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Supporting Information

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A Remarkably Efficient Fluoroalkylation of Cyclic Sulfates and Sulfamidates with $PhSO_2CF_2H$: Facile Entry into β-Difluoromethylated or β-Difluoromethylenated Alcohols and Amines

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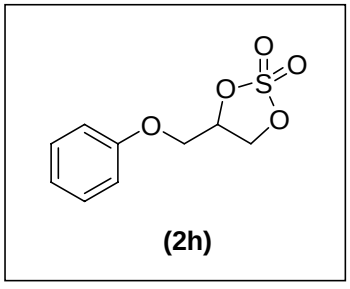
General:

Unless otherwise mentioned, reagents were purchased from commercial sources and used as received. The solvent THF is distilled from sodium. Melting points are uncorrected. High-resolution mass data were recorded on a high-resolution mass spectrometer in the EI , ESI or MALDI mode. ^{1}H NMR spectra were recorded at 300 MHz in $CDCl_3$ and were referenced to residual $CHCl_3$ or to tetramethylsilane (TMS). ^{19}F NMR spectra were recorded at 282 MHz using $CFCl_3$ as external standard. ^{13}C NMR spectra were recorded at 75, 100 or 125 MHz in $CDCl_3$. All chemical shifts are reported in δ parts per million and coupling constants are in hertz.

1. Preparation of the starting materials: 1,2-Cyclic sulfates were prepared from 1,2-diols according to the known procedures.[1] 1,2-Cyclic sulfamidates were prepared from corresponding amino alcohols.[2,3]

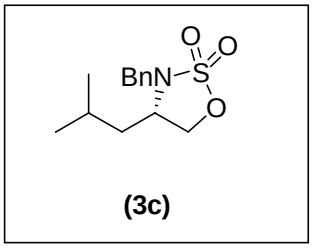
1. Gao, Y.; Sharpless, K. B. *J. Am. Chem. Soc*, **1988**, *110*, 7538-7539.
2. Posakony, J. J.; Tewson, T. J. *Synthesis*, **2002**, *6*, 766-770.
3. Williams, A. J.; Chakthong, S.; Gray, D.; Lawerence, R. M.; Gallagher, T. *Org. Lett.* **2003**, *5*, 811-814.



(2h)

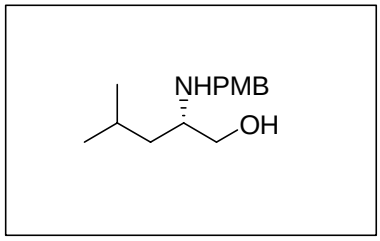
3-Phenoxypropane-1,2-cyclic sulfate, or *4-Phenoxymethyl-2,2-dioxo-1,3,2-dioxathiolane* **(2h)**
White solid , m.p. 48–49°C. ^{1}H NMR ($CDCl_3$, 300MHz): δ 4.30 (m, 2H), 4.68–4.90 (m, 2H), 5.24 (m, 1H), 6.91 (d, *J* = 7.9 Hz, 2H), 7.03 (t, *J* = 7.3 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR ($CDCl_3$,

75MHz): δ 65.7, 69.6, 78.8, 114.6, 122.2, 129.7, 157.4. MS (EI, *m/z*, %): 230(M^+, 33.0), 137(20.1), 107(84.5), 94(77.4), 79(52.9), 77(100.0). EA calcd. for $C_9H_{10}O_5S$: C, 46.95; H, 4.38; Found C, 46.89; H, 4.40. IR(KBr): 1600, 1787, 1501, 1490, 1393, 1247, 1209.

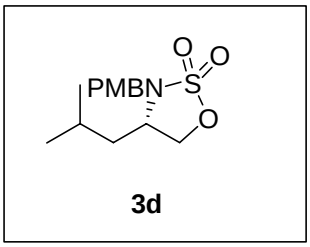


(3c)

3-Benzyl-(S)-4-isobutyl-[1,2,3]-oxathiazolidine-2,2-dioxide **(3c)**
White solid, mp 36–37°C. [α]^{25} 25.0(c=0.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300MHz): δ 0.77 (d, *J* = 6.5 Hz, 3H), 0.82 (d, *J* = 6.5 Hz, 3H), 1.39–1.57 (m, 3H), 3.62 (m, 1H), 4.17 (dd, *J* = 8.4, 6.4 Hz, 1H), 4.22 (d , *J* = 14.7 Hz, 1H), 4.40 (d , *J* = 14.7 Hz, 1H), 4.54 (dd, *J* = 8.4, 6.8 Hz, 1H), 7.28–7.44 (m, 5H). ^{13}C NMR ($CDCl_3$, 100MHz): δ 21.8, 23.1, 24.4, 41.0, 50.8, 57.9, 71.4, 128.3, 128.68, 128.73, 134.8. MS(EI, *m/z*): 270(M+H^+, 0.6), 212(2.8), 91(100.0). EA calcd. for $C_{13}H_{19}NO_3S$: C, 57.97; H, 7.11; N, 5.20; Found C, 57.91; H, 7.11; N, 4.96. IR(film): 2959, 2933, 2872, 1468, 1456, 1345, 1189.

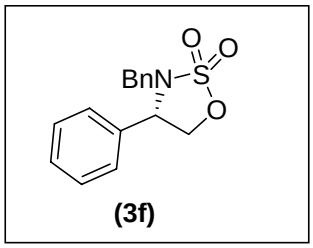


(S)-2-(4-Methoxybenzylamino)-4-methylpentan-1-ol
White solid, m.p. 49–50°C. [α]^{25} 26.0(c=1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300MHz): δ 0.88 (d, *J* = 4.9 Hz, 3H), 0.91 (d, *J* = 4.9 Hz, 3H), 1.23 (pent, *J* = 6.5 Hz, 1H), 1.41 (pent, *J* = 6.5 Hz, 1H), 1.62 (m, 1H), 1.70–2.18 (br, s, 2H), 2.74 (m, 1H), 3.26 (dd, *J* = 10.4, 6.4 Hz, 1H), 3.65 (dd, *J* = 10.9, 3.8 Hz, 1H), 3.72 (d , *J* = 5.3 Hz, 2H), 3.80 (s, 3H), 6.86 (d , *J* = 8.8 Hz, 2H), 7.24 (d , *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100MHz): δ 22.7, 23.0, 24.9, 41.2, 50.4, 55.2, 56.1, 63.2, 113.8, 129.2, 132.4, 158.7. MS(EI, *m/z*): 236(M–H^+, 0.1), 206(M–OCH_3, 13.9) 121(100.0), 77(5.2). EA calcd. for $C_{14}H_{23}NO_2$: C, 70.85; H, 9.77; N, 5.90; Found C, 70.87; H, 9.85; N, 5.70. IR(film): 3300(br), 2954, 2868, 1612, 1513, 1465, 1248.



3d

3-(4-Methoxybenzyl)-(S)-4-isobutyl-[1,2,3]-oxathiazolidine-2,2-dioxide **(3d)**
Colorless liquid. $[\alpha]^{25}$ 22.1(c=0.95, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300MHz): δ 0.79 (d, *J* = 6.0 Hz, 3H), 0.84 (d, *J* = 6.0 Hz, 3H), 1.39–1.58 (m, 3H), 3.61 (m, 1H), 3.81 (s, 3H), 4.15 (dd, *J* = 8.5, 6.0 Hz, 1H), 4.20 (d, *J* = 14.6 Hz, 1H), 4.30 (d, *J* = 14.6 Hz, 1H), 4.51 (dd, *J* = 8.5, 6.5 Hz, 1H), 6.88 (d , *J* = 8.8 Hz, 2H), 7.32 (d , *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100MHz): δ 21.8, 23.1, 24.4, 41.0, 50.2, 55.2, 57.5, 71.3, 114.0, 126.5, 130.2, 159.6. MS(EI, *m/z*): 299(M^+, 2.5), 218(1.0), 204(3.0), 162(3.0), 121(100.0). EA calcd. for $C_{14}H_{21}NO_4S$: C, 56.16; H, 7.07; N, 4.68; Found C, 56.21; H, 7.06; N, 4.56. IR(film): 2959, 2872, 1613, 1510, 1467, 1348, 1251.

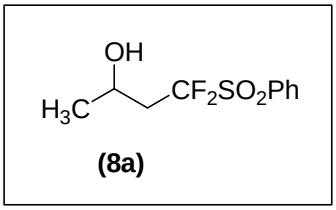


(3f)

3-Benzyl-(S)-4-phenyl-[1,2,3]-oxathiazolidine-2,2-dioxide **(3f)**
Yellow solid. $[\alpha]^{25}$102.2(c=1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300MHz): δ 4.08 (d, *J* = 15 Hz, 1H), 4.28 (d, *J* = 15 Hz, 1H), 4.37 (t, *J* = 8.7 Hz, 1H), 4.59 (t, *J* = 7.2 Hz, 1H), 4.69 (dd, *J* = 8.5, 6.7 Hz, 1H), 7.16–7.29 (m, 5H), 7.31–7.42 (m, 5H). ^{13}C NMR ($CDCl_3$, 125MHz): δ 49.3, 63.1, 72.5,127.7, 128.2, 128.4, 129.20, 129.22, 129.5, 133.7, 134.7. MS(ESI, *m/z*): 307.2($M+NH_4^+$, 100.0), 209.1($M+H^+$, 80.0). HRMS (MALDI): *m/z* calcd. for $C_{15}H_{15}NO_3SNa$($M+Na^+$) 312.0665, found 312.0683. IR(film): 3065, 3032, 1497, 1457, 1352, 1186.

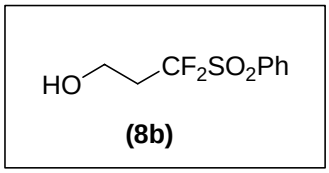
2. General procedure for nucleophilic difluoromethylation of 1,2-cyclic sulfates using difluoromethyl phenyl sulfone: Under N_2 atmosphere, into a 20-mL Schlenk flask containing 1,2-cyclic sulfate (**2**) (1.0 mmol) and $PhSO_2CF_2H$ (**1**, 211 mg, 1.1 mmol) in 5 ml THF and 0.5 ml HMPA at –78 ^{o}C, was added a THF solution (1.2 mL) of $(TMS)_2NLi$ (LHMDS, 1.0 M, 1.2 mmol) in 10 min. The reaction mixture was then stirred at this tempetature for another 20 min., followed by adding a 20% aqueous sulfuric acid (5 mL) at this temperature. The mixture was stired at room tempeture for at least 2 hours or overnight. Then the solution mixture was extracted with Et_2O (10 mL x 3) , and the combined organic phase was washed with saturated $NaHCO_3$ solution , then dried over $MgSO_4$. After the removal of volatile

solvents under vacuum, the crude product was further purified by silica gel column chromatography to give product **8 i**n 87-99% yields.



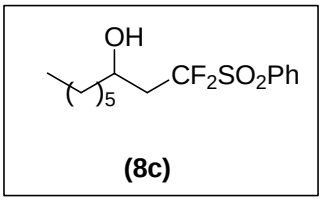
(8a)

4,4-Difluoro-4-(phenylsulfonyl)butan-2-ol **(8a)**
Colorless liquid. ^{1}H NMR ($CDCl_3$, 300MHz): δ 1.34 (d, *J* = 6.4 Hz, 3H), 2.22 (s, 1H), 2.37–2.69 (m, 2H), 4.33–4.47 (m, 1H), 7.59 –7.68 (m, 2H), 7.75–7.83 (m, 1H), 7.99 (d, *J* = 7.7 Hz, 2H). ^{19}F NMR ($CDCl_3$, 282MHz): δ –100.9 (td, *J* = 18.4, 4.6 Hz, 2F). ^{13}C NMR ($CDCl_3$, 100MHz): δ 23.8, 38.5 (t, *J* = 18 Hz), 62.1 (t, *J* = 3.6 Hz), 123.9 (t, *J* = 285 Hz), 129.1, 130.8, 131.9, 135.4. MS(EI, *m/z*): 235 (M–CH_3, 0.33), 187(0.6), 142(16.5), 125(9.1), 78(36.4), 45 (100). HRMS(MALDI): *m/z* calcd. for $C_{10}H_{12}O_3SF_2Na$ ($M+Na^+$) 273.0367, found 273.0387. IR(film): 3547, 3420, 2978, 2920, 1580, 1449, 1220, 1170, 1132.



(8b)

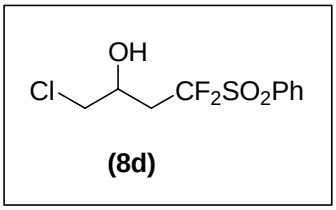
3,3-Difluoro-3-(phenylsulfonyl)propan-1-ol （**8b**）
White solid, m.p. 36–37°C. ^{1}H NMR ($CDCl_3$, 300MHz): δ 2.53–2.73 (m, 2H), 2.80 (s, 1H), 3.99 (t, *J* = 6.2 Hz, 2H), 7.58 –7.67 (m, 2H), 7.73–7.82 (m, 1H), 7.98 (d, *J* = 7.9 Hz, 2H). ^{19}F NMR ($CDCl_3$, 282MHz): δ –102.2 (t, *J* = 18 Hz, 2F). ^{13}C NMR ($CDCl_3$, 125MHz): δ 33.0 (t, *J* = 19 Hz), 55.5 (t, *J* = 4.5 Hz), 123.9 (t, *J* = 284 Hz), 129.3, 130.7, 131.9, 135.5. MS(EI, *m/z*): 237(M+1, 2.0), 219(6.0), 142(24.8), 125(25.5), 94(15.4), 78(100.0). EA calcd. for $C_9H_{10}F_2O_3S$: C, 45.76; H, 4.27; Found C, 45.85; H, 4.07. IR(film): 3543, 3416, 2949, 2899, 1584, 1449, 1336, 1164.



(8c)

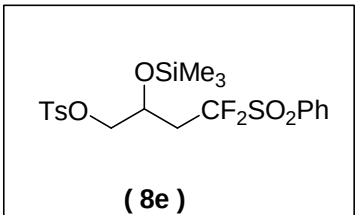
1,1-Difluoro-1-(phenylsulfonyl)nonan-3-ol **(8c)**
Colorless liquid. ^{1}H NMR ($CDCl_3$, 300MHz): δ 0.89 (t, *J* = 7 Hz, 3H), 1.23–1.65 (m, 10H), 2.18 (d, *J* = 4.3 Hz, 1H), 2.42–2.59 (m, 2H), 4.13 (m, 1H), 7.58 –7.68 (m, 2H), 7.73–7.81 (m, 1H), 7.99 (d, *J* = 7.7 Hz,

2H). ^{19}F NMR ($CDCl_3$, 282MHz): δ –100.0 (dt, *J* = 232, 18 Hz, 1F), –101.1 (dt, *J* = 232, 18 Hz, 1F). ^{13}C NMR ($CDCl_3$, 125MHz): δ 13.9, 22.4, 25.1, 28.9, 31.6, 37.1 (t, *J* = 18 Hz), 37.6, 65.6 (t, *J* = 2.8 Hz), 124.1 (t, *J* = 285 Hz), 129.2, 130.7, 132.0, 135.3. MS(EI, *m/z*): 321(M+1, 0.6), 303(3.1), 235(7.6), 143(55.1), 97(47.3), 55(100.0). EA calcd. for $C_{15}H_{22}F_2O_3S$: C, 56.23; H, 6.92; Found C, 56.55; H, 6.97. IR(film): 3556, 3069, 2980, 2857, 1585, 1449, 1350, 1170.



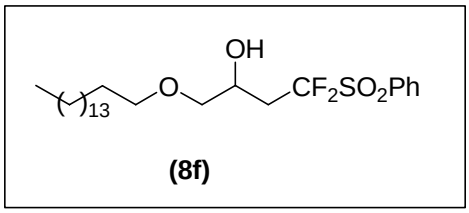
(8d)

1-Chloro-4,4-difluoro-4-(phenylsulfonyl)butan-2-ol **(8d)**
Colorless liquid. ^1H NMR ($CDCl_3$, 300MHz): δ 2.60–2.75 (m, 3H), 3.56–3.73 (m, 2H), 4.42 (m, 1H), 7.62 –7.67 (m, 2H), 7.77–7.82 (m, 1H), 7.99 (d, *J* = 8.0 Hz, 2H). ^{19}F NMR ($CDCl_3$, 282MHz): δ –101.0 (dd, *J* = 33, 16 Hz, 2F). ^{13}C NMR ($CDCl_3$, 75MHz): δ 34.4 (t, *J* = 18 Hz), 49.1, 65.6 (t, *J* = 2.7 Hz), 123.5 (t, *J* = 286 Hz), 129.5, 130.9, 131.7, 135.7. MS(EI, *m/z*): 285(M+1, 0.2), 142(32.6), 125(33.8), 94(9.1), 78(100.0). HRMS(MALDI): *m/z* calcd. for $C_{10}H_{11}O_3S^{35}ClF_2Na$ ($M+Na^+$) 306.9978, found 306.9987. IR(film): 3524, 1584, 1449, 1336, 1161, 1117.



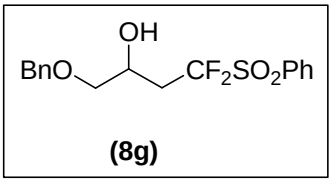
(8e)

4,4-Difluoro-4-(phenylsulfonyl)-2-(trimethylsilyloxy)butyl 4-methylbenzenesulfonate **(8e)**
White solid, m.p. 94–95°C. ^1H NMR ($CDCl_3$, 300MHz): δ 0.05(s, 9H), 2.25–2.65 (m, 2H), 2.44(s, 3H), 3.92(d, *J* = 5.3 Hz, 2H), 4.33 (m, 1H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 2H), 7.99 (d, *J* = 7.7 Hz, 2H), 7.77 (m, 3H), 7.94 (d, *J* = 8.0 Hz, 2H). ^{19}F NMR ($CDCl_3$, 282MHz): δ –101.4 (ddd, *J* = 230, 26, 11 Hz, 1F), –103.6 (ddd, *J* = 230, 25, 10 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100MHz): δ –0.15, 21.6, 33.4 (t, *J* = 18.8 Hz), 64.6, 72.2, 123.4 (t, *J* = 285 Hz), 127.9, 129.9, 130.8, 131.9, 132.6, 135.5, 145.1. MS(ESI, *m/z*): 531.0 ($M+K^+$, 12.0), 510.2 ($M+NH_4^+$, 70.0), 493.0 ($M+H^+$, 40.0), 421.0 ($M–OSiMe_3+NH_4^+$, 100.0). EA calcd. for $C_{20}H_{26}F_2O_6S_2Si$: C, 48.76; H, 5.32; Found C, 48.90; H, 5.22. IR(film): 3068, 2958, 1598, 1449, 1367, 1345, 1253, 1190, 1178, 1165, 1140.



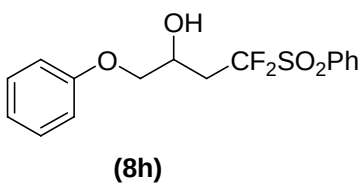
(8f)

4,4-Difluoro-1-(hexadecyloxy)-4-(phenylsulfonyl)butan-2-ol **(8f)**
White solid , m.p. 54–55°C. ^{1}H NMR ($CDCl_3$, 300MHz): δ 0.88 (t, *J* = 6.8 Hz, 3H), 1.18–1.39 (m, 26H), 1.57 (m, 2H), 2.48–2.68 (m, 3H), 3.36–3.57 (m, 4H), 4.30 (m, 1H), 7.63 (t, *J* = 7.7 Hz, 2H), 7.78 (t, *J* = 7.6 Hz, 1H), 8.00 (d, *J* = 7.9 Hz, 2H). ^{19}F NMR ($CDCl_3$, 282MHz): δ –101.7 (ddd, *J* = 280, 18, 18 Hz, 1F), –102.2 (ddd, *J* = 280, 18, 18 Hz, 1F). ^{13}C NMR ($CDCl_3$, 125MHz): δ 14.1, 22.7, 26.1, 29.3, 29.4, 29.6, 29.6, 29.6, 29.6, 29.7, 29.7, 31.9, 33.7 (t, *J* = 19 Hz), 64.8 (t, *J* = 2.8 Hz), 71.7, 73.8, 124.0 (t, *J* = 285 Hz), 129.3, 130.8, 132.2, 135.4. MS(EI, *m/z*): 330(M–$PhSO_2F$, 8.1), 235(23.6), 143(100.0), 125(33.6). EA calcd. for $C_{26}H_{44}F_2O_4S$: C, 63.64; H, 9.04; Found C, 63.73; H, 9.05. IR(film): 3544, 2944, 2854, 1466, 1449, 1346, 1165.



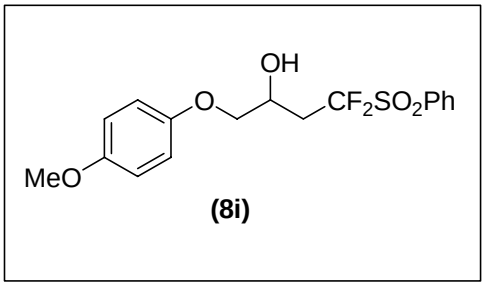
(8g)

1-(Benzyloxy)-4,4-difluoro-4-(phenylsulfonyl)butan-2-ol **(8g)**
Colorless oil. ^{1}H NMR ($CDCl_3$, 300MHz): δ 2.50–2.68 (m, 2H), 2.71 (br, d, *J* = 4.9 Hz, 1H), 3.48 (dd, *J* = 9.7, 6.1 Hz, 1H), 3.57 (dd, *J* = 9.7, 4.3 Hz, 1H), 4.34 (m, 1H), 4.58 (s, 2H), 7.29–7.41(m, 5H), 7.68 (m, 2H), 7.78 (m, 1H), 7.99 (m, 2H). ^{19}F NMR ($CDCl_3$, 282MHz): δ –101.7 (dt, *J* = 230, 19 Hz, 1F), –102.3 (dt, *J* = 230, 19 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100MHz): δ 33.6 (t, *J* = 19Hz), 64.8 (t, *J* = 2Hz), 73.3, 73.4, 123.9 (t, *J* = 285 Hz), 127.8, 127.9, 128.5, 129.3, 130.8, 132.0, 135.4, 137.5. MS(EI, *m/z*): 356(M^+, 0.8), 235(3.6), 143(21.0), 125(15.2), 107(10.4), 91(100.0). HRMS(MALDI): *m/z* calcd. for $C_{17}H_{18}O_4SF_2Na^{+1}$ ($M+Na^+$) 379.0786, found 379.0796. IR(film): 3565, 3440, 2919, 1449, 1334, 1162.



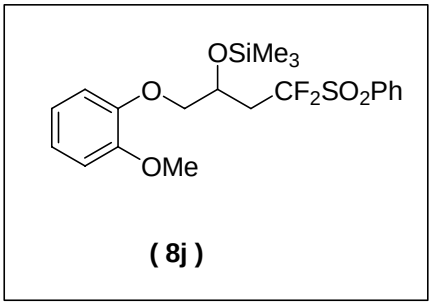
(8h)

4,4-Difluoro-1-phenoxy-4-(phenylsulfonyl)butan-2-ol **(8h)**
White solid , m.p. 43–45°C. ^{1}H NMR ($CDCl_3$, 300MHz): δ 2.65–2.82 (m, 3H), 4.00(dd, *J* = 9, 5.6 Hz, 1H), 4.06(dd, *J* = 9, 4.5 Hz, 1H), 4.55 (m, 1H), 6.88–7.03(m, 3H), 7.24–7.34(m, 2H), 7.64 (t, *J* = 7.9 Hz, 2H), 7.78 (m, 1H), 8.00 (d, *J* = 7.9 Hz, 2H). ^{19}F NMR ($CDCl_3$, 282MHz): δ –100.9 (dt, *J* = 230, 18 Hz, 1F), –101.1 (dt, *J* = 230, 18 Hz, 1F). ^{13}C NMR ($CDCl_3$, 125MHz): δ 33.8 (t, *J* = 19 Hz), 64.6, 71.0, 114.6, 121.4, 123.8 (t, *J* = 285 Hz), 126.6, 129.4, 129.5, 130.8, 131.83, 135.5. MS(EI, *m/z*): 342(M^+, 4.0), 249(4.8), 235(5.0), 143(61.6), 125(42.8), 107(31.3), 91(100.0), 77(59.0). HRMS(EI): *m/z* calcd. for $C_{16}H_{16}O_4F_2S$ (M^+) 342.0737, found 342.0742. IR(film): 3542, 3067, 2934, 1599, 1587, 1497, 1449, 1336, 1244, 1162.



(8i)

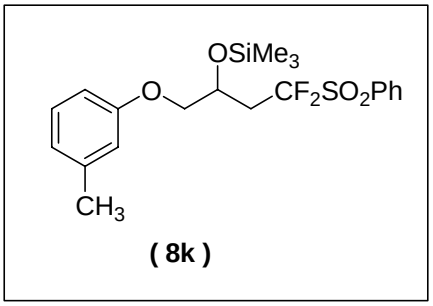
4,4-Difluoro-1-(4-methoxyphenoxy)-4-(phenylsulfonyl)butan-2-ol **(8i)**
White solid , m.p. 60–61°C. ^{1}H NMR ($CDCl_3$, 300MHz): δ 2.70 (m, 2H), 2.81 (d, *J* = 5 Hz, 1H), 3.76 (s, 3H), 3.96(m, 2H), 4.51 (m, 1H), 6.84(s, 4H), 7.62 (t, *J* = 7.9 Hz, 2H), 7.77 (m, 1H), 8.00 (d, *J* = 7.9 Hz, 2H). ^{19}F NMR ($CDCl_3$, 282MHz): δ –101.1 (ddd, *J* = 230, 18, 16 Hz, 1F), –101.3 (ddd, *J* = 230, 18, 16 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100MHz): δ 33.8 (t, *J* = 19 Hz), 55.7, 64.6, 71.8, 114.7, 115.7, 121.4, 123.8 (t, *J* = 285 Hz), 129.4, 130.8, 131.9, 135.5, 152.3, 154.4. MS(EI, *m/z*): 372(M^+, 2.5), 370(20.9), 248(8.3), 227(4.2), 143(25.5), 124(100.0), 109(39.7). EA calcd. for $C_{17}H_{18}F_2O_5S$: C, 54.83; H, 4.87; found C, 54.96; H, 4.78. IR(KBr): 3564, 2929, 1514, 1449, 1336, 1241, 1169.



(8j)

(4,4-difluoro-1-(2-methoxyphenoxy)-4-(phenylsulfonyl)butan-2-yloxy)trimethylsilane **(8j)**
White solid , m.p. 75–76°C. ^{1}H NMR ($CDCl_3$, 300MHz): δ 0.13(s, 9H), 2.56 (m, 1H), 2.87 (m, 1H), 3.84 (s, 3H), 3.91(dd, *J* = 9.6, 5.6 Hz, 1H), 3.99(dd, *J* = 9.6, 5.6 Hz, 1H), 4.56 (m, 1H), 6.88–7.00(m, 4H), 7.62 (t, *J* = 7.9 Hz, 2H), 7.76 (t, *J* = 7.3 Hz, 1H), 8.00 (d, *J* = 7.9 Hz, 2H). ^{19}F NMR ($CDCl_3$, 282MHz): δ –

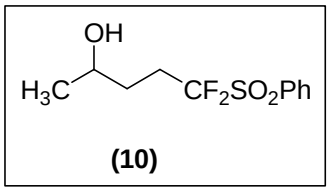
101.0 (ddd, *J* = 228, 30.0, 9.0 Hz, 1F), –103.7 (ddd, *J* = 228, 28.5, 8.0 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100MHz): δ –0.0, 33.8 (t, *J* = 18.5 Hz), 55.7, 65.6, 73.2, 112.3, 114.8, 120.8, 122.1, 124.1 (t, *J* = 285 Hz), 129.3, 130.8, 132.3, 148.1, 150.0. MS(EI, *m/z*): 445(M+1, 12.8), 320(4.0), 214(53.2), 195(27.8), 180(48.0), 164(40.1), 135(55.1), 125(100.0). EA calcd. for $C_{20}H_{26}F_2O_5SSi$: C, 54.03; H, 5.89; found C, 54.38; H, 5.93. IR(KBr) 2976, 2897, 1591, 1508, 1466, 1451, 1381, 1349, 1252.



(8k)

(4,4-Difluoro-4-(phenylsulfonyl)-1-(m-tolyloxy)butan-2-yloxy)trimethylsilane **(8k)**
White solid , m.p. 91–92°C. ^1H NMR ($CDCl_3$, 300MHz): δ 0.13(s, 9H), 2.13(s, 3H), 2.44–2.90 (m, 2H), 3.89 (m, 2H), 4.51 (m, 1H), 6.63–6.84(m, 3H), 7.16(t, *J* = 8.1 Hz, 1H), 7.64 (t, *J* = 7.9 Hz, 2H), 7.80 (t, *J* = 7.3 Hz, 1H), 8.00 (d, *J* = 7.9 Hz, 2H). ^{19}F NMR ($CDCl_3$, 282MHz): δ –101.0 (ddd, *J* = 228, 28.8, 8.0 Hz, 1F), –103.7 (ddd, *J* = 228, 27.5, 8.1 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100MHz): δ 0.1, 21.5, 33.8 (t, *J* = 18.6 Hz), 65.5, 71.4, 111.4, 115.3, 122.0, 124.0 (t, *J* = 285 Hz), 129.2, 129.3, 130.8, 132.2, 135.3, 139.6. MS(EI, *m/z*): 429(M+1, 5.9), 214(36.1), 198(23.8), 165(73.6), 135(34.6), 125(47.6), 73(100.0). EA calcd. for $C_{20}H_{26}F_2O_4SSi$: C, 56.05; H, 6.11; found C, 56.36; H, 6.16. IR(KBr) 2951, 1600, 1494, 1450, 1342, 1244, 1163.

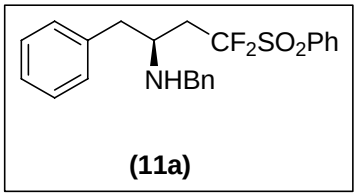
3. Nucleophilic difluoromethylation of 1,3-cyclic sulfate using difluoromethyl phenyl sulfone: Under N_2 atmosphere, into a Schlenk flask containing 1,3-cyclic sulfate (**9**) (1.0 mmol) and $PhSO_2CF_2H$ (**1**, 384 mg, 2.0 mmol) in 5 ml THF and 0.5 ml HMPA at –78 °C, was added a THF solution (2.2 mL) of $(TMS)_2Nli$ (LHMDS, 1.0 M, 2.2 mmol) in 10 min. The reaction mixture was then stirred at this tempetature for 8 hours, followed by adding a 20% aqueous sulfuric acid (5 mL) at this temperature. The mixture was stired at room tempeture for 2 hours. Then the solution mixture was extracted with Et_2O (10 mL x 3) , and the combined organic phase was washed with saturated $NaHCO_3$ solution then dried over $MgSO_4$. After the removal of the solvents under vacuum, the crude product was further purified by silica gel column chromatography to give **10 i**n 63% yield (166 mg).



(10)

5,5-Difluoro-5-(phenylsulfonyl)pentan-2-ol **(10)**
Colorless liquid. ^{1}H NMR ($CDCl_3$, 300MHz): δ 1.24 (d, *J* = 6.3 Hz, 3H), 1.80 (m, 2H), 2.03 (s, 1H), 2.28–2.73 (m, 2H), 3.86 (m, 1H), 7.62 (m, 2H), 7.76 (m, 1H), 7.99 (d, *J* = 7.7 Hz, 2H). ^{19}F NMR ($CDCl_3$, 282MHz): δ –103.2 (t, *J* = 18 Hz, 2F). ^{13}C NMR ($CDCl_3$, 75MHz): δ 23.5, 26.0 (t, *J* = 21 Hz), 30.0 (t, *J* = 3 Hz), 66.7, 124.7 (t, *J* = 285 Hz), 129.3, 130.6, 132.4, 135.3. MS(EI, *m/z* %): 247 (M^+–OH, 6.2), 143(20.8), 125(20.6), 103(33.1), 83(34.5), 77(100.0). HRMS(EI): *m/z* calcd. for $C_{10}H_{11}O_3F_2S$ (M^+–CH_3) 249.0397, found 249.0399. IR(film): 3545, 3402, 2971, 2932, 1449, 1340, 1140.

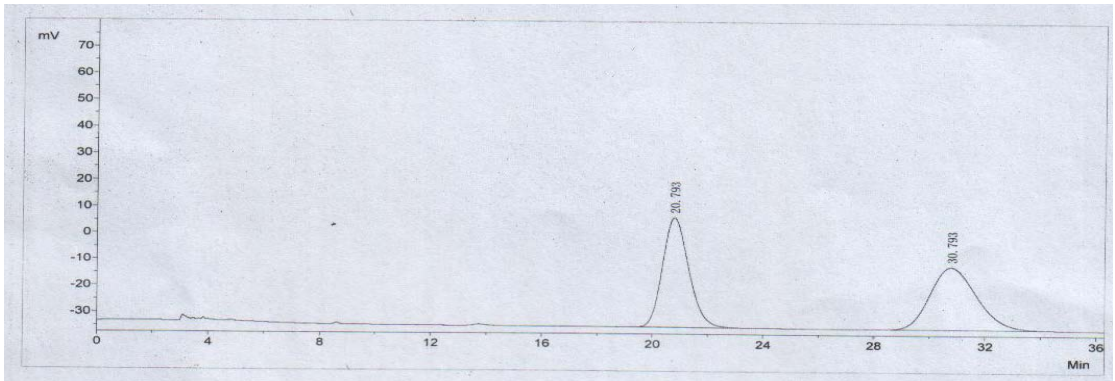
4. Typical procedure for nucleophilic difluoromethylation of 1,2-cyclic sulfamidate using difluoromethyl phenyl sulfone: Under N_2 atmosphere, into a Schlenk flask containing 1,2-cyclic sulfamidate (**3a**) (1.0 mmol) and $PhSO_2CF_2H$ (211 mg, 1.1 mmol) in 5 ml THF and 0.5 ml HMPA at –78 ^{o}C, was added a THF solution (1.2 mL) of $(TMS)_2NLi$ (LHMDS, 1.0 M, 1.2 mmol) in 10 minutes. The reaction mixture was then stirred at this tempetature for 30 min, followed by adding a 20% sulfuric acid solution (5 mL) at this temperature. The mixture was stired at room tempeture for 1 h. The aqueous phase was adjusted to pH 10-12 using NaOH aq solutions. The product was extracted with Et_2O (10 mL x 3), and the combined organic phase was washed with saturated $NaHCO_3$ solution then dried over Na_2SO_4. After the removal of volatile solvents under vacuum, the crude product was further purified by silica gel column chromatography to give **11a** as colorless oil, 399 mg (96% yield).



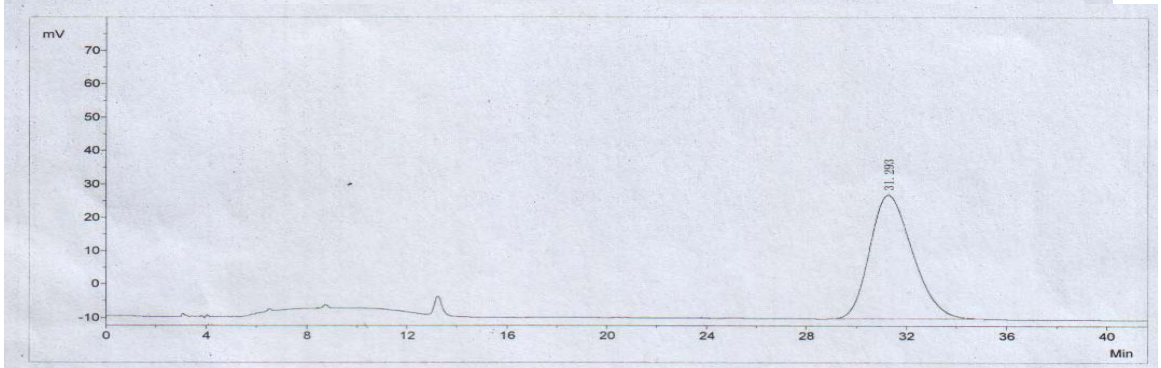
(11a)

(S)-N-benzyl-4,4-difluoro-1-phenyl-4-(phenylsulfonyl)butan-2-amine **(11a)**
Colorless oil. $[\alpha]^{25}$ –7.5(c=1.15, $CHCl_3$).

Chiral chromatography of **11a** on a Chiralcel® OJ-H coloum (t_R 31.29 min, hexane : *i*-propanol = 70:30, 0.6 mL/min) demonstrated > 99.5% ee.

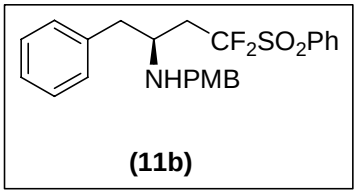


No.	R.Time	PeakHeight	PeakArea	PerCent
1	20.793	41308.2	2713059.5	49.8283
2	30.793	23454.1	2731760.6	50.1717
Total		64762.3	5444820.1	100.0000



No.	R.Time	PeakHeight	PeakArea	PerCent
1	31.293	37119.7	4411550.8	100.0000
Total		37119.7	4411550.8	100.0000

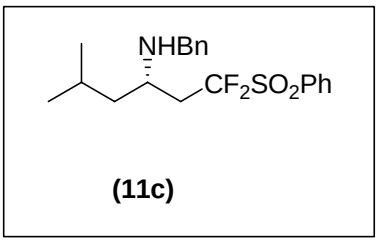
^{1}H NMR ($CDCl_3$, 300MHz): δ 1.52 (br, s, 1H), 2.35–2.67 (m, 2H), 2.78 (dd, *J* = 13.5, 8.0 Hz, 1H), 2.95 (dd, *J* = 13.5, 5.6 Hz, 1H), 3.37 (m, 1H), 3.70 (d , *J* = 13 Hz, 1H), 3.81 (d , *J* = 13 Hz, 1H), 7.12–7.18 (m, 4H), 7.21–7.33 (m, 6H), 7.61 (t, *J* = 7.9 Hz, 2H), 7.76 (t, *J* = 7.3 Hz, 1H), 7.97 (d, *J* = 7.9 Hz, 2H). ^{19}F NMR ($CDCl_3$, 282MHz): δ –101.2 (td, *J* = 19.5, 3.7 Hz, 2F). ^{13}C NMR ($CDCl_3$, 125MHz): δ 33.2 (t, *J* = 19 Hz), 41.2, 50.9, 52.8, 124.5 (t, *J* = 285 Hz), 126.6, 126.9, 128.0, 128.3, 128.6, 129.26, 129.31, 130.8, 132.3, 135.3, 137.4, 139.8. MS(EI, *m/z*): 324 (M–$PhCH_2$, 9.0), 210(1.6), 182 (38.0), 91(100.0). HRMS(MALDI): *m/z* calcd. for $C_{23}H_{24}NO_2SF_2$ ($M+H^+$) 416.1490, found 416.1496. IR(film): 3063, 3027, 2928, 1584, 1495, 1449, 1340, 1160.



