

Supporting Information for

Base-Promoted Cascade β -F-Elimination/Electrocyclization/Diels-Alder/Retro-Diels-Alder Reaction: Efficient Access to δ -Carboline Derivatives

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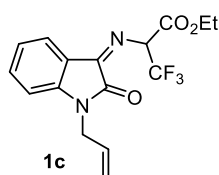
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¹H NMR (400 MHz, Chloroform-d) δ 7.80 – 7.75 (m, 1H), 7.52 – 7.44 (m, 1H), 7.17 – 7.09 (m, 1H), 6.84 (d, J = 7.8 Hz, 1H), 6.22 (q, J = 8.0 Hz, 1H), 4.38 – 4.22 (m, 2H), 3.20 (s, 3H), 1.32 (t, J = 7.1 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-d) δ 163.8 (d, J = 2.3 Hz), 158.5, 158.1, 146.7, 134.4, 123.7, 123.6, 123.3 (q, J = 280.3 Hz), 120.5, 108.9, 64.5 (q, J = 29.9 Hz), 62.6, 25.9, 14.0.

¹⁹F NMR (376 MHz, Chloroform-d) δ -71.85 (d, J = 8.0 Hz).

HRMS (ESI+) Calcd. For C₁₄H₁₄F₃N₂O₃⁺ ([M+H]⁺): 315.0951, found: 315.0945.



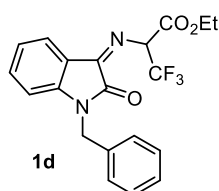
Ethyl (Z)-2-((1-allyl-2-oxoindolin-3-ylidene)amino)-3,3,3-trifluoropropanoate: Yellow solid; 93% yield.

¹H NMR (400 MHz, Chloroform-d) δ 7.82 – 7.75 (m, 1H), 7.50 – 7.36 (m, 1H), 7.17 – 7.08 (m, 1H), 6.84 (d, J = 7.9 Hz, 1H), 6.21 (q, J = 8.0 Hz, 1H), 5.90 – 5.75 (m, 1H), 5.31 – 5.23 (m, 2H), 4.39 – 4.24 (m, 4H), 1.31 (t, J = 7.1 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-d) δ 163.7 (d, J = 2.3 Hz), 158.2, 158.0, 146.0, 134.3, 130.5, 123.8, 123.6, 123.4 (q, J = 280.2 Hz), 120.6, 118.4, 109.8, 64.6 (q, J = 29.6 Hz), 62.6, 42.2, 14.0.

¹⁹F NMR (376 MHz, Chloroform-d) δ -71.85 (d, J = 8.0 Hz).

HRMS (ESI+) Calcd. For C₁₆H₁₆F₃N₂O₃⁺ ([M+H]⁺): 341.1108, found: 341.1103.



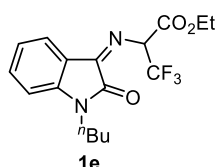
Ethyl (Z)-2-((1-benzyl-2-oxoindolin-3-ylidene)amino)-3,3,3-trifluoropropanoate: Yellow solid; 91% yield.

¹H NMR (400 MHz, Chloroform-d) δ 7.82 – 7.75 (m, 1H), 7.39 – 7.26 (m, 6H), 7.13 – 7.06 (m, 1H), 6.73 (d, J = 7.9 Hz, 1H), 6.26 (q, J = 8.0 Hz, 1H), 4.88 (q, J = 15.7 Hz, 2H), 4.43 – 4.21 (m, 2H), 1.31 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 163.7 (d, $J = 2.3$ Hz), 158.6, 158.0, 145.9, 134.8, 134.3, 129.0, 128.1, 123.8, 123.6, 123.4 (q, $J = 280.2$ Hz), 120.7, 109.9, 64.7 (q, $J = 29.9$ Hz), 62.7, 43.7, 14.0.

^{19}F NMR (376 MHz, Chloroform-d) δ -71.80 (d, $J = 8.0$ Hz).

HRMS (ESI+) Calcd. For $\text{C}_{20}\text{H}_{18}\text{F}_3\text{N}_2\text{O}_3^+$ ($[\text{M}+\text{H}]^+$): 391.1264, found: 391.1262.



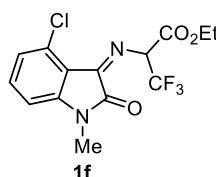
Ethyl (Z)-2-((1-butyl-2-oxoindolin-3-ylidene)amino)-3,3,3-trifluoropropanoate: Yellow solid; 98% yield.

^1H NMR (400 MHz, Chloroform-d) δ 7.81 – 7.73 (m, 1H), 7.50 – 7.41 (m, 1H), 7.15 – 7.07 (m, 1H), 6.85 (d, $J = 7.9$ Hz, 1H), 6.22 (q, $J = 8.0$ Hz, 1H), 4.38 – 4.19 (m, 2H), 3.75 – 3.59 (m, 2H), 1.70 – 1.60 (m, 2H), 1.44 – 1.35 (m, 2H), 1.30 (t, $J = 7.2$ Hz, 3H), 0.96 (t, $J = 7.3$ Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 163.8 (d, $J = 2.3$ Hz), 158.5, 158.3, 146.2, 134.3, 123.8, 123.4 (q, $J = 280.3$ Hz), 123.4, 120.7, 109.2, 64.5 (q, $J = 29.8$ Hz), 62.6, 39.7, 29.4, 20.2, 14.0, 13.7.

^{19}F NMR (376 MHz, Chloroform-d) δ -71.89 (d, $J = 8.0$ Hz).

HRMS (ESI+) Calcd. For $\text{C}_{17}\text{H}_{20}\text{F}_3\text{N}_2\text{O}_3^+$ ($[\text{M}+\text{H}]^+$): 357.1421, found: 357.1418.



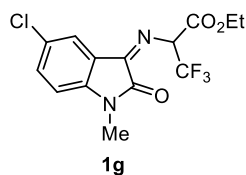
Ethyl (Z)-2-((4-chloro-1-methyl-2-oxoindolin-3-ylidene)amino)-3,3,3-trifluoropropanoate: Yellow solid; 76% yield.

^1H NMR (400 MHz, Chloroform-d) δ 7.41 – 7.33 (m, 1H), 7.14 – 7.06 (m, 1H), 6.77 – 6.71 (m, 1H), 6.13 (q, $J = 8.0$ Hz, 1H), 4.39 – 4.23 (m, 2H), 3.20 (s, 3H), 1.32 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 163.5 (d, $J = 2.4$ Hz), 157.6, 156.4, 148.0, 134.3, 132.6, 125.7, 123.4 (q, $J = 280.4$ Hz), 116.9, 107.2, 65.1 (q, $J = 30.1$ Hz), 62.6, 26.1, 14.0.

^{19}F NMR (376 MHz, Chloroform-d) δ -72.03 (d, $J = 8.0$ Hz).

HRMS (ESI+) Calcd. For $C_{14}H_{13}ClF_3N_2O_3^+$ ($[M+H]^+$): 349.0561, found: 349.0551.



