

## Supporting Information

### Rhodium-Catalyzed Regio- and Stereoselective 1-Seleno-2-Thiolation of 1-Alkynes

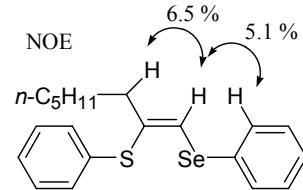
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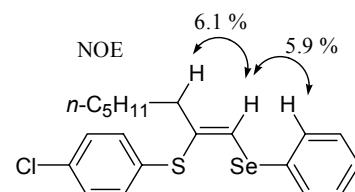
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**(Z)-1-Phenylseleno-2-phenylthio-1-octene (Table 2, entry 2)** (Z)-1-Phenylseleno-2-phenylthio-1-octene (72%), (Z)-1,2-bis(phenylthio)-1-octene (3%), and (Z)-7 (3%) were obtained ( $^1\text{H-NMR}$  yield). The major compound (68%) was isolated by preparative recycling reverse-phase HPLC using Cadenza CD-C18 column. (MeOH).  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.84 (3H, t,  $J = 7.2$  Hz), 1.14 - 1.30 (6H, m), 1.49, (2H, quintet,  $J = 7.2$  Hz), 2.23 (2H, t,  $J = 7.2$  Hz), 6.80 (1H, s), 7.21 (1H, t,  $J = 7.2$  Hz), 7.26 - 7.34 (5H, m), 7.36 (2H, d,  $J = 7.2$  Hz), 7.57 (2H, dd,  $J = 7.2, 1.6$  Hz).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  14.2, 22.6, 28.6, 28.5, 31.6, 37.9, 126.6, 127.3, 128.3 ( $^1J_{\text{C-Se}} = 105$  Hz), 128.8, 129.1, 130.0, 130.9, 132.6, 133.7, 135.7.  $^{77}\text{Se-NMR}$  (76 MHz,  $\text{CDCl}_3$ )  $\delta$  393.6. IR (neat) 3058, 2927, 2854, 1579  $\text{cm}^{-1}$ . MS (EI)  $m/z$  43 ( $M^+ - 333$ , 100), 376 ( $M^+$ , 78). HRMS. Calcd for  $\text{C}_{20}\text{H}_{24}\text{SSe}$ : 376.0764. Found: 376.0733. (Z)-1,2-Bis(phenylthio)-1-octene ( $\delta$  6.56) and (Z)-7 ( $\delta$  6.92) were assigned according to literature.<sup>4,8</sup>

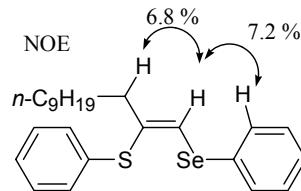


**(Z)-1-Phenylseleno-2-(4-chlorophenylthio)-1-octene (Table 2, entry 3)** (Z)-1-Phenylseleno-2-(4-chlorophenylthio)-1-octene (69%), (Z)-1,2-bis(4-chlorophenylthio)-1-octene (7%), and (Z)-7 (1%) were obtained ( $^1\text{H-NMR}$  yield). The spectroscopic data were obtained as a mixture.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.85 (3H, t,  $J = 6.4$  Hz), 1.15 - 1.32 (6H, m), 1.48 (2H, quintet  $J = 7.2$  Hz), 2.21 (2H, t,  $J = 7.2$  Hz), 6.83 (1H, s), 7.22 - 7.34 (7H, m), 7.55 (2H, dd,  $J = 7.2, 3.6$  Hz).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  14.1, 22.6, 28.4, 28.5, 31.5, 37.9, 127.3, 128.9, 129.1, 129.5 ( $^1J_{\text{C-Se}} = 103$  Hz), 130.8, 131.1, 132.3, 132.5, 132.6, 135.0.  $^{77}\text{Se-NMR}$  (76 MHz,  $\text{CDCl}_3$ )  $\delta$  397.2. IR (neat) 3057, 2927, 1576  $\text{cm}^{-1}$ . MS (EI)  $m/z$  43 ( $M^+ - 367$ , 100) 410 ( $M^+$ , 45). HRMS. Calcd for  $\text{C}_{20}\text{H}_{23}\text{ClSSe}$ : 410.0374. Found: 410.0384. (Z)-1,2-Bis(4-chlorophenylthio)-1-octene ( $\delta$  6.48) was assigned by analogy with (Z)-1,2-bis(phenylthio)-1-octene.<sup>4,8</sup>



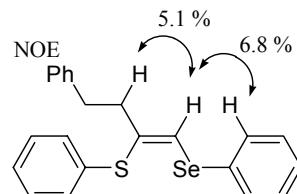
**(Z)-1-Phenylseleno-2-phenylthio-1-dodecene (Table 2, entry 4)** (Z)-1-Phenylseleno-2-phenylthio-1-dodecene (75%), (Z)-1,2-bis(phenylthio)-1-dodecene (2%), and

(Z)-1,2-bis(phenylseleno)-1-dodecene (5%) were obtained ( $^1\text{H-NMR}$  yield). The major compound (71%) was isolated by preparative recycling reverse-phase HPLC using Cadenza CD-C18 column (MeOH).  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.87 (3H, t,  $J = 7.6$  Hz), 1.15 - 1.34 (14H, m), 1.48 (2H, quintet,  $J = 7.2$ , Hz), 2.22 (2H, t,  $J = 7.2$  Hz), 6.80 (1H, s), 7.21 (1H, t,  $J = 7.2$  Hz), 7.25 - 7.32 (5H, m), 7.36 (2H, d,  $J = 8.0$  Hz), 7.56 (2H, dd,  $J = 7.6, 3.2$  Hz).  $^{13}\text{C-NMR}$  (150 MHz,  $\text{CDCl}_3$ )  $\delta$  14.3, 22.8, 28.6, 28.9, 29.4, 29.6, 29.7, 32.0, 37.8, 126.6, 127.3, 128.4 ( $^1\text{J}_{\text{C-Se}} = 101$  Hz), 128.9, 129.1, 130.0, 130.9, 132.6, 133.6, 135.7.  $^{77}\text{Se-NMR}$  (76 MHz,  $\text{CDCl}_3$ )  $\delta$  393.6. IR (neat) 3057, 2925, 2852, 1579  $\text{cm}^{-1}$ . MS (EI)  $m/z$  432 ( $\text{M}^+$ , 100). HRMS. Calcd for  $\text{C}_{24}\text{H}_{32}\text{SSe}$ : 432.1390. Found: 432.1421. (Z)-1,2-Bis(phenylthio)-1-dodecene ( $\delta$  6.54) and (Z)-1,2-bis(phenylseleno)-1-dodecene ( $\delta$  6.92) were assigned by analogy with (Z)-1,2-bis(phenylthio)-1-octene and (Z)-7, respectively.<sup>4, 8</sup>



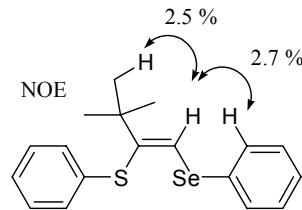
**(Z)-4-Phenyl-1-phenylseleno-2-phenylthio-1-butene (Table 2, entry 5)**

(Z)-4-Phenyl-1-phenylseleno-2-phenylthio-1-butene (65%), (Z)-4-phenyl-1,2-bis(phenylthio)-1-butene (2%), and (Z)-4-phenyl-1,2-bis(phenylseleno)-1-butene (10%) were obtained ( $^1\text{H-NMR}$  yield). The spectroscopic data were obtained as a mixture  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.52 (2H, t,  $J = 7.6$  Hz), 2.81 (2H, t,  $J = 7.6$  Hz), 6.72 (1H, s), 7.05 (2H, d,  $J = 7.2$  Hz), 7.17 (1H, d,  $J = 7.2$  Hz), 7.18 - 7.35 (8H, m) 7.39 (2H, d,  $J = 6.8$  Hz), 7.45 (2H, dd,  $J = 6.4, 2.8$  Hz).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  34.9, 39.6, 125.7, 126.7, 127.2, 128.1, 128.2, 128.9 ( $^1\text{J}_{\text{C-Se}} = 102$  Hz), 129.9, 129.2, 130.2, 130.7, 132.4, 133.3, 134.4, 140.7.  $^{77}\text{Se-NMR}$  (76 MHz,  $\text{CDCl}_3$ )  $\delta$  395.8. IR (neat) 3058, 3025, 2924, 2854, 1946, 1579  $\text{cm}^{-1}$ . MS (EI)  $m/z$  91 ( $\text{M}^+ - 305, 63$ ), 147 ( $\text{M}^+ - 249, 100$ ), 396 ( $\text{M}^+, 54$ ). HRMS. Calcd for  $\text{C}_{22}\text{H}_{20}\text{SSe}$ : 396.0451. Found: 396.0447. (Z)-1,2-Bis(phenylthio)-4-phenyl-1-butene ( $\delta$  6.42) was assigned according to literature.<sup>4</sup> (Z)-1,2-Bis(phenylseleno)-4-phenyl-1-butene ( $\delta$  6.84) was assigned by analogy with (Z)-7.<sup>8</sup>



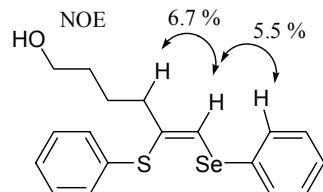
**(Z)-3,3-Dimethyl-1-phenylseleno-2-phenylthio-1-butene (Table 2, entry 6)**

(*Z*)-3,3-Dimethyl-1-phenylseleno-2-phenylthio-1-butene (61%) and (*Z*)-3,3-dimethyl-1,2-bis(phenylthio)-1-butene (25%) were obtained ( $^1\text{H-NMR}$  yield). The latter ( $\delta$  6.99) was assigned according to literature<sup>4</sup> The major compound (65%) was isolated by preparative recycling reverse-phase HPLC using Cadenza CD-C18 column (MeOH).  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.20 (9H, s), 7.12 (1H, tt,  $J$  = 7.6, 1.6 Hz), 7.23 - 7.32 (7H, m), 7.25 (1H, s) 7.52 (2H, dd,  $J$  = 6.0, 3.6 Hz).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  29.6, 41.0, 125.1, 126.7, 127.4, 128.7, 129.1, 131.0, 132.8, 134.9 ( $^1J_{\text{C-Se}} = 102$  Hz), 135.5, 141.5.  $^{77}\text{Se-NMR}$  (76 MHz,  $\text{CDCl}_3$ )  $\delta$  411.8. IR (neat) 2963, 1579, 1476  $\text{cm}^{-1}$ . MS (EI)  $m/z$  57 ( $\text{M}^+ - 291$ , 100), 348 ( $\text{M}^+$ , 34). HRMS. Calcd for  $\text{C}_{18}\text{H}_{20}\text{SSe}$ : 348.0451. Found: 348.0446. Anal. Calcd for  $\text{C}_{18}\text{H}_{20}\text{SSe}$ : C; 62.24, H; 5.80, S; 9.23 %. Found: C; 62.36, H; 5.88, S; 10.01 %.



