Supporting Information

Mild and Rapid Method for the Generation of *Ortho*-(Naphtho)Quinone Methide Intermediates

Abdul kadar Shaikh,[†] Alexander J. A. Cobb,[‡] and George Varvounis^{*,†}

[†]*Department of Chemistry, University of Ioannina, Section of Organic Chemistry and Biochemistry, 45110 Ioannina, Greece*

[‡]*School of Pharmacy, University of Reading, Whiteknights, Reading RG6 6AD, UK*

gvarvoun@cc.uoi.gr

Contents

1. General Experimental Procedures.....	S2
2. Materials.....	S2
3. Experimental Procedures and Characterization Data.....	S3
4. References	S17
5. NMR Spectra	S18

1. General Experimental Procedures

Unless otherwise noted, reactions were carried out under argon atmosphere, in flame dried, three-neck, with magnetic stirring. Organic solutions were concentrated by rotary evaporation at 23–40 °C under 15 Torr. Melting points were taken on a Büchi 510 apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were measured in CDCl_3 or $\text{DMSO-}d_6$ on a 250 or 400 MHz Brüker spectrometer. ^1H chemical shifts are reported in ppm from an internal standard TMS, residual chloroform (7.26 ppm) or $\text{DMSO-}d_6$ (2.50 ppm). ^{13}C NMR chemical shifts are reported in ppm from an internal standard TMS, residual chloroform (77.00 ppm) or $\text{DMSO-}d_6$ (39.43 ppm). High resolution ESI mass spectra were measured on a ThermoFisher Scientific Orbitrap XL system. Low resolution ESI spectra were measured with an Agilent 1100 LC-MS/MS spectrometer. IR spectra were acquired on a Perkin-Elmer 257 or a Perkin-Elmer GX FTIR spectrophotometer as liquids between sodium chloride discs or KBr discs and are reported in wave numbers (cm^{-1}). Elemental analyses were performed on a Carlo Erba 1106 elemental analyser. Analytical thin layer chromatography (TLC) was performed with TLC plates (Merck 70-230 mesh silica gel). Visualization was done under a 254 nm UV light source and generally by immersion in acidic aqueous-ethanolic vanillin solution, or in potassium permanganate (KMnO_4), followed by heating using a heat gun. Purification of reaction products was generally done by dry-column flash chromatography¹ using Merck silica gel 60 and/or flash chromatography² using Carlo Erba Reactifs-SDS silica gel 60.

2. Materials

Solvents, reagents and catalysts were used as received from the manufacturers (Aldrich, Acros, Fluka, and Alfa-Aesar) except for tetrahydrofuran, dichloromethane, ethanol, methanol, ethyl acetate, hexane and toluene that were purified and dried according to recommended procedures.

3. Experimental Procedures

(2-{{*tert*-Butyl(dimethyl)silyl}oxy}-1-naphthyl)methanol (**3b**)

To a solution of NaBH₄ (317 mg, 12 mmol) in MeOH (20 mL) was added **2b**³ (2.0 g, 10 mmol) in MeOH (10 mL). The mixture was stirred at room temperature for 6 h. MeOH was then removed and the resulting crude re-dissolved in EtOAc (30 mL) and washed with brine (10 mL). The organic layer was dried with sodium sulphate, filtered and the solvent was removed in vacuo. The residue was purified by dry-column flash chromatography (5 % ethyl acetate in hexane) gave **3b** (1.8 g, 89%) as a colourless oil. *R*_f = 0.25 (10% ethyl acetate in hexane). ¹H NMR (250 MHz, DMSO-*d*₆) δ: 8.17-8.14 (d, 1H, *J* = 8.5 Hz), 7.84-7.75 (m, 2H), 7.52-7.46 (t, 1H, *J* = 7.2 Hz, 7.7 Hz), 7.39-7.33 (t, 1H, *J* = 7.5 Hz, 7.2 Hz), 7.11-7.08 (d, 1H, *J* = 7.5 Hz), 4.95-4.88 (m, 3H), 1.03 (s, 9H), 0.23 (s, 6H); ¹³C NMR (63 MHz, DMSO-*d*₆) δ: ppm 18.04, 25.69, 53.88, 120.81, 123.51, 124.10, 124.48, 126.12, 127.97, 129.00, 129.21, 133.55, 150.23; IR (NaCl, neat): 3350, 2958, 2858, 1626, 1580, 1468, 1358, 1248, 1014, 838, 780, 665 cm⁻¹; HRMS (ESI) Calcd for C₁₇H₂₃OSi: 271.1512. Found: 271.1519.

General procedure for the synthesis of nitrate esters **4a,b**, **8**

To a stirred solution of aryl methyl alcohols **3** or **7**⁴ in THF at 25 °C silver nitrate was added followed by dropwise addition of thionyl chloride and the reaction mixture was left stirring overnight at 25 °C. After TLC analysis had shown complete conversion of the starting materials, water (20 mL) was added and the mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were dried with sodium sulphate, filtered and the solvent was removed in vacuo. The residue was purified by flash column chromatography with the indicated solvents to give the title products.

2-(*tert*-Butyldimethylsilyloxy)benzyl nitrate (**4a**)

According to the general procedure, {2-[(*tert*-butyldimethylsilyl)oxy]phenyl}-methanol **3a**⁴ (2.4 g, 10 mmol), silver nitrate (1.7 g, 10 mmol) and thionyl chloride (1.2 g, 10 mmol) were reacted in THF (20 mL) at 25 °C overnight. Subsequent workup and flash column chromatography (5% ethyl acetate in hexane) gave **4a** (1.57 g, 55%) as a colourless oil. R_f = 0.75 (20% ethyl acetate in hexane). ¹H NMR (250 MHz, CDCl₃) δ : 7.36-7.33 (d, 1H, J = 7.5 Hz), 7.23-7.17 (t, 1H, J = 7.5 Hz), 6.97-6.91 (t, 1H, J = 7.5 Hz), 6.86-6.83 (d, 1H, J = 8 Hz), 4.62 (s, 2H), 1.07 (s, 9H), 0.29 (s, 6H); ¹³C NMR (63 MHz, CDCl₃) δ : ppm 19.21, 26.73, 42.72, 119.58, 122.24, 129.17, 130.71, 131.83, 154.74; IR (NaCl, neat): 3284, 2958, 2860, 1914, 1602, 1492, 1456, 1284, 1258, 1102, 928, 826, 670 cm⁻¹; HRMS (ESI) Calcd for C₁₄H₂₄NaO₂Si: 275.1438. Found: 275.1428.

{2-[(*tert*-Butyldimethylsilyl)oxy]-1-naphthyl}methyl nitrate (4b**)**

According to the general procedure, {2[(*tert*-butyldimethylsilyl)oxy]naphthalen-1-yl}methanol **3b** (2.9 g, 10 mmol), silver nitrate (1.7 g, 10 mmol) and thionyl chloride (1.2 g, 10 mmol) were reacted in THF (25 mL) at 25 °C overnight. Subsequent workup and flash column chromatography (5% ethyl acetate in hexane) gave **4b** (2.12 g, 63%) as a yellow oil. R_f = 0.70 (20% ethyl acetate in hexane). ¹H NMR (250 MHz, CDCl₃) δ : 8.22-8.11 (q, 1H, J = 8.7 Hz, 9.2 Hz), 7.80-7.67 (m, 2H), 7.55-7.49 (t, 1H, J = 7.9 Hz, 7.0 Hz), 7.40-7.37 (d, 1H, J = 7.3 Hz), 7.14-7.06 (t, 1H, J = 8 Hz), 5.16 (s, 2H), 1.06 (s, 9H), 0.28 (s, 6H); ¹³C NMR (63 MHz, CDCl₃) δ : ppm 25.37, 29.29, 55.90, 120.18, 122.89, 123.36, 126.42, 126.70, 127.51, 127.98, 129.30; IR (NaCl, neat): 3206, 2958, 2858, 1954, 1626, 1468, 1358, 1248, 1014, 838 cm⁻¹; HRMS (ESI) Calcd for C₁₈H₂₆NaO₂Si: 325.1594. Found: 325.1589.

{5-(Benzyloxy)-2-[(*tert*-butyldimethylsilyl)oxy]}benzyl nitrate (8**)**

According to the general procedure, {5-(benzyloxy)-2-[(*tert*-butyldimethylsilyl)-oxy]phenyl}methanol **7⁴** (3.5 g, 10 mmol), silver nitrate (1.7 g, 10 mmol) and thionyl chloride (1.2 g, 10 mmol) were reacted in THF (30 mL) at 25 °C overnight. Subsequent workup and flash column chromatography (5% ethyl acetate in hexane) afforded **8** (1.18 g, 55% yield as a brown oil. R_f = 0.69 (20% ethyl acetate in hexane). ^1H NMR (250 MHz, CDCl_3) δ : 7.44-7.32 (m, 5H) 7.01-7.00 (d, 1H, J = 2.9 Hz) 6.84-6.79 (dd, 1H, J = 5.8 Hz, 3 Hz) 6.75-6.72 (d, 1H, J = 8.8 Hz) 5.01 (s, 2H) 4.58 (s, 2H) 1.03 (s, 9H) 0.24 (s, 6H); ^{13}C NMR (63 MHz, CDCl_3) δ : ppm 19.17, 26.69, 42.74, 71.56, 117.05, 117.72, 120.27, 128.87, 129.49, 129.60, 138.01, 148.59, 153.93; IR (NaCl, neat): 3222, 2956, 1874, 1500, 1466, 1278, 1228, 1026, 922, 840, 696 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{20}\text{H}_{28}\text{NaO}_3\text{Si}$: 367.1700. Found: 367.1691.

General procedure for the Michael addition reaction

The nitrate esters **4a** or **4b** were dissolved in THF, the reaction mixture was cooled to -78 °C, the appropriate nucleophile (RH, entry 1-11, Table 1, entry 1-2, Table 2) was added followed by TBAF (1M in THF) and the reaction was stirred at -78 °C for 2 min and then room temperature for 10 min. After TLC analysis had shown complete conversion of the starting materials, water (10 mL) was added, the mixture was extracted with EtOAc (3 $\times$ 10 mL), the combined organic extracts were dried with sodium sulphate, filtered and the solvent was removed in vacuo. Flash column chromatography using the stated solvent mixtures yielded the corresponding products **5a-m** and **10a,b** (yields are given in Table 1 and 2).

