**Supporting Information**

# Bridging of Terpenyl Aldehydes and Terpenes with Hydrazine

Li-Ming Zhang,[a,b] Su-Yang Xu,[a,b] Xue-Ting Li,[a,b] Ting-Ting Song,[a] Ding-Wei Ji,[a] Yanhua Lu,[c] Boshun Wan,[a,b] Qing-An Chen*[a,b]

[a]Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China
[b]University of Chinese Academy of Sciences, Beijing 100049, China
[c]Hubei Institute of Aerospace Chemotechnology, Xiangyang, 441003, China

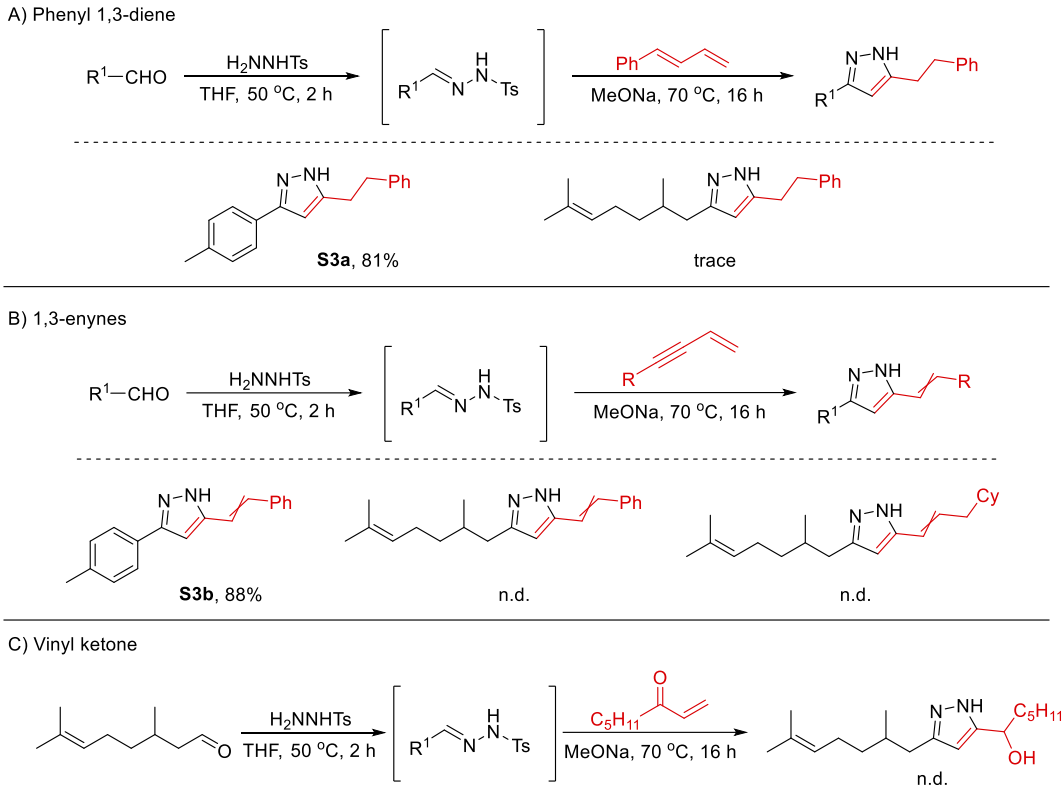
E-mail: *qachen@dicp.ac.cn

## Table of Contents

## 1. General experimental details

All the reagents were commercially available and were used without further purification unless otherwise stated. Solvents were treated prior to use according to the standard methods. Unless otherwise stated, all reactions were conducted under inert atmosphere using standard Schlenk techniques or in a nitrogen-filled glove-box. $^{1}H$ NMR and $^{13}C$ NMR spectra were recorded at room temperature in $CDCl_3$ on 400 MHz or 700 MHz instrument with tetramethylsilane (TMS) as internal standard. NMR data is reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, brs = broad singlet, m = multiplet), coupling constant (Hz), and integration. Flash column chromatography was performed on commercially available silica gel (200-300 mesh). All reactions were monitored by TLC, GC-FID, GC-MS or NMR analysis. HRMS data was obtained with Micromass HPLC-Q-TOF mass spectrometer (ESI) or Agilent 6540 Accurate-MS spectrometer (Q-TOF).

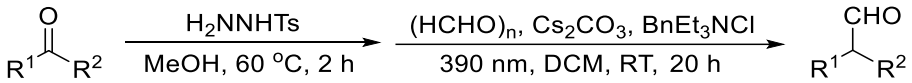
## 2. Supplementary substrates




**Figuer S1. Supplementary substrates.** Reaction conditions: aldehydes (0.21 mmol), $H_2NNHTs$ (0.20 mmol), alkenes (0.80 mmol), MeONa (0.50 mmol), THF (0.5 mL). Isolated yields were given.

## 3. Procedure for the synthesis of substrates

### 3.1 Procedure for the synthesis of terpenyl aldehydes 1l, 1q and 1r.

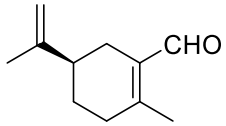



A modification of synthetic method from the literature (*1*). Tosylhydrazide (2.0 mmol) and ketone (2.0 mmol) were dissolved in MeOH (10 mL) at 60 °C. The reaction progress was monitored by TLC. After the completion of the reaction, the reaction mixture was concentrated in vacuo, gave the crude tosylhydrazones and directly used without further purification.

In a glove box, to a 50 mL seal tube with a magnetic stirring bar, crude tosylhydrazones (2.0 mmol, 1.0 eq.), $Cs_2CO_3$ (3.0 mmol, 1.5 eq.), $BnEt_3NCl$ (0.2 mmol, 10 mol%), paraformaldehyde (2.0 mmol, 1.0 eq.), and dry DCM (20 mL) were added. The reaction tube was sealed with a cap, removed from the glove box. Then, the reaction mixture was irradiated with a 390 nm LED at room temperature. After 20 h, the mixture was quenched with water and

extracted with DCM (20 mL *3). The combined organic phase was then washed with $H_2O$ (20 mL) and brine, dried over $Na_2SO_4$, and concentrated under vacuum. The residue was purified by silica gel flash chromatography to give the desired product.

**1l** was known compound.[1]



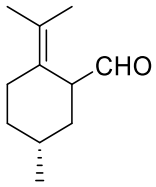

**1q**

**(*R*)-2-methyl-5-(prop-1-en-2-yl)cyclohex-1-ene-1-carbaldehyde (1q)**: colorless oil, $R_f$ = 0.5 (PE:EA = 20:1), 147.1 mg, 45% yield.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 10.14 (s, 1H), 4.76 – 4.69 (m, 2H), 2.54 (ddd, *J* = 17.0, 2.9, 1.3 Hz, 1H), 2.36 – 2.27 (m, 2H), 2.14 (s, 3H), 2.11 – 2.03 (m, 1H), 1.95 – 1.79 (m, 2H), 1.75 (s, 3H), 1.51 – 1.40 (m, 1H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 191.0, 155.8, 149.0, 133.3, 109.2, 40.3, 34.8, 27.6, 26.9, 20.9, 18.1.

**HRMS** calculated for $C_{11}H_{17}O$ $[M+H]^+$ 165.1274, found 165.1275.




**1r**

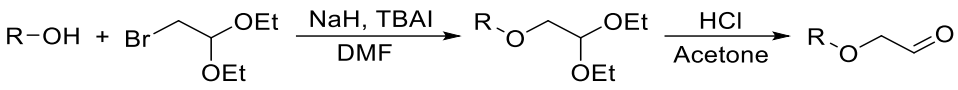
**(5*R*)-5-methyl-2-(propan-2-ylidene)cyclohexane-1-carbaldehyde (1r)**: colorless oil, $R_f$ = 0.5 (PE:EA = 20:1), 131.8 mg, 40% yield (d.r. = 1:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.54 (s, 1H), 3.54 (d, *J* = 5.6 Hz, 1H), 2.70 – 2.64 (m, 1H), 2.25 – 2.19 (m, 1H), 1.77 – 1.62 (m, 10H), 1.09 (dd, *J* = 11.9, 6.2 Hz, 1H), 0.87 (d, *J* = 6.4 Hz, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 203.6, 127.5, 126.2, 51.7, 35.3, 34.4, 29.1, 28.0, 22.5, 20.6, 20.5.

**HRMS** calculated for $C_{11}H_{19}O$ $[M+H]^+$ 167.1431, found 167.1430.

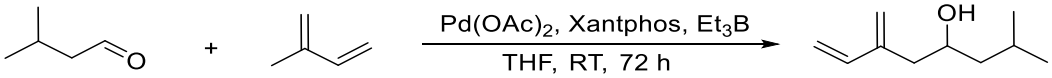
**3.2 Procedure for the synthesis of terpenyl aldehydes 1v and 1w.**




A modification of synthetic method from the literature (*2*). To a solution of alcohol (10.0 mmol, 1.0 eq.) in 30 mL DMF was added NaH (60% in oil, 15.0 mmol, 1.5 eq.) and TBAI (0.1 mmol, 0.01 eq..). After the solution was stirred at room temperature for 30 minutes, bromoacetaldehyde diethyl acetal (20.0 mmol, 2.0 eq.) was slowly added into the reaction at 0 °C. Then the reaction was heated to 40 °C and stirred overnight. The reaction was quenched by adding water and EA. The organic layer was separated, and the aqueous portion was extracted with EA for 3 times. The combined organic layers were washed with brine, dried over anhydrous $Na_2SO_4$, filtered, and concentrated to obtain the crude product which was purified by column chromatography to afford the pure acetal.

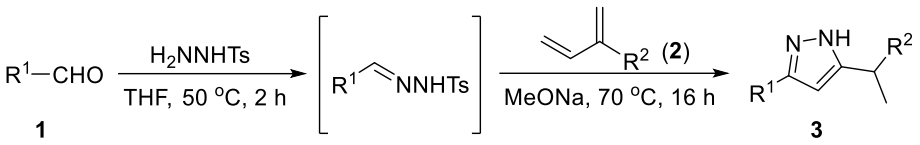
To a solution of the corresponding acetal (5.0 mmol, 1.0 eq.) in acetone (15 mL) was added concentrated HCl solution (1.5 mmol, 0.3 eq.). The reaction was monitored by TLC carefully. Upon formation of quite amount of desired aldehyde, the reaction was quenched immediately by adding $NaHCO_3$ solution slowly and extracted with EA. The extract was dried over $Na_2SO_4$ and concentrated to afford a crude product, which was purified by column chromatography to generate the corresponding α-alkoxy aldehydes. **1v** and **1w** were known compounds.[2]

### 3.3 Procedure for the synthesis of terpene 2af.



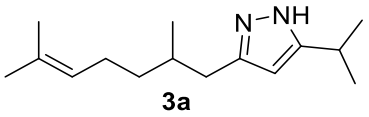

A modification of synthetic method from the literature (*3*). In a glove box, to a 30 mL seal tube with a magnetic stirring bar, $Pd(OAc)_2$ (45.2 mg, 0.2 mmol), Xantphos (115.6 mg, 0.2 mmol), isovaleraldehyde (172 mg, 2 mmol), isoprene (0.8 mL, 8 mmol), $Et_3B$ (4 mmol, 1.0 M THF solution) and dry THF (10 mL) were successively added. The reaction tube was sealed with a cap, removed from the glove box. Then, the reaction mixture was stirred at ambient temperature. After 72 h, the mixture was diluted with 30 mL of EA and washed with 2 M HCl, sat. $NaHCO_3$, and then brine. The extract was dried with $Na_2SO_4$ and concentrated in vacuo and the residual oil was subjected to column chromatography over silica gel (PE:EA = 10:1) to give product. **2af** was known compound (*3*).

## 4. General procedure for bridging of terpenyl aldehydes and terpenes




1 3

In a glove box, to a 4 mL seal tube with a magnetic stirring bar, $H_2NNHTs$ (0.20 mmol, 1.0 eq.), terpenyl aldehydes **1** (0.21 mmol, 1.05 eq.) and dry THF (0.5 mL) were successively added. The reaction tube was sealed with a cap, removed from the glove box and stirred at 50 °C for 2 h. Then, the reaction mixture was cooled to room temperature, MeONa (0.5 mmol, 2.5 eq.) and terpene **2** (0.8 mmol, 4.0 eq.) were added to the reaction mixture and stirred at 70 °C. After 16 h, the mixture was diluted with 2 mL of EA, washed with water and extracted with EA. The organic phase was dried over $Na_2SO_4$ and concentrated under reduced pressure. Purification by flash column chromatography over silica gel (PE/EA) to give product **3**.



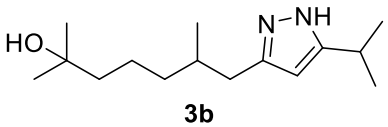

**3a**

**3-(2,6-dimethylhept-5-en-1-yl)-5-isopropyl-1*H*-pyrazole (3a)**: colorless oil, $R_f$ = 0.5 (PE:EA = 3:1), 36.2 mg, 77% yield.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.07 (brs, 1H), 5.84 (s, 1H), 5.10 – 5.06 (m, 1H), 2.96 (hept, *J* = 6.9 Hz, 1H), 2.61 (dd, *J* = 14.4, 6.0 Hz, 1H), 2.40 (dd, *J* = 14.4, 8.0 Hz, 1H), 2.00 (pd, *J* = 14.5, 7.0 Hz, 2H), 1.80 – 1.72 (m, 1H), 1.67 (s, 3H), 1.59 (s, 3H), 1.44 – 1.36 (m, 1H), 1.26 (d, *J* = 6.9 Hz, 6H), 1.22 – 1.14 (m, 1H), 0.89 (d, *J* = 6.6 Hz, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 155.4, 147.7, 131.4, 124.8, 100.9, 36.9, 34.7, 33.3, 27.0, 25.8, 25.7, 22.7, 19.7, 17.8.

**HRMS** calculated for $C_{15}H_{27}N_2$ $[M+H]^+$ 235.2169, found 235.2172.




**3b**

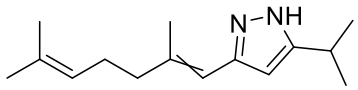
**7-(5-isopropyl-1*H*-pyrazol-3-yl)-2,6-dimethylheptan-2-ol (3b)**: colorless oil, $R_f$ = 0.2

(PE:EA = 1:1), 32.7 mg, 65% yield.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 5.83 (s, 1H), 5.34 (brs, 1H), 2.96 (hept, *J* = 6.9 Hz, 1H), 2.59 (dd, *J* = 14.4, 6.2 Hz, 1H), 2.43 (dd, *J* = 14.4, 7.7 Hz, 1H), 1.83 – 1.71 (m, 1H), 1.46 – 1.41 (m, 3H), 1.39 – 1.32 (m, 2H), 1.26 (d, *J* = 6.9 Hz, 6H), 1.20 (s, 6H),1.18 – 1.15 (m, 1H), 0.90 (d, *J* = 6.7 Hz, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 155.1, 147.6, 100.9, 71.0, 43.9, 37.1, 34.5, 33.5, 29.4, 29.3, 26.9, 22.7, 21.6, 19.8.

**HRMS** calculated for $C_{15}H_{29}N_2O$ $[M+H]^+$ 253.2275, found 253.2277.



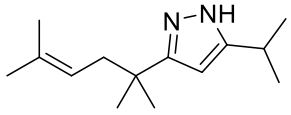

**3c**

**3-(2,6-dimethylhepta-1,5-dien-1-yl)-5-isopropyl-1*H*-pyrazole (3c)**: colorless oil, $R_f$ = 0.5 (PE:EA = 3:1), 32.2 mg, 69% yield (Z/E = 1/1.7).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.59 (brs, 1H), 6.15 (s, 0.63H), 6.13 (s, 0.37H), 6.07 (s, 0.63H), 6.03 (s, 0.37H), 5.21 – 5.09 (m, 1H), 3.06 – 2.93 (m, 1H), 2.38 – 2.14 (m, 4H), 1.95 (s, 1.90H), 1.89 (s, 1.10H), 1.70 (s, 1.10H), 1.68 (s, 1.90H), 1.64 (s, 1.10H), 1.61 (s, 1.90H), 1.28 (m, 6H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 156.4, 156.0, 144.9, 144.3, 141.4, 140.8, 132.2, 131.9, 123.9, 123.7, 115.1, 114.5, 101.0, 100.6, 40.9, 33.6, 27.1, 27.1, 26.7, 26.2, 25.8, 25.7, 24.5, 22.7, 18.6, 17.7.

**HRMS** calculated for $C_{15}H_{25}N_2$ $[M+H]^+$ 233.2013, found 233.2016.




**3d**

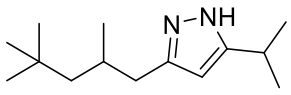
**3-(2,5-dimethylhex-4-en-2-yl)-5-isopropyl-1*H*-pyrazole (3d)**: colorless oil, $R_f$ = 0.5 (PE:EA = 3:1), 29.0 mg, 66% yield.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.04 (brs, 1H), 5.87 (s, 1H), 5.13 – 5.05 (m, 1H), 2.96 (hept, *J* = 6.9 Hz, 1H), 2.26 (d, *J* = 7.5 Hz, 2H), 1.68 (s, 3H), 1.53 (s, 3H), 1.28 (t, *J* = 3.5 Hz, 12H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 156.1, 155.3, 133.8, 120.9, 98.7, 41.7, 35.3, 27.7, 27.1, 26.1,

22.7, 17.9.

**HRMS** calculated for $C_{14}H_{25}N_2$ $[M+H]^+$ 221.2013, found 221.2013.



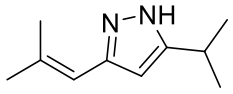
**3e**

**5-isopropyl-3-(2,4,4-trimethylpentyl)-1*H*-pyrazole (3e)**: colorless oil, $R_f$ = 0.5 (PE:EA = 3:1), 37.0 mg, 83% yield.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.58 (brs, 1H), 5.85 (s, 1H), 2.96 (hept, *J* = 6.9 Hz, 1H), 2.58 (dd, *J* = 14.3, 6.2 Hz, 1H), 2.40 (dd, *J* = 14.3, 8.1 Hz, 1H), 1.88 – 1.76 (m, 1H), 1.30 (dd, *J* = 14.0, 3.6 Hz, 1H), 1.26 (d, *J* = 6.9 Hz, 6H), 1.09 (dd, *J* = 13.9, 6.5 Hz, 1H), 0.94 (d, *J* = 6.6 Hz, 3H), 0.87 (s, 9H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 155.3, 148.0, 101.0, 50.7, 37.0, 31.2, 30.3, 30.1, 27.0, 22.8.

**HRMS** calculated for $C_{14}H_{27}N_2$ $[M+H]^+$ 223.2169, found 223.2172.



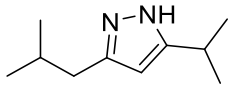
**3f**

**5-isopropyl-3-(2-methylprop-1-en-1-yl)-1*H*-pyrazole (3f)**: colorless oil, $R_f$ = 0.5 (PE:EA = 3:1), 21.7 mg, 66% yield.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 10.42 (brs, 1H), 6.15 (s, 1H), 6.05 (s, 1H), 3.01 (hept, *J* = 6.9 Hz, 1H), 1.95 (s, 3H), 1.90 (s, 3H), 1.28 (d, *J* = 6.9 Hz, 6H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 155.9, 145.1, 137.3, 115.1, 100.8, 27.1, 27.0, 22.8, 20.1.

**HRMS** calculated for $C_{10}H_{17}N_2$ $[M+H]^+$ 165.1387, found 165.1389.



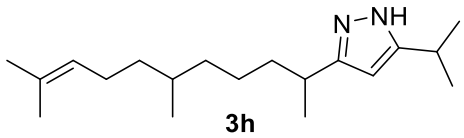
**3g**

**3-isobutyl-5-isopropyl-1*H*-pyrazole (3g)**: colorless oil, $R_f$ = 0.5 (PE:EA = 3:1), 21.4 mg, 64% yield.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.65 (brs, 1H), 5.84 (s, 1H), 2.96 (hept, *J* = 6.9 Hz, 1H), 2.47 (d, *J* = 7.1 Hz, 2H), 1.90 (m, 1H), 1.26 (d, *J* = 6.9 Hz, 6H), 0.92 (d, *J* = 6.6 Hz, 6H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 155.5, 147.9, 100.9, 36.4, 29.0, 27.0, 22.8, 22.6.

**HRMS** calculated for $C_{10}H_{19}N_2$ $[M+H]^+$ 167.1543, found 167.1546.



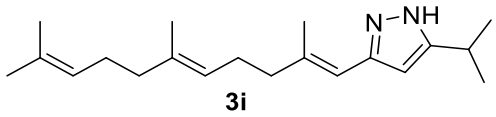

**3h**

**3-(6,10-dimethylundec-9-en-2-yl)-5-isopropyl-1*H*-pyrazole (3h)**: colorless oil, $R_f$ = 0.5 (PE:EA = 3:1), 40.8 mg, 70% yield (d.r. = 1:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.05 (brs, 1H), 5.85 (s, 1H), 5.08 (t, *J* = 7.1 Hz, 1H), 2.96 (hept, *J* = 6.9 Hz, 1H), 2.79 (h, *J* = 7.0 Hz, 1H), 1.94 (m, 2H), 1.67 (s, 3H), 1.64 – 1.56 (m, 4H), 1.54 – 1.45 (m, 1H), 1.38 – 1.34 (m, 1H), 1.32 – 1.19 (m, 13H), 1.13 – 1.05 (m, 2H), 0.83 (d, *J* = 6.5 Hz, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 155.1, 154.2, 131.1, 125.2, 98.6, 37.7, 37.7, 37.2, 37.2, 37.1, 32.5, 32.5, 32.4, 27.0, 25.8, 25.7, 24.9, 24.9, 22.7, 20.8, 20.7, 19.7, 17.7.

**HRMS** calculated for $C_{19}H_{35}N_2$ $[M+H]^+$ 291.2795, found 291.2798.



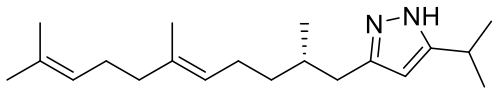

**3i**

**5-isopropyl-3-((1*E*,5*E*)-2,6,10-trimethylundeca-1,5,9-trien-1-yl)-1*H*-pyrazole (3i)**: colorless oil, $R_f$ = 0.5 (PE:EA = 3:1), 36.3 mg, 60% yield.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 6.12 (s, 1H), 6.06 (s, 1H), 5.14 (d, *J* = 1.1 Hz, 1H), 5.08 (ddd, *J* = 6.9, 4.1, 1.3 Hz, 1H), 2.99 (hept, *J* = 6.9 Hz, 1H), 2.19 (d, *J* = 3.2 Hz, 4H), 2.08 – 2.03 (m, 2H), 1.99 (d, *J* = 7.9 Hz, 2H), 1.96 (d, *J* = 1.0 Hz, 3H), 1.67 (s, 3H), 1.60 (d, *J* = 9.3 Hz, 6H), 1.29 (d, *J* = 6.9 Hz, 6H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 156.1, 145.0, 140.9, 135.7, 131.4, 124.4, 123.7, 114.6, 101.2, 40.9, 39.8, 27.2, 26.8, 26.7, 25.8, 22.8, 18.7, 17.8, 16.1.

**HRMS** calculated for $C_{20}H_{33}N_2$ $[M+H]^+$ 301.2639, found 301.2641.



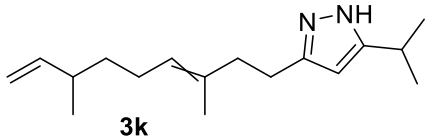
**3j**

**(*S*,*E*)-5-isopropyl-3-(2,6,10-trimethylundeca-5,9-dien-1-yl)-1*H*-pyrazole (3j)**: colorless oil, $R_f$ = 0.5 (PE:EA = 3:1), 40.5 mg, 67% yield.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.34 (brs, 1H), 5.85 (s, 1H), 5.12 – 5.05 (m, 2H), 2.96 (hept, *J* = 6.9 Hz, 1H), 2.61 (dd, *J* = 14.4, 5.9 Hz, 1H), 2.41 (dd, *J* = 14.5, 8.0 Hz, 1H), 2.09 – 2.02 (m, 3H), 2.01 – 1.94 (m, 3H), 1.82 – 1.72 (m, 1H), 1.67 (s, 3H), 1.59 (s, 6H), 1.44 – 1.37 (m, 1H), 1.26 (d, *J* = 6.9 Hz, 6H), 1.23 – 1.16 (m, 1H), 0.91 (d, *J* = 6.6 Hz, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 155.4, 147.7, 135.0, 131.4, 124.6, 124.5, 101.0, 39.9, 36.9, 34.7, 33.3, 27.0, 26.8, 25.8, 25.6, 22.7, 19.7, 17.8, 16.1.

**HRMS** calculated for $C_{20}H_{35}N_2$ $[M+H]^+$ 303.2795, found 303.2797.



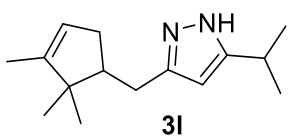
**3k**

**(*E*)-3-(3,7-dimethylnona-3,8-dien-1-yl)-5-isopropyl-1*H*-pyrazole (3k)**: colorless oil, $R_f$ = 0.5 (PE:EA = 3:1), 34.0 mg, 65% yield (Z/E = 1/5.7).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 5.88 (s, 0.15H), 5.86 (s, 0.85H), 5.68 (ddd, *J* = 17.6, 10.3, 7.6 Hz, 1H), 5.16 (td, *J* = 7.1, 1.0 Hz, 1H), 4.98 – 4.86 (m, 2H), 2.95 (hept, *J* = 6.9 Hz, 1H), 2.75 – 2.63 (m, 2H), 2.37 – 2.26 (m, 2H), 2.09 (dt, *J* = 13.9, 7.0 Hz, 1H), 2.00 – 1.91 (m, 2H), 1.71 (s, 0.46H), 1.63 (s, 2.62H), 1.34 – 1.24 (m, 8H), 0.98 (d, *J* = 6.7 Hz, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 155.1, 148.9, 144.8, 134.2, 126.4, 125.4, 112.7, 100.3, 39.3, 37.49, 37.46, 37.0, 36.7, 31.8, 26.93, 26.89, 26.0, 25.8, 25.7, 25.6, 23.4, 22.7, 20.3, 16.1.

**HRMS** calculated for $C_{17}H_{29}N_2$ $[M+H]^+$ 261.2326, found 261.2329.



**3l**

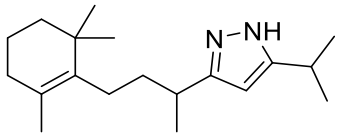
**5-isopropyl-3-((2,2,3-trimethylcyclopent-3-en-1-yl)methyl)-1*H*-pyrazole (3l)**: colorless oil,

$R_f$ = 0.5 (PE:EA = 3:1), 25.9 mg, 56% yield.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 5.88 (s, 1H), 5.22 (s, 1H), 2.96 (hept, *J* = 6.9 Hz, 1H), 2.76 (dd, *J* = 14.4, 4.2 Hz, 1H), 2.53 (dd, *J* = 14.4, 11.2 Hz, 1H), 2.29 – 2.20 (m, 1H), 2.14 – 2.05 (m, 1H), 1.97 – 1.87 (m, 1H), 1.63 – 1.59 (m, 3H), 1.26 (d, *J* = 6.9 Hz, 6H), 0.99 (s, 3H), 0.85 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 155.0, 148.6, 148.3, 121.7, 100.4, 50.1, 46.8, 35.9, 27.7, 26.8, 25.7, 22.7, 19.7, 12.6.

**HRMS** calculated for $C_{15}H_{25}N_2$ $[M+H]^+$ 233.2013, found 233.2018.



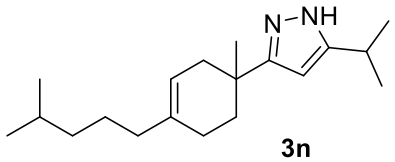

**3m**

**5-isopropyl-3-(4-(2,6,6-trimethylcyclohex-1-en-1-yl)butan-2-yl)-1*H*-pyrazole (3m)**: colorless oil, $R_f$ = 0.5 (PE:EA = 3:1), 33.0 mg, 57% yield.

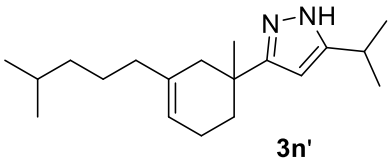
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.66 (brs, 1H), 5.88 (s, 1H), 2.97 (hept, *J* = 6.9 Hz, 1H), 2.79 (h, *J* = 6.9 Hz, 1H), 2.03 – 1.83 (m, 4H), 1.68 – 1.58 (m, 2H), 1.57 – 1.52 (m, 2H), 1.51 (s, 3H), 1.41 – 1.36 (m, 2H), 1.27 (t, *J* = 6.5 Hz, 9H), 0.93 (d, *J* = 3.8 Hz, 6H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 155.0, 154.3, 137.3, 127.0, 98.6, 40.0, 37.9, 35.1, 33.4, 32.9, 28.8, 28.7, 27.0, 26.7, 22.8, 22.7, 20.6, 19.9, 19.7.

**HRMS** calculated for $C_{19}H_{33}N_2$ $[M+H]^+$ 289.2639, found 289.2642.




**3n**




**3n'**

**3n+3n'** (**3n**:**3n'** = 1.8:1)

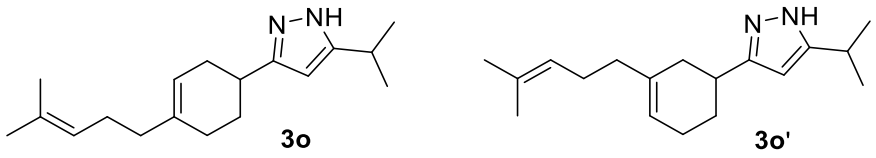
**5-isopropyl-3-(1-methyl-4-(4-methylpentyl)cyclohex-3-en-1-yl)-1*H*-pyrazole (3n)**: colorless oil, $R_f$ = 0.5 (PE:EA = 3:1), 44.4 mg, 77% yield (**3n**:**3n'** = 1.8:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.94 (brs, 1H), 5.88 (s, 1H), 5.43 (s, 1H), 3.01 – 2.89 (m, 1H), 2.42 (d, *J*=17.1 Hz, 0.64H), 2.32 (d, *J*=17.0 Hz, 0.36H), 2.13 – 1.77 (m, 6H), 1.73 – 1.64 (m,

1H), 1.55 – 1.48 (m, 1H), 1.43 – 1.33 (m, 2H), 1.30 – 1.24 (m, 9H), 1.17 – 1.10 (m, 2H), 0.88 – 0.84 (m, 6H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 156.1, 155.4, 137.7, 136.6, 120.0, 119.1, 98.5, 98.4, 40.8, 38.9, 38.8, 38.3, 37.9, 37.7, 35.0, 34.3, 33.5, 33.0, 28.0, 28.0, 27.19, 27.15, 27.0, 26.8, 26.0, 25.6, 25.5, 23.0, 22.8, 22.73, 22.70, 22.68.

**HRMS** calculated for $C_{19}H_{33}N_2$ $[M+H]^+$ 289.2639, found 289.2640.




**3o** **3o'**

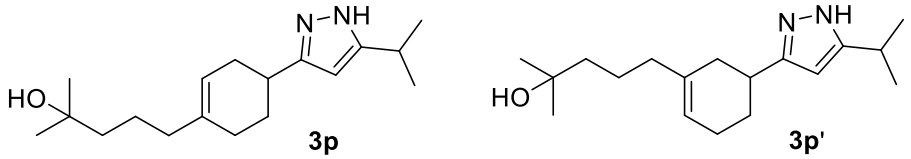
**3o+3o'** (**3o**:**3o'** = 1.8:1)

**5-isopropyl-3-(4-(4-methylpent-3-en-1-yl)cyclohex-3-en-1-yl)-1*H*-pyrazole (3o)**: colorless oil, $R_f$ = 0.5 (PE:EA = 3:1), 40.1 mg, 74% yield (**3o**:**3o'** = 1.8:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.90 (brs, 1H), 5.89 (s, 0.36H), 5.88 (s, 0.64H), 5.45 (s, 1H), 5.15 – 5.07 (m, 1H), 3.02 – 2.81 (m, 2H), 2.42 – 2.22 (m, 1H), 2.17 – 1.96 (m, 8H), 1.74 – 1.58 (m, 7H), 1.29 – 1.24 (m, 6H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 154.9, 153.5, 137.8, 136.9, 131.6, 124.4, 124.4, 120.7, 119.9, 98.7, 37.9, 37.8, 34.9, 33.1, 32.6, 31.7, 29.3, 28.9, 28.4, 26.98, 26.95, 26.5, 25.8, 25.3, 22.7, 17.82, 17.81.

**HRMS** calculated for $C_{18}H_{29}N_2$ $[M+H]^+$ 273.2326, found 273.2327.




**3p** **3p'**

**3p+3p'** (**3p**:**3p'** = 2.5:1)

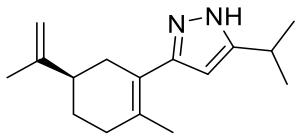
**5-(4-(5-isopropyl-1*H*-pyrazol-3-yl)cyclohex-1-en-1-yl)-2-methylpentan-2-ol (3p)**: colorless oil, $R_f$ = 0.2 (PE:EA = 1:1), 49.4 mg, 85% yield.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 5.88 (s, 0.28H), 5.87 (s, 0.72H), 5.45 (s, 1H), 3.01 – 2.80 (m, 2H), 2.41 – 2.08 (m, 3H), 2.07 – 1.94 (m, 4H), 1.74 – 1.61 (m, 1H), 1.50 – 1.39 (m, 4H), 1.26 (d, *J* = 6.9 Hz, 6H), 1.20 (s, 6H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 154.9, 153.4, 137.7, 136.8, 120.9, 120.0, 98.8, 71.1, 43.6, 43.6,

38.2, 38.1, 34.5, 33.0, 32.6, 31.6, 29.4, 29.3, 29.3, 29.2, 28.2, 26.9, 26.9, 25.1, 22.7, 22.6, 22.5, 22.4.

**HRMS** calculated for $C_{18}H_{31}N_2O$ $[M+H]^+$ 291.2431, found 291.2434.



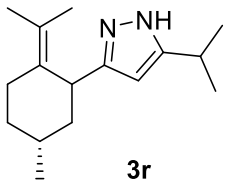
**3q**

**(*R*)-5-isopropyl-3-(2-methyl-5-(prop-1-en-2-yl)cyclohex-1-en-1-yl)-1*H*-pyrazole (3q)**: colorless oil, $R_f$ = 0.5 (PE:EA = 3:1), 31.7 mg, 65% yield.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.26 (brs, 1H), 5.99 (s, 1H), 4.74 (s, 2H), 2.99 (hept, *J* = 6.9 Hz, 1H), 2.46 (d, *J* = 13.1 Hz, 1H), 2.31 – 2.16 (m, 4H), 1.86 – 1.80 (m, 4H), 1.75 (s, 3H), 1.52 (m, 1H), 1.28 (d, *J* = 6.9 Hz, 6H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 155.6, 149.5, 147.7, 132.6, 121.9, 108.9, 101.2, 41.5, 35.1, 33.0, 27.6, 27.1, 22.7, 22.7, 21.1, 20.8.

**HRMS** calculated for $C_{16}H_{25}N_2$ $[M+H]^+$ 245.2013, found 245.2015.



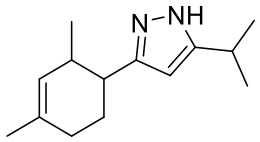
**3r**

**5-isopropyl-3-((5*R*)-5-methyl-2-(propan-2-ylidene)cyclohexyl)-1*H*-pyrazole (3r)**: colorless oil, $R_f$ = 0.5 (PE:EA = 3:1), 30.2 mg, 61% yield (d.r. = 1:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 5.88 (s, 1H), 4.06 (d, *J* = 4.5 Hz, 1H), 2.94 (hept, *J* = 6.9 Hz, 1H), 2.61 (d, *J* = 15.0 Hz, 1H), 2.14 (dd, *J* = 13.3, 2.2 Hz, 1H), 1.77 (s, 3H), 1.75 (s, 3H), 1.70 – 1.61 (m, 2H), 1.33 (m, 2H), 1.20 (d, *J* = 6.9, 1.8 Hz, 6H), 0.94 (m, 1H), 0.88 (d, *J* = 6.3 Hz, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 157.7, 148.8, 130.9, 124.8, 99.9, 39.2, 35.9, 35.7, 27.8, 27.5, 26.6, 22.8, 22.8, 22.5, 20.4, 20.3.

**HRMS** calculated for $C_{16}H_{27}N_2$ $[M+H]^+$ 247.2169, found 247.2172.



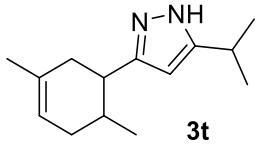
**3s**

**3-(2,4-dimethylcyclohex-3-en-1-yl)-5-isopropyl-1*H*-pyrazole (3s)**: colorless oil, $R_f$ = 0.5 (PE:EA = 3:1), 33.8 mg, 77% yield (d.r. = 1:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.07 (brs, 1H), 5.83 (s, 1H), 5.40 (s, 0.50H), 5.26 (s, 0.50H), 3.06 – 3.01 (m, 0.53H), 2.99 – 2.90 (m, 1H), 2.50 – 2.43 (m, 0.53H), 2.41 – 2.35 (m, 0.53H), 2.33 – 2.24 (m, 0.53H), 2.08 – 1.93 (m, 2H), 1.91 – 1.86 (m, 1.53H), 1.80 – 1.72 (m, 0.53H), 1.68 (s, 3H), 1.26 (d, *J* = 6.9, 6H), 0.90 (d, *J* = 6.8 Hz, 1.50H), 0.71 (d, *J* = 7.1 Hz, 1.52H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 155.7, 155.0, 153.0, 150.47, 133.33, 133.29, 127.28, 127.25, 100.3, 99.0, 40.8, 36.4, 36.3, 33.7, 30.2, 30.0, 29.8, 27.2, 27.0, 23.7, 23.6, 23.5, 22.8, 22.7, 20.8, 16.8.

**HRMS** calculated for $C_{14}H_{23}N_2$ $[M+H]^+$ 219.1856, found 219.1859.



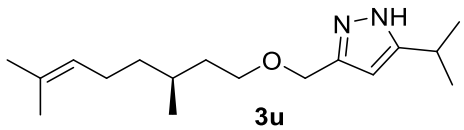
**3t**

**3-(3,6-dimethylcyclohex-3-en-1-yl)-5-isopropyl-1*H*-pyrazole (3t)**: colorless oil, $R_f$ = 0.5 (PE:EA = 3:1), 32.4 mg, 74% yield (d.r. = 1:1.5).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 5.85 (s, 0.40H), 5.84 (s, 0.60H), 5.41 (s, 1H), 3.00 – 2.92 (m, 1H), 2.65 – 2.45 (m, 1H), 2.29 – 2.05 (m, 3H), 1.92 – 1.73 (m, 2H), 1.67 (s, 3H), 1.27 (d, *J* = 6.9, 6H), 0.81 (m, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 155.5, 152.7, 133.8, 133.2, 120.7, 120.2, 99.2, 40.4, 39.8, 39.1, 37.6, 34.4, 34.0, 33.4, 32.9, 27.0, 23.5, 23.4, 22.7, 20.3, 20.1.

**HRMS** calculated for $C_{14}H_{23}N_2$ $[M+H]^+$ 219.1856, found 219.1858.



**3u**

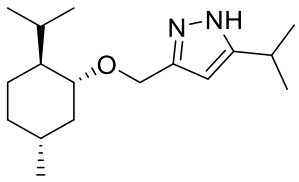
**(*S*)-3-(((3,7-dimethyloct-6-en-1-yl)oxy)methyl)-5-isopropyl-1*H*-pyrazole (3u)**: colorless oil,

$R_f$ = 0.5 (PE:EA =1:1), 32.4 mg, 58% yield.

**$^1$H NMR** (700 MHz, $CDCl_3$) δ 8.78 (brs, 1H), 6.07 (s, 1H), 5.09 (ddd, *J* = 7.1, 5.9, 1.3 Hz, 1H), 4.52 – 4.48 (m, 2H), 3.51 (ddd, *J* = 14.1, 8.4, 3.9 Hz, 2H), 2.98 (hept, *J* = 6.9 Hz, 1H), 2.01 – 1.92 (m, 2H), 1.69 – 1.65 (m, 4H), 1.60 – 1.55 (m, 4H), 1.43 – 1.391 (m, 1H), 1.34 – 1.31 (m, 1H), 1.28 (d, *J* = 7.0 Hz, 6H), 1.17 – 1.13 (m, 1H), 0.88 (d, *J* = 6.7 Hz, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 153.9, 147.3, 131.3, 124.9, 101.1, 69.1, 66.0, 37.3, 36.7, 29.7, 26.6, 25.8, 25.6, 22.6, 19.6, 17.8.

