

*Electronic Supplementary Information for*

## **Palladium Catalyzed Cascade Umpolung Allylation/Acetalation for the Construction of Quaternary 3-Amino Oxindoles**

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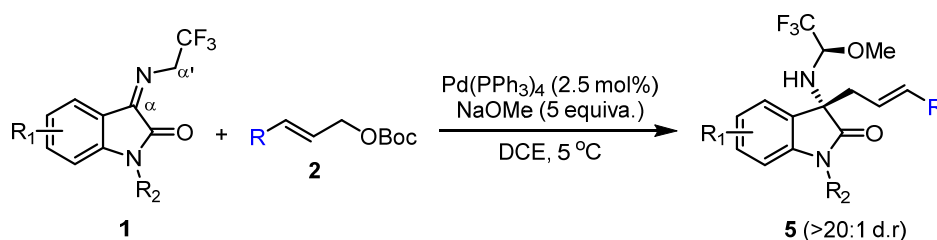
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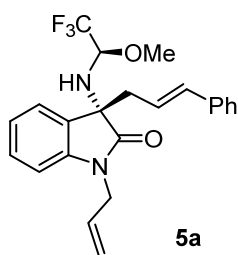
## 1. General remarks

<sup>1</sup>H NMR spectra were recorded on a Bruker 400 MHz spectrometer in CDCl<sub>3</sub>. Chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The data are reported as (s = single, d = double, t = triple, q = quarte, m = multiple or unresolved, brs = broad single, coupling constant(s) in Hz, integration). <sup>13</sup>C NMR spectra were recorded on a Bruker 100 MHz spectrometer in CDCl<sub>3</sub>. <sup>19</sup>F NMR spectra were recorded on a Bruker 376 MHz spectrometer in CDCl<sub>3</sub>. Chemical shifts are reported in ppm. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with silica gel-coated plates.

## 2. General procedure for Pd catalyzed allylic alkylation of *N*-2,2,2-trifluoroethylisatin ketamine

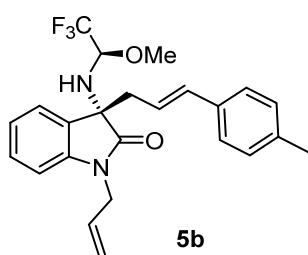


In a 25 mL nitrogen-filled dry Schlenk tube, Pd(PPh<sub>3</sub>)<sub>4</sub> (6.0 mg, 0.005 mmol), *N*-2,2,2-trifluoroethylisatin ketamine **1** (0.2 mmol), *tert*-butyl cinnamyl carbonates **2** (0.22 mmol) and degassed DCE (2 mL) were added. Once the temperature was reduced to 5 °C, Sodium methoxide (1.0 mmol) was added in one portion under N<sub>2</sub> atmosphere. The reaction was stirred for 12 h at 5 °C until starting material was consumed (monitored by TLC). The reaction mixture was concentrated via rotary evaporation under reduced pressure, and then purified by flash chromatography on silica gel (PE/EA = 10:1) to give the allylation products **5**.



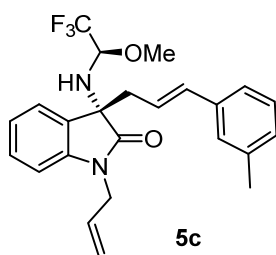
**1-allyl-3-cinnamyl-3-((2,2,2-trifluoro-1-methoxyethyl)amino)indolin-2-one:**

Yellow solid; 77% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 – 7.29 (m, 2H), 7.29 – 7.04 (m, 6H), 6.85 (d,  $J = 7.7$  Hz, 1H), 6.31 (d,  $J = 15.8$  Hz, 1H), 6.00 – 5.83 (m, 1H), 5.81 – 5.61 (m, 1H), 5.13 (dd,  $J = 49.4, 13.7$  Hz, 2H), 4.43 (dd,  $J = 16.1, 5.3$  Hz, 1H), 4.17 (dd,  $J = 16.1, 5.6$  Hz, 1H), 4.07 – 3.83 (m, 1H), 3.13 (d,  $J = 12.7$  Hz, 1H), 2.93 (s, 3H), 2.82 (dd,  $J = 13.2, 6.1$  Hz, 1H), 2.63 (dd,  $J = 13.2, 8.8$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  178.9, 143.5, 136.9, 135.0, 131.3, 129.7, 128.4, 127.4, 126.3, 126.2, 124.9, 123.3 (q,  $J = 285.9$  Hz), 122.7, 122.0, 118.1, 109.4, 85.0 (q,  $J = 31.8$  Hz), 63.3, 56.9, 56.8, 42.5.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -78.90 (d,  $J = 4.4$  Hz). HRMS Calcd. For  $\text{C}_{23}\text{H}_{23}\text{F}_3\text{N}_2\text{O}_2\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ): 439.1604, found: 439.1592.



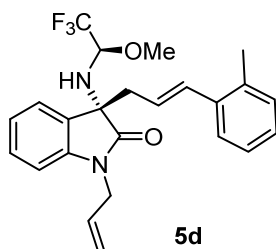
**(E)-1-allyl-3-(3-(p-tolyl)allyl)-3-((2,2,2-trifluoro-1-methoxyethyl)amino)indolin-2-one:**

Yellow solid; 77% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 – 7.28 (m, 2H), 7.20 – 6.96 (m, 5H), 6.85 (d,  $J = 7.7$  Hz, 1H), 6.27 (d,  $J = 15.8$  Hz, 1H), 5.92 – 5.79 (m, 1H), 5.79 – 5.62 (m, 1H), 5.29 – 4.99 (m, 2H), 4.42 (ddt,  $J = 16.1, 5.4, 1.5$  Hz, 1H), 4.17 (ddt,  $J = 16.1, 5.6, 1.3$  Hz, 1H), 3.96 (dq,  $J = 12.7, 4.8$  Hz, 1H), 3.12 (d,  $J = 12.7$  Hz, 1H), 2.93 (s, 3H), 2.80 (ddd,  $J = 13.2, 6.2, 1.3$  Hz, 1H), 2.61 (dd,  $J = 13.6, 8.8$  Hz, 1H), 2.29 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  179.0, 143.5, 137.2, 134.8, 134.2, 131.4, 129.7, 129.1, 126.4, 126.1, 124.9, 123.3 (q,  $J = 285.8$  Hz), 122.7, 120.9, 118.1, 109.3, 85.0 (q,  $J = 31.8$  Hz), 63.4, 56.8, 42.5, 42.5, 21.2.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -78.90 (d,  $J = 4.6$  Hz). HRMS Calcd. For  $\text{C}_{24}\text{H}_{25}\text{F}_3\text{N}_2\text{O}_2\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ): 453.1760, found: 453.1758.



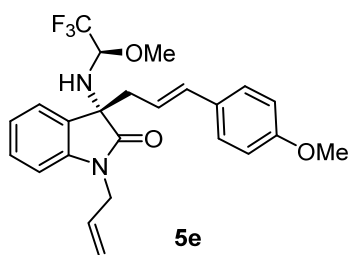
**(E)-1-allyl-3-(3-(m-tolyl)allyl)-3-((2,2,2-trifluoro-1-methoxyethyl)amino)indolin-2-one:**

Yellow solid; 73% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 (t,  $J = 8.2$  Hz, 2H), 7.12 (t,  $J = 6.0$  Hz, 2H), 7.00 (s, 3H), 6.85 (d,  $J = 7.6$  Hz, 1H), 6.28 (d,  $J = 15.8$  Hz, 1H), 5.90 (dt,  $J = 15.3, 7.5$  Hz, 1H), 5.82 – 5.61 (m, 1H), 5.15 (dd,  $J = 46.5, 13.7$  Hz, 2H), 4.43 (dd,  $J = 15.9, 4.5$  Hz, 1H), 4.18 (dd,  $J = 16.1, 5.0$  Hz, 1H), 4.05 – 3.85 (m, 1H), 3.13 (d,  $J = 12.6$  Hz, 1H), 2.93 (s, 3H), 2.80 (dd,  $J = 13.0, 6.0$  Hz, 1H), 2.62 (dd,  $J = 12.8, 9.0$  Hz, 1H), 2.29 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  177.94, 142.40, 136.92, 135.85, 134.02, 130.32, 128.68, 127.27, 127.15, 125.98, 125.32, 123.86, 122.30, 122.27 (q,  $J = 286.0$  Hz), 121.67, 120.73, 117.00, 108.32, 83.98 (q,  $J = 31.8$  Hz), 62.27, 55.80, 41.45, 41.42, 20.29.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -78.90 (d,  $J = 4.3$  Hz). HRMS Calcd. For  $\text{C}_{24}\text{H}_{25}\text{F}_3\text{N}_2\text{O}_2\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ): 453.1760, found: 453.1759.



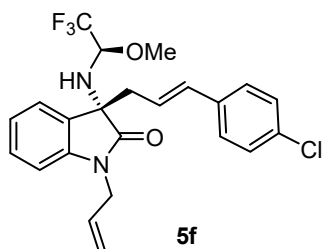
**(E)-1-allyl-3-(3-(o-tolyl)allyl)-3-((2,2,2-trifluoro-1-methoxyethyl)amino)indolin-2-one:**

Yellow solid; 61% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 – 7.29 (m, 2H), 7.22 – 7.01 (m, 5H), 6.86 (d,  $J = 7.8$  Hz, 1H), 6.49 (d,  $J = 15.7$  Hz, 1H), 5.85 – 5.61 (m, 2H), 5.28 – 5.00 (m, 2H), 4.39 (ddt,  $J = 16.0, 5.5, 1.5$  Hz, 1H), 4.20 (ddt,  $J = 16.1, 5.6, 1.4$  Hz, 1H), 3.97 (dq,  $J = 12.7, 4.8$  Hz, 1H), 3.13 (d,  $J = 12.7$  Hz, 1H), 2.94 (s, 3H), 2.82 (ddd,  $J = 13.1, 6.6, 1.3$  Hz, 1H), 2.65 (ddd,  $J = 13.2, 8.5, 0.5$  Hz, 1H), 2.14 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  178.9, 143.5, 136.2, 135.3, 133.3, 131.3, 130.0, 129.7, 127.3, 126.4, 125.9, 125.7, 124.9, 123.4, 123.3 (q,  $J = 285.9$  Hz), 122.7, 118.1, 109.4, 85.0 (q,  $J = 31.8$  Hz), 63.4, 56.7, 42.7, 42.5, 19.6.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -78.86 (d,  $J = 4.8$  Hz). HRMS Calcd. For  $\text{C}_{24}\text{H}_{25}\text{F}_3\text{N}_2\text{O}_2\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ): 453.1760, found: 453.1752.



**(E)-1-allyl-3-(3-(4-methoxyphenyl)allyl)-3-((2,2,2-trifluoro-1-methoxyethyl)amino)indolin-2-one:**

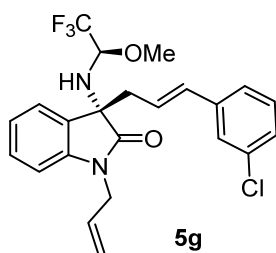
Yellow solid; 77% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 – 7.28 (m, 2H), 7.18 – 7.06 (m, 3H), 6.85 (d,  $J = 7.7$  Hz, 1H), 6.82 – 6.72 (m, 2H), 6.25 (d,  $J = 15.8$  Hz, 1H), 5.83 – 5.64 (m, 2H), 5.25 – 5.01 (m, 2H), 4.43 (ddt,  $J = 16.1, 5.3, 1.5$  Hz, 1H), 4.23 – 4.07 (m, 1H), 3.96 (dq,  $J = 12.7, 4.8$  Hz, 1H), 3.77 (s, 3H), 3.12 (d,  $J = 12.7$  Hz, 1H), 2.93 (s, 3H), 2.79 (ddd,  $J = 13.2, 6.2, 1.3$  Hz, 1H), 2.61 (dd,  $J = 13.4, 8.9$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  179.0, 159.1, 143.5, 134.3, 131.3, 129.8, 129.7, 127.4, 126.4, 124.9, 123.3 (q,  $J = 285.8$  Hz), 122.7, 119.7, 118.0, 113.8, 109.3, 85.0 (q,  $J = 31.8$  Hz), 63.4, 56.8, 55.3, 42.5, 42.4.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -78.91 (d,  $J = 4.6$  Hz). HRMS Calcd. For  $\text{C}_{24}\text{H}_{25}\text{F}_3\text{N}_2\text{O}_3\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ): 469.1709, found: 469.1706.



**(E)-1-allyl-3-(3-(4-chlorophenyl)allyl)-3-((2,2,2-trifluoro-1-methoxyethyl)amino)indolin-2-one:**

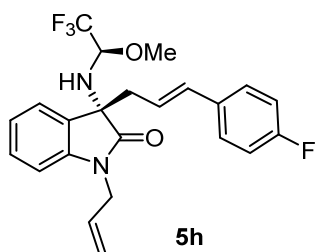
Yellow solid; 54% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 – 7.30 (m, 2H), 7.20 (d,  $J = 8.5$  Hz, 2H), 7.16 – 7.06 (m, 3H), 6.86 (d,  $J = 7.9$  Hz, 1H), 6.26 (d,  $J = 15.9$  Hz, 1H), 5.94 – 5.80 (m, 1H), 5.78 – 5.62 (m, 1H), 5.26 – 5.01 (m, 2H), 4.52 – 4.37 (m, 1H), 4.22 – 4.10 (m, 1H), 3.95 (dq,  $J = 12.7, 4.8$  Hz, 1H), 3.12 (d,  $J = 12.7$  Hz, 1H), 2.93 (s, 3H), 2.80 (ddd,  $J = 13.2, 6.2, 1.2$  Hz, 1H), 2.63 (dd,  $J = 13.3, 8.9$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  178.84, 143.43, 135.38, 133.73, 133.04, 131.26, 129.82, 128.58, 127.40, 126.20, 124.83, 123.28 (q,  $J = 285.9$  Hz), 122.79, 122.75, 118.07, 109.40, 85.00 (q,  $J = 31.8$  Hz), 63.28, 56.90, 42.44, 42.37.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -78.93 (d,  $J = 4.5$  Hz). HRMS Calcd. For  $\text{C}_{23}\text{H}_{22}\text{ClF}_3\text{N}_2\text{O}_2\text{Na}$

([M+Na]<sup>+</sup>): 473.1214, found: 473.1205.



**(E)-1-allyl-3-(3-(3-chlorophenyl)allyl)-3-((2,2,2-trifluoro-1-methoxyethyl)amino)indolin-2-one:**

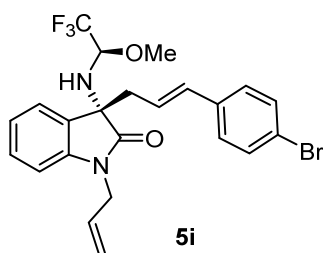
Yellow solid; 60% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.40 – 7.31 (m, 2H), 7.22 – 7.10 (m, 4H), 7.08 – 7.01 (m, 1H), 6.87 (d, *J* = 7.7 Hz, 1H), 6.25 (d, *J* = 15.8 Hz, 1H), 5.99 – 5.83 (m, 1H), 5.80 – 5.66 (m, 1H), 5.31 – 5.04 (m, 2H), 4.53 – 4.38 (m, 1H), 4.23 – 4.12 (m, 1H), 3.95 (dq, *J* = 12.7, 4.8 Hz, 1H), 3.12 (d, *J* = 12.7 Hz, 1H), 2.93 (s, 3H), 2.81 (ddd, *J* = 13.2, 6.3, 1.2 Hz, 1H), 2.63 (dd, *J* = 13.2, 8.8 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 178.82, 143.41, 138.75, 134.38, 133.66, 131.25, 129.87, 129.66, 127.37, 126.13, 126.10, 124.84, 124.46, 123.73, 123.28 (q, *J* = 285.9 Hz), 122.79, 118.14, 109.42, 85.01 (q, *J* = 31.7 Hz), 63.25, 56.90, 42.46, 42.35. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -78.92 (d, *J* = 4.5 Hz). HRMS Calcd. For C<sub>23</sub>H<sub>22</sub>ClF<sub>3</sub>N<sub>2</sub>O<sub>2</sub>Na ([M+Na]<sup>+</sup>): 473.1214, found: 473.1209.



**(E)-1-allyl-3-(3-(4-fluorophenyl)allyl)-3-((2,2,2-trifluoro-1-methoxyethyl)amino)indolin-2-one:**

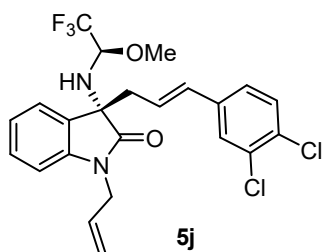
Yellow solid; 79% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.33 (t, *J* = 6.2 Hz, 2H), 7.13 (t, *J* = 6.6 Hz, 3H), 7.03 – 6.76 (m, 3H), 6.28 (d, *J* = 15.8 Hz, 1H), 5.90 – 5.61 (m, 2H), 5.12 (dd, *J* = 45.8, 13.7 Hz, 2H), 4.44 (dd, *J* = 16.1, 5.0 Hz, 1H), 4.16 (dd, *J* = 16.0, 5.3 Hz, 1H), 4.05 – 3.86 (m, 1H), 3.12 (d, *J* = 12.6 Hz, 1H), 2.93 (s, 3H), 2.80 (dd, *J* = 13.1, 5.9 Hz, 1H), 2.62 (dd, *J* = 13.1, 8.9 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 178.90, 162.19 (d, *J* = 247.7 Hz), 143.44, 133.76,

133.08 (d,  $J = 3.3$  Hz), 131.28, 129.78, 127.68 (d,  $J = 8.0$  Hz), 126.28, 124.84, 123.30 (q,  $J = 286.1$  Hz), 122.73, 121.75 (d,  $J = 2.1$  Hz), 118.02, 115.31 (d,  $J = 21.7$  Hz), 109.37, 85.01 (q,  $J = 31.8$  Hz), 63.31, 56.88, 42.43, 42.36.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -78.93 (d,  $J = 4.5$  Hz), -113.92 – -114.81 (m). HRMS Calcd. For  $\text{C}_{23}\text{H}_{22}\text{F}_4\text{N}_2\text{O}_2\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ): 457.1510, found: 457.1502.



**(E)-1-allyl-3-(3-(4-bromophenyl)allyl)-3-((2,2,2-trifluoro-1-methoxyethyl)amino)indolin-2-one:**

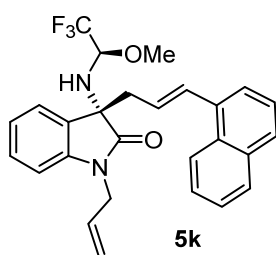
Yellow solid; 64% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41 – 7.30 (m, 4H), 7.19 – 7.08 (m, 1H), 7.03 (d,  $J = 8.5$  Hz, 2H), 6.93 – 6.76 (m, 1H), 6.25 (d,  $J = 15.9$  Hz, 1H), 5.95 – 5.82 (m, 1H), 5.77 – 5.60 (m, 1H), 5.26 – 5.03 (m, 2H), 4.43 (ddt,  $J = 16.1, 5.4, 1.5$  Hz, 1H), 4.24 – 4.10 (m, 1H), 3.95 (dq,  $J = 12.7, 4.8$  Hz, 1H), 3.12 (d,  $J = 12.7$  Hz, 1H), 2.93 (s, 3H), 2.80 (ddd,  $J = 13.2, 6.2, 1.4$  Hz, 1H), 2.62 (dd,  $J = 13.5, 9.0$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  178.83, 143.41, 135.81, 133.78, 131.53, 131.25, 129.82, 127.72, 126.18, 124.83, 123.27 (q,  $J = 281.4$  Hz), 122.94, 122.75, 121.18, 118.08, 109.39, 84.99 (q,  $J = 31.8$  Hz), 63.25, 56.89, 42.44, 42.37.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -78.93 (d,  $J = 4.8$  Hz). HRMS Calcd. For  $\text{C}_{23}\text{H}_{23}\text{BrF}_3\text{N}_2\text{O}_2$  ( $[\text{M}+\text{H}]^+$ ): 495.0890, found: 495.0890.



**(E)-1-allyl-3-(3-(3,4-dichlorophenyl)allyl)-3-((2,2,2-trifluoro-1-methoxyethyl)amino)indolin-2-one:**

Yellow solid; 79% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 – 7.27 (m, 3H), 7.24 (d,  $J = 2.0$

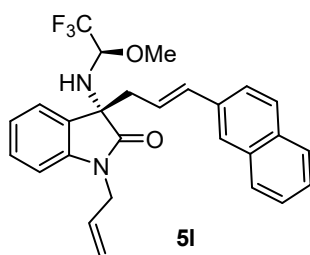
Hz, 1H), 7.14 (td,  $J = 7.6, 0.8$  Hz, 1H), 7.00 (dd,  $J = 8.3, 2.0$  Hz, 1H), 6.87 (d,  $J = 7.8$  Hz, 1H), 6.21 (d,  $J = 15.9$  Hz, 1H), 5.98 – 5.81 (m, 1H), 5.81 – 5.61 (m, 1H), 5.29 – 5.03 (m, 2H), 4.44 (ddt,  $J = 16.0, 5.4, 1.5$  Hz, 1H), 4.16 (ddt,  $J = 16.1, 5.6, 1.3$  Hz, 1H), 3.95 (dq,  $J = 12.7, 4.8$  Hz, 1H), 3.12 (d,  $J = 12.7$  Hz, 1H), 2.93 (s, 3H), 2.80 (ddd,  $J = 13.2, 6.3, 1.3$  Hz, 1H), 2.63 (dd,  $J = 13.5, 8.9$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  178.8, 143.4, 137.0, 132.7, 132.6, 131.2, 131.1, 130.4, 129.9, 127.9, 126.1, 125.4, 124.8, 124.3, 123.3 (q,  $J = 285.8$  Hz), 122.8, 118.2, 109.5, 85.0 (q,  $J = 31.8$  Hz), 63.2, 56.9, 42.5, 42.3.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -78.93 (d,  $J = 4.4$  Hz). HRMS Calcd. For  $\text{C}_{23}\text{H}_{21}\text{Cl}_2\text{F}_3\text{N}_2\text{O}_2\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ): 507.0824, found: 507.0818.



**(*E*)-1-allyl-3-(3-(naphthalen-1-yl)allyl)-3-((2,2,2-trifluoro-1-methoxyethyl)amino)indolin-2-one:**

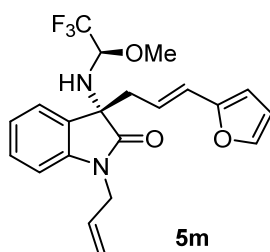
Yellow solid; 73% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 – 7.67 (m, 3H), 7.49 – 7.27 (m, 6H), 7.19 – 7.11 (m, 1H), 7.00 (d,  $J = 15.6$  Hz, 1H), 6.84 (d,  $J = 7.8$  Hz, 1H), 5.88 (ddd,  $J = 15.3, 8.4, 6.7$  Hz, 1H), 5.78 – 5.55 (m, 1H), 5.25 – 4.90 (m, 2H), 4.42 – 4.29 (m, 1H), 4.26 – 4.16 (m, 1H), 4.00 (dq,  $J = 12.7, 4.8$  Hz, 1H), 3.20 (d,  $J = 12.7$  Hz, 1H), 3.01 – 2.88 (m, 4H), 2.76 (dd,  $J = 13.0, 8.6$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  179.0, 143.6, 135.0, 133.4, 132.9, 131.3, 131.0, 129.8, 128.3, 127.8, 126.4, 125.9, 125.7, 125.5, 125.4, 125.0, 124.0, 123.9, 123.3 (q,  $J = 286.1$  Hz), 122.8, 118.2, 109.5, 85.0 (q,  $J = 31.7$  Hz), 63.5, 56.8, 42.7, 42.5.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -78.80 (d,  $J = 4.5$  Hz). HRMS Calcd. For  $\text{C}_{27}\text{H}_{25}\text{F}_3\text{N}_2\text{O}_2\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ): 489.1760, found: 489.1757.





**(E)-1-allyl-3-(3-(naphthalen-2-yl)allyl)-3-((2,2,2-trifluoro-1-methoxyethyl)amino)indolin-2-one:**

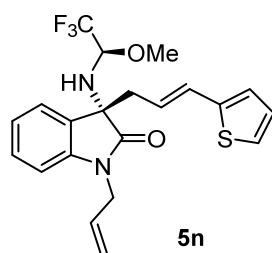
Yellow solid; 55% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.83 – 7.64 (m, 3H), 7.54 (s, 1H), 7.48 – 7.28 (m, 5H), 7.18 – 7.08 (m, 1H), 6.85 (d,  $J = 7.8$  Hz, 1H), 6.47 (d,  $J = 15.8$  Hz, 1H), 6.10 – 5.91 (m, 1H), 5.80 – 5.62 (m, 1H), 5.27 – 4.94 (m, 2H), 4.54 – 4.32 (m, 1H), 4.23 – 4.12 (m, 1H), 3.98 (dq,  $J = 12.7, 4.8$  Hz, 1H), 3.16 (d,  $J = 12.7$  Hz, 1H), 2.94 (s, 3H), 2.87 (ddd,  $J = 13.2, 6.2, 1.2$  Hz, 1H), 2.69 (dd,  $J = 13.3, 8.8$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  179.0, 143.5, 135.1, 134.4, 133.5, 132.9, 131.3, 129.8, 128.0, 127.9, 127.6, 126.3, 126.2, 126.1, 125.8, 124.9, 123.4, 123.3 (q,  $J = 31.7$  Hz), 122.8, 122.4, 118.1, 109.4, 85.1 (q,  $J = 31.7$  Hz), 63.4, 56.9, 42.6, 42.5.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -78.88 (d,  $J = 4.8$  Hz). HRMS Calcd. For  $\text{C}_{27}\text{H}_{25}\text{F}_3\text{N}_2\text{O}_2\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ): 489.1760, found: 489.1757.



