Supporting Information-

Oxaziridine Mediated Amination of Primary Amines: Scope and Application to a One-Pot Pyrazole Synthesis

Alan Armstrong,* Lyn H. Jones, Jamie D. Knight and Richard D. Kelsey

Triphenylphosphineimide sulfate **4**^{1a}

A mixture of triphenylphosphine (10.0 g, 38.1 mmol) in anhydrous methanol (65 mL) was heated to solution in a 150 mL round bottomed flask placed under an atmosphere of nitrogen. The reaction flask was then allowed to cool to room temperature. Over 5 min. a solution of hydroxylamine-O-sulfonic acid (4.3 g, 38.1 mmol) in anhydrous methanol (30 mL) was added. The reaction was stirred for 1 h. The contents of the flask were then poured into 200 mL of distilled water to afford a white precipitate, which was filtered *in vacuo* to afford the title compound (10.92 g, 29.12 mmol, 76%) as a white crystalline solid; m.p. 186-190 °C (lit.^{1a} m.p. 184-190 °C).

N-(Triphenylphosphoranylidene)-1H-imidazole-1-carboxamide **5**^{1a}

Triphenylphosphineimide sulfate (6.62 g, 17.7 mmol) was placed in a 150 mL round bottomed flask fitted with a water condenser and placed under an atmosphere of nitrogen. To the flask was added N,N-carbonyl diimidazole (2.86 g, 17.7 mmol), followed by anhydrous THF (60 mL) and triethylamine (4.9 mL, 35.3 mmol). The reaction flask was then heated to reflux and this was maintained for 6 h. The reaction vessel was then allowed to cool to room temperature and the solvent removed *in vacuo*. The residue was warmed in anhydrous toluene (50 mL) and redissolved. The flask was then allowed to cool to room temperature and upon addition of n-pentane (25 mL) afforded a white precipitate. The contents of the flask were filtered *in vacuo* and the precipitate was collected to afford the title compound (5.37 g, 14.47 mmol, 82%) as a white crystalline solid; m.p. 175-180 °C; ν_{max} (nujol)/cm⁻¹ 3055, 2180, 1651, 1483, 1363, 1302, 1265; δ_{H} (400 MHz, CDCl₃) 8.39 (1H, s, NCHN), 7.80-7.75 (6H, m, o-Ar), 7.64-7.60 (4H, m, p-Ar and NCHCHN), 7.54-7.50 (6H, m, m-Ar), 6.99 (1H, s, NCHCHN); δ_{C} (100 MHz, CDCl₃) 155.3 (C), 137.7 (CH), 133.0 (CH, o-Ar, ²J_{CP} 10.3), 132.9 (CH, p-Ar, ⁴J_{CP} 3), 128.9 (CH, m-Ar, ³J_{CP} 12.5), 128.7 (CH), 126.8 (C, s-Ar, ¹J_{CP} 102), 117.8 (CH); δ_{P} (161.9 MHz, CDCl₃) 23.7; m/z (CI, NH₃) 372 [M + H]⁺, found : [M + H]⁺, 372.1269. C₂₂H₁₈N₃OP requires [M + H]⁺, 372.1265.

tert-Butyl triphenylphosphoranylidene-carbamate **6**^{1b}

N-(Triphenylphosphoranylidene)-1H-imidazole-1-carboxamide (5.37 g, 14.5 mmol) was placed in a 150 mL round bottomed flask fitted with a water condenser and placed under an atmosphere of nitrogen. To the flask was added anhydrous THF (60 mL), followed by potassium tert-butoxide (3.24 g, 28.9 mmol). The reaction flask was then heated to reflux and this was maintained for 24 h. The reaction flask was then allowed to cool to room temperature. The contents of the flask were poured into 300 mL of ice-cold water to afford a white precipitate which was filtered *in vacuo* to afford the title compound (4.65 g, 12.33 mmol, 70%) as an off-white solid. Crystallization from ethyl acetate afforded analytically pure material (3.85 g, 10.21 mmol, 59%); m.p. 146-8 °C (lit.^{1b} m.p. 148 °C); $\nu_{\max}$ (nujol)/cm⁻¹ 3054, 2980, 1656, 1629, 1439, 1306, 1265, 1172, 1115; δ_{H} (400 MHz, CDCl₃) 7.77-7.62 (6H, m, Ar), 7.49-7.34 (9H, m, Ar), 1.30 [9H, s, C(CH₃)₃]; δ_{C} (100 MHz, CDCl₃) 161.2 (C), 133.1 (CH, o-Ar, ²J_{CP} 9.8), 132.1 (CH, p-Ar, ⁴J_{CP} 2.8), 128.8 (C, s-Ar, ¹J_{CP} 101.1), 128.5 (CH, m-Ar, ³J_{CP} 12.3), 94.6 (C), 28.1 (CH₃); δ_{P} (161.9 MHz, CDCl₃) 20.9; m/z (CI, NH₃) 378 (100), 322 (8), 304 (56), 278 (10).

General procedure for the preparation of diethylketomalonate derived oxaziridine **3^{1b,c}**

(i) tert-Butyl triphenylphosphoranylidene-carbamate (6.0 g, 15.9 mmol) was placed in a 50 mL round bottomed flask fitted with a water condenser and placed under an atmosphere of nitrogen. Anhydrous THF (20 mL) was added, followed by diethyl ketomalonate (2.4 mL, 15.9 mmol). The reaction flask was then heated to reflux and this was maintained for 24 h. The reaction flask was then allowed to cool to room temperature. The solvent was removed *in vacuo*. The residue was warmed in anhydrous toluene (30 mL) and redissolved. The flask was then allowed to cool to room temperature and upon addition of n-pentane (10 mL) afforded a white precipitate. The contents of the flask were filtered *in vacuo*. The filtrate was collected and the solvent removed *in vacuo* to afford the imine **7** as a pale yellow oil, 4.34 g, 15.9 mmol, 100%; (ii) To a well-stirred solution of imine (2.17 g, 7.95 mmol) in acetonitrile (30 mL) was added distilled water (20 mL). To the homogeneous solution was added a mixture of Oxone[®] (5.86 g, 19.1 mmol, KHSO₅) and NaHCO₃ (2.49 g, 29.7 mmol). The reaction was stirred for 5 h and then additional Oxone[®] (5.86 g, 19.1 mmol, KHSO₅) was added. The reaction was then stirred for 18 h. The contents of the flask were then poured into distilled water (100 mL) and extracted with dichloromethane (3 x 100 mL). The combined organic extracts were dried (MgSO₄), filtered and the solvent removed *in vacuo* to afford the crude compound as a pale yellow oil. Flash column chromatography (SiO₂; hexanes: dichloromethane : diethyl ether, 6:2.5:0.5) afforded the title compound (0.92 g, 3.18 mmol, 40%) as a clear oil; $\nu_{\max}$ (nujol)/cm⁻¹ 2986, 1777, 1765, 1373, 1244, 1151, 1071, 845; δ_{H} (250 MHz, CDCl₃) 4.41-4.31 [4H, m, CO₂CH₂CH₃], 1.52 [9H, s, C(CH₃)₃], 1.37-1.31 [6H, m, CO₂CH₂CH₃]; δ_{C} (62.5 MHz, CDCl₃) 162.1, 161.6 (C), 156.2 (C), 86.5 (C), 75.7 (C), 63.4, 63.2 (CH₂), 27.9 (CH₃), 13.8

(CH₃); m/z (CI, NH₃) 307 [M + H]⁺, found : [M + H]⁺, 307.1517. C₁₂H₂₃N₂O₇ requires [M + H]⁺, 307.1505.

