Supplementary Material

Ruthenium-catalyzed formation of pyrazoles or 3-hydroxynitriles from propargyl alcohols and hydrazines

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General Information

All reactions were carried out in a dry atmosphere under argon. The chemicals used were dried and purified according to common procedures. Products were purified by flash chromatography on silica and identified by spectroscopic analysis (1H NMR, 13C NMR, IR, MS, HRMS). Multiplicity was determined by DEPT spectra for all compounds. Infrared spectra were obtained with a PERKIN-ELMER FT-IR 2000. NMR spectra were recorded with a BRUKER DPX 400 or a BRUKER AVANCE 600 spectrometer. MS and HRMS data were obtained with a FINNIGAN MAT 95 or a WATERS ACQUITY UPLC-MS H-CLASS. Reactions using microwave irradiation were performed in a sealed tube with an ANTON PAAR MONOWAVE 300 reactor. Catalyst **1** has been prepared previously,[1] and its crystal structure has been solved.[2]

General Catalytic Procedure

Catalyst **1** (0.02 mmol) was dissolved in toluene (2 mL) and the propargyl alcohol (1 mmol) and hydrazine hydrate (2 mmol) or phenylhydrazine (1 mmol) were subsequently added. The mixture was heated to 150 °C for 15 or 30 minutes using microwave irradiation. Evaporation of the solvent and flash chromatography on silica (gradient: pentane/ethyl acetate) furnished the purified products as colorless or yellow oils or foams.
Spectral data of compounds **3a**[3], **3b**[4], **4a**[5], **4f**[6], **4k**[7], **4l**[8], **4m**[8], **4n**[9], **4o**[10], **7a**[11], **7b**[12], **8a**[11] and **8b**[13] are in agreement with the data previously reported by others.

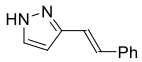
3-Methyl-1*H*-pyrazole (3a)[3]

Yield: 26 mg (0.32 mmol, 32%). Byproducts **4a** (30%) and **5a** (25%).
($C_4H_6N_2$): ^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.31 (d, *J* 1.5 Hz, 1H), 5.91 (d, *J* 1.5 Hz, 1H), 2.17 (s, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$): δ 143.1 (br, C), 134.4 (br, CH), 104.0 (CH), 11.6 (CH_3). HRMS (EI): *m*/*z* calcd. for $C_4H_6N_2$ $[M]^+$: 82.0526; Found: 82.0526.

3-Phenyl-1*H*-pyrazole (3b)[4]

Yield: 138 mg (0.96 mmol, 96%).
($C_9H_8N_2$): ^{1}H NMR (600 MHz, $CDCl_3$): δ 11.9 (br s, 1H), 7.85 (d, *J* 7.1 Hz, 2H), 7.64 (d, *J* 2.2 Hz, 1H), 7.45 (t, *J* 7.3 Hz, 2H), 7.39 (tt, *J* 7.3, 1.2 Hz, 1H), 6.66 (d, *J* 2.2 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 149.1 (br, C), 133.3 (br, CH), 132.2 (br, C), 128.8 (2CH), 128.0 (CH), 126.0 (2CH), 102.6 (CH). HRMS (EI): *m*/*z* calcd. for $C_9H_8N_2$ $[M]^+$: 144.0682; Found: 144.0682.

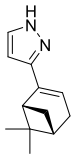
(*E*)-3-Styryl-1*H*-pyrazole (3c)



Yield: 166 mg (0.98 mmol, 98%).
($C_{11}H_{10}N_2$): ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.53 (d, *J* 2.2 Hz, 1H), 7.47 (t, *J* 7.6 Hz, 2H), 7.33 (t, *J* 7.4 Hz, 2H), 7.24 (tt, *J* 7.3, 1.3 Hz, 1H), 7.12 (d, *J* 16.6 Hz, 1H), 7.08 (d, *J* 16.6 Hz, 1H), 6.47 (d, *J* 2.2 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 146.7 (br, C), 136.8 (C, C2), 133.9 (br, CH), 130.5 (CH), 128.7 (2CH), 127.9 (CH), 126.4 (2CH), 118.2 (br, CH), 102.6 (CH). IR (ATR): ν 3181, 3035, 2956, 1672, 1467, 1369, 1205, 1098, 1048, 966, 768, 752, 694 cm^{-1}. MS

(EI): *m/z* (%): 170 $[M]^+$ (86), 169 (100), 142 (22), 84 (50). HRMS (EI): *m/z* calcd. for $C_{11}H_{10}N_2$ $[M]^+$: 170.0839; Found: 170.0839.

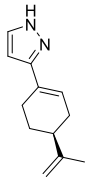
3-((1*R*,5*S*)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)-1*H*-pyrazole (3d)



Yield: 186 mg (0.99 mmol, 99%).

($C_{12}H_{16}N_2$): ^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.50 (d, *J* 2.1 Hz, 1H), 6.27 (d, *J* 2.1 Hz, 1H), 6.04 (tt, *J* 3.2, 1.5 Hz, 1H), 2.74 (td, *J* 5.6, 1.5 Hz, 1H), 2.50 (dt, *J* 8.7, 5.6 Hz, 1H), 2.46 (dt, *J* 18.6, 3.2 Hz, 1H), 2.39 (dt, *J* 18.6, 3.0 Hz, 1H), 2.20-2.15 (m, 1H), 1.36 (s, 3H), 1.29 (d, *J* 8.7 Hz, 1H), 0.87 (s, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$): δ 147.2 (br, C), 138.3 (C), 135.5 (br, CH), 120.1 (CH), 101.5 (CH), 44.0 (CH), 40.8 (CH), 38.1 (C), 31.8 (CH_2), 31.5 (CH), 26.3 (CH_3), 21.0 (CH_3). IR: v 3215, 2917, 2872, 1666, 1465, 1365, 1195, 1102, 1050, 909, 886, 765, 730, 647. MS (ESI): *m/z* (%): 188 $[M]^+$ (76), 173 (74), 146 (31), 145 (100), 144 (39), 107 (33), 84 (95). HRMS (EI): *m/z* calcd. for $C_{12}H_{16}N_2$ $[M]^+$: 188.1308; Found: 188.1308.

(*S*)-3-(4-(Prop-1-en-2-yl)cyclohex-1-en-1-yl)-1*H*-pyrazole (3e)



Yield: 187 mg (0.99 mmol, 99%).

($C_{12}H_{16}N_2$): ^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.52 (d, *J* 2.1 Hz, 1H), 6.32 (br s, 1H), 6.31 (d, *J* 2.1 Hz, 1H), 4.80-4.77 (m, 2H), 2.65-2.58 (m, 1H), 2.51-2.41 (m, 1H), 2.37-2.22 (m, 2H), 2.18-2.09 (m, 1H), 2.00-1.94 (m, 1H), 1.80 (s, 3H), 1.61 (dtd, *J* 12.7, 11.3, 5.5 Hz, 1H). ^{13}C-NMR (150 MHz, $CDCl_3$): δ 149.5 (C), 148.4 (br, C), 134.9 (br, CH), 128.0 (C), 124.3 (CH), 108.9 (CH_2), 101.2 (CH), 40.8 (CH), 30.9 (CH_2), 27.6 (CH_2), 26.8 (CH_2), 20.9 (CH_3). IR: v 3184, 3082, 2920, 1644, 1451, 1434, 1373, 1284, 1198, 1107, 1050, 934, 885, 831, 761 cm^{-1}. MS (EI): m/z (%): 188 $[M]^+$ (67), 147 (61), 120 (77), 119 (100), 93 (59), 81 (33). HRMS (EI): *m/z* calcd. for $C_{12}H_{16}N_2$ $[M]^+$: 188.1308; Found 188.1308.

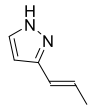
3-Pentyl-1*H*-pyrazole (3f)

Yield: 112 mg (0.81 mmol, 81%). Byproduct **4f** (10%).

($C_8H_{14}N_2$): ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.50 (d, *J* 1.9 Hz, 1H), 6.09 (d, *J* 1.9 Hz, 1H), 2.69 (t, *J* 7.8 Hz, 2H), 1.68 (br quint, *J* 7.6 Hz, 2H), 1.36-1.34 (m, 4H), 0.91 (t, *J* 7.0 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 147.9 (br, C), 135.1 (br, CH), 103.4 (CH), 31.6 (CH_2), 29.2 (CH_2), 26.7 (CH_2), 22.5 (CH_2), 14.1 (CH_3). IR (ATR): v 3194, 2955, 2928, 2867, 2859, 1686, 1466, 1434, 1377, 1295, 1202, 1111, 1050, 933, 827, 757 cm^{-1}. MS (EI): *m/z* (%): 138

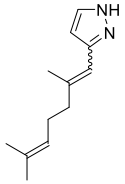
$[M]^+$ (82), 109 (59), 96 (79), 95 (91), 83 (82), 82 (100), 81 (92). HRMS (EI): *m/z* calcd. for $C_8H_{14}N_2$ $[M]^+$: 138.1152; Found: 138.1152.

(*E*)-3-(Prop-1-en-1-yl)-1*H*-pyrazole (3g)



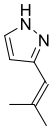
Yield: 40 mg (0.37 mmol, 37%). Byproduct **6g** (41%).
($C_6H_8N_2$): ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.50 (d, *J* 2.1 Hz, 1H), 6.40 (dq, *J* 16.0, 1.7 Hz, 1H), 6.30 (d, *J* 2.1 Hz, 1H), 6.24 (dq, *J* 15.9, 6.6 Hz, 1H), 1.89 (dd, *J* 6.6, 1.6 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 146.6 (br, C), 134.5 (br, CH), 128.3 (CH), 120.9 (CH), 102.0 (CH), 18.6 (CH_3). HRMS (EI): *m/z* calcd. for $C_6H_8N_2$ $[M]^+$: 108.0682; Found: 108.0683.

3-(2,6-Dimethylhepta-1,5-dien-1-yl)-1*H*-pyrazole (3h)



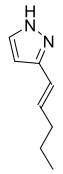
Yield: 160 mg (0,84 mmol, 84%). *E*:*Z*-ration 2:1 (as educt). Byproduct **6h** (8%).
($C_{12}H_{18}N_2$): *E*-Isomer: ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.56 (d, *J* 2.0 Hz, 1H), 6.29 (d, *J* 2.0 Hz, 1H), 6.22 (br s, 1H), 5.16-5.13 (m, 1H), 2.21-2.17 (m, 4H), 1.96 (d, *J* 1.2 Hz, 3H), 1.70 (br s, 3H), 1.63 (br s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 143.9 (br, C), 141.6 (C), 136.1 (br, CH), 132.1 (C), 123.7 (CH), 113.9 (CH), 104.3 (CH), 40.9 (CH_2), 26.7 (CH_2), 25.8 (CH_3), 18.6 (CH_3), 17.8 (CH_3). IR (ATR): ν 3186, 3110, 2967, 2855, 1660, 1447, 1376, 1275, 1206, 1169, 1107, 1050, 934, 868, 756 cm^{-1}. HRMS (EI): *m/z* calcd. for $C_{12}H_{18}N_2$: 190.1465 $[M]^+$; found: 190.1465. *Z*-Isomer: ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.54 (d, *J* 1.8 Hz, 1H), 6.24 (d, *J* 1.8 Hz, 1H), 6.17 (br s, 1H), 5.19-5.17 (m, 1H), 2.35 (dd, *J* 8.3, 7.4 Hz, 2H), 2.22-2.19 (m, 2H), 1.92 (d, *J* 1.1 Hz, 3H), 1.71 (br s, 3H), 1.64 (br s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 143.3 (br, C), 142.8 (C), 137.2 (br, CH), 132.9 (C), 124.1 (CH), 114.5 (CH), 104.4 (CH), 33.9 (CH_2), 26.4 (CH_2), 26.1 (CH_3), 24.8 (CH_3), 18.1 (CH_3). HRMS (EI): *m/z* calcd. for $C_{12}H_{18}N_2$: 190.1465 $[M]^+$; found: 190.1466.

3-(2-Methylprop-1-en-1-yl)-1*H*-pyrazole (3i)



Yield: 87 mg (0,71 mmol, 71%). Byproduct **6i** (11%).
($C_7H_{10}N_2$): ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.55 (d, *J* 1.8 Hz, 1H), 6.27 (d, *J* 1.8 Hz, 1H), 6.20 (br s, 1H), 1.96 (d, *J* 0.7 Hz, 3H), 1.93 (d, *J* 1.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 143.9 (br, C), 138.4 (C), 136.3 (br, CH), 114.2 (CH), 104.3 (CH), 27.1 (CH_3), 20.1 (CH_3). IR (ATR): ν 3179, 3101, 2927, 1665, 1462, 1441, 1377, 1280, 1207, 1109, 1051, 934, 839, 761 cm^{-1}. MS (EI): *m/z* (%): 122 $[M]^+$ (100), 107 (27), 94 (20); HRMS (EI): *m/z* calcd. for $C_7H_{10}N_2$: 122.0839 $[M]^+$; Found: 122.0838.

(*E*)-3-(Pent-1-en-1-yl)-1*H*-pyrazole (3j)

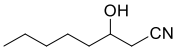


Yield: 71 mg (0,52 mmol, 52%). Byproduct **6j** (28%).
($C_8H_{12}N_2$): ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.51 (d, *J* 2.1 Hz, 1H), 6.40 (dt, *J* 16.0, 1.3 Hz, 1H), 6.32 (d, *J* 2.1 Hz, 1H), 6.25 (dt, *J* 16.0, 6.9 Hz, 1H), 2.19 (qd, *J* 7.1, 1.3 Hz, 2H), 1.50 (sext, *J* 7.4 Hz, 2H), 0.96 (t, *J* 7.4 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 146.5 (br, C), 134.6 (br, CH), 133.4 (CH), 119.7 (CH), 102.0 (CH), 35.1 (CH_2), 22.4 (CH_2), 13.8 (CH_3). IR (ATR): ν 3175, 3100, 2958, 2928, 2871, 1662, 1462, 1436, 1377, 1296, 1200, 1102, 1052, 962, 934, 759 cm^{-1}. MS (EI): *m/z* (%): 136 $[M]^+$ (94), 121 (62), 107 (100), 94 (49), 80 (69). HRMS (EI): *m/z* calcd. for $C_8H_{12}N_2$: 136.0995 $[M]^+$; Found: 136.0995.

