

SUPPORTING INFORMATION

[Ce(L-Pro)₂]₂ (Oxa) as a heterogeneous recyclable catalyst: Synthesis of pyrazoles under mild reaction conditions.

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General Information:

Analytical thin layer chromatography (TLC) was carried out using silica gel 60 F₂₅₄ pre-coated plates. Visualization was accomplished with UV lamp or I₂ stain. All products were characterized by their NMR and MS spectra. ¹H and ¹³C NMR was recorded on 50, 200 and 300 MHz, in CDCl₃ using TMS as the internal standard, Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane.

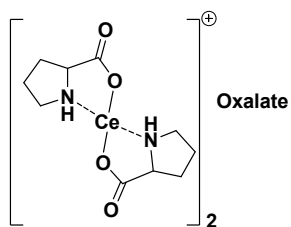
General procedure for the synthesis of pyrazoles:

General Procedure for the synthesis of pyrazole derivatives: Round-bottomed flask (25 mL) was charged with 1, 3-dicarbonyl compound (1.0 mmol) and phenyl hydrazine (1.0 mmol) was taken in ethanol (10 mL), a catalytic amount of [Ce(*L*-Pro)₂]₂ (Oxa) (5 mol %) was added and the mixture was stirred under room temperature for appropriate time. The progress of the reaction was monitored by TLC. After the completion of the reaction was indicated by TLC, then the catalyst ([Ce(*L*-Pro)₂]₂ (Oxa)) was filtered off from the reaction mixture. The remaining solvent was evaporated under reduced pressure. Further, the crude product was purified by column chromatography over silica gel to afford the corresponding product yields were obtained in 70-91% as shown in **Table 2**.

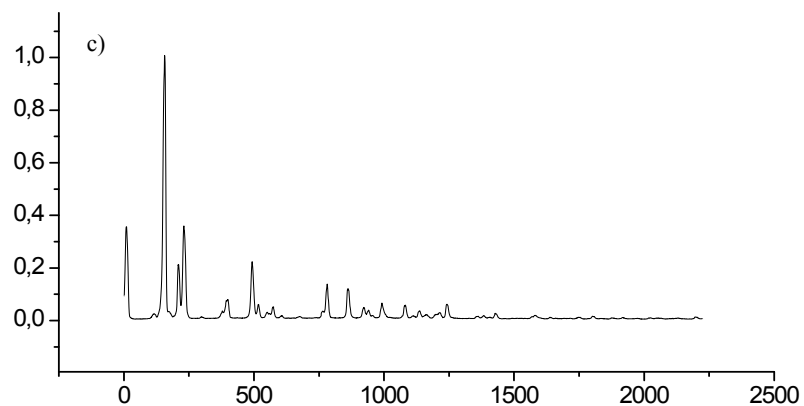
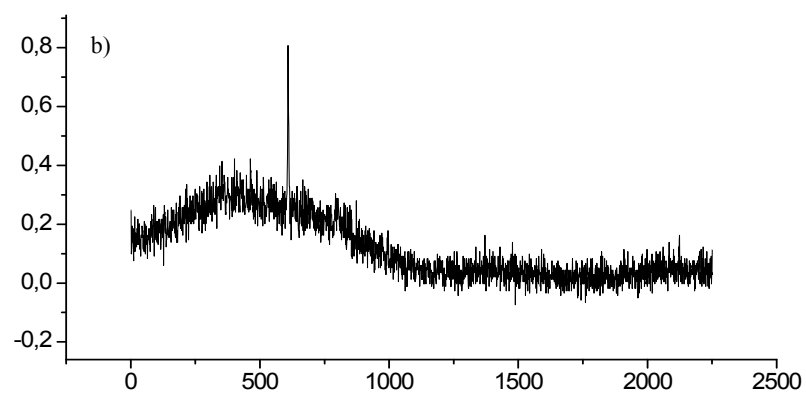
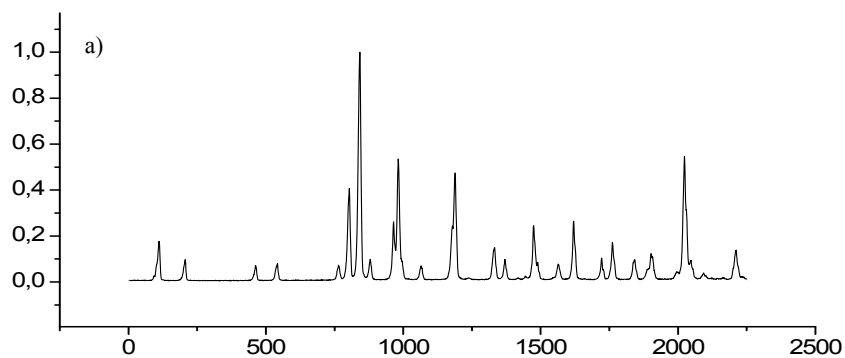
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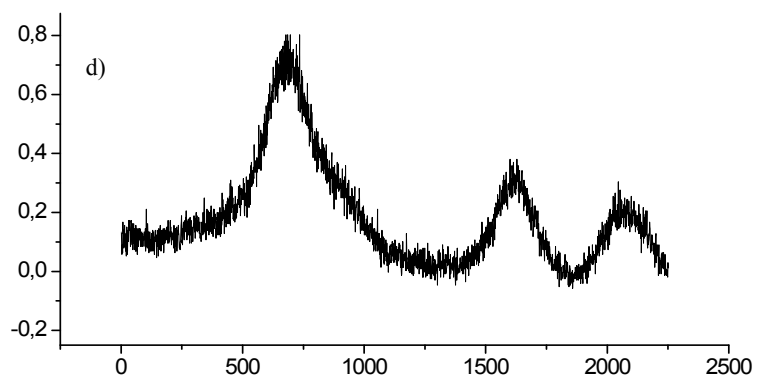
- (1) Chen, X.; She, J.; Shang, Z.; Wu, J.; Wu, H.; Zhang, P. *Synthesis*. **2008**, 21, 3478
- (2) Gosselin, F.; O'Shea, P. D.; Webster, R. A.; Reamer, R. A.; Tillyer, R. D.; Rabowski, E. J. *J. Synlett*. **2006**, 19, 3267.
- (3) Wang, Z.; Qin, H. *Green Chem.* **2004**, 6, 90;

Catalyst proposed structure for $[\text{Ce}(\text{L-Pro})_2]_2(\text{Oxa})$:

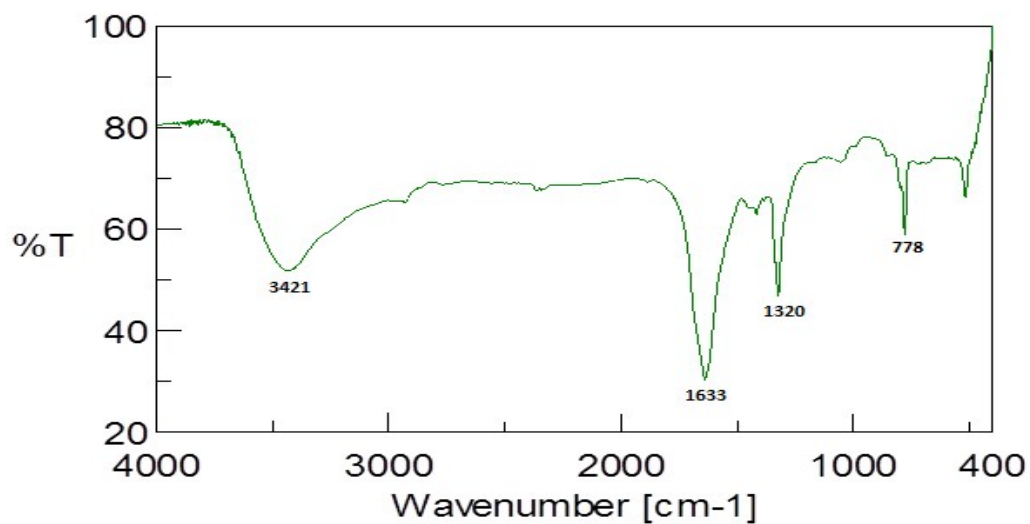


X-Ray diffraction patterns of proline (a), cerium chloride (b), sodium oxalate (c) and $[\text{Ce}(\text{L-Pro})_2]_2(\text{Oxa})$ (d):



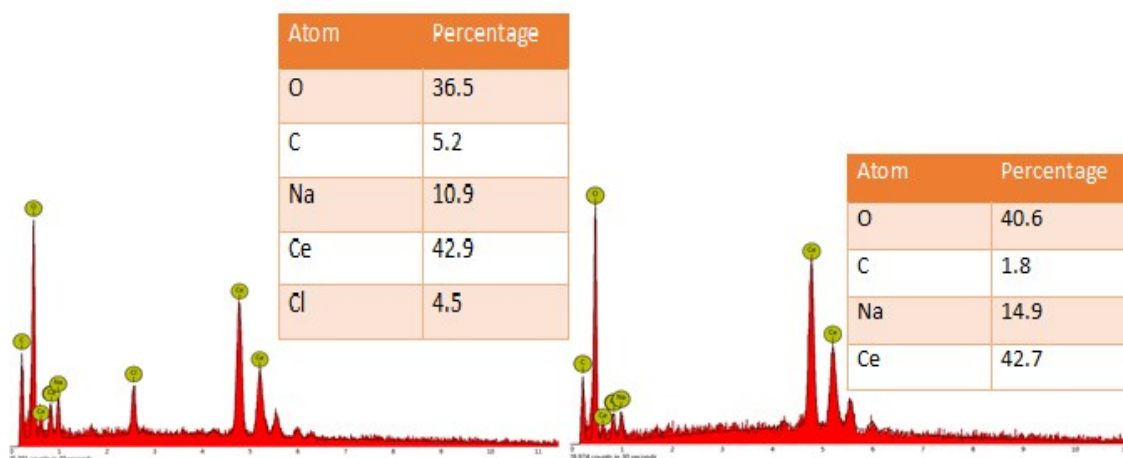


IR:



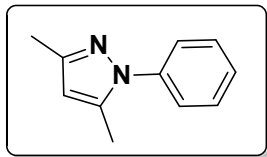
[A]

[B]

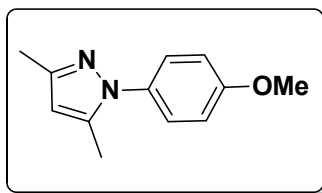


Catalyst EDS images of fresh [A] and after the reaction [B].

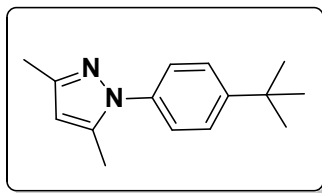
Spectral data :



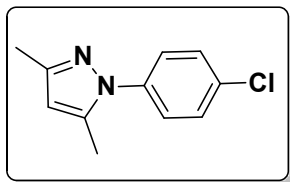
3, 5-dimethyl-1-phenyl-1H-pyrazole (Table 2, entry 1)¹: Light brown liquid; ¹H NMR (200 MHz, CDCl₃) δ: 7.46-7.33 (m, 4H), 7.29 -7.19 (m, 1H), 5.90 (s, 1H), 2.25 (s, 6H); ¹³C NMR (50 MHz, CDCl₃) δ: 148.1, 139.4, 138.4, 128.3, 126.4, 124.0, 106.4, 12.9, 11.8; MS (ESI): *m/z* = 173 [M+H]⁺.