Ethyl (Z)-2-((5-chloro-1-methyl-2-oxoindolin-3-ylidene)amino)-3,3,3-trifluoropropanoate:

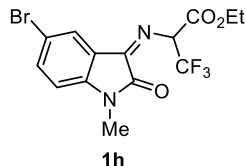
Yellow solid; 88% yield.

1H NMR (400 MHz, Chloroform-d) δ 7.76 (d, $J = 2.1$ Hz, 1H), 7.48 – 7.40 (m, 1H), 6.79 (d, $J = 8.3$ Hz, 1H), 6.18 (q, $J = 8.0$ Hz, 1H), 4.35 – 4.24 (m, 3H), 3.20 (s, 3H), 1.32 (t, $J = 7.1$ Hz, 4H).

^{13}C NMR (101 MHz, Chloroform-d) δ 163.4 (d, $J = 2.4$ Hz), 158.1, 157.3, 145.0, 133.9, 129.4, 123.9, 123.2 (q, $J = 280.3$ Hz), 121.7, 110.0, 64.7 (q, $J = 30.2$ Hz), 62.8, 26.1, 14.0.

^{19}F NMR (376 MHz, Chloroform-d) δ -71.80 (d, $J = 8.0$ Hz).

HRMS (ESI+) Calcd. For $C_{14}H_{13}ClF_3N_2O_3^+$ ($[M+H]^+$): 349.0561, found: 349.0555.



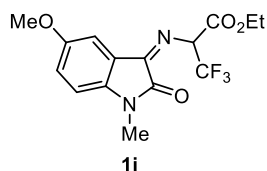
Ethyl (Z)-2-((5-bromo-1-methyl-2-oxoindolin-3-ylidene)amino)-3,3,3-trifluoropropanoate: Yellow solid; 68% yield.

1H NMR (400 MHz, Chloroform-d) δ 7.90 (d, $J = 2.0$ Hz, 1H), 7.64 – 7.54 (m, 1H), 6.74 (d, $J = 8.3$ Hz, 1H), 6.17 (q, $J = 7.9$ Hz, 1H), 4.36 – 4.25 (m, 2H), 3.19 (s, 3H), 1.32 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 163.5 (d, $J = 2.4$ Hz), 157.9, 157.1, 145.5, 136.8, 126.7, 123.2 (q, $J = 280.3$ Hz), 122.0, 116.5, 110.5, 64.7 (q, $J = 29.9$ Hz), 62.8, 26.0, 14.0.

^{19}F NMR (376 MHz, Chloroform-d) δ -71.79 (d, $J = 8.0$ Hz).

HRMS (ESI+) Calcd. For $C_{14}H_{13}BrF_3N_2O_3^+$ ($[M+H]^+$): 393.0056, found: 393.0046.



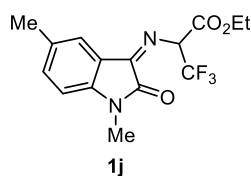
Ethyl (Z)-3,3,3-trifluoro-2-((5-methoxy-1-methyl-2-oxoindolin-3-ylidene)amino)propanoate: Yellow solid; 77% yield.

¹H NMR (400 MHz, Chloroform-d) δ 7.34 (d, $J = 2.7$ Hz, 1H), 7.07 – 7.00 (m, 1H), 6.75 (d, $J = 8.6$ Hz, 1H), 6.25 (q, $J = 8.0$ Hz, 1H), 4.37 – 4.23 (m, 2H), 3.83 (s, 3H), 3.17 (s, 3H), 1.32 (t, $J = 7.1$ Hz, 3H).

¹³C NMR (101 MHz, Chloroform-d) δ 163.8 (d, $J = 2.5$ Hz), 158.6, 156.6, 140.5, 123.3 (q, $J = 280.3$ Hz), 120.9, 109.8, 108.4, 64.4 (q, $J = 29.8$ Hz), 62.6, 56.0, 25.9, 14.0.

¹⁹F NMR (376 MHz, Chloroform-d) δ -71.80 (d, $J = 7.9$ Hz).

HRMS (ESI+) Calcd. For $C_{15}H_{16}F_3N_2O_4^+$ ($[M+H]^+$): 345.1057, found: 345.1053.



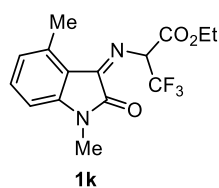
Ethyl (Z)-2-((1,5-dimethyl-2-oxoindolin-3-ylidene)amino)-3,3,3-trifluoropropanoate: Yellow solid; 87% yield.

¹H NMR (400 MHz, Chloroform-d) δ 7.63 – 7.58 (m, 1H), 7.26 (s, 1H), 6.72 (d, $J = 7.9$ Hz, 1H), 6.23 (q, $J = 8.0$ Hz, 1H), 4.38 – 4.21 (m, 2H), 3.18 (s, 3H), 2.34 (s, 3H), 1.31 (t, $J = 7.2$ Hz, 3H).

¹³C NMR (101 MHz, Chloroform-d) δ 163.8 (d, $J = 2.3$ Hz), 158.6, 158.4, 144.5, 134.7, 133.4, 124.2, 123.4 (q, $J = 280.3$ Hz), 120.4, 108.7, 64.4 (q, $J = 29.8$ Hz), 62.6, 25.9, 20.8, 14.0.

¹⁹F NMR (376 MHz, Chloroform-d) δ -71.87 (d, $J = 8.0$ Hz).

HRMS (ESI+) Calcd. For $C_{15}H_{16}F_3N_2O_3^+$ ($[M+H]^+$): 329.1108, found: 329.1109.



Ethyl (Z)-2-((1,4-dimethyl-2-oxoindolin-3-ylidene)amino)-3,3,3-trifluoropropanoate:

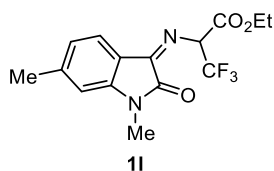
Yellow solid; 80% yield.

¹H NMR (400 MHz, Chloroform-d) δ 7.36 – 7.29 (m, 1H), 6.92 (d, $J = 7.8$ Hz, 1H), 6.66 (d, $J = 7.8$ Hz, 1H), 6.14 (q, $J = 8.0$ Hz, 1H), 4.42 – 4.18 (m, 2H), 3.18 (s, 3H), 2.60 (s, 3H), 1.32 (t, $J = 7.1$ Hz, 3H).

¹³C NMR (101 MHz, Chloroform-d) δ 164.0 (d, $J = 2.5$ Hz), 159.0, 158.4, 146.9, 139.6, 133.3, 126.3, 123.5 (q, $J = 280.2$ Hz), 117.8, 106.3, 64.8 (q, $J = 29.9$ Hz), 62.5, 25.8, 19.0, 14.0.

¹⁹F NMR (376 MHz, Chloroform-d) δ -72.29 (d, $J = 8.0$ Hz).

HRMS (ESI+) Calcd. For C₁₅H₁₆F₃N₂O₃⁺ ([M+H]⁺): 329.1108, found: 329.1100.



