

Supporting Information

Stereoselective Monofluoromethylation of *N*-*tert*-Butylsulfinyl Ketimines Using Pregenerated Fluoro(phenylsulfonyl)methyl Anion

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General Remarks:

The *N*-*tert*-butylsulfinyl ketimines¹ were prepared from the corresponding ketones according to the known condensation procedure in one step. Fluoromethyl phenyl sulfone **1**² was prepared according to the known procedures. Unless otherwise mentioned, all chemicals were purchased from commercial sources. THF was freshly distilled over sodium. Silica gel (300-400 mesh) was used for column chromatography, and in most cases petroleum ether/ethyl acetate combination was used as the eluent.

All the melting points were uncorrected. ¹H, ¹³C and ¹⁹F NMR spectra were recorded on 400 MHz or 300 MHz NMR spectrometer. ¹H NMR chemical shifts were determined relative to internal (CH₃)₄Si (TMS) at δ 0.0 or to the signal of a residual protonated solvent: CDCl₃ δ 7.26. ¹³C NMR chemical shifts were determined relative to internal TMS at δ 0.0. ¹⁹F NMR chemical shifts were determined relative to CFCI₃ at δ 0.0. Chemical shifts are reported in ppm. Mass spectra were obtained on a mass spectrometer. High-resolution mass data were recorded on a high-resolution mass spectrometer in the EI, ESI or MALDI mode.

Typical procedure for stereoselective nucleophilic monofluoromethylation of *N*-*tert*-butylsulfinyl ketimines using fluoromethyl phenyl sulfone:

Condition A (*n*BuLi as a base): Under N₂ atmosphere, *n*-butyllithium in hexane (1.3 mmol) was added dropwise into the THF (8 mL) solution of fluoromethyl phenyl sulfone (209 mg, 1.2 mmol) at -78°C , and after 30 min at that temperature, *N*-*tert*-butylsulfinyl ketimine (1.0 mmol) in 2mL THF was added slowly into the solution. The reaction mixture was then stirred vigorously at -78°C for 1 h , followed by adding a saturated NaCl water solution (10 mL). The solution mixture was extracted with Et₂O (10 mL \times 3), and the combined organic phase was dried over MgSO₄. After the removal of volatile solvents under vacuum, the crude product was further purified by silica gel column chromatography to give product **4'** and **4''**.

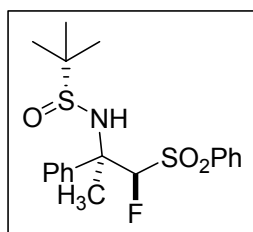
Condition B (KHMDS as a base): Under N₂ atmosphere, KHMDS in toluene (1.1 mmol) was added dropwise into the THF (4 mL) solution of fluoromethyl phenyl sulfone (174 mg, 1.0 mmol) at -78°C , and after 30 min at that temperature, *N*-*tert*-butylsulfinyl ketimine (0.5 mmol) in 1 mL of THF was added slowly into the solution. The reaction mixture was then stirred vigorously at -78°C for 2 h , followed by adding a saturated NaCl water solution (10 mL). The solution mixture was

extracted with Et₂O (10 mL×3), and the combined organic phase was dried over MgSO₄. After the removal of volatile solvents under vacuum, the crude product was further purified by silica gel column chromatography to give product **4'** and **4''**.

Sulfonamide **4a'**+**4a''**:

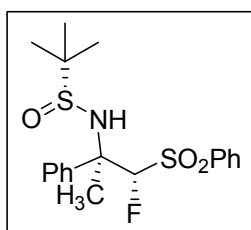
Using the typical procedure as condition A, the crude product was purified by silica gel column chromatography to afford two diastereoisomers **4a'** (198 mg) and **4a''** (158 mg) respectively, overall yield 90%.

Using the typical procedure as condition B, the crude product was purified by silica gel column chromatography to afford two diastereoisomers **4a'** (97mg) and **4a''** (30 mg) respectively, overall yield 64%.



4a'

White solid. mp 161–163 °C. $[\alpha]_D^{25} = -72.06$ (c = 0.98, CHCl₃); ¹H NMR: δ 7.81 (d, *J* = 7.5 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.53–7.58 (m, 2H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.31–7.37 (m, 3H), 5.81 (d, *J* = 45.0 Hz, 1H), 5.73 (brs, 1H), 1.97 (d, *J* = 2.4 Hz, 3H), 1.41 (s, 9H); ¹⁹F NMR: δ –174.4 (d, *J* = 44.9 Hz, 1F); ¹³C NMR: δ 139.7, 137.4, 134.3, 129.2, 129.0, 128.4, 128.3, 126.56, 126.52, 105.4 (d, *J* = 236.6 Hz), 62.4 (d, *J* = 16.7 Hz), 56.7, 25.4 (d, *J* = 4.8 Hz), 23.1; IR (KBr): 3293–2982–497, 1447, 1329, 1164, 1050, 569 cm^{–1}; Anal. Calcd. for C₁₉H₂₄FNO₃S₂: C, 57.41; H, 6.09; N, 3.52; Found C, 57.46; H, 6.10; N, 3.55; MS (ESI, *m/z*) 398.1 (M⁺+1).



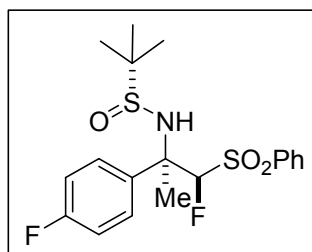
4a''

White solid. mp 155–156 °C. $[\alpha]_D^{25} = -85.68$ ($c = 0.94$, CHCl_3); ^1H NMR: δ 7.94 (d, $J = 7.8$ Hz, 2H), 7.71 (t, $J = 7.5$ Hz, 1H), 7.58 (t, $J = 7.8$ Hz, 2H), 7.46–7.51 (m, 2H), 7.33–7.41 (m, 3H), 5.35 (brs, 1H), 5.18 (d, $J = 44.1$ Hz, 1H), 2.15 (s, 3H), 1.30 (s, 9H); ^{19}F NMR: δ -178.2 (d, $J = 45.7$ Hz, 1F); ^{13}C NMR: δ 138.9, 137.2, 134.9, 129.5, 129.1, 128.7, 128.6, 127.8, 104.4 (d, $J = 228.2$ Hz), 63.5 (d, $J = 21.9$ Hz), 56.8, 22.9, 22.8; IR (KBr): 3271, 2938, 1585, 1475, 1450, 1327, 1150, 1057, 797, 686, 601 cm^{-1} ; Anal. Calcd. for $\text{C}_{19}\text{H}_{24}\text{FNO}_3\text{S}_2$: C, 57.41; H, 6.09; N, 3.52; Found C, 57.42; H, 6.24; N, 3.32; MS (ESI, m/z) 398.1 ($\text{M}^+ + 1$).

Sulfonamide **4b'**+**4b''**:

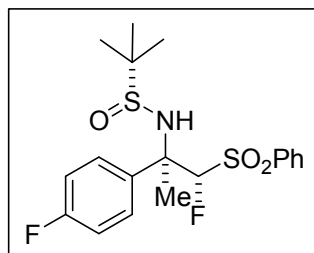
Using the typical procedure as condition A, the crude product was purified by silica gel column chromatography to afford two diastereoisomers **4b'** (185 mg) and **4b''** (151 mg) respectively, overall yield 81%.

Using the typical procedure as condition B, the crude product was purified by silica gel column chromatography to afford two diastereoisomers **4b'** (83 mg) and **4b''** (52 mg) respectively, overall yield 65%.



4b'

White solid. mp 178–180 °C. $[\alpha]_D^{25} = -70.96$ ($c = 0.98$, CHCl_3); ^1H NMR: δ 7.81 (d, $J = 7.5$ Hz, 2H), 7.65 (t, $J = 7.2$ Hz, 1H), 7.48–7.56 (m, 4H), 7.02 (t, $J = 8.7$ Hz, 2H), 5.80 (d, $J = 45.9$ Hz, 1H), 5.71 (brs, 1H), 1.95 (d, $J = 2.7$ Hz, 3H), 1.41 (s, 9H); ^{19}F NMR: δ -114.4 – -114.3 (m, 1F), -174.7 (d, $J = 46.0$ Hz, 1F); ^{13}C NMR: δ 162.6 (d, $J = 248.2$ Hz), 137.4, 135.7, 134.4, 129.3, 128.9, 128.4 (dd, $J = 8.4, 3.0$ Hz), 115.1 (d, $J = 21.4$ Hz), 105.3 (d, $J = 237.1$ Hz), 62.2 (d, $J = 16.7$ Hz), 56.7, 25.6 (d, $J = 5.1$ Hz), 23.0; IR (KBr): 3286, 2987, 1602, 1510, 1451, 1408, 1329, 1168, 1054, 836, 689, 620, 554 cm^{-1} ; Anal. Calcd. for $\text{C}_{19}\text{H}_{23}\text{F}_2\text{NO}_3\text{S}_2$: C, 54.92; H, 5.58; N, 3.37; Found C, 54.97; H, 5.72; N, 3.22; MS (ESI, m/z) 416.0 ($\text{M}^+ + 1$).



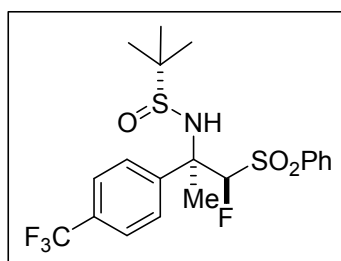
4b''

White solid. mp 162–163°C. $[\alpha]_D^{25} = -82.86$ ($c = 1.03$, CHCl_3); ^1H NMR: δ 7.94 (d, $J = 8.1$ Hz, 2H), 7.72 (t, $J = 7.2$ Hz, 1H), 7.59 (t, $J = 7.8$ Hz, 2H), 7.43–7.49 (m, 2H), 7.06 (t, $J = 8.4$ Hz, 2H), 5.33 (brs, 1H), 5.13 (d, $J = 44.7$ Hz, 1H), 2.14 (s, 3H), 1.29 (s, 9H); ^{19}F NMR: δ -113.3 – -113.2 (m, 1F), -178.7 (d, $J = 44.3$ Hz, 1F); ^{13}C NMR: δ 162.7 (d, $J = 249.1$ Hz), 137.2, 134.9, 134.7, 129.7 (d, $J = 8.4$ Hz), 129.5, 129.1, 115.5 (d, $J = 22.1$ Hz), 104.3 (d, $J = 229.4$ Hz), 63.1 (d, $J = 22.0$ Hz), 56.8, 22.9, 22.8; IR (KBr): 3276, 2956, 1739, 1604, 1513, 1450, 1325, 1311, 1148, 1056, 848, 729, 686, 595, 545 cm^{-1} . Anal. Calcd. for $\text{C}_{19}\text{H}_{23}\text{F}_2\text{NO}_3\text{S}_2$: C, 54.92; H, 5.58; N, 3.37; Found C, 54.99; H, 5.54; N, 3.13; MS (ESI, m/z) 416.0 ($\text{M}^+ + 1$).

Sulfinamide **4c'**+**4c''**:

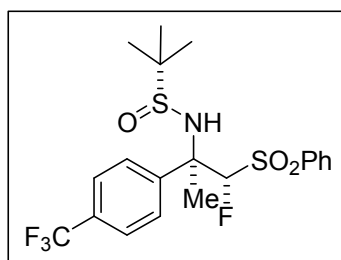
Using the typical procedure as condition A, the crude product was purified by silica gel column chromatography to afford two diastereoisomers **4c'** (218 mg) and **4c''** (182 mg) respectively, overall yield 86%.

Using the typical procedure as condition B, the crude product was purified by silica gel column chromatography to afford two diastereoisomers **4c'** (46 mg) and **4c''** (94 mg) respectively, overall yield 60%.



4c'

White solid. mp 142–144°C. $[\alpha]_D^{25} = -53.63$ ($c = 0.98$, CHCl_3); ^1H NMR: δ 7.78 (d, $J = 7.2$ Hz, 2H), 7.54–7.70 (m, 5H), 7.49 (t, $J = 7.5$ Hz, 2H), 5.89 (d, $J = 45.6$ Hz, 1H), 5.81 (brs, 1H), 1.96 (d, $J = 3.3$ Hz, 3H), 1.42 (s, 9H); ^{19}F NMR: δ -63.1 (s, 3F), -174.6 (d, $J = 47.1$ Hz, 1F); ^{13}C NMR: δ 144.1, 137.1, 134.6, 130.4 (q, $J = 31.3$ Hz), 129.3, 128.9, 126.95, 126.91, 125.2 (q, $J = 4.9$ Hz), 105.3 (d, $J = 237.3$ Hz), 62.4 (d, $J = 16.7$ Hz), 56.8, 25.5 (d, $J = 5.3$ Hz), 23.0; IR (KBr): 3287, 2974, 1622, 1450, 1328, 1164, 1121, 1054, 847, 687, 601, 519 cm^{-1} □ Anal. Calcd. for $\text{C}_{20}\text{H}_{23}\text{F}_4\text{NO}_3\text{S}_2$: C, 51.60; H, 4.98; N, 3.01; Found C, 51.70; H, 5.02; N, 2.83; MS (ESI, m/z) 466.0 ($\text{M}^+ + 1$).



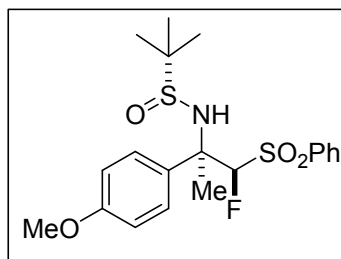
4c''

White solid. mp 180–182°C. $[\alpha]_D^{25} = -71.17$ ($c = 0.93$, CHCl_3); ^1H NMR: δ 7.93 (d, $J = 8.1$ Hz, 2H), 7.72 (t, $J = 7.5$ Hz, 1H), 7.55–7.64 (m, 6H), 5.39 (brs, 1H), 5.16 (d, $J = 44.7$ Hz, 1H), 2.18 (s, 3H), 1.31 (s, 9H); ^{19}F NMR: δ -63.2 (s, 3F), -178.8 (d, $J = 44.6$ Hz, 1F); ^{13}C NMR: δ 143.1, 136.9, 135.1, 130.8 (d, $J = 33.5$ Hz), 129.5, 129.2, 128.3, 125.5 (d, $J = 4.6$ Hz), 122.0, 104.0 (d, $J = 229.9$ Hz), 63.4 (d, $J = 22.0$ Hz), 57.1, 22.9, 22.8; IR (KBr): 3292, 2945, 1620, 1417, 1328, 1152, 1134, 1056, 850, 613, 572, 536 cm^{-1} □ Anal. Calcd. for $\text{C}_{20}\text{H}_{23}\text{F}_4\text{NO}_3\text{S}_2$: C, 51.60; H, 4.98; N, 3.01; Found C, 51.44; H, 4.97; N, 2.80; MS (ESI, m/z) 466.1 ($\text{M}^+ + 1$).

Sulfinamide **4d'**+**4d''**:

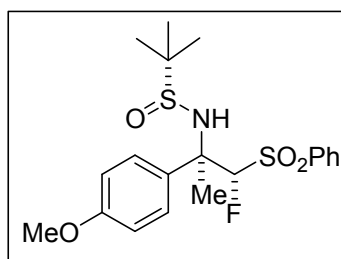
Using the typical procedure as condition A, the crude product was purified by silica gel column chromatography to afford two diastereoisomers **4d'** (188mg) and **4d''** (175mg) respectively, overall yield 85%.

Using the typical procedure as condition B, the crude product was purified by silica gel column chromatography to afford two diastereoisomers **4d'** (96 mg) and **4d''** (38 mg), respectively; overall yield 62%.



4d'

White solid. mp 100 –102°C. $[\alpha]_D^{25} = -54.44$ ($c = 1.05$, CHCl_3); ^1H NMR: δ 7.81 (d, $J = 7.5$ Hz, 2H), 7.63 (t, $J = 7.5$ Hz, 1H), 7.42–7.53 (m, 4H), 6.85 (d, $J = 9.0$ Hz, 2H), 5.74 (d, $J = 45.3$ Hz, 1H), 5.63 (brs, 1H), 3.81 (s, 3H), 1.96 (d, $J = 2.4$ Hz, 3H), 1.39 (s, 9H); ^{19}F NMR: δ –175.0 (d, $J = 44.0$ Hz, 1F); ^{13}C NMR: δ 159.5, 137.5, 134.3, 131.6, 129.2, 129.0, 127.8 (d, $J = 2.3$ Hz), 113.6, 105.6 (d, $J = 235.4$ Hz), 62.2 (d, $J = 16.4$ Hz), 56.6, 55.2, 25.3 (d, $J = 3.1$ Hz), 23.1; IR (KBr): 3452, 3286, 2977, 1614, 1516, 1323, 1256, 1186, 1141, 1055, 834, 689, 564, 515 cm^{-1} □ Anal. Calcd. for $\text{C}_{20}\text{H}_{26}\text{FNO}_4\text{S}_2$: C, 56.18; H, 6.13; N, 3.28; Found C, 56.07; H, 6.22; N, 2.97; MS (ESI, m/z) 428.1 ($\text{M}^+ + 1$).



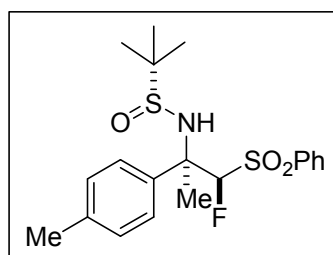
4d''

White solid. mp 171 –172°C. $[\alpha]_D^{26} = -82.73$ ($c = 0.95$, CHCl_3); ^1H NMR: δ 7.94 (d, $J = 8.1$ Hz, 2H), 7.71 (t, $J = 7.2$ Hz, 1H), 7.58 (t, $J = 7.2$ Hz, 2H), 7.38 (d, $J = 9.0$ Hz, 2H), 6.88 (d, $J = 9.0$ Hz, 2H), 5.29 (brs, 1H), 5.13 (d, $J = 44.7$ Hz, 1H), 3.80 (s, 3H), 2.12 (s, 3H), 1.29 (s, 9H); ^{19}F NMR: δ –178.5 (d, $J = 43.7$ Hz, 1F); ^{13}C NMR: δ 159.7, 137.3, 134.8, 130.7, 129.4, 129.1, 113.9, 104.5 (d, $J = 228.5$ Hz), 63.1 (d, $J = 21.7$ Hz), 56.7, 55.3, 22.9, 22.8; IR (KBr): 3295, 2953, 1612, 1517, 1309, 1259, 1151, 1058, 842, 728, 597 cm^{-1} □ Anal. Calcd. for $\text{C}_{20}\text{H}_{26}\text{FNO}_4\text{S}_2$: C, 56.18; H, 6.13; N, 3.28; Found C, 56.16; H, 6.09; N, 3.10; MS (ESI, m/z) 428.2 ($\text{M}^+ + 1$).

Sulfonamide **4e'**+**4e''**:

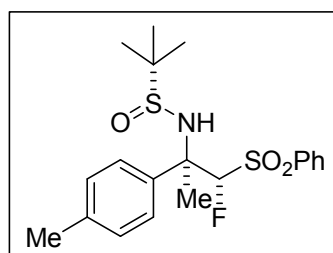
Using the typical procedure as condition A, the crude product was purified by silica gel column chromatography to afford two diastereoisomers **4e'** (218 mg) and **4e''** (163 mg) respectively, overall yield 93%.

Using the typical procedure as condition B, the crude product was purified by silica gel column chromatography to afford two diastereoisomers **4e'** (85mg) and **4e''** (55mg) respectively, overall yield 68%.



4e'

White solid. mp 145 –147 °C. $[\alpha]_D^{26} = -58.86$ ($c = 0.91$, CHCl₃); ¹H NMR: δ 7.80 (d, $J = 7.8$ Hz, 2H), 7.62 (t, $J = 7.5$ Hz, 1H), 7.48 (t, $J = 7.8$ Hz, 2H), 7.42 (d, $J = 7.5$ Hz, 2H), 6.85 (d, $J = 8.1$ Hz, 2H), 5.77 (d, $J = 45.3$ Hz, 1H), 5.66 (brs, 1H), 2.34 (s, 3H), 1.96 (d, $J = 2.7$ Hz, 3H), 1.39 (s, 9H); ¹⁹F NMR: δ -175.0 (d, $J = 47.1$ Hz, 1F); ¹³C NMR: δ 138.1, 137.5, 136.7, 134.2, 129.2, 129.0, 128.9, 126.4 (d, $J = 3.2$ Hz), 105.6 (d, $J = 236.9$ Hz), 62.3 (d, $J = 17.9$ Hz), 56.7, 25.3 (d, $J = 4.9$ Hz), 23.1, 21.1; IR (KBr): 3456, 3291, 2978, 1517, 1450, 1324, 1163, 1140, 1056, 818, 688, 532 cm⁻¹ □ Anal. Calcd. for C₂₀H₂₆FN₃O₃S₂: C, 58.37; H, 6.37; N, 3.40; Found C, 58.40; H, 6.57; N, 3.20; MS (ESI, m/z) 412.1 ($M^+ + 1$).



4e''

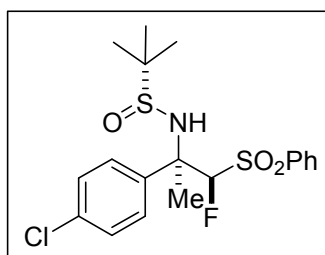
White solid. mp 175 –176 °C. $[\alpha]_D^{26} = -82.79$ ($c = 0.99$, CHCl₃); ¹H NMR: δ 7.93 (d, $J = 8.1$ Hz, 2H), 7.70 (t, $J = 7.2$ Hz, 1H), 7.57 (t, $J = 7.5$ Hz, 2H), 7.36 (d, $J = 8.1$ Hz, 2H), 6.88 (d, $J = 8.4$ Hz, 2H), 5.32 (brs, 1H), 5.16 (d, $J = 44.7$ Hz, 1H), 2.34 (s, 3H), 2.12 (s, 3H), 1.29 (s, 9H); ¹⁹F NMR: δ

–178.5 (d, $J = 46.3$ Hz, 1F); ^{13}C NMR: δ 138.7, 137.3, 135.9 (d, $J = 2.6$ Hz), 134.8, 129.4, 129.3, 129.1, 127.7, 104.5 (d, $J = 228.7$ Hz), 63.3 (d, $J = 22.3$ Hz), 56.8, 22.9, 22.8, 21.1; IR (KBr): 3290, 2945, 1449, 1310, 1150, 1056, 827, 729, 595 cm^{-1} □ Anal. Calcd. for $\text{C}_{20}\text{H}_{26}\text{FNO}_3\text{S}_2$: C, 58.37; H, 6.37; N, 3.40; Found C, 58.47; H, 6.36; N, 3.19; MS (ESI, m/z) 412.1 ($\text{M}^+ + 1$).

Sulfinamide **4f'**+**4f''**:

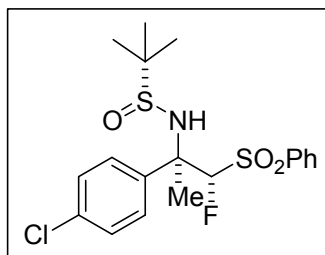
Using the typical procedure as condition A, the crude product was purified by silica gel column chromatography to afford two diastereoisomers **4f'** (180 mg) and **4f''** (152 mg), respectively; overall yield 77%.

Using the typical procedure as condition B, the crude product was purified by silica gel column chromatography to afford two diastereoisomers **4f'** (58 mg) and **4f''** (90 mg), respectively; overall yield 69%.



4f'

White solid. mp 163 –164 °C. $[\alpha]_{\text{D}}^{23} = -41.14$ (c = 1.02, CHCl_3); ^1H NMR: δ 7.80 (d, $J = 7.8$ Hz, 2H), 7.65 (t, $J = 7.5$ Hz, 1H), 7.46–7.55 (m, 4H), 7.26–7.31 (m, 2H), 5.82 (d, $J = 45.3$ Hz, 1H), 5.72 (brs, 1H), 1.94 (d, $J = 2.4$ Hz, 3H), 1.41 (s, 9H); ^{19}F NMR: δ –174.6 (d, $J = 45.5$ Hz, 1F); ^{13}C NMR: δ 138.5, 137.2, 134.4, 134.3, 129.3, 128.9, 128.4, 127.97, 127.91, 105.3 (d, $J = 236.5$ Hz), 62.2 (d, $J = 17.9$ Hz), 56.7, 25.4 (d, $J = 4.8$ Hz), 23.1; IR (KBr): 3285, 2985, 1496, 1451, 1404, 1326, 1164, 1054, 1014, 830, 687, 616, 528 cm^{-1} □ Anal. Calcd. for $\text{C}_{19}\text{H}_{23}\text{ClFNO}_3\text{S}_2$: C, 52.83; H, 5.37; N, 3.24; Found C, 52.83; H, 5.42; N, 3.08; MS (ESI, m/z) 432.1 ($\text{M}^+ + 1$).



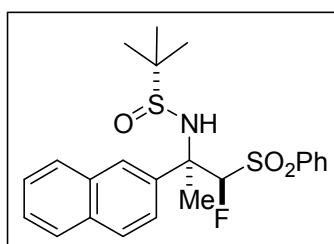
4f''

White solid. mp 167–168 °C. $[\alpha]_D^{24} = -79.14$ ($c = 1.01$, CHCl₃); ¹H NMR: δ 7.94 (d, $J = 7.8$ Hz, 2H), 7.74 (t, $J = 7.2$ Hz, 1H), 7.59 (t, $J = 8.1$ Hz, 2H), 7.42 (d, $J = 9.0$ Hz, 2H), 7.34 (d, $J = 9.0$ Hz, 2H), 5.33 (brs, 1H), 5.12 (d, $J = 44.7$ Hz, 1H), 2.13 (s, 3H), 1.29 (s, 9H); ¹⁹F NMR: δ -178.3 (d, $J = 46.0$ Hz, 1F); ¹³C NMR: δ 137.5, 137.1, 134.9, 134.8, 129.5, 129.2, 129.1, 128.8, 104.1 (d, $J = 229.3$ Hz), 63.2 (d, $J = 22.3$ Hz), 56.9, 22.9, 22.8; IR (KBr): 3310, 3276, 2939, 1498, 1449, 1328, 1151, 1057, 1013, 840, 722, 580, 536 cm⁻¹. Anal. Calcd. for C₁₉H₂₃ClFNO₃S₂: C, 52.83; H, 5.37; N, 3.24; Found C, 52.80; H, 5.42; N, 3.13; MS (ESI, m/z) 432.1 (M⁺+1).

Sulfonamide 4g'+4g'':

Using the typical procedure as condition A, the crude product was purified by silica gel column chromatography to afford two diastereoisomers **4g'** (170 mg) and **4g''** (148 mg) respectively, overall yield 72%.

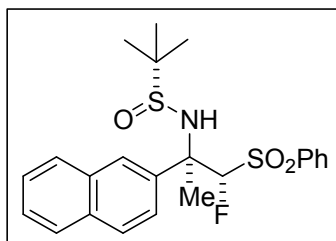
Using the typical procedure as condition B, the crude product was purified by silica gel column chromatography to afford two diastereoisomers **4g'** (51 mg) and **4g''** (101 mg) respectively, overall yield 68%.



4g'

White solid. mp 156–157 °C. $[\alpha]_D^{26} = -34.82$ ($c = 0.99$, CHCl₃); ¹H NMR: δ 7.98 (s, 1H), 7.71–7.84 (m, 5H), 7.45–7.64 (m, 4H), 7.36 (t, $J = 7.5$ Hz, 2H), 5.87 (d, $J = 45.6$ Hz, 1H), 5.78 (brs, 1H), 2.07 (d, $J = 2.7$ Hz, 3H), 1.45 (s, 9H); ¹⁹F NMR: δ -174.7 (d, $J = 44.6$ Hz, 1F); ¹³C NMR: δ

137.2, 137.1, 134.3, 133.0, 132.8, 129.1, 129.0, 128.6, 127.8, 127.5, 126.6, 126.3, 125.9, 124.5, 105.8 (d, $J = 237.1$ Hz), 62.7 (d, $J = 16.6$ Hz), 56.8, 25.4 (d, $J = 2.6$ Hz), 23.1; IR (KBr): 3291, 3063, 1448, 1330, 1161, 1069, 754, 687, 595, 534 cm^{-1} □ Anal. Calcd. for $\text{C}_{23}\text{H}_{26}\text{FNO}_3\text{S}_2$: C, 61.72; H, 5.86; N, 3.13; Found C, 61.69; H, 6.05; N, 2.96; MS (ESI, m/z) 448.1 ($\text{M}^+ + 1$).



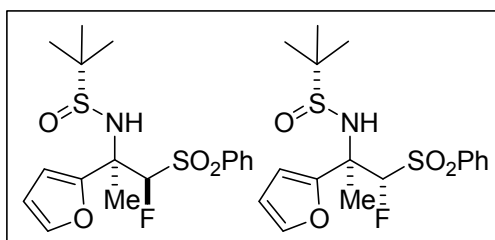
4g''

White solid. mp 170 –171 °C. $[\alpha]_{\text{D}}^{26} = -116.64$ ($c = 1.09$, CHCl_3); ^1H NMR: δ 7.93–7.97 (m, 3H), 7.79–7.86 (m, 3H), 7.69 (t, $J = 7.8$ Hz, 1H), 7.49–7.60 (m, 5H), 5.41 (brs, 1H), 5.30 (d, $J = 45.0$ Hz, 1H), 2.28 (s, 3H), 1.30 (s, 9H); ^{19}F NMR: δ –178.2 (d, $J = 44.3$ Hz, 1F); ^{13}C NMR: δ 137.2 □ 136.0 □ 134.9 □ 133.0 □ 132.9 □ 129.5 □ 129.1 □ 128.6 □ 128.4 □ 128.2 □ 127.5 □ 127.1 □ 126.6 □ 124.5 □ 104.1 (d, $J = 230.9$ Hz), 63.7 (d, $J = 22.5$ Hz), 56.9, 22.9, 22.8; IR (KBr): 3293, 2942, 1450, 1320, 1189, 1150, 1056, 823, 755, 684, 593, 543 cm^{-1} □ Anal. Calcd. for $\text{C}_{23}\text{H}_{26}\text{FNO}_3\text{S}_2$: C, 61.72; H, 5.86; N, 3.13; Found C, 61.80; H, 5.96; N, 2.97; MS (ESI, m/z) 448.1 ($\text{M}^+ + 1$).

Sulfonamide **4h'**+**4h''**:

Using the typical procedure as condition A, the crude product was purified by silica gel column chromatography to afford a mixture of two diastereoisomers **4h'** and **4h''** in the ratio 1:1 (determined by ^{19}F NMR of the crude reaction mixture), overall yield 81%.

Using the typical procedure as condition B, the crude product was purified by silica gel column chromatography to afford a mixture of two diastereoisomers **4h'** and **4h''** in the ratio 4:1 (determined by ^{19}F NMR of the crude reaction mixture), overall yield 77%.



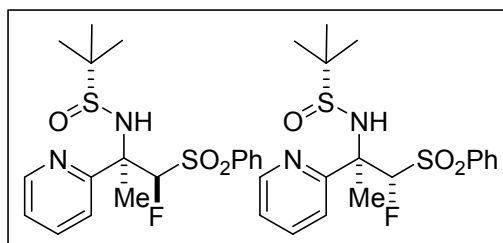
4h' + 4h''

^1H NMR: δ 7.88–7.97 (m, 2H), 7.52–7.76 (m, 3H), 7.43–7.46 (m, 0.4H), 7.39–7.41 (m, 0.6H), 6.55 (d, J = 3.6 Hz, 0.6H), 6.47 (d, J = 3.6 Hz, 0.4H), 6.40–6.43 (m, 0.4H), 6.36–6.39 (m, 0.6H), 5.62 (d, J = 45.6 Hz, 0.4H), 5.43 (d, J = 44.7 Hz, 0.6H), 5.15 (brs, 0.4H), 5.01 (brs, 0.6H), 2.06 (s, 1.8H), 1.98 (d, J = 2.4 Hz, 1.2H), 1.29 (s, 3.6H), 1.26 (s, 5.4H); ^{19}F NMR: δ -178.2 (d, J = 45.7 Hz, 0.6F) \square -179.3 (d, J = 45.1 Hz, 0.4F); IR (KBr): 3295, 2959, 1585, 1449, 1327, 1162, 1063, 1021, 726, 574, 537 cm^{-1} ; MS (ESI, m/z) 388.0 (M^+ +1); HRMS analysis (MALDI) m/z : Calcd. For $\text{C}_{17}\text{H}_{22}\text{NO}_4\text{FS}_2\text{Na}$ (M^+ +Na): 410.0857; Found 410.0866.

Sulfonamide 4i'+4i'':

Using the typical procedure as condition A, the crude product was purified by silica gel column chromatography to afford a mixture of two diastereoisomers **4i'** and **4i''** in the ratio 1.3:1 (determined by ^{19}F NMR of the crude reaction mixture), overall yield 81%.

Using the typical procedure as condition B, the crude product was purified by silica gel column chromatography to afford a mixture of two diastereoisomers **4i'** and **4i''** in the ratio 1.2:1 (determined by ^{19}F NMR of the crude reaction mixture), overall yield 74%.



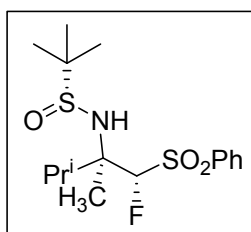
4i' + 4i''

^1H NMR: δ 8.62 (d, J = 4.8 Hz, 0.56H), 8.58 (d, J = 4.5 Hz, 0.44H), 7.47–7.92 (m, 7H), 7.24–7.34 (m, 1H), 5.88 (d, J = 45.0 Hz, 0.44H), 5.81 (d, J = 45.9 Hz, 0.56H), 5.64 (brs, 0.44H), 5.62 (brs, 0.56H), 2.11 (d, J = 1.2 Hz, 1.32H), 1.98 (d, J = 2.1 Hz, 1.68H), 1.30 (s, 3.96H), 1.26 (s, 5.04H); ^{19}F NMR: δ -179.0 (d, J = 44.6 Hz, 0.56F) \square -180.8 (d, J = 45.1 Hz, 0.44F); IR (KBr): 3469, 3290, 2960, 1589, 1469, 1449, 1330, 1155, 1067, 751, 720, 688, 564, 537 cm^{-1} ; MS (ESI, m/z) 399.1 (M^+ +1); HRMS analysis (MALDI) m/z : Calcd. For $\text{C}_{18}\text{H}_{23}\text{N}_2\text{O}_3\text{FS}_2\text{Na}$ (M^+ +Na): 421.1024; Found 421.1026.