3-Hydroxybutanenitrile (4a)[5]

Yield: 26 mg (0.30 mmol, 30%). Byproduct of **3a** (32%).
(C_4H_7NO): ^{1}H-NMR (600 MHz, $CDCl_3$): δ 3.97 (quint.d, *J* 6.2, 5.1 Hz, 1H), 2.40 (dd, *J* 16.6, 5.1 Hz, 1H), 2.34 (dd, *J* 16.6, 6.2 Hz, 1 H), 1.17 (d, *J* 6.2 Hz, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$): δ 118.2 (C), 62.9 (CH), 27.3 (CH_2), 22.5 (CH_3). HRMS (EI): *m/z* calcd. for C_4H_7NO: 85.0523 $[M]^+$; Found: 85.0523.

3-Hydroxyoctanenitrile (4f)[6]

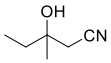


Yield: 14 mg (0.10 mmol, 10%). Byproduct of **3f** (81%).
($C_8H_{15}NO$): ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.98 (ddt, *J* 7.8, 6.5, 4.9 Hz, 1H), 2.57 (dd, *J* 16.6, 4.8 Hz, 1H), 2.50 (dd, *J* 16.6, 6.4 Hz, 1H), 1.65-1.56 (m, 2H), 1.51-1.44 (m, 1H), 1.39-1.25 (m, 5H), 0.90 (t, *J* 6.6 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 118.5 (C), 67.4 (CH), 36.7 (CH_2), 31.6 (CH_2), 26.3 (CH_2), 25.3 (CH_2), 22.6 (CH_2), 14.1 (CH_3). HRMS (EI): *m/z* calcd. for $C_8H_{15}NO$: 141.1149 $[M]^+$; Found: 141.1149.

3-Hydroxy-3-methylbutanenitrile (4k)[7]

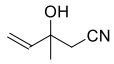
Yield: 90 mg (0.91 mmol, 91%).
(C_5H_9NO): ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.49 (s, 2H), 1.37 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 118.1 (C), 68.9 (C), 32.8 (CH_2), 29.1 ($2CH_3$). HRMS (EI): *m/z* calcd. for C_5H_9NO: 99.0679 $[M]^+$; Found: 99.0679.

3-Hydroxy-3-methylpentanenitrile (4l)[8]



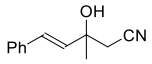
Yield: 111 mg (0,98 mmol, 98%).
($C_6H_{11}NO$): ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.47 (br s, 1H), 2.45 (d, *J* 16.6 Hz, 1H), 2.41 (d, *J* 16.6 Hz, 1 H), 1.59 (dq, *J* 16.8, 7.5 Hz, 1H), 1.56 (dq, *J* 16.8, 7.5 Hz, 1H), 1.26 (s, 3H), 0.88 (t, *J* 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 118.0 (C), 71.3 (C), 34.2 (CH_2), 30.8 (CH_2), 26.1 (CH), 8.1 (CH_3). HRMS (EI): *m/z* calcd. for $C_6H_{11}NO$: 113.0836 $[M]^+$; Found: 113.0835.

3-Hydroxy-3-methylpent-4-enenitrile (4m)[8]



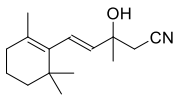
Yield: 51 mg (0,46 mmol, 46%). Byproducts **5m** (30%) and **10m** (14%).
(C_6H_9NO): ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.93 (dd, *J* 17.2, 10.8 Hz, 1H), 5.33 (d, *J* 17.2 Hz, 1H), 5.18 (d, *J* 10.8 Hz, 1H), 2.53 (s, 2H), 1.99 (br s, 1H), 1.42 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 141.6 (CH), 117.2 (C), 114.8 (CH_2), 71.2 (C), 31.8 (CH_2), 27.5 (CH_3). HRMS (EI): *m/z* calcd. for C_6H_9NO: 111.0679 $[M]^+$; Found: 111.0679.

(E)-3-Hydroxy-3-methyl-5-phenylpent-4-enenitrile (4n)[9]



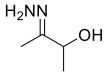
Yield: 60 mg (0.32 mmol, 32%). Byproduct **10g** (34%).
($C_{12}H_{13}NO$): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.27 (m, 5H), 6.74 (d, *J* 16.0 Hz, 1H), 6.32 (d, *J* 16.0 Hz, 1H), 2.68 (s, 2H), 1.59 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 135.9 (C), 132.6 (CH), 129.8 (CH), 128.8 (2CH), 128.3 (CH), 126.8 (2CH), 117.3 (C), 71.2 (C), 32.2 (CH_2), 27.9 (CH_3). HRMS (EI): *m/z* calcd. for $C_{12}H_{13}NO$: 187.0992 $[M]^+$; Found: 187.0992.

(E)-3-Hydroxy-3-methyl-5-(2,6,6-trimethylcyclohex-1-en-1-yl)pent-4-enenitrile (4o)[10]



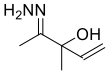
Yield: 146 mg (0.63 mmol, 63%). Byproduct **10f** (12%).
($C_{15}H_{23}NO$): ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.09 (br d, *J* 16.1 Hz, 1H), 5.48 (d, *J* 16.1 Hz, 1H), 2.52 (s, 2H), 1.96 (br t, *J* 6.3 Hz, 2H), 1.64 (d, *J* 0.8 Hz, 3H), 1.62-1.56 (m, 2H), 1.45-1.42 (m, 2H), 1.39 (s, 3H), 0.97 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.9 (CH), 136.6 (C), 129.0 (C), 126.7 (CH), 117.9 (C), 70.8 (C), 39.4 (CH_2), 34.1 (C), 33.1 (CH_2), 32.7 (CH_2), 28.8 ($2CH_3$), 28.7 (CH_3), 21.4 (CH_3), 19.3 (CH_2). HRMS (EI): *m/z* calcd. for $C_{15}H_{23}NO$ $[M]^+$: 233.1775; Found: 233.1775.

3-Hydrazonobutan-2-ol (5a)



Yield: 26 mg (0.25 mmol, 25%). Byproduct of **3a** (32%).
($C_4H_{10}N_2O$): ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.11 (q, *J* 6.6 Hz, 1H), 3.99 (br s, 3H), 1.62 (s, 3H), 1.14 (d, *J* 6.6 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 153.5 (C), 69.9 (CH), 20.6 (CH_3), 9.8 (CH_3). HRMS (EI): *m/z* calcd. for $C_4H_{10}N_2O$ $[M]^+$: 102.0788; Found: 102.0788.

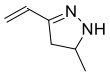
4-Hydrazono-3-methylpent-1-en-3-ol (5m)



Yield: 38 mg (0.30 mmol, 30%). Byproduct of **4m** (46%).
($C_6H_{12}N_2O$): ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.84 (dd, *J* 17.2, 10.6 Hz, 1H), 5.29 (dd *J* 17.2, 1.2 Hz, 1H), 5.11 (dd, *J* 10.6, 1.2 Hz, 1H), 3.34 (br s, 3H), 1.71 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 152.5 (C), 141.8 (CH),

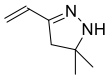
114.2 (CH_2), 74.8 (C), 25.0 (CH_3), 10.3 (CH_3). HRMS (EI): *m*/*z* calcd. for $C_4H_{10}N_2O$ $[M]^+$: 128.0945; Found: 128.0946.

5-Methyl-3-vinyl-4,5-dihydro-1*H*-pyrazole (6g)



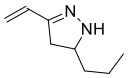
Yield: 45 mg (0.41 mmol, 41%). Byproduct of **3g** (37%).
($C_6H_{10}N_2$): ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.65 (dd, *J* 17.6, 10.8 Hz, 1H), 5.40 (dd *J* 10.8, 0.9 Hz, 1H), 5.31 (dd, *J* 17.6, 1.0 Hz, 1H), 3.88 (ddq, *J* 9.7, 7.9, 6.3 Hz, 1H), 2.88 (dd, *J* 16.0, 9.7 Hz, 1H), 2.40 (dd, *J* = 16.0, 7.9 Hz, 1H), 1.08 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 153.6 (C), 130.7 (CH), 118.6 (CH_2), 55.7 (CH), 37.6 (CH_2), 20.6 (CH_3). HRMS (EI): *m*/*z* calcd. for $C_6H_{10}N_2$ $[M]^+$: 110.0839; Found: 110.0840.

5,5-Dimethyl-3-vinyl-4,5-dihydro-1*H*-pyrazole (6i)



Yield: 14 mg (0.11 mmol, 11%). Byproduct of **3i** (71%).
($C_7H_{12}N_2$): ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.64 (dd, *J* 17.7, 10.8 Hz, 1H), 5.39 (dd *J* 10.8, 0.7 Hz, 1H), 5.29 (dd, *J* 17.7, 0.9 Hz, 1H), 2.80 (s, 2H), 1.10 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 153.2 (C), 131.1 (CH), 118.2 (CH_2), 62.7 (C), 43.9 (CH_2), 27.6 ($2CH_3$). HRMS (EI): *m*/*z* calcd. for $C_7H_{12}N_2$ $[M]^+$: 124.9995; Found: 124.9997.

5-Propyl-3-vinyl-4,5-dihydro-1*H*-pyrazole (6j)



Yield: 39 mg (0.28 mmol, 28%). Byproduct of **3j** (52%).
($C_8H_{14}N_2$): ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.63 (dd, *J* 17.6, 10.8 Hz, 1H), 5.38 (dd *J* 10.8, 0.7 Hz, 1H), 5.29 (dd, *J* 17.6, 0.9 Hz, 1H), 3.74 (ddt, *J* 9.8, 9.0, 6.7 Hz, 1H), 2.85 (dd, *J* 16.0, 9.7 Hz, 1H), 2.41 (dd, *J* 16.0, 8.9 Hz, 1H), 1.51-1.31 (m, 4H), 0.89 (d, *J* 6.7 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 153.8 (C), 130.7 (CH), 118.4 (CH_2), 60.4 (CH), 37.2 (CH_2), 36.2 (CH_2), 19.7 (CH_2), 14.0 (CH_3). HRMS (EI): *m*/*z* calcd. for $C_8H_{14}N_2$ $[M]^+$: 138.1152; Found: 138.1152.

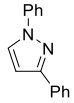
3-Methyl-1-phenyl-1*H*-pyrazole (7a)[11]

Yield: 63 mg (0.40 mmol, 40%). Byproducts **8a** (9%) and **9** (29%).
($C_{10}H_{10}N_2$): ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.80 (d, *J* 2.4 Hz, 1H), 7.66 (dd, *J* 8.6, 1.2 Hz, 2H), 7.43 (dd, *J* 8.4, 7.5 Hz, 2H), 7.27-7.23 (m, 1H), 6.26 (d, *J* 2.4 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 150.5 (C), 140.0 (C), 129.3 (2CH), 127.4 (CH), 125.9 (CH), 118.7 (2CH), 107.5 (CH), 13.6 (CH_3). HRMS (EI): *m*/*z* calcd. for $C_{10}H_{10}N_2$ $[M]^+$: 158.0840; Found: 158.0840.

5-Methyl-1-phenyl-1*H*-pyrazole (8a)[11]

Yield: 14 mg (0.09 mmol, 9%). Byproduct of **7a** (9%).
($C_{10}H_{10}N_2$): ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.62 (br d, *J* 1.7 Hz, 1H), 7.48-7.36 (m, 5H), 6.23 (br d, *J* 1.7 Hz, 1H), 2.34 (br s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 139.8 (CH), 139.7 (C), 138.7 (C), 129.0 (2CH), 127.3 (CH), 124.8 (2CH), 106.8 (CH), 12.2 (CH_3). HRMS (EI): *m*/*z* calcd. for $C_{10}H_{10}N_2$ $[M]^+$: 158.0840; Found: 158.0840.

1,3-Diphenyl-1*H*-pyrazole (7b)[12]

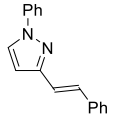


Yield: 32 mg (mmol, 15%). Byproduct of **8b** (39%).
($C_{15}H_{12}N_2$): ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.97-7.95 (m, 2H), 7.93 (d, *J* 2.5 Hz, 1H), 7.77 (d, *J* 7.4 Hz, 2H), 7.50-7.40 (m, 4H), 7.38-7.29 (m, 2H), 6.79 (d, *J* 2.5 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 152.9 (C), 140.1 (C), 133.0 (C), 129.4 (2CH), 128.7 (2CH), 128.1 (CH), 128.0 (CH), 126.3 (CH), 125.8 (2CH), 119.0 (2CH), 105.0 (CH). HRMS (EI): *m*/*z* calcd. for $C_{15}H_{12}N_2$ $[M]^+$: 220.0995; Found: 220.0995.

1,5-Diphenyl-1*H*-pyrazole (8b)[13]

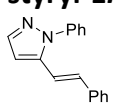
Yield: 86 mg (0.39 mmol, 39%). Byproduct **7b** (15%).
($C_{15}H_{12}N_2$): ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.73 (d, *J* 1.8 Hz, 1H), 7.40-7.22 (m, 10H), 6.53 (d, *J* 1.8 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 143.0 (C), 140.3 (CH), 139.9 (C), 130.4 (C), 128.9 (2CH), 128.7 (2CH), 128.4 (2CH), 128.2 (CH), 127.5 (CH), 125.2 (2CH), 107.8 (CH). HRMS (EI): *m*/*z* calcd. for $C_{15}H_{12}N_2$ $[M]^+$: 220.0995; Found: 220.0995.