Ethyl (Z)-2-((1,6-dimethyl-2-oxoindolin-3-ylidene)amino)-3,3,3-trifluoropropanoate:

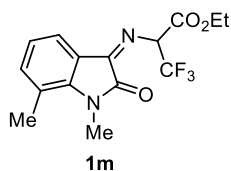
Yellow solid; 86% yield.

¹H NMR (400 MHz, Chloroform-d) δ 7.65 (d, $J = 7.7$ Hz, 1H), 6.97 – 6.89 (m, 1H), 6.67 – 6.61 (m, 1H), 6.21 (q, $J = 8.0$ Hz, 1H), 4.34 – 4.23 (m, 2H), 3.18 (s, 3H), 2.43 (s, 3H), 1.31 (t, $J = 7.1$ Hz, 3H).

¹³C NMR (101 MHz, Chloroform-d) δ 164.0 (d, $J = 2.3$ Hz), 159.0, 157.9, 146.9, 145.8, 124.2, 123.6, 123.4 (q, $J = 280.3$ Hz), 118.0, 109.7, 64.4 (q, $J = 29.8$ Hz), 62.5, 25.8, 22.5, 14.0.

¹⁹F NMR (376 MHz, Chloroform-d) δ -71.88 (d, $J = 8.1$ Hz).

HRMS (ESI+) Calcd. For C₁₅H₁₆F₃N₂O₃⁺ ([M+H]⁺): 329.1108, found: 329.1104.



Ethyl (Z)-2-((1,7-dimethyl-2-oxoindolin-3-ylidene)amino)-3,3,3-trifluoropropanoate:

Yellow solid; 90% yield.

¹H NMR (400 MHz, Chloroform-d) δ 7.70 – 7.55 (m, 1H), 7.20 (d, $J = 7.7$ Hz, 1H), 7.04 – 6.96 (m, 1H), 6.23 – 6.17 (q, $J = 8.1$ Hz, 1H), 4.36 – 4.22 (m, 2H), 3.46 (s, 3H), 2.54 (s, 3H), 1.31

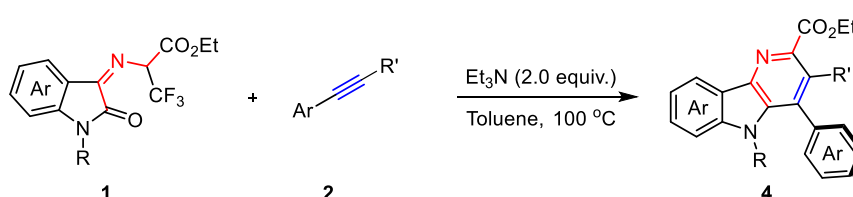
(t, $J = 7.1$ Hz, 3H).

^{13}C NMR (101 MHz, Chloroform- d) δ 163.8, 159.2, 158.1, 144.3, 142.3, 138.2, 123.5, 123.4 (q, $J = 280.3$ Hz), 121.7, 120.6, 64.6 (q, $J = 29.8$ Hz), 62.5, 29.2, 18.7, 14.0.

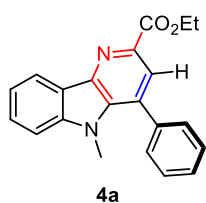
^{19}F NMR (376 MHz, Chloroform- d) δ -71.88 (d, $J = 8.1$ Hz).

HRMS (ESI+) Calcd. For $\text{C}_{15}\text{H}_{16}\text{F}_3\text{N}_2\text{O}_3^+$ ($[\text{M}+\text{H}]^+$): 329.1108, found: 329.1100.

3. General procedure for cascade β -F elimination/electrocyclization/Diels-Alder/retro-Diels-Alder reaction.



In a 25 mL nitrogen-filled dry Schlenk tube, isatin-activated ketoimine ester **1** (0.2 mmol), Arylalkyne **2** (0.4 mmol), Et_3N (0.4 mmol) and degassed toluene (2 mL) were added. The reaction was stirred for 12 h at $100\text{ }^\circ\text{C}$ until starting material was consumed (monitored by TLC, caution: the released COF_2 gas is toxic, please deal with the experiment in fume hood). 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 product **4**.

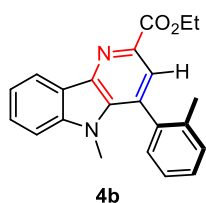


Ethyl 5-methyl-4-phenyl-5H-pyrido[3,2-b]indole-2-carboxylate: White solid; 81% yield.

^1H NMR (400 MHz, Chloroform- d) δ 8.58 (d, $J = 7.8$ Hz, 1H), 8.11 (s, 1H), 7.60 (t, $J = 7.6$ Hz, 1H), 7.52 (s, 5H), 7.45 – 7.33 (m, 2H), 4.53 (q, $J = 7.1$ Hz, 2H), 3.44 (s, 3H), 1.49 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (101 MHz, Chloroform- d) δ 166.1, 143.6, 143.0, 139.5, 137.3, 133.5, 132.2, 129.5, 128.64, 128.56, 128.4, 124.1, 122.0, 120.7, 109.2, 61.7, 32.5, 14.5.

HRMS (ESI+) Calcd. For $\text{C}_{21}\text{H}_{19}\text{N}_2\text{O}_2^+$ ($[\text{M}+\text{H}]^+$): 331.1441, found: 331.1443.

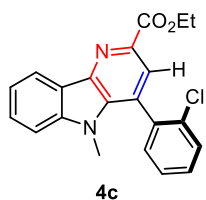


Ethyl 5-methyl-4-(*o*-tolyl)-5H-pyrido[3,2-*b*]indole-2-carboxylate: White solid; 90% yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.59 (d, *J* = 7.7 Hz, 1H), 8.05 (s, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.50 – 7.30 (m, 6H), 4.53 (q, *J* = 6.8 Hz, 2H), 3.35 (s, 3H), 2.08 (s, 3H), 1.49 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 166.2, 143.4, 142.7, 139.6, 136.6, 133.6, 131.5, 130.0, 129.8, 128.9, 128.6, 125.9, 123.8, 122.1, 122.0, 120.7, 109.1, 61.7, 30.9, 20.2, 14.5.

HRMS (ESI+) Calcd. For C₂₂H₂₁N₂O₂⁺ ([M+H]⁺): 345.1597, found: 345.1595.

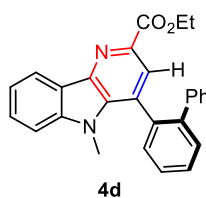


Ethyl 4-(2-chlorophenyl)-5-methyl-5H-pyrido[3,2-*b*]indole-2-carboxylate: White solid; 99% yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.59 (d, *J* = 7.8 Hz, 1H), 8.06 (s, 1H), 7.69 – 7.53 (m, 2H), 7.53 – 7.33 (m, 5H), 4.53 (q, *J* = 7.0 Hz, 2H), 3.42 (s, 3H), 1.49 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 166.0, 143.3, 142.9, 139.4, 136.2, 134.0, 133.5, 131.6, 130.3, 129.5, 128.9, 128.7, 127.0, 123.9, 122.0, 122.0, 120.7, 109.1, 61.7, 30.7, 14.5.