**(E)-1-allyl-3-(3-(furan-2-yl)allyl)-3-((2,2,2-trifluoro-1-methoxyethyl)amino)indolin-2-one:**

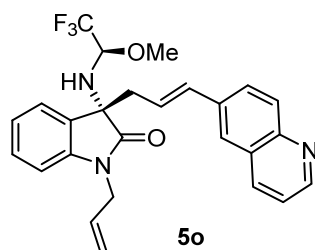
Yellow solid; 75% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 – 7.29 (m, 2H), 7.24 (d,  $J = 1.2$  Hz, 1H), 7.17 – 7.08 (m, 1H), 6.86 (d,  $J = 7.7$  Hz, 1H), 6.29 (dd,  $J = 3.2, 1.8$  Hz, 1H), 6.10 (dd,  $J = 21.3, 9.5$  Hz, 2H), 5.90 – 5.64 (m, 2H), 5.30 – 5.00 (m, 2H), 4.47 (ddt,  $J = 16.2, 5.1, 1.5$  Hz, 1H), 4.22 – 4.07 (m, 1H), 3.95 (dq,  $J = 12.7, 4.8$  Hz, 1H), 3.10 (d,  $J = 12.7$  Hz, 1H), 2.92 (s, 3H), 2.80 (ddd,  $J = 13.3, 6.3, 1.2$  Hz, 1H), 2.59 (dd,  $J = 13.3, 9.0$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  178.9, 152.4, 143.5, 141.7, 131.2, 129.8, 126.2, 124.8, 123.3 (q,  $J = 286.0$  Hz), 123.2, 122.7, 120.7, 117.8, 111.1, 109.4, 107.5, 85.0 (q,  $J = 31.7$  Hz), 63.3, 56.9, 42.4, 42.3.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -78.93 (d,  $J = 4.4$  Hz). HRMS Calcd. For  $\text{C}_{21}\text{H}_{21}\text{F}_3\text{N}_2\text{O}_3\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ):

429.1396, found: 429.1396.



**(E)-1-allyl-3-(3-(thiophen-2-yl)allyl)-3-((2,2,2-trifluoro-1-methoxyethyl)amino)indolin-2-one:**

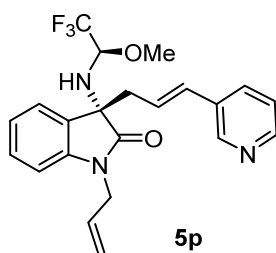
Yellow solid; 50% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 – 7.30 (m, 2H), 7.18 – 7.10 (m, 1H), 7.06 (d,  $J = 5.1$  Hz, 1H), 6.94 – 6.83 (m, 2H), 6.78 (d,  $J = 3.4$  Hz, 1H), 6.42 (d,  $J = 15.7$  Hz, 1H), 5.82 – 5.60 (m, 2H), 5.29 – 5.02 (m, 2H), 4.45 (ddt,  $J = 16.1, 5.3, 1.5$  Hz, 1H), 4.24 – 4.10 (m, 1H), 3.95 (dq,  $J = 12.7, 4.8$  Hz, 1H), 3.10 (d,  $J = 12.7$  Hz, 1H), 2.93 (s, 3H), 2.78 (ddd,  $J = 13.3, 6.4, 1.2$  Hz, 1H), 2.59 (dd,  $J = 13.3, 8.8$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  178.9, 143.5, 142.0, 131.3, 129.8, 128.0, 127.2, 126.1, 125.3, 124.9, 123.9, 123.3 (q,  $J = 285.8$  Hz), 122.8, 121.7, 118.1, 109.4, 85.0 (q,  $J = 31.8$  Hz), 63.3, 56.9, 42.5, 42.3.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -78.93 (d,  $J = 4.7$  Hz). HRMS Calcd. For  $\text{C}_{21}\text{H}_{21}\text{F}_3\text{N}_2\text{O}_2\text{SNa}$  ( $[\text{M}+\text{Na}]^+$ ): 445.1168, found: 445.1164.



**(E)-1-allyl-3-(3-(quinolin-6-yl)allyl)-3-((2,2,2-trifluoro-1-methoxyethyl)amino)indolin-2-one:**

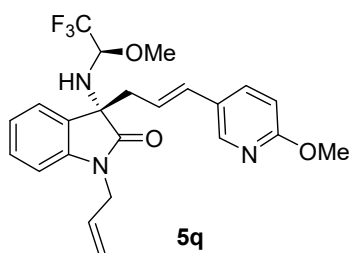
Yellow solid; 78% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.83 (dd,  $J = 4.1, 1.4$  Hz, 1H), 8.07 (d,  $J = 8.2$  Hz, 1H), 7.96 (d,  $J = 8.8$  Hz, 1H), 7.60 (dd,  $J = 8.8, 1.9$  Hz, 1H), 7.53 (d,  $J = 1.5$  Hz, 1H), 7.42 – 7.32 (m, 3H), 7.21 – 7.10 (m, 1H), 6.87 (d,  $J = 7.8$  Hz, 1H), 6.50 (d,  $J = 15.8$  Hz, 1H), 6.15 – 5.99 (m, 1H), 5.79 – 5.62 (m, 1H), 5.27 – 4.98 (m, 2H), 4.51 – 4.39 (m, 1H), 4.21 – 4.13 (m, 1H), 3.98 (dq,  $J = 12.7, 4.8$  Hz, 1H), 3.17 (d,  $J = 12.7$  Hz, 1H), 3.05 – 2.85 (m, 4H),

2.71 (dd,  $J = 13.3, 8.9$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  178.89, 150.03, 147.84, 143.45, 136.04, 135.09, 134.26, 131.23, 129.87, 129.43, 128.38, 127.11, 126.19, 125.58, 124.85, 123.81, 123.29 (q,  $J = 286.2$  Hz), 122.81, 121.44, 118.09, 109.45, 85.03 (q,  $J = 31.8$  Hz), 63.35, 56.92, 42.53, 42.45.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -78.91 (d,  $J = 4.4$  Hz). HRMS Calcd. For  $\text{C}_{26}\text{H}_{24}\text{F}_3\text{N}_3\text{O}_2\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ): 490.1713, found: 490.1708.



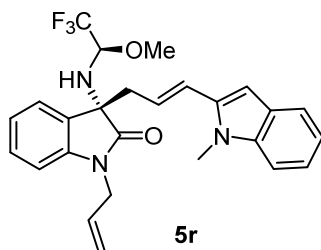
**(E)-1-allyl-3-(3-(pyridin-3-yl)allyl)-3-((2,2,2-trifluoro-1-methoxyethyl)amino)indolin-2-one:**

Yellow solid; 83% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.51 – 8.26 (m, 2H), 7.50 (dt,  $J = 7.9, 1.7$  Hz, 1H), 7.40 – 7.30 (m, 2H), 7.22 – 7.08 (m, 2H), 6.91 – 6.82 (m, 1H), 6.30 (d,  $J = 16.0$  Hz, 1H), 6.04 – 5.90 (m, 1H), 5.79 – 5.63 (m, 1H), 5.26 – 5.04 (m, 2H), 4.43 (ddt,  $J = 16.0, 5.5, 1.5$  Hz, 1H), 4.18 (ddt,  $J = 16.0, 5.5, 1.3$  Hz, 1H), 3.96 (dq,  $J = 12.7, 4.8$  Hz, 1H), 3.14 (d,  $J = 12.7$  Hz, 1H), 2.93 (s, 3H), 2.84 (ddd,  $J = 13.3, 6.2, 1.4$  Hz, 1H), 2.66 (dd,  $J = 13.7, 8.7$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  178.79, 148.40, 147.93, 143.39, 132.83, 132.53, 131.37, 131.23, 129.93, 126.04, 124.84, 124.79, 123.40, 123.26 (q,  $J = 285.9$  Hz), 122.83, 118.16, 109.45, 85.00 (q,  $J = 31.9$  Hz), 63.22, 56.92, 42.47, 42.41.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -78.94 (d,  $J = 4.5$  Hz). HRMS Calcd. For  $\text{C}_{22}\text{H}_{22}\text{F}_3\text{N}_3\text{O}_2\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ): 440.1556, found: 440.1553.



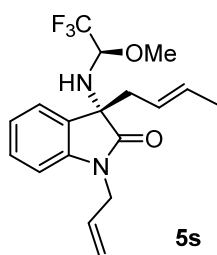
**(E)-1-allyl-3-(3-(6-methoxypyridin-3-yl)allyl)-3-((2,2,2-trifluoro-1-methoxyethyl)amino)indolin-2-one:**

Yellow solid; 64% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 (d,  $J = 2.2$  Hz, 1H), 7.44 (dd,  $J = 8.6, 2.4$  Hz, 1H), 7.40 – 7.29 (m, 2H), 7.19 – 7.08 (m, 1H), 6.86 (d,  $J = 8.2$  Hz, 1H), 6.63 (d,  $J = 8.6$  Hz, 1H), 6.24 (d,  $J = 15.9$  Hz, 1H), 5.88 – 5.62 (m, 2H), 5.27 – 5.03 (m, 2H), 4.53 – 4.38 (m, 1H), 4.23 – 4.11 (m, 1H), 4.01 – 3.87 (m, 4H), 3.12 (d,  $J = 12.7$  Hz, 1H), 2.93 (s, 3H), 2.81 (ddd,  $J = 13.2, 6.2, 1.2$  Hz, 1H), 2.63 (dd,  $J = 13.3, 8.8$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  178.87, 163.50, 145.19, 143.43, 135.46, 131.28, 131.03, 129.80, 126.21, 126.12, 124.83, 123.28 (q,  $J = 285.9$  Hz), 122.74, 121.42, 118.08, 110.75, 109.37, 85.00 (q,  $J = 31.8$  Hz), 63.31, 56.88, 56.87, 53.45, 42.43.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -78.94 (d,  $J = 4.7$  Hz). HRMS Calcd. For  $\text{C}_{23}\text{H}_{25}\text{F}_3\text{N}_3\text{O}_3$  ( $[\text{M}+\text{H}]^+$ ): 448.1843, found: 448.1842.



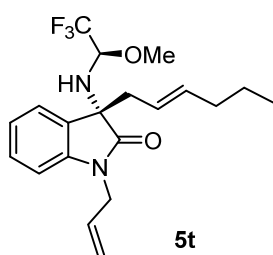
**(E)-1-allyl-3-(3-(1-methyl-1H-indol-2-yl)allyl)-3-((2,2,2-trifluoro-1-methoxyethyl)amino)indolin-2-one:**

Yellow solid; 76% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50 (d,  $J = 7.8$  Hz, 1H), 7.40 – 7.29 (m, 2H), 7.22 (d,  $J = 8.2$  Hz, 1H), 7.19 – 7.10 (m, 2H), 7.09 – 7.01 (m, 1H), 6.87 (d,  $J = 7.8$  Hz, 1H), 6.41 (s, 1H), 6.37 (d,  $J = 15.7$  Hz, 1H), 5.93 (ddd,  $J = 15.5, 8.7, 6.5$  Hz, 1H), 5.79 – 5.65 (m, 1H), 5.28 – 5.01 (m, 2H), 4.39 (ddt,  $J = 16.0, 5.5, 1.5$  Hz, 1H), 4.21 (ddt,  $J = 16.1, 5.5, 1.3$  Hz, 1H), 3.98 (dq,  $J = 12.7, 4.8$  Hz, 1H), 3.56 (s, 3H), 3.14 (d,  $J = 12.7$  Hz, 1H), 2.98 – 2.82 (m, 4H), 2.67 (dd,  $J = 13.4, 9.0$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  178.87, 143.53, 137.69, 137.66, 131.29, 129.85, 127.71, 126.15, 125.07, 124.93, 124.15, 123.30 (q,  $J = 286.0$  Hz), 122.73, 121.54, 120.27, 119.71, 118.20, 109.49, 109.10, 98.72, 85.00 (q,  $J = 31.8$  Hz), 63.43, 56.84, 42.68, 42.52, 29.73.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -78.87 (d,  $J = 4.7$  Hz). HRMS Calcd. For  $\text{C}_{26}\text{H}_{27}\text{F}_3\text{N}_3\text{O}_2$  ( $[\text{M}+\text{H}]^+$ ): 470.2050, found: 470.2046.



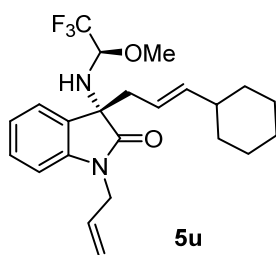
**(E)-1-allyl-3-(but-2-en-1-yl)-3-((2,2,2-trifluoro-1-methoxyethyl)amino)indolin-2-one:**

Yellow solid; 88% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 – 7.28 (m, 2H), 7.11 (td,  $J = 7.5$ , 0.8 Hz, 1H), 6.86 (d,  $J = 7.8$  Hz, 1H), 5.90 – 5.73 (m, 1H), 5.51 – 5.36 (m, 1H), 5.32 – 5.18 (m, 2H), 5.16 – 5.03 (m, 1H), 4.57 – 4.42 (m, 1H), 4.16 (ddt,  $J = 16.2$ , 5.5, 1.4 Hz, 1H), 3.92 (dq,  $J = 12.7$ , 4.8 Hz, 1H), 3.05 (d,  $J = 12.7$  Hz, 1H), 2.93 (s, 3H), 2.64 – 2.54 (m, 1H), 2.44 (dd,  $J = 13.2$ , 8.6 Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  179.1, 143.5, 131.5, 131.0, 129.5, 126.6, 124.7, 123.3 (q,  $J = 286.9$  Hz), 122.9, 122.6, 117.7, 109.2, 85.0 (q,  $J = 31.8$  Hz), 63.2, 56.8, 42.4, 42.2, 17.9.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -78.98 (d,  $J = 4.5$  Hz). HRMS Calcd. For  $\text{C}_{18}\text{H}_{21}\text{F}_3\text{N}_2\text{O}_2\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ): 377.1447, found: 377.1447.



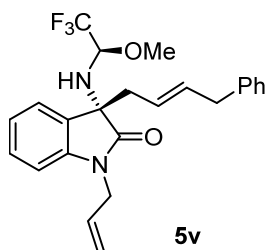
**(E)-1-allyl-3-(hex-2-en-1-yl)-3-((2,2,2-trifluoro-1-methoxyethyl)amino)indolin-2-one:**

Yellow solid; 98% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 – 7.27 (m, 2H), 7.11 (td,  $J = 7.5$ , 0.7 Hz, 1H), 6.86 (d,  $J = 7.8$  Hz, 1H), 5.92 – 5.71 (m, 1H), 5.47 – 5.33 (m, 1H), 5.33 – 5.20 (m, 2H), 5.15 – 5.01 (m, 1H), 4.42 (ddt,  $J = 16.1$ , 5.4, 1.5 Hz, 1H), 4.21 (ddt,  $J = 16.1$ , 5.5, 1.4 Hz, 1H), 3.93 (dq,  $J = 12.7$ , 4.9 Hz, 1H), 3.05 (d,  $J = 12.7$  Hz, 1H), 2.94 (s, 3H), 2.65 – 2.53 (m, 1H), 2.45 (dd,  $J = 13.2$ , 8.2 Hz, 1H), 1.94 – 1.74 (m, 2H), 1.29 – 1.14 (m, 2H), 0.75 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  179.1, 143.5, 136.4, 131.5, 129.5, 126.6, 124.8, 123.3 (q,  $J = 285.9$  Hz), 122.5, 121.8, 118.0, 109.2, 84.9 (q,  $J = 31.8$  Hz), 63.2, 56.7, 42.4, 42.3, 34.5, 22.3, 13.5.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -78.92 (d,  $J = 4.8$  Hz). HRMS Calcd. For  $\text{C}_{20}\text{H}_{25}\text{F}_3\text{N}_2\text{O}_2\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ): 405.1760, found: 405.1754.



**(E)-1-allyl-3-(3-cyclohexylallyl)-3-((2,2,2-trifluoro-1-methoxyethyl)amino)indolin-2-one:**

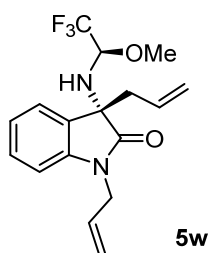
Yellow solid; 90% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34 – 7.27 (m, 2H), 7.10 (td,  $J = 7.5$ , 0.6 Hz, 1H), 6.86 (d,  $J = 7.8$  Hz, 1H), 5.90 – 5.69 (m, 1H), 5.38 – 5.17 (m, 3H), 5.13 – 4.98 (m, 1H), 4.37 (ddt,  $J = 15.9$ , 5.5, 1.3 Hz, 1H), 4.30 – 4.19 (m, 1H), 3.94 (dq,  $J = 12.7$ , 4.9 Hz, 1H), 3.05 (d,  $J = 12.7$  Hz, 1H), 2.94 (s, 3H), 2.56 (dd,  $J = 13.1$ , 6.5 Hz, 1H), 2.42 (dd,  $J = 13.1$ , 8.2 Hz, 1H), 1.83 – 1.70 (m, 1H), 1.68 – 1.38 (m, 5H), 1.26 – 1.00 (m, 3H), 0.96 – 0.79 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  179.1, 143.5, 142.5, 131.6, 129.5, 126.6, 124.8, 123.3 (q,  $J = 286.0$  Hz), 122.5, 119.0, 118.1, 109.1, 84.9 (q,  $J = 31.7$  Hz), 63.2, 56.6, 42.5, 42.2, 40.5, 32.8, 32.6, 26.1, 25.9, 25.8.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -78.90 (d,  $J = 4.8$  Hz). HRMS Calcd. For  $\text{C}_{23}\text{H}_{29}\text{F}_3\text{N}_2\text{O}_2\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ): 445.2073, found: 445.2067.



**(E)-1-allyl-3-(4-phenylbut-2-en-1-yl)-3-((2,2,2-trifluoro-1-methoxyethyl)amino)indolin-2-one:**

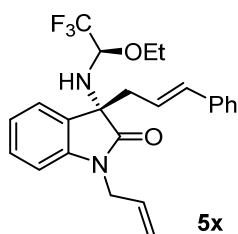
Yellow solid; 70% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 – 7.03 (m, 6H), 6.93 (d,  $J = 7.2$  Hz, 2H), 6.86 (d,  $J = 7.8$  Hz, 1H), 5.77 (ddd,  $J = 22.4$ , 10.6, 5.5 Hz, 1H), 5.62 – 5.48 (m, 1H), 5.34 – 5.14 (m, 3H), 4.27 (ddd,  $J = 48.0$ , 16.0, 5.4 Hz, 2H), 4.02 – 3.86 (m, 1H), 3.19 (d,  $J = 6.5$  Hz, 2H), 3.07 (d,  $J = 12.7$  Hz, 1H), 2.93 (s, 3H), 2.63 (dd,  $J = 13.2$ , 6.8 Hz, 1H), 2.50 (dd,  $J = 13.1$ , 7.9 Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  179.04, 143.51, 140.10, 134.71, 131.55, 129.55, 128.33, 128.31, 126.47, 125.93, 124.87, 123.54, 123.29 (q,  $J = 285.7$  Hz), 122.66, 118.10, 109.30, 84.94 (q,  $J = 31.7$  Hz), 63.16, 56.72, 42.45, 42.09, 38.80.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -78.88 (d,  $J = 4.4$  Hz). HRMS Calcd. For  $\text{C}_{24}\text{H}_{25}\text{F}_3\text{N}_2\text{O}_2\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ): 453.1760,

found: 453.1758.



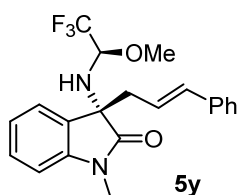
**1,3-diallyl-3-((2,2,2-trifluoro-1-methoxyethyl)amino)indolin-2-one:**

Yellow solid; 70% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 – 7.29 (m, 2H), 7.12 (td,  $J = 7.5$ , 0.8 Hz, 1H), 6.88 (d,  $J = 7.7$  Hz, 1H), 5.91 – 5.75 (m, 1H), 5.61 – 5.45 (m, 1H), 5.37 – 5.19 (m, 2H), 5.08 – 4.95 (m, 2H), 4.43 (ddt,  $J = 16.1$ , 5.4, 1.6 Hz, 1H), 4.23 (ddt,  $J = 16.1$ , 5.6, 1.4 Hz, 1H), 3.93 (dq,  $J = 12.7$ , 4.8 Hz, 1H), 3.06 (d,  $J = 12.7$  Hz, 1H), 2.93 (s, 3H), 2.72 – 2.60 (m, 1H), 2.49 (dd,  $J = 13.3$ , 8.4 Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  178.9, 143.5, 131.5, 130.6, 129.6, 126.3, 124.8, 123.3 (q,  $J = 286.0$  Hz), 122.6, 120.2, 118.1, 109.3, 84.9 (q,  $J = 31.8$  Hz), 62.8, 56.7, 43.2, 42.5.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -78.91 (d,  $J = 4.8$  Hz). HRMS Calcd. For  $\text{C}_{17}\text{H}_{19}\text{F}_3\text{N}_2\text{O}_2\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ): 363.1291, found: 363.1286.



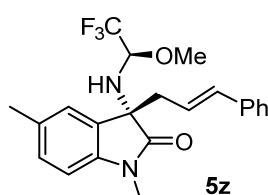
**1-allyl-3-cinnamyl-3-((1-ethoxy-2,2,2-trifluoroethyl)amino)indolin-2-one:**

Yellow solid; 77% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 – 7.28 (m, 2H), 7.25 – 7.08 (m, 6H), 6.83 (d,  $J = 7.7$  Hz, 1H), 6.30 (d,  $J = 15.9$  Hz, 1H), 5.95 – 5.80 (m, 1H), 5.76 – 5.59 (m, 1H), 5.22 – 4.98 (m, 2H), 4.56 (ddt,  $J = 16.1$ , 4.8, 1.6 Hz, 1H), 4.07 – 3.94 (m, 2H), 3.44 – 3.32 (m, 1H), 3.08 (d,  $J = 12.5$  Hz, 1H), 2.86 – 2.77 (m, 2H), 2.63 (dd,  $J = 13.2$ , 8.8 Hz, 1H), 0.96 (t,  $J = 7.0$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  178.5, 143.4, 136.9, 135.0, 131.2, 129.7, 128.4, 127.4, 126.6, 126.2, 124.8, 123.3 (q,  $J = 285.7$  Hz), 122.7, 122.0, 118.0, 109.3, 83.5 (q,  $J = 31.8$  Hz), 65.1, 63.5, 42.9, 42.4, 14.9.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -79.04 (d,  $J = 5.0$  Hz). HRMS Calcd. For  $\text{C}_{24}\text{H}_{25}\text{F}_3\text{N}_2\text{O}_2\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ): 453.1760, found: 453.1757.



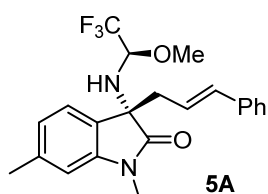
### 3-cinnamyl-1-methyl-3-((2,2,2-trifluoro-1-methoxyethyl)amino)indolin-2-one:

Yellow solid; 59% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 – 7.30 (m, 2H), 7.29 – 7.16 (m, 5H), 7.12 (t,  $J = 7.4$  Hz, 1H), 6.87 (d,  $J = 7.8$  Hz, 1H), 6.32 (d,  $J = 15.8$  Hz, 1H), 6.07 – 5.88 (m, 1H), 3.90 (dq,  $J = 12.7, 4.7$  Hz, 1H), 3.19 (s, 3H), 3.10 (d,  $J = 12.7$  Hz, 1H), 2.93 (s, 3H), 2.80 (ddd,  $J = 13.4, 6.1, 1.1$  Hz, 1H), 2.59 (dd,  $J = 13.4, 8.8$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  179.4, 144.2, 137.1, 134.8, 129.9, 128.5, 127.4, 126.4, 126.2, 125.0, 123.3 (q,  $J = 285.8$  Hz), 122.8, 122.2, 108.4, 85.3 (q,  $J = 31.8$  Hz), 63.2, 57.2, 42.0, 26.2.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -79.16 (d,  $J = 4.6$  Hz). HRMS Calcd. For  $\text{C}_{21}\text{H}_{21}\text{F}_3\text{N}_2\text{O}_2\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ): 413.1447, found: 413.1441.



### 3-cinnamyl-1,5-dimethyl-3-((2,2,2-trifluoro-1-methoxyethyl)amino)indolin-2-one:

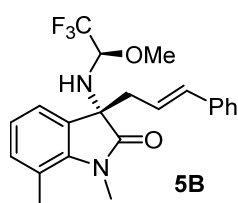
Yellow solid; 74% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28 – 7.11 (m, 7H), 6.75 (d,  $J = 7.8$  Hz, 1H), 6.33 (d,  $J = 15.8$  Hz, 1H), 5.99 – 5.86 (m, 1H), 3.92 (dq,  $J = 12.7, 4.8$  Hz, 1H), 3.16 (s, 3H), 3.08 (d,  $J = 12.7$  Hz, 1H), 2.94 (s, 3H), 2.77 (ddd,  $J = 13.5, 6.2, 1.2$  Hz, 1H), 2.60 (dd,  $J = 13.4, 8.8$  Hz, 1H), 2.37 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  179.3, 141.8, 137.2, 134.7, 132.4, 130.2, 128.4, 127.3, 126.4, 126.2, 125.6, 123.3 (q,  $J = 285.7$  Hz), 122.3, 108.2, 85.2 (q,  $J = 31.8$  Hz), 63.3, 57.2, 42.1, 26.2, 21.2.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -79.16 (d,  $J = 4.7$  Hz). HRMS Calcd. For  $\text{C}_{22}\text{H}_{23}\text{F}_3\text{N}_2\text{O}_2\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ): 427.1604, found: 427.1599.



