

Supporting Information

Enantioselective Intermolecular Bromoesterification of Allylic Sulfonamides

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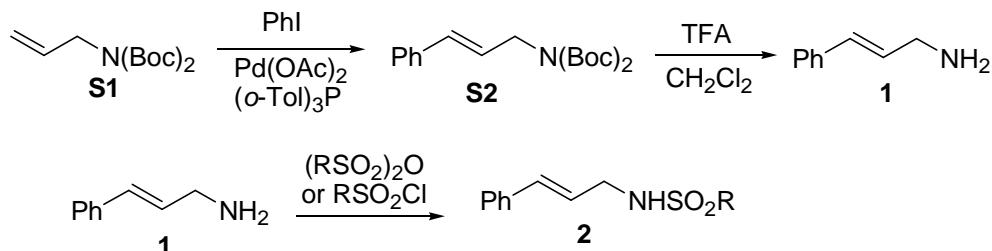
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General remarks

All reactions in non-aqueous media were conducted under a positive pressure of dry argon in glassware that had been oven dried prior to use unless noted otherwise. Anhydrous solutions of reaction mixtures were transferred via an oven dried syringe or cannula. Chloroform was freshly distilled to remove stabilizers. All solvents were dried prior to use unless noted otherwise. Thin layer chromatography was performed using precoated silica gel plates (EMD Chemical Inc. 60, F254). Flash column chromatography was performed with silica gel (Silicycle, 40-63 μ m). Infrared spectra (IR) were obtained as neat oils on a Bruker Equinox 55 Spectrophotometer. ¹H and ¹³C Nuclear magnetic resonance spectra (NMR) were obtained on a Varian Unity-Inova 400 MHz or 500 MHz recorded in ppm (δ) downfield of TMS ($\delta = 0$) in CDCl₃, DMSO. Signal splitting patterns were described as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), broad (b) or multiplet (m), with coupling constants (J) in hertz. High resolution mass spectra (HRMS) were performed by Analytical Instrument Center at the School of Pharmacy on an Electron Spray Injection (ESI) mass spectrometer. Enantiomeric excess was determined by chiral HPLC analysis. The optical rotation was determined by Perkin–Elmer 241 Polarimeter.

General methods for the preparation of allylic sulfonamides:

The procedure for Heck coupling was based on protocols in the following reference: Busacca, C. A.; Dong, Y. *Tetrahedron Lett.* **1996**, *37*, 3947. The procedure for sulfonamide formation was based on protocols in the following reference: Wang, X.; Mei, T.-S.; Yu, J.-Q. *J. Am. Chem. Soc.* **2009**, *131*, 7520. (Both were cited in the manuscript.)



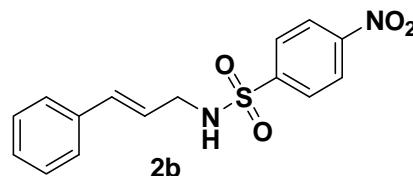
To a flask was added **S1** (1.30 g, 4.5 mmol), $\text{Pd}(\text{OAc})_2$ (50.5 mg, 0.225 mmol), and tri(*o*-tolyl)phosphine (137 mg, 0.45 mmol). The flask was filled with argon followed by addition of acetonitrile (10 mL), triethylamine (1.26 mL, 9.0 mmol) and iodobenzene (1.37 g, 6.7 mmol). The mixture was kept in oil bath at 85 °C for overnight followed by diluting with water (20 mL) and extracted with ether. The combined organic layer was dried over MgSO_4 and purified by flash chromatography to obtain **S2** (1.63 g, 91% yield).

To a stirred solution of **S2** (0.40 g, 1 mmol) in DCM (20 mL) was added trifluoroacetic acid (0.8 mL, 10 mmol). The mixture was stirred for 2 h at room temperature before the addition of 10% NaOH solution. The organic layer was separated and the aqueous layer was extracted with ether three times. The combined organic phase was dried over MgSO_4 and evaporated under vacuum. The crude product was used for the next step without further purification.

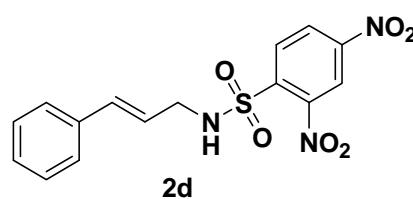
To a stirred solution of amine **1** (0.66 g, 5 mmol) in DCM (50 mL) was added triethylamine (1.0 mL, 7.5 mmol). Trifluoromethanesulfonic anhydride (0.96 mL, 5.5 mmol) was added dropwise at -78 °C and the mixture was stirred for 1 h at that temperature before being quenched by water (10 mL). The organic layer was separated and the aqueous layer was extracted with DCM three times. The combined organic phase was dried over Na_2SO_4 and purified by flash chromatography eluting with ethyl acetate and hexanes to obtain **2f** (0.95 g, 70% yield) as a yellow oil.

Other allylic amines were prepared according to either procedure described for **1** or procedures in the following reference: Jaganathan, A.; Garzan, A.; Whitehead, D. C.; Staples, R. J.; Borhan, B. *Angew. Chem. Int. Ed.* **2011**, *50*, 2593. All other allylic sulfonamides were prepared from the corresponding allylic amines according to procedures described for **2f**.

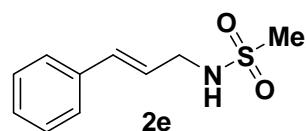
Characterization data for new allylic sulfonamides 2b, 2d, 2e, 2f, 4a – 4n, 6, and 7:



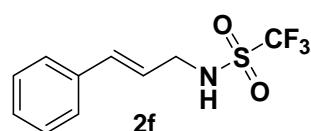
Yellow solid. mp. 107- 109 °C ^1H NMR (400 MHz, CDCl_3 , TMS): δ 8.32 (d, $J = 8.4$ Hz, 2H), 8.07 (d, $J = 8.4$ Hz, 2H), 7.31-7.21 (m, 5H), 6.46 (d, $J = 15.6$ Hz, 1H), 5.99 (dt, $J = 15.6, 6.4$ Hz, 1H), 4.90 (t, $J = 6$ Hz, 1H), 3.85 (t, $J = 6$ Hz, 2H), ^{13}C NMR (100 MHz, CDCl_3): δ 150.3, 146.4, 135.9, 134.2, 129.0, 128.7, 126.6, 126.7, 124.7, 123.5, 45.9. IR (CHCl_3) ν 1526, 1349, 1265, 1158 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_4\text{S}+\text{Na} (\text{M}+\text{Na})^+$ 341.0566, found 341.0563.



Yellow solid. mp. 133- 135 °C ^1H NMR (400 MHz, CDCl_3 , TMS): δ 8.63 (d, $J = 2$ Hz, 1H), 8.40 (dd, $J = 8.4, 2$ Hz, 1H), 8.32 (d, $J = 8.8$ Hz, 1H), 7.30-7.25 (m, 3H), 7.20-7.18 (m, 2H), 6.49 (d, $J = 15.6$ Hz, 1H), 5.98 (dt, $J = 15.6, 6.8$ Hz, 1H), 5.57 (b, 1H), 4.01 (t, $J = 6.4$ Hz, 2H), ^{13}C NMR (100 MHz, DMSO-d_6): δ 150.1, 148.2, 138.9, 136.5, 132.7, 132.2, 129.2, 128.5, 127.8, 126.9, 125.4, 120.7, 45.4. IR (CHCl_3) ν 1537, 1347, 1167, 735 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{13}\text{N}_3\text{O}_6\text{S}+\text{Na} (\text{M}+\text{Na})^+$ 386.0417, found 386.0415.

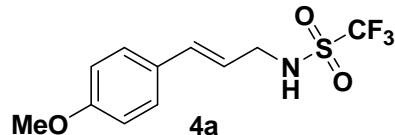


White solid. mp. 74- 76 °C ^1H NMR (400 MHz, CDCl_3 , TMS): δ 7.38-7.25 (m, 5H), 6.61 (d, $J = 16$ Hz, 1H), 6.20 (dt, $J = 16, 6.4$ Hz, 1H), 4.70 (b, 1H), 3.92 (t, $J = 6.4$ Hz, 2H), 2.98 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 136.3, 133.5, 128.9, 128.3, 126.8, 124.7, 45.6, 41.3. IR (CHCl_3) ν 1311, 1146, 963, 907 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{10}\text{H}_{13}\text{NO}_2\text{S}+\text{Na} (\text{M}+\text{Na})^+$ 234.0559, found 234.0547.

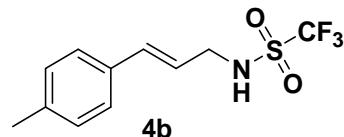


Yellow oil. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 7.37-7.26 (m, 5H), 6.58 (d, $J = 16$ Hz, 1H),

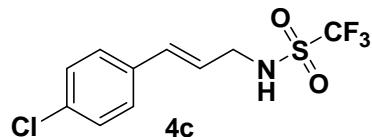
6.13 (dt, $J = 16, 6$ Hz, 1H), 5.10 (b, 1H), 4.02 (d, $J = 6.4$ Hz, 2H), ^{13}C NMR (100 MHz, CDCl_3): δ 135.8, 134.8, 129.0, 128.7, 126.9, 123.0, 119.9 (d, $J = 319$ Hz), 46.7. IR (CHCl_3) ν 1426, 1371, 1190, 1143 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{10}\text{H}_{10}\text{F}_3\text{NO}_2\text{S}+\text{Na} (\text{M}+\text{Na})^+$ 288.0277, found 288.0274.



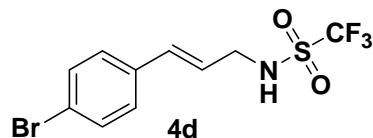
4a: (*E*)-1,1,1-trifluoro-N-(3-(4-methoxyphenyl)allyl)methanesulfonamide
Colorless oil. ^1H NMR (500 MHz, CDCl_3 , TMS): δ 7.29 - 7.35 (m, 2H), 6.84 - 6.92 (m, 2H), 6.57 (d, $J = 15.9$ Hz, 1H), 5.99 - 6.09 (m, 1H), 4.88 (b, 1H), 4.06 (t, $J = 6.2$ Hz, 2H), 3.80 - 3.86 (s, 3H), ^{13}C NMR (125 MHz, CDCl_3): δ 160.2, 134.6, 128.5, 128.2, 120.6, 119.9 (d, $J = 318$ Hz), 114.4, 55.6, 47.1. IR (CHCl_3) ν 2359, 1608, 1265, 1035, 738 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{11}\text{H}_{12}\text{F}_3\text{NO}_3\text{S}+\text{H} (\text{M}+\text{H})^+$ 296.0563, found 296.0567.



4b: (*E*)-1,1,1-trifluoro-N-(3-p-tolylallyl)methanesulfonamide
Yellow oil. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 7.26 (d, $J = 7.6$ Hz, 2H), 7.14 (d, $J = 7.6$ Hz, 2H), 6.56 (d, $J = 16$ Hz, 1H), 6.08 (dt, $J = 16, 6.4$ Hz, 1H), 4.98 (b, 1H), 4.02 (d, $J = 6.4$ Hz, 2H), 2.34 (s, 3H), ^{13}C NMR (125 MHz, CDCl_3): δ 138.7, 134.8, 133.0, 129.7, 126.7, 121.8, 120.0 (q, $J = 407$ Hz), 46.8, 21.4. IR (CHCl_3) ν 1426, 1370, 1042, 968 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{11}\text{H}_{12}\text{F}_3\text{NO}_2\text{S}+\text{Na} (\text{M}+\text{Na})^+$ 302.0433, found 302.0435.

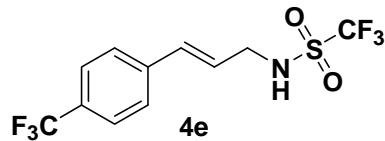


4c: (*E*)-N-(3-(4-chlorophenyl)allyl)-1,1,1-trifluoromethanesulfonamide
Yellow solid. mp. 84- 86°C ^1H NMR (500 MHz, CDCl_3 , TMS): δ 7.31 (d, $J = 1.2$ Hz, 2H), 7.26 (d, $J = 1.2$ Hz, 2H), 6.63 - 6.53 (m, 1H), 6.16 (dt, $J = 15.8, 6.5$ Hz, 1H), 4.87 (b, 1H), 4.08 (t, $J = 6.5$ Hz, 2H), ^{13}C NMR (125 MHz, CDCl_3): δ 134.5, 134.2, 133.5, 129.2, 128.1, 123.7, 119.8 (d, $J = 325$ Hz), 46.6. IR (CHCl_3) ν 1703, 1370, 1188, 734 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{10}\text{H}_9\text{ClF}_3\text{NO}_2\text{S}+\text{Na} (\text{M}+\text{Na})^+$ 321.9887, found 321.9875.



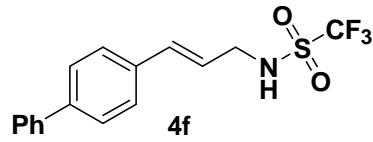
4d: (*E*)-N-(3-(4-bromophenyl)allyl)-1,1,1-trifluoromethanesulfonamide

White solid, mp. 85- 87°C ^1H NMR (400 MHz, CDCl_3 , TMS): δ 7.48 (d, $J = 8.4$ Hz, 2H), 7.29 - 7.22 (m, 2H), 6.57 (d, $J = 15.6$ Hz, 1H), 6.18 (dt, $J = 15.6, 6$ Hz, 1H), 4.90 (b, 1H), 4.08 (t, $J = 6$ Hz, 2H), ^{13}C NMR (100 MHz, CDCl_3): δ 134.6, 133.6, 132.1, 128.3, 123.8, 122.7, 119.8 (d, $J = 250$ Hz), 46.7. IR (CHCl_3) ν 1704, 1371, 1187, 792 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{10}\text{H}_9\text{BrF}_3\text{NO}_2\text{S}+\text{Na} (\text{M}+\text{Na})^+$ 365.9382, found 365.1048.



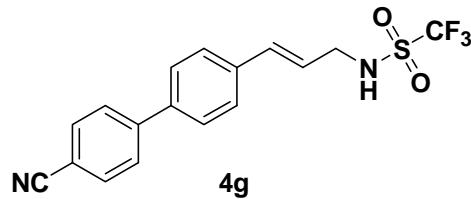
4e: (E)-1,1,1-trifluoro-N-(3-(4-(trifluoromethyl)phenyl)allyl)methanesulfonamide

Yellow oil. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 7.61 (d, $J = 8.2$ Hz, 2H), 7.49 (d, $J = 8.2$ Hz, 2H), 6.67 (d, $J = 15.8$ Hz, 1H), 6.29 (dt, $J = 15.8, 6.4$ Hz, 1H), 4.12 (d, $J = 6.4$ Hz, 2H), ^{13}C NMR (100 MHz, CDCl_3): δ 139.4, 133.2, 130.5 (q, $J = 26$ Hz), 127.1, 126.0 (q, $J = 2.7$ Hz), 125.9, 124.4 (d, $J = 217$ Hz), 119.9 (d, $J = 255$ Hz), 46.5. IR (CHCl_3) ν 2359, 1617, 1373, 1128, 906, 730 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{11}\text{H}_9\text{F}_6\text{NO}_2\text{S}+\text{Na} (\text{M}+\text{Na})^+$ 356.0150, found 356.0150.



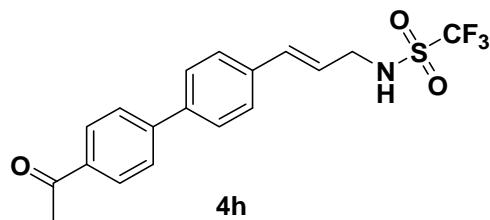
4f: (E)-N-(3-(biphenyl-4-yl)allyl)-1,1,1-trifluoromethanesulfonamide

White solid, mp. 103- 105°C ^1H NMR (400 MHz, CDCl_3 , TMS): δ 7.62- 7.55 (m, 4H), 7.47- 7.42 (m, 4H), 7.38- 7.35 (m, 1H), 6.63 (d, $J = 16$ Hz, 1H), 6.19 (dt, $J = 16, 6.4$ Hz, 1H), 4.96 (b, 1H), 4.07 (d, $J = 6.4$ Hz, 2H), ^{13}C NMR (125 MHz, CDCl_3): δ 141.5, 140.6, 134.7, 134.4, 129.1, 127.8, 127.7, 127.3, 127.2, 122.9, 119.9 (d, $J = 319$ Hz), 46.7. IR (CHCl_3) ν 1363, 1150, 763 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{14}\text{F}_3\text{NO}_2\text{S}+\text{Na} (\text{M}+\text{Na})^+$ 364.0590, found 364.0578.



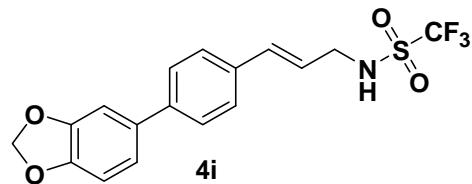
4g: (E)-N-(3-(4'-cyanobiphenyl-4-yl)allyl)-1,1,1-trifluoromethanesulfonamide

Yellow oil. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 7.73- 7.67 (m, 4H), 7.57 (d, $J = 6.4$ Hz, 2H), 7.49 (d, $J = 7.2$ Hz, 2H), 6.67 (d, $J = 16$ Hz, 1H), 6.26 (dt, $J = 16, 6.8$ Hz, 1H), 5.18 (b, 1H), 4.12 (m, 2H), ^{13}C NMR (100 MHz, CDCl_3): δ 145.1, 139.3, 136.2, 133.8, 132.9, 127.8, 127.7, 127.6, 124.2, 119.9 (d, $J = 319$ Hz), 119.1, 111.3, 46.7. IR (CHCl_3) ν 1373, 1266, 1230, 1192 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{13}\text{F}_3\text{N}_2\text{O}_2\text{S}+\text{Na} (\text{M}+\text{Na})^+$ 389.0542, found 389.0535.



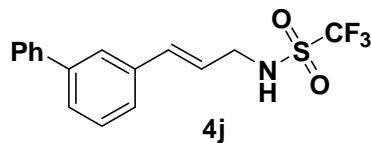
4h: (*E*)-*N*-(3-(4'-acetyl biphenyl-4-yl)allyl)-1,1,1-trifluoromethanesulfonamide

White solid, mp. 122- 125°C ¹H NMR (400 MHz, CDCl₃, TMS): δ 8.02 (d, *J* = 8 Hz, 2H), 7.66 (d, *J* = 8 Hz, 2H), 7.60 (d, *J* = 8 Hz, 2H), 7.46 (d, *J* = 8 Hz, 2H), 6.66 (d, *J* = 16 Hz, 1H), 6.25 (dt, *J* = 16, 6 Hz, 1H), 5.22 (b, 1H), 4.12 (t, *J* = 6 Hz, 2H), 2.64 (s, 3H), ¹³C NMR (100 MHz, CDCl₃): δ 198.2, 145.2, 140.0, 136.2, 135.8, 134.0, 129.2, 127.8, 127.5, 127.2, 123.8, 119.9 (d, *J* = 319 Hz), 46.8, 26.9. IR (CHCl₃) v 1679, 1603, 1363, 1190 cm⁻¹. HRMS (ESI) *m/z* calcd for C₁₈H₁₆F₃NO₃S+Na (M+Na)⁺ 406.0695, found 406.0693.



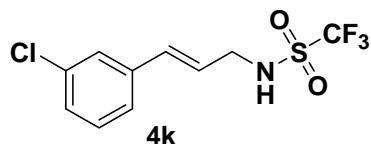
4i: (*E*)-*N*-(3-(4-(benzo[d][1,3]dioxol-5-yl)phenyl)allyl)-1,1,1-trifluoromethanesulfonamide

Yellow solid, mp. 98- 101°C ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.46 (d, *J* = 8 Hz, 2H), 7.41 (d, *J* = 8 Hz, 2H), 7.08- 7.05 (m, 2H), 6.88 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.64 (d, *J* = 16 Hz, 1H), 6.20 (dt, *J* = 16, 6 Hz, 1H), 6.00 (s, 2H), 4.95 (b, 1H), 4.09 (b, 2H), ¹³C NMR (125 MHz, CDCl₃): δ 148.4, 147.5, 141.2, 135.0, 134.43, 134.38, 127.33, 127.29, 122.8, 120.8, 119.9 (d, *J* = 310 Hz), 108.9, 107.6, 101.4, 46.9. IR (CHCl₃) v 1482, 1364, 1227, 1189 cm⁻¹. HRMS (ESI) *m/z* calcd for C₁₇H₁₄F₃NO₄S+Na (M+Na)⁺ 408.0488, found 408.0494.



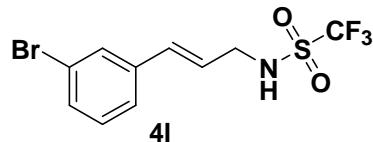
4j: (*E*)-*N*-(3-(biphenyl-3-yl)allyl)-1,1,1-trifluoromethanesulfonamide

Yellow solid, mp. 95- 97°C ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.60- 7.57 (m, 3H), 7.52 (d, *J* = 8 Hz, 1H), 7.48- 7.42 (m, 3H), 7.37 (t, *J* = 7.2 Hz, 2H), 6.69 (d, *J* = 16 Hz, 1H), 6.24 (dt, *J* = 16, 6.4 Hz, 1H), 4.89 (b, 1H), 4.10 (b, 2H), ¹³C NMR (125 MHz, CDCl₃): δ 142.1, 140.8, 136.2, 134.8, 129.4, 129.1, 127.8, 127.6, 127.4, 125.8, 125.7, 123.3, 120.0 (q, *J* = 319 Hz), 46.8. IR (CHCl₃) v 1372, 1229, 1188, 1147 cm⁻¹. HRMS (ESI) *m/z* calcd for C₁₆H₁₄F₃NO₂S+Na (M+Na)⁺ 364.0590, found 364.0592.



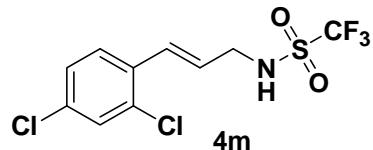
4k: (*E*)-*N*-(3-(3-chlorophenyl)allyl)-1,1,1-trifluoromethanesulfonamide

Yellow oil. ^1H NMR (500 MHz, CDCl_3 , TMS): δ 7.36 (s, 1H), 7.29 - 7.23 (m, 3H), 6.56 (d, J = 15.9 Hz, 1H), 6.14 - 6.23 (m, 1H), 5.15 (b, 1H), 4.07 (d, J = 6.4 Hz, 2H), ^{13}C NMR (125 MHz, CDCl_3): δ 137.6, 134.9, 133.2, 130.2, 128.6, 126.8, 125.0, 124.6, 119.8 (d, J = 325 Hz), 46.5. IR (CHCl_3) ν 2361, 1704, 1371, 1190, 738 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{10}\text{H}_9\text{ClF}_3\text{NO}_2\text{S}+\text{Na} (\text{M}+\text{Na})^+$ 321.9887, found 321.9891.



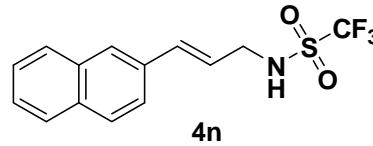
4l: (*E*)-*N*-(3-(3-bromophenyl)allyl)-1,1,1-trifluoromethanesulfonamide

Yellow solid, mp. 42- 45°C. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 7.50 (d, J = 1.2 Hz, 1H), 7.40 (dd, J = 8, 1.2 Hz, 1H), 7.27 (dd, J = 8, 1.2 Hz, 1H), 7.20 (t, J = 8 Hz, 1H), 6.53 (d, J = 16 Hz, 1H), 6.15 (dt, J = 16, 6.4 Hz, 1H), 5.19 (b, 1H), 4.05 (b, 2H), ^{13}C NMR (100 MHz, CDCl_3): δ 137.9, 133.1, 131.5, 130.5, 129.7, 125.5, 124.7, 123.1, 119.8 (d, J = 319 Hz), 46.5. IR (CHCl_3) ν 1370, 1229, 1188, 1144 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{10}\text{H}_9\text{BrF}_3\text{NO}_2\text{S}+\text{Na} (\text{M}+\text{Na})^+$ 365.9382, found 365.9384.



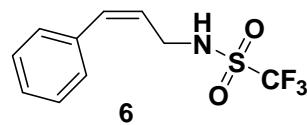
4m: (*E*)-*N*-(3-(2,4-dichlorophenyl)allyl)-1,1,1-trifluoromethanesulfonamide

Yellow oil. ^1H NMR (500 MHz, CDCl_3 , TMS): δ 7.40 (dd, J = 8, 2.4 Hz, 1H), 7.34 (d, J = 2.4 Hz, 1H), 7.20 (d, J = 8 Hz, 1H), 6.91 (d, J = 16 Hz, 1H), 6.13 (dt, J = 16, 5.2 Hz, 1H), 5.44 (b, 1H), 4.08 (d, J = 5.2 Hz, 2H), ^{13}C NMR (125 MHz, CDCl_3): δ 134.8, 134.1, 132.7, 129.91, 129.86, 128.1, 127.8, 126.6, 119.9 (q, J = 319 Hz), 46.7. IR (CHCl_3) ν 1471, 1188, 1144, 1103 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{10}\text{H}_8\text{F}_3\text{NO}_2\text{S}+\text{Na} (\text{M}+\text{Na})^+$ 355.9497, found 355.9497.



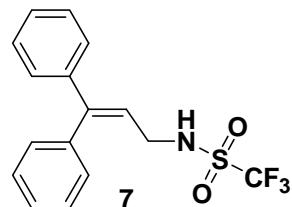
4n: (*E*)-1,1,1-trifluoro-*N*-(3-(naphthalen-2-yl)allyl)methanesulfonamide

White solid, mp. 85- 88°C. ^1H NMR (500 MHz, CDCl_3 , TMS): δ 7.85- 7.79 (m, 3H), 7.69 (s, 1H), 7.53- 7.44 (m, 3H), 6.69 (d, J = 16 Hz, 1H), 6.22 (dt, J = 16, 6 Hz, 1H), 5.11 (b, 1H), 4.05 (d, J = 6 Hz, 2H), ^{13}C NMR (125 MHz, CDCl_3): δ 134.8, 133.7, 133.6, 133.3, 128.7, 128.3, 128.0, 127.3, 126.8, 126.6, 123.5, 123.3, 120.0 (d, J = 319 Hz), 46.8. IR (CHCl_3) ν 1370, 1186, 1147, 1053 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{12}\text{F}_3\text{NO}_2\text{S}+\text{Na} (\text{M}+\text{Na})^+$ 338.0433, found 338.0437.



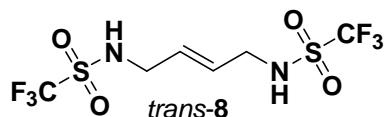
6: (Z)-1,1,1-trifluoro-N-(3-phenylallyl)methanesulfonamide

Yellow oil. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 7.36 (dd, $J = 7.6, 6$ Hz, 2H), 7.30 (d, $J = 6$ Hz, 1H), 7.16 (d, $J = 7.6$ Hz, 2H), 6.68 (d, $J = 11.6$ Hz, 1H), 5.67 (dt, $J = 11.6, 4.4$ Hz, 1H), 5.17 (b, 1H), 4.15 (b, 2H), ^{13}C NMR (100 MHz, CDCl_3): δ 135.6, 134.0, 128.9, 128.8, 128.1, 125.6, 119.9 (d, $J = 319$ Hz), 42.5. IR (CHCl_3) ν 1370, 1189, 1144, 1062 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{10}\text{H}_{10}\text{F}_3\text{NO}_2\text{S}+\text{Na} (\text{M}+\text{Na})^+$ 288.0277, found 288.0280.



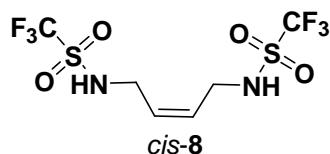
7: *N*-(3,3-diphenylallyl)-1,1,1-trifluoromethanesulfonamide

Yellow oil. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 7.41- 7.39 (m, 3H), 7.30- 7.29 (m, 3H), 7.23- 7.21 (m, 2H), 7.12 (dd, $J = 7.6, 1.6$ Hz, 2H), 6.07 (t, $J = 6.8$ Hz, 1H), 4.94 (b, 1H), 3.96 (t, $J = 6.8$ Hz, 2H), ^{13}C NMR (100 MHz, CDCl_3): δ 147.4, 141.0, 138.3, 129.6, 128.9, 128.6, 128.5, 128.4, 127.7, 121.8, 119.8 (d, $J = 317$ Hz), 43.7. IR (CHCl_3) ν 1424, 1370, 1190, 1142 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{14}\text{F}_3\text{NO}_2\text{S}+\text{Na} (\text{M}+\text{Na})^+$ 364.0590, found 364.0592.



Trans-8: (E)-N,N'-(but-2-ene-1,4-diyl)bis(1,1,1-trifluoromethanesulfonamide)

White solid, mp. 69- 72 °C. ^1H NMR (500 MHz, CDCl_3 , TMS): δ 5.80 (b, 2H), 5.02 (b, 2H), 3.95 (b, 4H), ^{13}C NMR (125 MHz, CDCl_3): δ 129.1, 119.8 (d, $J = 310$ Hz), 45.5. IR (CHCl_3) ν 1685, 1532, 1507, 1186 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_6\text{H}_8\text{F}_6\text{N}_2\text{O}_4\text{S}_2+\text{Na} (\text{M}+\text{Na})^+$ 372.9722, found 372.9720



Cis-8: (Z)-N,N'-(but-2-ene-1,4-diyl)bis(1,1,1-trifluoromethanesulfonamide)

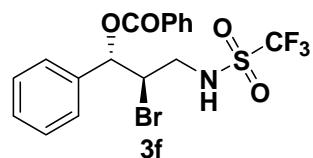
Colorless oil. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 5.73 (t, $J = 5$ Hz, 2H), 5.32 (b, 2H), 3.95 (d, $J = 5$ Hz, 4H), ^{13}C NMR (100 MHz, CDCl_3): δ 128.6, 119.7 (d, $J = 310$ Hz), 40.5. IR (CHCl_3) ν 1695, 1528, 1510, 1143 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_6\text{H}_8\text{F}_6\text{N}_2\text{O}_4\text{S}_2+\text{Na} (\text{M}+\text{Na})^+$ 372.9722, found 372.9720

General methods for enantioselective bromoesterification of allylic sulfonamides:

To a solution of allylic trifluoromethanesulfonamides **2f** (0.05 mmol) in freshly distilled CHCl₃ was added (DHQD)₂PHAL (7.7 mg, 0.01 mmol), (+) - CSA (2.3 mg, 0.01 mmol), benzoic acid (6.7 mg, 0.055 mmol) and NBS (9.8 mg, 0.055 mmol) sequentially. The reaction mixture was stirred at rt until the starting material disappeared as indicated by TLC (12 h). The reaction mixture was concentrated under vacuum and directly purified by flash column chromatography eluting with ethyl acetate and hexanes.

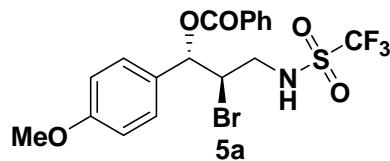
Note: The reaction was scaled up to 0.96 mmol for substrate **4n**.

Characterization Data for bromoesterification products **3f and **5a-5n**:**



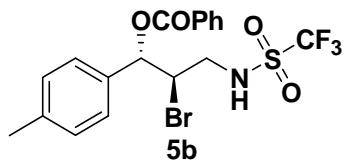
3f: 2-bromo-1-phenyl-3-(trifluoromethylsulfonamido)propyl benzoate

Colorless oil. 35.2mg, 75% yield. ¹H NMR (400 MHz, CDCl₃, TMS): δ 8.07 (d, *J* = 7.2 Hz, 2H), 7.62 (t, *J* = 8.8 Hz, 1H), 7.50- 7.36 (m, 7H), 6.24 (d, *J* = 6.8 Hz, 1H), 5.54 (b, 1H), 4.53- 4.49 (m, 1H), 3.90 (dd, *J* = 14.8, 3.6 Hz, 1H), 3.65 (dd, *J* = 14.4, 8 Hz, 1H), ¹³C NMR (100 MHz, CDCl₃): δ 165.4, 136.2, 134.1, 130.1, 129.6, 129.3, 129.2, 129.0, 127.3, 119.8 (d, *J* = 319 Hz), 76.4, 54.5, 47.0. IR (CHCl₃) ν 2358, 1727, 1264, 1146 cm⁻¹. HRMS (ESI) *m/z* calcd for C₁₇H₁₅BrF₃NO₄S+Na (M+Na)⁺ 487.9749, found 487.9746. [α]_D²⁵ = + 3.9 (c 2.0, CHCl₃). 80% ee under conditions in Table 3.



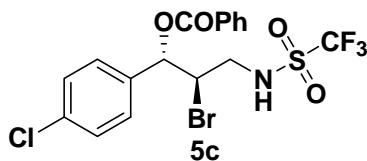
5a: 2-bromo-1-(4-methoxyphenyl)-3-(trifluoromethylsulfonamido)propyl benzoate

Yellow oil. 27.4mg, 55% yield. ¹H NMR (400 MHz, CDCl₃, TMS): δ 8.03 - 8.10 (m, 2H), 7.59 - 7.66 (m, 1H), 7.45 - 7.53 (m, 2H), 7.39 (s, 2H), 6.89 - 6.96 (m, 2H), 6.18 (d, *J* = 7.2 Hz, 1H), 5.47 (b, 1H), 4.50 (td, *J* = 7.5, 3.3 Hz, 1H), 3.92 (dd, *J* = 14.6, 2.9 Hz, 1H), 3.80 - 3.83 (m, 3H), 3.65 (dd, *J* = 14.6, 7.8 Hz, 1H), ¹³C NMR (125 MHz, CDCl₃): δ 165.4, 160.4, 133.9, 130.4, 130.0, 128.9, 128.6, 128.2, 119.7 (d, *J* = 319 Hz), 114.4, 76.0, 55.5, 54.7, 47.1. IR (CHCl₃) ν 2359, 1712, 1379, 1224, 1145 cm⁻¹. HRMS (ESI) *m/z* calcd for C₁₈H₁₇BrF₃NO₅S+Na (M+Na)⁺ 517.9855, found 517.9873.



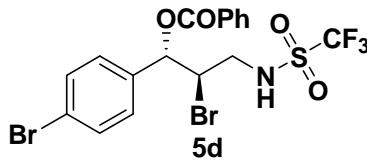
5b: 2-bromo-1-phenyl-3-(trifluoromethylsulfonamido)propyl benzoate

Colorless oil. 21.1mg, 87% yield. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 8.07- 8.05 (m, 2H), 7.61- 7.59 (m, 1H), 7.48 (t, J = 8 Hz, 2H), 7.33 (d, J = 6.4 Hz, 2H), 7.21 (d, J = 6.4 Hz, 2H), 6.20 (d, J = 6.8 Hz, 1H), 4.52- 4.48 (m, 1H), 3.90 (d, J = 14.4 Hz, 1H), 3.65 (dd, J = 14.4, 8 Hz, 1H), 2.35 (s, 3H), ^{13}C NMR (100 MHz, CDCl_3): δ 165.4, 139.5, 134.0, 130.4, 130.0, 129.8, 128.9, 128.7, 127.1, 119.8 (d, J = 334 Hz), 76.3, 54.5, 47.0, 21.4. IR (CHCl_3) ν 1700, 1376, 1266, 1195 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{17}\text{BrF}_3\text{NO}_4\text{S}+\text{Na} (\text{M}+\text{Na})^+$ 501.9906, found 501.9892. $[\alpha]_D^{25}= + 6.7$ (c 1.1, CHCl_3).



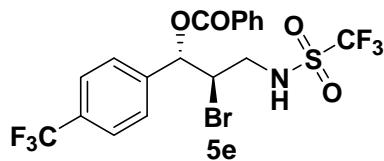
5c: 2-bromo-1-(4-chlorophenyl)-3-(trifluoromethylsulfonamido)propyl benzoate

Yellow oil. 38.7mg, 77% yield. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 8.08 - 8.02 (m, 2H), 7.68 - 7.60 (m, 1H), 7.54 - 7.46 (m, 2H), 7.41- 7.39 (m, 4H), 6.16 (dd, J = 7.4, 1.2 Hz, 1H), 5.51 (b, 1H), 4.55 - 4.42 (m, 1H), 3.92 (d, J = 14.4 Hz, 1H), 3.73 - 3.60 (m, 1H), ^{13}C NMR (125 MHz, CDCl_3): δ 165.2, 135.5, 134.8, 134.1, 130.0, 129.4, 129.3, 129.0, 128.8, 119.7 (d, J = 319 Hz), 75.6, 54.1, 47.1. IR (CHCl_3) ν 2360, 1728, 1377, 1092, 716 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{14}\text{BrClF}_3\text{NO}_4\text{S}+\text{Na} (\text{M}+\text{Na})^+$ 521.9360, found 521.9384. $[\alpha]_D^{25}= + 0.8$ (c 0.63, CHCl_3).

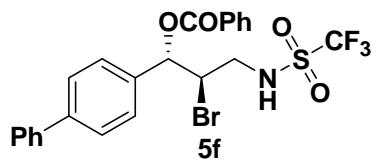


5d: 2-bromo-1-(4-bromophenyl)-3-(trifluoromethylsulfonamido)propyl benzoate

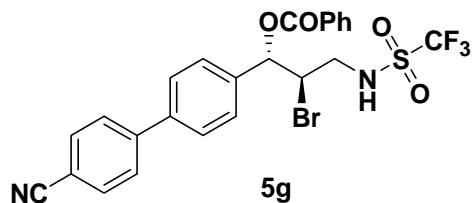
Yellow oil. 42.6mg, 78% yield. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 8.09 - 8.03 (m, 2H), 7.67 - 7.59 (m, 1H), 7.58 - 7.46 (m, 4H), 7.38 - 7.31 (m, 2H), 6.15 (d, J = 7.4 Hz, 1H), 5.58 (b, 1H), 4.48 (td, J = 7.4, 3.2 Hz, 1H), 3.92 (dd, J = 14.5, 3.2 Hz, 1H), 3.76 - 3.59 (m, 1H), ^{13}C NMR (100 MHz, CDCl_3): δ 165.3, 135.4, 134.2, 132.3, 130.1, 129.2, 129.1, 129.0, 123.8, 119.8 (q, J = 255 Hz), 75.7, 54.1, 47.1. IR (CHCl_3) ν 2360, 1721, 1378, 1094, 713 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{14}\text{Br}_2\text{F}_3\text{NO}_4\text{S}+\text{Na} (\text{M}+\text{Na})^+$ 565.8855, found 565.8875. $[\alpha]_D^{25}= + 9.5$ (c 0.84, CHCl_3).



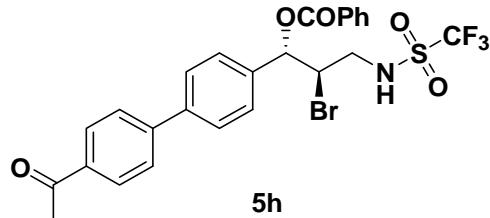
5e: 2-bromo-1-(4-(trifluoromethyl)phenyl)-3-(trifluoromethylsulfonamido)propyl benzoate
Yellow oil. 27.9mg, 52% yield. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 8.06 (t, $J = 6.4$ Hz, 2H), 7.75 - 7.56 (m, 5H), 7.54 - 7.44 (m, 2H), 6.31 - 6.17 (m, 1H), 4.50 (dt, $J = 6.6, 3.6$ Hz, 1H), 3.94 (d, $J = 14$ Hz, 1H), 3.70 (dd, $J = 14, 6.6$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 165.2, 140.2, 134.3, 131.8 (d, $J = 33$ Hz), 130.1, 129.0, 128.8, 127.9, 126.1 (q, $J = 3.8$ Hz), 123.9 (d, $J = 271$ Hz), 119.7 (d, $J = 319$ Hz), 75.6, 53.8, 47.1. IR (CHCl_3) v 2359, 1707, 1375, 1067, 714 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{14}\text{BrF}_6\text{NO}_4\text{S}+\text{Na} (\text{M}+\text{Na})^+$ 555.9623, found 555.9637. $[\alpha]_D^{25} = +1.4$ (c 0.87, CHCl_3).



5f: 1-(biphenyl-4-yl)-2-bromo-3-(trifluoromethylsulfonamido)propyl benzoate
Yellow solid, mp. 138- 141°C. 22.3mg, 82% yield. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 8.09 (dd, $J = 8, 1.2$ Hz, 2H), 7.65- 7.61 (m, 3H), 7.59- 7.56 (m, 2H), 7.53- 7.50 (m, 3H), 7.49- 7.42 (m, 3H), 7.36 (m, 1H), 6.27 (d, $J = 6.8$ Hz, 1H), 5.51 (b, 1H), 4.58- 4.53 (m, 1H), 3.94 (dd, $J = 14.4, 3.2$ Hz, 1H), 3.69 (dd, $J = 14.4, 8$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 165.4, 142.6, 140.5, 135.1, 134.1, 130.1, 129.3, 129.1, 129.0, 128.0, 127.9, 127.8, 127.5, 119.8 (d, $J = 320$ Hz), 76.3, 54.4, 47.1. IR (CHCl_3) v 1722, 1440, 1217, 1145 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{19}\text{BrF}_3\text{NO}_4\text{S}+\text{Na} (\text{M}+\text{Na})^+$ 564.0062, found 564.0053. $[\alpha]_D^{25} = -1.0$ (c 0.87, CHCl_3).

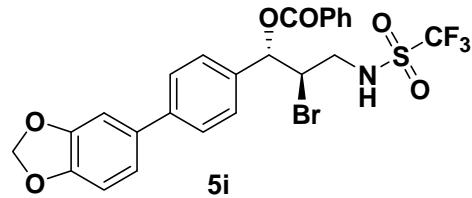


5g: 2-bromo-1-(4'-cyanobiphenyl-4-yl)-3-(trifluoromethylsulfonamido)propyl benzoate
Yellow oil. 22.5mg, 79% yield. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 8.12- 8.07 (m, 2H), 7.78- 7.56 (m, 9H), 7.50 (t, $J = 8$ Hz, 2H), 6.26 (d, $J = 7.2$ Hz, 1H), 5.83 (b, 1H), 4.57- 4.52 (m, 1H), 3.98- 3.92 (m, 1H), 3.74- 3.69 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 165.4, 145.0, 140.3, 136.9, 134.2, 133.0, 130.1, 129.2, 129.0, 128.2, 128.0, 127.9, 119.7 (d, $J = 357$ Hz), 119.1, 111.6, 76.1, 54.2, 47.1. IR (CHCl_3) v 2229, 1662, 1606, 1379, 1264 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{24}\text{H}_{18}\text{BrF}_3\text{N}_2\text{O}_4\text{S}+\text{Na} (\text{M}+\text{Na})^+$ 589.0015, found 589.0069. $[\alpha]_D^{25} = -4.4$ (c 0.73, CHCl_3).



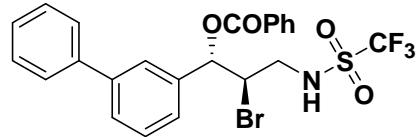
5h: 2-1-(4'-acetylphenyl-4-yl)-2-bromo-3-(trifluoromethylsulfonamido)propyl benzoate

Yellow oil. 22.6mg, 77% yield. ¹H NMR (400 MHz, CDCl₃, TMS): δ 8.13- 8.08 (m, 3H), 8.02 (d, J = 8.4 Hz, 2H), 7.67- 7.62 (m, 4H), 7.57- 7.55 (m, 2H), 7.49 (t, J = 6.4 Hz, 2H), 6.28 (d, J = 7.2 Hz, 1H), 6.03 (b, 1H), 4.59- 4.55 (m, 1H), 3.95 (d, J = 14 Hz, 1H), 3.72 (dd, J = 14, 8 Hz, 1H), 2.63 (s, 3H), ¹³C NMR (125 MHz, CDCl₃): δ 198.4, 165.4, 145.1, 141.1, 136.3, 134.2, 130.5, 130.1, 129.3, 129.0, 128.8, 128.1, 128.0, 127.5, 119.8 (d, J = 322 Hz), 76.1, 54.3, 47.2, 26.9. IR (CHCl₃) ν 1676, 1604, 1378, 1265, 1193 cm⁻¹. HRMS (ESI) m/z calcd for C₂₅H₂₁BrF₃NO₅S+Na (M+Na)⁺ 606.0168, found 606.0177. [α]_D²⁵ = - 5.2 (c 1.3, CHCl₃).



5i: 1-(4-(benzo[d][1,3]dioxol-5-yl)phenyl)-2-bromo-3-(trifluoromethylsulfonamido)propyl benzoate

White solid. mp. 146- 148°C. 20.9mg, 71% yield. ¹H NMR (400 MHz, CDCl₃, TMS): δ 8.08 (d, J = 8 Hz, 2H), 7.62 (t, J = 6.8 Hz, 1H), 7.55- 7.46 (m, 6H), 7.05- 7.03 (m, 2H), 6.87 (d, J = 8.8 Hz, 1H), 6.25 (d, J = 6.8 Hz, 1H), 6.00 (s, 2H), 5.58 (b, 1H), 4.55- 4.52 (m, 1H), 3.93 (d, J = 14 Hz, 1H), 3.68 (dd, J = 14, 8 Hz, 1H), ¹³C NMR (100 MHz, CDCl₃): δ 165.4, 148.4, 147.7, 142.2, 134.7, 134.1, 130.1, 129.2, 129.0, 128.9, 127.7, 127.5, 121.0, 119.8 (d, J = 309 Hz), 108.9, 107.8, 101.5, 76.2, 54.4, 47.0. IR (CHCl₃) ν 1724, 1483, 1229, 1145 cm⁻¹. HRMS (ESI) m/z calcd for C₂₄H₁₉BrF₃NO₆S+Na (M+Na)⁺ 607.9961, found 607.9969. [α]_D²⁵ = - 2.9 (c 2.0, CHCl₃).

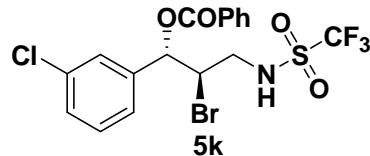


5j

5j: 1-(biphenyl-3-yl)-2-bromo-3-(trifluoromethylsulfonamido)propyl benzoate

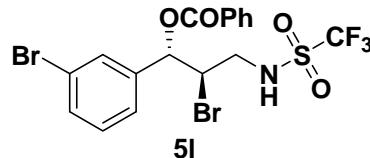
Colorless oil. 19.0mg, 70% yield. ¹H NMR (400 MHz, CDCl₃, TMS): δ 8.09- 8.07 (m, 2H), 7.65- 7.56 (m, 5H), 7.50- 7.41 (m, 6H), 7.35 (dt, J = 8, 0.8 Hz, 1H), 6.30 (d, J = 7.2 Hz, 1H), 5.57 (b, 1H), 4.58- 4.54 (m, 1H), 3.94 (d, J = 14.4 Hz, 1H), 3.69 (dd, J = 14.4, 8.4 Hz, 1H), ¹³C NMR (125 MHz, CDCl₃): δ 165.4, 142.3, 140.7, 136.8, 134.1, 130.1, 129.6, 129.3, 129.2, 129.0, 128.5, 128.0, 127.5, 126.2, 126.0, 119.8 (d, J = 319 Hz), 76.4, 54.5, 47.1. IR (CHCl₃) ν 1722, 1380, 1196, 1145 cm⁻¹. HRMS (ESI) m/z calcd for C₂₃H₁₉BrF₃NO₄S+Na (M+Na)⁺ 564.0062,

found 564.0068. $[\alpha]_D^{25} = -2.7$ (c 1.1, CHCl₃).



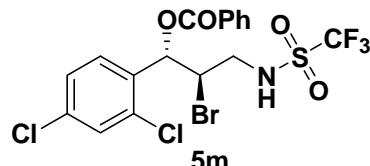
5k: 2-bromo-1-(3-chlorophenyl)-3-(trifluoromethylsulfonamido)propyl benzoate

Yellow oil. 26.8mg, 71% yield. ¹H NMR (400 MHz, CDCl₃, TMS): δ 8.10 - 8.04 (m, 2H), 7.68 - 7.60 (m, 1H), 7.54 - 7.44 (m, 3H), 7.39 - 7.32 (m, 3H), 6.21 - 6.14 (m, 1H), 4.54 - 4.43 (m, 1H), 3.96 - 3.85 (m, 1H), 3.74 - 3.61 (m, 1H), ¹³C NMR (100 MHz, CDCl₃): δ 165.2, 138.3, 135.1, 134.2, 130.3, 130.1, 129.8, 129.0, 128.9, 127.5, 125.7, 119.7 (d, *J* = 255 Hz), 75.6, 53.9, 47.0. IR (CHCl₃) ν 1709, 1434, 1362, 1148, 729 cm⁻¹. HRMS (ESI) *m/z* calcd for C₁₇H₁₄BrClF₃NO₄S+Na (M+Na)⁺ 521.9360, found 521.9347. $[\alpha]_D^{25} = -1.6$ (c 0.46, CHCl₃).



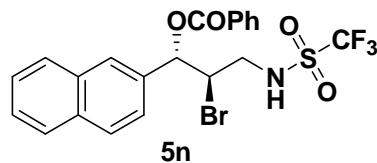
5l: 2-bromo-1-(3-bromophenyl)-3-(trifluoromethylsulfonamido)propyl benzoate

Yellow oil. 18.1mg, 66% yield. ¹H NMR (400 MHz, CDCl₃, TMS): δ 8.06 (dd, *J* = 7.2, 0.8 Hz, 2H), 7.65- 7.60 (m, 2H), 7.52- 7.48 (m, 3H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.28 (td, *J* = 8 Hz, 2 Hz, 1H), 6.15 (d, *J* = 7.6 Hz, 1H), 5.63 (b, 1H), 4.49- 4.45 (m, 1H), 3.91 (d, *J* = 14.4 Hz, 1H), 3.67 (dd, *J* = 14.4, 8 Hz, 1H), ¹³C NMR (100 MHz, CDCl₃): δ 165.2, 138.5, 134.2, 132.8, 130.6, 130.4, 130.1, 129.0, 128.9, 126.1, 123.1, 119.7 (d, *J* = 312 Hz), 75.5, 53.9, 47.0. IR (CHCl₃) ν 1725, 1266, 1195, 1155 cm⁻¹. HRMS (ESI) *m/z* calcd for C₁₇H₁₄Br₂F₃NO₄S+Na (M+Na)⁺ 565.8855, found 565.8855. $[\alpha]_D^{25} = -1.8$ (c 2.0, CHCl₃).



5m: 2-bromo-1-(2,4-dichlorophenyl)-3-(trifluoromethylsulfonamido)propyl benzoate

Yellow oil. 16.4mg, 61% yield. ¹H NMR (400 MHz, CDCl₃, TMS): δ 8.13- 8.07 (m, 2H), 7.65- 7.60 (m, 1H), 7.52- 7.42 (m, 4H), 7.30 (d, *J* = 8.8 Hz, 1H), 6.56 (d, *J* = 6.4 Hz, 1H), 5.58 (b, 1H), 4.66- 4.61 (m, 1H), 3.90 (d, *J* = 14 Hz, 1H), 3.69 (dd, *J* = 14, 8.4 Hz, 1H), ¹³C NMR (125 MHz, CDCl₃): δ 165.0, 136.2, 134.32, 134.27, 132.8, 130.4, 130.2, 129.3, 129.1, 128.9, 128.1, 119.8 (q, *J* = 319 Hz), 73.2, 52.6, 46.9. IR (CHCl₃) ν 1719, 1589, 1231, 1193 cm⁻¹. HRMS (ESI) *m/z* calcd for C₁₇H₁₃BrCl₂F₃NO₄S+Na (M+Na)⁺ 555.8970, found 555.8979. $[\alpha]_D^{25} = -23$ (c 1.0, CHCl₃).

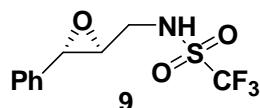


5n: 2-bromo-1-(naphthalen-2-yl)-3-(trifluoromethylsulfonamido)propyl benzoate

White solid. mp. 131- 134°C. 378mg, 76% yield. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 8.09 (d, J = 8.4 Hz, 2H), 7.91- 7.86 (m, 4H), 7.62 (t, J = 6.4 Hz, 1H), 7.56- 7.48 (m, 5H), 6.39 (d, J = 7.2 Hz, 1H), 5.55 (b, 1H), 4.65- 4.61 (m, 1H), 3.96 (d, J = 14 Hz, 1H), 3.71 (dd, J = 14, 8 Hz, 1H), ^{13}C NMR (125 MHz, CDCl_3): δ 165.4, 134.1, 133.9, 133.5, 133.2, 130.1, 129.3, 129.2, 129.0, 128.5, 128.1, 127.3, 127.2, 127.0, 124.1, 119.8 (d, J = 319 Hz), 76.6, 54.3, 47.2. IR (CHCl_3) ν 1727, 1428, 1380, 1265, 1145 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{17}\text{BrF}_3\text{NO}_4\text{S}+\text{Na} (\text{M}+\text{Na})^+$ 537.9906, found 537.9907. $[\alpha]_{\text{D}}^{25} = -10$ (c 0.87, CHCl_3).

Procedure for the preparation of epoxide **9**:

To a solution of **3f** (23 mg, 0.05 mmol) in water and THF (2 mL, volume ratio = 1:1) was added LiOH (10 mg, 0.25 mmol). After stirring for 8 h at 50 °C, the reaction mixture was diluted with water (3 mL) and extracted with ether. The combined organic phase was dried over MgSO_4 , concentrated under vacuum and purified by flash column chromatography eluting with ethyl acetate and hexanes to afford product **9** (8.4 mg, 60% yield).