HRMS (ESI+) Calcd. For C₂₁H₁₈ClN₂O₂⁺ ([M+H]⁺): 365.1051, found: 365.1048.



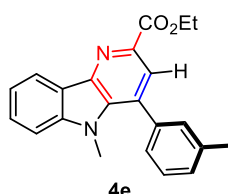
Ethyl 4-([1,1'-biphenyl]-2-yl)-5-methyl-5H-pyrido[3,2-*b*]indole-2-carboxylate: White solid; 65% yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.51 (d, *J* = 7.7 Hz, 1H), 8.05 (s, 1H), 7.64 – 7.45 (m, 5H), 7.37 – 7.27 (m, 2H), 7.12 – 6.97 (m, 5H), 4.49 (q, *J* = 6.9 Hz, 2H), 3.40 (s, 3H), 1.47 (t, *J*

= 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 165.1, 142.3, 141.6, 140.6, 138.7, 138.1, 134.4, 132.8, 130.6, 129.9, 129.3, 128.2, 128.1, 127.5, 127.1, 126.2, 126.1, 124.0, 120.9, 120.9, 119.5, 108.0, 60.6, 30.3, 13.4.

HRMS (ESI+) Calcd. For $\text{C}_{27}\text{H}_{23}\text{N}_2\text{O}_2^+$ ($[\text{M}+\text{H}]^+$): 407.1754, found: 407.1751.

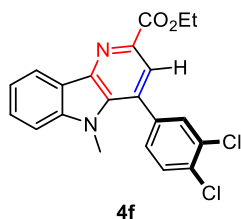


Ethyl 5-methyl-4-(*m*-tolyl)-5H-pyrido[3,2-*b*]indole-2-carboxylate: White solid; 83% yield.

^1H NMR (400 MHz, Chloroform-d) δ 8.58 (d, $J = 7.8$ Hz, 1H), 8.11 (s, 1H), 7.61 – 7.58 (m, 1H), 7.44 – 7.28 (m, 6H), 4.53 (q, $J = 7.1$ Hz, 2H), 3.45 (s, 3H), 2.46 (s, 3H), 1.49 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 166.2, 143.6, 143.0, 139.5, 138.2, 137.2, 133.6, 132.4, 130.2, 129.3, 128.6, 128.2, 126.6, 124.1, 122.1, 122.0, 120.6, 109.2, 61.7, 32.6, 21.5, 14.5.

HRMS (ESI+) Calcd. For $\text{C}_{22}\text{H}_{21}\text{N}_2\text{O}_2^+$ ($[\text{M}+\text{H}]^+$): 345.1597, found: 345.1596.

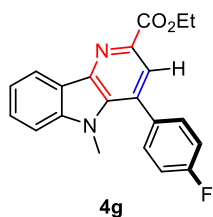


Ethyl 4-(3,4-dichlorophenyl)-5-methyl-5H-pyrido[3,2-*b*]indole-2-carboxylate: White solid; 87% yield.

^1H NMR (400 MHz, Chloroform-d) δ 8.53 (d, $J = 7.7$ Hz, 1H), 8.02 (s, 1H), 7.68 (d, $J = 1.6$ Hz, 1H), 7.66 – 7.57 (m, 2H), 7.44 – 7.34 (m, 3H), 4.53 (q, $J = 7.1$ Hz, 2H), 3.44 (s, 3H), 1.49 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 165.8, 143.6, 143.3, 139.5, 137.2, 133.1, 133.0, 132.8, 131.4, 130.4, 129.3, 128.93, 128.89, 123.7, 122.0, 121.9, 121.0, 109.3, 61.8, 32.8, 14.5.

HRMS (ESI+) Calcd. For $\text{C}_{21}\text{H}_{17}\text{Cl}_2\text{N}_2\text{O}_2^+$ ($[\text{M}+\text{H}]^+$): 399.0662, found: 399.0658.



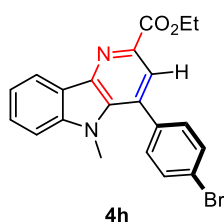
Ethyl 4-(4-fluorophenyl)-5-methyl-5H-pyrido[3,2-b]indole-2-carboxylate: White solid; 62% yield.

¹H NMR (400 MHz, Chloroform-d) δ 8.56 (d, $J = 7.8$ Hz, 1H), 8.07 (s, 1H), 7.62 – 7.60 (m, 1H), 7.55 – 7.46 (m, 2H), 7.44 – 7.34 (m, 2H), 7.23 (t, $J = 8.6$ Hz, 2H), 4.53 (q, $J = 7.1$ Hz, 2H), 3.44 (s, 3H), 1.49 (t, $J = 7.1$ Hz, 3H).

¹³C NMR (101 MHz, Chloroform-d) δ 166.1, 162.9 (d, $J = 249.7$ Hz), 143.6, 143.1, 139.5, 133.5, 133.2 (d, $J = 3.4$ Hz), 131.3 (d, $J = 8.2$ Hz), 131.1, 128.8, 124.2, 122.0, 122.0, 120.8, 115.5 (d, $J = 21.7$ Hz), 109.2, 61.7, 32.6, 14.5.

¹⁹F NMR (376 MHz, Chloroform-d) δ -112.75 – -112.82 (m).

HRMS (ESI+) Calcd. For $C_{21}H_{18}FN_2O_2^+$ ($[M+H]^+$): 349.1347, found: 349.1343.

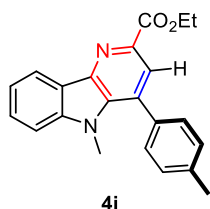


Ethyl 4-(4-bromophenyl)-5-methyl-5H-pyrido[3,2-b]indole-2-carboxylate: White solid; 74% yield.

¹H NMR (400 MHz, Chloroform-d) δ 8.57 (d, $J = 7.8$ Hz, 1H), 8.07 (s, 1H), 7.68 (d, $J = 8.3$ Hz, 2H), 7.64 – 7.60 (m, 1H), 7.45 – 7.36 (m, 4H), 4.53 (q, $J = 7.1$ Hz, 2H), 3.47 (s, 3H), 1.49 (t, $J = 7.1$ Hz, 3H).

¹³C NMR (101 MHz, Chloroform-d) δ 166.0, 143.6, 143.2, 139.6, 136.2, 133.3, 131.7, 131.1, 130.8, 128.8, 123.9, 123.0, 122.1, 122.0, 120.9, 109.2, 61.8, 32.7, 14.5.

HRMS (ESI+) Calcd. For $C_{21}H_{18}BrN_2O_2^+$ ($[M+H]^+$): 409.0546, found: 409.0540.

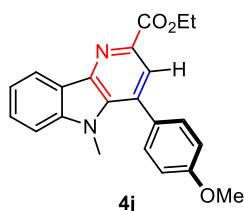


Ethyl 5-methyl-4-(*p*-tolyl)-5H-pyrido[3,2-*b*]indole-2-carboxylate: White solid; 99% yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.58 (d, *J* = 7.8 Hz, 1H), 8.10 (s, 1H), 7.62 – 7.58 (m, 1H), 7.42 – 7.31 (m, 6H), 4.53 (q, *J* = 7.1 Hz, 2H), 3.47 (s, 3H), 2.48 (s, 3H), 1.49 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 166.2, 143.6, 143.0, 139.5, 138.5, 134.3, 133.7, 132.4, 129.4, 129.1, 128.6, 124.3, 122.1, 122.0, 120.6, 109.2, 61.7, 32.6, 21.4, 14.5.