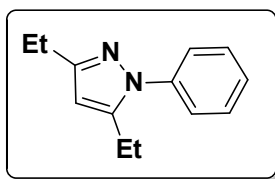
1-(4-methoxyphenyl)-3, 5-dimethyl-1H-pyrazole (Table 2, entry 2): brown liquid; ¹H NMR (200 MHz, CDCl₃) δ: 7.27 (d, 2H, *J* = 9.06 Hz), 6.90 (d, 2H, *J* = 9.06 Hz), 5.90 (s, 1H), 3.8 (s, 3H), 2.26 (s, 3H), 2.23 (s, 3H); ¹³C NMR (50 MHz, CDCl₃) δ: 158.7, 148.0, 139.1, 132.7, 125.9, 113.7, 105.9, 55.1, 13.1, 11.7; MS (ESI): *m/z* = 203 [M+H]⁺.



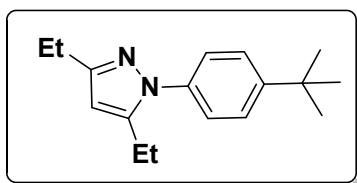
1-(4-tert-butylphenyl)-3,5-dimethyl-1H-pyrazole (Table 2, entry 3): brown liquid; ¹H NMR (200 MHz, CDCl₃) δ: 7.42 (d, 2H, *J* = 8.68 Hz), 7.32 (d, 2H, *J* = 8.68 Hz), 5.91 (s, 1H), 2.34 (s, 3H), 2.20 (s, 3H), 1.34 (s, 9H); ¹³C NMR (50 MHz, CDCl₃) δ: 150.1, 148.4, 139.3, 137.3, 125.7, 124.5, 106.5, 34.8, 31.3, 13.5, 12.4; MS (ESI): *m/z* = 229 [M+H]⁺.



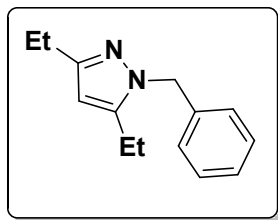
1-(4-chlorophenyl)-3, 5-dimethyl-1H-pyrazole (Table 2, entry 4)¹: thick brown liquid; ¹H NMR (200 MHz, CDCl₃) δ: 7.45(m, 4H), 5.95 (s, 1H), 2.29 (s, 3H), 2.27 (s, 3H); ¹³C NMR (50 MHz, CDCl₃) δ: 148.7, 138.8, 137.7, 132.7, 128.7, 125.3, 107, 13.0, 12.0. MS (ESI): *m/z* = 207 [M+H]⁺.



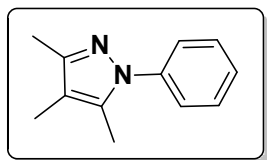
3, 5-diethyl-1-phenyl-1H-pyrazole (Table 2, entry 5): brown liquid; ¹H NMR (200 MHz, CDCl₃) δ: 7.42 (m, 5H), 6.08 (s, 1H), 2.68 (m, 4H), 1.36-1.21(m, 6H); ¹³C NMR (50 MHz, CDCl₃) δ: 154.7, 145.8, 140.2, 129.2, 127.3, 125.2, 103.2, 21.7, 19.6, 14.2, 13.15; MS (ESI): *m/z* = 201 [M+H]⁺.



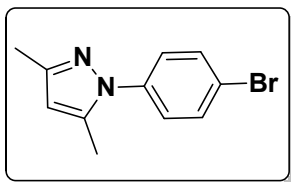
1-(4-tert-butylphenyl)-3, 5-diethyl-1H-pyrazole (Table 2, entry 6): brown liquid; ¹H NMR (200 MHz, CDCl₃) δ: 7.42 (d, 2H, *J* = 8.79 Hz), 7.33 (d, 2H, *J* = 8.05 Hz), 6.0 (s, 1H), 2.69-2.59 (m, 4H), 1.33 (s, 9H), 1.29-1.16 (m, 6H); ¹³C NMR (50 MHz, CDCl₃) δ: 151.1, 147.3, 140.2, 136.2, 124.9, 119.2, 107.3, 40.2, 31.2, 23.1, 21.2 18.1; MS (ESI): *m/z* = 257 [M+H]⁺.



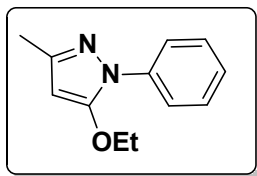
1-benzyl-3, 5-diethyl-1H-pyrazole (Table 2, entry 7): ^1H NMR (200 MHz, CDCl_3) δ : 7.28-7.16 (m, 3H), 7.03 (d, 2H, $J = 7.16$ Hz), 5.82 (s, 1H), 5.20 (s, 2H), 2.60 (q, 2H, $J = 7.5$ Hz), 2.41 (q, $J = 7.5$ Hz, 2H), 1.24 (t, $J = 7.55$, 3H), 1.14 (t, 3H, $J = 7.55$); ^{13}C NMR (50 MHz, CDCl_3) δ : 147.6, 141.2, 138.3, 129.5, 128.5, 127.3, 106.7, 53.5, 22.2, 20.1, 14.2, 12.6; MS (ESI): $m/z = 215$ $[\text{M}+\text{H}]^+$.



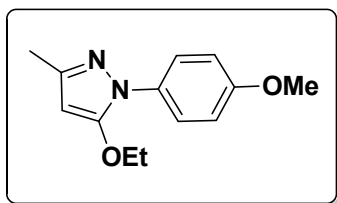
3, 4, 5-trimethyl-1-phenyl-1H-pyrazole (Table 2, entry 8): yellow liquid; ^1H NMR (300 MHz, CDCl_3) δ : 7.39- 7.31 (m, 5H) 2.10 (s, 6H), 1.96 (s, 3H); ^{13}C NMR (50 MHz, CDCl_3) δ : 148.4, 138.6, 135.9, 132.3, 129.0, 125.5, 113.6, 11.8, 10.9, 8.1; MS (ESI): $m/z = 187$ $[\text{M}+\text{H}]^+$.



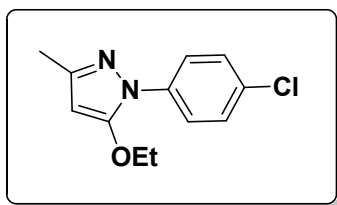
1-(4-bromophenyl)-3, 5-dimethyl-1H-pyrazole (Table 2, entry 9)³: brown liquid; ^1H NMR (200 MHz, CDCl_3) δ : 7.52 (d, 2H, $J = 8.3$ Hz), 7.36 (d, 2H, $J = 9.0$ Hz), 5.91 (s, 1H), 2.28 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (50 MHz, CDCl_3) δ : 148.4 138.4, 137.3, 132.4, 128.5, 125.4, 107.8, 13.2, 12.2; MS (ESI): $m/z = 251$ $[\text{M}+\text{H}]^+$.



5-ethoxy-3-methyl-1-phenyl-1H-pyrazole (Table 2, entry 10): ^1H NMR (200 MHz, CDCl_3) δ : 7.68 (d, 2H, $J = 7.74$ Hz), 7.35 (t, 2H, $J = 7.74$ Hz), 7.17 (t, 1H, $J = 7.74$ Hz), 5.40 (s, 1H), 4.12 (q, 2H, $J = 6.98$ Hz), 2.42 (s, 3H), 1.44 (t, 3H, $J = 6.98$ Hz); ^{13}C NMR (50 MHz, CDCl_3) δ : 154.6, 148.3, 138.8, 128.6, 125.5, 121.6, 86.1, 67.5, 14.6, 14.5; MS (ESI): $m/z = 203$ $[\text{M}+\text{H}]^+$.

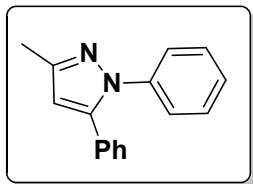


5-ethoxy-1-(4-methoxyphenyl)-3-methyl-1H-pyrazole (Table 2, entry 11): brown solid; mp. 53-55 $^{\circ}\text{C}$; ^1H NMR (300 MHz, CDCl_3) δ : 7.52 (d, 2H, $J = 8.78$ Hz), 6.85 (d, 2H, $J = 8.78$ Hz), 5.37 (s, 1H), 4.08 (q, 2H, $J = 6.83$ Hz), 3.80 (s, 3H), 2.22 (s, 3H), 1.42 (t, 3H, $J = 7.80$ Hz); ^{13}C NMR (50 MHz, CDCl_3) δ : 157.7, 154.4, 148.0, 132.2, 124.0, 113.8, 85.5, 67.2, 55.5, 14.6, 14.4; MS (ESI): $m/z = 233$ $[\text{M}+\text{H}]^+$.

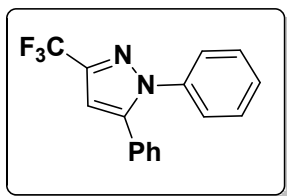


1-(4-chlorophenyl)-5-ethoxy-3-methyl-1H-pyrazole (Table 2, entry 12): mp. 58-61 $^{\circ}\text{C}$; ^1H NMR (300 MHz, CDCl_3) δ : 7.58 (d, 2H, $J = 8.87$ Hz), 7.47 (d, 2H, $J = 8.87$ Hz), 5.39 (s, 1H), 4.10 (q, 2H, $J = 6.98$ Hz), 2.22 (s, 3H), 1.45 (t, 3H, $J = 6.98$ Hz); ^{13}C NMR

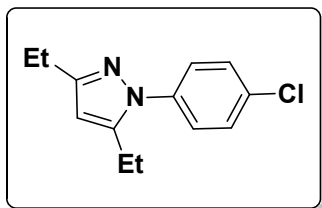
(50 MHz, CDCl₃) δ : 155.1, 148.9, 137.8, 132.4, 122.8, 118.7, 86.6, 68.0, 14.7, 14.6; MS (ESI): m/z = 237 [M+H]⁺.



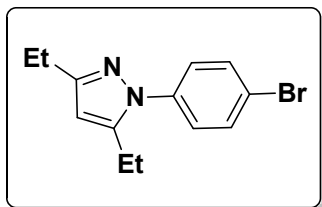
3-methyl-1, 5-diphenyl-1H-pyrazole (Table 2, entry 13): yellow oil; ¹H NMR (200 MHz, CDCl₃) δ : 7.37-7.19 (m, 10H), 6.28 (s, 1H), 2.40 (s, 3H); ¹³C NMR (50 MHz, CDCl₃) δ : 148.7, 142.9, 139.7, 130.3, 128.2, 128.1, 127.9, 127.5, 126.4, 124.5, 107.5, 13.2; MS (ESI): m/z = 235 [M+H]⁺.