(11b)

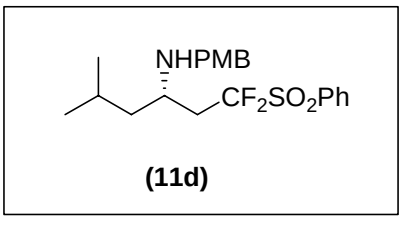
(S)-N-(4-methoxybenzyl)-4,4-difluoro-1-phenyl-4-(phenylsulfonyl)butan-2-amine **(11b)**

Colorless oil. [α]^{25} –7.3(c=1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300MHz): δ 1.50 (br, s, 1H), 2.51 (m, 2H), 2.73 (dd, *J* = 14, 7.9 Hz, 1H), 2.95 (dd, *J* = 14, 5.3 Hz, 1H), 3.35 (m, 1H), 3.63 (d , *J* = 12.7 Hz, 1H), 3.75 (d , *J* = 12.7 Hz, 1H), 3.77 (s, 1H), 6.78 (m, 2H), 7.06 (m, 2H), 7.14 (m, 2H), 7.19–7.34 (m, 3H), 7.61 (t, *J* = 7.9 Hz, 2H), 7.75 (m, 1H), 7.97 (d, *J* = 7.5 Hz, 2H). ^{19}F NMR ($CDCl_3$, 282MHz): δ –101.2 (t, *J* = 17.9 Hz, 2F). ^{13}C NMR ($CDCl_3$, 100MHz): δ 33.2 (t, *J* = 18.7 Hz), 41.2, 50.3, 52.6, 55.2, 113.7, 124.5 (t, *J* = 285 Hz), 126.6, 128.6, 129.1, 129.2, 129.3, 130.8, 131.9, 132.3, 135.3, 137.8, 158.6. MS(ESI, *m/z*): 446.2(M+H$^+$, 100.0). EA calcd. for $C_{24}H_{25}F_2NO_3S$: C, 64.70; H, 5.66; N, 3.14; Found C, 64.80; H, 5.65; N, 2.98. IR(film): 3063, 3026, 2835, 1612, 1512, 1448, 1335, 1247, 1163.



(11c)

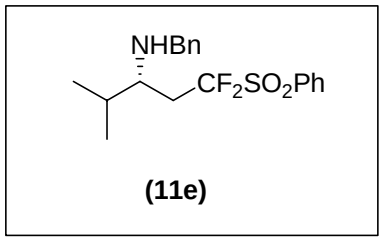
(S)-N-benzyl-1,1-difluoro-5-methyl-1-(phenylsulfonyl)hexan-3-amine **(11c)**
Colorless oil. [α]^{25} –6.6(c=1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300MHz): δ 0.83 (d, *J* = 6.5 Hz, 3H), 0.89 (d, *J* = 6.5 Hz, 3H), 1.21–1.58 (m, 3H), 1.72 (m, 1H), 2.27–2.73 (m, 2H), 3.12 (m, 1H), 3.72 (d , *J* = 12.7 Hz, 1H), 3.81 (d , *J* = 12.7 Hz, 1H), 7.18–7.36 (m, 5H), 7.62 (t, *J* = 8.0 Hz, 2H),7.76 (m, 1H), 7.99 (d, *J* = 7.5 Hz, 2H). ^{19}F NMR ($CDCl_3$, 282MHz): δ –101.7 (t, *J* = 15 Hz, 1F), –101.8 (t, *J* = 15 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100MHz): δ 22.1, 23.0, 24.7, 33.4 (t, *J* = 18.5 Hz), 44.9, 49.7, 50.4, 124.7 (t, *J* = 285 Hz), 127.0, 127.6, 128.2, 128.3, 129.2, 130.7, 132.2, 135.2, 140.2. MS(ESI, *m/z*): 382.2(M+H$^+$, 100.0). EA calcd. for $C_{20}H_{25}F_2NO_2S$: C, 62.97; H, 6.61; N, 3.67; Found C, 62.99; H, 6.53; N, 3.67. IR(film): 3063, 3027, 2956, 2869, 1449, 1338, 1160.



(11d)

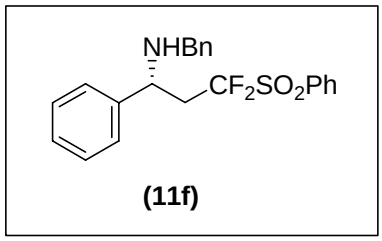
(S)-N-(4-methoxybenzyl)-1,1-difluoro-5-methyl-1-(phenylsulfonyl)hexan-3-amine **(11d)**
White solid, m.p. 40–41°C. [α]^{25}–6.1(c=1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300MHz): δ 0.84 (d, *J* = 6.8 Hz, 3H), 0.89 (d, *J* = 6.8 Hz, 3H), 1.23–1.56 (m, 3H), 1.72 (m, 1H), 2.28–2.72 (m, 2H), 3.15 (m, 1H), 3.65 (d , *J* = 12.9 Hz, 1H), 3.95 (d , *J* = 12.9 Hz, 1H), 3.79 (s, 3H), 6.84 (d, *J* = 8.7 Hz, 2H), 7.22 (d, *J* = 8.7 Hz, 2H), 7.62 (t, *J* = 7.9 Hz, 2H), 7.77 (t, *J* = 7.3 Hz, 1H), 7.99 (d, *J* = 7.9 Hz, 2H). ^{19}F NMR ($CDCl_3$, 282MHz): δ –101.68 (dd, *J* = 17.7, 9.2 Hz, 1F), –101.76 (dd, *J* = 17.7, 9.2 Hz, 1F). ^{13}C NMR ($CDCl_3$,

100MHz): δ 22.1, 23.1, 24.7, 33.4 (t, *J* = 18.4 Hz), 45.0, 49.6, 49.9, 55.2, 113.8, 124.7 (t, *J* = 285 Hz), 129.2, 129.3, 130.8, 132.30, 132.33, 135.2, 158.7. MS(ESI, *m/z*): 412.2($M+H^+$, 100.0). EA calcd. for $C_{21}H_{27}F_2NO_3S$: C, 61.29; H, 6.61; N, 3.40; Found C, 61.04; H, 6.41; N, 3.19. IR(film): 3065, 3025, 2956, 2689, 2837, 1612, 1585, 1512, 1466, 1449, 1339.



(11e)

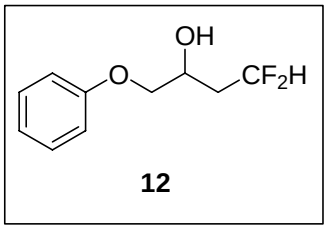
(R)-N-benzyl-1,1-difluoro-4-methyl-1-(phenylsulfonyl)pentan-3-amine **(11e)**
Colorless oil. $[\alpha]^{25}$ 23.1(c=1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 300MHz): δ 0.92 (d, *J* = 3.0 Hz, 3H), 0.94 (d, *J* = 3.0 Hz, 3H), 1.40 (br, s, 1H), 1.97 (m, 1H), 2.34–2.64 (m, 2H), 2.96 (m, 1H), 3.74 (d, *J* = 12.8 Hz, 1H), 3.79 (d, *J* = 12.8 Hz, 1H), 7.18–7.36 (m, 5H), 7.62 (m, 2H),7.76 (m, 1H), 7.99 (d, *J* = 7.8 Hz, 2H). ^{19}F NMR ($CDCl_3$, 282MHz): δ –101.4 (ddd, *J* = 226, 29.6, 11.6 Hz, 1F), –102.5 (ddd, *J* = 226, 18.7, 10.2 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100MHz): δ 17.4, 17.9, 30.2 (t, *J* = 19 Hz), 30.7, 51.6, 56.5, 125.0 (t, *J* = 285 Hz), 16.9, 128.1, 128.3, 129.2, 130.8, 132.3, 135.2, 140.4. MS(ESI, *m/z*): 368.2($M+H^+$, 100.0). HRMS (MALDI): *m/z* calcd. for $C_{19}H_{24}NO_2SF_2(M+H^+)$ 368.1490, found 368.1505. IR(film): 3065, 3028, 2960, 1449, 1338, 1164.



(11f)

(R)-N-benzyl-3,3-difluoro-1-phenyl-3-(phenylsulfonyl)propan-1-amine **(11f)**
White solid, mp 86–87°C. $[\alpha]^{25}$ 1.3(c=0.95, $CHCl_3$); ^1H NMR ($CDCl_3$, 300MHz): δ 1.62 (br, s, 1H), 2.76 (m, 2H), 3.37 (m, 1H), 3.53 (d , *J* = 13.6 Hz, 1H), 3.63 (d , *J* = 13.6 Hz, 1H), 4.17 (t, *J* = 6.5 Hz, 1H), 7.17–7.42 (m, 10H), 7.60 (t, *J* = 7.9 Hz, 2H), 7.75 (t, *J* = 7.3 Hz, 1H), 7.95 (d, *J* = 7.9 Hz, 2H). ^{19}F NMR ($CDCl_3$, 282MHz): δ –100.8 (ddd, *J* = 228, 27.5, 10.4 Hz, 1F), –102.1 (ddd, *J* = 228, 27.0, 11.5 Hz, 1F). ^{13}C NMR ($CDCl_3$, 125MHz): δ 37.1 (t, *J* = 18.5 Hz), 51.3, 56.3, 124.0 (t, *J* = 285 Hz), 127.0, 127.1, 127.8, 128.0, 128.4, 128.8, 129.3, 130.8, 132.2, 135.3, 139.9, 142.2. MS(ESI, *m/z*): 402.2($M+H^+$, 100.0), 446.2($M+Na^+$, 15.0). EA calcd. for $C_{22}H_{21}F_2NO_2S$: C, 65.82; H, 5.27; N, 3.49; Found C, 65.84; H, 5.34; N, 3.33. IR(film): 3053, 3025, 2844, 1492, 1449, 1338, 1163.

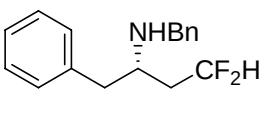
5. Reductive desulfonylation of 8h: Into a 50-mL Schlenk flask containing sulfone compound **8h (**171 mg, 0.5 mmol**)** in 5 mL DMF at room temperature was added 3 mL HOAc-NaOAc (1:1) buffer solution (8 mol/L). Magnesium turnings (192mg, 8 mmol) was added in portions. The reaction mixture was stirred at room temperature for 3 h, followed by adding 30mL water. The solution mixture was extracted with Et_2O (20 mL x 3), and the combined organic phase was washed with saturated $NaHCO_3$ solution and brine, then dried over $MgSO_4$. After the removal of ethyl ether, the crude product was purified by silica gel column chromatography using petroleum ether-ethyl acetate(8 : 1) as eluent to give product **12** as a white solid (84 mg , 83 % yield).



12

4,4-Difluoro-1-phenoxybutan-2-ol **(12)**
White solid , m.p. 49–50°C. ^{1}H NMR ($CDCl_3$, 300MHz): δ 1.99–2.29 (m, 2H), 2.46 (br, d, *J* = 3.7 Hz, 1H), 3.90 (dd, *J* = 9.3, 7.2 Hz, 1H), 4.02 (dd, *J* = 9.3, 3.4 Hz, 1H), 4.28 (m, 1H), 6.11 (tdd, *J* = 57, 6.1, 3.8 Hz, 1H), 6.91 (d, *J* = 7.9 Hz, 2H), 6.99 (t, *J* = 7.2 Hz, 1H), 7.27–7.34(m, 2H). ^{19}F NMR ($CDCl_3$, 282MHz): δ –116.0 (ddt, *J* = 285, 58, 13 Hz, 1F), –101.1 (dddd, *J* = 285, 58, 23, 16 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100MHz): δ 37.8 (t, *J* = 22 Hz), 65.5 (dd, *J* = 8.4, 4.4 Hz), 71.5, 114.6, 115.8 (t, *J* = 238 Hz), 121.5, 129.6, 158.2. MS(EI, *m/z*): 202(M^+, 12.5), 119(4.5), 107(14.0), 94(100.0), 77(33.7). HRMS(EI): *m/z* calcd. for $C_{10}H_{12}O_2F_2$ (M^+) 202.0805, found 202.0806. IR(film): 3415, 2933, 1600, 1497, 1243, 1105.

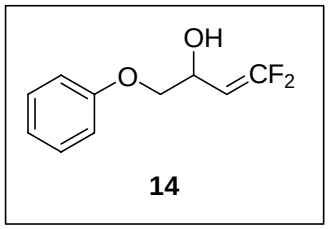
6. Reductive desulfonylation of 11a: Into a 50-mL Schlenk flask containing sulfone compound **11a (**160 mg, 0.385 mmol**)** in 4 mL DMF at room temperature was added 2.5 mL HOAc-NaOAc (1:1) buffer solution (8 mol/L). Magnesium turnings (166 mg, 6 mmol) was added in portions. The reaction mixture was stirred at room temperature for 3 h, followed by adding 30mL water and adjusted to pH 10-12 using NaOH aqueous solution. The solution mixture was extracted with Et_2O (20 mL x 3), and the combined organic phase was washed with brine, then dried over Na_2SO_4. After the removal of ethyl ether, the crude product was purified by flash column chromatography using petroleum ether-ethyl acetate(5 : 1) as eluent to give product **13** 86 mg (81 % yield).



13

(S)-N-benzyl-4,4-difluoro-1-phenylbutan-2-amine **(13)**
Pale yellow oil. $[\alpha]^{25}$ 5.7(c=0.90, $CHCl_3$); ^1H NMR ($CDCl_3$, 300MHz): δ 1.43 (br, s, 1H), 1.72–2.07 (m, 2H), 2.77 (dd, *J* = 13.6, 6.7 Hz, 1H), 2.85 (dd, *J* = 13.6, 6.3 Hz, 1H), 3.07 (m, 1H), 3.77 (d , *J* = 13.2 Hz, 1H), 3.80 (d , *J* = 13.2 Hz, 1H), 6.01 (tdd, *J* = 54, 5.4, 3.7 Hz, 1H), 7.10–7.35 (m, 10H). ^{19}F NMR ($CDCl_3$, 282MHz): δ –115.3 (dt, *J* = 57, 17.4 Hz, 2F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 38.7 (t, *J* = 19 Hz), 40.6, 51.0, 53.4 (t, *J* = 5.4 Hz), 116.8 (t, *J* = 236 Hz), 126.6, 127.0, 128.0, 128.4, 128.6, 129.3, 138.0, 140.1. MS(EI, *m/z*): 276(M+1, 4.9), 184(22.5), 91(100.0). HRMS(EI): *m/z* calcd. for $C_{17}H_{19}NF_2$ (M^+) 275.1486, found 275.1477. IR(film): 3063, 3028, 2928, 2851, 1495, 1454, 1397, 1116.

7. Preparation of β-difluoromethylenated alcohol (14) with base-mediated α,β- elimination: Under an nitrogen atmosphere, into a Schlenk flask containing **8h** (171 mg, 0.5 mmol) in THF (4 mL) at 0°C, was added dropwise via a syringe LHMDS (1.0M in THF, 1.5 mL, 1.5 mmol). The reaction mixture was stirred at 0 °C to room temperature for 1 h, and the completion of the reaction was monitored by TLC. The reaction was then quenched by adding saturated NH_4Cl solution followed by extraction with Et_2O (15 mL x 3). The combined organic phase was dried over anhydrous Na_2SO_4, filtered, and the solvent was removed. The crude product was purified by a flash chromatography (PE : EA = 7:1) to give **14** as a colorless oil (82 mg, 82 % yield).

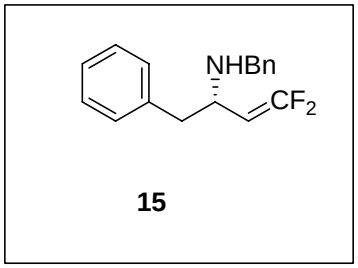


14

4,4-Difluoro-1-phenoxybut-3-en-2-ol **(14)**
Colorless oil. ^1H NMR ($CDCl_3$, 300MHz): δ 2.50 (br, d, *J* = 3.8 Hz, 1H), 3.92 (dd, *J* = 9.0, 7.0 Hz, 1H), 4.03 (dd, *J* = 9.0, 3.5 Hz, 1H), 4.51 (ddd, *J* = 18.8, 9.5, 7.9 Hz, 1H), 4.78 (m, 1H), 6.88–6.96 (m, 2H), 6.96–7.04 (m, 1H), 7.26–7.35 (m, 2H). ^{19}F NMR ($CDCl_3$, 282MHz): δ –84.6 (s, 1F), –84.7 (dd, *J* = 45, 36 Hz, 1F). ^{13}C NMR ($CDCl_3$, 125MHz): δ 64.1 (d, *J* = 6 Hz), 71.2 (d, *J* = 2 Hz), 78.8 (t, *J* = 18 Hz), 114.6, 121.5, 129.6, 157.2 (t, *J* = 288 Hz), 158.2. MS(EI, *m/z*): 200(M^+, 10.5), 108(58.2), 94(61.4), 77(100.0). HRMS(EI): *m/z* calcd. for $C_{10}H_{10}O_2F_2$ (M^+) 200.0649, found 202.0656. IR(film): 3398, 2930, 1750, 1600, 1589, 1497, 1290, 1245.

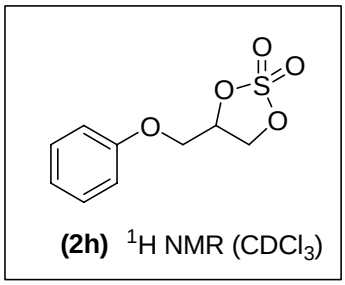
8. Preparation of β-difluoromethylenated amine (15) with base-mediated α,β- elimination: Under an nitrogen atmosphere, into a Schlenk flask containing **11a** (145 mg, 0.35 mmol) in THF (3 mL) at 0°C, was added dropwise via a syringe LHMDS (1.0M in THF, 1.4 mL, 1.4 mmol). The reaction mixture was

stirred at room temperature for 6 h, and the completion of the reaction was monitored by TLC. The reaction was then quenched by adding saturated NH_4Cl solution followed by extraction with Et_2O (15 mL x 3). The combined organic phase was dried over anhydrous Na_2SO_4, filtered, and the solvent was removed. The crude product was purified by a flash chromatography (PE : EA = 10:1) to give **15** 67 mg (70 % yield).

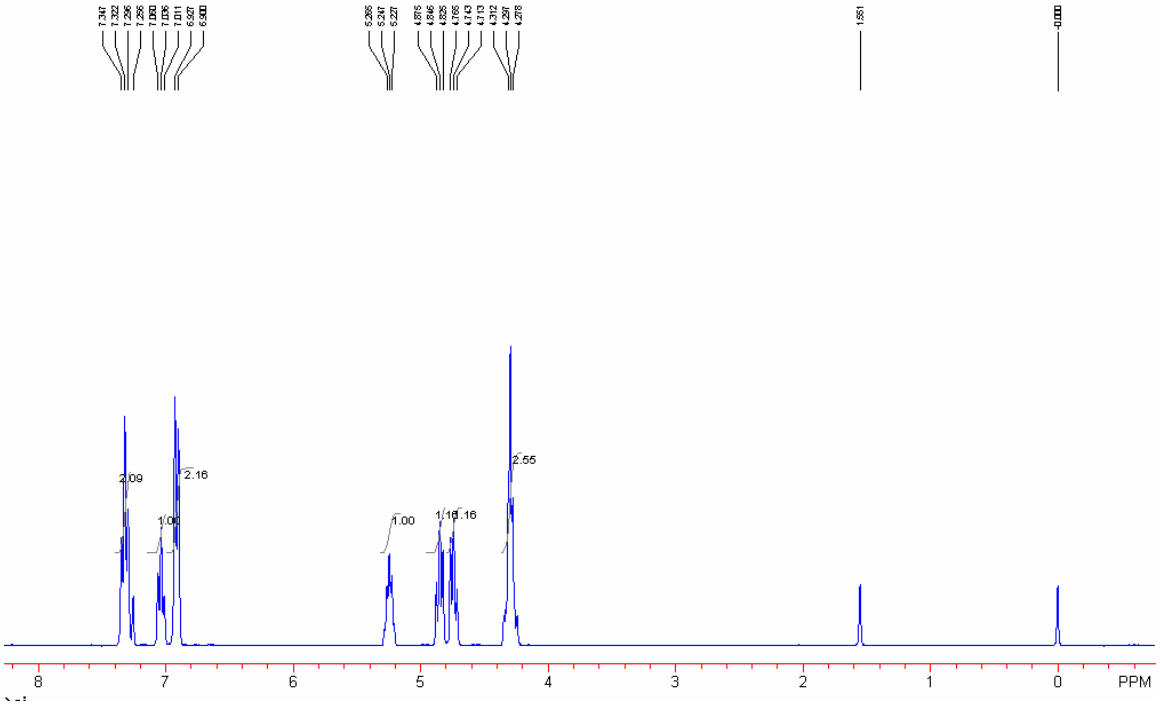


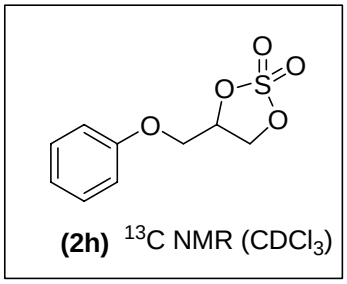
15

(S)-N-benzyl-4,4-difluoro-1-phenylbut-3-en-2-amine **(15)**
Pale yellow oil. $[\alpha]^{25}$–22.2(c=1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300MHz): δ 1.52 (br, s, 1H), 2.80 (d, *J* = 6.8 Hz, 2H), 3.60 (d , *J* = 13.3 Hz, 1H), 3.82 (d , *J* = 13.3 Hz, 1H), 3.55–3.65 (m, 1H), 4.15 (ddd, *J* = 25.3, 9.9, 2.7 Hz, 1H), 7.10–7.33 (m, 10H). ^{19}F NMR ($CDCl_3$, 282MHz): δ –86.5 (d, *J* = 44 Hz, 1F), –88.3 (dd, *J* = 44, 25 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 42.5, 51.3, 52.9 (d, *J* = 6 Hz), 81.5 (t, *J* = 18 Hz), 126.6, 126.9, 127.9, 128.4, 128.5, 129.3, 137.7, 140.0, 157.0 (t, *J* = 287 Hz). MS(EI, *m/z*): 182(M^+–Bn, 38.7), 91(100.0). HRMS(EI): *m/z* calcd. for $C_{10}H_{10}NF_2$ (M^+–Bn) 182.0781, found 182.0786. IR(film): 3063, 3028, 2928, 2850, 1741, 1496, 1454.

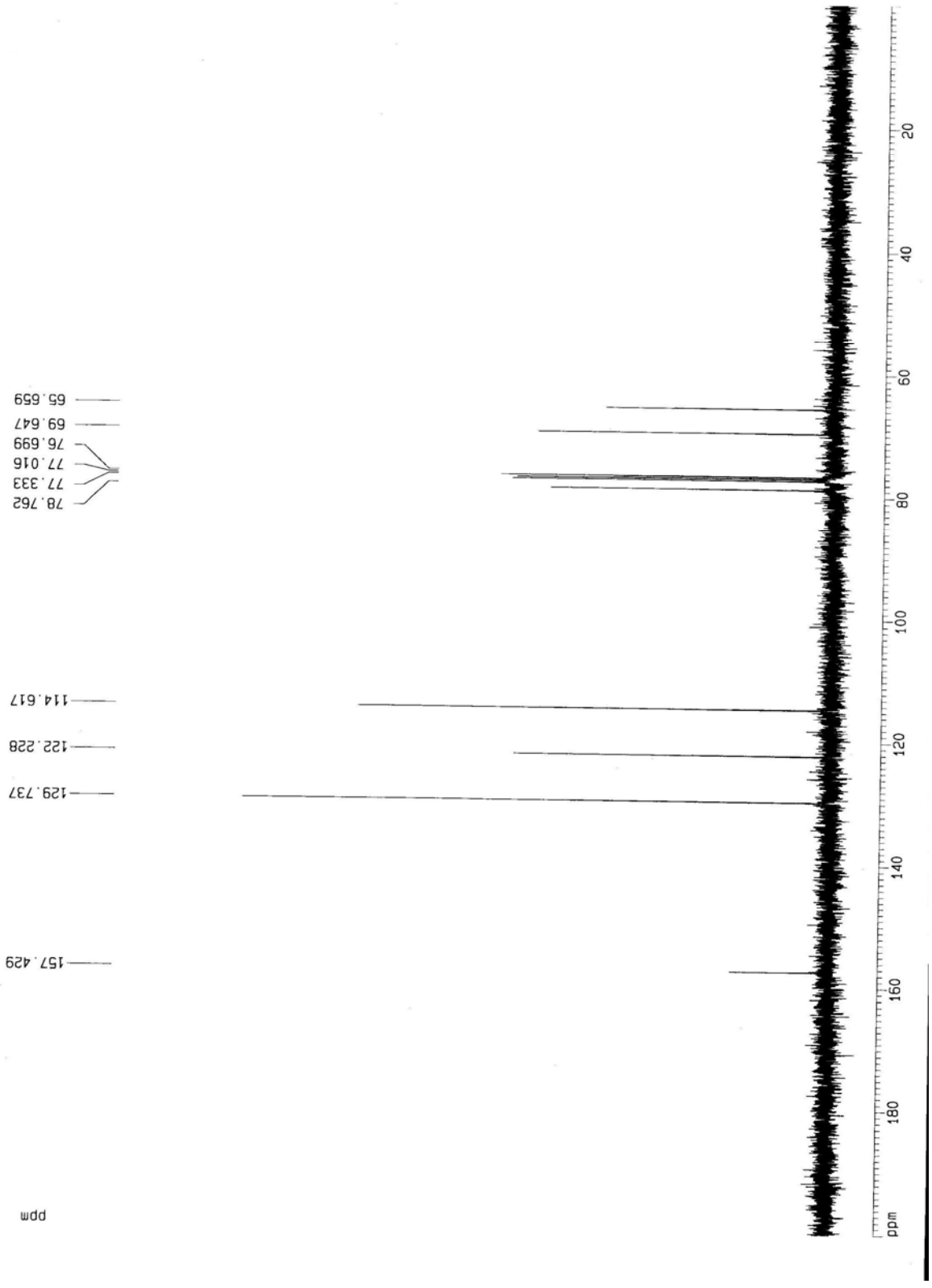


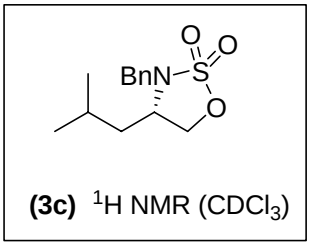
(2h) ^{1}H NMR ($CDCl_3$)



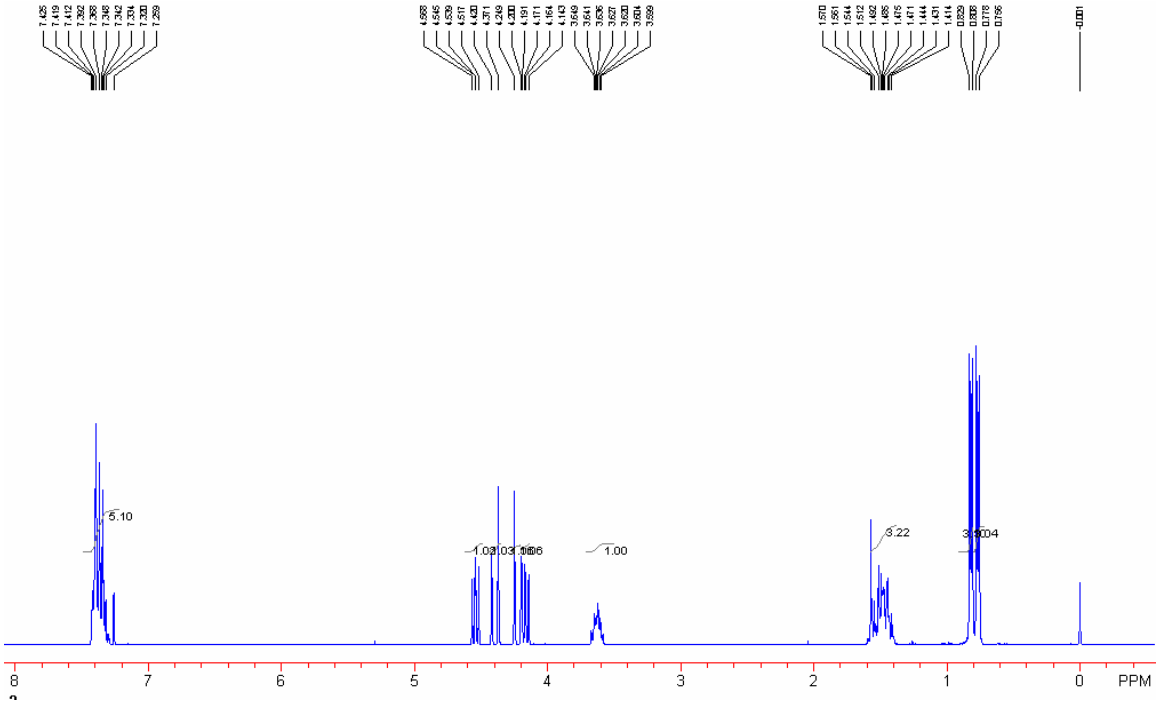


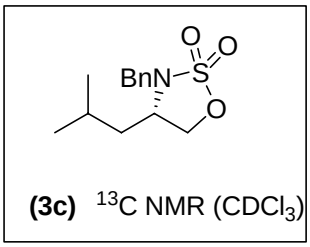
(2h) ^{13}C NMR ($CDCl_3$)



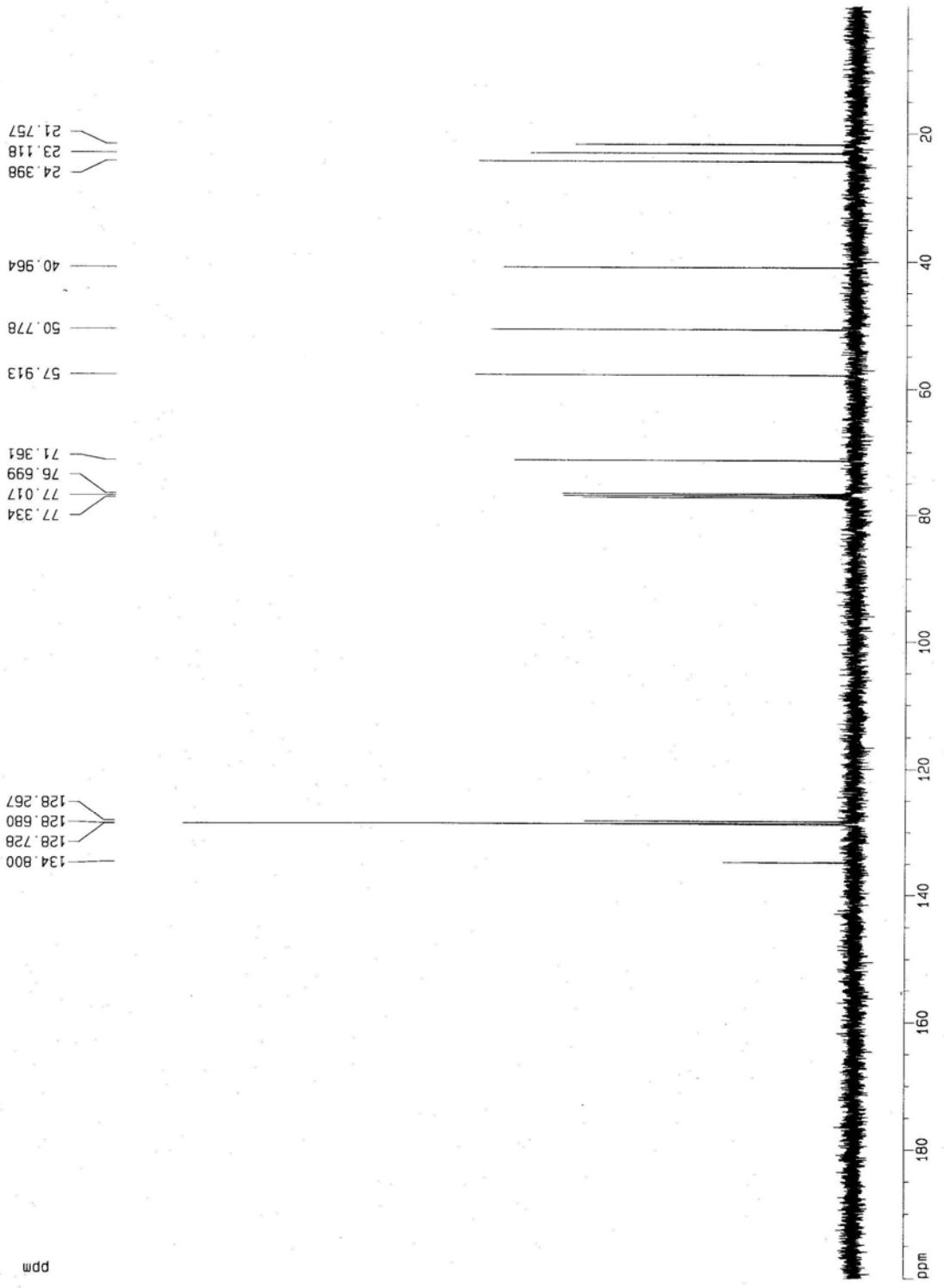


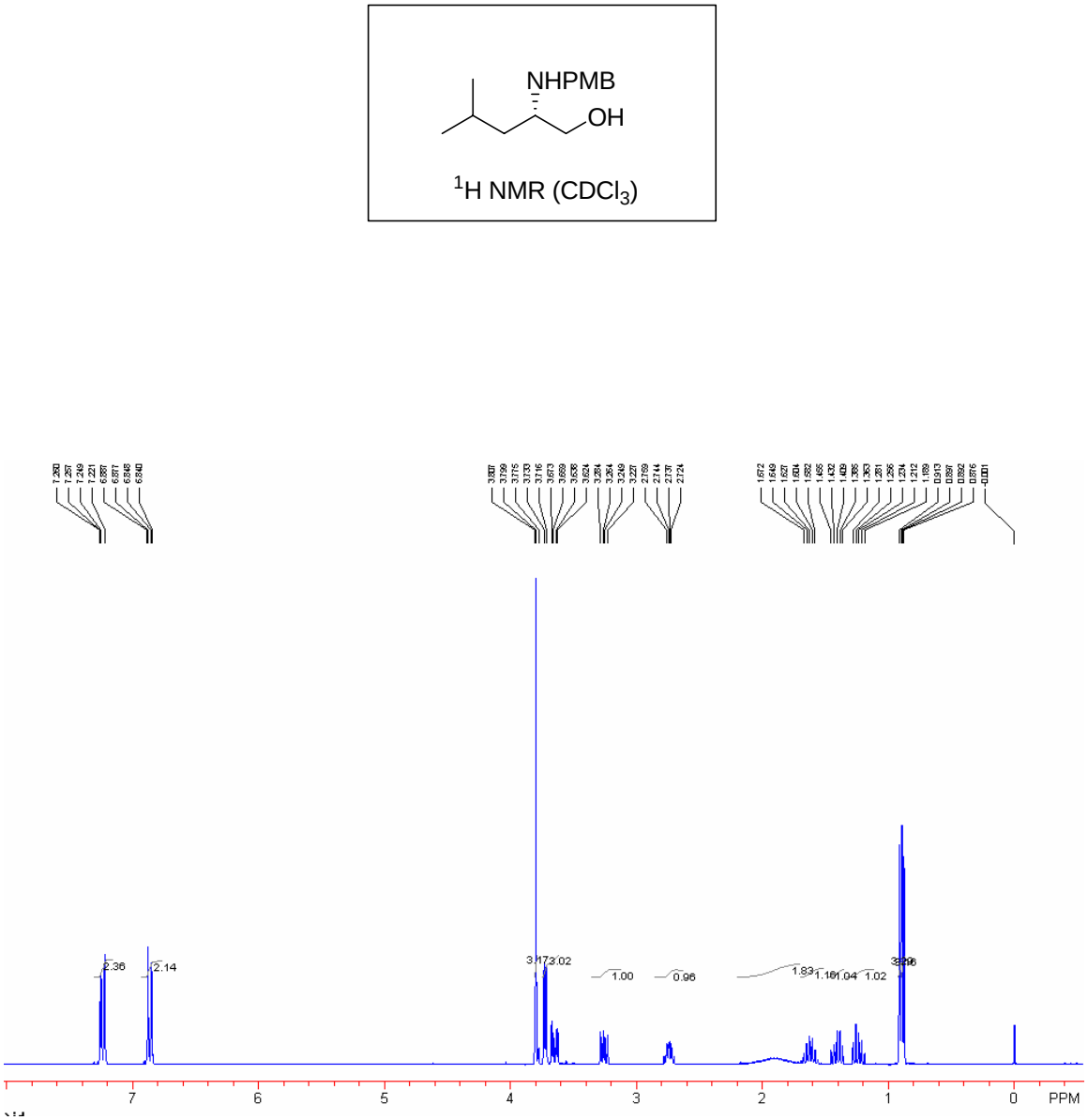
(3c) ^{1}H NMR ($CDCl_3$)

