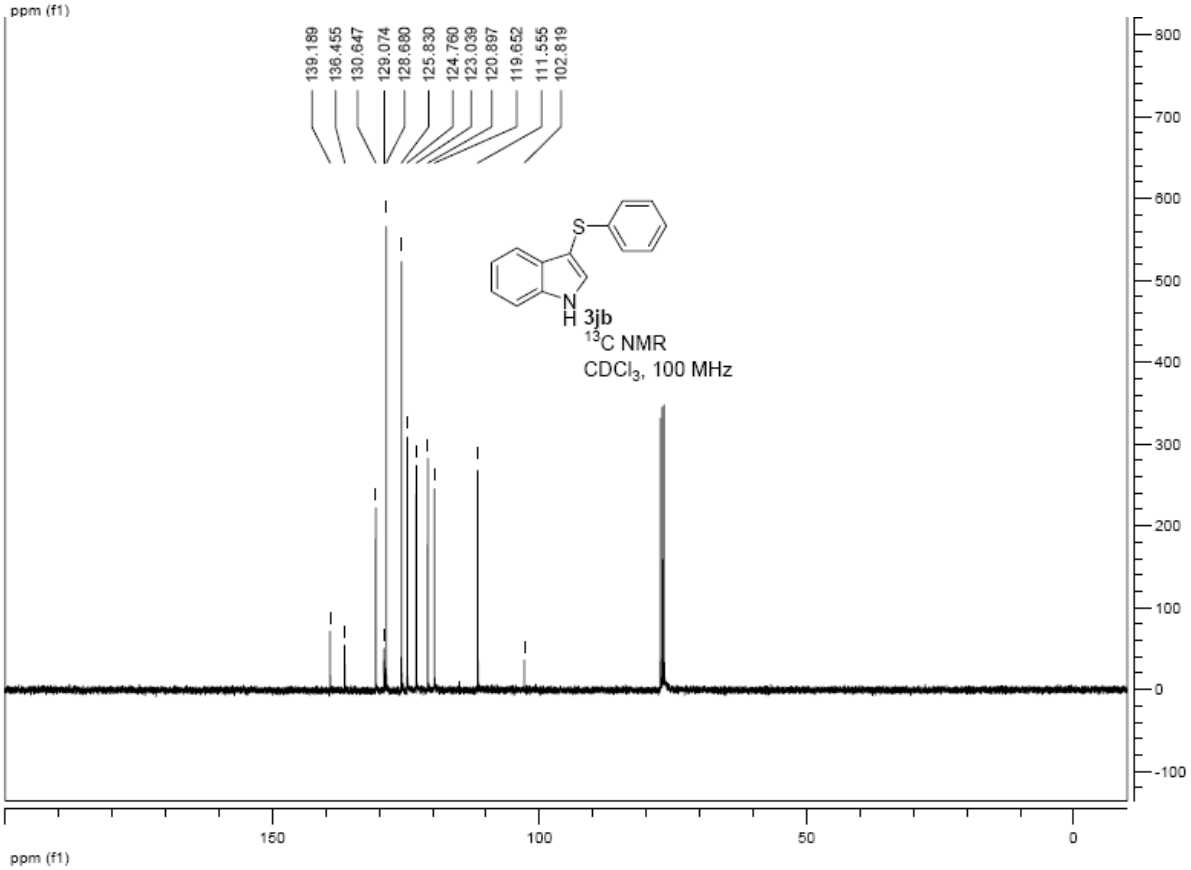




Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012

3-Phenylthioindole (3jb)





Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012

3-(4-Chlorophenylthio)-indole (3je)