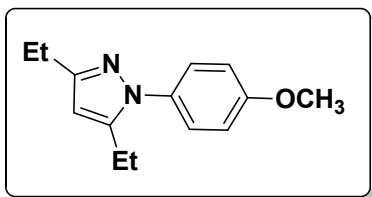
1, 5-diphenyl-3-(trifluoromethyl)-1H-pyrazole (Table 2, entry 14)²: light yellow solid; mp. 86-90 °C; ¹H NMR (200 MHz, CDCl₃) δ : 7.36-7.26 (m, 8H), 7.23 -7.18 (m, 2H), 6.71 (s, 1H); ¹³C NMR (50 MHz, CDCl₃) δ : 144.8, 139.2, 129.0, 128.9, 128.7, 128.6, 128.3, 125.4, 105.5; MS (ESI): m/z = 289 [M+H]⁺.



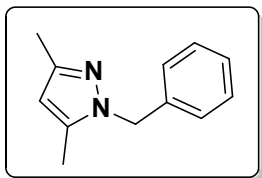
1-(4-chlorophenyl)-3, 5-diethyl-1H-pyrazole (Table 2, entry 15): ¹H NMR (200 MHz, CDCl₃) δ : 7.41-7.31 (m, 4H), 6.01 (s, 1H), 2.69-2.57 (m, 4H), 1.33-1.19 (m, 6H); ¹³C NMR (50 MHz, CDCl₃) δ : 154.5, 145.4, 140.5, 128.9, 127.8, 125.9, 103.5, 21.5, 19.9, 14.3, 13.3; MS (ESI): m/z = 235 [M+H]⁺.



1-(4-bromophenyl)-3, 5-diethyl-1H-pyrazole (Table 2, entry 16): ^1H NMR (200 MHz, CDCl_3) δ : 7.55 (d, 2H, $J = 8.79$ Hz), 7.29 (d, 2H, $J = 8.05$), 6.05 (s, 1H), 2.70-2.59 (m, 4H), 1.33-1.20 (m, 6H); ^{13}C NMR (50 MHz, CDCl_3) δ : 151.8, 147.7, 140.1, 136.3, 124.4, 119.2, 107.0, 21.6, 20.4, 15.1, 14.2; MS (ESI): $m/z = 279$ $[\text{M}+\text{H}]$.



3, 5-diethyl-1-(4-methoxyphenyl)-1H-pyrazole (Table 2, entry 17): brown liquid; ^1H NMR (200 MHz, CDCl_3) δ : 7.26 (d, 2H, $J = 9.06$ Hz), 6.81 (d, 2H, $J = 8.3$ Hz), 5.92 (s, 1H), 3.84 (s, 3H), 2.69-2.52 (m, 4H), 1.30-1.15 (m, 6H); ^{13}C NMR (50 MHz, CDCl_3) δ : 158.8, 148.3, 139.4, 133.5, 126, 114, 108, 55, 22.3, 19.8, 13.7, 12.8; MS (ESI): $m/z = 231.15$ $[\text{M}+\text{H}]^+$.



1-benzyl-3, 5-dimethyl-1H-pyrazole (Table 2, entry 18): liquid; ^1H NMR 200 MHz, CDCl_3) δ : 7.28-7.15 (m, 3H), 7.02 (d, 2H, $J = 7.32$), 5.85 (s, 1H), 5.14 (s, 2H), 2.22 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (50 MHz, CDCl_3) δ : 147.2, 138.9, 137.2, 128.9, 127.5, 126.5, 105.7, 52.5, 13.5, 11.3; MS (ESI): $m/z = 187.16$ $[\text{M}+\text{H}]^+$.

Copies of ^1H -NMR & ^{13}C -NMR:

Table 2, entry 1:

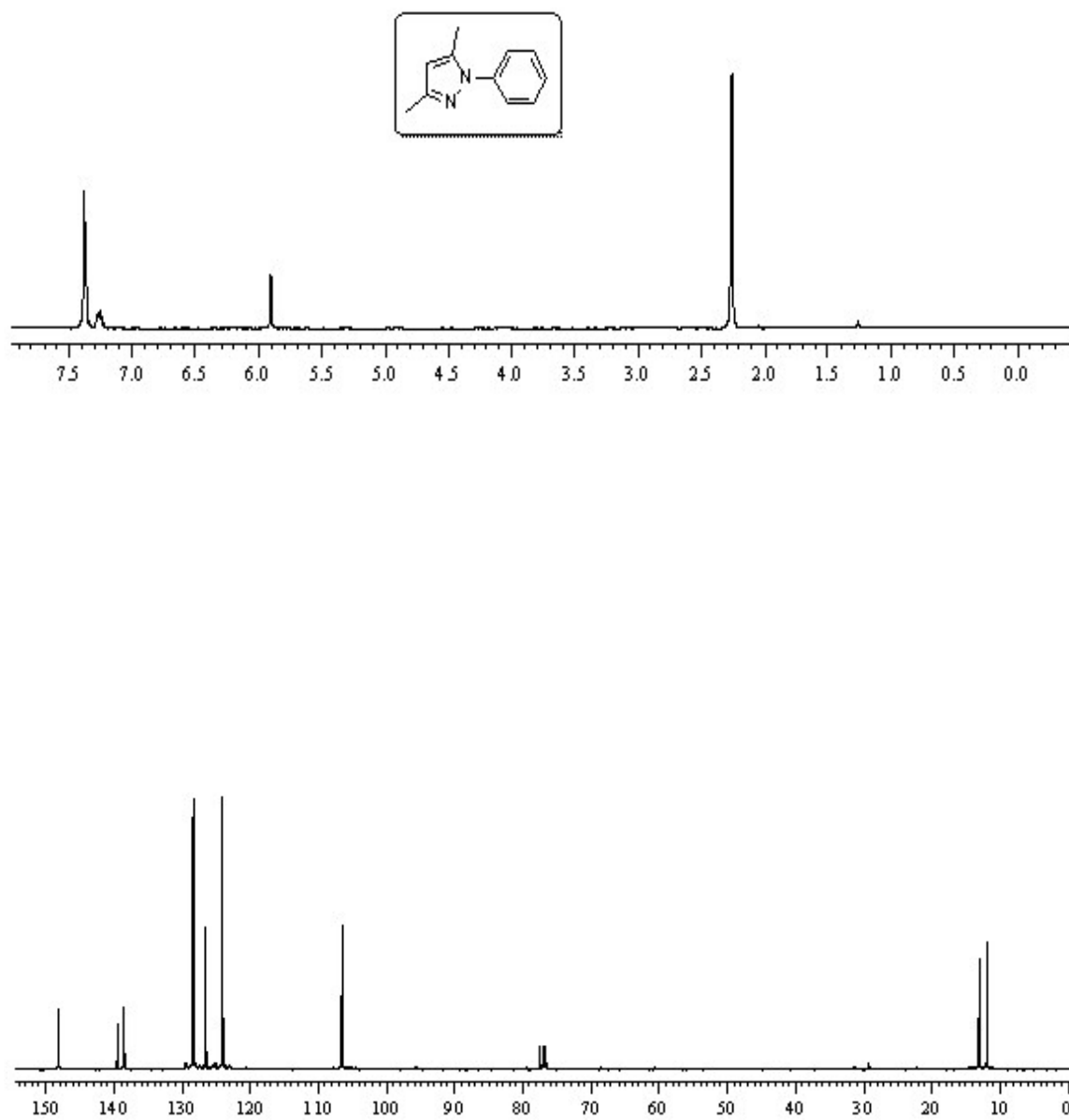


Table 2, entry 2:

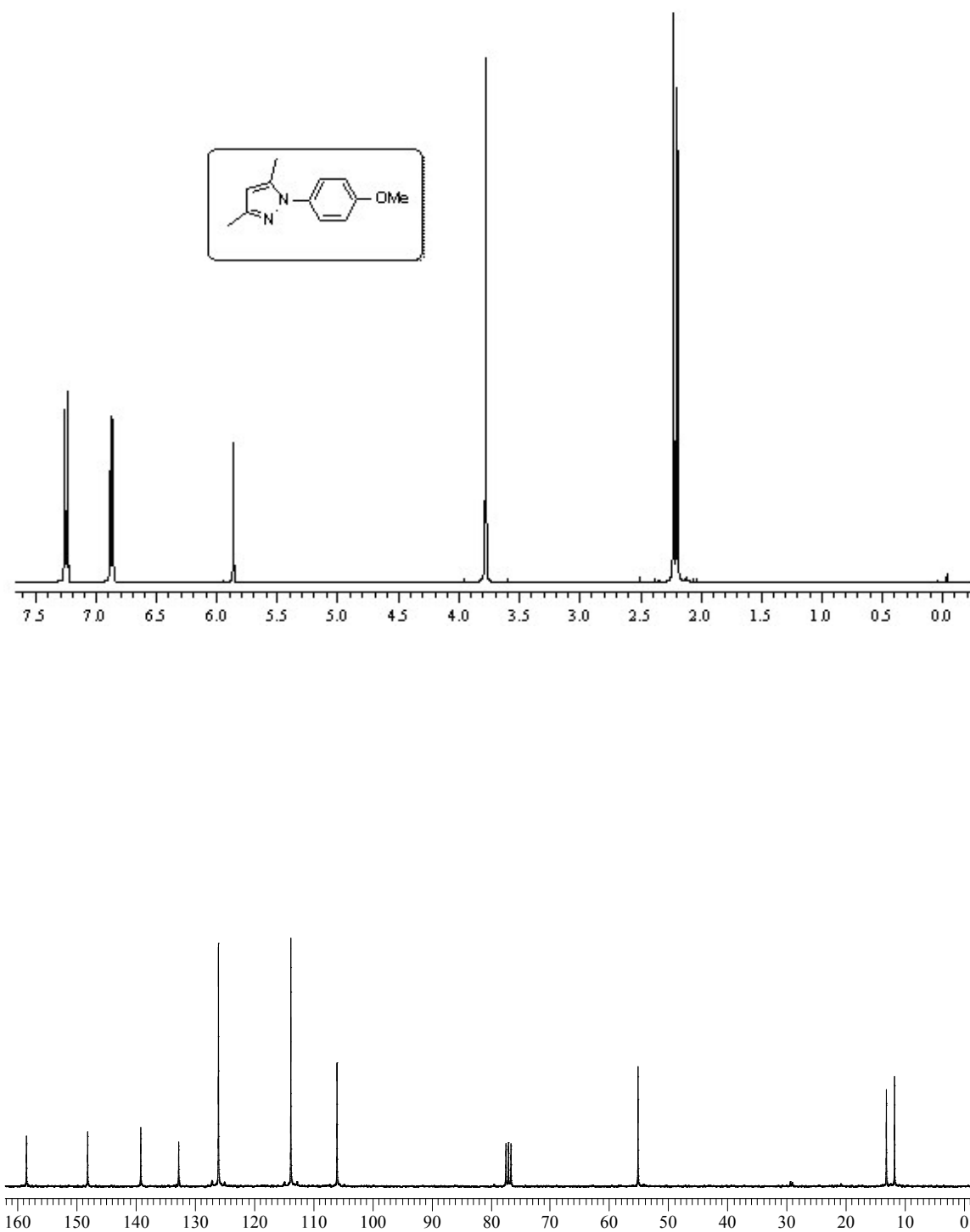


Table 2, entry 3:

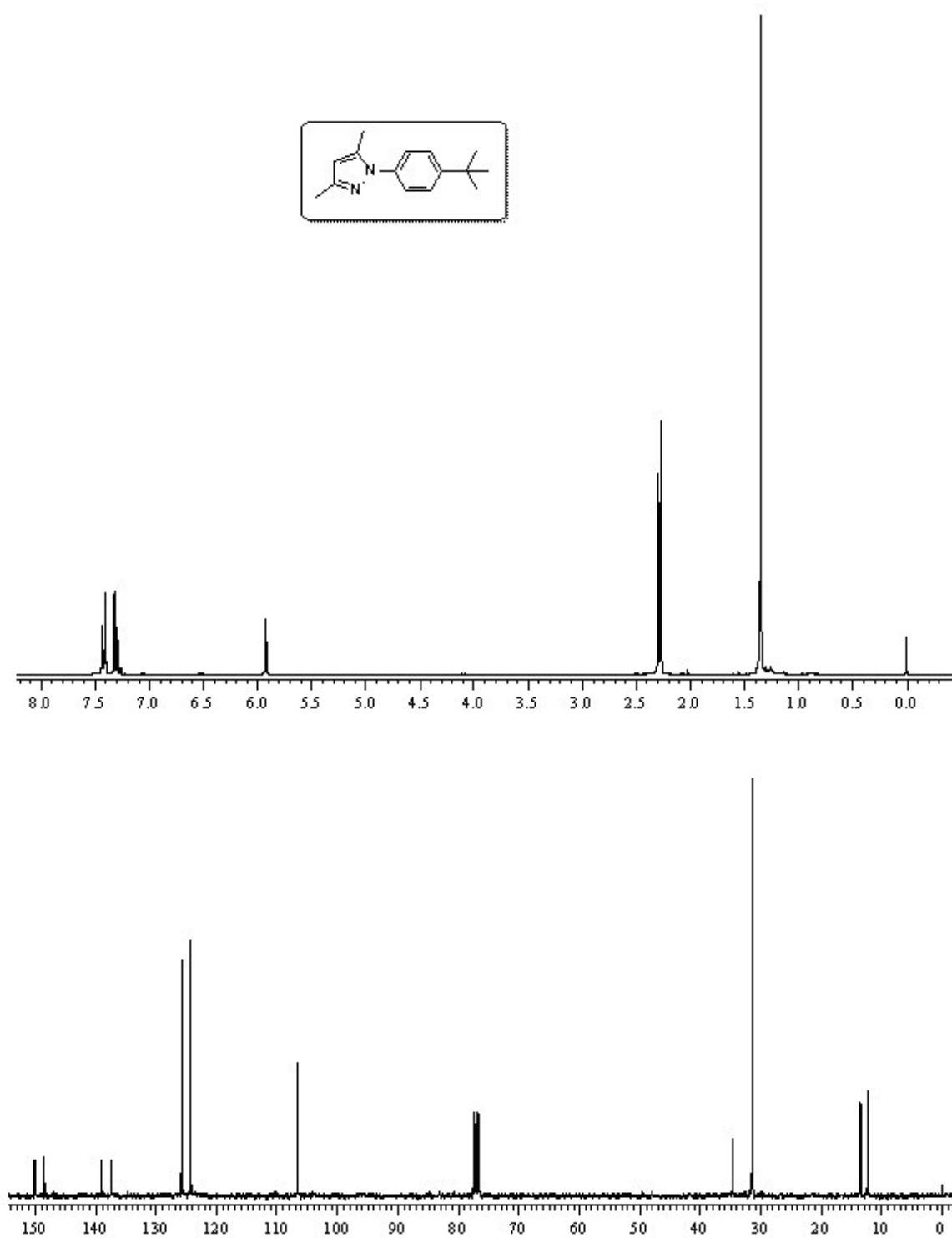


Table 2, entry 4:

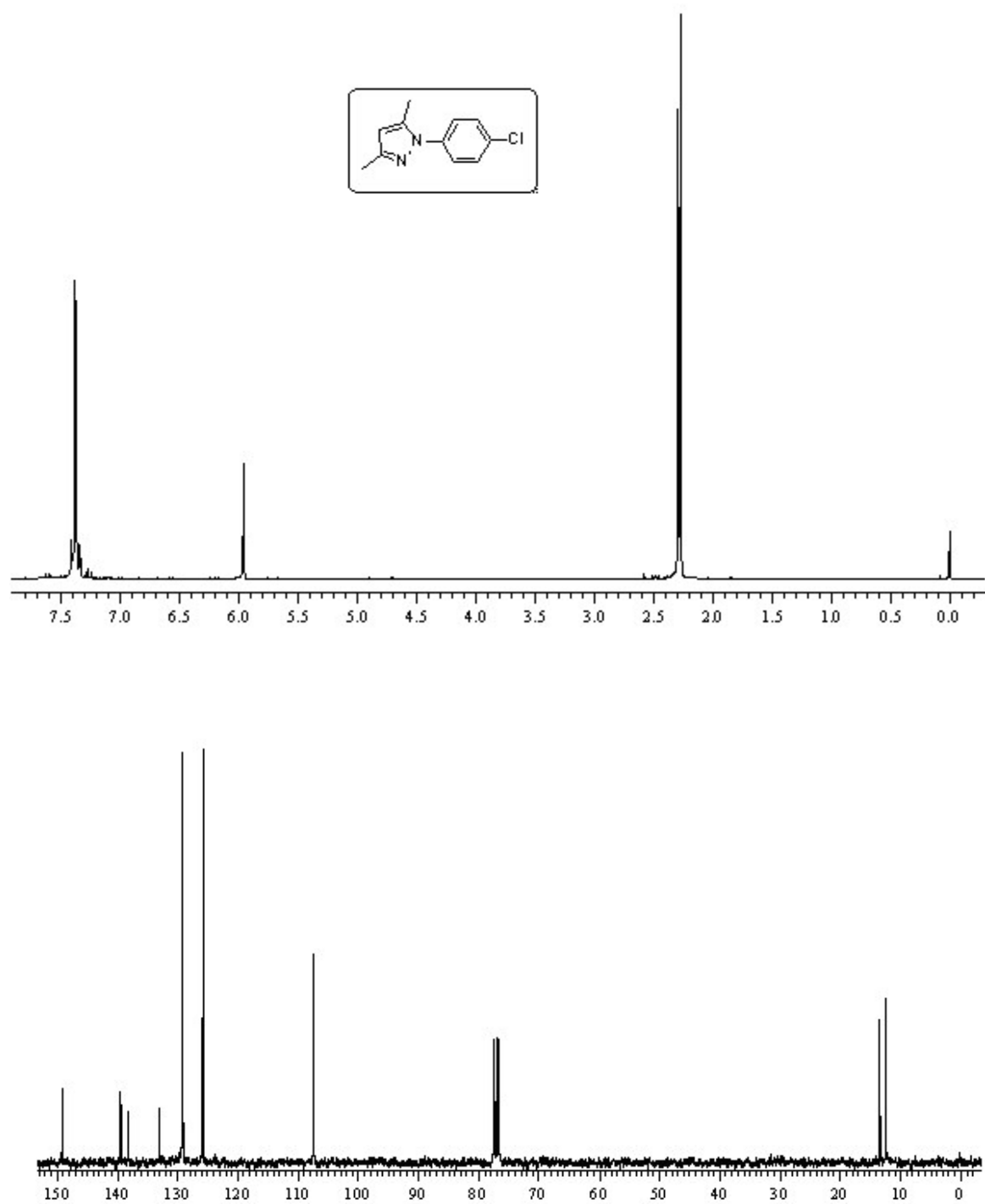


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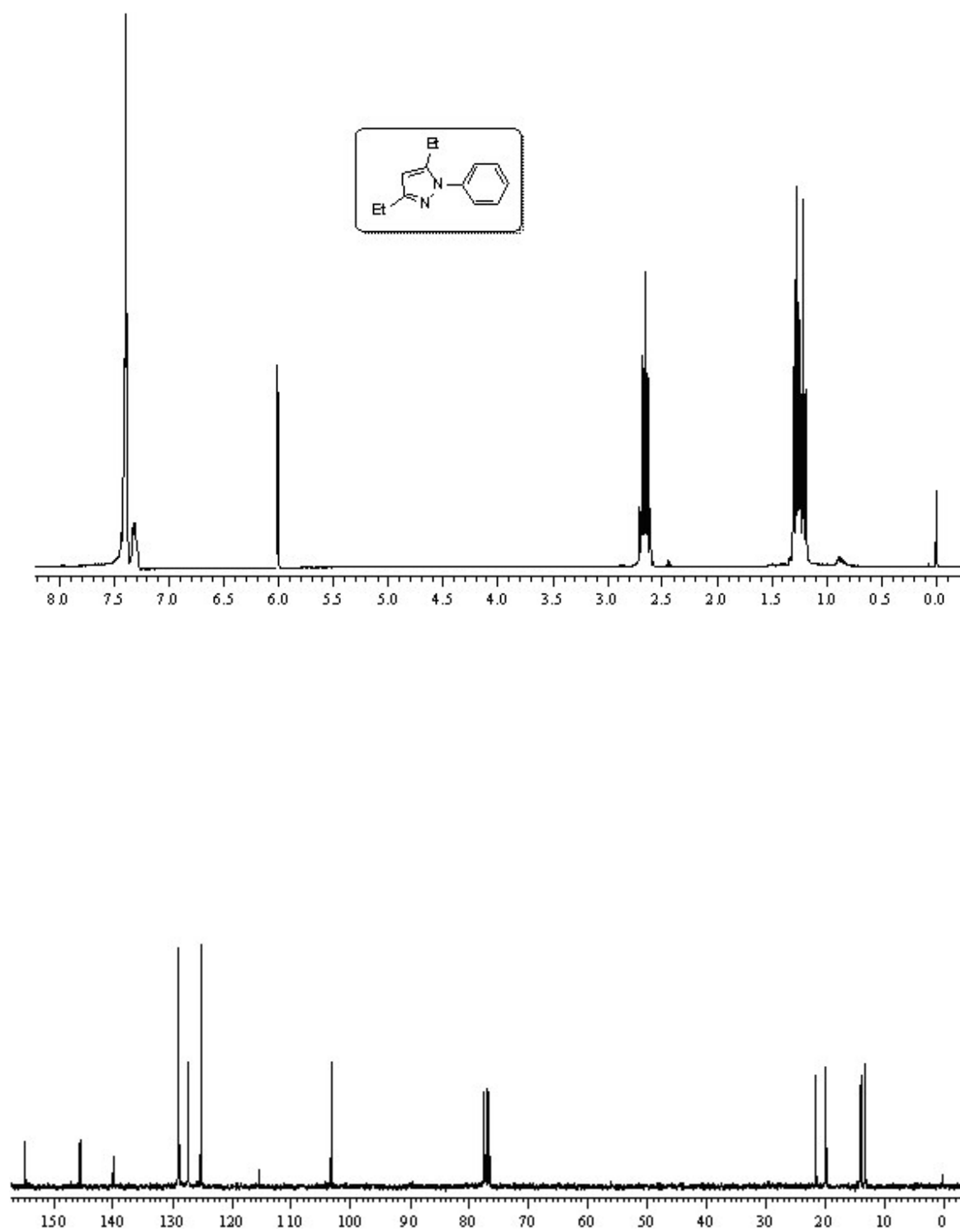


Table 2, entry 6:

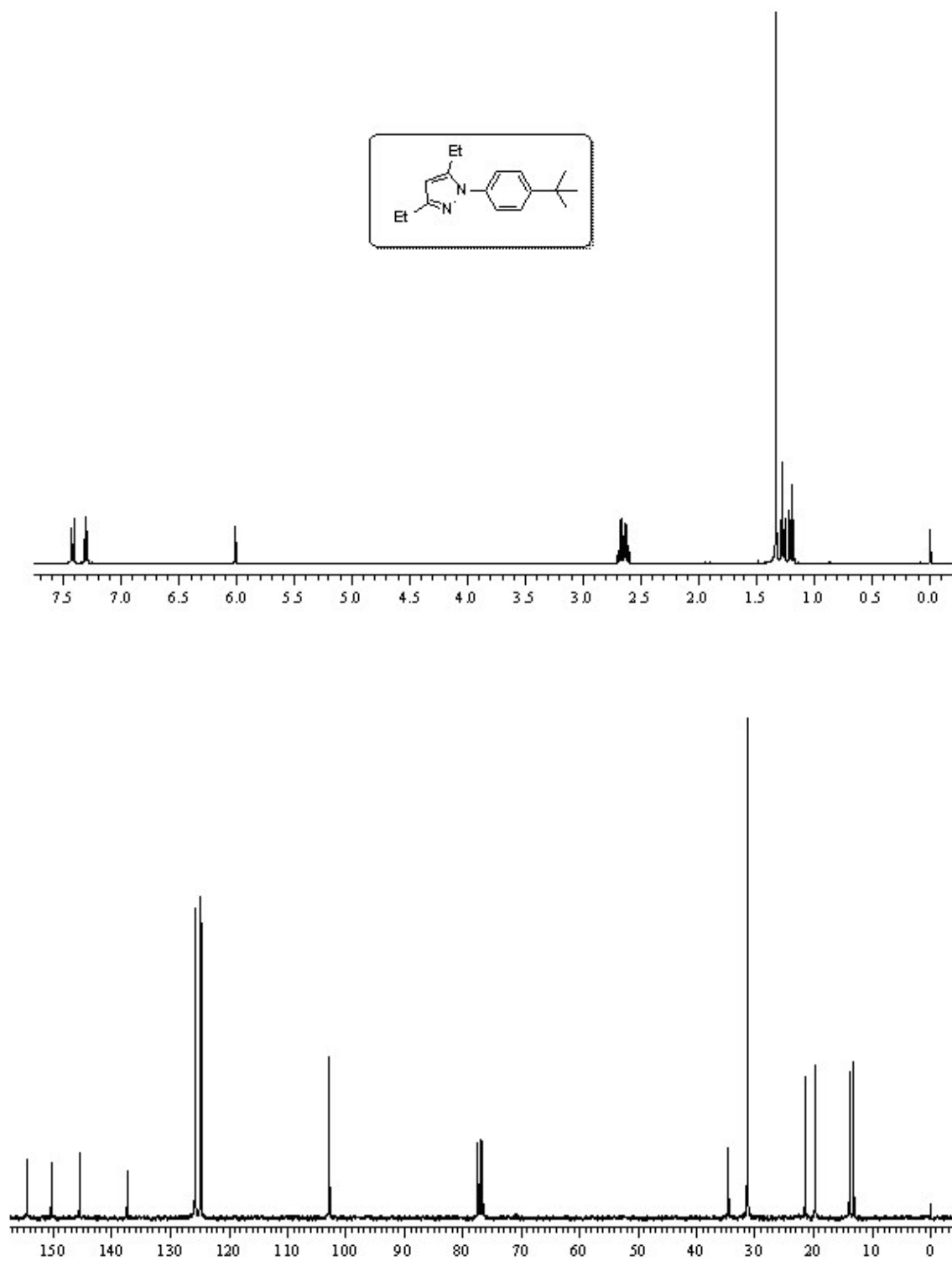


Table 2, entry 7:

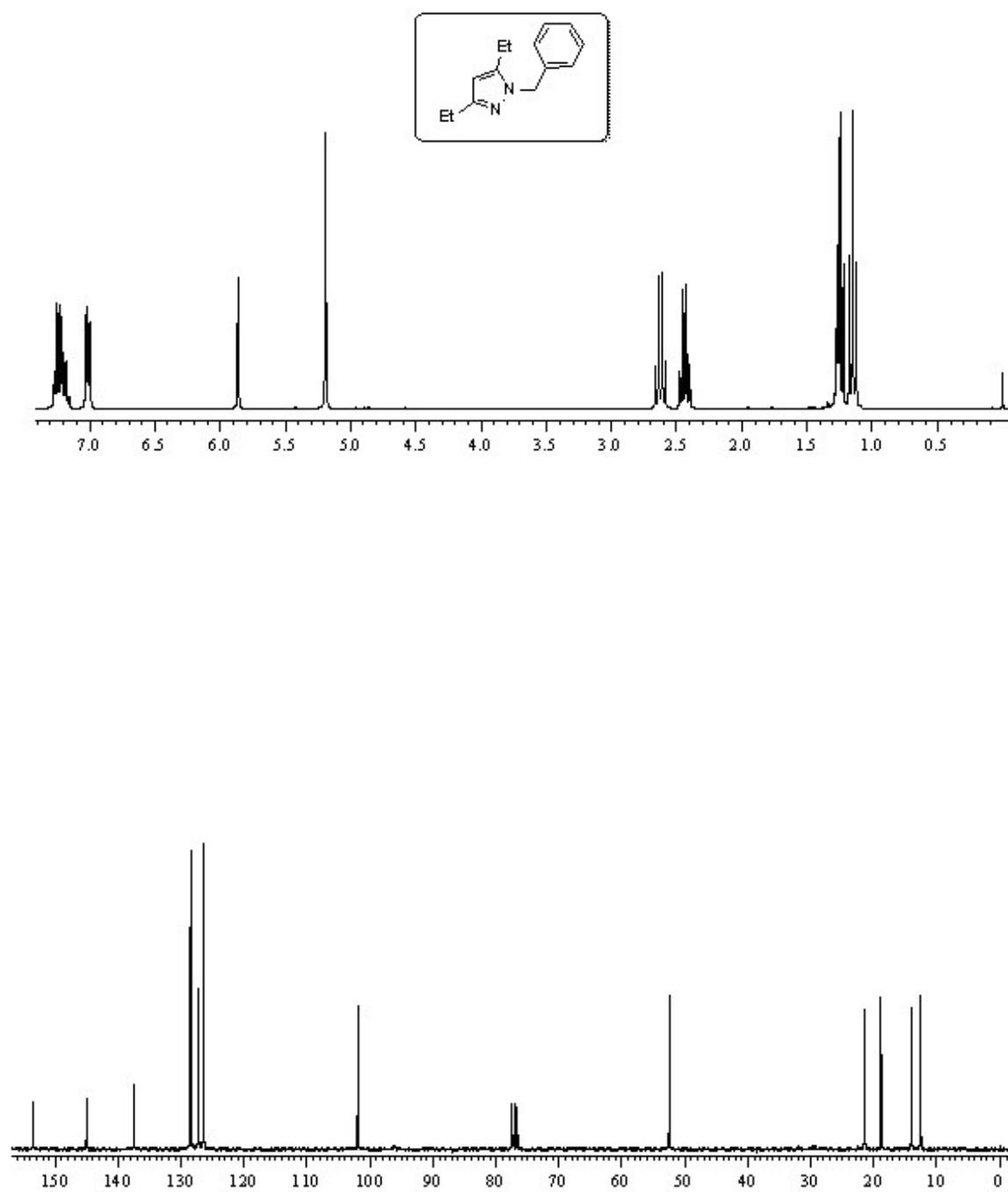


Table 2, entry 8:

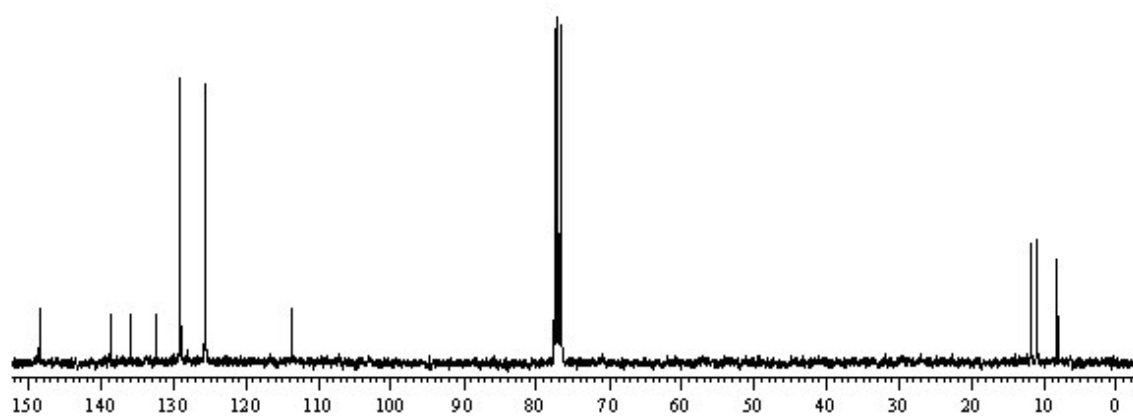
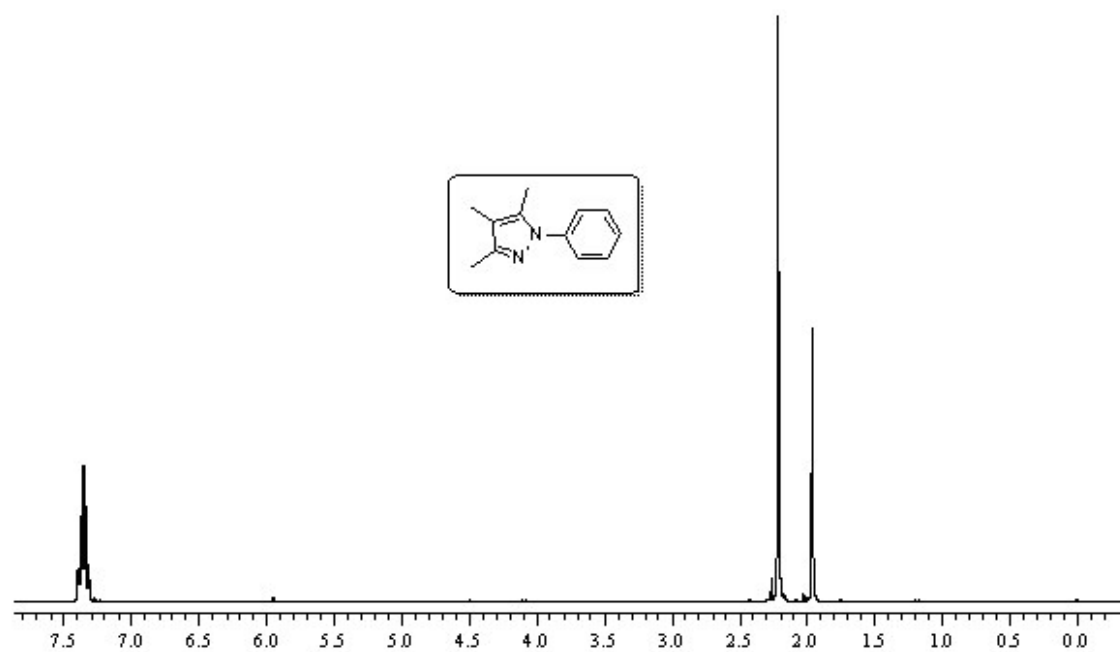


Table 2, entry 9:

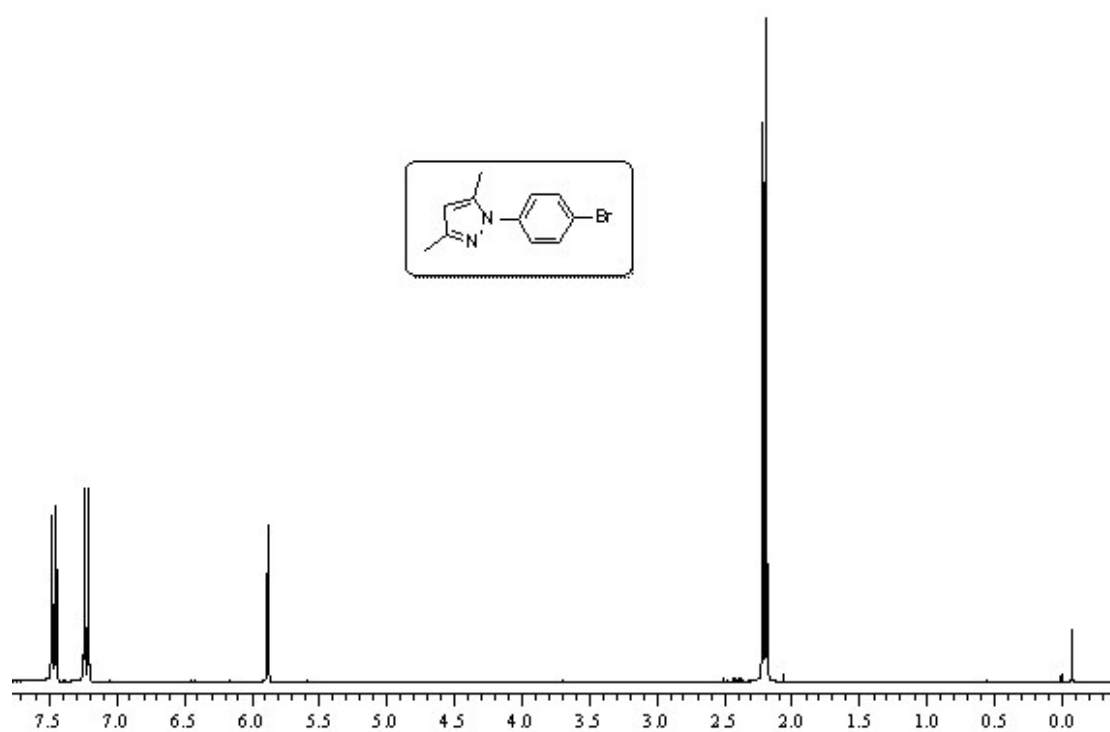


Table 2, entry 10:

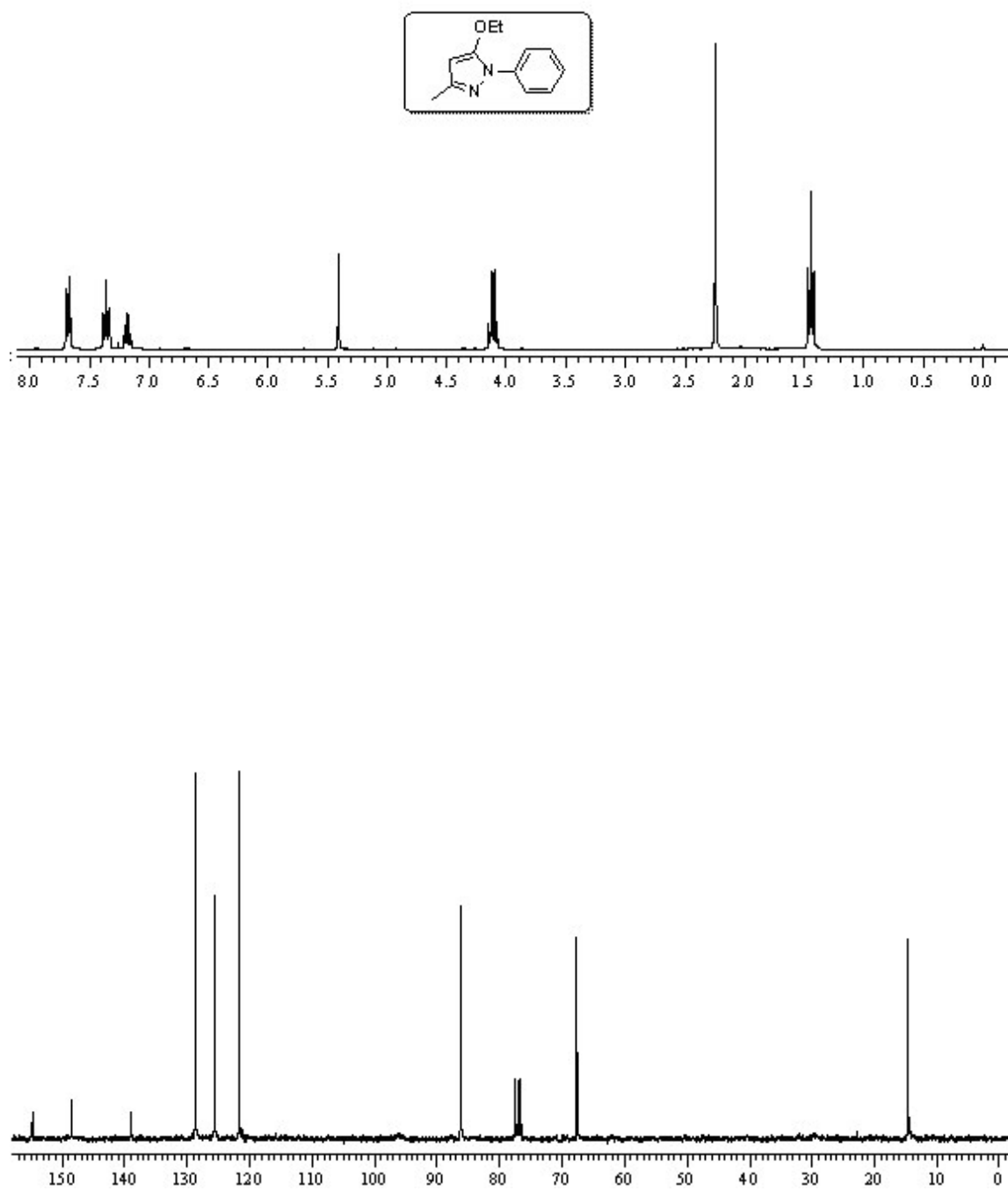


Table 2, entry 11:

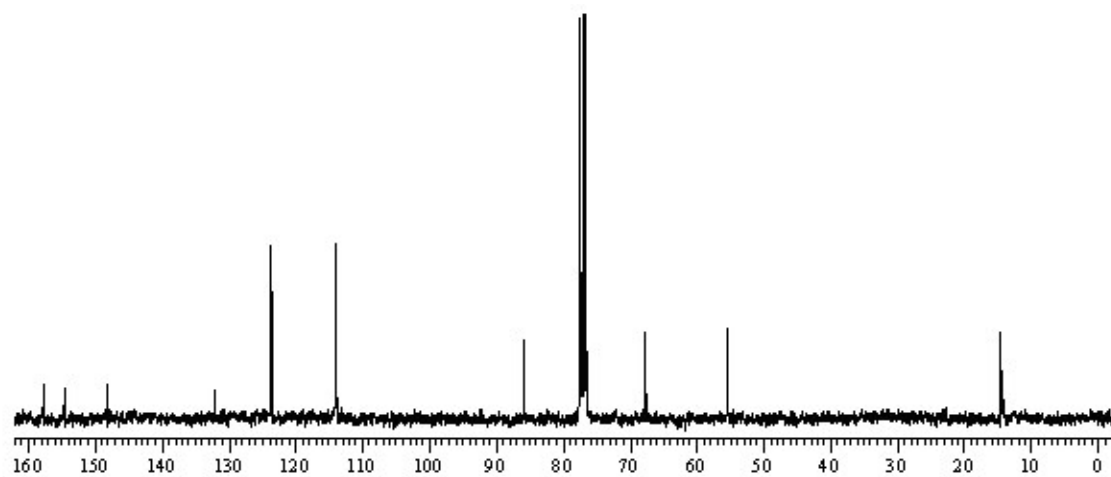
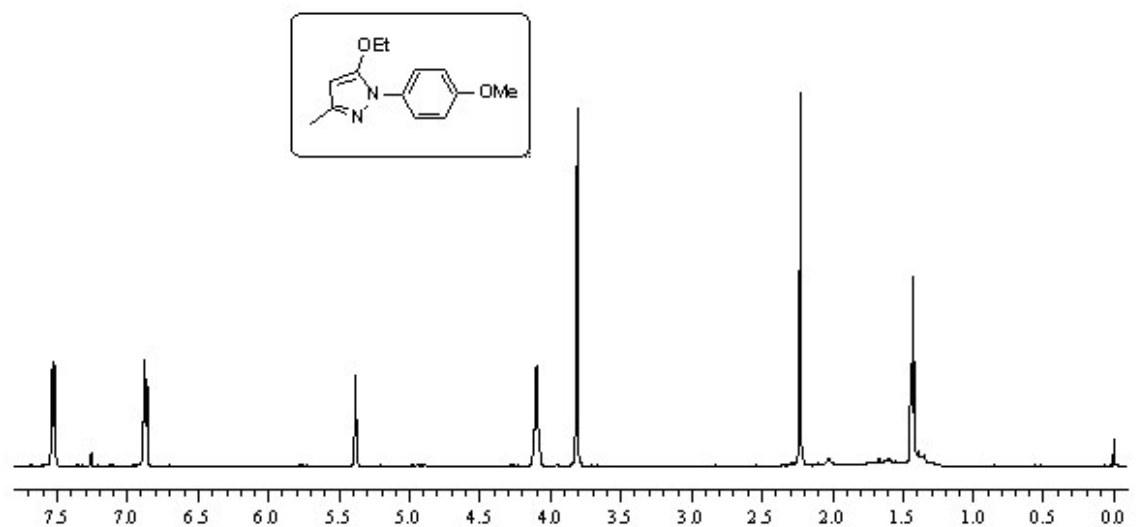


Table 2, entry 12:

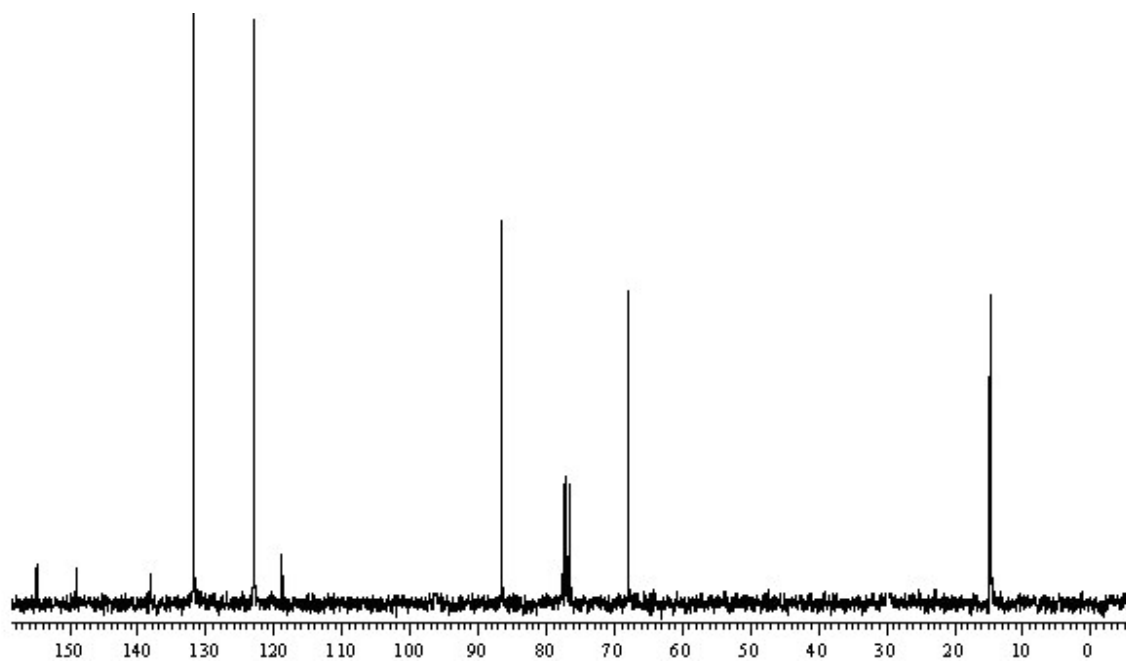
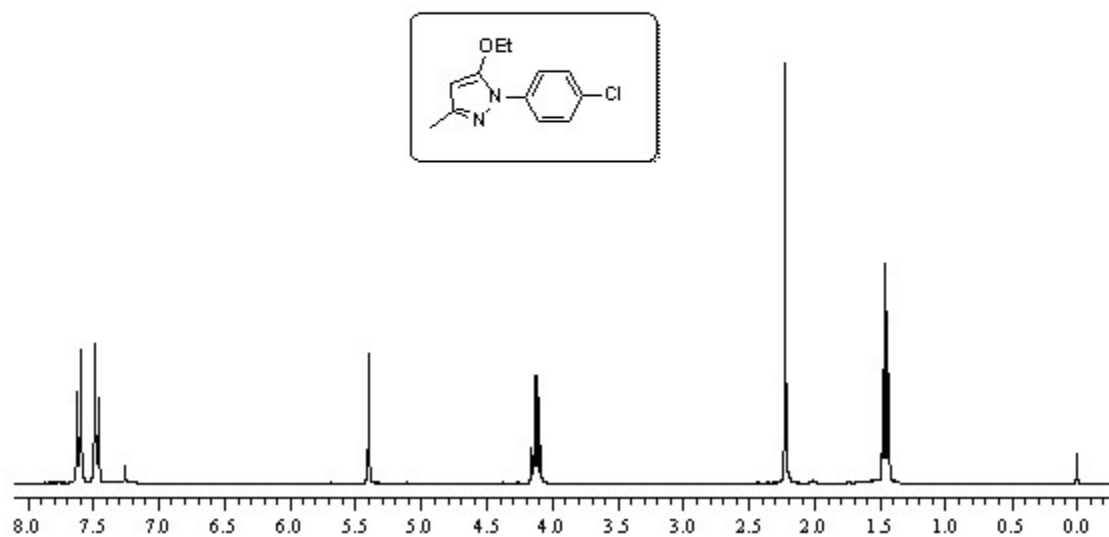


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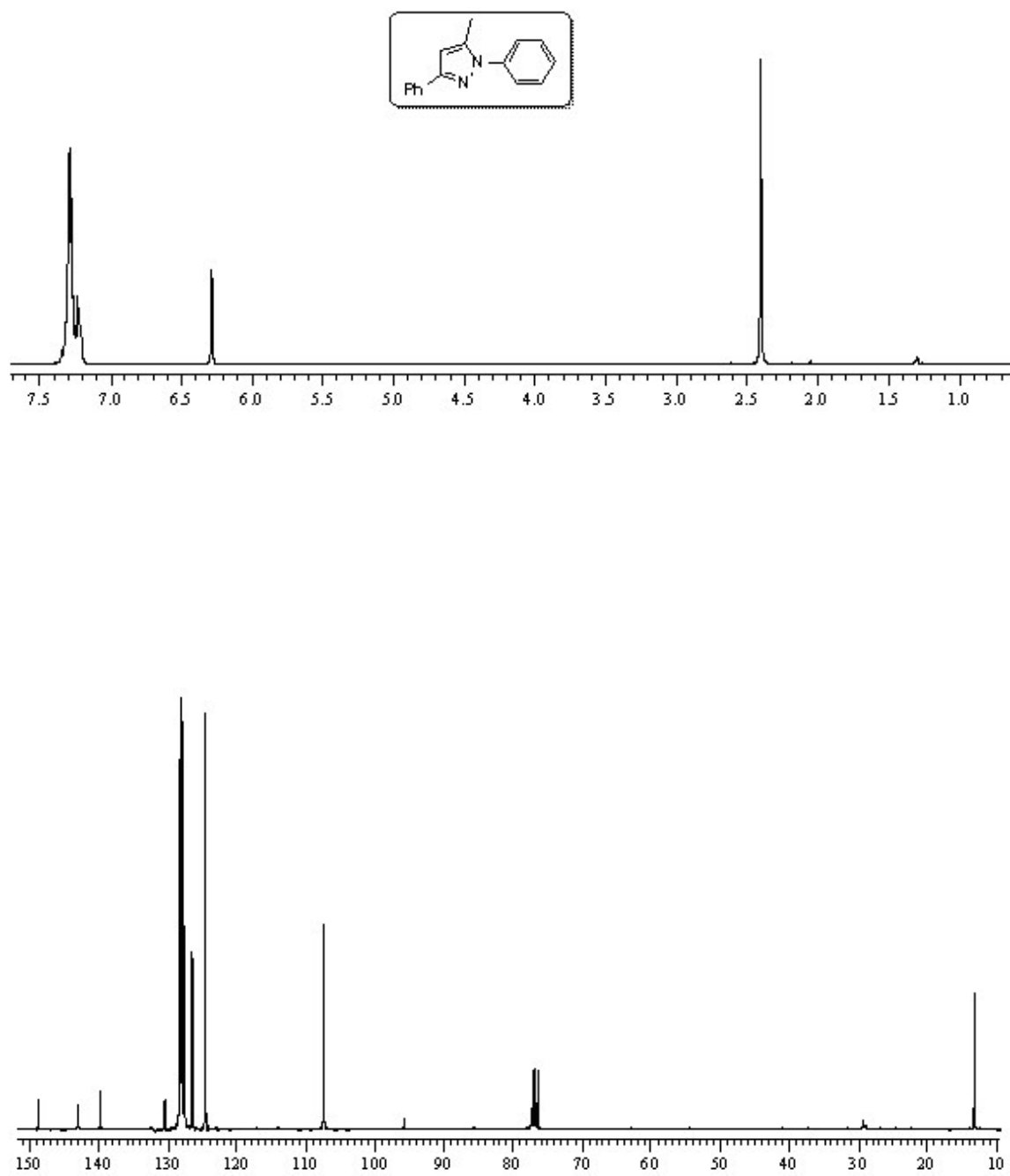


Table 2, entry 14:

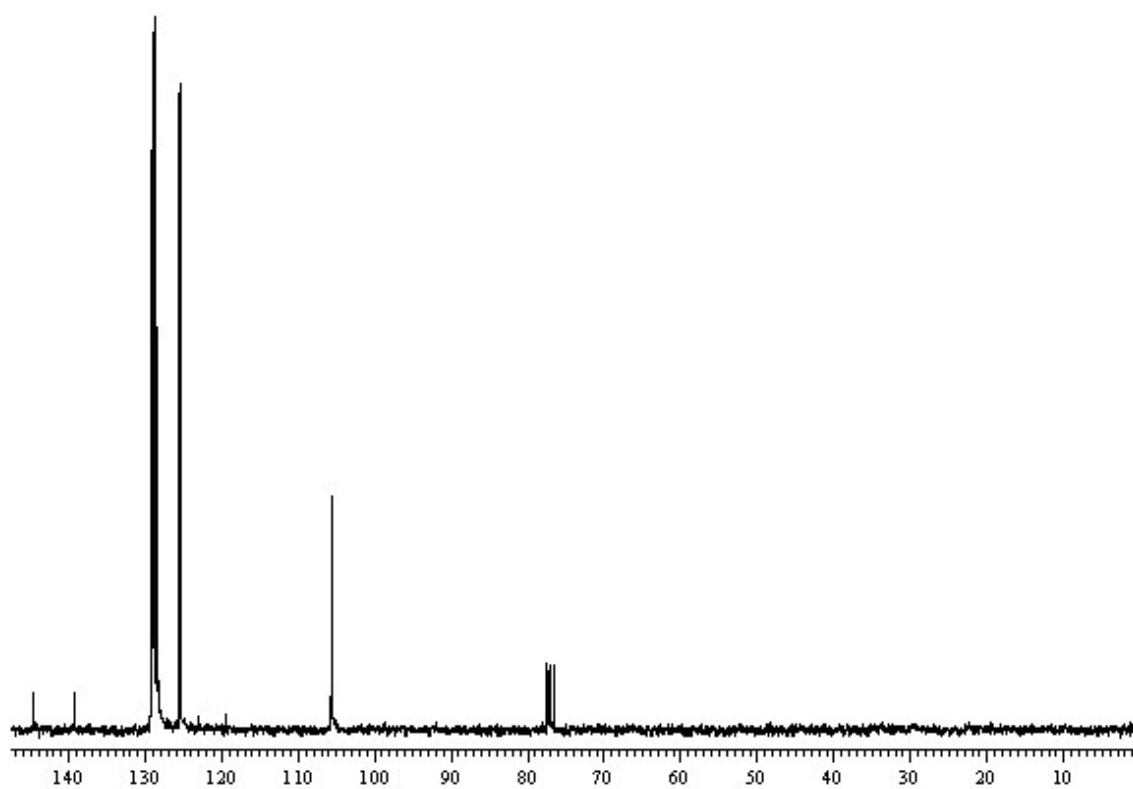
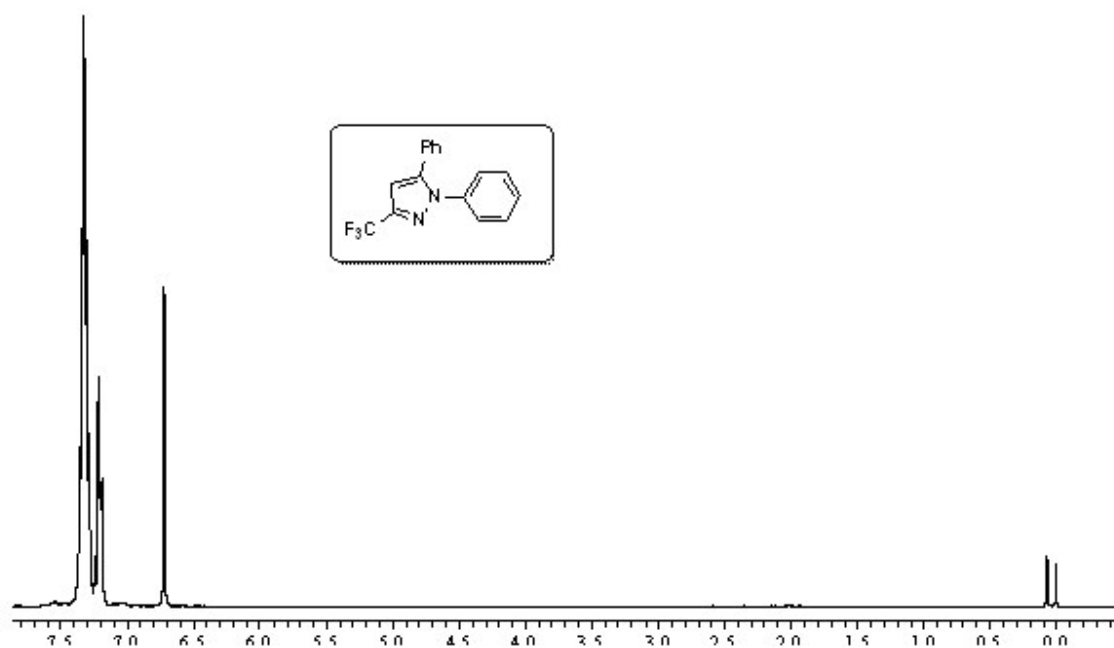


