

Supplementary Material

An alkynylboronic ester cycloaddition route to functionalised aromatic boronic esters

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General Procedures

Infrared (IR) Spectra were recorded on a Perkin Elmer Paragon 100 FTIR spectrophotometer, ν_{\max} in cm^{-1} . Samples were recorded as thin films using sodium chloride plates, as a DCM solution. Bands are characterised as broad (br), strong (s), medium (m), and weak (w). ^1H NMR spectra were recorded on a Bruker AC-250 (250 MHz) or AMX-400 (400 MHz) supported by an Aspect 3000 data system, unless otherwise stated. Chemical shifts are reported in ppm from tetramethylsilane with the residual protic solvent resonance as the internal standard (CHCl_3 : $\delta 7.27\text{ppm}$). Data are reported as follows: chemical shift, integration, multiplicity (s=singlet, d=doublet, q=quartet, pent=pentet, sext=sextet, br=broad, m=multiplet, app=apparent), coupling constants (Hz), and assignment. ^{13}C NMR spectra were recorded on a Bruker AC-250 (62.9 MHz) or AMX-400 (100.6 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent as the internal reference (CDCl_3 : $\delta 77.0\text{ppm}$). Low resolution mass spectra were recorded on Micromass Autospec, operating in E.I., C.I. or FAB mode; or a Perkin-Elmer Turbomass Benchtop GC-MS operating in either E.I. or C.I. mode. High-resolution mass spectra (HRMS) recorded for accurate mass analysis, were performed on either a MicroMass LCT operating in Electrospray mode (TOF ES^+) or a MicroMass Prospec operating in FAB (FAB^+), EI (EI^+) or CI (CI^+) mode. Elemental microanalysis was performed using a Perkin-Elmer 2400 CHNS / O Series II Elemental Analyser. Melting points performed on recrystallised solids, were recorded on a Gallenkamp melting point apparatus and are uncorrected. All solvents and reagents were purified using standard laboratory techniques according to methods published in "Purification of Laboratory Chemicals" by Perrin, Armarego, and Perrin (Pergamon Press, 1966). Starting alkynylboronates¹ and pyranones² were prepared according to established procedures. Methyl coumalate was purchased from Aldrich chemical co. and used as received. Flash chromatography was performed on silica gel (BDH Silica Gel 60 43-60). Thin layer chromatography (TLC) was performed on aluminium backed plates pre-coated with

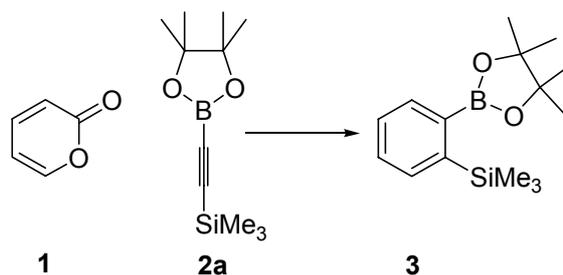
¹ H. C. Brown, N. G. Bhat, M. Srebink, *Tetrahedron Lett*, 1982, **29**, 2631.

² A. Haneda, H. Uenakai, T. Imawaga, M. Kawanisi, *Synth. Comm*, 1976, **6**, 141; I.W. Ashworth, M.C. Bowden, B. Dembofsky, D. Levin, W. Moss, E. Robinson, N. Szczur, J. Virica, *Org. Proc. Res. Dev.*, 2003, **7**, 74; C.G. Cho, Y.W. Kim, Y.K. Lim, J.S. Park, H. Lee, S. Koo, *J. Org. Chem*, 2002, **67**, 290.

silica (0.2 mm, Merck DC-alufolien Kieselgel 60 F₂₅₄) which were developed using standard visualizing agents: Ultraviolet light or potassium permanganate. X-Ray data for compounds **13** and **15** have been deposited with the CCDC, supplementary entry numbers: 608269 and 608270 respectively.

1.1. [4+2] Cycloaddition

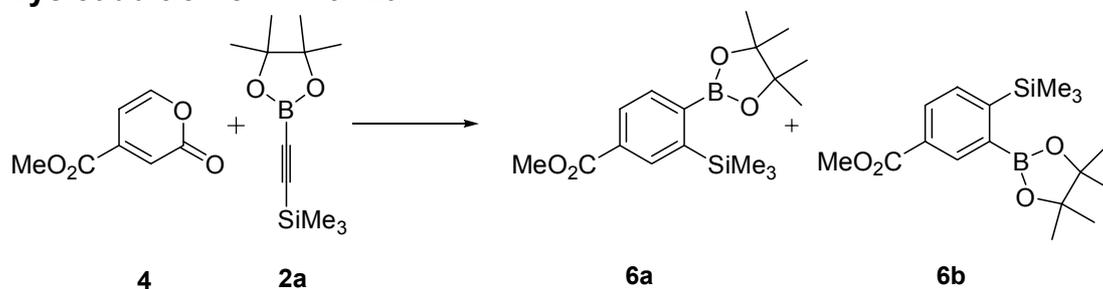
Cycloaddition of **1** with **2a**



A mixture of **1** (0.1 g, 1.04 mmol) and **2a** (0.466 g, 2.08 mmol) was heated at 170 °C and stirred for 15 h under N₂. The product was purified by flash column chromatography (eluting solvent petroleum ether/ethyl acetate 25:1 ratio) to give compound **3** as crystalline colourless solid, wt. 0.247 g, 86% yield.

Mp 84-86 °C **¹H NMR** (250 MHz, CDCl₃): δ 0.33 (9H, s, SiMe₃), 1.34 (12H, s, 4 x CH₃), 7.36 (2H, m, Ar-H) 7.61 (1H, m, Ar-H), 7.90 (1H, m, Ar-H); **¹³C NMR** (62.9 MHz, CDCl₃) δ 1.1, 25.0, 83.8, 127.8, 129.7, 134.3, 136.1, 146.0; **FTIR**: ν_{max}/CHCl₃, 2981 (s) cm⁻¹; **HRMS (EI⁺)** calcd for. C₁₅H₂₅BO₂Si: 276.1717. Found: 276.1715.

Cycloaddition of **4** with **2a**



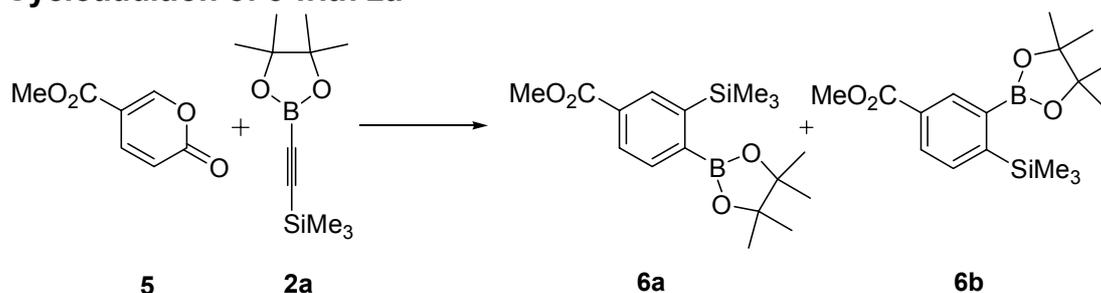
A mixture of **4** (0.1 g, 0.649 mmol) and **2a** (0.291 g, 1.298 mmol) was heated at 170 °C and stirred for 15 h under N₂. The product was purified by flash column chromatography (eluting solvent petroleum ether/ethyl acetate 25:1 ratio) to give **6a** and **6b** (3:1 ratio) as colourless

oils, wt. 0.152 g, 70% yield. *The regiochemistry was determined by 2-D NMR experiment (nOesy) of the major regioisomer 6a.*

6a : $^1\text{H NMR}$ (250 MHz, CDCl_3): δ 0.29 (9H, s, SiMe_3), 1.29 (12H, s, CH_3), 3.86 (3H, s, CO_2CH_3), 7.62 (1H, d, $J=8.0$ Hz, Ar-H), 7.93 (1H, dd, $J=8.0, 1.5$ Hz, Ar-H), 8.43 (1H, d, $J=1.5$ Hz, Ar-H); $^{13}\text{C NMR}$ (62.9 MHz, CDCl_3) δ 0.8, 25.0, 52.0, 84.1, 129.7, 130.2, 134.4, 136.4, 153.3, 167.4; **FTIR**: $\nu_{\text{max}}/\text{CHCl}_3$, 2979 (m), 2951 (w), 2901 (w), 1726 (s), 1593 (w), 1551 (w) cm^{-1} ; **HRMS** (EI^+) calcd. for $\text{C}_{17}\text{H}_{27}\text{O}_4\text{BSi}$ 335.1850 Found: 335.1857

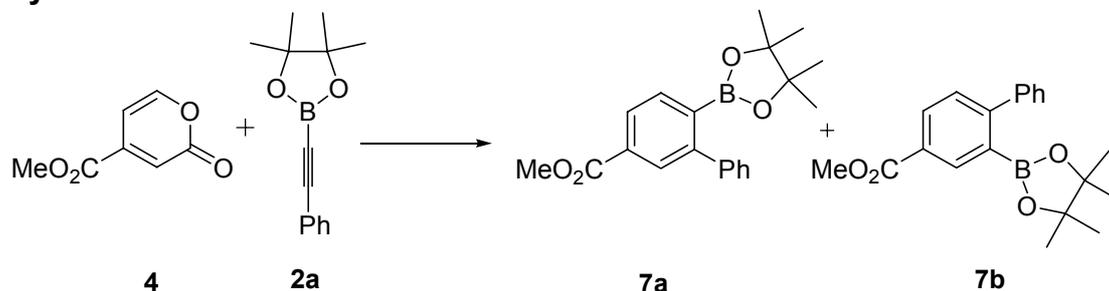
6b : $^1\text{H NMR}$ (250 MHz, CDCl_3) δ 0.36 (9H, s, SiMe_3), 1.35 (12H, s, CH_3), 3.91 (3H, s, CO_2CH_3), 7.96 (2H, m, Ar-H), 8.24 (1H, d, $J=1.5$ Hz, Ar-H); $^{13}\text{C NMR}$ (62.9 MHz, CDCl_3) δ 0.4, 25.0, 52.1, 84.2, 128.5, 130.5, 134.8, 135.9, 147.3, 167.5; **FTIR** $\nu_{\text{max}}/\text{CHCl}_3$ 2979 (m), 2952 (w), 1726 (s), 1595 (w), 1548 (w) cm^{-1} ; **HRMS** (EI^+) calcd. for $\text{C}_{17}\text{H}_{27}\text{O}_4\text{BSi}$ 335.1850 Found: 335.1839

Cycloaddition of 5 with 2a



A mixture of **5** (0.2 g, 1.298 mmol) and **2a** (0.582 g, 2.595 mmol) was heated at 170 °C and stirred for 15 h under N_2 . The product was purified by flash column chromatography (eluting solvent petroleum ether/ethyl acetate 25:1 ratio) to give the separated title compounds **6a** and **6b** (1:1 ratio) as colourless oils, wt. 0.384 g, 83% yield.

Cycloaddition of 4 with 2b



A mixture of **4** (0.1 g, 0.649 mmol) and **2a** (0.296 g, 1.298 mmol) was heated at 170 °C and stirred for 15 h under N_2 . The product was purified by flash column chromatography (eluting

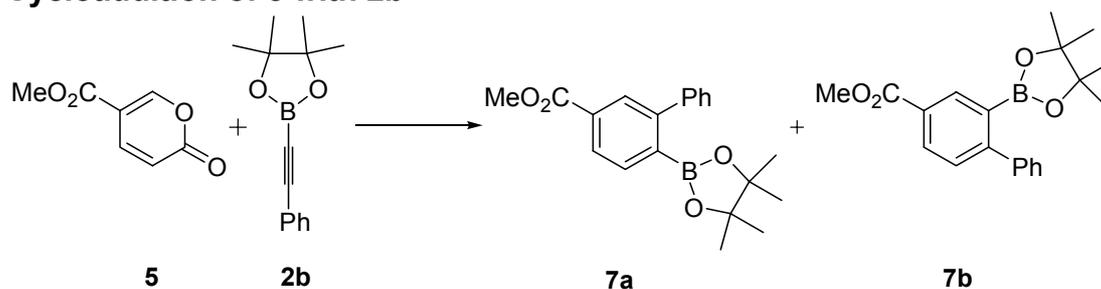
solvent petroleum ether/ethyl acetate 25:1 ratio) to give **7a** and **7b** (1:1 ratio) as a clear oil, 0.092g, 42%.

