Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

"On Water" Synthesis of *N*-Unsubstituted Pyrazoles: Semicarbazide Hydrochloride as an Alternative to Hydrazine for Preparation of Pyrazole-3-carboxylate Derivatives and 3,5-disubstituted Pyrazoles

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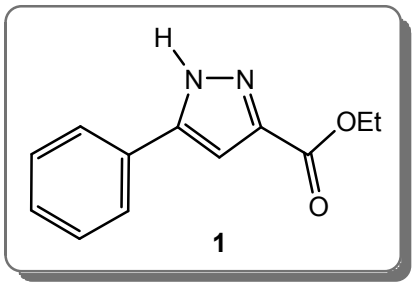
General Information.

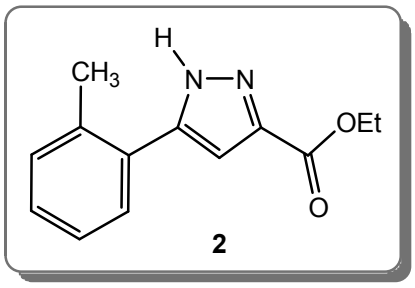
Melting points were measured by Stuart melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer with a KBr disc. ^{1}H and ^{13}C-NMR spectra were recorded on a Varian Gemini 200 MHz and a Bruker Avance III 500 MHz spectrometer. Single-crystal X-ray diffraction data for compound **9** and **16** were collected at room temperature (294(2) K) on an Agilent Gemini S diffractometer equipped with Mo *Kα* radiation (λ = 0.71073 Å) and Sapphire3 CCD detector. Data collection, integration and scaling of the reflections were performed with the *CRYSALISPRO* software.

Characterization data.



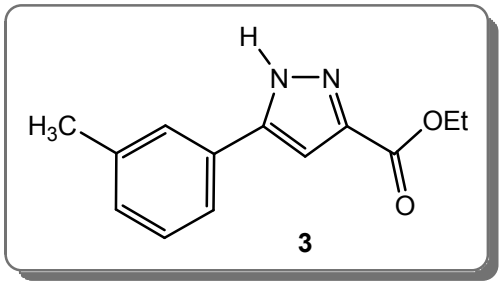
1

Ethyl 5-phenyl-1H-pyrazole-3-carboxylate (**1**): White powder (95% yield); **mp** 137-138 °C; **IR** (KBr): 3192; 1726; 1242; 1139; 762 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$) δ = 1.22 (t, *J* = 7.2 Hz, 3H, CH_3), 4.20 (q, *J* = 7.2 Hz, 2H, CH_2), 6.99 (s, 1H, Pz-H), 7.31-7.43 (m, 3H, Ar-H), 7.71 (dd, *J* = 8.0 and 1.6 Hz, 2H, Ar-H), 13.05 (bs, 1H, N-H) ppm; **^{13}C NMR** (50 MHz, $CDCl_3$) δ = 13.8, 60.7, 104.7, 125.5, 128.3, 128.7, 129.6, 141.3, 146.5, 161.2 ppm; Anal. Calcd. For $C_{12}H_{12}N_2O_2$ (216.24 g/mol): C, 66.65; H, 5.59; N, 12.96; Found: C, 66.51; H, 5.57; N, 12.98.



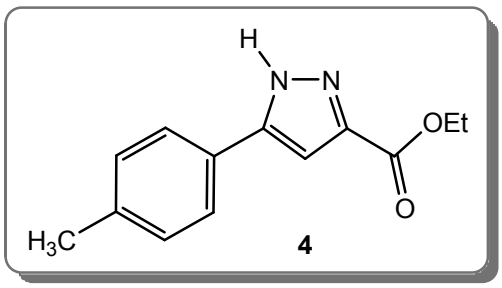
2

Ethyl 5-o-tolyl-1H-pyrazole-3-carboxylate (**2**): White crystalline solid (93% yield); **mp** 78-79 °C; **IR** (KBr): 3140; 1731; 1720; 1246; 1150; 765 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$) δ = 1.17 (t, *J* = 7.2 Hz, 3H, CH_3), 2.38 (s, 3H, CH_3), 4.16 (q, *J* = 7.2 Hz, 2H, CH_2), 6.88 (s, 1H, Pz-H), 7.12-7.26 (m, 3H, Ar-H), 7.44 (d, *J* = 7.2 Hz, 1H, Ar-H), 11.59 (bs, 1H, N-H) ppm; **^{13}C NMR** (50 MHz, $CDCl_3$) δ = 14.0, 20.8, 60.9, 108.1, 126.0, 128.6, 128.9, 129.5, 130.9, 135.9, 141.1, 146.1, 161.6 ppm; Anal. Calcd. For $C_{13}H_{14}N_2O_2$ (230.27 g/mol): C, 67.81; H, 6.13; N, 12.17; Found: C, 67.69; H, 6.15; N, 12.13.



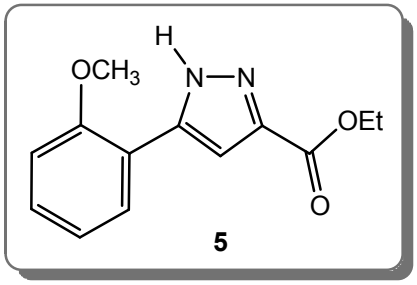
3

Ethyl 5-m-tolyl-1H-pyrazole-3-carboxylate (**3**): White powder (87% yield); **mp** 107-108 °C; **IR** (KBr): 3256; 1723; 1716; 1256; 1170; 780 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$) δ = 1.16 (t, *J* = 7.2 Hz, 3H, CH_3), 2.32 (s, 3H, CH_3), 4.14 (q, *J* = 7.2 Hz, 2H, CH_2), 6.96 (s, 1H, Pz-H), 7.09-7.13 (m, 1H, Ar-H), 7.24 (t, *J* = 7.2 Hz, 1H, Ar-H), 7.47-7.51 (m, 2H, Ar-H), 12.96 (bs, 1H, N-H) ppm; **^{13}C NMR** (50 MHz, $CDCl_3$) δ = 13.8, 21.2, 60.7, 104.8, 122.6, 126.2, 128.6, 129.1, 129.6, 138.3, 141.0, 147.0, 161.2 ppm; Anal. Calcd. For $C_{13}H_{14}N_2O_2$ (230.27 g/mol): C, 67.81; H, 6.13; N, 12.17; Found: C, 67.72; H, 6.11; N, 12.21.



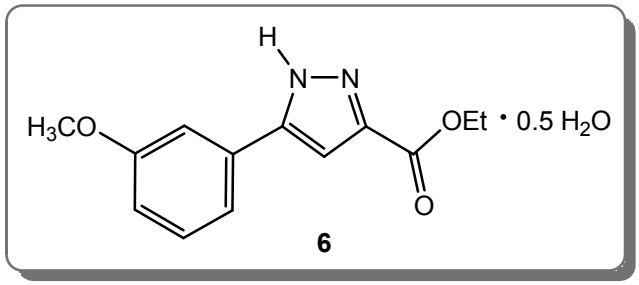
4

Ethyl 5-p-tolyl-1H-pyrazole-3-carboxylate (**4**): White powder (94% yield); **mp** 155-156 °C; **IR** (KBr): 3232; 3138; 1728; 1720; 1242; 1131; 816 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$) δ = 1.28 (t, *J* = 7.2 Hz, 3H, CH_3), 2.39 (s, 3H, CH_3), 4.27 (q, *J* = 7.2 Hz, 2H, CH_2), 7.00 (s, 1H, Pz-H), 7.21 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.62 (d, *J* = 8.0 Hz, 2H, Ar-H), 12.47 (bs, 1H, N-H) ppm; **^{13}C NMR** (50 MHz, $CDCl_3$) δ = 14.1, 21.2, 61.0, 105.0, 125.6, 127.6, 129.5, 138.4, 140.1, 148.4, 161.0 ppm; Anal. Calcd. For $C_{13}H_{14}N_2O_2$ (230.27 g/mol): C, 67.81; H, 6.13; N, 12.17; Found: C, 67.73; H, 6.12; N, 12.20.



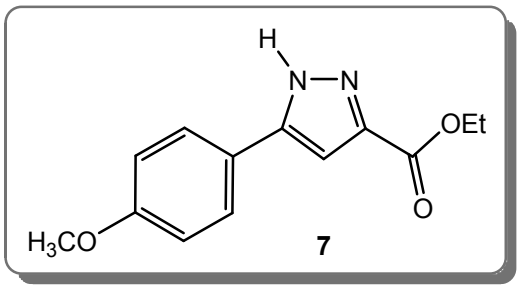
5

Ethyl 5-(2-methoxyphenyl)-1H-pyrazole-3-carboxylate (**5**): White crystalline solid (90% yield); **mp** 95-96 °C; **IR** (KBr): 3317; 1734; 1493; 1265; 1249; 1145; 748 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$) δ = 1.39 (t, *J* = 7.2 Hz, 3H, CH_3), 3.96 (s, 3H, OCH_3), 4.40 (q, *J* = 7.2 Hz, 2H, CH_2), 6.98-7.08 (m, 2H, Ar-H), 7.18 (s, 1H, Pz-H), 7.28-7.37 (m, 1H, Ar-H), 7.70 (dd, *J* = 7.6 and 1.6 Hz, 1H, Ar-H), 11.95 (bs, 1H, N-H) ppm; **^{13}C NMR** (50 MHz, $CDCl_3$) δ = 14.2, 55.7, 60.8, 105.6, 111.5, 117.1, 121.4, 127.9, 129.7, 142.4, 143.1, 155.9, 162.4 ppm; Anal. Calcd. For $C_{13}H_{14}N_2O_3$ (246.27 g/mol): C, 63.40; H, 5.73; N, 11.38; Found: C, 63.22; H, 5.71; N, 11.38.



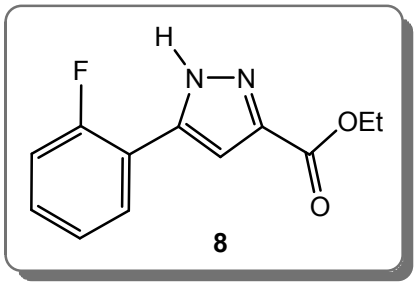
6

Ethyl 5-(3-methoxyphenyl)-1H-pyrazole-3-carboxylate · 0.5 H_2O (**6**): White powder (93% yield); **mp** 97-98 °C; **IR** (KBr): 3257; 1726; 1709; 1268; 1222; 776 cm^{-1}; **1H NMR** (200 MHz, $CDCl_3$) δ = 1.20 (t, *J* = 7.2 Hz, 3H, CH_3), 3.76 (s, 3H, OCH_3), 4.19 (q, *J* = 7.2 Hz, 2H, CH_2), 6.82-6.91 (m, 1H, Ar-H), 6.96 (s, 1H, Pz-H), 7.26-7.28 (m, 3H, Ar-H), 12.16 (bs, 1H, N-H) ppm; **^{13}C NMR** (50 MHz, $CDCl_3$) δ = 14.0, 55.2, 61.0, 105.2, 110.6, 114.6, 118.1, 129.9, 131.4, 140.2, 147.9, 159.9, 160.9 ppm; Anal. Calcd. For $C_{13}H_{14}N_2O_3 \cdot 0.5H_2O$ (255.27 g/mol): C, 61.17; H, 5.93; N, 10.97; Found: C, 61.33; H, 5.91; N, 11.01.



7

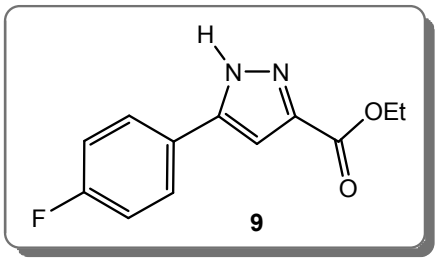
Ethyl 5-(4-methoxyphenyl)-1H-pyrazole-3-carboxylate (**7**): White crystalline solid (98% yield); **mp** 156-157 °C; **IR** (KBr): 3192; 1724; 1511; 1280; 1244; 773 cm^{-1}; **1H NMR** (200 MHz, $CDCl_3$) δ = 1.21 (t, *J* = 7.2 Hz, 3H, CH_3), 3.81 (s, 3H, OCH_3), 4.19 (q, *J* = 7.2 Hz, 2H, CH_2), 6.88 (s, 1H, Pz-H), 6.89 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.62 (d, *J* = 8.8 Hz, 2H, Ar-H), 12.47 (bs, 1H, N-H) ppm; **^{13}C NMR** (50 MHz, $CDCl_3$) δ = 14.0, 55.2, 60.9, 104.5, 114.3, 123.0, 127.0, 140.3, 147.8, 159.9, 161.1 ppm; Anal. Calcd. For $C_{13}H_{14}N_2O_3$ (246.27 g/mol): C, 63.40; H, 5.73; N, 11.38; Found: C, 63.25; H, 5.74; N, 11.34.



8

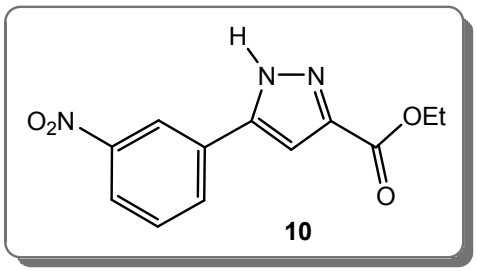
Ethyl 5-(2-fluorophenyl)-1H-pyrazole-3-carboxylate (**8**): White powder (89% yield); **mp** 120-121 °C; **IR** (KBr): 3162; 1733; 1722; 1423; 1253; 1202; 762 cm^{-1}; **1H NMR** (200 MHz, $CDCl_3$) δ = 1.42 (t, *J* = 7.2 Hz, 3H, CH_3), 4.43 (q, *J* = 7.2 Hz, 2H, CH_2), 7.13-7.20 (m, 1H, Ar-H), 7.23-7.28 (m, 2H, Ar-H and Pz-H), 7.30-7.41 (m, 1H, Ar-H), 7.87 (td, *J* = 7.6 and 1.8 Hz, 1H, Ar-H), 11.41 (bs, 1H, N-H) ppm; **^{13}C NMR** (50 MHz, $CDCl_3$) δ = 14.1, 61.2, 108.0 (d, J_{CF} = 7 Hz), 116.2 (d, J_{CF} = 22 Hz), 118.4 (d, J_{CF} = 12 Hz), 124.5 (d, J_{CF} = 3 Hz), 128.1 (d, J_{CF} = 3 Hz),

129.9 (d, J_{CF} = 8 Hz), 139.8, 143.0, 159.6 (d, J = 248 Hz), 160.9 ppm; Anal. Calcd. For $C_{12}H_{11}N_2O_2F$ (234.23 g/mol): C, 61.54; H, 4.74; N, 11.96; Found: C, 61.32; H, 4.73; N, 11.92.



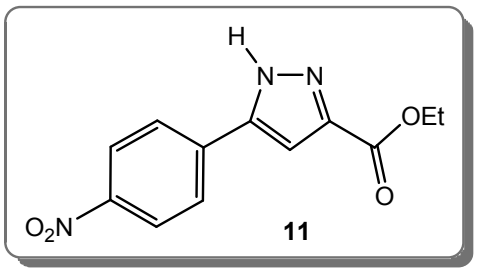
9

Ethyl 5-(4-fluorophenyl)-1H-pyrazole-3-carboxylate (**9**): White powder (98% yield); **mp** 152-153 °C; **IR** (KBr): 3196; 3170; 3134; 1728; 1508; 1247; 841; 779 cm^{-1}; **1H NMR** (200 MHz, $CDCl_3$) δ = 1.27 (t, J = 7.2 Hz, 3H, CH_3), 4.26 (q, J = 7.2 Hz, 2H, CH_2), 6.95 (s, 1H, Pz-H), 7.07 (t, J = 8.6 Hz, 2H, Ar-H), 7.70 (dd, J = 8.6 and 5.3 Hz, 2H, Ar-H), 12.61 (bs, 1H, N-H) ppm; **^{13}C NMR** (50 MHz, $CDCl_3$) δ = 14.2, 61.4, 105.4, 115.8 (d, J_{CF} = 22 Hz), 127.5 (d, J_{CF} = 8 Hz), 137.8, 150.0, 160.1, 163.0 (d, J_{CF} = 247 Hz); Anal. Calcd. For $C_{12}H_{11}N_2O_2F$ (234.23 g/mol): C, 61.54; H, 4.74; N, 11.96; Found: C, 61.42; H, 4.75; N, 11.94.



10

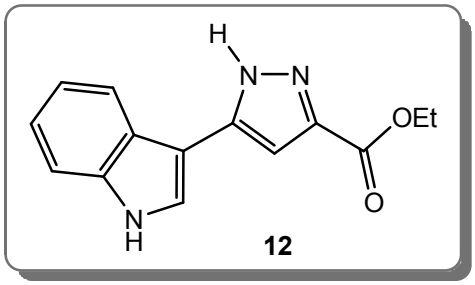
Ethyl 5-(3-nitrophenyl)-1H-pyrazole-3-carboxylate (**10**): Light yellow powder (85% yield); **mp** 147-148 °C; **IR** (KBr): 3313; 1741; 1700; 1534; 1348; 1246; 745 cm^{-1}; **1H NMR** (200 MHz, $(CD_3)_2CO$) δ = 1.36 (t, J = 7.2 Hz, 3H, CH_3), 4.37 (q, J = 7.2 Hz, 2H, CH_2), 7.40 (s, 1H, Pz-H), 7.72 (t, J = 8.0 Hz, 1H, Ar-H), 8.18 (ddd, J = 8.0, 2.4 and 1.0 Hz, 1H, Ar-H), 8.30 (ddd, J = 8.0, 2.4 and 1.0 Hz, 1H, Ar-H), 8.71 (t, J = 2.4 Hz, 1H, Ar-H), 13.35 (bs, 1H, N-H) ppm; **^{13}C NMR** (50 MHz, $(CD_3)_2CO$) δ = 14.5, 61.7, 106.8, 120.6, 123.2, 130.9, 132.2, 135.0, 138.2, 149.7, 160.1 ppm; Anal. Calcd. For $C_{12}H_{11}N_3O_4$ (261.24 g/mol): C, 55.17; H, 4.24; N, 16.08; Found: C, 55.09; H, 4.25; N, 16.05.



11

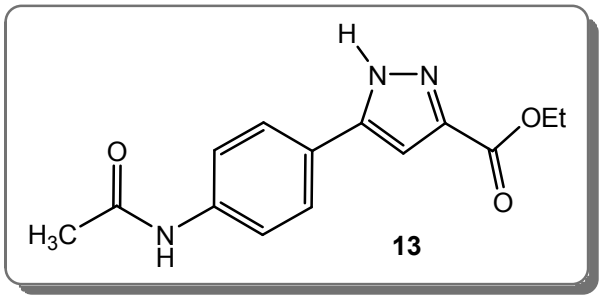
Ethyl 5-(4-nitrophenyl)-1H-pyrazole-3-carboxylate (**11**): Light yellow powder (90% yield); **mp** 209-210 °C; **IR** (KBr): 3139; 1736; 1523; 1338; 1260; 854 cm^{-1}; **1H NMR** (200 MHz, $(CD_3)_2CO$) δ = 1.36 (t, J = 7.2 Hz, 3H, CH_3), 4.37 (q, J = 7.2 Hz, 2H, CH_2), 7.45 (s, 1H, Pz-H), 8.19 (d, J = 9.0 Hz, 2H, Ar-H), 8.32 (d, J = 9.0 Hz, 2H, Ar-H), 13.42 (s, 1H, N-H) ppm; **^{13}C**

NMR (125 MHz, $(CD_3)_2CO$) δ = 15.0, 62.3, 108.0, 125.4, 127.6, 137.4, 140.8, 148.8, 151.4, 160.2 ppm; Anal. Calcd. For $C_{12}H_{11}N_3O_4$ (261.24 g/mol): C, 55.17; H, 4.24; N, 16.08; Found: C, 55.32; H, 4.23; N, 16.12.



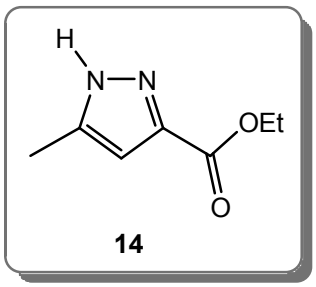
12

Ethyl 5-(1H-indol-3-yl)-1H-pyrazole-3-carboxylate (**12**): White powder (97% yield); **mp** 152-153 °C; **IR** (KBr): 3349; 3305; 1712; 1702; 1257; 1244; 743 cm^{-1}; **1H NMR** (200 MHz, $(CD_3)_2CO$) δ = 1.37 (t, *J* = 7.2 Hz, 3H, CH_3), 4.36 (q, *J* = 7.2 Hz, 2H, CH_2), 7.11 (s, 1H, Pz-H), 7.15-7.25 (m, 2H, Ar-H), 7.46-7.52 (m, 1H, Ar-H), 7.86 (d, *J* = 2.6 Hz, 1H, Ar-H), 8.08 (s, 1H, Ar-H), 10.57 (s, 1H, NH_{indole}), 12.83 (s, 1H, $NH_{pyrazole}$); **^{13}C NMR** (50 MHz, $(CD_3)_2CO$) δ = 14.6, 61.1, 105.3, 112.6, 120.9, 122.9, 124.2, 126.1, 137.8; Anal. Calcd. For $C_{14}H_{13}N_3O_2$ (255.28 g/mol): C, 65.87; H, 5.13; N, 16.46; Found: C, 65.62; H, 5.11; N, 16.48.



13

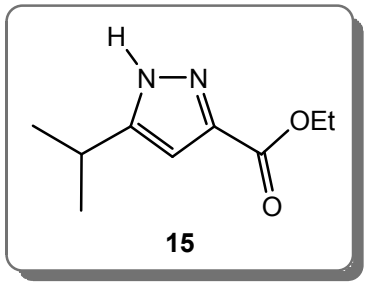
Ethyl 5-(4-acetamidophenyl)-1H-pyrazole-3-carboxylate (**13**, main tautomer): White powder (96% yield); **mp** 226-227 °C; **IR** (KBr): 3343; 3211; 1715; 1542; 1253; 836; 773 cm^{-1}; **1H NMR** (200 MHz, DMSO-d_6) δ = 1.30 (t, *J* = 7.2 Hz, 3H, CH_3), 2.05 (s, 3H, CH_3CO), 4.29 (q, *J* = 7.2 Hz, 2H, CH_2), 7.10 (s, 1H, Pz-H), 7.62-7.77 (m, 4H, Ar-H), 10.10 (s, 1H, NH-CO), 13.84 (s, 1H, NH); **^{13}C NMR** (50 MHz, DMSO-d_6) δ = 14.4, 24.2, 60.7, 104.8, 119.6, 125.2, 126.1, 139.6, 140.6, 146.7, 161.2, 168.9; Anal. Calcd. For $C_{14}H_{15}N_3O_3$ (273.29 g/mol): C, 61.53; H, 5.53; N, 15.38; Found: C, 61.67; H, 5.55; N, 15.40.



