Supplementary Material

An Alkynylboronate Cycloaddition Strategy to Functionalised Benzyne Precursors.

James D. Kirkham,† Patrick M. Delaney,† George J. Ellames,‡ Eleanor C. Row,‡ Joseph P. A. Harrity*,†

†*Department of Chemistry, University of Sheffield, Sheffield, S3 7HF, U. K. and* ‡*Sanofi Aventis, Willowburn Avenue, Alnwick, NE66 2JH, U. K.*

j.harrity@sheffield.ac.uk

General Procedures

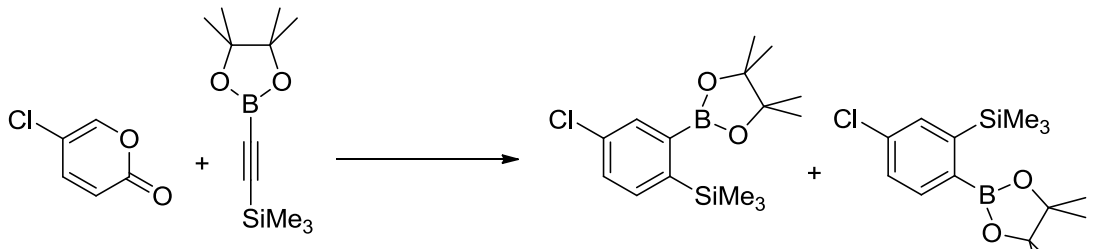
Infrared (IR) Spectra were recorded on a Perkin Elmer Paragon 100 FTIR spectrophotometer, v_{max} in cm^{-1}. Samples were recorded as thin films using sodium chloride plates, as a DCM solution. Bands are characterised as broad (br), strong (s), medium (m), and weak (w). ^{1}H NMR spectra were recorded 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 ($CHCl_3$: δ7.27ppm). 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 ($CDCl_3$: δ77.0ppm). 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.

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 alkynylboronates[1] and pyranones[2] were prepared according to established procedures. Coumalic acid and methyl coumalate were purchased from Aldrich chemical co. and used as received. 3-Bromo-methyl coumalate was prepared as previously reported.[3] 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 silica (0.2 mm, Merck DC-alufolien Kieselgel 60 F254) which were developed using standard visualizing agents: Ultraviolet light or potassium permanganate.

General Procedure 1: The cycloaddition of halo-pyranones with trimethylsilylalkynyl boronic ester

A mixture of the pyranone (0.2 mmol) and trimethylsilylalkynylboronate (0.4 mmol) in mesitylene (0.2 mL) was heated at 155 ^{o}C and stirred for 16 h under N_2. The product was purified by flash column chromatography (starting with petroleum ether, ending with 10% ethyl acetate in petroleum ether).

Synthesis of (4-chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl) trimethylsilane 10a and (5-chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) phenyl)trimethylsilane 10b



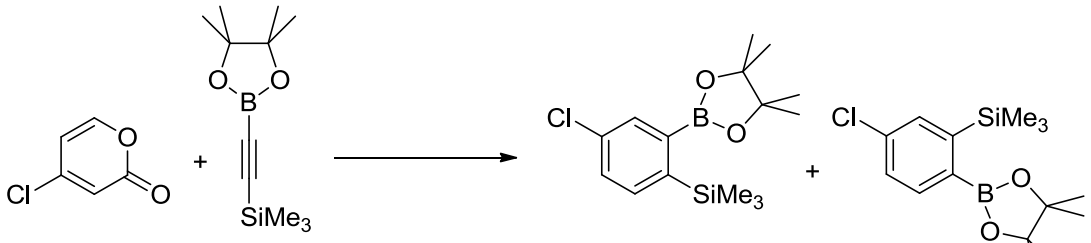
1 **9** **10a** **10b**

[1] H.C. Brown, N.G. Bhat, M. Srebink, *Tetrahedron Lett*, **1982**, *29*, 2631.
[2] (a) Afarinkia, K.; Bearpark, M.J.; Ndibwami, A. *J. Org. Chem.* **2005**, *70*, 1122. (b) Afarinkia, K.; Bearpark, M.J.; Ndibwami, A. *J. Org. Chem.* **2003**, *68*, 7158. (c) Cho, C.-G.; Park, J.-S.; Jung, I.-H.; Lee, H. *Tetrahedron Lett.* **2001**, *42*, 1065. (d) Posner, G.H.; Afarinkia, K.; Dai, H. *Org. Synth.* **1995**, *73*, 231. (e) Kvita, V.; Sauter, H. *Helv. Chim. Acta* **1990**, *73*, 883. (f) Ashworth, I.W.; Bowden, M.C.; Dembofsky, B.; Levin, D.; Moss, W.; Robinson, E.; Szczur, N.; Virica, J. *Org. Process Res. Dev.* **2003**, *7*, 74.
[3] Delaney, P.M.; Browne, D.L.; Adams, H.; Plant, A.; Harrity, J.P.A. *Tetrahedron* **2008**, *64*, 866.

Using General Procedure 1, with pyranone **1** (25 mg, 0.19 mmol), the product was isolated as an inseparable mixture of compounds **10a** and **10b** (4:3 ratio), as a clear oil, 41 mg, 70% yield.

^{1}H NMR (250 MHz, $CDCl_3$): **10a**: δ 0.35 (9H, s, Si-C*H*$_3$), 1.38 (12H, s, C*H*$_3$), 7.38 (1H, dd, *J* = 2.0, 8.0 Hz, Ar-*H*), 7.55 (1H, d, *J* = 8.0 Hz, Ar-*H*), 7.89 (1H, d, *J* = 2.0 Hz, Ar-*H*); **10b**: δ 0.37 (9H, s, Si-C*H*$_3$), 1.38 (12H, s, C*H*$_3$), 7.34 (1H, dd, *J* = 2.0, 8.0 Hz, Ar-*H*), 7.57 (1H, d, *J* = 2.0 Hz, Ar-*H*), 7.87 (1H, d, *J* = 8.0 Hz, Ar-*H*). ^{13}C NMR (62.9 MHz, $CDCl_3$): **10a/b**: δ 0.0, 0.1, 24.6 (x2), 83.6, 86.9, 127.4, 129.2, 130.7, 132.3, 133.8, 135.0, 135.4, 135.5, 136.3, 137.3. FTIR (CH_2Cl_2, thin film): 2980 (s), 1570 (m), 1388 (s), 1340 (s), 1145 (s), 845 (s) cm^{-1}. HRMS calculated for $C_{15}H_{24}B^{35}ClO_2Si$ (EI^+): 310.1327. Found: 310.1335.

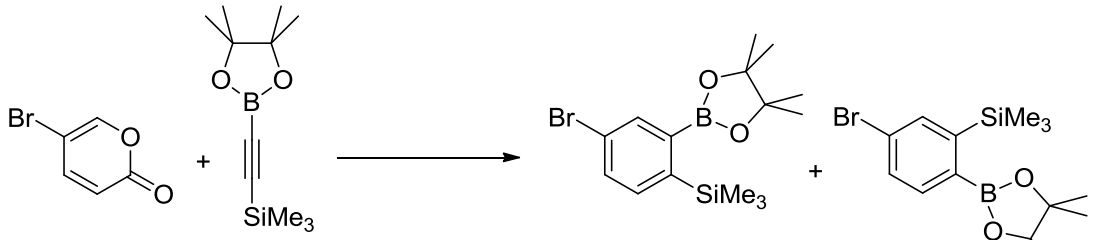
Synthesis of (4-chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl) trimethylsilane 10a and (5-chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) phenyl)trimethylsilane 10b



2 **9** **10a** **10b**

Using General Procedure 1, with pyranone **2** (25 mg, 0.19 mmol), the product was isolated as an inseparable mixture of compounds **10a** and **10b** (3:5 ratio), as a clear oil, 40 mg, 70% yield. The mixture provided the same spectroscopic data as for the compounds above.

Synthesis of (4-bromo-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl) trimethylsilane 11a and (5-bromo-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) phenyl)trimethylsilane 11b

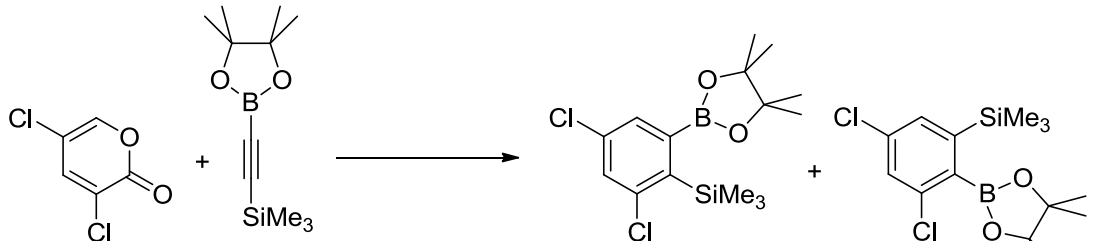


3 **9** **11a** **11b**

Using General Procedure 1, with pyranone **3** (50 mg, 0.29 mmol), the product was isolated as an inseparable mixture of compounds **11a** and **11b** (3:2 ratio), as a clear oil, 82 mg, 80% yield.

^{1}H NMR (400 MHz, $CDCl_3$): **11 a or b**: δ 0.36 (9H, s, Si-C*H*$_3$), 1.38 (12H, s, C*H*$_3$), 7.50 (1H, m, Ar-*H*), 7.54 (1H, m, Ar-*H*), 8.06 (1H, d, *J* = 2.0 Hz, Ar-*H*); **11 a or b**: δ 0.38 (9H, s, Si-C*H*$_3$), 1.38 (12H, s, C*H*$_3$), 7.48 (1H, m, Ar-*H*), 7.74 (1H, d, *J* = 2.0 Hz, Ar-*H*), 7.80 (1H, d, *J* = 8.0 Hz, Ar-*H*). ^{13}C NMR (62.9 MHz, $CDCl_3$): **11a/b:** δ 0.5 (x2), 25.0 (x2), 84.0, 84.2, 123.4, 125.9, 130.8, 132.6, 136.0, 137.0, 137.9, 138.7, 145.6, 150.3. FTIR (CH_2Cl_2, thin film): 2980 (s), 2977 (w), 1454 (w) cm^{-1}. HRMS calculated for $C_{15}H_{24}B^{79}BrO_2Si$ (EI^+): 355.1504. Found: 355.1507.

Synthesis of 2-(2,4-dichloro-6-trimethylsilanyl-phenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane 12a and 2-(3,5-dichloro-2-trimethylsilanyl-phenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane 12b



4 **9** **12a** **12b**

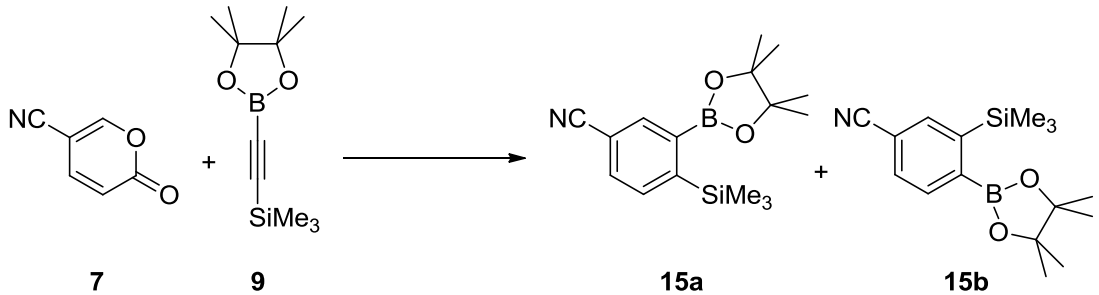
Using General Procedure 1, with pyranone **4** (25 mg, 0.15 mmol), the product was isolated as an inseparable mixture of compounds **12a** and **12b** (1:1 ratio), as a clear oil, 37 mg, 71% yield.

^{1}H NMR (250 MHz, $CDCl_3$): **12a/b**: δ 0.36 (9H, s, Si-CH_3), 0.43 (9H, s, Si-CH_3), 1.39 (12H, s, CH_3), 1.45 (12H, s, CH_3), 7.34 – 7.44 (4H, m, Ar-*H*). ^{13}C NMR (62.9 MHz, $CDCl_3$): **12a/b**: δ 0.0, 1.7, 25.3, 25.8, 84.6, 84.9, 113.2, 115.6, 119.1, 128.7, 130.3, 131.9 (x2), 135.0, 135.3, 138.7. FTIR (CH_2Cl_2, thin film): 2981 (s), 1562 (m), 1318 (s), 1142 (s), 1050 (m), 846 (s) cm^{-1}. HRMS calculated for $C_{15}H_{23}B^{35}Cl_2O_2Si$ (EI$^+$): 344.0937. Found: 344.0932.

General Procedure 2: The cycloaddition of nitrile-pyranones with trimethylsilyl alkynyl boronic ester

A mixture of the pyranone (0.2 mmol) and trimethylsilyl alkynyl boronate (0.4 mmol) in *o*-dichlorobenzene (0.2 mL) was heated at 175 ^{o}C and stirred for 18 h under N_2. The product was purified by flash column chromatography (starting with petroleum ether, ending with 10% ethyl acetate in petroleum ether).

Synthesis of 3-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-4-trimethylsilanyl-benzonitrile 15a and 4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-3-trimethylsilanyl-benzonitrile 15b



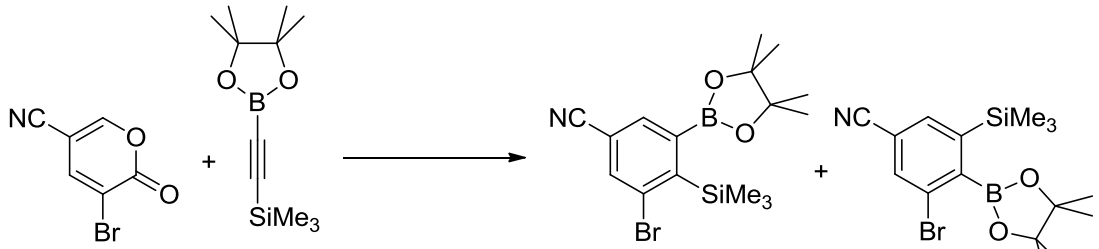
7 **9** **15a** **15b**

Using General Procedure 2, with pyranone **7** (25 mg, 0.21 mmol), the product was isolated as an inseparable mixture of compounds **15a** and **15b** (1:1 ratio), as a clear oil, 62 mg, 99% yield.

^{1}H NMR (250 MHz, $CDCl_3$): **15a/b**: δ 0.37 (18H, s, Si-CH_3), 1.38 (24H, s, CH_3), 7.60 – 7.73 (3H, m, Ar-*H*), 7.85 (1H, d, *J* = 1.0 Hz, Ar-*H*), 7.98 (1H, d, *J* = 7.5 Hz, Ar-*H*), 8.17 (1H, d, *J* = 1.0 Hz, Ar-*H*). ^{13}C NMR (62.9 MHz, $CDCl_3$): **15a/b**: δ 0.0, 0.1, 24.7 (x2), 84.3 (x2), 111.6, 113.1, 118.8, 119.1, 130.6, 132.1, 134.3, 135.8, 137.0, 138.7, 148.4, 153.4. FTIR (CH_2Cl_2, thin film): 2980 (s), 2229 (s), 1342 (s), 1143 (s), 1053 (m), 843 (s) cm^{-1}. HRMS calculated for $C_{16}H_{24}BNO_2Si$ (EI$^+$): 302.1748. Found: 302.1735.

Synthesis of **15a** and **15b** was also performed on gram scale: Using General Procedure 2, with pyranone **7** (0.50 g, 4.13 mmol), the product was isolated as an inseparable mixture of compounds **15a** and **15b** (1:1 ratio), as a clear oil, 1.28 g, quant.

Synthesis of 3-bromo-5-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-4-trimethylsilanyl-benzonitrile 16a and 3-bromo-4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-5-trimethylsilanyl-benzonitrile 16b



8 **9** **16a** **16b**

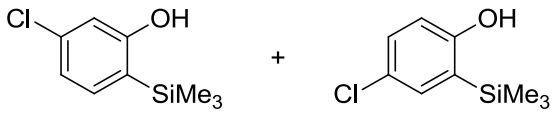
Using General Procedure 2, with pyranone **8** (25 mg, 0.13 mmol), the product was isolated as an inseparable mixture of compounds **16a** and **16b** (1:1 ratio), as a clear oil, 46 mg, 96% yield.

^{1}H NMR (250 MHz, $CDCl_3$): **16a/b**: δ 0.38 (9H, s, Si-CH_3), 0.48 (9H, s, Si-CH_3), 1.39 (12H, s, CH_3), 1.48 (12H, s, CH_3), 7.71 (1H, d, *J* = 1.5 Hz, Ar-*H*), 7.75 (1H, d, *J* = 1.5 Hz, Ar-*H*), 7.77 (1H, d, *J* = 1.5 Hz, Ar-*H*), 7.81 (1H, d, *J* = 1.5 Hz, Ar-*H*). ^{13}C NMR (62.9 MHz, $CDCl_3$): **16a/b**: δ 0.0, 1.9, 25.5, 26.1, 85.1, 85.6, 113.5, 113.8, 117.6, 117.9, 127.9, 131.3, 131.5, 134.8, 135.2, 135.3, 136.5, 149.0. FTIR (CH_2Cl_2, thin film): 2981 (s), 2232 (m), 1332 (s), 1140 (s), 1048 (m), 847 (s) cm^{-1}. HRMS calculated for $C_{16}H_{23}B^{79}BrNO_2Si$ (EI^+): 379.0774. Found: 379.0777.

General Procedure 3: The oxidation of aromatic boronic esters

To a mixture of the aromatic boronic ester (0.2 mmol) dissolved in ethanol (8 mL), was added Na_2CO_3 (0.2 mmol). To this mixture 30% w/v H_2O_2 (2 mL) was added dropwise. The reaction was stirred at r.t.. Upon completion of reaction, 20 mL H_2O was added, and the product extracted from DCM (3 x 20 mL). The organic layers were combined and dried over $MgSO_4$, then concentrated in vacuo. The product was purified by flash column chromatography (eluting solvent 10 % ethyl acetate in petroleum ether).

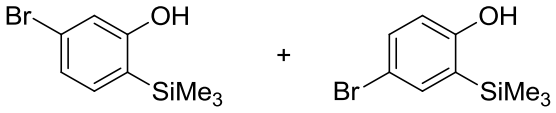
Synthesis of 5-chloro-2-trimethylsilanyl-phenol and 4-chloro-2-trimethylsilanyl-phenol



Using General Procedure 3, with **10a,b** (63 mg, 0.20 mmol), the product was isolated as an inseparable mixture of compounds (5:3 ratio) as a clear oil, 30 mg, 75 % yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.32 (3.4H, s, Si-C*H*$_3$), 0.33 (5.6H, s, Si-C*H*$_3$), 4.87 (0.6H, br s, O*H*), 4.98 (0.4H, br s, O*H*), 6.63 (0.6H, d, *J* = 8.5 Hz, Ar-*H*), 6.72 (0.4H, d, *J* = 2.0 Hz, Ar-*H*), 6.94 (0.4H, dd, *J* = 2.0, 8.0 Hz, Ar-*H*), 7.19 (0.6H, dd, *J* = 2.5, 8.5 Hz, Ar-*H*), 7.28 – 7.30 (1H, m, Ar-*H*). ^{13}C NMR (100.6 MHz, $CDCl_3$): -0.7, -0.6, 115.2, 116.3, 121.2, 124.4, 126.1, 128.5, 130.6, 135.2, 136.3, 136.6, 159.1, 161.3. FTIR (CH_2Cl_2, thin film): 3425 (br, s), 2956 (m), 1589 (m), 1479 (m), 1381 (s), 840 (s) cm^{-1}. HRMS calculated for $C_9H_{14}{}^{35}ClOSi$ (M^+): 200.0424. Found: 200.0428.

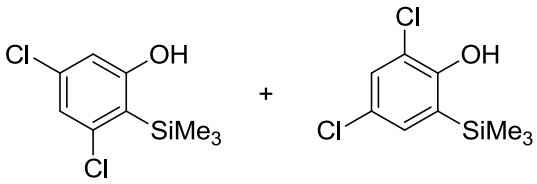
Synthesis of 5-bromo-2-trimethylsilanyl-phenol and 4-bromo-2-trimethylsilanyl-phenol



Using General Procedure 3, with **11a,b** (130 mg, 0.37 mmol), the product was isolated as an inseparable mixture of compounds (3:2 ratio) as a clear oil, 67 mg, 75 % yield.

^{1}H NMR (250 MHz, $CDCl_3$): δ 0.33 (5.4H, s, Si-C*H*$_3$), 0.34 (3.6H, s, Si-C*H*$_3$), 5.01 (0.6H, br s, O*H*), 5.13 (0.4H, br s, O*H*), 6.59 (0.4H, d, *J* = 8.5 Hz, Ar-*H*), 6.88 (0.6H, d, *J* = 1.5 Hz, Ar-*H*), 7.10 (0.6H, dd, *J* = 1.5, 8.0 Hz, Ar-*H*), 7.24 (0.6H, d, *J* = 8.0 Hz, Ar-*H*), 7.34 (0.4H, dd, *J* = 2.0, 8.5 Hz, Ar-*H*), 7.45 (0.4H, d, *J* = 2.0 Hz, Ar-*H*). ^{13}C NMR (100.6 MHz, $CDCl_3$): -0.7, -0.6, 113.8, 116.9, 118.1, 124.1, 124.4, 125.0, 129.3, 133.6, 136.9, 138.1, 160.0, 161.4. FTIR (CH_2Cl_2, thin film): 3347 (br, s), 2956 (m), 2232 (s), 1588 (s), 1401 (s), 842 (s) cm^{-1}. HRMS calculated for $C_9H_{13}{}^{79}BrOSi$ (EI^+): 243.9919. Found: 243.9925.

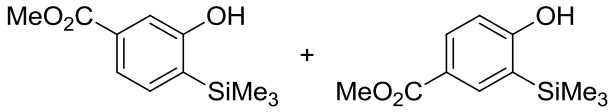
Synthesis of 3,5-dichloro-2-trimethylsilanyl-phenol and 2,4-dichloro-6-trimethylsilanyl-phenol



Using General Procedure 3, with **12a,b** (123 mg, 0.36 mmol), the product was isolated as an inseparable mixture of compounds (1:1 ratio) as a clear oil, 56 mg, 95 % yield.

^{1}H NMR (250 MHz, $CDCl_3$): δ 0.33 (9H, s, Si-C*H*$_3$), 0.46 (9H, s, Si-C*H*$_3$), 4.70 – 6.23 (2H, br, O*H*), 6.65 (1H, d, *J* = 2.0 Hz, Ar-*H*), 6.96 (1H, d, *J* = 2.0 Hz, Ar-*H*), 7.20 (1H, d, *J* = 2.5 Hz, Ar-*H*), 7.34 (1H, d, *J* = 2.5 Hz, Ar-*H*). ^{13}C NMR (100.6 MHz, $CDCl_3$): -1.3, 1.7, 114.2, 119.9, 121.9, 122.4, 125.4, 129.0, 129.1, 133.4, 136.0, 142.1, 153.9, 161.8. FTIR (CH_2Cl_2, thin film): 3415 (br, s), 2959 (s), 1698 (s), 1577 (s), 1378 (s), 847 (s) cm^{-1}. HRMS calculated for $C_9H_{12}{}^{35}Cl_2OSi$ (EI^+): 234.0034. Found: 234.0024.

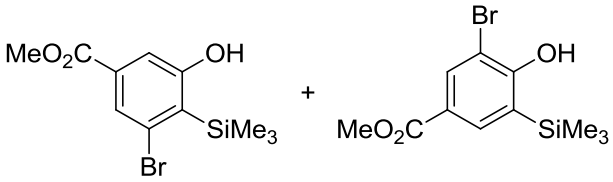
Synthesis of 3-hydroxy-4-trimethylsilanyl-benzoic acid methyl ester and 4-hydroxy-3-trimethylsilanyl-benzoic acid methyl ester



Using General Procedure 3, with **13a,b** (385 mg, 1.15 mmol), the product was isolated as an inseparable mixture of compounds (3:2 ratio) as a clear oil, 180 mg, 70 % yield.

^{1}H NMR (250 MHz, $CDCl_3$): δ 0.35 (9H, s, Si-C*H*$_3$), 3.92 (1.2H, s, C*H*$_3$), 3.94 (1.8H, s, C*H*$_3$), 5.60 (0.6H, br s, O*H*), 5.77 (0.4H, br s, O*H*), 6.74 (0.4H, d, *J* = 8.5 Hz, Ar-*H*), 7.45 (1.2H, m, Ar-*H*), 7.59 (0.6H, dd, *J* = 1.5, 7.5 Hz, Ar-*H*), 7.96 (0.4H, dd, *J* = 2.0, 8.5 Hz, Ar-*H*), 8.09 (0.4H, d, *J* = 2.0 Hz, Ar-*H*). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ -1.1, -1.2, 51.9, 52.3, 114.3, 114.9, 121.3, 122.3, 125.7, 132.1 (x2), 132.9, 135.4, 137.6, 160.6, 164.5, 167.3, 167.4. FTIR (CH_2Cl_2, thin film): 3375 (br, s), 2957 (m), 1687 (s), 1593 (m), 1395 (s), 1266 (s), 837 (s) cm^{-1}. HRMS calculated for $C_{11}H_{16}O_3Si$ (MH^+): 225.0947. Found: 225.0948.

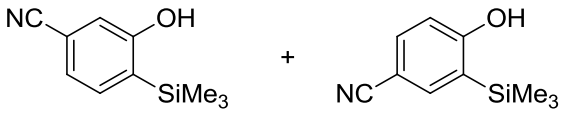
Synthesis of 3-bromo-5-hydroxy-4-trimethylsilanyl-benzoic acid methyl ester and 3-bromo-4-hydroxy-5-trimethylsilanyl-benzoic acid methyl ester



Using General Procedure 3, with **14a,b** (201 mg, 0.49 mmol), the product was isolated as an inseparable mixture of compounds (3:2 ratio) as a colourless solid, 119 mg, 81 % yield, m.pt. = 97 – 99 ^{o}C.

^{1}H NMR (250 MHz, $CDCl_3$): δ 0.35 (5.4H, s, Si-C*H*$_3$), 0.50 (3.6H, s, Si-C*H*$_3$), 3.91 (1.2H, s, C*H*$_3$), 3.92 (1.8H, s, C*H*$_3$), 6.22 (0.6H, br s, O*H*), 6.85 (0.4H, br s, O*H*), 7.45 (0.4H, d, *J* = 1.5 Hz, Ar-*H*), 7.74 (0.4H, d, *J* = 1.5 Hz, Ar-*H*). 8.00 (0.6H, d, *J* = 2.0 Hz, Ar-*H*), 8.19 (0.6H, d, *J* = 2.0 Hz, Ar-*H*). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ -0.9, -0.3, 52.6, 52.8, 110.7, 123.2, 124.1, 127.4, 127.5, 131.8, 133.2, 133.8, 135.2, 136.4, 136.8, 140.7, 166.3, 166.6. FTIR (CH_2Cl_2, thin film): 3315 (br, s), 2951 (m), 1703 (s), 1687 (s), 1258 (s), 1247 (s), 843 (s) cm^{-1}. HRMS calculated for $C_{11}H_{15}{}^{79}BrO_3Si$ (MH^+): 303.0052. Found: 303.0057.

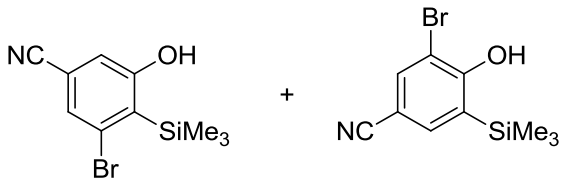
Synthesis of 3-hydroxy-4-trimethylsilanyl-benzonitrile 36a and 4-hydroxy-3-trimethylsilanyl-benzonitrile 36b



Using General Procedure 3, with **15a,b** (49 mg, 0.16 mmol), the product was isolated as an inseparable mixture of compounds (1:1 ratio) as a colourless solid, 11 mg, 71 % yield, m.pt. = 82 – 84 ^{o}C.

^{1}H NMR (250 MHz, $CDCl_3$): δ 0.34 (18H, s, Si-C*H*$_3$), 5.34 (1H, br s, O*H*), 5.75 (1H, br s, O*H*), 7.00 (1H, d, *J* = 1.0 Hz, Ar-*H*), 7.24 (1H, dd, *J* = 1.0, 7.5 Hz, Ar-*H*), 7.46 (1H, d, *J* = 7.5 Hz, Ar-*H*), 7.48 (1H, dd, *J* = 2.0, 8.0 Hz, Ar-*H*), 7.74 (1H, d, *J* = 2.0 Hz, Ar-*H*), 7.80 (1H, d, *J* = 8.0 Hz, Ar-*H*). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ -1.3 (x2), 103.6, 113.3, 115.1, 116.9, 118.8, 119.7, 123.9, 127.9, 133.3, 134.9, 136.1, 139.9, 160.6, 164.1. FTIR (CH_2Cl_2, thin film): 3347 (br, s), 2956 (m), 2232 (s), 1588 (s), 1401 (s), 842 (s) cm^{-1}. HRMS calculated for $C_{10}H_{13}NOSi$ (MH^+): 192.0845. Found: 192.0846.

Synthesis of 3-bromo-5-hydroxy-4-trimethylsilanyl-benzonitrile and 3-bromo-4-hydroxy-5-trimethylsilanyl-benzonitrile



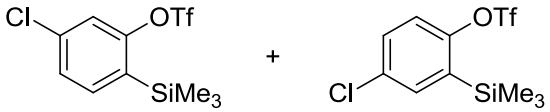
Using General Procedure 3, with **16a,b** (43 mg, 0.14 mmol), the product was isolated as an inseparable mixture of compounds (3:2 ratio) as a clear oil, 26 mg, 84 % yield.

^{1}H NMR (250 MHz, $CDCl_3$): δ 0.34 (5.4H, s, Si-C*H*$_3$), 0.50 (3.6H, s, Si-C*H*$_3$), 6.21 (0.4H, br s, O*H*), 6.24 (0.6H, br s, O*H*), 6.96 (0.6H, d, *J* = 1.5 Hz, Ar-*H*), 7.40 (0.6H, d, *J* = 1.5 Hz, Ar-*H*), 7.59 (0.4H, d, *J* = 2.0 Hz, Ar-*H*), 7.80 (0.4H, d, *J* = 2.0 Hz, Ar-*H*). ^{13}C NMR (100.6 MHz, $CDCl_3$): -1.1, 2.3, 105.7, 110.9, 114.8, 117.2, 117.6, 118.5, 128.9, 129.4, 131.6, 133.4, 136.9, 139.2, 160.1, 162.2. FTIR (CH_2Cl_2, thin film): 3354 (br s), 2925 (s), 2232 (m), 1580 (m), 1249 (s), 844 (s) cm^{-1}. HRMS calculated for $C_{10}H_{11}{}^{79}BrNOSi$ (M^-): 267.9793. Found: 267.9793.

General Procedure 4: The sulfonylation of *o*-trimethylsilyl phenols

A solution of the phenol (1.0 mmol) and $^{i}Pr_2NEt$ (2.0 mmol),in DCM (1 mL) was cooled to 0 ^{o}C and stirred for 10 mins. To this mixture Tf_2O (1.5 mmol) was added dropwise. The reaction was stirred at 0 ^{o}C for a further 10 mins, then left stirring overnight at r.t.. To the reaction was added Et_2O (approx. 20 mL), then this mixture washed successively with sat. aq. NH_4Cl, sat. aq. $NaHCO_3$ and sat. aq. NaCl. The organic layers were then combined, dried with $MgSO_4$ and concentrated in vacuo. If necessary, products were purified by flash column chromatography (eluting solvent 10 % ethyl acetate in petroleum ether).

Synthesis of trifluoromethanesulfonic acid 5-chloro-2-trimethylsilanyl-phenyl ester 17a and trifluoromethanesulfonic acid 4-chloro-2-trimethylsilanyl-phenyl ester 17b

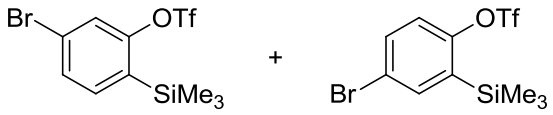


17a **17b**

Using General Procedure 4 with the appropriate phenol (30 mg, 0.10 mmol), the product was isolated as an inseparable mixture of compounds **17a** and **17b** (5:3 ratio) as a brown oil, 48 mg, 94 % yield.

^{1}H NMR (250 MHz, $CDCl_3$): **17a/b**: δ 0.37 (3.4H, s, *C*H_3), 0.39 (5.6H, s, *C*H_3), 7.24 – 7.52 (3H, m, Ar-*H*). ^{13}C NMR (100.6 MHz, $CDCl_3$): **17a/b**: δ -1.0, -0.9, 118.4 (x2) (q, *J* = 320 Hz, *C*F_3), 120.2, 121.0, 127.9, 131.0, 131.1, 133.5, 135.3, 135.9, 136.6, 136.9, 153.1, 154.7. FTIR (CH_2Cl_2, thin film): 2928 (m), 1587 (s), 1424 (s), 1214 (s), 1140 (s), 845 (s) cm^{-1}. HRMS calculated for $C_{10}H_{12}{}^{35}ClF_3O_3SSi$ (AP^+): 332.9992. Found: 332.9995.

Synthesis of trifluoromethanesulfonic acid 5-bromo-2-trimethylsilanyl-phenyl ester 18a and trifluoromethanesulfonic acid 4-bromo-2-trimethylsilanyl-phenyl ester 18b

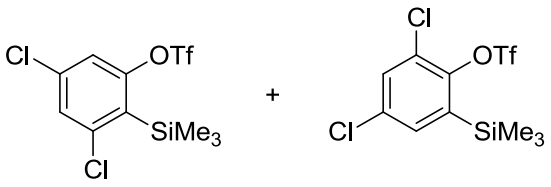


18a **18b**

Using General Procedure 4 with the appropriate phenol (67 mg, 0.27 mmol), the product was isolated as an inseparable mixture of compounds **18a** and **18b** (3:2 ratio) as a brown oil, 114 mg, 100 % yield.

^{1}H NMR (250 MHz, $CDCl_3$): **18a/b**: δ 0.38 (5.4H, s, C*H*$_3$), 0.40 (3.6H, s, C*H*$_3$), 7.24 (0.4H, d, *J* = 9.0 Hz, Ar-*H*), 7.43 (0.6H, m, Ar-*H*), 7.51 (1.2H, m, Ar-*H*), 7.57 (0.4H, dd, *J* = 2.5, 9.0 Hz, Ar-*H*), 7.63 (0.4H, d, *J* = 2.5 Hz, Ar-*H*). ^{13}C NMR (100.6 MHz, $CDCl_3$): **18a/b**: δ -0.6, -0.5, 118.8 (x2) (q, *J* = 320 Hz, *C*F_3), 121.8, 122.1, 123.4, 124.6, 131.2, 132.0, 134.4, 136.2, 137.6, 139.2, 154.1, 155.1. FTIR (CH_2Cl_2, thin film): 2960 (m), 1581 (s), 1424 (s), 1215 (s), 1141 (s), 845 (s) cm^{-1}. HRMS calculated for $C_{10}H_{12}{}^{79}BrF_3O_3SSi$ (EI^+): 375.9412. Found: 375.9412.

Synthesis of trifluoromethanesulfonic acid 3,5-dichloro-2-trimethylsilanyl-phenyl ester 19a and trifluoromethanesulfonic acid 2,4-dichloro-6-trimethylsilanyl-phenyl ester 19b

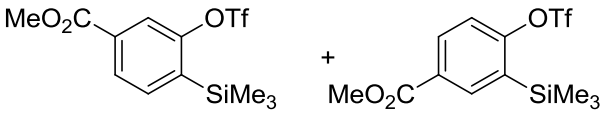


19a **19b**

Using General Procedure 4 with the appropriate phenol (21 mg, 0.09 mmol), the product was isolated as an inseparable mixture of compounds **19a** and **19b** (1:1 ratio) as a brown oil, 18 mg, 53 % yield.

^{1}H NMR (250 MHz, $CDCl_3$): **19 a or b**: δ 0.50 (9H, s, *C*H_3), 7.29 (1H, d, *J* = 2.0 Hz, Ar-*H*), 7.41 (1H, d, *J* = 2.0 Hz, Ar-*H*). **19 a or b**: δ 0.43 (9H, s, *C*H_3), 7.40 (1H, d, *J* = 2.5 Hz, Ar-*H*), 7.52 (1H, d, *J* = 2.5 Hz, Ar-*H*). ^{13}C NMR (100.6 MHz, $CDCl_3$): **19a/b:** δ 0.2, 1.7, 118.9 (q, *J* = 321 Hz, *C*F_3), 119.0 (q, *J* = 321 Hz, *C*F_3), 120.0, 128.9, 130.2, 130.9, 132.4, 134.8, 134.9, 136.8, 139.8, 143.3, 147.0, 154.6. FTIR (CH_2Cl_2, thin film): 2927 (s), 1732 (w), 1607 (m), 1416 (s), 1211 (s), 820 (s) cm^{-1}. HRMS calculated for $C_{10}H_{11}Cl_2F_3O_3SSi$ (EI^+): 365.9527. Found: 365.9541.

Synthesis of 3-trifluoromethanesulfonyloxy-4-trimethylsilanyl-benzoic acid methyl ester 20a and 4-trifluoromethanesulfonyloxy-3-trimethylsilanyl-benzoic acid methyl ester 20b



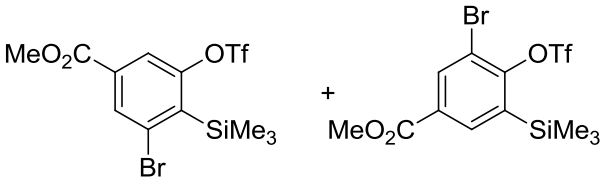
20a **20b**

Using General Procedure 4 with the appropriate phenol (120 mg, 0.54 mmol), the product was isolated as an inseparable mixture of compounds **20a** and **20b** (3:2 ratio) as a clear oil, 187 mg, 98 % yield.

^{1}H NMR (250 MHz, $CDCl_3$): **20a/b**: δ 0.41 (9H, s, *C*H_3), 3.95 (1.2H, s, *C*H_3), 3.96 (1.8H, s, *C*H_3) 7.44 (0.4H, d, *J* = 9.0 Hz, Ar-*H*), 7.64 (0.6H, d, *J* = 7.5 Hz, Ar-*H*), 7.97 (0.6H, m, Ar-*H*), 8.01 (0.6H, dd, *J* = 1.5, 7.5 Hz, Ar-*H*), 8.12 (0.4H, dd, *J* = 2.0, 9.0 Hz, Ar-*H*), 8.22 (0.4H, d, *J* = 2.0 Hz, Ar-*H*). ^{13}C NMR (100.6 MHz, $CDCl_3$): **20a/b**: δ -0.6 (x2), 52.9, 53.1, 118.9 (x2) (q, *J*

= 320 Hz, *C*F_3), 119.7, 120.8, 128.6, 129.6, 133.2, 133.5, 133.7, 136.8, 138.2, 139.1, 155.2, 158.3, 165.8, 166.3. FTIR (CH_2Cl_2, thin film): 2958 (m), 1732 (s), 1602 (w), 1424 (s), 1214 (s), 842 (s) cm^{-1}. HRMS calculated for $C_{12}H_{15}F_3O_5SSi$ (ES^+): 357.0440. Found: 357.0432.

Synthesis of 3-bromo-5-trifluoromethanesulfonyloxy-4-trimethylsilanyl-benzoic acid methyl ester 21a and 3-bromo-4-trifluoromethanesulfonyloxy-5-trimethylsilanyl-benzoic acid methyl ester 21b

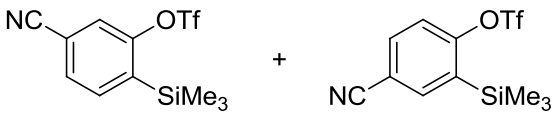


21a **21b**

Using General Procedure 4 with the appropriate phenol (121 mg, 0.40 mmol), the product was isolated as an inseparable mixture of compounds **21a** and **21b** (3:2 ratio) as a clear oil, 132 mg, 76 % yield.

^{1}H NMR (250 MHz, $CDCl_3$): **21a/b**: δ 0.46 (5.4H, s, C*H*$_3$), 0.55 (3.6H, s, C*H*$_3$), 3.95 – 3.99 (3H, br, C*H*$_3$), 7.90 (0.4H, d, *J* = 1.5 Hz, Ar-*H*), 8.18 (0.6H, d, *J* = 2.0 Hz, Ar-*H*), 8.23 (0.4H, d, *J* = 1.5 Hz, Ar-*H*), 8.34 (0.6H, d, *J* = 2.0 Hz, Ar-*H*). ^{13}C NMR (100.6 MHz, $CDCl_3$): **21a/b**: δ 0.0, 1.5, 52.7, 52.9, 116.8, 118.5 (q, *J* = 321 Hz, *C*F_3), 118.6 (q, *J* = 321 Hz, *C*F_3), 120.3, 130.8, 131.4, 133.4, 134.0, 136.8, 136.9, 138.3, 139.8, 151.8, 154.2, 164.1, 164.7. FTIR (CH_2Cl_2, thin film): 2960 (m), 1732 (s), 1428 (s), 1214 (s), 844 (s) cm^{-1}. HRMS calculated for $C_{12}H_{14}{}^{79}BrF_3O_5SSi$ (AP^+): 434.9545. Found: 434.9541.

Synthesis of trifluoromethanesulfonic acid 5-cyano-2-trimethylsilanyl-phenyl ester 22a and trifluoromethanesulfonic acid 4-cyano-2-trimethylsilanyl-phenyl ester 22b

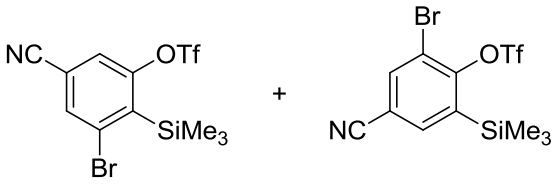


22a **22b**

Using General Procedure 4 with the appropriate phenol (200 mg, 1.05 mmol), the product was isolated as an inseparable mixture of compounds **22a** and **22b** (1:1 ratio) as a brown oil, 375 mg, 100 % yield.

^{1}H NMR (250 MHz, $CDCl_3$): **22a/b**: δ 0.41 (18H, s, *C*H_3), 7.50 (1H, d, *J* = 8.5 Hz, Ar-*H*), 7.65 (3H, m, Ar-*H*), 7.77 (1H, dd, *J* = 2.0, 8.5 Hz, Ar-*H*), 7.84 (1H, d, *J* = 2.0 Hz, Ar-*H*). ^{13}C NMR (100.6 MHz, $CDCl_3$): **22a/b**: δ -0.72, -0.68, 114.8 (x2) (q, *J* = 478 Hz, *C*F_3), 115.3, 117.5, 118.1, 120.4, 120.6, 123.1, 131.1, 135.4, 135.5, 137.6, 140.3, 140.7, 154.7, 157.5. FTIR (CH_2Cl_2, thin film): 2924 (s), 2236 (s), 1426 (s), 1216 (s), 846 (s) cm^{-1}. HRMS calculated for $C_{11}H_{12}F_3NO_3SSi$ (AP^+): 324.0338. Found: 324.0329.