General procedure for the amination of amines 9a-m

To a 50 mL round bottomed flask was added oxaziridine **3** (100 mg, 0.346 mmol, 1 eq.) followed by the respective amine **8** (1 eq.) and placed under an atmosphere of nitrogen. To the flask was added anhydrous dichloromethane (i) or toluene (ii) (4 mL). The reaction was stirred for a period of 72 h at room temperature until no more starting material could be detected by thin layer chromatography (hexanes : diethyl ether, 1:1). The solvent was then removed *in vacuo* and the crude residue purified by flash column chromatography (SiO₂; hexanes: diethyl ether, 1:1). The isolated yields for compounds **9**, **10** and **11** in both dichloromethane (i) and toluene (ii) are reported in Table 2 of this letter.

Spectroscopic data for 9a-h and k-m

N'-Phenethyl-hydrazinecarboxylic acid tert-butyl ester **9a**²

White crystalline solid, m.p. 87-90 °C (lit.² m.p. 90-92 °C); $\nu_{\max}$ (film)/cm⁻¹ 3363, 2992, 2970, 2361, 1764, 1692, 1658, 1529, 1493; δ_{H} (250 MHz, CDCl₃) 7.33-7.18 (5H, m, Ar-H), 6.12 (1H, bs, NH), 3.15 (2H, t, *J* 7.5, CH₂N), 2.78 (2H, t, *J* 7.5, CH₂Ar), 1.45 [9H, s, (CH₃)₃]; δ_{C} (125 MHz, CDCl₃) 156.7 (C), 139.5 (C), 128.6 (CH), 128.4 (CH), 126.2 (CH), 80.5 (C), 53.0 (CH₂), 34.4 (CH₂), 28.3 (CH₃); m/z (CI, NH₃) 237 (37), 198 (100), 181 (93), 137 (32).

N'-Benzyl-hydrazinecarboxylic acid tert-butyl ester **9b**²

Colorless oil; $\nu_{\max}$ (film)/cm⁻¹ 3063, 2978, 2933, 1711, 1604, 1455, 1373, 1281, 1248, 1164; δ_{H} (250 MHz, CDCl₃) 7.37-7.24 (5H, m, Ar-H), 6.09 (1H, bs, NH), 4.20 (1H, bs, NH), 3.99 (2H, bs, CH₂), 1.46 [9H, bs, (CH₃)₃]; δ_{C} (125 MHz, CDCl₃) 156.6 (C), 137.6 (C), 128.9, 128.4, 127.4 (CH), 80.4 (C), 55.8 (CH₂), 28.3 (CH₃); m/z (CI, NH₃) 223 (17), 184 (72), 165 (73), 121 (43).

N'-[(R)-1-Phenyl-ethyl]-hydrazinecarboxylic acid t-butyl ester **9c**²

White crystalline solid, m.p. 70-71 °C (lit.² m.p. 72-73 °C); $\nu_{\max}$ (film)/cm⁻¹ 3054, 2964, 2922, 1724, 1611, 1443, 1382, 1287, 1254, 1172; δ_{H} (250 MHz, CDCl₃) 7.39-7.22 (5H, m, Ar-H), 6.15 (1H, bs, NH), 4.18 [1H, q(distorted), *J* 6.5, CH], 1.43 [9H, s, (CH₃)₃], 1.32 (3H, d, *J* 6.5, CH₃); δ_{C} (100

MHz, CDCl₃) 156.6 (C), 143.3 (C), 128.4, 127.2, 126.7 (CH), 80.4 (C), 59.5 (CH), 28.2 (CH₃), 21.1 (CH₃); *m/z* (CI, NH₃) 237 (28), 198 (37), 181 (55), 137 (13).

N'-Benzhydryl-hydrazinecarboxylic acid tert-butyl ester **9d**²

Colorless crystals, m.p. 113-116 °C (lit.² m.p. 97-99 °C); $\nu_{\max}$ (film)/cm⁻¹ 2978, 1711, 1493, 1452, 1382, 1295, 1280, 1170; δ_{H} (250 MHz, CDCl₃) 7.48-7.15 (10H, m, Ar-H), 6.07 (1H, bs, NH), 5.28 (1H, bs, NCH), 4.39 (1H, bs, NH), 1.41 [9H, bs, (CH₃)₃]; δ_{C} (100 MHz, CDCl₃) 156.6 (C), 141.45 (C), 128.5, 128.4, 128.3, 128.2, 127.9, 127.8, 127.7, 127.6, 127.4, 127.3 (CH), 80.5 (C), 68.2 (CH), 28.3 (CH₃); *m/z* (CI, NH₃) 299 (99), 260 (45), 243 (65), 199 (29), 184 (30), 167 (100).

Phenyl-carbamic acid t-butyl ester **9e**² (N'-Phenyl-hydrazinecarboxylic acid tert-butyl ester)

White crystalline solid, m.p. 97-98 °C (lit.² m.p. 90-92 °C); $\nu_{\max}$ (film)/cm⁻¹ 3067, 2963, 2922, 1704, 1605, 1503, 1485, 1380, 1251, 1142; δ_{H} (250 MHz, CDCl₃) 7.27-7.19 (2H, m, Ar-H), 6.92-6.88 (1H, m, Ar-H), 6.86-6.81 (2H, m, Ar-H), 6.38 (1H, bs, NH), 5.73 (1H, bs, NH), 1.46 [9H, bs, (CH₃)₃]; δ_{C} (62.5 MHz, CDCl₃) 156.2 (C), 148.1 (C), 129.0, 120.7, 112.9 (CH), 81.2 (C), 28.2 (CH₃); *m/z* (CI, NH₃) 226 (7), 209 (5), 170 (100), 153 (16), 109 (16).