2-(Pyrrolidin-1-ylmethyl)phenol (**5a**)

According to the general procedure, the nitrate ester **4a** (200 mg, 0.7 mmol) and pyrrolidine (55 mg, 0.77 mmol) were reacted with TBAF (0.7 mL, 0.7 mmol) in THF (8 mL) at -78 °C. Subsequent workup and flash column chromatography (10% ethyl

acetate in hexane) afforded **5a** as a pale yellow oil (100 mg, 80%). $R_f = 0.53$ (40% ethyl acetate in hexane) identical in all respects to an authentic sample.⁵

^1H NMR (250 MHz, CDCl_3) δ : 7.18-7.12 (t, 1H, $J = 7.7$ Hz), 6.98-6.95 (d, 1H, $J = 7.3$ Hz), 6.82-6.73 (m, 2H), 3.81 (s, 2H), 2.67-2.59 (m, 4H), 1.87-1.82 (s, 4H); ^{13}C NMR (63 MHz, CDCl_3) δ : ppm 24.68, 54.44, 59.81, 116.84, 119.70, 123.25, 128.72, 129.46, 158.85.

2-[(Benzylamino)methyl]phenol (**5b**) and

2,2'-[(Benzylazanediyl)bis(methylene)]diphenol (**5c**)

According to the general procedure, the nitrate ester **4a** (200 mg, 0.7 mmol) and benzylamine (83 mg, 0.77 mmol) were reacted with TBAF (0.7 mL, 0.7 mmol) in THF (8 mL) at -78°C . Subsequent workup and flash column chromatography (10% ethyl acetate in hexane) afforded **5b** as colourless oil (20 mg, 13% yield $R_f = 0.45$ (40% ethyl acetate in hexane) identical in all respects to an authentic sample.⁶

^1H NMR (250 MHz, $\text{DMSO}-d_6$) δ : 7.33-7.23 (m, 7H), 7.08-7.04 (m, 2H), 6.75-6.70 (m, 2H), 3.78 (s, 2H), 3.69 (s, 2H); ^{13}C NMR (63 MHz, $\text{DMSO}-d_6$) δ : ppm 49.59, 51.74, 115.33, 118.54, 124.12, 126.88, 127.86, 128.13, 128.28, 128.63, 139.58, 157.22.

The second product obtained flash column chromatography was recrystallized from hexane to afford **5c** as colourless microcrystals (45 mg, 20%). $R_f = 0.62$ (40% ethyl acetate in hexane), m.p. $129-131^\circ\text{C}$. ^1H NMR (250 MHz, $\text{DMSO}-d_6$) δ : 10.07 (s, 2H), 7.26-7.35 (m, 5H), 7.18-7.16 (d, 2H, $J = 6.6\text{ Hz}$), 7.11-7.05 (t, 2H, $J = 7.6$ Hz), 6.79-6.74 (t, 4H, $J = 7.9$ Hz, 5.6 Hz), 3.58 (s, 6H); ^{13}C NMR (63 MHz, $\text{DMSO}-d_6$) δ : ppm 53.16, 57.19, 115.33, 118.94, 123.18, 127.25, 128.35, 129.14, 129.89, 137.46, 156.39; IR (KBr, neat): 3234, 2240, 1702, 1460, 1274, 1252, 1098, 922, 762 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{21}\text{H}_{22}\text{NO}_2$: 320.1645. Found: 320.1647.

2-[(4-Methoxyphenyl)amino]methyl]phenol (**5d**)

2, 2'-{[(4-Methoxyphenyl)azanediy]bis(methylene)}diphenol (5e)

According to the general procedure, the nitrate ester **4a** (200 mg, 0.7 mmol) and *p*-anisidine (95 mg, 0.77 mmol) were reacted with TBAF (0.7 mL, 0.7 mmol) in THF (8 mL) at -78 °C. Subsequent workup and flash column chromatography (5% ethyl acetate in hexane) yielded **5d** as an off white solid which was recrystallized from hexane to afford **5d** as off white microcrystals (50 mg, 30% yield). R_f = 0.52 (40% ethyl acetate in hexane), m.p. 129-131 °C, identical in all respects to an authentic sample.⁷ ^1H NMR (250 MHz, DMSO- d_6) δ : 8.92 (s, 1H), 7.21-7.18 (t, 1H, J = 8.0 Hz, 10 Hz), 7.14-7.11 (d, 1H, J = 7.0 Hz), 6.90-6.86 (m, 2H), 6.82 (s, 4H), 4.38 (s, 2H), 3.76 (s, 3H); ^{13}C NMR (63 MHz, CDCl_3) δ : ppm 51.18, 56.59, 115.73, 117.61, 118.77, 120.79, 123.75, 129.49, 130.08, 141.40, 155.56, 158.12.

The second product obtained from flash column chromatography was recrystallized from toluene-hexane to afford **5e** as colourless microcrystals (46 mg, 20% yield). R_f = 0.44 (40% ethyl acetate in hexane), m.p. 163-165 °C. ^1H NMR (250 MHz, DMSO- d_6) δ : 9.59 (s, 2H), 7.06-6.98 (q, 4H, J = 7.6 Hz, 6.4 Hz), 6.82-6.79 (d, 2H, J = 7.7 Hz), 6.72-6.70 (d, 4H, J = 6.6 Hz), 6.57-6.53 (d, 2H, J = 8.9 Hz), 4.44 (s, 4H), 3.60 (s, 3H); ^{13}C NMR (63 MHz, CDCl_3) δ : ppm 56.28, 58.19, 115.26, 115.72, 116.92, 118.83, 120.73, 124.97, 129.54, 130.13, 131.30, 142.61, 156.99, 157.67; IR (KBr, neat): 3308, 2986, 1588, 1512, 1462, 1378, 1246, 1188, 1038, 928, 832, 760 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{21}\text{H}_{22}\text{NO}_3$: 336.1594. Found: 336.1591.

2-(Azidomethyl)phenol (5f)

According to the general procedure, the nitrate ester **4a** (200 mg, 0.7 mmol), sodium azide (55 mg, 0.84 mmol) and 18-crown-6 (5 mg) were reacted with TBAF (0.7 mL, 0.7 mmol) in THF (8 mL) at -78 °C. Subsequent workup and flash column chromatography (10% ethyl acetate in hexane) yielded **5f** as pale yellow oil (66 mg, 63%). R_f = 0.53 (40% ethyl acetate in hexane) identical in all respects to an authentic sample.⁸ ^1H NMR (250 MHz, CDCl_3) δ : 7.22-7.12 (m, 2H), 6.98-6.91 (m, 1H), 6.85-6.82 (d, 1H, J = 7.6 Hz), 5.23 (s, 1H), 4.17 (s, 2H); ^{13}C NMR (63 MHz, CDCl_3) δ : ppm 55.39, 115.58, 120.08, 121.76, 129.04, 130.49, 154.54.

2-(Methoxymethyl)phenol (**5g**)

According to the general procedure, the nitrate ester **4a** (200 mg, 0.7 mmol) was reacted with TBAF (0.7 mL, 0.7 mmol) in MeOH (8 mL) instead of THF at -78 °C. Methanol was then evaporated under reduced pressure, subsequent workup and flash column chromatography (5% ethyl acetate in hexane) yielded **5g** as colourless oil (45 mg, 94%). R_f = 0.52 (40% ethyl acetate in hexane) identical in all respects to an authentic sample.⁹ ^1H NMR (250 MHz, CDCl_3) δ : 7.01-6.95 (t, 1H, J = 8.0 Hz), 6.80-6.77 (d, 1H, J = 7.2 Hz), 6.67-6.58 (m, 2H), 4.43 (s, 2H), 3.21 (s, 3H); ^{13}C NMR (63 MHz, CDCl_3) δ : ppm 59.15, 75.01, 117.39, 120.80, 122.95, 129.15, 130.45, 157.12.

2-(*iso*-Propoxymethyl)phenol (**5h**)

According to the general procedure, the nitrate ester **4a** (200 mg, 0.7 mmol) was reacted with TBAF (0.7 mL, 0.7 mmol) in *i*-PrOH (8 mL) at -78 °C. The solvent was then evaporated under reduced pressure, subsequent workup and flash column chromatography (5% ethyl acetate in hexane) yielded **5h** as a colourless oil (76 mg, 65%). R_f = 0.58 (40% ethyl acetate in hexane). ^1H NMR (250 MHz, DMSO-d_6) δ :

9.36 (s, 1H), 7.23-7.20 (d, 1H, $J = 7.4$ Hz), 7.08-7.03 (t, 1H, $J = 8.4$ Hz), 6.79-6.73 (t, 2H, $J = 7.6$ Hz, 8 Hz), 4.41 (s, 2H), 3.70-3.56 (m, 1H), 1.14-1.12 (d, 6H); ^{13}C NMR (63 MHz, CDCl_3) δ : ppm 22.77, 70.72, 72.79, 117.46, 120.64, 123.49, 128.67, 130.16, 157.41; IR (NaCl, neat) 3258, 2974, 1898, 1590, 1490, 1458, 1382, 1242, 1122, 1034, 754 cm^{-1} ; Elemental Analysis: Found: C, 72.22; H, 8.47. $\text{C}_{10}\text{H}_{14}\text{O}_2$ requires C, 72.26; H, 8.49.

2-(Phenoxymethyl)phenol (**5i**)

According to the general procedure, the nitrate ester **4a** (200 mg, 0.7 mmol) and phenol (132 mg, 1.4 mmol) were reacted with TBAF (0.7 mL, 0.7 mmol) in THF (8 mL) at -78°C . Subsequent workup and flash column chromatography (5% ethyl acetate in hexane) yielded **5i** as a colourless oil (73 mg, 52%). $R_f = 0.57$ (40% ethyl acetate in hexane) identical in all respects to an authentic sample.¹⁰

^1H NMR (250 MHz, $\text{DMSO}-d_6$) δ : 7.00-6.91 (m, 5H), 6.78-6.61 (m, 4H), 4.94 (s, 1H), 3.72 (s, 2H); ^{13}C NMR (63 MHz, CDCl_3) δ : ppm 36.48, 116.28, 116.74, 117.11, 121.76, 122.47, 127.86, 128.99, 130.65, 131.74, 153.42.

Diethyl 2-(2-hydroxybenzyl)malonate (**5j**)

According to the general procedure, the nitrate ester **4a** (200 mg, 0.7 mmol) and diethyl malonate (124 mg, 0.77 mmol) [it was reacted first with sodium hydride (20 mg) in THF (8 mL) to generate the carbanion] were reacted with TBAF (0.7 mL, 0.7 mmol) at -78°C . Subsequent workup and flash column chromatography (5% ethyl acetate in hexane) yielded **5j** as a colourless oil (112 mg, 60%). $R_f = 0.47$ (40% ethyl acetate in hexane). ^1H NMR (250 MHz, $\text{DMSO}-d_6$) δ : 9.51 (s, 1H), 7.05-6.97 (q, 2H, $J = 7.4$ Hz), 6.78-6.75 (d, 1H, $J = 7.9$ Hz), 6.70-6.64 (t, 1H, $J = 7.4$ Hz), 4.09-4.01 (q, 4H), 3.82-3.75 (t, 1H), 3.01-2.98 (d, 2H), 1.12-1.06 (m, 6H); ^{13}C NMR (63 MHz, CDCl_3) δ : ppm 14.87, 30.32, 53.69, 62.84, 117.68, 121.51, 125.11, 129.36, 132.00,

155.42, 170.90; IR (NaCl, neat): 3228, 1952, 1732, 1458, 1372, 1232, 1154, 1102, 1032, 860, 754 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{14}\text{H}_{18}\text{NaO}_5$: 289.1046. Found: 280.1046.