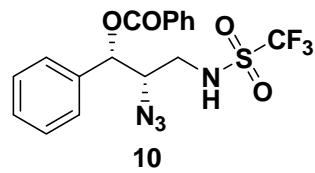


9: 1,1,1-trifluoro-N-((3-phenyloxiran-2-yl)methyl)methanesulfonamide

Colorless oil. ^1H NMR (500 MHz, CDCl_3 , TMS): δ 7.39- 7.33 (m, 3H), 7.26 (d, J = 6 Hz, 2H), 3.86 (d, J = 2.5 Hz, 1H), 3.81 (d, J = 14.5 Hz, 1H), 3.50 (dd, J = 15, 5 Hz, 1H), 3.26 (dd, J = 5, 2.5 Hz, 1H), ^{13}C NMR (125 MHz, CDCl_3): δ 135.5, 129.1, 129.0, 126.0, 112.0 (d, J = 320 Hz), 60.4, 57.1, 45.3. IR (CHCl_3) ν 1375, 1230, 1191, 1148, 1087 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{10}\text{H}_{10}\text{F}_3\text{NO}_3\text{S}+\text{Na} (\text{M}+\text{Na})^+$ 304.0226, found 304.0223. $[\alpha]_{\text{D}}^{25} = -21$ (c 0.54, CHCl_3).

Procedure for the preparation of compound **10**:

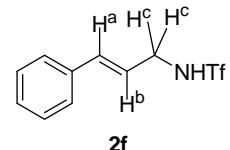
To a solution of **3f** (23 mg, 0.05 mmol) in HMPA (1 mL) was added NaN_3 (10 mg, 0.15 mmol). After stirring for 24 h at 50 °C, the reaction mixture was diluted with water (3 mL) at 0 °C, extracted with ether, and then the combined organic phase was washed with brine and dried over MgSO_4 . The reaction mixture was concentrated under vacuum and purified by flash column chromatography eluting with ethyl acetate and hexanes to afford product **10** (18 mg, 83% yield).



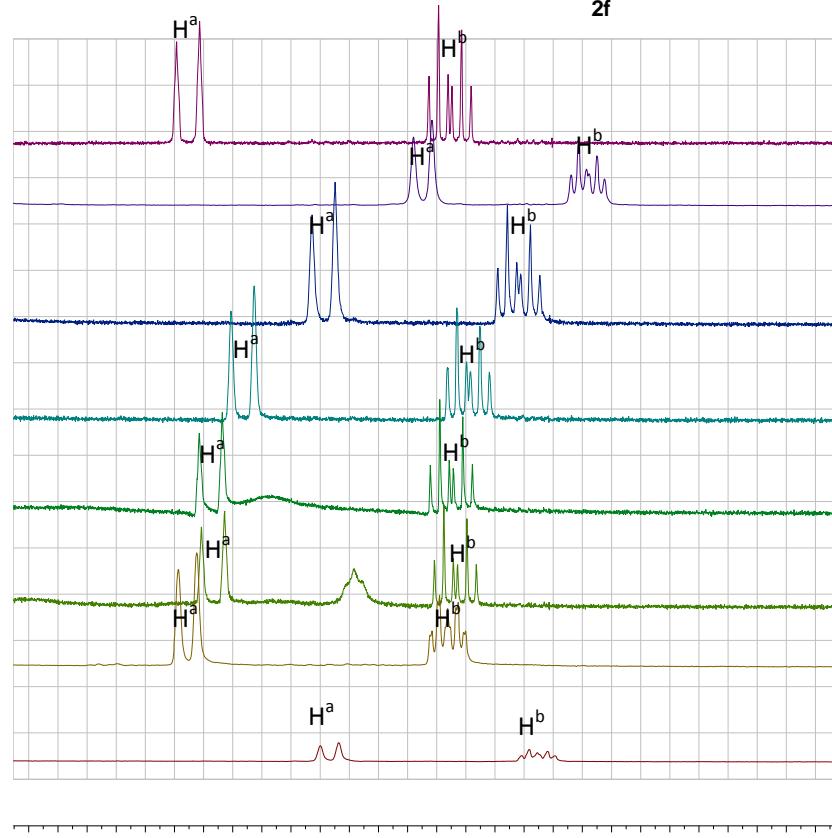
10: 2-azido-1-phenyl-3-(trifluoromethylsulfonamido)propyl benzoate

Colorless oil. ^1H NMR (500 MHz, CDCl_3 , TMS): δ 8.07 (d, $J = 8$ Hz, 2H), 7.57 (t, $J = 7.5$ Hz, 1H), 7.49 (d, $J = 8$ Hz, 2H), 7.45- 7.38 (m, 5H), 6.20 (d, $J = 8.5$ Hz, 1H), 4.15- 4.13 (m, 1H), 3.63 (dd, $J = 13, 4$ Hz, 1H), 3.27 (dd, $J = 13, 3$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 166.6, 135.8, 134.0, 130.2, 129.9, 129.6, 129.2, 128.8, 127.5, 119.7 (d, $J = 319$ Hz), 75.0, 59.2, 52.8. IR (CHCl_3) ν 2108, 1702, 1381, 1269, 1198 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{15}\text{F}_3\text{N}_4\text{O}_4\text{S}+\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 451.0658, found 451.0646. $[\alpha]_D^{25} = +8$ (c 0.86, CHCl_3).

¹H NMR of **2f** in the presence of catalyst and/or (+)-CSA



2f : (DHQD)₂PHAL : (+)-CSA		
1:	0:	0
1:	1:	0
1:	1:	1
1:	1:	2
1:	1:	3
1:	1:	4
1: 0: 1		
Substrate:		
(DHQD) ₂ PHAL:CSA:BzOH		
1 : 1 : 1 : 5.5		



2f : (DHQD)₂PHAL : (+)-CSA		
1:	0:	0
1:	1:	0
1:	1:	1
1:	1:	2
1:	1:	3
1:	1:	4
1: 0: 1		

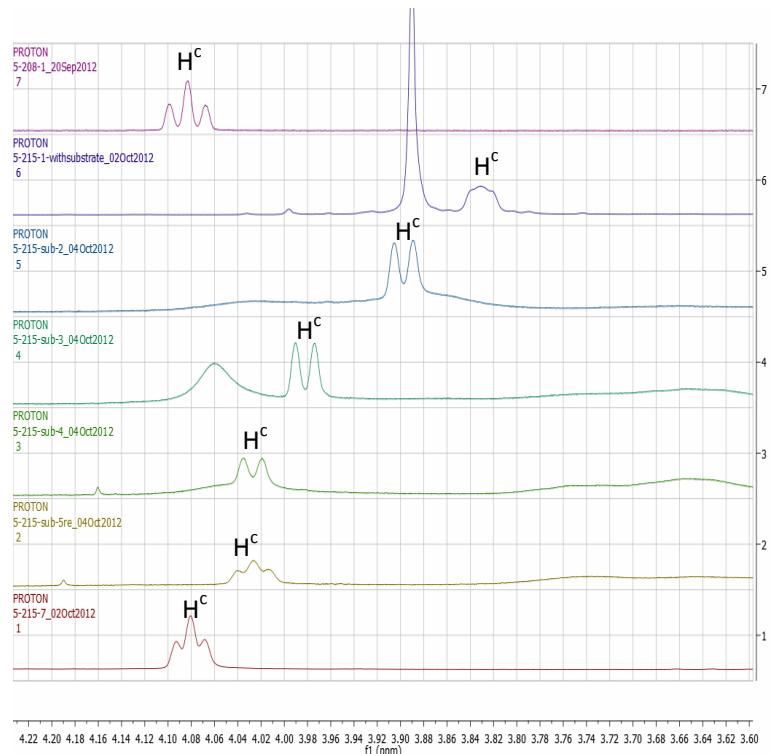
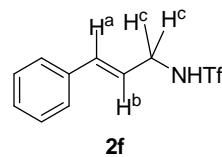


Table S1. Summary of ^1H NMR of **2f** in the presence of catalyst and/or (+)-CSA



2f : (DHQD)₂PHAL : (+)-CSA	H^a	H^b	H^c
1: 0: 0	6.63	6.18	4.08
1: 1: 0	6.22	5.94	3.83
1: 1: 1	6.39	6.06	3.90
1: 1: 2	6.53	6.15	3.98
1: 1: 3	6.59	6.17	4.03
1: 1: 4	6.58	6.16	4.03
1: 0: 1	6.62	6.18	4.08
Substrate: (DHQD) ₂ PHAL:CSA:BzOH 1 : 1 : 1 : 5.5	6.39	6.04	Mixed with other peaks

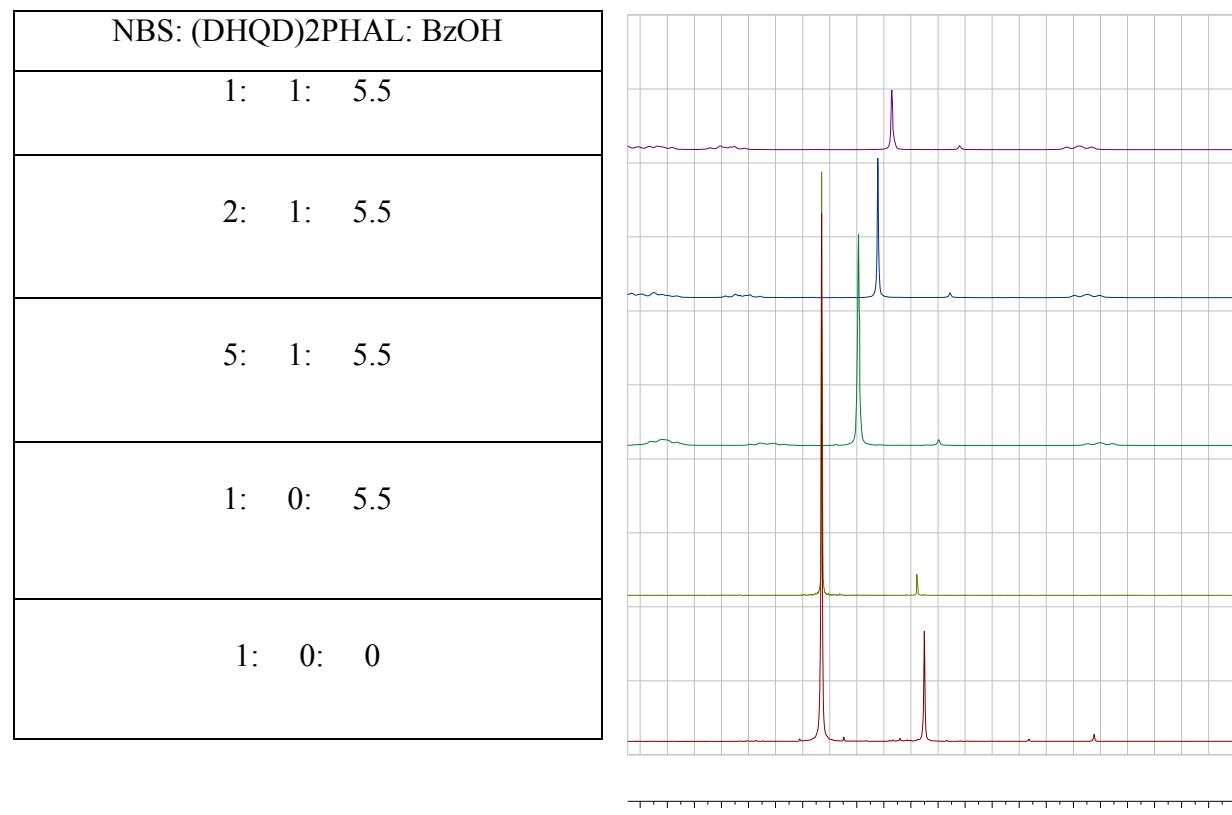
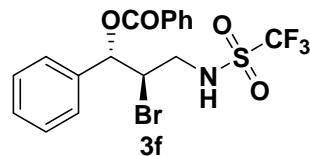


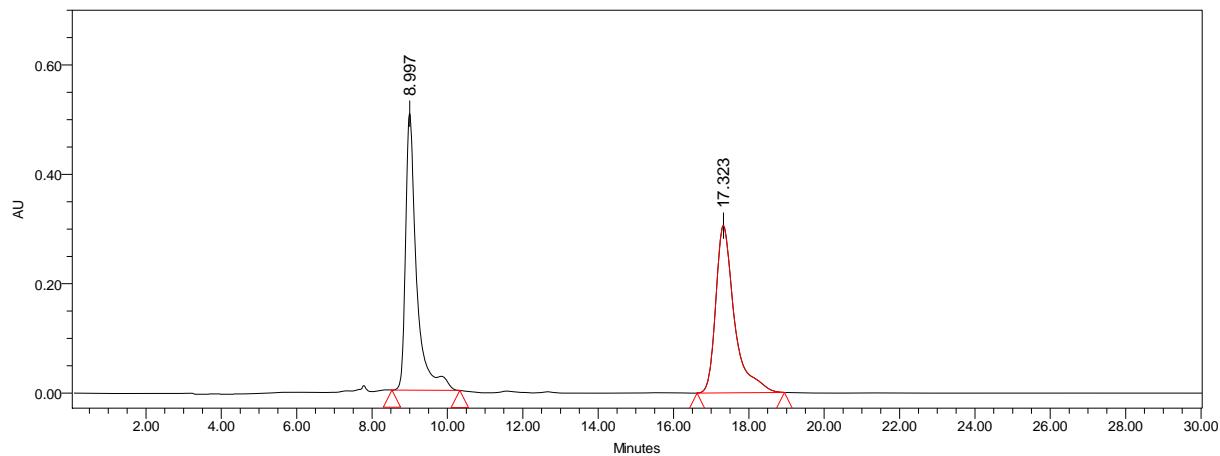
Table S2. Summary of ^1H NMR of **NBS** in the presence of catalyst and/or PhCOOH

NBS: (DHQD)2PHAL: BzOH	H of NBS
1: 1: 5.5	2.84
2: 1: 5.5	2.86
5: 1: 5.5	2.89
1: 0: 5.5	2.96
1: 0: 0	2.96

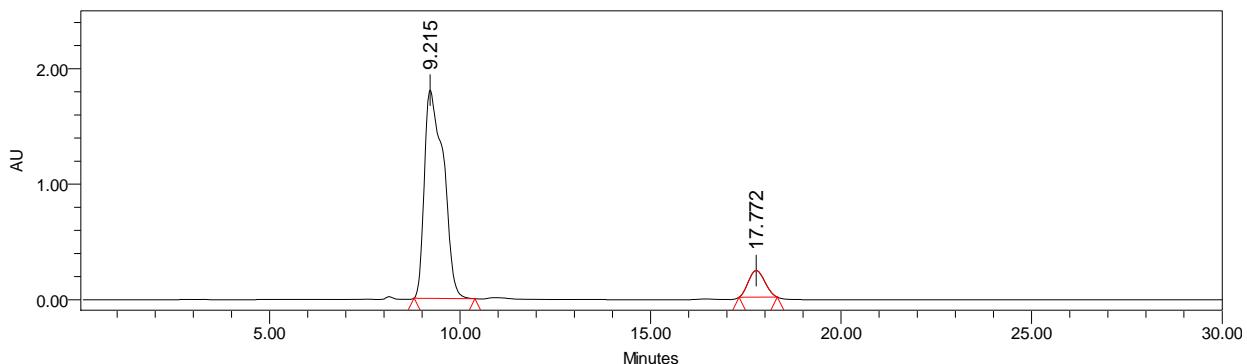
HPLC spectra of racemic and enantio-enriched compounds **3f** and **5b- 5n**.



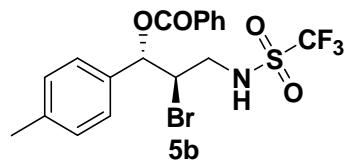
HPLC (Chiralcel AD-H; eluent: hexane/2-propanol = 90/10; flow rate: 0.7 mL/min; detection: at 230 nm): retention times $t_1 = 9.0\text{min}$ $t_2 = 17.3\text{min}$;



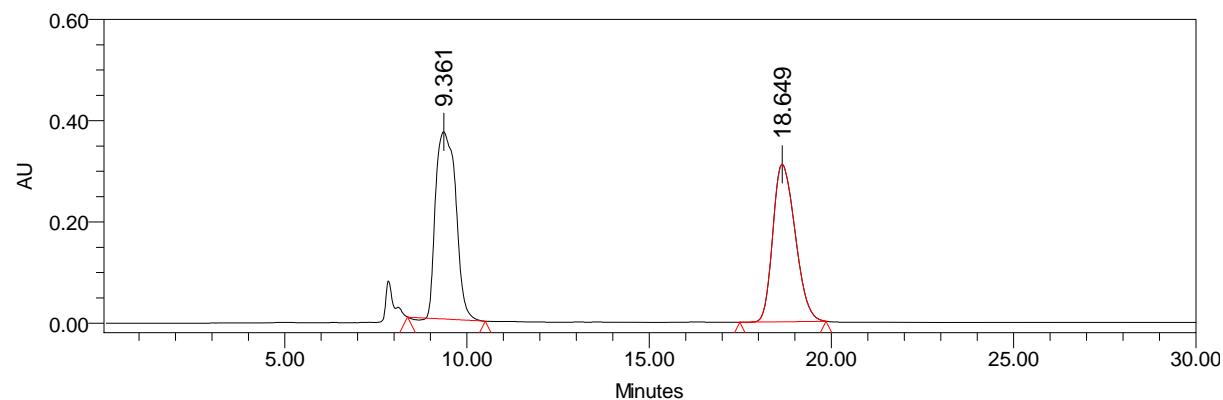
Retention Time	Area	Area%	Height
8.997	10254310	49.34	506851
17.323	10527576	50.66	306039



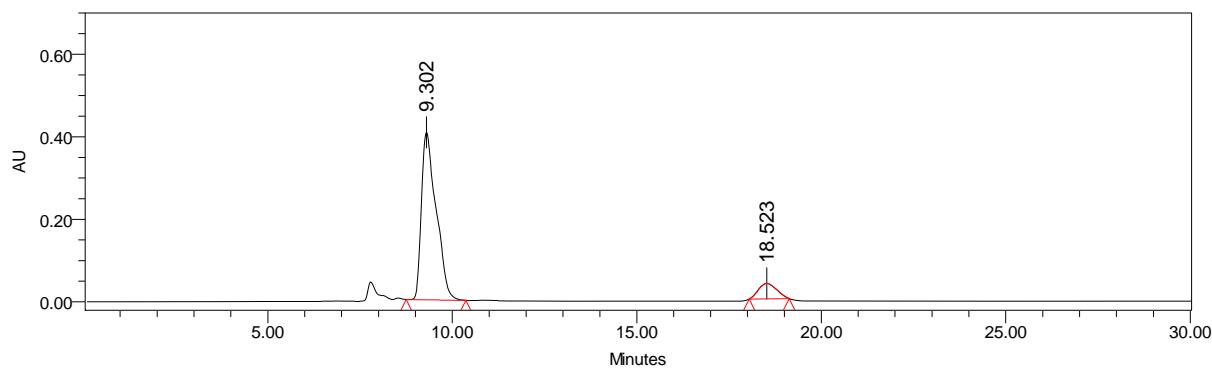
Retention Time	Area	Area%	Height
9.215	62847212	90.15	1804512
17.772	6870661	9.85	231045



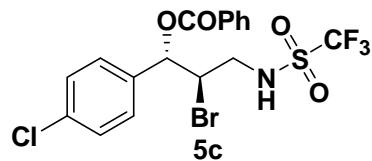
HPLC (Chiralcel AD-H; eluent: hexane/2-propanol = 90/10; flow rate: 0.7 mL/min; detection: at 225 nm): retention times $t_1 = 9.4$ min $t_2 = 18.6$ min;



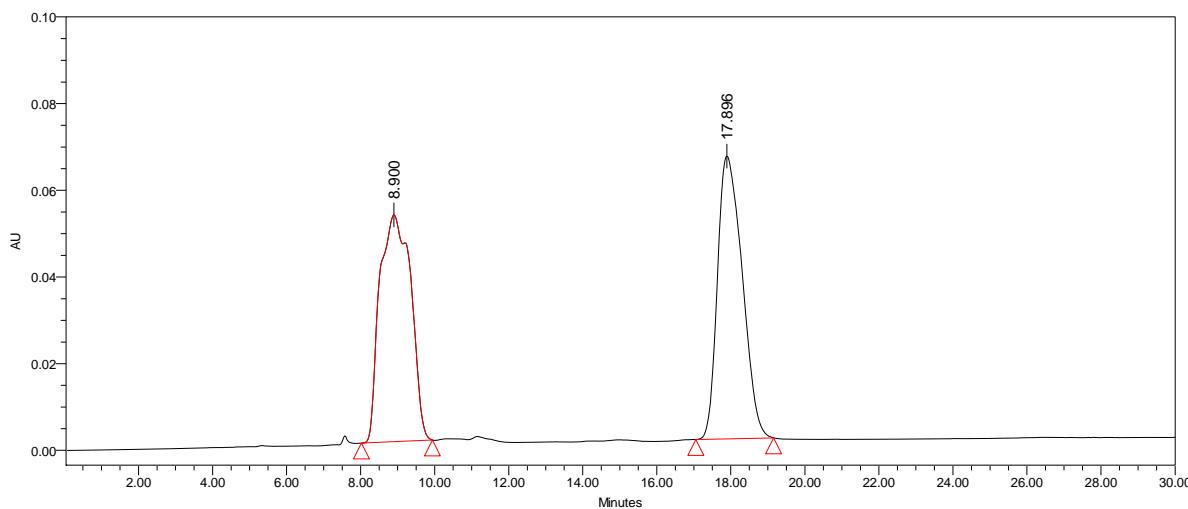
Retention Time	Area	Area%	Height
9.361	14375710	51.98	369565
18.649	13282723	48.02	311095



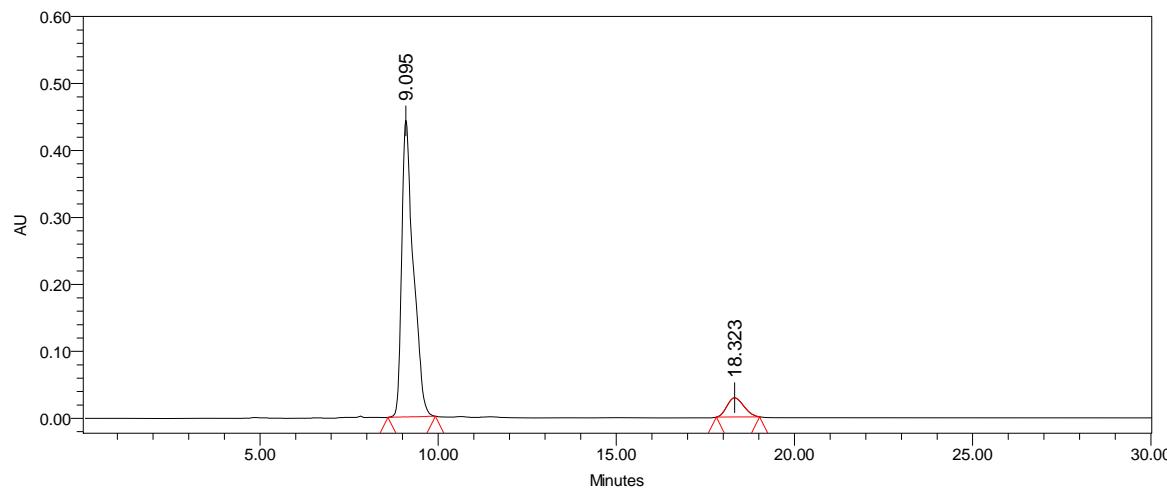
Retention Time	Area	Area%	Height
9.302	11281179	89.82	406245
18.523	1278905	10.18	37386



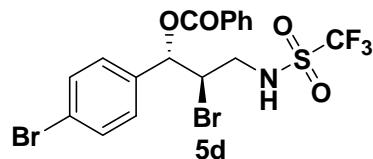
HPLC (Chiralcel AD-H; eluent: hexane/2-propanol = 90/10; flow rate: 0.7 mL/min; detection: at 220 nm): retention times $t_1 = 8.9$ min $t_2 = 17.9$ min;



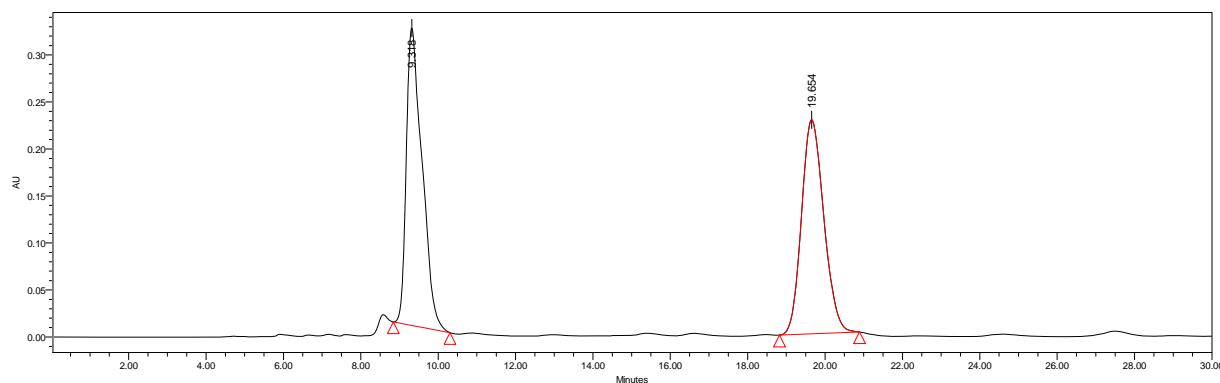
	Retention Time	Area	% Area	Height
1	8.900	3044432	50.11	52319
2	17.896	3031013	49.89	65277



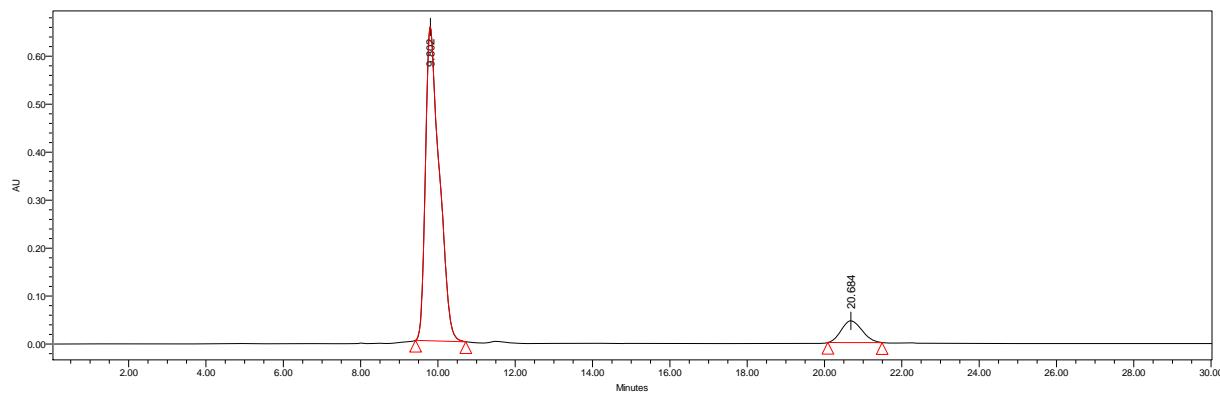
	Retention Time	Area	% Area	Height
1	9.095	9974703	91.43	443386
2	18.323	935169	8.57	28770



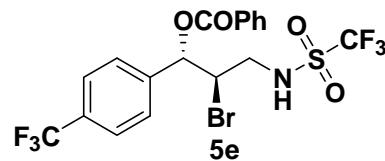
HPLC (Chiralcel AD-H; eluent: hexane/2-propanol = 90/10; flow rate: 0.7 mL/min; detection: at 220 nm): retention times $t_1 = 9.3$ min $t_2 = 19.7$ min;



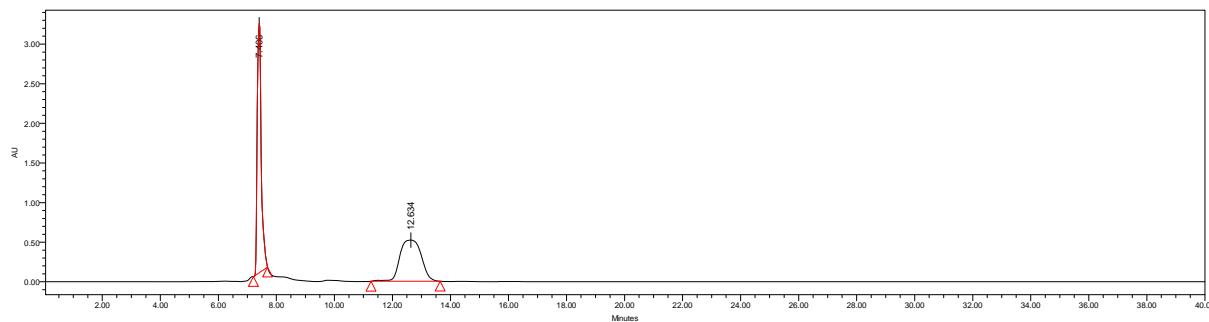
Retention Time	Area%	Start Time	End Time
9.318	51.03	8.407	10.590
19.654	48.97	18.790	21.023



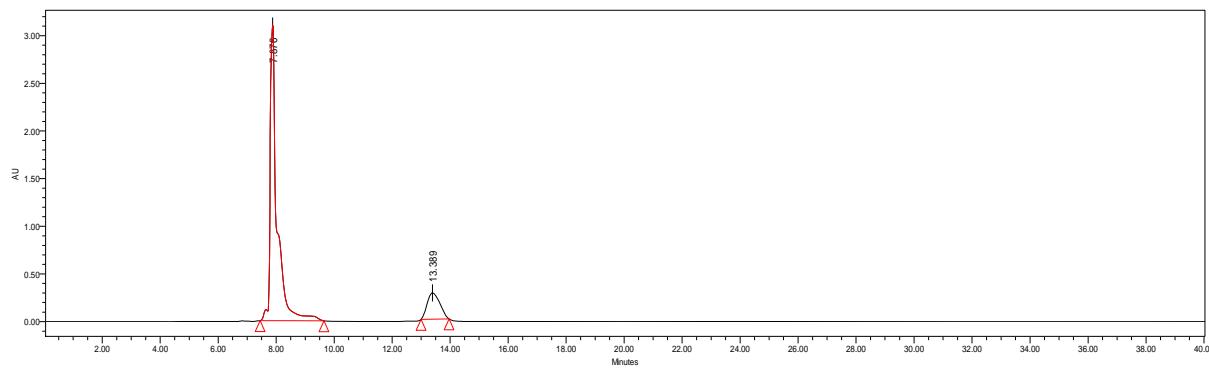
Retention Time	Area%	Start Time	End Time
9.802	90.53	9.422	10.722
20.684	9.47	20.088	21.488



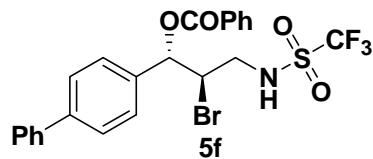
HPLC (Chiralcel AD-H; eluent: hexane/2-propanol = 90/10; flow rate: 0.7 mL/min; detection: at 225 nm): retention times $t_1 = 7.4$ min $t_2 = 12.6$ min.



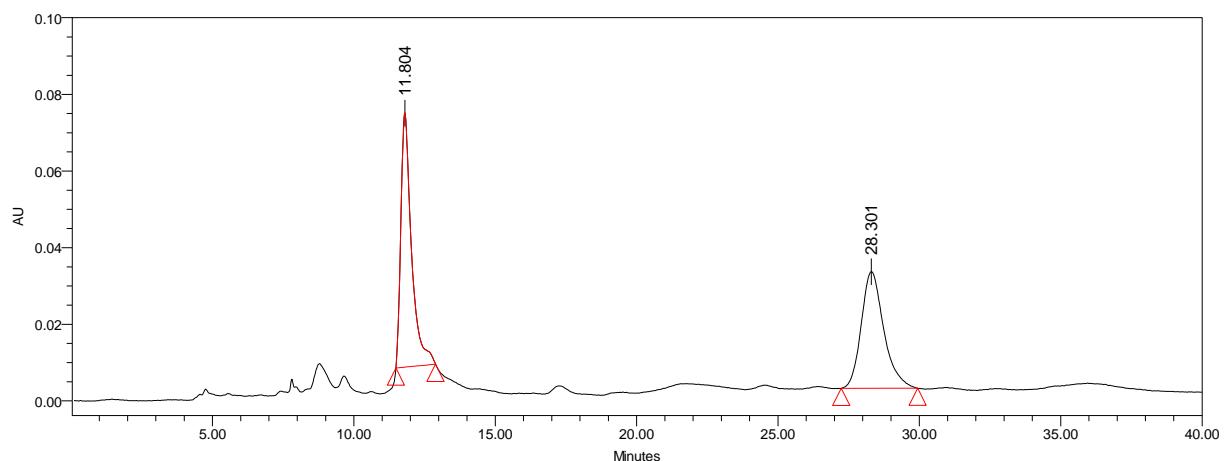
Retention Time	% Area	Start Time	End Time
7.406	51.24	7.383	8.867
12.634	48.76	10.333	13.200



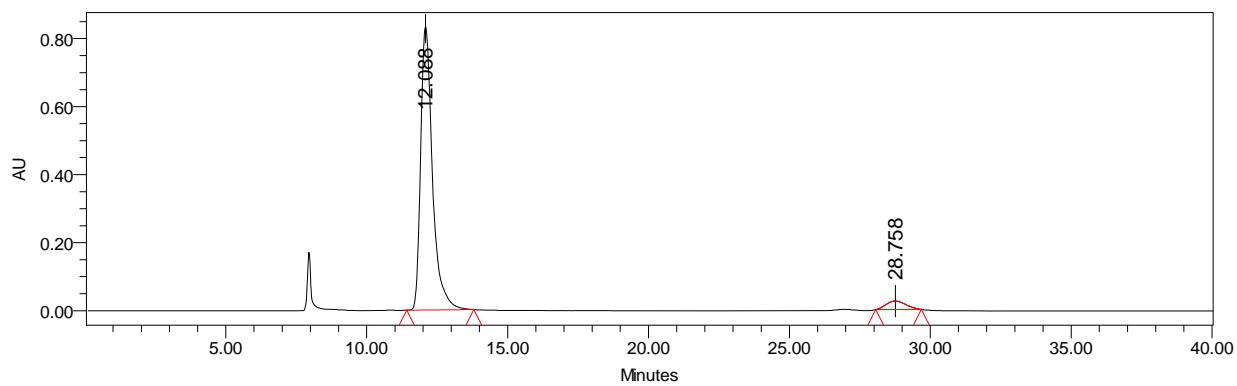
Retention Time	Area%	Start Time	End Time
7.876	85.75	7.445	9.645
13.389	14.25	12.995	13.962



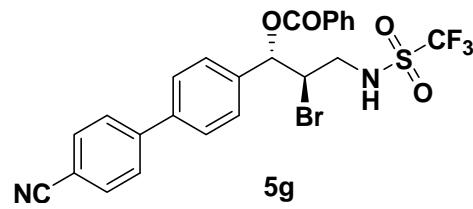
HPLC (Chiralcel AD-H; eluent: hexane/2-propanol = 90/10; flow rate: 0.7 mL/min; detection: at 250 nm): retention times $t_1 = 11.8$ min $t_2 = 28.3$ min;



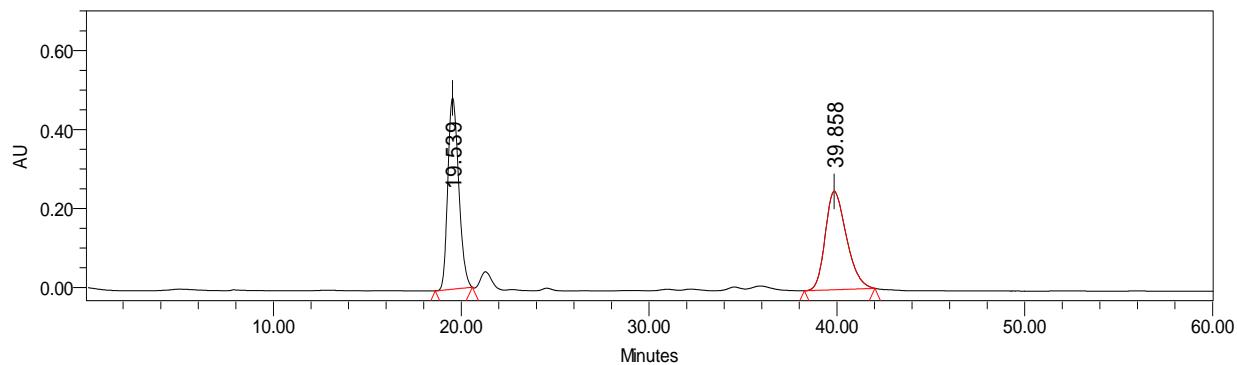
Retention Time	Area	Area%	Height
11.804	1736181	50.84	66341
28.301	1678740	49.16	30442



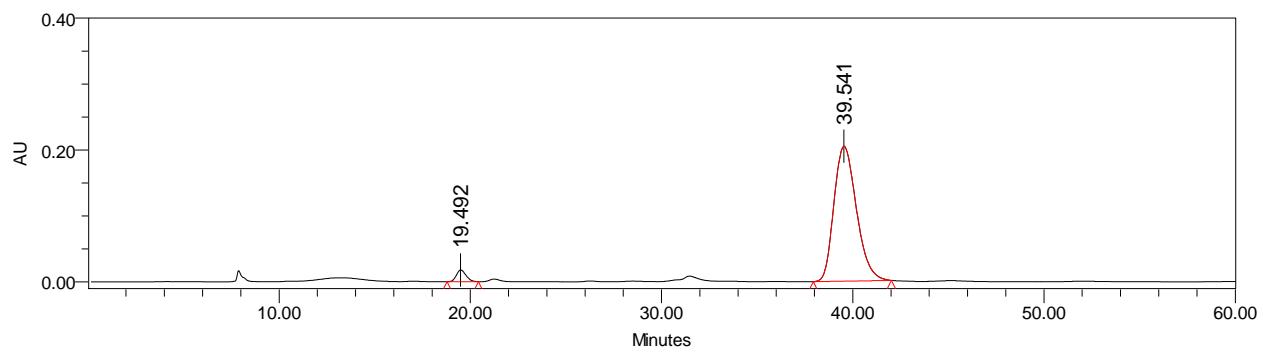
Retention Time	Area	Area%	Height
12.088	24166656	95.18	832897
28.758	1224103	4.82	25003



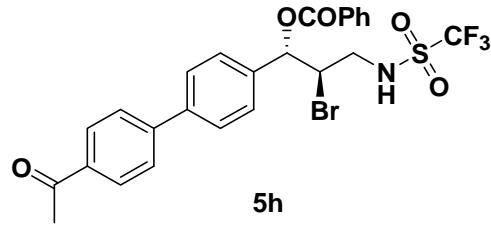
HPLC (Chiralcel AD-H; eluent: hexane/2-propanol = 90/10; flow rate: 0.7 mL/min; detection: at 270 nm): retention times $t_1 = 19.5$ min $t_2 = 39.9$ min;



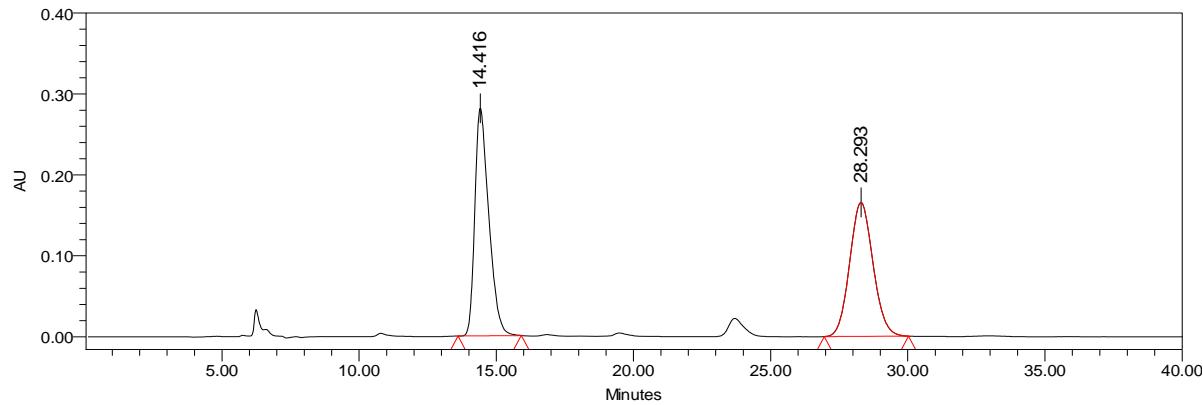
Retention Time	Area	Area%	Height
19.539	19641042	50.05	484426
39.858	19598872	49.95	249503



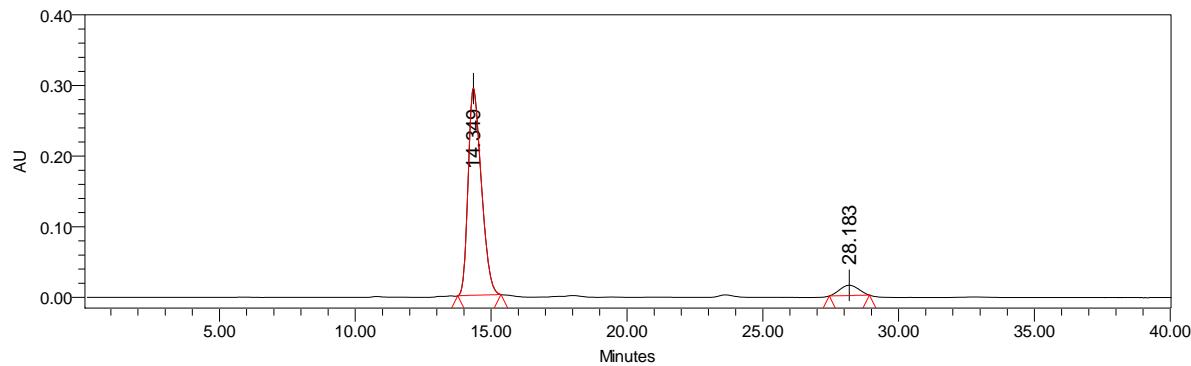
Retention Time	Area	Area%	Height
19.492	620915	3.58	17866
39.541	16715053	96.42	204585



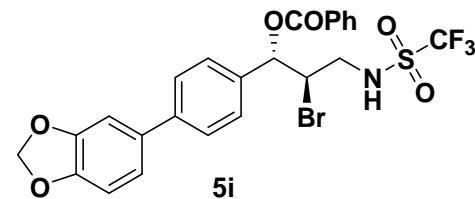
HPLC (Chiralcel AD-H; eluent: hexane/2-propanol = 80/20; flow rate: 0.7 mL/min; detection: at 280 nm): retention times $t_1 = 14.4$ min $t_2 = 28.3$ min;



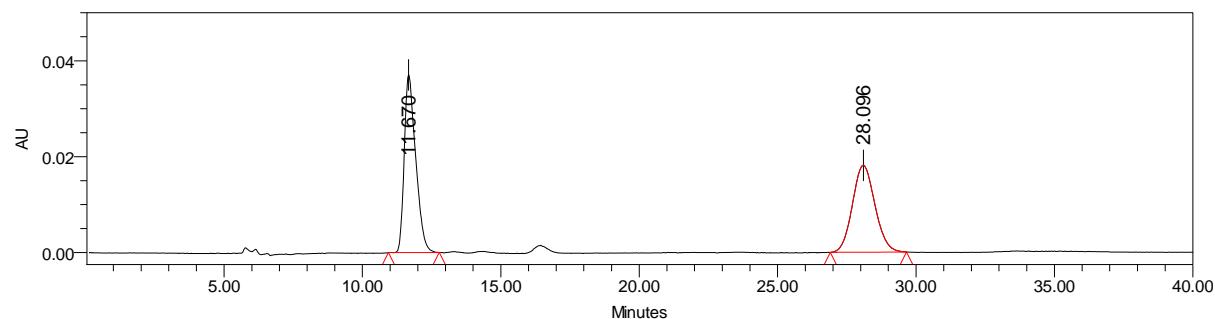
Retention Time	Area	Area%	Height
14.416	9933811	50.35	281245
28.293	9795204	49.65	165459



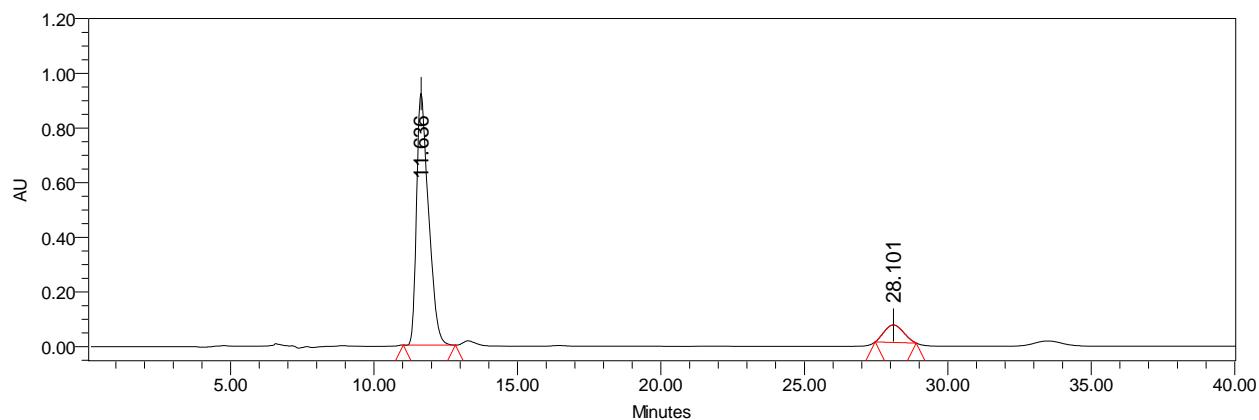
Retention Time	Area	Area%	Height
14.349	9879958	93.41	293061
28.183	697192	6.59	14570



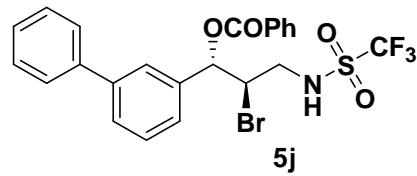
HPLC (Chiralcel AD-H; eluent: hexane/2-propanol = 80/20; flow rate: 0.7 mL/min; detection: at 230 nm): retention times $t_1 = 11.7$ min $t_2 = 28.1$ min;



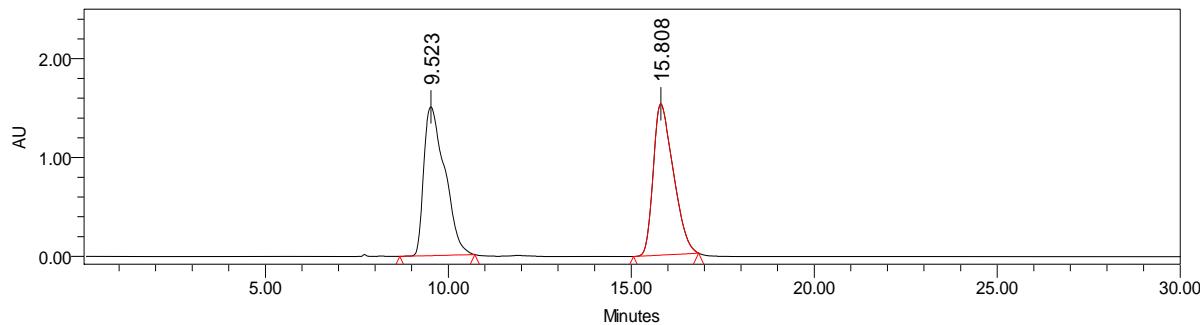
Retention Time	Area	Area%	Height
11.670	1062075	50.97	37068
28.096	1021530	49.03	18111



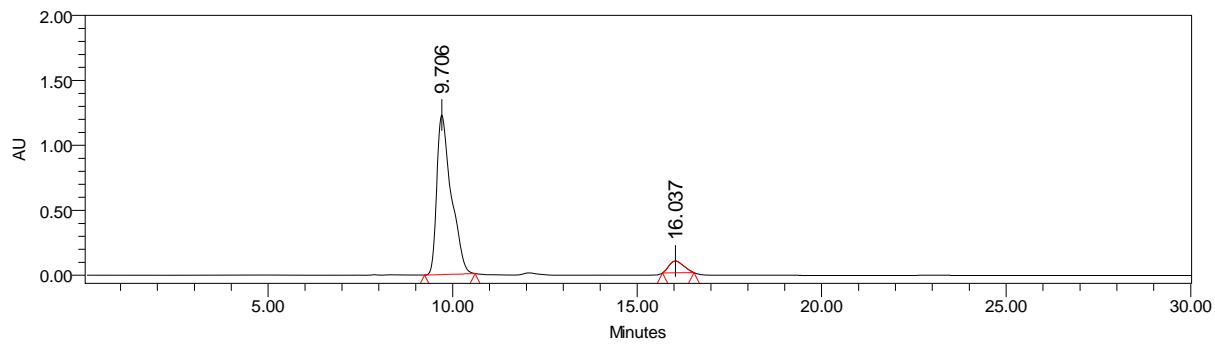
Retention Time	Area	Area%	Height
11.636	26557029	89.94	920492
28.101	2970763	10.06	64071



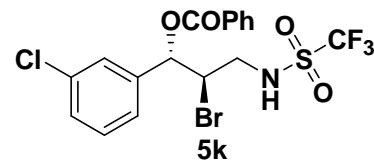
HPLC (Chiralcel AD-H; eluent: hexane/2-propanol = 90/10; flow rate: 0.7 mL/min; detection: at 235 nm): retention times $t_1 = 9.5$ min $t_2 = 15.8$ min;



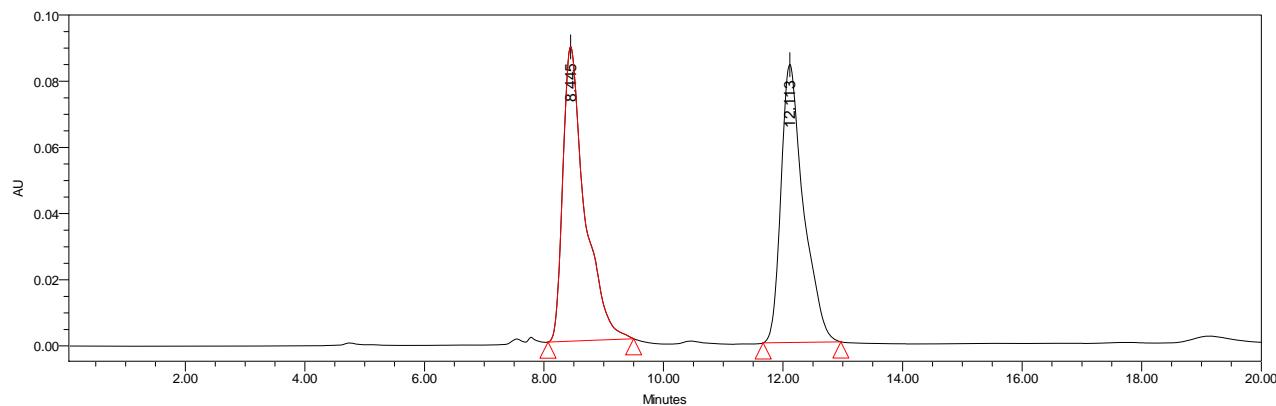
Retention Time	Area	Area%	Height
9.523	59873217	50.67	1504066
15.808	58298128	49.33	1529292



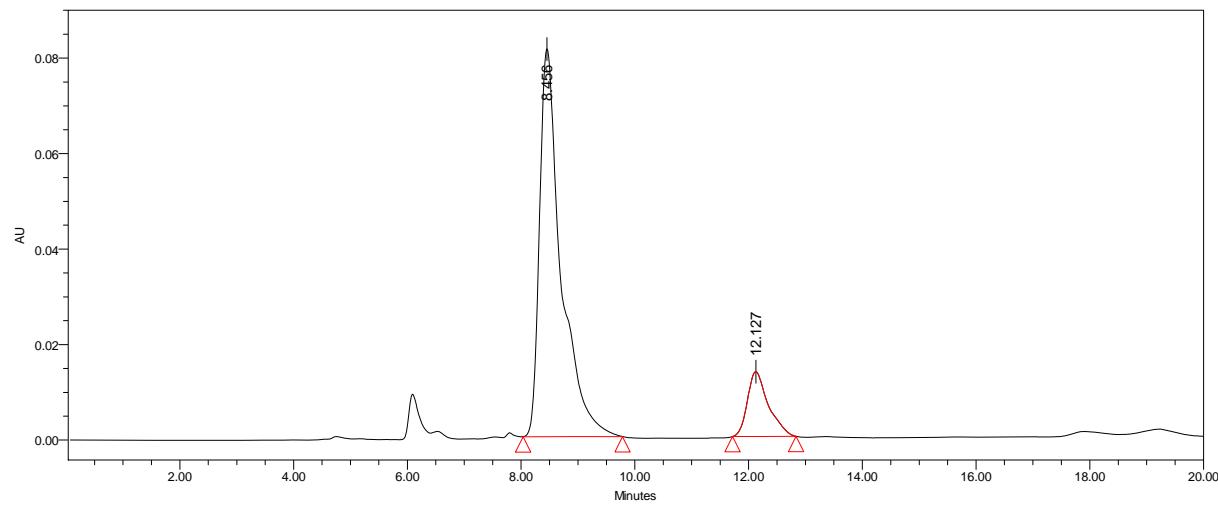
Retention Time	Area	Area%	Height
9.706	33368001	93.09	1227280
16.037	2475852	6.91	91247