### 3-cinnamyl-1,6-dimethyl-3-((2,2,2-trifluoro-1-methoxyethyl)amino)indolin-2-one:

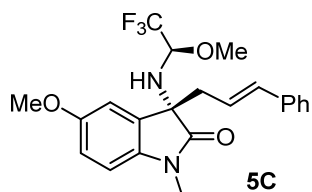


Yellow solid; 67% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 – 7.14 (m, 6H), 6.92 (d,  $J = 7.4$  Hz, 1H), 6.69 (s, 1H), 6.32 (d,  $J = 15.8$  Hz, 1H), 6.05 – 5.91 (m, 1H), 3.90 (dq,  $J = 12.6, 4.8$  Hz, 1H), 3.18 (s, 3H), 3.06 (d,  $J = 12.7$  Hz, 1H), 2.94 (s, 3H), 2.84 – 2.73 (m, 1H), 2.56 (dd,  $J = 13.4, 8.9$  Hz, 1H), 2.40 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  179.69, 144.25, 140.19, 137.16, 134.64, 128.44, 127.34, 126.25, 124.75, 123.34, 123.32 (q,  $J = 287.3$  Hz), 123.31, 122.47, 109.34, 85.22 (q,  $J = 31.8$  Hz), 63.08, 57.19, 42.04, 26.11, 21.95.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -79.16 (d,  $J = 4.6$  Hz). HRMS Calcd. For  $\text{C}_{22}\text{H}_{23}\text{F}_3\text{N}_2\text{O}_2\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ): 427.1604, found: 427.1601.



**3-cinnamyl-1,7-dimethyl-3-((2,2,2-trifluoro-1-methoxyethyl)amino)indolin-2-one:**

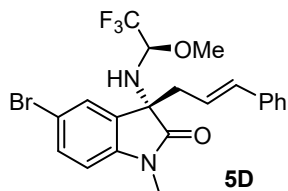
Yellow solid; 68% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29 – 7.13 (m, 6H), 7.08 (d,  $J = 7.5$  Hz, 1H), 7.00 (t,  $J = 7.5$  Hz, 1H), 6.32 (d,  $J = 15.8$  Hz, 1H), 6.06 – 5.84 (m, 1H), 3.91 (dq,  $J = 12.7, 4.8$  Hz, 1H), 3.46 (s, 3H), 3.08 (d,  $J = 12.7$  Hz, 1H), 2.98 (s, 3H), 2.75 (ddd,  $J = 13.3, 6.1, 1.0$  Hz, 1H), 2.64 – 2.51 (m, 4H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  180.1, 142.0, 137.2, 134.7, 133.5, 128.5, 127.4, 127.1, 126.3, 123.3 (q,  $J = 285.8$  Hz), 122.8, 122.7, 122.3, 120.1, 85.1 (q,  $J = 31.8$  Hz), 62.5, 57.0, 42.4, 29.6, 19.1.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -79.10 (d,  $J = 4.6$  Hz). HRMS Calcd. For  $\text{C}_{22}\text{H}_{23}\text{F}_3\text{N}_2\text{O}_2\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ): 427.1604, found: 427.1603.



**3-cinnamyl-5-methoxy-1-methyl-3-((2,2,2-trifluoro-1-methoxyethyl)amino)indolin-2-one:**

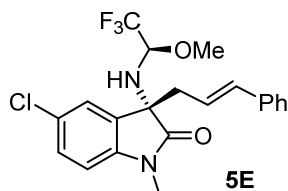
Yellow solid; 64% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 – 7.15 (m, 5H), 6.94 (d,  $J = 2.5$  Hz, 1H), 6.89 (dd,  $J = 8.5, 2.5$  Hz, 1H), 6.77 (d,  $J = 8.5$  Hz, 1H), 6.34 (d,  $J = 15.8$  Hz, 1H), 6.02 – 5.87 (m, 1H), 3.93 (dq,  $J = 12.6, 4.7$  Hz, 1H), 3.78 (s, 3H), 3.17 (s, 3H), 3.10 (d,  $J = 12.7$  Hz, 1H), 2.96 (s, 3H), 2.78 (ddd,  $J = 13.3, 6.2, 1.2$  Hz, 1H), 2.60 (dd,  $J = 13.4, 8.8$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  179.0, 156.1, 137.6, 137.1, 134.9, 128.5, 127.7, 127.4, 126.2, 123.3

(q,  $J = 285.9$  Hz), 122.1, 114.2, 112.0, 108.9, 85.2 (q,  $J = 31.9$  Hz), 63.7, 57.3, 55.8, 42.1, 26.2.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -79.20 (d,  $J = 4.4$  Hz). HRMS Calcd. For  $\text{C}_{22}\text{H}_{23}\text{F}_3\text{N}_2\text{O}_3\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ): 443.1553, found: 443.1549.



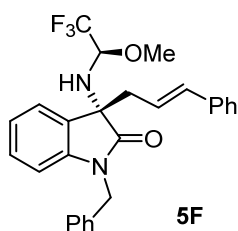
**5-bromo-3-cinnamyl-1-methyl-3-((2,2,2-trifluoro-1-methoxyethyl)amino)indolin-2-one:**

Yellow solid; 87% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50 (dd,  $J = 8.3, 2.0$  Hz, 1H), 7.46 (d,  $J = 1.9$  Hz, 1H), 7.29 – 7.16 (m, 5H), 6.74 (d,  $J = 8.3$  Hz, 1H), 6.35 (d,  $J = 15.8$  Hz, 1H), 5.96 – 5.79 (m, 1H), 3.99 – 3.85 (m, 1H), 3.16 (s, 3H), 3.12 (d,  $J = 12.7$  Hz, 1H), 2.97 (s, 3H), 2.76 (ddd,  $J = 13.3, 6.3, 1.2$  Hz, 1H), 2.62 (dd,  $J = 13.4, 8.7$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  178.7, 143.3, 136.9, 135.4, 132.8, 128.6, 128.5, 127.9, 127.6, 126.3, 123.1 (q,  $J = 286.0$  Hz), 121.3, 115.5, 109.9, 85.2 (q,  $J = 32.0$  Hz), 63.4, 57.2, 42.1, 26.2.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -79.01 (d,  $J = 4.3$  Hz). HRMS Calcd. For  $\text{C}_{21}\text{H}_{20}\text{BrF}_3\text{N}_2\text{O}_2\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ): 491.0552, found: 491.0547.



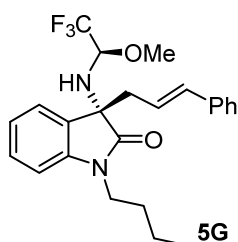
**5-chloro-3-cinnamyl-1-methyl-3-((2,2,2-trifluoro-1-methoxyethyl)amino)indolin-2-one:**

Yellow solid; 68% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 – 7.30 (m, 2H), 7.28 – 7.15 (m, 5H), 6.79 (d,  $J = 8.2$  Hz, 1H), 6.34 (d,  $J = 15.8$  Hz, 1H), 5.96 – 5.81 (m, 1H), 3.91 (dq,  $J = 12.8, 4.7$  Hz, 1H), 3.17 (s, 3H), 3.12 (d,  $J = 12.7$  Hz, 1H), 2.97 (s, 3H), 2.77 (ddd,  $J = 13.3, 6.3, 1.3$  Hz, 1H), 2.62 (dd,  $J = 13.4, 8.7$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  178.85, 142.77, 136.86, 135.37, 129.93, 128.49, 128.28, 128.27, 127.55, 126.28, 125.16, 123.14 (q,  $J = 286.0$  Hz), 121.37, 109.37, 85.18 (q,  $J = 31.9$  Hz), 63.42, 57.19, 42.08, 26.27.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -79.03 (d,  $J = 4.4$  Hz). HRMS Calcd. For  $\text{C}_{21}\text{H}_{20}\text{ClF}_3\text{N}_2\text{O}_2\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ): 447.1058, found: 447.1050.



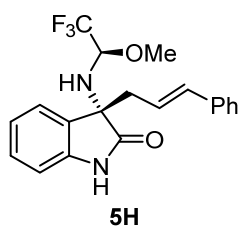
**1-benzyl-3-cinnamyl-3-((2,2,2-trifluoro-1-methoxyethyl)amino)indolin-2-one:**

Yellow solid; 56% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 (dd,  $J = 7.3, 0.7$  Hz, 1H), 7.28 – 7.06 (m, 10H), 7.00 (t,  $J = 7.6$  Hz, 2H), 6.72 (d,  $J = 7.8$  Hz, 1H), 6.38 (d,  $J = 15.9$  Hz, 1H), 5.93 – 5.77 (m, 1H), 5.15 (d,  $J = 15.6$  Hz, 1H), 4.58 (d,  $J = 15.6$  Hz, 1H), 3.96 (dq,  $J = 12.7, 4.8$  Hz, 1H), 3.16 (d,  $J = 12.7$  Hz, 1H), 2.89 (ddd,  $J = 13.2, 6.1, 1.4$  Hz, 1H), 2.84 (s, 3H), 2.73 (dd,  $J = 13.3, 9.1$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  179.33, 143.57, 136.87, 135.43, 135.13, 129.83, 128.70, 128.51, 127.53, 127.48, 127.36, 126.35, 126.25, 124.83, 123.34 (q,  $J = 285.8$  Hz), 122.81, 121.98, 109.54, 85.04 (q,  $J = 31.8$  Hz), 63.41, 56.83, 44.01, 42.56.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -78.89 (d,  $J = 4.8$  Hz). HRMS Calcd. For  $\text{C}_{27}\text{H}_{25}\text{F}_3\text{N}_2\text{O}_2\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ): 489.1760, found: 489.1755.



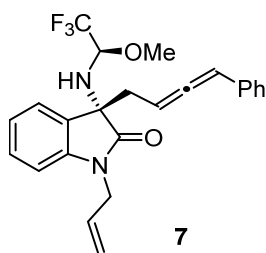
**1-butyl-3-cinnamyl-3-((2,2,2-trifluoro-1-methoxyethyl)amino)indolin-2-one:**

Yellow solid; 60% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 – 7.31 (m, 2H), 7.25 – 7.13 (m, 5H), 7.11 (td,  $J = 7.5, 0.6$  Hz, 1H), 6.86 (d,  $J = 7.7$  Hz, 1H), 6.30 (d,  $J = 15.9$  Hz, 1H), 5.95 – 5.79 (m, 1H), 3.95 (dq,  $J = 12.7, 4.8$  Hz, 1H), 3.84 – 3.69 (m, 1H), 3.53 (dt,  $J = 14.2, 7.2$  Hz, 1H), 3.09 (d,  $J = 12.7$  Hz, 1H), 2.92 (s, 3H), 2.80 (ddd,  $J = 13.2, 6.1, 1.3$  Hz, 1H), 2.61 (dd,  $J = 13.3, 8.9$  Hz, 1H), 1.59 – 1.47 (m, 2H), 1.37 – 1.22 (m, 2H), 0.81 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  179.0, 143.8, 137.0, 134.8, 129.8, 128.4, 127.4, 126.5, 126.2, 125.0, 123.3 (q,  $J = 285.9$  Hz), 122.5, 122.1, 108.6, 85.1 (q,  $J = 31.7$  Hz), 63.3, 56.9, 42.5, 39.9, 29.8, 20.2, 13.6.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -78.98 (d,  $J = 4.6$  Hz). HRMS Calcd. For  $\text{C}_{24}\text{H}_{27}\text{F}_3\text{N}_2\text{O}_2\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ): 455.1917, found: 455.1914.



**3-cinnamyl-3-((2,2,2-trifluoro-1-methoxyethyl)amino)indolin-2-one:**

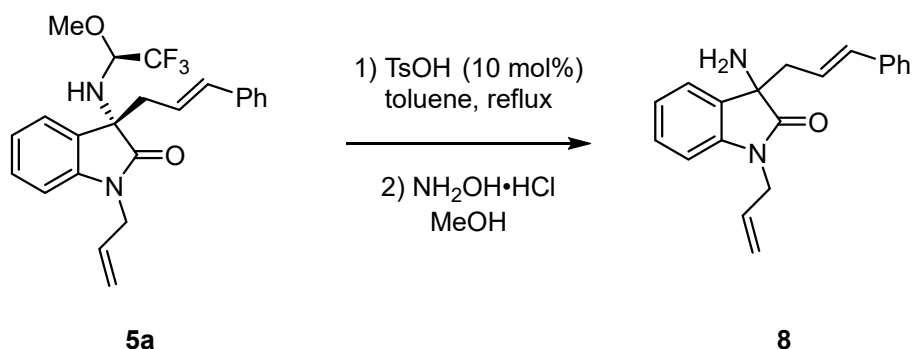
Yellow solid; 17% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 (s, 1H), 7.33 – 7.28 (m, 2H), 7.25 – 7.16 (m, 5H), 7.13 – 7.08 (m, 1H), 6.91 (d,  $J = 7.6$  Hz, 1H), 6.34 (d,  $J = 15.6$  Hz, 1H), 6.05 – 5.90 (m, 1H), 3.99 – 3.89 (m, 1H), 3.11 (d,  $J = 12.8$  Hz, 1H), 3.00 (s, 3H), 2.80 (dd,  $J = 13.6, 6.4$  Hz, 1H), 2.61 (dd,  $J = 13.6, 8.8$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  181.0, 141.1, 137.0, 135.0, 129.8, 128.4, 127.4, 126.7, 126.2, 125.3, 123.3 (q,  $J = 285.8$  Hz), 122.8, 121.9, 110.2, 85.3 (q,  $J = 31.3$  Hz), 63.6, 57.5, 42.2.  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -79.19 (d,  $J = 4.5$  Hz). HRMS Calcd. For  $\text{C}_{20}\text{H}_{19}\text{F}_3\text{N}_2\text{O}_2\text{Na}^+$  ( $[\text{M}+\text{Na}]^+$ ): 399.1291, found: 399.1321.



**1-allyl-3-(4-phenylbuta-2,3-dien-1-yl)-3-((2,2,2-trifluoro-1-methoxyethyl)amino)indolin-2-one:**

Yellow solid; 46% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 – 7.32 (m, 2H), 7.30 – 7.21 (m, 2H), 7.21 – 7.09 (m, 4H), 6.90 (d,  $J = 7.8$  Hz, 1H), 5.97 – 5.75 (m, 2H), 5.49 – 5.17 (m, 3H), 4.52 – 4.23 (m, 2H), 4.07 – 3.90 (m, 1H), 3.16 (d,  $J = 12.8$  Hz, 1H), 2.95 (s, 3H), 2.72 (ddd,  $J = 13.7, 6.3, 3.4$  Hz, 1H), 2.56 (ddd,  $J = 13.7, 9.0, 1.4$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  207.3, 178.8, 143.6, 133.9, 131.4, 129.8, 128.5, 126.9, 126.8, 126.1, 125.1, 123.3 (q,  $J = 286.0$  Hz), 122.7, 118.4, 109.5, 94.5, 87.6, 84.9 (q,  $J = 31.9$  Hz), 62.6, 56.7, 42.6, 38.7.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -78.81 (d,  $J = 4.8$  Hz). HRMS Calcd. For  $\text{C}_{24}\text{H}_{23}\text{F}_3\text{N}_2\text{O}_2\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ): 451.1603, found: 451.1603.

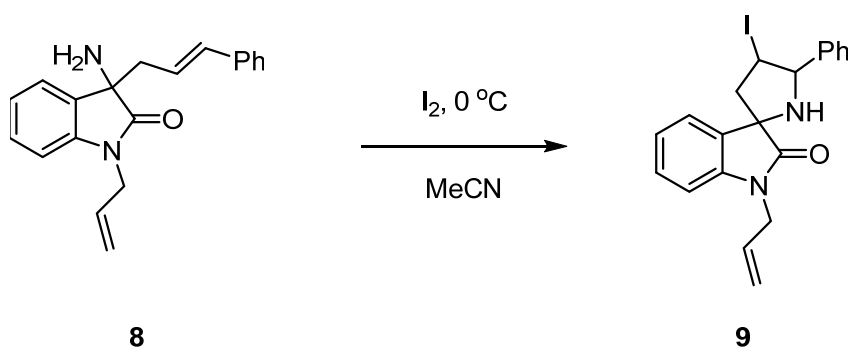
### 3. Synthetic Applications



In a 50 mL round-bottom flask, **5a** (2.0 mmol) and TsOH (0.2 mmol) were dissolved in 20 mL toluene. Equipped with a reflux condenser, a magnetic stirring bar and Dean-Stark trap, the system was heated to reflux for 3 hours.<sup>[1]</sup> After cooling to rt,  $\text{NH}_2\text{OH}\cdot\text{HCl}$  was added. The reaction was stirred for 0.5 h at rt, then solvent was removed by rotary evaporation, **8** were obtained by chromatography on silica gel (PE/EA/ $\text{Et}_3\text{N}$  = 5:1:1) as colorless oil.

#### 1-allyl-3-amino-3-cinnamylindolin-2-one:

Colourless oil; 81% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 (dd,  $J$  = 7.4, 0.8 Hz, 1H), 7.31 – 7.13 (m, 6H), 7.09 (td,  $J$  = 7.6, 0.9 Hz, 1H), 6.80 (d,  $J$  = 7.8 Hz, 1H), 6.37 (d,  $J$  = 15.8 Hz, 1H), 6.02 – 5.83 (m, 1H), 5.71 (ddt,  $J$  = 17.1, 10.4, 5.3 Hz, 1H), 5.22 – 4.97 (m, 2H), 4.43 (ddt,  $J$  = 16.3, 5.0, 1.7 Hz, 1H), 4.13 (ddt,  $J$  = 16.3, 5.4, 1.5 Hz, 1H), 2.77 (ddd,  $J$  = 13.2, 6.5, 1.4 Hz, 1H), 2.66 (ddd,  $J$  = 13.2, 8.6, 0.8 Hz, 1H), 2.10 (brs, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  179.8, 142.4, 137.0, 134.6, 131.4, 131.2, 129.0, 128.4, 127.3, 126.2, 123.9, 122.9, 122.8, 117.6, 109.2, 61.4, 42.9, 42.3. HRMS Calcd. For  $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}$  ( $[\text{M}+\text{Na}]^+$ ): 327.1468, found: 327.1463.

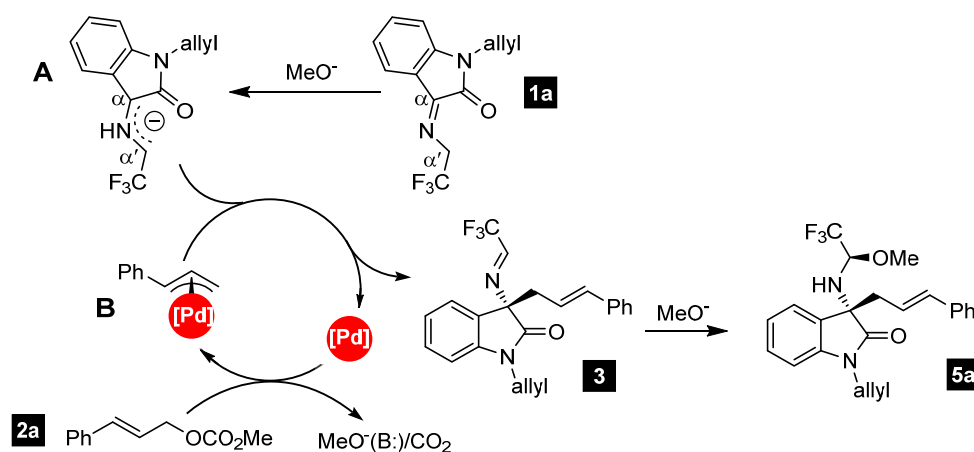


**8** (0.2 mmol), I<sub>2</sub> (0.4 mmol) and CH<sub>3</sub>CN (1 mL) were added to a 5-mL vial equipped with stirring bar. The mixture was stirred at 0 °C for 4 h, and TLC showed that **8** was disappeared. The mixture was stirred for 10 min before quenched by addition of CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and saturated Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (5 mL), and the aqueous layer was extracted with additional portions of CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were combined, concentrated, purified by flash chromatography on silica gel (PE/EA = 5:1) to give the inseparable products **9**.

#### 1-allyl-4'-iodo-5'-phenylspiro[indoline-3,2'-pyrrolidin]-2-one:

Colourless oil; 81% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.70 – 7.61 (m, 1H), 7.60 – 7.53 (m, 1H), 7.50 – 7.26 (m, 5H), 7.17 – 7.07 (m, 1H), 6.83 (dd, *J* = 7.7, 3.9 Hz, 1H), 5.92 – 5.74 (m, 1H), 5.31 – 5.17 (m, 2H), 4.97<sub>major</sub> (d, *J* = 10.0 Hz, 0.6H), 4.71<sub>minor</sub> (d, *J* = 10.0 Hz, 0.4H), 4.66 – 4.16 (m, 3H), 2.90 (ddd, *J* = 14.9, 13.2, 8.8 Hz, 1H), 2.77 – 2.62 (m, 1H), 2.39 (brs, 1H). Major: <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) 179.53, 142.21, 138.94, 133.63, 131.23, 129.05, 128.57, 128.39, 127.44, 123.27, 123.08, 117.81, 109.31, 72.12, 66.96, 49.65, 42.54, 26.39. Minor: <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 179.59, 142.21, 138.98, 132.83, 131.17, 129.09, 128.75, 128.45, 127.83, 123.46, 123.22, 117.83, 109.25, 74.17, 67.85, 50.53, 42.54, 26.59. HRMS Calcd. For C<sub>20</sub>H<sub>20</sub>IN<sub>2</sub>O ([M+Na]<sup>+</sup>): 431.0615, found: 431.0607.

#### 4. Proposed mechanism for cascade umpolung allylation/acetalation



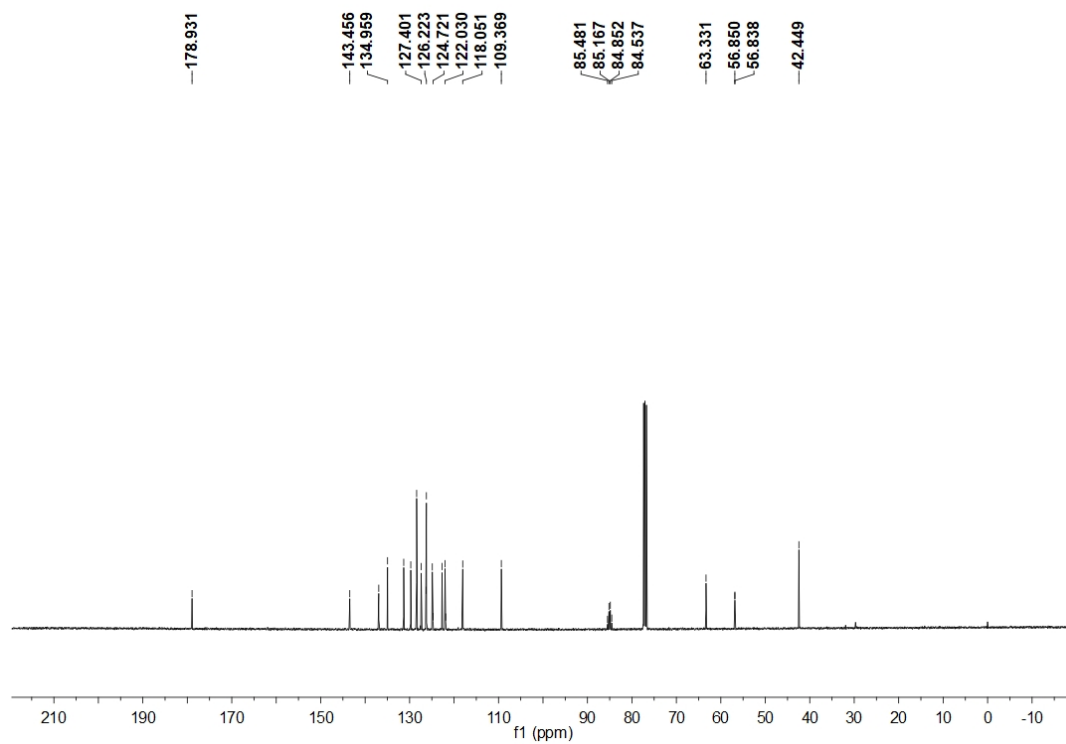
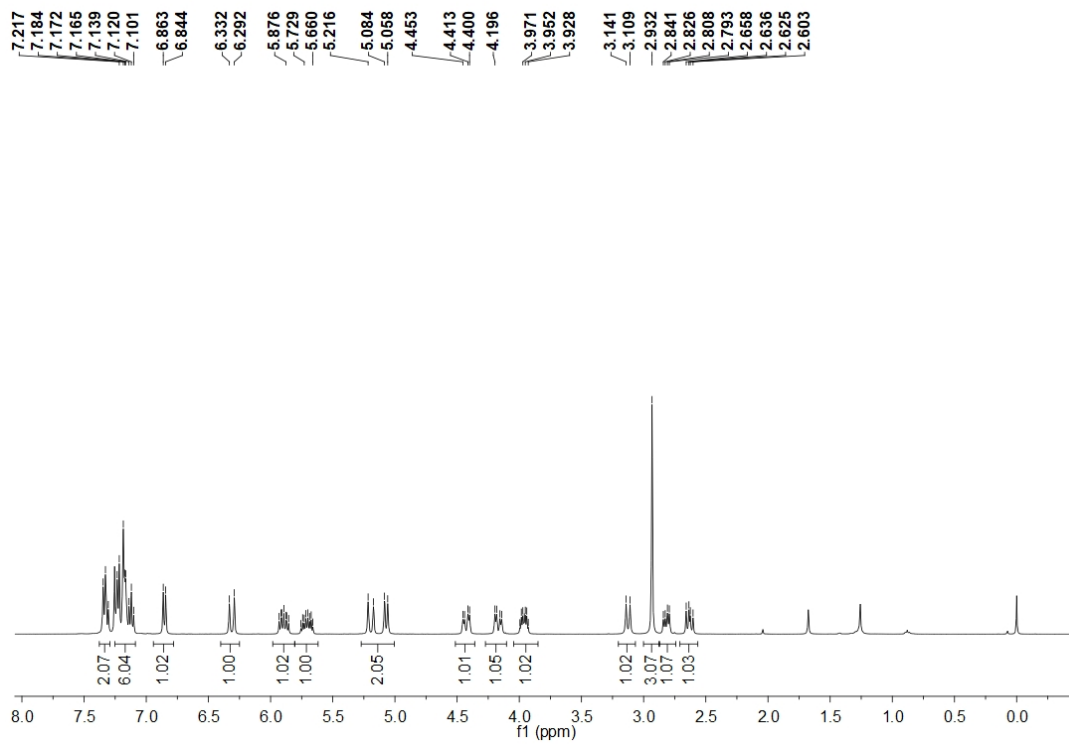
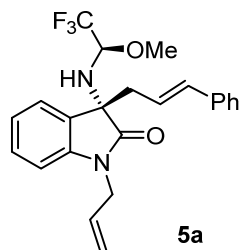
**Scheme S1.** Proposed Mechanism for cascade umpolung allylation/Acetalation

Under basic condition, *N*-2,2,2-trifluoroethylisatin ketimine **1a** is deprotonated to form 2-azaallyl carbanion **A**. Coordination of allylic carbonate **2a** to Pd(0) followed by oxidative addition-decarboxylation gives Pd- $\pi$ -Allyl species (**B**). The nucleophilic attack of 2-azaallyl carbanion **A** to electrophilic  $\pi$ -allyl Pd (**B**) generates the allylation product **3** and completes the catalytic cycles. Then, the imine moiety of **3** is attacked by methoxide to form the final product **5a**.