7a ¹H NMR: δ1.23 (12H, s, 4 x CH₃), 3.95 (3H, s, CO₂CH₃), 7.35-7.48 (6H, m, Ar-H), 8.12 (1H, dd, J=8.0, 2.0 Hz, Ar-H) 8.38 (1H, dd, J=2.0, 0.5 Hz, Ar-H); ¹³C NMR (62.9 MHz, CDCl₃) δ24.6, 52.1, 84.0, 127.0, 127.5, 127.9, 128.9, 129.0, 130.0, 135.6, 142.1, 151.9, 167.0.

7b ¹H NMR: δ1.21 (12H, s, 4 x CH₃), 3.92 (3H, s, CO₂CH₃), 7.35-7.48 (5H, m, Ar-H), 7.56 (1H, d, J=8.0 Hz, Ar-H), 7.98 (1H, dd, J=8.0, 1.5 Hz, Ar-H), 8.04 (1H, dd, J= 1.0, 0.5 Hz, Ar-H); ¹³C NMR (62.9 MHz, CDCl₃) δ24.7, 52.2, 84.1, 127.0, 127.2, 127.5, 128.0, 129.0, 129.1, 135.7, 142.0, 147.9, 167.0.

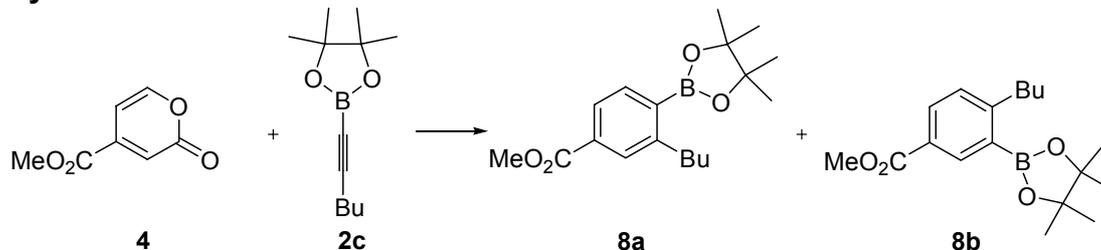
FTIR: ν_{max}/CHCl₃, 2991 (w), 2979 (w), 2940 (w), 1723 (s), 1600 (w) cm⁻¹; HRMS (EI⁺) calcd. for C₂₀H₂₃O₄B: 338.1689 Found: 338.1687.

Cycloaddition of **5** with **2b**



A mixture of **5** (0.1 g, 0.649 mmol) and **2b** (0.296 g, 1.298 mmol) was heated at 170 °C and stirred for 15 h under N₂. The product was purified by flash column chromatography (eluting solvent petroleum ether/ethyl acetate 25:1 ratio) to give compounds **7a** and **7b** (1:14 ratio) as a clear oil, 0.127g, 57% yield. *The regiochemistry was determined by 2-D NMR experiment (nOesy) of the major regioisomer 7b.*

Cycloaddition of **4** with **2c**



A mixture of **4** (0.1 g, 0.649 mmol) and **2c** (0.270 g, 1.298 mmol) was heated at 170 °C and stirred for 15 h under N₂. The product was purified by flash column chromatography (eluting solvent petroleum ether/ethyl acetate 25:1 ratio) to give compounds **8a** and **8b** (10:1 ratio) as

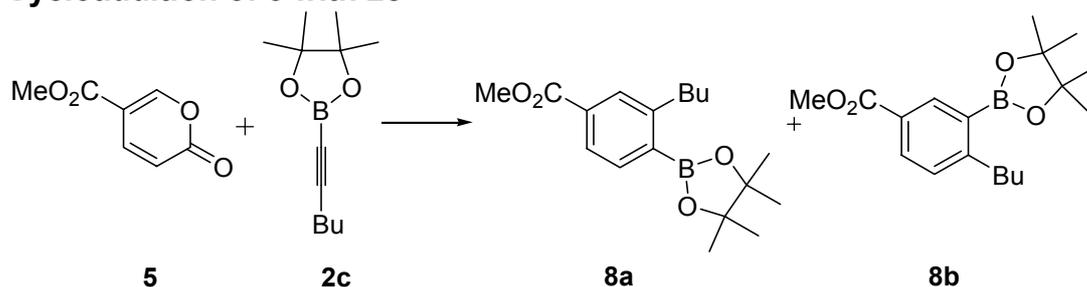
a clear oil, wt. 0.050 g, 24% yield. *The regiochemistry was determined by 2-D NMR experiment (nOesy) of the major regioisomer 8a.*

8a $^1\text{H NMR}$: δ 0.85 (3H, t, $J=7.5$ Hz, CH_2CH_3), 1.28 (12H, s, 4 x CH_3), 1.22-1.37 (2H, m, CH_2CH_3), 1.38-1.56 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.85 (2H, app t, $J=8.0$ Hz, $\text{C}=\text{CCH}_2$), 3.88 (3H, s, CO_2CH_3), 7.16 (1H, d, $J=8.0$ Hz, Ar- H), 7.92 (1H, dd, $J=8.0, 2.0$ Hz, Ar- H), 8.34 (1H, d, $J=2.0$ Hz, Ar- H); $^{13}\text{C NMR}$ (62.9 MHz, CDCl_3) δ 13.9, 22.7, 24.8, 35.3, 35.6, 51.9, 83.7, 126.8, 129.3, 131.8, 137.2, 155.5, 167.3.

8b $^1\text{H NMR}$: δ 0.85 (3H, t, $J=7.5$ Hz, CH_2CH_3), 1.28 (12H, s, 4 x CH_3), 1.22-1.37 (2H, m, CH_2CH_3), 1.38-1.56 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.85 (2H, app t, $J=8.0$ Hz, $\text{C}=\text{CCH}_2$), 3.89 (3H, s, CO_2CH_3), 7.79 (2H, s, Ar- H), 7.81 (1H, s, Ar- H); $^{13}\text{C NMR}$ (62.9 MHz, CDCl_3) δ 13.9, 22.7, 24.8, 35.2, 35.4, 52.0, 83.8, 125.6, 129.9, 131.8, 135.8, 150.2, 167.3.

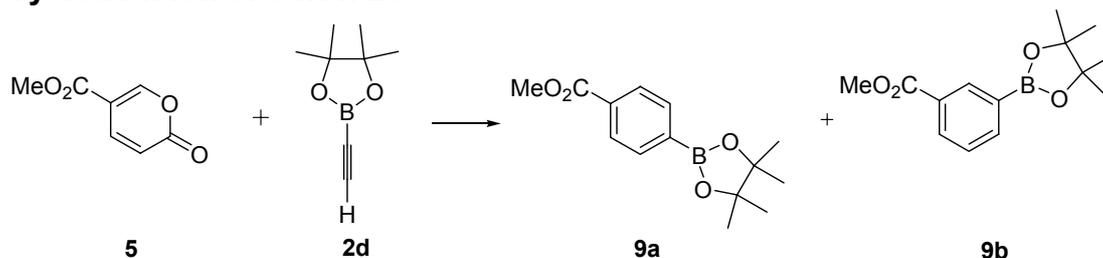
FTIR: $\nu_{\text{max}}/\text{CHCl}_3$, 2977 (m), 2956 (m), 2931 (m), 2870 (m), 1723 (s) cm^{-1} **HRMS** (EI^+) calcd. for $\text{C}_{18}\text{H}_{27}\text{O}_4\text{B}$: 318.2002 Found: 318.2012

Cycloaddition of 5 with 2c



A mixture of **5** (0.1 g, 0.649 mmol) and **2c** (0.270 g, 1.298 mmol) was heated at 170 °C and stirred for 15 h under N_2 . The product was purified by flash column chromatography (eluting solvent petroleum ether/ethyl acetate 25:1 ratio) to give compounds **8a** and **8b** (1: 3 ratio) as a clear oil, wt. 0.127 g, 59% yield. *The regiochemistry was determined by 2-D NMR experiment (nOesy) of the major regioisomer 8b.*

Cycloaddition of 5 with 2d



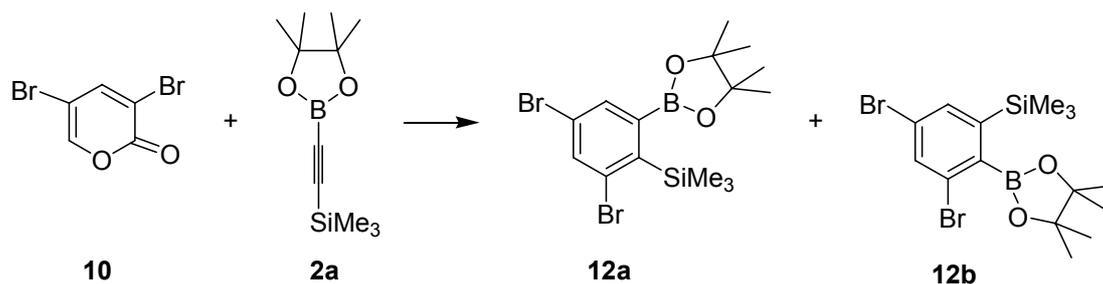
A mixture of **5** (0.1 g, 0.649 mmol), **2d** (0.09 g, 0.649 mmol) and diphenylether (1 mL) were heated at 170 °C with stirring, for 15 hours under a nitrogen atmosphere. The product was purified by flash column chromatography (eluting solvent 100: 1 petroleum ether: EtOAc) to give colourless crystalline solid of regioisomers in 5: 1 ratio (Major regioisomer was **9a**) wt. 0.130 g, 77% yield.

9a³: ¹H NMR (250 MHz, CDCl₃): δ1.28 (12H, s, CH₃), 3.84 (3H, s, CH₃OCO), 7.79 (2H, d, *J*=8.5 Hz, ArH), 7.96 (2H, d, *J*=8.5 Hz, ArH). ¹³C NMR (62.9 MHz, CDCl₃): δ24.8, 52.1, 84.1, 127.8, 135.8, 134.6, 167.1

9b: ¹H NMR δ1.28 (12H, s, CH₃), 3.84 (3H, s, CH₃OCO), 7.38 (1H, t, *J*=8.0 Hz, ArH), 7.90 (1H, m, ArH), 8.05 (1H, dt, *J*=8.0, 1.0 Hz, ArH), 8.39 (1H, br, ArH). ¹³C NMR (62.9 MHz, CDCl₃): δ24.8, 52.0, 84.1, 128.6 (x 2), 132.3 (x 2), 139.1, 167.1.

FTIR: ν_{\max} /CHCl₃, cm⁻¹ 2979 (w), 1727 (s), 1606 (w), 1510 (w), 1399 (m), 1361 (s). **HRMS** (EI⁺) Calcd for C₂₉H₂₄O₄ 262.1376 Found: 262.1377.

Cycloaddition of **10** with **2a**



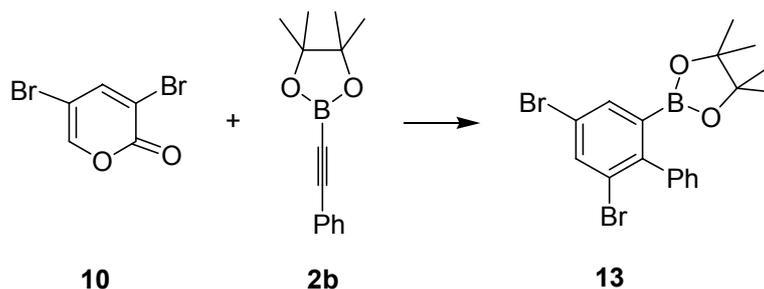
A mixture of **10** (0.100 g, 0.394 mmol) and **2a** (0.176 g, 0.788 mmol) and mesitylene (1 mL) was heated at 155 °C and stirred for 15 h under N₂. The product was purified by flash column chromatography (eluting solvent petroleum ether/ethyl acetate 25:1 ratio) to give compounds **12a** and **12b** (1:1 ratio) as a brown oil, wt. 0.111 g, 65% yield.

12a/b mixture: ¹H NMR δ0.29 (9H, s, CH₃), 0.37 (9H, s, CH₃), 1.29 (12H, s, CH₃), 1.37 (12H, s, CH₃), 7.47 (1H, d, *J*=2.0 Hz, ArH), 7.51 (1H, d, *J*=2.0 Hz, ArH), 7.59 (1H, d, *J*=2.0 Hz, ArH), 7.64 (1H, d, *J*=2.0 Hz, ArH). ¹³C NMR (62.9 MHz, CDCl₃): δ-0.5, 1.8, 24.7, 25.3, 84.5, 85.5, 112.5(x2), 134.3(x2), 134.8(x2), 135.0(x2), 136.3(x2).