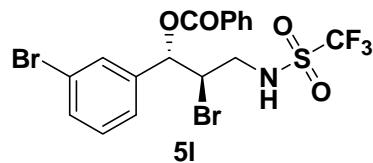
HPLC (Chiralcel AD-H; eluent: hexane/2-propanol = 90/10; flow rate: 0.7 mL/min; detection: at 220 nm): retention times $t_1 = 8.4$ min $t_2 = 12.1$ min;



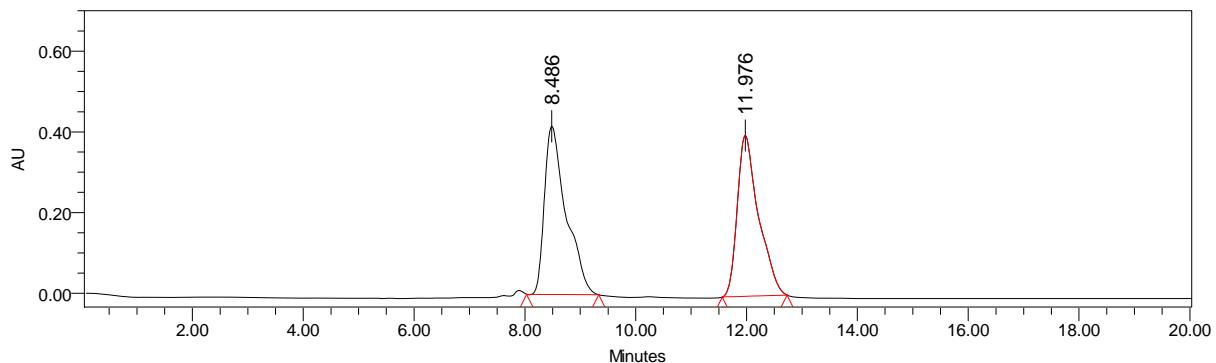
Retention Time	Area	% Area	Height
8.445	2265427	50.81	89030
12.113	2192798	49.19	84059



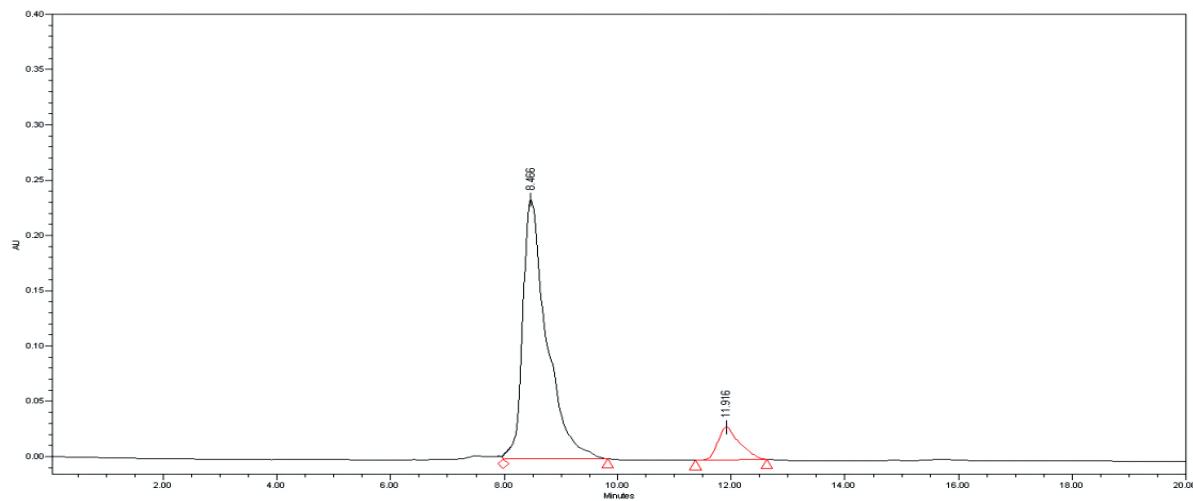
Retention Time	Area	% Area	Height
8.456	1995939	86.61	78234
12.127	308475	13.39	12710



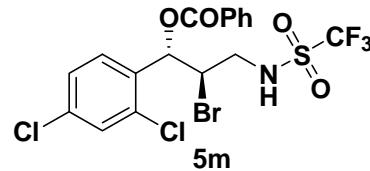
HPLC (Chiralcel AD-H; eluent: hexane/2-propanol = 90/10; flow rate: 0.7 mL/min; detection: at 225 nm): retention times $t_1 = 8.5$ min $t_2 = 11.9$ min;



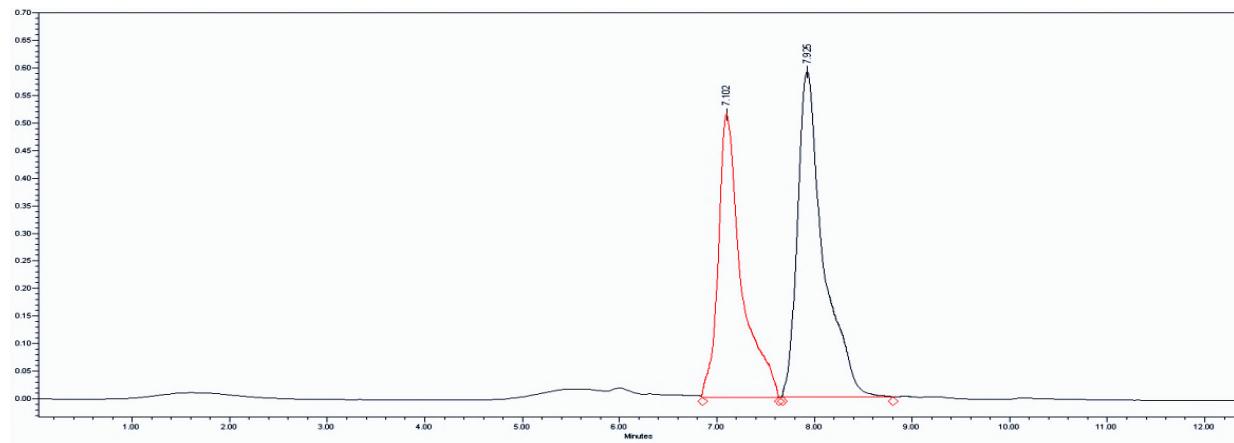
Retention Time	Area	Area%	Height
8.486	11299618	51.59	417013
11.976	10604837	48.41	398766



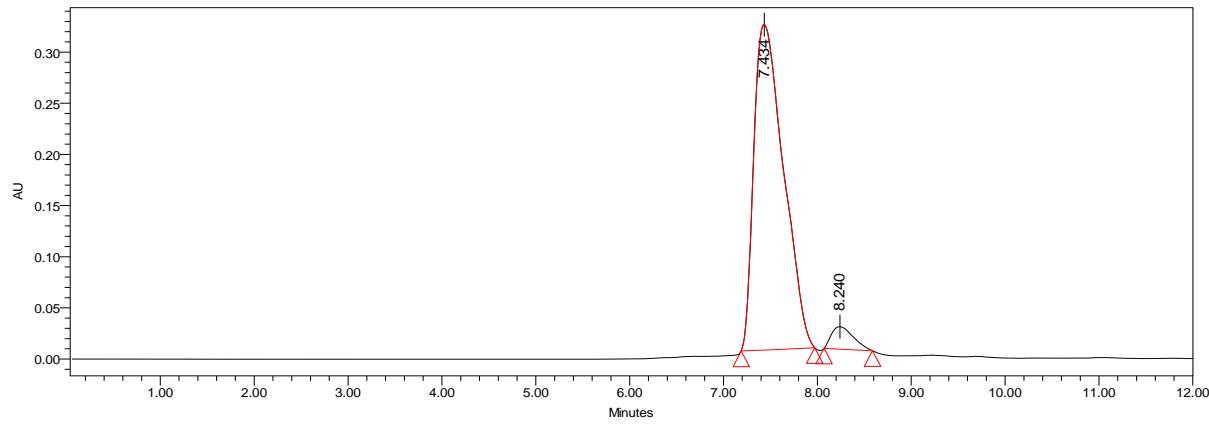
Retention Time	Area	% Area	Height
8.466	6420251	90.56	209880
11.916	669233	9.44	26058



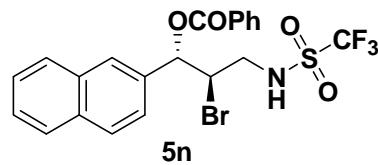
HPLC (Chiralpak- IC; eluent: hexane/2-propanol = 90/10; flow rate: 0.6 mL/min; detection: at 230 nm): retention times $t_1 = 7.1$ min $t_2 = 7.9$ min;



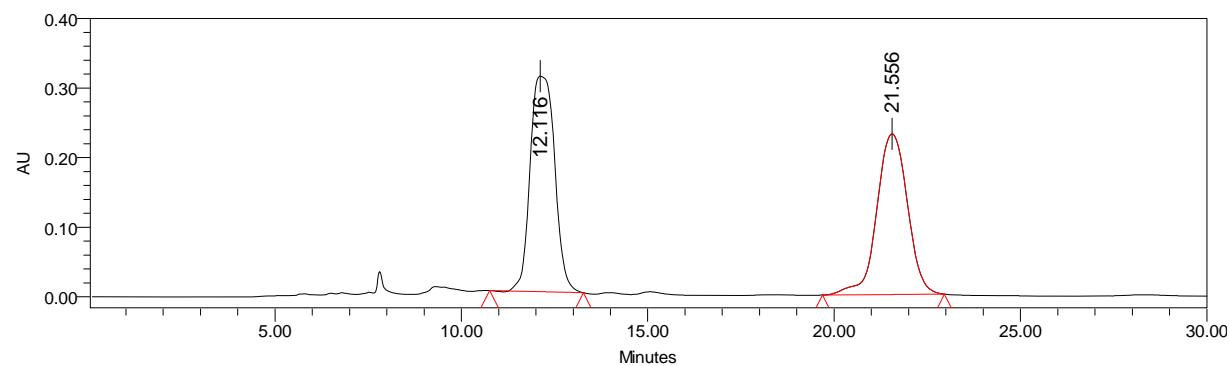
Retention Time	Area	% Area	Height
7.120	2993039	48.20	186809
7.944	3216073	51.80	205086



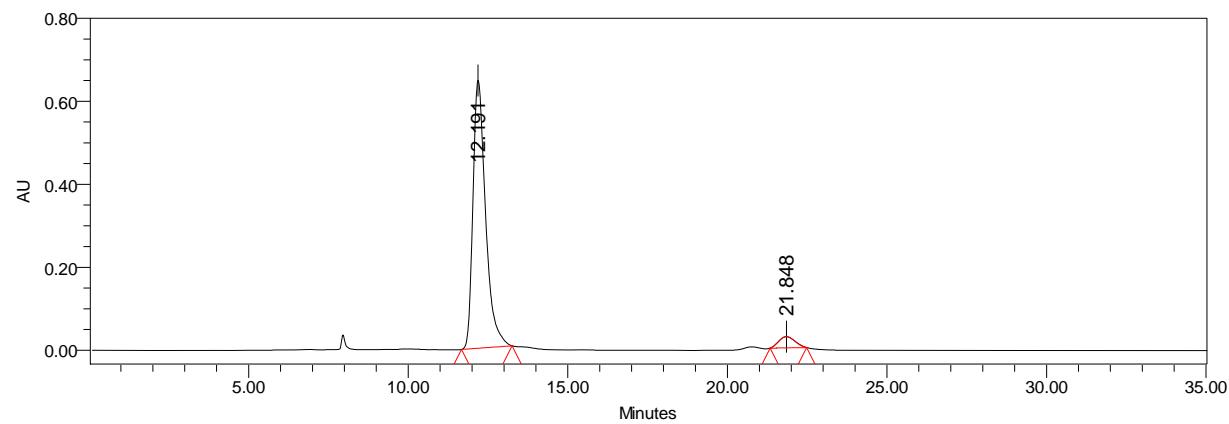
Retention Time	Area	Area%	Height
7.449	31224009	91.69	1270702
8.257	2831021	8.31	145042



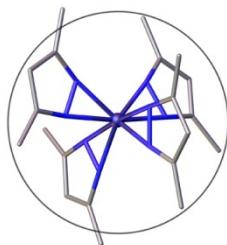
HPLC (Chiralcel AD-H; eluent: hexane/2-propanol = 90/10; flow rate: 0.7 mL/min; detection: at 220 nm): retention times $t_1 = 12.1$ min $t_2 = 21.6$ min;



Retention Time	Area	Area%	Height
12.116	14205976	51.76	309857
21.556	13242498	48.24	230914



Retention Time	Area	Area%	Height
12.191	17678656	94.85	645704
21.848	960797	5.15	27261



MOLECULAR STRUCTURE LABORATORY

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Structural report on compound 5i

Crystallographic Experimental Section

Data Collection

A colorless crystal with approximate dimensions $0.55 \times 0.18 \times 0.13 \text{ mm}^3$ was selected under oil under ambient conditions and attached to the tip of a MiTeGen MicroMount©. The crystal was mounted in a stream of cold nitrogen at 100(1) K and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker SMART APEXII diffractometer with Cu K α ($\lambda = 1.54178 \text{ \AA}$) radiation and the diffractometer to crystal distance of 4.03 cm.

The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 41 frames collected at intervals of 0.6° in a 25° range about ω with the exposure time of 10 seconds per frame. The reflections were successfully indexed by an automated indexing routine built in the APEXII program. The final cell constants were calculated from a set of 9300 strong reflections from the actual data collection.

The data were collected by using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.82 \AA . A total of 22391 data were harvested by collecting 19 sets of frames with 0.7° scans in ω and ϕ with an exposure time 3/6 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements. [1]

Structure Solution and Refinement

The systematic absences in the diffraction data were consistent for the space groups $P2_1$ and $P2_1/m$. The E -statistics strongly suggested the non-centrosymmetric space group $P2_1$ that yielded chemically reasonable and computationally stable results of refinement [2-4].

A successful solution by the direct methods provided most non-hydrogen atoms from the E -map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

Atom Br1 is disordered over two positions with the major component being present 78.1(8)% of the time. Atoms C22-C24 and O6 are disordered over two positions with the major components being present

65.3(10)% of the time. The disordered parts were refined with constraints and restraints.

The final least-squares refinement of 410 parameters against 5359 data resulted in residuals R (based on F^2 for $I \geq 2\sigma$) and wR (based on F^2 for all data) of 0.0258 and 0.0646, respectively. The final difference Fourier map was featureless.

The molecular diagram is drawn with 50% probability ellipsoids.

References

- [1] Bruker-AXS. (2007-2011) APEX2, SADABS, and SAINT Software Reference Manuals. Bruker-AXS, Madison, Wisconsin, USA.
- [2] Sheldrick, G. M. (2008) SHELXL. *Acta Cryst. A* **64**, 112-122.
- [3] Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. "OLEX2: a complete structure solution, refinement and analysis program". *J. Appl. Cryst.* (2009) **42**, 339-341.
- [4] Guzei, I.A. (2006-2012). Internal laboratory computer programs "G1,2,3", "ResIns", "FCF_filter", "Modicifer".

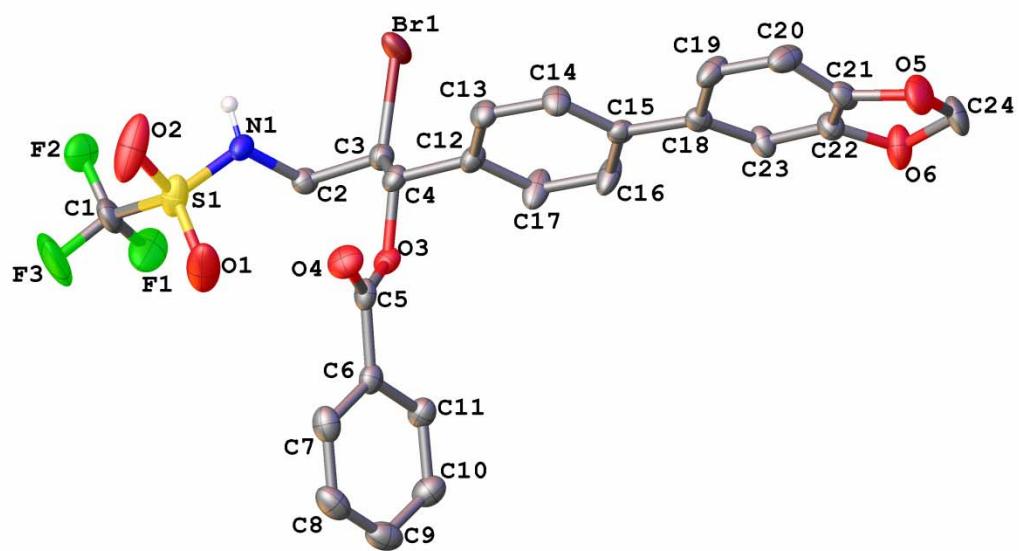


Figure 1. A molecular drawing of **5i**. The minor disorder components, solvent molecule, and H atoms are omitted.

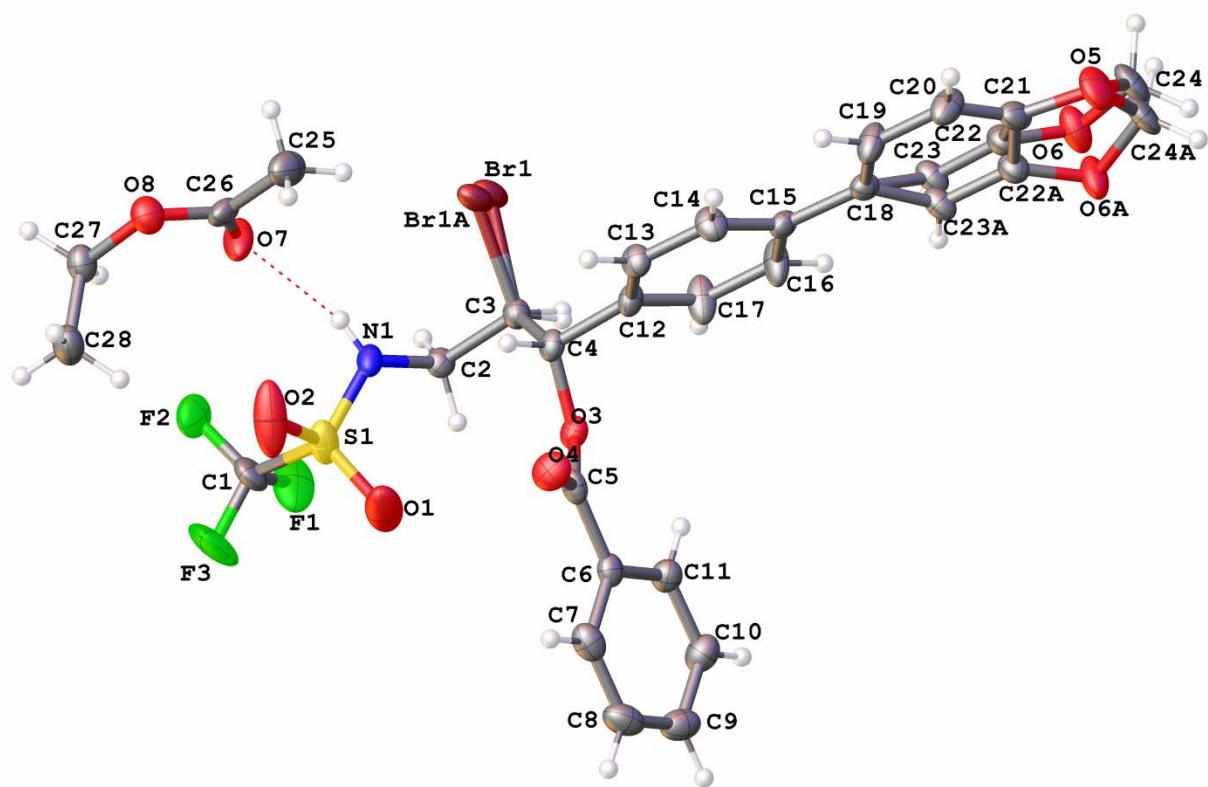


Figure 2. A molecular drawing of **5i**. The content of the asymmetric unit. All disorder components are shown.

Table 1. Crystal data and structure refinement for **5i**.

Identification code	5i
Empirical formula	C ₂₈ H ₂₇ BrF ₃ N O ₈ S
Formula weight	674.48
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	P2 ₁
Unit cell dimensions	a = 11.663(4) Å b = 5.822(2) Å c = 21.566(8) Å
Volume	1438.0(9) Å ³
Z	2
Density (calculated)	1.558 Mg/m ³
Absorption coefficient	3.255 mm ⁻¹
F(000)	688
Crystal size	0.55 x 0.18 x 0.13 mm ³
Theta range for data collection	2.09 to 72.19°.
Index ranges	-14<=h<=14, -7<=k<=7, -26<=l<=24
Reflections collected	22391
Independent reflections	5359 [R(int) = 0.0200]
Completeness to theta = 67.00°	99.4 %
Absorption correction	Numerical with SADABS
Max. and min. transmission	0.6714 and 0.2667
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5359 / 6 / 410
Goodness-of-fit on F ²	1.070
Final R indices [I>2sigma(I)]	R1 = 0.0258, wR2 = 0.0645
R indices (all data)	R1 = 0.0260, wR2 = 0.0646
Absolute structure parameter	0.006(11)
Extinction coefficient	0.00050(12)
Largest diff. peak and hole	0.375 and -0.332 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

for **5i**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij}^{eq} tensor.

	x	y	z	U(eq)
Br(1)	6361(1)	3808(2)	6694(1)	33(1)
Br(1A)	6241(3)	4480(7)	6700(1)	33(1)
S(1)	5855(1)	7824(2)	8568(1)	36(1)
F(1)	5474(2)	4302(5)	9247(1)	66(1)
F(2)	3927(1)	6029(4)	8785(1)	44(1)
F(3)	4983(2)	7558(6)	9590(1)	100(1)
O(1)	7000(2)	8033(5)	8934(1)	64(1)
O(2)	5160(2)	9766(4)	8337(2)	73(1)
O(3)	8908(1)	6279(3)	8120(1)	23(1)
O(4)	9074(2)	10139(4)	8133(1)	35(1)
O(5)	13677(2)	5679(4)	4514(1)	44(1)
O(6)	13984(4)	3256(8)	5396(2)	40(1)
O(6A)	13438(9)	2575(11)	5127(5)	42(2)
N(1)	5885(2)	6145(4)	8001(1)	27(1)
C(1)	4998(2)	6348(6)	9082(1)	39(1)
C(2)	6684(2)	4194(4)	8038(1)	23(1)
C(3)	7389(2)	4223(4)	7512(1)	24(1)
C(4)	8149(2)	6349(4)	7500(1)	23(1)
C(5)	9340(2)	8287(4)	8362(1)	23(1)
C(6)	10233(2)	7923(4)	8949(1)	24(1)
C(7)	10463(2)	9685(4)	9391(1)	32(1)
C(8)	11315(2)	9393(5)	9929(1)	38(1)
C(9)	11942(2)	7369(5)	10025(1)	36(1)
C(10)	11722(2)	5611(5)	9587(1)	34(1)
C(11)	10857(2)	5870(5)	9052(1)	28(1)
C(12)	8905(2)	6275(4)	7004(1)	24(1)
C(13)	8870(2)	7969(5)	6556(1)	26(1)
C(14)	9626(2)	7923(5)	6129(1)	29(1)
C(15)	10439(2)	6170(4)	6134(1)	22(1)
C(16)	10451(2)	4439(5)	6583(1)	37(1)
C(17)	9701(2)	4493(5)	7009(1)	39(1)
C(18)	11273(2)	6123(4)	5688(1)	23(1)
C(19)	11222(2)	7728(5)	5212(1)	35(1)
C(20)	11991(2)	7718(6)	4782(1)	36(1)
C(21)	12808(2)	6052(5)	4854(1)	30(1)
C(22)	12927(7)	4591(16)	5358(4)	40(2)
C(22A)	12804(13)	4160(40)	5277(9)	40(2)
C(23)	12230(4)	4557(9)	5795(3)	28(1)

C(23A)	11955(9)	4131(14)	5651(6)	28(1)
C(24)	14293(5)	3661(9)	4795(2)	40(1)
C(24A)	13952(10)	3278(10)	4606(5)	40(1)
O(7)	3569(2)	6667(5)	7307(1)	48(1)
O(8)	2472(1)	9808(4)	7042(1)	34(1)
C(25)	3957(2)	9095(7)	6471(1)	46(1)
C(26)	3335(2)	8370(5)	6987(1)	34(1)
C(27)	1874(2)	9458(5)	7570(1)	32(1)
C(28)	2261(2)	11256(5)	8062(1)	41(1)

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Table 3. Bond lengths [\AA] and angles [$^\circ$] for **5i**.

Br(1)-C(3)	1.950(2)	C(12)-C(13)	1.376(3)
Br(1A)-C(3)	1.998(4)	C(12)-C(17)	1.391(3)
S(1)-O(1)	1.422(2)	C(13)-C(14)	1.389(3)
S(1)-O(2)	1.425(2)	C(13)-H(13)	0.9500
S(1)-N(1)	1.572(2)	C(14)-C(15)	1.392(3)
S(1)-C(1)	1.839(3)	C(14)-H(14)	0.9500
F(1)-C(1)	1.334(4)	C(15)-C(16)	1.395(3)
F(2)-C(1)	1.305(3)	C(15)-C(18)	1.492(3)
F(3)-C(1)	1.306(3)	C(16)-C(17)	1.385(3)
O(3)-C(5)	1.339(3)	C(16)-H(16)	0.9500
O(3)-C(4)	1.457(3)	C(17)-H(17)	0.9500
O(4)-C(5)	1.201(3)	C(18)-C(19)	1.382(3)
O(5)-C(21)	1.377(3)	C(18)-C(23A)	1.417(5)
O(5)-C(24A)	1.439(5)	C(18)-C(23)	1.426(4)
O(5)-C(24)	1.448(4)	C(19)-C(20)	1.407(3)
O(6)-C(24)	1.430(4)	C(19)-H(19)	0.9500
O(6)-C(22)	1.446(6)	C(20)-C(21)	1.347(4)
O(6A)-C(22A)	1.262(15)	C(20)-H(20)	0.9500
O(6A)-C(24A)	1.428(5)	C(21)-C(22)	1.366(9)
N(1)-C(2)	1.461(3)	C(21)-C(22A)	1.43(2)
N(1)-H(1)	0.80(3)	C(22)-C(23)	1.357(12)
C(2)-C(3)	1.523(3)	C(22A)-C(23A)	1.39(2)
C(2)-H(2A)	0.9900	C(23)-H(23)	0.9500
C(2)-H(2B)	0.9900	C(23A)-H(23A)	0.9500
C(3)-C(4)	1.526(3)	C(24)-H(24A)	0.9900
C(3)-H(3A)	1.0000	C(24)-H(24B)	0.9900
C(3)-H(3B)	1.0000	C(24A)-H(24C)	0.9900
C(4)-C(12)	1.510(3)	C(24A)-H(24D)	0.9900
C(4)-H(4)	1.0000	O(7)-C(26)	1.210(3)
C(5)-C(6)	1.496(3)	O(8)-C(26)	1.332(3)
C(6)-C(7)	1.391(3)	O(8)-C(27)	1.458(3)
C(6)-C(11)	1.395(3)	C(25)-C(26)	1.499(3)
C(7)-C(8)	1.389(4)	C(25)-H(25A)	0.9800
C(7)-H(7)	0.9500	C(25)-H(25B)	0.9800
C(8)-C(9)	1.381(4)	C(25)-H(25C)	0.9800
C(8)-H(8)	0.9500	C(27)-C(28)	1.498(4)
C(9)-C(10)	1.383(4)	C(27)-H(27A)	0.9900
C(9)-H(9)	0.9500	C(27)-H(27B)	0.9900
C(10)-C(11)	1.389(3)	C(28)-H(28A)	0.9800
C(10)-H(10)	0.9500	C(28)-H(28B)	0.9800
C(11)-H(11)	0.9500	C(28)-H(28C)	0.9800
O(1)-S(1)-O(2)		O(2)-S(1)-N(1)	108.47(15)
O(1)-S(1)-N(1)		O(1)-S(1)-C(1)	105.43(14)

O(2)-S(1)-C(1)	104.09(13)	O(3)-C(5)-C(6)	110.89(16)
N(1)-S(1)-C(1)	105.86(12)	C(7)-C(6)-C(11)	119.7(2)
C(5)-O(3)-C(4)	116.80(16)	C(7)-C(6)-C(5)	119.3(2)
C(21)-O(5)-C(24A)	104.3(3)	C(11)-C(6)-C(5)	121.0(2)
C(21)-O(5)-C(24)	105.2(2)	C(8)-C(7)-C(6)	119.8(2)
C(24A)-O(5)-C(24)	22.3(4)	C(8)-C(7)-H(7)	120.1
C(24)-O(6)-C(22)	102.6(4)	C(6)-C(7)-H(7)	120.1
C(22A)-O(6A)-C(24A)	110.3(10)	C(9)-C(8)-C(7)	120.3(2)
C(2)-N(1)-S(1)	123.27(15)	C(9)-C(8)-H(8)	119.9
C(2)-N(1)-H(1)	120(2)	C(7)-C(8)-H(8)	119.9
S(1)-N(1)-H(1)	112(2)	C(8)-C(9)-C(10)	120.3(2)
F(2)-C(1)-F(3)	109.0(2)	C(8)-C(9)-H(9)	119.8
F(2)-C(1)-F(1)	108.4(2)	C(10)-C(9)-H(9)	119.8
F(3)-C(1)-F(1)	109.2(3)	C(9)-C(10)-C(11)	119.9(2)
F(2)-C(1)-S(1)	110.42(17)	C(9)-C(10)-H(10)	120.1
F(3)-C(1)-S(1)	110.4(2)	C(11)-C(10)-H(10)	120.1
F(1)-C(1)-S(1)	109.41(17)	C(10)-C(11)-C(6)	120.0(2)
N(1)-C(2)-C(3)	112.23(17)	C(10)-C(11)-H(11)	120.0
N(1)-C(2)-H(2A)	109.2	C(6)-C(11)-H(11)	120.0
C(3)-C(2)-H(2A)	109.2	C(13)-C(12)-C(17)	118.1(2)
N(1)-C(2)-H(2B)	109.2	C(13)-C(12)-C(4)	122.26(19)
C(3)-C(2)-H(2B)	109.2	C(17)-C(12)-C(4)	119.58(19)
H(2A)-C(2)-H(2B)	107.9	C(12)-C(13)-C(14)	120.9(2)
C(2)-C(3)-C(4)	114.72(18)	C(12)-C(13)-H(13)	119.6
C(2)-C(3)-Br(1)	110.26(13)	C(14)-C(13)-H(13)	119.6
C(4)-C(3)-Br(1)	110.25(15)	C(13)-C(14)-C(15)	121.7(2)
C(2)-C(3)-Br(1A)	106.70(16)	C(13)-C(14)-H(14)	119.1
C(4)-C(3)-Br(1A)	102.74(18)	C(15)-C(14)-H(14)	119.1
Br(1)-C(3)-Br(1A)	12.03(9)	C(14)-C(15)-C(16)	116.92(19)
C(2)-C(3)-H(3A)	107.1	C(14)-C(15)-C(18)	122.32(19)
C(4)-C(3)-H(3A)	107.1	C(16)-C(15)-C(18)	120.76(19)
Br(1)-C(3)-H(3A)	107.1	C(17)-C(16)-C(15)	121.3(2)
Br(1A)-C(3)-H(3A)	118.9	C(17)-C(16)-H(16)	119.4
C(2)-C(3)-H(3B)	110.8	C(15)-C(16)-H(16)	119.4
C(4)-C(3)-H(3B)	110.8	C(16)-C(17)-C(12)	121.1(2)
Br(1)-C(3)-H(3B)	99.0	C(16)-C(17)-H(17)	119.5
Br(1A)-C(3)-H(3B)	110.8	C(12)-C(17)-H(17)	119.5
H(3A)-C(3)-H(3B)	8.1	C(19)-C(18)-C(23A)	117.2(6)
O(3)-C(4)-C(12)	108.33(16)	C(19)-C(18)-C(23)	118.4(3)
O(3)-C(4)-C(3)	102.52(16)	C(23A)-C(18)-C(23)	19.1(4)
C(12)-C(4)-C(3)	114.04(18)	C(19)-C(18)-C(15)	121.7(2)
O(3)-C(4)-H(4)	110.6	C(23A)-C(18)-C(15)	119.5(6)
C(12)-C(4)-H(4)	110.6	C(23)-C(18)-C(15)	119.5(3)
C(3)-C(4)-H(4)	110.6	C(18)-C(19)-C(20)	122.9(2)
O(4)-C(5)-O(3)	125.1(2)	C(18)-C(19)-H(19)	118.5
O(4)-C(5)-C(6)	123.94(19)	C(20)-C(19)-H(19)	118.5

C(21)-C(20)-C(19)	116.9(2)	O(6A)-C(24A)-H(24C)	110.6
C(21)-C(20)-H(20)	121.6	O(5)-C(24A)-H(24C)	110.6
C(19)-C(20)-H(20)	121.6	O(6A)-C(24A)-H(24D)	110.6
C(20)-C(21)-C(22)	120.2(3)	O(5)-C(24A)-H(24D)	110.6
C(20)-C(21)-O(5)	128.9(2)	H(24C)-C(24A)-H(24D)	108.7
C(22)-C(21)-O(5)	110.5(3)	C(26)-O(8)-C(27)	117.60(18)
C(20)-C(21)-C(22A)	122.7(4)	C(26)-C(25)-H(25A)	109.5
C(22)-C(21)-C(22A)	13.1(14)	C(26)-C(25)-H(25B)	109.5
O(5)-C(21)-C(22A)	108.0(4)	H(25A)-C(25)-H(25B)	109.5
C(23)-C(22)-C(21)	125.3(4)	C(26)-C(25)-H(25C)	109.5
C(23)-C(22)-O(6)	124.7(7)	H(25A)-C(25)-H(25C)	109.5
C(21)-C(22)-O(6)	109.7(5)	H(25B)-C(25)-H(25C)	109.5
O(6A)-C(22A)-C(23A)	131(2)	O(7)-C(26)-O(8)	123.8(2)
O(6A)-C(22A)-C(21)	109.0(11)	O(7)-C(26)-C(25)	124.5(2)
C(23A)-C(22A)-C(21)	117.8(9)	O(8)-C(26)-C(25)	111.7(2)
C(22)-C(23)-C(18)	115.6(6)	O(8)-C(27)-C(28)	109.30(19)
C(22)-C(23)-H(23)	122.2	O(8)-C(27)-H(27A)	109.8
C(18)-C(23)-H(23)	122.2	C(28)-C(27)-H(27A)	109.8
C(22A)-C(23A)-C(18)	119.5(14)	O(8)-C(27)-H(27B)	109.8
C(22A)-C(23A)-H(23A)	120.2	C(28)-C(27)-H(27B)	109.8
C(18)-C(23A)-H(23A)	120.2	H(27A)-C(27)-H(27B)	108.3
O(6)-C(24)-O(5)	108.9(3)	C(27)-C(28)-H(28A)	109.5
O(6)-C(24)-H(24A)	109.9	C(27)-C(28)-H(28B)	109.5
O(5)-C(24)-H(24A)	109.9	H(28A)-C(28)-H(28B)	109.5
O(6)-C(24)-H(24B)	109.9	C(27)-C(28)-H(28C)	109.5
O(5)-C(24)-H(24B)	109.9	H(28A)-C(28)-H(28C)	109.5
H(24A)-C(24)-H(24B)	108.3	H(28B)-C(28)-H(28C)	109.5
O(6A)-C(24A)-O(5)	105.8(5)		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **5i**. The anisotropic displacement factor exponent takes the form: $-2\Box^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^{*} b^{*} U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Br(1)	36(1)	41(1)	23(1)	-11(1)	12(1)	-15(1)
Br(1A)	36(1)	41(1)	23(1)	-11(1)	12(1)	-15(1)
S(1)	30(1)	24(1)	58(1)	-10(1)	21(1)	-7(1)
F(1)	63(1)	92(2)	51(1)	44(1)	29(1)	25(1)
F(2)	33(1)	58(1)	46(1)	8(1)	18(1)	-8(1)
F(3)	89(2)	164(3)	57(1)	-65(2)	39(1)	-14(2)
O(1)	39(1)	73(2)	85(2)	-51(1)	20(1)	-21(1)
O(2)	58(1)	22(1)	156(3)	12(1)	66(2)	2(1)
O(3)	20(1)	20(1)	29(1)	6(1)	4(1)	2(1)
O(4)	39(1)	21(1)	43(1)	5(1)	3(1)	3(1)
O(5)	48(1)	57(1)	36(1)	10(1)	27(1)	4(1)
O(6)	39(2)	53(2)	35(2)	14(2)	22(2)	17(2)
O(6A)	48(5)	34(3)	53(5)	-2(3)	32(4)	3(3)
N(1)	21(1)	40(1)	22(1)	9(1)	7(1)	7(1)
C(1)	42(1)	56(2)	25(1)	-6(1)	18(1)	-2(1)
C(2)	23(1)	24(1)	22(1)	5(1)	6(1)	-2(1)
C(3)	23(1)	26(1)	25(1)	2(1)	7(1)	2(1)
C(4)	20(1)	23(1)	28(1)	4(1)	6(1)	4(1)
C(5)	26(1)	17(1)	31(1)	1(1)	14(1)	2(1)
C(6)	23(1)	23(1)	29(1)	3(1)	11(1)	0(1)
C(7)	39(1)	23(1)	38(1)	-2(1)	17(1)	-2(1)
C(8)	48(1)	37(2)	29(1)	-7(1)	10(1)	-12(1)
C(9)	37(1)	43(1)	28(1)	3(1)	2(1)	-13(1)
C(10)	29(1)	30(1)	41(1)	5(1)	3(1)	0(1)
C(11)	26(1)	25(1)	32(1)	-1(1)	6(1)	-1(1)
C(12)	17(1)	26(1)	30(1)	5(1)	6(1)	0(1)
C(13)	27(1)	24(1)	28(1)	5(1)	5(1)	6(1)
C(14)	35(1)	27(1)	26(1)	10(1)	10(1)	6(1)
C(15)	16(1)	26(1)	23(1)	2(1)	2(1)	-3(1)
C(16)	32(1)	38(1)	48(1)	22(1)	22(1)	19(1)
C(17)	38(1)	37(1)	49(1)	27(1)	24(1)	16(1)
C(18)	21(1)	26(1)	22(1)	0(1)	3(1)	-5(1)
C(19)	22(1)	45(1)	40(1)	20(1)	9(1)	8(1)
C(20)	26(1)	53(1)	30(1)	19(1)	5(1)	-1(1)
C(21)	29(1)	39(1)	21(1)	-1(1)	9(1)	-8(1)
C(22)	59(2)	19(4)	50(3)	2(3)	36(2)	4(3)
C(22A)	59(2)	19(4)	50(3)	2(3)	36(2)	4(3)
C(23)	36(3)	22(2)	28(3)	2(2)	14(2)	0(2)
C(23A)	36(3)	22(2)	28(3)	2(2)	14(2)	0(2)
C(24)	53(3)	45(2)	31(2)	-7(2)	27(2)	2(2)
C(24A)	53(3)	45(2)	31(2)	-7(2)	27(2)	2(2)

O(7)	32(1)	80(2)	34(1)	22(1)	10(1)	25(1)
O(8)	35(1)	32(1)	36(1)	4(1)	12(1)	-1(1)
C(25)	32(1)	72(2)	34(1)	0(2)	10(1)	-15(1)
C(26)	19(1)	55(2)	25(1)	0(1)	-1(1)	-5(1)
C(27)	29(1)	30(1)	38(1)	1(1)	14(1)	0(1)
C(28)	32(1)	45(1)	48(2)	-9(1)	15(1)	0(1)

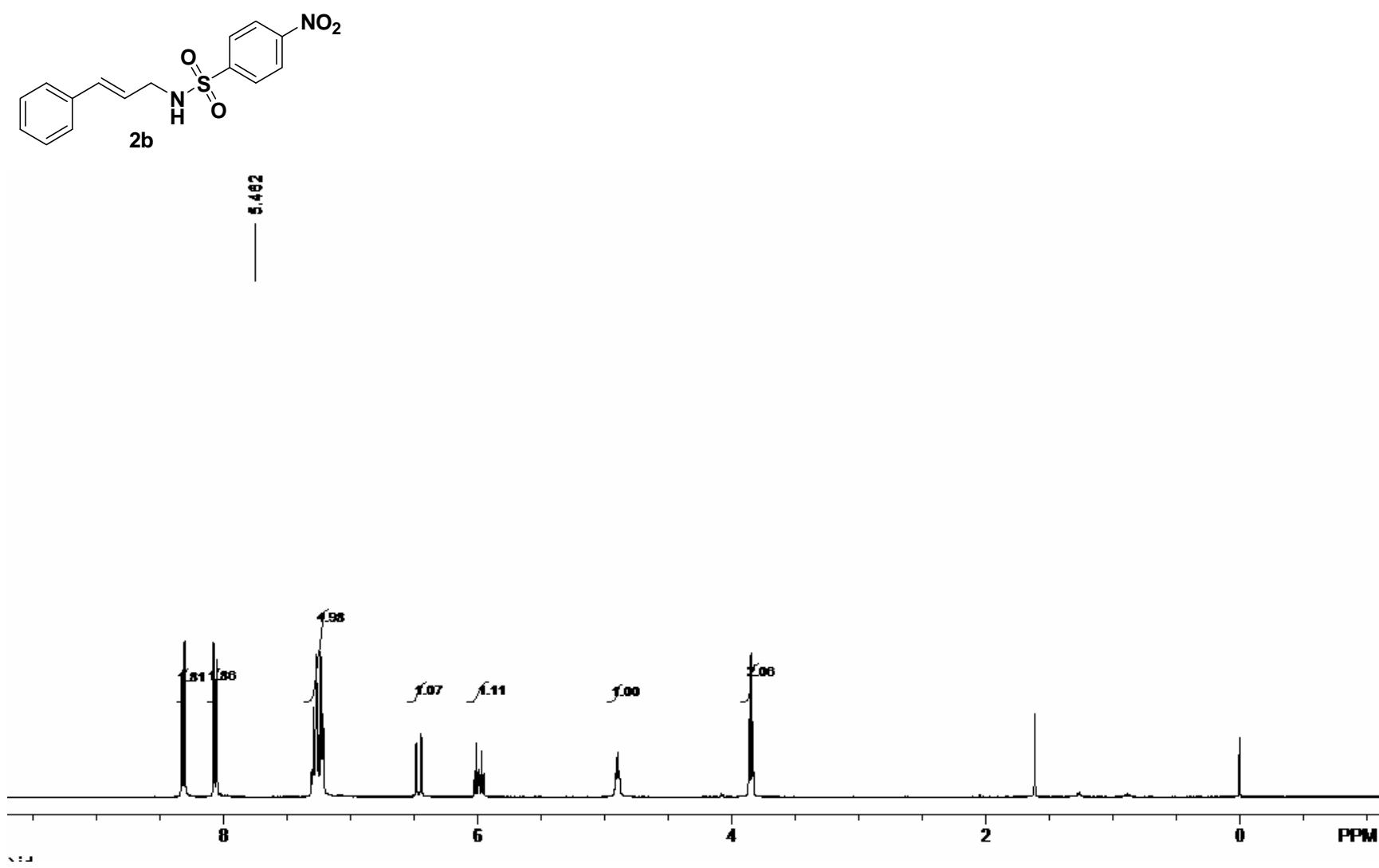
Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **5i**.

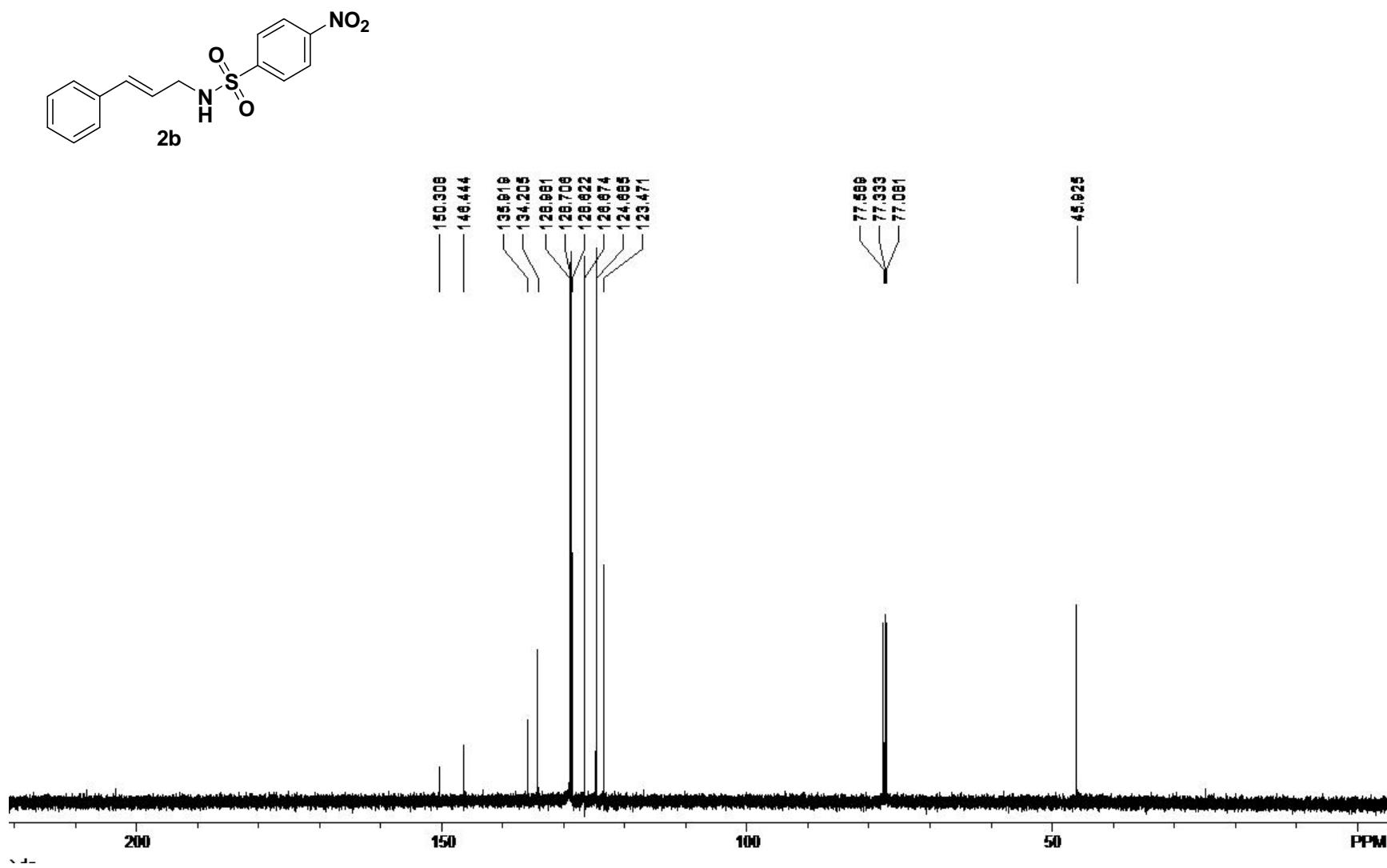
	x	y	z	U(eq)
H(1)	5280(30)	6130(60)	7754(15)	45(9)
H(2A)	6229	2750	8014	28
H(2B)	7225	4223	8451	28
H(3A)	7924	2867	7579	29
H(3B)	7864	2790	7519	29
H(4)	7660	7772	7454	28
H(7)	10039	11084	9324	39
H(8)	11468	10590	10233	45
H(9)	12526	7183	10393	44
H(10)	12162	4230	9651	41
H(11)	10691	4650	8756	33
H(13)	8322	9185	6538	32
H(14)	9586	9119	5826	35
H(16)	10986	3200	6596	45
H(17)	9729	3292	7310	47
H(19)	10642	8892	5173	42
H(20)	11938	8832	4456	44
H(23)	12371	3556	6150	33
H(23A)	11834	2788	5881	33
H(24A)	14078	2314	4517	48
H(24B)	15146	3901	4846	48
H(24C)	13622	2388	4223	48
H(24D)	14808	3045	4703	48
H(25A)	3421	8993	6063	69
H(25B)	4627	8083	6468	69
H(25C)	4229	10682	6544	69
H(27A)	2058	7912	7753	38
H(27B)	1019	9559	7421	38
H(28A)	1824	11085	8405	61
H(28B)	2115	12784	7872	61
H(28C)	3097	11077	8230	61

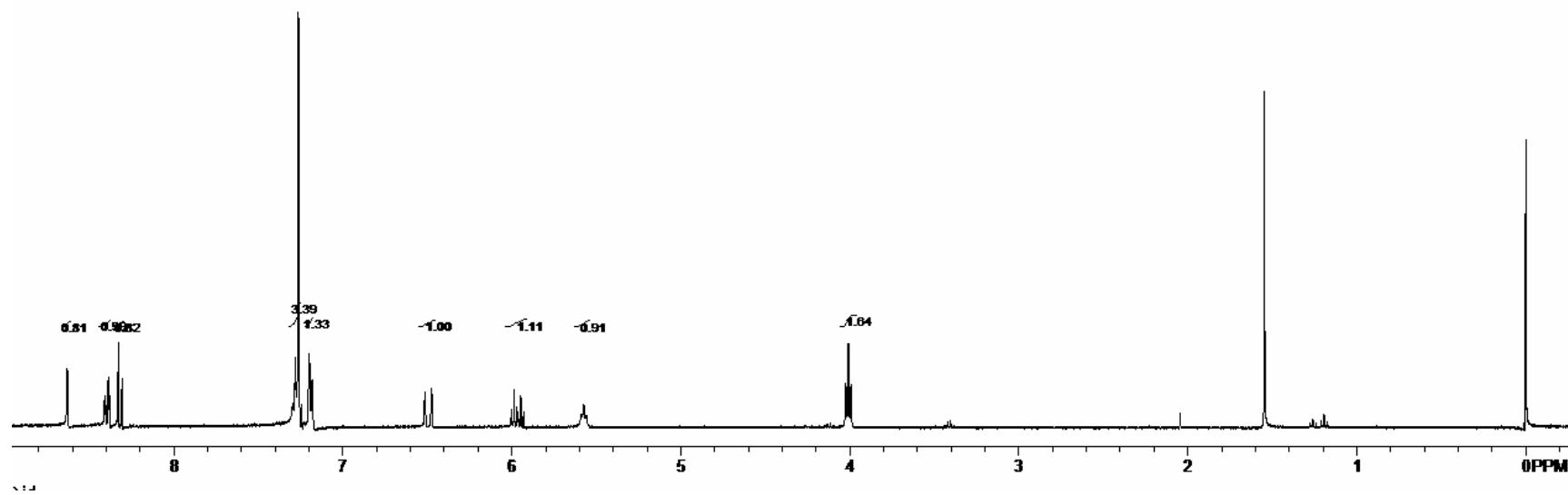
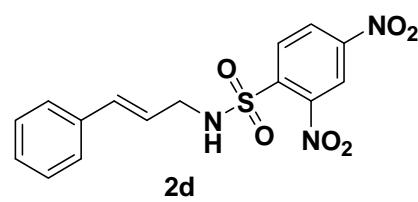
Table 6. Torsion angles [°] for **5i**.

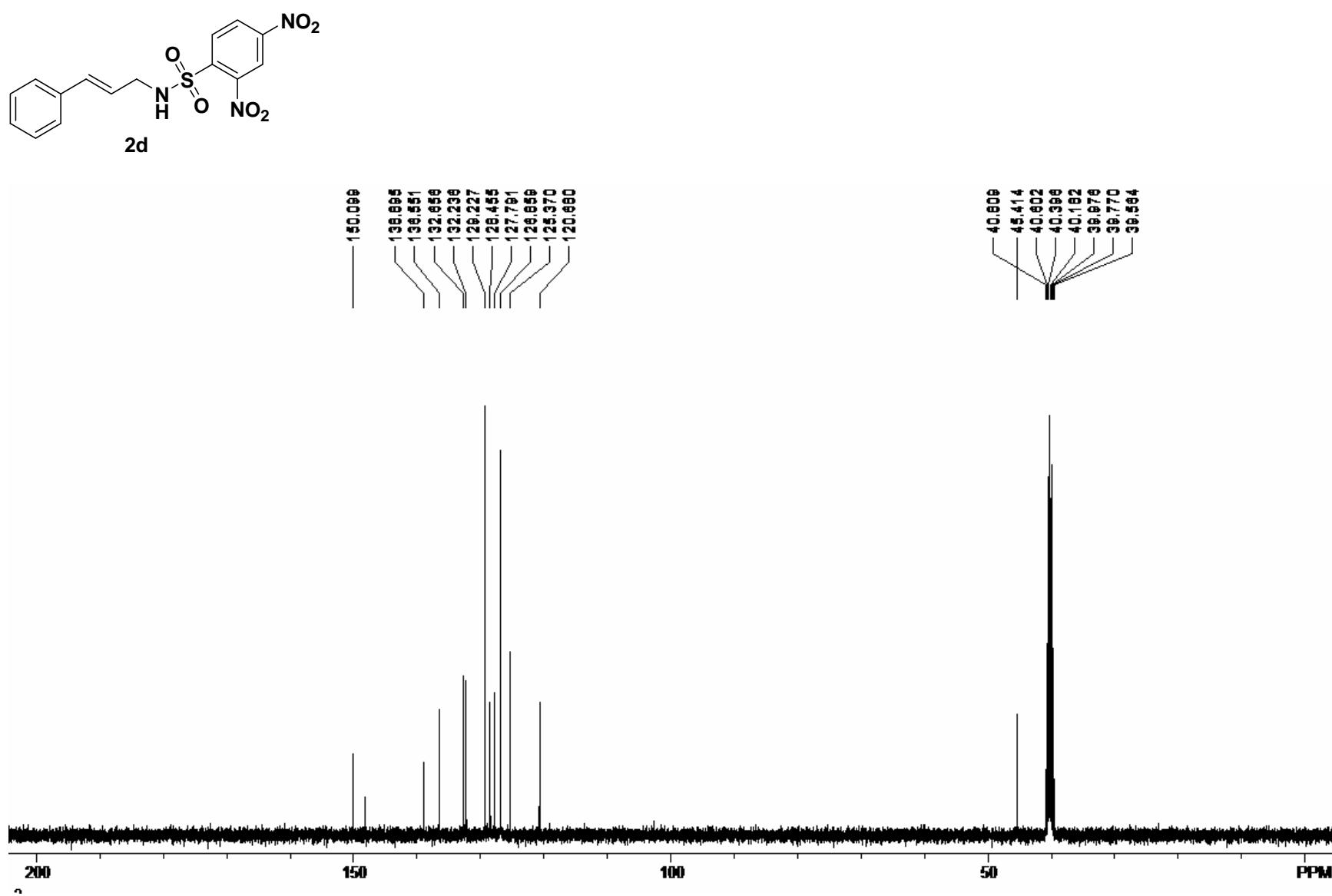
O(1)-S(1)-N(1)-C(2)	32.6(2)	C(12)-C(13)-C(14)-C(15)	0.4(4)
O(2)-S(1)-N(1)-C(2)	168.36(17)	C(13)-C(14)-C(15)-C(16)	0.8(3)
C(1)-S(1)-N(1)-C(2)	-80.4(2)	C(13)-C(14)-C(15)-C(18)	-178.7(2)
O(1)-S(1)-C(1)-F(2)	-178.84(18)	C(14)-C(15)-C(16)-C(17)	-1.0(4)
O(2)-S(1)-C(1)-F(2)	51.0(2)	C(18)-C(15)-C(16)-C(17)	178.4(2)
N(1)-S(1)-C(1)-F(2)	-63.3(2)	C(15)-C(16)-C(17)-C(12)	0.1(4)
O(1)-S(1)-C(1)-F(3)	60.6(3)	C(13)-C(12)-C(17)-C(16)	1.1(4)
O(2)-S(1)-C(1)-F(3)	-69.6(3)	C(4)-C(12)-C(17)-C(16)	-176.5(2)
N(1)-S(1)-C(1)-F(3)	176.1(2)	C(14)-C(15)-C(18)-C(19)	-5.1(3)
O(1)-S(1)-C(1)-F(1)	-59.7(2)	C(16)-C(15)-C(18)-C(19)	175.4(2)
O(2)-S(1)-C(1)-F(1)	170.2(2)	C(14)-C(15)-C(18)-C(23A)	-170.5(6)
N(1)-S(1)-C(1)-F(1)	55.9(2)	C(16)-C(15)-C(18)-C(23A)	10.1(6)
S(1)-N(1)-C(2)-C(3)	-126.57(17)	C(14)-C(15)-C(18)-C(23)	167.5(4)
N(1)-C(2)-C(3)-C(4)	59.8(2)	C(16)-C(15)-C(18)-C(23)	-11.9(4)
N(1)-C(2)-C(3)-Br(1)	-65.4(2)	C(23A)-C(18)-C(19)-C(20)	-13.9(6)
N(1)-C(2)-C(3)-Br(1A)	-53.3(2)	C(23)-C(18)-C(19)-C(20)	7.7(5)
C(5)-O(3)-C(4)-C(12)	85.4(2)	C(15)-C(18)-C(19)-C(20)	-179.6(2)
C(5)-O(3)-C(4)-C(3)	-153.78(16)	C(18)-C(19)-C(20)-C(21)	-0.4(4)
C(2)-C(3)-C(4)-O(3)	59.1(2)	C(19)-C(20)-C(21)-C(22)	-5.5(7)
Br(1)-C(3)-C(4)-O(3)	-175.72(14)	C(19)-C(20)-C(21)-O(5)	-178.2(2)
Br(1A)-C(3)-C(4)-O(3)	174.47(18)	C(19)-C(20)-C(21)-C(22A)	9.6(13)
C(2)-C(3)-C(4)-C(12)	175.96(16)	C(24A)-O(5)-C(21)-C(20)	-156.9(6)
Br(1)-C(3)-C(4)-C(12)	-58.9(2)	C(24)-O(5)-C(21)-C(20)	-179.9(4)
Br(1A)-C(3)-C(4)-C(12)	-68.7(2)	C(24A)-O(5)-C(21)-C(22)	29.8(7)
C(4)-O(3)-C(5)-O(4)	6.6(3)	C(24)-O(5)-C(21)-C(22)	6.7(6)
C(4)-O(3)-C(5)-C(6)	-171.70(16)	C(24A)-O(5)-C(21)-C(22A)	16.2(12)
O(4)-C(5)-C(6)-C(7)	25.4(3)	C(24)-O(5)-C(21)-C(22A)	-6.9(11)
O(3)-C(5)-C(6)-C(7)	-156.24(19)	C(20)-C(21)-C(22)-C(23)	4.2(12)
O(4)-C(5)-C(6)-C(11)	-152.8(2)	O(5)-C(21)-C(22)-C(23)	178.2(7)
O(3)-C(5)-C(6)-C(11)	25.5(3)	C(22A)-C(21)-C(22)-C(23)	-101(3)
C(11)-C(6)-C(7)-C(8)	0.2(3)	C(20)-C(21)-C(22)-O(6)	-169.4(4)
C(5)-C(6)-C(7)-C(8)	-178.0(2)	O(5)-C(21)-C(22)-O(6)	4.5(8)
C(6)-C(7)-C(8)-C(9)	0.6(4)	C(22A)-C(21)-C(22)-O(6)	85.7(18)
C(7)-C(8)-C(9)-C(10)	-0.3(4)	C(24)-O(6)-C(22)-C(23)	172.5(8)
C(8)-C(9)-C(10)-C(11)	-0.8(4)	C(24)-O(6)-C(22)-C(21)	-13.7(8)
C(9)-C(10)-C(11)-C(6)	1.7(4)	C(24A)-O(6A)-C(22A)-C(23A)	164.8(19)
C(7)-C(6)-C(11)-C(10)	-1.3(3)	C(24A)-O(6A)-C(22A)-C(21)	2(2)
C(5)-C(6)-C(11)-C(10)	176.9(2)	C(20)-C(21)-C(22A)-O(6A)	161.8(10)
O(3)-C(4)-C(12)-C(13)	-122.3(2)	C(22)-C(21)-C(22A)-O(6A)	-115(3)
C(3)-C(4)-C(12)-C(13)	124.2(2)	O(5)-C(21)-C(22A)-O(6A)	-11.8(19)
O(3)-C(4)-C(12)-C(17)	55.2(3)	C(20)-C(21)-C(22A)-C(23A)	-4(2)
C(3)-C(4)-C(12)-C(17)	-58.3(3)	C(22)-C(21)-C(22A)-C(23A)	79(2)
C(17)-C(12)-C(13)-C(14)	-1.4(3)	O(5)-C(21)-C(22A)-C(23A)	-177.4(15)
C(4)-C(12)-C(13)-C(14)	176.1(2)	C(21)-C(22)-C(23)-C(18)	3.1(12)

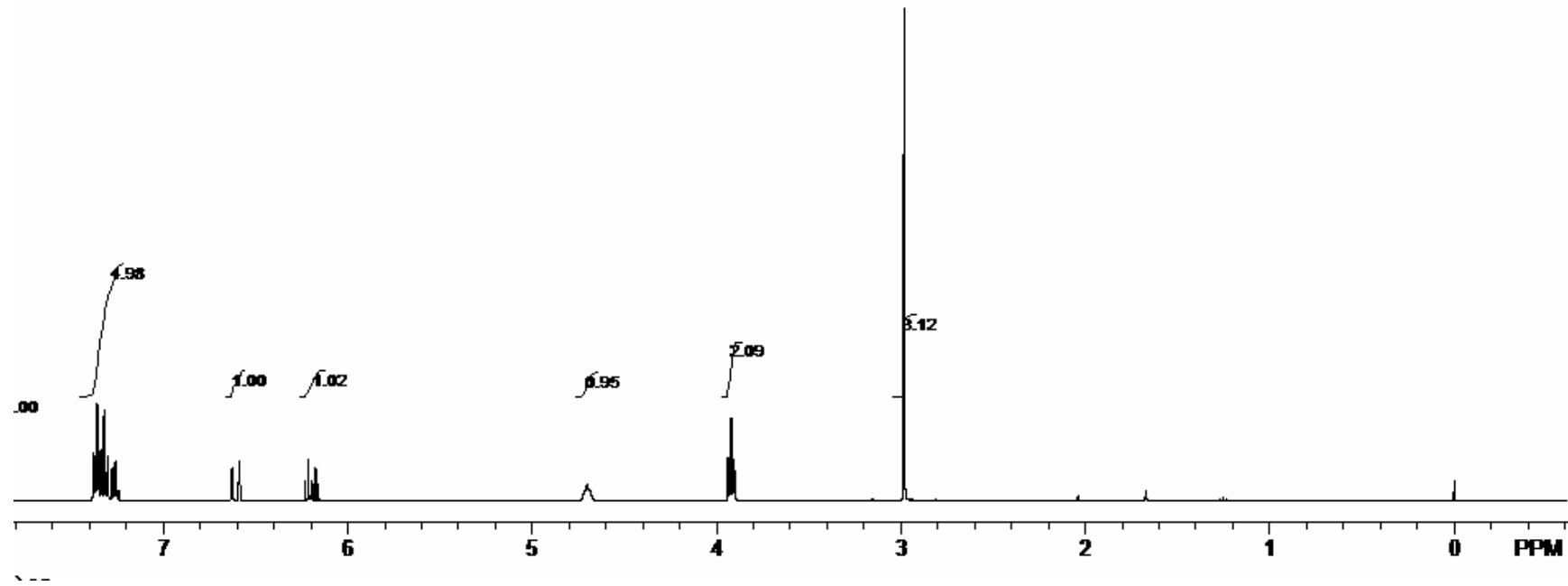
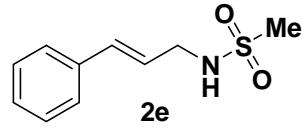
O(6)-C(22)-C(23)-C(18)	175.9(7)
C(19)-C(18)-C(23)-C(22)	-8.7(7)
C(23A)-C(18)-C(23)-C(22)	83(2)
C(15)-C(18)-C(23)-C(22)	178.4(6)
O(6A)-C(22A)-C(23A)-C(18)	-173.0(17)
C(21)-C(22A)-C(23A)-C(18)	-11(2)
C(19)-C(18)-C(23A)-C(22A)	19.6(15)
C(23)-C(18)-C(23A)-C(22A)	-79(2)
C(15)-C(18)-C(23A)-C(22A)	-174.5(13)
C(22)-O(6)-C(24)-O(5)	17.8(6)
C(21)-O(5)-C(24)-O(6)	-15.7(4)
C(24A)-O(5)-C(24)-O(6)	-106.3(10)
C(22A)-O(6A)-C(24A)-O(5)	8.3(15)
C(21)-O(5)-C(24A)-O(6A)	-15.0(8)
C(24)-O(5)-C(24A)-O(6A)	80.4(9)
C(27)-O(8)-C(26)-O(7)	7.9(3)
C(27)-O(8)-C(26)-C(25)	-173.43(19)
C(26)-O(8)-C(27)-C(28)	105.1(2)

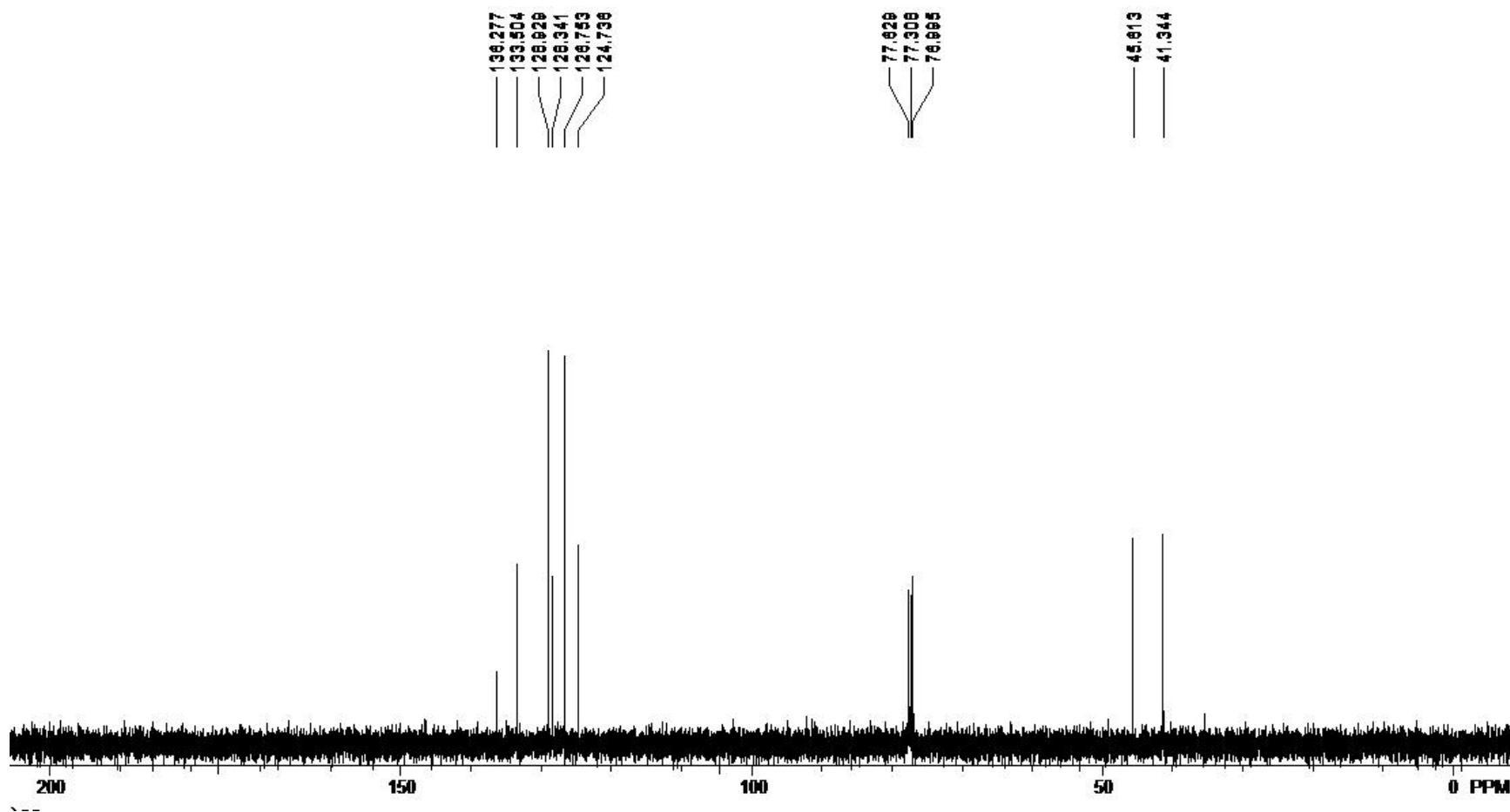
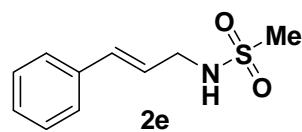


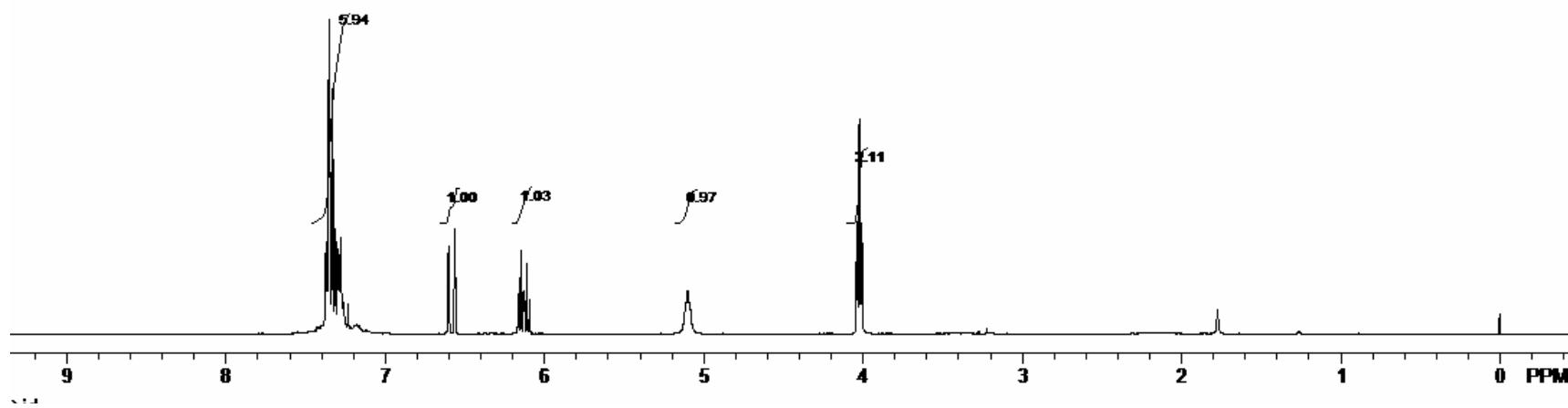
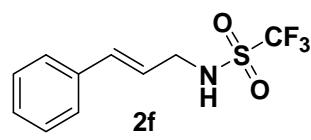


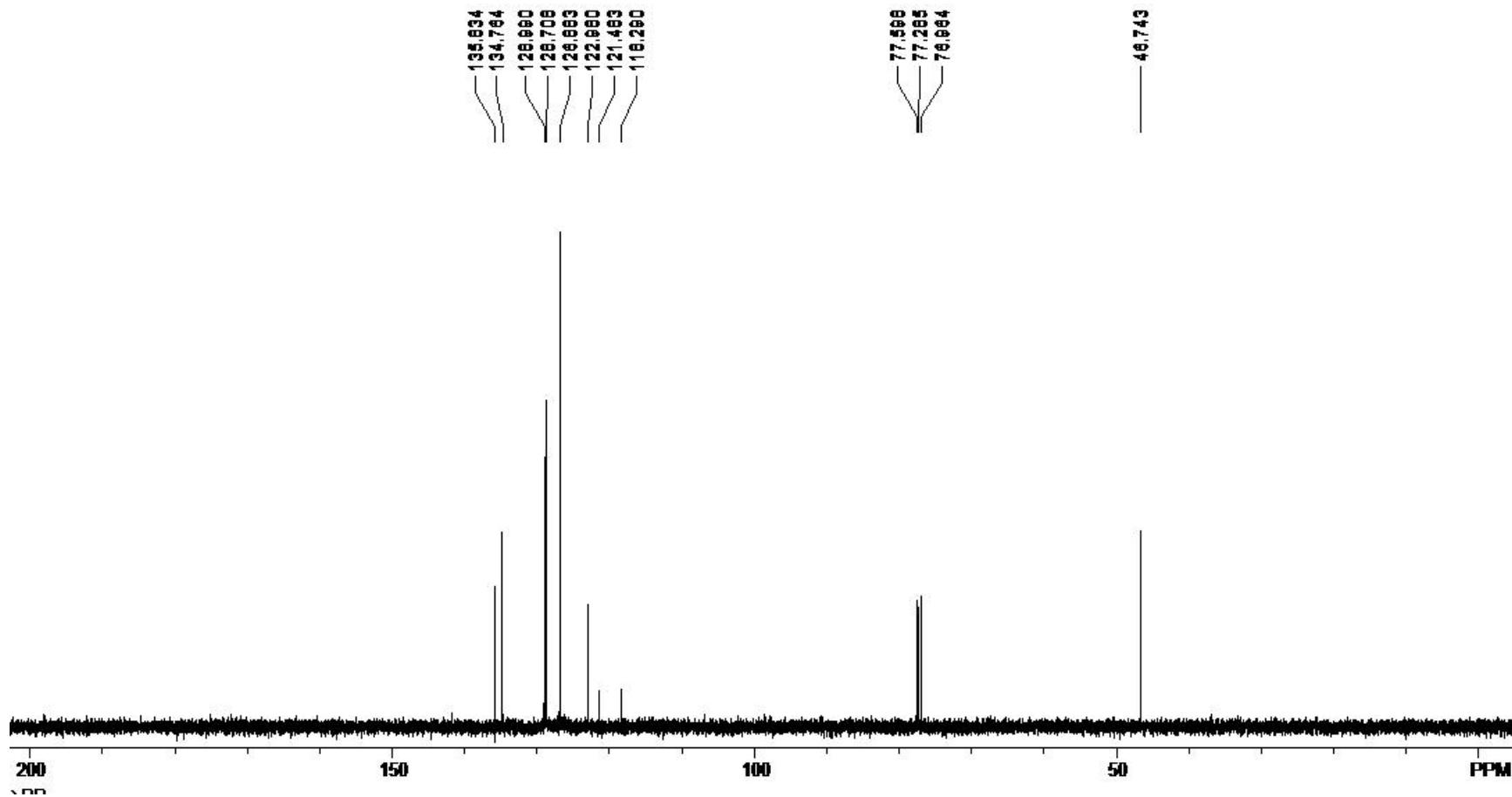
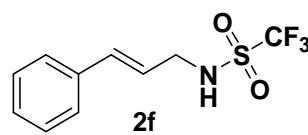


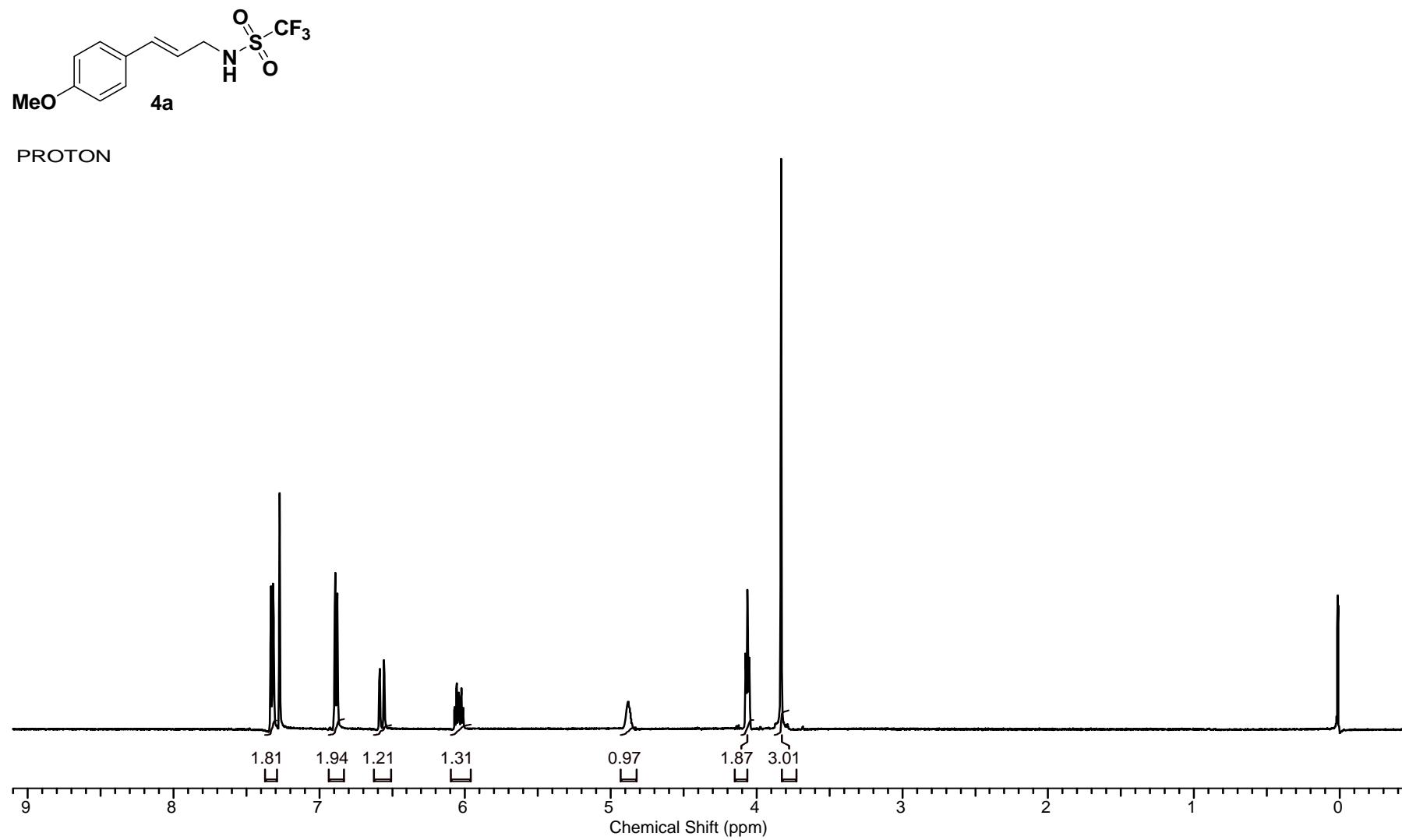


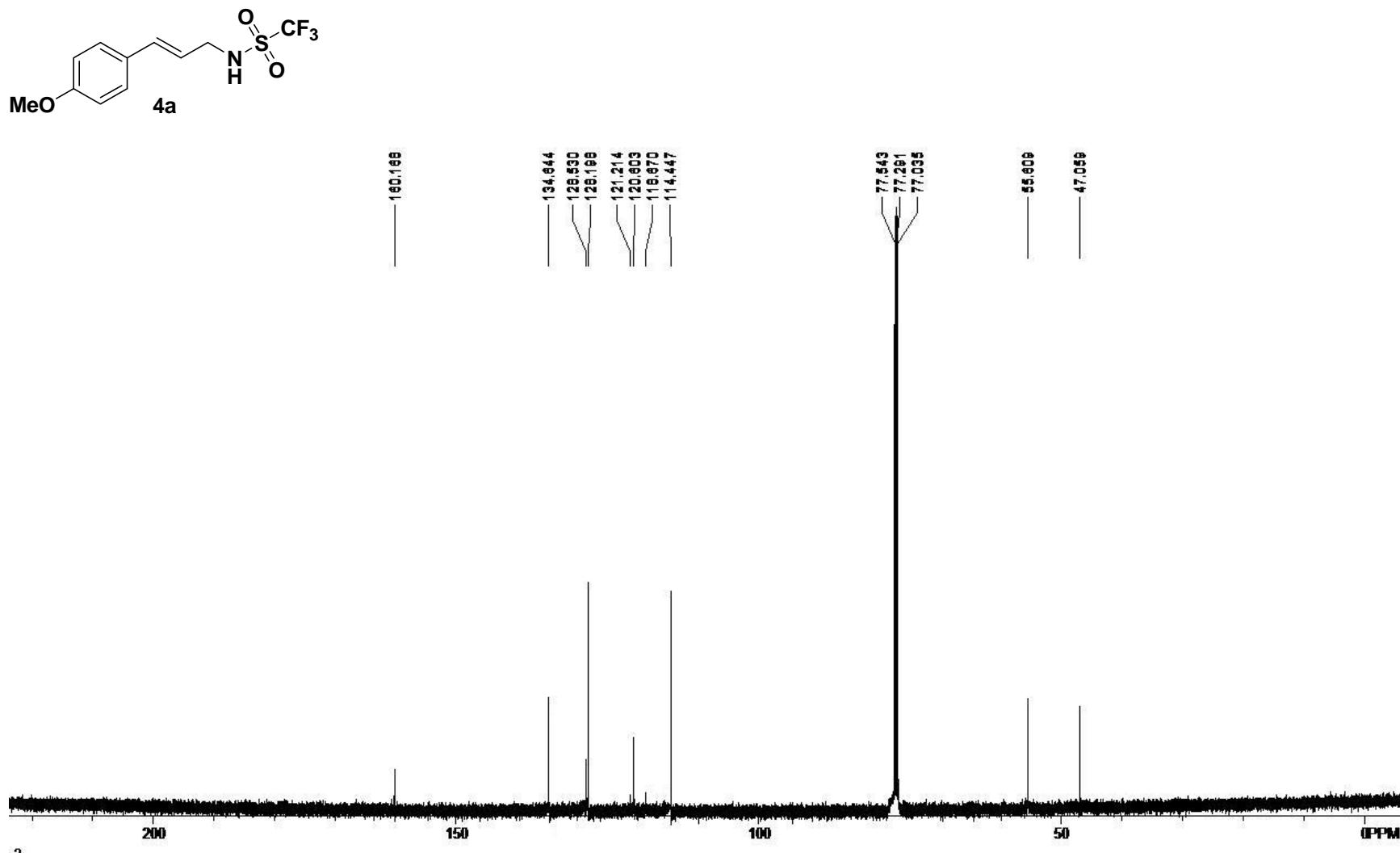


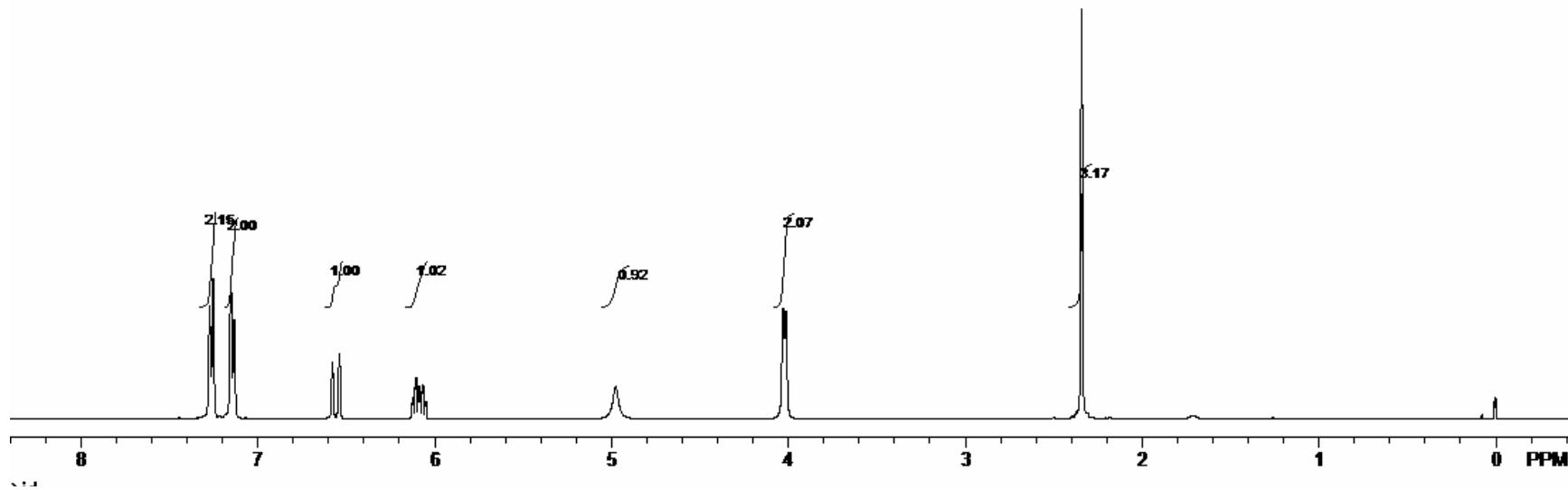
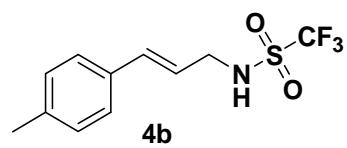


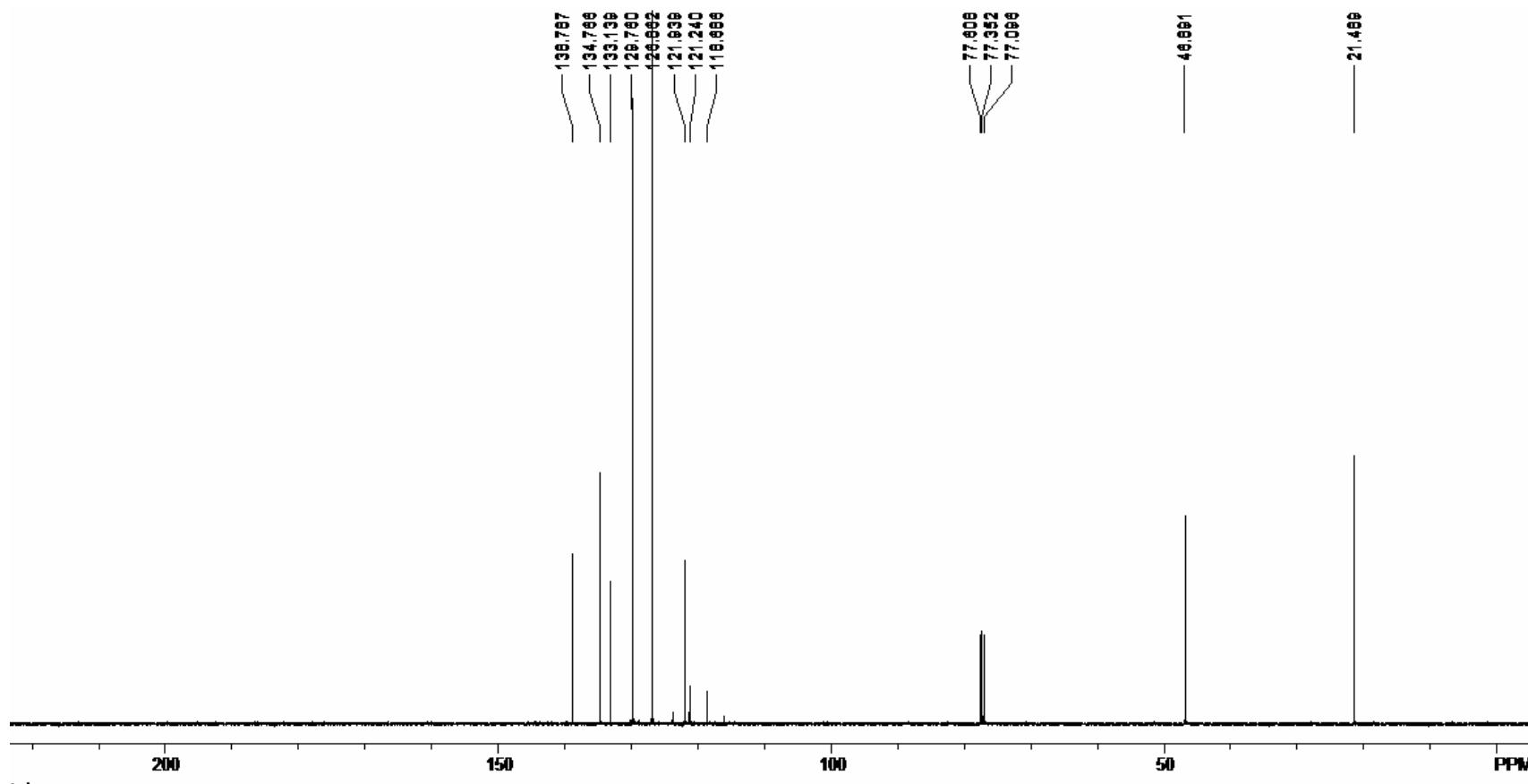
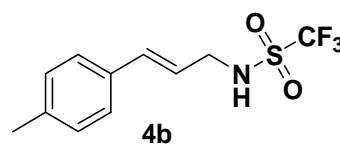


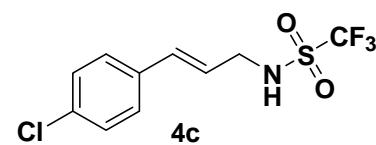




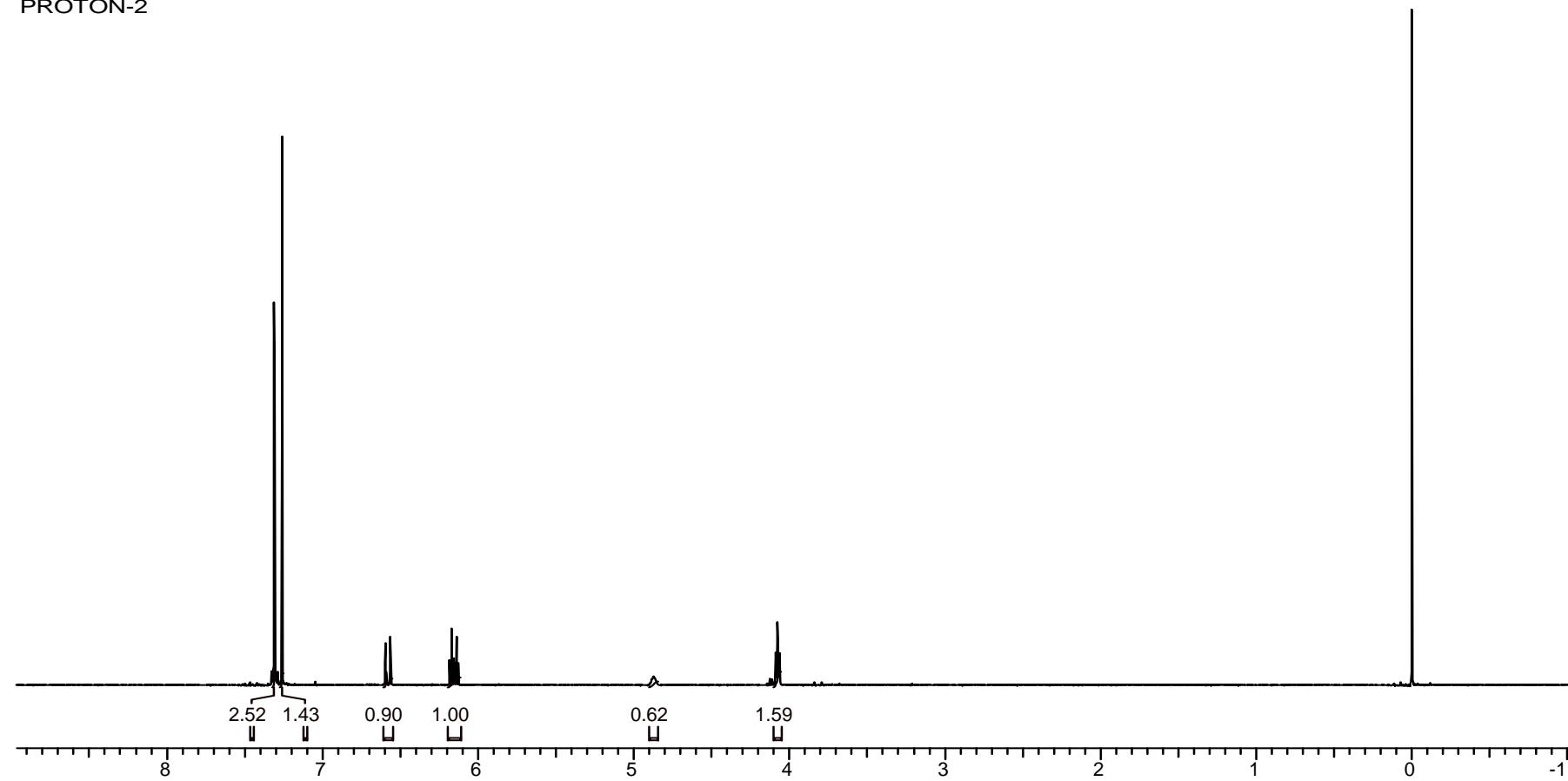


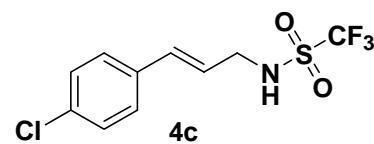




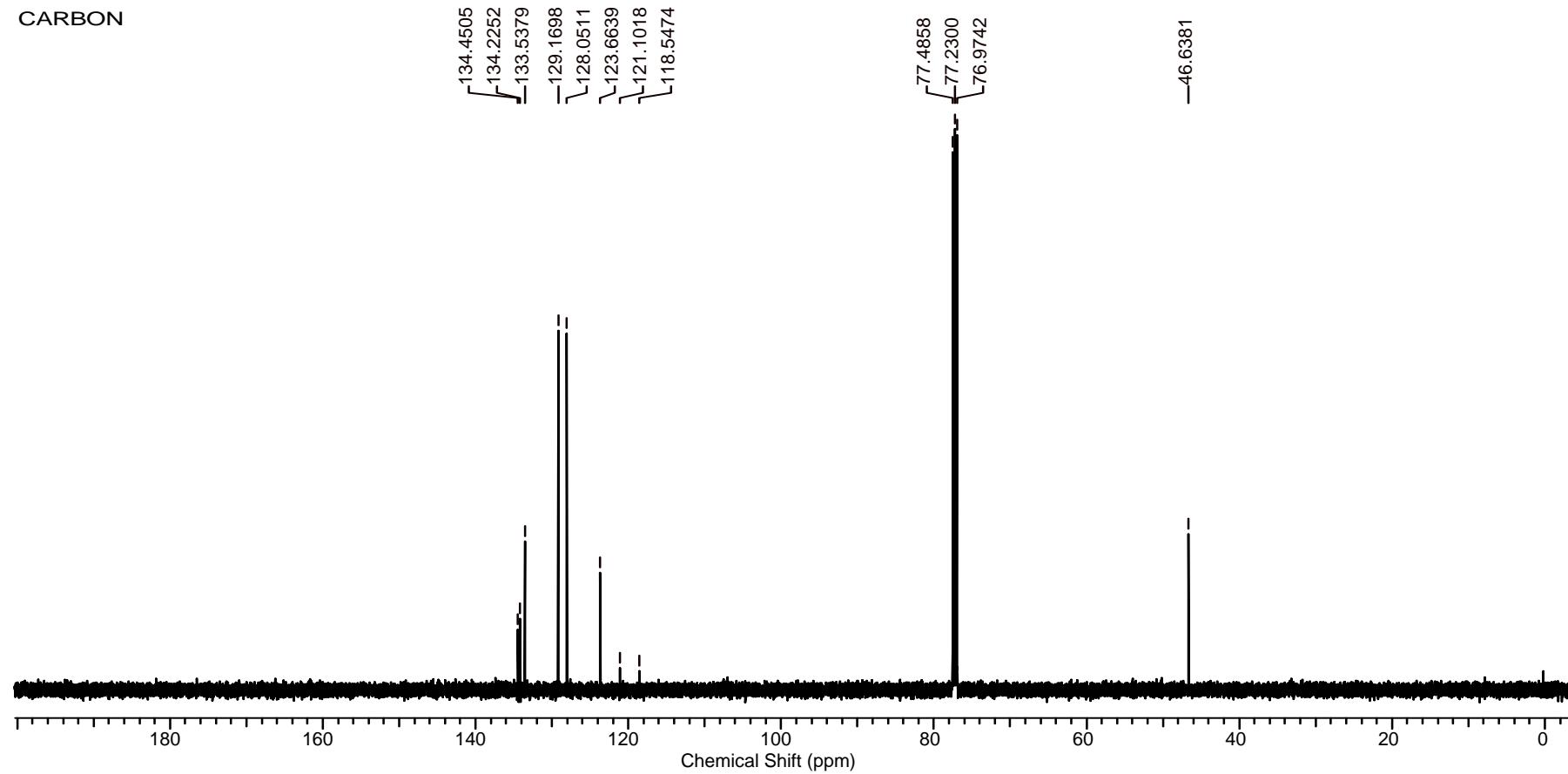


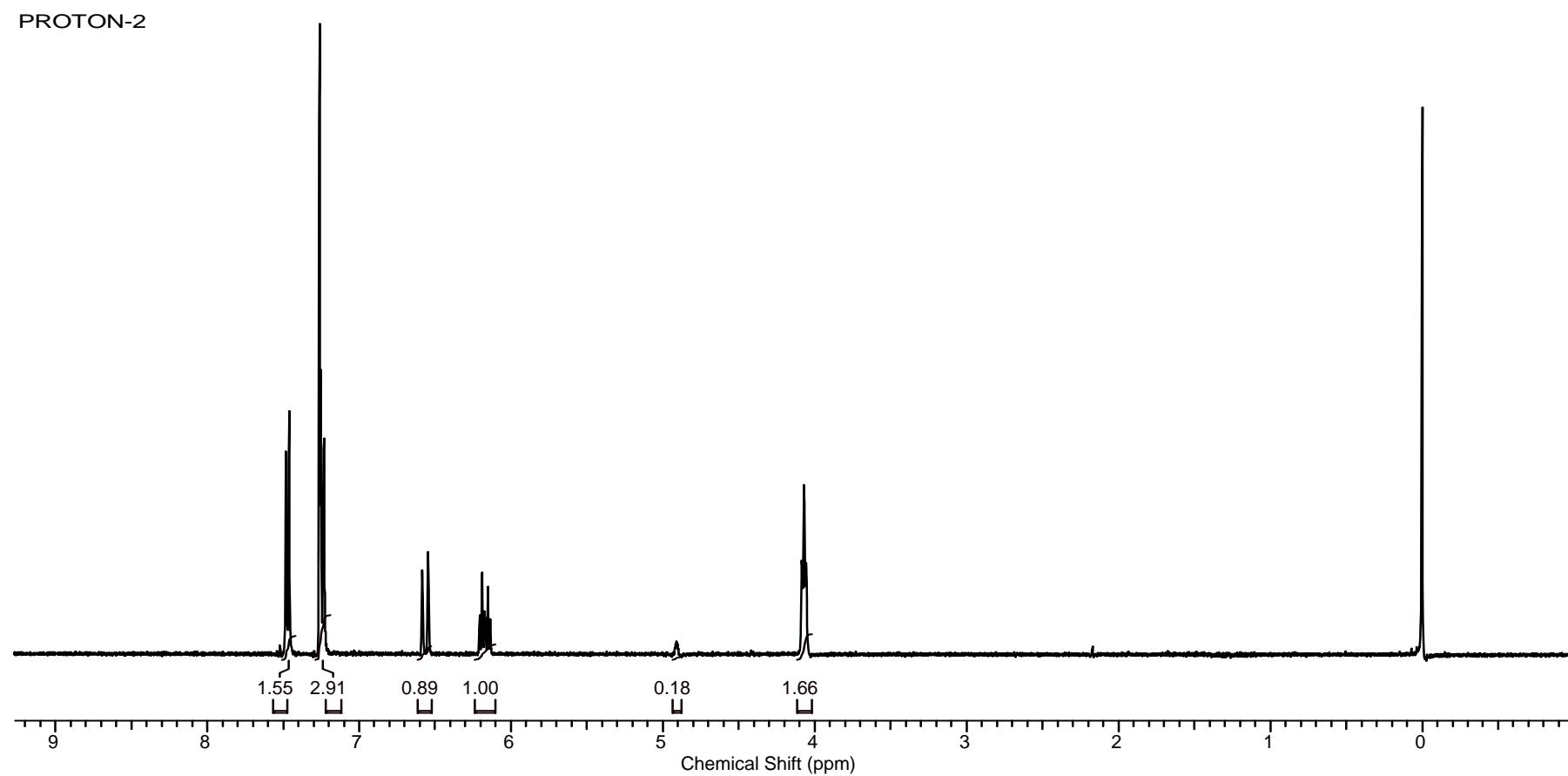
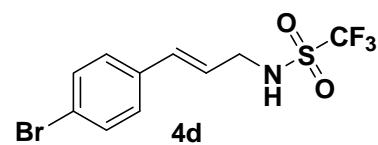
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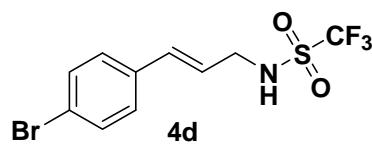




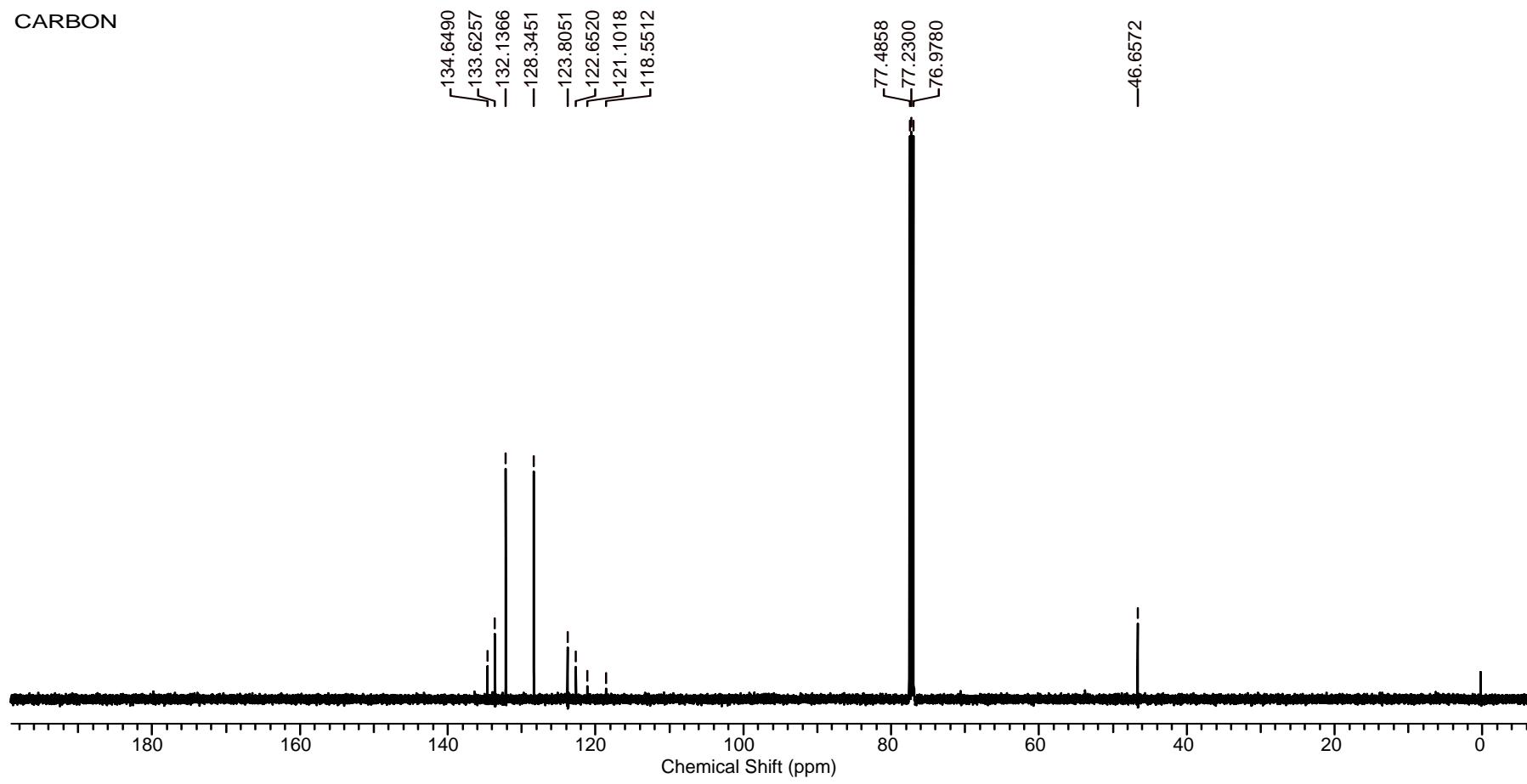
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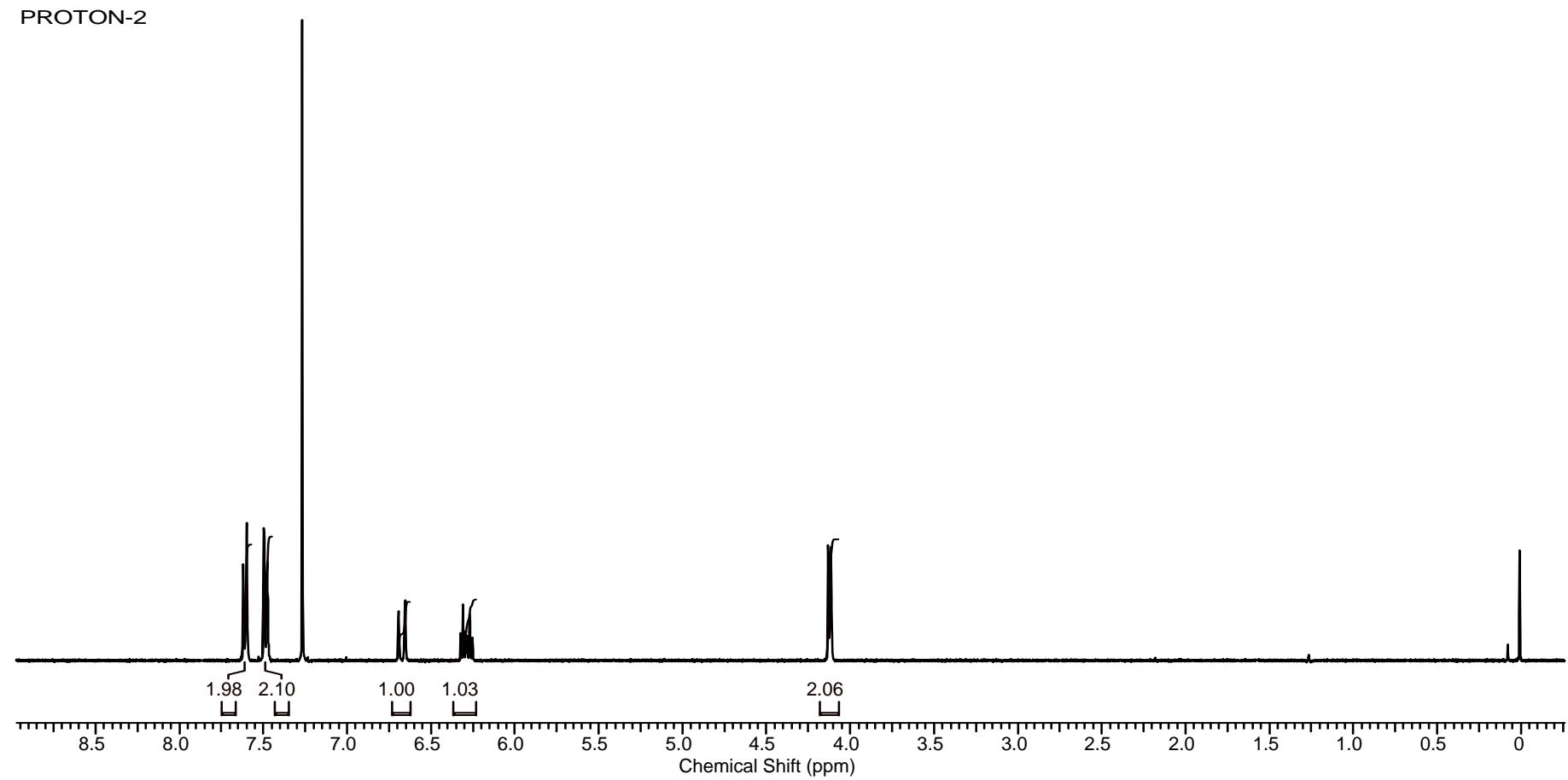
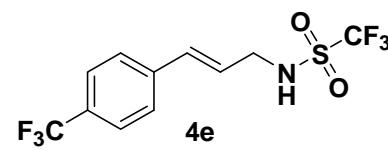