Synthesis of trifluoromethanesulfonic acid 3-bromo-5-cyano-2-trimethylsilanyl-phenyl ester 23a and trifluoromethanesulfonic acid 2-bromo-4-cyano-6-trimethylsilanyl-phenyl ester 23b



23a **23b**

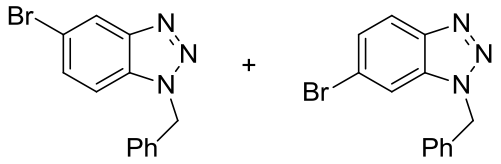
Using General Procedure 4 with the appropriate phenol (248 mg, 0.92 mmol), the product was isolated as an inseparable mixture of compounds **23a** and **23b** (1:1 ratio) as a clear oil, 220 mg, 60 % yield.

^{1}H NMR (250 MHz, $CDCl_3$): **23a/b**: δ 0.44 (9H, s, *C*H_3), 0.55 (9H, s, *C*H_3), 7.58 (1H, d, *J* = 1.5 Hz, Ar-*H*), 7.80 (1H, d, *J* = 1.5 Hz, Ar-*H*), 7.87 (1H, d, *J* = 2.0 Hz, Ar-*H*), 7.98 (1H, d, *J* = 2.0 Hz, Ar-*H*). ^{13}C NMR (100.6 MHz, $CDCl_3$): **23a/b**: δ 0.3, 1.8, 115.8, 116.0, 116.2 (q, *J* = 403 Hz, *C*F_3), 116.7, 118.9 (q, *J* = 321 Hz, *C*F_3), 123.0, 132.5, 136.3, 139.1, 139.8, 139.1, 139.8, 140.6, 141.7, 152.0, 154.2. FTIR (CH_2Cl_2, thin film): 2926 (m), 2237 (s), 1524 (m), 1414 (s), 1136 (s), 844 (s) cm^{-1}. HRMS calculated for $C_{11}H_{11}BrF_3NO_3SSi$ (AP^+): 401.9443. Found: 401.9429.

General Procedure 5: The cycloaddition of benzyne precursors with benzyl azide

To a mixture of benzyne precursor (0.12 mmol) and benzyl azide (0.10 mmol), dissolved in MeCN (0.12 mL), was added CsF (0.2 mmol). The reaction was then left to stir at r.t. for 18 hrs. The mixture was poured onto sat. aq. $NaHCO_3$, and then extracted with DCM (3 x 10 mL). The organic layers were combined, dried over $MgSO_4$, and concentrated in vacuo. The crude product was purified via flash column chromatography (eluting solvent 10 % ethyl acetate in petroleum ether).

Synthesis of 1-benzyl-5-bromo-1H-benzotriazole 24a and 1-benzyl-6-bromo-1H-benzotriazole 24b

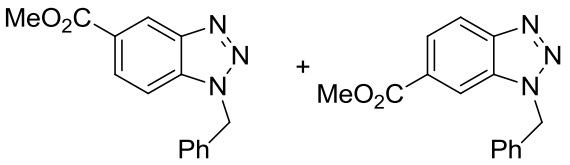


24a **24b**

Using General Procedure 5, with benzyne precursor **18a,b** (50 mg, 0.08 mmol), the product was isolated as an inseparable mixture of compounds **24a** and **24b** (2:1 ratio), as a brown solid, 23 mg, 70 % yield, m.pt.= 83 – 85 ^{o}C.

^{1}H NMR (250 MHz, $CDCl_3$): **24a/b**: δ 5.84 (0.7H, s, C*H*$_2$), 5.86 (1.3H, s, *CH*$_2$), 7.25 (0.7H, dd, *J* = 0.5, 9.0 Hz, Ar-*H*), 7.27 – 7.42 (5H, m, Ar-*H*), 7.47 (0.3H, dd, *J* = 1.5, 9.0 Hz, Ar-*H*), 7.51 (0.7H, dd, *J* = 1.5, 9.0 Hz, Ar-*H*), 7.57 (0.3H, dd, *J* = 0.5, 1.5 Hz, Ar-*H*), 7.96 (0.3H, dd, *J* = 0.5, 9.0 Hz, Ar-*H*), 8.25 (0.7H, dd, *J* = 0.5, 1.5 Hz, Ar-*H*). ^{13}C NMR (100.6 MHz, $CDCl_3$): **24a/b**: δ 52.8, 53.0, 111.5, 113.0, 117.7, 121.7, 122.2, 123.1, 126.4, 128.0, 128.2, 129.1, 129.5, 129.6, 131.2, 132.2, 134.3, 134.7, 141.2, 145.6, 148.0, 151.2. FTIR (CH_2Cl_2, thin film): 2923 (m), 1605 (m), 1474 (m), 1203 (s), 734 (s) cm^{-1}. HRMS calculated for $C_{13}H_{10}{}^{79}BrN_3$ (ES^+): 288.0136. Found: 288.0132.

Synthesis of 1-benzyl-1H-benzotriazole-5-carboxylic acid methyl ester 25a and 3-benzyl-3H-benzotriazole-5-carboxylic acid methyl ester 25b

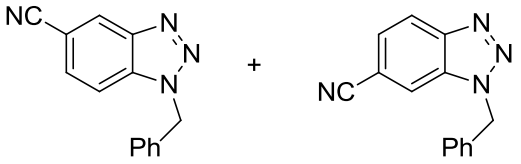


25a **25b**

Using General Procedure 5, with benzyne precursor **20a,b** (50 mg, 0.14 mmol), the product was isolated as an inseparable mixture of compounds **25a** and **25b** (1:1 ratio), as a brown solid, 21 mg, 67 % yield, m.pt.= 75 – 78 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$): **25a/b**: δ 3.97 (3H, s, *C*H_3), 3.99 (3H, s, *C*H_3), 5.90 (2H, s, C*H*$_2$), 5.92 (2H, s, *C*H_2), 7.30 – 7.43 (11H, m, Ar-*H*), 8.05 (1H, dd, *J* = 1.5, 8.5 Hz, Ar-*H*), 8.10 – 8.15 (2H, m, Ar-*H*), 8.19 (1H, dd, *J* = 1.0, 1.5 Hz, Ar-*H*), 8.82 (1H, dd, *J* = 1.0, 1.5 Hz, Ar-*H*). ^{13}C NMR (100.6 MHz, $CDCl_3$): **25a/b**: δ 52.9 (x3), 53.0, 110.0, 112.7, 120.4, 123.4, 125.1, 126.8, 128.0 (x2), 128.7, 129.1, 129.6, 129.7, 133.0, 134.7, 134.8, 135.5, 146.5, 148.7, 149.1, 157.0, 166.9 (x2). FTIR (CH_2Cl_2, thin film): 2953 (m), 1722 (s), 1436 (s), 1288 (s), 733 (s) cm^{-1}. HRMS calculated for $C_{15}H_{13}N_3O_2$ (M^+): 268.1086. Found: 268.1086.

Synthesis of 1-benzyl-1H-benzotriazole-5-carbonitrile 26a and 3-benzyl-3H-benzotriazole-5-carbonitrile 26b



26a **26b**

Using General Procedure 5, with benzyne precursor **22a,b** (25 mg, 0.08 mmol), the product was isolated as an inseparable mixture of compounds **26a** and **26b** (2:1 ratio), as a brown solid, 10 mg, 65 % yield, m.pt.= 72 – 74 ^{o}C.

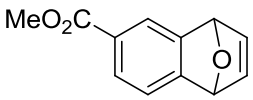
^{1}H NMR (250 MHz, $CDCl_3$): δ 5.91 (1.3H, s, C*H*$_2$), 5.92 (0.7H, s, C*H*$_2$), 7.29 – 7.43 (5H, m, Ar-*H*), 7.47 (0.7H, dd, *J* = 0.5, 8.5 Hz), 7.57 (0.3H, dd, *J* = 1.5, 8.5 Hz, Ar-*H*), 7.63 (0.7H, dd, *J* = 1.5, 8.5 Hz, Ar-*H*), 7.74 (0.3H, s, Ar-*H*), 8.19 (0.3H, dd, *J* = 0.5, 8.5 Hz, Ar-*H*), 8.47 (0.7H, s, Ar-*H*). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 52.8, 53.0, 107.9 (x2), 111.3 (x2), 115.7 (x2),

118.5, 119.1, 121.6 (x2), 126.3, 126.4, 127.7, 129.0, 129.3, 129.7, 133.8, 134.4, 135.8, 138.0, 141.4, 145.5. FTIR (CH_2Cl_2, thin film): 2924 (m), 2232 (m), 1569 (m), 1432 (m), 1205 (m), 720 (m) cm^{-1}. HRMS calculated for $C_{14}H_{10}N_4$ (MH^+): 235.0984. Found: 235.0975.

General Procedure 6: The cycloaddition of benzyne precursors with furans

To a mixture of benzyne precursor (0.10 mmol) and furan (0.50 mmol), dissolved in MeCN (3 mL), was added CsF (0.30 mmol). The reaction was then left to stir at r.t. for 18 hrs. The mixture was then poured onto sat. aq. $NaHCO_3$, and then extracted from DCM (3 x 10 mL). The organic layers were combined, dried over $MgSO_4$, and concentrated in vacuo. The crude product was purified via flash column chromatography (eluting solvent 10 % ethyl acetate in petroleum ether).

Synthesis of 11-Oxa-tricyclo[6.2.1.0^{2,7}]undeca-2,4,6,9-tetraene-4-carboxylic acid methyl ester 27



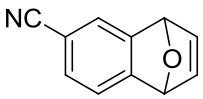
27

Using General Procedure 6, with benzyne precursor **20a,b** (25 mg, 0.07 mmol), the product **27** was isolated as a colourless solid, 10 mg, 68 % yield. The compound gave satisfactory spectroscopic data in comparison with the literature.[4]

^{1}H NMR (250 MHz, $CDCl_3$): δ 3.91 (3H, s, C*H*$_3$), 5.77 (2H, m, C*H*), 7.05 (2H, m, C*H*), 7.32 (1H, d, *J* = 7.5 Hz, Ar-*H*), 7.78 (1H, d, *J* = 7.5 Hz, Ar-*H*), 7.89 (1H, s, Ar-*H*). ^{13}C NMR (100.6 MHz, $CDCl_3$): 52.5, 82.6 (x2), 120.4, 121.1, 127.7, 128.5, 142.8, 143.8, 150.0, 154.8, 167.4.

4. Kitamura, T.; Wasai, K.; Todaka, M.; Fujiwara, Y. *Synlett.* **1999**, *6*, 731

Synthesis of 11-Oxa-tricyclo[6.2.1.0^{2,7}]undeca-2,4,6,9-tetraene-4-carbonitrile 28

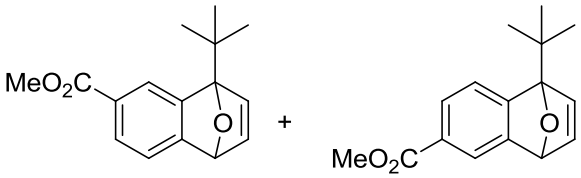


28

Using General Procedure 6, with benzyne precursor **22a,b** (50 mg, 0.16 mmol), the product **28** was isolated as a colourless solid, 17 mg, 66 % yield. The compound gave satisfactory spectroscopic data in comparison with the literature [5]

^{1}H NMR (250 MHz, $CDCl_3$): δ 5.79 (2H, m, C*H*), 7.06 (2H, m, C*H*), 7.36 (2H, m, Ar-*H*), 7.48 (1H, s, Ar-*H*). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 82.3, 82.6, 119.6, 121.1, 123.2, 131.4, 135.4, 140.9, 143.0, 143.5, 155.8.

Synthesis of 1-tert-Butyl-11-oxa-tricyclo[6.2.1.0^{2,7}]undeca-2,4,6,9-tetraene-4-carboxylic acid methyl ester 29a and 8-tert-Butyl-11-oxa-tricyclo[6.2.1.0^{2,7}]undeca-2,4,6,9-tetraene-4-carboxylic acid methyl ester 29b



29a **29b**

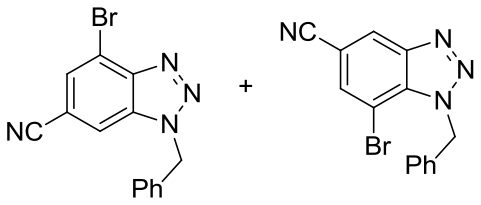
Using General Procedure 6, with benzyne precursor **20a,b** (30 mg, 0.08 mmol), the product was isolated as an inseparable mixture of compounds **29a** and **29b** (1:1 ratio), 14 mg, 63 % yield.

^{1}H NMR (250 MHz, $CDCl_3$): **29a/b:** δ 1.29 (9H, s, CH_3), 1.33 (9H, s, CH_3), 3.90 (3H, s, CH_3) 3.91 (3H, s, CH_3), 5.69 (1H, m, C*H*), 5.70 (1H, m, C*H*), 6.93 – 7.08 (4H, m, C*H*), 7.26 (1H, d, *J* = 7.5 Hz, Ar-*H*), 7.45 (1H, d, *J* = 7.5 Hz, Ar-*H*), 7.74 (2H, m, Ar-*H*), 7.82 (1H, d, *J* = 1.0 Hz, Ar-*H*), 8.00 (1H, m, Ar-*H*). ^{13}C NMR (100.6 MHz, $CDCl_3$): **29a/b**: δ 27.0 (x2), 32.9 (x2), 52.5 (x2), 81.6, 81.7, 100.1 (x2), 120.0, 120.6, 121.7, 122.4, 127.0, 127.1, 127.9, 128.0, 142.7,

5. Sapountzis, I.; Lin, W.; Fischer, M.; Knochel, P. *Angew. Chem. Int. Ed.* **2004**, *43*, 4364

143.6, 144.2, 145.2, 150.2, 153.1, 155.3, 158.0, 167.4, 167.5. FTIR (CH_2Cl_2, thin film): 2958 (m), 1720 (s), 1435 (s), 1258 (s), 769 (s) cm^{-1}. HRMS calculated for $C_{16}H_{18}O_3$ (ES^+): 259.1334. Found: 259.1337.

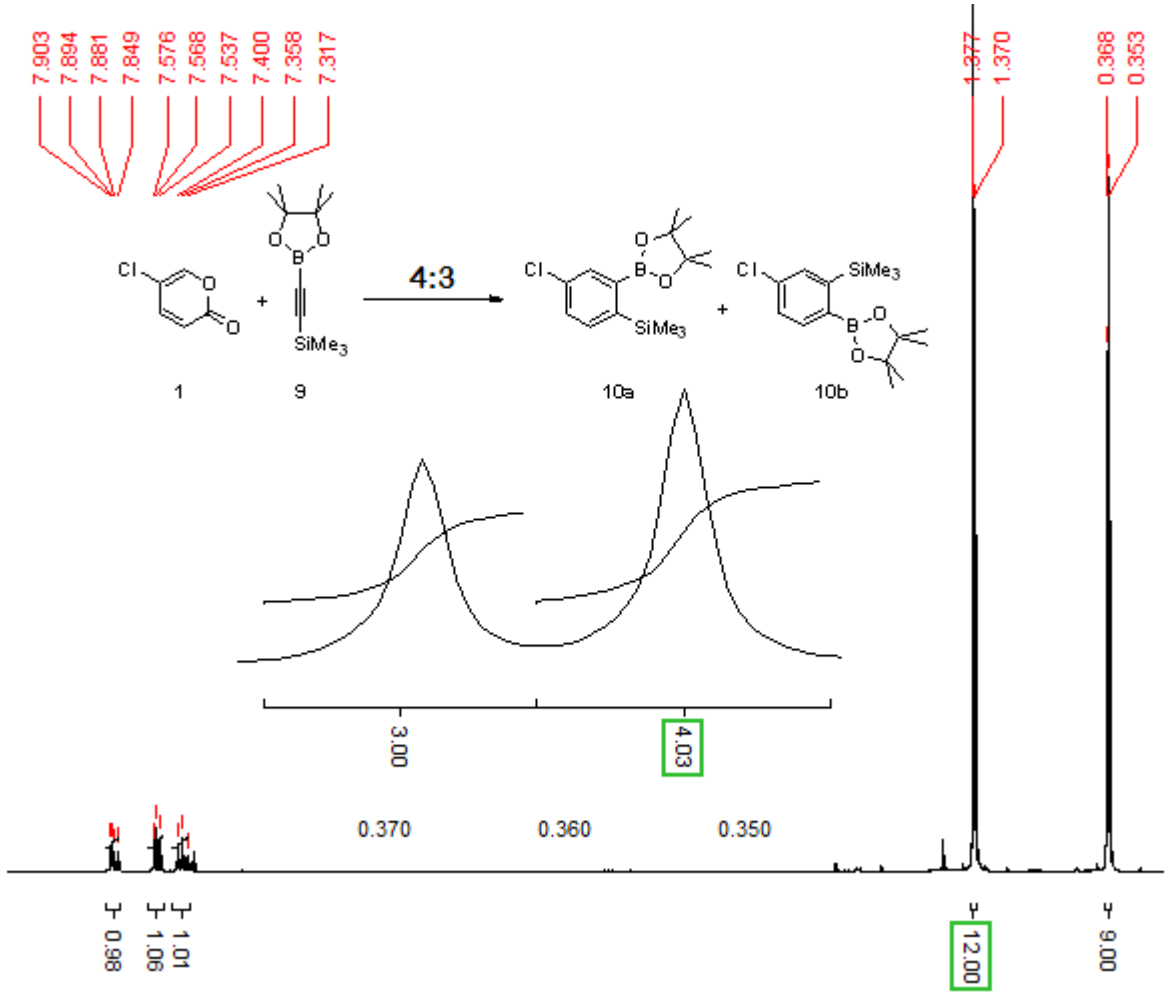
Synthesis of 3-benzyl-7-bromo-3H-benzotriazole-5-carbonitrile 30a and 1-benzyl-7-bromo-1H-benzotriazole-5-carbonitrile 30b



30a **30b**

To a mixture of benzyne precursor **23a/b** (50 mg, 0.12 mmol) and benzyl azide (80 mg, 0.60 mmol), dissolved in MeCN (0.6 mL), was added CsF (91 mg, 0.60 mmol). The reaction was then left to stir at r.t. for 18 hrs. The mixture was then poured onto sat. aq. $NaHCO_3$, and then extracted from DCM (3 x 10 mL). The organic layers were combined, dried over $MgSO_4$, and concentrated in vacuo. The crude product was purified via flash column chromatography (eluting solvent 10 % ethyl acetate in petroleum ether). The product was isolated as an inseparable mixture of compounds **30a** and **30b** (5:1 ratio), as a brown oil, 11 mg, 29 % yield.

^{1}H NMR (250 MHz, $CDCl_3$): **30a/b**: δ 5.92 (1.7H, s, C*H*$_2$), 6.23 (0.3H, s, C*H*$_2$), 7.08 – 7.46 (5H, m, Ar-*H*), 7.67 (0.8H, d, *J* = 1.0 Hz, Ar-*H*), 7.78 (1H, d, *J* = 0.8 Hz, Ar-*H*), 7.87 (0.2H, d, *J* = 1.0 Hz, Ar-*H*), 8.45 (0.2H, d, *J* = 1.0 Hz, Ar-*H*). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 52.9, 53.6, 112.0, 112.7, 114.5, 114.8 (x2), 115.2, 117.1, 117.3, 117.9, 123.4, 123.9, 125.3, 126.8, 127.1, 127.7, 128.6, 129.0, 129.1, 129.4, 129.5, 133.1, 133.3. FTIR (CH_2Cl_2, thin film): 2924 (m), 2232 (m), 1569 (m), 1432 (m), 1205 (m), 720 (m) cm^{-1}. HRMS calculated for $C_{14}H_9{}^{79}BrN_4$ (ES^+): 313.0078. Found: 313.0089.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7.576
7.568
7.537
7.400
7.358
7.317
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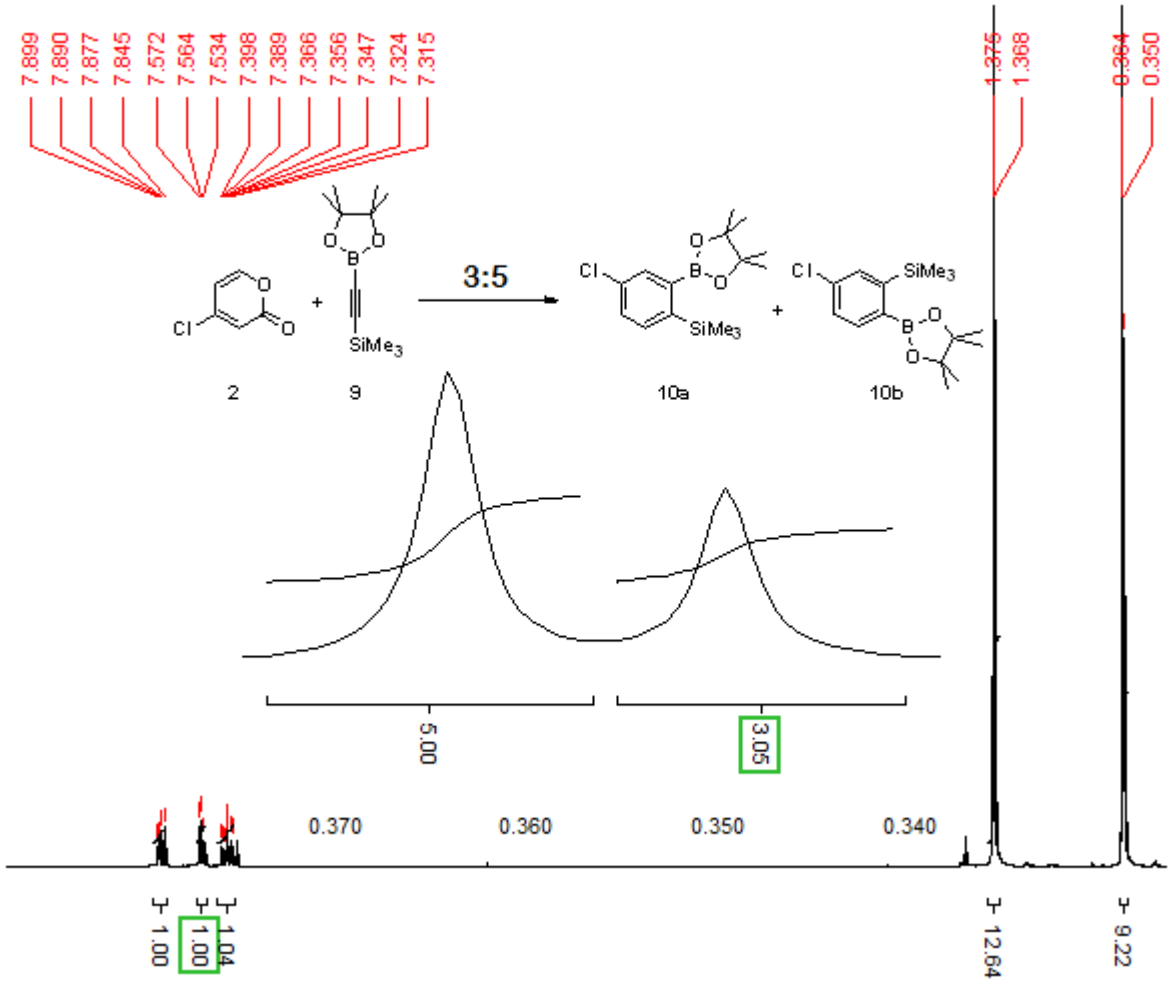
1.370
0.368
0.353
4:3
SiMe3
1
9
10a
10b
3.00
4.03
0.370
0.360
0.350
0.98
1.06
1.01
12.00
9.00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7.564
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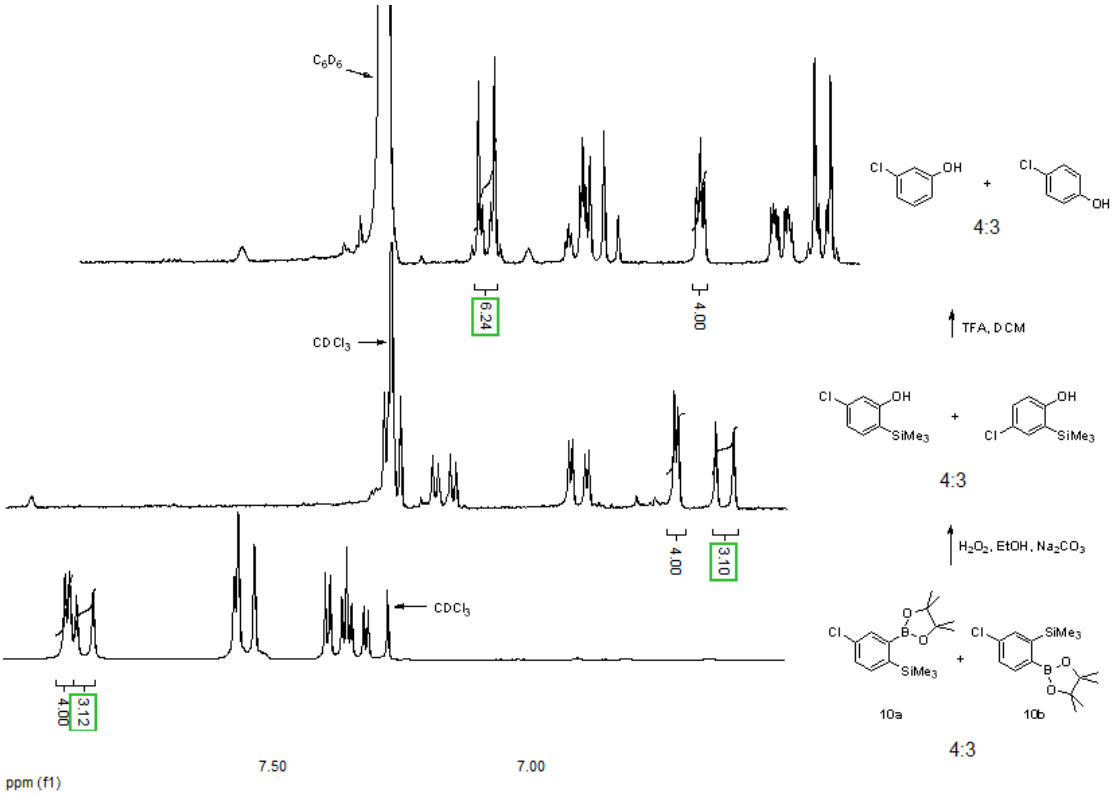
7.389
7.366
7.356
7.347
7.324
7.315
1.375
1.368
0.364
0.350
3:5
SiMe3
2
9
10a
10b
5.00
3.09
0.370
0.360
0.350
0.340
1.00
1.00
1.04
12.64
9.22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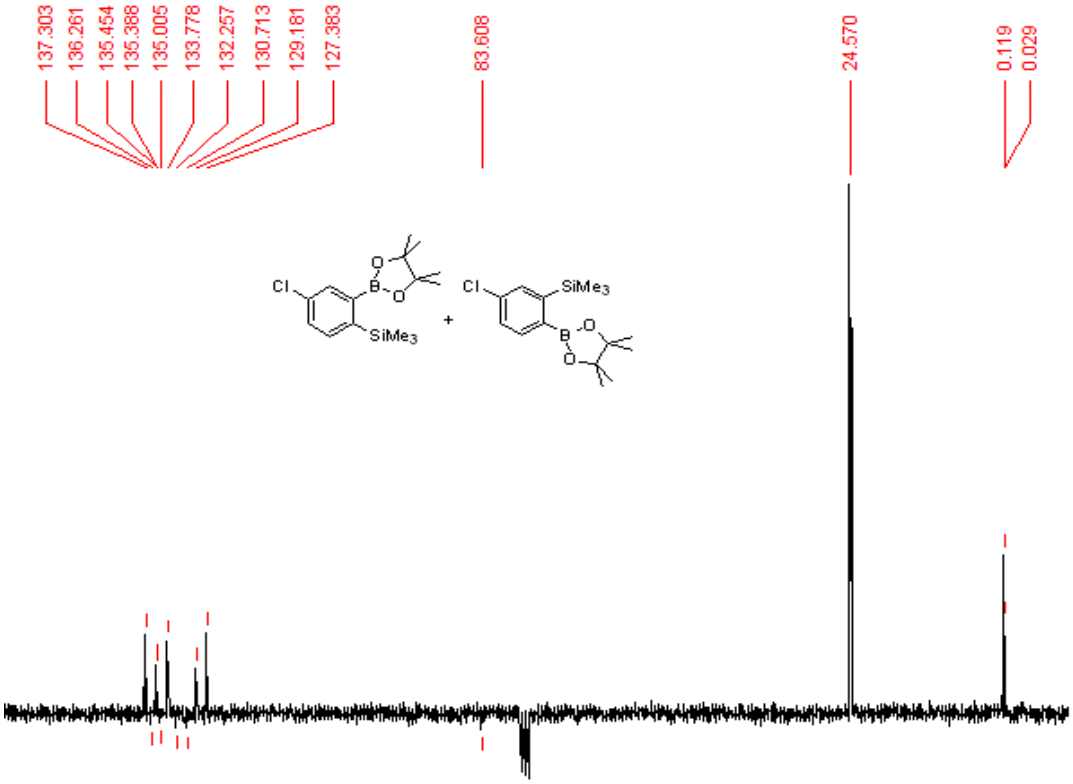
CDCl3
6.24
4.00
4.00
3.10
CDCl3
4.00
3.12
7.50
7.00
ppm (f1)
4:3
TFA, DCM
4:3
H2O2, EtOH, Na2CO3
10a
10b
4:3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135.005
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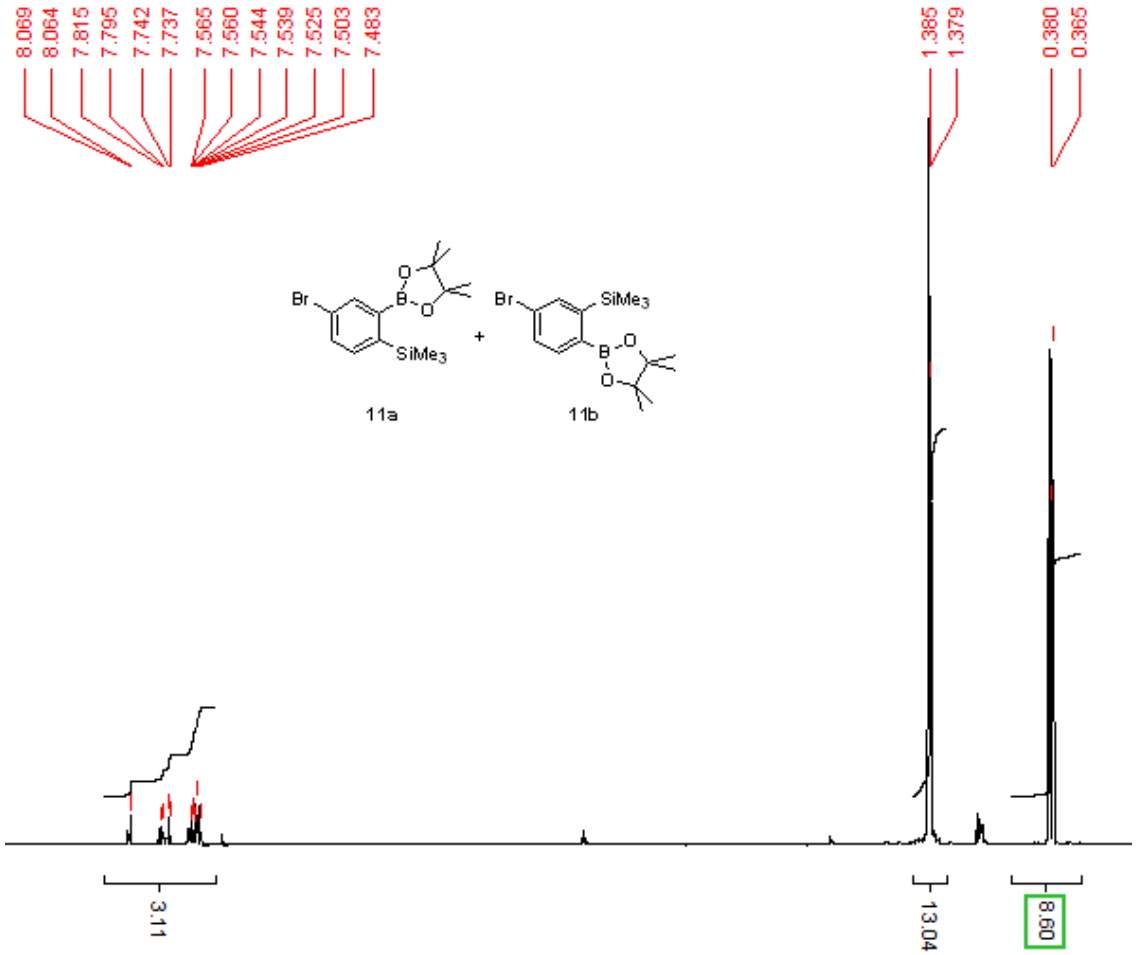
127.383
83.608
24.570
0.119
0.029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7.742
7.737
7.565
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7.544
7.539
7.525
7.503
7.483
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0.380
0.365
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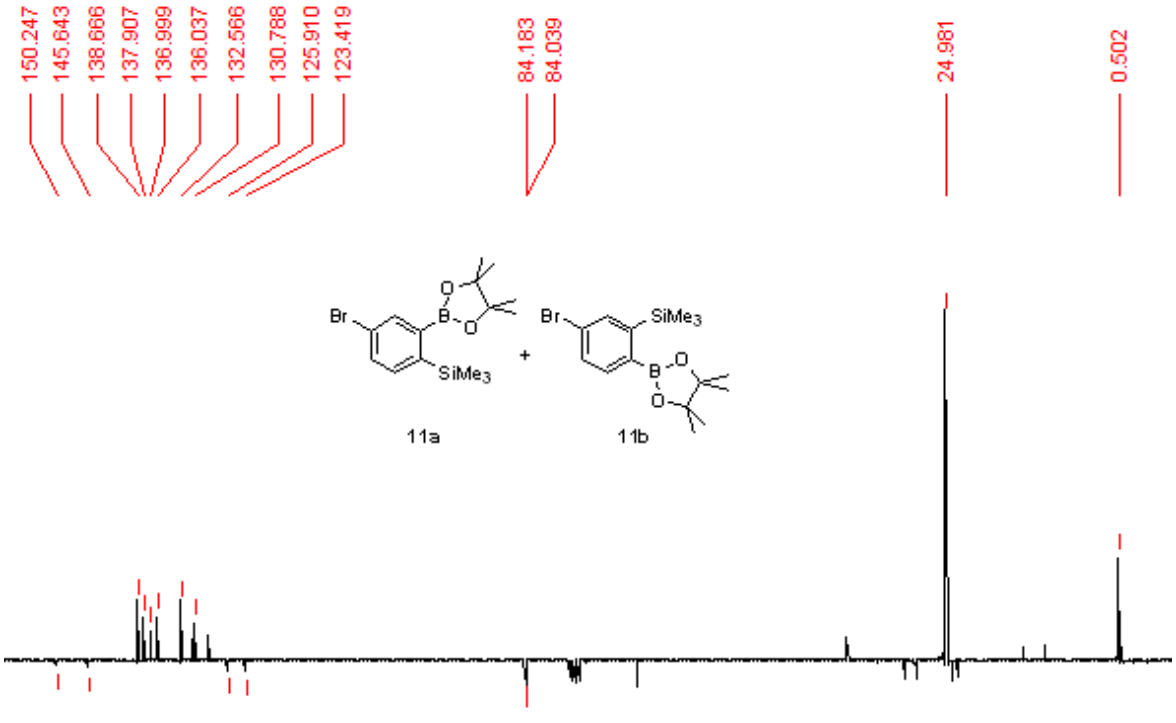
B
O
11a
11b
3.11
13.04
8.00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84.039
