

**Supporting Information for**  
**Gold-catalyzed synthesis of oxazoles from alkynyl triazenes**  
**and dioxazoles**

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## 1. General information

Reactions were monitored by thin layer chromatography (TLC) using silicycle pre-coated silica gel plates. Column chromatography was performed over silica gel (200–300mesh).

Melting points were measured with X–4 micro melting point apparatus.

HRMS were performed on Agilent Technologies 6546-LC/Q-TOF mass spectrometer (ESI-TOF).

$^1\text{H}$  NMR spectra and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AV-600 spectrometer or a WNMRI-400 spectrometer in chloroform-*d* ( $\text{CDCl}_3$ , contain internal TMS). Chemical shifts of  $^1\text{H}$  NMR spectra were reported in ppm with the internal TMS signal at 0 ppm as a standard, and chemical shifts of  $^{13}\text{C}$  NMR spectra were reported in ppm with the chloroform signal at 77.16 ppm as a standard.<sup>1</sup> The data is being reported as (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, hept = heptet, dd = double doublet, dt = double of triplet, m = multiplet or unresolved, br = broad singlet, coupling constant(s) in Hz, integration).

## 2. Starting materials

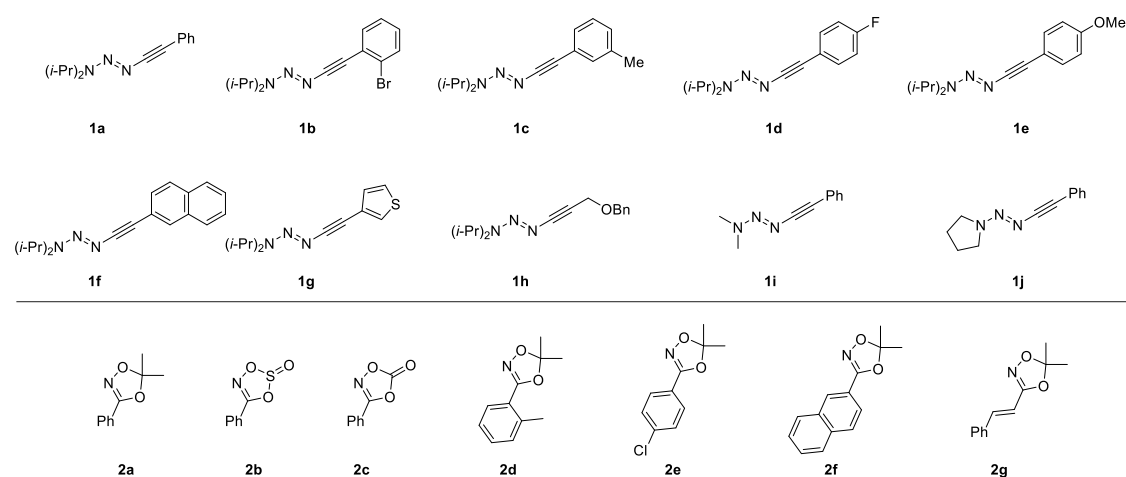
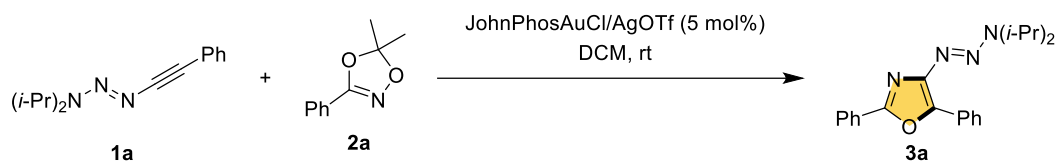


Figure S1. Starting materials

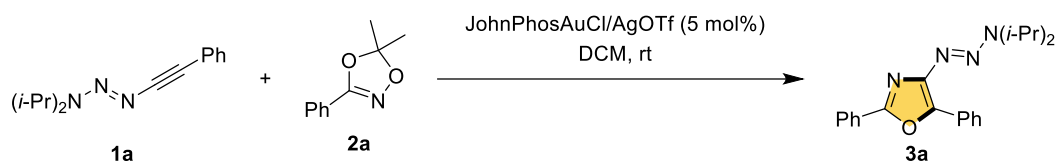
All starting materials are listed as Figure S1. Alkynyl triazene **1a-1j** were prepared according to the reported methods.<sup>2</sup> dioxzole **2a-2g** were synthesized according to the literature.<sup>3</sup>

### 3. Typical procedure for the synthesis of 3a



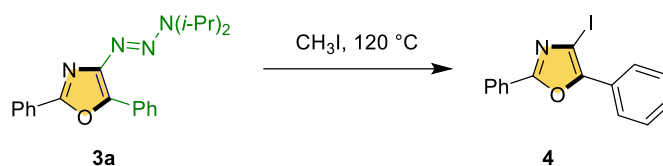
An oven-dried Schlenk tube equipped with a magnetic stirrer bar was charged with JohnPhosAuCl (5.3 mg, 5 mol%) and AgOTf (2.6 mg, 5 mol%), then purged with argon three times. Anhydrous CH<sub>2</sub>Cl<sub>2</sub> (1 mL) was added as solvent and the mixture was stirred for 15 mins. Alkynyl triazene **1a** (46 mg, 0.2 mmol) and dioxazole **2a** (43 mg, 0.24 mmol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) and added. The reaction was stirred until TLC analysis showed the completion of the reaction. The reaction mixture was concentrated to obtain the residue, which was purified by silica gel column chromatography eluting with PE/EA = 20/1 to give the desired product **3a** (56.5 mg, 81% yield) as a light red solid.

### 4. Gram-scale reaction for synthesizing 3a



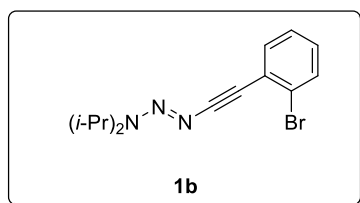
An oven-dried Schlenk tube equipped with a magnetic stirrer bar was charged with JohnPhosAuCl (132.5 mg, 5 mmol%) and AgOTf (65 mg, 5 mol%), then purged with argon three times. Anhydrous CH<sub>2</sub>Cl<sub>2</sub> (25 mL) was added as solvent and the mixture was stirred for 15 mins. Alkynyl triazene **1a** (1.15 g, 5 mmol) and dioxazole **2a** (1.1 g, 6.2 mmol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (25 mL) and added. The reaction was stirred until TLC analysis showed the completion of the reaction. The reaction mixture was concentrated to obtain the residue, which was purified by silica gel column chromatography eluting with PE/EA = 20/1 to give the desired product **3a** (1.36 g, 78% yield) as a light red solid.

## 5. Iodination

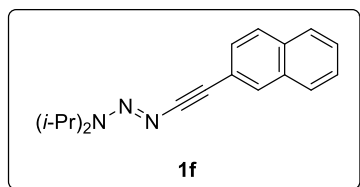


An oven-dried Schlenk pressure tube equipped with a magnetic stirrer bar was charged with **3a** (70 mg, 0.2 mmol) and  $\text{CH}_3\text{I}$  (2 mL), then purged with argon three times and sealed. The mixture was stirred at 120 °C for 12 h. The mixture was concentrated to obtain the residue, which was further purified by silica gel column chromatography eluting with PE/EA = 20/1 to give **4** (38 mg, 55% yield) as a off-white solid.

## 6. Characterization of new alkynyl triazenes and products

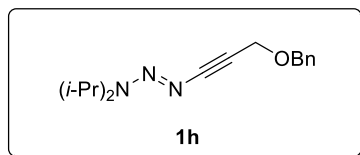


**(E)-1-((2-bromophenyl)ethynyl)-3,3-diisopropyltriaz-1-ene (1b)**: yellow crystal (recrystallized from pentane).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 1.2$  Hz, 1H), 7.48 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 1.6$  Hz, 1H), 7.28 – 7.20 (m, 1H), 7.11 – 7.04 (m, 1H), 5.28 – 5.08 (m, 1H), 4.14 – 3.96 (m, 1H), 1.37 (d,  $J = 6.8$  Hz, 6H), 1.24 (d,  $J = 6.8$  Hz, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  132.91, 132.30, 128.08, 127.06, 126.95, 125.09, 98.37, 78.78, 50.55, 47.63, 23.51, 19.21. **HRMS (ESI-TOF)**  $m/z$ : (M+H) $^+$  calcd. For  $\text{C}_{14}\text{H}_{19}\text{BrN}_3$ , 308.0762; found, 308.0761.

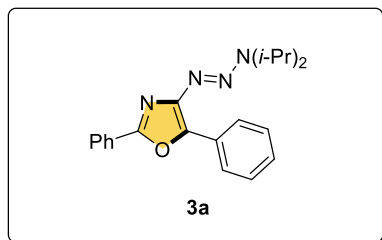


**(E)-3,3-diisopropyl-1-(naphthalen-2-ylethynyl)triaz-1-ene (1f)**: yellow crystal (recrystallized from pentane).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (s, 1H), 7.82 – 7.72 (m, 3H), 7.53 (dd,  $J = 8.5, 1.6$  Hz, 1H), 7.50 – 7.38 (m, 2H), 5.23 – 5.05 (m, 1H), 4.14

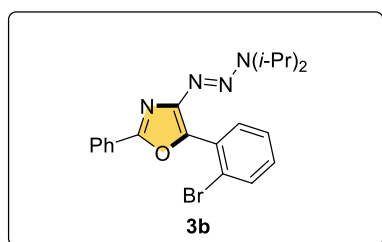
– 3.97 (m, 1H), 1.39 (d,  $J = 6.6$  Hz, 5H), 1.25 (d,  $J = 6.8$  Hz, 5H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  133.36, 132.36, 130.33, 128.80, 127.79, 127.74, 126.34, 126.07, 122.31, 94.44, 80.65, 50.55, 47.63, 23.52, 19.22. HRMS (ESI-TOF)  $m/z$ : ( $\text{M}+\text{H}$ ) $^+$  calcd. For  $\text{C}_{18}\text{H}_{22}\text{N}_3$ , 280.1814; found, 180.1815.



**(E)-1-(3-(benzyloxy)prop-1-yn-1-yl)-3,3-diisopropyltriazen-1-ene (1h)**: yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 (d,  $J = 7.3$  Hz, 2H), 7.35 – 7.30 (m, 2H), 7.28 – 7.23 (m, 1H), 5.05 (hept,  $J = 6.8$  Hz, 1H), 4.64 (s, 2H), 4.48 (s, 2H), 3.99 (hept,  $J = 6.6$  Hz, 1H), 1.32 (d,  $J = 6.7$  Hz, 6H), 1.19 (d,  $J = 6.8$  Hz, 6H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  138.04, 128.35, 128.10, 127.64, 90.67, 74.43, 71.25, 58.46, 50.23, 47.32, 23.36, 19.01. HRMS (ESI-TOF)  $m/z$ : ( $\text{M}+\text{H}$ ) $^+$  calcd. for  $\text{C}_{16}\text{H}_{24}\text{N}_3\text{O}$ : 274.1919; Found: 274.1919.

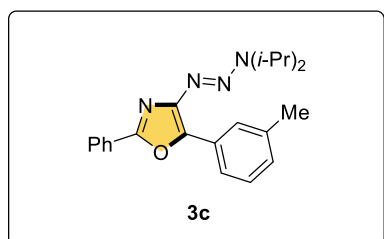


**(E)-4-(3,3-diisopropyltriazen-1-en-1-yl)-2,5-diphenyloxazole (3a)**: Light yellow solid, 56 mg, 81% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.21 – 8.15 (m, 2H), 8.12 – 8.03 (m, 2H), 7.51 – 7.41 (m, 5H), 7.30 – 7.23 (m, 1H), 5.31 – 4.90 (m, 1H), 4.38 – 3.95 (m, 1H), 1.56 – 1.30 (m, 12H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  158.78, 146.48, 138.83, 130.30, 129.61, 128.71, 128.61, 127.83, 126.98, 126.78, 125.13, 51.36, 47.23, 23.38, 19.22. HRMS (ESI-TOF)  $m/z$ : ( $\text{M}+\text{H}$ ) $^+$  calcd. For  $\text{C}_{21}\text{H}_{25}\text{N}_4\text{O}$ , 349.2028; found, 349.2025.



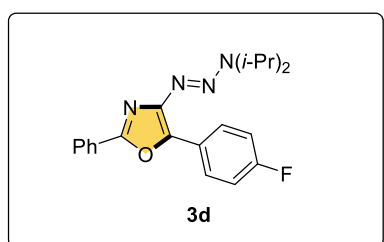
**(E)-5-(2-bromophenyl)-4-(3,3-diisopropyltriazen-1-en-1-yl)-2-phenyloxazole (3b)**: Light yellow solid, 61 mg, 71% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.11 – 8.06 (m,

2H), 7.62 – 7.56 (m, 2H), 7.40 – 7.34 (m, 3H), 7.32 – 7.26 (m, 1H), 7.15 – 7.09 (m, 1H), 5.29 – 5.04 (m, 1H), 4.02 – 3.76 (m, 1H), 1.16 (d,  $J = 6.8$  Hz, 6H), 1.05 (d,  $J = 6.8$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.31, 148.01, 135.28, 133.46, 132.45, 131.15, 130.28, 129.57, 128.74, 127.80, 126.96, 126.59, 123.33, 49.81, 46.24, 23.33, 19.37. HRMS (ESI-TOF)  $m/z$ : ( $\text{M}+\text{H}$ ) $^+$  calcd. For  $\text{C}_{21}\text{H}_{24}\text{BrN}_4\text{O}_2$ , 427.1133, 429.1113; found, 427.1133, 429.1131.



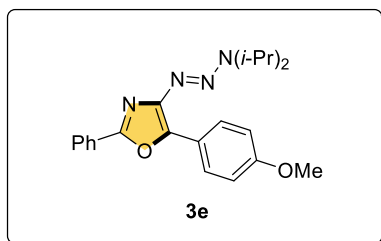
**(E)-4-(3,3-diisopropyltriaz-1-en-1-yl)-5-(4-methoxyphenyl)-2-phenyloxazole (3c):**

Light yellow solid, 51 mg, 71% yield  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.13 – 8.05 (m, 2H), 7.84 (s, 1H), 7.77 (d,  $J = 7.8$  Hz, 1H), 7.42 – 7.31 (m, 3H), 7.28 – 7.20 (m, 1H), 7.00 (d,  $J = 7.5$  Hz, 1H), 5.05 – 4.79 (m, 1H), 4.23 – 3.98 (m, 1H), 2.33 (s, 3H), 1.43 – 1.27 (m, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.67, 146.24, 138.99, 138.05, 130.24, 129.39, 128.66, 128.50, 127.81, 127.76, 126.73, 125.80, 122.20, 51.53, 47.30, 23.25, 21.74, 19.12. HRMS (ESI-TOF)  $m/z$ : ( $\text{M}+\text{H}$ ) $^+$  calcd. For  $\text{C}_{22}\text{H}_{27}\text{N}_4\text{O}$ , 363.2185; found, 363.2185.