**HRMS** calculated for $C_{17}H_{31}N_2O$ $[M+H]^+$ 279.2431, found 279.2434.



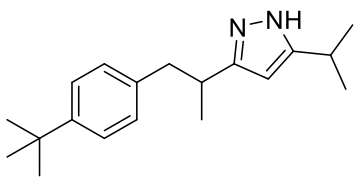

**3v**

**5-isopropyl-3-((((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)methyl)-1*H*-pyrazole (3v)**: colorless oil, $R_f$ = 0.5 (PE:EA =1:1), 29.4 mg, 53% yield.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.13 (brs, 1H), 6.06 (s, 1H), 4.65 (d, *J* = 12.0 Hz, 1H), 4.43 (d, *J* = 12.0 Hz, 1H), 3.16 (td, *J* = 10.6, 4.2 Hz, 1H), 2.98 (hept, *J* = 6.9 Hz, 1H), 2.25 – 2.12 (m, 2H), 1.67 – 1.59 (m, 2H), 1.27 (d, *J* = 6.9 Hz, 8H), 0.95 – 0.86 (m, 9H), 0.67 (d, *J* = 6.9 Hz, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 154.1, 147.6, 101.0, 78.6, 63.4, 48.3, 40.3, 34.7, 31.6, 26.6, 25.6, 23.4, 22.7, 22.6, 22.4, 21.1, 16.1.

**HRMS** calculated for $C_{17}H_{31}N_2O$ $[M+H]^+$ 279.2431, found 279.2433.



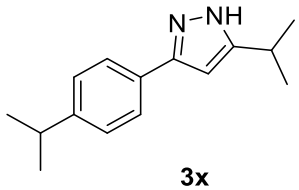

**3w**

**3-(1-(4-(tert-butyl)phenyl)propan-2-yl)-5-isopropyl-1*H*-pyrazole (3w)**: colorless oil, $R_f$ = 0.5 (PE:EA = 3:1), 42.1 mg, 74% yield.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.3 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 5.89 (s, 1H), 3.16 – 3.06 (m, 1H), 3.05 – 2.93 (m, 2H), 2.71 (dd, *J* = 13.4, 8.7 Hz, 1H), 1.32 (s, 9H), 1.28 (d, *J* = 6.9 Hz, 6H), 1.24 (d, *J* = 6.9 Hz, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ154.8, 153.7, 148.9, 137.4, 128.9, 125.2, 99.1, 43.2, 34.5, 34.3, 31.5, 26.9, 22.7, 19.8.

**HRMS** calculated for $C_{19}H_{29}N_2$ $[M+H]^+$ 285.2326, found 285.2326.



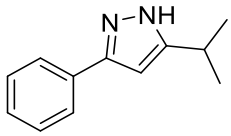

**3x**

**5-isopropyl-3-(4-isopropylphenyl)-1*H*-pyrazole (3x)**: colorless oil, $R_f$ = 0.4 (PE:EA = 3:1), 28.2 mg, 62% yield.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 10.69 (brs, 1H), 7.63 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 6.31 (s, 1H), 3.02 – 2.85 (m, 2H), 1.26 (dd, *J* = 6.7, 5.8 Hz, 12H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 154.4, 149.5, 148.6, 130.3, 126.8, 125.8, 99.1, 34.0, 26.6, 24.1, 22.7.

**HRMS** calculated for $C_{15}H_{21}N_2$ $[M+H]^+$ 229.1700, found 229.1704.



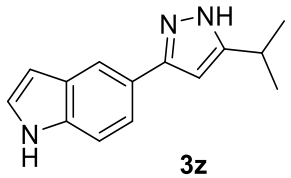

**3y**

**5-isopropyl-3-phenyl-1*H*-pyrazole (3y)**: light yellow solid (m.p. = 106.6 – 107.6 °C), $R_f$ = 0.4 (PE:EA = 3:1), 28.7 mg, 77% yield.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.06 (brs, 1H), 7.75 – 7.71 (m, 2H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.32– 7.27 (m, 1H), 6.37 (s, 1H), 3.00 (hept, *J* = 6.9 Hz, 1H), 1.30 (d, *J* = 6.9 Hz, 6H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 154.1, 149.7, 132.8, 128.7, 127.8, 125.8, 99.2, 26.5, 22.6.

**HRMS** calculated for $C_{12}H_{15}N_2$ $[M+H]^+$ 187.1230, found 187.1231.



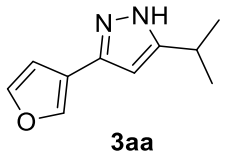
**3z**

**5-(5-isopropyl-1*H*-pyrazol-3-yl)-1*H*-indole (3z)**: yellow oil, $R_f$ = 0.5 (PE:EA =1:1), 27.9 mg, 62% yield.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.93 (brs, 1H), 8.60 (s, 1H), 7.98 (s, 1H), 7.56 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.30 (d, *J* = 8.5 Hz, 1H), 7.18 – 7.13 (m, 1H), 6.53 (s, 1H), 6.41 (s, 1H), 3.02 (hept, *J* = 6.9 Hz, 1H), 1.32 (d, *J* = 6.9 Hz, 6H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 155.4, 150.0, 135.8, 128.2, 125.1, 124.1, 120.4, 118.0, 111.5, 102.9, 99.0, 26.9, 22.7.

**HRMS** calculated for $C_{14}H_{16}N_3$ $[M+H]^+$ 226.1339, found 226.1339.



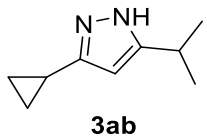
**3aa**

**3-(furan-3-yl)-5-isopropyl-1*H*-pyrazole (3aa)**: white solid (m.p. = 109.7 – 110.7 °C), $R_f$ = 0.5 (PE:EA =1:1), 24.7 mg, 70% yield.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.73 (brs, 1H), 7.72 (s, 1H), 7.44 – 7.37 (m, 1H), 6.68 (d, *J* = 1.0 Hz, 1H), 6.14 (s, 1H), 2.95 (hept, *J* = 6.9 Hz, 1H), 1.26 (d, *J* = 6.9 Hz, 6H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 153.5, 143.4, 142.8, 139.2, 119.3, 109.0, 99.4, 26.4, 22.6.

**HRMS** calculated for $C_{10}H_{13}N_2O$ $[M+H]^+$ 177.1023, found 177.1025.



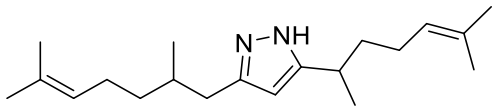
**3ab**

**3-cyclopropyl-5-isopropyl-1*H*-pyrazole (3ab)**: colorless oil, $R_f$ = 0.5 (PE:EA = 3:1), 18.7 mg, 62% yield.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.04 (brs, 1H), 5.72 (s, 1H), 2.94 (hept, *J* = 6.9 Hz, 1H), 1.93 – 1.85 (m, 1H), 1.25 (d, *J* = 6.9 Hz, 6H), 0.93 – 0.87 (m, 2H), 0.73 – 0.68 (m, 2H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 154.3, 152.0, 97.8, 26.6, 22.6, 8.3, 7.7.

**HRMS** calculated for $C_9H_{15}N_2$ $[M+H]^+$ 151.1230, found 151.1232.



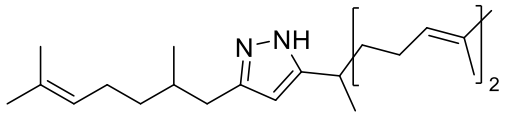
**3ac**

**3-(2,6-dimethylhept-5-en-1-yl)-5-(6-methylhept-5-en-2-yl)-1*H*-pyrazole (3ac)**: colorless oil, $R_f$ = 0.5 (PE:EA = 3:1), 38.3 mg, 63% yield (d.r. = 1:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 5.83 (s, 1H), 5.11 – 5.06 (m, 2H), 2.81 (h, *J* = 7.0 Hz, 1H), 2.61 (dd, *J* = 14.4, 6.0 Hz, 1H), 2.41 (dd, *J* = 14.4, 8.0 Hz, 1H), 2.06 – 1.91 (m, 4H), 1.80 – 1.71 (m, 1H), 1.67 (d, *J* = 1.6 Hz, 6H), 1.64 – 1.50 (m, 8H), 1.44 – 1.35 (m, 1H), 1.24 (d, *J* = 7.0 Hz, 3H), 1.22 – 1.15 (m, 1H), 0.90 (d, *J* = 6.6 Hz, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 154.3, 147.8, 131.7, 131.4, 124.8, 124.4, 101.3, 37.5, 36.9, 34.7, 33.3, 32.0, 26.0, 25.8, 25.7, 20.9, 19.6, 17.8.

**HRMS** calculated for $C_{20}H_{35}N_2$ $[M+H]^+$ 303.2795, found 303.2796.



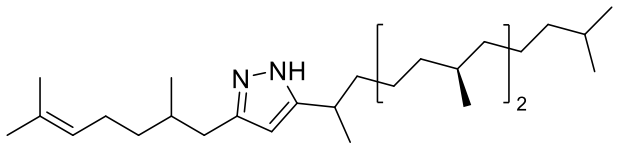
**3ad**

**(*E*)-3-(2,6-dimethylhept-5-en-1-yl)-5-(6,10-dimethylundeca-5,9-dien-2-yl)-1*H*-pyrazole (3ad)**: colorless oil, $R_f$ = 0.5 (PE:EA = 3:1), 47.0 mg, 63% yield (d.r. = 1:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 5.83 (s, 1H), 5.10 (dd, *J* = 15.6, 7.3 Hz, 3H), 2.81 (h, *J* = 7.0 Hz, 1H), 2.61 (dd, *J* = 14.4, 6.0 Hz, 1H), 2.41 (dd, *J* = 14.4, 8.0 Hz, 1H), 2.09 – 1.93 (m, 8H), 1.81 – 1.74 (m, 1H), 1.68 (s, 6H), 1.60 (s, 6H), 1.54 (s, 3H), 1.42 – 1.36 (m, 1H), 1.29 – 1.14 (m, 5H), 0.90 (d, *J* = 6.6 Hz, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 154.1, 147.9, 135.4, 131.4, 131.4, 124.8, 124.5, 124.3, 101.3, 39.8, 37.5, 36.9, 34.8, 33.3, 32.0, 26.8, 25.8, 25.8, 25.8, 25.7, 20.8, 19.7, 17.8, 17.8, 16.0.

**HRMS** calculated for $C_{25}H_{43}N_2$ $[M+H]^+$ 371.3421, found 371.3422.



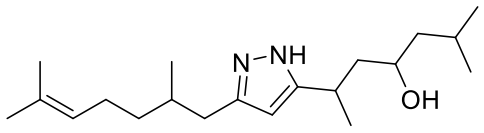

**3ae**

**3-(2,6-dimethylhept-5-en-1-yl)-5-((6*R*,10*R*)-6,10,14-trimethylpentadecan-2-yl)-1*H*-pyrazole (3ae)**: colorless oil, $R_f$ = 0.5 (PE:EA = 3:1), 53.4 mg, 60% yield (d.r. = 1:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 5.83 (s, 1H), 5.12 – 5.05 (m, 1H), 2.79 (h, *J* = 6.9 Hz, 1H), 2.61 (dd, *J* = 14.4, 6.0 Hz, 1H), 2.41 (dd, *J* = 14.4, 8.0 Hz, 1H), 2.10 – 1.91 (m, 2H), 1.81 – 1.72 (m, 1H), 1.68 (s, 3H), 1.61 – 1.47 (m, 6H), 1.40 – 1.31 (m, 4H), 1.30 – 1.19 (m, 12H), 1.17 – 1.11 (m, 3H), 1.09 – 0.99 (m, 4H), 0.90 (d, *J* = 6.6 Hz, 3H), 0.86 (d, *J* = 6.6 Hz, 6H), 0.84 (d, *J* = 6.6 Hz, 3H), 0.81 (dd, *J* = 6.5, 2.8 Hz, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 154.6, 147.6, 131.4, 124.8, 101.3, 39.5, 37.8, 37.6, 37.6, 37.4, 37.2, 36.9, 33.3, 32.9, 32.8, 32.8, 28.1, 25.8, 25.7, 24.9, 24.6, 22.9, 22.8, 20.9, 20.8, 19.9, 19.8, 19.7, 17.8.

**HRMS** calculated for $C_{30}H_{57}N_2$ $[M+H]^+$ 445.4517, found 445.4519.



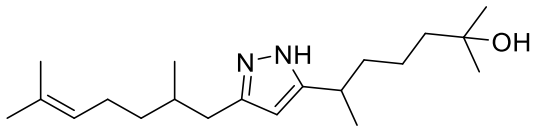

**3af**

**2-(3-(2,6-dimethylhept-5-en-1-yl)-1*H*-pyrazol-5-yl)-6-methylheptan-4-ol (3af)**: colorless oil, $R_f$ = 0.2 (PE:EA =1:1), 49.7 mg, 78% yield (d.r. = 2.7:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.16 (brs, 2H), 5.82 (s, 0.70H), 5.81 (s, 0.30H), 5.08 – 5.05 (m, 1H), 3.82 – 3.76 (m, 0.73H), 3.47 – 3.43 (m, 0.23H), 3.13 – 3.06 (m, 1H), 2.65 – 2.51 (m, 1H), 2.44 – 2.33 (m, 1H), 2.06 – 1.90 (m, 2H), 1.84 – 1.70 (m, 3H), 1.66 (m, 3H), 1.61 – 1.54 (m, 4H), 1.43 – 1.33 (m, 2H), 1.27 – 1.12 (m, 5H), 0.90 – 0.75 (m, 9H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 155.2, 147.1, 131.2, 124.6, 124.6, 101.1, 100.5, 100.4, 68.2, 66.7, 47.5, 47.1, 46.0, 45.8, 36.8, 36.7, 34.4, 33.2, 33.2, 29.6, 29.0, 25.7, 25.6, 24.6, 23.4, 23.1, 23.1, 22.3, 22.2, 21.8, 20.2, 19.5, 19.4, 17.7.

**HRMS** calculated for $C_{20}H_{37}N_2O$ $[M+H]^+$ 321.2901, found 321.2905.



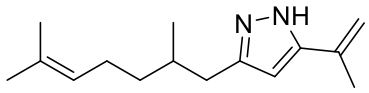

**3ag**

**6-(3-(2,6-dimethylhept-5-en-1-yl)-1*H*-pyrazol-5-yl)-2-methylheptan-2-ol (3ag)**: colorless oil, $R_f$ = 0.2 (PE:EA = 1:1), 45.1 mg, 70% yield (d.r. = 1:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 5.81 (s, 1H), 5.07 (dd, *J* = 10.0, 4.1 Hz, 1H), 2.90 – 2.78 (m, 1H), 2.61 (dd, *J* = 14.4, 6.0 Hz, 1H), 2.41 (dd, *J* = 14.4, 8.1 Hz, 1H), 2.08 – 1.90 (m, 2H), 1.81 – 1.71 (m, 1H), 1.67 (s, 3H), 1.63 – 1.57 (m, 4H), 1.56 – 1.30 (m, 6H), 1.24 (d, *J* = 6.9 Hz, 3H), 1.21 – 1.14 (m, 7H), 0.89 (d, *J* = 6.6 Hz, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 154.4, 147.5, 131.3, 124.8, 101.0, 71.1, 43.5, 37.8, 36.9, 34.7, 33.3, 32.2, 29.5, 29.2, 25.8, 25.7, 22.1, 21.0, 19.6, 17.7.

**HRMS** calculated for $C_{20}H_{37}N_2O$ $[M+H]^+$ 321.2901, found 321.2904.



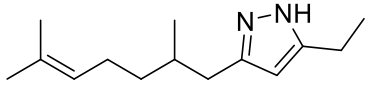

**3ah**

**3-(2,6-dimethylhept-5-en-1-yl)-5-(prop-1-en-2-yl)-1*H*-pyrazole (3ah)**: colorless oil, $R_f$ = 0.5 (PE:EA = 3:1), 21.7 mg, 47% yield.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.17 (brs, 1H), 6.14 (s, 1H), 5.43 (s, 1H), 5.11 – 5.03 (m, 2H), 2.62 (dd, *J* = 14.5, 6.0 Hz, 1H), 2.42 (dd, *J* = 14.5, 8.0 Hz, 1H), 2.11 (s, 3H), 2.06 – 1.92 (m, 2H), 1.82 – 1.72 (m, 1H), 1.68 (s, 3H), 1.60 (s, 3H), 1.44 – 1.36 (m, 1H), 1.24 – 1.16 (m, 1H), 0.90 (d, *J* = 6.6 Hz, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 150.1, 147.0, 135.6, 131.5, 124.6, 111.9, 101.7, 36.8, 34.3, 33.3, 25.8, 25.7, 20.5, 19.6, 17.8.

**HRMS** calculated for $C_{15}H_{25}N_2$ $[M+H]^+$ 233.2013, found 233.2009.




**3ai**

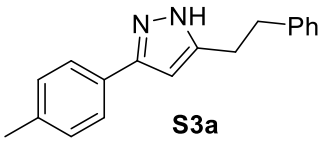
**3-(2,6-dimethylhept-5-en-1-yl)-5-ethyl-1*H*-pyrazole (3ai)**: colorless oil, $R_f$ = 0.5 (PE:EA =

3:1), 38.8 mg, 88% yield.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.95 (brs, 1H), 5.84 (s, 1H), 5.10 – 5.06 (m, 1H), 2.67 – 2.58 (m, 3H), 2.41 (dd, *J* = 14.4, 8.0 Hz, 1H), 2.09 – 1.90 (m, 2H), 1.80 – 1.72 (m, 1H), 1.67 (s, 3H), 1.59 (s, 3H), 1.43 – 1.35 (m, 1H), 1.25 (t, *J* = 7.6 Hz, 3H), 1.21 – 1.15 (m, 1H), 0.90 (d, *J* = 6.6 Hz, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 150.9, 147.7, 131.4, 124.7, 102.2, 36.9, 34.6, 33.3, 25.8, 25.7, 20.5, 19.6, 17.8, 13.7.

**HRMS** calculated for $C_{14}H_{25}N_2$ $[M+H]^+$ 221.2013, found 221.2015.



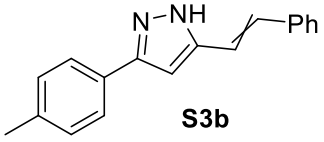

**S3a**

**5-phenethyl-3-(p-tolyl)-1*H*-pyrazole (S3a):** colorless oil, $R_f$ = 0.5 (PE:EA = 3:1), 42.4 mg, 81% yield.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 10.15 (brs, 1H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 2H), 7.12 – 7.02 (m, 5H), 6.22 (s, 1H), 2.87 – 2.79 (m, 4H), 2.25 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 149.3, 147.8, 141.2, 137.8, 129.5, 128.5, 128.5, 126.2, 125.7, 101.1, 35.6, 28.6, 21.4.

**HRMS** calculated for $C_{18}H_{19}N_2$ $[M+H]^+$ 263.1543, found 263.1545.




**S3b**

**5-styryl-3-(p-tolyl)-1*H*-pyrazole (S3b):** colorless oil, $R_f$ = 0.5 (PE:EA = 3:1), 45.8 mg, 88% yield (Z/E = 1/1.1).

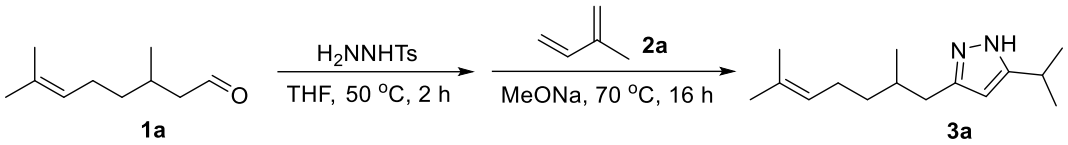
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 11.27 (s, 1H), 7.59 (d, J = 7.8 Hz, 1.05H), 7.54 (d, J = 7.7 Hz, 0.95H), 7.40 – 7.22 (m, 5H), 7.14 (dd, J = 8.0, 5.1 Hz, 2H), 7.06 (d, J = 16.4 Hz, 0.51H), 6.97 (d, J = 16.5 Hz, 0.51H), 6.68 (d, J = 11.9 Hz, 1H), 6.47 (d, J = 12.2 Hz, 0.46H), 6.37 (s, 0.46H), 2.32 (s, 3H).

**$^{13}$C NMR** (176 MHz, CDCl3) δ 138.0, 137.8, 137.3, 136.8, 131.4, 130.7, 129.56, 129.55, 129.5,

128.74, 128.66, 128.5, 127.92, 127.85, 126.6, 125.8, 125.7, 102.6, 99.7, 21.3.

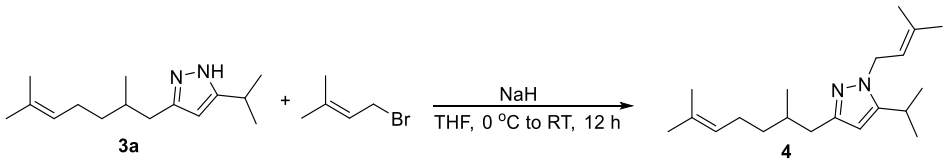
**HRMS** calculated for $C_{18}H_{17}N_2$ $[M+H]^+$ 261.1387, found 261.1388.

## 5. Scale-up reactions




In a glove box, to a 120 mL seal tube with a magnetic stirring bar, $H_2NNHTs$ (20.0 mmol, 1.0 eq.), citronellal **1a** (20.2 mmol, 1.01 eq.) and dry THF (50 mL) were successively added. The reaction tube was sealed with a cap, removed from the glove box and stirred at 50 °C for 2 h. Then, the reaction mixture was cooled to room temperature, MeONa (50.0 mmol, 2.5 eq.) and isoprene **2a** (80.0 mmol, 4.0 eq.) were added into the reaction mixture and stirred at 70 °C. After 16 h, the mixture was diluted with 50 mL of EA, washed with water and extracted with EA. The organic phase was dried over $Na_2SO_4$ and concentrated under reduced pressure. Purification by flash column chromatography over silica gel (PE/EA= 3/1) to give product **3a** (3.59 g, 77% yield).

## 6. Synthetic transformations



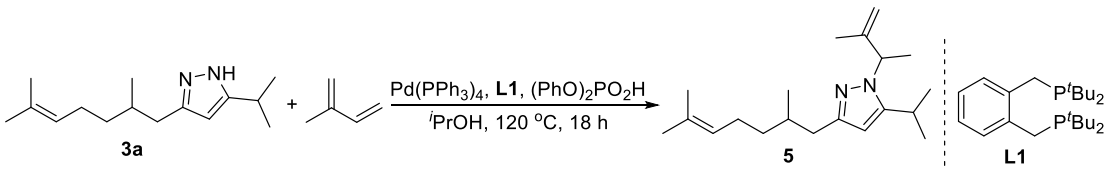

In a Schlenk tube (50 mL), **3a** (3.0 mmol) was dissolved in THF (20.0 mL). After cooling to 0 ºC, NaH (1.5 eq.) was added, and stirred for 1 h. Then prenyl bromide (1.5 eq.) was added dropwise at 0 ºC, and the mixture was stirred at room temperature for 12 h. The reaction was quenched by water and extracted with DCM. The organic phase was dried over sodium sulfate and concentrated under reduced pressure. Purification by flash column chromatography over silica gel (PE/EA= 20/1) to give the desired product **4** (*4*).

**3-(2,6-dimethylhept-5-en-1-yl)-5-isopropyl-1-(3-methylbut-2-en-1-yl)-1*H*-pyrazole (4)**: colorless oil, $R_f$ = 0.6 (PE:EA = 10:1), 740 mg, 81% yield ($N^1$:$N^2$ = 4.5:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 5.81 (s, 0.81H), 5.78 (s, 0.18H), 5.31 – 5.22 (m, 1H), 5.12 – 5.04 (m, 1H), 4.65 – 4.58 (m, 2H), 2.99 – 2.83 (m, 1H), 2.60 – 2.49 (m, 1H), 2.39 – 2.28 (m, 1H), 2.06 – 1.92 (m, 2H), 1.75 – 1.65 (m, 10H), 1.59 (s, 3H), 1.45 – 1.36 (m, 1H), 1.25 – 1.18 (m, 7H), 0.93 – 0.88 (m, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 157.9, 151.0, 149.4, 141.9, 134.28, 134.26, 131.5, 131.0, 125.1, 124.5, 121.0, 120.9, 101.5, 100.9, 47.5, 47.2, 37.1, 37.0, 36.1, 33.4, 33.3, 32.6, 27.9, 25.8, 25.7, 25.60, 25.59, 25.4, 23.2, 22.92, 22.88, 19.7, 19.6, 18.2, 18.1, 17.7.

**HRMS** calculated for $C_{20}H_{35}N_2$ $[M+H]^+$ 303.2795, found 303.2797.




In glove box, a 4 mL sealed tube was charged with $Pd(PPh_3)_4$ (0.01 mmol, 5 mol%), **L1** (0.01 mmol, 5 mol%), **3a** (0.2 mmol, 1.0 eq.), $(PhO)_2PO_2H$ (0.1 mmol, 50 mol%), $^i$PrOH (1.0 mL) and isoprene (1.0 mmol, 5.0 eq.) at room temperature. The reaction tube was sealed with a cap, removed from the glove box. Then, the reaction mixture was stirred at 120 ºC for 18 h. And the crude reaction mixture was purified by column chromatography over silica gel (PE/EA= 20/1)

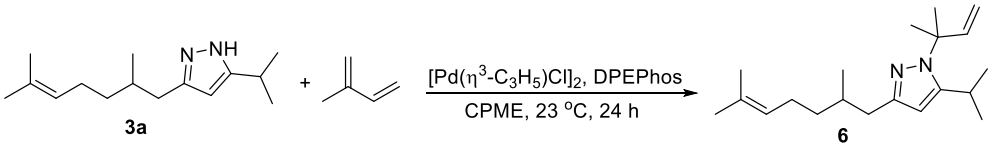
to give the desired product **5** (*5*).

**3-(2,6-dimethylhept-5-en-1-yl)-5-isopropyl-1-(3-methylbut-3-en-2-yl)-1*H*-pyrazole (5)**: colorless oil, $R_f$ = 0.5 (PE:EA = 15:1), 32.0 mg, 53% yield ($N^1$:$N^2$ = 2.0:1, d.r. = 1:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 5.81 (s, 0.67H), 5.79 (s, 0.33H), 5.08 (s, 1H), 4.84 (s, 0.33H), 4.82 (s, 0.67H), 4.74 – 4.60 (m, 2H), 3.02 – 2.85 (m, 1H), 2.62 – 2.48 (m, 1H), 2.42 – 2.27 (m, 1H), 2.05 – 1.93 (m, 2H), 1.79 – 1.71 (m, 1H), 1.67 (d, *J* = 13.3, 6H), 1.61 – 1.56 (m, 6H), 1.46 – 1.35 (m, 1H), 1.26 – 1.16 (m, 7H), 0.93 – 0.86 (m, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 157.7, 150.8, 150.7, 145.0, 149.9, 146.19, 146.16, 146.12, 146.09, 142.23, 142.21, 131.6, 131.5, 131.0, 130.9, 125.13, 125.10, 124.6, 124.5, 111.4, 111.3, 101.2, 101.1, 100.9, 100.8, 58.3, 58.0, 57.9, 37.0, 36.9, 36.0, 35.9, 33.5, 33.4, 33.3, 33.2, 32.4, 32.3, 27.9, 25.8, 25.7, 25.59, 25.56, 25.2, 23.54, 23.51, 23.48, 23.1, 22.72, 22.67, 19.8, 19.64, 19.60, 19.59, 19.55, 19.5, 18.9, 18.72, 18.69, 17.71, 17.68.

**HRMS** calculated for $C_{20}H_{35}N_2$ $[M+H]^+$ 303.2795, found 303.2799.




In glove box, a 4 mL sealed tube was charged with with $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (0.01 mmol, 5 mol%), DPEphos (0.02 mmol, 10 mol%), **3a** (0.2 mmol), isoprene (1.0 mmol, 5.0 eq.) and CPME (1.0 mL) at room temperature. The reaction tube was sealed with a cap, removed from the glove box. Then, the reaction mixture was stirred at 23 ºC for 24 h. And the crude reaction mixture was purified by column chromatography over silica gel (PE/EA= 20/1) to give the desired product **6** (*6*).

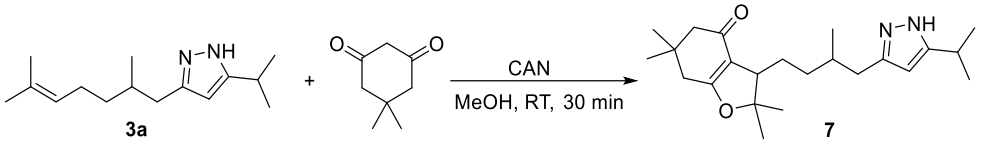
**3-(2,6-dimethylhept-5-en-1-yl)-5-isopropyl-1-(2-methylbut-3-en-2-yl)-1*H*-pyrazole (6)**: colorless oil, $R_f$ = 0.4 (PE:EA = 15:1), 33.3 mg, 55% yield ($N^1$:$N^2$ = 1.6:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 5.80 (s, 0.62H), 5.78 (s, 0.38H), 5.29 – 5.25(m, 1H), 5.12 – 5.06 (m, 1H), 4.66 – 4.57 (m, 2H), 2.97 – 2.83 (m, 1H), 2.60 – 2.49 (m, 1H), 2.39 – 2.28 (m, 1H), 2.07 – 1.93 (m, 2H), 1.80 – 1.69 (m, 7H), 1.68 (s, 1.82H), 1.67 (s, 1.18H), 1.59 (s, 3H), 1.46 – 1.35 (m, 1H), 1.24 – 1.18 (m, 7H), 0.92 – 0.87 (m, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 156.7, 149.9, 148.4, 140.9, 133.3, 133.2, 130.5, 130.0, 124.0,

123.4, 119.9, 119.7, 100.4, 99.8, 46.4, 46.2, 35.99, 35.95, 35.0, 32.4, 32.2, 31.6, 26.8, 24.7, 24.6, 24.53, 24.51, 24.3, 22.1, 21.84, 21.80, 18.63, 18.56, 17.08, 17.05, 16.62, 16.60.

**HRMS** calculated for $C_{20}H_{35}N_2$ $[M+H]^+$ 303.2795, found 303.2796.



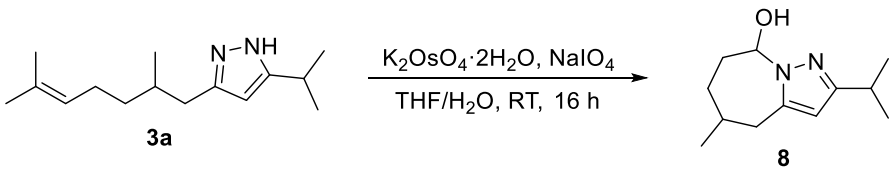

In a Schlenk tube (25 mL), **3a** (0.3 mmol, 1.0 eq.) and 5,5-dimethylcyclohexane-1,3-dione (1.2 mmol, 4.0 eq.) was dissolved in MeOH (8.0 mL), then CAN (3.0 mmol, 10 eq.) was added, and stirred for 30 min. The reaction was quenched by water and extracted with DCM. The organic phase was dried over sodium sulfate and concentrated under reduced pressure. Purification by flash column chromatography over silica gel (EA/PE = 2/1) to give the desired product **7** (*7*).

**3-(4-(5-isopropyl-1*H*-pyrazol-3-yl)-3-methylbutyl)-2,2,6,6-tetramethyl-3,5,6,7-tetrahydrobenzofuran-4(2*H*)-one (7)**: colorless oil, $R_f$ = 0.3 (EA:PE = 2:1), 67.9 mg, 61% yield (d.r. = 1.3:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.78 (brs, 1H), 5.81 (s, 0.43H), 5.80 (s, 0.57H), 2.93 (hept, *J* = 6.9 Hz, 1H), 2.76 – 2.64 (m, 1H), 2.61 – 2.35 (m, 2H), 2.34 – 2.08 (m, 4H), 1.85 – 1.66 (m, 2H), 1.54 – 1.41 (m, 1H), 1.40 – 1.27 (m, 7H), 1.26 – 1.20 (m, 7H), 1.05 (s, 6H), 0.88 (d, 2.8 Hz, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 195.7, 174.9, 174.8, 156.0, 155.6, 146.7, 146.6, 115.6, 115.4, 101.1, 100.9, 92.97, 92.95, 51.4, 48.2, 48.1, 38.2, 34.8, 34.5, 34.0, 34.0, 33.84, 33.78, 29.8, 28.91, 28.89, 28.52, 28.49, 27.1, 27.0, 26.7, 26.6, 22.78, 22.75, 22.73, 22.30, 22.28, 19.9, 19.8.

**HRMS** calculated for $C_{23}H_{37}N_2O_2$ $[M+H]^+$ 373.2850, found 373.2851.




In a Schlenk tube (10 mL), **3a** (0.3 mmol, 1.0 eq.) was dissolved in THF (2.0 mL) and

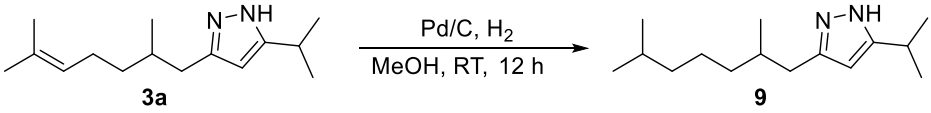
$H_2O$ (1.0 mL), then $NaIO_4$ (0.7 mmol, 2.4 eq.) was added. After cooling to 0 °C, $K_2OsO_4 \cdot 2H_2O$ (0.015 mmol, 5 mol%) was added, and the mixture was stirred at room temperature for 16 h. The reaction was quenched by aqueous $Na_2S_2O_3$ and stirred for 30 min. The reaction mixture was then extracted with EA, and the combined organic layers were washed with brine, dried over sodium sulfate and concentrated under reduced pressure. Purification by flash column chromatography over silica gel (PE/EA= 5/1) to give the desired product **8** (*8*).

**2-isopropyl-5-methyl-5,6,7,8-tetrahydro-4*H*-pyrazolo[1,5-*a*]azepin-8-ol (8)**: white solid (m.p. = 93.8 – 94.8 °C), $R_f$ = 0.5 (PE:EA = 3:1), 40.3 mg, 64% yield (d.r. = 3.5:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 6.56 (brs, 1H), 5.93 (d, *J* = 3.6 Hz, 0.78H), 5.86 (t, *J* = 3.5 Hz, 0.22H), 5.74 (s, 0.23H), 5.74 (s, 0.76H), 2.85 – 2.48 (m, 3H), 2.27 – 2.14 (m, 1H), 2.04 – 1.94 (m, 1H), 1.80 (t, *J* = 13.7 Hz, 1H), 1.74 – 1.38 (m, 2H), 1.16 – 0.99 (m, 9H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 157.1, 156.8, 142.8, 141.6, 104.3, 103.1, 83.0, 82.8, 45.8, 34.4, 33.8, 33.3, 32.0, 31.4, 29.4, 29.0, 28.4, 27.4, 24.1, 23.0, 22.7, 17.8.

**HRMS** calculated for $C_{12}H_{21}N_2O$ $[M+H]^+$ 209.1649, found 209.1651.




**3a** **9**

In a single-necked flask, a mixture of **3a** (0.3 mmol, 1.0 eq.), Pd/C ( 0.03 mmol, 0.10 eq.; Pd 5 mol%) and MeOH (3.0 mL) was stirred under a $H_2$ atmosphere (5 atm) for 12 h at room temperature. After releasing the $H_2$ gas, Pd/C was removed by filtration, and the solvent was removed under reduced pressure. Purification by flash column chromatography over silica gel (PE/EA= 5/1) to give the desired product **9**.

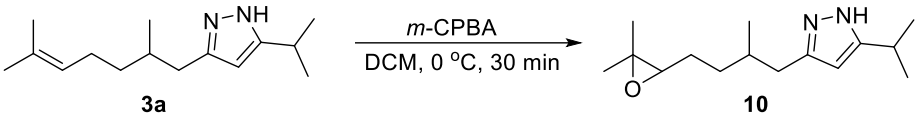
**3-(2,6-dimethylheptyl)-5-isopropyl-1*H*-pyrazole (9)**: colorless oil, $R_f$ = 0.5 (PE:EA = 3:1), 58.9 mg, 83% yield.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.54 (brs, 1H), 5.84 (s, 1H), 2.96 (hept, *J* = 6.9 Hz, 1H), 2.60 (dd, *J* = 14.4, 5.9 Hz, 1H), 2.40 (dd, *J* = 14.4, 8.1 Hz, 1H), 1.81 – 1.69 (m, 1H), 1.58 – 1.44 (m, 1H), 1.37 – 1.30 (m, 2H), 1.29 – 1.23 (m, 7H), 1.17 – 1.09 (m, 3H), 0.89 (d, *J* = 6.6 Hz, 3H), 0.86 (d, *J* = 6.6 Hz, 6H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 155.3, 147.7, 100.8, 39.3, 37.1, 34.8, 33.7, 28.1, 27.0, 24.9,

22.80, 22.77, 22.7, 19.7.

**HRMS** calculated for $C_{15}H_{29}N_2$ $[M+H]^+$ 237.2326, found 237.2330.




**3a** **10**

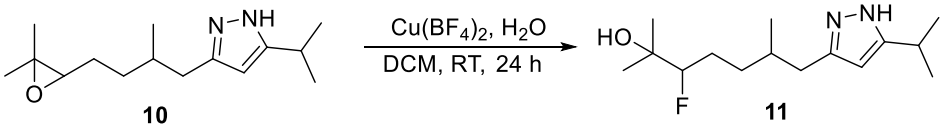
In a Schlenk tube (10 mL), **3a** (2.0 mmol, 1.0 eq.) was dissolved in DCM (2.0 mL). After cooling to 0 °C, *m*-CPBA (2.02 mmol, 1.01 eq.) was added, and the mixture was stirred at 0 °C for 30 min. The reaction was quenched by NaOH 10% aq., the reaction mixture was then extracted with DCM, and the combined organic layers were washed with brine, dried over sodium sulfate and concentrated under reduced pressure. Purification by flash column chromatography over silica gel (PE/EA= 2/1) to give the desired product **10**.

**3-(4-(3,3-dimethyloxiran-2-yl)-2-methylbutyl)-5-isopropyl-1*H*-pyrazole (10)**: colorless oil, $R_f$ = 0.3 (PE:EA = 2:1), 440 mg, 88% yield (d.r. = 1:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.05 (brs, 1H), 5.85 (s, 1H), 2.96 (hept, *J* = 6.9 Hz, 1H), 2.70 (t, *J* = 6.1 Hz, 1H), 2.66 – 2.57 (m, 1H), 2.49 – 2.41 (m, 1H), 1.88 – 1.77 (m, 1H), 1.69 – 1.34 (m, 4H), 1.30 (s, 3H), 1.27 (s, 3H), 1.26 (s, 6H), 0.93 (d, *J* = 6.6 Hz, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 154.9, 147.7, 100.8, 64.6, 58.4, 58.3, 34.8, 34.5, 33.51, 33.45, 33.3, 26.8, 26.5, 25.0, 22.7, 19.7, 19.6, 18.8, 18.7.

**HRMS** calculated for $C_{15}H_{27}N_2O$ $[M+H]^+$ 251.2118, found 251.2122.




**10** **11**

In a Schlenk tube (50 mL), **10** (2.0 mmol, 1.0 eq.) was dissolved in DCM (12.0 mL), $Cu(BF_4)_2$ (4.6 mmol, 2.3 eq., 45% in $H_2O$) was added, and the mixture was stirred at room temperature for 24 h. The reaction mixture was washed with brine, dried over sodium sulfate and concentrated under reduced pressure. Purification by flash column chromatography over silica gel (PE/EA= 1/1) to give the desired product **11**.

**3-fluoro-7-(5-isopropyl-1*H*-pyrazol-3-yl)-2,6-dimethylheptan-2-ol (11)**: colorless oil, $R_f$ =

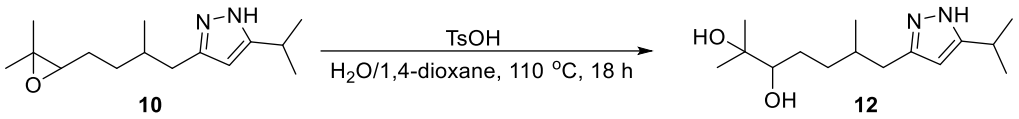
0.2 (PE:EA = 1:1), 171.8 mg, 32% yield (d.r. = 1:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 6.28 (brs, 1H), 5.83 (s, 1H), 3.62 – 3.45 (m, 1H), 2.96 (hept, *J* = 6.9 Hz, 1H), 2.63 – 2.43 (m, 2H), 1.89 – 1.76 (m, 1H), 1.73 – 1.38 (m, 3H), 1.37 – 1.33 (m, 3H), 1.29 (d, *J* = 1.9 Hz, 3H), 1.27 – 1.17 (m, 7H), 0.91 (d, *J* = 6.6 Hz, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 154.8, 154.6, 147.9, 147.4, 100.9, 100.7, 97.97 (d, J = 166.1 Hz), 97.96 (d, J = 166.1 Hz), 76.8 (d, J = 75.1 Hz), 76.5 (d, J = 75.1 Hz), 34.6, 34.0, 33.4, 32.9, 32.8, 28.47 (d, J = 65.9 Hz), 28.43 (d, J = 66.2 Hz), 26.8, 26.7, 23.5, 23.4, 23.3, 23.2, 22.74, 22.72, 22.13, 22.06, 21.9, 21.8, 20.0, 19.6.

