**Supporting Information for**

# Gold-Catalyzed formation of aryl-fused pyrazolooxazepines *via* intramolecular regioselective *7-exo-dig* cyclization†

**Ravinder Guduru,[a,b,c] N. S. V. M. Rao Mangina,[a,b,c] Balasubramanian Sridhar,[d] and Galla V. Karunakar*[a,b]**

[a]Division of Fluoro and Agrochemicals, CSIR-Indian Institute of Chemical Technology, Hyderabad, 500007, India.

[b]Academy of Scientific and Innovative Research, Ghaziabad- 201002, India.

[c]Authors contributed equally.

[d]Center for X-ray Crystallography, CSIR-Indian Institute of Chemical Technology, Hyderabad, 500007, India.

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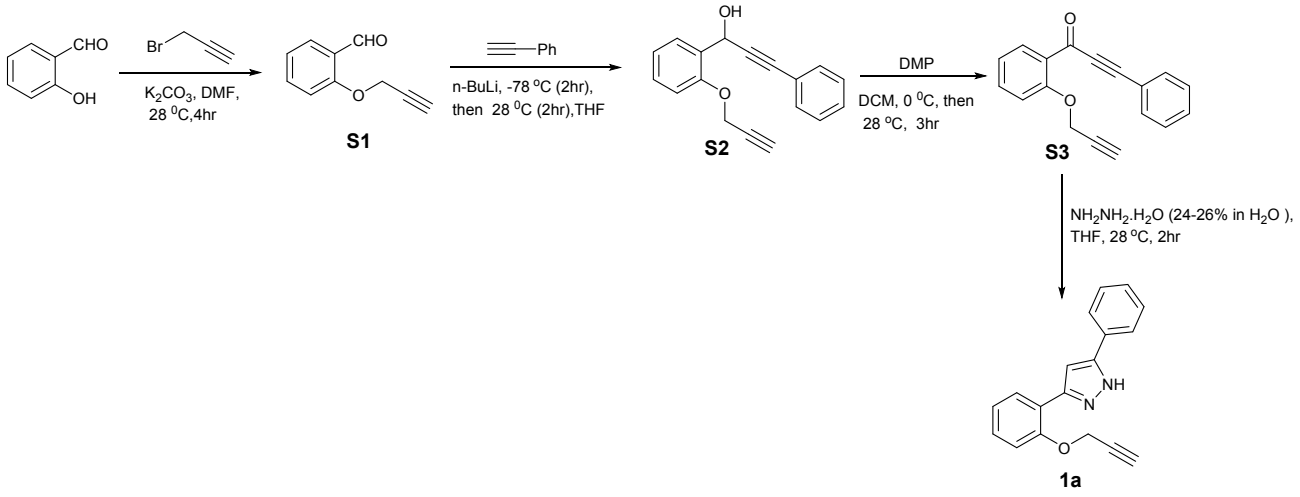
## 1.1 General

Reactions were carried out in oven dried reaction flasks under nitrogen atmosphere and also solvents and reagents were transferred by oven-dried syringes to ambient temperature. TLC was performed on Merck silica gel aluminium sheets using UV as a visualizing agent and a 0.5% aqueous potassium permanganate solution and heat as developing agents. Solvents were removed under reduced pressure. Columns were packed as slurry of silica gel in hexane and ethyl acetate solvent mixture. The elution was assisted by applying pressure with an air pump. $^{13}C$ NMR spectra were recorded on 75 and 125 MHz spectrometers. $^{1}HNMR$ spectra were recorded on 300 MHz and 500 MHz spectrometers in appropriate solvents using TMS as internal standard. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, dd = double doublet, t = triplet, m = multiplet. All reactions were performed under nitrogen atmosphere with freshly distilled and dried solvents. All solvents were distilled using standard procedures. Unless otherwise noted, reagents were obtained from Aldrich, Alfa Aesar, and TCI used without further purification. Synthesis of aryl-fused pyrazolooxazepines **(1a-1ab)** were prepared by following reported procedures.[1]

## 1.2 General procedure for synthesis of *ortho-O*-propargyl aryl pyrazoles (1a-1aa).

1.2.1 Synthesis of 5-phenyl-3-(2-(prop-2-yn-1-yloxy)phenyl)-1*H*-pyrazole-**1a**



Procedure for synthesis of 2-(prop-2-yn-1-yloxy)benzaldehyde - **S1**

To a stirred solution of 2-hydroxy benzaldehyde (1g, 8.19 mmol) in DMF (20 mL) added potassium carbonate (1.69g, 12.29 mmol) under nitrogen atmosphere. Resulting solution was stirred for 15min., to this reaction mixture propargyl bromide (1.2mL, 10.65 mmol) was added dropwise and stirred for 4hrs at 28 $^{o}$C. After completion of reaction (monitored by TLC), it was quenched by ice water (20 mL) and extracted with ethyl acetate (2x25 mL). The organic layer was washed with brine solution (20 mL) and dried over anhydrous $Na_2SO_4$. The combined organic layer was evaporated under reduced pressure to afford a crude residue. The crude product was purified on $SiO_2$ (100-200 mesh) using hexane/EtOAc mixture (94:6) as eluents to afford the pure 2-(prop-2-yn-1-yloxy)benzaldehyde (**S1**) as white solid (1.15g, 88% yield).

Procedure for synthesis of 3-phenyl-1-(2-(prop-2-yn-1-yloxy)phenyl)prop-2-yn-1-ol - **S2**

To a 50 mL round-bottomed flask equipped with magnetic stir bar added THF (20 mL) and allowed to stirred at -78 $^{o}$C. n-Butyl lithium (2.5M) (3.3 mL, 8.25 mmol) was added dropwise under nitrogen atmosphere . To this reaction mixture phenyl acetylene (0.9 mL, 8.25 mmol) was added dropwise and the reaction mixture stirred at -78 $^{o}$C for 2hrs. To this reaction mixture **S1** (1.1g, 6.87 mmol) was added, the resulting reaction mixture allowed to stir at 28 $^{o}$C for 2hrs. After completion of reaction (monitored by TLC), it was quenched by ice water (10 mL) and the reaction mixture was extracted with ethyl acetate (2x25 mL). The combined organic layer was washed with brine solution (20 mL) and dried over anhydrous $Na_2SO_4$ . The solution was concentrated under reduced pressure and the crude residue was purified by silica gel flash column chromatography (Hexane/EtOAc mixture = 90:10), affording 3-phenyl-1-(2-(prop-2-yn-1-yloxy)phenyl)prop-2-yn-1-ol (**S2**) as Yellow liquid (1.33g, 74 % yield).

Procedure for synthesis of 3-phenyl-1-(2-(prop-2-yn-1-yloxy) phenyl) prop-2-yn-1-one - **S3**

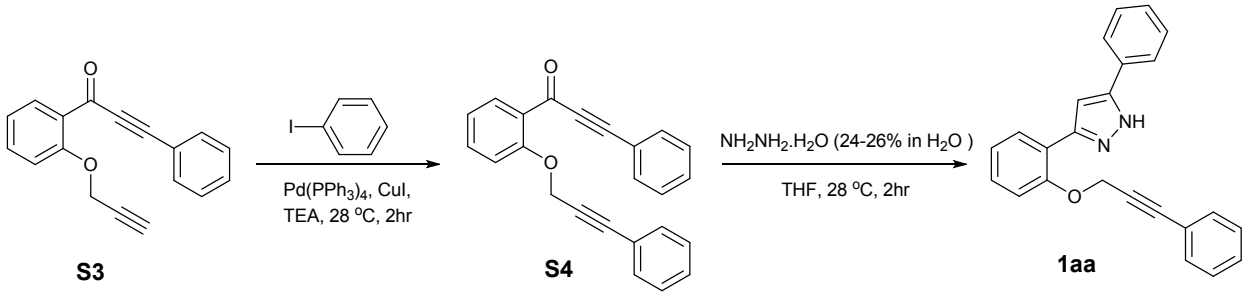
To a solution of 3-phenyl-1-(2-(prop-2-yn-1-yloxy) phenyl) prop-2-yn-1-ol (**S2**) (1.2g, 4.58 mmol) in DCM (20 mL) added DMP (2.52g, 5.95 mmol) at 0 $^{o}$C. Then the reacton mixture warmed to room temperature (28 $^{o}$C) and stirred for 3hrs. After completion of the reaction (monitored by TLC), reaction mixture was quenched by 10% sodium thiosulphate solution (10 mL) and saturated sodium bicarbonate solution (10 mL) (to neutralize the reaction mixture ). Then the organic layer was extracted with DCM (2x25 mL) and washed with brine solution (20 mL). The organic layer was dried over anhydrous $Na_2SO_4$ and solvent was evaporated under reduced pressure to afford a crude residue. The crude residue was purified by silica gel flash column chromatography (Hexane/EtOAc mixture = 95:5), affording 3-phenyl-1-(2-(prop-2-yn-1-yloxy) phenyl) prop-2-yn-1-one (**S3**) as Yellow solid (0.84g, 71% yield).

Procedure for synthesis of 5-phenyl-3-(2-(prop-2-yn-1-yloxy) phenyl)-1*H*-pyrazole - **1a**

To a solution of 3-phenyl-1-(2-(prop-2-yn-1-yloxy) phenyl) prop-2-yn-1-one (**S3**) (0.8g, 3.07 mmol) in THF (8 mL) added hydrazine hydrate solution (0.67 mL, 3.38 mmol). Then the reaction mixture was stirred at 28 $^{o}$C for 2hrs. After completion of the reaction (monitored by TLC), reaction mixture was extracted with ethyl acetate (2x25 mL) and dried over anhydrous $Na_2SO_4$. The solvent was evaporated under reduced pressure to afford a crude residue and purified by silica gel flash column chromatography (Hexane/EtOAc mixture = 90:10), affording, 5-phenyl-3-(2-(prop-2-yn-1-yloxy) phenyl)-1*H*-pyrazole (**1a**) as light Yellow solid (0.72g,

85% yield). The above similar synthetic procedure was followed for the synthesis of the starting materials **1b - 1z.**

1.2.2 General procedure for synthesis of 5-phenyl-3-(2-((3-phenylprop-2-yn-1-yl)oxy)phenyl)-1*H*-pyrazole - **1aa**




Procedure for synthesis of 3-phenyl-1-(2-((3-phenylprop-2-yn-1-yl)oxy)phenyl)prop-2-yn-1-one - **S4**

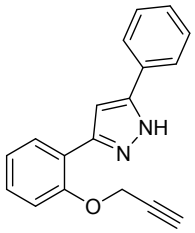
To a solution of 3-phenyl-1-(2-(prop-2-yn-1-yloxy) phenyl) prop-2-yn-1-one (**S3**) (0.5g, 1.92 mmol) in triethyl amine (5 mL) added iodobenzene (0.26 mL, 2.3 mmol). To this reaction mixture tetrakis(triphenylphosphine)palladium(0) (0.044g, 0.038 mmol) and copper iodide (0.014g, 0.076 mmol) was added. The resulting reaction mixture was stirred at room temperature (28 °C) for 2hrs. After completion of the reaction (monitored by TLC), reaction mixture was extracted with ethyl acetate (2x5 mL). Then the organic layer was washed with ice water and brine solution (10 mL). The comboined organic layer was dried over anhydrous $Na_2SO_4$ and solvent was evaporated under reduced pressure to afford a crude residue. The crude residue was purified by silica gel flash column chromatography (Hexane/EtOAc mixture = 94:6), afford the desired 3-phenyl-1-(2-((3-phenylprop-2-yn-1-yl)oxy)phenyl)prop-2-yn-1-one (**S4**) as brown liquid (0.41g, 64% yield).

Procedure for synthesis of 5-phenyl-3-(2-((3-phenylprop-2-yn-1-yl)oxy)phenyl)-1*H*-pyrazole - **1aa**

To a solution of 3-phenyl-1-(2-((3-phenylprop-2-yn-1-yl)oxy)phenyl)prop-2-yn-1-one (**S4**) (0.4g, 1.19 mmol) in THF (4 mL) added hydrazine hydrate solution (0.26 mL, 1.309 mmol). Then the reaction mixture was stirred at 28 °C for 2hrs. After completion of the reaction (monitored by TLC), reaction mixture was extracted with ethyl acetate (2x5 mL) and dried over anhydrous $Na_2SO_4$. The solvent was evaporated under reduced pressure to afford a crude residue and purified by silica gel flash column chromatography (Hexane/EtOAc mixture = 91:9), affording, 5-phenyl-3-(2-((3-phenylprop-2-yn-1-yl)oxy)phenyl)-1*H*-pyrazole (**1aa**) as yellow solid (0.35g, 84% yield). A similar procedure was followed for the synthesis of substrate **1ab**.

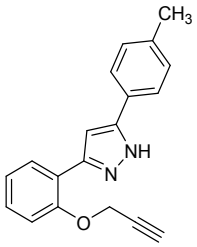
**1.3 Spectroscopic data of *ortho-O*-propargyl aryl pyrazole derivatives (1a-1ab).**

5-Phenyl-3-(2-(prop-2-yn-1-yloxy)phenyl)-1*H*-pyrazole : **1a**



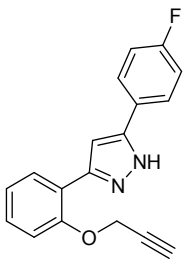
$R_f$: 0.45; Hexane: Ethyl acetate mixture (10 : 1); Yield: 85%, light Yellow solid; Melting Point: 84-86 °C; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.89-7.86 (m, 2H), 7.78-7.75 (m, 1H), 7.45-7.41 (m, 2H), 7.35-7.31 (m, 2H), 7.14-7.10 (m, 2H), 6.97 (s, 1H), 4.87 (d, $J$ = 2.4 Hz, 2H), 2.61 (t, $J$ = 2.4 Hz, 1H) ppm; $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 153.8, 151.3, 141.7, 133.2, 129.1, 128.6, 128.2, 127.7, 125.6, 122.3, 118.3, 113.0, 100.2, 77.6, 76.6, 56.5 ppm.

3-(2-(Prop-2-yn-1-yloxy)phenyl)-5-(p-tolyl)-1*H*-pyrazole : **1b**



$R_f$: 0.65; Hexane: Ethyl acetate mixture (10 : 0.7); Yield: 87%, Yellow liquid; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.78-7.74 (m, 3H), 7.33-7.28 (m, 1H), 7.25-7.22 (d, $J$ = 7.8 Hz, 2H), 7.12-7.07 (d, $J$ = 8.4 Hz, 2H), 6.93 (s, 1H), 4.83 (d, $J$ = 2.4 Hz, 2H), 2.59 (t, $J$ = 2.4 Hz, 1H),2.38 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 153.8, 151.3, 141.7, 137.4, 130.4, 129.3, 129.0, 128.2, 125.5, 122.3, 118.4, 113.0, 100.0, 77.6, 76.6, 56.5, 21.2 ppm.

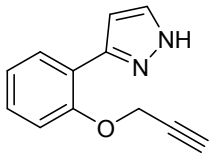
5-(4-Fluorophenyl)-3-(2-(prop-2-yn-1-yloxy)phenyl)-1*H*-pyrazole : **1c**



$R_f$: 0.5; Hexane: Ethyl acetate mixture (10 : 0.6); Yield: 78%, white solid; Melting Point: 133-135 °C; $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ 7.86-7.82 (m, 2H), 7.75-7.73 (m, 1H), 7.35-7.31 (m,

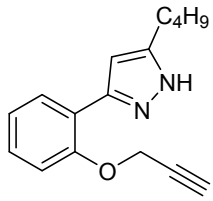
1H), 7.13-7.09 (m, 4H), 6.90 (s, 1H), 4.85 (d, $J$ = 2.4 Hz, 2H), 2.61 (t, $J$ = 2.4 Hz, 1H) ppm; $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 162.5 (d, $J$ = 246.488 Hz, 1C), 153.8, 150.6, 141.7, 129.6, 129.5, 129.2, 128.1, 127.2 (d, $J$ = 8.070 Hz, 1C), 122.4, 118.1, 115.5 (d, $J$ = 22.008 Hz, 2C), 113.0, 99.9, 77.5, 76.7, 56.6 ppm.