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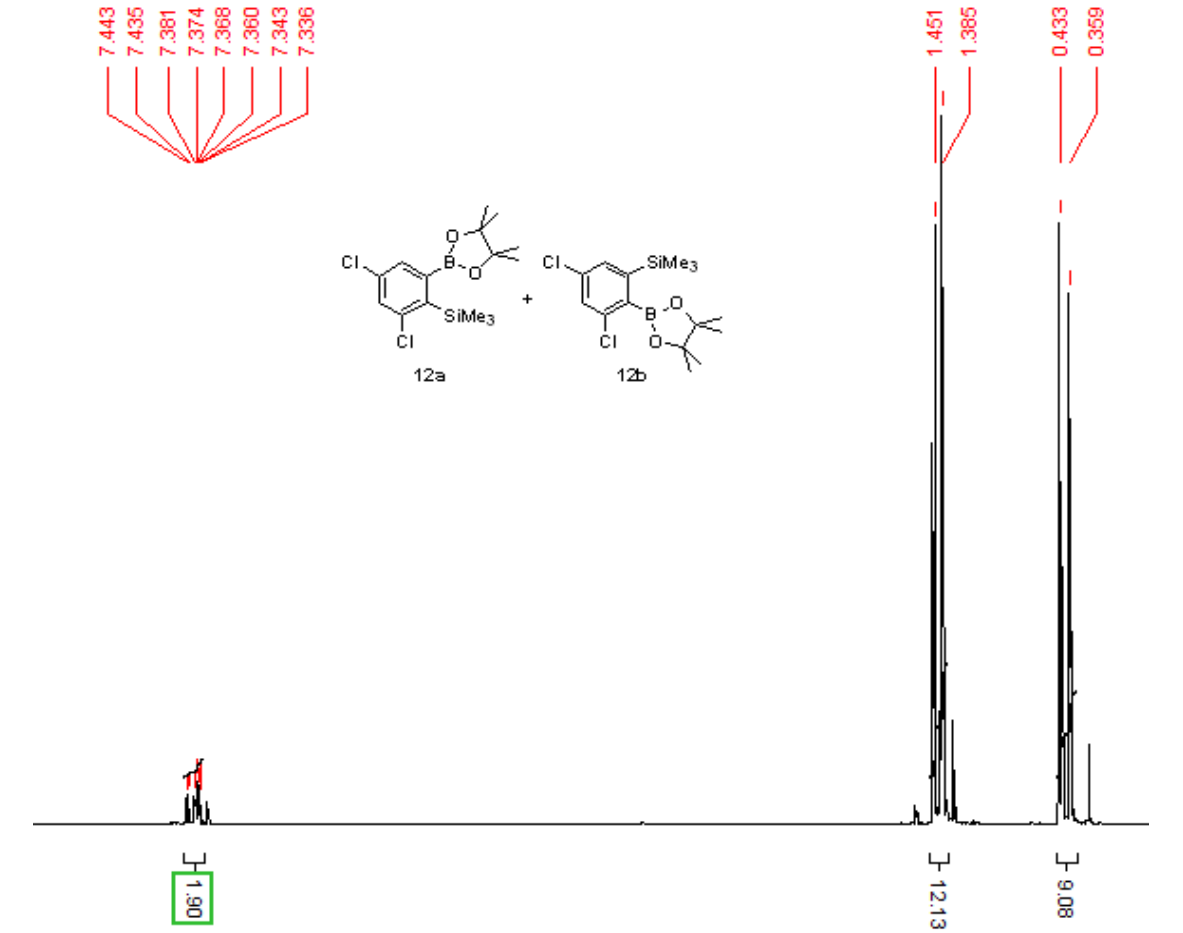
0.502
Br
SiMe3
B
O
11a
11b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7.381
7.374
7.368
7.360
7.343
7.336
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0.359
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B
O
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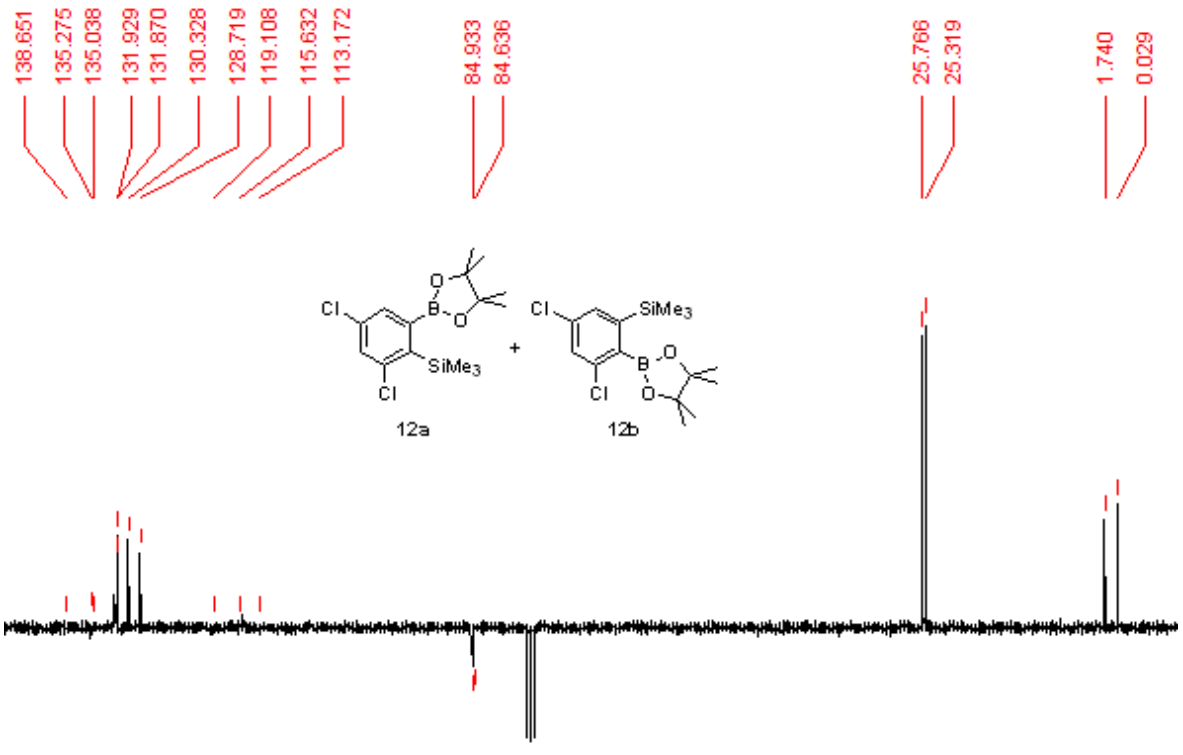
12a
12b
1.90
12.13
9.08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135.038
131.929
131.870
130.328
128.719
119.108
115.632
113.172
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84.636
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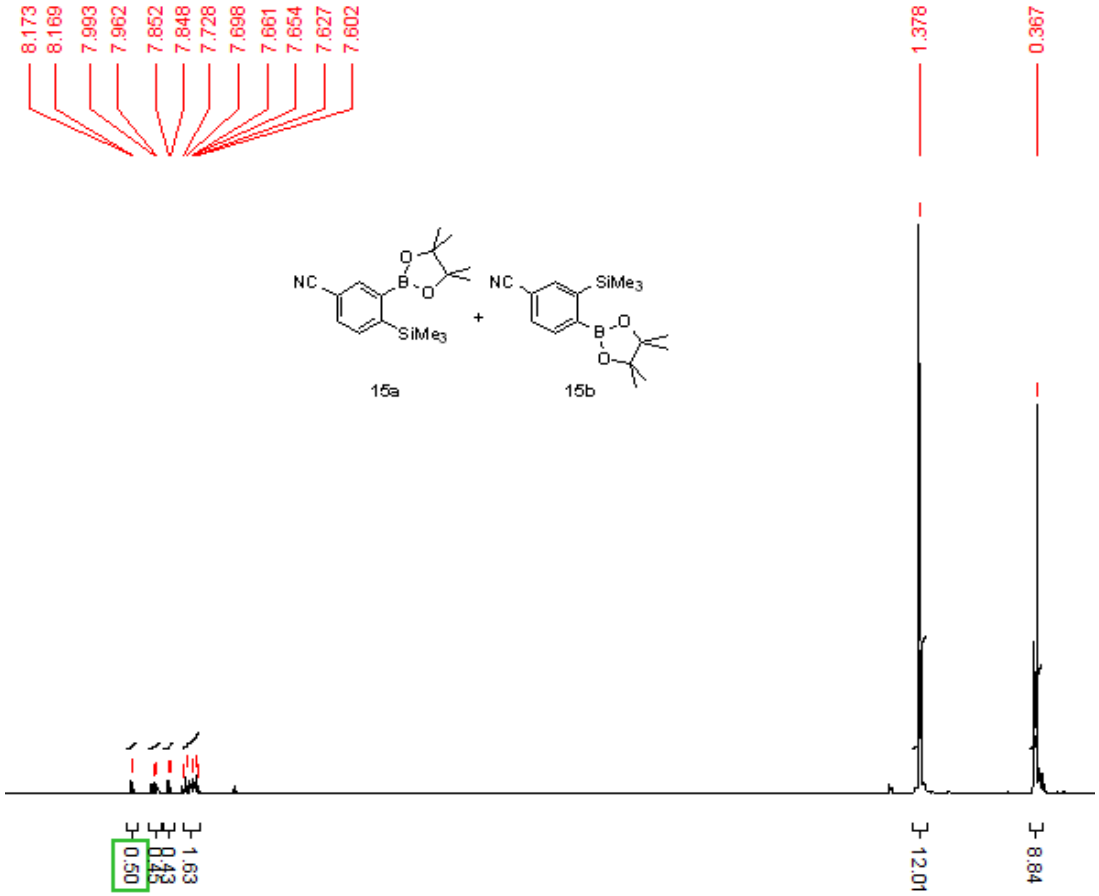
25.319
1.740
0.029
Cl
B
O
SiMe3
12a
12b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7.728
7.698
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7.654
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SiMe3
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15b
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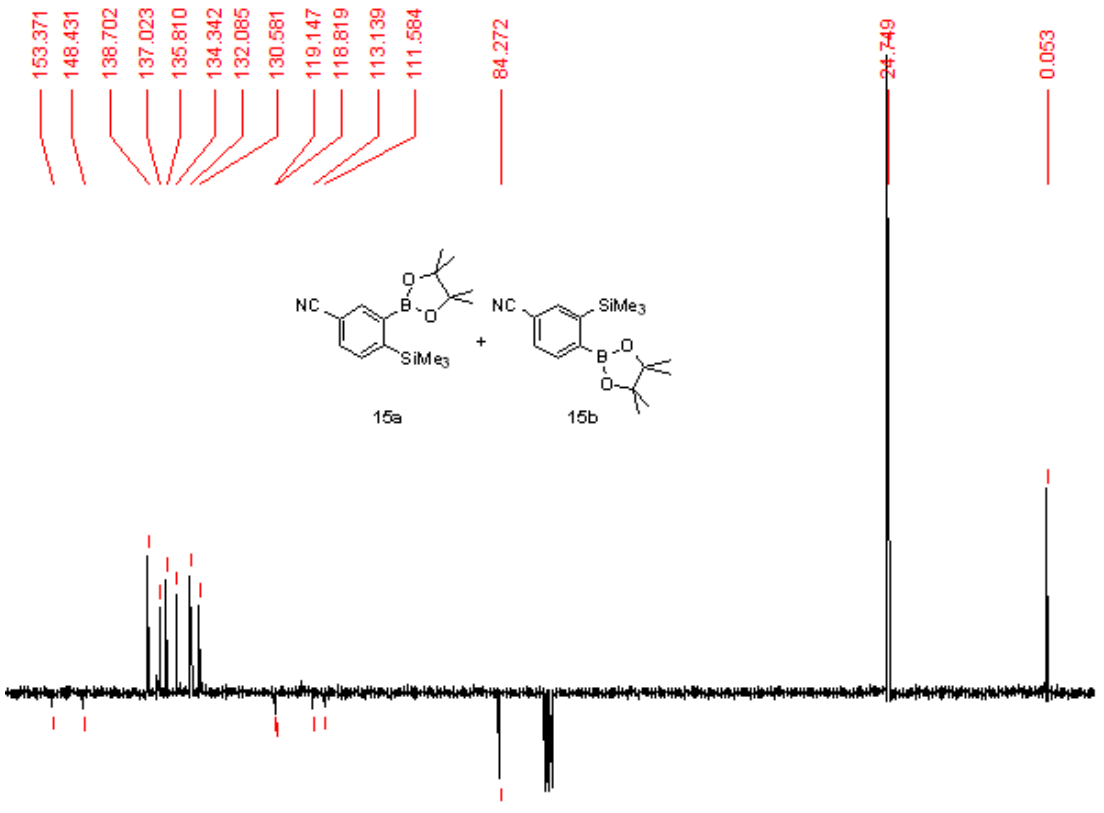
8.84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135.810
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118.819
113.139
111.584
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NC
SiMe3
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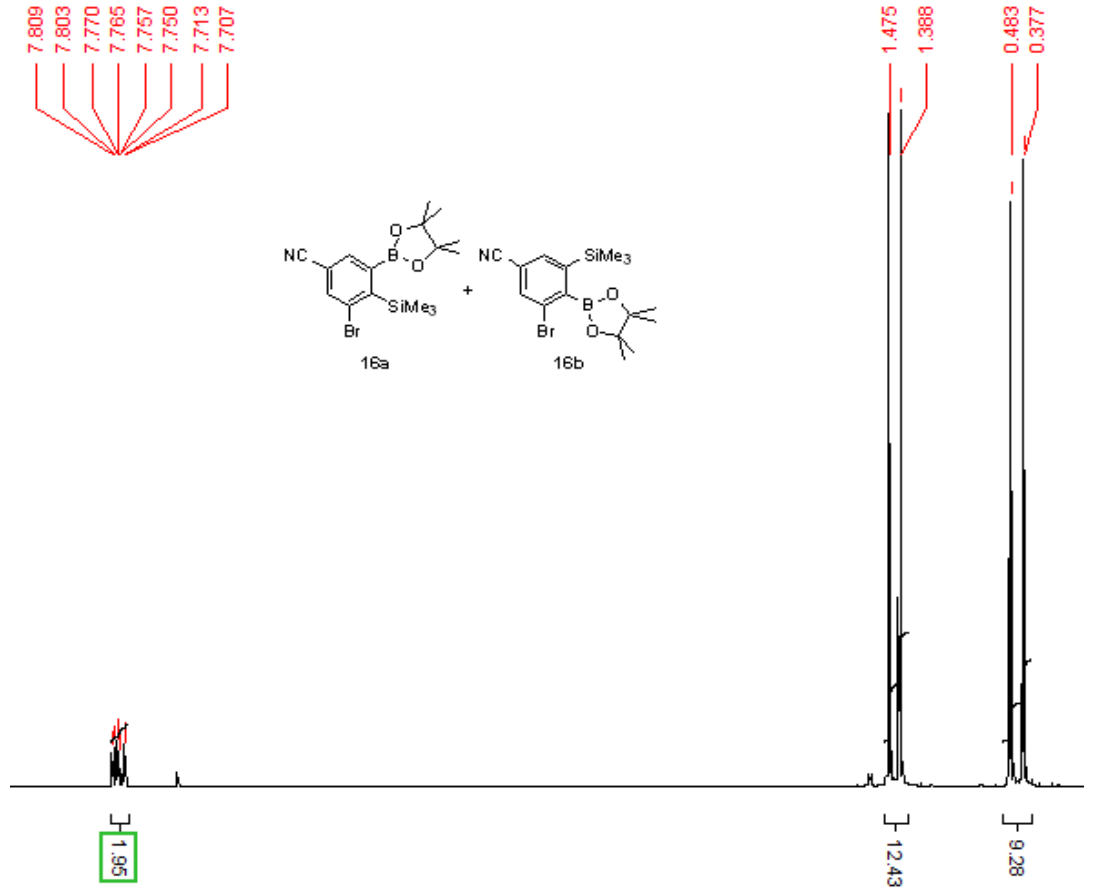
15b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7.803
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7.765
7.757
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7.713
7.707
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1.388
0.483
0.377
NC
B
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O
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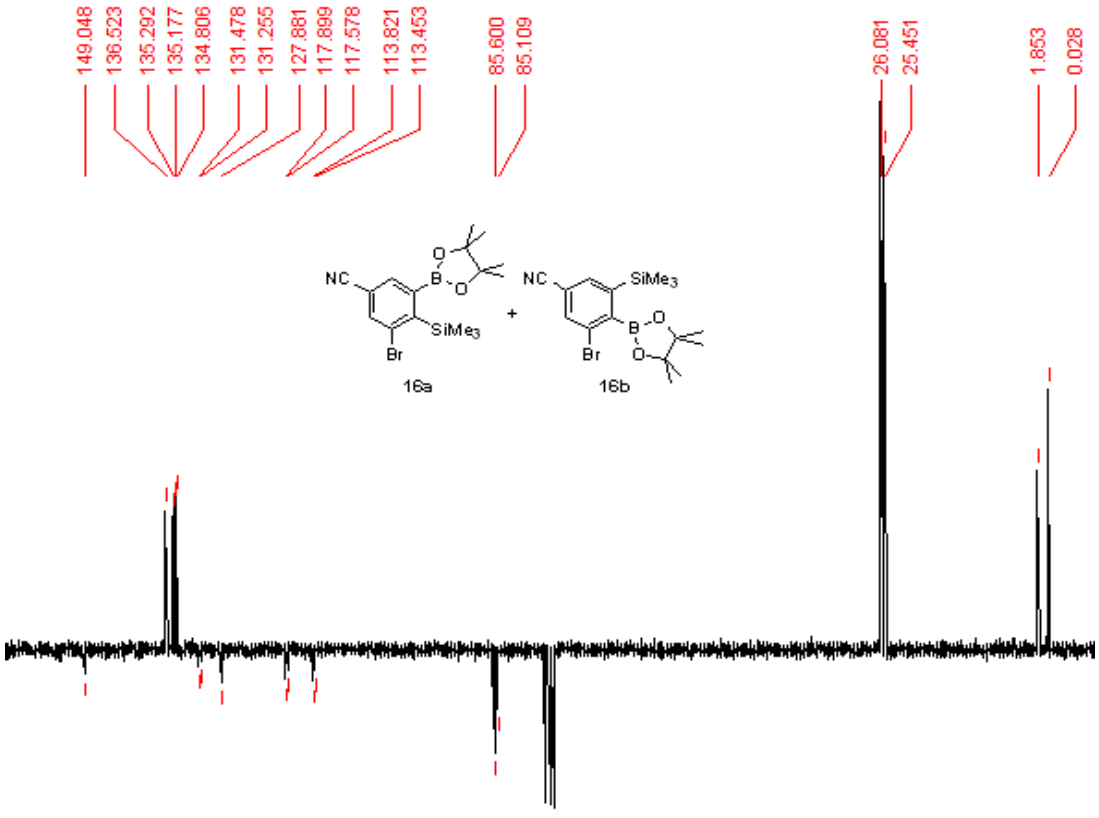
Br
16a
+
NC
SiMe3
B
O
O
Br
16b
1.95
12.43
9.28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117.578
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85.109