2-[(Phenylthio)methyl]phenol (**5k**)

According to the general procedure, the nitrate ester **4a** (200 mg, 0.7 mmol) and thiophenol (93 mg, 0.84 mmol) were reacted with TBAF (0.7 mL, 0.7 mmol) in THF (8 mL) at $-78\text{ }^{\circ}\text{C}$. Subsequent workup and flash column chromatography (5% ethyl acetate in hexane) yielded **5k** as colourless oil (103 mg, 68%). $R_f = 0.67$ (40% ethyl acetate in hexane) identical in all respects to an authentic sample.¹¹ ^1H NMR (250 MHz, CDCl_3) δ : 7.29 (s, 1H), 7.22-7.11 (m, 4H), 7.08-7.05 (d, 1H, $J = 8.0$ Hz), 6.98-6.96 (d, 1H, $J = 7.0$ Hz), 6.80-6.71 (m, 2H), 5.84 (s, 1H), 4.09 (s, 2H); ^{13}C NMR (63 MHz, CDCl_3) δ : ppm 36.49, 117.68, 121.77, 123.58, 128.03, 129.90, 131.75, 135.56, 155.55.

Methyl 2-[(2-hydroxybenzyl)thio]acetate (**5l**)

According to the general procedure, the nitrate ester **4a** (200 mg, 0.7 mmol) and methyl thioglycolate (82 mg, 0.77 mmol) were reacted with TBAF (0.7 mL, 0.7 mmol) in THF (8 mL) at $-78\text{ }^{\circ}\text{C}$. Subsequent workup and flash column chromatography (5% ethyl acetate in hexane) yielded **5l** as a colourless oil (84 mg, 56% yield). $R_f = 0.43$ (40% ethyl acetate in hexane). ^1H NMR (250 MHz, $\text{DMSO}-d_6$) δ : 9.54 (s, 1H), 7.14-7.11 (d, 1H, $J = 7.4$ Hz), 7.07-7.04 (d, 1H, $J = 7.5$ Hz), 6.81-6.78 (d, 1H, $J = 7.7$ Hz), 6.76-6.70 (t, 1H, $J = 7.4$ Hz), 3.72 (s, 2H), 3.62 (s, 3H), 3.26 (s, 2H); ^{13}C NMR (63 MHz, CDCl_3) δ : ppm 32.77, 32.96, 53.74, 117.91, 121.53, 123.28, 130.19, 131.77, 155.88, 172.66; IR (NaCl, neat): 3322, 1954, 1954, 1726, 1712, 1634, 1456,

1300, 1170, 1006, 850, 756 cm^{-1} ; HRMS (ESI): Calcd for $\text{C}_{10}\text{H}_{12}\text{NaO}_3\text{S}$: 235.0399. Found: 235.0395.

2-[(Butylthio)methyl]phenol(**5m**)

According to the general procedure, the nitrate ester **4a** (200 mg, 0.7 mmol) and methyl 1-buthylmercaptan (70 mg, 0.77 mmol) were reacted with TBAF (0.7 mL, 0.7 mmol) in THF (8 mL) at $-78\text{ }^{\circ}\text{C}$. Subsequent workup and flash column chromatography (5% ethyl acetate in hexane) yielded **5m** as a colourless oil (91 mg, 66%). $R_f = 0.56$ (40% ethyl acetate in hexane) identical in all respects to an authentic sample.¹² ^1H NMR (250 MHz, CDCl_3) δ : 7.23-7.17 (t, 1H, $J = 7.3$ Hz), 7.10-7.07 (d, 1H, $J = 7.0$ Hz), 6.92-6.83 (m, 2H), 3.81 (s, 2H), 2.44-2.38 (t, 2H, $J = 7.4$ Hz, 7.1 Hz), 1.60-1.49 (m, 2H), 1.40-1.31 (m, 2H), 0.91-0.85 (t, 3H, $J = 7.3$ Hz, 7.1 Hz); ^{13}C NMR (63 MHz, CDCl_3) δ : ppm 14.54, 22.77, 31.36, 31.99, 33.60, 118.041, 121.41, 123.50, 129.98, 131.39, 156.34.

1-[(Phenylthio)methyl]naphthalen-2-ol (**10a**)

According to the general procedure, the nitrate ester **4b** (200 mg, 0.59 mmol) and thiophenol (72 mg, 0.65 mmol) were reacted with TBAF (0.59 mL, 0.59 mmol) in THF (8 mL) at $-78\text{ }^{\circ}\text{C}$. Subsequent workup and flash column chromatography (5% ethyl acetate in hexane) yielded a brown solid which was recrystallized from ethanol to afford **10a** as colourless microcrystals (120 mg, 75%). $R_f = 0.52$ (40% ethyl acetate in hexane) m.p. $123\text{--}125\text{ }^{\circ}\text{C}$ identical in all respects to an authentic sample.¹³ ^1H NMR (250 MHz, $\text{DMSO}-d_6$) δ : 10.12 (s, 1H), 7.94-7.91 (d, 1H, $J = 8.5$ Hz), 7.80-7.77 (d, 1H, $J = 8.1$ Hz), 7.73-7.70 (d, 1H, $J = 8.8$ Hz), 7.49-7.42 (m, 3H), 7.36-7.26 (m, 3H), 7.22-7.16 (m, 2H), 4.62 (s, 2H); ^{13}C NMR (63 MHz, CDCl_3) δ : ppm 30.80, 115.33, 119.08, 123.61, 124.43, 127.74, 127.84, 129.54, 129.88, 130.33, 130.57,

131.36, 133.83, 136.90, 152.97; HRMS (ESI) Calcd for $C_{17}H_{15}OS$: 267.0838. Found: 267.0838.

1-{[(4-Methoxyphenyl)amino]methyl}naphthalen-2-ol (**10b**)

According to the general procedure, the nitrate ester **4b** (200 mg, 0.59 mmol) and *p*-anisidine (81 mg, 0.65 mmol) were reacted with TBAF (0.59 mL, 0.59 mmol) in THF (8 mL) at -78 °C. Subsequent workup and flash column chromatography (10% ethyl acetate in hexane) yielded a yellow solid which was recrystallized from chloroform-hexane to afford **10b** colourless microcrystals (126 mg, 75%). R_f = 0.55 (40% ethyl acetate in hexane), m.p. 125-127 °C identical in all respects to an authentic sample.¹⁴ 1H NMR (250 MHz, $DMSO-d_6$) δ : 9.93(s, 1H), 7.95-7.91 (d, 1H, J = 8.3 Hz), 7.79-7.76 (d, 1H, J = 8.0 Hz), 7.73-7.69 (d, 1H, J = 8.8 Hz), 7.46-7.40 (t, 1H, J = 7.6 Hz, 7.0 Hz), 7.30-7.24 (t, 1H, J = 7.5 Hz, 7.1 Hz), 7.20-7.17 (d, 1H, J = 8.8 Hz), 6.71 (s, 4H), 5.21 (s, 1H), 4.48 (s, 2H), 3.63 (s, 3H); ^{13}C NMR (63 MHz, $DMSO-d_6$) δ : ppm 55.35, 113.10, 114.51, 115.93, 118.19, 122.41, 123.30, 126.26, 128.15, 128.72, 133.63, 143.61, 150.67, 153.07; HRMS (ESI) Calcd for $C_{18}H_{18}NO_2$: 280.1332. Found: 280.1328.

General procedure for hetero Diels-Alder reaction of the nitrate ester (**4a**)

The nitrate ester **4a** was dissolved in toluene (20 mL) and the reaction mixture was cooled to -78 °C. Ethyl vinyl ether or ethyl vinyl sulfide was added followed by dropwise addition of TBAF (1M in THF) for a period of about 4 h. After TLC analysis had shown complete conversion of the starting material the precipitated solid was filtered off, washed with hexane and recrystallized from acetone to give the trimer of *o*-quinone methide as colourless needles m.p. 188-190 °C [lit.¹⁵ m.p. = 190-192 °C]. The filtrate was evaporated under reduced pressure and the residue was

purified using preparative TLC (5% ethyl acetate in hexane) to yield the corresponding products **6a,b**.

2-Ethoxychroman (6a)

According to the general procedure, the benzyl nitrate **4a** (200 mg, 0.7 mmol) and ethyl vinyl ether (5 g, 70 mmol) were reacted with TBAF (0.7 mL, 0.7 mmol) in toluene (20 mL) at -78 °C. Subsequent workup and purification yielded **6a** as colourless oil (20 mg, 16%). $R_f = 0.68$ (40% ethyl acetate in hexane) identical in all respects to an authentic sample.¹⁶ ^1H NMR (250 MHz, CDCl_3) δ : 7.14–7.03 (m, 2H), 6.89–6.81 (m, 2H), 5.26–5.24 (t, $J = 2.7$ Hz, 1H), 3.96–3.83 (m, 1H), 3.70–3.58 (m, 1H), 3.05–2.91 (m, 1H), 2.69–2.59 (m, 1H), 2.09–1.89 (m, 2H), 1.22–1.16 (t, 3H, $J = 7.0$ Hz); ^{13}C NMR (63 MHz, CDCl_3) δ : ppm 16.08, 21.48, 27.48, 64.62, 97.85, 117.86, 121.49, 123.57, 128.17, 130.19, 153.15.

2-(Ethylthio)chroman (6b)

According to the general procedure, the benzyl nitrate **4a** (200 mg, 0.7 mmol) and ethyl vinyl sulfide (6.2 g, 70 mmol) were reacted with TBAF (0.7 mL, 0.7 mmol) in toluene (20 mL) at -78 °C. Subsequent workup and purification yielded **6b** as pale yellow oil (28 mg, 23%). $R_f = 0.60$ (40% ethyl acetate in hexane) identical in all respects to an authentic sample.¹⁶ ^1H NMR (250 MHz, CDCl_3) δ : 7.16–7.05 (m, 2H), 6.91–6.83 (m, 2H), 5.56–5.53 (t, 1H, $J = 4.0$ Hz, 3.7 Hz), 3.04–2.59 (m, 4H), 2.37–2.23 (m, 1H), 2.18–2.06 (m, 1H), 1.37–1.31 (t, 3H, $J = 7.4$ Hz); ^{13}C NMR (63 MHz, CDCl_3) δ : ppm 15.30, 23.02, 24.81, 27.55, 80.30, 117.36, 120.99, 123.07, 127.67, 129.69, 152.64.