14

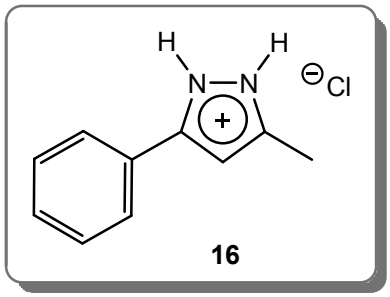
Ethyl 5-methyl-1H-pyrazole-3-carboxylate (**14**, mixture of tautoisomers): White powder (86% yield); **mp** 77-78 °C; **IR** (KBr): 3209, 3145, 1720, 1580, 1221, 1174, 779 cm^{-1}; **^{1}H NMR** (200

MHz, $CDCl_3$) δ = 1.36 (t, *J* = 7.2 Hz, 3H, CH_3), 2.36 and 2.37 (s, 3H, CH_3), 4.36 (q, *J* = 7.2 Hz, 2H, CH_2), 6.57 and 6.58 (s, 1H, Pz-H), 9.29 (bs, 1H, N-H) ppm; **^{13}C NMR** (50 MHz, $CDCl_3$) δ = 11.3, 14.2, 60.8, 107.1, 141.8, 142.7, 162.0 ppm; Anal. Calcd. For $C_7H_{10}N_2O_2$ (154.17 g/mol): C, 54.53; H, 6.54; N, 18.17; Found: C, 54.38; H, 6.56; N, 18.15.



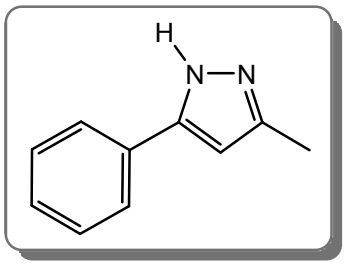
15

Ethyl 5-isopropyl-1H-pyrazole-3-carboxylate (**15**, mixture of tautoisomers): White powder (95% yield); **mp** 62-63 °C; **IR** (KBr): 3245, 3136, 1712, 1212, 1174, 782 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$) δ = 1.27 (d, *J* = 7.0 Hz, 6H, CH_3), 1.32 (t, *J* = 7.2 Hz, 3H, CH_3), 3.03 and 3.04 (septet, *J* = 7.0 Hz, 1H, CH), 4.34 (q, *J* = 7.2 Hz, 2H, CH_2), 6.58 and 6.59 (s, 1H, Pz-H), 10.16 (bs, 1H, N-H) ppm; **^{13}C NMR** (50 MHz, $CDCl_3$) δ = 14.2, 22.3, 26.3, 60.8, 104.6, 140.8, 154.2, 161.7 ppm; Anal. Calcd. For $C_9H_{14}N_2O_2$ (182.22 g/mol): C, 59.32; H, 7.74; N, 15.37; Found: C, 59.25; H, 7.72; N, 15.39.

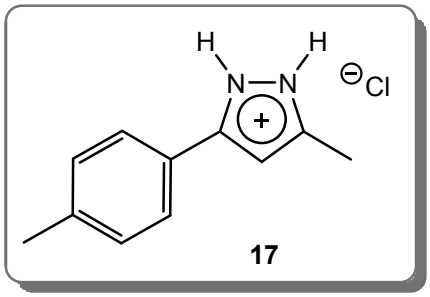


16

3(5)-Methyl-5(3)-phenyl-1H-pyrazolium chloride (**16**, mixture of tautoisomers): White powder (77% yield); **IR** (KBr): 3128, 3062, 1590, 1583, 1077, 762 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$) δ = 2.340 and 2.342 (s, 3H, CH_3), 6.38 (s, 1H, Pz-H), 7.32-7.43 (m, 3H, Ar-H), 7.71-7.77 (m, 2H, Ar-H), 9.87 (s, 2H, N-H) ppm; **^{13}C NMR** (50 MHz, $CDCl_3$) δ = 11.6, 102.7, 126.3, 128.9 (2C, overlapped), 130.0, 144.1, 148.6 ppm.

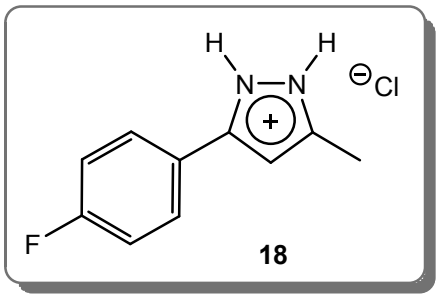


3(5)-Methyl-5(3)-phenyl-1H-pyrazole (mixture of tautoisomers): **^{1}H NMR** (200 MHz, $CDCl_3$) δ = 2.23 (s, 3H, CH_3), 6.31 and 6.32 (s, 1H, Pz-H), 7.22-7.38 (m, 3H, Ar-H), 7.68-7.72 (m, 2H, Ar-H), 11.63 (bs, 1H, N-H) ppm; **^{13}C NMR** (50 MHz, $CDCl_3$) δ = 11.5, 102.0, 125.7, 127.7, 128.6, 132.6, 143.2, 149.9 ppm.



17

3(5)-Methyl-5(3)-(4-methylphenyl)-1H-pyrazolium chloride (**17**, mixture of tautoisomers): White powder (80% yield); **IR** (KBr): 3134, 1619, 1612, 1454, 1271, 796 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$) δ = 2.32 and 2.33 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 6.32 and 6.35 (s, 1H, Pz-H), 7.17 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.61 (d, *J* = 8.2 Hz, 2H, Ar-H), 8.76 (bs, 2H, N-H) ppm; **^{13}C NMR** (50 MHz, $CDCl_3$) δ = 11.7, 21.2, 102.3, 126.1, 127.7, 129.5, 138.6, 144.0, 148.7 ppm.



18

3(5)-Methyl-5(3)-(4-fluorophenyl)-1H-pyrazolium chloride (**18**, mixture of tautoisomers): White powder (75% yield); **IR** (KBr): 3080, 1610, 1594, 1523, 1223, 837 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$) δ = 2.291 and 2.294 (s, 3H, CH_3), 6.28 and 6.29 (s, 1H, Pz-H), 6.99-7.10 (m, 2H, Ar-H), 7.62 (bs, 2H, Pz-H) 7.63-7.73 (m, 2H, Ar-H) ppm; **^{13}C NMR** (50 MHz, $CDCl_3$) δ = 11.5, 102.0, 115.6 (d, J_{CF} = 22 Hz), 127.5 (d, J_{CF} = 8 Hz), 128.7 (d, J_{CF} = 3 Hz), 142.7, 149.5, 162.7 (d, J_{CF} = 246 Hz) ppm.

Copies of ^{1}H and ^{13}C NMR spectra.

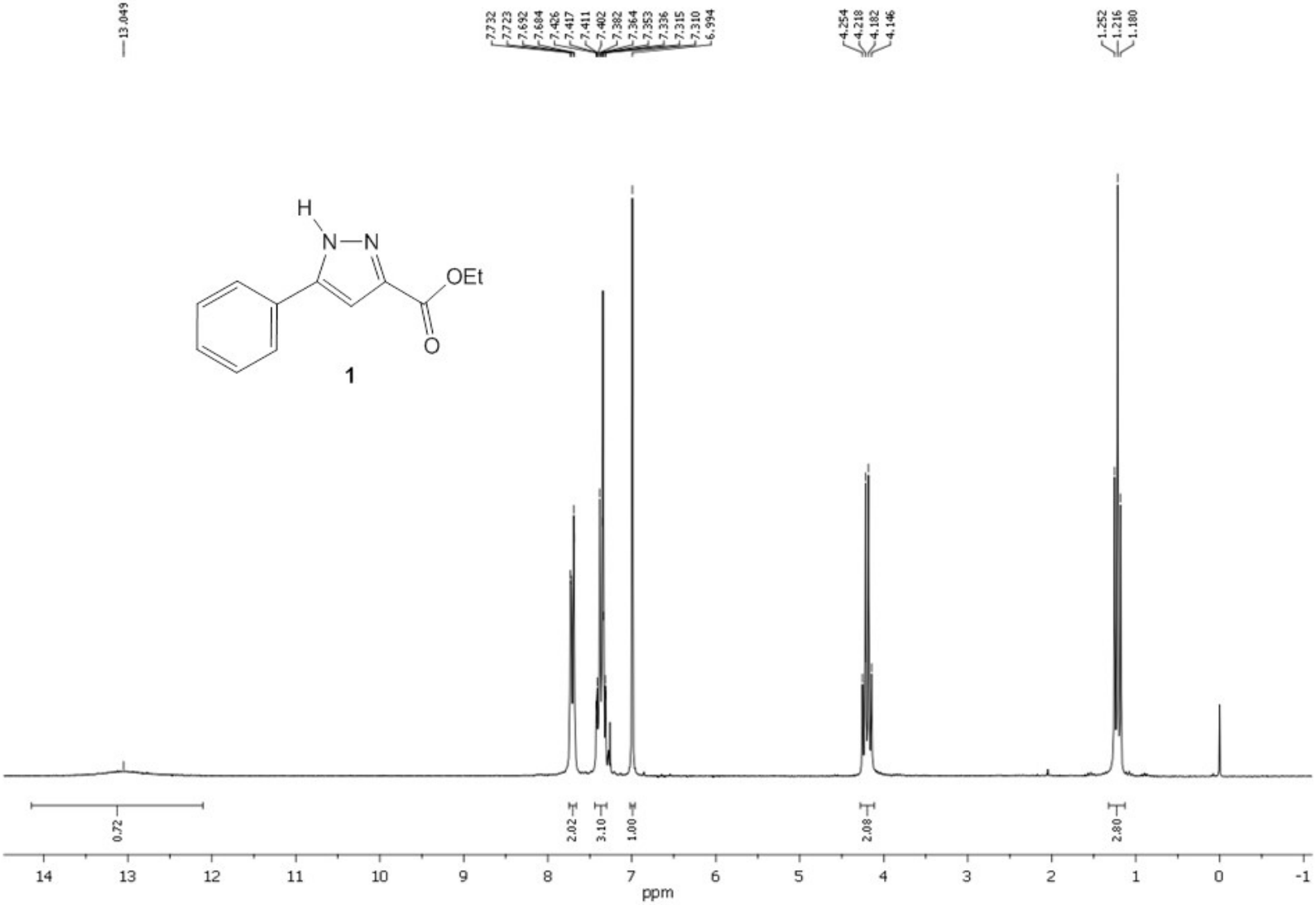


Fig. S1. ^{1}H NMR spectrum of **1** in $CDCl_3$ (200 MHz).

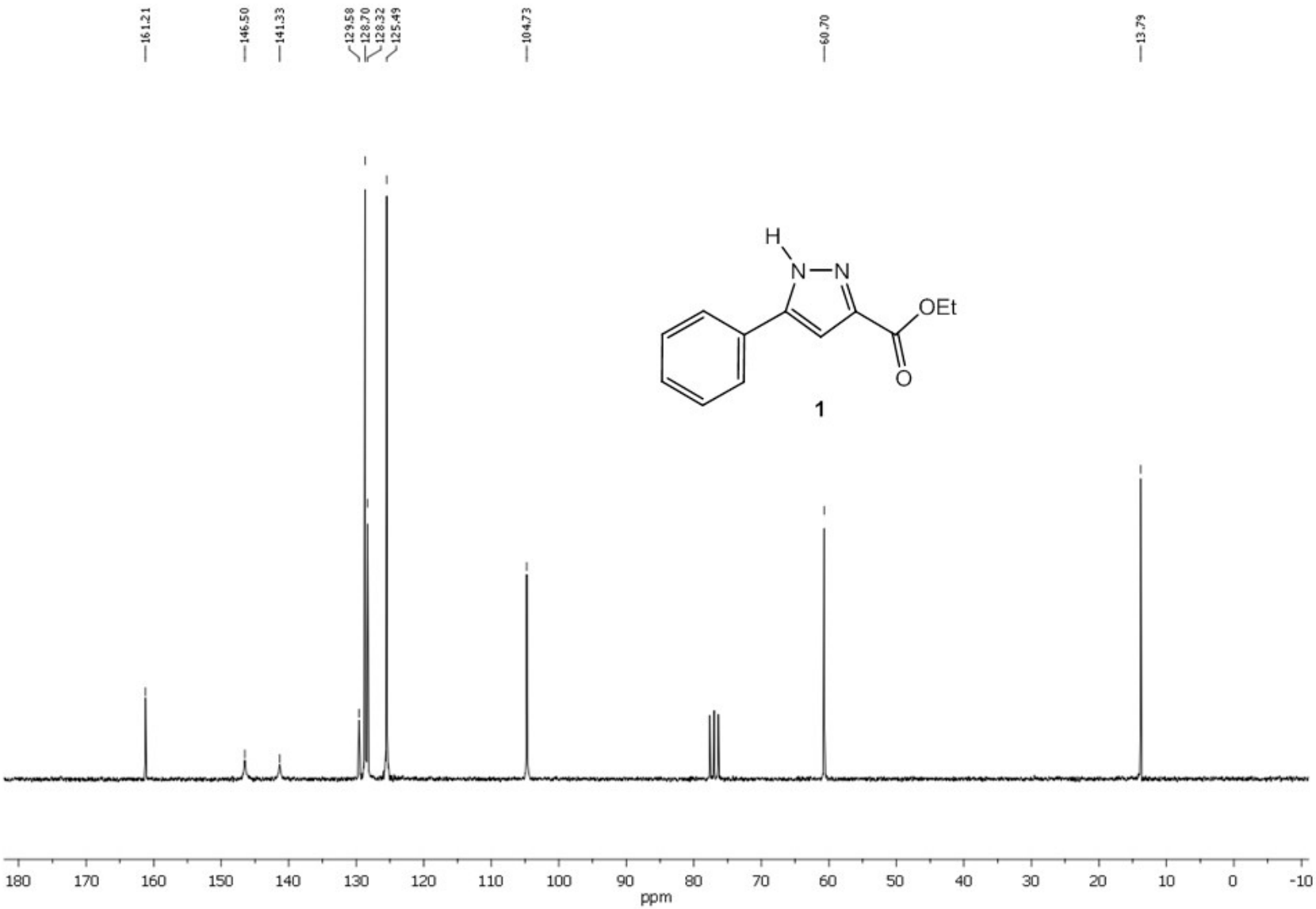


Fig. S2. ^{13}C NMR spectrum of **1** in $CDCl_3$ (50 MHz).

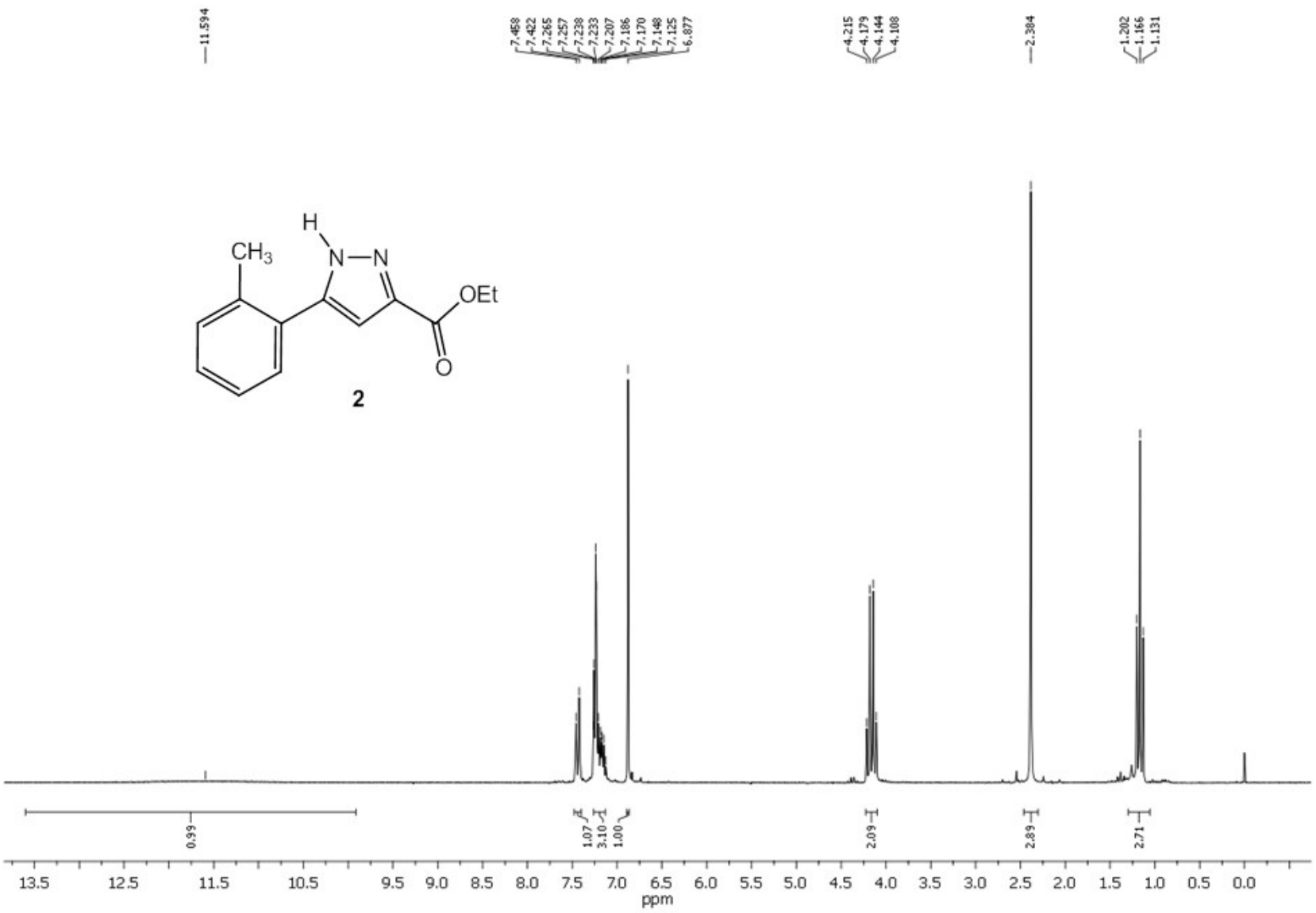


Fig. S3. ^{1}H NMR spectrum of **2** in $CDCl_3$ (200 MHz).

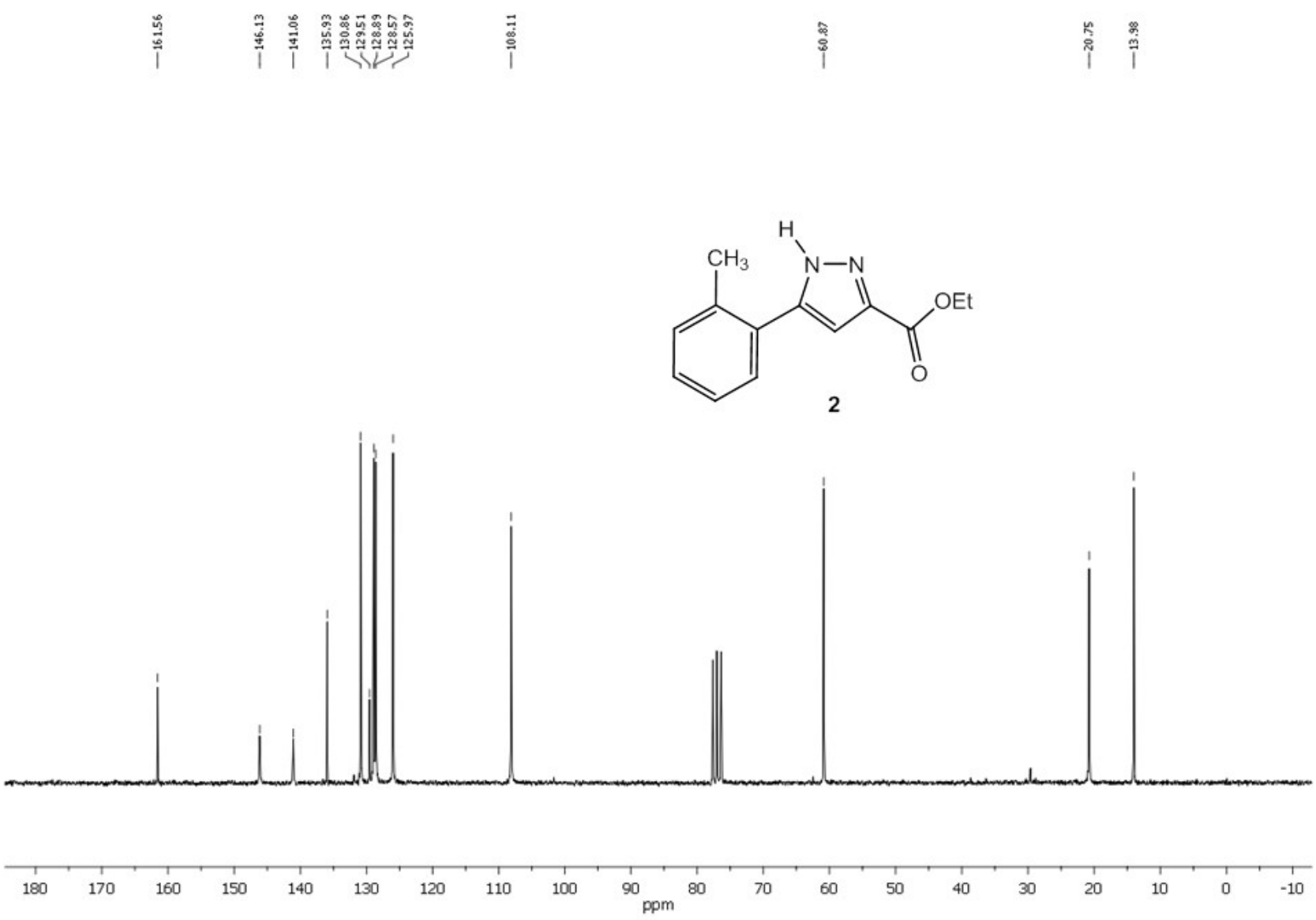


Fig. S4. ^{13}C NMR spectrum of **2** in $CDCl_3$ (50 MHz).