3-(2-(Prop-2-yn-1-yloxy)phenyl)-1*H*-pyrazole : **1d**



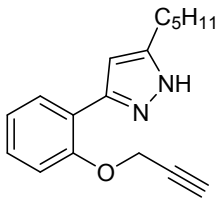

$R_f$: 0.7; Hexane: Ethyl acetate mixture (10 : 0.7); Yield: 63%, Colorless liquid; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.73-7.70 (dd, $J$ = 7.7, 9.4 Hz, 1H), 7.62 (d, $J$ = 1.9 Hz, 1H), 7.33-7.28 (m, 1H), 7.12-7.07 (m, 2H), 6.67 (d, $J$ = 1.9 Hz, 1H), 4.85 (d, $J$ = 2.3 Hz, 2H), 2.60-2.58 (t, $J$ = 2.3 Hz, 1H) ppm; $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 153.7, 140.7, 138.7, 128.9, 128.2, 122.2, 118.6, 112.9, 103.2, 77.6, 76.5, 56.4 ppm.

5-Butyl-3-(2-(prop-2-yn-1-yloxy)phenyl)-1*H*-pyrazole : **1e**




$R_f$: 0.45; Hexane: Ethyl acetate mixture (10 : 0.6); Yield: 81%, Yellow liquid; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.70-7.67 (m, 1H), 7.31-7.27 (m, 1H), 7.10-7.05 (m, 2H), 6.47 (s, 1H), 4.83 (d, $J$ = 2.3 Hz, 2H), 2.69 (t, $J$ = 7.7 Hz, 2H), 2.58 (t, $J$ = 2.3 Hz, 1H), 1.73-1.65 (m, 2H), 1.47-1.37 (m, 2H), 0.95 (t, $J$ = 7.3 Hz, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 153.8, 128.7, 128.2, 122.2, 119.0, 112.9, 102.0, 77.7, 76.4, 56.5, 31.7, 27.6, 22.4, 13.9 ppm.

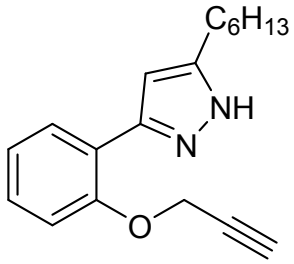
5-Pentyl-3-(2-(prop-2-yn-1-yloxy)phenyl)-1*H*-pyrazole : **1f**




$R_f$: 0.4; Hexane: Ethyl acetate mixture (10 : 0.9); Yield: 65%, white solid; Melting Point: 80-82 °C; $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ 7.70-7.68 (m, 1H), 7.30-7.27 (m, 1H), 7.09-7.06 (m, 2H),

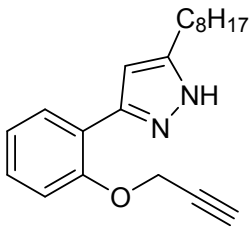
6.46 (s, 1H), 4.83 (d, $J$ = 2.4 Hz, 2H), 2.68 (t, $J$ = 7.7 Hz, 2H), 2.58 (t, $J$ = 2.4 Hz, 1H), 1.74-1.68 (m, 2H), 1.40-1.35 (m, 4H), 0.91 (t, $J$ = 7.3 Hz, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 153.8, 152.5, 141.4, 128.7, 128.1, 122.2, 119.0, 112.9, 102.0, 77.7, 76.4, 56.4, 31.5, 29.2, 27.8, 22.4, 14.0 ppm.

5-Hexyl-3-(2-(prop-2-yn-1-yloxy)phenyl)-1*H*-pyrazole : **1g**



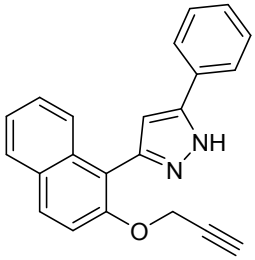

$R_f$: 0.3; Hexane: Ethyl acetate mixture (10 : 0.8); Yield: 73%, Yellow liquid; $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 7.72-7.66 (m, 1H), 7.33-7.27 (m, 1H), 7.12-7.04 (m, 2H), 6.46 (s, 1H), 4.84 (d, $J$ = 2.4 Hz, 2H), 2.68 (t, $J$ = 7.7 Hz, 2H), 2.58 (t, $J$ = 2.4 Hz, 1H), 1.75-1.64 (m, 2H), 1.43-1.30 (m, 6H), 0.89 (t, $J$ = 6.9 Hz, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 153.8, 152.5, 141.3, 128.7, 128.2, 122.2, 119.0, 113.0, 102.0, 77.7, 76.4, 56.5, 31.6, 29.5, 29.1, 27.9, 22.5, 14.0 ppm.

5-Octyl-3-(2-(prop-2-yn-1-yloxy)phenyl)-1*H*-pyrazole : **1h**



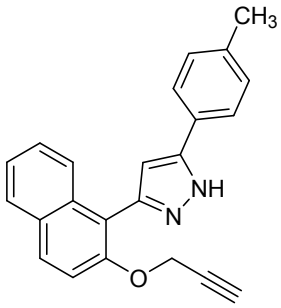

$R_f$: 0.4; Hexane: Ethyl acetate mixture (10 : 0.8); Yield: 76%, white solid; Melting Point: 67-69 °C; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.70-7.67 (m, 1H), 7.31-7.27 (m, 1H), 7.09-7.05 (m, 2H), 6.46 (s, 1H), 4.82 (d, $J$ = 2.4 Hz, 2H), 2.68 (t, $J$ = 7.7 Hz, 2H), 2.58 (t, $J$ = 2.4 Hz, 1H), 1.74-1.66 (m, 2H), 1.43-1.22 (m, 10H), 0.88 (t, $J$ = 7.3 Hz, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 153.8, 152.6, 141.3, 128.7, 128.1, 122.2, 119.0, 112.9, 101.9, 77.7, 76.4, 56.5, 31.8, 29.5, 29.4, 29.2, 27.9, 22.6, 14.0 ppm.

5-Phenyl-3-(2-(prop-2-yn-1-yloxy)naphthalen-1-yl)-1*H*-pyrazole : **1i**



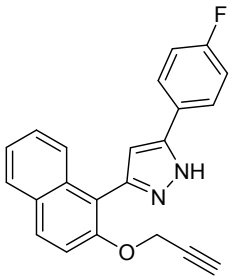

$R_f$: 0.5; Hexane: Ethyl acetate mixture (10 : 0.6); Yield: 62%, Yellow semi solid; $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ 8.04 (d, $J$ = 8.5 Hz, 1H), 7.92 (d, $J$ = 9.0 Hz, 1H), 7.90-7.88 (m, 2H), 7.85 (d, $J$ = 7.6 Hz, 1H), 7.49-7.40 (m, 5H), 7.36-7.32 (m, 1H), 6.87 (s, 1H), 4.78 (d, $J$ = 2.4 Hz, 2H), 2.50 (t, $J$ = 2.4 Hz, 1H) ppm; $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 152.8, 150.7, 138.9, 133.0, 132.9, 130.6, 129.6, 128.6, 128.0, 127.7, 127.2, 125.6, 124.9, 124.5, 115.2, 114.9, 105.1, 78.5, 76.1, 57.4 ppm.

3-(2-(Prop-2-yn-1-yloxy)naphthalen-1-yl)-5-(p-tolyl)-1*H*-pyrazole : **1j**



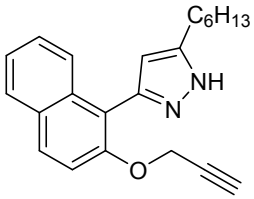

$R_f$: 0.3; Hexane: Ethyl acetate mixture (10 : 0.8); Yield: 70%, light yellow solid; Melting Point: 172-174 °C; $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ 8.04 (d, $J$ = 8.3 Hz, 1H), 7.90 (d, $J$ = 9.0 Hz, 1H), 7.83 (d, $J$ = 7.7 Hz, 1H), 7.75 (d, $J$ = 7.4 Hz, 2H), 7.47-7.38 (m, 3H), 7.21 (d, $J$ = 7.0 Hz, 2H), 6.82 (s, 1H), 4.74 (s, 2H), 2.48 (s, 1H), 2.38 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 152.8, 150.6, 139.0, 137.5, 133.0, 130.5, 130.0, 129.6, 129.3, 128.0, 127.2, 125.5, 125.0, 124.5, 115.2, 104.9, 78.5, 76.1, 57.4, 21.2 ppm.

5-(4-Fluorophenyl)-3-(2-(prop-2-yn-1-yloxy)naphthalen-1-yl)-1*H*-pyrazole : **1k**



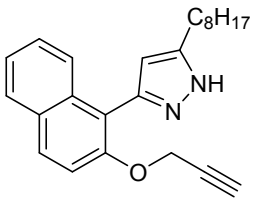

$R_f$: 0.4; Hexane: Ethyl acetate mixture (10 : 0.8); Yield: 66%, white solid; Melting Point: 189-191 °C; $^1$H NMR ($CDCl_3$+DMSO, 300 MHz): $\delta$ 12.48 (s, 1H), 7.96-7.83 (m, 5H), 7.53-7.49 (m, 1H), 7.47-7.37 (m, 2H), 6.73 (s, 1H), 4.79 (d, $J$ = 2.2 Hz, 2H), 2.66 (t, $J$ = 2.2 Hz, 1H) ppm; $^{13}$C NMR ($CDCl_3$+DMSO,75 MHz): $\delta$ 161.5 (d, $J$ = 245.930 Hz, 1C), 152.5, 132.8, 129.7, 128.8, 127.3, 126.5 (d, $J$ = 7.703 Hz, 1C), 126.3, 124.4, 123.7, 114.7 (d, $J$ = 20.907 Hz, 2C), 103.8, 78.2, 75.7, 56.8 ppm.

5-Hexyl-3-(2-(prop-2-yn-1-yloxy)naphthalen-1-yl)-1*H*-pyrazole : **1l**




$R_f$: 0.4; Hexane: Ethyl acetate mixture (10 : 2); Yield: 91%, Yellow liquid; $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ 7.94 (d, $J$ = 8.3 Hz, 1H), 7.86 (d, $J$ = 9.0 Hz, 1H), 7.80 (d, $J$ = 8.5 Hz, 1H), 7.44-7.36 (m, 3H), 6.30 (s, 1H), 4.71 (d, $J$ = 2.2 Hz, 2H), 2.65 (t, $J$ = 7.6 Hz, 2H), 2.47 (t, $J$ = 2.2 Hz, 1H), 1.72-1.65 (m, 2H), 1.40-1.34 (m, 2H), 1.33-1.28 (m, 4H), 0.90 (t, $J$ = 7.0 Hz, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 152.8, 150.4, 140.0, 133.3, 130.1, 129.7, 127.9, 126.8, 125.2, 124.3, 115.6, 106.2, 78.7, 75.8, 57.5, 31.6, 29.2, 29.1, 27.3, 22.5, 14.0 ppm.

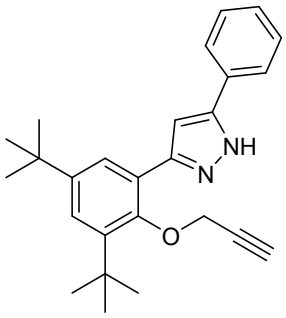
5-Octyl-3-(2-(prop-2-yn-1-yloxy)naphthalen-1-yl)-1*H*-pyrazole : **1m**




$R_f$: 0.3; Hexane: Ethyl acetate mixture (10 : 0.9); Yield: 87%, brown liquid; $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ 7.95 (d, $J$ = 8.3 Hz, 1H), 7.87 (d, $J$ = 9.0 Hz, 1H), 7.81 (d, $J$ = 7.9 Hz, 1H), 7.44-7.36 (m, 3H), 6.30 (s, 1H), 4.71 (d, $J$ = 2.4 Hz, 2H), 2.67 (t, $J$ = 7.6 Hz, 2H), 2.47 (t, $J$ = 2.4 Hz, 1H), 1.73-1.66 (m, 2H), 1.41-1.27 (m, 10H), 0.89 (t, $J$ = 7.0 Hz, 3H) ppm; $^{13}$C NMR ($CDCl_3$,

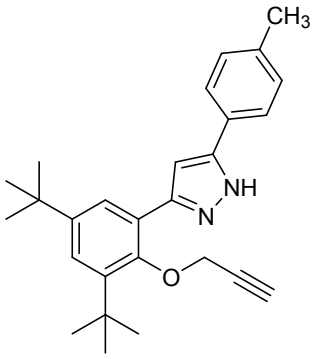
100 MHz): $\delta$ 152.8, 150.6, 139.9, 133.3, 130.1, 129.7,127.9, 126.9, 125.2, 124.3, 115.5, 106.3, 78.7, 75.8, 57.5, 31.8, 29.4, 29.3, 29.2, 27.4, 22.6, 14.0 ppm.

3-(3,5-Di-tert-butyl-2-(prop-2-yn-1-yloxy)phenyl)-5-phenyl-1*H*-pyrazole : **1n**



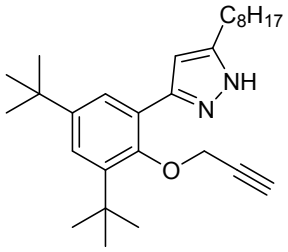

$R_f$: 0.4; Hexane: Ethyl acetate mixture (10 : 0.9); Yield: 59%, light Yellow solid; Melting Point: 151-153 °C; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.8 (d, $J$ = 7.3 Hz, 2H), 7.46-7.38 (m, 4H), 7.33(t, $J$ = 7.3 Hz, 1H), 6.90 (s, 1H), 4.24 (d, $J$ = 2.2 Hz, 2H), 2.50 (t, $J$ = 2.2 Hz, 1H), 1.48 (s, 9H), 1.34 (s, 9H) ppm; $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 152.2, 151.0, 147.2, 143.0, 132.7, 128.6, 127.8, 125.6, 125.0, 124.8, 123.4, 101.6, 78.5, 75.4, 60.7, 35.4, 34.6, 31.3, 31.0 ppm.

3-(3,5-Di-tert-butyl-2-(prop-2-yn-1-yloxy)phenyl)-5-(p-tolyl)-1*H*-pyrazole : **1o**



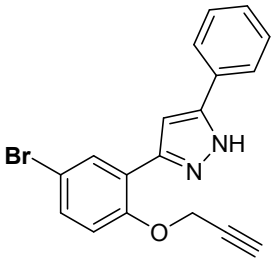

$R_f$: 0.5; Hexane: Ethyl acetate mixture (10 : 0.9); Yield: 71%, Yellow solid; Melting Point: 173-175 °C; $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ 7.76 (d, $J$ = 8.1 Hz, 2H), 7.43-7.38 (m,2H), 7.24 (d, $J$ = 7.9 Hz, 2H), 6.87 (s, 1H), 4.24 (d, $J$ = 2.4 Hz, 2H), 2.49 (t, $J$ = 2.4 Hz, 1H), 2.39 (s, 3H), 1.48 (s, 9H), 1.34(s, 9H) ppm; $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 152.2, 147.1, 143.0, 137.7, 129.7, 129.3, 125.5, 125.0, 124.7, 101.5, 78.6, 75.3, 60.8, 35.4, 34.6, 31.4, 31.0, 21.2 ppm.

3-(3,5-Di-tert-butyl-2-(prop-2-yn-1-yloxy)phenyl)-5-octyl-1*H*-pyrazole : **1p**



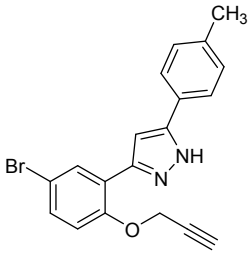

$R_f$: 0.4; Hexane: Ethyl acetate mixture (10 : 0.8); Yield: 68%, brown liquid; $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ 7.38 (d, $J$ = 2.4 Hz, 1H), 7.35 (d, $J$ = 2.4 Hz, 1H), 6.43 (s, 1H), 4.19 (d, $J$ = 2.4 Hz, 2H), 2.69 (t, $J$ = 7.6 Hz, 2H), 2.48 (t, $J$ = 2.4 Hz, 1H), 1.74-1.68 (m, 2H), 1.46 (s, 9H), 1.44-1.35 (m, 4H), 1.32 (s, 9H), 1.31-1.27 (m, 6H), 0.88 (t, $J$ = 7.0 Hz, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 152.3, 146.8, 142.7, 124.8, 124.5,123.7, 106.3, 103.2, 99.1, 78.8, 74.9, 60.4, 35.3, 35.1, 34.5, 31.8, 31.4, 31.0, 30.2, 29.2, 28.3, 27.4, 22.6, 14.0 ppm.