**$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -144.39, -144.41.

**HRMS** calculated for $C_{15}H_{28}FN_2O$ $[M+H]^+$ 271.2181, found 271.2184.




**10** **12**

In a Schlenk tube (25 mL), **10** (0.3 mmol, 1.0 eq.), TsOH (0.015 mmol, 5 mol%) was dissolved in 1,4-dioxane (3.0 mL) and $H_2O$ (3.0 mL). After refluxing for 18 h, the mixture was cooled, quenched with sat. $NaHCO_3$, the reaction mixture was then extracted with DCM, dried over sodium sulfate and concentrated under reduced pressure. Purification by flash column chromatography over silica gel (DCM/MeOH= 10/1) to give the desired product **12**.

**7-(5-isopropyl-1*H*-pyrazol-3-yl)-2,6-dimethylheptane-2,3-diol (12)**: colorless oil, $R_f$ = 0.4 (DCM:MeOH= 10:1), 65.6 mg, 81% yield (d.r. = 1:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 5.81 (s, 1H), 5.38 (brs, 2H), 3.36 (dd, *J* = 21.4, 9.2 Hz, 1H), 2.94 (hept, *J* = 6.9 Hz, 1H), 2.59 – 2.44 (m, 2H), 1.89 – 1.74 (m, 1H), 1.71 – 1.26 (m, 4H), 1.24 (d, *J* = 6.9 Hz, 6H), 1.18 (s, 3H), 1.14 (d, *J* = 3.6 Hz, 3H), 0.93 – 0.88 (m, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 153.8, 153.7, 147.2, 146.5, 100.2, 100.0, 78.1, 77.2, 72.3, 33.7, 33.0, 32.7, 32.5, 32.0, 31.8, 28.3, 27.4, 25.8, 25.8, 25.5, 25.4, 22.4, 21.8, 21.8, 19.3, 18.7.

**HRMS** calculated for $C_{15}H_{29}N_2O_2$ $[M+H]^+$ 269.2224, found 269.2224.

## 7. Mechanistic study

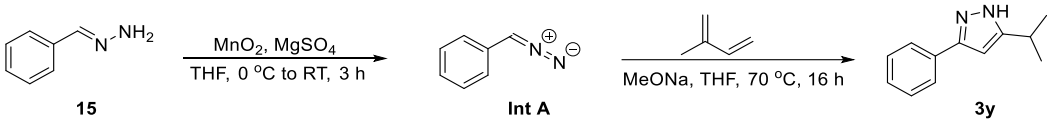
### 7.1 Control experiments

In a glove box, to a 4 mL seal tube with a magnetic stirring bar, Ts-hydrazone (0.20 mmol, 1.0 eq.), MeONa (0.5 mmol, 2.5 eq.), dry THF (0.5 mL) and alkene (0.8 mmol, 4.0 eq.) were successively added. The reaction tube was sealed with a cap, removed from the glove box and stirred at 70 °C for 16 h. The mixture was detected by TLC and GC-MS.

### 7.2 Temperature effect

In a glove box, to a 4 mL seal tube with a magnetic stirring bar, $H_2NNHTs$ (0.20 mmol, 1.0 eq.), citronellal **1a** (0.21 mmol, 1.05 eq.) and dry THF (0.5 mL) were successively added. The reaction tube was sealed with a cap, removed from the glove box and stirred at 50 °C for 2 h. Then, the reaction mixture was cooled to room temperature, MeONa (0.5 mmol, 2.5 eq.) and isoprene **2a** (0.8 mmol, 4.0 eq.) were added into the reaction mixture and stirred at different temperature (40 °C, 50 °C, 60 °C, 70 °C, 90 °C and 110 °C) for 16 h, respectively. The yields were determined by GC-FID analysis of crude mixture with 1,3,5-trimethoxybenzene as the internal standard.

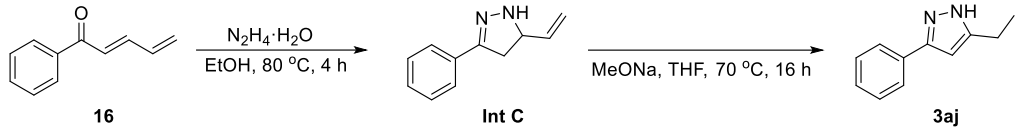
### 7.3 Verification of intermediates




To a solution of benzylidenehydrazine **15** (0.2 mmol) in THF (0.5 mL) with a magnetic stirring bar was added activated $MnO_2$ (0.8 mmol, 4.0 eq.) and $MgSO_4$ (0.8 mmol, 4.0 eq.) at 0 °C. The reaction mixture was stirred at 0 °C for 2 h and at room temperature for 1 h, then filtered through celite, washed with THF (0.5 mL) giving **Int A** and used in the next step immediately without further purification (*9*).

In a glove box, to a 4 mL seal tube with a magnetic stirring bar, a solution of **Int A** in THF, MeONa (0.5 mmol, 2.5 eq.) and isoprene (0.8 mmol, 4.0 eq.) were successively added. The reaction tube was sealed with a cap, removed from the glove box and stirred at 70 °C. After 16 h, the mixture was diluted with 2 mL of EA, washed with water and extracted with EA. The

organic phase was dried over $Na_2SO_4$ and concentrated under reduced pressure. Purification by flash column chromatography over silica gel (PE/EA = 3/1) to give product **3y** (5.9 mg, 16% yield).




16 Int C 3aj

To a solution of 1-phenylpenta-2,4-dien-1-one **16** (0.5 mmol) in absolute ethyl alcohol (1.0 mL) with a magnetic stirring bar was added hydrazine monohydrate (1.0 mmol, 2.0 eq.). The reaction mixture was stirred at 80 °C for 4 h, then the solvent was removed under reduced pressure gaving **Int C** and used in the next step without further purification (*10*).

**3-phenyl-5-vinyl-4,5-dihydro-1*H*-pyrazole (Int C)**

**$^1$H NMR** (700 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.8 Hz, 2H), 7.36 (m, 3H), 5.97 – 5.91 (m, 1H), 5.70 (brs, 1H), 5.24 (d, *J* = 17.1 Hz, 1H), 5.12 (d, *J* = 10.1 Hz, 1H), 4.34 (dd, *J* = 17.7, 8.5 Hz, 1H), 3.20 (dd, *J* = 16.0, 10.0 Hz, 1H), 2.85 (dd, *J* = 16.0, 8.3 Hz, 1H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 152.1, 138.1, 132.8, 128.8, 128.5, 126.0, 116.5, 63.6, 38.6.

**HRMS** calculated for $C_{11}H_{13}N_2$ $[M+H]^+$ 173.1073, found 173.1075.

In a glove box, to a 4 mL seal tube with a magnetic stirring bar, a solution of **Int C** in THF (1.0 mL), and MeONa (0.75 mmol, 1.5 eq.) were successively added. The reaction tube was sealed with a cap, removed from the glove box and stirred at 70 °C. After 16 h, the mixture was diluted with 2 mL of EA, washed with water and extracted with EA. The organic phase was dried over $Na_2SO_4$ and concentrated under reduced pressure. Purification by flash column chromatography over silica gel (PE/EA = 3/1) to give product **3aj**.

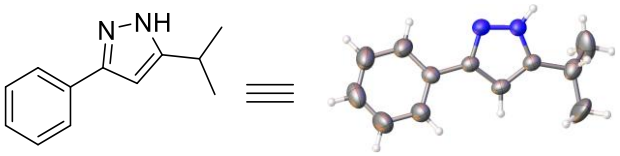
**5-ethyl-3-phenyl-1H-pyrazole (3aj)**: yellow solid (m.p. = 71.1 – 72.1 °C), $R_f$ = 0.4 (PE:EA= 3:1), 43.8 mg, 51% yield.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 10.06 (brs, 1H), 7.76 – 7.70 (m, 2H), 7.40 – 7.33 (m, 2H), 7.32 – 7.27 (m, 1H), 6.37 (s, 1H), 2.66 (q, *J* = 7.6 Hz, 2H), 1.26 (t, *J* = 7.6 Hz, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 149.9, 149.5, 132.8, 128.7, 127.8, 125.8, 100.5, 19.8, 13.6.

**HRMS** calculated for $C_{11}H_{13}N_2$ $[M+H]^+$ 173.1073, found 173.1076.

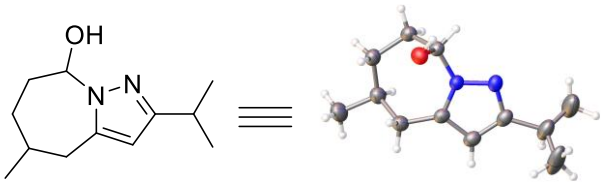
## 8. X-ray crystal structures




**3y** CCDC: 2433436

**Table S1 Crystal data and structure refinement for 3y.**

| | |
|---|---|
| Identification code | **3y** |
| Empirical formula | $C_{12}H_{14}N_2$ |
| Formula weight | 186.25 |
| Temperature/K | 293(2) |
| Crystal system | monoclinic |
| Space group | Pc |
| a/Å | 11.4118(6) |
| b/Å | 10.9978(7) |
| c/Å | 18.1346(10) |
| α/° | 90 |
| β/° | 90.638(5) |
| γ/° | 90 |
| Volume/Å$^3$ | 2275.8(2) |
| Z | 8 |
| $\rho_{calc}$g/cm$^3$ | 1.087 |
| μ/mm$^{-1}$ | 0.504 |
| F(000) | 800.0 |
| Crystal size/mm$^3$ | 0.22 × 0.16 × 0.11 |
| Radiation | CuKα (λ = 1.54178) |
| 2Θ range for data collection/° | 7.748 to 153.418 |
| Index ranges | -14 ≤ h ≤ 14, -13 ≤ k ≤ 13, -22 ≤ l ≤ 16 |
| Reflections collected | 30705 |
| Independent reflections | 7636 [$R_{int}$ = 0.0724, $R_{sigma}$ = 0.0596] |
| Data/restraints/parameters | 7636/2/531 |
| Goodness-of-fit on F$^2$ | 0.942 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0635, w$R_2$ = 0.1584 |
| Final R indexes [all data] | $R_1$ = 0.1222, w$R_2$ = 0.1980 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.17/-0.18 |




**8** CCDC: 2433435

**Table S2 Crystal data and structure refinement for 8.**

| | |
|---|---|
| Identification code | **8** |
| Empirical formula | $C_{12}H_{20}N_2O$ |
| Formula weight | 208.30 |
| Temperature/K | 293(2) |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 5.8209(3) |
| b/Å | 9.6111(4) |
| c/Å | 11.5153(5) |
| α/° | 74.895(4) |
| β/° | 88.396(4) |
| γ/° | 84.626(4) |
| Volume/Å$^3$ | 619.23(5) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.117 |
| μ/mm$^{-1}$ | 0.563 |
| F(000) | 228.0 |
| Crystal size/mm$^3$ | 0.19 × 0.16 × 0.12 |
| Radiation | CuKα (λ = 1.54178) |
| 2Θ range for data collection/° | 7.952 to 159.276 |
| Index ranges | -7 ≤ h ≤ 7, -12 ≤ k ≤ 12, -14 ≤ l ≤ 14 |
| Reflections collected | 11389 |
| Independent reflections | 2496 [$R_{int}$ = 0.0532, $R_{sigma}$ = 0.0342] |
| Data/restraints/parameters | 2496/0/143 |
| Goodness-of-fit on F$^2$ | 1.087 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0693, w$R_2$ = 0.2201 |
| Final R indexes [all data] | $R_1$ = 0.1014, w$R_2$ = 0.2524 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.28/-0.21 |

## 9. References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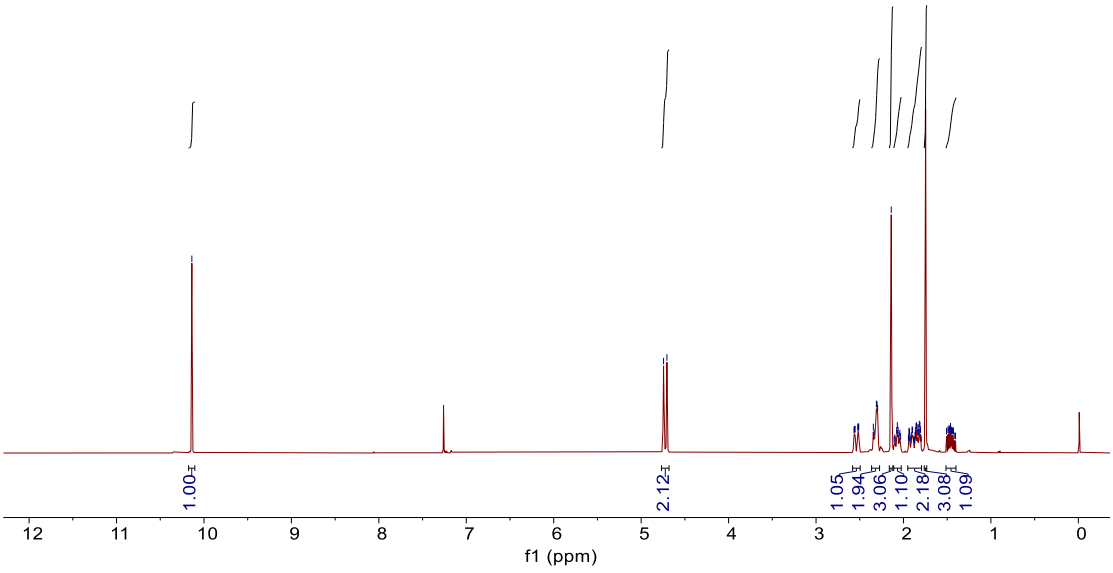
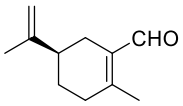
## 10. Copies of NMR spectra


A5747-ZLM-4-34

PROTON CDCl3 {D:\NMR400\02T4} nmr-new 27




**1q**

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**


A8550-ZLM-4-34

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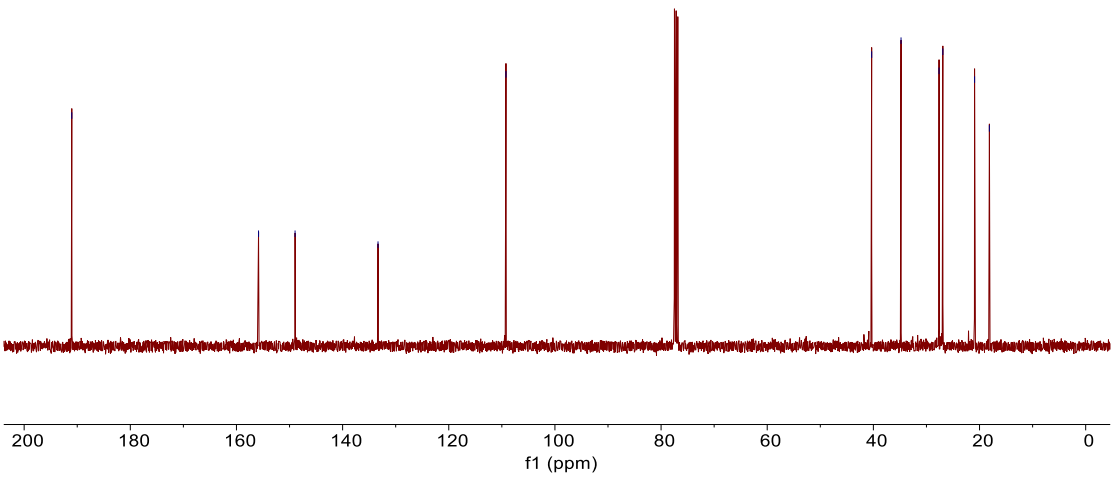


A6106-ZLM-4-42B

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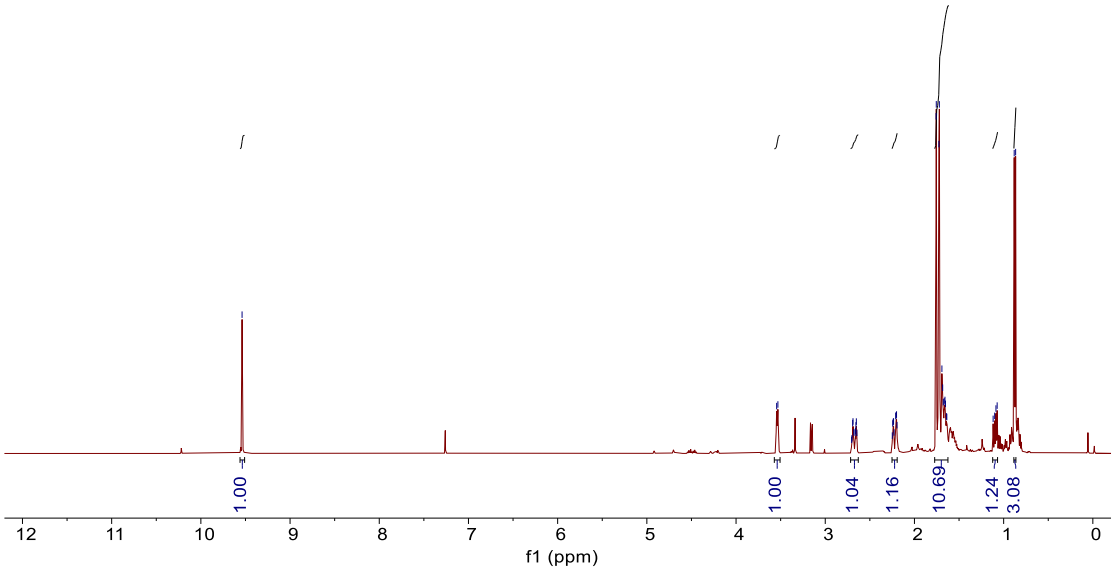


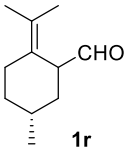


**1r**

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**


A6106-ZLM-4-42B

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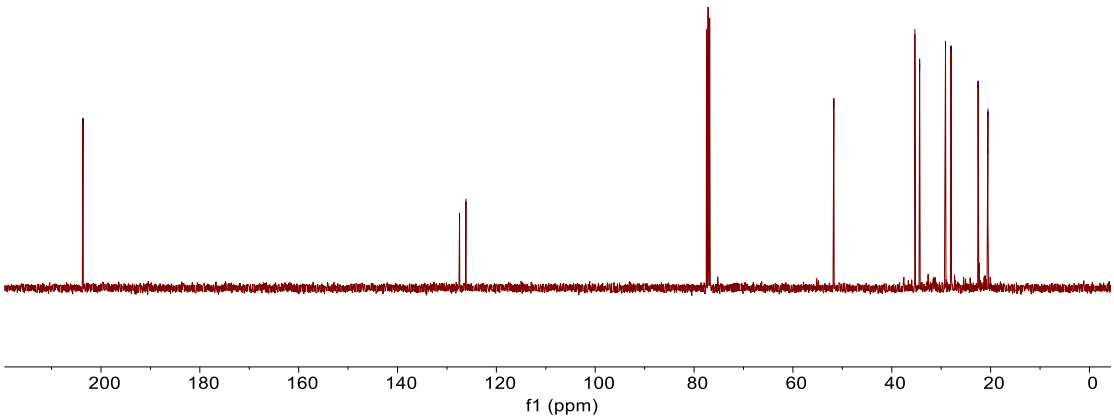

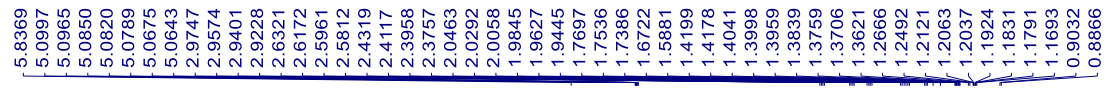


A1386-ZLM-2-36C

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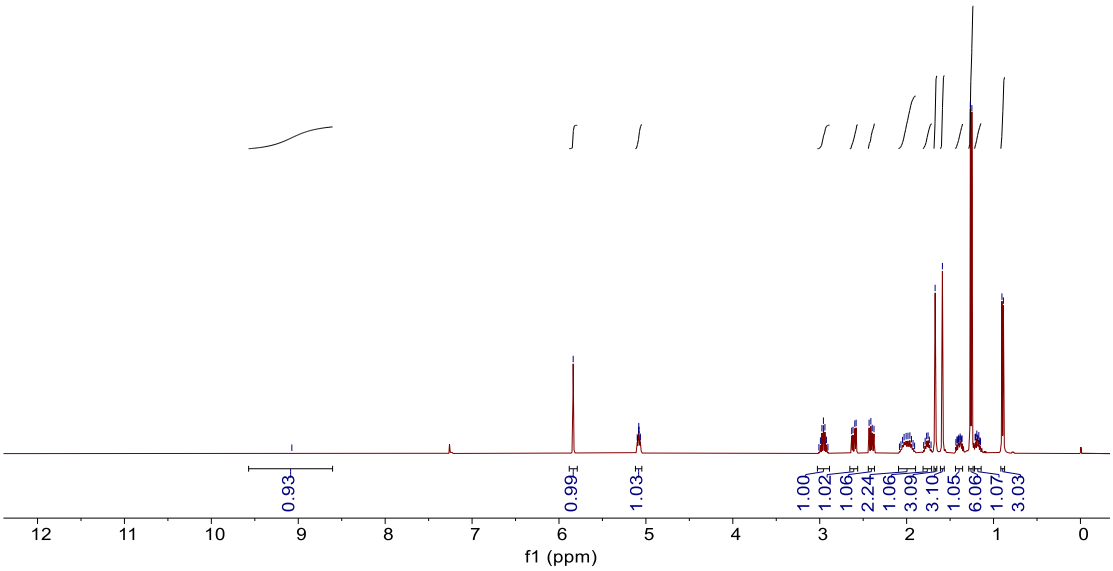
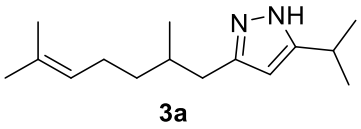


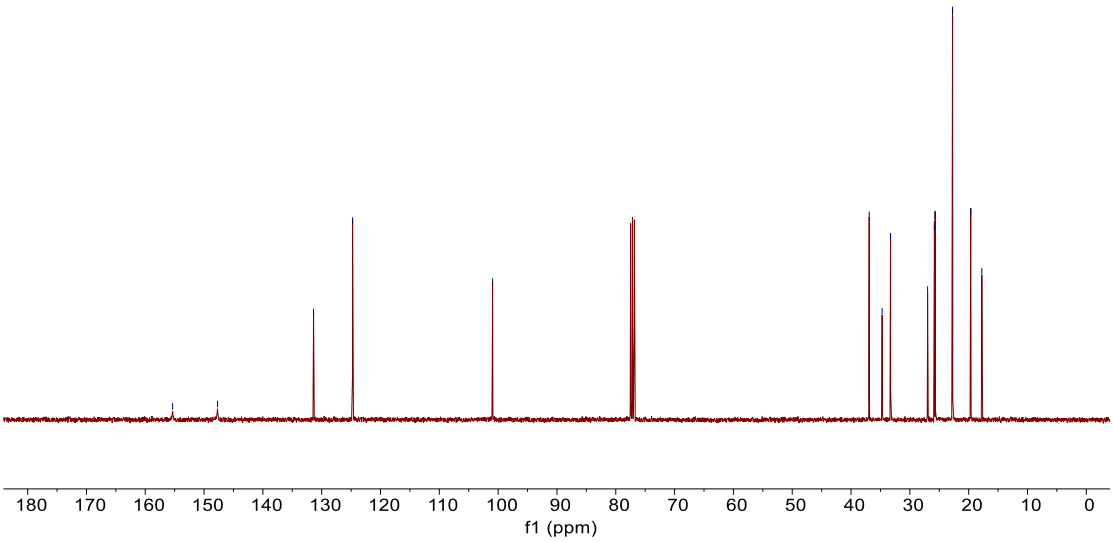

**3a**

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**


A1387-ZLM-2-36C

C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 45




A1722-ZLM-2-53C

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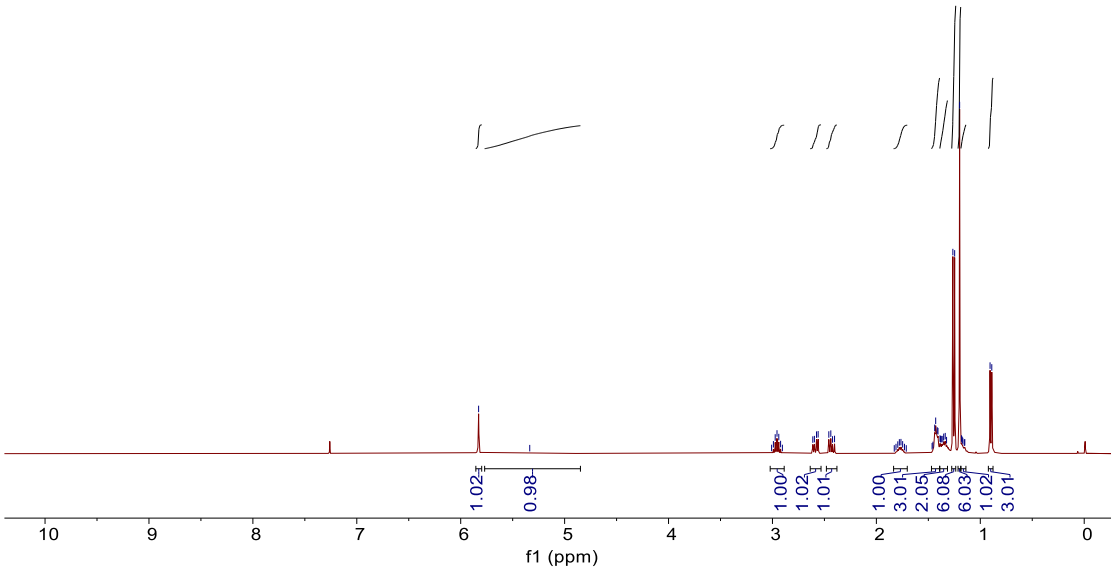
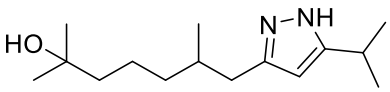


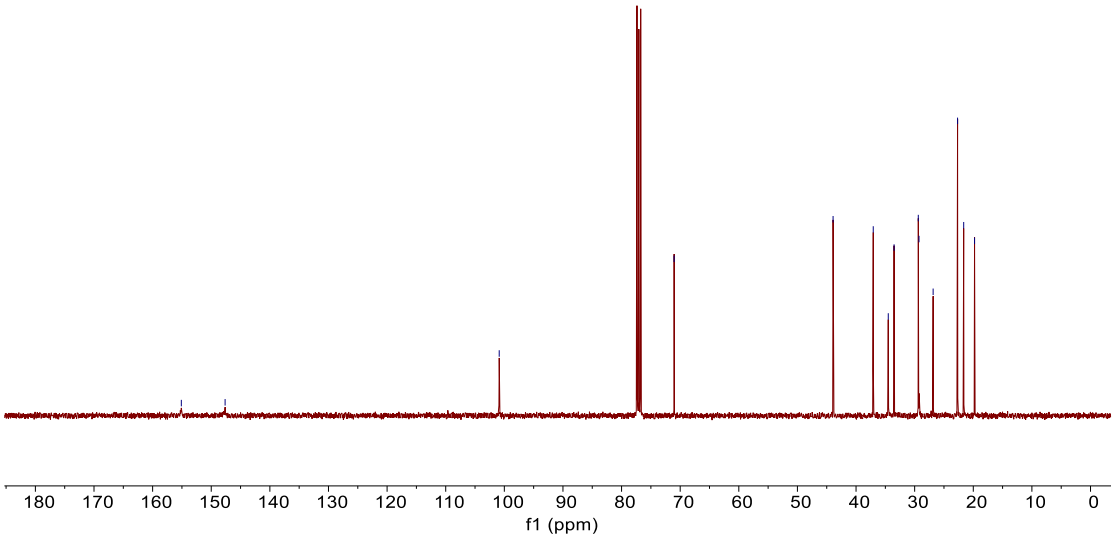

3b

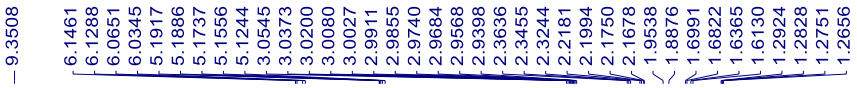
**$^{1}$H NMR (400 MHz, $CDCl_3$)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**


A1806-ZLM-2-53C

C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 34






A1386-ZLM-2-36B

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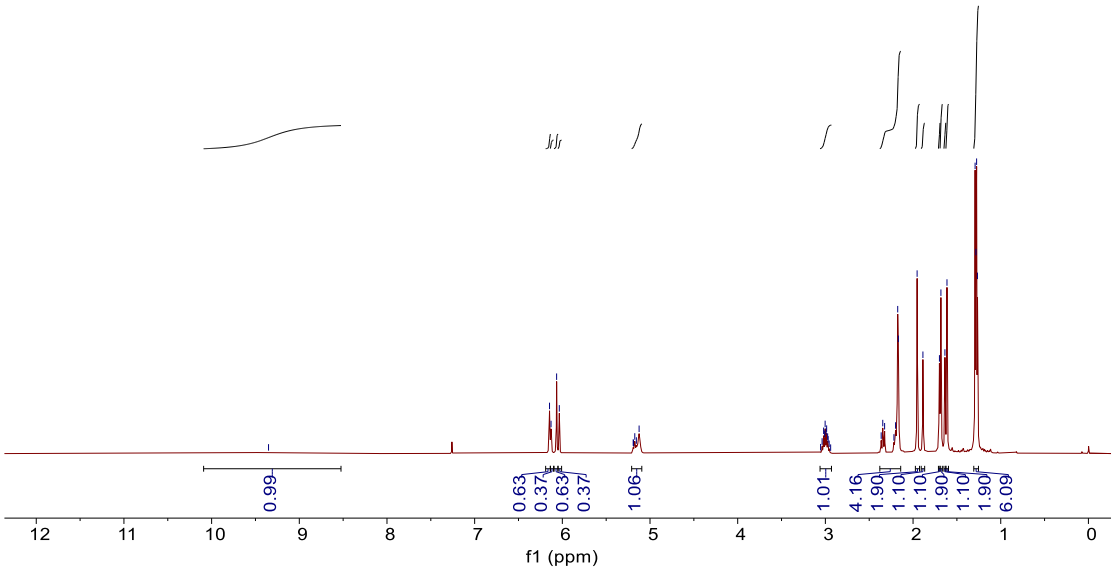
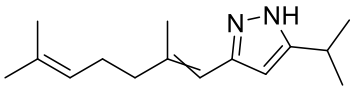


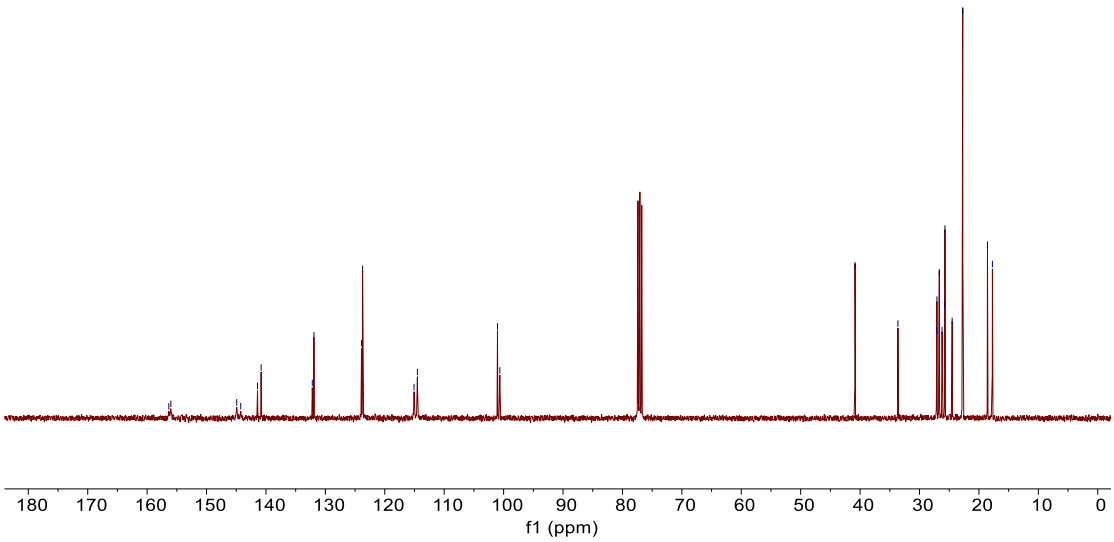

**3c**

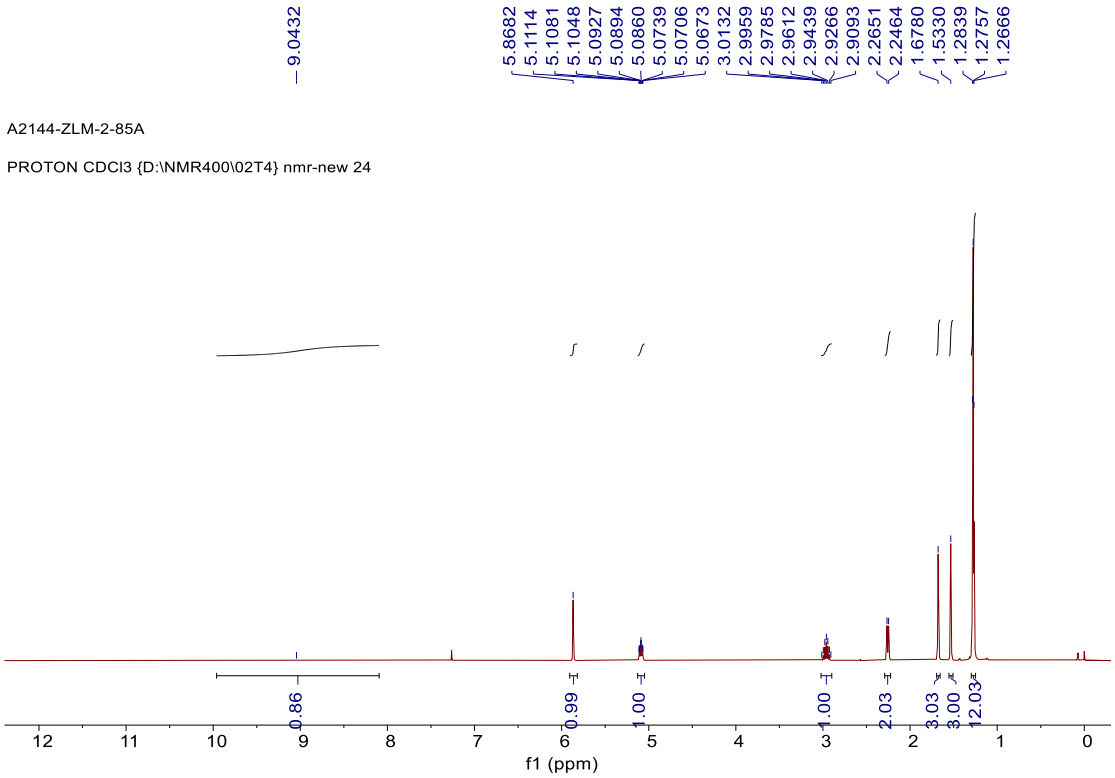
**$^{1}$H NMR (400 MHz, $CDCl_3$)**

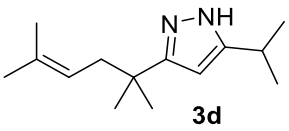
**$^{13}$C NMR (100 MHz, $CDCl_3$)**


A1481-ZLM-2-36B

C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 28



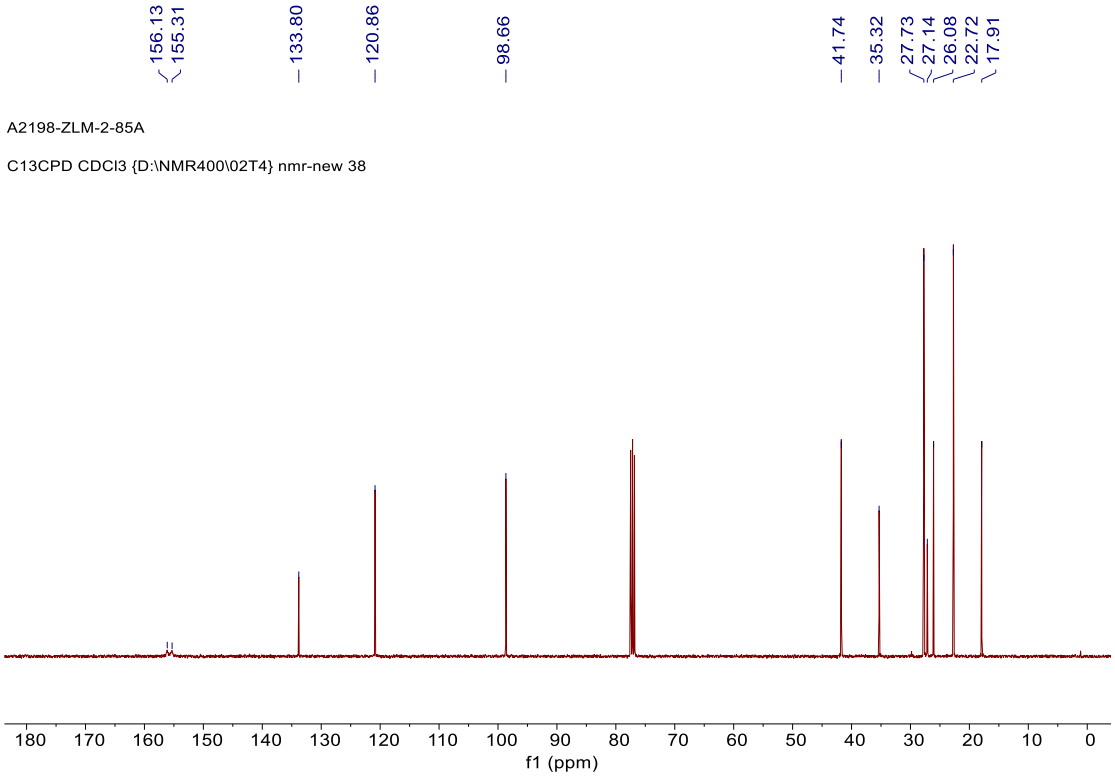



3d

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**




A5999-ZLM-4-37A

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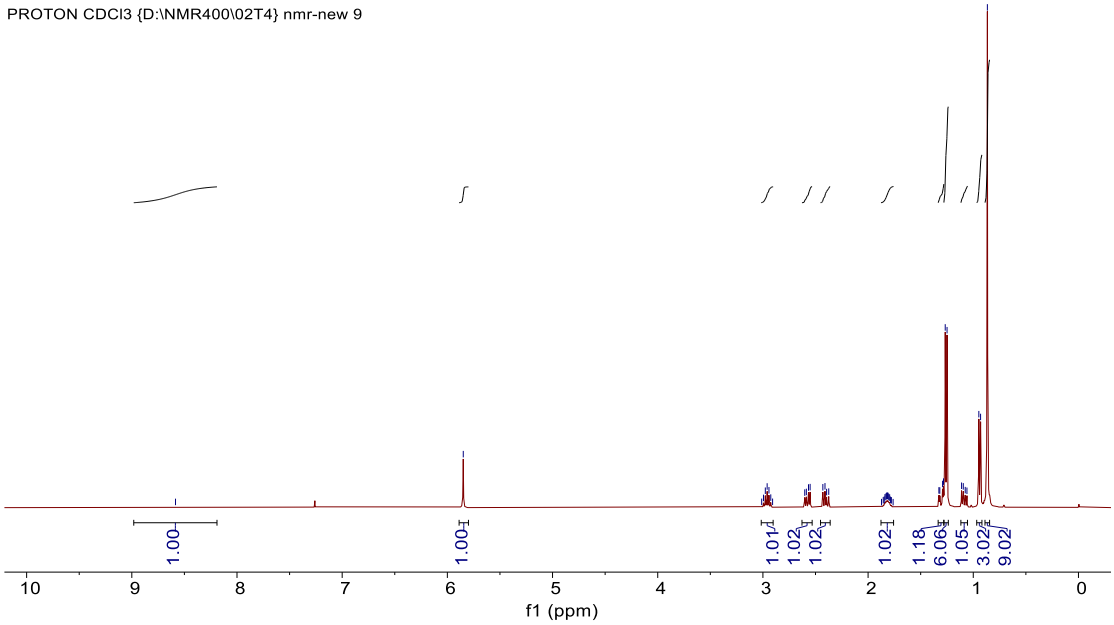
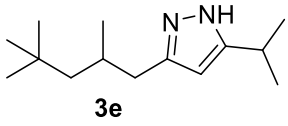