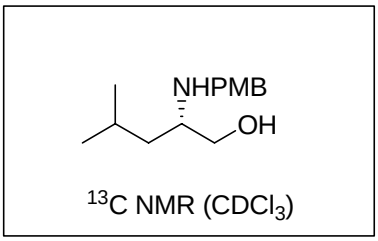




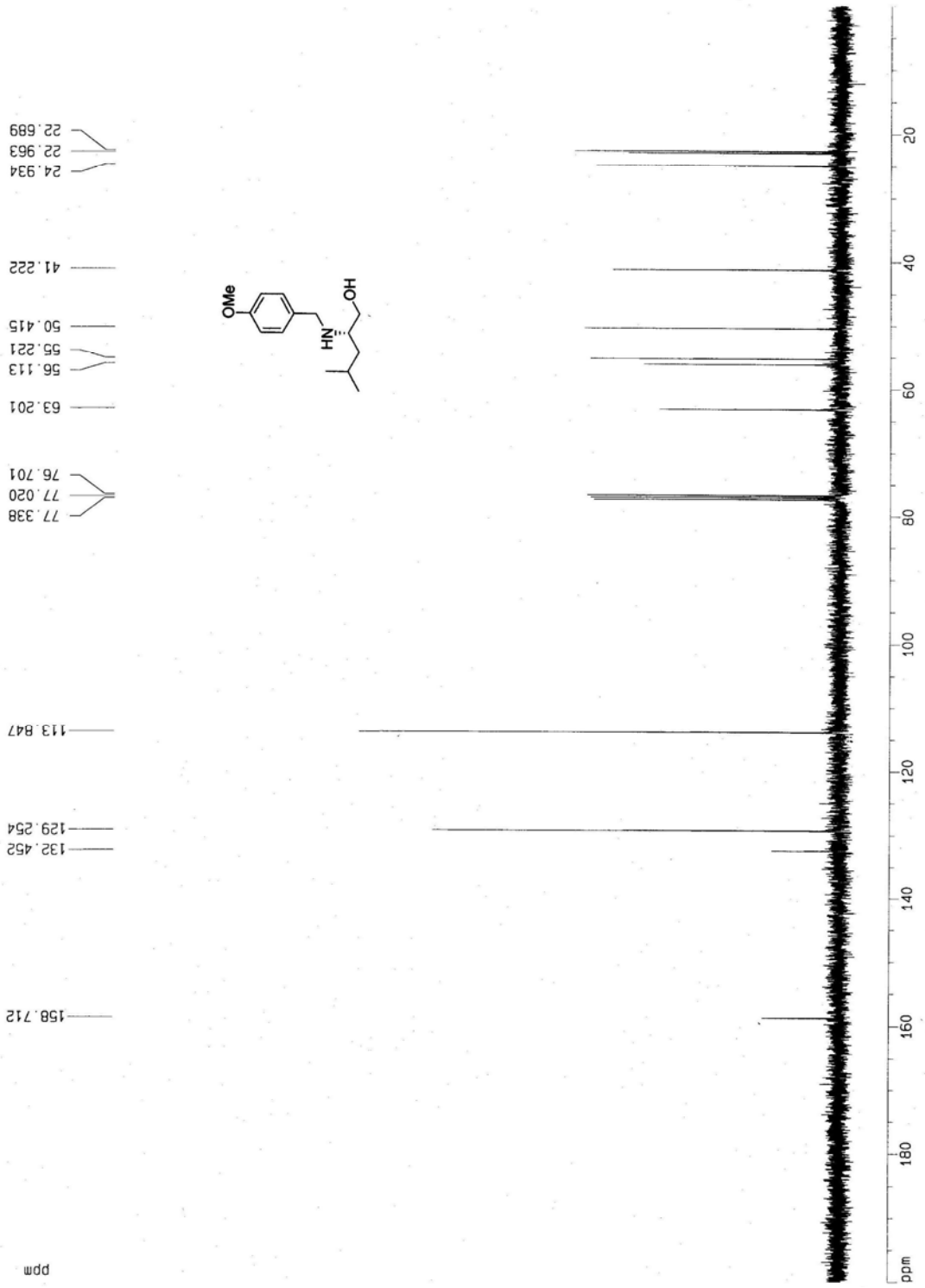
(3c) ^{13}C NMR ($CDCl_3$)

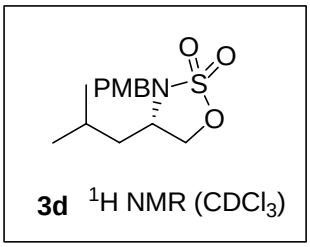



NHPMB
OH
^{1}H NMR ($CDCl_3$)
2.36
2.14
3.17
3.02
1.00
0.96
1.83
1.18
1.04
1.02
7
6
5
4
3
2
1
0
PPM

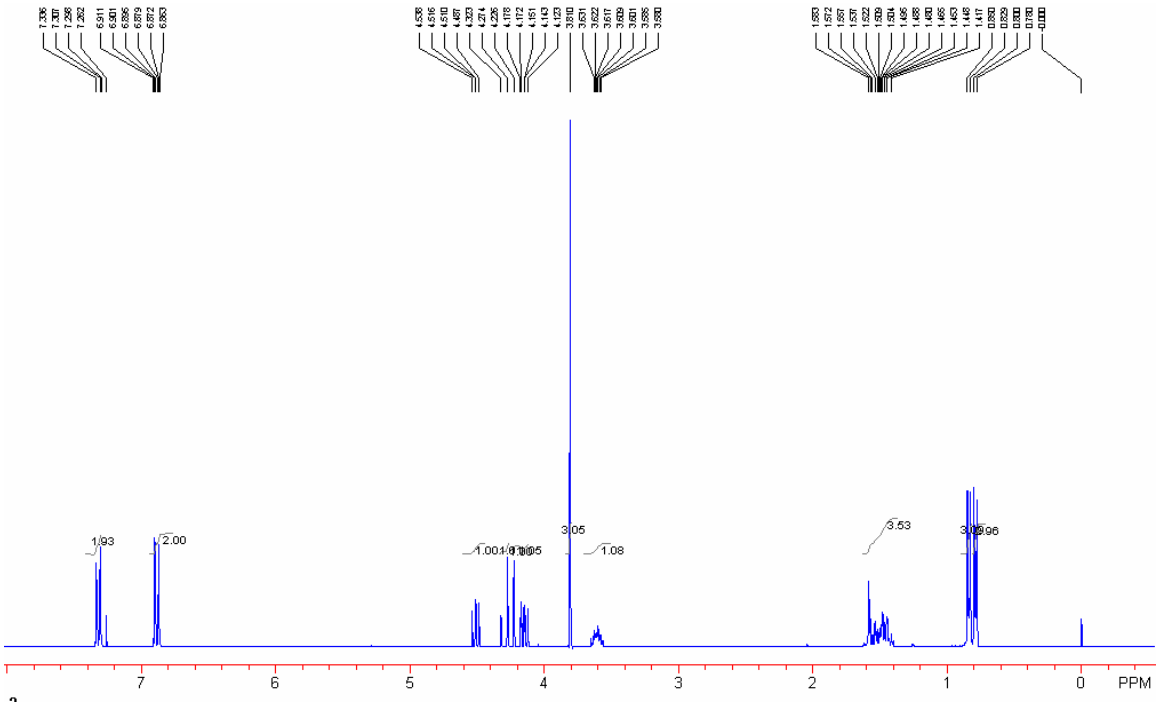


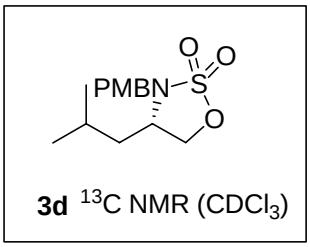
^{13}C NMR ($CDCl_3$)



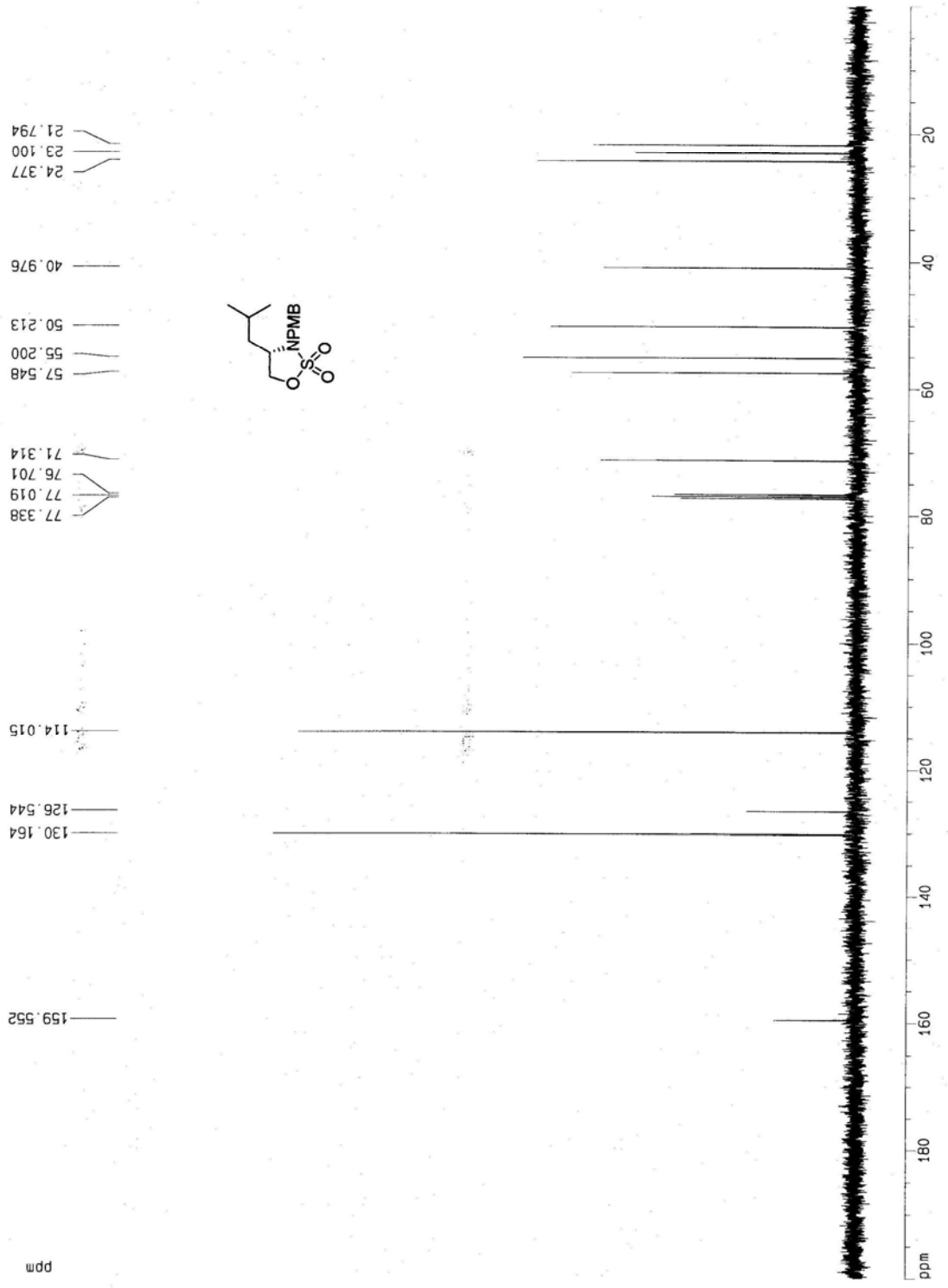


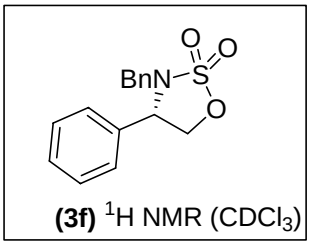
3d ^{1}H NMR ($CDCl_3$)



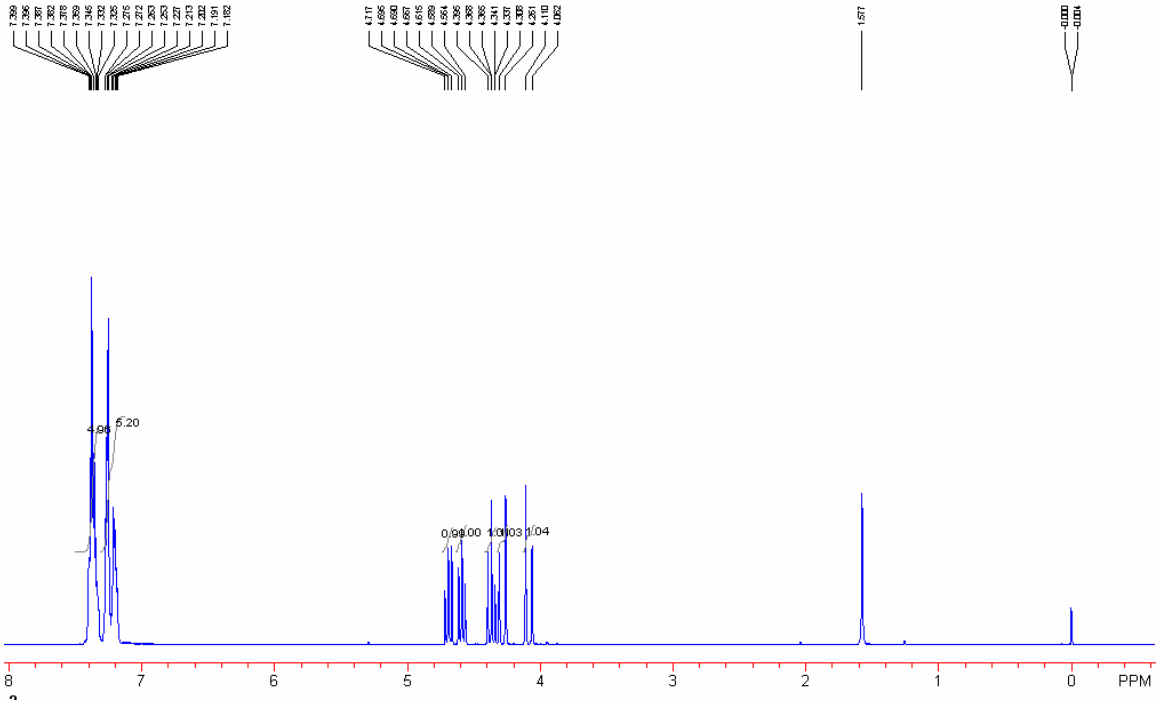


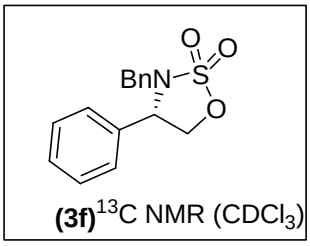
3d ^{13}C NMR ($CDCl_3$)



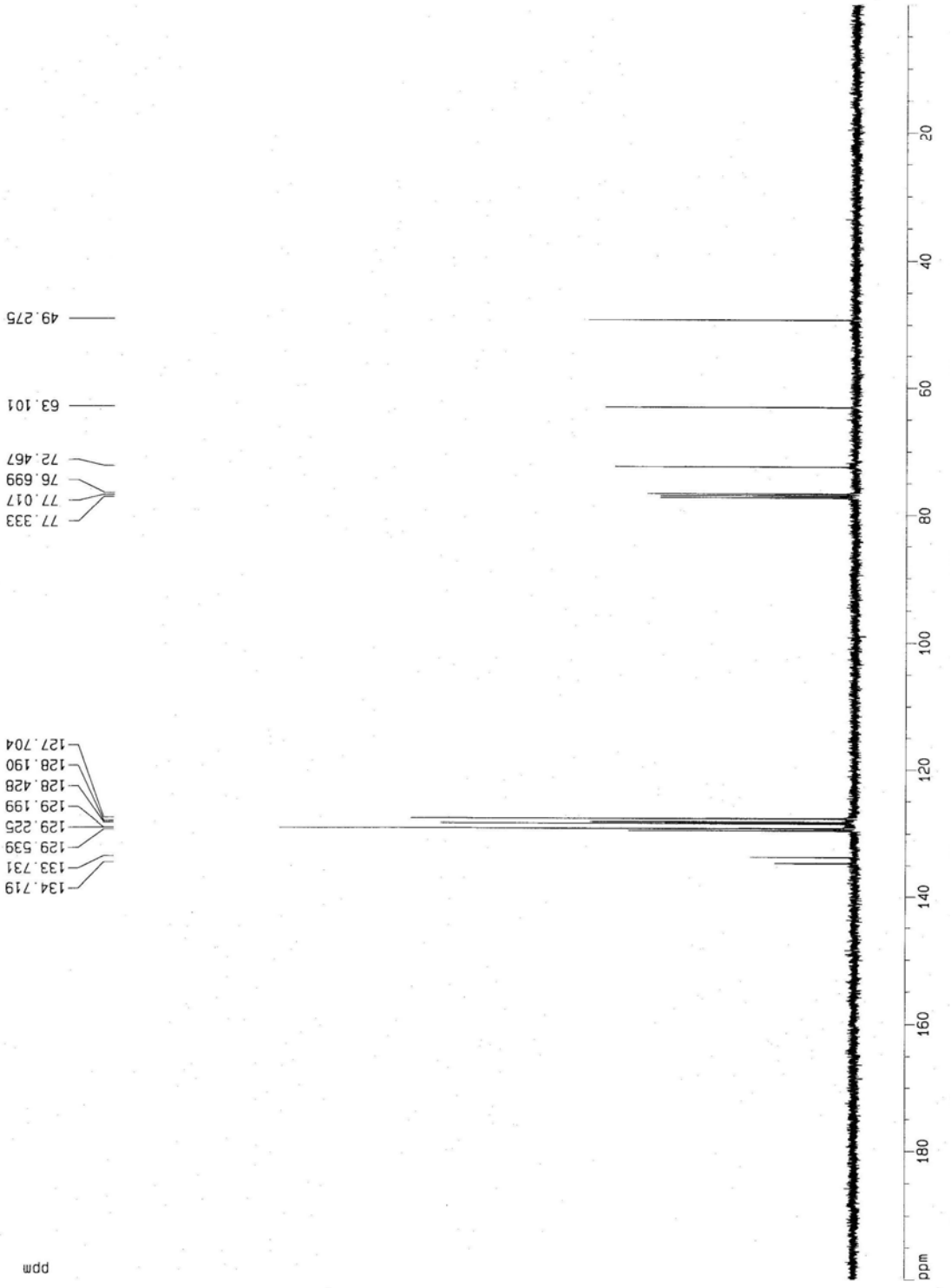


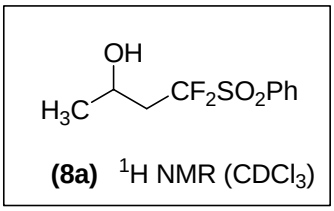
(3f) ^{1}H NMR ($CDCl_3$)



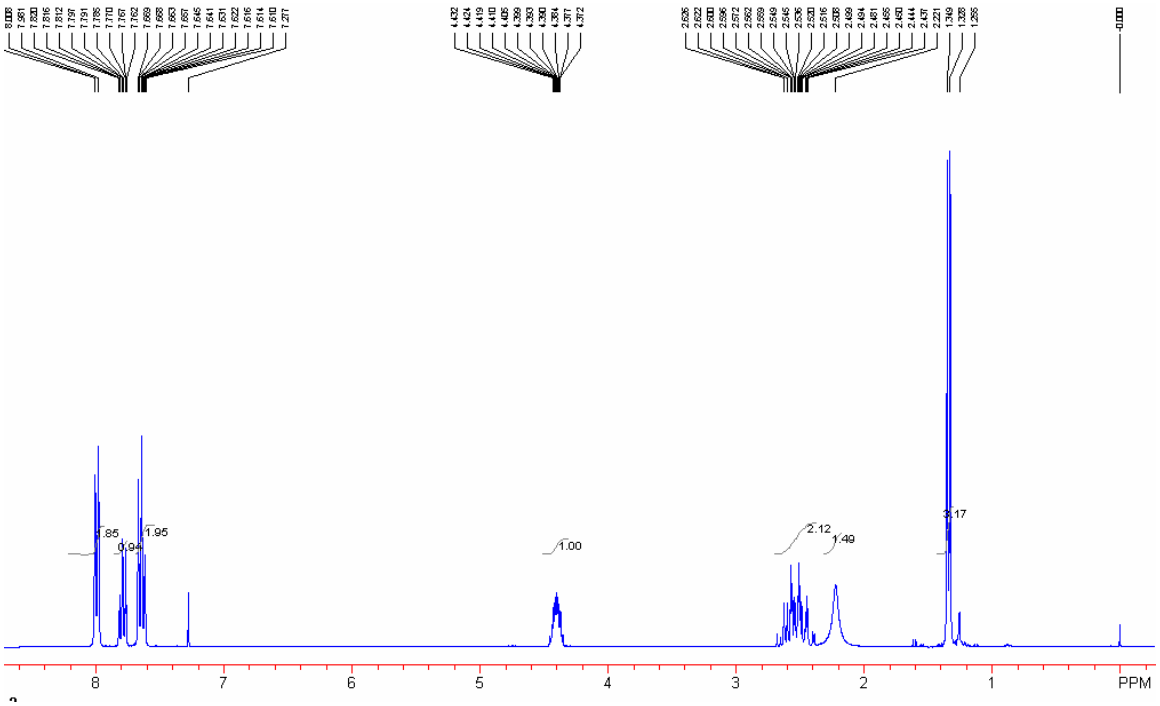


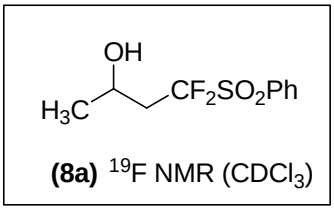
(3f) ^{13}C NMR ($CDCl_3$)



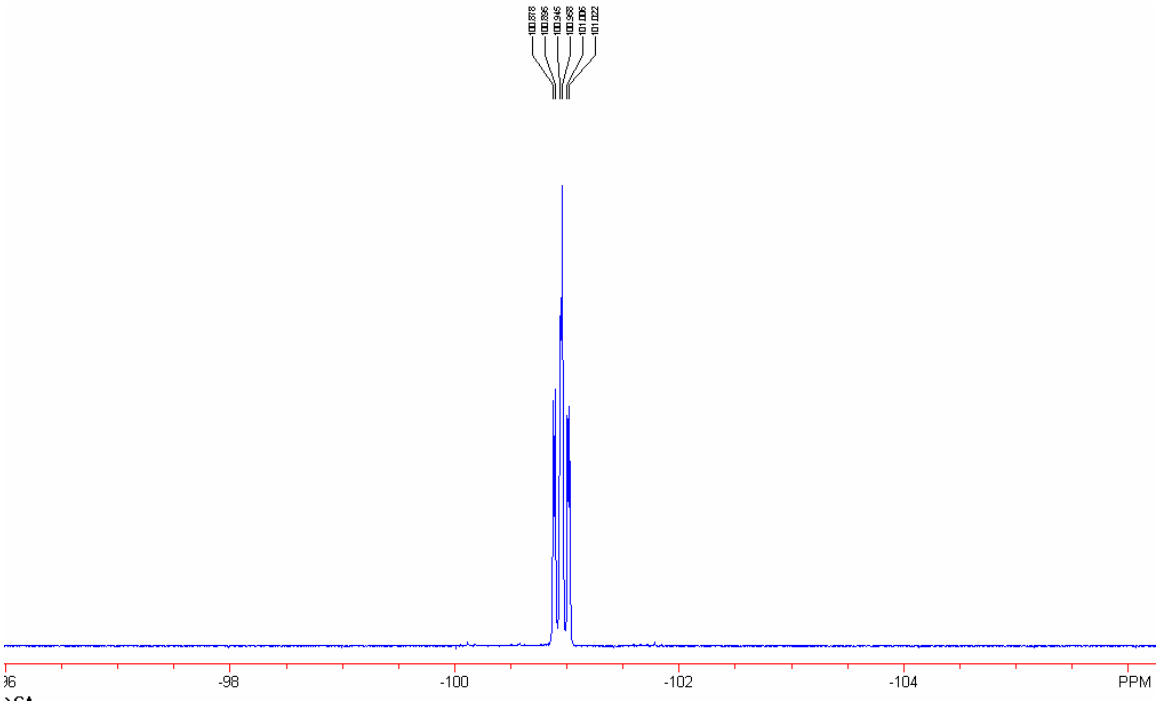


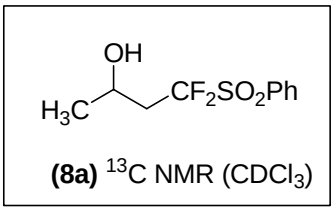
(8a) ^{1}H NMR ($CDCl_3$)



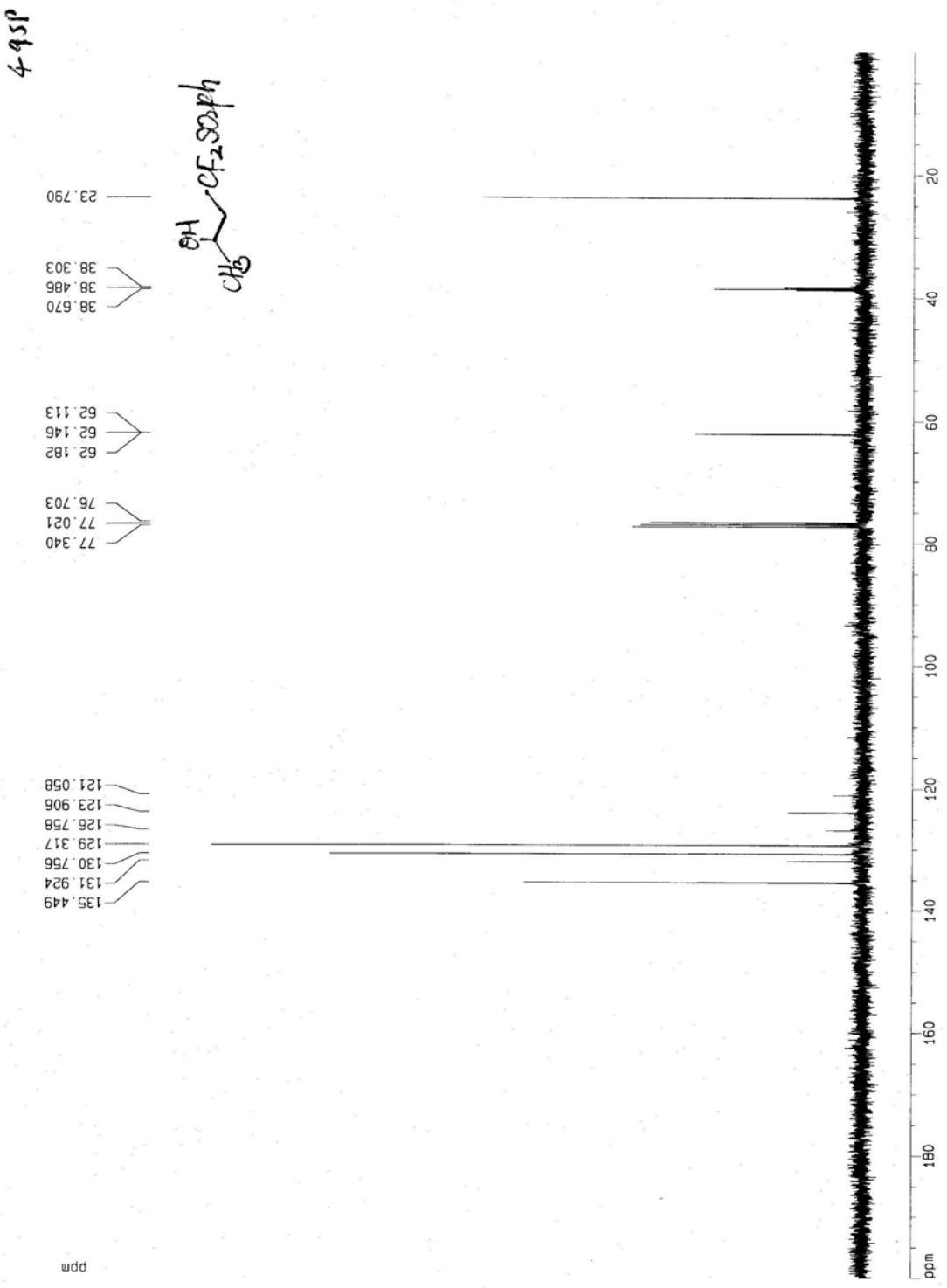


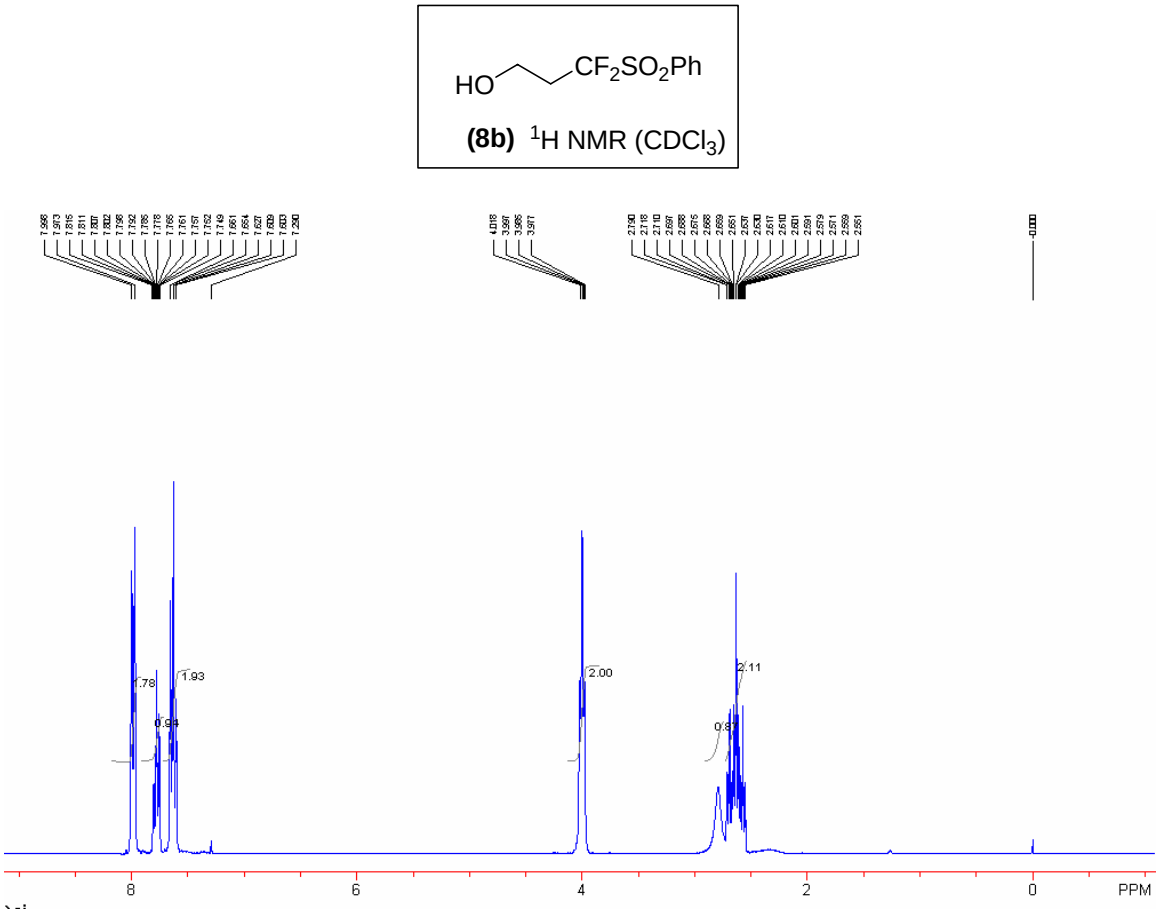
(8a) ^{19}F NMR ($CDCl_3$)

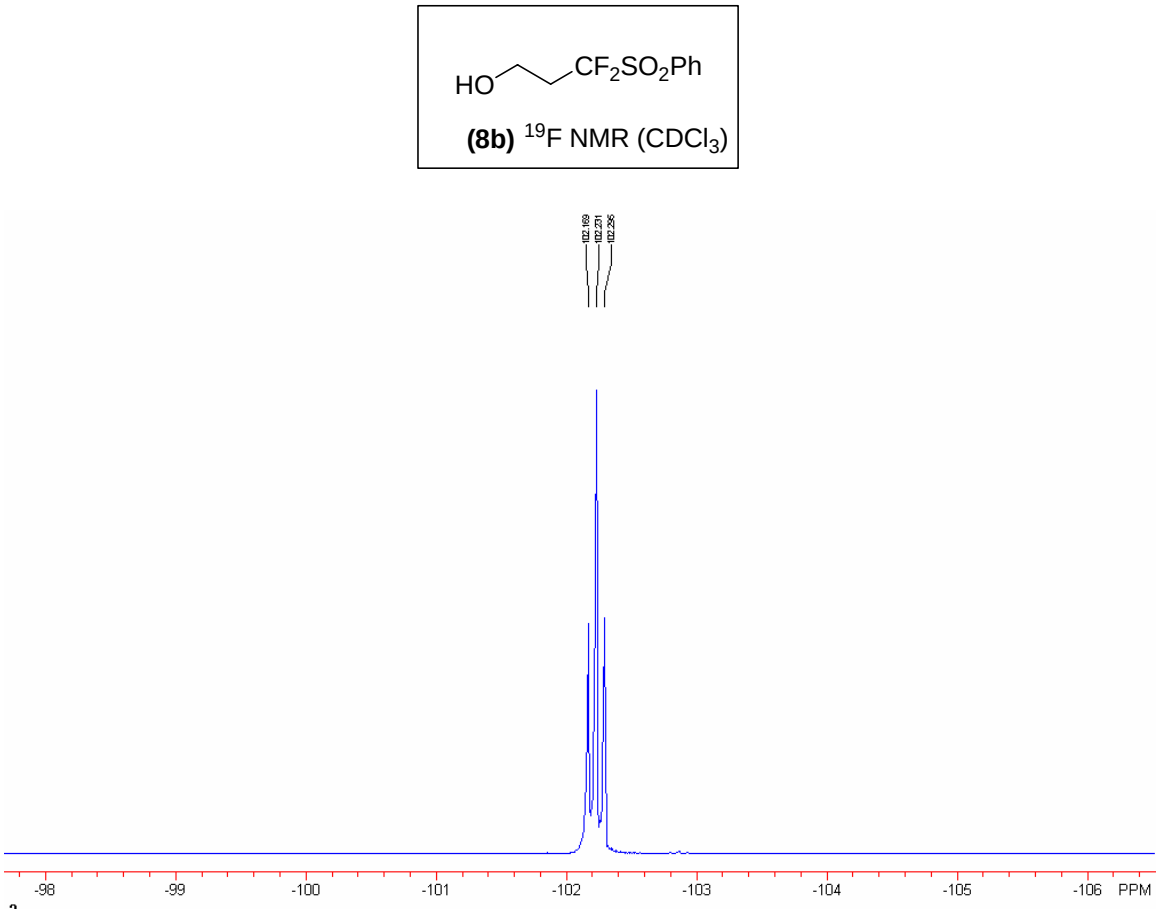


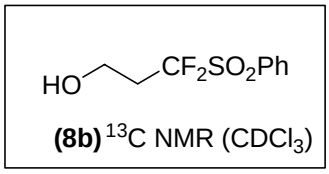


(8a) ^{13}C NMR ($CDCl_3$)

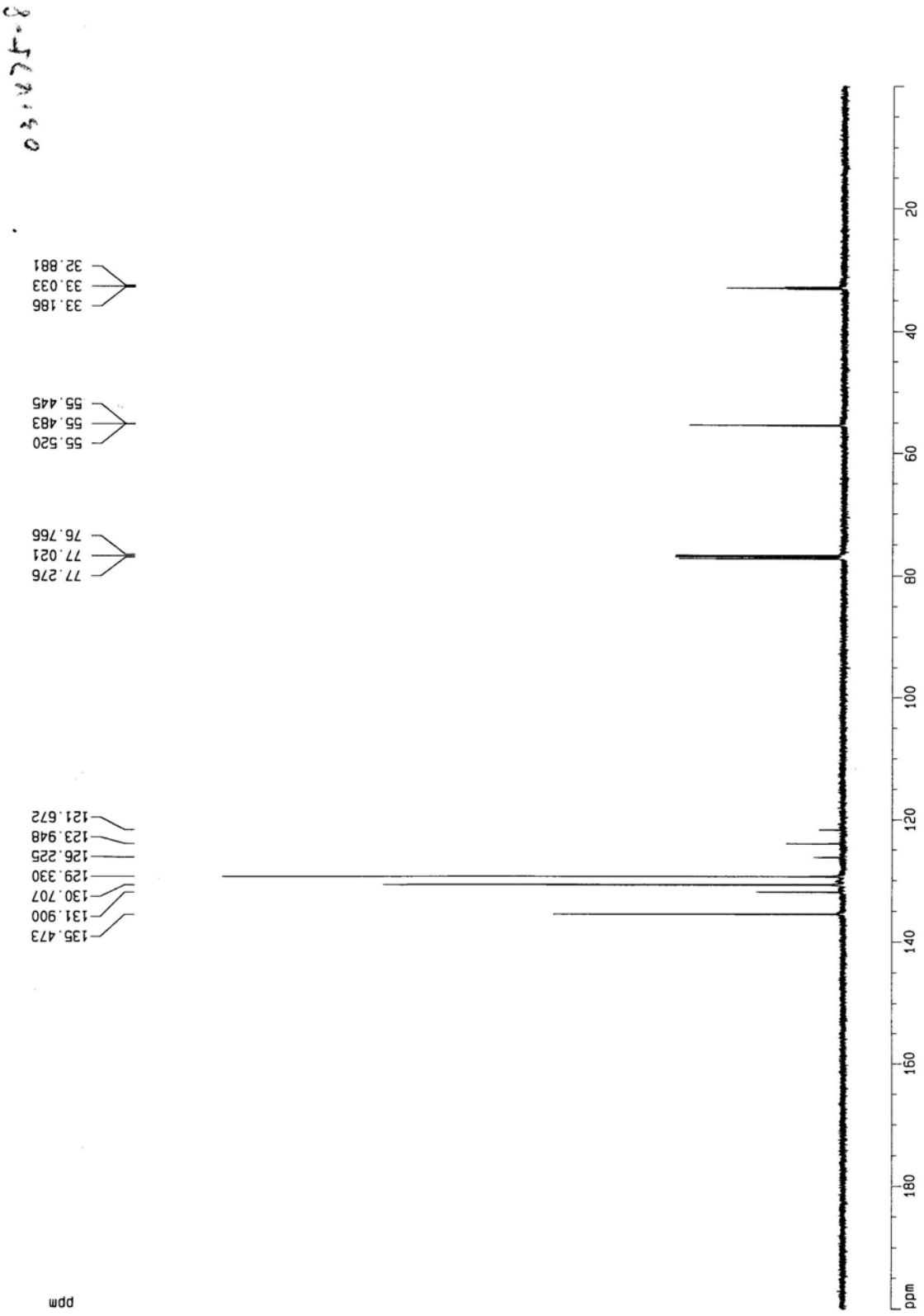


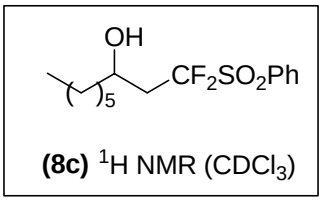

HO
CF2SO2Ph
(8b) 1H NMR (CDCl3)
1.78
1.93
0.94
2.00
2.11
0.83
8
6
4
2
0
PPM


HO
CF2SO2Ph
(8b) 19F NMR (CDCl3)
-98
-99
-100
-101
-102
-103
-104
-105
-106
PPM

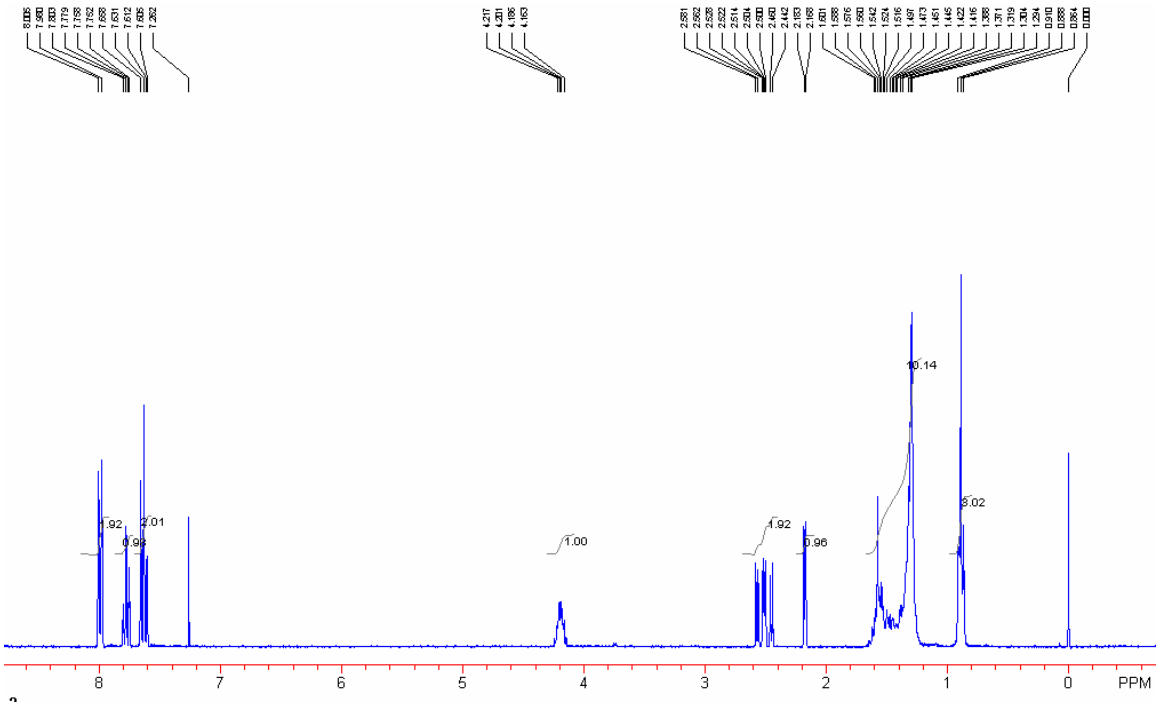


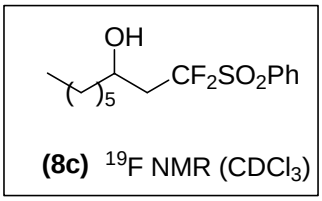
(8b) ^{13}C NMR ($CDCl_3$)



