A General Route to 1,5-Disubstituted 1,2,3-Triazoles with Alkyl/Alkyl, Alkyl/Aryl, Aryl/Aryl Combinations: A Metal-Free, Regioselective, One-pot Three Component Approach

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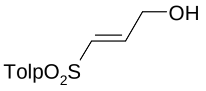
Experimental section:

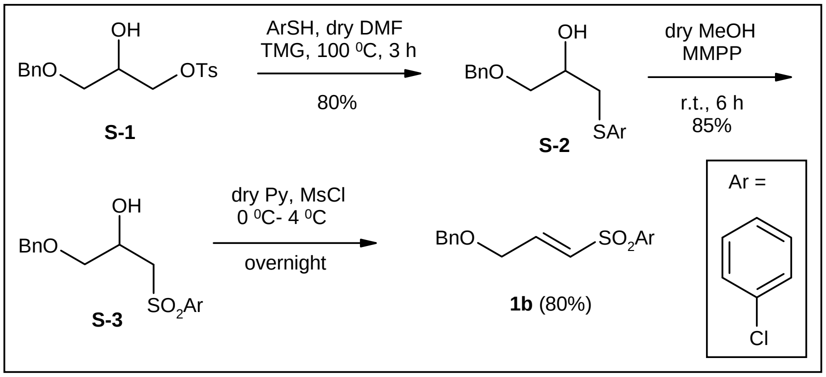
General methods: Melting points were determined in open-end capillary tubes and are uncorrected. All the fine chemicals were obtained from commercial suppliers and are used without purification. Solvents were dried and distilled following the standard procedures. TLC was carried out on pre-coated plates (Merck silica gel 60, f_{254}) and the spots were visualized with UV light or by charring the plate dipped in 5% H_2SO_4-MeOH, 5% H_2SO_4-vaniline solution and 5% HOAc-nihydrine solution. Column chromatography was performed on silica gel (230-400 mesh and 60-120 mesh). ^{1}H and ^{13}C NMR spectra for new compounds were recorded at 200 and/or 400 MHz NMR respectively using both $CDCl_3$ and DMSO-d_6 as the solvent unless stated otherwise. DEPT experiments have been carried out to identify the methylene carbons and quaternary carbons. Optical rotations were recorded at 589 nm. High Resolution Mass Spectra (HRMS) were recorded by quadrupole-equipped TOF mass spectrometer.

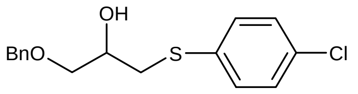


Compound **1a**

Synthesis and characterization of vinyl sulfone 1a[1]: A mixture of sodium *p*-toluene sulfinate (6.13 g, 34.43 mmol), 2,3-dibromo-propan-1-ol **2** (5.0 g, 22.95 mmol) and dry DMF (10 ml) were added to a flask equipped with a magnetic stir bar and the mixture was stirred at 80 ^{0}C for 12 h. After cooling to room temperature the reaction mixture was treated with water (10 ml) and the compound was extracted with EtOAc (3 x 30 ml). The combined organic layers were washed with brine (30 ml), dried over anhydrous Na_2SO_4, filtered and the filtrate was concentrated under reduced pressure to get a residue. The residue was further purified by silica gel column chromatography to afford compound **1a** (4.3 g, 88 %) in pure form. [Eluent: 1:9 = EtOAc:Hexane]. Colourless gum. **Spectral data:** ^{1}H NMR ($CDCl_3$): δ 2.46 (s, 3H); 3.91-4.12 (m, 2H); 6.64 (d, 1H, *J* = 15 Hz); 6.95-7.04 (m, 1H); 7.30-7.37 (m, 2H); 7.67-7.77 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$): δ 21.8 (CH_3); 60.8 (CH_2); 128.1; 128.9; 130.0; 130.3; 135.5 (4 °C); 145.3 (4 °C) ppm. HRMS [ES$^+$, $(M+H)^+$]: for $C_{10}H_{13}O_3S$ found 213.0500, calcd. 213.0507.

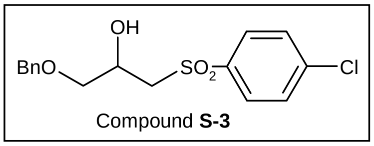
Scheme S-1: Synthesis of vinyl sulfone **1b** from monotosylated derivative of glycerol **S-1**.





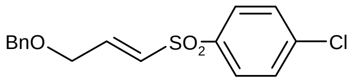
Compound **S-2**

Synthesis and characterization of compound S-2: To a well-stirred solution of mono tosylated benzyl derivative **S-1** (2 g, 5.95 mmol) in dry DMF (20 ml), 4-chlorobenzenethiol (1.29 g, 8.93 mmol) and TMG (1,1,3,3-tetramethylguanidine) (0.9 ml, 7.142 mmol) was added. The reaction mixture was heated at 100 ^{0}C with stirring under N_2 atmosphere for 3 h. After completion of the reaction the reaction mixture was cooled and poured into saturated $NaHCO_3$ solution, and the product was extracted with EtOAc (3 x 30 ml). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and the filtrate was concentrated under reduced pressure to get a residue. Then the residue was purified over silica gel column chromatography to afford the desired sulfide derivative **S-2** (1.46 g, 80%) in pure form. [Eluent: EtOAc:Hexane (1:5)]. Yellowish gum. **Spectral data:** ^{1}H NMR: δ 2.92 (m, 2H); 3.43-3.52 (m, 2H); 3.79-3.90 (m, 1H); 4.48 (s, 2H); 7.17-7.36 (m, 9 H) ppm. ^{13}C NMR: δ 37.7 (CH_2); 69.1; 72.5 (CH_2); 73.5 (CH_2); 127.9 (2C); 128.6; 129.2; 130.9; 132.4 (4 °C); 133.5 (4 °C); 137.8 (4 °C) ppm. HRMS [ES$^+$, (M+Na)$^+$]: for $C_{16}H_{17}O_2SClNa$ found 331.0548, calcd. 331.0535.



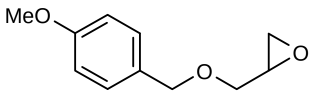
Compound **S-3**

Synthesis and characterization of compound S-3: To a well stirred solution of the compound **S-2** (2 g, 6.493 mmol) in dry MeOH (30 ml) MMPP [magnesium bis(monoperoxyphthalate) hexahydrate] (6.42 g, 12.99 mmol) was added, and the reaction mixture was stirred at room temperature under N_2 atmosphere. After completion of the reaction monitored by TLC, MeOH was evaporated to dryness under reduced pressure, and the residue was poured into saturated $NaHCO_3$ solution. The product was extracted with EtOAc (3 x 30 ml). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and the filtrate was concentrated under reduced pressure to get a residue. The residue was purified over silica gel column to afford the desired sulfone derivative **S-3** (1.87 g, 85%) in pure form. [Eluent: EtOAc:Hexane (1:4)]. White solid. M.P.: 106 ^{0}-110 ^{0}C. **Spectral data:** ^{1}H NMR: δ 3.24 (bs, 1H); 3.32 (d, 2H, *J* = 5.6 Hz); 3.48 (d, 2H, *J* = 5.2 Hz); 4.28-4.38 (m, 1H); 4.42-4.55 (m, 2H); 7.14-7.32 (m, 5H); 7.41-7.52 (m, 2H); 7.77-7.87 (m, 2H) ppm. ^{13}C NMR: δ 59.7 (CH_2); 65.6; 72.5 (CH_2); 73.6 (CH_2); 127.9; 128.1; 128.6; 129.7 (2xC); 137.5 (4 °C); 138.1 (4 °C); 140.7 (4 °C) ppm. HRMS [ES$^+$, (M+Na)$^+$]: for $C_{16}H_{17}O_4SClNa$ found 363.0453, calcd. 363.0434.



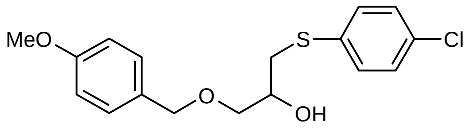
Compound **1b**

Synthesis and characterization of compound 1b: To a well-stirred solution of compound **S-3** (2.3 g, 6.764 mmol) in dry pyridine (25 ml), MsCl (methanesulfonyl chloride) (1 ml, 13.53 mmol) in pyridine (2 ml) was added dropwise with the help of a dropping funnel at 0 ^{0}C under N_2 atmosphere and kept the reaction mixture at +4 ^{0}C for overnight. After completion of the reaction monitored by TLC, the reaction mixture was poured into saturated $NaHCO_3$ solution and the product was extracted with EtOAc (3 x 30 ml). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and the filtrate was concentrated under reduced pressure to get a residue. The residue was purified over silica gel column to afford the desired vinyl sulfone **1b** (1.74 g, 80%) in pure form. [Eluent: EtOAc:Hexane (1:5)]. White solid. M.P.: 93 ^{0}-96 ^{0}C. **Spectral data:** ^{1}H NMR: δ 4.19 (t, 2H, *J* = 2.4 Hz); 4.52 (s, 2H); 6.59-6.68 (m, 1H); 6.94-7.05 (m, 1H); 7.29-7.32 (m, 5H); 7.48 (d, 2H, *J* = 8.4 Hz); 7.80 (d, 2H, *J* = 8.6 Hz) ppm. ^{13}C NMR: δ 67.6 (CH_2); 73.1 (CH_2); 127.7; 127.9; 128.5; 129.2; 129.5; 129.8; 137.1 (4 ^{o}C); 138.8 (4 ^{o}C); 139.9 (4 ^{o}C); 143.3 ppm. HRMS [ES^{+}, (M+Na)$^{+}$]: for $C_{16}H_{15}O_3SClNa$ found 345.0339, calcd 345.0328.



Compound **4**

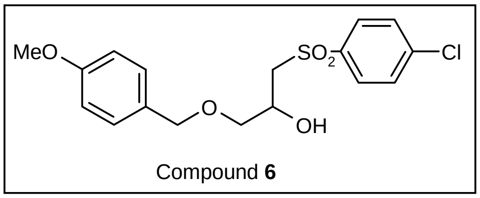
Synthesis and characterization of compound 4: A solution of 4-methoxybenzyl alcohol (PMB-OH) (1 g, 7.24 mmol) in dry DMF (20 ml) was cooled to 0 ^{0}C. Then at 0 ^{0}C NaH (0.521 g, 10.86 mmol) was added and stirred at N_2 atmosphere. After 1 hour epichlorohydrin **3** (0.85 ml, 10.85 mmol) was added to the reaction mixture and it was allowed to stir for overnight. On completion of the reaction, the reaction mixture was poured in brine solution and stirred for few hours. The product was extracted with EtOAc (2 x 50 ml) and the combined organic layer was dried over anhydrous Na_2SO_4, filtered and the filtrate was evaporated to dryness under reduced pressure to get a residue. Then the residue was purified over silica gel column to get compound **4** (1.37 g, 65%) in pure form. [Eluent: Hexane]. Yellow gum. **Spectral data:** ^1H NMR ($CDCl_3$): δ 2.52-2.55 (m, 1H); 2.72 (t, 1H, *J* = 5,4.2 Hz); 3.09-3.13 (m, 1H); 3.29-3.38 (m, 1H); 3.65-3.68 (m, 1H); 3.72 (s, 3H); 4.46 (q, 2H, *J* = 13 Hz); 6.84 (d, 2H, *J* = 8.4 Hz); 7.23(d, 2H, *J* = 8.4 Hz) ppm. ^{13}C NMR ($CDCl_3$): δ 44.0 (CH_2); 50.7; 55.0 (CH_3); 70.4 (CH_2); 72.7 (CH_2); 113.6; 129.2; 129.8 (4 ^oC); 159.1 (4 ^oC) ppm. HRMS [ES^+, $(M+H)^+$]: for $C_{11}H_{15}O_3$ found 195.0948, calcd. 195.0943.



Compound **5**

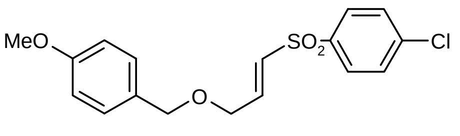
Synthesis and characterization of compound 5: A solution of 4-chlorobenzenethiol (3.84 g, 26.57 mmol), dry DMF (20 ml) and TMG (4.1 ml, 33.215 mmol) was stirred well for 1hour. Then to the reaction mixture compound **4** (4.2957 g, 22.143 mmol) was added and heated at 90 ^0C for overnight under N_2 atmosphere. On completion of the reaction the reaction mixture was poured into brine solution and stirred for few hours. The product was extracted with EtOAc (2 x 50ml) and the combined organic layer was dried over anhydrous Na_2SO_4, filtered and the filtrate was evaporated to dryness under reduced pressure to get a residue. Then the residue was purified over silica gel column to get compound **5** (6.29 gm, 84%) in pure form. [Eluent: (1:6) EtOAc:Hexane]. Yellow gum. **Spectral data:** ^1H NMR ($CDCl_3$): δ 2.96-3.09 (m, 3H); 3.44-3.47 (m, 2H); 3.74 (s, 3H); 3.85 (bs, 1H); 4.40 (s, 2H);

6.84 (d, 2H, *J* = 8.2 Hz); 7.17-7.26 (m, 6H) ppm. ^{13}C NMR ($CDCl_3$): δ 37.4 (CH_2); 55.2 (CH_3); 69.0; 72.2 (CH_2); 73.0 (CH_2); 113.8; 129.0; 129.4; 129.7; 130.6 (4 °C); 132.0 (4 °C); 134.5 (4 °C); 159.2 (4 °C) ppm. HRMS [ES^+, $(M+H)^+$]: for $C_{17}H_{20}ClO_3S$ found 339.0751, calcd. 339.0743.



Compound **6**

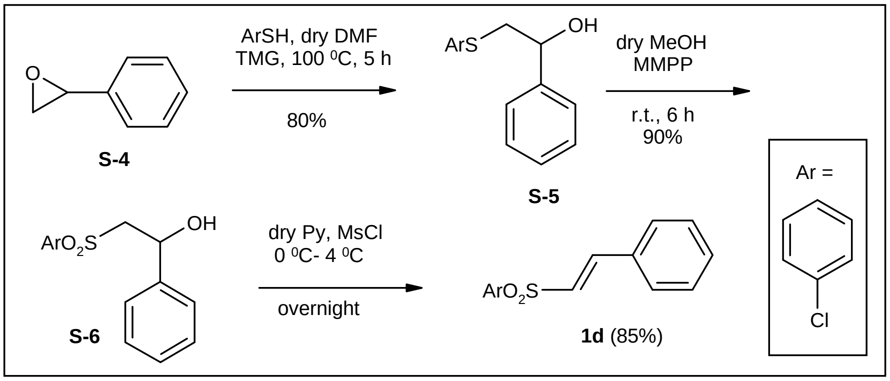
Synthesis and characterization of compound 6: To a well-stirred solution of compound **5** (1.2304 g, 3.64 mmol) in dry MeOH (30 ml), MMPP (2.697 g, 5.45 mmol) was added at 0 ^{0}C and stirred for 6 h under N_2 atmosphere. On completion of the reaction, MeOH was evaporated to dryness under reduced pressure and the residue was dissolved in aq. saturated $NaHCO_3$ solution. Then the product was extracted with EtOAc (3 x 30 ml). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and the filtrate was concentrated under reduced pressure to get a residue. The residue was purified over silica gel column to afford desired sulfone derivative **6** (1.33 g, 99%) in pure form. [Eluent: (1:5) EtOAc:Hexane]. Colourless gum. **Spectral data:** ^{1}H NMR ($CDCl_3$): δ 3.26-3.41(m, 5H); 3.69(s, 3H); 4.22-4.32 (m, 2H); 4.45 (s, 1H); 6.75 (d, 2H, *J* = 8.6 Hz); 7.08-7.17 (m, 2H); 7.36-7.41 (m, 2H); 7.70-7.80 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$): δ 54.8 (CH_3); 59.2 (CH_2); 64.0 (CH_2); 65.1; 69.0 (CH_2); 72.1(CH_2); 72.6 (CH_2); 113.5; 121.1; 128.2; 129.1; 129.2; 129.3; 133.0 (4 °C); 138.0 (4 °C); 139.9 (4 °C); 140.0 (4 °C); 159.0 (4 °C) ppm. HRMS [ES^+, $(M+H)^+$]: for $C_{17}H_{20}ClO_5S$ found 371.0639, calcd. 371.0642.

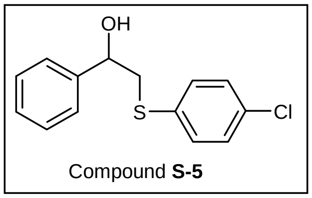


Compound **1c**

Synthesis and characterization of compound 1c: To a well-stirred solution of compound **6** (1.3308 g, 3.59 mmol) in dry pyridine (30 ml), MsCl (0.5 ml, 7.18 mmol) was added at 0 ^{0}C under N_2 atmosphere and the reaction mixture was kept at +4 ^{0}C for overnight. After completion of the reaction monitored by TLC, the reaction mixture was poured into saturated $NaHCO_3$ solution and the product was extracted with EtOAc (3 x 30 ml). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and the filtrate was concentrated under reduced pressure to get a residue. The crude residue was dissolved in dry DCM (20 ml) and Et_3N (1.5 mmol) was added and stirred at room temperature. After 1 h the solvent was evaporated to dryness to get a residue. The residue was purified over silica gel to afford the derired vinylsulfone **1c** (1.05 g, 83%) in pure form. [Eluent: (1:5) EtOAc:Hexane]. Colourless gum. **Spectral data:** ^{1}H NMR ($CDCl_3$): δ 3.79 (s, 3H); 4.18 (t, 2H, *J* = 2.8, 2.4 Hz); 4.47 (s, 2H); 6.58-6.68 (m, 1H); 6.92 (d, 2H, *J* = 13.4 Hz); 6.95-7.06 (m, 1H); 7.21 (d, 2H, *J* = 8.6 Hz); 7.49 (d, 2H, *J* = 8.6 Hz); 7.80 (d, 2H, *J* = 6.8 Hz) ppm. ^{13}C NMR ($CDCl_3$): δ 55.4 (CH_3); 67.4 (CH_2); 73.0 (CH_2); 114.0; 129.4; 129.6; 129.7; 130.0; 139.0 (4 °C); 140.0 (4 °C); 143.4; 159.6 (4 °C) ppm. HRMS [ES$^+$, (M+H)$^+$]: for $C_{17}H_{18}ClO_4S$ found 353.0530, calcd. 353.0536.

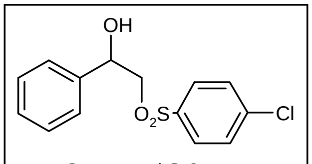
Scheme S-2: Synthesis of vinyl sulfone **1d** from styrene oxide **S-4**.





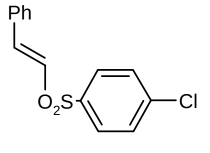
Compound **S-5**

Synthesis and characterization of compound S-5: To a well-stirred solution of the epoxide **S-4** (2 g, 16.66 mmol) in DMF (20 ml) was added 4-chlorobenzenethiol (3.61 g, 24.99 mmol) and TMG (2.5 ml, 19.99 mmol). The mixture was heated at 100 ^{0}C with stirring under N_2 atmosphere. After 5 h the reaction mixture was cooled and poured into saturated $NaHCO_3$ solution, and the product was extracted with EtOAc (3 x 30 ml). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and the filtrate was concentrated under reduced pressure. The residue was purified over silica gel column to afford the desired sulfide derivative **S-5** (3.30 g, 80%) in pure form. [Eluent: EtOAc:Hexane (1:5)]. Yellow gum. **Spectral data:** ^{1}H NMR: δ 3.00-3.25 (m, 3H); 4.63-4.70 (m, 1H); 7.16-7.29 (m, 9 H) ppm. ^{13}C NMR: δ 43.9 (CH_2); 72.0; 126.0; 128.2; 128.7; 129.3; 131.4; 132.7 (4 ^{o}C); 133.9 (4 ^{o}C); 142.2 (4 ^{o}C) ppm. HRMS [ES$^+$, (M+H)$^+$]: for $C_{14}H_{14}OSCl$ found 265.0372, calcd. 265.0376.



Compound **S-6**

Synthesis and characterization of compound S-6: To a well stirred solution of sulfide **S-5** (2 g, 8.064 mmol) in dry MeOH (20 ml), MMPP (8 g, 16.13mmol), and the mixture was stirred at room temperature under N_2 atmosphere. After completion of the reaction monitored by TLC, the volatile matters were evaporated to dryness under reduced pressure to get a residue, and the residue was dissolved in aq. saturated $NaHCO_3$ solution. The product was extracted with EtOAc (3 x 30 ml). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to get a residue. The residue was purified over silica gel column to afford desired sulfone derivative **S-6** (2.03 g, 90%) in pure form. [Eluent: EtOAc:Hexane (1:4)]. White solid. M.P.: 105 ^{0}-108 ^{0}C. **Spectral data:** ^{1}H NMR: δ 3.24-3.56 (m, 2H); 3.74 (bs, 1H); 5.17-5.24 (m, 1H); 7.13-7.31 (m, 5H); 7.44 (d, 2H, *J* = 8.6 Hz); 7.79 (d, 2H, *J* = 8.6 Hz) ppm. ^{13}C NMR: δ 63.7 (CH_2); 68.5; 125.7; 128.3; 128.7; 129.6; 137.9 (4 ^{o}C); 140.5 (4 ^{o}C); 140.9 (4 ^{o}C) ppm. HRMS [ES$^+$, (M+H)$^+$]: for $C_{14}H_{13}O_3SClNa$ found 319.0150, calcd. 319.0172.



Compound **1d**

Synthesis and characterization of compound 1d: To a well-stirred solution of sulfone **S-6** (2 g, 7.142 mmol) in pyridine (20 ml) MsCl (1.1 ml, 14.285 mmol) in pyridine (5 ml) was added dropwise at 0 ^{0}C under N_2 atmosphere. After completion of the addition, the reaction mixture was kept at +4 ^{0}C for overnight. After completion of the reaction monitored by TLC, the reaction mixture was poured into an aq. saturated $NaHCO_3$ solution and the product was extracted with EtOAc (3 x 30 ml). The combined organic layer was dried over anhyd. Na_2SO_4 and concentrated under reduced pressure to get a residue. The crude residue was dissolved in dry DCM (20 ml) and Et_3N (1.5 mmol) was added and stirred at room temperature. After 1 h the solvent was evaporated to dryness to get a residue. The residue was purified over silica gel to afford the desired vinyl sulfone **1d** (1.66 g, 85%) in pure form. [Eluent: EtOAc:Hexane (1:5)]. White solid. M.P.: 62 ^{0}-66 ^{0}C. **Spectral data:** ^{1}H NMR: δ 6.95 (d, 1H, *J* = 15.4 H); 7.34-7.48 (m, 7H); 7.69 (d, 1H, *J* = 15.4 Hz); 7.89 (d, 2H, *J* = 8.6 Hz) ppm. ^{13}C NMR: δ 126.8; 128.5; 128.9; 129.0; 129.4; 131.2; 132.0 (4 ^{o}C); 139.2 (4 ^{o}C); 139.7 (4 ^{o}C); 142.8 ppm. HRMS [ES$^+$, (M+H)$^+$]: for $C_{14}H_{12}O_2SCl$ found 279.0255, calcd. 279.0247.

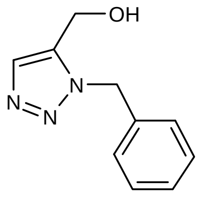
General procedure for one-pot multicomponent reaction:

(i) From bromides/tosylates/mesylates: A well-stirred solution of an appropriate halide, tosylate or mesylates (2 mmol), vinyl sulfone (1 mmol) and sodium azide (2 mmol) in dry DMF (20 ml) was heated at 100 ^{0}C. After completion of the reaction (TLC) the reaction mixture was treated with satd. $NaHCO_3$ solution and the product was extracted with EtOAc (3 x 30 ml). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and the filtrate was evaporated to dryness under reduced pressure to get a residue. Then the residue was purified over silica gel column chromatography to afford the corresponding 1,5-DTs in moderate to good yields.

(ii) From aryl amines:[2] To a well-stirred solution of an aryl amine (1 mmol) in HOAc (2 ml), aq. $NaNO_2$ (1.5 mmol in 3 ml H_2O) was added followed by NaN_3 (2 mmol in 3 ml H_2O) at 0 ^{0}C. After 10 minutes, vinyl sulfone (1 mmol) was added into it and the mixture was heated at

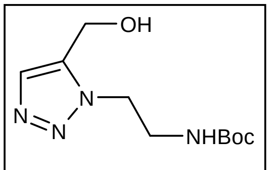
100 ^{0}C. After completion of the reaction (TLC) the reaction mixture was treated with satd. $NaHCO_3$ solution and the product was extracted with EtOAc (3 x 30 ml). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and the filtrate was evaporated to dryness under reduced pressure to get a residue. Then the residue was purified over silica gel column chromatography to afford the corresponding 1,5-DTs in good yields.

(iii) From aryl iodides:[3] A mixture of aryl iodides (2 mmol), sodium azide (2.4 mmol), CuI (0.2 mmol), L-proline (0.4 mmol) and NaOH (0.4 mmol) in 4 ml DMSO was stirred at 60 ^{0}C. After 5-7 h, vinyl sulfone (1.5 mmol) was added and the reaction mixture was heated at 90 ^{0}C. After completion of the reaction (TLC) the reaction mixture was treated with satd. $NaHCO_3$ solution and the product was extracted with EtOAc (3 x 30 ml). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and the filtrate was evaporated to dryness under reduced pressure to get a residue. Then the residue was purified over silica gel column chromatography to afford the corresponding 1,5-DTs in moderate to good yields.



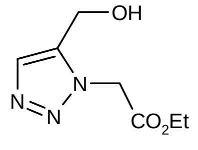
Compound **7a**

Characterization of compound 7a: Using the general procedure, compound **1a** (0.5 g, 2.36 mmol) afforded compound **7a** (0.388 g, 87%) in pure form. [Eluent: (1:3) EtOAc:Hexane]. Colourless gum. **Spectral data:** ^{1}H NMR ($CDCl_3$): δ 4.55 (s, 2H); 5.46 (bs, 1H); 5.54 (s, 2H); 7.15-7.27 (m, 5H); 7.42 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$): δ 52.1 (CH_2); 52.7 (CH_2); 127.5; 128.4; 128.9; 132.9; 134.6 (4 ^{o}C); 137.0 (4 ^{o}C) ppm. HRMS [ES^+, $(M+H)^+$]: for $C_{10}H_{12}N_3O$ found 190.0908, calcd. 190.0902.



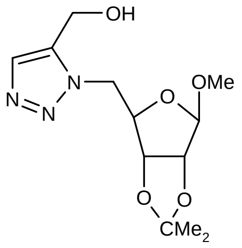
Compound **10a**

Characterization of compound 10a: Using the general procedure, compound **1a** (0.5 g, 2.36 mmol) afforded compound **10a** (0.451 g, 79%) in pure form. [Eluent: (1:1) EtOAc:Hexane]. **Spectral data:** ^{1}H NMR ($CDCl_3$): δ 1.30 (s, 9H); 3.53 (q, 2H, *J* = 11.8 Hz); 4.41 (t, 2H, *J* = 6 Hz); 4.65 (d, 2H, *J* = 3.2 Hz); 5.19 (bs, 1H); 5.61 (t, 1H, *J* = 6 Hz); 7.43 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$): δ 28.3 (CH_3); 40.1 (CH_2); 48.0 (CH_2); 52.5 (CH_2); 79.9 (4 ^{0}C); 132.8; 137.1 (4 ^{0}C); 156.4 (4 ^{0}C) ppm. HRMS [ES$^+$, $(M+H)^+$]: for $C_{10}H_{19}N_4O_3$ found 243.1384, calcd. 243.1379.



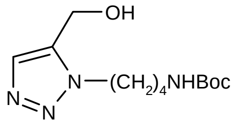
Compound **11a**

Characterization of compound 11a: Using the general procedure, compound **1a** (0.5 g, 2.36 mmol) afforded compound **11a** (0.384 g, 88%) in pure form. [Eluent: (1:2) EtOAc:Hexane]. Yellow gum. **Spectral data:** ^{1}H NMR ($CDCl_3$): δ 1.22 (t, 3H, *J* = 7.2 Hz); 4.17 (q, 2H, *J* = 14.2 Hz); 4.64 (s, 2H); 4.83 (bs, 1H); 5.19 (s, 2H); 7.41 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$): δ 14.1 (CH_3); 49.7 (CH_2); 53.1 (CH_2); 62.5 (CH_2); 132.6; 137.5 (4 ^{o}C); 167 (4 ^{o}C) ppm. HRMS [ES$^+$, $(M+H)^+$]: for $C_7H_{12}N_3O_3$ found 186.0809, calcd. 186.0800.



Compound **13a**

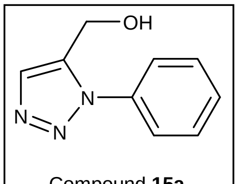
Characterization of compound 13a: Using the general procedure, compound **1a** (0.5 g, 2.36 mmol) afforded compound **13a** (0.598 g, 89%) in pure form. This reaction was carried out in 2 equiv $NaHCO_3$. [Eluent: (1:1) EtOAc:Hexane]. $[\alpha]^{28}_{D}$: 1.16 (c 0.2059, $CHCl_3$). Yellow gum. **Spectral data:** ^1H NMR ($CDCl_3$): δ 1.26 (s, 3H); 1.41 (s, 3H); 3.36 (s, 3H); 4.24 (bs, 1H); 4.45-4.65 (m, 4 H); 4.72 (s, 2H); 4.87 (d, 1H, *J* = 6 Hz); 4.97 (s, 1H); 7.48 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$): δ 25.0 (CH_3); 26.5 (CH_3); 51.1 (CH_2); 52.9 (CH_2); 55.7; 81.8; 84.9; 85.1; 110.3; 112.9 (4 °C); 133.1; 136.9 (4 °C) ppm. HRMS [ES$^+$, $(M+H)^+$]: for $C_{12}H_{20}N_3O_5$ found 286.1320, calcd. 286.1325.



Compound **14a**

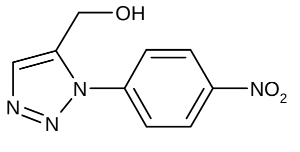
Characterization of compound 14a: Using the general procedure, compound **1a** (0.5 g, 2.36 mmol) afforded compound **14a** (0.535 g, 84%) in pure form. [Eluent: (1:2) EtOAc:Hexane]. Yellow gum. **Spectral data:** ^1H NMR ($CDCl_3$): 1.36 (s, 9H); 1.41-1.48 (m, 2H); 1.77-1.92 (m, 2H); 3.00-3.09 (m, 2H); 4.29 (t, 2H, *J* = 7 Hz); 4.67 (s, 2H); 4.98 (bs, 1H); 7.55 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$): δ 27.0 (CH_2); 27.4 (CH_2); 28.4 (CH_3); 39.6 (CH_2); 49.9 (CH_2); 56.0

(CH_2); 79.3 (4 °C); 122.1; 148.0 (4 °C); 156.3 (4 °C) ppm. HRMS [ES$^+$, (M+H)$^+$]: for $C_{12}H_{23}N_4O_3$ found 271.1697, calcd. 271.1692.



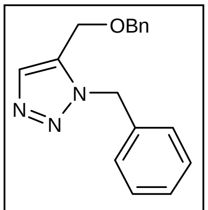
Compound **15a**

Characterization of compound 15a: Using the general procedure, compound **1a** (0.354 g, 1.67 mmol) afforded compound **15a** (0.234 g, 80%) in pure form. [Eluent: 1:3 = EtOAc:Hexane]. Yellow gum. **Spectral data:** ^{1}H NMR ($CDCl_3$): δ 4.89 (s, 2H); 7.42-7.45 (m, 1H); 7.49-7.53 (m, 2H); 7.71 (d, 2H, J = 8 Hz); 7.99 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$): δ 56.7 (CH_2); 120.2; 120.8; 129.0; 130.0; 137.2 (4 °C); 148.6 (4 °C) ppm. HRMS [ES$^+$, (M+H)$^+$]: for $C_9H_{10}N_3O$ found 176.0138, calcd. 176.0129.



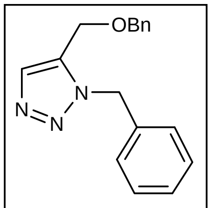
Compound **18a**

Characterization of compound 18a: Using the general procedure, compound **1a** (0.45 g, 2.12 mmol) afforded compound **18a** (0.37 g, 79%) in pure form. [Eluent: 1:3 = EtOAc:Hexane]. Yellow gum. **Spectral data:** ^{1}H NMR (DMSO-d_6): δ 4.64 (s, 2H); 5.40 (bs, 1H); 8.22 (d, 2H, J = 9 Hz); 8.43 (d, 2H, J = 9 Hz); 8.89 (s, 1H) ppm. ^{13}C NMR (DMSO-d_6): δ 55.3 (CH_2); 120.8; 121.8; 126.0; 141.4 (4 ^{0}C); 147.0 (4 ^{0}C); 150.3 (4 ^{0}C) ppm. HRMS [ES$^+$, (M+H)$^+$]: for $C_9H_9N_4O_3$ found 221.0715, calcd. 221.0711.



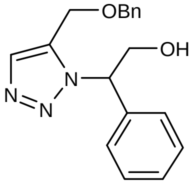
Compound **7b**

Characterization of compound 7b[4]: Using the general procedure compound **1b** (0.130 g, 0.40 mmol) was converted to compound **7b** (0.090 g, 80%) in pure form. [Eluent: 1:4 = EtOAc:Hexane]. Yellow gum. **Spectral data:** ^{1}H NMR: δ 4.39 (d, 4H, *J* = 3.4 Hz); 5.56 (s, 2H); 7.10-7.13 (m, 2H); 7.21-7.33 (m, 8H); 7.61 (s, 1H) ppm.



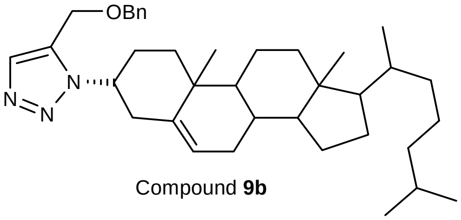
Compound **7b**

Synthesis of compound 7b[4] in the presence of Cu (I) salt: A mixture of benzyl bromide (0.19 ml, 1.56 mmol), sodium azide (0.1 gm, 1.56 mmol), CuI (0.2 mmol), L-proline (0.4 mmol) and NaOH (0.4 mmol) in 4 ml DMSO was heated at 60 ^{0}C to yield benzyl azide.[3] After that vinyl sulfone **1b** (0.25 gm, 0.78 mmol) was added in the reaction flask and the mixture was heated at 90 ^{0}C for 10 h. After completion of the reaction (TLC) the reaction mixture was treated with satd. $NaHCO_3$ solution and the product was extracted with EtOAc (3 x 30 ml). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and the filtrate was evaporated to dryness under reduced pressure to get a residue. Then the residue was purified over silica gel column chromatography to afford compound **7b** (0.16 gm, 73%) in pure form. [Eluent: 1:5 = EtOAc:Hexane]. Yellow gum. **Spectral data:** ^{1}H NMR ($CDCl_3$): δ 4.46 (d, 2H, *J* = 2.8 Hz); 5.63 (t, 2H, *J* = 15 Hz); 7.19-7.40 (m, 10H); 7.69 (s, 1H) ppm.



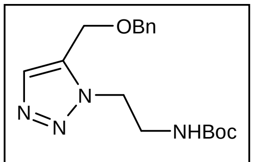
Compound **8b**

Characterization of compound 8b[4]: Using the general procedure compound **1b** (0.156 g, 0.48 mmol) was converted to compound **8b** (0.12 g, 77%) in pure form. [Eluent: 1:4 = EtOAc:Hexane]. White solid. M.p.: 95 ^{0}C-97 ^{0}C. **Spectral data:** ^{1}H NMR: δ 3.37 (bs, 1H); 4.10-4.65 (m, 6H); 5.62-5.68 (m, 1H); 7.05-7.09 (m, 2H); 7.16-7.31 (m, 8H); 7.62 (s, 1H) ppm.



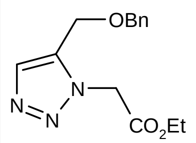
Compound **9b**

Characterization of compound 9b[4]: Using the general procedure compound **1b** (0.100 g, 0.31 mmol) was converted to compound **9b** (0.130 g, 75%) in pure form. [Eluent: 1:4 = EtOAc:Hexane]. White solid. M.p.: 71 ^{0}C-72 ^{0}C. $[\alpha]^2_D$: 2.21 (c 0.6314, $CHCl_3$). **Spectral data:** ^{1}H NMR: δ 0.65 (s, 3H); 0.75-1.08 (m, 9H) 1.17-1.24 (m, 11H); 1.30-1.78 (m, 13H); 1.84-2.09 (m, 6H); 2.33 (d, 1H, *J* = 15.4 Hz); 2.80 (d, 1H, *J* = 15 Hz); 4.46 (s, 2H); 4.54 (s, 2H); 4.67 (bs, 1H); 5.17 (d, 1H, *J* = 3 Hz); 7.23-7.37 (m, 5H); 7.56 (s, 1H) ppm.



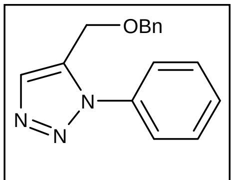
Compound **10b**

Characterization of compound 10b: Using the general procedure compound **1b** (0.150 g, 0.47 mmol) was converted to compound **10b** (0.135 g, 87%) in pure form. [Eluent: 1:2 = EtOAc:Hexane]. Yellow gum. **Spectral data:** ^{1}H NMR: δ 1.40 (s, 9H); 3.59-3.68 (m, 2H); 4.40-4.45 (m, 2H); 4.53-4.60 (m, 4H); 5.03 (bs, 1H); 7.32-7.36 (m, 5H); 7.61 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$): δ 28.0 (CH_3); 46.2 (CH_2); 59.4 (CH_2); 63.3 (CH_2); 72.0 (CH_2); 80.1 (4 °C); 123.1; 127.7; 127.8; 128.1; 133.6 (4 °C); 137.6 (4 °C); 155.1 (4 °C) ppm. HRMS [ES$^+$, (M+H)$^+$]: for $C_{17}H_{25}N_4O_3$ found 333.2047, calcd. 333.2045.



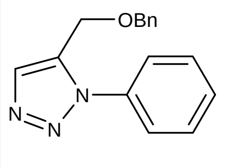
Compound **11b**

Characterization of compound 11b: Using the general procedure compound **1b** (0.117 g, 0.36 mmol) was converted to compound **11b** (0.085 g, 85%) in pure form. [Eluent: 1:2 = EtOAc:Hexane]. Yellow gum. **Spectral data:** ^{1}H NMR: δ 1.19 (t, 3H, *J* = 0.8 Hz); 4.12 (q, 2H, *J* = 14.3 Hz); 4.44 (s, 2H); 4.58 (s, 2H); 5.17 (s, 2H); 7.23-7.33 (m, 5H); 7.59 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$): δ 14.0 (CH_3); 49.7 (CH_2); 60.1 (CH_2); 62.2 (CH_2); 72.6 (CH_2); 127.8; 128.0; 128.2; 128.4; 128.6; 133.9 (4 °C); 136.7 (4 °C); 166.4 (4 °C) ppm. HRMS [ES$^+$, (M+H)$^+$]: for $C_{14}H_{18}N_3O_3$ found 276.1319, calcd. 276.1321.



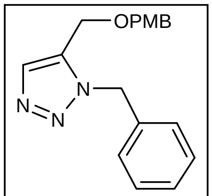
Compound **15b**

Characterization of compound 15b[4] (from aniline): Using the general procedure, compound **1b** (0.25 g, 0.78 mmol) afforded compound **15b** (0.16 g, 77%) in pure form. [Eluent: 1:5 = EtOAc:Hexane]. Yellow gum. **Spectral data:** ^{1}H NMR (CDCl$_3$): δ 4.52 (s, 4H); 7.23-7.33 (m, 5H); 7.47-7.50 (m, 3H); 7.58-7.63 (m, 2H); 7.79 (s, 1H) ppm.



Compound **15b**

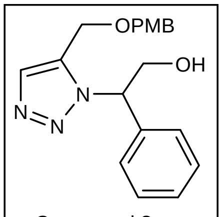
Characterization of compound 15b[4] (from iodobenzene): Using the general procedure, compound **1b** (0.25 g, 0.78 mmol) afforded compound **15b** (0.155 g, 75%) in pure form. [Eluent: 1:5 = EtOAc:Hexane]. Yellow gum. **Spectral data:** ^{1}H NMR (CDCl$_3$): δ 4.39-4.61 (m, 4H); 7.21-7.35 (m, 5H); 7.44-7.77 (m, 5H); 7.88 (s, 1H) ppm.



Compound **7c**

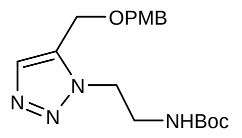
Characterization of compound 7c: Using the general procedure, compound **1c** (0.5 g, 1.42 mmol) afforded compound **7c** (0.351 g, 80%) in pure form. [Eluent: (1:5) EtOAc:Hexane].

Yellow gum. **Spectral data:** ^{1}H NMR ($CDCl_3$): δ 3.81 (s, 3H); 4.37 (d, 4H, *J* = 3.8 Hz); 5.50-5.60 (m, 2H); 6.86-6.90 (m, 2H); 7.11-7.23 (m, 4H); 7.28-7.35 (m, 3H); 7.63 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$): δ 52.4 (CH_2); 55.4 (CH_3); 59.4 (CH_2); 72.2 (CH_2); 114.1; 127.7; 128.4; 129.0; 129.9; 134.9 (4 ^{o}C); 159.7 (4 ^{o}C) ppm. HRMS [ES$^+$, (M+H)$^+$]: for $C_{18}H_{20}N_3O_2$ found 310.1473, calcd. 310.1477.



Compound **8c**

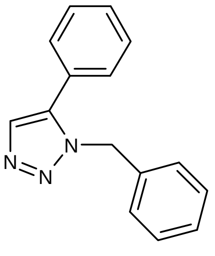
Characterization of compound 8c: Using the general procedure, compound **1c** (0.5 g, 1.42 mmol) afforded compound **8c** (0.371 g, 77%) in pure form. [Eluent: (1:4) EtOAc:Hexane]. Yellow gum. **Spectral data:** ^{1}H NMR ($CDCl_3$): δ 3.79-3.82 (m, 3H); 4.13-4.68 (m, 6H); 5.65-5.71 (m, 1H); 6.85-6.89 (m, 2H); 7.12-7.16 (m, 4H); 7.26-7.32 (m, 4H); 7.66 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$): δ 29.9, 55.5 (CH_3); 59.5 (CH_2); 60.1; 65.4 (CH_2); 65.7; 66.0; 68.4; 72.2 (CH_2); 114.1; 114.2; 127.1; 127.2; 127.4; 128.6; 128.8; 129.0; 129.2; 129.2; 129.4; 129.9; 130.0 (4 ^{o}C); 130.3 (4 ^{o}C); 134.5 (4 ^{o}C); 134.7 (4 ^{o}C); 136.1 (4 ^{o}C); 159.8 (4 ^{o}C) ppm. HRMS [ES$^+$, (M+H)$^+$]: for $C_{19}H_{22}N_3O_3$ found 340.1579, calcd. 340.1583.



Compound **10c**

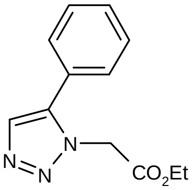
Characterization of compound 10c: Using the general procedure, compound **1c** (0.5 g, 1.42 mmol) afforded compound **10c** (0.422 g, 82%) in pure form. [Eluent: (1:3) EtOAc:Hexane].

Colourless gum. **Spectral data:** ^{1}H NMR (CDCl$_3$): δ 1.42 (s, 9H); 3.64 (q, 2H, *J* = 8.4 Hz); 3.82 (s, 3H); 4.40-4.48 (m, 4H); 5.11 (bs, 1H); 6.90 (d, 2H, *J* = 8.6 Hz); 7.25 (d, 2H, *J* = 8.6 Hz); 7.61 (s, 1H) ppm. ^{13}C NMR (CDCl$_3$): δ 28.5 (CH$_3$); 29.9 (CH$_2$); 40.3 (CH$_2$); 48.4 (CH$_2$); 55.5 (CH$_3$); 59.3 (CH$_2$); 72.4 (CH$_2$); 79.9 (4 ^{o}C); 114.2; 129.0; 130.0 (4 ^{o}C); 134.2 (4 ^{o}C); 156.0 (4 ^{o}C); 159.8 (4 ^{o}C) ppm. HRMS [ES$^+$, (M+H)$^+$]: for $C_{18}H_{27}N_4O_4$ found 363.1959, calcd. 363.1954.



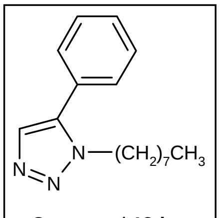
Compound **7d**

Characterization of compound 7d^5: Using the general procedure compound **1d** (0.127 g, 0.46 mmol) afforded compound **7d** (0.086 g, 80%) in pure form. [Eluent: EtOAc: pet ether (1:5)]. Yellow gum. **Spectral data:** ^{1}H NMR (CDCl$_3$): δ 5.55 (s, 2H); 7.06-7.08 (m, 2H); 7.24-7.28 (m, 5H); 7.39-7.48 (m, 3H); 7.74 (s, 1H) ppm.



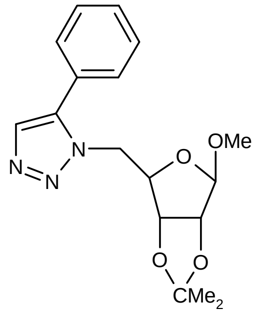
Compound **11d**

Characterization of compound 11d: Using the general procedure compound **4** (0.2 g, 0.72 mmol) was converted to compound **11d** (0.130 g, 78%) in pure form. [Eluent: EtOAc: pet ether (1:4)]. White solid. M.p.: 70 ^{0}C -72 ^{0}C. **Spectral data:** ^{1}H NMR (CDCl$_3$): δ 1.12 (t, 3H, *J* = 14.4 Hz); 4.09 (q, 2H, *J* = 14.4 Hz); 5.03 (s, 2H); 7.27-7.40 (m, 5H); 7.64 (s, 1H) ppm. ^{13}C NMR (CDCl$_3$): δ 14.0 (CH$_3$); 49.3 (CH$_2$); 62.3 (CH$_2$); 126.5 (4 ^{o}C); 128.7; 129.2; 129.8; 132.9; 138.9 (4 ^{o}C); 166.6 (4 ^{o}C) ppm. HRMS [ES$^+$, (M+H)$^+$]: for $C_{12}H_{14}N_3O_2$ found 232.1057, calcd. 232.1041.



Compound **12d**

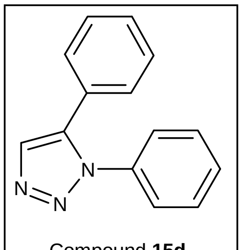
Characterization of compound 12d[4]: Using the general procedure compound **1d** (0.127 g, 0.46 mmol) afforded compound **12d** (0.092 g, 78%) in pure form. [Eluent: EtOAc: pet ether (1:6)]. Colorless gum. **Spectral data:** ^{1}H NMR (CDCl$_3$): δ 0.85 (t, 3H, *J* = 6.8 Hz); 1.22 (bs, 10H); 1.80-1.84 (m, 2H); 4.33-4.34 (m, 2H); 7.37-7.49 (m, 5H); 7.69 (s, 1H) ppm.



Compound **13d**

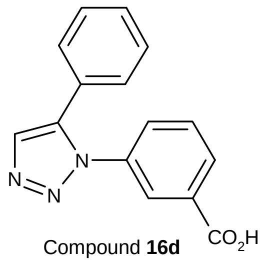
Characterization of compound 13d: Using the general procedure compound **1d** (0.2 g, 0.72 mmol) was converted to compound **13d** (0.198 g, 83%) in pure form. This reaction was carried out in 2 equiv NaHCO$_3$. [Eluent: EtOAc: pet ether (1:3)]. Yellow gum. $[\alpha]^{28}{}_D$: -31.52

(c 1.3825, $CHCl_3$). **Spectral data:** ^{1}H NMR ($CDCl_3$): δ 1.41 (s, 3H); 1.60 (s, 3H); 3.25 (s, 3H); 4.40-4.66 (m, 5H); 4.83-4.93 (m, 2H); 7.40-7.52 (m, 5H); 7.73 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$): δ 24.9 (CH_3); 26.4 (CH_3); 53.1 (CH_2); 55.6; 81.8; 85.0; 85.2; 110.1; 112.9 (4 °C); 119.9; 125.7; 128.2; 128.8; 130.5 (4 °C); 148.0 (4 °C) ppm. HRMS [ES$^+$, (M+H)$^+$]: for $C_{17}H_{22}N_3O_4$ found 332.1554, calcd. 332.1572.



Compound **15d**

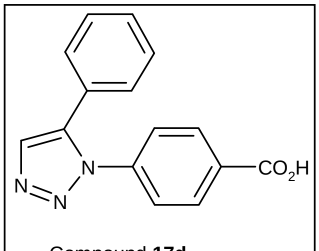
Characterization of compound 15d[4] (from aniline): Using the general procedure, compound **1d** (0.4 g, 1.44 mmol) afforded compound **15d** (0.25 g, 78%) in pure form. [Eluent: 1:4 = EtOAc:Hexane]. Yellow gum. **Spectral data:** ^{1}H NMR ($CDCl_3$): δ 7.22-7.43 (m, 10H); 7.87 (s, 1H) ppm.



Compound **16d**

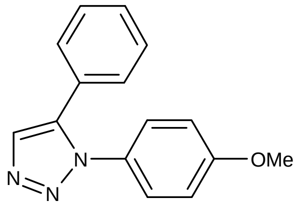
Characterization of compound 16d: Using the general procedure, compound **1d** (0.416 g, 1.50 mmol) afforded compound **16d** (0.321 g, 81%) in pure form. [Eluent: 1:4 = EtOAc:Hexane]. Yellow gum. **Spectral data:** ^{1}H NMR (DMSO-d_6): δ 7.35-7.54 (m, 3H); 7.77 (t, 1H, $J = 7.8$ Hz); 7.96-8.08 (m, 3H); 8.24 (d, 1H, $J = 8$ Hz); 8.49 (s, 1H); 9.47 (s, 1H);

13.45 (bs, 1H) ppm. ^{13}C NMR (DMSO-d$_6$): δ 120.5; 121.0; 124.7; 126.1; 129.0; 129.7; 129.9; 130.8; 131.1 (4 ^{o}C); 137.5 (4 ^{o}C); 148.2 (4 ^{o}C); 165.9 (4 ^{o}C) ppm. HRMS [ES$^+$, (M+H)$^+$]: for $C_{15}H_{12}N_3O_2$ found 266.0592, calcd. 266.0598.



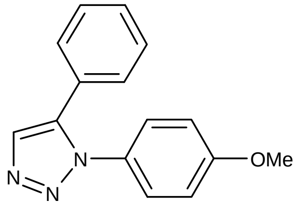
Compound **17d**

Characterization of compound 17d: Using the general procedure, compound **1d** (0.315 g, 1.13 mmol) afforded compound **17d** (0.23 g, 78%) in pure form. [Eluent: 1:4 = EtOAc:Hexane]. Yellow gum. **Spectral data:** ^{1}H NMR (DMSO-d$_6$): δ 7.36-7.55 (m, 3H); 7.96 (d, 2H, $J = 8$ Hz); 8.04-8.20 (m, 4H); 9.42 (s, 1H) ppm. ^{13}C NMR (DMSO-d$_6$): δ 120.4; 126.1; 126.2; 129.1; 129.3; 129.7; 130.7; 131.3 (4 ^{0}C); 131.8; 140.2 (4 ^{0}C); 148.3 (4 ^{0}C); 167.1 (4 ^{0}C); 173.5 (4 ^{0}C) ppm. HRMS [ES$^+$, (M+H)$^+$]: for $C_{15}H_{12}N_3O_2$ found 266.0615, calcd. 266.0610.



Compound **19d**

Characterization of compound 19d[4] (from *p*-OMeC$_6$H$_4$I): Using the general procedure, compound **1d** (0.3 g, 1.08 mmol) afforded compound **19d** (0.203 g, 75%) in pure form. [Eluent: 1:4 = EtOAc:Hexane]. Yellow gum. **Spectral data:** ^{1}H NMR (CDCl$_3$): δ 3.84 (s, 3H); 6.92 (d, 2H, $J = 8.8$ Hz); 7.21-7.28 (m, 4H); 7.32-7.36 (m, 3H); 7.85 (s, 1H) ppm.



Compound **19d**

Characterization of compound 19d[4] **(from *p*-anisidine):** Using the general procedure, compound **1d** (0.5 g, 1.80 mmol) afforded compound **19d** (0.33 g, 73%) in pure form. [Eluent: 1:4 = EtOAc:Hexane]. Yellow gum. **Spectral data:** ^{1}H NMR (CDCl$_3$): δ 3.84 (s, 3H); 6.89-6.97 (m, 2H); 7.20-7.37 (m, 7H); 7.85 (s, 1H) ppm.

References:

(1) Z. H. Guan, W. Zuo, L. B. Zhao, Z. H. Ren and Y. M. Liang, *Synthesis*, 2007, **10**, 1465.

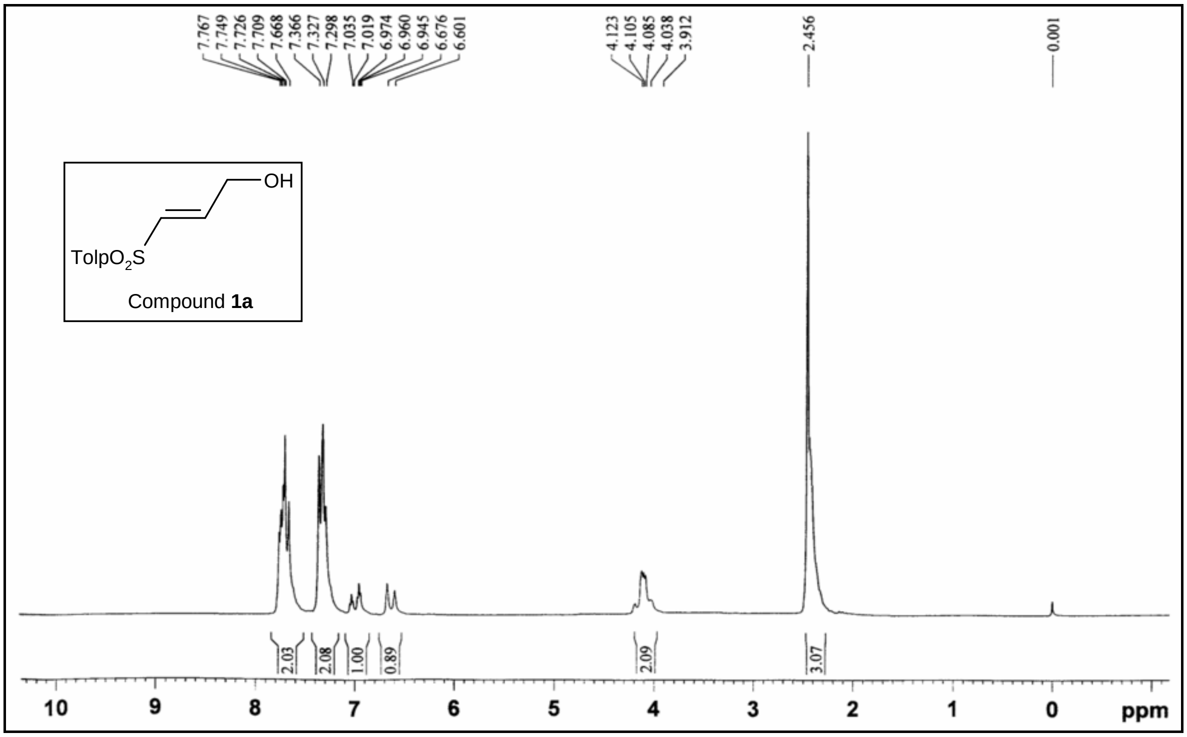
(2) (a) S. Xu, X. Zhuang, X. Pan, Z. Zhang, L. Duan, Y. Liu, L. Zhang, X. Ren and K. Ding, *J. Med. Chem.*, 2013, **56**, 4631; (b) V. Haridas, S. Sahu and P. P. P. Kumar, *Tetrahedron Lett.*, 2011, **52**, 6930.

(3) W. Zhu and D. Ma, *Chem. Commun.*, 2004, **7**, 888.

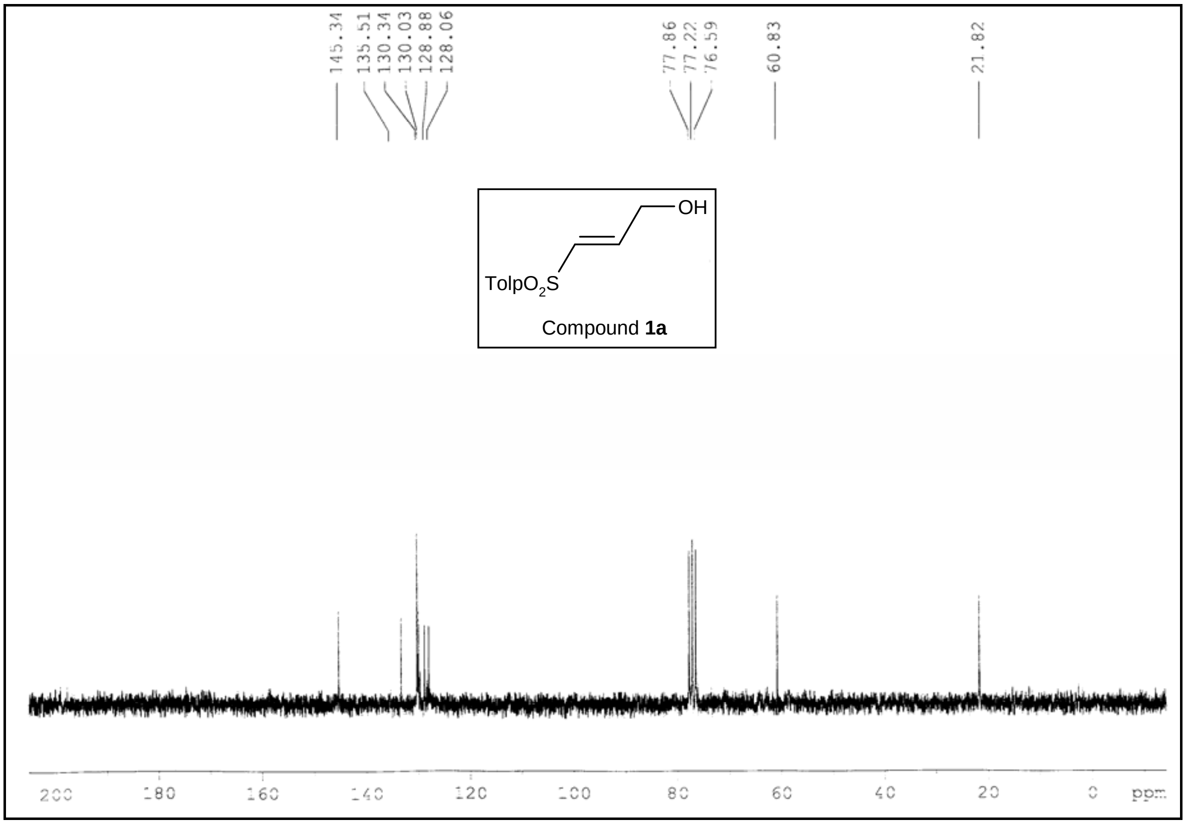
(4) S. Dey, D. Datta and T. Pathak, *Synlett*, 2011, 2521-2524.

(5) M. Lamberti, G. C. Fortman, A. Poater, J. Broggi, A. M. Z. Slawin, L. Cavallo and S. P. Nolan, *Organometallics*, 2012, **31**, 756.

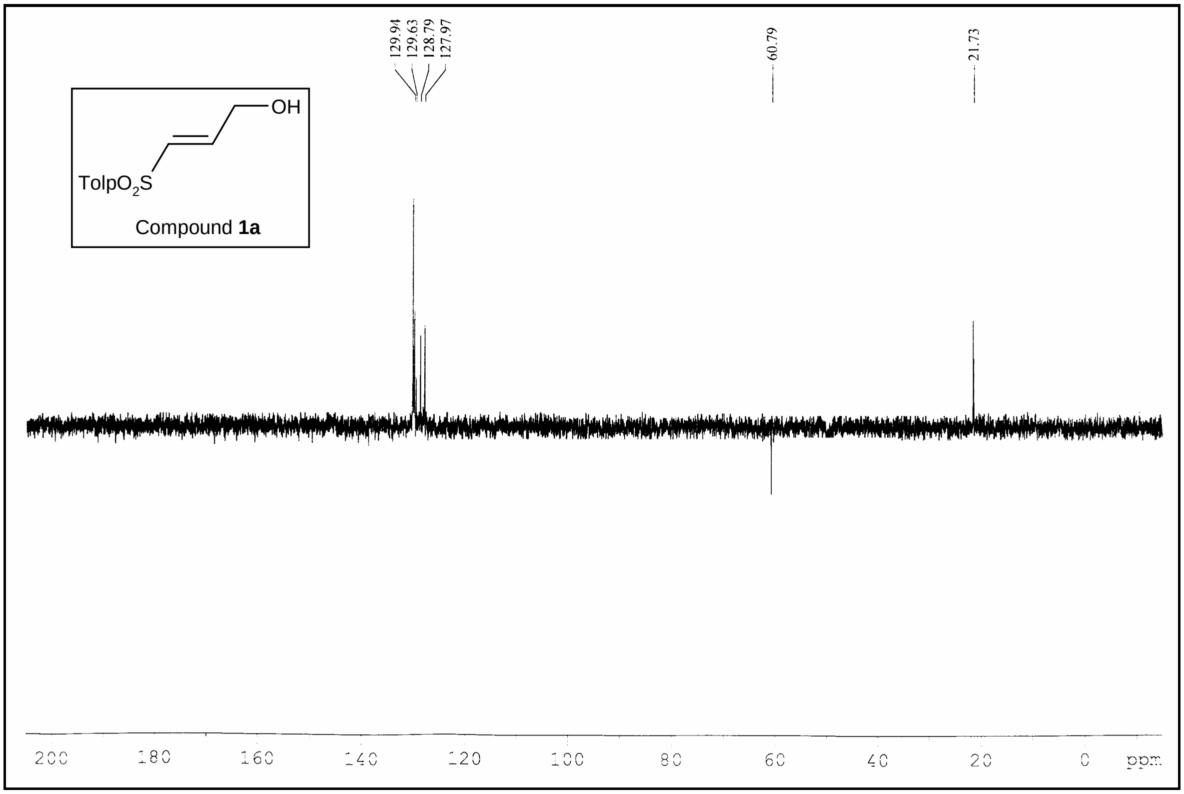
^{1}H-NMR spectra of **1a**



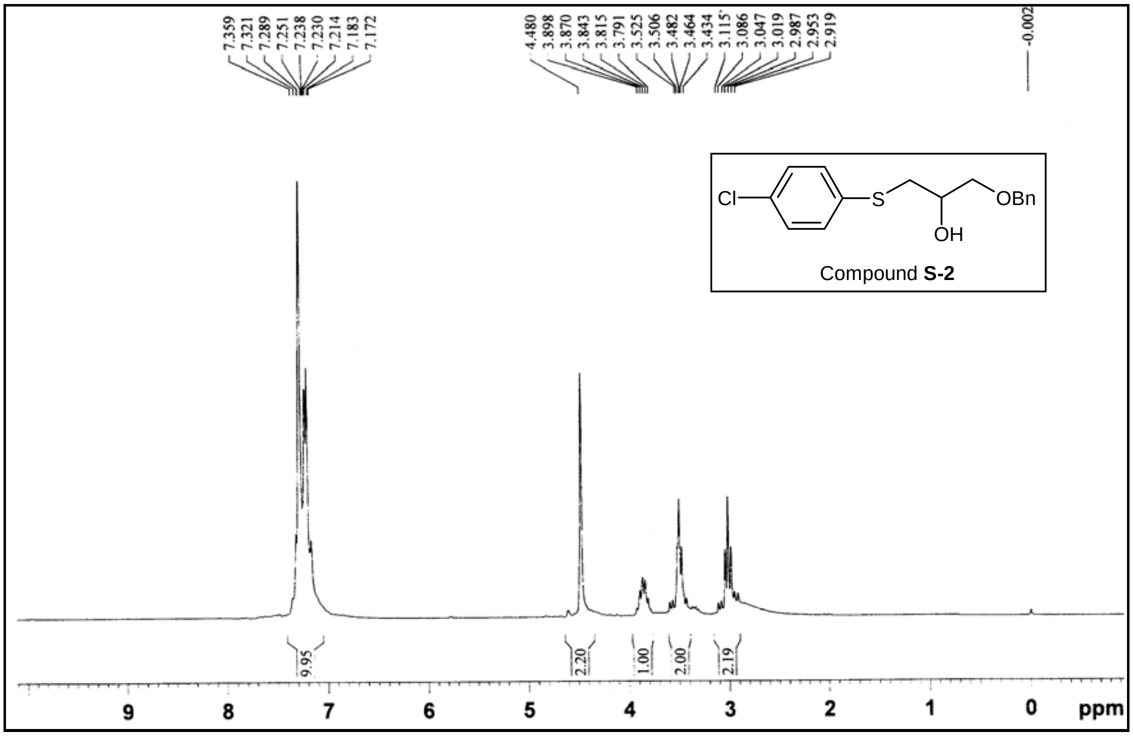
^{13}C-NMR spectra of **1a**



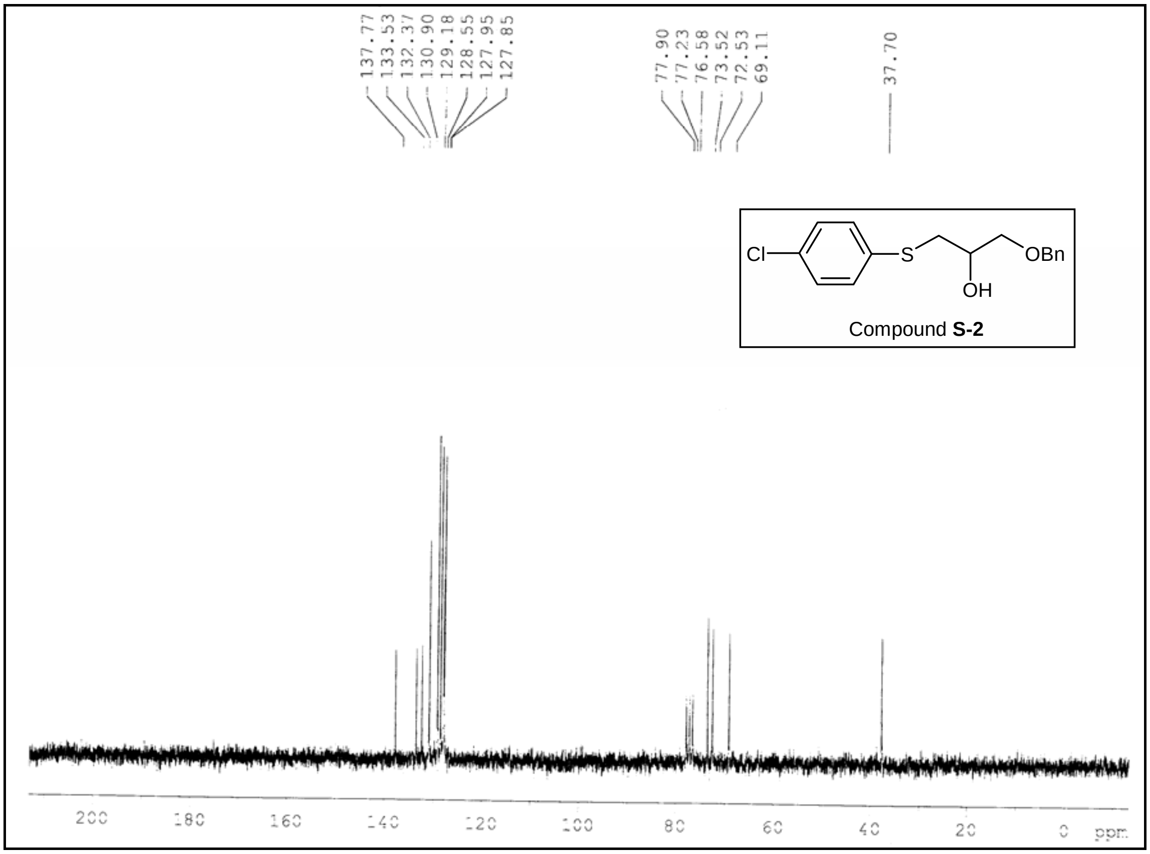
DEPT spectra of **1a**



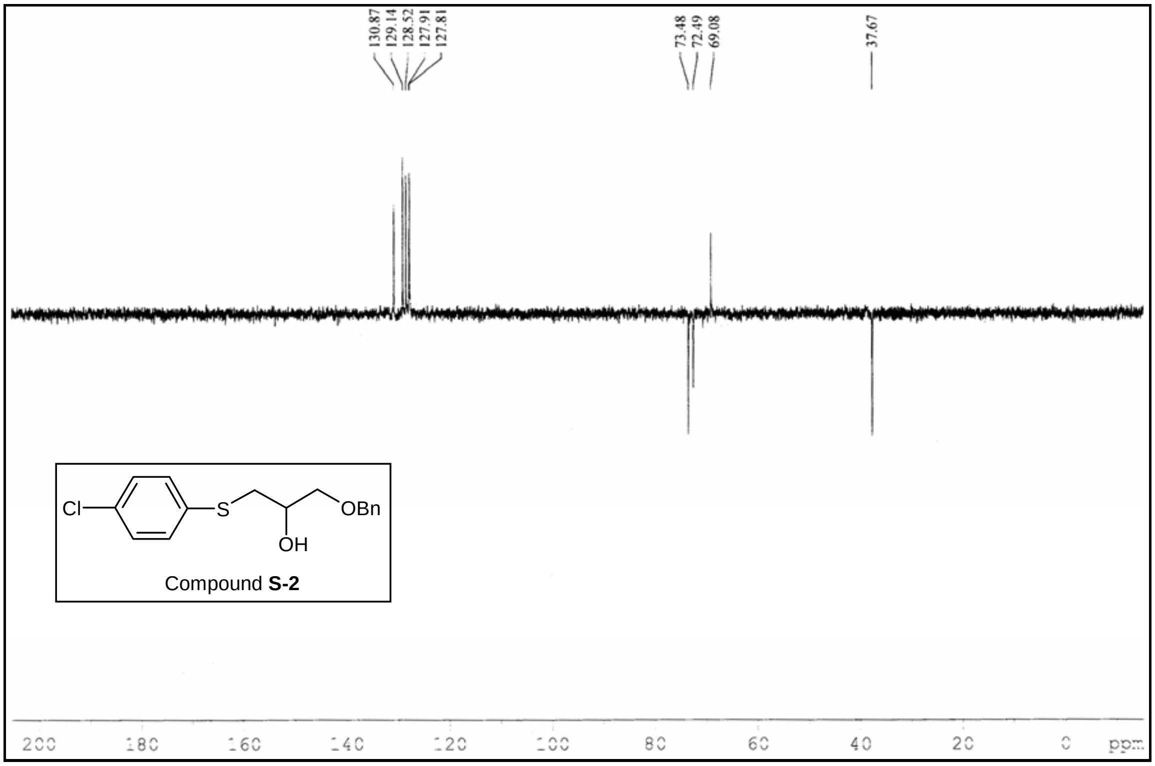
^{1}H-NMR spectra of **S-2**



^{13}C-NMR spectra of **S-2**



DEPT spectra of **S-2**



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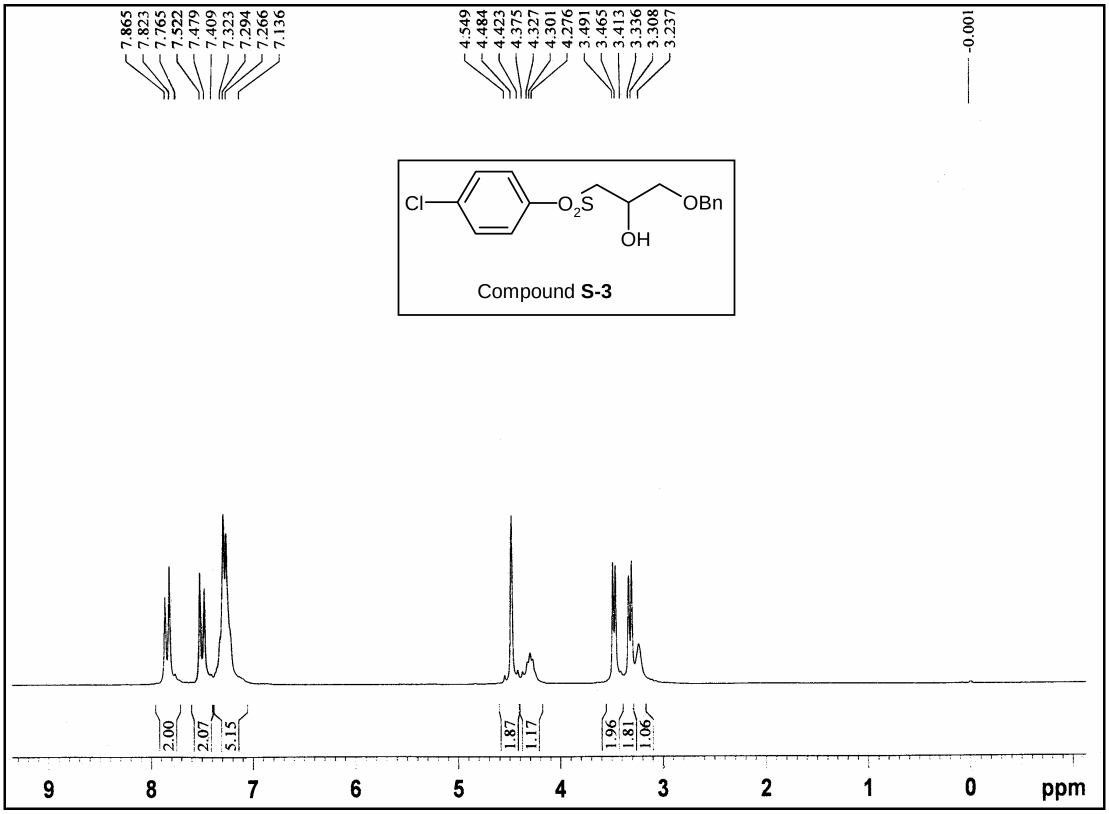

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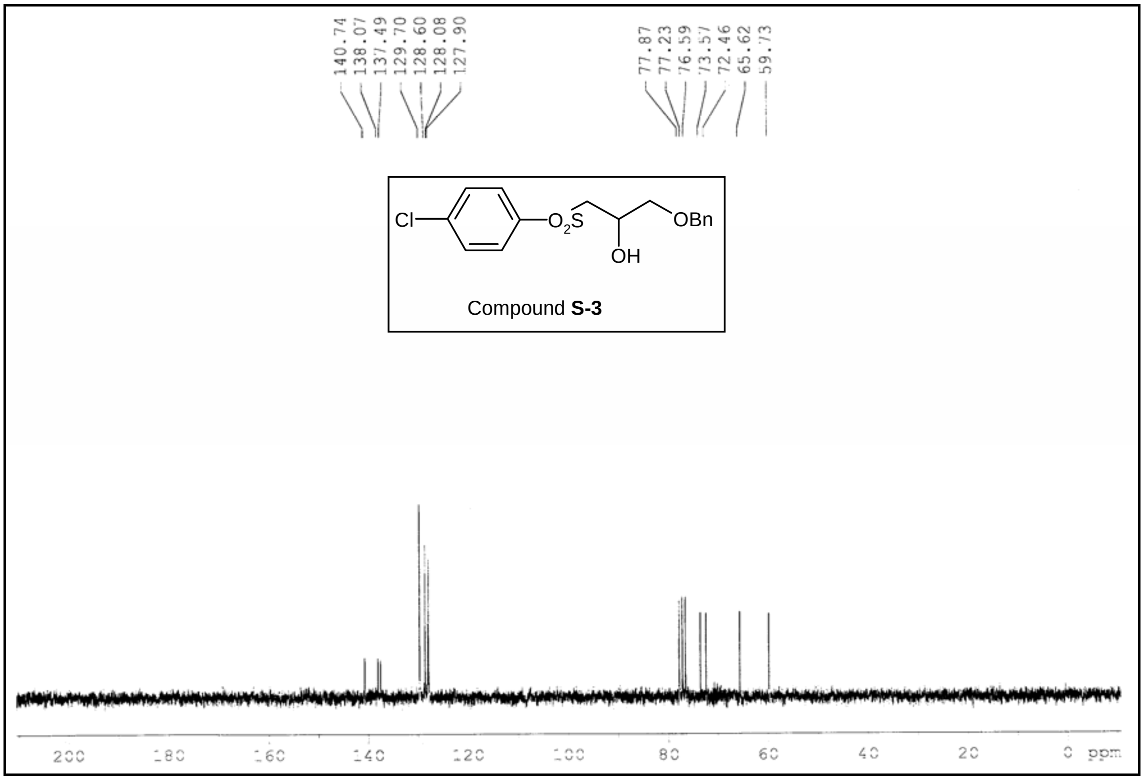
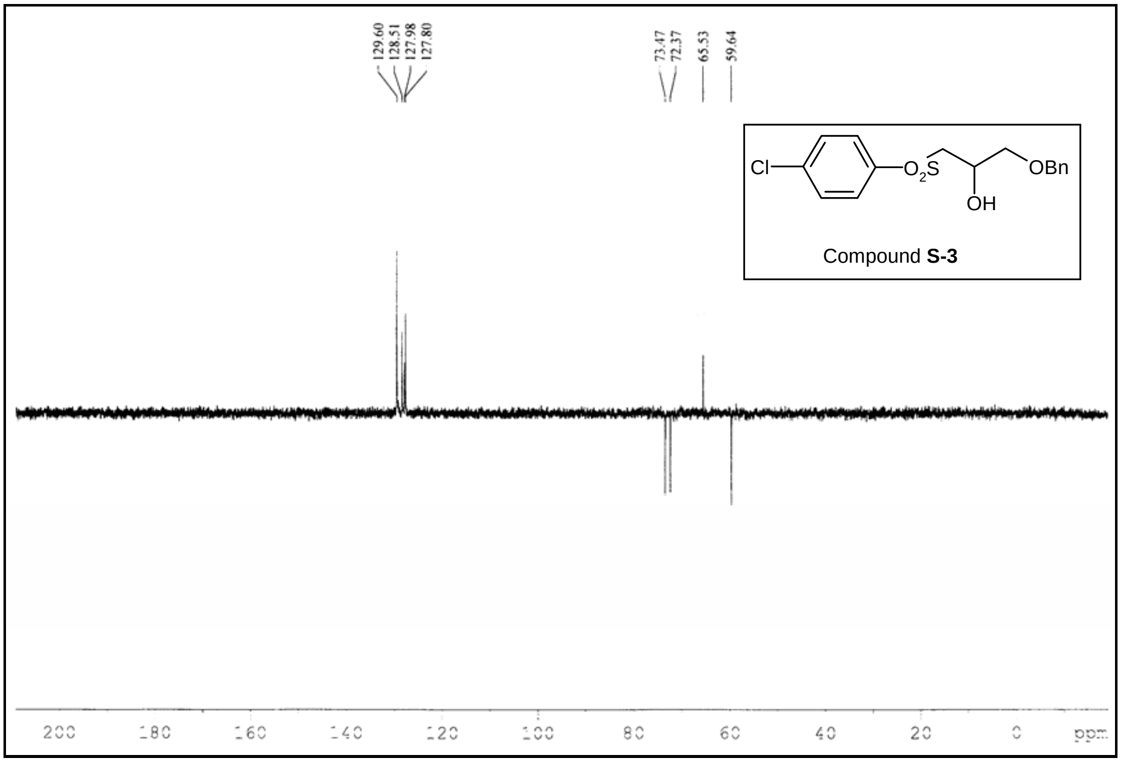
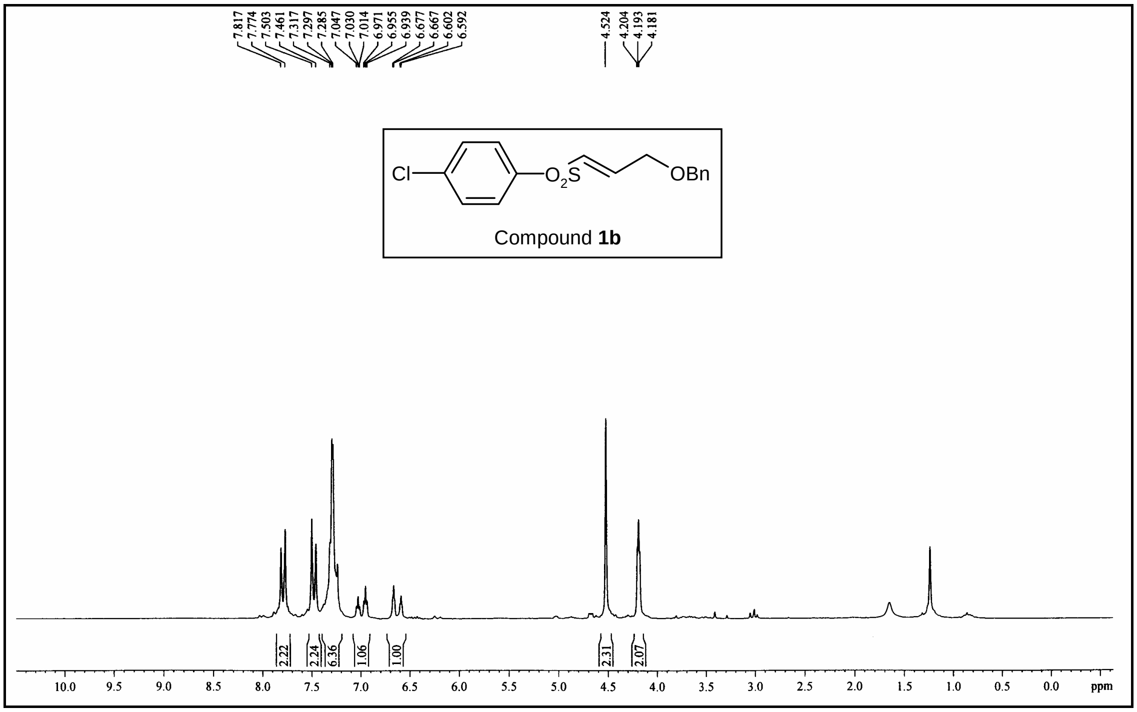


DEPT spectra of **S-3**



^{1}H-NMR spectra of **1b**



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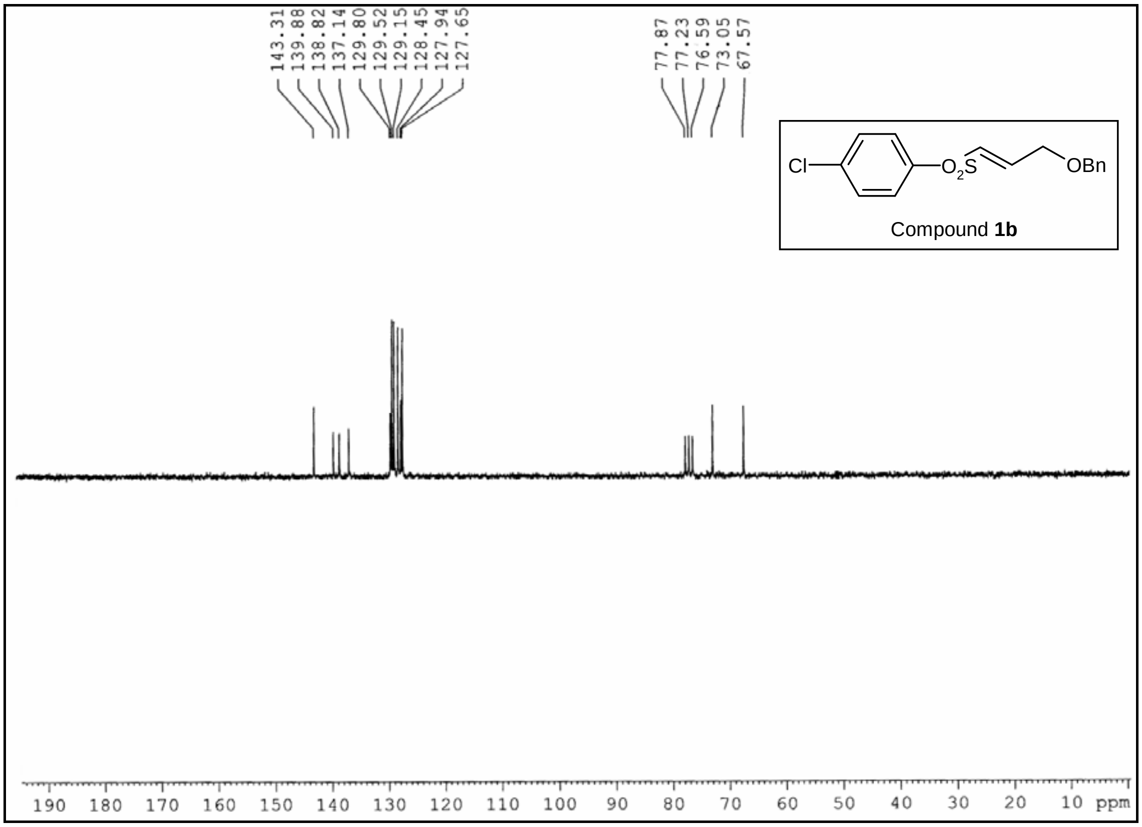

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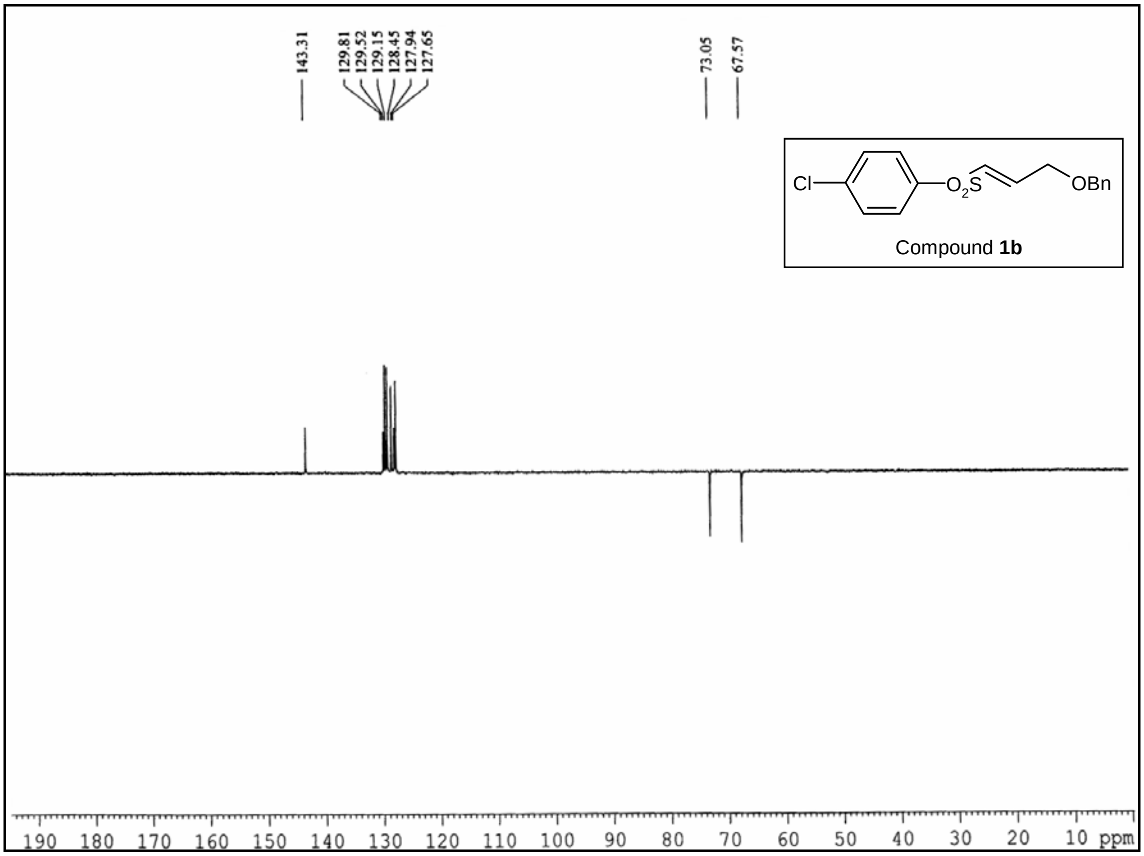
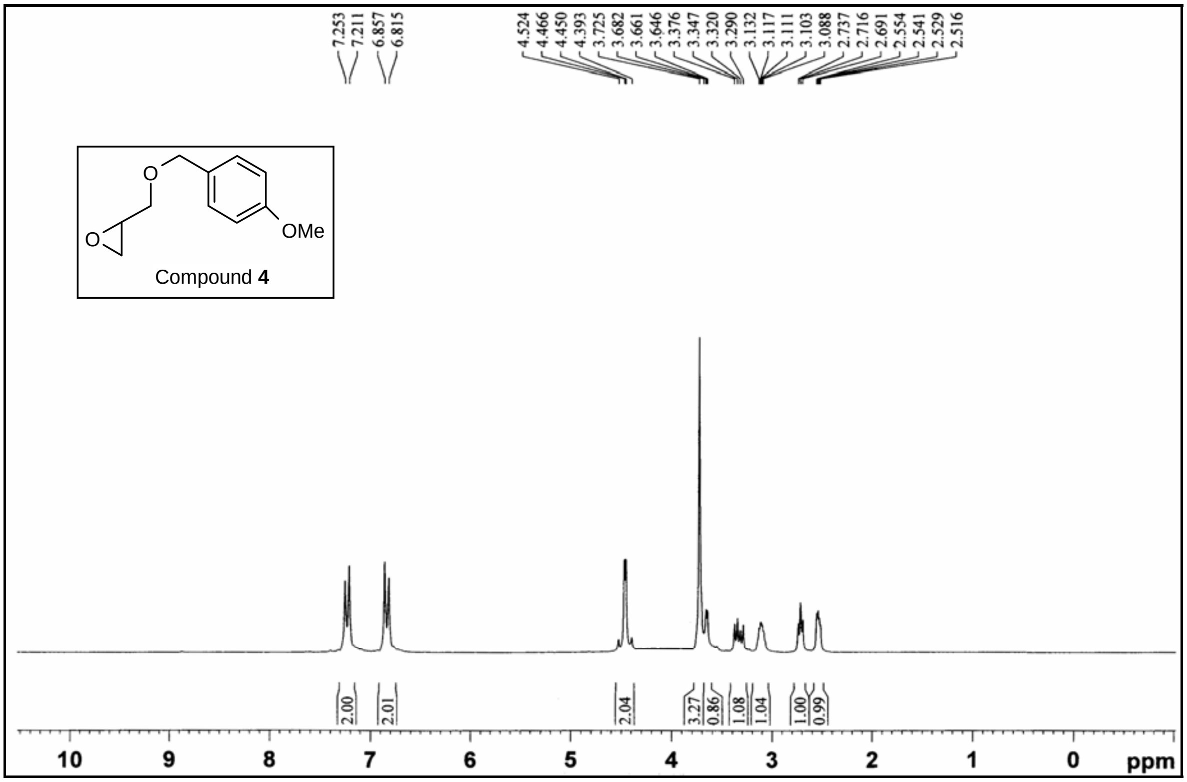


^{1}H-NMR spectra of **4**



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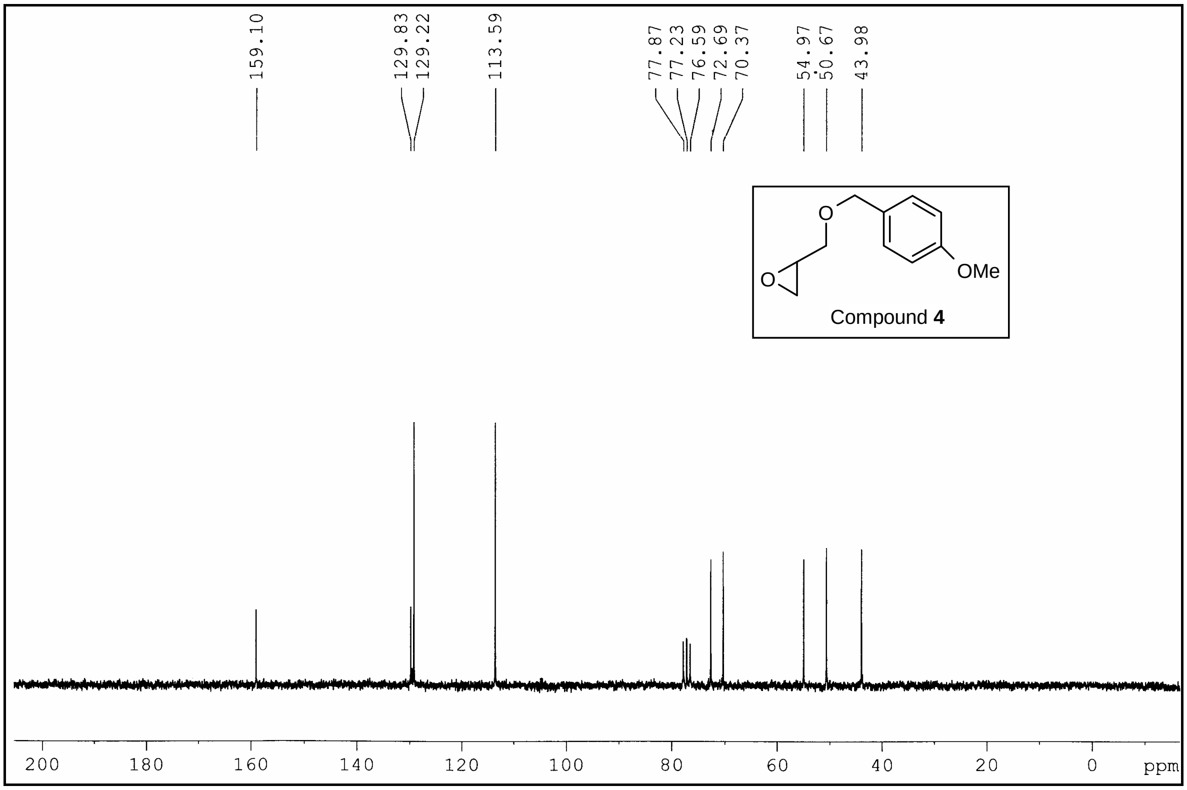

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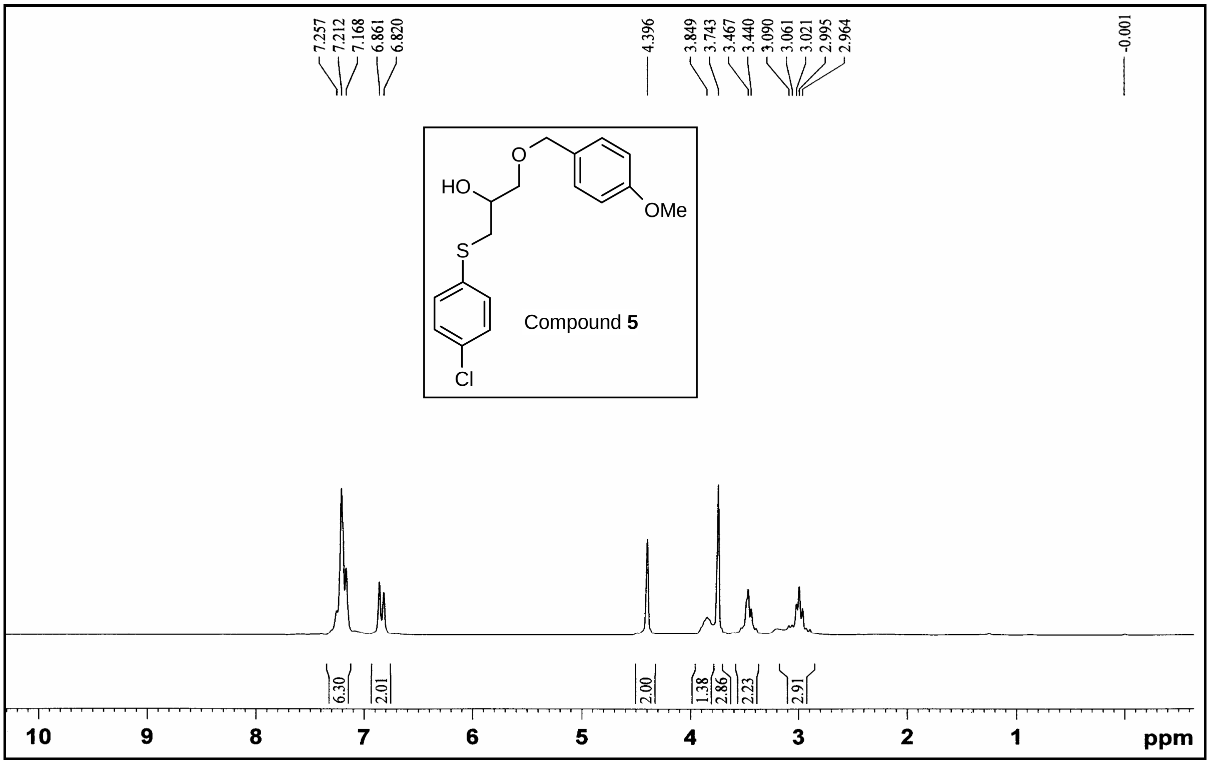

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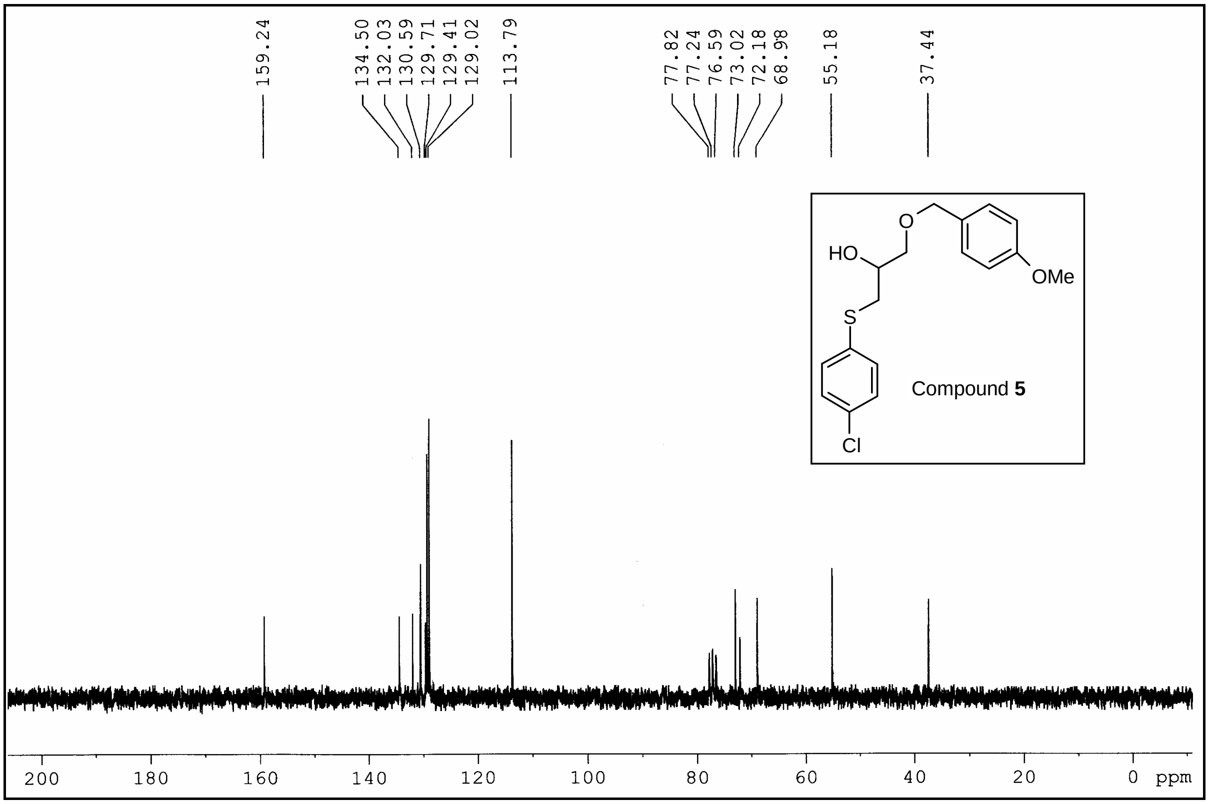

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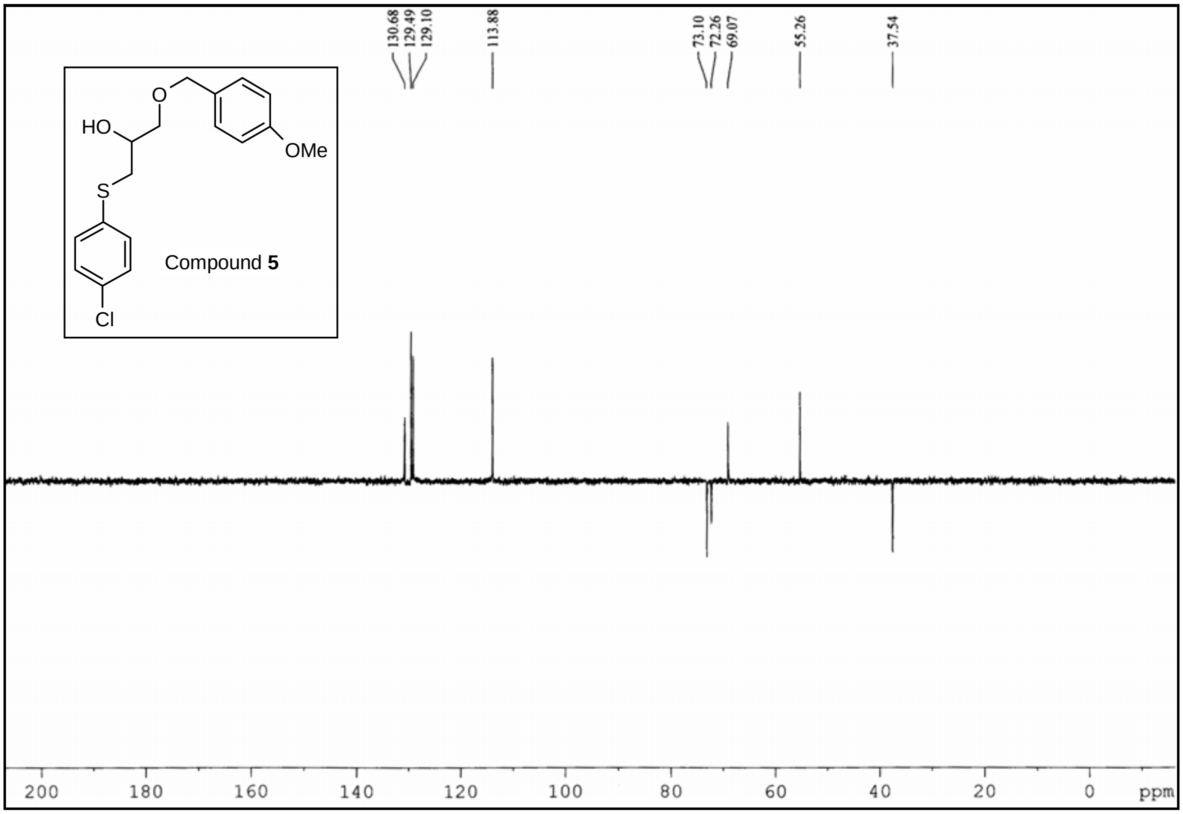
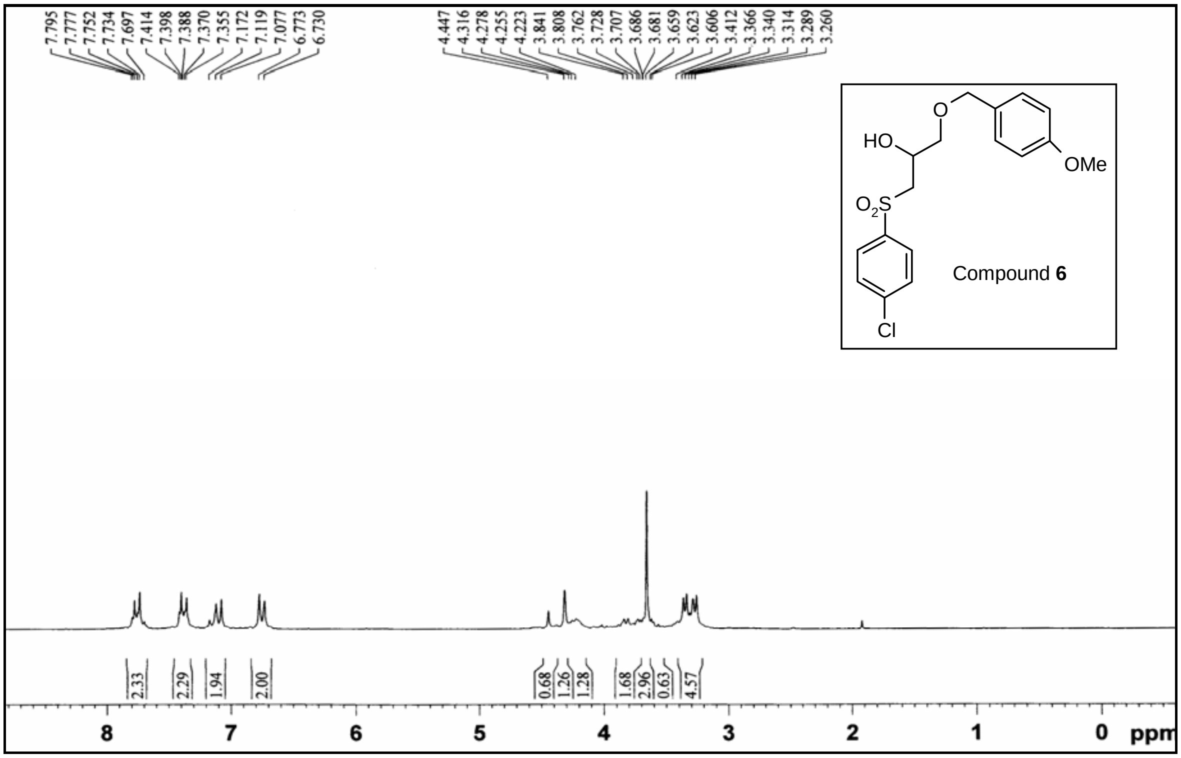


^{1}H-NMR spectra of **6**



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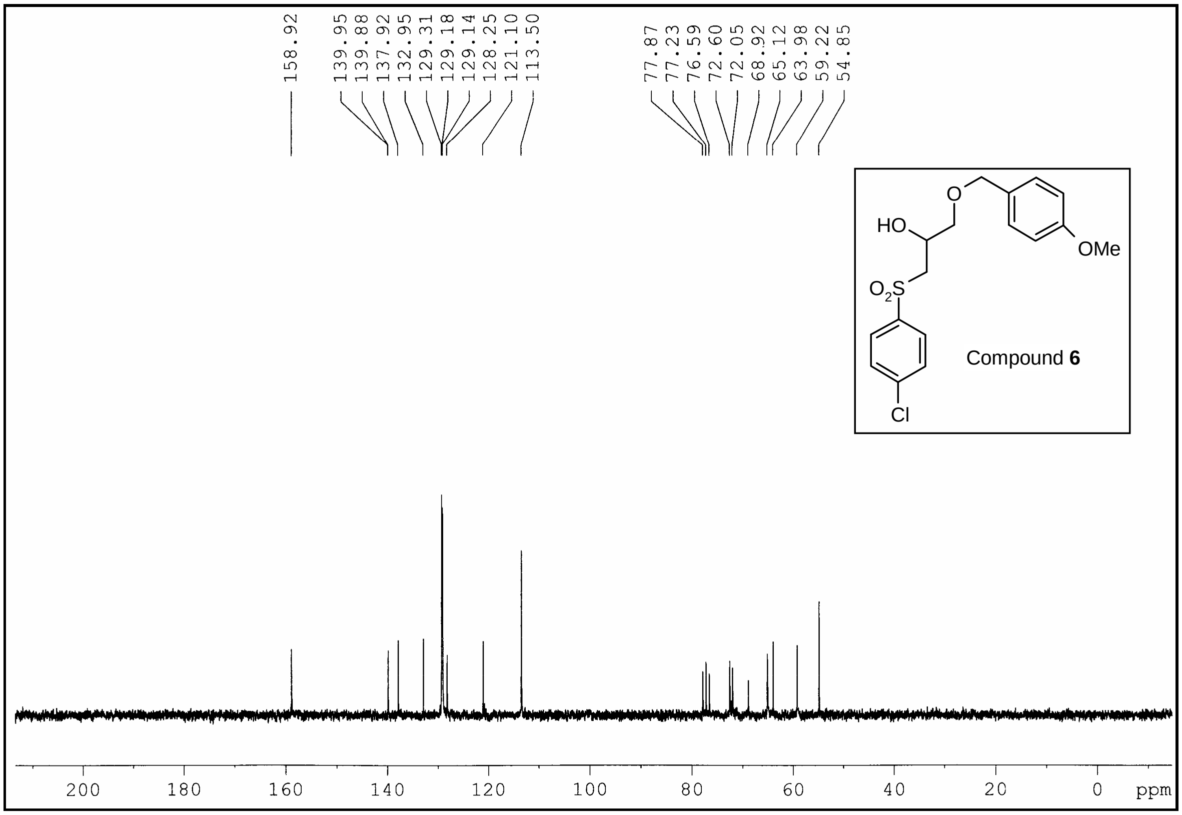

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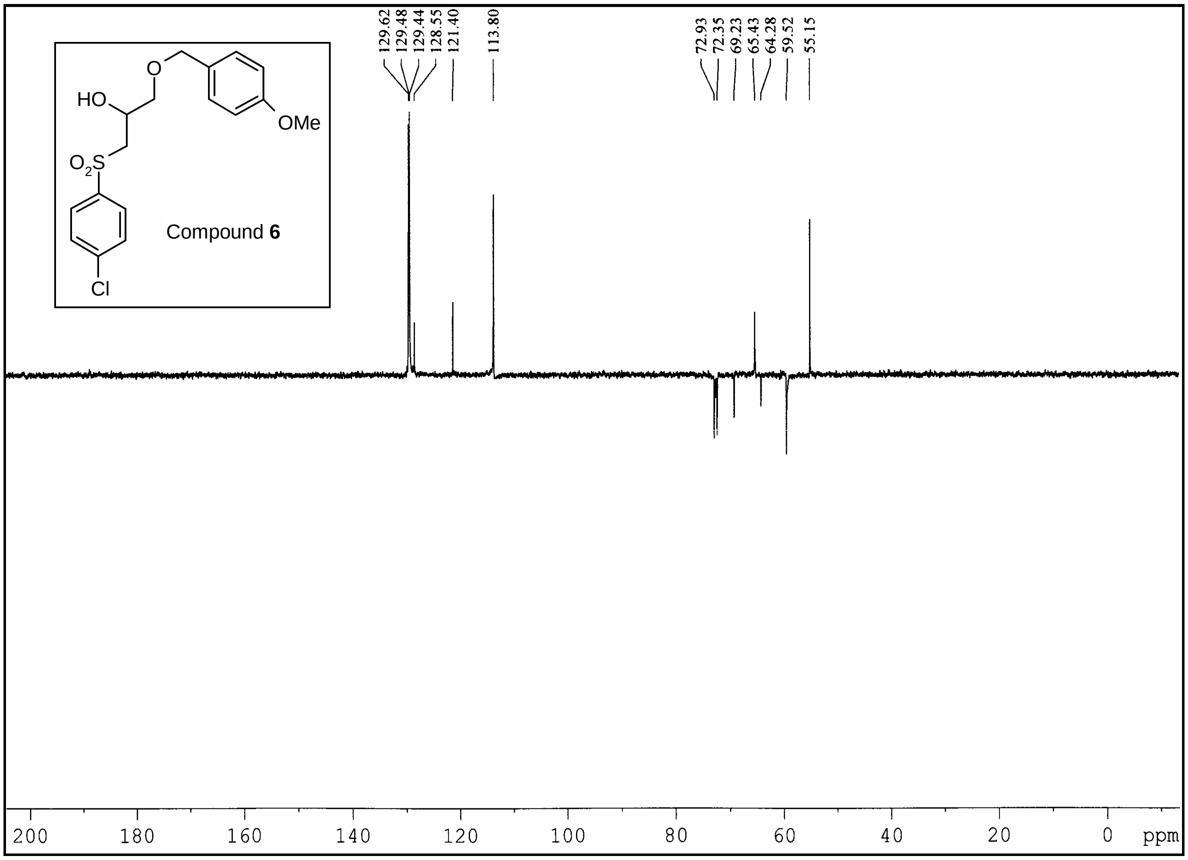
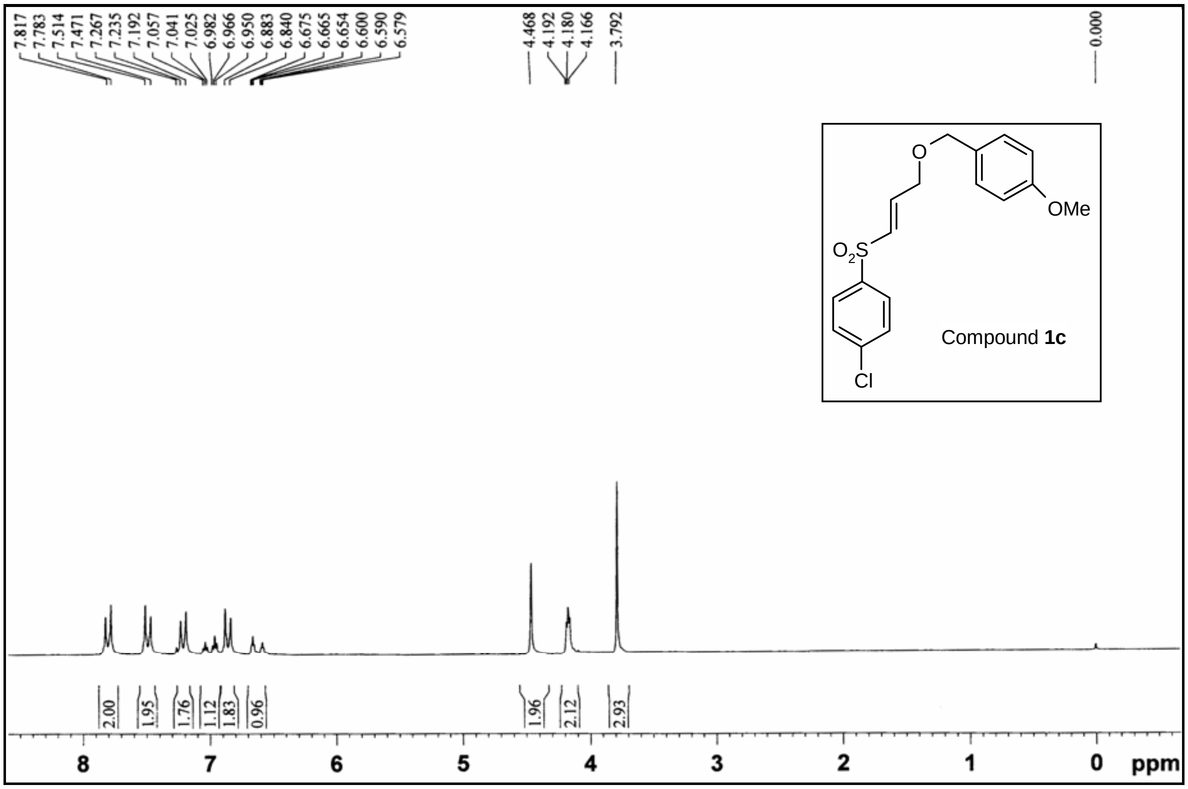
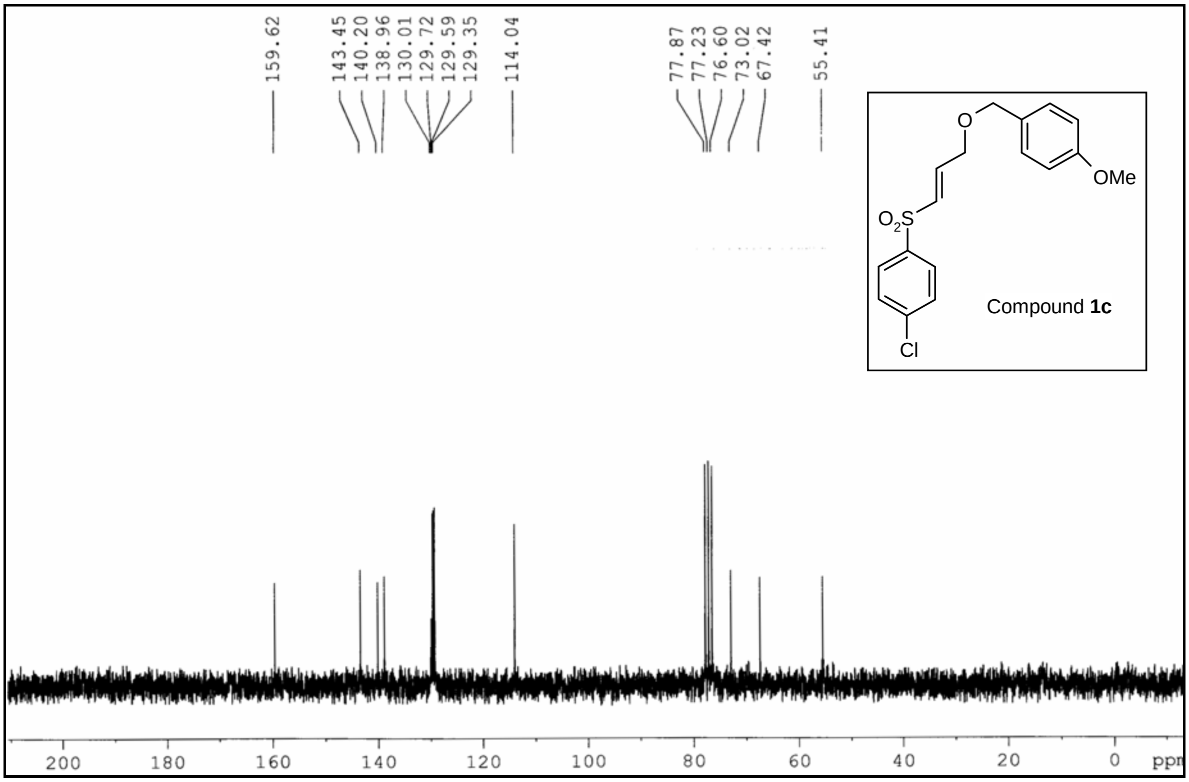


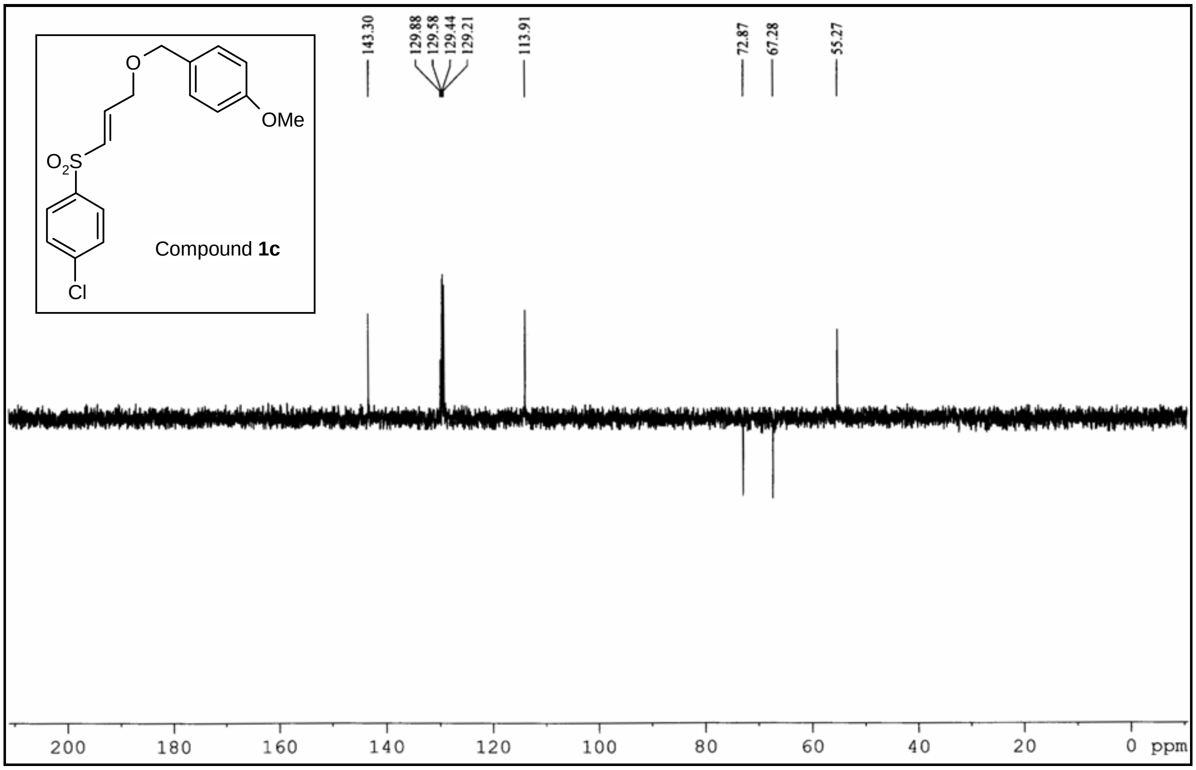
^{1}H-NMR spectra of **1c**



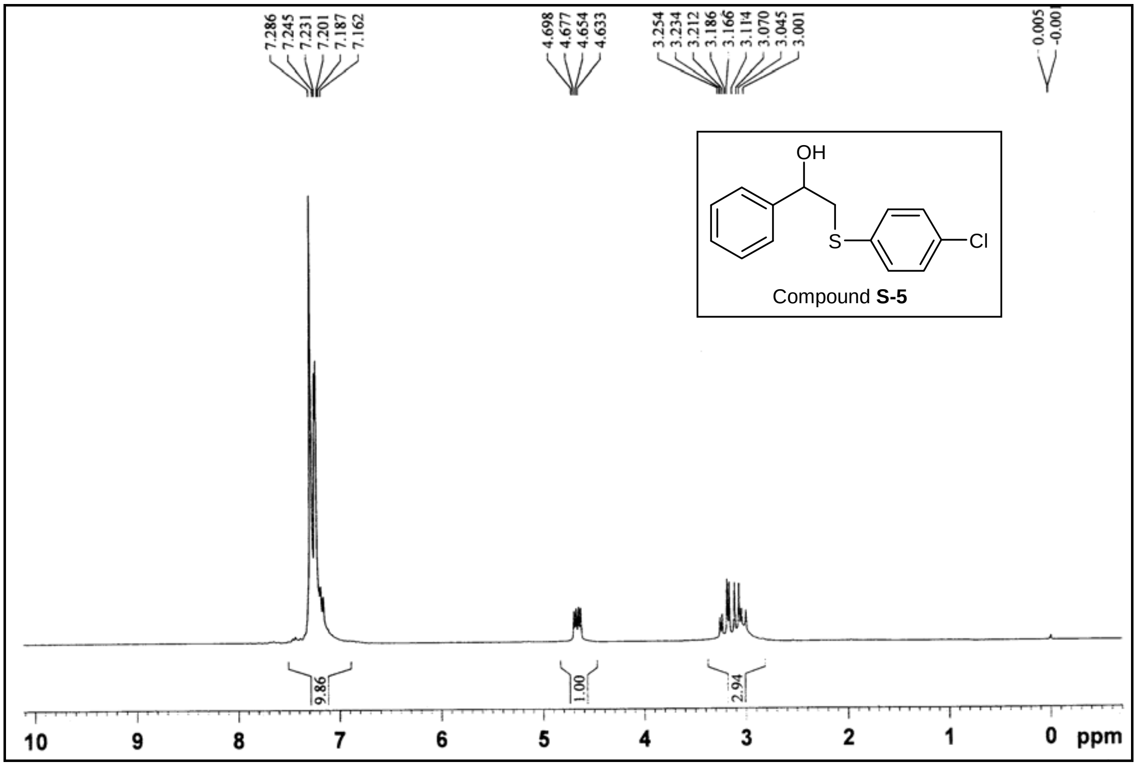
^{13}C-NMR spectra of **1c**



DEPT spectra of **1c**



^{1}H-NMR spectra of **S-5**



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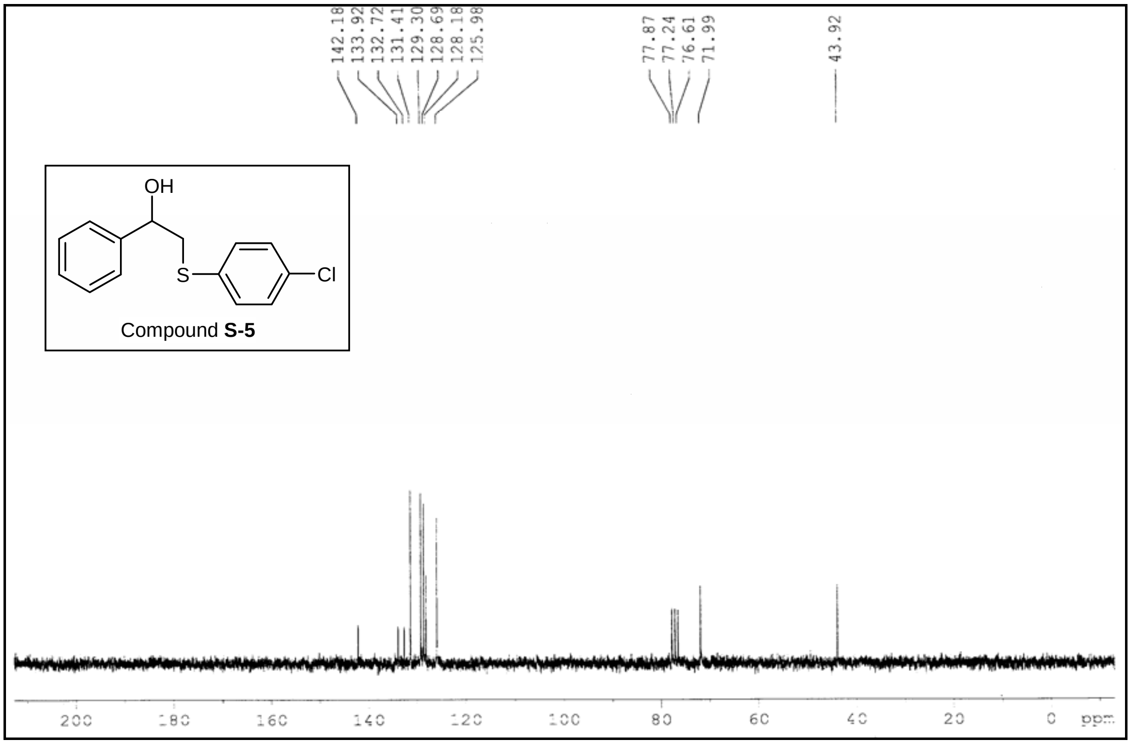

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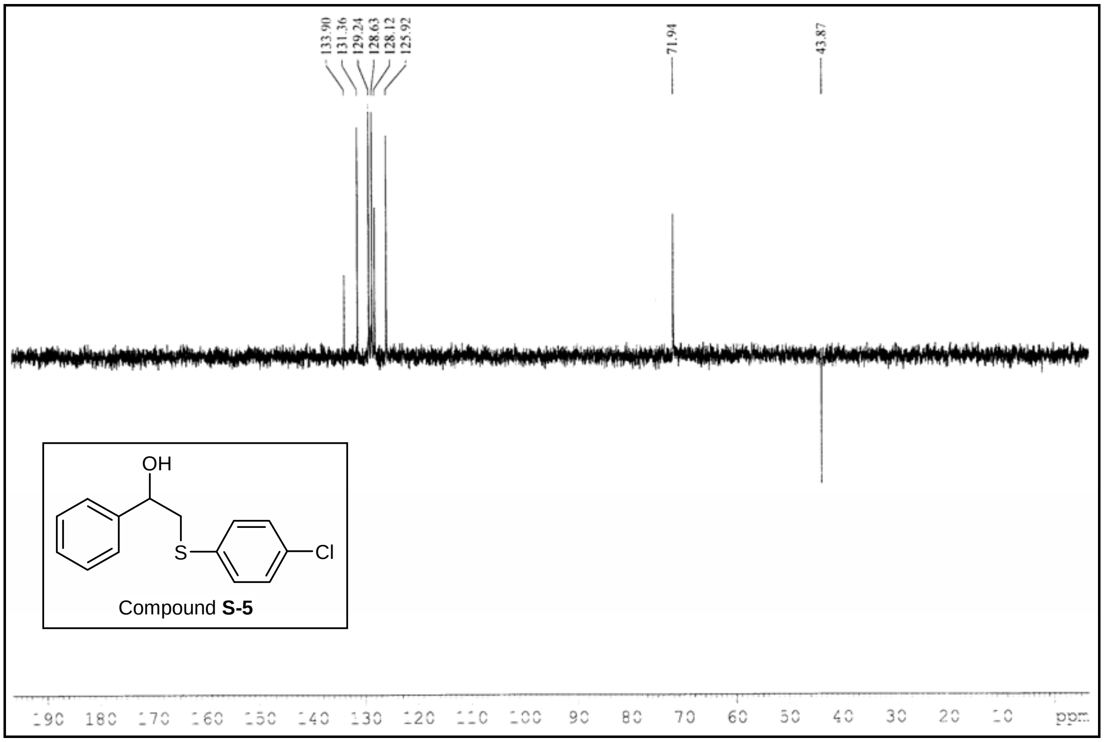
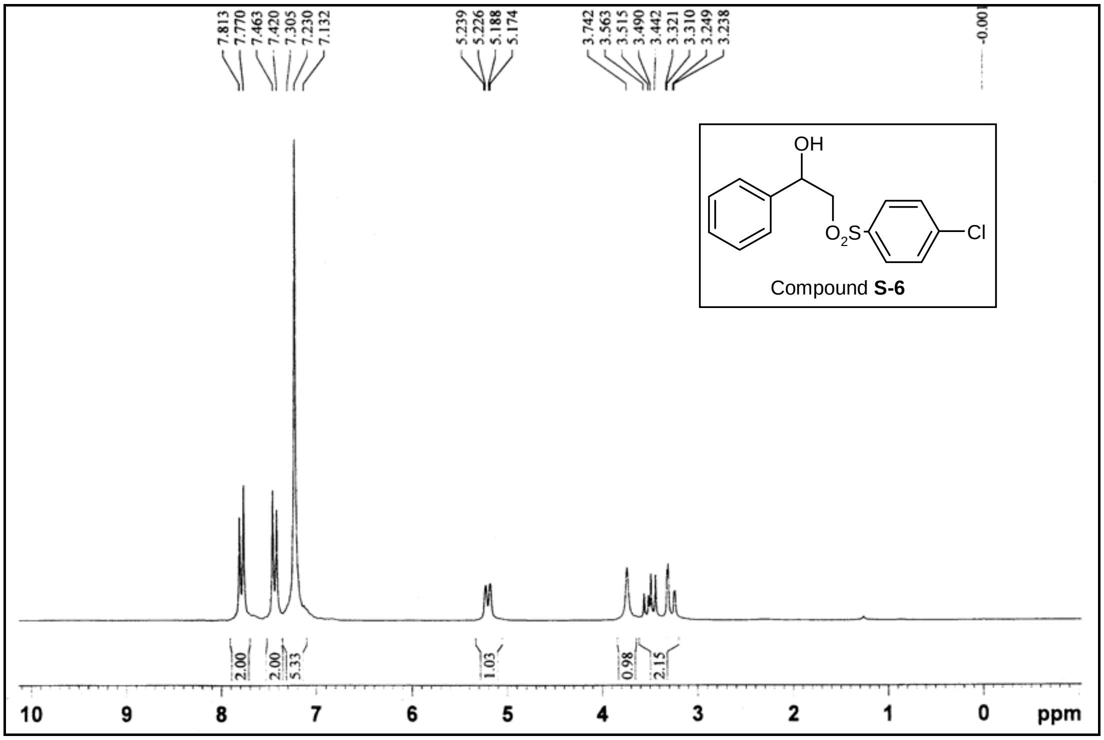


^{1}H-NMR spectra of **S-6**



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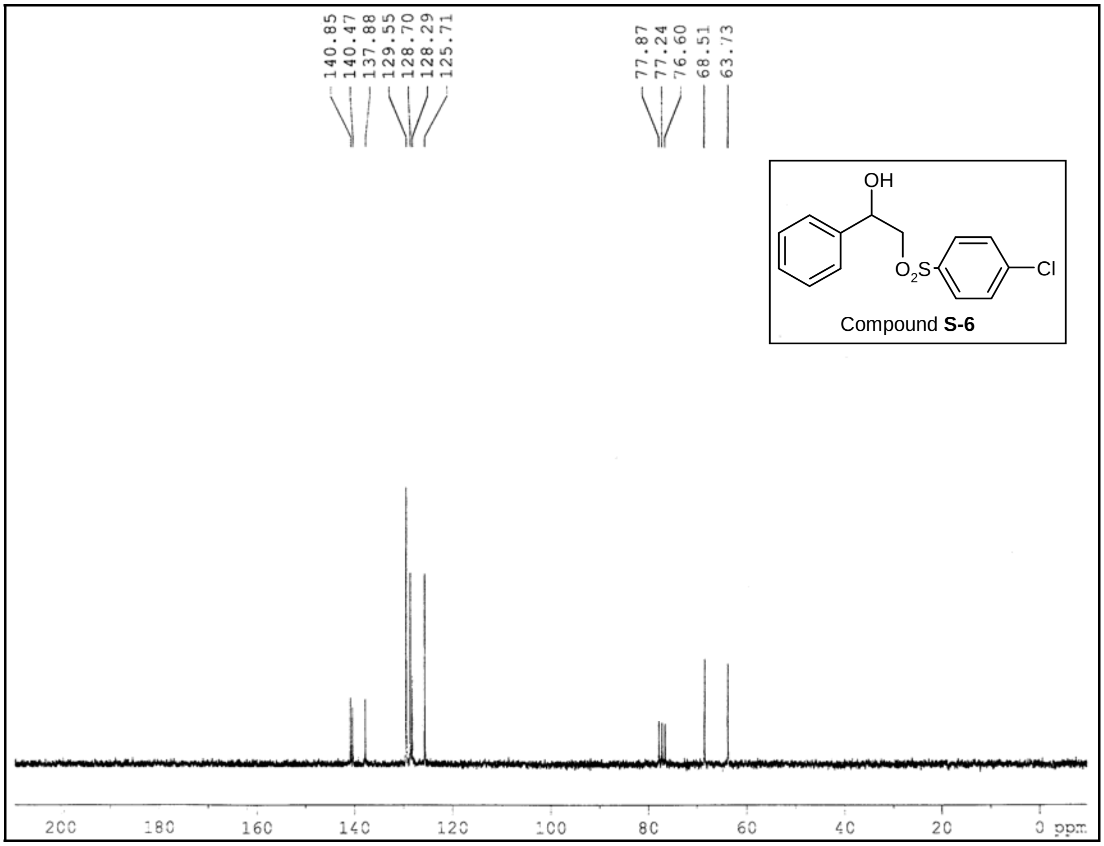

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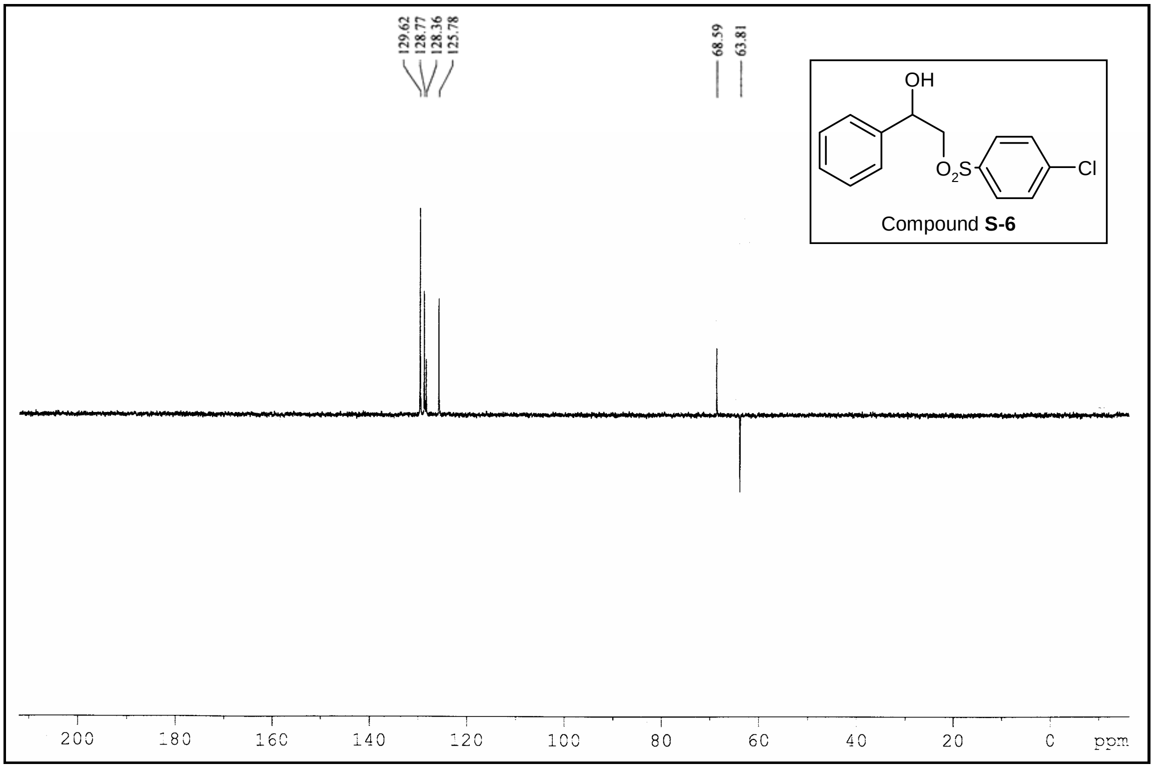

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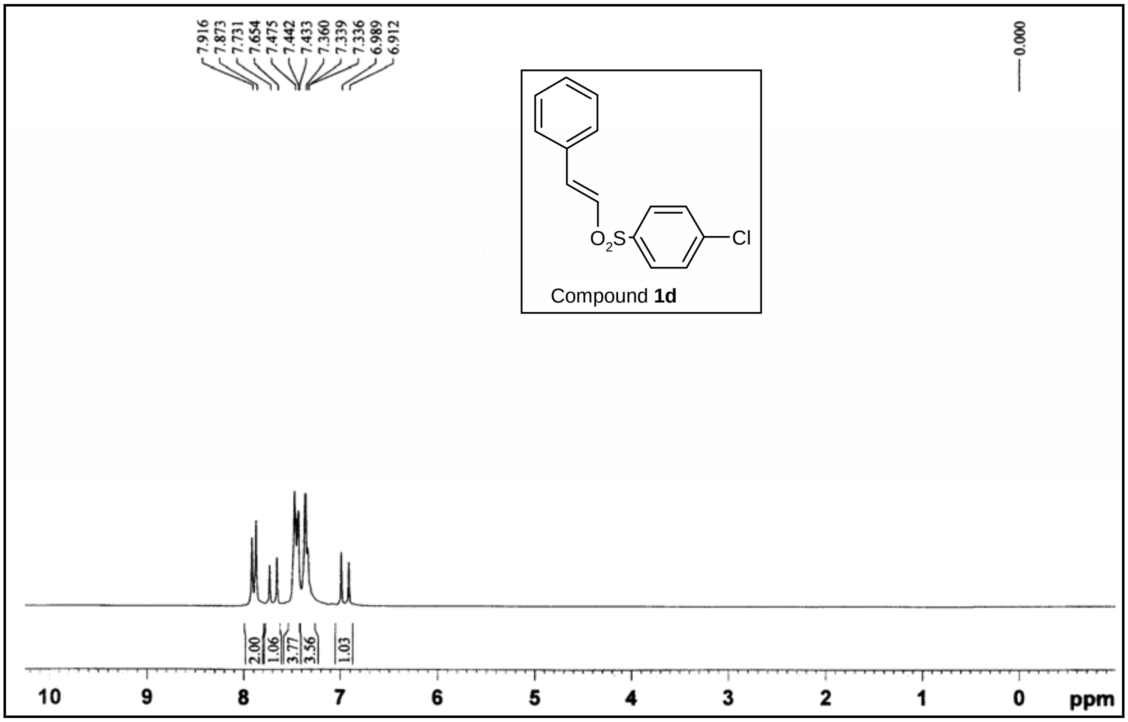

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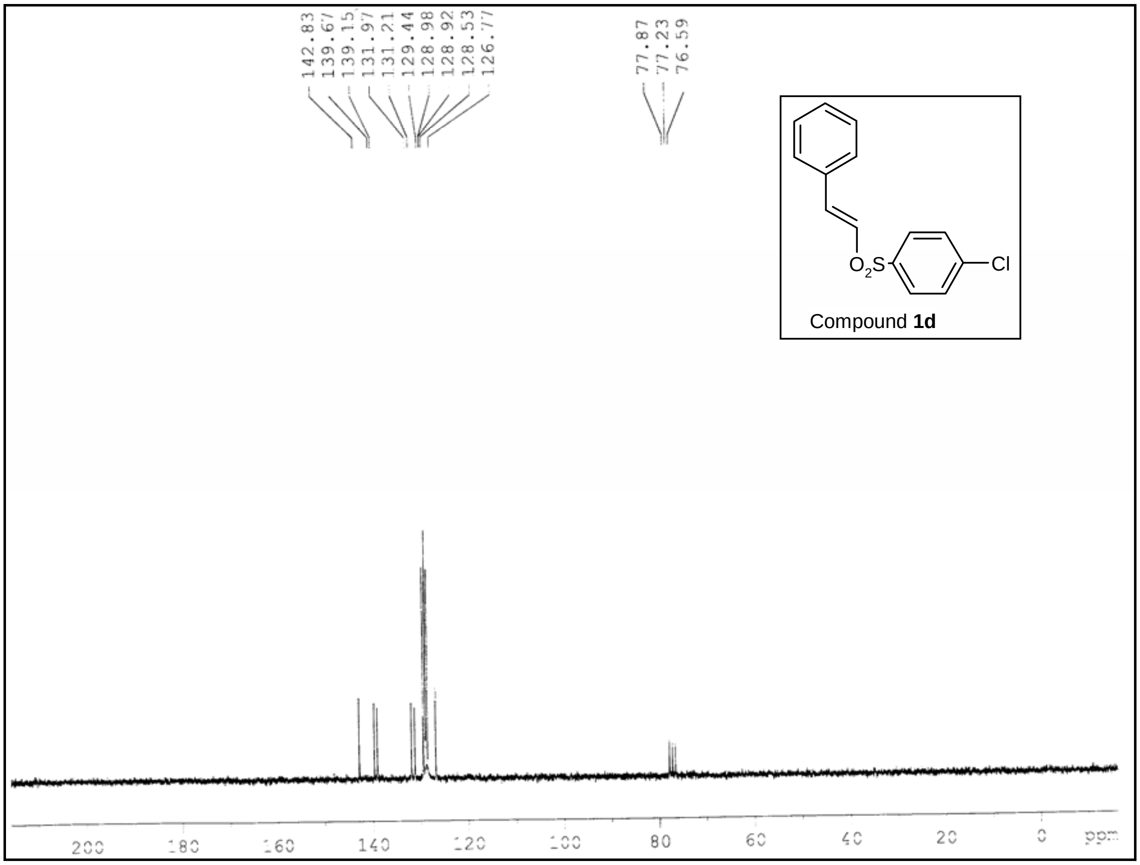

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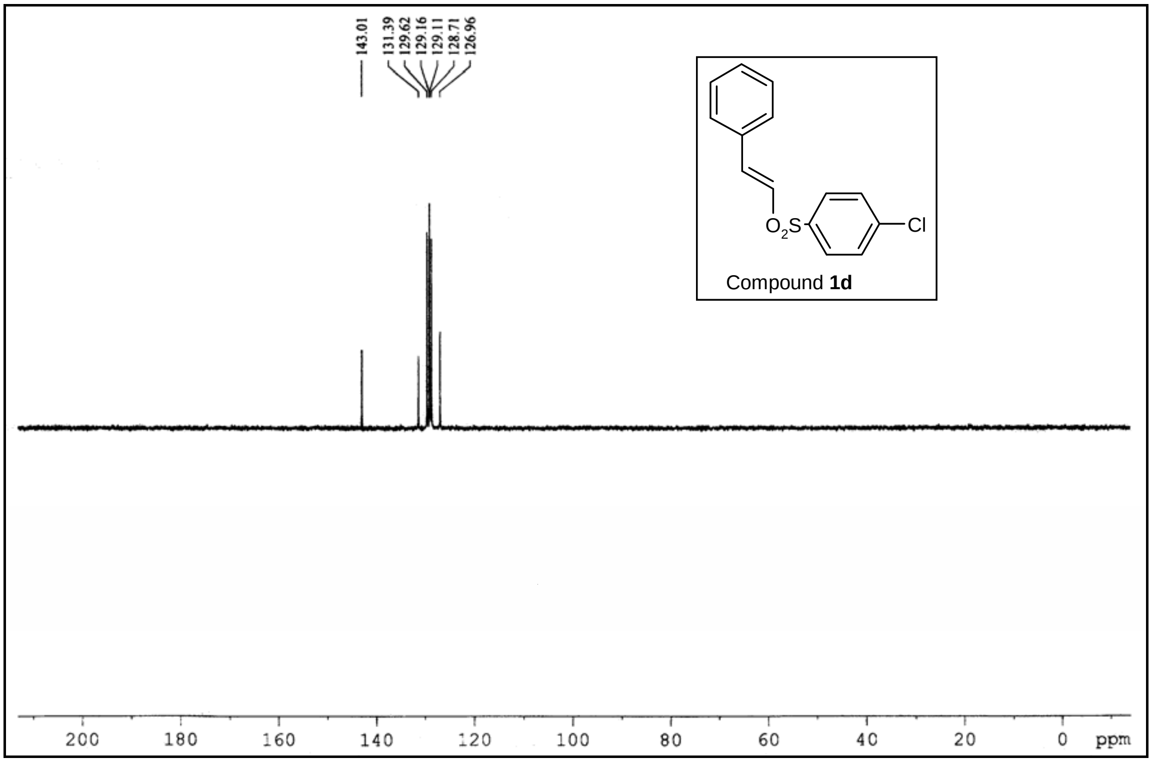
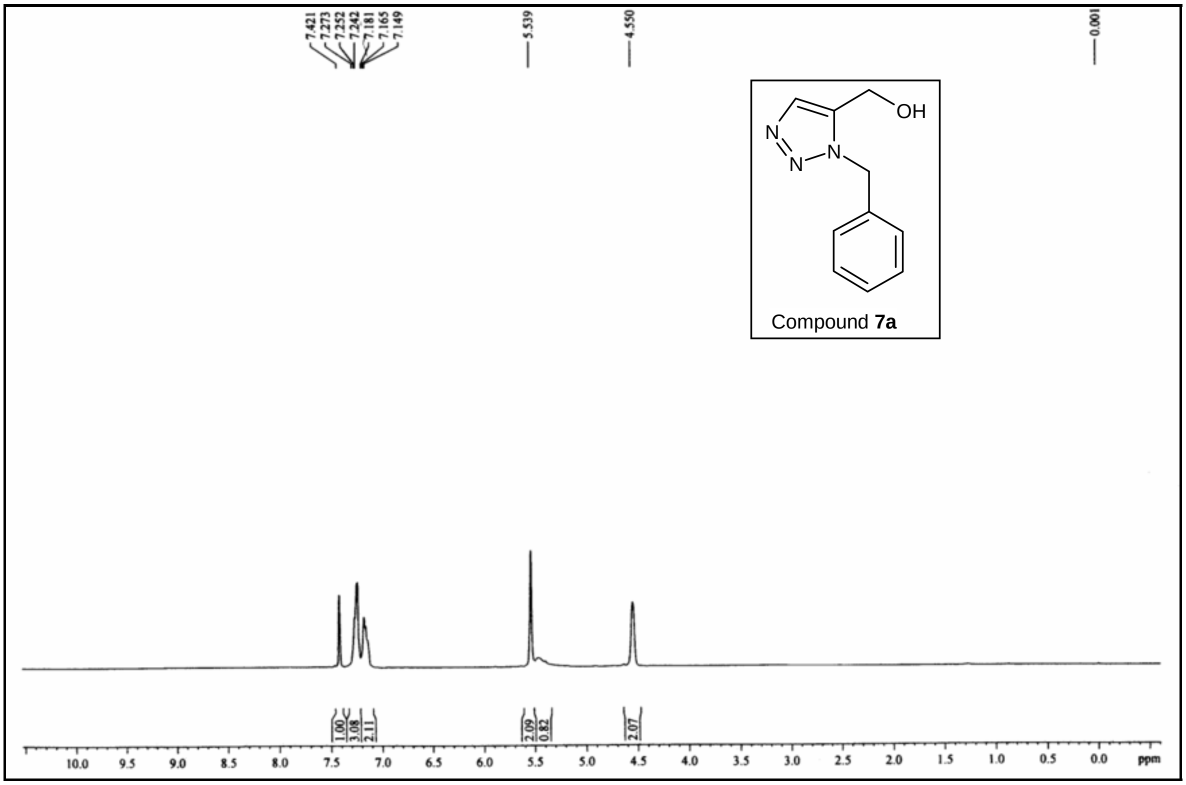


^{1}H-NMR spectra of **7a**



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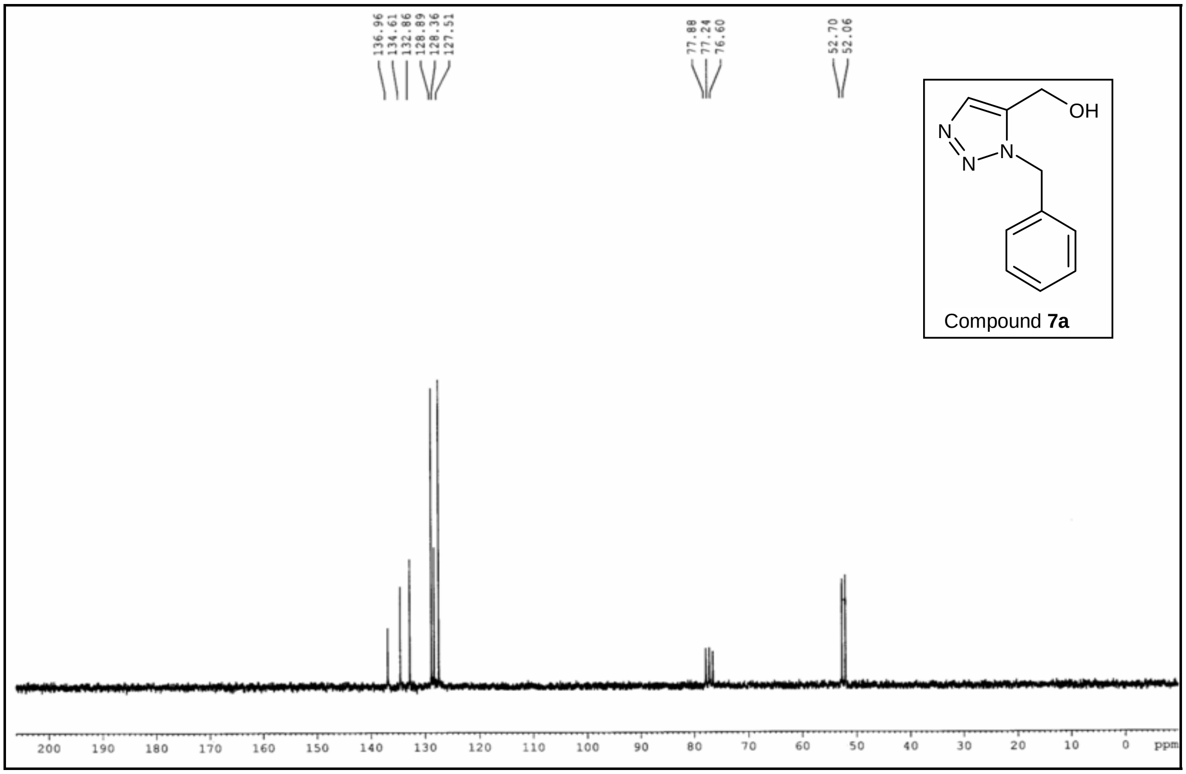

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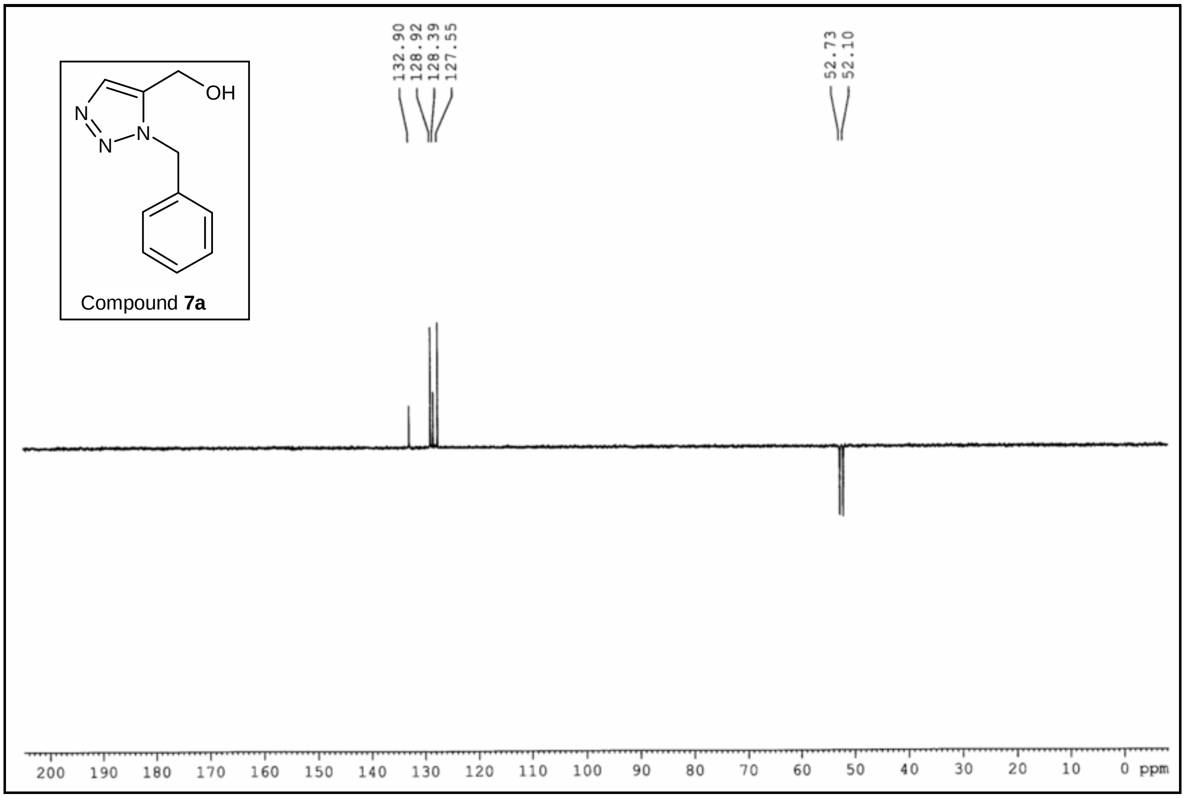
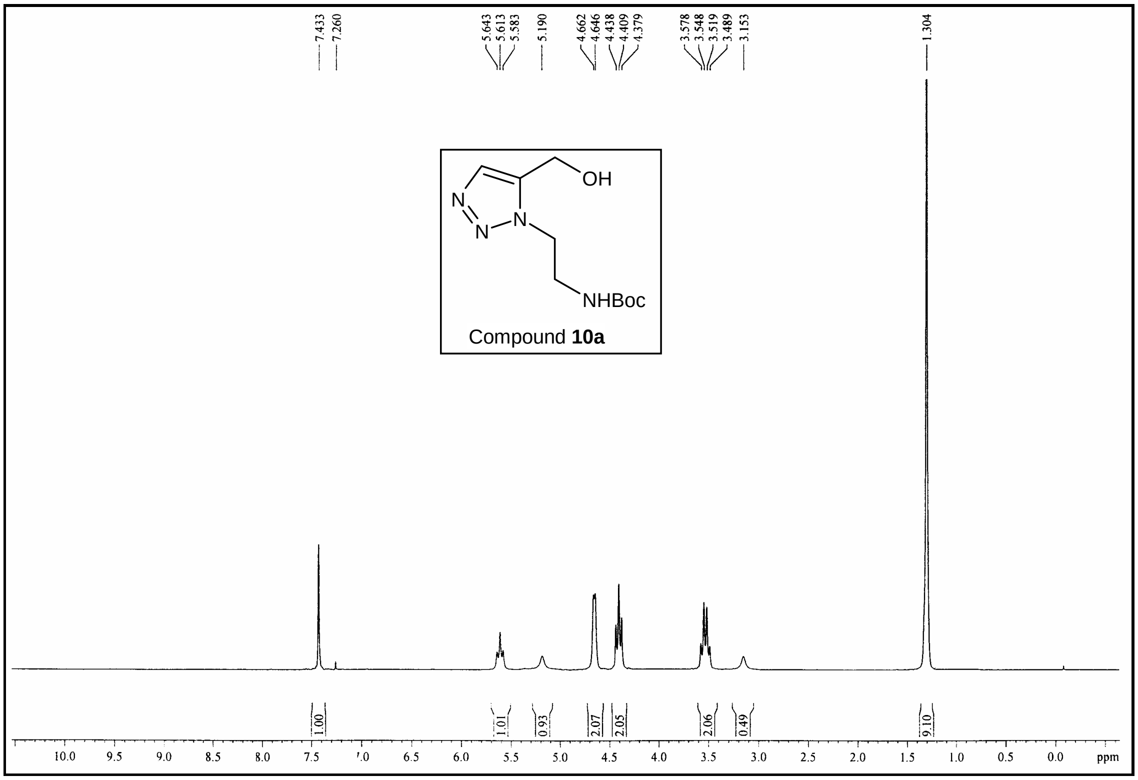


^{1}H-NMR spectra of **10a**



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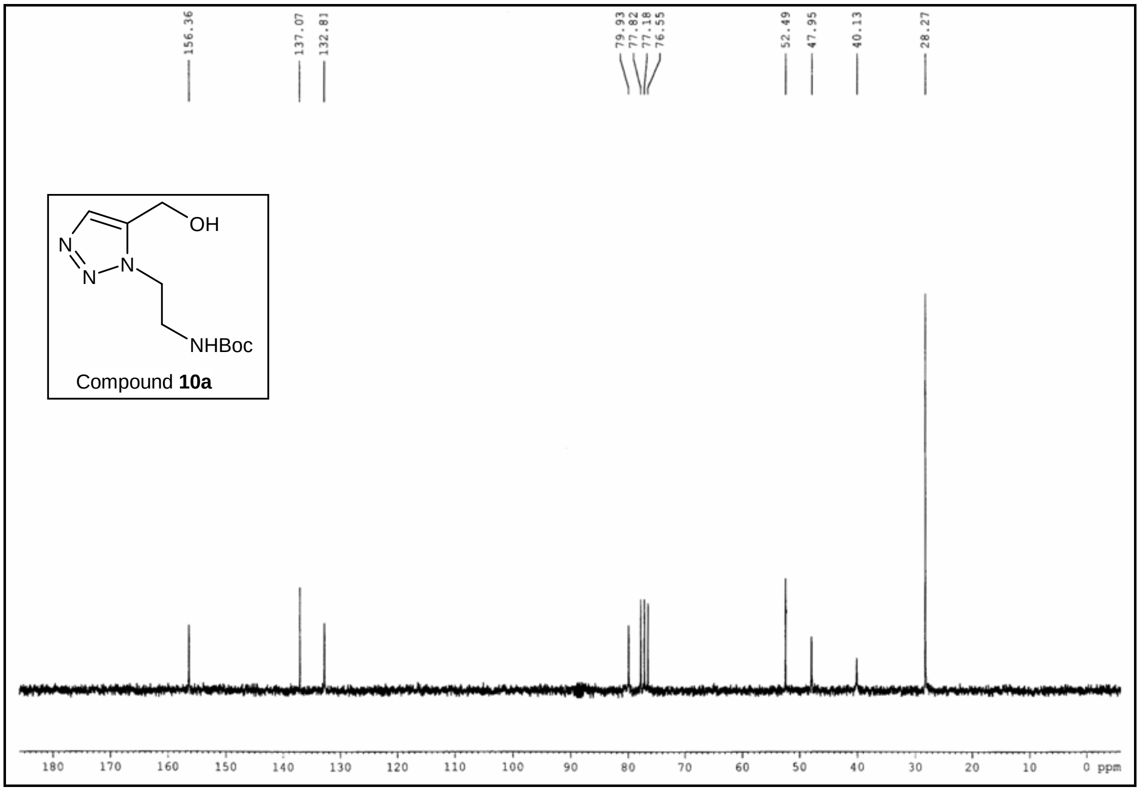

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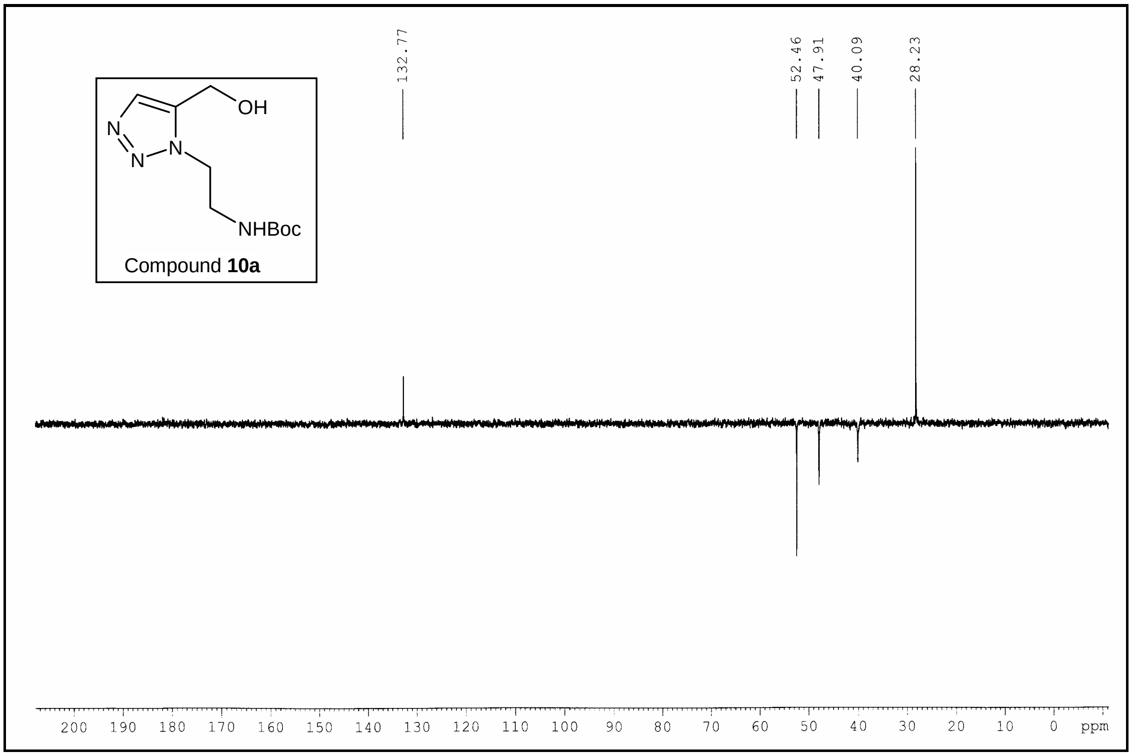
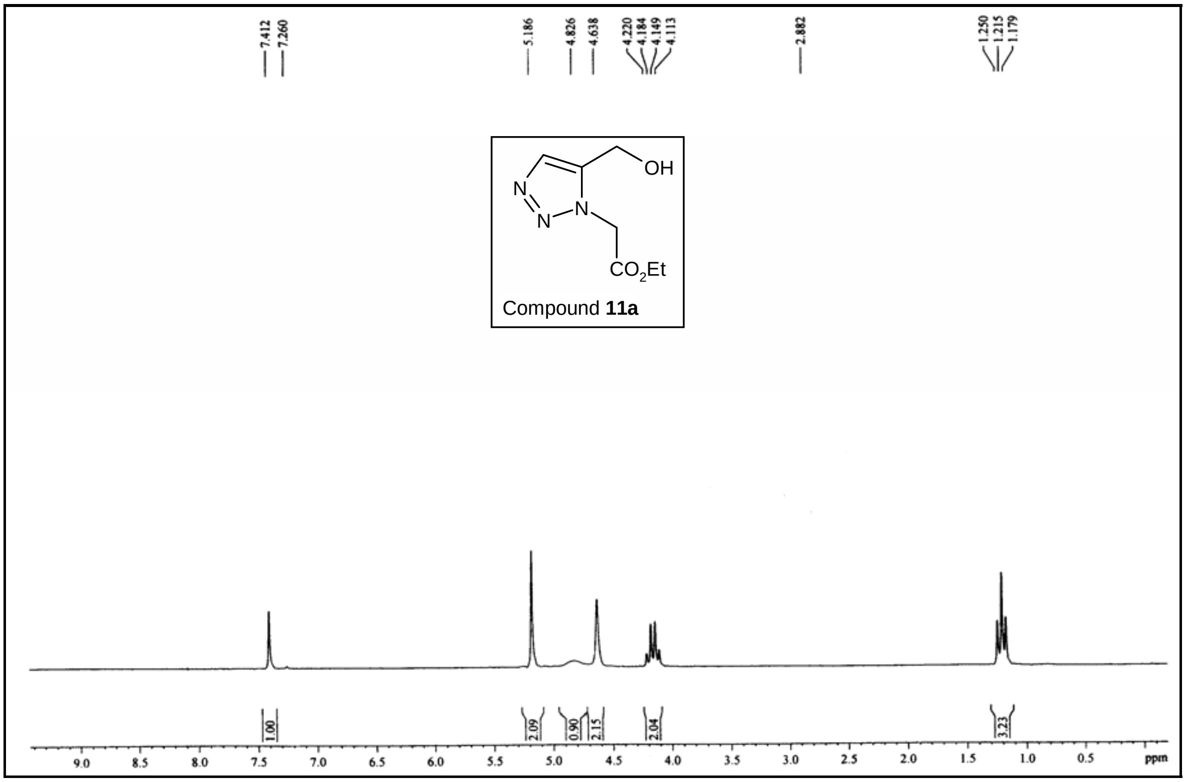


^{1}H-NMR spectra of **11a**



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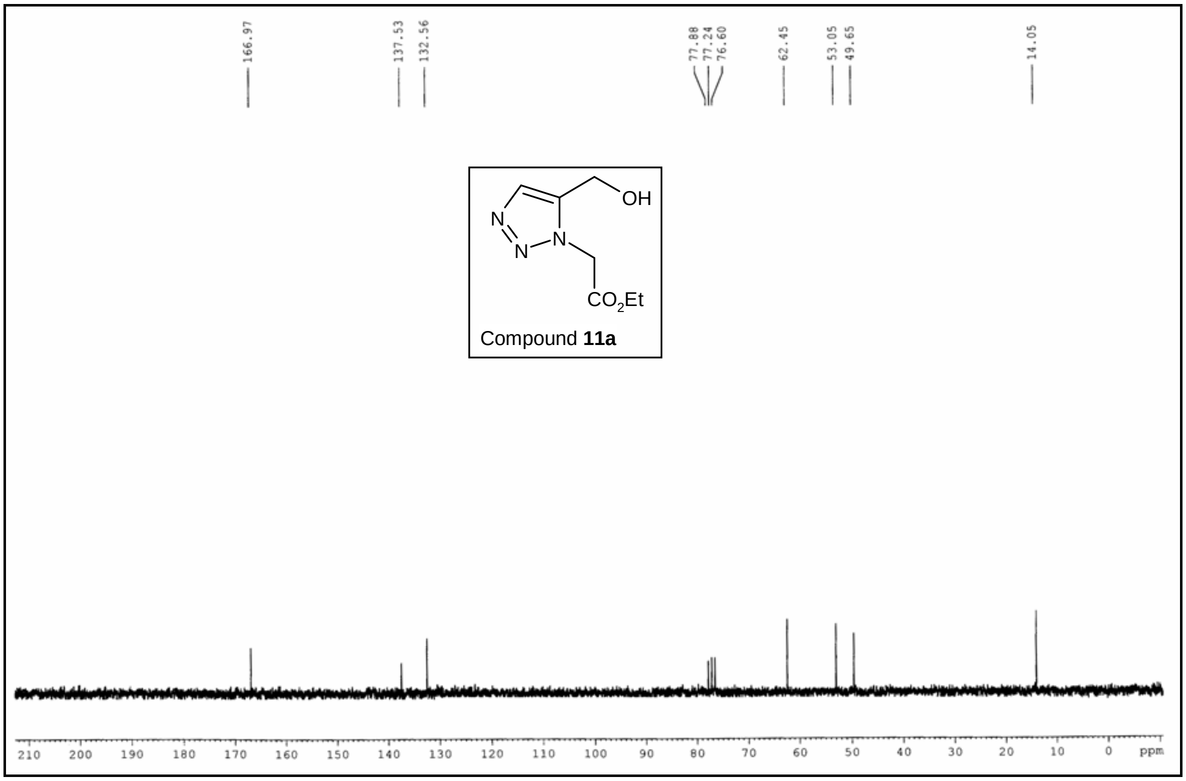

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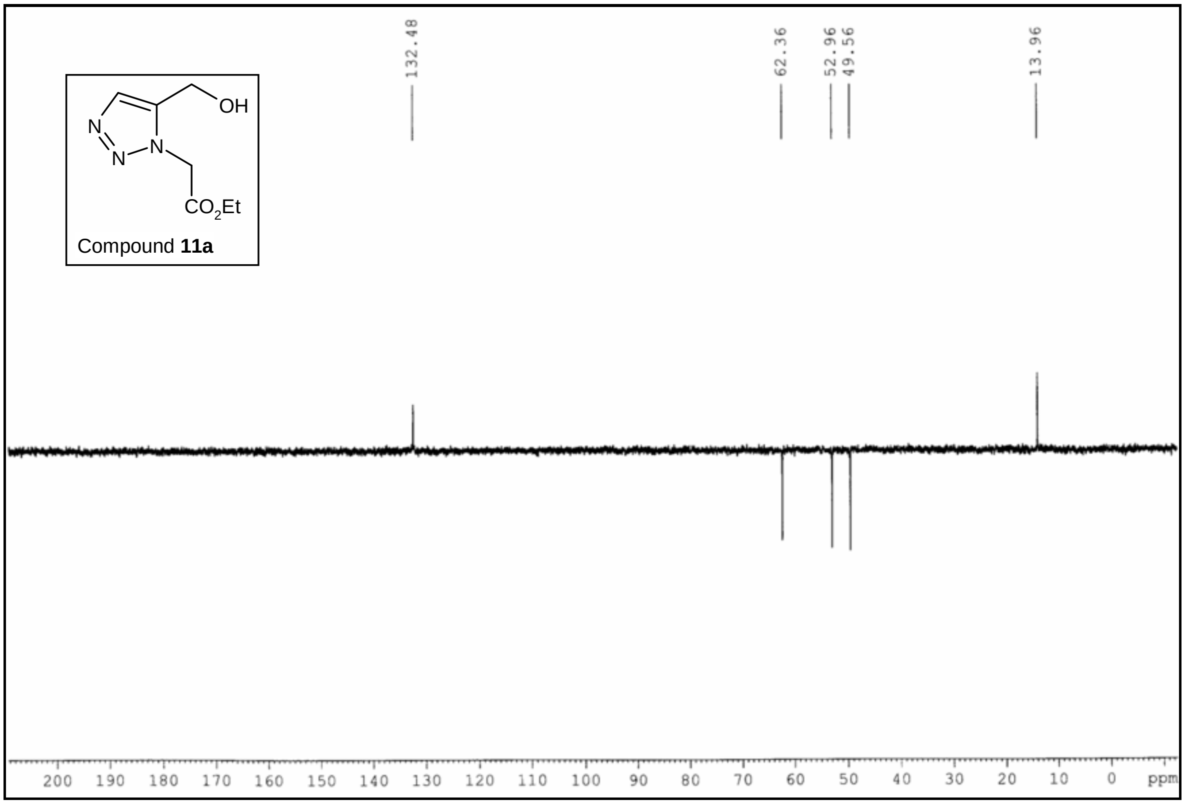

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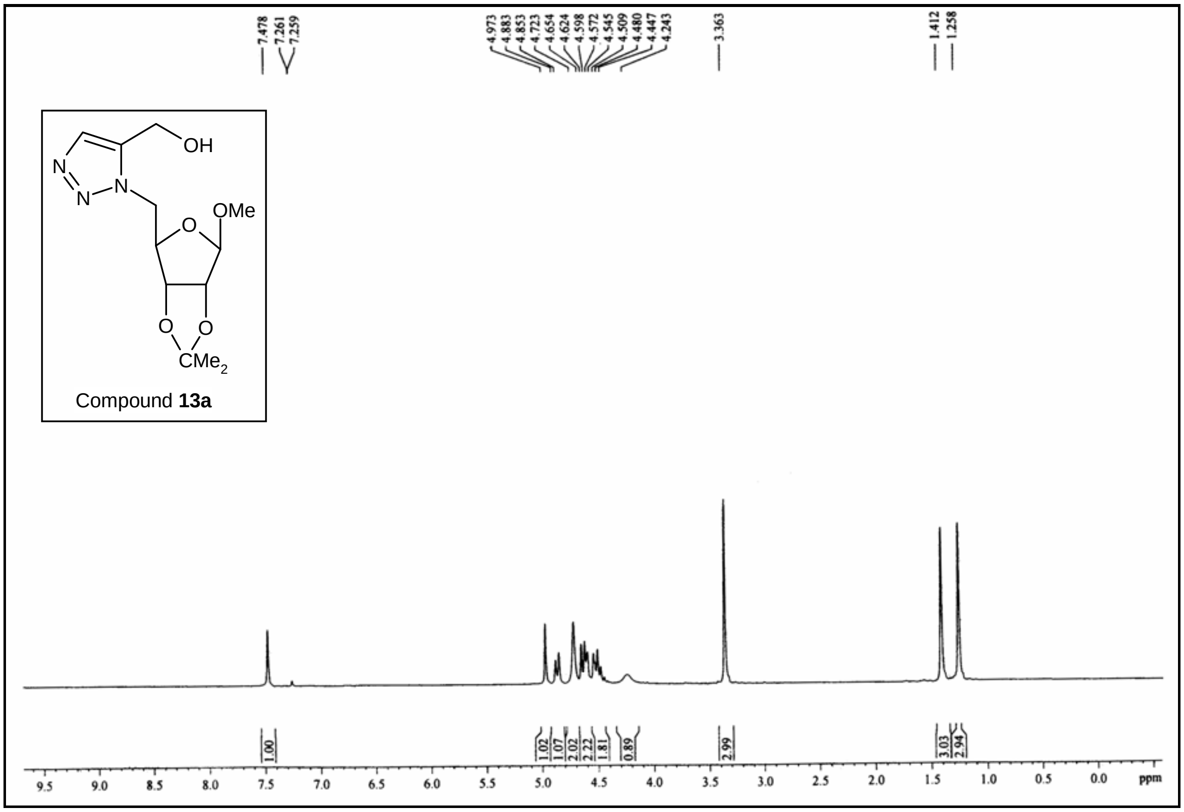

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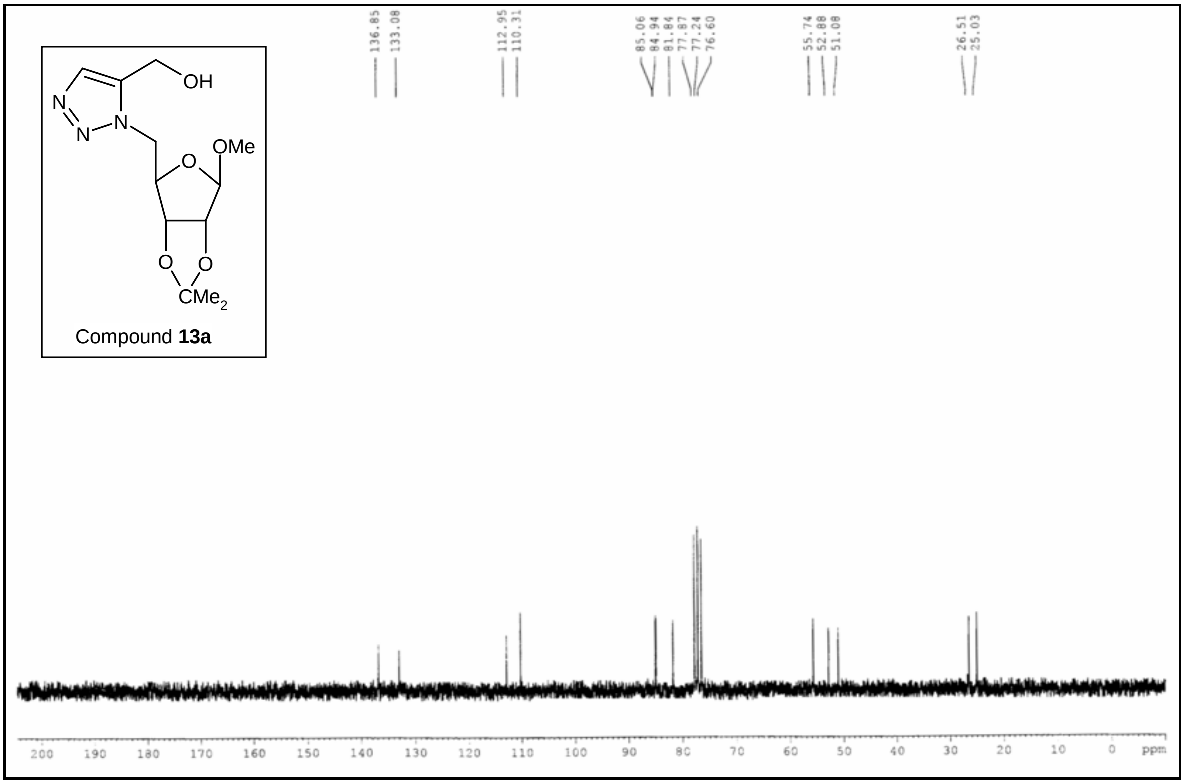

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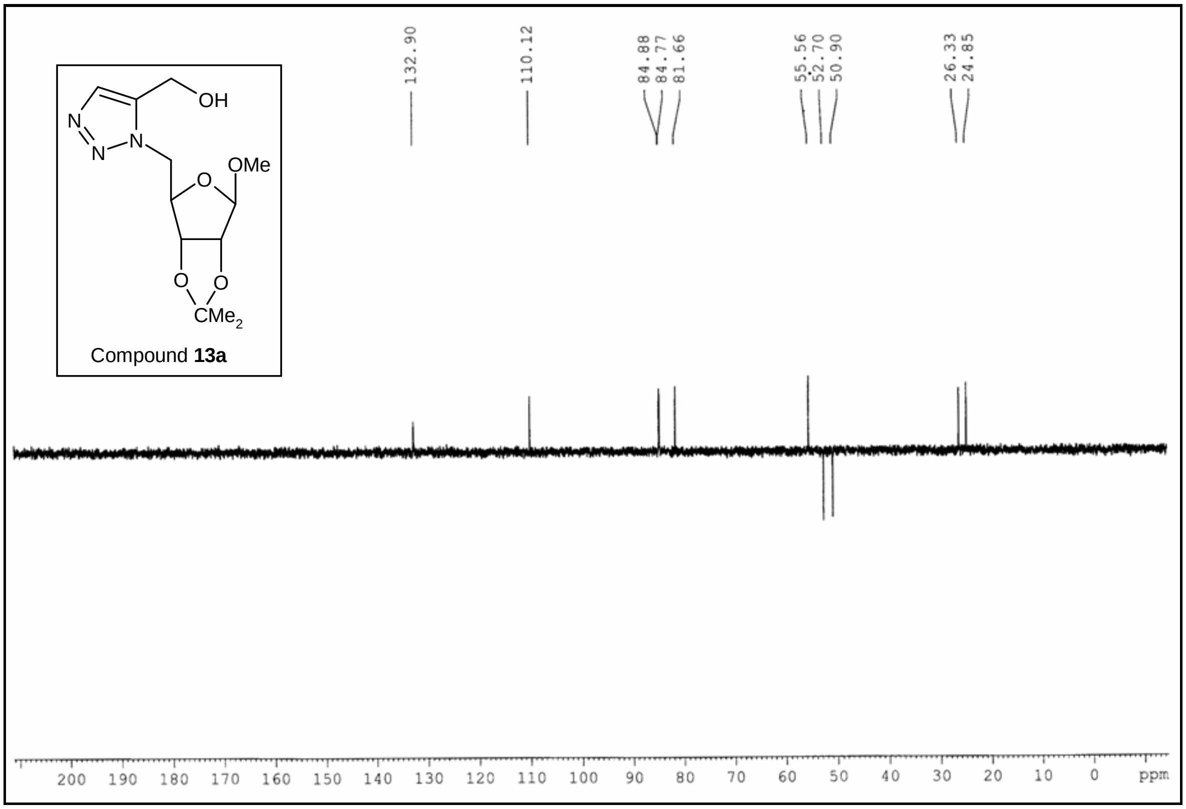

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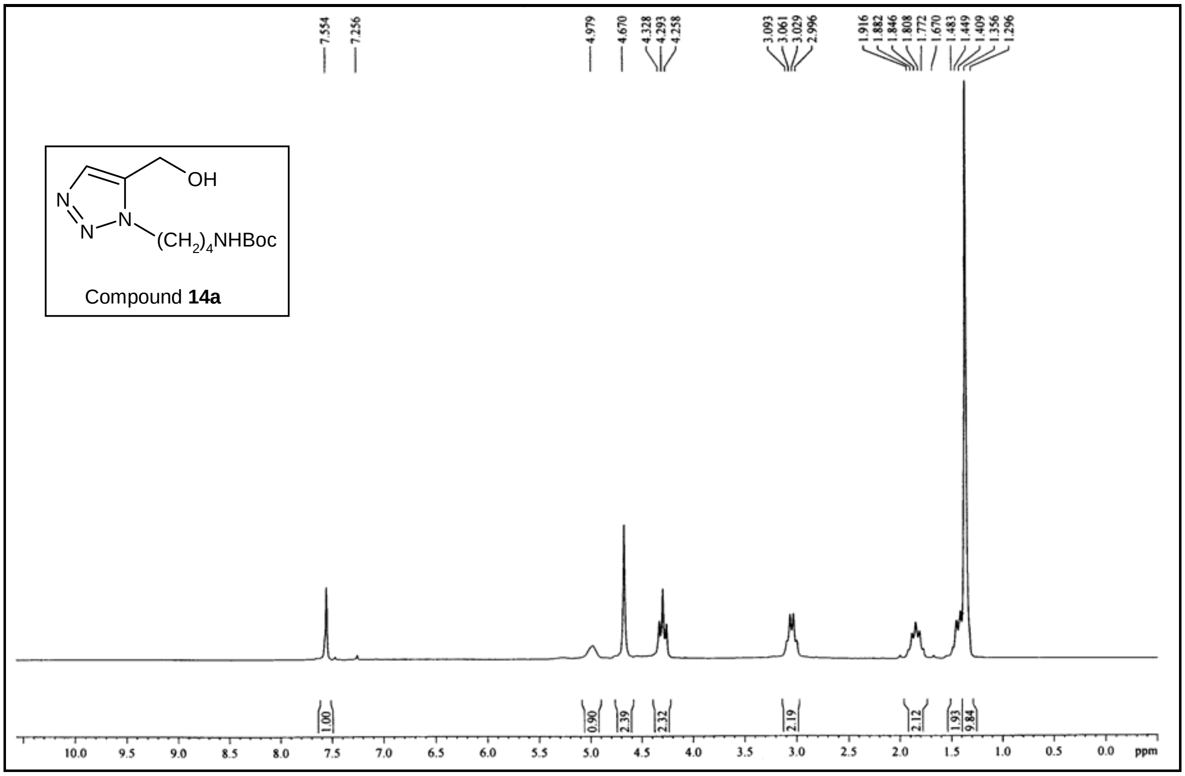

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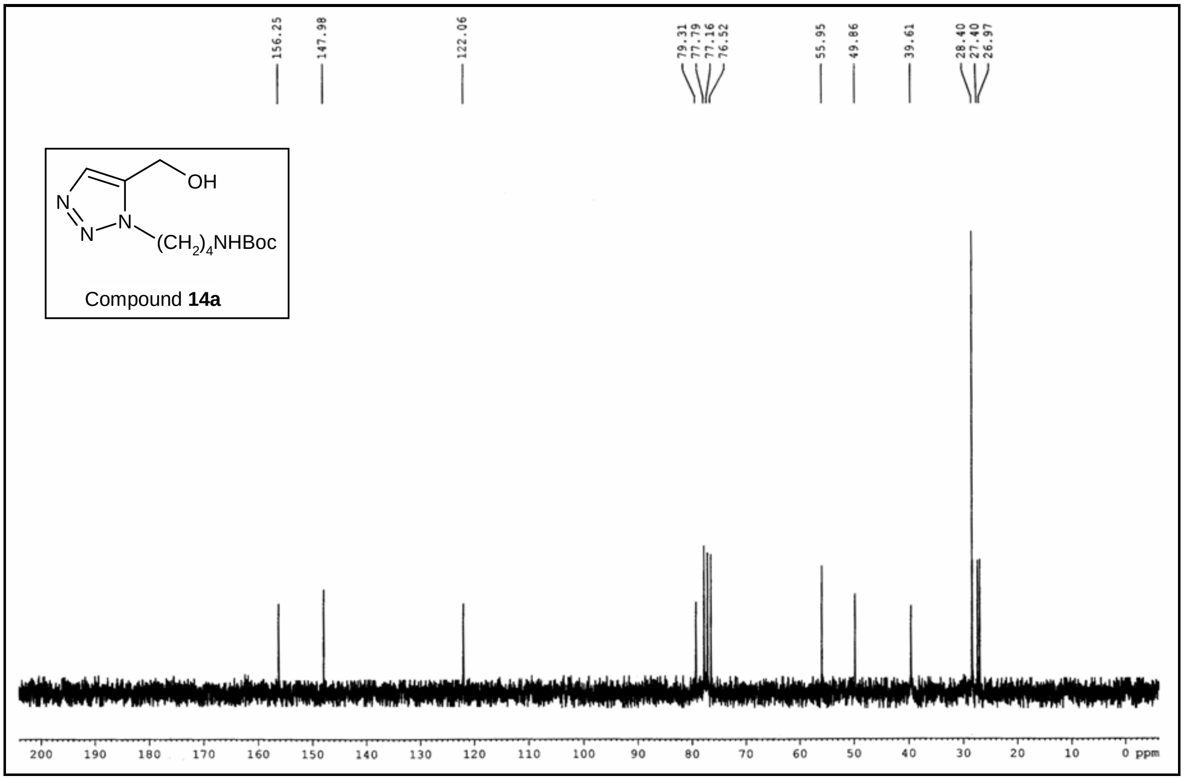

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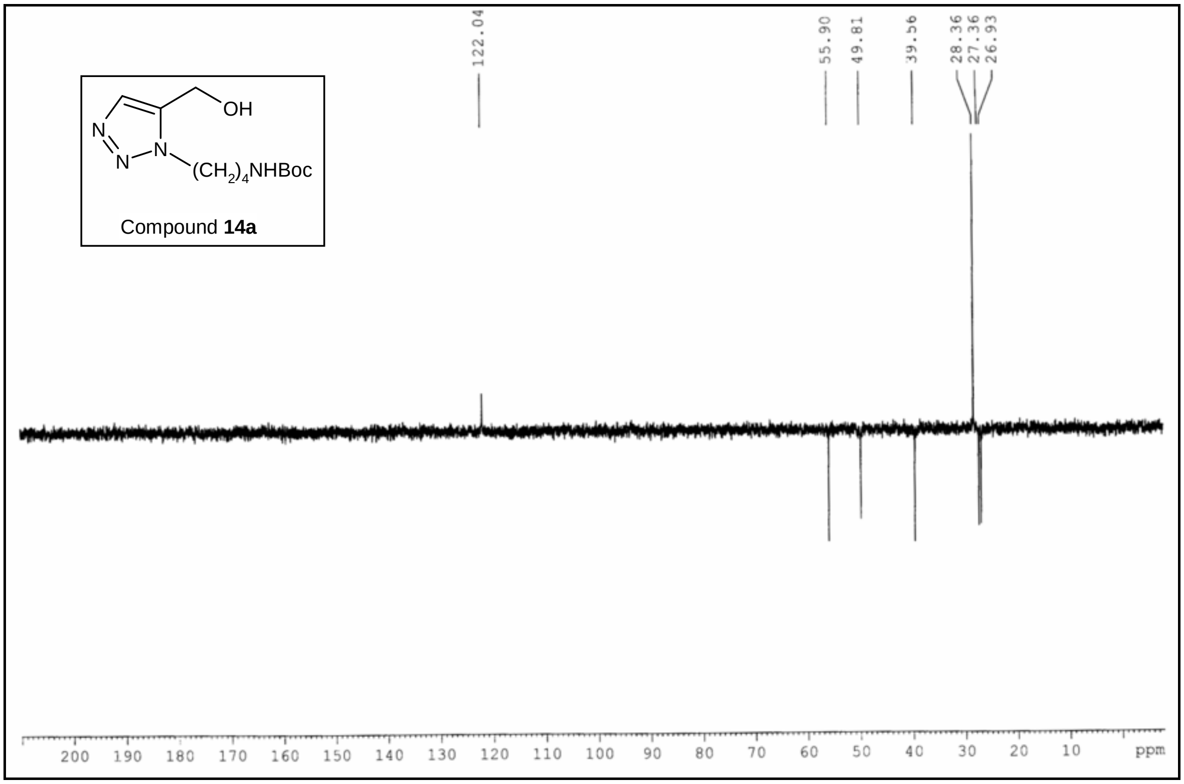

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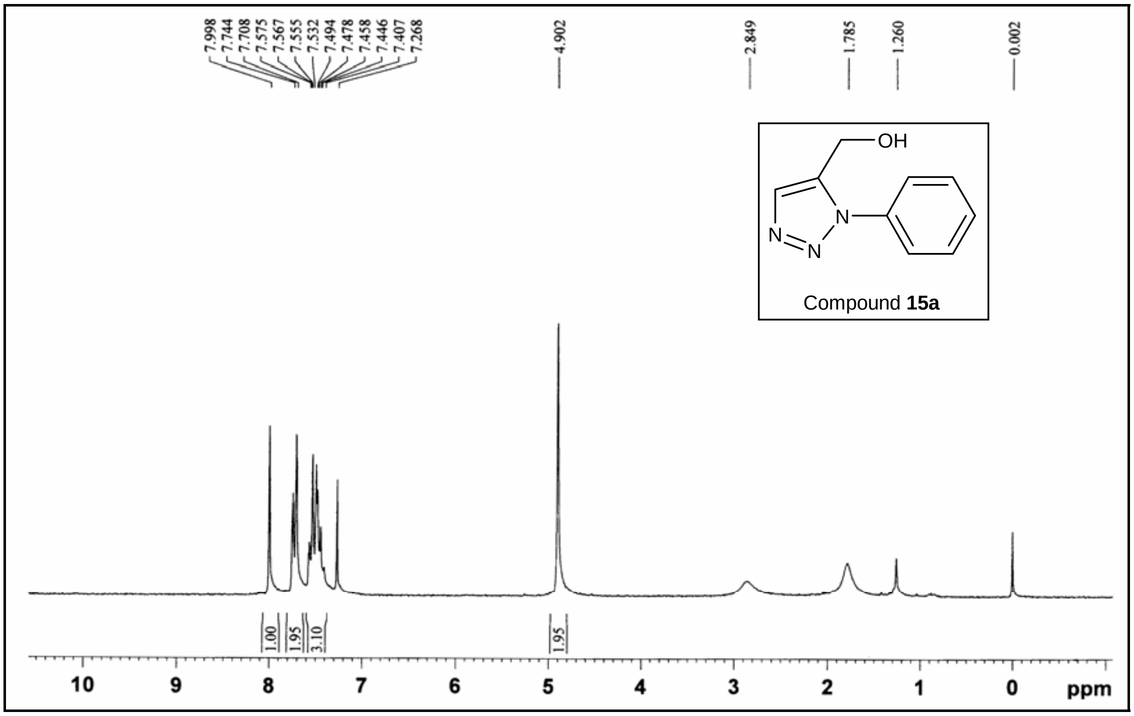

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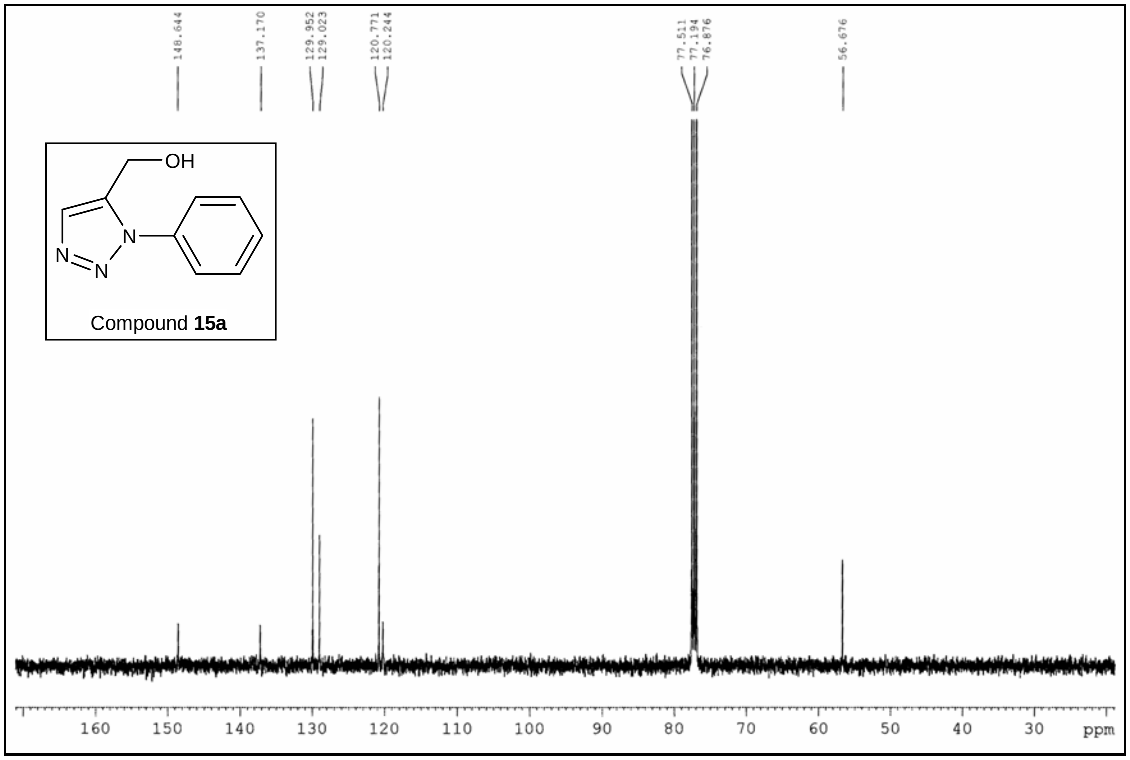

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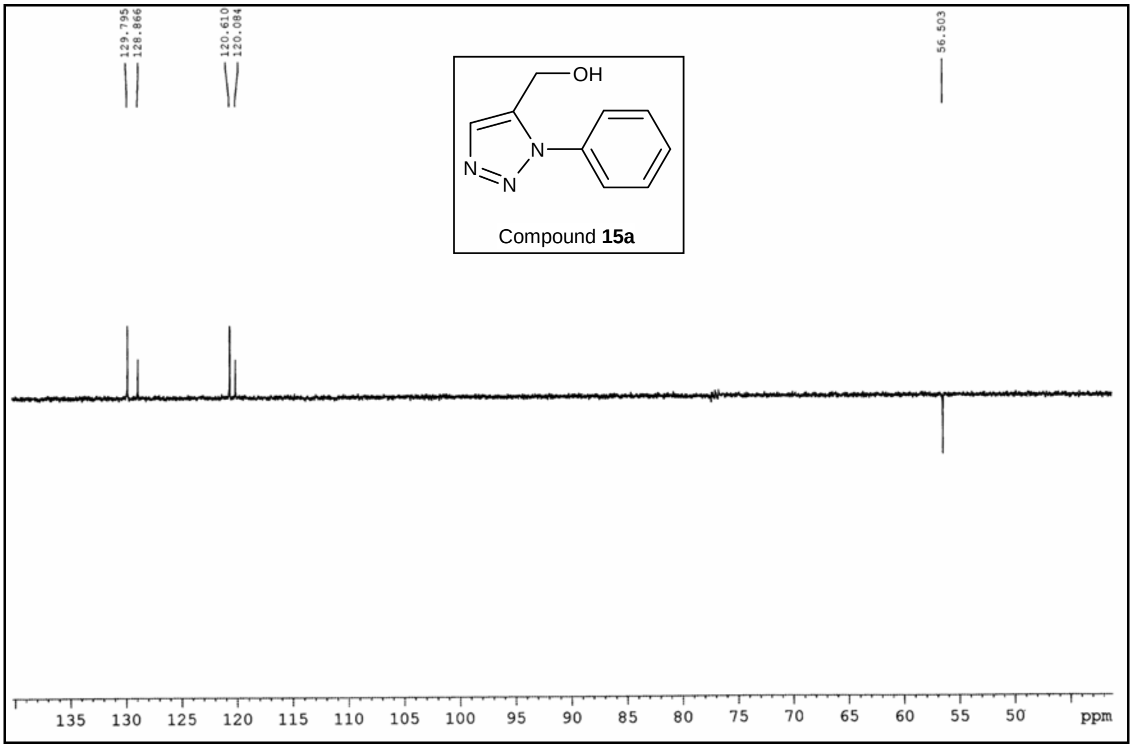

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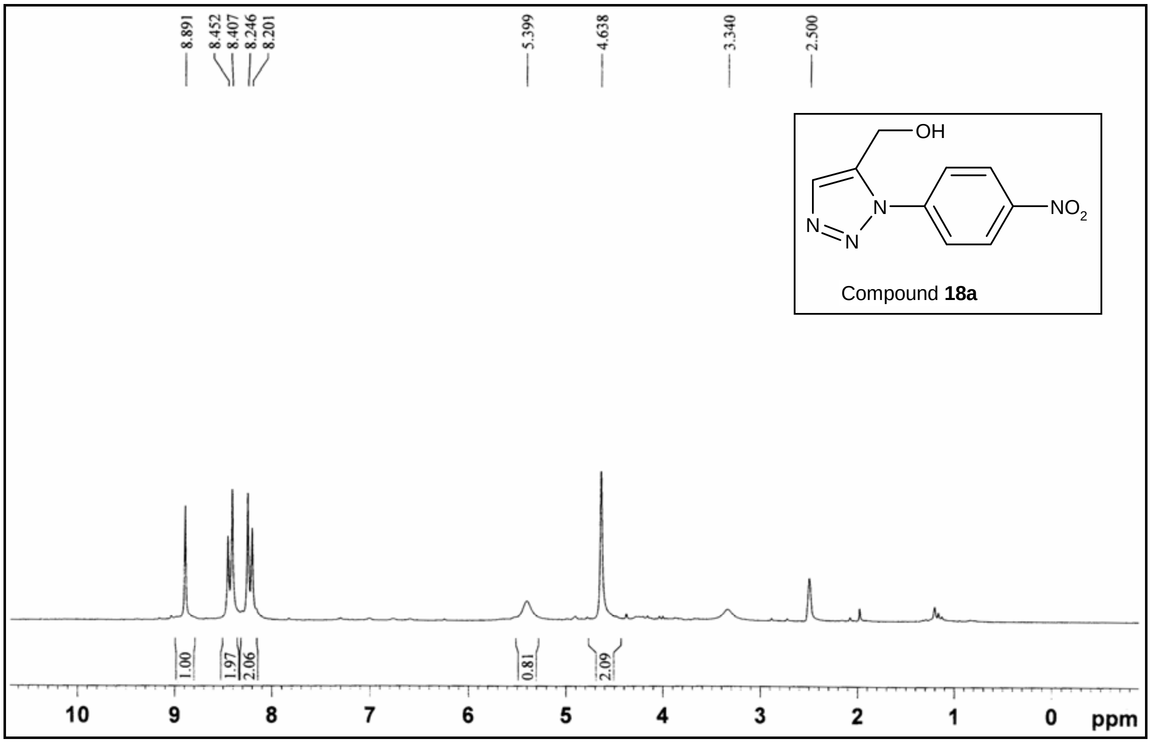

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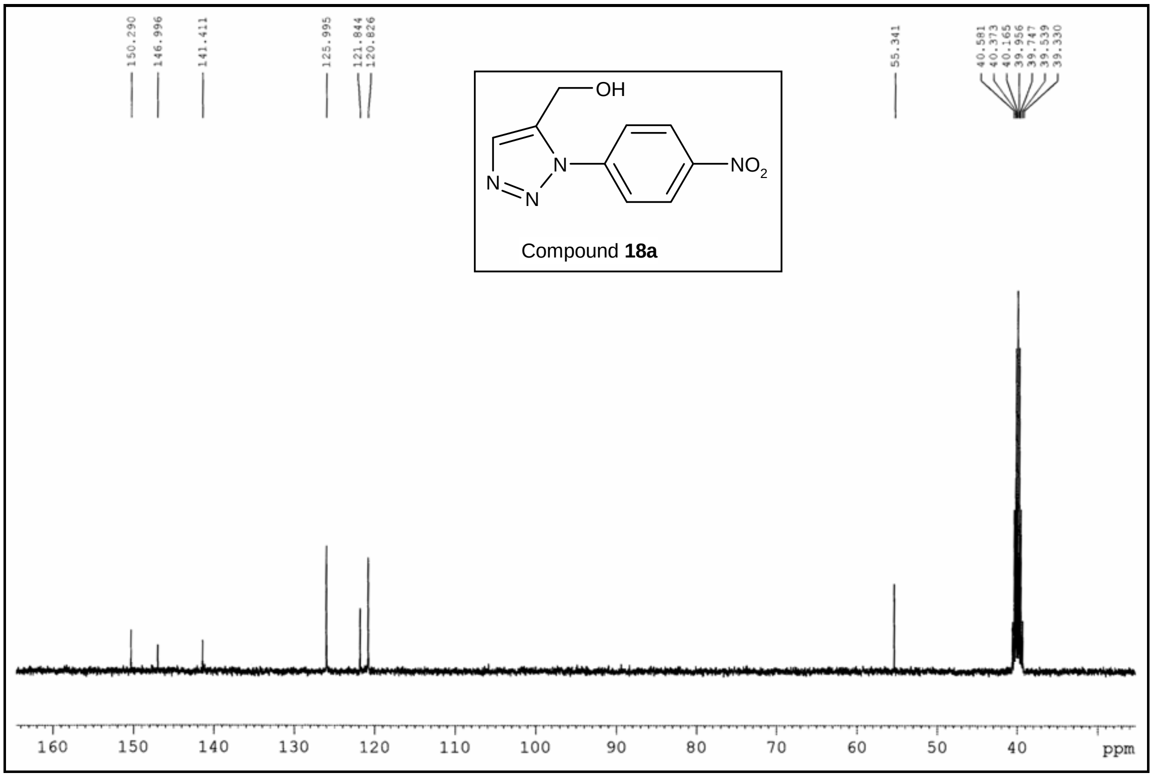

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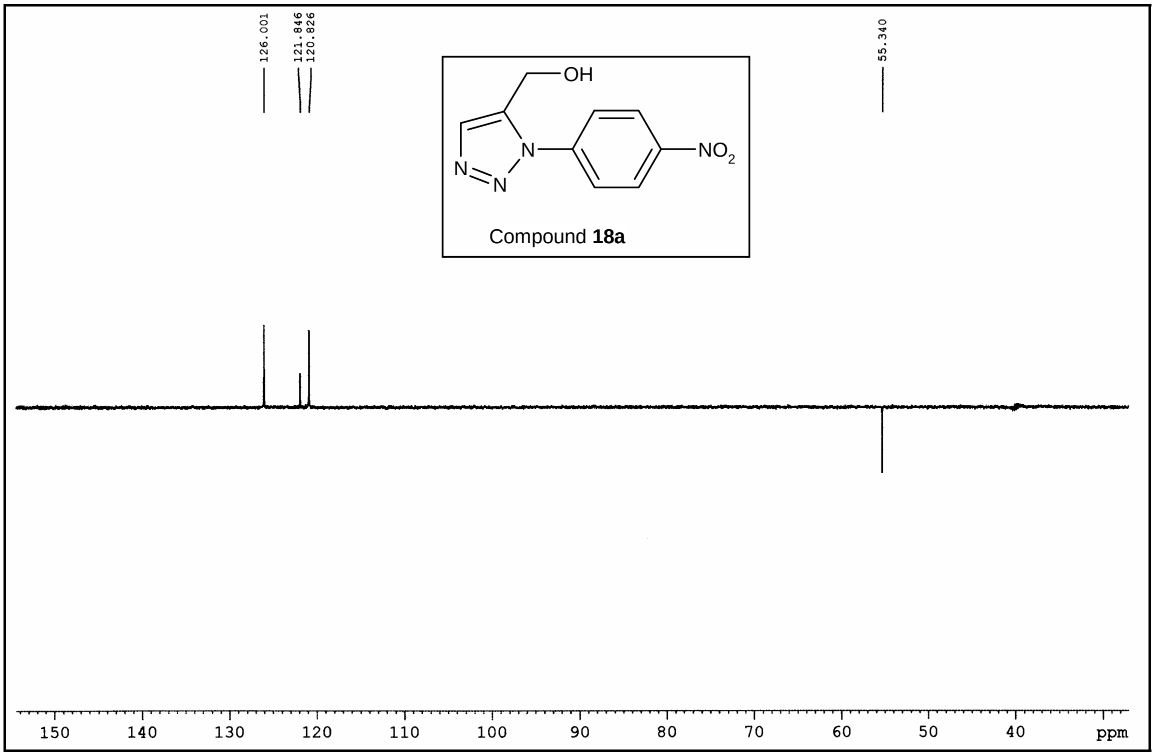
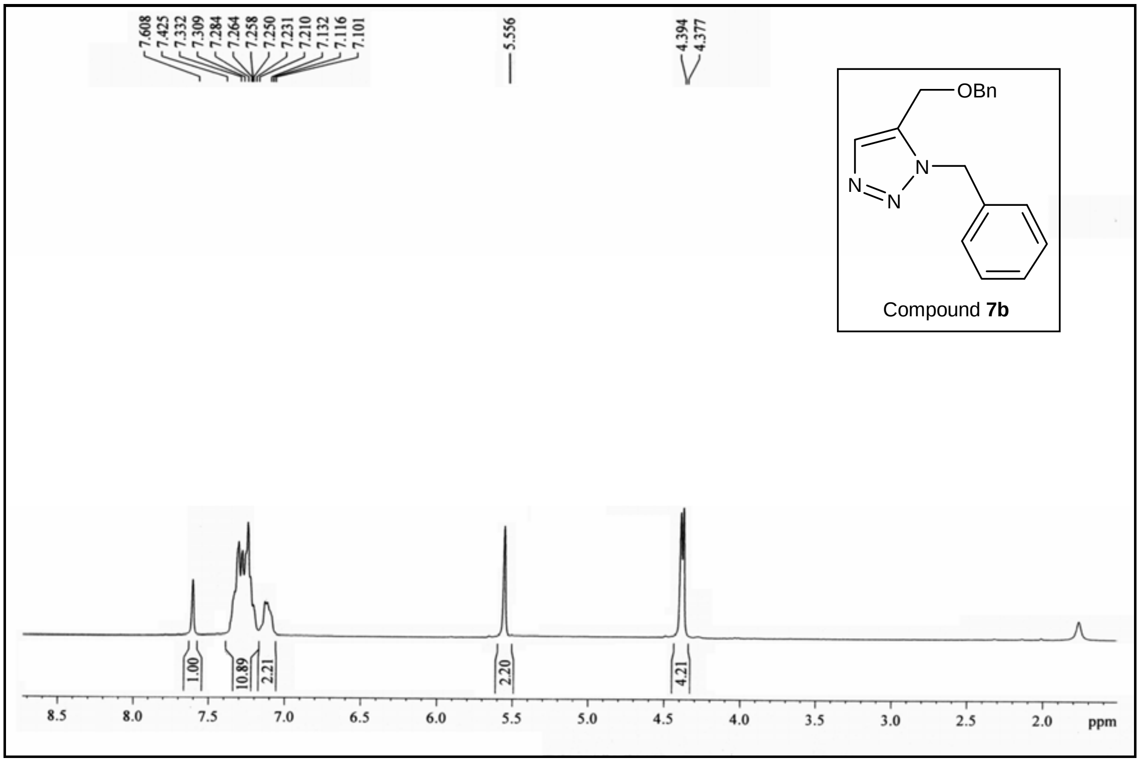
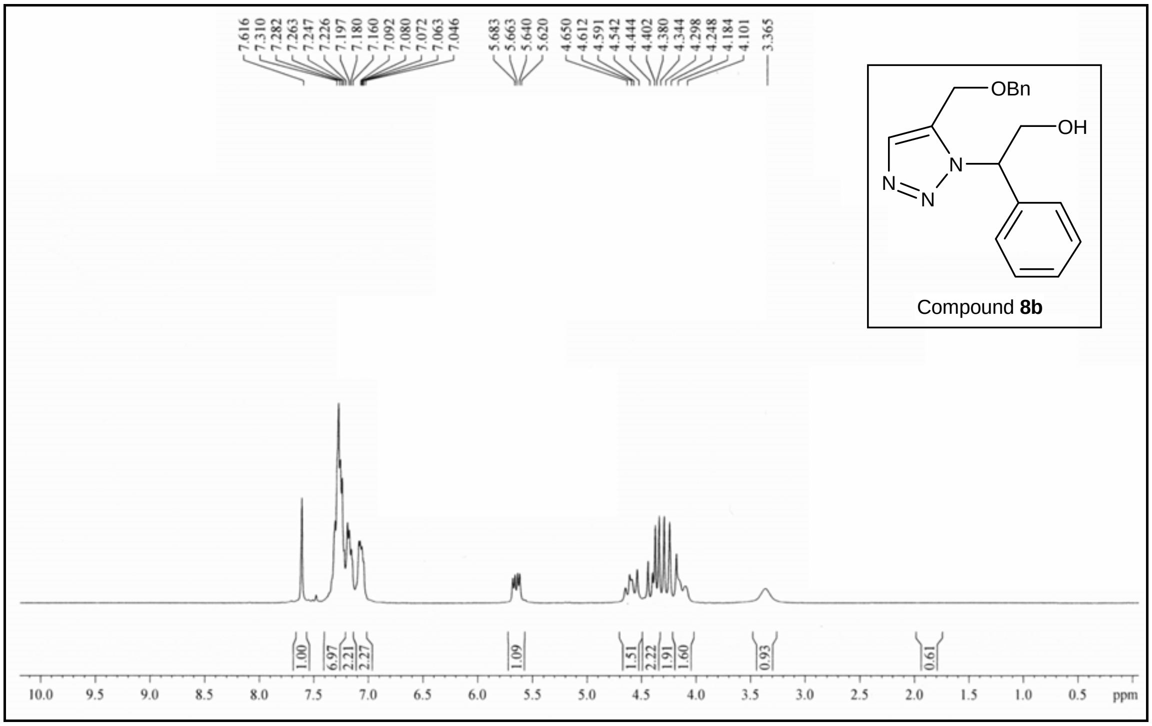


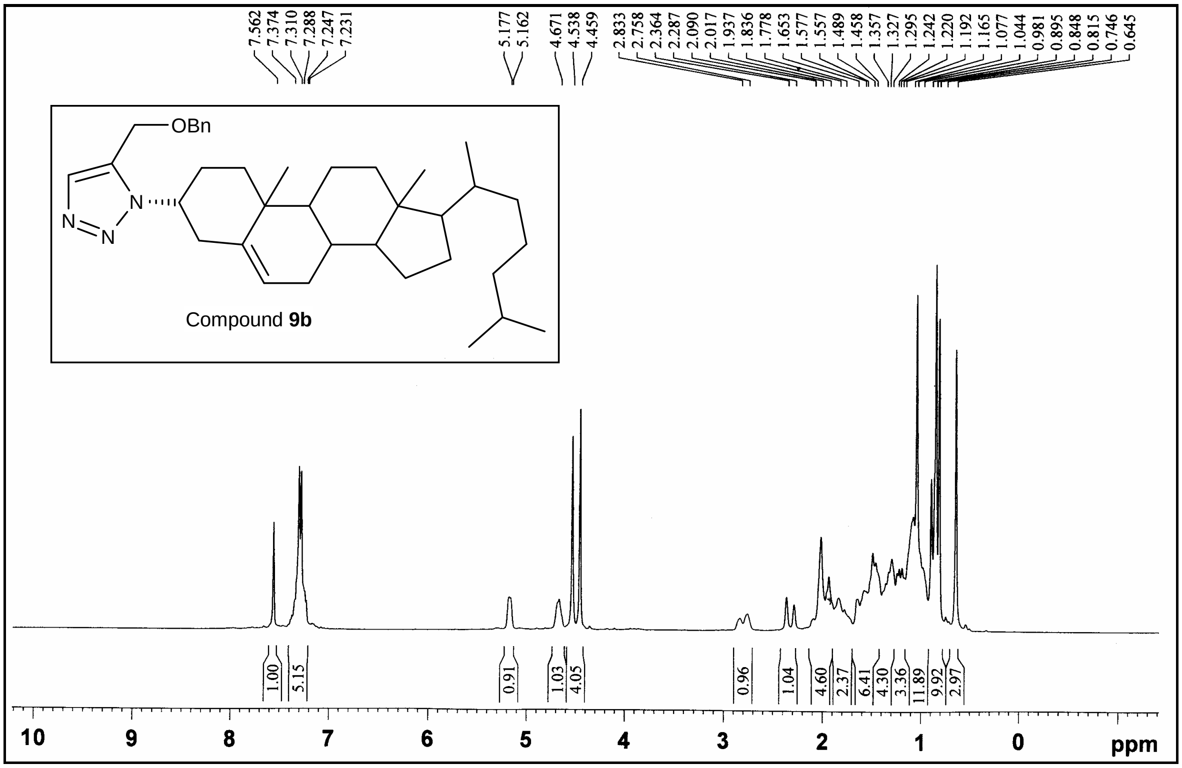
^{1}H-NMR spectra of **7b**



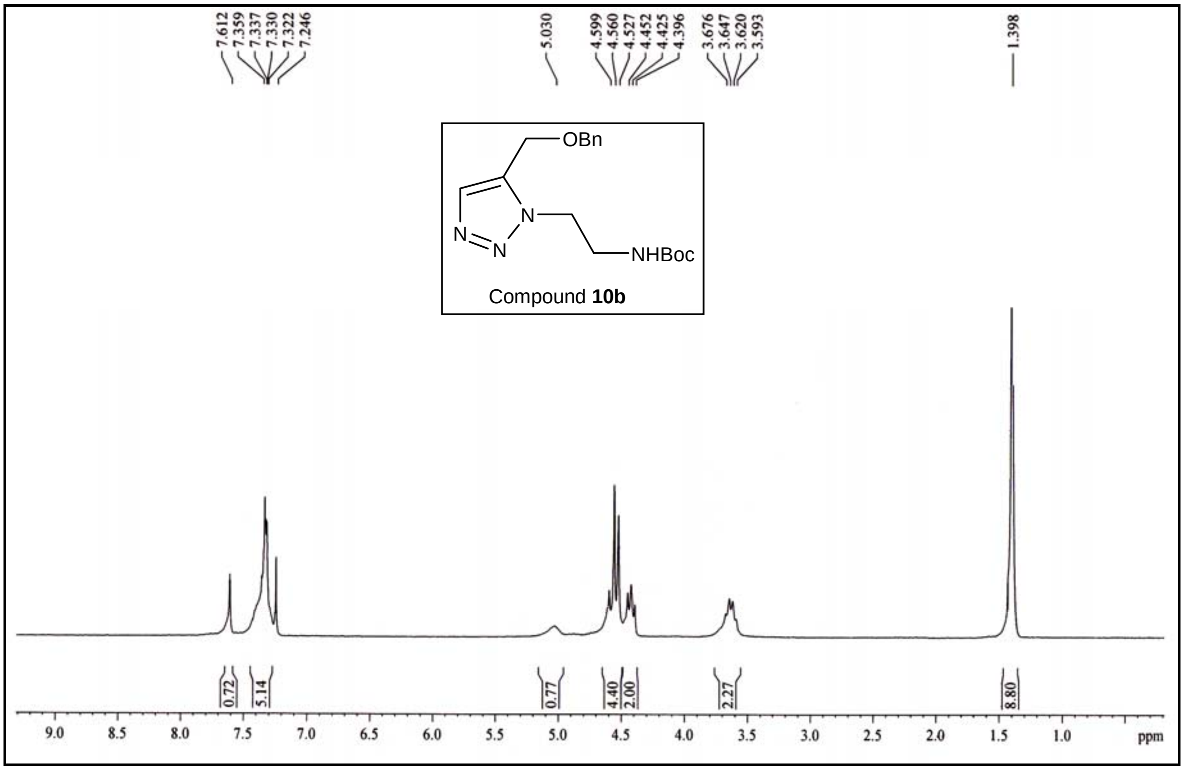
^{1}H-NMR spectra of **8b**



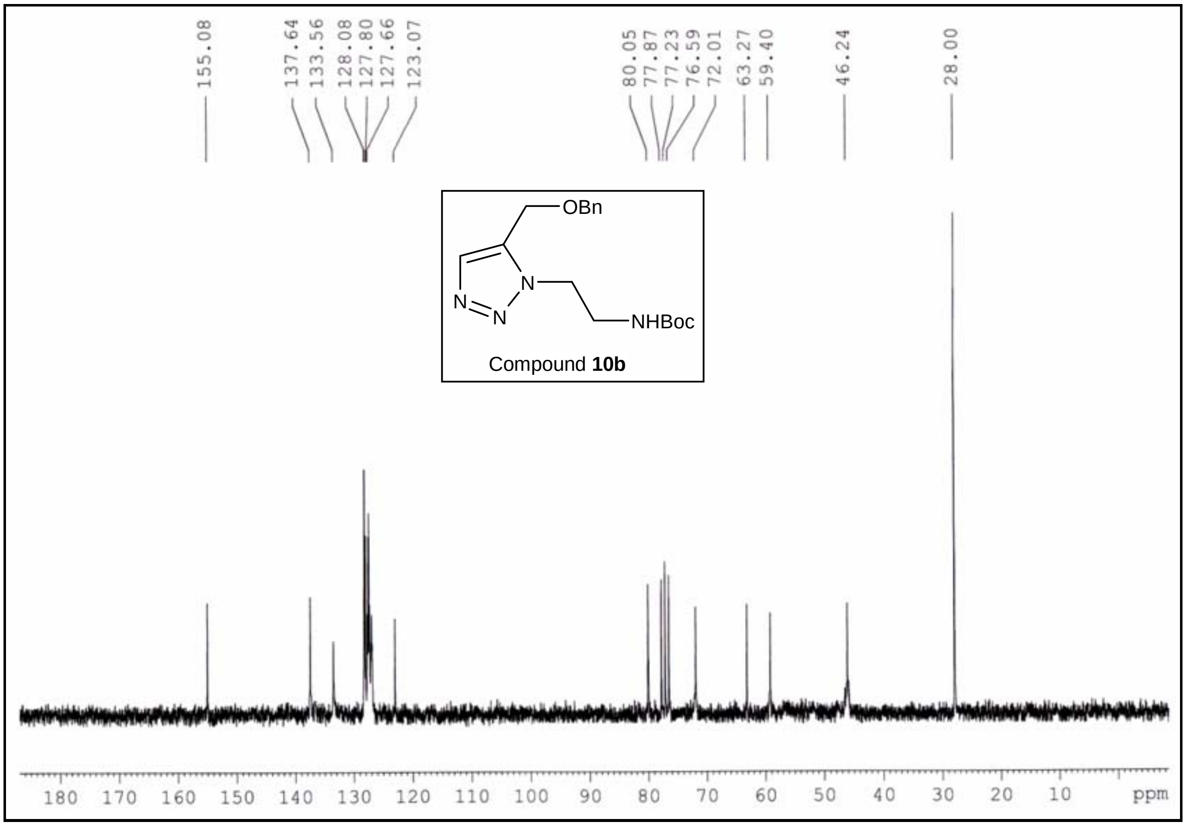
^{1}H-NMR spectra of **9b**



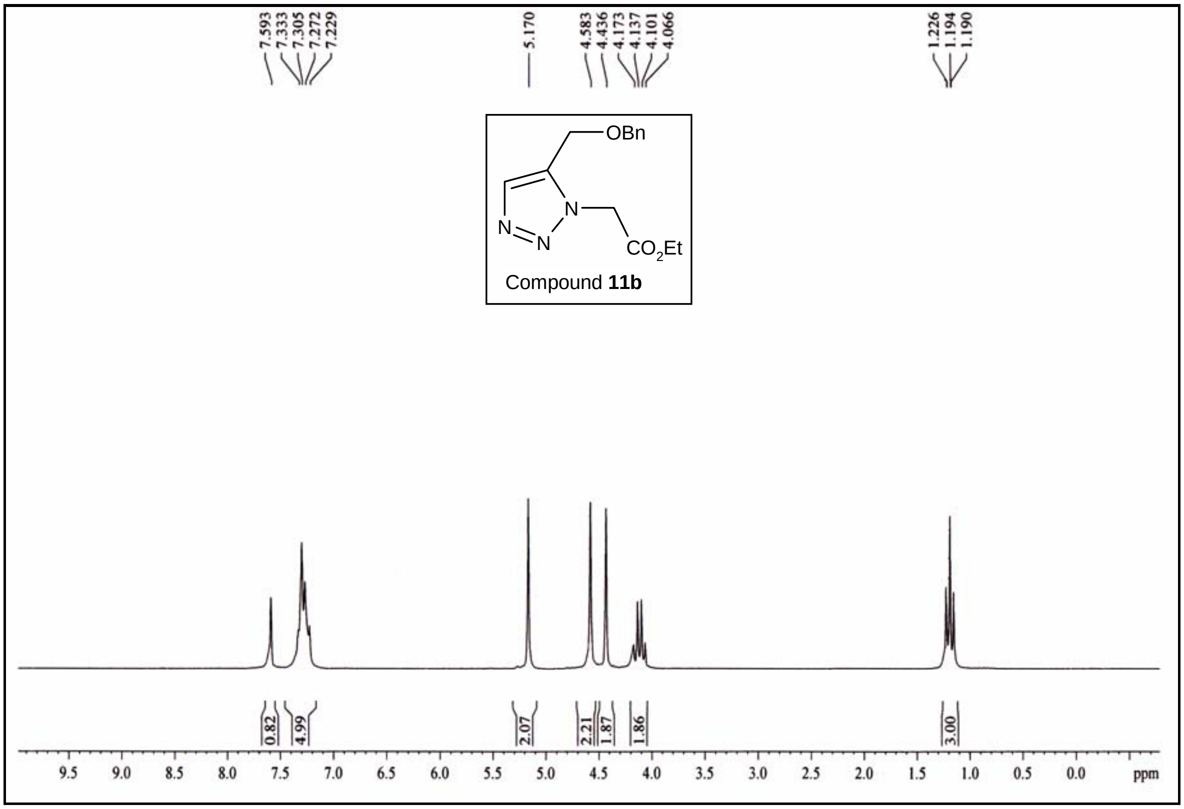
^{1}H-NMR spectra of **10b**



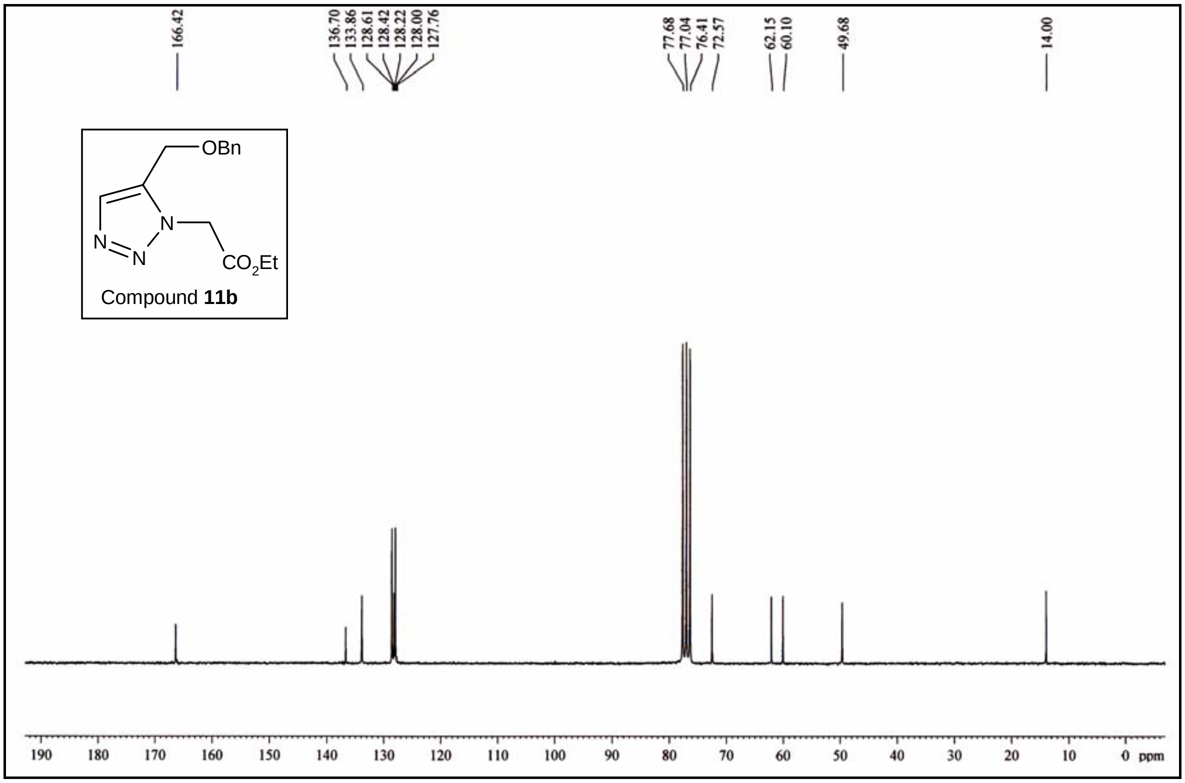
^{13}C-NMR spectra of **10b**



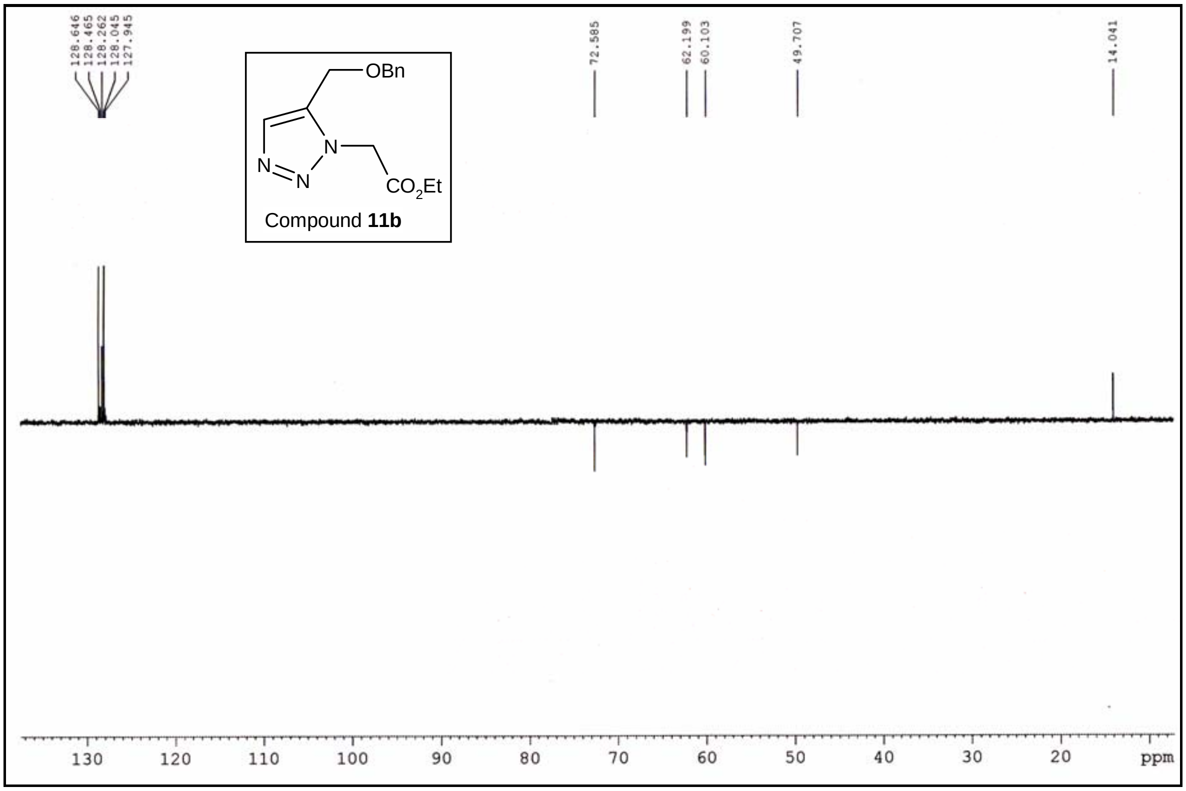
^{1}H-NMR spectra of **11b**



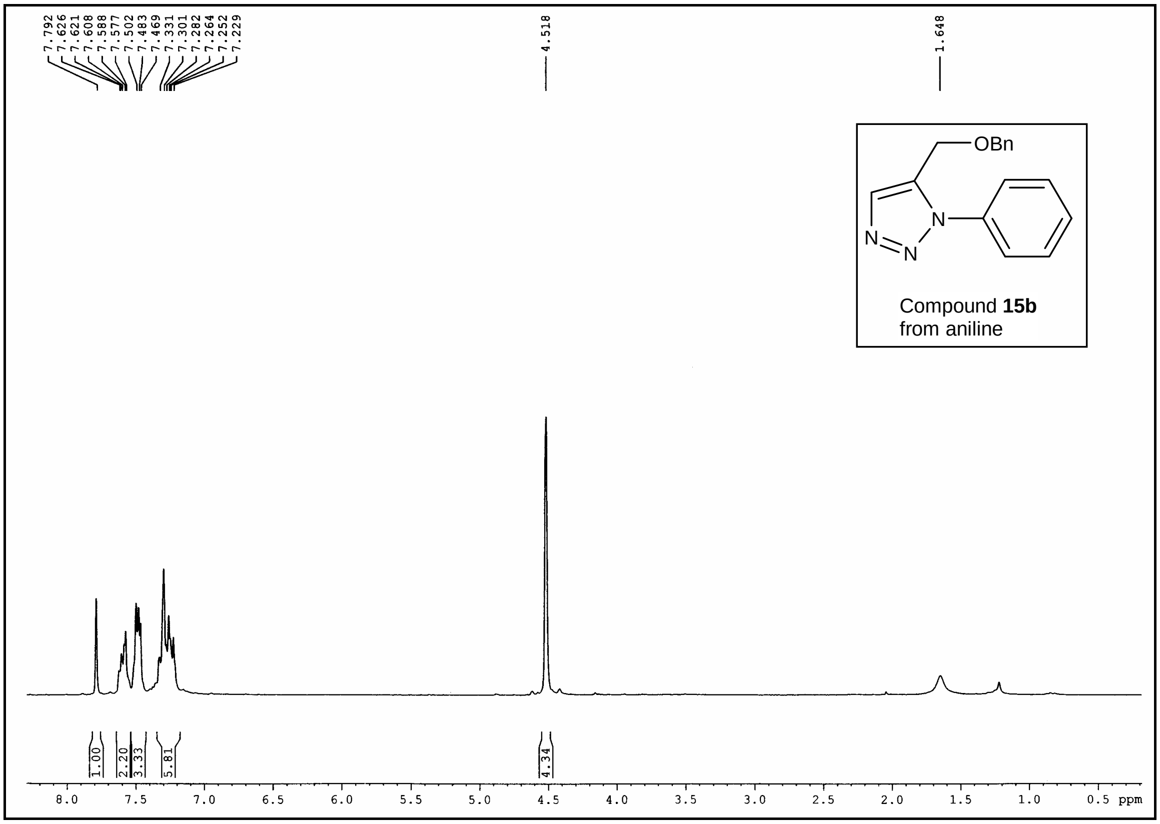
^{13}C-NMR spectra of **11b**



DEPT spectra of **11b**



^{1}H-NMR spectra of **15b**



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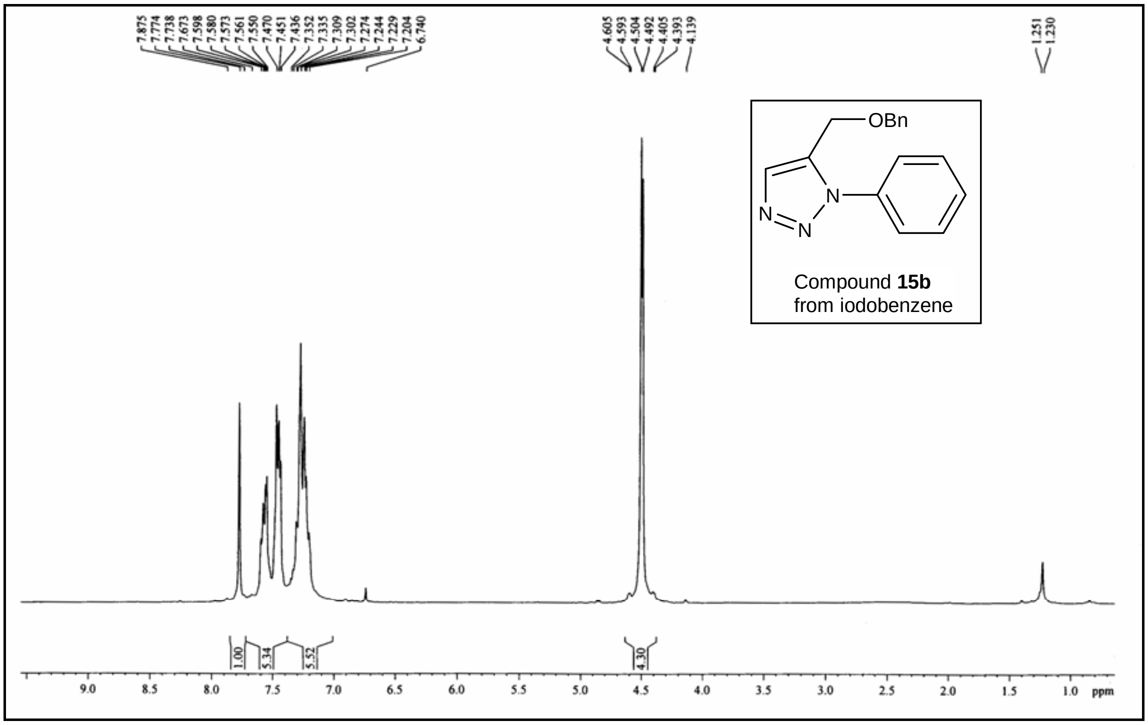

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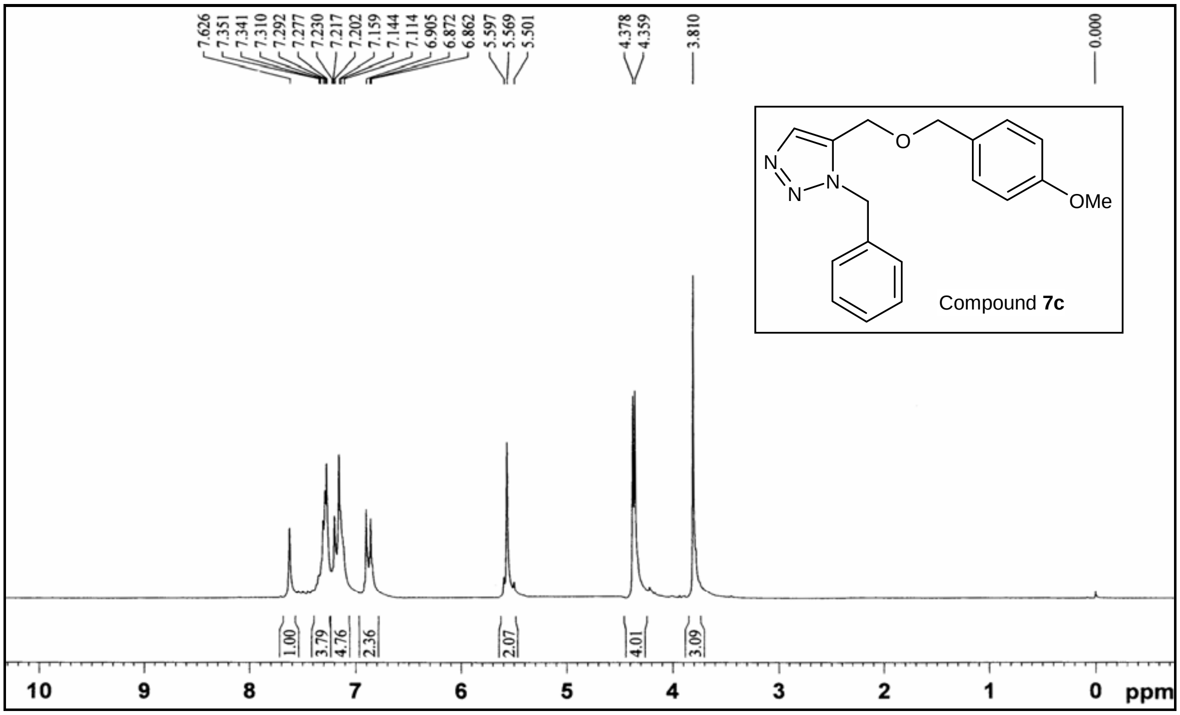

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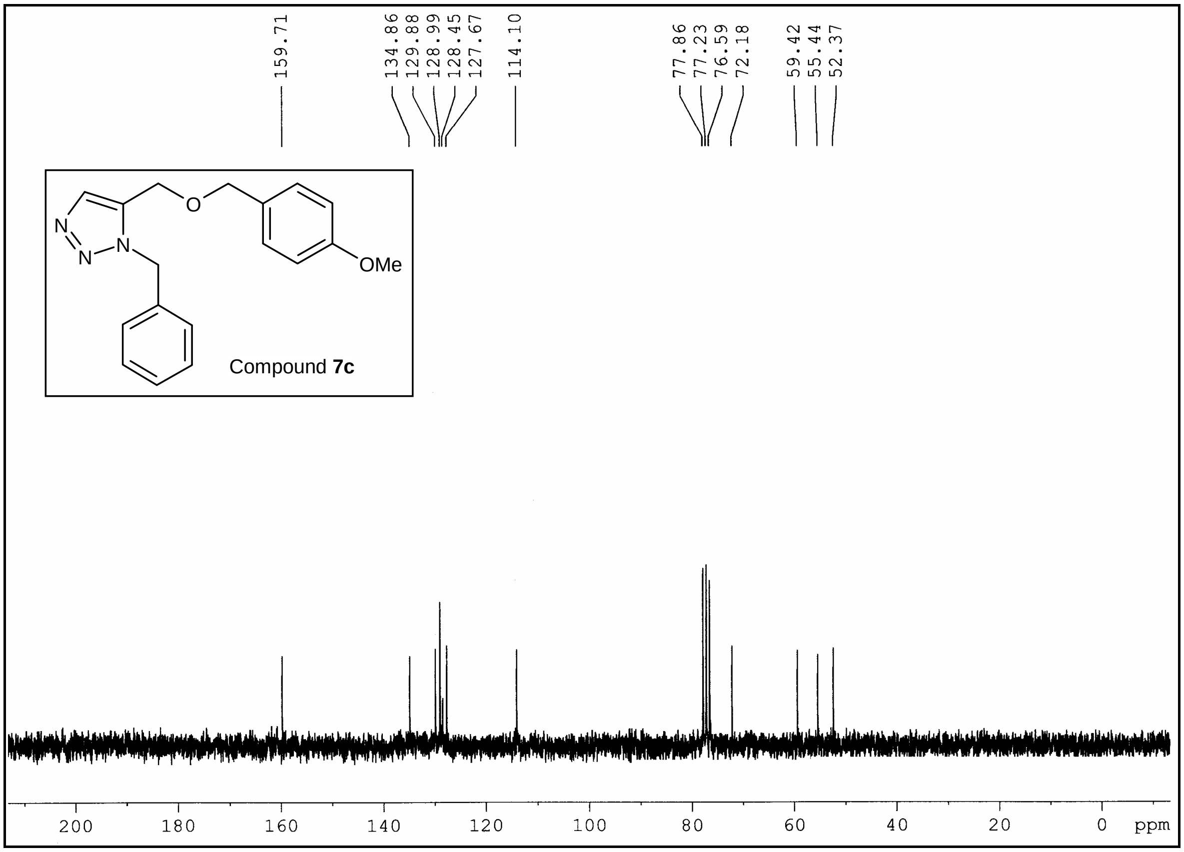

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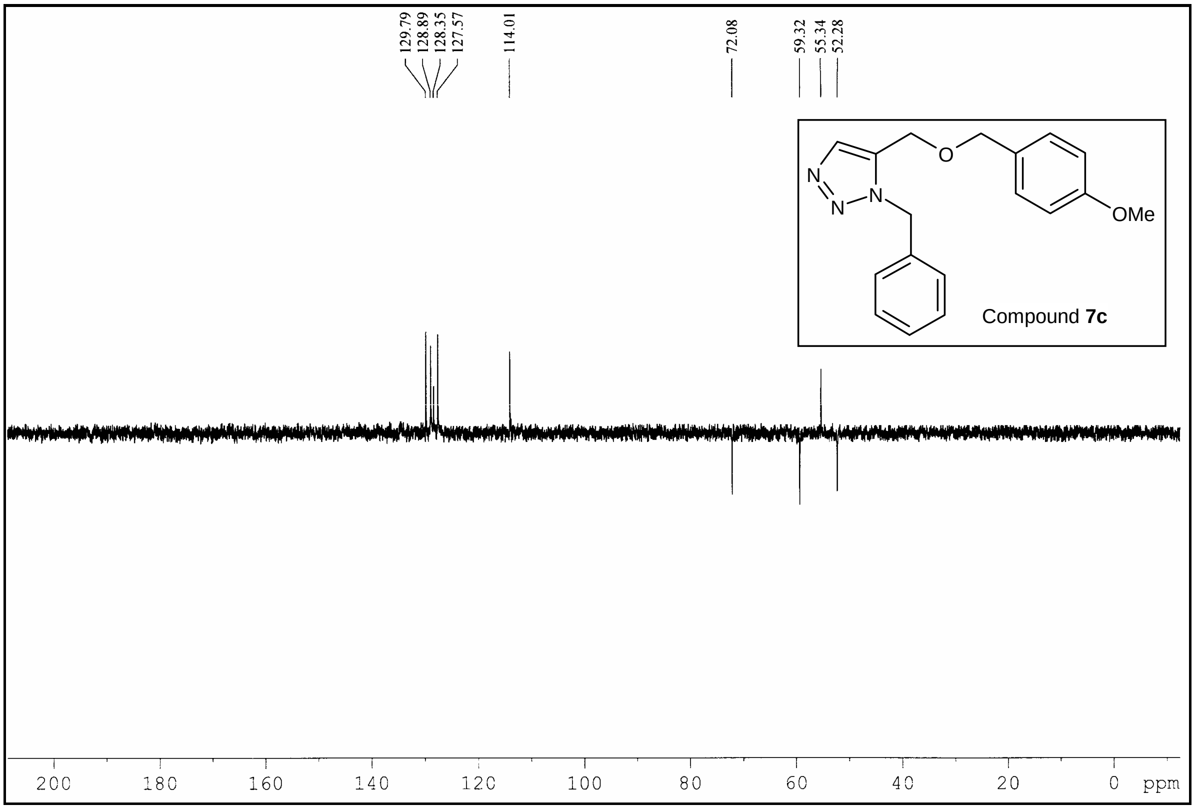
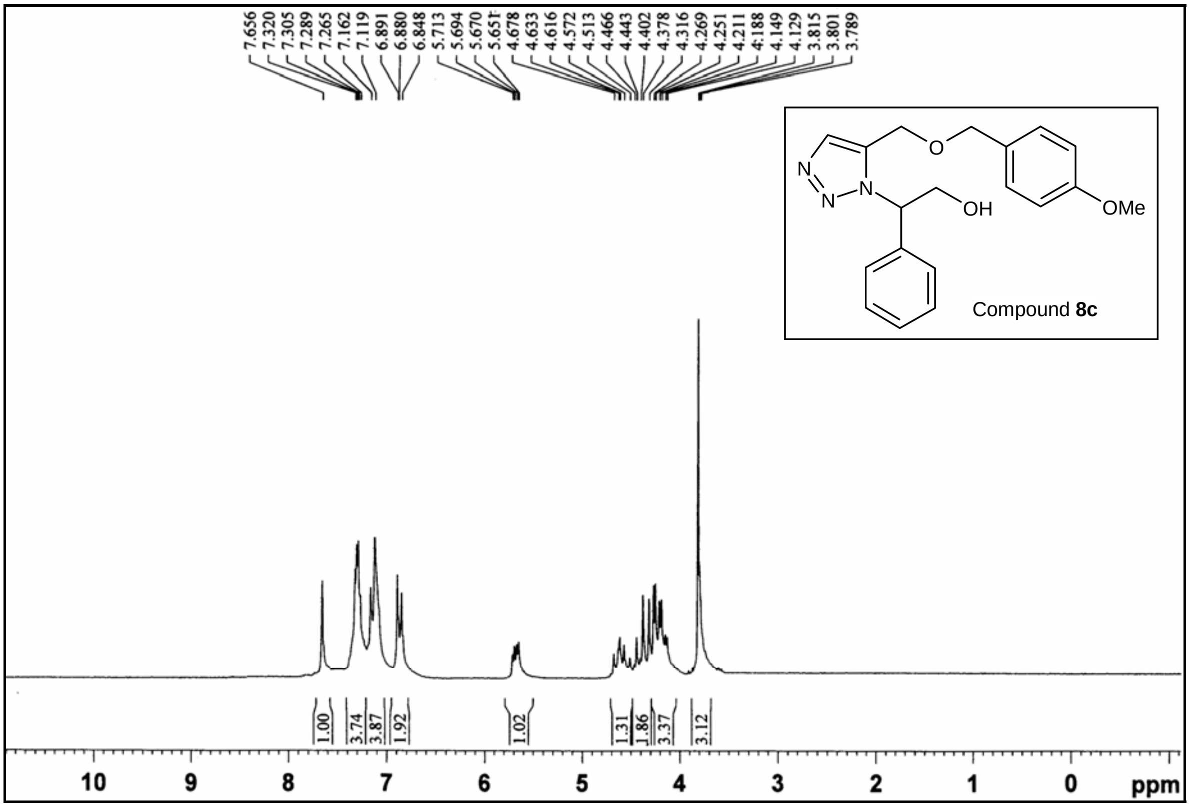


^{1}H-NMR spectra of **8c**



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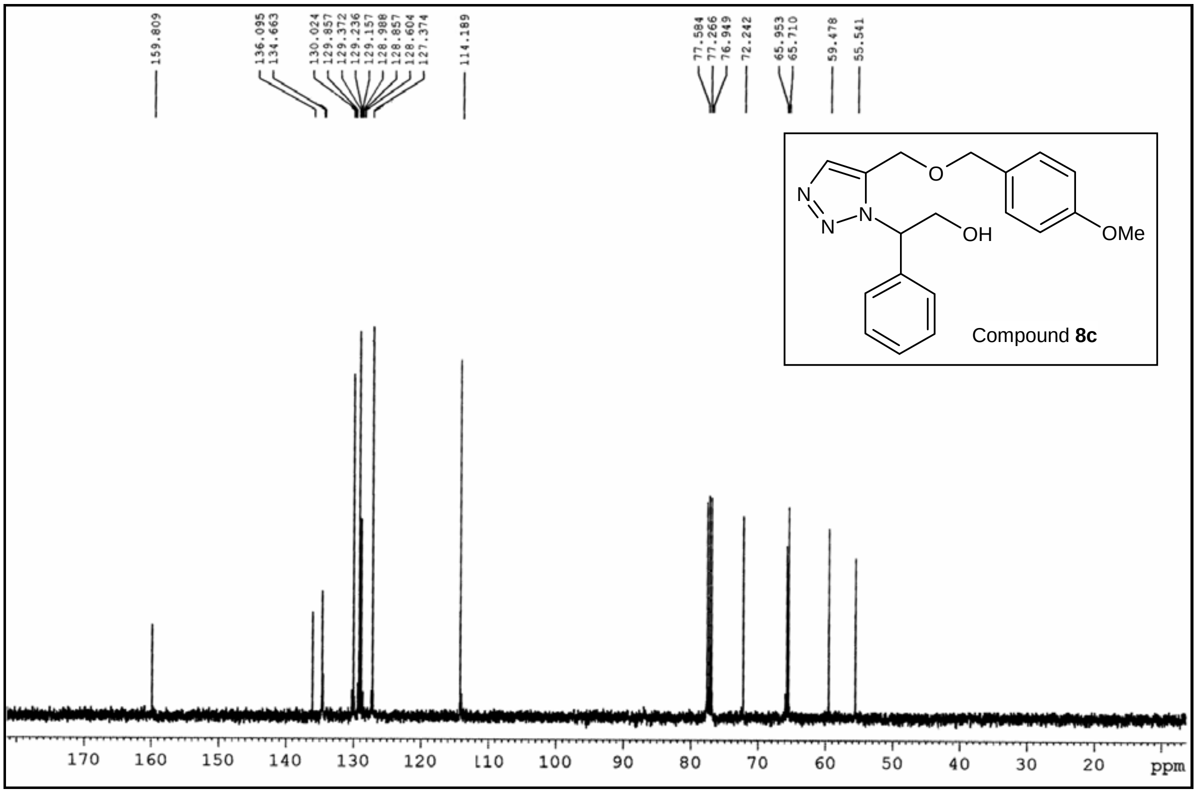

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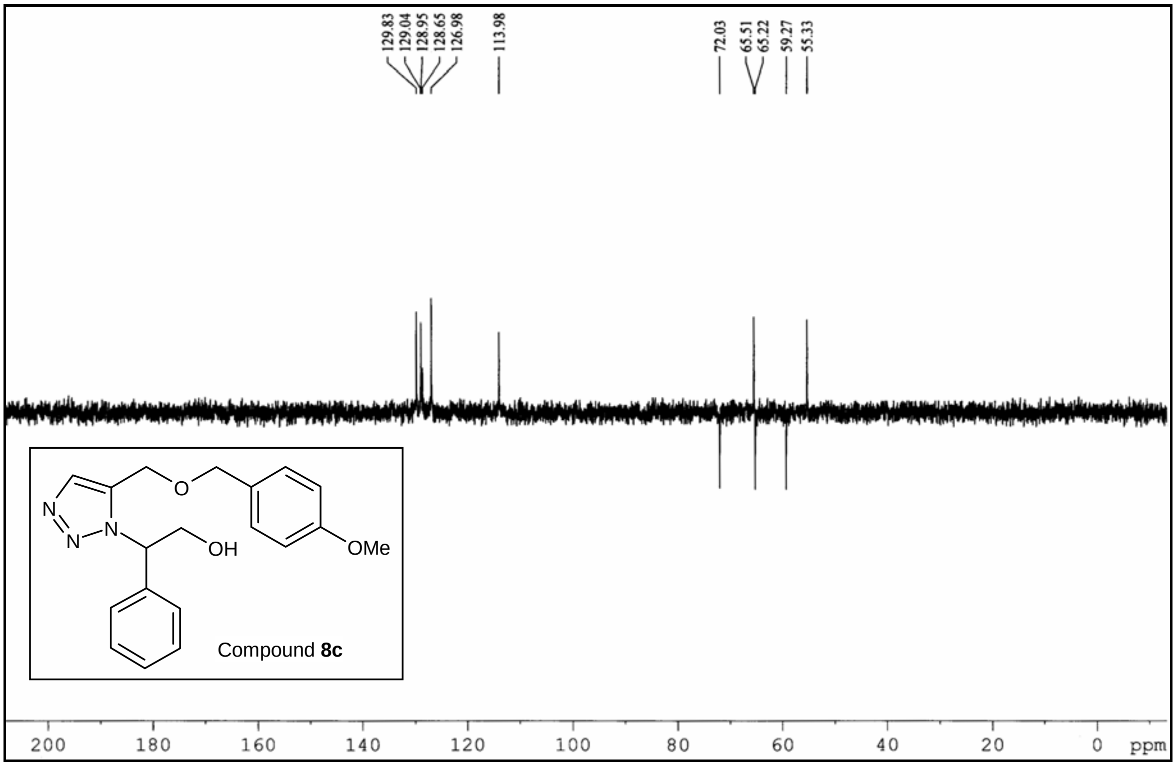
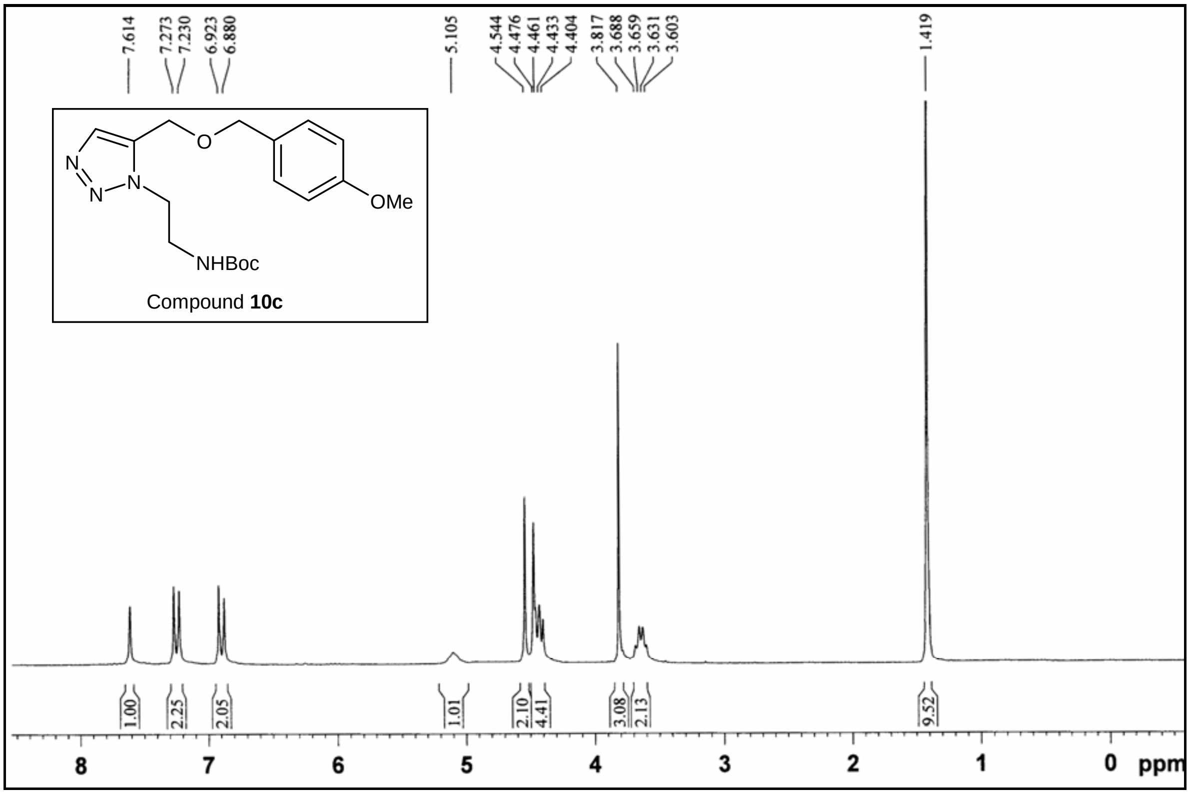


^{1}H-NMR spectra of **10c**



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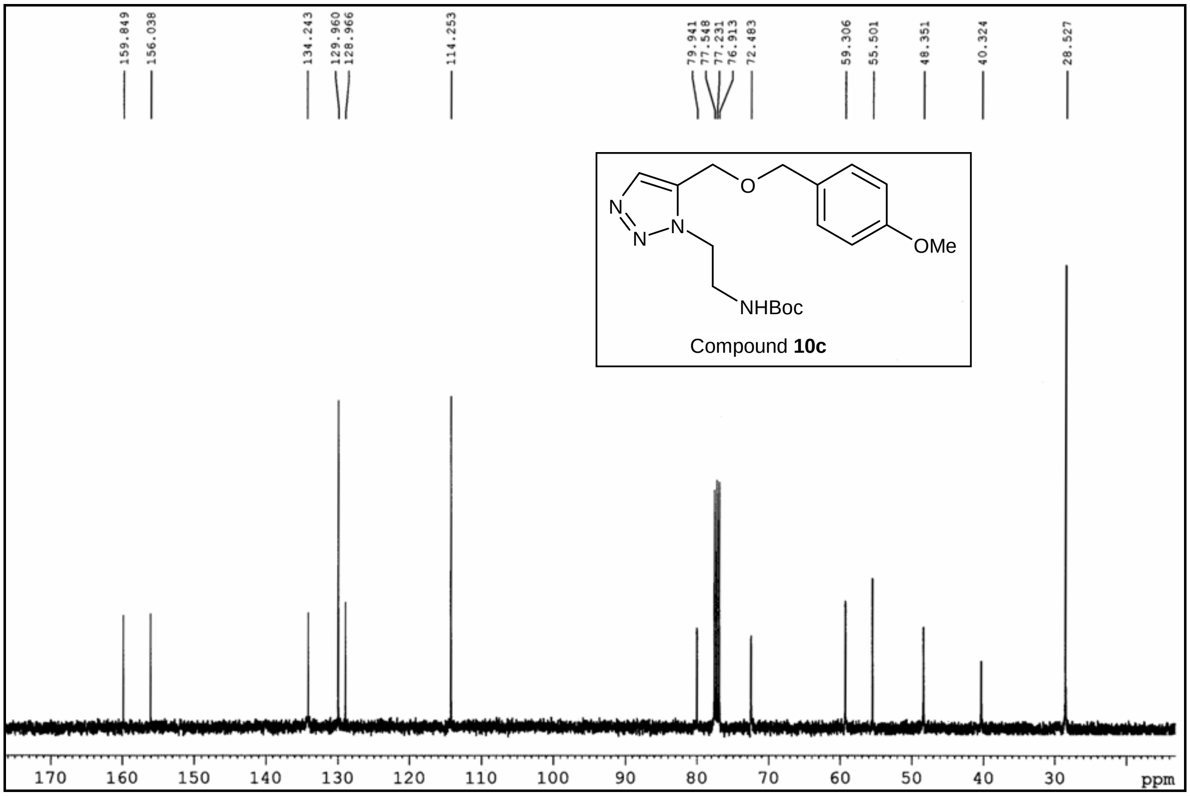

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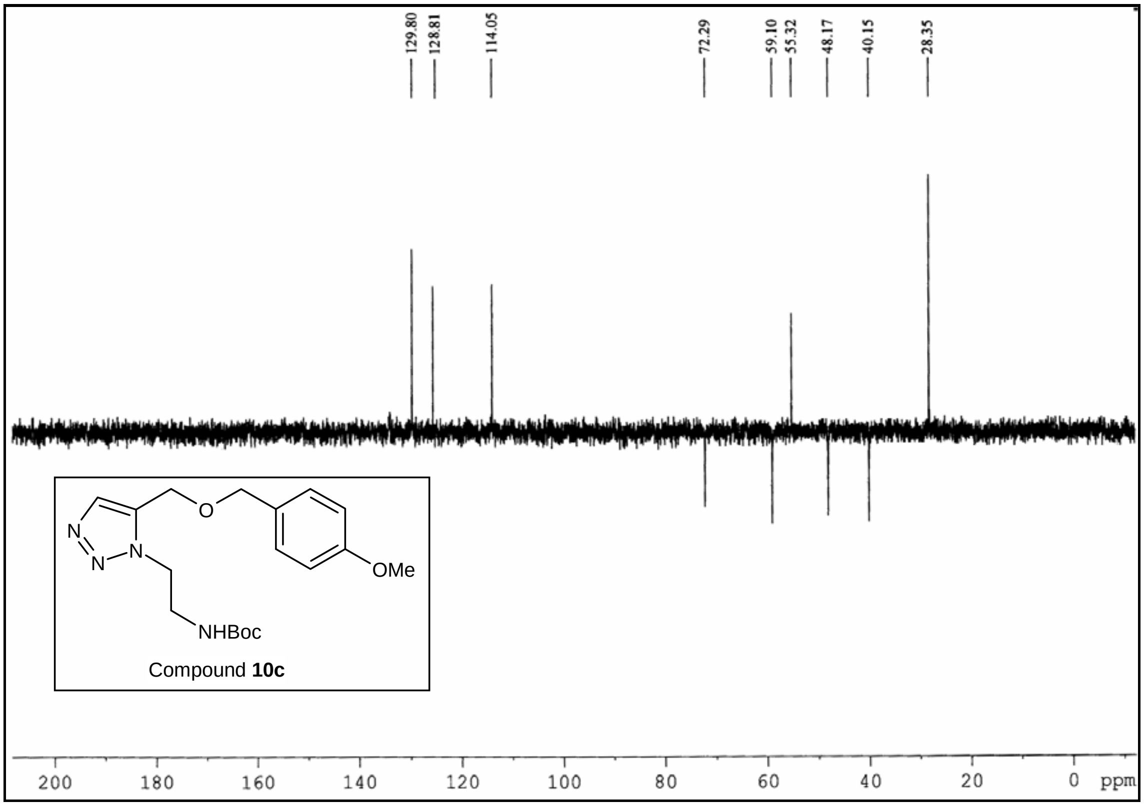
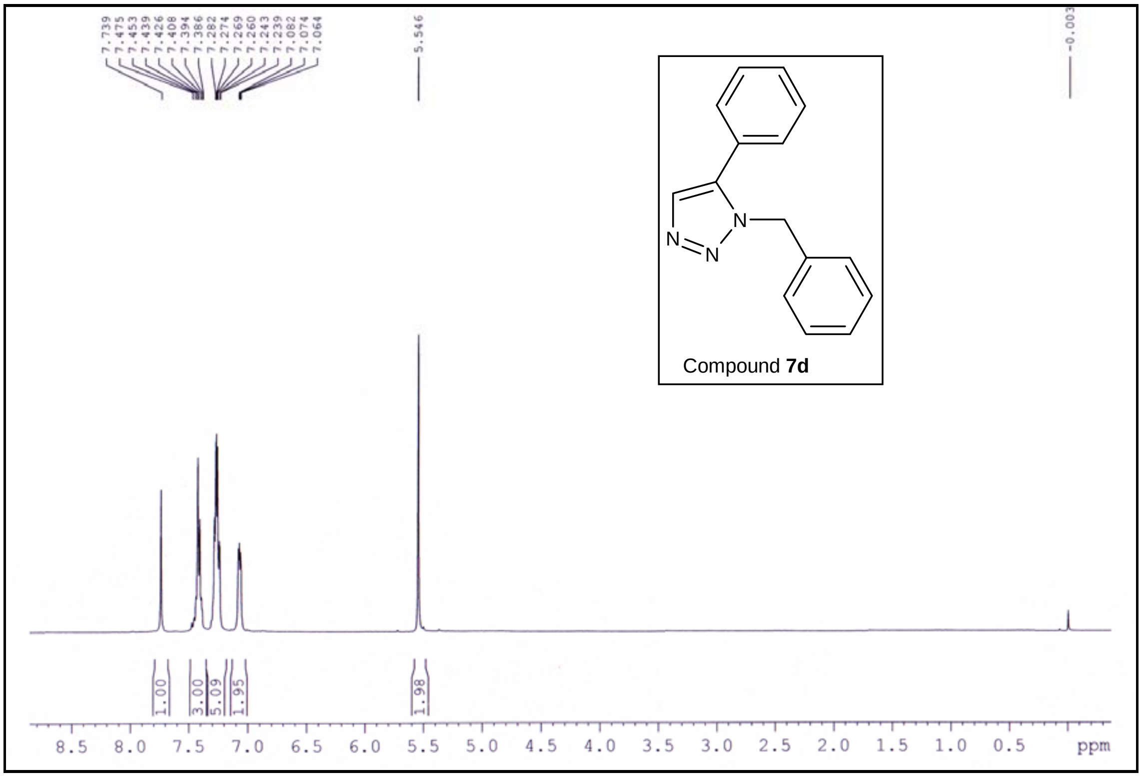
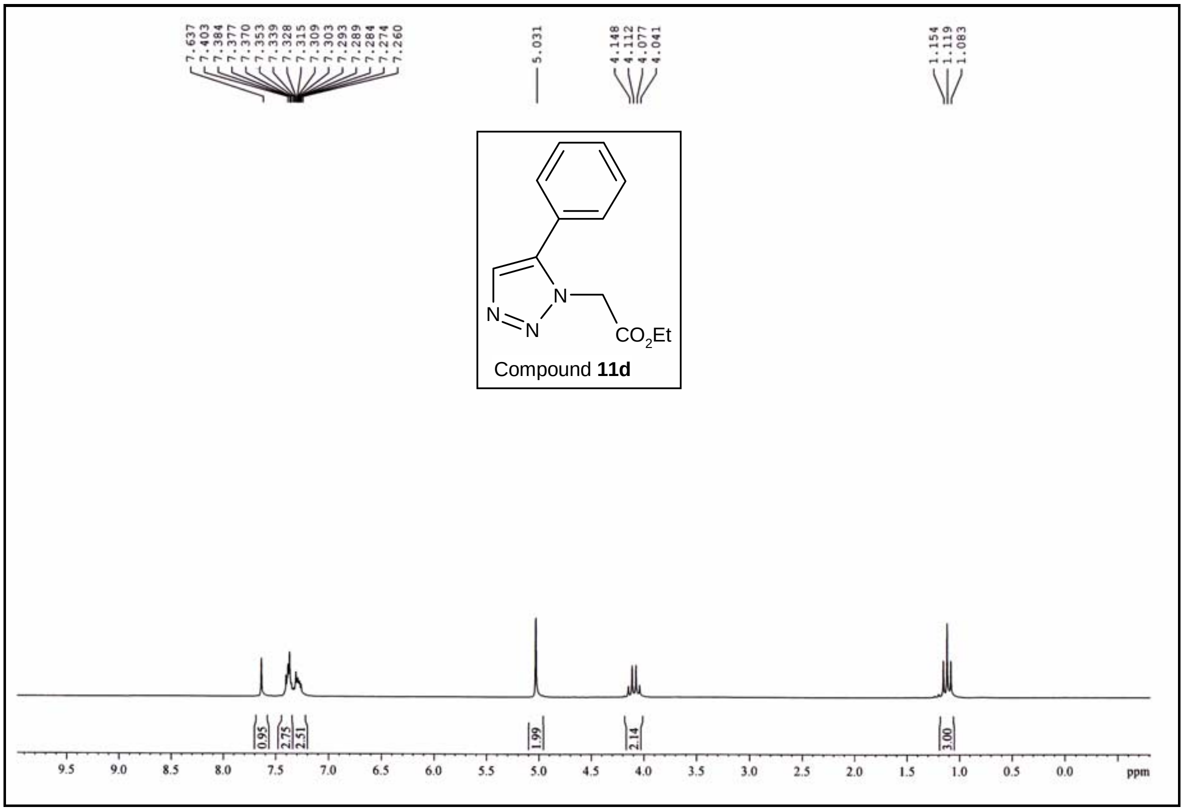