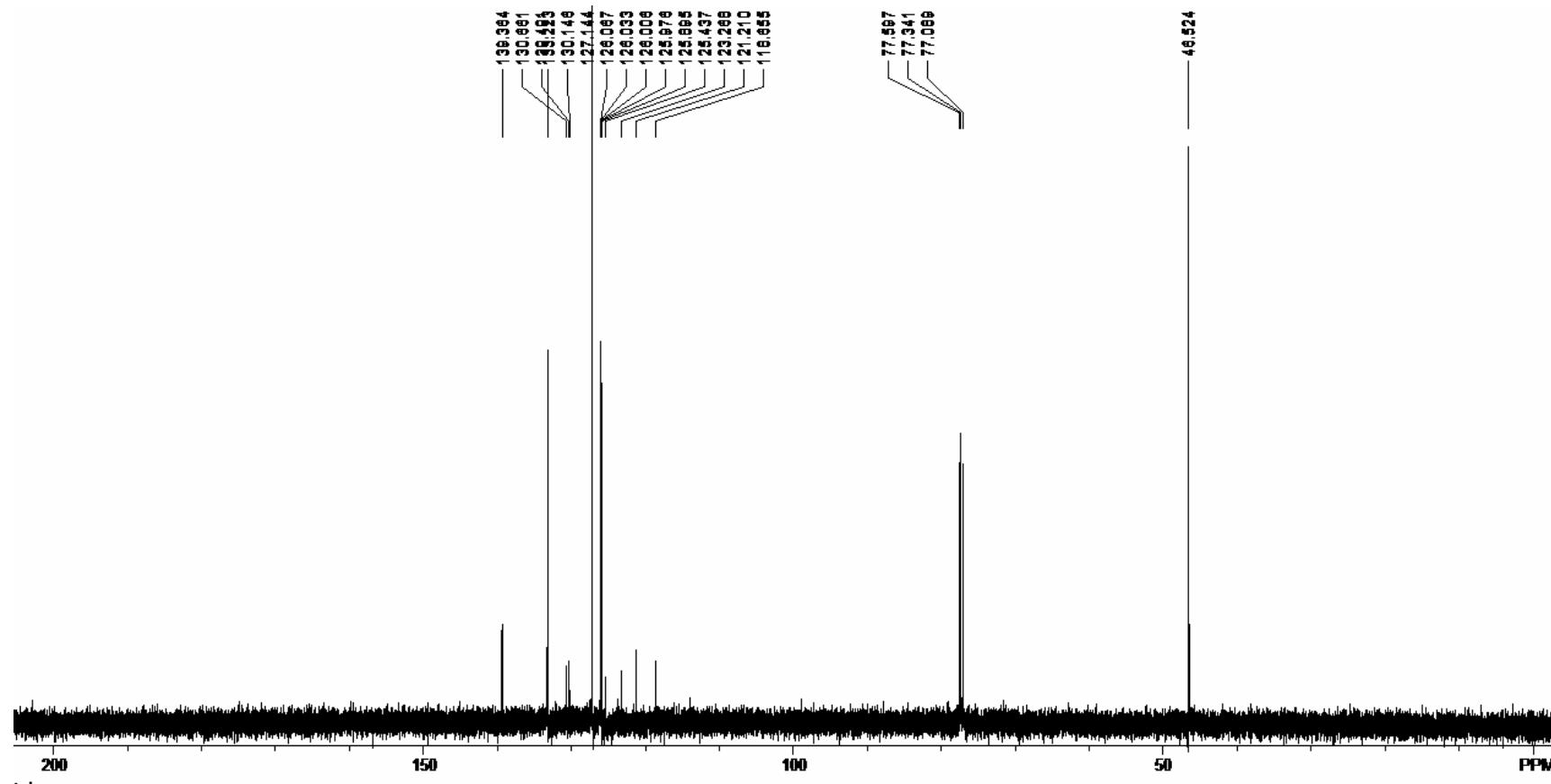
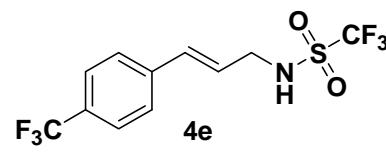


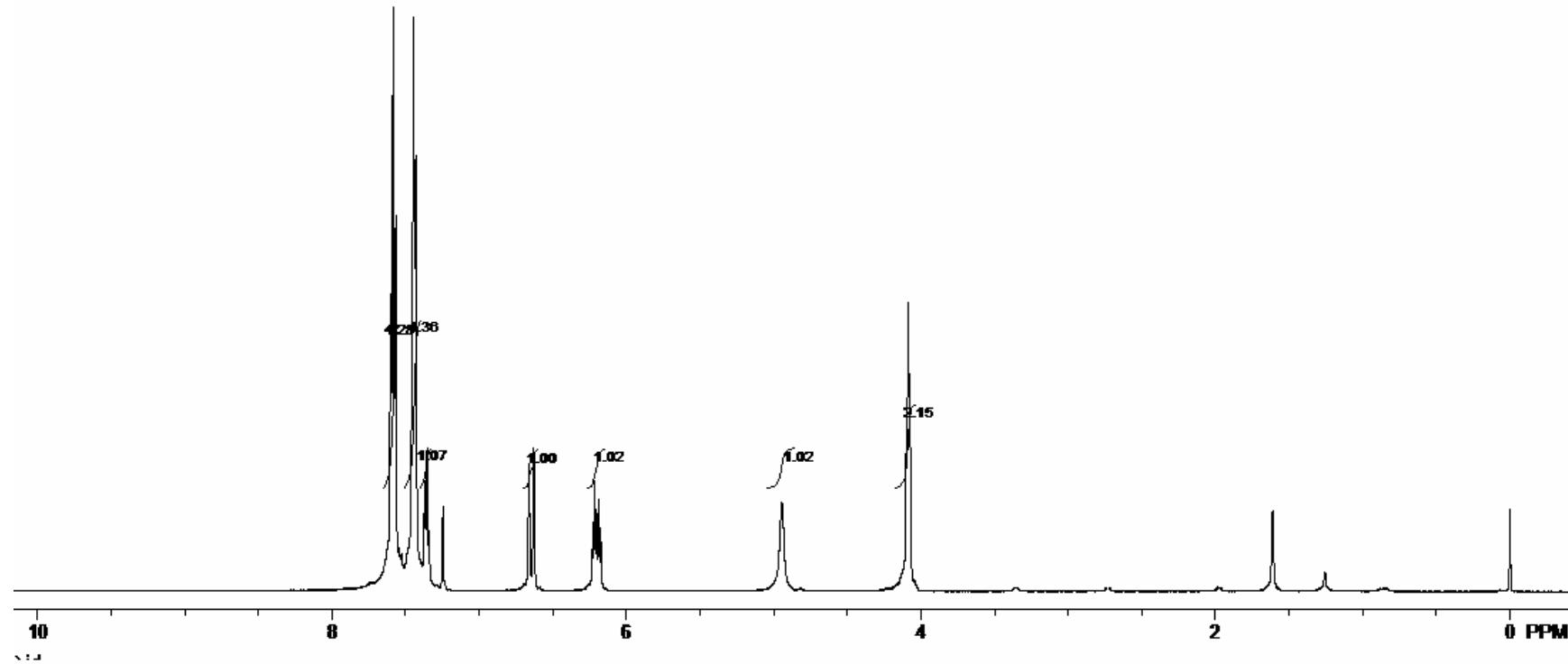
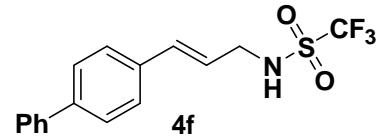


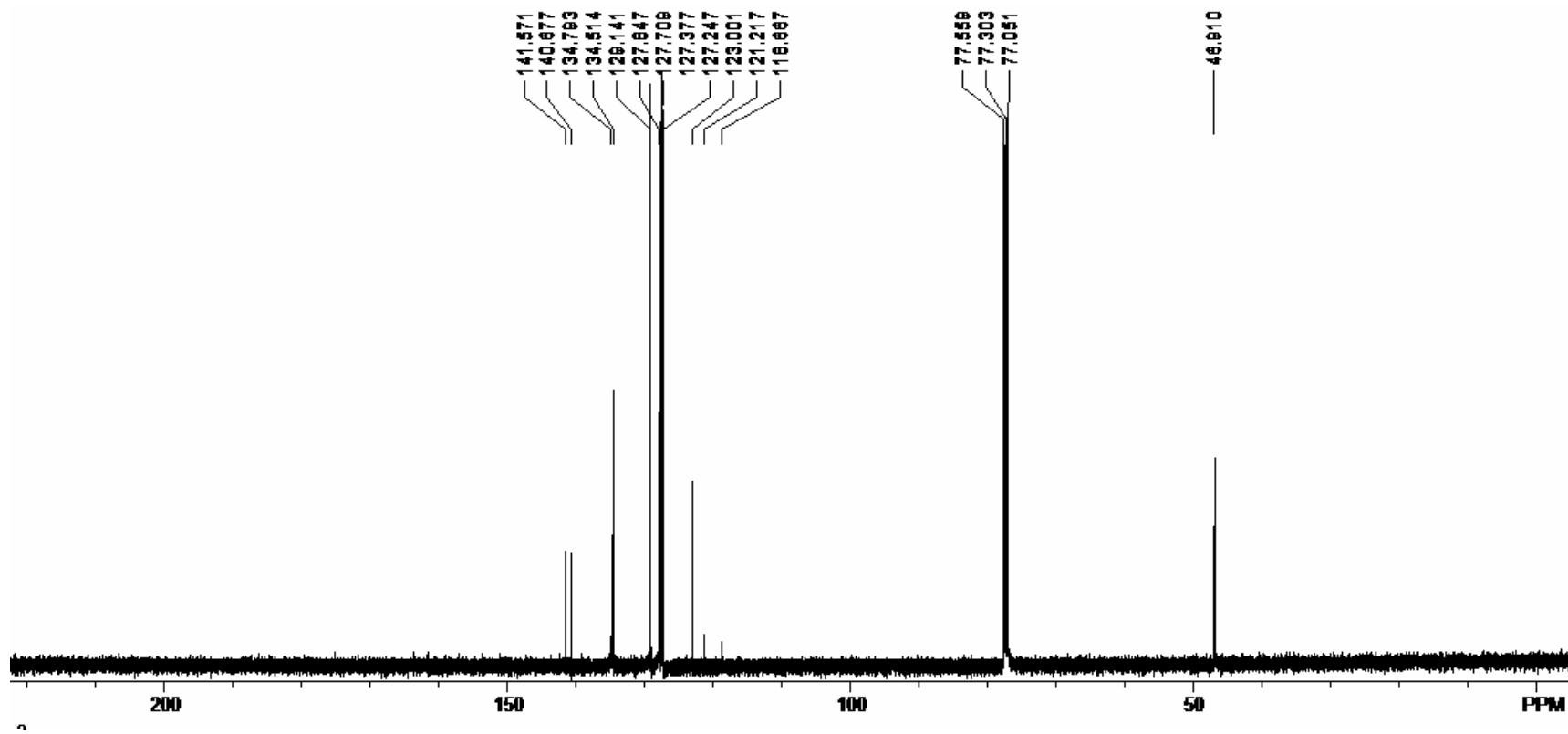
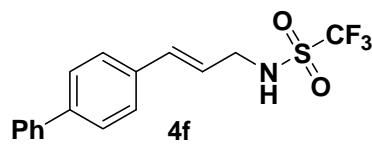
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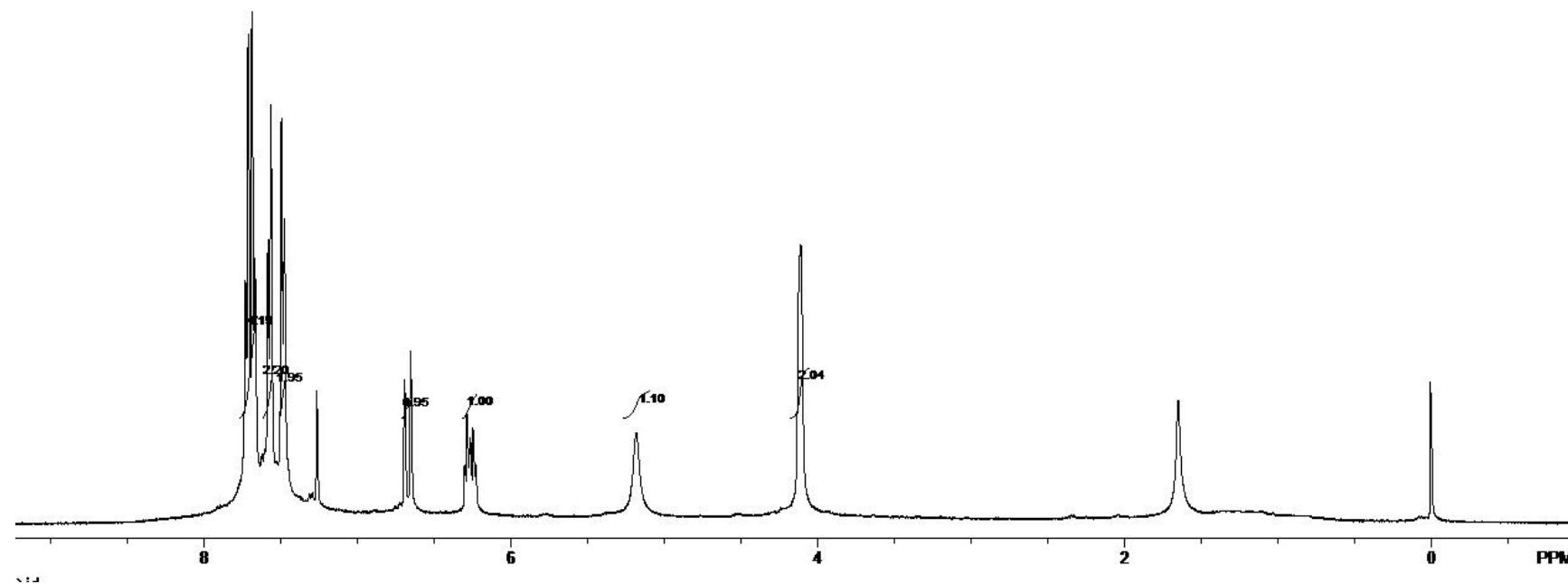
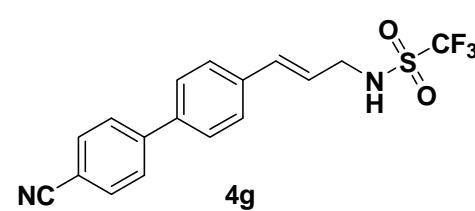


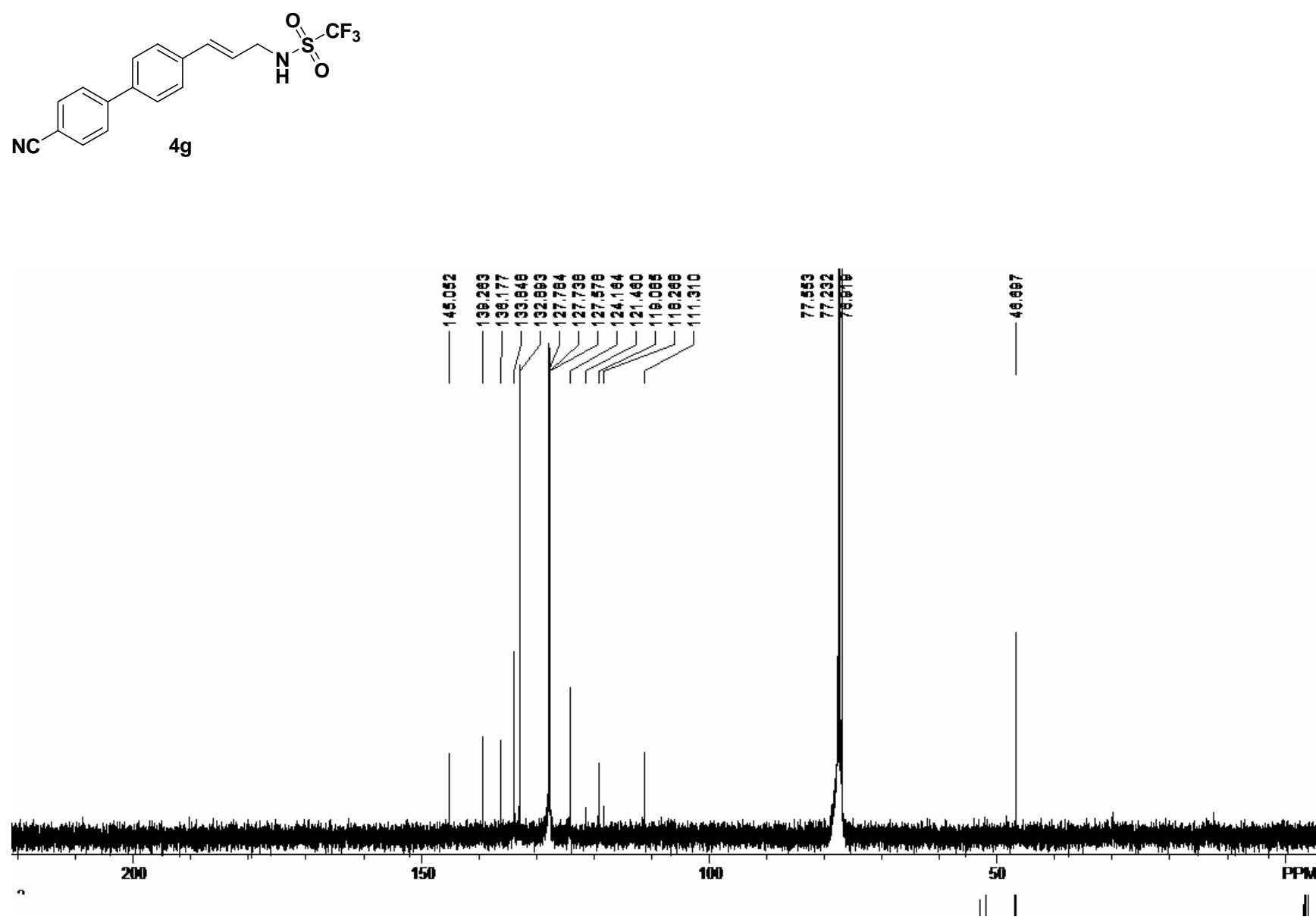


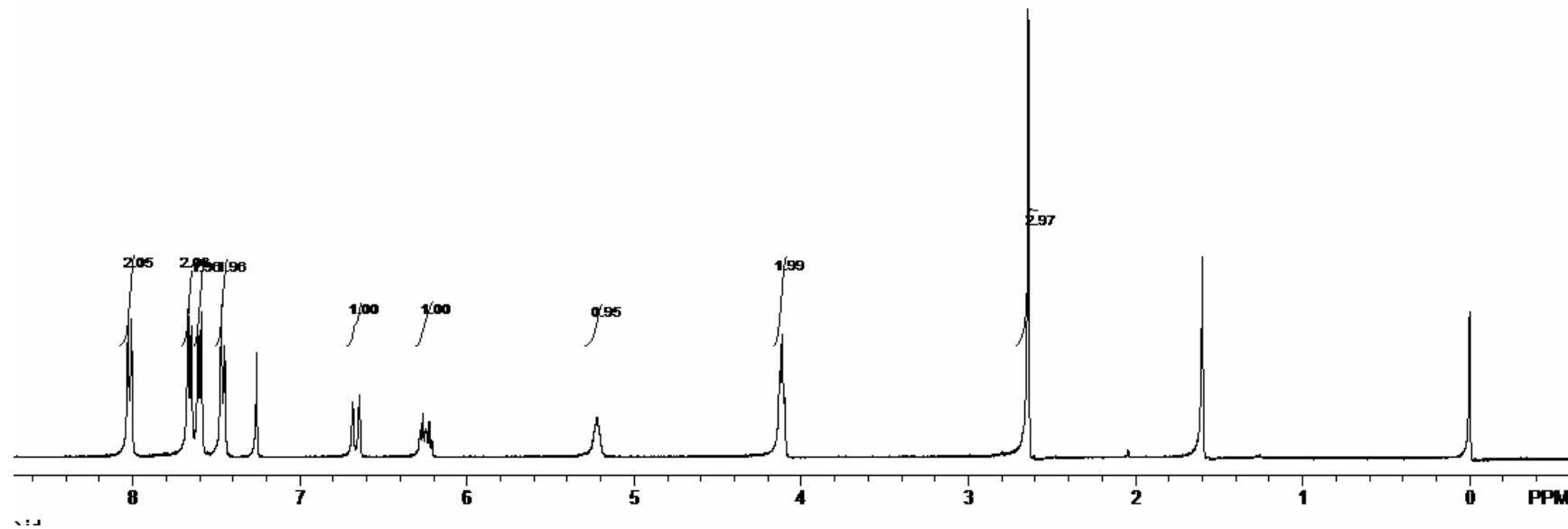
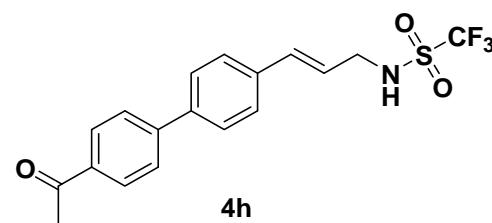


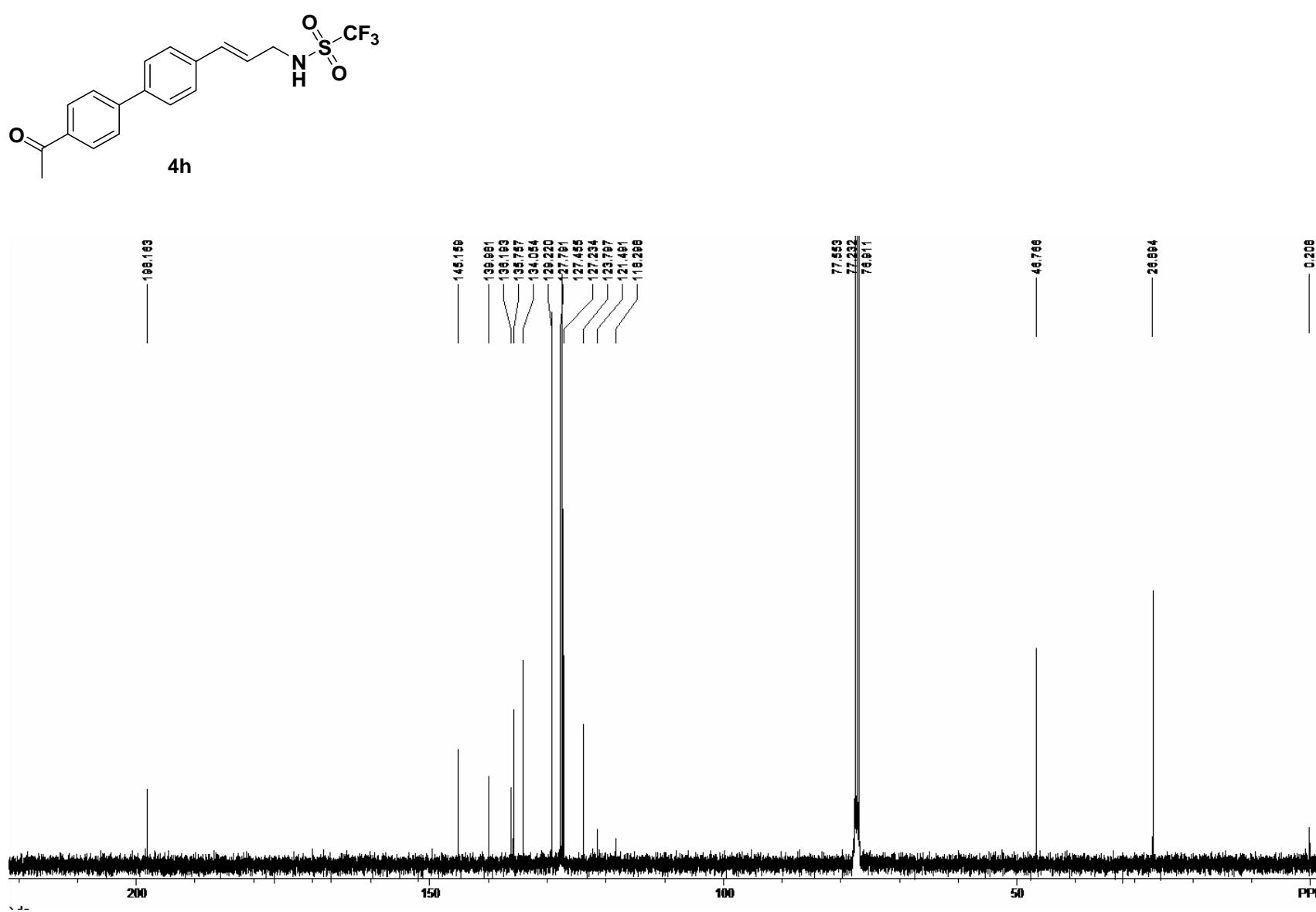


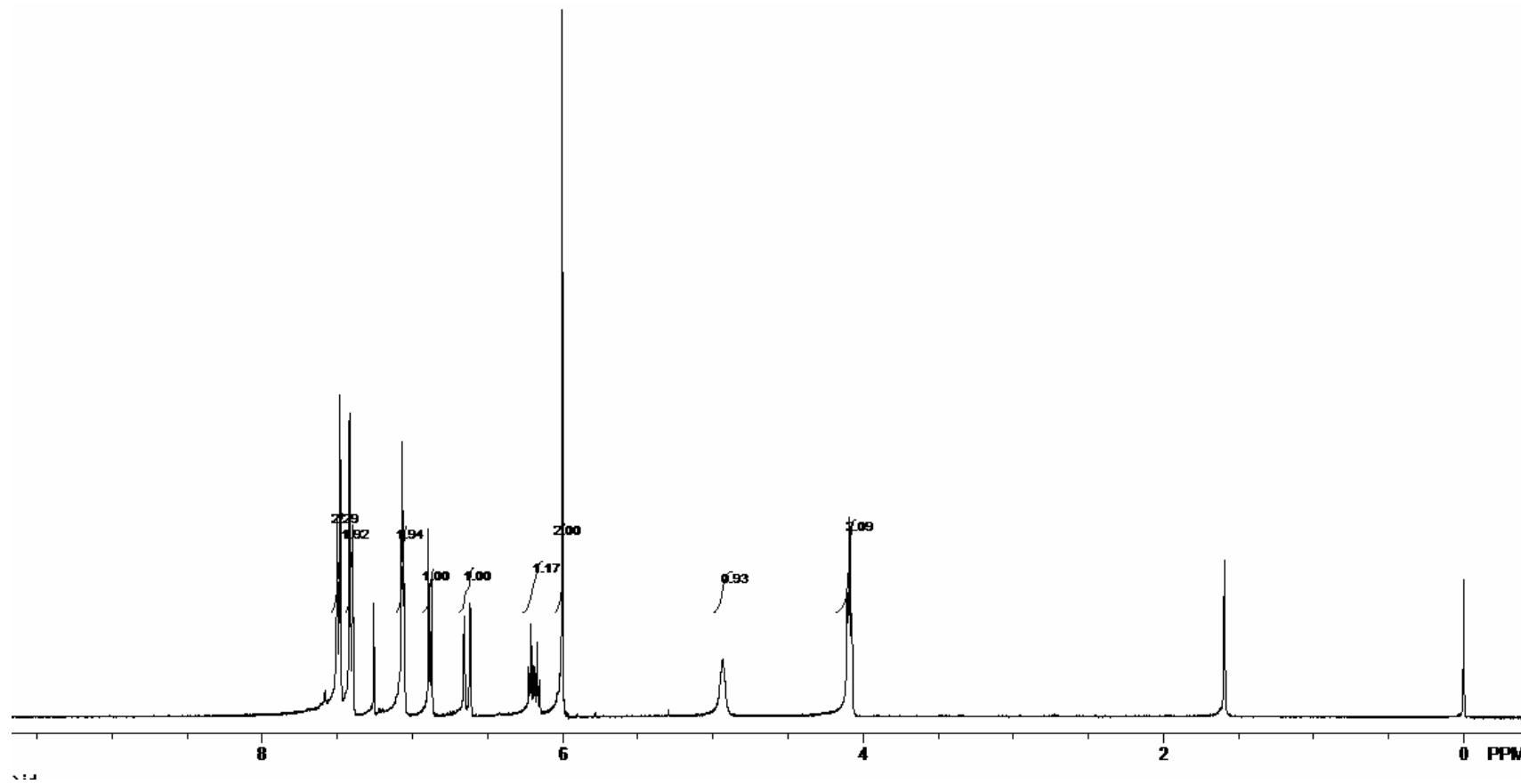
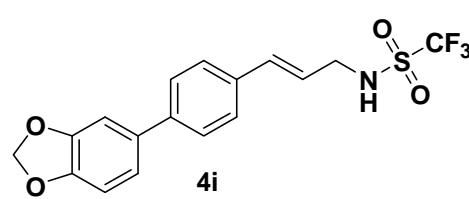


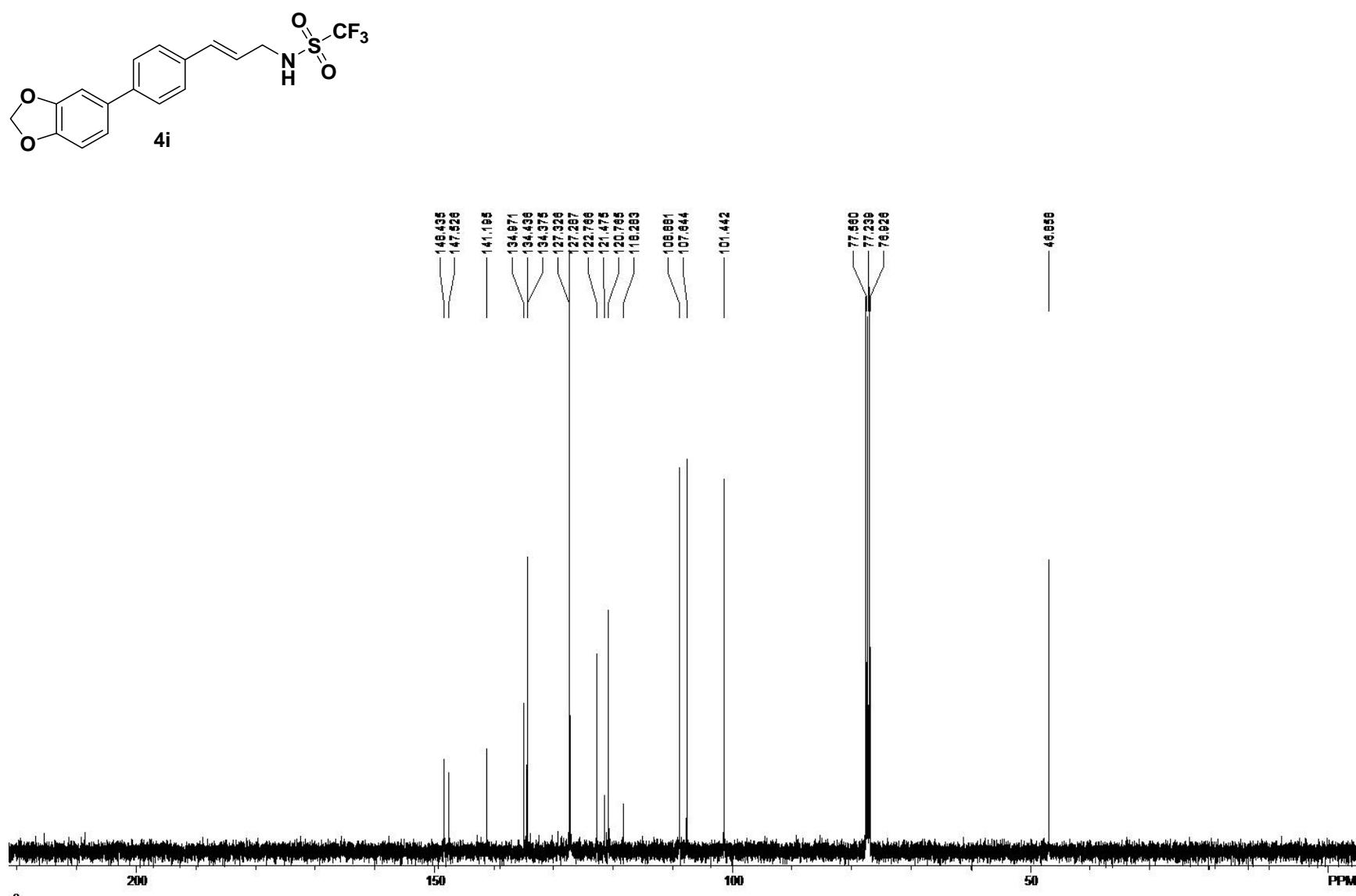


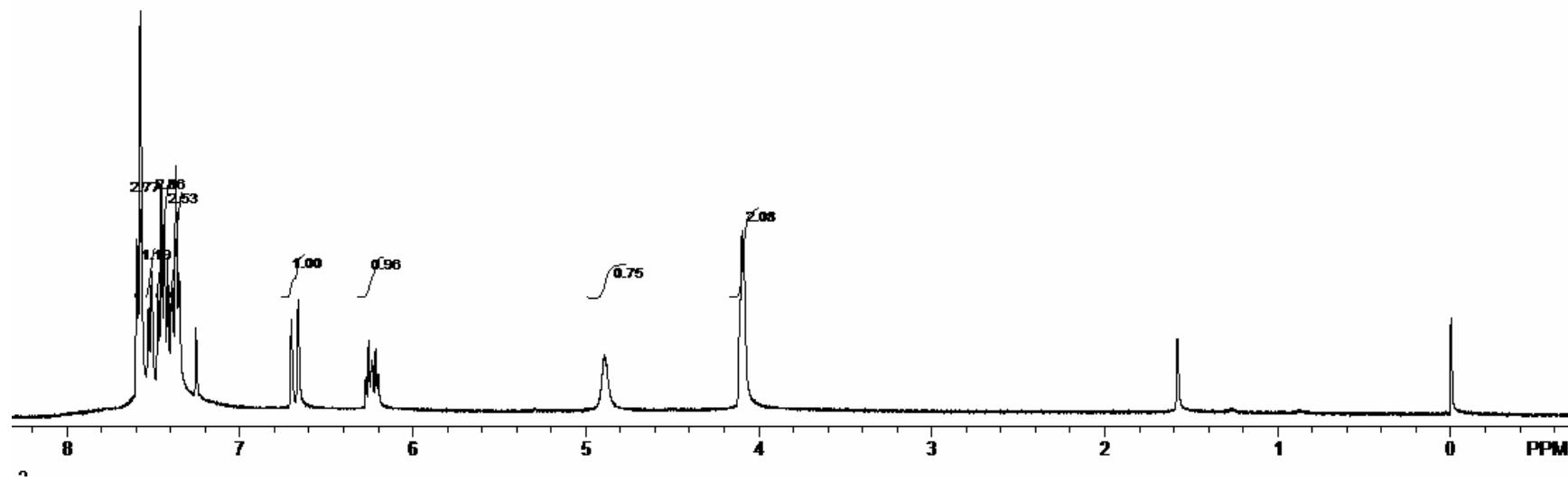
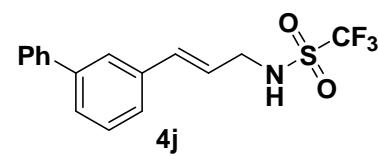


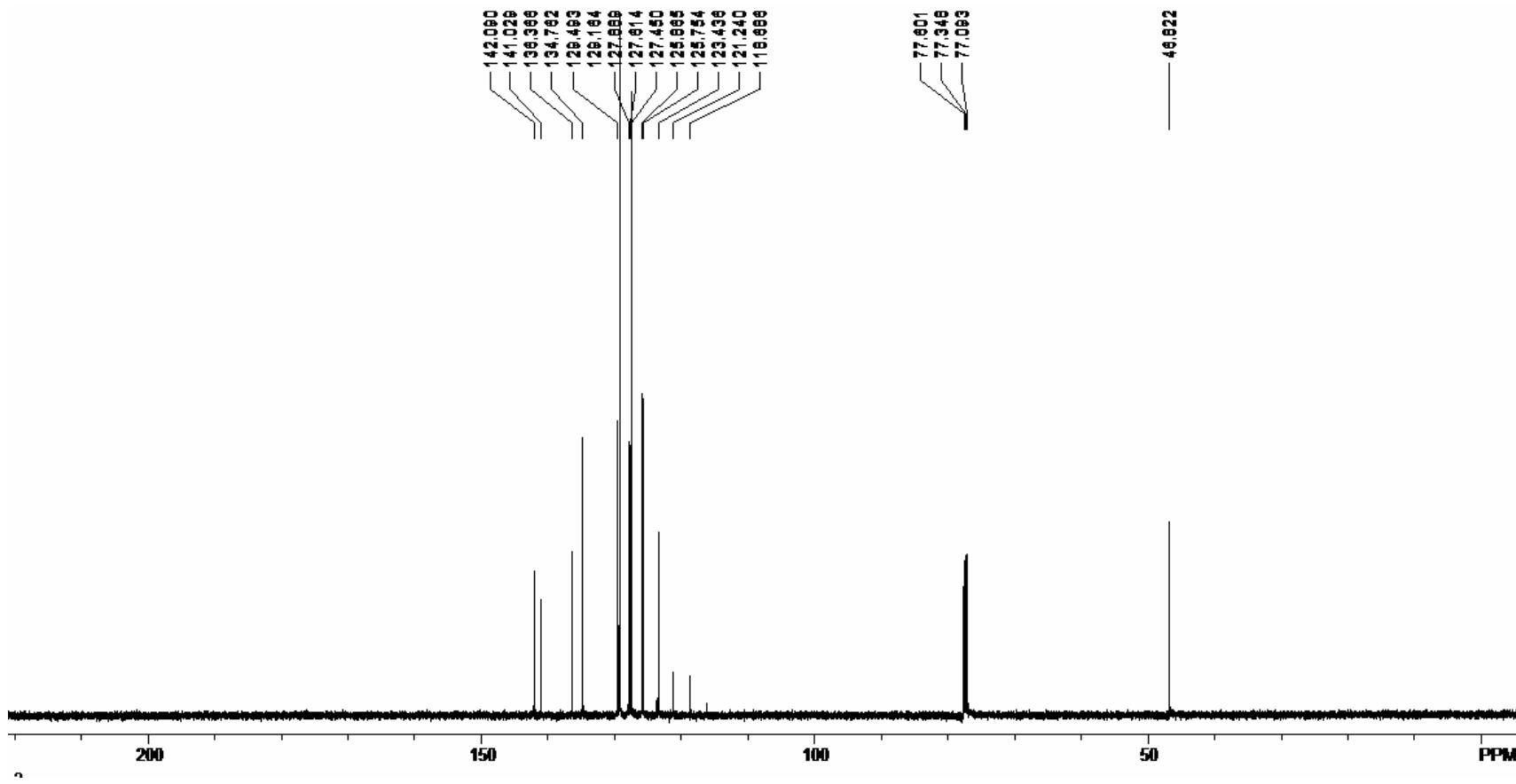
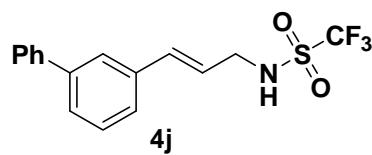


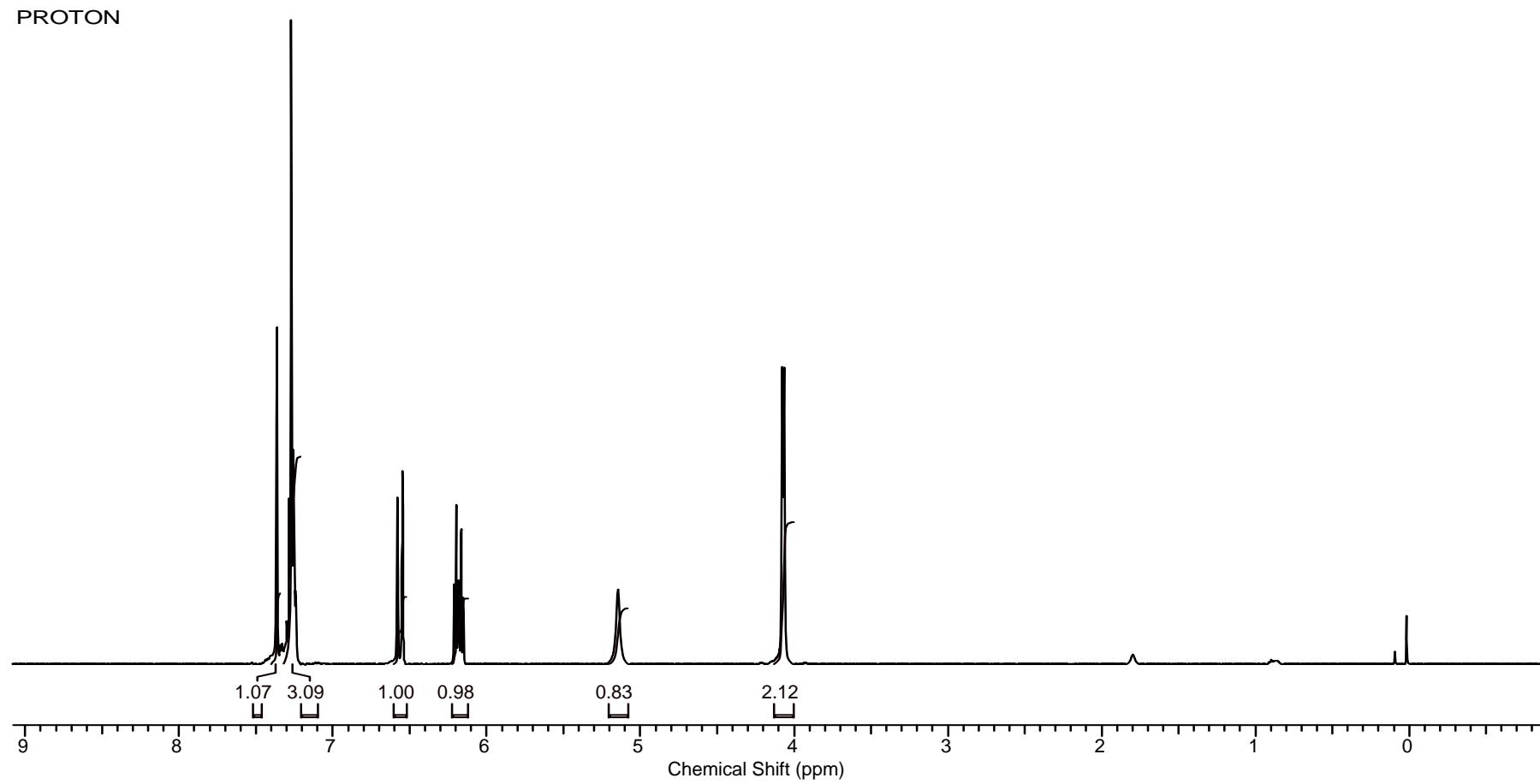
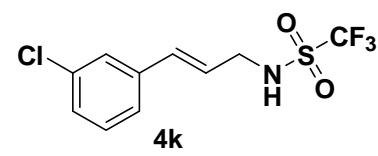


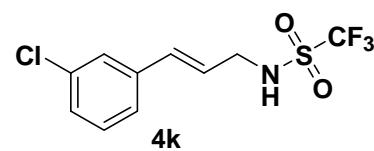




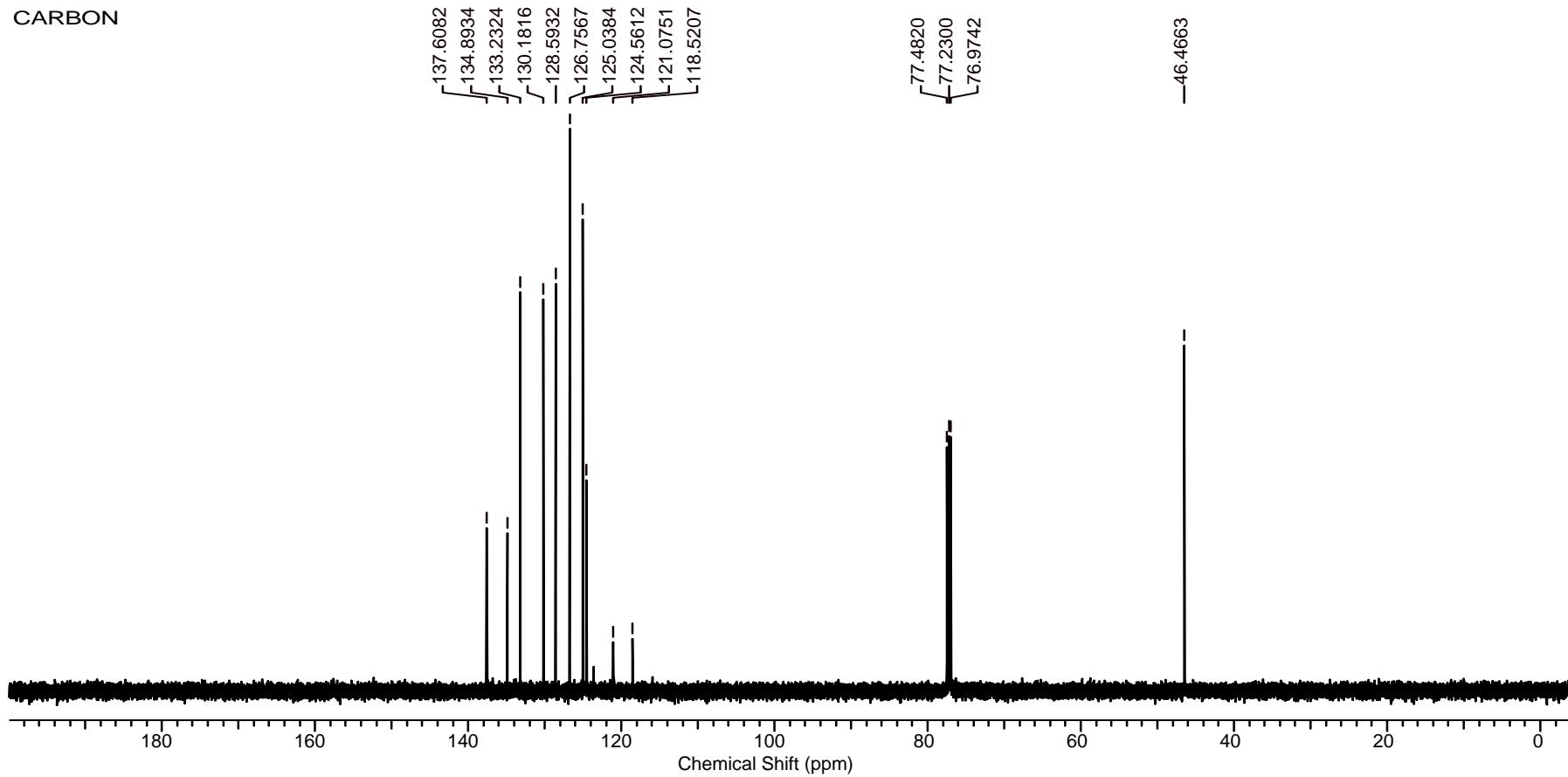


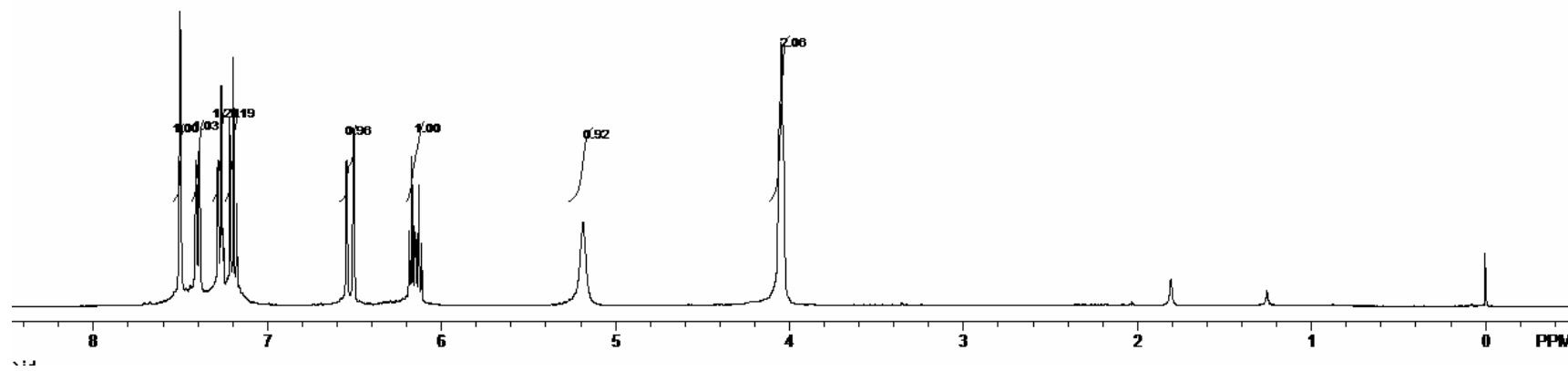
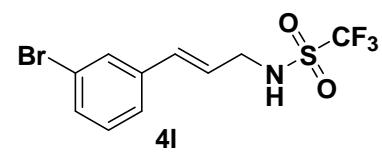


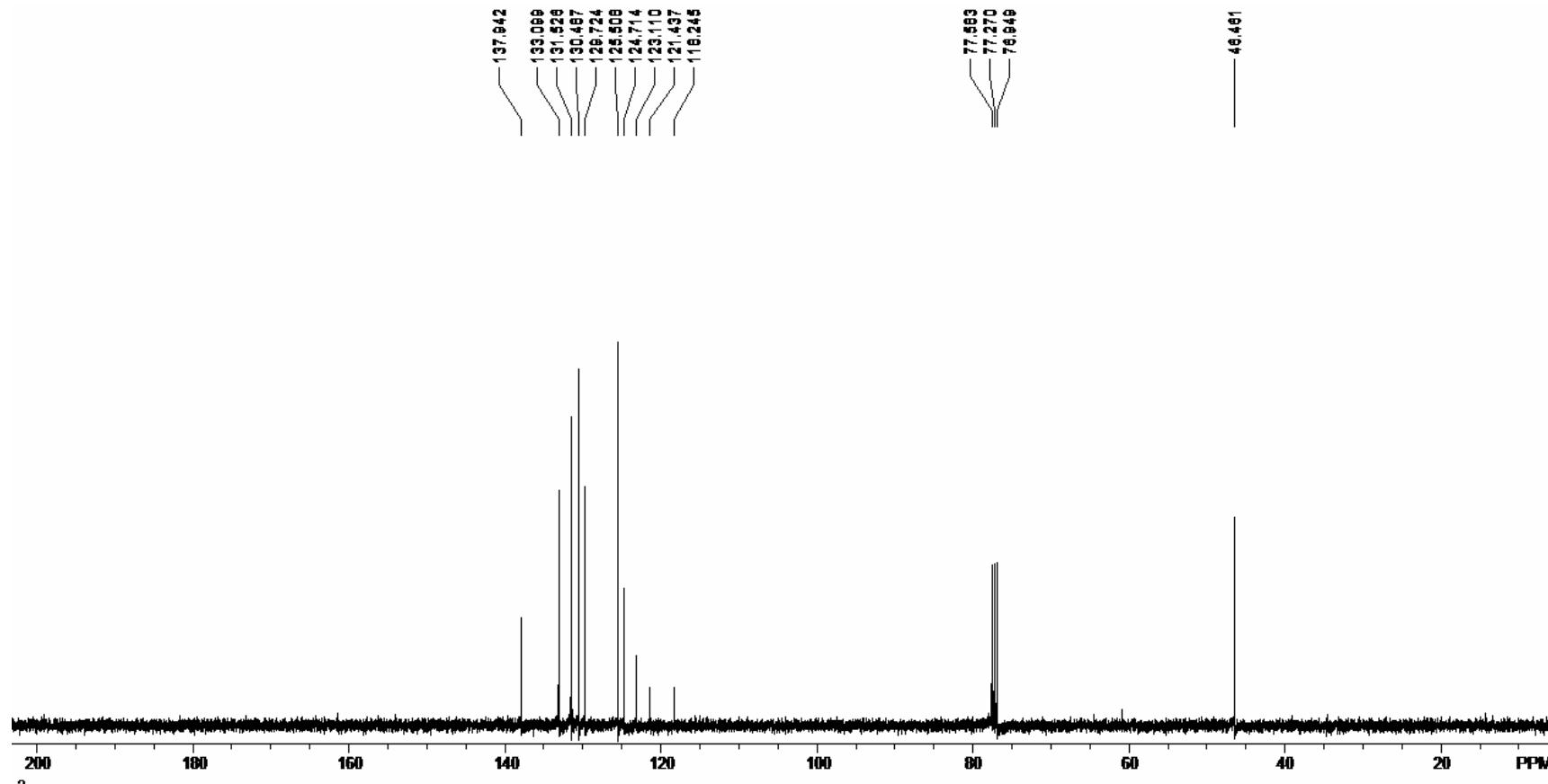
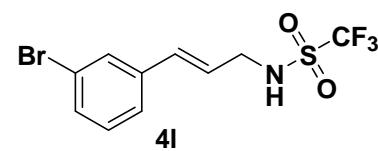


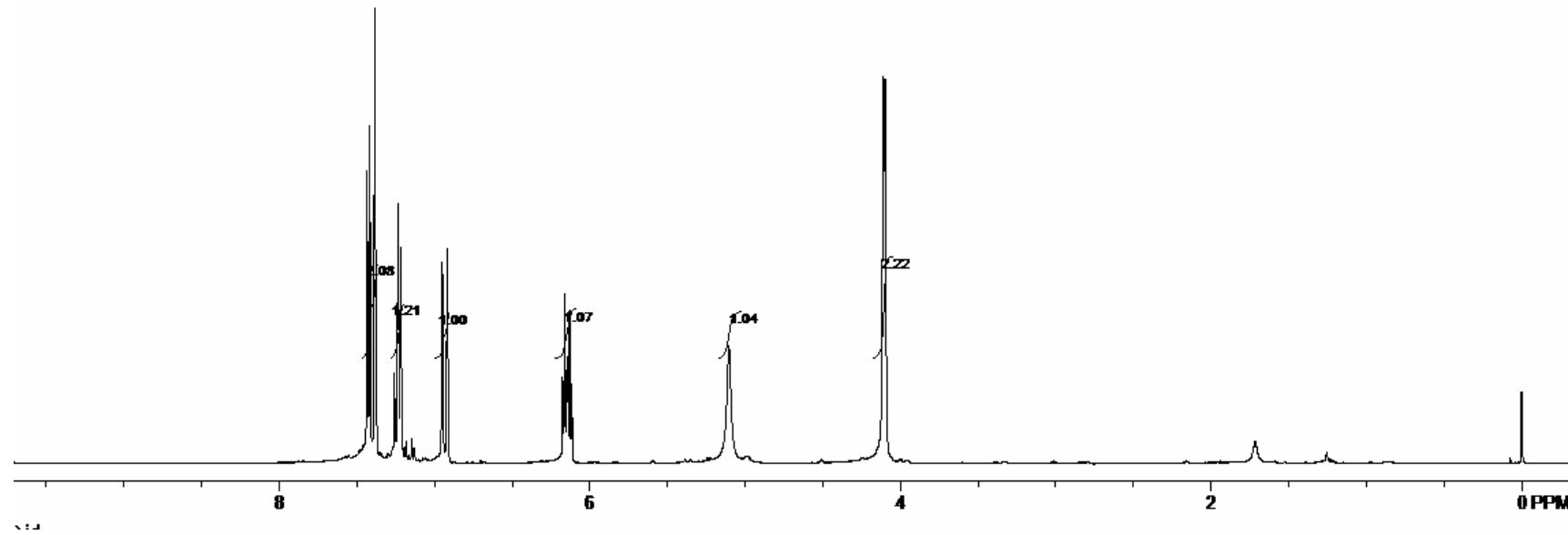
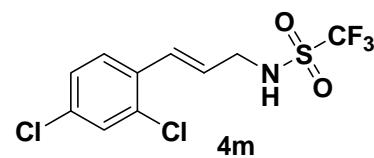


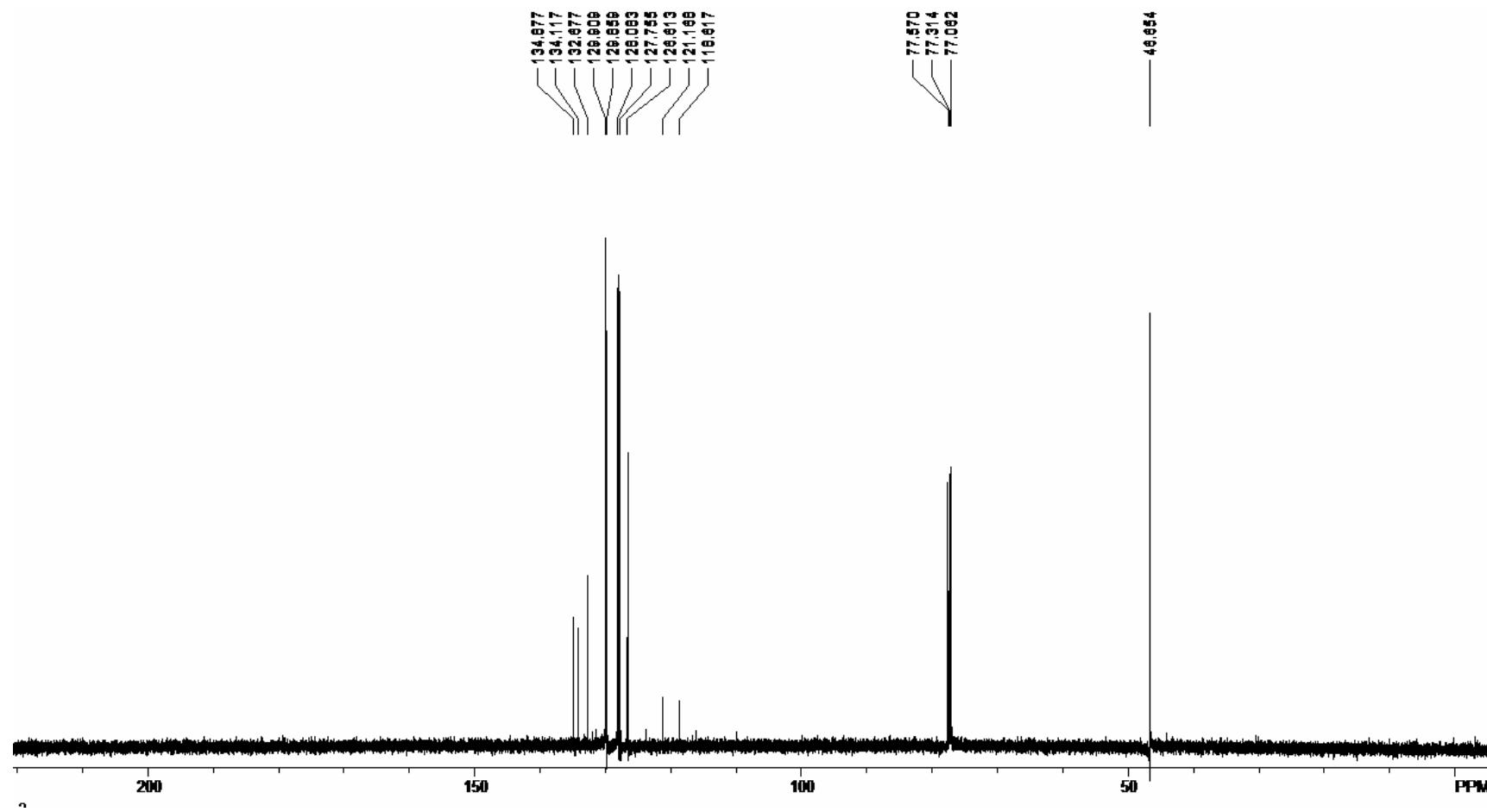
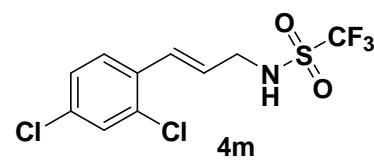
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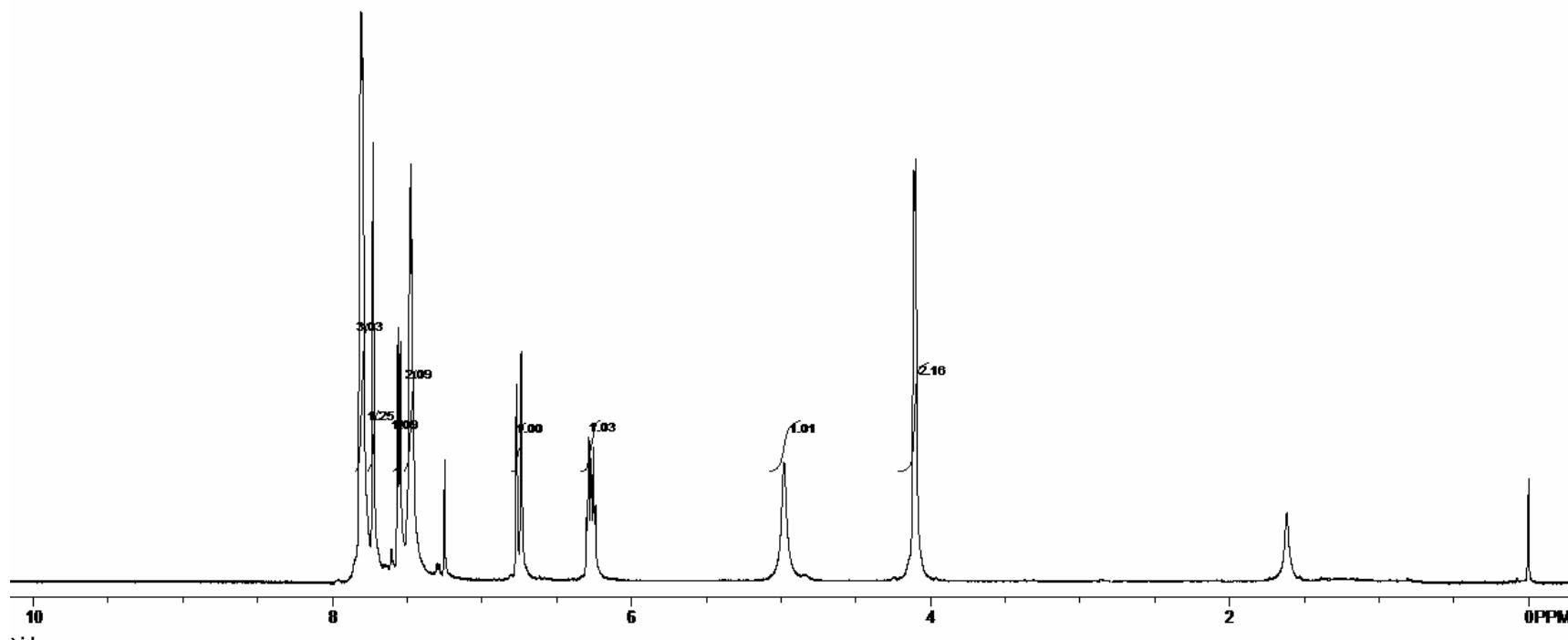
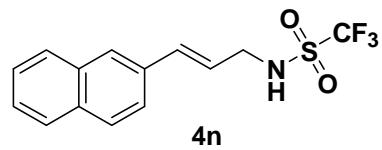


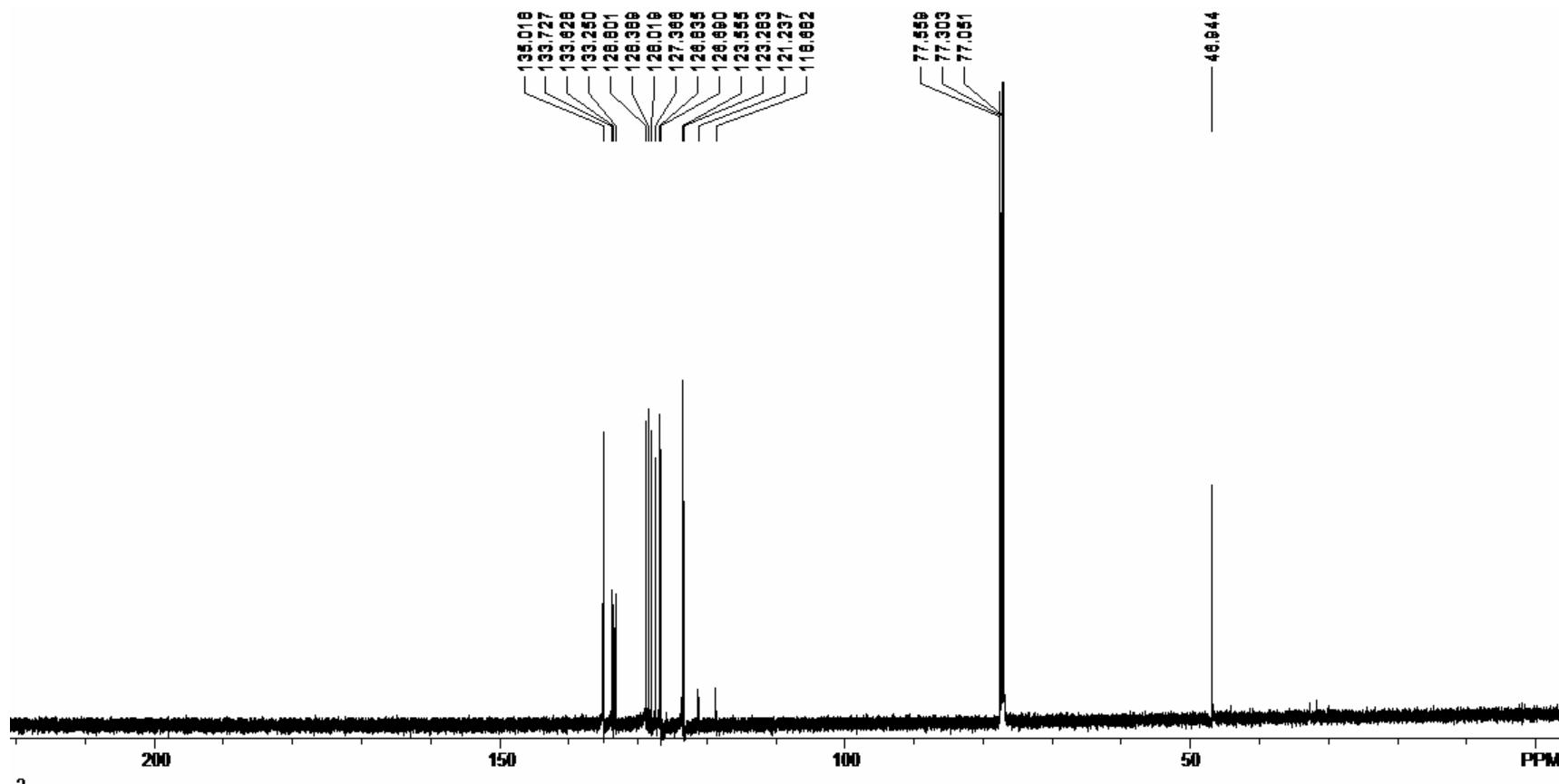
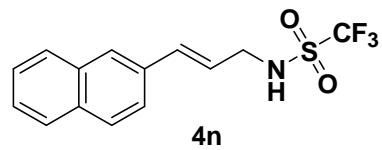


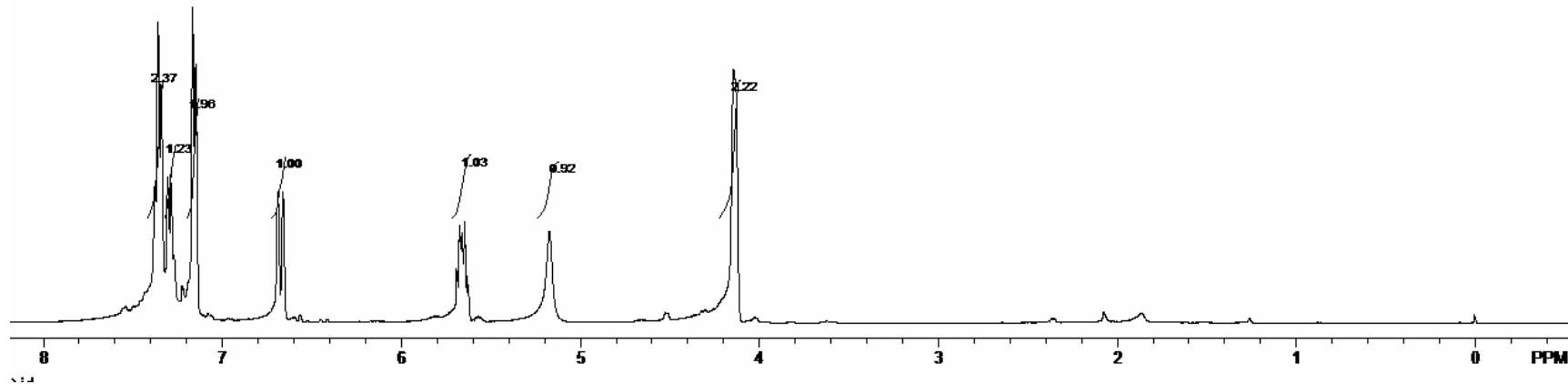
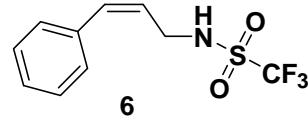


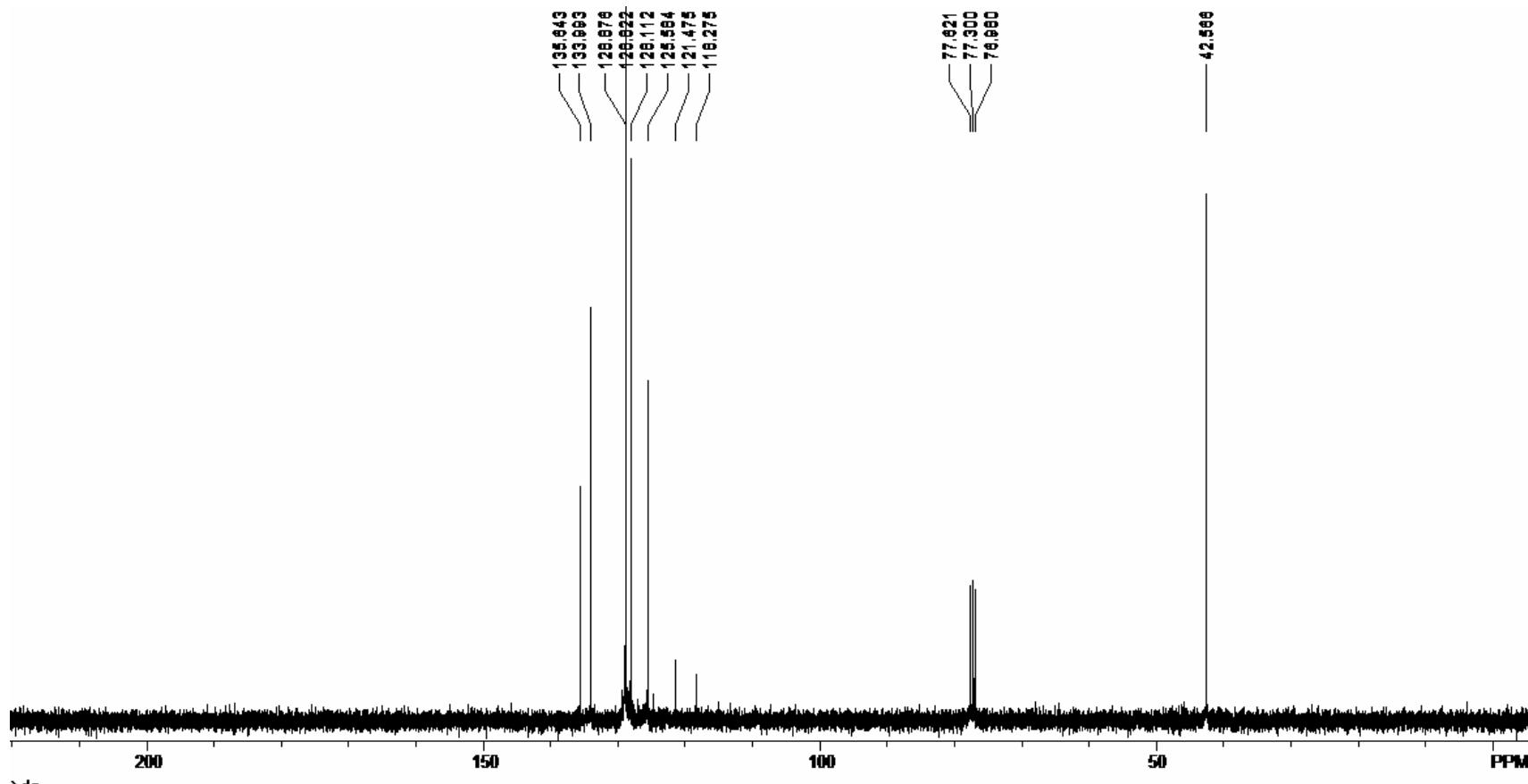
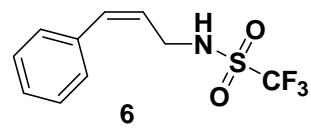


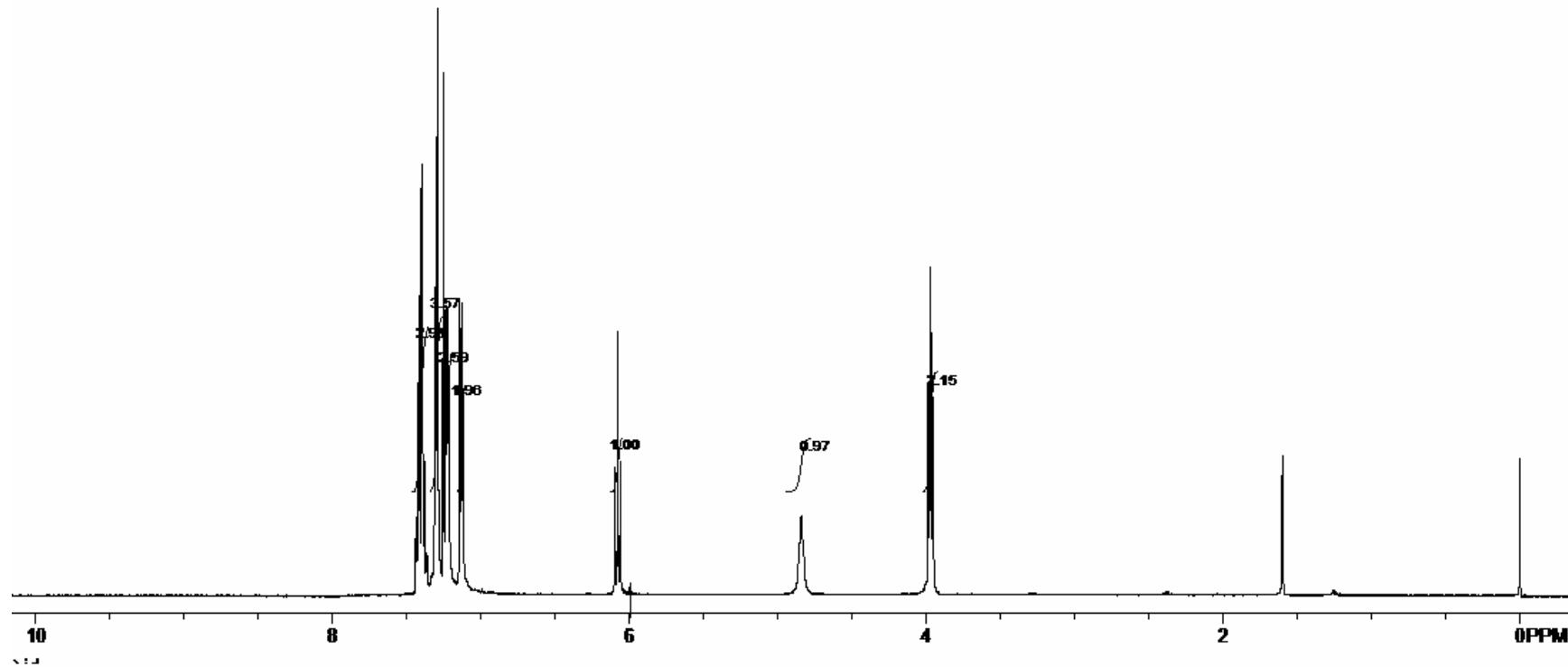
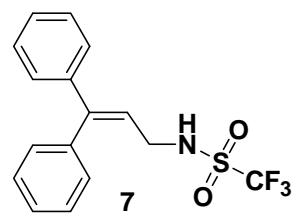


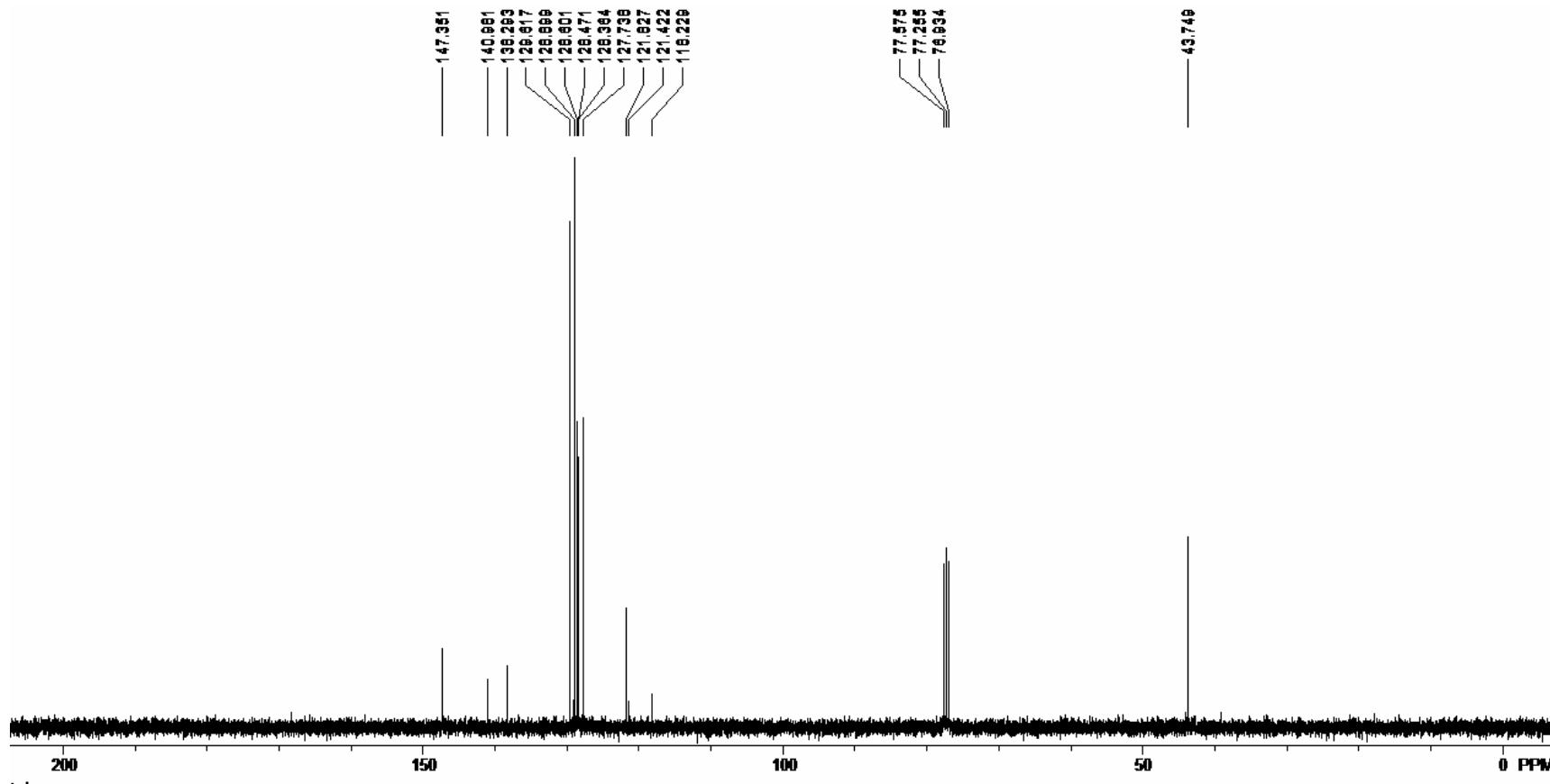
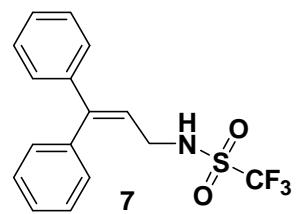


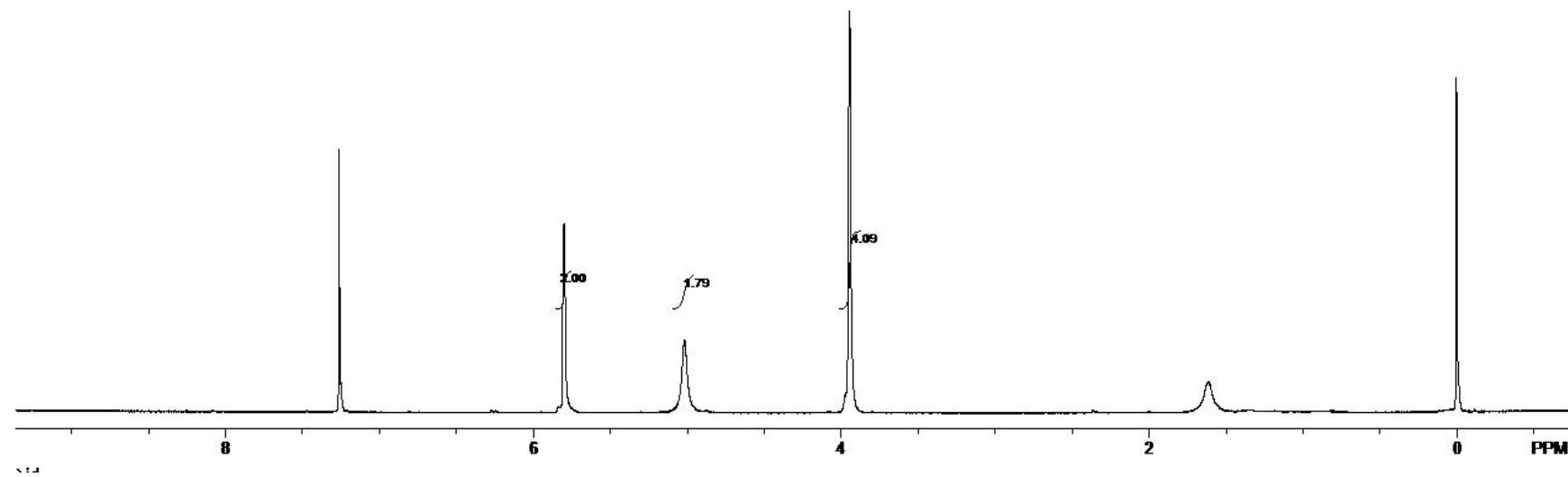
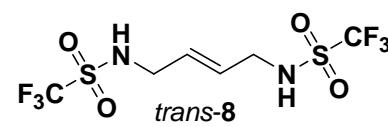


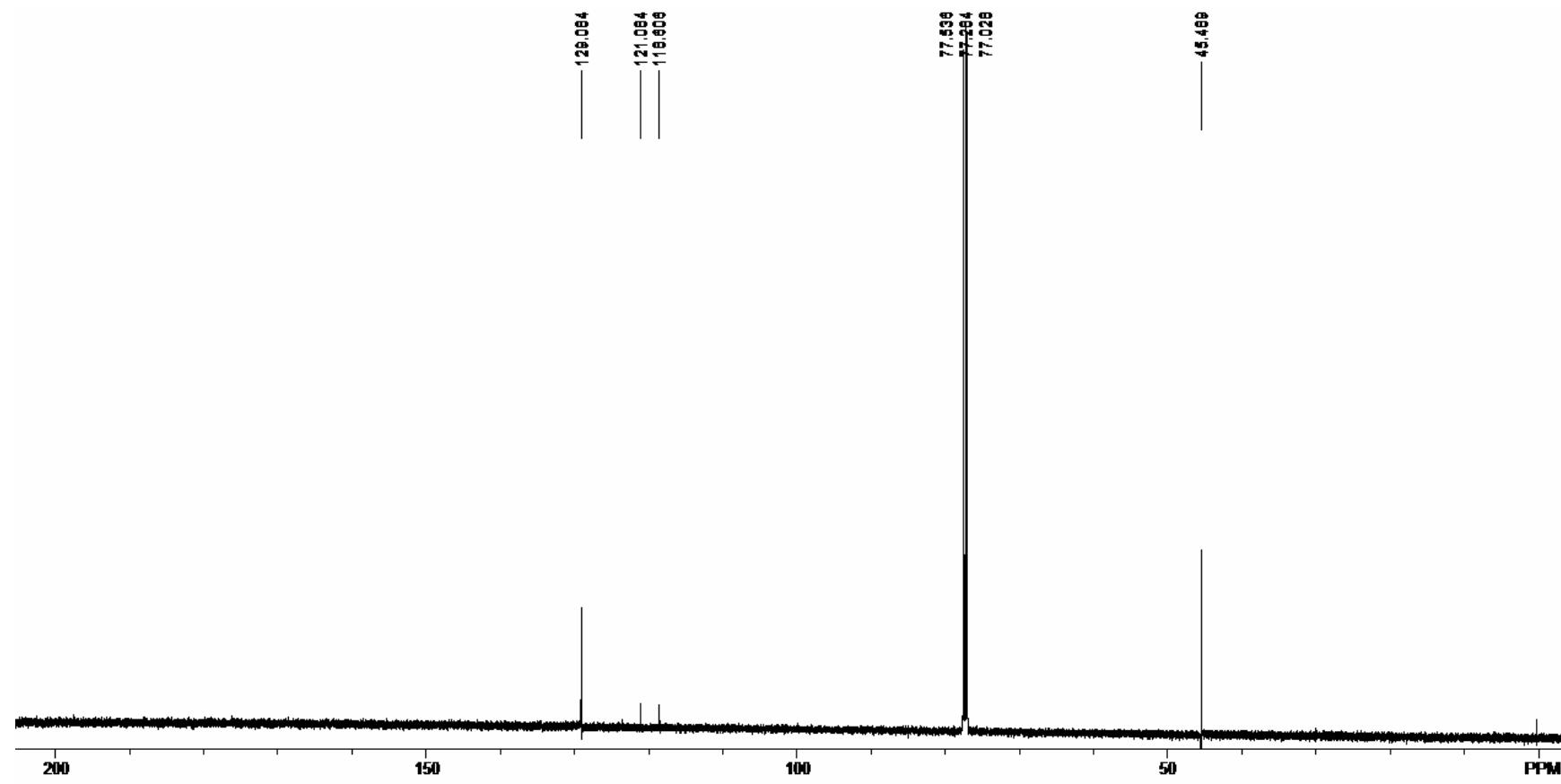
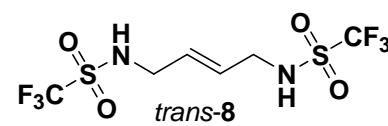


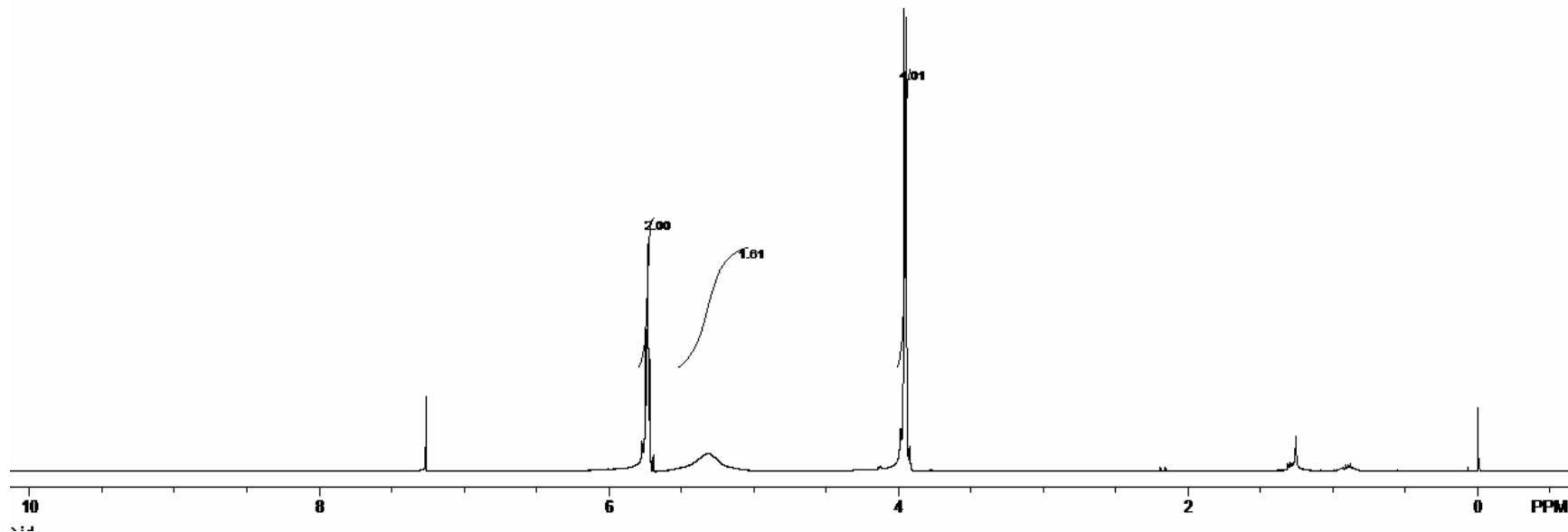
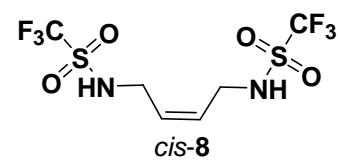


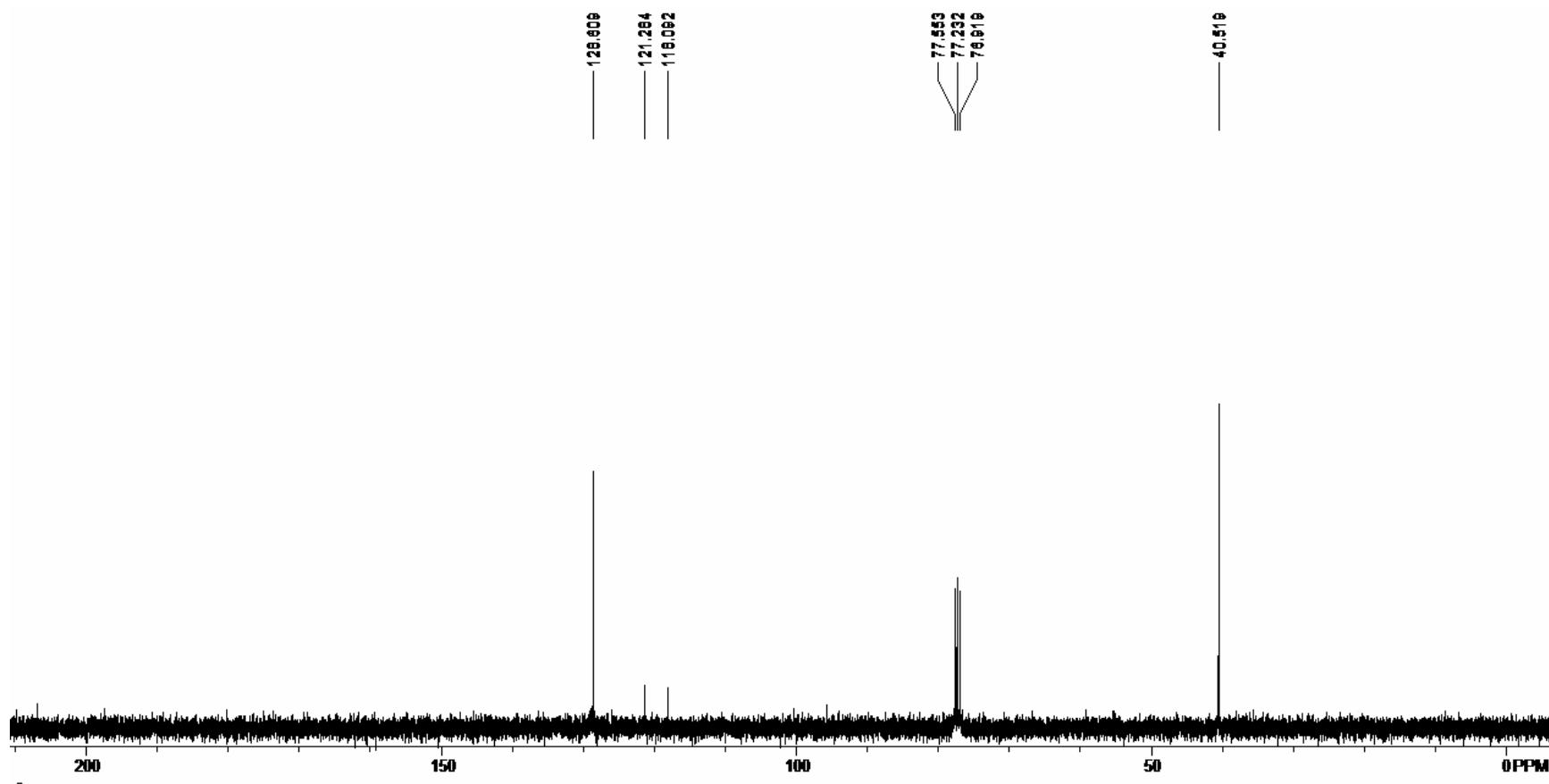
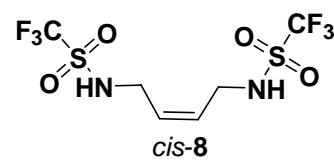


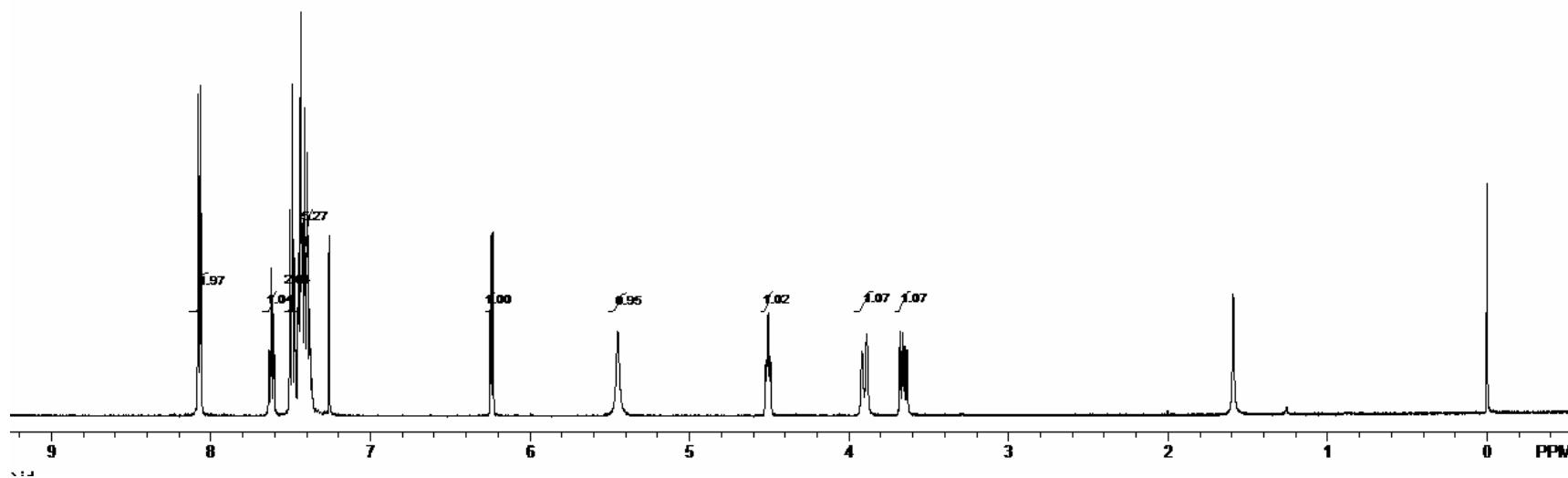
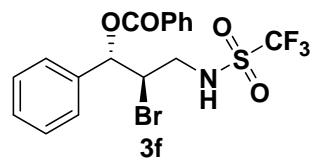


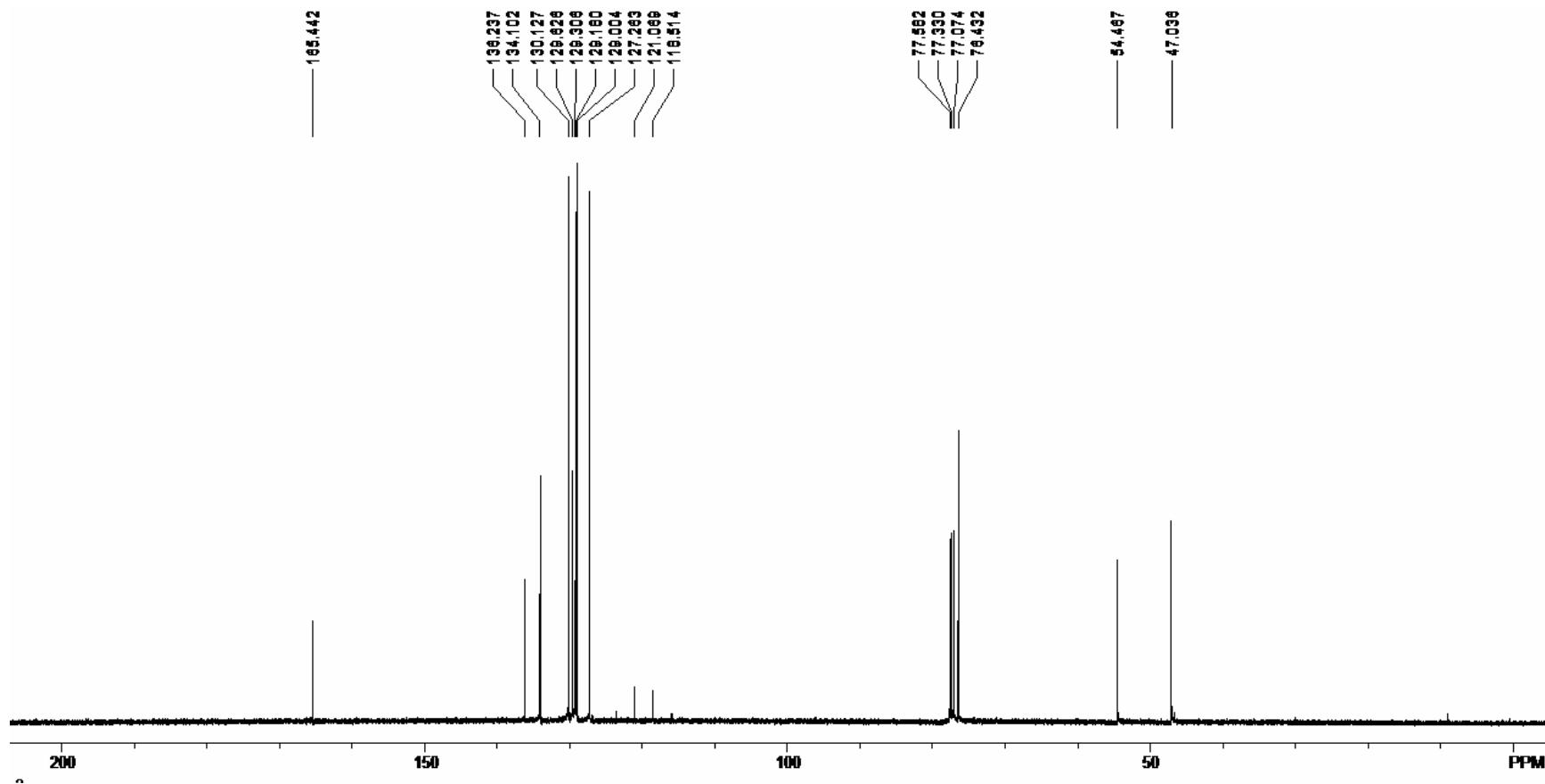
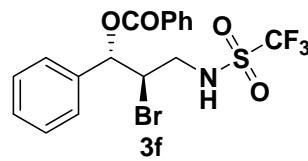


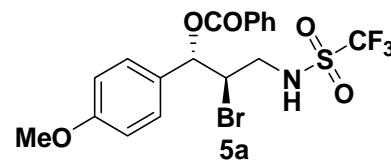




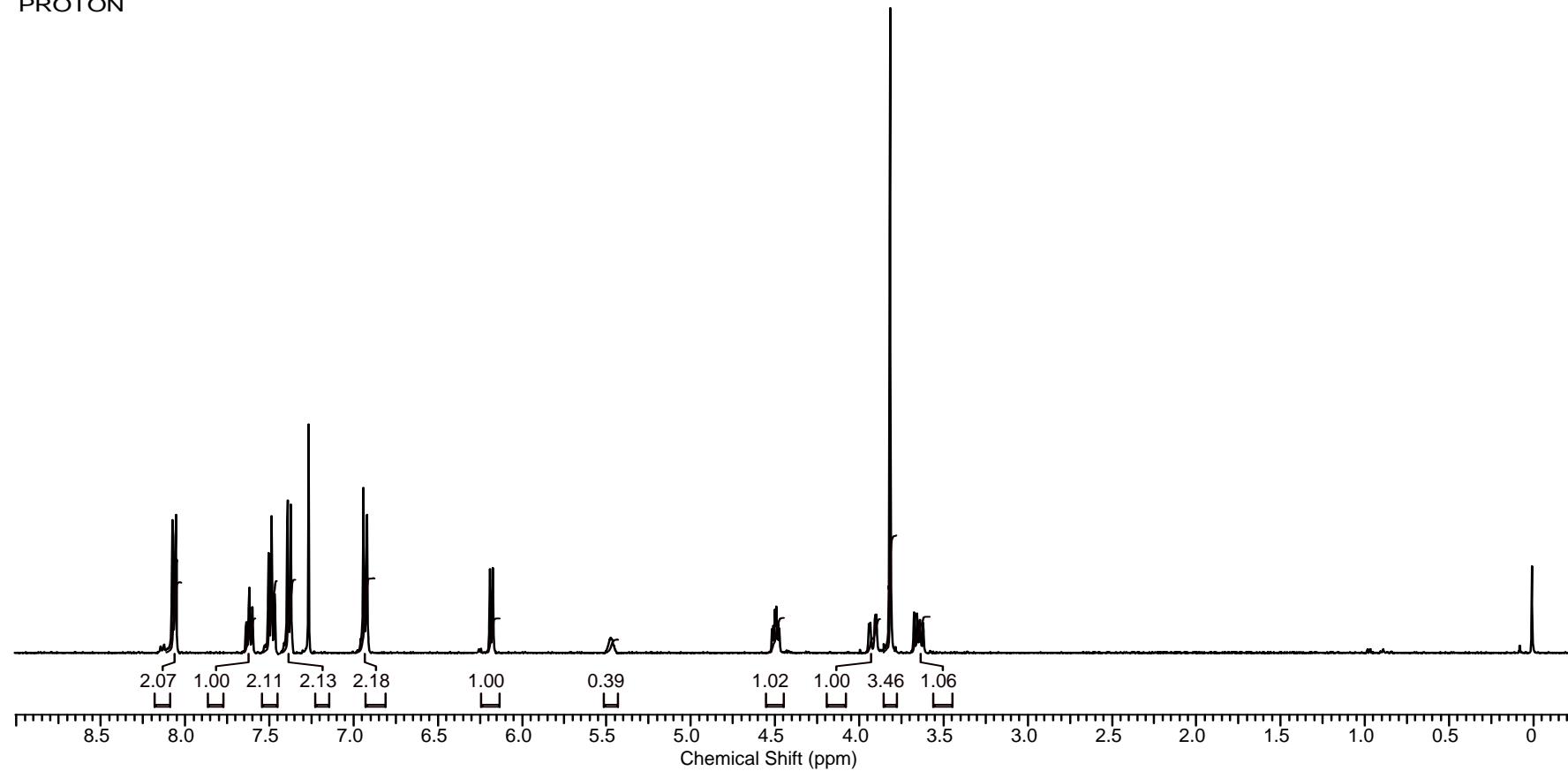


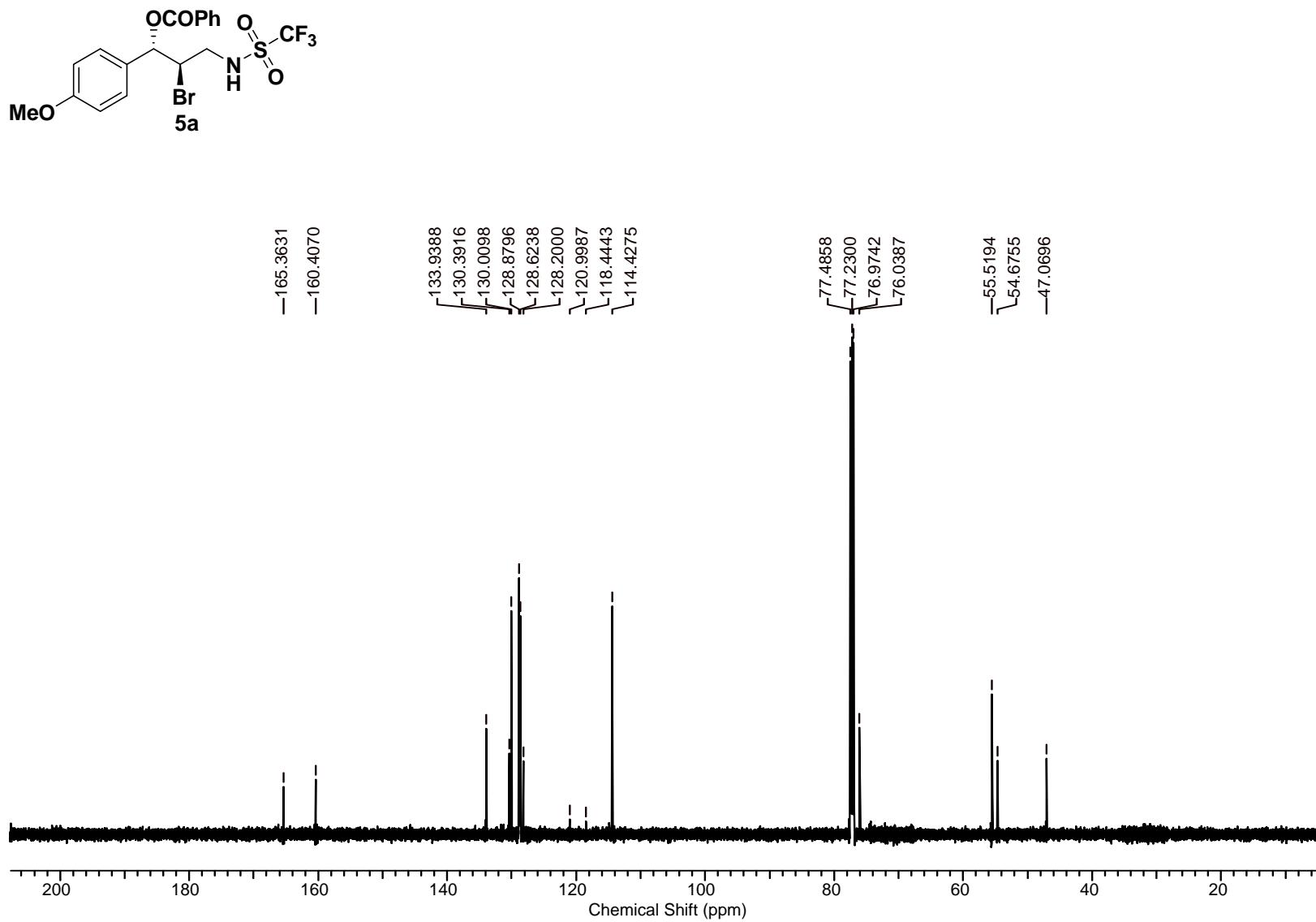


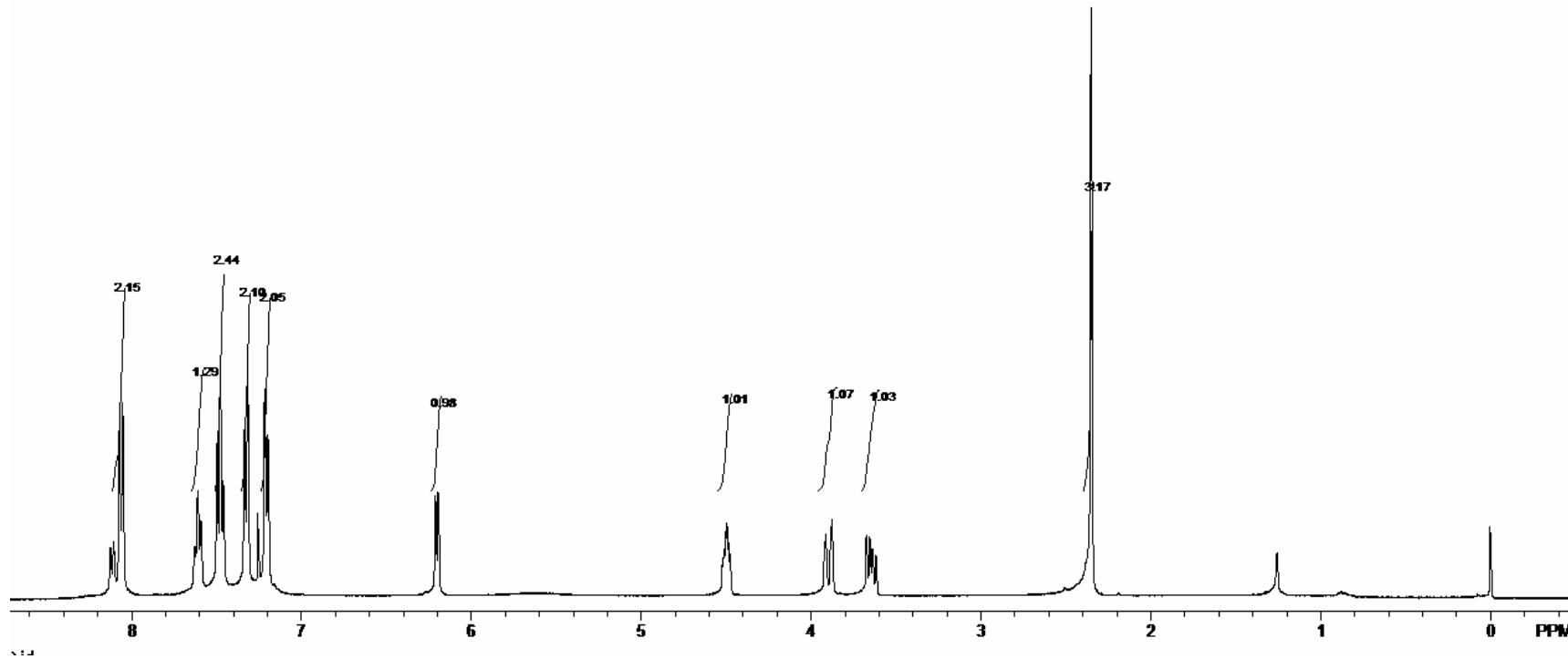
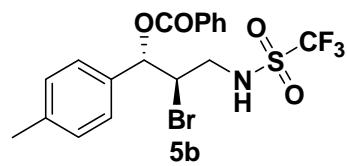


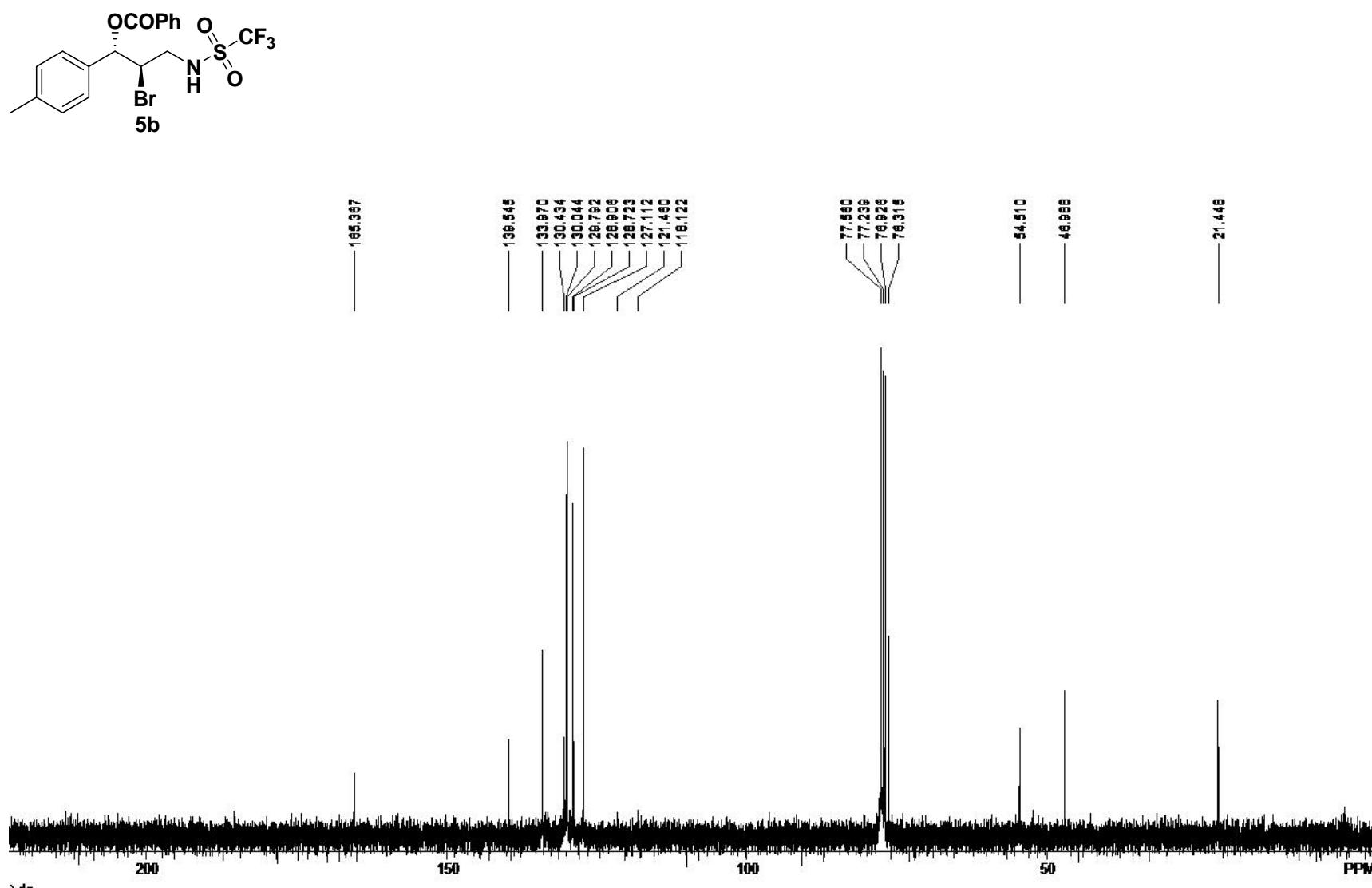


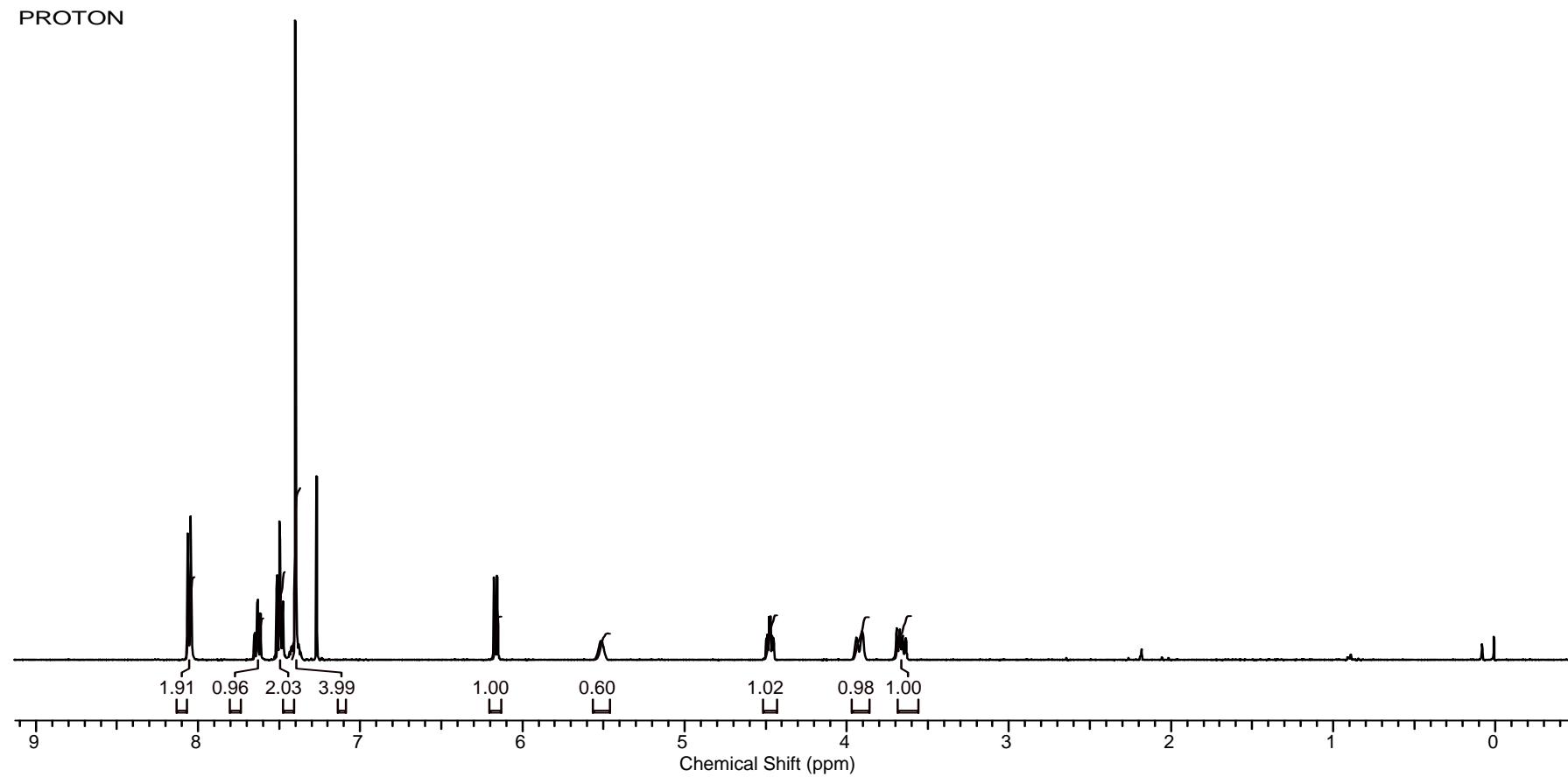
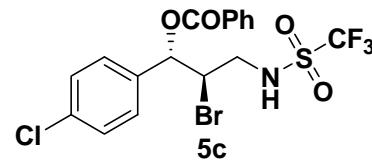
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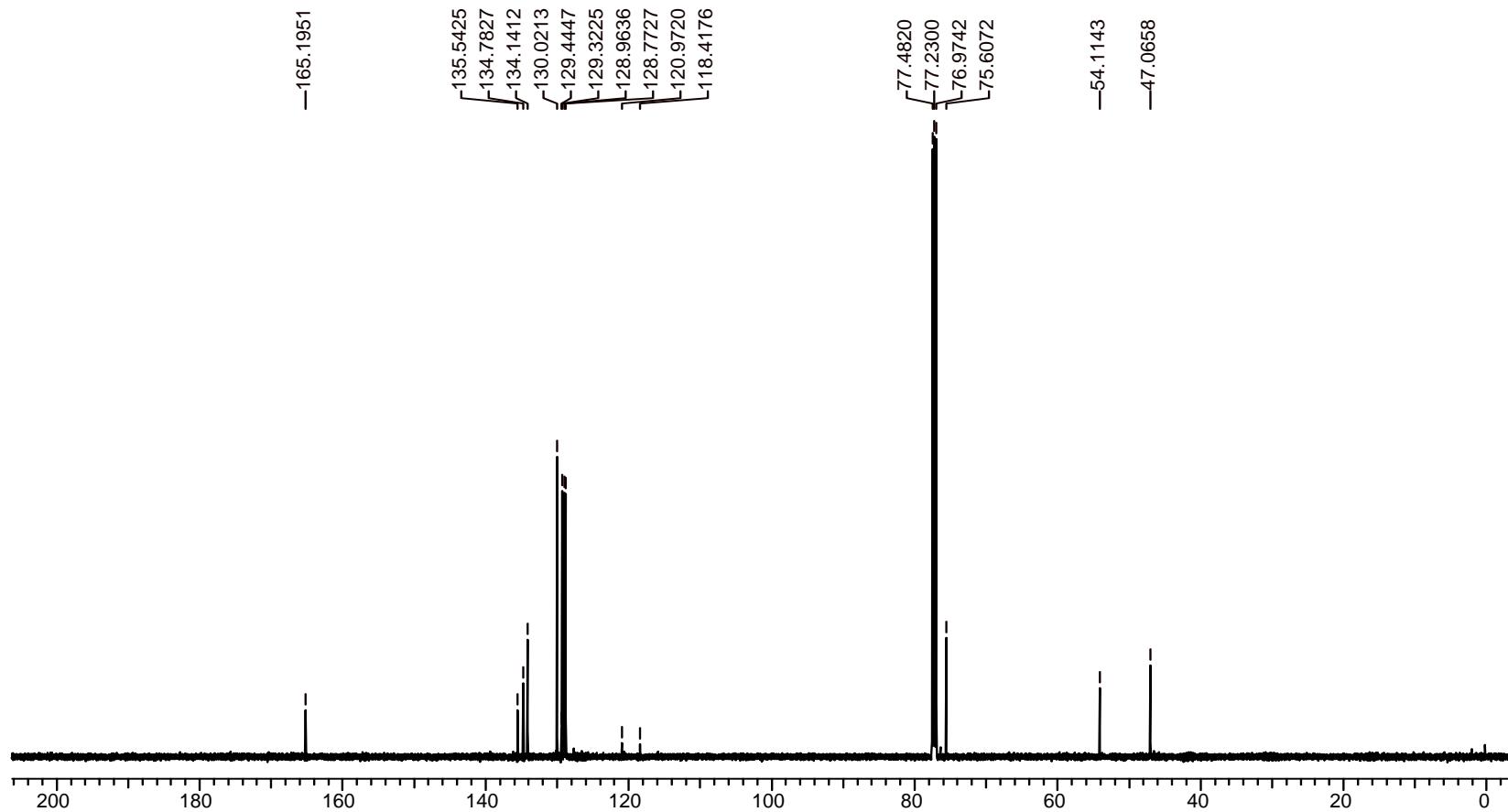
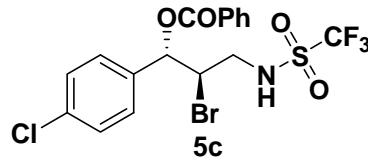


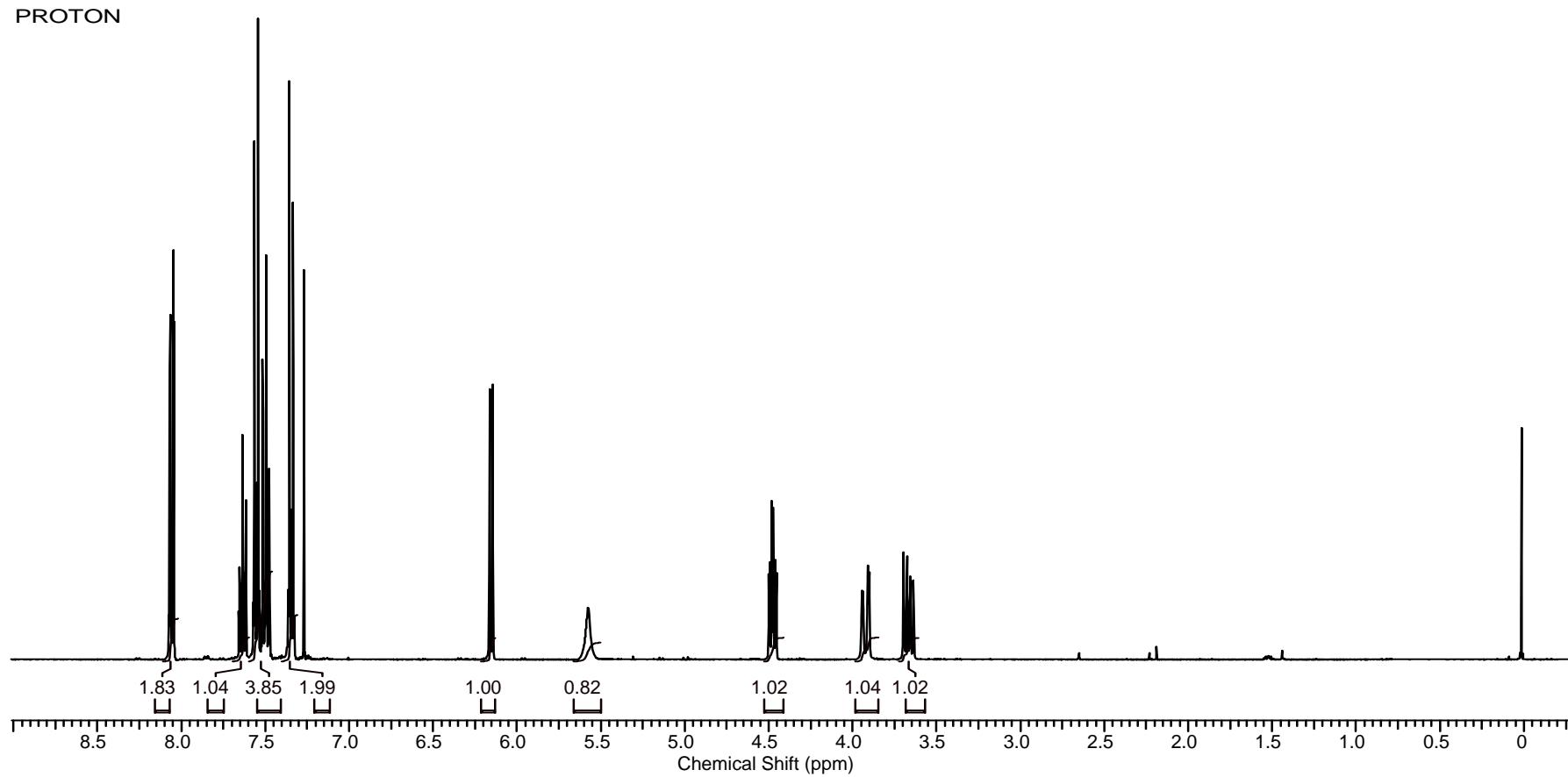
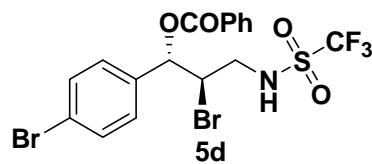


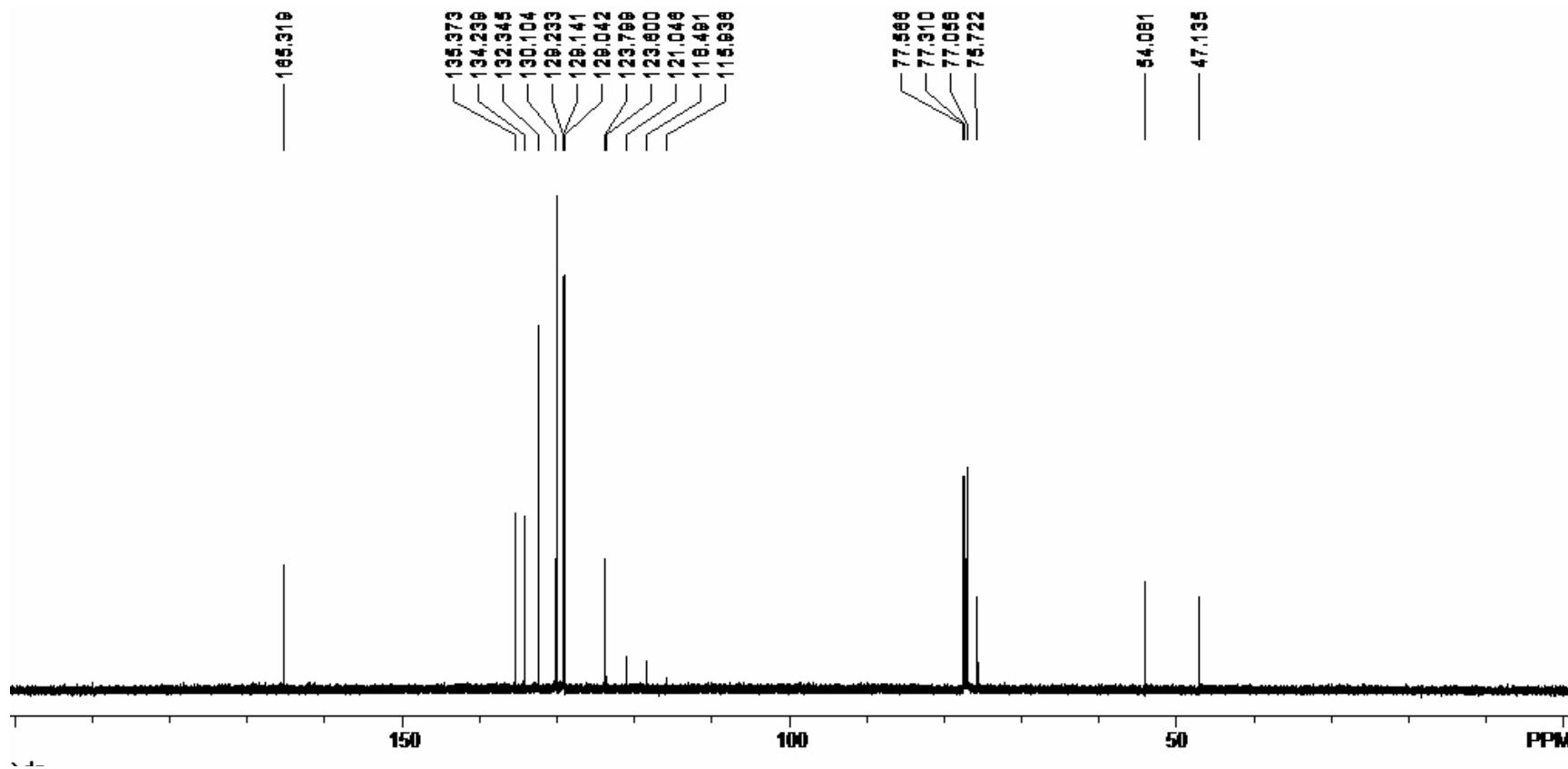
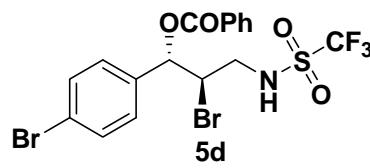


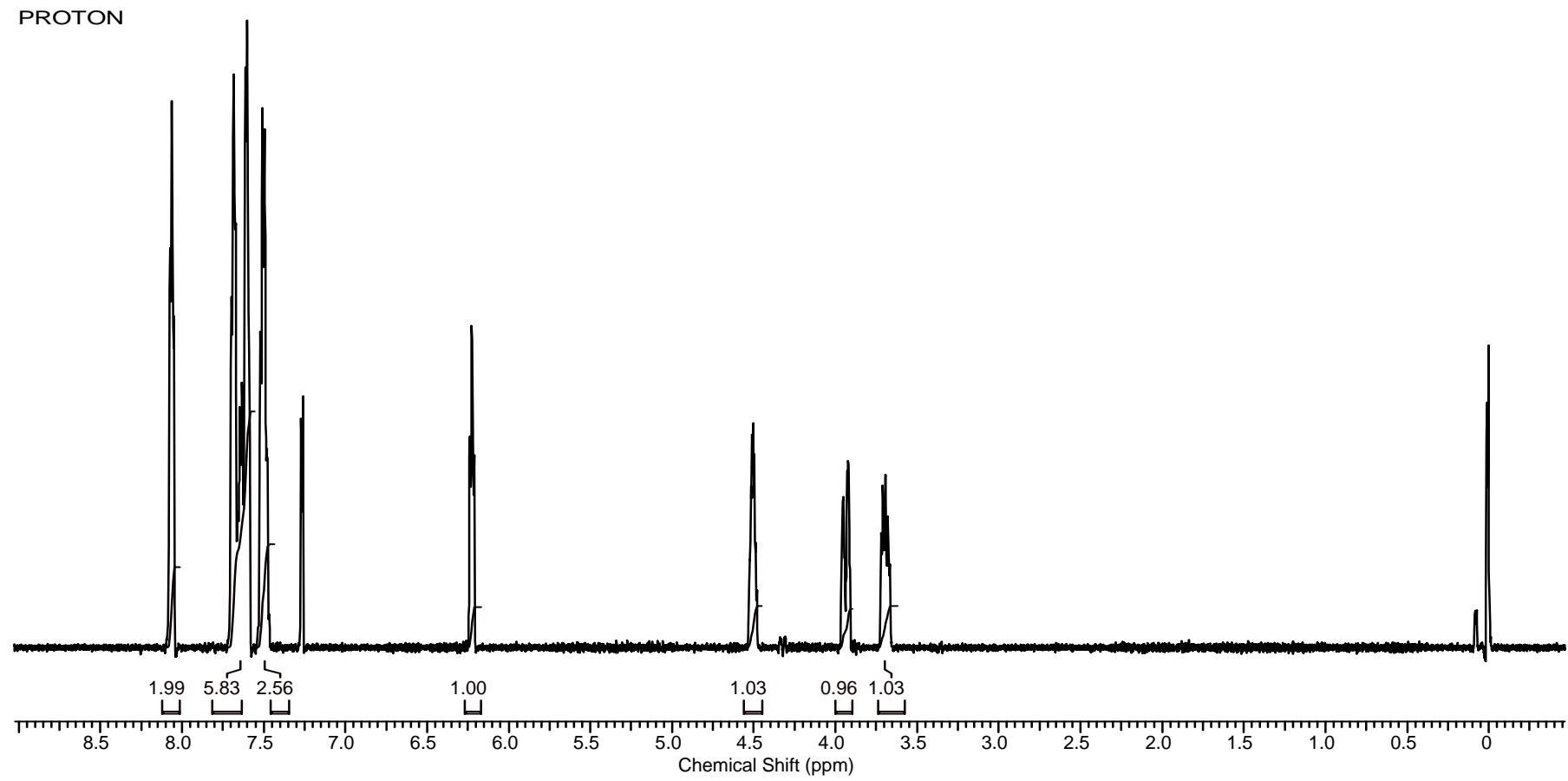
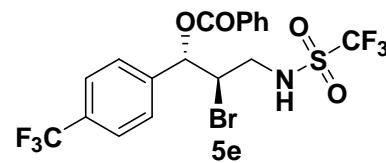


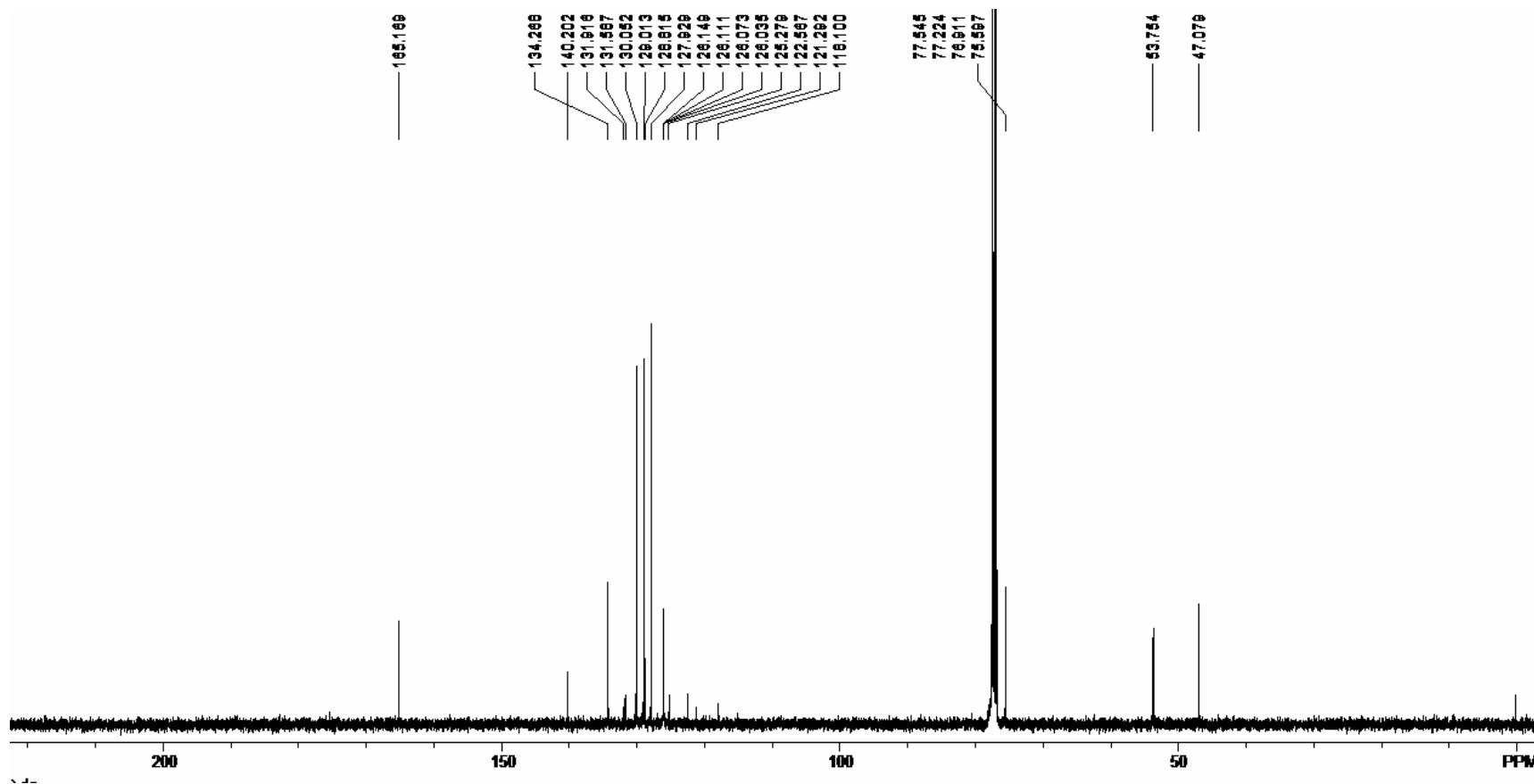
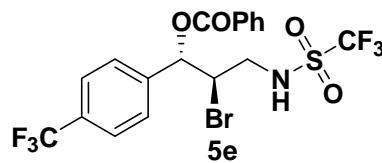


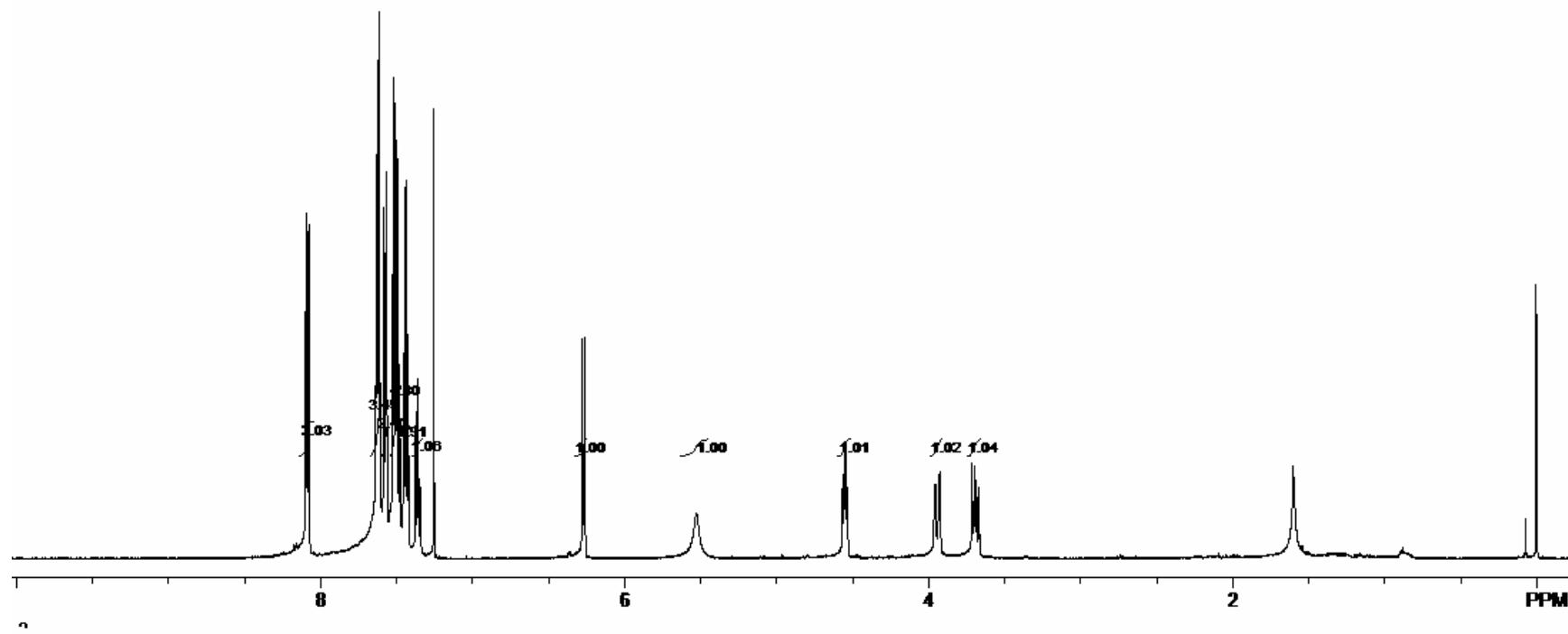
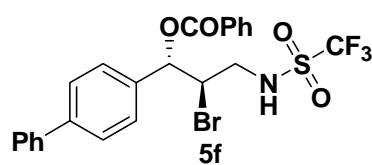


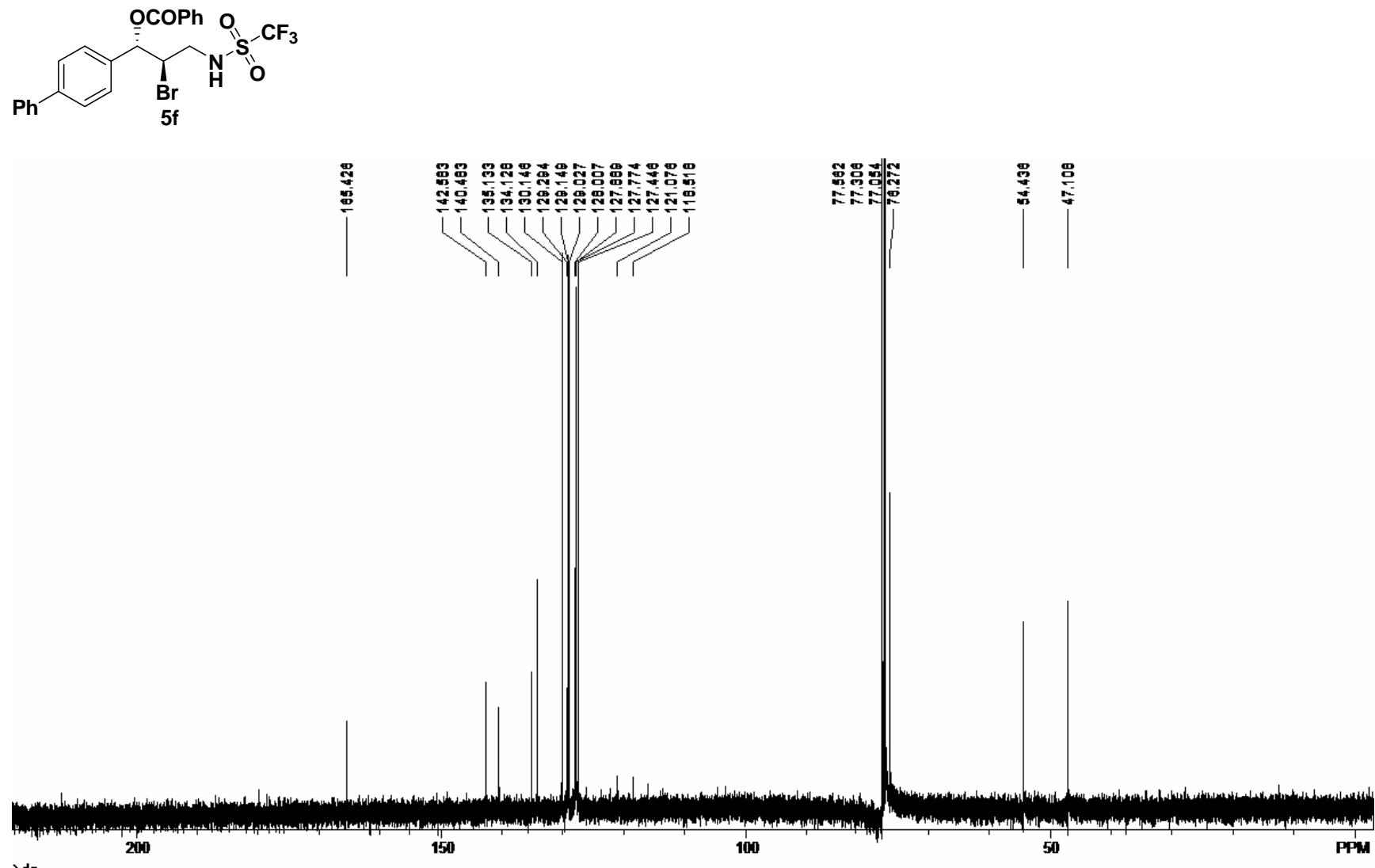


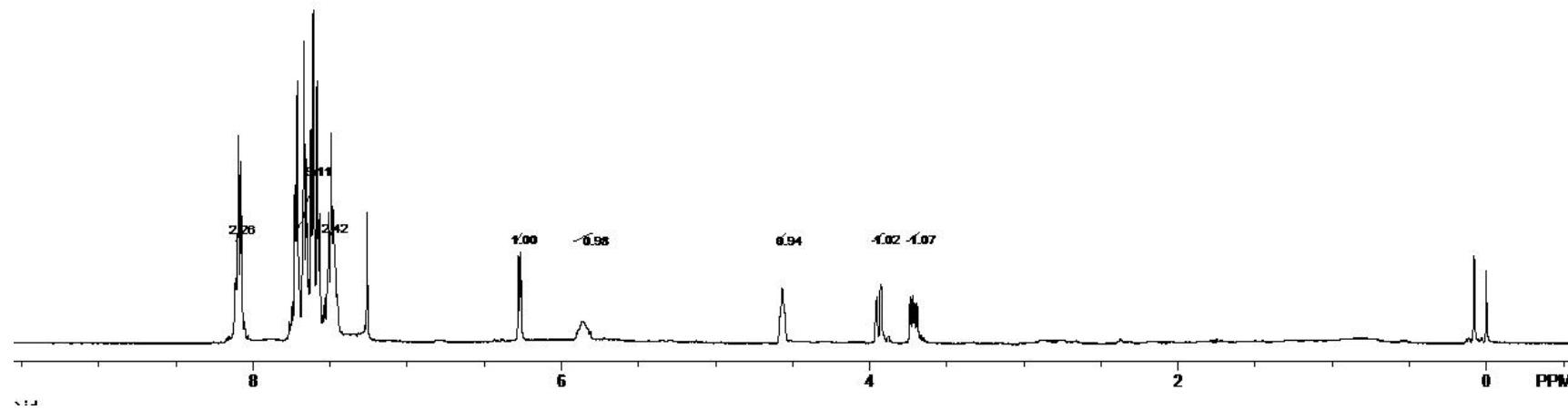
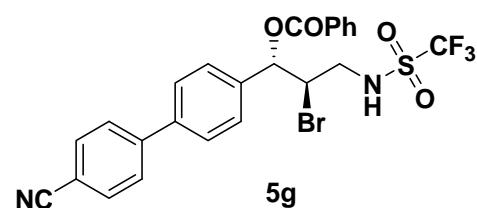


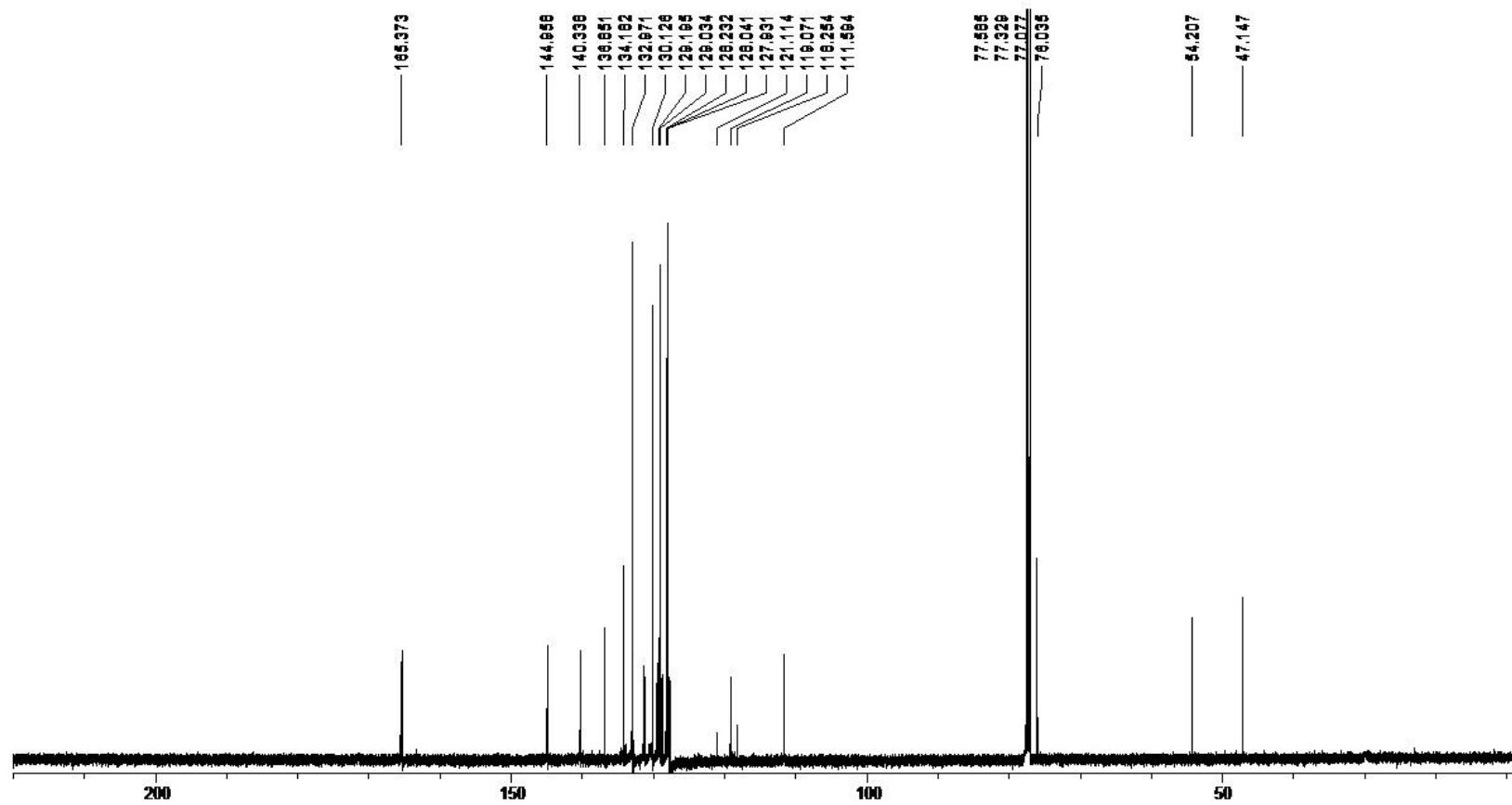
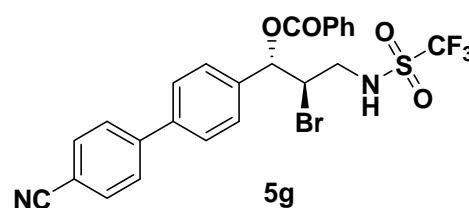


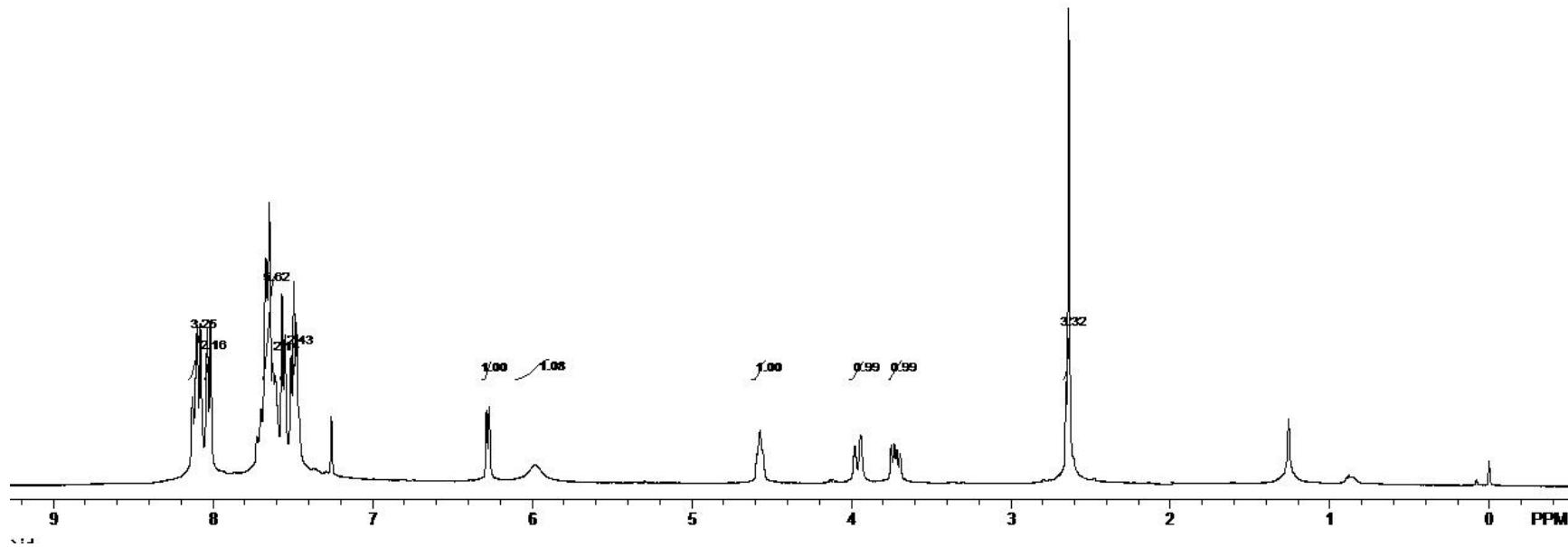
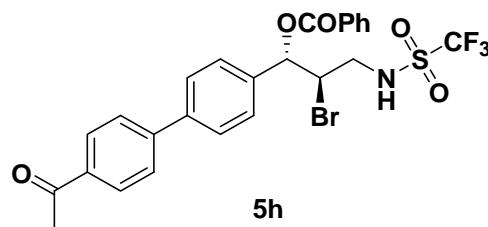


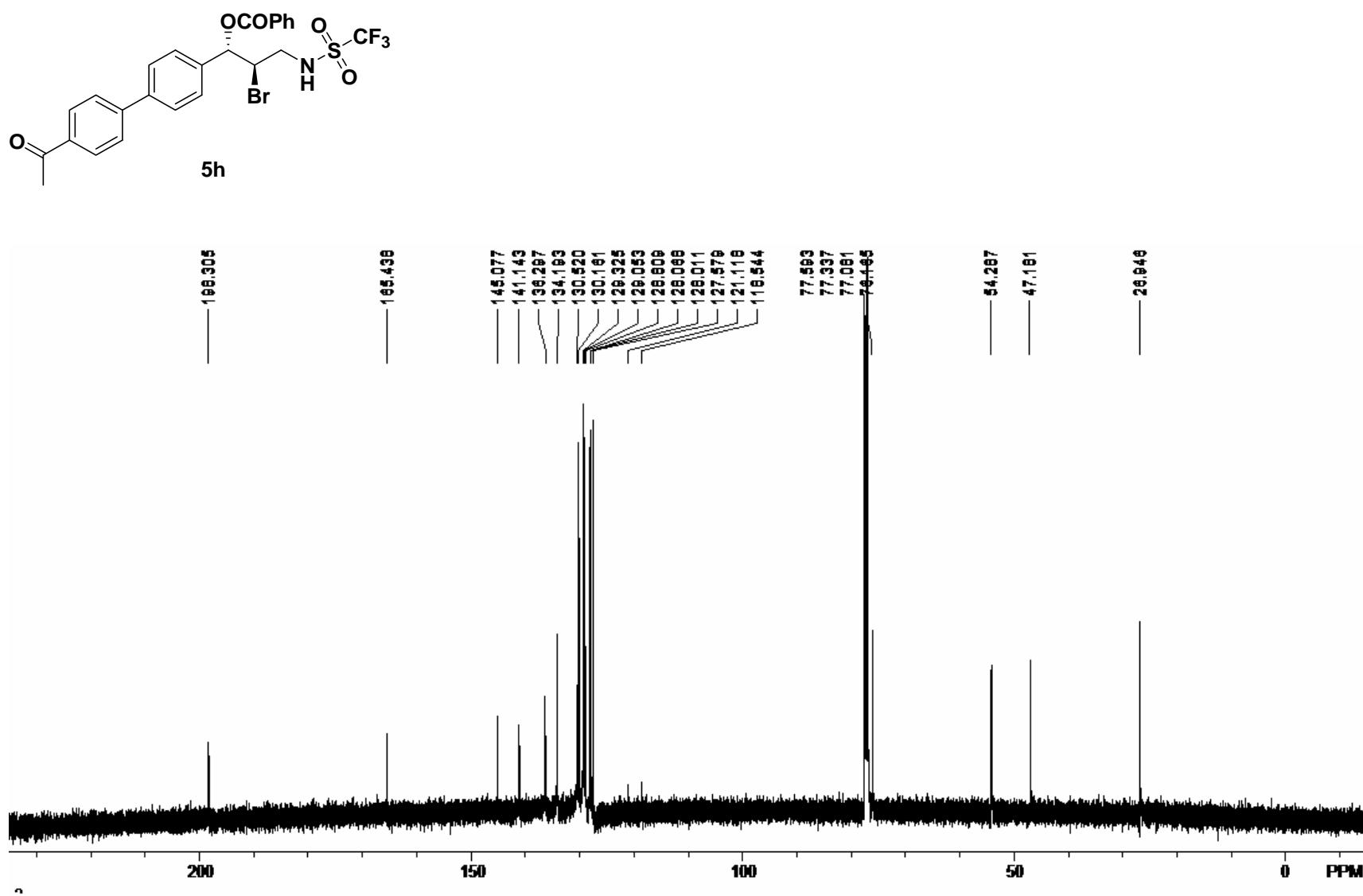


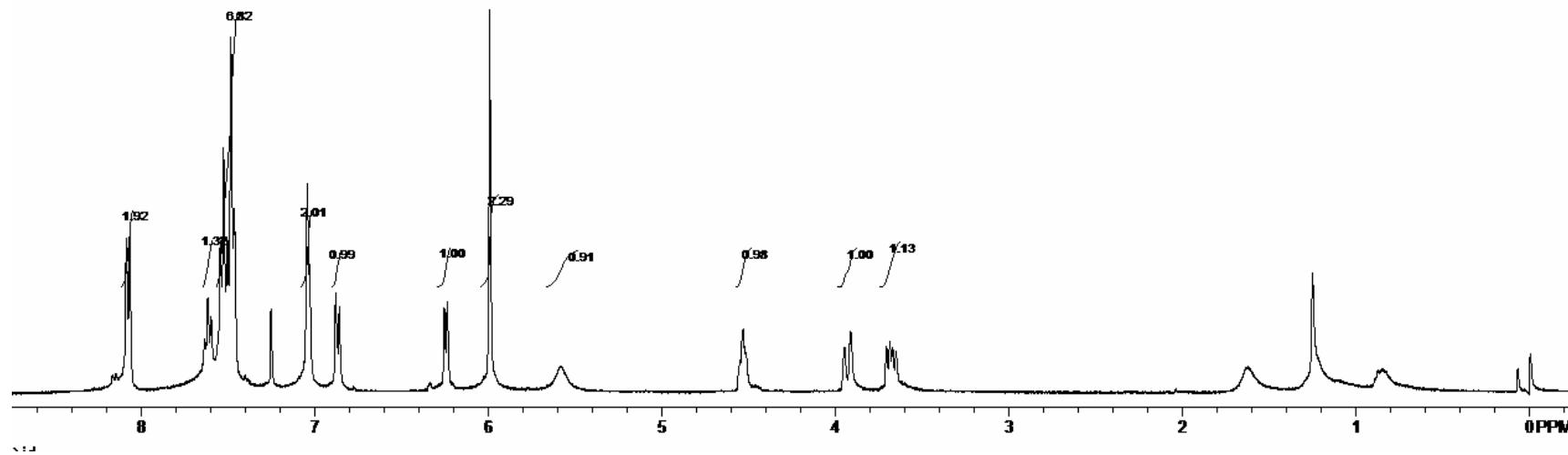
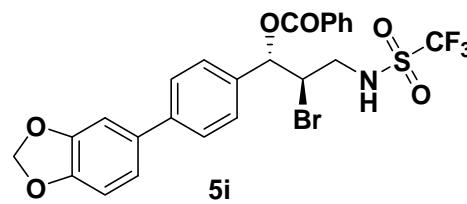


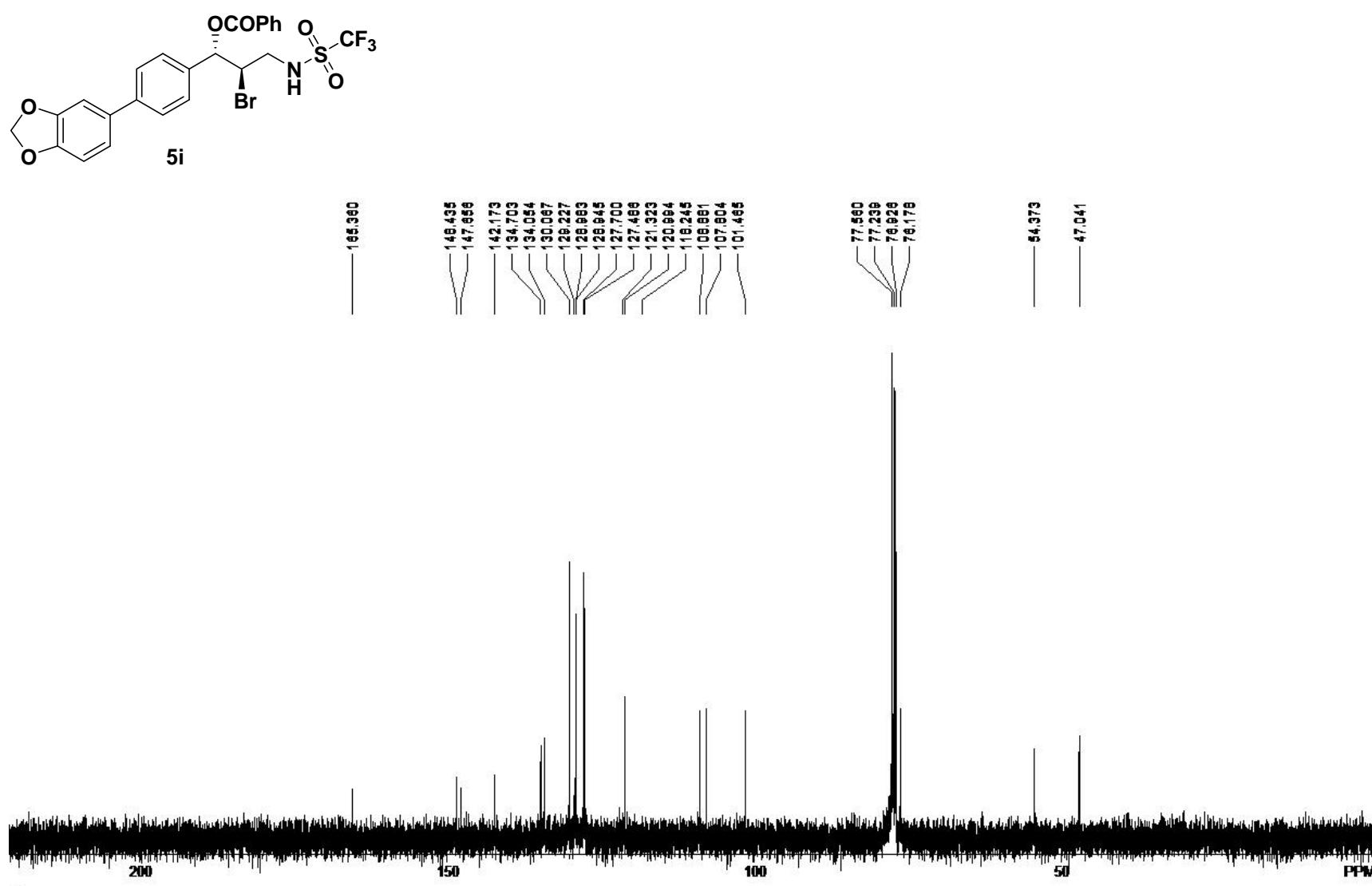


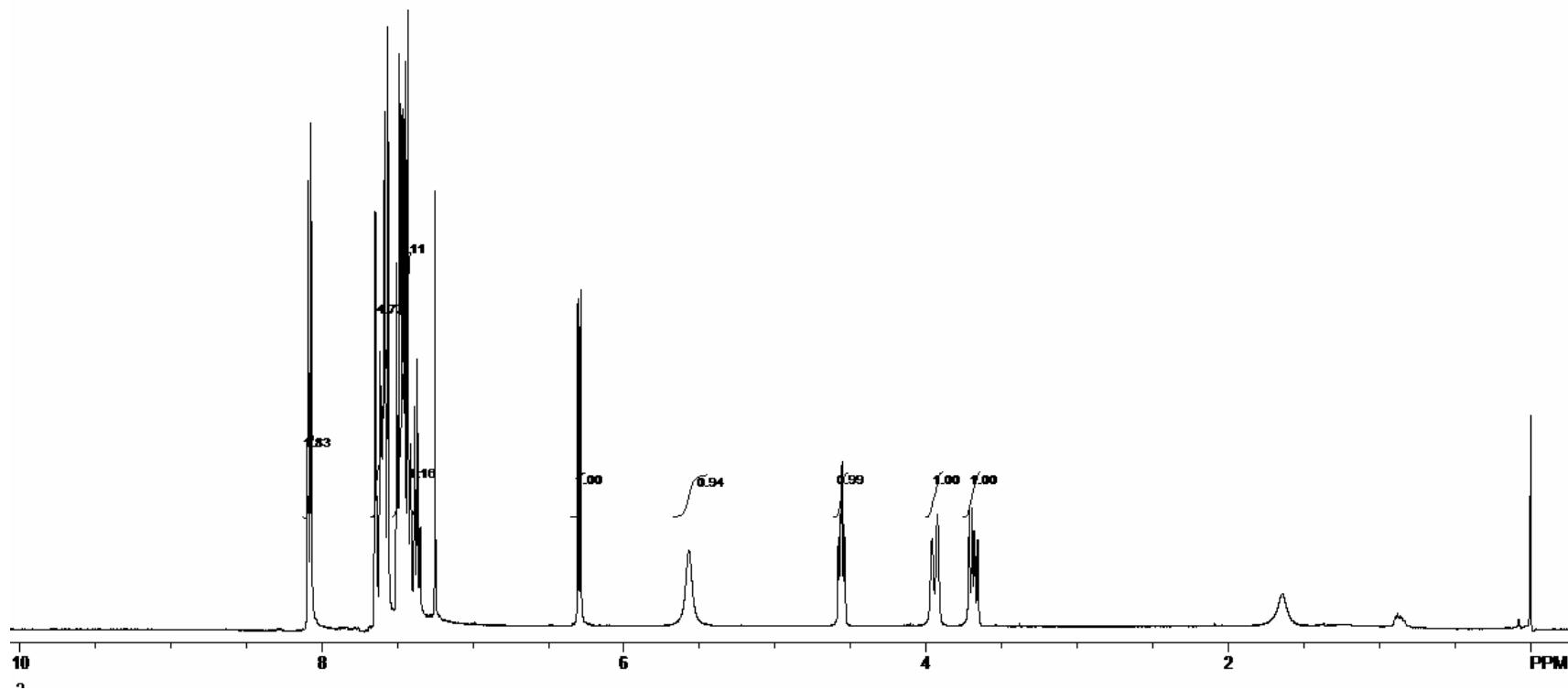
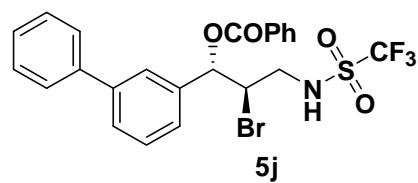


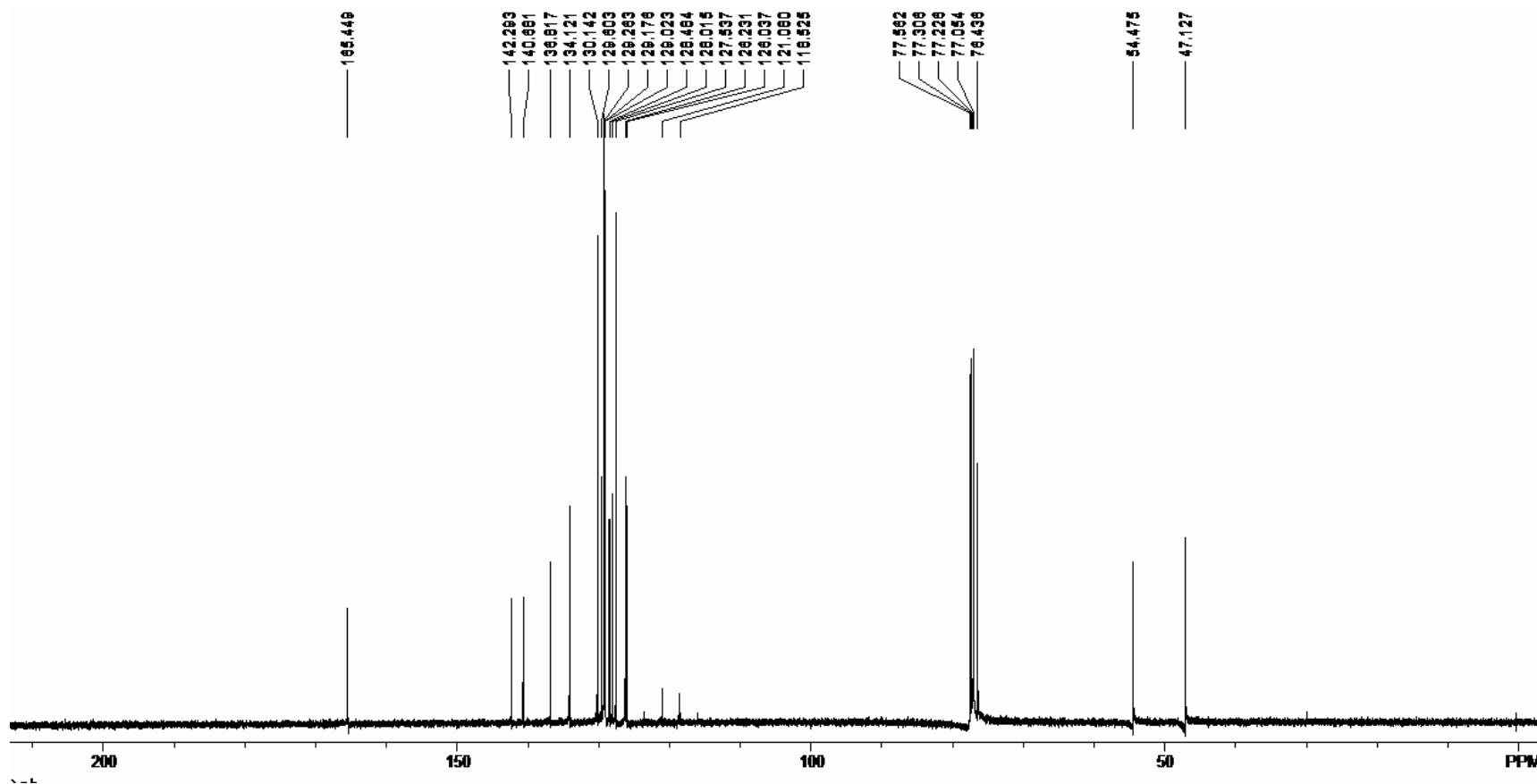
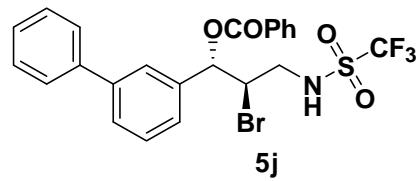


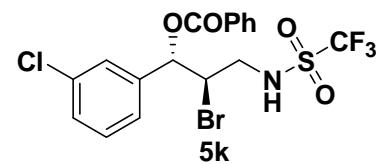




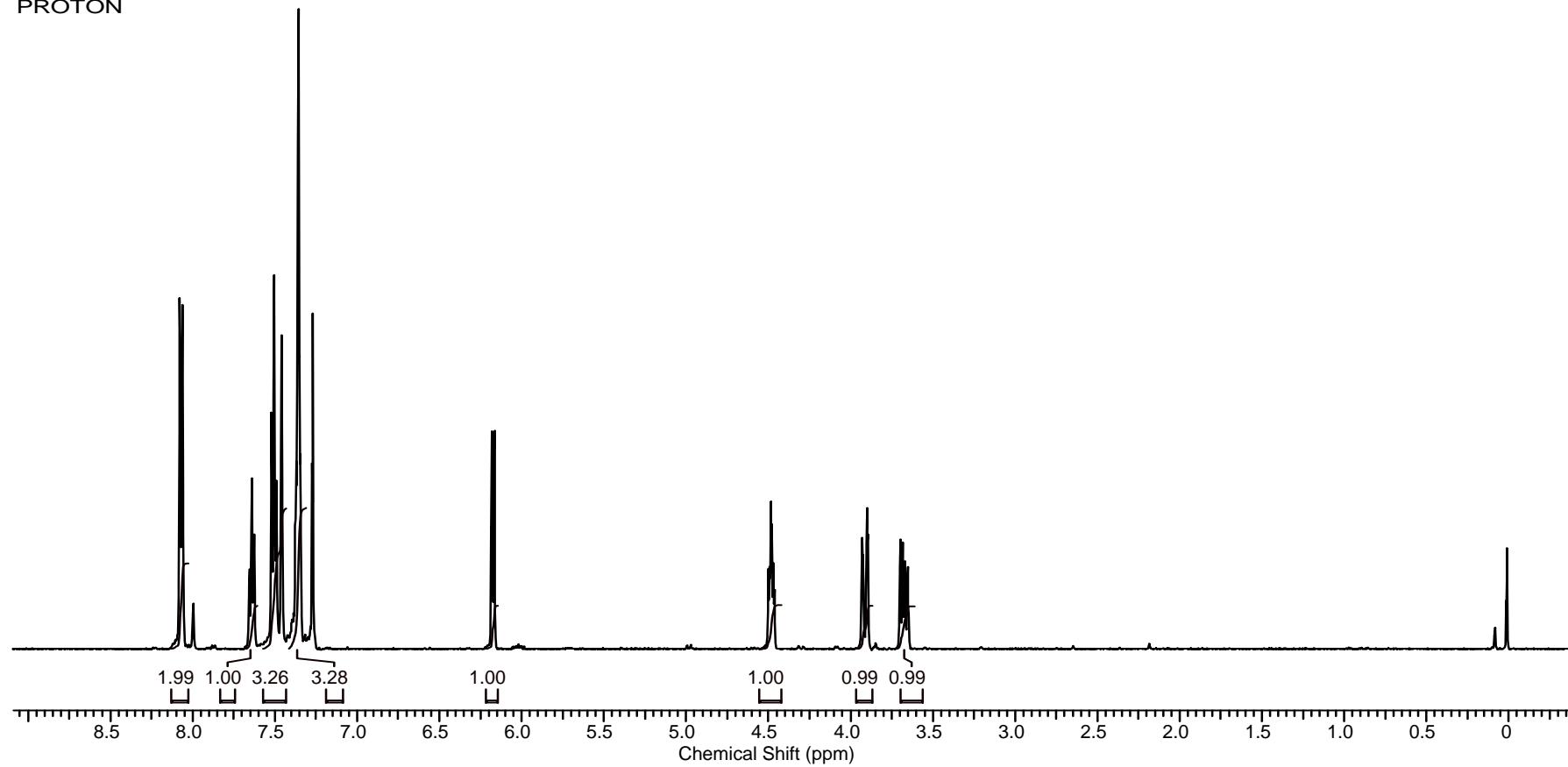


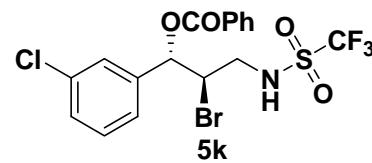




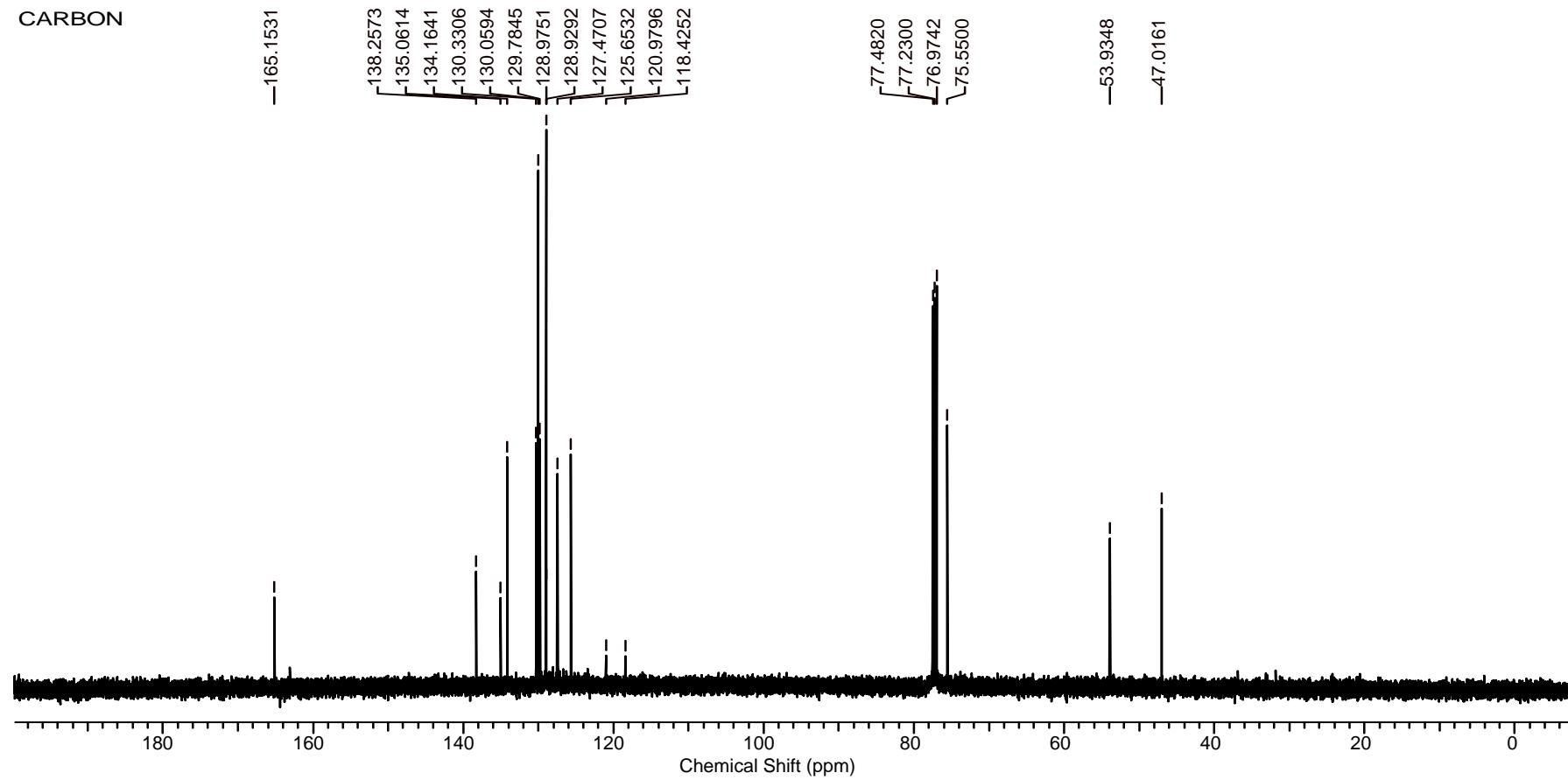


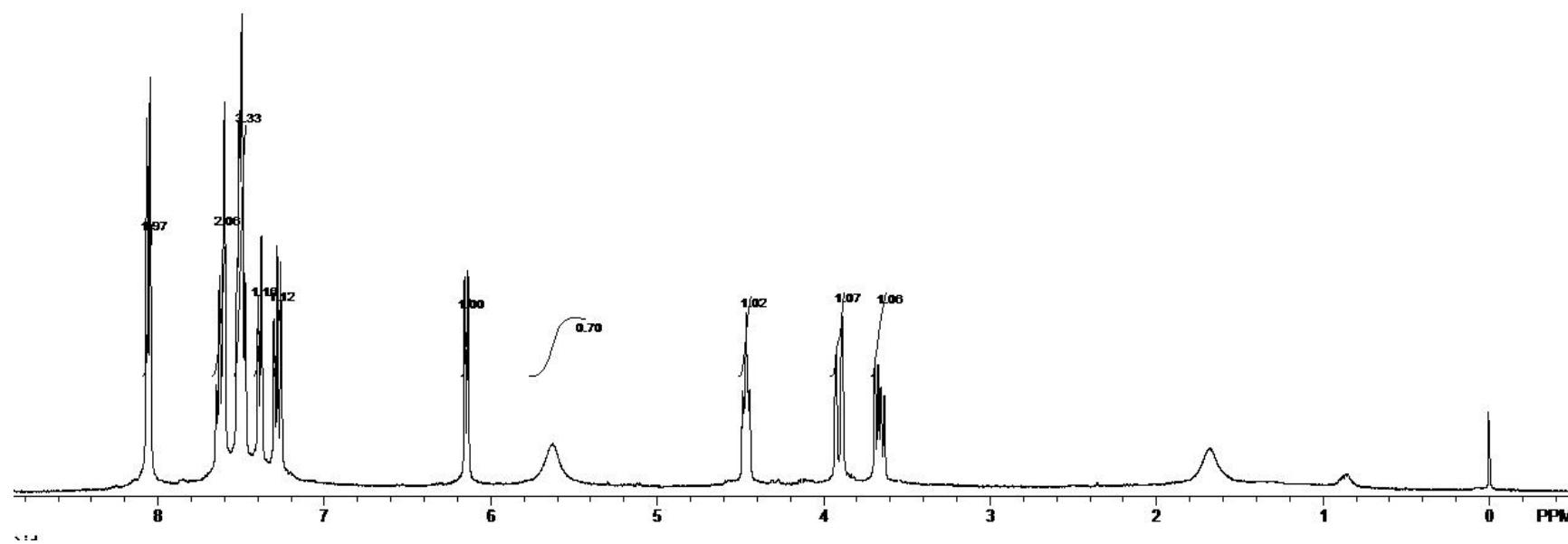
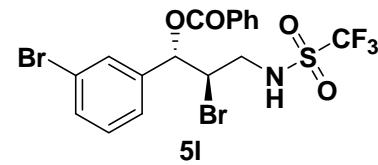
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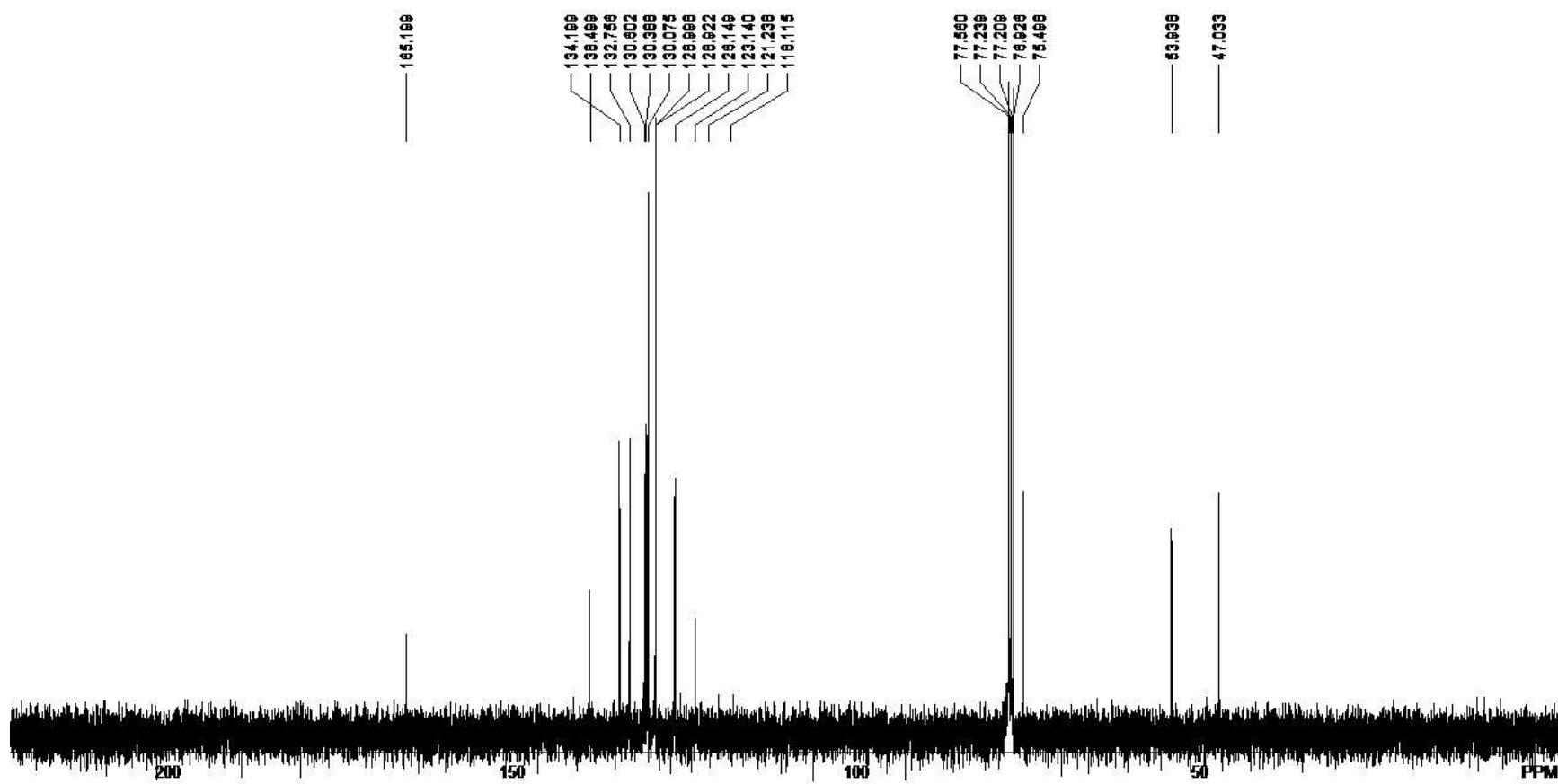
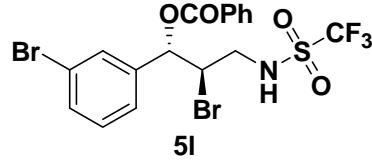


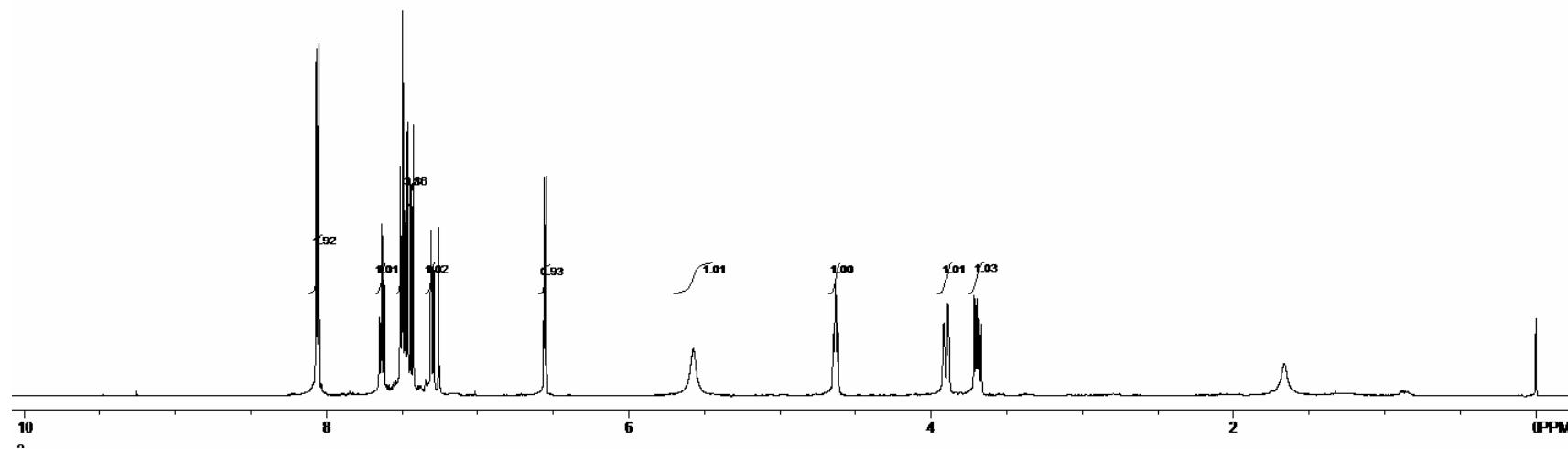
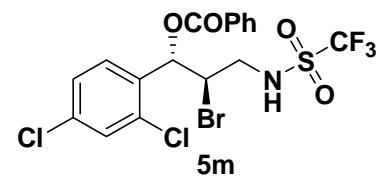


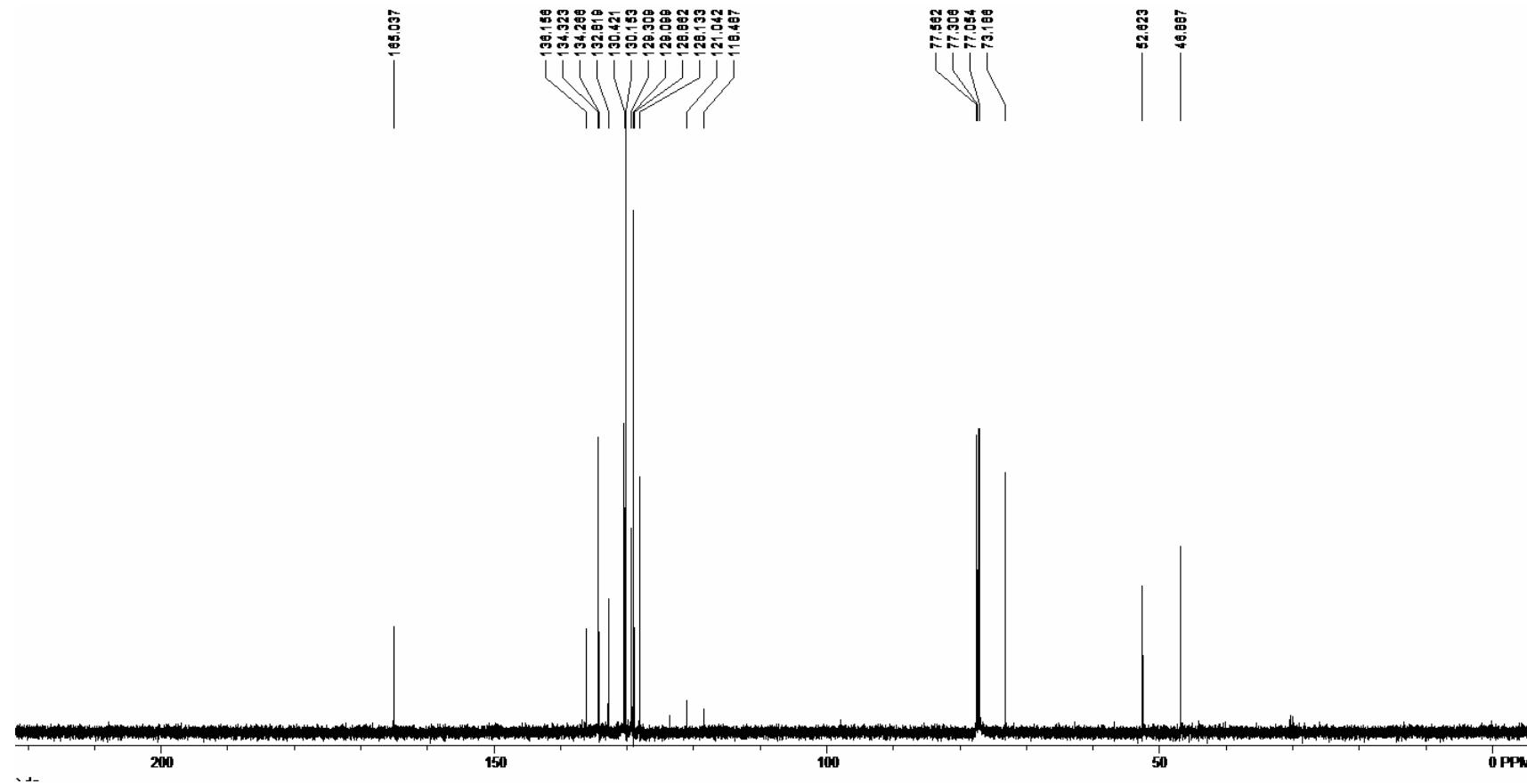
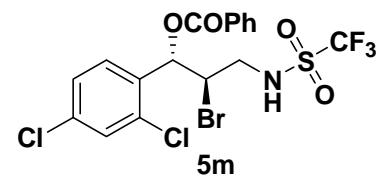
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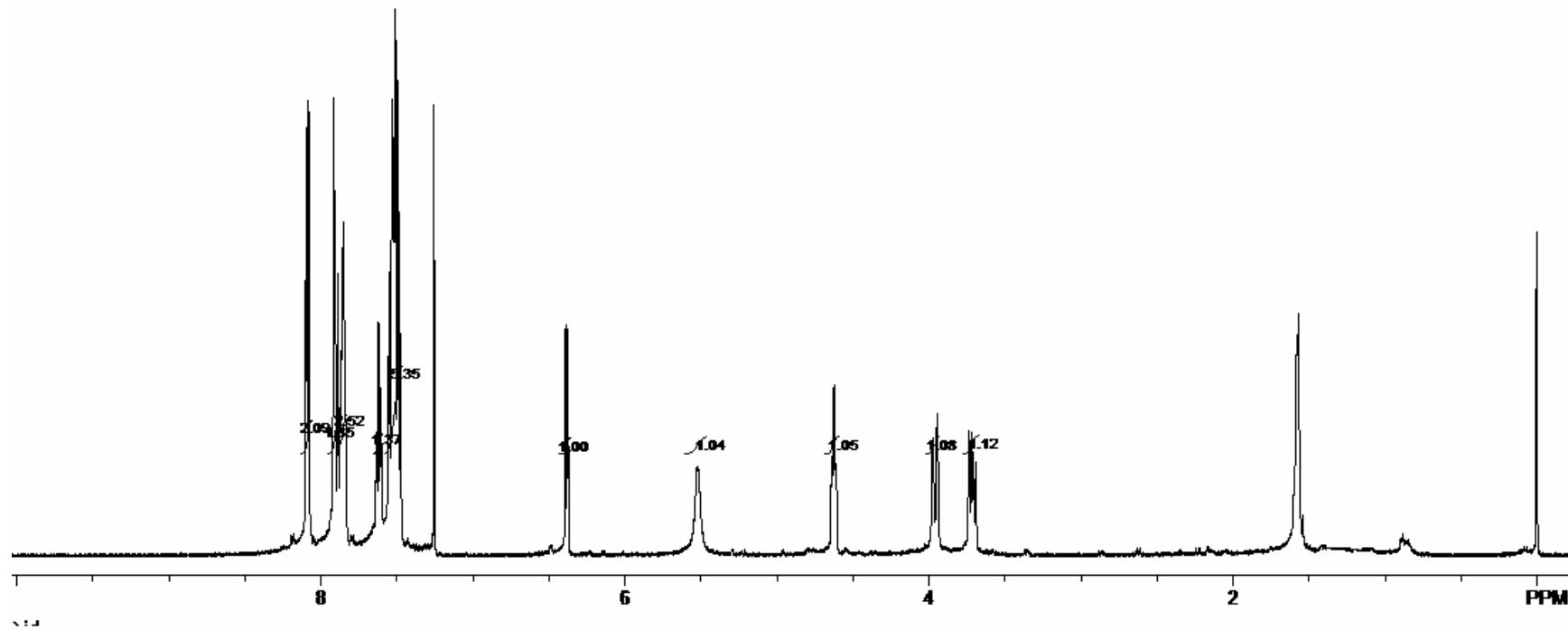
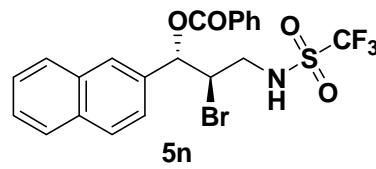


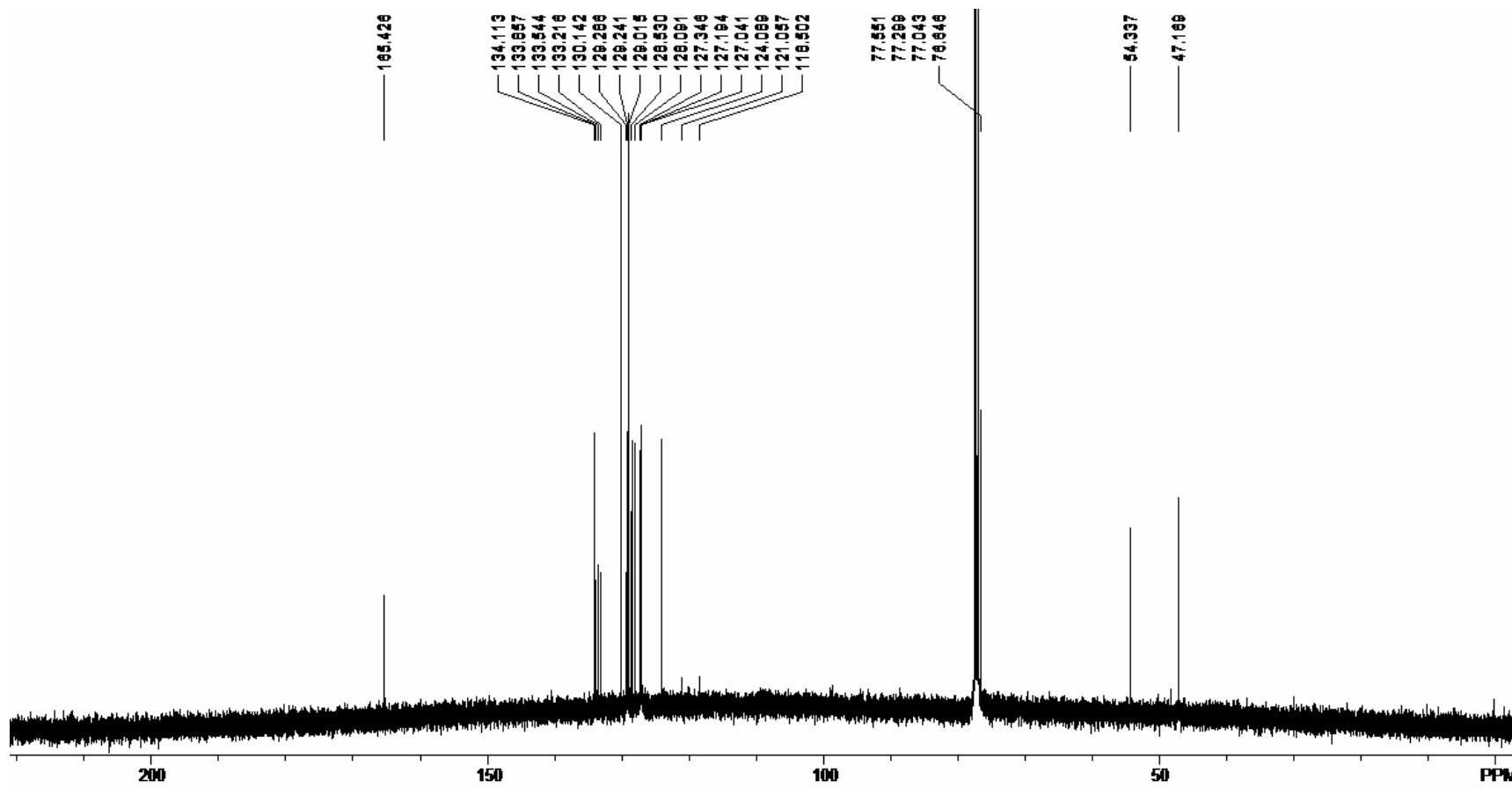
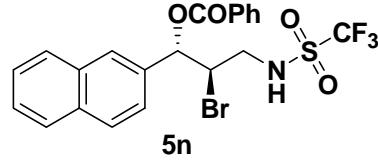


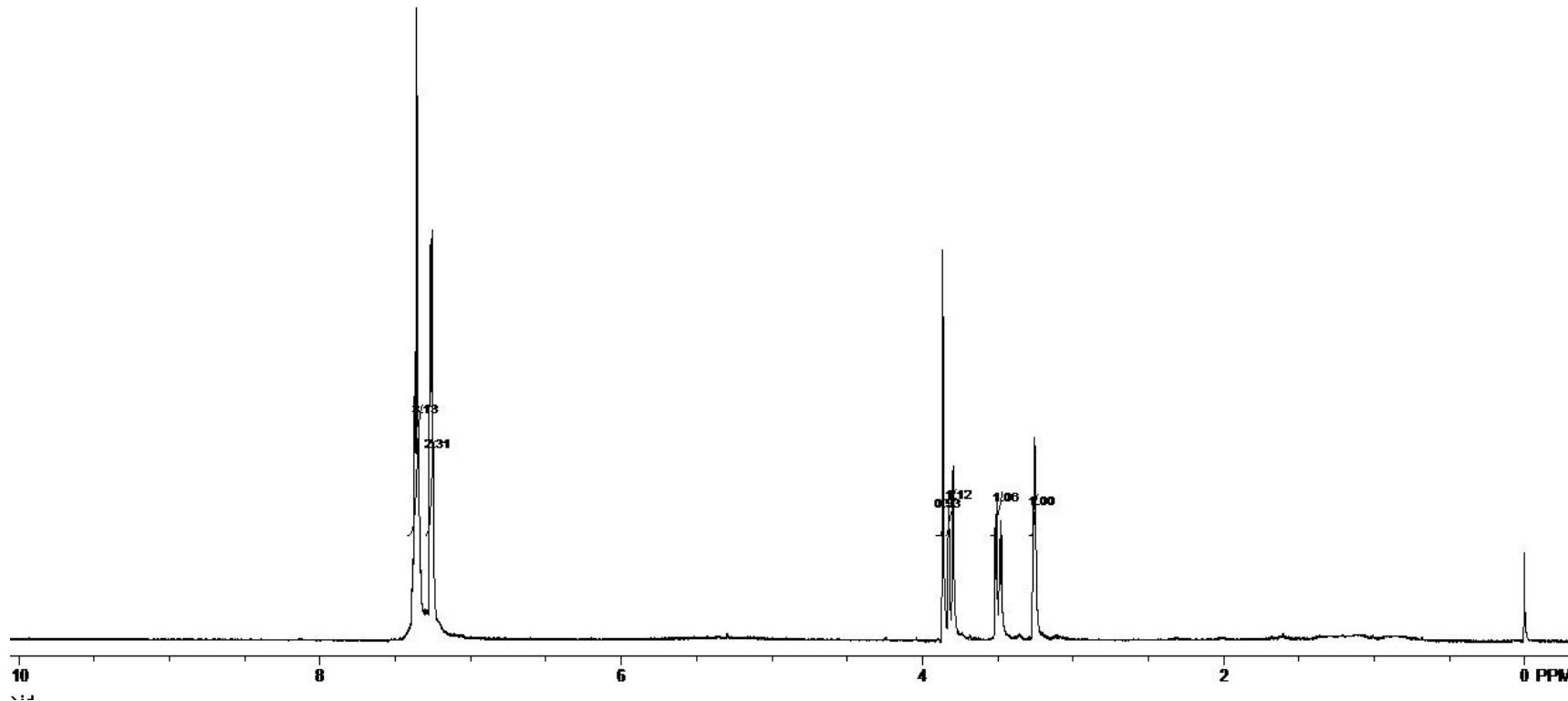
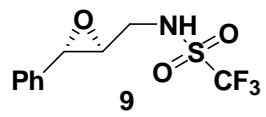




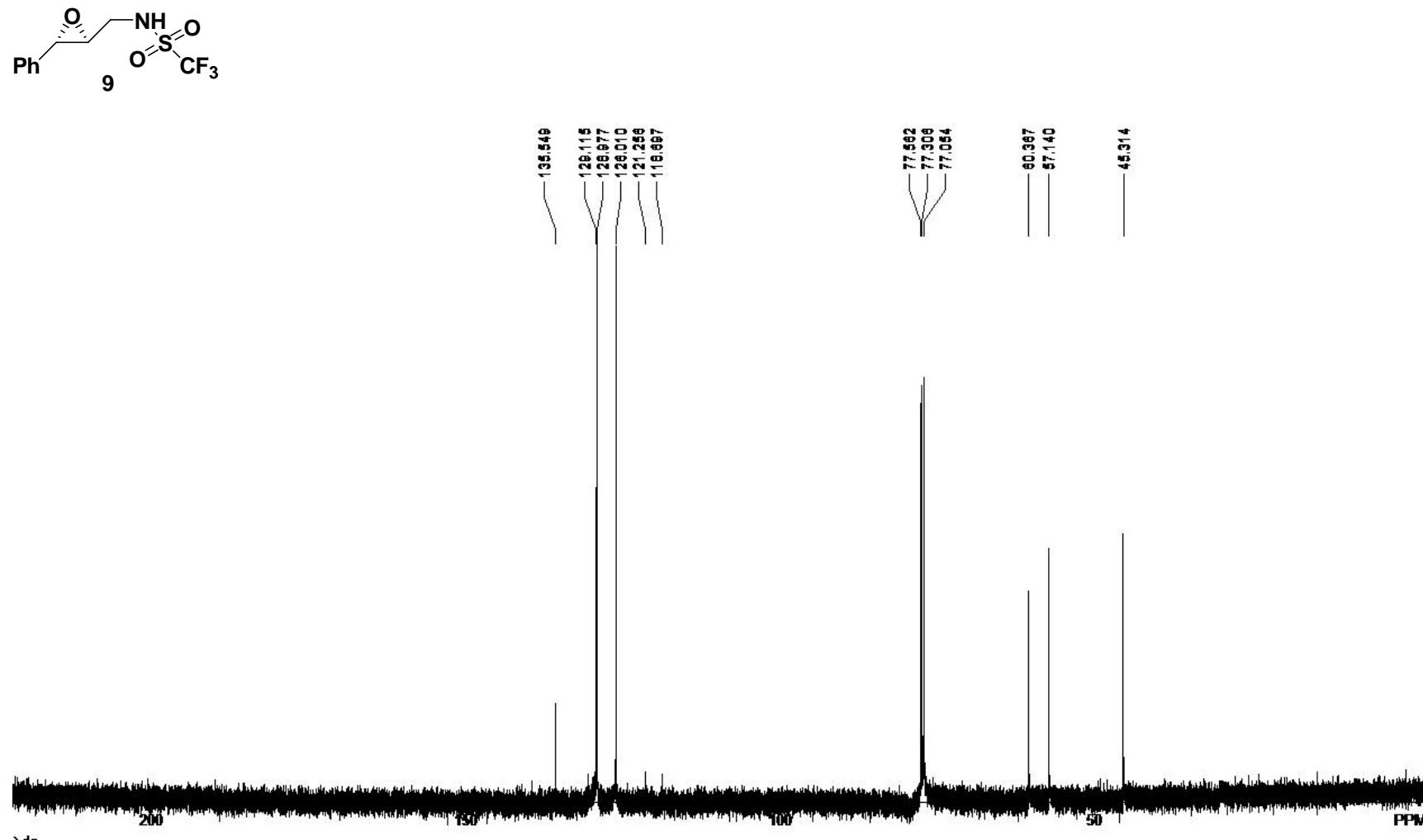


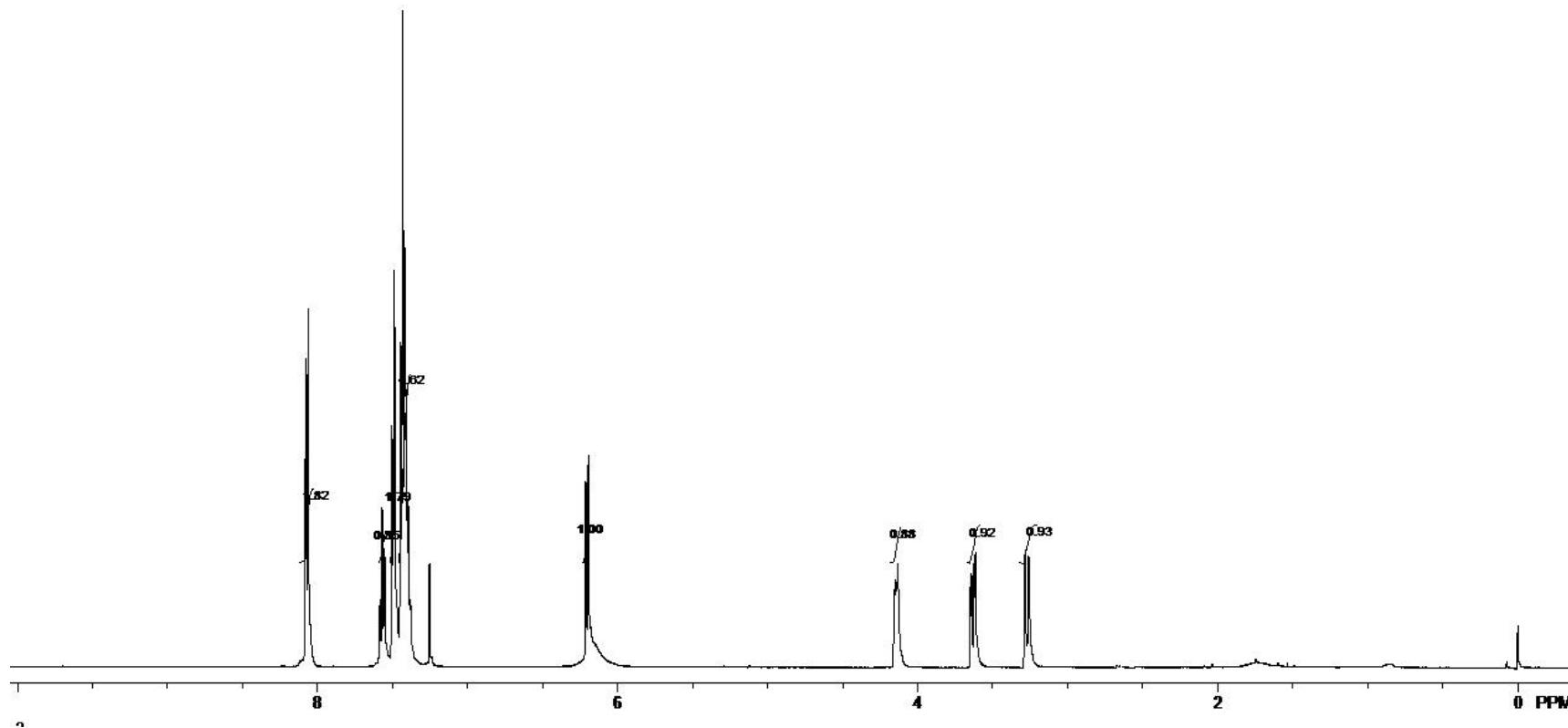
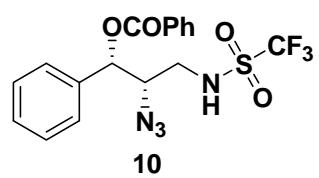


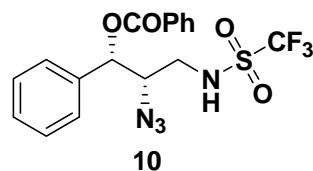




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