**(*Z*)-1-Phenylseleno-2-phenylthio-1-hexen-6-ol (Table 2, entry 7)**

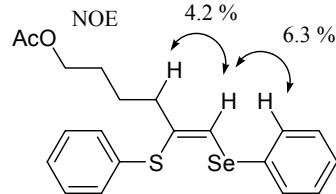
(*Z*)-1-Phenylseleno-2-phenylthio-1-hexen-6-ol (71%), (*Z*)-1,2-bis(phenylthio)-1-hexen-6-ol (1%), and (*Z*)-1,2-bis(phenylseleno)-1-hexen-6-ol (5%) were obtained ( $^1\text{H-NMR}$  yield). The major compound (62%) was isolated by preparative recycling reverse-phase HPLC using Cadenza CD-C18 column (MeOH).  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.30 (1H, s, br), 1.51 (2H, quintet,  $J$  = 6.4 Hz), 1.57 (2H, quintet,  $J$  = 6.8 Hz), 2.26 (2H, t,  $J$  = 7.2 Hz), 3.57 (2H, t,  $J$  = 6.8 Hz), 6.83 (1H, s), 7.23 (1H, t,  $J$  = 6.4 Hz), 7.26 - 7.34 (5H, m), 7.36 (2H, d,  $J$  = 8.0 Hz), 7.57 (2H, d,  $J$  = 3.2, 8.4 Hz).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  24.7, 31.9, 37.5, 62.6, 126.7, 127.3, 128.9, 129.1 ( $^1J_{\text{C-Se}} = 95$  Hz), 129.1, 130.1, 130.7, 132.7, 133.5, 135.0.  $^{77}\text{Se-NMR}$  (76 MHz,  $\text{CDCl}_3$ )  $\delta$  396.0. IR (neat) 3349, 3057, 2935, 1578  $\text{cm}^{-1}$ . MS (EI)  $m/z$  147 ( $\text{M}^+ - 217, 58$ ), 364 ( $\text{M}^+$ , 100). HRMS. Calcd for  $\text{C}_{18}\text{H}_{20}\text{OSSe}$ : 364.0400. Found: 364.0370. (*Z*)-1,2-Bis(phenylthio)-1-hexen-6-ol ( $\delta$  6.58) and (*Z*)-1,2-bis(phenylseleno)-1-hexen-6-ol ( $\delta$  6.95) were assigned by analogy with (*Z*)-1,2-bis(phenylthio)-1-octene and (*Z*)-7, respectively.<sup>4,8</sup>



**(Z)-6-Acetyloxy-1-phenylseleno-2-phenylthio-1-hexene** (Table 2, entry 8)

(Z)-6-Acetyloxy-1-phenylseleno-2-phenylthio-1-hexene (78%),

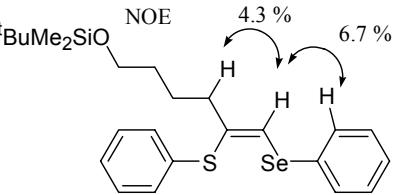
(Z)-6-acetyloxy-1,2-bis(phenylthio)-1-hexene (3%), and (Z)-6-acetyloxy-1,2-bis(phenylseleno)-1-hexene (6%) were obtained ( $^1\text{H}$ -NMR yield). The major compound (70%) was isolated by recycling HPLC using Cadenza CD-C18 column (MeOH).  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.56 (4H, m), 2.00 (3H, s), 2.26 (2H, t,  $J$  = 6.8 Hz), 3.99 (2H, t,  $J$  = 6.0 Hz), 6.83 (1H, s), 7.22 (2H, t,  $J$  = 7.2 Hz), 7.26 - 7.34 (4H, m), 7.36 (2H, d,  $J$  = 7.6 Hz), 7.57 (2H, dd,  $J$  = 8.0, 2.8 Hz).  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  21.1, 24.9, 27.8, 37.3, 64.2, 126.7, 127.4, 128.9, 129.1 ( $^{1}\text{J}_{\text{C-Se}} = 108$  Hz), 129.3, 130.1, 130.7, 132.7, 133.4, 134.8, 170.9.  $^{77}\text{Se}$ -NMR (76 MHz,  $\text{CDCl}_3$ )  $\delta$  396.6. IR (neat) 3057, 2945, 1739, 1578  $\text{cm}^{-1}$ . MS (EI)  $m/z$  43 ( $\text{M}^+ - 363$ , 100), 147 ( $\text{M}^+ - 259$ , 68), 406 ( $\text{M}^+$ , 69). HRMS. Calcd for  $\text{C}_{20}\text{H}_{22}\text{O}_2\text{SSe}$ : 406.0506. Found: 406.0496. (Z)-6-Acetyloxy-1,2-bis(phenylthio)-1-hexene ( $\delta$  6.58) and (Z)-6-acetyloxy-1,2-bis(phenylseleno)-1-hexene ( $\delta$  6.95) were assigned by analogy with (Z)-1,2-bis(phenylthio)-1-octene and (Z)-7, respectively.<sup>4,8</sup>



**(Z)-6-(*t*-Butyldimethylsilyloxy)-1-phenylseleno-2-phenylthio-1-hexene** (Table 2, entry 9)

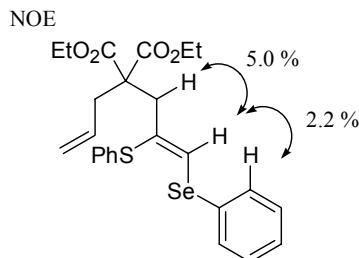
(Z)-6-(*t*-Butyldimethylsilyloxy)-1-phenylseleno-2-phenylthio-1-hexene (72%), and

(Z)-1,2-bis(phenylseleno)-6-(*t*-butyldimethylsilyloxy)-1-hexene (3%) were obtained ( $^1\text{H}$ -NMR yield). The major compound (70%) was isolated by preparative recycling reverse-phase HPLC using Cadenza CD-C18 column (MeOH).  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.01 (6H, s), 0.86 (9H, s), 1.44 (2H, quintet,  $J$  = 6.0 Hz), 1.54 (2H, quintet,  $J$  = 6.4 Hz), 2.25 (2H, t,  $J$  = 6.4 Hz), 3.53 (2H, t,  $J$  = 6.8 Hz), 6.82 (1H, s), 7.18 - 7.32 (6H, m), 7.35 (2H, d,  $J$  = 8.0 Hz), 7.56 (2H, dd,  $J$  = 8.0, 2.4 Hz).  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  -5.1, 18.5, 24.9, 26.1, 32.1, 37.6, 62.9, 126.6, 127.3, 128.7 ( $^{1}\text{J}_{\text{C-Se}} = 100$  Hz), 128.9, 129.0, 130.1, 130.9, 132.6, 133.6, 135.5.  $^{77}\text{Se}$ -NMR (76 MHz,  $\text{CDCl}_3$ )  $\delta$  394.6. IR (neat) 3059, 2928, 1579  $\text{cm}^{-1}$ . MS (EI)  $m/z$  75 ( $\text{M}^+ - 403$ , 100), 478 ( $\text{M}^+$ , 20). HRMS. Calcd for  $\text{C}_{24}\text{H}_{34}\text{OSSeSi}$ : 478.1265. Found: 478.1240. Anal.  $\text{C}_{24}\text{H}_{34}\text{OSSeSi}$ : Calcd for C; 60.35, H; 7.17. Found: C; 60.42, H; 7.06. (Z)-1,2-Bis(phenylseleno)-6-(*t*-butyldimethylsilyloxy)-1-hexene ( $\delta$  6.92) was assigned by analogy with (Z)-7.<sup>8</sup>



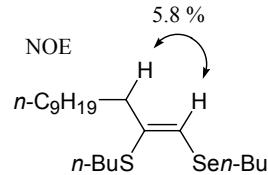
**(Z)-4,4-Bis(ethoxycarbonyl)-1-phenylseleno-2-phenylthio-1,6-heptadiene (Table 2, entry 10)**

(*Z*)-4,4-Bis(ethoxycarbonyl)-1-phenylseleno-2-phenylthio-1,6-heptadiene (73%), and (*Z*)-4,4-bis(ethoxycarbonyl)-1,2-bis(phenylthio)-1,6-heptadiene (6%) were obtained ( $^1\text{H}$ -NMR yield). The spectroscopic data were obtained as a mixture.  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.15 (6H, t,  $J$  = 7.2 Hz), 2.77 (2H, d,  $J$  = 7.2 Hz), 2.95 (2H, s), 4.06 (2H, q,  $J$  = 7.2 Hz), 4.14 (2H, q,  $J$  = 7.2 Hz), 5.01 (1H, d,  $J$  = 8.0 Hz), 5.04 (1H, d,  $J$  = 16.8 Hz), 5.57 (1H, ddt,  $J$  = 16.8, 7.2, 6.4 Hz), 7.10 (1H, s), 7.16 - 7.33 (8H, m), 7.54 (2H, dd,  $J$  = 7.2, 3.6 Hz).  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  13.9, 36.6, 39.1, 57.4, 61.3, 118.9, 126.1, 127.2, 128.6, 128.9, 129.1, 130.0, 130.1, 132.2, 132.8, 133.6, 138.8 ( $^1J_{\text{C-Se}} = 105$  Hz), 170.0.  $^{77}\text{Se}$ -NMR (76 MHz,  $\text{CDCl}_3$ )  $\delta$  416.1. IR (neat) 3074, 2980, 1732, 1640, 1579  $\text{cm}^{-1}$ . MS (EI)  $m/z$  147 ( $\text{M}^+ - 357$ , 100), 273 ( $\text{M}^+ - 231$ , 64), 347 ( $\text{M}^+ - 157$ , 70) 504 ( $\text{M}^+$ , 55). HRMS. Calcd for  $\text{C}_{25}\text{H}_{28}\text{OSSe}$ : 504.0874. Found: 504.0857. (*Z*)-4,4-Bis(ethoxycarbonyl)-1,2-bis(phenylthio)-1,6-heptadiene ( $\delta$  6.86) was assigned according to literature.<sup>8</sup>



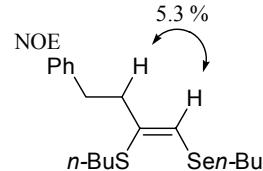
**(Z)-1-Butylseleno-2-butylthio-1-dodecene (Table 4, entry 2)** (*Z*)-1-Butylseleno-2-butylthio-1-dodecene (53%), (*Z*)-2-butylseleno-1-butylthio-1-dodecene (5%), (*Z*)-1,2-bis(butylthio)-1-dodecene (5%), and (*Z*)-1,2-bis(butylseleno)-1-dodecene (19%) were obtained ( $^1\text{H}$ -NMR yield). The spectroscopic data were obtained as a mixture.  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.88 (3H, t,  $J$  = 8.0 Hz), 0.91 (3H, t,  $J$  = 6.8 Hz), 0.92 (3H, t,  $J$  = 7.6 Hz), 1.19 - 1.38 (16H, m), 1.42 (2H, sextet,  $J$  = 7.6 Hz), 1.42 (2H, sextet,  $J$  = 7.6 Hz), 1.48 - 1.60 (2H, m), 1.69 (2H, quintet,  $J$  = 7.6 Hz), 2.25, (2H, t,  $J$  = 7.6 Hz), 2.68 (2H, t,  $J$  = 7.6 Hz), 2.69 (2H, t,  $J$  = 7.2 Hz), 6.32 (1H, s).  $^{13}\text{C}$ -NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  13.6, 13.7, 14.1, 21.9, 22.7, 22.8, 26.4, 28.5, 29.0, 29.3, 29.4, 29.6, 29.6, 31.3, 31.9, 32.0, 33.0, 37.4, 122.4 ( $^1J_{\text{C-Se}} = 102$  Hz), 135.7.  $^{77}\text{Se}$ -NMR (76 MHz,  $\text{CDCl}_3$ )  $\delta$  257.2. IR (neat) 2925, 2854, 1574  $\text{cm}^{-1}$ . MS (EI)  $m/z$  392 ( $\text{M}^+$ , 100). HRMS. Calcd for

$C_{20}H_{40}SSe$ : 392.2016. Found: 392.1998. (*Z*)-1,2-Bis(butylthio)-1-dodecene ( $\delta$  6.03) and (*Z*)-1,2-bis(butylseleno)-1-dodecene ( $\delta$  6.54) were assigned by analogy with (*Z*)-**12** and (*Z*)-**13**, respectively.<sup>4,8</sup> A peak at  $\delta$  6.21 was assigned to (*Z*)-2-butylseleno-1-butylthio-1-dodecene tentatively.



**(*Z*)-1-Butylseleno-2-butylthio-4-phenyl-1-butene (Table 4, entry 3)**

(*Z*)-1-Butylseleno-2-butylthio-4-phenyl-1-butene (41%), (*Z*)-2-butylseleno-1-butylthio-4-phenyl-1-butene (3%), (*Z*)-1,2-bis(butylthio)-4-phenyl-1-butene (5%), and (*Z*)-1,2-bis(butylseleno)-4-phenyl-1-butene (21%) were obtained ( $^1H$ -NMR yield). The spectroscopic data were obtained as a mixture.  $^1H$ -NMR (400 MHz,  $CDCl_3$ )  $\delta$  0.91 (3H, t,  $J$  = 7.2 Hz), 0.92 (3H, t,  $J$  = 7.2 Hz), 1.38 (2H, sextet,  $J$  = 7.2 Hz), 1.44 (2H, sextet,  $J$  = 7.6 Hz), 1.48 - 1.70 (4H, m), 2.55 (2H, t,  $J$  = 7.6 Hz), 2.65 (2H, t,  $J$  = 7.2 Hz), 2.72 (2H, t,  $J$  = 7.6 Hz), 2.85 (2H, t,  $J$  = 8.0 Hz), 6.30 (1H, s), 7.15 - 7.21 (3H, m), 7.28 (2H, t,  $J$  = 7.6 Hz).  $^{13}C$ -NMR (100 MHz,  $CDCl_3$ )  $\delta$  13.7, 13.8, 22.0, 22.9, 26.5, 31.5, 32.1, 33.1, 35.1, 39.6, 124.0 ( $^1J_{C-Se}$  = 104 Hz), 125.8, 128.2, 128.3, 134.1, 141.2.  $^{77}Se$ -NMR (76 MHz,  $CDCl_3$ )  $\delta$  262.1. IR (neat) 3026, 2956, 2927, 2871, 1603  $cm^{-1}$ . MS (EI)  $m/z$  91 ( $M^+$  - 265, 66), 356 ( $M^+$ , 100). HRMS. Calcd for  $C_{18}H_{28}SSe$ : 356.1077. Found: 356.1094. (*Z*)-1,2-Bis(butylthio)-4-phenyl-1-butene ( $\delta$  6.00) and (*Z*)-1,2-bis(butylseleno)-4-phenyl-1-butene ( $\delta$  6.51) were assigned by analogy with (*Z*)-**12** and (*Z*)-**13**, respectively.<sup>4,8</sup> A peak at  $\delta$  6.17 was assigned to (*Z*)-2-butylseleno-1-butylthio-4-phenyl-1-butene tentatively.

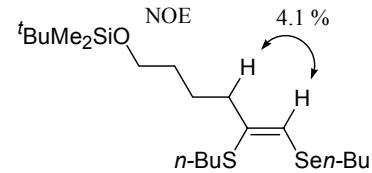


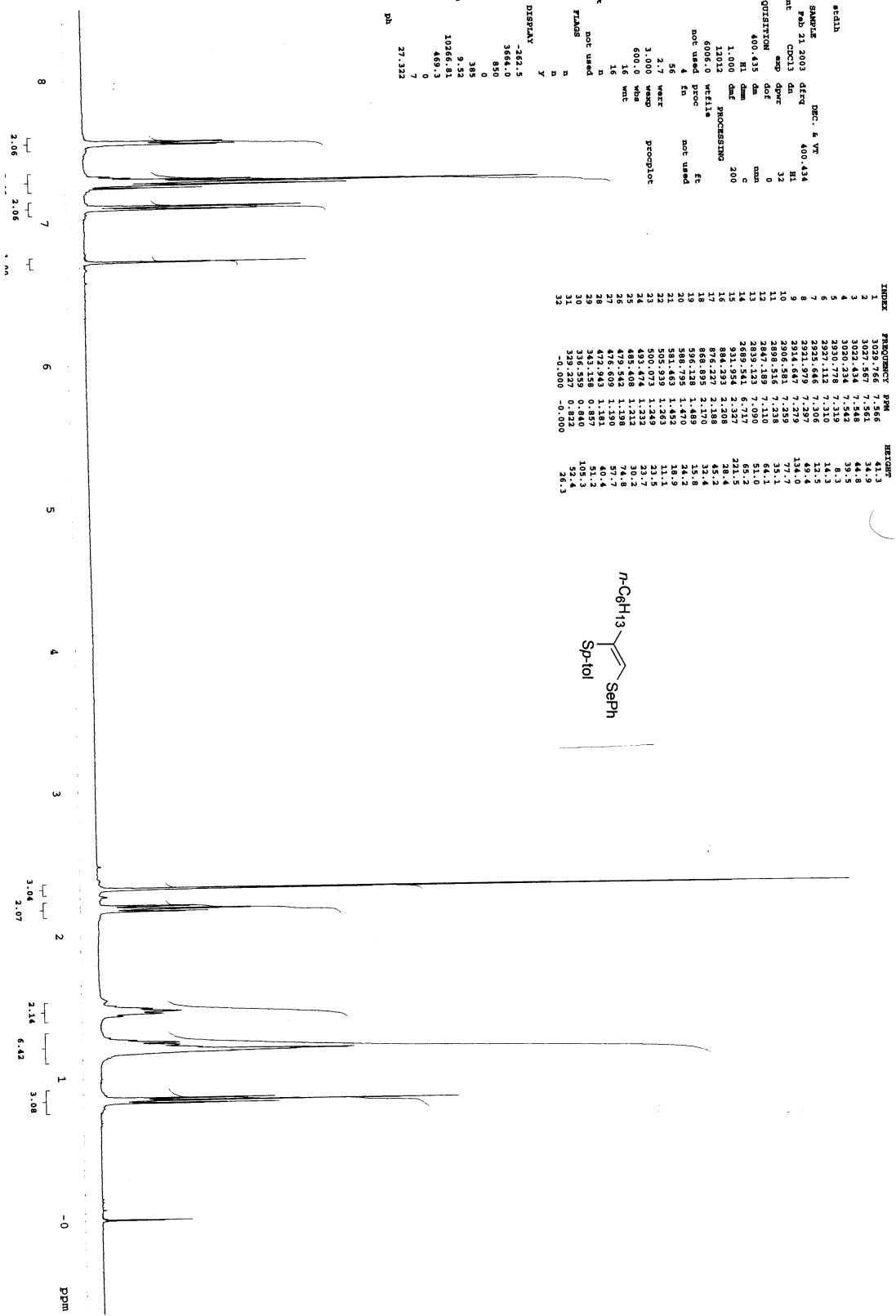
**(*Z*)-6-(*t*-Butyldimethylsilyloxy)-1-butylseleno-2-butylthio-1-hexene (Table 4, entry 4)**

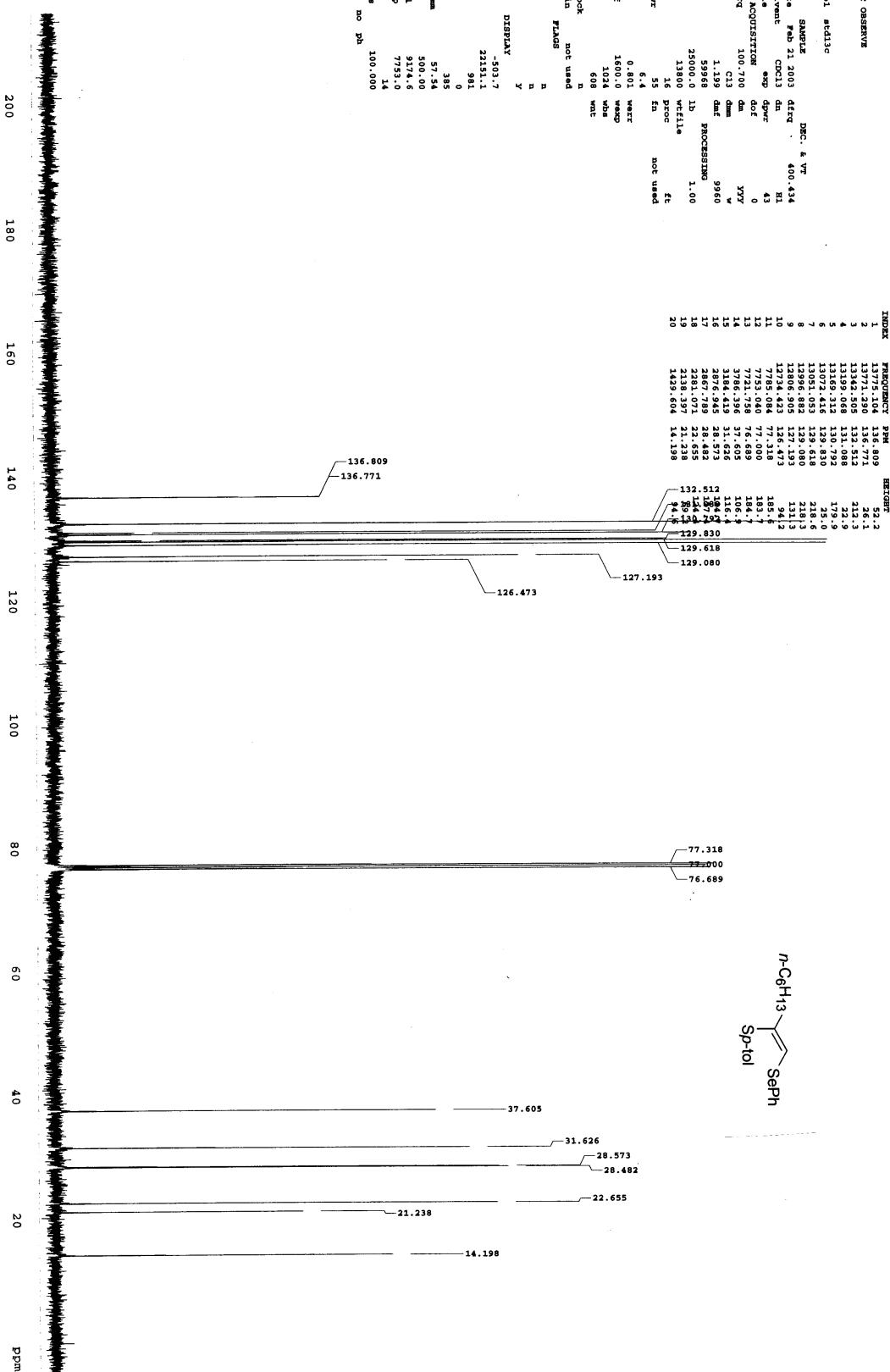
(*Z*)-6-(*t*-Butyldimethylsilyloxy)-1-butylseleno-2-butylthio-1-hexene (50%), (*Z*)-6-(*t*-butyldimethylsilyloxy)-2-butylseleno-1-butylthio-1-hexene (4%), (*Z*)-1,2-bis(butylthio)-6-(*t*-butyldimethylsilyloxy)-1-hexene (5%), and

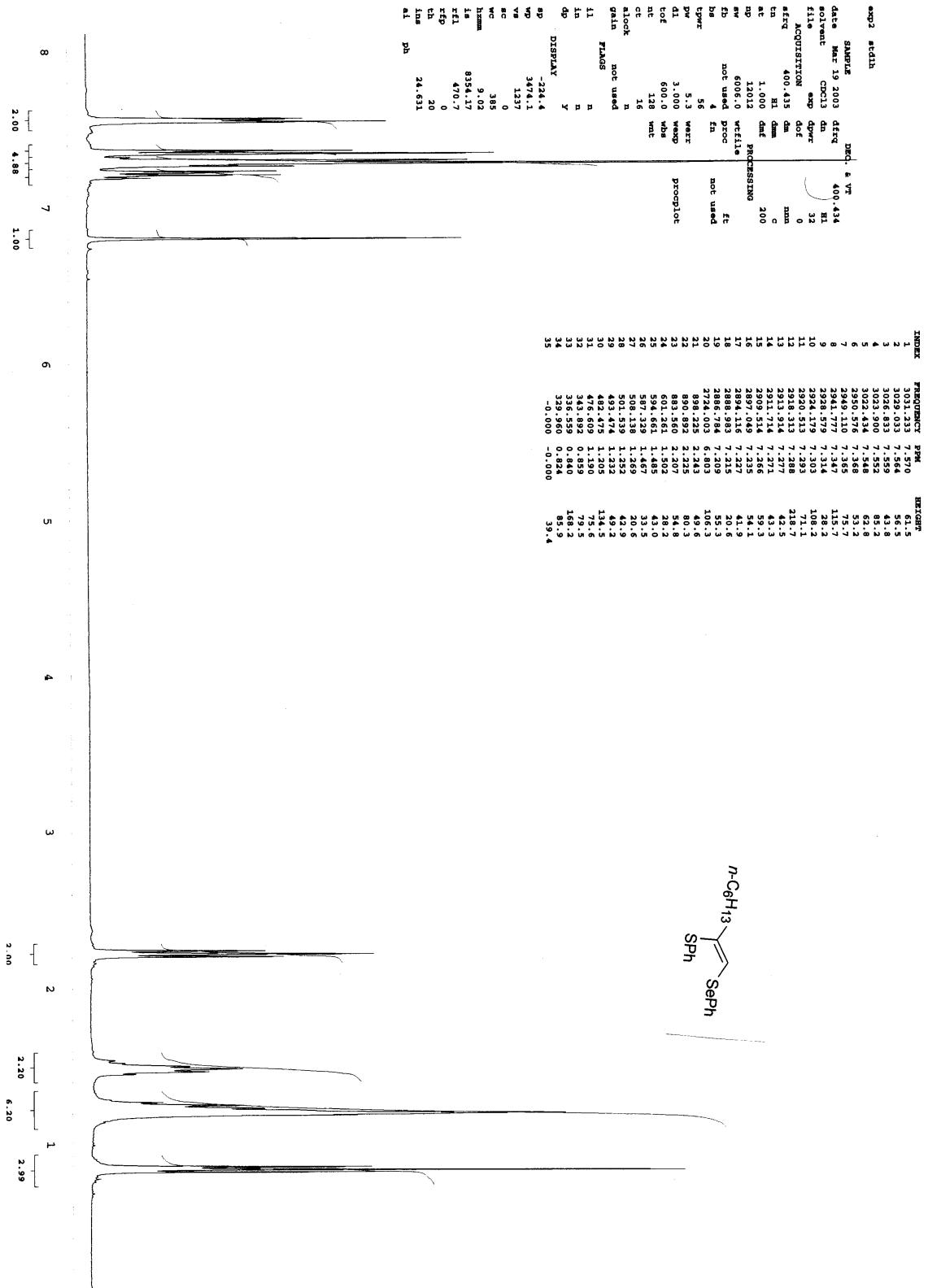
(Z)-1,2-bis(butylseleno)-6-(*t*-butyldimethylsilyloxy)-1-hexene (17%) were obtained (<sup>1</sup>H-NMR yield). The major compound (48%) was isolated by preparative recycling reverse-phase HPLC using Cadenza CD-C18 column (MeOH). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 0.05 (6H, s), 0.89 (9H, s), 0.91 (3H, t, *J* = 7.6 Hz), 0.92 (3H, t, *J* = 7.6 Hz), 1.41 (2H, sextet, *J* = 7.2 Hz), 1.42 (2H, sextet, *J* = 7.2 Hz), 1.48 - 1.62 (6H, m), 1.69 (2H, quintet, *J* = 7.2 Hz), 2.28 (2H, t, *J* = 7.2 Hz), 2.68 (2H, t, *J* = 7.2 Hz), 2.68 (2H, t, *J* = 7.2 Hz), 3.62 (2H, t, *J* = 6.0 Hz), 6.34 (1H, s). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ -5.1, 13.7, 13.8, 18.5, 22.0, 23.0, 24.9, 26.1, 26.5, 31.4, 32.1, 32.2, 33.1, 37.3, 63.0, 122.7 (<sup>1</sup>*J*<sub>C-Se</sub> = 102 Hz), 135.2. <sup>77</sup>Se-NMR (76 MHz, CDCl<sub>3</sub>) δ 258.5. IR (neat) 2928, 2857, 2736, 1574 cm<sup>-1</sup>. MS (EI) *m/z* 75 (M<sup>+</sup> - 363, 100), 438 (M<sup>+</sup>, 60). HRMS. Calcd for C<sub>20</sub>H<sub>42</sub>OSeSi: 438.1891. Found: 438.1870.

(Z)-1,2-Bis(butylthio)-6-(*t*-butyldimethylsilyloxy)-1-hexene (δ 6.05), and (Z)-1,2-bis(butylseleno)-6-(*t*-butyldimethylsilyloxy)-1-hexene (δ 6.56) were assigned by analogy with (Z)-12 and (Z)-13, respectively.<sup>4,</sup> <sup>8</sup> A peak at δ 6.23 was assigned to (Z)-6-(*t*-butyldimethylsilyloxy)-2-butylseleno-1-butylthio-1-hexene tentatively.

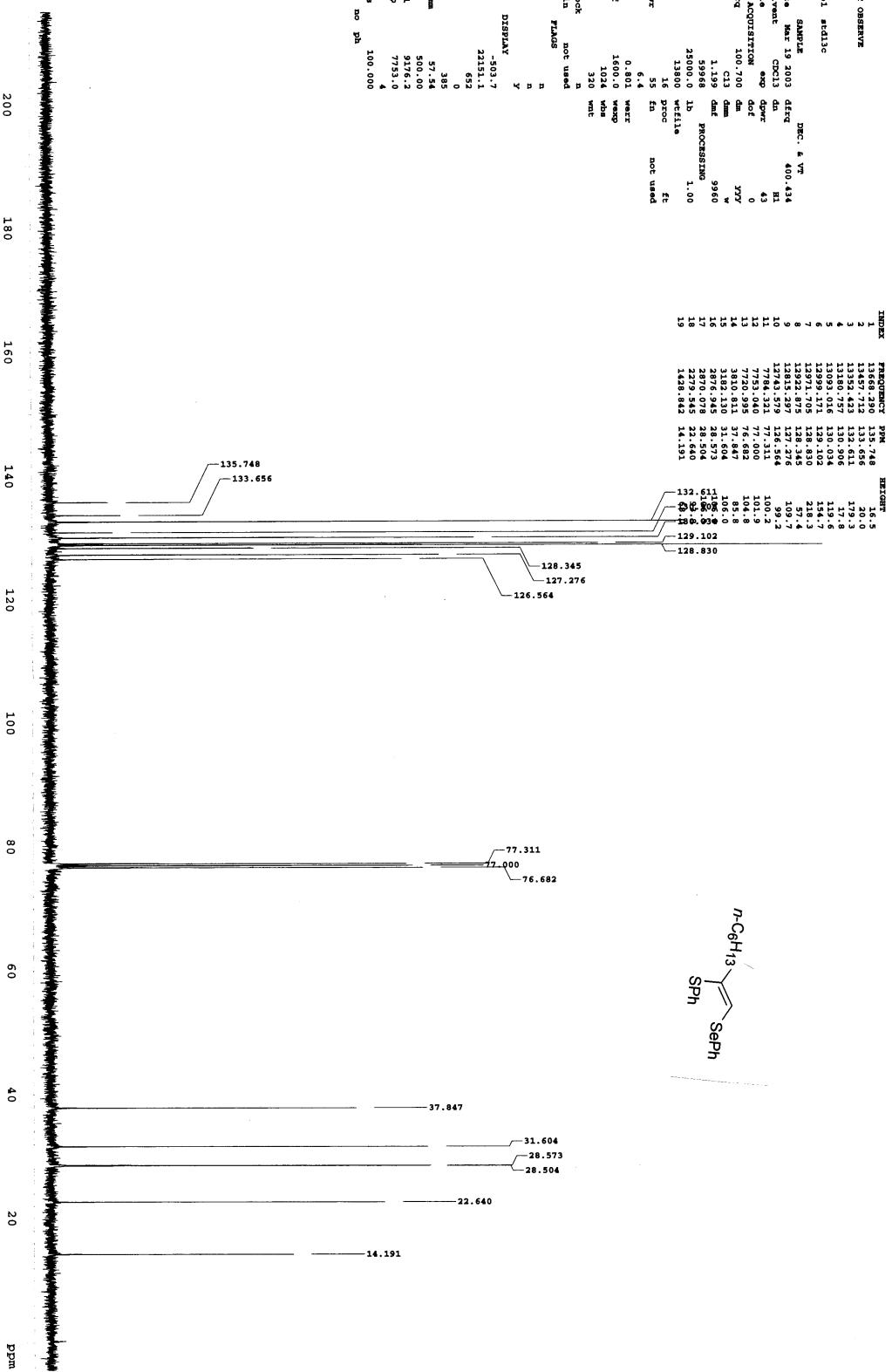


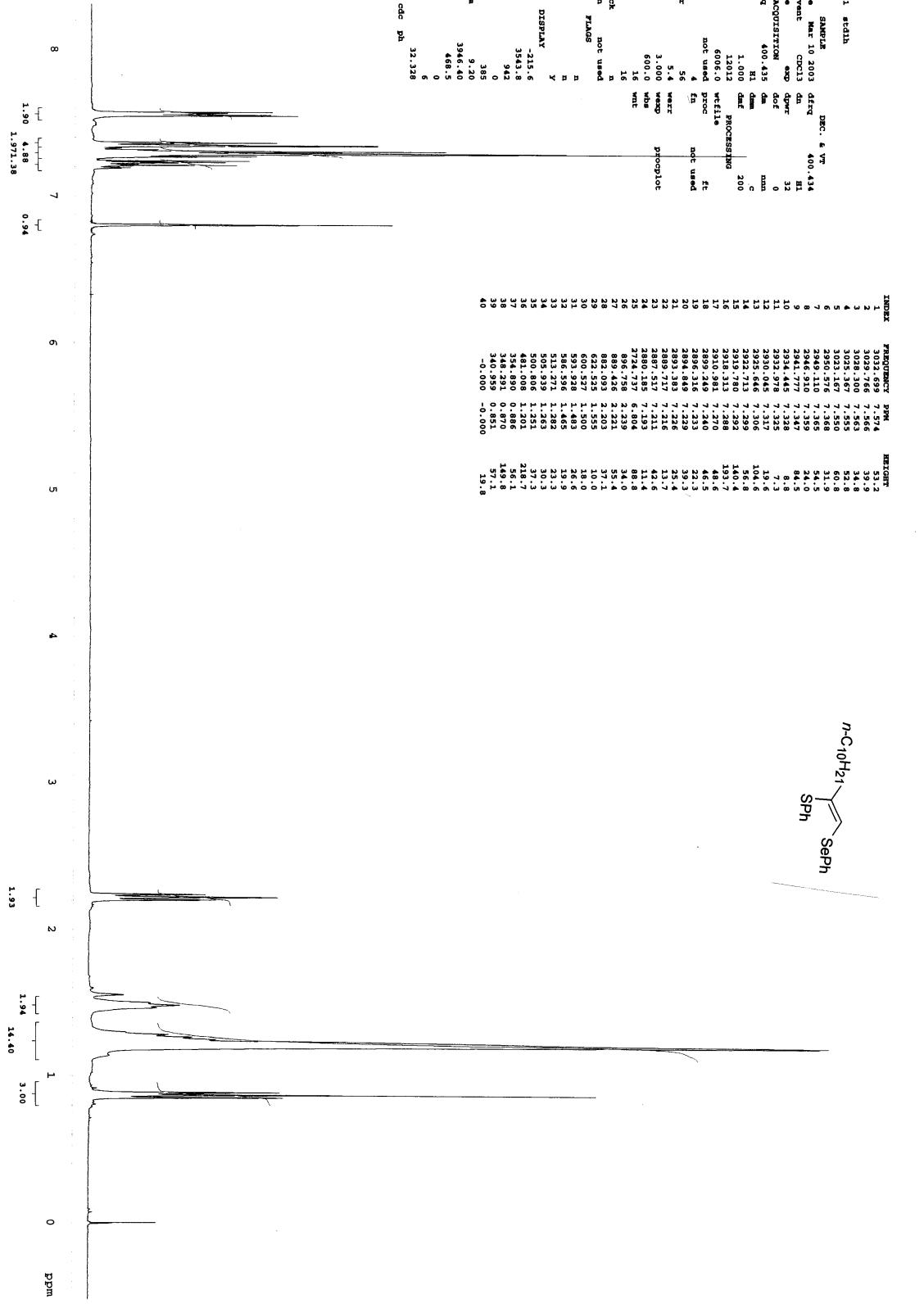


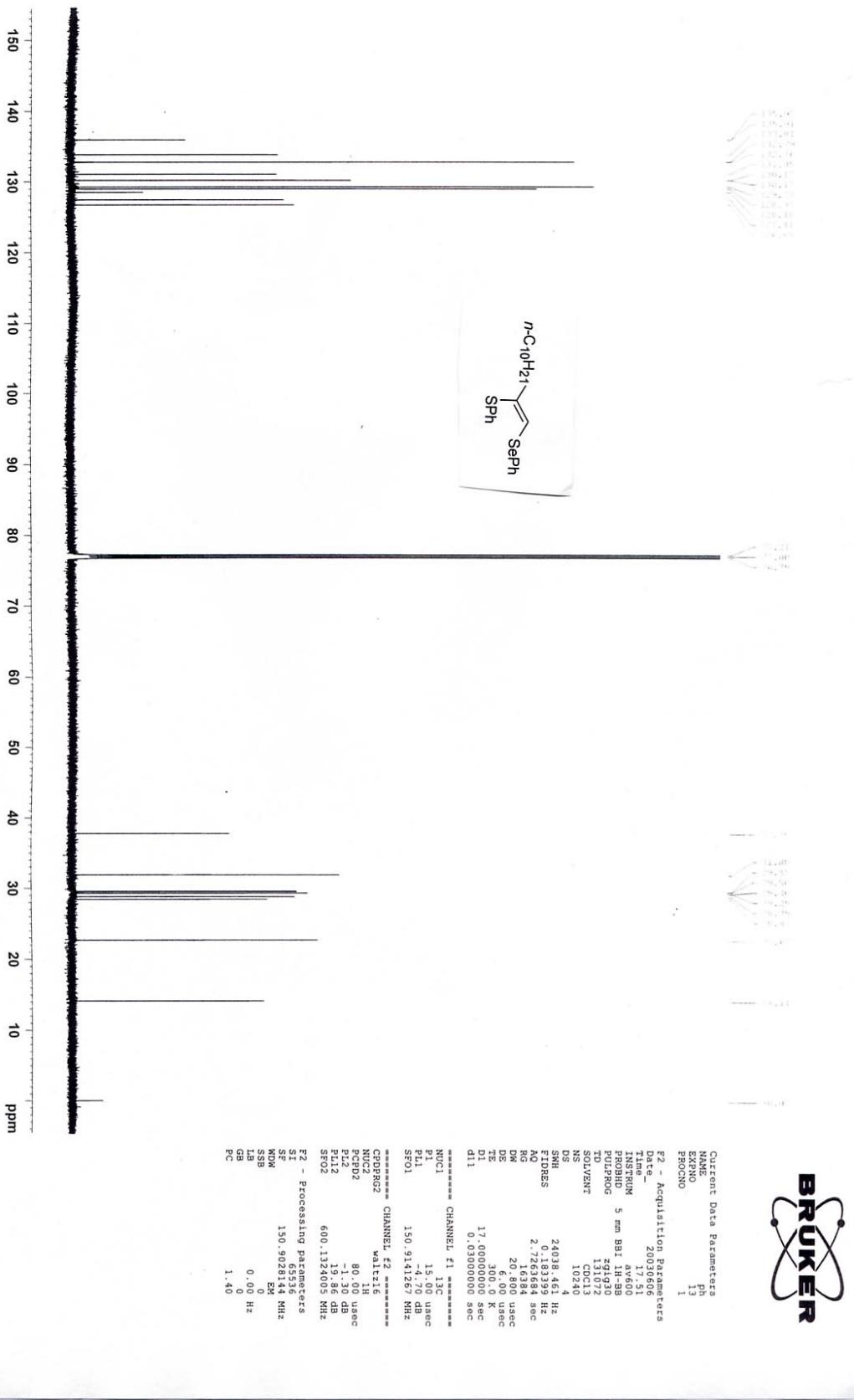


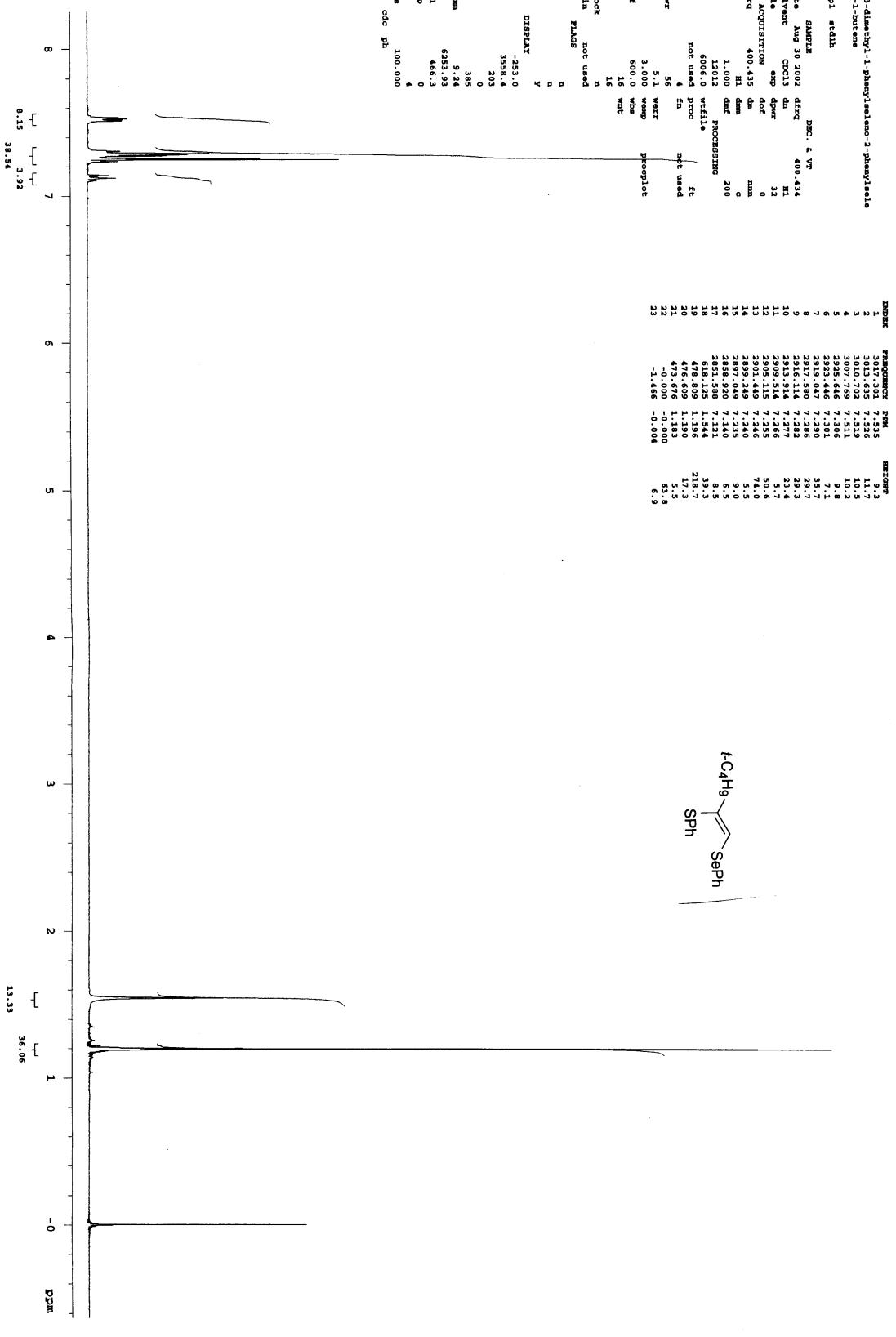


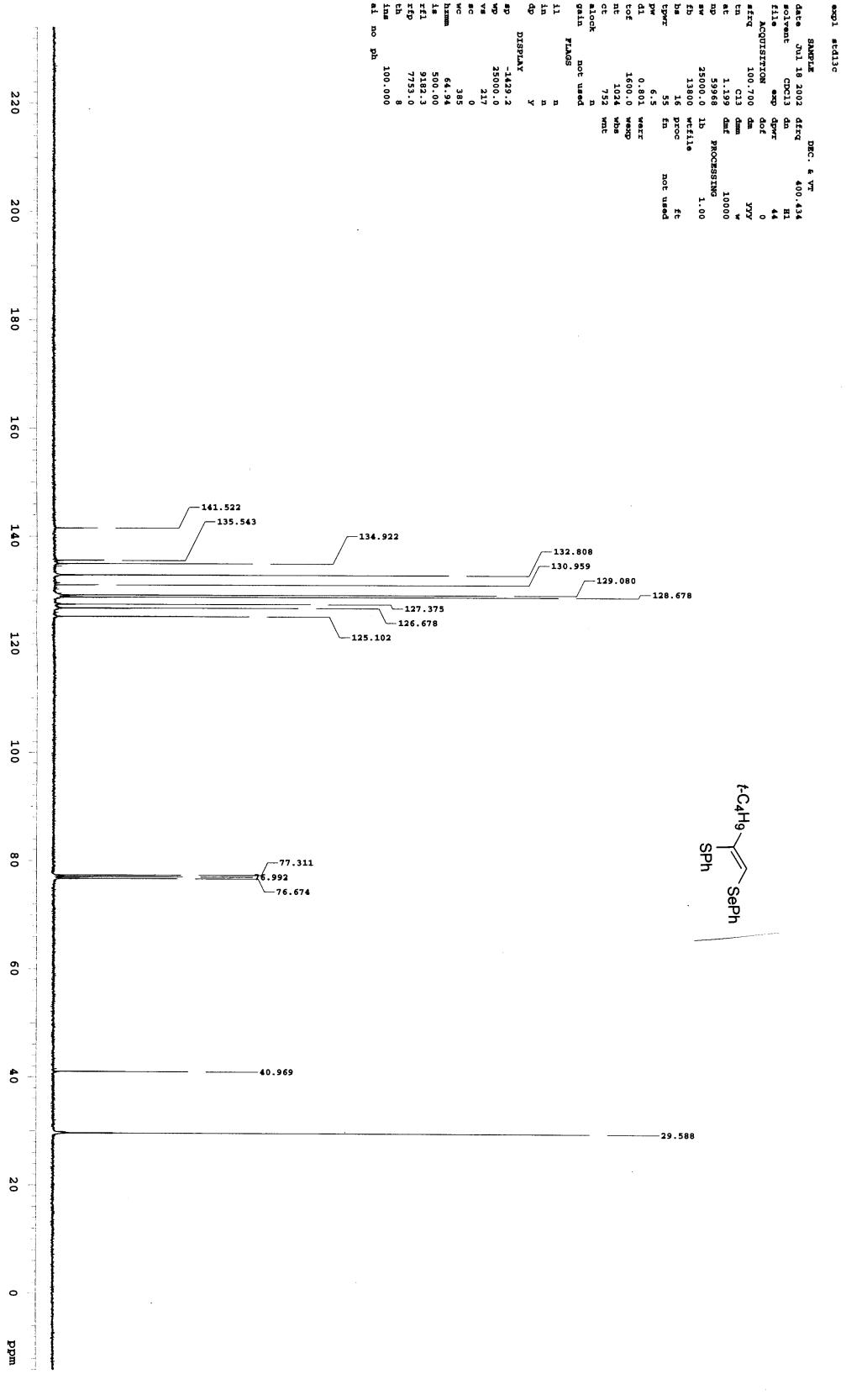
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4 11093.656 132.611 17.3  
5 11093.656 130.034 139.6  
6 11999.437 130.032 134.7  
7 12971.705 128.820 238.3  
8 12932.875 128.345 57.4  
9 12815.287 127.266 109.7  
10 12773.559 126.314 109.7  
11 12724.621 125.311 101.9  
12 7720.599 77.000 101.9  
13 7720.599 76.982 104.8  
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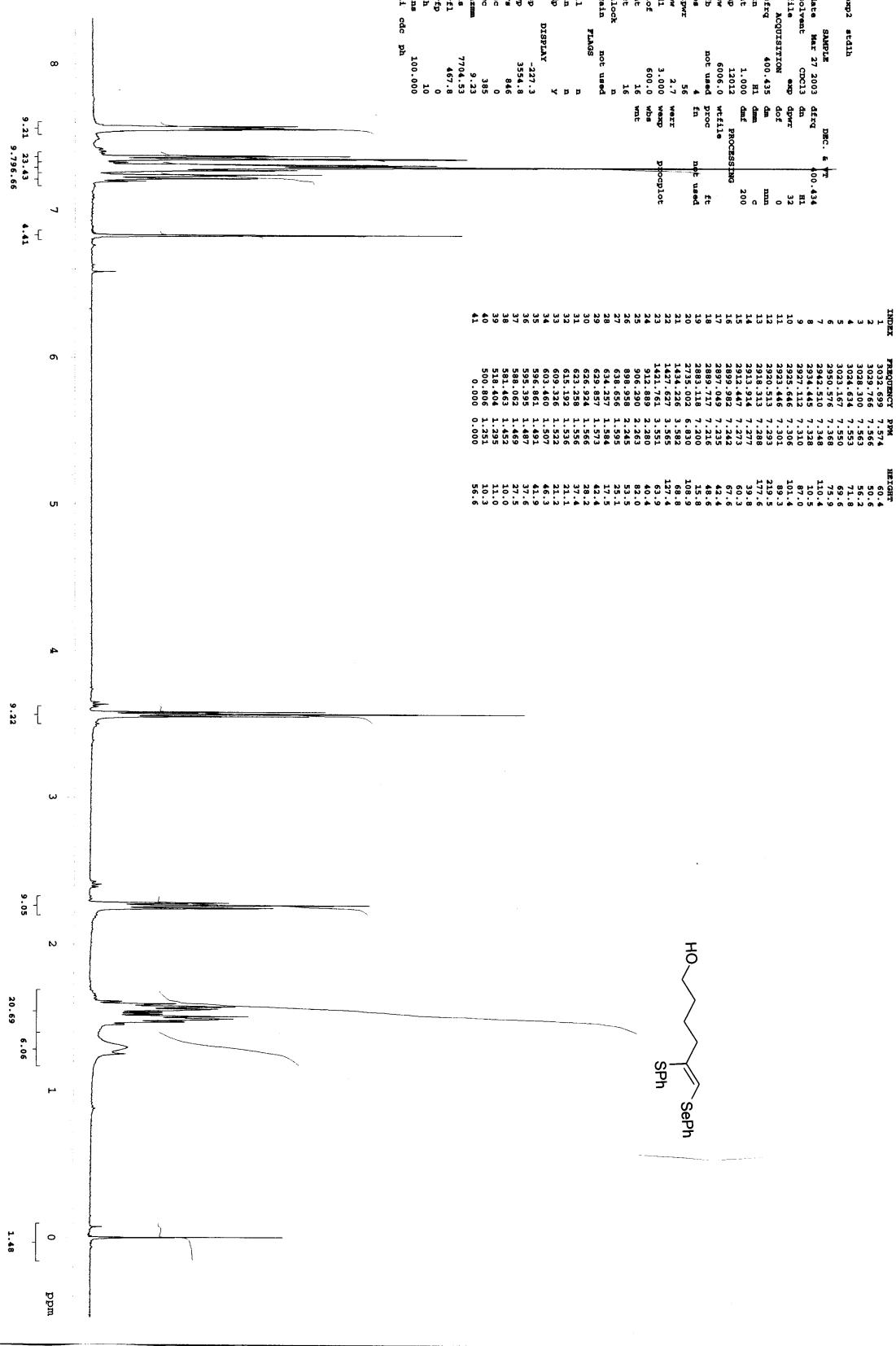


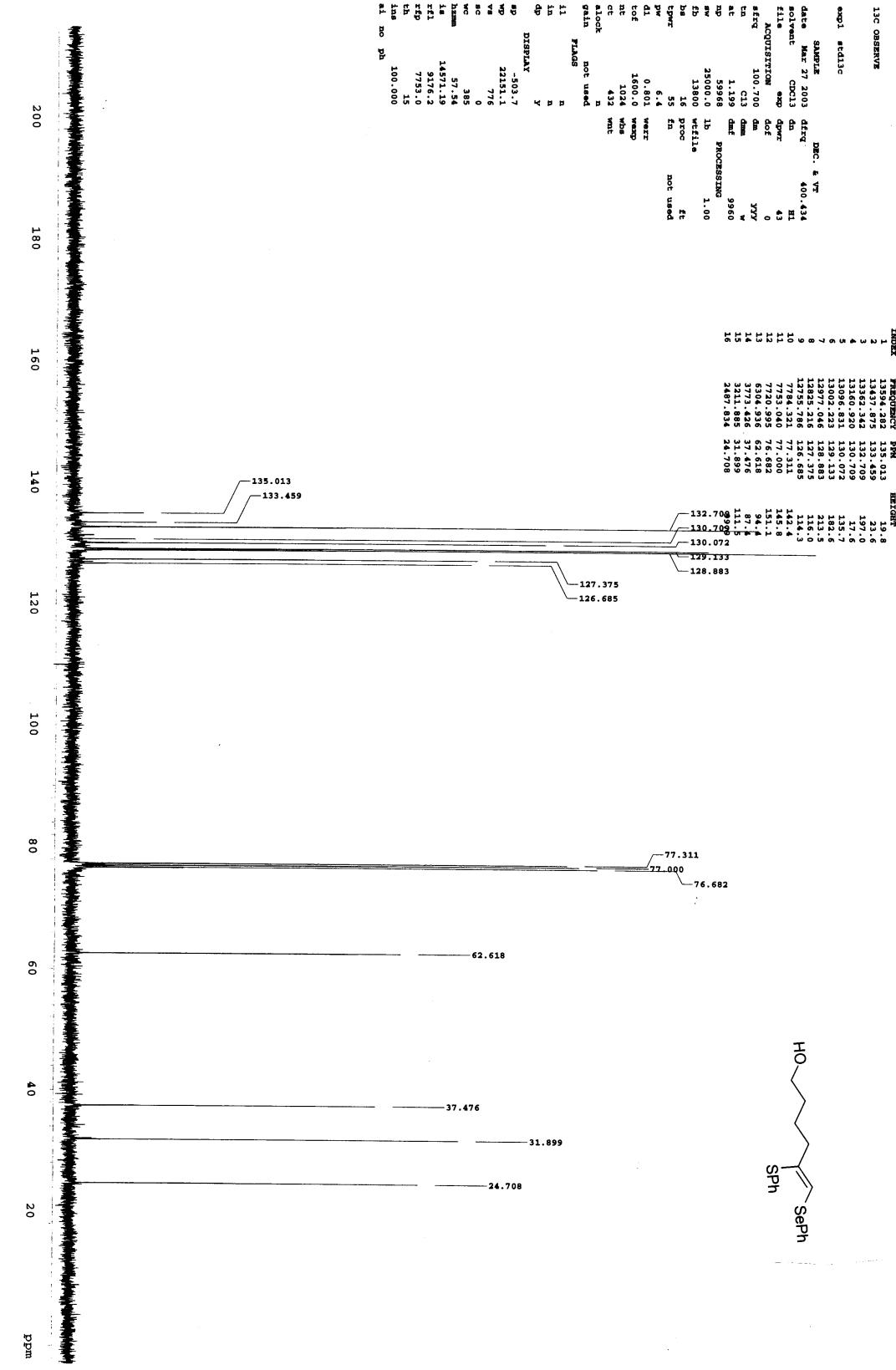


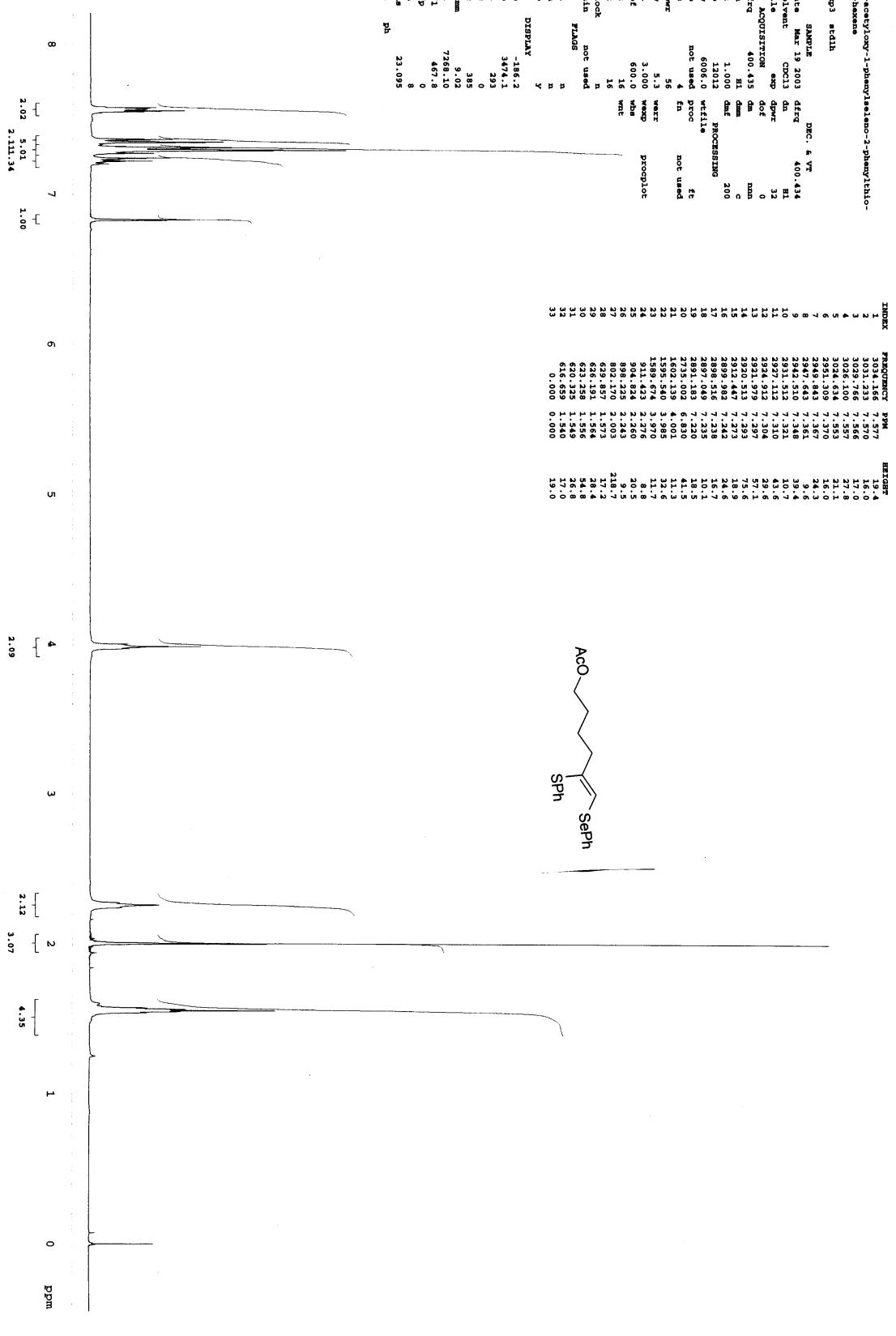


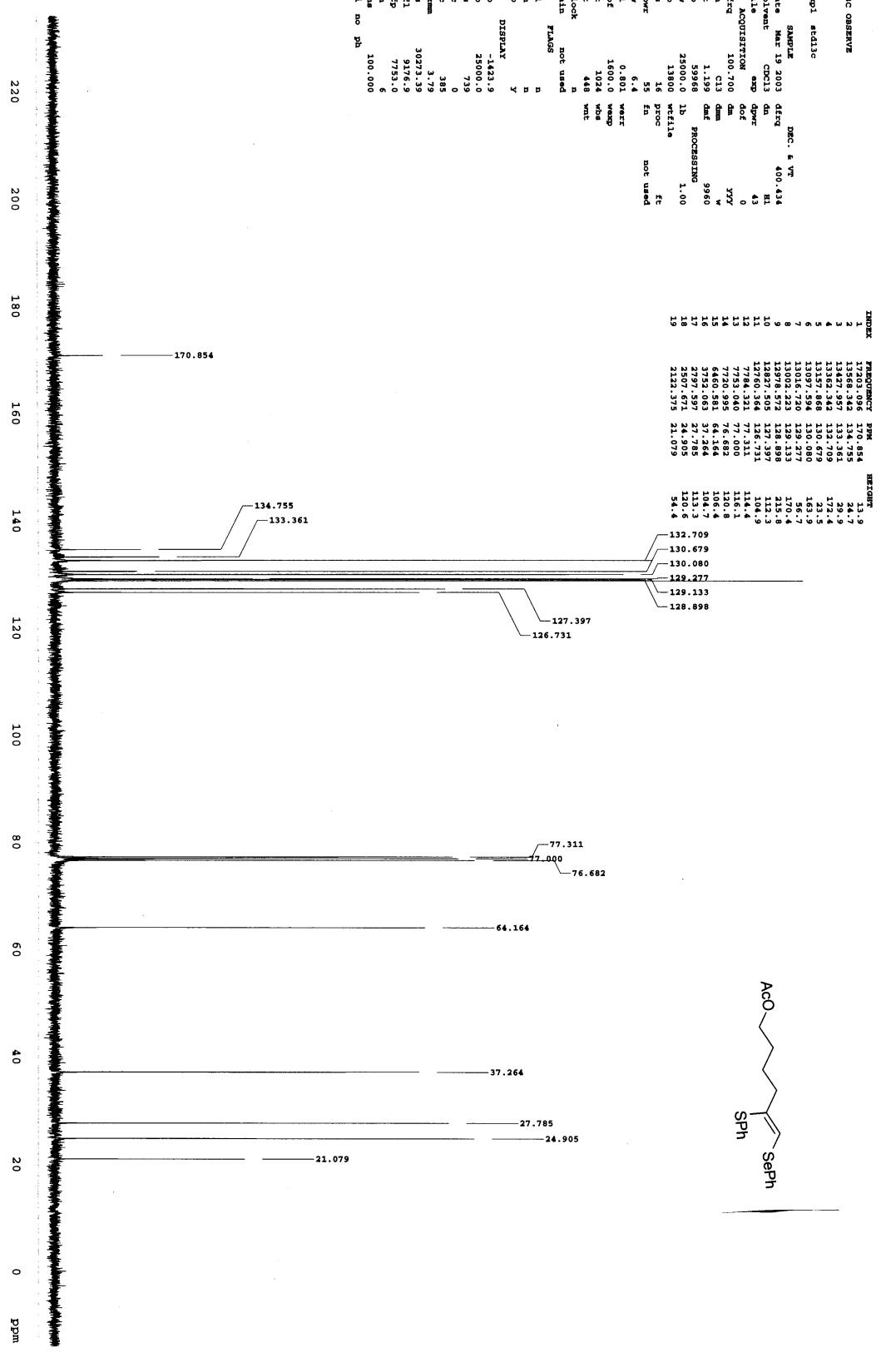






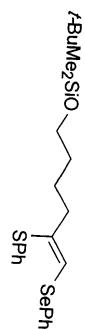




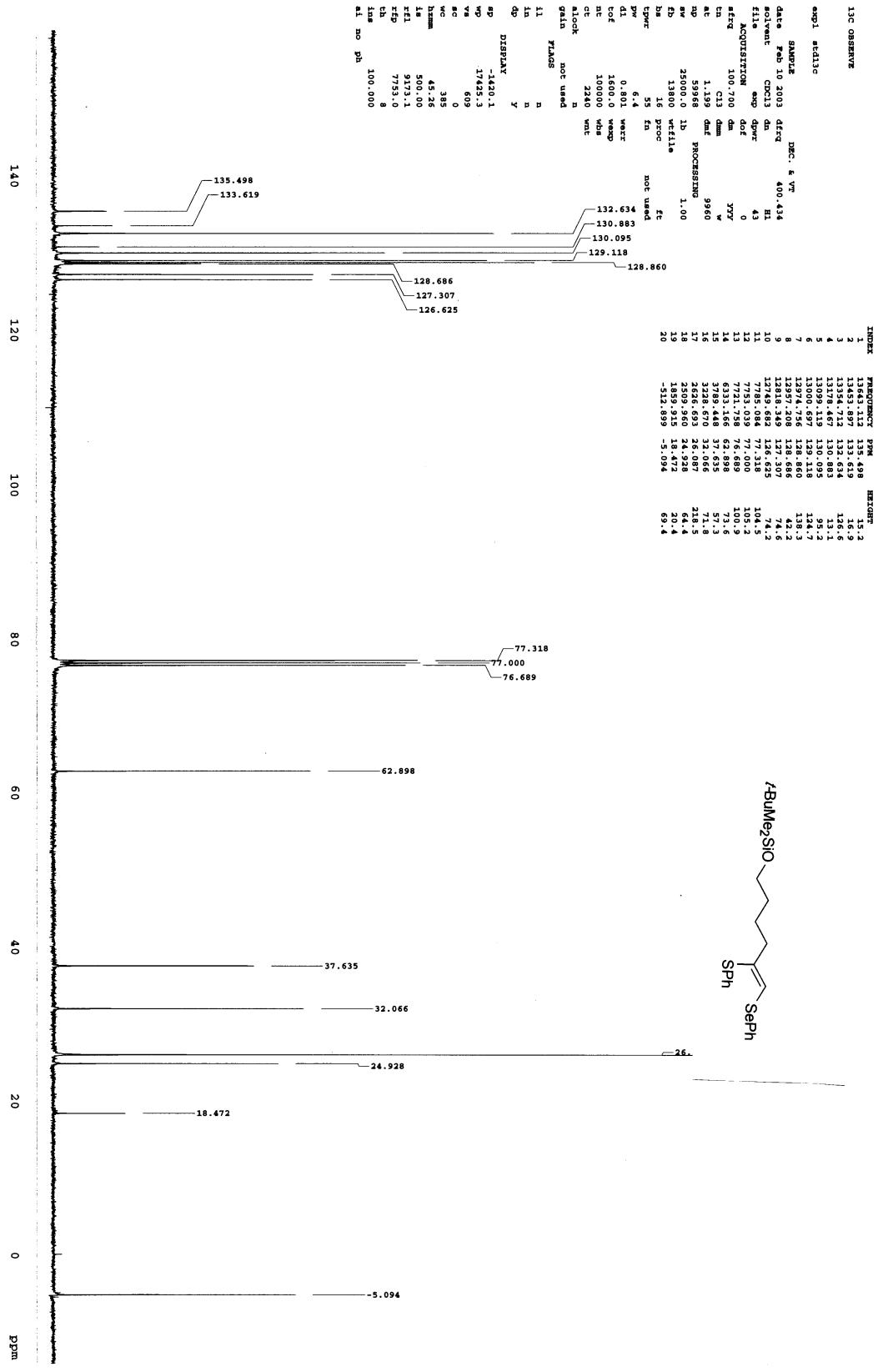


STANDARD IN OBSERVE

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2	3023.467	7.550	7.1
3	3021.701	7.546	6.4
4	3019.935	7.537	10.8
5	3016.508	7.533	9.8
6	2981.574	7.522	9.5
7	2922.779	7.516	15.2
8	2922.713	7.509	4.4
9	2919.047	7.500	16.9
10	2916.847	7.494	10.7
11	2913.381	7.475	26.7
12	2911.714	7.471	31.1
13	2905.848	7.457	4.1
14	2904.382	7.453	7.8
15	2894.116	7.427	10.9
16	2890.450	7.424	3.9
17	2889.450	7.418	6.4
18	2887.517	7.411	2.7
19	2881.851	7.403	2.2
20	2881.651	7.196	6.7
21	2725.470	6.806	14.4
22	1417.362	3.540	9.8
23	1410.762	3.523	17.0
24	1404.897	3.508	9.9
25	903.387	2.456	5.8
26	896.025	2.438	10.5
27	888.692	2.419	6.5
28	643.526	1.549	3.9
29	619.192	1.536	2.7
30	612.259	1.529	6.1
31	607.860	1.518	3.5
32	601.261	1.502	5.3
33	586.556	1.465	2.5
34	580.730	1.450	2.9
35	571.931	1.428	3.5
36	566.085	1.414	3.9