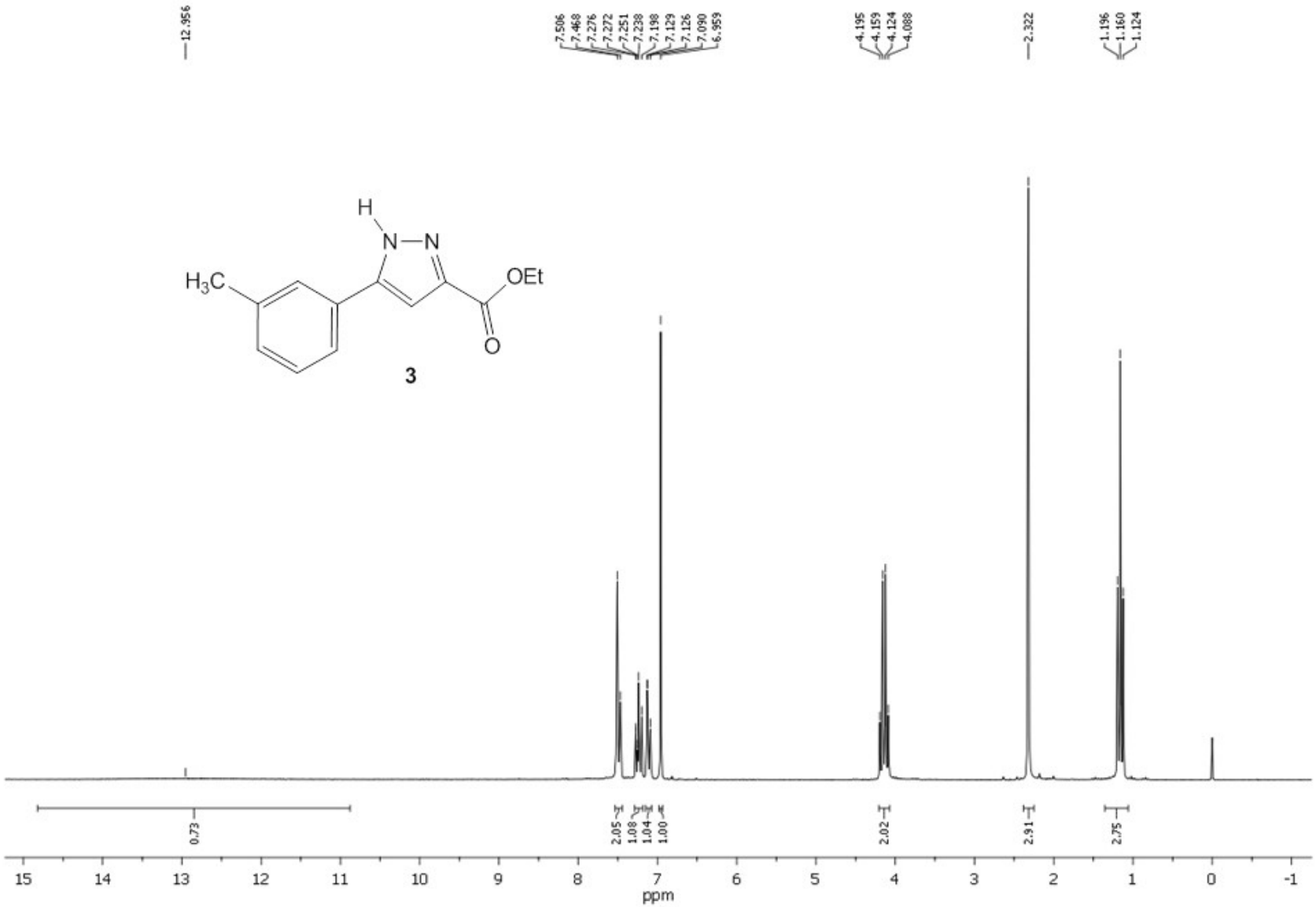


Fig. S5. ^{13}H NMR spectrum of **3** in $CDCl_3$ (200 MHz).

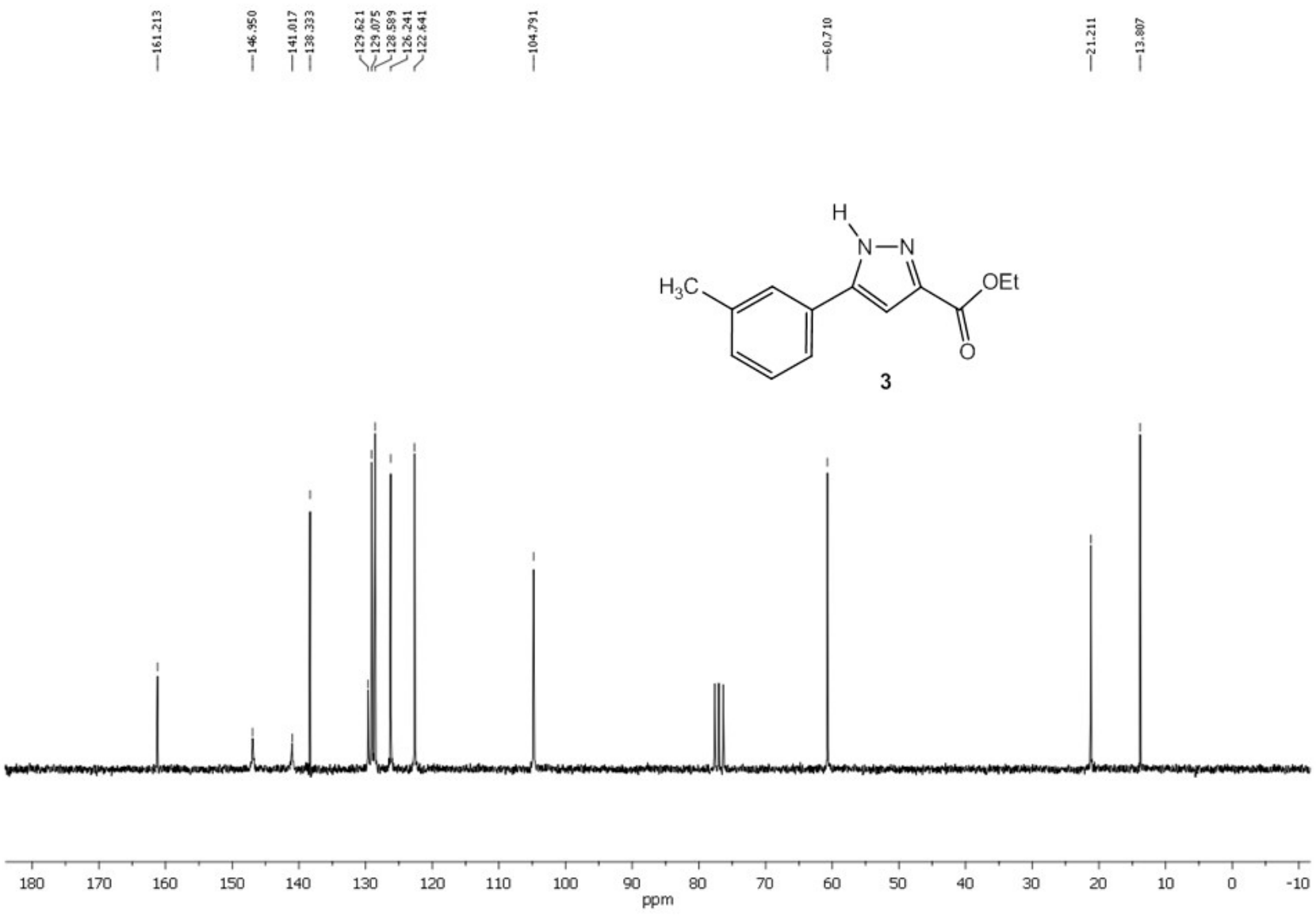


Fig. S6. ^{13}C NMR spectrum of **3** in $CDCl_3$ (50 MHz).

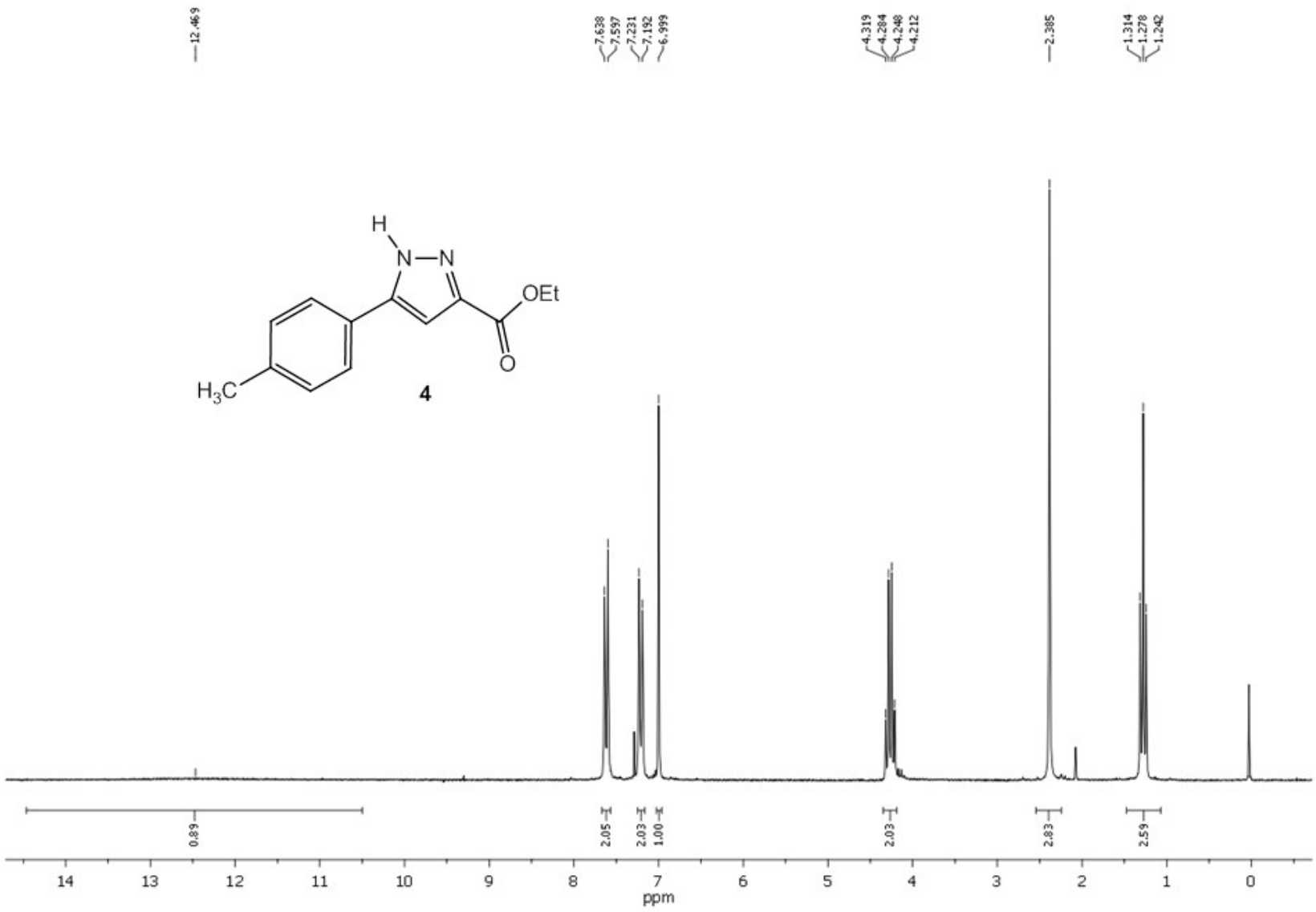


Fig. S7. ^{13}H NMR spectrum of **4** in $CDCl_3$ (200 MHz).

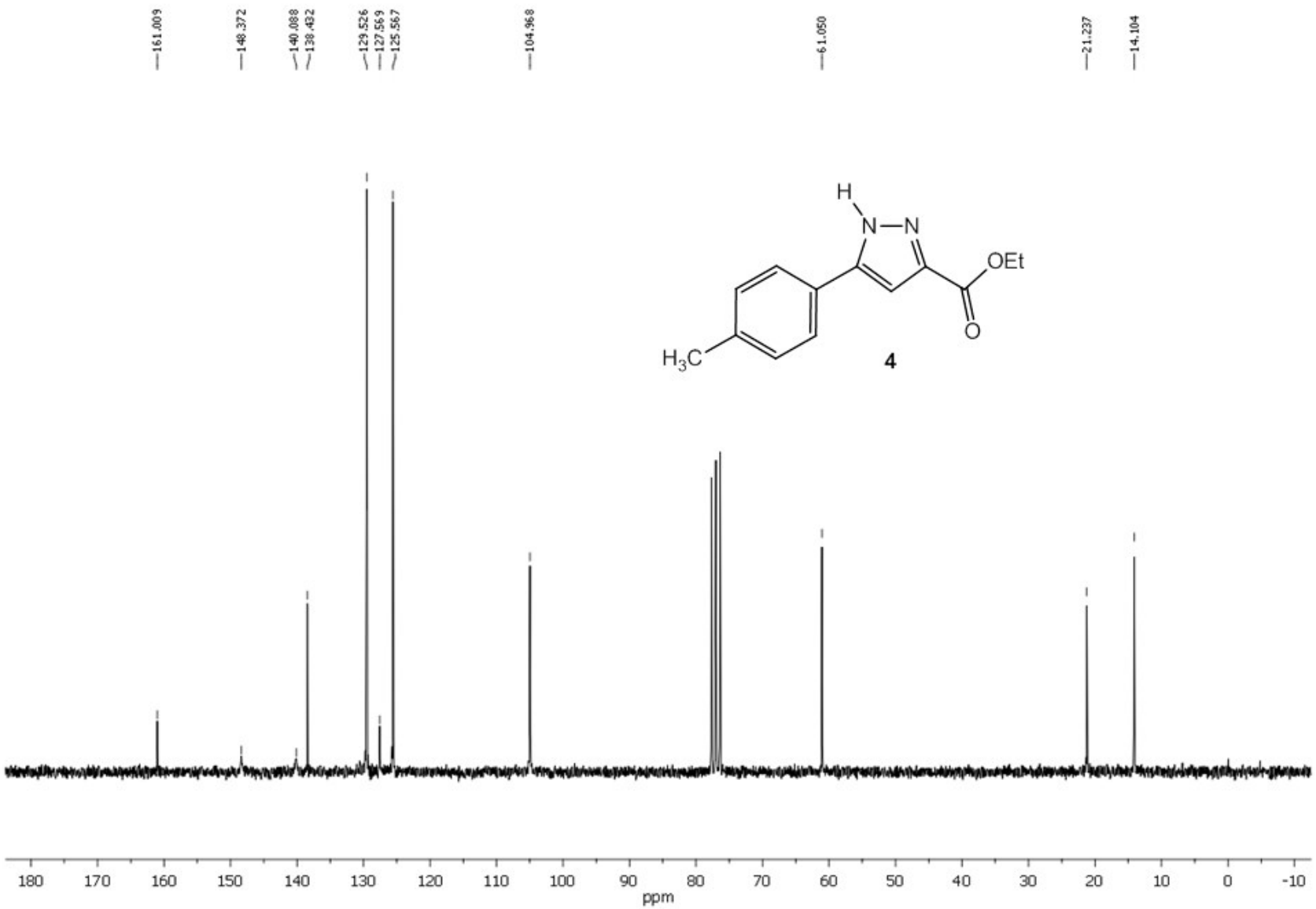


Fig. S8. ^{13}C NMR spectrum of **4** in $CDCl_3$ (50 MHz).

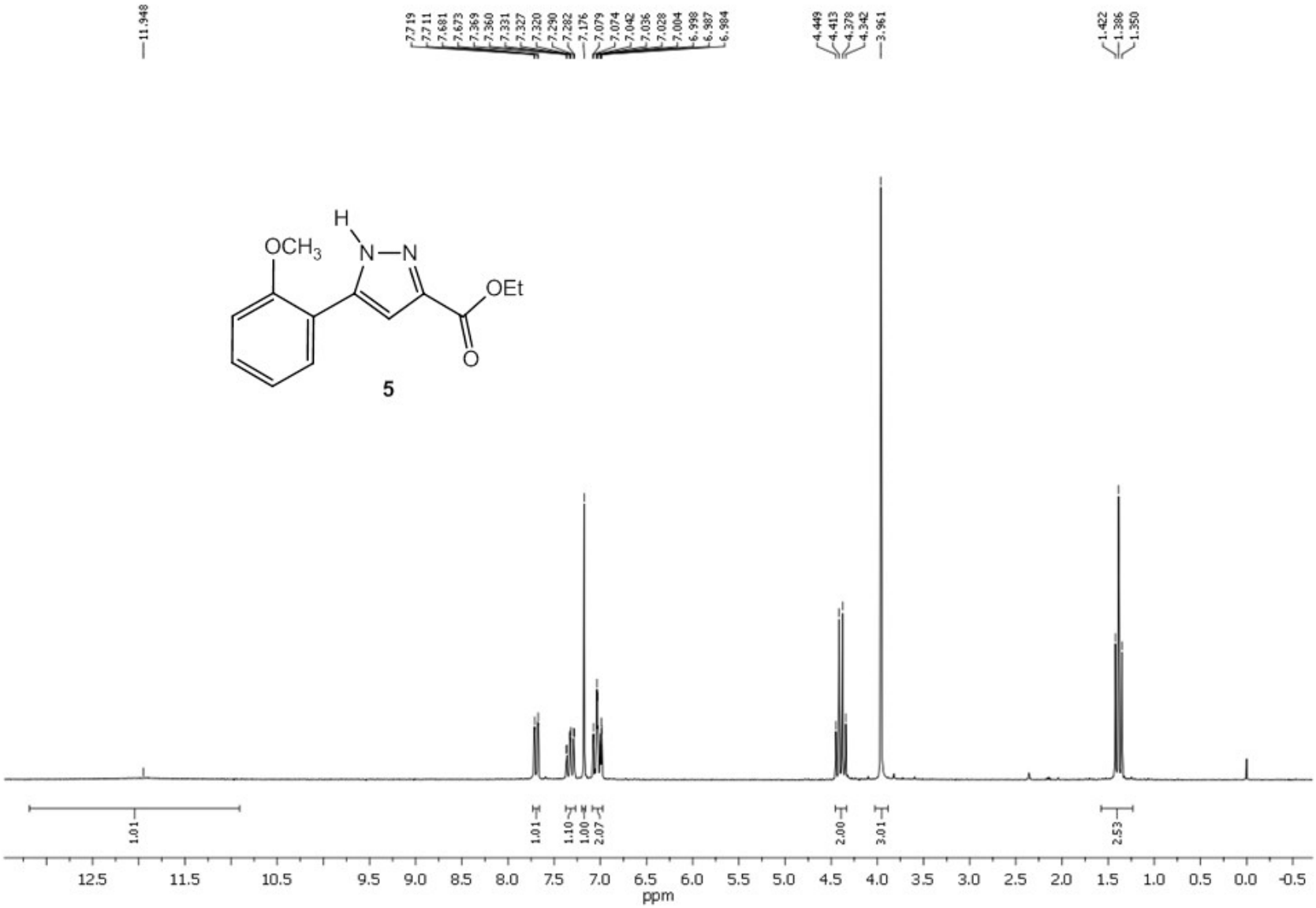


Fig. S9. ^{13}H NMR spectrum of **5** in $CDCl_3$ (200 MHz).

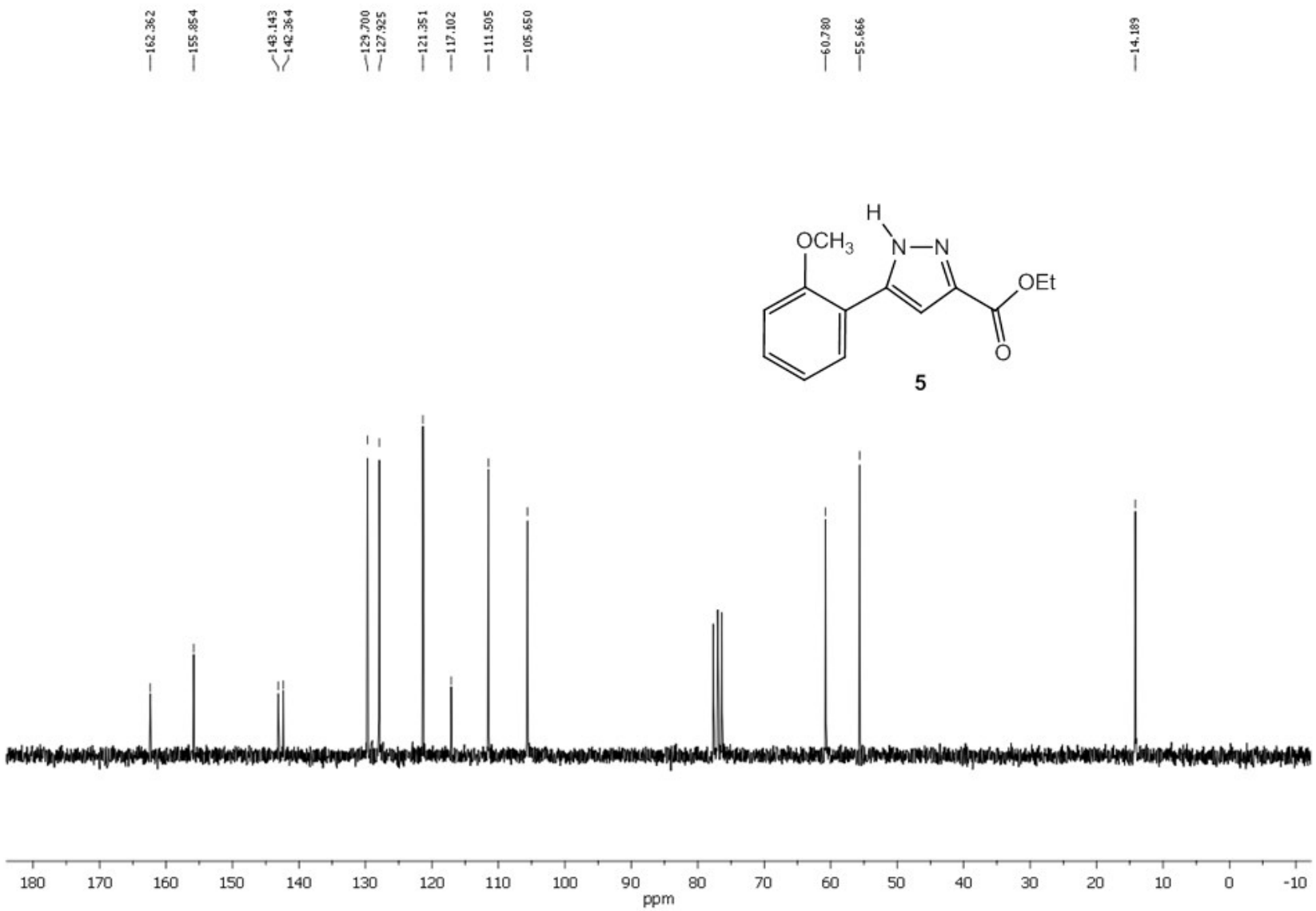


Fig. S10. ^{13}C NMR spectrum of **5** in $CDCl_3$ (50 MHz).