HRMS (ESI+) Calcd. For C₂₂H₂₁N₂O₂⁺ ([M+H]⁺): 345.1597, found: 345.1594.

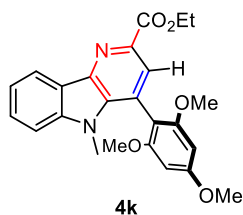


Ethyl 4-(4-methoxyphenyl)-5-methyl-5H-pyrido[3,2-*b*]indole-2-carboxylate: White solid; 85% yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.57 (d, *J* = 7.8 Hz, 1H), 8.09 (s, 1H), 7.66 – 7.55 (m, 1H), 7.49 – 7.32 (m, 4H), 7.05 (d, *J* = 8.7 Hz, 2H), 4.53 (q, *J* = 7.1 Hz, 2H), 3.91 (s, 3H), 3.47 (s, 3H), 1.49 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 166.2, 159.9, 143.6, 143.0, 139.6, 133.8, 132.1, 130.7, 129.4, 128.6, 124.4, 122.1, 122.0, 120.6, 113.8, 109.2, 61.7, 55.4, 32.6, 14.5.

HRMS (ESI+) Calcd. For C₂₂H₂₁N₂O₃⁺ ([M+H]⁺): 361.1547, found: 361.1543.

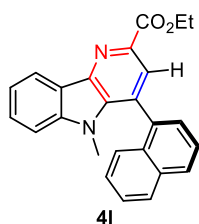


Ethyl (*r*)-5-methyl-4-(2,4,6-trimethoxyphenyl)-5H-pyrido[3,2-*b*]indole-2-carboxylate: White solid; 90% yield.

¹H NMR (400 MHz, Chloroform-d) δ 8.58 (d, $J = 7.7$ Hz, 1H), 8.02 (s, 1H), 7.57 (t, $J = 7.6$ Hz, 1H), 7.43 – 7.30 (m, 2H), 6.27 (s, 2H), 4.51 (q, $J = 7.0$ Hz, 2H), 3.92 (s, 3H), 3.67 (s, 6H), 3.48 (s, 3H), 1.48 (t, $J = 7.1$ Hz, 3H).

¹³C NMR (101 MHz, Chloroform-d) δ 166.5, 162.1, 158.9, 143.1, 142.5, 139.3, 135.3, 128.1, 126.3, 124.9, 122.1, 121.9, 120.2, 108.8, 106.8, 90.5, 61.5, 55.7, 55.5, 30.1, 14.5.

HRMS (ESI+) Calcd. For C₂₄H₂₅N₂O₅⁺ ([M+H]⁺): 421.1758, found: 421.1758.

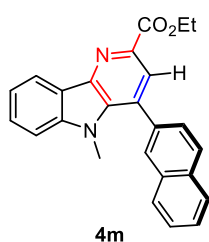


Ethyl 5-methyl-4-(naphthalen-1-yl)-5H-pyrido[3,2-b]indole-2-carboxylate: White solid; 99% yield.

¹H NMR (400 MHz, Chloroform-d) δ 8.64 (d, $J = 7.8$ Hz, 1H), 8.19 (s, 1H), 7.99 (dd, $J = 18.8$, 8.0 Hz, 2H), 7.66 – 7.49 (m, 4H), 7.44 – 7.29 (m, 4H), 4.53 (q, $J = 7.1$ Hz, 2H), 3.08 (s, 3H), 1.47 (t, $J = 7.1$ Hz, 3H).

¹³C NMR (101 MHz, Chloroform-d) δ 166.1, 143.3, 142.7, 139.7, 134.7, 134.4, 133.2, 132.4, 130.2, 129.2, 128.7, 128.5, 127.8, 127.0, 126.5, 125.8, 125.2, 124.8, 122.1, 122.0, 120.7, 109.1, 61.7, 31.1, 14.5.

HRMS (ESI+) Calcd. For C₂₅H₂₁N₂O₂⁺ ([M+H]⁺): 381.1598, found: 381.1593.

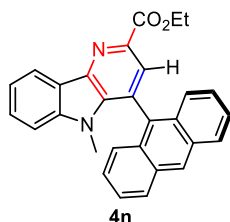


Ethyl 5-methyl-4-(naphthalen-2-yl)-5H-pyrido[3,2-b]indole-2-carboxylate: White solid; 93% yield.

¹H NMR (400 MHz, Chloroform-d) δ 8.60 (d, $J = 7.7$ Hz, 1H), 8.20 (s, 1H), 8.02 – 7.89 (m, 4H), 7.65 – 7.55 (m, 4H), 7.42 – 7.33 (m, 2H), 4.53 (q, $J = 7.1$ Hz, 2H), 3.42 (s, 3H), 1.49 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (101 MHz, Chloroform- d) δ 166.1, 143.7, 143.1, 139.5, 134.7, 133.7, 133.0, 132.9, 132.2, 128.7, 128.6, 128.2, 128.0, 127.9, 127.3, 127.0, 126.9, 124.4, 122.1, 120.8, 109.2, 61.7, 32.7, 14.5.

HRMS (ESI+) Calcd. For $\text{C}_{25}\text{H}_{21}\text{N}_2\text{O}_2^+$ ($[\text{M}+\text{H}]^+$): 381.1598, found: 381.1593.

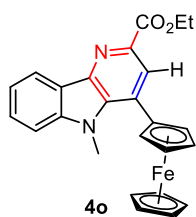


Ethyl (*r*)-4-(anthracen-9-yl)-5-methyl-5H-pyrido[3,2-*b*]indole-2-carboxylate: White solid; 99% yield.

^1H NMR (400 MHz, Chloroform- d) δ 8.70 (d, $J = 7.8$ Hz, 1H), 8.65 (s, 1H), 8.22 (s, 1H), 8.12 (d, $J = 8.5$ Hz, 2H), 7.59 - 7.57 (m, 1H), 7.54 - 7.46 (m, 2H), 7.46 - 7.31 (m, 5H), 7.28 (s, 1H), 4.52 (q, $J = 7.1$ Hz, 2H), 2.80 (s, 3H), 1.45 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (101 MHz, Chloroform- d) δ 166.1, 143.3, 142.9, 139.9, 135.1, 131.1, 130.7, 130.3, 128.8, 128.7, 128.2, 126.7, 126.2, 125.7, 125.6, 122.2, 122.1, 120.8, 109.1, 61.7, 30.3, 14.5.

HRMS (ESI+) Calcd. For $\text{C}_{29}\text{H}_{23}\text{N}_2\text{O}_2^+$ ($[\text{M}+\text{H}]^+$): 431.1754, found: 431.1753.