Sulfinamide **4j'**+**4j''**:

Using the typical procedure as condition A, the crude product was purified by silica gel column chromatography to afford only a diastereoisomer **4j''** (the other diastereoisomer **4j'** was mixed with unreacted fluoromethyl phenyl sulfone **1**, the ratio of **4j'** and **4j''** 1:1.6), overall yield (determined by ^{19}F NMR of the crude reaction mixture) 81%.

Using the typical procedure as condition B, the crude product was purified by silica gel column chromatography to afford only a diastereoisomer **4j''** (the other diastereoisomer **4j'** was mixed with unreacted fluoromethyl phenyl sulfone **1**, the ratio of **4j'** and **4j''** is 1:1.6), overall yield 73% (determined by ^{19}F NMR of the crude reaction mixture).



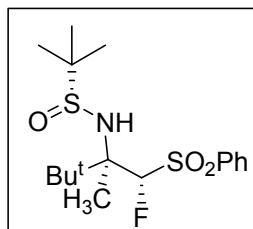
4j''

White solid. mp 125 –126°C. $[\alpha]_{\text{D}}^{24} = -89.71$ ($c = 0.90$, CHCl_3); ^1H NMR: δ 7.97 (d, $J = 7.5$ Hz, 2H), 7.69 (t, $J = 7.2$ Hz, 1H), 7.58 (t, $J = 7.5$ Hz, 2H), 5.19 (d, $J = 45.6$ Hz, 1H), 4.47 (brs, 1H), 2.52-2.62 (m, 1H), 1.64 (s, 3H), 1.26 (s, 9H), 1.11 (dd, $J = 6.9, 2.4$ Hz, 3H), 1.04 (d, $J = 6.0$ Hz, 3H); ^{19}F NMR: δ -175.7 (d, $J = 43.7$ Hz, 1F); ^{13}C NMR: δ 137.3, 134.6, 129.3, 105.4 (d, $J = 226.9$ Hz), 63.0 (d, $J = 16.4$ Hz), 56.5, 34.8, 22.8, 20.4 (d, $J = 3.8$ Hz), 17.9, 17.7 (d, $J = 5.7$ Hz); IR (KBr): 3307, 2946, 1451, 1319, 1273, 1150, 1073, 897, 838, 687, 593, 557 cm^{-1} □ Anal. Calcd. for $\text{C}_{16}\text{H}_{26}\text{FNO}_3\text{S}_2$: C, 52.87; H, 7.21; N, 3.85; Found C, 52.88; H, 7.28; N, 3.68; MS (ESI, m/z) 364.1 ($\text{M}^+ + 1$).

Sulfinamide **4k'**+**4k''**:

Using the typical procedure as condition A, the crude product was purified by silica gel column chromatography to afford only a diastereoisomer **4k''** (the other diastereoisomer **4k'** was mixed with unreacted fluoromethyl phenyl sulfone **1**, the ratio of **4k'** and **4k''** 1:1.8), overall yield 77% (determined by ^{19}F NMR of the crude reaction mixture).

Using the typical procedure as condition B, the crude product was purified by silica gel column chromatography to afford only a diastereoisomer **4k''** (the other diastereoisomer **4k'** was mixed with unreacted fluoromethyl phenyl sulfone **1**, the ratio of **4k'** and **4k''** is 1:2.9), overall yield 47% (determined by ^{19}F NMR of the crude reaction mixture).



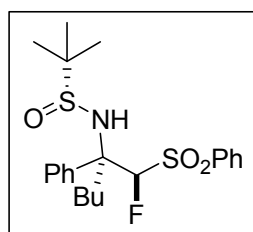
4k''

White solid. mp 142 –143 °C. $[\alpha]_D^{24} = -117.72$ ($c = 1.03$, CHCl_3); ^1H NMR: δ 8.00 (d, $J = 7.5$ Hz, 2H), 7.68 (t, $J = 7.8$ Hz, 1H), 7.57 (t, $J = 7.5$ Hz, 2H), 5.26 (d, $J = 43.8$ Hz, 1H), 4.76 (brs, 1H), 1.65 (d, $J = 2.7$ Hz, 3H), 1.28 (s, 9H), 1.16 (s, 9H); ^{19}F NMR: δ -173.4 (d, $J = 57.9$ Hz, 1F); ^{13}C NMR: δ 137.8, 134.5, 129.4, 129.3, 104.9 (d, $J = 225.7$ Hz), 67.3 (d, $J = 16.6$ Hz), 56.8, 39.2, 26.5, 23.0, 17.5 (d, $J = 6.9$ Hz); IR (KBr): 3317, 2955, 1585, 1450, 1324, 1273, 1162, 1084, 1071, 903, 688, 589 cm^{-1} ; Anal. Calcd. for $\text{C}_{17}\text{H}_{28}\text{FNO}_3\text{S}_2$: C, 54.08; H, 7.48; N, 3.71; Found C, 54.07; H, 7.54; N, 3.51; MS (ESI, m/z) 378.1 ($\text{M}^+ + 1$).

Sulfonamide **4l'**+**4l''**:

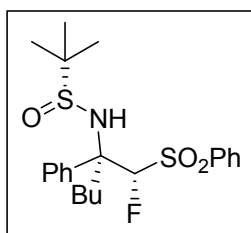
Using the typical procedure as condition A, the crude product was purified by silica gel column chromatography to afford two diastereoisomers **4l'** (127 mg) and **4l''** (263 mg), respectively; overall yield 88%.

Using the typical procedure as condition B, the crude product was purified by silica gel column chromatography to afford two diastereoisomers **4l'** (42 mg) and **4l''** (154 mg), respectively; overall yield 67%.



4l'

White solid. mp 170–172°C. $[\alpha]_D^{24} = -60.81$ ($c = 1.05$, CHCl_3); ^1H NMR: δ 7.87 (d, $J = 7.5$ Hz, 2H), 7.64 (t, $J = 7.2$ Hz, 1H), 7.36–7.56 (m, 7H), 5.45 (d, $J = 45.9$ Hz, 1H), 5.44 (brs, 1H), 2.55–2.67 (m, 1H), 2.17–2.29 (m, 1H), 1.38 (s, 9H), 1.19–1.32 (m, 3H), 0.87–1.02 (m, 1H), 0.81 (t, $J = 6.6$ Hz, 3H); ^{19}F NMR: δ -172.2 (d, $J = 47.1$ Hz, 1F); ^{13}C NMR: δ 137.0, 136.8, 134.5, 129.5, 129.2, 128.6, 128.4, 126.9, 104.5 (d, $J = 236.0$ Hz), 65.9 (d, $J = 19.8$ Hz), 57.3, 35.5, 24.8, 23.2, 22.6, 13.8; IR (KBr): 3298, 2958, 1467, 1448, 1324, 1256, 1158, 1071, 779, 687, 572, 541 cm^{-1} ; Anal. Calcd. for $\text{C}_{22}\text{H}_{30}\text{FNO}_3\text{S}_2$: C, 60.11; H, 6.88; N, 3.19; Found C, 60.28; H, 6.85; N, 3.10; MS (ESI, m/z) 440.1 ($\text{M}^+ + 1$).



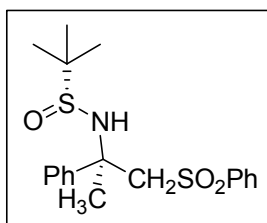
41''

White solid. mp 162–164°C. $[\alpha]_D^{24} = -50.56$ ($c = 0.99$, CHCl_3); ^1H NMR: δ 7.79 (d, $J = 7.5$ Hz, 2H), 7.60 (t, $J = 7.5$ Hz, 1H), 7.43–7.51 (m, 4H), 7.30–7.38 (m, 3H), 6.07 (d, $J = 45.6$ Hz, 1H), 5.81 (brs, 1H), 2.29–2.39 (m, 2H), 1.45 (s, 9H), 1.12–1.30 (m, 3H), 0.77 (t, $J = 6.9$ Hz, 3H), 0.58–0.72 (m, 1H); ^{19}F NMR: δ -175.8 (d, $J = 46.9$ Hz, 1F); ^{13}C NMR: δ 137.8, 134.1, 129.2, 128.9, 128.2, 128.1, 126.53, 126.50, 105.3 (d, $J = 235.6$ Hz), 64.9 (d, $J = 18.6$ Hz), 57.0, 34.2 (d, $J = 1.9$ Hz), 23.8, 23.1, 22.4, 13.9; IR (KBr): 3287, 2870, 1447, 1332, 1164, 1055, 871, 757, 702, 577, 527 cm^{-1} ; Anal. Calcd. for $\text{C}_{22}\text{H}_{30}\text{FNO}_3\text{S}_2$: C, 60.11; H, 6.88; N, 3.19; Found C, 60.00; H, 6.81; N, 3.10; MS (ESI, m/z) 440.1 ($\text{M}^+ + 1$).

Addition of Lithiated Methyl Sulfones to **2a**:

Under N_2 atmosphere, *n*-Butyllithium in hexane (1.3 mmol) was added dropwise into the THF (8 mL) solution of methyl phenyl sulfone (188 mg, 1.2 mmol) at -78 °C, and after 30 min at that temperature, *N*-*tert*-butanesulfinyl ketimine **2a** (224mg, 1.0 mmol) in 2 mL of THF was added slowly into the solution. The reaction mixture was then stirred vigorously at -78 °C for 3.5 h ,

followed by adding a saturated NaCl water solution (10 mL) at this temperature. The solution mixture was extracted with Et₂O (10 mL×3), and the combined organic phase was dried over MgSO₄. After the removal of volatile solvents under vacuum, the crude product was further purified by silica gel column chromatography to give product **7** in 58% yield (222 mg).



7

White solid. mp 104–105°C. $[\alpha]_D^{23} = -61.83$ ($c = 0.95$, CHCl₃); ¹H NMR: δ 7.79 (d, $J = 7.2$ Hz, 2H), 7.58 (t, $J = 7.2$ Hz, 1H), 7.38–7.50 (m, 4H), 7.24–7.32 (m, 3H), 5.92 (s, 1H), 3.89 (d, $J = 14.7$ Hz, 1H), 3.78 (d, $J = 14.7$ Hz, 1H), 1.91 (s, 3H), 1.37 (s, 9H); ¹³C NMR: δ 142.8, 140.9, 133.6, 129.2, 128.4, 127.8, 127.6, 126.0, 66.9, 60.2, 56.4, 28.7, 23.1; IR (KBr): 3284, 2971, 2497, 1495, 1448, 1309, 1147, 1057, 773, 680, 611 cm⁻¹. Anal. Calcd. for C₁₉H₂₅NO₃S₂: C, 60.13; H, 6.64; N, 3.69; Found C, 60.00; H, 6.55; N, 3.43; MS (ESI, m/z) 380.2 ($M^+ + 1$).

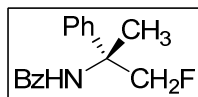
Procedure for magnesium-mediated reductive desulfonylation and deprotection of the *tert*-butylsulfinyl group and benzylation of **4a:**

Into a 50-mL Schlenk flask containing **4a** (210 mg, 0.52 mmol) in 5 mL DMF at room temperature was added 3 mL of HOAc/NaOAc (1:1) buffer solution (8 mol/L). Magnesium turnings (183 mg, 7.5 mmol) were added in portions. The reaction mixture was stirred at room temperature for 8 h followed by adding 10 mL of water. The solution mixture was extracted with Et₂O (20 mL x 3), and the combined organic phase was washed with saturated NaHCO₃ solution and brine, then dried over MgSO₄ and the solvent was removed to give the intermediate product without further purification.

The intermediate product was dissolved in 5 mL of anhydrous methanol. Then 0.5 mL of HCl/Dioxane (4N) was added. The reaction mixture was stirred at room temperature for 30 min and was then concentrated to near dryness. Diethyl ether was added to precipitate out the amine hydrochloride.

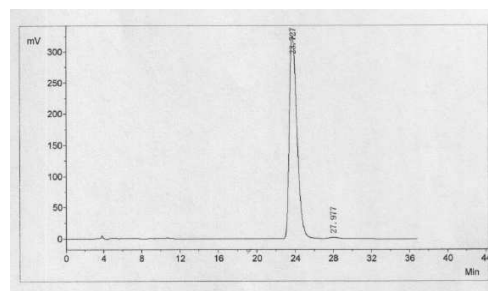
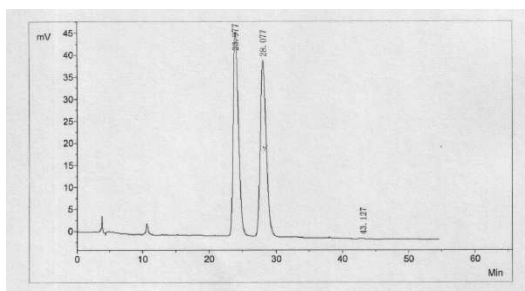
Under N₂ atmosphere, a flask containing the amine hydrochloride without further purification

PhCOCl (1.5 mmol), Et₃N (1.5 mmol) and K₂CO₃ (0.5 mmol) in 5 mL of dioxane was stirred at 60 °C for 5 h. Then removal of the solvents under reduced pressure and flash chromatography afforded **10** (96 mg) as a white solid in total 72% yield.

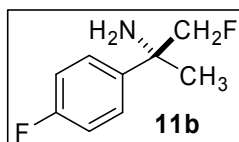


10

HPLC: CHIRALPAK OD hexane/2-propanol= 95:5; 0.7mL/min; UV 214 nm; (R)-, *r*_t= 23.9 min, (S)-, *r*_t= 28.0 min (98.7% ee);

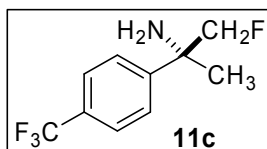


White solid. mp 141–142°C. [α]_D²³ = 21.08 (*c* = 0.97, CHCl₃); ¹H NMR: δ 7.80 (d, *J* = 7.5 Hz, 2H), 7.25–7.55 (m, 8H), 6.61 (brs, 1H), 4.84 (dd, *J* = 25.2, 9.0 Hz, 1H), 4.69 (dd, *J* = 24.6, 9.0 Hz, 1H), 1.90 (d, *J* = 2.1 Hz, 3H); ¹⁹F NMR: δ –221.9 (t, *J* = 48.0 Hz, 1F); ¹³C NMR: δ 166.9, 141.4, 134.9, 131.7, 128.7, 128.6, 127.7, 127.0, 125.5, 87.6 (d, *J* = 179.9 Hz), 59.3, 22.6 (d, *J* = 4.0 Hz); IR (KBr): 3255, 3062, 1638, 1540, 1494, 1317, 1035, 1022, 699, 607 cm^{–1}; Anal. Calcd. for C₁₆H₁₆FNO: C, 74.69; H, 6.27; N, 5.44; Found C, 74.58; H, 6.12; N, 5.24; MS (ESI, *m/z*) 258.4 (*M*⁺+1).

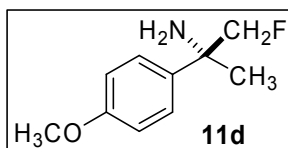


¹H NMR: δ 7.49 (dd, *J* = 9.0, 5.1 Hz, 2H), 7.04 (t, *J* = 8.7 Hz, 2H), 4.36 (d, *J* = 48.0 Hz, 2H), 1.67 (s, 2H), 1.50 (d, *J* = 1.8 Hz, 3H); ¹⁹F NMR: δ –116.0 to –116.2 (m, 1F), –220.1 (t, *J* = 52.7 Hz, 1F); ¹³C NMR: δ 136.1, 127.4 (d, *J* = 1.6 Hz), 127.3, 115.1 (d, *J* = 20.9 Hz), 91.0 (d, *J* = 177.3 Hz), 55.1, 26.6 (d, *J* = 3.6 Hz); IR (KBr): 2929, 1602, 1512, 1233, 1165, 1012, 836, 572 cm^{–1}; MS (EI,

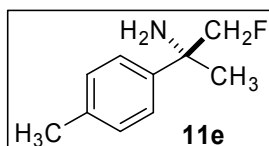
m/z , %) 42 (39.14), 138 (M-CH₂F, 100.00); HRMS analysis (EI) m/z : Calcd. For C₉H₁₁NF₂ (M⁺): 171.0860; Found 171.0855.



¹H NMR: δ 7.66 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 9.0 Hz, 2H), 4.49 (dd, J = 15.3, 9.0 Hz, 1H), 4.33 (dd, J = 15.0, 9.0 Hz, 1H), 1.67 (s, 2H), 1.51 (d, J = 2.4 Hz, 3H); ¹⁹F NMR: δ - 62.6 (s, 3F), - 220.7 (t, J = 42.0 Hz, 1F); ¹³C NMR: δ 148.6, 129.3 (q, J = 95.8 Hz), 126.1, 125.3 (q, J = 3.8 Hz), 90.7 (d, J = 178.4 Hz), 55.4 (d, J = 17.6 Hz), 26.5 (d, J = 2.6 Hz); IR (KBr): 3379, 2979, 1620, 1412, 1330, 1168, 1118, 1016, 842, 617 cm⁻¹; MS (EI, m/z , %) 42 (30.94), 188 (M-CH₂F, 100.00); HRMS analysis (EI) m/z : Calcd. For C₁₀H₁₁NF₄ (M⁺): 221.0828; Found 221.0828.

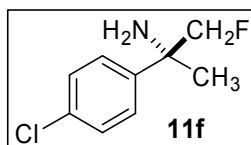


¹H NMR: δ 7.43 (d, J = 9.3 Hz, 2H), 7.11 (d, J = 8.7 Hz, 2H), 4.34 (d, J = 47.7 Hz, 2H), 3.80 (s, 3H), 1.70 (s, 2H), 1.50 (d, J = 1.8 Hz, 3H); ¹⁹F NMR: δ - 219.9 (t, J = 45.4 Hz, 1F); ¹³C NMR: δ 158.6, 136.4 (d, J = 4.3 Hz), 126.7, 113.7, 91.2 (d, J = 177.0 Hz), 55.2, 54.9 (d, J = 17.8 Hz), 26.5 (d, J = 4.2 Hz); IR (KBr): 2970, 1611, 1514, 1251, 1182, 1034, 831, 410 cm⁻¹; MS (EI, m/z , %) 42 (18.09), 150 (M-CH₂F, 100.00); HRMS analysis (EI) m/z : Calcd. For C₁₀H₁₄NOF (M⁺): 183.1059; Found 183.1060.

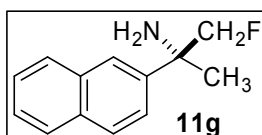


¹H NMR: δ 7.32 (d, J = 8.4 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 4.30 (d, J = 48.0 Hz, 2H), 2.27 (s, 2H), 1.61 (s, 3H), 1.43 (d, J = 1.5 Hz, 3H); ¹⁹F NMR: δ - 220.5 (t, J = 52.2 Hz, 1F); ¹³C NMR: δ 141.4, 136.8, 129.1, 125.4, 91.2 (d, J = 177.2 Hz), 55.1 (d, J = 17.8 Hz), 26.5 (d, J = 3.7 Hz), 20.9; IR (KBr): 3378, 2972, 1514, 1010, 817, 424, 404 cm⁻¹; MS (EI, m/z , %) 42 (27.99), 134 (M-CH₂F,

100.00); HRMS analysis (EI) m/z : Calcd. For $C_{10}H_{14}NF$ (M^+): 167.1110; Found 167.1104.



1H NMR: δ 7.46 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 9.0 Hz, 2H), 4.44 (dd, J = 10.8, 8.4 Hz, 1H), 4.28 (dd, J = 11.1, 9.3 Hz, 1H), 1.78 (s, 2H), 1.49 (d, J = 1.8 Hz, 3H); ^{19}F NMR: δ - 220.2 (t, J = 51.3 Hz, 1F); ^{13}C NMR: δ 142.9, 133.0, 128.5, 127.1, 90.8 (d, J = 178.4 Hz), 55.1 (d, J = 18.4 Hz), 26.5 (d, J = 3.8 Hz); IR (KBr): 2975, 1594, 1494, 1096, 1013, 829, 579, 410 cm^{-1} ; MS (EI, m/z , %) 42 (39.00), 154 ($M-CH_2F$, 100.00), 156 (32.20); HRMS analysis (EI) m/z : Calcd. For $C_9H_{11}NFCI$ (M^+): 187.0564; Found 187.0561.

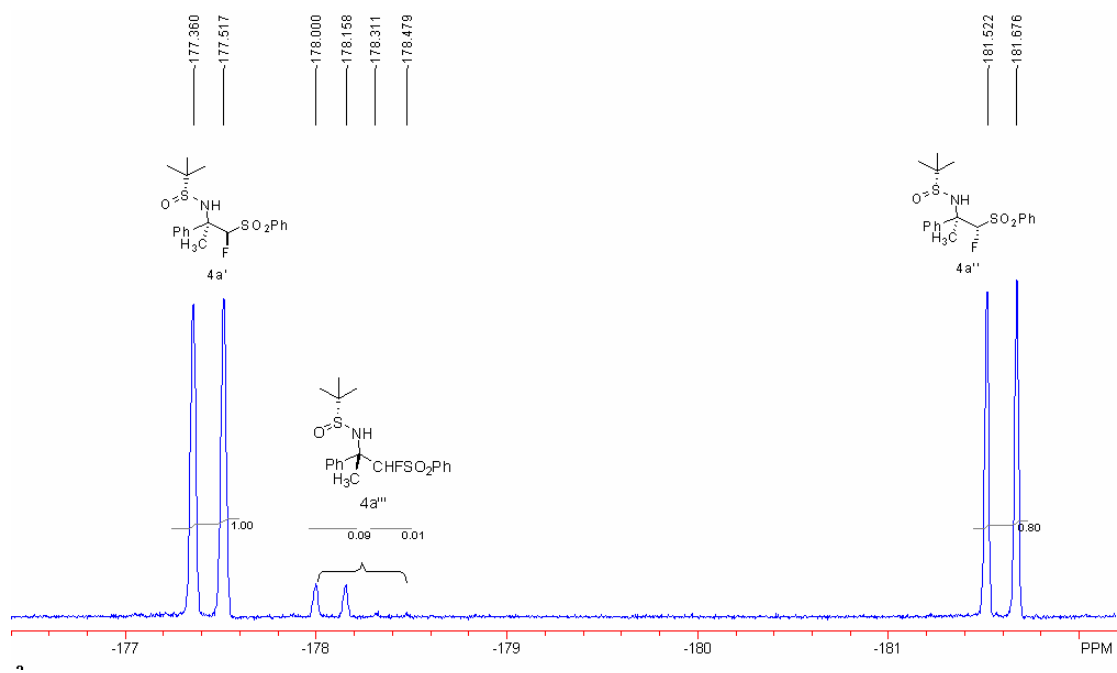


1H NMR: δ 7.96 – 7.99 (m, 1H), 7.79 – 7.88 (m, 3H), 7.62 (dd, J = 8.7, 1.8 Hz, 1H), 7.44 – 7.52 (m, 2H), 4.49 (d, J = 47.4 Hz, 2H), 1.84 (s, 2H), 1.60 (d, J = 2.1 Hz, 3H); ^{19}F NMR: δ - 220.6 (t, J = 52.7 Hz, 1F); ^{13}C NMR: δ 133.2, 132.4, 128.2, 128.1, 127.4, 126.2, 126.0, 124.3, 123.9, 91.0 (d, J = 177.5 Hz), 55.5 (d, J = 17.9 Hz), 26.5 (d, J = 3.6 Hz); IR (KBr): 3059, 2971, 1601, 1506, 1276, 1011, 819, 749, 479, 405 cm^{-1} ; MS (EI, m/z , %) 129 (26.43), 170 ($M-CH_2F$, 100.00); HRMS analysis (EI) m/z : Calcd. For $C_{13}H_{14}NF$ (M^+): 203.1110; Found 203.1114.

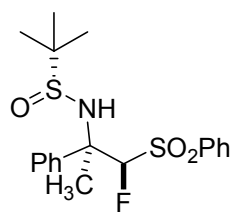
References:

1. Liu, G.; Cogan, D.A.; Owens, T.D.; Tang, T.P.; Ellman, J.A. *J. Org. Chem.* **1999**, *64*, 1278.
2. *Encyclopedia of Reagents for Organic Synthesis*, Vol. 4, pp 2558-2561, Paquette, L. A., et.al Eds; John Wiley & Sons: Chichester, 2002.

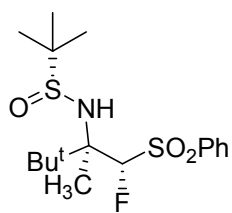
Example of determination of facial selectivity ratio of 4 (the organic phase of the reaction mixture after saturated NaCl water solution was added) by ¹⁹F NMR:



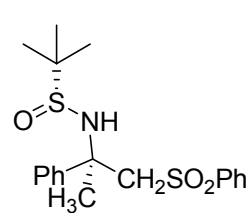
Determination of the absolute configuration of 4a', 4k'' and 7 by X-ray analysis



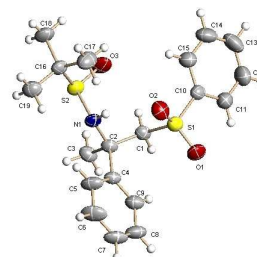
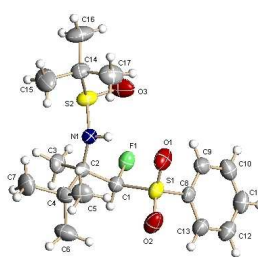
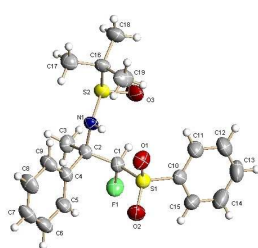
4a'



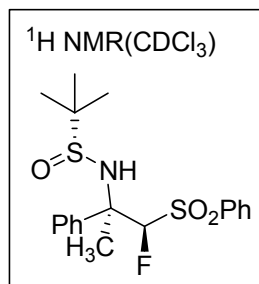
4k'



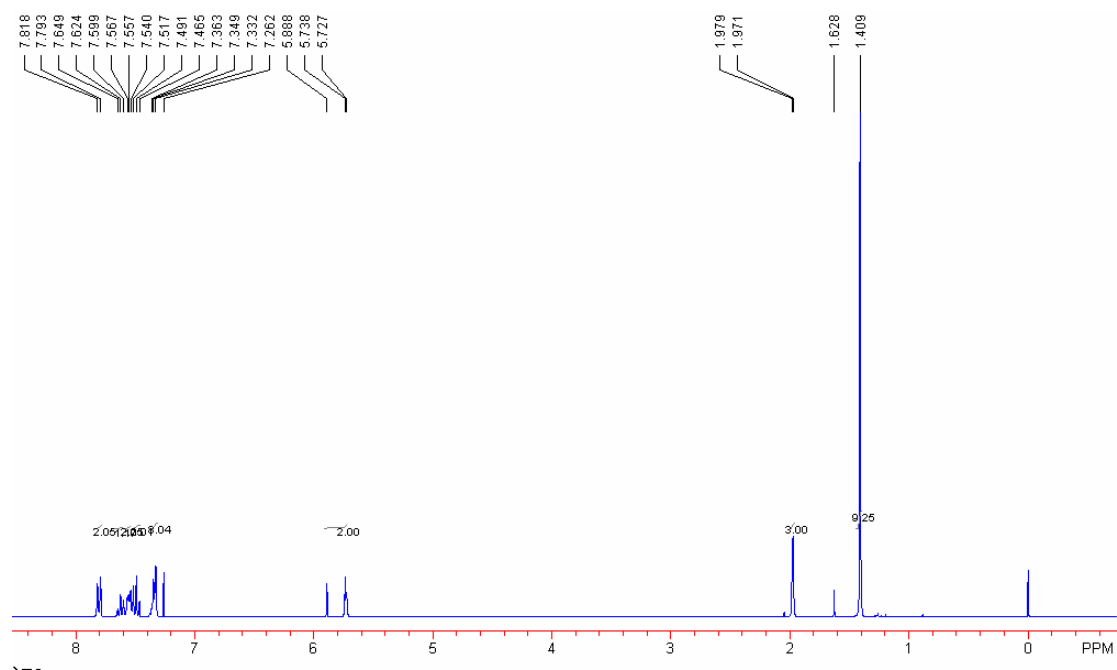
7

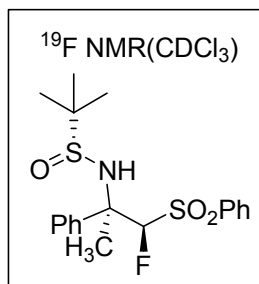


NMR spectra for all isolated products

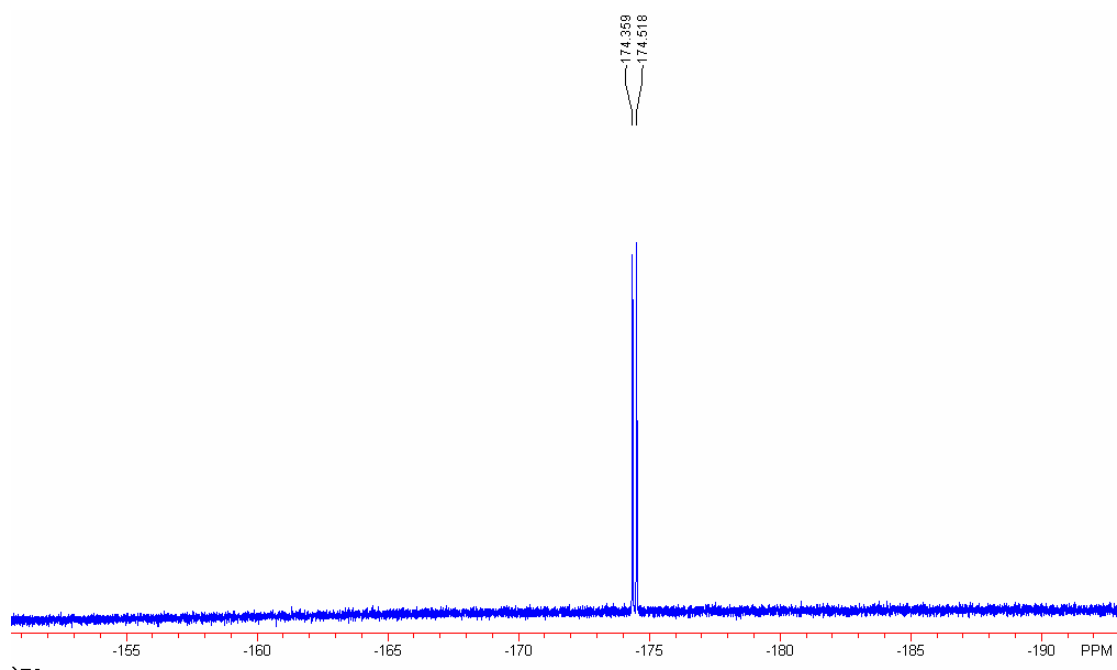


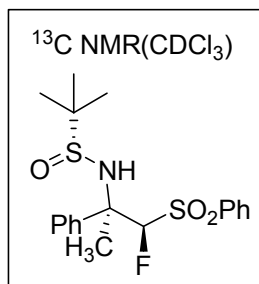
4a'



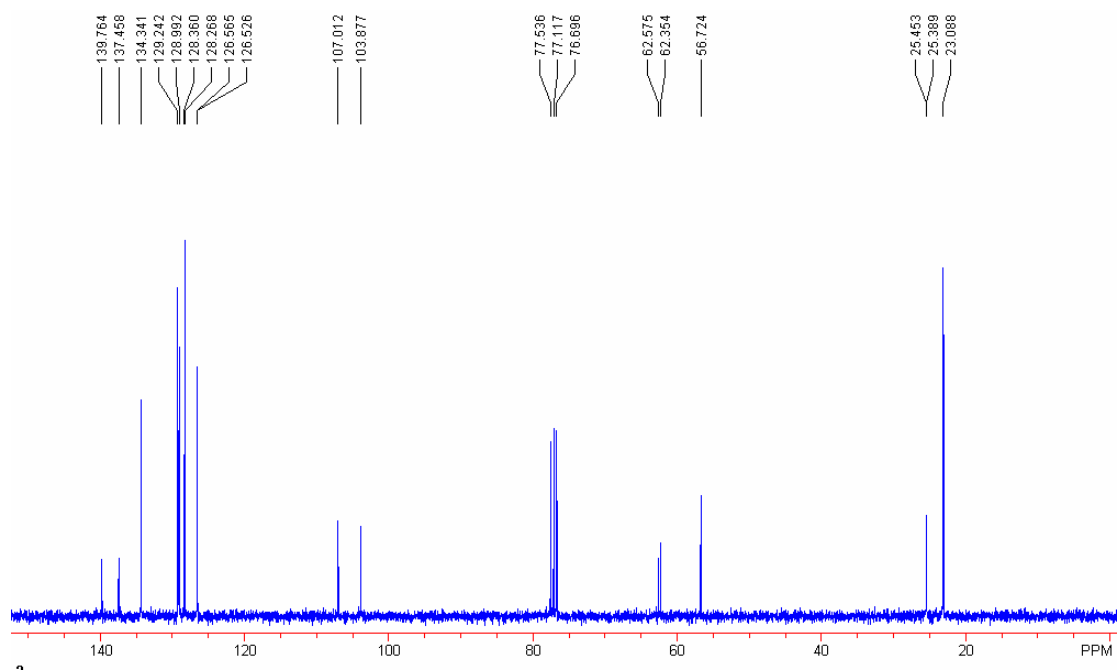


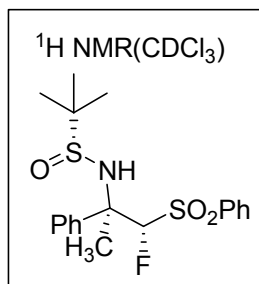
4a'