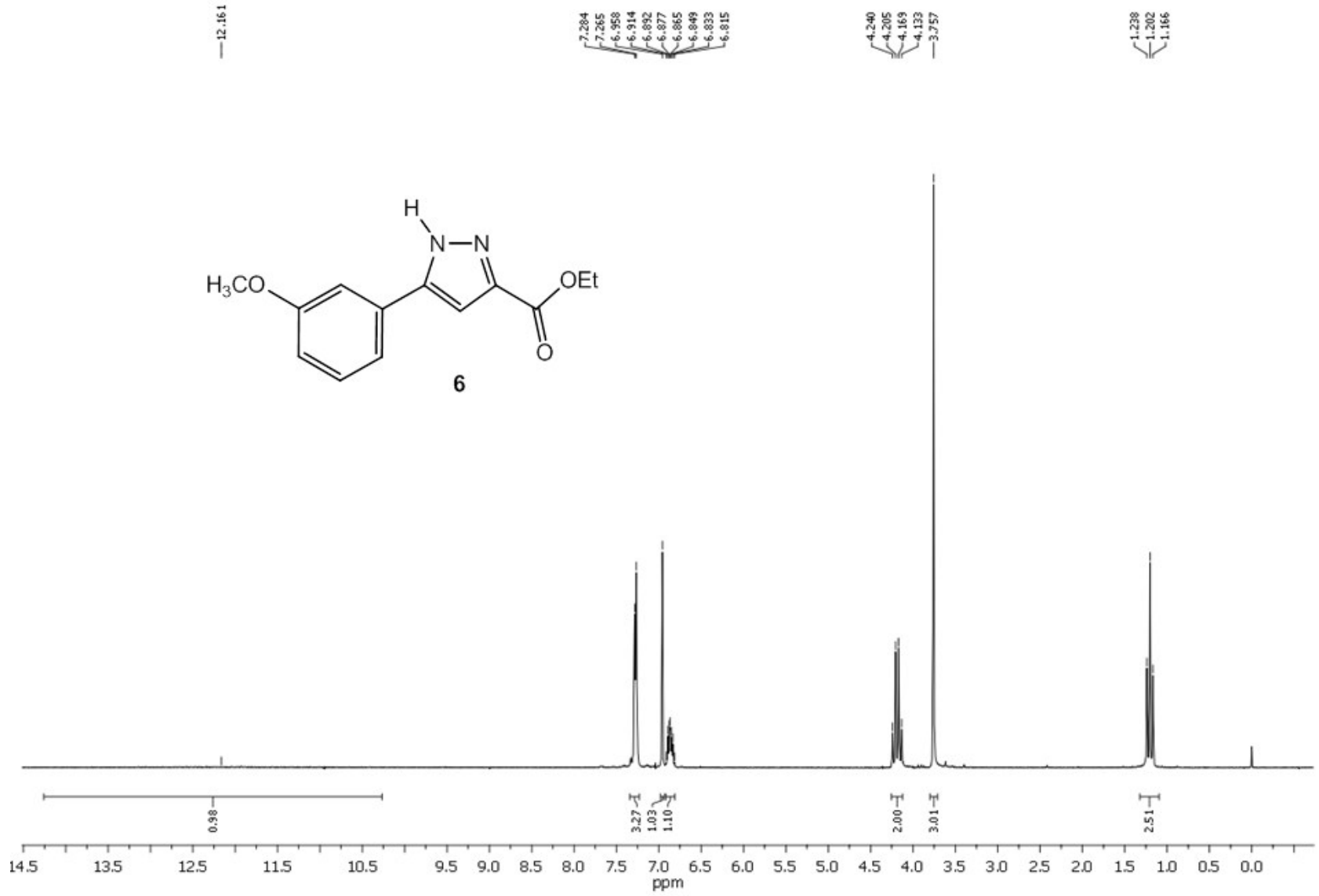


Fig. S11. ^{13}H NMR spectrum of **6** in $CDCl_3$ (200 MHz).

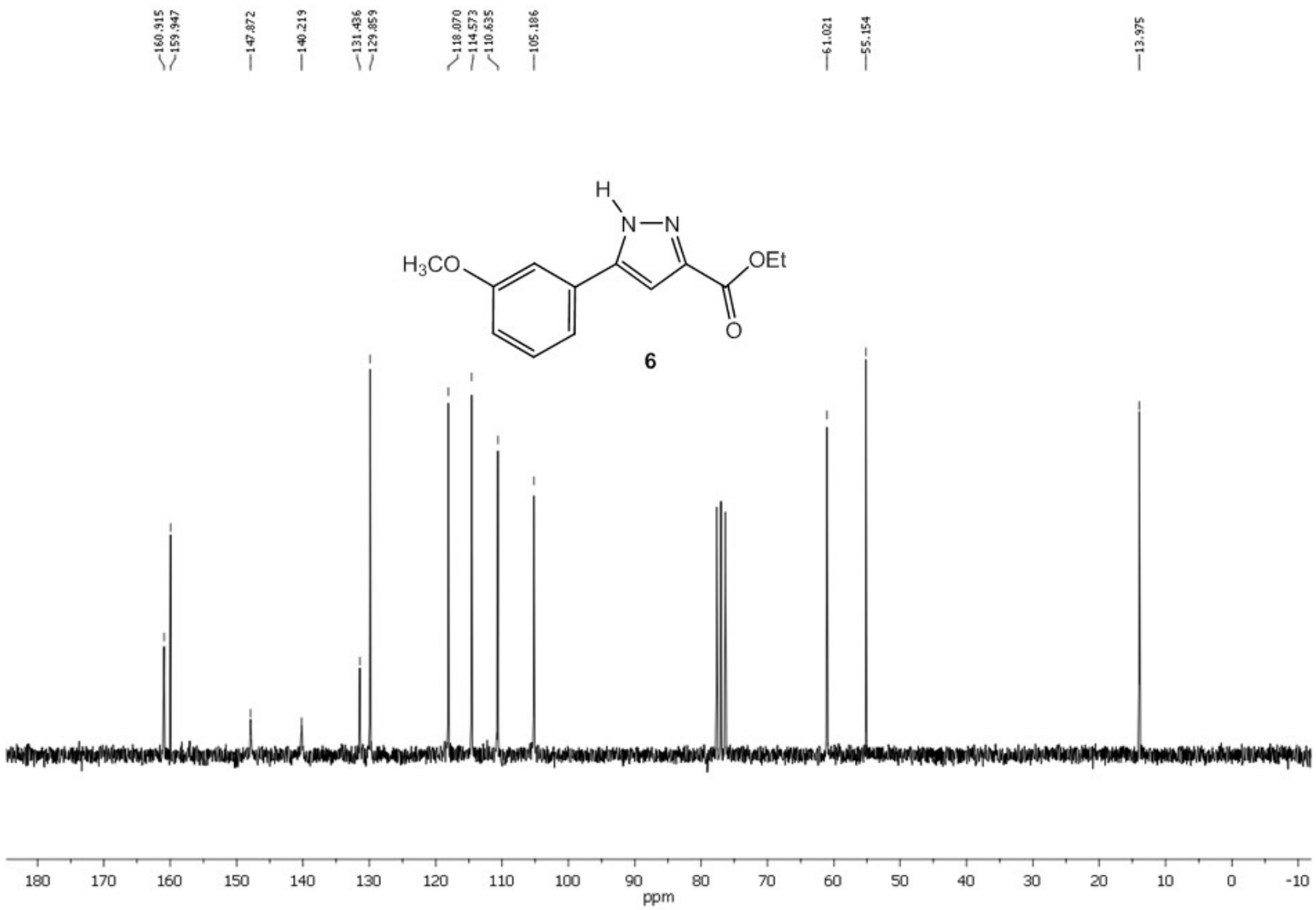


Fig. S12. ^{13}C NMR spectrum of **6** in $CDCl_3$ (50 MHz).

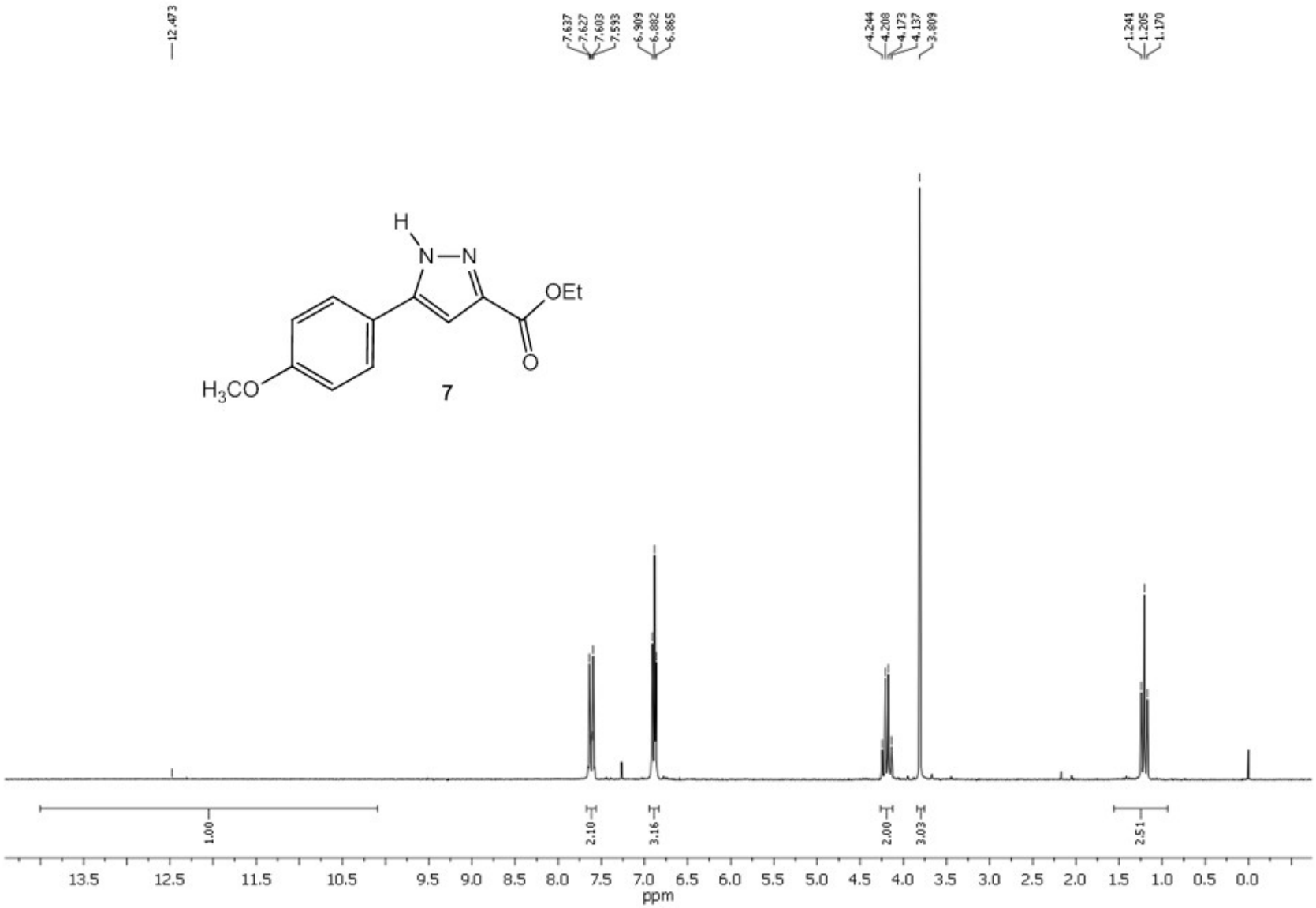


Fig. S13. ^{13}H NMR spectrum of **7** in $CDCl_3$ (200 MHz).

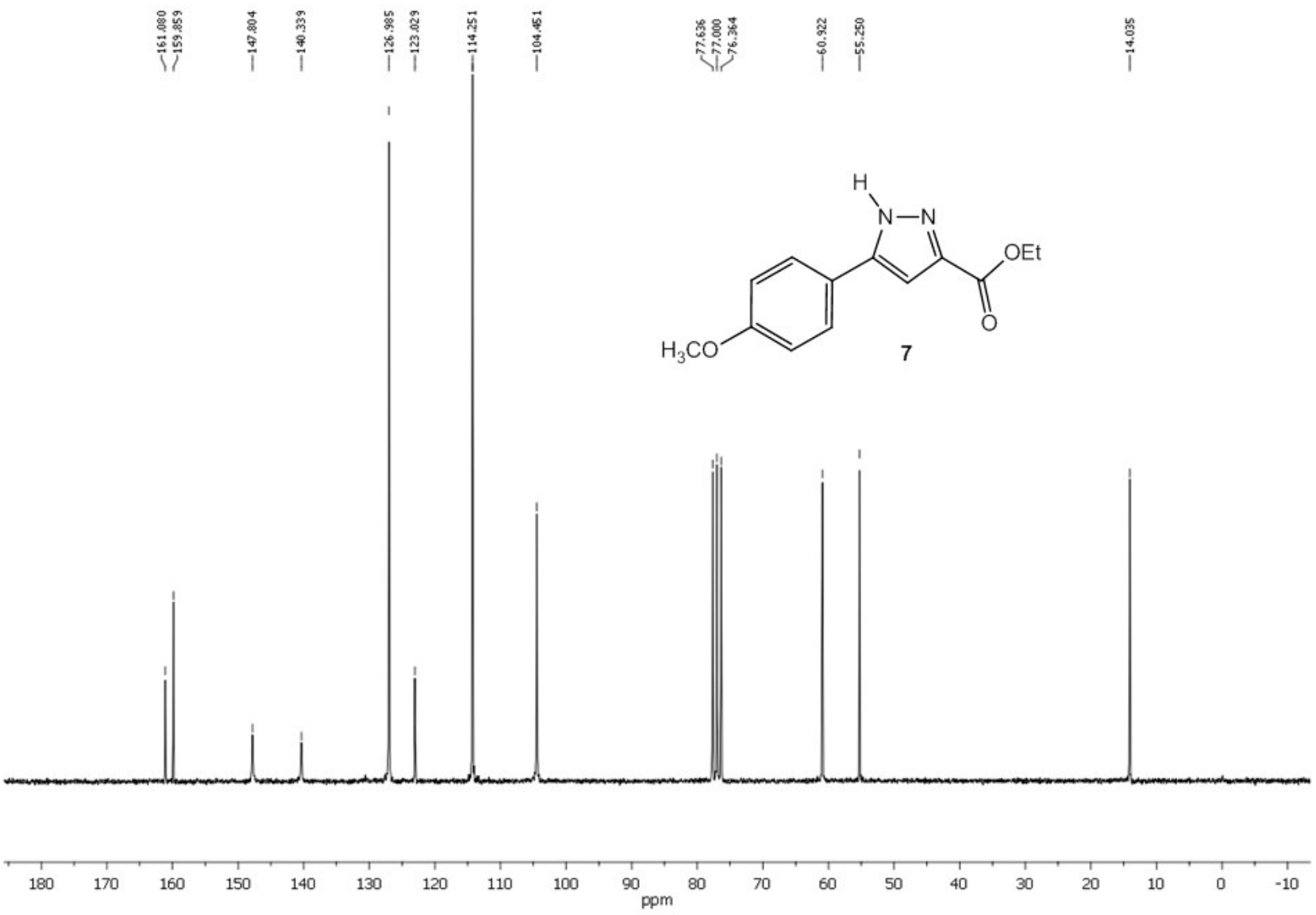


Fig. S14. ^{13}C NMR spectrum of **7** in $CDCl_3$ (50 MHz).

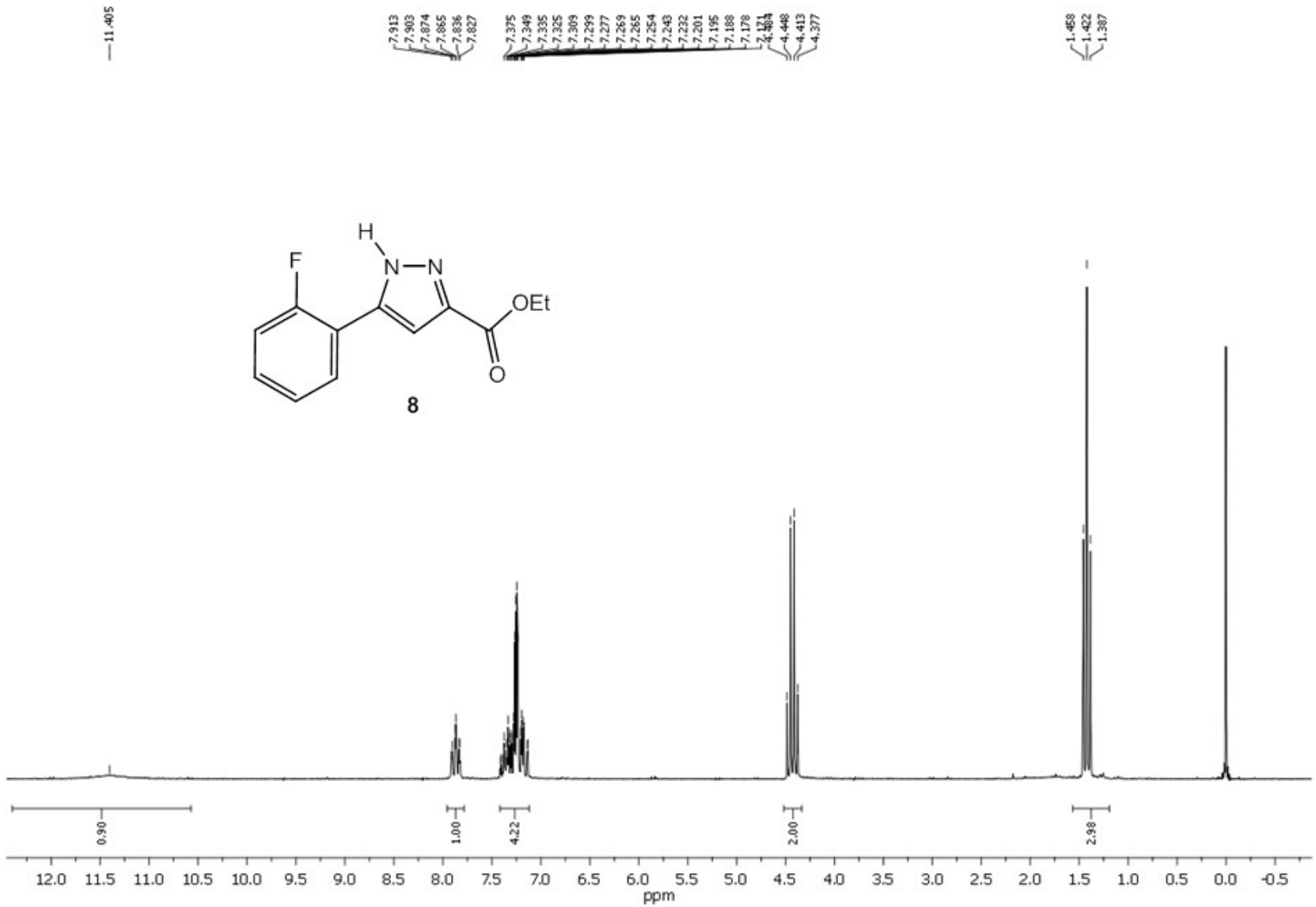


Fig. S15. ^{13}H NMR spectrum of **8** in $CDCl_3$ (200 MHz).

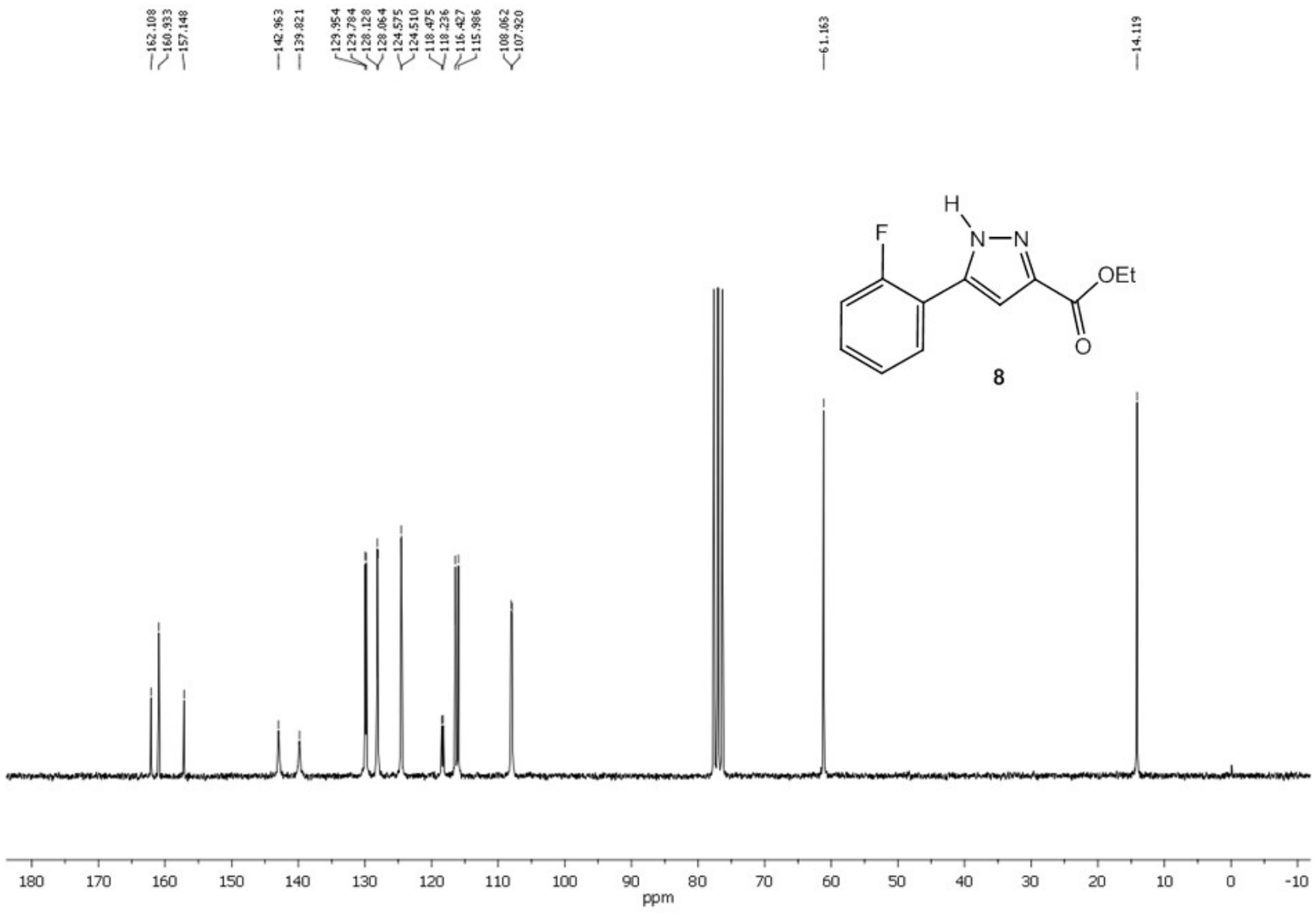


Fig. S16. ^{13}C NMR spectrum of **8** in $CDCl_3$ (50 MHz).