(*E*)-1-Phenyl-3-styryl-1*H*-pyrazole (7c)



Yield: 94 mg (0.38 mmol, 38%). Byproduct of **8c** (56%).
($C_{17}H_{14}N_2$): ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.92 (d, *J* 2.5 Hz, 1H), 7.73 (dd, *J* 8.5, 1.1 Hz, 2H), 7.57 (d, *J* 7.3 Hz, 2H), 7.55 (d, *J* 7.4 Hz, 2H), 7.48 (dd, *J* 8.5, 7.5 Hz, 2H), 7.39 (t, *J* 7.6 Hz, 2H), 7.30 (t, *J* 7.3 Hz, 1H), 7.29 (t, *J* 7.5 Hz, 1H), 7.26 (d, *J* 16.6 Hz, 1H), 7.20 (d, *J* 16.6 Hz, 1 H), 6.71 (d, *J* 2.5 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 152.4 (C), 140.2 (C), 137.2 (C), 130.9 (CH), 129.6 (2CH), 128.8 (2CH), 128.0 (CH), 127.9 (CH), 126.7 (2CH), 126.5 (CH, C13), 120.6 (CH), 119.1 (2CH), 105.1 (CH). IR (ATR): ν 3047, 3000, 1598, 1515, 1499, 1381, 1256, 1052, 963, 946, 761, 747, 688 cm^{-1}. MS (EI): *m*/*z* (%): 246 $[M]^+$ (84), 245 (100), 169 (39), 168 (31), 158 (39). HRMS (EI): *m*/*z* calcd. for $C_{17}H_{14}N_2$ $[M]^+$: 246.1152; Found: 246.1152.

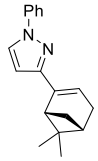
(*E*)-1-Phenyl-5-styryl-1*H*-pyrazole (8c)



Yield: 138 mg (0.56 mmol, 56%). Byproduct **7c** (38%).

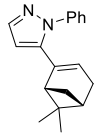
($C_{17}H_{14}N_2$): ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.69 (d, *J* 1.9 Hz, 1H), 7.53 (d, *J* 4.3 Hz, 4H), 7.45 (q, *J* 4.3 Hz, 1H), 7.43 (d, *J* 7.9 Hz, 2H), 7.35 (t, *J* 7.6 Hz, 2 H), 7.29 (tt, *J* 7.4, 1.1 Hz, 1H), 7.11 (d, *J* 16.3 Hz, 1H), 6.92 (d, *J* 16.3 Hz, 1 H), 6.69 (d, *J* 1.9 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 141.3 (C), 140.4 (CH), 139.7 (C), 136.5 (C), 132.2 (CH), 129.3 (2CH), 128.9 (2CH), 128.4 (CH), 128.1 (CH), 126.7 (2CH), 125.6 (2CH), 115.8 (CH), 104.2 (CH). IR (ATR): ν 3046, 3026, 3002, 1598, 1515, 1499, 1455, 1389, 1328, 1256, 1237, 1071, 1052, 962, 946, 925, 761, 747, 689 cm^{-1}. MS (EI): *m/z* (%): 246 $[M]^+$ (100), 245 (97), 169 (34), 158 (85), 157 (62). HRMS (EI): *m/z* calcd. for $C_{17}H_{14}N_2$ $[M]^+$: 246.1152; Found: 246.1152.

3-((1*R*,5*S*)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)-1-phenyl-1*H*-pyrazole (7d)



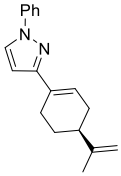
Yield: 74 mg (0.28 mmol, 28%). Byproduct of **8d** (60%).
($C_{18}H_{20}N_2$): ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.86 (d, *J* 2.5 Hz, 1H), 7.70 (dd, *J* 8.7, 1.2 Hz, 2H), 7.44 (dd, *J* 8.5, 7.4 Hz, 2H), 7.26 (tt, *J* 7.5, 1.1 Hz, 2H), 6.55 (d, *J* 2.5 Hz, 1H), 6.19 (tt, *J* 3.3, 1.5 Hz, 1H), 3.12 (td, *J* 5.7, 1.4 Hz, 1H), 2.55 (dt, *J* 8.8, 5.7 Hz, 1H), 2.51 (dt, *J* 18.4, 3.2 Hz, 1H), 2.44 (dt, *J* 18.4, 3.0 Hz, 1H), 2.22 (septd, *J* 2.9, 1.2 Hz, 1H), 1.41 (s, 3H), 1.34 (d, *J* 8.9 Hz, 1H), 0.93 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 153.7 (C), 140.9 (C), 140.4 (C), 129.4 (2CH), 127.7 (CH), 126.0 (CH), 120.7 (CH), 119.0 (2CH), 104.1 (CH), 43.0 (CH), 41.0 (CH), 38.0 (C), 32.0 (CH_2), 31.6 (CH_2), 26.4 (CH_3), 21.1 (CH_3). IR (ATR): ν 2931, 2913, 1599, 1517, 1501, 1461, 1365, 1315, 1254, 1220, 1199, 1176, 1155, 1140, 1121, 1081, 1046, 1029, 946, 927, 902, 885, 807, 751, 689, 667 cm^{-1}. MS (EI): *m/z* (%): 264 $[M]^+$ (92), 249 (78), 221 (100), 182 (40), 105 (37). HRMS (EI): *m/z* calcd. for $C_{18}H_{20}N_2$ $[M]^+$: 264.1621; Found: 264.1621.

5-((1*R*,5*S*)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)-1-phenyl-1*H*-pyrazole (8d)



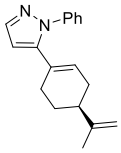
Yield: 158 mg (0.60 mmol, 60%). Byproduct **7d** (28%).
($C_{18}H_{20}N_2$): ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.60 (d, *J* 1.9 Hz, 1H), 7.47 (dd, *J* 8.5, 1.2 Hz, 2H), 7.42 (t, *J* 7.9 Hz, 2H), 7.34 (tt, *J* 7.3, 1.3 Hz, 1H), 6.25 (d, *J* 1.9 Hz, 1H), 5.75 (tt, *J* 3.3, 1.4 Hz, 1H), 2.40 (dt, *J* 18.6, 3.1 Hz, 1H), 2.31 (dt, *J* 8.8, 5.7 Hz, 1H), 2.29 (dt, *J* 18.6, 3.1, 1H), 2.11-2.08 (m, 1H), 2.07 (td, *J* 5.6, 1.5 Hz, 1H), 1.25 (d, *J* 8.8 Hz, 1H), 1.18 (s, 3H), 0.87 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 144.1 (C), 141.0 (C), 140.1 (CH), 137.6 (C), 129.0 (2CH), 127.6 (CH), 125.2 (CH), 124.9 (2CH), 106.2 (CH), 45.8 (CH), 40.2 (CH), 38.0 (C), 32.1 (CH_2), 31.9 (CH_2), 26.2 (CH_3), 20.9 (CH_3). IR (ATR): ν 2946, 2933, 2915, 1597, 1499, 1468, 1448, 1383, 1366, 1349, 1263, 1219, 1117, 1070, 1055, 1021, 952, 924, 900, 885, 811, 778, 760, 691, 652 cm^{-1}. MS (EI): *m/z* (%): 264 $[M]^+$ (64), 221 (100), 195 (58), 194 (51), 94 (25). HRMS (EI): *m/z* calcd. for: $C_{18}H_{20}N_2$ $[M]^+$: 264.1621; Found: 264.1621.

(*S*)-1-Phenyl-3-(4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)-1*H*-pyrazole (7e)



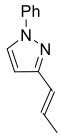
Yield: 82 mg (0.31 mmol, 31%). Byproduct of **8e** (62%).
($C_{18}H_{20}N_2$): ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.86 (d, *J* 2.3 Hz, 1H), 7.70 (dd, *J* 8.5, 1.1 Hz, 2H), 7.44 (dd, *J* 8.4, 7.4 Hz, 2H), 7.26 (tt, *J* 7.5, 1.1 Hz, 1H), 6.53 (d, *J* 2.4 Hz, 1H), 6.43 (dtd, *J* 5.2, 2.4, 0.9 Hz, 1H), 4.80-4.78 (m, 2H), 2.84-2.79 (m, 1H), 2.56-2.49 (m, 1H), 2.40-2.35 (m, 1H), 2.32-2.27 (m, 1H), 2.17 (dddt, *J* 17.6, 10.5, 3.9, 2.6 Hz, 1H), 2.02-1.98 (m, 1H), 1.81 (s, 3H), 1.64 (dtd, *J* 12.7, 11.5, 5.3 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 154.7 (C), 150.0 (C), 140.4 (C), 130.4 (C), 129.5 (2CH), 127.4 (CH), 126.1 (CH), 124.8 (CH), 118.9 (2CH), 108.9 (CH_2), 104.0 (CH), 41.1 (CH), 31.1 (CH_2), 27.7 (CH_2), 26.5 (CH_2), 21.0 (CH_3). IR (ATR): ν 3069, 2964, 2917, 1599, 1515, 1501, 1451, 1434, 1401, 1372, 1346, 1329, 1294, 1254, 1236, 1093, 1039, 948, 886, 830, 750, 688 cm^{-1}. MS (EI): *m/z* (%): 264 $[M]^+$ (89), 249 (33), 223 (87), 195 (100), 182 (82), 169 (45). HRMS (EI): *m/z* calcd. for: $C_{18}H_{20}N_2$ $[M]^+$: 264.1621; Found: 264.1621.

(*S*)-1-Phenyl-5-(4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)-1*H*-pyrazole (8e)



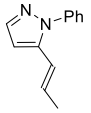
Yield: 164 mg (0.62 mmol, 62%). Byproduct **7e** (31%).
($C_{18}H_{20}N_2$): ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.62 (d, *J* 1.9 Hz, 1H), 7.49 (dd, *J* 8.3, 1.0 Hz, 2H), 7.43 (t, *J* 7.9 Hz, 2H), 7.35 (tt, *J* 7.4, 1.2 Hz, 1H), 6.28 (d, *J* 1.8 Hz, 1H), 5.87-5.85 (m, 1H), 4.79 (quint, *J* 1.4 Hz, 1H), 4.72-4.71 (m, 1H), 2.27-2.21 (m, 1H), 2.20-2.16 (m, 1H), 2.15-2.10 (m, 2H), 2.07-2.01 (m, 1H), 1.82-1.78 (m, 1H), 1.74 (s, 3H), 1.49 (dddd, *J* 12.8, 11.2, 10.1, 6.1 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 149.3 (C), 145.1 (C), 140.9 (C), 139.9 (CH), 130.0 (CH), 129.1 (2CH), 128.0 (C), 127.5 (CH), 124.6 (2CH), 109.1 (CH_2), 106.5 (CH), 40.3 (CH), 31.0 (CH_2), 28.5 (CH_2), 27.5 (CH_2), 20.9 (CH_3). IR (ATR): ν 3046, 2964, 2917, 1597, 1515, 1500, 1473, 1449, 1384, 1328, 1312, 1258, 1229, 1122, 1070, 1052, 963, 945, 925, 889, 833, 760, 690, 651 cm^{-1}. MS (EI): *m/z* (%): 264 $[M]^+$ (77), 263 (44), 196 (33), 195 (92), 94 (100). HRMS (EI): *m/z* calcd. for: $C_{18}H_{20}N_2$ $[M]^+$: 264.1621; Found: 264.1621.

(*E*)-1-Phenyl-3-(prop-1-en-1-yl)-1*H*-pyrazole (7g)



Yield: 46 mg (0.25 mmol, 25%). Byproduct of **8g** (62%).
($C_{12}H_{12}N_2$): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* 2.5 Hz, 1H), 7.67 (dd, *J* 8.5, 1.1 Hz, 2H), 7.44 (dd, *J* 8.3, 7.5 Hz, 2H), 7.26 (tt, *J* 7.4, 1.1 Hz, 2H), 6.53 (dq, *J* 16.0, 1.5 Hz, 1H), 6.51 (d, *J* 2.5 Hz, 1H), 6.35 (dq, *J* 15.9, 6.6 Hz, 1H), 1.92 (dd, *J* 6.6, 1.6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 152.7 (C), 140.2 (C), 129.5 (2CH), 128.6 (CH), 127.7 (CH), 126.2 (CH), 123.2 (CH), 119.0 (2CH), 104.4 (CH), 18.6 (CH_3). IR (ATR): ν 3048, 3013, 2962, 2931, 2912, 1598, 1518, 1500, 1457, 1386, 1369, 1257, 1048, 963, 949, 930, 750, 689 cm^{-1}. MS (EI): *m/z* (%): 184 $[M]^+$ (100), 183 (29), 77 (39). HRMS (EI): *m/z* calcd. for $C_{12}H_{12}N_2$ $[M]^+$: 184.0995; Found: 184.0995.

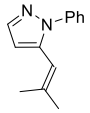
(*E*)-1-Phenyl-5-(prop-1-en-1-yl)-1*H*-pyrazole (8g)



Yield: 114 mg (0.62 mmol, 62%). Byproduct **7g** (25%).