p-Methoxyphenyl-carbamic acid t-butyl ester **9f** [N'-(4-Methoxy-phenyl)-hydrazinecarboxylic acid tert-butyl ester]

Brown oil; $\nu_{\max}$ (film)/cm⁻¹ 3337, 2954, 1712, 1510, 1456, 1364, 1274, 1237, 1148; δ_{H} (250 MHz, CDCl₃) 6.84-6.76 (4H, m, Ar-H), 6.39 (1H, bs, NH), 4.31 (1H, bs, NH), 3.75 (3H, s, OCH₃), 1.45 [9H, s, (CH₃)₃]; δ_{C} (62.5 MHz, CDCl₃) 156.4 (C), 154.3 (C), 142.2 (C), 114.6 (CH), 81.1 (C), 55.6 (CH₃), 28.2 (CH₃); *m/z* (CI, NH₃) 239 [M + H]⁺, found : [M + H]⁺, 239.1402. C₁₂H₁₉N₂O₃ requires [M + H]⁺, 239.1396.

p-Cyanophenyl-carbamic acid t-butyl ester **9g** [N'-(4-Cyano-phenyl)-hydrazinecarboxylic acid tert-butyl ester]

Colorless oil; $\nu_{\max}$ (film)/ cm^{-1} 3325, 2220, 1714, 1609, 1512, 1352, 1236, 1155; δ_{H} (250 MHz, CDCl_3) 7.53-7.48 (2H, m, Ar-H), 6.86-6.81 (2H, m, Ar-H), 6.39 (1H, bs, NH), 6.05 (1H, bs, NH), 1.46 [9H, bs, $(\text{CH}_3)_3$]; δ_{C} (62.5 MHz, CDCl_3) 155.6 (C), 151.9 (C), 133.7 (CH), 119.6 (CH), 112.6 (CH), 82.1 (C), 28.2 (CH_3); m/z (CI, NH_3) 234 $[\text{M} + \text{H}]^+$, found : $[\text{M} + \text{H}]^+$, 234.1242. $\text{C}_{12}\text{H}_{16}\text{N}_3\text{O}_2$ requires $[\text{M} + \text{H}]^+$, 234.1243.

Cyclopropyl-carbamic acid t-butyl ester **9h** (N'-Cyclopropyl-hydrazinecarboxylic acid tert-butyl ester)

Colorless oil; $\nu_{\max}$ (film)/ cm^{-1} 2954, 2360, 2342, 1706, 1508 1364, 1232, 1155; δ_{H} (250 MHz, CDCl_3) 6.16 (1H, bs, NH), 3.51 (1H, bs, NH), 2.74-2.66 (1H, m, CH), 1.47 [9H, s, $(\text{CH}_3)_3$], 0.47-0.43 (4H, m, CH_2); δ_{C} (62.5 MHz, CDCl_3) 156.8 (C), 80.4 (C), 32.3 (CH), 28.3 (CH_3), 5.5 (CH_2); m/z (CI, NH_3) 173 $[\text{M} + \text{H}]^+$, found : $[\text{M} + \text{H}]^+$, 173.1292. $\text{C}_8\text{H}_{17}\text{N}_2\text{O}_2$ requires $[\text{M} + \text{H}]^+$, 173.1290.

Cyclohexyl-carbamic acid t-butyl ester **9i** (N'-Cyclohexyl-hydrazine carboxylic acid tert-butyl ester)

White crystalline solid; m.p. 76-77 °C; $\nu_{\max}$ (film)/ cm^{-1} 2964, 2350, 2342, 1712, 1532 1372, 1236, 1163; δ_{H} (250 MHz, CDCl_3) 6.04 (1H, bs, NH), 4.29 (1H, bs, NH), 2.81-2.75 (1H, m, CH), 1.83-1.58 [5H, m, from CH_2], 1.46 [9H, s, $\text{C}(\text{CH}_3)_3$], 1.29-1.02 (5H, m, from CH_2); δ_{C} (62.5 MHz, CDCl_3) 172.9 (C), 80.4 (C), 58.5 (CH), 31.2 (CH_2), 28.4 (CH_3), 26.1 (CH_2), 24.4 (CH_2); m/z (CI, NH_3) 215 $[\text{M} + \text{H}]^+$, found : $[\text{M} + \text{H}]^+$, 215.1758. $\text{C}_{11}\text{H}_{23}\text{N}_2\text{O}_2$ requires $[\text{M} + \text{H}]^+$, 215.1759.

n-Heptyl-carbamic acid t-butyl ester **9j** (N'-n-heptyl-hydrazine carboxylic acid tert-butyl ester)

Clear oil; $\nu_{\max}$ (film)/ cm^{-1} 2931, 2253, 1712, 1467, 1458, 1369, 1272, 1253, 1161; δ_{H} (400 MHz, CDCl_3) 2.82 (2H, t, J 7.3, CH_2N), 1.45 [9H, s, $\text{C}(\text{CH}_3)_3$], 1.28-1.26 (10H, m, CH_2), 0.87 (3H, t, J 7.3, CH_3); δ_{C} (100 MHz, CDCl_3) 156.6 (C), 80.4 (C), 52.1, 31.7, 29.2 (CH_2), 28.3 (CH_3), 27.8, 27.0

22.6 (CH₂), 14.0 (CH₃); m/z (CI, NH₃) 231 [M + H]⁺, found : [M + H]⁺, 231.2081. C₁₂H₂₆N₂O₃ requires [M + H]⁺, 231.2072.

N'-(1-Benzyl-3-ethoxy-2-oxo-propyl)-hydrazinecarboxylic acid tert-butyl ester **9k**³

Pale yellow oil; $\nu_{\max}$ (CHCl₃)/cm⁻¹ 2983, 2934, 2253, 1728, 1455, 1369, 1251, 1160; δ_{H} (400 MHz, CDCl₃) 7.30-7.21 (5H, m, Ar-H), 6.15 (1H, bs, NH), 4.15 (2H, q, *J* 7.1, CO₂CH₂CH₃), 3.95 (1H, dd, *J* 6.5 and 6.5, CHN), 3.07-2.97 [2H, m, PhCH₂], 1.41 [9H, s, (CH₃)₃], 1.20 (3H, t, *J* 7.1, CO₂CH₂CH₃); δ_{C} (100 MHz, CDCl₃) 172.6 (C), 156.1 (C), 136.5 (C), 129.1, 128.5, 126.8 (CH), 80.5 (C), 64.0 (CH), 60.9 (CH₂), 37.1 (CH₂), 28.2, 28.1 (CH₃), 14.1 (CH₃); m/z (CI, NH₃) 326 (21), 309 (30), 270 (98), 209 (100), 194 (13).