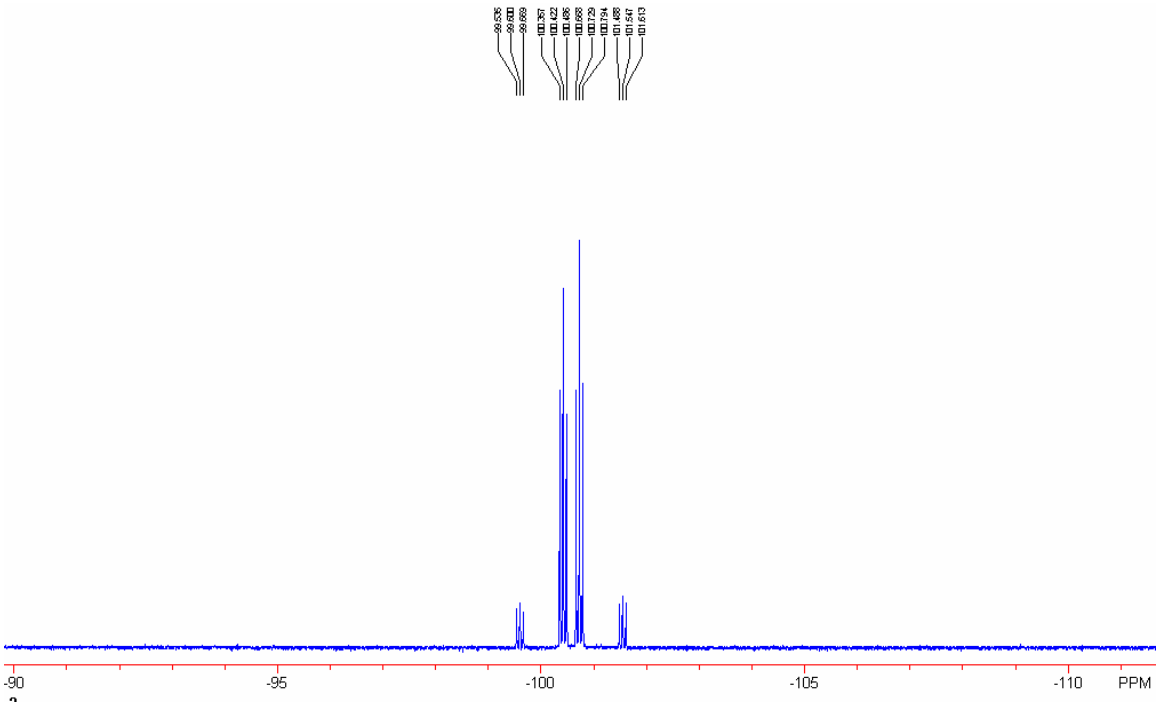


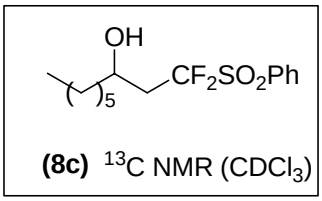
(8c) ^{1}H NMR ($CDCl_3$)



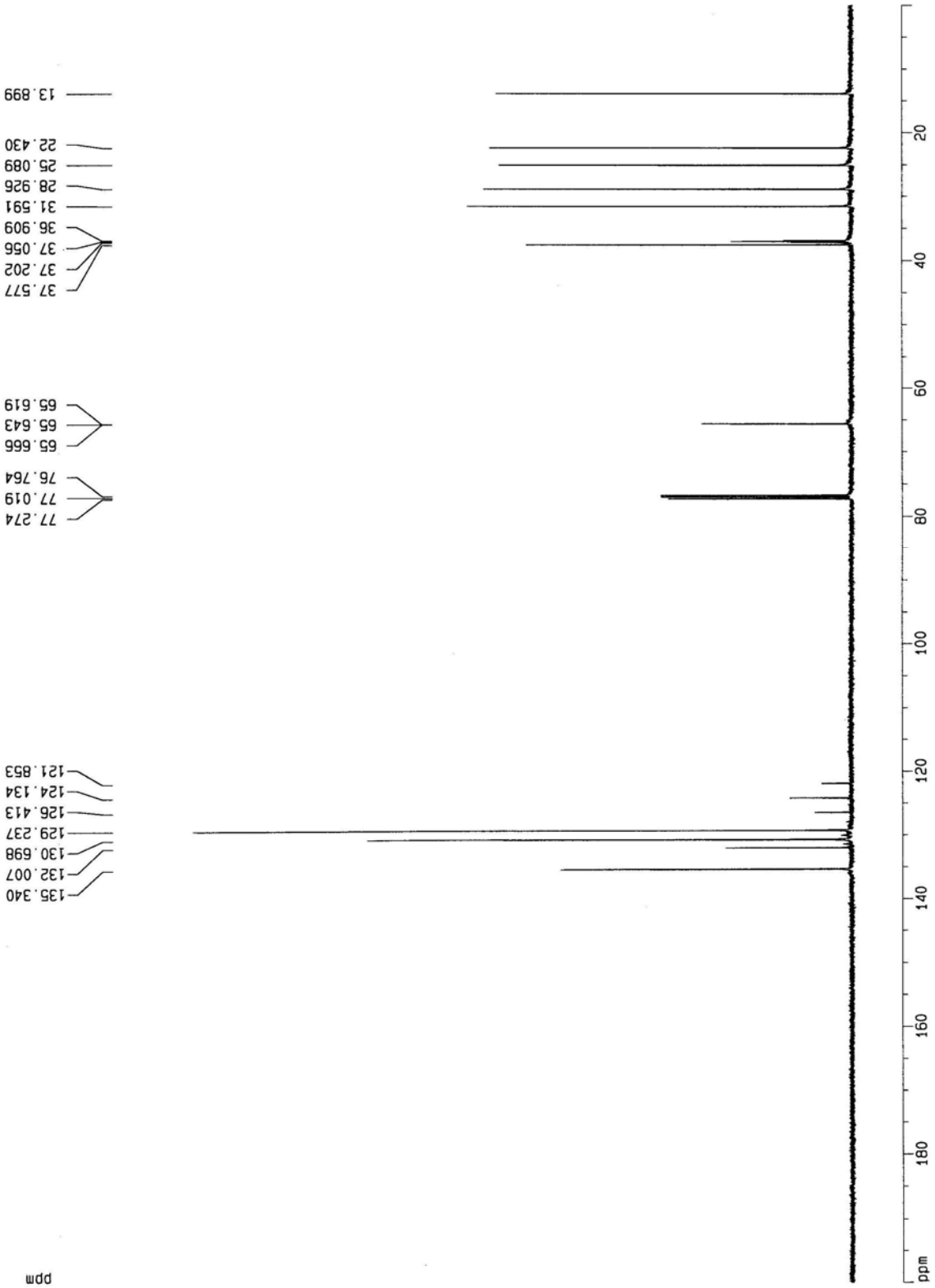


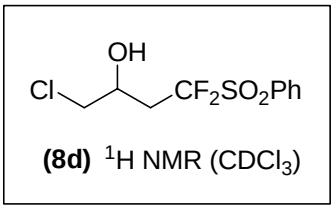
(8c) ^{19}F NMR ($CDCl_3$)

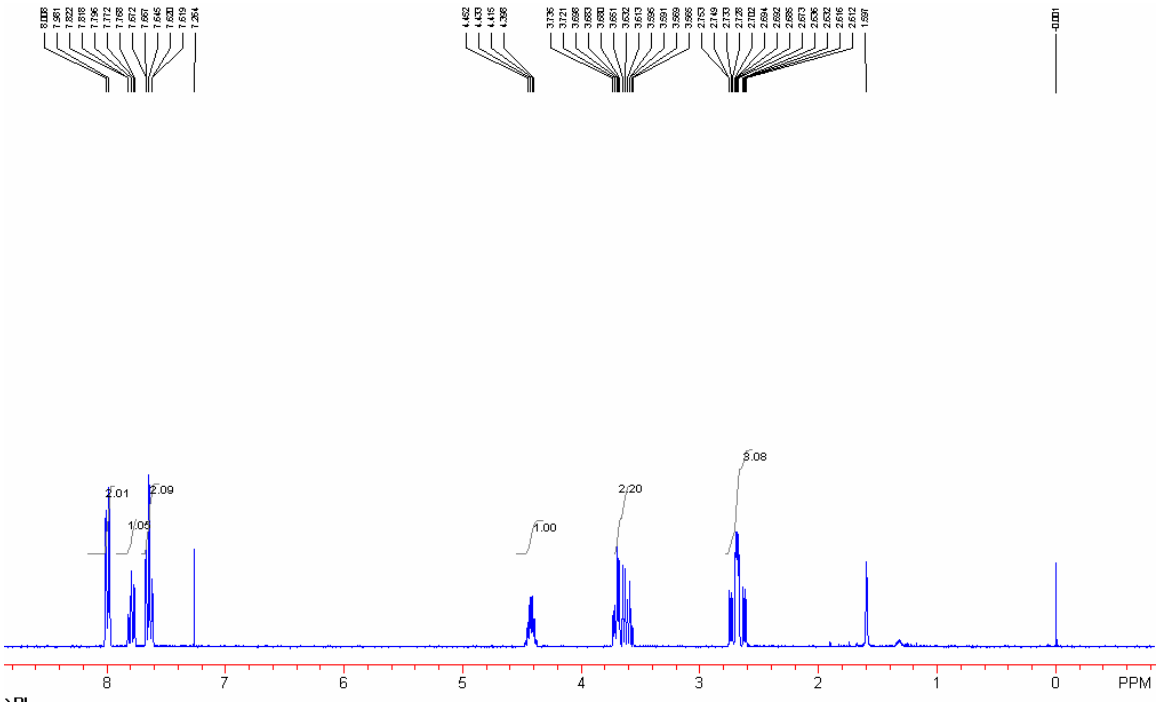


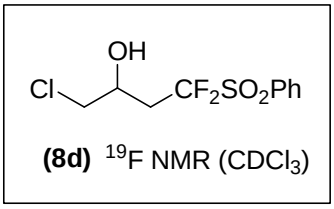


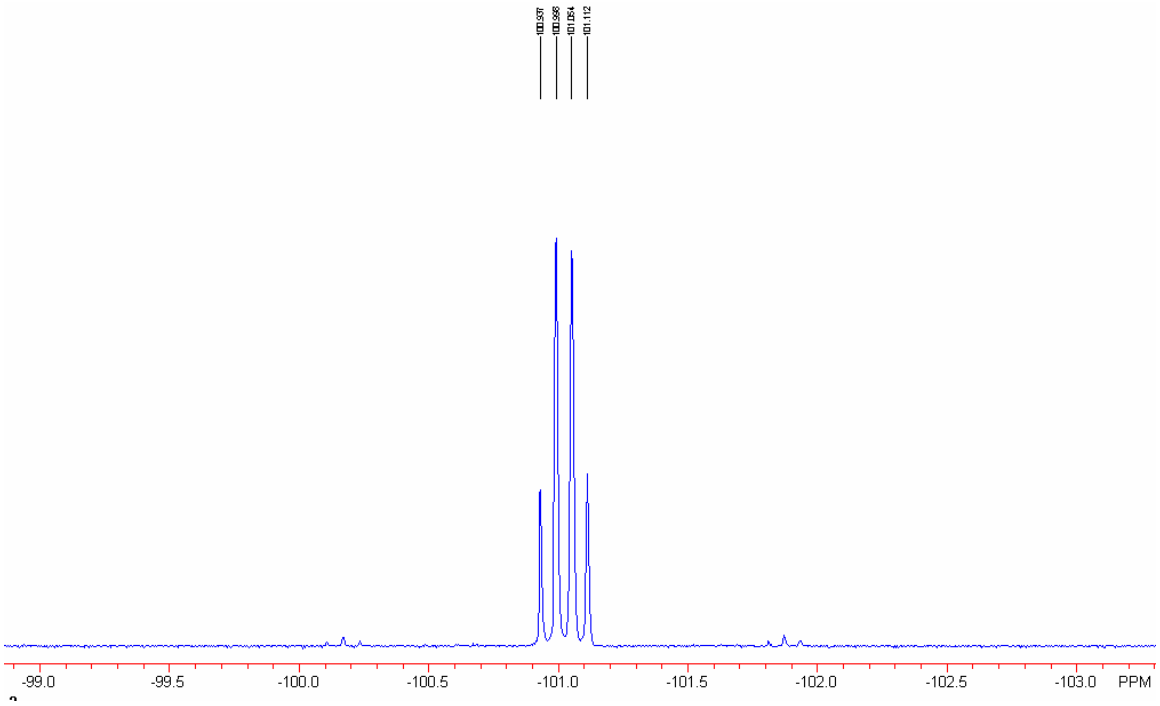
(8c) ^{13}C NMR ($CDCl_3$)

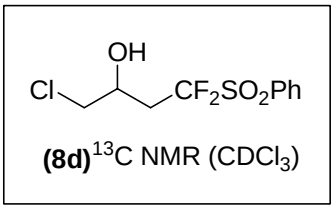



OH
Cl
CF2SO2Ph
(8d) 1H NMR (CDCl3)

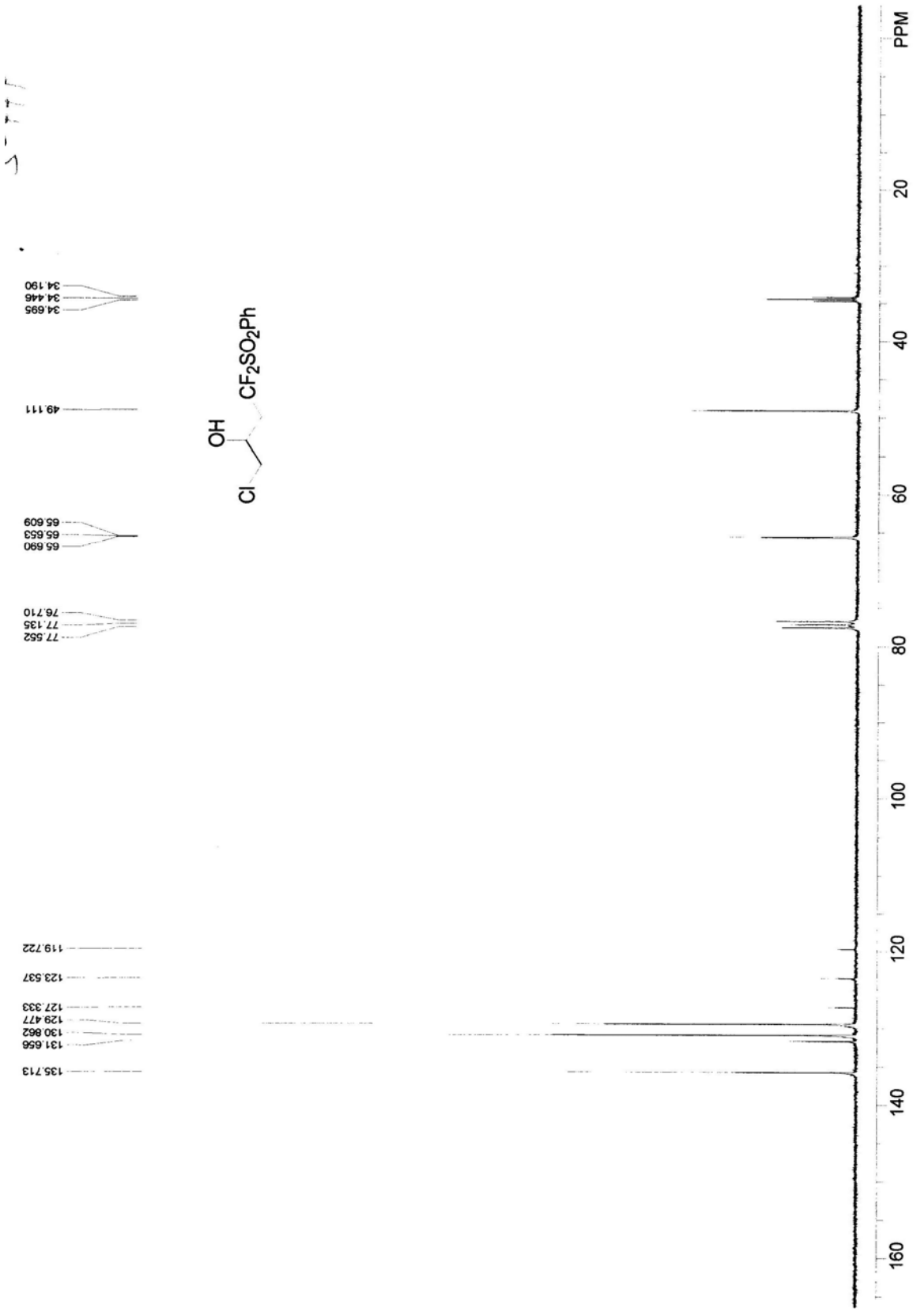

2.01
2.09
1.05
1.00
2.20
3.08
8
7
6
5
4
3
2
1
0
PPM

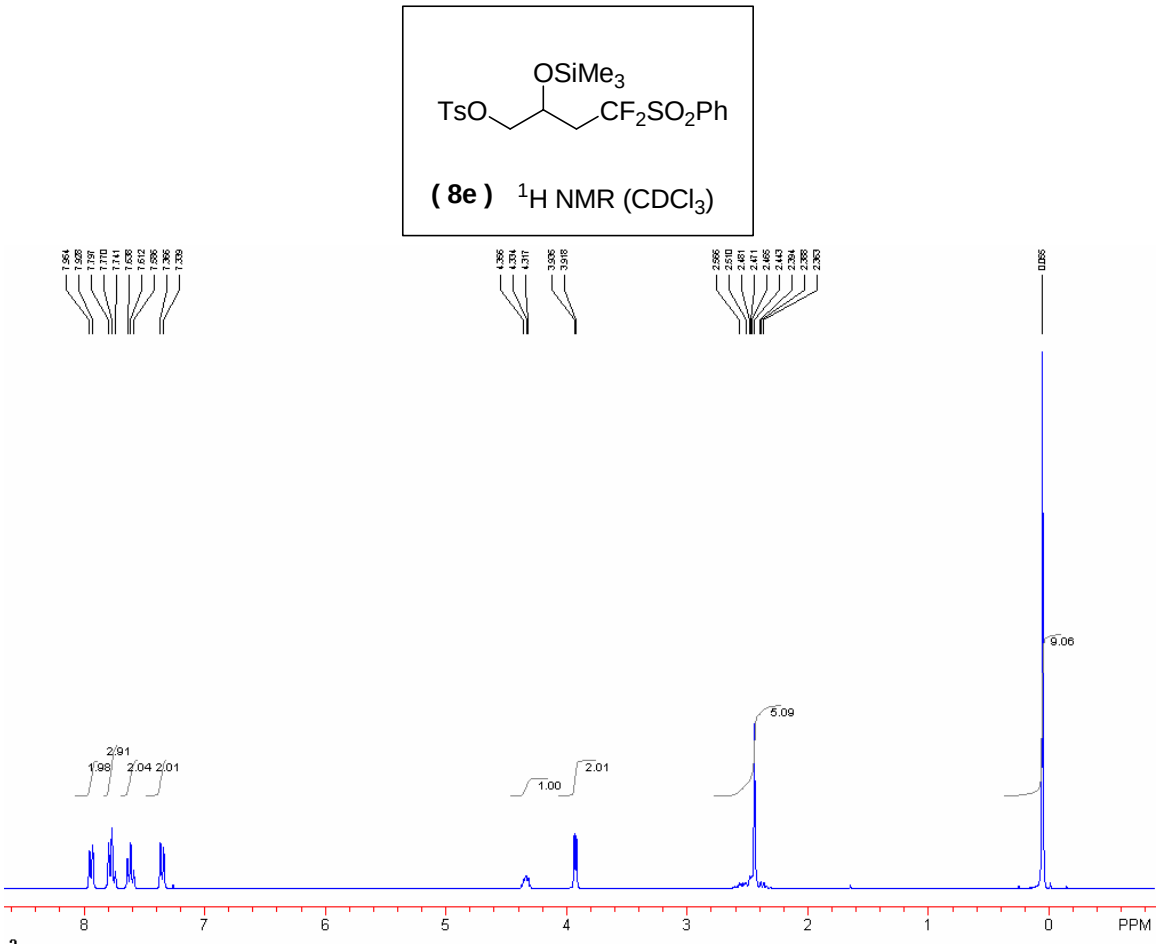

OH
Cl
CF2SO2Ph
(8d) 19F NMR (CDCl3)

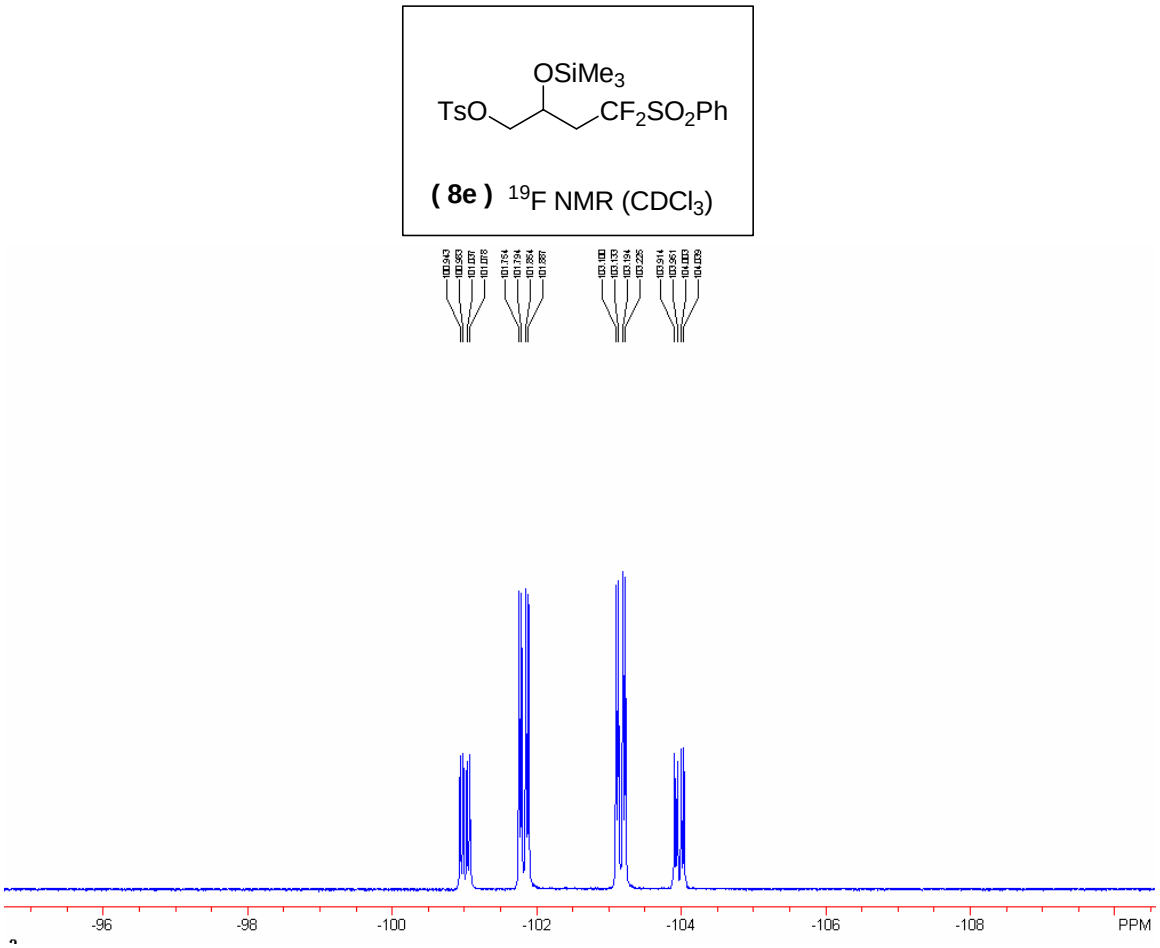

-99.0
-99.5
-100.0
-100.5
-101.0
-101.5
-102.0
-102.5
-103.0
PPM

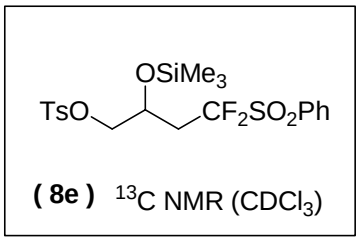


(8d) ^{13}C NMR ($CDCl_3$)

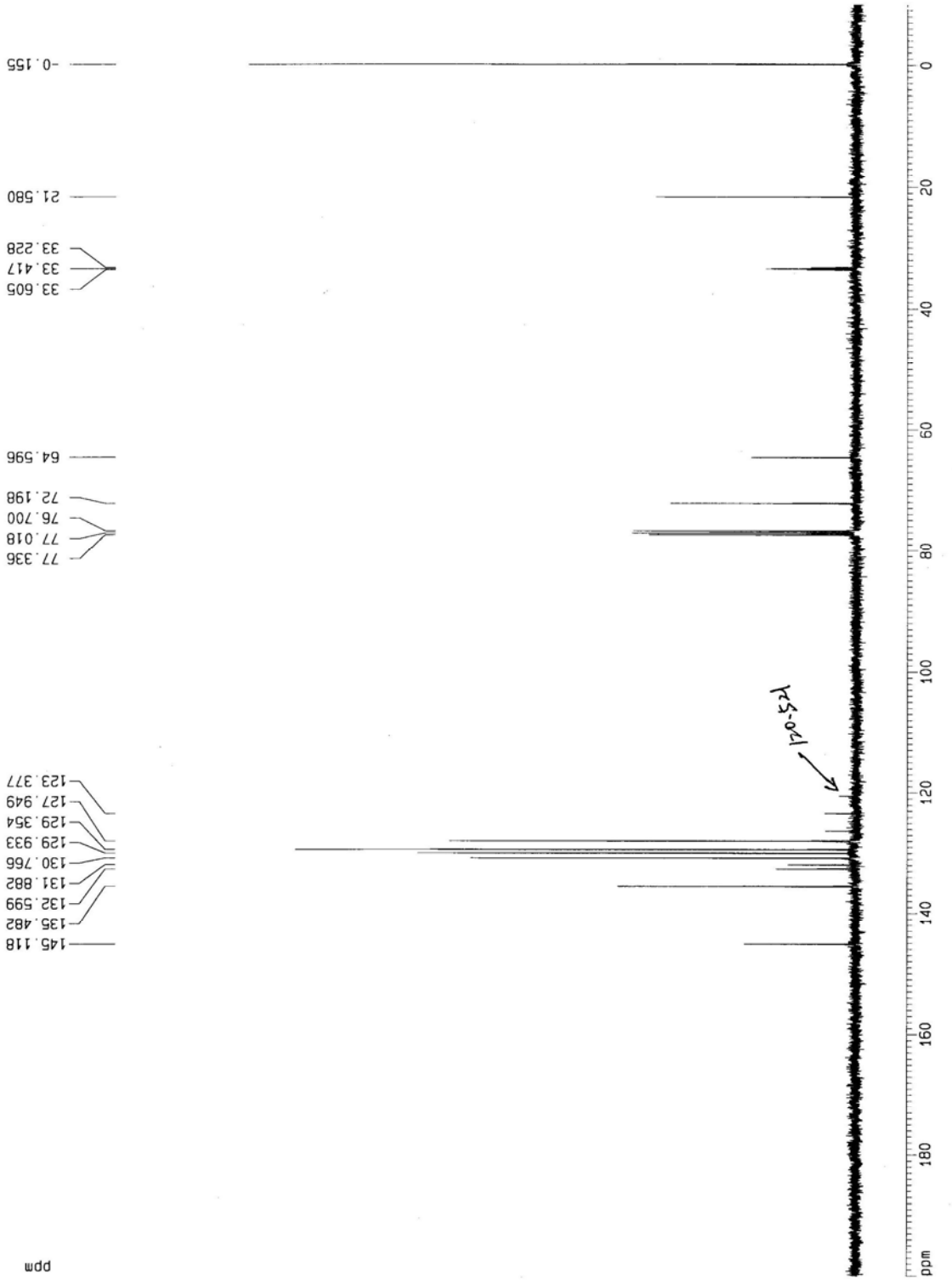


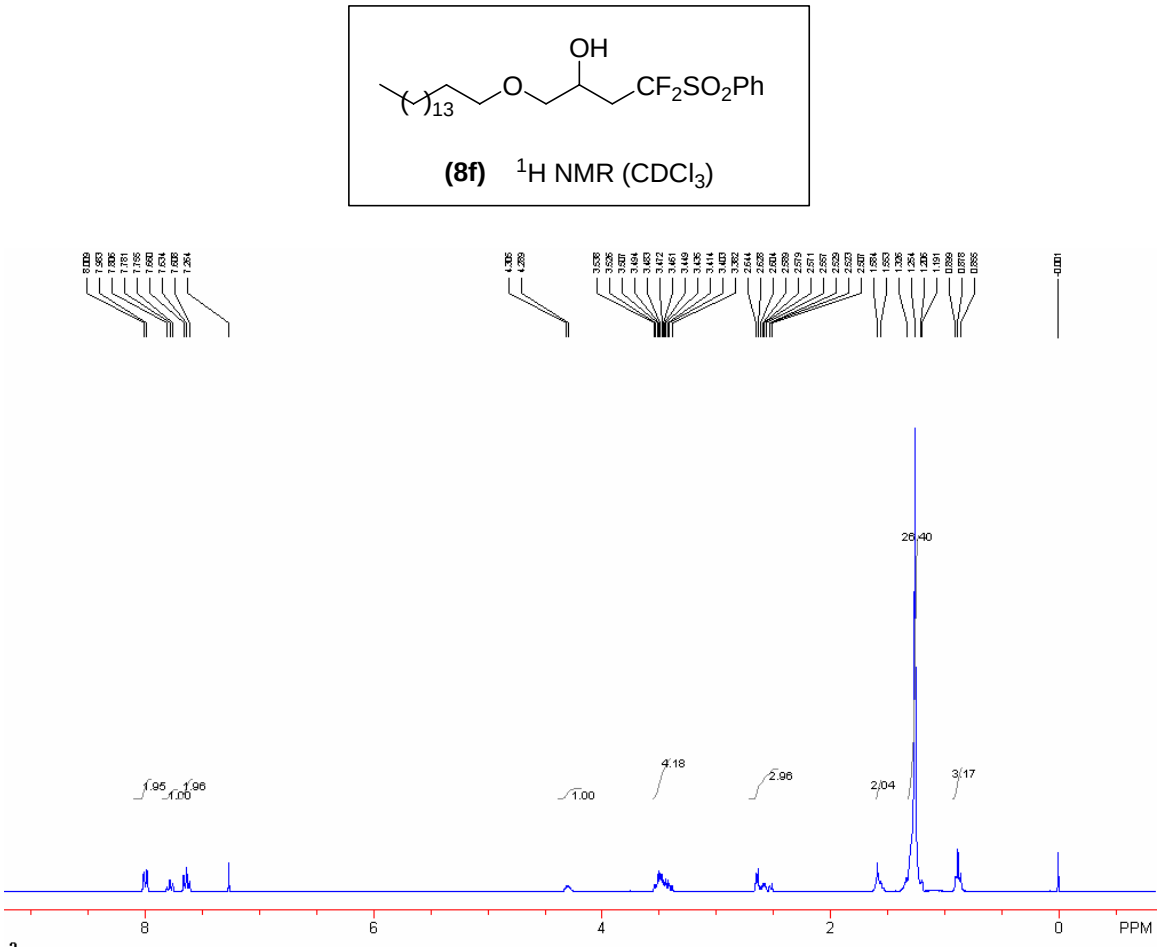

OSiMe3
TsO
CF2SO2Ph
(8e) 1H NMR (CDCl3)
9.06
5.09
2.91
1.98
2.04
2.01
1.00
2.01
8
7
6
5
4
3
2
1
0
PPM

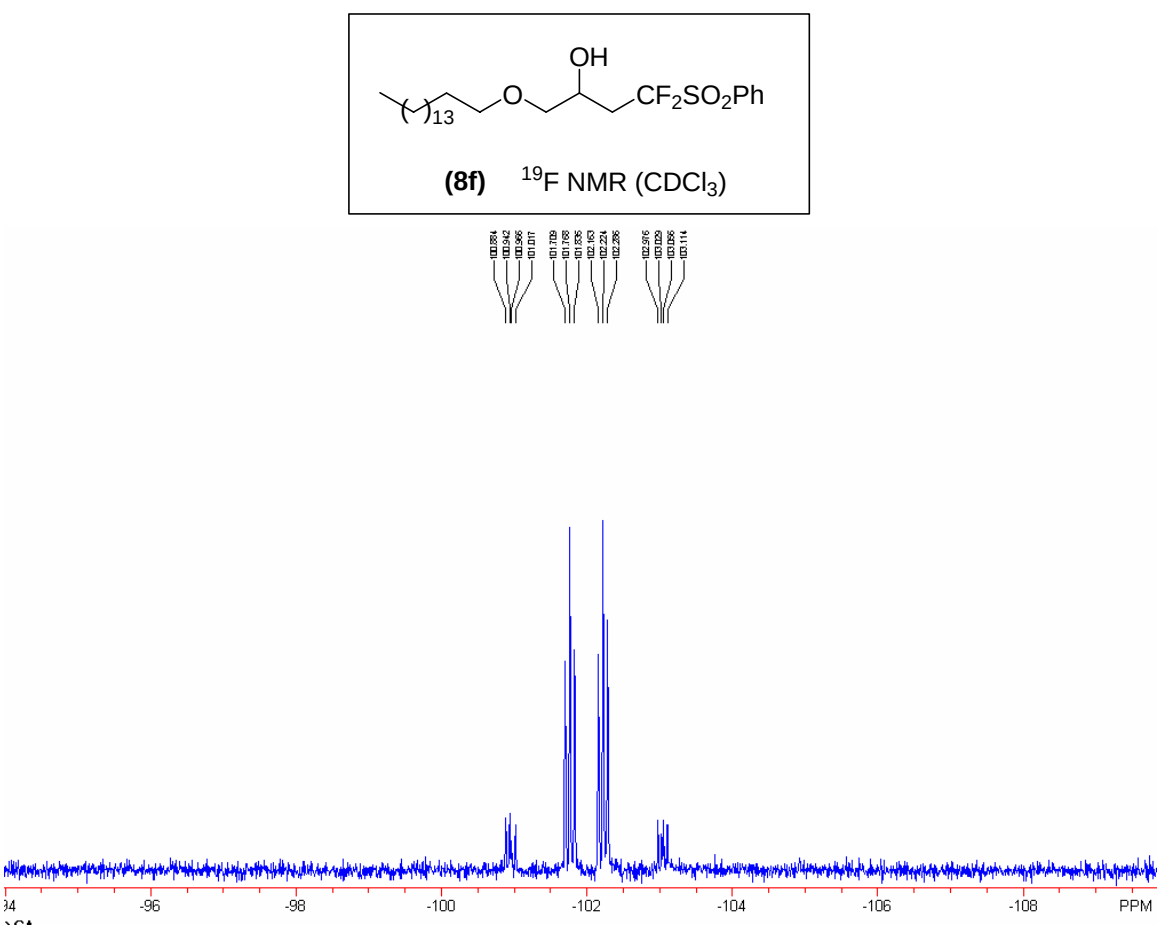

OSiMe3
TsO
CF2SO2Ph
(8e) 19F NMR (CDCl3)
-96
-98
-100
-102
-104
-106
-108
PPM

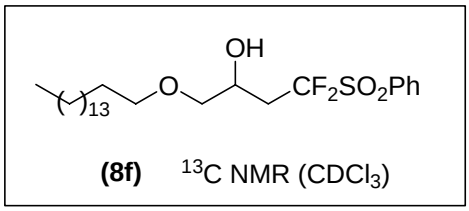


(8e) ^{13}C NMR ($CDCl_3$)