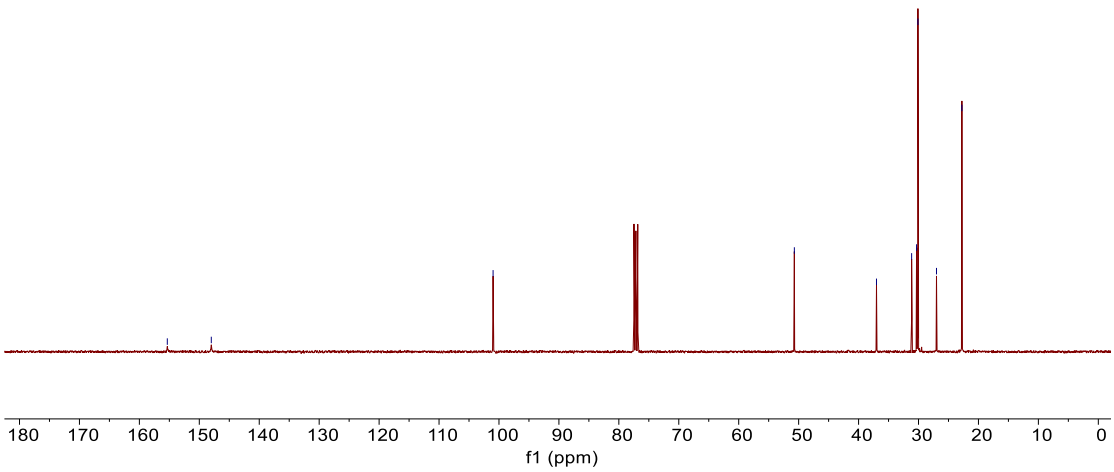

3e

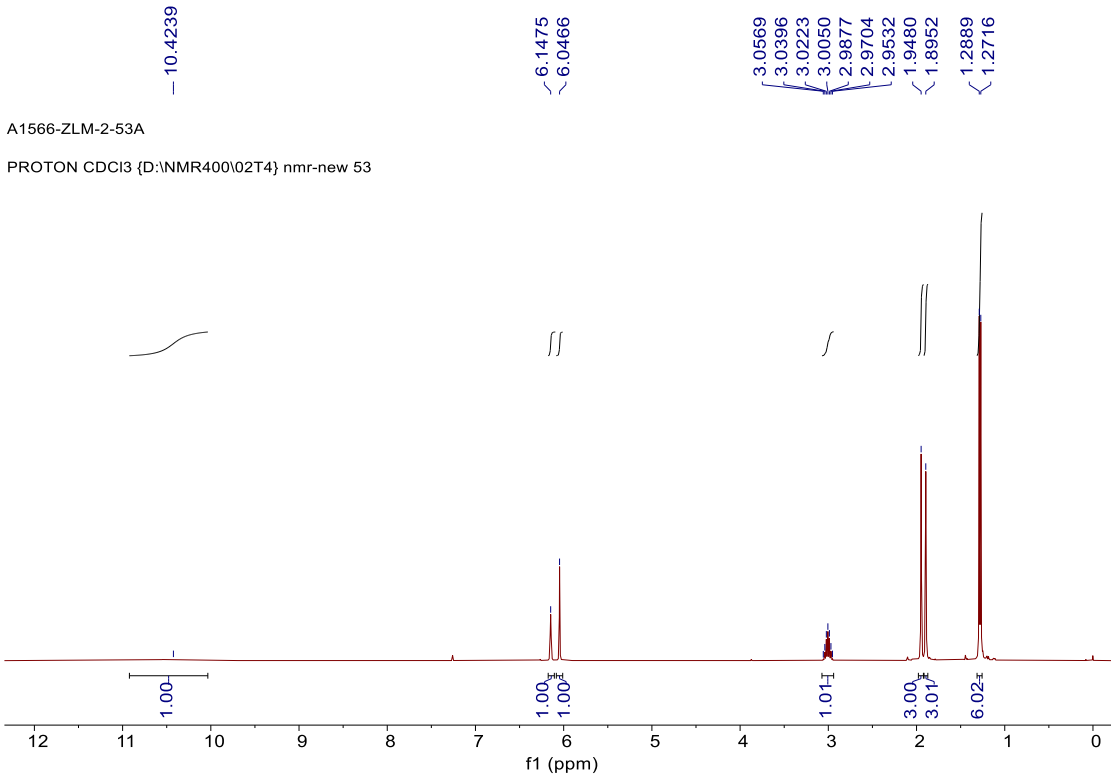
**$^{1}$H NMR (400 MHz, $CDCl_3$)**

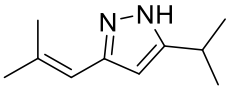
**$^{13}$C NMR (100 MHz, $CDCl_3$)**


A6106-ZLM-4-37A

C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 38



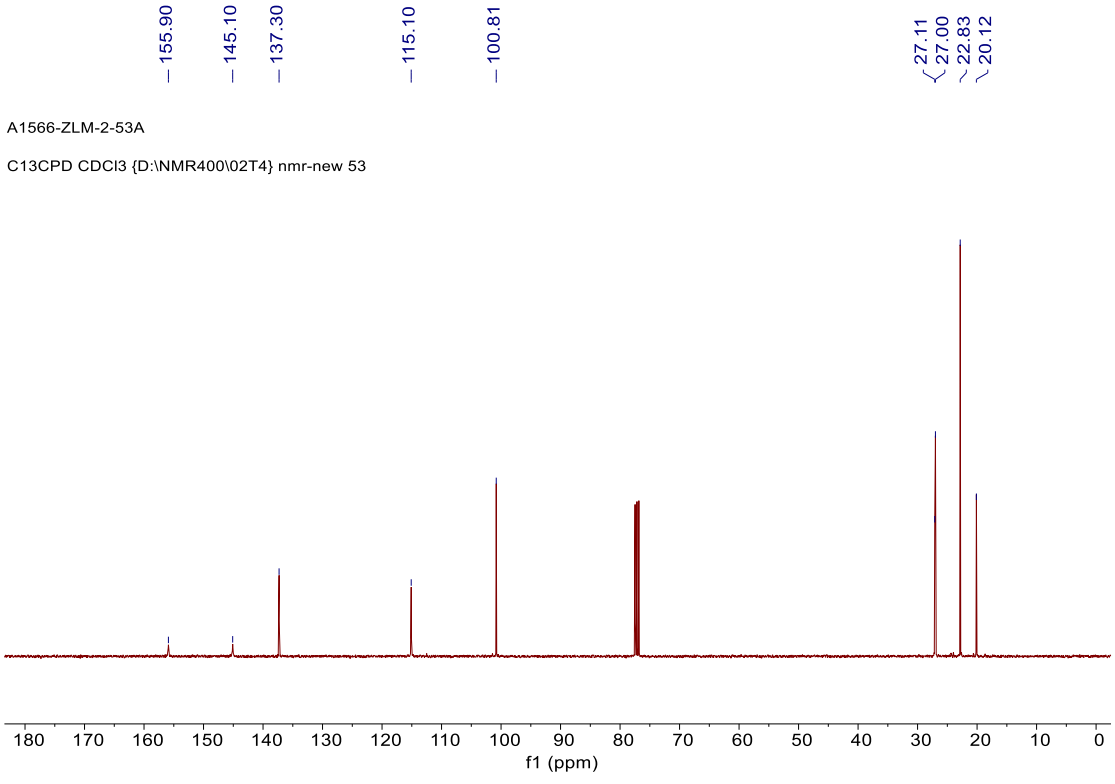


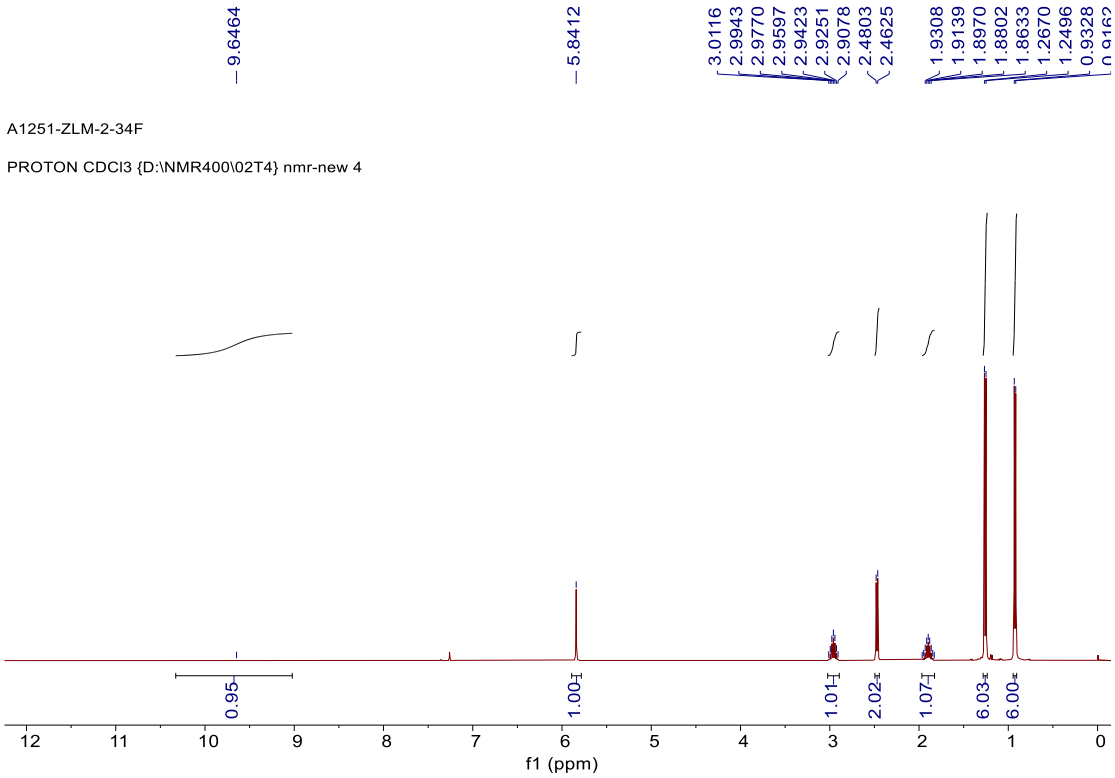



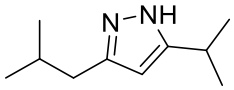

**3f**

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**



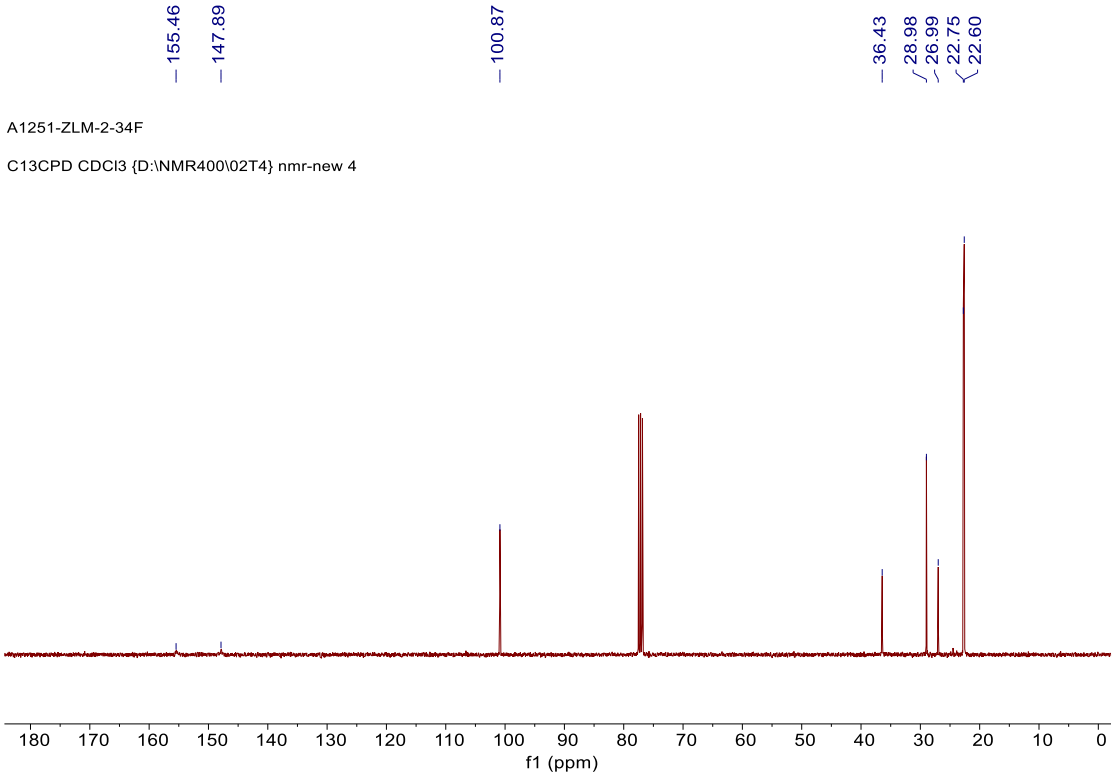



3g

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**




A1860-ZLM-2-70C

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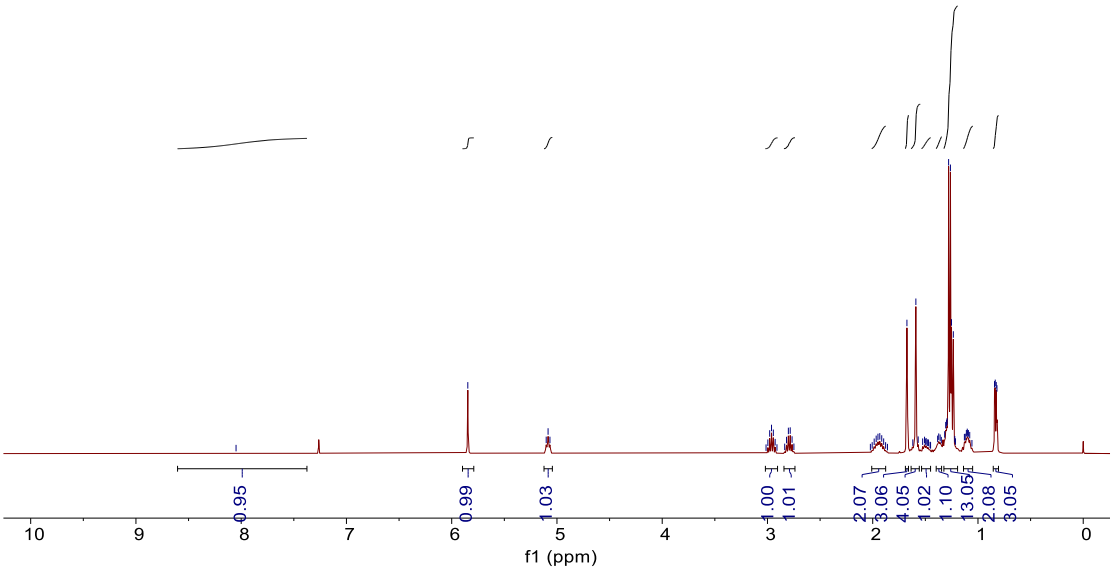


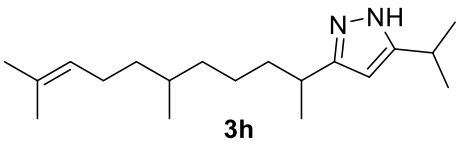


3h

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**


A1899-ZLM-2-70C

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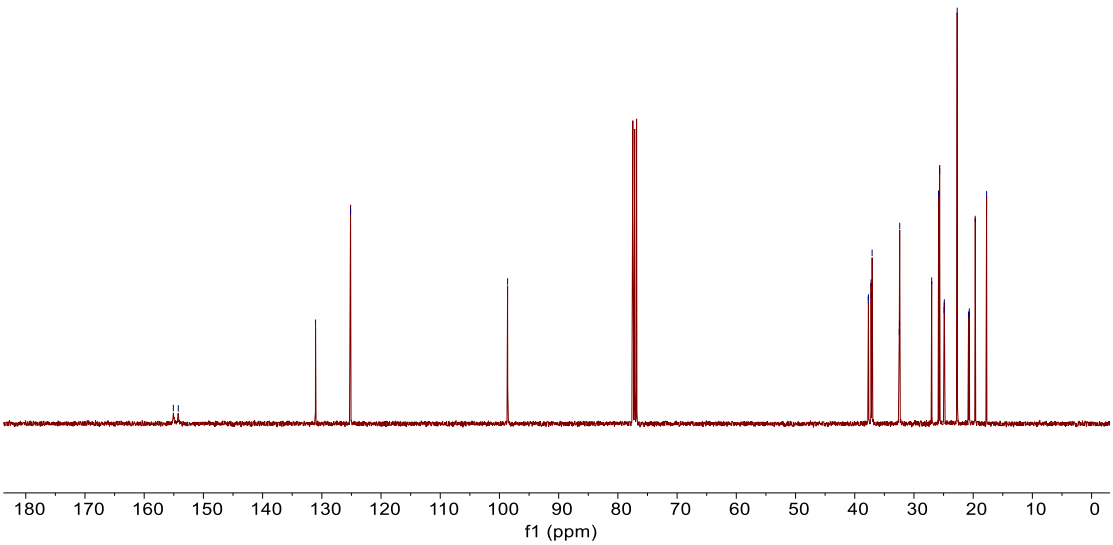
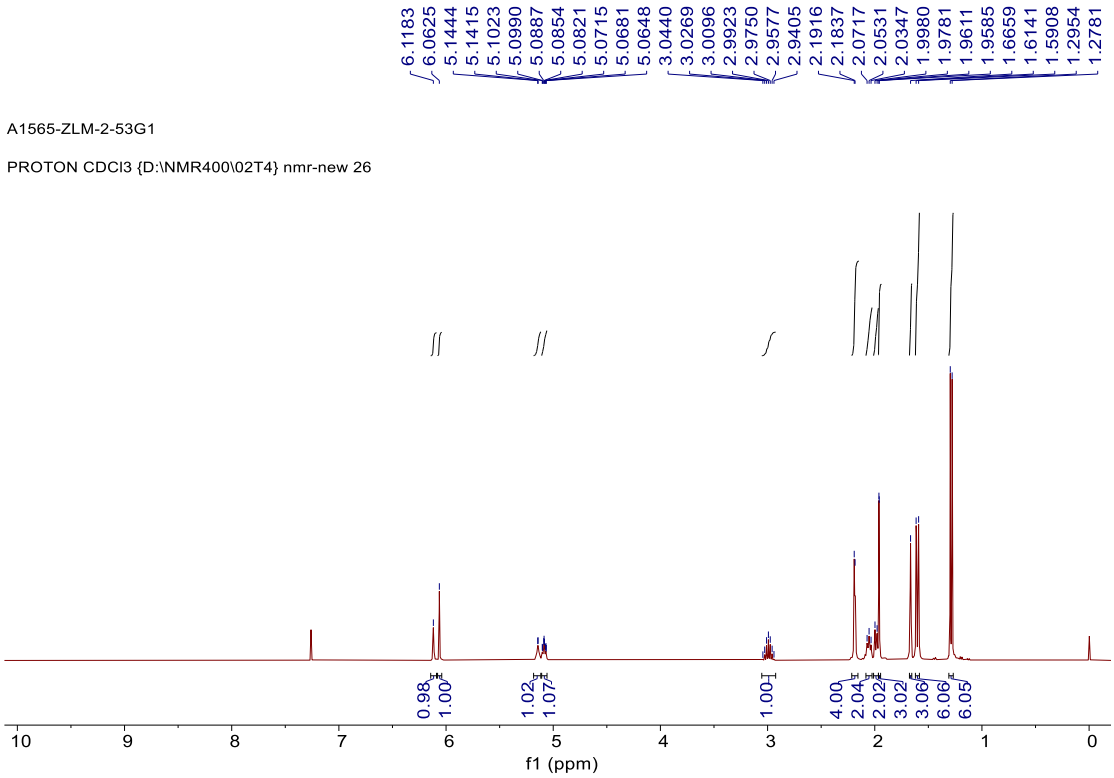
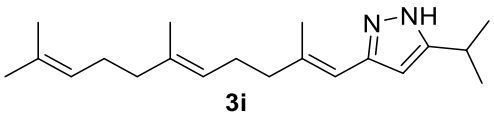


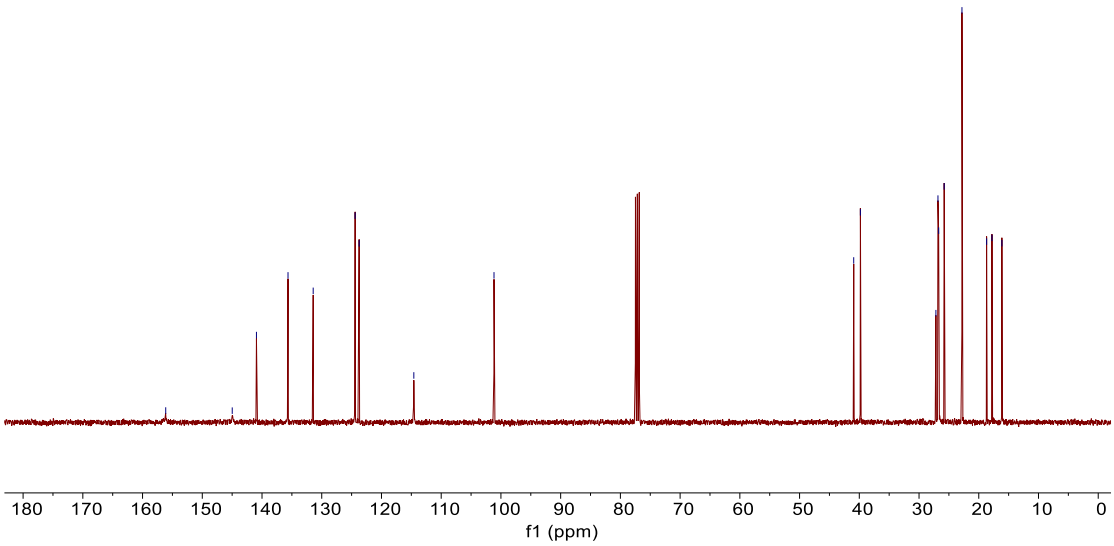



3i

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**


A2198-ZLM-2-85C

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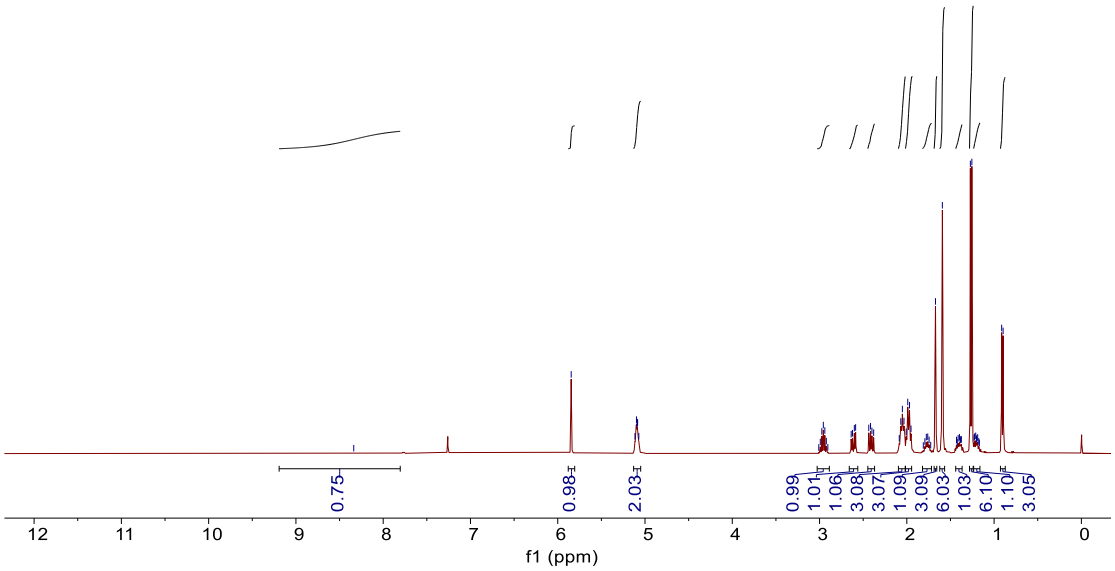


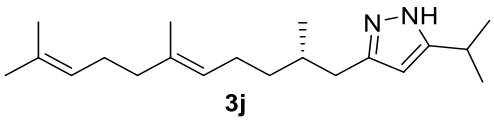


**3j**

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**

155.35
147.71
135.02
131.39
124.62
124.48
100.96
39.85
36.88
34.72
33.28
26.99
26.83
25.81
25.59
22.73
19.68
17.79
16.08

A2197-ZLM-2-85C

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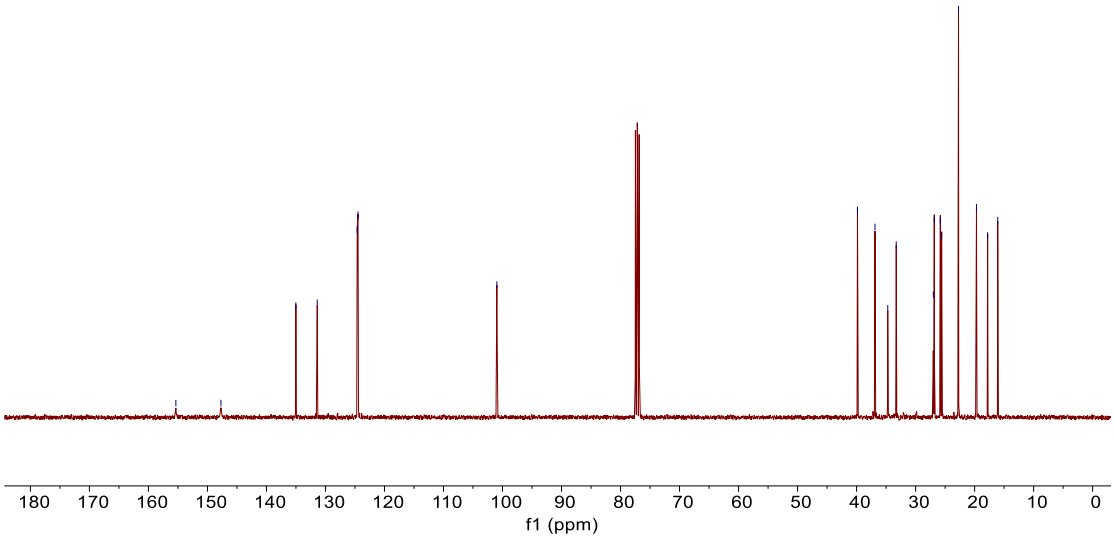
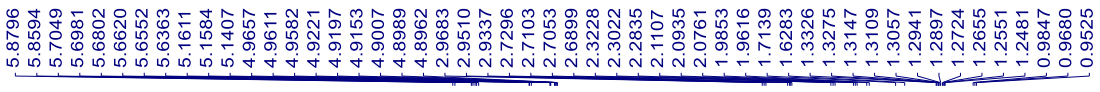
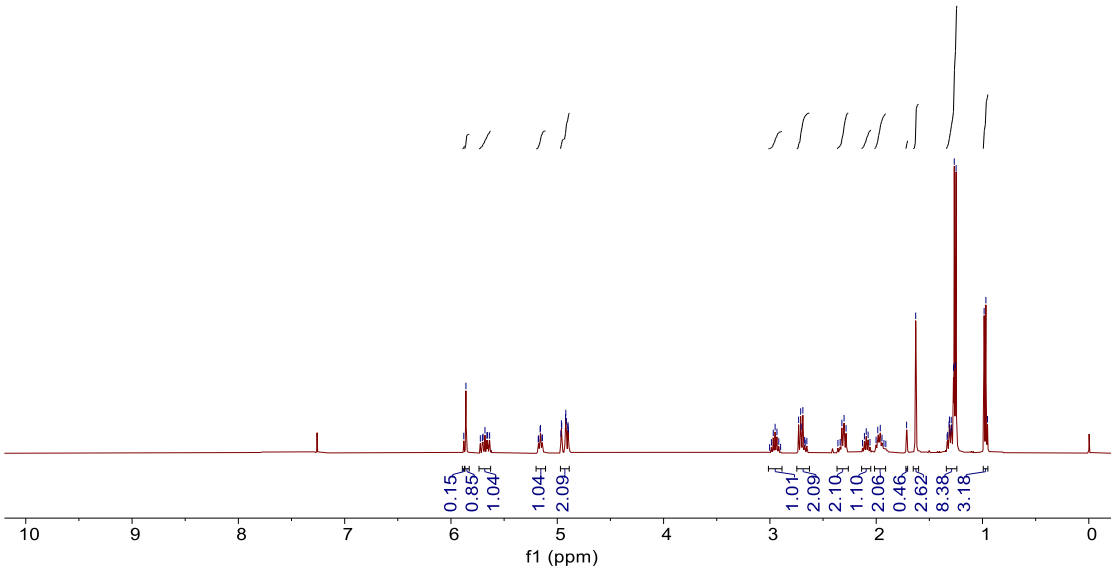
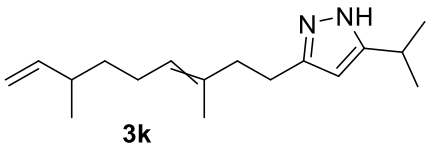





A2268-ZLM-2-75D

PROTON CDCl3 {D:\NMR400\02T4} nmr-new 39



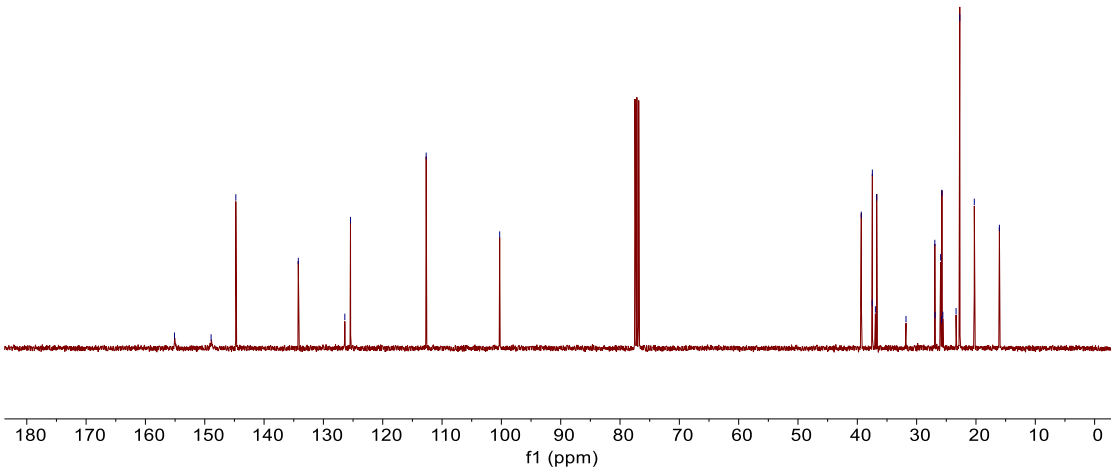

3k

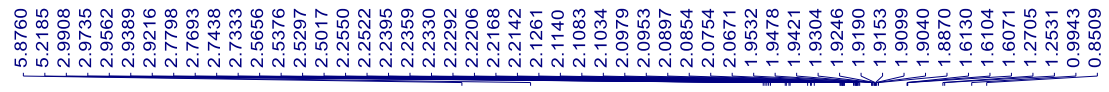
**$^{1}$H NMR (400 MHz, $CDCl_3$)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**


A2346-ZLM-2-75D

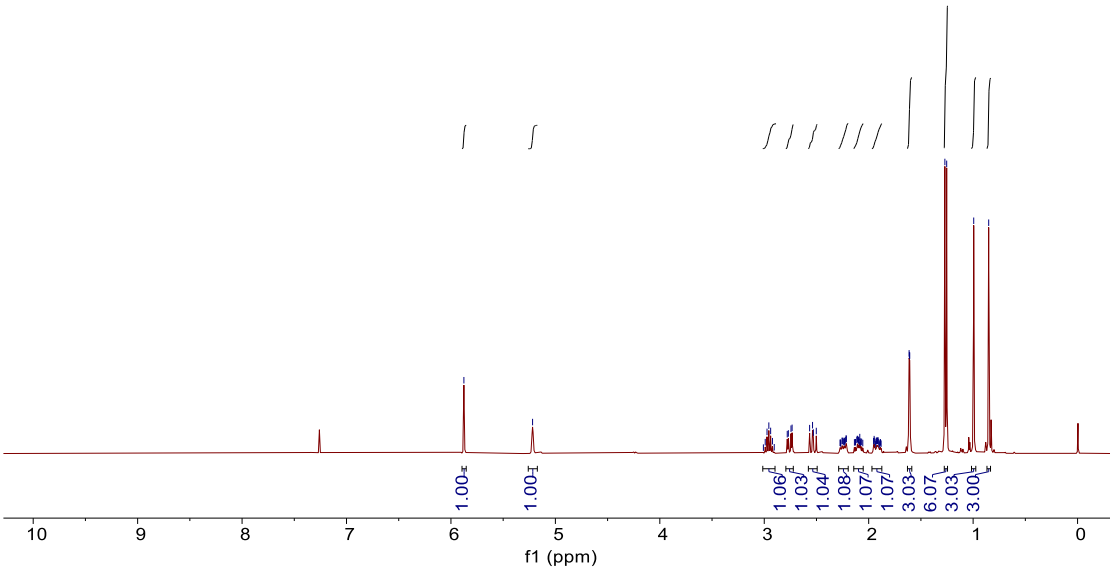
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 29

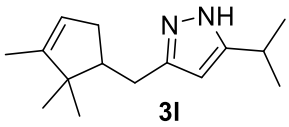





A1857-ZLM-2-70E

PROTON CDCl3 {D:\NMR400\02T4} nmr-new 7



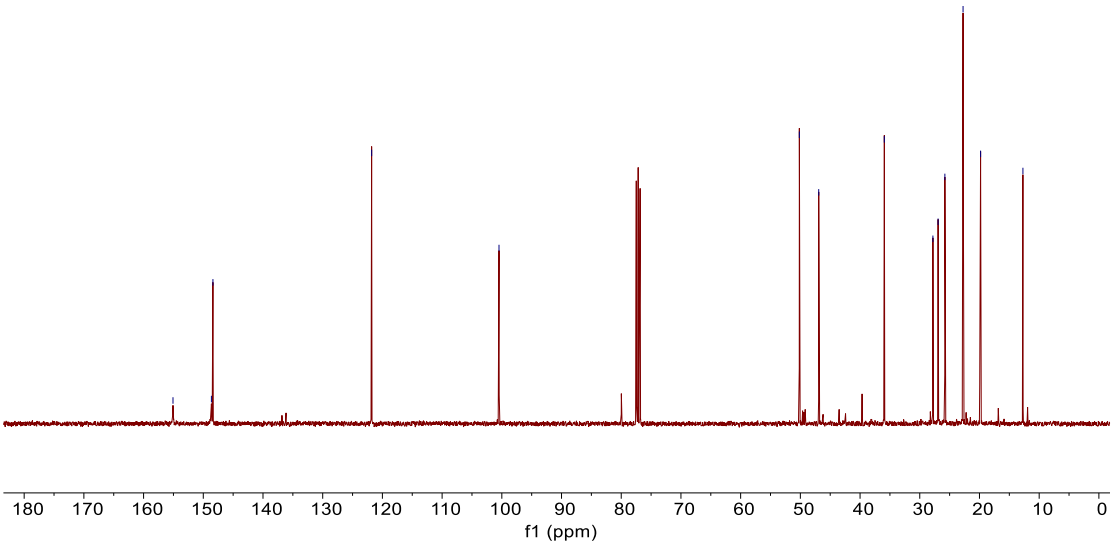

3l

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**

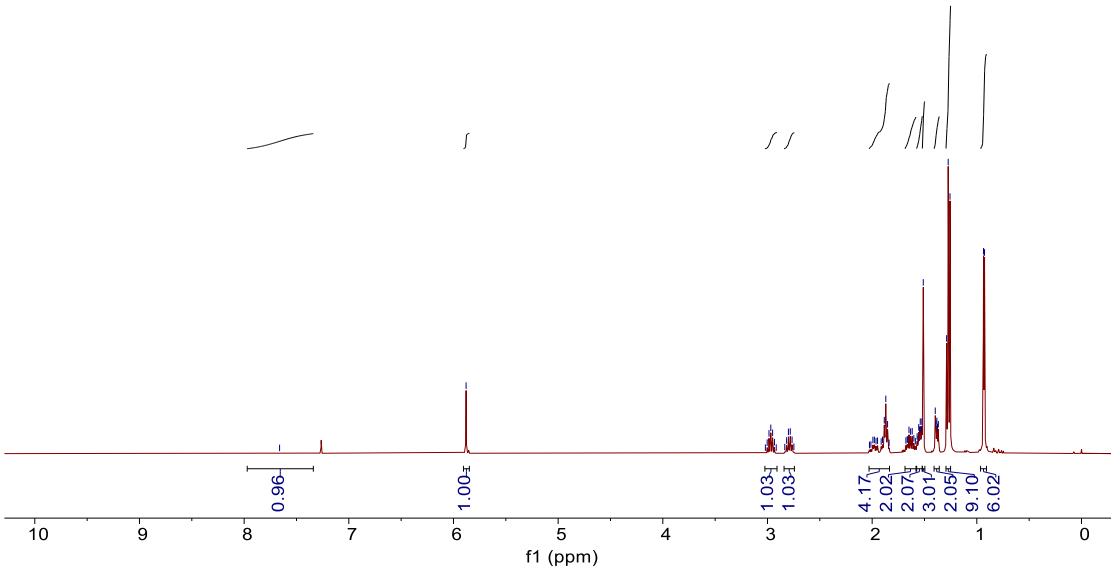

A1899-ZLM-2-70E

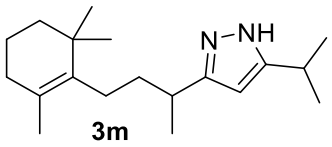
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 1




A5820-ZLM-4-37C

PROTON CDCl3 {D:\NMR400\02T4} nmr-new 22



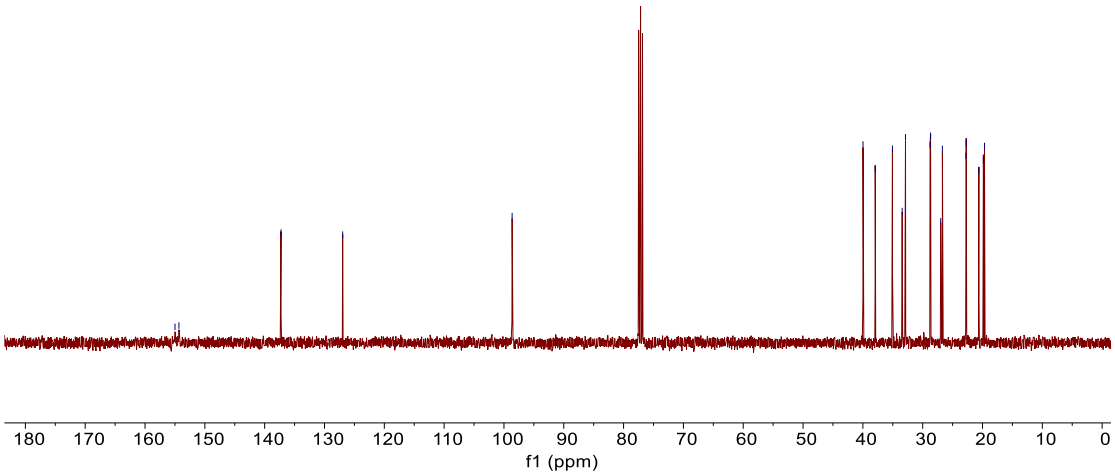

3m

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**

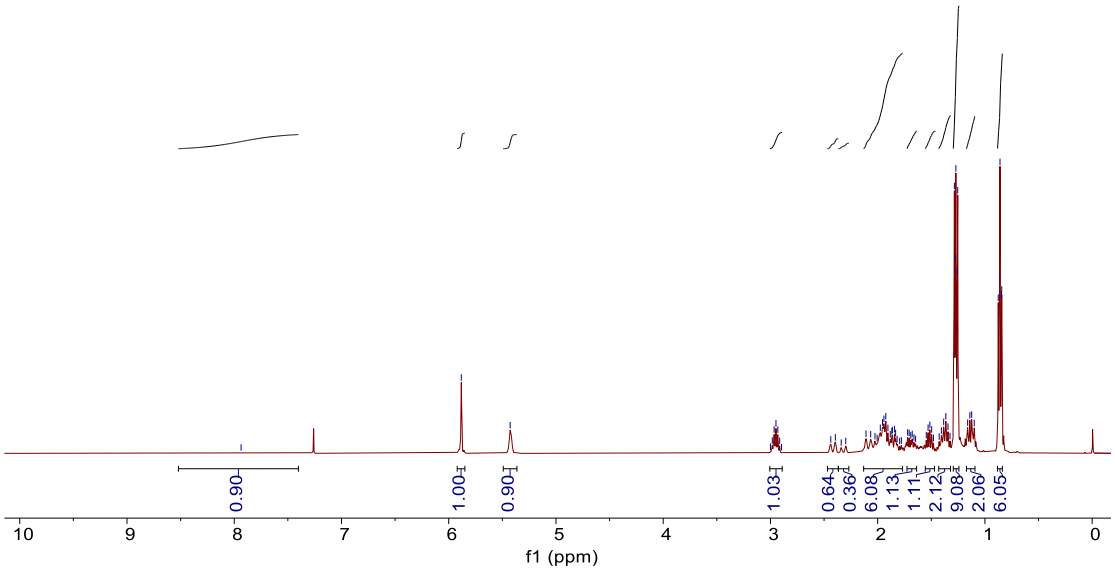

A5820-ZLM-4-37C

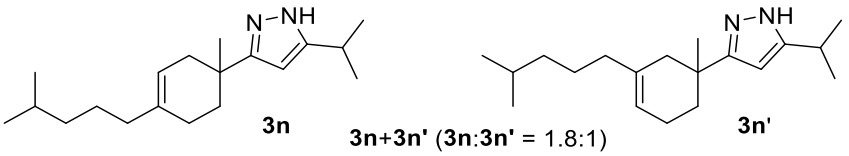
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 22




A1860-ZLM-2-70B

PROTON CDCl3 {D:\NMR400\02T4} nmr-new 41



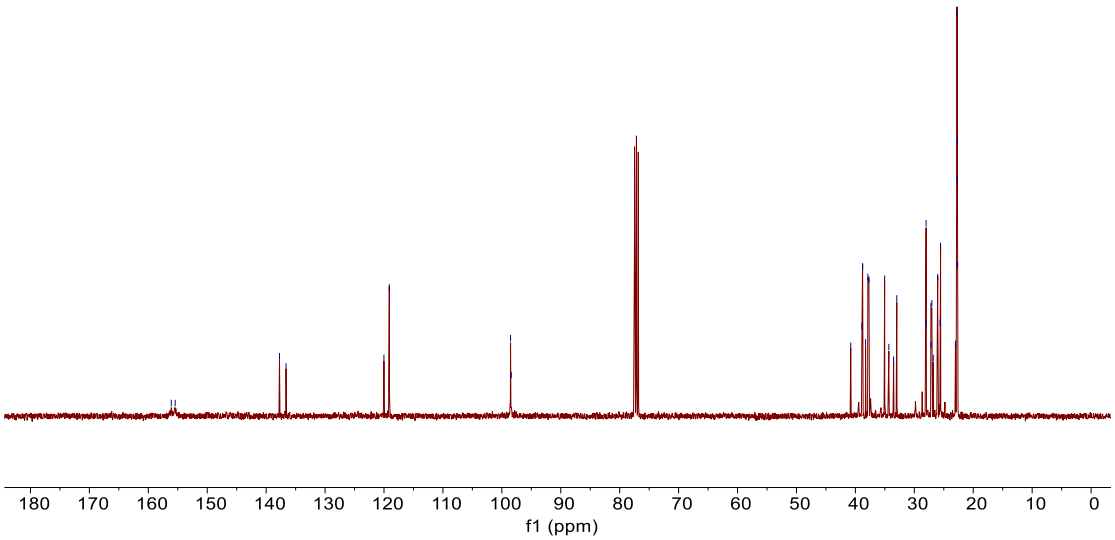

**3n** **3n+3n'** (**3n**:**3n'** = 1.8:1) **3n'**

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**

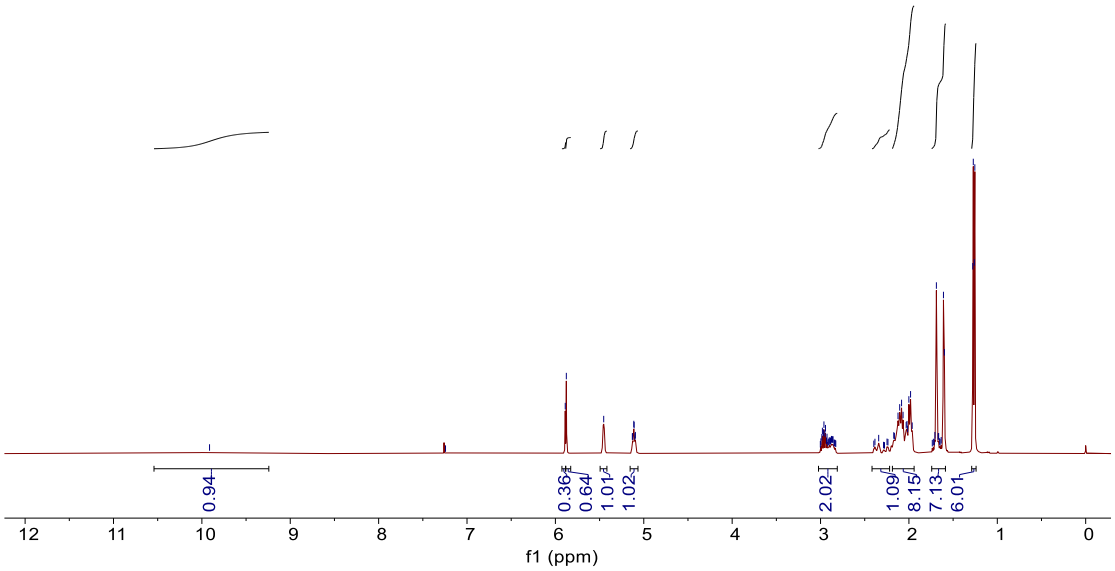

A1899-ZLM-2-70B

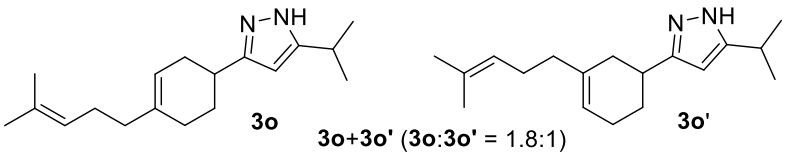
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 3




A1504-ZLM-2-44C

PROTON CDCl3 {D:\NMR400\02T4} nmr-new 29




**3o** **3o'**

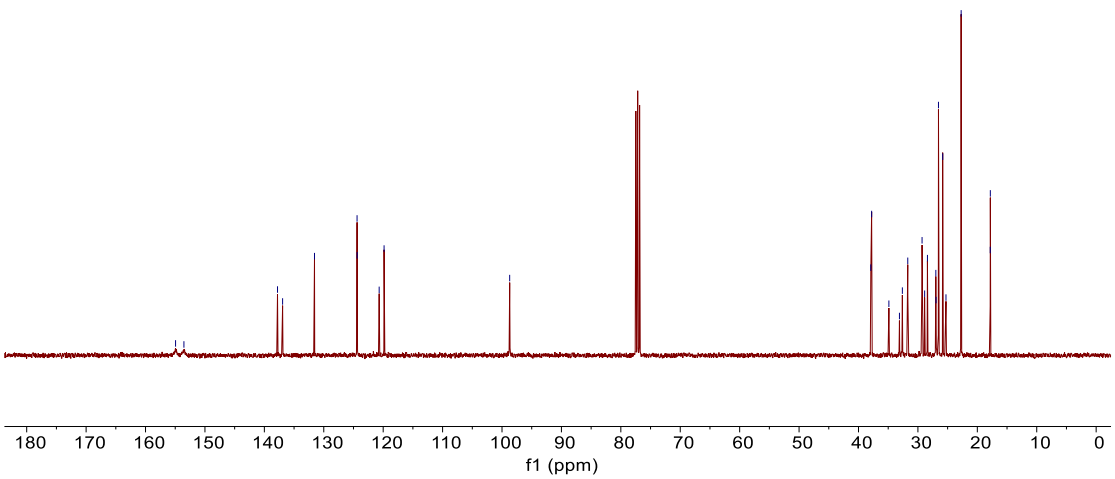
**3o+3o' (3o:3o' = 1.8:1)**

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**

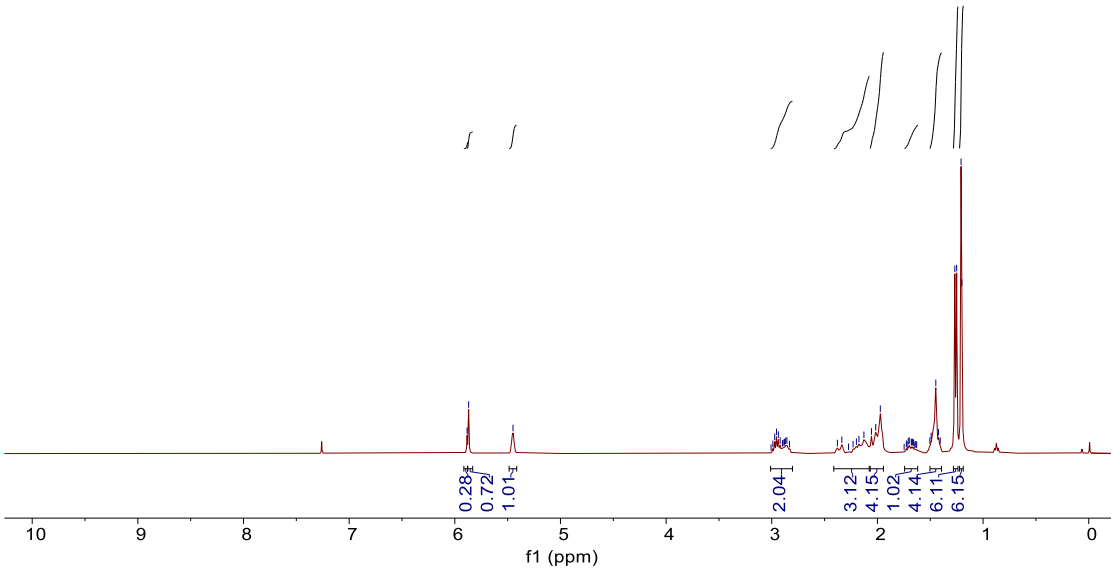

A1504-ZLM-2-44C

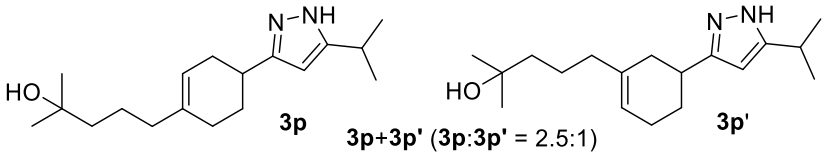
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 29




A1722-ZLM-2-53E

PROTON CDCl3 {D:\NMR400\02T4} nmr-new 56




**3p** **3p'**

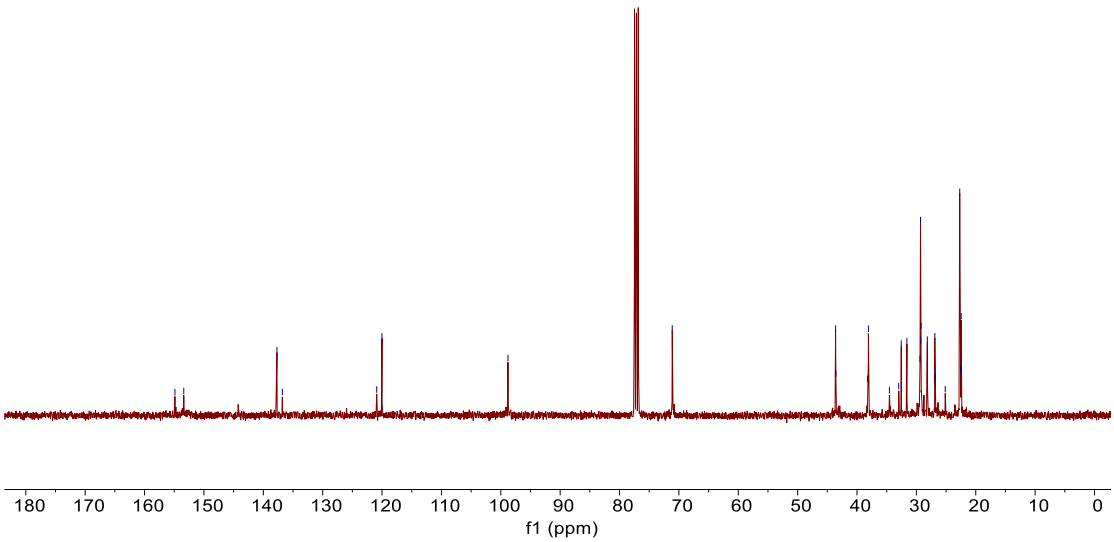
**3p+3p'** (**3p**:**3p'** = 2.5:1)

**$^{1}$H NMR (400 MHz, CDCl$_3$)**

**$^{13}$C NMR (100 MHz, CDCl$_3$)**

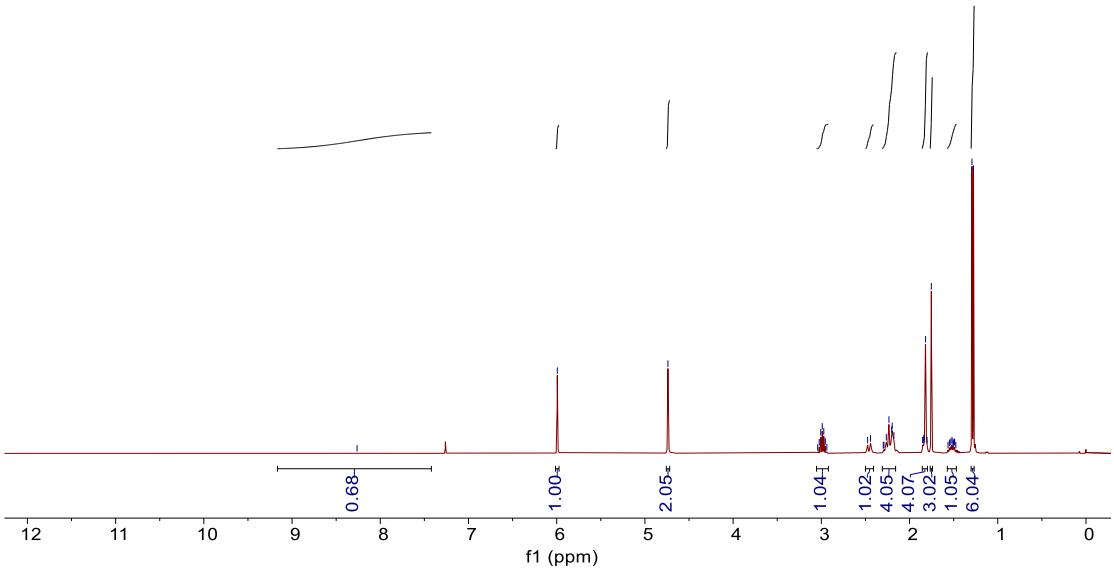

A9424-ZLM-2-53E

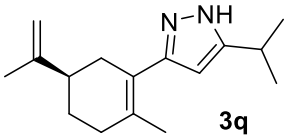
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 11




A5820-ZLM-4-37B

PROTON CDCl3 {D:\NMR400\02T4} nmr-new 21



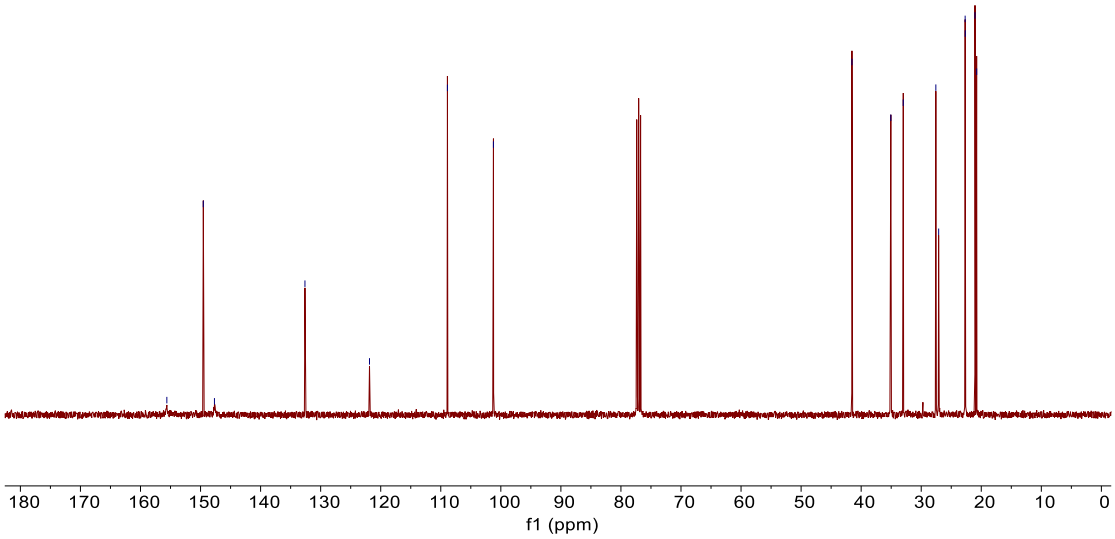

3q

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**

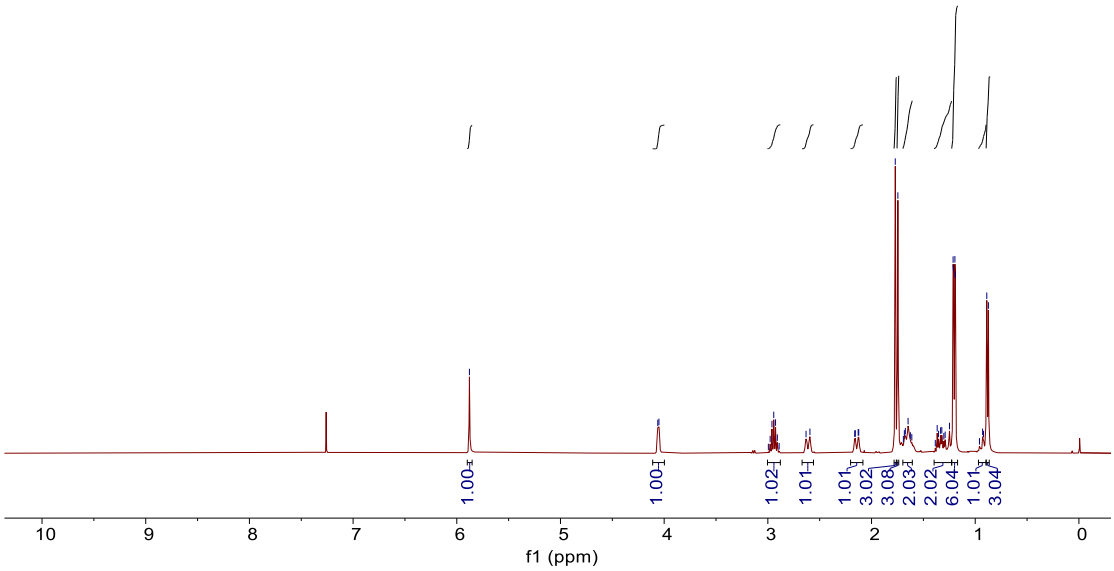

A5920-ZLM-4-37B

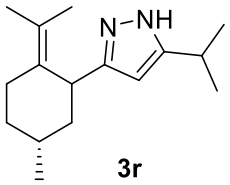
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 27




A6126-ZLM-4-37E

PROTON CDCl3 {D:\NMR400\02T4} nmr-new 2



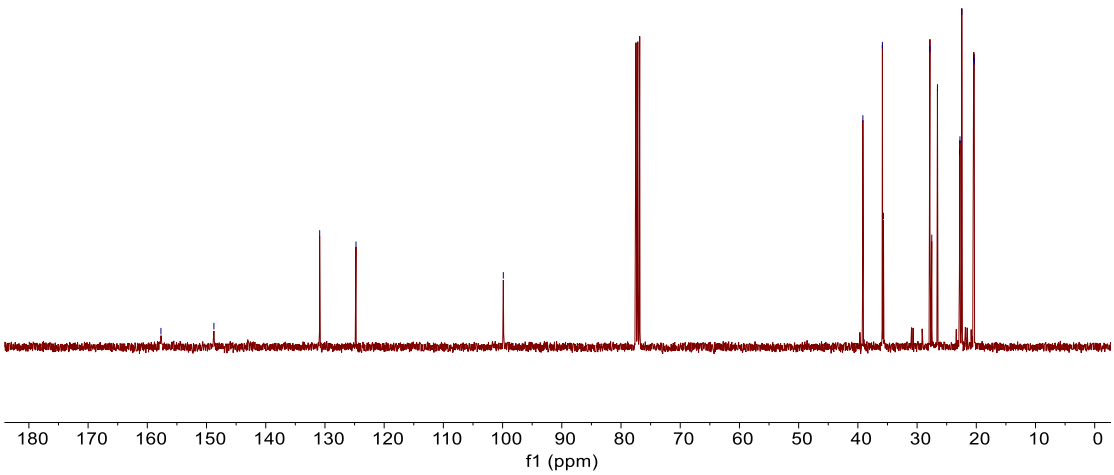

3r

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**

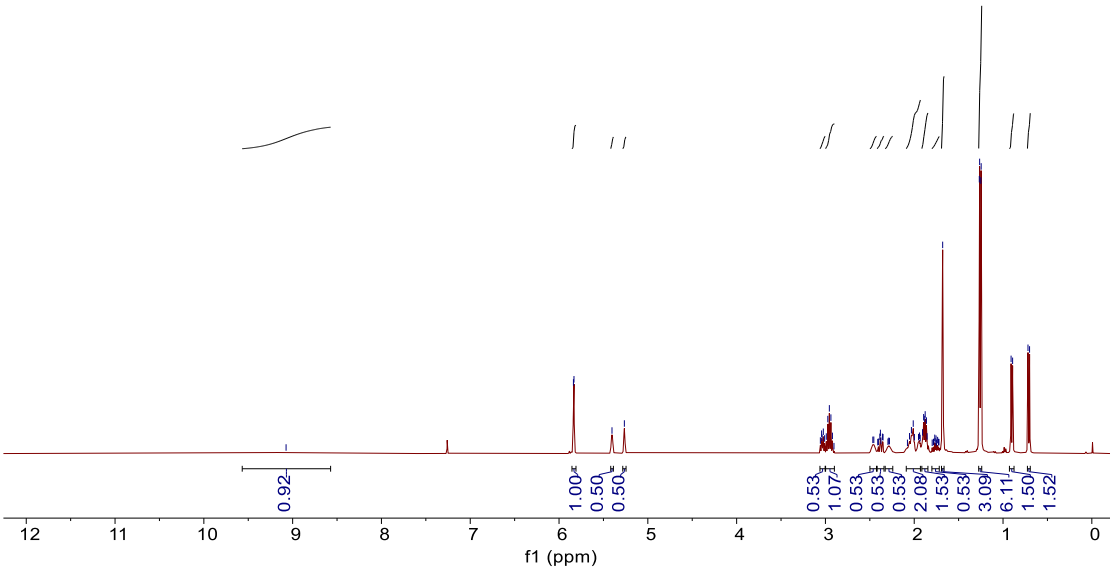

A6106-ZLM-4-37E

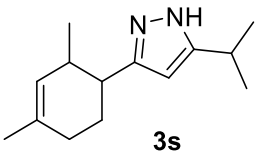
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 39




A1386-ZLM-2-36E

PROTON CDCl3 {D:\NMR400\02T4} nmr-new 13



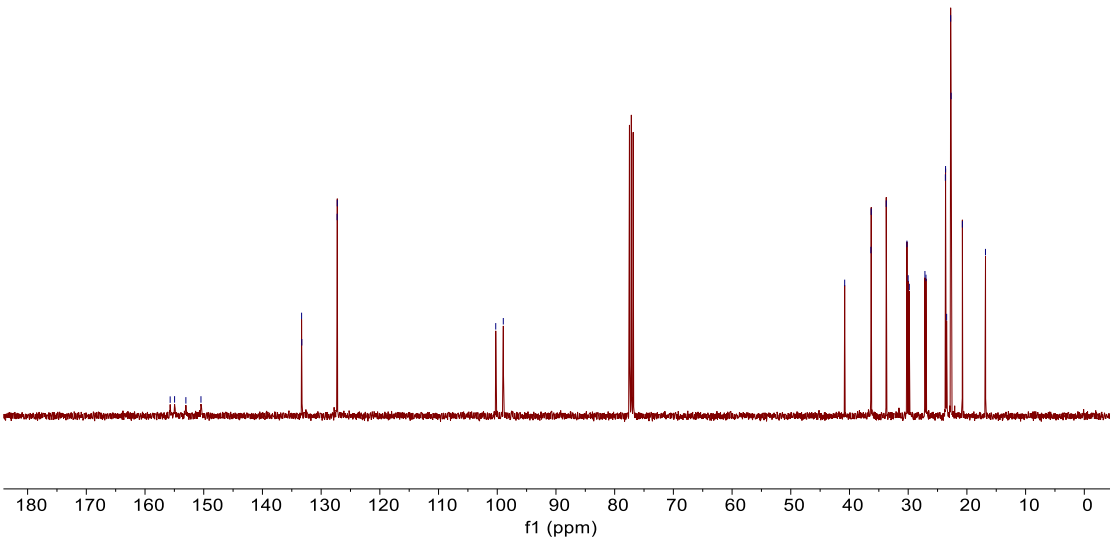

3s

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**

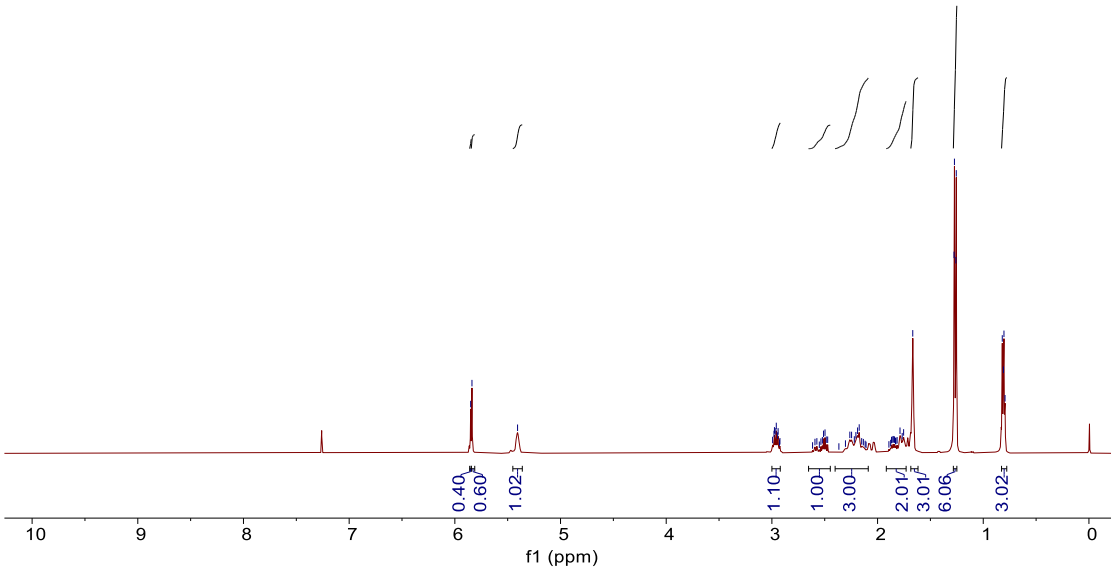

A1481-ZLM-2-36E

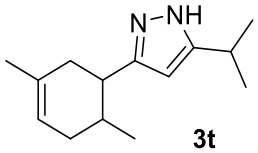
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 29




A1857-ZLM-2-70A

PROTON CDCl3 {D:\NMR400\02T4} nmr-new 6



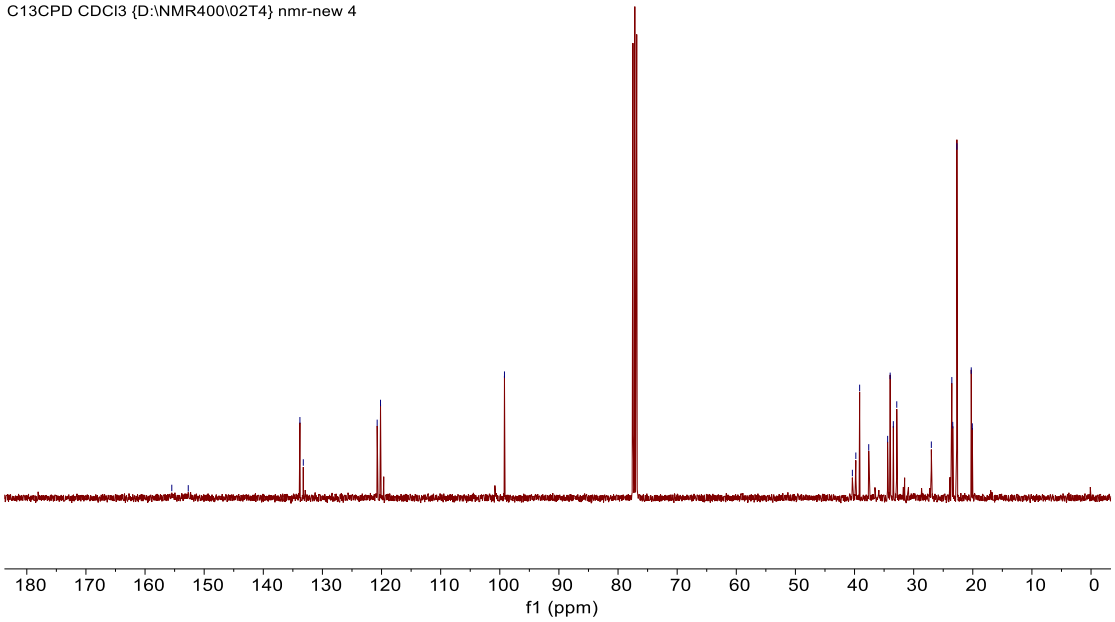

3t

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

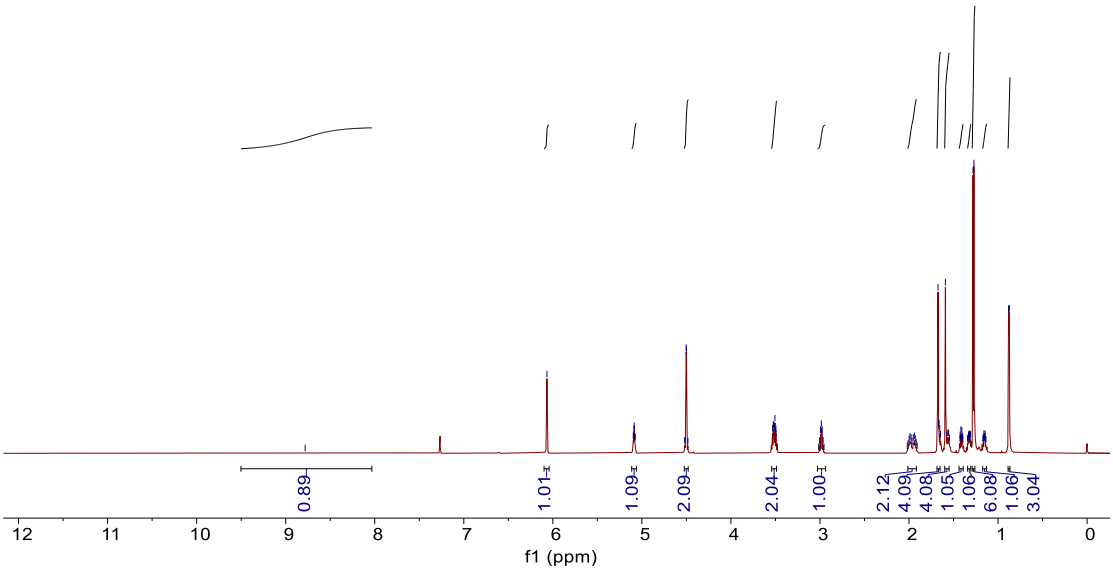
**$^{13}$C NMR (100 MHz, $CDCl_3$)**

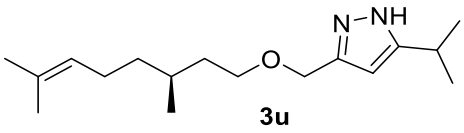

A1899-ZLM-2-70A

C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 4




5670-ZLM-2-57B



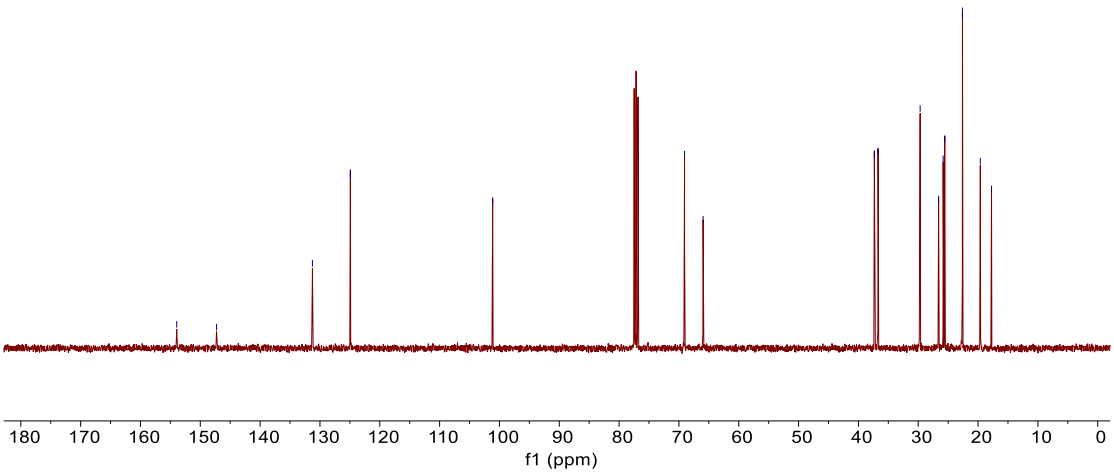

3u

**$^{1}$H NMR (700 MHz, $CDCl_3$)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**

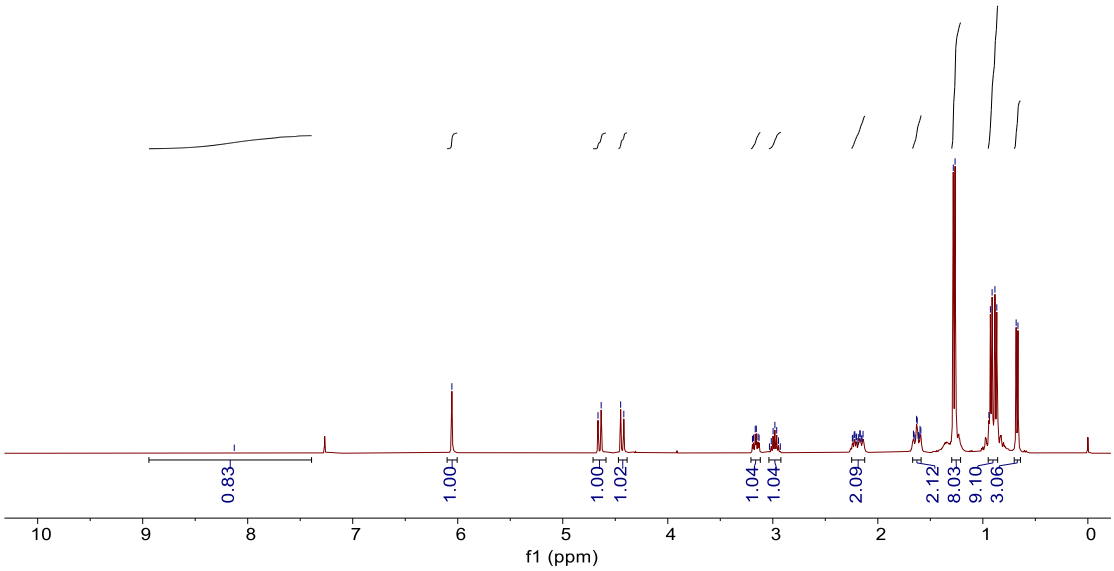

A1566-ZLM-2-57B

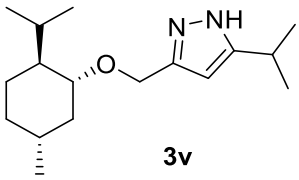
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 57