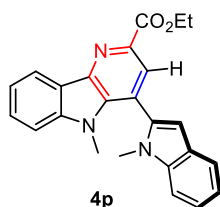


Ethyl 5-methyl-4-ferrocene-5H-pyrido[3,2-*b*] indole-2-carboxylate: White solid; 80% yield.

^1H NMR (400 MHz, Chloroform- d) δ 8.78 (s, 1H), 8.54 (d, $J = 7.7$ Hz, 1H), 7.57 (t, $J = 7.6$ Hz, 1H), 7.38 - 7.31 (m, 2H), 4.64 - 4.54 (m, 4H), 4.45 - 4.41 (m, 2H), 4.31 (s, 5H), 3.54 (s, 3H), 1.54 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (101 MHz, Chloroform- d) δ 166.3, 143.8, 142.7, 139.0, 135.4, 129.2, 128.5, 126.9, 122.0, 120.6, 109.2, 85.6, 71.7, 69.9, 68.3, 61.7, 32.7, 14.5.

HRMS (ESI+) Calcd. For $\text{C}_{25}\text{H}_{23}\text{FeN}_2\text{O}_2^+$ ($[\text{M}+\text{H}]^+$): 439.1104, found: 439.1096.

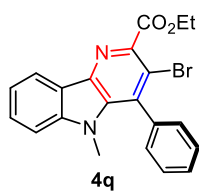


Ethyl 5-methyl-4-(1-methyl-1H-indol-2-yl)-5H-pyrido[3,2-b]indole-2-carboxylate: White solid; 87% yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.61 (d, *J* = 7.7 Hz, 1H), 8.22 (s, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.45 – 7.31 (m, 4H), 7.25 – 7.19 (m, 1H), 6.75 (s, 1H), 4.53 (q, *J* = 7.1 Hz, 2H), 3.54 (s, 3H), 3.39 (s, 3H), 1.49 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 165.9, 143.6, 143.1, 139.5, 137.5, 134.7, 134.4, 129.0, 127.9, 125.1, 122.6, 122.2, 122.1, 122.0, 121.1, 121.1, 120.5, 109.7, 109.3, 104.3, 61.8, 30.8, 30.5, 14.5.

HRMS (ESI+) Calcd. For C₂₄H₂₂N₃O₂⁺ ([M+H]⁺): 384.1707, found: 384.1702.

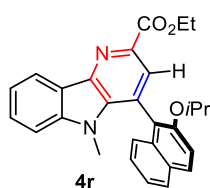


Ethyl 3-bromo-5-methyl-4-phenyl-5H-pyrido[3,2-b]indole-2-carboxylate: White solid; 80% yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.43 – 8.39 (m, 1H), 7.60 – 7.46 (m, 4H), 7.37 – 7.29 (m, 4H), 4.54 (q, *J* = 7.2 Hz, 2H), 3.15 (s, 3H), 1.48 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 167.1, 143.3, 142.7, 140.5, 136.2, 133.4, 133.2, 129.9, 129.0, 128.8, 128.5, 121.5, 121.1, 120.8, 116.1, 109.3, 62.2, 31.6, 14.3.

HRMS (ESI+) Calcd. For C₂₁H₁₈BrN₂O₂⁺ ([M+H]⁺): 409.0546, found: 409.0542.

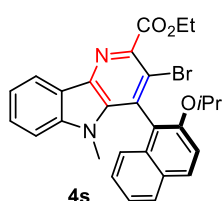


Ethyl 4-(2-isopropoxynaphthalen-1-yl)-5-methyl-5H-pyrido[3,2-b]indole-2-carboxylate: White solid; 81% yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.65 (d, *J* = 7.8 Hz, 1H), 8.12 (s, 1H), 7.99 (d, *J* = 9.1 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.62 – 7.54 (m, 1H), 7.44 – 7.29 (m, 5H), 7.21 (d, *J* = 8.3 Hz, 1H), 4.63 – 4.47 (m, 3H), 3.22 (s, 3H), 1.47 (t, *J* = 7.1 Hz, 3H), 1.10 (d, *J* = 6.1 Hz, 3H), 1.06 (d, *J* = 6.1 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 166.3, 153.3, 143.3, 142.7, 139.5, 135.3, 133.8, 130.5, 128.8, 128.4, 128.1, 127.3, 127.0, 125.8, 125.0, 124.2, 122.1, 122.0, 121.0, 120.4, 116.3, 109.0, 72.0, 61.6, 30.2, 22.5, 22.2, 14.5.

HRMS (ESI+) Calcd. For C₂₈H₂₇N₂O₃⁺ ([M+H]⁺): 439.2016, found: 439.2011.

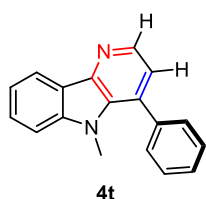


Ethyl 3-bromo-4-(2-isopropoxynaphthalen-1-yl)-5-methyl-5H-pyrido[3,2-b]indole-2-carboxylate: White solid; 66% yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.50 (d, *J* = 7.8 Hz, 1H), 8.02 (d, *J* = 9.1 Hz, 1H), 7.91 – 7.82 (m, 1H), 7.63 – 7.49 (m, 1H), 7.42 – 7.26 (m, 5H), 7.10 – 7.01 (m, 1H), 4.71 – 4.61 (m, 1H), 4.55 (q, *J* = 7.1 Hz, 2H), 3.04 (s, 3H), 1.48 (t, *J* = 7.1 Hz, 3H), 1.17 (d, *J* = 6.1 Hz, 3H), 1.13 (d, *J* = 6.1 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 167.1, 153.5, 143.2, 142.8, 140.3, 134.6, 133.3, 131.1, 129.3, 128.5, 128.5, 128.2, 127.6, 124.4, 124.2, 121.6, 121.4, 120.6, 119.5, 118.0, 115.2, 109.2, 71.4, 62.1, 30.0, 22.6, 22.4, 14.3.

HRMS (ESI+) Calcd. For C₂₈H₂₆BrN₂O₃⁺ ([M+H]⁺): 517.1121, found: 517.1115.



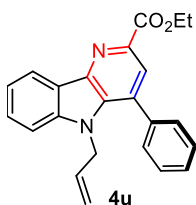
5-methyl-4-phenyl-5H-pyrido[3,2-b]indole: White solid; 46% yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.54 (d, *J* = 4.8 Hz, 1H), 8.50 – 8.37 (m, 1H), 7.59 – 7.53 (m, 1H), 7.52 – 7.46 (m, 5H), 7.38 (d, *J* = 8.3 Hz, 1H), 7.36 – 7.30 (m, 1H), 7.19 (d, *J* = 4.8 Hz,

1H), 3.40 (s, 3H).

¹³C NMR (101 MHz, Chloroform-d) δ 142.8, 142.6, 141.2, 137.9, 132.9, 132.0, 129.5, 128.3, 127.9, 122.0, 120.9, 120.1, 109.1, 32.5.

HRMS (ESI+) Calcd. For C₁₈H₁₅N₂⁺ ([M+H]⁺): 259.1230, found: 259.1224.

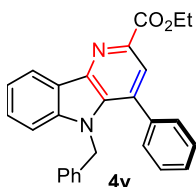


Ethyl 5-allyl-4-phenyl-5H-pyrido[3,2-b]indole-2-carboxylate: White solid; 67% yield.

¹H NMR (400 MHz, Chloroform-d) δ 8.60 (d, *J* = 7.8 Hz, 1H), 8.08 (s, 1H), 7.65 – 7.52 (m, 1H), 7.42 – 7.33 (m, 5H), 7.39 – 7.36 (m, 2H), 5.64 – 5.57 (m, 1H), 5.01 (d, *J* = 10.4 Hz, 1H), 4.76 – 4.41 (m, 5H), 1.49 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-d) δ 166.1, 143.3, 143.1, 139.7, 137.2, 133.0, 132.5, 132.0, 129.3, 128.73, 128.68, 128.3, 124.3, 122.3, 122.1, 120.9, 116.7, 110.0, 61.7, 46.8, 14.5.

HRMS (ESI+) Calcd. For C₂₃H₂₁N₂O₂⁺ ([M+H]⁺): 357.1598, found: 357.1592.

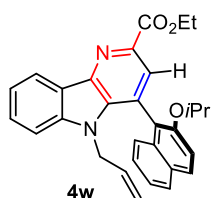


Ethyl 5-benzyl-4-phenyl-5H-pyrido[3,2-b]indole-2-carboxylate: White solid; 85% yield.

¹H NMR (400 MHz, Chloroform-d) δ 8.69 – 8.54 (m, 1H), 8.05 (s, 1H), 7.57 – 7.49 (m, 1H), 7.42 – 7.34 (m, 2H), 7.33 – 7.26 (m, 3H), 7.25 – 7.20 (m, 2H), 7.17 – 7.05 (m, 3H), 6.58 – 6.45 (m, 2H), 5.18 (s, 2H), 4.53 (q, *J* = 7.1 Hz, 2H), 1.48 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-d) δ 166.1, 143.5, 143.4, 139.9, 136.9, 136.5, 133.1, 132.8, 129.2, 128.9, 128.5, 128.2, 127.2, 125.5, 124.4, 122.3, 122.2, 121.1, 109.9, 61.7, 48.0, 14.5.

HRMS (ESI+) Calcd. For C₂₇H₂₃N₂O₂⁺ ([M+H]⁺): 407.1754, found: 407.1749.



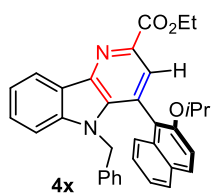
Ethyl 5-allyl-4-(2-isopropoxynaphthalen-1-yl)-5H-pyrido[3,2-b]indole-2-carboxylate:

White solid; 98% yield.

¹H NMR (400 MHz, Chloroform-d) δ 8.65 (d, J = 7.8 Hz, 1H), 8.10 (s, 1H), 7.98 (d, J = 9.1 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.59 – 7.52 (m, 1H), 7.42 – 7.26 (m, 5H), 7.15 (d, J = 8.4 Hz, 1H), 5.41 – 5.27 (m, 1H), 4.69 (dd, J = 10.3, 0.9 Hz, 1H), 4.63 – 4.41 (m, 4H), 4.39 – 4.21 (m, 2H), 1.47 (t, J = 7.1 Hz, 3H), 1.11 (d, J = 6.1 Hz, 3H), 1.07 (d, J = 6.0 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-d) δ 166.3, 153.2, 143.0, 142.8, 139.7, 134.6, 133.6, 132.1, 130.6, 128.7, 128.4, 128.1, 127.2, 127.1, 125.9, 125.1, 124.1, 122.5, 122.0, 120.6, 120.5, 116.7, 115.9, 109.8, 71.8, 61.6, 46.4, 22.5, 22.2, 14.5.

HRMS (ESI+) Calcd. For C₃₀H₂₉N₂O₃⁺ ([M+H]⁺): 465.2173, found: 465.2166.



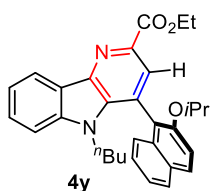
Ethyl 5-benzyl-4-(2-isopropoxynaphthalen-1-yl)-5H-pyrido[3,2-b]indole-2-carboxylate:

White solid; 79% yield.

¹H NMR (400 MHz, Chloroform-d) δ 8.69 (d, J = 7.7 Hz, 1H), 8.07 (s, 1H), 7.89 (d, J = 9.0 Hz, 1H), 7.77 (d, J = 8.1 Hz, 1H), 7.53 – 7.51 (m, 1H), 7.40 – 7.38 (m, 1H), 7.34 – 7.17 (m, 3H), 7.13 – 7.11 (m, 1H), 7.01 – 6.87 (m, 2H), 6.83 – 6.81 (m, 2H), 6.31 (d, J = 7.4 Hz, 2H), 4.95 (s, 2H), 4.51 (q, J = 7.0 Hz, 2H), 4.39 – 4.33 (m, 1H), 1.46 (t, J = 7.1 Hz, 3H), 1.02 (d, J = 6.1 Hz, 3H), 0.98 (d, J = 6.1 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-d) δ 166.3, 153.2, 143.4, 143.2, 139.9, 136.8, 134.8, 133.7, 130.5, 128.7, 128.5, 128.0, 127.8, 127.5, 127.0, 126.8, 126.1, 125.4, 124.7, 123.9, 122.4, 122.1, 120.8, 120.2, 115.7, 109.7, 71.5, 61.6, 47.3, 22.5, 22.0, 14.5.

HRMS (ESI+) Calcd. For C₃₄H₃₁N₂O₃⁺ ([M+H]⁺): 515.2329, found: 515.2322.



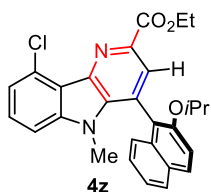
Ethyl 5-butyl-4-(2-isopropoxynaphthalen-1-yl)-5H-pyrido[3,2-b]indole-2-carboxylate:

White solid; 93% yield.

¹H NMR (400 MHz, Chloroform-d) δ 8.65 (d, $J = 7.8$ Hz, 1H), 8.10 (s, 1H), 7.99 (d, $J = 9.1$ Hz, 1H), 7.88 (d, $J = 8.0$ Hz, 1H), 7.57 – 7.55 (m, 1H), 7.44 – 7.27 (m, 5H), 7.17 (d, $J = 8.4$ Hz, 1H), 4.64 – 4.61 (m, 1H), 4.52 (q, $J = 7.1$ Hz, 2H), 3.75 – 3.51 (m, 2H), 1.47 (t, $J = 7.1$ Hz, 3H), 1.42 – 1.28 (m, 1H), 1.13 (d, $J = 6.1$ Hz, 3H), 1.09 (d, $J = 6.0$ Hz, 3H), 1.06 – 0.95 (m, 1H), 0.74 – 0.59 (m, 1H), 0.59 – 0.43 (m, 1H), 0.37 (t, $J = 7.3$ Hz, 3H).