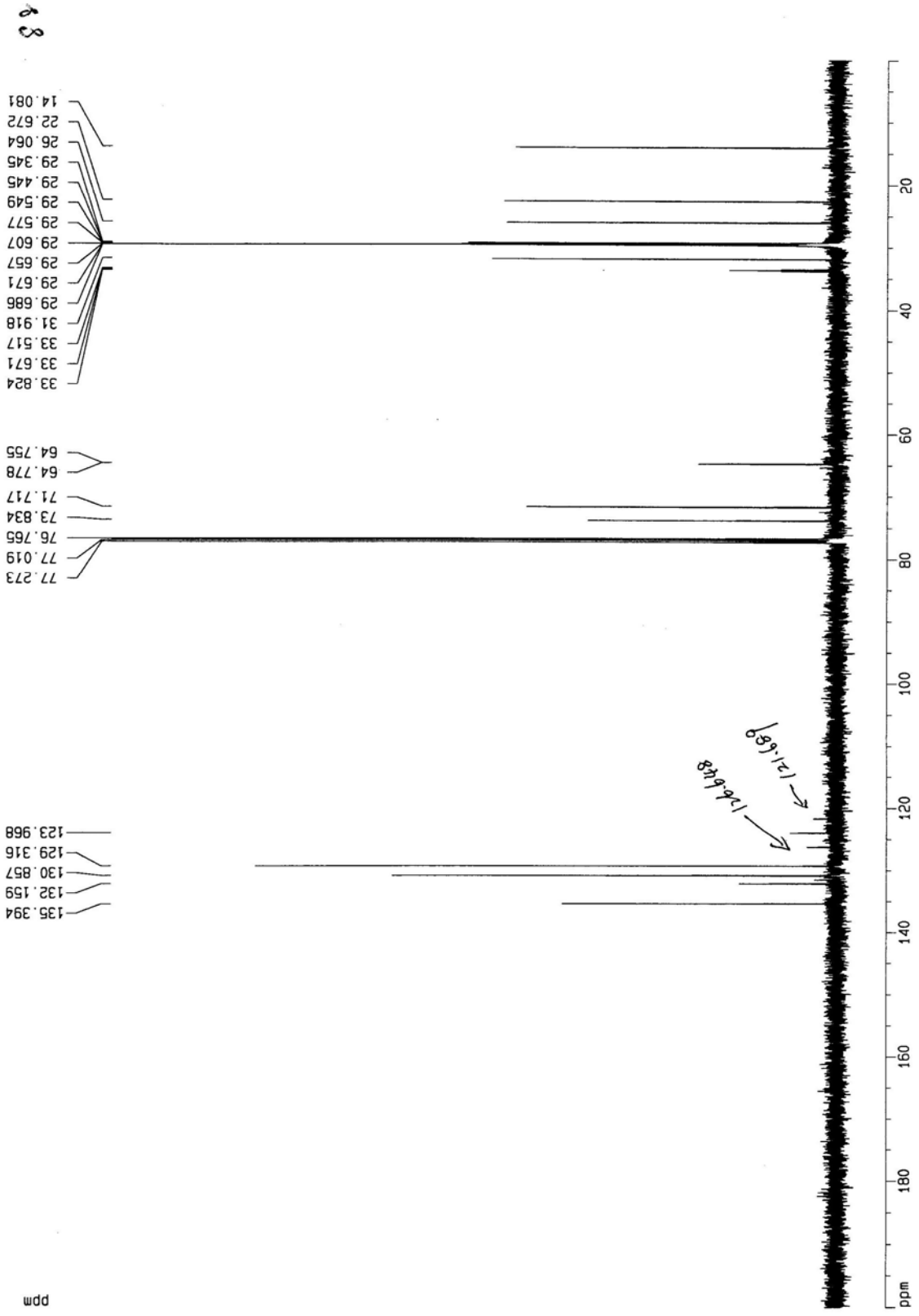


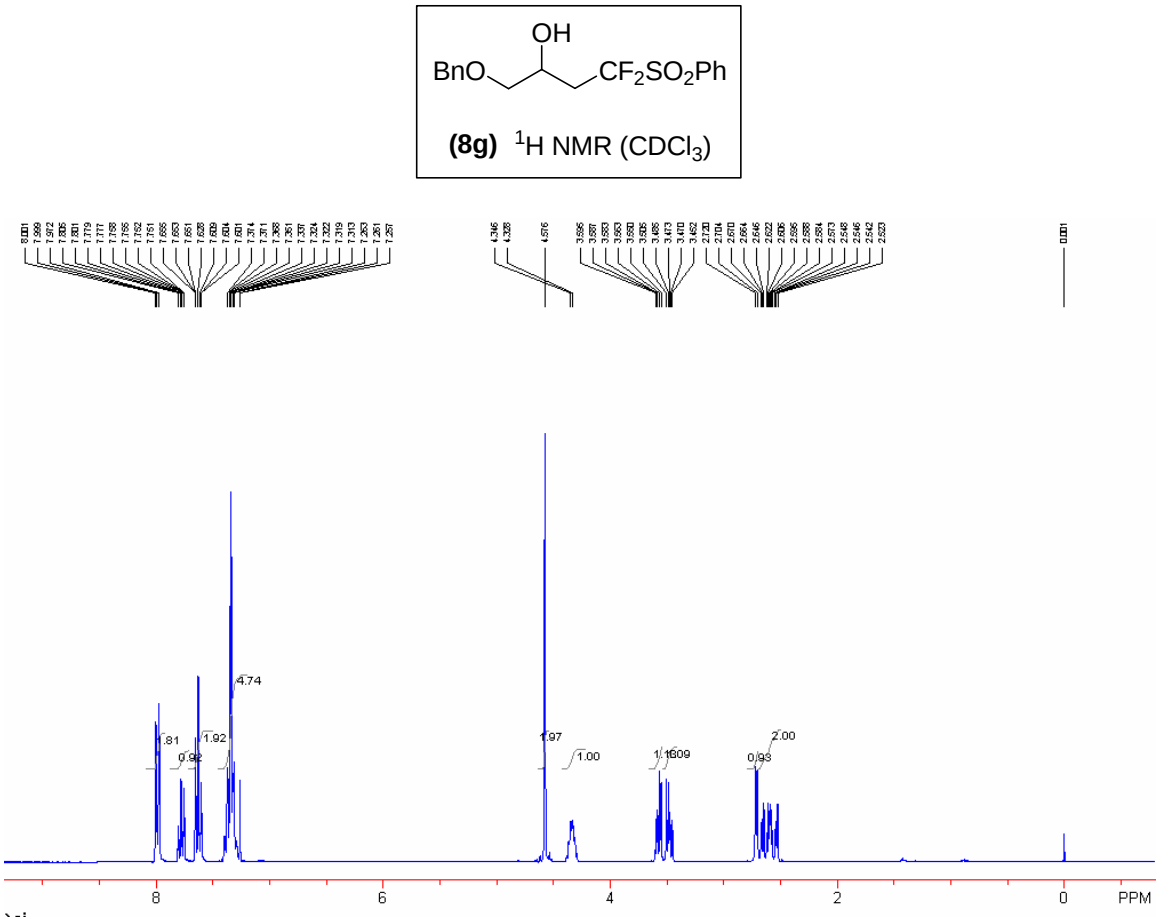

OH
O
13
CF2SO2Ph
(8f) 1H NMR (CDCl3)
26.40
4.18
2.96
2.04
3.17
1.95
1.96
1.00
1.00
8
6
4
2
0
PPM

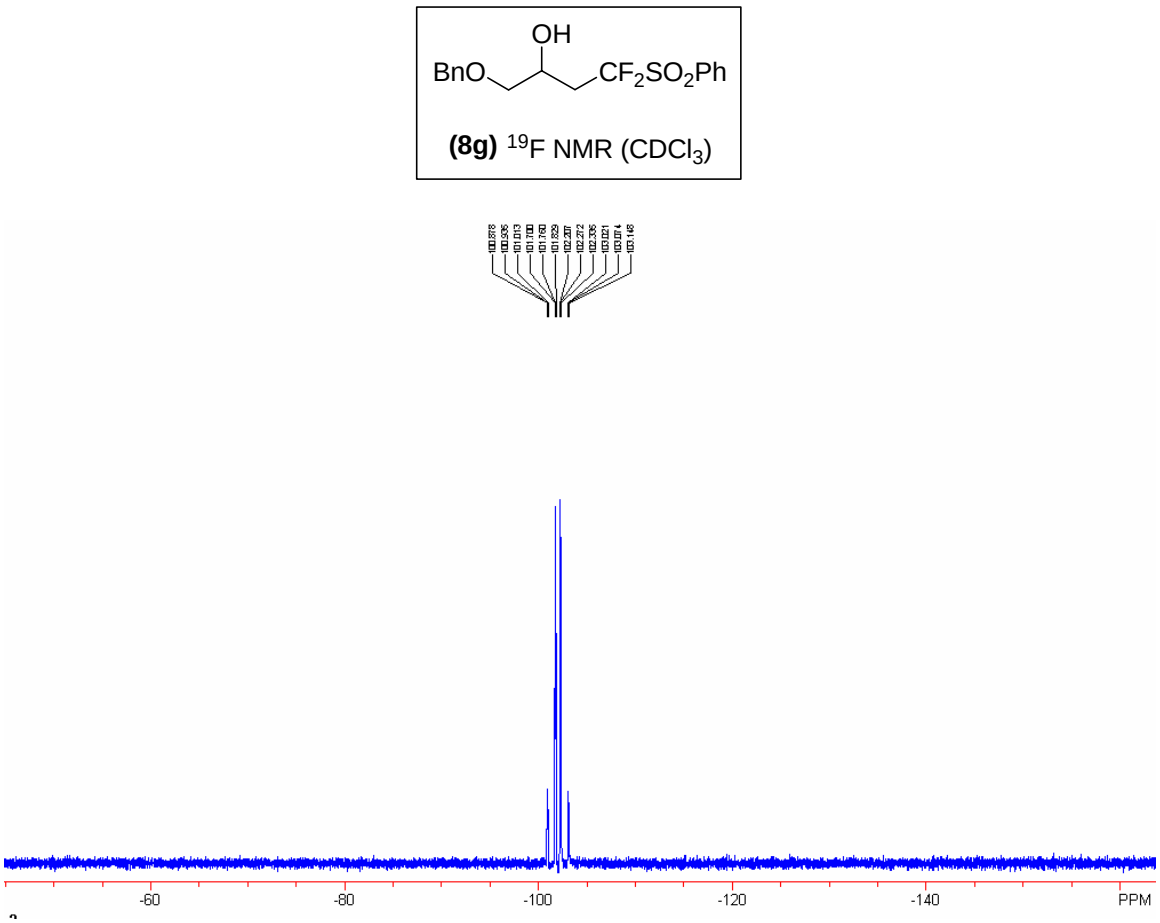

OH
O
13
CF2SO2Ph
(8f) 19F NMR (CDCl3)
-96
-98
-100
-102
-104
-106
-108
PPM

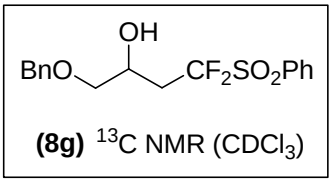


(8f) ^{13}C NMR ($CDCl_3$)

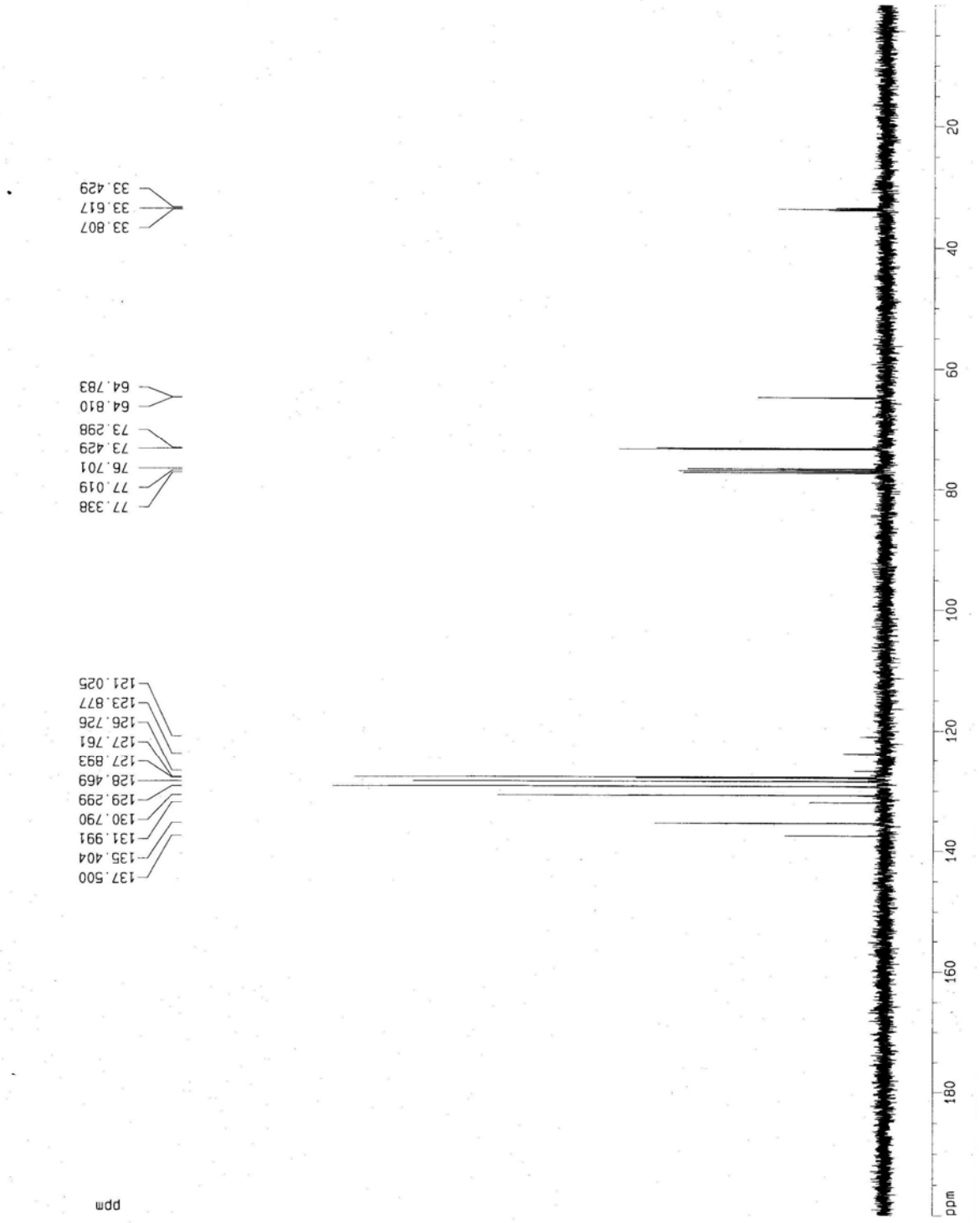


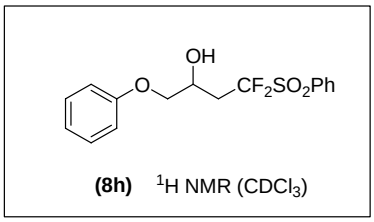

OH
BnO
CF2SO2Ph
(8g) 1H NMR (CDCl3)
4.74
1.81
1.92
0.92
1.97
1.00
1.1609
0.93
2.00
8
6
4
2
0
PPM


OH
BnO
CF2SO2Ph
(8g) 19F NMR (CDCl3)
-60
-80
-100
-120
-140
PPM

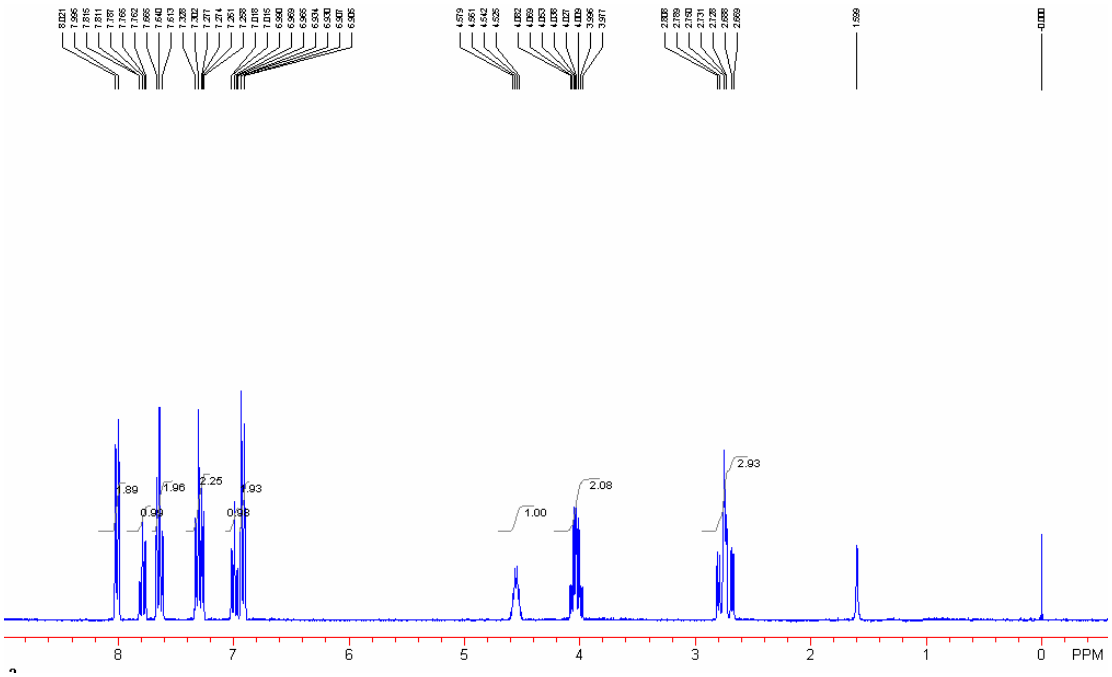


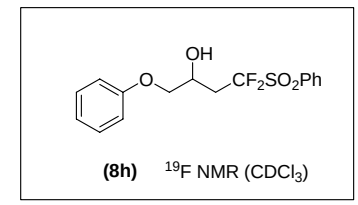
(8g) ^{13}C NMR ($CDCl_3$)



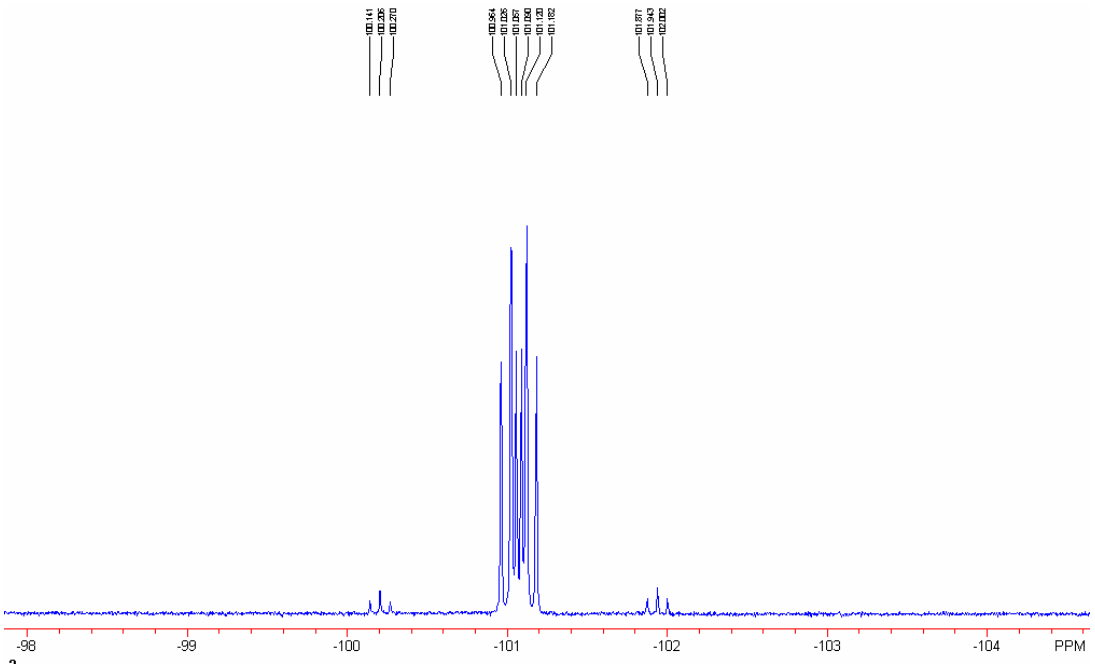


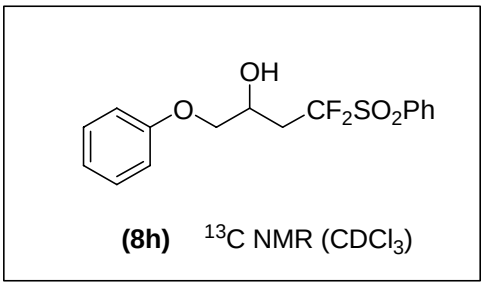
(8h) ^1H NMR ($CDCl_3$)



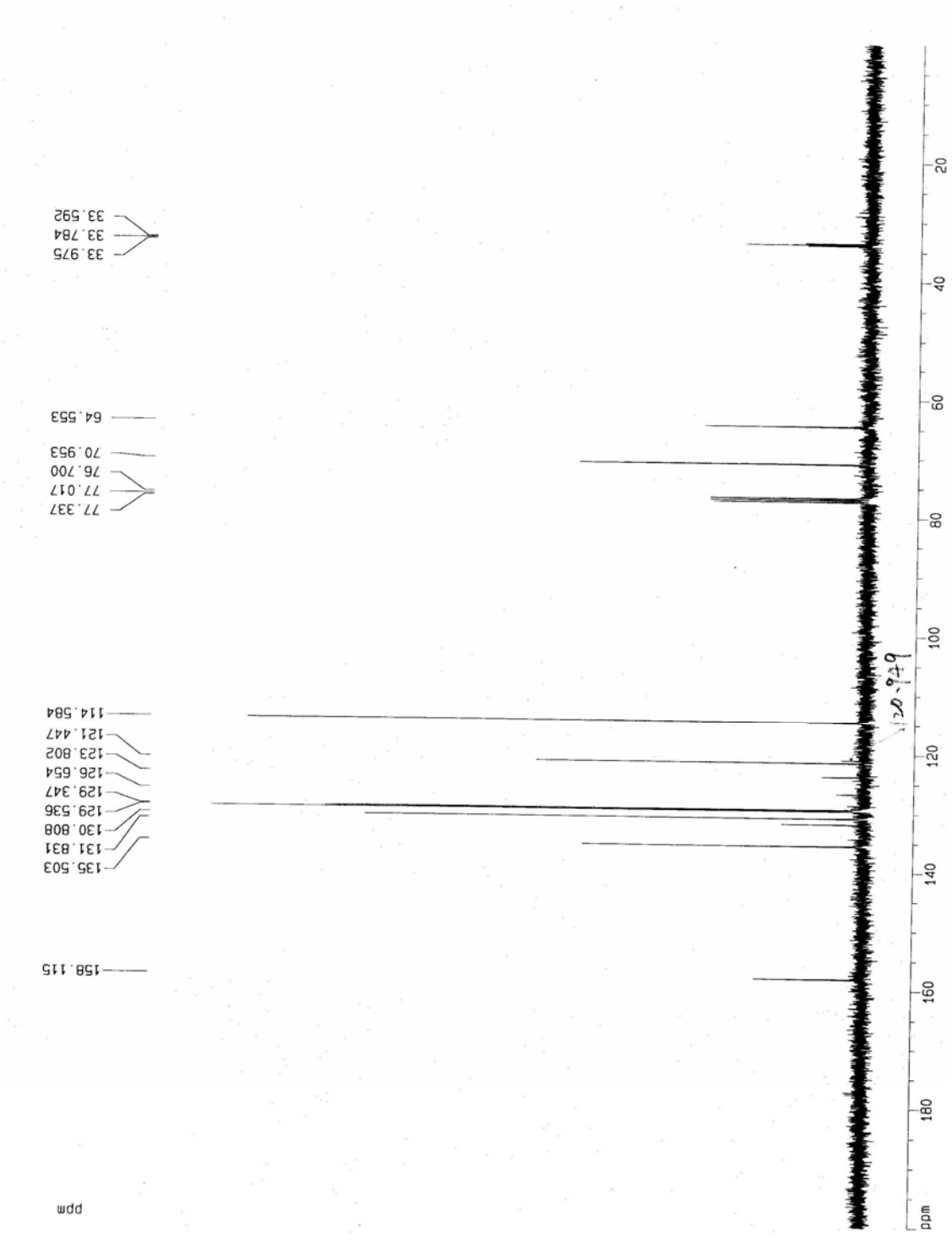


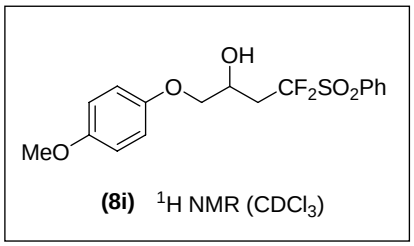
(8h) ^{19}F NMR ($CDCl_3$)



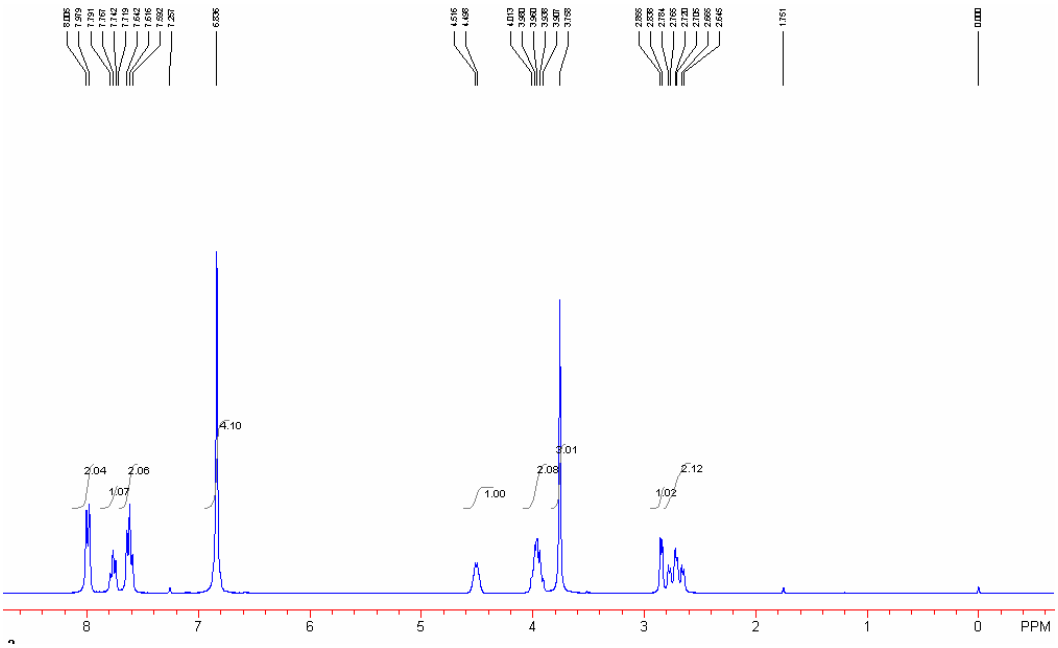


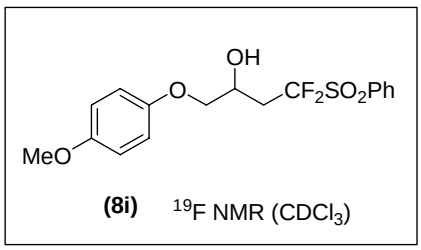
(8h) ^{13}C NMR ($CDCl_3$)



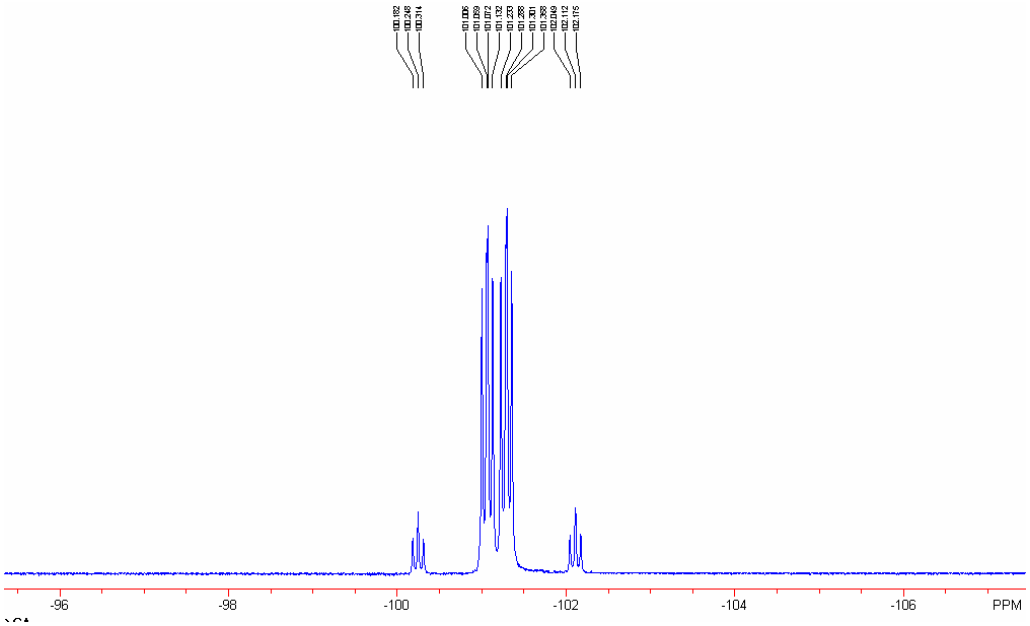


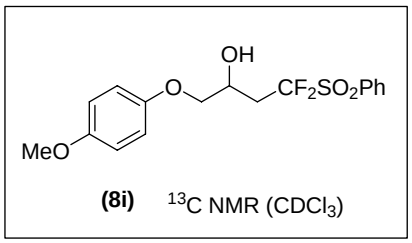
(8i) ^{1}H NMR ($CDCl_3$)



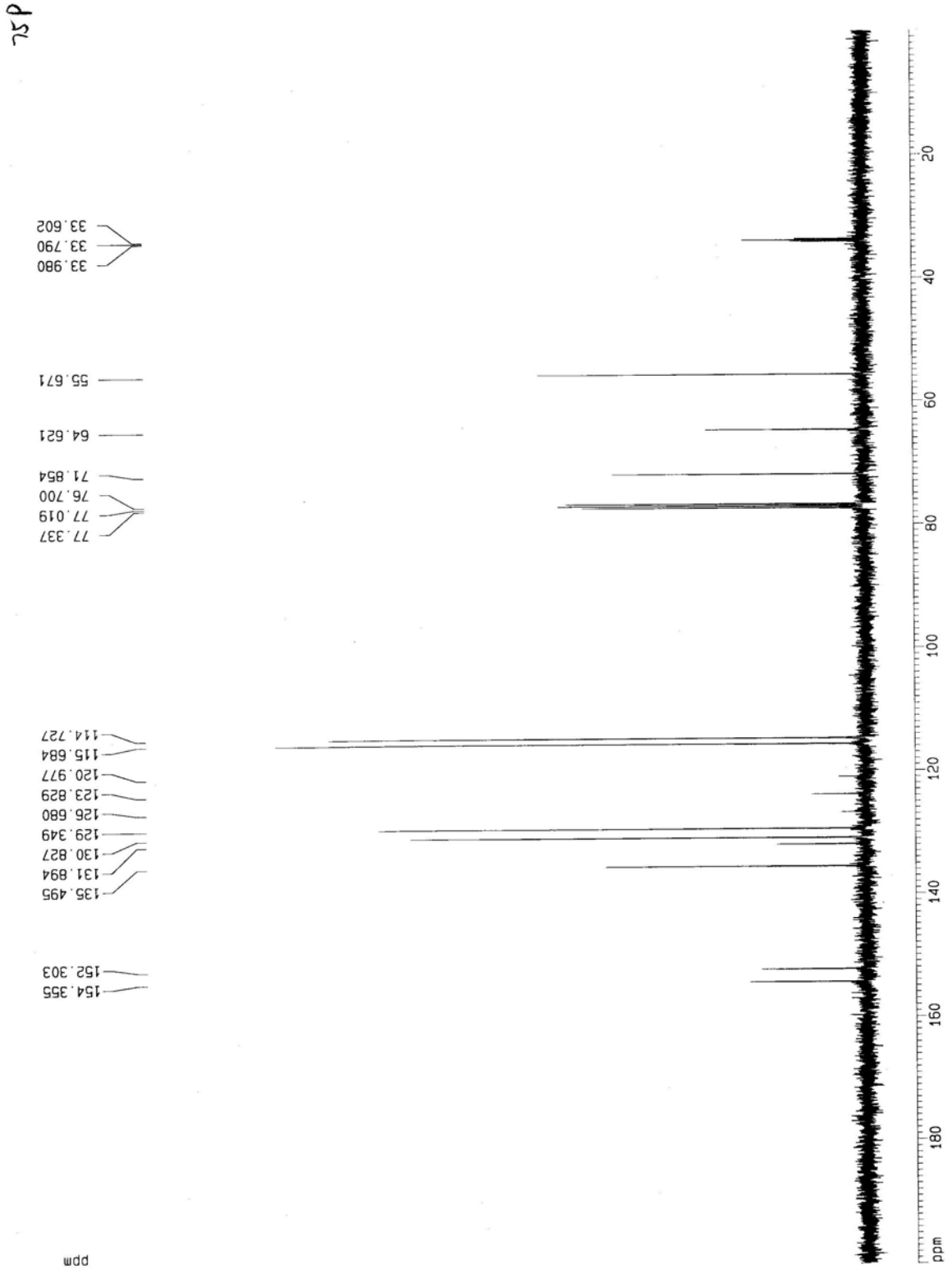


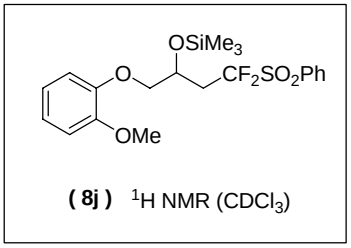
(8i) ^{19}F NMR ($CDCl_3$)



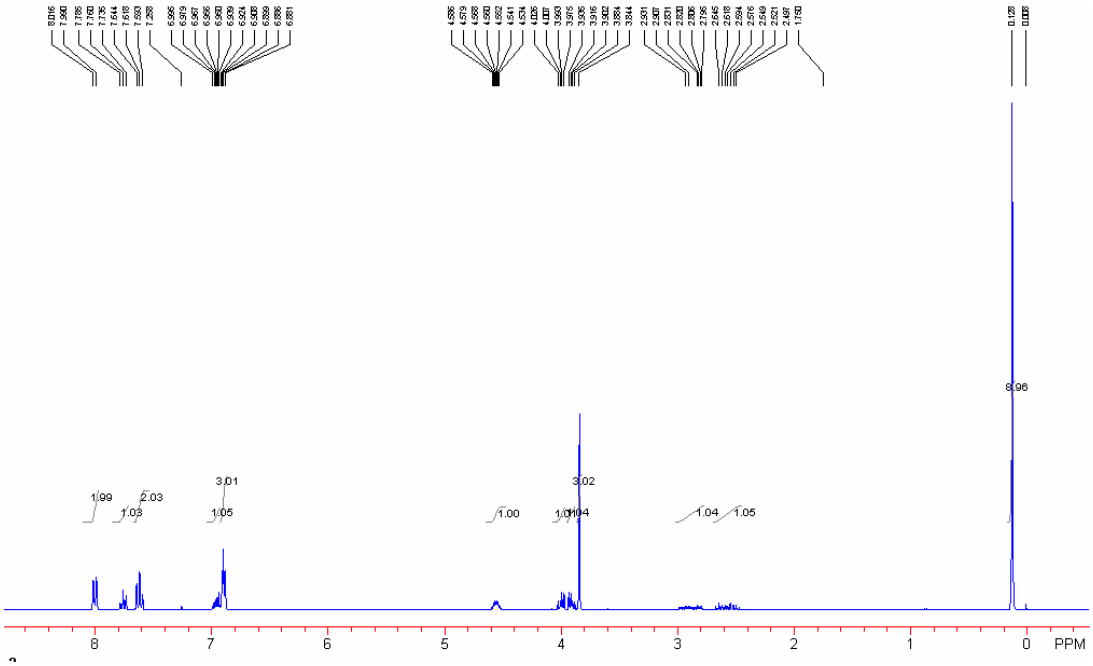


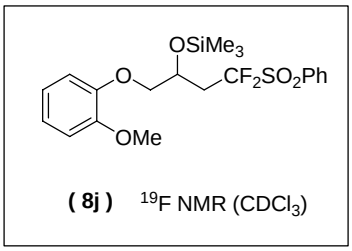
(8i) ^{13}C NMR ($CDCl_3$)



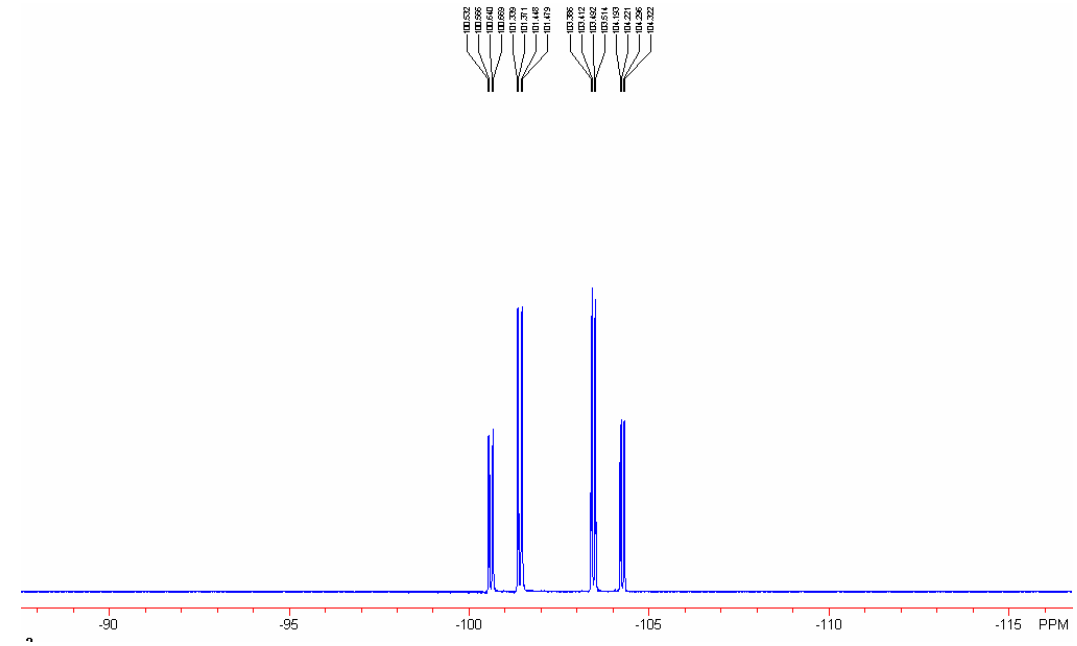


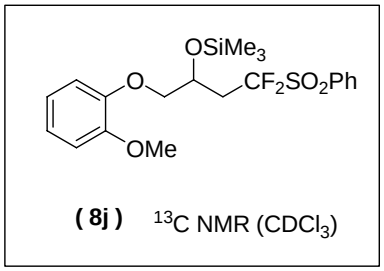
(8j) ^{1}H NMR ($CDCl_3$)