N'-(3-Ethoxy-1-isopropyl-2-oxopropyl)-hydrazinecarboxylic acid tert-butyl ester **9l**⁴

Pale yellow oil; $\nu_{\max}$ (CHCl₃)/cm⁻¹ 2962, 2933, 2254, 1727, 1458, 1369, 1252, 1158; δ_{H} (250 MHz, CDCl₃) 6.16 (1H, bs, NH), 4.24 (2H, q, *J* 7.1, CO₂CH₂CH₃), 3.41 (1H, d, *J* 4.9, CHN), 2.10-1.97 [1H, m, (CH₃)₂CH], 1.43 [9H, s, (CH₃)₃], 1.28 (3H, t, *J* 7.1, CO₂CH₂CH₃), 0.99 [3H, d, *J* 7.2, (CH₃)₂CH]; δ_{C} (125 MHz, CDCl₃) 173.1 (C), 156.2 (C), 80.5 (C), 69.2 (CH), 60.7 (CH₂), 30.0 (CH), 28.3 (CH₃), 18.9 (CH₃), 18.4 (CH₃), 14.2 (CH₃); m/z (CI, NH₃) 278 (24), 261 (53), 222 (100), 205 (68), 101 (50), 146 (20).

N'-Pyridin-3-ylmethyl-hydrazinecarboxylic acid tert-butyl ester **9m**

Pale yellow oil; $\nu_{\max}$ (CHCl₃)/cm⁻¹ 2982, 2253, 1719, 1504, 1482, 1369, 1249, 1148; δ_{H} (500 MHz, CDCl₃) 8.56 (1H, s, Ar-H), 8.50 (1H, d, *J* 4.9, Ar-H), 7.67 (1H, d, *J* 7.9, Ar-H), 7.27 (1H, dd, *J* 7.9 and 4.9, Ar-H), 6.14 (1H, bs, NH), 4.00 (2H, s, ArCH₂), 1.45 [9H, s, (CH₃)₃]; δ_{C} (125 MHz, CDCl₃) 156.7 (C), 150.0, 148.5, 136.9 (CH), 133.5 (C), 123.5 (CH), 80.8 (C), 53.0 (CH₂), 28.3 (CH₃); m/z (CI, NH₃) 224 [M + H]⁺, found : [M + H]⁺, 224.1392. C₁₁H₁₈N₃O₂ requires [M + H]⁺, 224.1399.

Spectroscopic data for 10a-b, f-g and j-m

10a

White crystalline solid; m.p. 142-143 °C; $\nu_{\max}$ (CHCl₃)/cm⁻¹ 3152, 2982, 2931, 2253, 1721, 1712, 1478, 1460, 1369, 1244, 1154; δ_{H} (250 MHz, CDCl₃) 7.30-7.11 (5H, m, Ar-H), 3.50 (2H, t, *J* 7.8, CH₂N), 2.81 (2H, t, *J* 7.8, ArCH₂), 1.45 [9H, s, (CH₃)₃]; δ_{C} (125 MHz, CDCl₃) 154.7 (C), 139.2 (C), 128.7, 128.3, 126.1 (CH), 80.9 (C), 60.5 (CH₂), 34.1 (CH₂), 28.3 (CH₃); m/z (CI, NH₃) 352 [M + H]⁺, found : [M + H]⁺, 352.2234. C₁₈H₃₀N₃O₄ requires [M + H]⁺, 352.2236.

10b

White crystalline solid; m.p. 116-117 °C; $\nu_{\max}$ (CHCl₃)/cm⁻¹ 3154, 2927, 2855, 2253, 1725, 1712, 1478, 1468, 1381, 1251, 1157; δ_{H} (250 MHz, CDCl₃) 7.39-7.26 (5H, m, Ar-H), 4.48 (2H, s, ArCH₂), 1.46 [9H, s, (CH₃)₃]; δ_{C} (125 MHz, CDCl₃) 154.6 (C), 136.1 (C), 129.4, 128.2, 127.6 (CH), 87.2 (C), 62.8 (C) and 28.3 (CH₃); m/z (CI, NH₃) 338 [M + H]⁺, found : [M + H]⁺, 338.2070. C₁₇H₂₈N₃O₄ requires [M + H]⁺, 352.2079.

10f

Pale yellow oil; $\nu_{\max}$ (CHCl₃)/cm⁻¹ 3152, 2986, 2931, 2253, 1725, 1711, 1478, 1462, 1381, 1247, 1155; δ_{H} (250 MHz, CDCl₃) 6.93-6.78 (4H, m, Ar-H), 3.75 (1H, s, OCH₃), 1.47 [9H, s, (CH₃)₃]; δ_{C} (100 MHz, CDCl₃) 154.8 (C), 154.6 (C), 143.1 (C), 122.6 (C), 115.1, 114.7, 114.3, 114.2 (CH), 81.6 (C), 55.5 (CH₃), 28.2 (CH₃); m/z (CI, NH₃) 354 [M + H]⁺, found : [M + H]⁺, 354.2021. C₁₇H₂₈N₃O₅ requires [M + H]⁺, 352.2028.

10g

White crystalline solid; m.p. 197-198 °C; $\nu_{\max}$ (CHCl₃)/cm⁻¹ 3282, 2982, 2934, 2253, 1733, 1705, 1608, 1508, 1370, 1250, 1155; δ_{H} (250 MHz, CDCl₃) 7.53 (2H, d, *J* 9.2, Ar-H), 7.02 (2H, d, *J* 9.2, Ar-H), 1.48 [9H, s, (CH₃)₃]; δ_{C} (125 MHz, CDCl₃) 154.2 (C), 152.4 (C), 133.5 (CH), 119.3 (C), 113.8 (CH), 104.6 (C), 82.7 (C), 28.2 (CH₃); m/z (CI, NH₃) 366 [M + NH₄]⁺, found : [M + NH₄]⁺, 366.2131. C₁₇H₂₈N₅O₄ requires [M + NH₄]⁺, 366.2141.

10j

White crystalline solid, m.p. 140-141 °C; $\nu_{\max}$ (film)/cm⁻¹ 2931, 2253, 1713, 1479, 1455, 1393, 1369, 1250, 1155; δ_{H} (250 MHz, CDCl₃) 7.14 (1H, bs, NH), 4.34 (2H, t, *J* 7.3, CH₂N), 1.45 [9H, bs, (CH₃)₃], 1.36-1.20 (10H, m, CH₂), 0.86 (CH₃, t, *J* 7.3, CH₃); δ_{C} (62.5 MHz, CDCl₃) 154.7 (C), 80.7 (C), 59.1, 31.7, 29.0 (CH₂), 28.3 (CH₃), 27.4, 26.7, 22.6 (CH₂), 14.0 (CH₃); m/z (CI, NH₃) 346 [M + H]⁺, found : [M + H]⁺, 346.2703. C₁₇H₃₅N₃O₄ requires [M + H]⁺, 346.2705.