37	342.445	0.855	216.9
38	337.222	0.848	4.1
39	318.420	0.855	2.1
40	44.421	0.077	5.9
41	42.422	0.070	4.2
42	-0.000	0.000	110.4
43	-4.399	0.011	11.5
44	-6.599	-0.016	2.0



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cpwr	56	not used		
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dr		wt		
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6	6	3013.67	7.553	102.3
7	7	2961.84	7.400	71.4
8	8	2951.97	7.396	100.7
9	9	2951.09	7.396	144.0
10	10	2951.00	7.390	74.9
11	11	2950.98	7.394	39.8
12	12	2951.77	7.326	29.8
13	13	2951.77	7.326	7.35
14	14	2929.31	7.315	172.3
15	15	2923.44	7.301	112.0
16	16	2921.346	7.285	115.8
17	17	2918.313	7.288	163.6
18	18	2916.947	7.284	105.2
19	19	2911.501	7.275	24.6
20	20	2911.501	7.275	24.6
21	21	2905.112	7.221	39.3
22	22	2903.64	7.221	70.6
23	23	2902.482	7.248	35.0
24	24	2898.516	7.238	100.6
25	25	2898.415	7.233	100.7
26	26	2898.415	7.233	30.9
27	27	2898.415	7.233	25.5
28	28	2744.603	6.847	64.9
29	29	2731.536	6.836	194.8
30	30	2726.936	6.810	218.7
31	31	2718.871	6.790	60.7
32	32	-0.000	-0.000	59.0