FTIR: ν_{\max} /CHCl₃, cm⁻¹ 2980 (s), 1315 (s), 846 (s). **HRMS** (EI⁺) Calcd for C₁₅H₂₃BBR₂O₂Si 431.9927 Found: 431.9909.

³ N. Miyaura, M. Murata, I. Tatsuo, *J. Org. Chem.*, 1995, **60**, 7508.

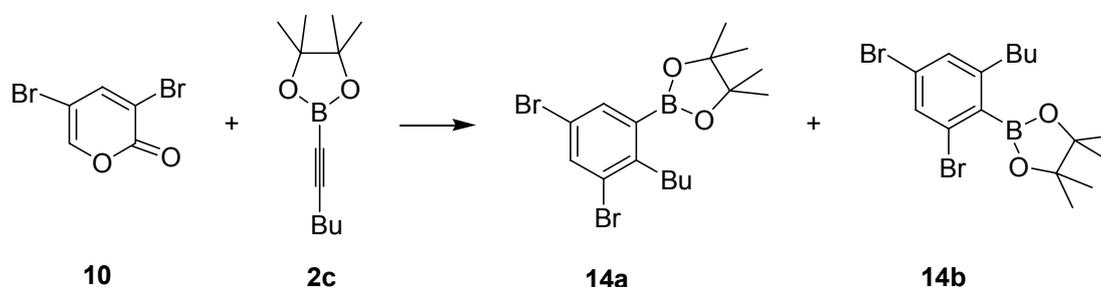
Cycloaddition of **10** with **2b**



A mixture of **10** (0.200 g, 0.788 mmol) and **2b** (0.269 g, 1.182 mmol) and mesitylene (1 mL) was heated at 155 °C and stirred for 15 h under N₂. The product was purified by flash column chromatography (eluting solvent petroleum ether/ethyl acetate 25:1 ratio) to give compound **13** as brown solid, 0.214g, 62% yield. *The regiochemistry was determined by X-ray crystallography.*

Mp 54-56 °C. **¹H NMR** δ1.06 (12H, s, CH₃), 7.28 (2H, m, ArH), 7.36 (3H, m, ArH), 7.72 (1H, d, *J*=2.0 Hz, ArH), 7.85 (1H, d, *J*=2.0 Hz, ArH). **¹³C NMR** (62.9 MHz, CDCl₃): δ24.4, 84.2, 113.3, 114.0, 115.0, 117.5, 122.0, 127.6, 129.5, 135.4, 136.3. **FTIR:** ν_{max}/CHCl₃, cm⁻¹ 2979 (w), 2979(s), 1458 (w), 1145 (w). **HRMS** (EI⁺) Calcd for C₁₈H₁₉BBr₂O₂ 381.0490 Found: 381.0486.

Cycloaddition of **10** with **2c**

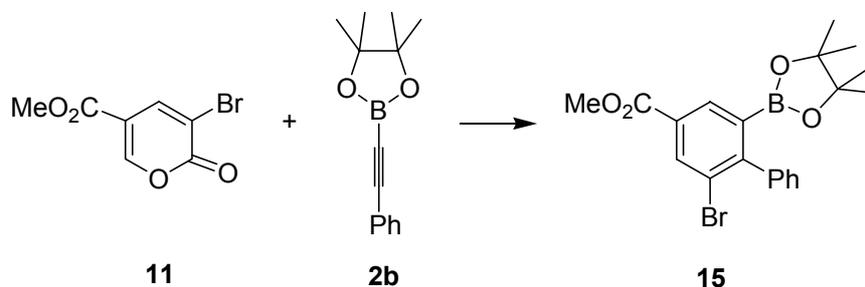


A mixture of **10** (0.100 g, 0.394 mmol) and **2c** (0.123 g, 0.591 mmol) and mesitylene (1 mL) was heated at 155 °C and stirred for 15 h under N₂. The product was purified by flash column chromatography (eluting solvent petroleum ether/ethyl acetate 25:1 ratio) to give compounds **14a** and **14b** as a brown oil, wt. 0.077 g, 47% yield. *The regiochemistry was determined by NMR experiment (nOe) of the major regioisomer 14a.*

14a: **¹H NMR** δ0.87 (3H, t, CH₂CH₃), 1.26 (12H, s, CH₃), 1.27-1.36 (4H, m, CH₂CH₂CH₃), 2.92 (2H, t, *J*=8.0 Hz, C=CCH₂), 7.66 (1H, d, *J*=1.0 Hz, ArH), 7.73 (1H, d, *J*=1.0 Hz, ArH). **¹³C NMR** (62.9 MHz, CDCl₃): δ13.9, 22.9, 24.8, 34.4, 35.4, 81.5, 125.6, 130.4, 134.9, 137.3, 137.7.

FTIR: ν_{\max}/CHCl_3 , cm^{-1} 2958 (s). **HRMS** (EI^+) Calcd for $\text{C}_{16}\text{H}_{23}\text{BBr}_2\text{O}_2$ 416.0158 Found: 416.0162.

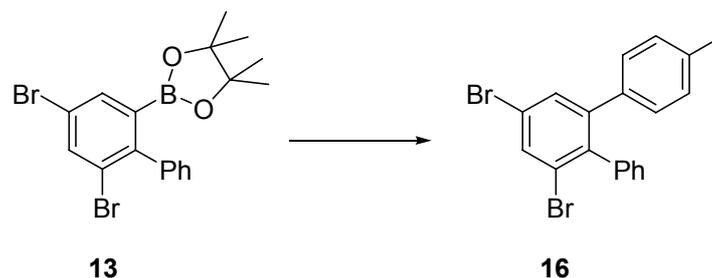
Cycloaddition of **11** with **2b**



A mixture of **11** (0.1 g, 0.429 mmol) and **2b** (0.391 g, 1.716 mmol) was heated at 170 °C and stirred for 15 h under vacuum 10 mmHg. The product was purified by flash column chromatography (eluting solvent petroleum ether/ethyl acetate 25:1 ratio) to give compound **89** as brown solid, 0.099 g, 56% yield. *The regiochemistry was determined by X-ray crystallography.*

Mp 109-111 °C. $^1\text{H NMR}$ δ 1.01 (12H, s, CH_3), 3.85 (3H, s, CH_3OCO), 7.30 (2H, m, ArH), 7.71 (3H, m, ArH), 8.17 (1H, d, $J=2.0$ Hz, ArH), 8.28 (1H, d, $J=2.0$ Hz, ArH). $^{13}\text{C NMR}$ (62.9 MHz, CDCl_3): δ 24.9, 52.6, 82.1, 122.9, 128.5, 128.8, 129.5, 130.9, 131.6, 134.7, 140.6, 147.4, 166.1. **FTIR:** ν_{\max}/CHCl_3 , cm^{-1} 2978 (w), 1727 (s). **HRMS** (EI^+) Calcd for $\text{C}_{20}\text{H}_{22}\text{BBrO}_4$ 417.0873 Found: 417.0886.

Suzuki reaction of **13** with *p*-iodotoluene

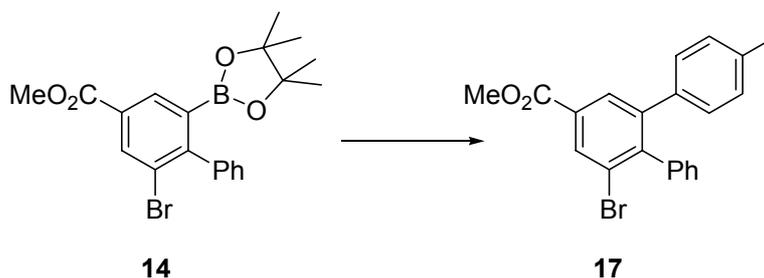


A round bottom flask was charged with **13** (0.260 g, 0.594 mmol), $\text{PdCl}_2(\text{dppf})\text{DCM}$ (0.043 g, 0.059 mmol), K_3PO_4 (0.378 g, 1.780 mmol), dioxane (1 ml) and iodotoluene (0.259 g, 1.187 mmol). The flask was fitted with a reflux condenser and heated at 85 °C under N_2 . After stirring for 48 h the reaction was cooled to room temperature and quenched by the addition of distilled water (10 ml), the product was extracted into dichloromethane (3 x 10 ml), dried (MgSO_4), filtered and conc. *in vacuo*. The product was purified by flash column

chromatography (eluting solvent petroleum ether/ethyl acetate 15:1 ratio) to give compound **16** as clear oil, wt. 0.133 g, 56% yield.

¹H NMR δ2.24 (3H, s, CH₃), 6.86-6.95 (4H, m, ArH), 7.24-7.20 (2H, m, ArH), 7.49-7.50 (3H, m, ArH), 7.49 (1H, d, J=2.0 Hz, ArH), 7.81 (1H, d, J=2.0, Hz, ArH). **¹³C NMR** (62.9 MHz, CDCl₃): δ21.3, 113.1, 113.9, 114.2, 115.1, 126.5, 127.3, 127.7, 128.5, 129.3, 130.1, 130.4, 133.8, 134.3, 135.0. **FTIR:** ν_{max}/CHCl₃, cm⁻¹ 2923 (w). **HRMS** (EI⁺) Calcd for C₁₉H₁₄Br₂ 399.9462 Found: 399.9462.

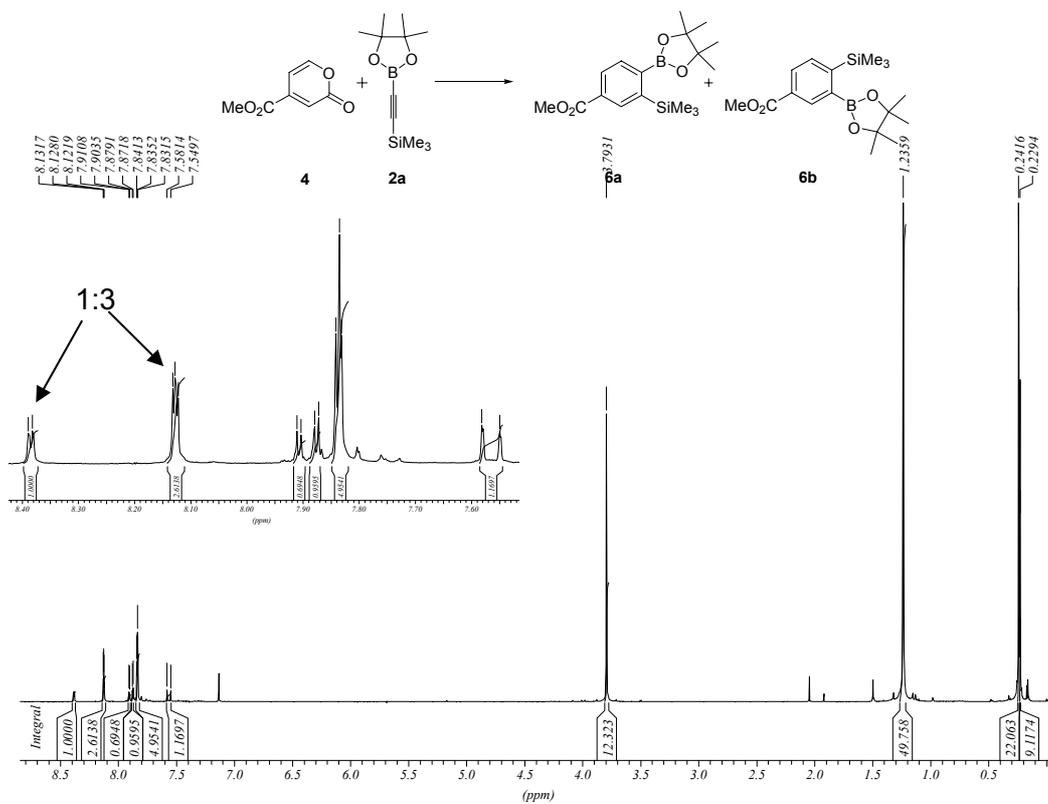
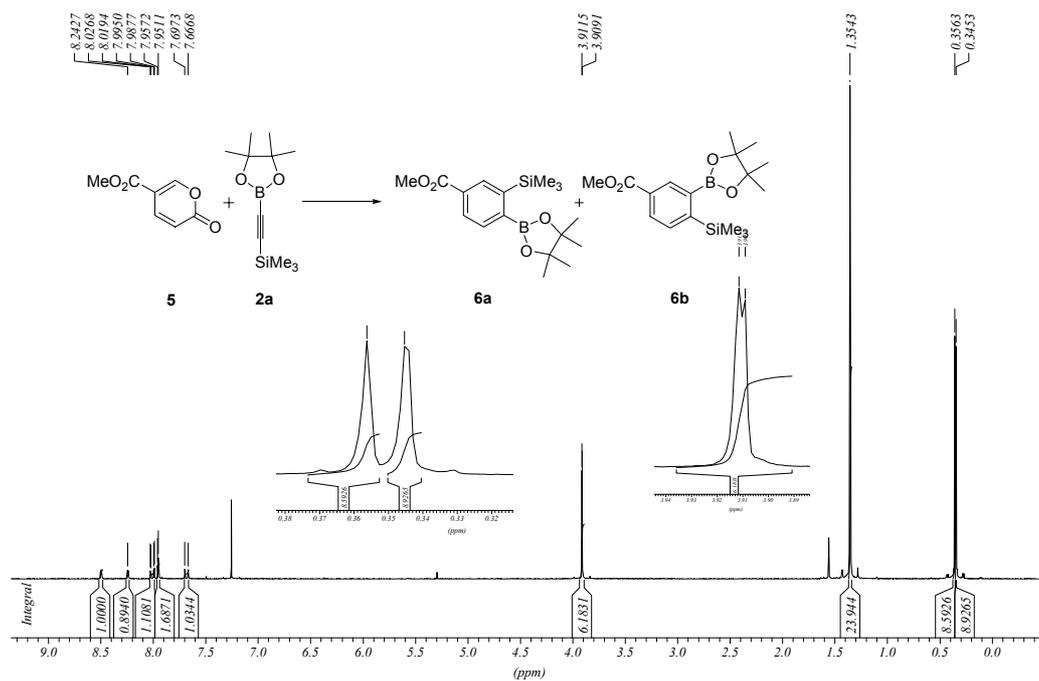
Suzuki reaction of **13** with *p*-iodotoluene