10l

Pale yellow oil; $\nu_{\max}$ (CHCl₃)/cm⁻¹ 2981, 2933, 2253, 1727, 1725, 1580, 1479, 1369, 1266, 1237, 1144; δ_{H} (250 MHz, CDCl₃) 7.17 (1H, bs, NH), 4.18 (2H, t, *J* 7.0, CO₂CH₂CH₃), 3.55 (1H, d, *J* 7.9, CHN), 2.07-1.93 [1H, m, (CH₃)₂CH], 1.42 [9H, s, (CH₃)₃], 1.27 (3H, t, *J* 7.0, CO₂CH₂CH₃), 1.05 [3H, d, *J* 6.7, CH₃(CH₃)CH], 0.92 [3H, d, *J* 6.7, CH₃(CH₃)CH]; δ_{C} (125 MHz, CDCl₃) 162.6 (C), 152.5 (C), 81.4 (C), 75.6 (CH), 61.3 (CH₂), 31.8 (CH), 28.2 (CH₃), 20.3 (CH₃), 13.9 (CH₃); m/z (CI, NH₃) 376 [M + H]⁺, found : [M + H]⁺, 376.2463. C₁₇H₃₄N₃O₆ requires [M + H]⁺, 376.2447.

10m

Pale yellow oil; $\nu_{\max}$ (CHCl₃)/cm⁻¹ 2982, 2929, 2253, 1716, 1633, 1609, 1476, 1454, 1390, 1368, 1293, 1252, 1164; δ_{H} (250 MHz, CDCl₃) 8.86 (1H, s, Ar-H), 8.72 (1H, d, *J* 6.7, Ar-H), 7.73 (1H, d, *J* 7.6, Ar-H), 7.48 (1H, dd, *J* 7.6 and 6.7, Ar-H), 6.17 (1H, bs, NH), 4.09 (2H, s, ArCH₂), 1.52 [9H, s, (CH₃)₃], 1.44 [9H, s, (CH₃)₃]; δ_{C} (125 MHz, CDCl₃) Carbonyl peaks not observed, 142.3, 141.1 (CH), 137.9 (C), 135.4, 125.3 (CH), 81.8, 77.9 (C), 52.2 (CH₂), 28.7, 28.2 (CH₃); *m/z* (FAB, Na) 339 [M + H]⁺, found : [M + H]⁺, 339.2034. C₁₆H₂₇N₄O₄ requires [M + H]⁺, 339.1987.

Spectroscopic data for 11d, 11f

2-Benzhydrylimino-malonic acid diethyl ester **11d**

Pale yellow oil; $\nu_{\max}$ (CHCl₃)/cm⁻¹ 2984, 2253, 1736, 1623, 1598, 1466, 1447; δ_{H} (250 MHz, CDCl₃) 7.71-7.18 (10H, m, Ar-H), 4.84 (1H, s, CH), 4.25 (2H, q, *J* 7.2, CO₂CH₂CH₃), 4.23 (2H, q, *J* 7.2, CO₂CH₂CH₃), 1.27 [6H, t, *J* 7.2, CO₂(CH₂CH₃)₂]; δ_{C} (125 MHz, CDCl₃) 173.8 (C), 167.2 (C), 139.0 (C), 135.5 (C), 130.8 (C), 129.3, 129.1, 128.6, 128.5, 128.0, 127.8, 126.7 (C), 69.7 (CH), 61.8 (CH₂), 14.0 (CH₃); *m/z* (CI, NH₃) 340 [M + H]⁺, found : [M + H]⁺, 340.1548. C₂₀H₂₂N₁O₄ requires [M + H]⁺, 340.1548.

2-(4-Methoxy-phenylimino)-malonic acid diethyl ester **11f**⁵

Pale yellow oil; δ_{H} (250 MHz, CDCl₃) 6.92 (2H, d, *J* 9.4, Ar-H), 6.81 (2H, d, *J* 9.4, Ar-H), 4.23 (2H, q, *J* 7.0, CO₂CH₂CH₃), 4.27 (2H, q, *J* 7.0, CO₂CH₂CH₃), 3.75 (3H, s, OCH₃), 1.25 (2H, t, *J* 7.0, CO₂CH₂CH₃), 1.18 (2H, t, *J* 7.0, CO₂CH₂CH₃).

General procedure for the one-pot synthesis of 1,3,5-trisubstituted pyrazoles 12a-c, e and g

To a 50 mL round bottomed flask was added oxaziridine **3** (200 mg, 0.692 mmol, 1 eq.) followed by the respective amine **8** (1 eq.) and placed under an atmosphere of nitrogen. To the flask was added anhydrous dichloromethane (4 mL) and the reaction was stirred for 72 h. The crude reaction was then washed with a saturated sodium hydrogen carbonate solution (4 mL). The aqueous layer was pipetted off and to the flask was added MgSO₄ (~1 g). This was followed by the sequential addition of trifluoroacetic acid (2 mL, 25.9 mmols, 37.5 eq.) for 0.5 h and next hepta-3,5-dione (94 μ L 0.692mmol, 1.0 eq.). The reaction was left to stir for a period of 24 h and monitored by thin layer chromatography (hexanes:diethyl ether, 1:1). The reaction was then filtered, the solvent evaporated *in vacuo* and the crude residue subjected to flash column chromatography (hexanes : diethyl ether, 1:1) to afford the desired pyrazole product.

3,5-Diethyl-1-phenethyl-1*H*-pyrazole **12a**

Pale yellow oil; 56.2 mg, 36%; $\nu_{\max}$ (film)/cm⁻¹ 2253, 1741, 1682, 1604, 1547, 1497; δ_{H} (400 MHz, CDCl₃) 7.25-7.19 (3H, m, *m*- and *p*-Ar), 7.00-6.98 (2H, m, *o*-Ar), 5.92 (1H, s, CH), 4.37 (2H, t, *J* 7, CH₂N), 3.10 (2H, t, *J* 7, ArCH₂), 2.75 (2H, q, *J* 7.5, CH₂), 2.13 (2H, q, *J* 7.5, CH₂), 1.26 (3H, t, *J* 7.5, CH₃), 1.05 (3H, t, *J* 7.5, CH₃); δ_{C} (100 MHz, CDCl₃) 152.3, 148.4, (C), 136.9 (C), 128.7, 128.6, 126.9, (CH), 102.6 (CH), 49.5 (CH₂), 36.3 (CH₂), 19.7, 18.0 (CH₂), 13.1, 11.8 (CH₃); *m/z* (CI, NH₃) *m/z* (CI, NH₃) 229 [M + H]⁺, found : [M + H]⁺, 229.1710. C₁₅H₂₀N₂ requires [M + H]⁺, 229.1704.