A2083-ZLM-2-75A

PROTON CDCl3 {D:\NMR400\02T4} nmr-new 19



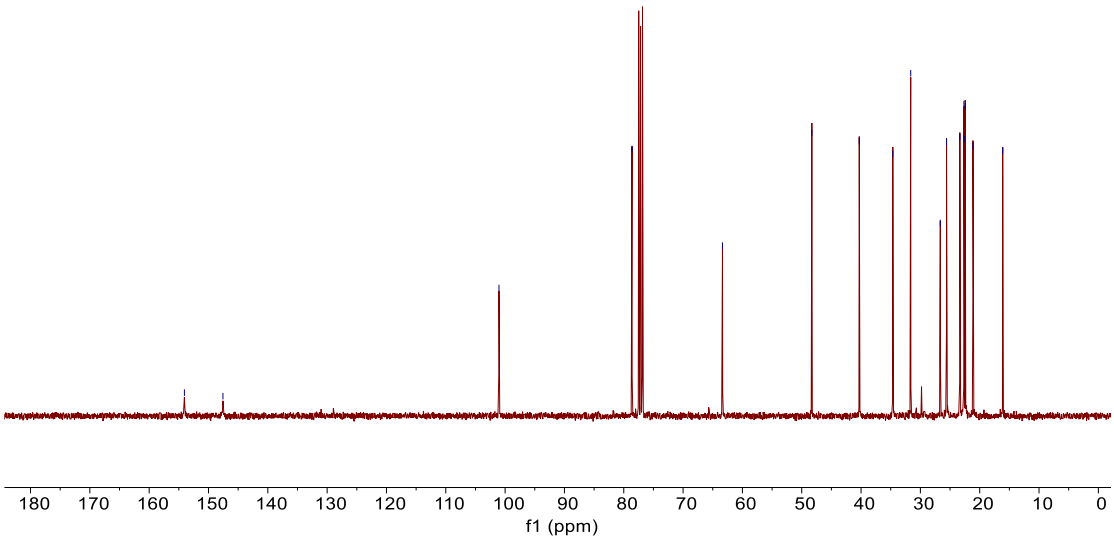

3v

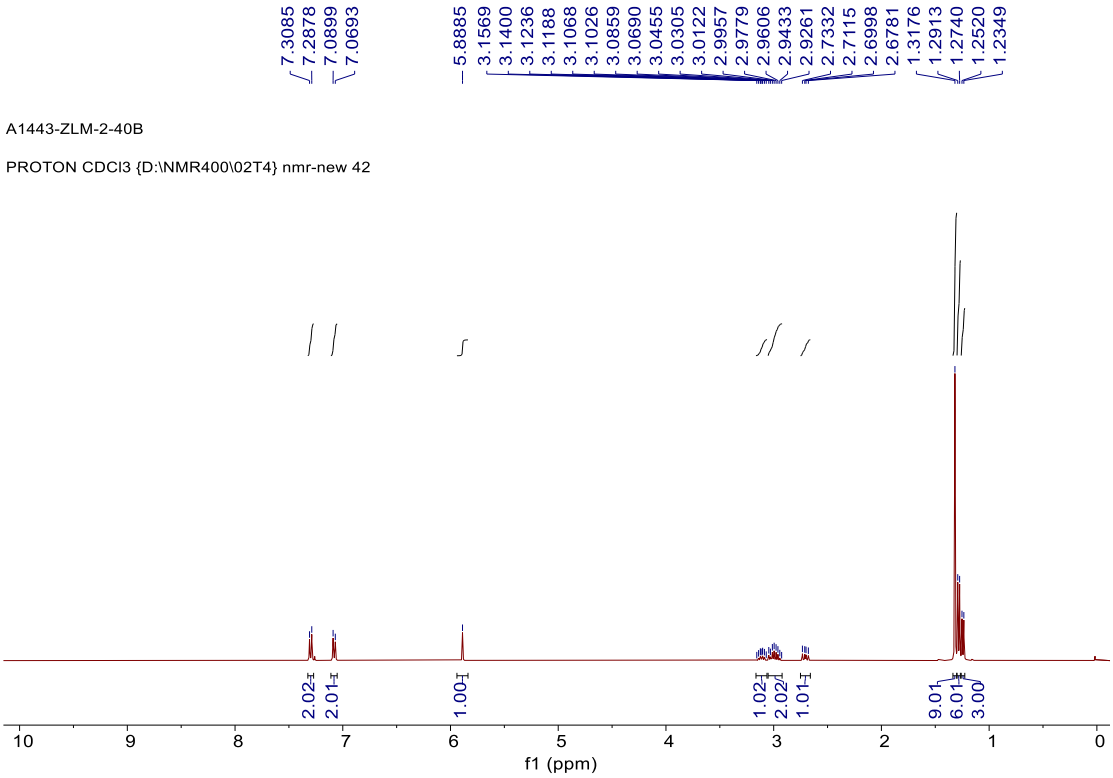
**$^{1}$H NMR (400 MHz, $CDCl_3$)**

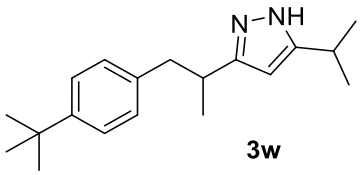
**$^{13}$C NMR (100 MHz, $CDCl_3$)**


A2100-ZLM-2-75A

C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 57



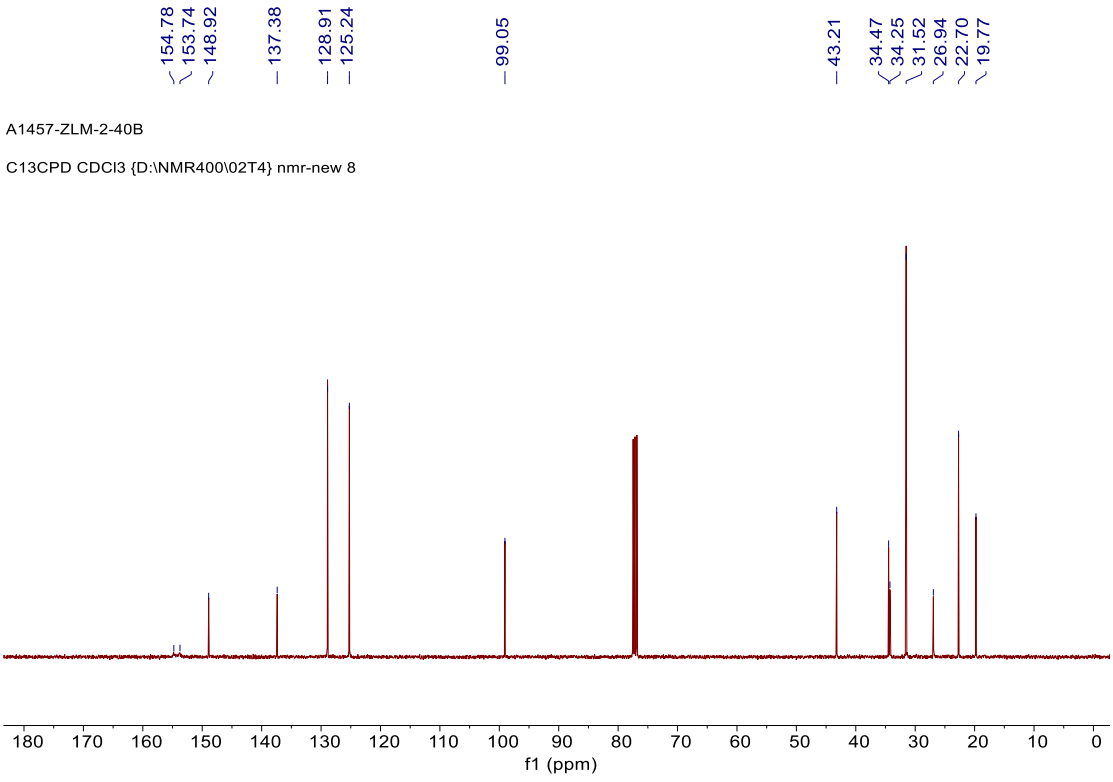


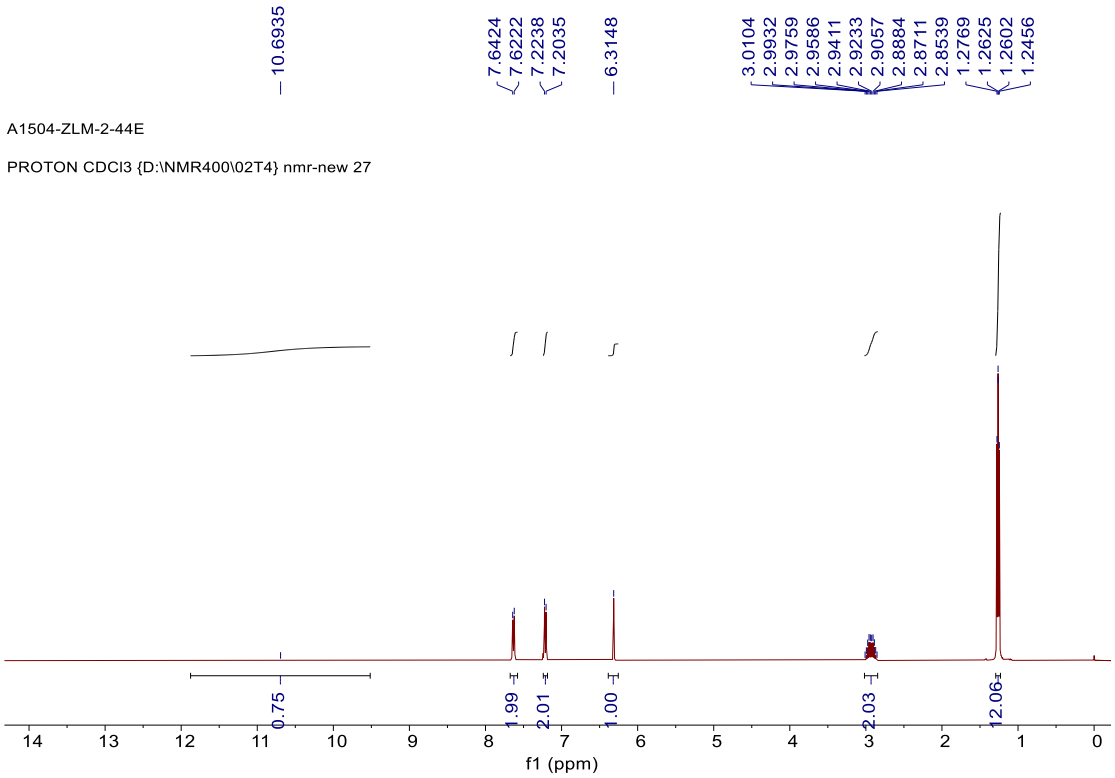



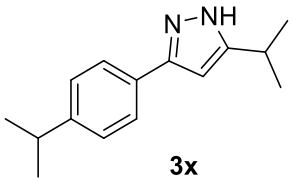

3w

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**



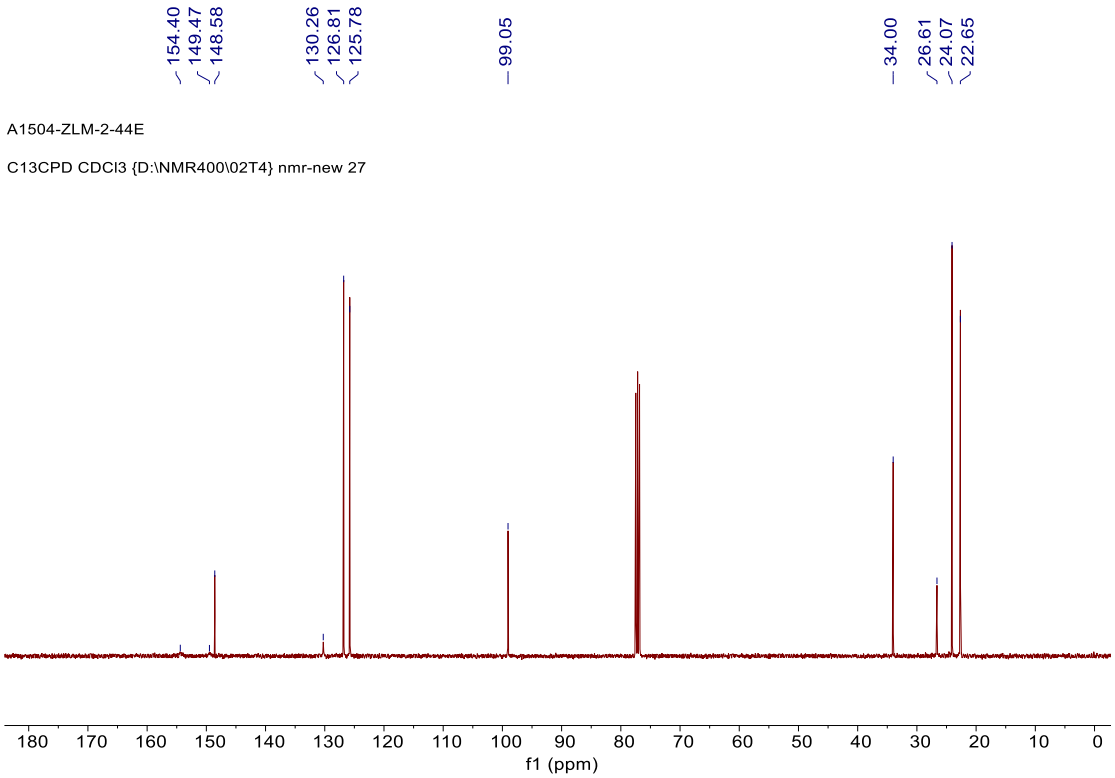


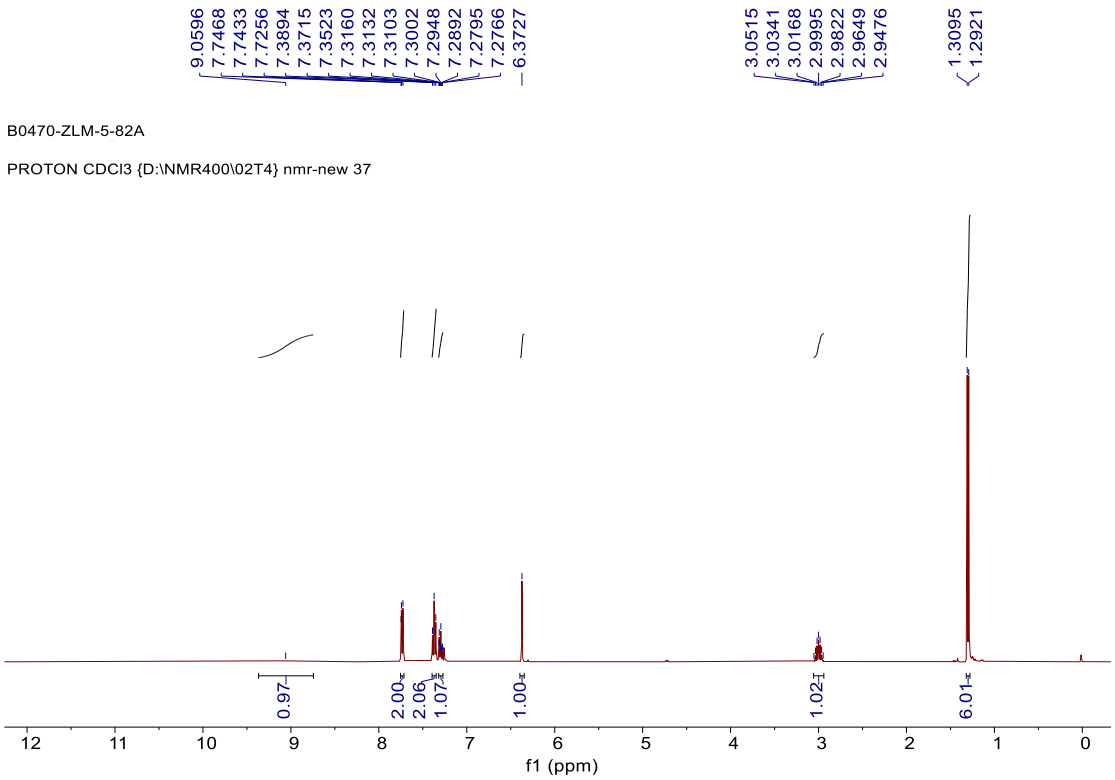



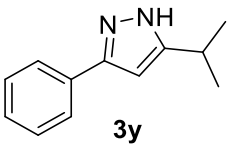

**3x**

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**



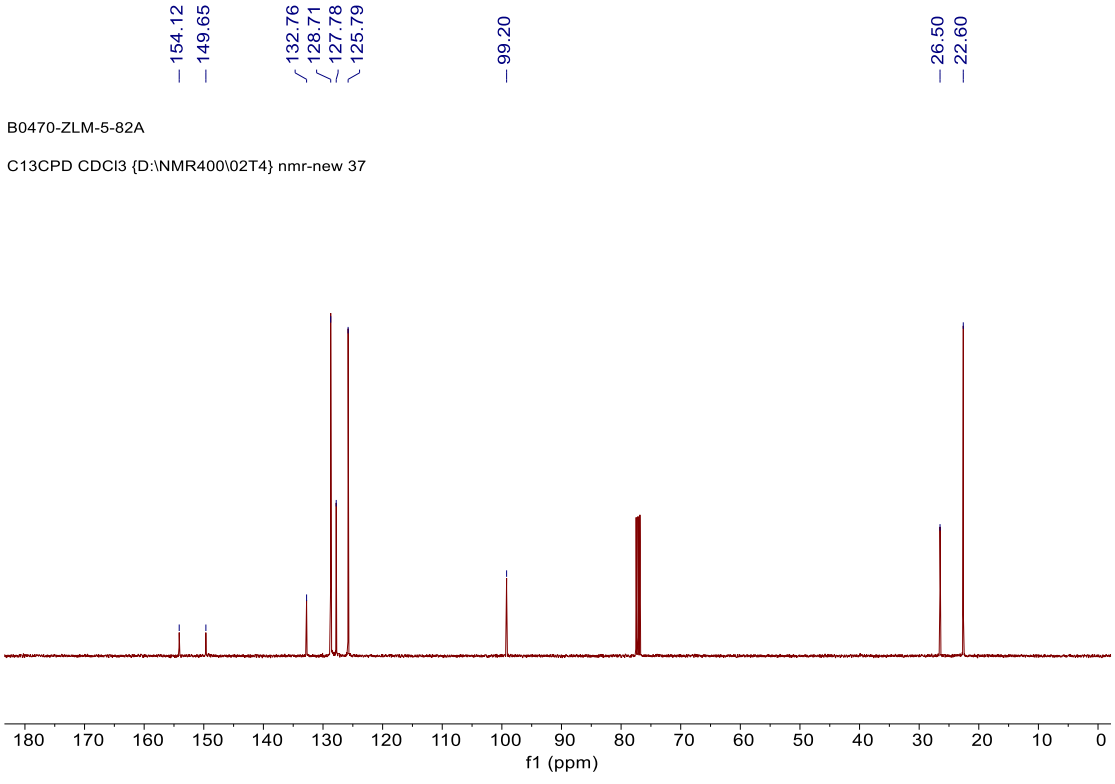


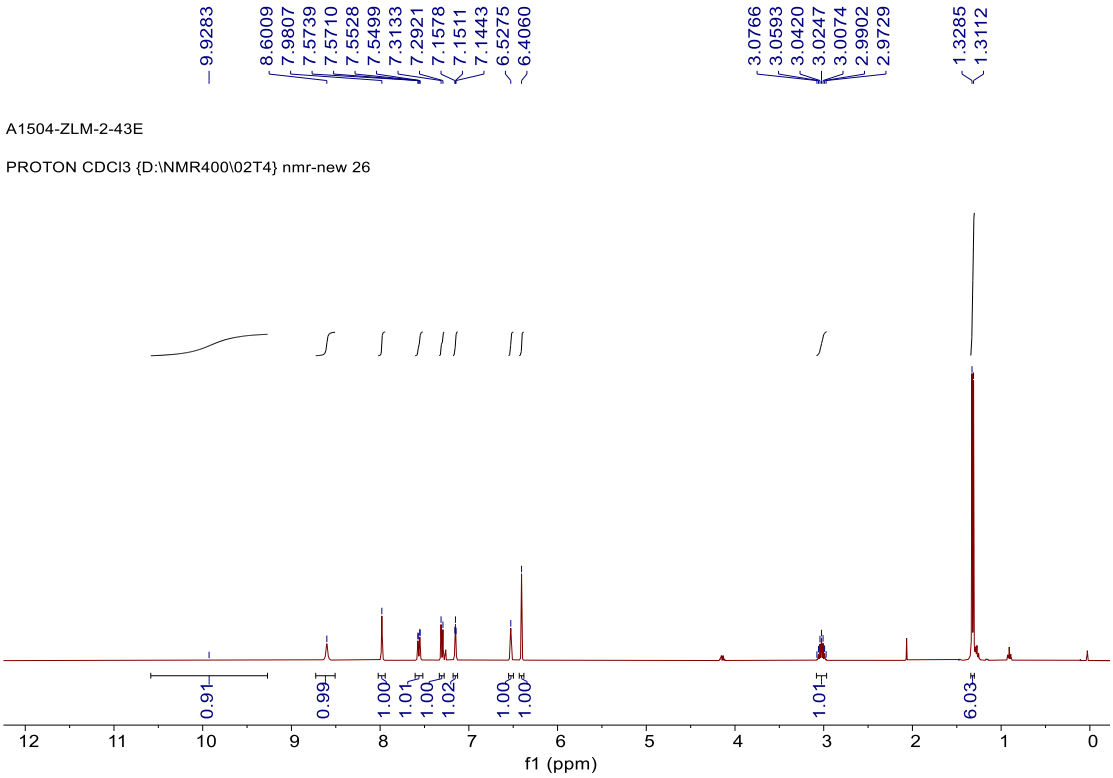




3y

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

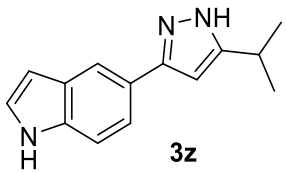
**$^{13}$C NMR (100 MHz, $CDCl_3$)**






A1504-ZLM-2-43E

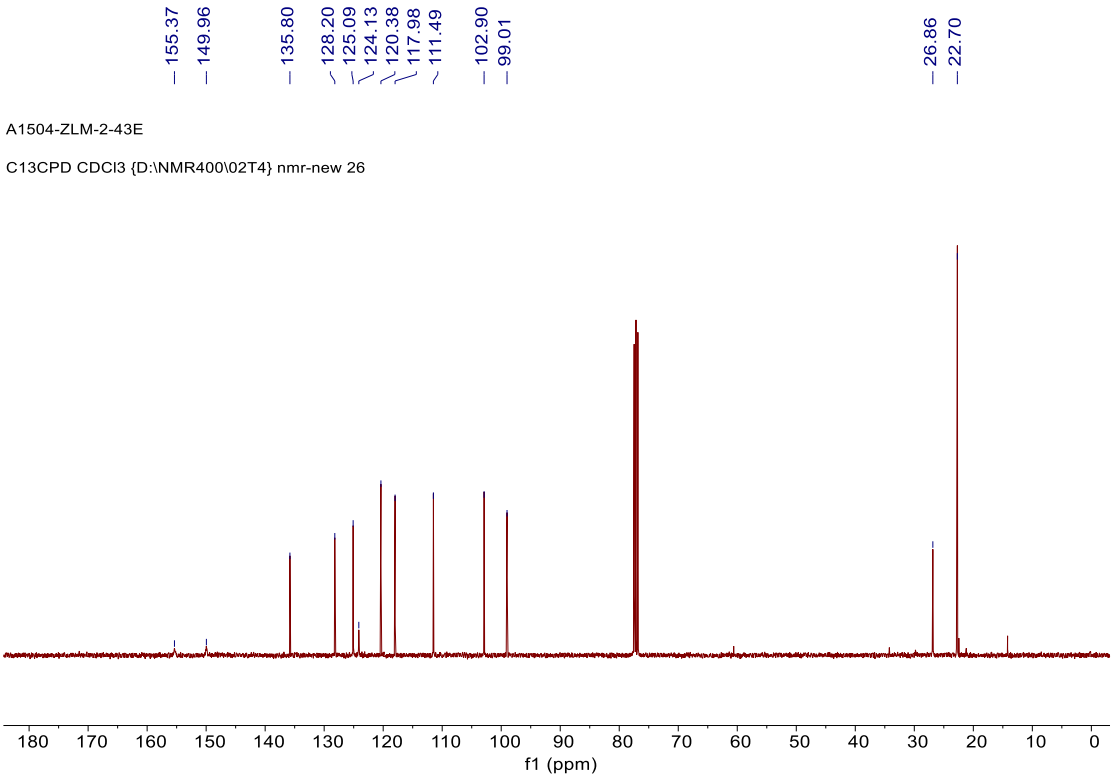
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 26




3z

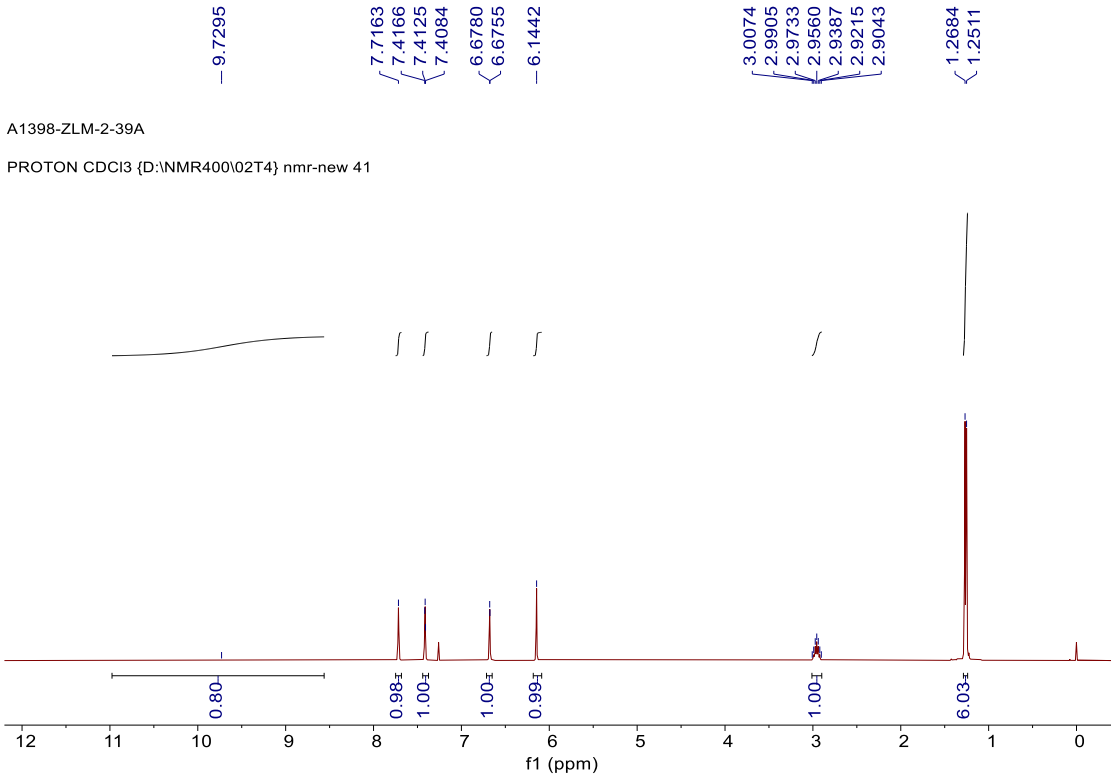
**$^{1}$H NMR (400 MHz, $CDCl_3$)**

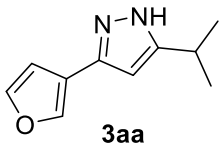
**$^{13}$C NMR (100 MHz, $CDCl_3$)**




A1504-ZLM-2-43E

C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 26

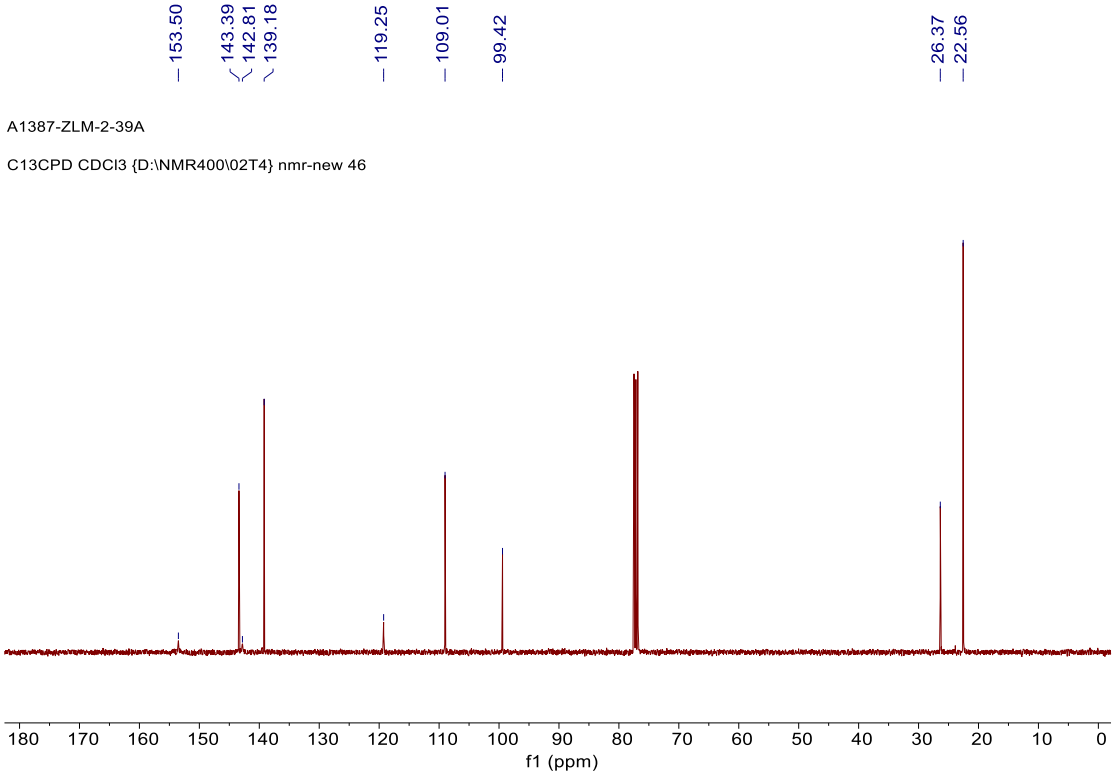


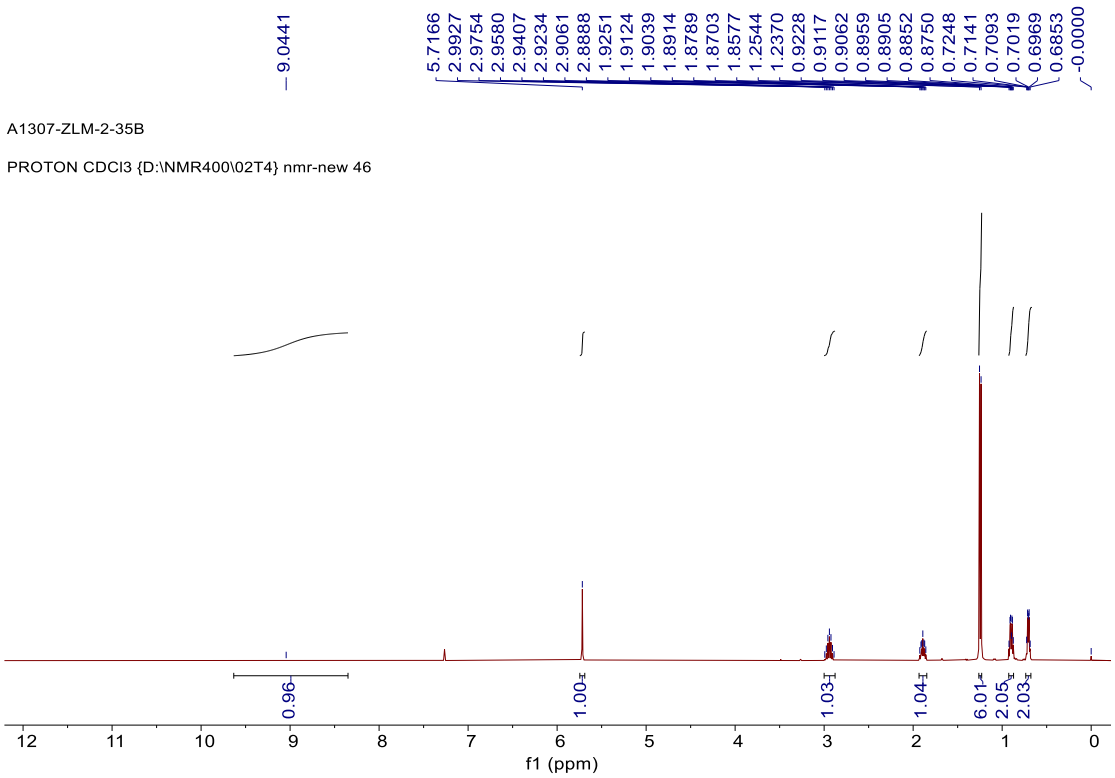



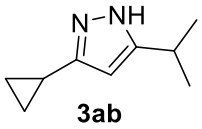

**3aa**

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**



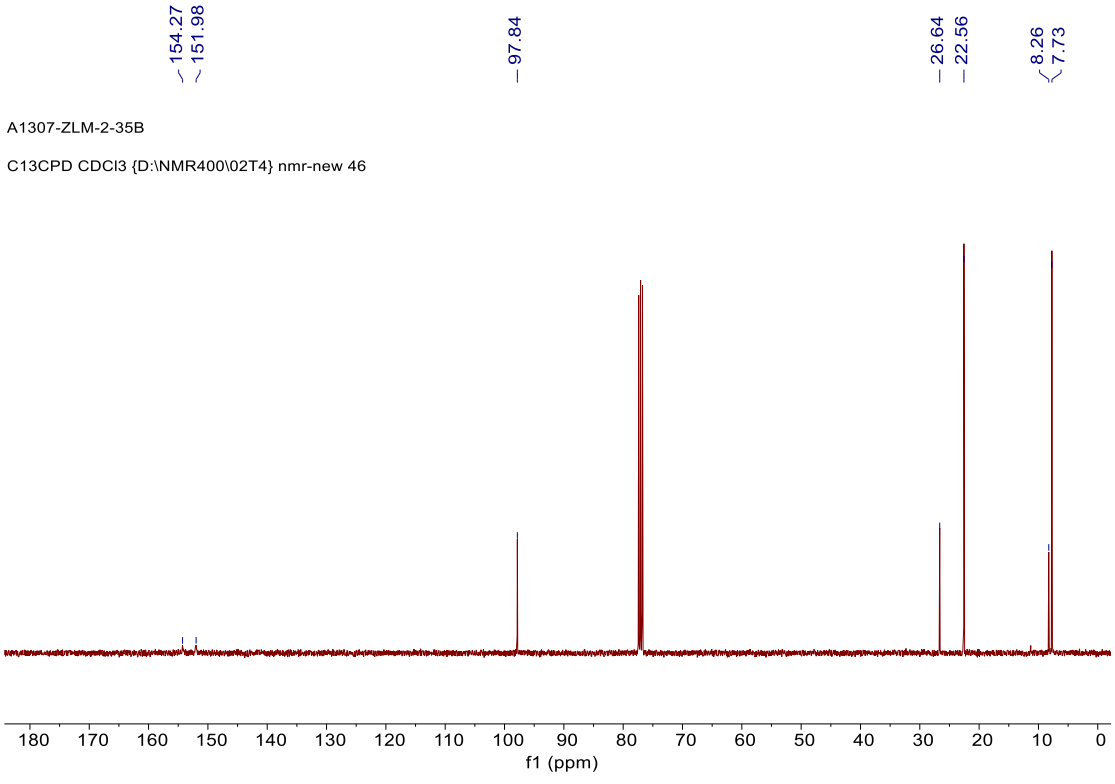



3ab

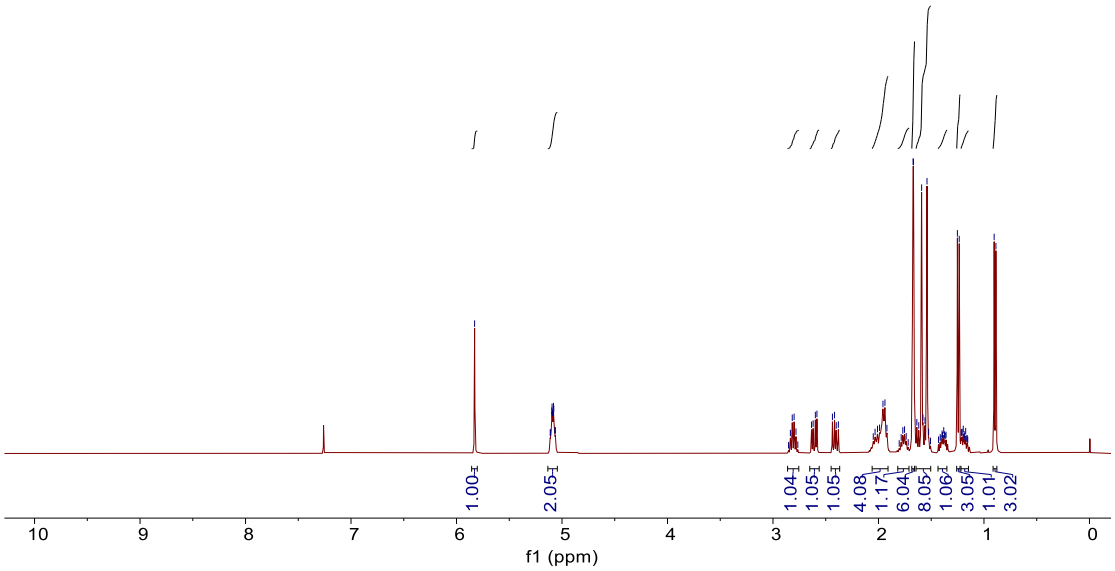
**$^{1}$H NMR (400 MHz, $CDCl_3$)**

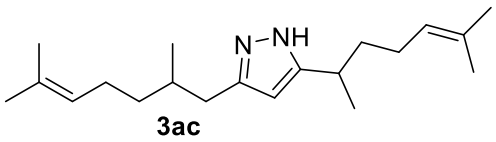
**$^{13}$C NMR (100 MHz, $CDCl_3$)**




A1565-ZLM-2-59A

PROTON CDCl3 {D:\NMR400\02T4} nmr-new 45




3ac

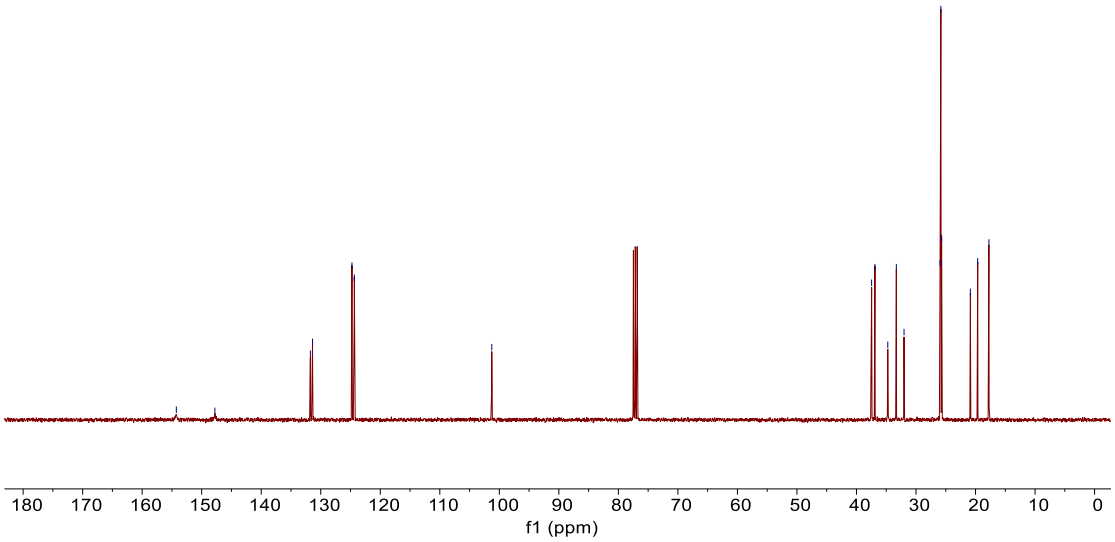
**$^{1}$H NMR (400 MHz, $CDCl_3$)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**

154.26
147.78
131.74
131.38
124.76
124.36
101.27
37.46
36.90
34.74
33.31
32.01
25.96
25.82
25.70
20.87
19.64
17.75

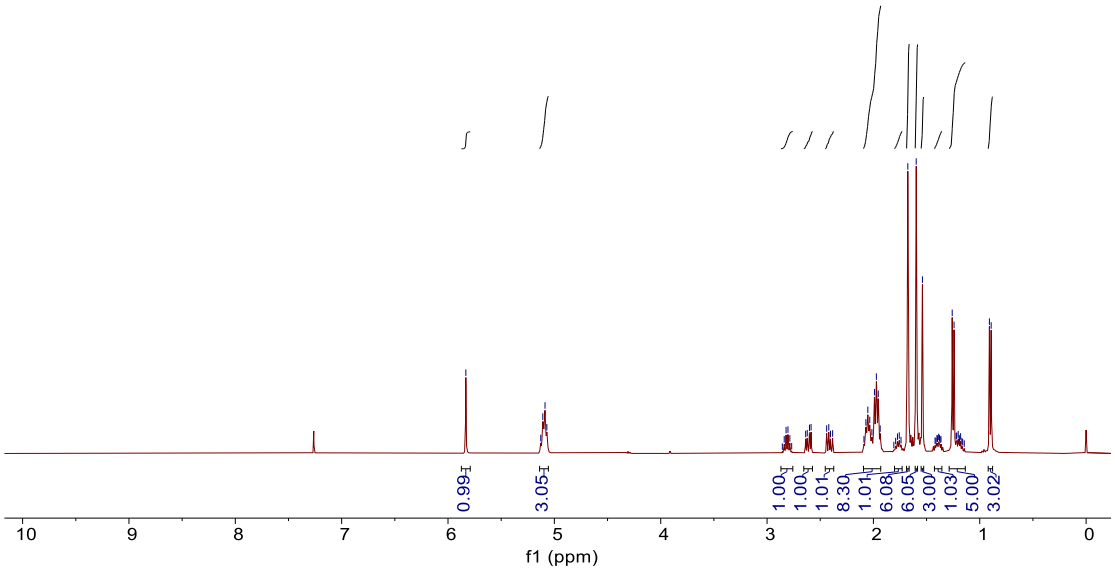
A1586-ZLM-2-59A

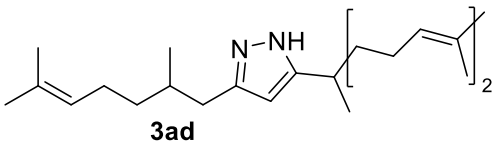
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 41




A2083-ZLM-2-76A

PROTON CDCl3 {D:\NMR400\02T4} nmr-new 23




3ad

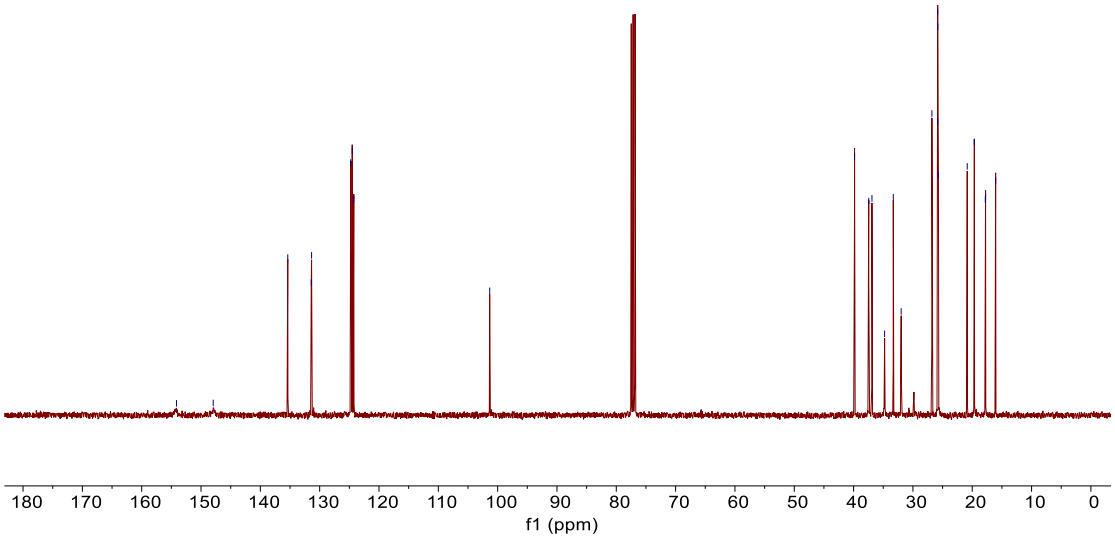
**$^{1}$H NMR (400 MHz, $CDCl_3$)**

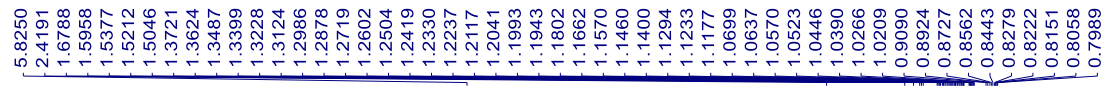
**$^{13}$C NMR (100 MHz, $CDCl_3$)**

154.14
147.94
135.38
131.41
131.37
124.77
124.51
124.25
101.34
39.84
37.45
36.90
34.77
33.31
31.98
26.80
25.84
25.82
25.81
25.70
20.84
19.65
17.80
17.75
16.05