3-(5-Bromo-2-(prop-2-yn-1-yloxy)phenyl)-5-phenyl-1*H*-pyrazole : **1q**




$R_f$: 0.3; Hexane: Ethyl acetate mixture (10 : 1); Yield: 78%, white semi solid; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.89-7.83 (m, 3H), 7.45-7.38 (m, 3H), 7.36-7.31 (m, 1H), 6.98 (d, $J$ = 8.8 Hz, 1H), 6.95 (s, 1H), 4.82 (d, $J$ = 2.4 Hz, 2H), 2.61 (t, $J$ = 2.4 Hz, 1H) ppm; $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 152.8, 151.0, 140.7, 132.8, 131.5, 130.7, 128.6, 127.9, 125.6, 120.6, 114.8, 114.7, 100.9, 77.1, 76.9, 56.8 ppm.

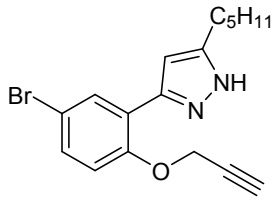
3-(5-Bromo-2-(prop-2-yn-1-yloxy)phenyl)-5-(p-tolyl)-1*H*-pyrazole : **1r**




$R_f$: 0.45; Hexane: Ethyl acetate mixture (10 : 0.9); Yield: 77%, Yellow solid; Melting Point: 106-108°C; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.87 (d, $J$ = 2.4 Hz, 1H), 7.73 (d, $J$ = 8.0 Hz, 2H), 7.41-7.37 (m, 1H), 7.24 (d, $J$ = 7.9 Hz, 2H), 6.97(d, $J$ = 8.8 Hz, 1H), 6.92 (s, 1H), 4.81 (s, 2H), 2.6 (s,

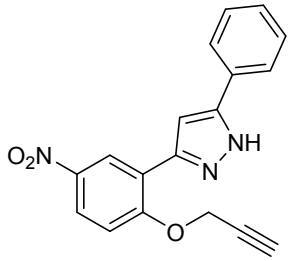
1H), 2.39 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 152.9, 137.7, 131.4, 130.7, 129.9, 129.3, 125.5, 120.7, 114.8, 114.7, 100.7, 77.1, 76.9, 56.8, 21.2 ppm.

3-(5-Bromo-2-(prop-2-yn-1-yloxy)phenyl)-5-pentyl-1*H*-pyrazole : **1s**



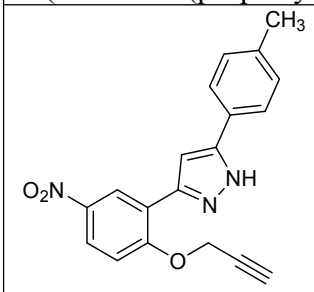

$R_f$: 0.4; Hexane: Ethyl acetate mixture (10 : 1); Yield: 65%, white solid; Melting Point: 109-111 °C; $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ 7.83 (d, $J$ = 2.4 Hz, 1H), 7.37 (dd, $J$ = 2.4, 8.8 Hz, 1H), 6.97 (d, $J$ = 8.8 Hz, 1H), 6.48 (s, 1H), 4.80 (d, $J$ = 2.4 Hz, 2H), 2.68 (t, $J$ = 7.7 Hz, 2H), 2.59 (t, $J$ = 2.4 Hz, 1H), 1.73-1.67 (m, 2H), 1.39-1.34 (m, 4H), 0.91 (t, $J$ = 7.0 Hz, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 152.9, 151.8, 140.9, 131.1, 130.8, 121.5, 114.8, 114.6, 102.7, 77.3, 76.7, 56.7, 31.5, 29.1, 27.6, 22.4, 14.0 ppm.

3-(5-Nitro-2-(prop-2-yn-1-yloxy)phenyl)-5-phenyl-1*H*-pyrazole : **1t**



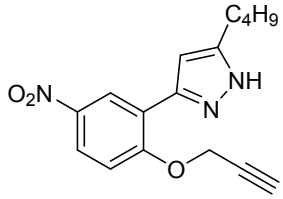

$R_f$: 0.3; Hexane: Ethyl acetate mixture (10 : 2); Yield: 68%, white solid; Melting Point: 171-173 °C; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 8.69 (d, $J$ = 2.8 Hz, 1H), 8.22 (dd, $J$ = 2.8, 9.1 Hz, 1H), 7.85-7.81 (m, 2H), 7.47-7.42 (m, 2H), 7.38-7.34 (m, 1H), 7.21 (d, $J$ = 9.1 Hz, 1H), 7.09 (s, 1H), 4.97 (d, $J$ = 2.3 Hz, 2H), 2.67 (t, $J$ = 2.3 Hz, 1H) ppm; $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 158.0, 150.4, 142.5, 140.9, 132.0, 128.8, 128.2, 125.6, 124.4, 123.9, 120.1, 112.8, 102.0, 77.8, 76.3, 57.2 ppm.

3-(5-Nitro-2-(prop-2-yn-1-yloxy)phenyl)-5-(p-tolyl)-1*H*-pyrazole : **1u**



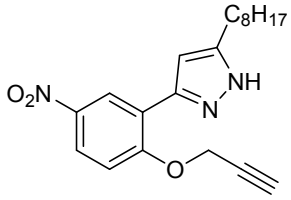
$R_f$: 0.45; Hexane: Ethyl acetate mixture (10 : 0.8); Yield: 73%, Yellow solid; Melting Point: 186-188 °C; $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ 8.68 (s, 1H), 8.22-8.17 (m, 1H), 7.70 (d, $J$ = 7.7 Hz, 2H), 7.25-7.17 (m, 3H), 7.05 (s, 1H), 4.94 (s, 2H), 2.66 (s, 1H), 2.39 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$+DMSO,75 MHz): $\delta$ 158.1, 141.7, 137.2, 129.0, 128.1, 125.0, 123.6, 123.4, 112.3, 102.4, 76.9, 76.7, 56.4, 20.8 ppm

5-Butyl-3-(5-nitro-2-(prop-2-yn-1-yloxy)phenyl)-1*H*-pyrazole : **1v**



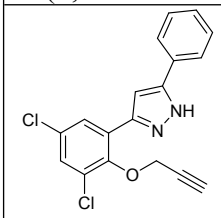
$R_f$: 0.2; Hexane: Ethyl acetate mixture (10 : 2); Yield: 65%, white solid; Melting Point: 125-127 °C; $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ 8.67 (d, $J$ = 2.7 Hz, 1H), 8.18 (dd, $J$ = 2.8, 9.1 Hz, 1H), 7.18 (d, $J$ = 9.1 Hz, 1H), 6.61 (s, 1H), 4.94 (d, $J$ = 2.2 Hz, 2H), 2.71 (t, $J$ = 7.7 Hz, 2H), 2.64 (t, $J$ = 2.2 Hz, 1H), 1.73-1.67(m, 2H), 1.46-1.39 (m, 2H), 0.96 (t, $J$ = 7.3 Hz, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 158.2, 142.3, 124.1, 124.0, 121.4, 112.7, 103.9, 77.4, 77.2, 57.0, 31.4, 26.8, 22.3, 13.8 ppm.

3-(5-Nitro-2-(prop-2-yn-1-yloxy)phenyl)-5-octyl-1*H*-pyrazole : **1w**



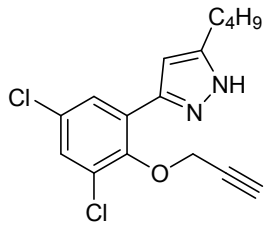
$R_f$: 0.4; Hexane: Ethyl acetate mixture (10 :1.2); Yield: 83%, white solid; Melting Point: 92-94 °C; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 8.67 (d, $J$ = 2.8 Hz, 1H), 8.18 (dd, $J$ = 2.8, 9.1 Hz, 1H), 7.18 (d, $J$ = 9.1 Hz, 1H), 6.61 (s, 1H), 4.93 (d, $J$ = 2.4 Hz, 2H), 2.70 (t, $J$ = 7.7 Hz, 2H), 2.64 (t, $J$ = 2.4 Hz, 1H), 1.75-1.66 (m, 2H), 1.42-1.27 (m, 10H),0.88 (t, $J$ = 7.0 Hz, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 158.2, 142.3, 124.1, 124.0, 121.4, 112.7, 103.8, 77.4, 77.1, 57.0, 31.8, 29.4, 29.3, 29.2, 27.1, 22.6, 14.0 ppm.

3-(3,5-Dichloro-2-(prop-2-yn-1-yloxy)phenyl)-5-phenyl-1*H*-pyrazole : **1x**



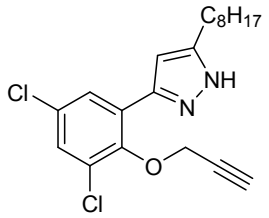
$R_f$: 0.4; Hexane: Ethyl acetate mixture (10 : 0.9); Yield: 74%, white solid; Melting Point: 177-179 °C; $^1$H NMR ($CDCl_3$+DMSO, 300 MHz): $\delta$ 13.38 (s, 1H), 7.85-7.77 (m, 2H), 7.47-7.30 (m, 5H), 7.20 (s, 1H), 4.64 (d, $J$ = 2.2 Hz, 2H), 2.93 (t, $J$ = 2.2 Hz, 1H) ppm; $^{13}$C NMR ($CDCl_3$+DMSO,75 MHz): $\delta$ 147.9, 128.6, 128.3, 127.4, 127.2, 126.6, 125.3, 124.0, 101.6, 77.1, 76.0, 58.9 ppm.

5-Butyl-3-(3,5-dichloro-2-(prop-2-yn-1-yloxy)phenyl)-1*H*-pyrazole : **1y**



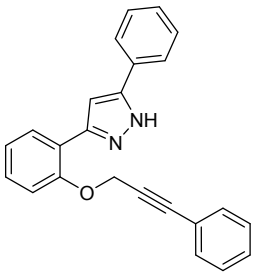
$R_f$: 0.45; Hexane: Ethyl acetate mixture (10 : 0.8); Yield: 80%, light Yellow solid; Melting Point: 83-85 °C; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.66 (d, $J$ = 2.4 Hz, 1H), 7.34 (d, $J$ = 2.4 Hz, 1H), 6.57 (s, 1H), 4.62 (d, $J$ = 2.4 Hz, 2H), 2.70 (t, $J$ = 7.7 Hz, 2H), 2.50 (t, $J$ = 2.4 Hz, 1H), 1.73-1.65 (m, 2H), 1.47-1.37 (m, 2H), 0.95(t, $J$ = 7.3 Hz, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 149.2, 130.5, 129.7, 129.0, 128.5, 103.9, 77.5, 76.4, 60.6, 31.3, 26.4, 22.2, 13.8 ppm.

3-(3,5-Dichloro-2-(prop-2-yn-1-yloxy)phenyl)-5-octyl-1*H*-pyrazole : **1z**



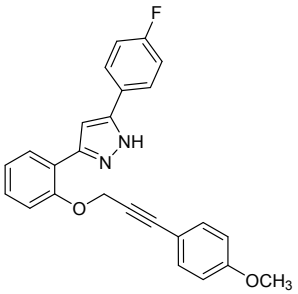
$R_f$: 0.5; Hexane: Ethyl acetate mixture (10 : 1); Yield: 67%, light yellow solid; Melting Point: 56-58 °C; $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ 7.6 (d, $J$ = 2.5 Hz, 1H), 7.33 (d, $J$ = 2.5 Hz, 1H), 6.57 (s, 1H), 4.61 (d, $J$ = 2.4 Hz, 2H), 2.68 (t, $J$ = 7.6 Hz, 2H), 2.49 (t, $J$ = 2.4 Hz, 1H), 1.72-1.65 (m, 2H), 1.43-1.27 (m, 10H), 0.88 (t, $J$ = 7.0 Hz, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 149.2, 142.6, 130.6, 129.7, 129.0, 128.4, 126.9, 103.9, 77.5, 76.5, 60.6, 31.8, 29.6, 29.4, 29.3, 29.2, 26.8, 22.4, 14.0 ppm.

5-Phenyl-3-(2-((3-phenylprop-2-yn-1-yl)oxy)phenyl)-1*H*-pyrazole : **1aa**



$R_f$: 0.45; Hexane: Ethyl acetate mixture (10 : 0.9); Yield: 84%, yellow solid; Melting Point: 134-136 °C; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.89-7.86 (m, 2H), 7.77 (dd, $J$ = 1.7, 7.8 Hz, 1H), 7.46-7.40 (m, 4H), 7.37-7.28 (m, 5H), 7.22-7.19 (m, 1H), 7.14-7.10 (m, 1H), 6.97 (s, 1H), 5.08 (s, 2H) ppm; $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 154.1, 151.3, 141.8, 133.3, 131.8, 129.1, 128.8, 128.5, 128.2, 128.1, 127.6, 125.6, 122.2, 121.8, 118.3, 113.3, 100.2, 88.1, 82.8, 57.5 ppm.

5-(4-Fluorophenyl)-3-(2-((3-(4-methoxyphenyl)prop-2-yn-1-yl)oxy)phenyl)-1*H*-pyrazole : **1ab**

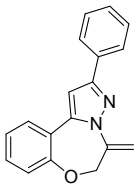


$R_f$: 0.3; Hexane: Ethyl acetate mixture (10 : 1); Yield: 67%, light yellow solid; Melting Point: 141-143 °C; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.86-7.81 (m, 2H), 7.74 (dd, $J$ = 1.7, 7.8 Hz, 1H), 7.41-7.32 (m, 3H), 7.22-7.19 (m, 1H), 7.14-7.08 (m, 3H), 6.91 (s, 1H), 6.86-6.81 (m,2H), 5.08 (s, 2H), 3.81 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 162.5 (d, $J$ = 246.488 Hz, 1C), 160.0, 154.2, 141.9, 133.4, 129.6, 129.2, 128.0, 127.2 (d, $J$ = 8.070 Hz, 1C), 122.1, 118.1, 115.4 (d, $J$ = 22.008 Hz, 2C), 113.9, 113.8, 113.3, 99.9, 88.2, 81.4, 57.6, 55.2 ppm.

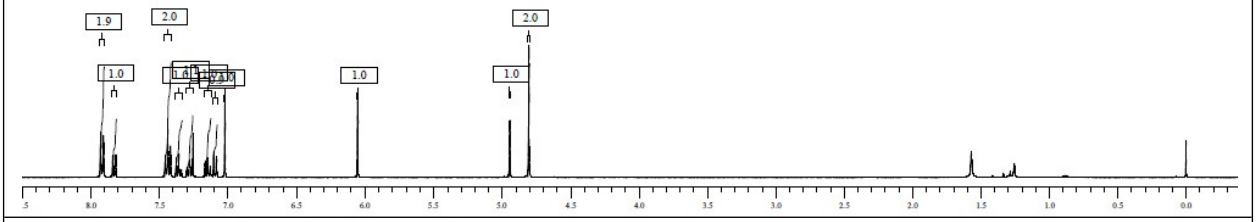
1) (a) H. -L. Liu, H. -F. Jiang, M. Zhang, W. -J.; Yao, Q. -H. Zhu, Z. Tang, *Tetrahedron Lett*. **2008**, *49*, 3805. (b) B. Willy, T. J. J. Müller, *Eur. J. Org. Chem.* **2008**, 4157. (c) B. Willy, T. J. J. Müller, *Org. Lett.* **2011**, *13*, 2082.