General procedure for the Diels-Alder reaction of the nitrate esters **4b**, **8**

The nitrate ester **4b** or **8** was dissolved in the designated solvent, the reaction mixture was cooled to $-78\text{ }^{\circ}\text{C}$ and the appropriate dienophile was added followed by dropwise addition of TBAF (1M in THF) for a period of about 4 h. After TLC analysis had shown complete conversion of the starting materials, water (10 mL) was added, the mixture was extracted with EtOAc ($3 \times 10\text{ mL}$), the combined extracts were dried with sodium sulphate, filtered and the solvent was removed in vacuo. Flash column chromatography using the stated solvent mixtures yielded the corresponding products **9a,b**, **11** and **12** (yields are given in Scheme 3 and 4).

6-(Benzyloxy)-2-ethoxychroman (**9a**)

According to the general procedure, the nitrate ester **8** (200 mg, 0.5 mmol) and ethyl vinyl ether (3.69 g, 50 mmol) were reacted with TBAF (0.24 mL, 0.5 mmol) in toluene (20 mL) at $-78\text{ }^{\circ}\text{C}$. Subsequent workup and flash column chromatography (5% ethyl acetate in hexane) yielded **9a** as a colourless oil (168 mg, 84%). $R_f = 0.55$ (20% ethyl acetate in hexane) identical in all respects to an authentic sample.⁴

^1H NMR (250 MHz, CDCl_3) δ : 7.43–7.31 (m, 5H), 6.75 (s, 2H), 6.69 (s, 1H), 5.22–5.20 (t, 1H, $J = 2.7\text{ Hz}$), 4.99 (s, 2H), 3.93–3.80 (m, 1H), 3.68–3.56 (m, 1H), 3.02–2.89 (m, 1H), 2.65–2.55 (m, 1H), 2.05–1.91 (m, 2H), 1.21–1.16 (t, 3H, $J = 7.1\text{ Hz}$); ^{13}C NMR (63 MHz, CDCl_3) δ : ppm 15.95, 21.72, 27.37, 64.41, 71.47, 97.62, 115.03, 115.93, 118.27, 124.10, 128.31, 128.68, 129.38, 138.28, 147.15, 153.61.

6-(Benzyloxy)-2-(ethylthio)chroman (**9b**)

According to the general procedure, the nitrate ester **8** (200 mg, 0.5 mmol) and ethyl vinyl sulfide (4.5 g, 50 mmol) were reacted with TBAF (0.24 mL, 0.5 mmol) in Toluene (20 mL) at $-78\text{ }^{\circ}\text{C}$. Subsequent workup and flash column chromatography

(2% ethyl Acetate in hexane) yielded **9b** as a colourless oil (158 mg, 74%). $R_f = 0.53$ (20% ethyl acetate in hexane) identical in all respects to an authentic sample.⁴

^1H NMR (250 MHz, CDCl_3) δ : 7.43–7.31 (m, 5H), 6.75 (s, 2H), 6.69 (s, 1H), 5.54–5.51 (t, 1H, $J = 3.9$ Hz), 4.99 (s, 2H), 3.02–2.88 (m, 1H), 2.84–2.54 (m, 3H), 2.35–2.21 (m, 1H), 2.15–2.04 (m, 1H), 1.35–1.29 (t, 3H, $J = 7.4$ Hz); ^{13}C NMR (63 MHz, CDCl_3) δ : ppm 15.96, 23.68, 25.47, 28.20, 71.44, 80.96, 115.30, 116.08, 118.93, 123.39, 128.33, 128.72, 129.40, 138.24, 147.32, 153.98.

1,2-Dihydro-2'H-spiro(benzo[f]chromene-3,1'-naphthalen)-2'-one (11)

According to the general procedure, the nitrate ester **4b** (200 mg, 0.59 mmol) was reacted with TBAF (0.59 mL, 0.59 mmol) in THF (10 mL) at -78°C . Subsequent workup and flash column chromatography (5% ethyl Acetate in hexane) yielded a yellow viscous oil that crystallized on standing to give **11** (75 mg, 40%). $R_f = 0.65$ (20% ethyl acetate in hexane). m.p. $143\text{--}145^\circ\text{C}$ identical in all respects to an authentic sample.¹⁷ ^1H NMR (250 MHz, CDCl_3) δ : 7.83–7.72 (m, 3H), 7.65–7.62 (d, 1H, $J = 7.0$ Hz), 7.52–7.46 (t, 1H, $J = 7.0$ Hz, 8.0 Hz), 7.43–7.34 (m, 6H), 6.17–6.13 (d, 1H, $J = 9.0$ Hz), 3.16–3.06 (m, 1H), 2.92–2.79 (m, 1H), 2.55–2.46 (m, 1H), 2.24–2.12 (m, 1H); ^{13}C NMR (63 MHz, CDCl_3) δ : ppm 19.27, 34.49, 83.59, 113.27, 119.55, 122.93, 124.53, 126.97, 127.34, 129.10, 129.38, 129.52, 130.04, 130.49, 131.41, 133.53, 144.82, 145.14, 153.56, 201.62; HRMS (ESI) Calcd for $\text{C}_{22}\text{H}_{17}\text{O}_2$: 313.1223. Found: 313.1223.

3-Ethoxy-2,3-dihydro-1H-benzo[f]chromene (12)

According to the general procedure, the nitrate ester **4b** (200 mg, 0.59 mmol) and ethyl vinyl ether (216 mg, 2.9 mmol) were reacted with TBAF (0.59 mL, 0.59 mmol)

in THF (8 mL) at -78 °C. Subsequent workup and flash column chromatography (5% ethyl acetate in hexane) yielded **12** as colourless oil (32 mg, 23% yield. R_f = 0.51 (20% ethyl acetate in hexane) identical in all respects to an authentic sample.¹⁸

¹H NMR (250 MHz, CDCl₃) δ : 7.86-7.83 (d, 1H, J = 8.3 Hz), 7.78-7.75 (d, 1H, J = 8.0 Hz), 7.65-7.62 (d, 1H, J = 8.8 Hz), 7.51-7.46 (t, 1H, J = 7.0 Hz), 7.37-7.31 (t, 1H, J = 7.0 Hz), 7.08-7.05 (d, 1H, J = 8.8 Hz), 5.33-5.31 (t, 1H, J = 3.0 Hz), 3.94-3.84 (m, 1H), 3.74-3.65 (m, 1H), 3.14-3.06 (m, 2H), 2.28-2.19 (m, 1H), 2.17-2.07 (m, 1H), 1.22-1.16 (t, 3H, J = 7.0 Hz); ¹³C NMR (63 MHz, CDCl₃) δ : ppm 16.14, 18.46, 27.39, 64.78, 97.83, 115.40, 120.06, 122.97, 124.30, 127.23, 128.68, 129.35, 130.09, 133.76, 150.34. ; HRMS (ESI) Calcd for C₁₅H₁₅O₂: 227.1066. Found: 227.1065.

1-{2-[(*tert*-Butyldimethylsilyl)oxy]benzyl}pyrrolidine (**13**)

The nitrate ester **4a** (200 mg, 0.7 mmol) and pyrrolidine (60 mg, 0.84 mmol) were dissolved in THF (10 mL) at -78 °C and stirred for 6 h from -78 °C to 0 °C then at rt for 1 h as there was no major change in starting material it was refluxed for 24 h. After TLC analysis had shown complete conversion of the starting material water (10 mL) was added, the mixture was extracted with EtOAc (3 × 10 mL), the combined extracts were dried with sodium sulphate, filtered and the solvent was removed in vacuo. Flash column chromatography (50% ethyl acetate in hexane) yielded **13** as colourless oil (94 mg, 45%). R_f = 0.26 (10% ethyl acetate in hexane). ¹H NMR (250 MHz, CDCl₃) δ : 7.38-7.35 (d, 1H, J = 7.4 Hz), 7.14-7.08 (t, 1H, J = 7.8 Hz), 6.96-6.90 (t, 1H, J = 7.2 Hz), 6.81-6.78 (d, 1H, J = 7.9 Hz), 3.65 (s, 2H), 2.55 (s, 4H), 1.77 (s, 4H) 1.03 (s, 9H), 0.23 (s, 6H); ¹³C NMR (63 MHz, CDCl₃) δ : ppm 18.45, 23.61, 26.01, 54.20, 118.74, 121.05, 127.55, 129.99, 130.64, 153.69; IR (NaCl, neat): 2929, 1591, 1471, 1409, 1255, 1102, 913, 835, 751 cm⁻¹; HRMS (ESI) Calcd for C₁₇H₃₀ONSi: 292.2091. Found: 292.2077.

4. References

1. Leonard, J.; Lygo, B.; Procter, G. *Advanced Practical Organic Chemistry*, Nelson Thornes Ltd. UK, 2001
2. Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
3. Nagamochi, M.; Fang, Y.Q.; Lauten, M. *Org. Lett.* **2007**, *9*, 2955.
4. Barrero, A. F.; Quílez del Moral, J. F.; Herrador, M. M.; Arteaga, P.; Cortés, M.; Benites, J.; Rosellón, A. *Tetrahedron* **2006**, *62*, 6012.
5. Dilman, A. D.; Arkhipov, D. E.; Belyakov, P.A.; Struchkova, M. I.; Tartakovsky, V. A. *Russ. Chem. Bull.* **2006**, *55*, 517.
6. Andreu, R. and Ronda, J. C. *Synth. Commun.* **2008**, *38*, 2316.
7. Davion, Y.; Guillaumet, G.; Léger, J. M.; Jarry, C.; Lesur, B.; and Mérour J.Y. *Heterocycles* **2003**, *60*, 1793.
8. Zhang, Q.; Takacs, J. M. *Org. Lett.* **2008**, *10*, 545.
9. Kawada, A.; Yasuda, K.; Abe, H.; Harayama, T. *Chem. Pharm. Bull.* **2002**, *50*, 380.
10. Latowski, T.; Latowska, E.; Poplawska, B.; Przytarska, M.; Walczak, M.; Zelent, B. *Pol. J. Chem.* **1980**, *54*, 1073.
11. Sato, K.; Inoue, S.; Ozawa, K.; Kobayashi, T.; Ota, T.; Tazaki, M. *J. Chem. Soc. Perkin Trans. I* **1987**, 1753.
12. Tsay, S. C.; Lin, L. C.; Furth, P. A.; Shum, C. C.; King, D. B.; Yu, S. F.; Chen, B. L.; Hwu, J. R. *Synthesis* **1993**, 329.
13. Katritzky, A. R.; Zhang, Z.; Lan, X.; Lang, H. *J. Org. Chem.* **1994**, *59*, 1900.
14. Bilgiç, S.; Bilgiç, O.; Bilgiç, M.O.; Gündüz, M.; Karakoç, N. *Arkivoc* **2009**, *xiii*, 185.
15. Cavitt, S. B.; Sarrafizadeh, H. R.; Gardner, P. D. *J. Org. Chem.* **1962**, *27*, 1211.
16. Bray, C. D. *Org. Biomol. Chem.* **2008**, *6*, 2815.
17. Belyanin, M. L.; Filimonov, V. D.; Raldugin, V. A.; Krasnov, E. A. *Russ. Chem. Bull.* **2001**, *50*, 914.
18. Matsumoto, J.; Ishizu, M.; Kawano, R.; Hesaka, D.; Shiragami, T.; Hayashi, Y.; Yamashita, T.; Yasuda, M. *Tetrahedron*, **2005**, *61*, 5735.