1-Benzyl-3,5-Diethyl-1*H*-pyrazole **12b**⁶

Pale yellow oil; 87.2 mg, 28%; $\nu_{\max}$ (film)/cm⁻¹ 2252, 1738, 1699, 1610, 1548, 1498; δ_{H} (400 MHz, CDCl₃) 7.35-7.27 (3H, m, *m*- and *p*-Ar), 7.13-1.11 (2H, m, *o*-Ar), 6.07 (1H, s, CH), 5.44 (2H, m, ArCH₂), 2.75 (2H, q, *J* 7.5, CH₂), 2.56 (2H, q, *J* 7.5, CH₂), 1.27 (3H, t, *J* 7.5, CH₃), 1.22 (3H, t, *J* 7.5, CH₃); δ_{C} (100 MHz, CDCl₃) 152.5, 148.2 (C), 134.6 (C), 129.0, 128.4, 126.9 (CH), 103.6 (CH), 51.8 (CH₂), 19.8, 18.7 (CH₂), 13.1, 11.9 (CH₃); *m/z* (CI, NH₃) 215 (100), 214 (13), 194 (11), 185 (4), 146 (12), 129 (11), 123 (7).

(*R*)-3,5-Diethyl-1-(1-phenyl-ethyl)-1*H*-pyrazole **12c**

Pale yellow oil; 69.4 mg, 43%; $[\alpha]_D^{25} + 30^\circ$ (c 1.00 CH₂Cl₂); $\nu_{\max}$ (film)/cm⁻¹ 2974, 2939, 2253, 1792, 1733, 1602, 1547, 1465, 1379; δ_H (250 MHz, CDCl₃) 7.31-7.06 (5H, m, Ar-H), 5.9 (1H, s, CH), 5.34 (1H, q, *J* 7.0, CHCH₃), 2.68 (2H, q, *J* 7.6, CH₂), 2.59-2.29 (2H, m, CH₂), 1.90 (3H, d, *J* 7.0, CHCH₃), 1.26 (3H, t, *J* 7.6, CH₂CH₃), 1.14 (3H, t, *J* 7.6, CH₂CH₃); δ_C (100 MHz, CDCl₃) 153.1 (C), 145.2 (C), 143.1 (C), 128.5 (CH), 127.1 (CH), 125.9 (CH), 101.8 (CH), 57.2 (CH), 21.8 (CH₃), 21.6 (CH₂), 18.9 (CH₂), 14.2 (CH₃), 12.5 (CH₃); *m/z* (CI, NH₃) 229 [M + H]⁺, found : [M + H]⁺, 229.1696. C₁₅H₂₁N₂ requires [M + H]⁺, 229.1704.

3,5-Diethyl-1-phenyl-1*H*-pyrazole **12e**

Pale yellow oil; 70.2 mg, 51%; $\nu_{\max}$ (film)/cm⁻¹ 2253, 1700, 1699, 1598, 1548, 1504; δ_H (400 MHz, CDCl₃) 7.46-7.34 (Ar), 6.07 (1H, s, CH), 2.70 (2H, q, *J* 7.5, CH₂), 2.63 (2H, q, *J* 7.5, CH₂), 1.28 (3H, t, *J* 7.5, CH₃), 1.20 (3H, t, *J* 7.5, CH₃); δ_C (100 MHz, CDCl₃) 154.7, 146.1 (C), 139.4 (C), 129.0, 127.7, 125.3 (CH), 103.2 (CH), 21.3, 19.7 (CH₂), 13.7, 13.0 (CH₃); *m/z* (CI, NH₃) 201 [M + H]⁺, found : [M + H]⁺, 201.1391. C₁₃H₁₆N₂ requires [M + H]⁺, 201.1391.

4-(3,5-Diethyl-pyrazol-1-yl)-benzonitrile **12g**

Pale yellow oil; 65.4 mg, 42%; $\nu_{\max}$ (film)/cm⁻¹ 2253, 1793, 1608, 1551, 1514, 1464; δ_H (500 MHz, CDCl₃) 7.74 (2H, d, *J* 8.5, Ar-H), 7.59 (2H, d, *J* 8.5, Ar-H), 6.12 (CH), 2.73-2.66 (4H, m, CH₂), 1.29-1.24 (6H, m, CH₃); δ_C (100 MHz, CDCl₃) 156.4 (C), 146.1 (C), 143.6 (C), 133.1 (CH), 124.5 (CH), 118.3 (C), 110.3 (C), 105.2 (CH), 21.4, 20.3 (CH₂), 13.6, 13.1 (CH₃); *m/z* (CI, NH₃) 226 [M + H]⁺, found : [M + H]⁺, 226.1345. C₁₄H₁₆N₃ requires [M + H]⁺, 226.1344.

References

1. (a). Tomcufcik, A. S.; Emma, J. E.; Eudy, N. H.; Marsico, J. W.; Newman, H. US Patent No. 4767749, 1988; *Chem. Abstr.* **1988**, *109*, 231197. (b) Armstrong, A.; Cooke, R. S. *Chem. Commun.*, **2002**, 904-905. (c) Armstrong, A.; Draffan, A. G. *J. Chem. Soc., Perkin Trans. 1.* **2001**, 2681-2873.
2. Baumgarten, H. E.; Chen, P. Y. N.; Taylor, H. W.; Hwang, D. -R. *J. Org. Chem.* **1976**, *41*, 3805-3811.
3. Grupe, R.; Niedrich, H. *Chem. Ber.*, **1967**, *100*, 3283-3288 and *ibid.*, **1966**, *99*, 3914-3924.
4. Agadzhanyan, Ts. E.; Arutyunyan, A. D.; Garibdzhanyan, B. T.; Chachoyan, A. A. *Armyanskii Khimicheskii Zhurnal*, **1976**, *29*, 879
5. Alves, M. J.; Almeida, I. G.; Fortes, A. G.; Freitas, A. P. *Tetrahedron Lett.*, **2003**, *44*, 6561-6565.
6. Yeng, F. -W.; Chiu, J. -Y.; Wang, J. C. -L.; Lu, H. -H.; Liu, S. -H.; Huang, S. -L.; Chiang, R. -S. *Chinese Pharmaceutical Journal*, **1994**, *46*, 517-534.