A2100-ZLM-2-76A

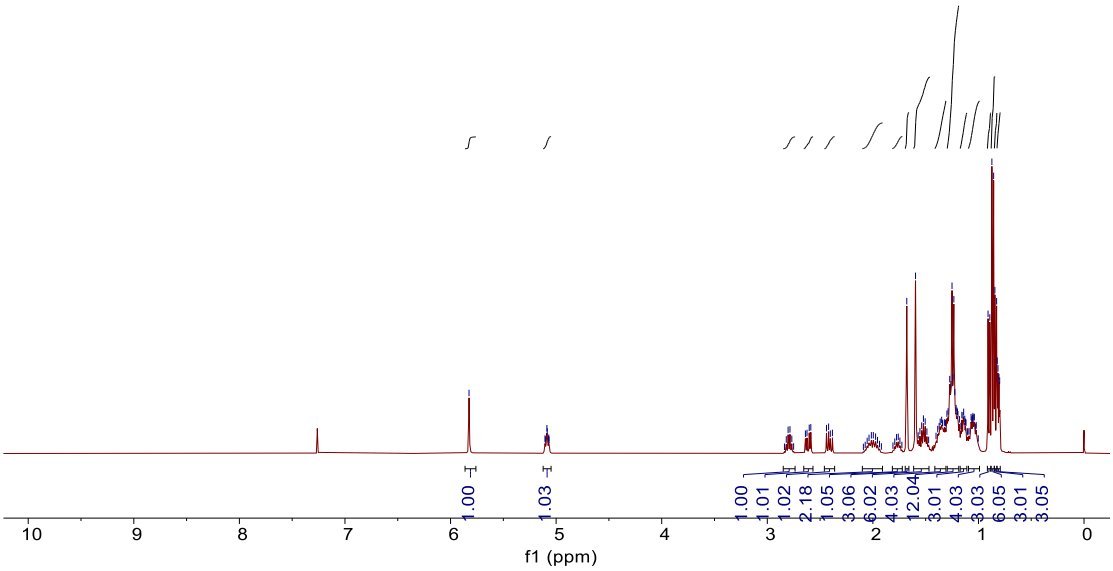
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 58

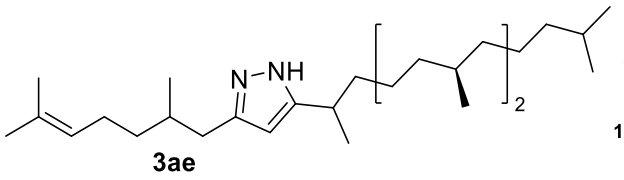





A2225-ZLM-2-90A

PROTON CDCl3 {D:\NMR400\02T4} nmr-new 10

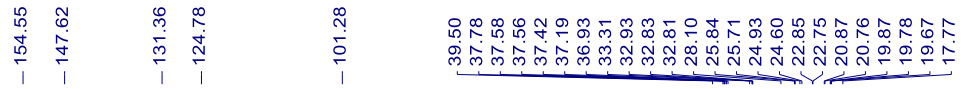



**3ae**

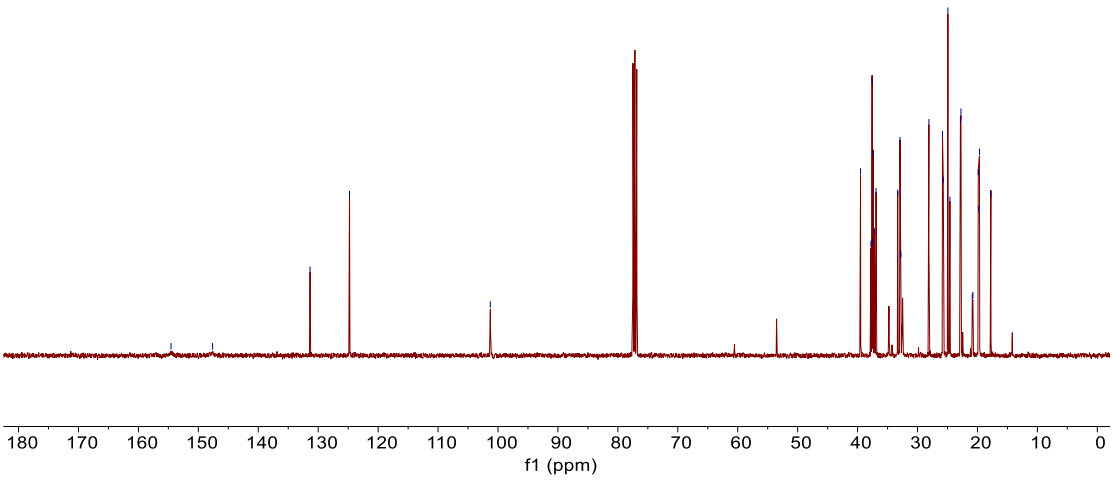
**$^{1}$H NMR (400 MHz, $CDCl_3$)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**



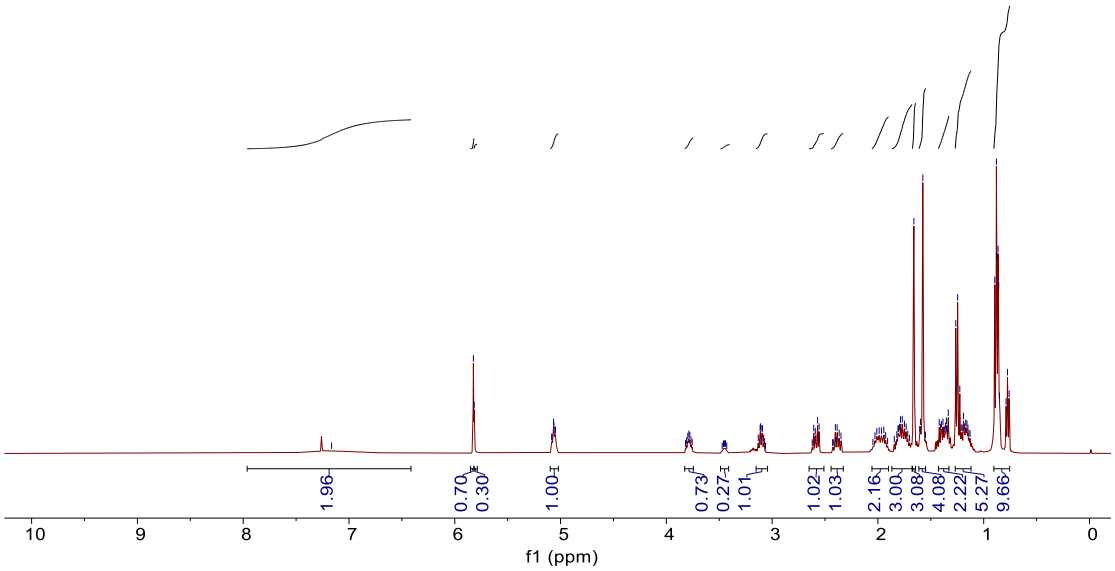

A2225-ZLM-2-90A

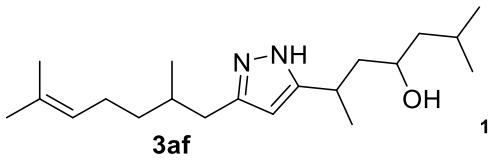
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 10




A6940-ZLM-4-79B

PROTON CDCl3 {D:\NMR400\02T4} nmr-new 25



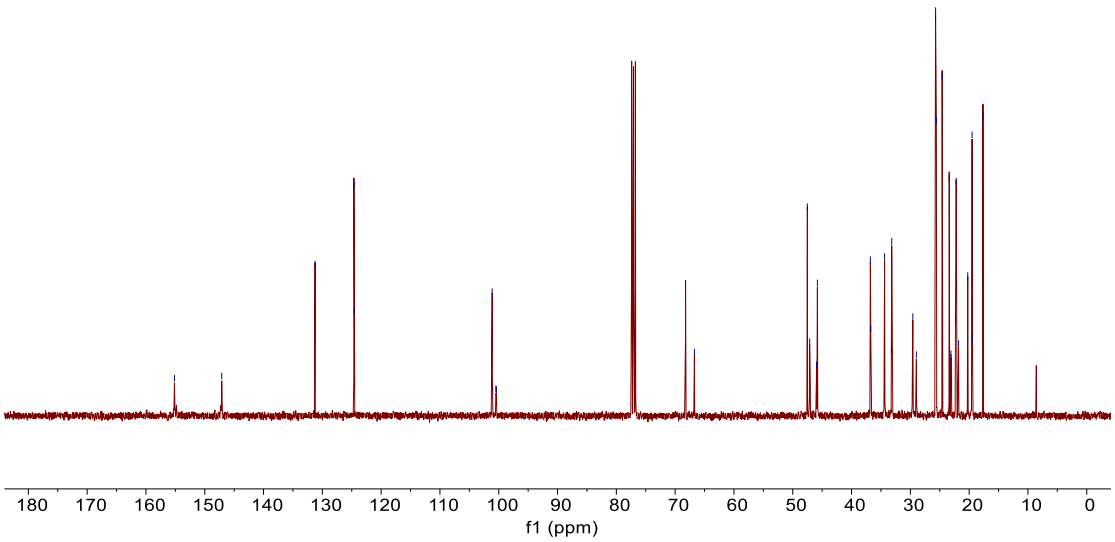

**3af**

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**

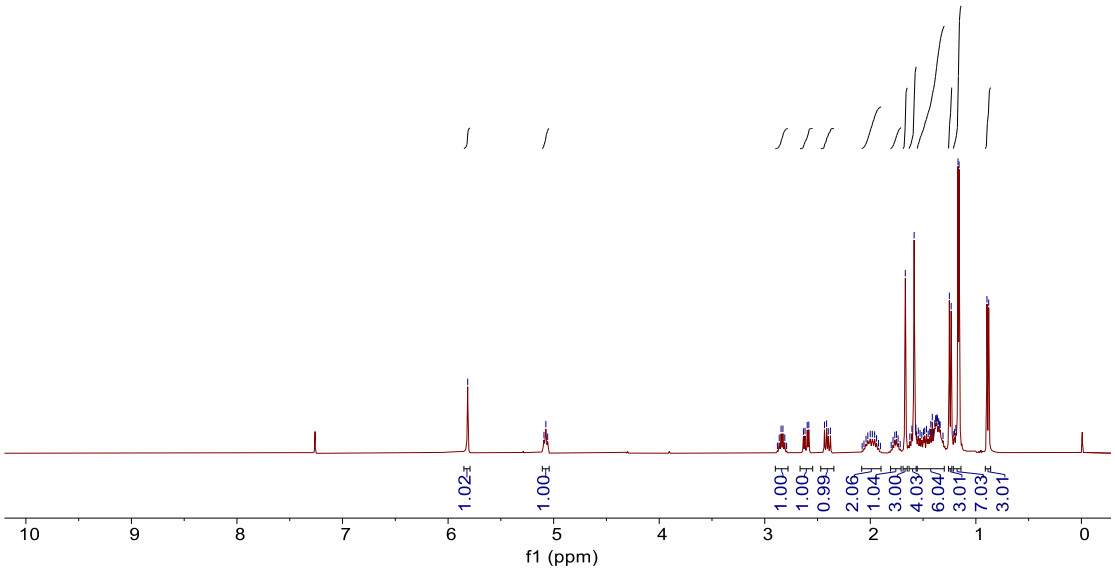

A7260-ZLM-4-79B

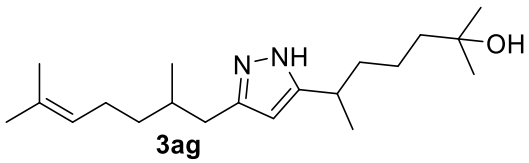
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 16




A2083-ZLM-2-76B

PROTON CDCl3 {D:\NMR400\02T4} nmr-new 21




3ag

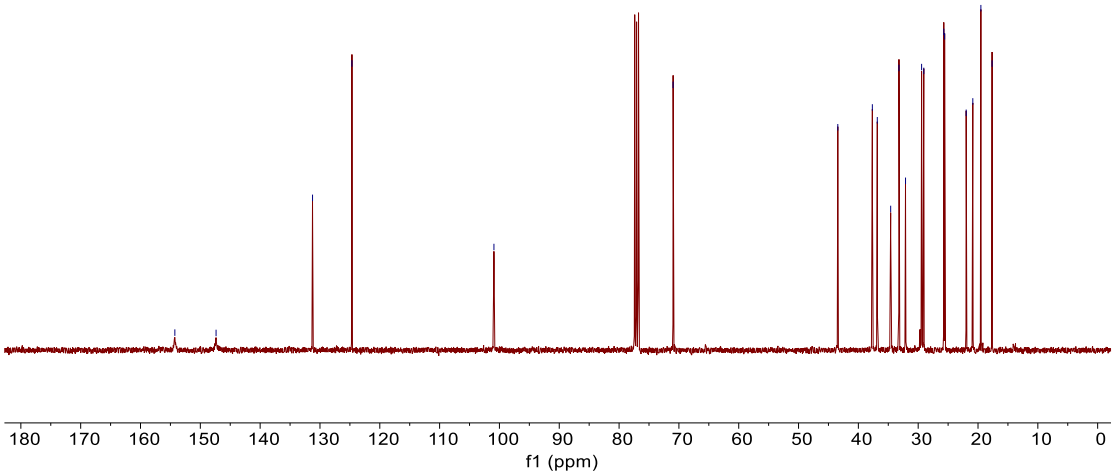
**$^{1}$H NMR (400 MHz, $CDCl_3$)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**

154.26
147.37
131.24
124.66
100.92
70.97
43.44
37.66
36.84
34.60
33.22
32.12
29.43
29.06
25.72
25.58
21.98
20.87
19.52
17.65

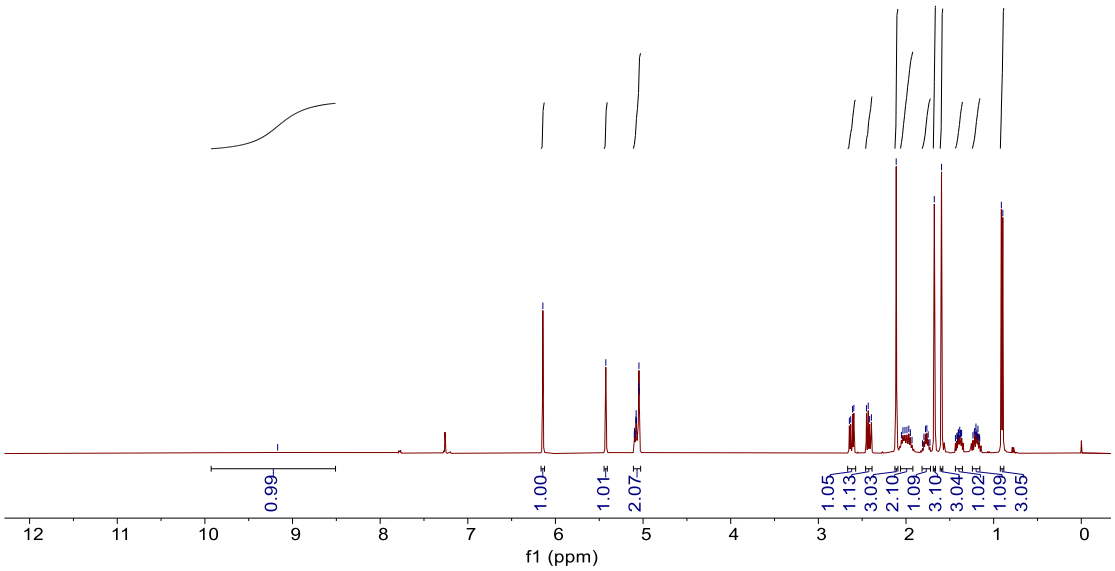
A2100-ZLM-2-76B

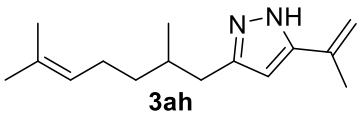
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 59




A1566-ZLM-2-56E

PROTON CDCl3 {D:\NMR400\02T4} nmr-new 52



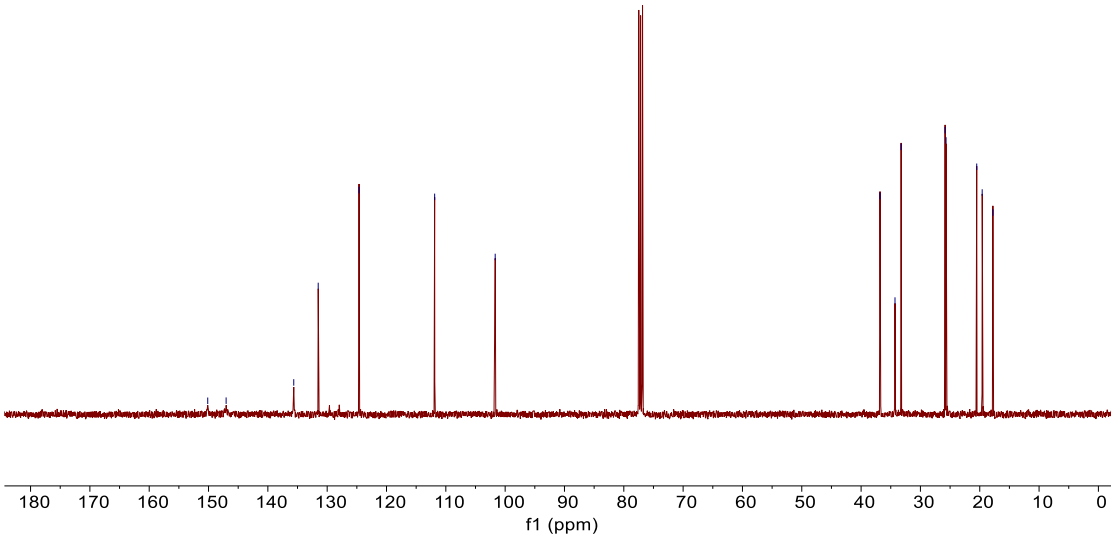

3ah

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**

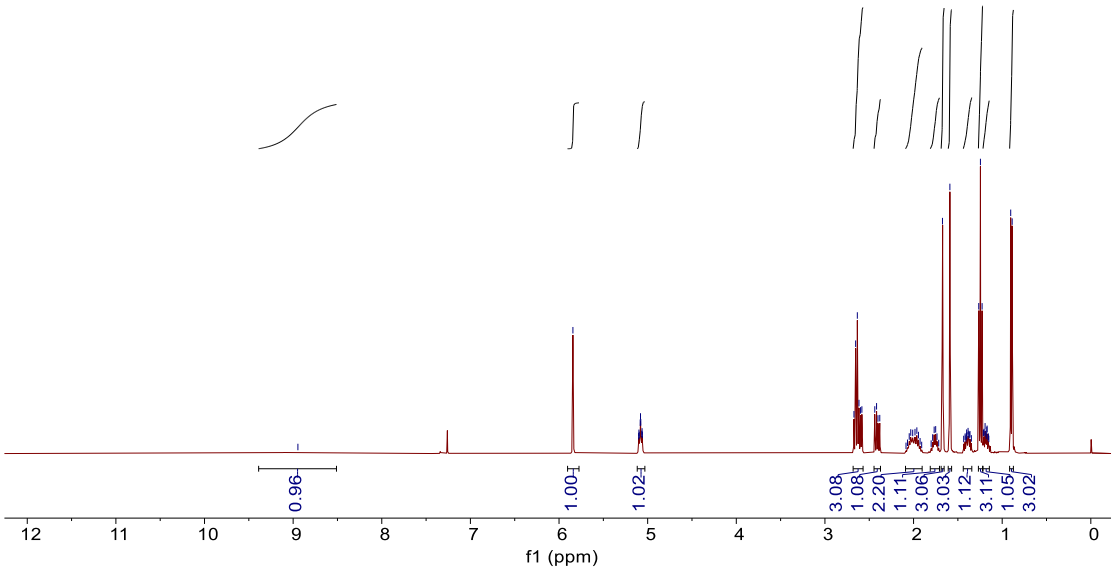

A1566-ZLM-2-56E

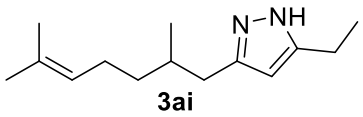
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 52




A1565-ZLM-2-59B

PROTON CDCl3 {D:\NMR400\02T4} nmr-new 46



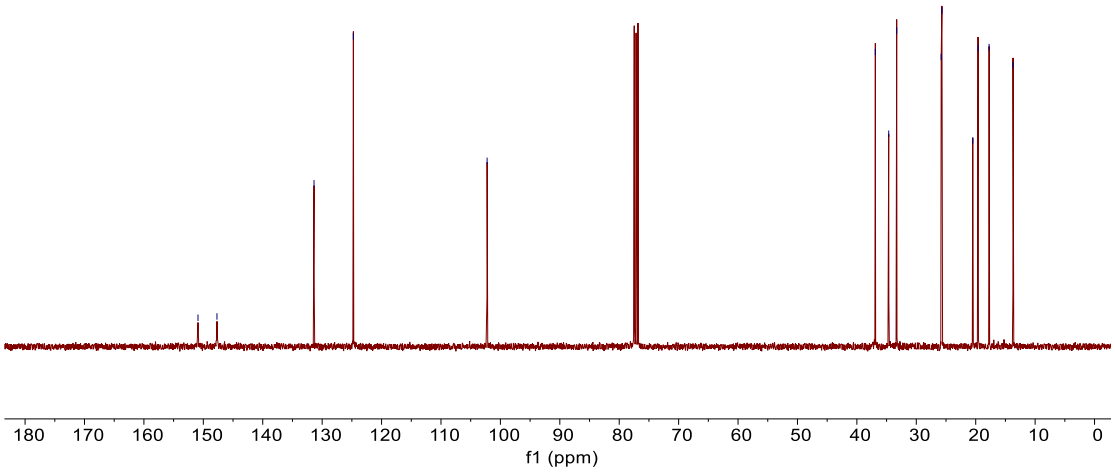

3ai

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**

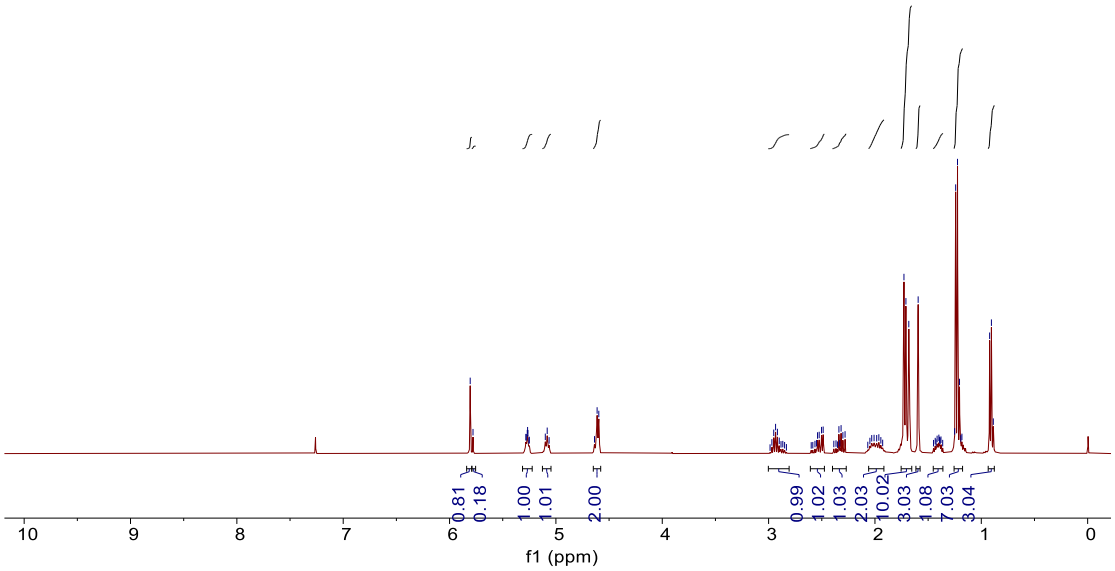

A1566-ZLM-2-59B

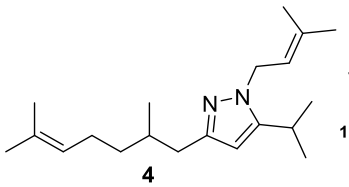
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 54




A2100-ZLM-2-81

PROTON CDCl3 {D:\NMR400\02T4} nmr-new 16



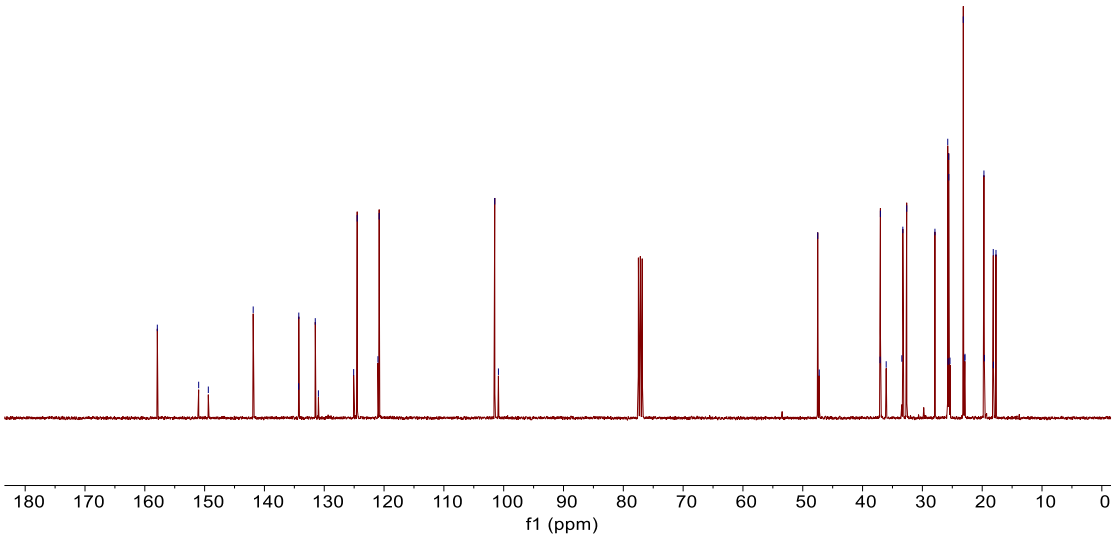
**4**

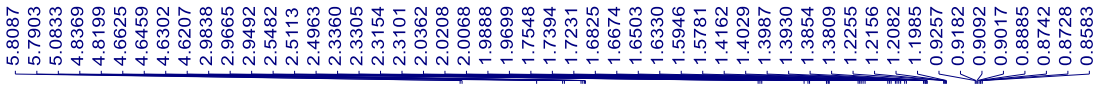
**$^{1}$H NMR (400 MHz, $CDCl_3$)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**


A2100-ZLM-2-81

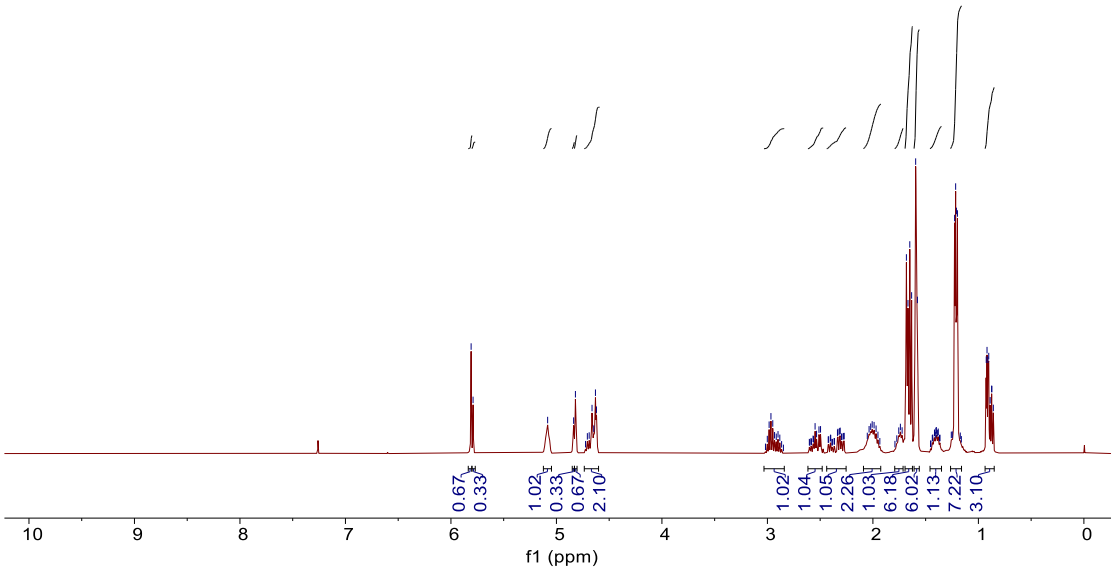
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 16

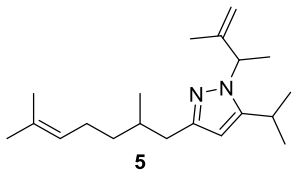





A2886-ZLM-3-14-1 new

PROTON CDCl3 {D:\NMR400\02T4} nmr-new 46



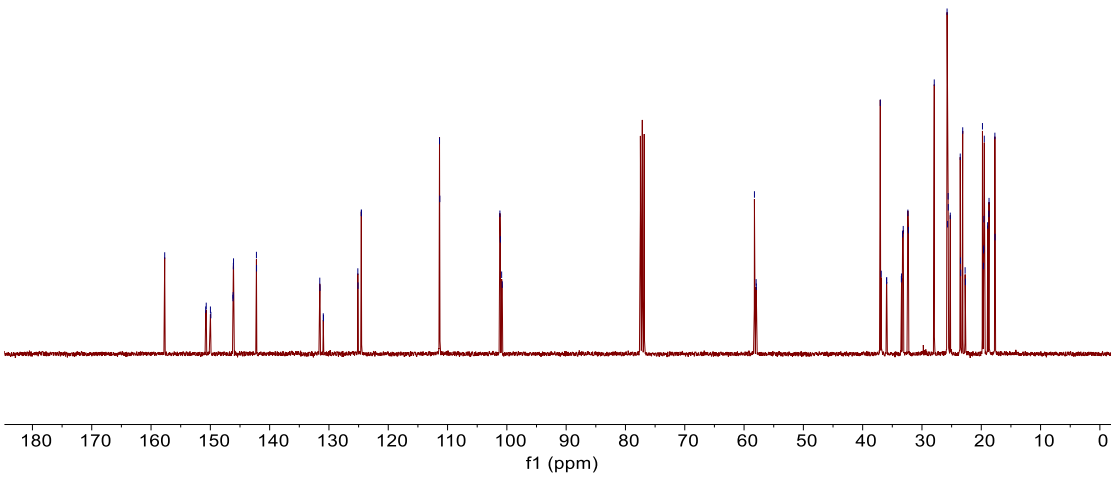

**5**

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**

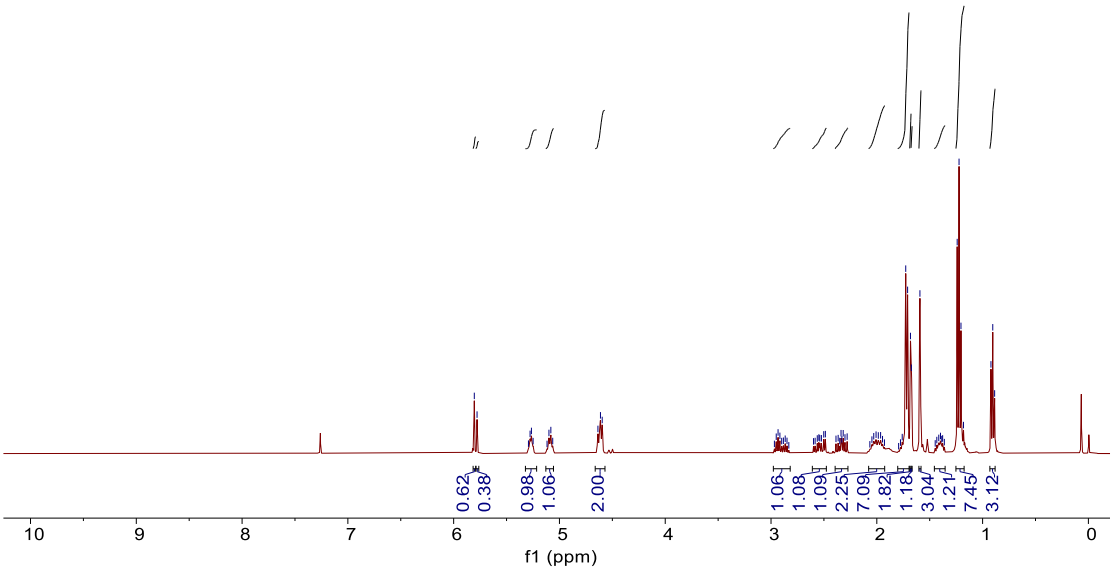

A2921-ZLM-3-14-1 NEW

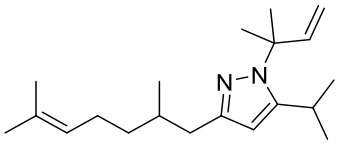
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 23




A2845-ZLM-3-15

PROTON CDCl3 {D:\NMR400\02T4} nmr-new 23

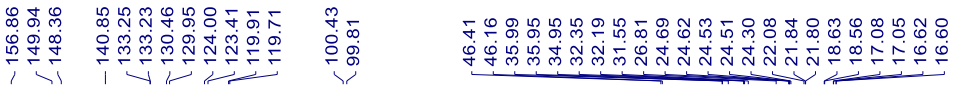


**6**

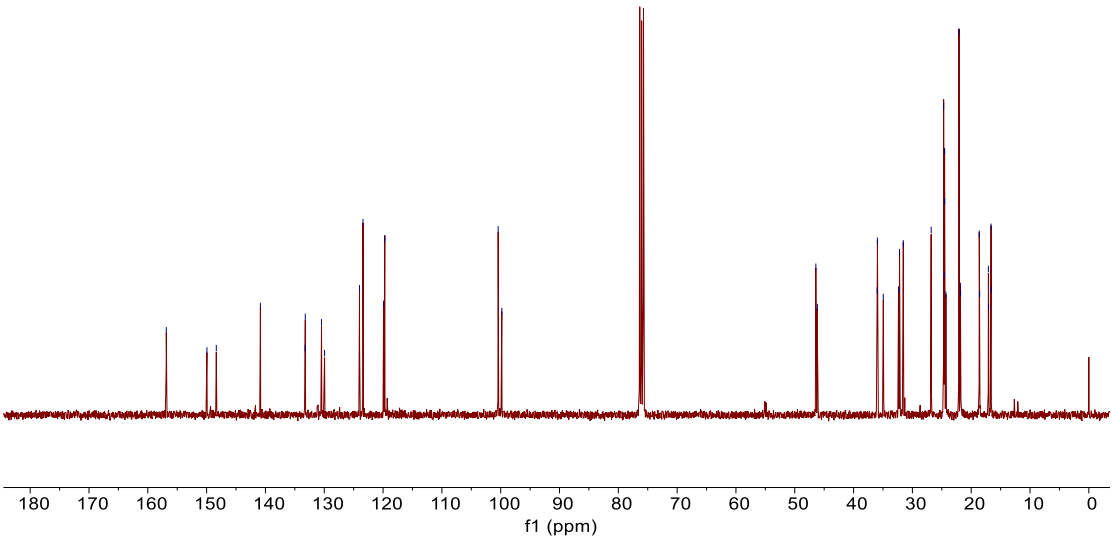
**$^{1}$H NMR (400 MHz, $CDCl_3$)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**



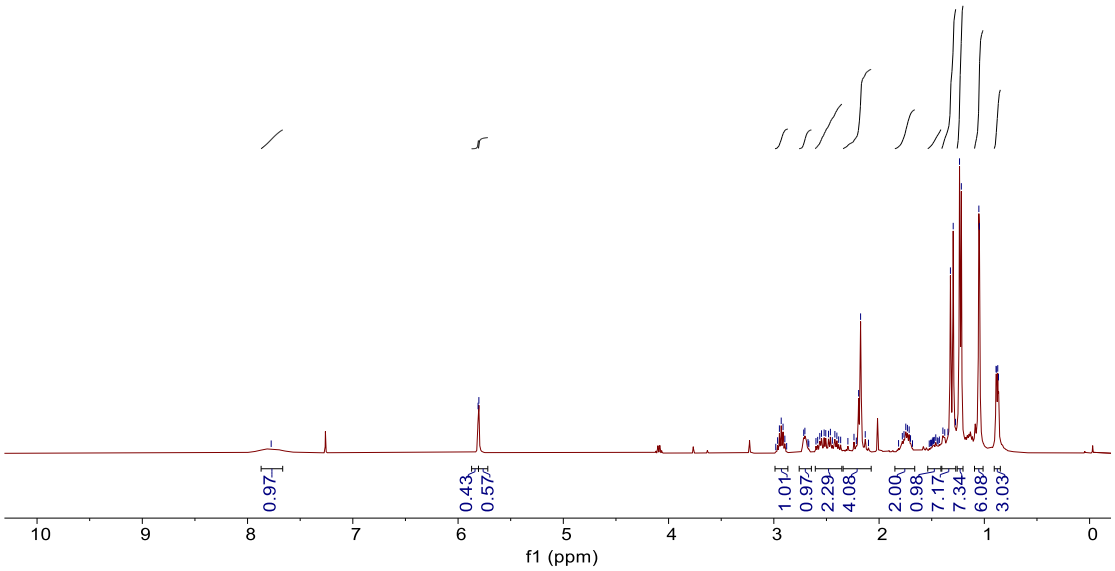

A3000-ZLM-3-15

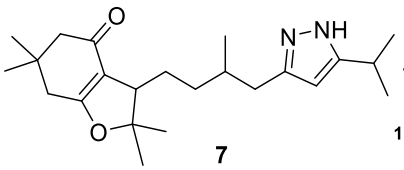
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 3




A9645-ZLM-3-32

PROTON CDCl3 {D:\NMR400\02T4} nmr-new 30



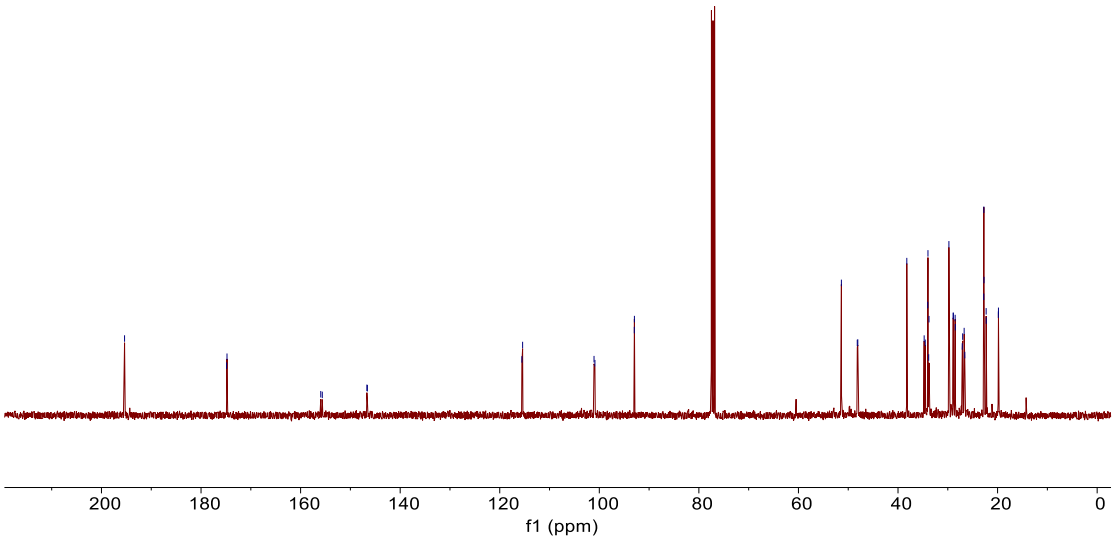

7

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**

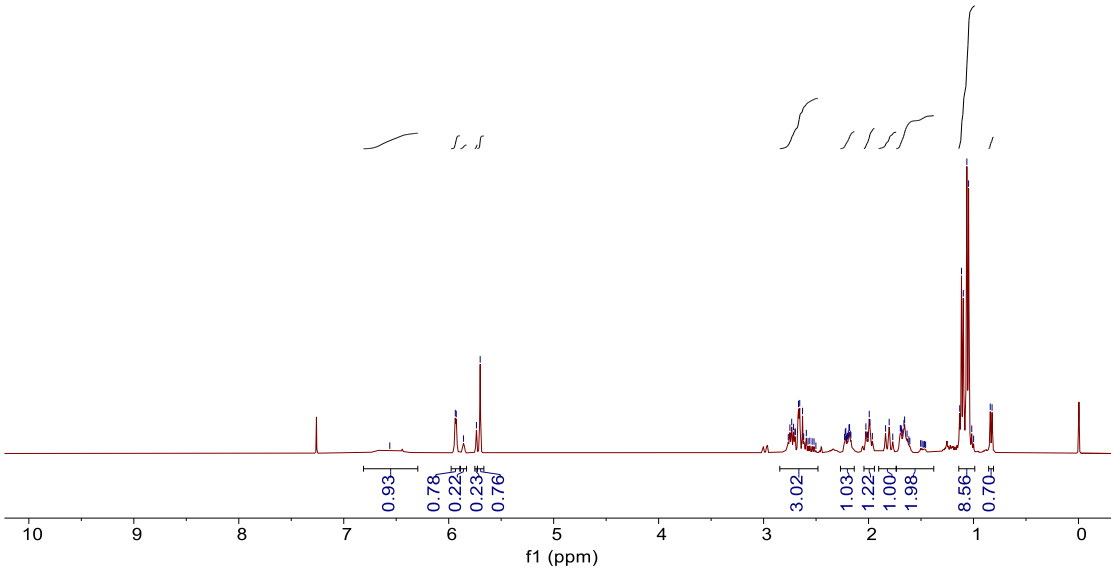

A9645-ZLM-3-32

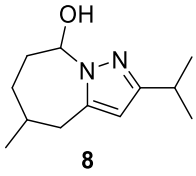
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 30