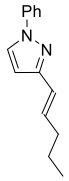
($C_{12}H_{12}N_2$): ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.59 (d, *J* 1.9 Hz, 1H), 7.51-7.44 (m, 4H), 7.42-7.38 (m, 1H), 6.47 (d, *J* 1.9 Hz, 1H), 6.32-6.21 (m, 2H), 1.87-1.83 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 141.5 (C), 140.2 (CH), 139.8 (C), 130.2 (CH), 129.2 (2CH), 127.9 (CH), 125.5 (2CH), 118.9 (CH), 103.6 (CH), 18.7 (CH_3). IR (ATR): ν 3033, 2963, 2933, 1596, 1499, 1452, 1391, 1070, 956, 931, 924, 910, 761, 695, 684, 648 cm^{-1}. MS (EI): *m*/*z* (%): 184 $[M]^+$ (100), 183 (35), 77 (33). HRMS (EI): *m*/*z* calcd. for $C_{12}H_{12}N_2$: 184.0995 $[M]^+$; Found: 184.0995.

5-(2-Methylprop-1-en-1-yl)-1-phenyl-1H-pyrazole (8i)



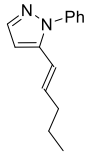
Yield: 116 mg (0.59 mmol, 59%).
($C_{13}H_{14}N_2$): ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.65 (d, *J* 1.8 Hz, 1H), 7.48 (dd, *J* 8.4, 1.1 Hz, 2H), 7.43 (t, *J* 7.6 Hz, 2H), 7.34 (tt, *J* 7.4, 1.2 Hz, 1H), 6.37 (d, *J* 1.8 Hz, 1H), 5.97 (br s, 1H), 1.92 (d, *J* 1.0 Hz, 3H), 1.86 (d, *J* 1.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 140.1 (C), 140.0 (C), 139.9 (CH), 139.4 (C), 129.0 (2CH), 127.5 (CH), 125.2 (2CH), 113.5 (CH), 106.9 (CH), 26.8 (CH_3), 20.1 (CH_3).
HRMS (EI): *m*/*z* calcd. for $C_{13}H_{14}N_2$: 198.1152 $[M]^+$; Found: 198.1152.

(*E*)-3-(Pent-1-en-1-yl)-1-phenyl-1*H*-pyrazole (7j)



Yield: 44 mg (0.21 mmol, 21%). Byproduct of **8j** (59%).
($C_{14}H_{16}N_2$): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* 2.5 Hz, 1H), 7.68 (dd, *J* 8.5, 1.3 Hz, 1H), 7.44 (dd, *J* 8.5, 7.5 Hz, 2H), 7.26 (tt, *J* 7.4, 1.1 Hz, 1H), 6.53 (dt, *J* 16.0, 1.4 Hz, 1H), 6.52 (d, *J* 2.5 Hz, 1H), 6.34 (dt, *J* 16.0, 6.9 Hz, 1H), 2.23 (qd, *J* 7.0, 1.4 Hz, 2H), 1.53 (sext, *J* 7.4 Hz, 2H), 0.98 (t, *J* 7.3 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 152.8 (C), 140.3 (C), 133.8 (CH), 129.5 (2CH), 127.6 (CH), 126.2 (CH), 122.1 (CH), 118.9 (2CH), 104.5 (CH), 35.1 (CH_2), 22.4 (CH_2), 13.9 (CH_3). IR (ATR): ν 3047, 2958, 2928, 1599, 1518, 1501, 1456, 1257, 1046, 965, 947, 749, 689 cm^{-1}. MS (EI): *m*/*z* (%): 212 $[M]^+$ (100), 197 (80), 183 (38), 131 (34), 77 (31). HRMS (EI): *m*/*z* calcd. for $C_{14}H_{16}N_2$ $[M]^+$: 212.1308; Found: 212.1308.

(*E*)-5-(Pent-1-en-1-yl)-1-phenyl-1*H*-pyrazole (8j)



Yield: 125 mg (0.59 mmol, 59%). Byproduct **7j** (21%).
($C_{14}H_{16}N_2$): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* 1.9 Hz, 1H), 7.51-7.45 (m, 4H), 7.42-7.38 (m, 1H), 6.48 (d, *J* 1.9 Hz, 1H), 6.30-6.20 (m, 2H), 2.18-2.13 (m, 2H), 1.47 (sext, *J* 7.3 Hz, 2H), 0.94 (t, *J* 7.4 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 141.5 (C), 140.2 (CH), 139.8 (C), 135.3 (CH), 129.2 (2CH), 127.8 (CH), 125.5 (2CH), 117.8 (CH), 103.6 (CH), 35.2 (CH_2), 22.3 (CH_2), 13.8 (CH_3). IR (ATR): ν 3034, 2958, 2929, 1598, 1500, 1448, 1391, 961, 931, 924, 761, 695, 685, 649 cm^{-1}. MS (EI): *m*/*z* (%): 212 $[M]^+$ (70), 208 (30), 183 (70), 169 (100), 131 (33), 77 (45). HRMS (EI): *m*/*z* calcd. for $C_{14}H_{16}N_2$ $[M]^+$: 212.1308; Found: 212.1308.

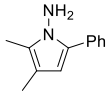
1-(But-3-en-2-ylidene)-2-phenylhydrazine (9a)

Yield: 46 mg (0.29 mmol, 29%). Byproduct of **7a** (40%).
($C_{10}H_{12}N_2$): ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.23 (dd, *J* 8.4, 7.4 Hz, 2H), 6.96 (tt, *J* 7.3, 1.2 Hz, 1H), 6.73 (dd, *J* 8.4, 1.2 Hz, 2H), 6.71 (dd, *J* 17.7, 10.9 Hz, 3H), 5.48 (d, *J* 17.7 Hz, 1H), 5.36 (d, *J* 11.0 Hz, 1H), 3.51 (br s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 144.7 (C), 143.1 (C), 137.9 (CH), 129.1 (2CH), 120.1 (CH), 114.2 (CH_2), 113.1 (2CH). HRMS (EI): *m*/*z* calcd. for $C_{10}H_{12}N_2$ $[M]^+$: 160.0995; Found: 160.0994.

2,3-Dimethyl-1*H*-pyrrol-1-amine (10m)

Yield: 15 mg (0.14 mmol, 14%). Byproduct of **4m** (40%).
($C_6H_{10}N_2$): ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.57 (d, *J* 2.8 Hz, 1H), 5.79 (d, *J* 2.8 Hz, 1H), 4.46 (br s, 2H), 2.11 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 125.4 (C), 119.7 (CH), 112.6 (C), 105.9 (CH), 11.7 (CH_3), 8.9 (CH_3). HRMS (EI): *m*/*z* calcd. for $C_6H_{10}N_2$ $[M]^+$: 110.0839; Found: 110.0840.

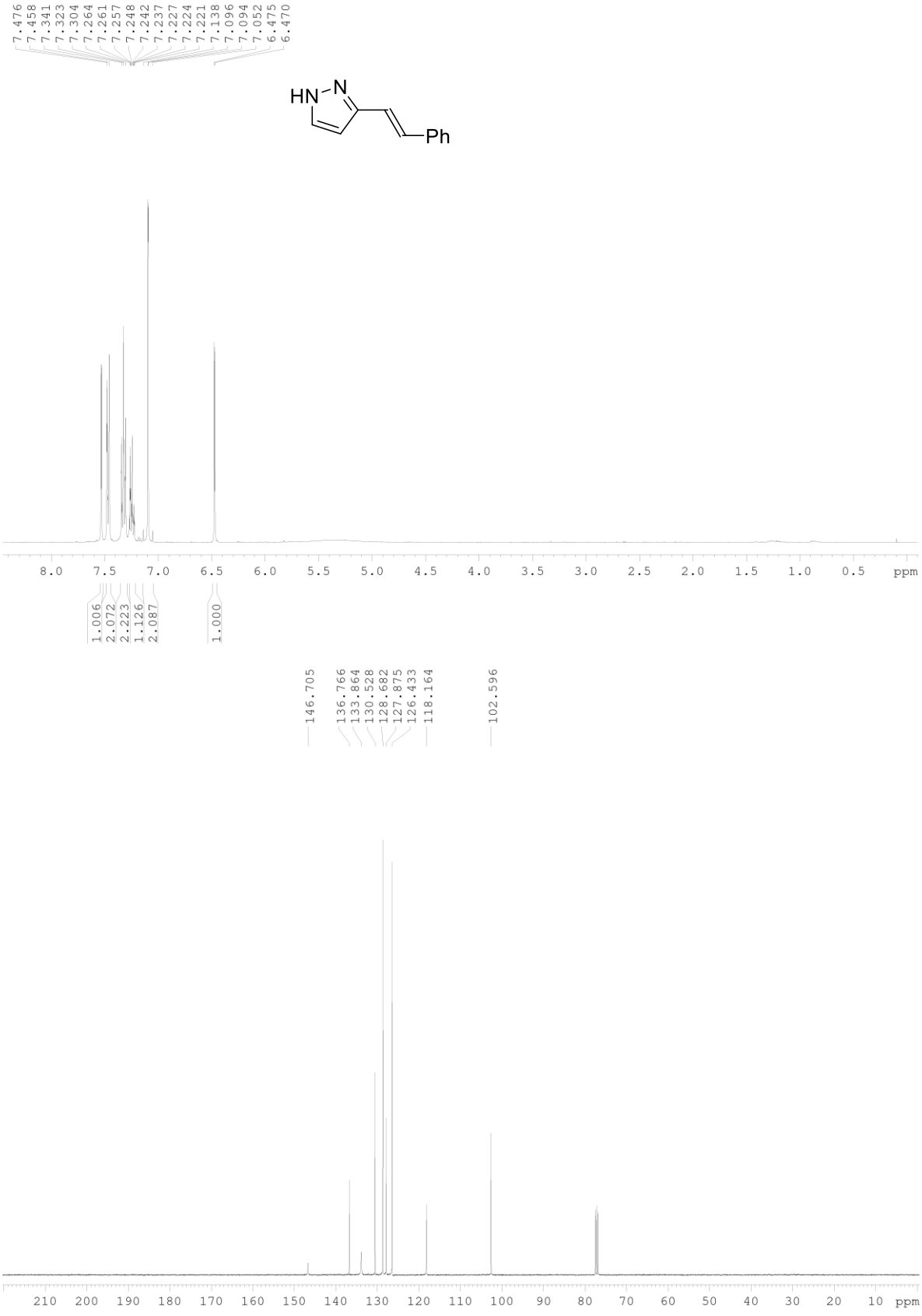
2,3-Dimethyl-5-phenyl-1*H*-pyrrol-1-amine (10n)



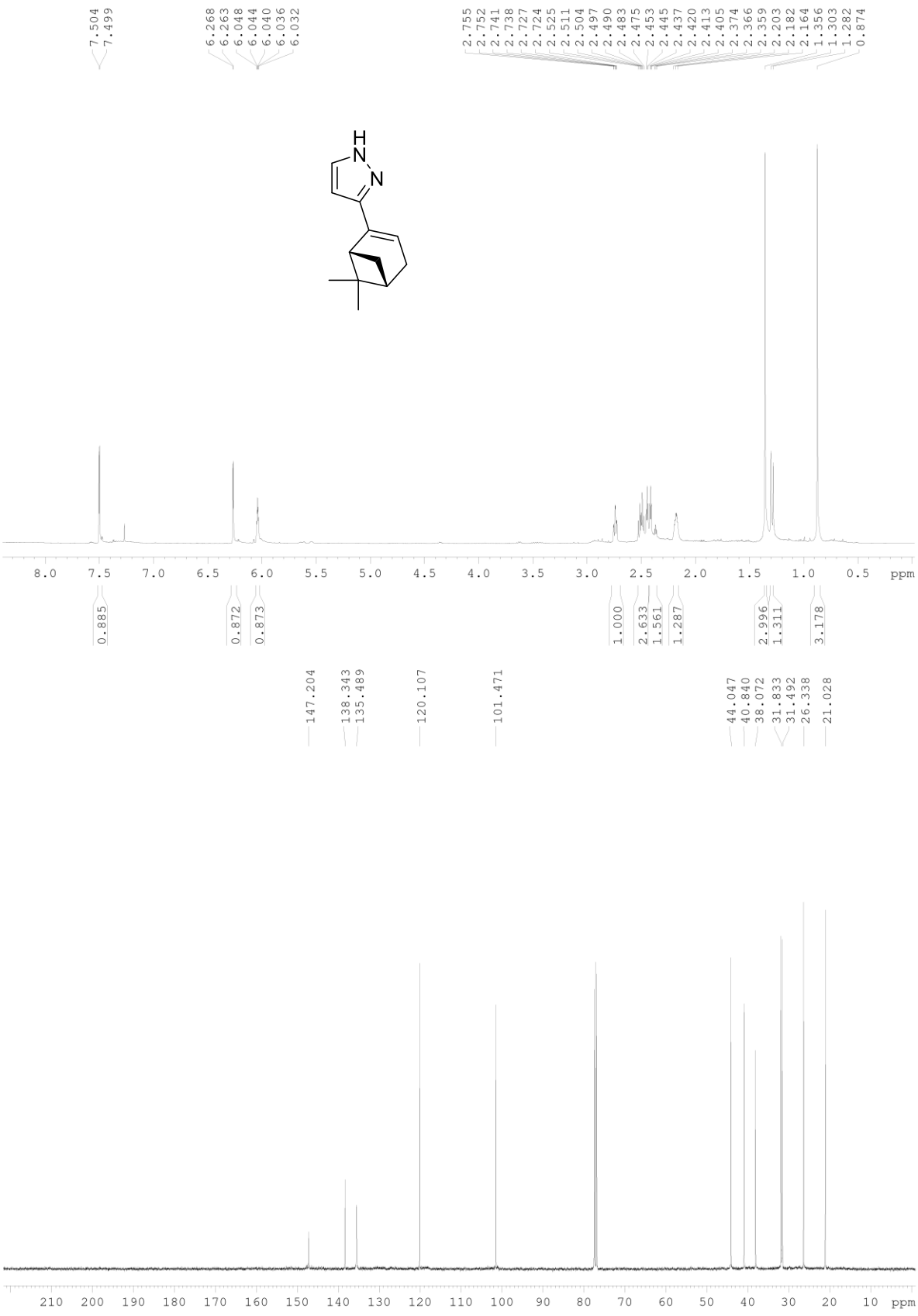
Yield: 63 mg (0.34 mmol, 34%). Byproduct of **4n** (32%).
($C_{12}H_{14}N_2$): ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.54-7.52 (m, 2H), 7.40-7.37 (m, 2H), 7.33-7.31 (m, 1H), 6.04 (s, 1H), 4.41 (br s, 2H), 2.23 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 132.9 (C), 131.8 (C), 128.4 (2CH), 128.1 (2CH), 127.4 (C), 126.3 (CH), 112.3 (C), 106.9 (CH), 11.5 (CH_3), 9.5 (CH_3). HRMS (EI): *m*/*z* calcd. for $C_{12}H_{14}N_2$ $[M]^+$: 186.1152; Found: 186.1152.

