Sequential Cross-Metathesis / Electrophilic Fluorodesilylation: a Novel Entry to Functionalized Allylic Fluorides

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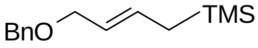
Supporting Information

General Procedure A: Cross-Metathesis reaction

A solution of starting material **3** (0.3 M) in dichloromethane and allyltrimethylsilane (3 eq.) was heated to reflux under argon. Catalyst **2** (5% mol) was added as a solid (in three portions over 48 hours), the reaction left to reflux for 48 hours, and followed by TLC. The mixture was then concentrated *in vacuo*.

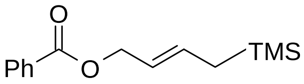
General Procedure B: Electrophilic Fluorodesilylation

A solution of Cross-Metathesis product **4** (0.1 M) in acetonitrile and Selectfluor^{TM} (1eq.) was stirred at room temperature under argon for 2 days. When the reaction was complete the mixture was concentrated *in vacuo*.

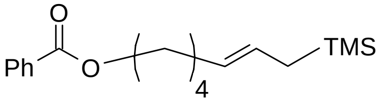


Compound 4a: (4-Benzyloxy-but-2-enyl)-trimethyl-silane. General procedure A was followed, starting from 156 mg of allyloxymethyl-benzene **3a** (1.05 mmol) and 0.5 ml of allyltrimethylsilane in DCM (3ml) using 5% of catalyst **2** (44 mg, 0.05 mmol). Purification by flash column chromatography (3/97: diethylether/hexane) afforded 143 mg of the title compound (E/Z ratio: 4/1) as a white oil (58%). ^{1}H NMR (400.132 MHz, $CDCl_3$, ppm) : δ 0.02 and 0.03 (9H, 2s, $Si(Me)_3$), 1.53 (2H, d, J= 8.4 Hz, CH_2, H_1), 3.98 (1.6H, d, J = 6.6 Hz, H_{4trans}), 4.05 (0.4H, d, J = 5.9 Hz, H_{4cis}), 4.51 and 4.53 (2H, 2s, -O-CH_2-Ph), 5.47 (0.8H, dddm, J = 15.2 Hz, J = 6.8 Hz, J = 5.9 Hz, H_{2trans}), 5.54 (0.2H, m, H_{2cis}), 5.70 (1H, m, H_2), 7.36-7.59 (5H, m, H_{arom}). ^{13}C NMR (100.624 MHz, $CDCl_3$, ppm) : δ -1.9 (CH_3, $Si(Me)_3$), 22.9 (CH_2, C_1),71 (CH_2, C_4 or -CH_2-Ph), 71.3 (CH_2, C_4 or -O-CH_2-Ph), 123.6 (CH, C_{2cis}), 124.7 (CH, C_{2trans}), 127.5 (CH, $C_{arom\ para}$), 127.7 (CH, $C_{arom\ ortho}$), 128.3 (CH, $C_{arom\ meta}$),

130.0 (CH, C_{3cis}), 131.9 (CH, C_{3trans}), 138.6 (CH, $C_{arom\ IPSO}$). MS (GCT, CI^+): *m/z* (relative intensity %) 252 $[M+NH_4]^+$ (100). HRMS (GCT, CI^+): Calc for $C_{14}H_{26}NOSi$: 252.1784, found 252.1781.

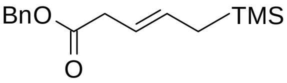


Compound 4b: Benzoic acid 4-trimethylsilanyl-but-2-enyl ester. General procedure A was followed, starting from 162 mg of benzoic acid allyl ester **3b** (1 mmol) and 0.48 ml of allyltrimethylsilane in DCM (3ml) using 5% of catalyst **2** (42 mg, 0.05 mmol). Purification by flash column chromatography (2/98: diethylether/hexane then 5/95: diethylether/hexane) afforded 208 mg of the title compound (E/Z ratio: 4/1) as an oil (84%). ^1H NMR (400.132 MHz, $CDCl_3$, ppm) : δ 0.05 and 0.06 (9H, 2s, $Si(Me)_3$), 1.55 (1.6H, d, J= 4.5 Hz, H_{4trans}), 1.65 (0.4H, d, J= 4.3 Hz, H_{4cis}), 4.76 (1.6H, d, J = 6.8 Hz, H_{1trans}), 4.94 (0.4H, d, J = 6.6 Hz, H_{1cis}), 5.57 (1H, m, H_2), 5.77 (0.2H, q, J = 6.7 Hz, H_{3cis}), 5.90 (0.8, dt, J = 16.0 Hz, J = 8.0 Hz, H_{3trans}), 7.44 (2H, t, J = 7.6 Hz, $H_{arom\ meta}$), 7.55 (1H, m, $H_{arom\ para}$), 8.06 (2H, m, $H_{arom\ ortho}$). ^{13}C NMR (100.624 MHz, $CDCl_3$, ppm) : δ -2.0 (CH_3, $Si(Me)_3$), 19.3 (CH_2, C_4), 23.1 (CH_2, C_4), 60.7 (CH_2, C_1), 66.1 (CH_2, C_1), 120.7 (CH, C_{2cis}), 122.1 (CH, C_{2trans}), 128.3 (CH, $C_{arom\ meta}$), 129.6 (CH, $C_{arom\ ortho}$), 131.0 (CH, $C_{arom\ IPSO}$), 132.1 (CH, C_{3cis}), 132.7 (CH, C_{3trans}), 134.1 (CH, $C_{arom\ para}$), 166.5 (CO). MS (GCT, CI^+): *m/z* (relative intensity %) 179 $[M-CH_2SiMe_3+NH_4]^+$ (100), 248 $[M]^+$ (5). HRMS (GCT, CI^+): Calc for $C_{14}H_{20}O_2Si$: 248.1233, found 248.1238.

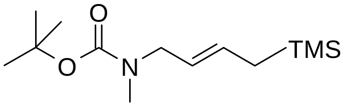


Compound 4c: Benzoic acid 7-trimethylsilanyl-hept-5-enyl ester. General procedure A was followed, starting from 449 mg of benzoic acid hex-5-enyl ester **3c** (2.36 mmol) and 1.12 ml of allyltrimethylsilane in DCM (6ml) using 5% of catalyst **2** (100 mg, 0.17 mmol). Purification by flash column chromatography (2/98: diethylether/hexane) afforded 370 mg of the title compound (E/Z ratio: 5/1) as a white oil (54%). ^1H NMR (400.132 MHz, $CDCl_3$, ppm) : δ -0.01 and 0.00 (9H, 2s, $Si(Me)_3$), 1.41 (2H, d, J= 7.6 Hz, H_7), 1.50 (2H, tt, J= 7.6 Hz, J= 7.6 Hz, H_3), 1.78 (2H, tt, J= 6.8 Hz, J= 6.8 Hz, H_2), 2.06 (1.66H, q, J= 7.2 Hz, H_{4trans}), 2.16 (0.33H, q, J= 6.8 Hz, H_{4cis}), 4.32 (2H, t, J= 6.4 Hz, H_1), 5.25 (0.83H, dt, J = 15.1 Hz, J = 7.6 Hz, H_{6trans}), 5.27 (0.16H, m, H_{6cis}), 5.42 (0.83, dt, J= 15.1 Hz, J= 7.2 Hz,

H_{5trans}), 5.45 (0.16H, m, H_{5cis}), 7.45 (2H, t, J= 8.0 Hz, $H_{arom\ meta}$), 7.56 (1H, m, $H_{arom\ para}$), 8.05 (2H, dm, J = 7.2 Hz, $H_{arom\ ortho}$). ^{13}C NMR (100.624 MHz, $CDCl_3$, ppm) : δ -2.0 and -1.8 (CH_3, $Si(Me)_3$), 22.6 (CH_2, C_7), 26.3 (CH_2, C_3), 28.1 (CH_2, C_2), 32.3 (CH_2, C_4), 65.8 (CH_2, C_1), 126.8 (CH, C_6), 128.1 (CH, C_5), 128.3 (CH, $C_{arom\ meta}$), 129.5 (CH, $C_{arom\ ortho}$), 130.5 (CH, $C_{arom\ IPSO}$), 132.8 (CH, $C_{arom\ para}$), 166.7 (CO). MS (GCT, CI^+): *m/z* (relative intensity %) 291 $[M+H]^+$ (100). HRMS (GCT, CI^+): Calc for $C_{17}H_{27}O_2Si$: 291.1780, found 291.1774.

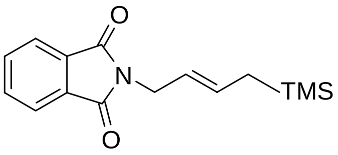


Compound 4d: 5-Trimethylsilanyl-pent-3-enoic acid benzyl ester. General procedure A was followed, starting from 217 mg of but-3-enoic acid phenyl ester **3d** (1.23 mmol) and 0.59 ml of allyltrimethylsilane in DCM (3ml) using 5% of catalyst **2** (52 mg, 0.06 mmol). Purification by flash column chromatography (5/95: diethylether/hexane) afforded 265 mg of the title compound (E/Z ratio: 3/1) as a white oil (82%). ^1H NMR (400.132 MHz, $CDCl_3$, ppm) : δ -0.02 and 0.03 (9H, 2s, $Si(Me)_3$), 1.46 (1.5H, d, J= 12.7 Hz, H_{5trans}), 1.52 (0.5H, d, J= 9.4 Hz, H_{5cis}), 3.10 (1.5H, d, J= 6.9 Hz, H_{2trans}), 3.13 (0.5H, d, J= 7.1 Hz, H_{2cis}), 5.15 (1.5H, s, -O-CH_2-Ph), 5.16 (0.5H, s, -O-CH_2-Ph), 5.40 (1H, m, H_4), 5.58 (0.75, dt, J= 15.2 Hz, J= 7.6 Hz, H_{3trans}), 5.65 (0.25H, dm, J= 10.8 Hz, H_{3cis}), 7.34 (5H, m, H_{arom}). ^{13}C NMR (100.624 MHz, $CDCl_3$, ppm) : δ -2.0 and -1.8 (CH_3, $Si(Me)_3$), 18.8 and 22.9 (CH_2, C_5), 32.8 and 38.3 (CH_2, C_2), 66.3 (CH_2, O-CH_2-Ph), 118.2 (CH, C_{4cis}), 119.6 (CH, C_{4trans}), 128.2 and 128.5 (3CH, $C_{arom\ ortho\text{-}meta\text{-}para}$), 129.4 (CH, C_{3cis}), 131.2 (CH, C_{3trans}), 136.0 (CH, $C_{arom\ IPSO}$), 172.0 (CO). MS (GCT, CI^+): *m/z* (relative intensity %) 280 $[M+NH_4]^+$ (20), 263 $[M+H]^+$ (100). HRMS (GCT, CI^+): Calc for $C_{15}H_{23}O_2Si$: 263.1467, found 263.1461.

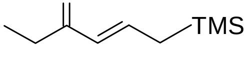


Compound 4e: Methyl-(4-trimethylsilanyl-but-2-enyl)-carbamic acid *tert*-butyl ester. General procedure A was followed, starting from 171 mg of Allyl-methyl-carbamic acid *tert*-butyl ester **3e** (1 mmol) and 0.48 ml of allyltrimethylsilane in DCM (3ml) using 5% of catalyst **2** (42 mg, 0.05 mmol). Purification by flash column chromatography (10/90: diethylether/hexane) afforded

180 mg of the title compound (E/Z ratio: 9/1) as a white oil (70%). ^{1}H NMR (400.132 MHz, CDCl$_3$, ppm) : δ 0.00 and 0.01 (9H, 2s, Si(Me)$_3$), 1.48 (11H, brs, H$_4$ and (CH$_3$)3C-O-), 2.78 (2.7H, s, N-CH$_{3\ \mathrm{trans}}$), 2.80 (0.3H, s, N-CH$_{3\ \mathrm{cis}}$), 3.74 (1.8H, d, J= 4.8 Hz, H$_{1\mathrm{trans}}$), 3.82 (0.2H, d, J= 2.4 Hz, H$_{1\mathrm{cis}}$), 5.23 (0.9H, dt, J= 15.4 Hz, J= 6.4 Hz H$_{3\mathrm{trans}}$), 5.28 (0.1H, dm, J= 10.8 Hz, H$_{3\mathrm{cis}}$), 5.54 (0.9H, dt, J= 15.5 Hz, J= 8.4 Hz, H$_{2\mathrm{trans}}$), 5.58 (0.1H, m, H$_{2\mathrm{cis}}$). ^{13}C NMR (100.624 MHz, CDCl$_3$, ppm): δ -2.0 and -1.8 (CH$_3$, Si(Me)$_3$), 18.8 (CH$_2$, C$_4$), 22.6 (CH$_2$, C$_1$), 28.4 (3 CH$_3$, (CH$_3$)3C-O-), 33.2 (CH$_3$, N-CH$_3$) 79.1 ((CH$_3$)3$\underline{\mathrm{C}}$-O-), 123.5 (2CH, C$_2$ and C$_3$), 155.7 (CO). MS (GCT, CI$^+$): *m/z* (relative intensity %) 202 [M-SiMe$_3$+NH$_4$]$^+$ (100), 258 [M+H]$^+$ (7). HRMS (GCT, CI$^+$): Calc for C$_{13}$H$_{28}$NO$_2$Si: 258.1889, found 258.1881.