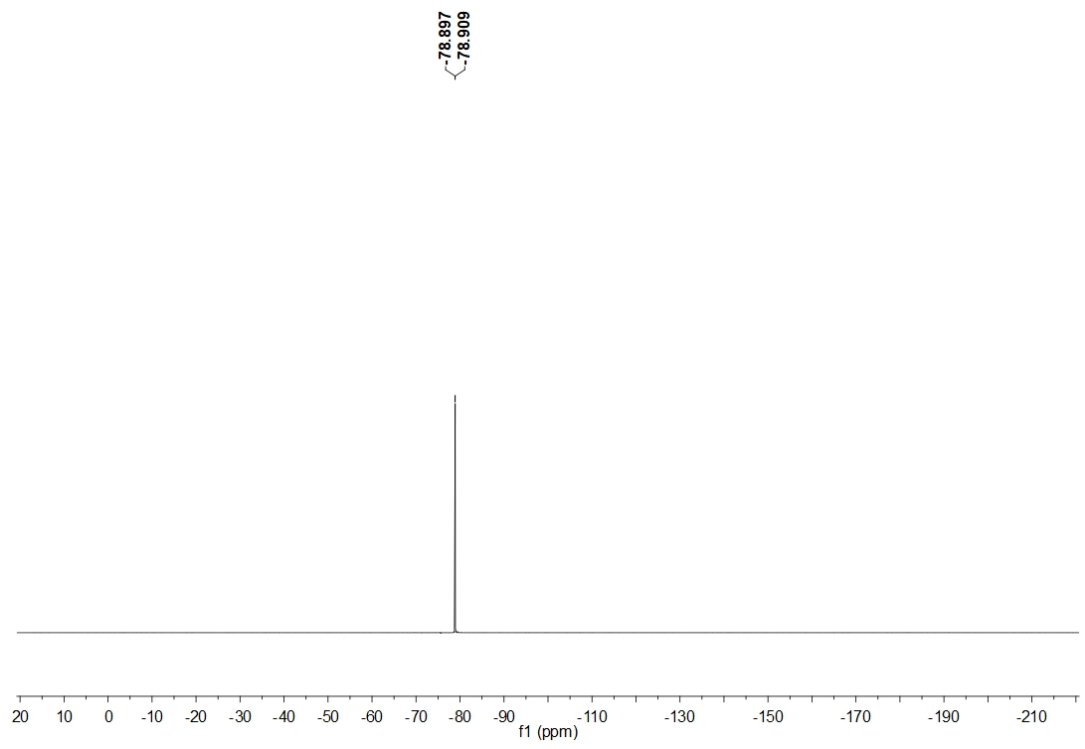
## 5. References

[1] H. Mimura, K. Kawada, T. Yamashita, T. Sakamoto, Y. Kikugawa, *J. Fluorine Chem.* **2010**, *131*, 477-486.

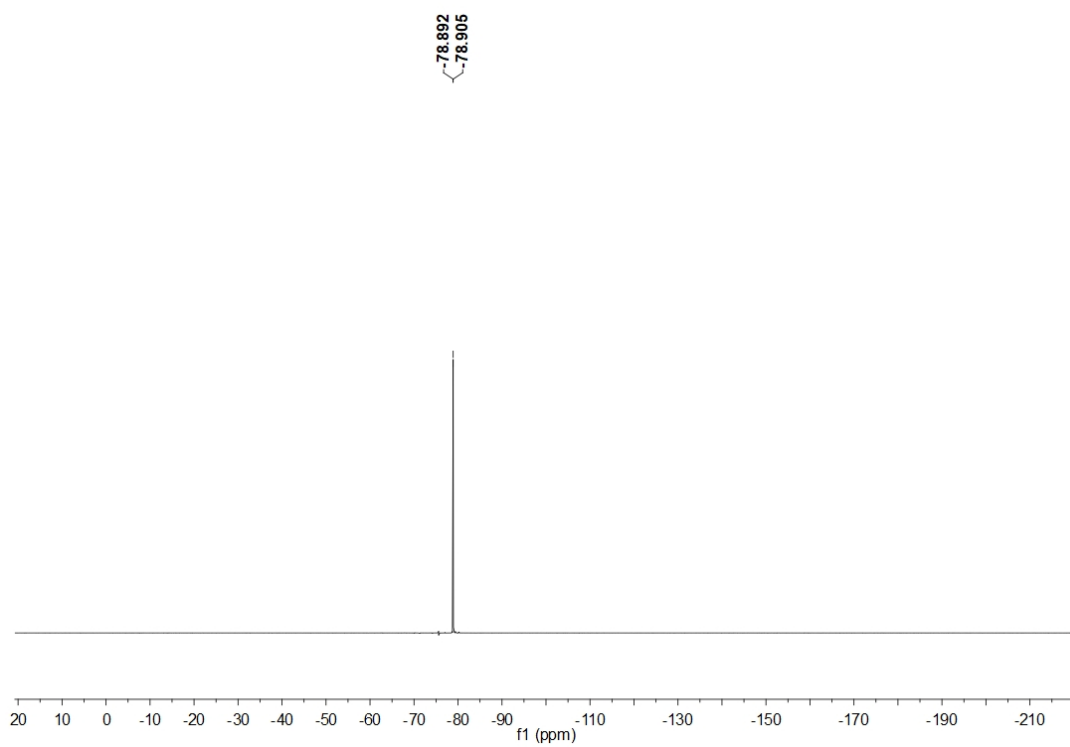
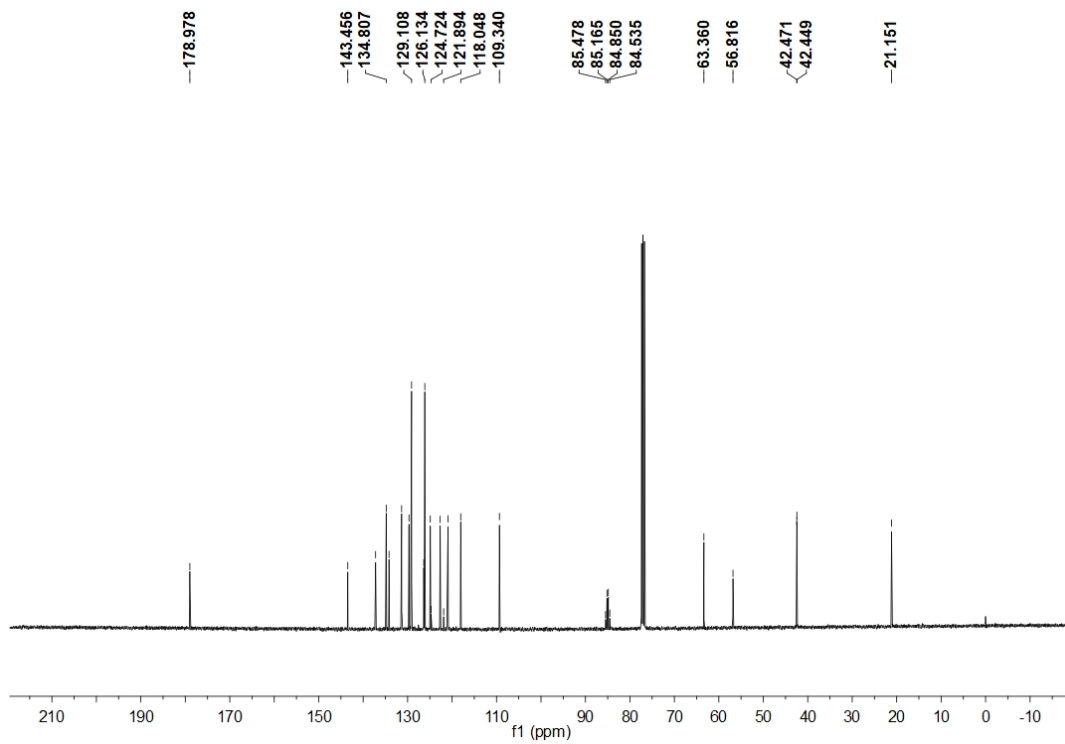
## 6. NMR spectra

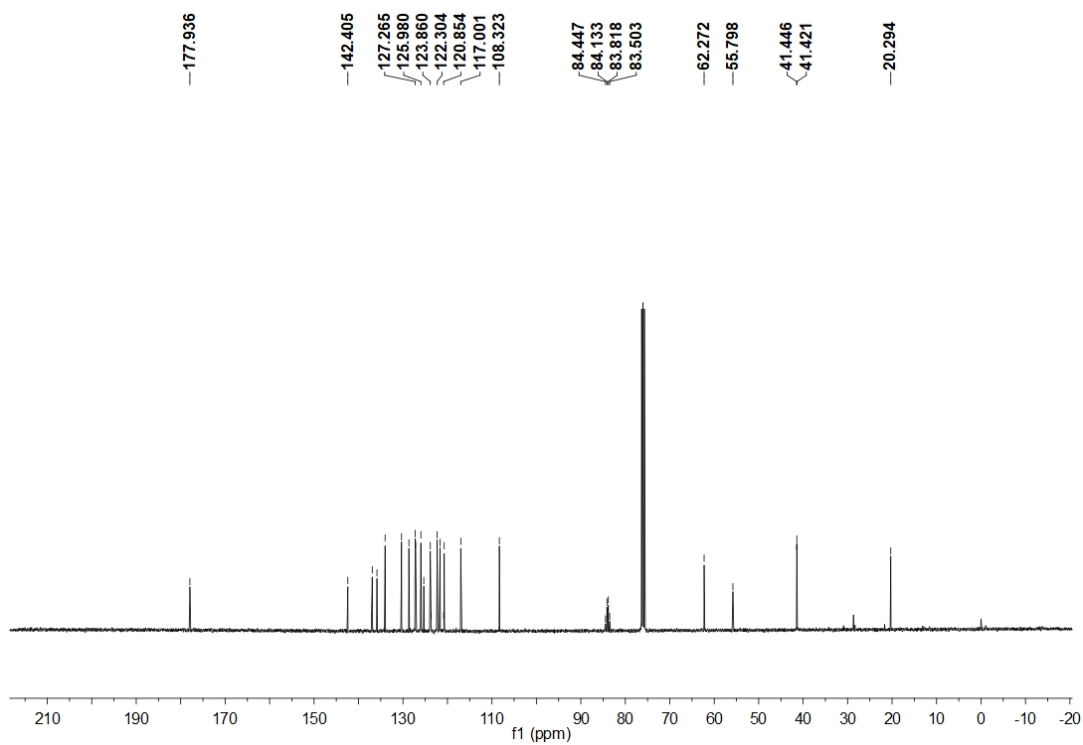
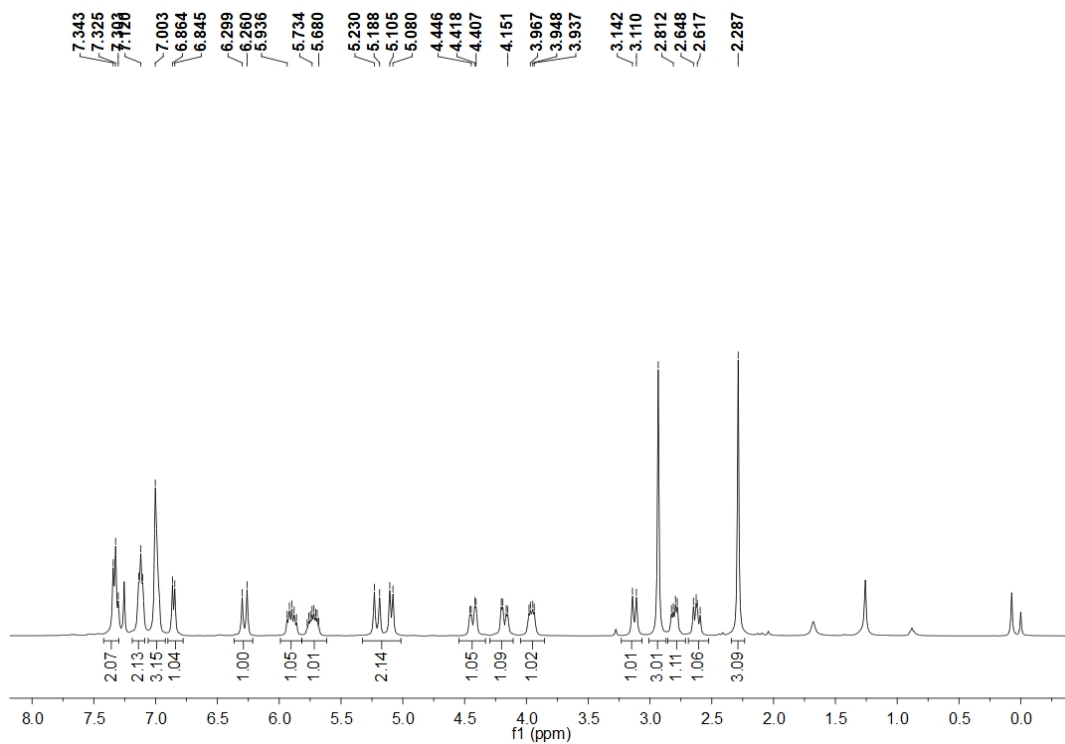
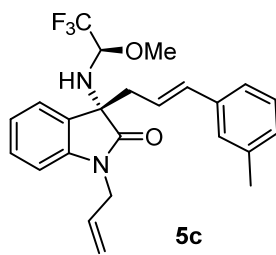


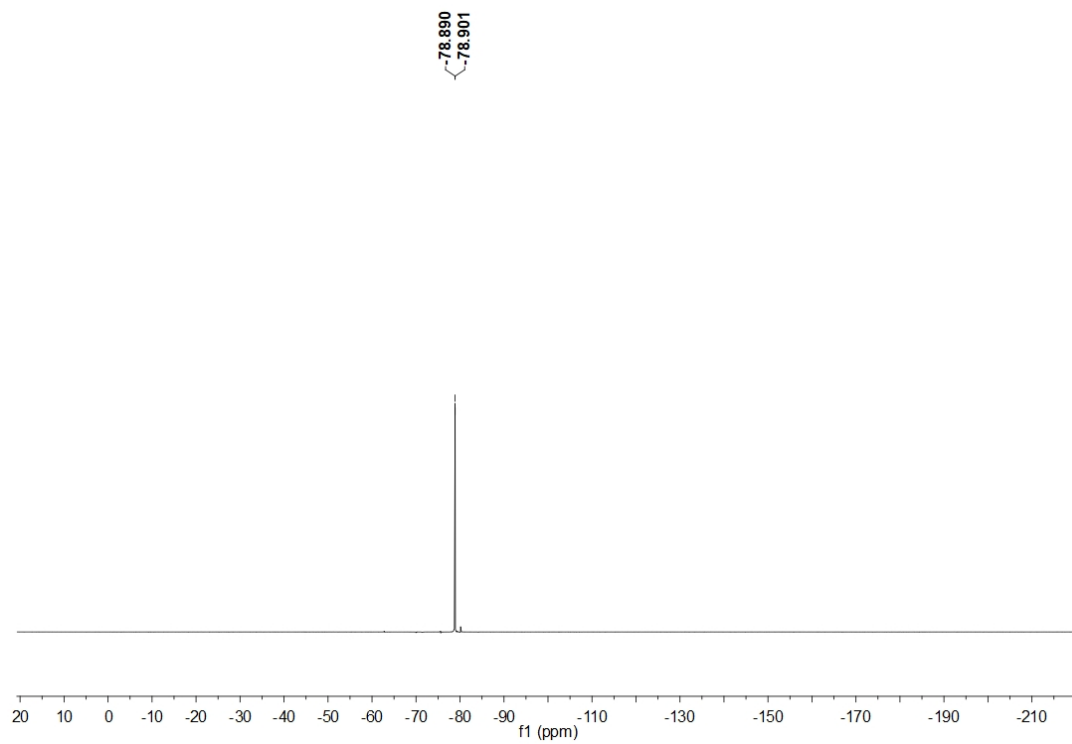


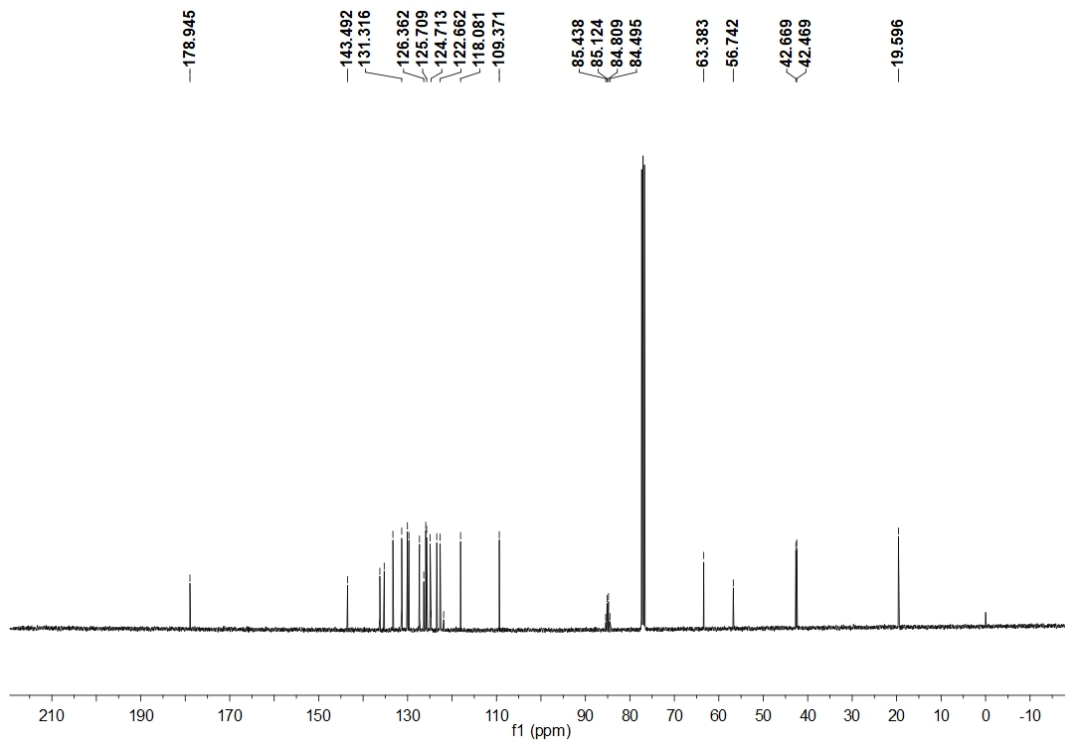
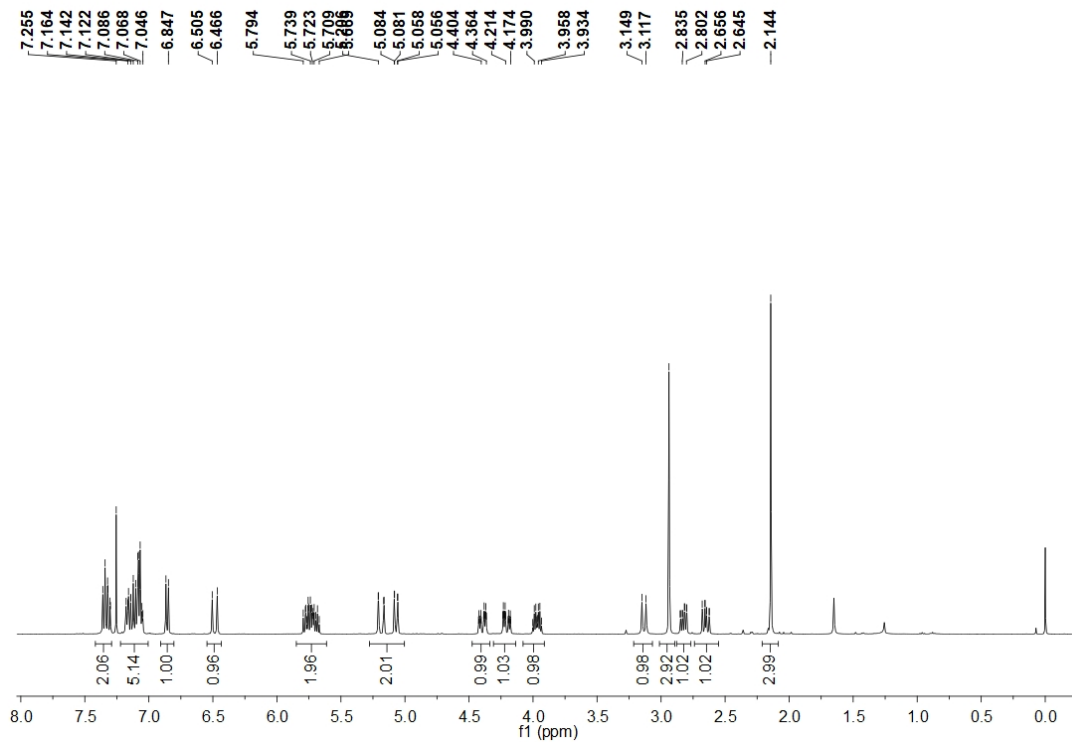
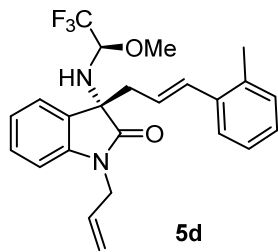


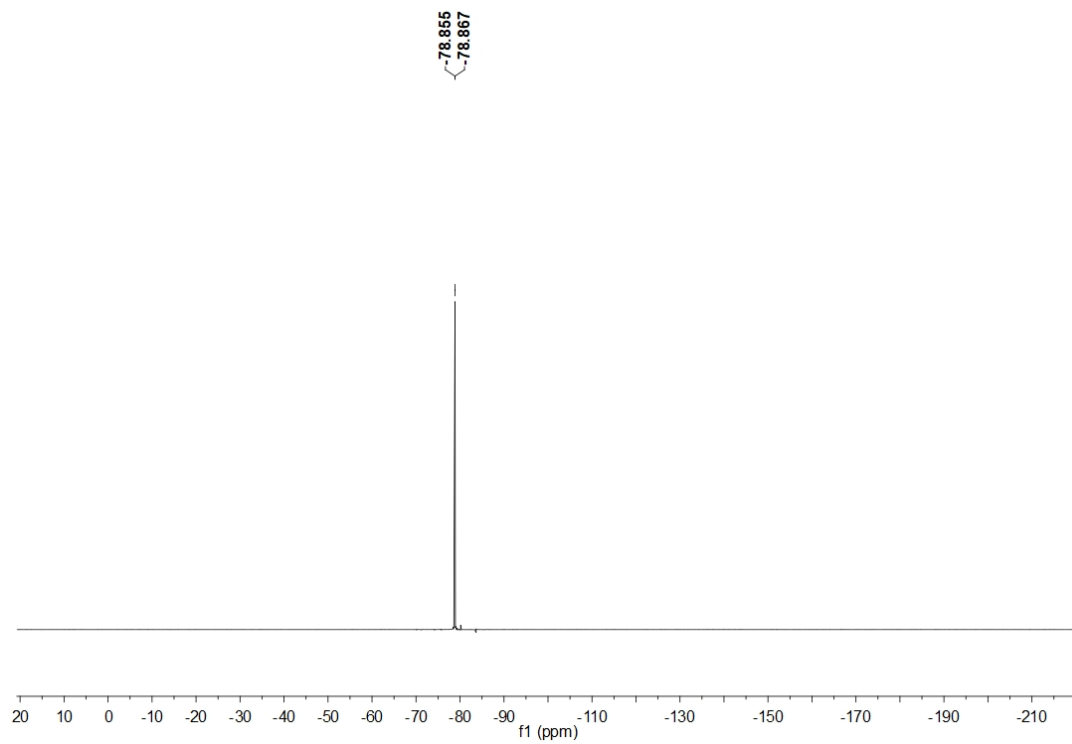


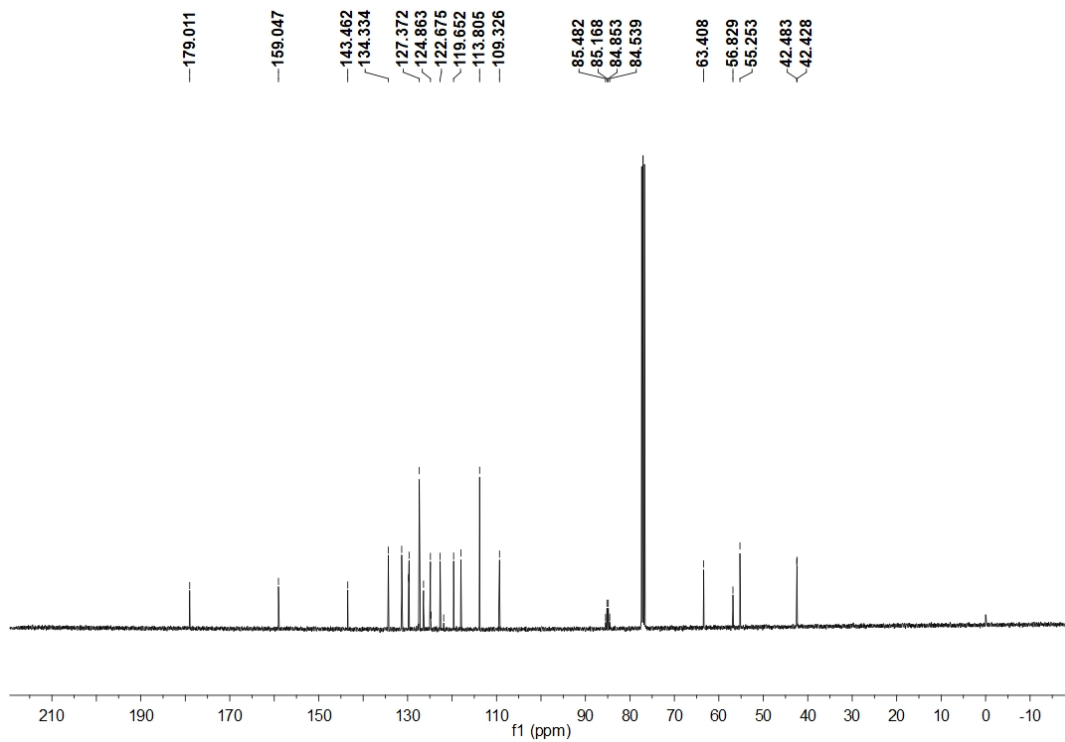
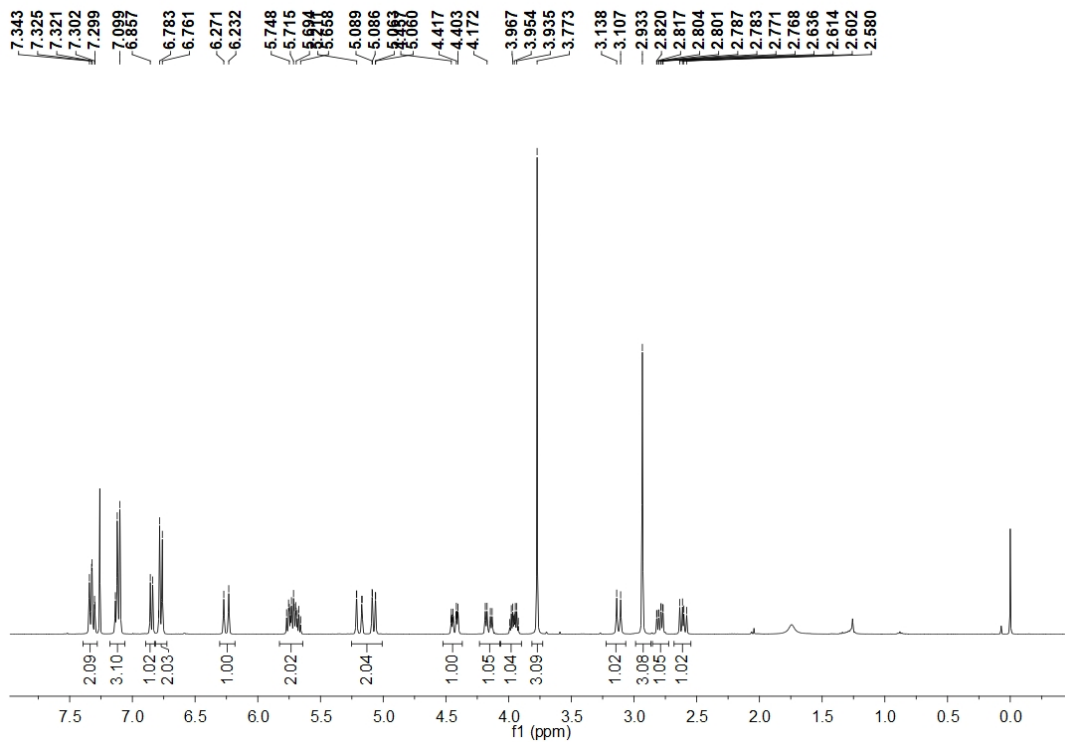
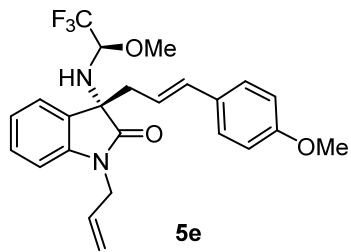