Copies of 1H and 13C NMR spectra for new major products

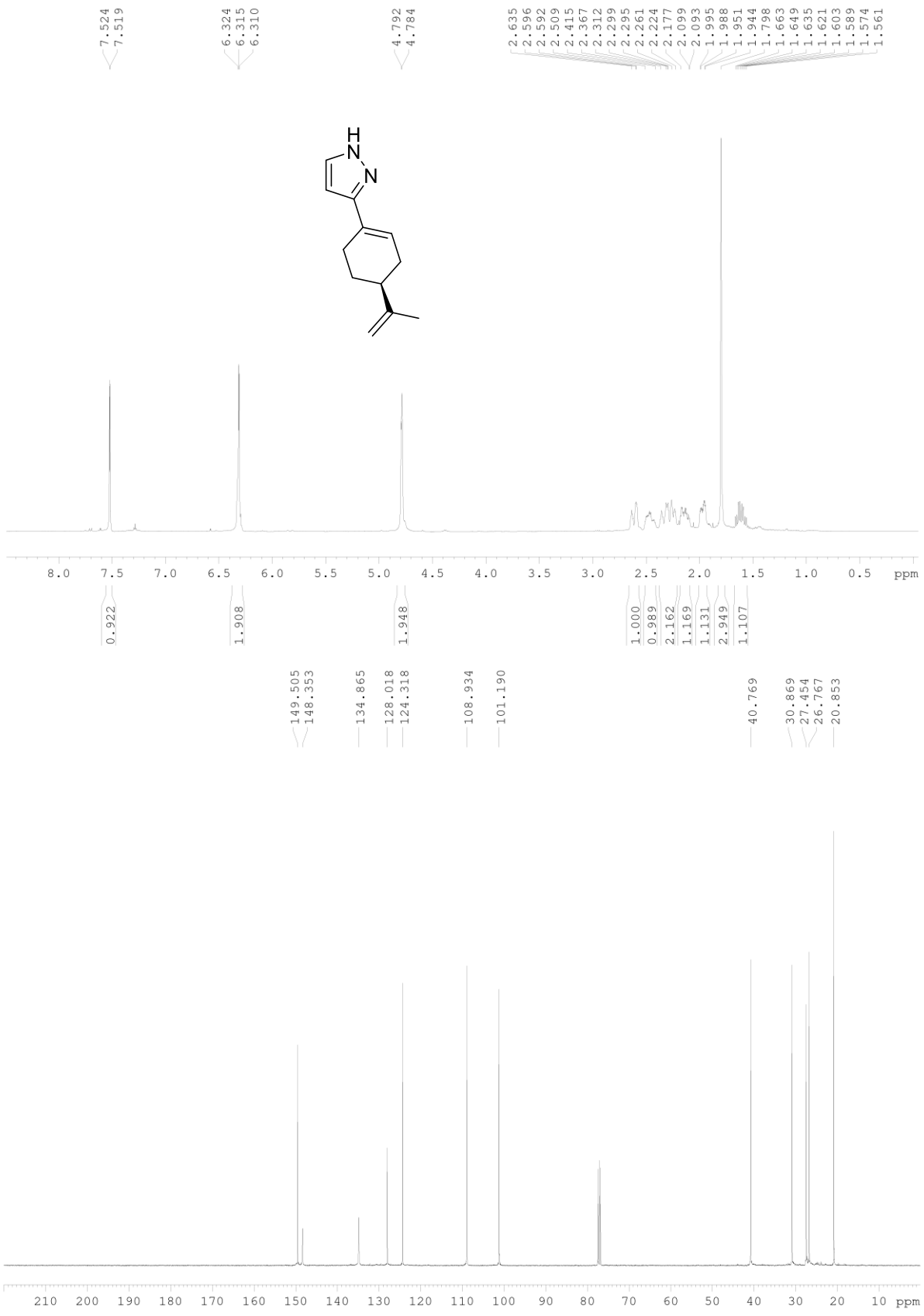
(*E*)-3-Styryl-1*H*-pyrazole (3c)



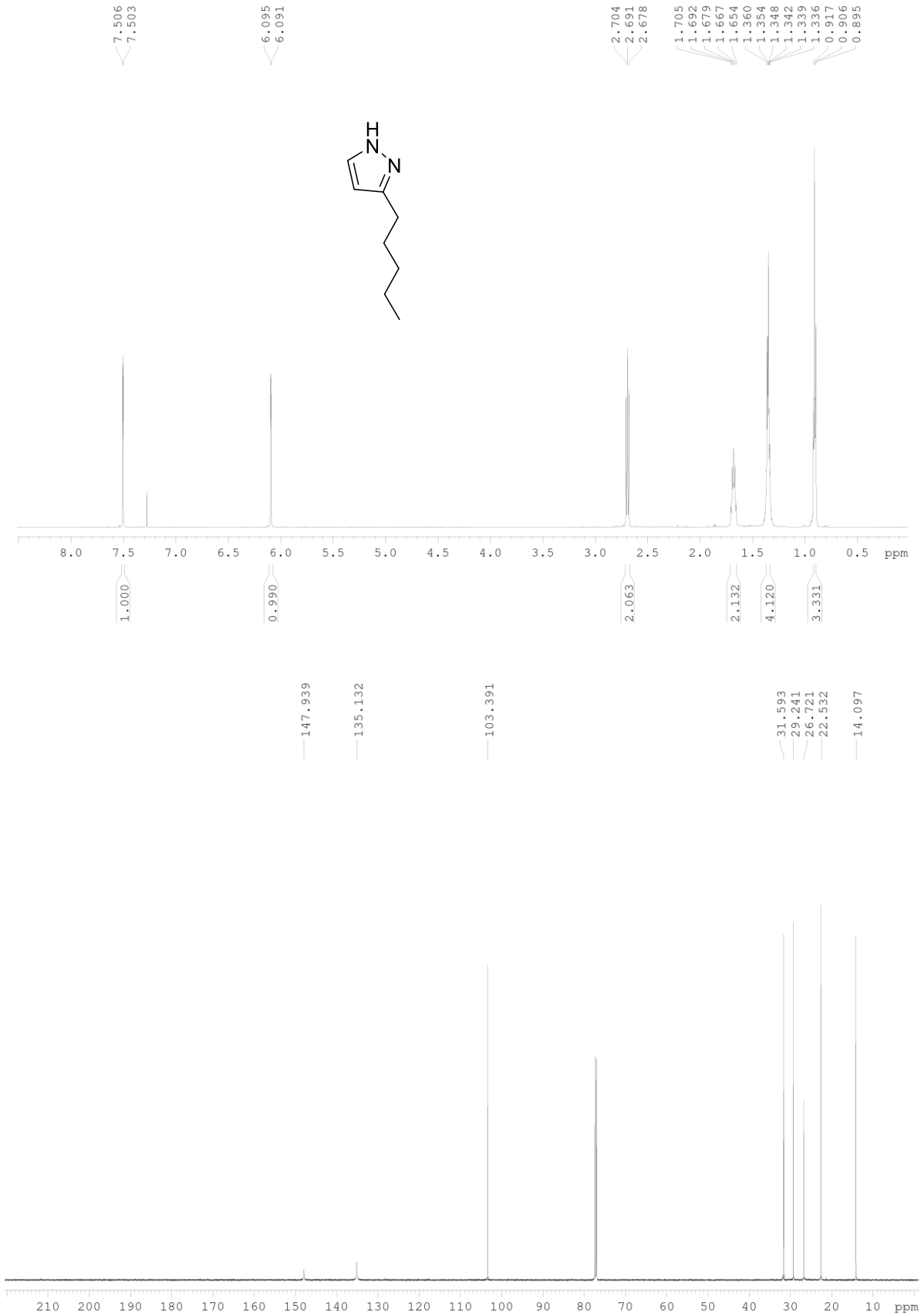
3-((1*R*,5*S*)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)-1*H*-pyrazole (3d)



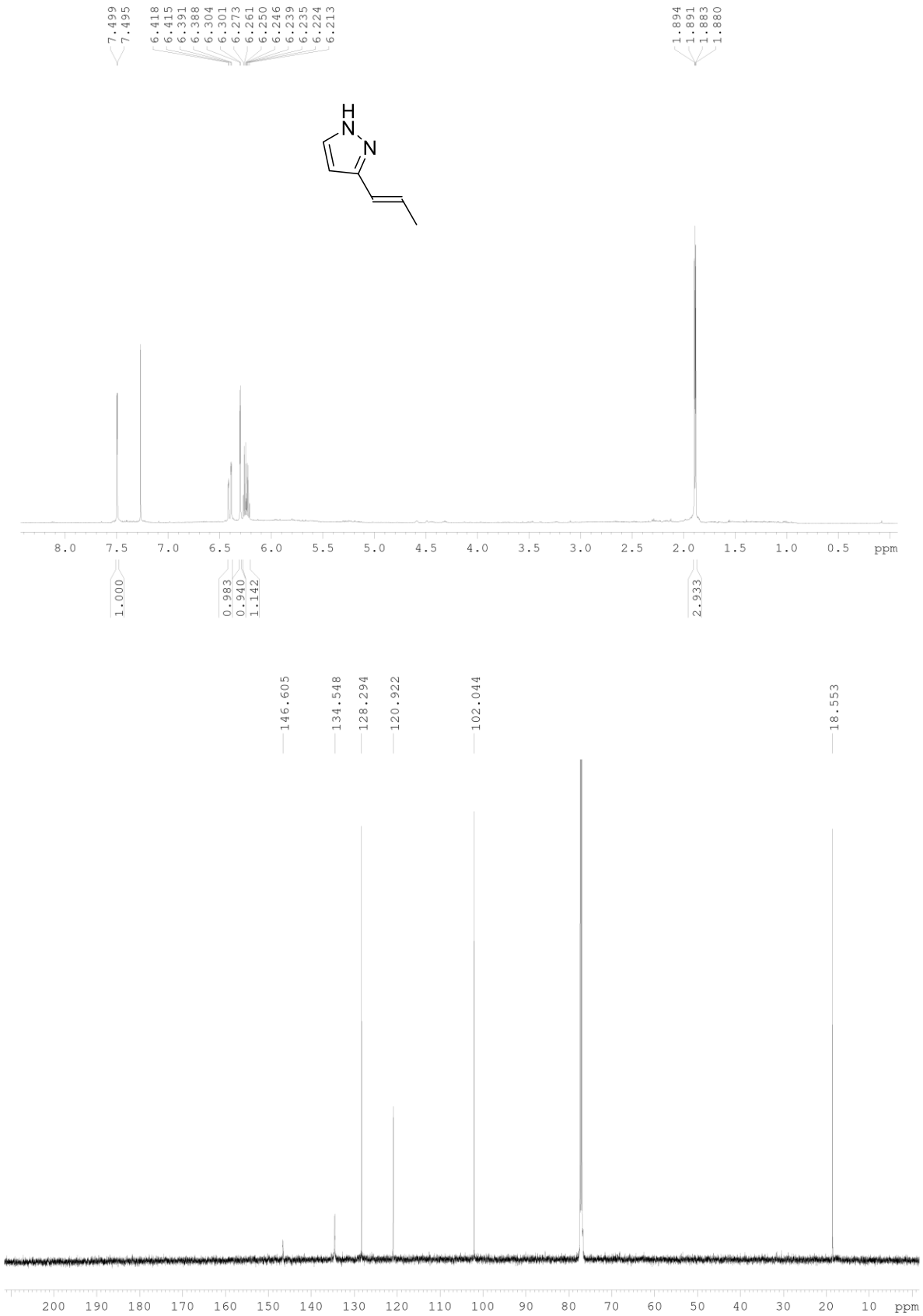
(*S*)-3-(4-(Prop-1-en-2-yl)cyclohex-1-en-1-yl)-1*H*-pyrazole (3e)



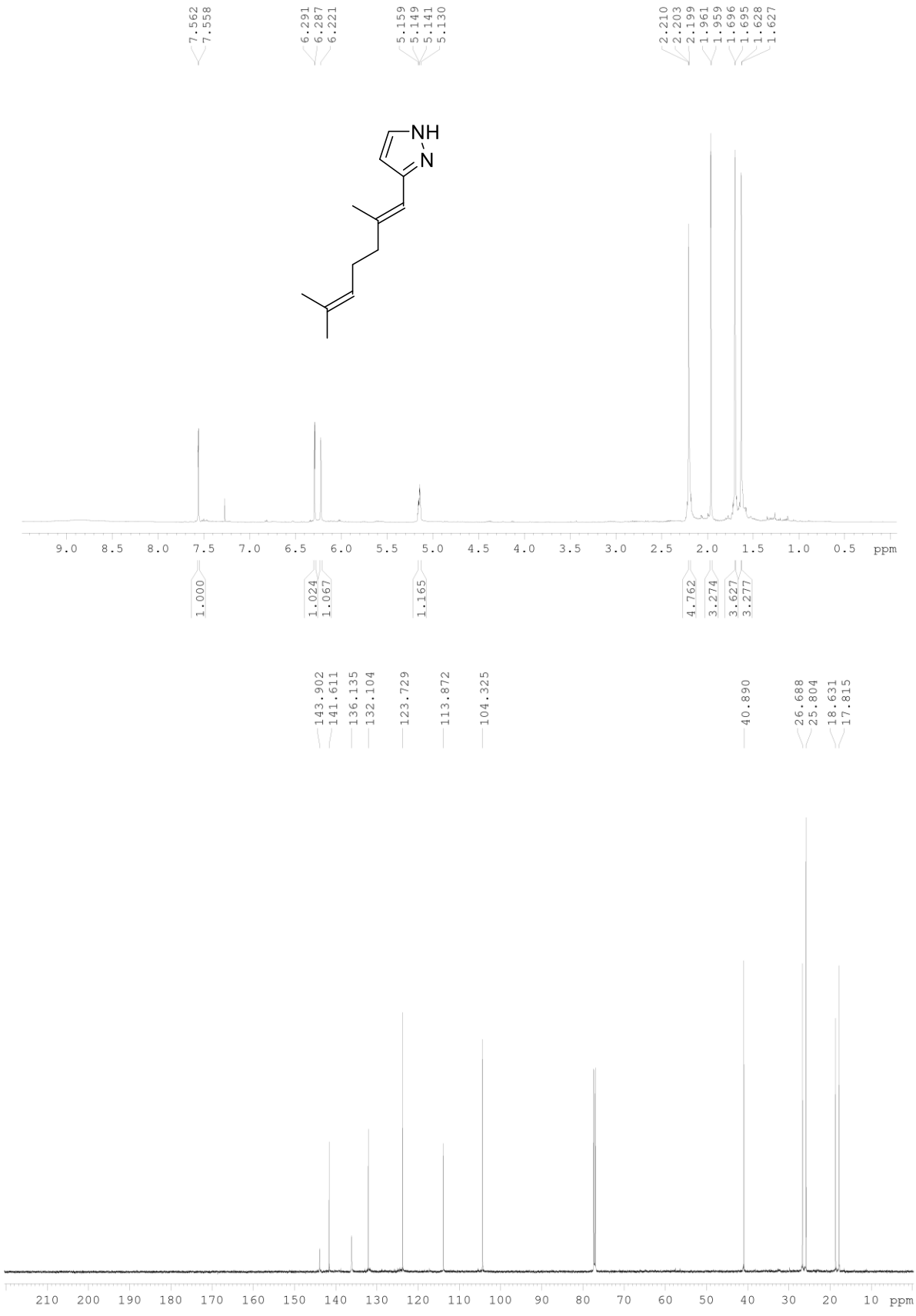
3-Pentyl-1*H*-pyrazole (3f)



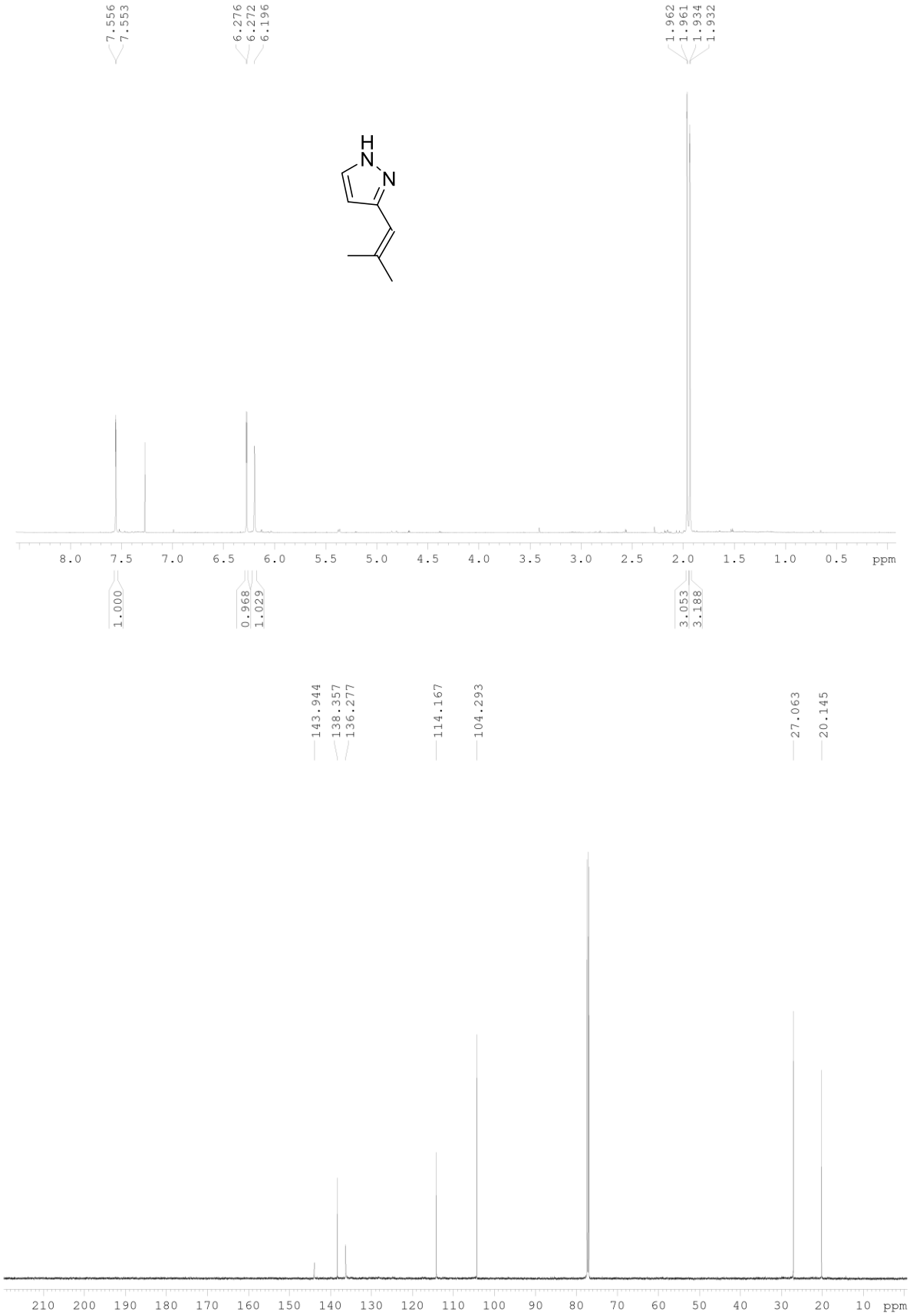
(*E*)-3-(Prop-1-en-1-yl)-1*H*-pyrazole (3g)



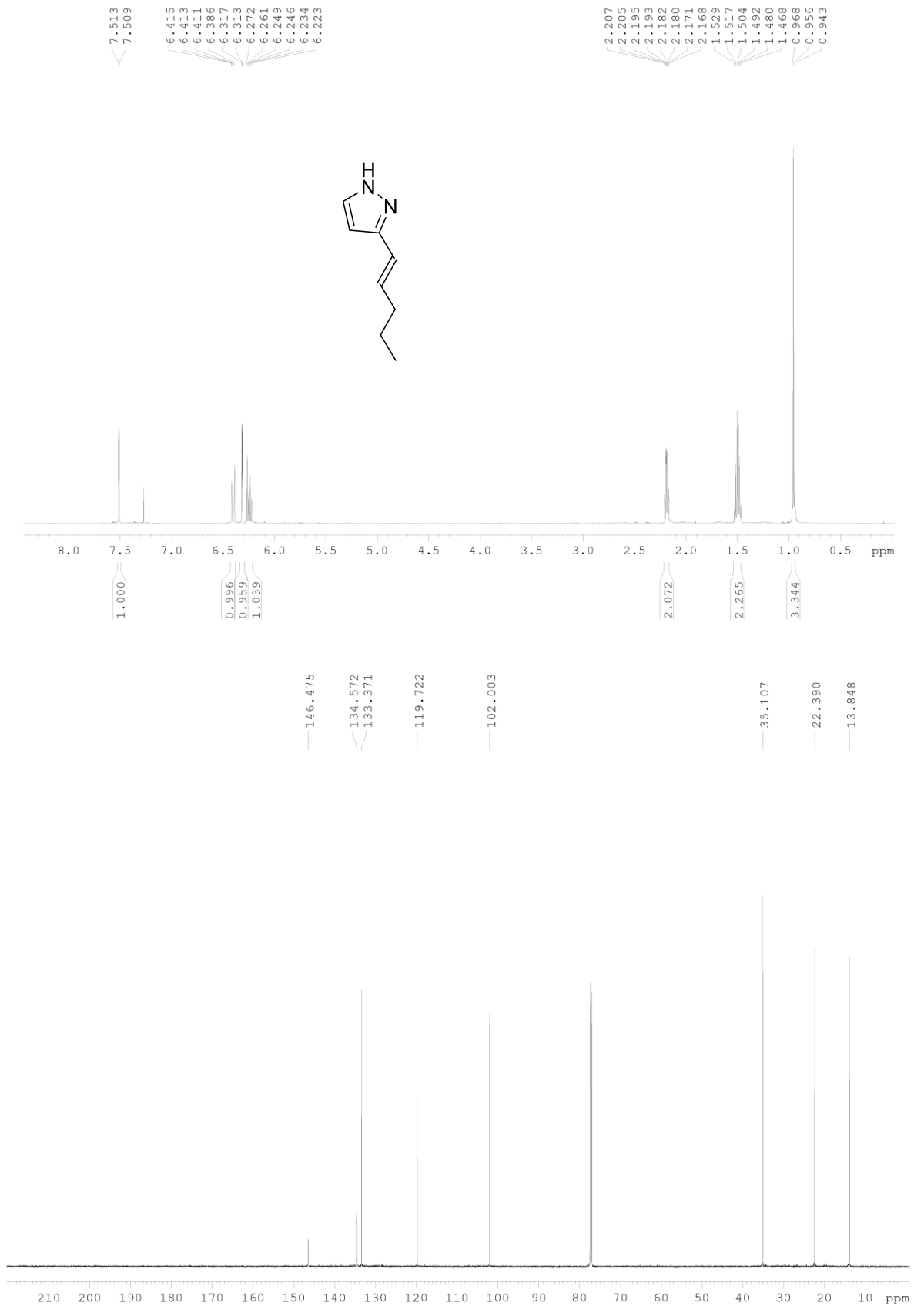
(*E*)-3-(2,6-Dimethylhepta-1,5-dien-1-yl)-1*H*-pyrazole (3h)



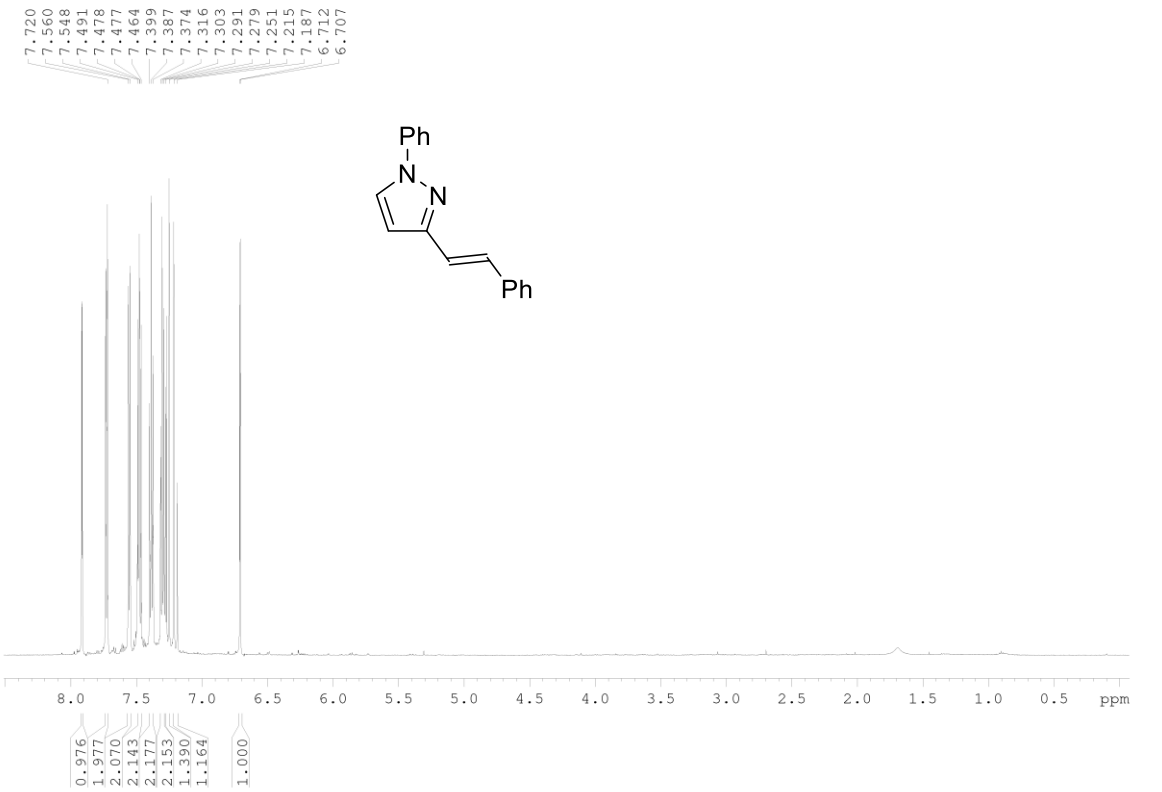
3-(2-Methylprop-1-en-1-yl)-1*H*-pyrazole (3i)