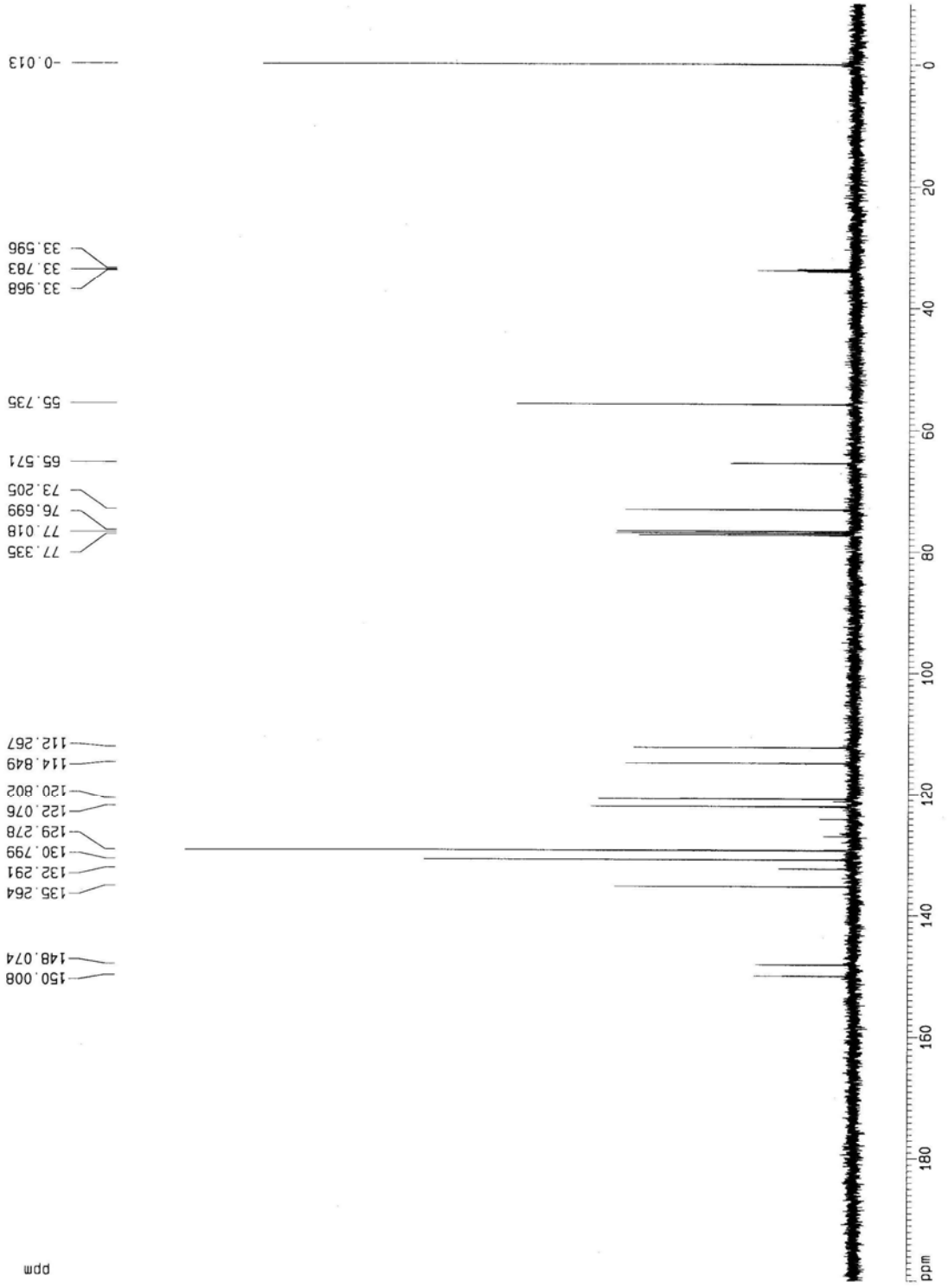


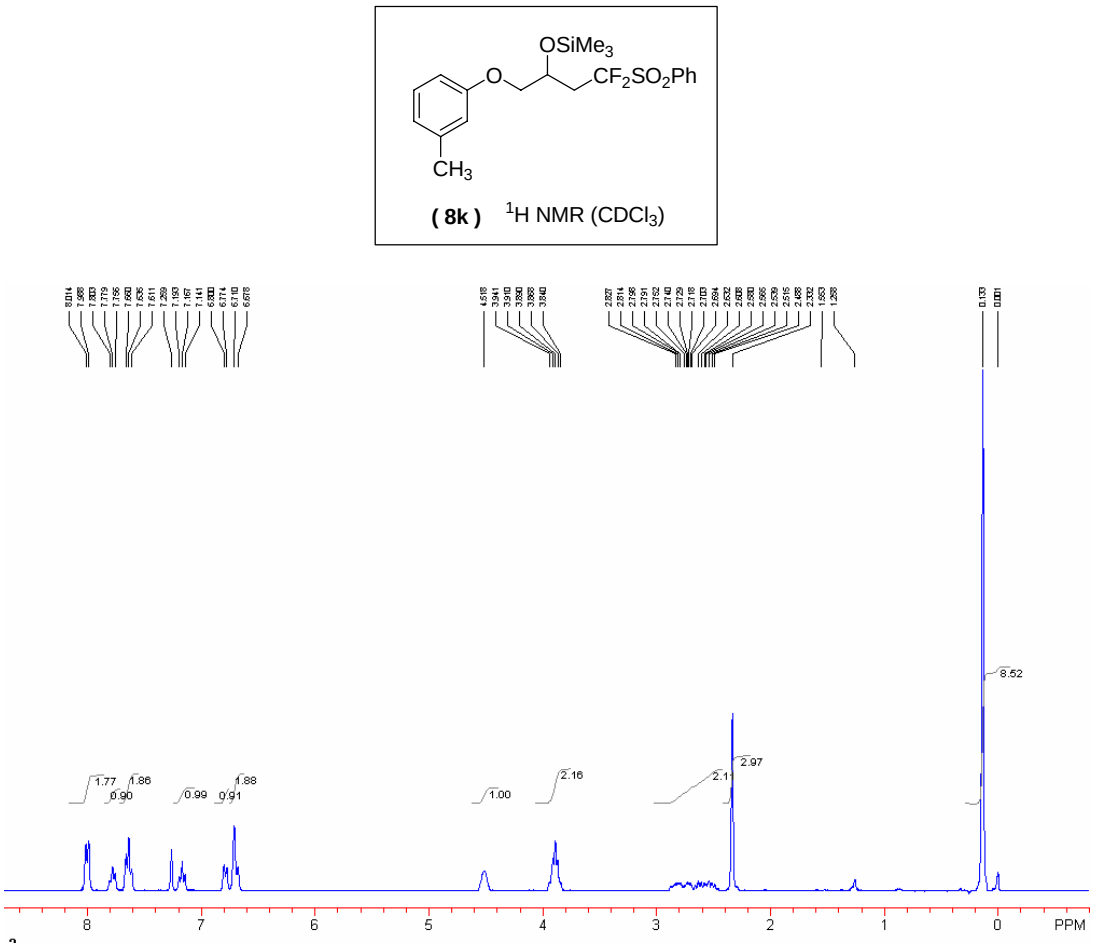
(8j) ^{19}F NMR ($CDCl_3$)

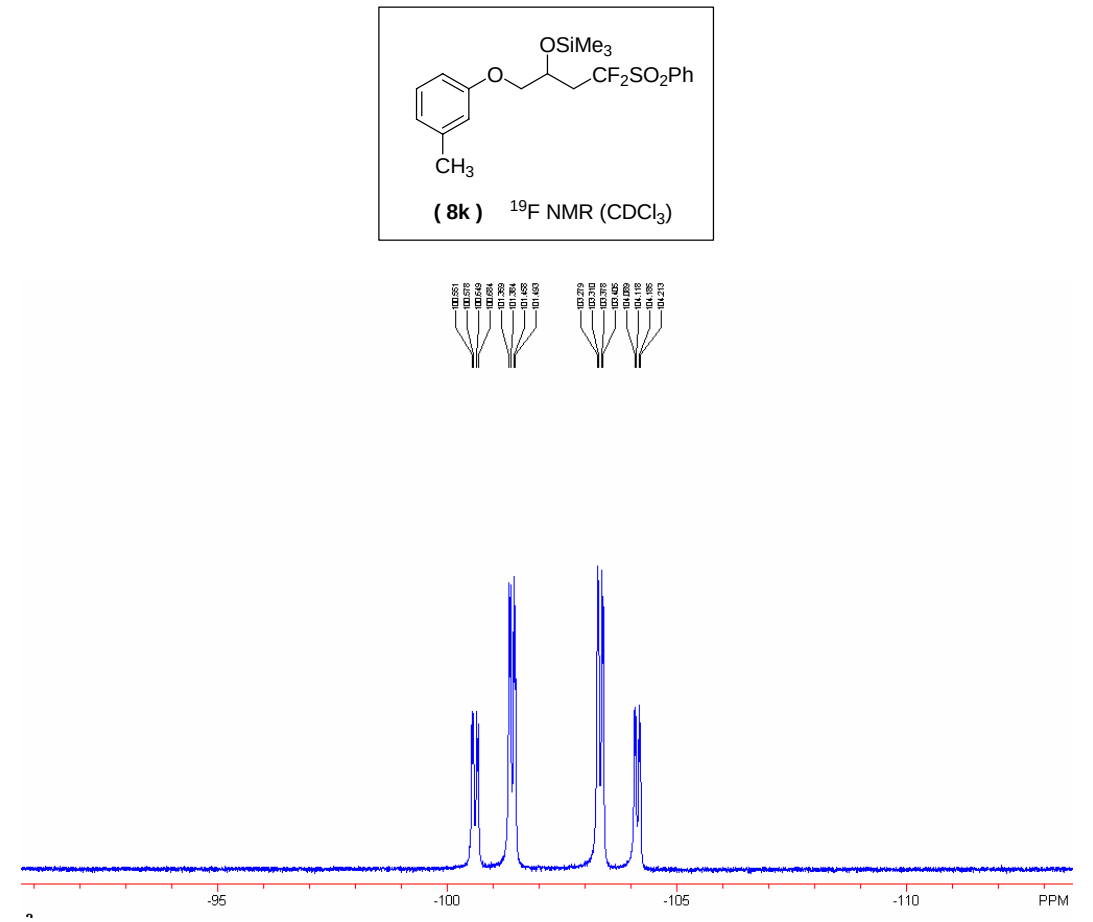


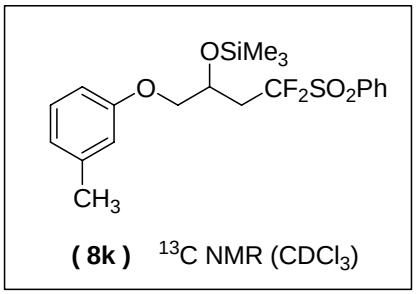


(8j) ^{13}C NMR ($CDCl_3$)

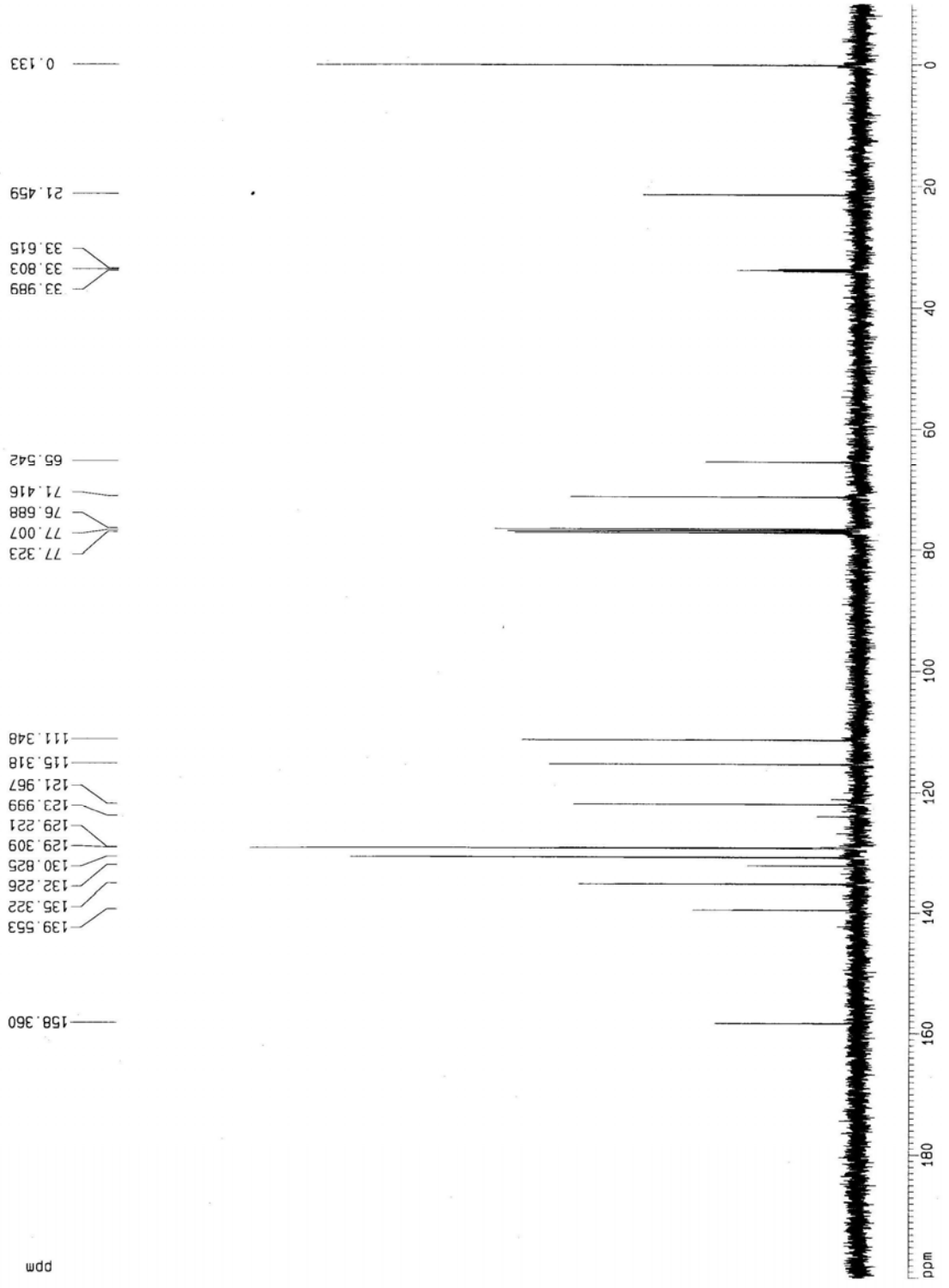


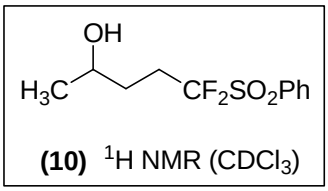

OSiMe3
O
CF2SO2Ph
CH3
(8k) 1H NMR (CDCl3)
1.77
1.86
0.90
0.99
1.88
0.91
1.00
2.16
2.11
2.97
8.52
8
7
6
5
4
3
2
1
0
PPM


OSiMe3
O
CF2SO2Ph
CH3
(8k) 19F NMR (CDCl3)
-95
-100
-105
-110
PPM

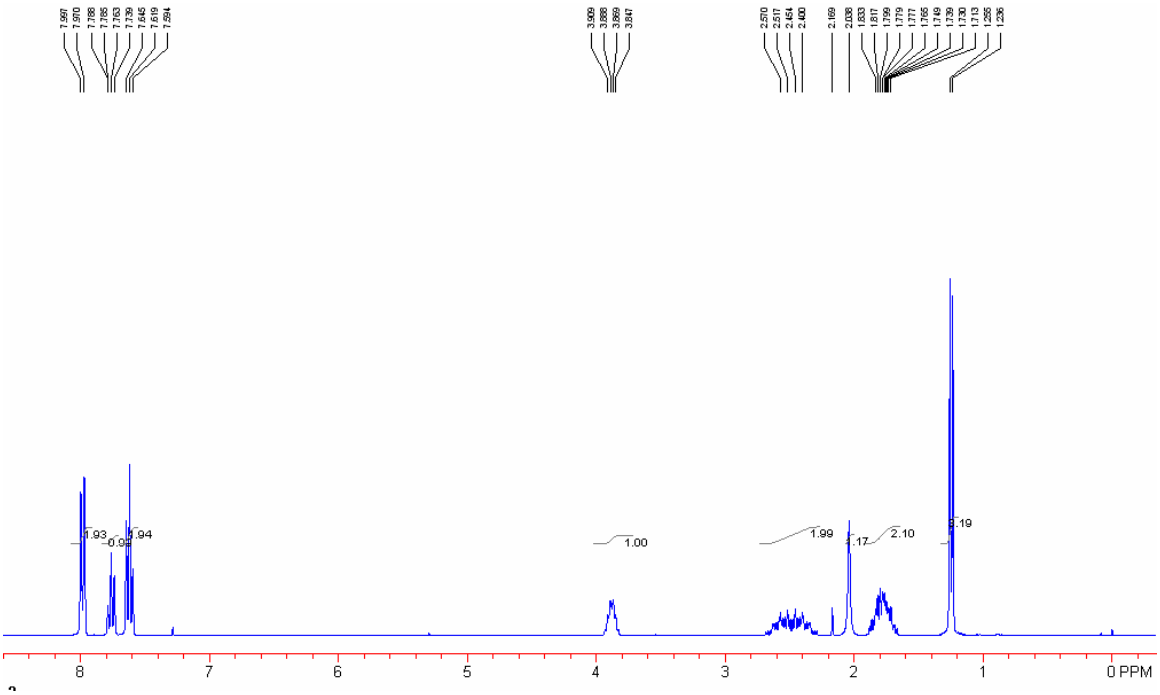


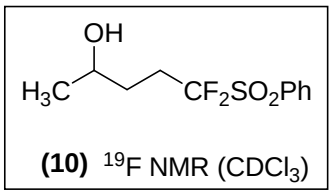
(8k) ^{13}C NMR ($CDCl_3$)



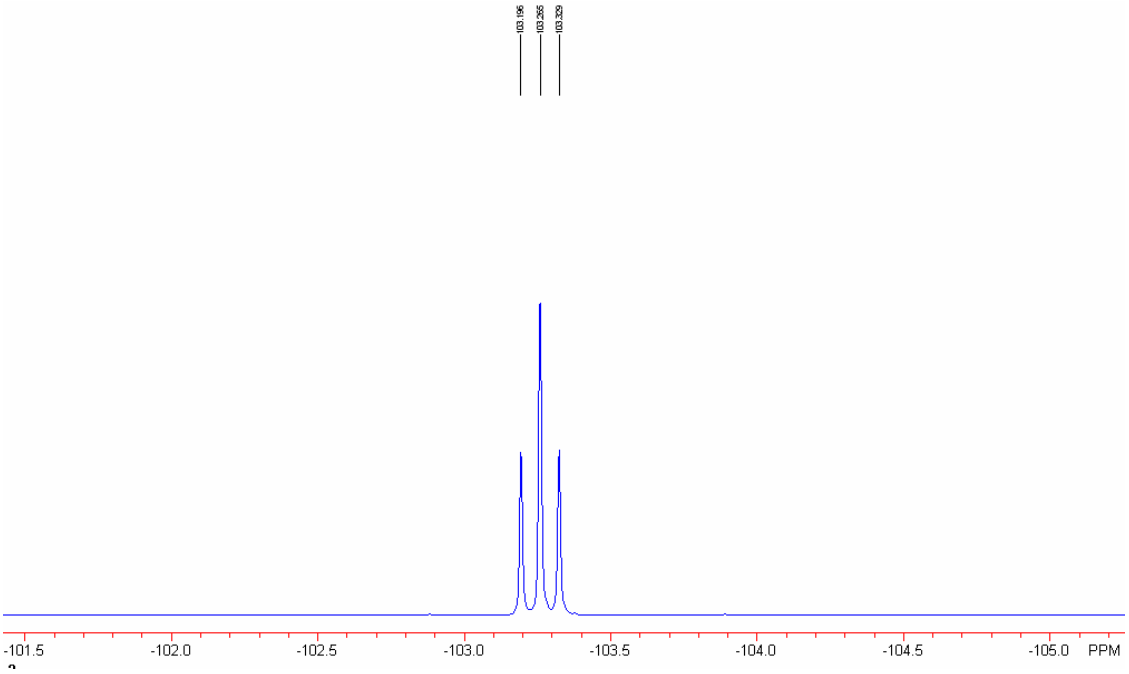


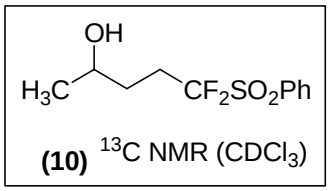
(10) ^{1}H NMR ($CDCl_3$)



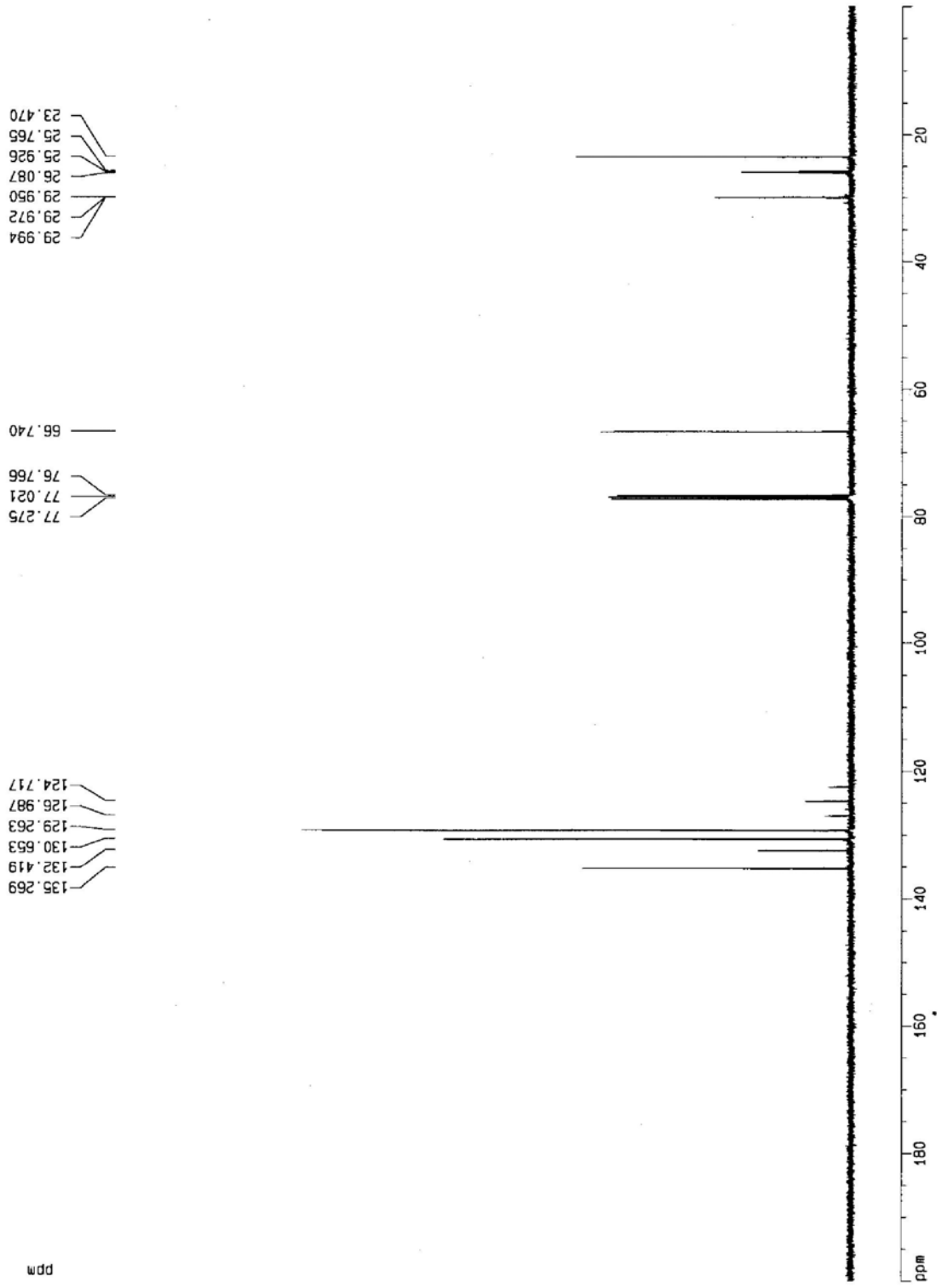


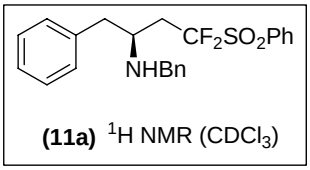
(10) ^{19}F NMR ($CDCl_3$)



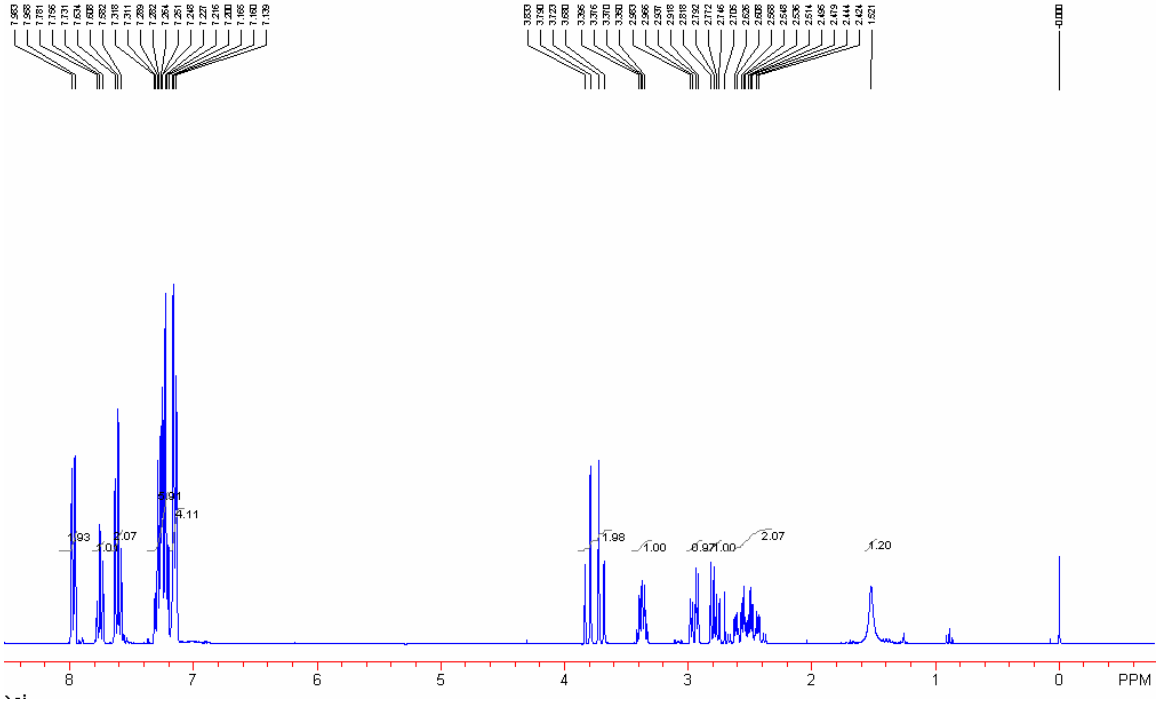


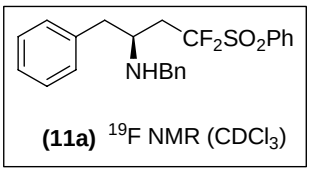
(10) ^{13}C NMR ($CDCl_3$)



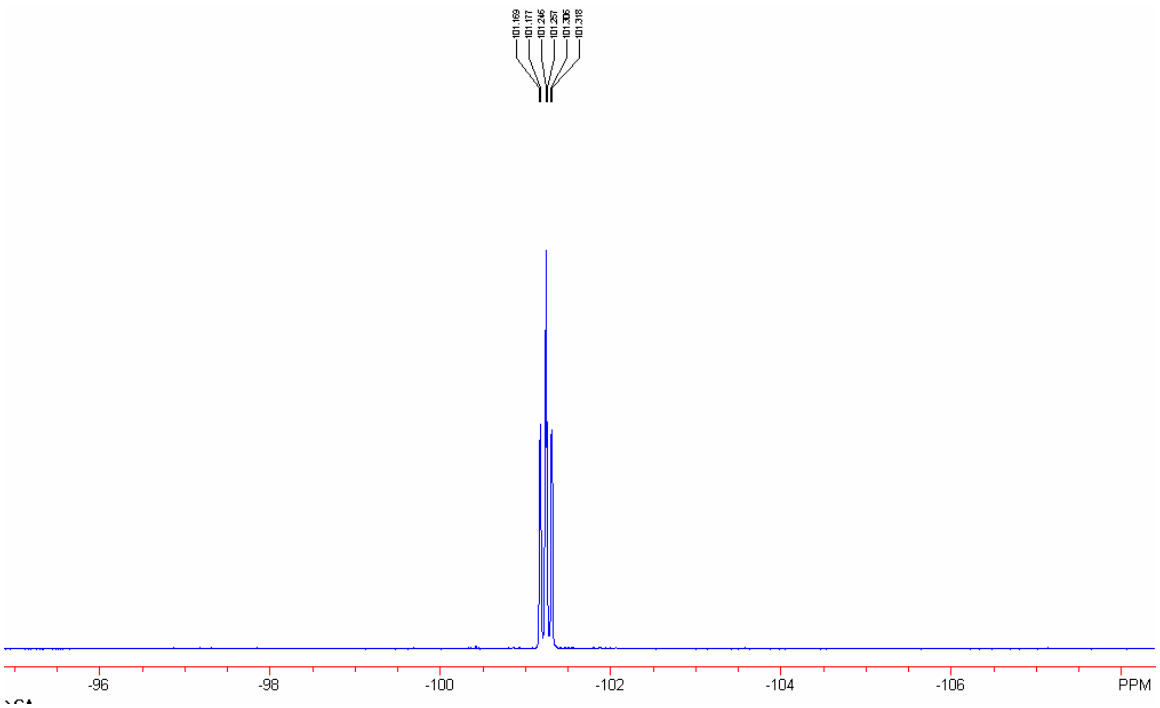


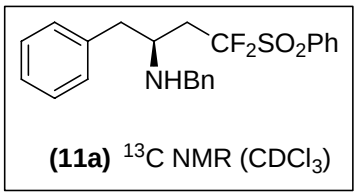
(11a) ^{1}H NMR ($CDCl_3$)



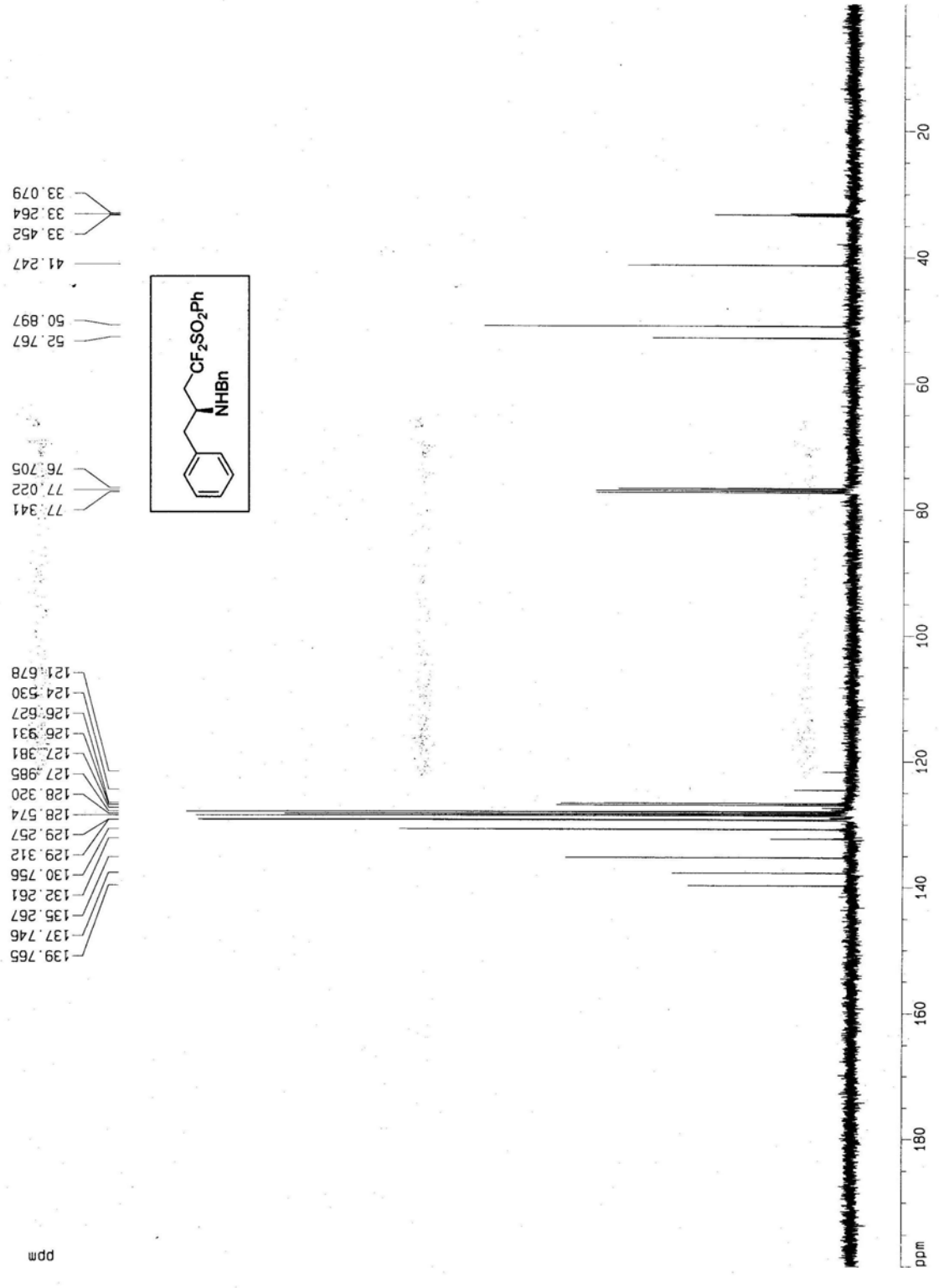


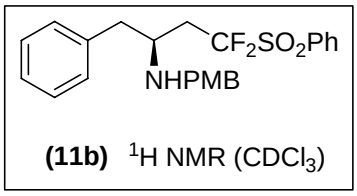
(11a) ^{19}F NMR ($CDCl_3$)



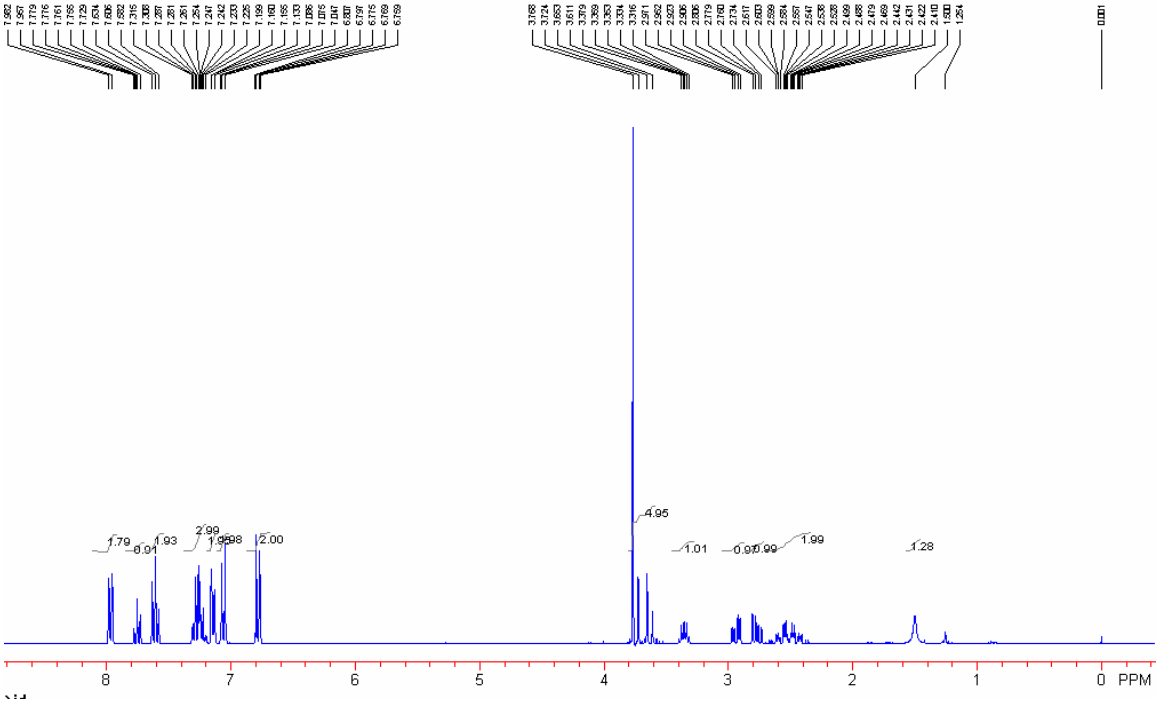


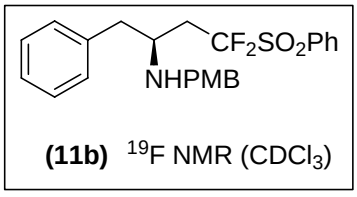
(11a) ^{13}C NMR ($CDCl_3$)