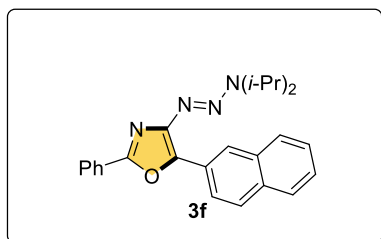
**(E)-4-(3,3-diisopropyltriaz-1-en-1-yl)-5-(4-fluorophenyl)-2-phenyloxazole (3d):**

Light yellow solid, 60 mg, 82% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.17 – 8.01 (m, 2H), 8.01 – 7.85 (m, 2H), 7.49 – 7.26 (m, 3H), 7.16 – 6.94 (m, 2H), 5.23 – 4.69 (m, 1H), 4.36 – 3.91 (m, 1H), 1.49 – 1.20 (m, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.86 (d,  $J = 247.3$  Hz), 158.66, 145.99, 138.04, 130.32, 128.69, 127.66, 126.79 (d,  $J = 7.9$  Hz), 126.70, 125.89 (d,  $J = 2.8$  Hz), 115.65 (d,  $J = 21.9$  Hz), 51.24, 47.17, 23.35, 19.16. HRMS (ESI-TOF)  $m/z$ : ( $\text{M}+\text{H}$ ) $^+$  calcd. For  $\text{C}_{21}\text{H}_{24}\text{FN}_4\text{O}_2$ , 367.1934; found, 367.1935.



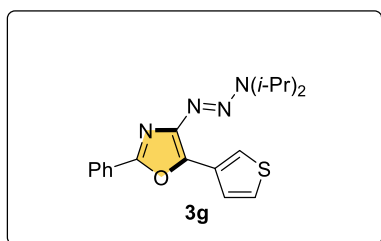
**(E)-4-(3,3-diisopropyltriaz-1-en-1-yl)-5-(4-methoxyphenyl)-2-phenyloxazole (3e):**

Light yellow solid, 60 mg, 80% yield.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.14 – 8.04 (m, 2H), 7.99 – 7.83 (m, 2H), 7.41 – 7.30 (m, 3H), 6.96 – 6.86 (m, 2H), 5.17 – 4.72 (m, 1H), 4.24 – 4.00 (m, 1H), 3.77 (s, 3H), 1.46 – 1.23 (m, 12H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.84, 158.19, 145.06, 139.05, 130.08, 128.66, 127.85, 126.61, 122.49, 114.16, 55.45, 51.15, 47.03, 23.36, 19.22. **HRMS (ESI-TOF)**  $m/z$ :  $(\text{M}+\text{H})^+$  calcd. For  $\text{C}_{22}\text{H}_{27}\text{N}_4\text{O}_2$ , 379.2134; found, 379.2135.



**(E)-4-(3,3-diisopropyltriaz-1-en-1-yl)-5-(naphthalen-2-yl)-2-phenyloxazole (3f):**

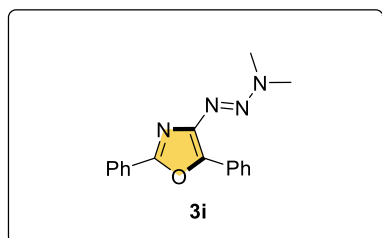
Light yellow solid, 60 mg, 75% yield.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.40 (s, 1H), 8.21 – 8.09 (m, 3H), 7.84 – 7.70 (m, 3H), 7.47 – 7.31 (m, 5H), 5.15 – 4.84 (m, 1H), 4.25 – 4.04 (m, 1H), 1.38 (d,  $J = 6.8$  Hz, 12H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.96, 146.82, 138.99, 133.62, 132.43, 130.35, 128.71, 128.32, 128.15, 127.86, 127.74, 127.00, 126.82, 126.46, 125.95, 123.71, 123.30, 51.61, 47.46, 23.30, 19.21. **HRMS (ESI-TOF)**  $m/z$ :  $(\text{M}+\text{H})^+$  calcd. For  $\text{C}_{25}\text{H}_{27}\text{N}_4\text{O}$ , 399.2185; found, 399.2185.



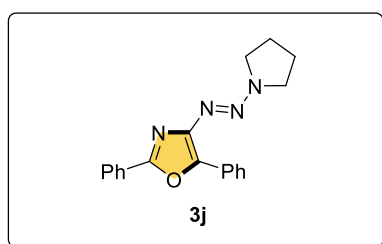
**(E)-4-(3,3-diisopropyltriaz-1-en-1-yl)-2-phenyl-5-(thiophen-3-yl)oxazole (3g):**

Light yellow solid, 57 mg, 80% yield.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.10 – 8.04 (m, 2H), 7.67 – 7.61 (m, 2H), 7.41 – 7.34 (m, 3H), 7.33 – 7.29 (m, 1H), 5.22 – 4.78 (m, 1H), 4.33 – 3.91 (m, 1H), 1.48 – 1.23 (m, 12H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.38,

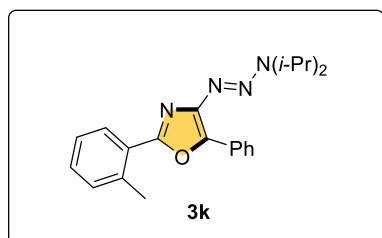
145.11, 137.05, 130.29, 130.21, 128.67, 127.74, 126.68, 125.89, 125.49, 119.81, 51.13, 47.01, 23.36, 19.21. **HRMS (ESI-TOF)  $m/z$ :** (M+H)<sup>+</sup> calcd. For C<sub>19</sub>H<sub>23</sub>N<sub>4</sub>O<sub>S</sub>, 355.1593; found, 355.1595.



**(E)-4-(3,3-dimethyltriaz-1-en-1-yl)-2,5-diphenyloxazole (3i):** Light yellow solid, 36 mg, 61% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.22 – 8.15 (m, 2H), 8.12 – 8.07 (m, 2H), 7.50 – 7.41 (m, 5H), 7.32 – 7.25 (m, 1H), 3.64 (s, 3H), 3.32 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 158.89, 145.53, 139.51, 130.52, 129.14, 128.70, 128.65, 127.35, 127.26, 126.82, 125.20, 43.58, 36.64. **HRMS (ESI-TOF)  $m/z$ :** (M+H)<sup>+</sup> calcd. For C<sub>17</sub>H<sub>17</sub>N<sub>4</sub>O, 293.1402; found, 293.1401.



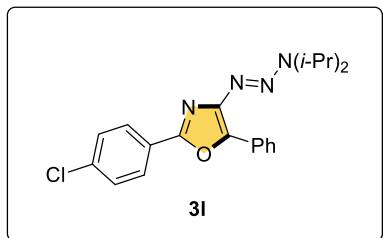
**(E)-2,5-diphenyl-4-(pyrrolidin-1-yl)diaz-enyl)oxazole (3j):** Yellow solid, 39 mg, 62% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.16 – 8.08 (m, 2H), 8.03 – 7.95 (m, 2H), 7.44 – 7.34 (m, 5H), 7.25 – 7.19 (m, 1H), 3.90 – 3.81 (m, 4H), 1.77 – 1.63 (m, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.05, 145.59, 139.79, 130.56, 129.12, 128.70, 127.36, 126.88, 125.27, 44.89, 44.01, 24.38. **HRMS (ESI-TOF)  $m/z$ :** (M+H)<sup>+</sup> calcd. For C<sub>19</sub>H<sub>19</sub>N<sub>4</sub>O, 319.1559; found, 319.1558.



**(E)-4-(3,3-diisopropyltriaz-1-en-1-yl)-5-phenyl-2-(o-tolyl)oxazole (3k):** Light yellow solid, 51 mg, 70% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.08 – 8.03 (m, 1H), 7.99 – 7.93 (m, 2H), 7.39 – 7.31 (m, 2H), 7.26 – 7.14 (m, 4H), 5.18 – 4.94 (m, 1H),

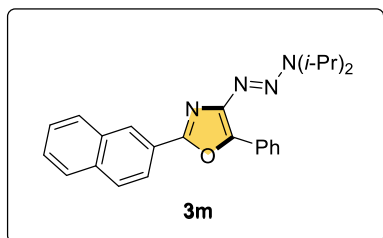


4.21 – 3.92 (m, 1H), 2.71 (s, 3H), 1.39 – 1.26 (m, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.37, 146.19, 138.49, 137.62, 131.68, 129.90, 129.65, 129.23, 128.60, 126.87, 126.84, 125.95, 125.03, 50.75, 47.07, 23.51, 22.18, 19.23. HRMS (ESI-TOF)  $m/z$ :  $(\text{M}+\text{H})^+$  calcd. For  $\text{C}_{22}\text{H}_{27}\text{N}_4\text{O}$ , 363.2185; found, 363.2187.



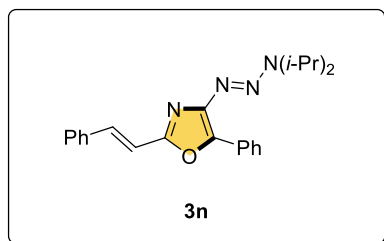
**(E)-2-(4-chlorophenyl)-4-(3,3-diisopropyltriaz-1-en-1-yl)-5-phenyloxazole (3l):**

Light yellow solid, 62 mg, 81% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.08 – 7.89 (m, 4H), 7.41 – 7.27 (m, 4H), 7.24 – 7.11 (m, 1H), 5.14 – 4.75 (m, 1H), 4.20 – 3.95 (m, 1H), 1.52 – 1.22 (m, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.75, 146.44, 138.99, 136.27, 129.33, 128.99, 128.58, 127.95, 127.08, 126.23, 125.08, 51.28, 47.25, 23.33, 19.14. HRMS (ESI-TOF)  $m/z$ :  $(\text{M}+\text{H})^+$  calcd. For  $\text{C}_{21}\text{H}_{24}\text{ClN}_4\text{O}$ , 383.1639; found, 383.1637.

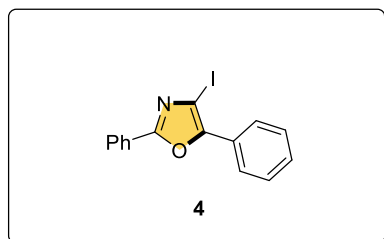


**(E)-4-(3,3-diisopropyltriaz-1-en-1-yl)-2-(naphthalen-2-yl)-5-phenyloxazole (3m):**

Yellow solid, 70 mg, 88% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.56 (d,  $J = 1.6$  Hz, 1H), 8.17 (dd,  $J = 8.6, 1.6$  Hz, 1H), 8.06 – 7.98 (m, 2H), 7.90 – 7.82 (m, 1H), 7.81 (d,  $J = 8.6$  Hz, 1H), 7.79 – 7.71 (m, 1H), 7.45 – 7.38 (m, 2H), 7.40 – 7.31 (m, 2H), 7.22 – 7.14 (m, 1H), 5.11 – 4.85 (m, 1H), 4.26 – 4.03 (m, 1H), 1.47 – 1.24 (m, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.86, 146.58, 139.02, 134.23, 133.15, 129.54, 128.82, 128.59, 128.44, 127.95, 127.17, 126.99, 126.71, 126.51, 125.14, 125.07, 123.84, 51.38, 47.24, 23.33, 19.16. HRMS (ESI-TOF)  $m/z$ :  $(\text{M}+\text{H})^+$  calcd. For  $\text{C}_{25}\text{H}_{27}\text{N}_4\text{O}$ , 399.2185; found, 399.2184.



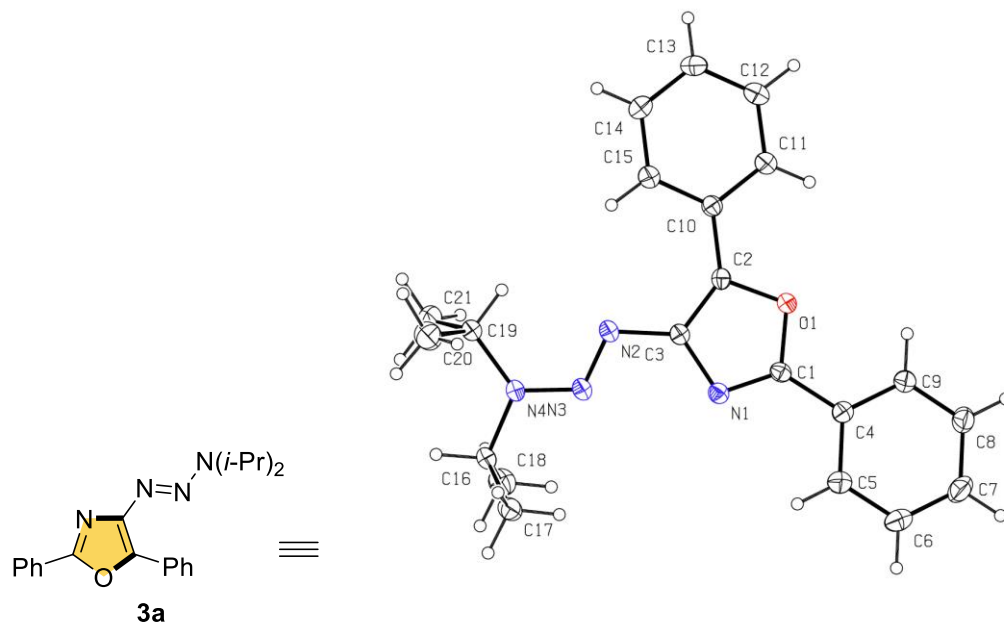
**4-((E)-3,3-diisopropyltriaz-1-en-1-yl)-5-phenyl-2-((E)-styryl)oxazole (3n):** Yellow solid, 64 mg, 85% yield.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (d,  $J = 7.3$  Hz, 2H), 7.56 – 7.44 (m, 3H), 7.40 – 7.28 (m, 4H), 7.30 – 7.21 (m, 1H), 7.23 – 7.14 (m, 1H), 6.96 (d,  $J = 16.4$  Hz, 1H), 5.08 – 4.82 (m, 1H), 4.33 – 3.94 (m, 1H), 1.44 – 1.26 (m, 12H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.68, 146.45, 138.70, 135.94, 129.43, 129.13, 129.01, 128.60, 127.31, 127.03, 125.15, 114.56, 51.48, 47.33, 23.30, 19.17. **HRMS (ESI-TOF)**  $m/z$ :  $(\text{M}+\text{H})^+$  calcd. For  $\text{C}_{23}\text{H}_{27}\text{N}_4\text{O}$ , 375.2185; found, 375.2185.



**4-iodo-2,5-diphenyloxazole (4):** Off-white solid, 38 mg, 55% yield.  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.13 – 8.08 (m, 2H), 8.07 – 8.02 (m, 3H), 7.51 – 7.47 (m, 6H), 7.44 – 7.39 (m, 1H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.05, 150.10, 131.01, 129.14, 128.97, 128.81, 127.44, 126.52, 126.48, 126.09, 80.00. **HRMS (ESI-TOF)**  $m/z$ :  $(\text{M}+\text{H})^+$  calcd. For  $\text{C}_{15}\text{H}_{11}\text{INO}$ , 347.9885; found, 347.9885.

## 7. X-Ray Crystallographic Data

Compound **3a** was crystallized from CDCl<sub>3</sub>. Intensity data for **3a** was collected on Bruker D8 Venture Ims3.0.



Bond precision: C-C = 0.0018 Å      Wavelength=0.71073  
 Cell:                    a=20.6474 (5)      b=8.3478 (2)      c=11.4696 (3)  
                           alpha=90            beta=102.688 (1)    gamma=90  
 Temperature:        169 K

	Calculated	Reported
Volume	1928.63 (8)	1928.63 (8)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C21 H24 N4 O	C21 H24 N4 O
Sum formula	C21 H24 N4 O	C21 H24 N4 O
Mr	348.44	348.44
Dx, g cm <sup>-3</sup>	1.200	1.200
Z	4	4
Mu (mm <sup>-1</sup> )	0.076	0.076
F000	744.0	744.0
F000'	744.26	
h, k, lmax	26, 10, 14	26, 10, 14
Nref	4260	4258
Tmin, Tmax	0.967, 0.983	0.710, 0.746
Tmin'	0.966	

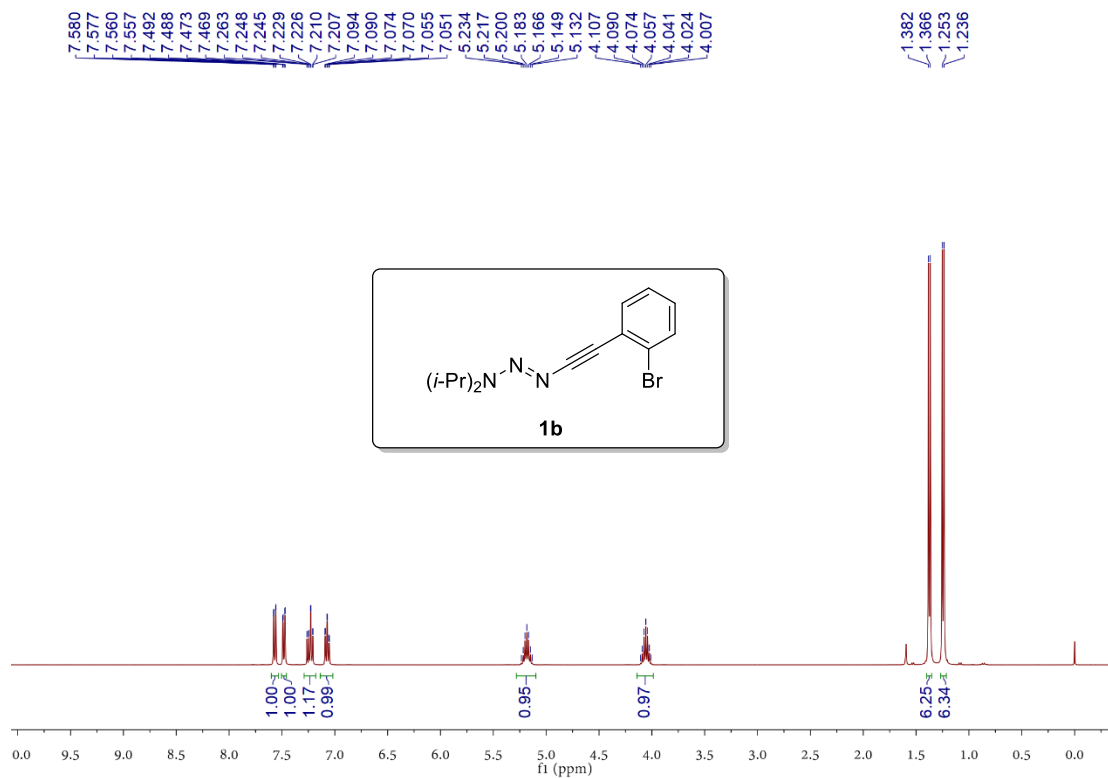
Correction method= # Reported T Limits: Tmin=0.710 Tmax=0.746  
 AbsCorr = MULTI-SCAN

Data completeness= 1.000      Theta(max)= 27.119

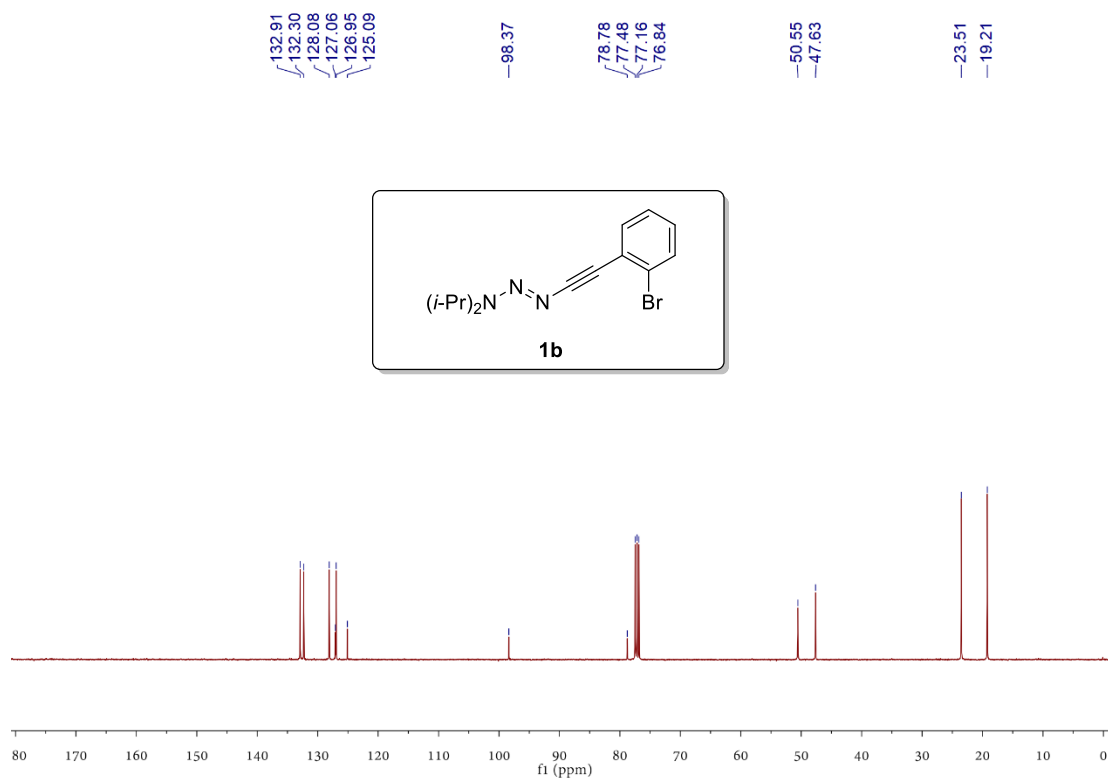
R(reflections)= 0.0400 ( 3708)      wR2(reflections)=  
 S = 1.025      Npar= 239      0.1014 ( 4258)

**Figure S2.** X-ray crystallographic structure **3a** (ORTEP view with 50% thermal ellipsoid contour probability)

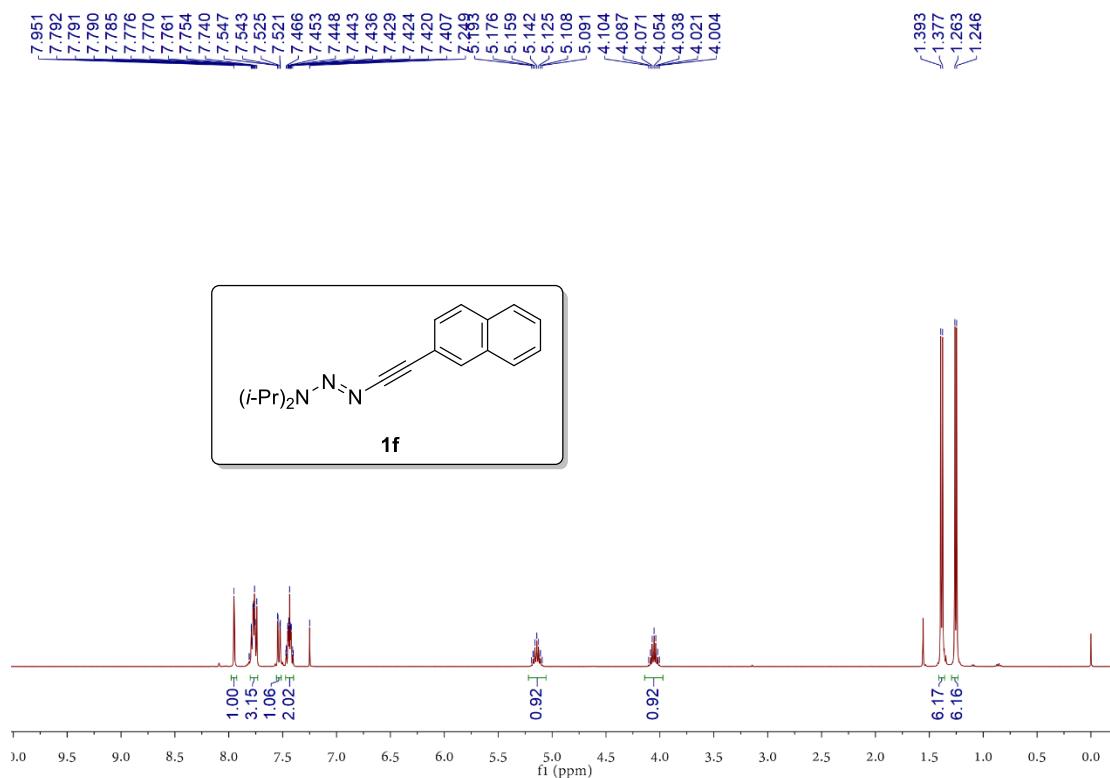
## 8. Copies of NMR Spectra



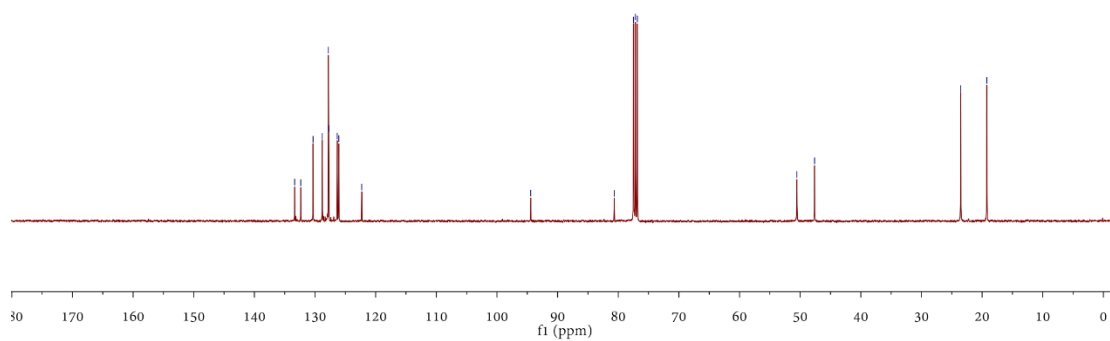
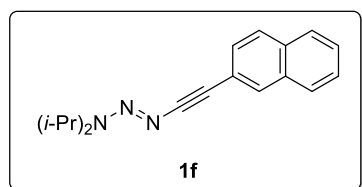
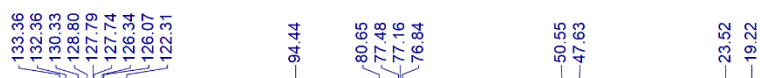
$^1\text{H NMR}$  of **1b** ( $\text{CDCl}_3$ , 400 MHz)



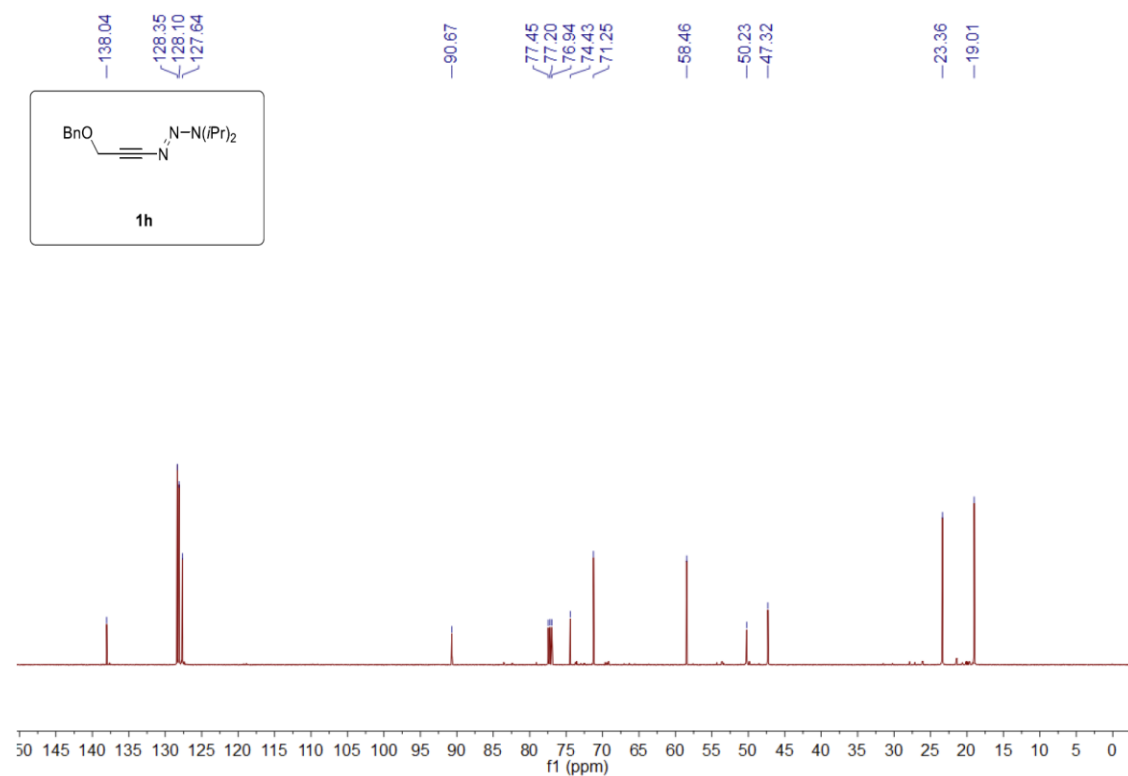
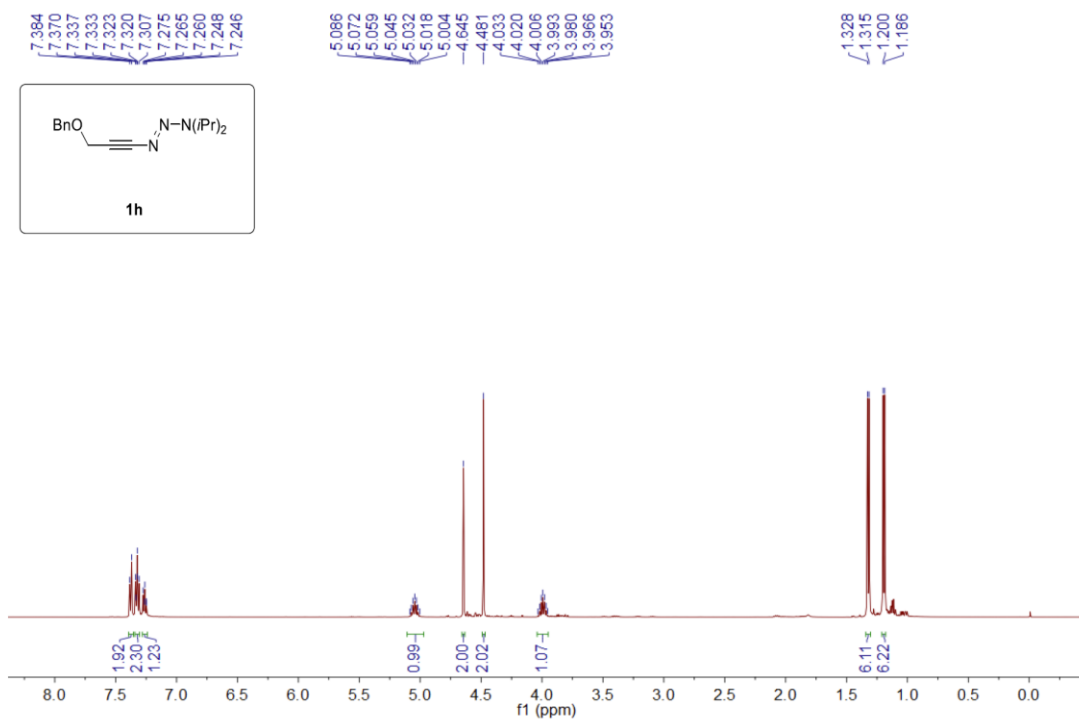
$^{13}\text{C NMR}$  of **1b** ( $\text{CDCl}_3$ , 100 MHz)

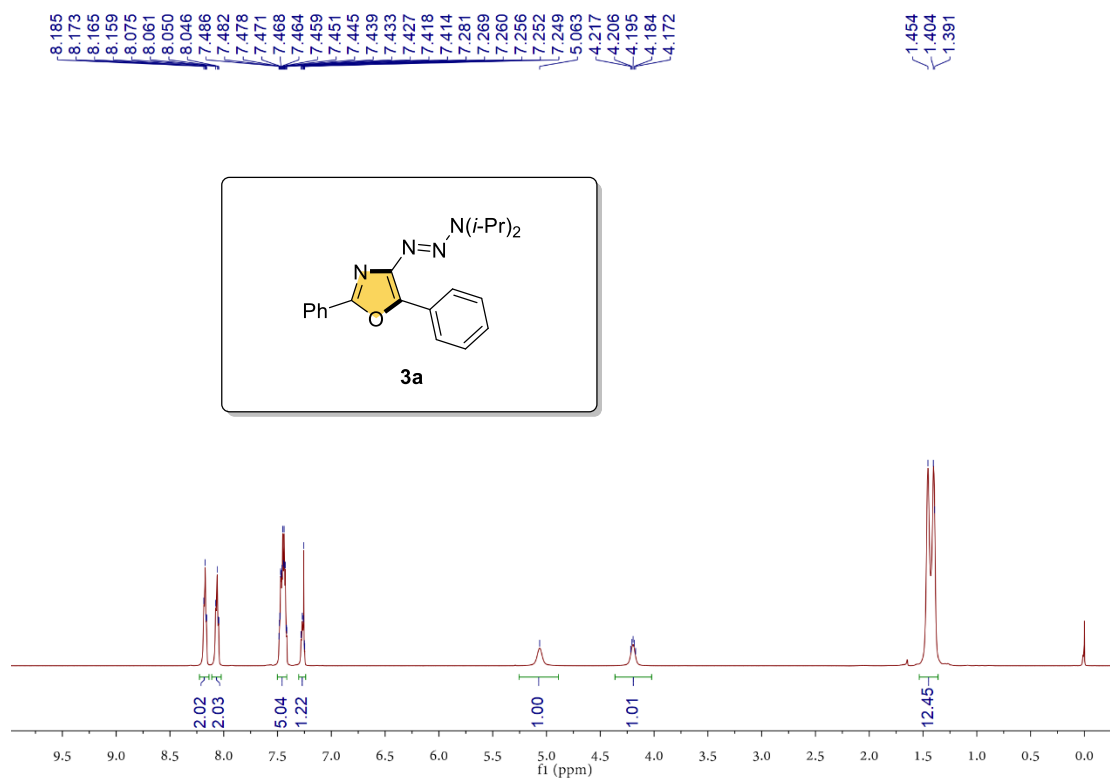


$^1\text{H NMR}$  of **1f** ( $\text{CDCl}_3$ , 400 MHz)

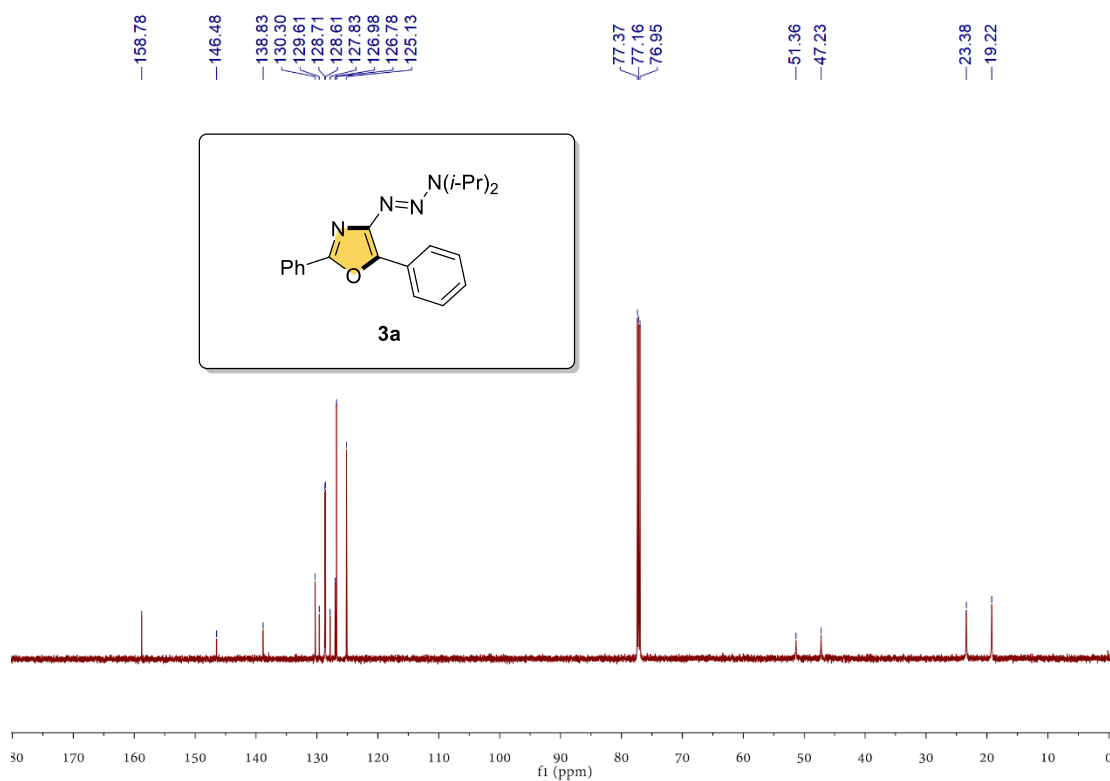


$^{13}\text{C NMR}$  of **1f** ( $\text{CDCl}_3$ , 100 MHz)



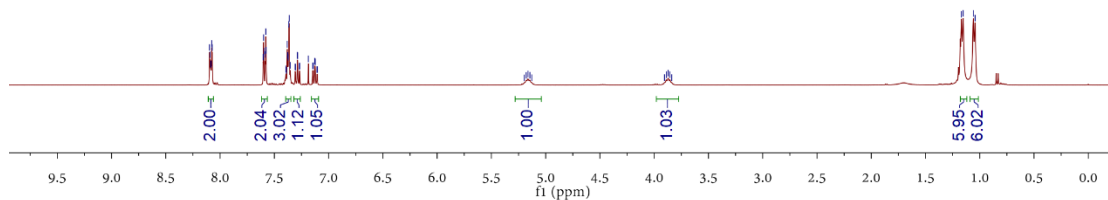
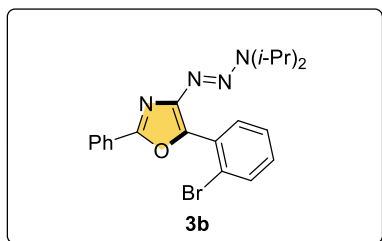


$^1\text{H NMR}$  of **3a** ( $\text{CDCl}_3$ , 600 MHz)



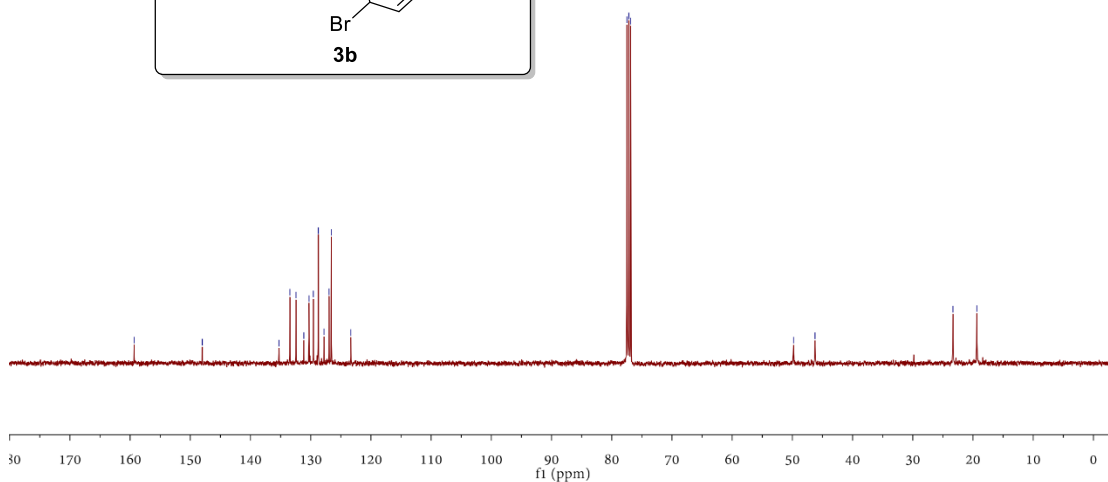
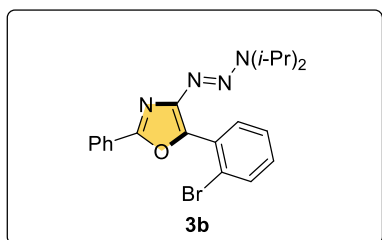
$^{13}\text{C NMR}$  of **3a** ( $\text{CDCl}_3$ , 150 MHz)

8.097  
8.091  
8.085  
8.083  
8.077  
8.073  
7.603  
7.599  
7.596  
7.583  
7.579  
7.576  
7.394  
7.389  
7.381  
7.377  
7.373  
7.367  
7.362  
7.355  
7.308  
7.305  
7.289  
7.286  
7.270  
7.267  
7.187  
7.146  
7.142  
7.127  
7.123  
7.107  
7.103  
5.197  
5.180  
5.162  
5.145  
5.128  
3.905  
3.888  
3.872  
3.855  
3.838  
1.170  
1.153  
1.060  
1.043



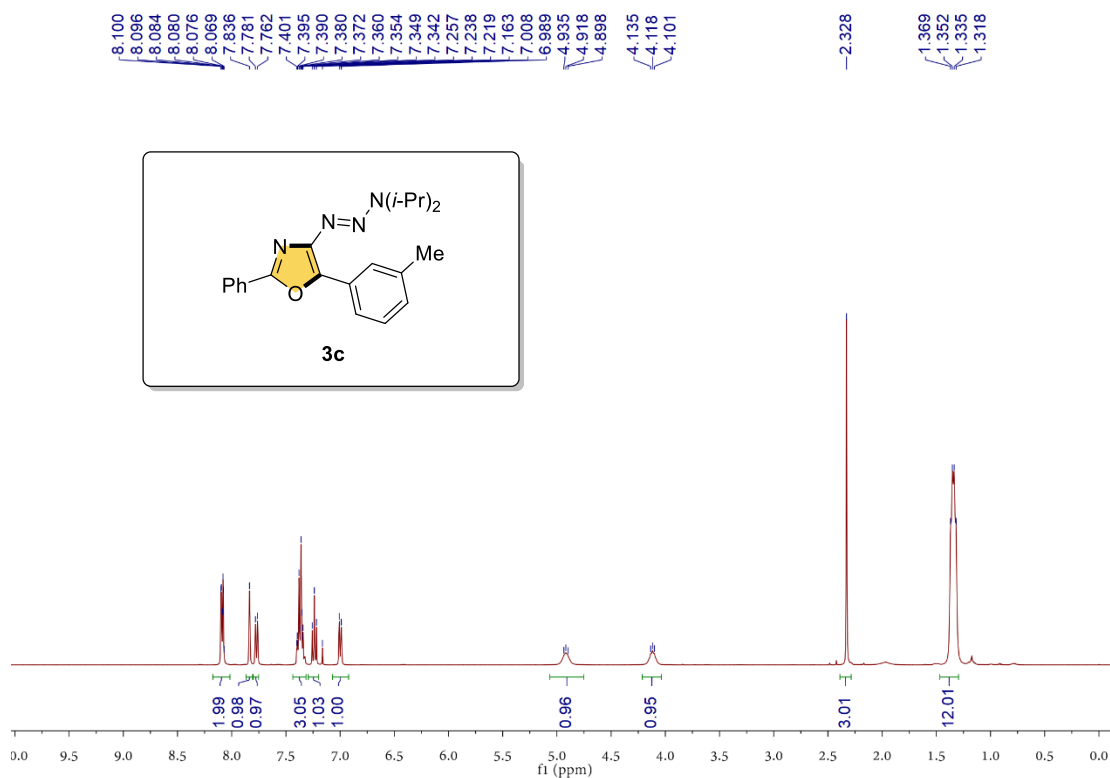
$^1\text{H NMR}$  of **3b** ( $\text{CDCl}_3$ , 400 MHz)

159.31  
148.01  
135.28  
133.46  
132.45  
131.15  
130.28  
129.57  
128.74  
127.80  
126.96  
126.59  
123.33  
77.48  
77.16  
76.84  
49.81  
46.24  
23.33  
19.37

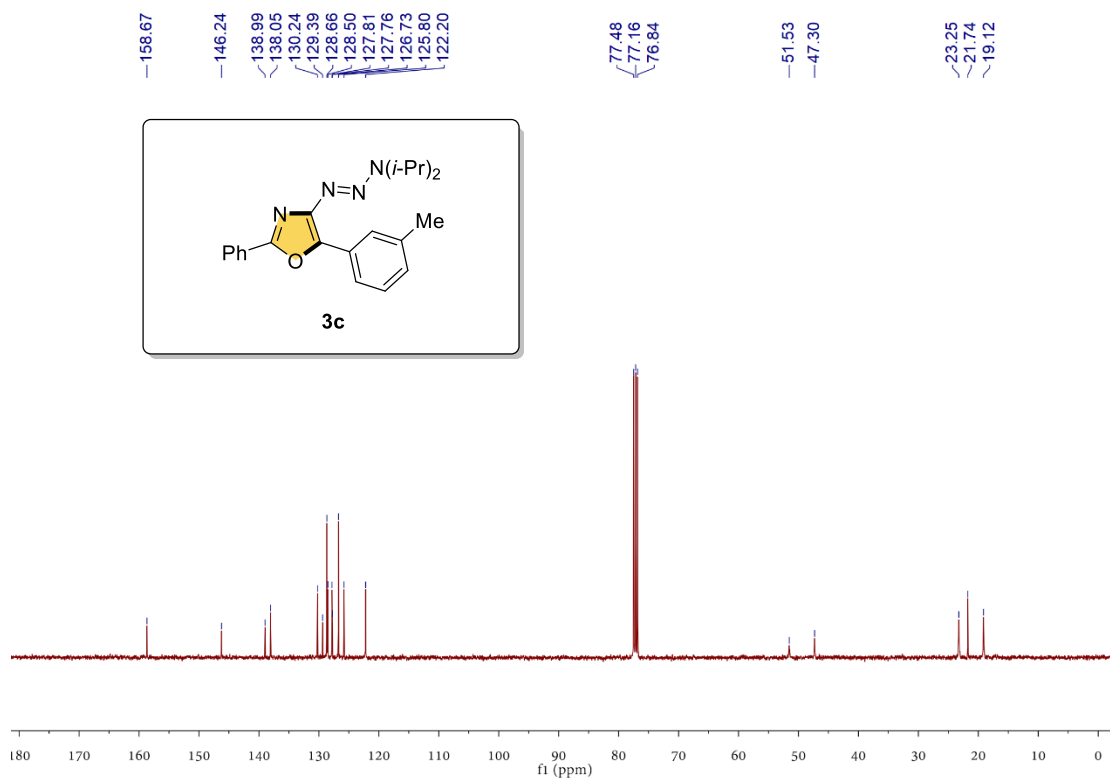


$^{13}\text{C NMR}$  of **3b** ( $\text{CDCl}_3$ , 100 MHz)

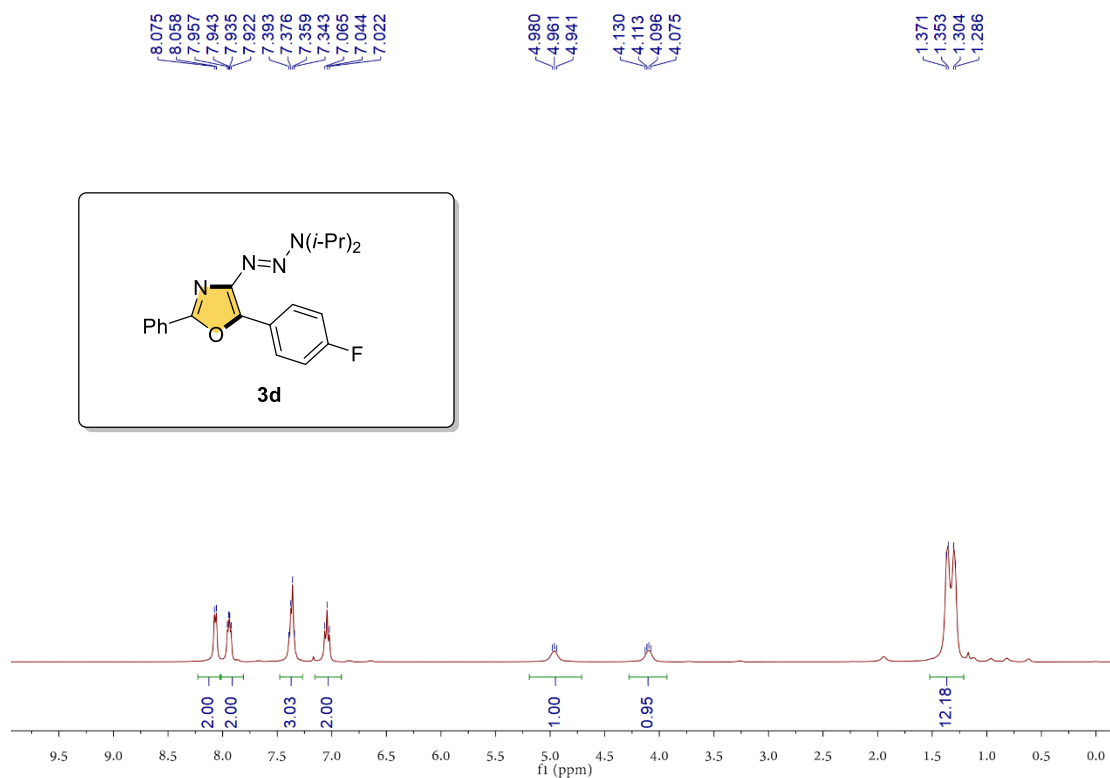




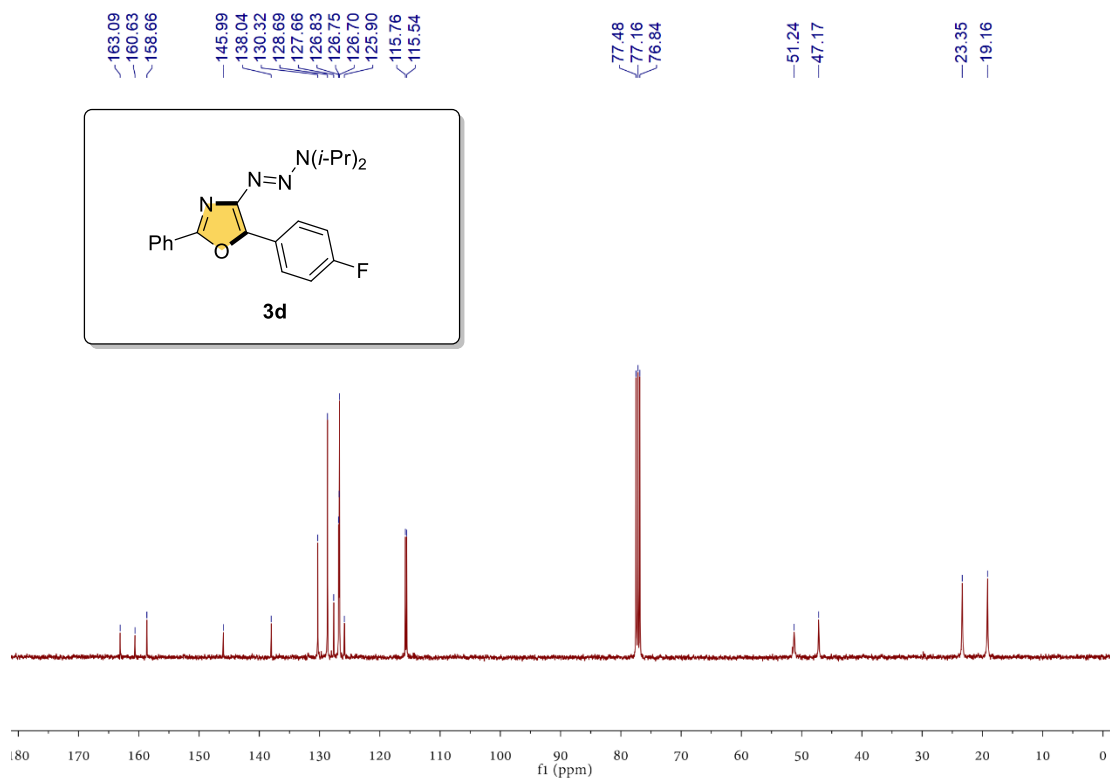
*<sup>1</sup>H NMR of 3c (CDCl<sub>3</sub>, 400 MHz)*



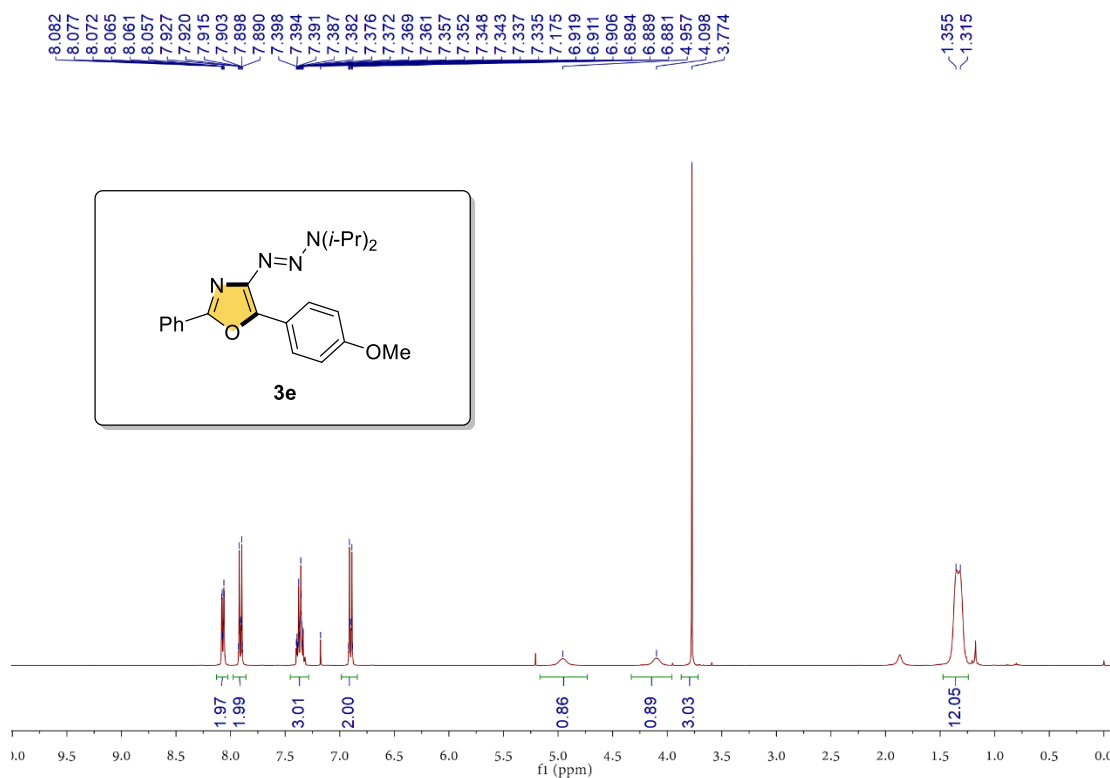
*<sup>13</sup>C NMR of 3c (CDCl<sub>3</sub>, 100 MHz)*



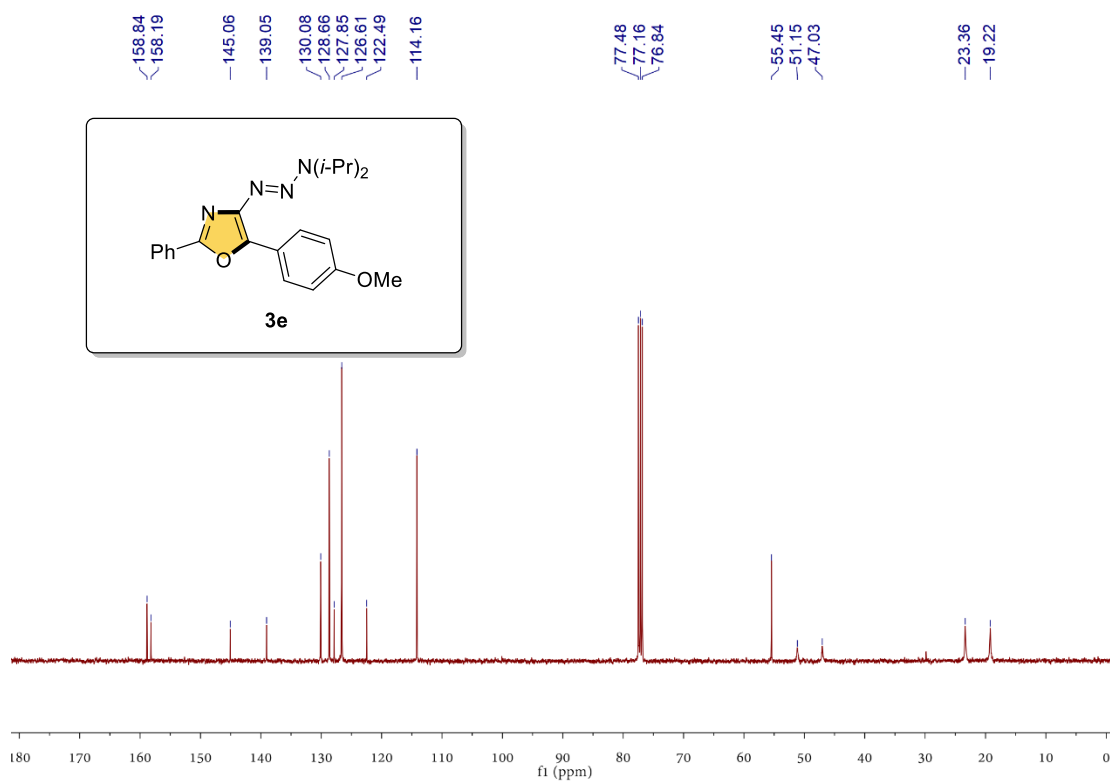
*<sup>1</sup>H NMR of 3d (CDCl<sub>3</sub>, 400 MHz)*



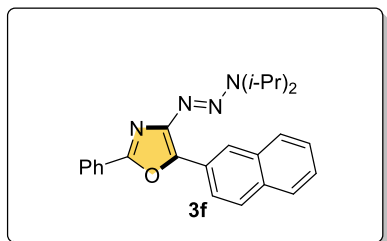
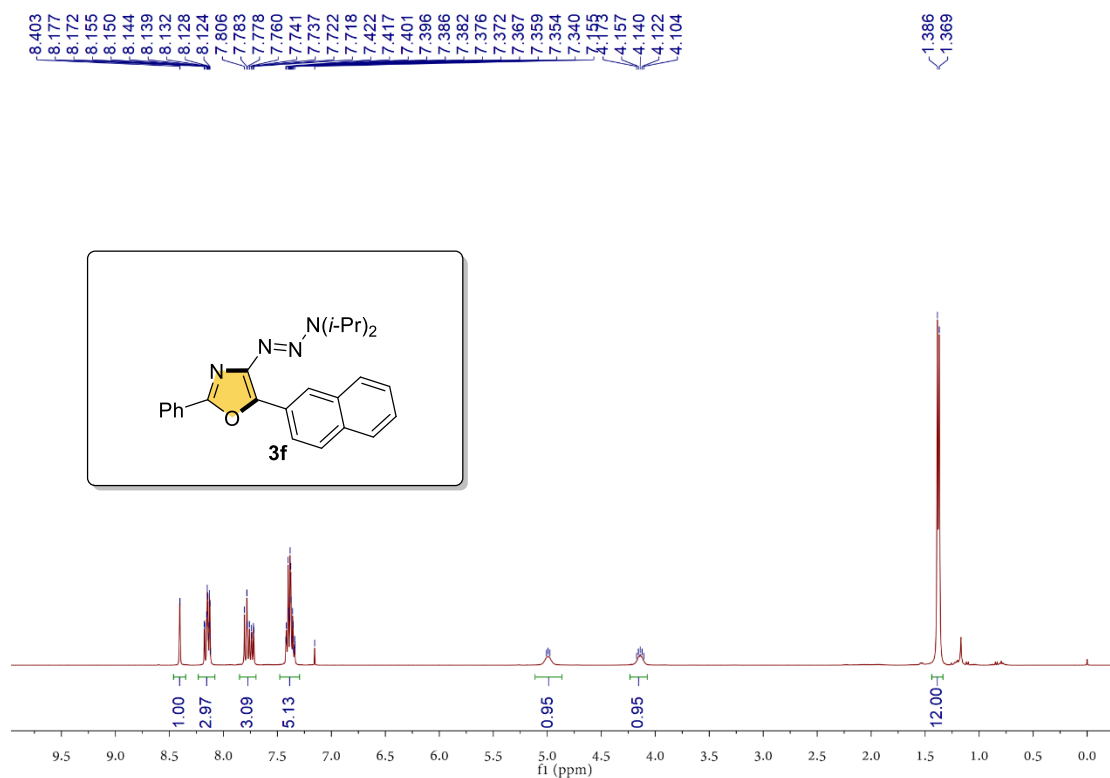
*<sup>13</sup>C NMR of 3d (CDCl<sub>3</sub>, 100 MHz)*



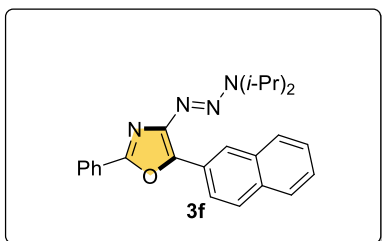
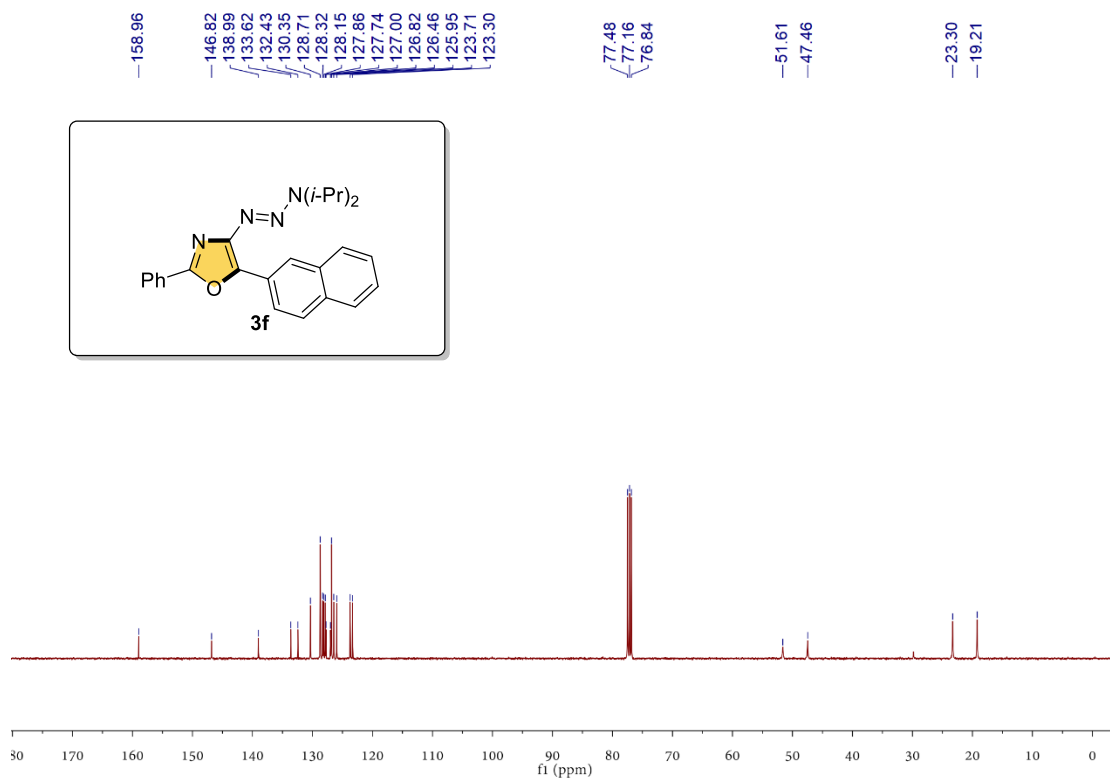
*<sup>1</sup>H NMR of 3e (CDCl<sub>3</sub>, 400 MHz)*



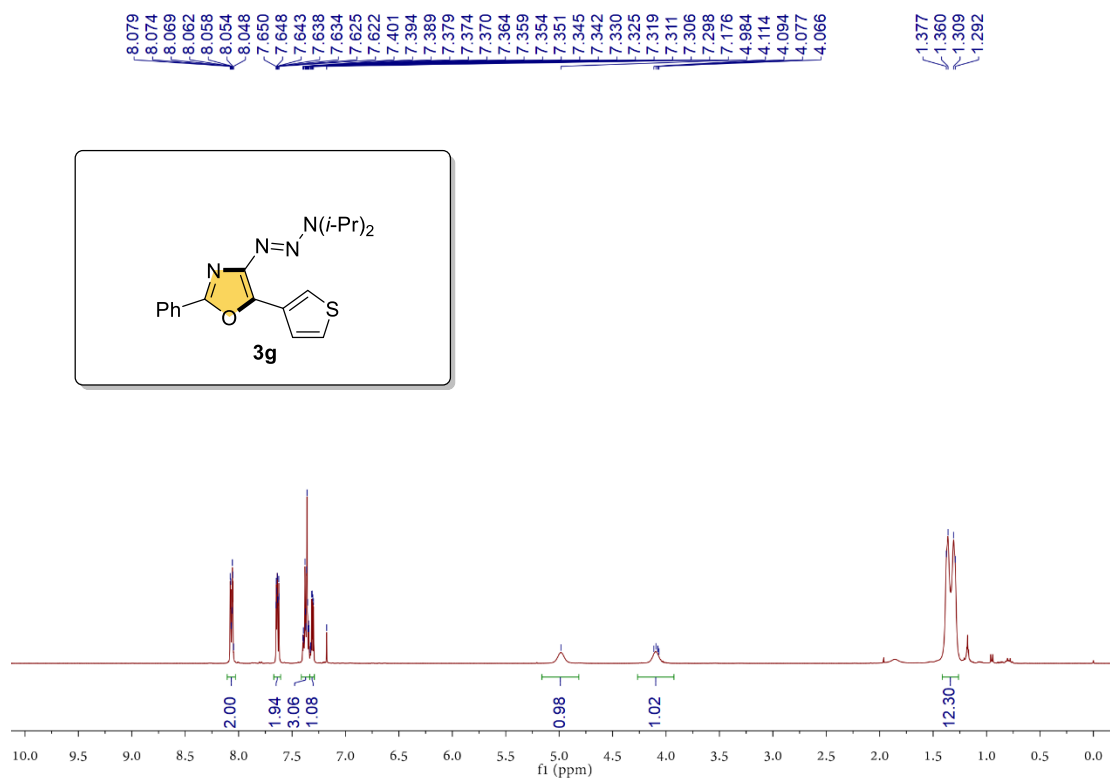
*<sup>13</sup>C NMR of 3e (CDCl<sub>3</sub>, 100 MHz)*



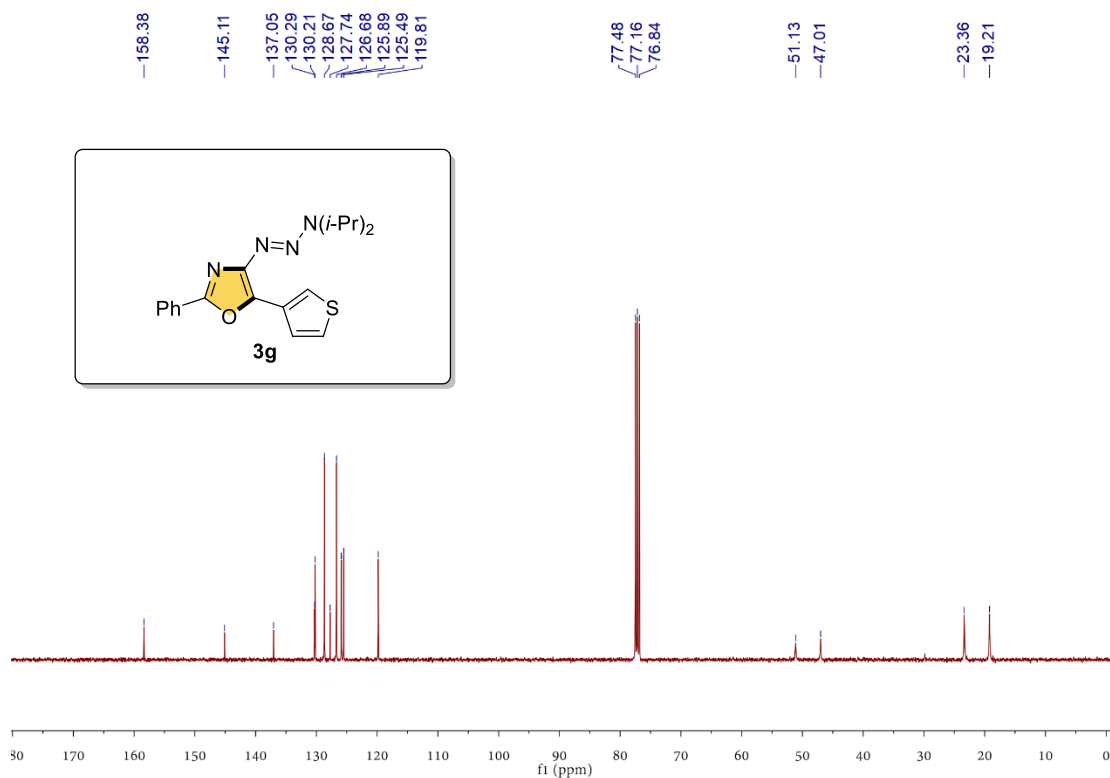
$^1\text{H NMR}$  of **3f** ( $\text{CDCl}_3$ , 400 MHz)



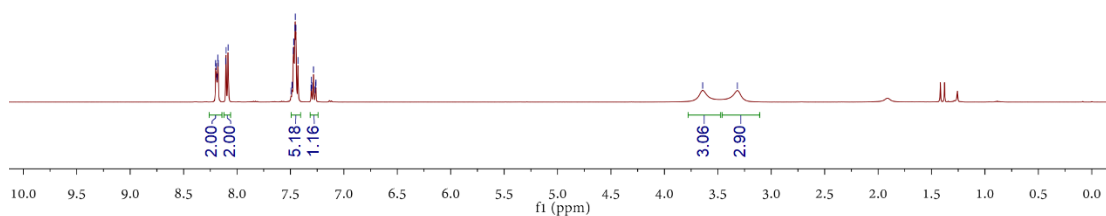
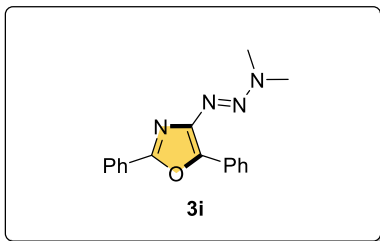
$^{13}\text{C NMR}$  of **3f** ( $\text{CDCl}_3$ , 100 MHz)



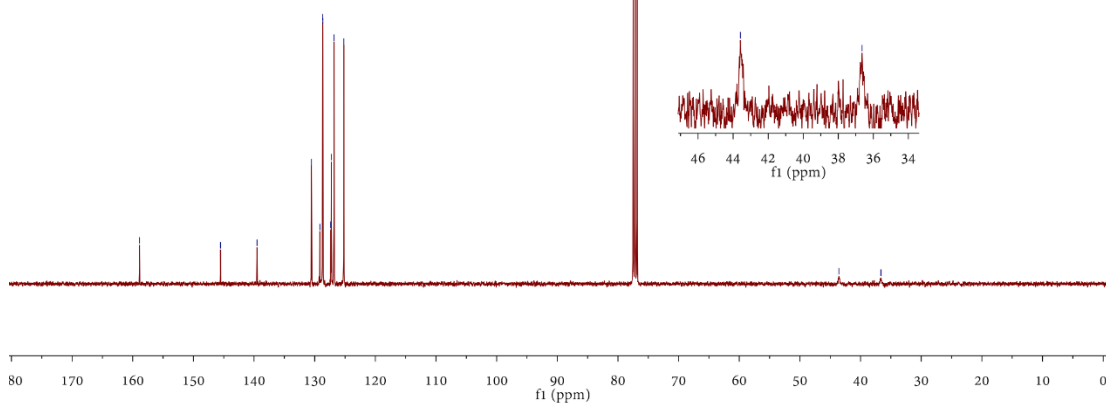
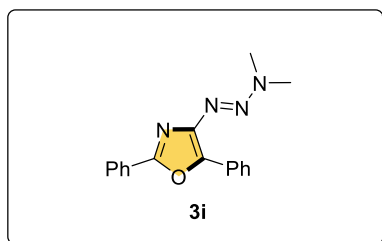
<sup>1</sup>H NMR of **3g** (CDCl<sub>3</sub>, 400 MHz)



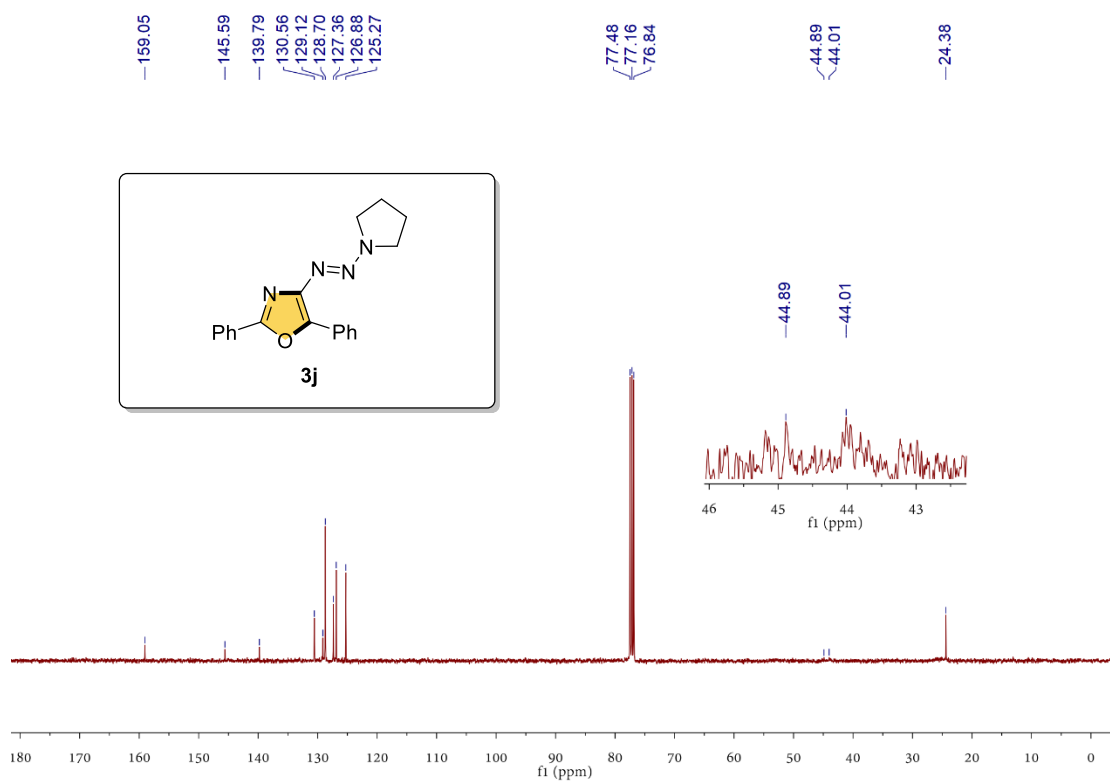
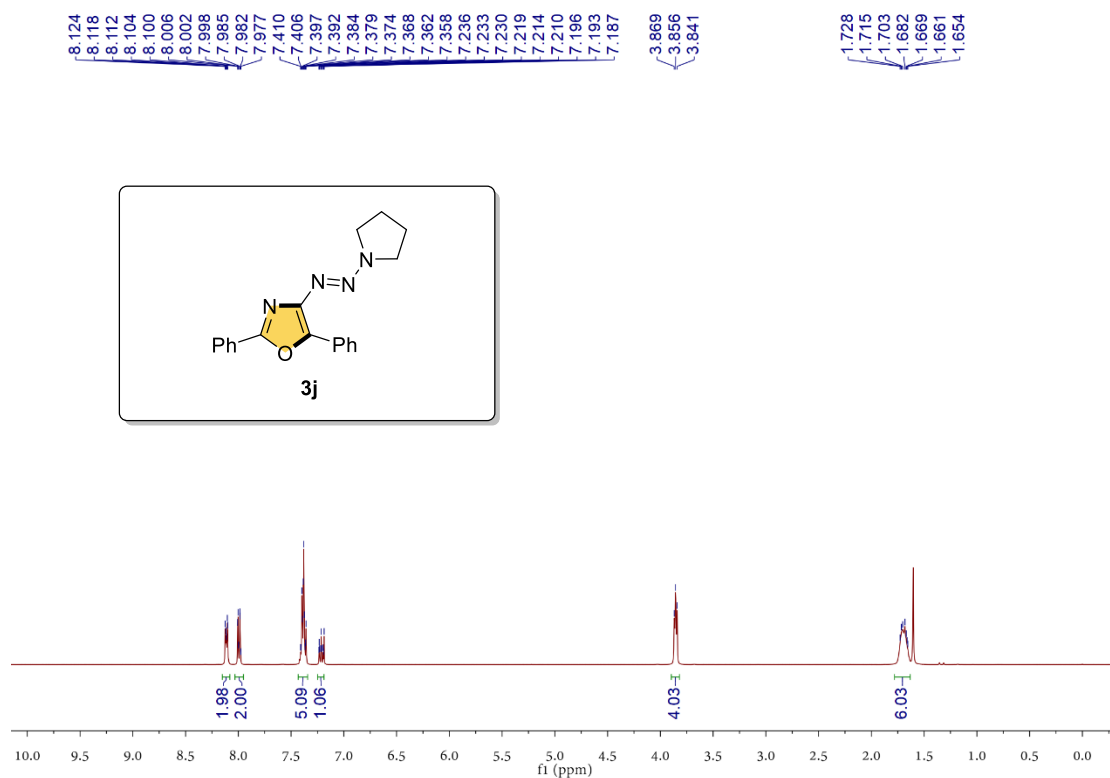
<sup>13</sup>C NMR of **3g** (CDCl<sub>3</sub>, 100 MHz)

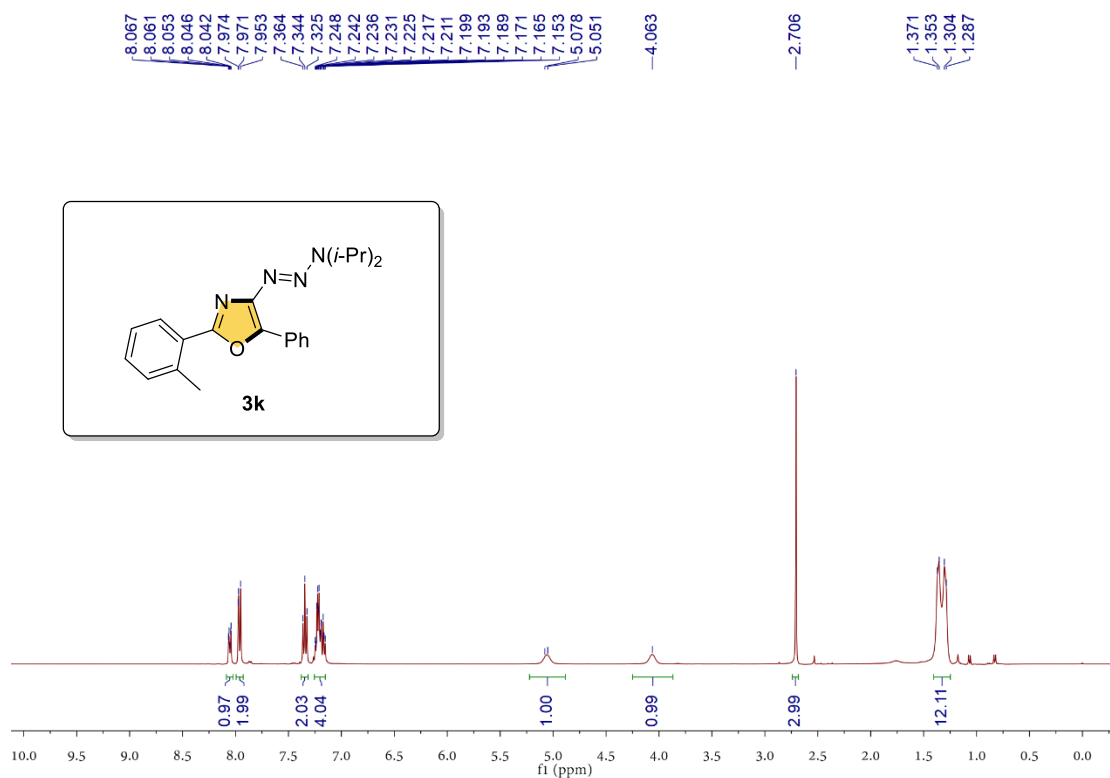


$^1\text{H NMR of } \mathbf{3i} \text{ (CDCl}_3\text{, 400 MHz)}$

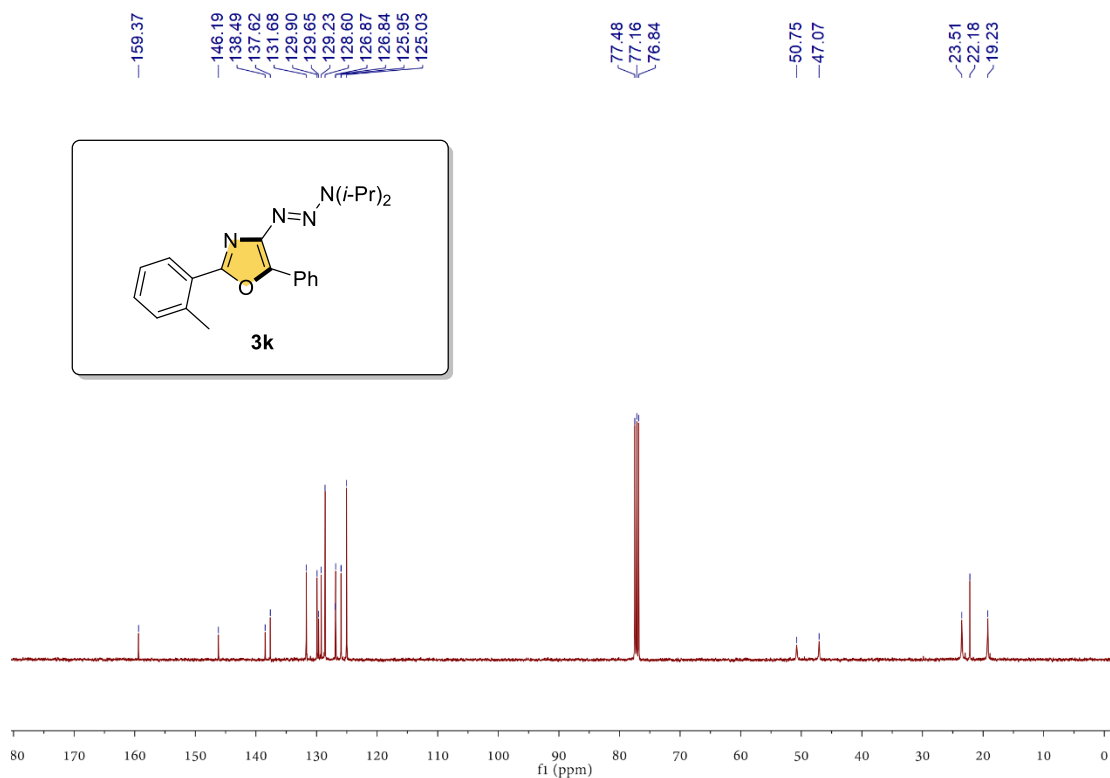


$^{13}\text{C NMR of } \mathbf{3i} \text{ (CDCl}_3\text{, 100 MHz)}$



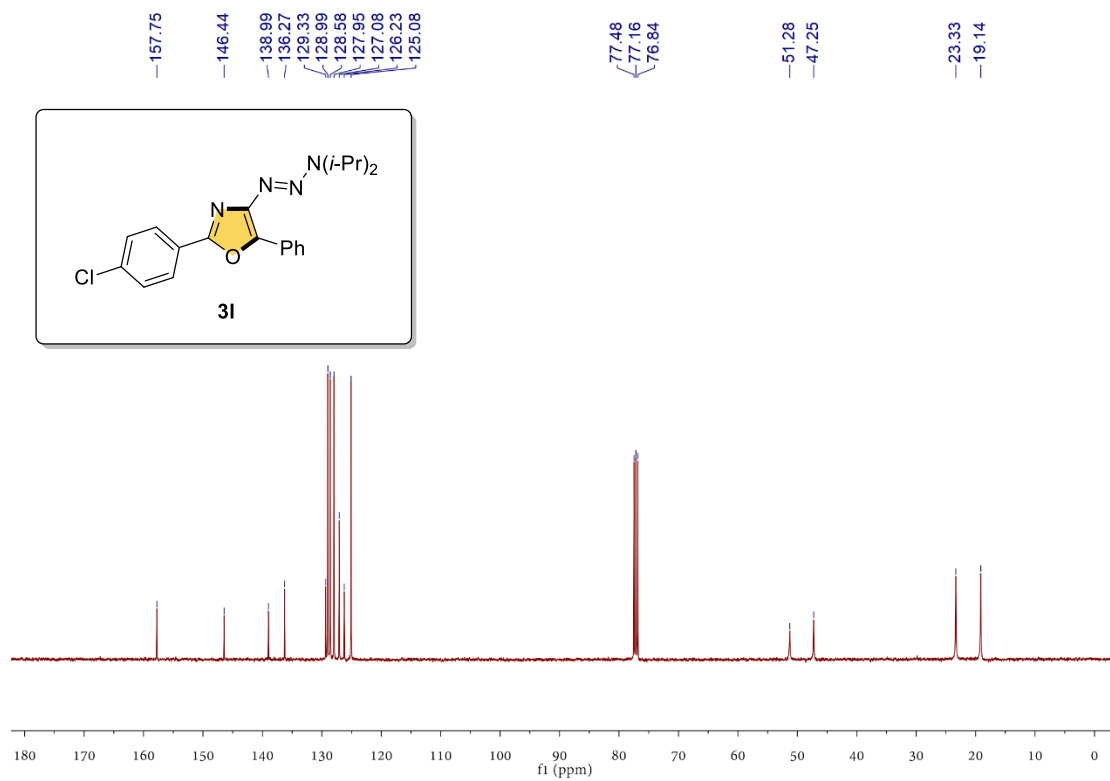
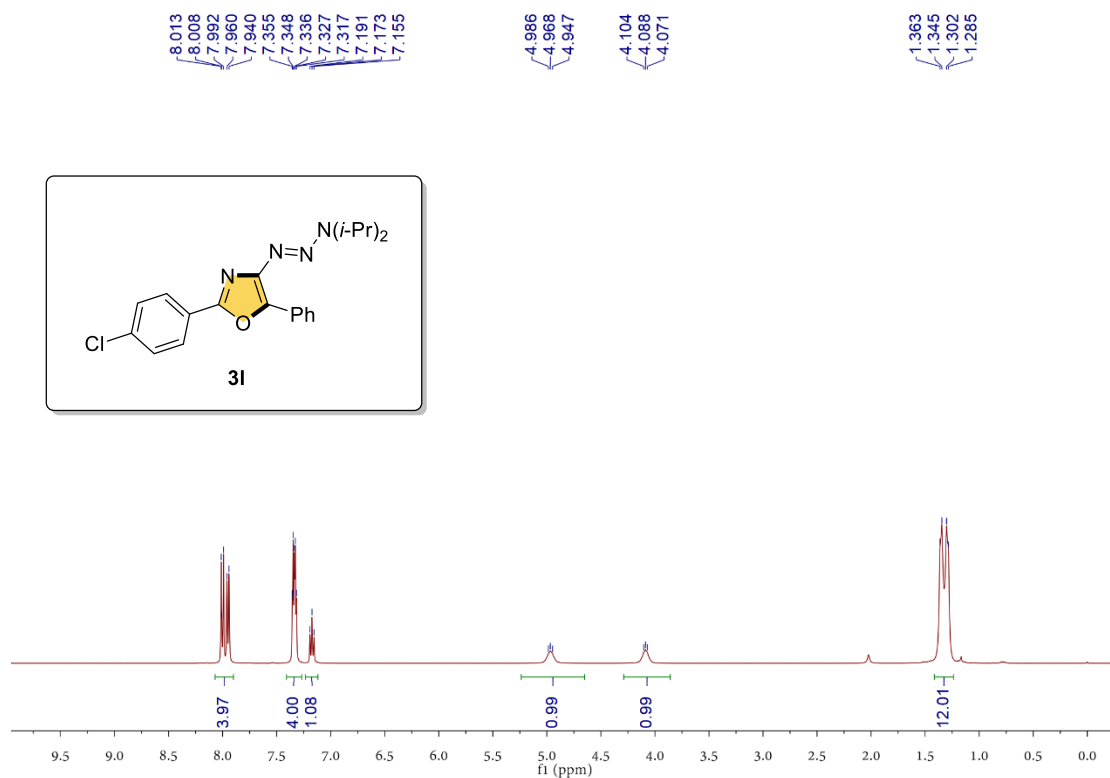


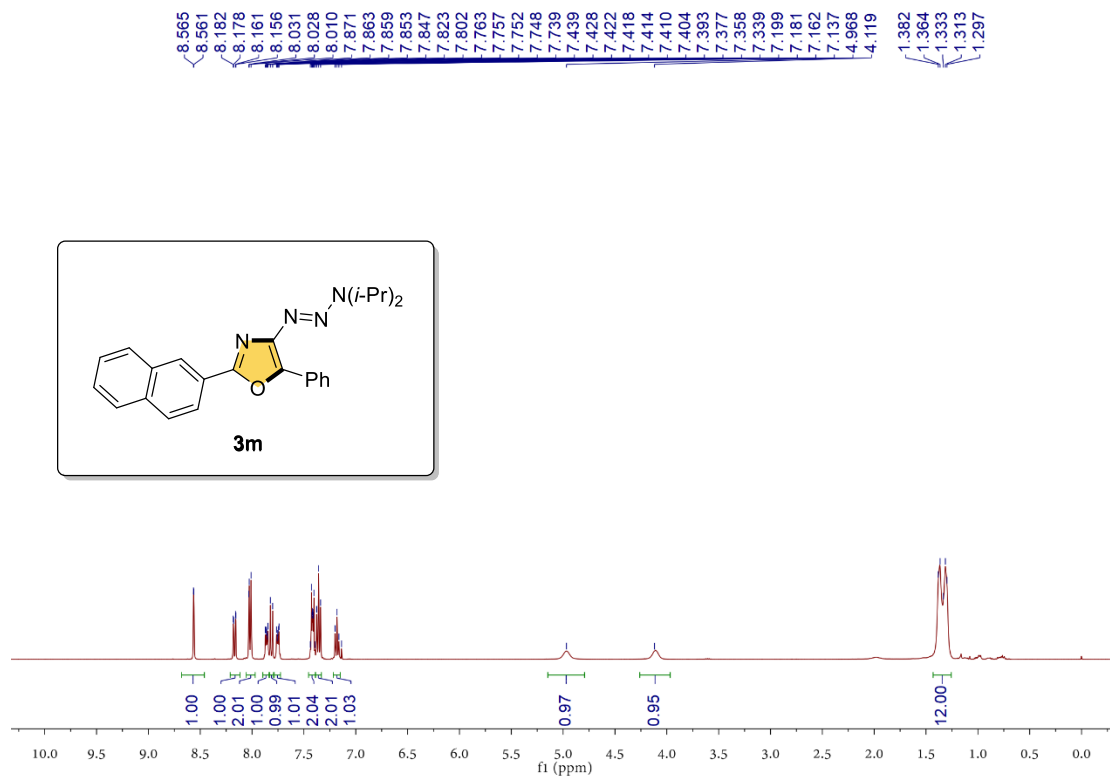
*<sup>1</sup>H NMR of 3k (CDCl<sub>3</sub>, 400 MHz)*



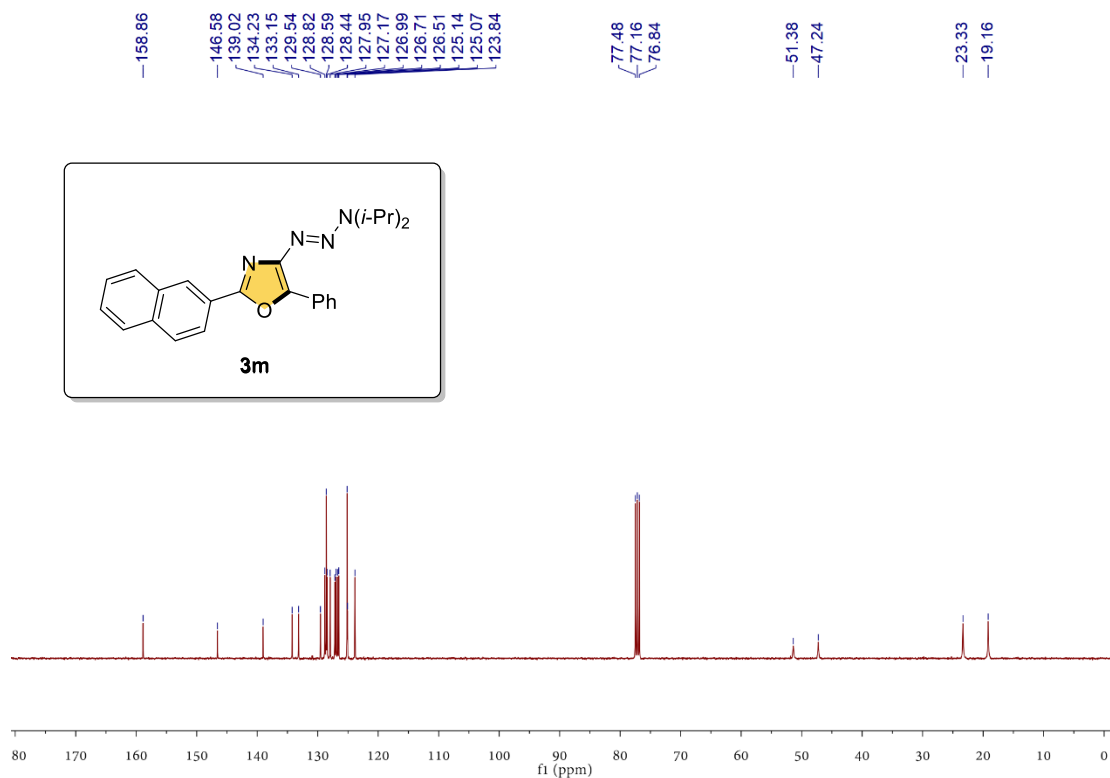
*<sup>13</sup>C NMR of 3k (CDCl<sub>3</sub>, 100 MHz)*



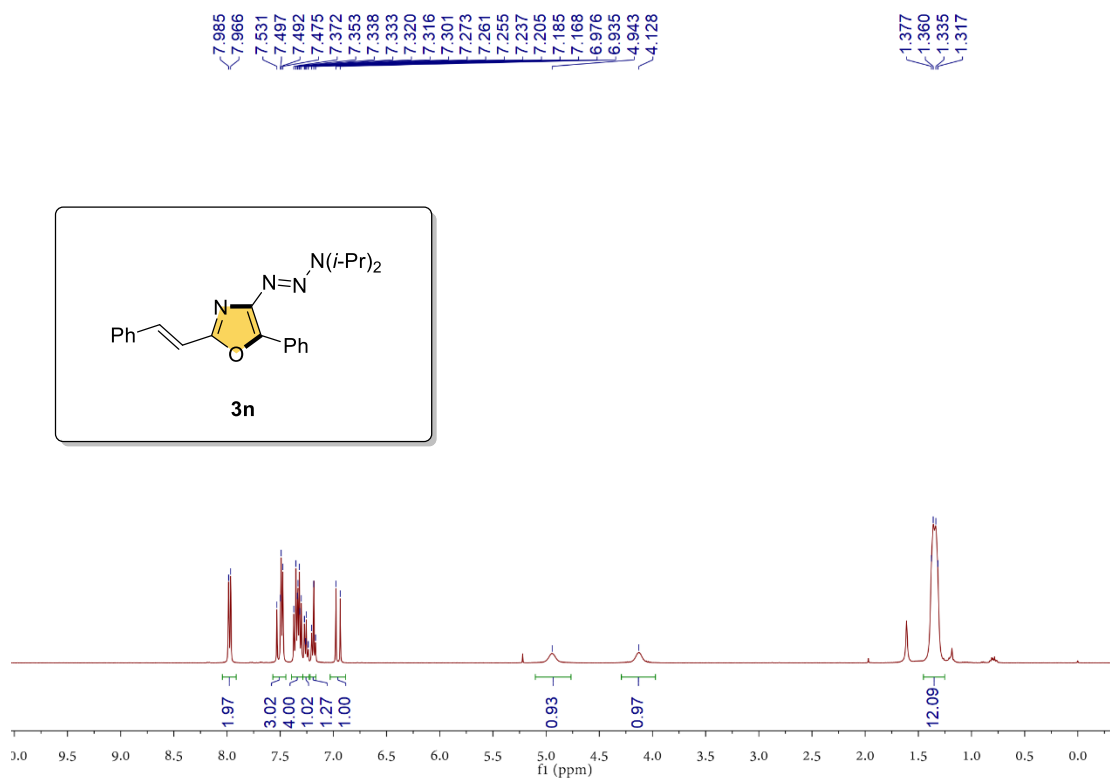




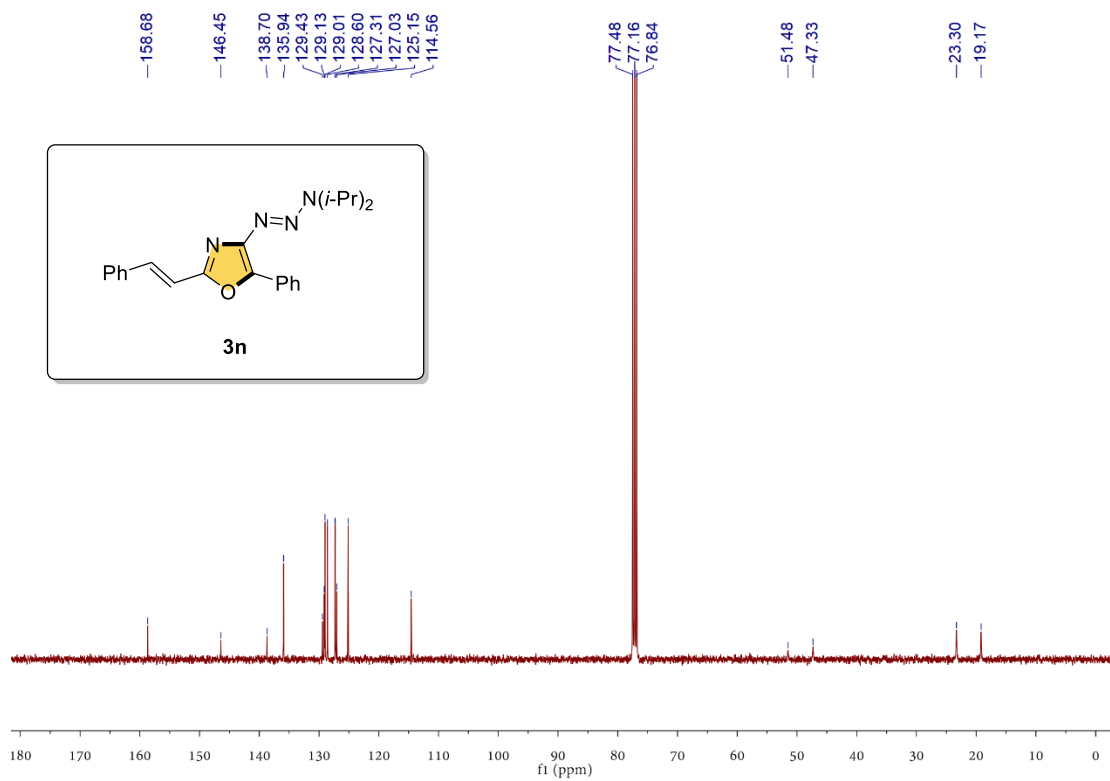
$^1\text{H NMR}$  of **3m** ( $\text{CDCl}_3$ , 400 MHz)



$^{13}\text{C NMR}$  of **3m** ( $\text{CDCl}_3$ , 100 MHz)

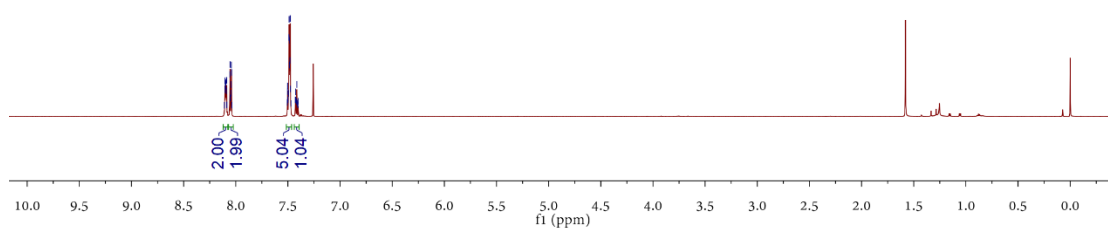
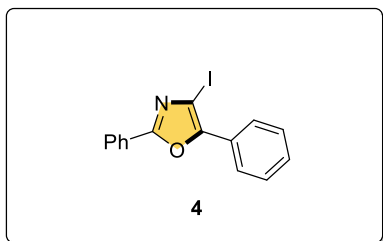


*<sup>1</sup>H NMR of 3n (CDCl<sub>3</sub>, 400 MHz)*



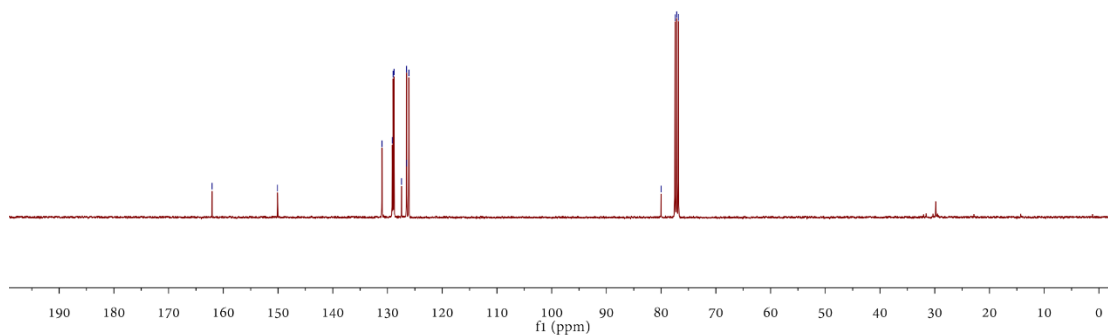
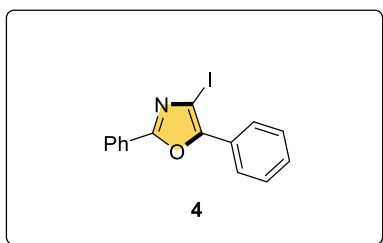
*<sup>13</sup>C NMR of 3n (CDCl<sub>3</sub>, 100 MHz)*

8.104  
8.102  
8.100  
8.097  
8.095  
8.093  
8.091  
8.088  
8.057  
8.055  
8.045  
8.043  
8.041  
8.036  
7.504  
7.503  
7.500  
7.495  
7.491  
7.489  
7.486  
7.483  
7.481  
7.478  
7.474  
7.471  
7.429  
7.427  
7.424  
7.417  
7.414  
7.411  
7.404  
7.402



$^1\text{H NMR}$  of **4** ( $\text{CDCl}_3$ , 600 MHz)

162.05  
150.10  
131.01  
129.14  
128.97  
128.81  
127.44  
126.52  
126.48  
126.09  
80.00  
77.48  
77.16  
76.84



$^{13}\text{C NMR}$  of **4** ( $\text{CDCl}_3$ , 100 MHz)

## 9. References

1. H. E. Gottlieb, V. Kotlyar and A. Nudelman, *J. Org. Chem.* 1997, **62**, 7512.
2. L. Zeng, Z. Lai, C. Zhang, H. Xie and S. Cui, *Org. Lett.*, 2020, **22**, 2220-2224.
3. M. Chen, N. Sun, H. Chen and Y. Liu, *Chem. Commun.*, 2016, **52**, 6324-6327.