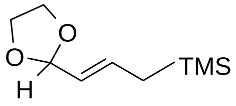


Compound 4f: 2-(4-Trimethylsilanyl-but-2-enyl)-isoindole-1,3-dione. General procedure A was followed, starting from 187 mg of 2-Allyl-isoindole-1,3-dione **3f** (1 mmol) and 0.48 ml of allyltrimethylsilane in DCM (3ml) using 5% of catalyst **2** (42 mg, 0.05 mmol). Purification by flash column chromatography (15/85: diethylether/hexane) afforded 243 mg of the title compound (E/Z ratio: 3/1) as a white solid (89%). ^{1}H NMR (400.132 MHz, CDCl$_3$, ppm) : δ -0.02 and 0.04 (9H, 2s, Si(Me)$_3$), 1.44 (1.5H, d, J= 8.5 Hz, H$_{4'\mathrm{trans}}$), 1.73 (0.5H, d, J= 8.9 Hz, H$_{4'\mathrm{cis}}$), 4.22 (1.5H, d, J= 6.6 Hz, H$_{1'\mathrm{trans}}$), 4.27 (0.5H, d, J= 6.0 Hz, H$_{1'\mathrm{cis}}$), 5.40 (1H, m, H$_{3'}$), 5.62 (0.25H, dt, J= 7.7 Hz, J= 7.6 Hz, H$_{2'\mathrm{cis}}$), 5.78 (0.75H, dt, J= 15.2 Hz, J= 8.2 Hz, H$_{2'\mathrm{trans}}$), 7.70 (2H, dd, J= 5.6 Hz, J= 3.2 Hz, H$_{\mathrm{arom}\ 6\ \mathrm{and}\ 7}$), 7.83 (2H, dd, J= 5.6 Hz, J= 3.2 Hz, H$_{\mathrm{arom}\ 5\ \mathrm{and}\ 8}$). ^{13}C NMR (100.624 MHz, CDCl$_3$, ppm) : δ -2.3 and -2.0 (CH$_3$, Si(Me)$_3$), 18.9 (CH$_2$, C$_{4'}$), 22.7 (CH$_2$, C$_{4'}$), 34.7 (CH$_2$, C$_{1'}$), 39.9 (CH$_2$, C$_{1'}$), 120.5 (CH, C$_{3'\mathrm{cis}}$), 121.3 (CH, C$_{3'\mathrm{trans}}$), 130.8 (CH, C$_{2'\mathrm{cis}}$), 132.2 (CH, C$_{2'\mathrm{trans}}$), 132.3 (2C$_{\mathrm{arom}}$, C$_4$ and C$_9$), 133.8 (2C$_{\mathrm{arom}}$, C$_5$ and C$_8$), 168.0 (CO). mp:92-93°C. MS (GCT, CI$^+$): *m/z* (relative intensity %) 274 [M+H]$^+$ (100). HRMS (GCT, CI$^+$): Calc for C$_{15}$H$_{20}$NO$_2$Si: 274.1263, found 274.1255.

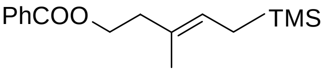


Compound 4g: 6-Trimethylsilanyl-hex-4-en-3-one. A solution of 0.16 ml of allyltrimethylsilane (1 mmol) and 0.3 ml of ethylvinyl ketone

3g (3 eq.) in dichloromethane (4 ml) was heated to reflux under argon. Catalyst **2** (42 mg, 0.05 mmol) was then added as a solid (in three portions over 48 hours) and the reaction left to reflux for 48 hours. The mixture was then concentrated *in vacuo*. Purification by flash column chromatography (4/96: diethylether/hexane then 6/94: ether/hexane) afforded 106 mg of the title compound (E>95 %) as an oil (62%). Spectroscopic data are in accordance with literature.[8e]

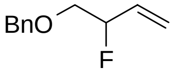


Compound 4h: (3-[1,3]Dioxalan-2-yl-allyl)trimethyl-silane. General procedure A was followed, starting from 1 ml of 2-Vinyl-[1,3]dioxalane **3h** (1 mmol) and 0.48 ml of allyltrimethylsilane in DCM (3ml) using 5% of catalyst **2** (42 mg, 0.05 mmol). Purification by flash column chromatography (4/96: diethylether/hexane) afforded 140 mg of the title compound (E>95 %) as an oil (75%). ^{1}H NMR (400.132 MHz, $CDCl_3$, ppm) : δ 0.03 (9H, s, $Si(Me)_3$), 1.55 (2H, dd, J= 8.4 Hz, J= 1.6 Hz, H_1), 3.88 and 4.00 (4H, 2m, -O-CH_2-CH_2-O-), 5.18 (1H, d, J= 6.8 Hz, -O-CHR-O-), 5.33 (1H, ddt, J= 15.2 Hz, J= 6.8 Hz, J= 1.6 Hz, H_3), 5.93 (1H, dt, J= 15.2 Hz, J= 8.4 Hz, H_2). ^{13}C NMR (100.624 MHz, $CDCl_3$, ppm): δ -2.0 CH_3, $Si(Me)_3$), 23.1 (CH_2, C_1), 64.8 (2CH_2, -O-CH_2-CH_2-O-), 104.7 (CH, -O-CHR-O-), 124.5 (CH, C_2), 134.9 (CH, C_3). MS (GCT, CI^+): *m/z* (relative intensity %) 187 $[M+H]^+$ (100). HRMS (GCT, CI^+): Calc for $C_9H_{19}O_2Si$: 187.1154, found 187.1155.

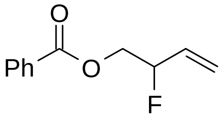


Compound 4i: Benzoic acid 3-methyl-5-trimethylsilanyl-pent-3-enyl ester. A solution of 190 mg of Benzoic acid 3-methyl-but-3-enyl ester **3i** (1 mmol) and 0.48 ml of allyltrimethylsilane in dichloromethane (3 ml) was heated to reflux under argon. Catalyst **2** (85 mg, 0.1 mmol) was then added as a solid (in five portions over 96 hours) and the reaction left to reflux for 4 days. The mixture was then concentrated *in vacuo*. Purification by flash column chromatography (5/95: diethylether/hexane) afforded 36 mg of the title compound (E/Z ratio: 1/1) as an oil (13%). ^{1}H NMR (400.132 MHz, $CDCl_3$, ppm) : δ -0.04 and 0.01 (9H, 2s, $Si(Me)_3$), 1.44 (2H, m, H_5), 1.65 (1.5H, s, CH_3), 1.80 (1.5H, d, J= 15.2 Hz, CH_3), 2.47 (2H, q, J= 1.2 Hz, H_2), 4.35 (1H, t, J= 7.2 Hz, H_1), 4.38 (1H, t, J= 6.8 Hz, H_1), 5.31 (1H, m, H_4), 7.44 (2H, m, $H_{arom\ meta}$), 7.55 (1H, m, $H_{arom\ para}$), 8.04 (2H,

m, $H_{arom\ ortho}$). ^{13}C NMR (100.624 MHz, $CDCl_3$, ppm) : δ -1.8 and -1.7 (CH_3, $Si(Me)_3$), 15.9 (CH_3cis), 18.6 and 18.9 (CH_2, C_5), 23.7 (CH_3trans), 39.0 (CH_2, C_2), 63.3 and 63.8 (CH_2, C_1), 123.3 and 123.5 (CH, C_4), 128.1 ($C_{arom\ IPSO}$), 128.2 (2CH, $C_{arom\ meta}$), 129.5 (2CH, $C_{arom\ ortho}$), 130.4 (C_3), 132.8 (CH, $C_{arom\ para}$), 166.6 (CO). MS (GCT, CI$^+$): *m/z* (relative intensity %) 277 $[M+H]^+$ (85). HRMS (GCT, CI$^+$): Calc for $C_{16}H_{25}O_2Si$: 277.1624, found 277.1621.

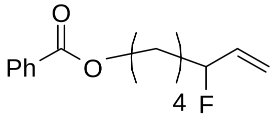


Compound 5a: (2-Fluoro-but-3-enyloxymethyl)-benzene. General procedure B was followed, starting from 76 mg of **4a** (0.31 mmol) and 115 mg of Selectfluor^{TM} (1 eq.) in CH_3CN (5ml). Purification by flash column chromatography (5/95: diethylether/hexane) afforded 39 mg of the title compound as a white oil (71%). ^{1}H NMR (400.132 MHz, $CDCl_3$, ppm) : δ 3.60 (1H, m, H_{1a}), 3.67 (1H, d, J = 4.8 Hz, H_{1b}), 4.62 (2H, d, J = 4.8 Hz, -O-CH_2-Ph), 5.11 (1H, ddt, J = 48.8 Hz, J = 11.6 Hz, J = 1.2 Hz, H_2), 5.32 (1H, dt, J = 10.8 Hz, J = 1.2 Hz, H_{4a}), 5.44 (1H, dq^5, J = 17.2 Hz, J = 1.2 Hz, H_{4b}), 5.92 (1H, dddd, J = 22.8 Hz, J = 17.2 Hz, J = 11.6 Hz, J = 10.2 Hz, H_3), 7.27-7.38 (5H, m, H_{arom}). ^{13}C NMR (100.624 MHz, CDCl3, ppm) : δ 72.3 (CH_2, d, J = 23 Hz, C_1), 73.5 (CH_2, -O-CH_2-Ph), 92.3 (CH, d, J = 171 Hz, C_2), 118.4 (CH, d, J = 11 Hz, C_4), 127.7 (CH, $C_{arom\ ortho}$), 127.8 (CH, $C_{arom\ para}$), 128.4 (CH, $C_{arom\ meta}$), 132.9 (CH, d, J = 19 Hz, C_3), 137.8 ($C_{arom\ IPSO}$). ^{19}F{^{1}H} NMR (376.508 MHz, $CDCl_3$, ppm): δ –189.8. MS (GCT, CI$^+$): *m/z* (relative intensity %) 198 $[M+NH_4]^+$ (90), 161 $[M-HF+H]^+$ (40). HRMS (GCT, CI$^+$): Calc for $C_{11}H_{13}O$: 161.0966, found 161.0968.

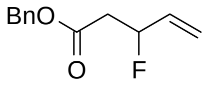


Compound 5b: Benzoic acid 2-fluoro-but-3-enyl ester. General procedure B was followed, starting from 95 mg of **4b** (0.38 mmol) and 132 mg of Selectfluor^{TM} (1 eq.) in CH_3CN (5ml). Purification by flash column chromatography (4/96: diethylether/hexane) afforded 55 mg of the title compound as a white oil (74%). ^{1}H NMR (400.132 MHz, $CDCl_3$, ppm) : δ 4.43 (1H, ddd, J = 19.2 Hz, J = 12.4 Hz, J = 6.8 Hz, H_{1a}), 4.52 (1H, ddd, J = 26.4 Hz, J = 12.4 Hz, J = 3.2 Hz, H_{1b}), 5.25 (1H, dm, J = 44.6 Hz, H_2), 5.40 (1H, dt, J = 10.8 Hz, J = 1.2 Hz, H_{4a}), 5.54 (1H, dq^5, J

= 17.2 Hz, J = 1.2 Hz, H$_{4b}$), 5.97 (1H, dddd, J = 20.8 Hz, J = 17.2 Hz, J = 10.8 Hz, J = 6.0 Hz, H$_3$), 7.46 (2H, dd, J = 8.0 Hz, J = 7.2 Hz, H$_{\text{arom meta}}$), 7.58 (1H, t, J = 7.2 Hz, H$_{\text{arom para}}$), 8.09 (2H, d, J = 8.0 Hz, H$_{\text{arom ortho}}$). ^{13}C NMR (100.624 MHz, CDCl3, ppm) : δ 65.8 (CH$_2$, d, J = 8 Hz, C$_1$), 90.6 (CH, d, J = 173 Hz, C$_2$), 119.4 (CH, d, J = 12 Hz, C$_4$), 128.4 (CH, C$_{\text{arom meta}}$), 129.6 (C$_{\text{arom IPSO}}$), 129.7 (CH, C$_{\text{arom ortho}}$), 132.0 (CH, d, J = 19 Hz, C$_3$), 132.2 (CH, C$_{\text{arom para}}$), 166.2 (CO). ^{19}F{^{1}H} NMR (376.508 MHz, CDCl$_3$, ppm): δ –185.9. MS (GCT, CI$^+$): *m/z* (relative intensity %) 212 [M+NH$_4$]$^+$ (70), 195 [M+H]$^+$ (18). HRMS (GCT, CI$^+$): Calc for C$_{11}$H$_{12}$FO$_2$: 195.0821, found 195.0815.