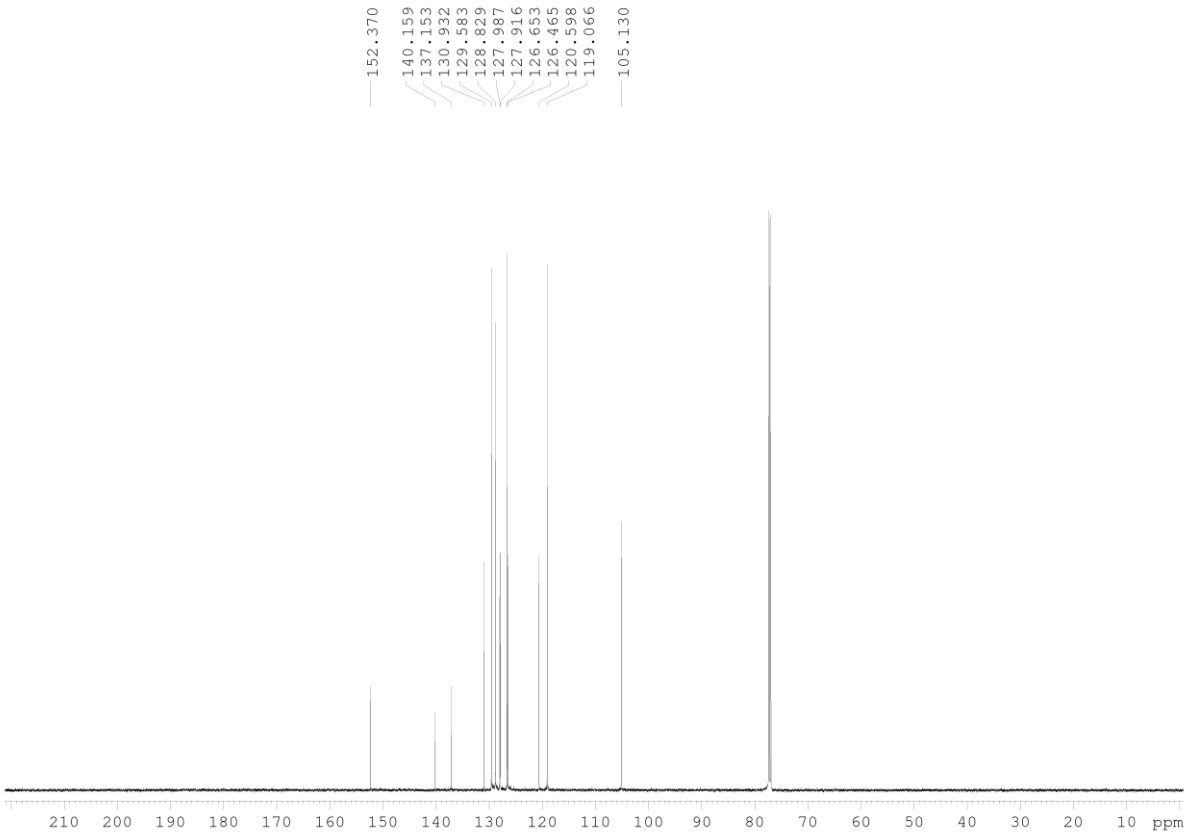


(*E*)-3-(Pent-1-en-1-yl)-1*H*-pyrazole (3j)

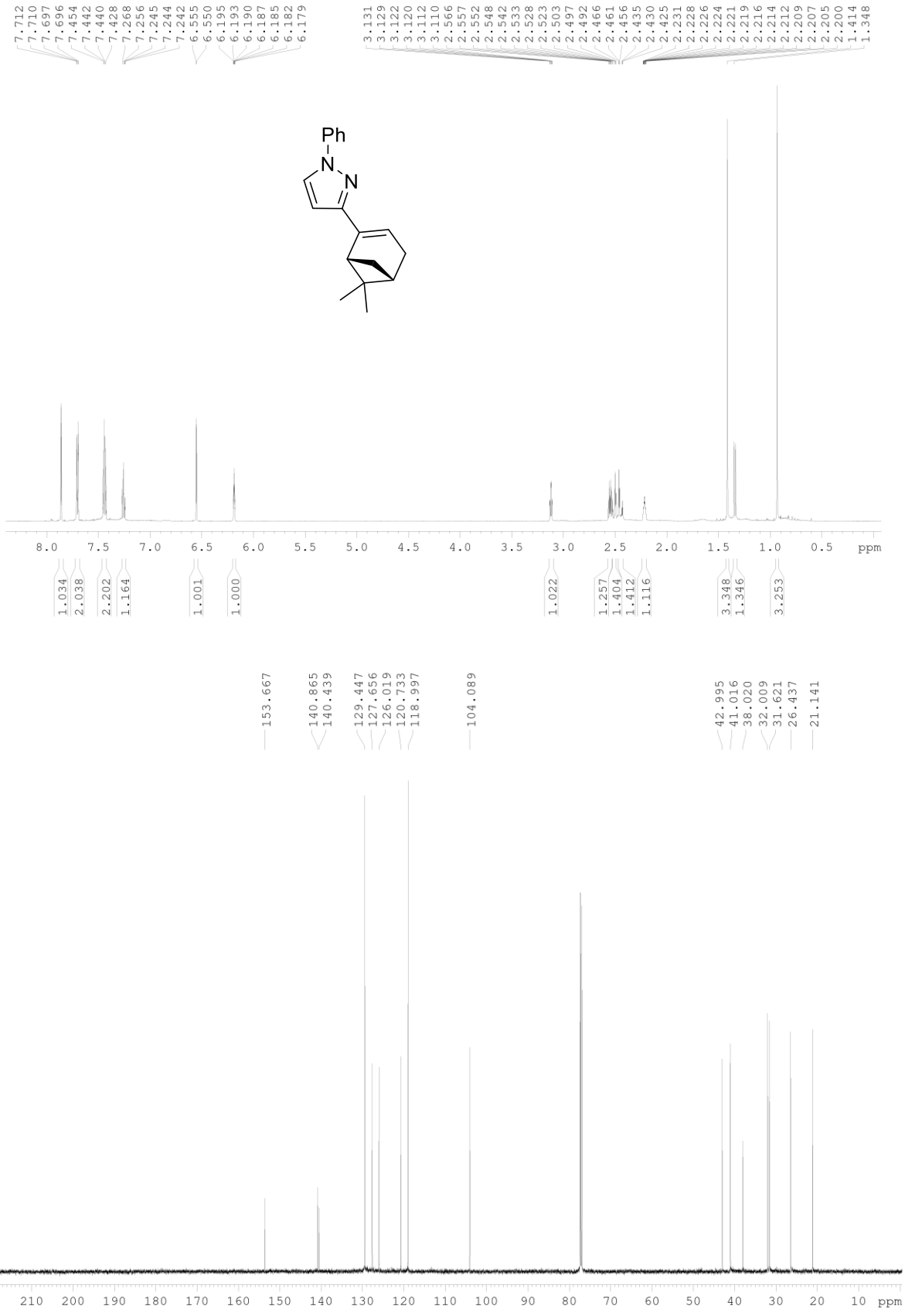


(*E*)-1-Phenyl-3-styryl-1*H*-pyrazole (7c)

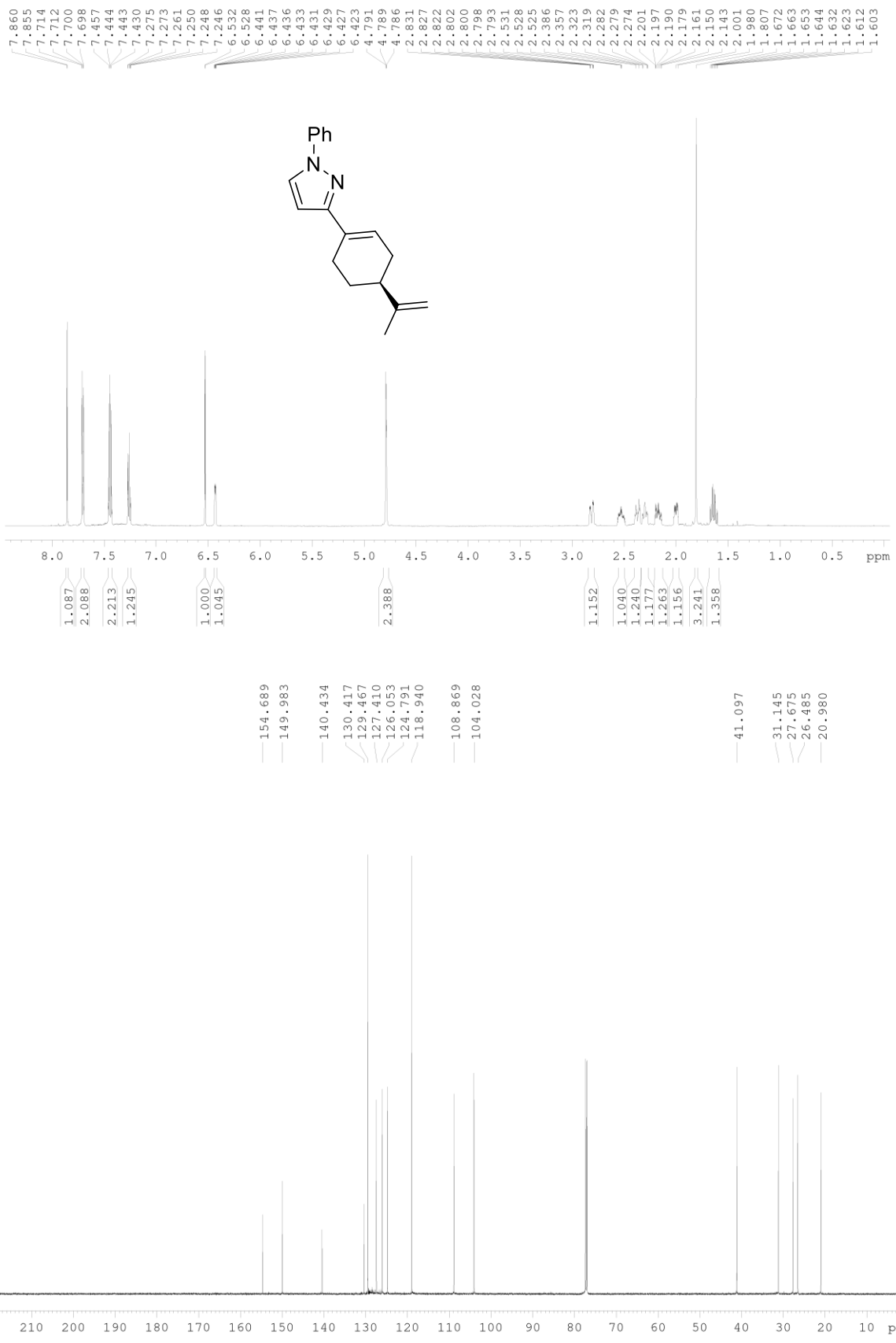




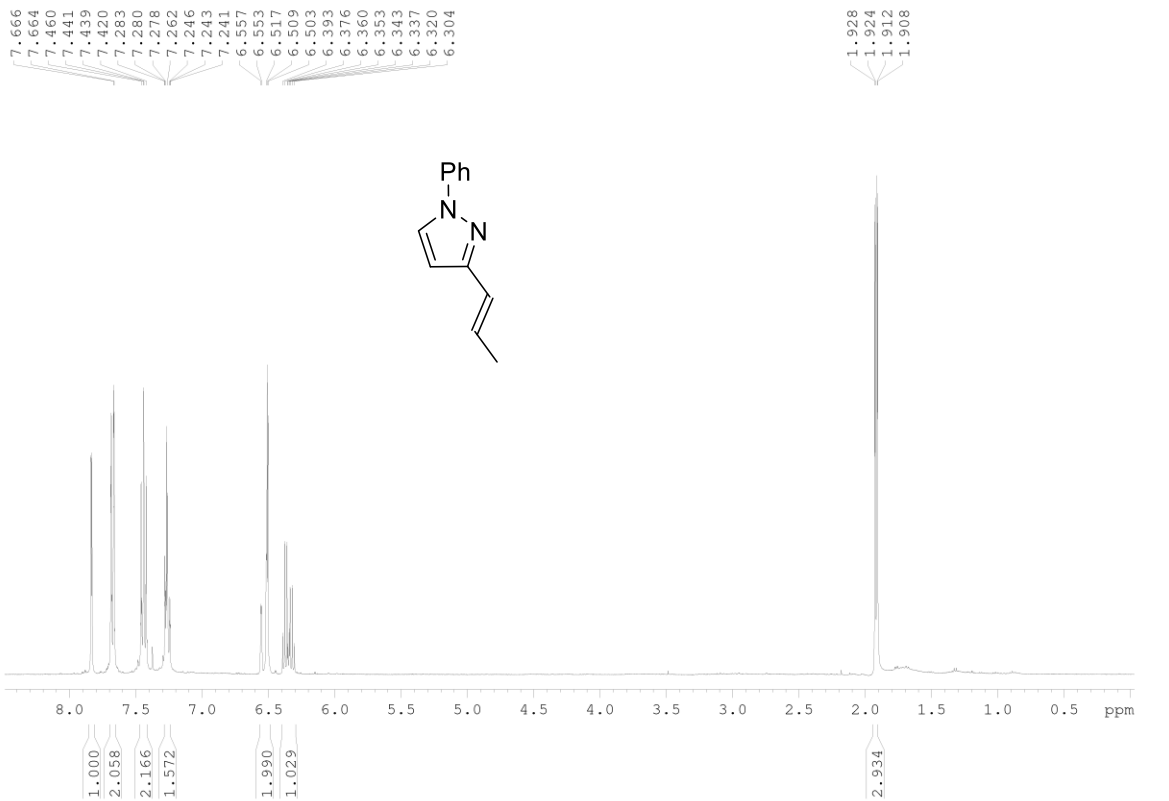
3-((1*R*,5*S*)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)-1-phenyl-1*H*-pyrazole (7d)

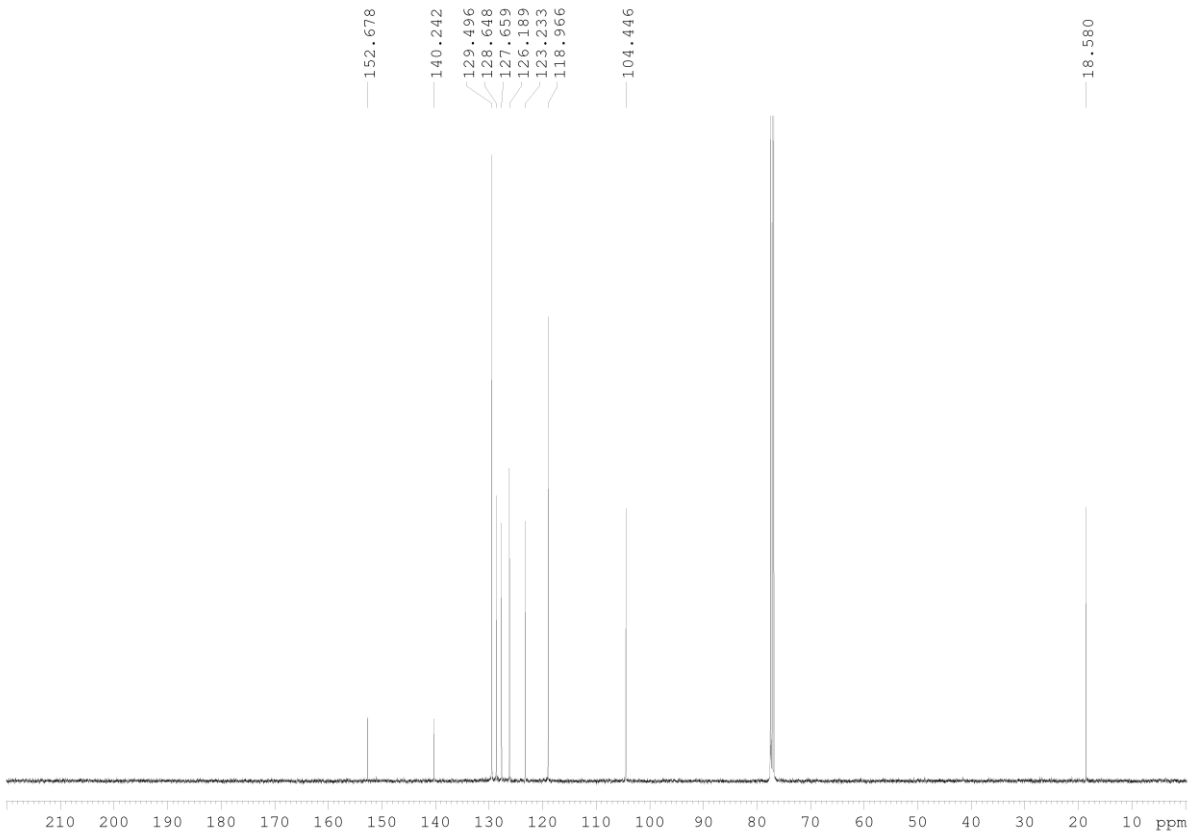


(*S*)-1-Phenyl-3-(4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)-1*H*-pyrazole (7e)

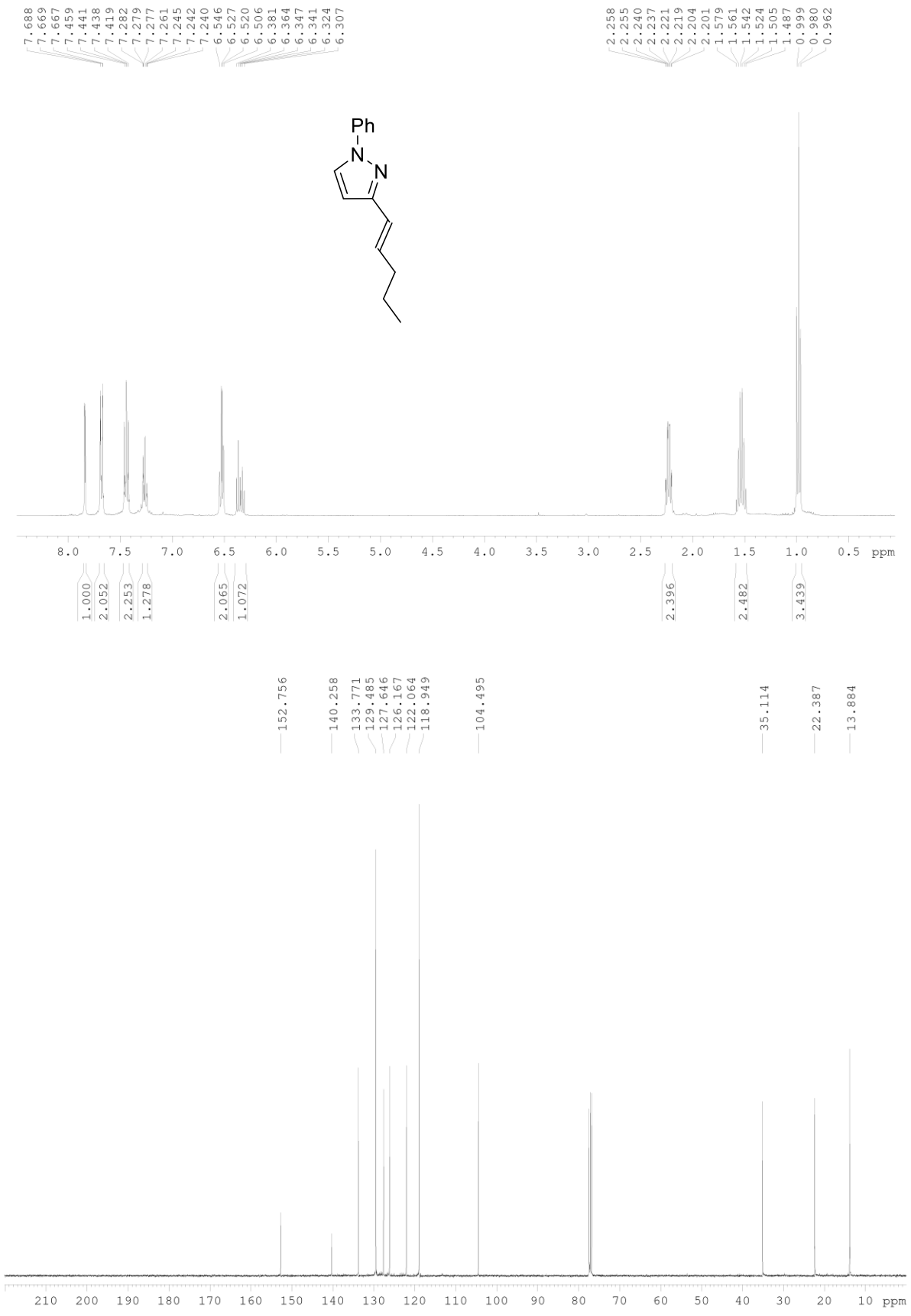


(*E*)-1-Phenyl-3-(prop-1-en-1-yl)-1*H*-pyrazole (7g)

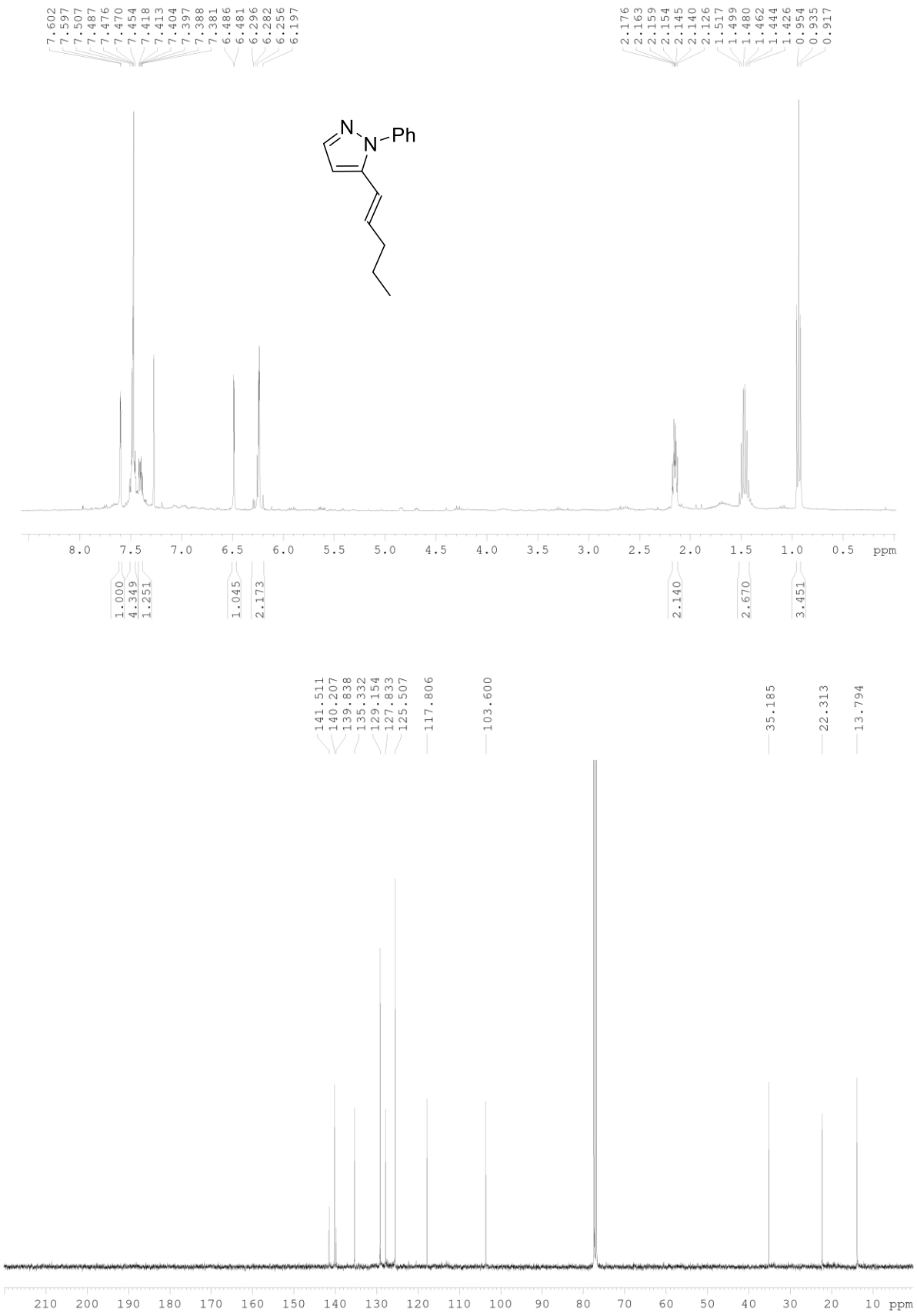




(*E*)-3-(Pent-1-en-1-yl)-1-phenyl-1*H*-pyrazole (7j)



(*E*)-5-(Pent-1-en-1-yl)-1-phenyl-1*H*-pyrazole (8j)



References

1. Haak, E. *Eur. J. Org. Chem.* **2007**, 2815-2824.
2. Thies, N.; Hrib, C. G.; Haak, E. *Chem. Eur. J.* **2012**, *18*, 6302-6308.
3. Levanova, E. P; Grabel'nykh, V. A.; Volkova, K. A.; Russavskaya, N. V.; Klyba, L. V.; Albanov, A. I.; Korchevin, N. A. *Chem. Heterocycl. Compd.* **2009**, *45*, 1009-1010.
4. Pleier, A._K.; Glas, H.; Grosche, M.; Sirsch, P.; Thiel, W. R. *Synthesis* **2001**, 55-62.
5. Ma, D.-Y.; Wang, D.-X.; Pan, J.; Huang, Z.-T.; Wang, M.-X. *J. Org. Chem.* **2008**, *73*, 4087-4091.
6. Yamasaki, S.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2001,** *123,* 1256-1257.
7. Kisanga, P.; McLeod, D.; D'Sa, B.; Verkade, J. *J. Org. Chem.* **1999,** *64,* 3090-3094.
8. Majeric´ Elenkov, M.; Hauer, B.; Janssena, D. B. *Adv. Synth. Catal.* **2006**, *348*, 579-585.
9. Jinzaki, T.; Arakawa, M.; Kinoshita, H.; Ichikawa, J.; Miura, K. *Org. Lett*. **2013**, *15*, 3750-3753.
10. Pori, M.; Galletti, P.; Soldati, R.; Calzà, L.; Mangano, C.; Giacomini, D. *Eur. J. Med. Chem.* **2013**, *70*, 857-863.
11. Cristau, H.-J.; Cellier, P. P.; Spindler, J.-F.; Taillefer, M. *Eur. J. Org. Chem.* **2004**, 695-709.
12. Browne, D. L.; Taylor, J. B.; Plant, A.; Harrity, J. P. A. *J. Org. Chem.* **2010**, *75*, 984-987.
13. Begtrup, M.; Vedsø, P.; Cabildo, P.; Claramunt, R. M.; Elguero, J.; Meuter-Mans, W. *Magn. Reson. Chem.* **1992**, *30*, 455-459.