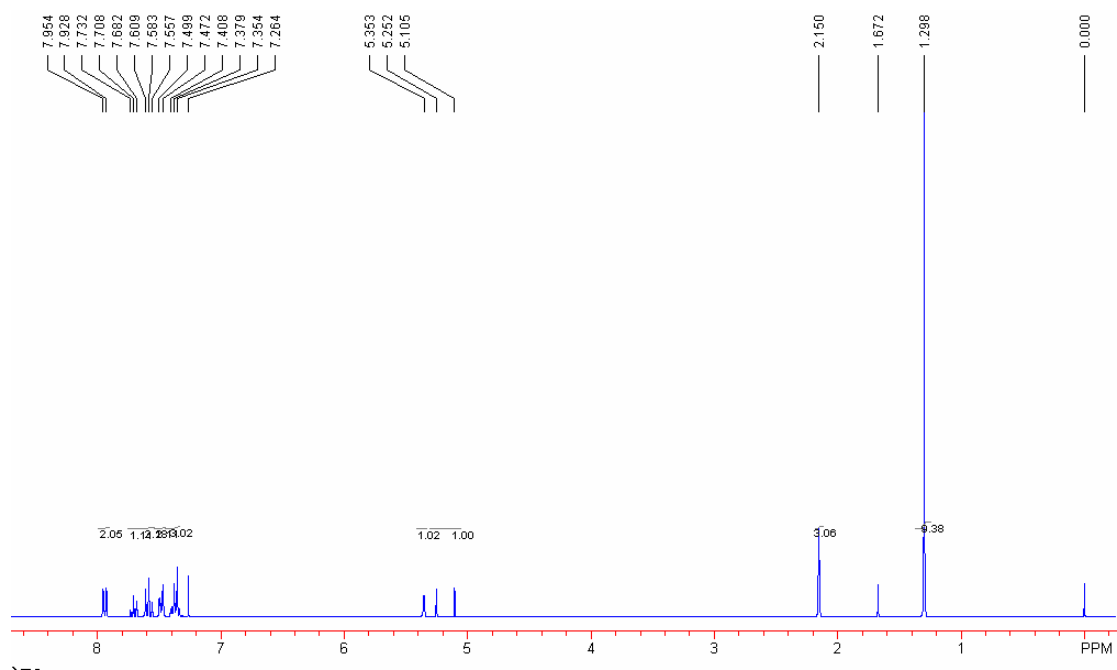


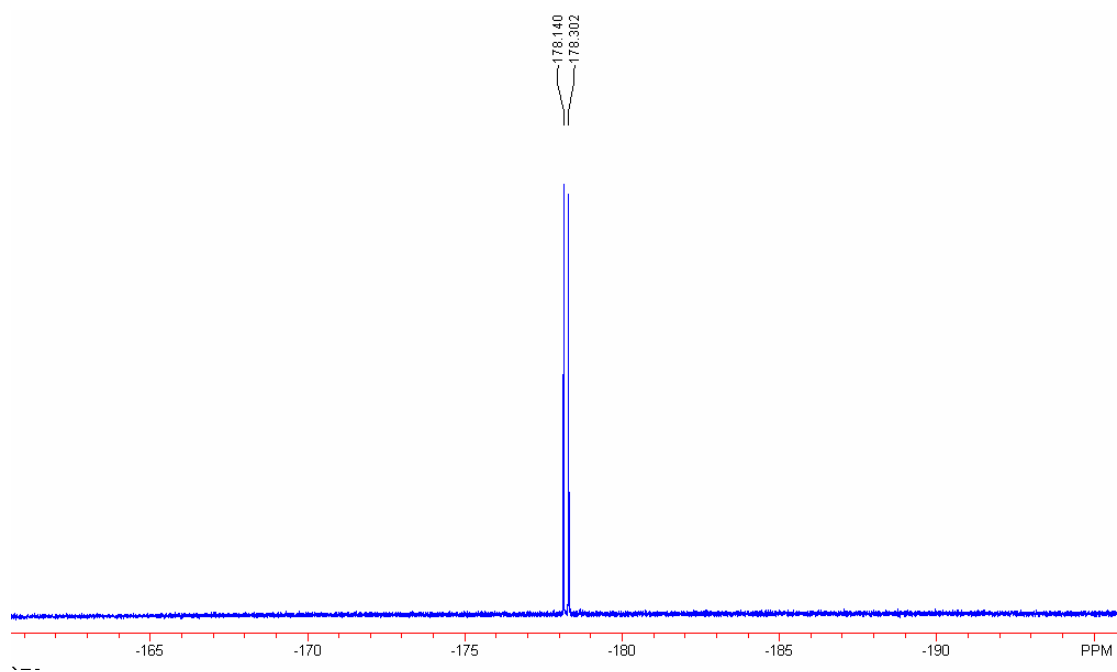
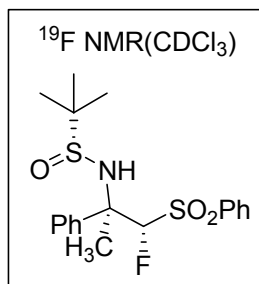
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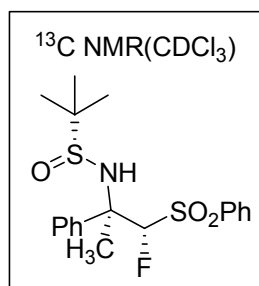




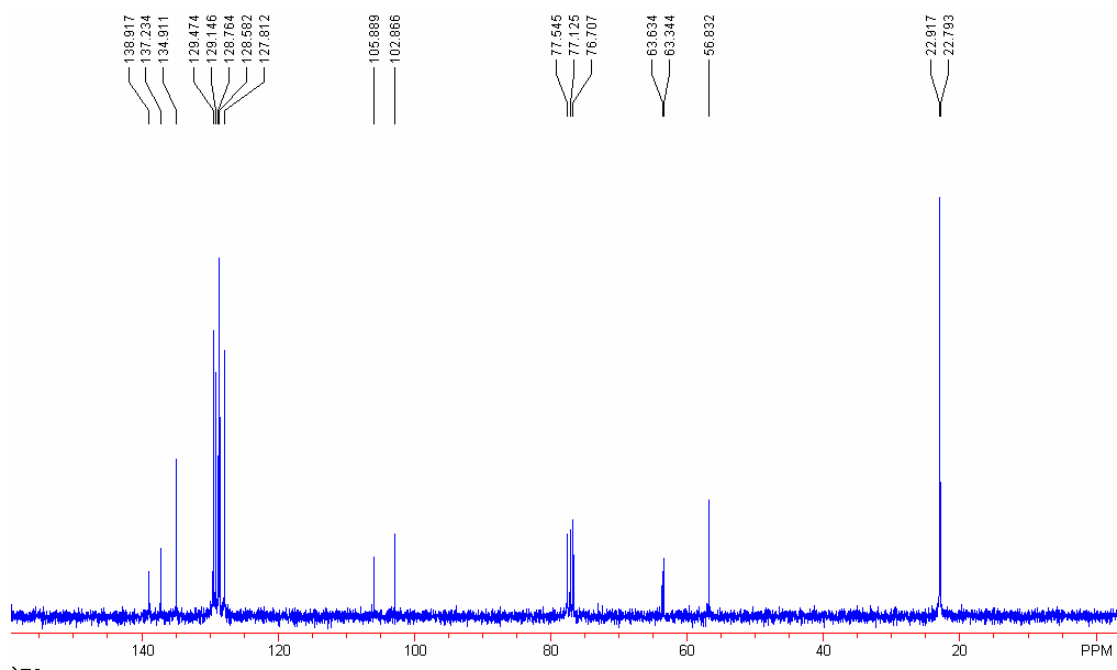
4a''

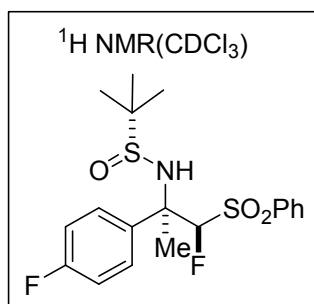




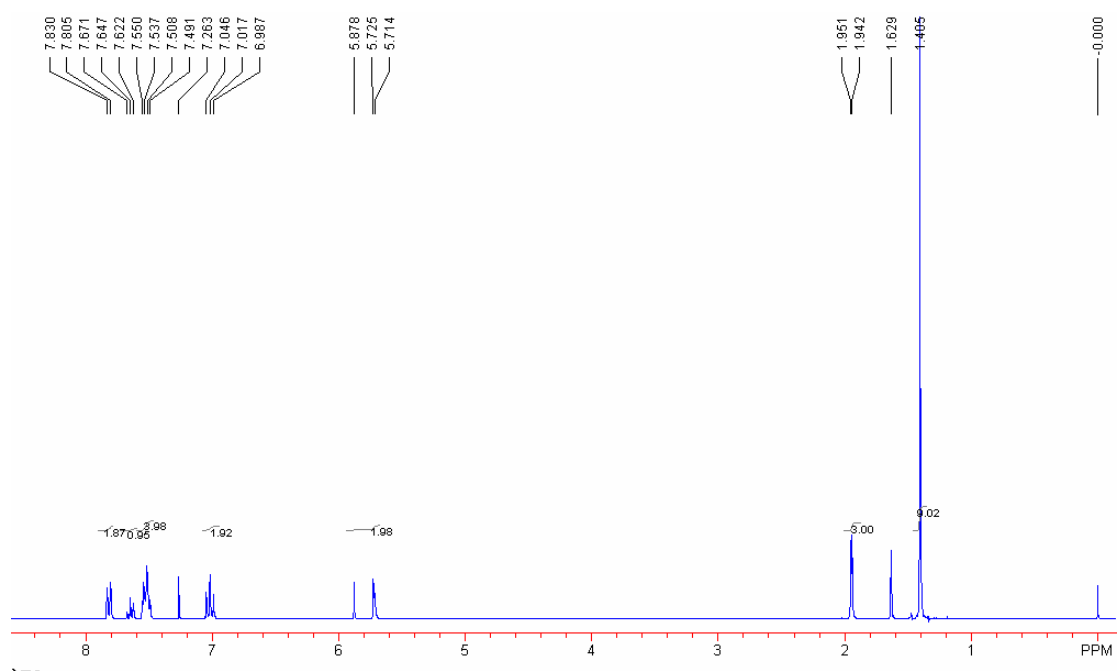


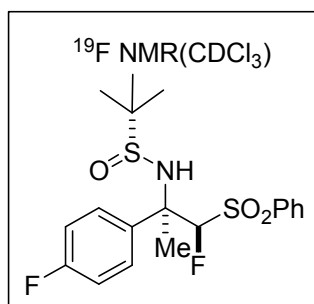
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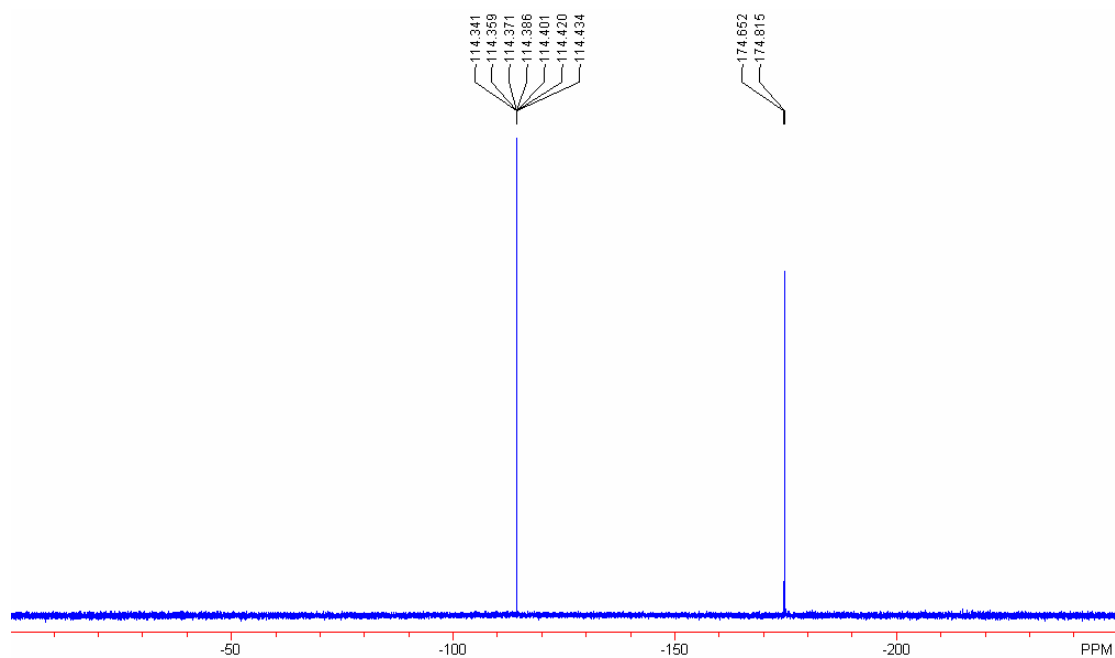


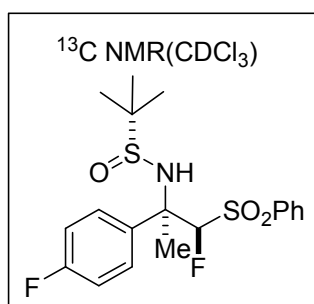
4b'



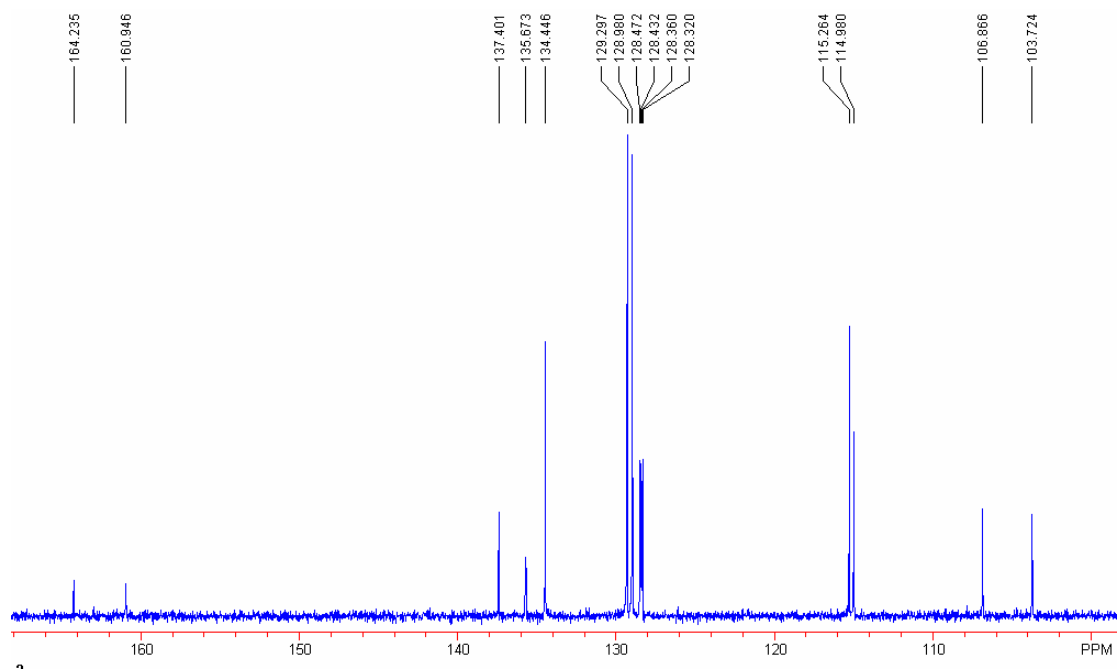


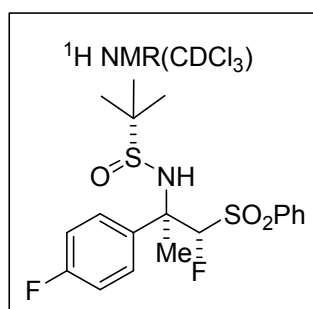
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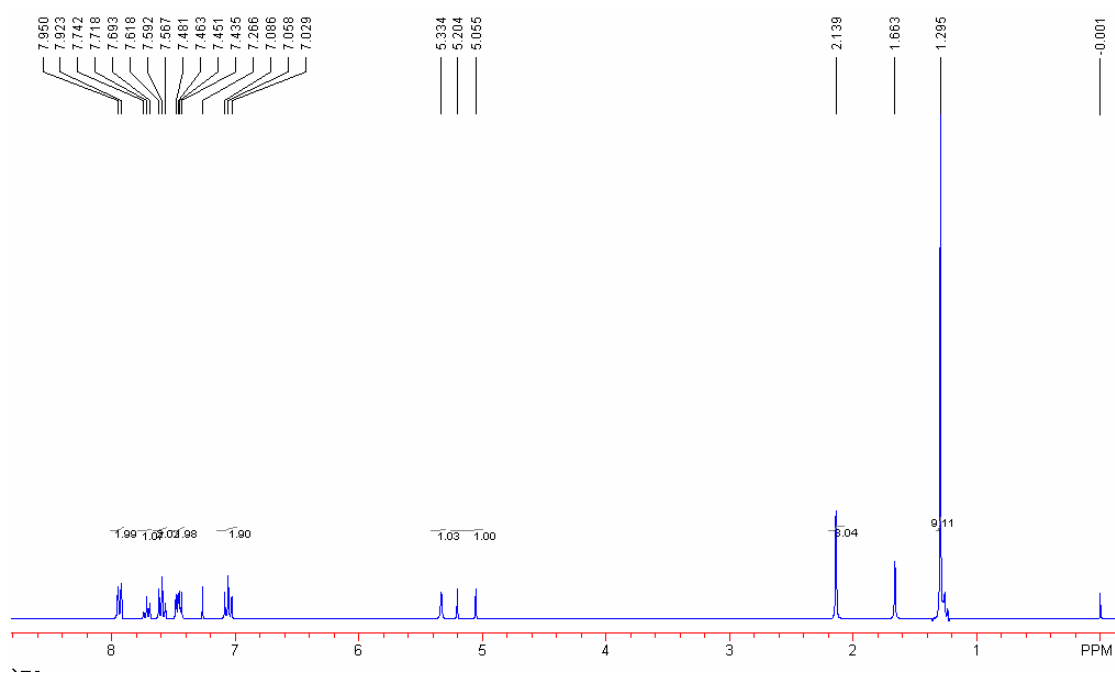


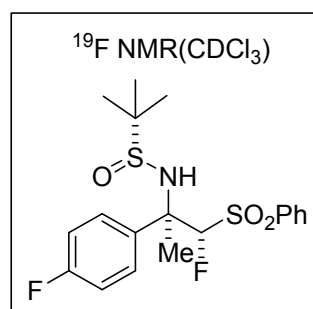
4b'



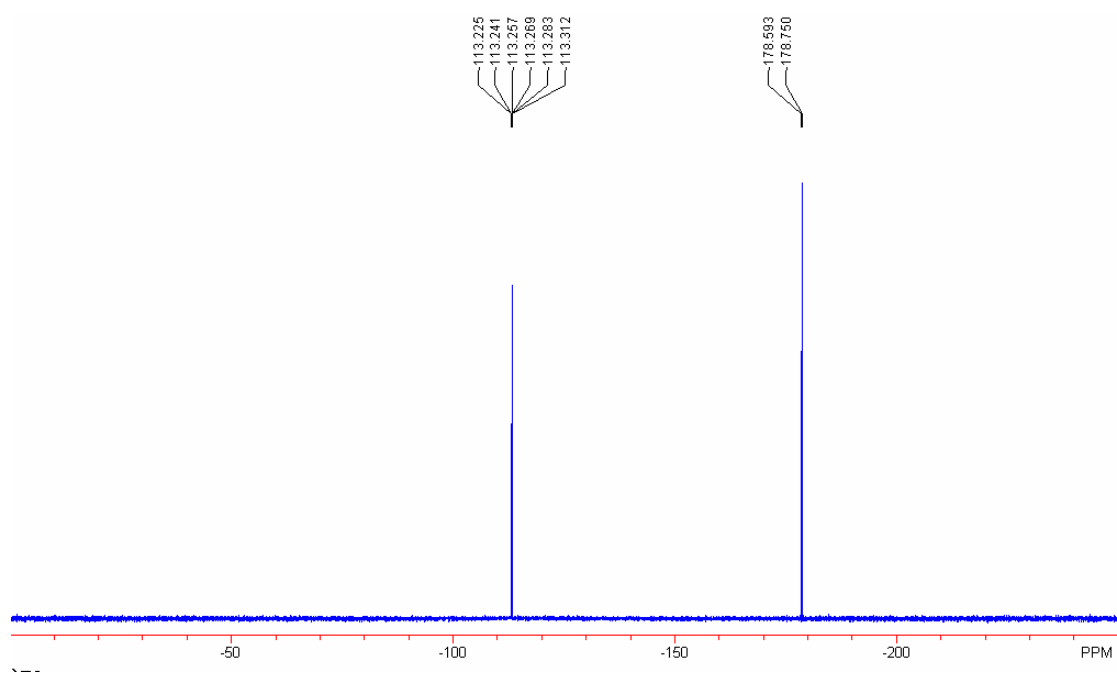


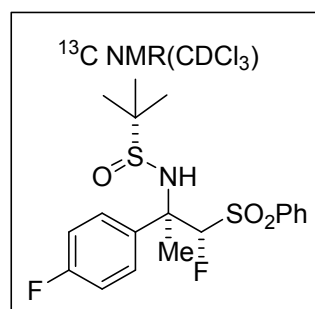
4b''



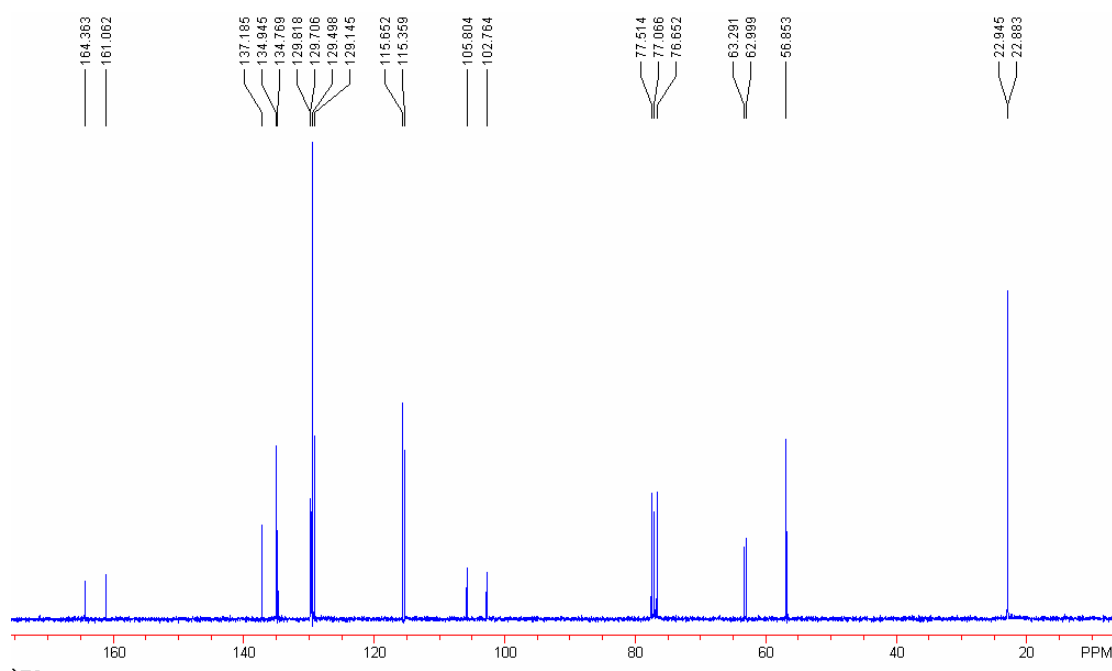


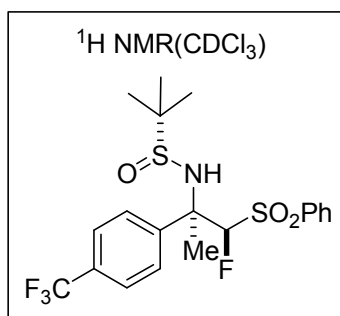
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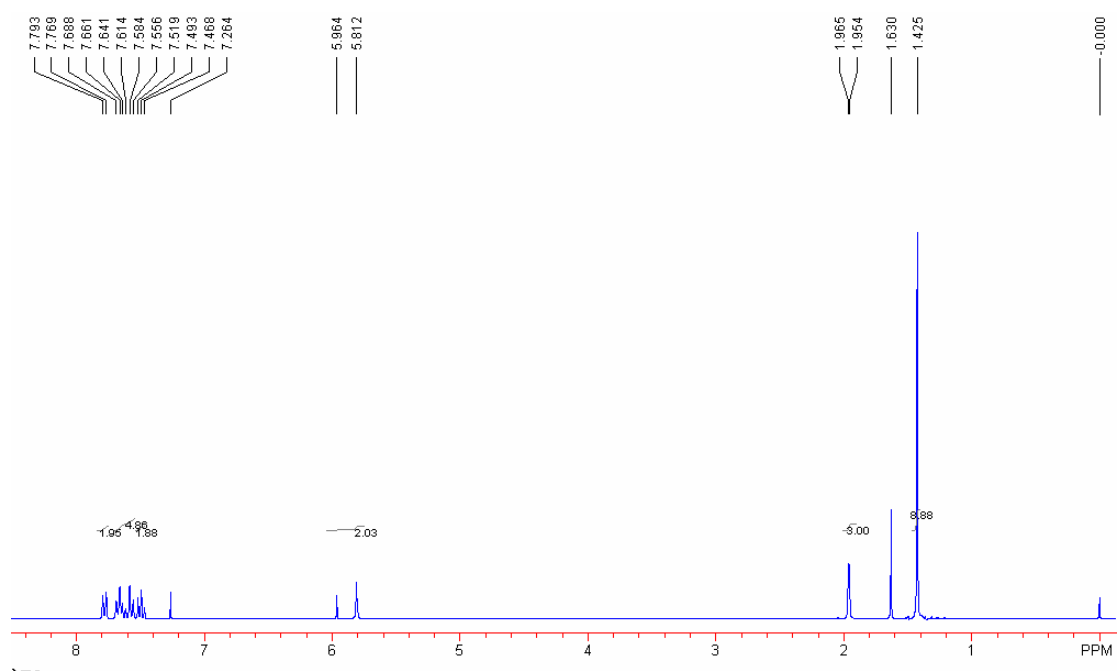


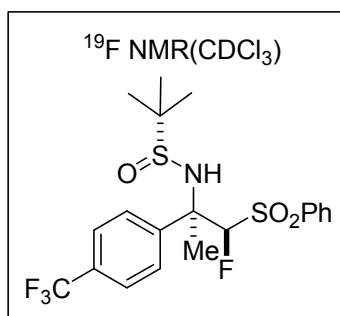
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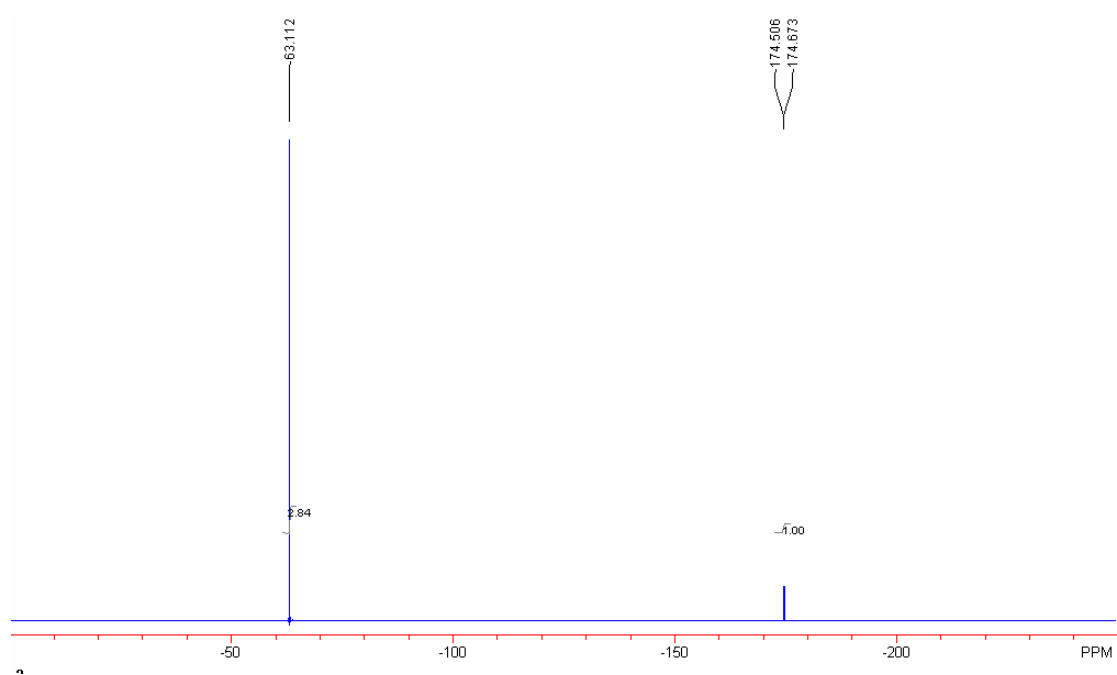


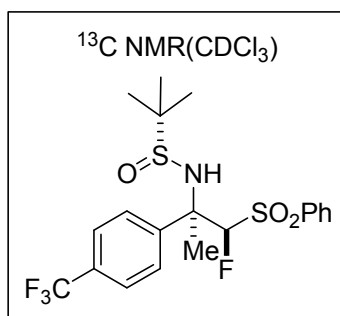
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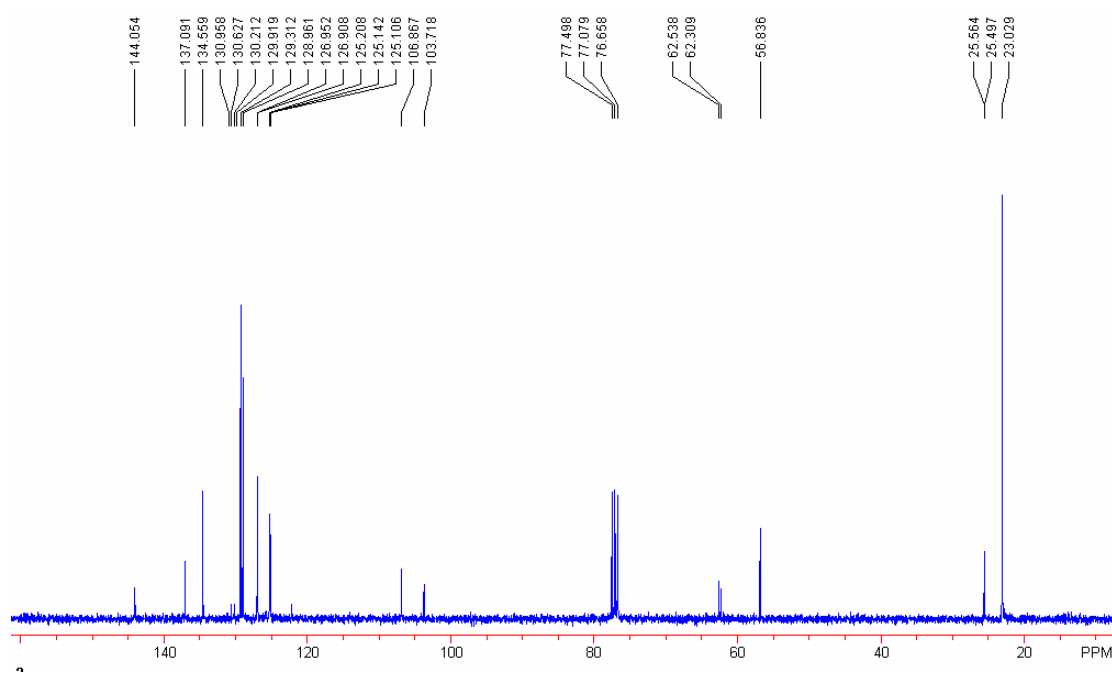


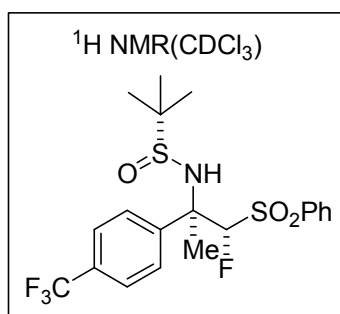
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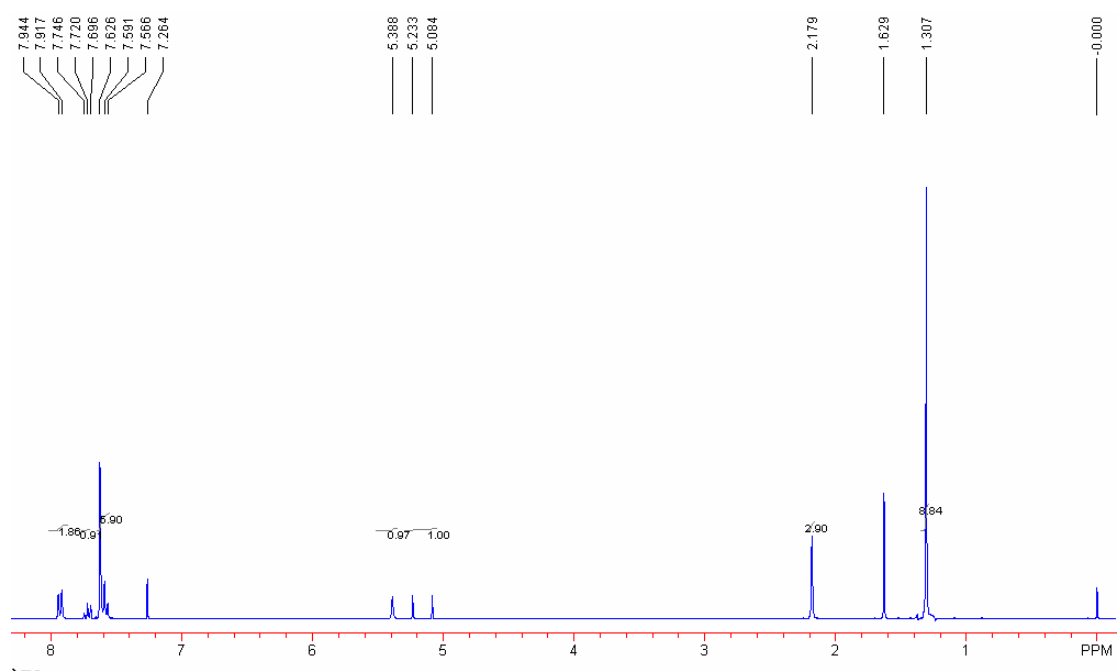


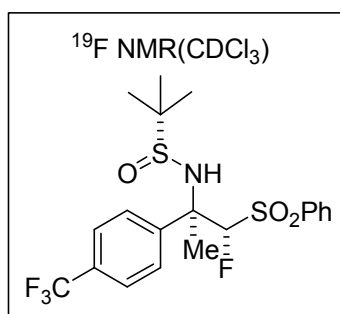
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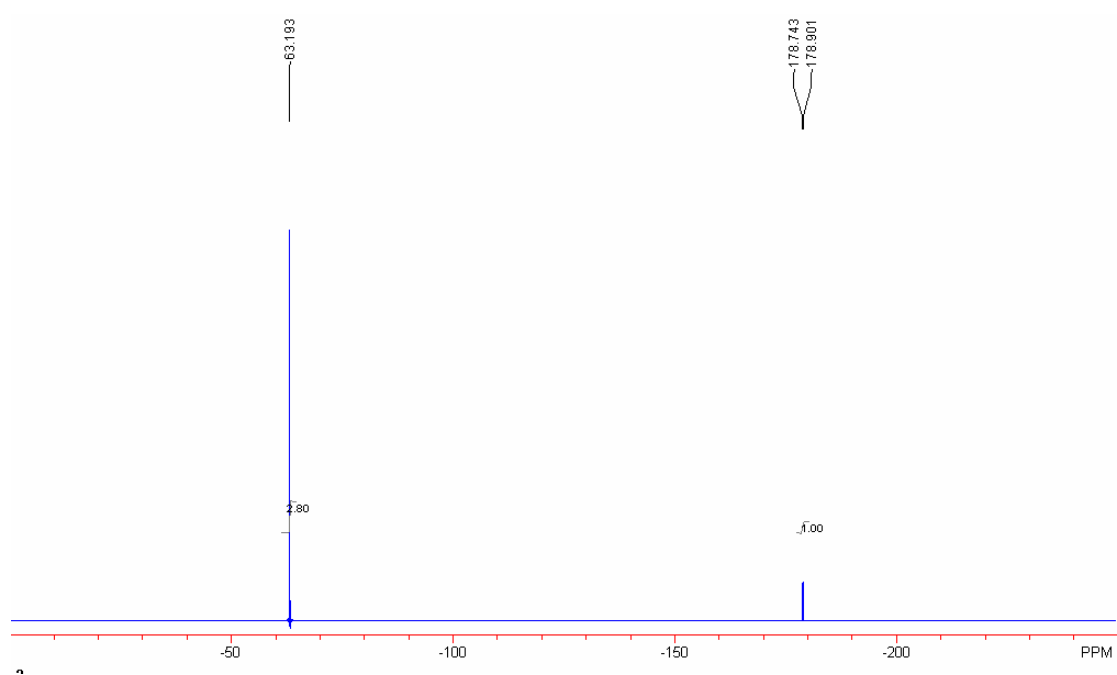


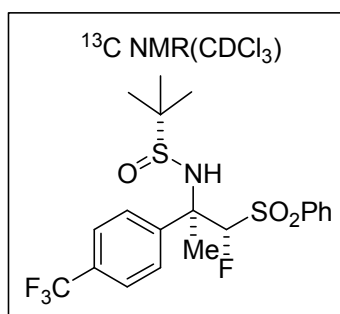
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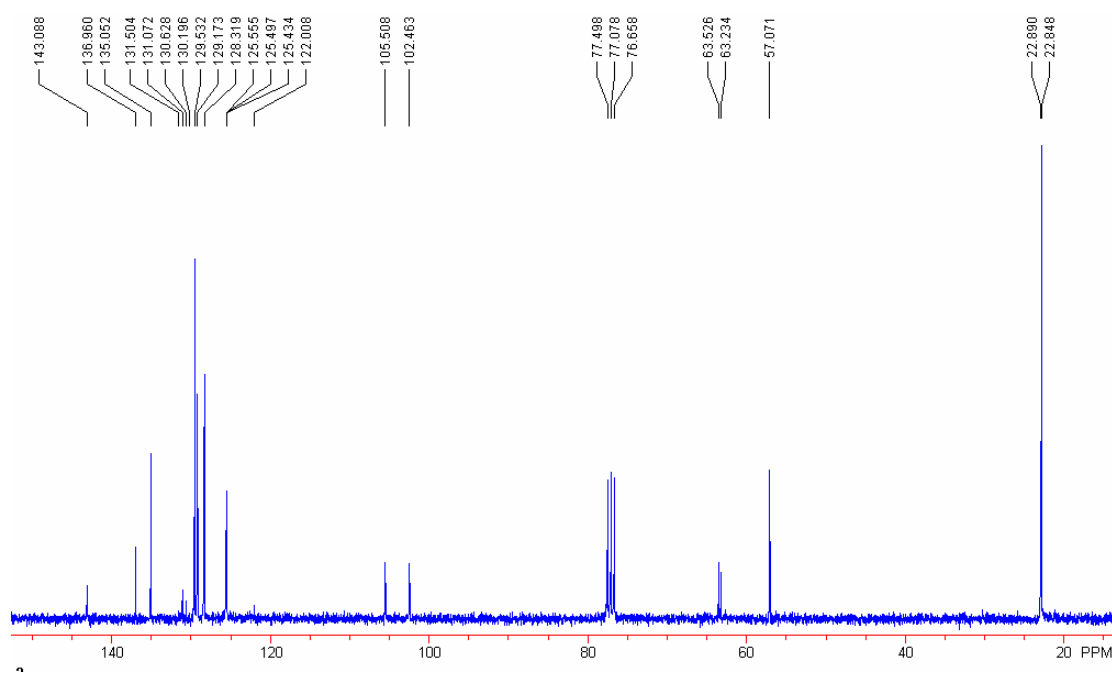


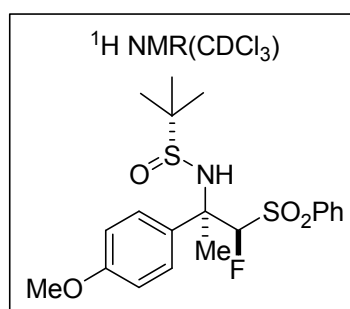
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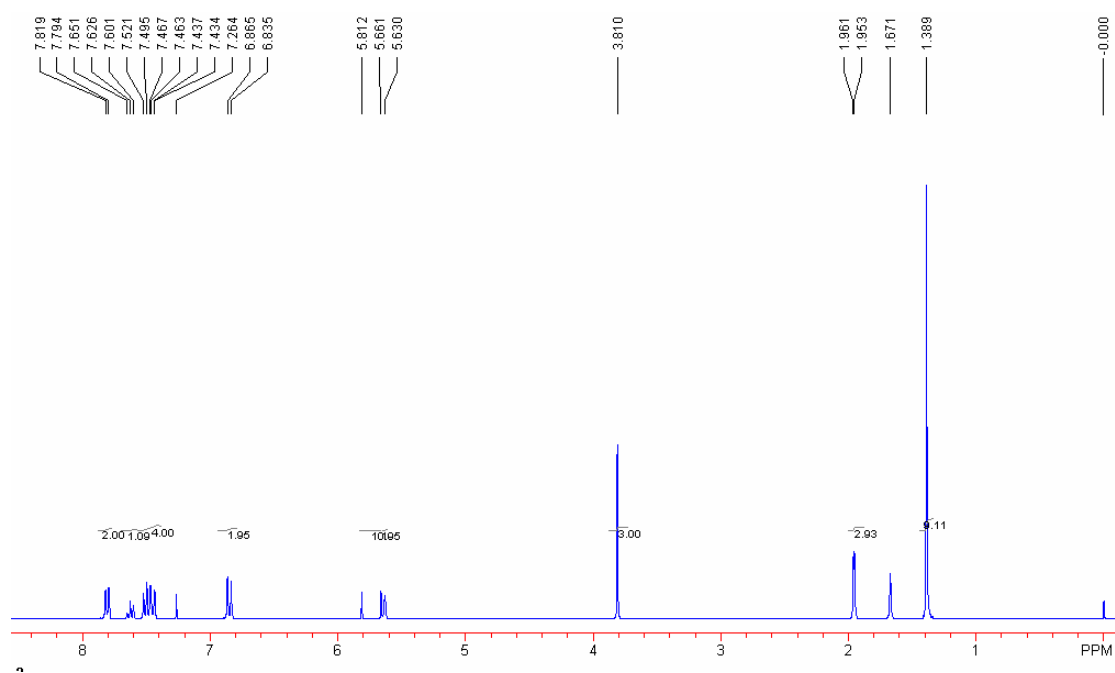


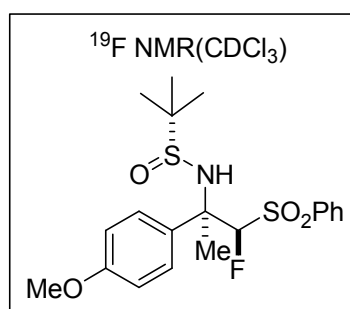
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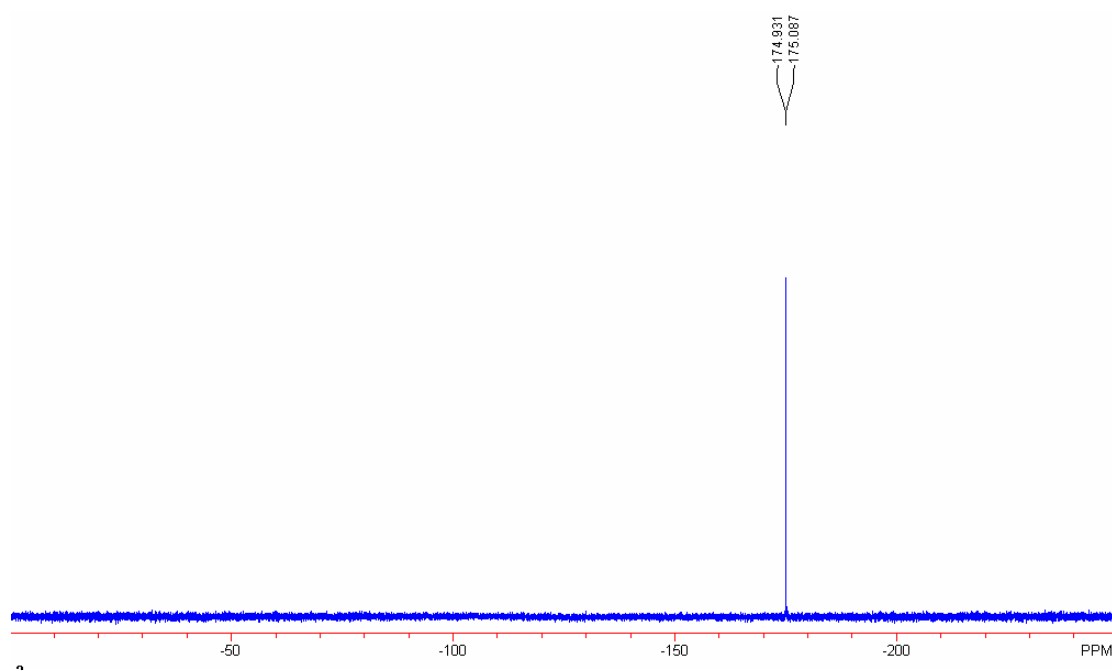


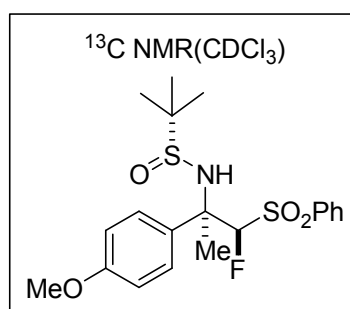
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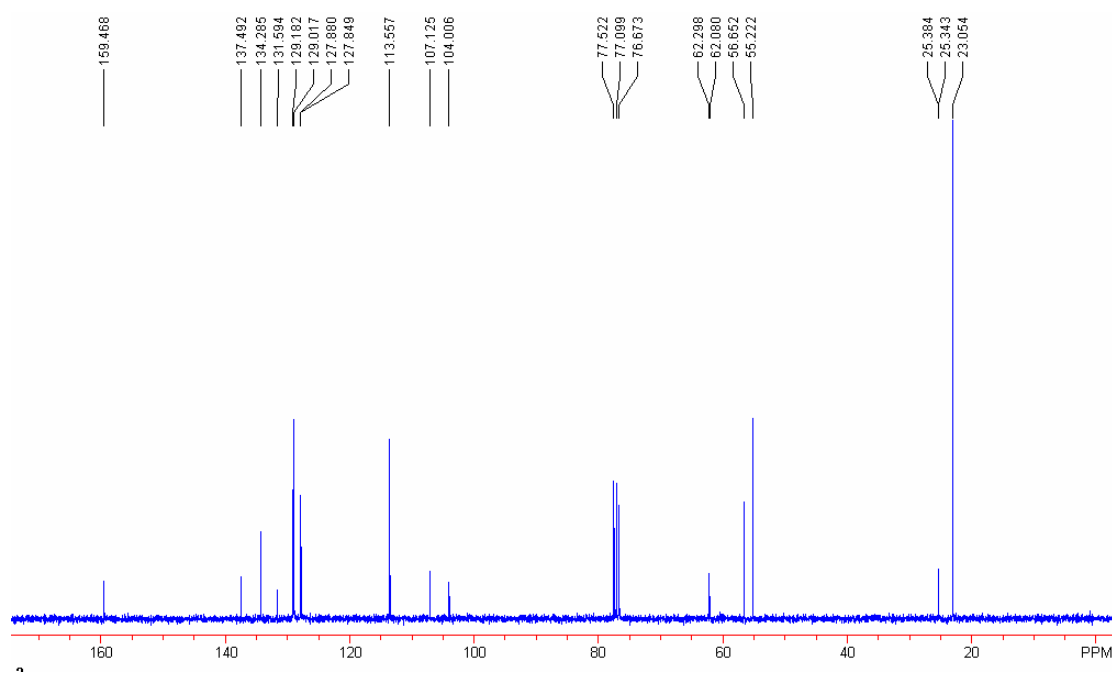


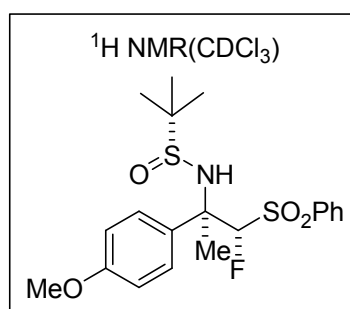
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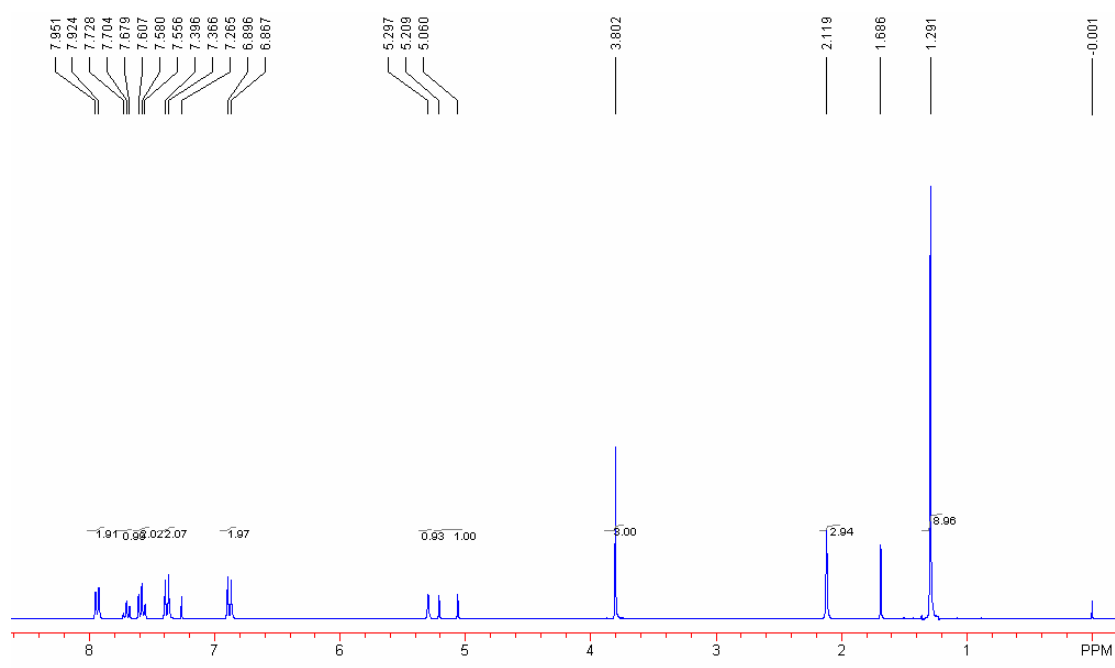


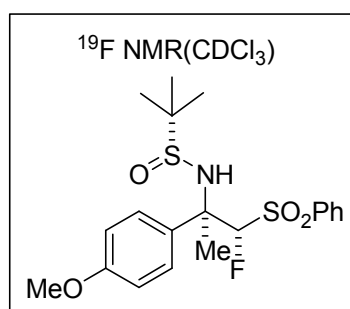
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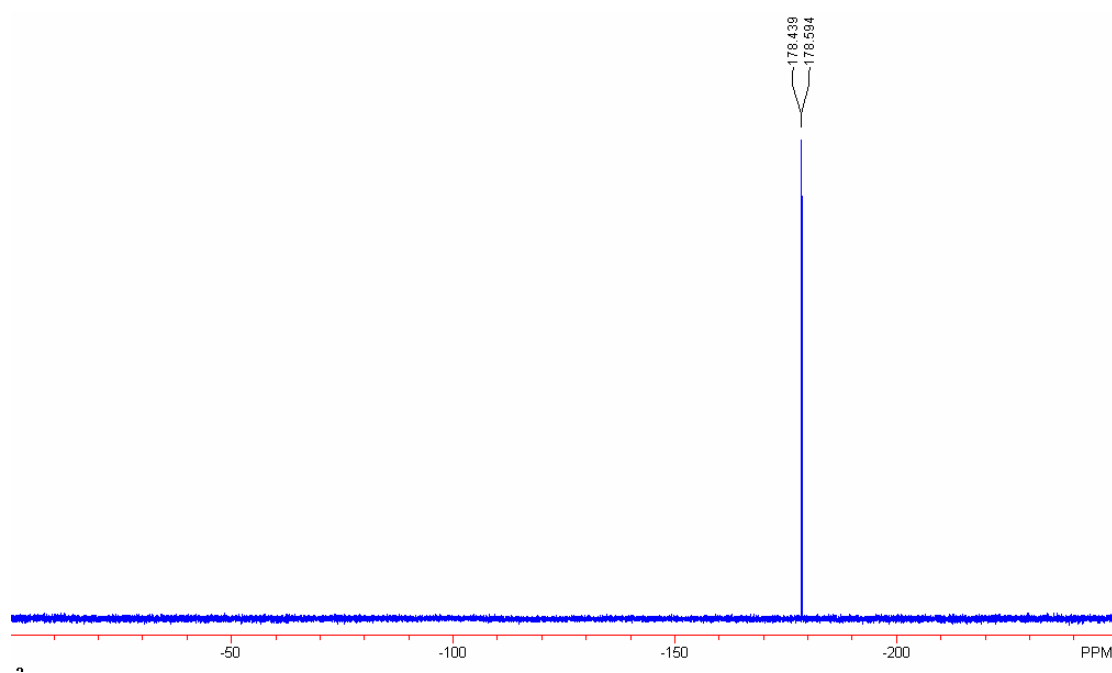


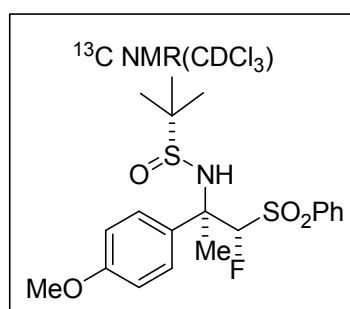
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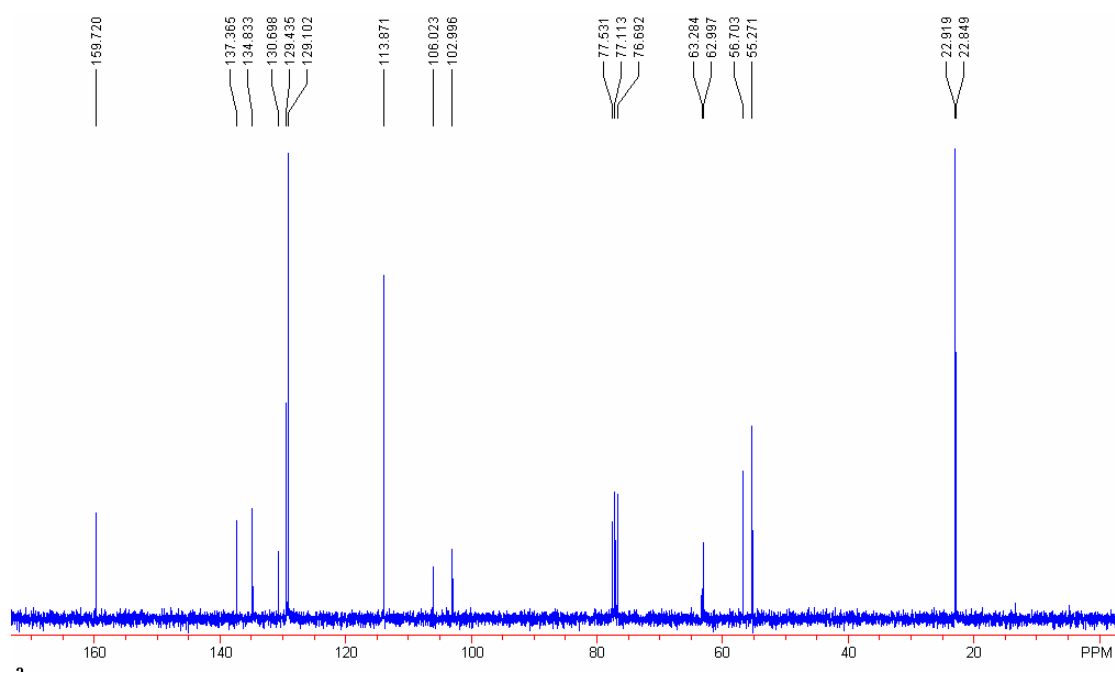


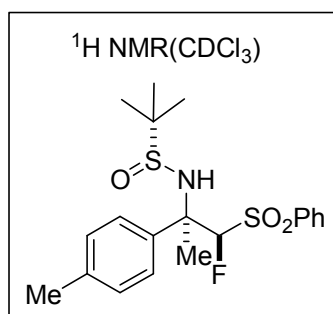
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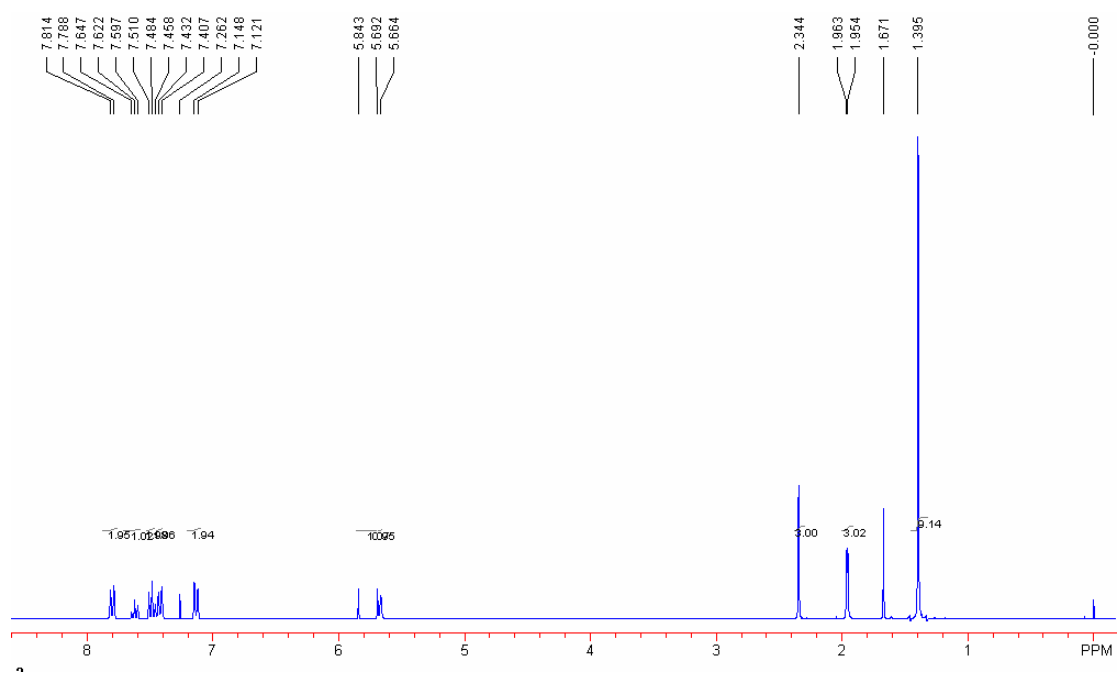


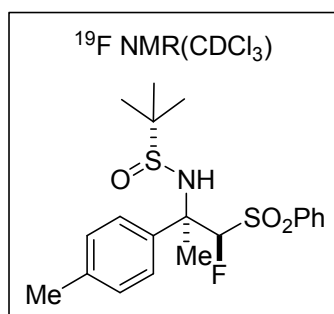
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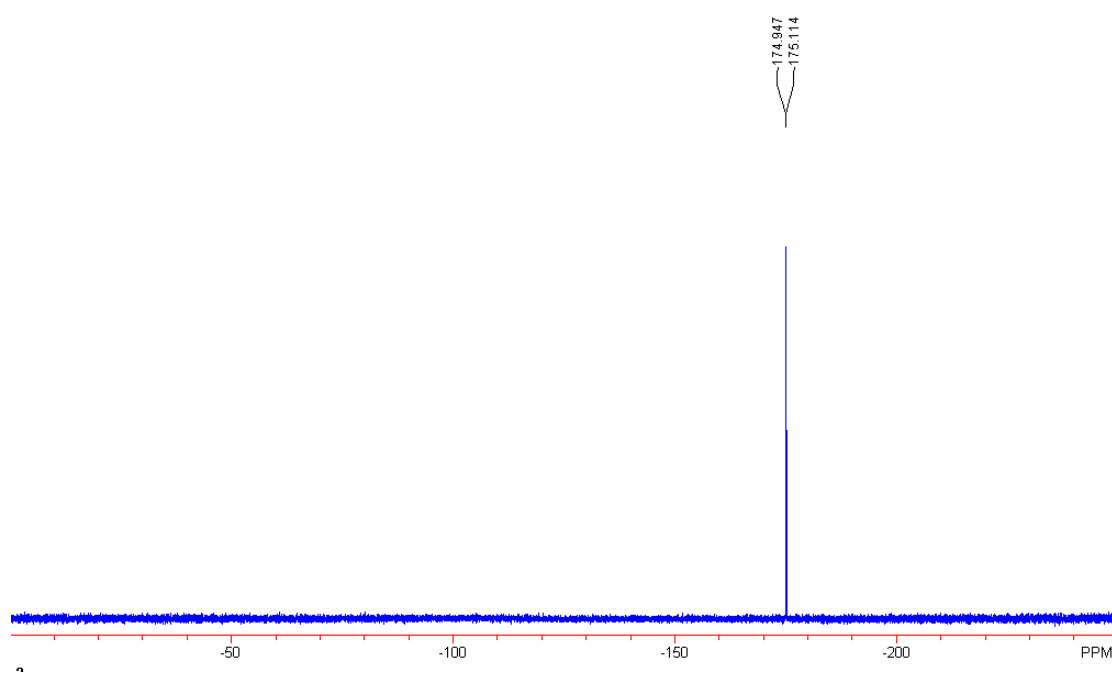


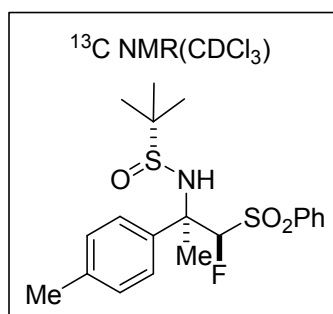
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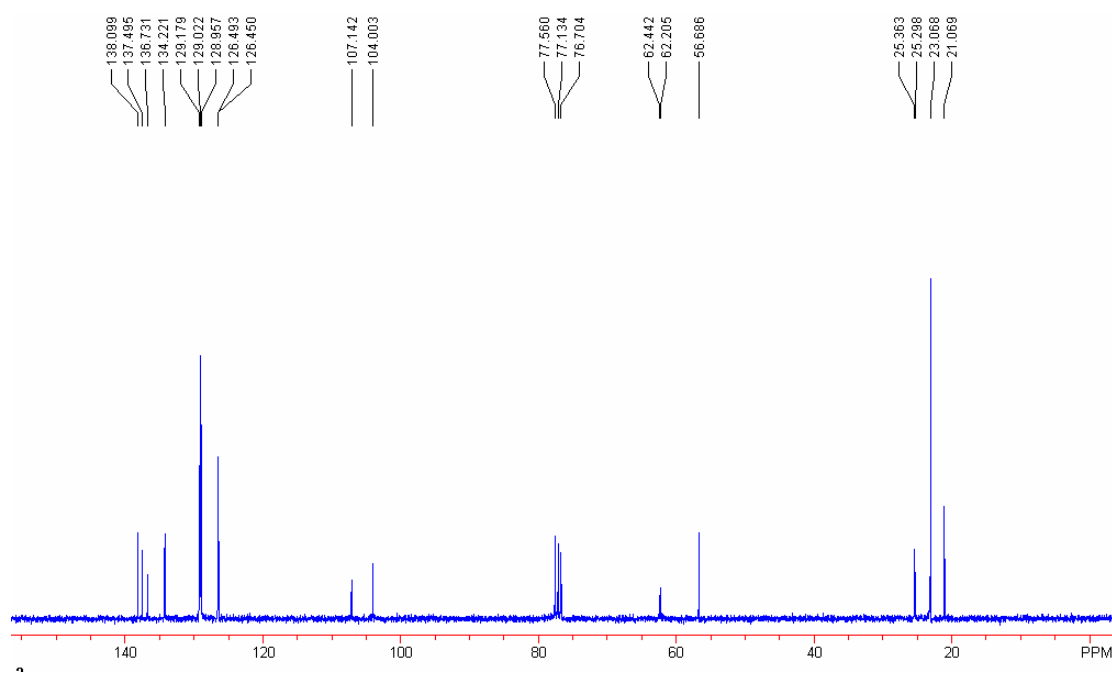


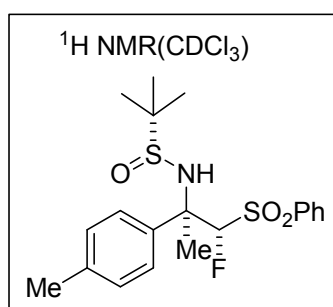
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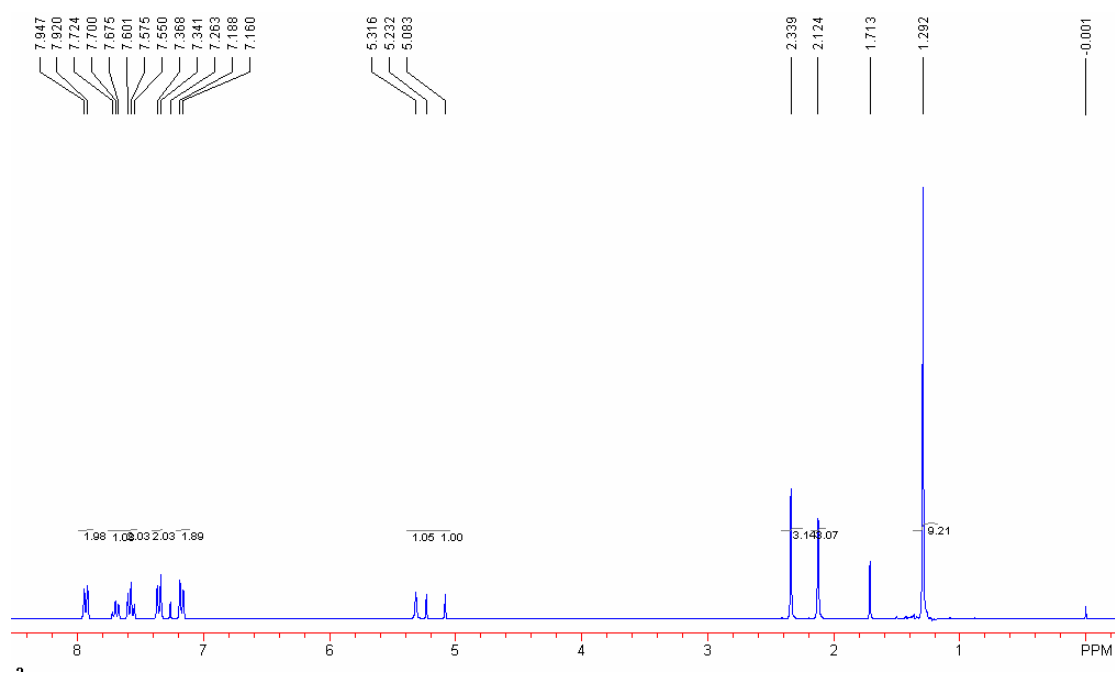


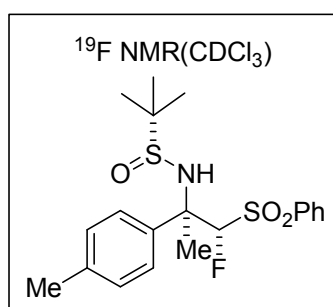
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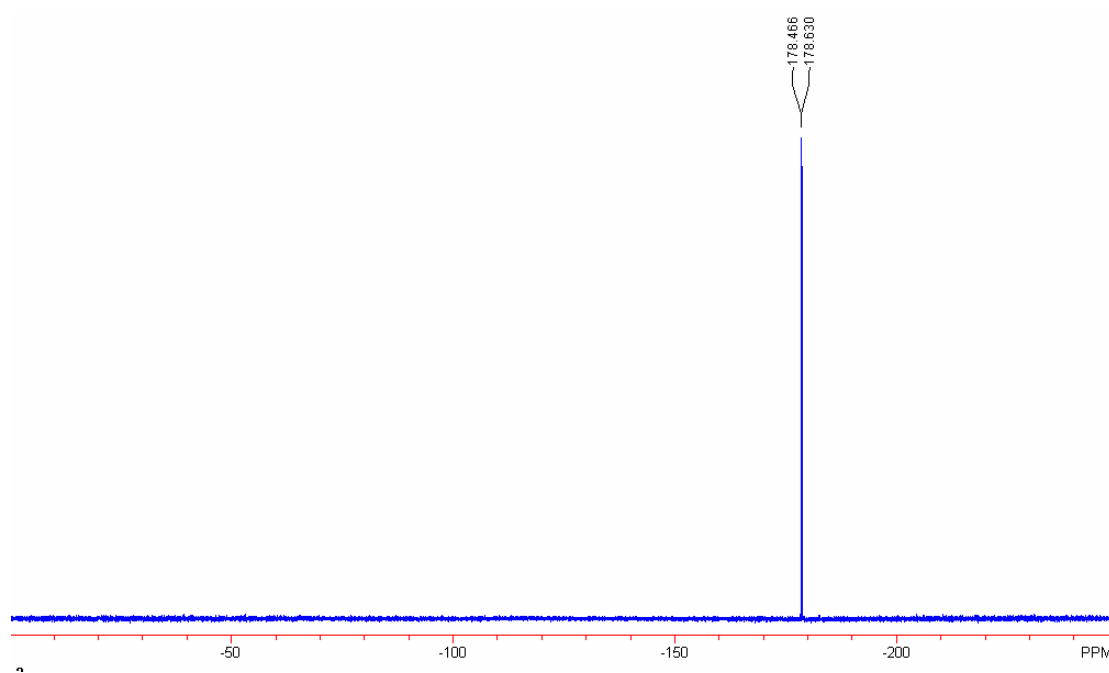


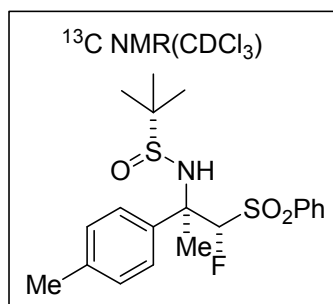
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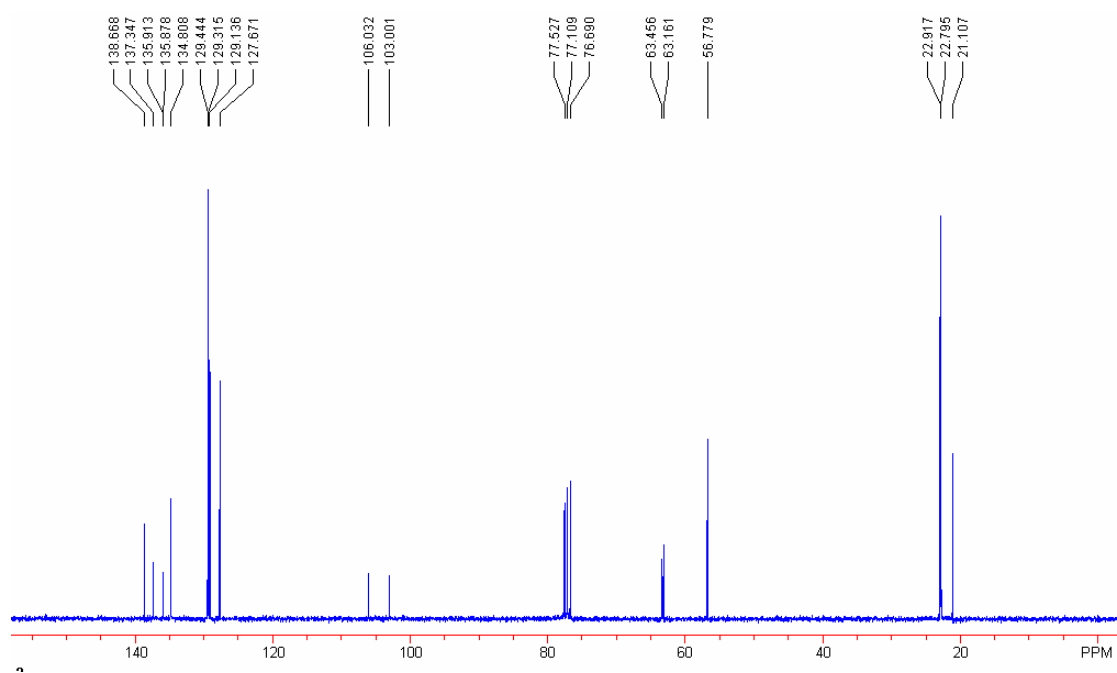


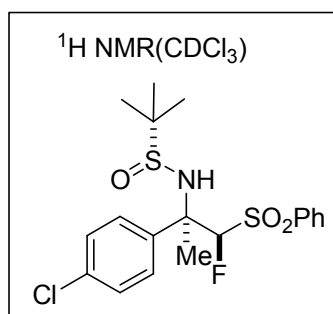
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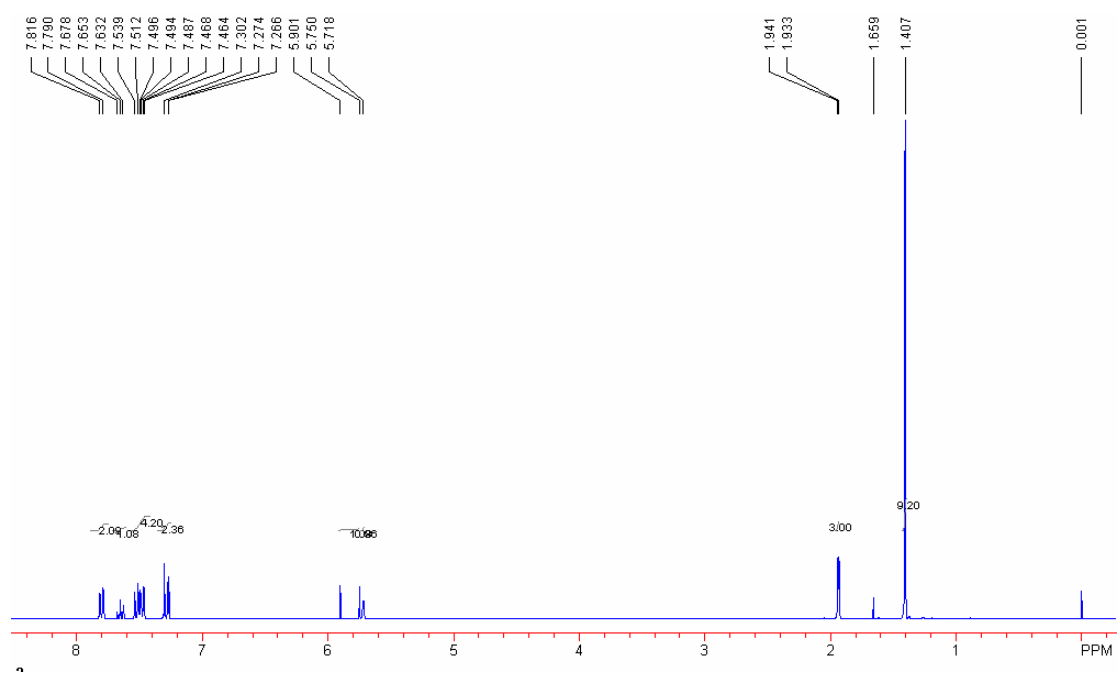


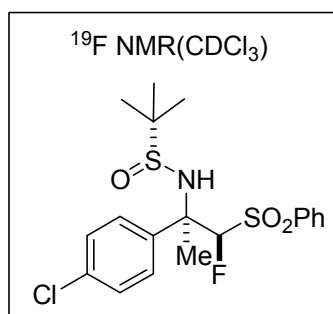
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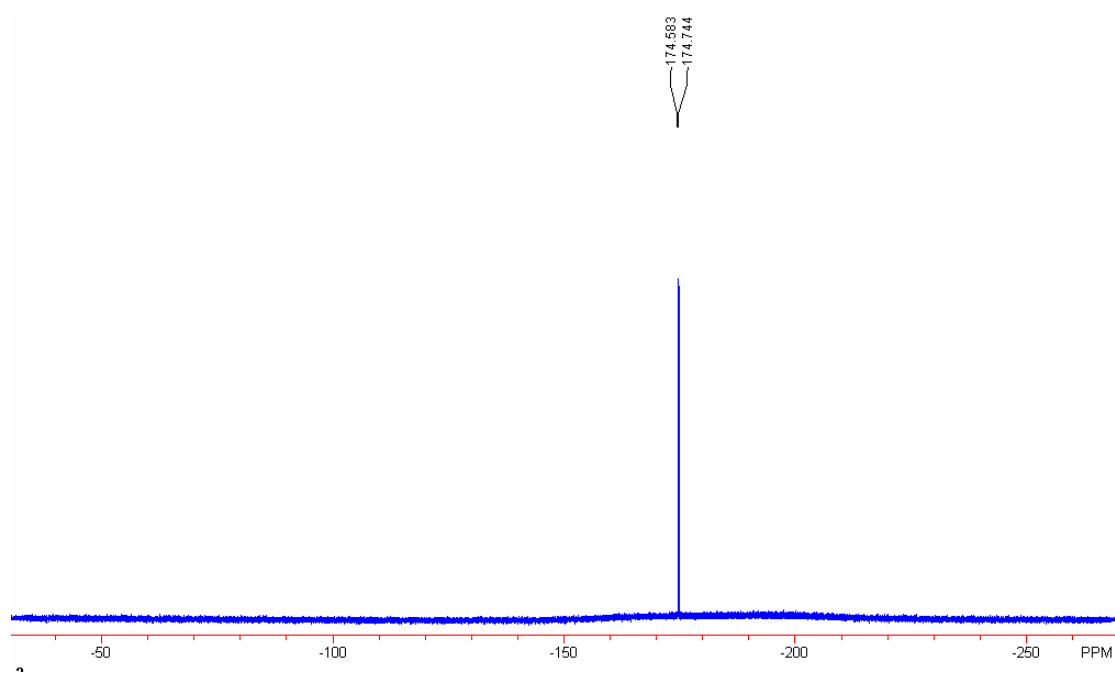


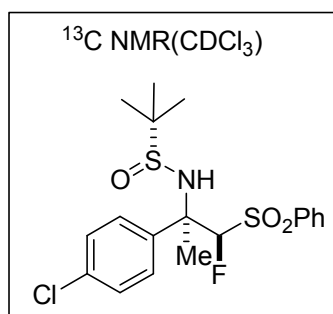
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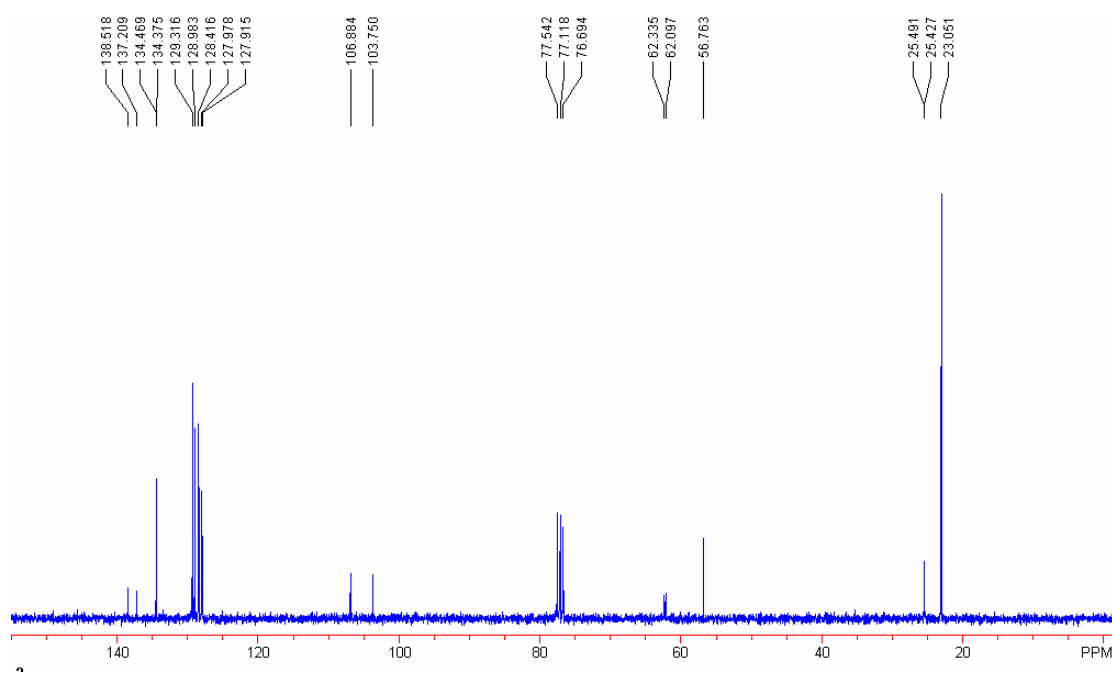


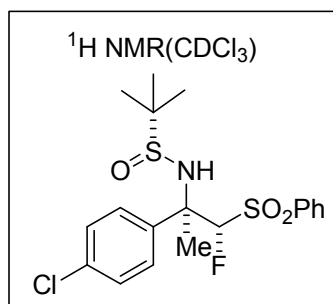
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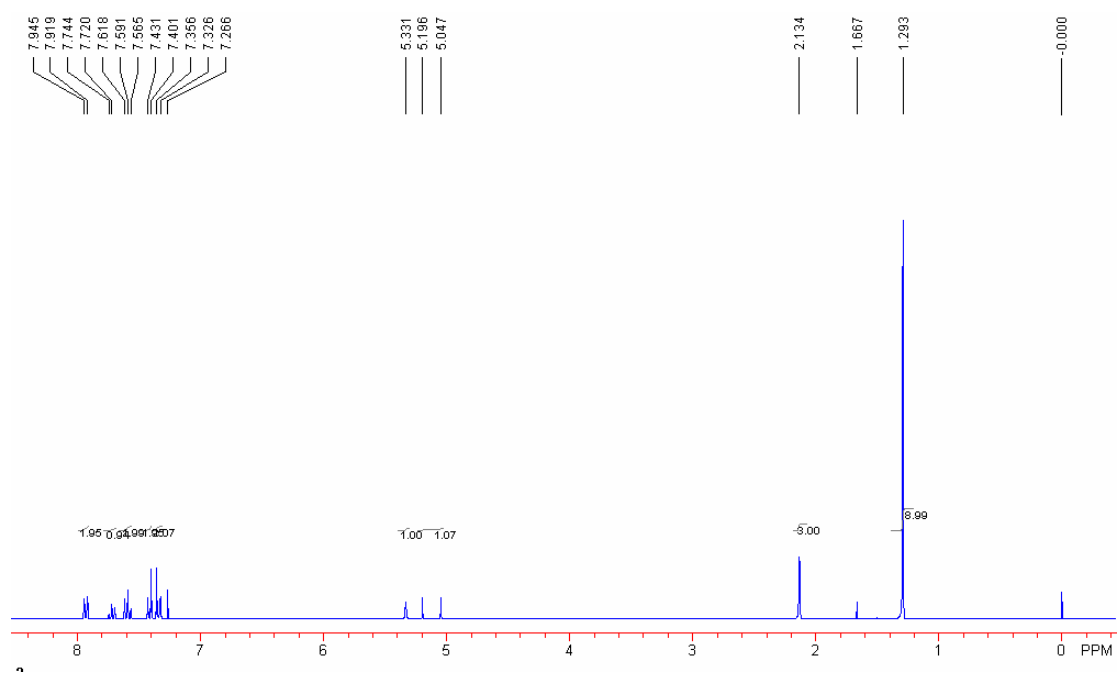


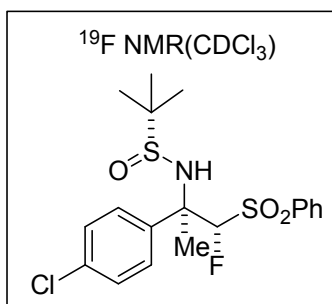
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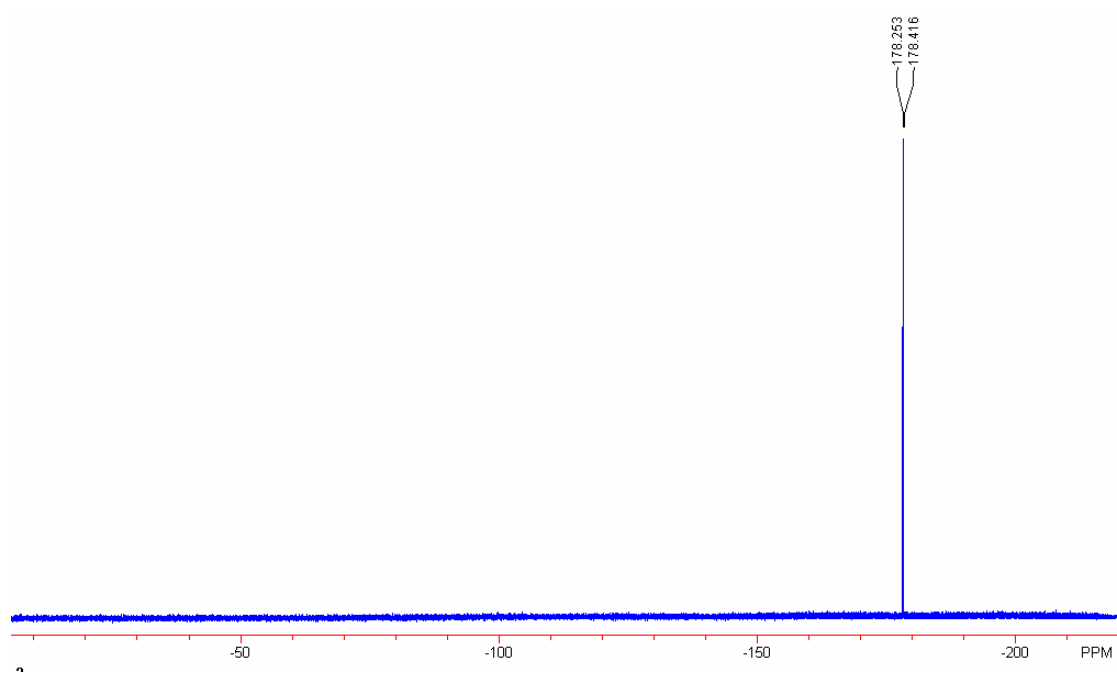


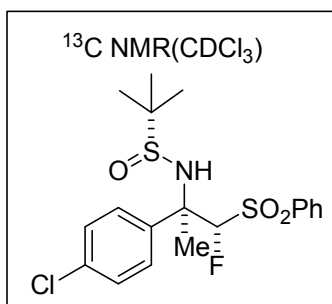
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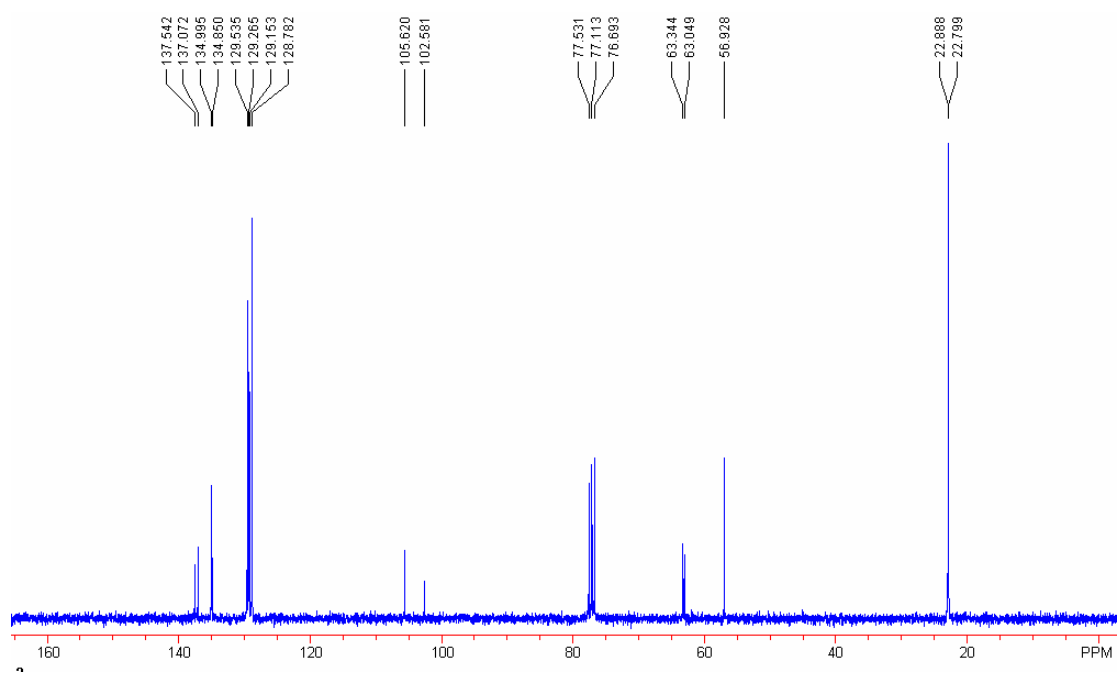


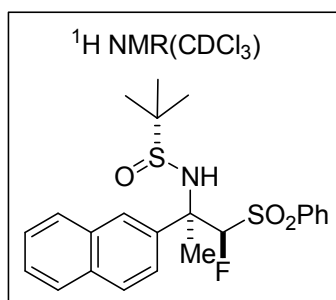
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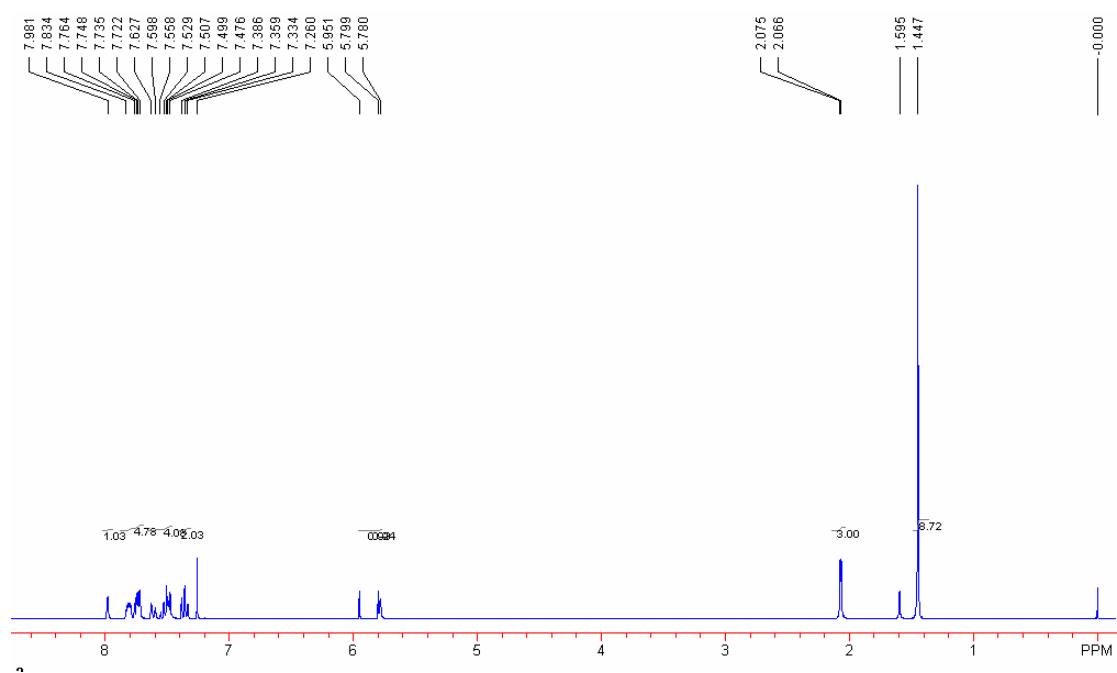


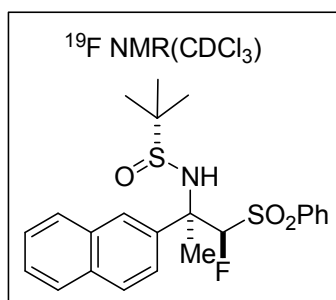
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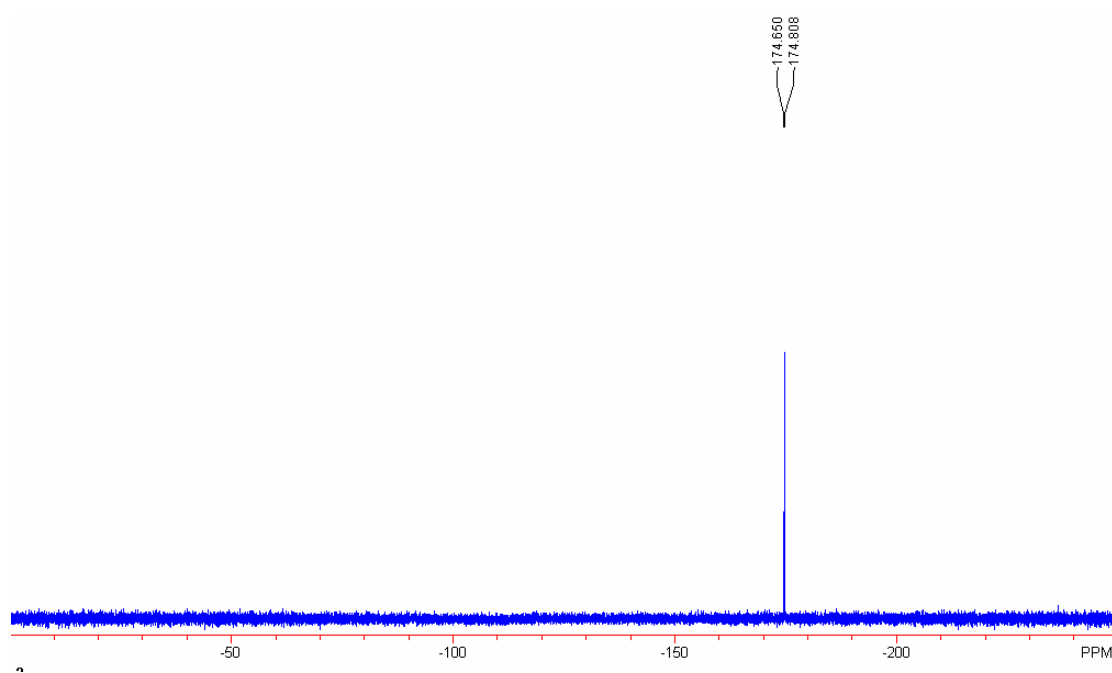


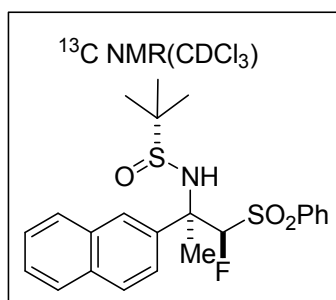
4g



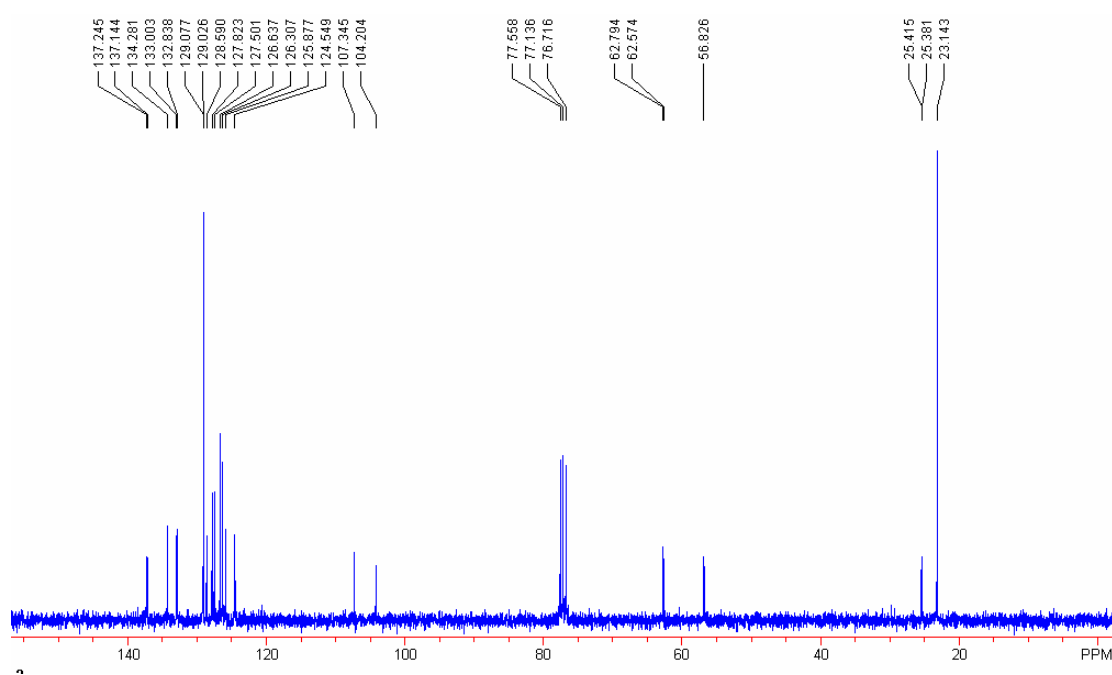


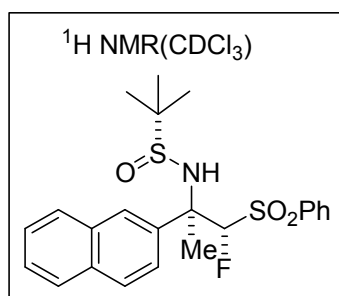
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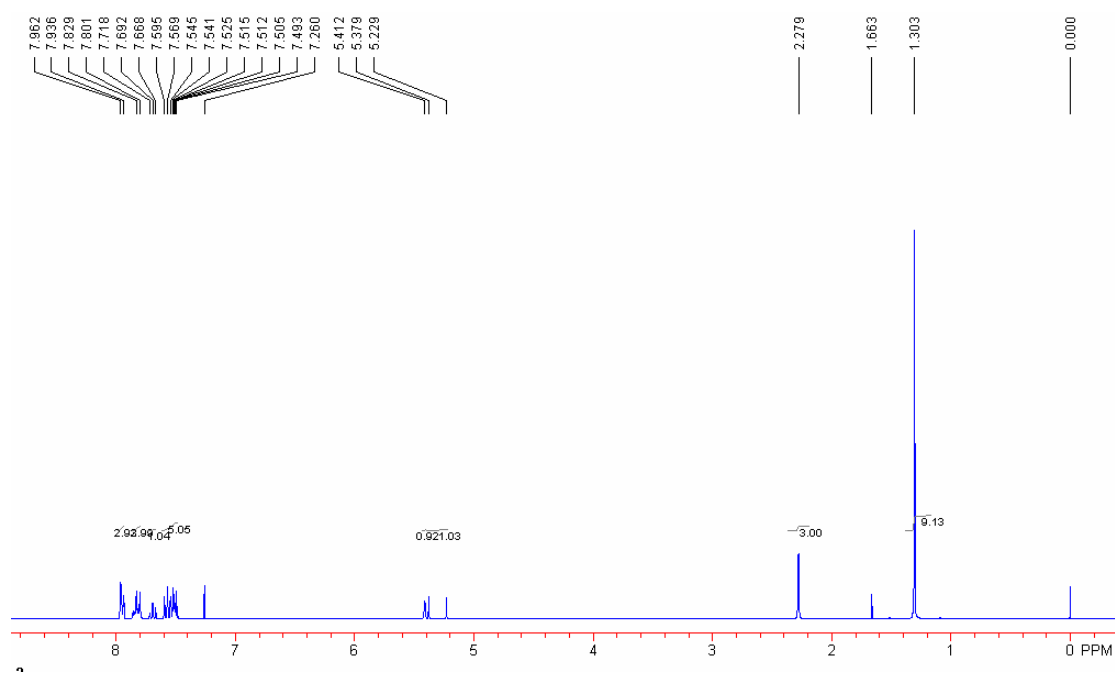


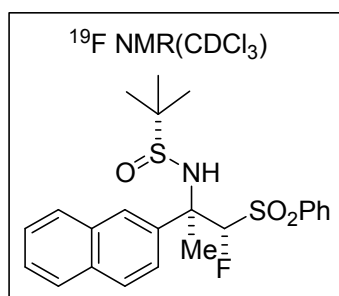
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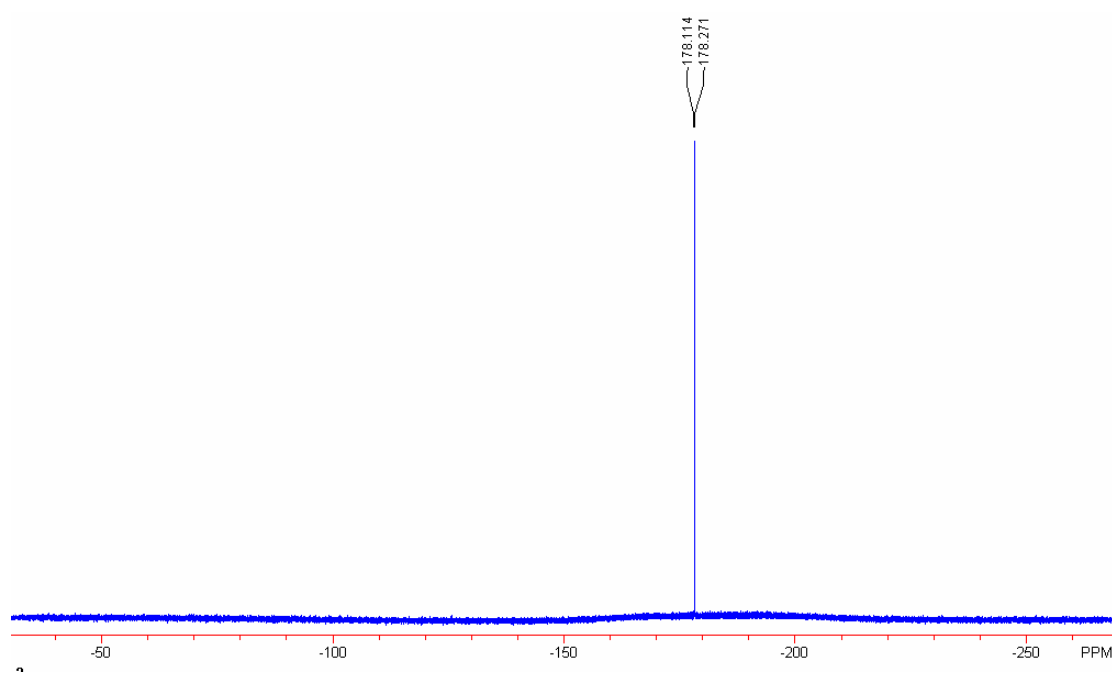