¹H NMR spectrum of 9f

RD0RXN364/1

DC04099.002
DATE 23-8-2

SF	250.133
SFO	250.130
O1	4355.105
SI	32768
TD	32768
SW	5000.000
HZ/PT	.305
PW	3.0
RD	0.0
AG	3.277
RG	10
NS	16
TE	297
FW	6300
O2	1.000
DP	OL P0
LB	0.0
GB	0.0
CX	23.00
CY	0.0
F1	8.000f
F2	.000f
HZ/CM	87.002
PPM/CM	.348
SR	2854.18

¹³C NMR spectrum of 9f

~~BUK R~~
 MART535.001
 DATE 27-8-2
 SF 62.896
 SF0 62.894
 O1 10761.923
 SI 16384
 TD 16384
 SW 20000.000
 HZ/PT 2.441
 PM 2.0
 RD 1.000
 AQ .410
 RG 400
 NS 1006
 TE 297
 FW 25000
 O2 4100.000
 DP 18H CPD
 LB 1.000
 GB 0.0
 CX 23.00
 CY 0.0
 F1 180.019f
 F2 .027f
 HZ/CM 492.209
 PPM/CM 7.826
 SR 1956.53

¹H NMR spectrum of 9g

RDKH357.001
 DATE 2-8-2
 SF 250.133
 SFO 4355.105
 SI 32768
 TD 32768
 SW 5000.000
 HZ/PT .305
 PM 3.0
 RD 0.0
 AG 3.277
 RG 20
 NS 15
 TE 297
 FW 6300
 O2 1.000
 DP OL PO
 LB 0.0
 GB 0.0
 CX 23.00
 CY 0.0
 F1 8.0014
 F2 .0014
 HZ/CM 87.002
 PPM/CM .348
 SR 2854.39

¹³C NMR spectrum of 9g

~~BUK R~~
 RDKD348.001
 DATE 4-8-2
 SF 62.896
 SFO 62.894
 O1 10781.923
 S1 16384
 TD 16384
 SW 20000.000
 HZ/PT 2.441
 PW 2.0
 RD 1.000
 AG .410
 RG 400
 NS 5539
 TE 297
 FW 25000
 O2 4100.000
 DP 18H CPD
 LB 1.000
 GB 0.0
 CX 23.00
 CY 0.0
 F1 200.010f
 F2 .027f
 HZ/CW 546.875
 PPM/CW 8.695
 SR 1956.53

¹H NMR spectrum of 9h

¹³C NMR spectrum of 9h

RDKC361.001
 DATE 24-8-2
 SF 62.896
 SFO 62.894
 O1 10761.923
 SI 16384
 TD 16384
 SW 20000.000
 HZ/PT 2.441
 PW 2.0
 RD 1.000
 AG .410
 RG 400
 NS 1598
 TE 297
 FW 25000
 O2 4100.000
 DP 18H CPD
 LB 1.000
 GB 0.0
 CX 23.00
 CY 0.0
 F1 180.019f
 F2 -9.988f
 HZ/CW 519.595
 PPM/CW 8.261
 SR 1956.53

¹H NMR spectrum of 9i

¹³C NMR spectrum of 9i

¹H NMR spectrum of 9j

J Knight JK121.2 in CDCl₃ ; ¹H spectrum using DRX400 ; Nov05/110

¹³C NMR spectrum of 9j

¹H NMR spectrum of 9m

JK300604.001
 DATE 30-6-4
 SF 500.135
 SY 83.0
 O1 8000.000
 SI 32768
 TD 32768
 SW 6097.564
 HZ/PT .372
 PM 9.0
 RD 1.000
 AQ 2.687
 RG 32
 NS 32
 TE 297
 FW 7700
 DZ 1.000
 DP 63L P0
 LB 0.0
 GB 0.0
 CX 23.00
 CY 0.0
 F1 10.000P
 F2 10.000P
 HZ/CW 228.315
 PPM/CW 457
 SR 5421.50

¹³C NMR spectrum of 9m

~~BLISS~~
 JK300604.002
 DATE 30-6-4
 SF 93.6 125.759
 O1 3650.000
 SI 32768
 TD 32768
 SM 31230.000
 HZ/P1 1.907
 PW 2.5
 RD 1.000
 AG .524
 RG 320
 NS 1101
 TE 297
 FM 39100
 O2 8000.000
 DP 14H CPD
 LB 4.000
 GB 0.0
 CX 23.00
 CY 0.0
 F1 200.002P
 F2 -9.996P
 HZ/CM 1.148E3
 PPM/CM 9.130
 SR 23150.62

¹H NMR spectrum of 10a

JK10.2

JKS10.002
 DATE 11-3-3
 SF 250.133
 SF0 250.130
 O1 4355.105
 SI 32768
 TD 32768
 SW 5000.000
 HZ/PT .305
 PW 3.0
 RD 0.0
 AQ 3.277
 RG 4
 NS 8
 TE 297
 FW 6300
 O2 1.000
 DP OL PD
 LB 0.0
 GB 0.0
 CX 23.00
 CY 0.0
 F1 10.000f
 F2 .000f
 HZ/CM 108.749
 PPM/CM .435
 SR 2854.18

¹³C NMR spectrum of 10a

~~BRUKER~~
 JK130303.004
 DATE 13-3-3
 SF 93.1 125.759
 O1 36500.000
 ST 32768
 TD 32768
 SW 31250.000
 HZ/PT 1.907
 PW 2.5
 RD 1.000
 AG 1.524
 RG 40
 NS 1985
 TE 297
 FW 39100
 O2 8000.000
 DP 14H CPD
 LB 2.000
 GB 23.400
 CX 0.0
 CY 0.0
 F1 200.002P
 F2 -0.01P
 HZ/CM 1.093E3
 PPM/CM 8.696
 SR 23152.53

¹H NMR spectrum of 10b

JK12.2

~~BUKER~~

JDKS12.002
DATE 12-3-3

SF 250.133
SF0 250.130
O1 4355.105
SI 32768
TD 32768
SW 5000.000
HZ/PT .305

PW 3.0
RD 0.0
AQ 3.277
RG 10
NS 8
TE 297

FW 6300
O2 1.000
DP 0L P0

LB 0.0
GB 0.0
CX 23.00
CY 0.0
F1 10.000f
F2 .000f
HZ/CM 108.749
PPM/CM .435
SR 2854.18

¹³C NMR spectrum of 10b

~~BJK-R~~
 JK140303.003
 DATE 14-3-3
 SF 125.759
 SY 93.0
 O1 36500.000
 SI 32768
 TD 32768
 SM 31250.000
 HZ/PT 1.907
 PM 2.5
 RD 1.000
 AG .524
 RG 40
 NS 5730
 TE 297
 FW 39100
 O2 8000.000
 DP 14H CPD
 LB 3.000
 GB 0.0
 CX 23.00
 CY 0.0
 F1 200.002P
 F2 -9.996P
 HZ/CW 1.148E3
 PPM/CW 9.130
 SR 23150.62