26.081
25.451
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+
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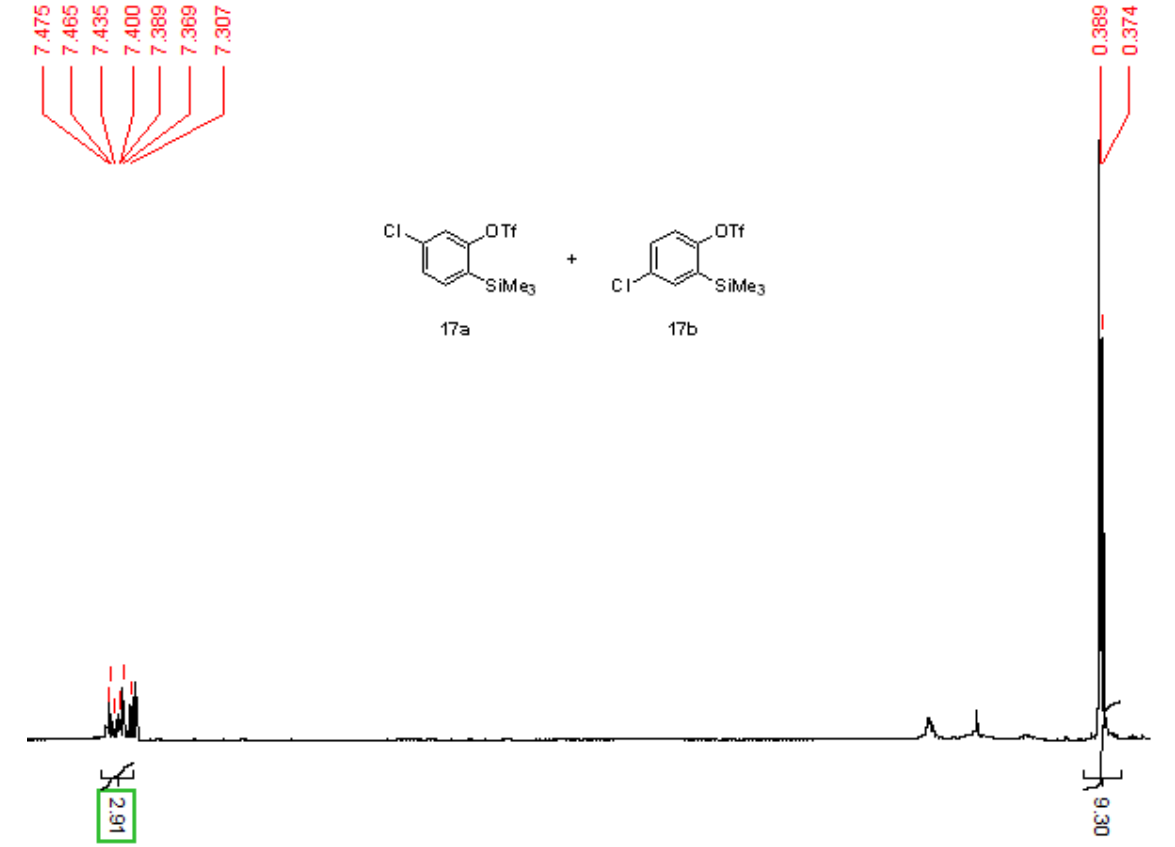
Br
16b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SiMe3
+
Cl
OTf
SiMe3
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17b
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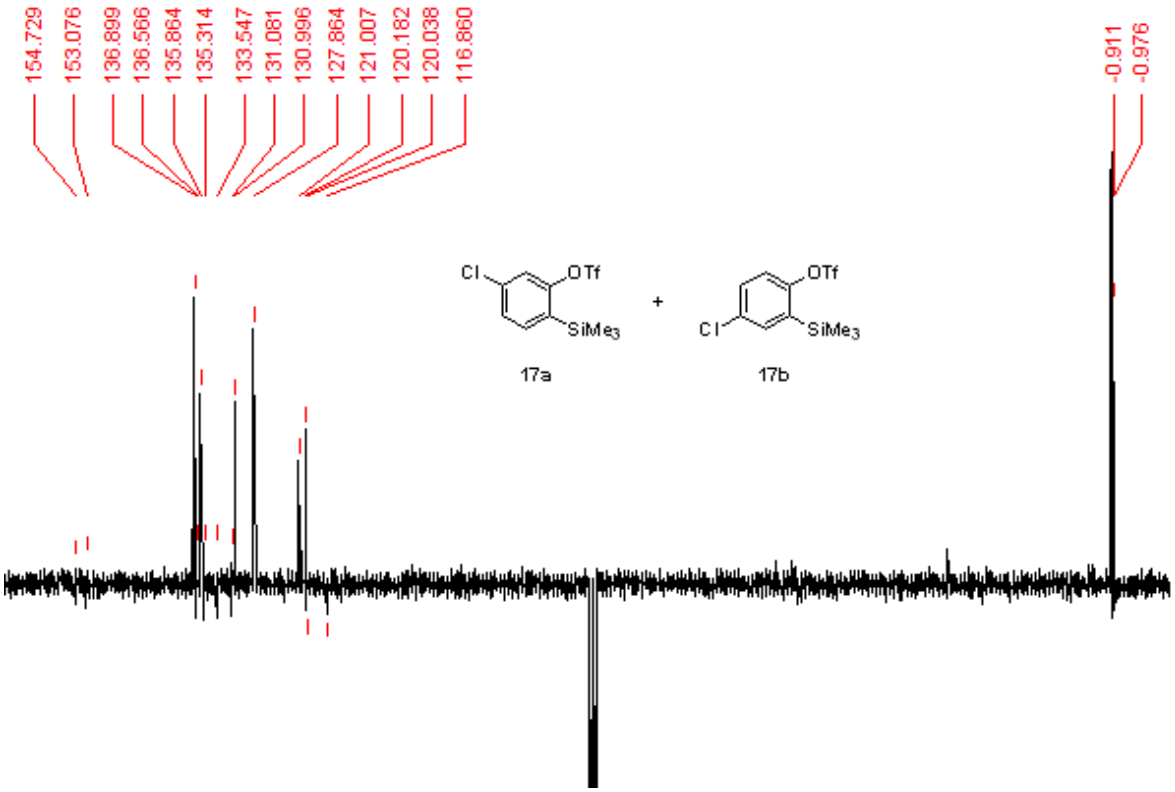
9.30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135.314
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131.081
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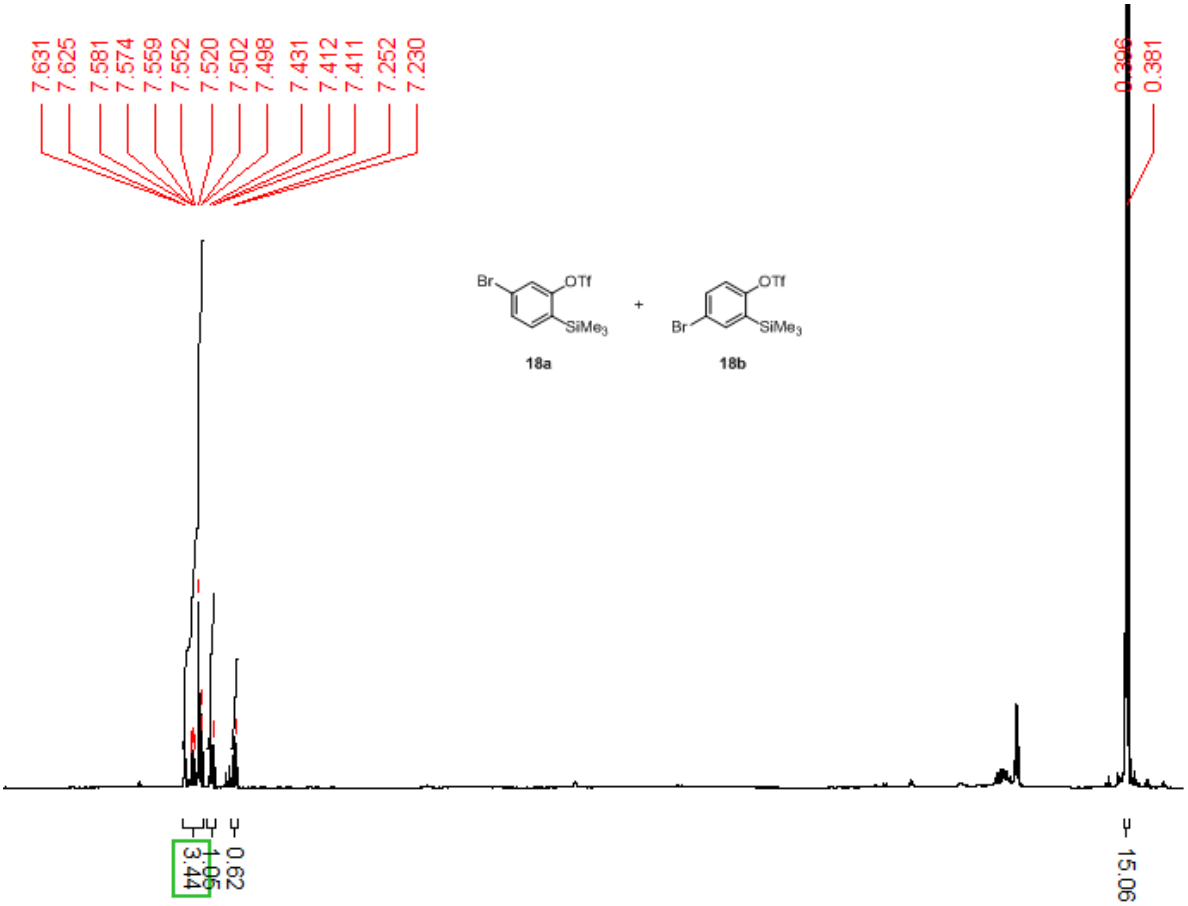
127.864
121.007
120.182
120.038
116.860
-0.911
-0.976
Cl
OTf
SiMe3
+
Cl
OTf
SiMe3
17a
17b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Br
OTf
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18a
18b
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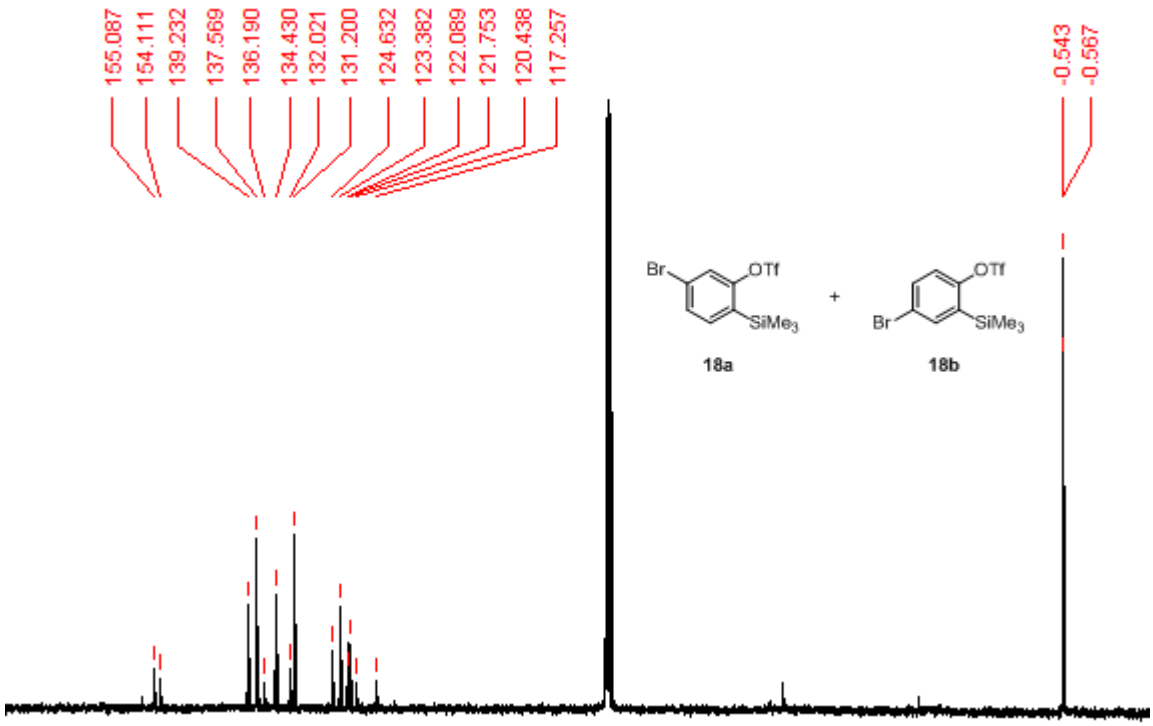
0.62
15.06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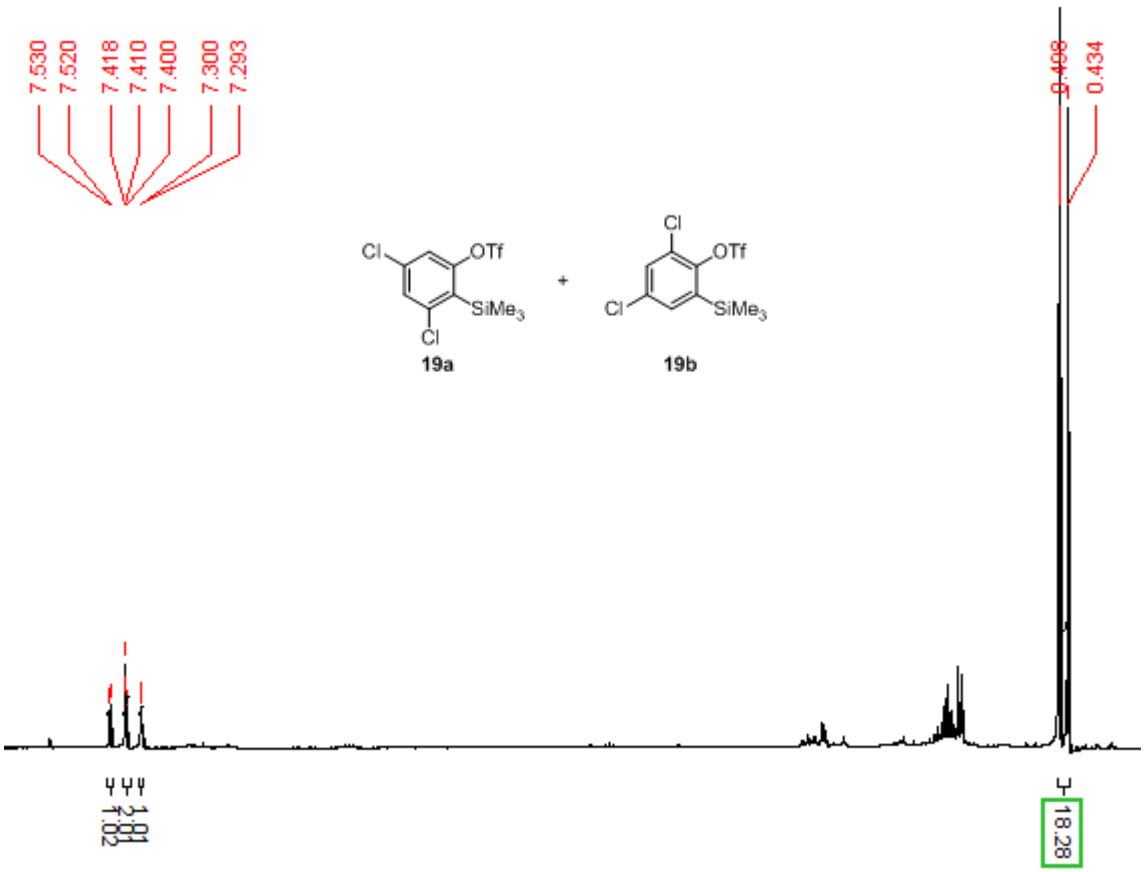
-0.567
Br
OTf
SiMe3
18a
18b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+
Cl
OTf
Cl
SiMe3
19b
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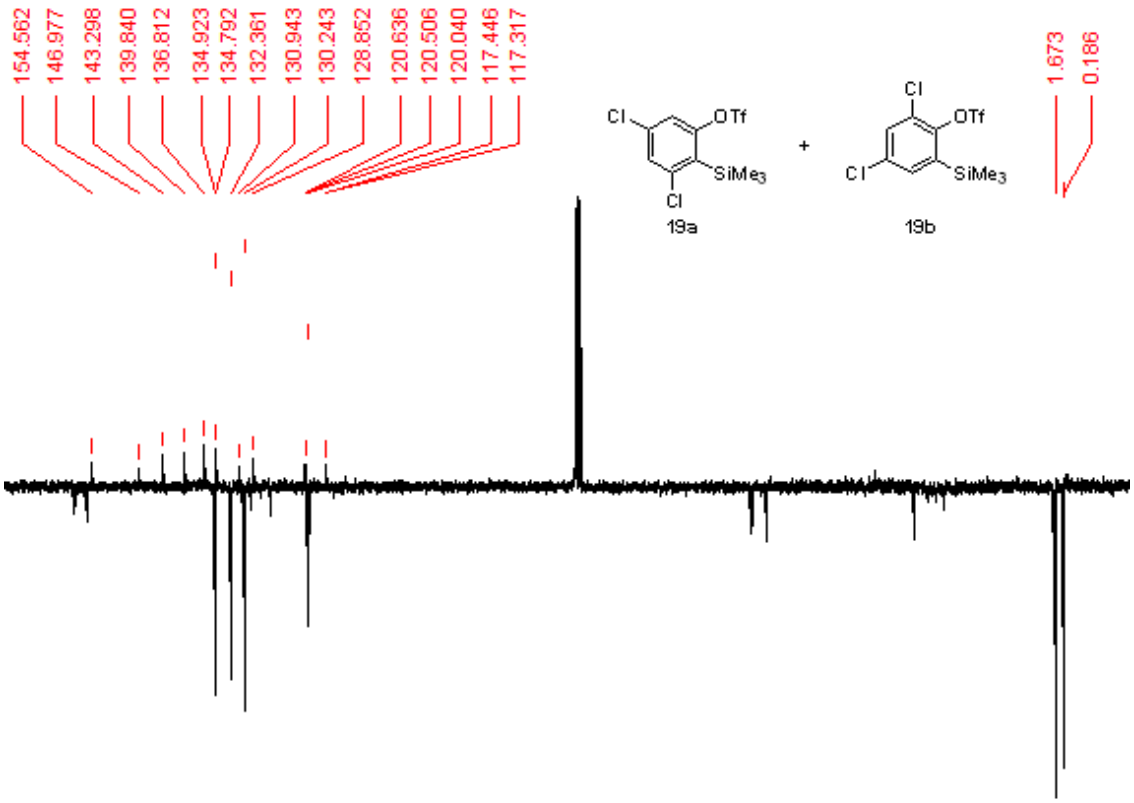
2.02
18.28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120.506
120.040
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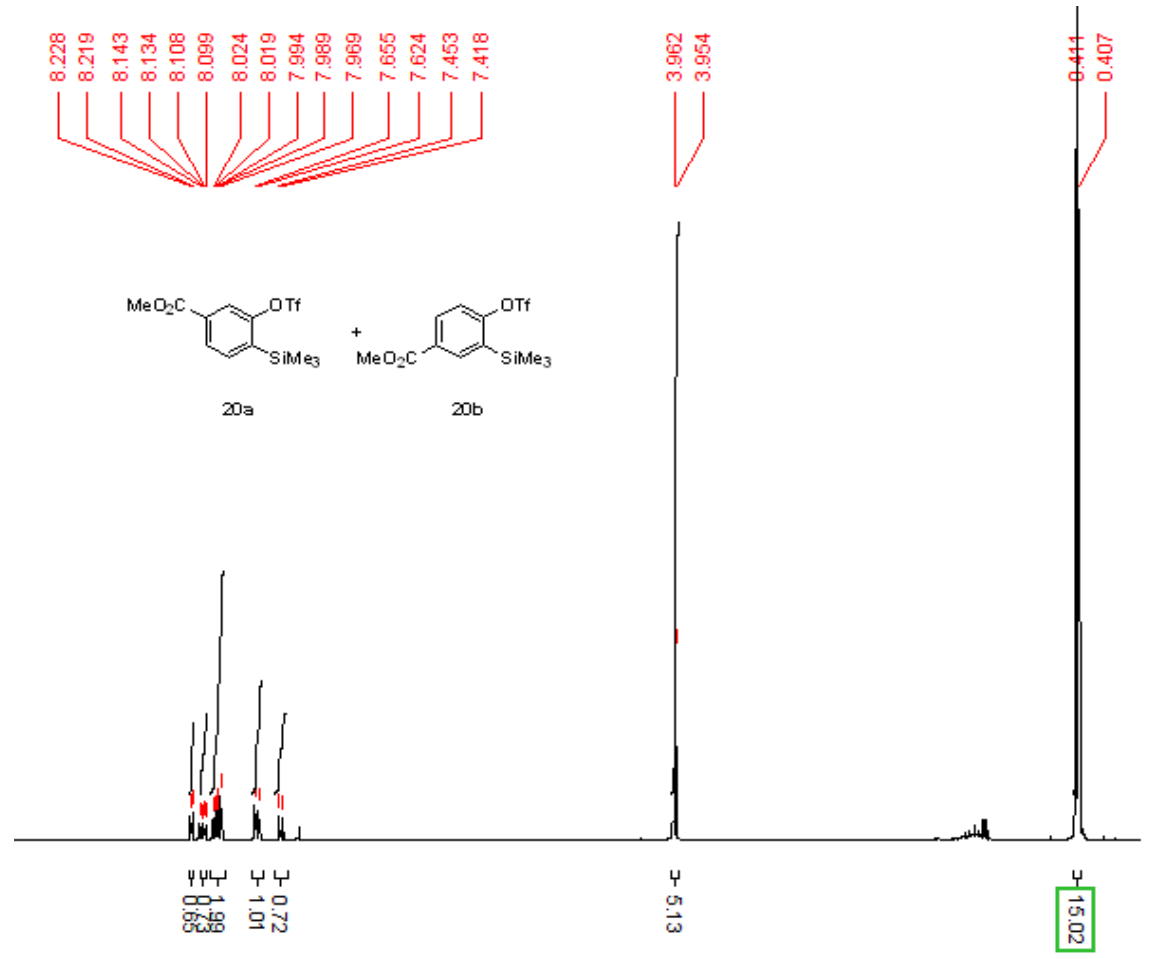
OTf
SiMe3
Cl
19a
+
Cl
OTf
Cl
SiMe3
19b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7.989
7.969
7.655
7.624
7.453
7.418
3.962
3.954
0.411
0.407
MeO2C
OTf
SiMe3
+
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20b
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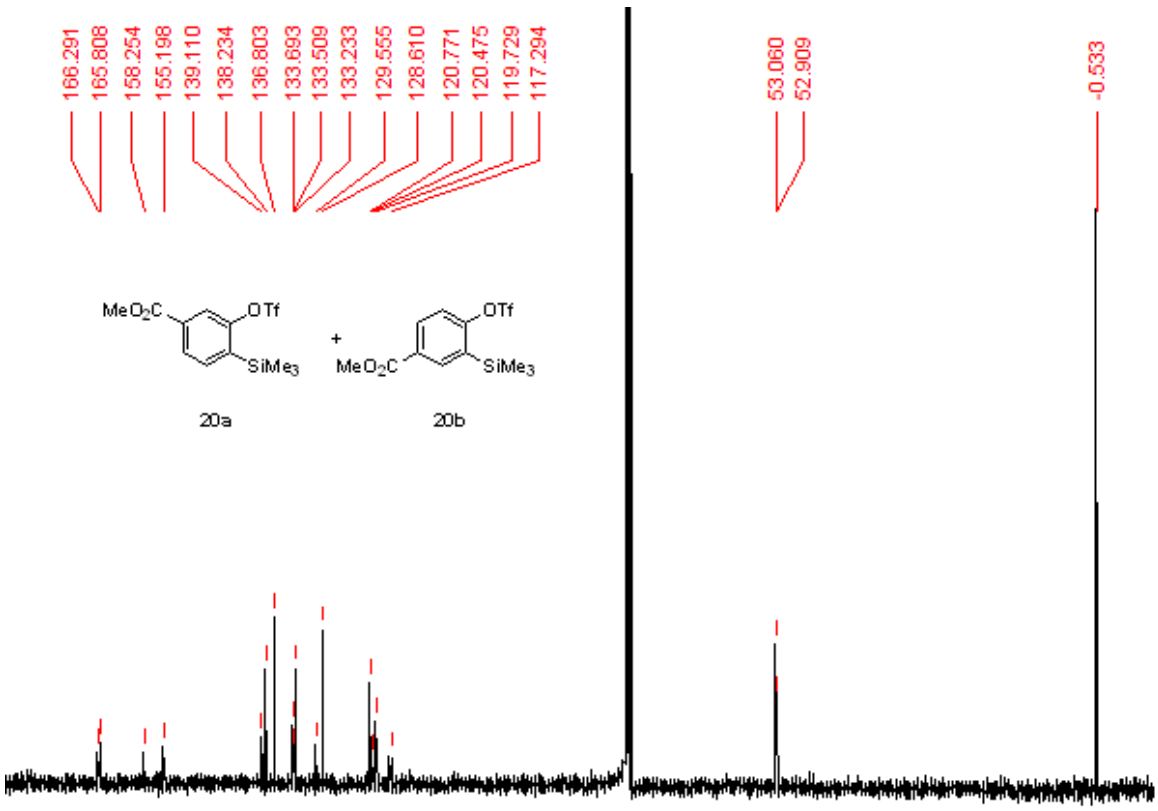
0.99
1.01
0.72
5.13
15.02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155.198
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133.693
133.509
133.233
129.555
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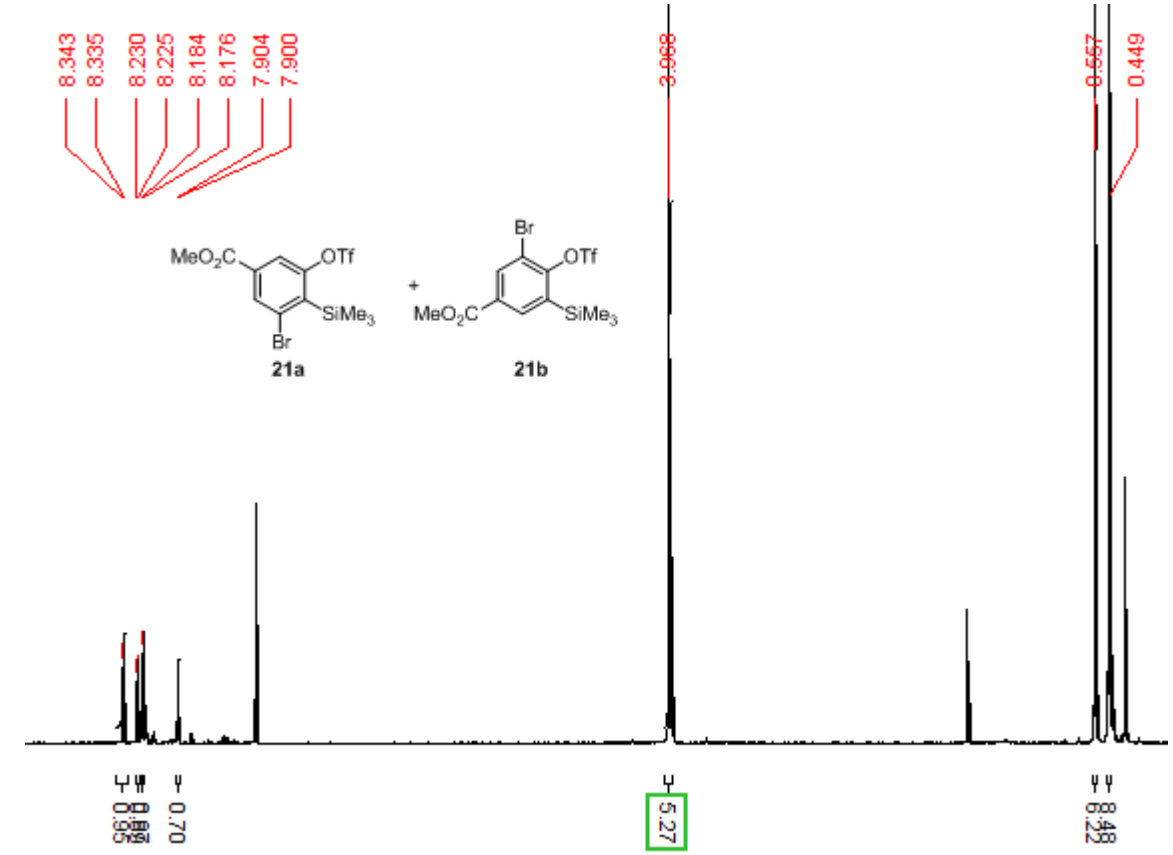
120.475
119.729
117.294