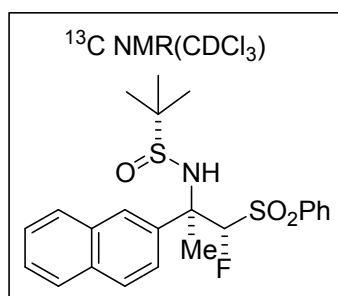
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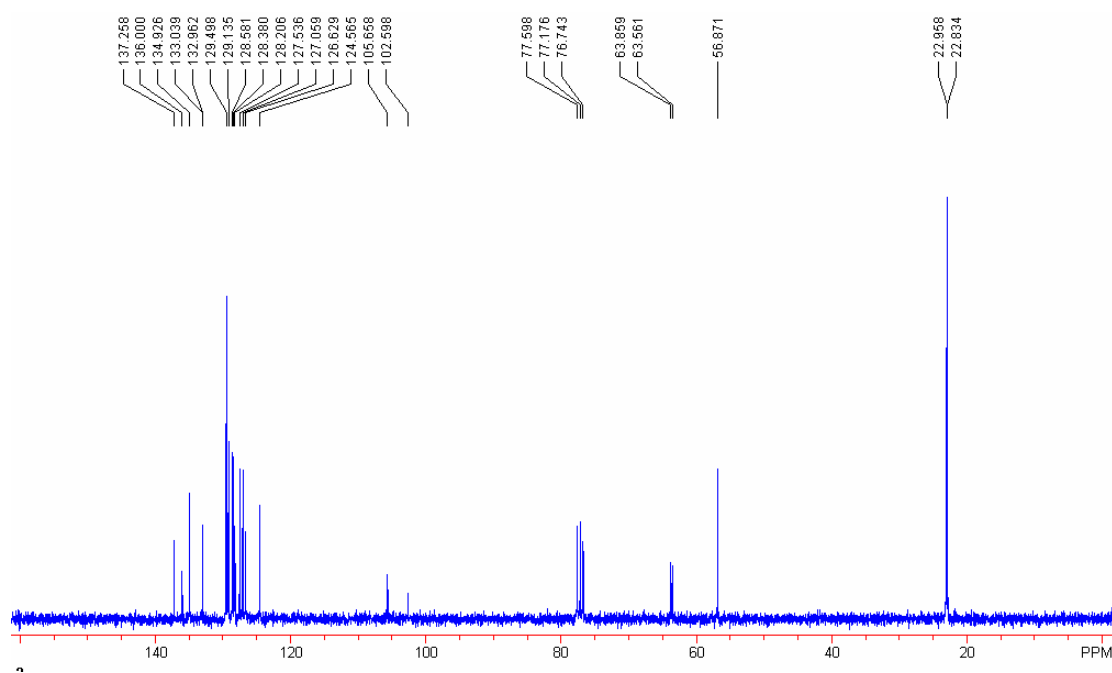


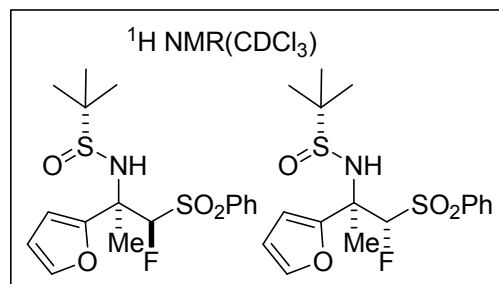
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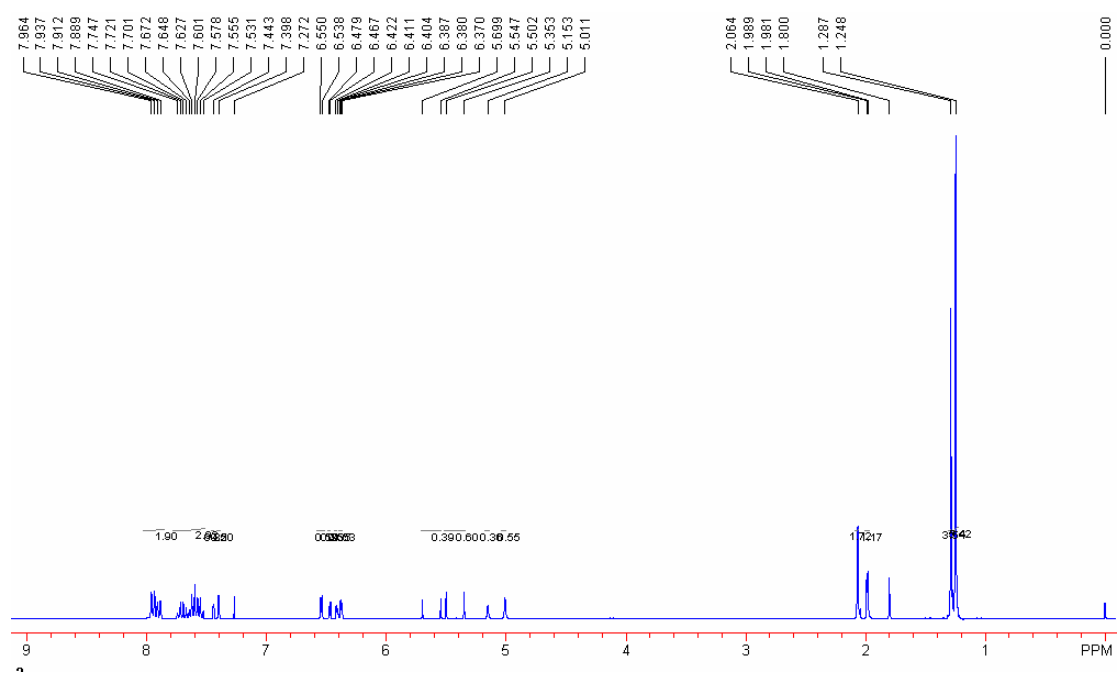


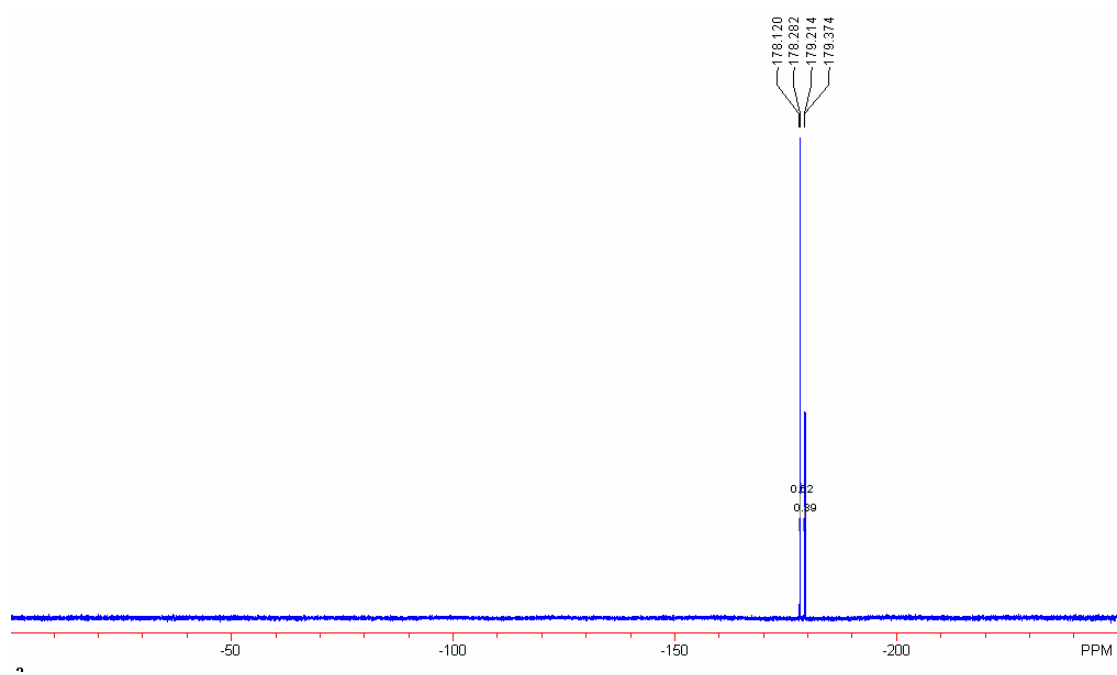
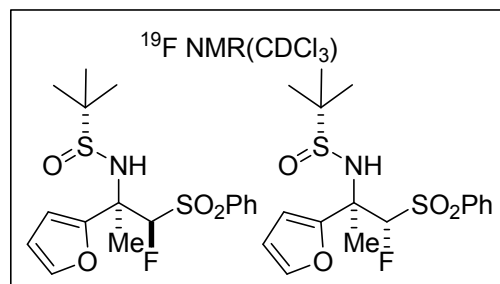
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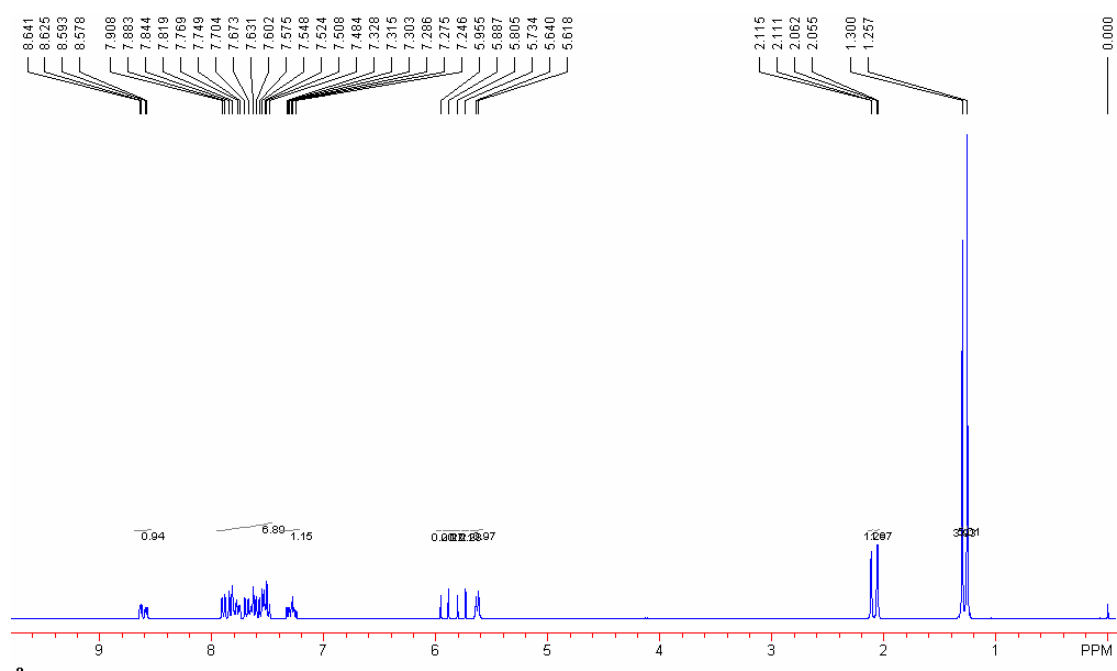
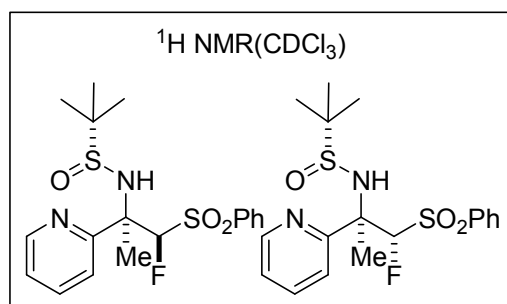


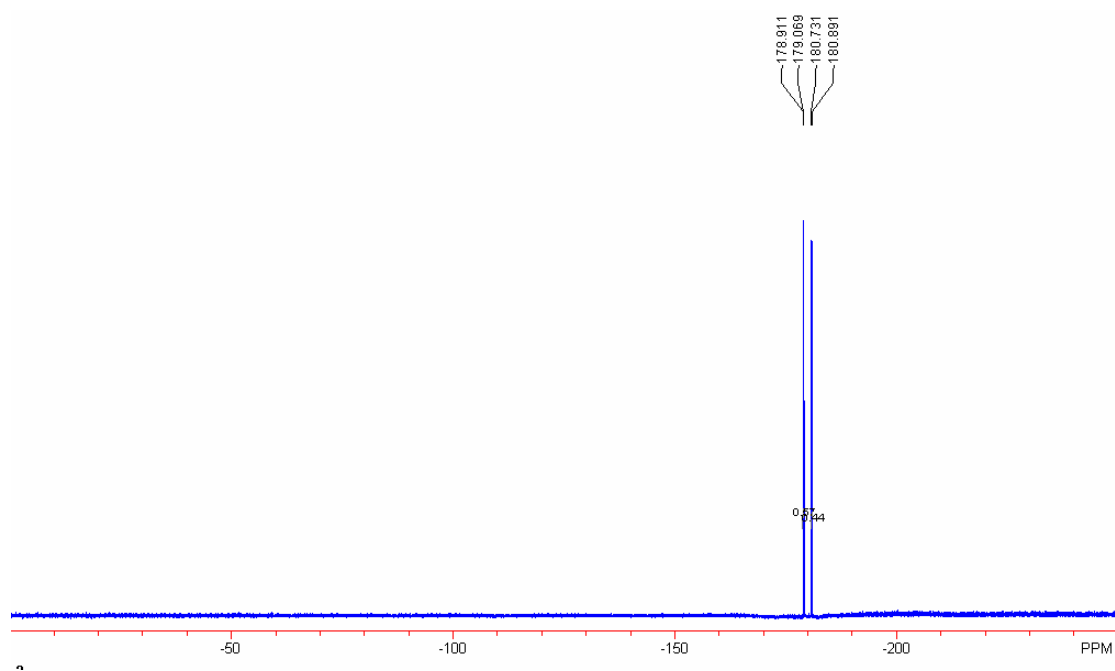
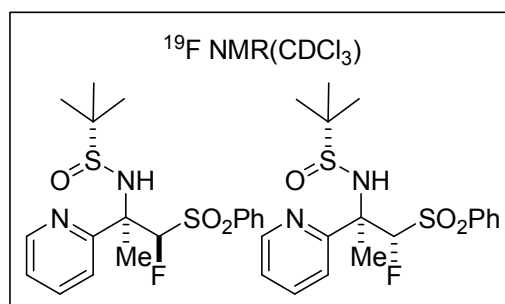


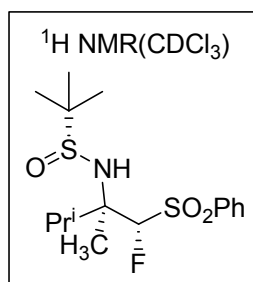
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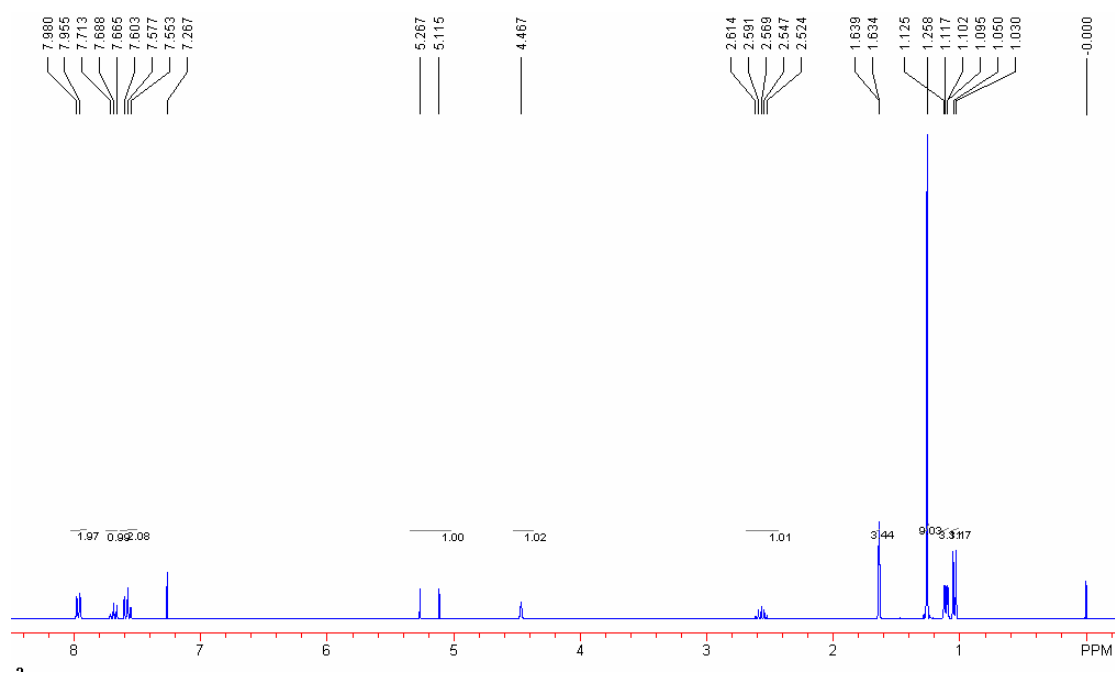


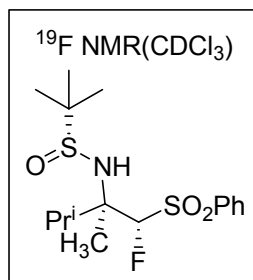




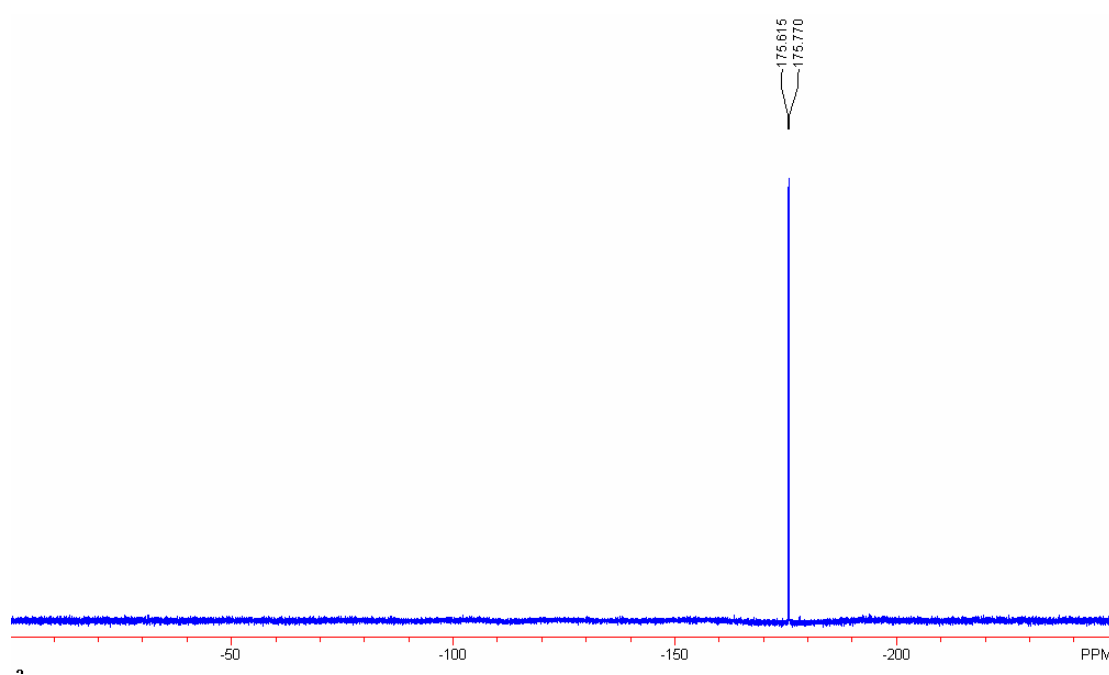


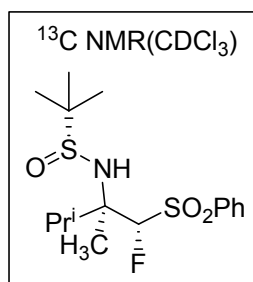
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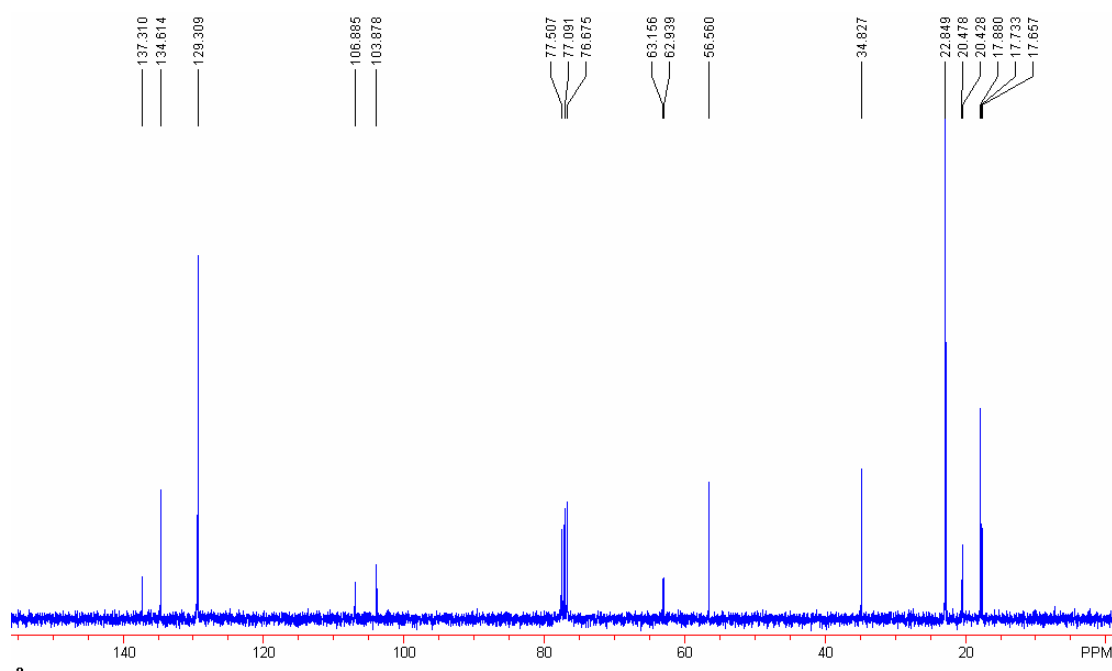


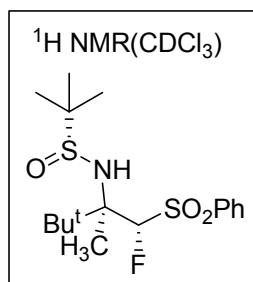
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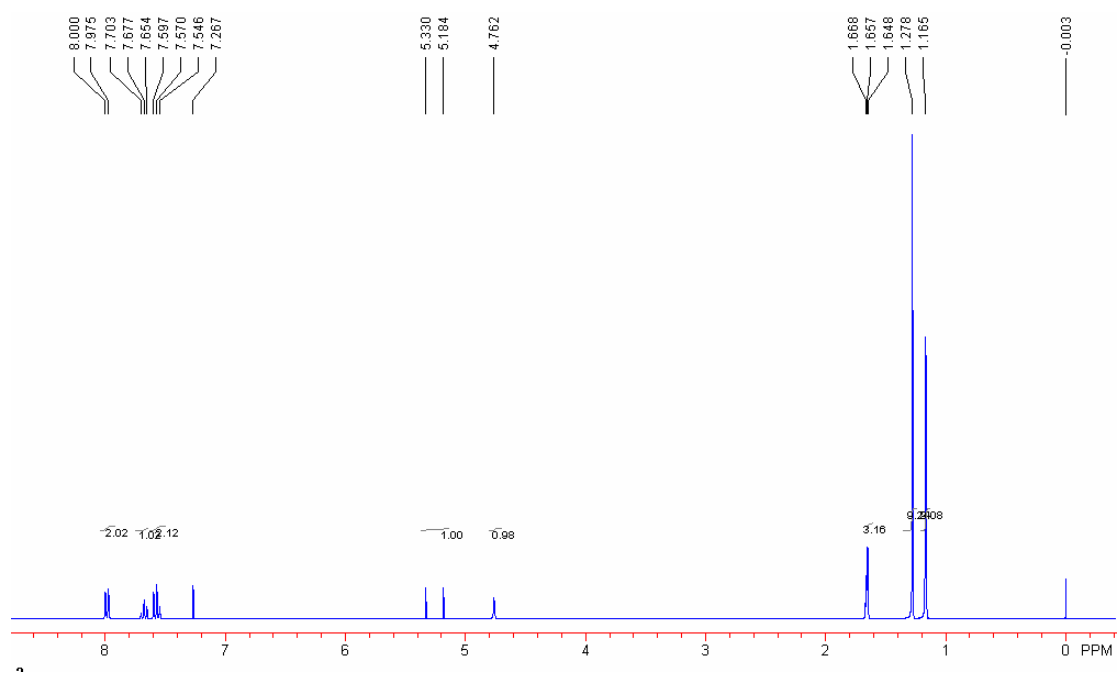


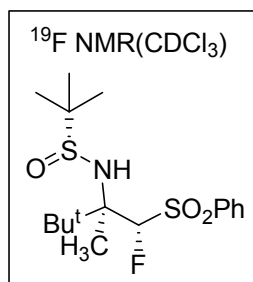
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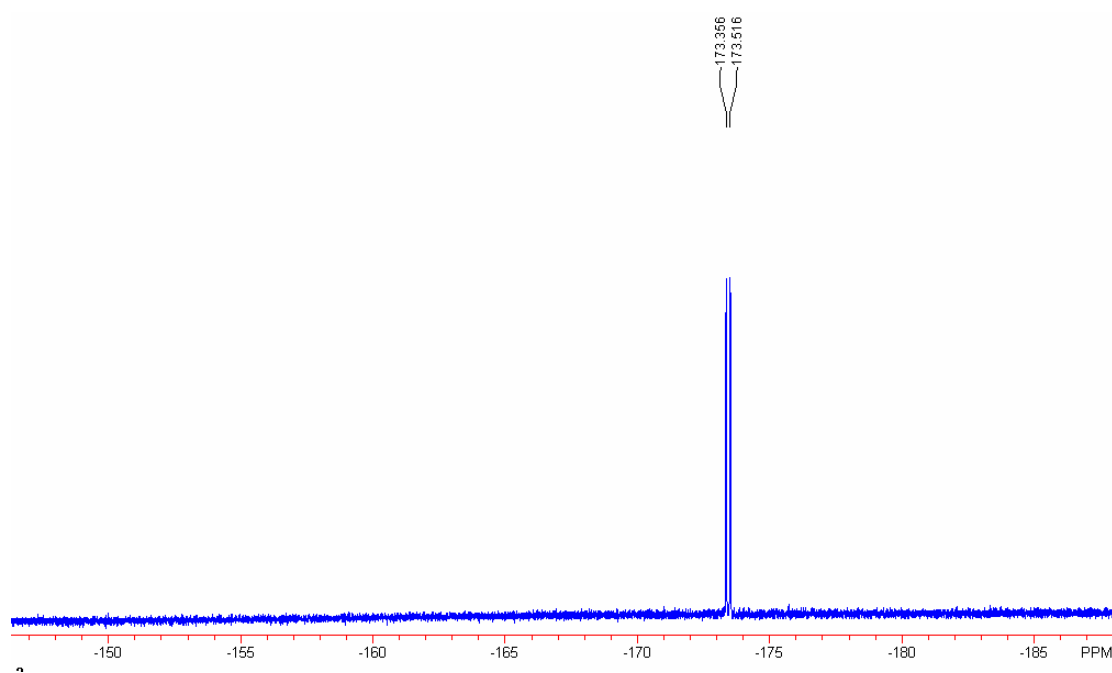


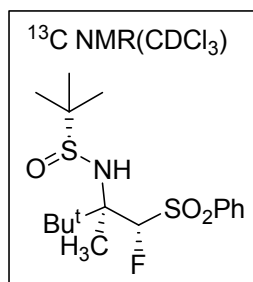
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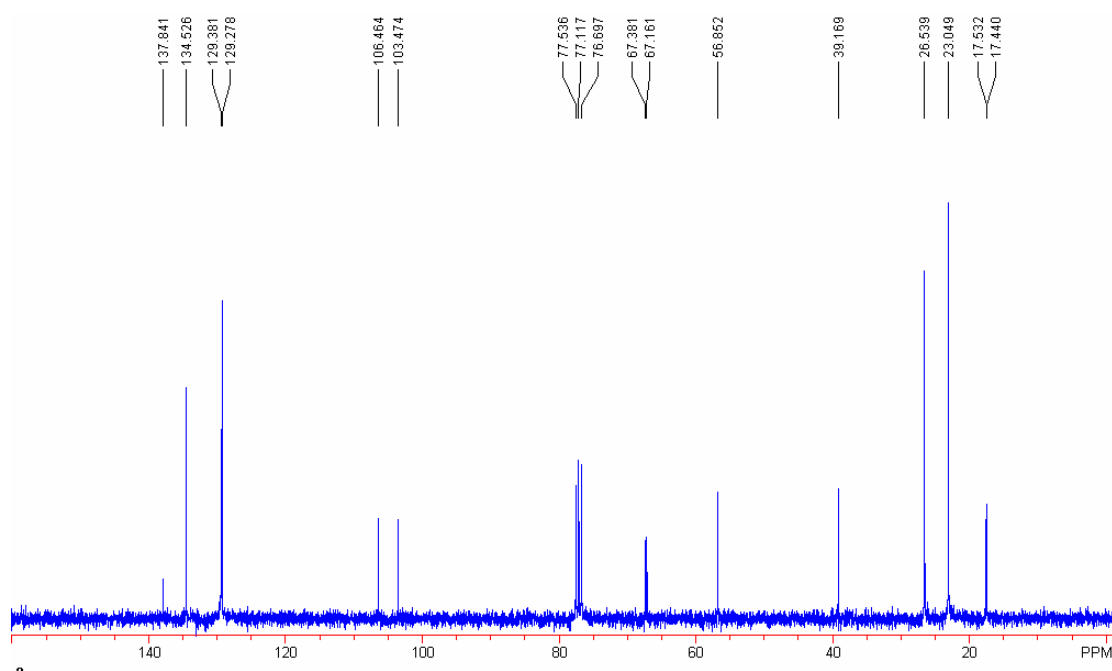


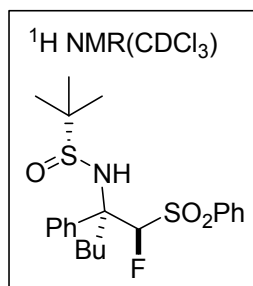
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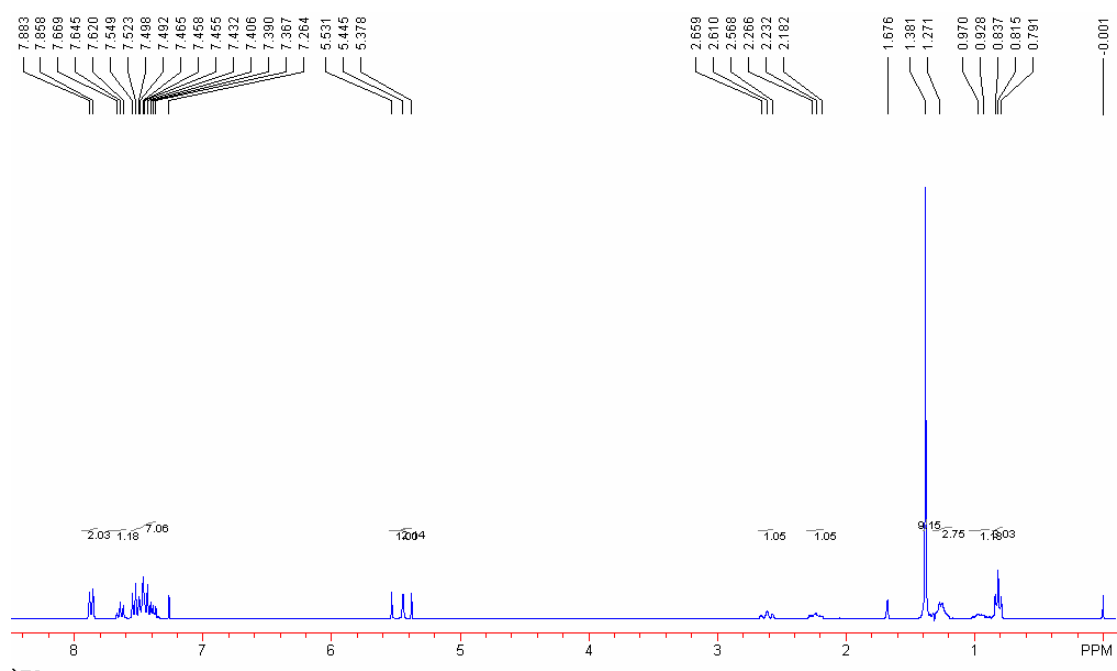