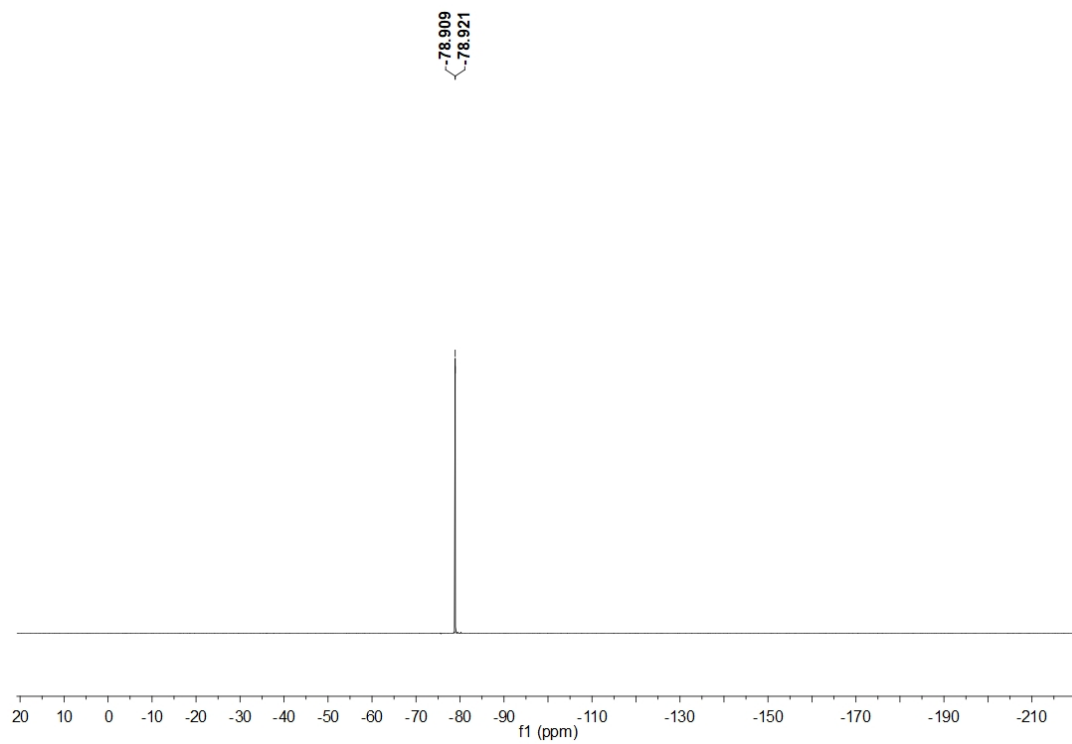


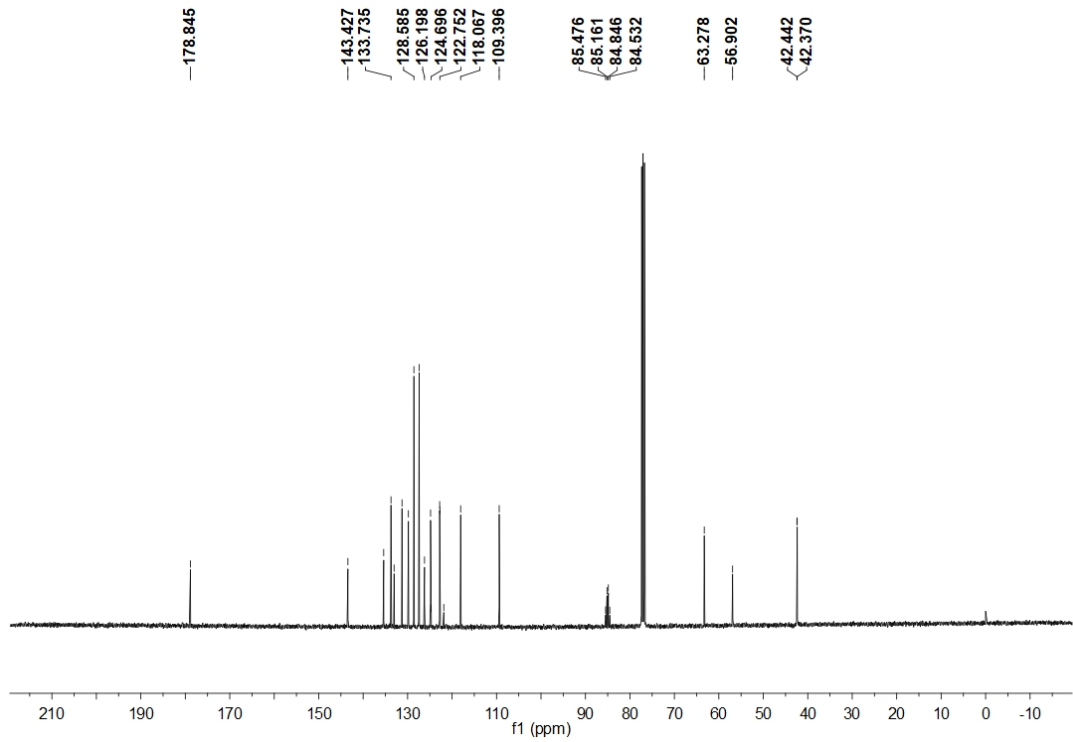
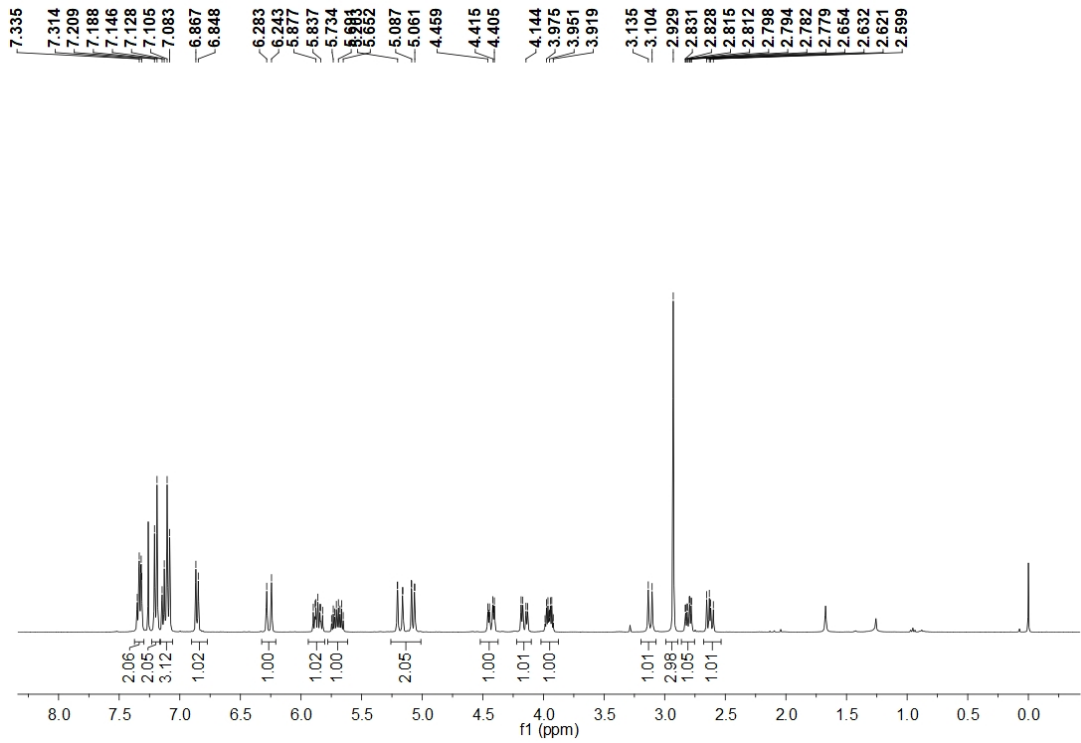
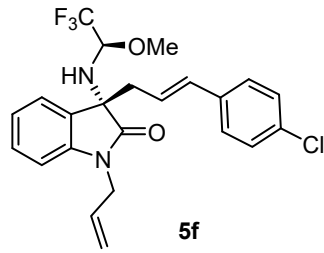


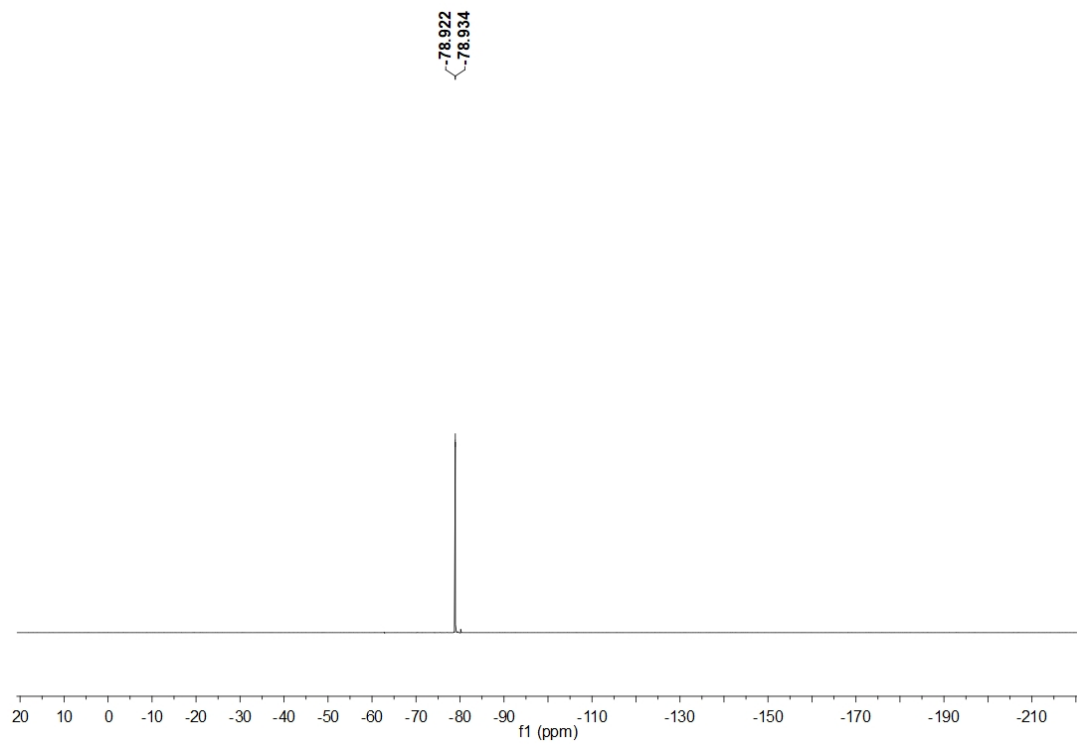


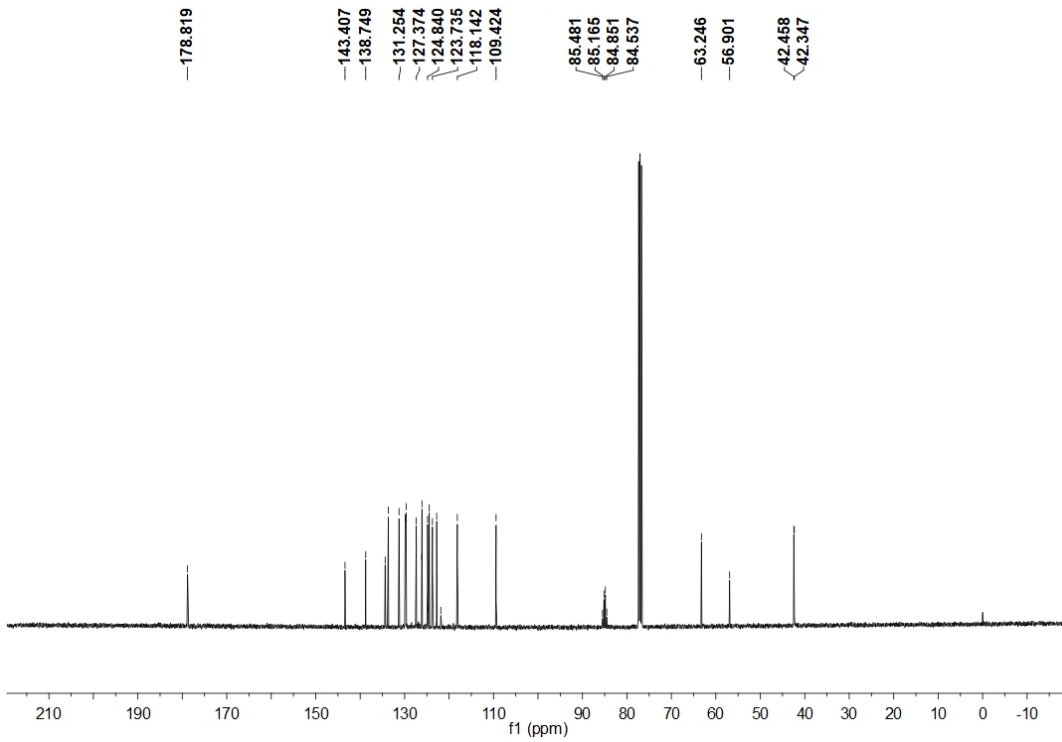
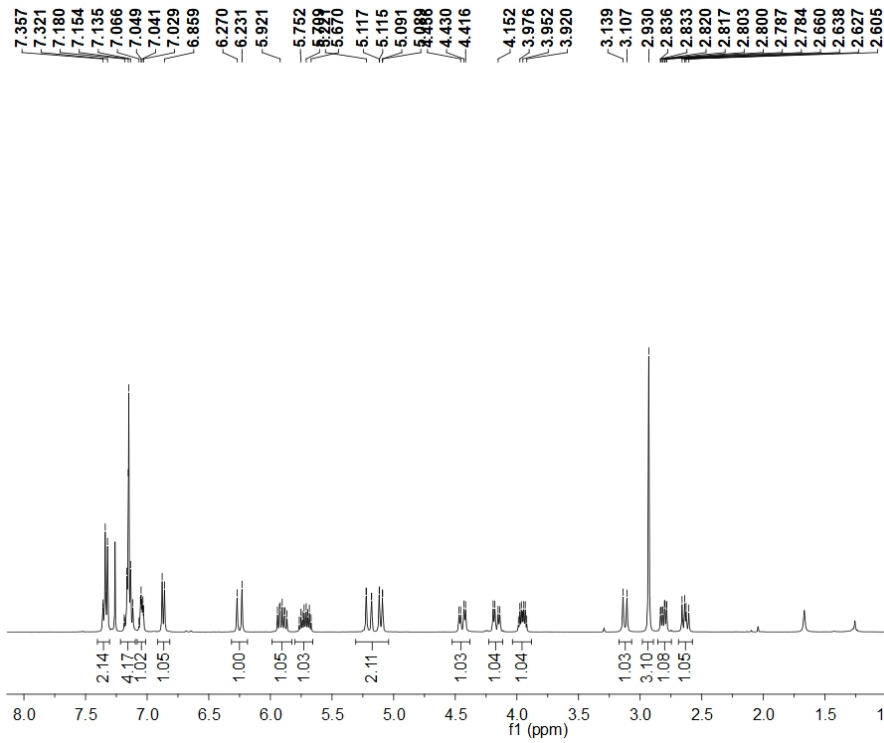
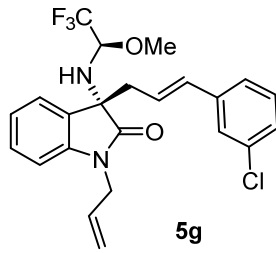


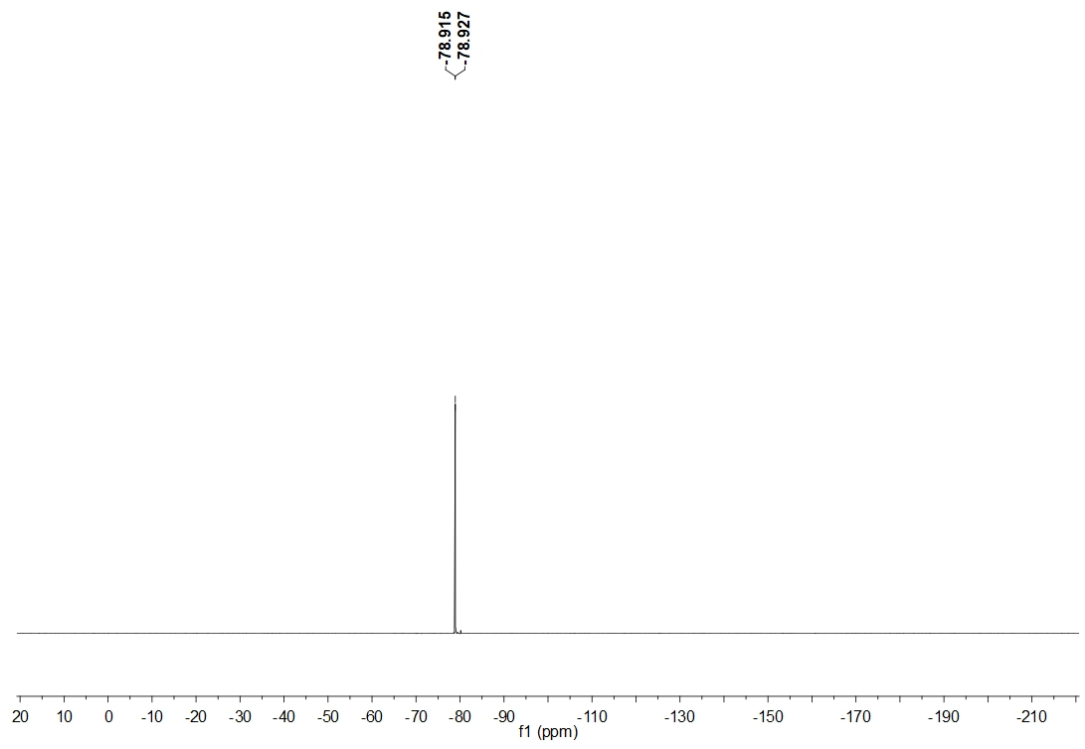


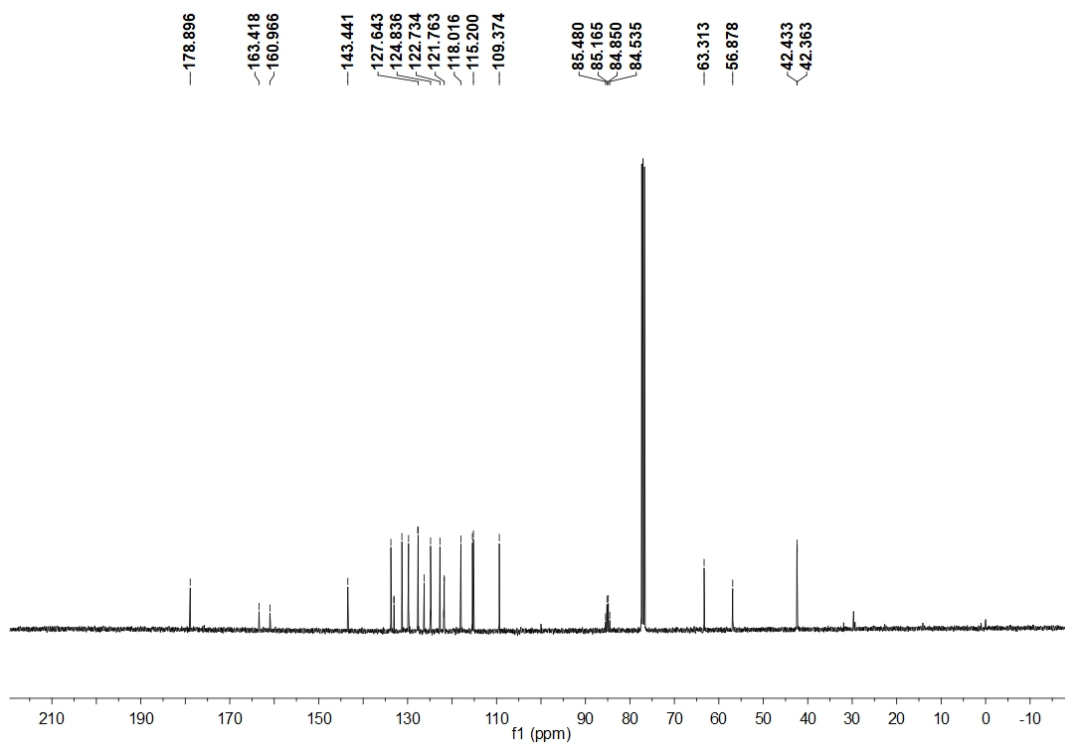
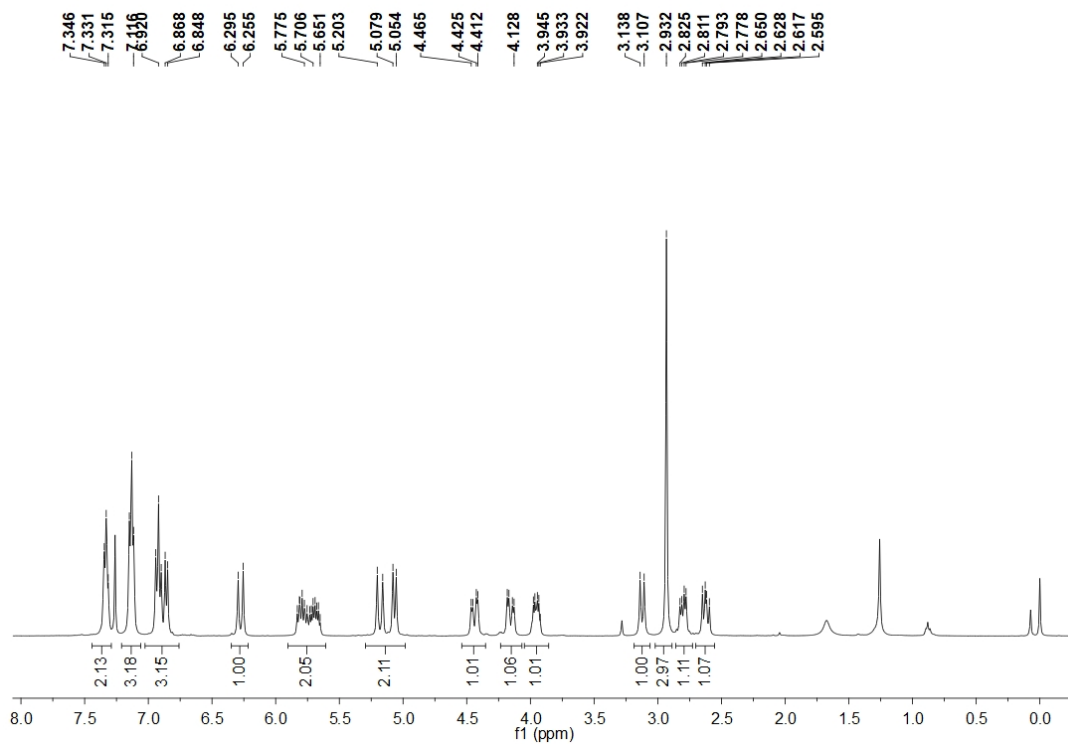
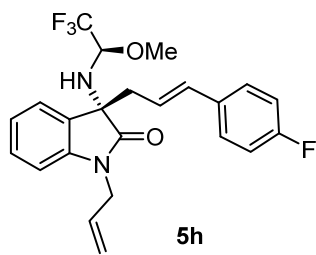


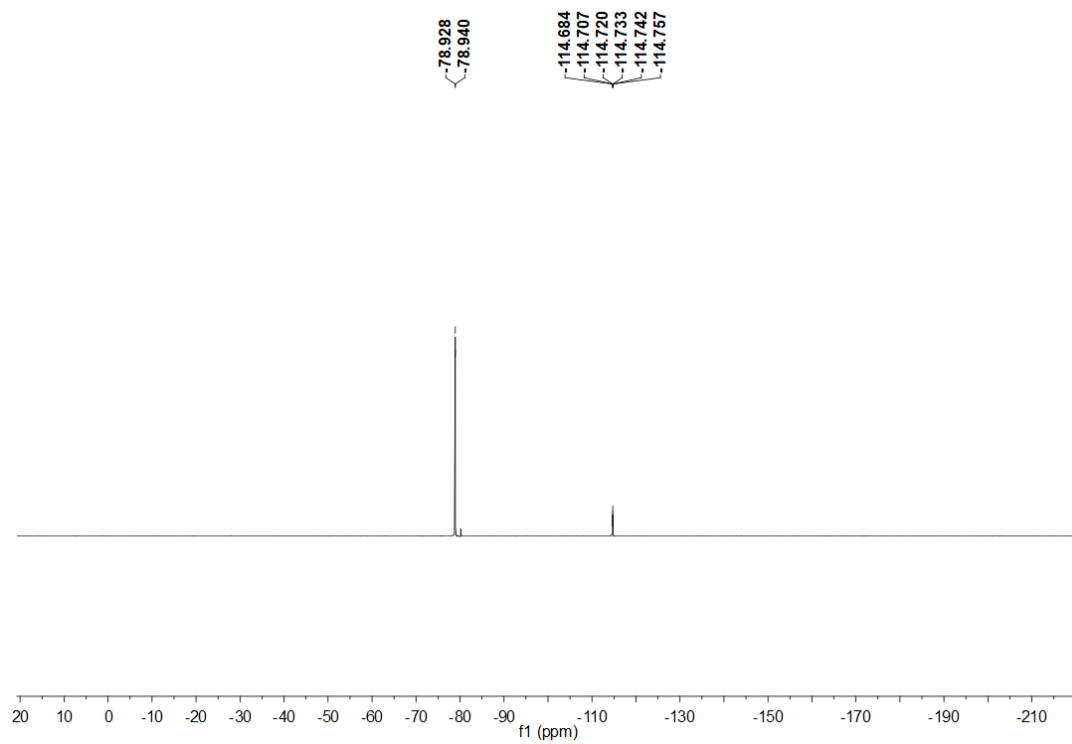


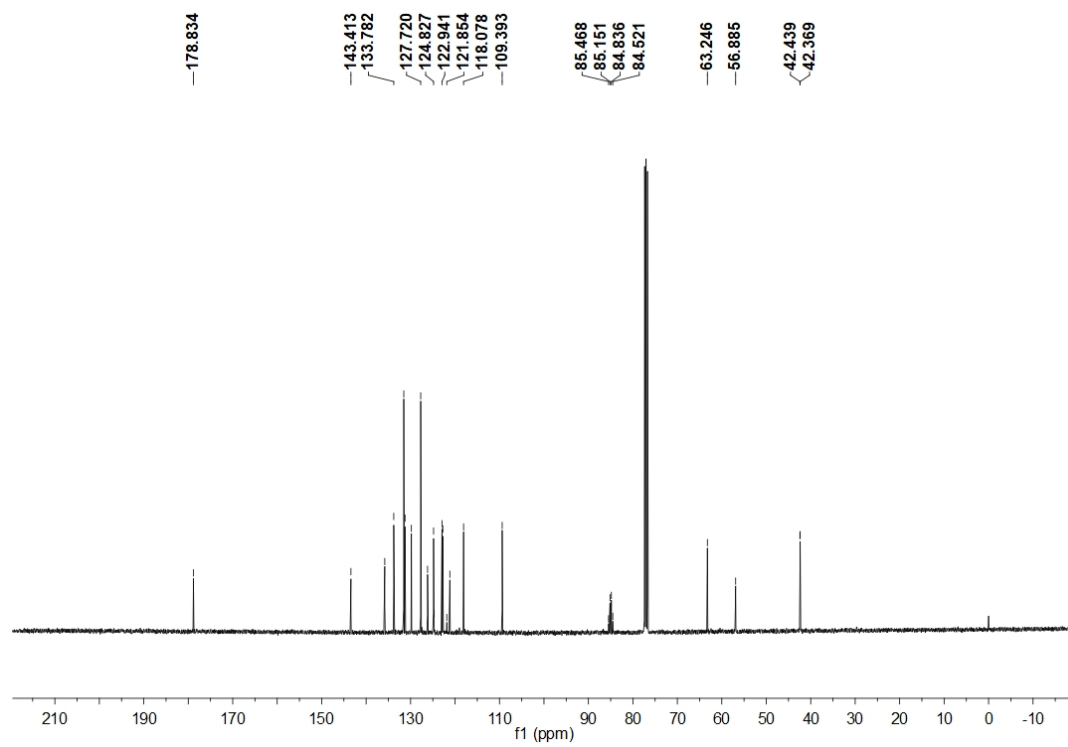
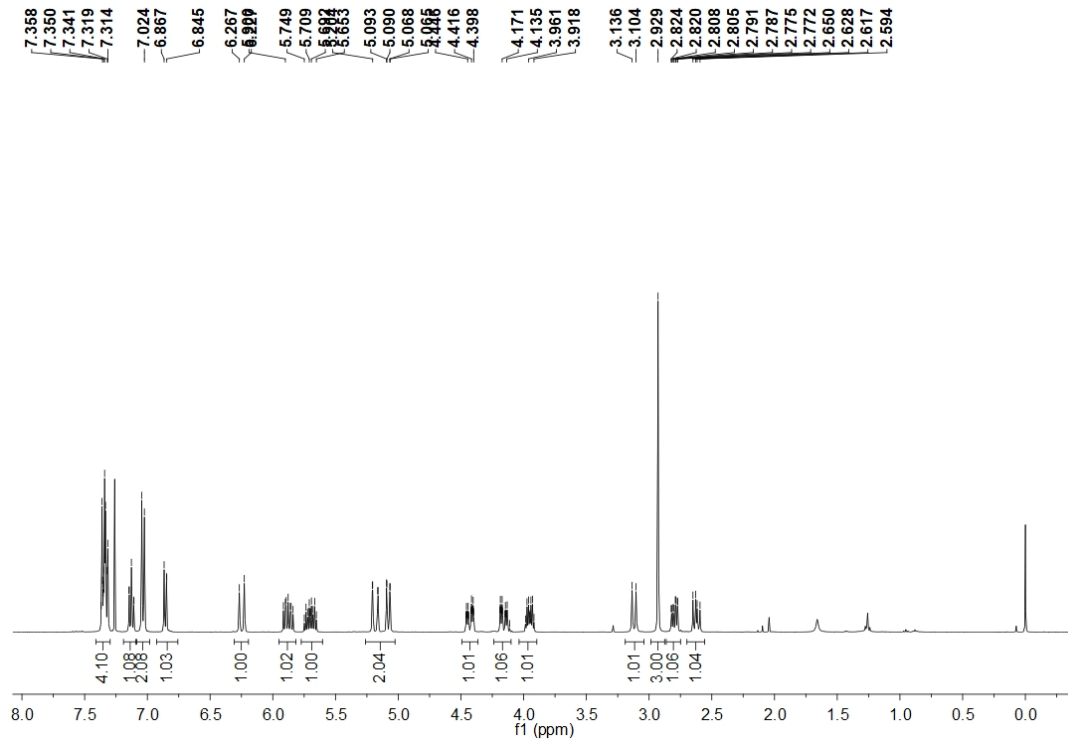
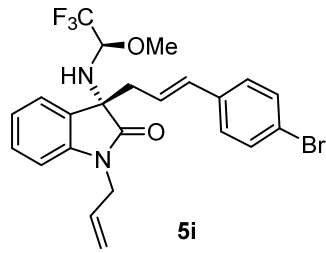




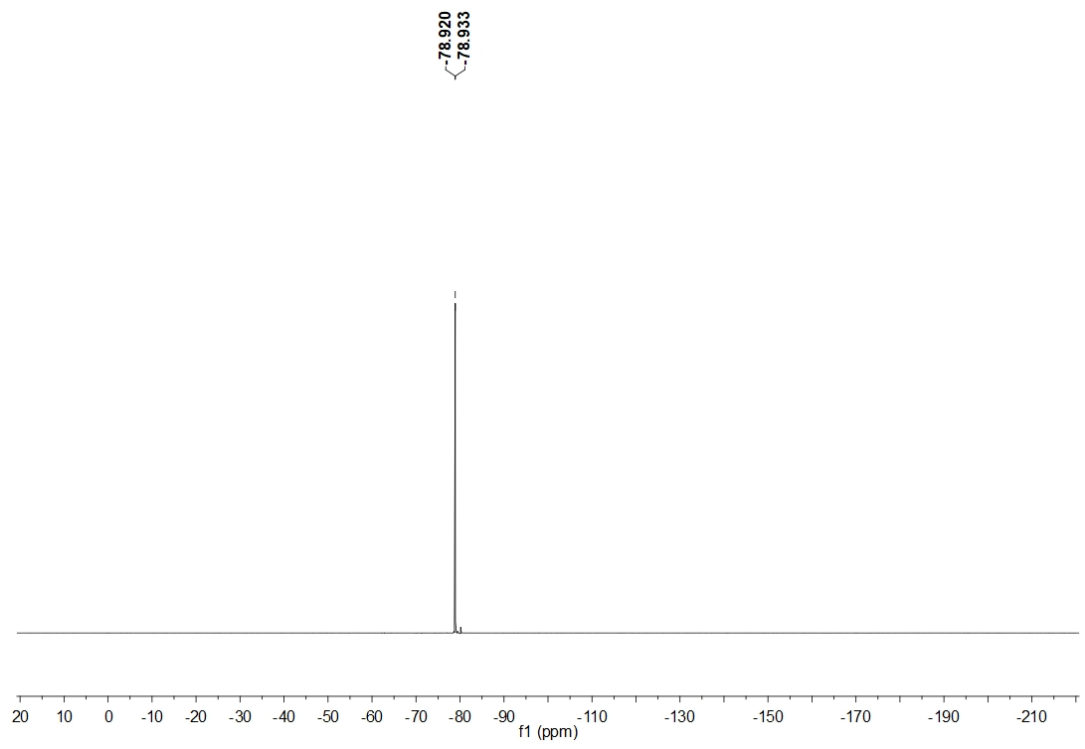


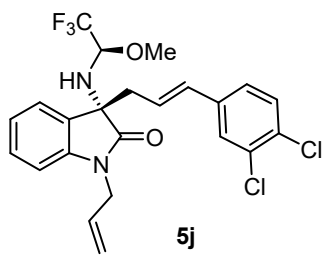




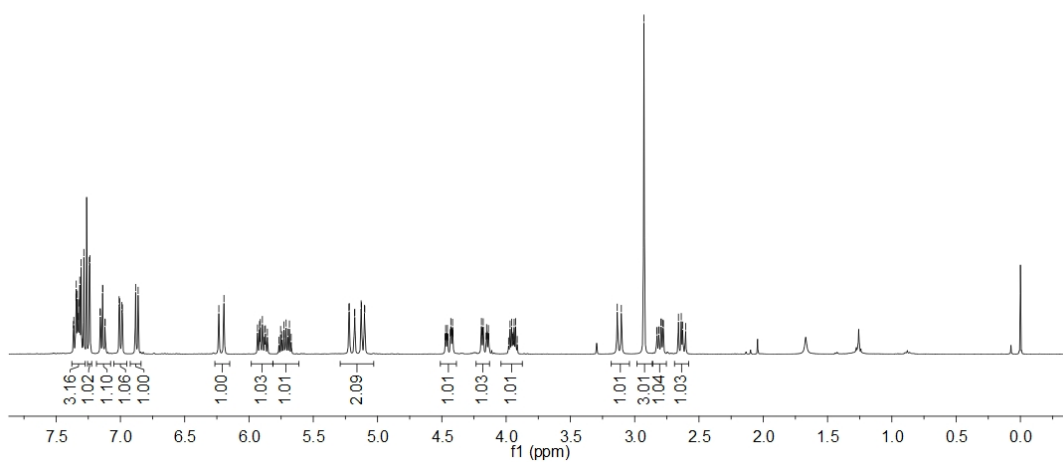




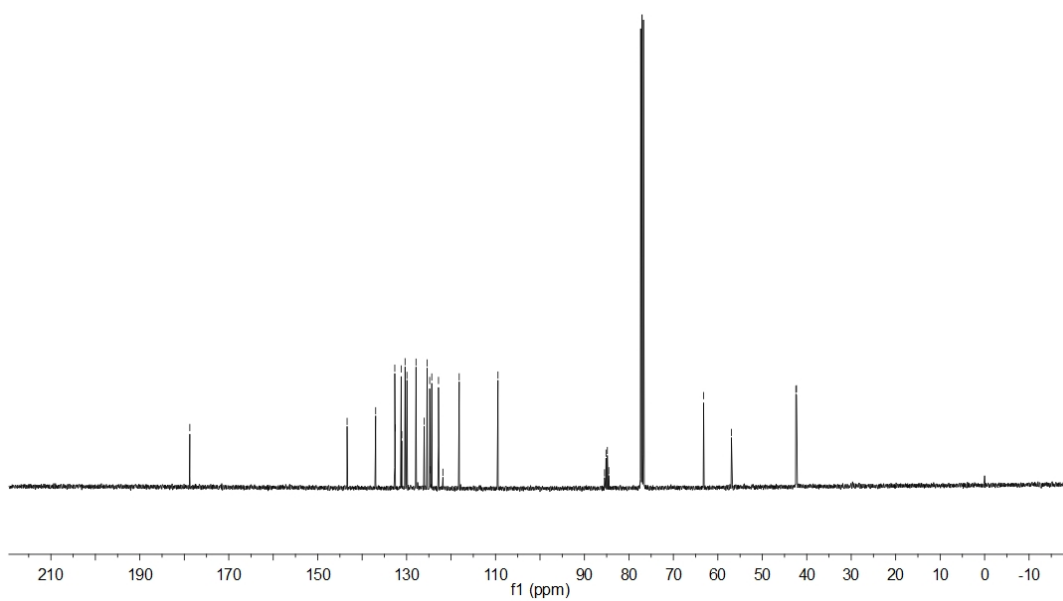


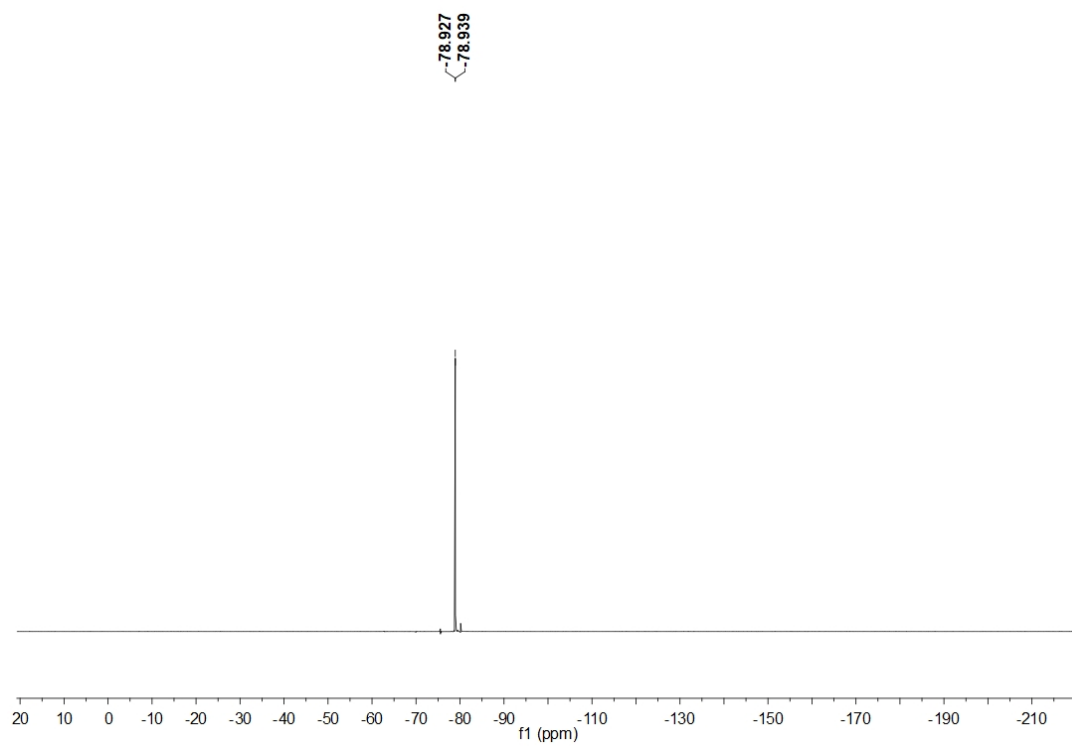


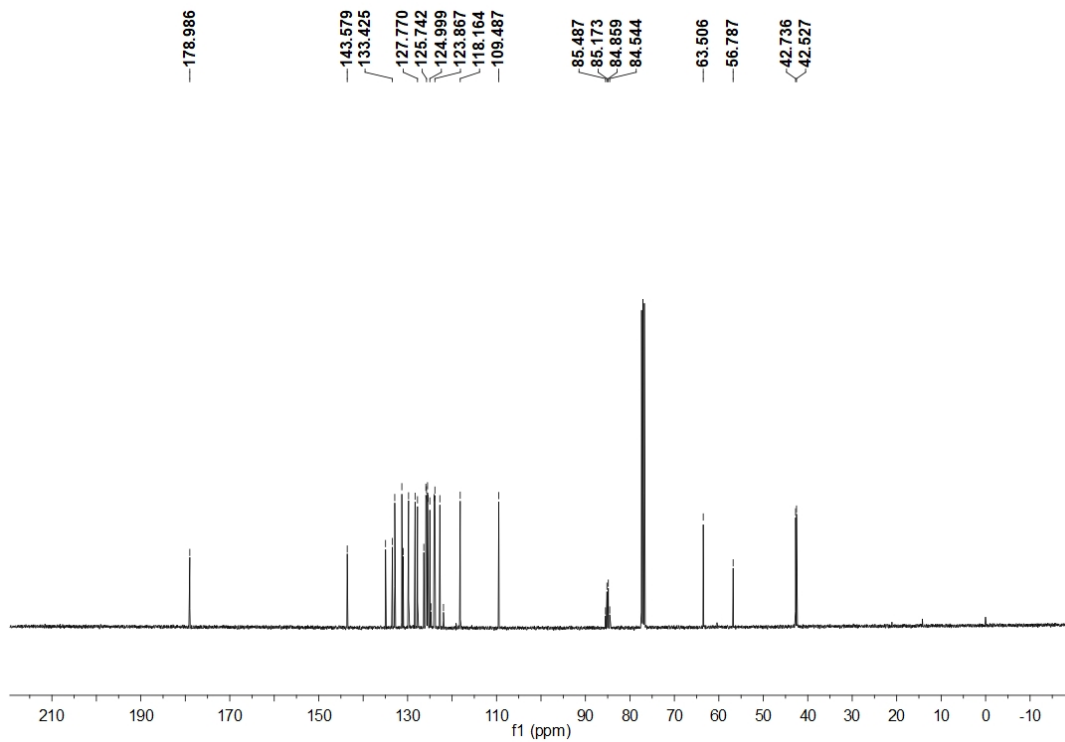
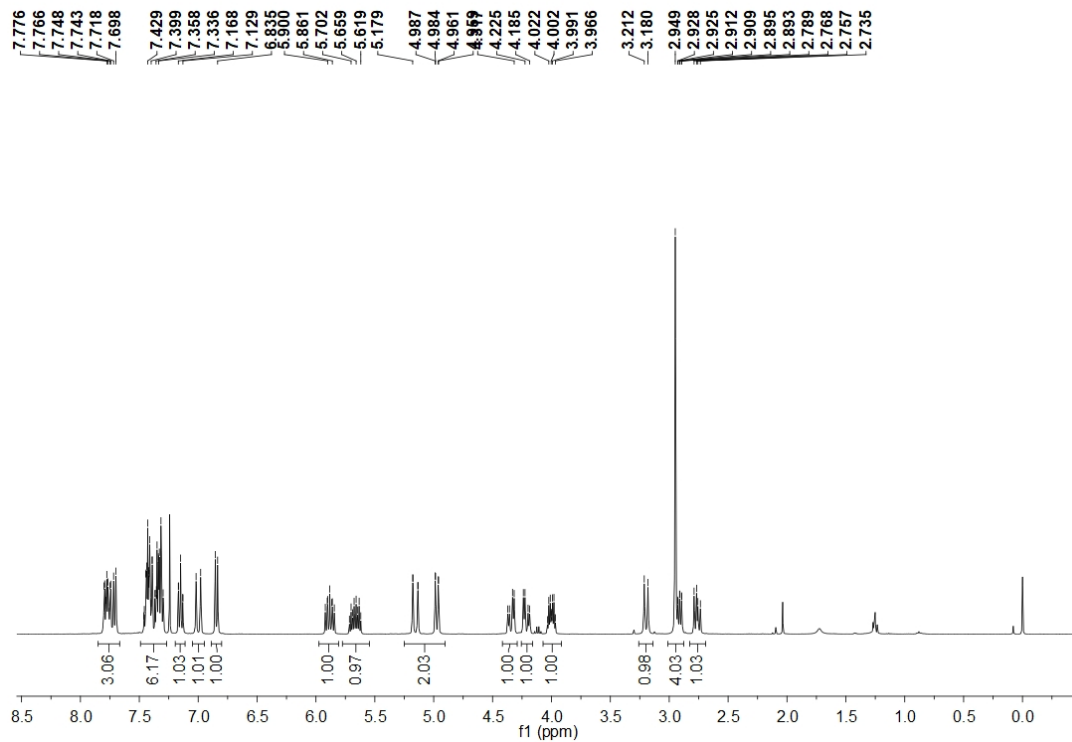
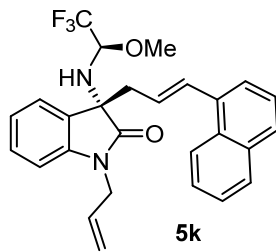
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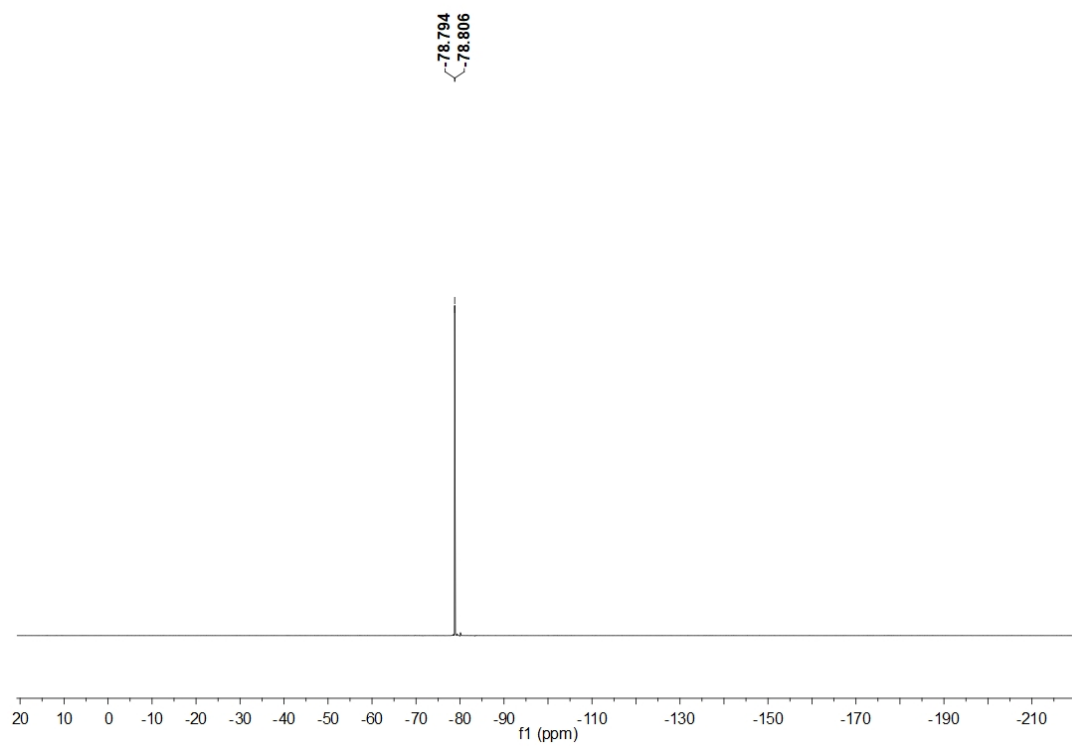


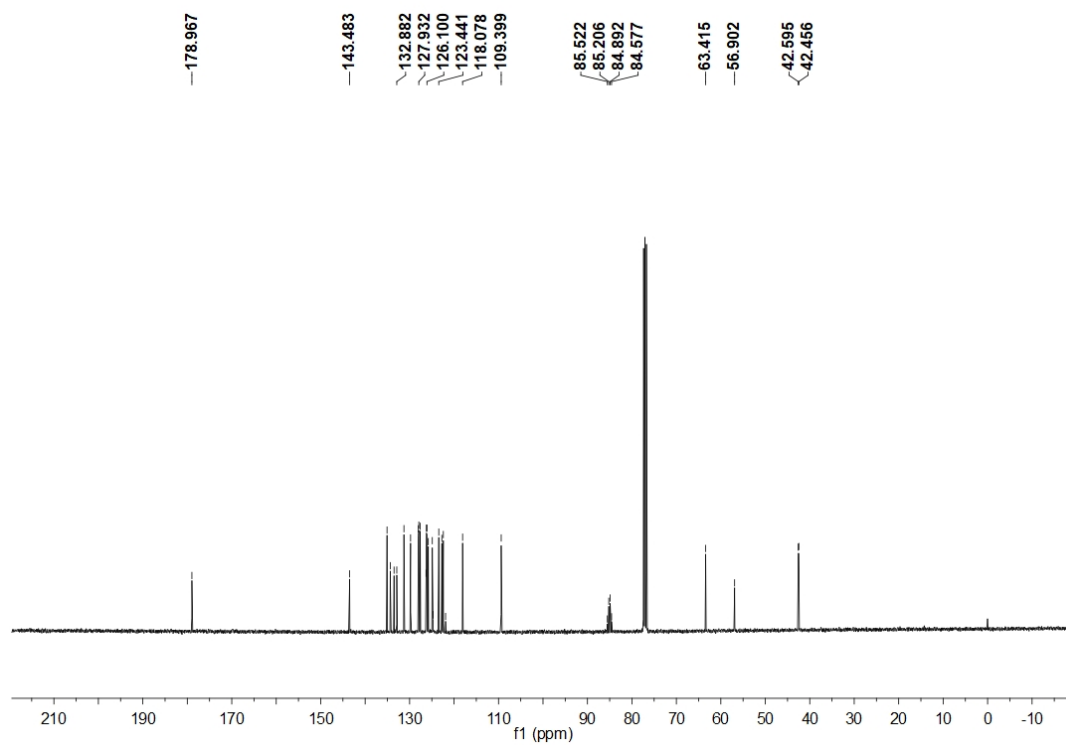
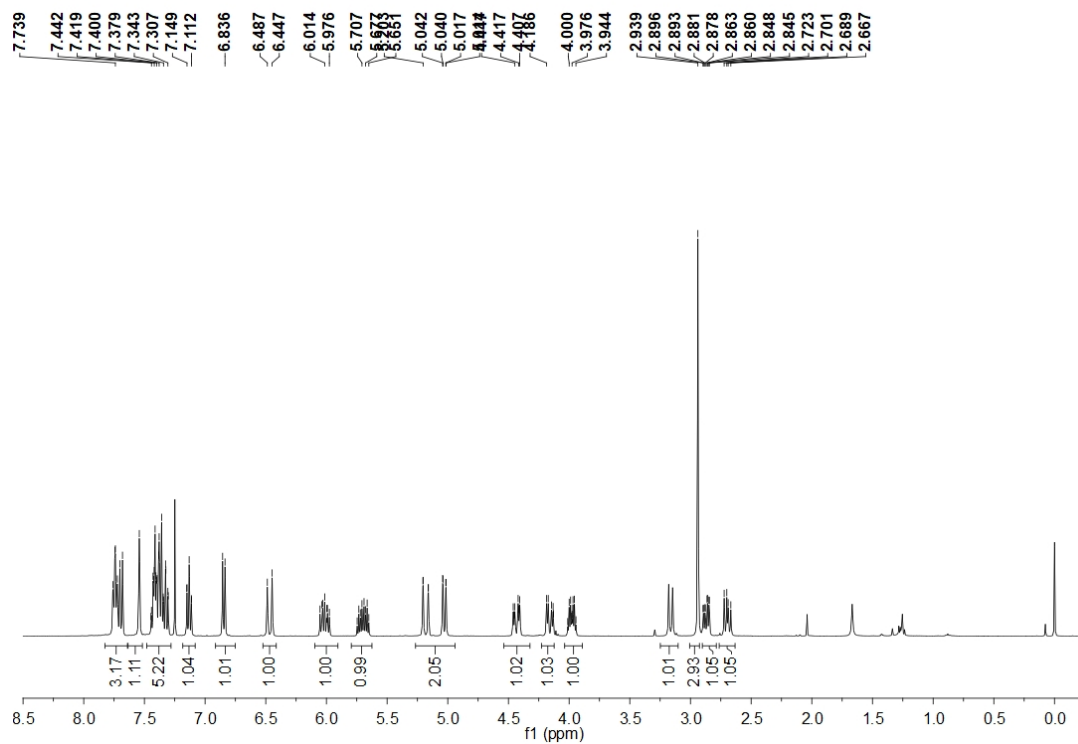
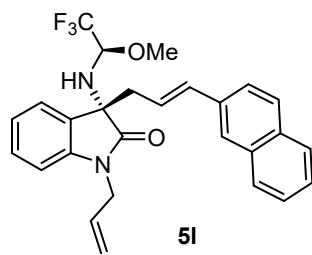
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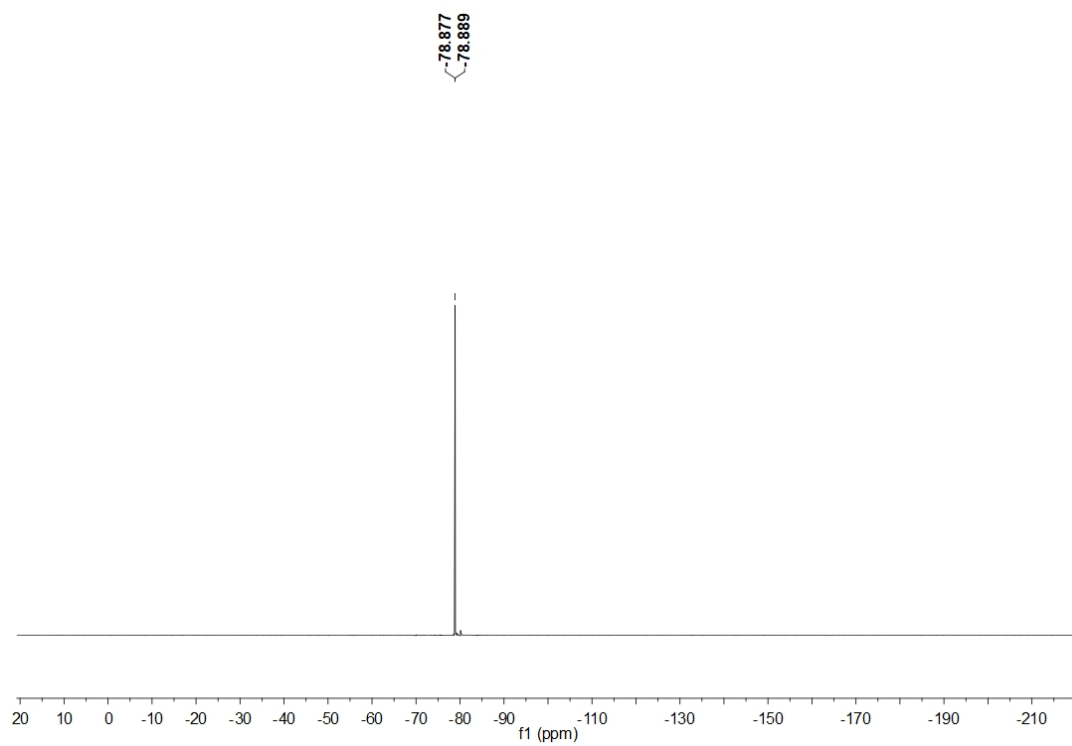


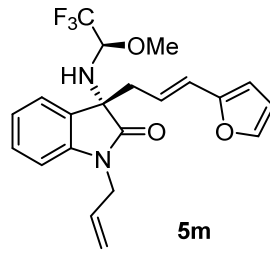




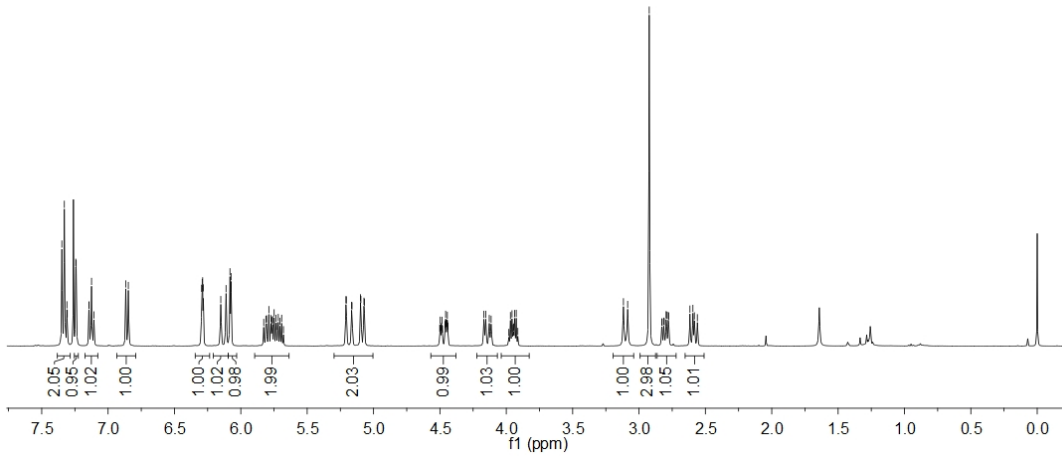




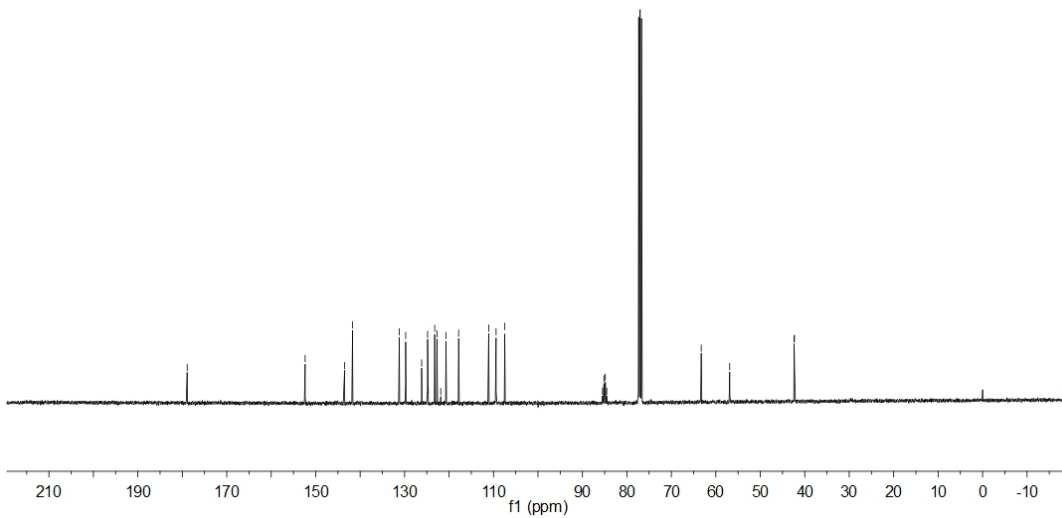




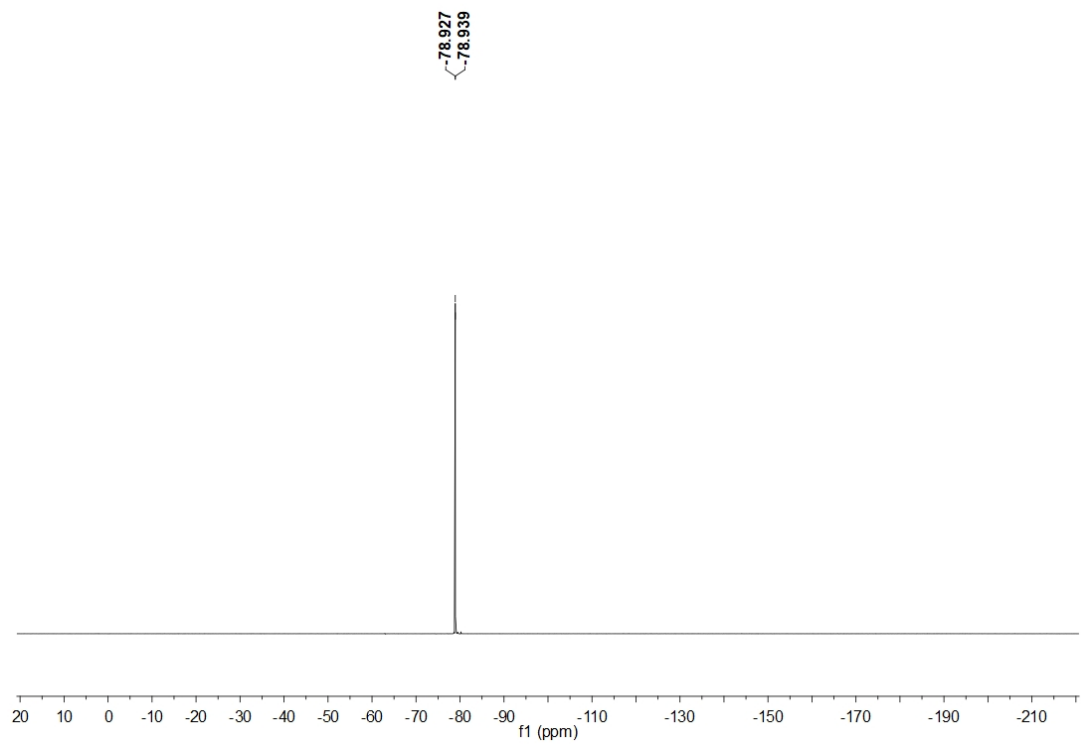
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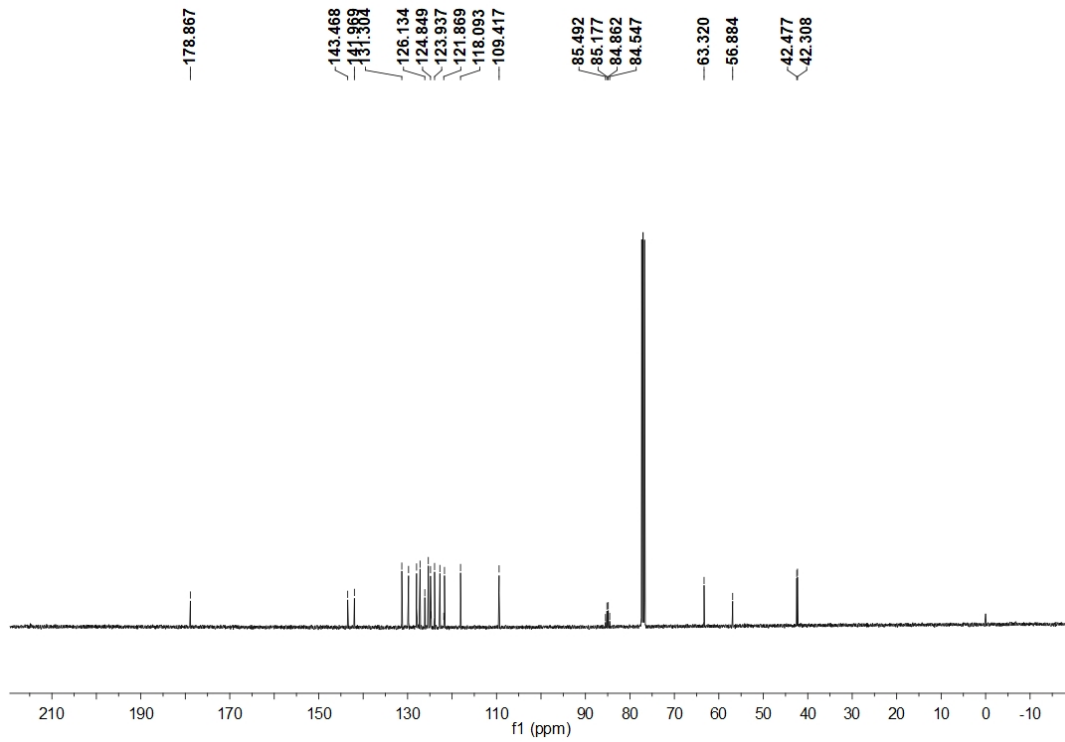
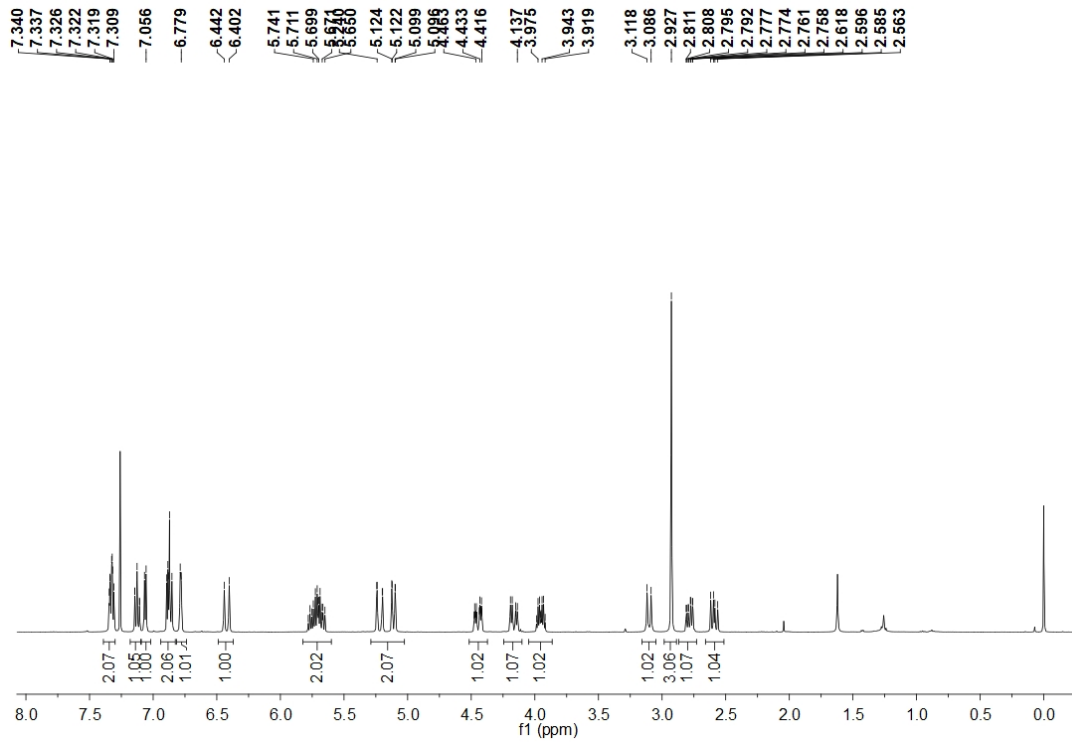
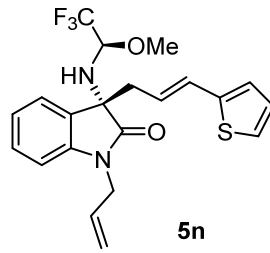


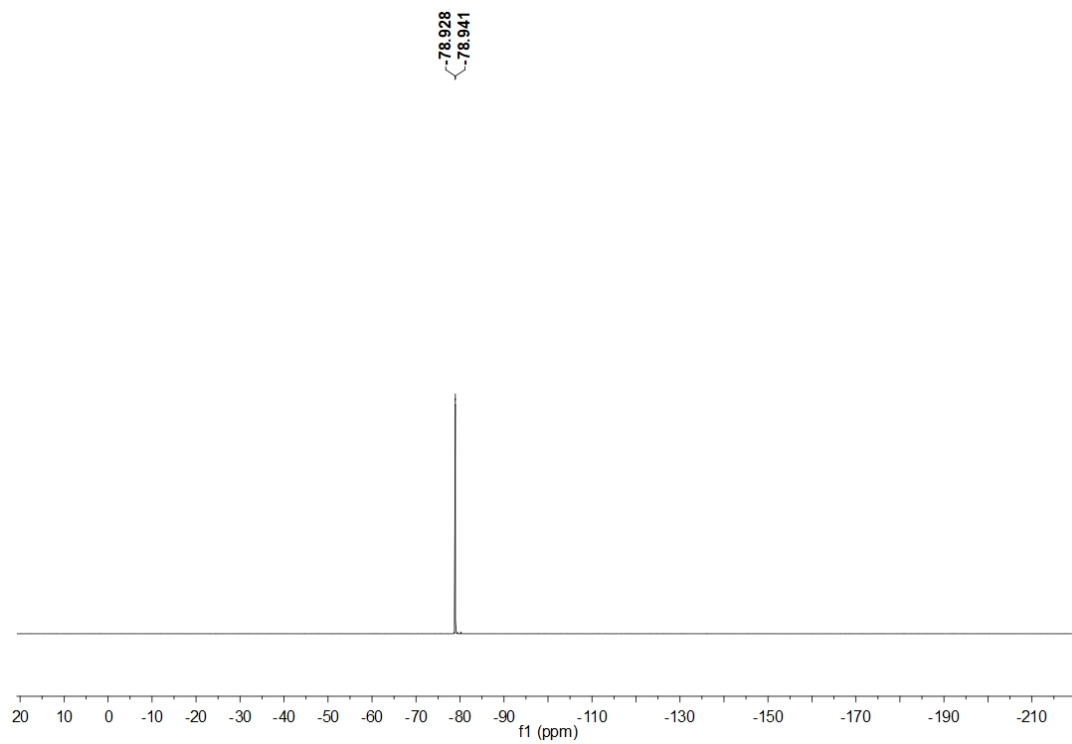
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121.874  
117.841  
111.080  
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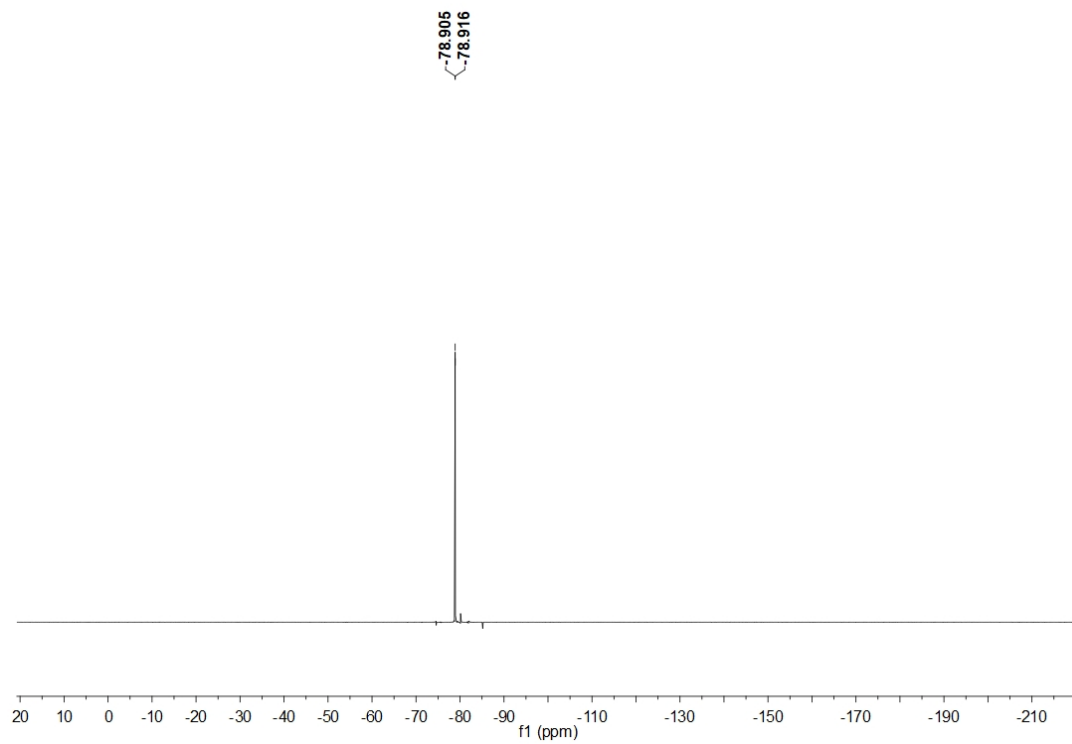




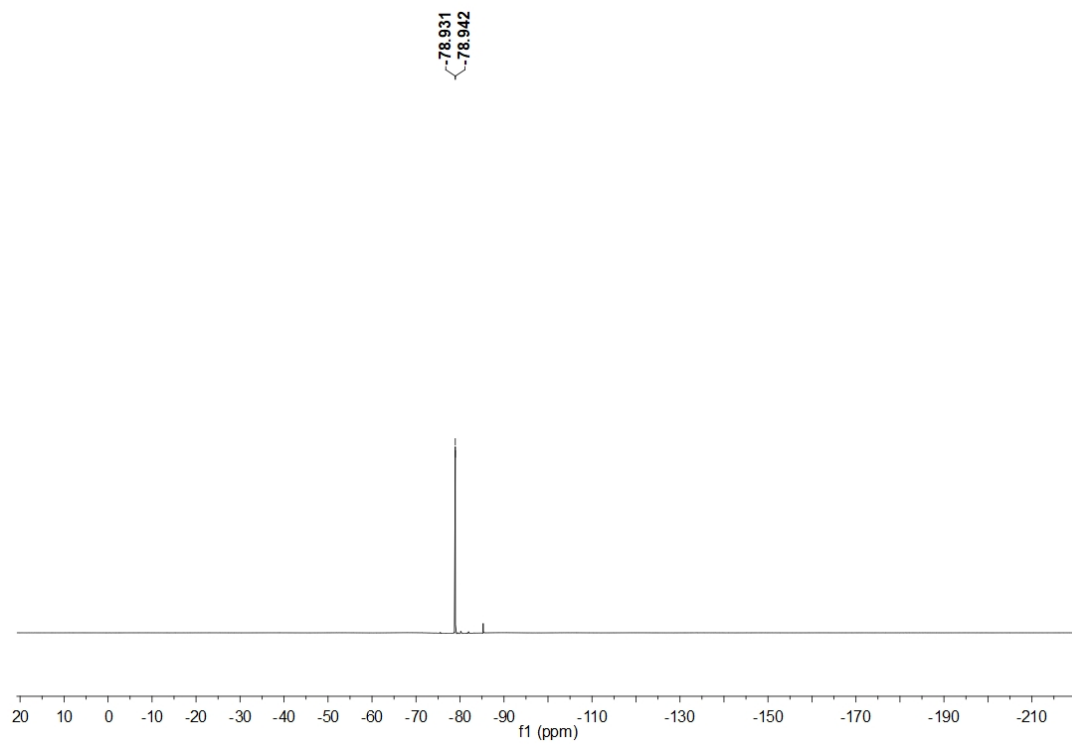


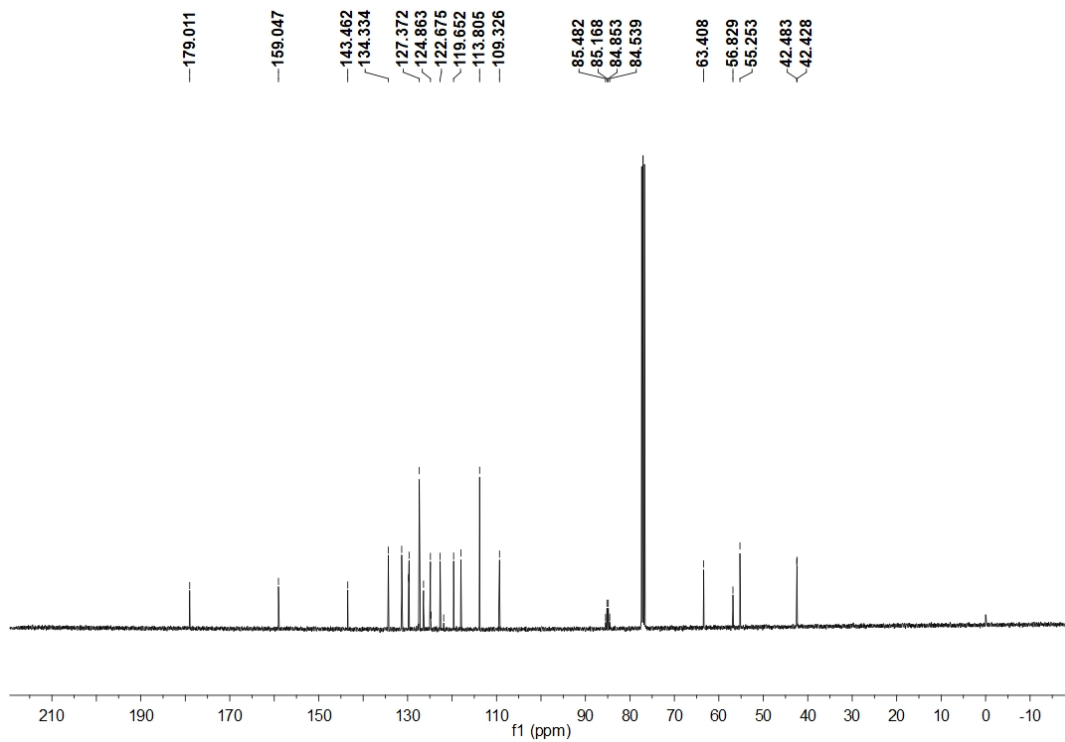
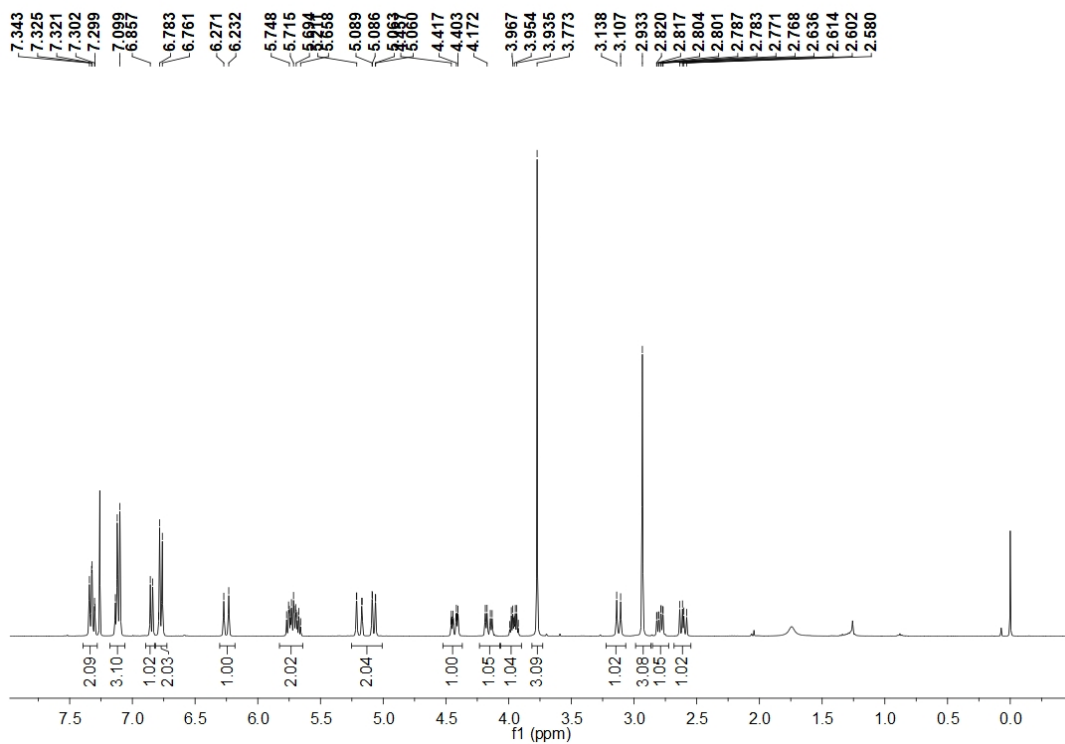
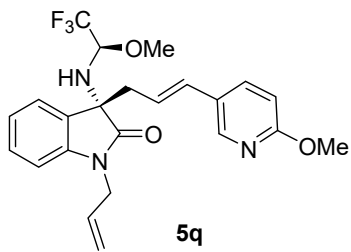




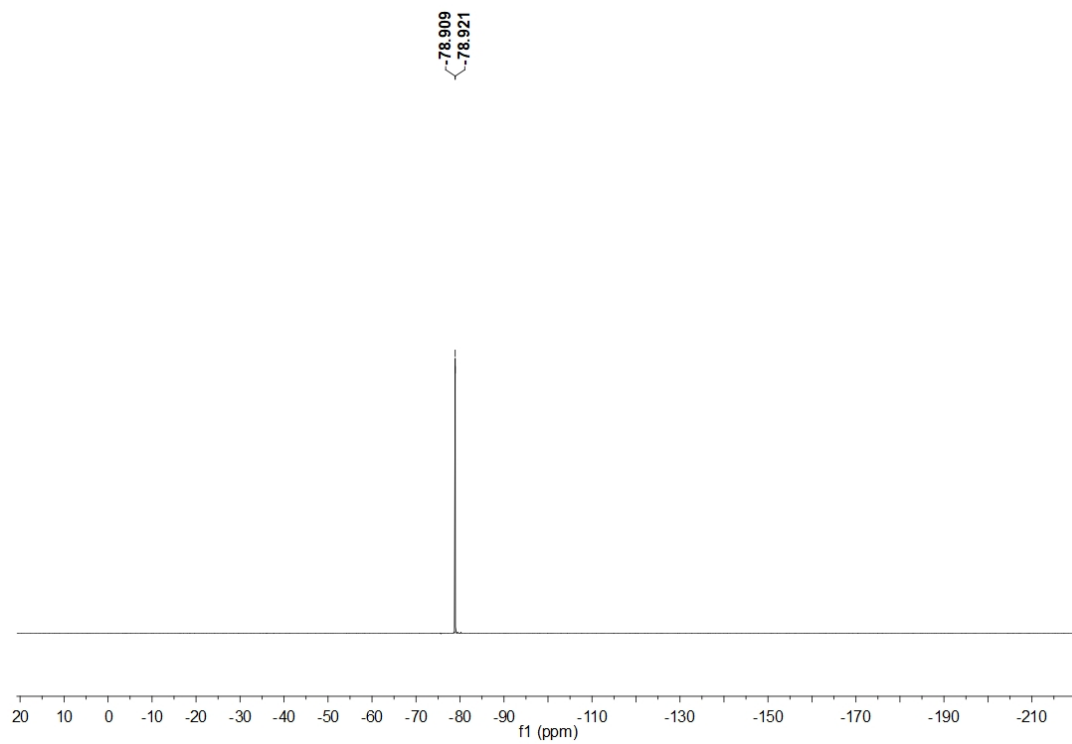


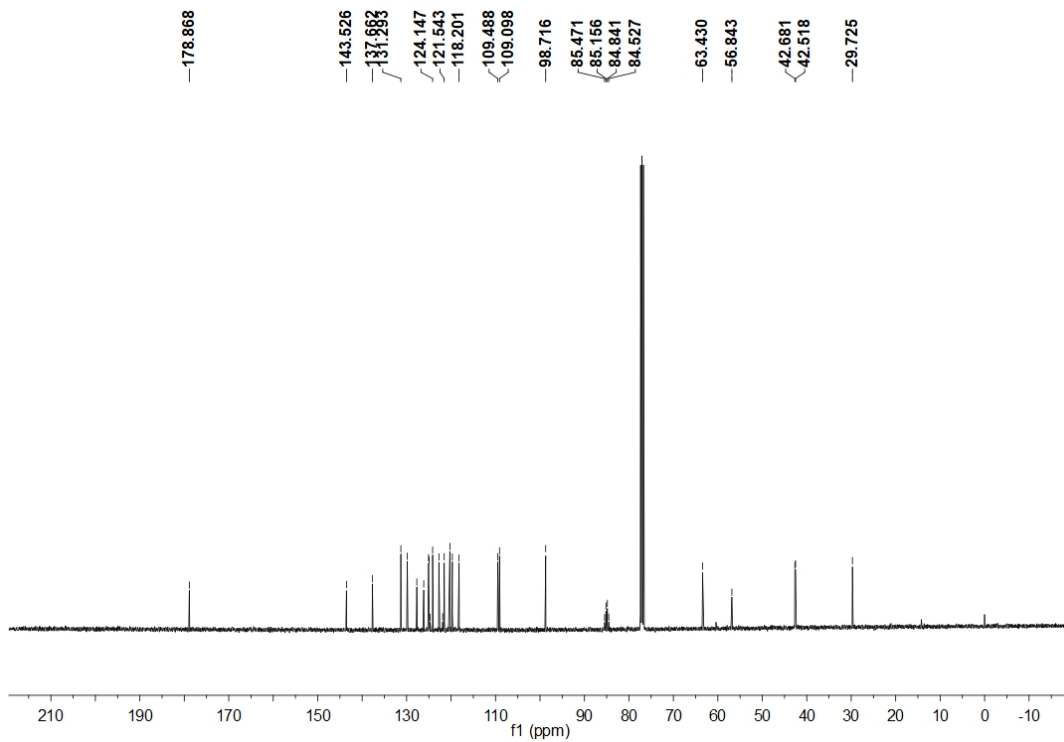
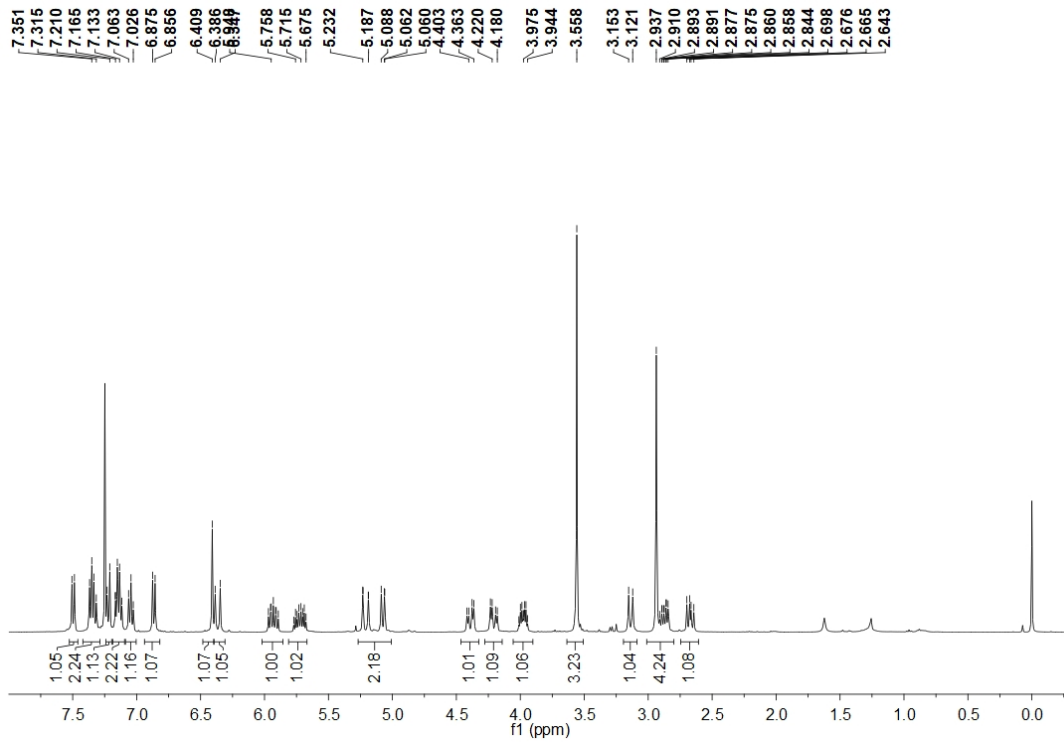
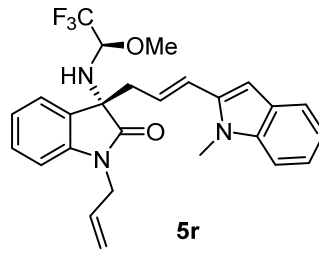


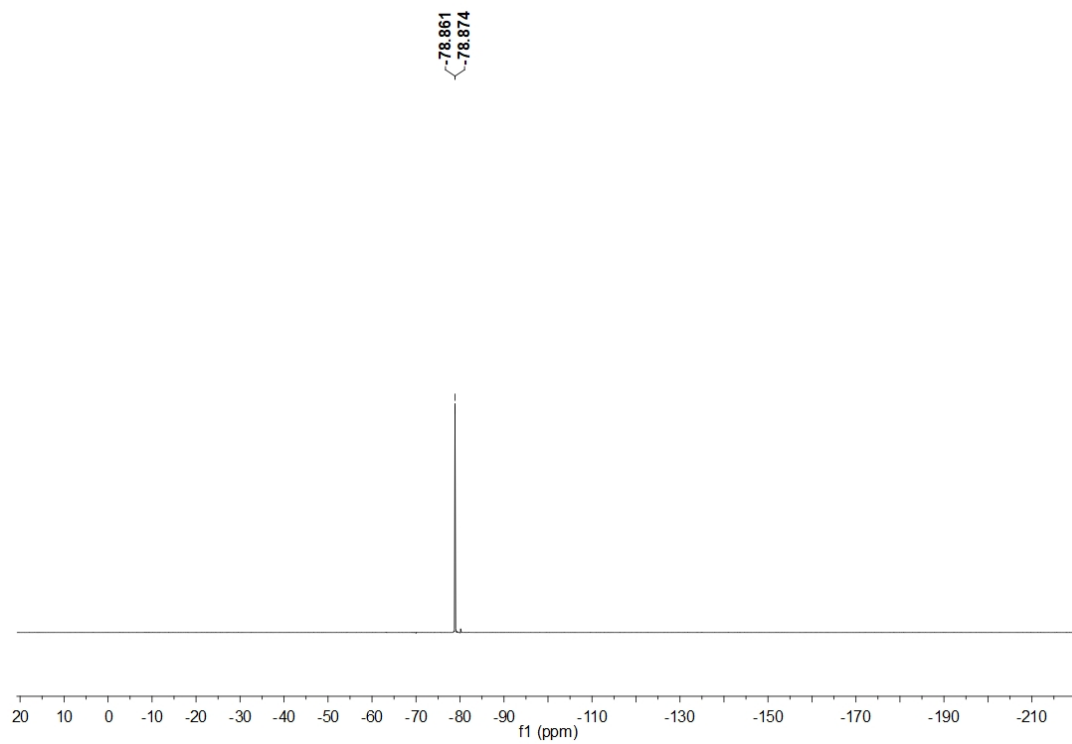


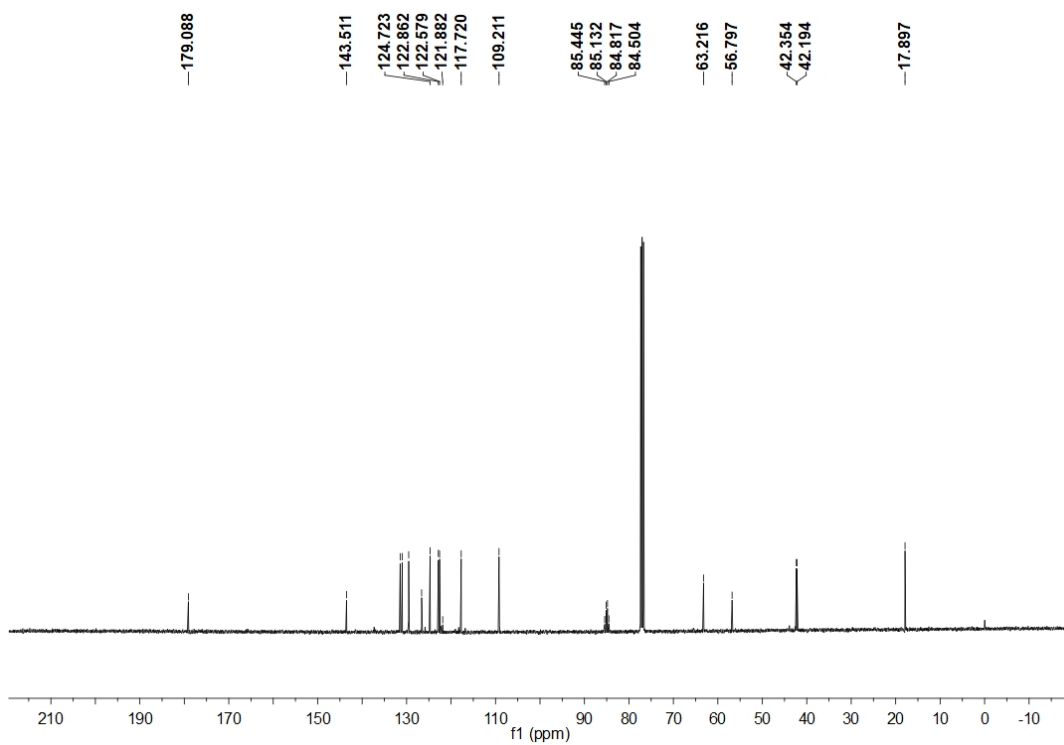
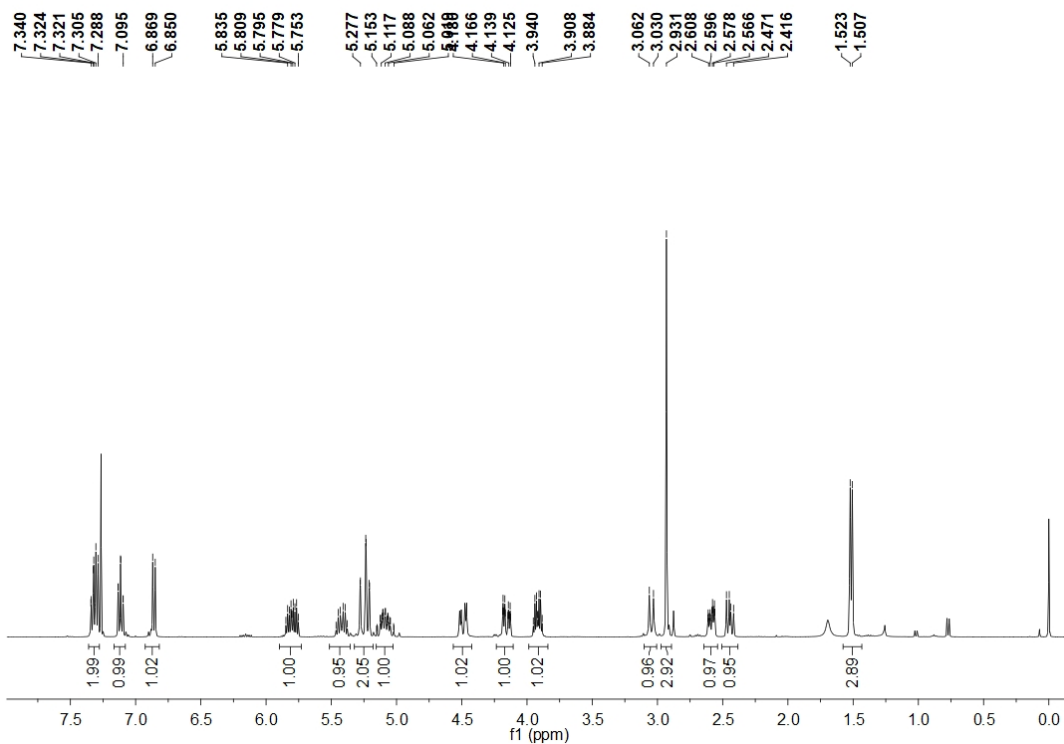
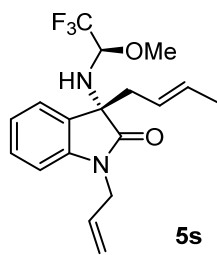


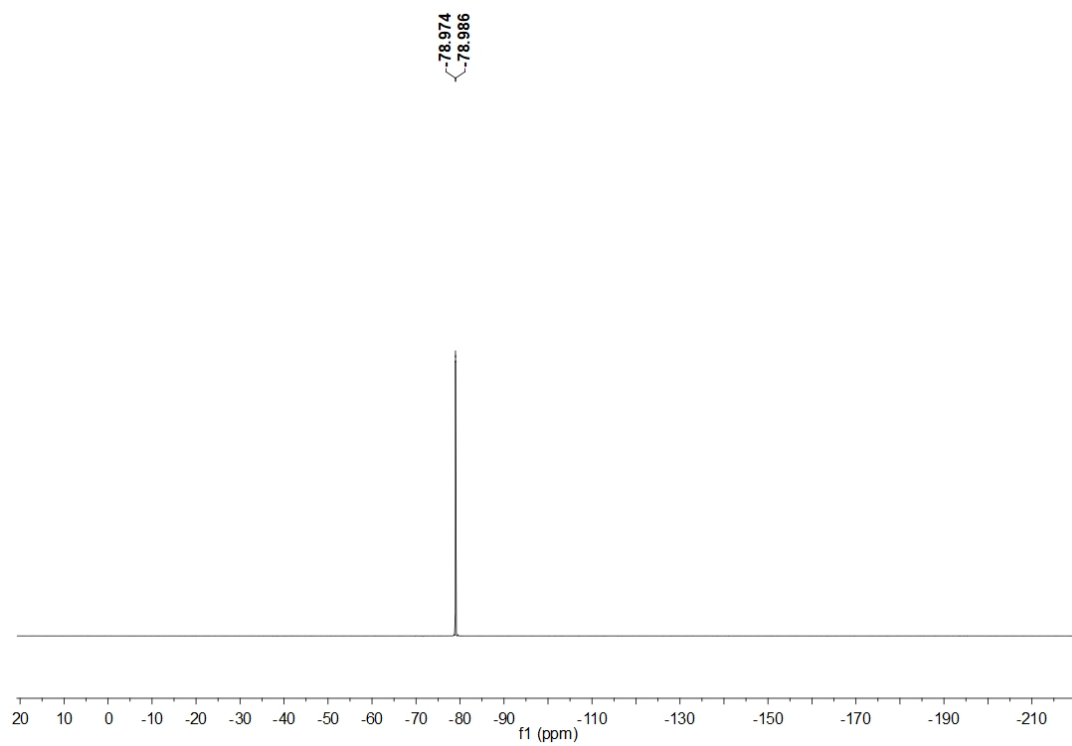


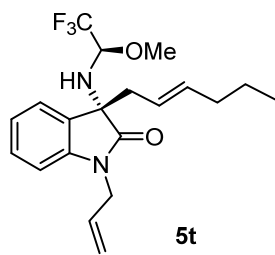




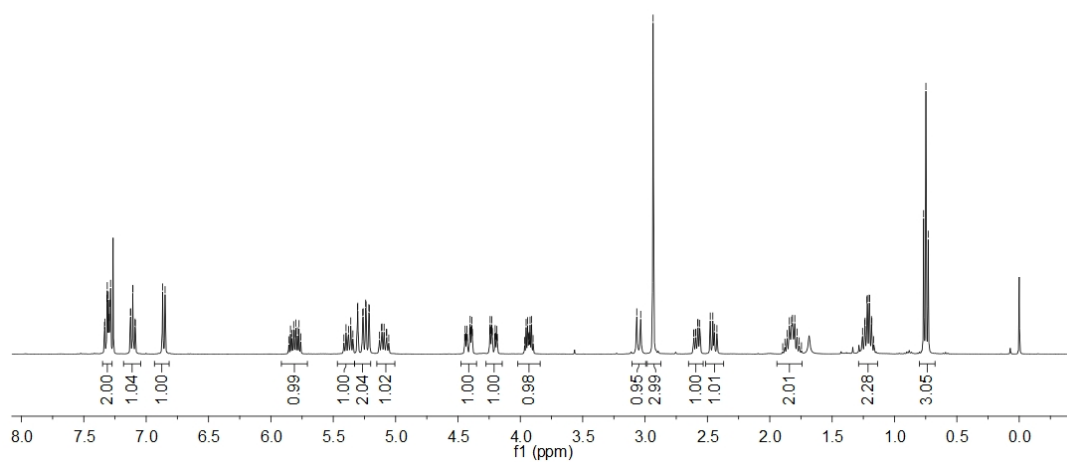








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