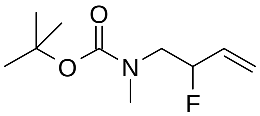


Compound 5c: Benzoic acid 5-fluoro-hept-6-enyl ester. General procedure B was followed, starting from 338 mg of **4c** (1.17 mmol) and 425 mg of Selectfluor$^{\text{TM}}$ (1 eq.) in CH$_3$CN (10ml). Purification by flash column chromatography (4/96: diethylether/hexane) afforded 91 mg of the title compound as a yellow oil (33%). ^{1}H NMR (400.132 MHz, CDCl$_3$, ppm) : δ 1.80 (6H, m, H$_{2,3,4}$), 4.34 (2H, t, J = 6.4 Hz, H$_1$), 4.91 (0.75H, dq, J = 48.8 Hz, J = 6.4 Hz, H$_5$), 5.01 (0.25H, dq, J = 49.6 Hz, J = 6.0 Hz, H$_5$), 5.24 (1H, d, J = 10.4 Hz, H$_{7a}$), 5.34 (1H, dm, J = 17.2 Hz, H$_{7b}$), 5.89 (1H, dddd, J = 20.0 Hz, J = 17.2 Hz, J = 10.5 Hz, J = 6.0 Hz, H$_6$), 7.45 (2H, t, J = 8.0 Hz, H$_{\text{arom meta}}$), 7.57 (1H, t, J = 7.6 Hz, H$_{\text{arom para}}$), 8.05 (2H, d, J = 6.8 Hz, H$_{\text{arom ortho}}$). ^{13}C NMR (100.624 MHz, CDCl3, ppm) : δ 21.3 (CH$_2$, C$_3$), 28.5 (CH$_2$, C$_2$), 34.8 (CH$_2$, d, J = 22 Hz, C$_4$), 64.7 (CH$_2$, C$_1$), 93.4 (CH, d, J = 166 Hz, C$_5$), 117.1 (CH$_2$, d, J = 12 Hz, C$_7$), 128.3 and 129.5 (CH, C$_{\text{arom ortho, meta}}$), 130.3 (C$_{\text{arom IPSO}}$), 132.9 (CH, C$_{\text{arom para}}$), 136.4 (CH, d, J = 20 Hz, C$_6$), 166.6 (CO). ^{19}F{^{1}H} NMR (376.508 MHz, CDCl$_3$, ppm): δ –177.4. MS (GCT, CI$^+$): *m/z* (relative intensity %) 234 [M-HF+NH$_4$]$^+$ (50). HRMS (GCT, CI$^+$): Calc for C$_{14}$H$_{20}$NO$_2$: 234.1494, found 234.1490.

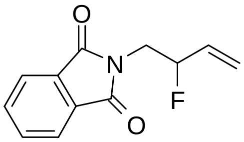


Compound 5d: 3-Fluoro-pent-4-enoic acid benzyl ester. A solution of 94 mg of **4d** (0.35 mmol) and 130 mg of Selectfluor$^{\text{TM}}$ (1 eq.) in CH$_3$CN (3ml) was stirred at room temperature for 48 hours. Without any evaporation the

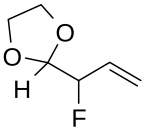
crude is directly subjected to flash column chromatography (4/96: diethylether/hexane) to afford 52 mg of the title compound as a white oil (69%). ^{1}H NMR (400.132 MHz, CDCl$_3$, ppm) : δ 2.69 (1H, ddd, J = 29.6 Hz, J = 16.0 Hz, J = 4.8 Hz, H$_{2a}$), 2.85 (1H, ddd, J = 16.0 Hz, J = 14.8 Hz, J = 8.4 Hz, H$_{2b}$), 5.18 (2H, s, -O-CH$_2$-Ph), 5.29 (1H, dt, J = 10.8 Hz, J = 1.0 Hz, H$_{5a}$), 5.39 (1H, dm, J = 46.8 Hz, H$_3$), 5.40 (1H, ddt, J = 18.8 Hz, J = 3.6 Hz, J = 1.2 Hz, H$_{5b}$), 5.93 (1H, dddd, J = 24.8 Hz, J = 18.8 Hz, J = 10.4 Hz, J = 6.0 Hz, H$_4$), 7.36 (5H, m, H$_{arom}$). ^{13}C NMR (100.624 MHz, CDCl3, ppm) : δ 40.5 (CH$_2$, d, J = 25 Hz, C$_2$), 66.7 (CH$_2$, -O-CH$_2$-Ph), 89.5 (CH, d, J = 169 Hz, C$_3$), 118.1 (CH$_2$, d, J = 12 Hz, C$_5$), 128.3, 128.4 and 128.6 (CH, C$_{\text{arom ortho, meta and para}}$), 134.8 (CH, d, J = 20 Hz, C$_4$), 135.5 (C$_{\text{arom IPSO}}$), 169.4 (CO). ^{19}F{^{1}H} NMR (376.508 MHz, CDCl$_3$, ppm): δ –177.3. MS (GCT, CI$^+$): *m/z* (relative intensity %) 189 [M+H-HF]$^+$ (65). HRMS (GCT, CI$^+$): Calc for $C_{12}H_{13}O_2$: 189.0916, found 189.0918.



Compound 5e: (2-Fluoro-but-3-enyl)-methyl-carbamic acid *tert*-butyl ester. General procedure B was followed, starting from 165 mg of **4e** (0.64 mmol) and 310 mg of Selectfluor^{TM} (1.3 eq.) in CH$_3$CN (5ml). Purification by flash column chromatography (5/95: diethylether/hexane) afforded 68 mg of the title compound as a white oil (52%). ^{1}H NMR (400.132 MHz, CDCl$_3$, ppm) : δ 1.46 (9H, s, (CH$_3$)3C-O-), 2.94 (3H, s, N-CH$_3$), 3.39 (2H, m, H$_1$), 5.06 (1H, dm, J = 48.4 Hz, H$_2$), 5.28 (1H, dm, J = 8.4 Hz, H$_{4a}$), 5.39 (1H, dm, J = 17.2 Hz, H$_{4b}$), 5.85 (1H, m, H$_3$). ^{13}C NMR (100.624 MHz, CDCl3, ppm) : δ 28.3 (CH$_3$, (CH$_3$)3C-O-), 36.3 (CH$_3$, N-CH$_3$), 52.9 (CH$_2$, d, J = 23 Hz, C$_1$), 79.7 ((CH$_3$)3$\underline{\text{C}}$-O), 92.8 (CH, d, J = 172 Hz, C$_2$), 118.1 (CH$_2$, d, J = 9 Hz, C$_4$), 133.8 (CH$_2$, d, J = 18 Hz, C$_3$). ^{19}F{^{1}H} NMR (376.508 MHz, CDCl$_3$, ppm): δ –185.8. MS (GCT, CI$^+$): *m/z* (relative intensity %) 204 [M+H]$^+$ (50). HRMS (GCT, CI$^+$): Calc for $C_{10}H_{19}NO_2F$: 204.1400, found 204.1401.

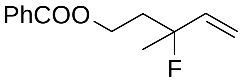


Compound 5f: 2-(2-Fluoro-but-3-enyl)-isoindole-1,3-dione. General procedure B was followed, starting from 174 mg of **4f** (0.64 mmol) and 232 mg of Selectfluor^{TM} (1 eq.) in CH_3CN (3ml). Purification by flash column chromatography (30/70: diethylether/hexane) afforded 114 mg of the title compound as a white solid (82%). ^1H NMR (400.132 MHz, $CDCl_3$, ppm): δ 3.83 (1H, ddd, J = 26.4 Hz, J = 14.4 Hz, J = 4.0 Hz, $H_{1'a}$), 4.04 (1H, ddd, J = 22.0 Hz, J = 14.0 Hz, J = 8.4 Hz, $H_{1'b}$), 5.21 (1H, dm, J = 48.4 Hz, $H_{2'}$), 5.36 (1H, dt, J = 10.8 Hz, J = 1.2 Hz, $H_{4'a}$), 5.36 (1H, ddt, J = 16.8 Hz, J = 13.6 Hz, J = 1.2 Hz, $H_{4'b}$), 5.95 (1H, dddd, J = 25.6 Hz, J = 16.8 Hz, J = 10.8 Hz, J = 6.0 Hz, $H_{3'}$), 7.75 (2H, dd, J= 5.2 Hz, J= 2.8 Hz, $H_{arom\ 6\ and\ 7}$), 7.90 (2H, dd, J= 5.2 Hz, J= 2.8 Hz, $H_{arom\ 5\ and\ 8}$). ^{13}C NMR (100.624 MHz, CDCl3, ppm) : δ 41.5 (CH_2, d, J = 25 Hz, $C_{1'}$), 90.1 (CH, d, J = 173 Hz, $C_{2'}$), 119.7 (CH_2, d, J = 12 Hz, $C_{4'}$), 131.9 ($2C_{arom}$, C_4 and C_9), 132.9 (CH, d, J = 19 Hz, $C_{3'}$), 134.1 ($2C_{arom}$, C_6 and C_7), 168.0 (CO). $^{19}F\{^1H\}$ NMR (376.508 MHz, $CDCl_3$, ppm): δ –184.5. mp:52-53°C. MS (GCT, CI^+): *m/z* (relative intensity %) 237 $[M+NH_4]^+$ (30) 220 $[M+H]^+$ (40) 200 $[M-HF+H]^+$ (100). HRMS (GCT, CI^+): Calc for $C_{12}H_{11}FNO_2$: 220.0774, found 220.0771.

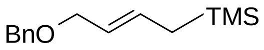


Compound 5h: 2-(1-Fluoro-allyl)-[1,3]dioxalane. A solution of 140 mg of **4h** (0.75 mmol) and 270 mg of Selectfluor^{TM} (1 eq.) in CH_3CN (3ml) was stirred at room temperature for 48 hours. Without any evaporation the crude (100% conversion) is directly subjected to flash column chromatography (4/96: diethylether/hexane) to afford the title compound contaminated with diethylether (30 %). ^1H NMR (400.132 MHz, $CDCl_3$, ppm) : δ 3.99 and 4.03 (4H, 2m, -O-CH_2-CH_2-O-), 4.80 (1H, dm, J= 47.2 Hz, $H_{1'}$), 5.02 (1H, dd, J= 10.8 Hz, J= 3.2 Hz, -O-CHR-O-), 5.40 (1H, dt, J= 10.4 Hz, J= 0.8 Hz, $H_{3'a}$), 5.48 (1H, dq[5], J= 17.6 Hz, J= 1.2 Hz, $H_{3'b}$), 5.94 (1H, dddd, J= 21.6 Hz, J= 17.6 Hz, J= 10.8 Hz, J= 6.0 Hz, $H_{2'}$). ^{13}C NMR (100.624 MHz, $CDCl_3$, ppm) : δ 65.6 ($2CH_2$, -O-CH_2-CH_2-O-), 92.2 (CH, d, J= 175 Hz, $C_{1'}$), 103.06 (CH, d, J= 24 Hz, -O-CHR-O-), 119.7 (CH, d, J= 12 Hz, $C_{3'}$), 131.3

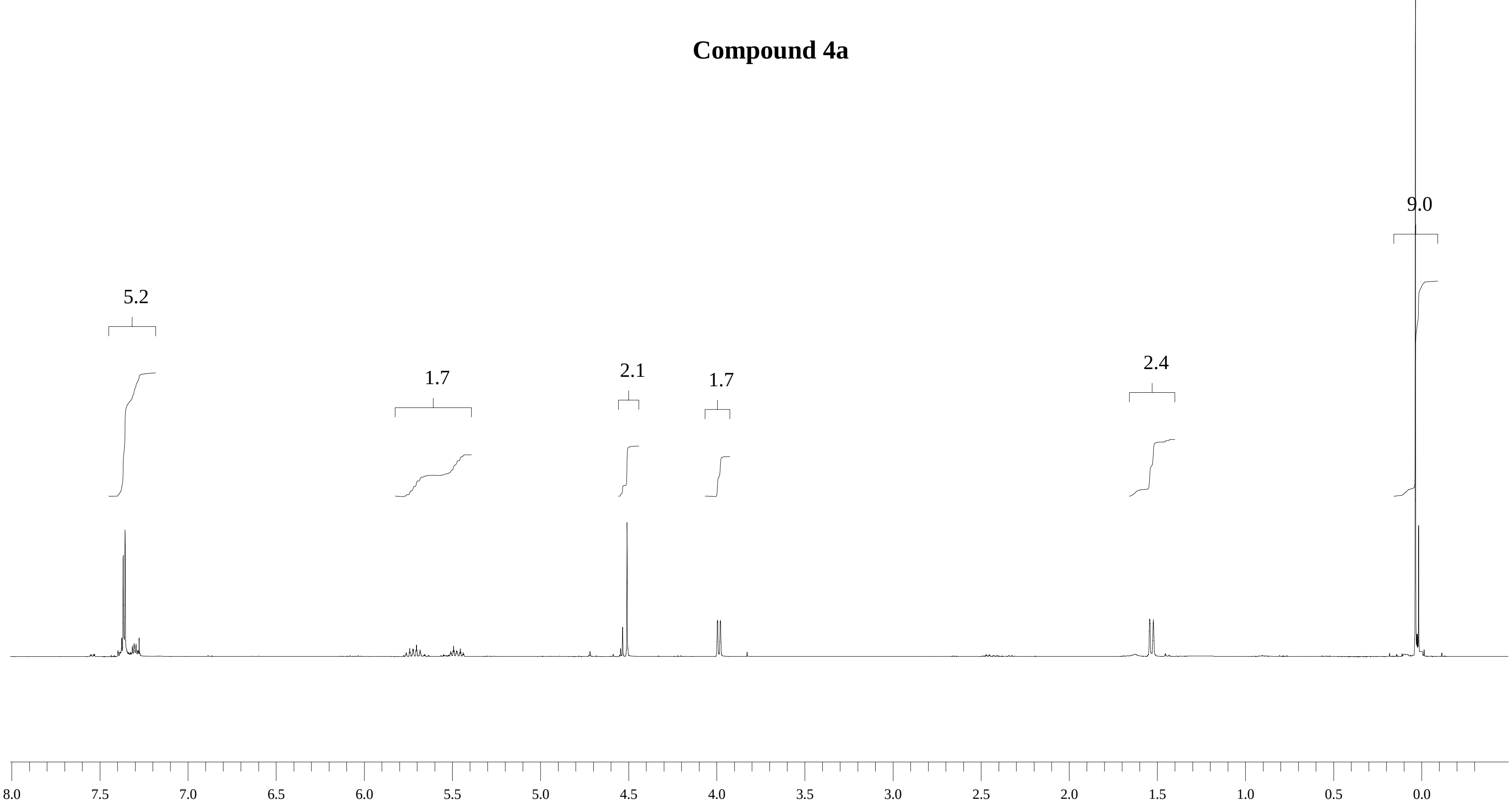
(CH, d, J= 19 Hz $C_{2'}$). $^{19}F\{^1H\}$ NMR (376.508 MHz, $CDCl_3$, ppm): δ –195.1. MS (GCT, CI^+): *m/z* (relative intensity %) 150 $[M+NH_4]^+$ (25), 113 $[M-HF+H]^+$ (25). HRMS (GCT, CI^+): Calc for $C_6H_{13}FNO_2$: 150.0930, found 150.0926.



Compound 5i: Benzoic acid 3-Fluoro-3-methyl-pent-4-enyl ester. General procedure B was followed, starting from 15 mg of **4i** (0.05 mmol) and 20 mg of Selectfluor™ (1 eq.) in CH_3CN (1ml). Purification by flash column chromatography (5/95: diethylether/hexane) afforded 9.6 mg of the title compound as an oil (79%). ^1H NMR (400.132 MHz, $CDCl_3$, ppm): δ 1.52 (3H, d, J = 22.0 Hz, CH_3), 2.20 (2H, m, H_2), 4.45 (2H, d, J = 6.8 Hz, H_1), 5.18 (1H, d, J = 11.2 Hz, H_{5a}), 5.35 (1H, d, J = 17.2 Hz, H_{5b}), 5.95 (1H, td, J = 17.6 Hz, J = 11.2 Hz, H_4), 7.45 (2H, m, $H_{arom\ meta}$), 7.57 (1H, tm, J = 7.6 Hz, $H_{arom\ para}$), 8.04 (2H, dm, J= 7.2 Hz, $H_{arom\ ortho}$). ^{13}C NMR (100.624 MHz, CDCl3, ppm) : δ 25.8 (CH_3, d, J = 25 Hz, CH_3), 38.8 (CH_2, d, J = 23 Hz, C_2), 60.7 (CH_2, d, J = 5 Hz, C_1), 113.9 (CH_2, d, J = 11 Hz, C_5), 128.3 (CH, $C_{arom\ meta}$), 129.5 (CH, $C_{arom\ ortho,}$), 130.2 ($C_{arom\ IPSO}$), 132.9 (CH, $C_{arom\ para}$), 135.9 (CH, d, J = 22 Hz, C_4), 166.5 (CO). $^{19}F\{^1H\}$ NMR (376.508 MHz, $CDCl_3$, ppm): δ –148.8. MS (GCT, CI^+): *m/z* (relative intensity %) 203 $[M-HF+H]^+$ (100). HRMS (GCT, CI^+): Calc for $C_{13}H_{15}O_2$: 203.1072, found 203.1065.


BnO
TMS

Compound 4a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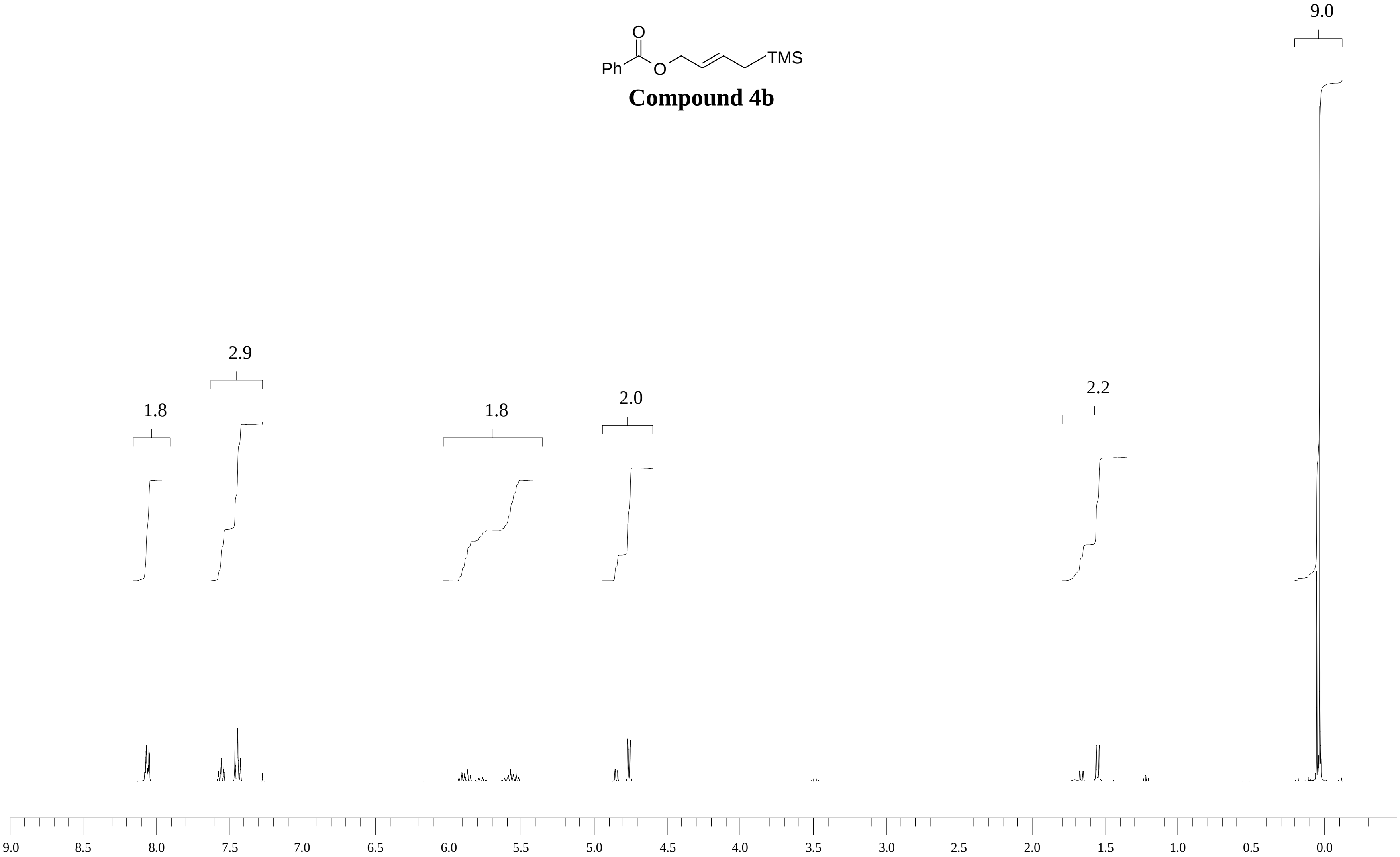

Compound 4b

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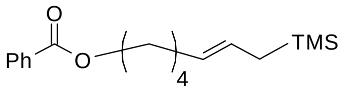
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Ph
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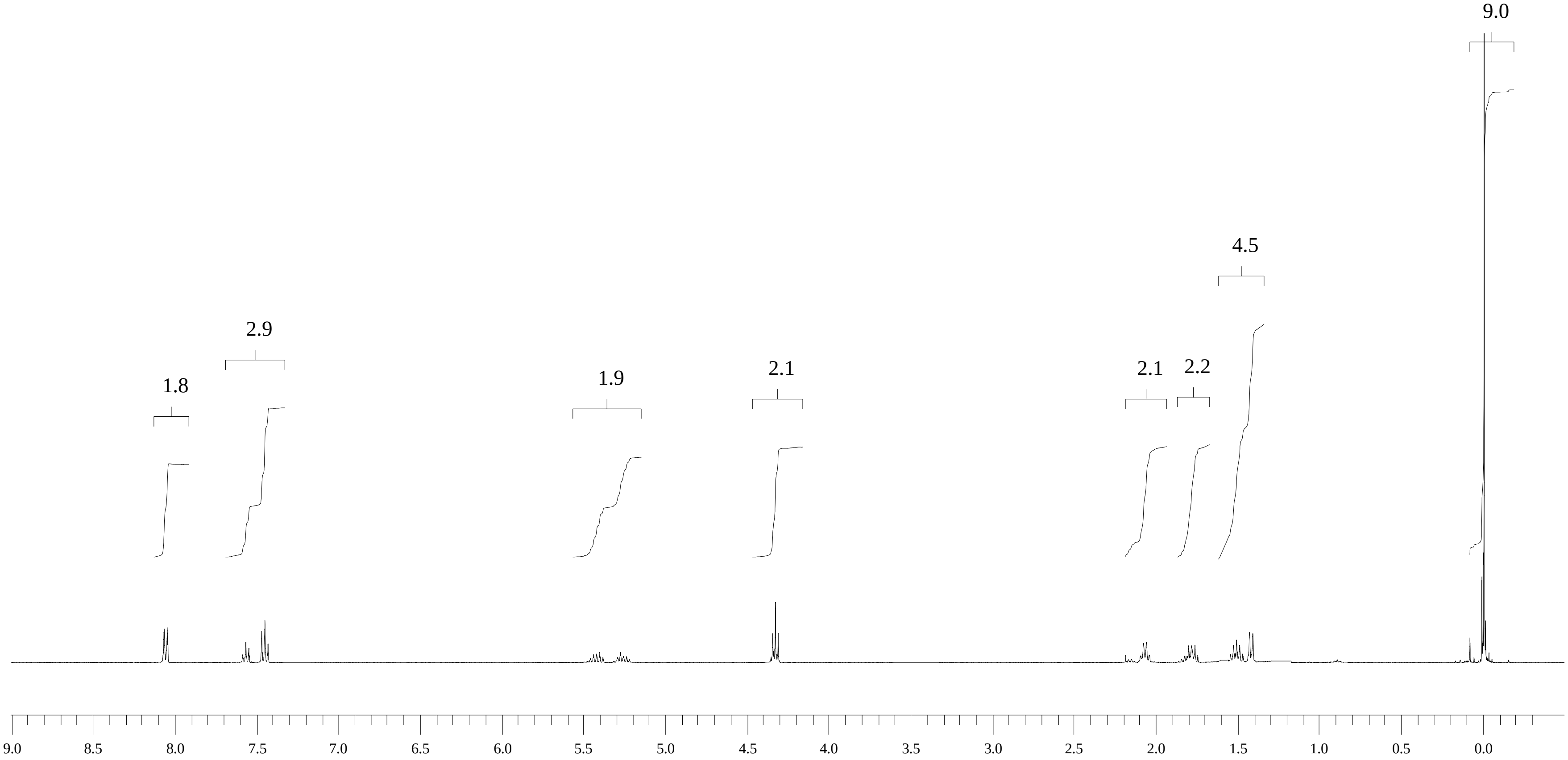
Compound 4c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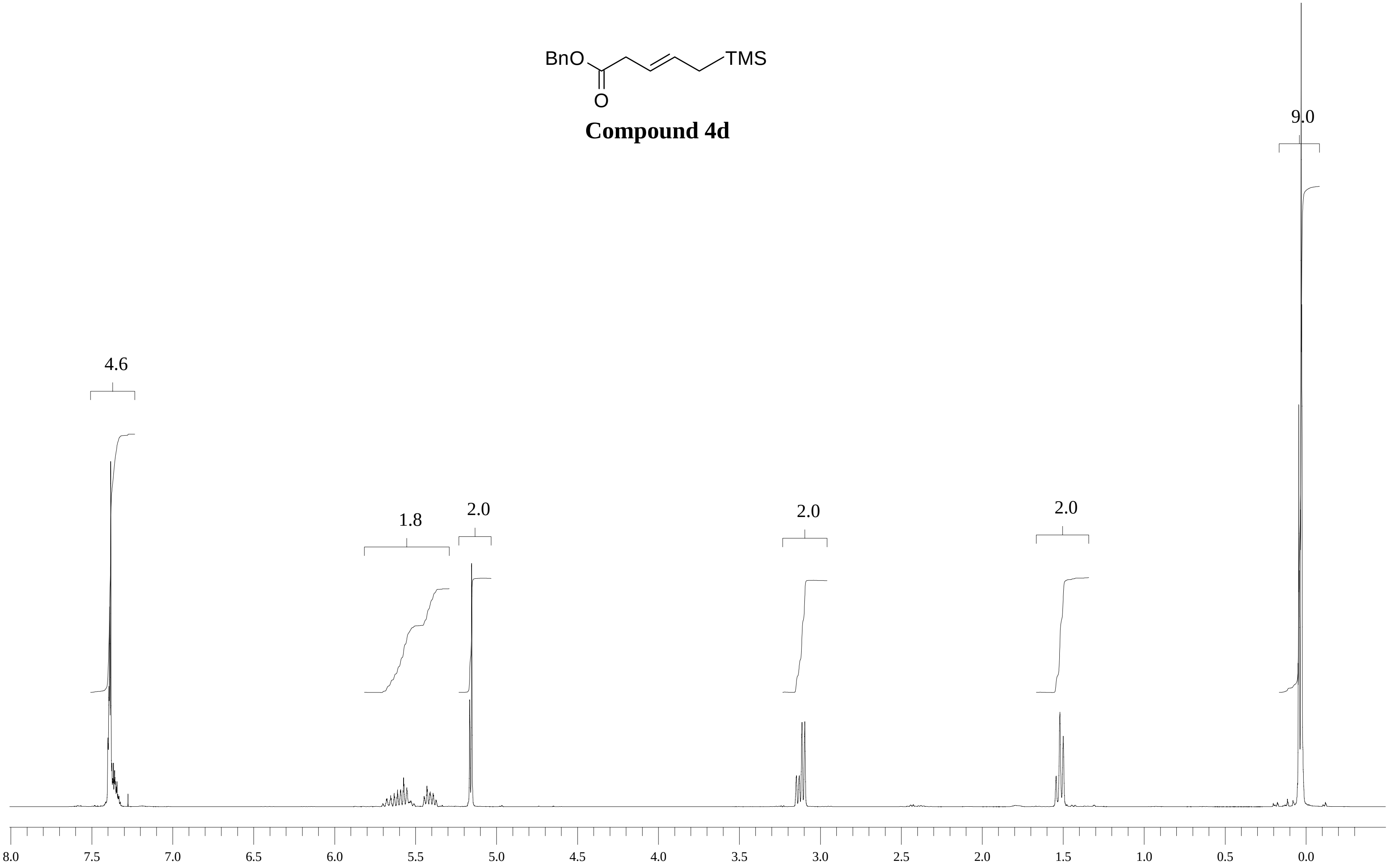
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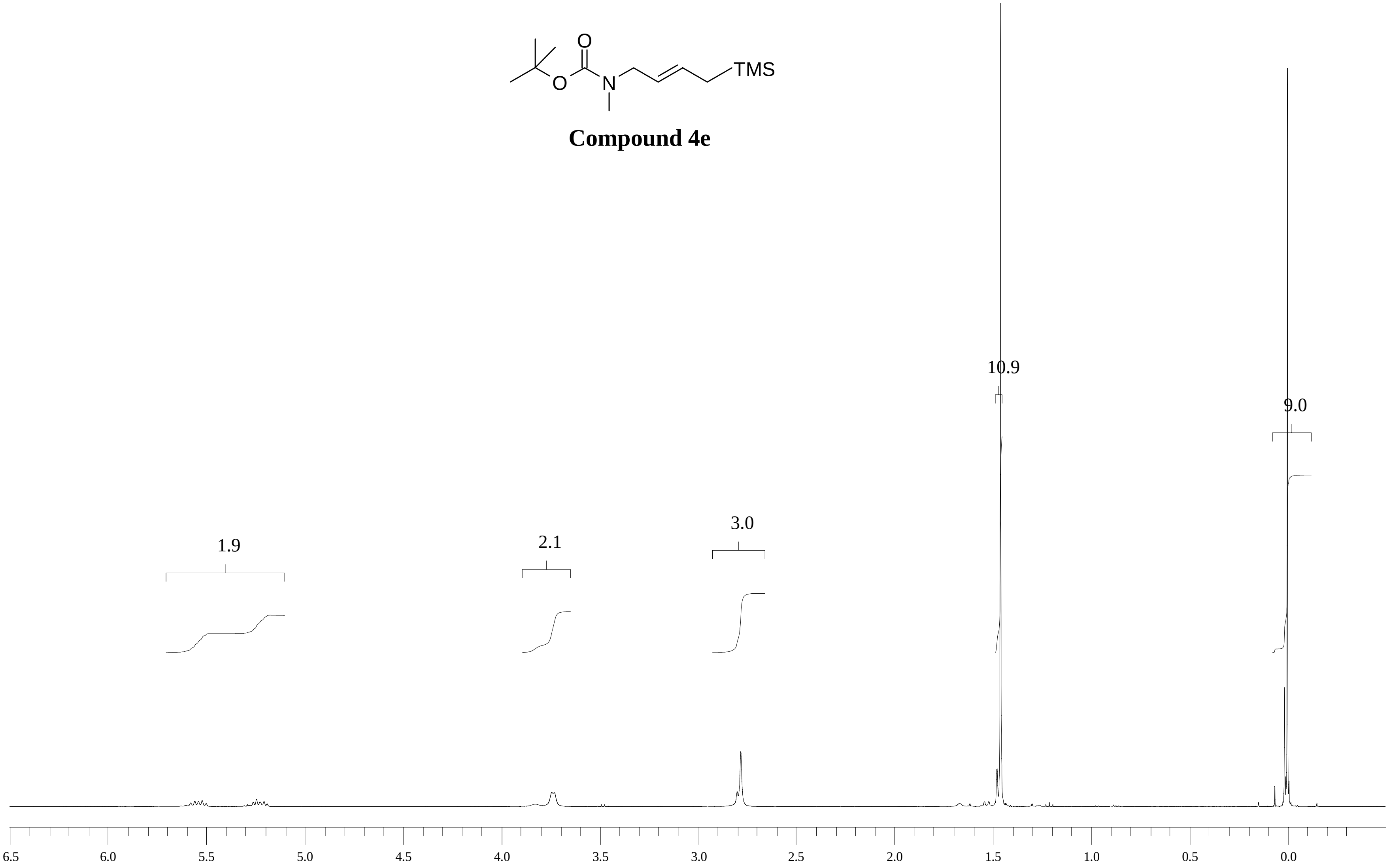
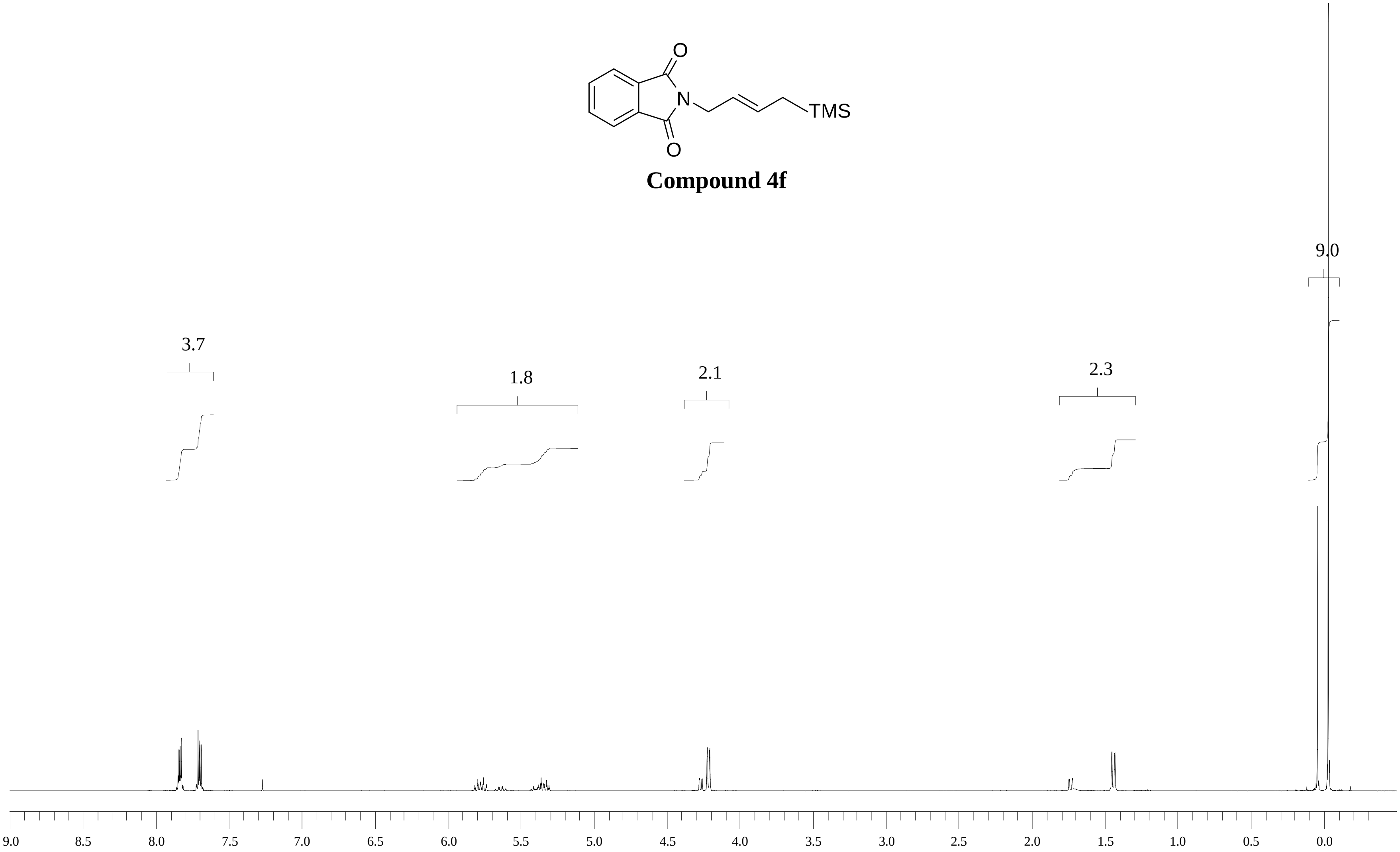
Compound 4d



Compound 4e

O
N
TMS
O

Compound 4f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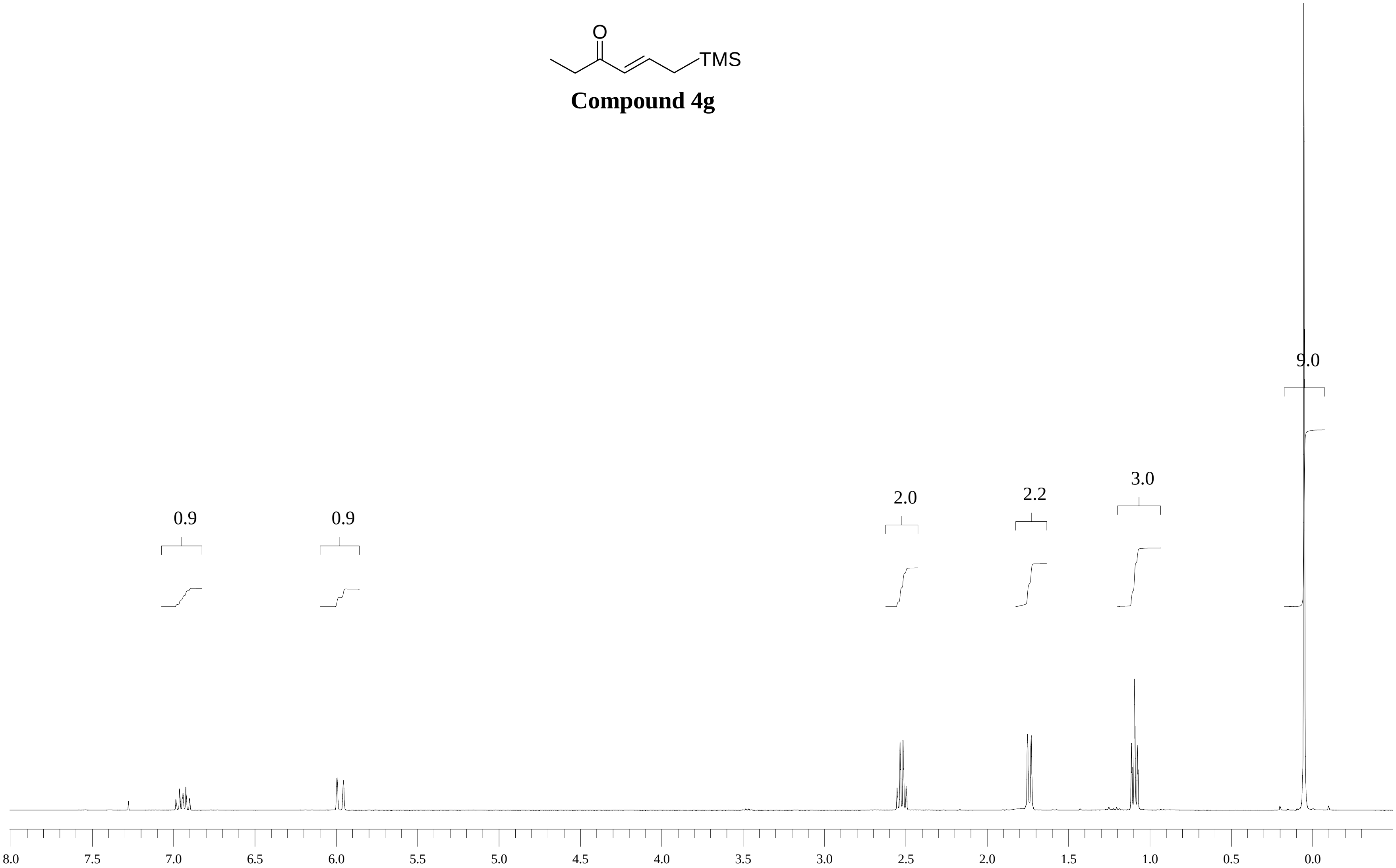
O
TMS

Compound 4g

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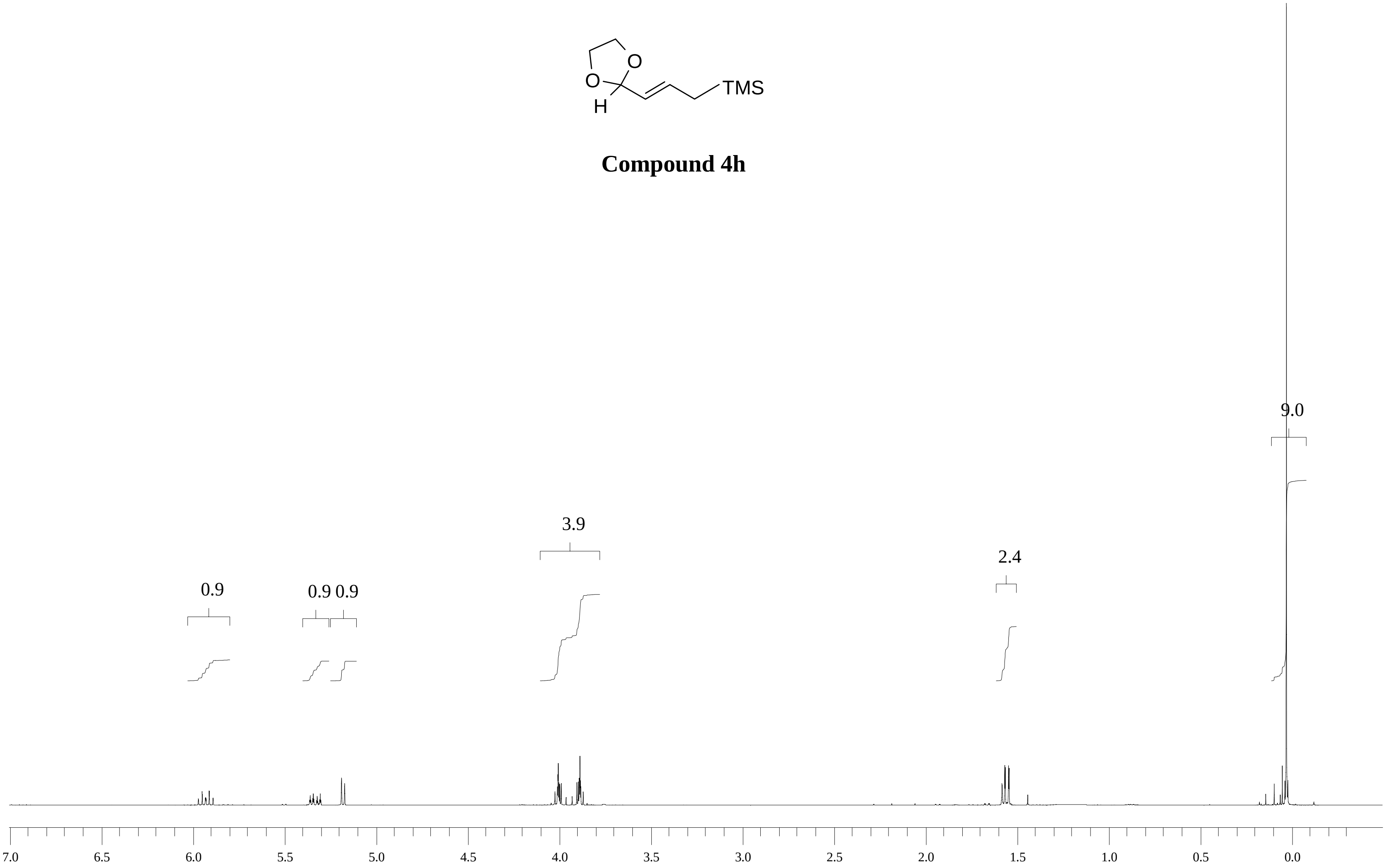
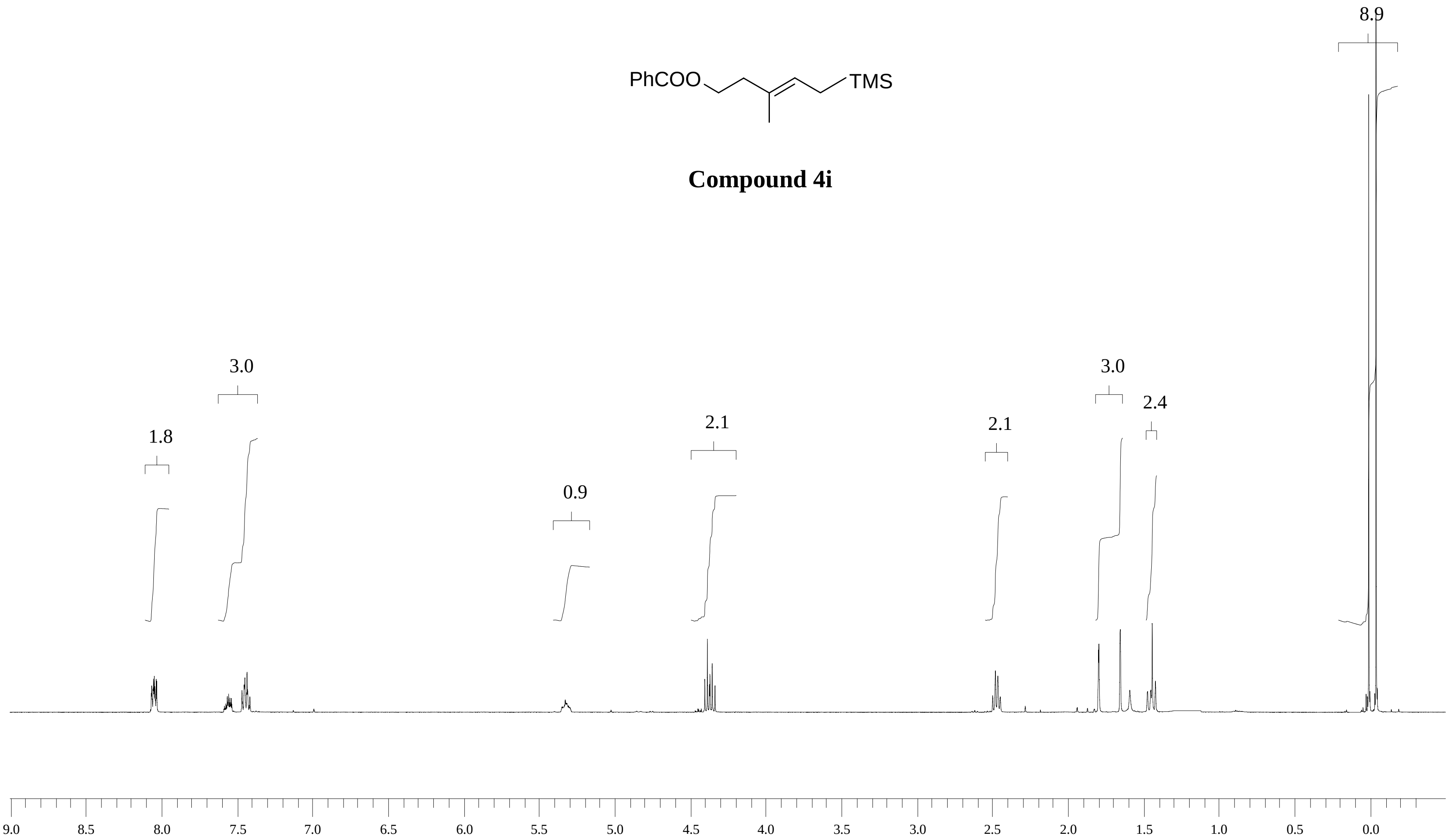


Compound 4h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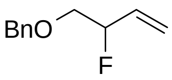
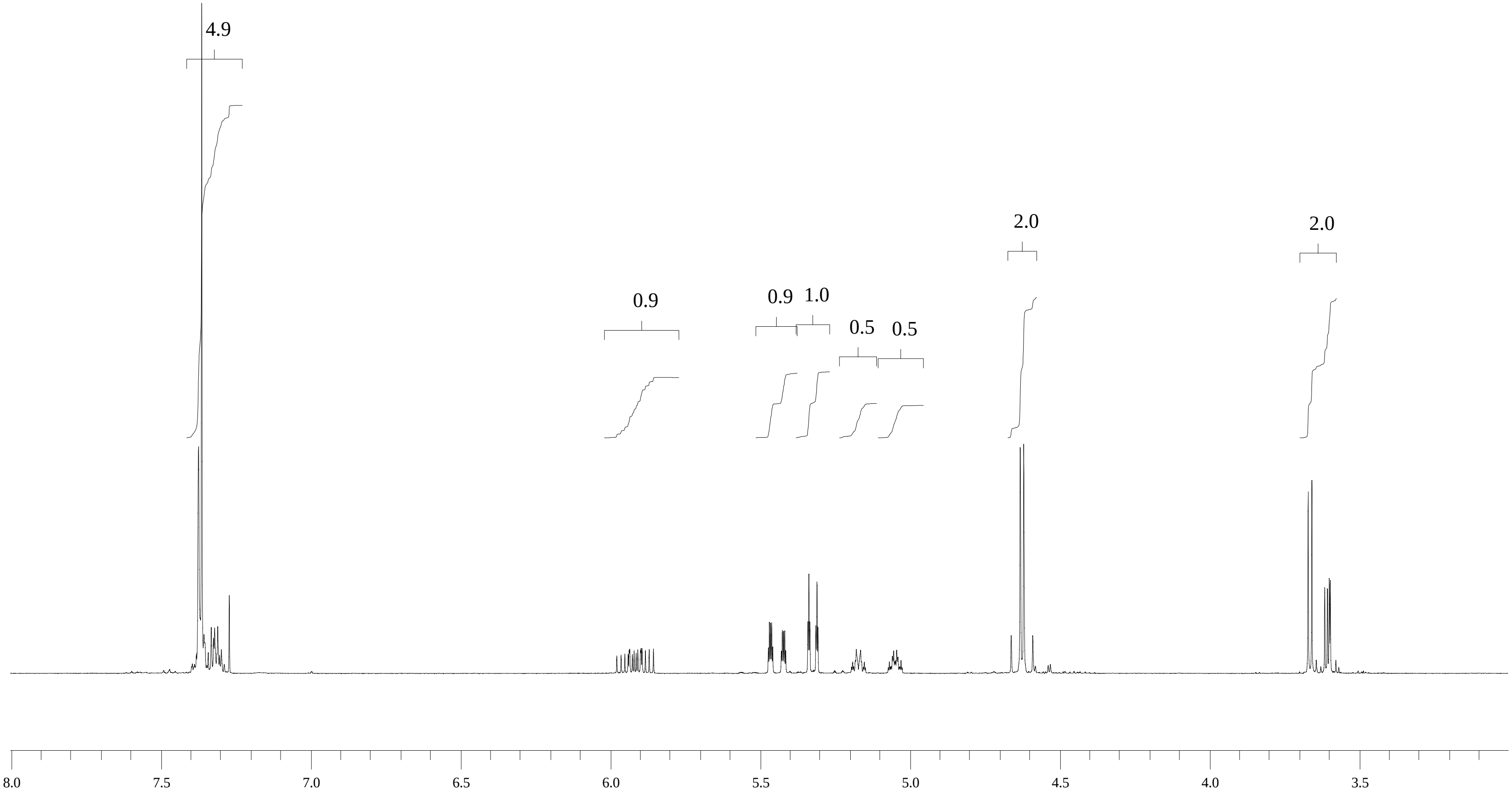
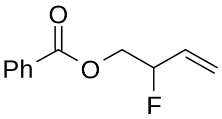
Compound 4i



Compound 5a

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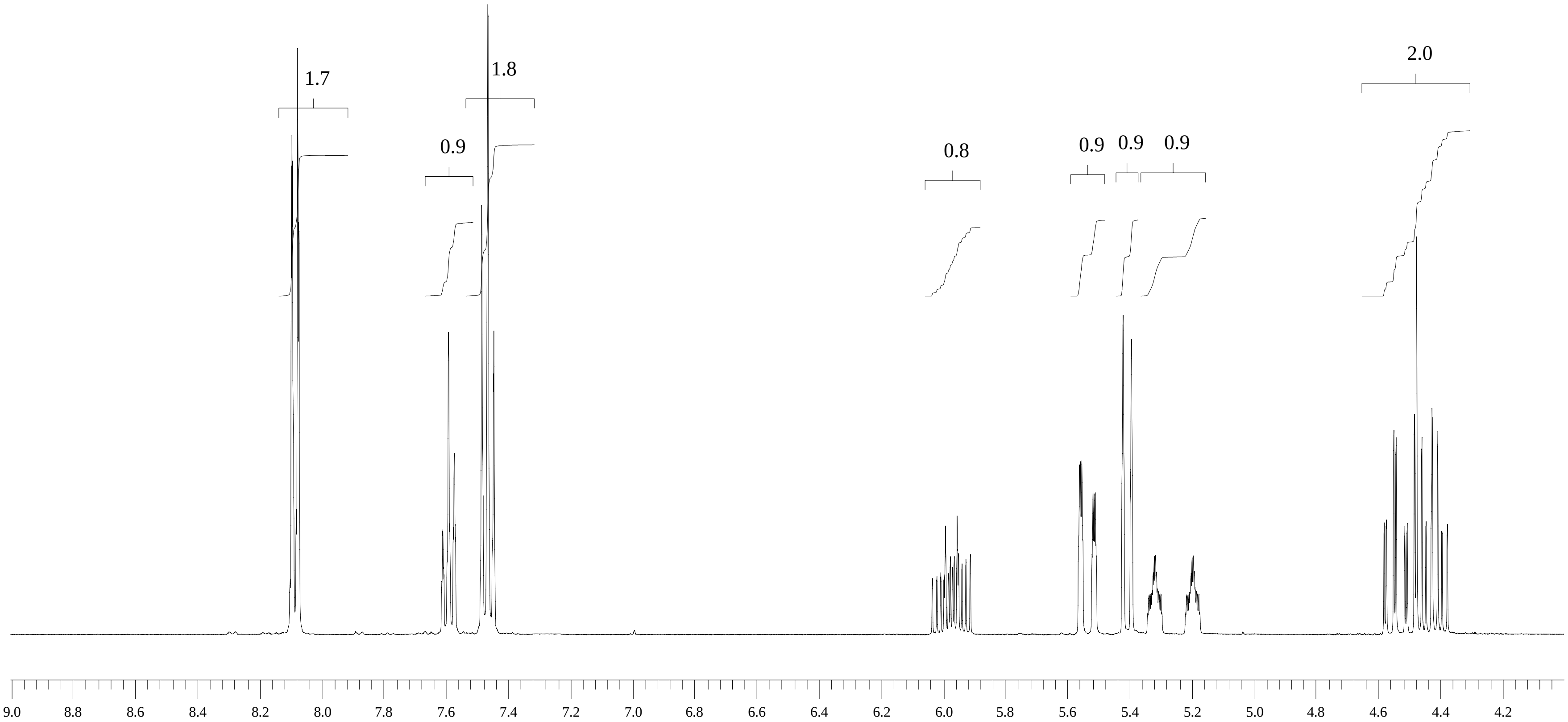
Ph
O
F

Compound 5b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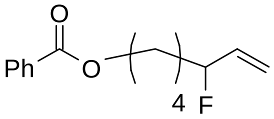
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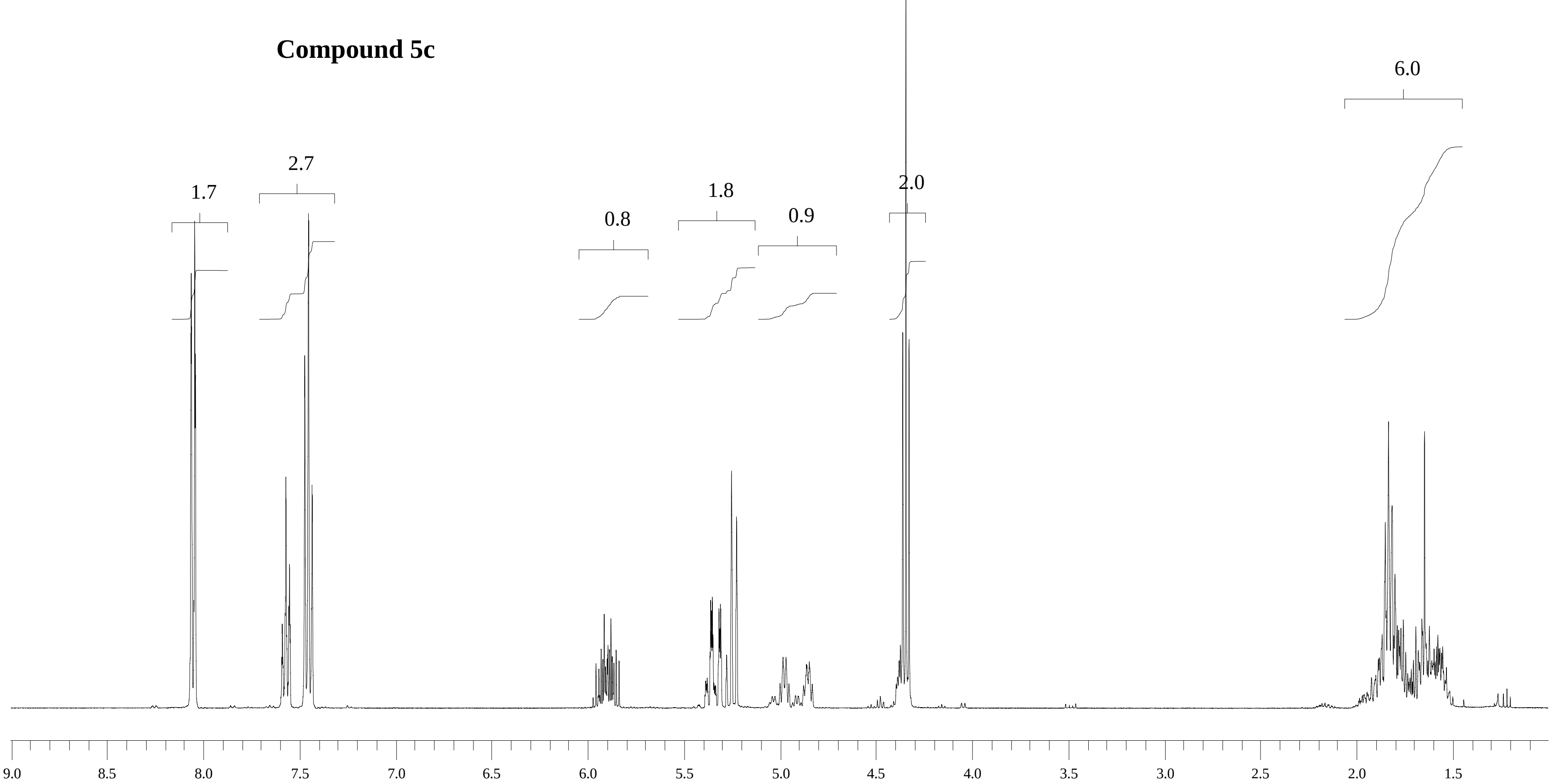
Compound 5c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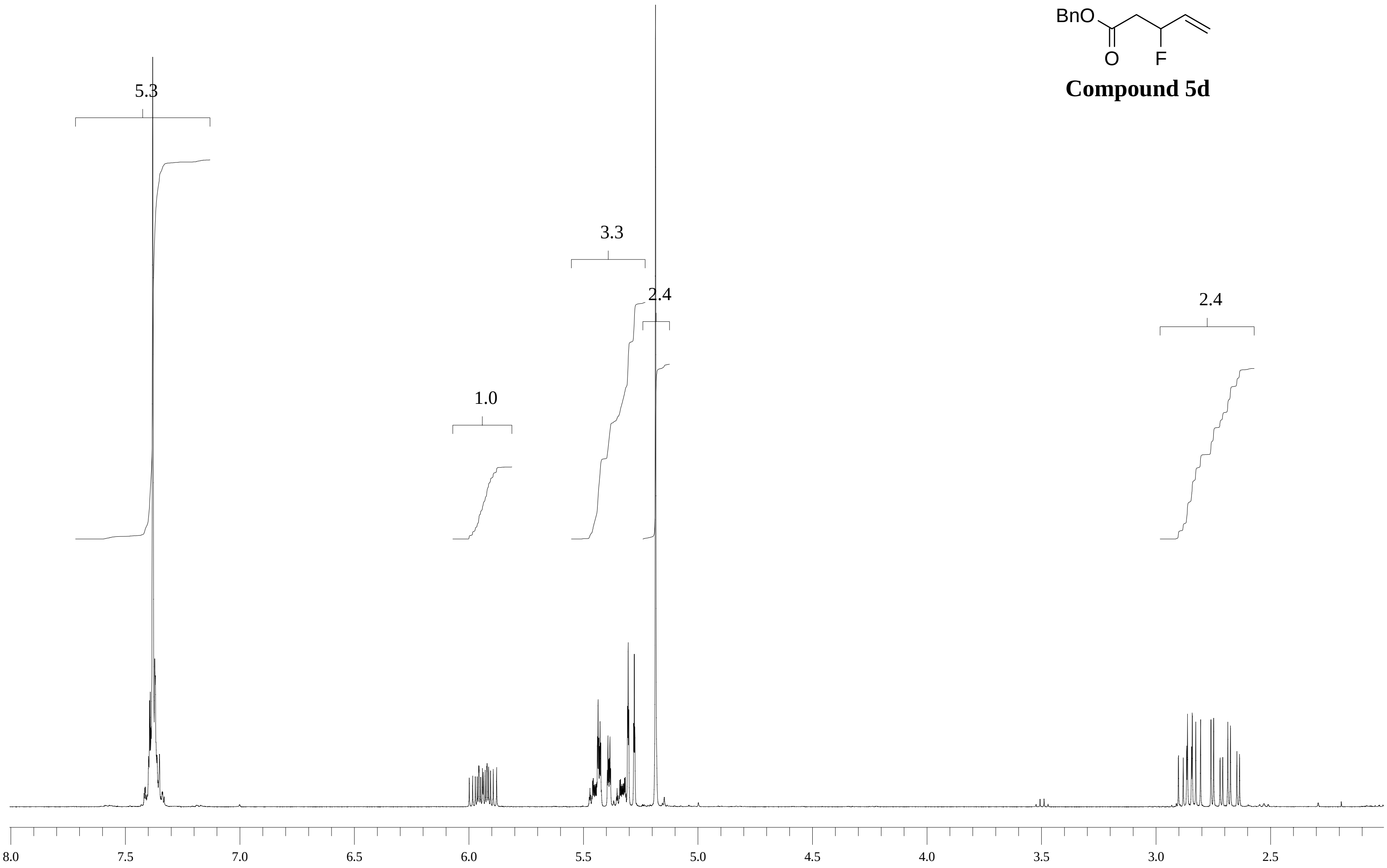
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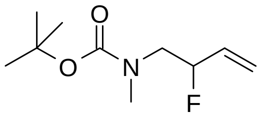
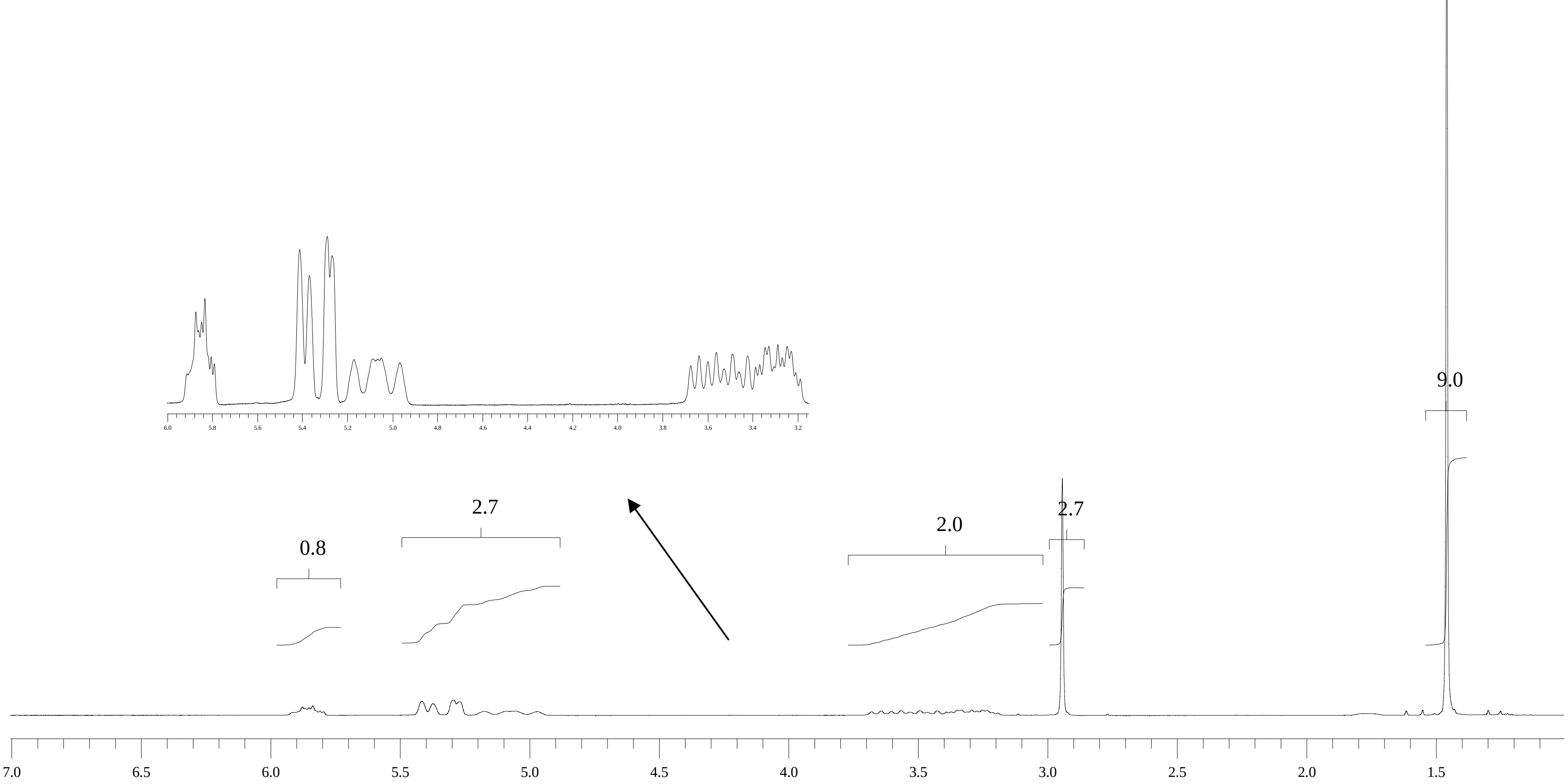


Compound 5e



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2.7
2.0
2.7
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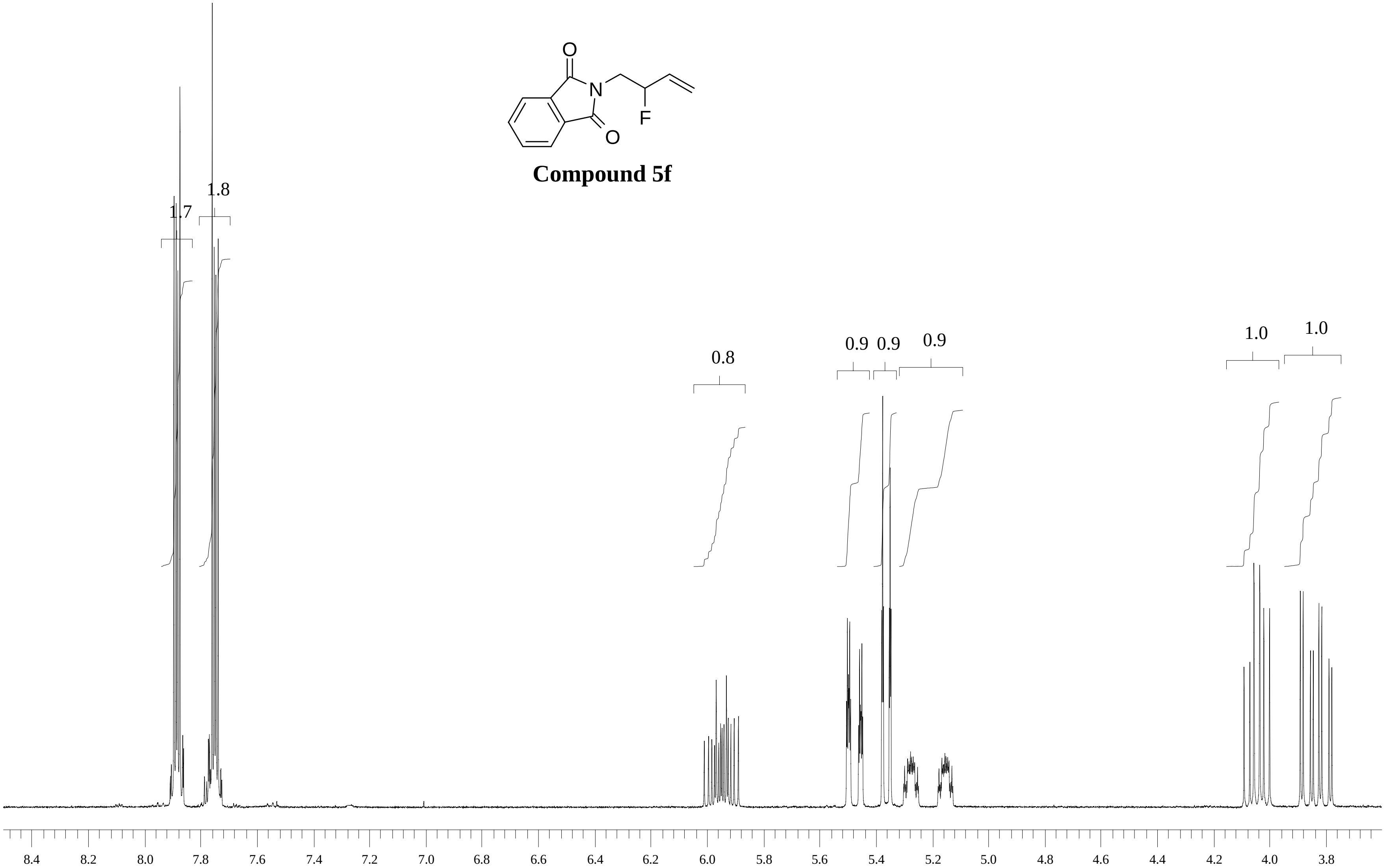
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5



Compound 5f

O
N
O
F
1.7
1.8
0.8
0.9
0.9
0.9
1.0
1.0
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
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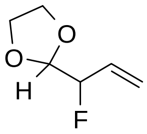
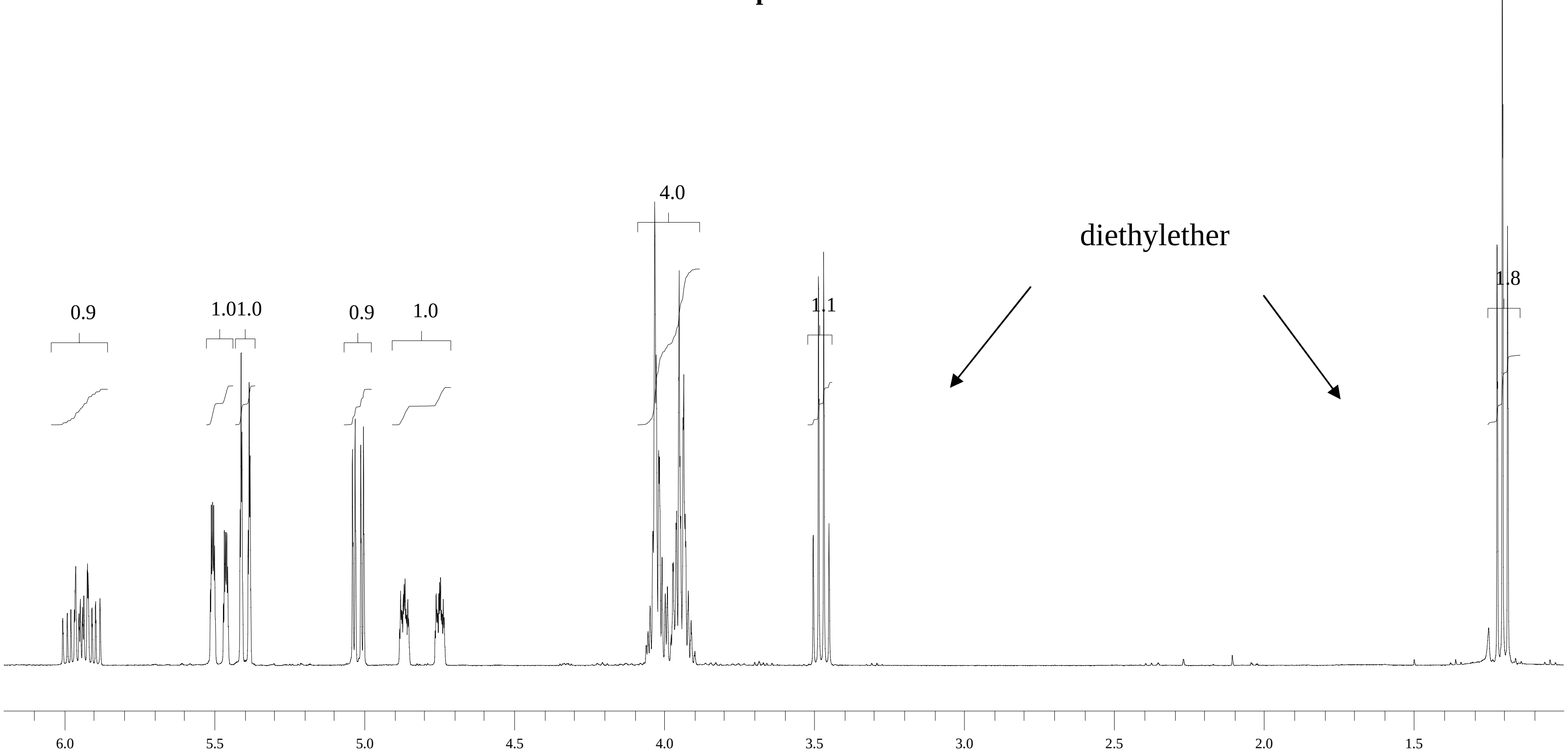
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8


O
O
H
F

Compound 5h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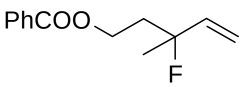
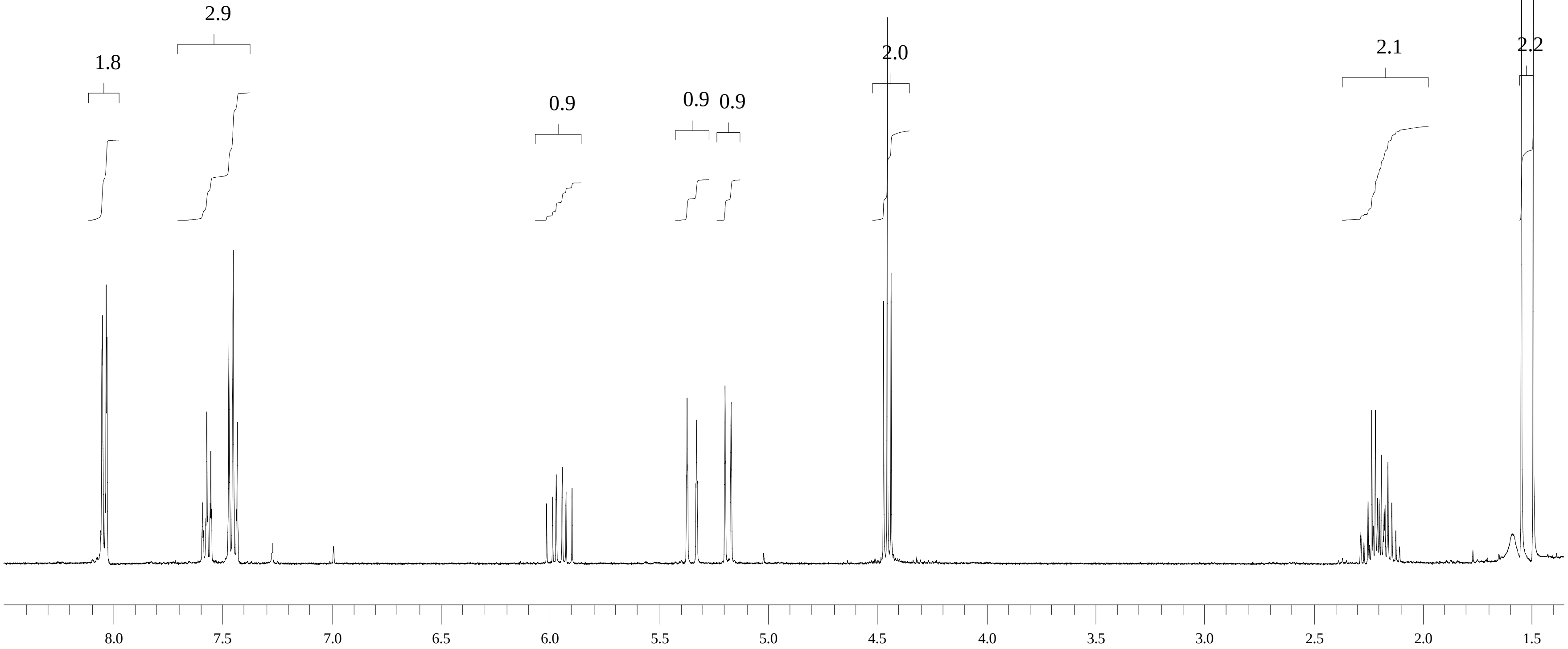
1.0
0.9
1.0
4.0
1.1
1.8
diethylether
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5


PhCOO
F

Compound 5i


1.8
2.9
0.9
0.9
0.9
2.0
2.1
2.2
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
1.5