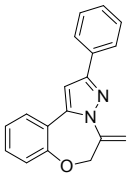
## 1.4 Copies of $^{1}H$ and $^{13}C$ NMR spectra (2a-2ab)

5-Methylene-2-phenyl-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: **2a**

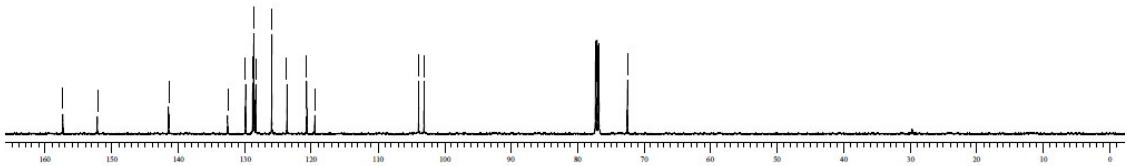


$^{1}$HNMR, $CDCl_3$, 400 MHz

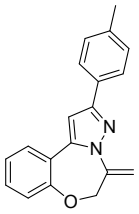




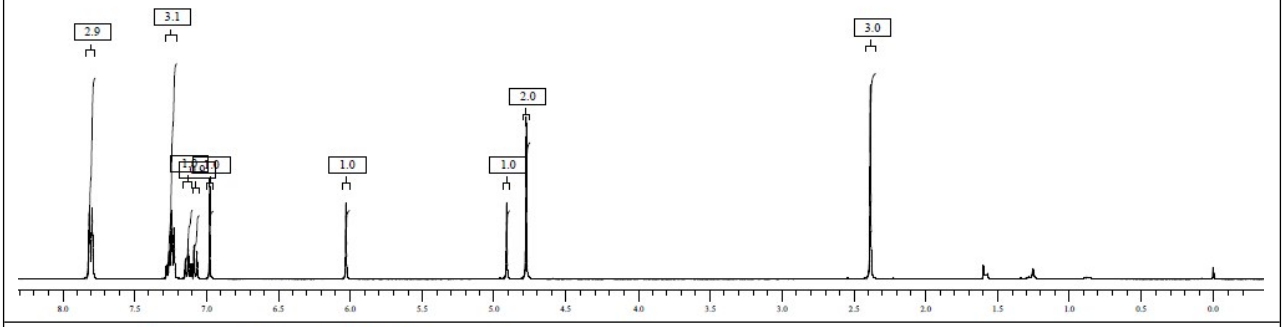
$^{13}$CNMR, $CDCl_3$, 125 MHz



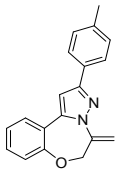
5-Methylene-2-(p-tolyl)-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: **2b**



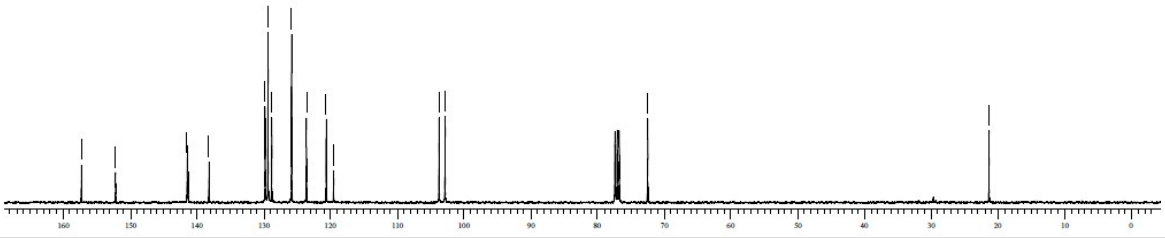
$^{1}$HNMR, $CDCl_3$, 400 MHz



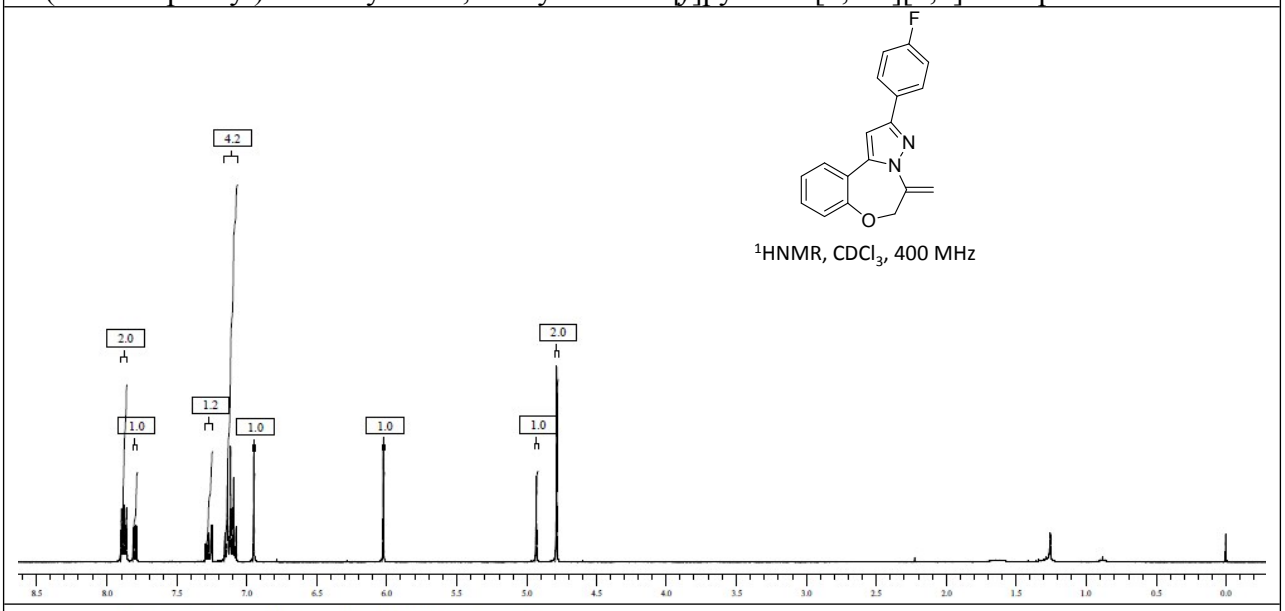




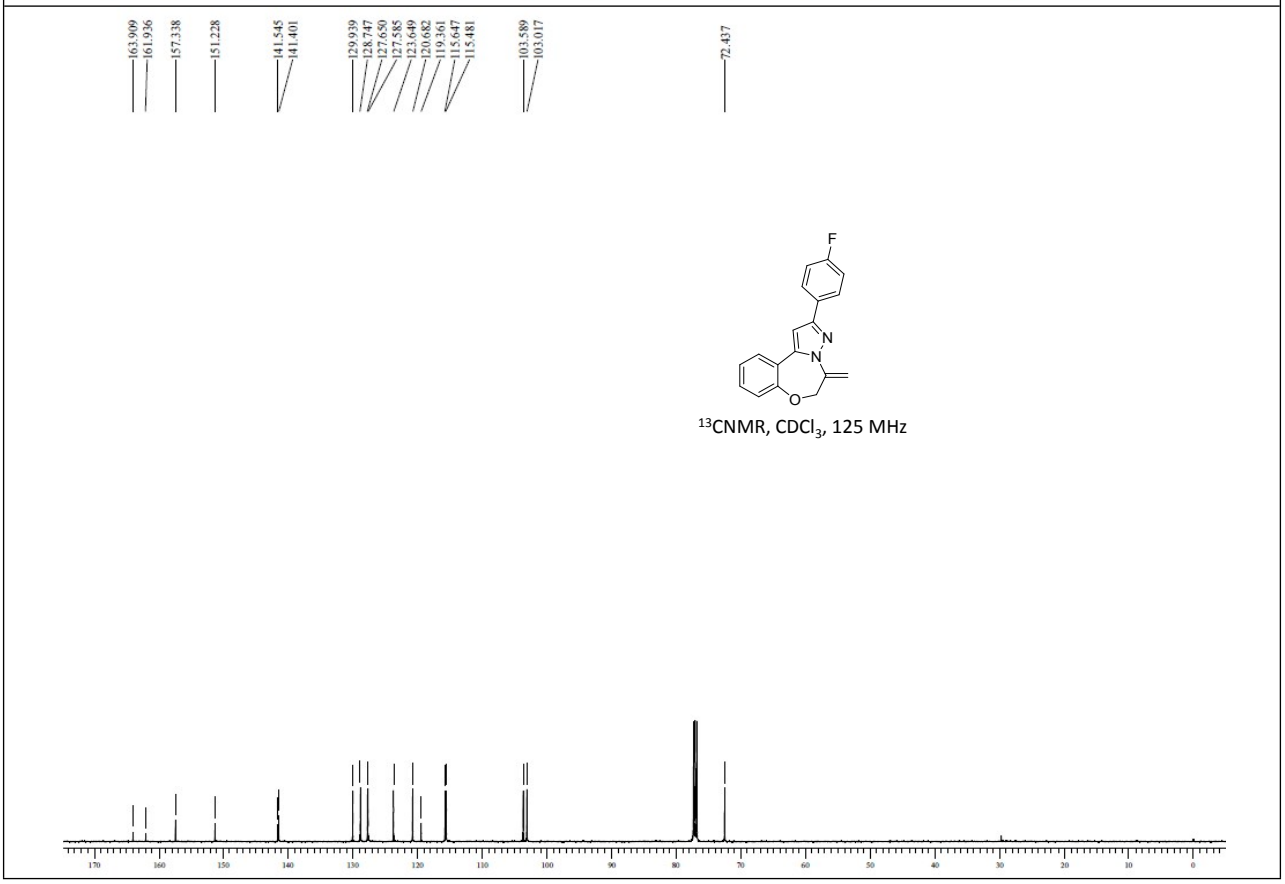
$^{13}$CNMR, $CDCl_3$, 100 MHz



2-(4-Fluorophenyl)-5-methylene-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: **2c**

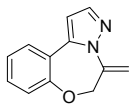



$^{1}$HNMR, $CDCl_3$, 400 MHz

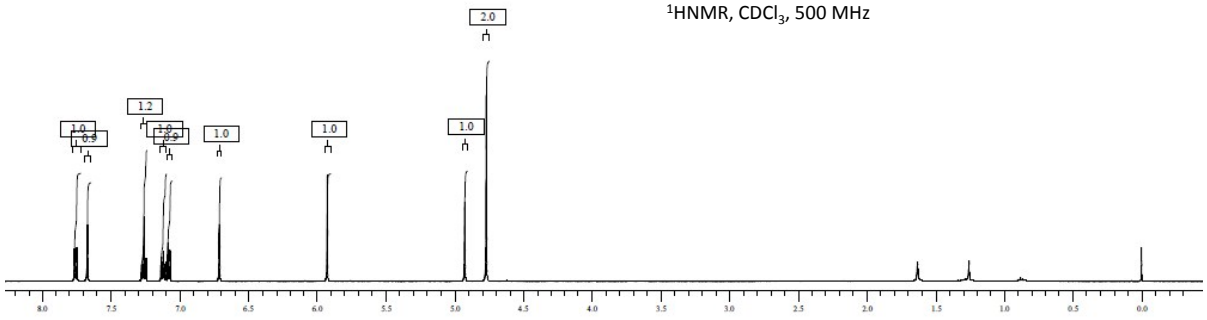


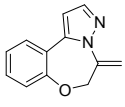

$^{13}$CNMR, $CDCl_3$, 125 MHz

5-Methylene-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: **2d**

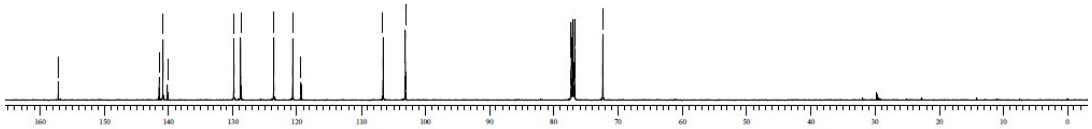


$^{1}$HNMR, $CDCl_3$, 500 MHz

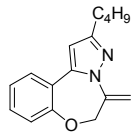


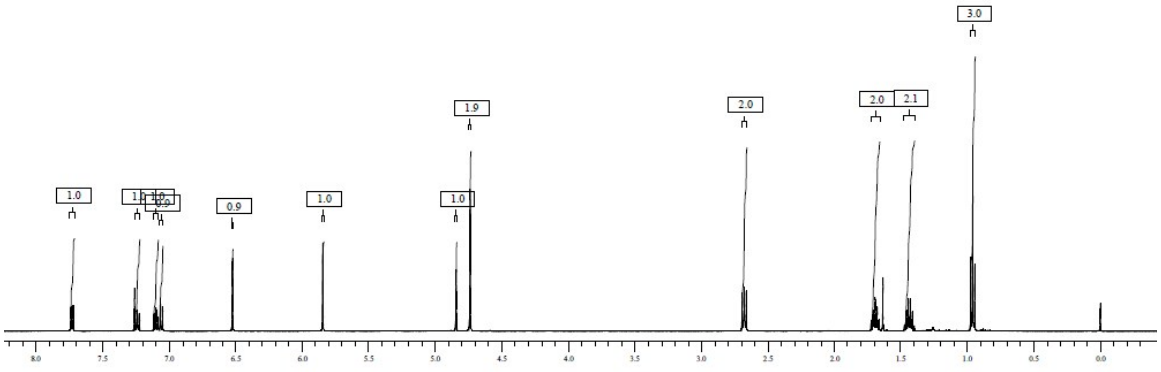
$^{13}$CNMR, $CDCl_3$, 125 MHz



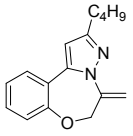
2-Butyl-5-methylene-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: **2e**