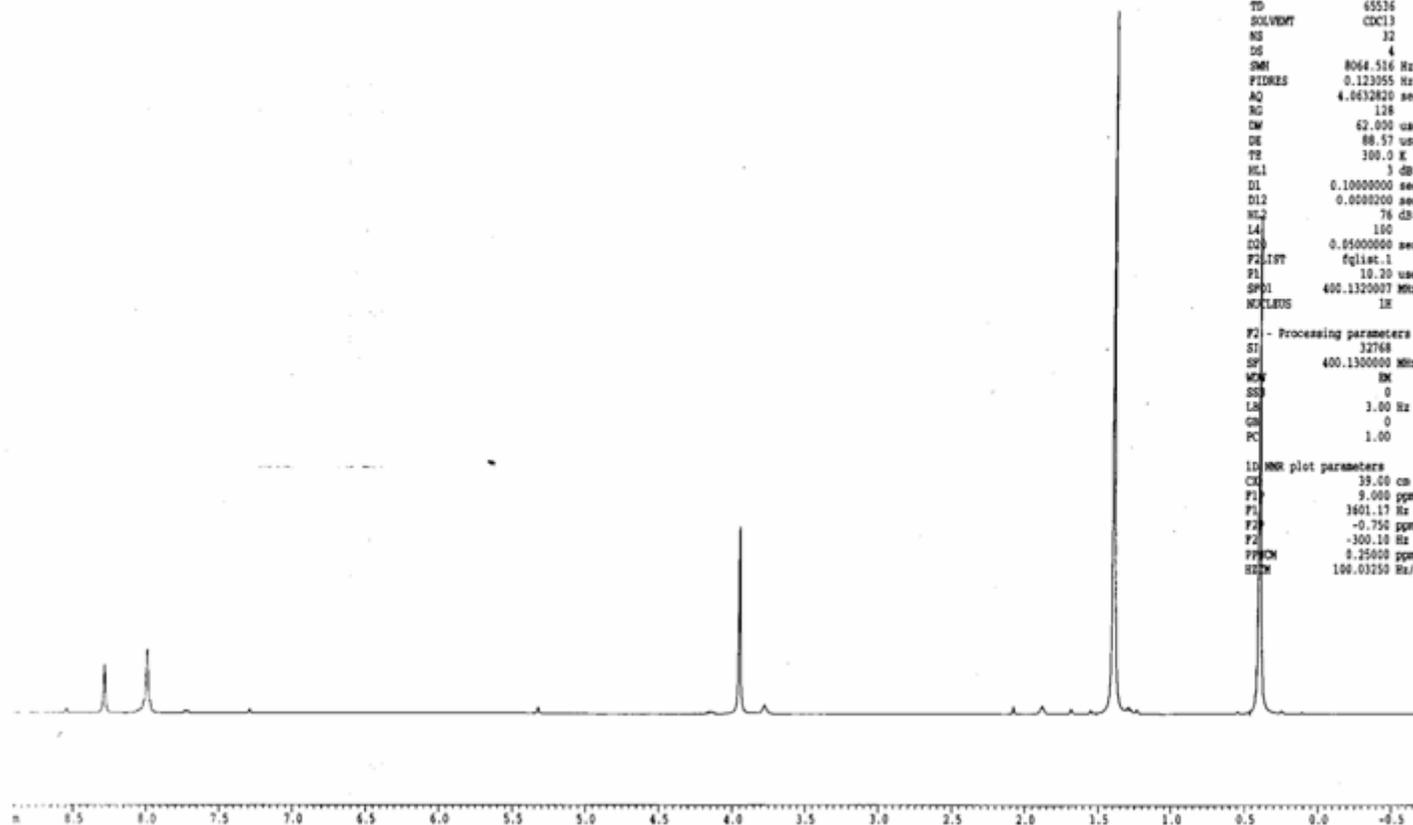
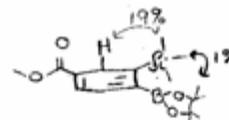
A round bottom flask was charged with **14** (0.088 g, 0.211 mmol), PdCl₂(dppf)DCM (0.015 g, 0.021 mmol), K₃PO₄ (.134 g, 0.633 mmol), dioxane (1 ml) and iodotoluene (0.092 g, 0.422 mmol). The flask was fitted with a reflux condenser and heated at 85 °C under N₂. After stirring for 48 h the reaction was cooled to room temperature and quenched by the addition of distilled water (10 ml), the product was extracted into dichloromethane (3 x 10 ml), dried (MgSO₄), filtered and conc. *in vacuo*. The product was purified by flash column chromatography (eluting solvent petroleum ether/ethyl acetate 15:1 ratio) to give compound **17** as colourless oil, wt. 0.076 g, 70% yield.

¹H NMR δ2.18 (3H, s, CH₃), 3.85 (3H, s, CH₃OCO), 6.82-6.90 (4H, m, ArH), 6.98-7.02 (2H, m, ArH), 7.18 (3H, m, ArH), 7.94 (1H, d, J=1.5 Hz, ArH), 8.25 (1H, d, J=1.5 Hz, ArH). **¹³C NMR** (62.9 MHz, CDCl₃): δ21.1, 52.4, 124.7, 127.4, 127.7, 128.5, 129.4, 130.2, 130.4, 132.5, 133.4, 136.7, 137.2, 139.5, 143.7, 145.5, 165.7. **FTIR:** ν_{max}/CHCl₃, cm⁻¹ 2360 (w) 1725 (s), 1240 (s). **HRMS** (EI⁺) Calcd for C₂₁H₁₇BrO₂ 380.0412 Found: 380.0413.

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Jane Moore E27 Sample ref: JMS40B in CDCl3



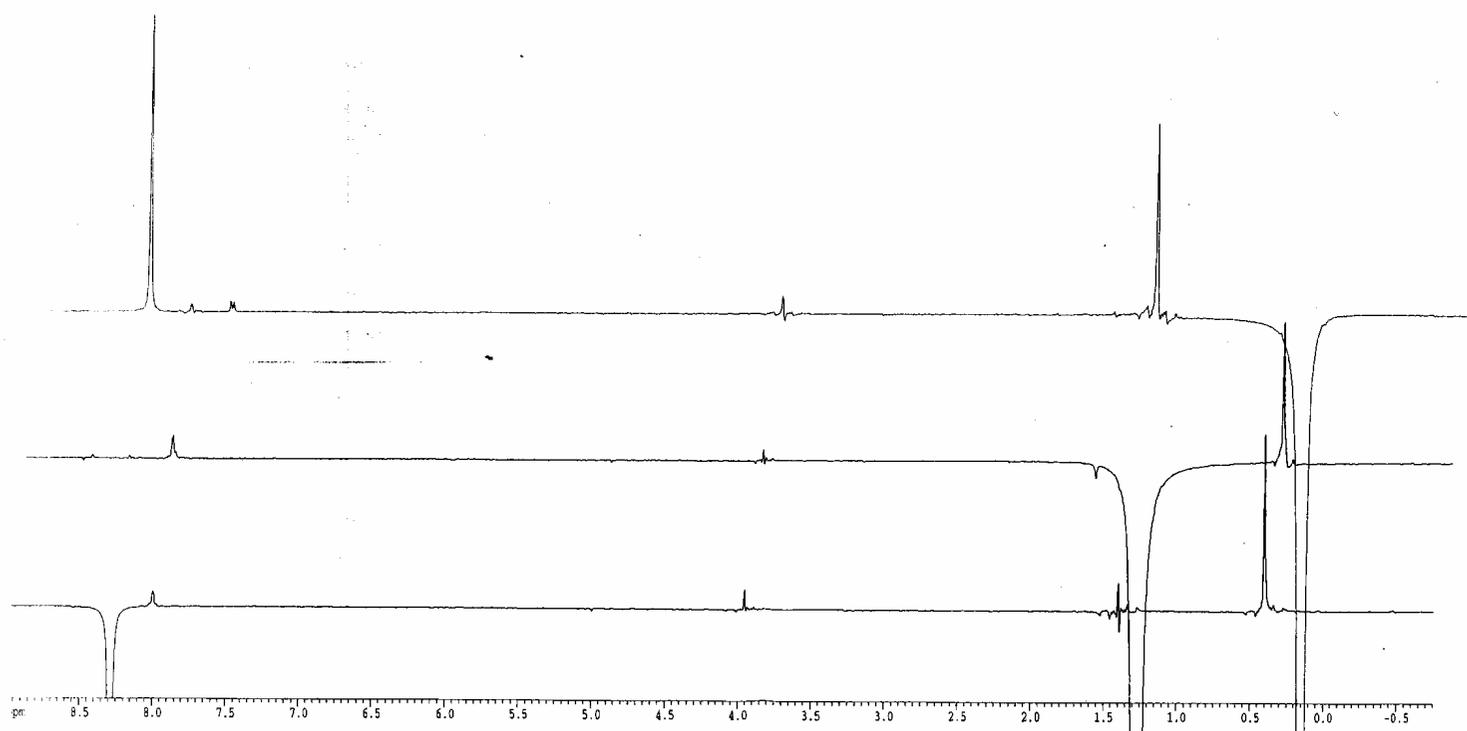
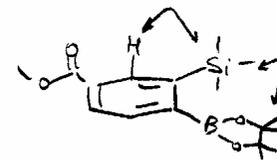
Current Data Parameters
NAME ny12
EXPNO 100
PROCNO 2

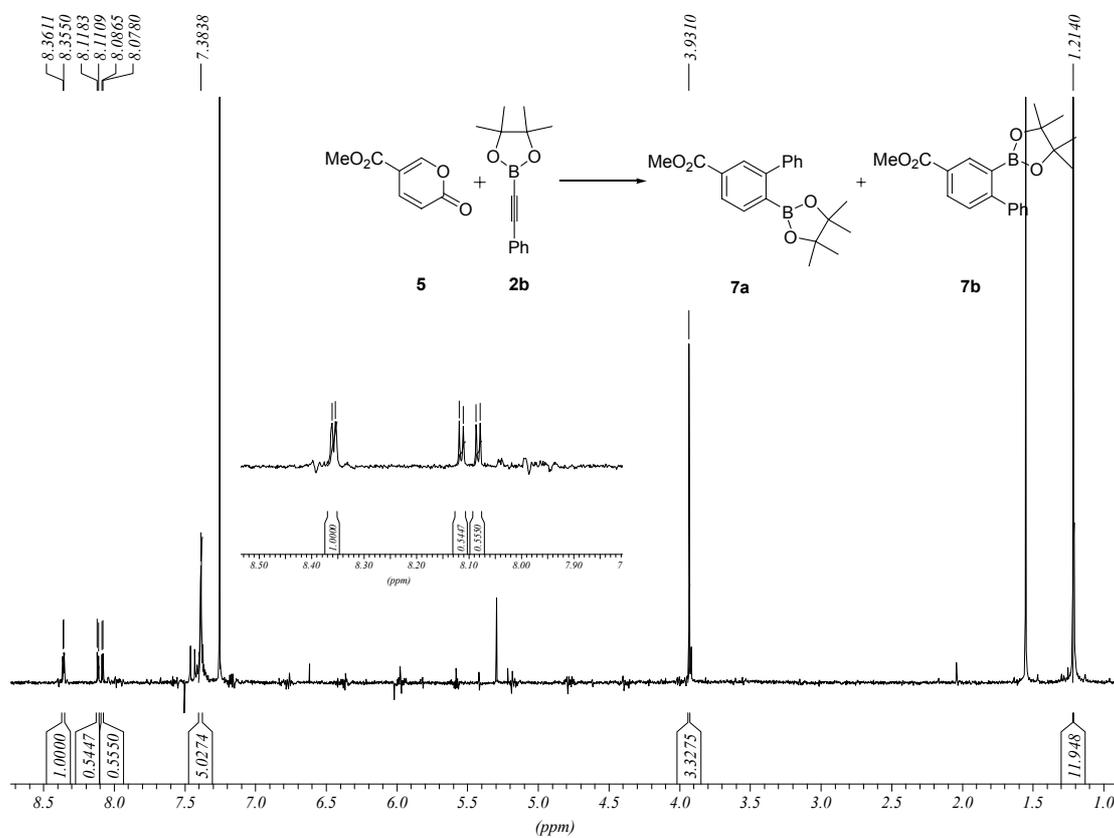
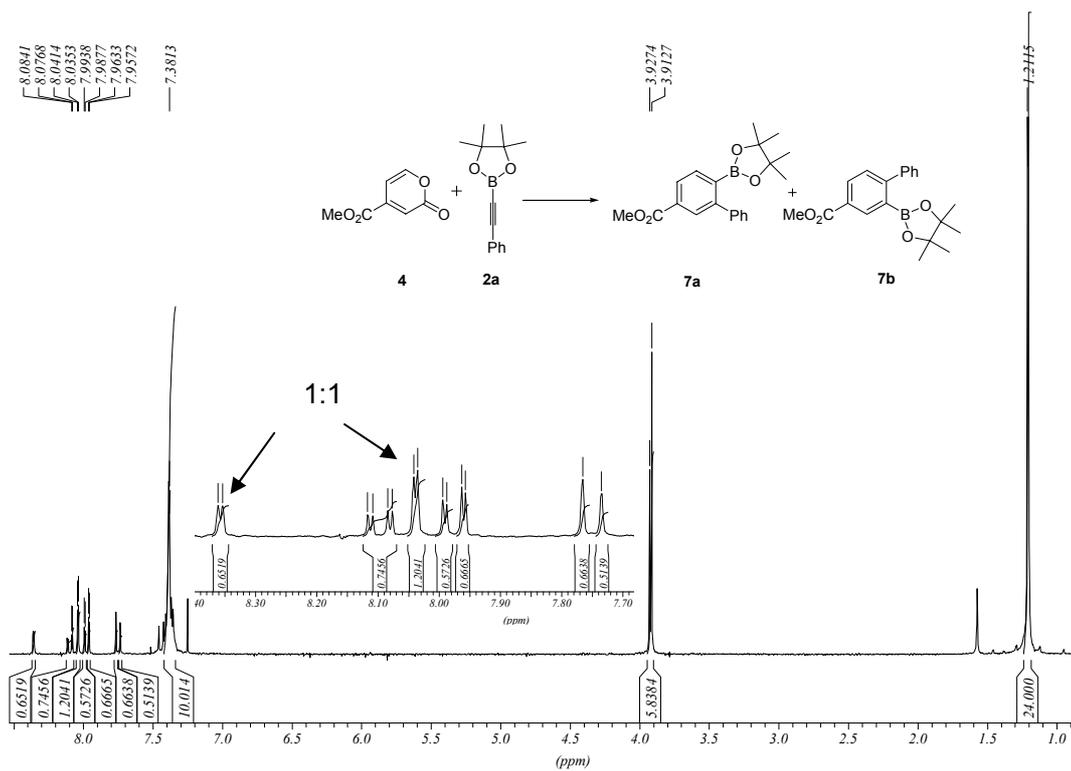
F2 - Acquisition Parameters
Date_ 20040512
Time 11.14
INSTRUM amx400
PROBHD 5 mm Multinu
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 32
DS 4
SFO 8064.516 Hz
FIDRES 0.123055 Hz
AQ 4.0632820 sec
RG 128
DM 62.000 usec
DE 88.57 usec
TE 300.0 K
NUC1 13C
D1 0.1000000 sec
D12 0.0000000 sec
NUC2 1H
L4 160
DQ 0.0500000 sec
F2LIST f2list.1
P1 10.20 usec
SFO1 400.1320007 MHz
NUCLEUS 1H

F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

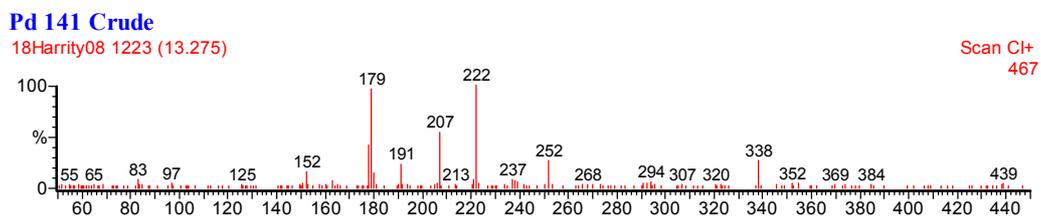
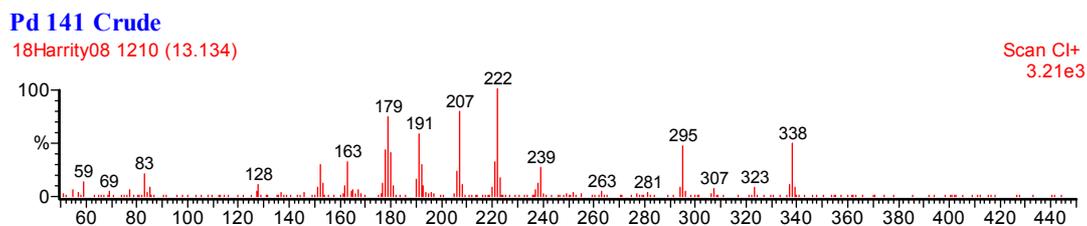
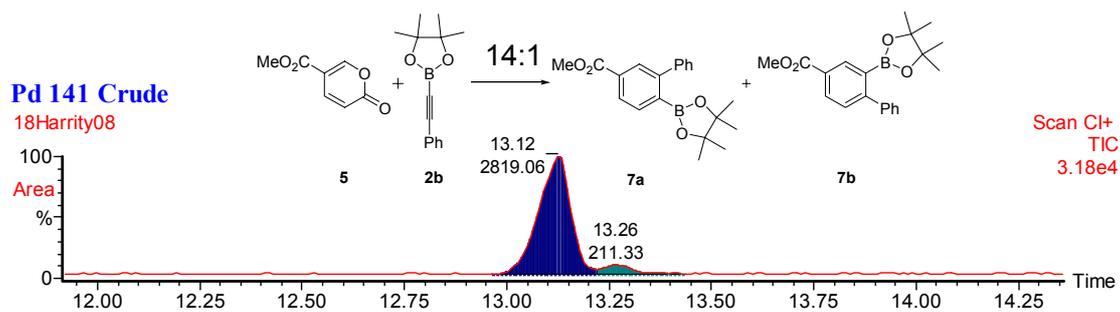
1D NMR plot parameters
CH 39.00 cm
F1 9.000 ppm
F2 3401.17 Hz
F3 -0.750 ppm
F4 -300.10 Hz
PPHM 8.25000 ppm/cm
SFO 400.1320007 MHz