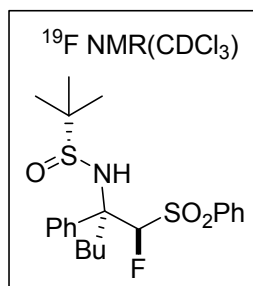
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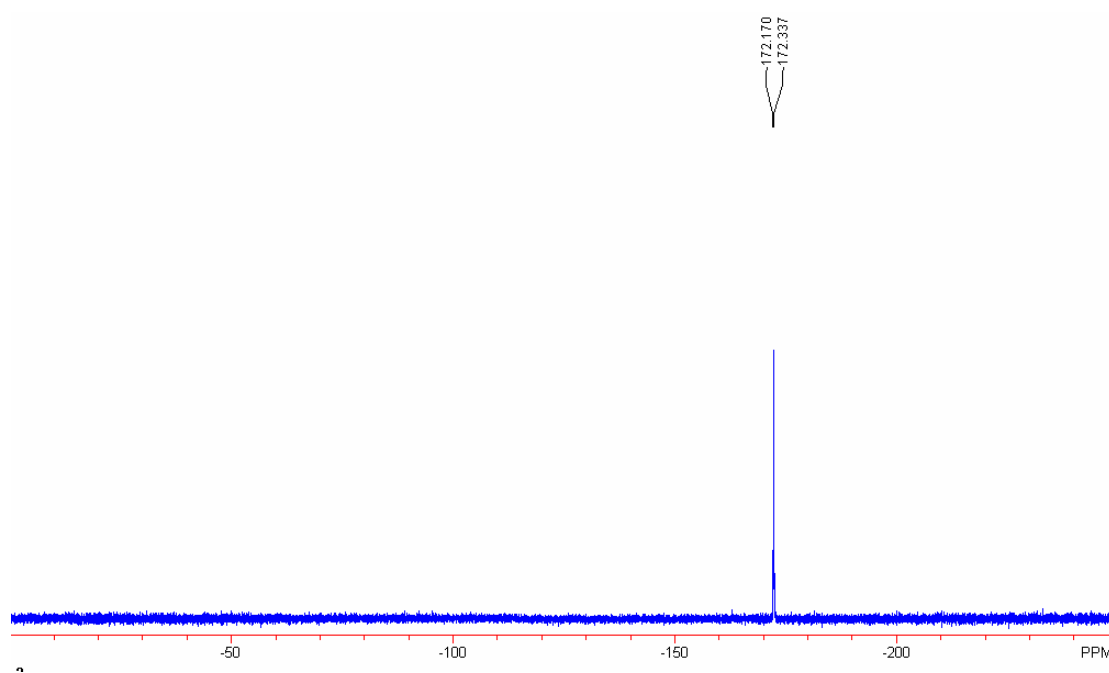


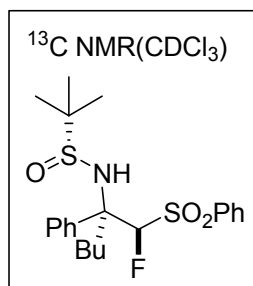
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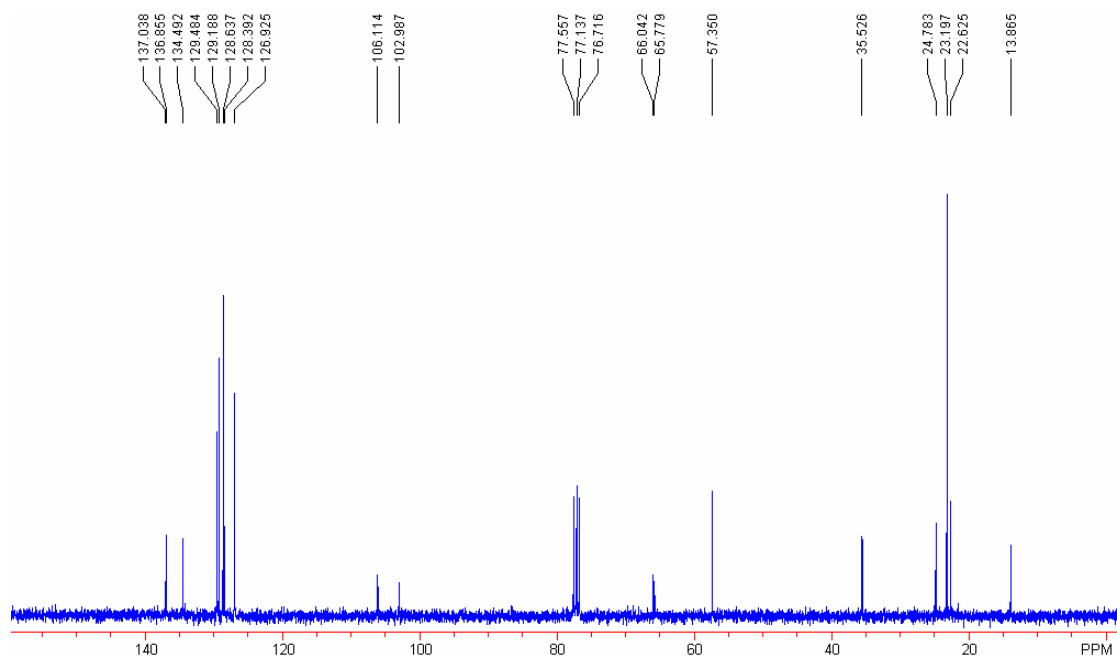


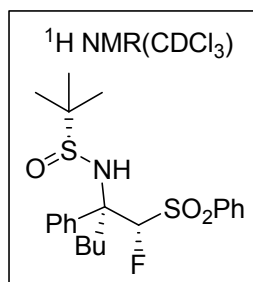
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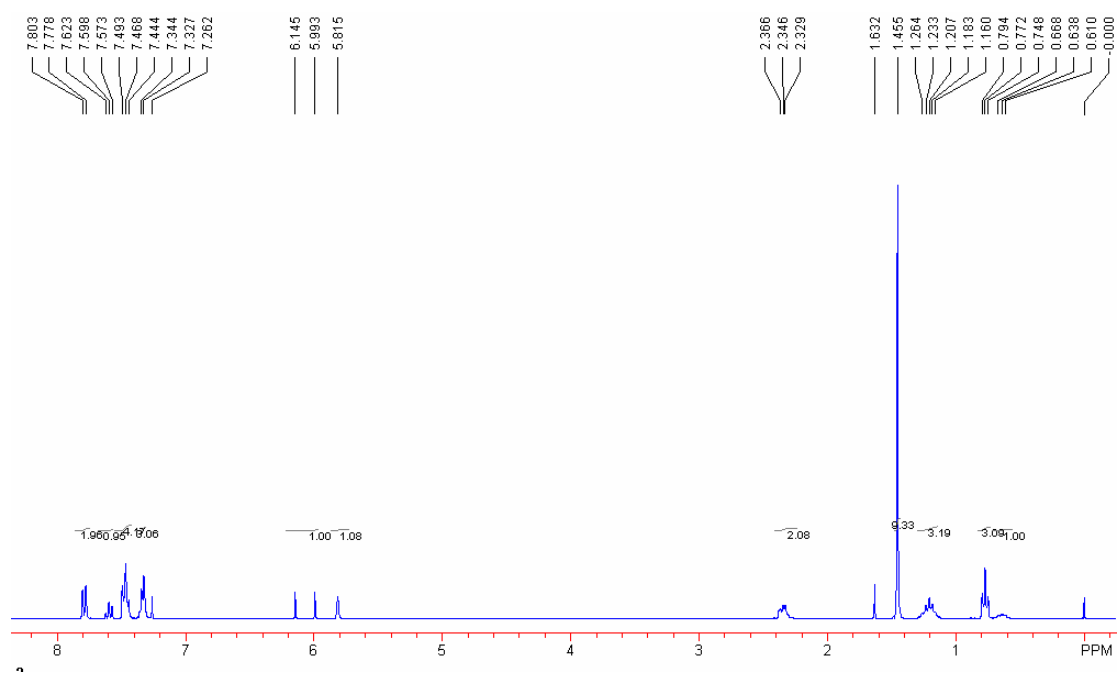


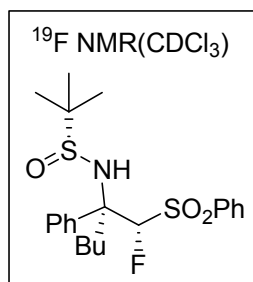
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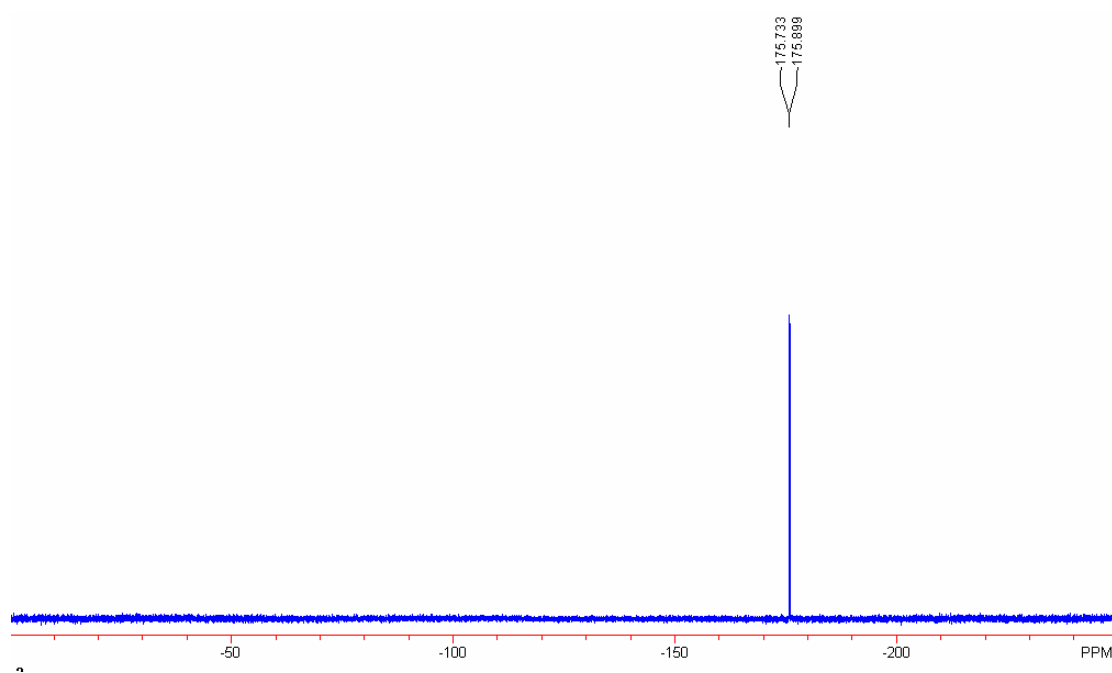


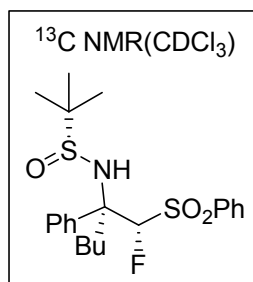
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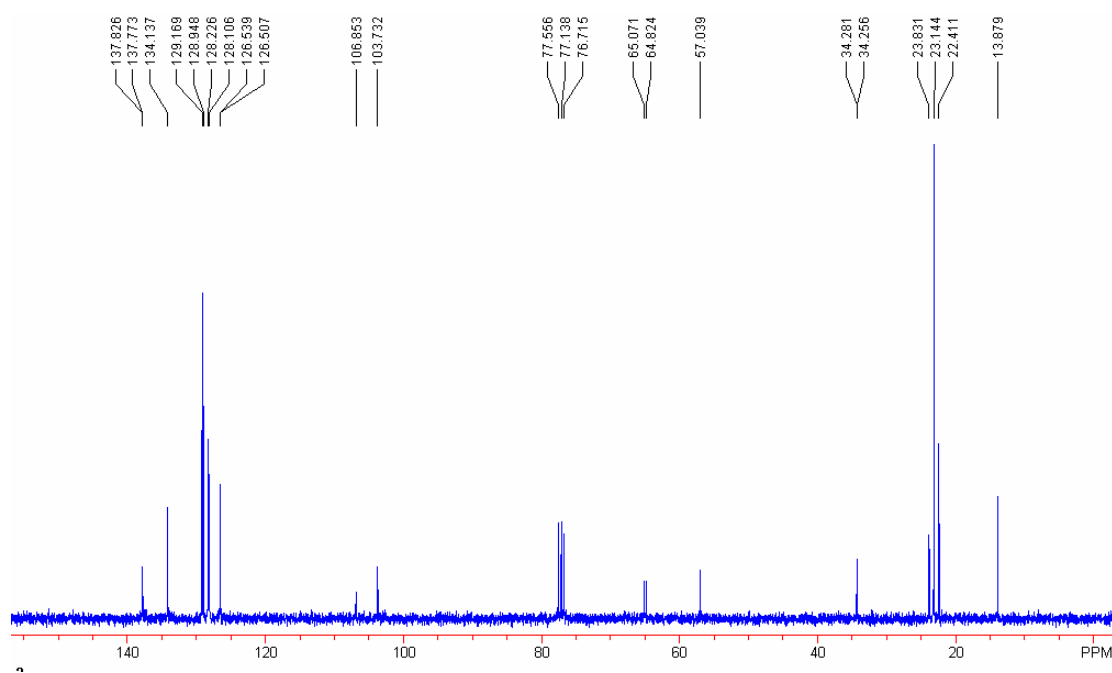


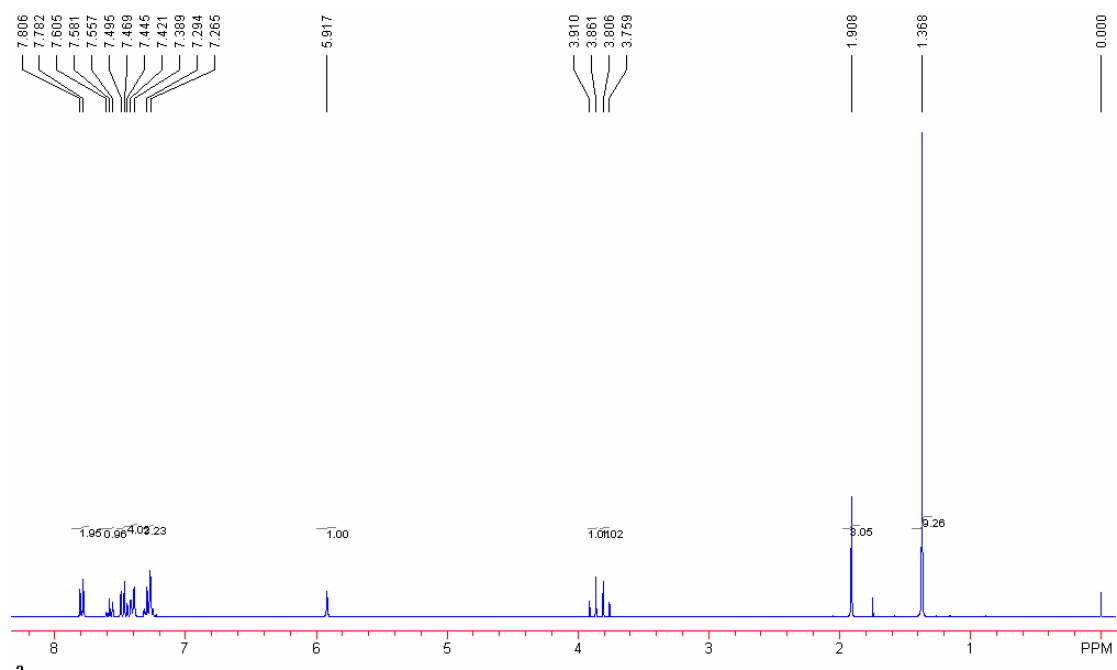
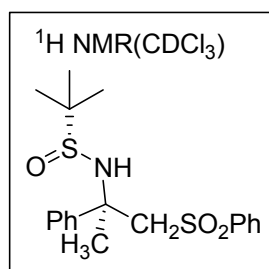
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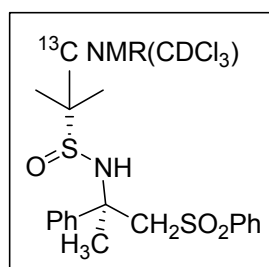




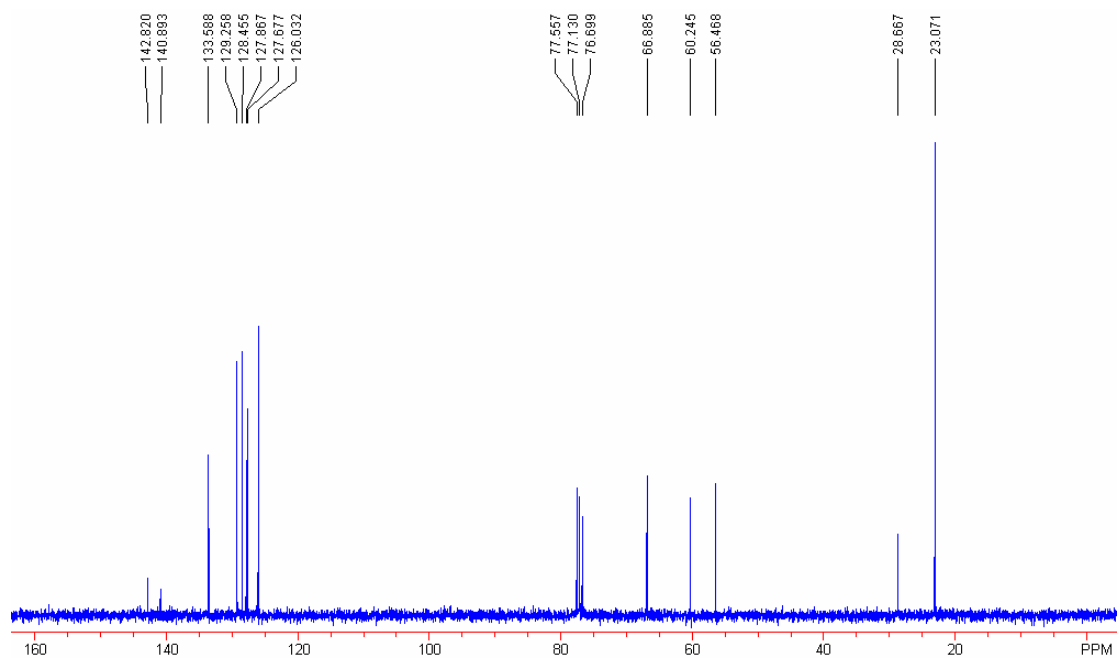
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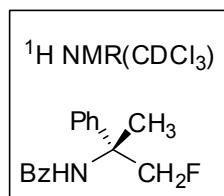




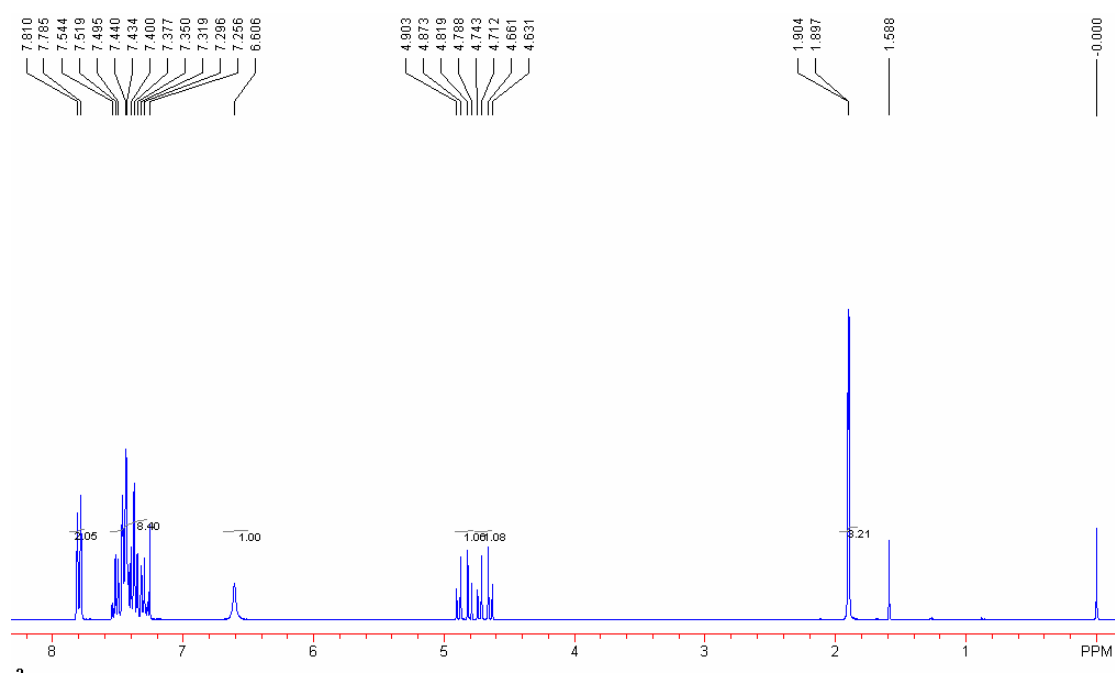


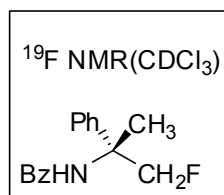
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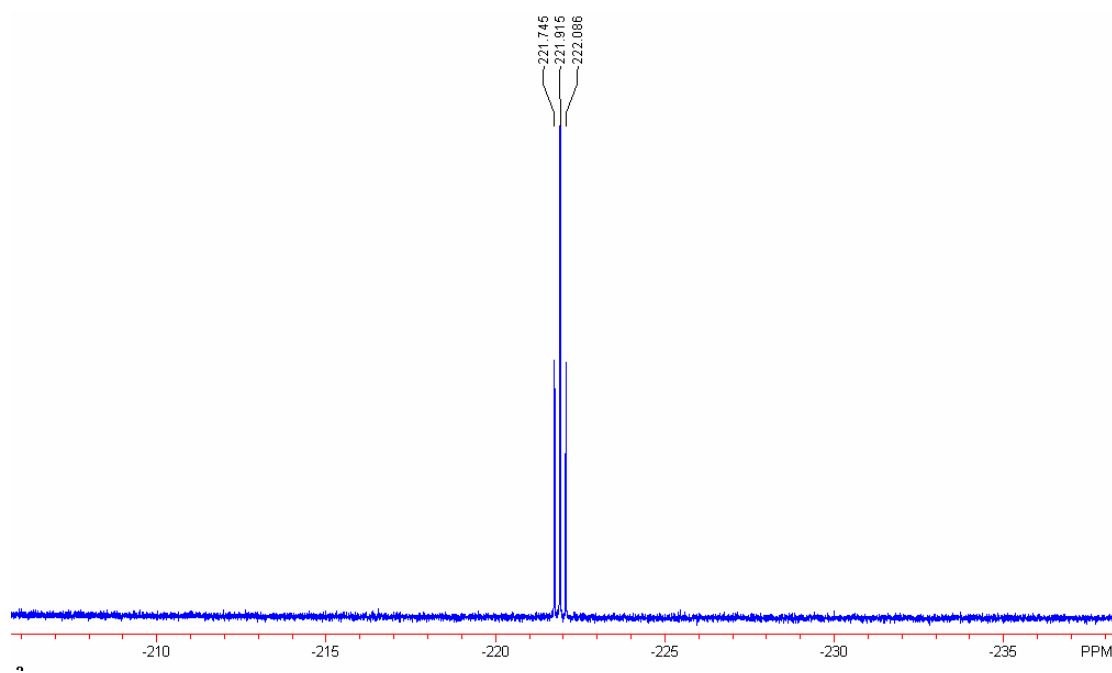


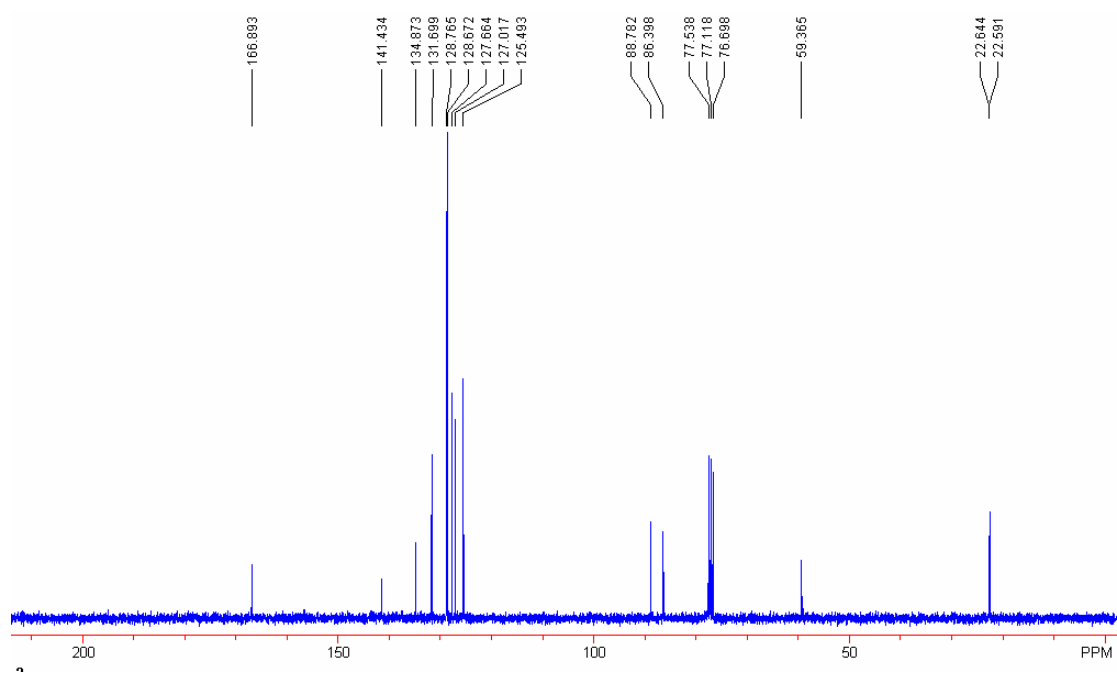
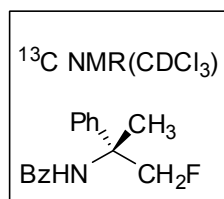
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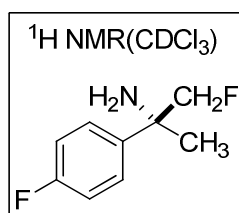




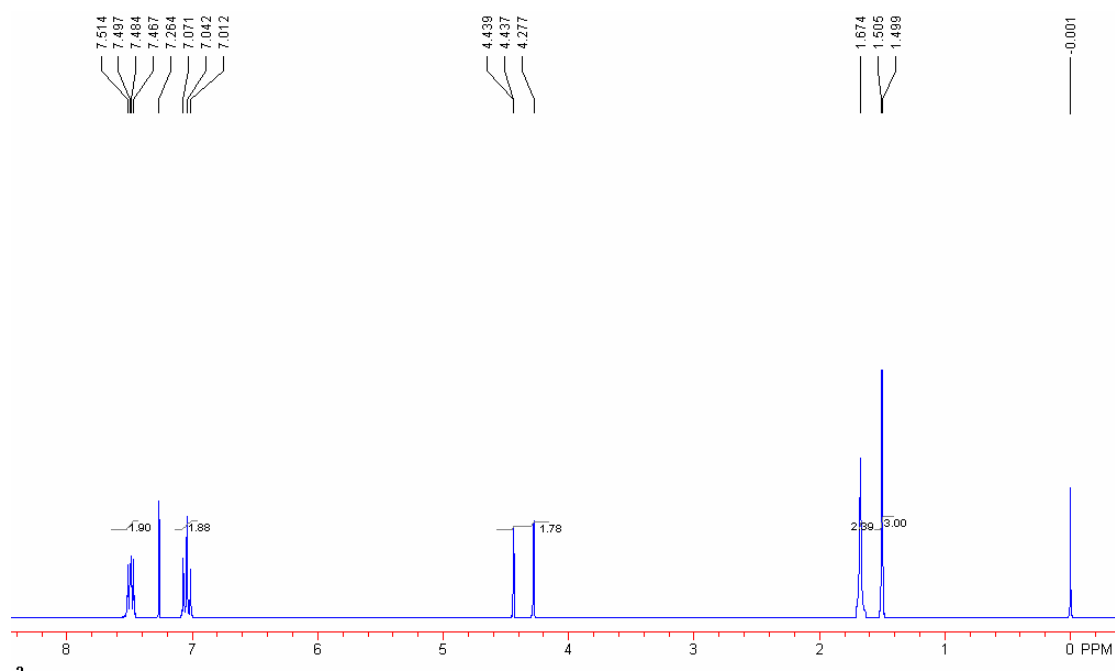
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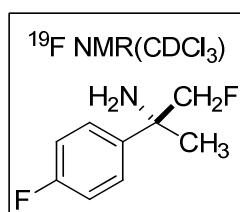




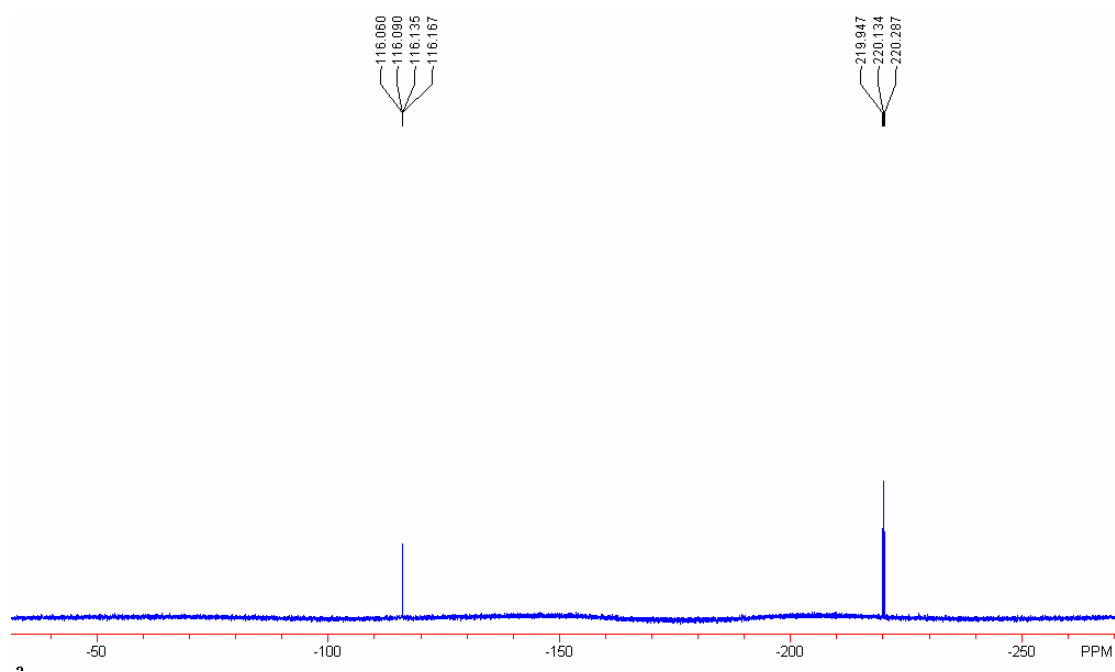


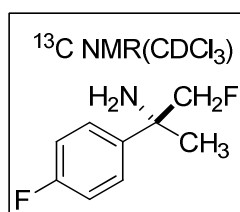
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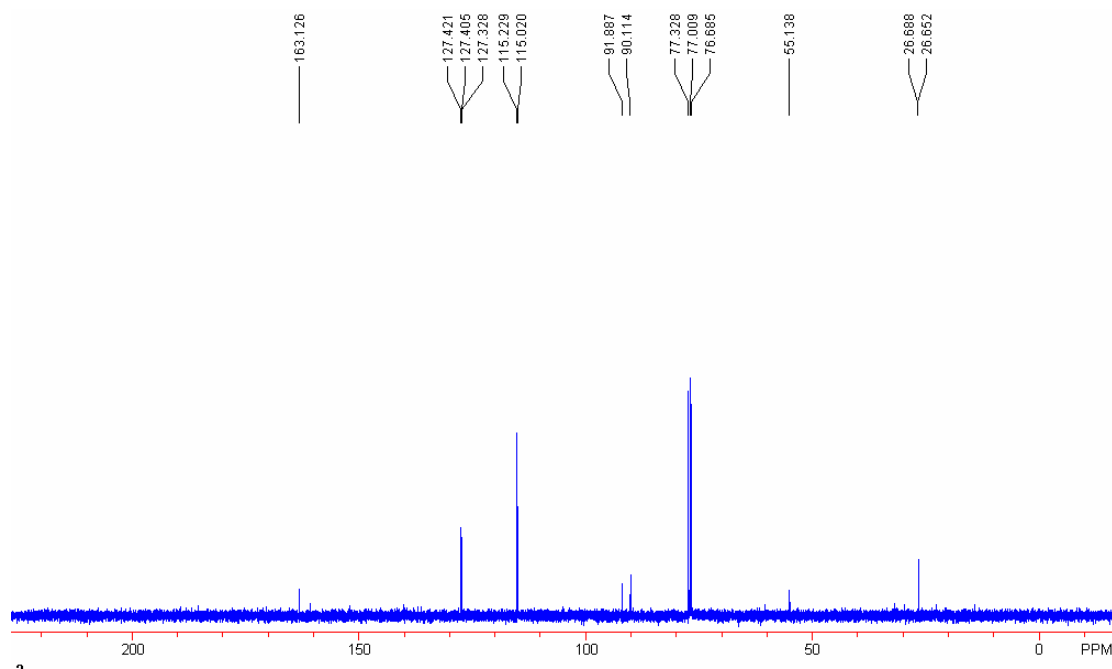


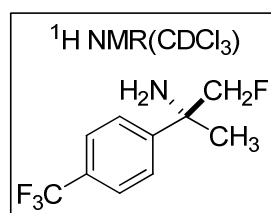
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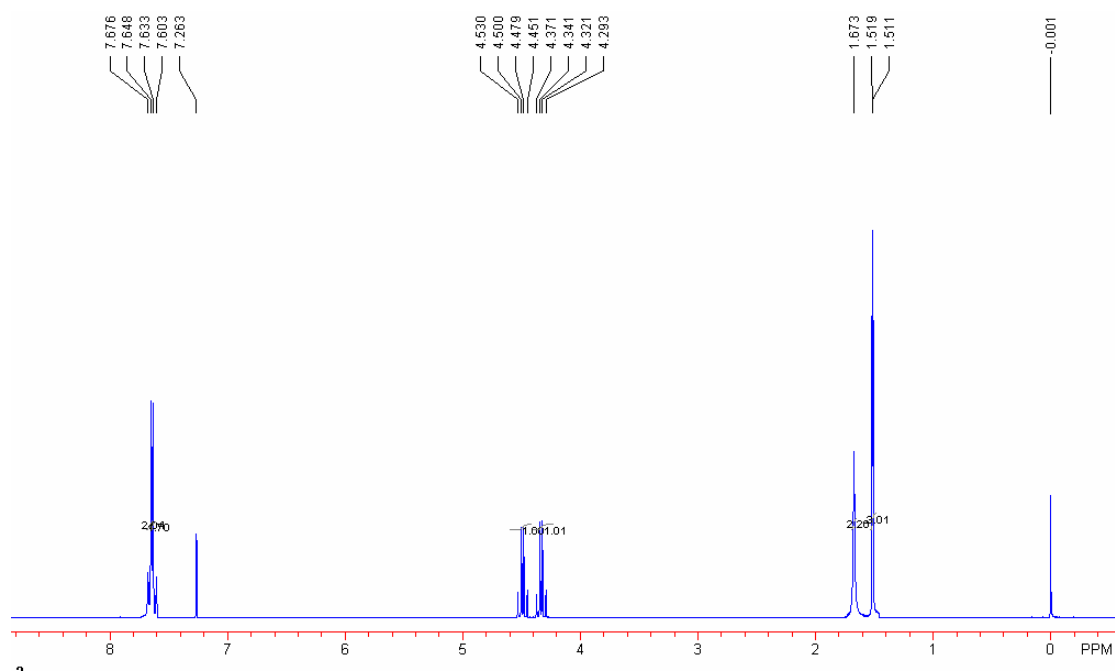


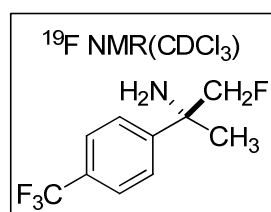
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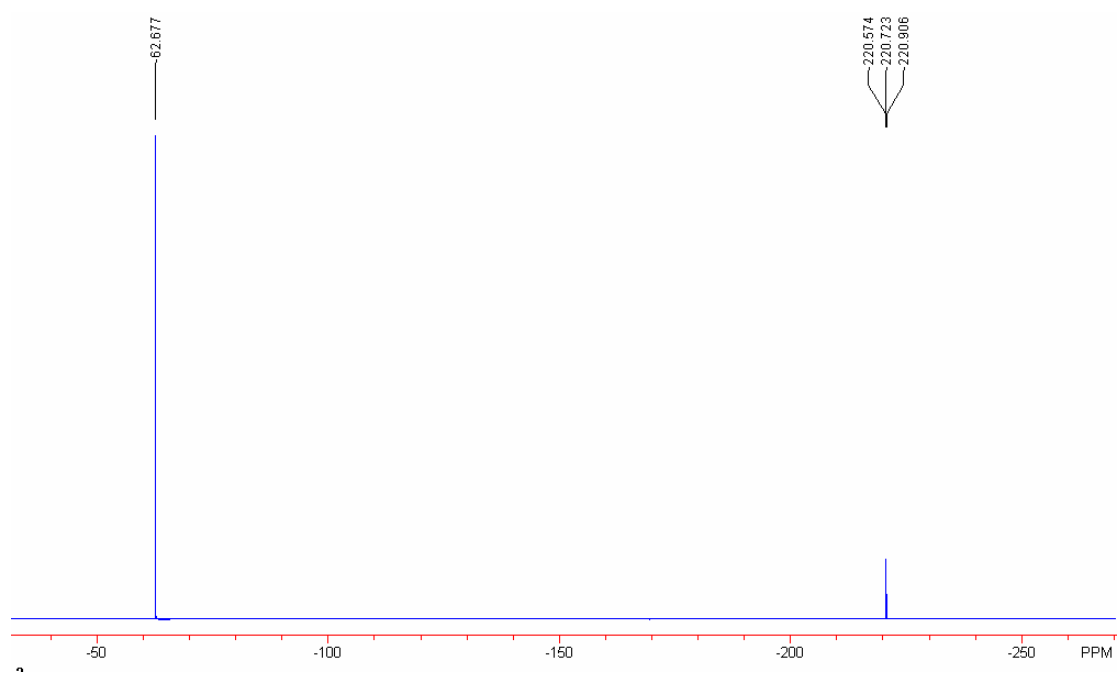


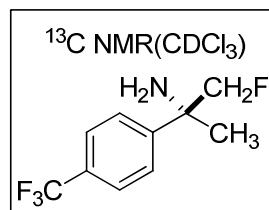
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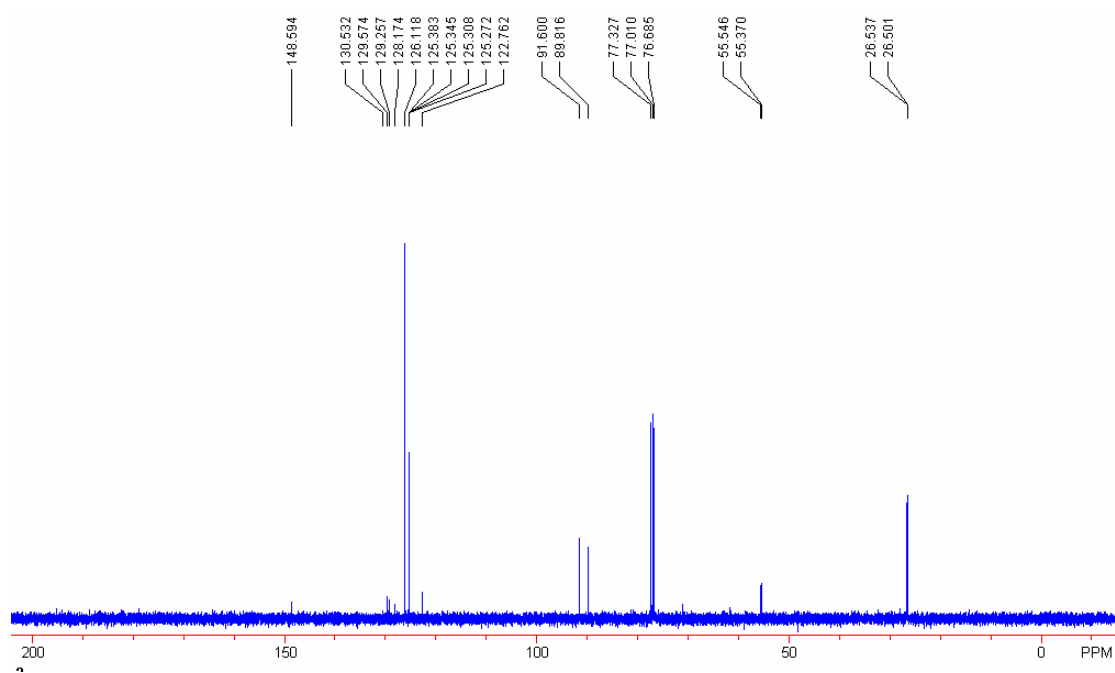


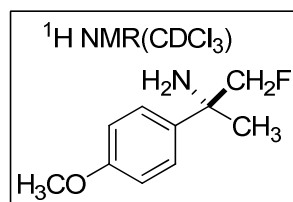
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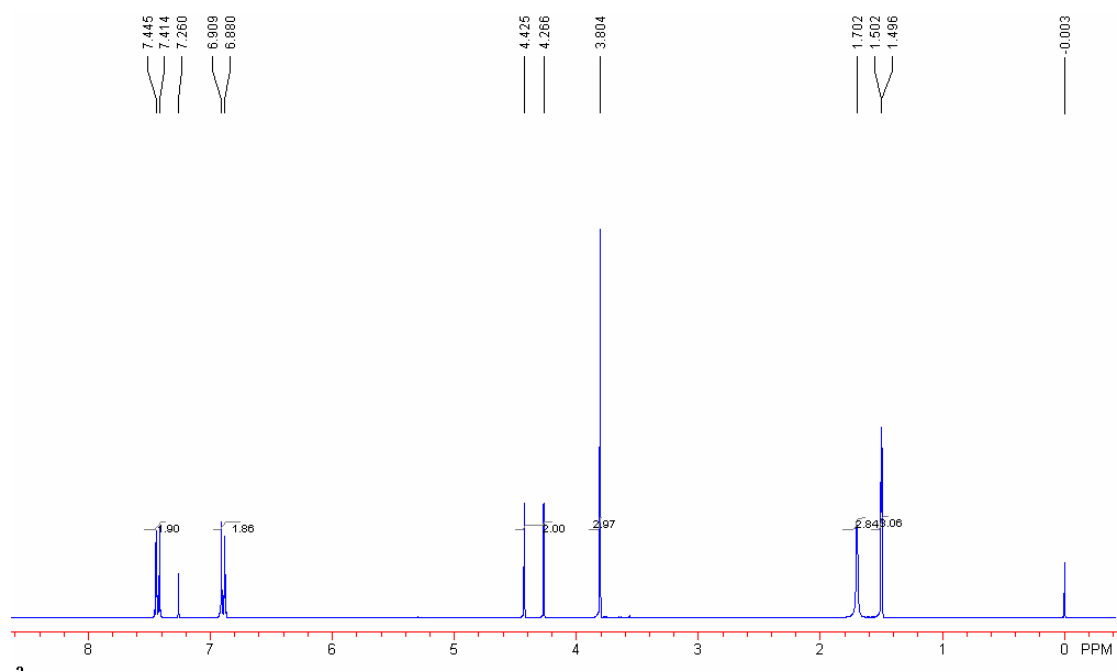


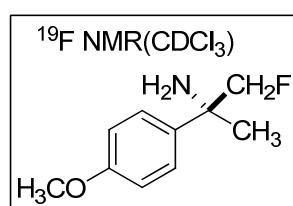
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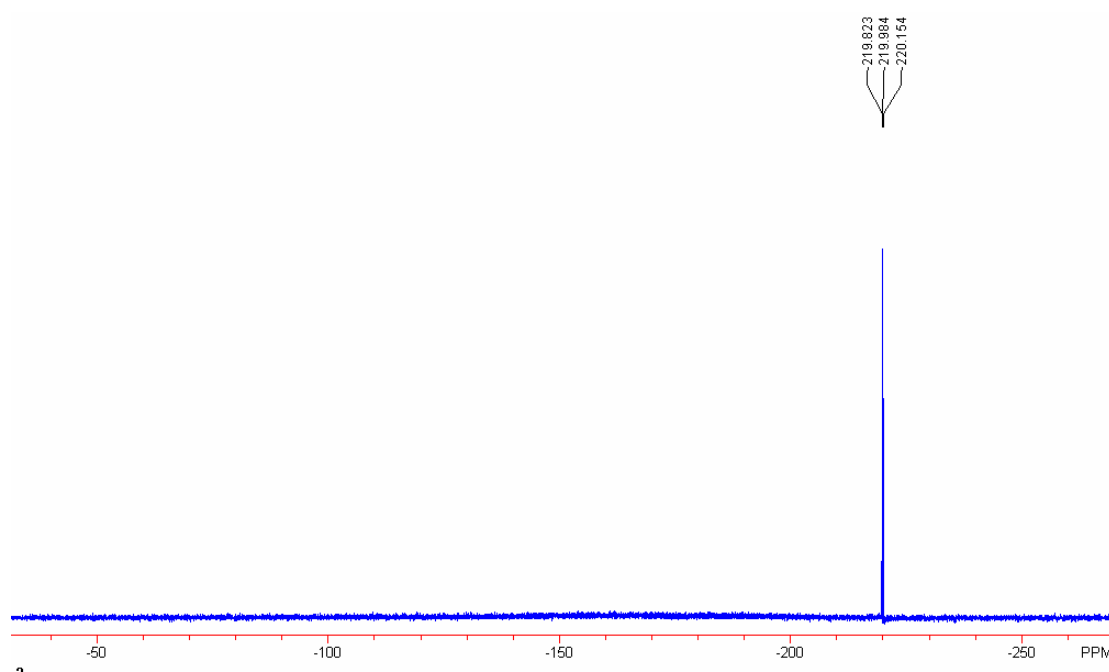


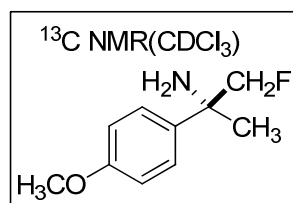
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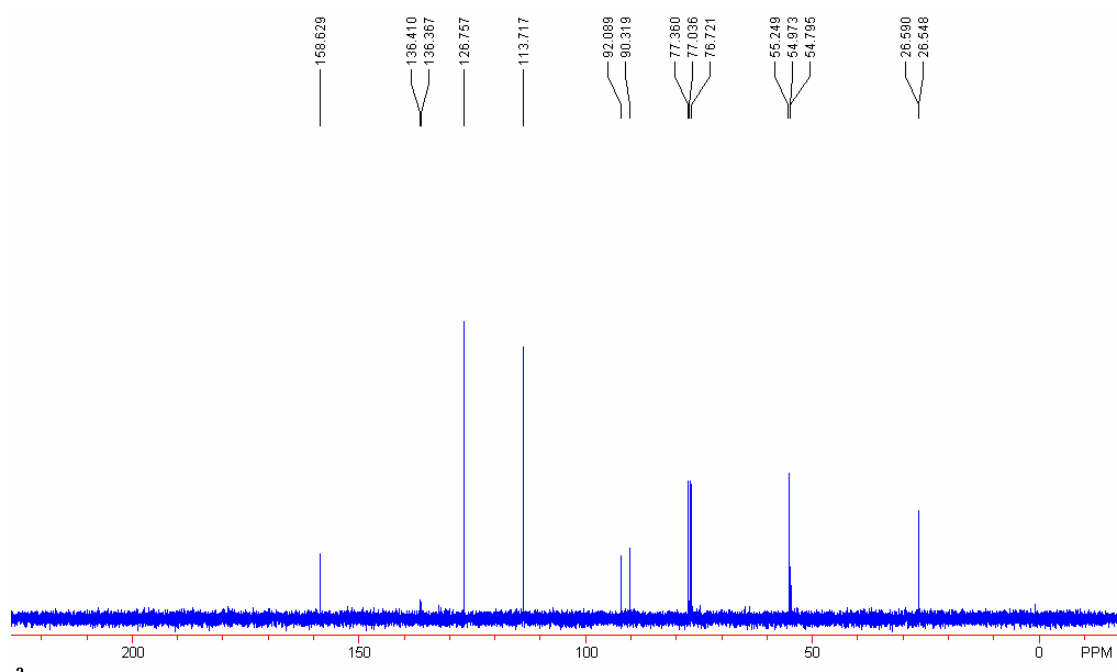


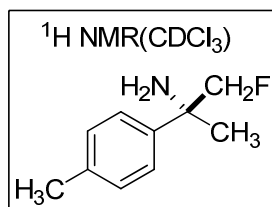
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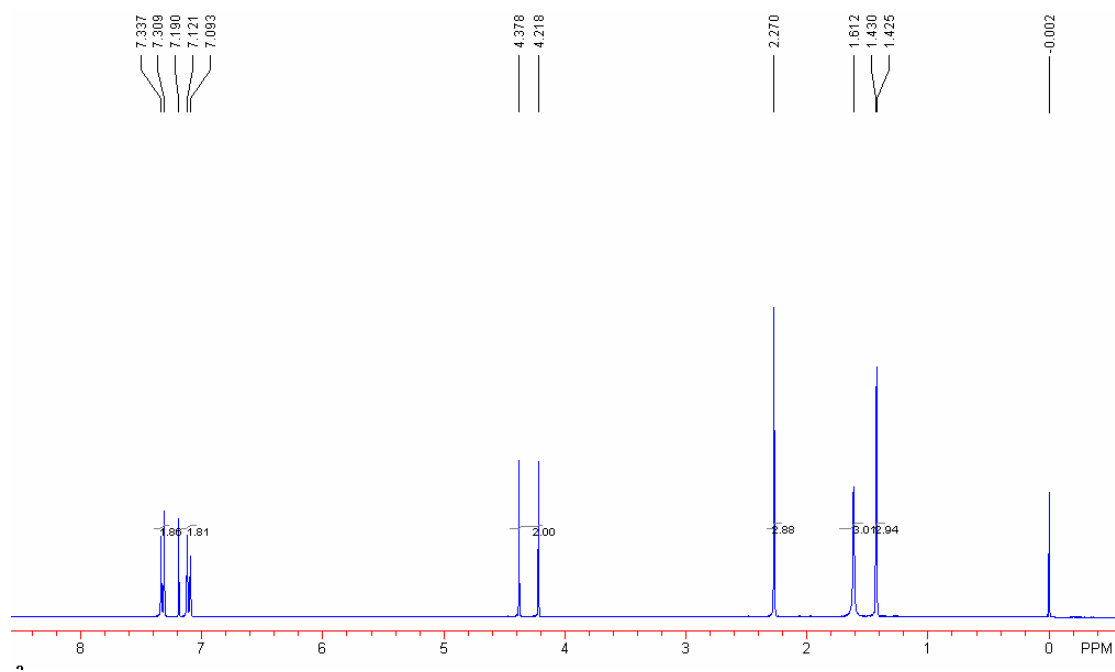


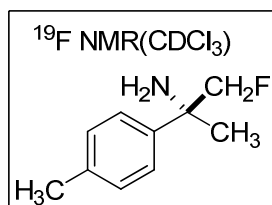
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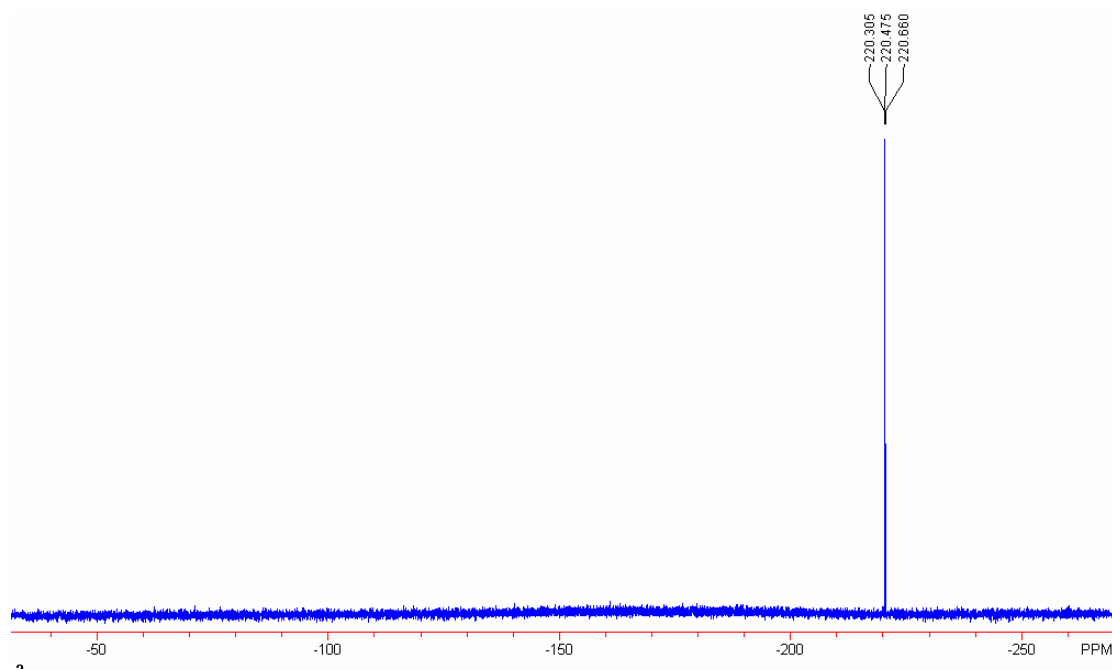


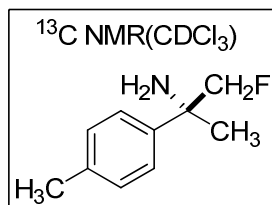
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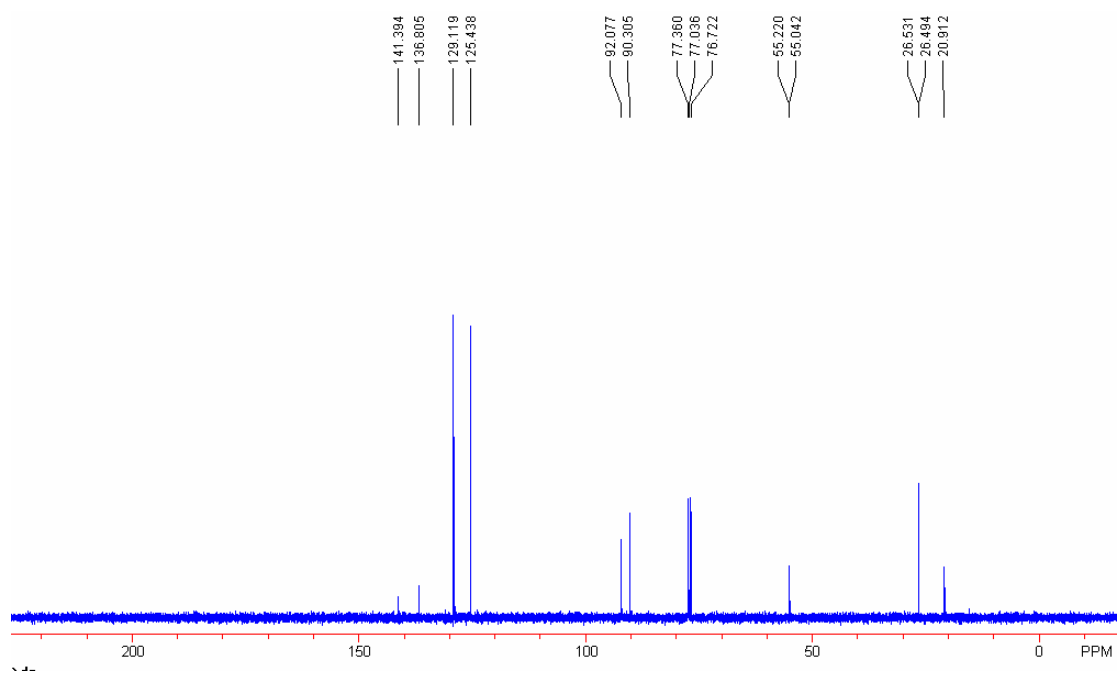


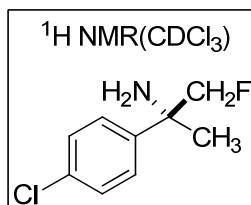
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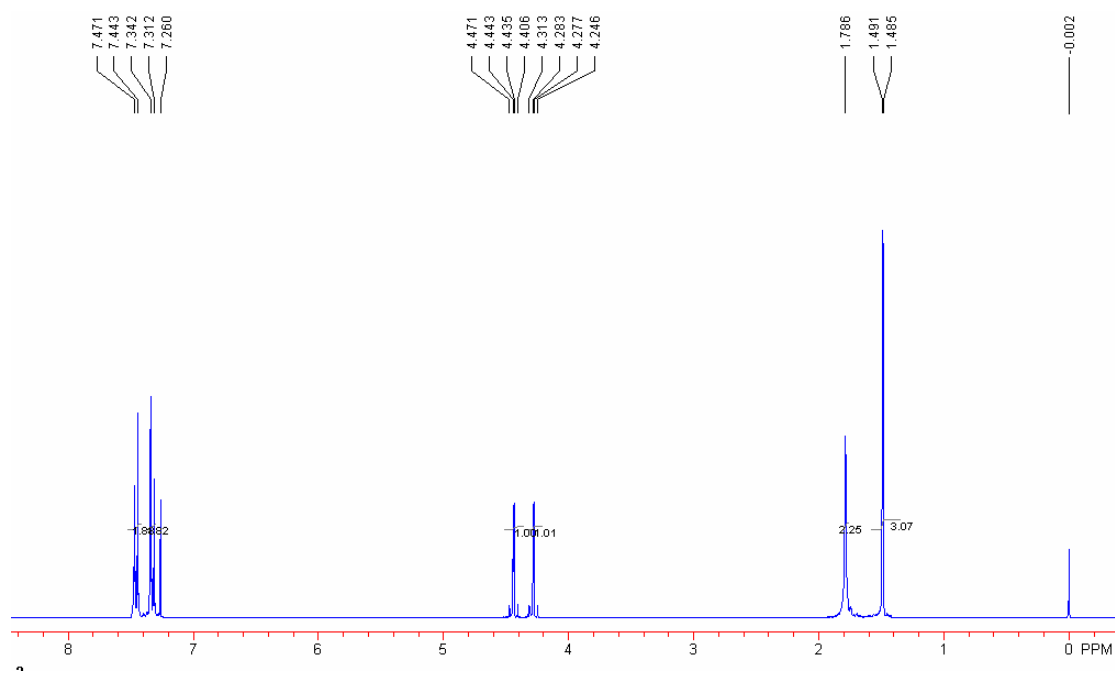


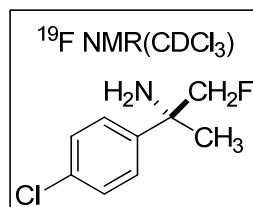
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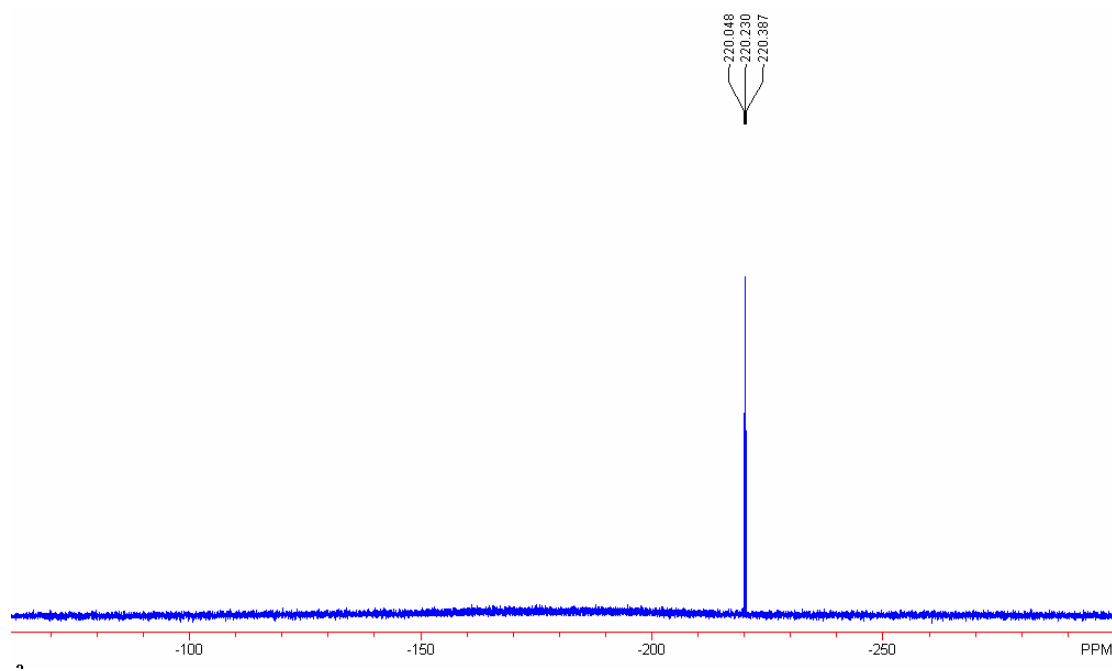


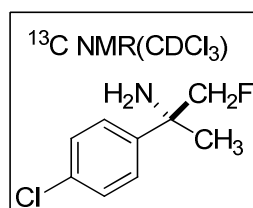
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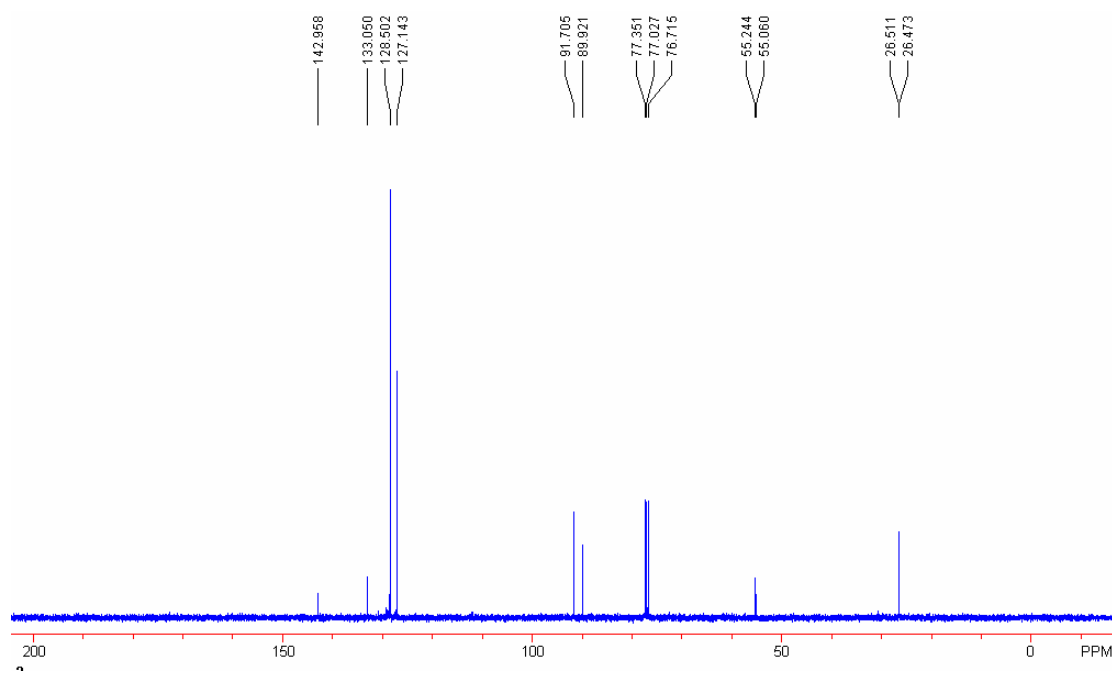


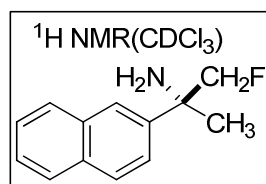
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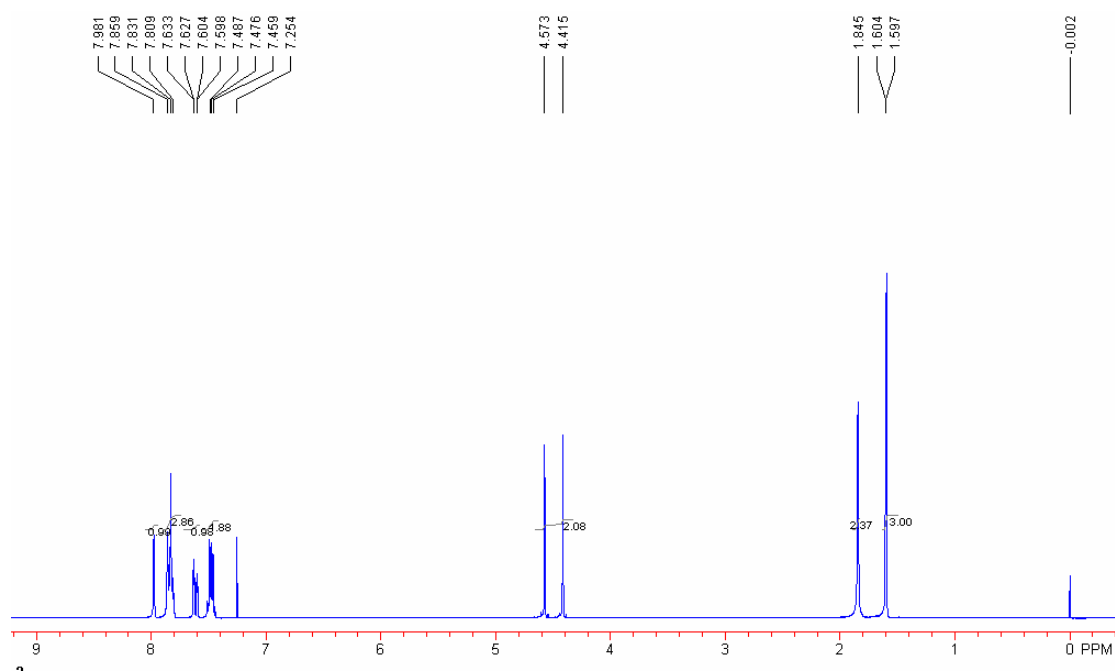


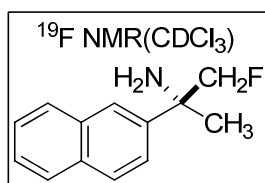
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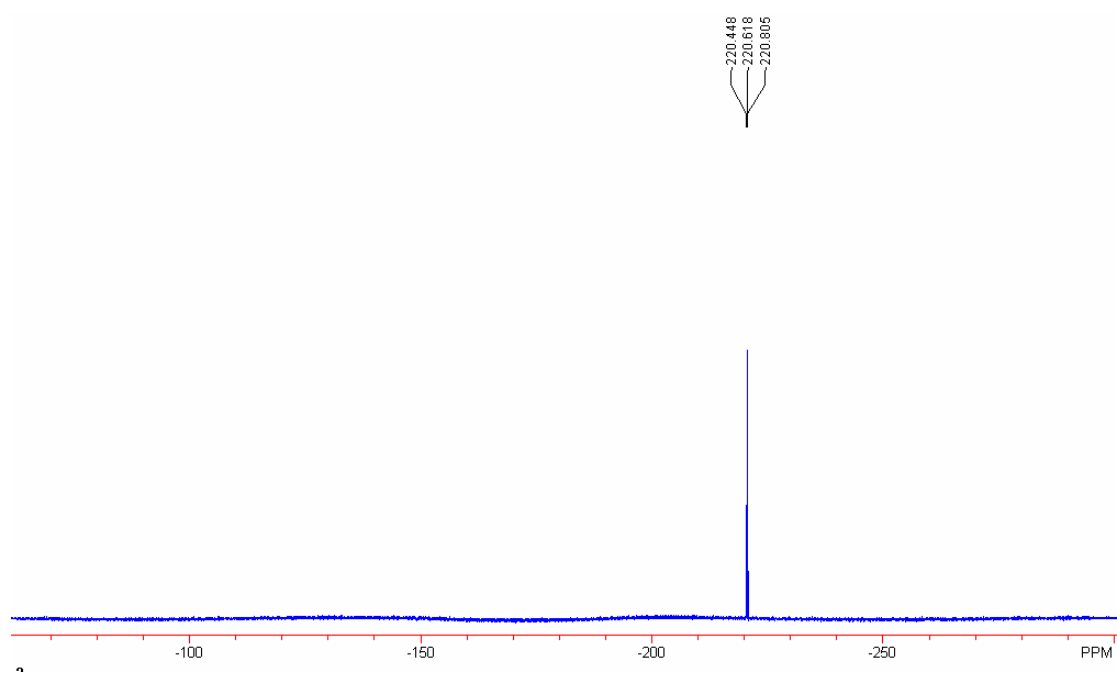


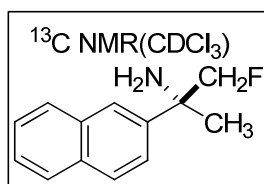
11g





11g





11g