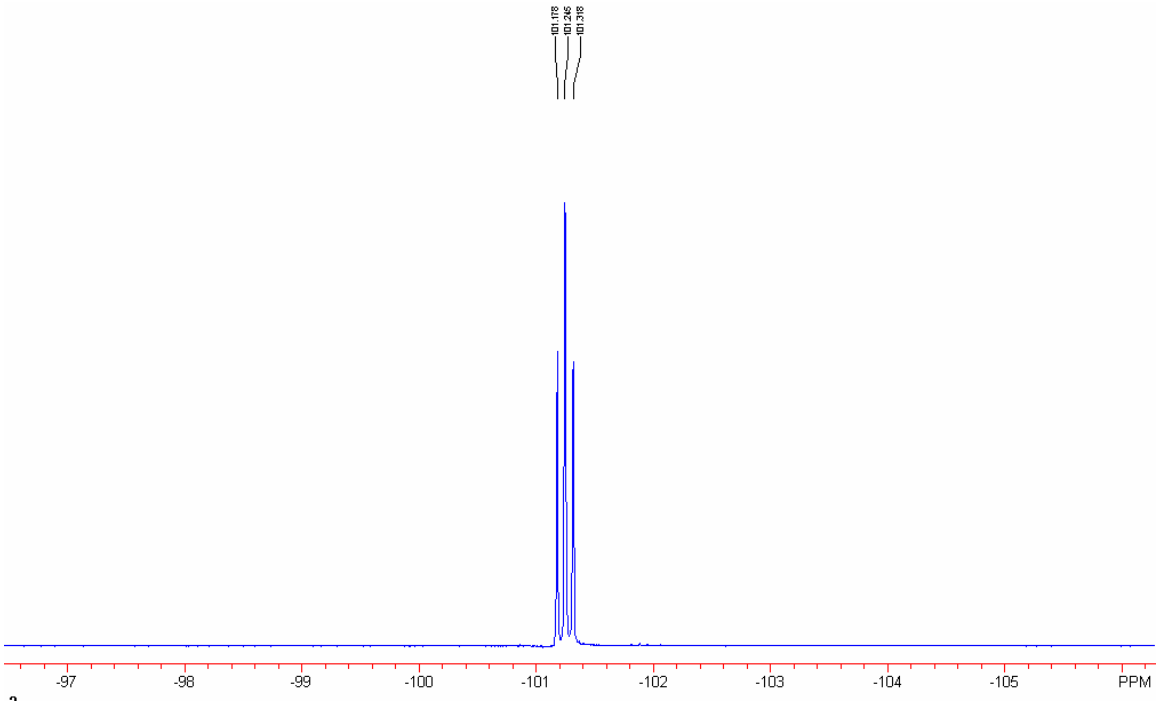


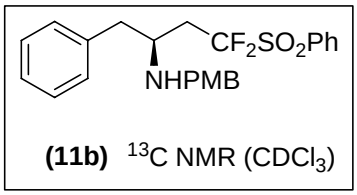
(11b) ^{1}H NMR ($CDCl_3$)



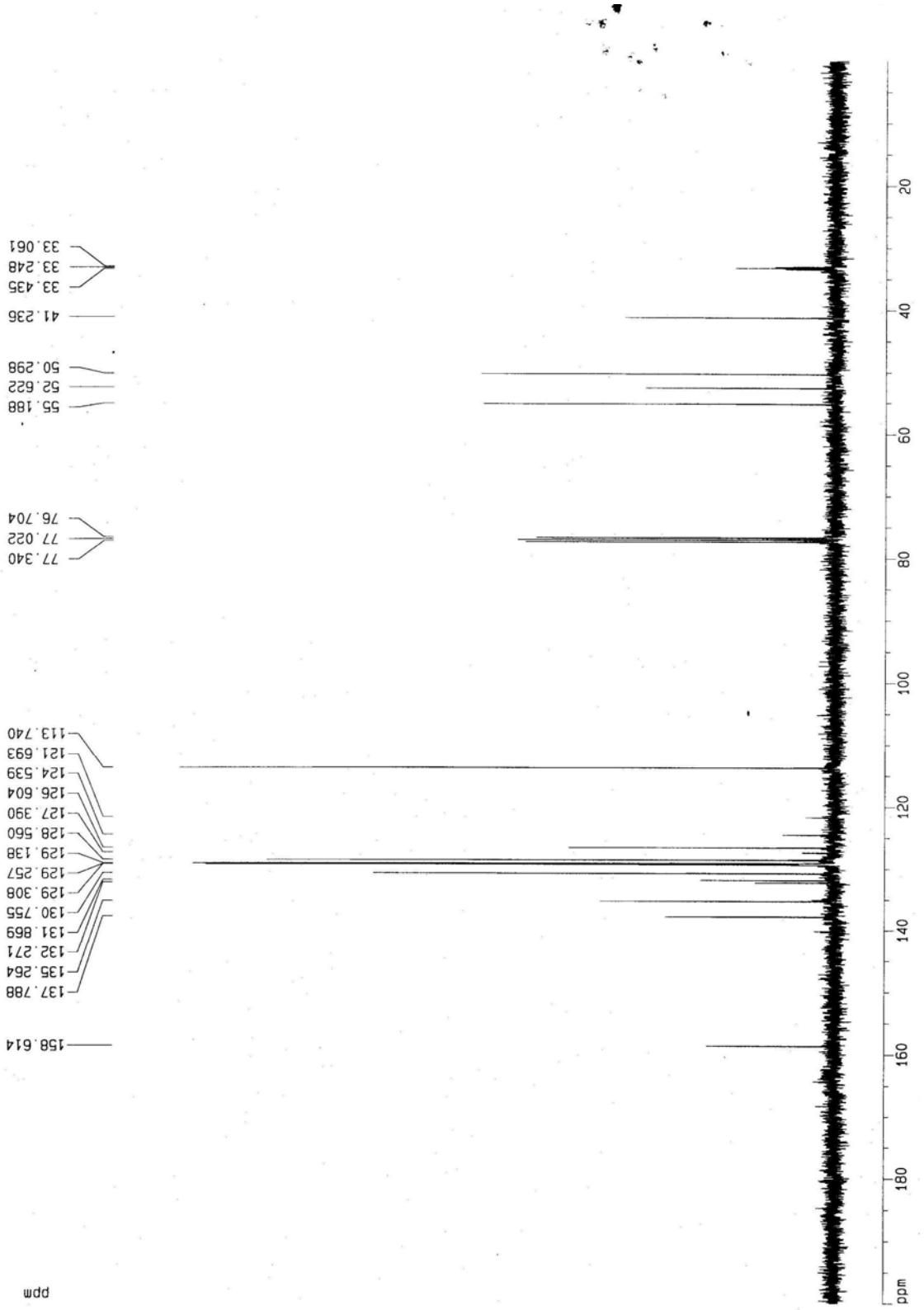


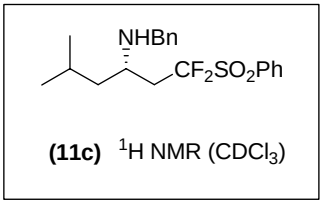
(11b) ^{19}F NMR ($CDCl_3$)



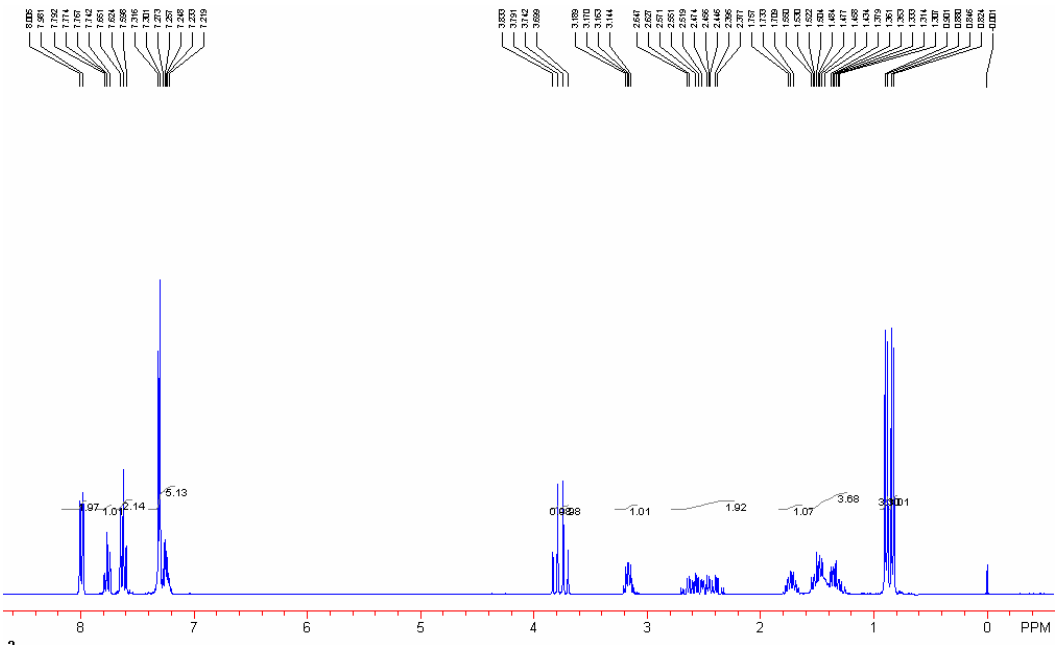


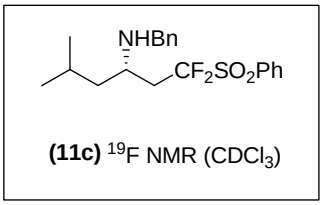
(11b) ^{13}C NMR ($CDCl_3$)



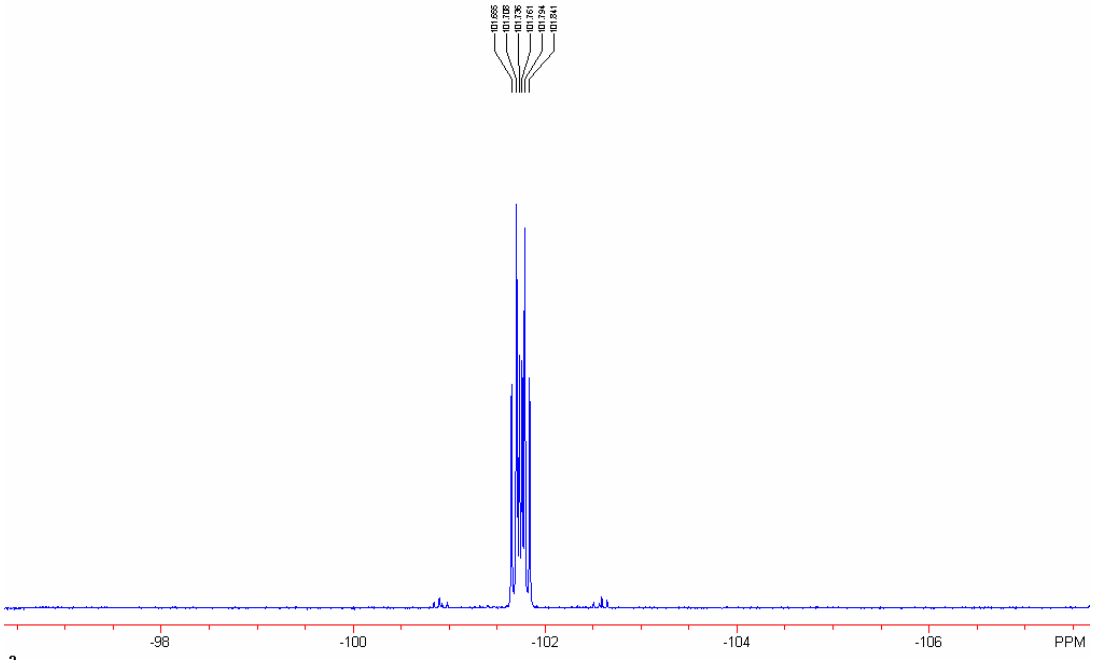


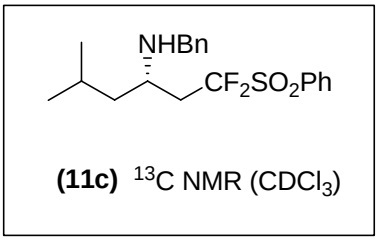
(11c) ^{1}H NMR ($CDCl_3$)



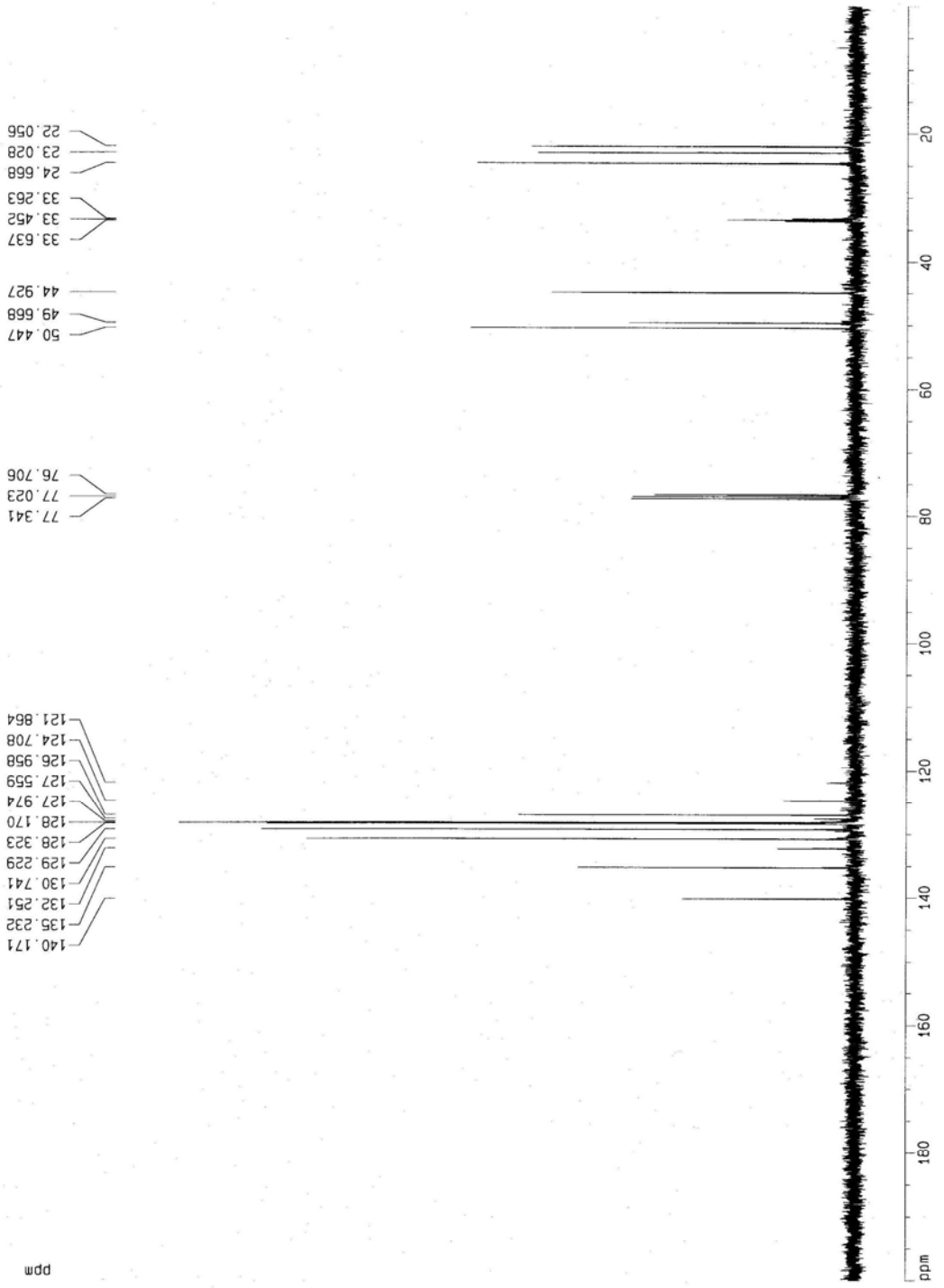


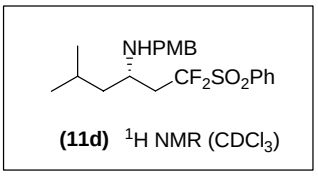
(11c) ^{19}F NMR ($CDCl_3$)



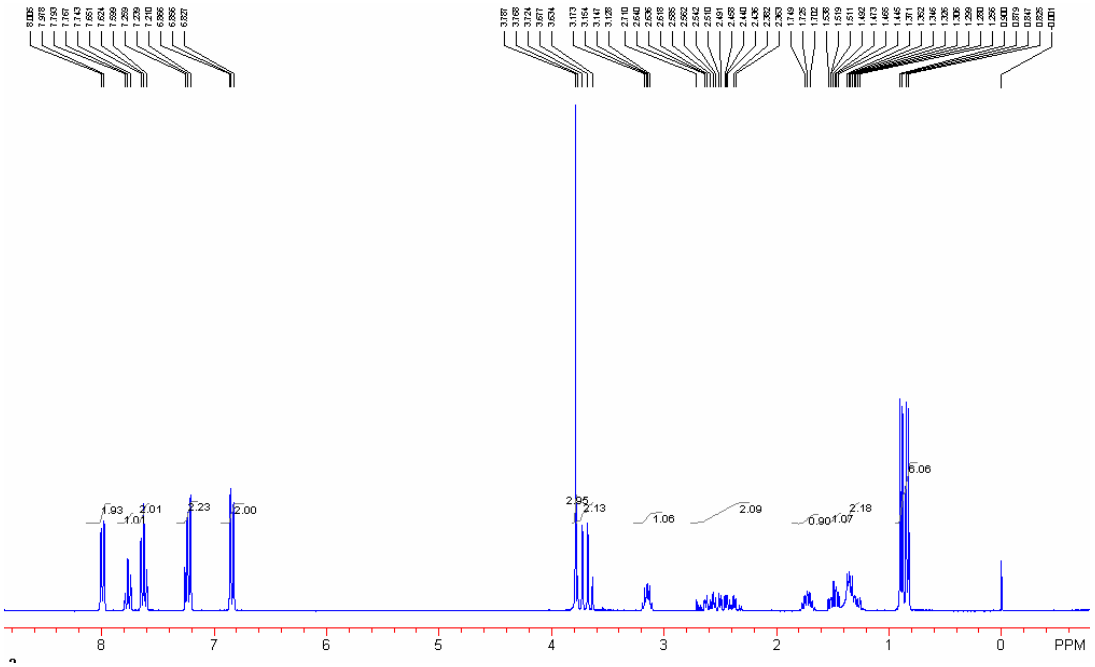


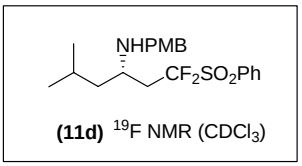
(11c) ^{13}C NMR ($CDCl_3$)



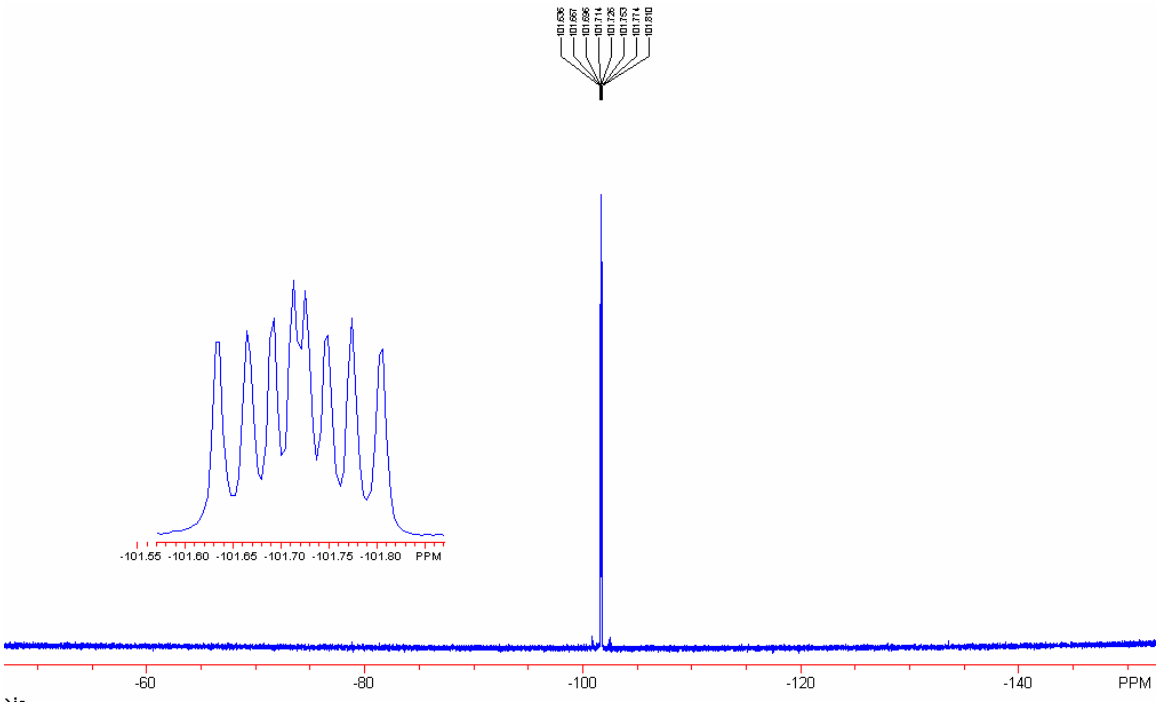


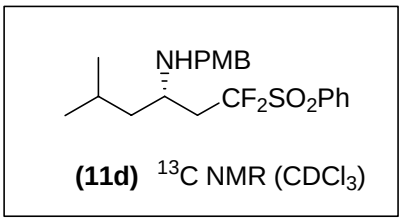
(11d) ^{1}H NMR ($CDCl_3$)



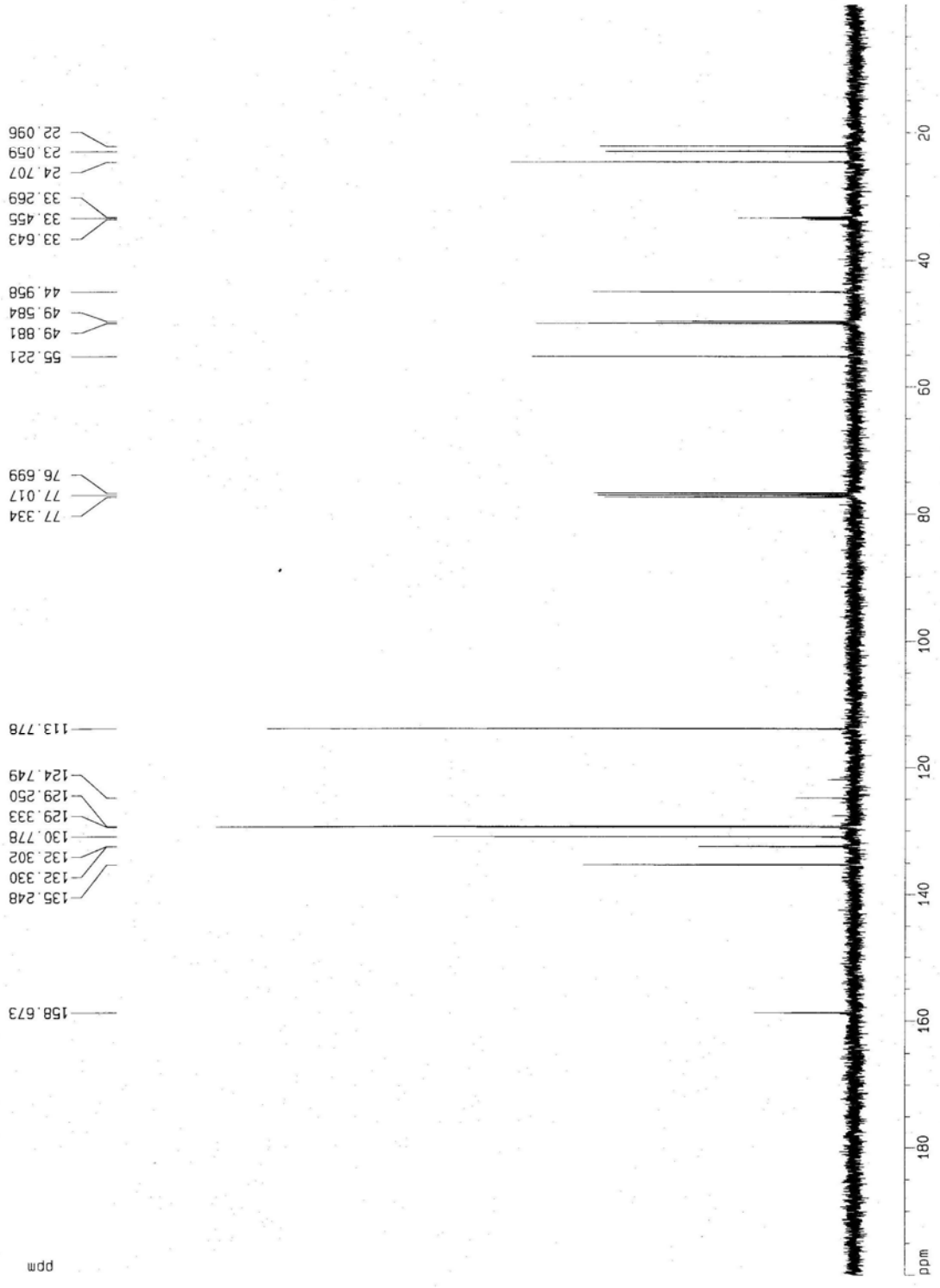


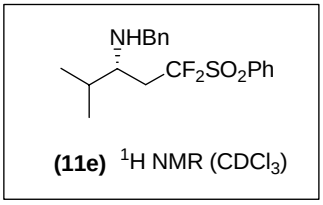
(11d) ^{19}F NMR ($CDCl_3$)



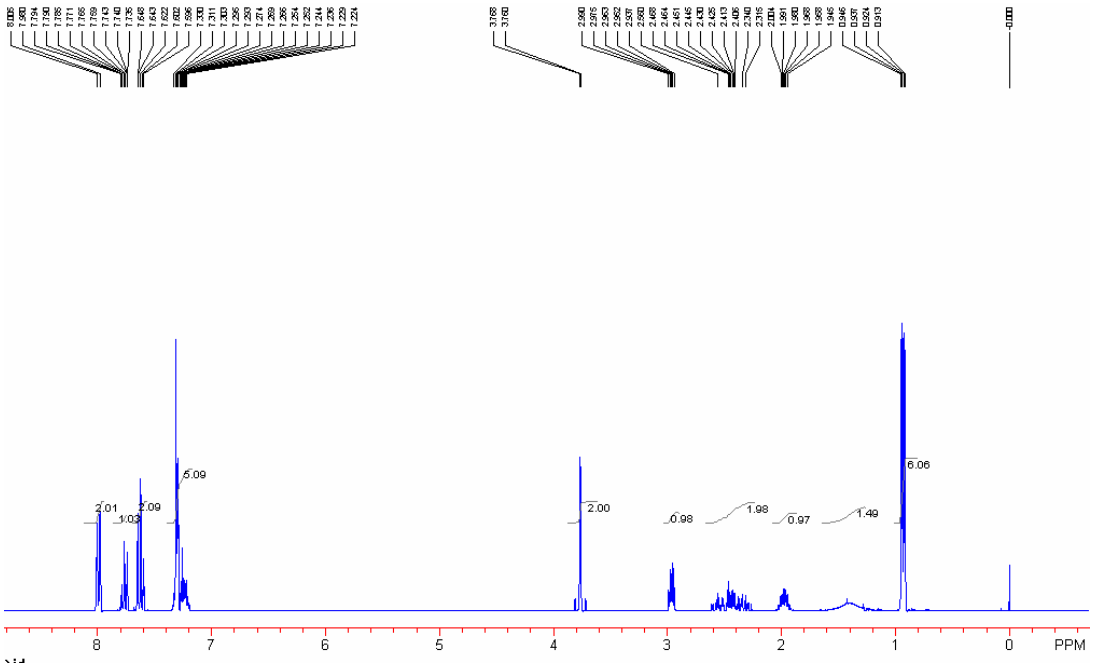


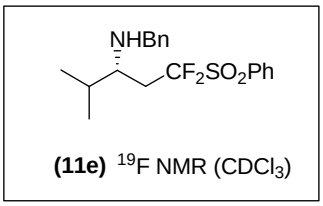
(11d) ^{13}C NMR ($CDCl_3$)



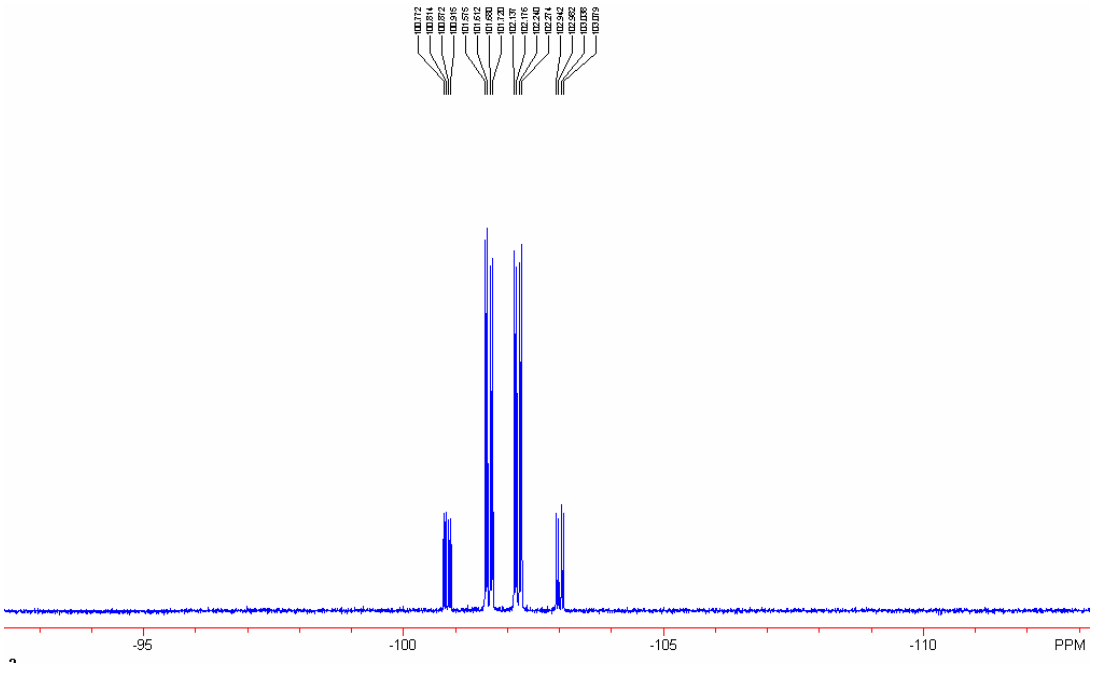


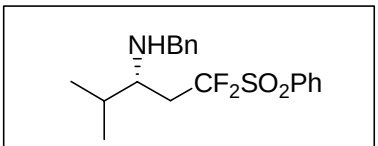
(11e) ^{1}H NMR ($CDCl_3$)



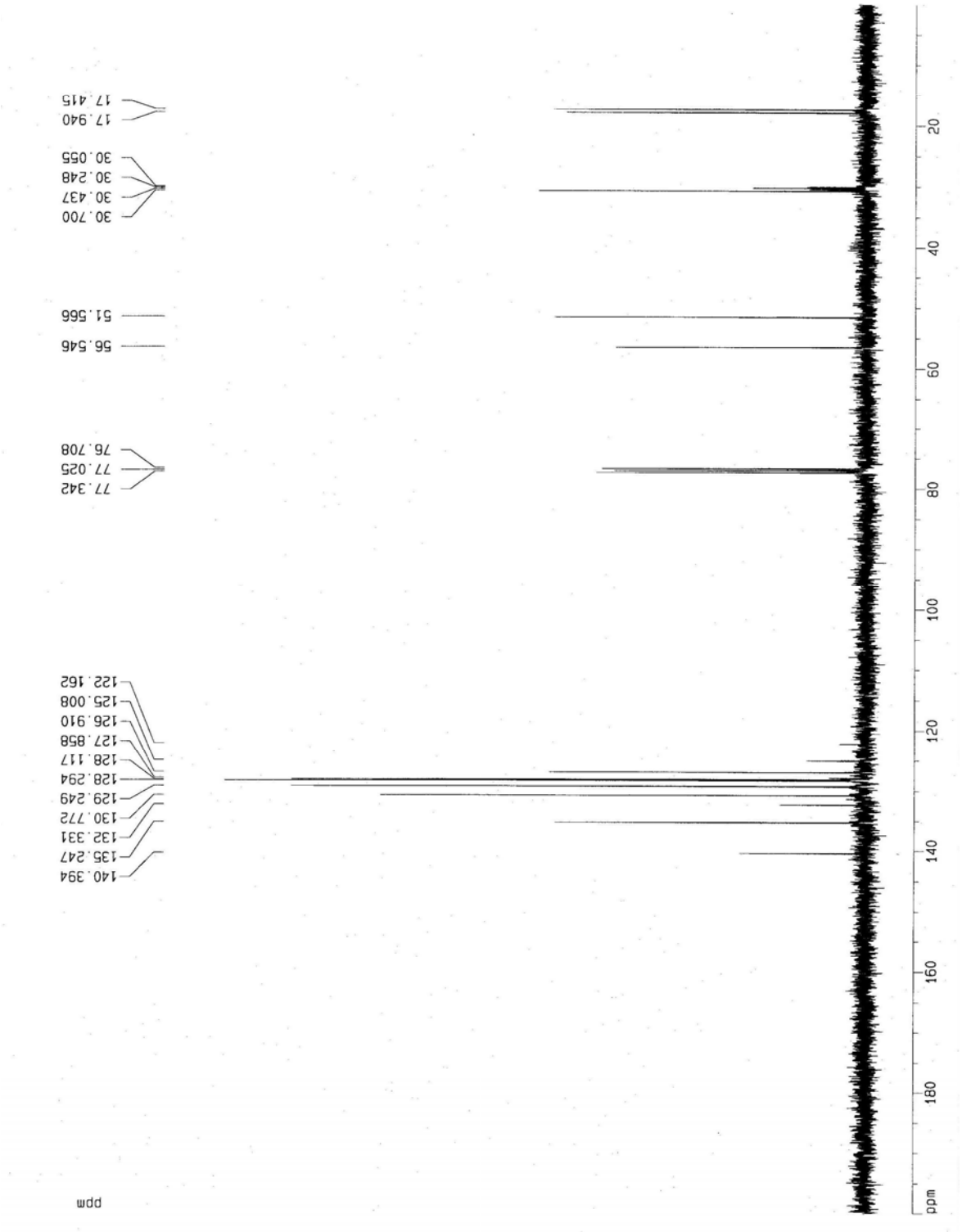


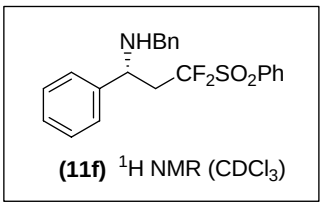
(11e) ^{19}F NMR ($CDCl_3$)



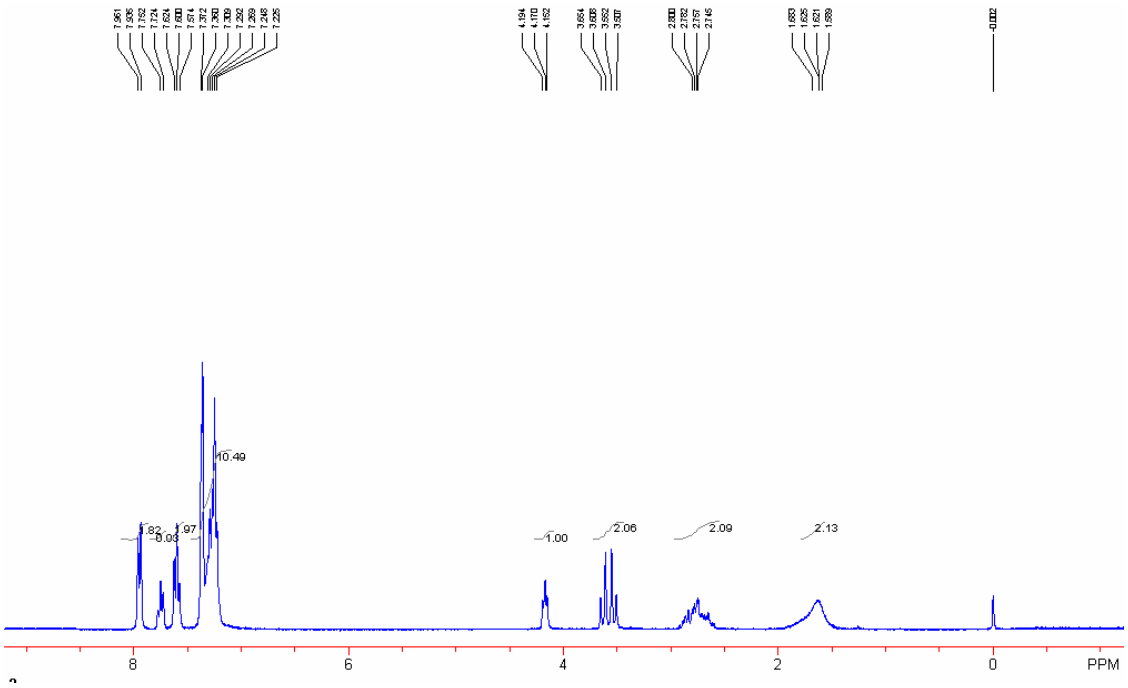


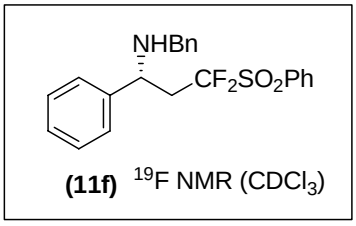
(11e) ^{13}C NMR ($CDCl_3$)



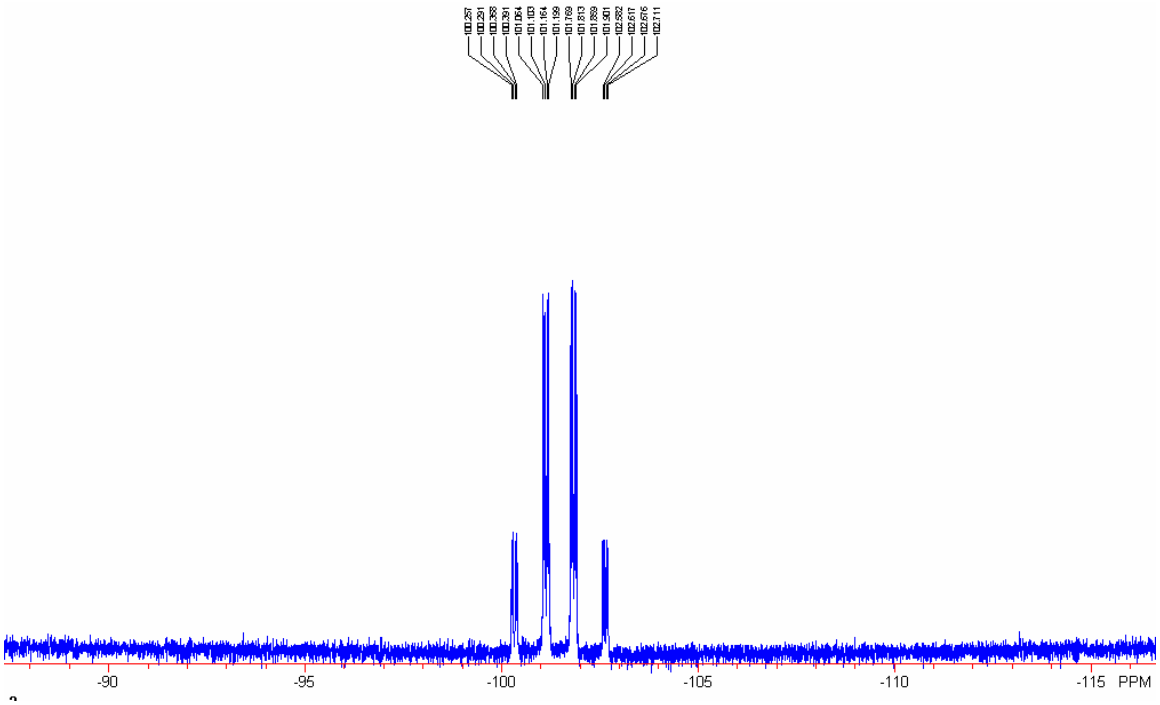


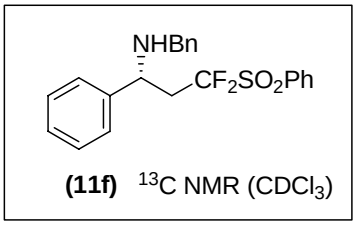
(11f) ^{1}H NMR ($CDCl_3$)



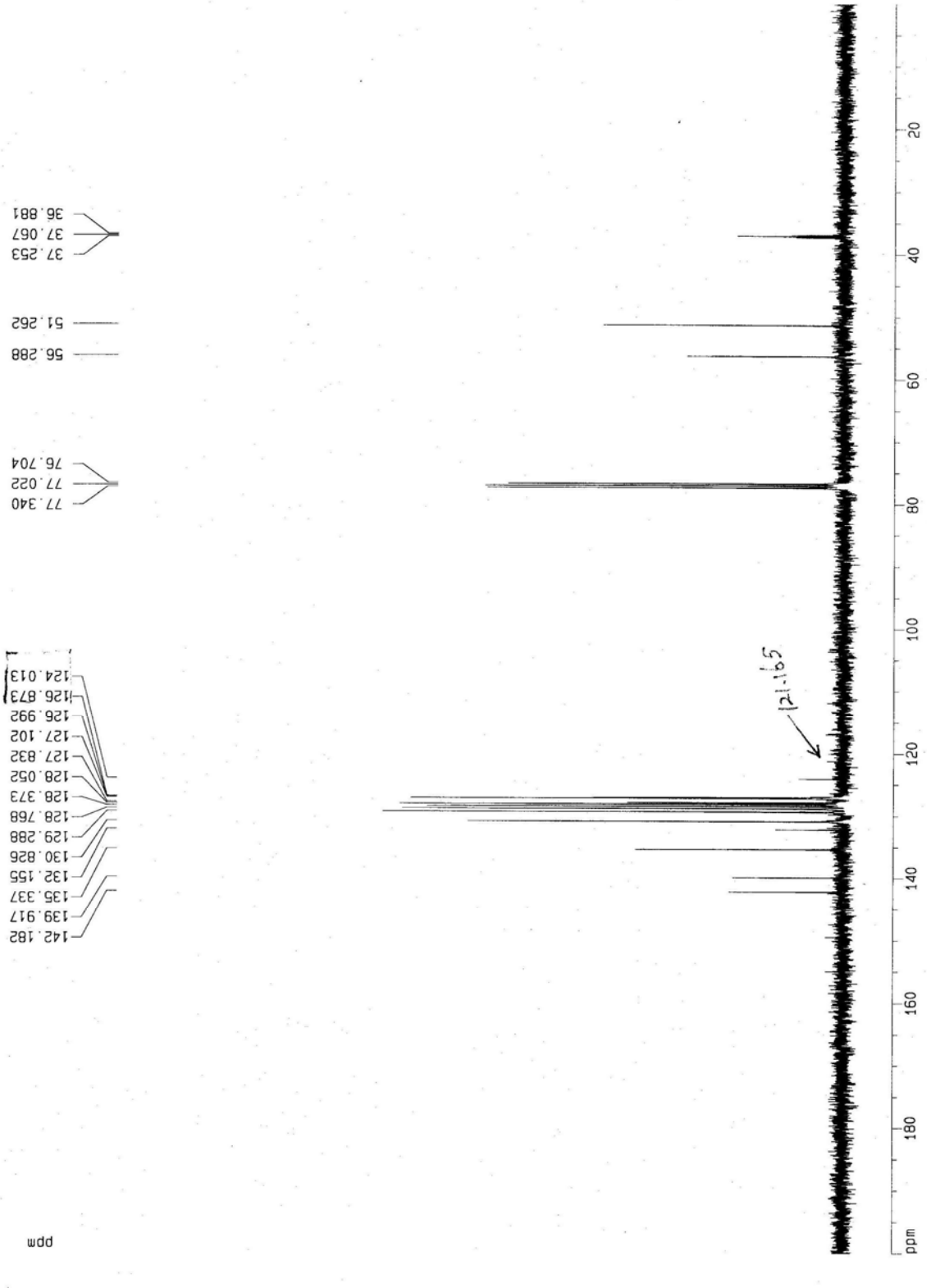


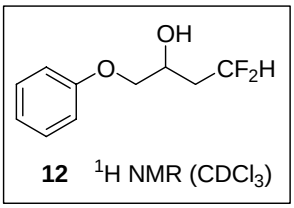
(11f) ^{19}F NMR ($CDCl_3$)



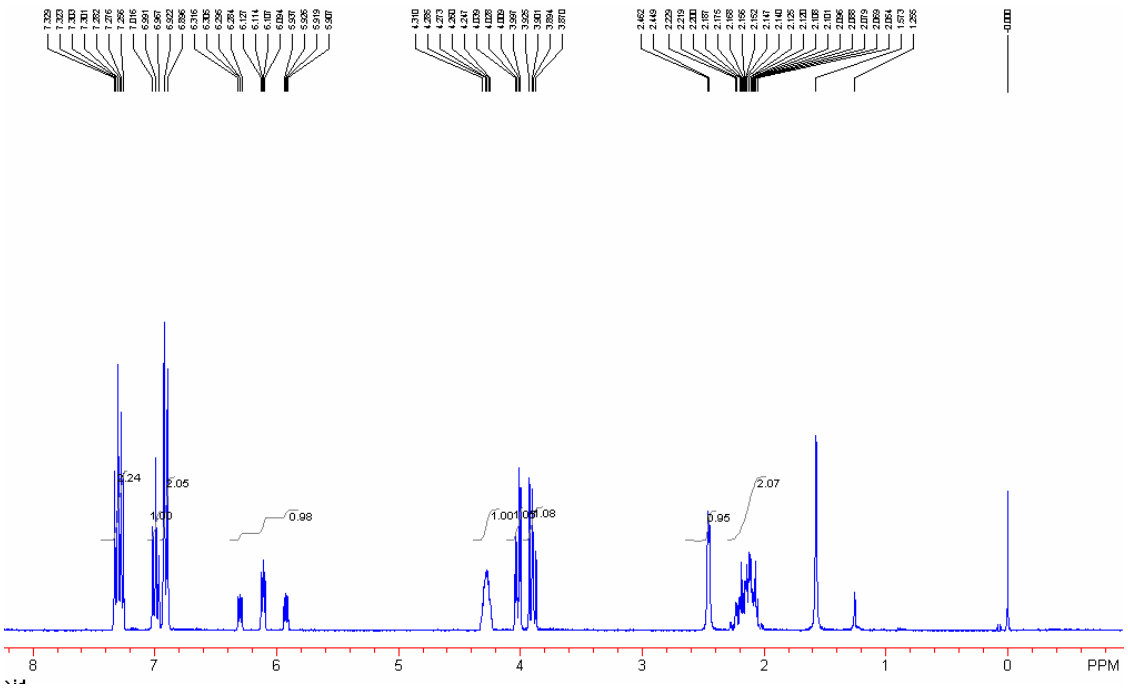


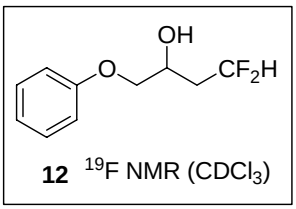
(11f) ^{13}C NMR ($CDCl_3$)



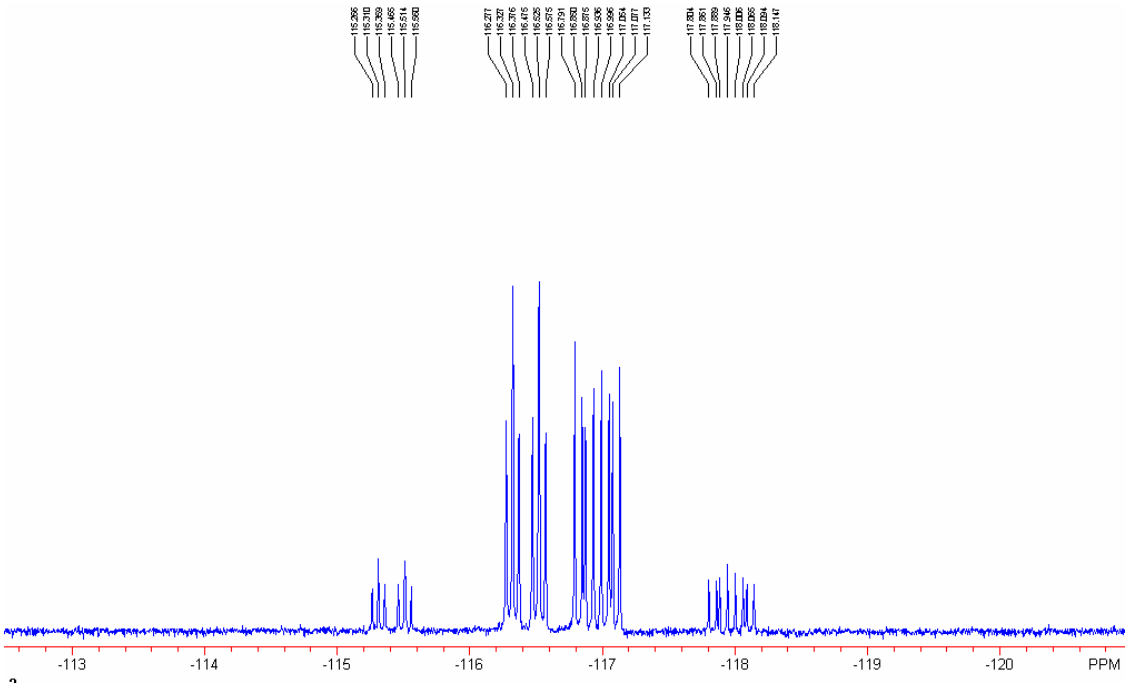


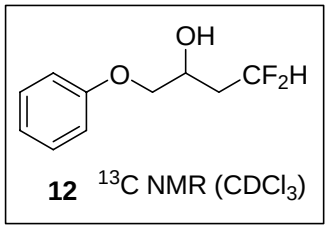
12 ^{1}H NMR ($CDCl_3$)



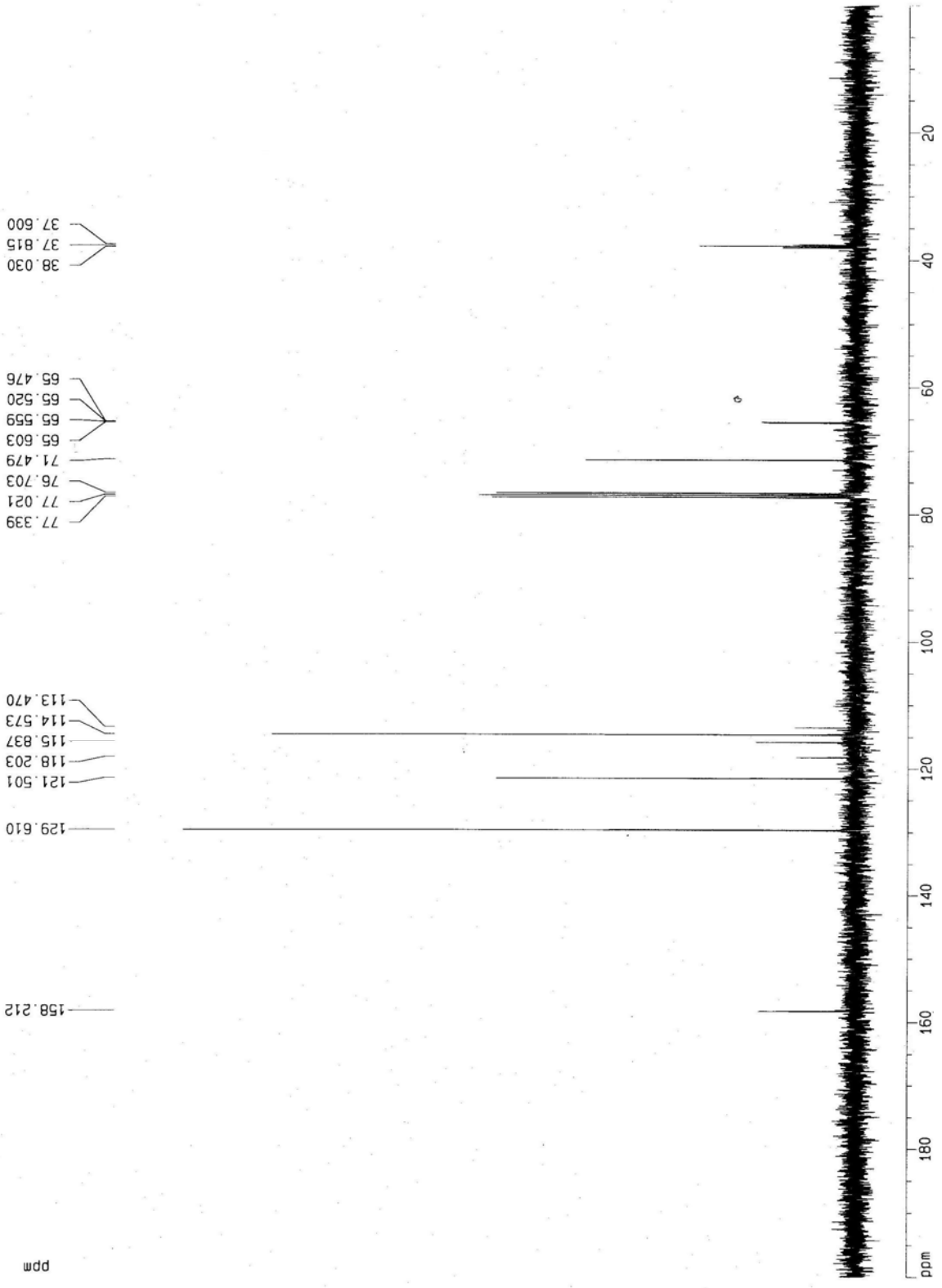


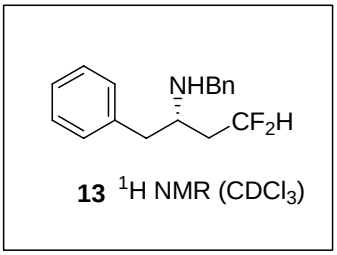
12 ^{19}F NMR ($CDCl_3$)



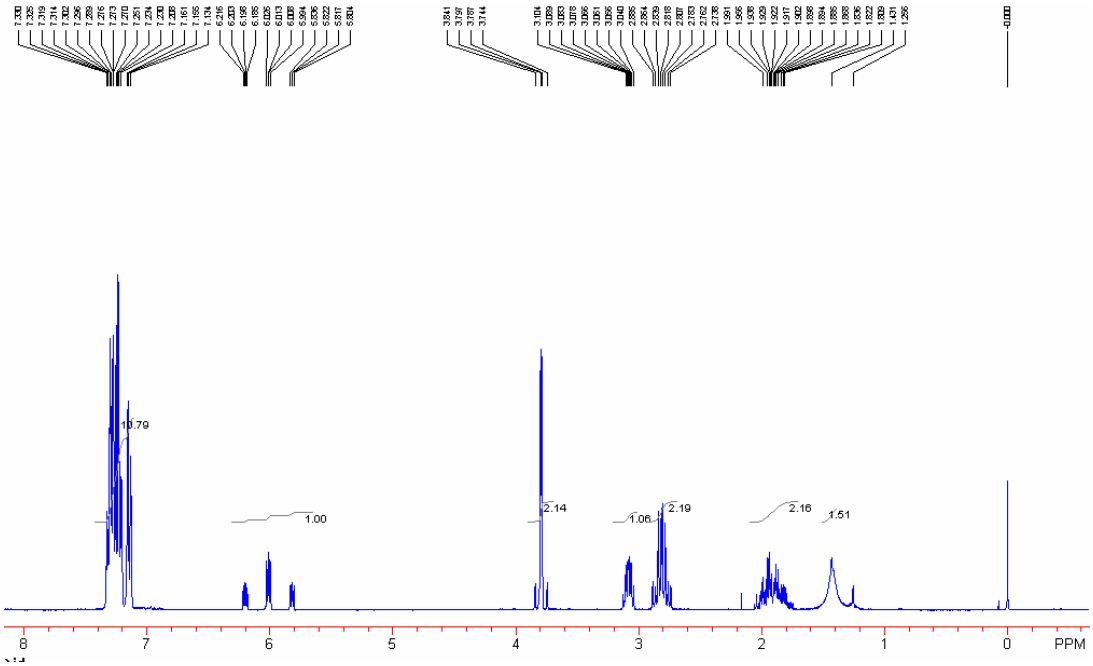


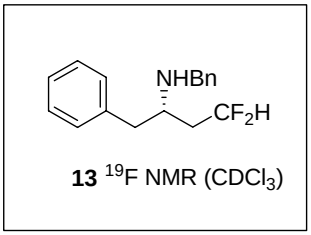
12 ^{13}C NMR ($CDCl_3$)



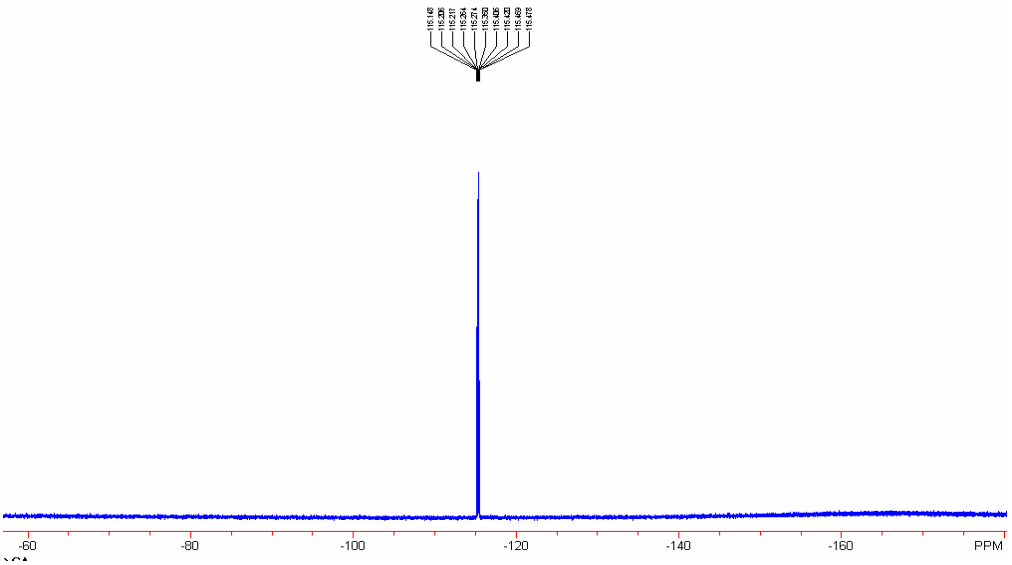


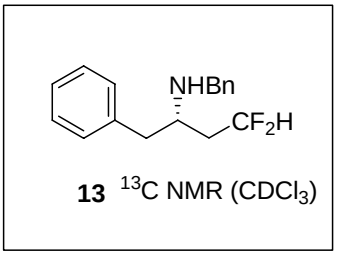
13 ^{1}H NMR ($CDCl_3$)



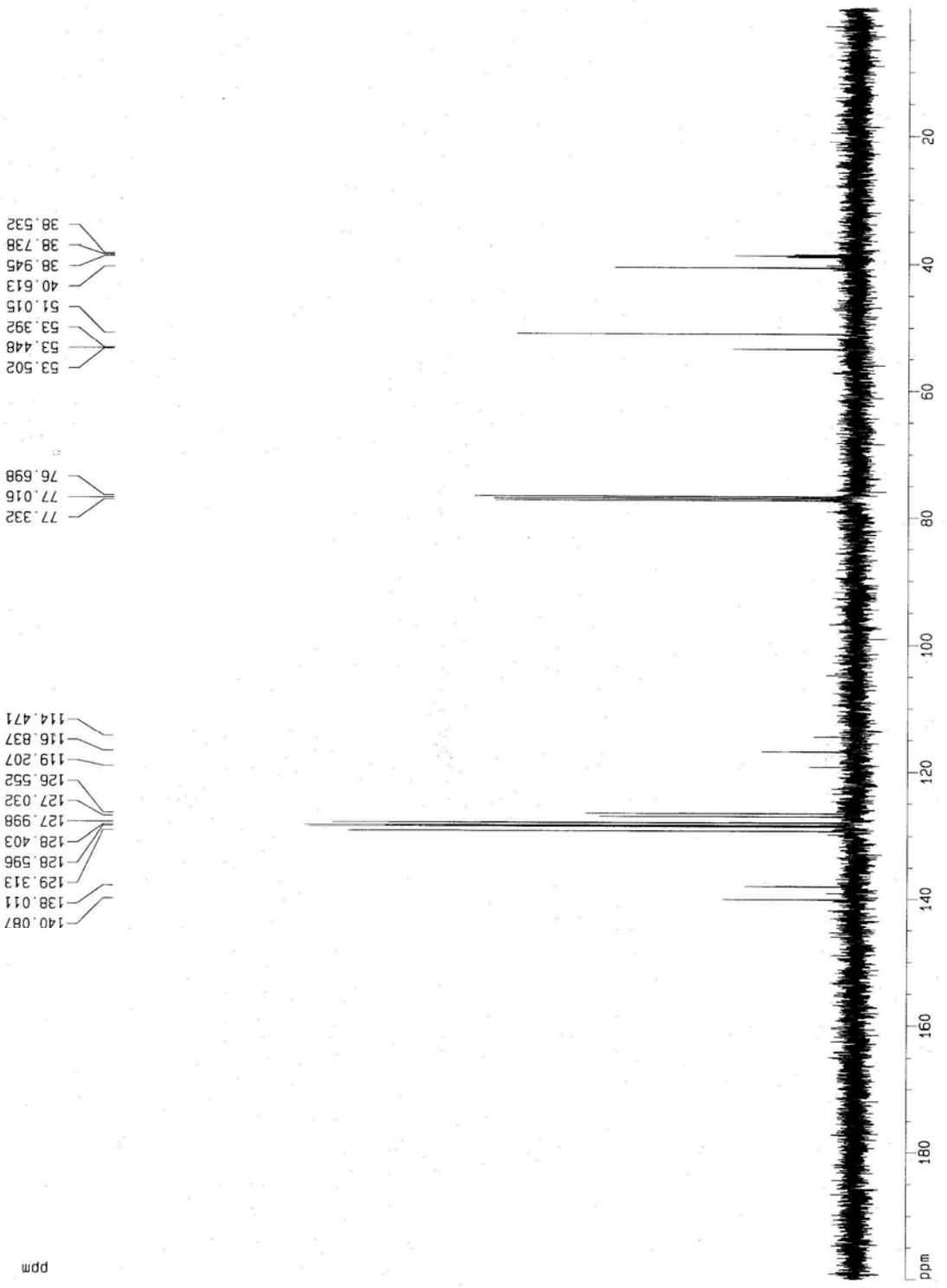


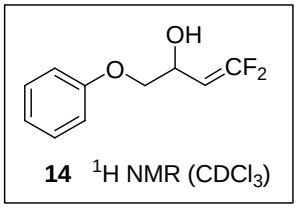
13 ^{19}F NMR ($CDCl_3$)



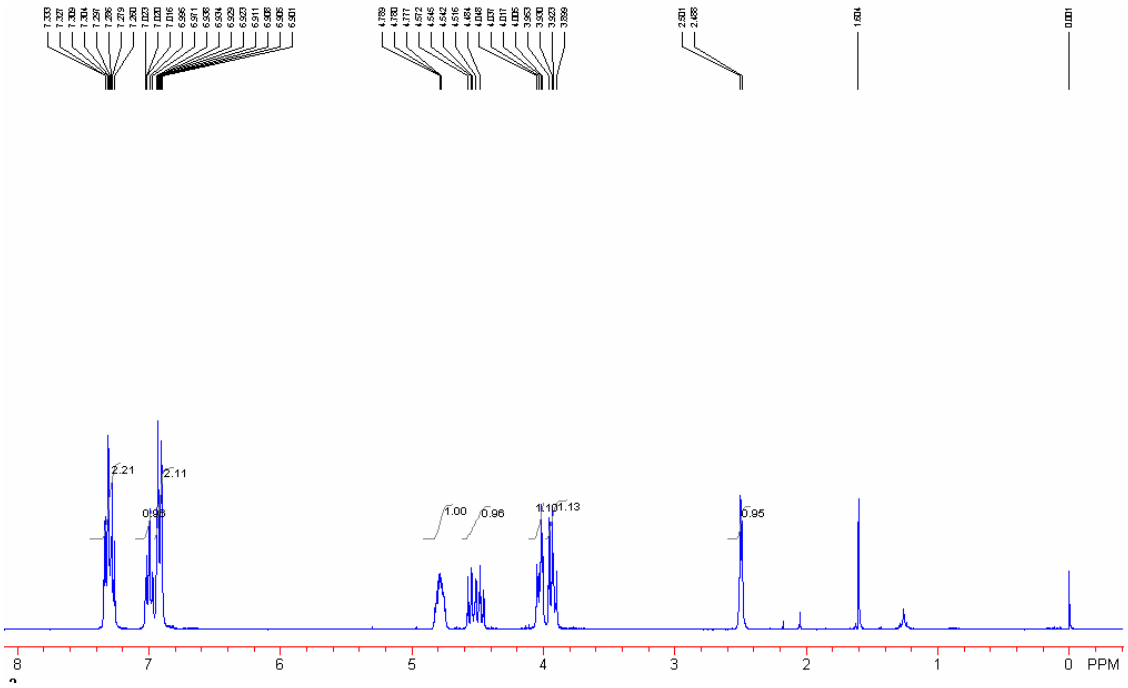


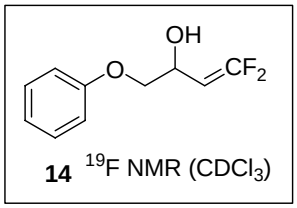
13 ^{13}C NMR ($CDCl_3$)



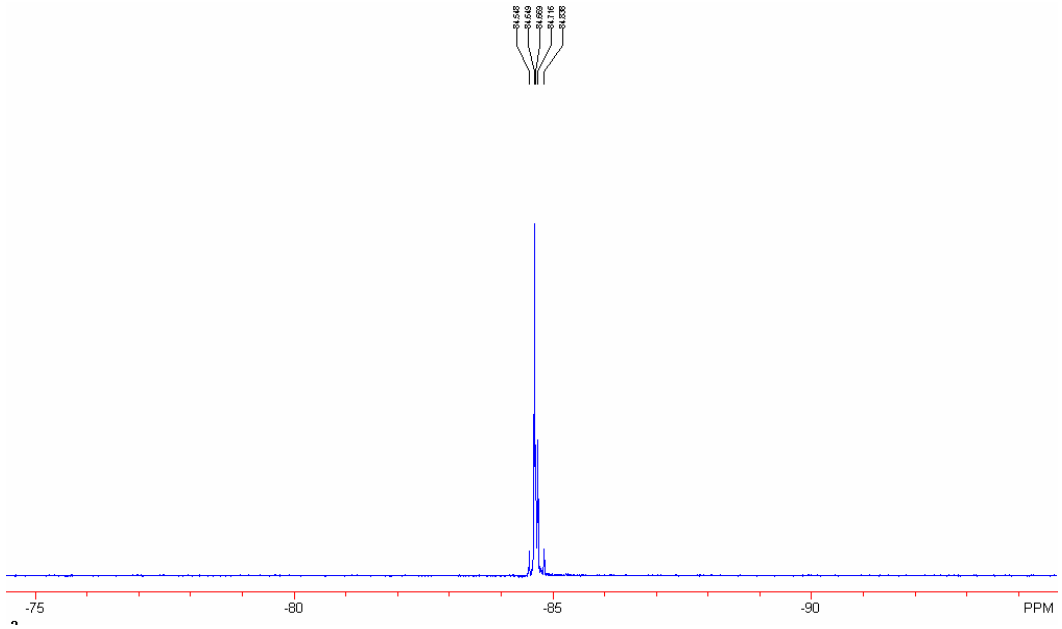


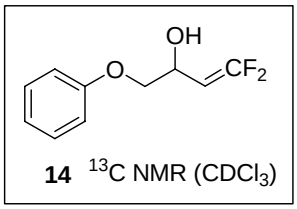
14 ^{1}H NMR ($CDCl_3$)



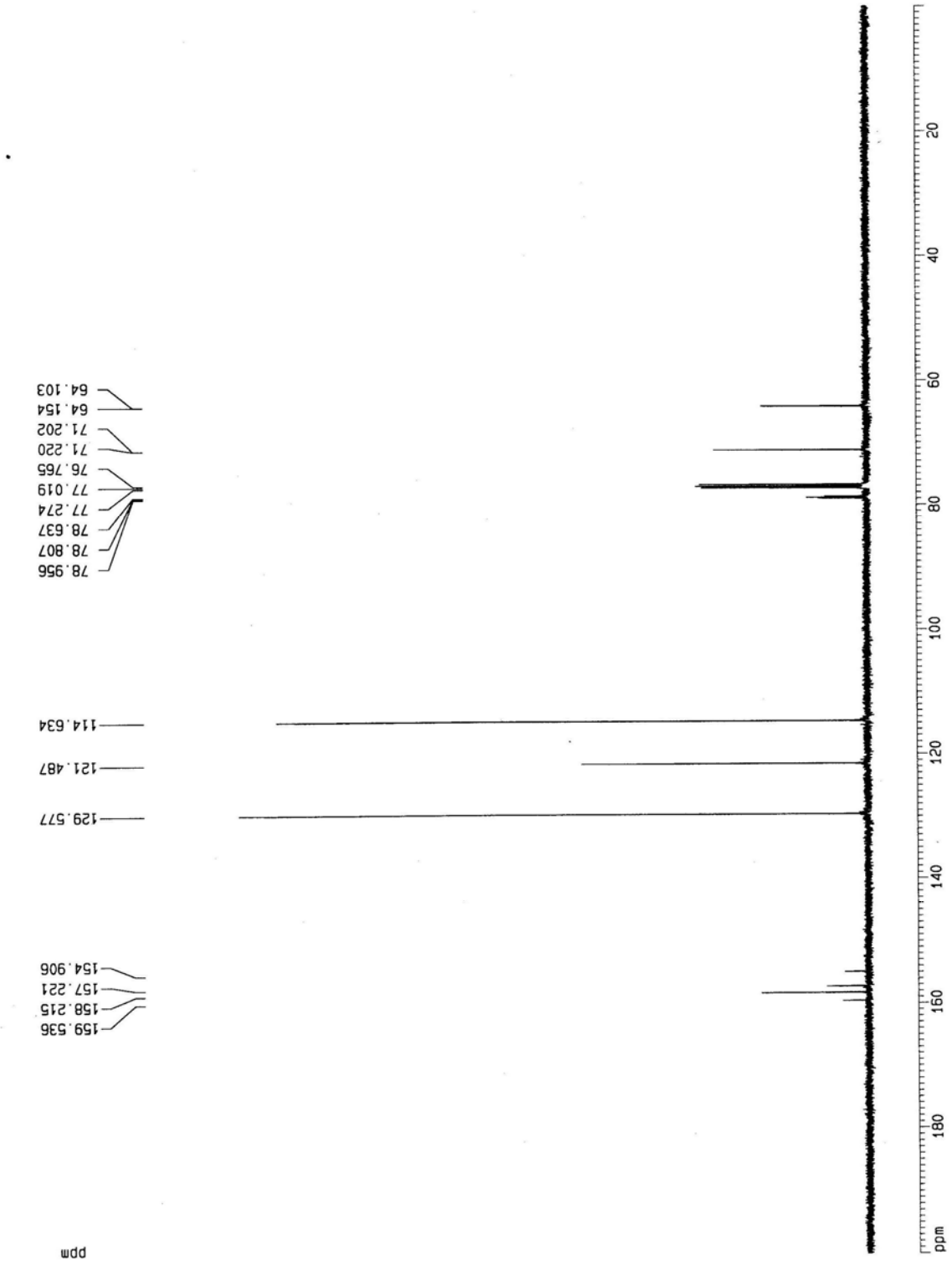


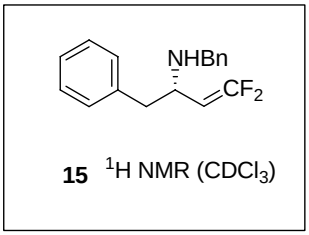
14 ^{19}F NMR ($CDCl_3$)



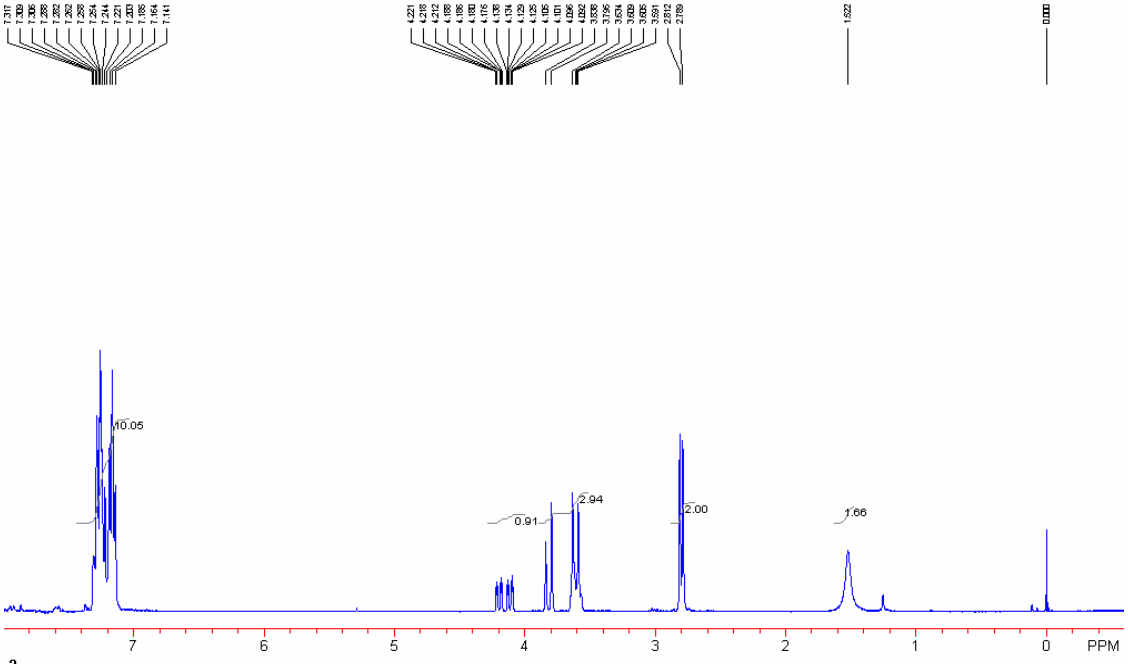


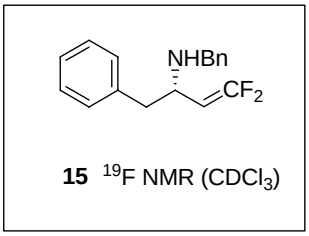
14 ^{13}C NMR ($CDCl_3$)



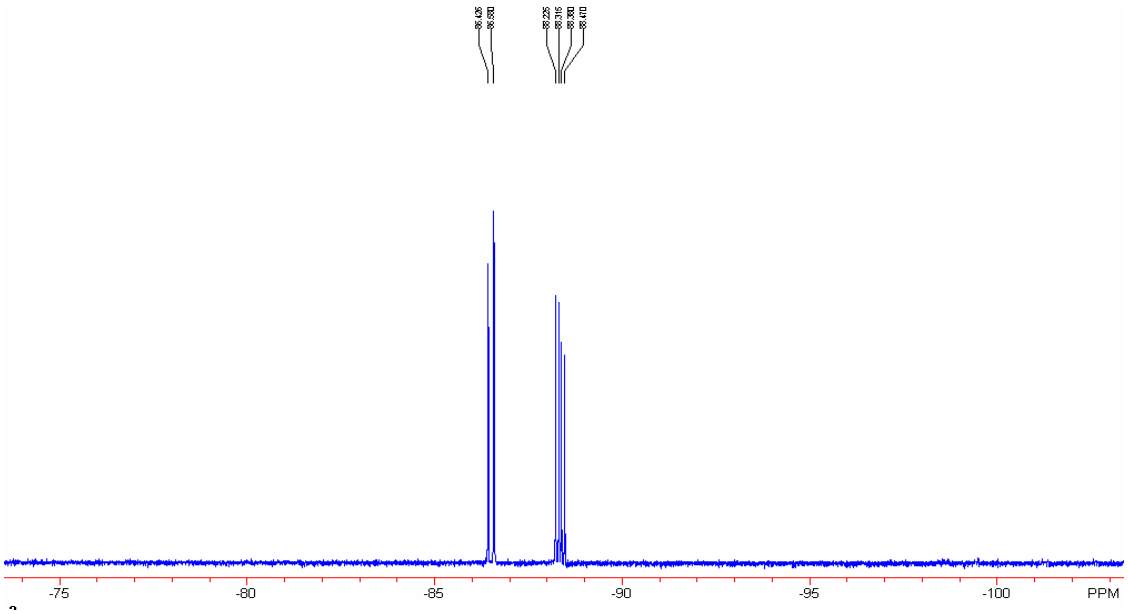


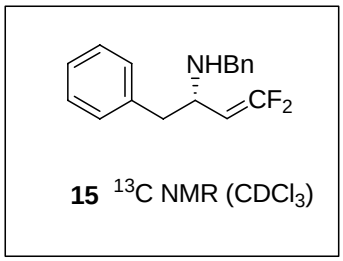
15 ^{1}H NMR ($CDCl_3$)





15 ^{19}F NMR ($CDCl_3$)





15 ^{13}C NMR ($CDCl_3$)