Phylogenetic tree of GVA sequences. The tree shows a hierarchical clustering of sequences based on their GVA values. The values are listed at the top of the tree, and the branching structure indicates the evolutionary relationships between them.

Sequence	GVA
8.1795	8.1795
8.1453	8.1453
7.8412	7.8412
7.8095	7.8095
7.788	7.788
7.7521	7.7521
7.5281	7.5281
7.499	7.499
7.468	7.468
7.394	7.394
7.364	7.364
7.335	7.335
7.118	7.118
7.082	7.082

4.954
4.937
4.903
4.887

NAME	GVAS2
EXPNO	460
PROCNO	1
Date_	20111221
Time_	20.04
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zg
TD	32768
SOLVENT	DMSO
NS	8
DS	0
SWH	3676.471 Hz
FDRES	0.112197 Hz
F2	4.4564981 sec
AQ	128
DW	136.000000 sec
DE	6.00 usec
TE	294.8 K
D1	5.00000000 sec
TD0	1

```

===== CHANNEL f1 =====
NUC1              1H
P1                9.00 usec
PL1              4.00 dB
PL1W             7.67000008 W
SFO1            250.1315259 MHz
SI               32768
SF              250.1299971 MHz
WDW              EM
SSB              0
LB              1.00 Hz
GB              0
PC              1.40

```

¹³C NMR of Compound 3b

GVAS43@250 C-13

150.23350

133.556
129.210
129.001
127.973
126.128
124.483
124.101
123.510
120.818

53.8888

NAME	GVAS2
EXPNO	461
PROCNO	1
Date_	20111221
Time	20.10
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zgdc
TD	22010
SOLVENT	DMSO
NS	1200
DS	4
SWH	15723.271 Hz
FIDRES	0.714369 Hz
AQ	0.6999680 sec
RG	362
DW	31.800 usec
DE	6.00 usec
TE	295.0 K
D1	0.50000000 sec
D11	0.03000000 sec
TD0	1

```
===== CHANNEL f1 =====
NUC1                13C
P1                  2.32 usec
PL1                 -2.00 dB
PL1W                54.14257431 W
SFO1                62.9031528 MHz
```

```
===== CHANNEL f2 =====
CPDRG2          wait1216
NUTC            1H
PCPD2           135.00 usec
PL2             120.00 dB
PL12            22.00 dB
PL2W            0.00000000 W
PL12W           0.12156131 W
SFO2            250.1311770 MHz
SI              32768
SF              62.8952668 MHz
WDW             EM
SSB             0
LSB             0
GB              0
PC              0.80
```

HRMS of Compound 3b

GVAS43_6_12_11_inf_111130114211 #50 RT: 1.15 AV: 1 NL: 6.23E8

T: FTMS + p ESI Full ms [150.00-2000.00]

¹H NMR of Compound 5a

GVAS24-D@250 H-1

7.18
7.15
7.12
6.98
6.95
6.82
6.79
6.76
6.73

NAME GVAS2
EXPNO 47
PROCNO 1
Date_ 20100408
Time 18.39
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 34
DS 0
SWH 3676.471 Hz
FIDRES 0.112197 Hz
AQ 4.4564981 sec
RG 512
DW 136.000 usec
DE 6.00 usec
TE 298.0 K
D1 5.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 9.00 usec
PL1 4.00 dB
PL1W 7.67000008 W
SFO1 250.1315259 MHz
SI 32768
SF 250.1300024 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

2.67
2.65
2.63
2.60
2.59

1.87
1.86
1.84
1.83
1.82

8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 ppm

1.13
1.19
2.01

2.00

4.15

4.15

¹³C NMR of Compound 5a

GVAS24-D@250 C-13

—158.859

—129.467
—128.729

—123.253
—119.706
—116.841

—59.811

—54.448

—24.685

NAME GVAS2
EXPNO 50
PROCNO 1
Date_ 20100409
Time 9.53
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgdc
TD 22010
SOLVENT CDCl3
NS 25000
DS 4
SWH 15723.271 Hz
FIDRES 0.714369 Hz
AQ 0.6999680 sec
RG 512
DW 31.800 usec
DE 6.00 usec
TE 298.0 K
D1 0.50000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 2.32 usec
PL1 -2.00 dB
PL1W 54.14257431 W
SFO1 62.9031528 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 120.00 dB
PL2 22.00 dB
PL2W 0.00000000 W
PL12W 0.12156131 W
SFO2 250.1311770 MHz
SI 32768
SF 62.8951782 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 0.80

¹H NMR of Compound 5b

GVAS26B@250 H-1

7.339
7.323
7.284
7.266
7.250
7.230
7.088
7.075
7.062
7.047
6.753
6.738
6.725
6.703

3.787
3.695

NAME GVAS2
EXPNO 462
PROCNO 1
Date_ 20111221
Time 20.41
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg
TD 32768
SOLVENT DMSO
NS 8
DS 0
SWH 3676.471 Hz
FIDRES 0.112197 Hz
AQ 4.4564981 sec
RG 128
DW 136.000 usec
DE 6.00 usec
TE 294.8 K
D1 5.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 9.00 usec
PL1 4.00 dB
PL1W 7.67000008 W
SFO1 250.1315259 MHz
SI 32768
SF 250.1299971 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

¹³C NMR of Compound **5b**

GVAS26B@250 C-13

— 157.223 —
— 139.587 —
128.637
128.281
128.137
127.862
126.882
124.124
— 118.543 —
— 115.334 —

— 51.748 —
— 49.594 —

NAME GVAS2
EXPNO 463
PROCNO 1
Date_ 20111221
Time 21.24
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgdc
TD 22010
SOLVENT DMSO
NS 1800
DS 4
SWH 15723.271 Hz
FIDRES 0.714369 Hz
AQ 0.6999680 sec
RG 362
DW 31.800 usec
DE 6.00 usec
TE 295.0 K
D1 0.50000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 2.32 usec
PL1 -2.00 dB
PL1W 54.14257431 W
SFO1 62.9031528 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 120.00 dB
PL12 22.00 dB
PL2W 0.00000000 W
PL12W 0.12156131 W
SFO2 250.1311770 MHz
SI 32768
SF 62.8952662 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 0.80

¹H NMR of compound **5c**

¹³C NMR of compound **5c**

```
NAME          GVAS2
EXPNO         368
PROCNO        1
Date_         20110726
Time          14.07
INSTRUM       spect
PROBHD        5 mm Multinucl
PULPROG       zgdc
TD            22010
SOLVENT       DMSO
NS            6000
DS            4
SWH           15723.271 Hz
FIDRES        0.714369 Hz
AQ            0.6999680 sec
RG            1024
DW            31.800 usec
DE            6.00 usec
TE            295.1 K
D1            0.50000000 sec
D11           0.03000000 sec
TD0           1
```

```
===== CHANNEL f1 =====
NUC1           13C
P1             2.32 usec
PL1            -2.00 dB
PL1W           54.14257431 W
SFO1           62.9031528 MHz
```

```
===== CHANNEL f2 =====
CPDPRG2       waltz16
NUC2           1H
PCPD2         135.00 usec
PL2           120.00 dB
PL12          22.00 dB
PL2W           0.00000000 W
PL12W         0.12156131 W
SFO2          250.1311770 MHz
SI            32768
SF            62.8952645 MHz
WDW            EM
SSB            0
LB             3.00 Hz
GB            0
PC            0.80
```

RT: 0.00 - 11.50

250711-GVAS-26-A #357 RT: 4.96 AV: 1 NL: 2.90E6

F: FTMS + p ESI Full ms [150.00-1000.00]

¹H NMR of Compound 5d

GVAS27A@250 H-1

¹³C NMR of Compound 5d

GVAS27-A@250 C-13

NAME GVAS2
EXPNO 60
PROCNO 1
Date_ 20100429
Time 17.28
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgdc
TD 22010
SOLVENT CDCl3
NS 6000
DS 4
SWH 15723.271 Hz
FIDRES 0.714369 Hz
AQ 0.6999680 sec
RG 574.7
DW 31.800 usec
DE 6.00 usec
TE 298.0 K
D1 0.50000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 2.32 usec
PL1 -2.00 dB
PL1W 54.14257431 W
SFO1 62.9031528 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 120.00 dB
PL12 22.00 dB
PL2W 0.00000000 W
PL12W 0.12156131 W
SFO2 250.1311770 MHz
SI 32768
SF 62.8951781 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 0.80

¹H NMR of compound **5e**

NAME nmr
EXPNO 363
PROCNO 1
Date_ 20110725
Time 14.18
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg
TD 32768
SOLVENT DMSO
NS 8
DS 0
SWH 3676.471 Hz
FIDRES 0.112197 Hz
AQ 4.4564981 sec
RG 1024
DW 136.000 usec
DE 6.00 usec
TE 295.4 K
D1 5.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 9.00 usec
PL1 4.00 dB
PL1W 7.67000008 W
SFO1 250.1315259 MHz
SI 32768
SF 250.1299972 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

¹³C NMR of compound **5e**

```
NAME          GVAS2
EXPNO         61
PROCNO        1
Date_         20100430
Time          0.41
INSTRUM       spect
PROBHD        5 mm Multinucl
PULPROG       zgdc
TD            22010
SOLVENT       CDCl3
NS            6000
DS            4
SWH           15723.271 Hz
FIDRES        0.714369 Hz
AQ            0.6999680 sec
RG            256
DW            31.800 usec
DE            6.00 usec
TE            298.0 K
D1            0.50000000 sec
D11           0.03000000 sec
TD0           1

===== CHANNEL f1 =====
NUC1          13C
P1            2.32 usec
PL1           -2.00 dB
PL1W          54.14257431 W
SFO1          62.9031528 MHz

===== CHANNEL f2 =====
CPDPRG2       waltz16
NUC2          1H
PCPD2         135.00 usec
PL2           120.00 dB
PL12          22.00 dB
PL2W          0.00000000 W
PL12W         0.12156131 W
SFO2          250.1311770 MHz
SI            32768
SF            62.8951779 MHz
WDW           EM
SSB           0
LB            3.00 Hz
GB            0
PC            0.80
```

RT: 0.00 - 11.49

250711-GVAS-27-B #359 RT: 5.14 AV: 1 NL: 2.50E6

F: FTMS + p ESI Full ms [150.00-1000.00]

GVAS290250 H-1

7.220
7.189
7.151
7.121
6.989
6.961
6.918
6.858
6.828

—5.234

—4.172

NAME GVAS2
EXPNO 456
PROCNO 1
Date_ 20110220
Time 21.06
INSTRUM spect
PROBHD 5 mm Multiscale
PULPROG zgpg30
TD 32768
F2 -
SOLVENT DMSO-d
NS 16
DS 4
SWH 3676.411 Hz
FREQ 400.142 MHz
WDW EM
SSB 0
GB 0
PC 1.00
RG 327.68
AQ 0.02468 sec
FIDRES 0.001200 Hz
AQRES 0.001200 sec
SFO 400.142 MHz
SF01 400.142 MHz
SF02 400.142 MHz
SF03 400.142 MHz
SF04 400.142 MHz
SF05 400.142 MHz
SF06 400.142 MHz
SF07 400.142 MHz
SF08 400.142 MHz
SF09 400.142 MHz
SF10 400.142 MHz
SF11 400.142 MHz
SF12 400.142 MHz
SF13 400.142 MHz
SF14 400.142 MHz
SF15 400.142 MHz
SF16 400.142 MHz
SF17 400.142 MHz
SF18 400.142 MHz
SF19 400.142 MHz
SF20 400.142 MHz
SF21 400.142 MHz
SF22 400.142 MHz
SF23 400.142 MHz
SF24 400.142 MHz
SF25 400.142 MHz
SF26 400.142 MHz
SF27 400.142 MHz
SF28 400.142 MHz
SF29 400.142 MHz
SF30 400.142 MHz
SF31 400.142 MHz
SF32 400.142 MHz
SF33 400.142 MHz
SF34 400.142 MHz
SF35 400.142 MHz
SF36 400.142 MHz
SF37 400.142 MHz
SF38 400.142 MHz
SF39 400.142 MHz
SF40 400.142 MHz
SF41 400.142 MHz
SF42 400.142 MHz
SF43 400.142 MHz
SF44 400.142 MHz
SF45 400.142 MHz
SF46 400.142 MHz
SF47 400.142 MHz
SF48 400.142 MHz
SF49 400.142 MHz
SF50 400.142 MHz
SF51 400.142 MHz
SF52 400.142 MHz
SF53 400.142 MHz
SF54 400.142 MHz
SF55 400.142 MHz
SF56 400.142 MHz
SF57 400.142 MHz
SF58 400.142 MHz
SF59 400.142 MHz
SF60 400.142 MHz
SF61 400.142 MHz
SF62 400.142 MHz
SF63 400.142 MHz
SF64 400.142 MHz
SF65 400.142 MHz
SF66 400.142 MHz
SF67 400.142 MHz
SF68 400.142 MHz
SF69 400.142 MHz
SF70 400.142 MHz
SF71 400.142 MHz
SF72 400.142 MHz
SF73 400.142 MHz
SF74 400.142 MHz
SF75 400.142 MHz
SF76 400.142 MHz
SF77 400.142 MHz
SF78 400.142 MHz
SF79 400.142 MHz
SF80 400.142 MHz
SF81 400.142 MHz
SF82 400.142 MHz
SF83 400.142 MHz
SF84 400.142 MHz
SF85 400.142 MHz
SF86 400.142 MHz
SF87 400.142 MHz
SF88 400.142 MHz
SF89 400.142 MHz
SF90 400.142 MHz
SF91 400.142 MHz
SF92 400.142 MHz
SF93 400.142 MHz
SF94 400.142 MHz
SF95 400.142 MHz
SF96 400.142 MHz
SF97 400.142 MHz
SF98 400.142 MHz
SF99 400.142 MHz
SF100 400.142 MHz

CHANNEL f1
NUC1 1H
P1 7.00 usec
PL1 0.00 dB
PL2 0.00 dB
PL3 0.00 dB
PL4 0.00 dB
PL5 0.00 dB
PL6 0.00 dB
PL7 0.00 dB
PL8 0.00 dB
PL9 0.00 dB
PL10 0.00 dB
PL11 0.00 dB
PL12 0.00 dB
PL13 0.00 dB
PL14 0.00 dB
PL15 0.00 dB
PL16 0.00 dB
PL17 0.00 dB
PL18 0.00 dB
PL19 0.00 dB
PL20 0.00 dB
PL21 0.00 dB
PL22 0.00 dB
PL23 0.00 dB
PL24 0.00 dB
PL25 0.00 dB
PL26 0.00 dB
PL27 0.00 dB
PL28 0.00 dB
PL29 0.00 dB
PL30 0.00 dB
PL31 0.00 dB
PL32 0.00 dB
PL33 0.00 dB
PL34 0.00 dB
PL35 0.00 dB
PL36 0.00 dB
PL37 0.00 dB
PL38 0.00 dB
PL39 0.00 dB
PL40 0.00 dB
PL41 0.00 dB
PL42 0.00 dB
PL43 0.00 dB
PL44 0.00 dB
PL45 0.00 dB
PL46 0.00 dB
PL47 0.00 dB
PL48 0.00 dB
PL49 0.00 dB
PL50 0.00 dB
PL51 0.00 dB
PL52 0.00 dB
PL53 0.00 dB
PL54 0.00 dB
PL55 0.00 dB
PL56 0.00 dB
PL57 0.00 dB
PL58 0.00 dB
PL59 0.00 dB
PL60 0.00 dB
PL61 0.00 dB
PL62 0.00 dB
PL63 0.00 dB
PL64 0.00 dB
PL65 0.00 dB
PL66 0.00 dB
PL67 0.00 dB
PL68 0.00 dB
PL69 0.00 dB
PL70 0.00 dB
PL71 0.00 dB
PL72 0.00 dB
PL73 0.00 dB
PL74 0.00 dB
PL75 0.00 dB
PL76 0.00 dB
PL77 0.00 dB
PL78 0.00 dB
PL79 0.00 dB
PL80 0.00 dB
PL81 0.00 dB
PL82 0.00 dB
PL83 0.00 dB
PL84 0.00 dB
PL85 0.00 dB
PL86 0.00 dB
PL87 0.00 dB
PL88 0.00 dB
PL89 0.00 dB
PL90 0.00 dB
PL91 0.00 dB
PL92 0.00 dB
PL93 0.00 dB
PL94 0.00 dB
PL95 0.00 dB
PL96 0.00 dB
PL97 0.00 dB
PL98 0.00 dB
PL99 0.00 dB
PL100 0.00 dB

¹H NMR of Compound 5g

GVAS31@250 H-1

¹³C NMR of Compound **5g**

GVAS31@250 C-13

¹H NMR of compound **5h**

¹³C NMR of compound **5h**

NAME GVAS2
EXPNO 74
PROCNO 1
Date_ 20100518
Time 21.39
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgdc
TD 22010
SOLVENT CDCl3
NS 5000
DS 4
SWH 15723.271 Hz
FIDRES 0.714369 Hz
AQ 0.6999680 sec
RG 512
DW 31.800 usec
DE 6.00 usec
TE 295.0 K
D1 0.50000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 2.32 usec
PL1 -2.00 dB
PL1W 54.14257431 W
SFO1 62.9031528 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 120.00 dB
PL12 22.00 dB
PL2W 0.00000000 W
PL12W 0.12156131 W
SFO2 250.1311770 MHz
SI 32768
SF 62.8951800 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 0.80

¹NMR of Compound 5i

GVAS34@250 H-1

NAME GVAS34
EXPNO 1
PROCNO 1
F2 20111127
TIME 22.12
INSTRUM spect
PROBHD 5 mm NMR
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1
DS 0
SWH 3678.470 Hz
FIDRES 0.112191 Hz
AQ 4.456198 sec
RG 1024
SR 136.000 MHz
SC 6.00 us
EC 294.6 Hz
SI 5.0000000 sec
LUG 1

----- CHANNEL f1 -----
NUC1 1H
P1 19.00 dB
PT 4.00 dB
PL1 1.6120000 Hz
RG1 250.1313779 MHz
AF 32768
CF 490.1429990 MHz
MAG 201
SFO 500
TA 1.00 Hz
GB 0
PC 1.40

¹³C NMR of Compound 5i

GVAS340250 C-13

—153.42

131.748
130.650
128.990
127.866
122.471
121.761
117.115
116.749
116.280

—36.489

NAME GVAS340250
EXPNO 1
PROCNO 1
Date_ 20110903
Time 02.11
INSTRUM spect
PROBHD 5 mm BBO-1H/13C
PULPROG zgpg30
TD 65536
SOLVENT DMSO-d6
NS 1024
DS 4
SWH 12722.171 Hz
FIDRES 0.713250 Hz
AQ 0.0000000 sec
RG 326
OR 31.000 cm-1
SR 1.00 cm-1
DE 2.00
TE 300.2 K
D1 0.0000000 sec
d11 0.0100000 sec
DELTA 1

===== CHANNEL f1 =====
NUC1 13C
P1 0.0000000 sec
PL1 0.00 dB
PL12 0.00 dB
PL13 0.00 dB
PL14 0.00 dB

===== CHANNEL f2 =====
NAME2 1H
NUC2 1H
P2 0.0000000 sec
PL2 0.00 dB
PL22 0.00 dB
PL23 0.00 dB
PL24 0.00 dB
PL25 0.00 dB
PL26 0.00 dB
PL27 0.00 dB
PL28 0.00 dB
PL29 0.00 dB
PL30 0.00 dB
PL31 0.00 dB
PL32 0.00 dB
PL33 0.00 dB
PL34 0.00 dB
PL35 0.00 dB
PL36 0.00 dB
PL37 0.00 dB
PL38 0.00 dB
PL39 0.00 dB
PL40 0.00 dB

¹H NMR of compound 5j

¹³C NMR of compound **5j**

NAME GVAS2
EXPNO 87
PROCNO 1
Date_ 20100602
Time 23.16
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgdc
TD 22010
SOLVENT CDCl3
NS 3500
DS 4
SWH 15723.271 Hz
FIDRES 0.714369 Hz
AQ 0.6999680 sec
RG 362
DW 31.800 usec
DE 6.00 usec
TE 294.8 K
D1 0.50000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 2.32 usec
PL1 -2.00 dB
PL1W 54.14257431 W
SFO1 62.9031528 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 120.00 dB
PL12 22.00 dB
PL2W 0.00000000 W
PL12W 0.12156131 W
SFO2 250.1311770 MHz
SI 32768
SF 62.8951805 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 0.80

RT: 0.00 - 11.51

NL:
1.73E7
TIC F: FTMS +
p ESI Full ms
[150.00-
1000.00] MS
250711-GVAS-
35

250711-GVAS-35 #449 RT: 6.37 AV: 1 NL: 4.09E6

F: FTMS + p ESI Full ms [150.00-1000.00]

¹H NMR of Compound 5k

GVAS32@250 H-1

```
NAME          GVAS2
EXPNO         68
PROCNO        1
Date_         20100513
Time          19.52
INSTRUM       spect
PROBHD        5 mm Multinucl
PULPROG       zg
TD            32768
SOLVENT       CDCl3
NS            4
DS            0
SWH           3676.471 Hz
FIDRES        0.112197 Hz
AQ            4.4564981 sec
RG            256
DW            136.000 usec
DE            6.00 usec
TE            298.0 K
D1            5.00000000 sec
TD0           1

===== CHANNEL f1 =====
NUC1          1H
P1            9.00 usec
PL1           4.00 dB
PL1W          7.67000008 W
SFO1          250.1315259 MHz
SI            32768
SF            250.1300210 MHz
WDW           EM
SSB           0
LB            1.00 Hz
GB            0
PC            1.40
```

¹³C NMR of Compound 5k

GVAS32@250 C-13

NAME GVAS2
EXPNO 108
PROCNO 1
Date_ 20100606
Time 18.34
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgdc
TD 22010
SOLVENT CDCl3
NS 3000
DS 4
SWH 15723.271 Hz
FIDRES 0.714369 Hz
AQ 0.6999680 sec
RG 256
DW 31.800 usec
DE 6.00 usec
TE 294.7 K
D1 0.50000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 2.32 usec
PL1 -2.00 dB
PL1W 54.14257431 W
SFO1 62.9031528 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 120.00 dB
PL12 22.00 dB
PL2W 0.00000000 W
PL12W 0.12156131 W
SFO2 250.1311770 MHz
SI 32768
SF 62.8951776 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 0.80

¹H NMR of compound **5l**

¹³C NMR of compound **51**

NAME GVAS2
EXPNO 100
PROCNO 1
Date_ 20100605
Time 22.28
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgdc
TD 22010
SOLVENT CDCl3
NS 4500
DS 4
SWH 15723.271 Hz
FIDRES 0.714369 Hz
AQ 0.6999680 sec
RG 574.7
DW 31.800 usec
DE 6.00 usec
TE 294.5 K
D1 0.50000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 2.32 usec
PL1 -2.00 dB
PL1W 54.14257431 W
SFO1 62.9031528 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 120.00 dB
PL12 22.00 dB
PL2W 0.00000000 W
PL12W 0.12156131 W
SFO2 250.1311770 MHz
SI 32768
SF 62.8951830 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 0.80

GVAS-36_110726101010 #3 RT: 0.09 AV: 1 NL: 5.15E5

F: FTMS + p ESI Full ms [85.00-1500.00]

¹H NMR of Compound 5m

GVAS38@250 H-1

¹³C NMR of Compound 5m

GVAS38@250 C-13

NAME GVAS2
EXPNO 96
PROCNO 1
Date_ 20100605
Time 19.54
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgdc
TD 22010
SOLVENT CDCl3
NS 4000
DS 4
SWH 15723.271 Hz
FIDRES 0.714369 Hz
AQ 0.6999680 sec
RG 181
DW 31.800 usec
DE 6.00 usec
TE 294.4 K
D1 0.50000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 2.32 usec
PL1 -2.00 dB
PL1W 54.14257431 W
SFO1 62.9031528 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 120.00 dB
PL12 22.00 dB
PL2W 0.00000000 W
PL12W 0.12156131 W
SFO2 250.1311770 MHz
SI 32768
SF 62.8951814 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 0.80

¹H NMR of Compound 6a

GVAS61B-1 crude@250 H-1

¹³C NMR of Compound 6a

GVAS61B-1@250 C-13

153.146

130.197

128.170

123.574

121.492

117.863

97.852

64.623

27.489

21.487

16.085

```
NAME          GVAS2
EXPNO         233
PROCNO        1
Date_         20101213
Time          12.37
INSTRUM       spect
PROBHD        5 mm Multinucl
PULPROG       zgpg
TD            22010
SOLVENT       CDCl3
NS            400
DS            4
SWH           15723.271 Hz
FIDRES        0.714369 Hz
AQ            0.6999680 sec
RG            512
DW            31.800 usec
DE            6.00 usec
TE            294.5 K
D1            0.50000000 sec
D11           0.03000000 sec
TD0           1

===== CHANNEL f1 =====
NUC1          13C
P1            2.32 usec
PL1           -2.00 dB
PL1W          54.14257431 W
SFO1          62.9031528 MHz

===== CHANNEL f2 =====
CPDPRG2       waltz16
NUC2          1H
PCPD2         135.00 usec
PL2           120.00 dB
PL12          22.00 dB
PL2W          0.00000000 W
PL12W         0.12156131 W
SFO2          250.1311770 MHz
SI            32768
SF            62.8951784 MHz
WDW           EM
SSB           0
LB            3.00 Hz
GB            0
PC            0.80
```

GVAS72A0250 H-1

NAME GVAS72
EXPNO 250
PROCNO 1
Date_ 20110322
Time 1.01
INSTRUM spect
PROBHD 5 mm MSL-100
SOLVENT CDCl3
ID 12709
SOLVENT CDCl3
NS 8
DS 2
SWH 1600.401 Hz
FIDRES 0.112187 Hz
AQ 4.4561961 sec
RG 1024
ZG 135.000 MHz
PC 6.00 sec
TE 290.0 K
D1 5.0000000 sec
TD 1

----- CHANNEL f1 -----
NUC1 13C
P1 8.00 usec
PL1 0.00 dB
PL1F 7.6700000 MHz
NUC1 13C
PC 250.1300016 MHz
PDW 0
SOL 0
LB 1.00 Hz
GB 0
PR 1.18

NAME: 02K42
 CYNO: 201
 PROCNO: 20110122
 DATE: 1-12
 TIME: 10:00
 INSTRUM: spect
 PULPROG: zgpg30
 TD: 65536
 FIDRES: 0.000100
 AQ: 0.000100
 RG: 327.68
 DQ: 0.000100
 SFO: 125.760 MHz
 P1: 0.000100
 PL2: 0.000100
 PL3: 0.000100
 PL4: 0.000100
 PL5: 0.000100
 PL6: 0.000100
 PL7: 0.000100
 PL8: 0.000100
 PL9: 0.000100
 PL10: 0.000100
 PL11: 0.000100
 PL12: 0.000100
 PL13: 0.000100
 PL14: 0.000100
 PL15: 0.000100
 PL16: 0.000100
 PL17: 0.000100
 PL18: 0.000100
 PL19: 0.000100
 PL20: 0.000100
 PL21: 0.000100
 PL22: 0.000100
 PL23: 0.000100
 PL24: 0.000100
 PL25: 0.000100
 PL26: 0.000100
 PL27: 0.000100
 PL28: 0.000100
 PL29: 0.000100
 PL30: 0.000100
 PL31: 0.000100
 PL32: 0.000100
 PL33: 0.000100
 PL34: 0.000100
 PL35: 0.000100
 PL36: 0.000100
 PL37: 0.000100
 PL38: 0.000100
 PL39: 0.000100
 PL40: 0.000100
 PL41: 0.000100
 PL42: 0.000100
 PL43: 0.000100
 PL44: 0.000100
 PL45: 0.000100
 PL46: 0.000100
 PL47: 0.000100
 PL48: 0.000100
 PL49: 0.000100
 PL50: 0.000100
 PL51: 0.000100
 PL52: 0.000100
 PL53: 0.000100
 PL54: 0.000100
 PL55: 0.000100
 PL56: 0.000100
 PL57: 0.000100
 PL58: 0.000100
 PL59: 0.000100
 PL60: 0.000100
 PL61: 0.000100
 PL62: 0.000100
 PL63: 0.000100
 PL64: 0.000100
 PL65: 0.000100
 PL66: 0.000100
 PL67: 0.000100
 PL68: 0.000100
 PL69: 0.000100
 PL70: 0.000100
 PL71: 0.000100
 PL72: 0.000100
 PL73: 0.000100
 PL74: 0.000100
 PL75: 0.000100
 PL76: 0.000100
 PL77: 0.000100
 PL78: 0.000100
 PL79: 0.000100
 PL80: 0.000100
 PL81: 0.000100
 PL82: 0.000100
 PL83: 0.000100
 PL84: 0.000100
 PL85: 0.000100
 PL86: 0.000100
 PL87: 0.000100
 PL88: 0.000100
 PL89: 0.000100
 PL90: 0.000100
 PL91: 0.000100
 PL92: 0.000100
 PL93: 0.000100
 PL94: 0.000100
 PL95: 0.000100
 PL96: 0.000100
 PL97: 0.000100
 PL98: 0.000100
 PL99: 0.000100
 PL100: 0.000100

¹H NMR of Compound 9a

GVAS70B@250 H-1

```
NAME          GVAS2
EXPNO         269
PROCNO        1
Date_         20110223
Time          19.48
INSTRUM       spect
PROBHD        5 mm Multinucl
PULPROG       zg
TD            32768
SOLVENT       CDCl3
NS            8
DS            0
SWH           3676.471 Hz
FIDRES        0.112197 Hz
AQ            4.4564981 sec
RG            1024
DW            136.000 usec
DE            6.00 usec
TE            298.0 K
D1            5.00000000 sec
TD0           1

===== CHANNEL f1 =====
NUC1          1H
P1            9.00 usec
PL1           4.00 dB
PL1W          7.67000009 W
FO1           250.1315259 MHz
SI            32768
SF            250.1300012 MHz
WDW           EM
SSB           0
LB            1.00 Hz
GB            0
PC            1.40
```

GVAS70B@250 C-13

```
NAME          GVAS2
EXPNO         272
PROCNO        1
Date_         20110302
Time          20.19
INSTRUM       spect
PROBHD        5 mm Multinucl
PULPROG       zgpg30
TD            22010
SOLVENT       CDCl3
NS            10000
DS            4
SHE           15723.271 Hz
FIDRES        0.714369 Hz
AQ            0.6999680 sec
RG            1024
DW            31.800 usec
DE            6.00 usec
TE            298.0 K
D1            0.50000000 sec
D11           0.03000000 sec
TD0           1
----- CHANNEL f1 -----
NUC1          13C
P1            2.32 usec
PL1           -2.00 dB
PL1W          54.14257431 W
SFO1          62.9031528 MHz
----- CHANNEL f2 -----
CPDPRG2       waltz16
NUC2          1H
PCPD2         135.00 usec
PL2           120.00 dB
PL12          0.00000000 W
PL2W          0.12156131 W
SFO2          250.1311770 MHz
S1            32768
SF            62.8951846 MHz
WDW           EM
SSB           0
LB            3.00 Hz
GB            0
PC            0.80
```


GVAS71B@250 H-1

¹³C NMR of Compound 9b

GVAS71B@250 C-13

```
NAME      GVAS71B
EXPNO     1
PROCNO    1
Date_     20110304
Time      7.38
INSTRUM   spect
PROBHD    5 mm Multinucl
PULPROG   zgpg30
TD        22010
SOLVENT   CDCl3
NS        30000
DS        4
SWH       15723.271 Hz
FIDRES    0.714369 Hz
AQ        0.6999680 sec
RG        1024
DW        31.800 usec
DE        6.00 usec
TE        298.0 K
D1        0.50000000 sec
D11       0.03000000 sec
TD0       1

===== CHANNEL f1 =====
NUC1      13C
P1        2.32 usec
PL1       -2.00 dB
PL1W      54.14257431 W
SFO1      62.9031528 MHz

===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2      1H
PCPD2     135.00 usec
PL2       120.00 dB
PL12      22.00 dB
PL2W      0.00000000 W
PL12W     0.12156131 W
SFO2      250.1311770 MHz
SI        32768
SF        62.8951831 MHz
WDW       EM
SSB       0
LB        3.00 Hz
GB        0
PC        0.80
```

¹H NMR of Compound 10a

GVAS62@250 H-1

10.128

7.945
7.912
7.807
7.775
7.739
7.704
7.494
7.451
7.421
7.362
7.332
7.299
7.262
7.226
7.201
7.167

NAME GVAS2
EXPNO 445
PROCNO 1
Date_ 20111217
Time 19.49
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg
TD 32768
SOLVENT DMSO
NS 8
DS 0
SWH 3676.471 Hz
FIDRES 0.112197 Hz
AQ 4.4564981 sec
RG 1024
DW 136.000 usec
DE 6.00 usec
TE 298.0 K
D1 5.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 9.00 usec
PL1 4.00 dB
PL1W 7.67000008 W
SF01 250.1315259 MHz
SI 32768
SF 250.1299972 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

4.625

¹³C NMR of Compound 10a

GVAS62@250 C-13

NAME GVAS2
EXPNO 257
PROCNO 1
Date_ 20110208
Time 3.21
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgdc
TD 22010
SOLVENT CDCl3
NS 20000
DS 4
SWH 15723.271 Hz
FIDRES 0.714369 Hz
AQ 0.6999680 sec
RG 1024
DW 31.800 usec
DE 6.00 usec
TE 298.0 K
D1 0.50000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 2.32 usec
PL1 -2.00 dB
PL1W 54.14257431 W
SFO1 62.9031528 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 120.00 dB
PL12 22.00 dB
PL2W 0.00000000 W
PL12W 0.12156131 W
SFO2 250.1311770 MHz
SI 32768
SF 62.8951794 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 0.80

HRMS of Compound 10a

GVAS62_20_12_11_inf_111219131550 #108 RT: 1.55 AV: 1 NL: 8.54E7

T: FTMS + p ESI Full ms [150.00-2000.00]

HRMS of Compound 10a

C₁₇H₁₄O₂ +H: C₁₇ H₁₅ O₁ S₁ p(gss, s/p:40) Chrg 1R:...

¹H NMR of Compound 10b

GVAS66@250 H-1

NAME GVAS2
EXPNO 446
PROCNO 1
Date_ 20111217
Time 20.02
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg
TD 32768
SOLVENT DMSO
NS 8
DS 0
SWH 3676.471 Hz
FIDRES 0.112197 Hz
AQ 4.4564981 sec
RG 1024
DW 136.000 usec
DE 6.00 usec
TE 298.0 K
D1 5.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 9.00 usec
PL1 4.00 dB
PL1W 7.67000008 W
SFO1 250.1315259 MHz
SI 32768
SF 250.1299970 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

¹³C NMR of Compound 10b

GVAS66@250 C-13

— 153.075
— 150.672

— 143.617

— 133.639

— 128.727
— 128.155

— 126.261

— 123.304
— 122.411

— 118.199

— 115.936

— 114.515
— 113.104

— 55.352

```
NAME          GVAS2
EXPNO         454
PROCNO        1
Date_         20111220
Time          8.09
INSTRUM       spect
PROBHD        5 mm Multinucl
PULPROG       zgdc
TD            22010
SOLVENT       DMSO
NS            35000
DS            4
SWH           15723.271 Hz
FIDRES        0.714369 Hz
AQ            0.6999680 sec
RG            512
DW            31.800 usec
DE            6.00 usec
TE            294.8 K
D1            0.50000000 sec
D11           0.03000000 sec
TD0           1

===== CHANNEL f1 =====
NUC1          13C
P1            2.32 usec
PL1           -2.00 dB
PL1W          54.14257431 W
SFO1          62.9031528 MHz

===== CHANNEL f2 =====
CPDPRG2       waltz16
NUC2          1H
PCPD2         135.00 usec
PL2           120.00 dB
PL12          22.00 dB
PL2W          0.00000000 W
PL12W         0.12156131 W
SFO2          250.1311770 MHz
SI            32768
SF            62.8952660 MHz
WDW           EM
SSB           0
LB            3.00 Hz
GB            0
PC            0.80
```

HRMS of Compound 10b

GVAS66new_20_12_11_inf_111219131550 #20 RT: 0.54 AV: 1 NL: 1.91E8
T: FTMS + p ESI Full ms [150.00-2000.00]

NAME	SVTYPE
REFID	185
PROCID	1
DATE	20101023
TIME	9:58
LOCATION	SPACT
REFPROG	5 sec Multitask
CLPROG	4.0
ID	32160
NOEVENT	66623
MS	4
PM	3
TIME	3076.471 HP
TIMESEC	0.13137 HP
PC	0.0564985 HP
GS	128
DM	136,3000 ADDR
DE	8,000 ADDR
SE	288,0 HP
SI	2,00000000 ADDR
TIME	1

----- CHANGES: 11 -----

PLC1	14
P1	9,10 ADDR
P12	1,10 ADDR
P13	1,80000000 HP
SV1	232,137275 HP
SV2	32748
IF	282,137012 ADDR
MDM	HP
DE1	0
DE2	1,0 HP
DE3	0
DE4	1,00

¹³C NMR of Compound 11

GVAS53@250 C-13

```
NAME          GVAS2
EXPNO         186
PROCNO        1
Date_         20101013
Time          11.10
INSTRUM       spect
PROBHD        5 mm Multinucl
PULPROG       zgdc
TD            22010
SOLVENT       CDCl3
NS            3000
DS            4
SWH           15723.271 Hz
FIDRES        0.714369 Hz
AQ            0.6999680 sec
RG            512
DW            31.800 usec
DE            6.00 usec
TE            294.7 K
D1            0.50000000 sec
D11           0.03000000 sec
TD0           1

===== CHANNEL f1 =====
NUC1          13C
P1            2.32 usec
PL1           -2.00 dB
PL1W          54.14257431 W
SFO1          62.9031528 MHz

===== CHANNEL f2 =====
CPDPRG2       waltz16
NUC2          1H
PCPD2         135.00 usec
PL2           120.00 dB
PL12          22.00 dB
PL2W          0.00000000 W
PL12W         0.12156131 W
SFO2          250.1311770 MHz
SI            32768
SF            62.8951753 MHz
WDW           EM
SSB           0
LB            3.00 Hz
GB            0
PC            0.80
```

HRMS of Compound 11

GVAS53_20_12_11_inf_111219131550 #35 RT: 0.94 AV: 1 NL: 1.70E8
T: FTMS + p ESI Full ms [150.00-2000.00]

¹H NMR of Compound 12

GVAS52-B@250 H-1

¹³C NMR of Compound 12

GVAS52-B@250 C-13

NAME GVAS2
EXPNO 182
PROCNO 1
Date_ 20100924
Time 5.19
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgdc
TD 22010
SOLVENT CDCl3
NS 28000
DS 4
SWH 15723.271 Hz
FIDRES 0.714369 Hz
AQ 0.6999680 sec
RG 512
DW 31.800 usec
DE 6.00 usec
TE 298.0 K
D1 0.50000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 2.32 usec
PL1 -2.00 dB
PL1W 54.14257431 W
SFO1 62.9031528 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 120.00 dB
PL12 22.00 dB
PL2W 0.00000000 W
PL12W 0.12156131 W
SFO2 250.1311770 MHz
SI 32768
SF 62.8951753 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 0.80

HRMS of Compound 12

GVAS52_20_12_11_inf_111219131550 #8 RT: 0.19 AV: 1 NL: 1.61E8

T: FTMS + p ESI Full ms [150.00-2000.00]

¹H NMR of compound 13

GVAS23@250 H-1

7.386
7.357
7.149
7.143
7.113
7.088
7.082
6.961
6.931
6.903
6.819
6.787

```
NAME      GVAS2
EXPNO     417
PROCNO    1
Date_     20111124
Time      23.11
INSTRUM   spect
PROBHD    5 mm Multinucl
PULPROG   zg
TD        32768
SOLVENT   CDCl3
NS        8
DS        0
SWH       3676.471 Hz
FIDRES    0.112197 Hz
AQ        4.4564981 sec
RG        32
DW        136.000 usec
DE        6.00 usec
TE        294.6 K
D1        5.00000000 sec
TD0       1

----- CHANNEL f1 -----
NUC1      1H
P1        9.00 usec
PL1       4.00 dB
PL1W      7.67000008 W
SFO1      250.1315259 MHz
SI        32768
SF        250.1300014 MHz
WDW       EM
SSB       0
LB        1.00 Hz
GB        0
PC        1.40
```

— 3.660

— 2.551

— 1.777

— 1.037

— 0.236

7.5

7.0

6.5

6.0

5.5

5.0

4.5

4.0

3.5

3.0

2.5

2.0

1.5

1.0

0.5

0.0

ppm

0.97

1.01

1.00

1.02

2.00

4.07

4.02

9.09

6.02

¹³C NMR of compound 13

GVAS23@250 C-13

— 153.690

— 130.649

— 129.999

— 127.550

— 121.057

— 118.746

```
NAME          GVAS2
EXPNO         418
PROCNO        1
Date_         20111124
Time          23.14
INSTRUM       spect
PROBHD        5 mm Multinucl
PULPROG       zgpg
TD            22010
SOLVENT       CDCl3
NS            50
DS            4
SWH           15723.271 Hz
FIDRES        0.714369 Hz
AQ            0.6999680 sec
RG            1024
DW            31.800 usec
DE            6.00 usec
TE            294.5 K
D1            0.5000000 sec
D11           0.0300000 sec
TD0           1
```

```
----- CHANNEL f1 -----
NUC1          13C
P1            2.32 usec
PL1           -2.00 dB
PL1W          54.14257431 W
SFO1          62.9031528 MHz
```

```
----- CHANNEL f2 -----
CPDPRG2       waltz16
NUC2          1H
PCPD2         135.00 usec
PL2           120.00 dB
PL12          22.00 dB
PL2W          0.0000000 W
PL12W         0.12156131 W
SFO2          250.1311770 MHz
SI            32768
SF            62.8952320 MHz
WDW           EM
SSB           0
LB            3.00 Hz
GB            0
PC            0.80
```

— 54.203

— 26.017

— 23.617

— 18.450

HRMS of Compound 13

GVAS23_14_12_11_inf_110728101420 #8 RT: 0.11 AV: 1 NL: 1.48E9
T: FTMS + p ESI Full ms [150.00-2000.00]