Table 2, entry 15:

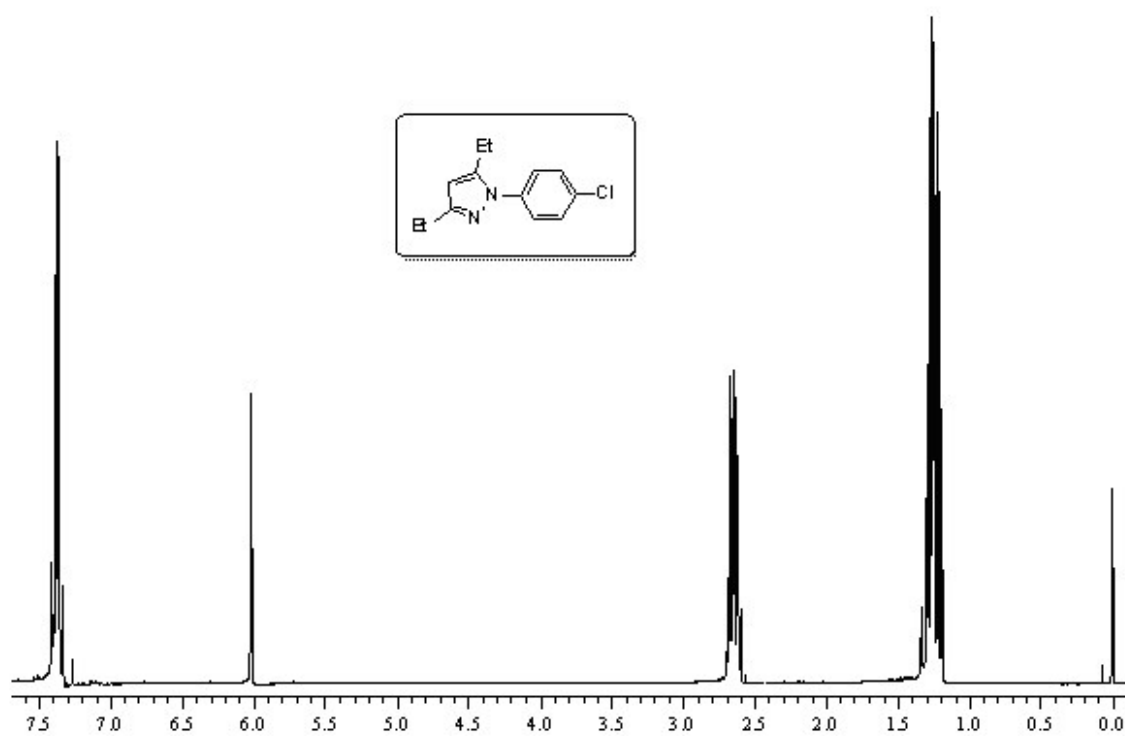


Table 2, entry 16:

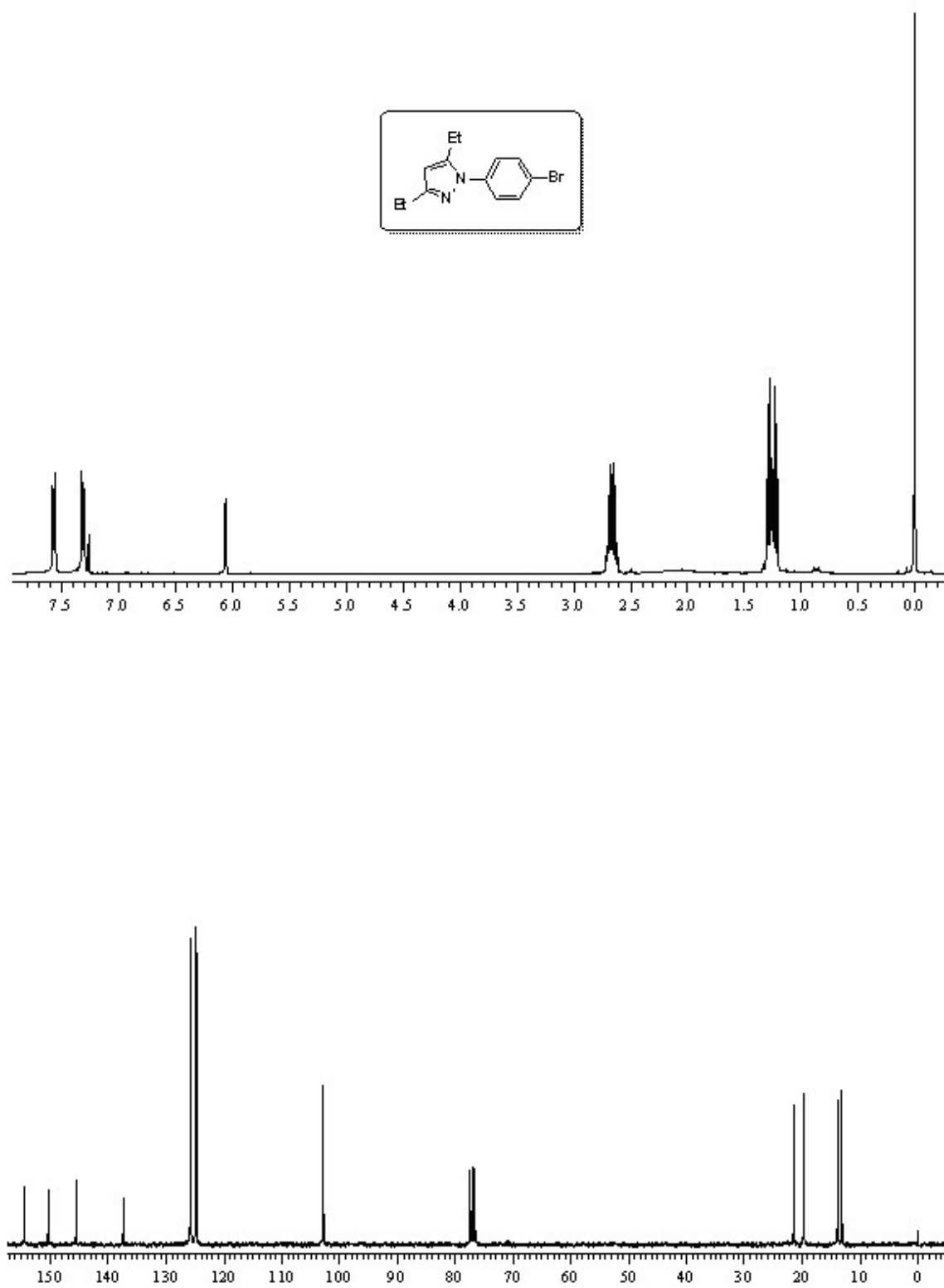


Table 2, entry 17:

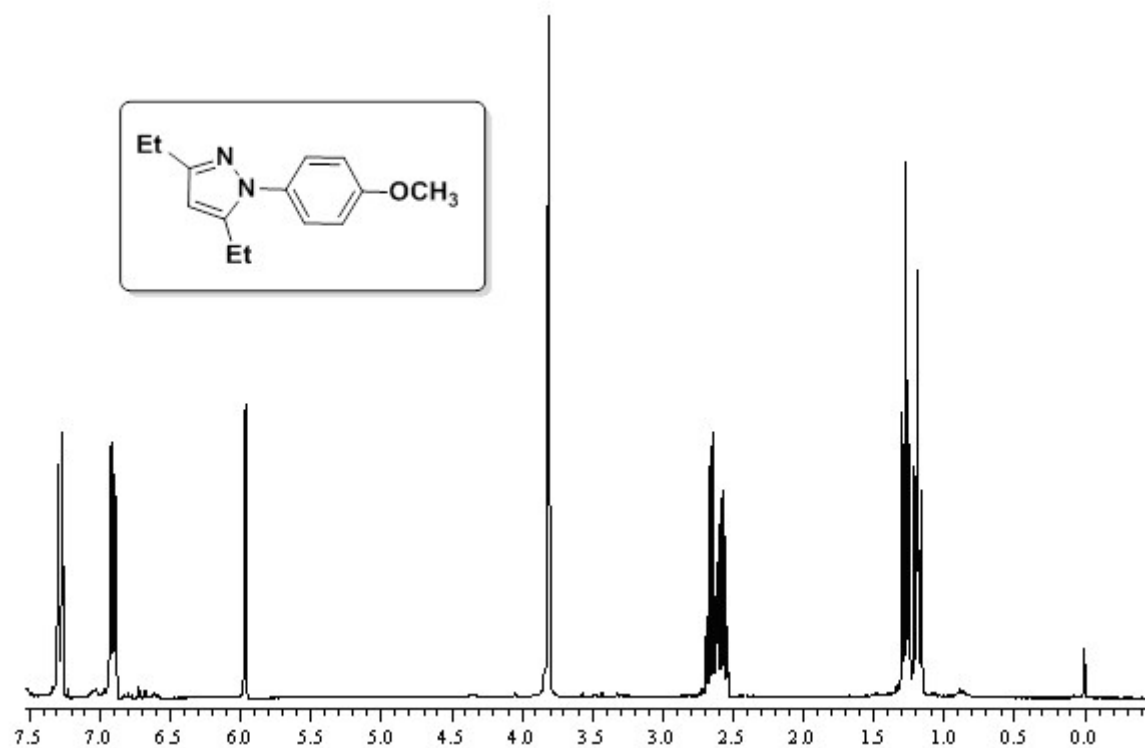


Table 2, entry 18:

