

Electronic Supplementary Information

Magnetically recyclable γ -Fe₂O₃–HAP nanoparticles for the cycloaddition reaction of alkynes, halides and azides in aqueous media

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1. Experimental
2. Characterization of compounds
3. Copies of ¹H and ¹³C NMR spectra
4. GC-MS spectra of compounds 4a-4q

1. Experimental

Preparation of the γ -Fe₂O₃/HAP nanoparticles catalyst

A solution of FeCl₂·4H₂O (3.7 mmol) and FeCl₃·6H₂O (7.4 mmol) was prepared by dissolving these salts in 100 ml distilled water under nitrogen atmosphere at room temperature. 25% of NH₄OH solution (20 ml) was then added with constant stirring. A black precipitate of γ -Fe₂O₃ was produced. Dropwise addition of NH₄OH helps to obtain small and uniform particle size. After 30 min, 200 ml of Ca(NO₃)₂·4H₂O (33.7 mmol) and (NH₄)₂HPO₄ (40 mmol) solution adjusted to pH=11 were added dropwise to the obtained precipitate for 1 h with vigorous stirring. The obtaining solution was then heated to 90 °C. After 2 h. the reaction mixture was cooled to room temperature and aged overnight. The dark brown precipitate was washed with distilled water. The synthesized catalyst was calcined at 300 °C for 3 h, yielding γ -Fe₂O₃/HAP (Fe content by ICP-AES: 1.093 mmol/g). The catalyst was characterized using various techniques such as XRD, FT-IR, ICP-AES, DSC-TGA, SEM and TEM.

General procedure for the synthesis of 1,2,3-triazoles

In a 10 ml round bottom flask fitted with a magnetic stirrer, the catalyst (5 mol % of Fe), phenyl acetylene (1 mmol), sodium azide (1.2 mmol) and benzyl bromide (1 mmol) were stirred in water (5 ml) at 100 °C for 5 h. The reaction progress was monitored by TLC. After 5 h, the reaction was quenched and the product was extracted with ethyl acetate. The organic layer was then separate out using separating funnel. The separated layer was washed with water and dried over sodium sulfate. The ethyl acetate solvent was removed using rotary evaporator, which left 94% pure desired product. The recovered catalyst was reused for further run without removing catalyst from the flask. All the prepared compounds were confirmed by GC-MS, IR, ¹H and ¹³C NMR.

2. Characterization of the γ -Fe₂O₃/HAP nanoparticles

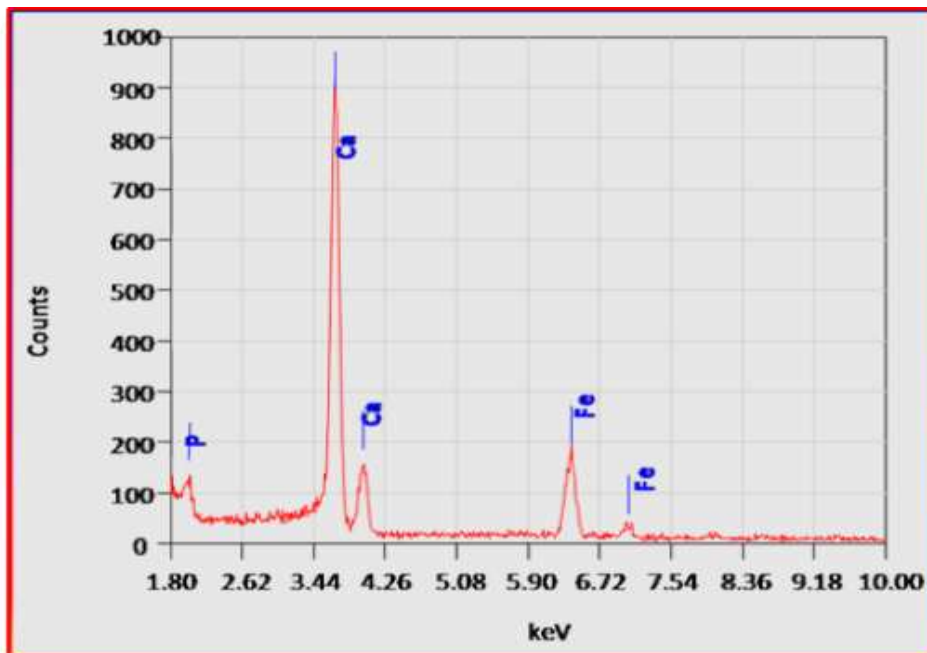


Fig.1 EDAX of γ -Fe₂O₃/HAP

The elemental analysis of the γ -Fe₂O₃/HAP was done by ICP-AES analysis technique. The ICP-AES analysis clearly shows presence of Fe metal ion.

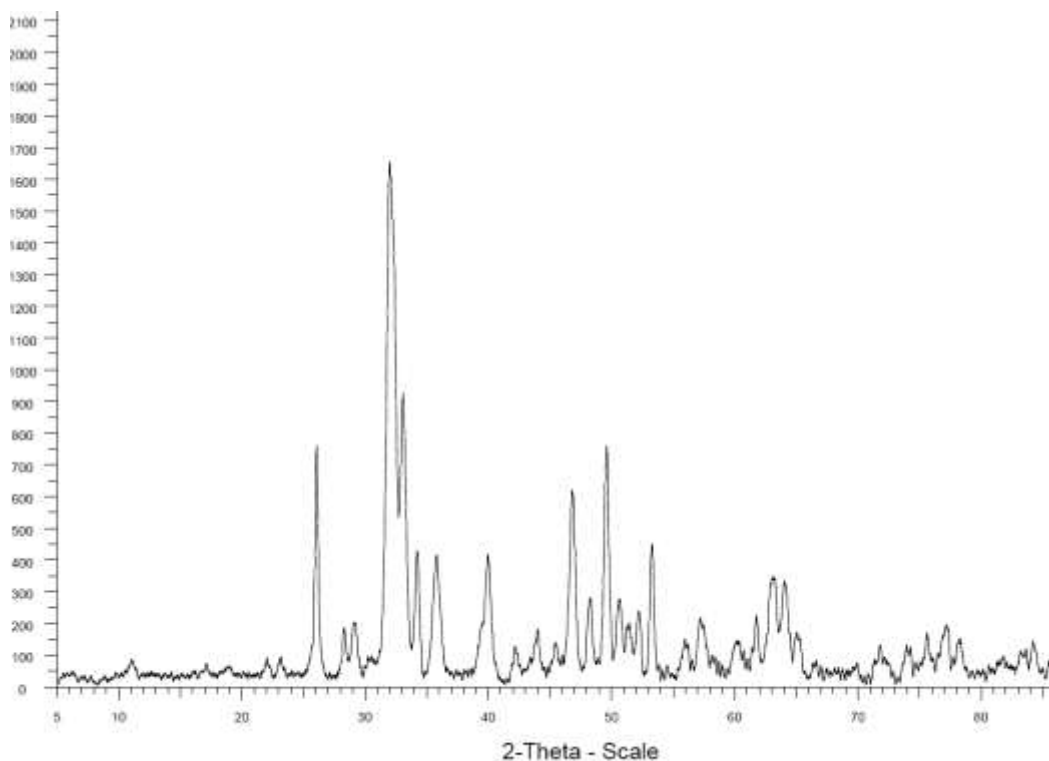


Fig.2 XRD of γ -Fe₂O₃/HAP

The XRD spectrum of γ -Fe₂O₃/HAP is depicted in Fig. 2. XRD of the γ -Fe₂O₃/HAP shows crystalline nature of the catalyst. The observed diffraction peaks agree well with that of the tetragonal structure of γ -Fe₂O₃.

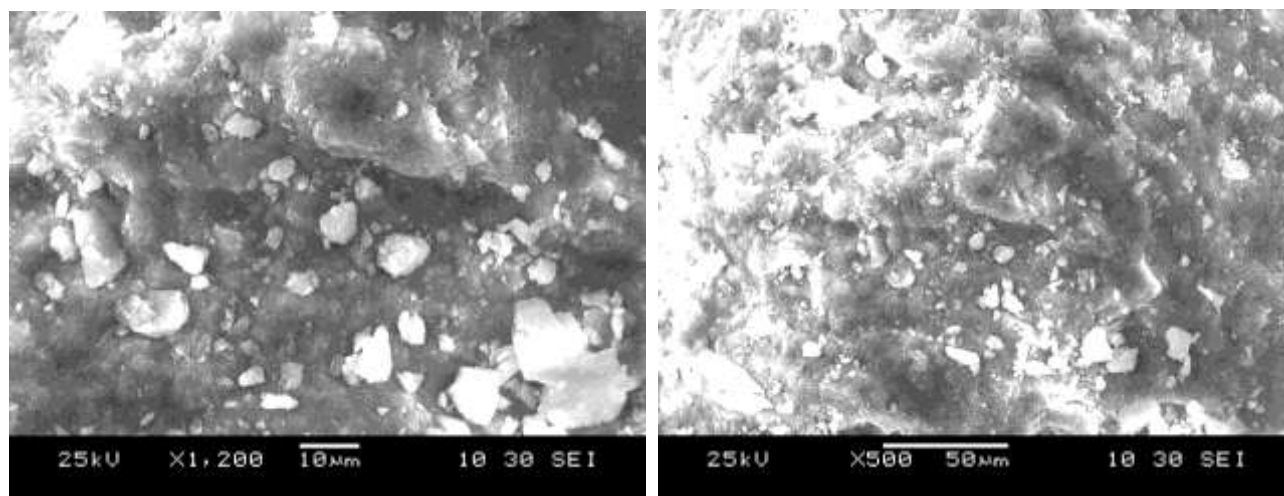


Fig.3 SEM images of γ -Fe₂O₃/HAP

The scanning electron micrograph of the γ -Fe₂O₃/HAP showed uniform particles size.

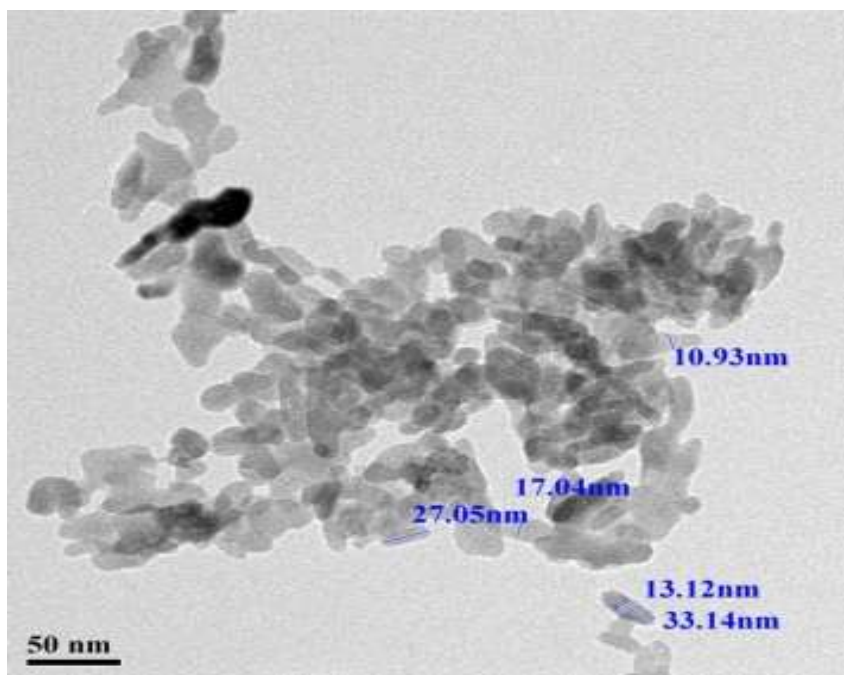


Fig.4 TEM images of γ -Fe₂O₃/HAP

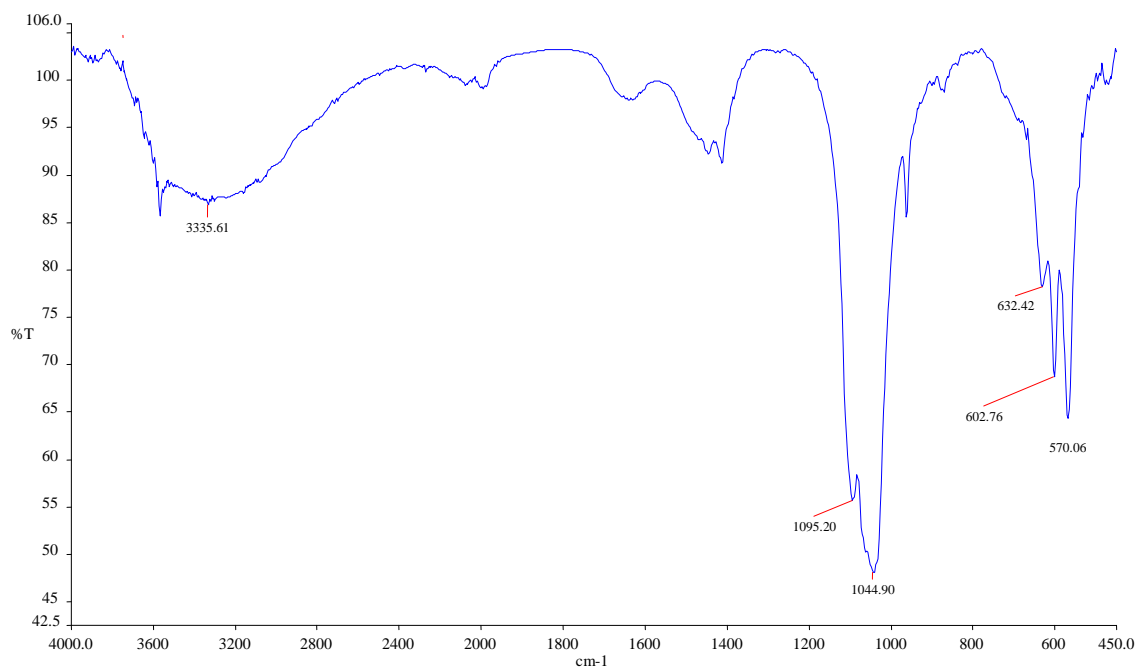


Fig. 5 FTIR spectrum of $\gamma\text{-Fe}_2\text{O}_3/\text{HAP}$

The characteristic absorption bands due to the bending vibration mode of O–P–O surface phosphate groups in the hydroxyapatite shell were observed at 570 and 602 cm^{-1} which were in overlap with Fe–O stretching. Also the stretching of P–O bond appeared at 1044 cm^{-1} overlapped with S–O stretching peak.

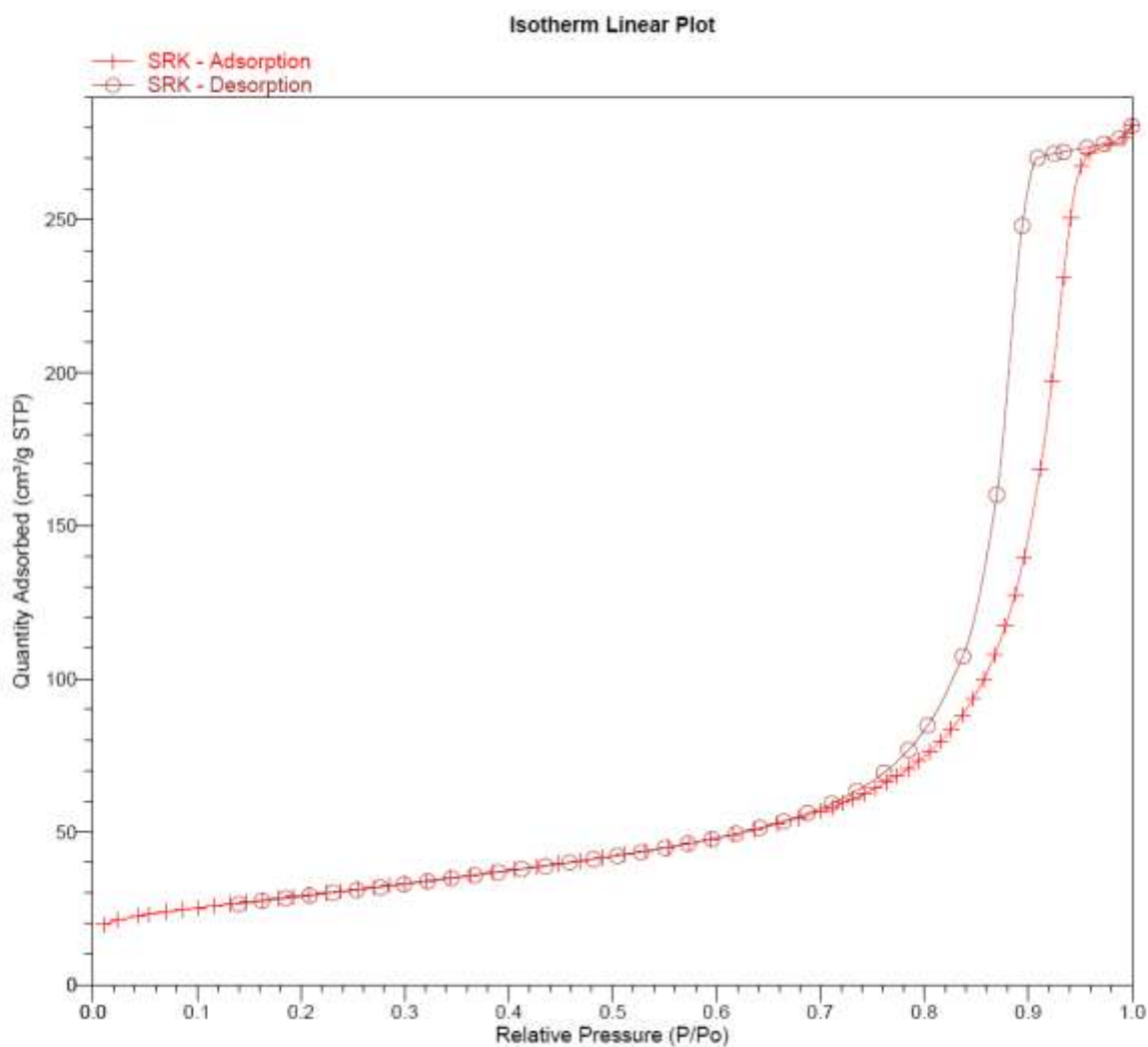
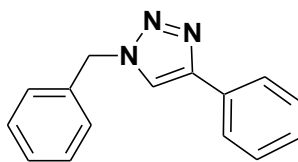


Fig.6 Isotherm plot of γ -Fe₂O₃/HAP

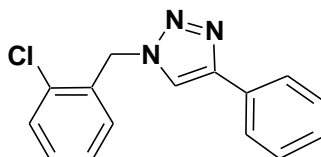
Nitrogen adsorption–desorption isotherms are shown in Fig. 6 and reveal that the adsorption–desorption process is not reversible. The surface area was calculated using BET method, and a value of $103 \text{ m}^2\text{g}^{-1}$ was found for hydroxyapatite coated magnetic nanoparticle (γ -Fe₂O₃/HAP).

3. Characterization of compounds:



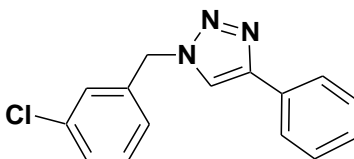
1-Benzyl-4-phenyl-1H-1,2,3-triazole:

GC (capillary column, 30 m × 60 mm, ID-BP1 0.25 UM.): oven rate (10 °C · min⁻¹), initial column temp. (353 K), final column temp. (523 K), injection temperature (533 K), detection temperature (543 K), halt (2 min.), retention time (17.85 min); White solid, mp 126-128°C; IR (KBr): 694, 729, 768, 1049, 1076, 1223, 1358, 1466, 3121 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ: 5.23(2H, s, CH₂), 7.26-7.41(6H, m, Ar), 7.69(1H, s, CH), 7.79-7.82(4H, m, Ar); ¹³C NMR (75 MHz, CDCl₃) δ: 54.1, 119.7, 125.7, 128, 128.2, 128.7, 128.8, 129.1, 130.6, 134.7, 148.1; MS: m/z (%): 235 (20), 207 (12), 206 (52), 180 (9), 179(7), 116 (100), 91 (98), 65 (30), 77 (5), 51 (10); Elemental analysis: found C 75.62, H 5.48, N 18.12, Calcd for C 75.59, H 5.53, N 17.87



1-(2-chlorobenzyl)-4-phenyl-1H-1,2,3-triazole:

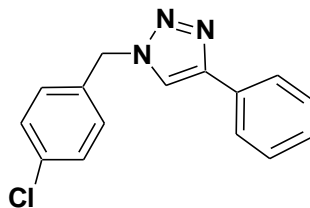
GC (capillary column, 30 m × 60 mm, ID-BP1 0.25 UM.): oven rate (10 °C · min⁻¹), initial column temp. (353 K), final column temp. (523 K), injection temperature (533 K), detection temperature (543 K), halt (2 min.), retention time (19.17 min); White solid, mp 90-92 °C; ¹H NMR (300 MHz, CDCl₃) δ: 5.67 (2H, s, N-CH₂), 7.16-7.46 (7H, m, 3H of Ar & 4H of Ar-Cl), 7.78 (1H, s, CH of triazole ring), 7.80-7.83 (2H, d, Ar); ¹³C NMR (75 MHz, CDCl₃) δ: 51.36, 119.91, 125.64, 127.56, 128.14, 128.76, 129.83, 130.13, 130.15, 130.40, 132.49, 133.31, 147.99; MS: m/z (%): 269 (12), 240 (10), 206 (50), 207(5), 179 (5), 138 (9), 116 (100), 89 (48), 63 (18), 77 (5), 51(5).



1-(3-chlorobenzyl)-4-phenyl-1H-1,2,3-triazole:

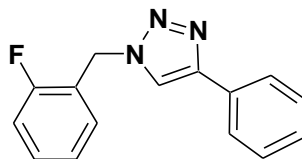
GC (capillary column, 30 m × 60 mm, ID-BP1 0.25 UM.): oven rate (10 °C · min⁻¹), initial column temp. (353 K), final column temp. (523 K), injection temperature (533 K), detection temperature (543 K), halt (2 min.), retention time (19.44 min); White solid, mp 106-108°C; ¹H NMR (300 MHz, CDCl₃) δ: 5.54 (2H, s, N-CH₂), 7.16-7.43 (7H, m, 3H of Ar & 4H of Ar-Cl), 7.69 (1H, s, CH of triazole ring), 7.79-7.82 (2H, d, Ar); ¹³C NMR (75 MHz, CDCl₃) δ: 53.4, 119.72, 125.68, 128.05, 128.01, 128.28, 128.85, 128.91, 130.33, 130.43, 134.92,

136.67, 148.31; MS: m/z (%): 269 (12), 240 (20), 206 (12), 207(5), 179 (5), 138 (9), 116 (100), 89 (35), 63 (18), 77 (5), 51(5).



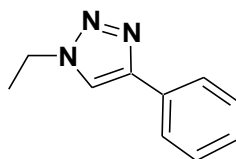
1-(4-chlorobenzyl)-4-phenyl-1H-1,2,3-triazole:

GC (capillary column, 30 m × 60 mm, ID-BP1 0.25 UM.): oven rate (10 °C · min⁻¹), initial column temp. (353 K), final column temp. (523 K), injection temperature (533 K), detection temperature (543 K), halt (2 min.), retention time (19.14 min); White solid, mp 140-142°C; ¹H NMR (300 MHz, CDCl₃) δ: 5.52(2H, s, CH₂), 7.17 (2H, d, *J* = 8.4 Hz, Ar), 7.24-7.44 (5H, m, Ar), 7.67 (1H, s, CH), 7.80 (2H, d, *J* = 8.4 Hz, Ar); ¹³C NMR (75 MHz, CDCl₃) δ: 53.4, 119.7, 125.6, 128.2, 128.8, 129.31, 129.35, 130.37, 133.24, 134.76, 148.32; MS: m/z (%): 269 (8), 240 (16), 206 (12), 179 (7), 138 (8), 125 (38) 116 (100), 89 (32), 63 (15), 77 (5), 51(5).



1-(2-Fluorobenzyl)-4-phenyl-1H-1,2,3-triazole:

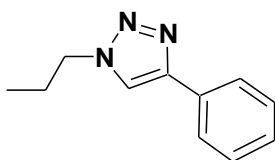
GC (capillary column, 30 m × 60 mm, ID-BP1 0.25 UM.): oven rate (10 °C · min⁻¹), initial column temp. (353 K), final column temp. (523 K), injection temperature (533 K), detection temperature (543 K), halt (2 min.), retention time (17.46 min); White solid, mp 102-104°C; ¹H NMR (300 MHz, CDCl₃) δ: 5.62 (2H, s, N-CH₂), 7.09-7.42 (7H, m, Ar), 7.76-7.82 (2H, m, Ar); ¹³C NMR (75 MHz, CDCl₃) δ: 47.67, 115.63, 115.90, 119.75, 121.88, 122.07, 124.83, 125.66, 128.71, 130.46, 130.81, 130.91, 148.14, 158.82, 162.11; MS: m/z (%): 253 (20), 224 (32), 198 (10), 130 (7), 124 (20), 116 (100), 109 (68), 102 (5), 89 (26), 83 (18), 77 (5), 63 (12), 51(5).



1-ethyl-4-phenyl-1H-1,2,3-triazole:

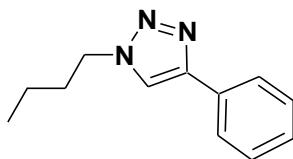
GC (capillary column, 30 m × 60 mm, ID-BP1 0.25 UM.): oven rate (10 °C · min⁻¹), initial column temp. (353 K), final column temp. (523 K), injection temperature (533 K), detection temperature (543 K), halt (2 min.), retention time (12.14 min); White solid, mp 54-56°C; ¹H NMR (300 MHz, CDCl₃) δ: 1.57 (3H, triplet, *J* = 7.33 Hz, CH₃), 4.45 (2H, quartet, *J* = 7.33 Hz, N-CH₂), 7.76 (1H, s, N-CH), 7.26-7.38 (3H, m, Ar), 7.80-7.83 (2H, d, ortho to Ar); ¹³C NMR (75 MHz, CDCl₃) δ: 15.50, 15.57, 45.23, 45.34, 119.02, 125.65, 128.06, 128.81, 129.78,

130.69, 147.74; MS: m/z (%): 173 (35), 144 (25), 130 (68), 117 (100) 103 (22), 90 (70), 89 (60), 77 (10), 63 (26), 51(15).



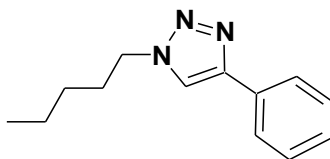
1-propyl-4-phenyl-1H-1.2.3-triazole:

GC (capillary column, 30 m × 60 mm, ID-BP1 0.25 UM.): oven rate (10 °C · min⁻¹), initial column temp. (353 K), final column temp. (523 K), injection temperature (533 K), detection temperature (543 K), halt (2 min.), retention time (12.86 min); White solid, mp 62-64°C, ¹H NMR (300 MHz, CDCl₃) δ: 0.85-0.98 (3H, t, CH₃), 1.88-1.98 (2H, m, CH₂-CH₃), 4.30-4.35 (2H, t, N-CH₂-CH₂-CH₃), 7.26-7.43 (3H, m, Ar), 7.81-7.84 (2H, d, Ar), 7.75 (1H, s, CH); ¹³C NMR (75 MHz, CDCl₃) δ: 23.72, 29.68, 51.92, 119.52, 125.62, 128.01, 128.78, 130.70, 147.61; MS: m/z (%): 187 (25), 144 (13), 131 (35), 117 (100), 103 (26), 90 (35), 77 (15), 41(25).



1-butyl-4-phenyl-1H-1.2.3-triazole:

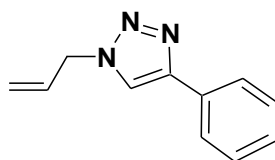
GC (capillary column, 30 m × 60 mm, ID-BP1 0.25 UM.): oven rate (10 °C · min⁻¹), initial column temp. (353 K), final column temp. (523 K), injection temperature (533 K), detection temperature (543 K), halt (2 min.), retention time (14.24 min); White solid, mp 48-50°C; ¹H NMR (300 MHz, CDCl₃) δ: 0.96 (3H, t, *J* = 7.33 Hz, CH₃-CH₂), 1.38 (2H, sextet, *J* = 7.33 Hz, CH₂-CH₂-CH₃), 1.92 (2H, quintet, *J* = 7.33 Hz, CH₂-CH₂-CH₂), 4.39 (2H, t, *J* = 7.33 Hz, N-CH₂), 7.26-7.44 (3H, m, Ar), 7.74 (1H, s, N-CH), 7.82 (2H, d, Ar); ¹³C NMR (75 MHz, CDCl₃) δ: 13.57, 19.78, 32.37, 50.19, 119.48, 125.73, 128.12, 128.88, 130.79, 147.76; MS: m/z (%): 201 (24), 172 (18), 145 (14), 144 (12), 130 (17), 117 (100), 90 (24), 89 (22), 77 (12), 41 (25); Elemental analysis: found C 71.56, H 7.39, N 20.68, Calcd for C 71.64, H 7.46, N 20.89



1-pentyl-4-phenyl-1H-1.2.3-triazole:

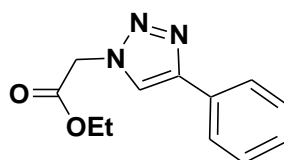
GC (capillary column, 30 m × 60 mm, ID-BP1 0.25 UM.): oven rate (10 °C · min⁻¹), initial column temp. (353 K), final column temp. (523 K), injection temperature (533 K), detection temperature (543 K), halt (2 min.), retention time (13.14 min); White solid, mp 68-70°C; ¹H NMR (300 MHz, CDCl₃) δ: 0.91 (3H, triplet, CH₃), 1.32-1.41 (4H, m, CH₂-CH₂), 1.95 (2H, quintet, *J* = 7.33 Hz, CH₂), 4.39 (2H, triplet, *J* = 7.33 Hz, N-CH₂), 7.32-7.45 (3H, m, ortho to Ar), 7.74 (1H, s, N-CH), 7.82-7.85 (2H, d, *J* = 8.4 Hz, Ar); ¹³C NMR (75 MHz, CDCl₃) δ: 13.83, 22.07, 28.55, 30.01, 50.37, 119.35, 125.62, 128.012, 128.77, 130.69, 147.65; MS: m/z (%): 215 (25),

186 (20), 172 (9), 158 (5), 145(1), 144(15), 130 (17), 117 (100), 104(25), 89 (24), 77 (14), 63 (10), 41 (50);
Elemental analysis: found C 71.58, H 7.54, N 19.97, Calcd for C 71.55, H 7.90, N 19.53



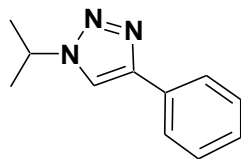
1-allyl-4-phenyl-1H-1.2.3-triazole:

GC (capillary column, 30 m × 60 mm, ID-BP1 0.25 UM.): oven rate (10 °C · min⁻¹), initial column temp. (353 K), final column temp. (523 K), injection temperature (533 K), detection temperature (543 K), halt (2 min.), retention time (13.20 min); White solid, mp 58-60°C; ¹H NMR (300 MHz, CDCl₃) δ: 4.96-4.99 (2H, d, *J* = 6.2 Hz, N-CH₂), 5.27-5.36 (2H, dd, *J* = 8 Hz & 16.86 Hz, allylic CH₂), 6.01-6.09 (1H, m, allylic CH), 7.27-7.43 (3H, m, Ar), 7.76 (1H, s, CH of triazole ring), 7.80-7.83 (2H, d, Ar); ¹³C NMR (75 MHz, CDCl₃) δ: 51.36, 119.91, 120.08, 125.63, 128.08, 128.77, 130.54, 131.26, 147.88; MS: *m/z* (%): 185 (20), 156 (18), 116 (100), 89 (30), 63 (15), 77 (5), 41(16).



4-Phenyl-1,2,3-triazole-1-yl)-acetic acid ethyl ester:

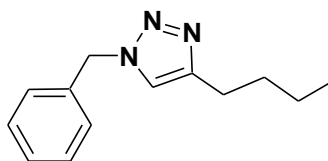
GC (capillary column, 30 m × 60 mm, ID-BP1 0.25 UM.): oven rate (10 °C · min⁻¹), initial column temp. (353 K), final column temp. (523 K), injection temperature (533 K), detection temperature (543 K), halt (2 min.), retention time (15.64 min); White solid, mp 102-104°C; IR (KBr): 768, 1045, 1078, 1223, 1466, 1758, 2950, 3004, 3079, 3125 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ: 1.33 (3H, triplet, *J* = 7.69 Hz), 4.26 (2H, quartet, *J* = 7.69 Hz), 5.20 (2H, s, N-CH₂), 7.40-7.41 (3H, m), 7.83-7.86 (2H, m, ortho to Ar), 7.91 (1H, s, CH); ¹³C NMR (75 MHz, CDCl₃) δ: 14.05, 51.01, 62.39, 121.08, 125.74, 128.21, 128.80, 130.32, 148.12, 166.28; MS: *m/z* (%): 231 (30), 203 (14), 160 (18), 146 (20), 131 (40), 130 (50), 116 (100), 103 (62), 77 (42), 51 (18); Elemental analysis: found C 61.80, H 5.39, N 17.49, Calcd for C 61.63 H 5.62 N 17.58



1-isopropyl-4-phenyl-1H-1.2.3-triazole:

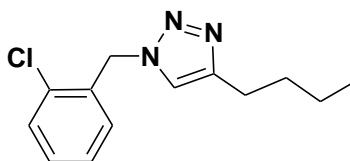
GC (capillary column, 30 m × 60 mm, ID-BP1 0.25 UM.): oven rate (10 °C · min⁻¹), initial column temp. (353 K), final column temp. (523 K), injection temperature (533 K), detection temperature (543 K), halt (2 min.), retention time (15.92 min); Light Yellow solid; ¹H NMR (300 MHz, CDCl₃) δ: 1.59 (6H, d, *J* = 8.4 Hz, 2 CH₃), 4.85 (1H, m, *J* = 8.4 Hz, N-CHMe₂), 7.26-7.43 (3H, m, Ar), 7.77 (1H, s, N-CH), 7.82 (2H, d, ortho to Ar); ¹³C NMR (.....MHz, CDCl₃) δ: 23.08, 23.14, 53.02, 53.17, 117.18, 125.71, 128.06, 128.85, 130.90, 147.54; MS:

m/z (%): 187 (30), 159 (10), 144 (50), 132 (5), 117 (100), 103 (20), 102 (10), 89 (38), 77 (5), 63 (16), 51 (10), 43 (25), 41 (20).



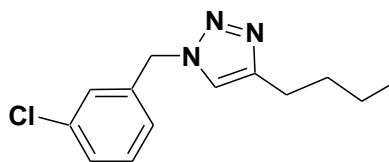
1-benzyl-4-butyl-1H-1,2,3-triazole:

GC (capillary column, 30 m × 60 mm, ID-BP1 0.25 UM.): oven rate (10 °C · min⁻¹), initial column temp. (353 K), final column temp. (523 K), injection temperature (533 K), detection temperature (543 K), halt (2 min.), retention time (15.72 min); White solid, mp 56-58°C; ¹H NMR (300 MHz, CDCl₃) δ: 0.90 (3H, triplet, *J* = 7.69 Hz, CH₃), 1.25-1.39 (2H, sextet, *J* = 7.69 Hz, CH₂), 1.60 (2H, quintet, *J* = 7.69 Hz, CH₂), 2.68 (2H, triplet, *J* = 7.69 Hz, CH₂), 5.48 (2H, singlet, N-CH₂), 7.19-7.39 (6H, m, Ar); ¹³C NMR (75 MHz, CDCl₃) δ: 13.78, 22.29, 25.36, 31.48, 53.92, 120.44, 120.55, 127.92, 128.54, 129.01, 134.99, 148.89; MS: m/z (%): 215 (2), 173 (7), 144 (5), 130 (4), 104 (6), 91 (100), 69 (4), 65 (12), 41(10).



1-(2-chlorobenzyl)-4-butyl-1H-1,2,3-triazole:

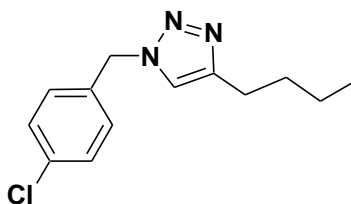
GC (capillary column, 30 m × 60 mm, ID-BP1 0.25 UM.): oven rate (10 °C · min⁻¹), initial column temp. (353 K), final column temp. (523 K), injection temperature (533 K), detection temperature (543 K), halt (2 min.), retention time (17.12 min); White solid, mp 90-92°C; ¹H NMR (300 MHz, CDCl₃) δ: 5.52(2H, s, CH₂), 7.17 (2H, d, *J* = 8.4 Hz, Ar), 7.24-7.44 (5H, m, Ar), 7.67 (1H, s, CH), 7.80 (2H, d, *J* = 8.4 Hz, Ar); ¹³C NMR (75 MHz, CDCl₃) δ: 53.4, 119.7, 125.6, 128.2, 128.8, 129.31, 129.35, 130.37, 133.24, 134.76, 148.32; MS: m/z (%): 249 (2), 214 (2), 207 (7), 186 (4), 144 (4), 127 (32), 125 (100), 96 (3), 89 (21), 69 (6), 41 (15).



1-(3-chlorobenzyl)-4-butyl-1H-1,2,3-triazole:

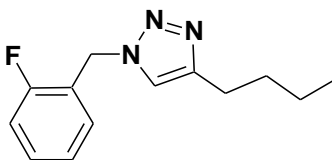
GC (capillary column, 30 m × 60 mm, ID-BP1 0.25 UM.): oven rate (10 °C · min⁻¹), initial column temp. (353 K), final column temp. (523 K), injection temperature (533 K), detection temperature (543 K), halt (2 min.), retention time (16.62 min); Light yellow solid, mp 50-52°C; ¹H NMR (300 MHz, CDCl₃) δ: 0.98 (3H, triplet, *J* = 7.69 Hz), 1.35 (2H, sextet, *J* = 7.69 Hz), 1.63 (2H, quintet, *J* = 7.69 Hz), 2.69 (2H, triplet, *J* = 7.69 Hz), 5.46 (2H, singlet, N-CH₂), 7.20-7.33 (5H, m); ¹³C NMR (75 MHz, CDCl₃) δ: 13.74, 22.23, 25.29, 31.38, 53.12,

120.67, 120.57, 125.87, 128.68, 130.26, 134.78, 136.96, 149.03; MS: m/z (%): 249 (1), 220 (2), 207 (10), 178 (3), 164 (2), 138 (4), 127 (31), 125 (100), 89 (20), 69 (8), 41 (18).



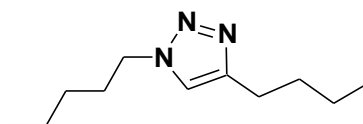
1-(4-chlorobenzyl)-4-butyl-1H-1,2,3-triazole:

GC (capillary column, 30 m × 60 mm, ID-BP1 0.25 UM.): oven rate (10 °C · min⁻¹), initial column temp. (353 K), final column temp. (523 K), injection temperature (533 K), detection temperature (543 K), halt (2 min.), retention time (20.97 min); White solid, mp 54-56°C; ¹H NMR (300 MHz, CDCl₃) δ: 0.91 (3H, triplet, *J* = 7.69 Hz), 1.38 (2H, sextet, *J* = 7.69 Hz), 1.63 (2H, quintet, *J* = 7.69 Hz), 2.63 (2H, triplet, *J* = 7.69 Hz), 5.46 (2H, singlet, N-CH₂), 7.17-7.39 (5H, m); ¹³C NMR (75 MHz, CDCl₃) δ: 13.84, 22.37, 25.43, 31.53, 53.27, 120.54, 129.31, 133.58, 134.68, 149.20; MS: m/z (%): 249 (1), 207 (8), 178 (2), 164 (1), 138 (4), 127 (30), 125 (100), 89 (18), 69 (3), 41 (15).



1-(2-fluorobenzyl)-4-butyl-1H-1,2,3-triazole:

GC (capillary column, 30 m × 60 mm, ID-BP1 0.25 UM.): oven rate (10 °C · min⁻¹), initial column temp. (353 K), final column temp. (523 K), injection temperature (533 K), detection temperature (543 K), halt (2 min.), retention time (17.10 min); Brown oil; ¹H NMR (300 MHz, CDCl₃) δ: 0.91 (3H, triplet, *J* = 7.69 Hz), 1.37 (2H, sextet, *J* = 7.69 Hz), 1.62 (2H, quintet, *J* = 7.69 Hz), 2.69 (2H, triplet, *J* = 7.69 Hz), 5.45 (2H, singlet, N-CH₂), 7.10-7.39 (5H, m); ¹³C NMR (75 MHz, CDCl₃) δ: 13.76, 22.25, 25.29, 31.43, 47.40, 115.79, 120.74, 122.29, 124.72, 130.59, 148.85, 158.76, 162.05; MS: m/z (%): 233 (1), 204 (2), 191 (8), 176 (2), 162 (6), 122 (5), 109 (100), 96 (6), 83 (12), 69 (5), 41(11).



1-pentyl-4-butyl-1H-1,2,3-triazole:

GC (capillary column, 30 m × 60 mm, ID-BP1 0.25 UM.): oven rate (10 °C · min⁻¹), initial column temp. (353 K), final column temp. (523 K), injection temperature (533 K), detection temperature (543 K), halt (2 min.), retention time (12.49 min); Yellow oil; ¹H NMR (300 MHz, CDCl₃) δ: 0.87-0.95 (6H, m, 2CH₃), 1.29-1.44 (6H, m, 3CH₂), 1.65 (2H, quintet, *J* = 7.33 Hz, CH₂), 1.86 (2H, quintet, *J* = 7.33 Hz, CH₂), 2.71 (2H, triplet, *J* = 7.33 Hz, CH₂), 4.30 (2H, triplet, *J* = 7.33 Hz, N-CH₂), 7.27 (1H, s, N-CH); ¹³C NMR (75 MHz, CDCl₃) δ: 13.91, 22.16, 22.37, 25.42, 28.67, 29.74, 30.11, 31.66, 50.21, 120.44, 148.45; MS: m/z (%): 195 (9), 151 (4), 152 (16), 124 (20), 110 (25), 96 (26), 82 (40), 68 (26), 54 (70), 41 (100).

Table 2, Entry 1:

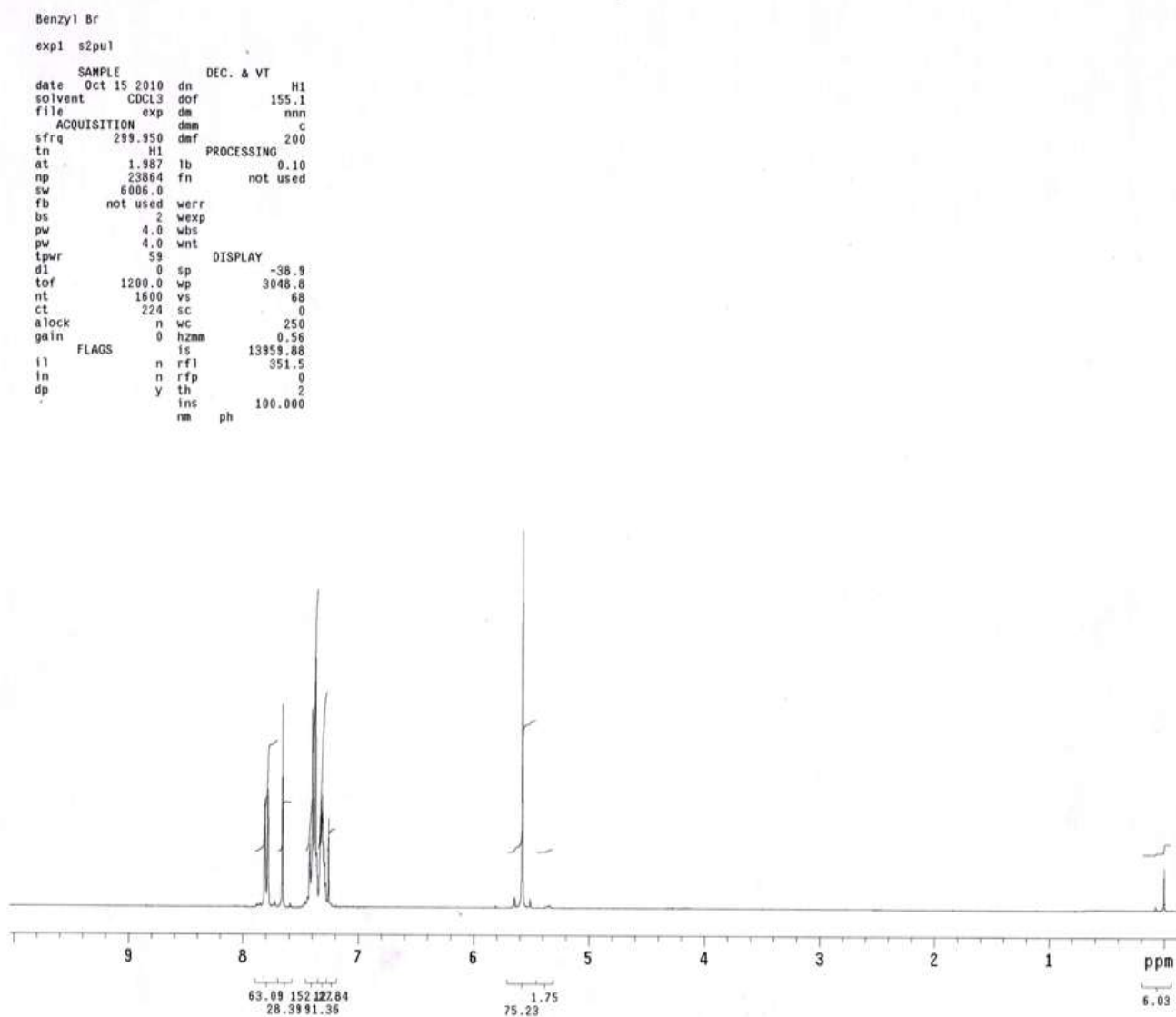
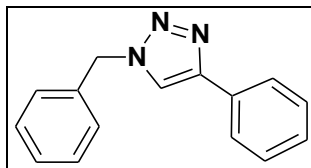
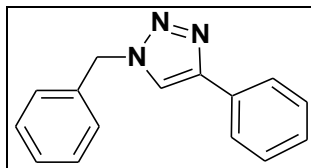


Table 2, Entry 1:



```
Benzyl Br
exp3 s2pu1
SAMPLE
date Oct 15 2010 temp not used
solvent CDCL3 gain not used
file exp spin not used
ACQUISITION
sw 25000.0 hst 0.008
at 1.280 pw90 9.500
np 64000 alfa 20.000
fb 13800 il FLAGS n
bs 4 in n
d1 3.000 dp y
nt 12000 hs nn
ct 248 PROCESSING
tn C13 fb 2.00
sfrq 75.430 fn not used
tof 748.9 sp DISPLAY -55.0
tpwr 59 wp 16855.0
pw 6.000 rfl 10042.6
DECOUPLER rfp 5815.0
dn H1 rp -139.1
dof 0 lp -333.9
dm yyy PLOT
dmm w wc 250
dpwr 39 sc 0
dmf 10900 vs 29
th 5
al ph
```

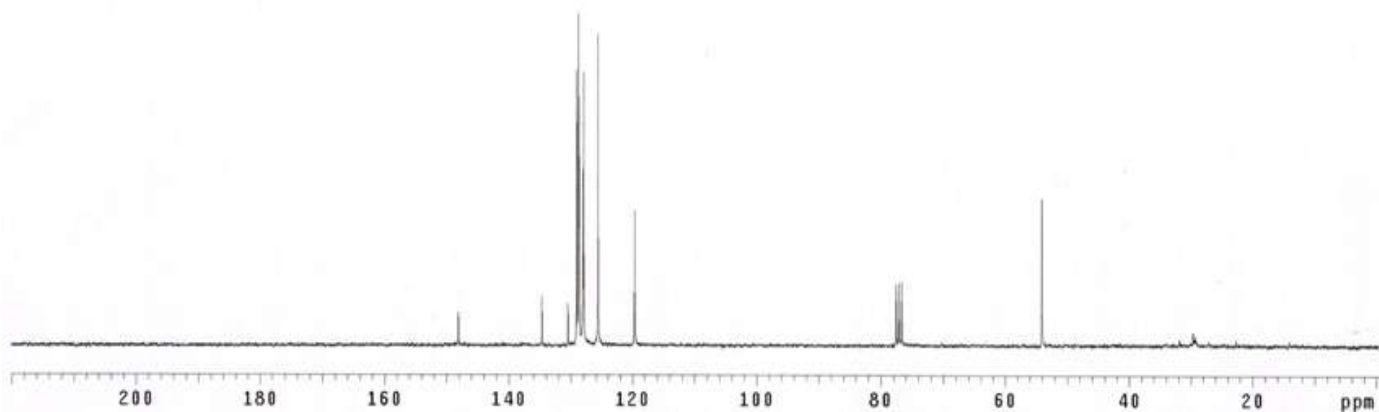


Table 2, Entry 3:

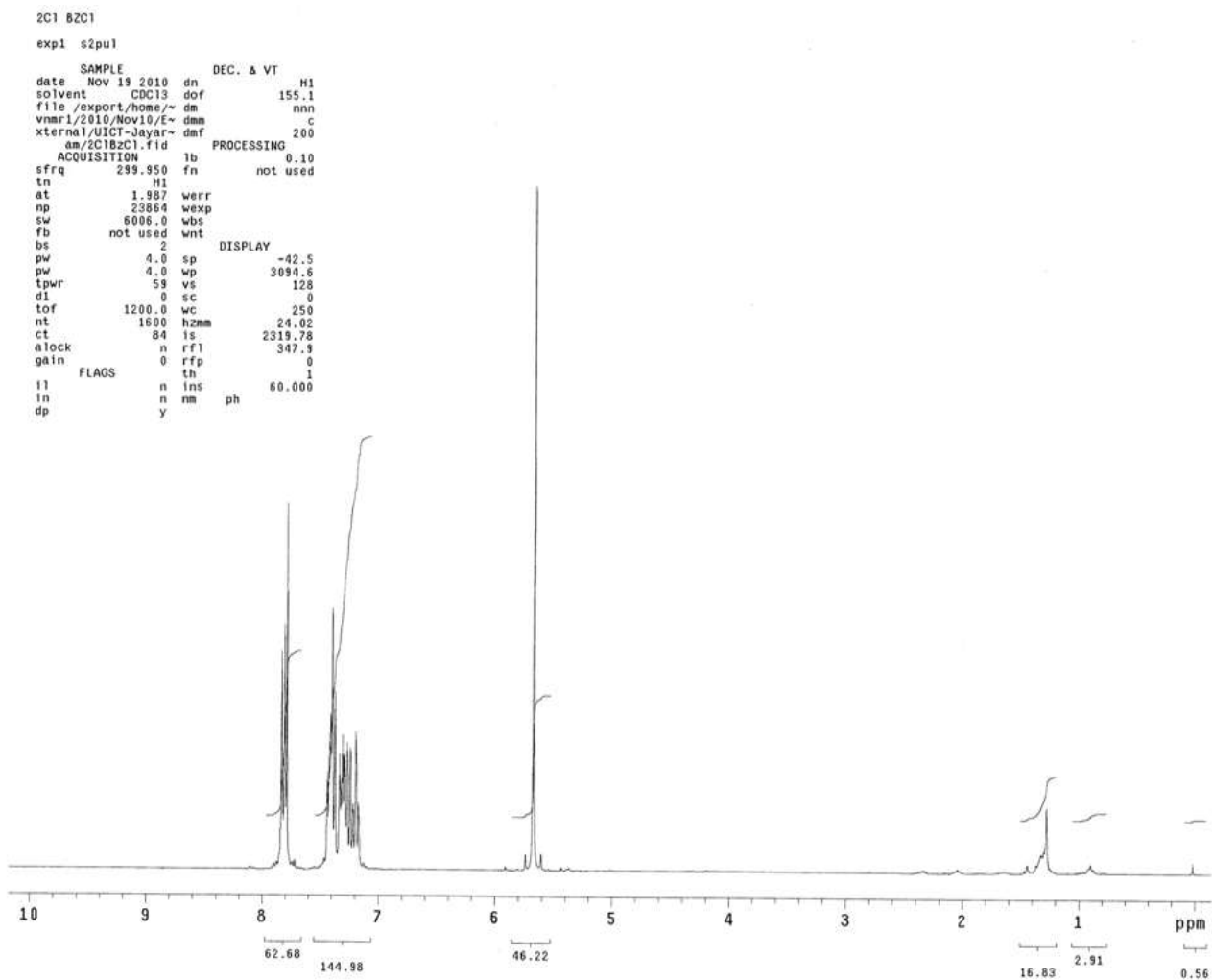
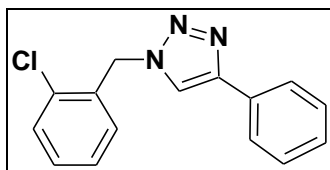


Table 2, Entry 3:

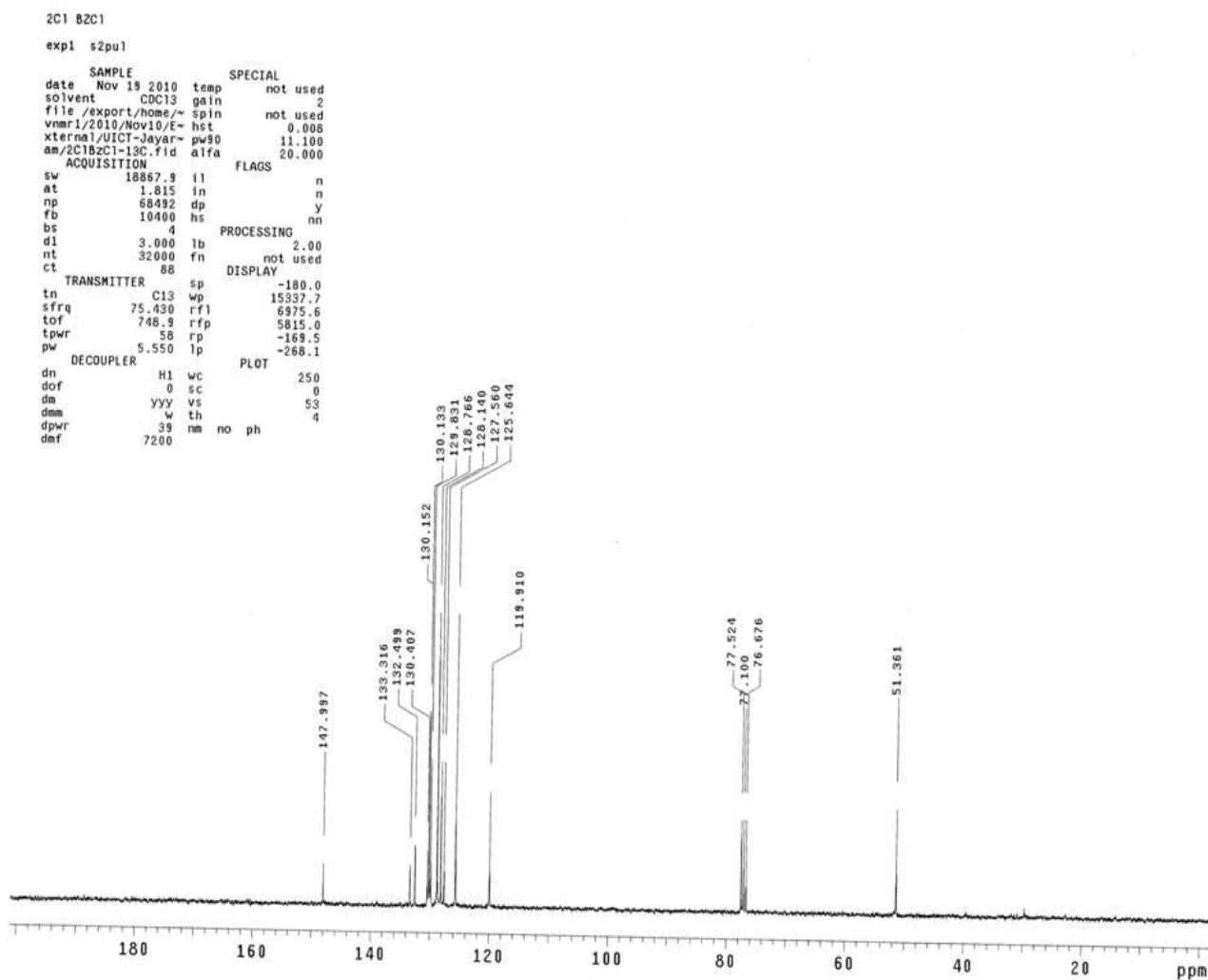
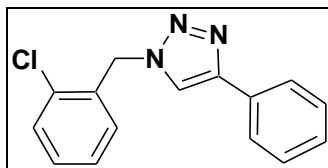


Table 2, Entry 4:

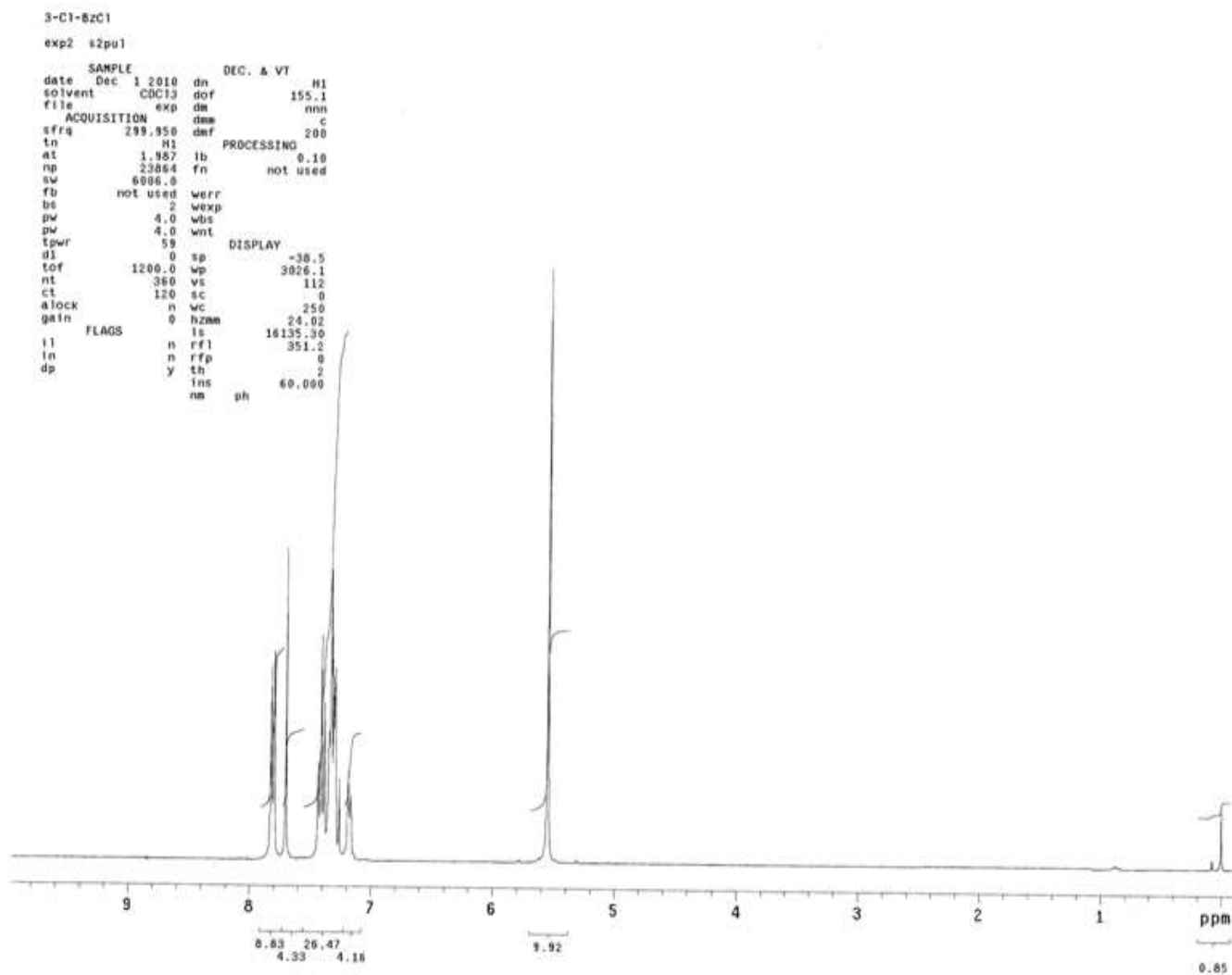
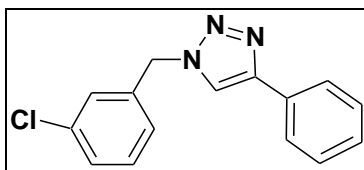


Table 2, Entry 4:

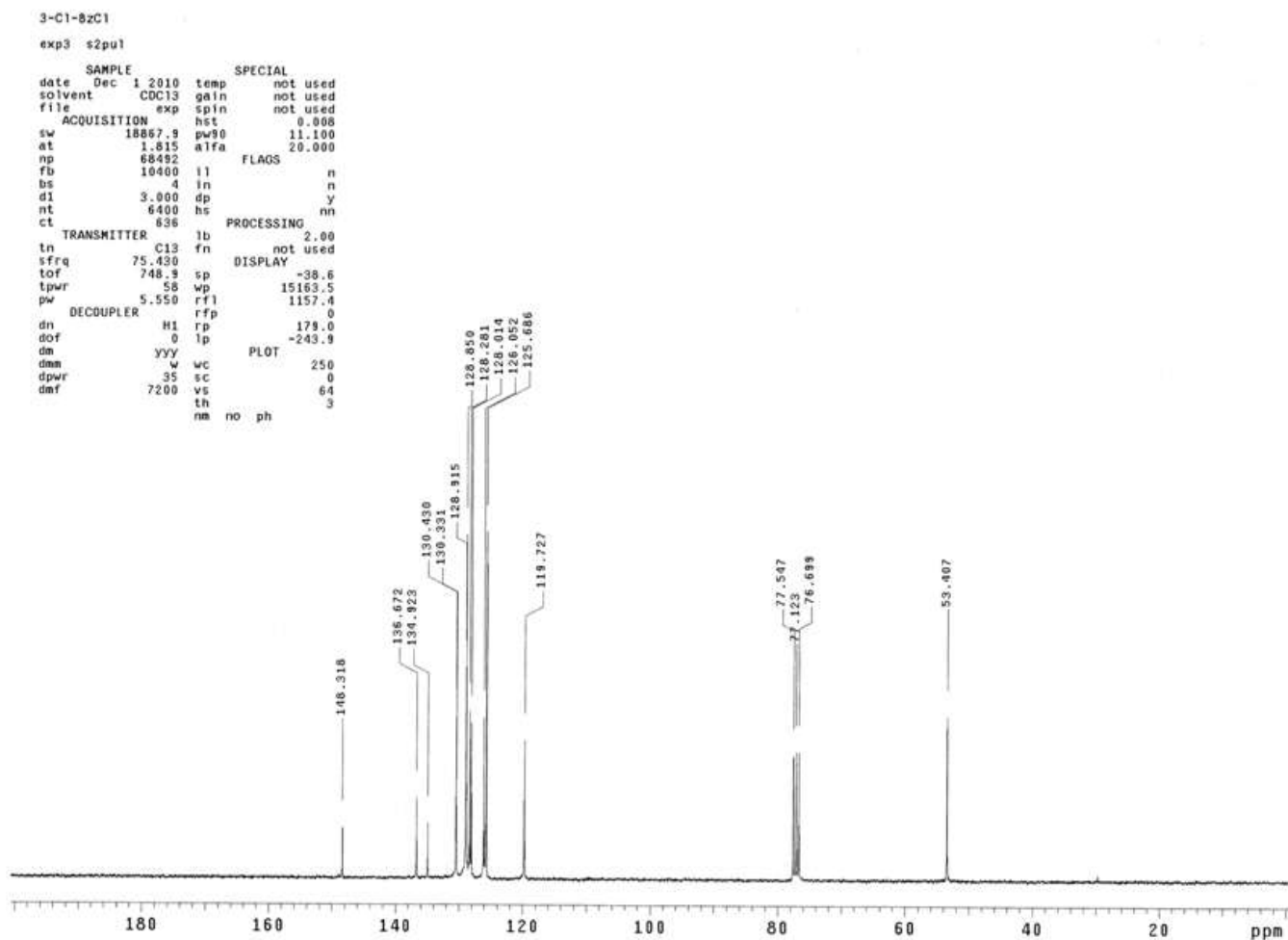
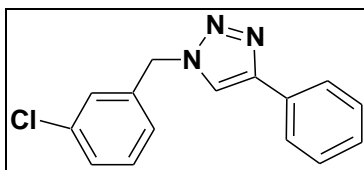


Table 2, Entry 5:

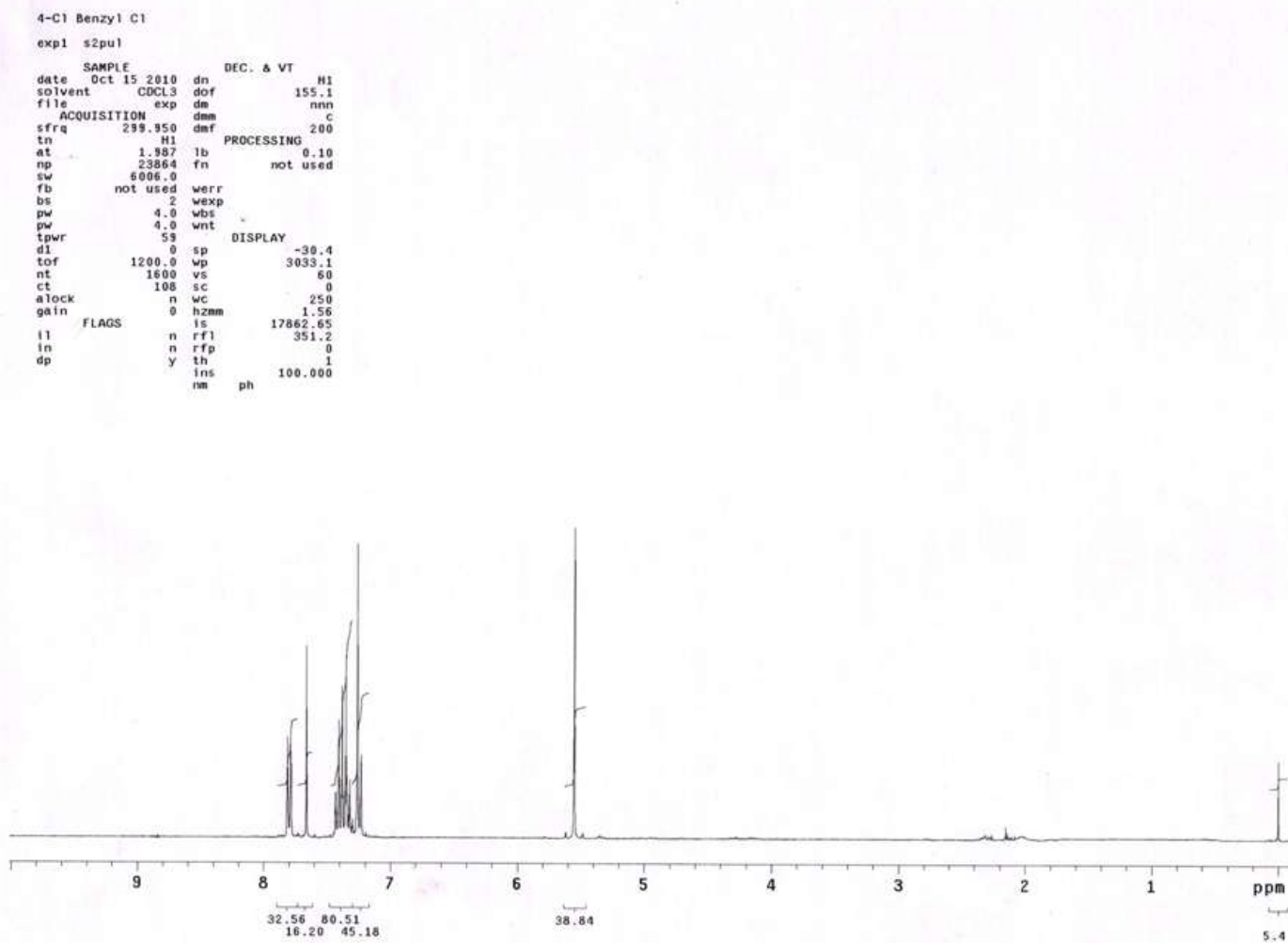
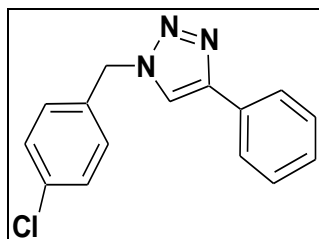
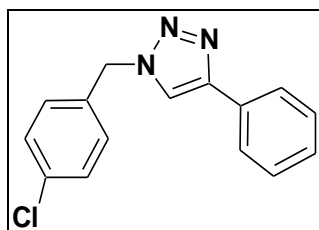


Table 2, Entry 5:



```
4-Cl Benzyl C1
exp3 s2pu1
SAMPLE          SPECIAL
date Oct 15 2010 temp not used
solvent CDCl3 gain not used
file exp spin not used
ACQUISITION    hst 0.008
sw 25000.0 pw90 9.500
at 1.280 alfa 20.000
np 64000
fb 13800 ll
bs 4 ln
d1 3.000 dp
nt 12000 hs
ct 164
TRANSMITTER    Tb 2.00
tn C13 fn not used
sfrq 75.430
tof 748.9 sp
tpwr 59 wp 16687.8
pw 6.000 rfl 10036.5
DECOUPLER      rfp 5815.0
dn H1 rp -144.3
dof 0 lp -337.9
dm yyw
dma w wc 250
dpwr 39 sc 0
dmf 10900 vs 37
ai th 2
al ph
```

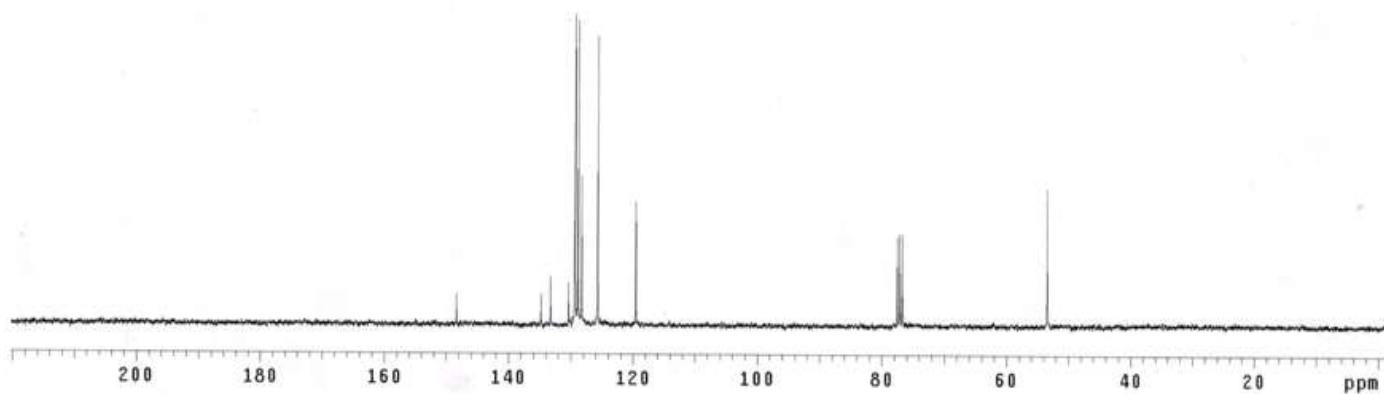


Table 2, Entry 6:

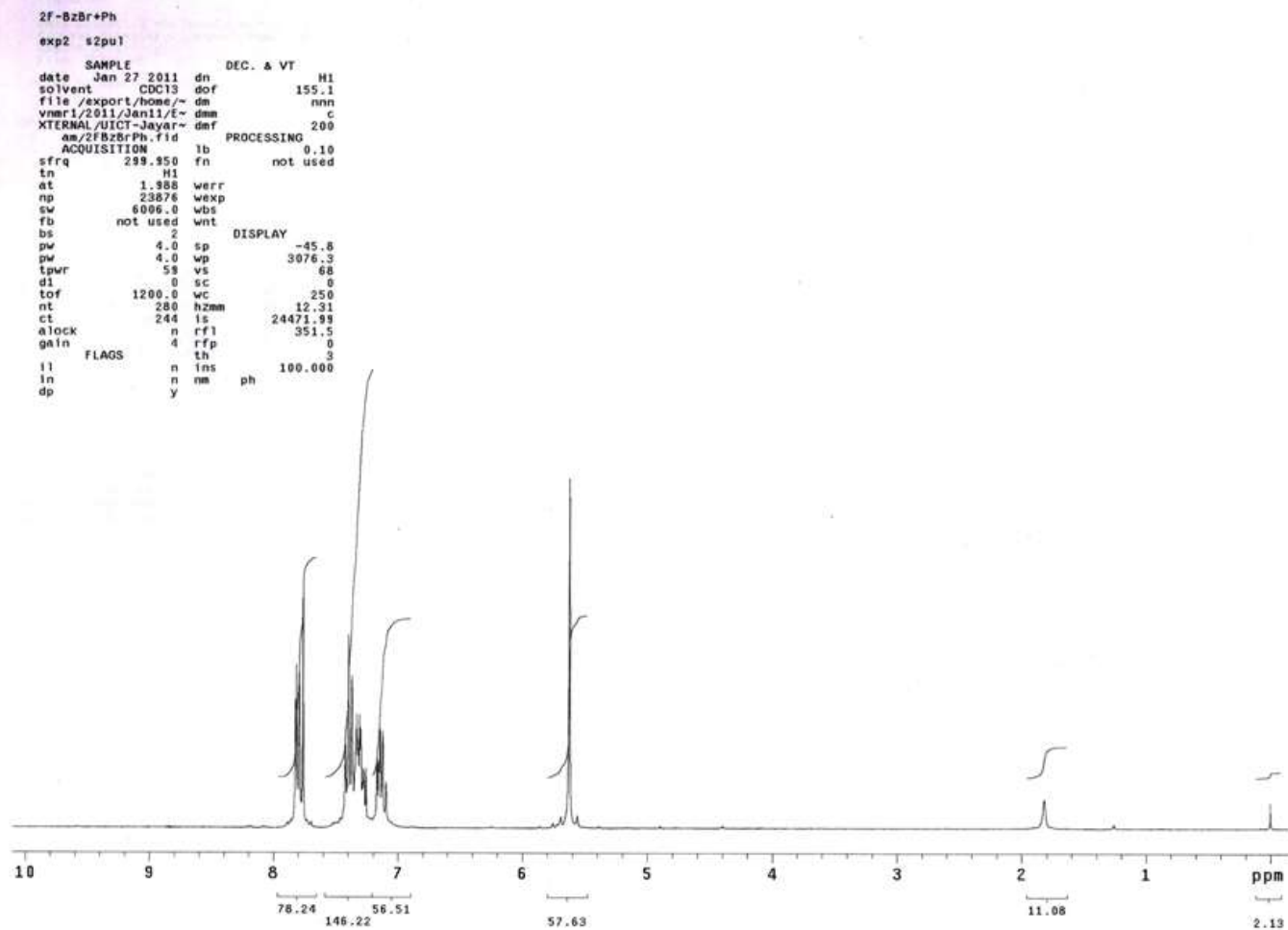
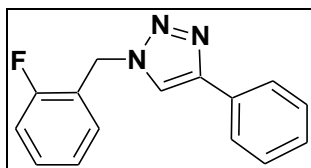
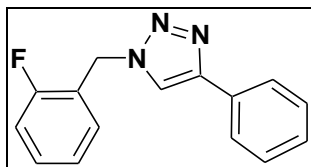


Table 2, Entry 6:



2F-BzBr+Ph

expl1 s2pu1

SAMPLE		SPECIAL	
date	Jan 25 2011	temp	not used
solvent	CDCl3	gain	not used
file	/export/home/~	spin	20
nmr1	/2011/Jan11/f~	hst	0.008
XTERNAL	/UIC-T-Jayar~	pw30	9.500
an/2FBzBrPh-13C.f1~	alfa	20.000	
	d	FLAGS	
ACQUISITION	il	n	
sw	25000.0	in	n
at	1.280	dp	y
np	64000	hs	nn
fb	13800	PROCESSING	
bs	4	lb	4.00
d1	2.000	fn	not used
nt	3200	DISPLAY	
ct	304	sp	-39.0
TRANSMITTER		wp	15205.4
tn	C13	rf1	10039.5
sfrq	75.430	rpf	5815.0
tof	748.9	rp	-136.8
tpwr	59	lp	-369.0
pw	6.000	PLOT	
DECOUPLER	wc	250	
dn	H1	sc	0
dof	0	vs	153
dm	yyy	th	3
dsm	w	al	ph
dpwr	39		
dmf	10900		

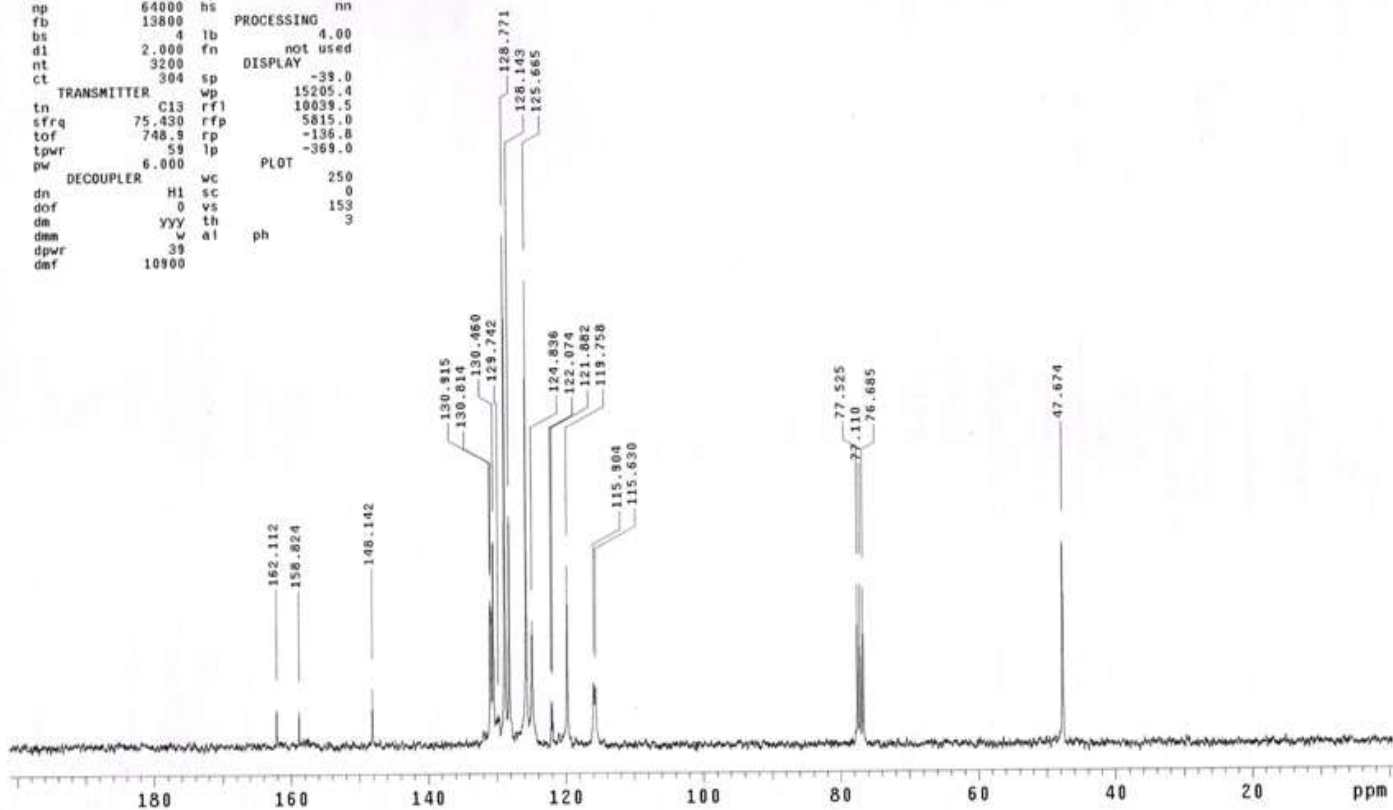


Table 2, Entry 7:

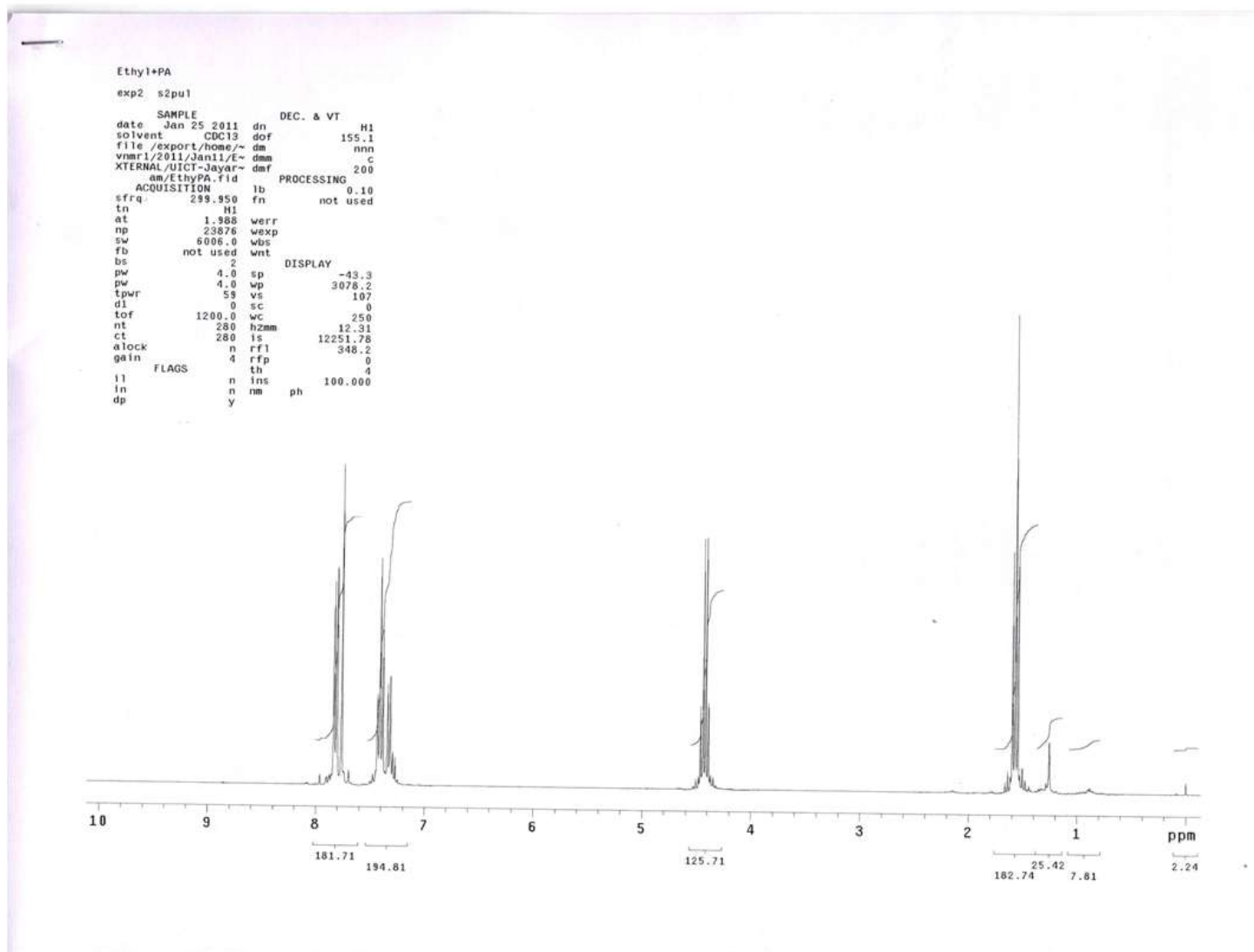
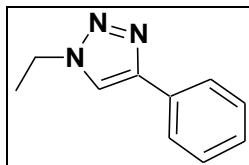
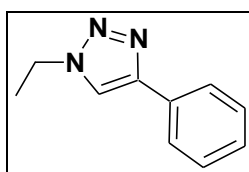


Table 2, Entry 7:



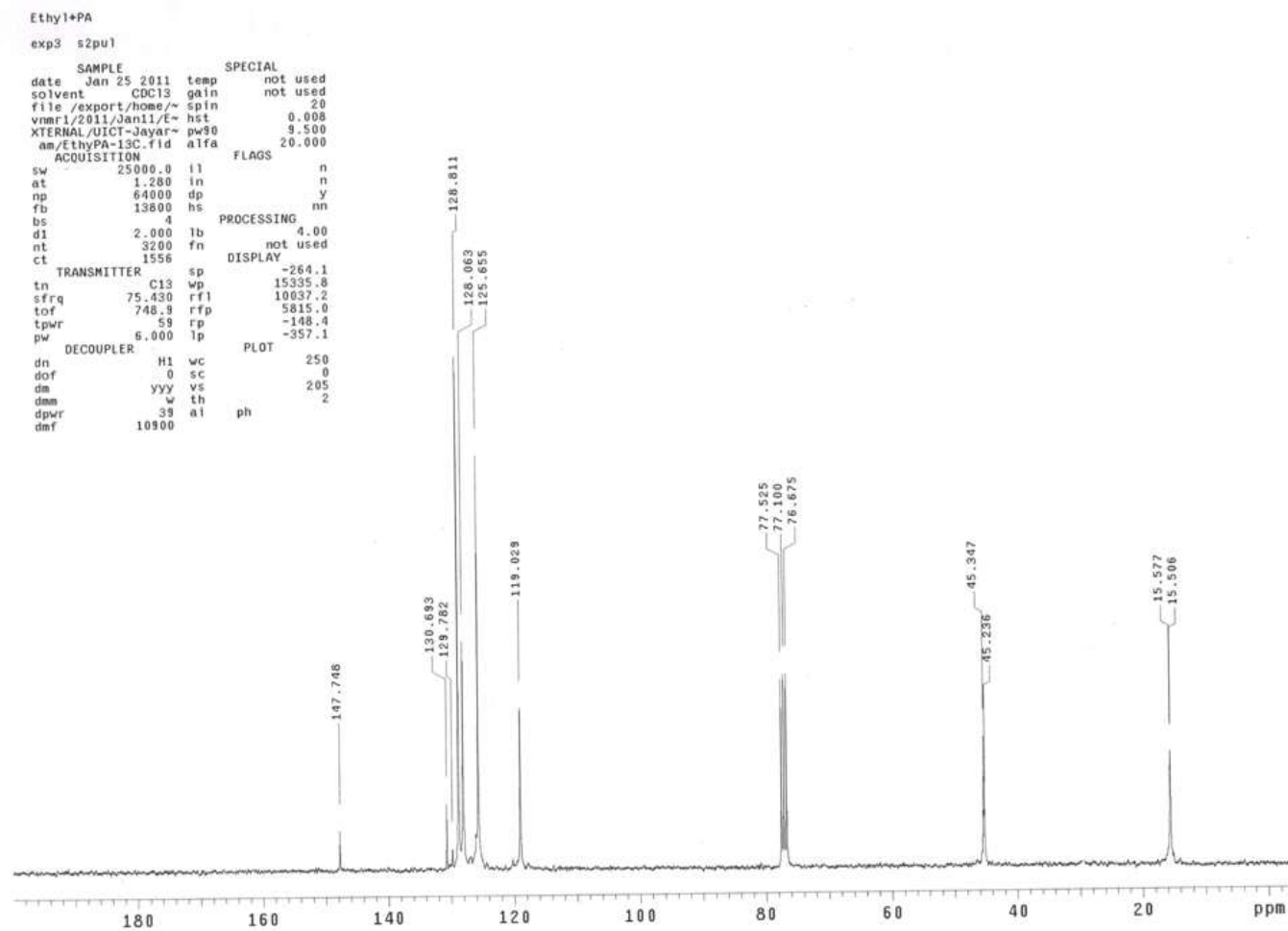
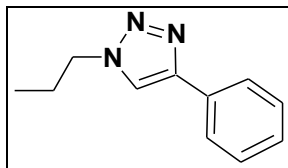