A2724-ZLM-3-9 H

PROTON CDCl3 {D:\NMR400\02T4} nmr-new 47



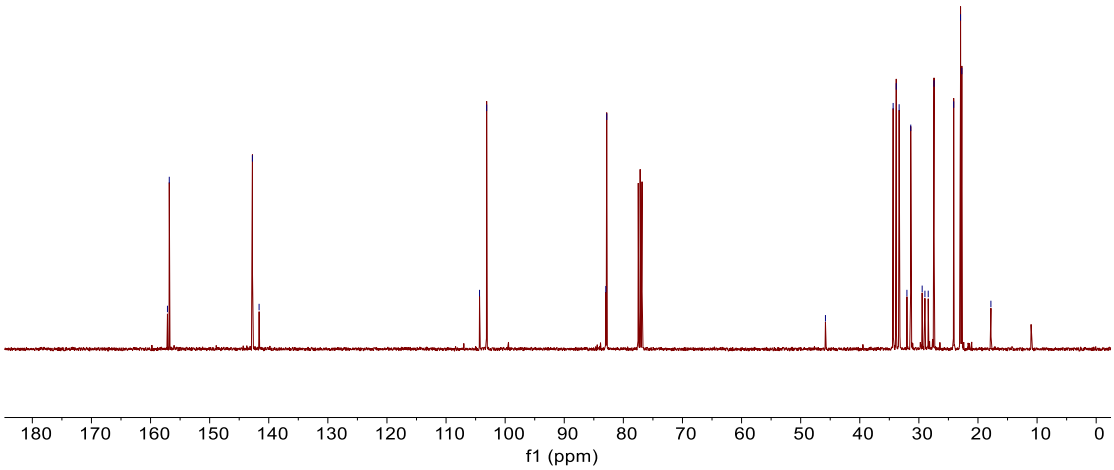

8

$^{1}$H NMR (400 MHz, $CDCl_3$)

$^{13}$C NMR (100 MHz, $CDCl_3$)

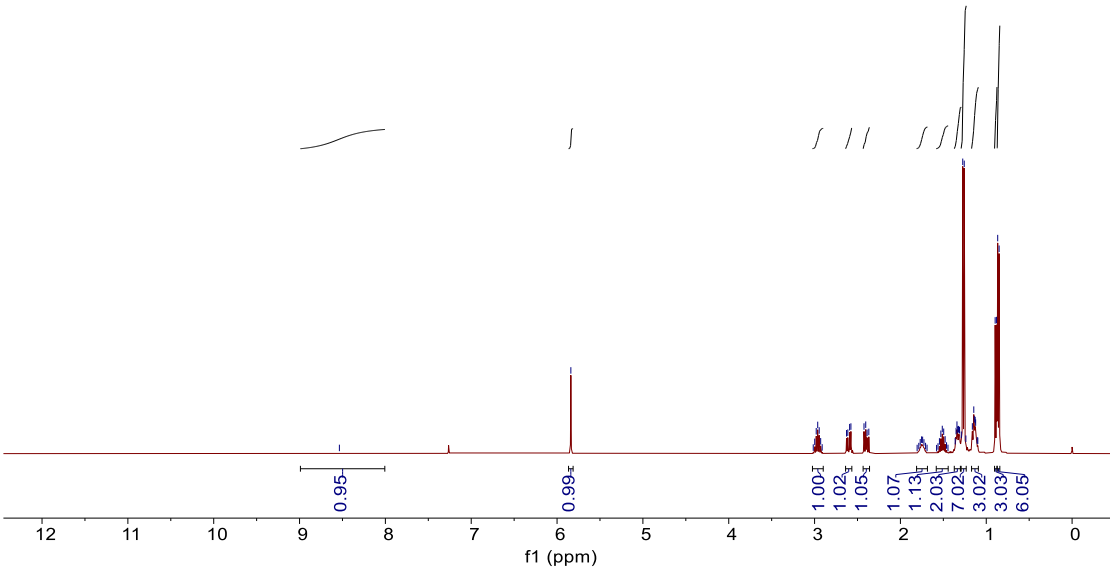

A2724-ZLM-3-9 C

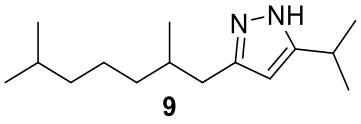
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 46




A2707-ZLM-3-12

PROTON CDCl3 {D:\NMR400\02T4} nmr-new 23




9

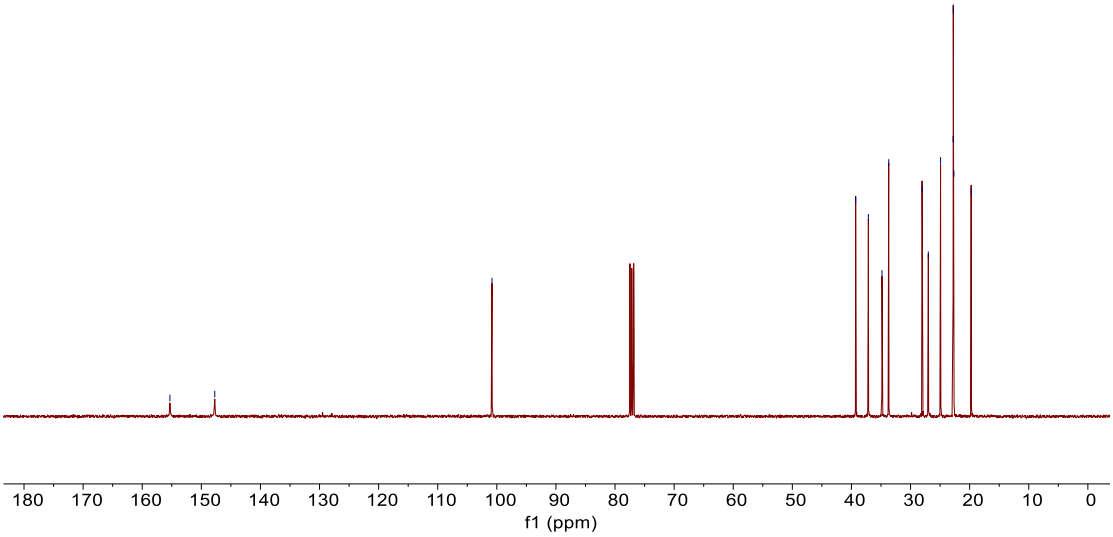
$^{1}$H NMR (400 MHz, $CDCl_3$)

$^{13}$C NMR (100 MHz, $CDCl_3$)

155.32
147.73
100.82
39.29
37.14
34.83
33.69
28.05
26.99
24.92
22.80
22.77
22.68
19.74

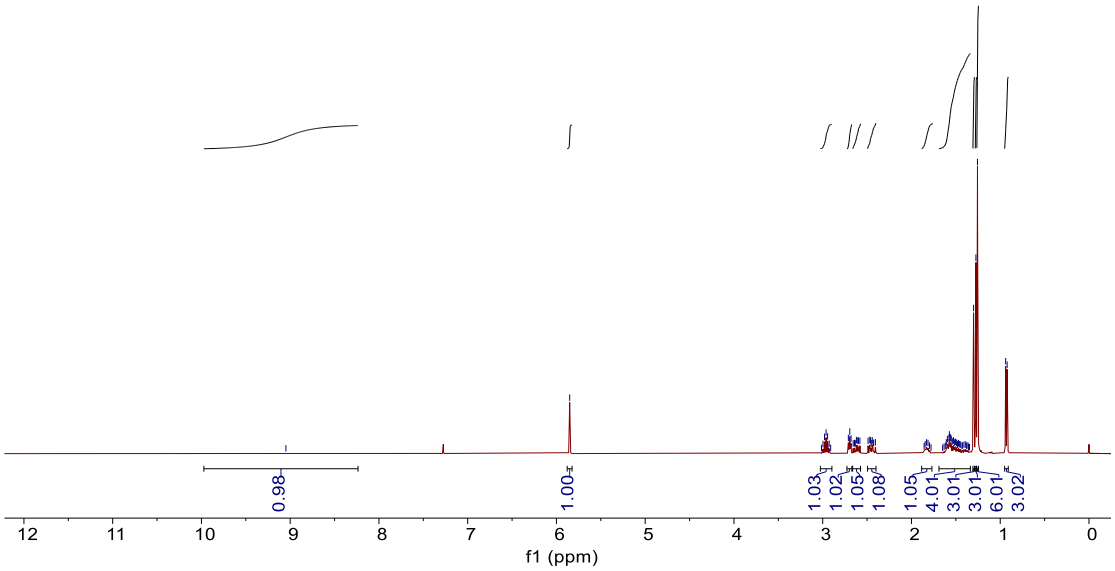
A2754-ZLM-3-12

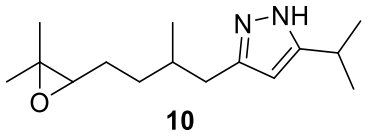
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 46




A2100-ZLM-2-78

PROTON CDCl3 {D:\NMR400\02T4} nmr-new 15



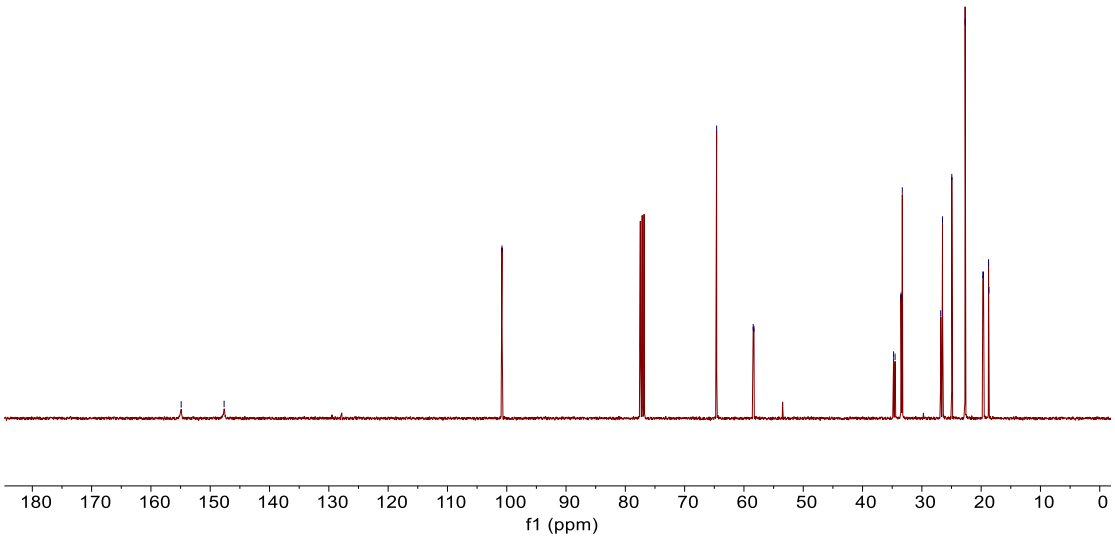

10

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**

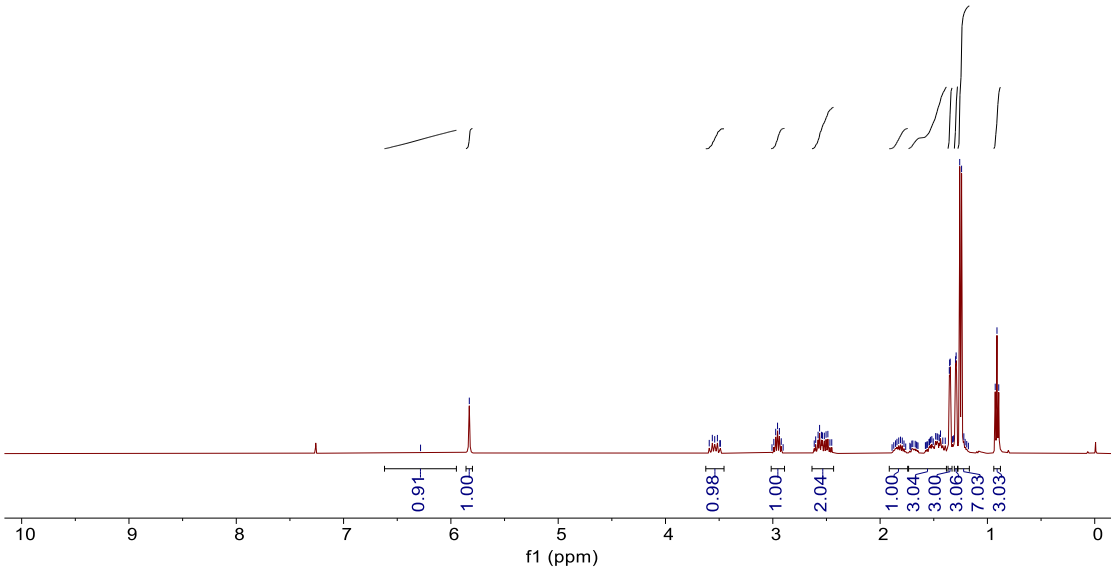

A2100-ZLM-2-78

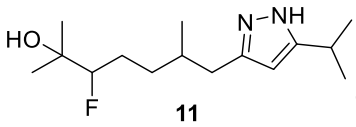
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 15




A2687-ZLM-3-10A

PROTON CDCl3 {D:\NMR400\02T4} nmr-new 39



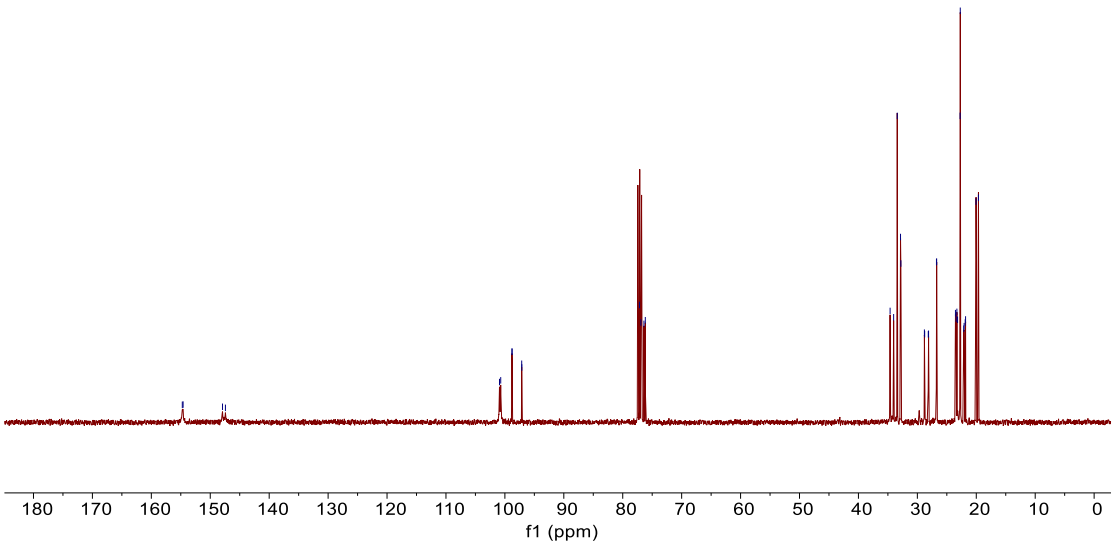

**11**

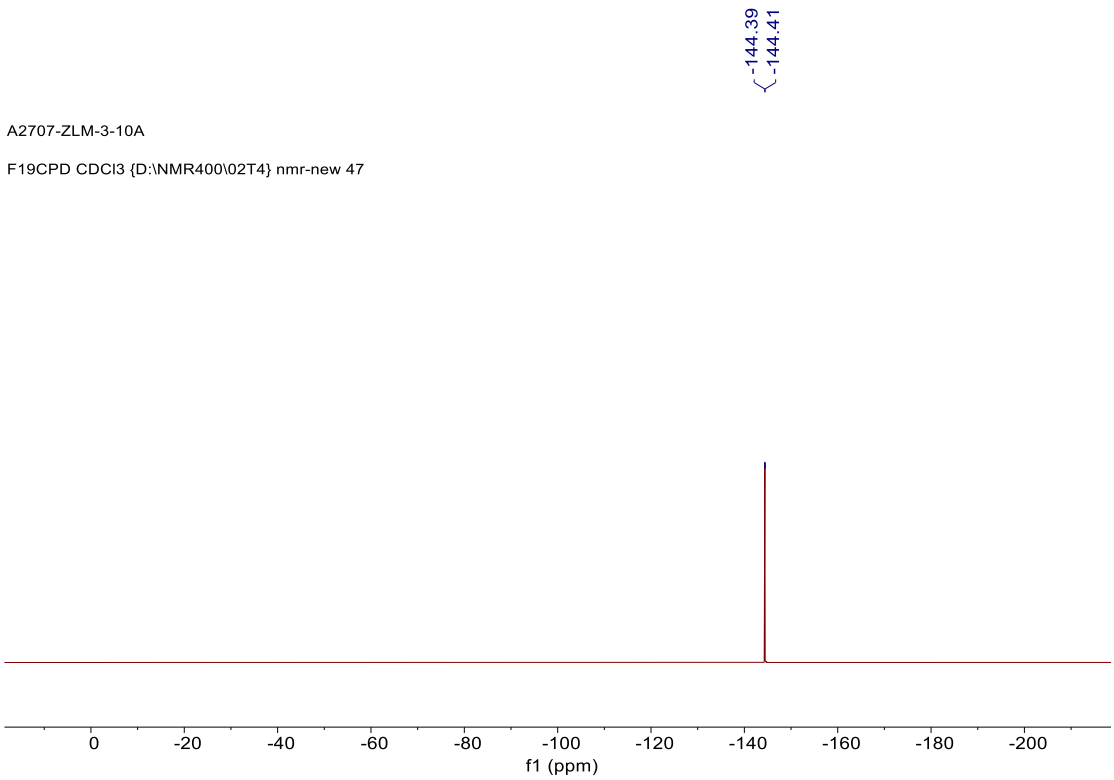
**$^{1}$H NMR (400 MHz, $CDCl_3$)**

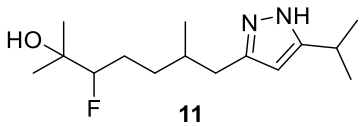
**$^{13}$C NMR (100 MHz, $CDCl_3$)**


A2707-ZLM-3-10A

C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 47





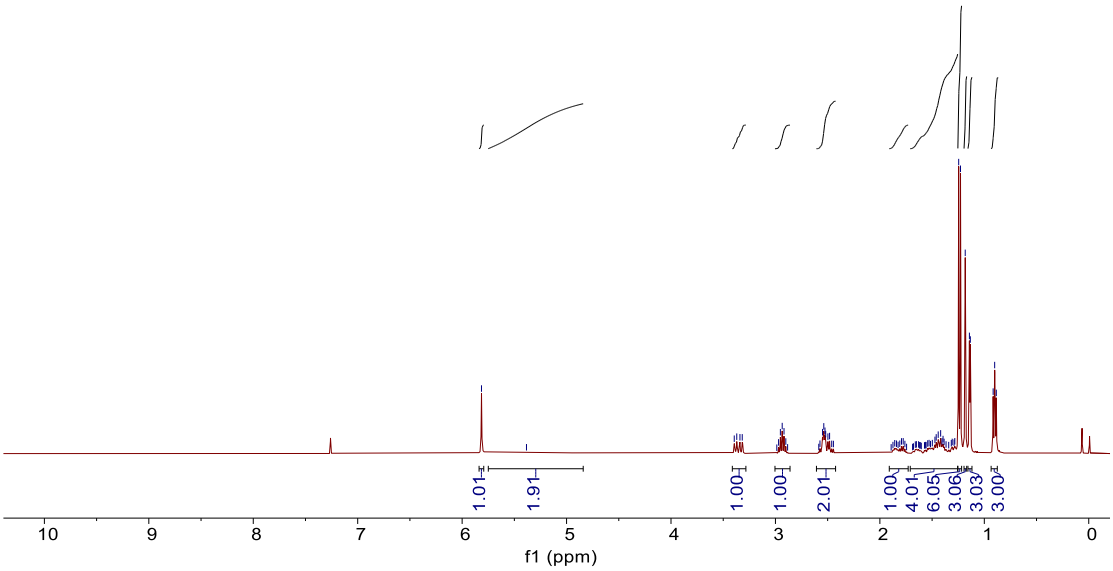



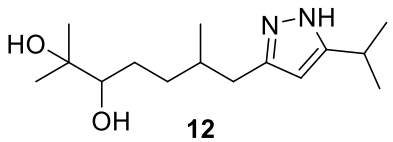

**11**

**$^{19}$F NMR (375 MHz, $CDCl_3$)**


A2554-ZLM-3-4

PROTON CDCl3 {D:\NMR400\02T4} nmr-new 4



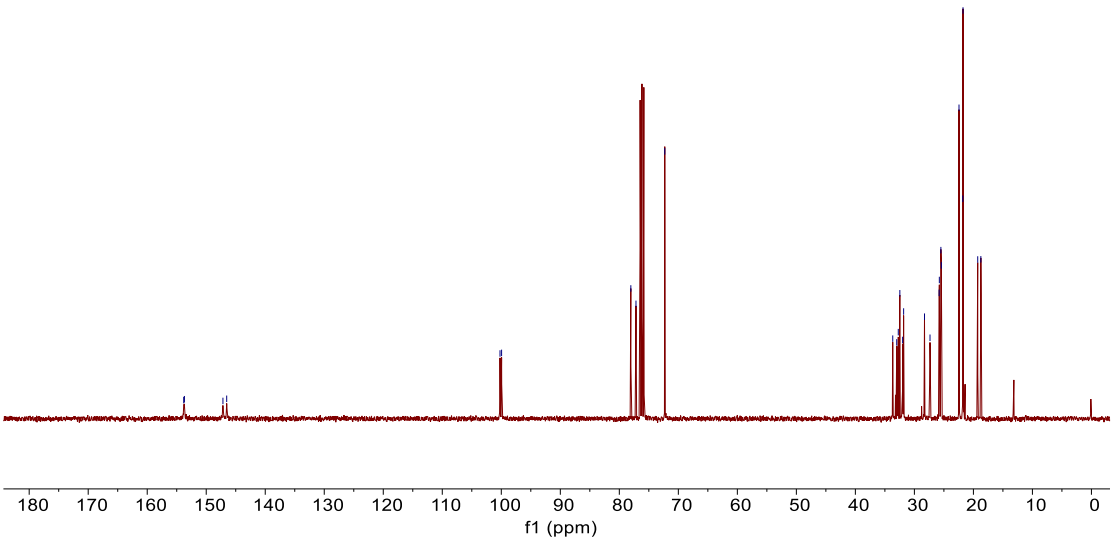

**12**

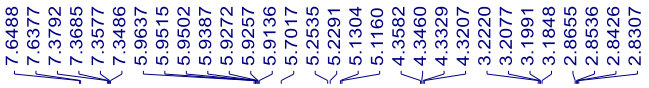
**$^{1}$H NMR (400 MHz, $CDCl_3$)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**

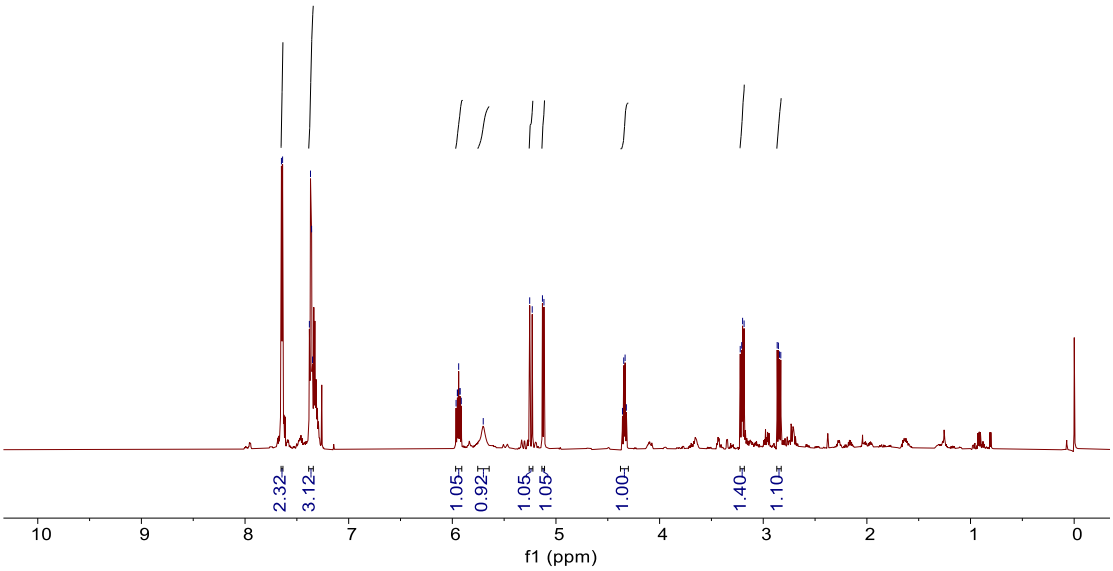

A2197-ZLM-3-4

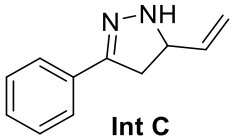
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 10






7422-ZLM-5-66



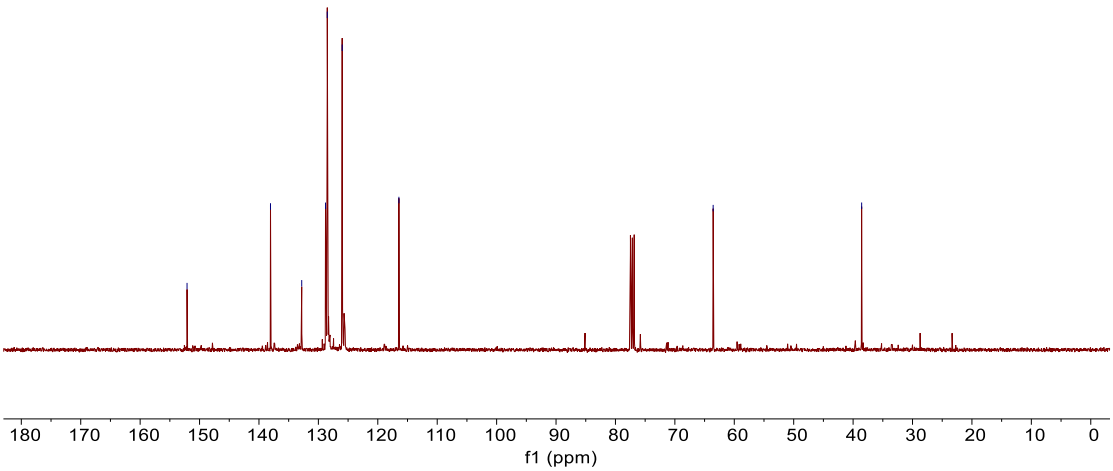

Int C

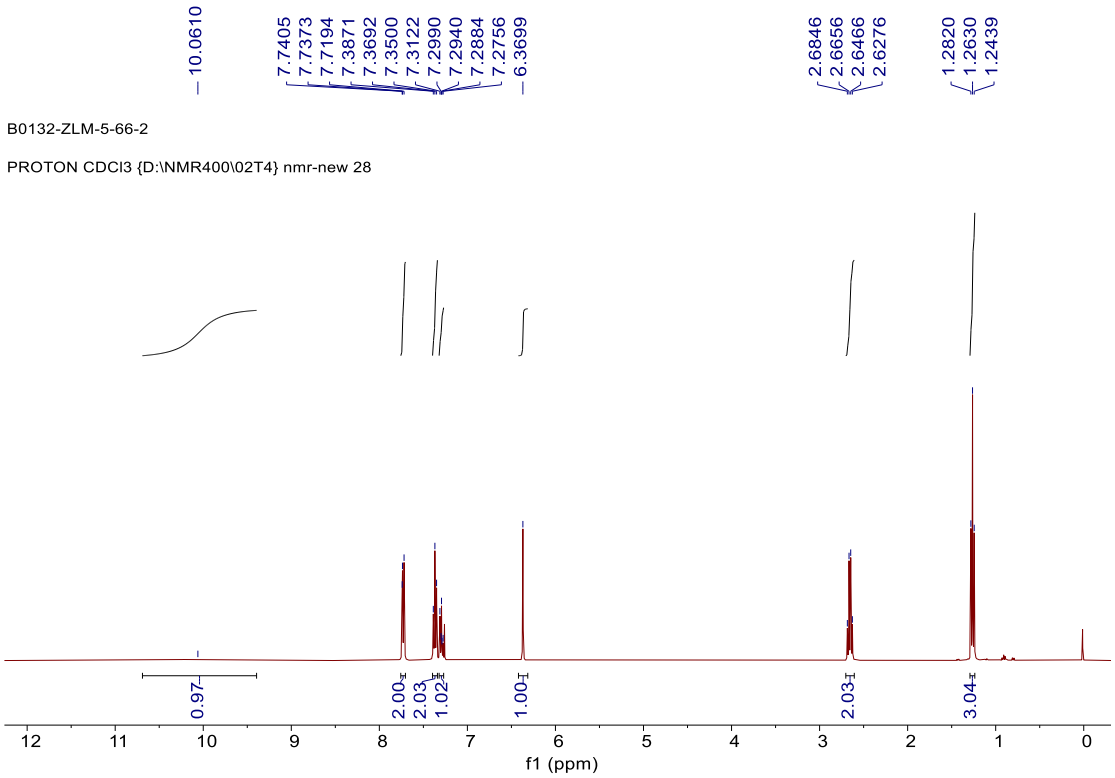
**$^{1}$H NMR (700 MHz, $CDCl_3$)**

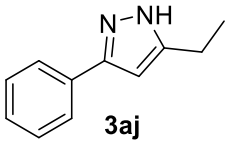
**$^{13}$C NMR (100 MHz, $CDCl_3$)**


B0160-ZLM-5-66

C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 24



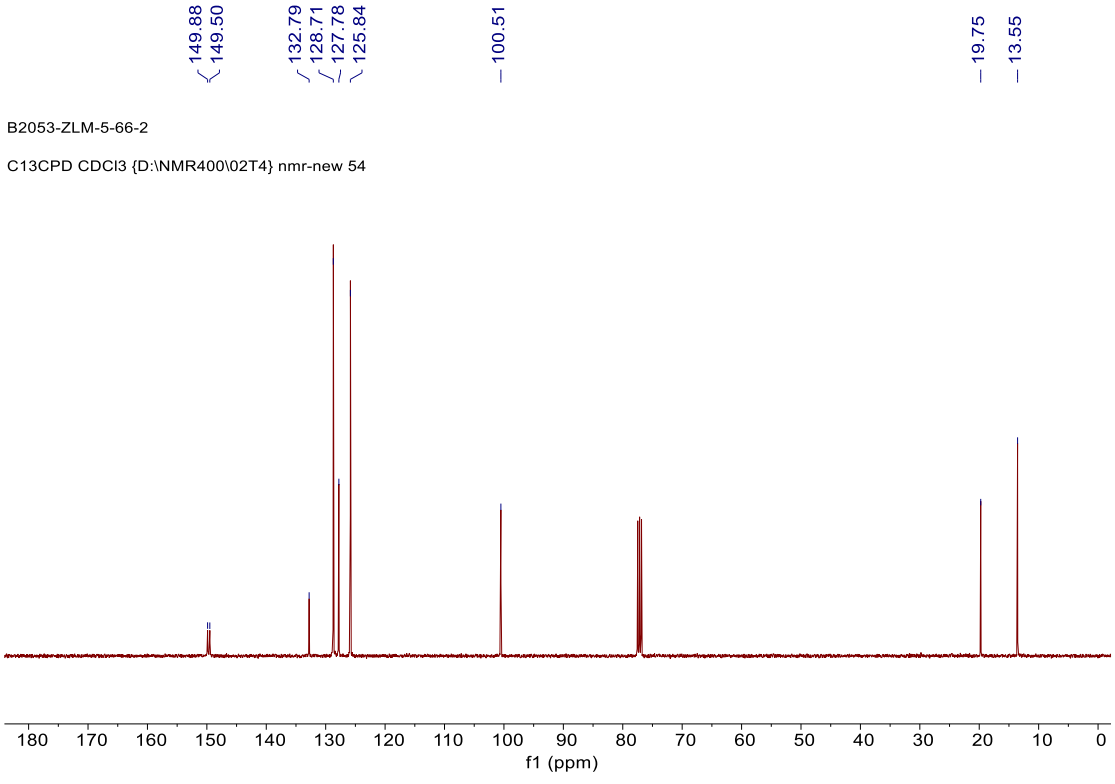


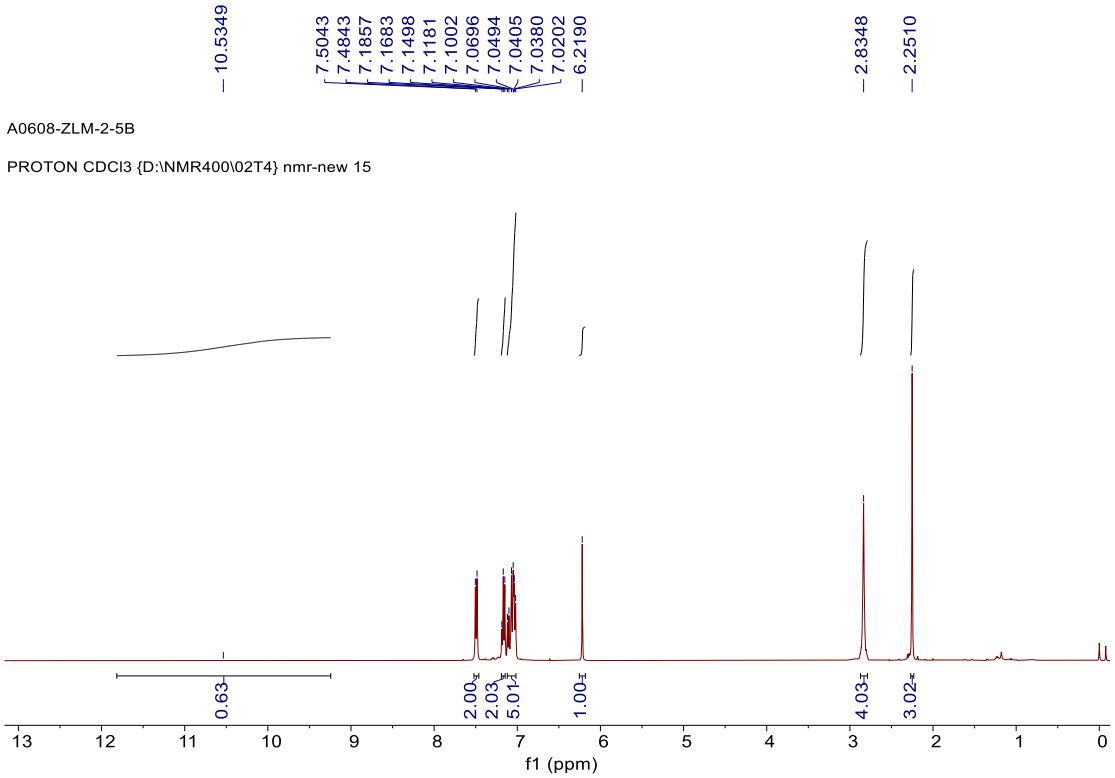



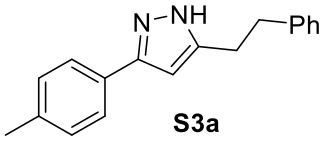

3aj

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**



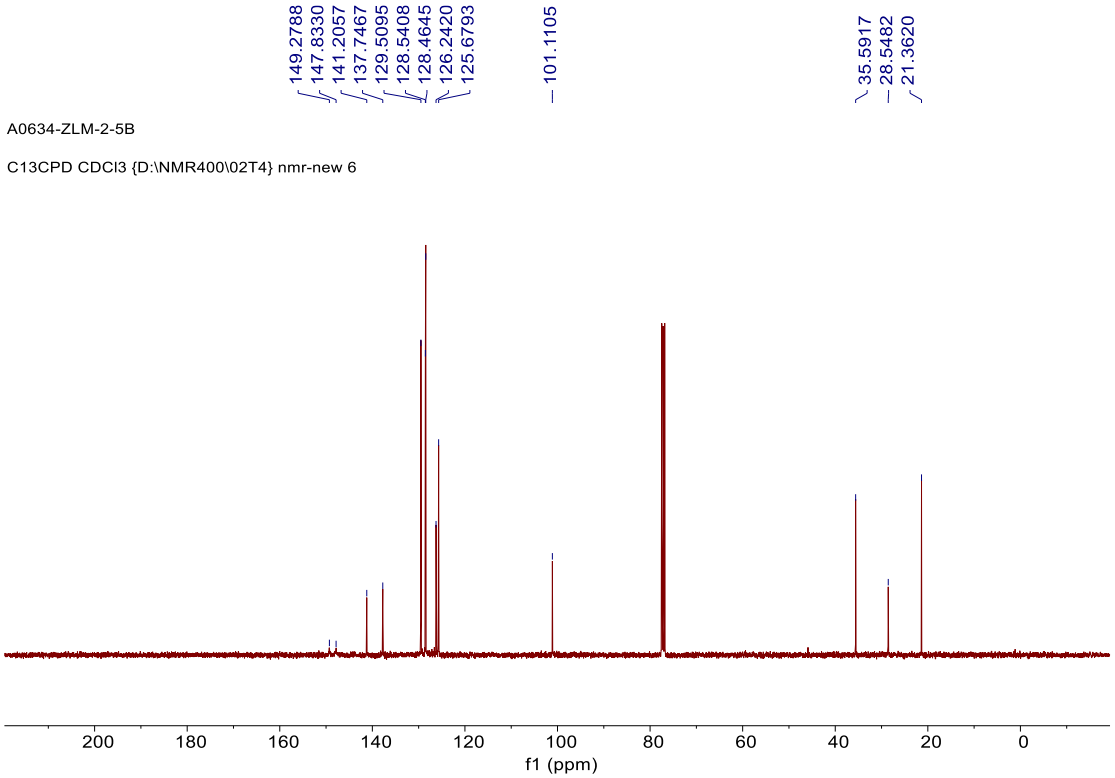


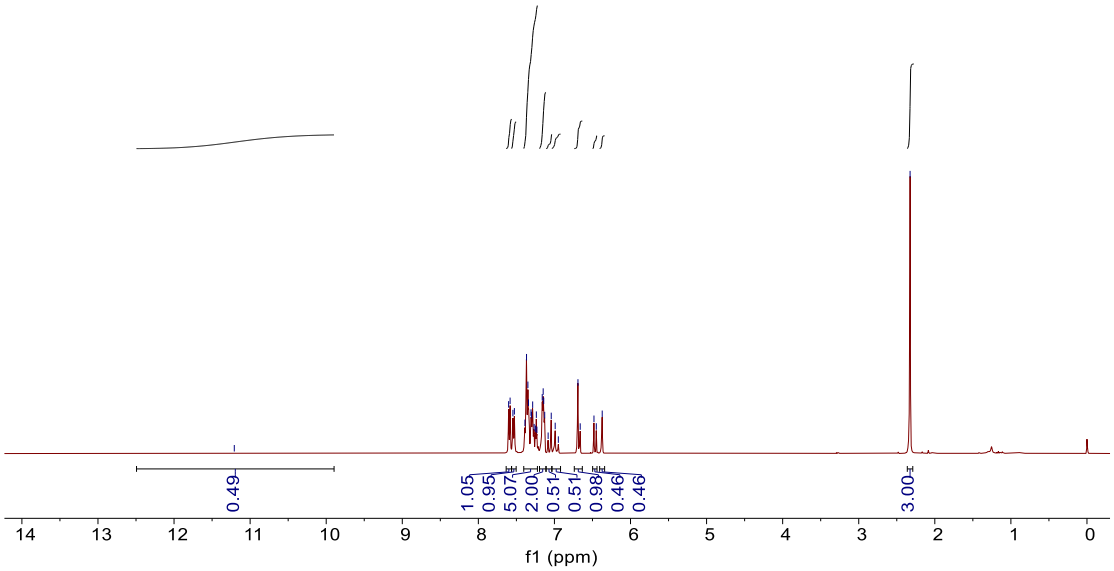

**S3a**

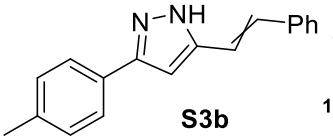
**$^{1}$H NMR (400 MHz, $CDCl_3$)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**




B3858-ZLM-2-5C.10.1.1r
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 25




S3b

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

**$^{13}$C NMR (176 MHz, $CDCl_3$)**


8964-ZLM-2-5C.13.1.1r