Difference spectra plotted with a Y-gain of 32

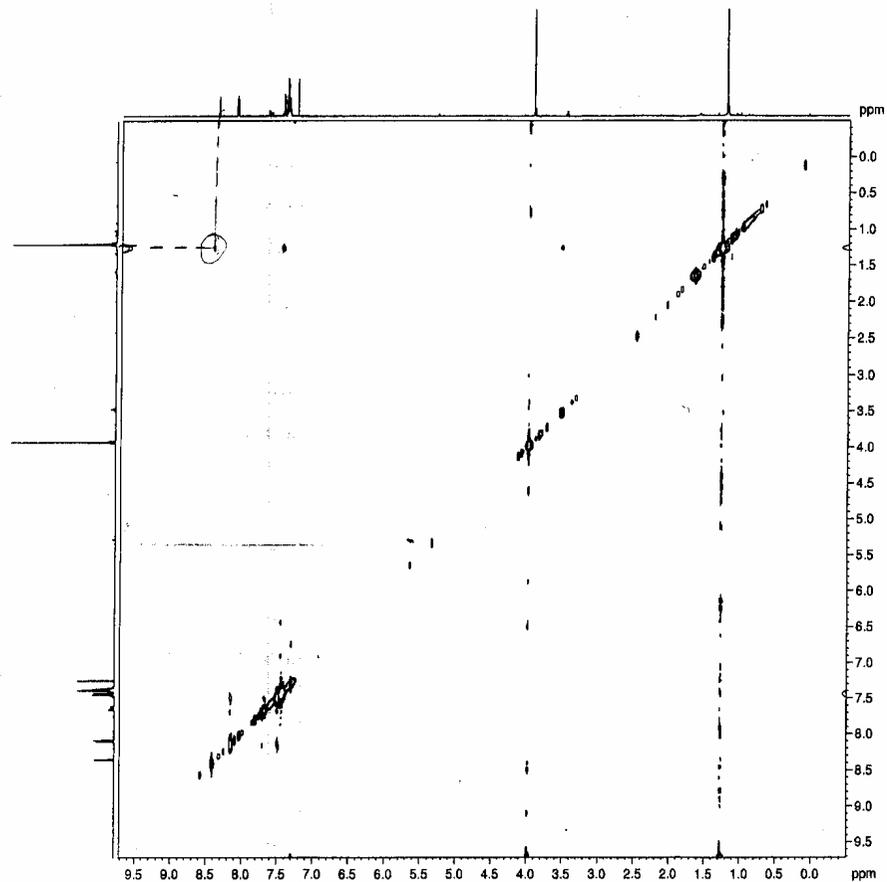




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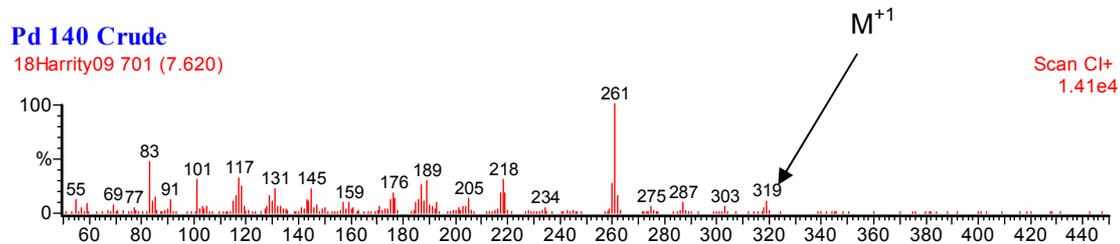
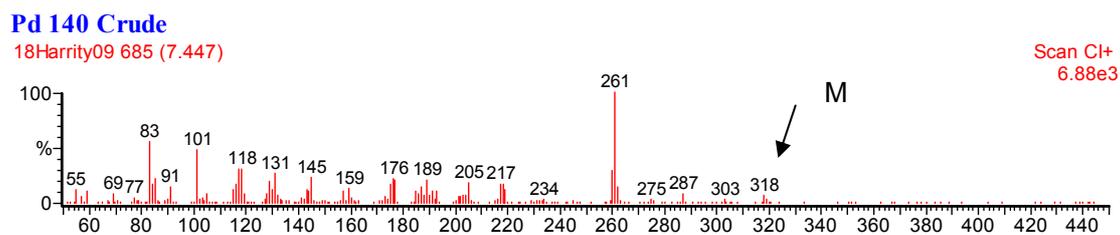
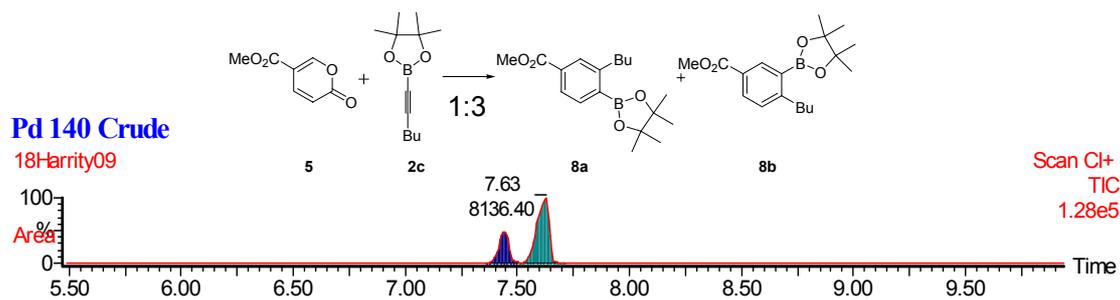
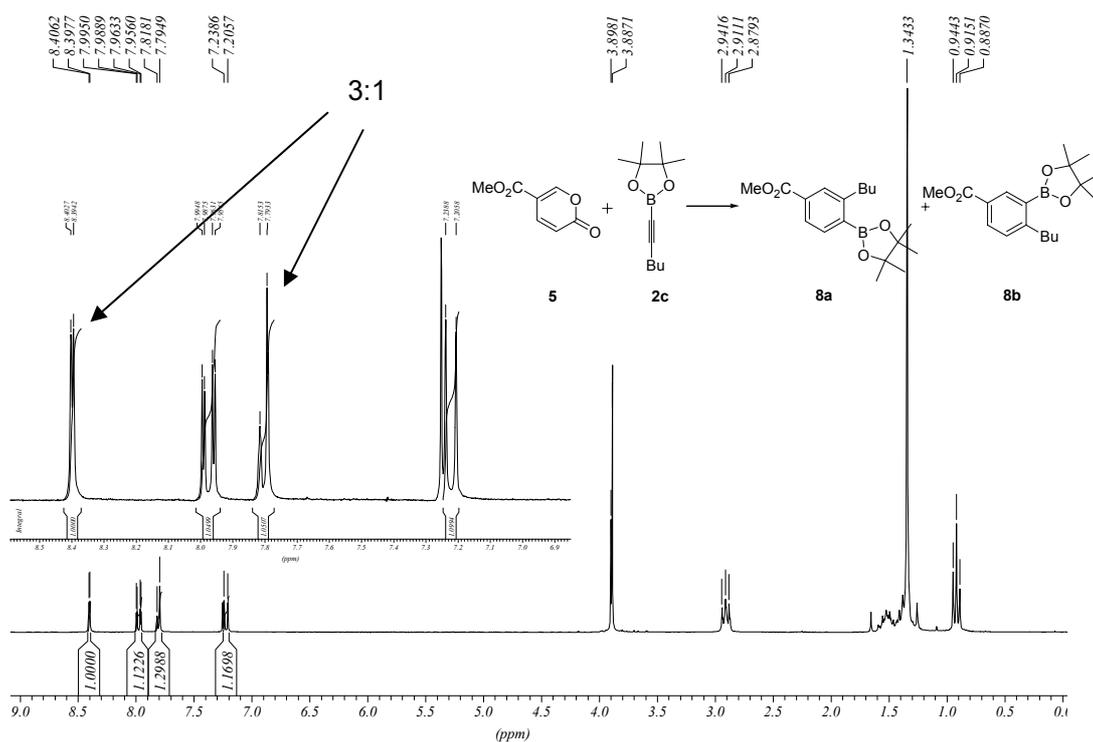


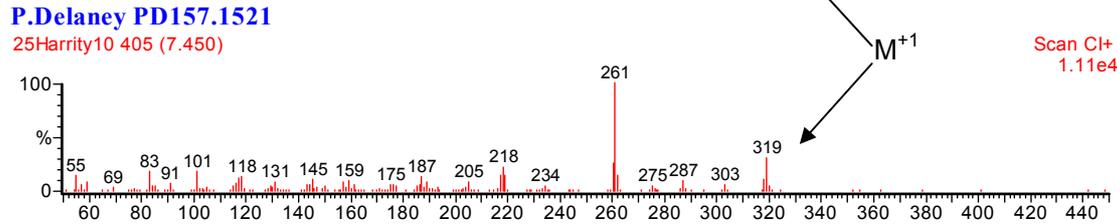
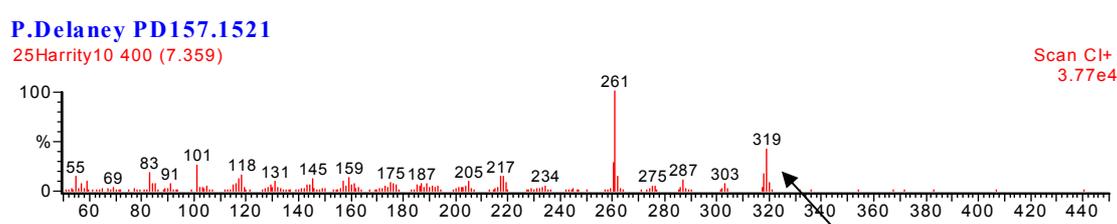
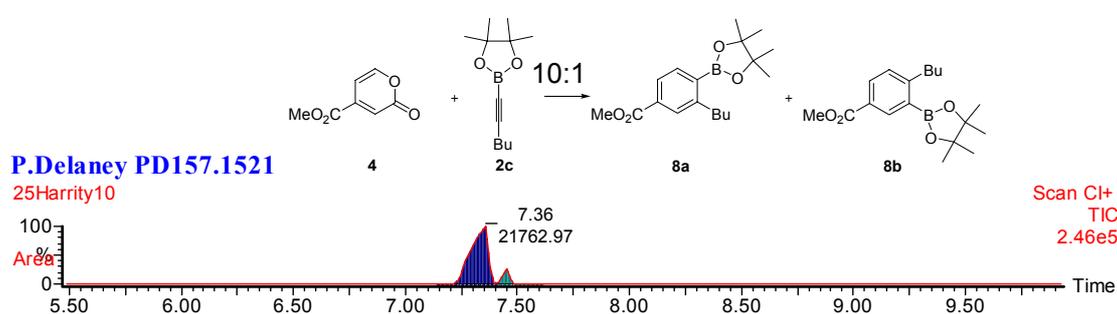
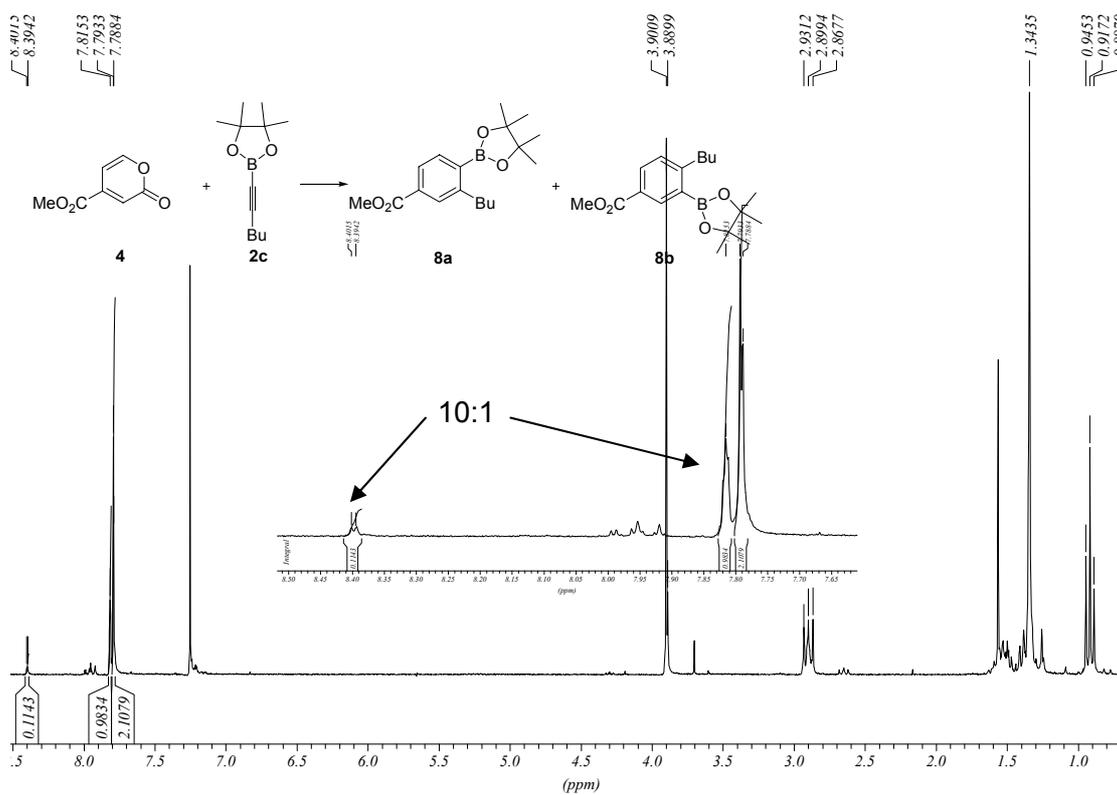
Jane Moore E27 Sample ref: JM 613c in CDC13



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NAME          oc29
EXPNO        4
PROCNO       1
F2 - Acquisition Parameters
Date_        20041229
Time         16.14
INSTRUM      dx500
PROBHD       5 mm BBI 1H-3B
PULPROG      zgpg30
TD           65536
SOLVENT      CDC13
NS           16
DS           4
SWE          5112.475 Hz
FIDRES       2.486325 Hz
AQ           0.2003444 sec
RG           64
DW           97.800 usec
DE           6.00 usec
TE           292.2 K
CO           0.0000000 sec
D1           2.0000000 sec
D8           0.0000001 sec
D9           0.0000000 sec
ZM0          0.0000000 sec
MCRMAT       0.0000000 sec
MCWIND       1.0000000 sec
SOLICNT      128
----- CHANNEL f1 -----
NUC1          1H
P1            7.68 usec
PL1          -3.00 dB
SFO1         500.1323022 MHz
F1 - Acquisition parameters
WDW           3
SSB           0
SF01         500.1323 MHz
FIDRES       19.970404 Hz
SN           10.222 ppm
F2 - Processing parameters
SI           1024
SF           500.1300000 MHz
WDW          EM
SSB          0
LB           0.00 Hz
GB           0
PC           1.00
F1 - Processing parameters
SI           1024
MC2          States-PP1
SF           500.1300000 MHz
WDW          EM
SSB          0
LB           0.00 Hz
GB           0
```

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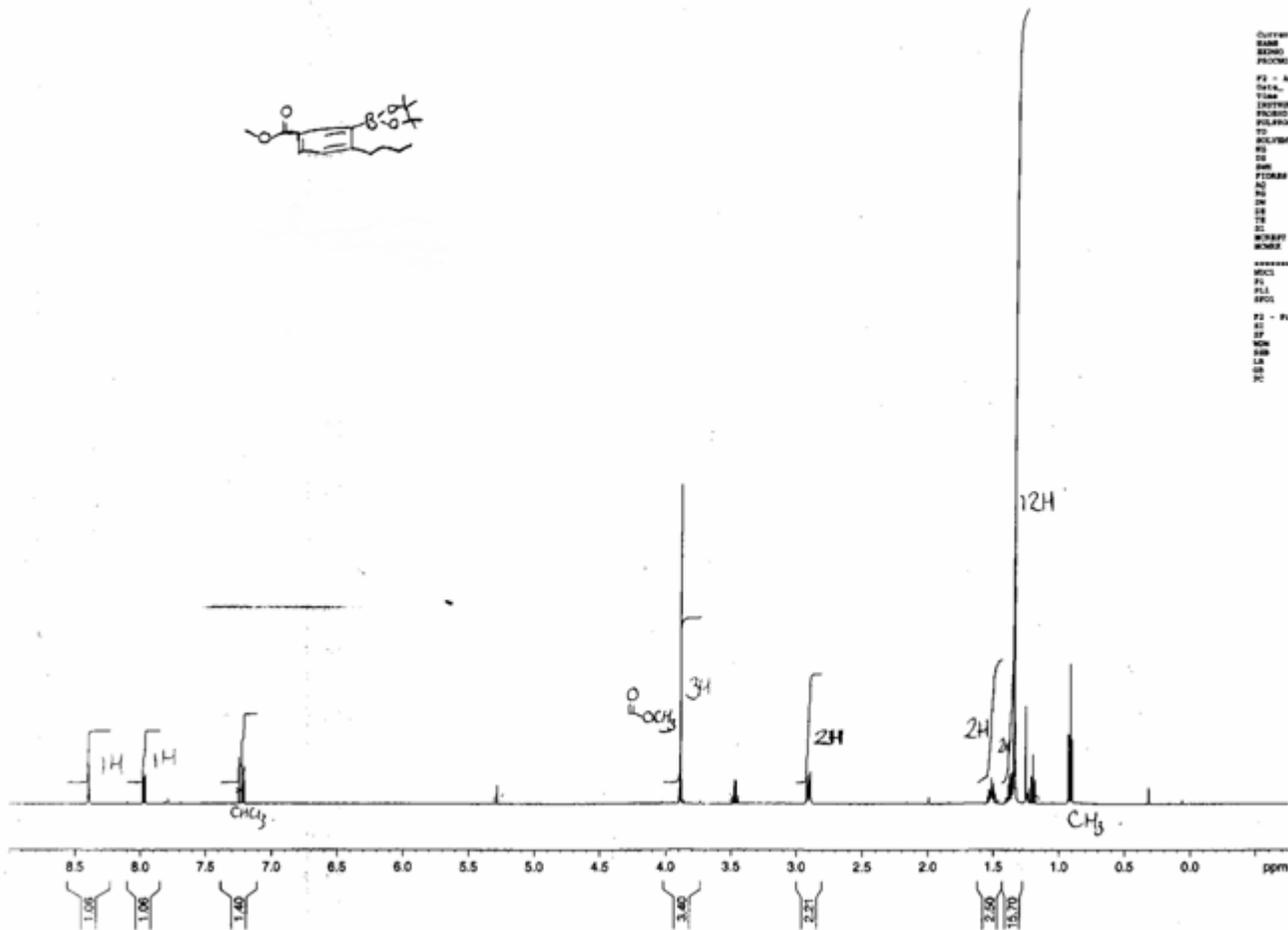




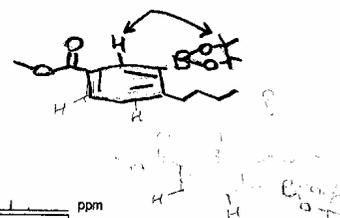
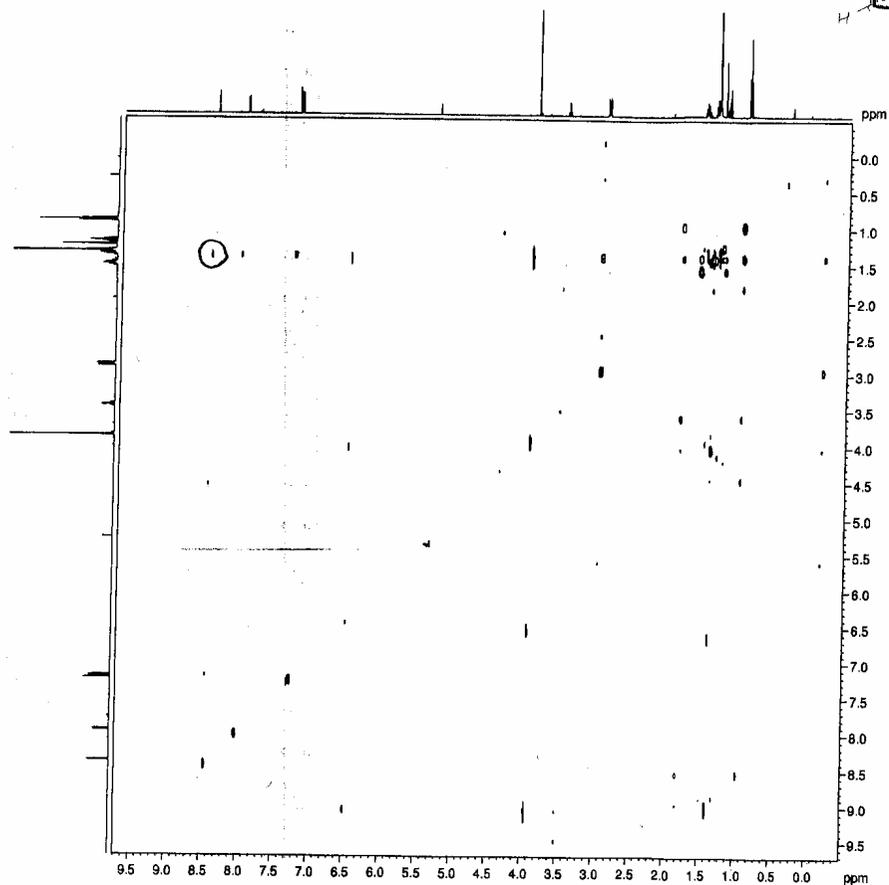
Jane Moore E27 Sample ref. JM 5340 in CDCl3



Current Data Parameters
NAME: JM5340
EXPNO: 1
PROCNO: 1
F2 - Acquisition Parameters
Date_: 20061007
Time: 14.01
INSTRUM: spect
PULPROG: zgpg30
TD: 65536
SOLVENT: CDCl3
NS: 32
DS: 4
SWH: 5995.204 Hz
FIDRES: 0.001480 Hz
AQ: 0.4407324 sec
RG: 100
GB: 0.0000000
PC: 0.0000000
SC: 1.0000000
WBW1: 0.0000000 Hz
WBW2: 0.0100000 Hz
***** CHANNEL f1 *****
NUC1: 13
P1: 7.00 usec
PL1: -2.00 dB
SFO1: 500.137050 MHz
F2 - Processing parameters
SI: 32768
SF: 500.130024 MHz
WDW: EM
SSB: 0
LB: 0.00 Hz
GB: 0
PC: 1.00



Moore E27 Sample ref: JM 534c in CDC13



```
Current Data Parameters
NAME      cc27
EXPNO     1
PROCNO    1

F2 - Acquisition Parameters
Date_     20041027
Time      14.30
INSTRUM   drx500
PROBHD    5 mm BBI 1H-5B
PULPROG   zgpg30
TD        65536
SOLVENT   CDCl3
NS        4
DS        4
SWH        312.475 Hz
FIDRES     0.496322 Hz
AQ         0.2003444 sec
RG         314.4
DM         97.800 usec
DE         6.00 usec
TE         293.1 K
AQ         0.0008802 sec
Q1         2.0000000 sec
Q2         0.1000001 sec
Q3         0.1000001 sec
Q4         0.00019560 sec
RG         0.1000000 sec
MCMRG     1.0000000 sec
STICNT    128

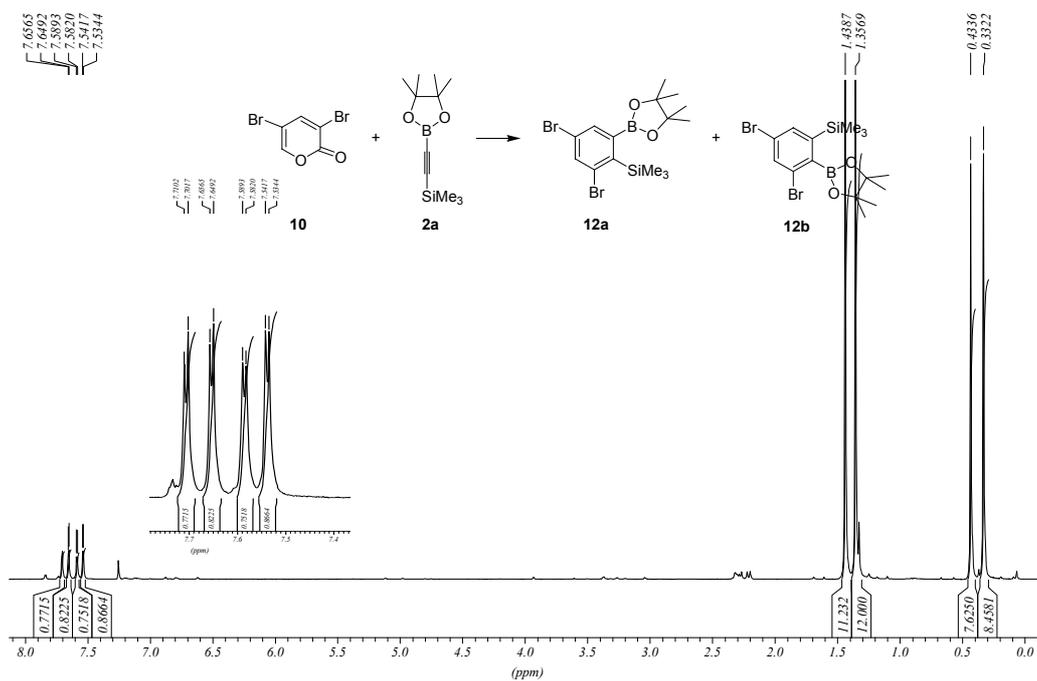
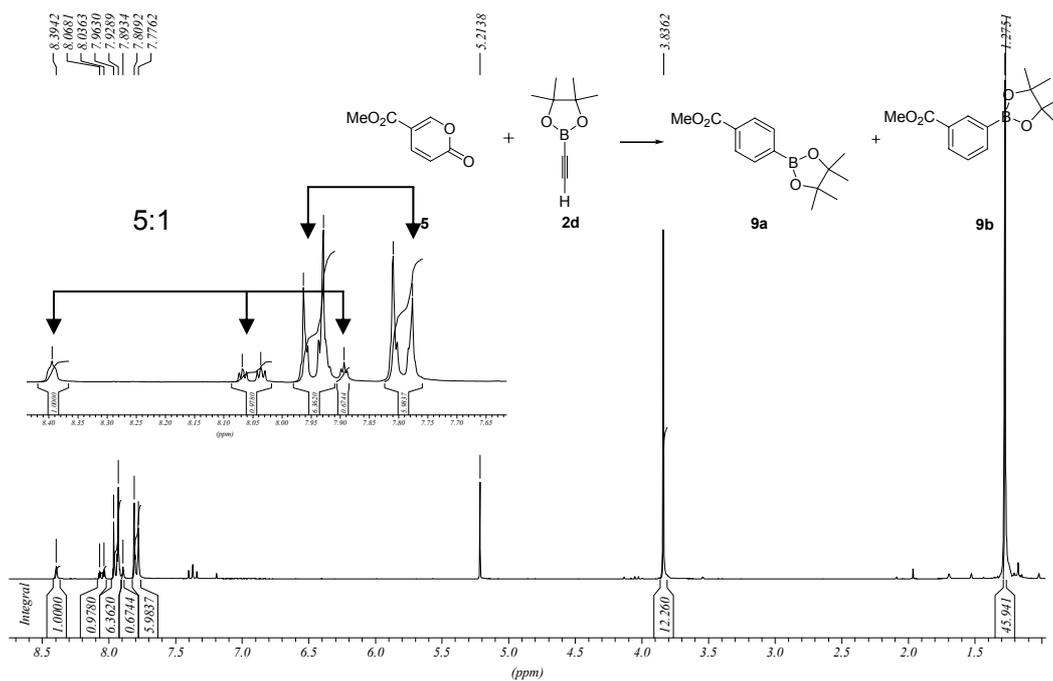
----- CHANNEL f1 -----
NUC1       13H
P1         7.68 usec
PL1        -3.00 dB
SFO1       500.132022 MHz

F1 - Acquisition parameters
ND0        256
SFO1       500.1323 MHz
FIDRES     19.970684 Hz
SW         16.222 ppm
PRMODE     States-TPPI

F2 - Processing parameters
SI         3274
SF         500.1300000 MHz
WDW        QSIW2
SSB        0
GB         0.00 Hz
FC         1.00

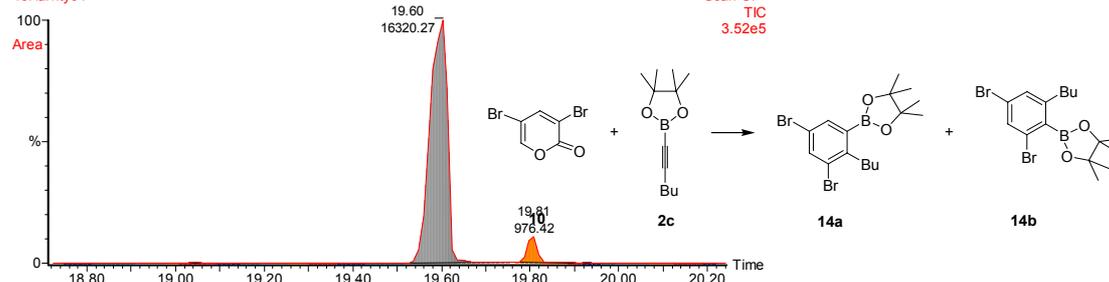
F1 - Processing parameters
SI         1024
MC2        States-TPPI
SF         500.1300000 MHz
WDW        QSIW2
SSB        2
GB         0.00 Hz
FC         0
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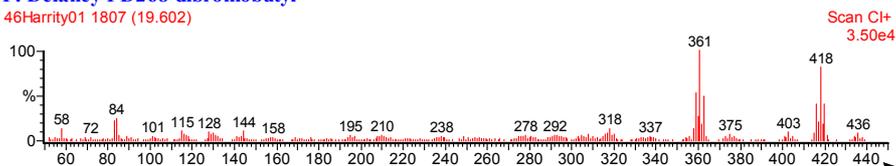
P. Delaney PD268 dibromobutyl

46Harrity01



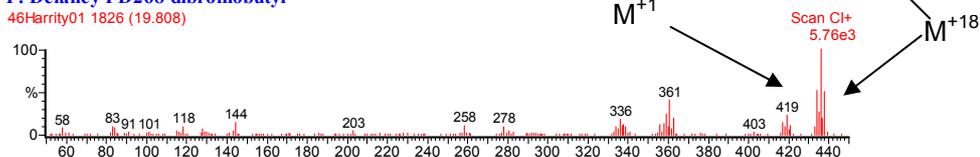
P. Delaney PD268 dibromobutyl

46Harrity01 1807 (19.602)



P. Delaney PD268 dibromobutyl

46Harrity01 1826 (19.808)



M^{+18} = mass ion + NH_3

Patrik Delany E27 Sample ref: PD 282 in CDCl3



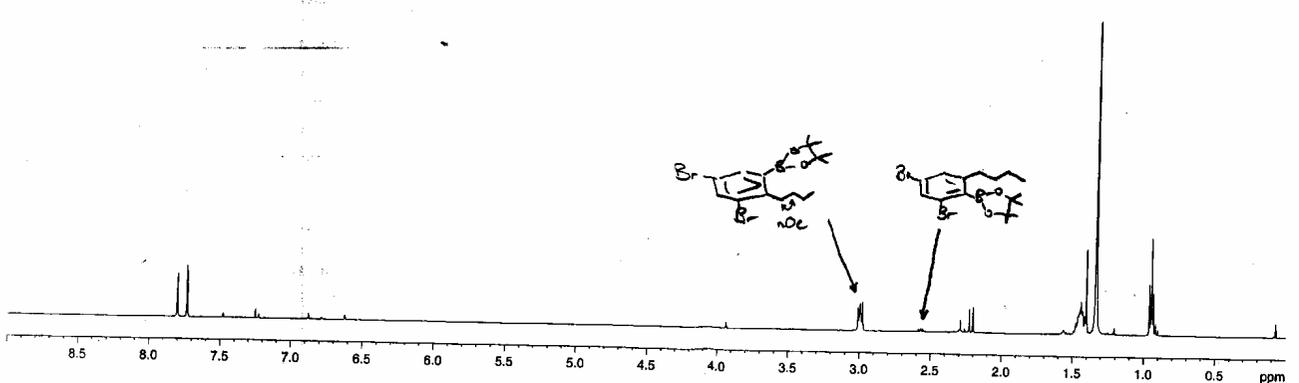
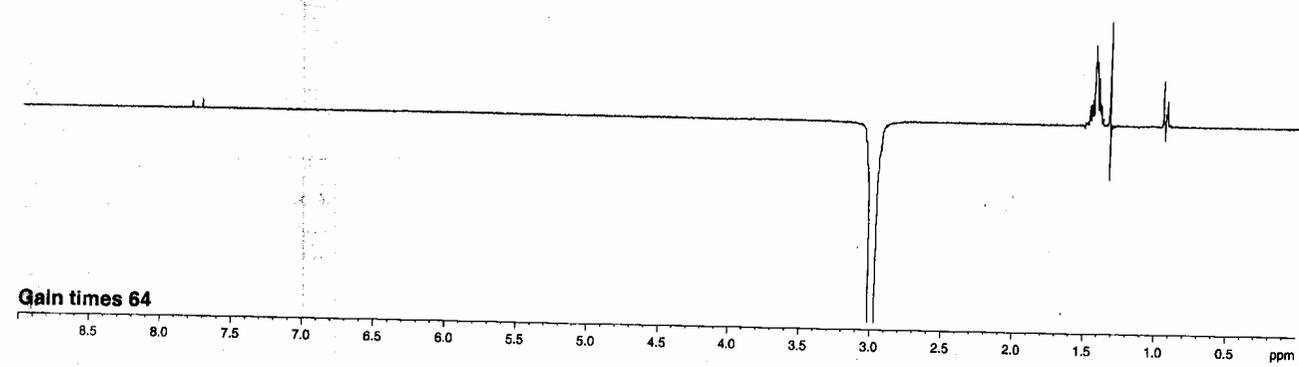
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Current Data Parameters
NAME          PD282
PROCNO       101
PROCNAME

#2 - Acquisition Parameters
Date_        20060516
Time         9.31
INSTRUM      dr2500
PROBHD       5 mm BBI 1H/2H
PULPROG      zgpg30
TD           32768
SOLVENT      DMSO
NS           32
DS           4
SWH          9999.304
FIDRES       0.182959
AQ           2.732801
RG           351.9
DM           60.000
DE           6.00
TE           299.9
D1           2.0000000
D8           0.0000000
D16          0.0000000
E1           0.24879999
MCHRG1       0.0000000
MCHRG2       0.0100000

***** CHANNEL f1 *****
NUC1          1H
P1           14
PL1          7.48
PC1          15.16
PR1          50000.00
PC2          100.00
PL2          -3.00
PC3          500.1100004
PR2          59.10
SFO1         500.130000
SFO2         99.625000
SFO3         999.130000

***** GRADIENT CHANNELS *****
GPRMG1       0.00
GPRMG2       0.00
GPRMG3       0.00
GPRMG4       0.00
GPRMG5       0.00
GPRMG6       0.00
GPRMG7       0.00
GPRMG8       0.00
GPRMG9       0.00
GPRMG10      0.00
GPRMG11      0.00
GPRMG12      0.00
GPRMG13      0.00
GPRMG14      0.00
GPRMG15      0.00
GPRMG16      0.00
GPRMG17      0.00
GPRMG18      0.00
GPRMG19      0.00
GPRMG20      0.00

#2 - Processing parameters
SI           32768
SF           500.1300217
WDW          EM
SSB          0
LB           0.30
GB           0
PC           1.00
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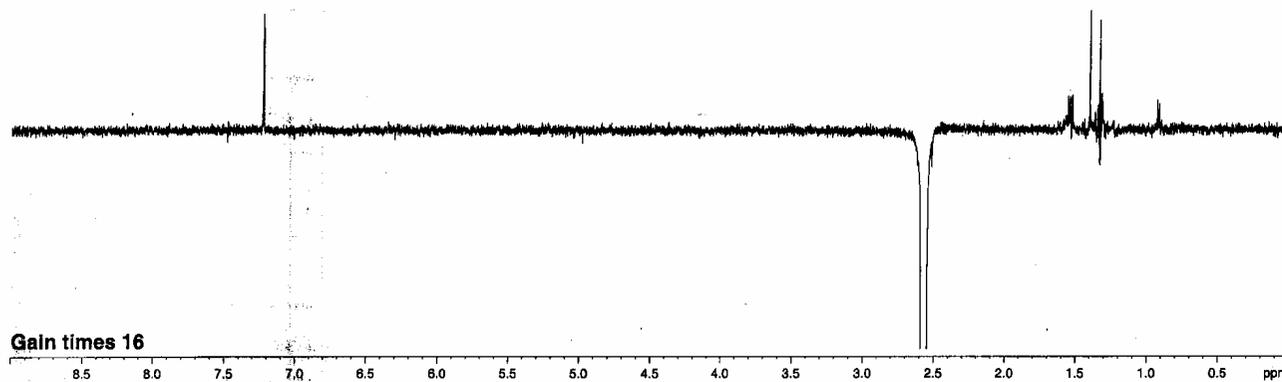


Patrick Delany E27 Sample ref: PD 282 in CDCl3



Current Data Parameters
NAME: m01c
EXPNO: 102
PROCNO: 1

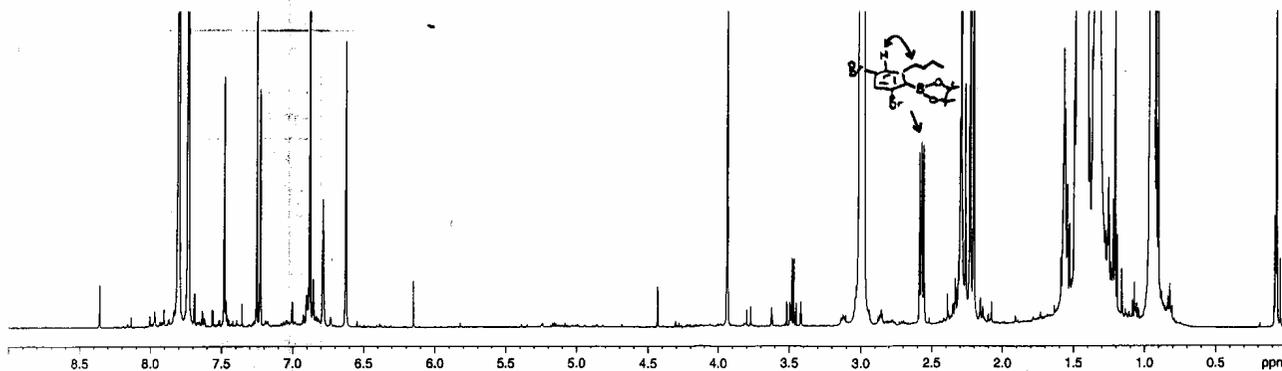
F2 - Acquisition Parameters
Date_: 20060516
Time: 9.38
INSTRUM: spect
PROBHD: 5 mm BBO 1H/13
PULPROG: zgpg30
TD: 32768
SOLVENT: DMSO
NS: 32
DS: 4
SWH: 5999.204
FIDRES: 0.182559
AQ: 2.7329011
RG: 32.0
SR: 82.400
DE: 6.00
TE: 293.2
D1: 3.0000000
D2: 0.5000000
D3: 0.0000000
AQ2: 0.24879999
MCWST: 0.0000000
MCWXR: 0.0100000



***** CHANNEL f1 *****
NUC1: 13C
P1: 7.48
P2: 19.16
PL1: 50000.00
PL2: 100.00
PL3: -1.00
SFO1: 500.1300000
SFO2: 89.80
SFO3: 0.0000000
SFOF3: -1192.89

***** GRADIENT CHANNEL *****
GPRAM1: 2182.150
GPRAM2: 2182.150
GPT1: 0.00
GPT2: 0.00
GPT3: 0.00
GPT4: 0.00
GPT5: 0.00
GPT6: 0.00
GPT7: 0.00
GPT8: 0.00
GPT9: 0.00
GPT10: 0.00

F2 - Processing parameters
SI: 32768
SF: 500.1300000
WDW: EM
SSB: 0
LA: 0.00
GB: 0
PC: 1.00



Patrick Delany E27 Sample ref. PD 262 in CDCl3



Current Data Parameters
NAME: M16
EXPNO: 103
PROCNO: 1
F2 - Acquisition Parameters
Date_: 20060516
Time: 7.34
INSTRUM: dr2500
PROBHD: 5 mm BBI 1H-13
PULPROG: zgpg30
TD: 32768
SOLVENT: DMSO
NS: 32
DS: 4
SWH: 5994.204
FIDRES: 0.182955
AQ: 2.7329011
RG: 38.9
DM: 83.400
DE: 16.00
TE: 303.2
D1: 2.00000000
DE: 0.80000000
D11: 0.00000000
dS0: 0.24878989
MCHRES: 2.00000000
MCHW: 0.01000000
***** CHANNEL f1 ****
NUC1: 13C
P1: 7.48
SFO: 101.626120
P13: 10000.00
PL3: 120.00
PC1: 1.00
SFO1: 100.62612004
SFO2: 400.14701500
SFO3: 101.62612004
SFO4: 113.691
***** GRADIENT CHANNEL *****
OPM1: SINE 100
OPM2: SINE 100
OPM3: 0.00
OPM4: 0.00
OPM5: 0.00
OPM6: 18.00
OPM7: 40.00
P16: 1000.00
F2 - Processing parameters
SI: 32768
SF: 100.62612004
WDW: EM
SSB: 0
GB: 0
PC: 1.00