¹H NMR spectrum of 10f

JK3601

~~BJK-R~~

JKS36.002
DATE 11-7-3

SF	250.133
SF0	250.130
01	4355.105
SI	32768
TD	32768
SW	5000
HZ/PT	.305
PW	3.0
RD	0.0
AG	3.277
RG	10
NS	8
TE	297
FW	6300
02	1.000
DP	OL P0
LB	0.0
GB	0.0
CX	23.00
CY	0.0
F1	10.000f
F2	.000f
HZ/CM	108.749
PPM/CM	.435
SR	2854.18

¹³C NMR spectrum of 10f

¹H NMR spectrum of 10g

~~BJK-R~~
 JKS37.003
 DATE 16-7-3
 SF 250.133
 SF0 250.130
 01 4355.105
 SI 32768
 TD 32768
 SW 5000.000
 HZ/PT .305
 PW 3.0
 RD 0.0
 AQ 3.277
 RG 40
 NS 8
 TE 297
 FW 6300
 02 1.000
 DP 0L P0
 LB 0.0
 GB 0.0
 CX 23.00
 CY 0.0
 F1 10.000f
 F2 .000f
 HZ/CM 108.749
 PPM/CM .435
 SR 2859.08

¹³C NMR spectrum of 10g

BJR
 JK270904.002
 DATE 27-9-4
 SF 125.759
 SY 93.0
 O1 36500.000
 S1 32768
 T0 32768
 SW 31250.000
 HZ/PT 1.907
 PM 2.5
 RD 1.000
 AQ .524
 RG 320
 NS 5470
 TE 297
 FW 39100
 O2 8000.000
 DP 14H CPD
 LB 4.000
 GB 0.0
 CX 23.00
 CY 0.0
 F1 200.002P
 F2 -.001P
 HZ/CM 1.093E3
 PPM/CM 8.696
 SR 23148.71

¹H NMR spectrum of 10j

SF 250.133
 SFO 250.130
 O1 4355.105
 S1 32768
 TD 32768
 SW 5000.000
 HZ/PT .305
 PM 3.0
 RD 0.0
 AG 3.277
 RG 2
 NS 8
 TE 297
 FW 6300
 O2 1.000
 DP OL PO
 LB 0.0
 GB 0.0
 CX 23.00
 CY 0.0
 F1 10.000f
 F2 .000f
 HZ/CM 108.749
 PPM/CM .435
 SR 2854.18

BULKY
 R

SES223.001
 DATE 4-11-4

¹³C NMR spectrum of 10j

¹H NMR spectrum of 10l

¹³C NMR spectrum of 10l

JK020804.002
 DATE 2-8-4
 SF 125.759
 SY 93.0
 O1 36500.000
 SI 32768
 TD 32768
 SW 31250.000
 HZ/PT 1.907
 PW 2.5
 RD 1.000
 AQ 524
 RG 320
 NS 1088
 TE 297
 FW 39100
 O2 8000.000
 DP 14H CPD
 LB 5.000
 GB 0.0
 CX 23.00
 CY 0.0
 F1 200.002P
 F2 -.001P
 HZ/CM 1.093E3
 PPM/CM 8.696
 SR 23150.62

B
 J
 K
 R

¹H NMR spectrum of 10m

~~BJK-R~~
 JK 109.3
 JKS109.003
 DATE 4-8-4
 SF 250.133
 SF0 250.130
 O1 4355.105
 S1 32768
 TD 32768
 SW 5000.000
 HZ/PT .305
 PW 3.0
 RD 0.0
 AG 3.277
 RG 20
 NS 16
 TE 297
 FW 6300
 O2 1.000
 DP OL P0
 LB 0.0
 GB 0.0
 CX 23.00
 CY 0.0
 F1 10.000f
 F2 .000f
 HZ/CM 108.749
 PM/CM .435
 SR 2854.18

¹³C NMR spectrum of 10m

¹H NMR spectrum of 11d

~~BRUKER~~
 JDS112.001
 DATE 7-9-4
 SF 250.133
 SF0 250.130
 O1 4355.105
 SI 32768
 TD 32768
 SW 5000.000
 HZ/PT .305
 PW 3.0
 RD 0.0
 AG 3.277
 RG 10
 NS 16
 TE 297
 FW 6300
 O2 1.000
 DP 0L P0
 LB 0.0
 GB 0.0
 CX 23.00
 CY 0.0
 F1 10.000f
 F2 108.000f
 HZ/CM 108.749
 PPM/CM .435
 SR 2854.18

¹³C NMR spectrum of 11d

BK
 JK R
 JK070904.001
 DATE 7-9-4
 SF 125.759
 SY 93.0
 OI 36500.000
 SI 32768
 TI 32768
 SM 31250.000
 HZ/PT 1.907
 PM 2.5
 RD 1.000
 AG .324
 RG 320
 NS 596
 TE 297
 FW 39100
 OZ 8000.000
 DP 14H D0
 LB 3.000
 GB 0.0
 CX 23.00
 CY 0.0
 F1 200.002P
 F2 1.093E3
 PPM/CM 8.696
 SR 23152.53

¹H NMR spectrum of 11f

¹H NMR spectrum of 12a

¹³C NMR spectrum of 12a

¹H NMR spectrum of 12c

JK 118.1

JKS118.001
DATE 1-10-4

SF 250.133
SF0 250.130
O1 4355.105
SI 32768
TD 32768
SW 5000.000
HZ/Pt .305

PW 3.0
RD 0.0
AQ 3.277
RG 10
NS 16
TE 297

FW 6300
O2 1.000
DP OL PO

LB 0.0
GB 0.0
CX 23.00
CY 0.0
F1 10.000f
F2 10.000f
HZ/CM 108.749
PPM/CM 435
SR 2854.18

¹³C NMR spectrum of 12c

¹H NMR spectrum of 12e

¹³C NMR spectrum of 12e

¹H NMR spectrum of 12g

BK113.5
 JK071004.001
 DATE 7-10-4
 SF 500.135
 SY 83.0
 O1 8000.000
 SI 32768
 TD 32768
 SW 6097.561
 HZ/PT .372
 PW 9.0
 RD 1.000
 AQ 2.687
 RG 32
 NS 16
 TE 297
 FW 7700
 O2 1.000
 DP 63L P0
 LB 0.0
 GB 0.0
 CX 23.00
 CY 0.0
 F1 10.000P
 F2 10.000P
 HZ/CM 217.442
 PPM/CM .435
 SR 5421.50

¹³C NMR spectrum of 12g