53.060
52.909
-0.533
MeO2C
OTf
SiMe3
+
20a
20b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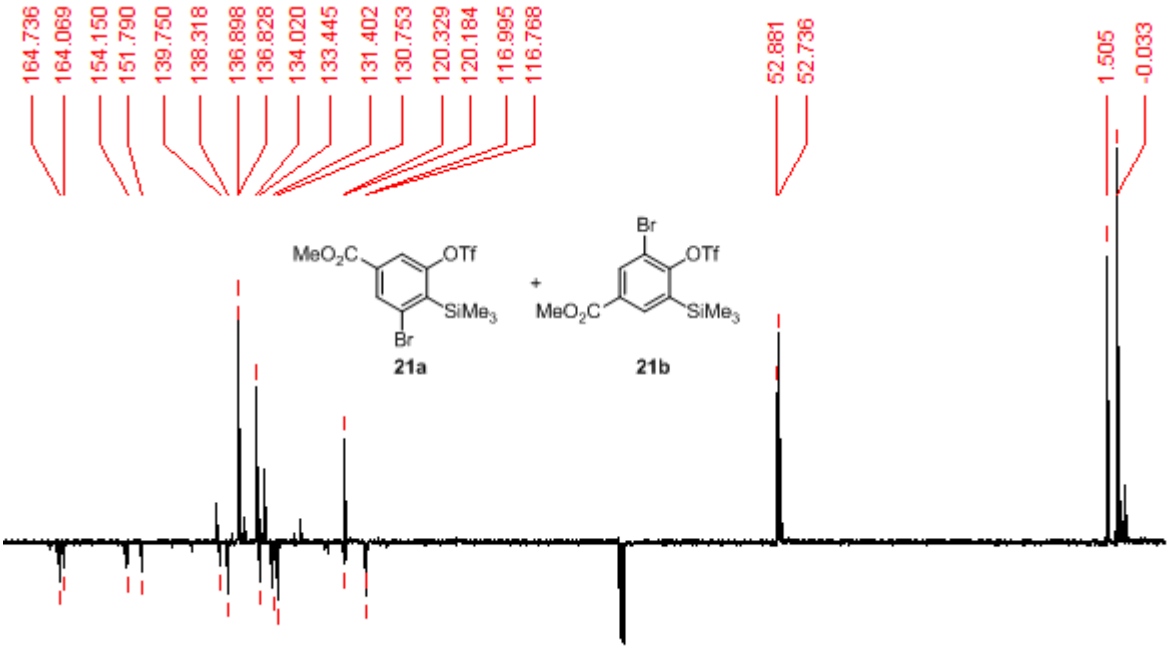
MeO2C
OTf
SiMe3
Br
21a
+
Br
OTf
MeO2C
SiMe3
21b
0.96
0.70
5.27
8.48
8.22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164.069
154.150
151.790
139.750
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136.898
136.828
134.020
133.445
131.402
130.753
120.329
120.184
116.995
116.768
52.881
52.736
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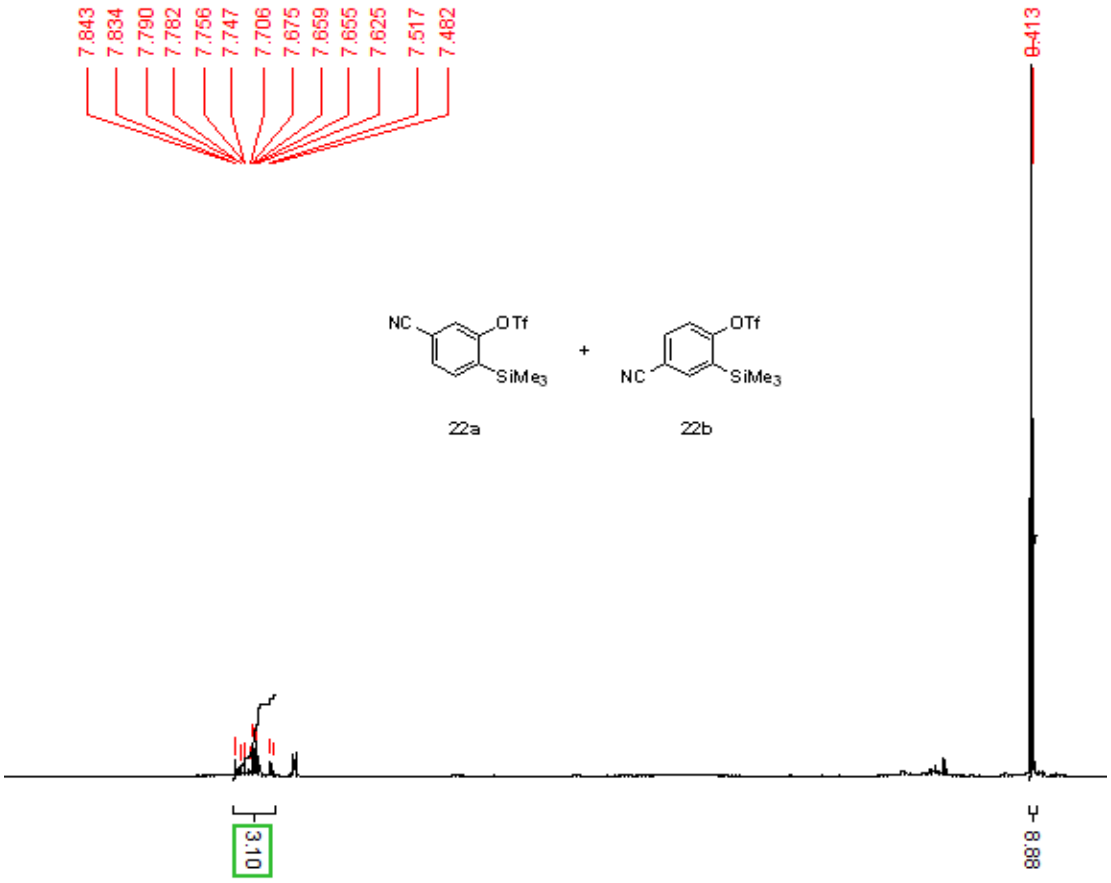
-0.033
MeO2C
OTf
SiMe3
Br
21a
+
Br
OTf
MeO2C
SiMe3
21b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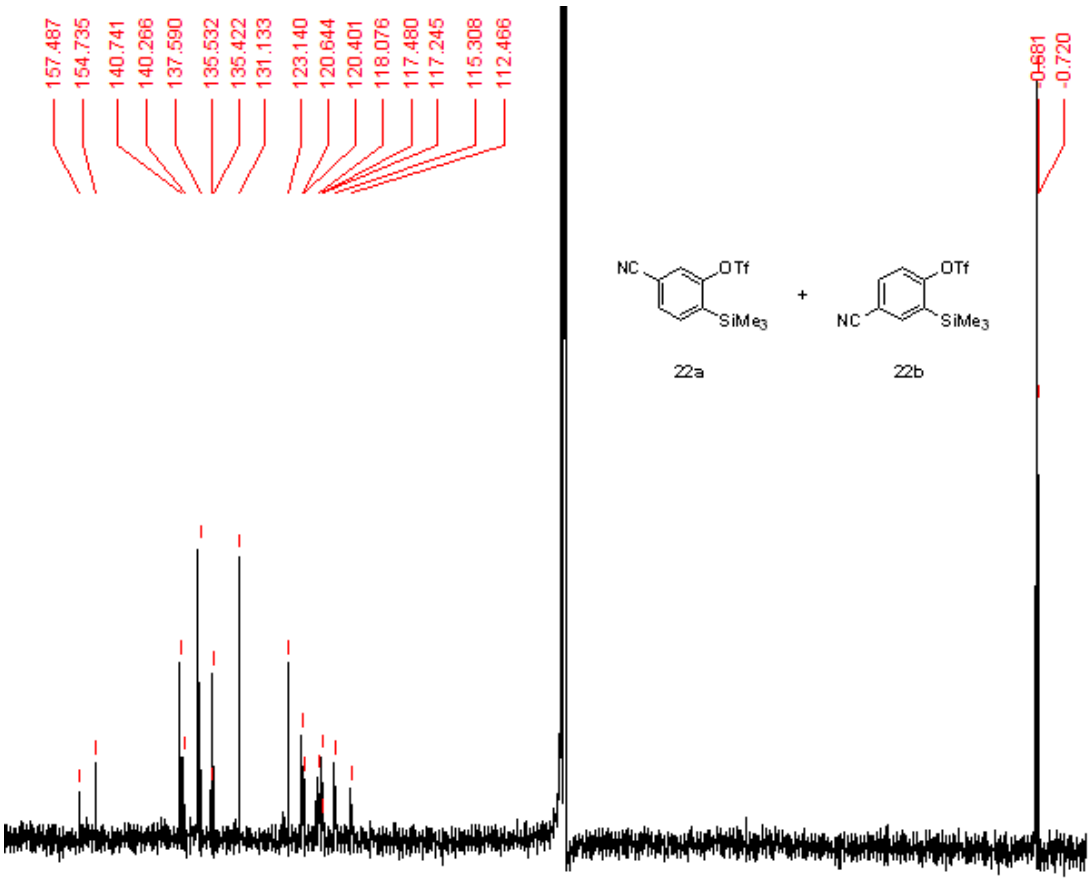
7.790
7.782
7.756
7.747
7.706
7.675
7.659
7.655
7.625
7.517
7.482
9.413
NC
OTf
SiMe3
+
OTf
NC
SiMe3
22a
22b
3.10
8.88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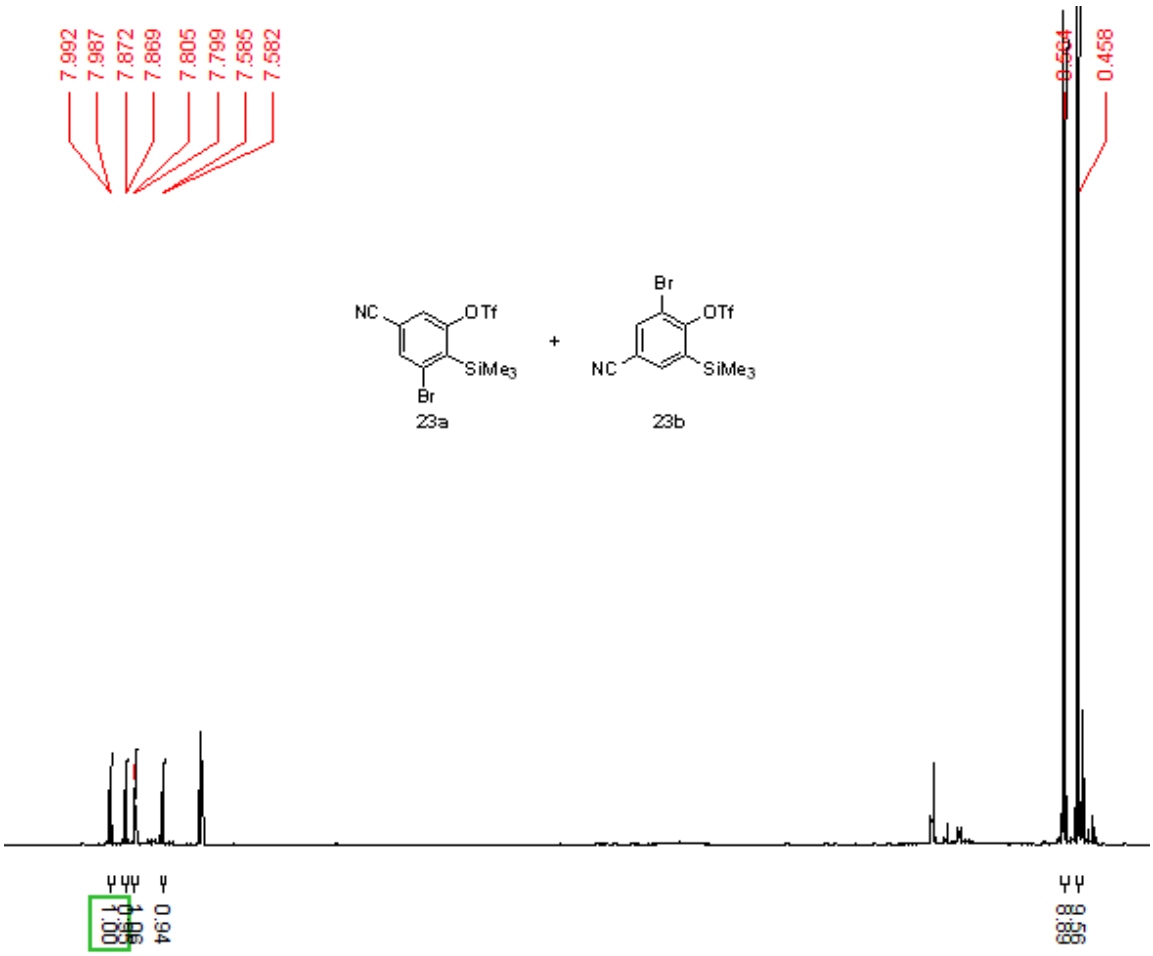
154.735
140.741
140.266
137.590
135.532
135.422
131.133
123.140
120.644
120.401
118.076
117.480
117.245
115.308
112.466
0.681
-0.720
NC
OTf
SiMe3
+
OTf
NC
SiMe3
22a
22b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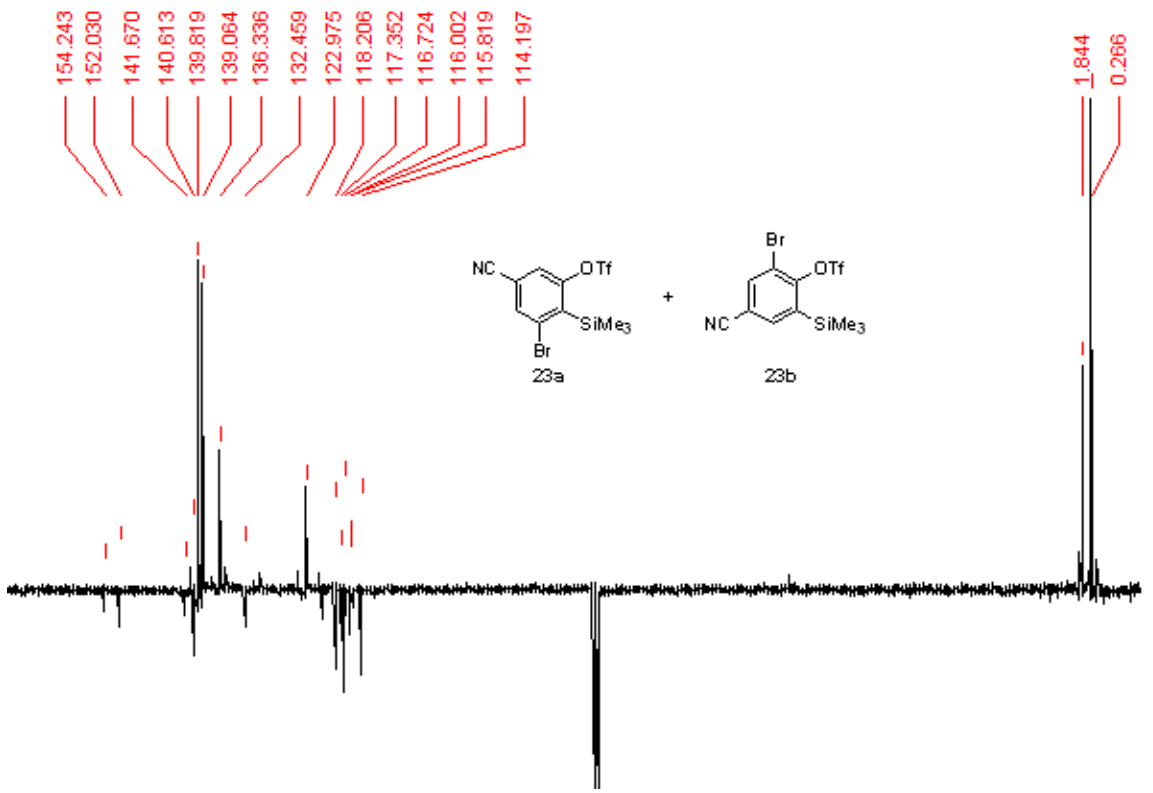
7.987
7.872
7.869
7.805
7.799
7.585
7.582
0.564
0.458
NC
OTf
SiMe3
Br
23a
+
Br
OTf
NC
SiMe3
23b
7.00
0.98
0.94
8.56
8.89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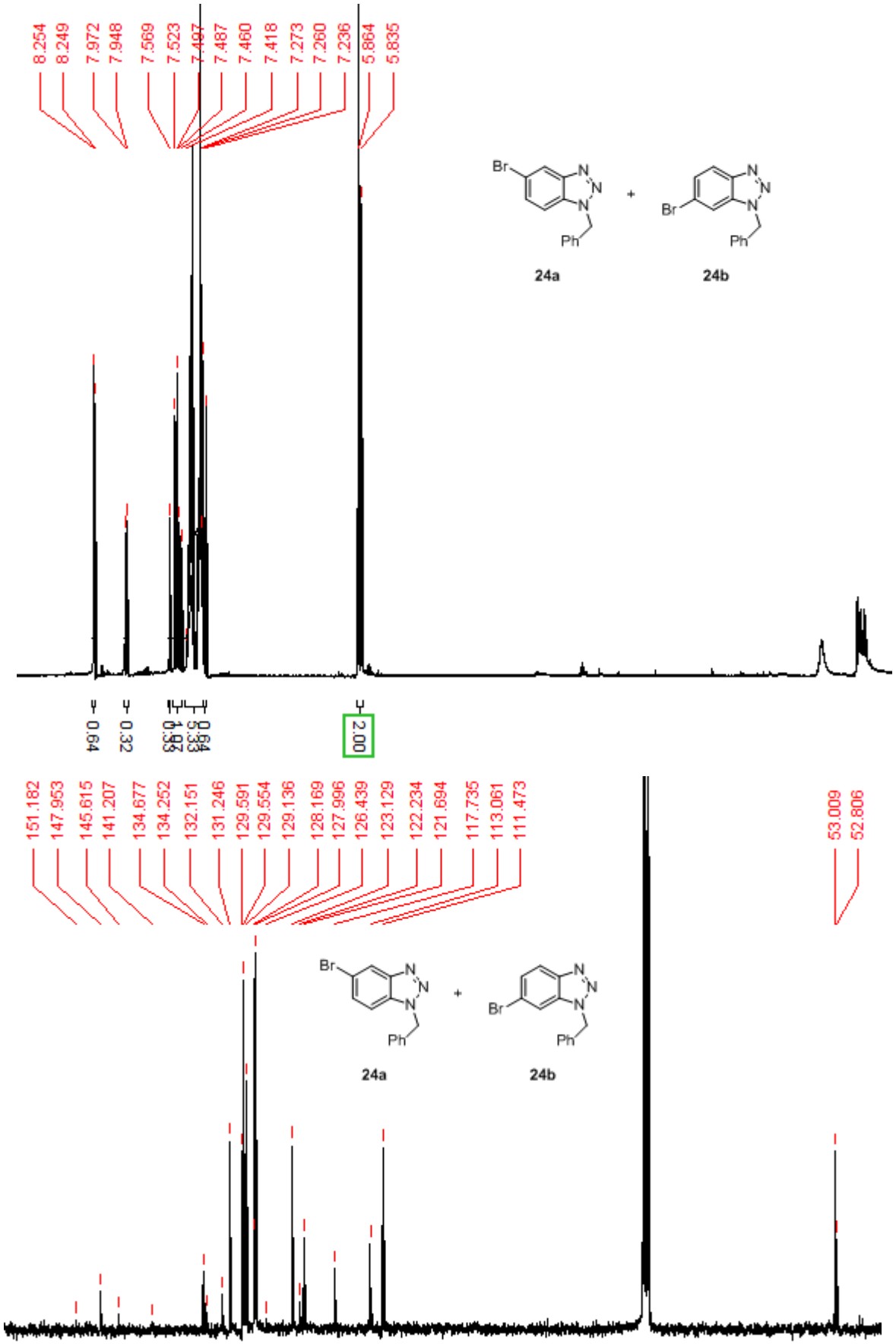
152.030
141.670
140.613
139.819
139.064
136.336
132.459
122.975
118.206
117.352
116.724
116.002
115.819
114.197
1.844
0.266
NC
OTf
SiMe3
Br
23a
+
Br
OTf
NC
SiMe3
23b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8.249
7.972
7.948
7.569
7.523
7.497
7.487
7.460
7.418
7.273
7.260
7.236
5.864
5.835
Br
N
N
N
Ph
+
24a
24b
0.64
0.32
0.93
0.97
3.83
3.84
2.00
151.182
147.953
145.615
141.207
134.677
134.252
132.151
131.246
129.591
129.554
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127.996
126.439
123.129
122.234
121.694
117.735
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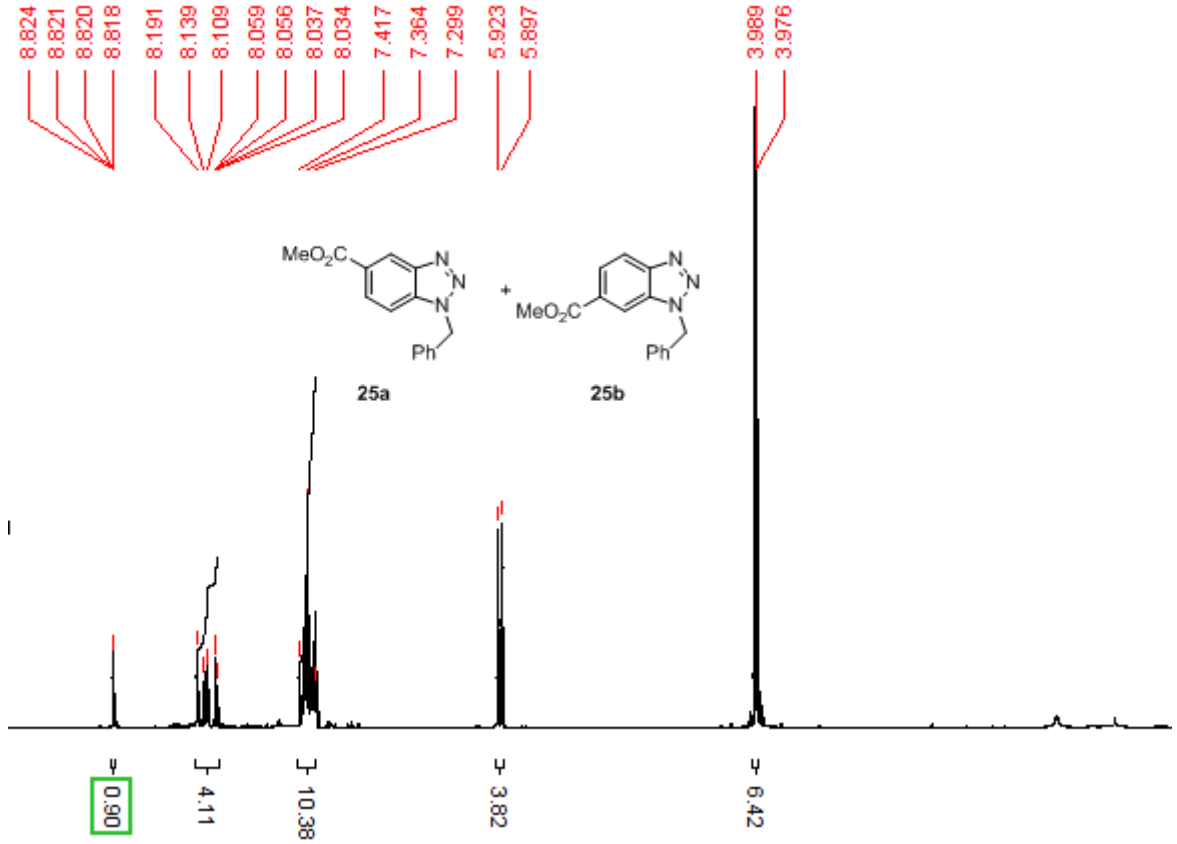