^{1}H-NMR spectra of **7d**



^{1}H-NMR spectra of **11d**



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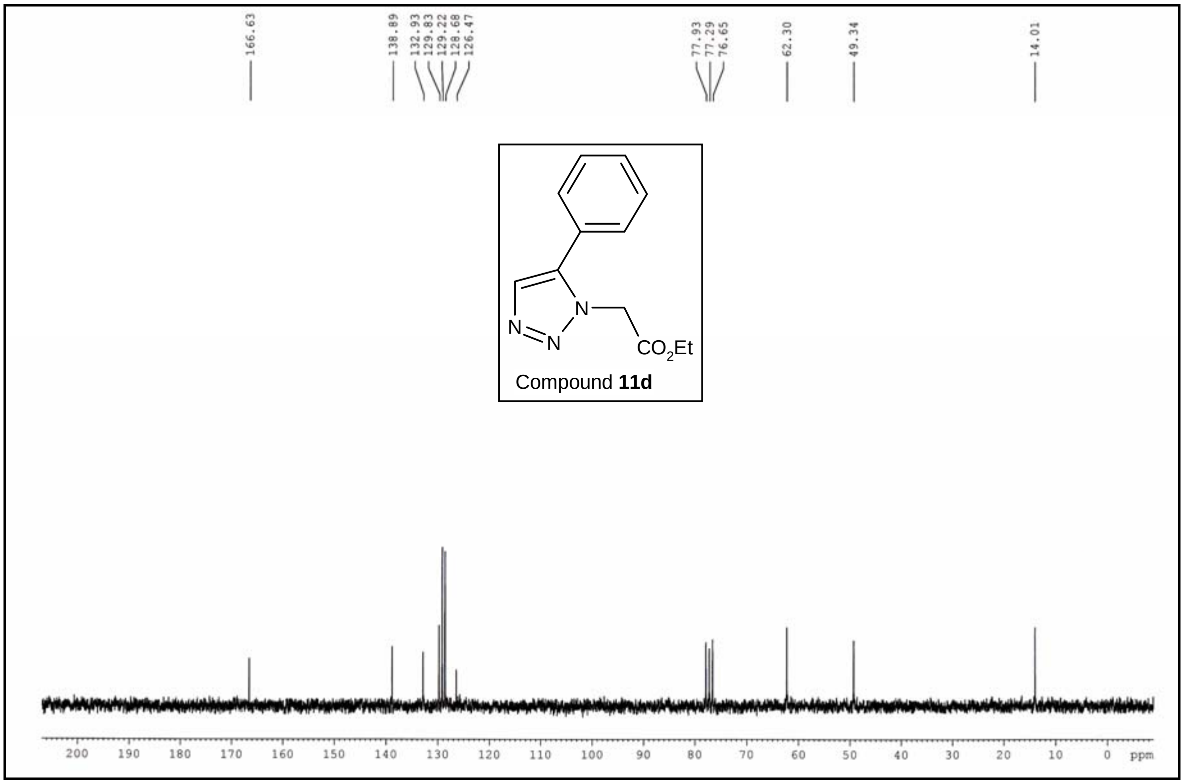

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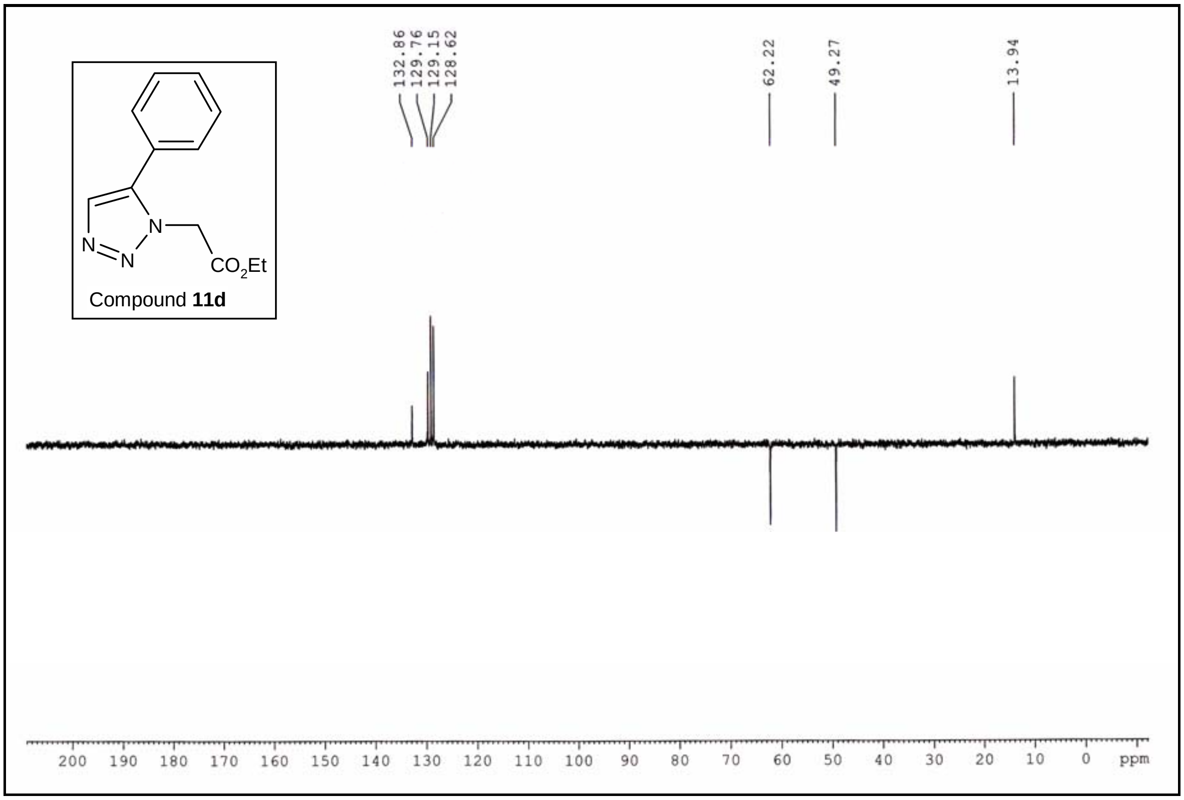
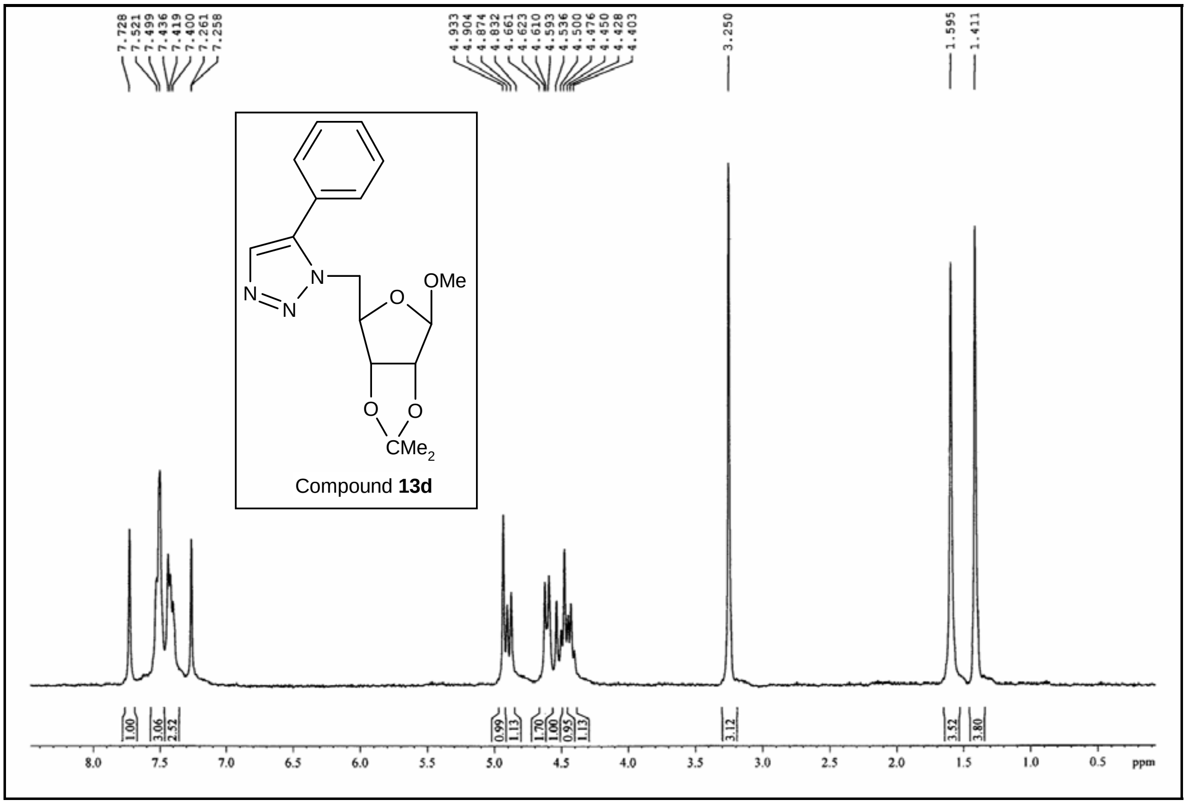
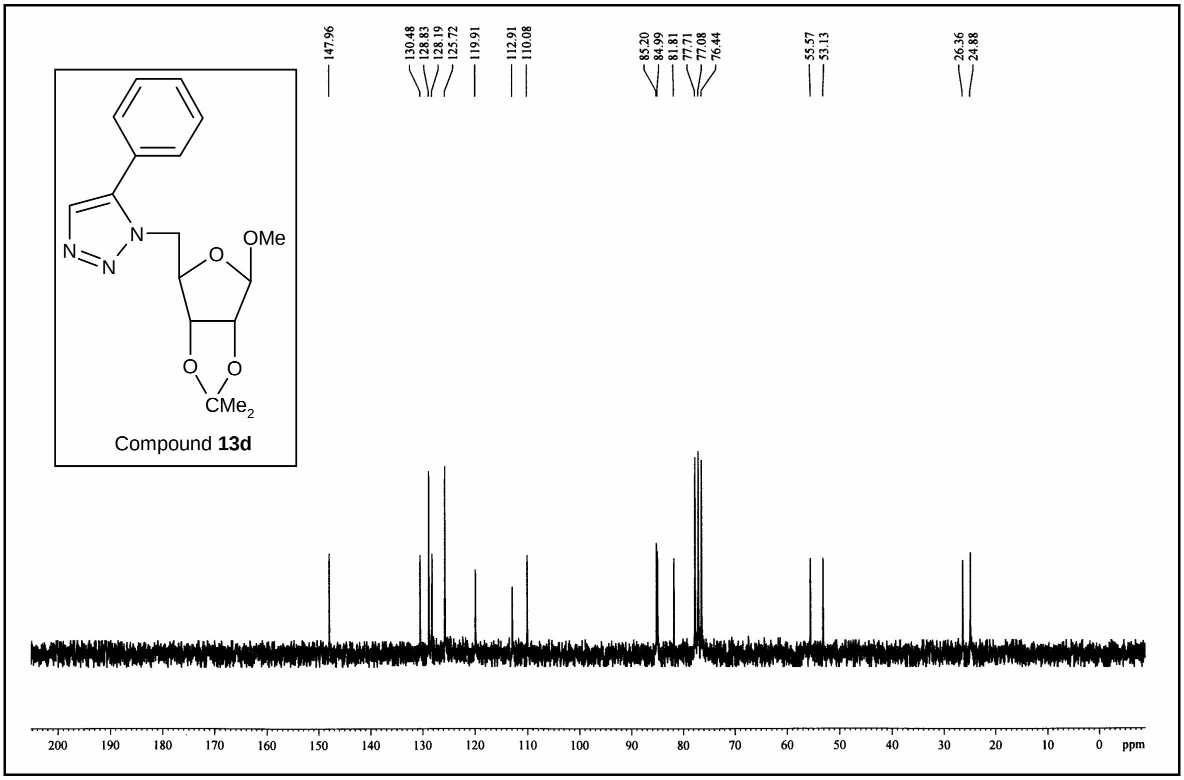


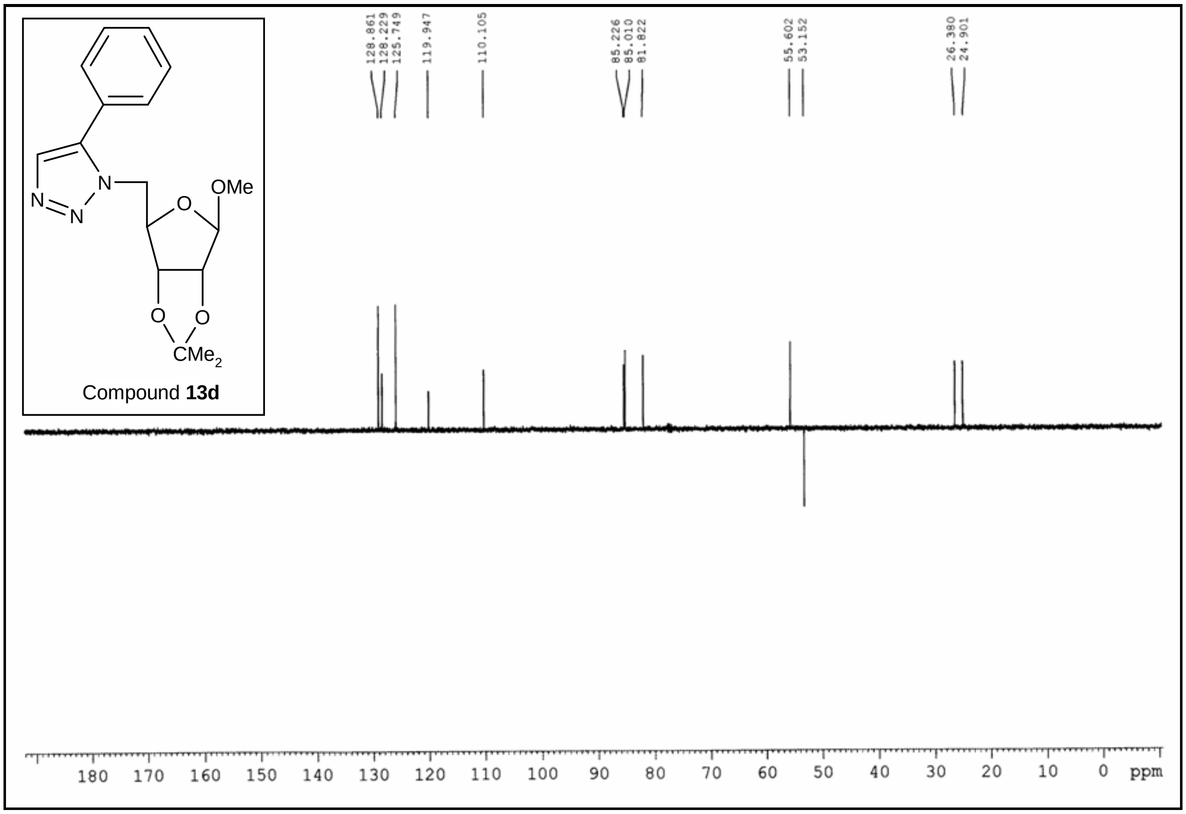
^{1}H-NMR spectra of **13d**



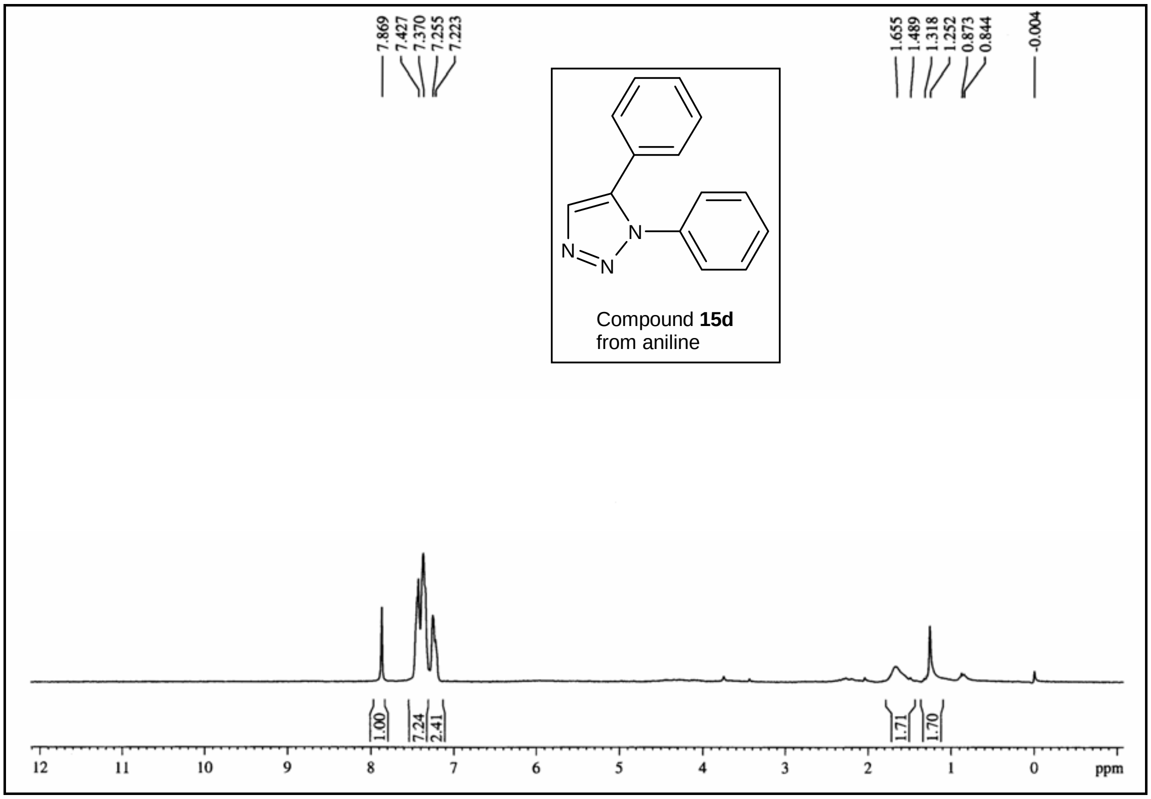
^{13}C-NMR spectra of **13d**



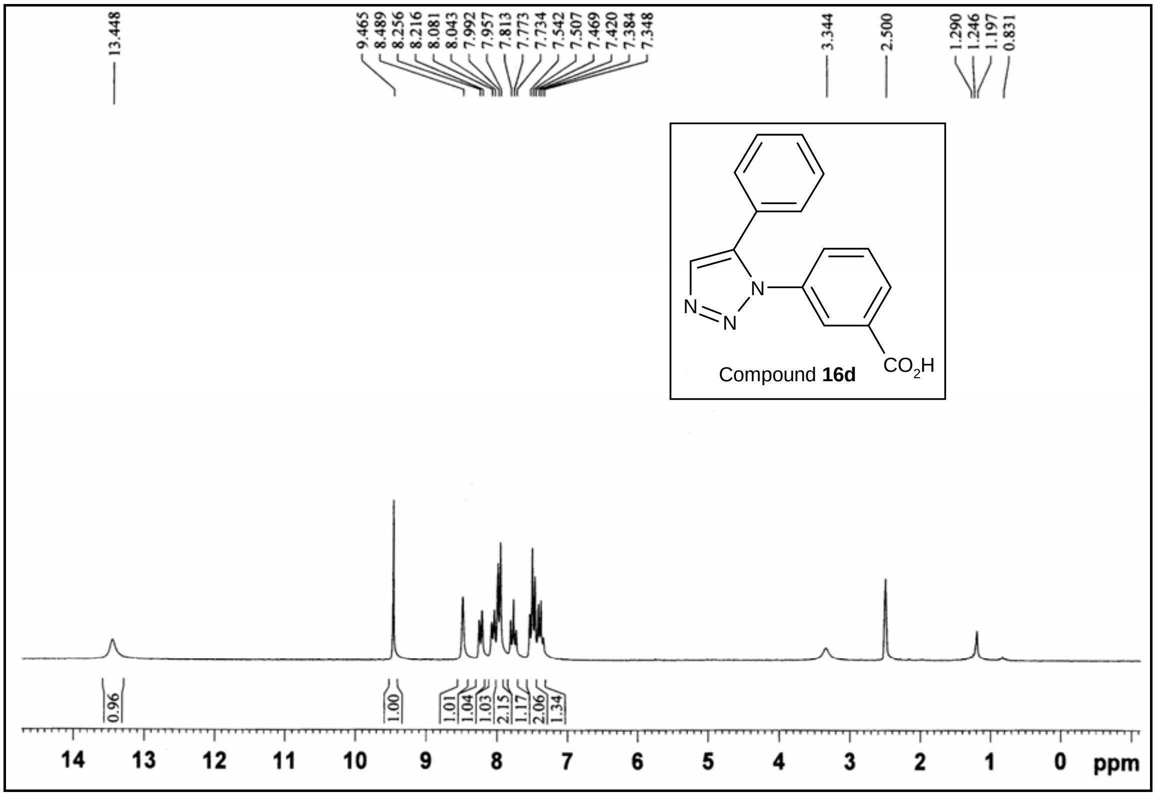
DEPT spectra of **13d**



^{1}H-NMR spectra of **15d**



^{1}H-NMR spectra of **16d**



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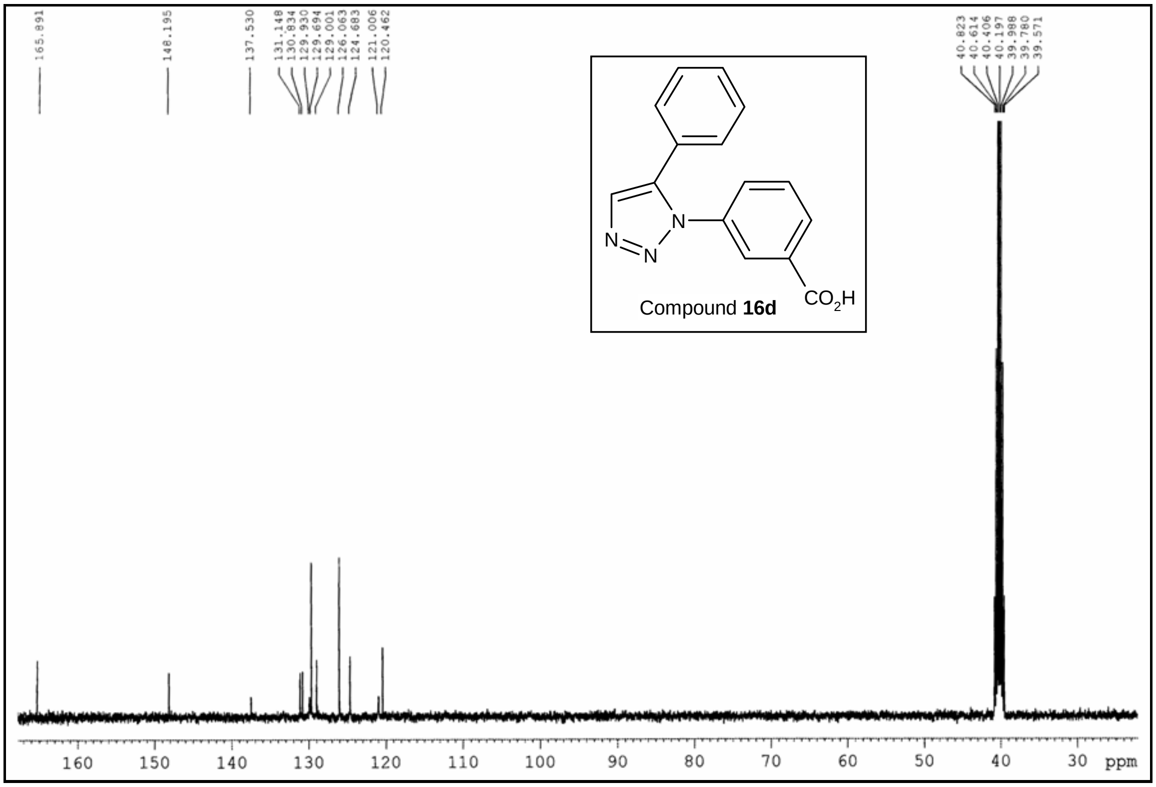

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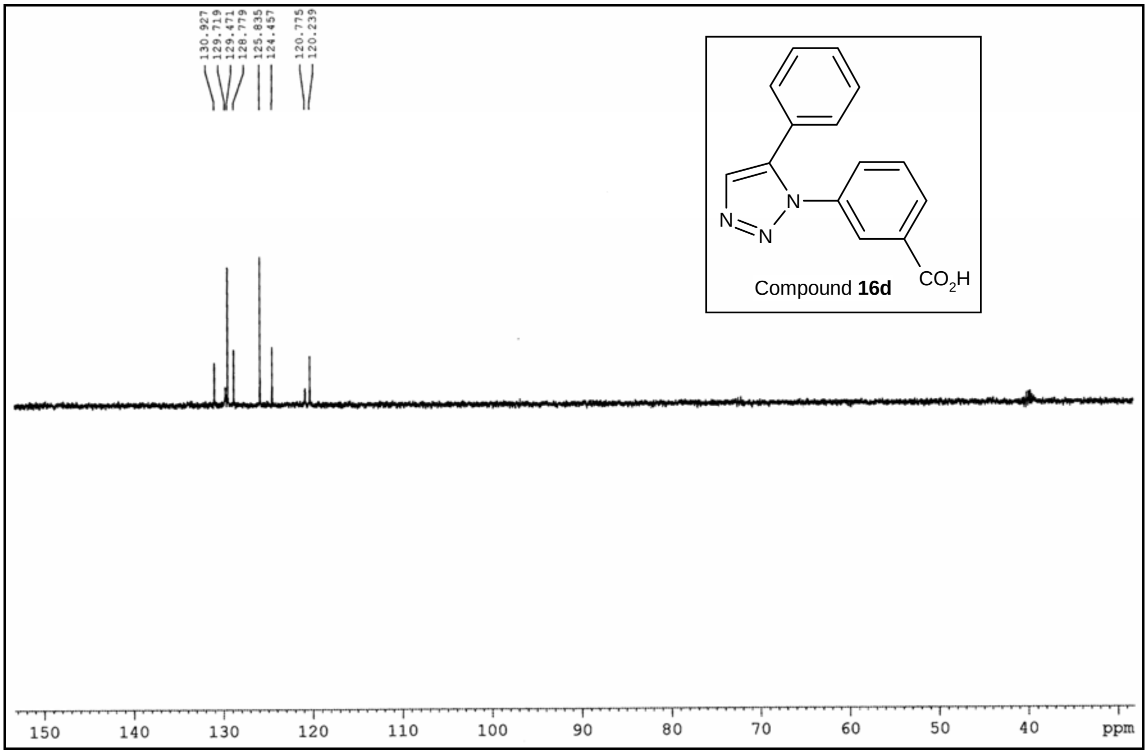

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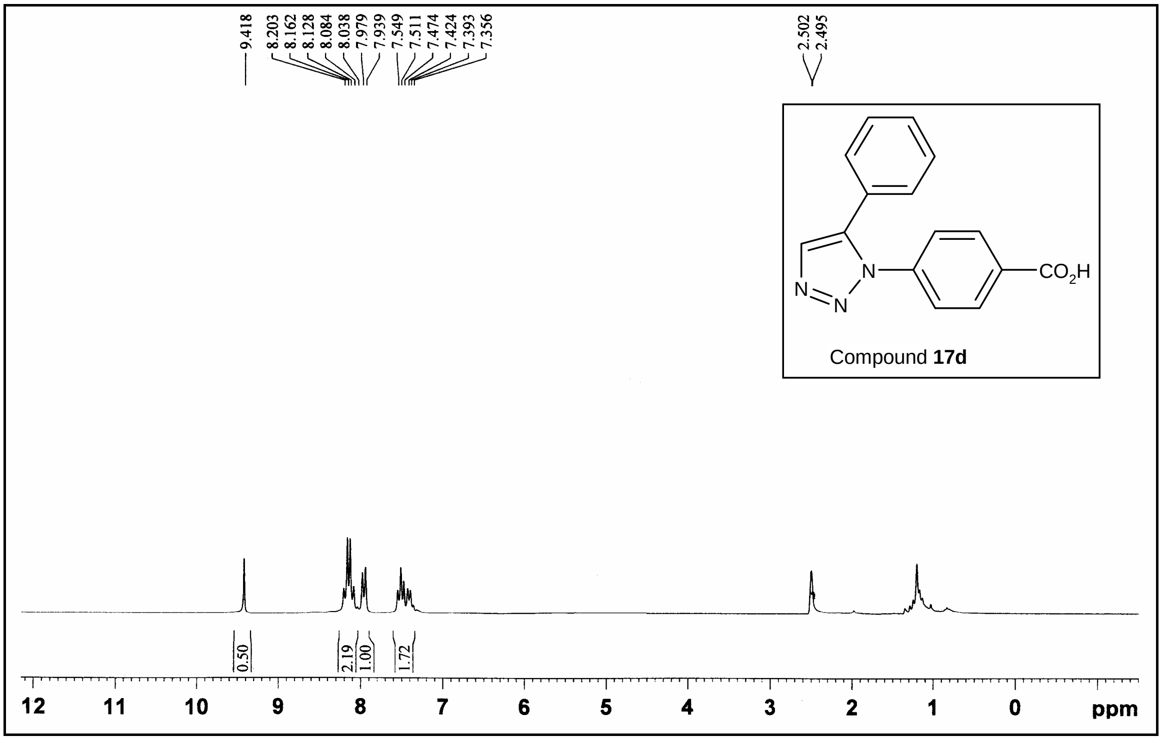

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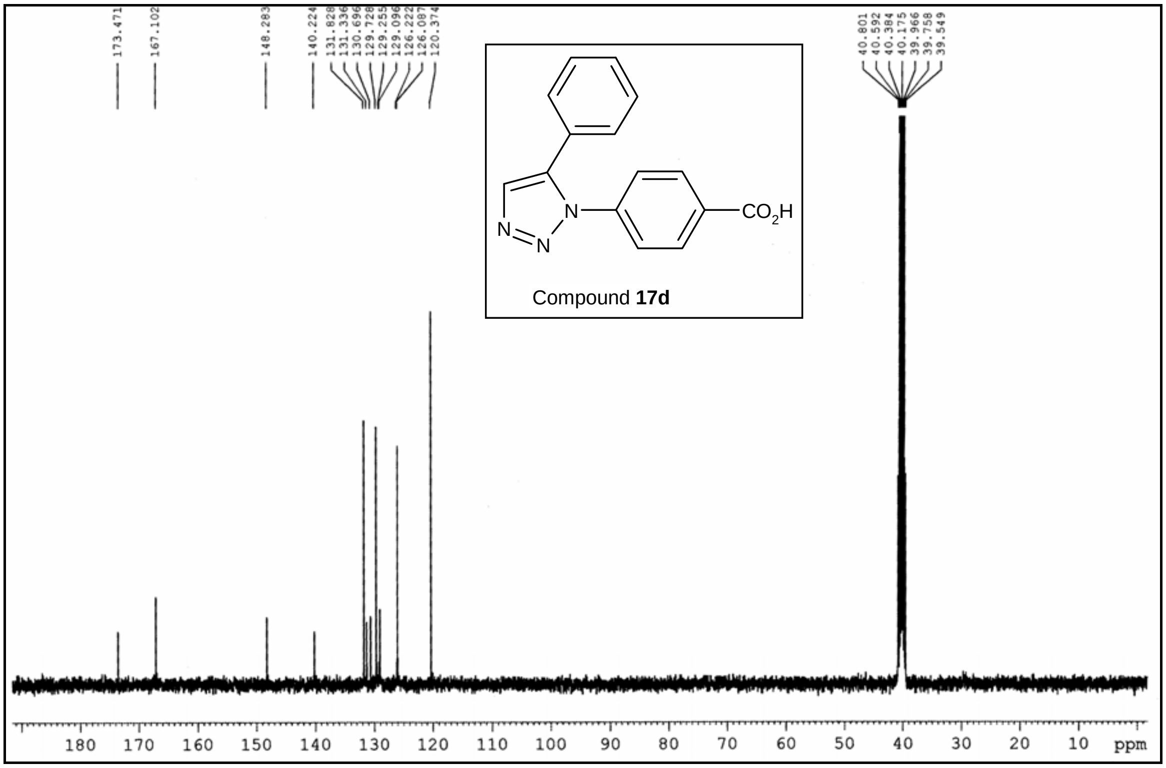

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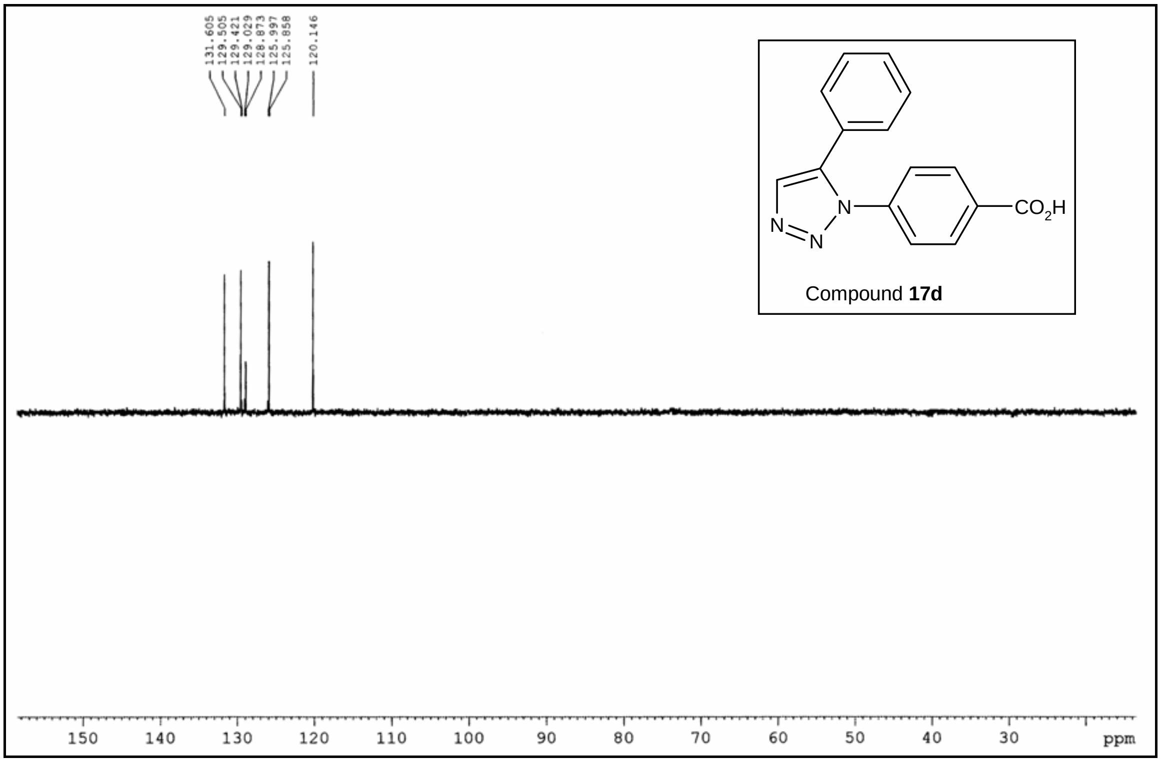
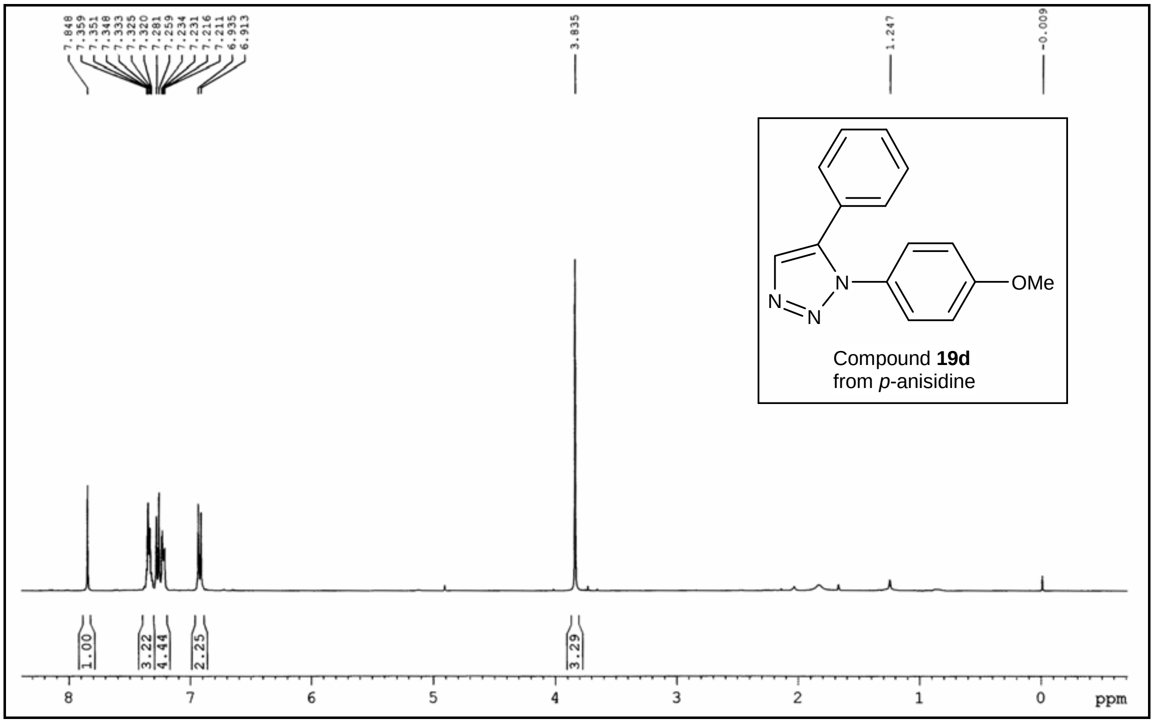


^{1}H-NMR spectra of **19d**



^{1}H-NMR spectra of **19d**