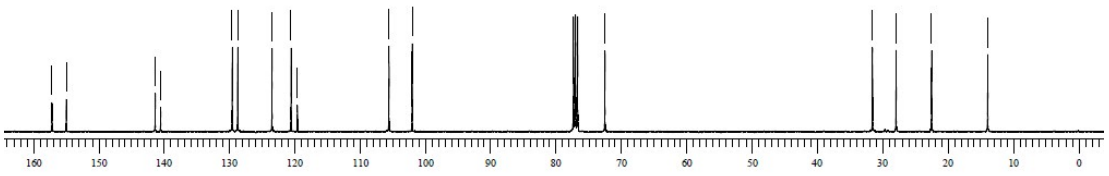

$^1$HNMR, $CDCl_3$, 400 MHz



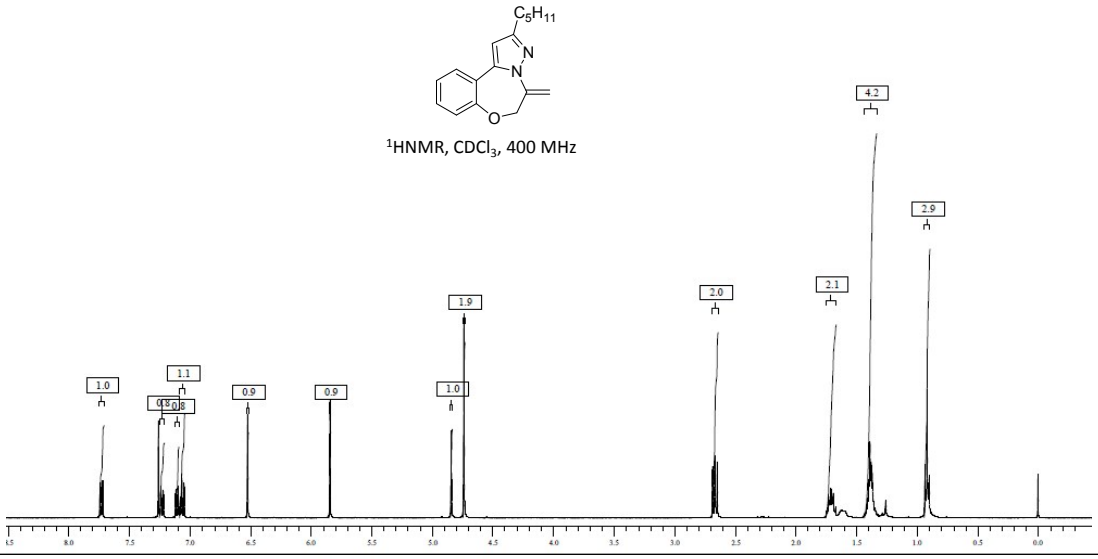




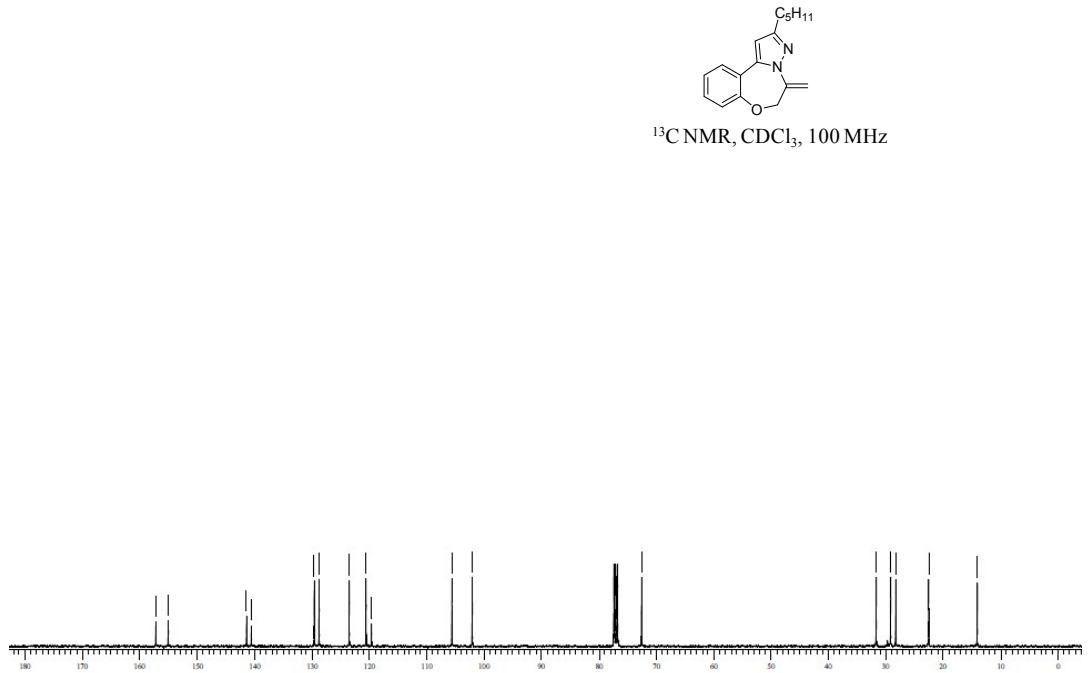

$^{13}$CNMR, $CDCl_3$, 100 MHz



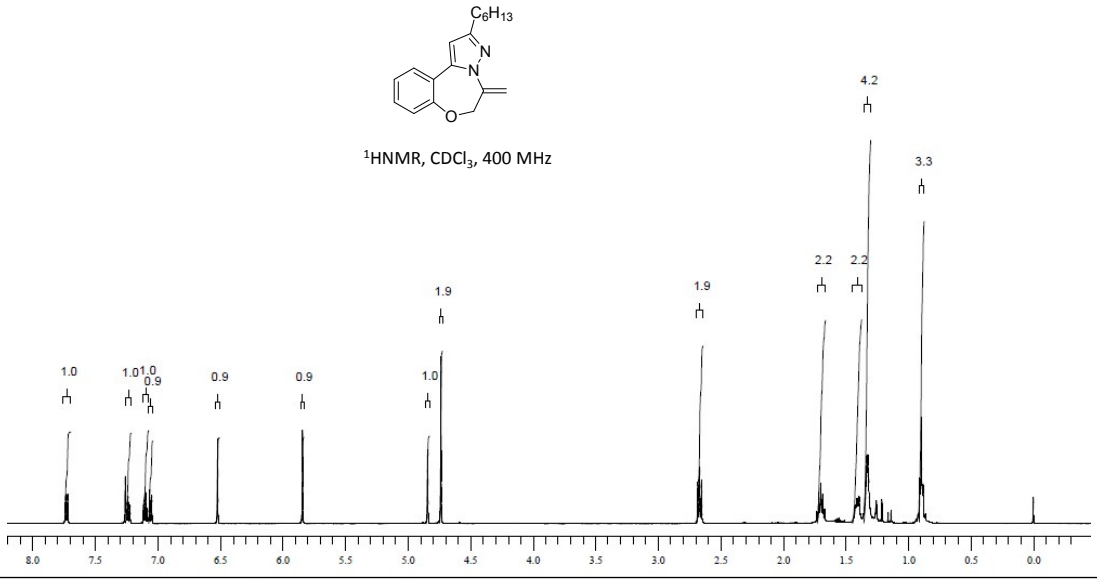
5-Methylene-2-pentyl-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: **2f**



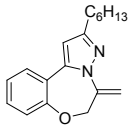




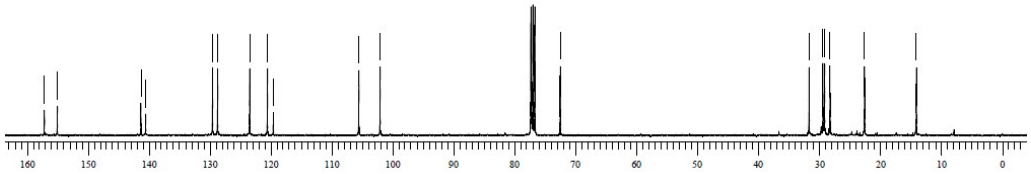
2-Hexyl-5-methylene-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: **2g**



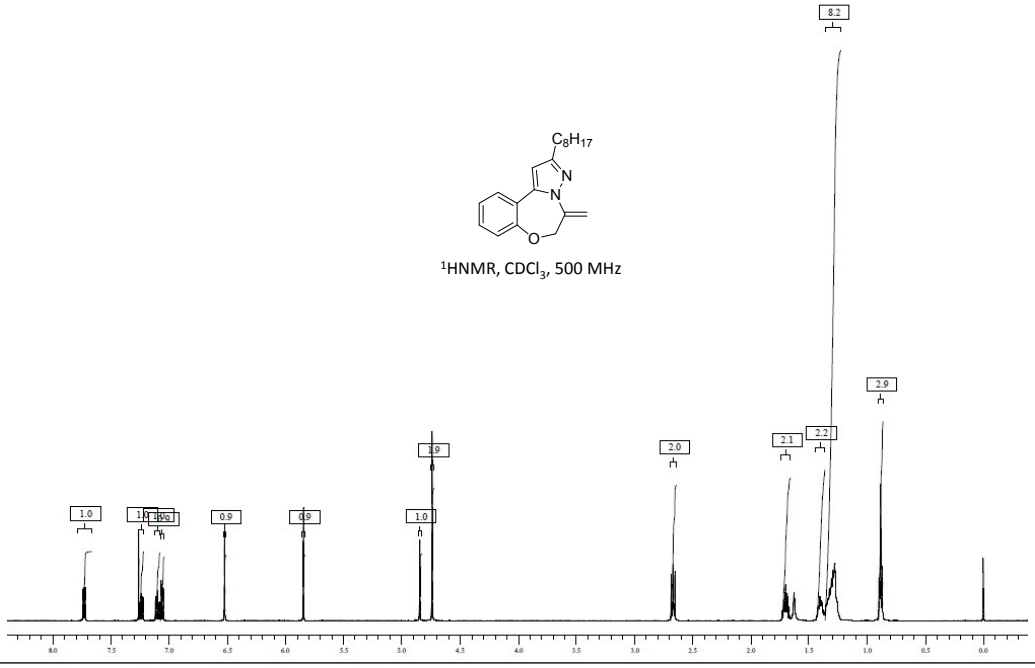




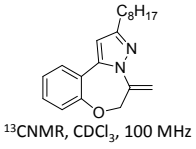

$^{13}$CNMR, $CDCl_3$, 100 MHz



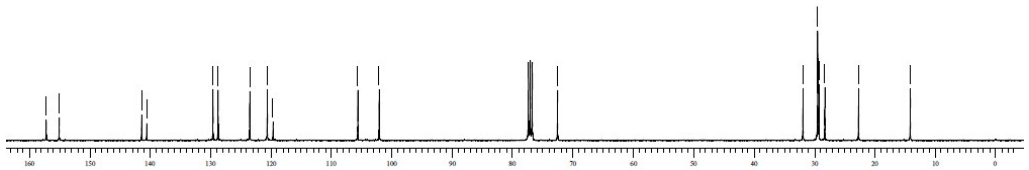
5-Methylene-2-octyl-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: **2h**



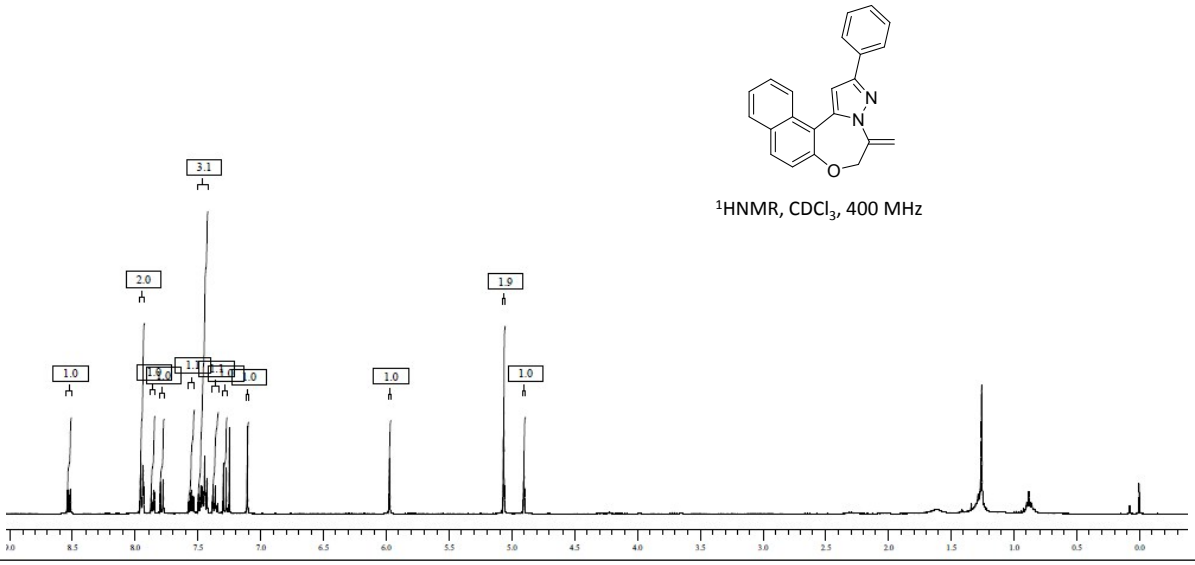

$^1$HNMR, $CDCl_3$, 500 MHz

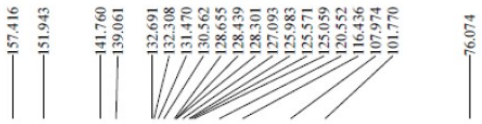

$^{13}$CNMR, $CDCl_3$, 100 MHz



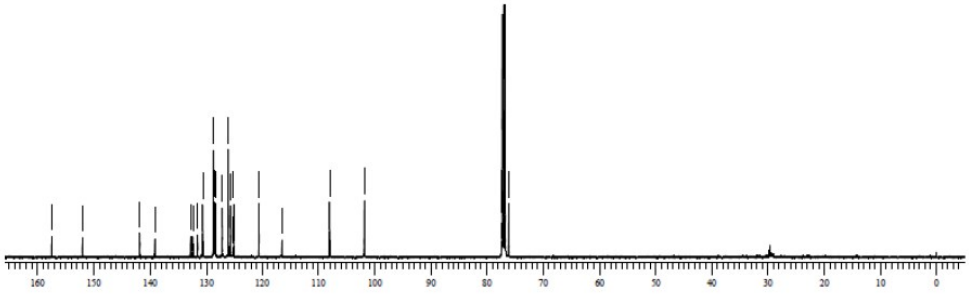
5-Methylene-2-phenyl-5,6-dihydronaphtho[1,2-*f*]pyrazolo[1,5-*d*][1,4]oxazepine: **2i**



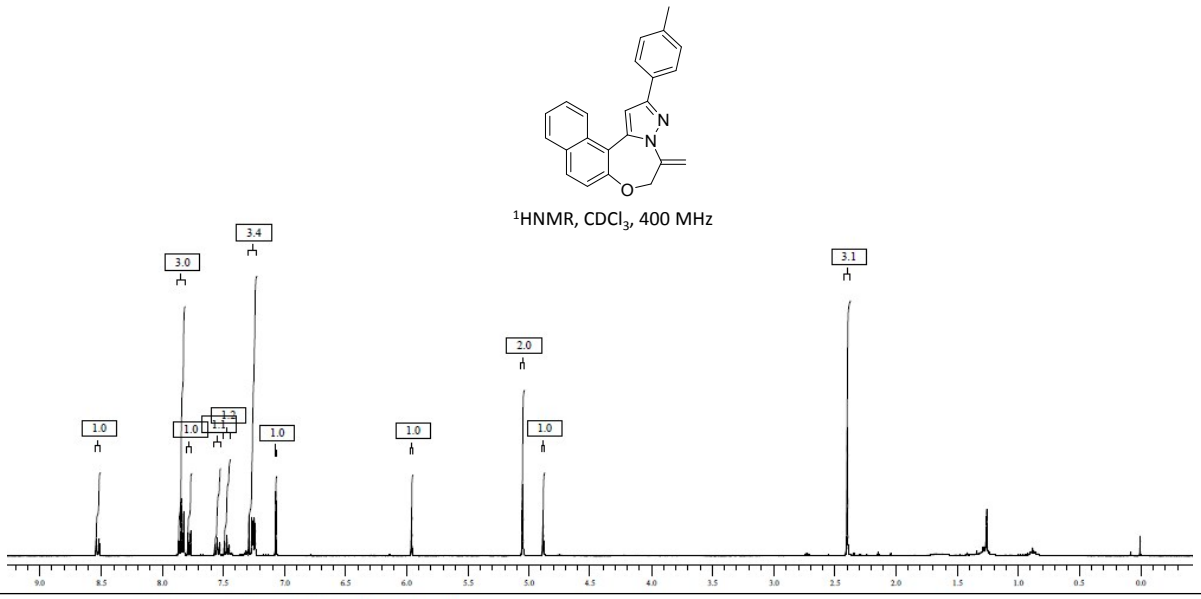

$^{1}$HNMR, $CDCl_3$, 400 MHz



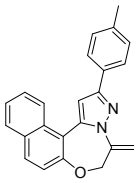

$^{13}$CNMR, $CDCl_3$, 125 MHz



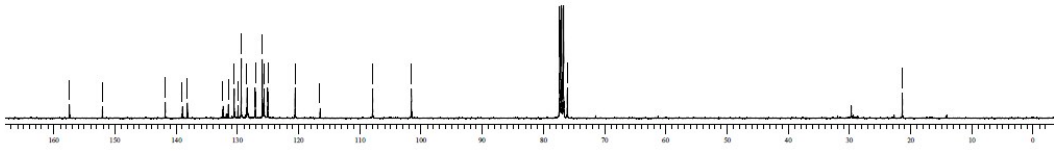
5-Methylene-2-(p-tolyl)-5,6-dihydronaphtho[1,2-*f*]pyrazolo[1,5-*d*][1,4]oxazepine: **2j**



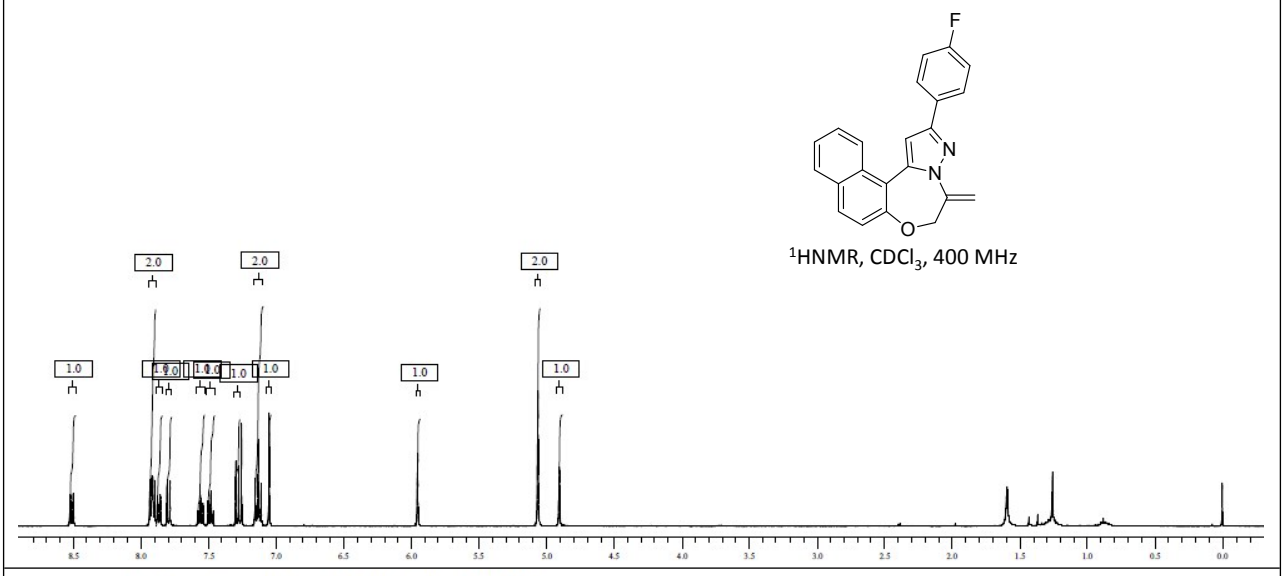




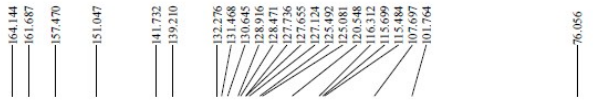

$^{13}$CNMR, CDCl$_3$, 100 MHz

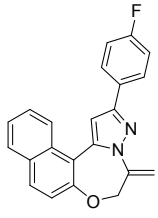


2-(4-Fluorophenyl)-5-methylene-5,6-dihydronaphtho[1,2-*f*]pyrazolo[1,5-*d*][1,4]oxazepine: **2k**

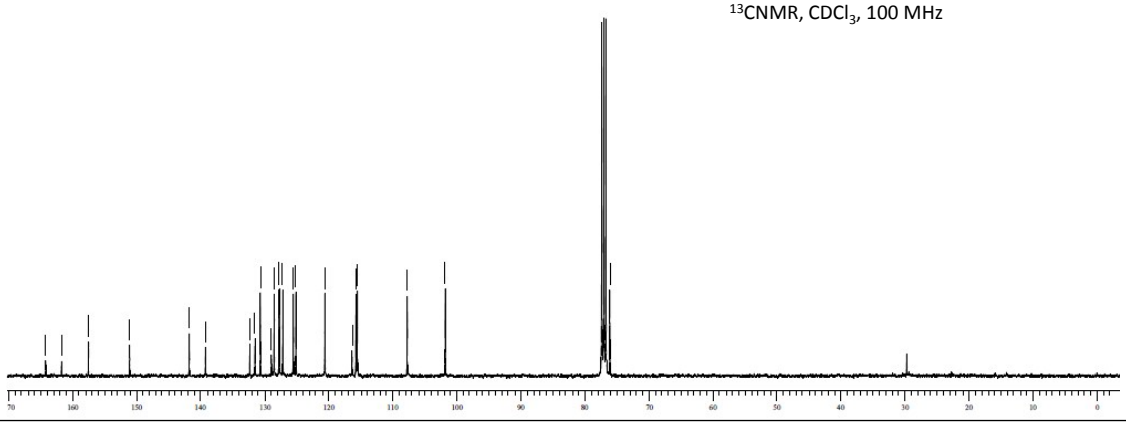



$^{1}$HNMR, $CDCl_3$, 400 MHz

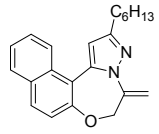


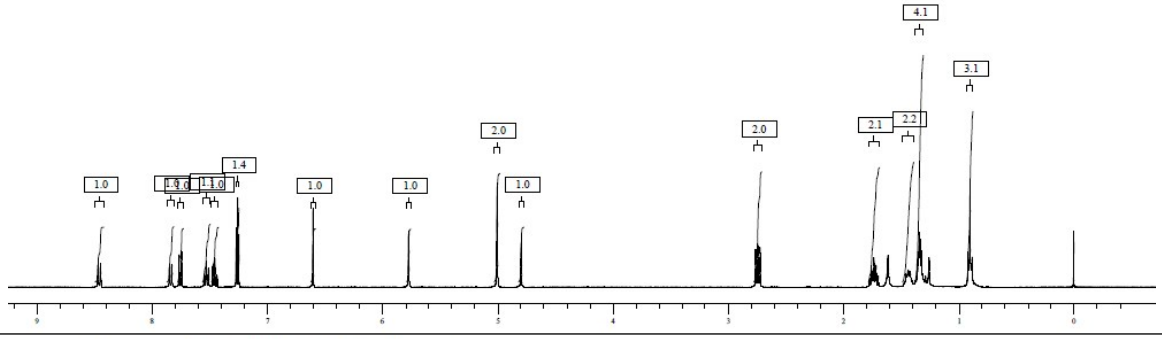

$^{13}$CNMR, $CDCl_3$, 100 MHz



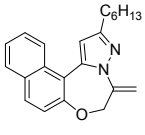
2-Hexyl-5-methylene-5,6-dihydronaphtho[1,2-*f*]pyrazolo[1,5-*d*][1,4]oxazepine: **2l**



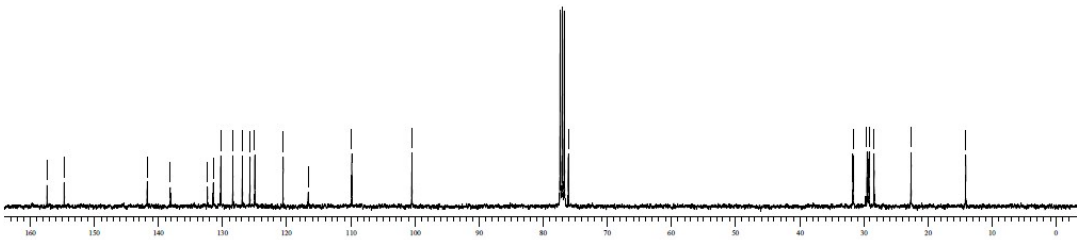

$^{1}$HNMR, $CDCl_3$, 400 MHz



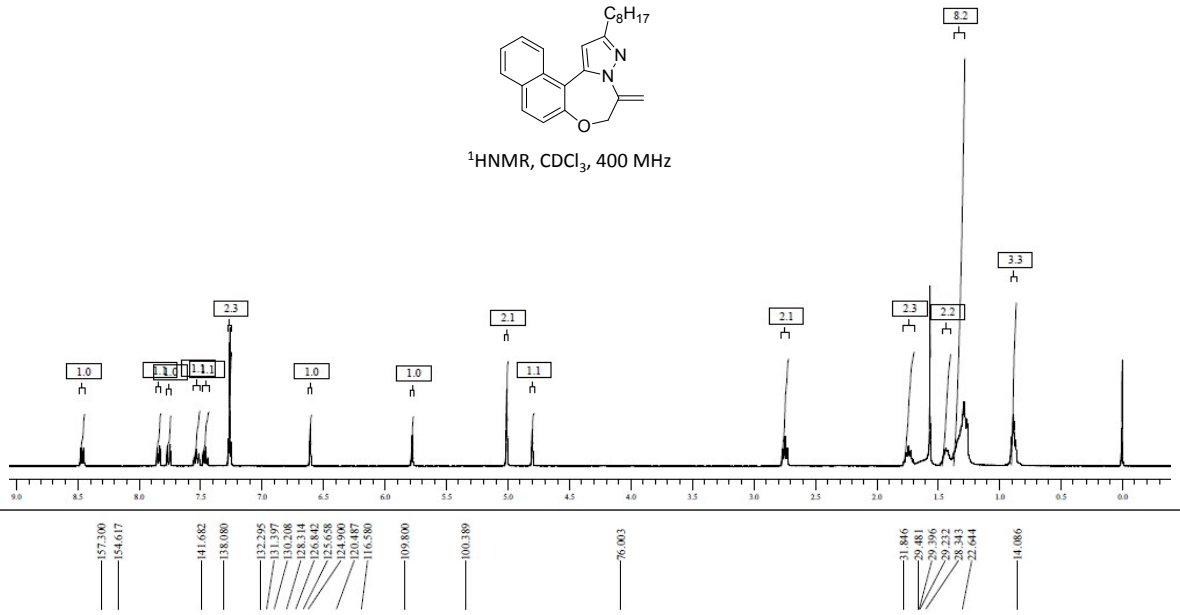





$^{13}$CNMR, $CDCl_3$, 100 MHz

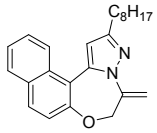


5-Methylene-2-octyl-5,6-dihydronaphtho[1,2-*f*]pyrazolo[1,5-*d*][1,4]oxazepine: **2m**

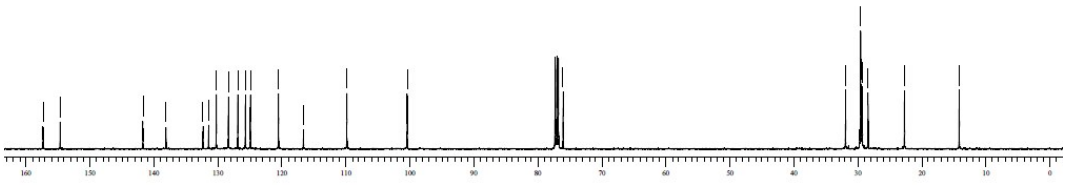



$^{1}$HNMR, $CDCl_3$, 400 MHz

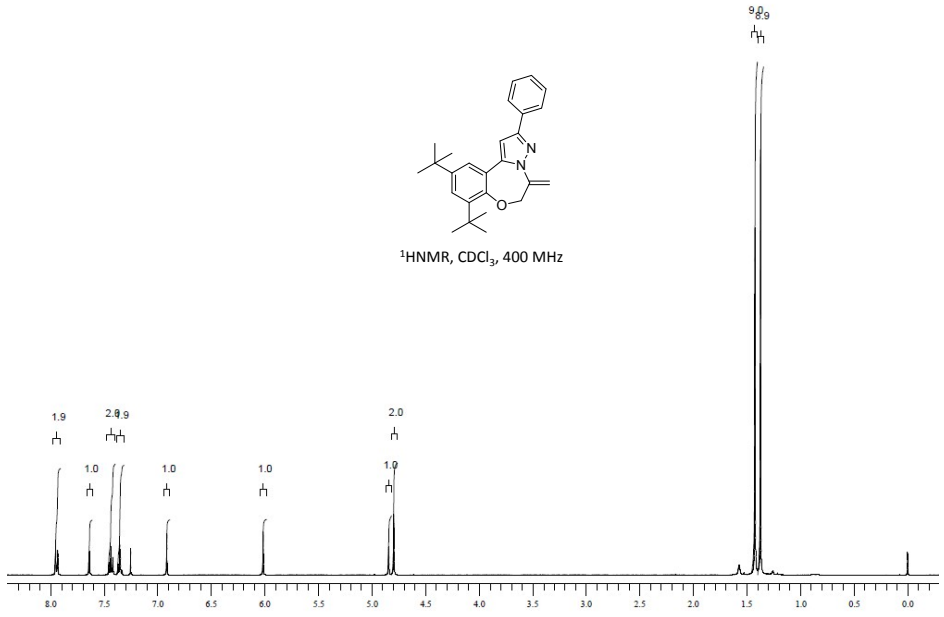


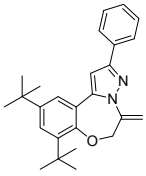

$^{13}$CNMR, $CDCl_3$, 125 MHz



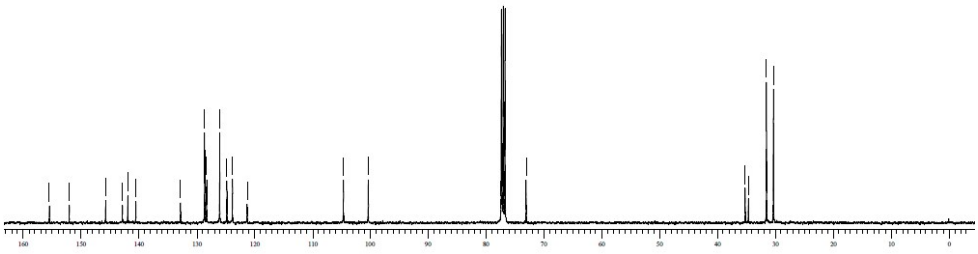
8,10-Di-tert-butyl-5-methylene-2-phenyl-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: **2n**



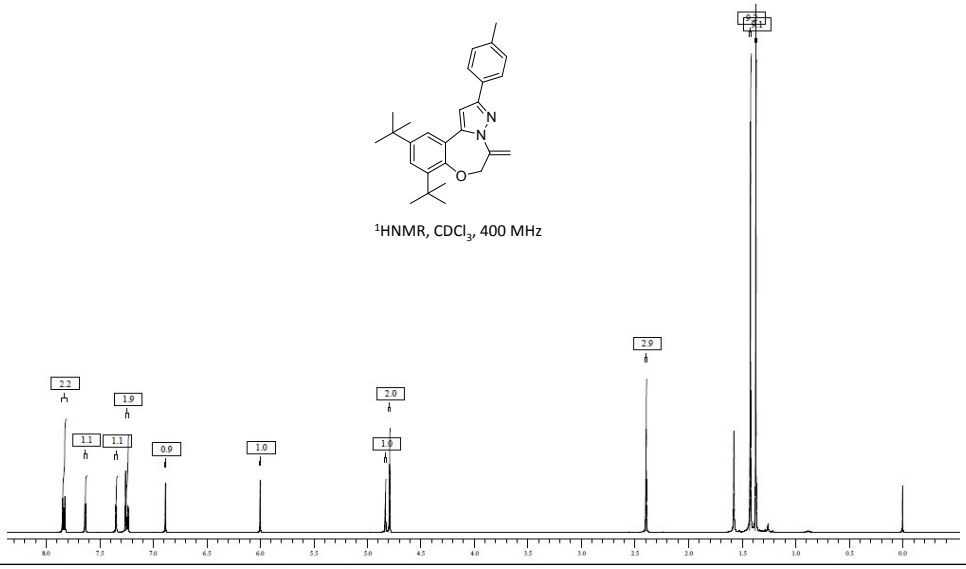

$^{1}$HNMR, $CDCl_3$, 400 MHz

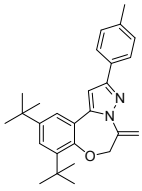
$^{13}$CNMR, $CDCl_3$, 100 MHz



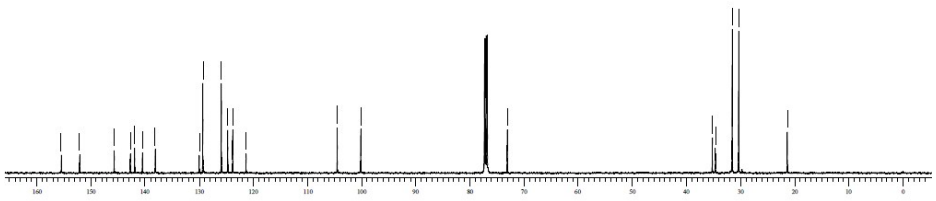
8,10-Di-tert-butyl-5-methylene-2-(p-tolyl)-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: **2o**



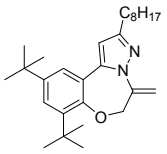

$^{1}$HNMR, $CDCl_3$, 400 MHz

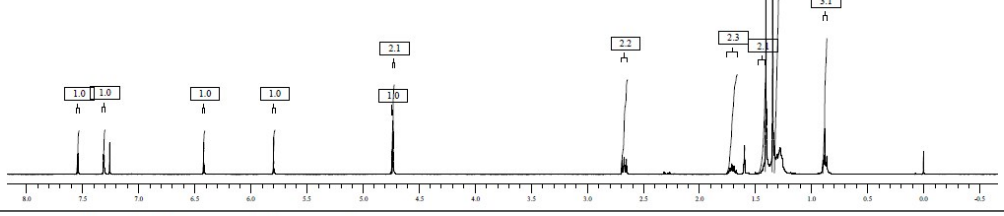
$^{13}$CNMR, $CDCl_3$, 125 MHz



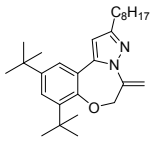
8,10-Di-tert-butyl-5-methylene-2-octyl-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: **2p**



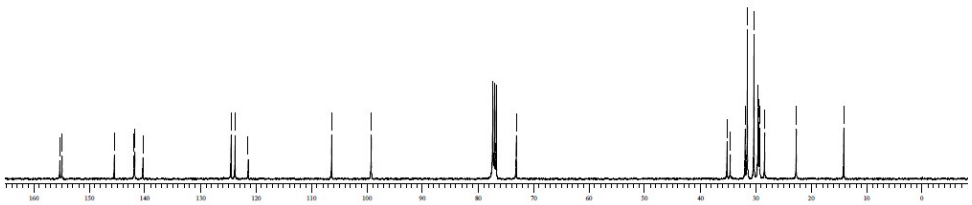

$^1$HNMR, $CDCl_3$, 400 MHz



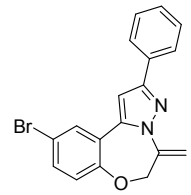




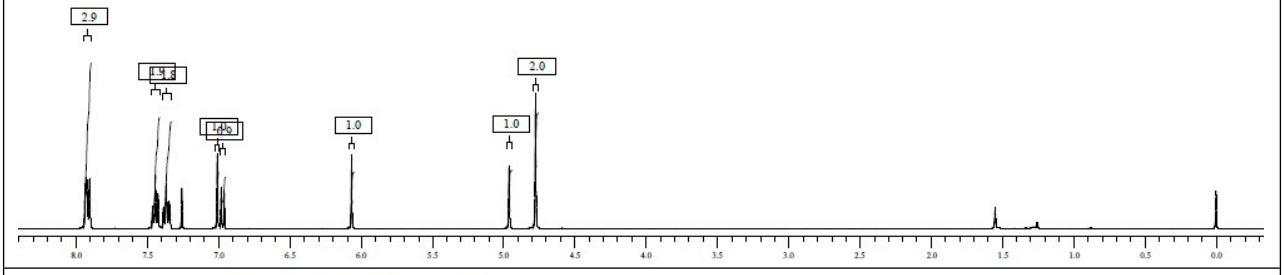

$^{13}$CNMR, $CDCl_3$, 100 MHz



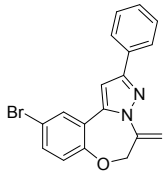
10-Bromo-5-methylene-2-phenyl-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: **2q**



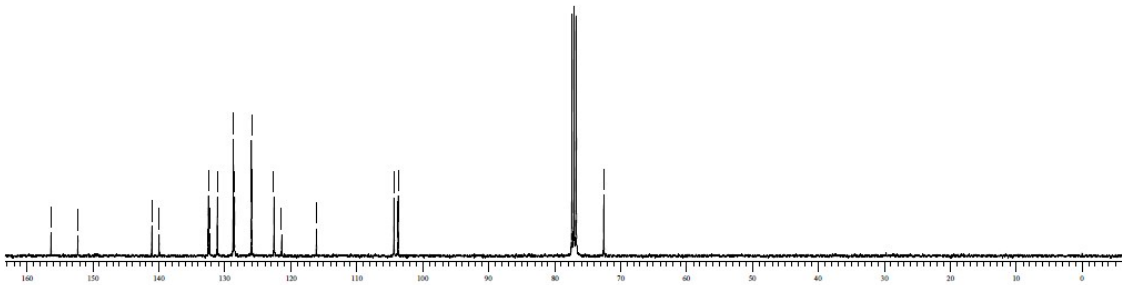

$^{1}$HNMR, $CDCl_3$, 400 MHz



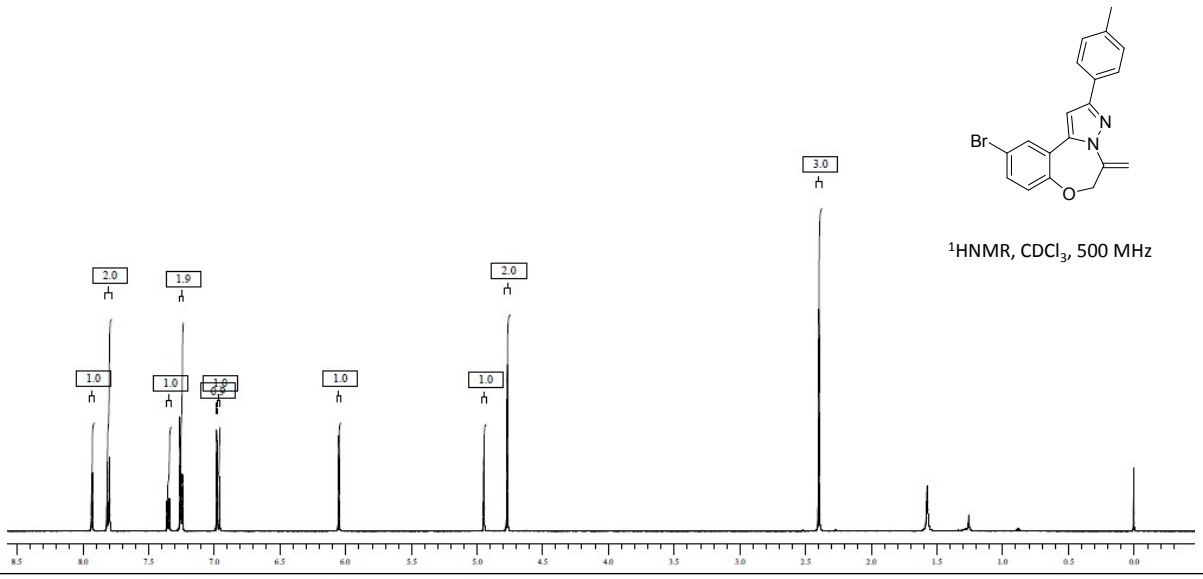




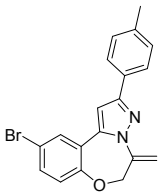

$^{13}$CNMR, $CDCl_3$, 100 MHz



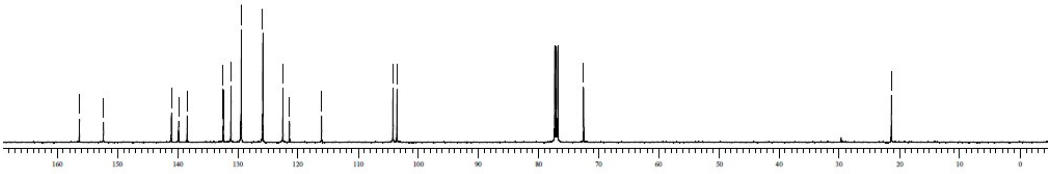
10-Bromo-5-methylene-2-(p-tolyl)-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: **2r**



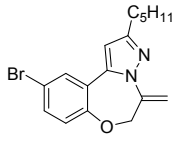

$^{1}$HNMR, $CDCl_3$, 500 MHz

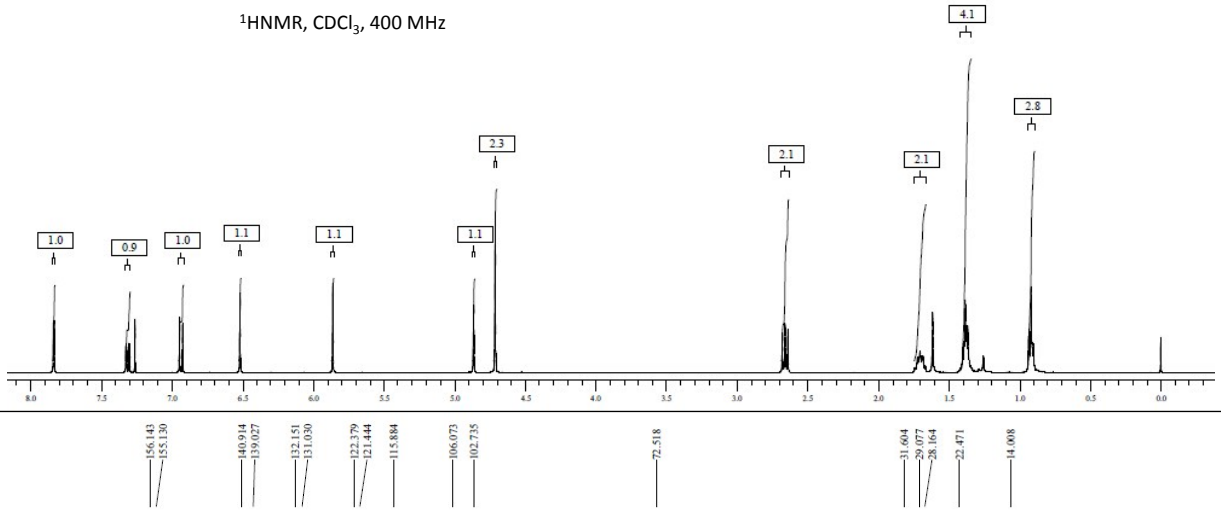

$^{13}$CNMR, $CDCl_3$, 125 MHz



10-Bromo-5-methylene-2-pentyl-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: **2s**

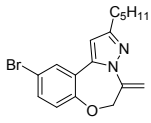



$^1$HNMR, $CDCl_3$, 400 MHz

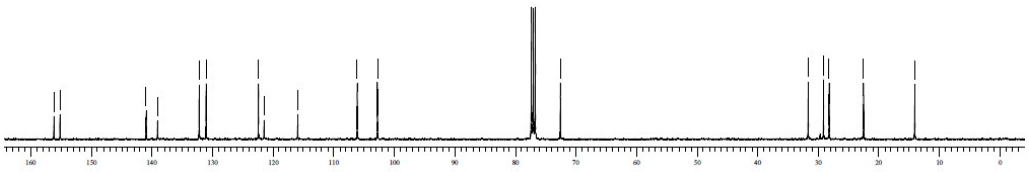




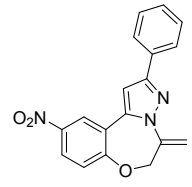




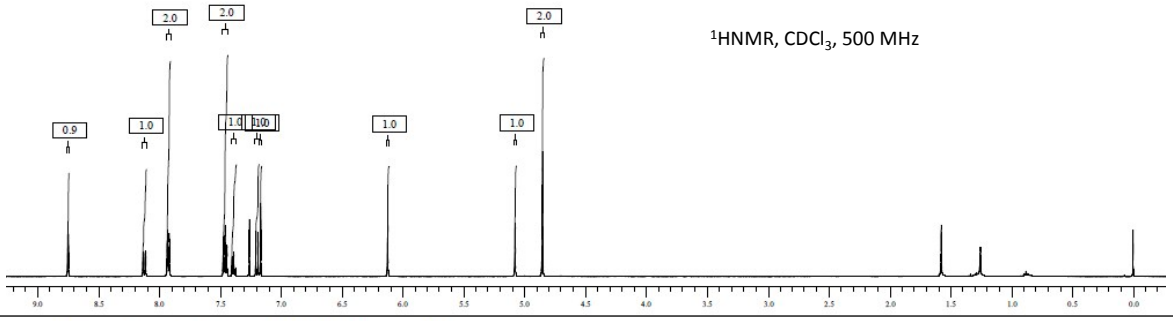

$^{13}$CNMR, $CDCl_3$, 100 MHz

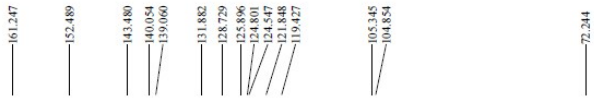


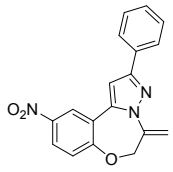
5-Methylene-10-nitro-2-phenyl-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: **2t**



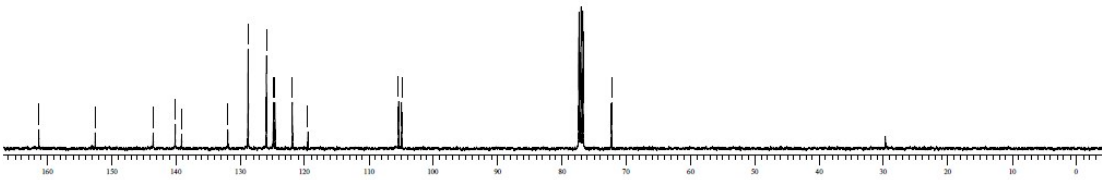
$^{1}$HNMR, $CDCl_3$, 500 MHz



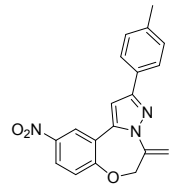




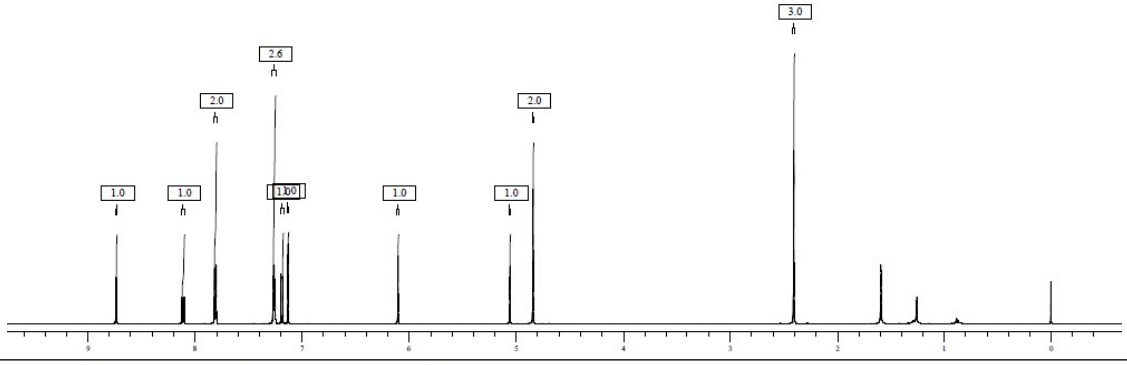
$^{13}$CNMR, $CDCl_3$, 100 MHz



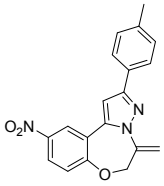
5-Methylene-10-nitro-2-(p-tolyl)-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: **2u**



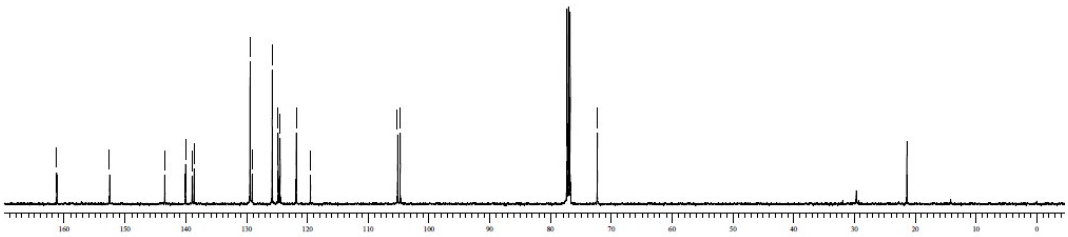
$^{1}$HNMR, $CDCl_3$, 500 MHz



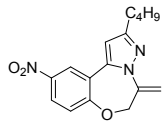




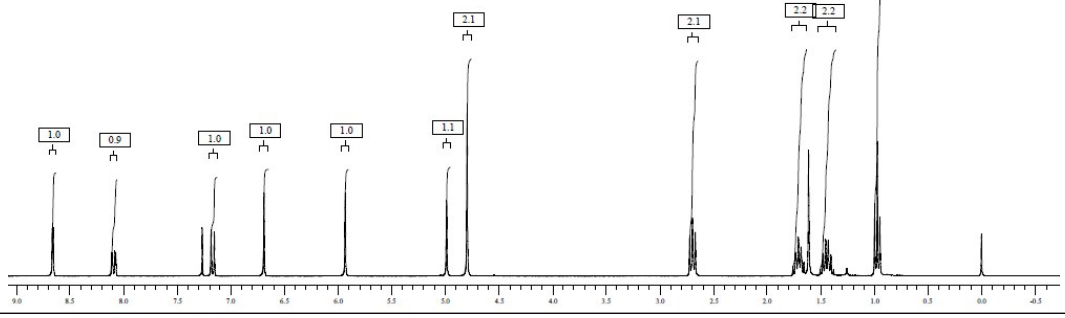
$^{13}$CNMR, $CDCl_3$, 125 MHz



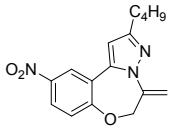
2-Butyl-5-methylene-10-nitro-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: **2v**



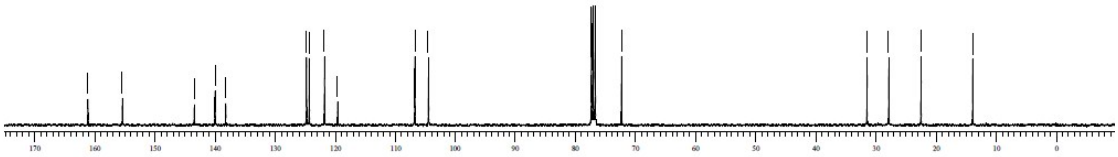

$^1$HNMR, $CDCl_3$, 300 MHz



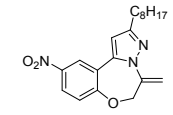





$^{13}$CNMR, $CDCl_3$, 100 MHz



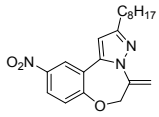
5-Methylene-10-nitro-2-octyl-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: **2w**



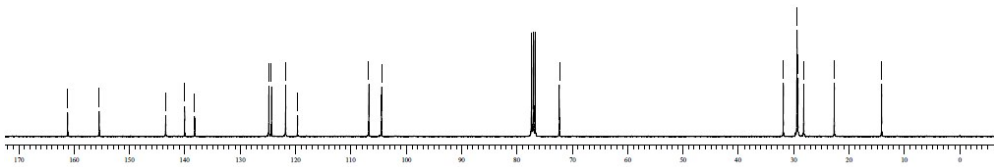

$^1$HNMR, $CDCl_3$, 500 MHz



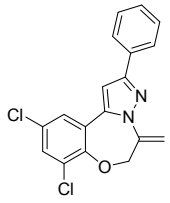




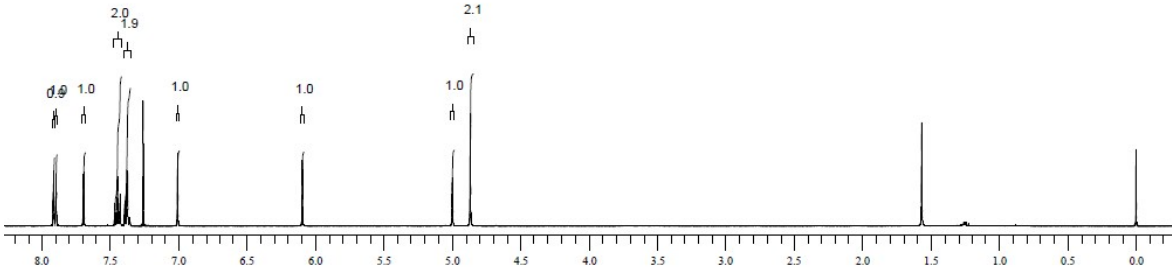

$^{13}$CNMR, $CDCl_3$, 100 MHz

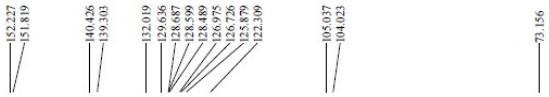


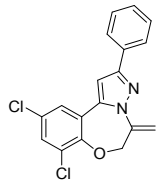
8,10-Dichloro-5-methylene-2-phenyl-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: **2x**



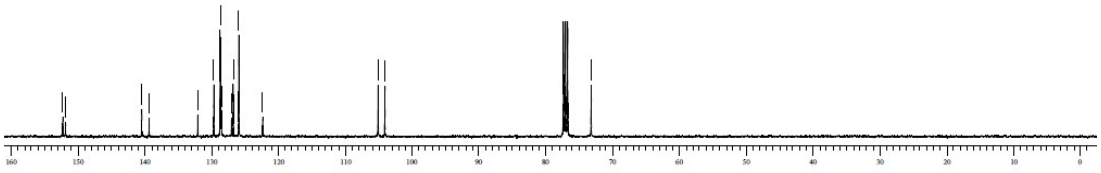

$^{1}$HNMR, $CDCl_3$, 400 MHz



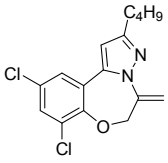



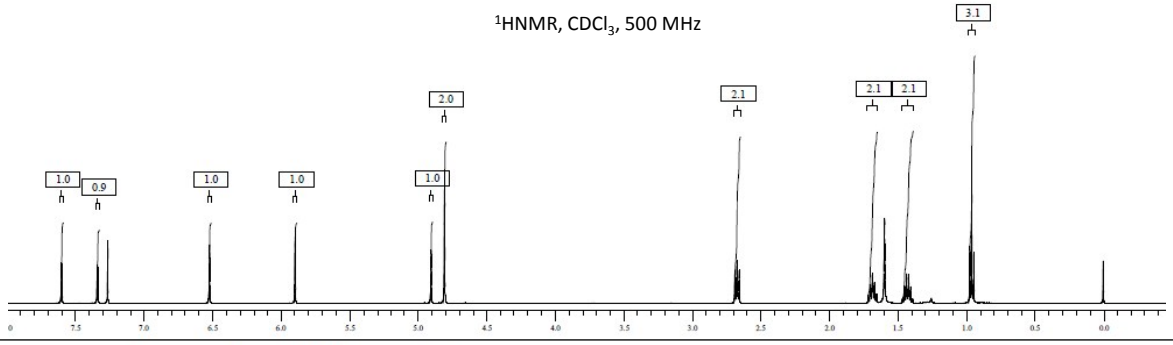

$^{13}$CNMR, $CDCl_3$, 100 MHz



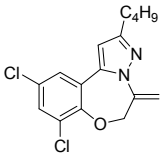
2-Butyl-8,10-dichloro-5-methylene-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: **2y**



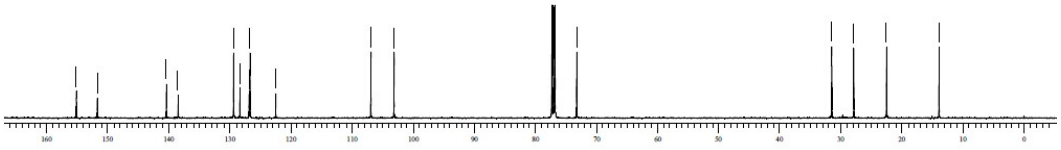

$^{1}$HNMR, $CDCl_3$, 500 MHz



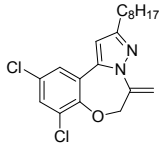




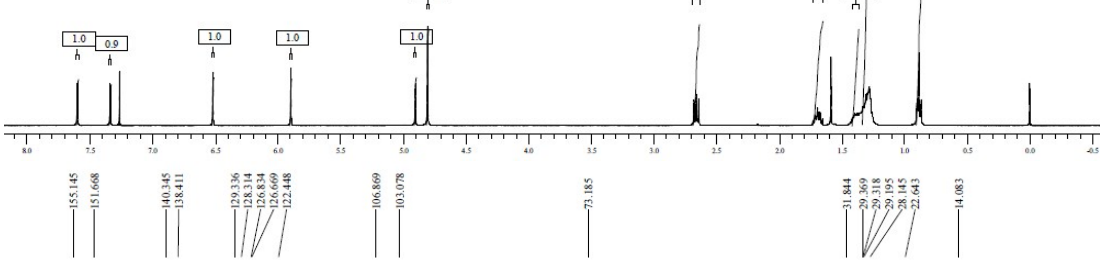

$^{13}$CNMR, $CDCl_3$, 125 MHz

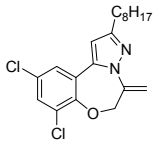


8,10-Dichloro-5-methylene-2-octyl-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: **2z**

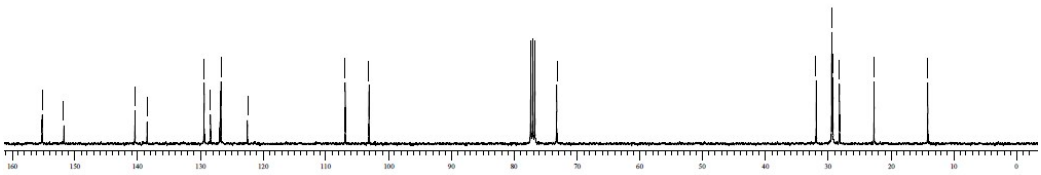



$^{1}$HNMR, $CDCl_3$, 400 MHz

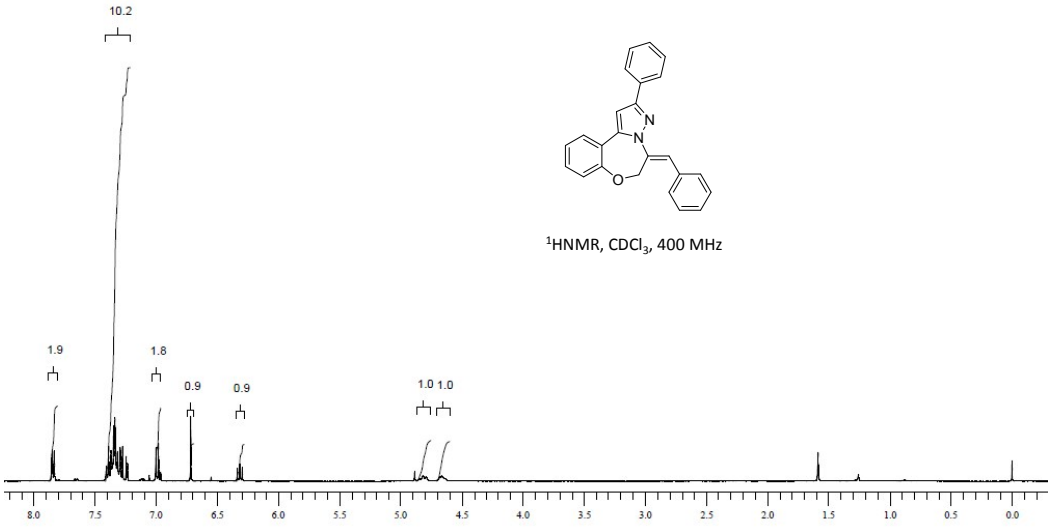


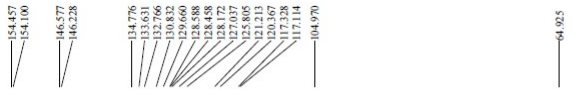

$^{13}$CNMR, $CDCl_3$, 100 MHz

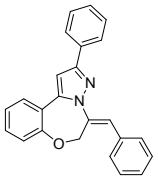


(*E*)-5-Benzylidene-2-phenyl-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: **2aa**

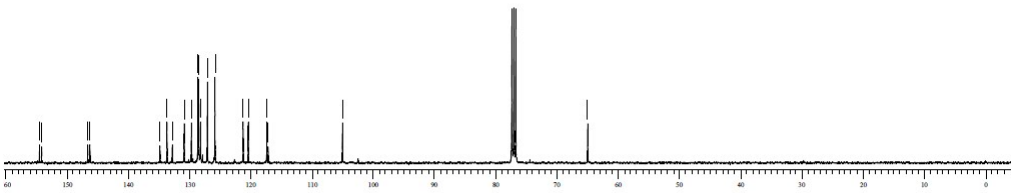



$^{1}$HNMR, $CDCl_3$, 400 MHz

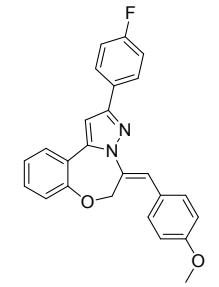


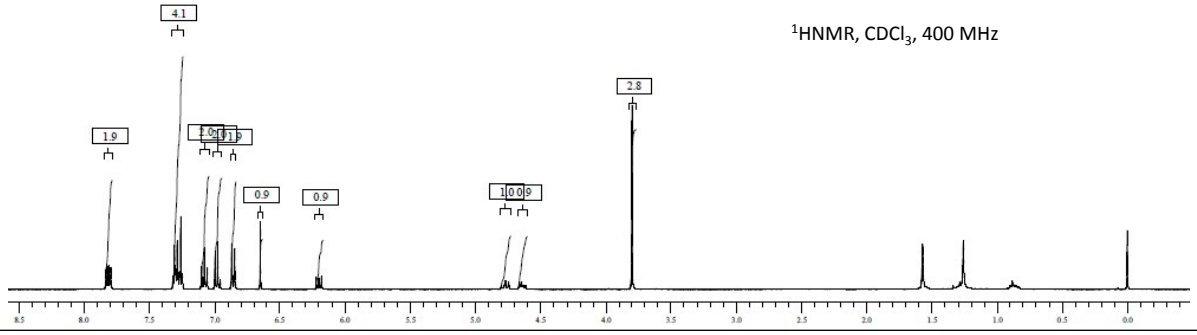
$^{13}$CNMR, $CDCl_3$, 100 MHz

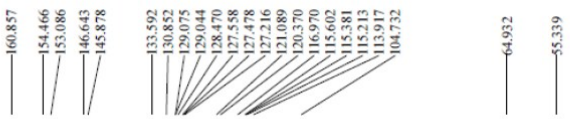


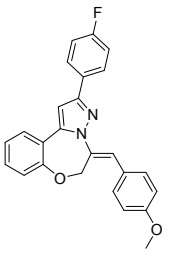
(*E*)-2-(4-Fluorophenyl)-5-(4-methoxybenzylidene)-5,6-dihydrobenzo[*f*]pyrazolo[1,5-*d*][1,4]oxazepine: **2ab**




$^{1}$HNMR, $CDCl_3$, 400 MHz




$^{13}$CNMR, $CDCl_3$, 100 MHz

## 1.5 X-ray crystallography data of compound 2u.

X-ray data for the compound KA263 was collected at 100 K on a Bruker D8 QUEST instrument with an IμS Mo microsource (λ = 0.7107 A) and a PHOTON-100 detector. The raw data frames were reduced and corrected for absorption effects using the Bruker Apex 3 software suite programs.[2] The structure was solved using intrinsic phasing method[3] and further refined with the SHELXL program and expanded using Fourier techniques.[3] Anisotropic displacement parameters were included for all non-hydrogen atoms. All C bound H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å, and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H or $1.2U_{eq}(C)$ for other H atoms].

**Crystal Data for KA263**: $C_{19}H_{15}N_3O_3$ ($M$ =333.35 g/mol): monoclinic, space group $P2_1/c$ (no. 14), $a$ = 7.021(9) Å, $b$ = 20.14(3) Å, $c$ = 21.54(3) Å, $\beta$ = 95.79(2)°, $V$ = 3030(7) Å$^3$, $Z$ = 8, $T$ = 100.0 K, μ(Mo Kα) = 0.101 mm$^{-1}$, *Dcalc* = 1.4612 g/cm$^3$, 38713 reflections measured (4.46° ≤ 2Θ ≤ 61.62°), 9422 unique ($R_{int}$ = 0.0356, $R_{sigma}$ = 0.0330) which were used in all calculations. The final $R_1$ was 0.0454 (I>2σ(I)) and $wR_2$ was 0.1193 (all data). CCDC 1574971 contains supplementary Crystallographic data for the structure. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; email: deposit@ccdc.cam.ac.uk].

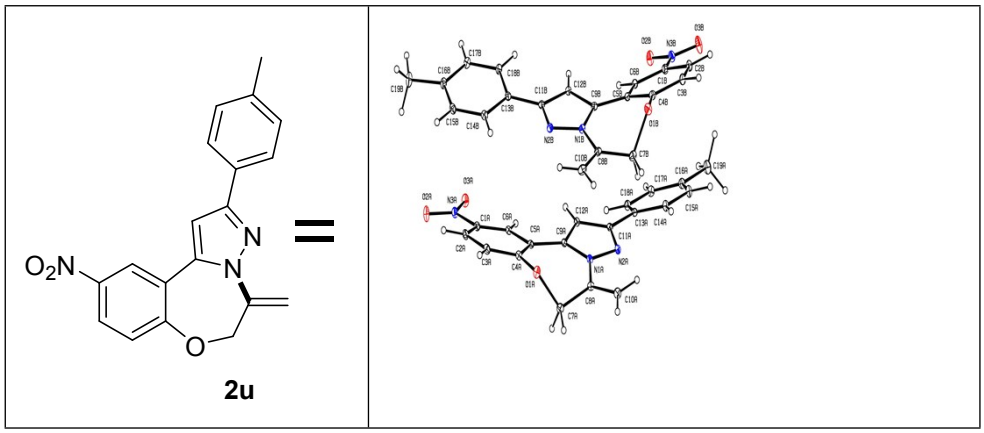



**Figure 1**. A view of **KA263**, showing the atom-labelling scheme. Two molecules were present in the asymmetric unit. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by circles of arbitrary radii.

2. Bruker (2001). SAINT (Version 6.28a) &SMART (Version 5.625), Bruker AXS Inc., Madison, Wisconsin, USA.
3. Sheldrick, G. M. (2015)*ActaCrystallogr* C71: 3-8.