111.473
53.009
52.806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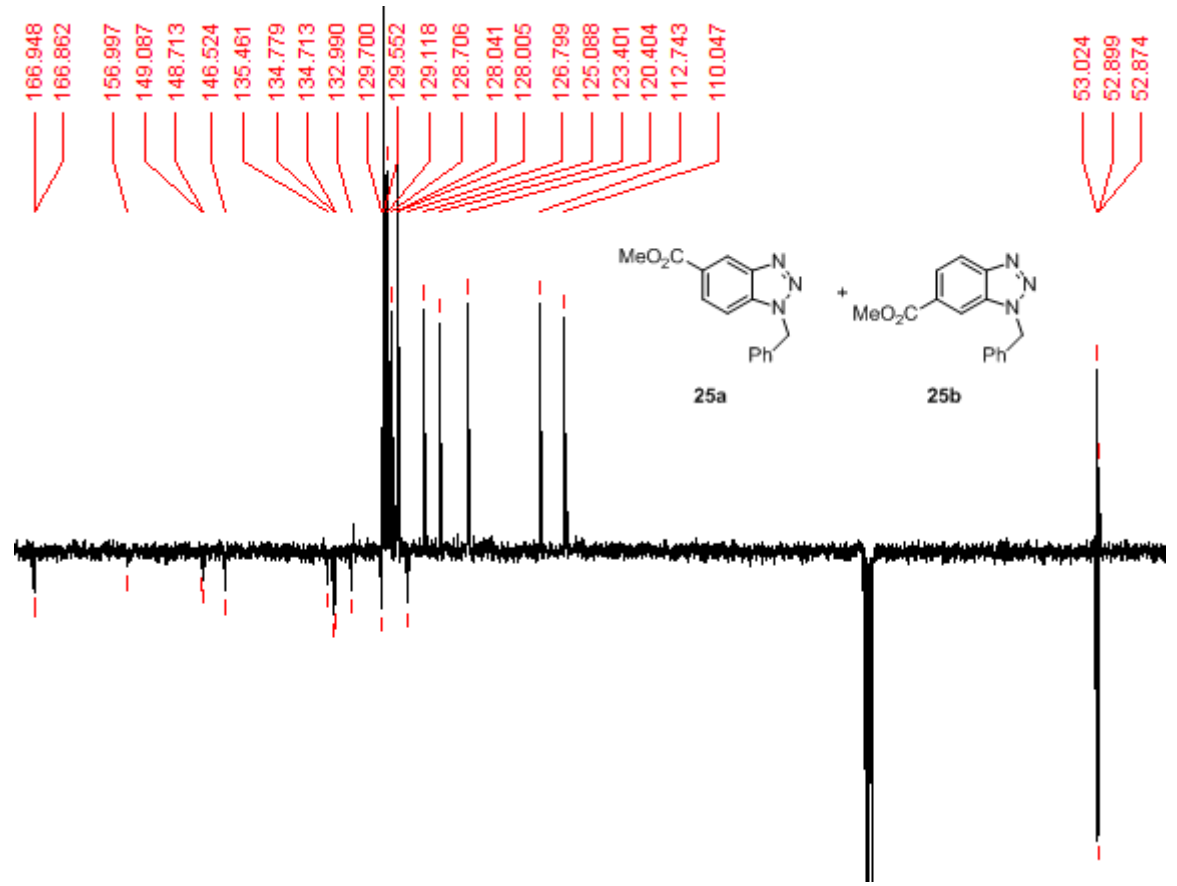
8.821
8.820
8.818
8.191
8.139
8.109
8.059
8.056
8.037
8.034
7.417
7.364
7.299
5.923
5.897
3.989
3.976
MeO2C
N
N
N
Ph
+
MeO2C
N
N
N
Ph
25a
25b
0.90
4.11
10.38
3.82
6.42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166.862
156.997
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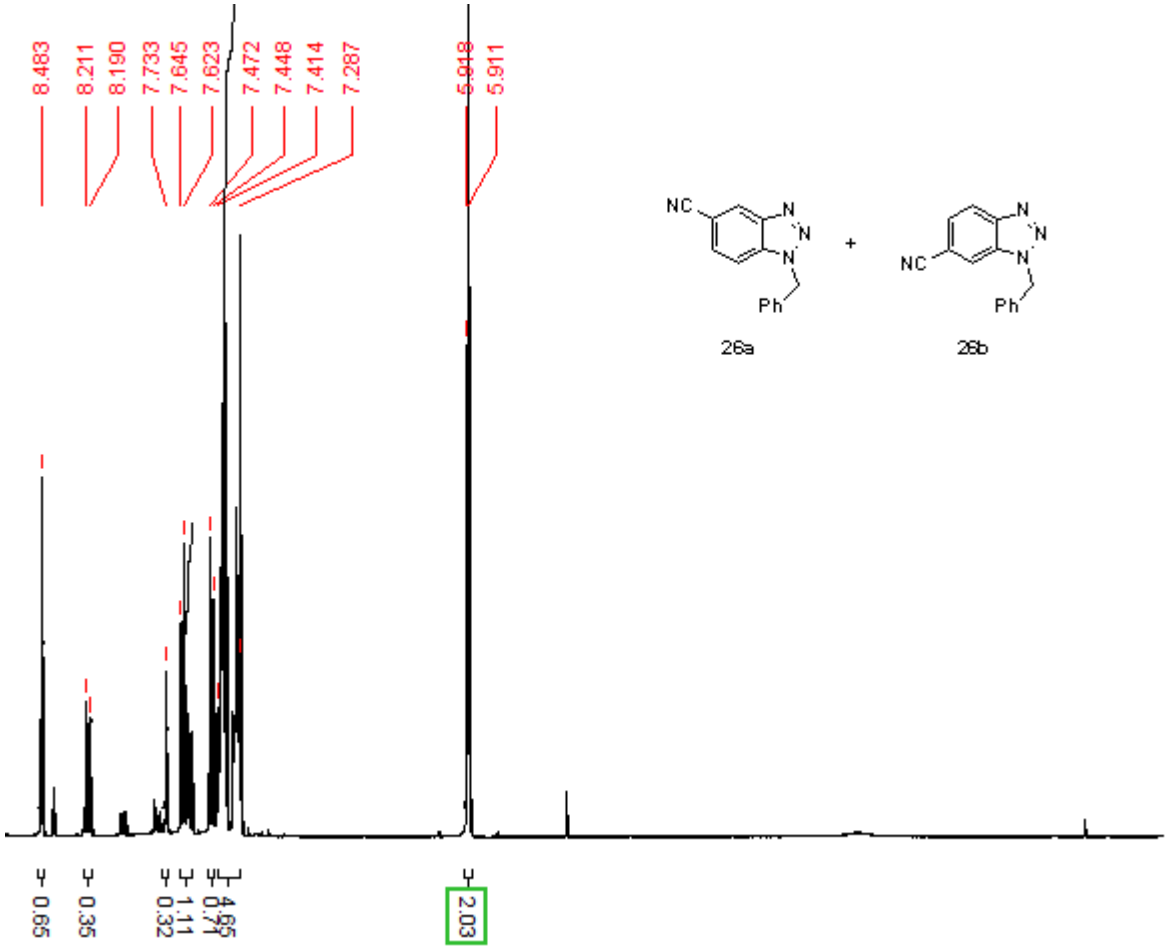
148.713
146.524
135.461
134.779
134.713
132.990
129.700
129.552
129.118
128.706
128.041
128.005
126.799
125.088
123.401
120.404
112.743
110.047
53.024
52.899
52.874
MeO2C
N
N
N
Ph
+
MeO2C
N
N
N
Ph
25a
25b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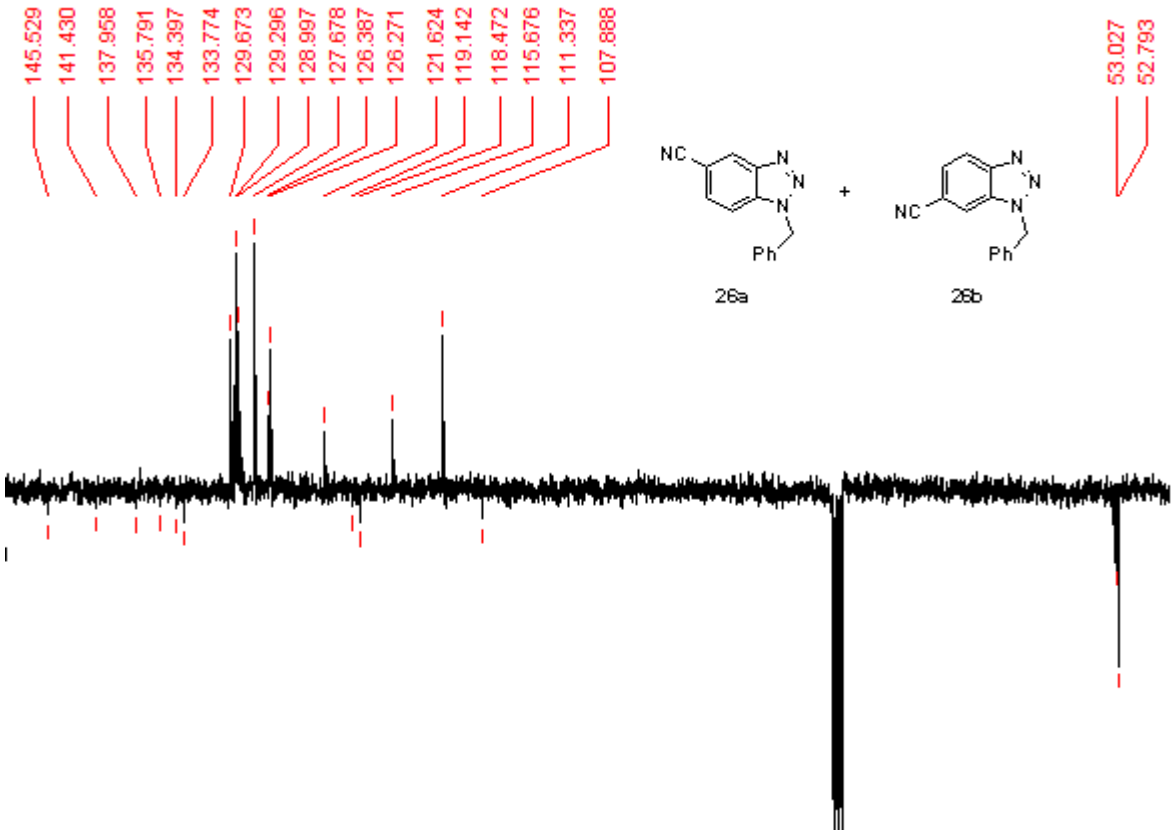
8.211
8.190
7.733
7.645
7.623
7.472
7.448
7.414
7.287
5.918
5.911
0.65
0.35
0.32
1.11
0.97
4.95
2.03
NC
N
N
N
Ph
+
26a
26b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134.397
133.774
129.673
129.296
128.997
127.678
126.387
126.271
121.624
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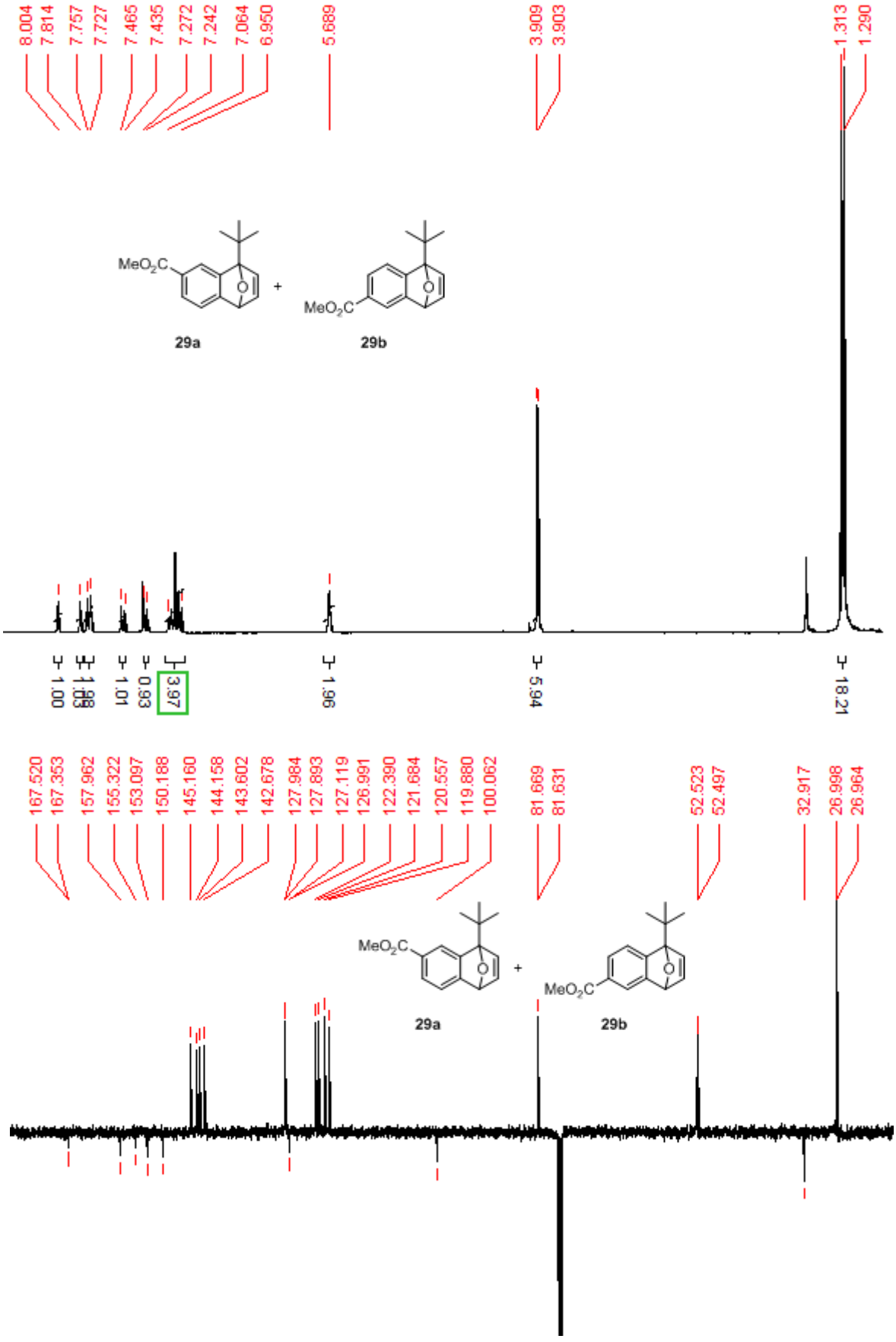
118.472
115.676
111.337
107.888
53.027
52.793
NC
N
N
N
Ph
+
26a
26b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7.757
7.727
7.465
7.435
7.272
7.242
7.064
6.950
5.689
3.909
3.903
1.313
1.290
MeO2C
29a
MeO2C
29b
1.00
1.03
1.01
0.93
3.97
1.96
5.94
18.21
167.520
167.353
157.962
155.322
153.097
150.188
145.160
144.158
143.602
142.678
127.984
127.893
127.119
126.991
122.390
121.684
120.557
119.880
100.062
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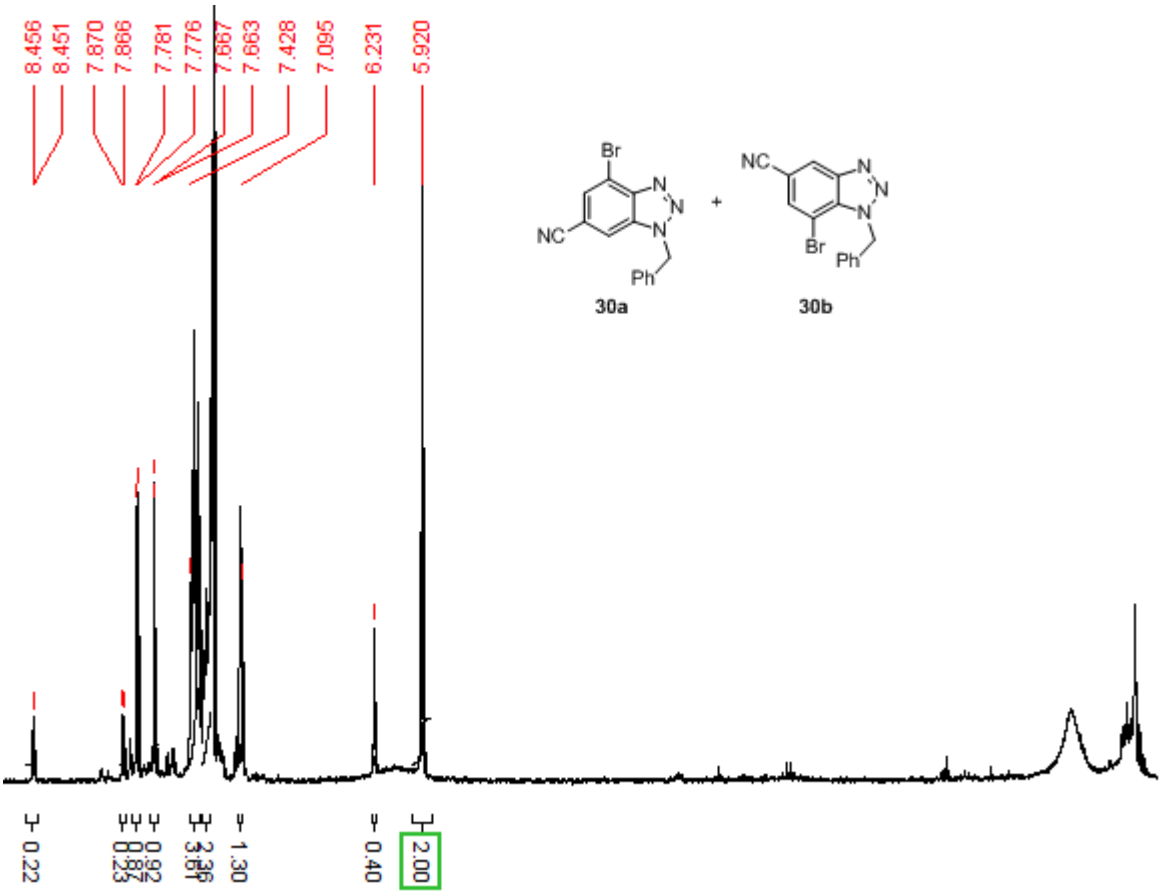
81.631
52.523
52.497
32.917
26.998
26.964
MeO2C
29a
MeO2C
29b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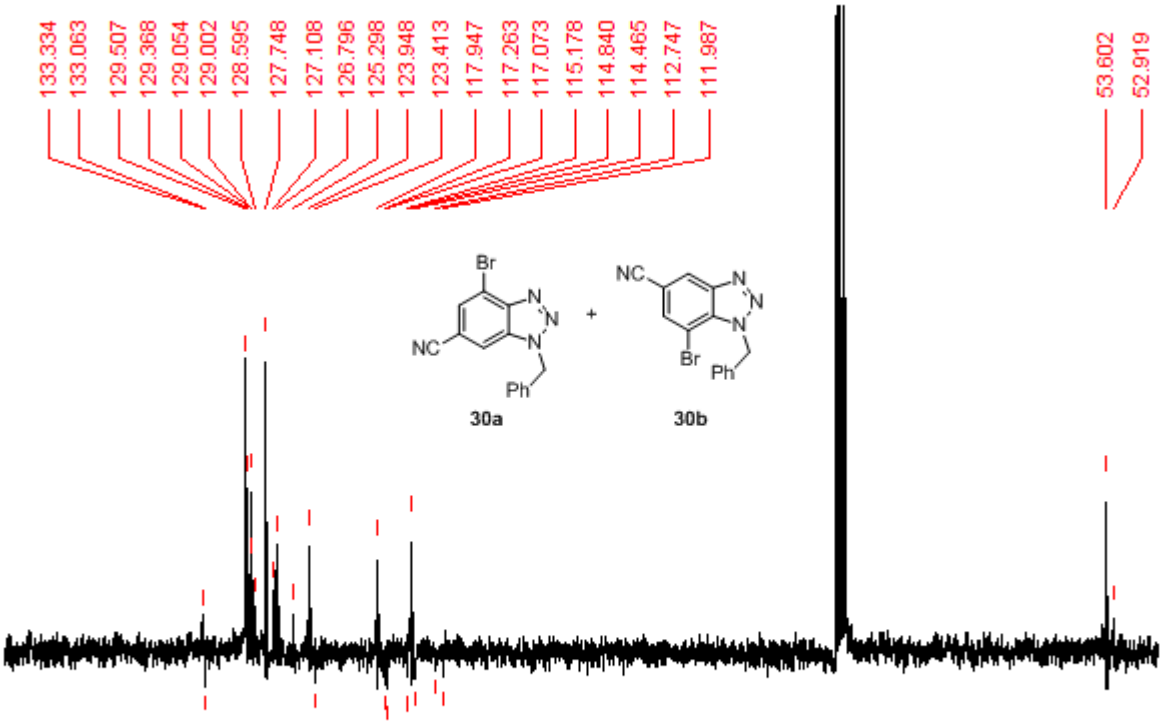
8.451
7.870
7.866
7.781
7.776
7.667
7.663
7.428
7.095
6.231
5.920
0.22
0.23
0.82
0.92
3.36
3.39
1.30
0.40
2.00
Br
NC
N
N
N
Ph
30a
NC
N
N
N
Br
Ph
30b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52.919
Br
NC
N
N
N
Ph
30a
NC
N
N
N
Br
Ph
30b