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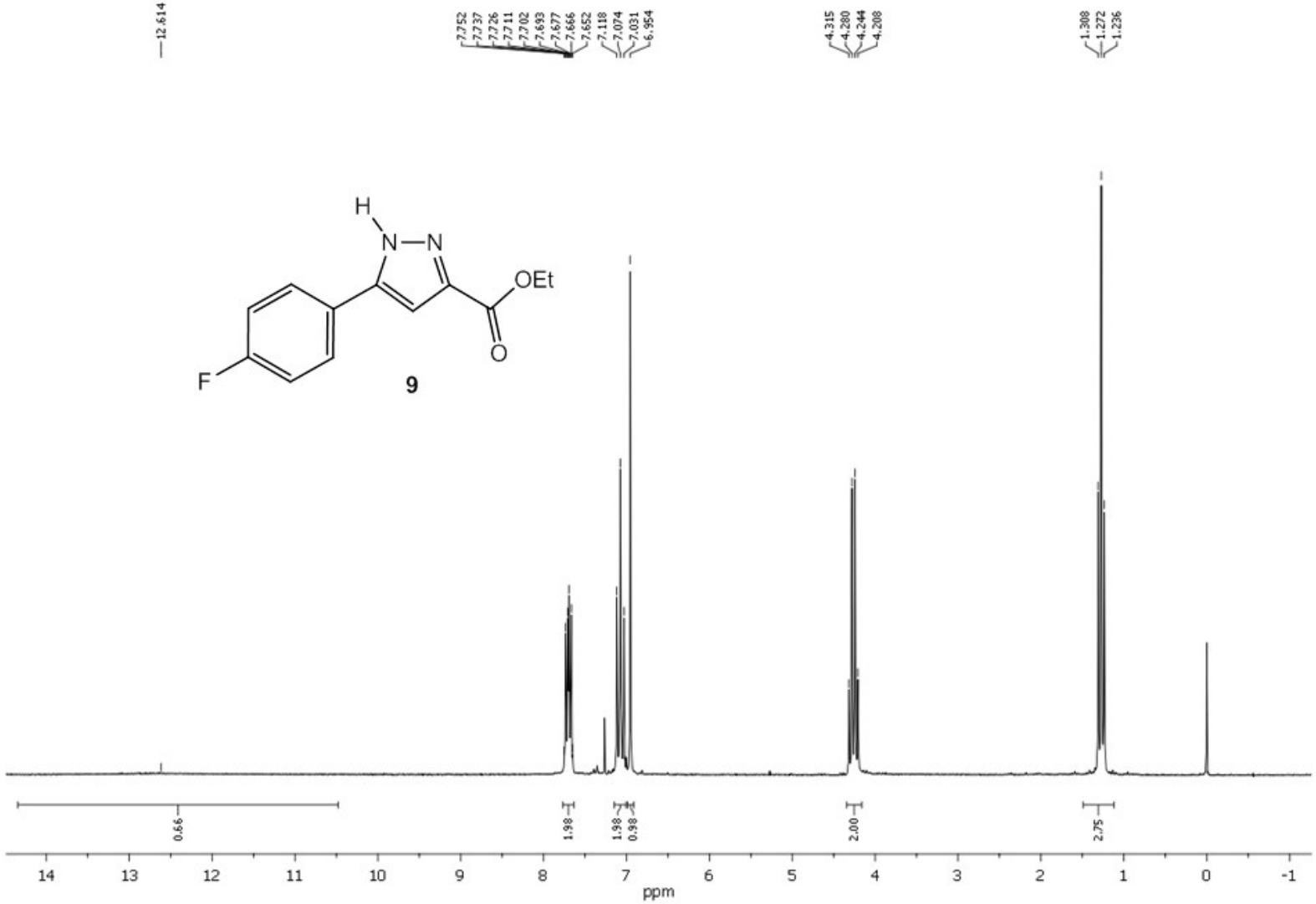

Fig. S17. ^{13}H NMR spectrum of **9** in $CDCl_3$ (200 MHz).

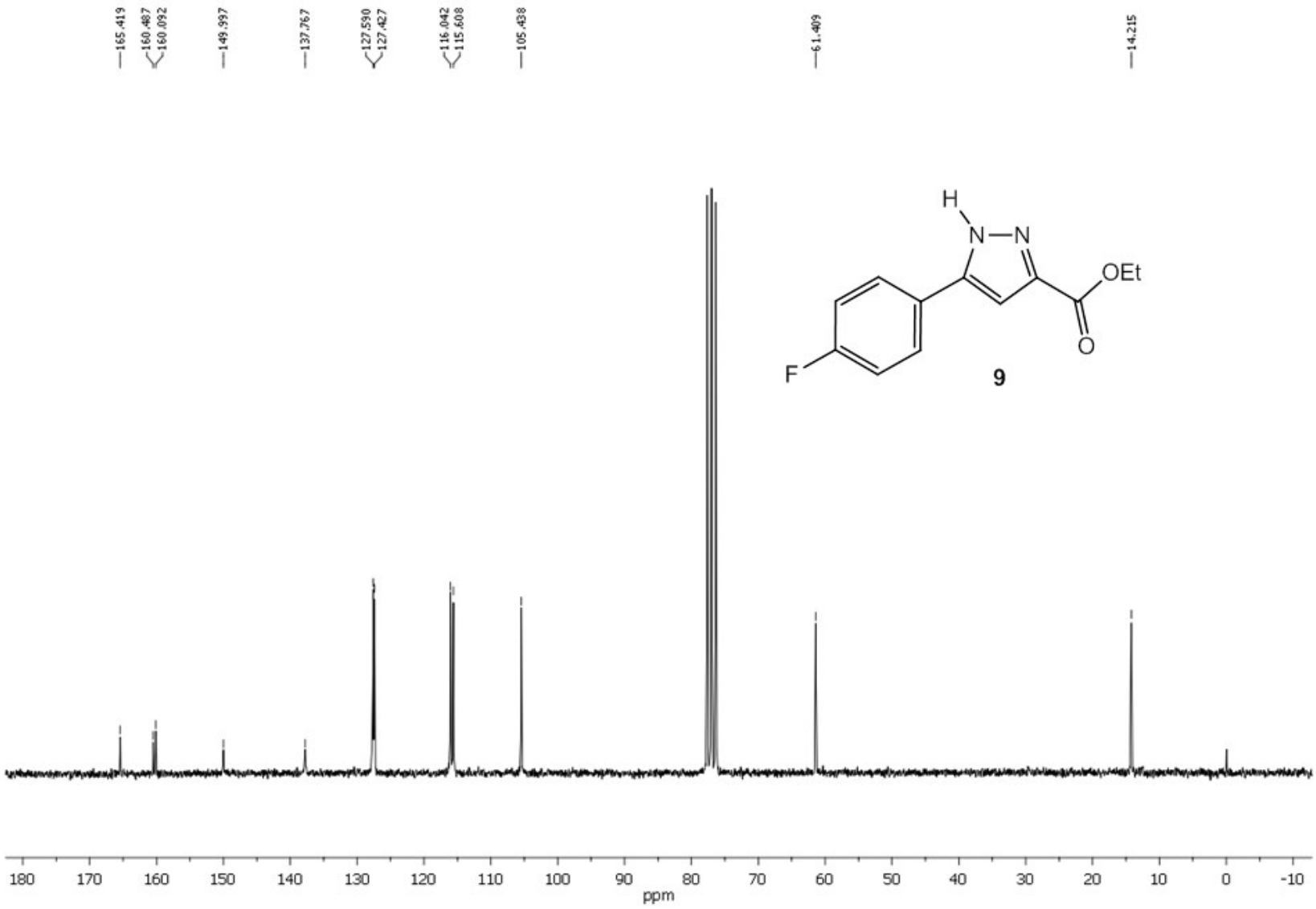

Fig. S18. ^{13}C NMR spectrum of **9** in $CDCl_3$ (50 MHz).

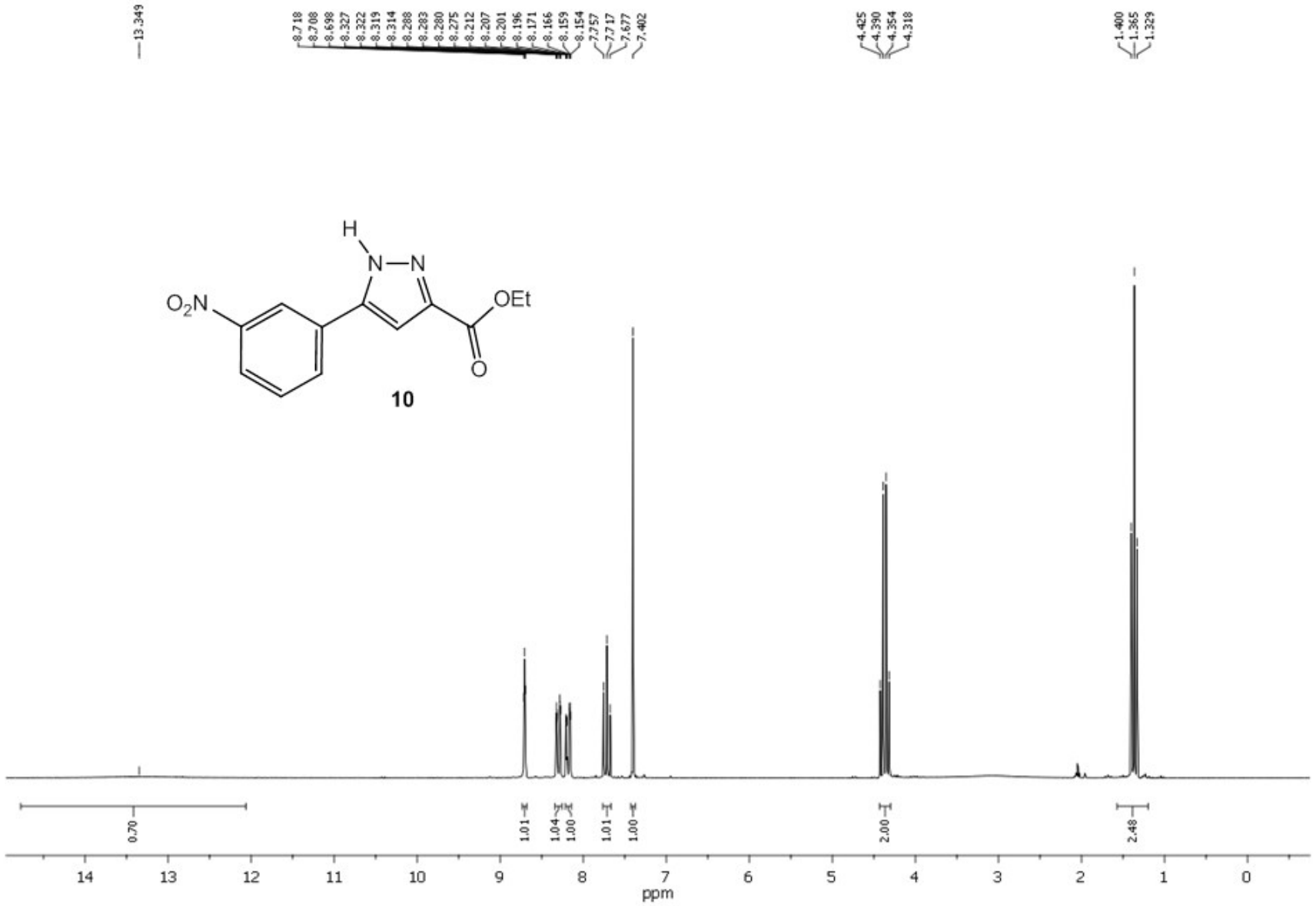

Fig. S19. ^{13}H NMR spectrum of **10** in $(CD_3)_2CO$ (200 MHz).

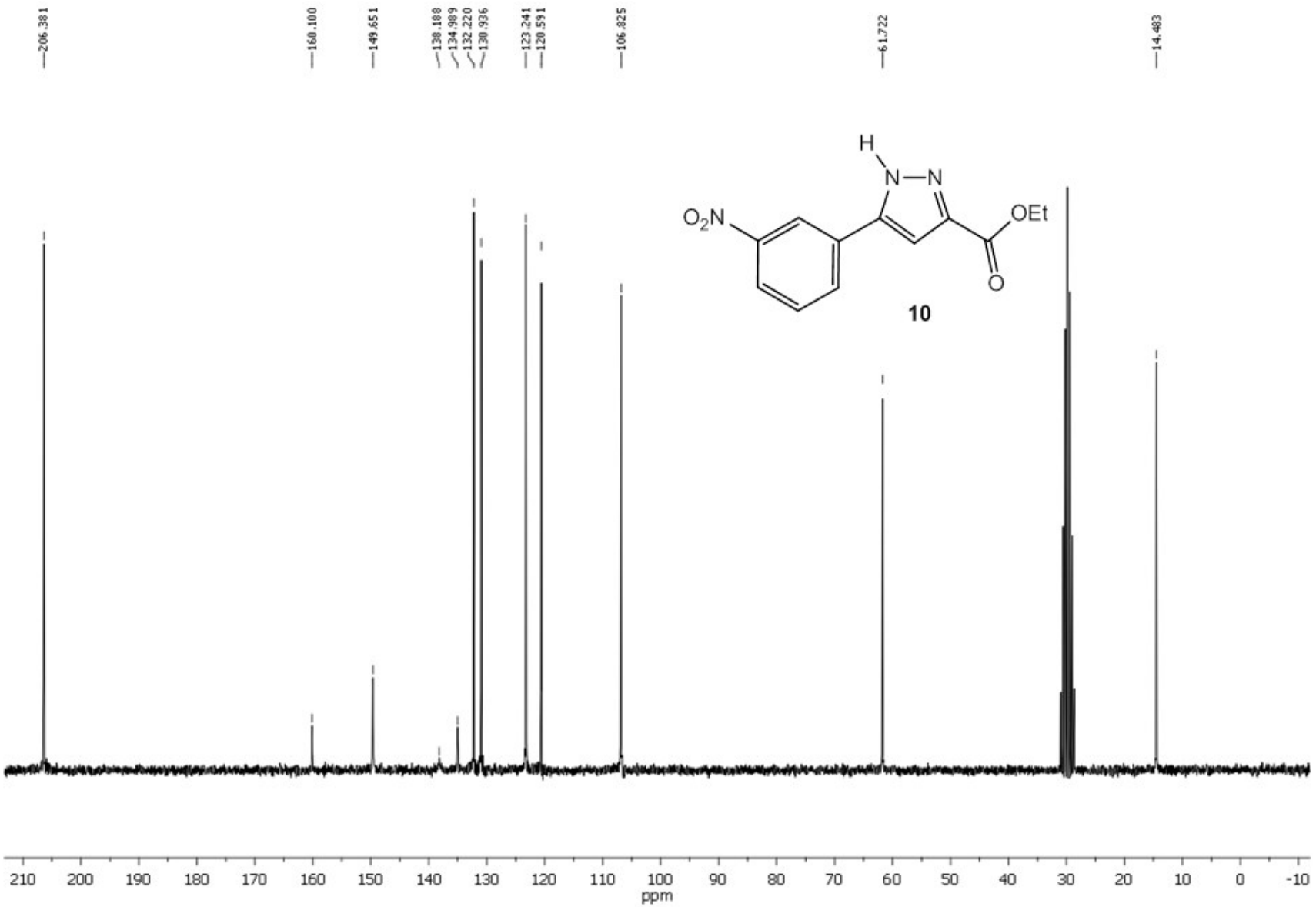

Fig. S20. ^{13}C NMR spectrum of **10** in $(CD_3)_2CO$ (50 MHz).

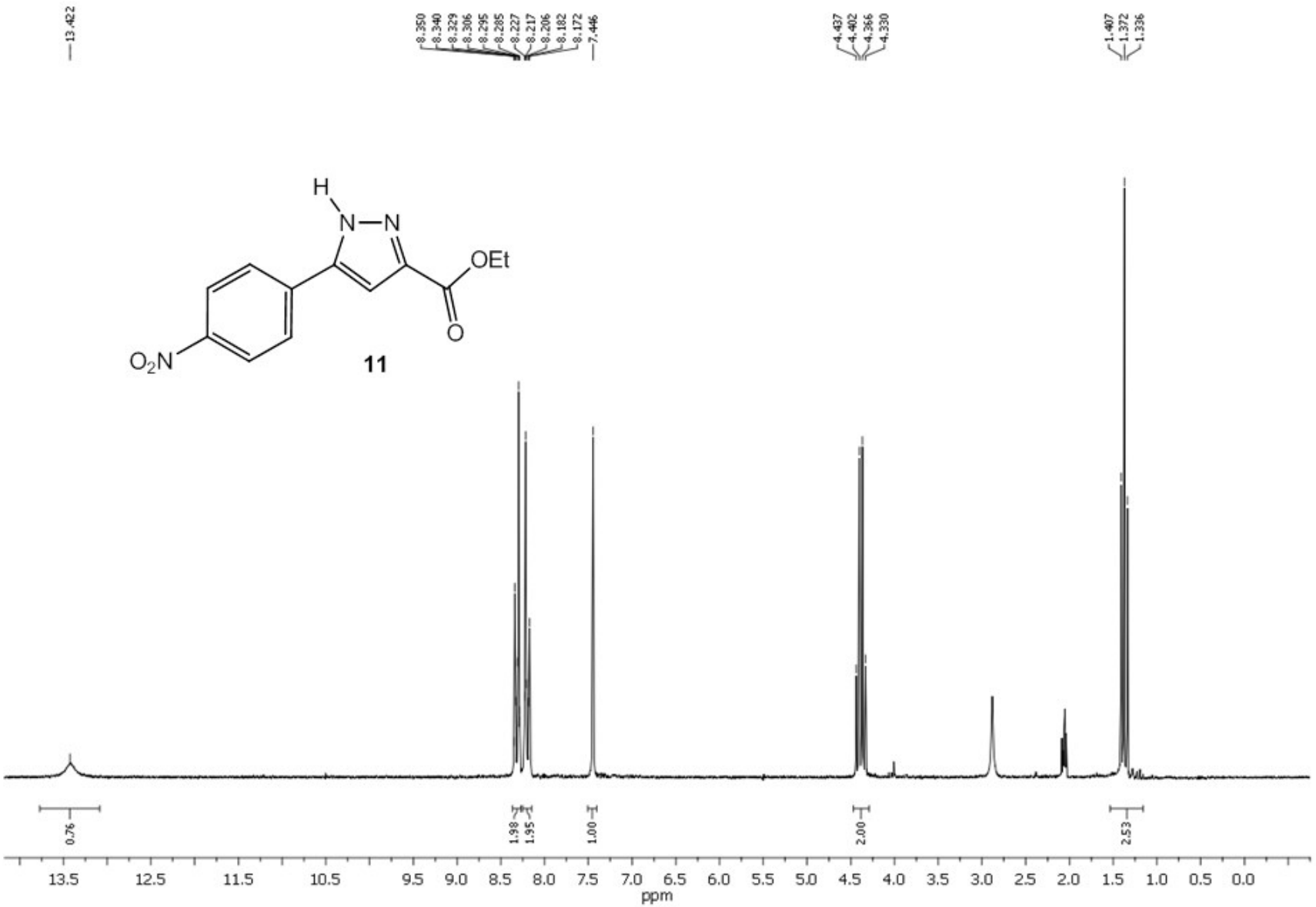

Fig. S21. ^{13}H NMR spectrum of **11** in $(CD_3)_2CO$ (200 MHz).

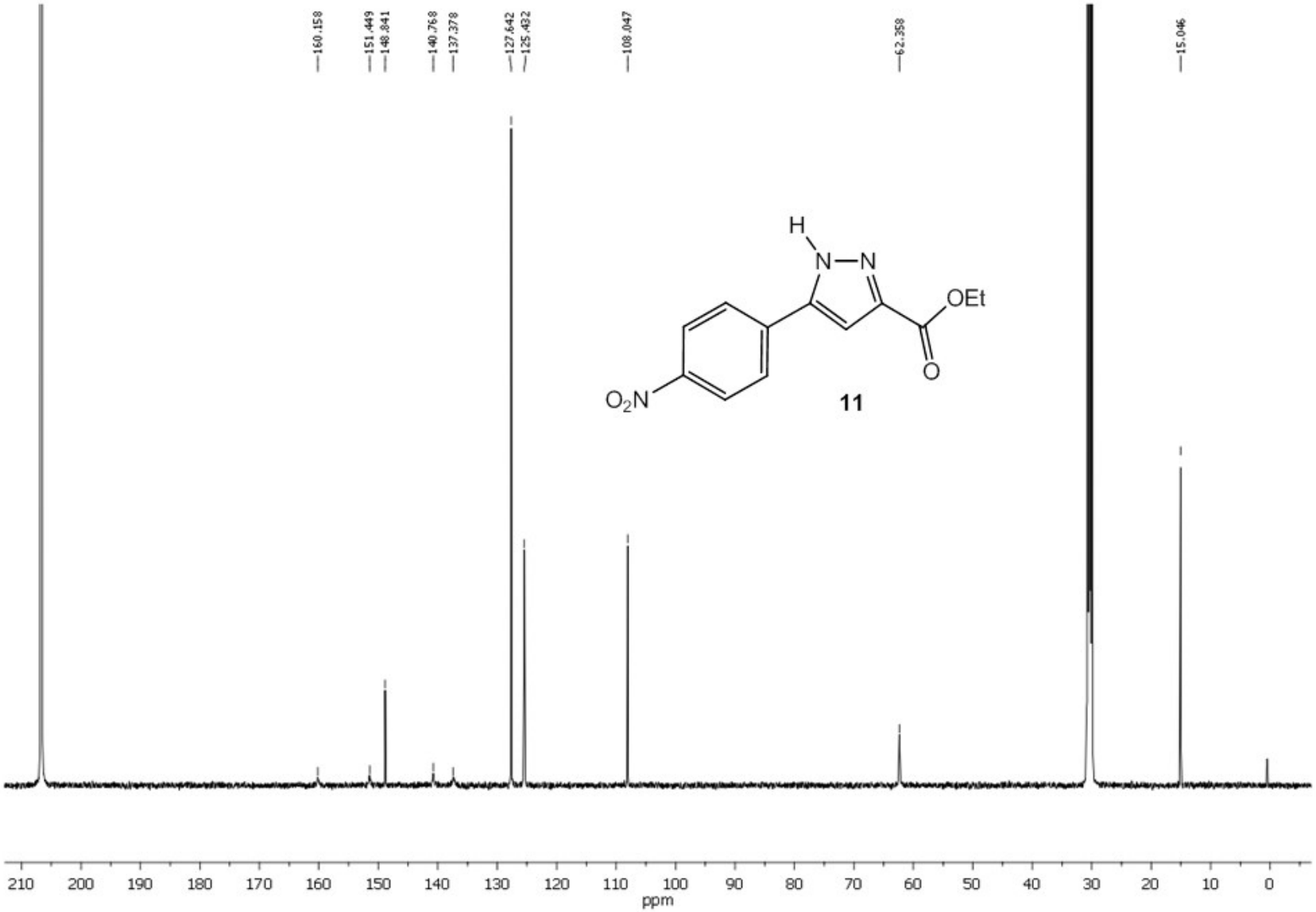

Fig. S22. ^{13}C NMR spectrum of **11** in $(CD_3)_2CO$ (125 MHz).

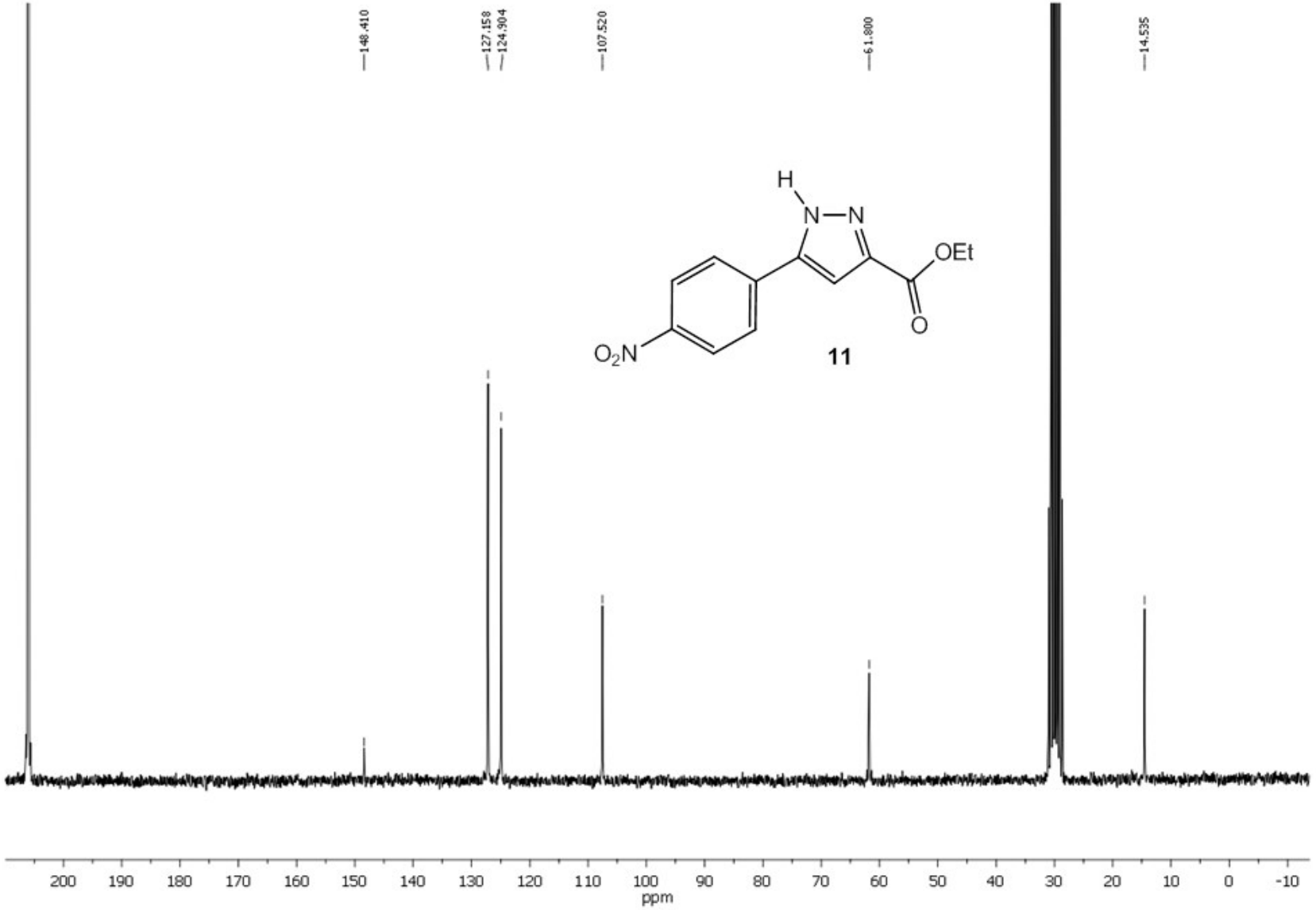

Fig. S23. ^{13}C NMR spectrum of **11** in $(CD_3)_2CO$ (50 MHz).

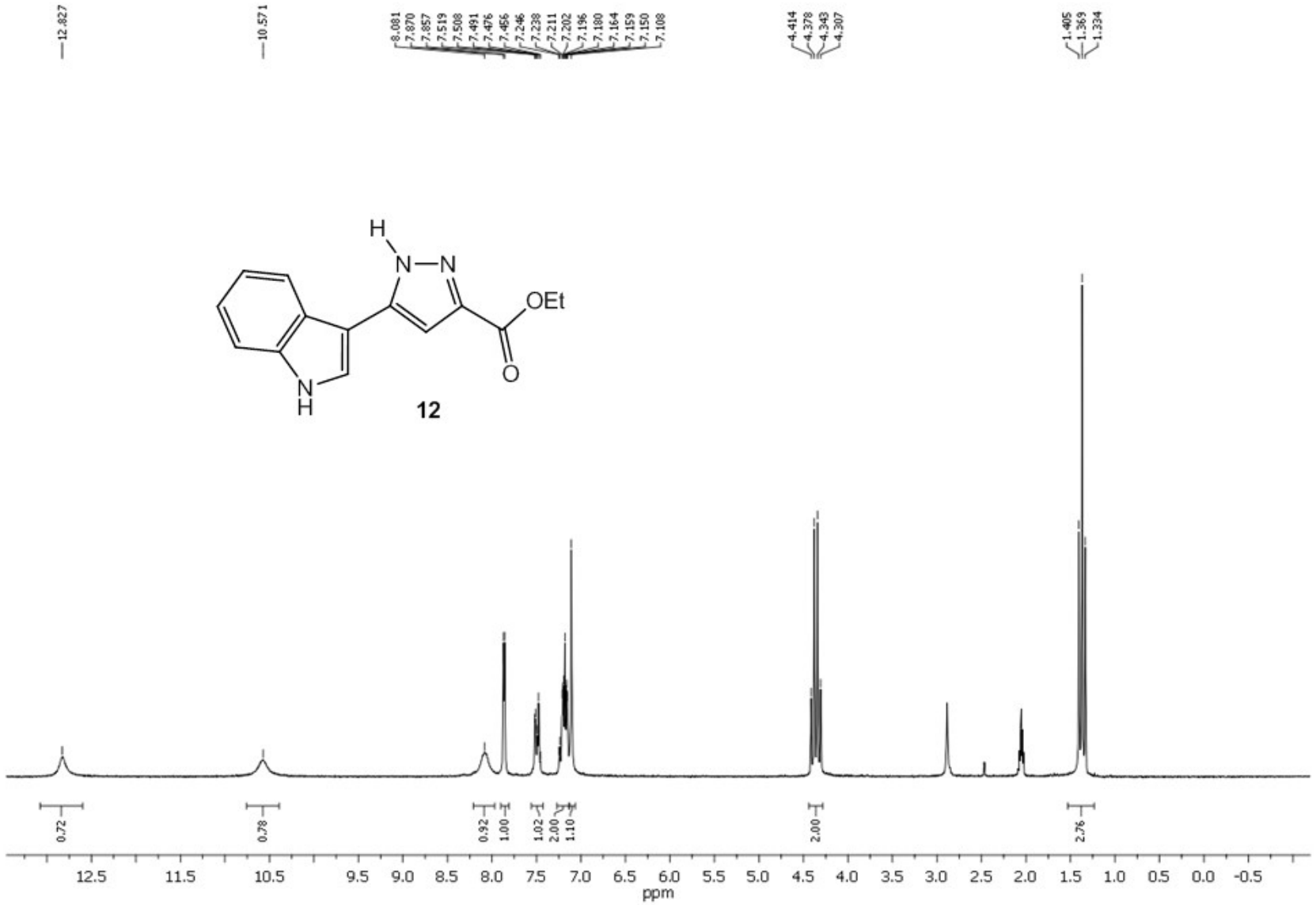

Fig. S24. ^{13}H NMR spectrum of **12** in $(CD_3)_2CO$ (200 MHz).

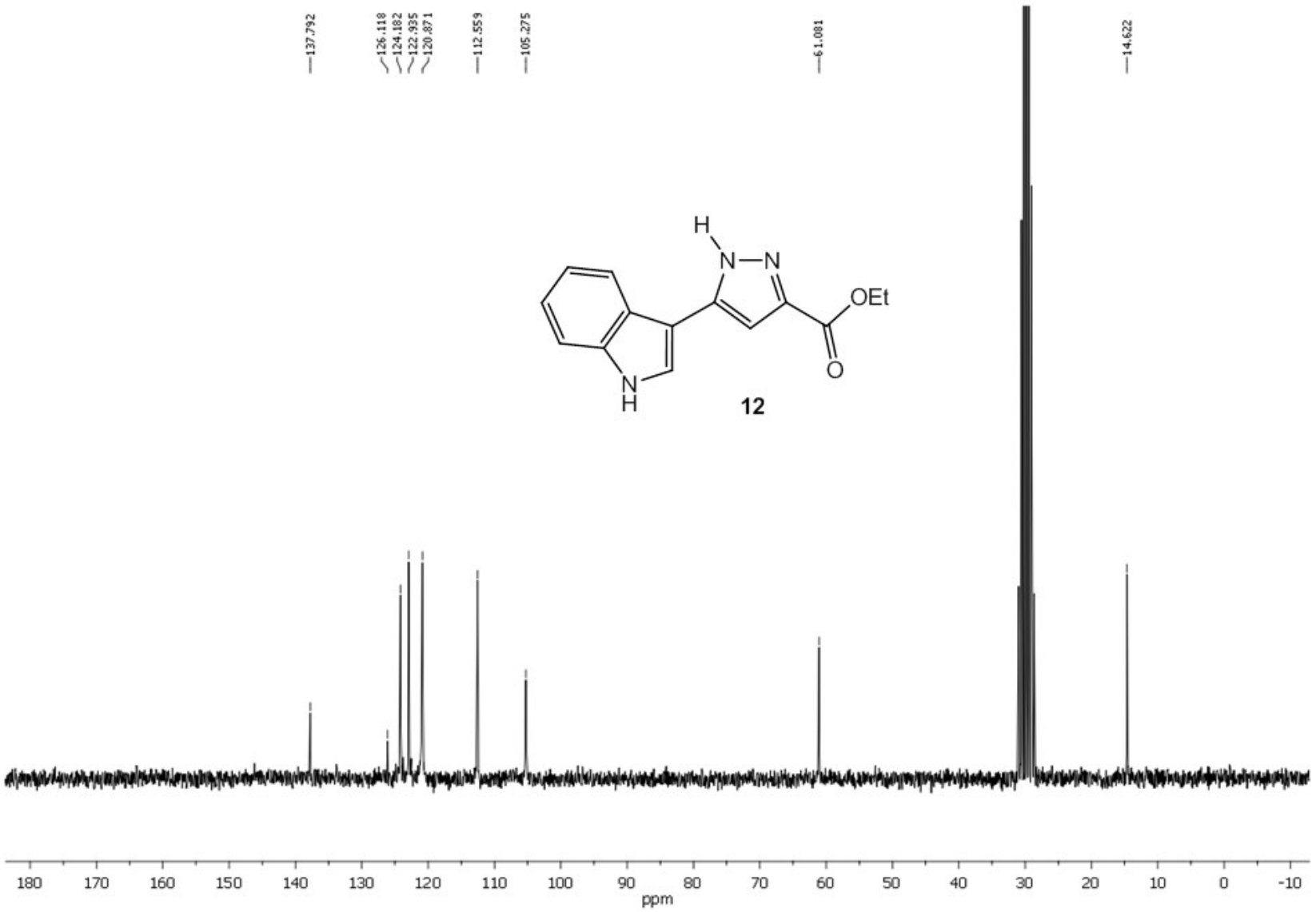

Fig. S25. ^{13}C NMR spectrum of **12** in $(CD_3)_2CO$ (50 MHz).

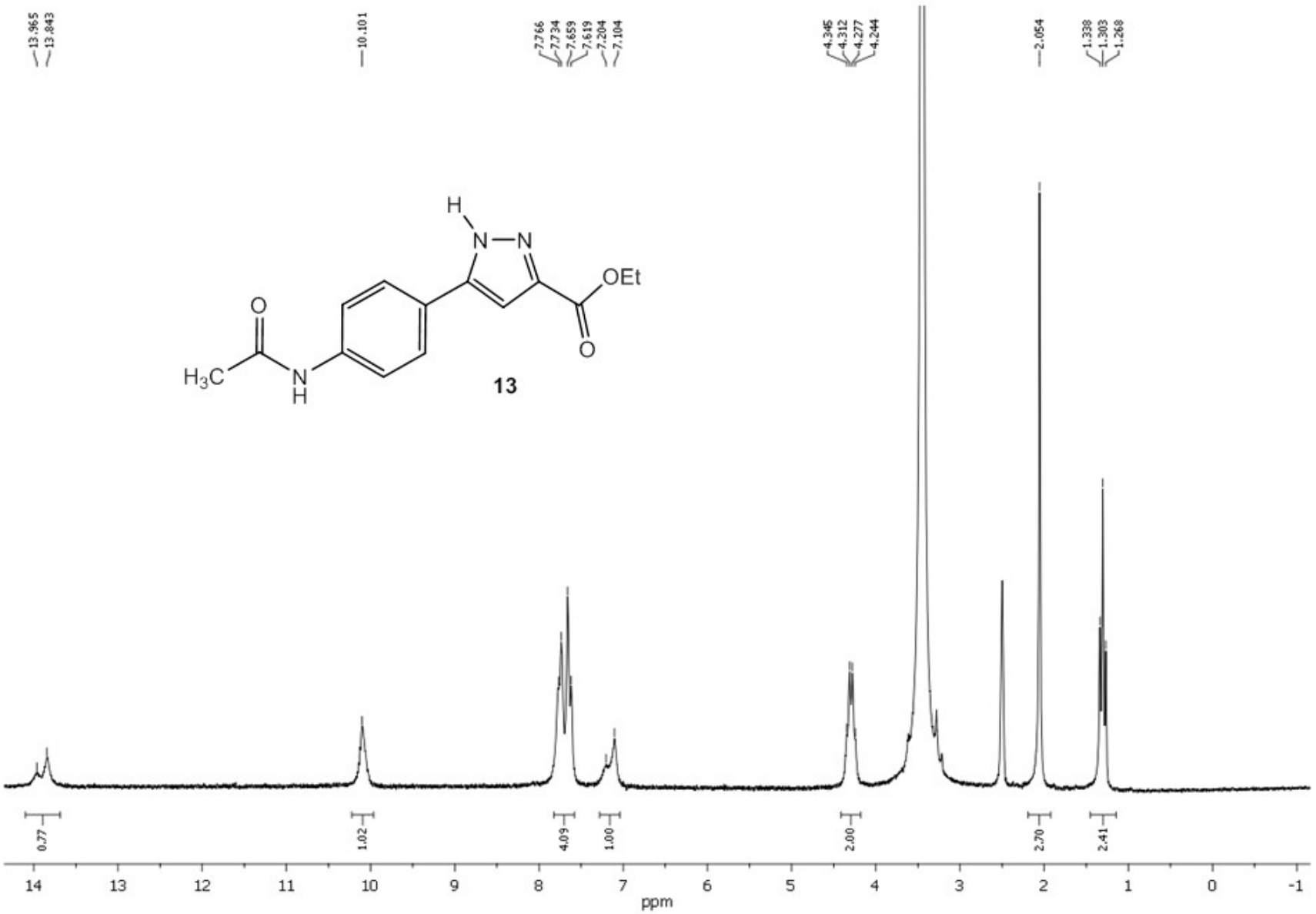

Fig. S26. ^{13}H NMR spectrum of **13** in DMSO-d_6 (200 MHz).

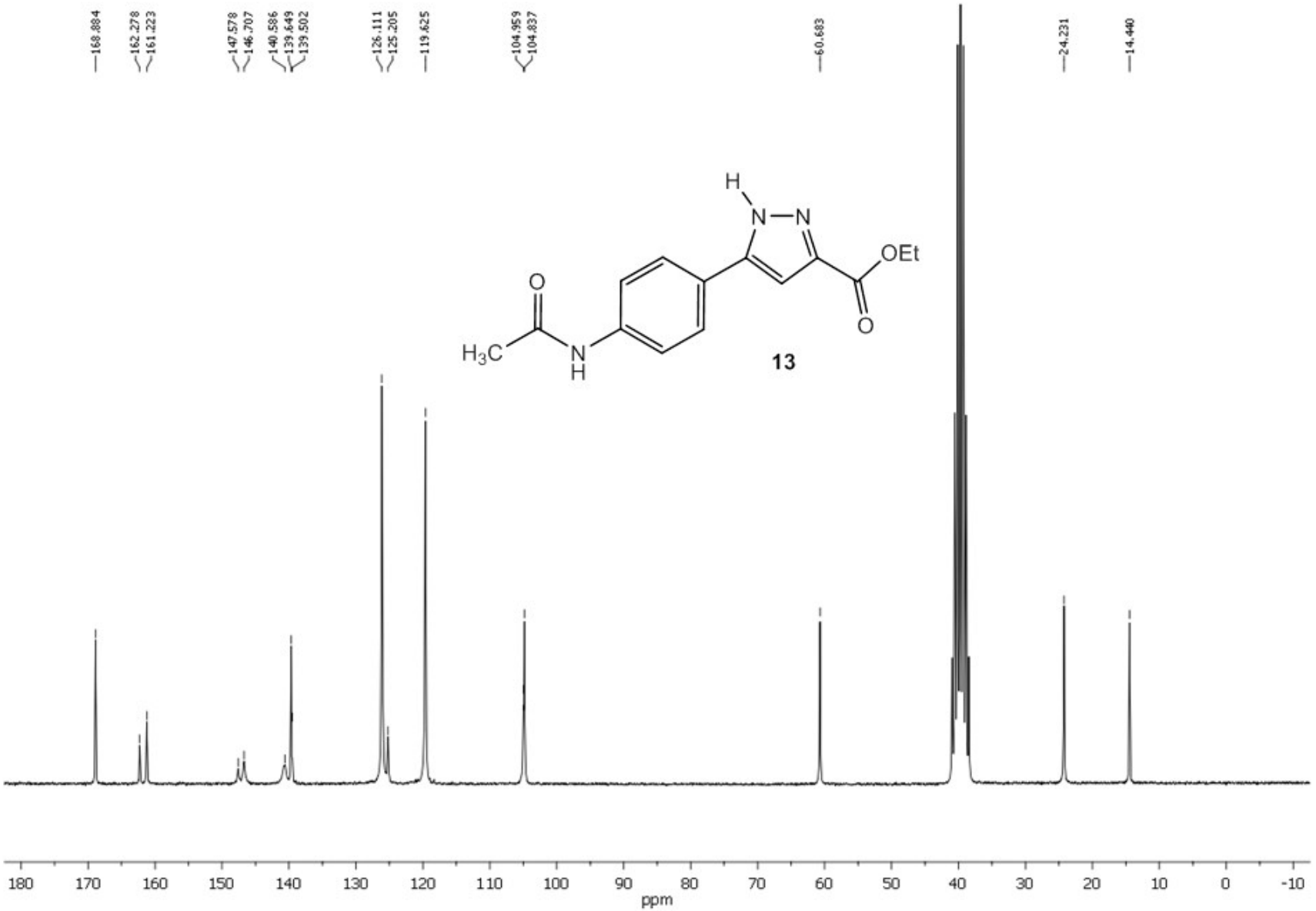

Fig. S27. ^{13}C NMR spectrum of **13** in DMSO-d_6 (50 MHz).

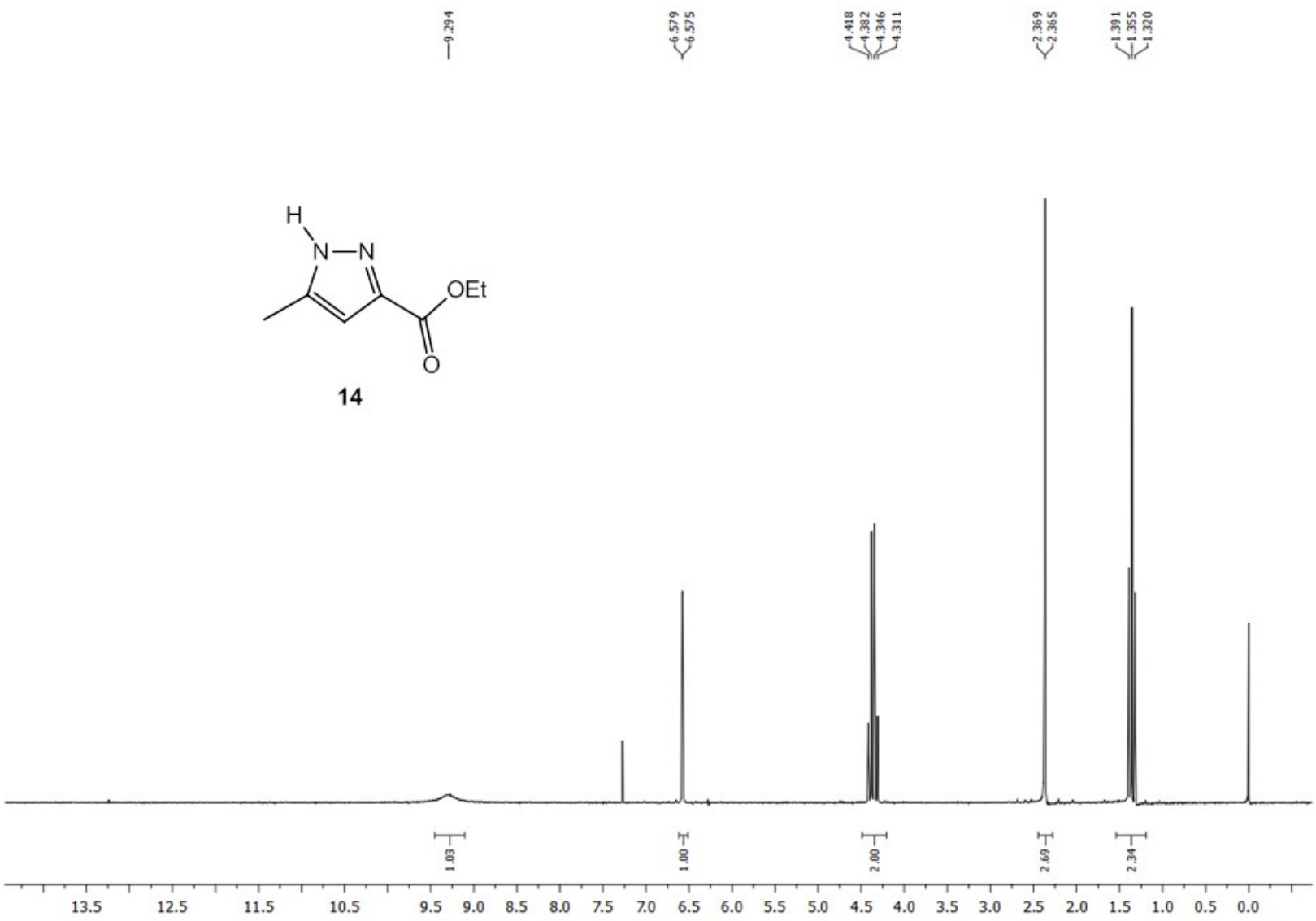

Fig. S28. ^{13}H NMR spectrum of **14** in $CDCl_3$ (200 MHz).

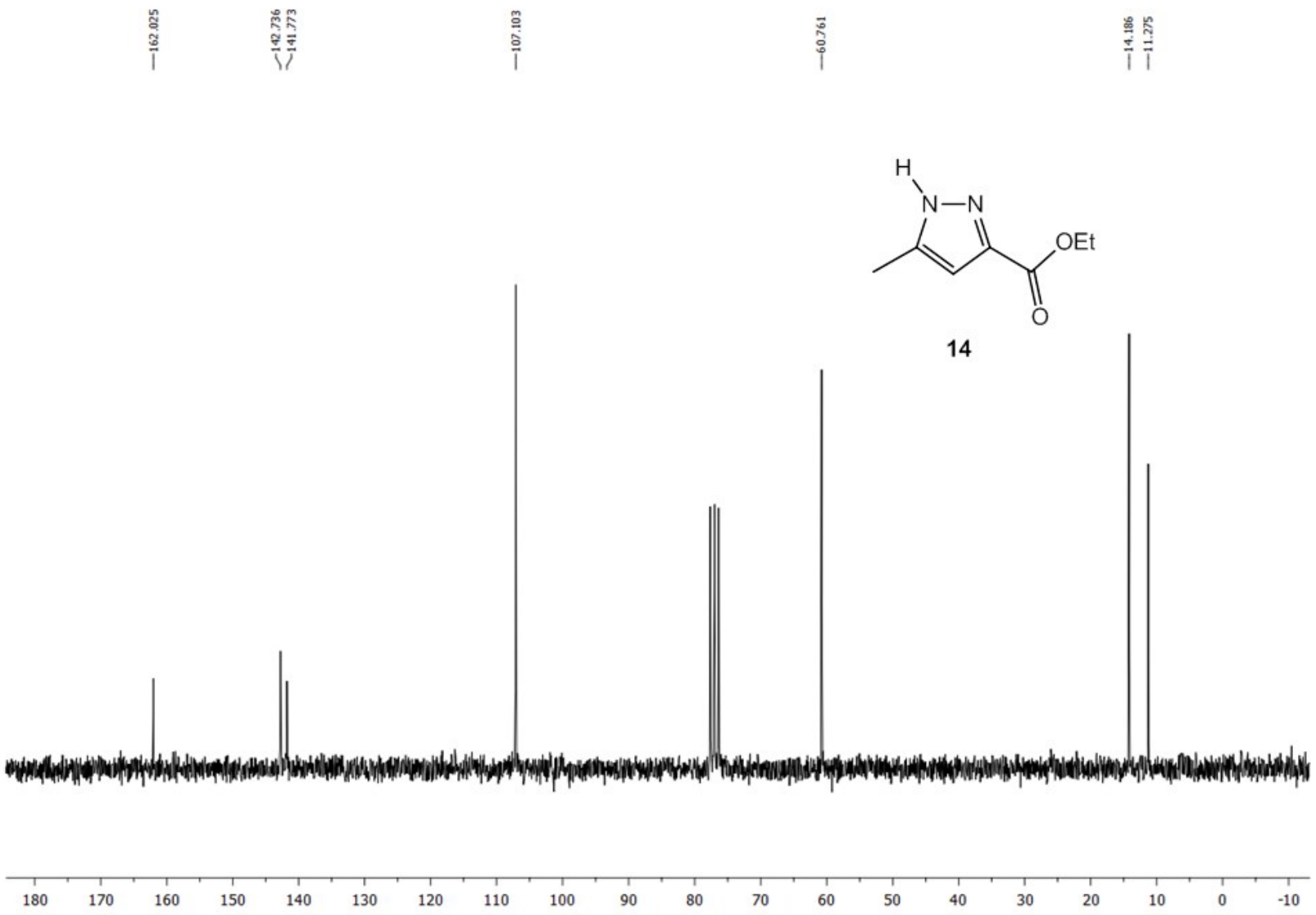

Fig. S29. ^{13}C NMR spectrum of **14** in $CDCl_3$ (50 MHz).

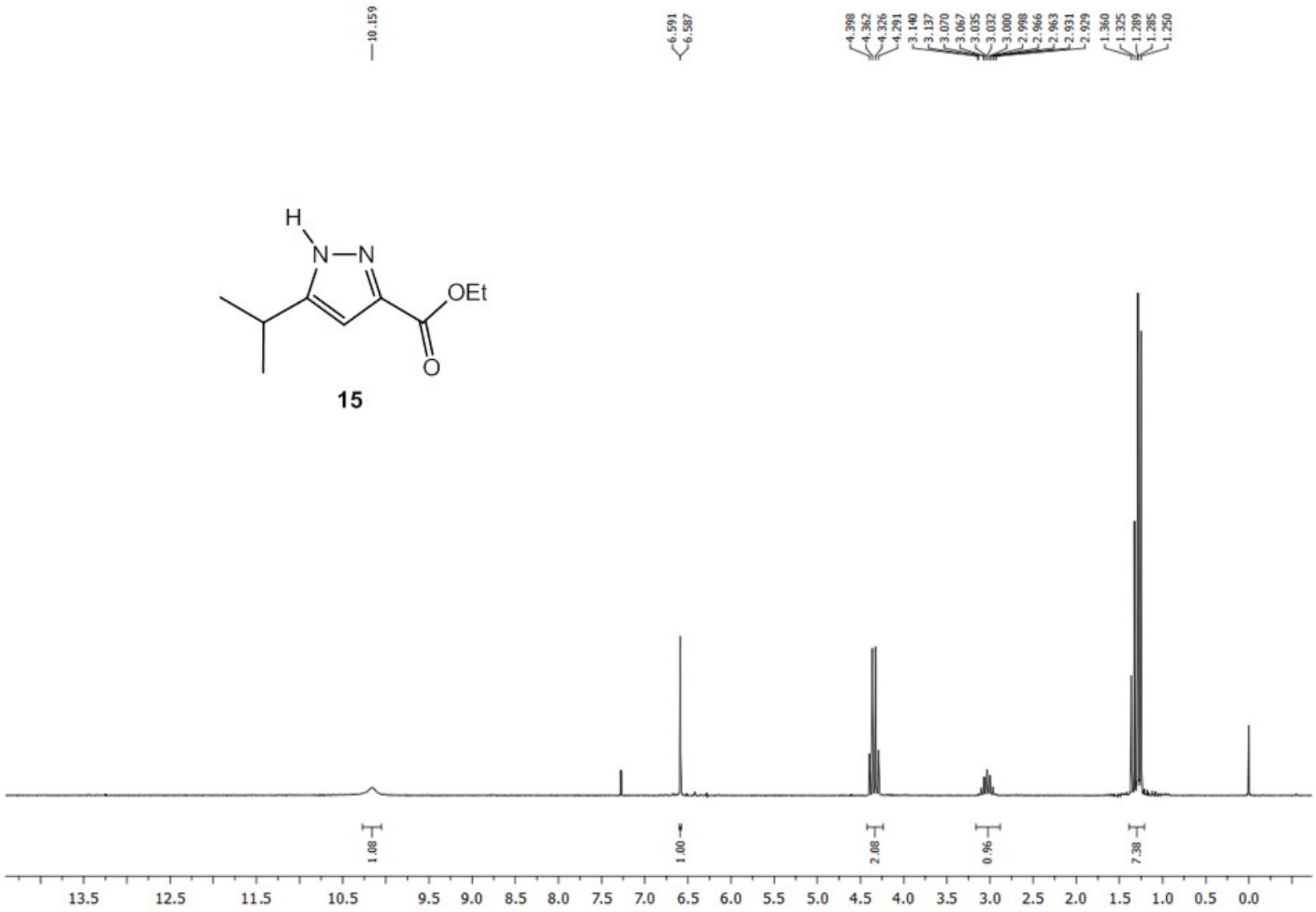

Fig. S30. ^{13}H NMR spectrum of **15** in $CDCl_3$ (200 MHz).

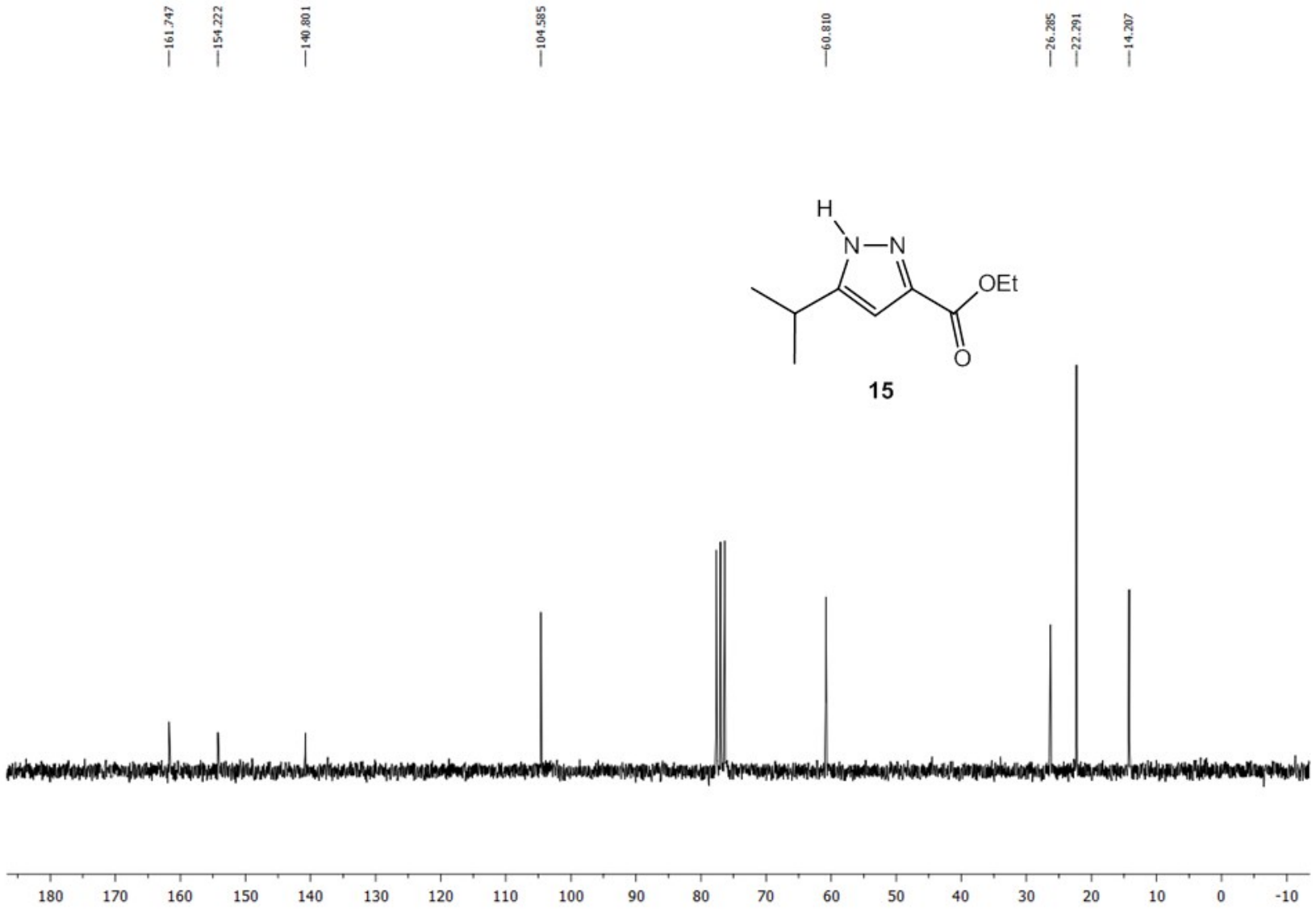

Fig. S31. ^{13}C NMR spectrum of **15** in $CDCl_3$ (50 MHz).

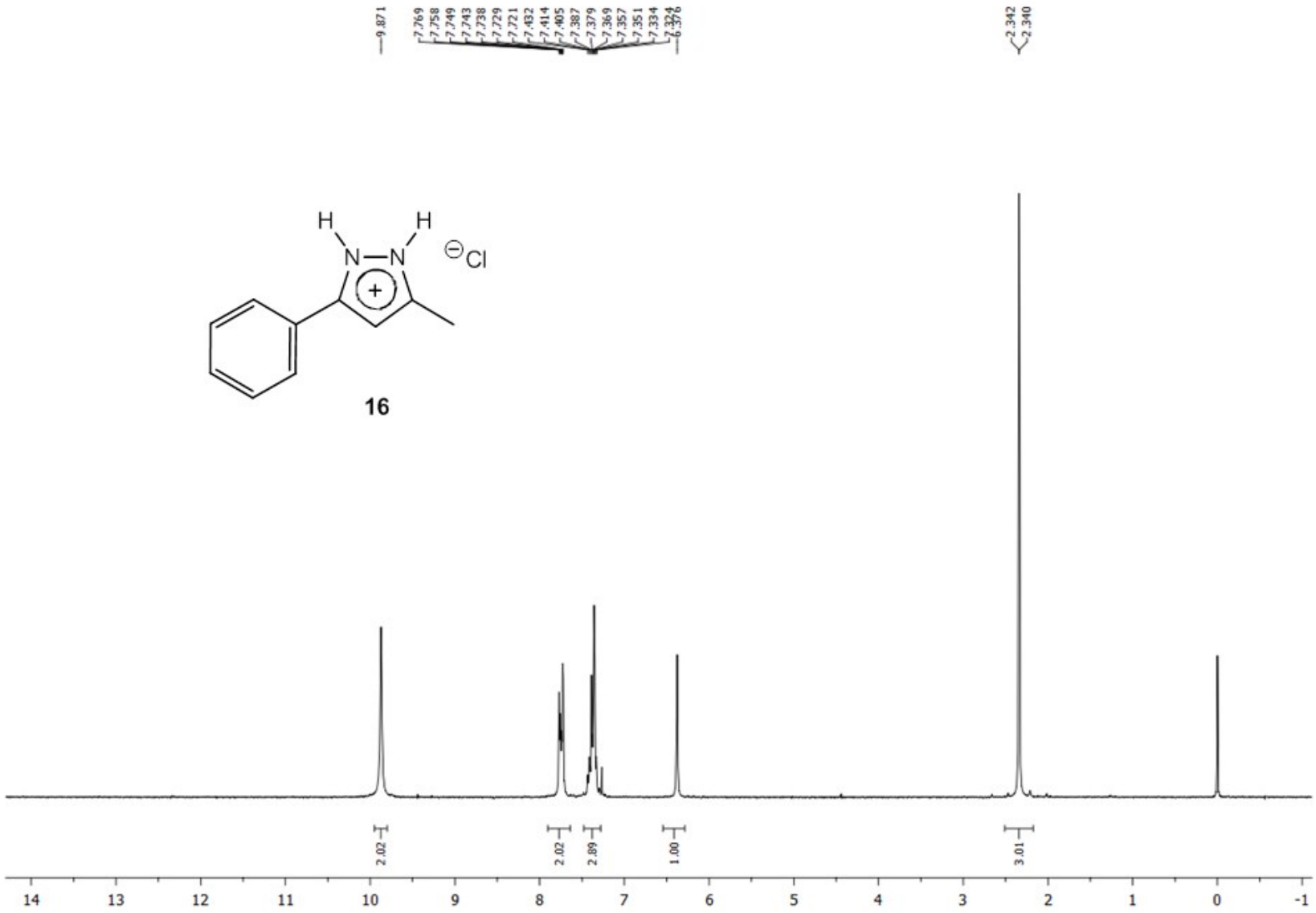

Fig. S32. ^{13}H NMR spectrum of **16** in $CDCl_3$ (200 MHz).

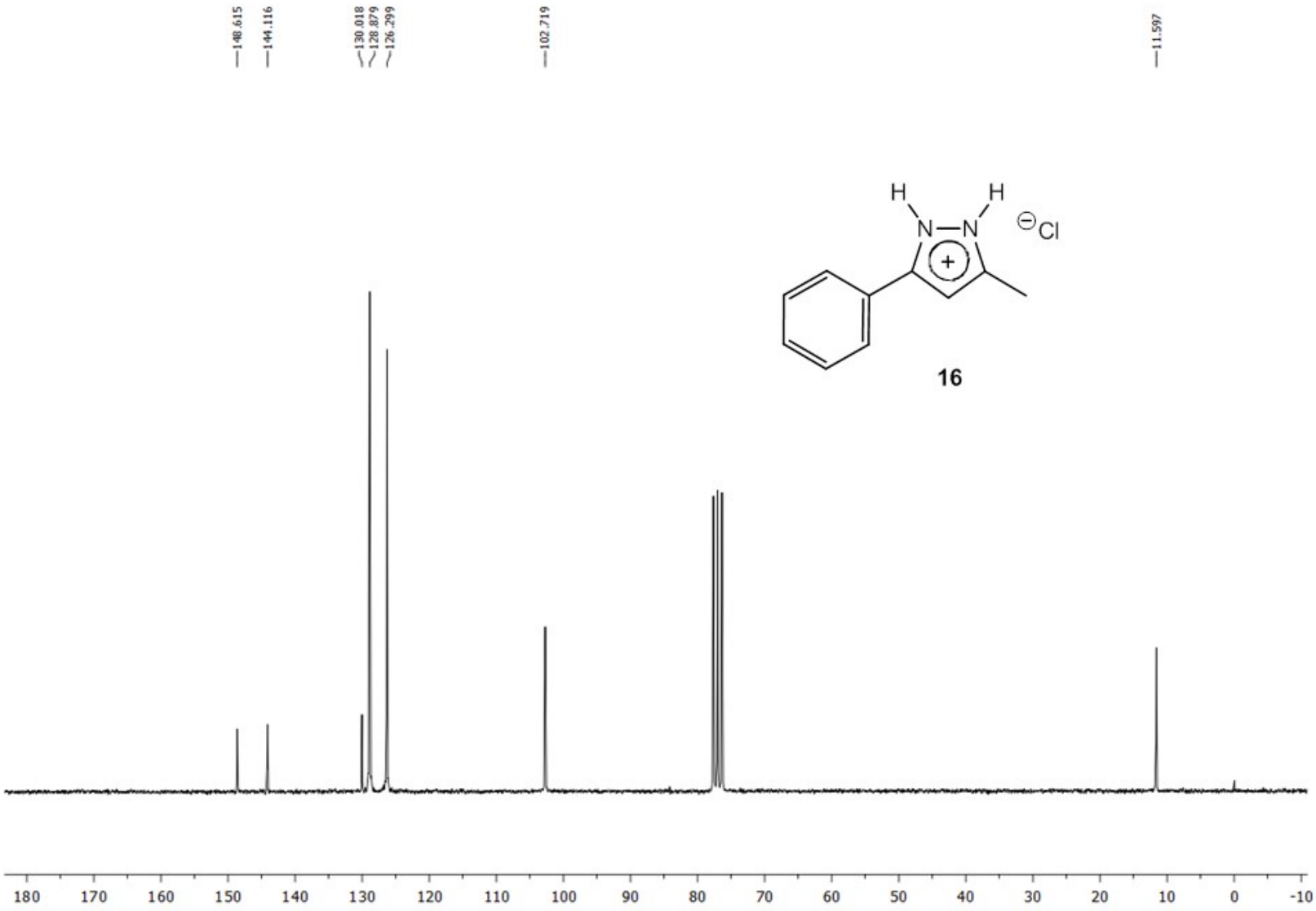

Fig. S33. ^{13}C NMR spectrum of **16** in $CDCl_3$ (50 MHz).

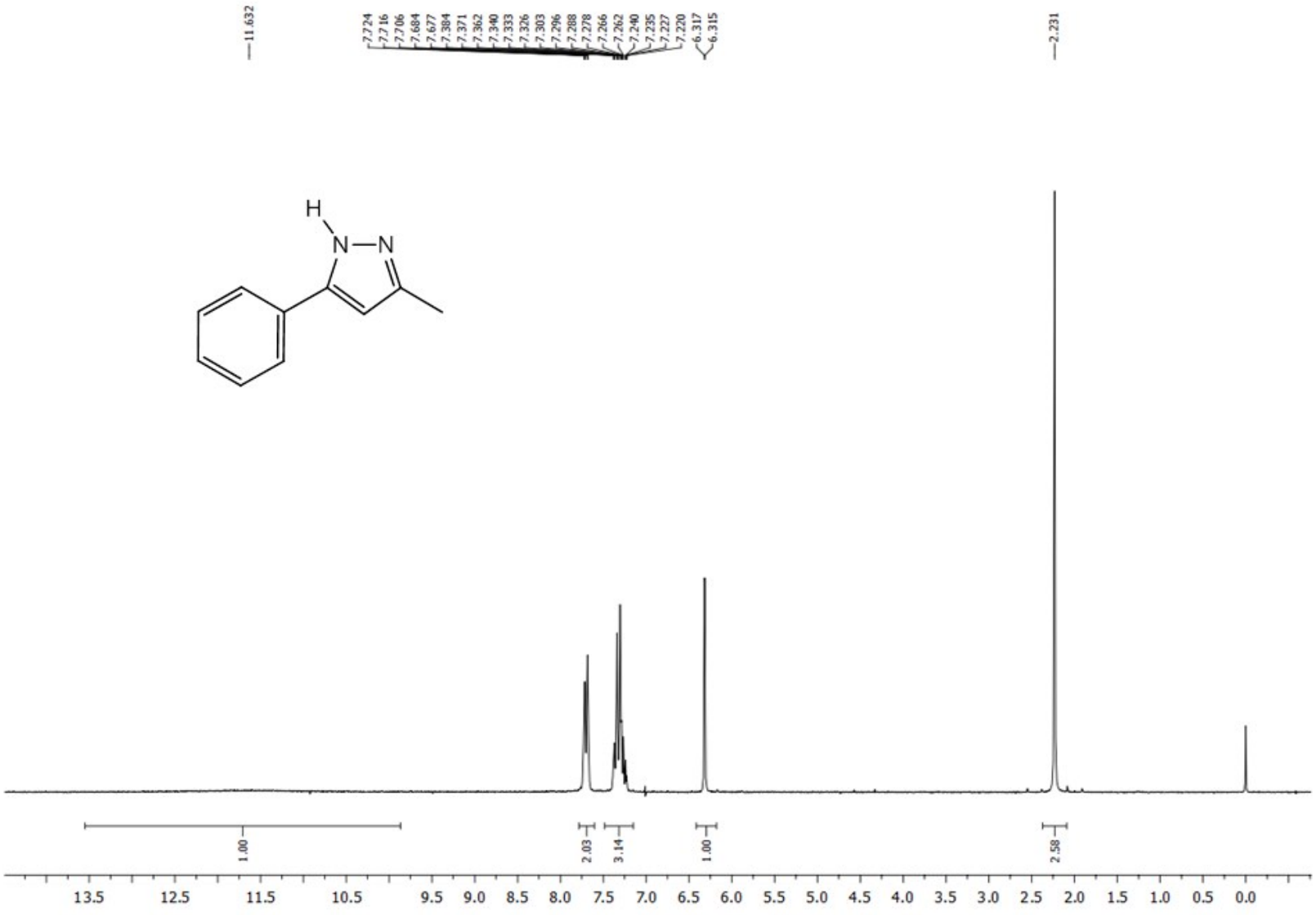

Fig. S34. ^{13}H NMR spectrum of 3(5)-methyl-5(3)-phenyl-1*H*-pyrazole in $CDCl_3$ (200 MHz).

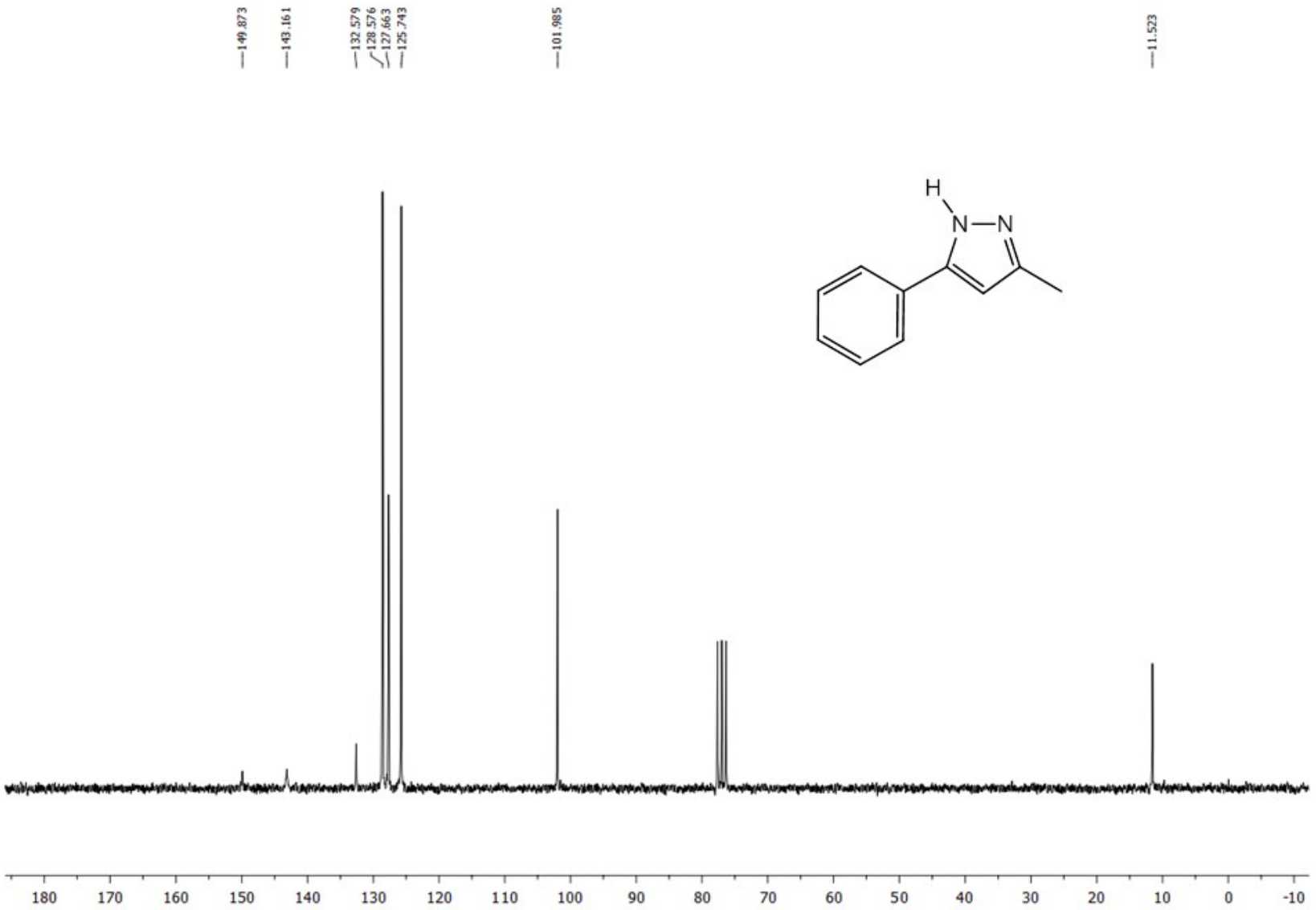

Fig. S35. ^{13}C NMR spectrum of 3(5)-methyl-5(3)-phenyl-1*H*-pyrazole in $CDCl_3$ (50 MHz).

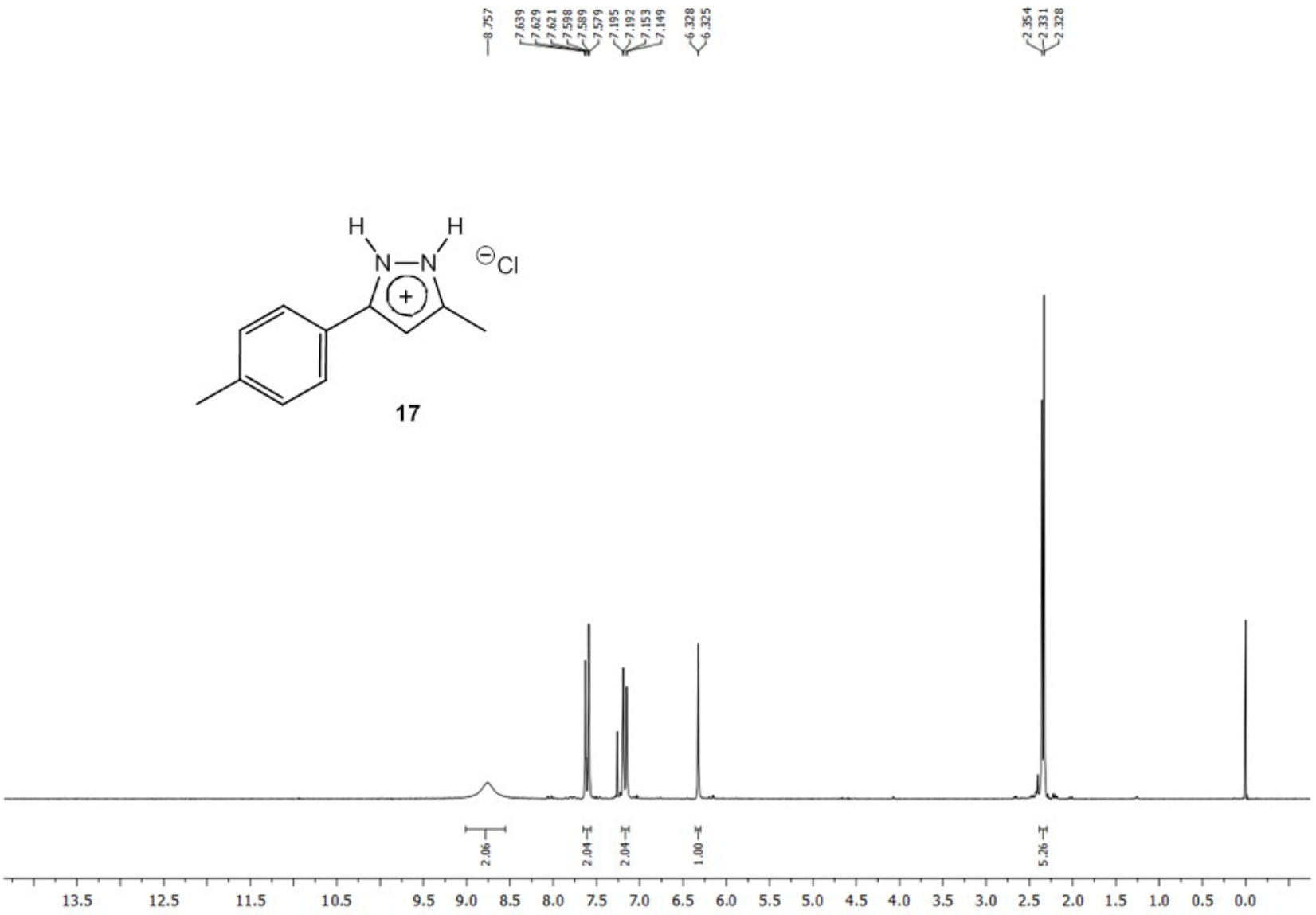

Fig. S36. ^{13}H NMR spectrum of **17** in $CDCl_3$ (200 MHz).

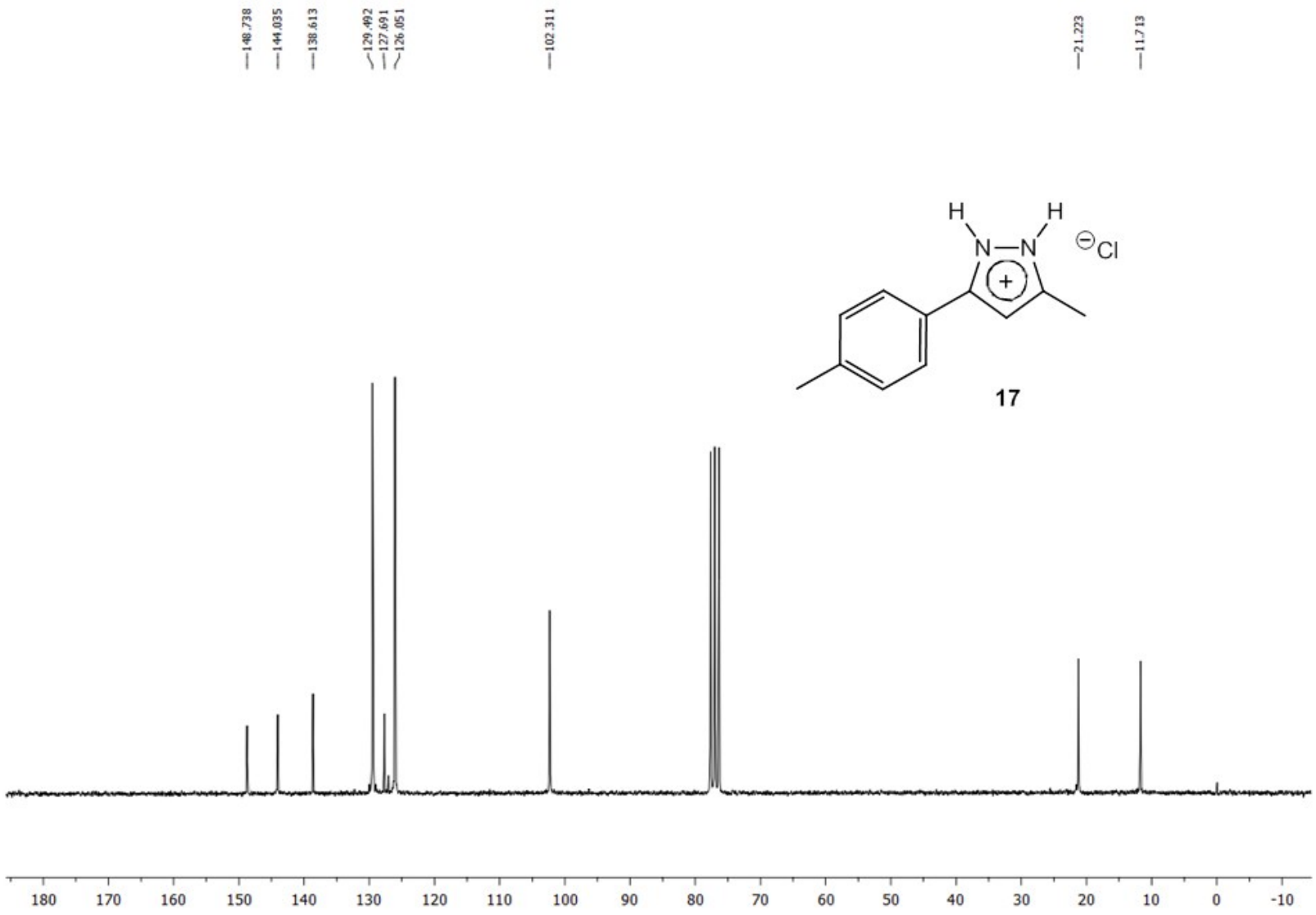

Fig. S37. ^{13}C NMR spectrum of **17** in $CDCl_3$ (50 MHz).

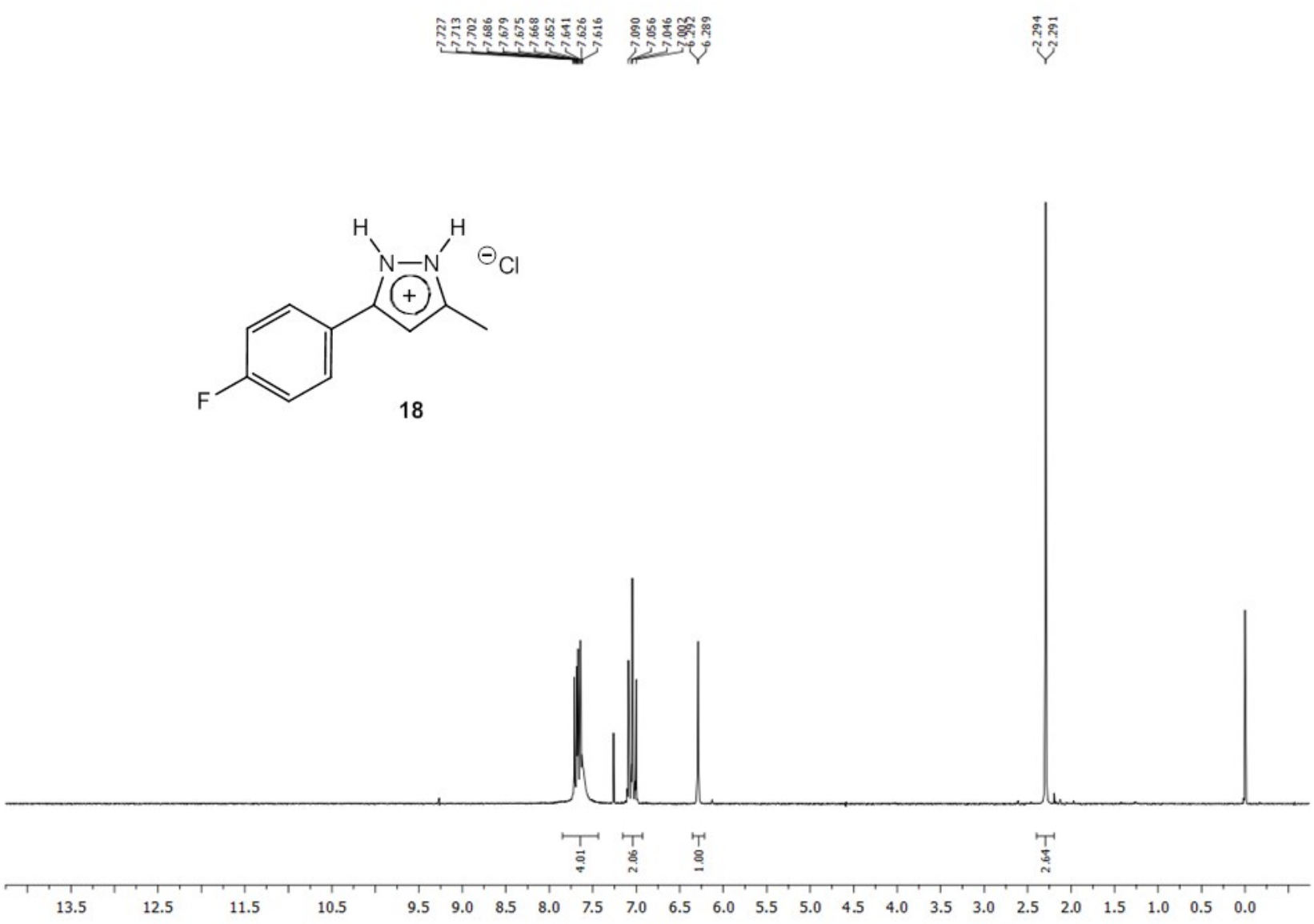

Fig. S38. ^{13}H NMR spectrum of **18** in $CDCl_3$ (200 MHz).

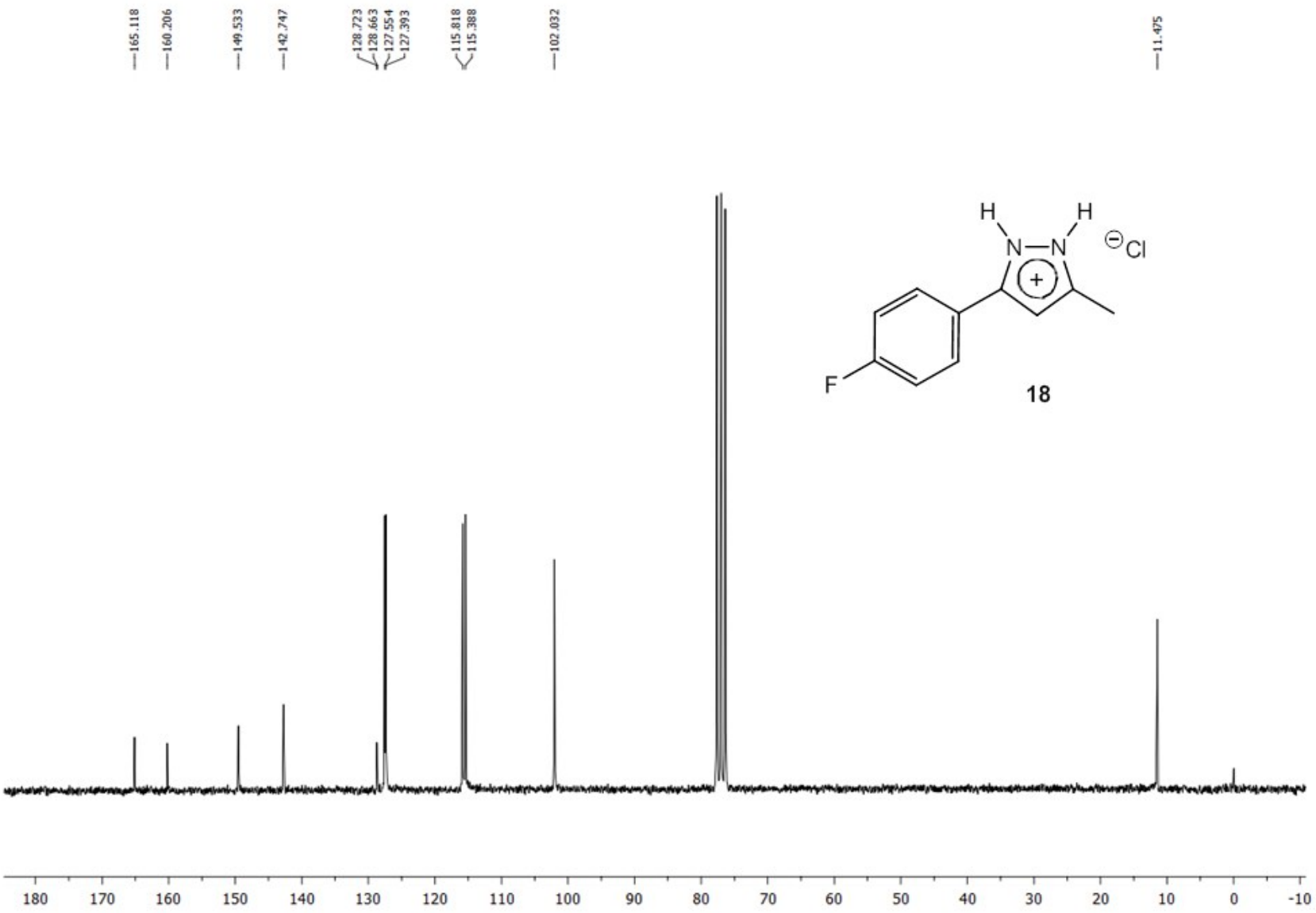

Fig. S39. ^{13}C NMR spectrum of **18** in $CDCl_3$ (50 MHz).