Table 2, Entry 8:



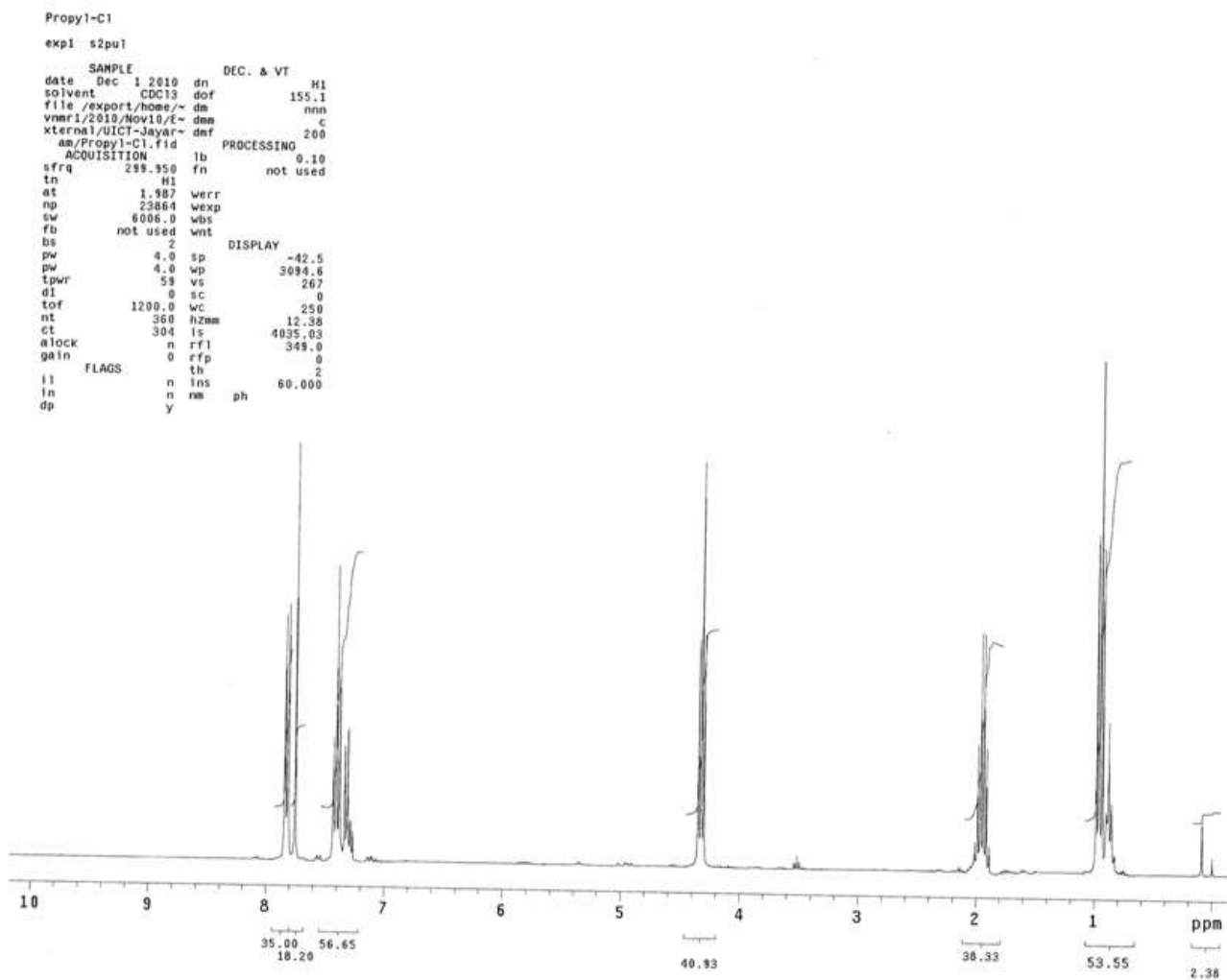
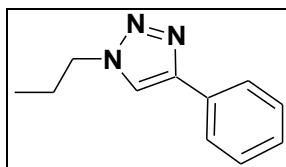


Table 2, Entry 8:



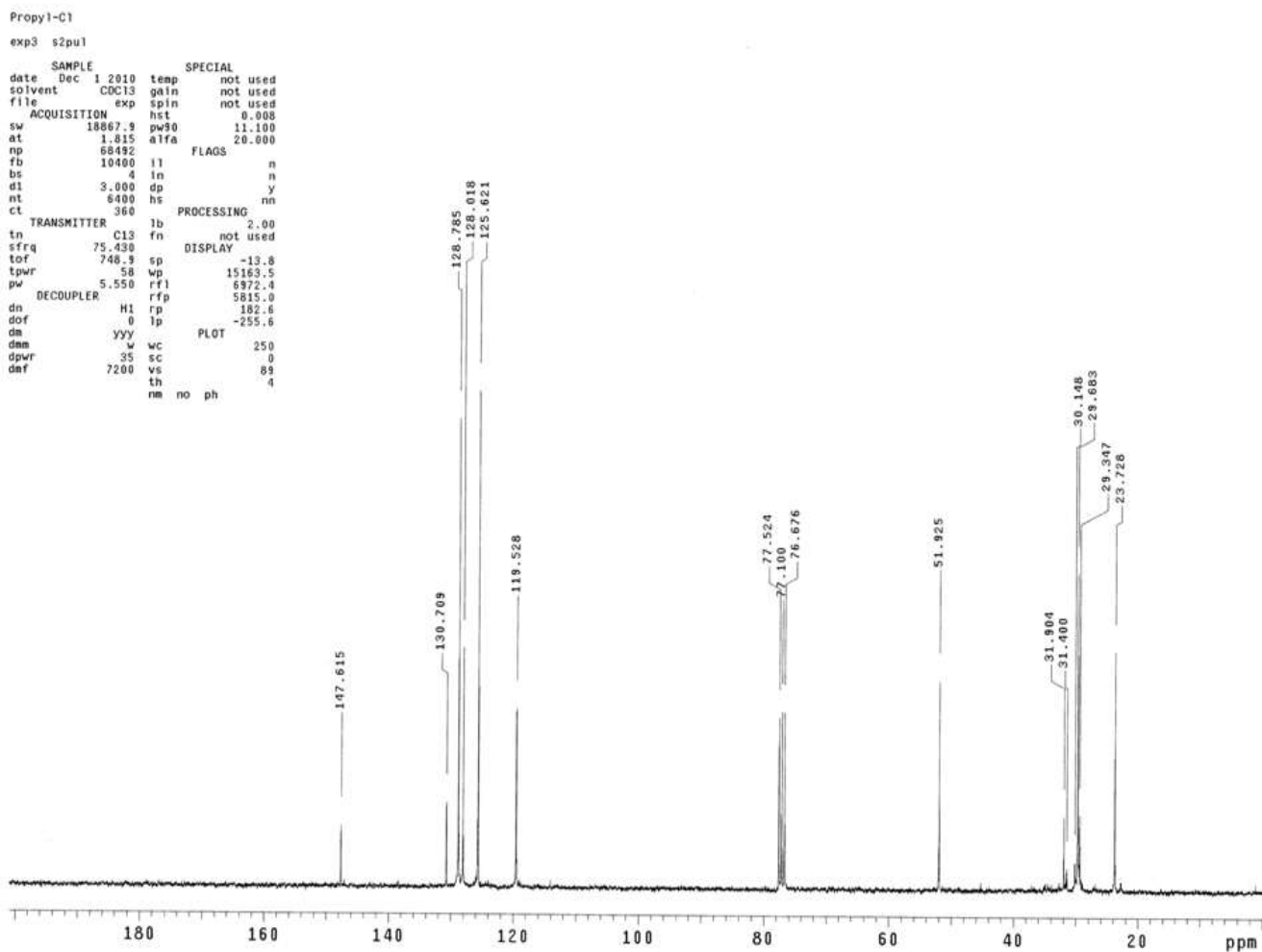
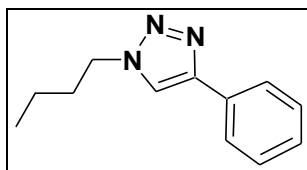


Table 2, Entry 9:



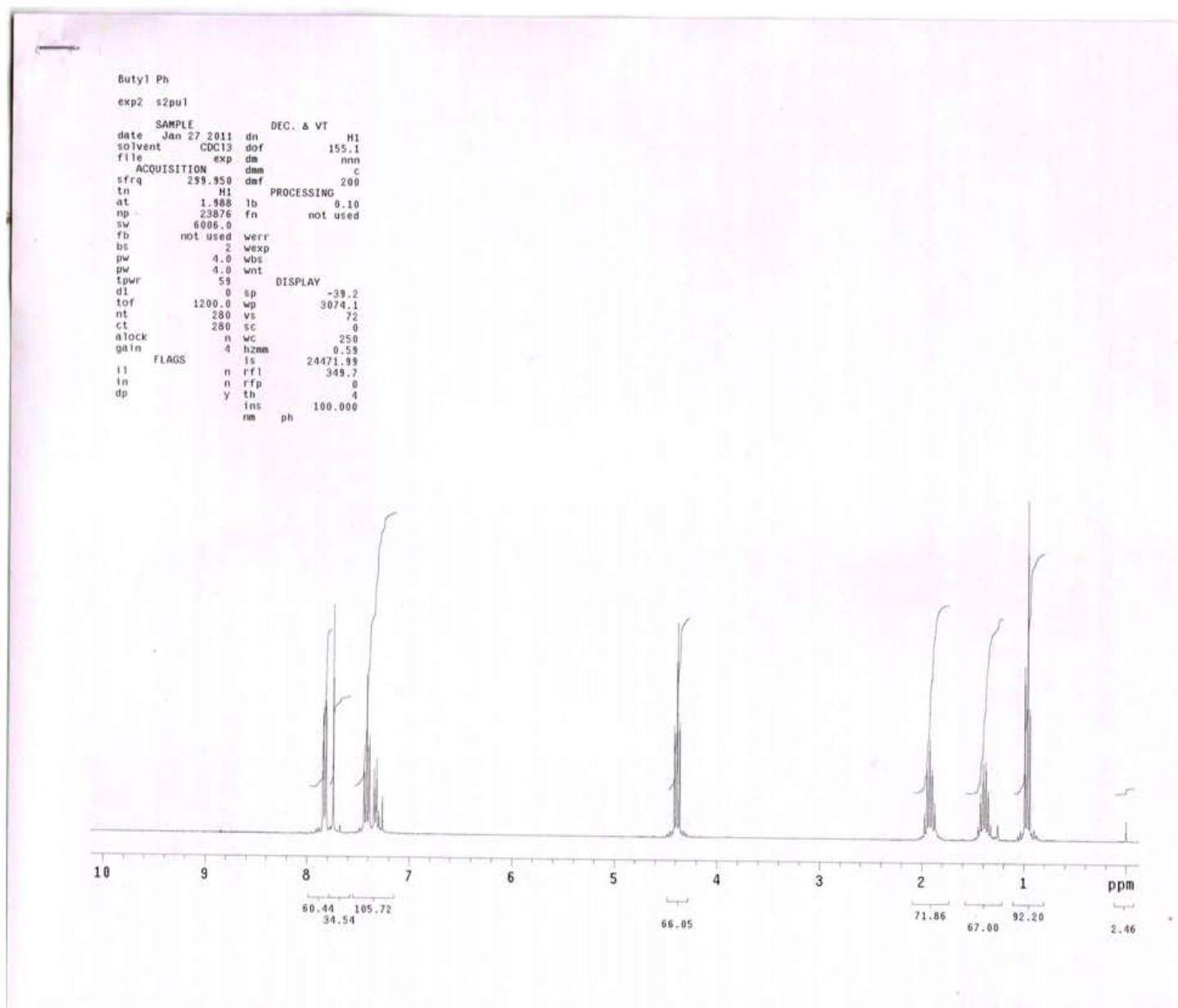
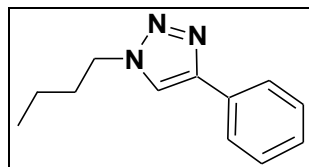


Table 2, Entry 9:



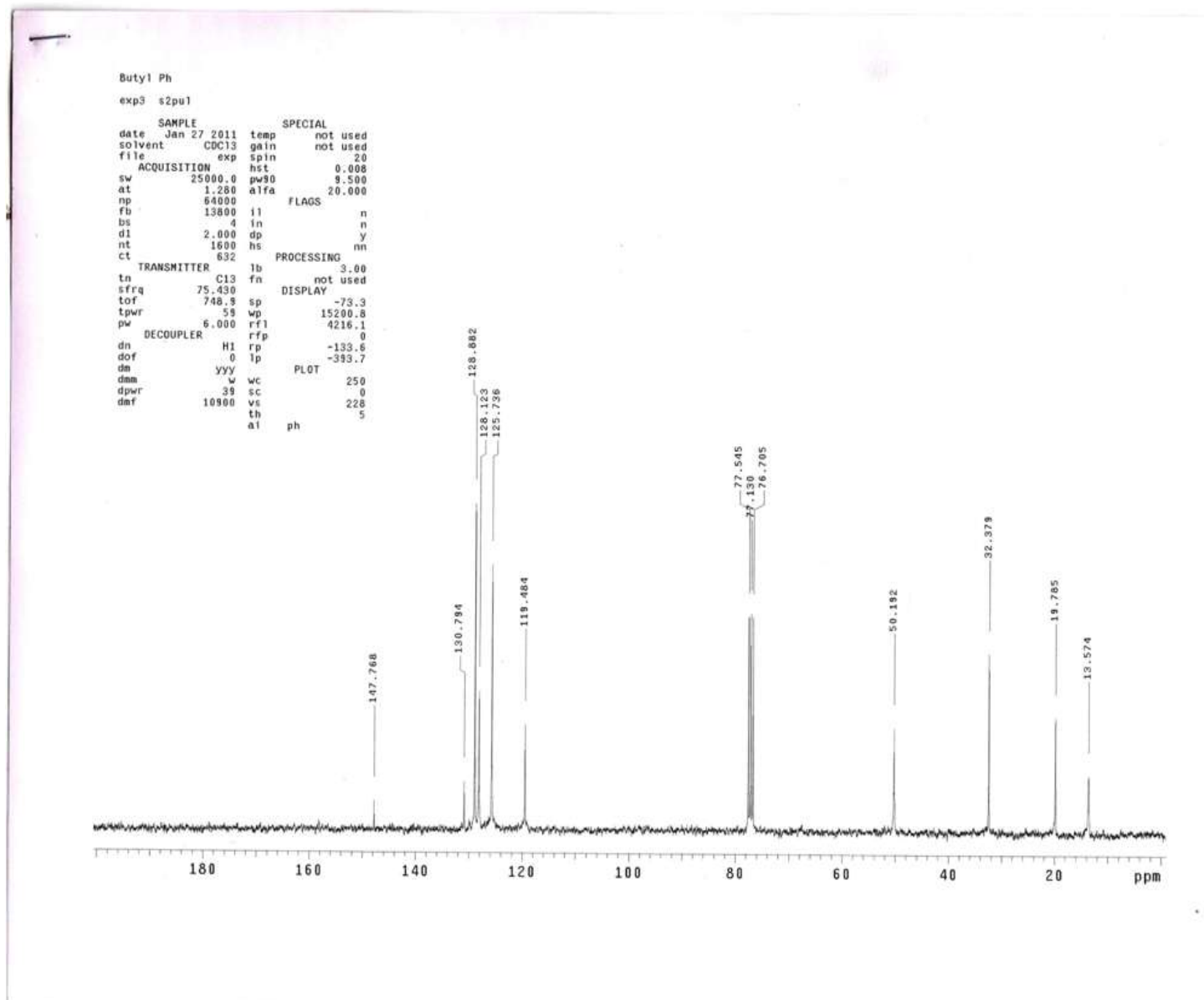
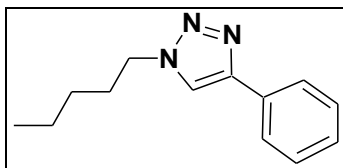


Table 2, Entry 11:



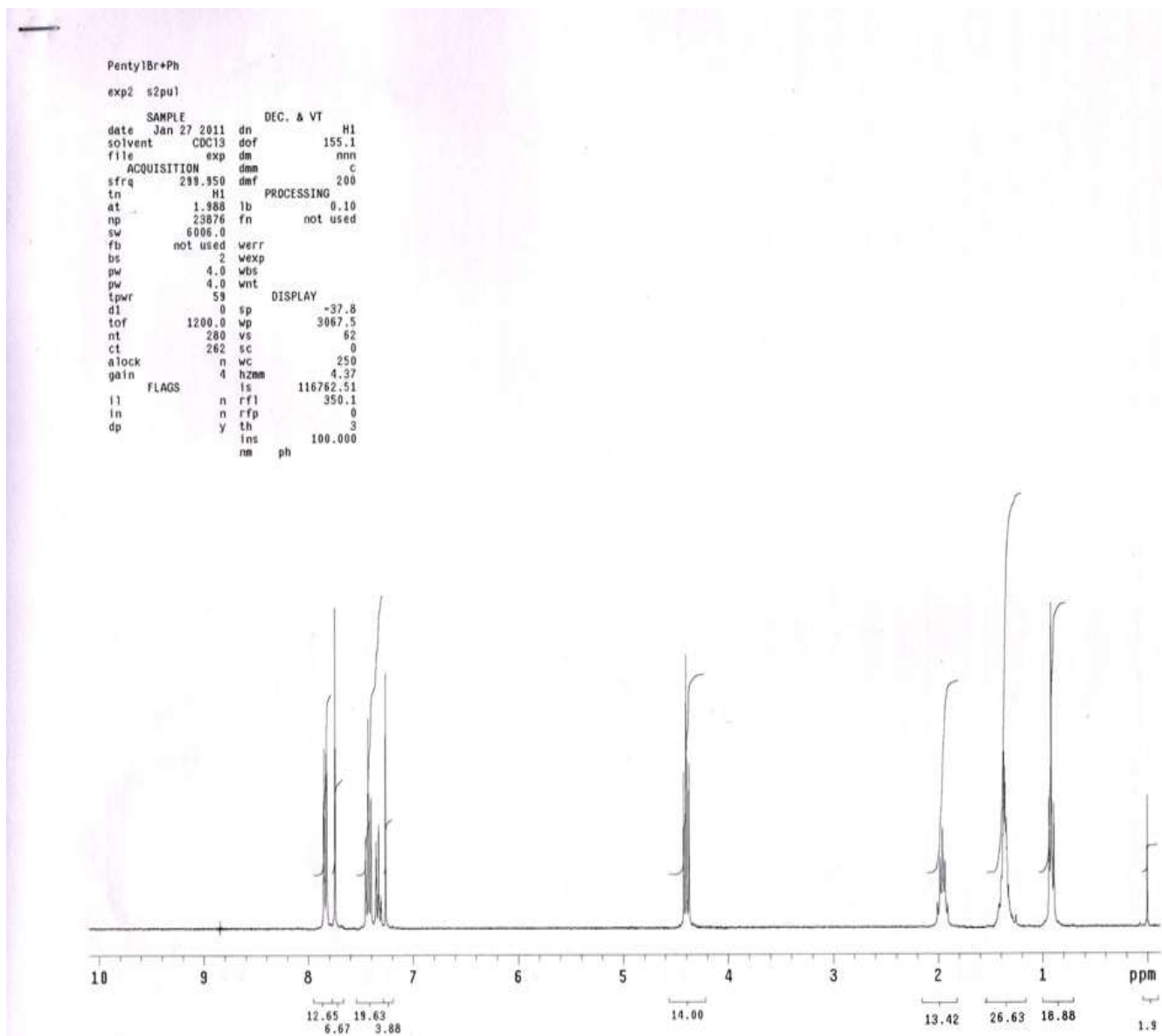
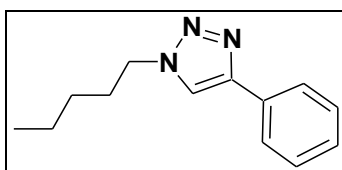


Table 2, Entry 11:



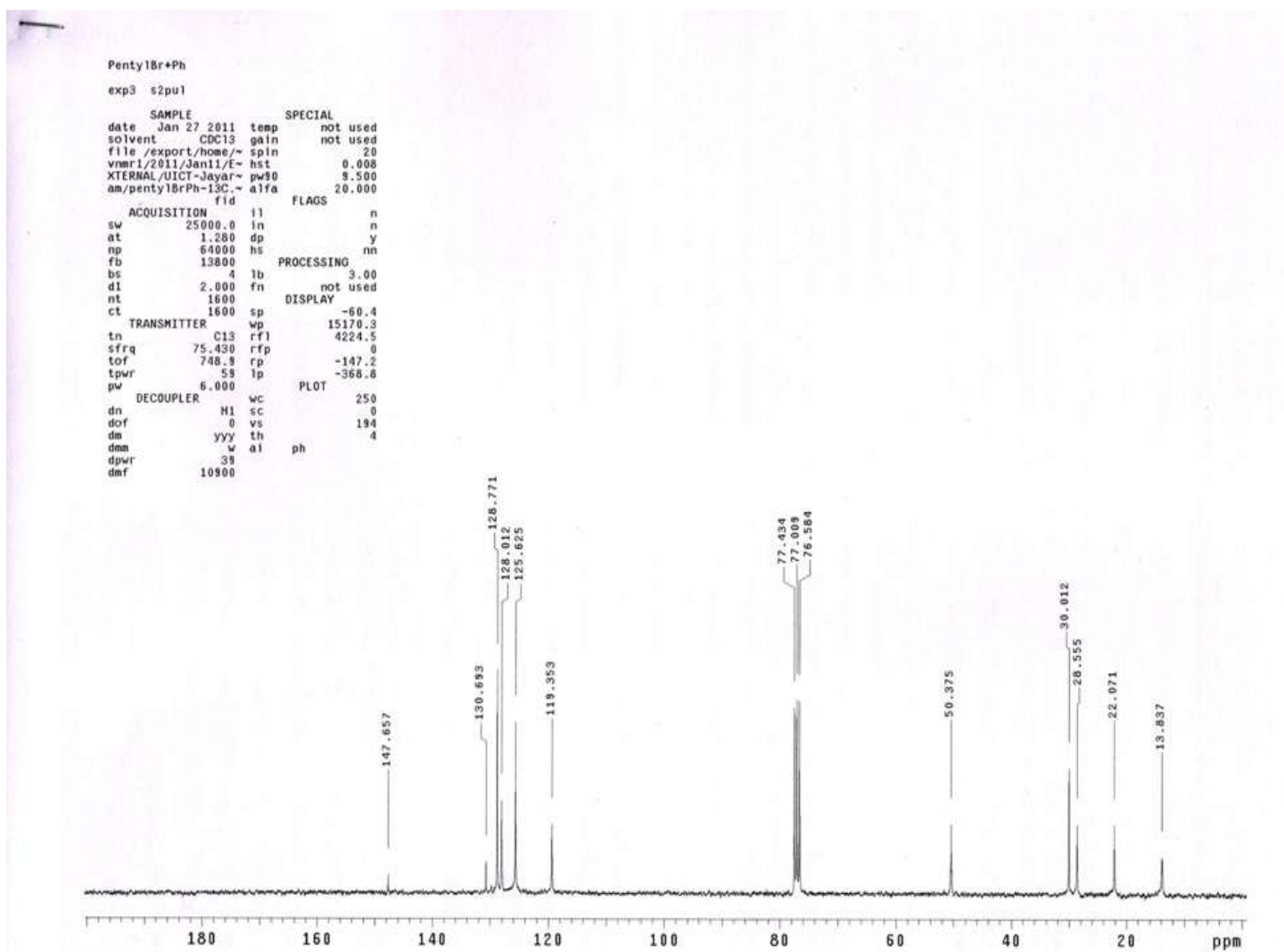
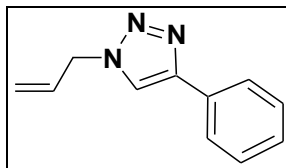


Table 2, Entry 12:



```
Allyl Cl
expl s2pu1
SAMPLE
date Nov 19 2010 dn DEC. & VT H1
solvent CDCl3 dof 155.1
file /export/home/~ dm nnn
vnmr1/2010/Nov19/E~ dnm c
xternal/UCT-Jayar~ dmf 200
am/AllylCl1.fid
ACQUISITION lb PROCESSING
sfrq 299.950 fn not used
tn H1
at 1.987 werr
np 23864 wexp
sw 6006.0 wbs
fb not used wnt
bs 2
pw 4.0 sp DISPLAY -62.7
pw 4.0 wp 3005.8
tpwr 59 vs 104
dl 0 sc 0
tof 1200.0 wc 250
nt 1600 hzmm 12.34
ct 90 ls 4608.41
alock n rfl 347.9
gain 0 rfp 0
FLAGS n th 1
il n lns ph 60.000
in n nm
dp y
```

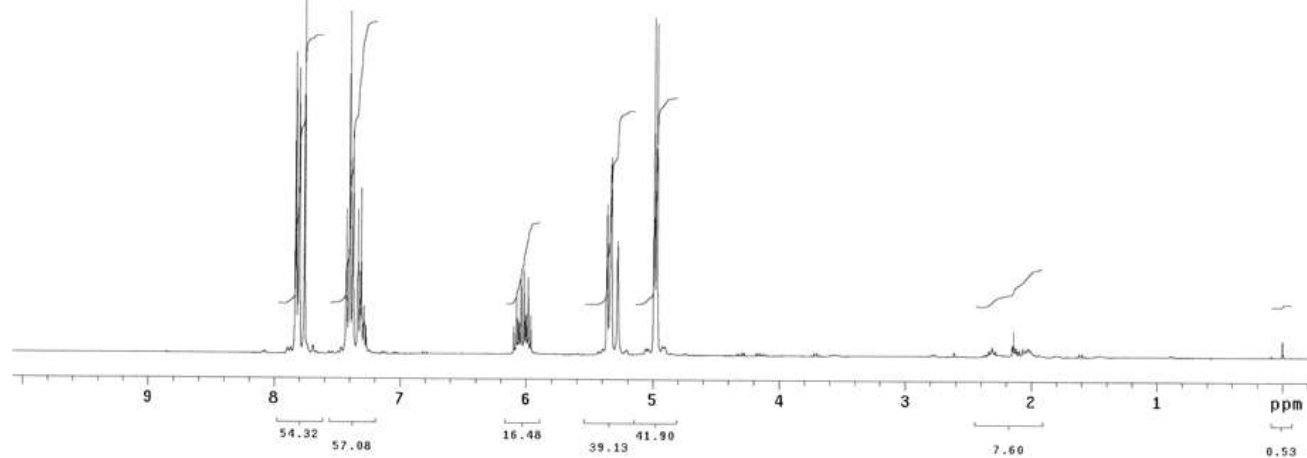
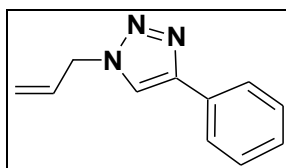


Table 2, Entry 12:



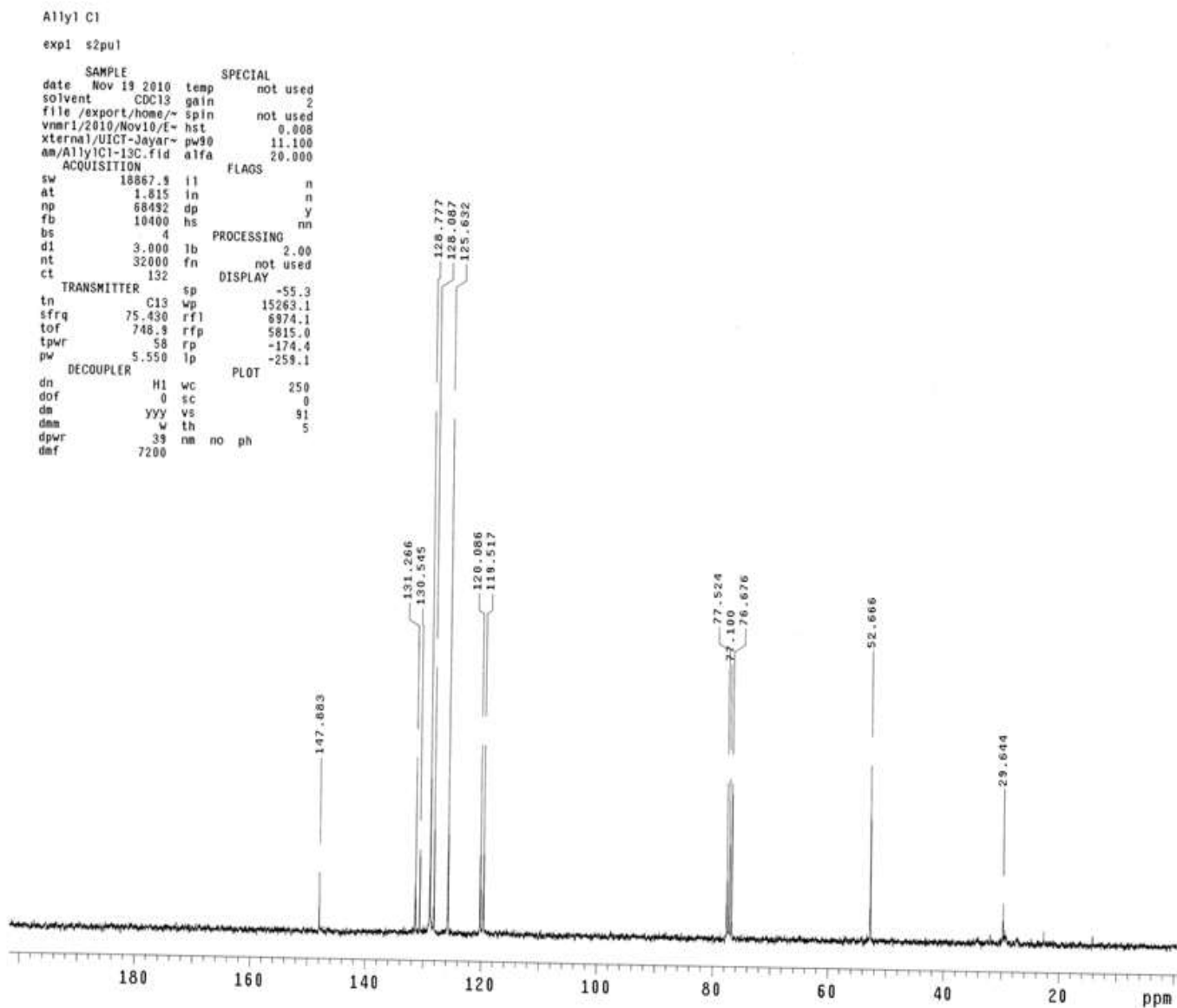
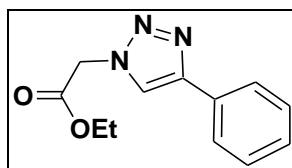


Table 2, Entry 14:



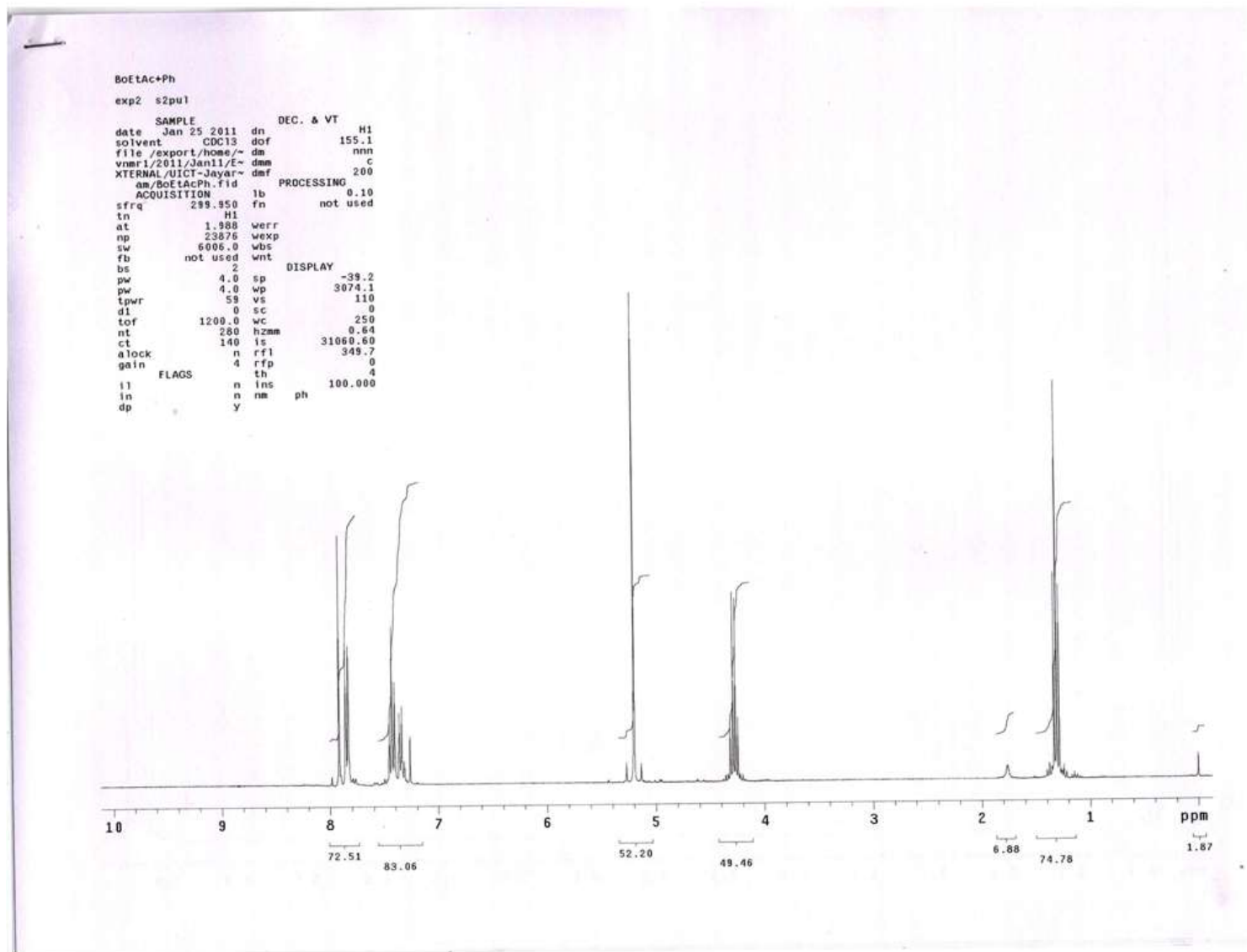
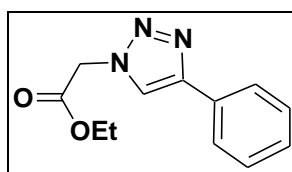


Table 2, Entry 14:



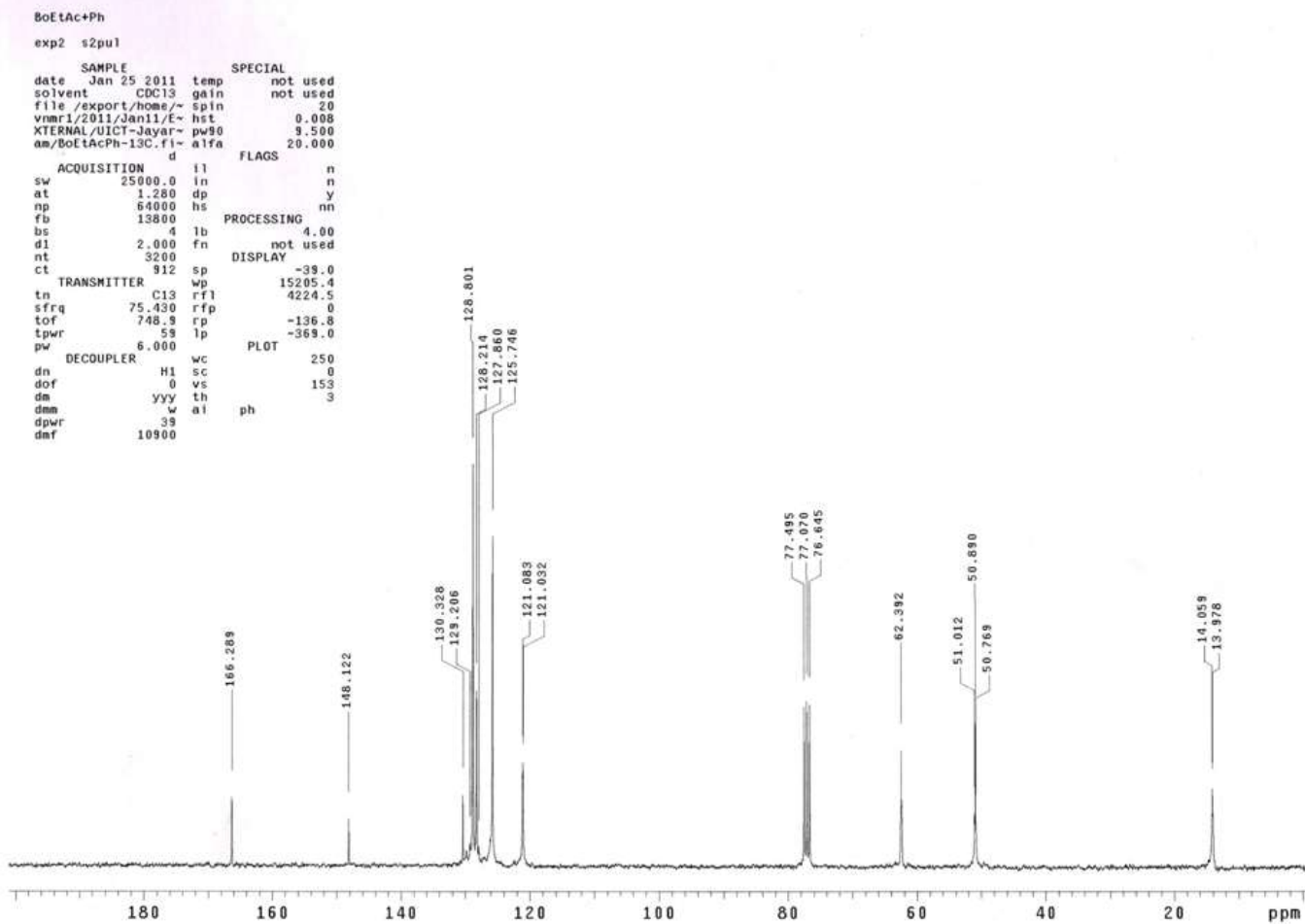
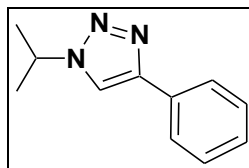


Table 2, Entry 15:



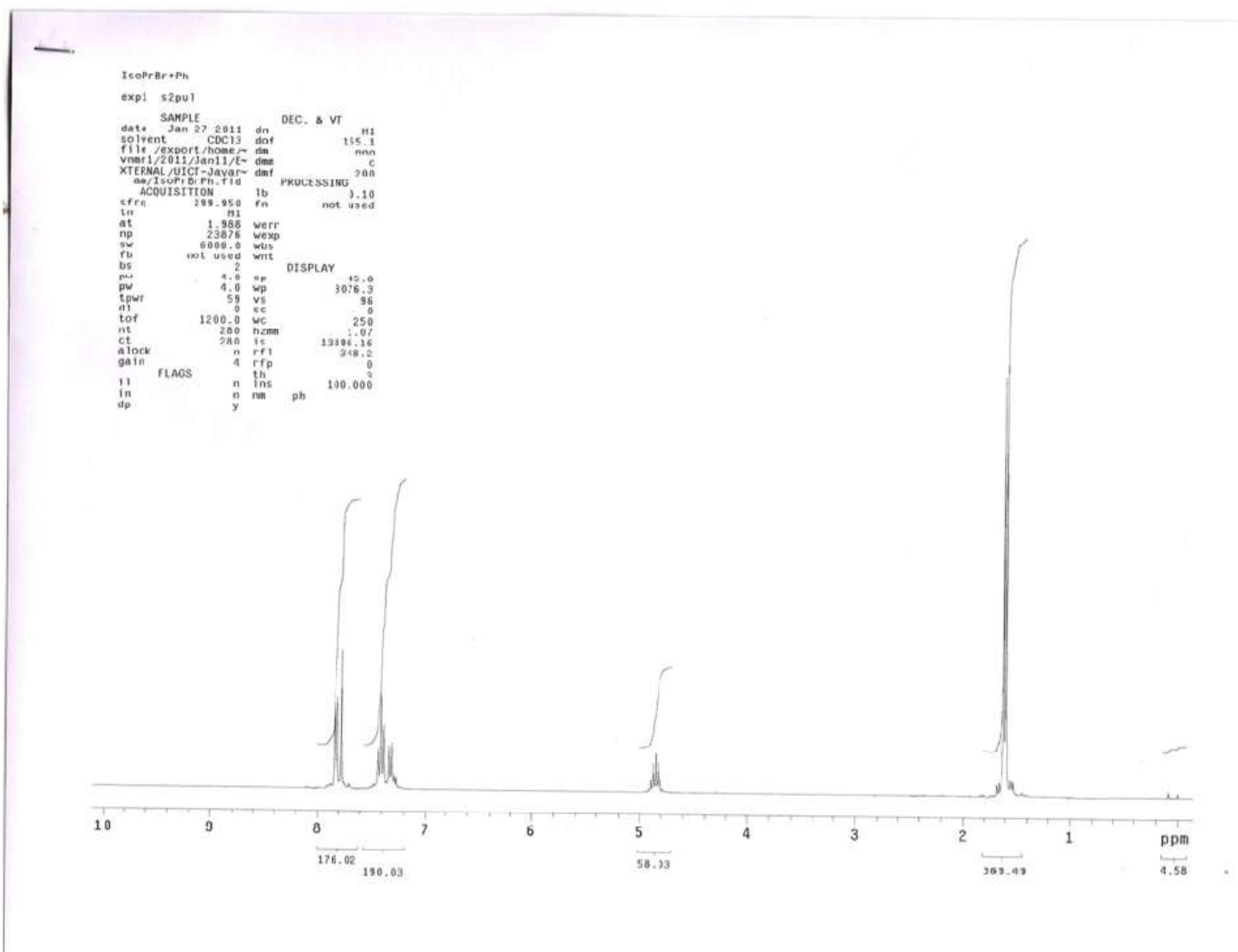
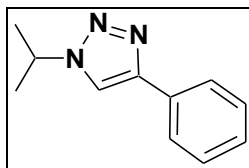


Table 2, Entry 15:



IsoPrBr+Ph
exp3 s2pu1

SAMPLE		SPECIAL	
date	Jan 27 2011	temp	not used
solvent	CDCl3	gain	not used
file		spin	20
ACQUISITION			
exp	hst	0.008	
sw	25000.0	pw90	1.500
at	1.280	alfa	20.000
np	64000	FLAGS	
fb	13800	l1	n
bs	4	in	n
d1	2.000	dp	y
nt	1600	hc	nn
ct	668	PROCESSING	
TRANSMITTER		lb	3.00
tn	C13	fn	not used
sfrq	75.430	DISPLAY	
tof	748.8	sp	-60.4
tpwr	59	wp	15170.3
pw	6.000	rfl	4216.1
DECOUPLER		rpf	0
dn	H1	rp	-143.3
dof	0	lp	-374.0
dm	yyv	PLOT	
dma	w	wc	250
dpwr	39	sc	0
dmf	10900	vs	115
		th	4
		al	ph

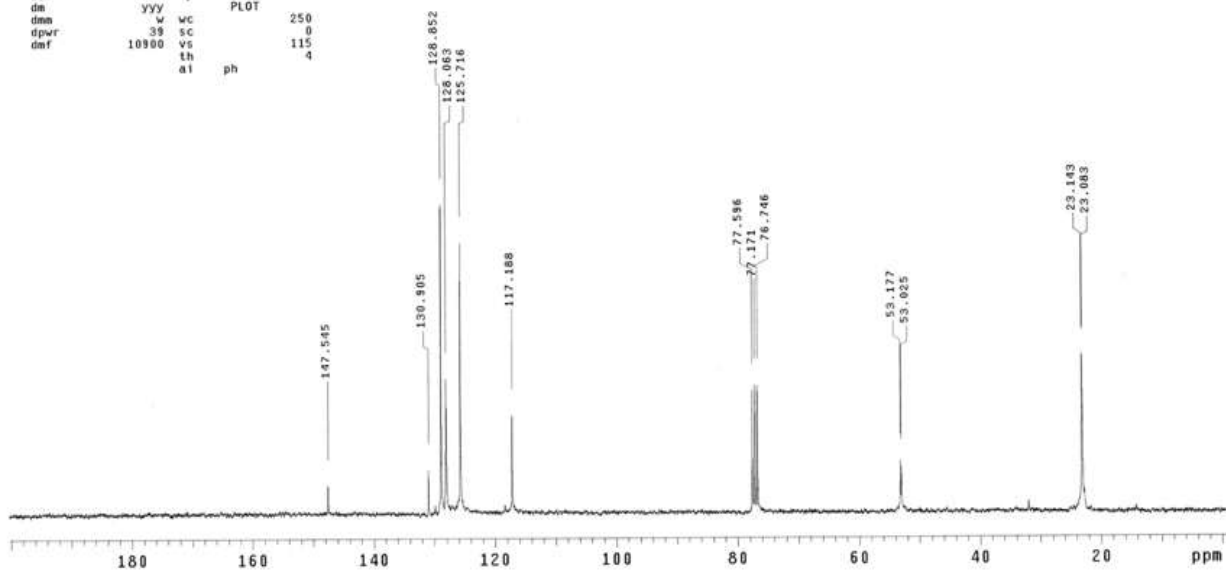
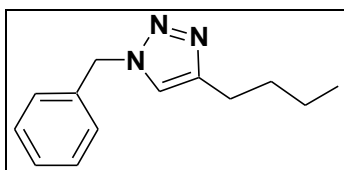


Table 2, Entry 16:



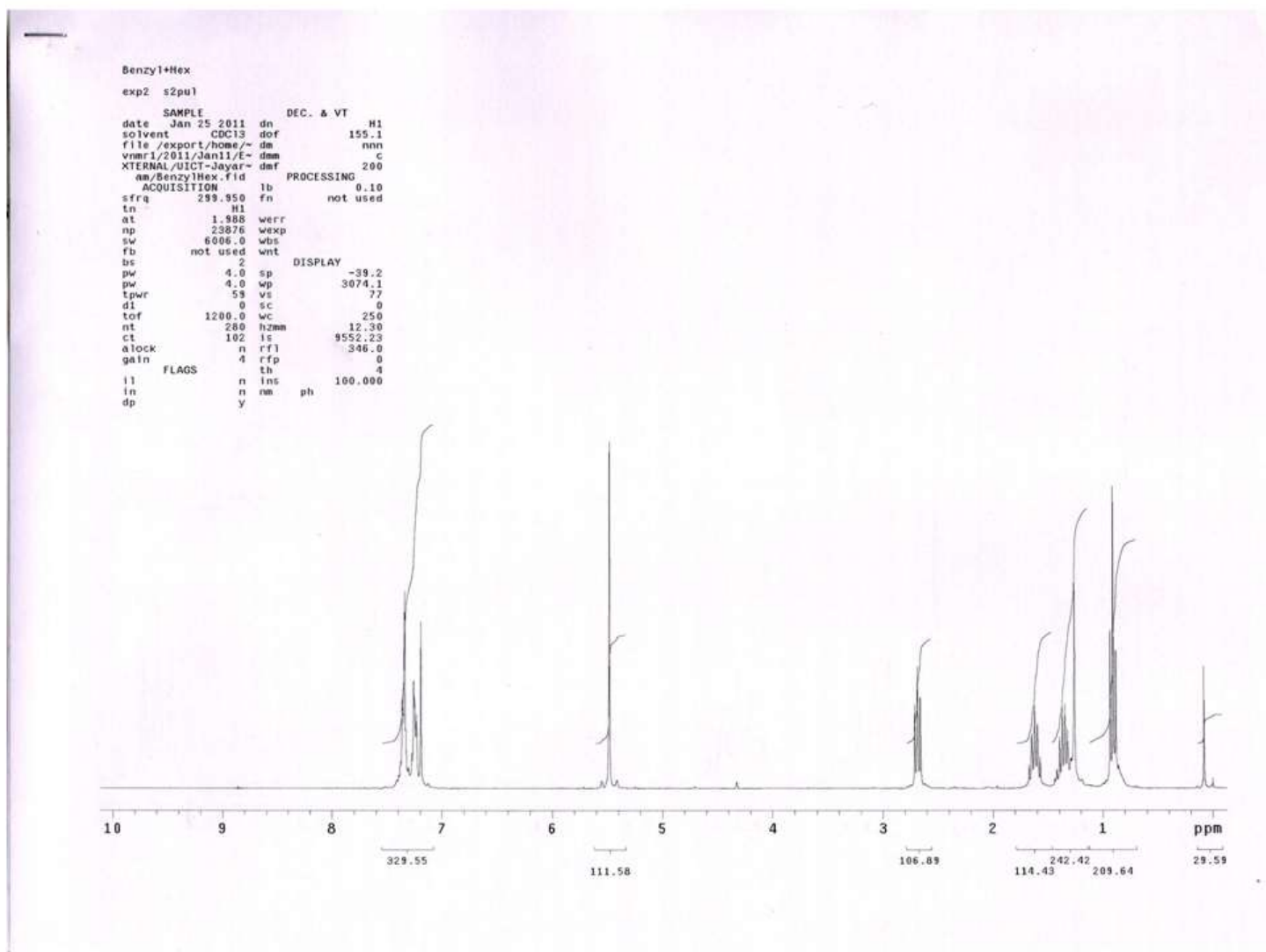
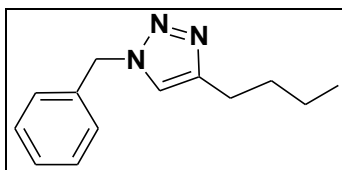


Table 2, Entry 16:



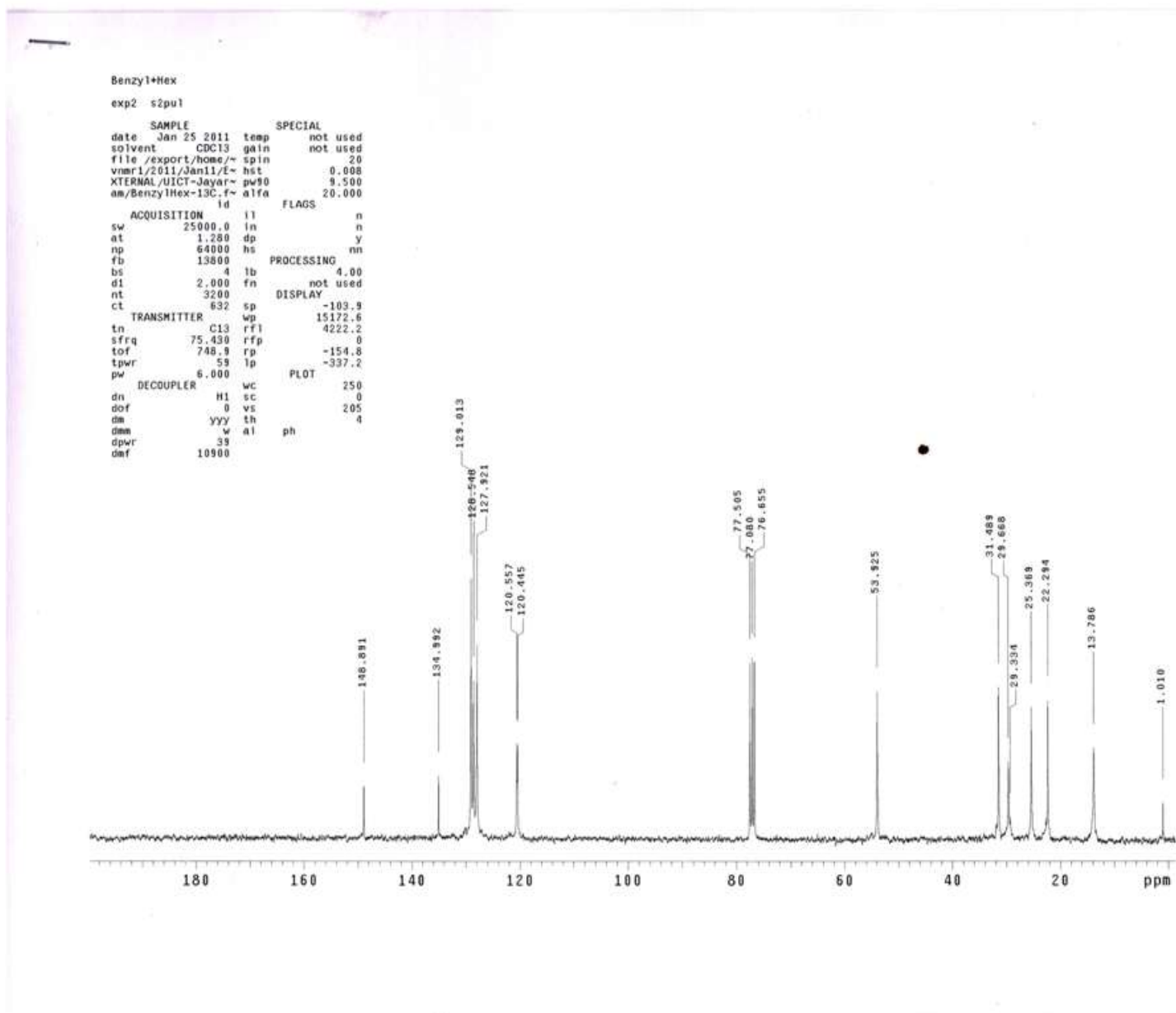
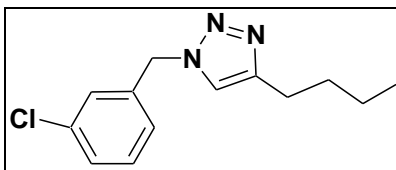


Table 2, Entry 19:



3C1+Hex

exp2 s2pu1

SAMPLE		DEC. & VT	
date	Jan 27 2011	dn	H1
solvent	CDCl3	dof	155.1
file	exp	dm	nnn
ACQUISITION			
sfrq	299.950	dmf	200
tn	H1	PROCESSING	
at	1.988	lb	0.10
np	23876	fn	not used
sw	6006.0		
fb	not used	werr	
bs	2	wexp	
pw	4.0	wbs	
pw	4.0	wnt	
tpwr	59	DISPLAY	
d1	0	sp	-45.8
tof	1200.0	wp	3076.3
nt	280	vs	109
ct	280	sc	0
atock	n	wc	250
gain	4	hzmm	3.99
FLAGS			
il	n	rf1	8571.46
in	n	rfp	337.6
dp	y	th	0
		ins	3
		nm	100.000
		ph	

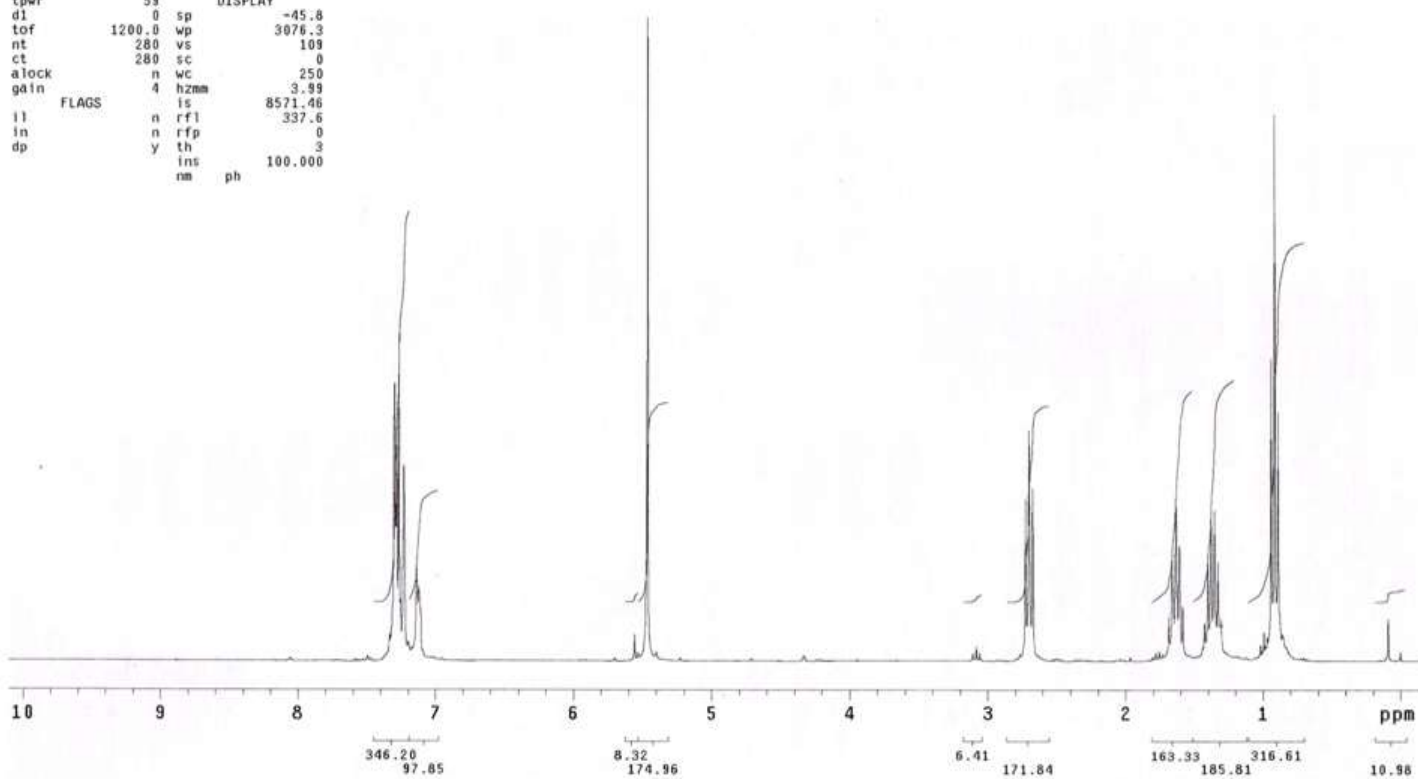
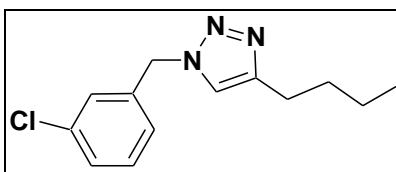


Table 2, Entry 19:



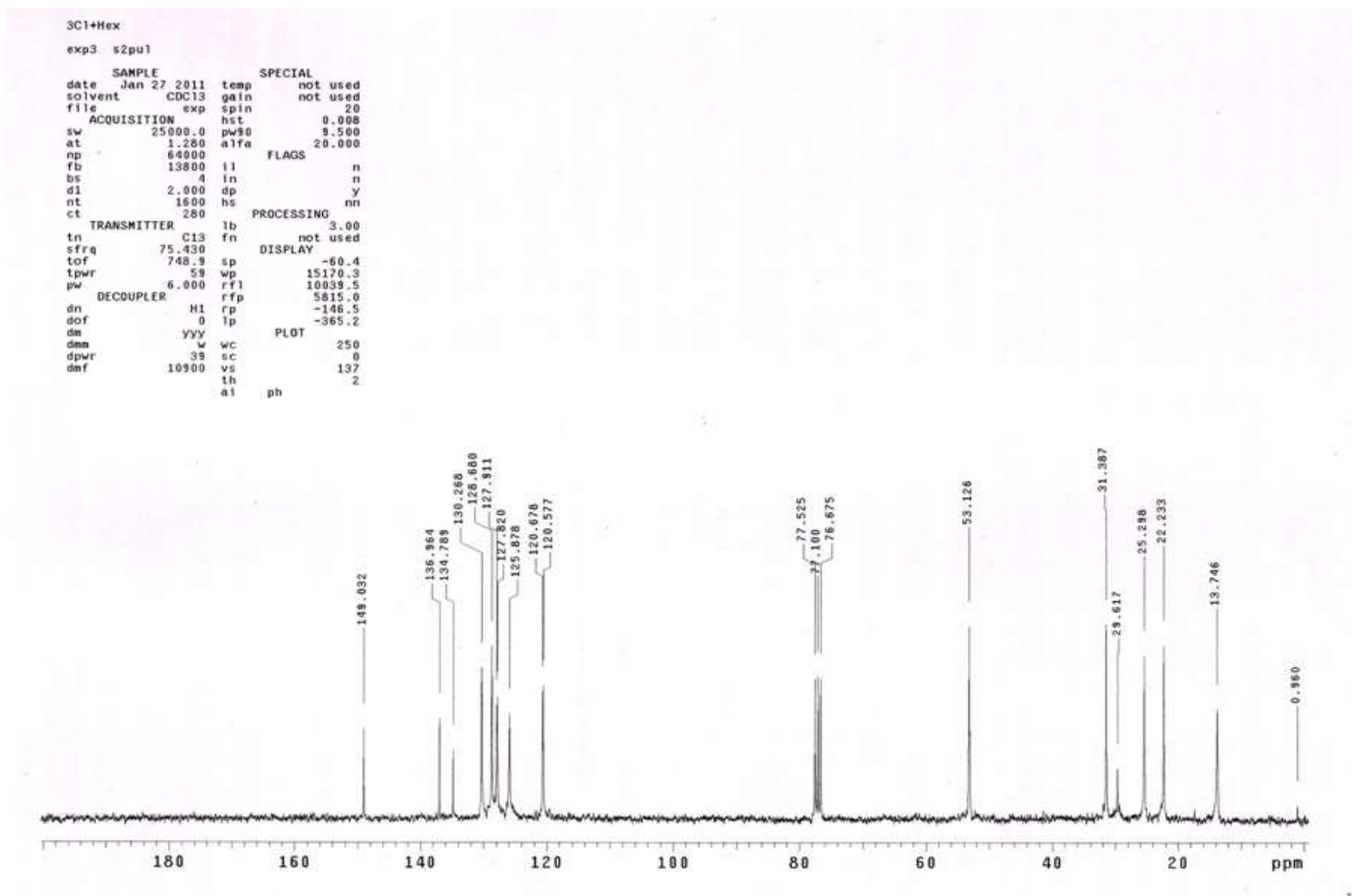
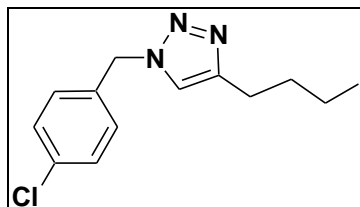


Table 2, Entry 20:



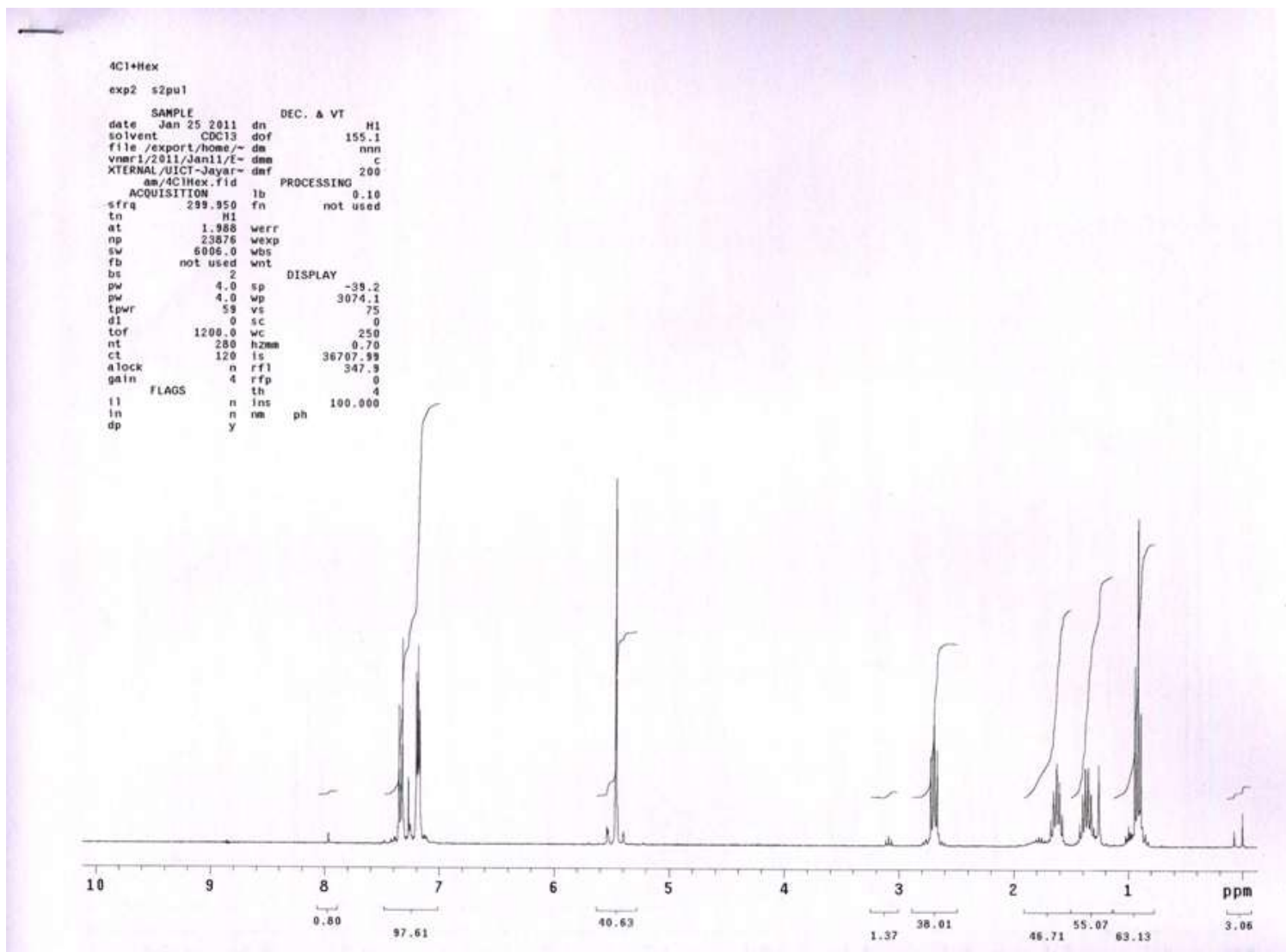
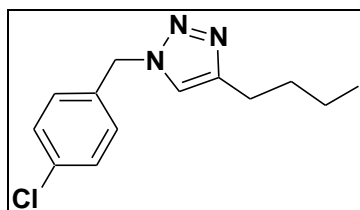


Table 2, Entry 20:



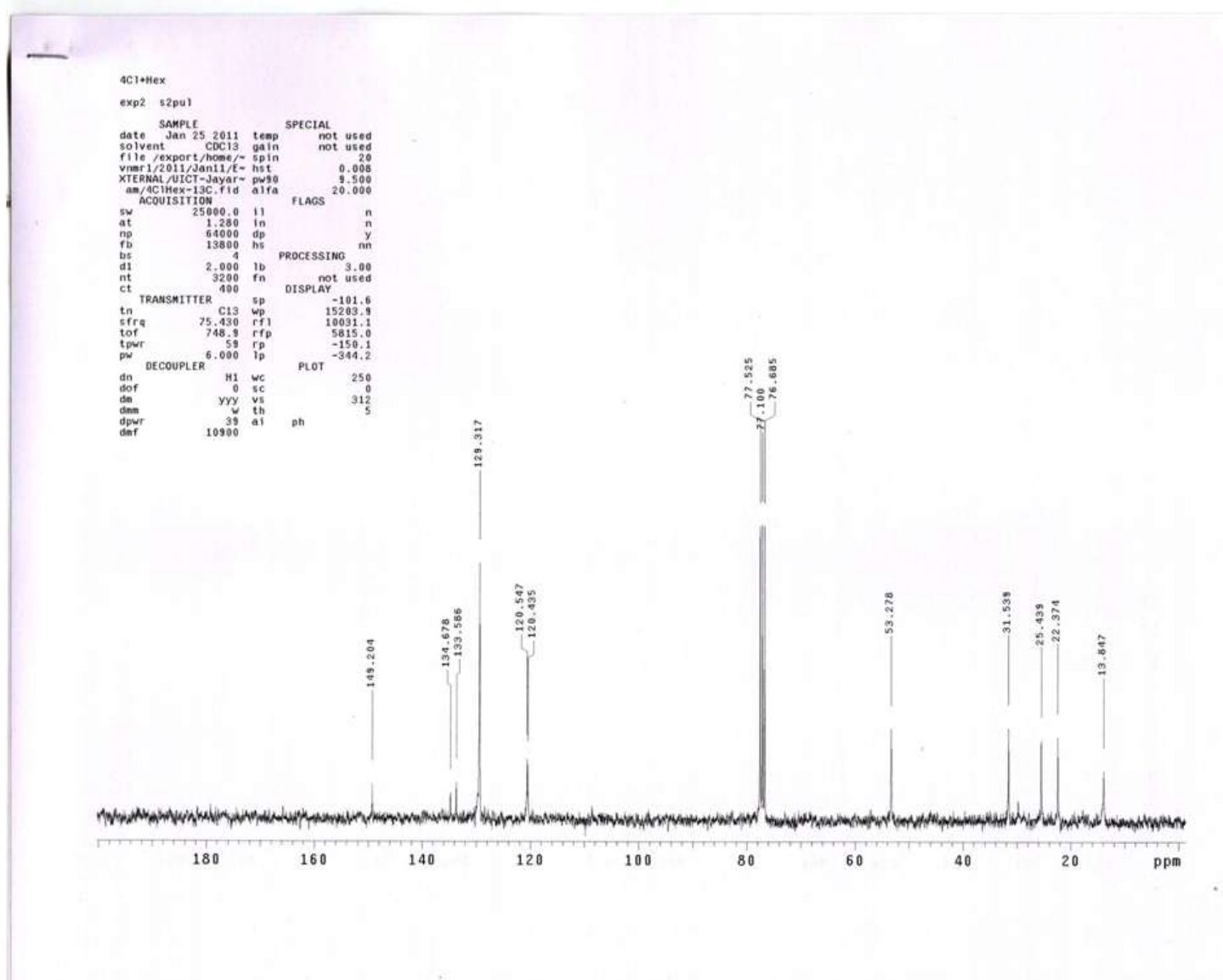
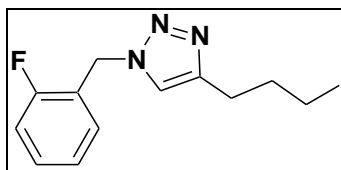


Table 2, Entry 21:



2F-BzBr+Hex

exp1 s2pul

```
SAMPLE          DEC. & VT
date  Jan 27 2011  dn
solvent  CDC13  dof      155.1
file  /export/home/~  dm      nnn
vnmr1/2011/Jan11/E~  dam      c
XTERNAL/UICT-Jayar~  dmf      200
am/2FbZBr-Hex.fid  PROCESSING
ACQUISITION      lb      0.10
sfrq      299.950  fn      not used
tn      H1
at      1.988  werr
np      23876  wexp
sw      6006.0  wbs
fb      not used  wnt
bs      2
pw      4.0  sp      -45.8
pw      4.0  wp      3076.3
tpwr     59  vs      59
d1      0  sc      0
tof     1200.0  wc      250
nt      280  hzmm     0.41
ct      106  is     14683.20
alock   n  rfl     346.0
gain    4  rfp      0
        FLAGS      th      3
ll      n  ins     100.000
in      n  nm
dp      y
```

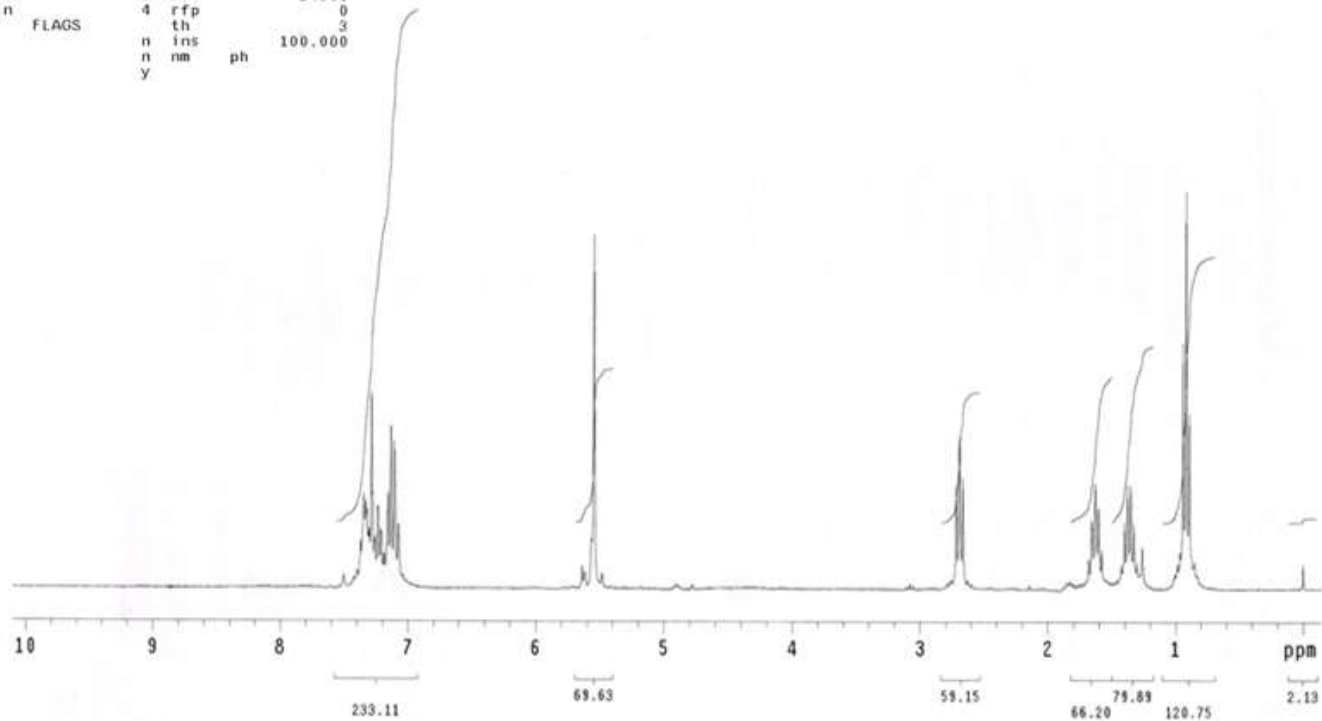


Table 2, Entry 21:

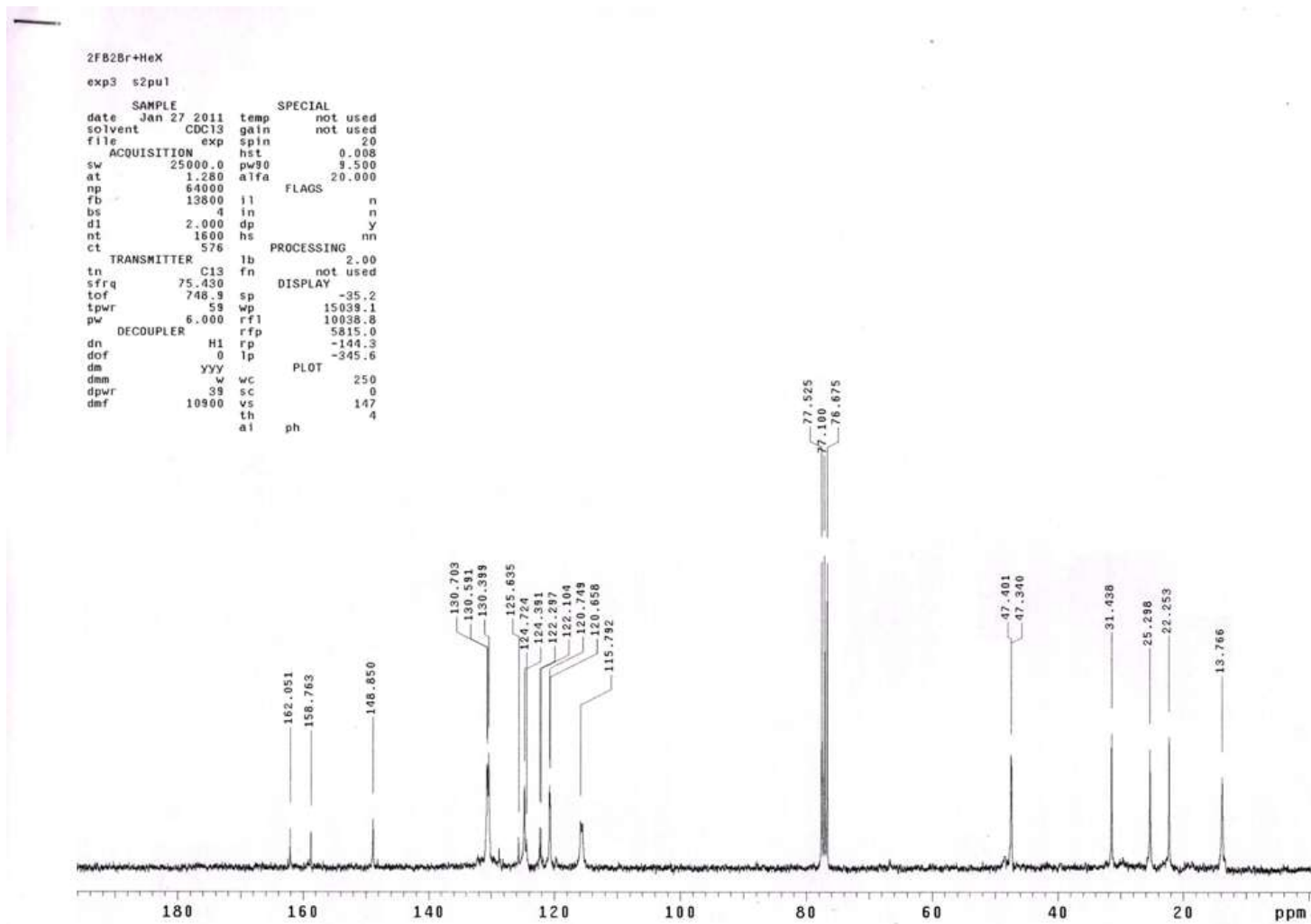
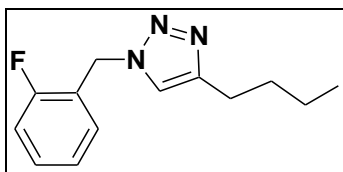
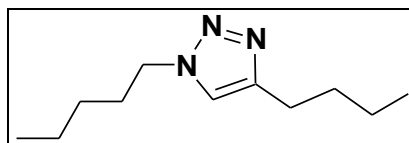


Table 2, Entry 22:



```
C5+Hex
exp2 s2pu1
SAMPLE
date Jan 25 2011 dn
solvent CDC13 dof 155.1
file /export/home/~ dm nnn
vnmr1/2011/Jan11/E~ dma c
XTERNAL/UICT-Jayar~ dmf 200
am/C5Hex.fid
ACQUISITION lb 0.10
sfrq 299.950 fn not used
tn H1
at 1.988 verr
np 23876 wexp
sw 6006.0 wbs
fb not used wnt
bs 2
pw 4.0 sp DISPLAY -69.3
pw 4.0 wp 3089.9
tpwr 59 vs 75
d1 0 sc 0
tof 1200.0 wc 250
nt 280 hzmm 12.36
ct 280 is 22221.69
alock n rfl 346.8
gain 4 rfp 0
FLAGS th 4
ll n ins 100.000
ln n nm ph
dp y
```

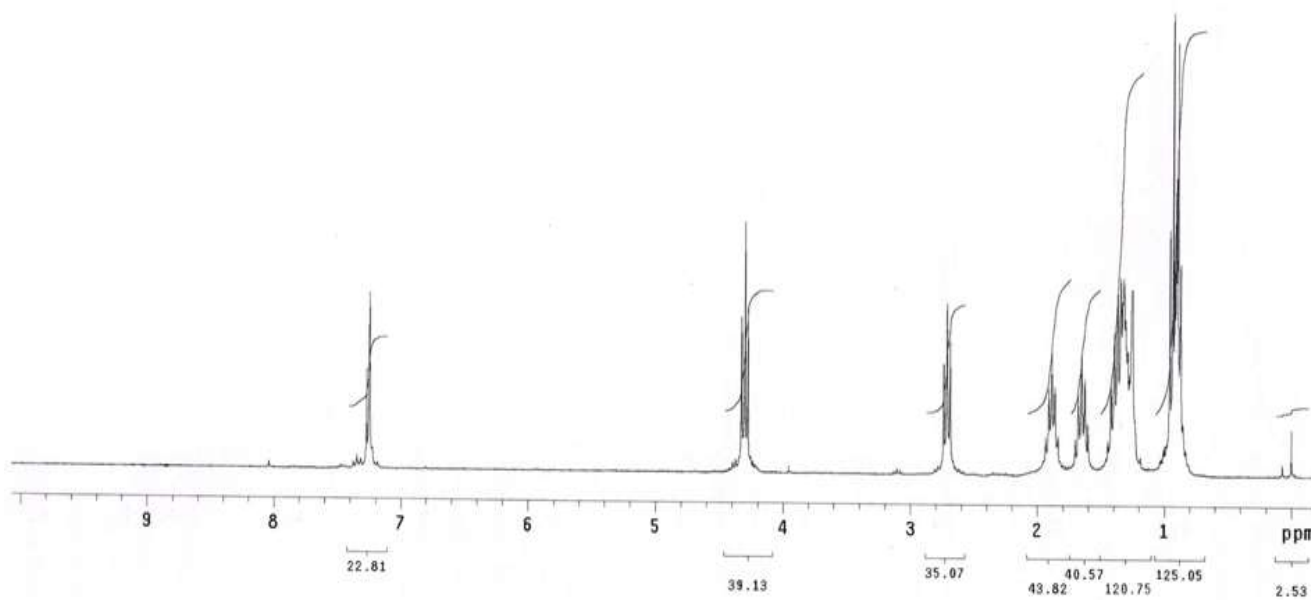
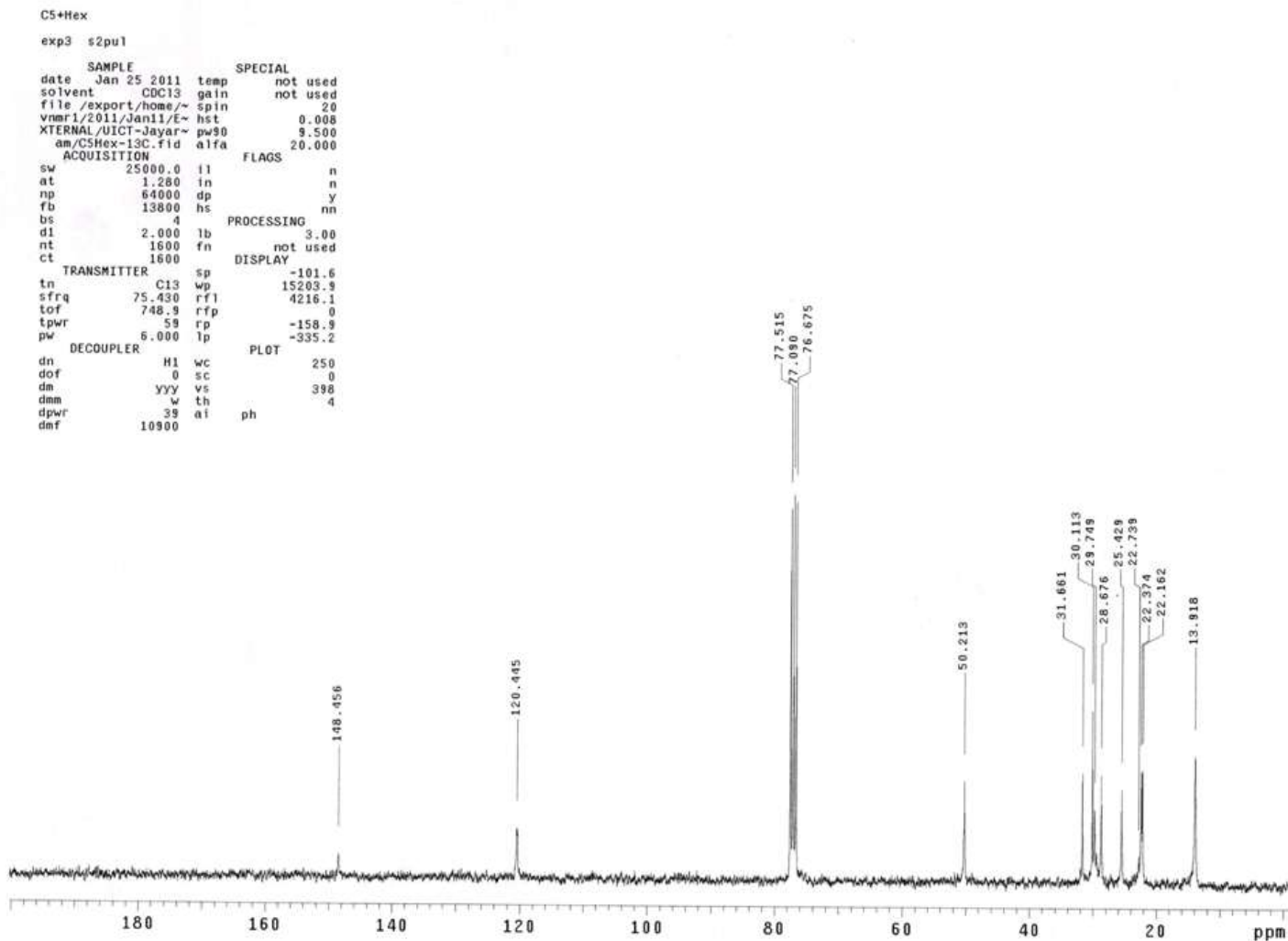
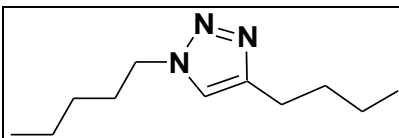


Table 2, Entry 22:



5. GC-MS spectra:



