

Supporting Information for

DAST-Promoted Beckmann Rearrangement/Intramolecular Cyclization of Acyclic Ketoximes: Access to 2-Oxazolines, Benzimidazoles and Benzoxazoles

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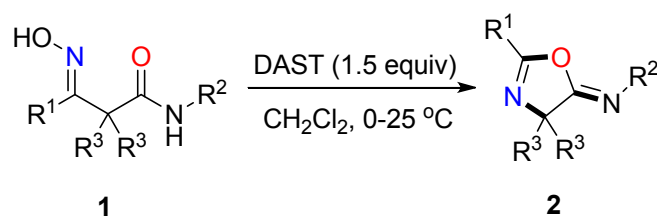
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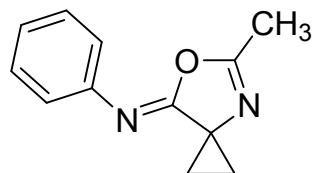
I. General information

All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. The products were purified by column chromatography over silica gel. ¹H-NMR and ¹³C-NMR spectra were recorded at 25 °C on a Varian 500 MHz and 125 MHz, respectively, and TMS was used as internal standard. Mass spectra were recorded on BRUKER AutoflexIII Smartbeam MS-spectrometer. High resolution mass spectra (HRMS) were recorded on Bruck microTof by using ESI method.

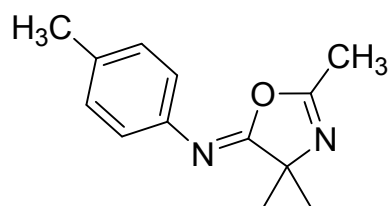
II. Synthesis and analytical data of compounds 2a-2o



General procedure (with **1a** as an example): The (*E*)-1-(1-(hydroxyimino)ethyl)-*N*-phenylcyclopropanecarboxamide **1a** (0.5 mmol) was dissolved in anhydrous DCM (1.0 mL) at ambient temperature. The solution of oxime in DCM was cooled to 0 °C. The diethylaminosulfur trifluoride (DAST) was added slowly to the solution of **1a** in DCM and the reaction was stirred and allowed to warm to 25 °C until the **1a** was consumed (monitored by TLC). The reaction mixture was concentrated in vacuo and purified by flash chromatography (petroleum ether : diethyl ether = 15 : 1) to afford compound **2a** in 87% yield.

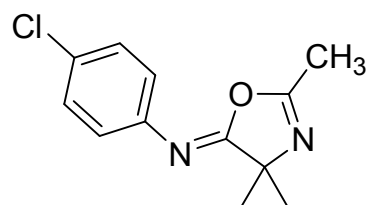


(**2a**) White solid, m.p. 78-79 °C; ¹H-NMR (500 MHz, CDCl₃) δ 1.52-1.58 (m, 2H), 1.60-1.65 (m, 2H), 2.18 (s, 3H), 7.08-7.14 (m, 3H), 7.28-7.35 (m, 2H); ¹³C-NMR (CDCl₃, 125 MHz) δ 14.9, 18.7, 49.5, 122.7, 124.3, 128.7, 145.3, 161.7, 162.2; HRMS (ESI) m/z calculated for C₁₂H₁₂N₂O [M+H]⁺ : 201.1028, found: 201.1054.



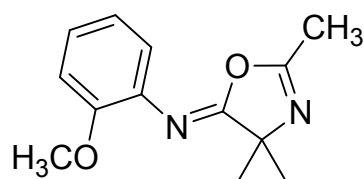
(2b) White solid, m.p. 67-68 °C; **¹H-NMR** (500 MHz, CDCl₃) δ 1.52-1.57 (m, 2H), 1.58-1.63 (m, 2H), 2.19 (s, 3H), 2.32 (s, 3H), 7.03 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 15.0, 18.7, 20.9, 49.5, 122.7, 129.3, 134.0, 142.7, 161.3, 162.3; **HRMS** (ESI) *m/z* calculated for C₁₃H₁₄N₂O [M+H]⁺ : 215.1184, found: 215.1189.

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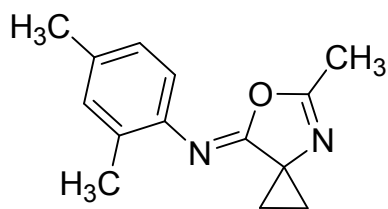
(2c) Semisolid; **¹H-NMR** (500 MHz, CDCl₃) δ 1.50-1.59 (m, 2H), 1.61-1.67 (m, 2H), 2.21 (s, 3H), 7.03-7.10 (m, 2H), 7.24-7.30 (m, 2H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 14.9, 18.9, 49.7, 124.3, 128.8, 129.6, 143.9, 162.1, 162.5; **HRMS** (ESI) *m/z* calculated for C₁₂H₁₁ClN₂O [M+H]⁺ : 235.0638, found: 235.0630.

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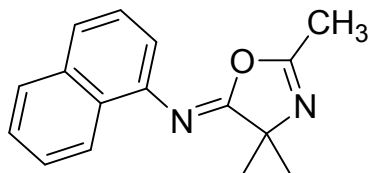
(2d) Semisolid; **¹H-NMR** (500 MHz, CDCl₃) δ 1.59-1.63 (m, 4H), 2.15 (s, 3H), 3.81 (s, 3H), 6.87-6.94 (m, 2H), 6.96-7.01 (m, 1H), 7.04-7.12 (m, 1H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 14.8, 18.8, 49.3, 55.7, 111.5, 120.5, 122.6, 124.9, 135.0, 151.0, 162.3, 162.8; **HRMS** (ESI) *m/z* calculated for C₁₃H₁₄N₂O₂ [M+H]⁺ : 231.1134, found: 231.1150.

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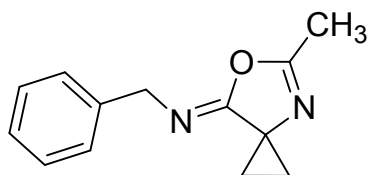
(**2e**) Semisolid; **¹H-NMR** (500 MHz, CDCl₃) δ 1.53-1.60 (m, 2H), 1.61-1.68 (m, 2H), 2.16 (s, 3H), 2.18 (s, 3H), 2.31 (s, 3H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 7.01 (s, 1H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 15.0, 17.7, 18.6, 20.8, 49.1, 121.0, 126.6, 129.9, 130.9, 133.5, 141.7, 160.9, 162.4; **HRMS** (ESI) *m/z* calculated for C₁₄H₁₆N₂O [M+H]⁺ : 229.1341, found: 229.1349.

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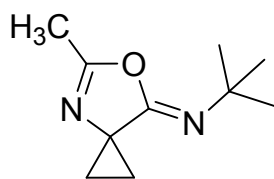
(**2f**) White solid, m.p. 84-85°C; **¹H-NMR** (500 MHz, CDCl₃) δ 1.68-1.76 (m, 4H), 2.14 (s, 3H), 7.19 (d, *J* = 7.0 Hz, 1H), 7.39-7.49 (m, 3H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.78-7.84 (m, 1H), 8.00-8.06 (m, 1H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 14.9, 19.0, 49.7, 116.8, 123.4, 124.2, 125.4, 125.6, 126.0, 127.8, 128.0, 134.0, 141.8, 162.4, 162.5; **HRMS** (ESI) *m/z* calculated for C₁₆H₁₄N₂O [M+H]⁺ : 251.1184, found: 251.1181.

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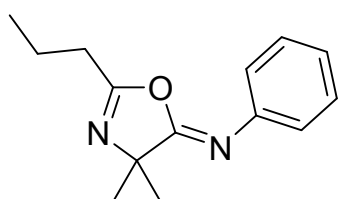
(**2g**) Colorless liquid; **¹H-NMR** (500 MHz, CDCl₃) δ 1.46-1.51 (m, 2H), 1.52-1.57 (m, 2H), 1.85 (s, 3H), 4.52 (s, 2H), 7.19-7.24 (m, 1H), 7.27-7.35 (m, 4H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 10.0, 18.3, 30.2, 50.6, 126.5, 127.6, 128.2, 140.3, 162.9, 165.1; **HRMS** (ESI) *m/z* calculated for C₁₃H₁₄N₂O [M+H]⁺ : 215.1184, found: 215.1186.

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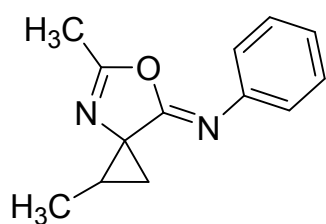
(2h) White solid, m.p. 57-58 °C; **¹H-NMR** (500 MHz, CDCl₃) δ 1.26 (s, 9H), 1.34-1.37 (m, 2H), 1.37-1.39 (m, 2H), 1.82 (s, 3H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 10.1, 18.2, 30.0, 30.7, 53.3, 158.2, 164.4; **HRMS** (ESI) m/z calculated for C₁₀H₁₆N₂O [M+H]⁺ : 181.1341, found: 181.1344.

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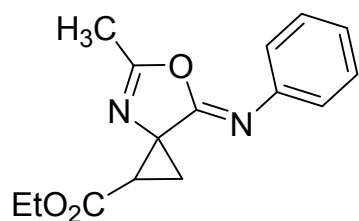


(2i) White solid, m.p. 40-41 °C; **¹H-NMR** (500 MHz, CDCl₃) δ 1.01 (t, *J* = 7.5 Hz, 3H), 1.53-1.59 (m, 2H), 1.62-1.67 (m, 2H), 1.68-1.77 (m, 2H), 2.44 (t, *J* = 7.5 Hz, 2H), 7.08-7.15 (m, 3H), 7.28-7.35 (m, 2H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 13.6, 18.8, 18.9, 30.6, 49.5, 122.9, 124.3, 128.7, 145.3, 161.8, 165.3; **HRMS** (ESI) m/z calculated for C₁₄H₁₆N₂O [M+H]⁺ : 229.1341, found: 229.1337.

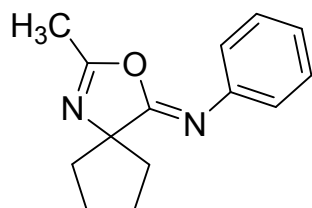
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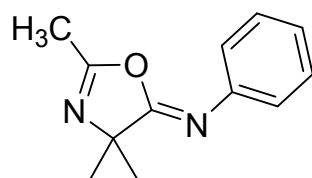
(2j) Semisolid; **¹H-NMR** (500 MHz, CDCl₃) δ 1.32 (dd, *J* = 5.0 Hz, *J* = 8.0 Hz 1H), 1.43 (d, *J* = 6.0 Hz, 3H), 1.80 (dd, *J* = 5.0 Hz, *J* = 9.0 Hz 1H), 1.92-2.01 (m, 1H), 2.13 (d, *J* = 3.0 Hz, 3H), 7.06-7.16 (m, 3H), 7.27-7.35 (m, 2H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 10.2, 14.5, 25.0, 25.7, 52.3, 122.5, 123.9, 128.5, 145.5, 159.3, 161.2; **HRMS** (ESI) m/z calculated for C₁₃H₁₄N₂O [M+H]⁺ : 215.1184, found: 215.1202.



(**2k**) Yellow liquid; $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 1.30 (t, $J = 7.0$ Hz, 3H), 1.86 (dd, $J = 5.0$ Hz, $J = 8.0$ Hz 1H), 2.21 (s, 3H), 2.33 (dd, $J = 5.0$ Hz, $J = 7.5$ Hz 1H), 2.60-2.65 (m, 1H), 4.20-4.28 (m, 2H), 7.10-7.17 (m, 3H), 7.29-7.35 (m, 2H); $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ 14.1, 15.0, 21.6, 31.9, 55.0, 61.3, 122.9, 124.8, 128.7, 144.5, 158.9, 164.3, 167.9; **HRMS** (ESI) m/z calculated for $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$: 273.1239, found: 273.1269.

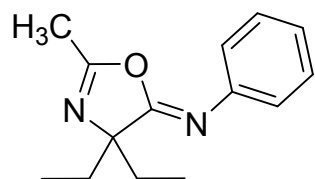


(**2l**) Colorless liquid; $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 1.91-2.00 (m, 6H), 2.08-2.15 (m, 5H), 7.07-7.15 (m, 3H), 7.28-7.35 (m, 2H); $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ 14.7, 25.5, 40.4, 77.0, 122.5, 124.5, 128.7, 145.6, 160.1, 165.1; **HRMS** (ESI) m/z calculated for $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$: 229.1341, found: 229.1324.

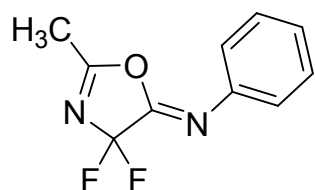


(**2m**) Colorless liquid; $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 1.41 (s, 6H), 2.02 (s, 3H), 7.05-7.23 (m, 3H), 7.26-7.35 (m, 2H); $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ 10.5, 23.6, 49.5, 122.9, 124.3, 128.6, 145.4, 165.4, 168.2; **HRMS** (ESI) m/z calculated for $\text{C}_{12}\text{H}_{14}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$: 203.1184, found:

203.1170.

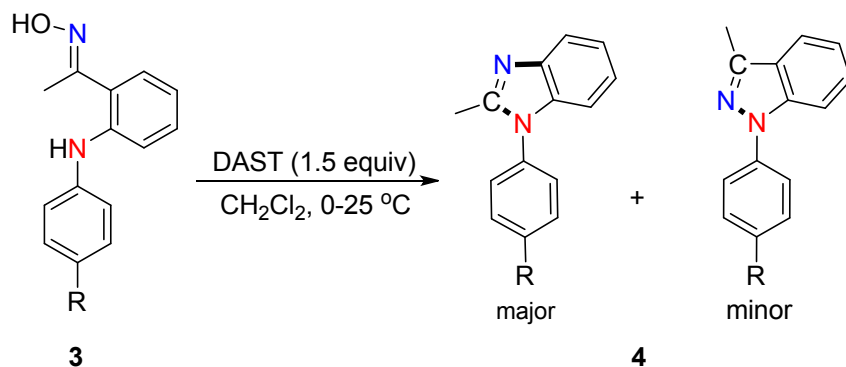


(**2n**) White solid, m.p. 53-54 °C; $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 0.81-0.89 (m, 6H), 1.67-1.76 (m, 2H), 1.85-1.94 (m, 2H), 1.99 (s, 3H), 7.05 (t, $J = 7.5$ Hz, 1H), 7.15 (d, $J = 7.5$ Hz, 2H), 7.32 (t, $J = 7.5$ Hz, 2H); $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ 8.9, 10.8, 29.8, 60.5, 122.7, 124.3, 128.7, 145.8, 163.8, 165.7; **HRMS** (ESI) m/z calculated for $\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$: 231.1497, found: 231.1503.



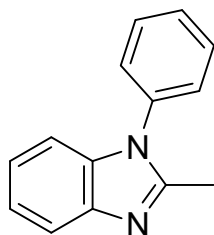
(**2o**) Light yellow liquid; $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 2.14 (t, $J = 1.5$ Hz, 3H), 7.15 (t, $J = 7.5$ Hz, 1H), 7.24-7.32 (m, 2H), 7.36 (d, $J = 7.5$ Hz, 2H); $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ 9.0, 114.8 (t, $J = 250$ Hz), 125.3, 127.4, 128.9, 142.1, 146.0 (t, $J = 25$ Hz), 156.1 (t, $J = 25$ Hz); **HRMS** (ESI) m/z calculated for $\text{C}_{10}\text{H}_8\text{F}_2\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$: 211.0683, found: 211.0663.

III. Synthesis and analytical data of compounds 4a-4d



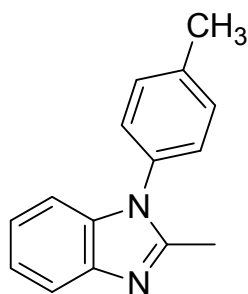
General procedure (with **3a** as an example): The (*E*)-1-(2-(phenylamino)phenyl)ethanone oxime

3a (0.5 mmol) was dissolved in anhydrous DCM (1.0 mL). The solution of oxime in DCM was cooled to 0 °C. The diethylaminosulfur trifluoride (DAST) was added slowly to the solution of **3a** in DCM and the reaction was stirred and allowed to warm to 25 °C until the **3a** was consumed (monitored by TLC). The reaction mixture was concentrated in vacuo and purified by flash chromatography (petroleum ether : diethyl ether = 15 : 1) to afford compounds **4aa** and **4ab** in 63% and 21% yield, respectively.



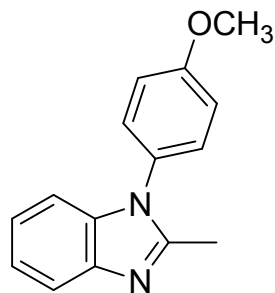
(**4aa**) Yellow solid, **¹H-NMR** (500 MHz, CDCl₃) δ 2.49 (s, 3H), 7.07-7.37 (m, 5H), 7.45-7.59 (m, 3H), 7.74 (d, *J* = 8.0 Hz, 1H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 14.2, 109.7, 118.7, 122.2, 122.4, 126.8, 128.6, 129.7, 135.8, 136.2, 142.4, 151.3; **HRMS** (ESI) *m/z* calculated for C₁₄H₁₂N₂ [M+H]⁺ : 209.1079, found: 209.1075.

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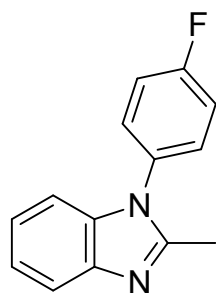
(**4ba**) Yellow solid, **¹H-NMR** (500 MHz, CDCl₃) δ 2.45 (s, 3H), 2.47 (s, 3H), 7.09 (d, *J* = 8.0 Hz, 1H), 7.12-7.27 (m, 4H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 1H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 14.2, 21.1, 109.8, 118.7, 122.1, 122.3, 126.7, 130.3, 133.2, 136.4, 138.7, 142.4, 151.5; **HRMS** (ESI) *m/z* calculated for C₁₅H₁₄N₂ [M+H]⁺ : 223.1235, found: 223.1235.

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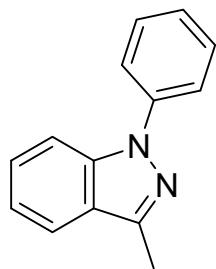
(4ca) Tan solid, $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 2.48 (s, 3H), 3.89 (s, 3H), 7.03-7.10 (m, 3H), 7.15-7.20 (m, 1H), 7.22-7.28 (m, 3H), 7.73 (d, $J = 8.0$ Hz, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ 14.2, 55.5, 109.8, 114.9, 118.8, 122.1, 122.3, 128.2, 128.5, 136.7, 142.4, 151.8, 159.6; **HRMS** (ESI) m/z calculated for $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$: 239.1184, found: 239.1176.

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(4da) Tan solid, $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 2.48 (s, 3H), 7.07 (d, $J = 8.0$ Hz, 1H), 7.15-7.37 (m, 6H), 7.73 (d, $J = 8.0$ Hz, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ 14.1, 109.5, 116.7 (d, $J = 22.8$ Hz), 118.9, 122.3, 122.6, 128.8 (d, $J = 8.8$ Hz), 132.0 (d, $J = 3.4$ Hz), 136.4, 142.3, 151.3, 161.3 (d, $J = 248$ Hz); **HRMS** (ESI) m/z calculated for $\text{C}_{14}\text{H}_{11}\text{FN}_2$ $[\text{M}+\text{H}]^+$: 227.0985, found: 227.0989.

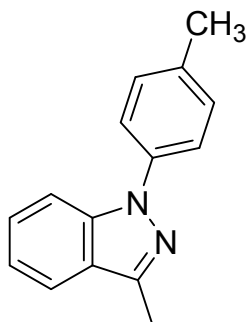
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(4ab) Yellow solid, $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 2.66 (s, 3H), 7.18-7.23 (m, 1H), 7.29-7.34 (m,

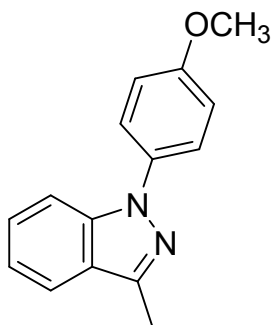
1H), 7.39-7.44 (m, 1H), 7.49-7.54 (m, 2H), 7.67-7.77 (m, 4H); ¹³C-NMR (CDCl₃, 125 MHz) δ 11.9, 110.3, 120.6, 120.8, 122.4, 125.0, 126.1, 127.1, 129.4, 139.5, 140.3, 144.0; **HRMS** (ESI) m/z calculated for C₁₄H₁₂N₂ [M+H]⁺ : 209.1079, found: 209.1075.

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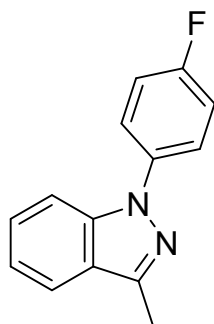
(4bb) Yellow solid, ¹H-NMR (500 MHz, CDCl₃) δ 2.43 (s, 3H), 2.67 (s, 3H), 7.17-7.22 (m, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.38-7.43 (m, 1H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H); ¹³C-NMR (CDCl₃, 125 MHz) δ 11.9, 21.0, 110.2, 120.47, 120.54, 122.3, 124.7, 126.9, 129.9, 135.9, 137.8, 139.4, 143.5; **HRMS** (ESI) m/z calculated for C₁₅H₁₄N₂ [M+H]⁺ : 223.1235, found: 223.1235.

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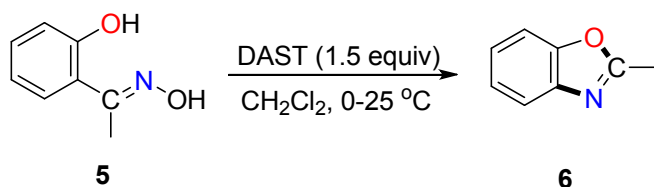
(4cb) Yellow solid, ¹H-NMR (500 MHz, CDCl₃) δ 2.65 (s, 3H), 3.85 (s, 3H), 7.00-7.06 (m, 2H), 7.17 (t, *J* = 7.0 Hz, 1H), 7.36-7.41 (m, 1H), 7.54-7.61 (m, 3H), 7.70 (d, *J* = 8.0 Hz, 1H); ¹³C-NMR (CDCl₃, 125 MHz) δ 11.9, 55.5, 110.0, 114.6, 120.4, 120.5, 124.2, 124.4, 126.8, 133.4, 139.6, 143.3, 158.0; **HRMS** (ESI) m/z calculated for C₁₅H₁₄N₂O [M+H]⁺ : 239.1184, found: 239.1186.

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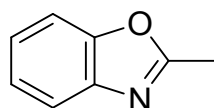


(**4db**) Pale yellow solid, $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 2.64 (s, 3H), 7.16-7.22 (m, 3H), 7.40-7.43 (m, 1H), 7.57-7.66 (m, 3H), 7.69-7.74 (m, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ 11.9, 109.9, 116.1 (d, $J = 22.6$ Hz), 120.6, 120.8, 124.1 (d, $J = 8.3$ Hz), 124.7, 127.2, 136.4, 139.5, 144.0, 159.8 (d, $J = 244.5$ Hz); **HRMS** (ESI) m/z calculated for $\text{C}_{14}\text{H}_{11}\text{N}_2\text{F}$ $[\text{M}+\text{H}]^+$: 227.0985, found: 227.0989.

IV. Synthesis and analytical data of compound 6

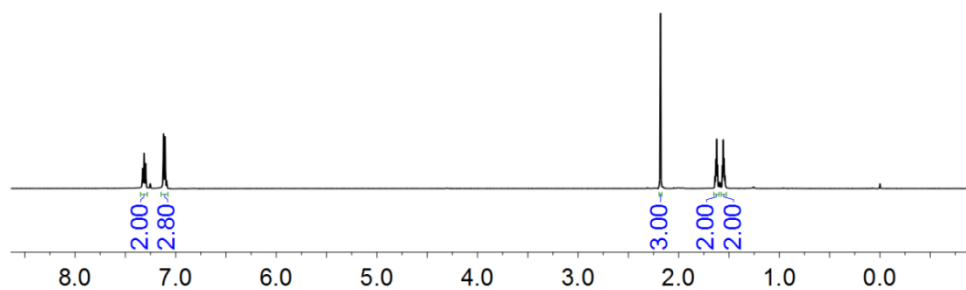
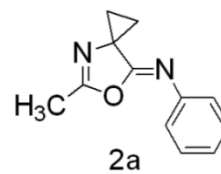


General procedure: The (*E*)-1-(2-hydroxyphenyl)ethanone oxime **5** (0.5 mmol) was dissolved in anhydrous DCM (1.0 mL). The solution of **5** in DCM was cooled to 0 °C. The diethylaminosulfur trifluoride (DAST) was added slowly to the solution of oxime in DCM and the reaction was stirred and allowed to warm to 25 °C until the **5** was consumed (monitored by TLC). The reaction mixture was concentrated in vacuo and purified by flash chromatography (petroleum ether : diethyl ether = 15 : 1) to afford 2-methylbenzoxazole **6** in 41% yield.



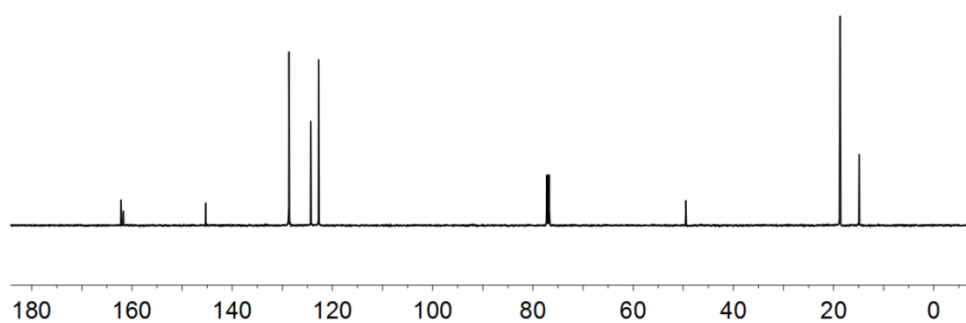
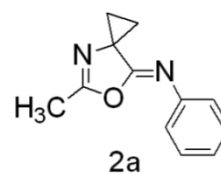
(**6**) Light yellow liquid, $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 2.58 (s, 3H), 7.20-7.26 (m, 2H), 7.37-7.43 (m, 1H), 7.55-7.62 (m, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ 14.5, 110.2, 119.4, 124.1, 124.4, 141.4, 150.9, 163.8; **HRMS** (ESI) m/z calculated for $\text{C}_8\text{H}_7\text{NO}$ $[\text{M}+\text{H}]^+$: 134.0606, found: 134.0607.

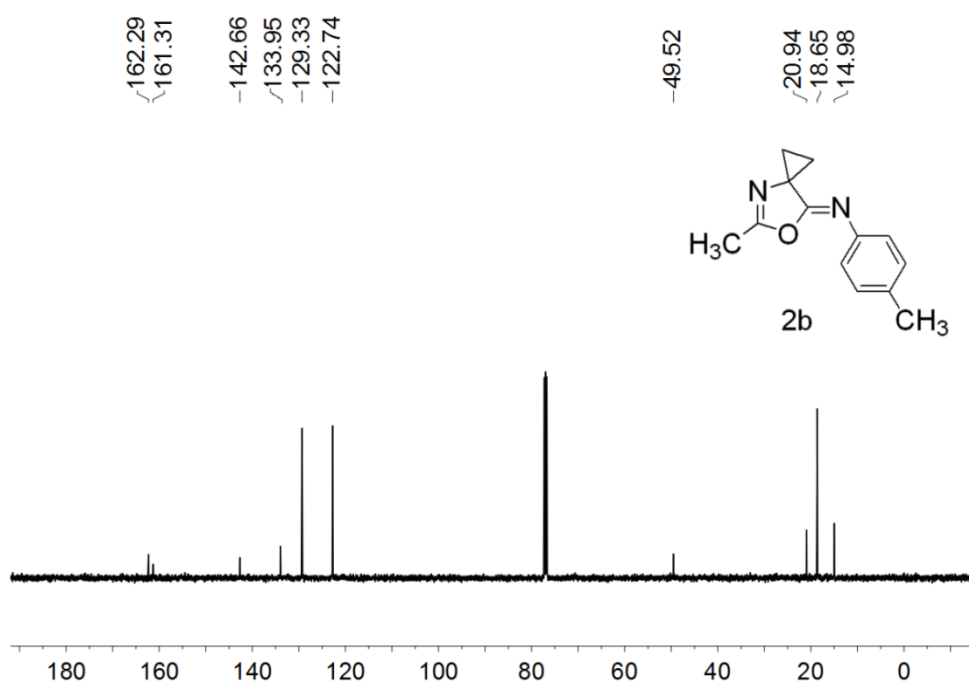
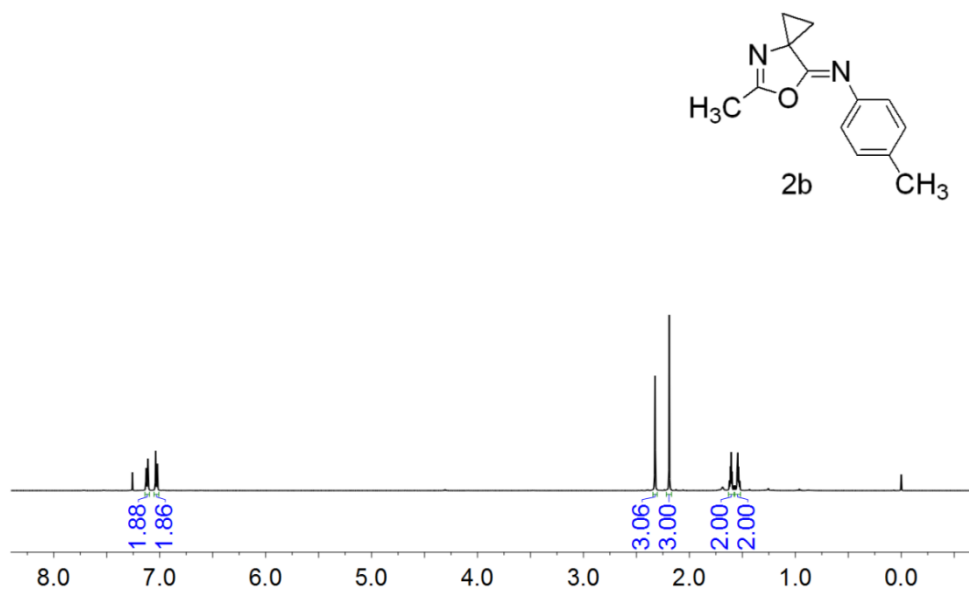
V. NMR spectra of all compounds

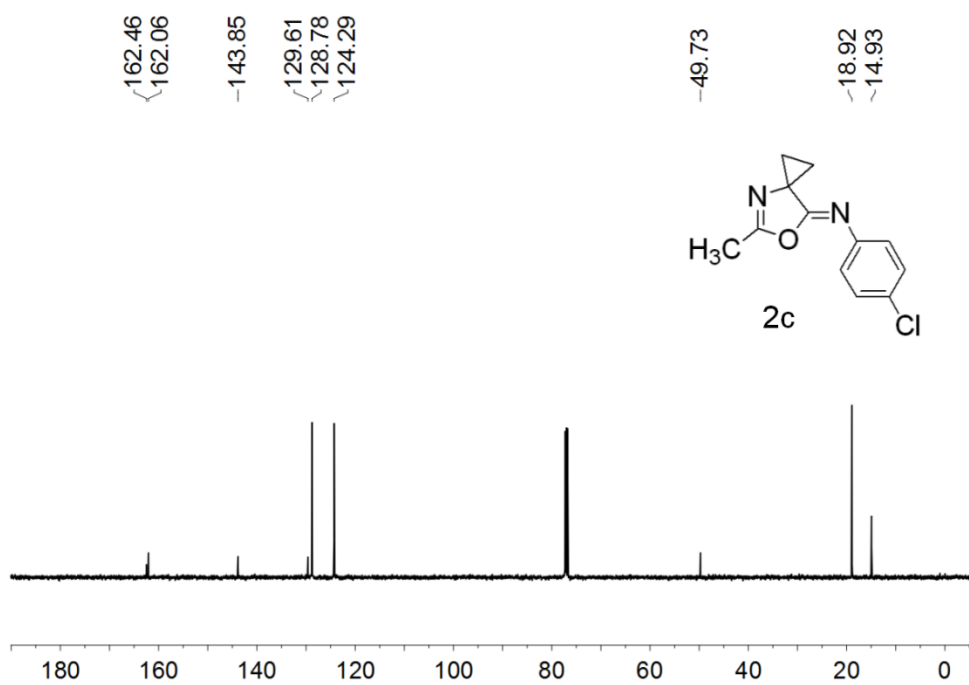
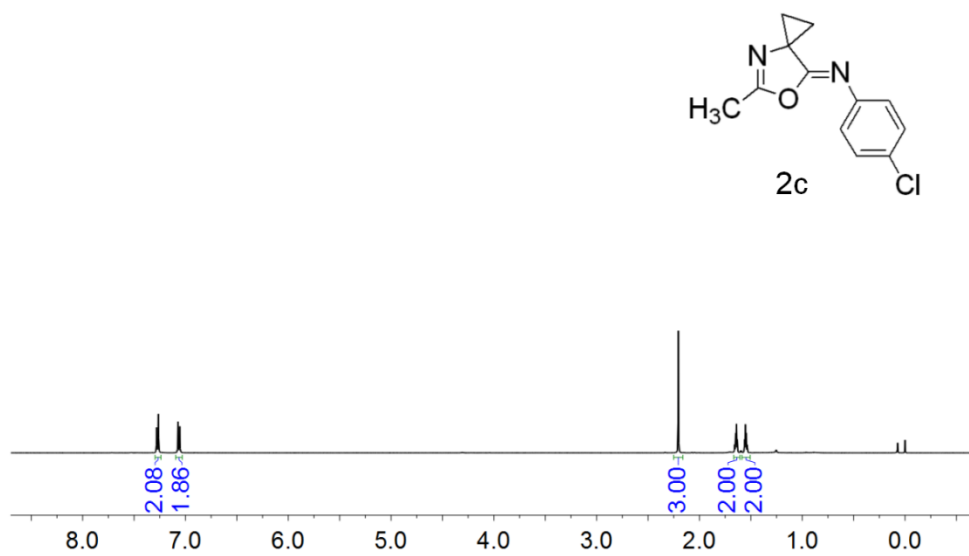


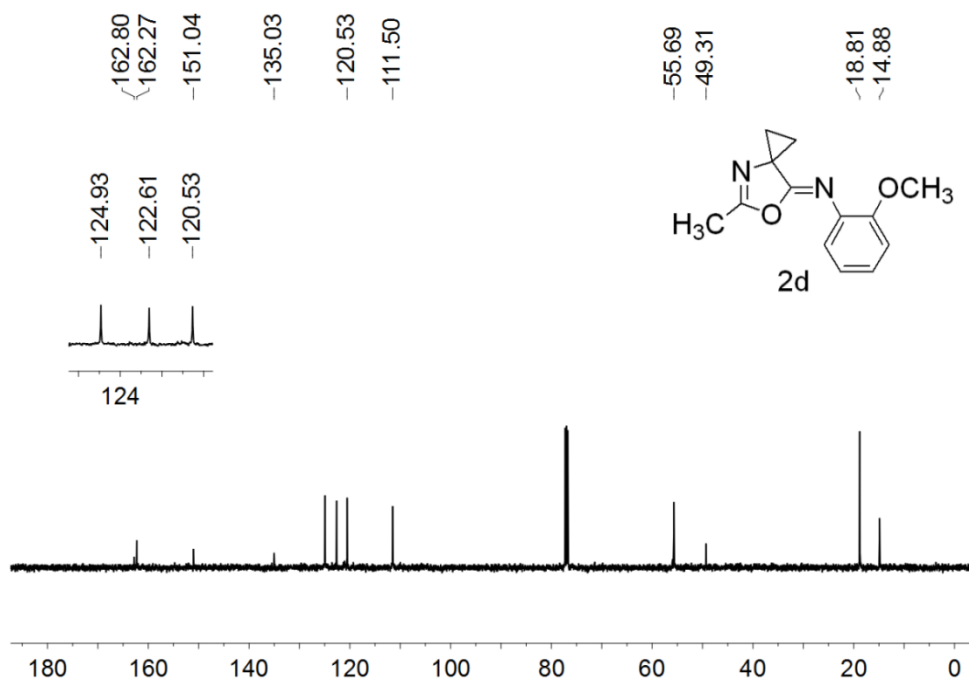
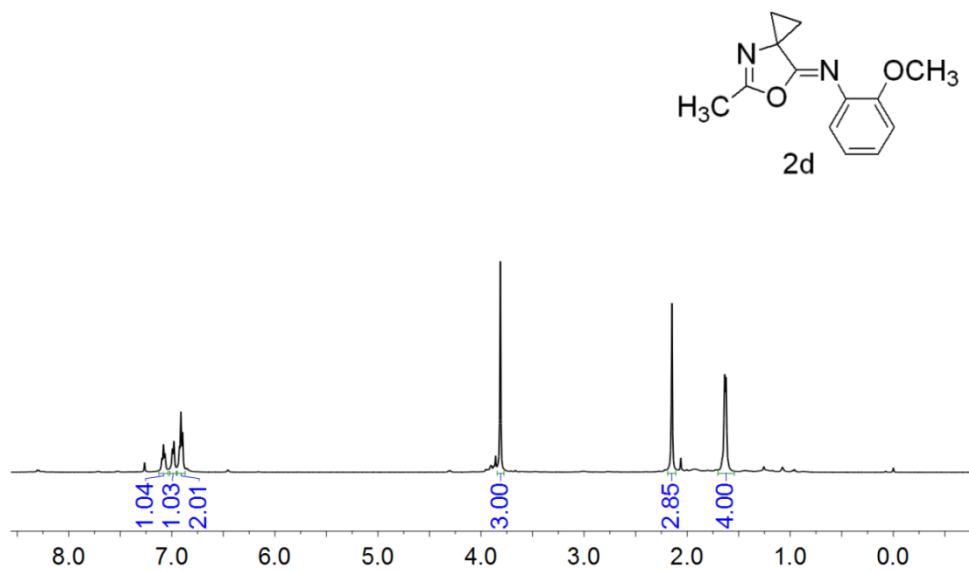
162.19
161.72
-145.29
128.67
124.32
122.73

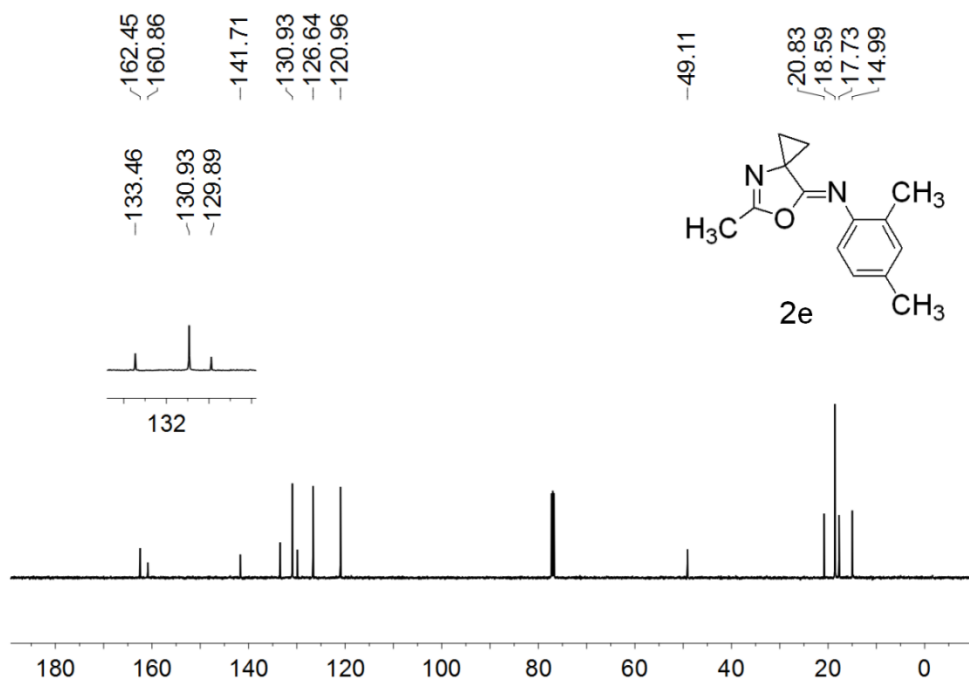
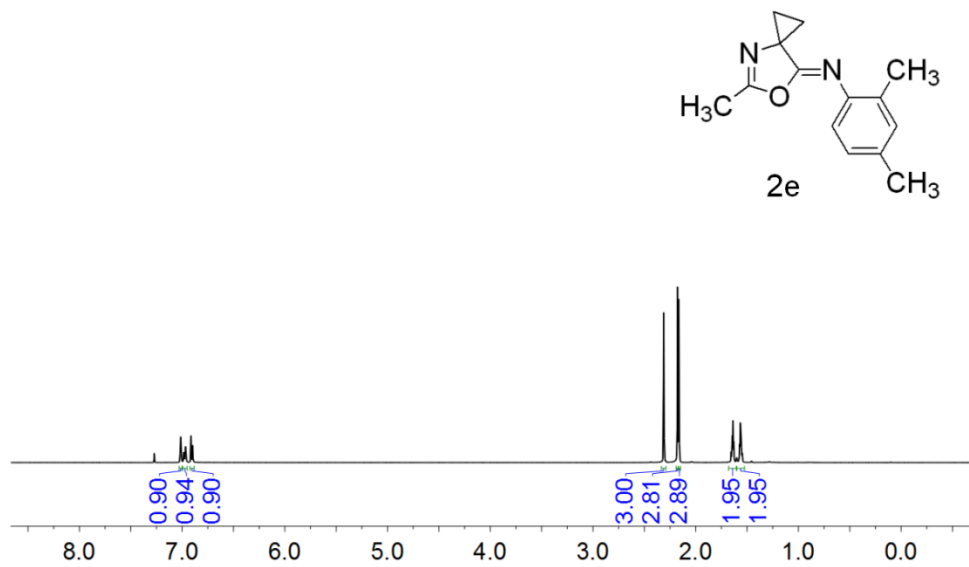
-49.50
18.70
14.90

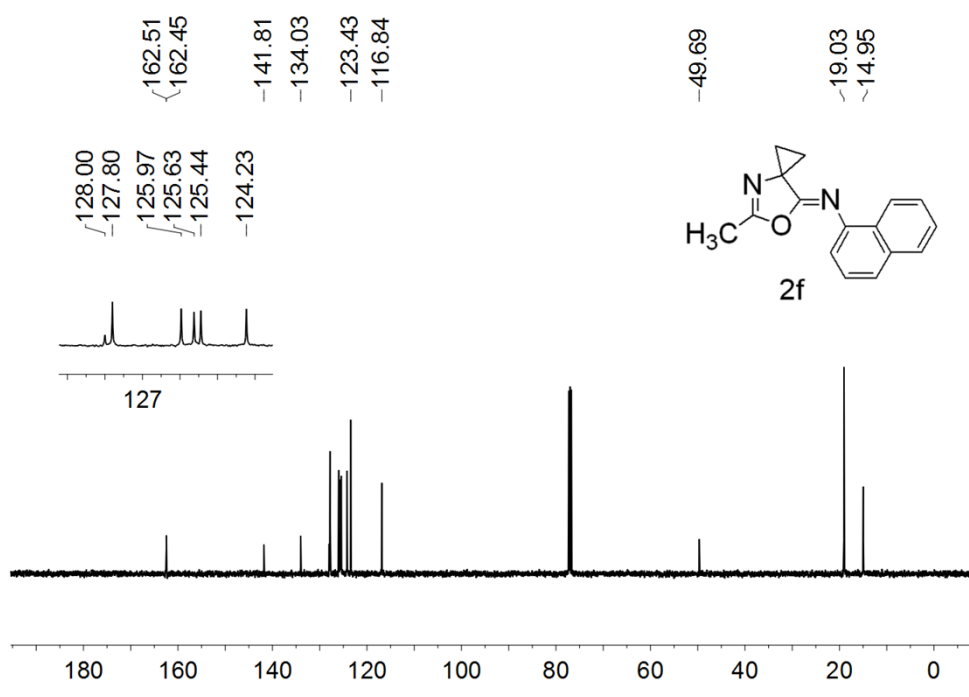
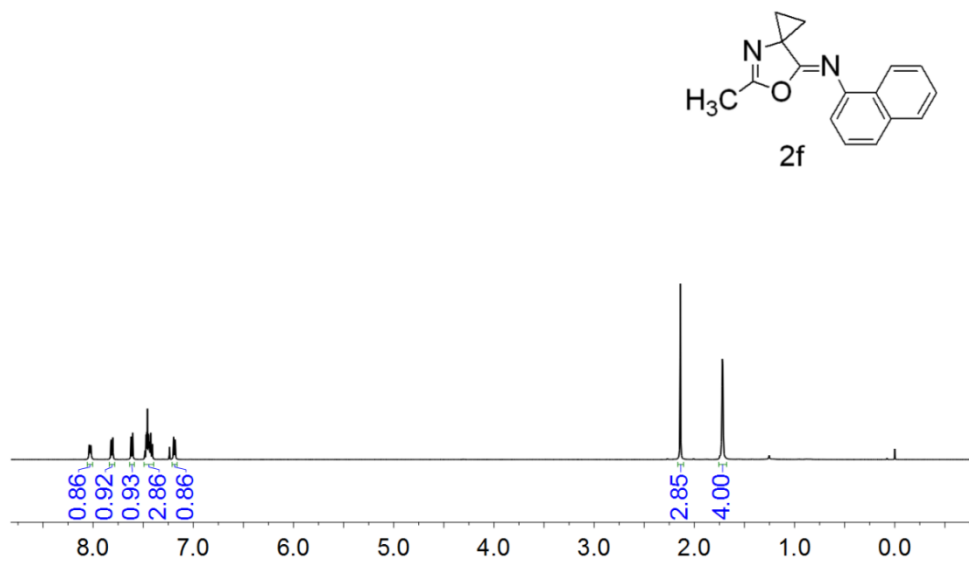


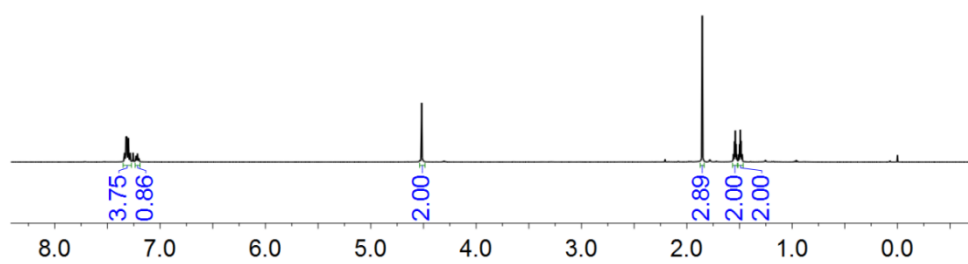
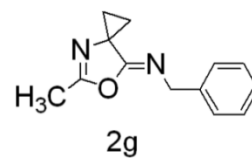








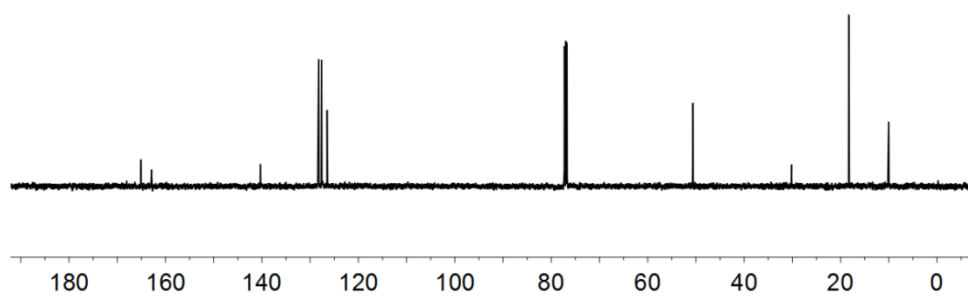
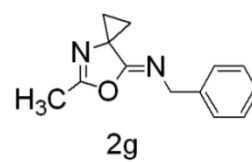


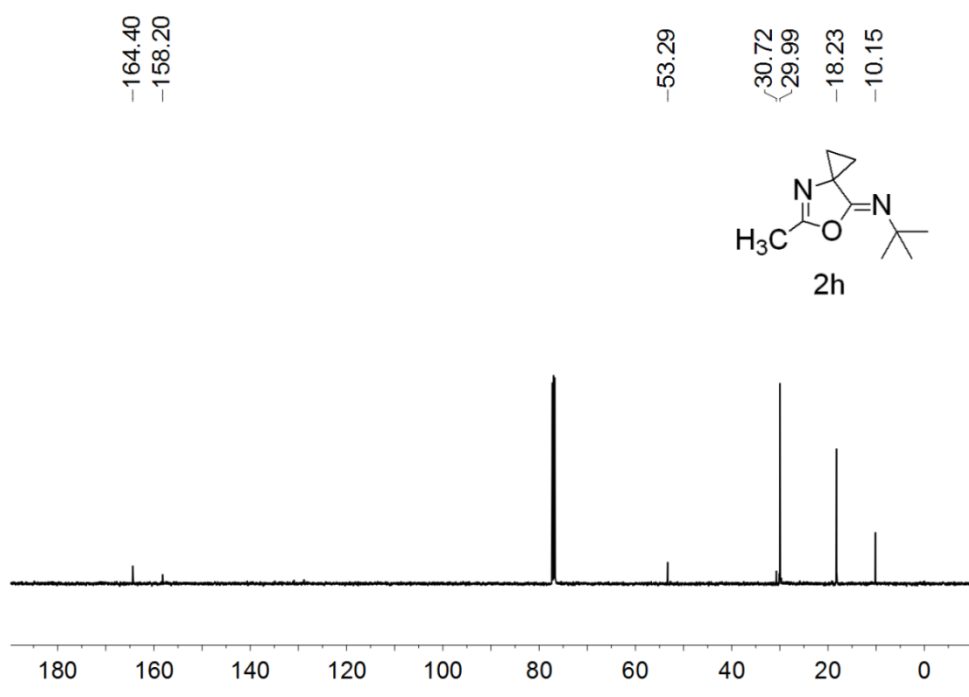
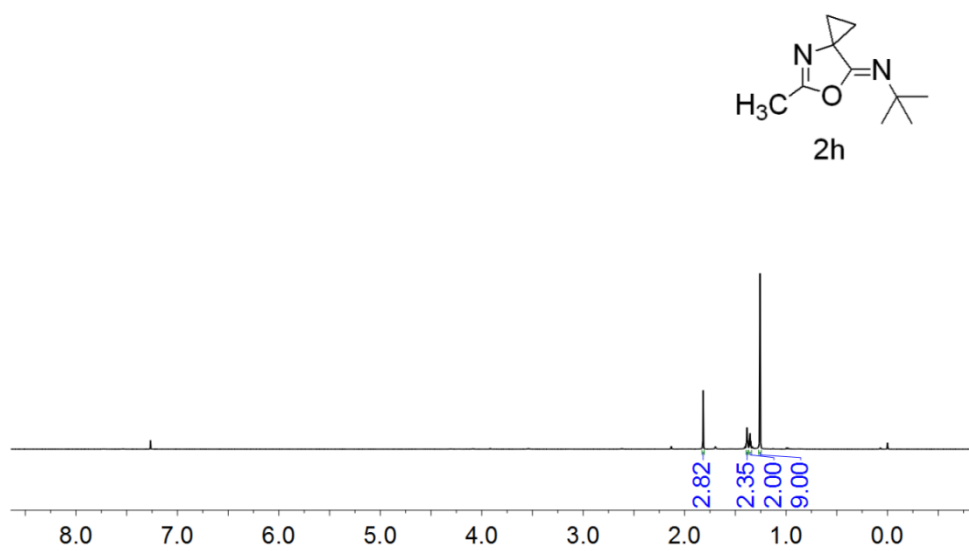


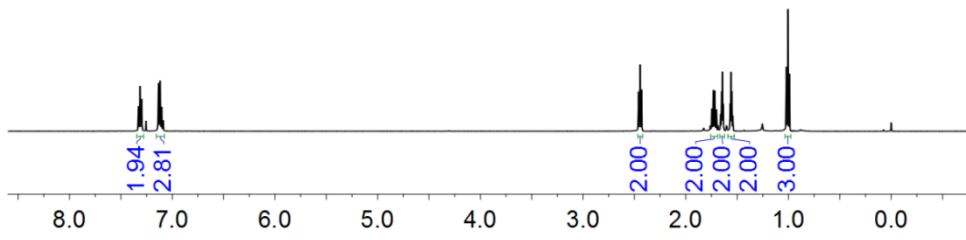
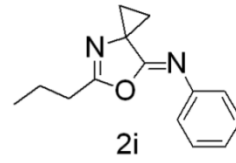
165.10
162.89

140.32
128.22
127.63
126.50

50.64
30.16
18.28
10.01







~165.28
~161.82

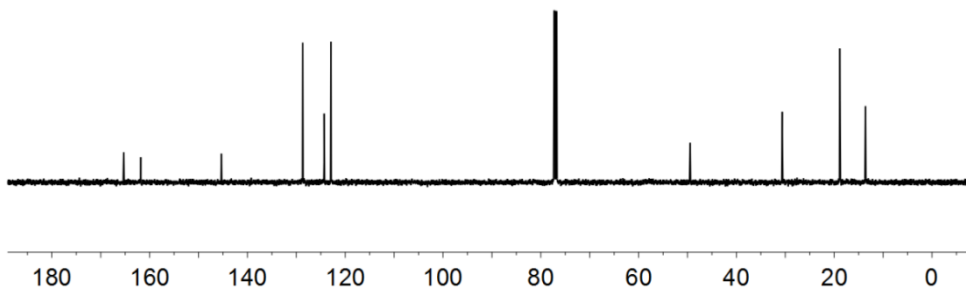
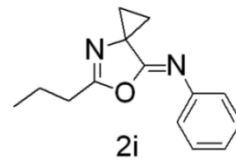
~145.33

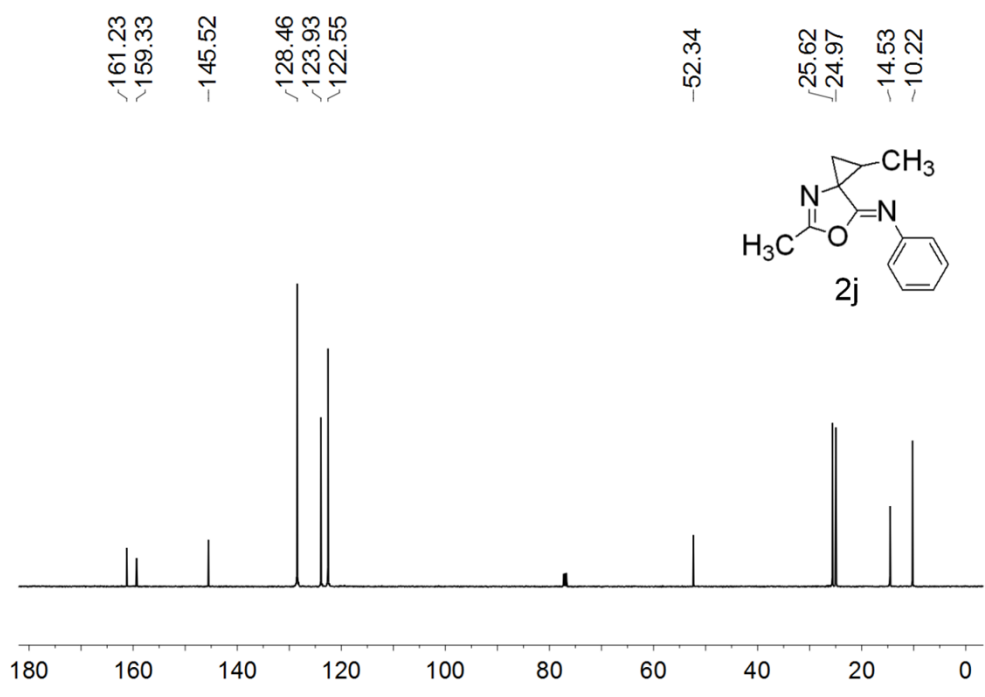
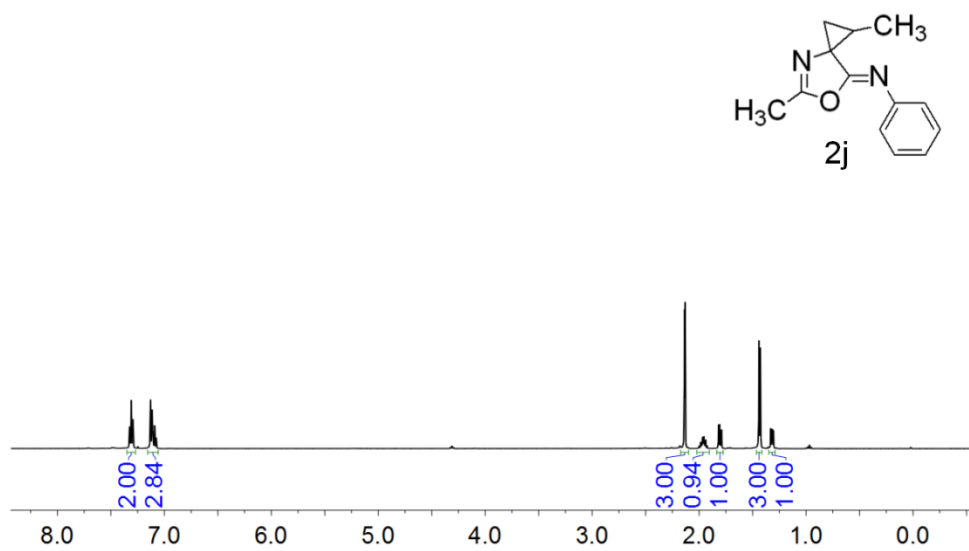
~128.68
~124.31
~122.91

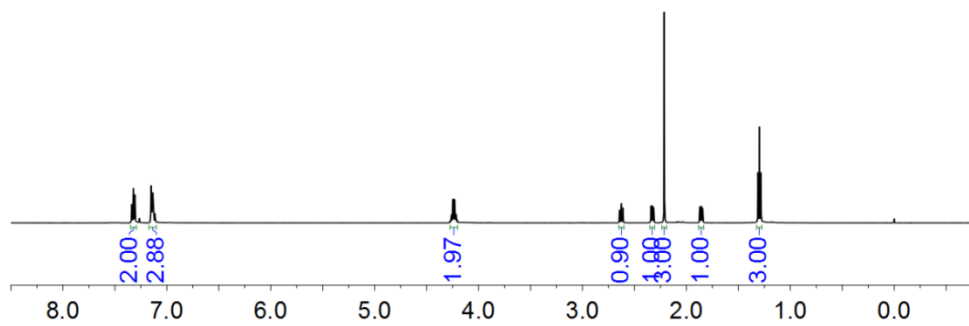
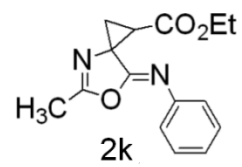
~49.46

~30.63

~18.86
~18.80
~13.60







167.89
164.29
158.90

144.48

128.67
124.79
122.87

61.25
55.04

31.86
21.62
15.01
14.12