¹³C NMR (101 MHz, Chloroform-d) δ 166.4, 153.2, 143.0, 142.7, 139.4, 134.4, 133.6, 130.5, 128.7, 128.3, 128.1, 127.2, 126.9, 125.9, 124.9, 124.1, 122.3, 122.0, 120.8, 120.3, 115.7, 109.3, 71.7, 61.5, 44.1, 31.2, 22.5, 22.2, 19.8, 14.5, 13.2.

HRMS (ESI+) Calcd. For $C_{31}H_{33}N_2O_3^+$ ($[M+H]^+$): 481.2486, found: 481.2480.

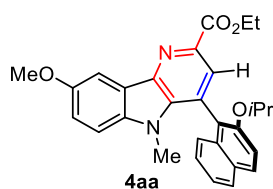


Ethyl 9-chloro-4-(2-isopropoxynaphthalen-1-yl)-5-methyl-5H-pyrido[3,2-b]indole-2-carboxylate: White solid; 87% yield.

¹H NMR (400 MHz, Chloroform-d) δ 8.15 (s, 1H), 7.99 (d, $J = 9.0$ Hz, 1H), 7.89 (d, $J = 7.9$ Hz, 1H), 7.48 - 7.46 (m, 1H), 7.42 – 7.30 (m, 4H), 7.26 (d, $J = 7.9$ Hz, 1H), 7.19 (d, $J = 8.4$ Hz, 1H), 4.60 – 4.55 (m, 1H), 4.51 (q, $J = 7.1$ Hz, 2H), 3.23 (s, 3H), 1.50 (t, $J = 7.1$ Hz, 3H), 1.09 (d, $J = 6.1$ Hz, 3H), 1.04 (d, $J = 6.0$ Hz, 3H).

¹³C NMR (101 MHz, Chloroform-d) δ 166.2, 153.3, 144.2, 141.5, 140.2, 135.3, 133.7, 130.7, 129.6, 128.8, 128.3, 128.2, 127.4, 127.3, 125.8, 124.8, 124.2, 121.8, 120.8, 119.1, 116.2, 107.5, 72.1, 61.6, 30.5, 22.5, 22.2, 14.4.

HRMS (ESI+) Calcd. For $C_{28}H_{26}ClN_2O_3^+$ ($[M+H]^+$): 473.1626, found: 473.1624.

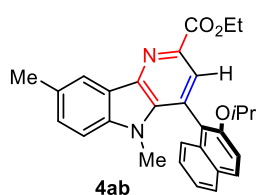


Ethyl 4-(2-isopropoxynaphthalen-1-yl)-8-methoxy-5-methyl-5H-pyrido[3,2-b]indole-2-carboxylate: White solid; 87% yield.

¹H NMR (400 MHz, Chloroform-d) δ 8.11 (d, J = 10.6 Hz, 2H), 7.98 (d, J = 9.0 Hz, 1H), 7.88 (d, J = 7.9 Hz, 1H), 7.46 – 7.15 (m, 6H), 4.65 – 4.44 (m, 3H), 3.99 (s, 3H), 3.19 (s, 3H), 1.47 (t, J = 7.0 Hz, 3H), 1.10 (d, J = 6.1 Hz, 3H), 1.07 (d, J = 6.4 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-d) δ 166.3, 154.6, 153.3, 142.4, 139.0, 138.2, 135.6, 133.8, 130.5, 128.8, 128.1, 127.3, 127.0, 125.5, 125.0, 124.2, 122.4, 121.0, 118.7, 116.3, 110.0, 103.3, 72.0, 61.6, 56.1, 30.3, 22.5, 22.2, 14.5.

HRMS (ESI+) Calcd. For C₂₉H₂₉N₂O₄⁺ ([M+H]⁺): 469.2122, found: 469.2119.

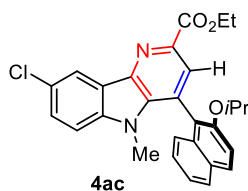


Ethyl 4-(2-isopropoxynaphthalen-1-yl)-5,8-dimethyl-5H-pyrido[3,2-b]indole-2-carboxylate: White solid; 80% yield.

¹H NMR (400 MHz, Chloroform-d) δ 8.46 (s, 1H), 8.10 (s, 1H), 7.98 (d, J = 9.0 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.45 – 7.29 (m, 4H), 7.22 (dd, J = 8.3, 3.3 Hz, 2H), 4.62 – 4.46 (m, 3H), 3.19 (s, 3H), 2.57 (s, 3H), 1.47 (t, J = 7.1 Hz, 3H), 1.09 (d, J = 6.1 Hz, 3H), 1.06 (d, J = 6.0 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-d) δ 166.3, 153.3, 142.5, 141.6, 139.2, 135.4, 133.8, 130.4, 130.0, 129.8, 128.8, 128.1, 127.2, 126.7, 125.6, 125.0, 124.2, 122.2, 121.8, 121.1, 116.3, 108.7, 72.0, 61.5, 30.2, 22.5, 22.2, 21.3, 14.5.

HRMS (ESI+) Calcd. For C₂₉H₂₉N₂O₃⁺ ([M+H]⁺): 453.2173, found: 453.2168.

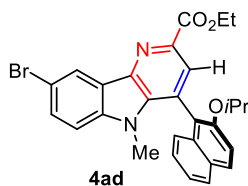


Ethyl 8-chloro-4-(2-isopropoxynaphthalen-1-yl)-5-methyl-5H-pyrido[3,2-b]indole-2-carboxylate: White solid; 81% yield.

¹H NMR (400 MHz, Chloroform-d) δ 8.62 (d, $J = 2.0$ Hz, 1H), 8.13 (s, 1H), 8.00 (d, $J = 9.1$ Hz, 1H), 7.89 (d, $J = 7.8$ Hz, 1H), 7.52 (dd, $J = 8.7, 2.1$ Hz, 1H), 7.43 – 7.30 (m, 3H), 7.26 (d, $J = 8.7$ Hz, 1H), 7.21 (d, $J = 8.4$ Hz, 1H), 4.64 – 4.47 (m, 3H), 3.21 (s, 3H), 1.47 (t, $J = 7.1$ Hz, 3H), 1.10 (d, $J = 6.0$ Hz, 3H), 1.06 (d, $J = 6.0$ Hz, 3H).

¹³C NMR (101 MHz, Chloroform-d) δ 166.1, 153.3, 141.6, 141.5, 140.0, 135.7, 133.7, 130.7, 128.8, 128.4, 128.2, 127.6, 127.4, 126.23, 126.19, 124.8, 124.2, 123.2, 121.6, 120.5, 116.1, 110.1, 72.0, 61.7, 30.4, 22.5, 22.2, 14.5.

HRMS (ESI+) Calcd. For $C_{28}H_{26}ClN_2O_3^+$ ($[M+H]^+$): 473.1626, found: 473.1620.

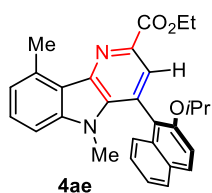


Ethyl 8-bromo-4-(2-isopropoxynaphthalen-1-yl)-5-methyl-5H-pyrido[3,2-b]indole-2-carboxylate: White solid; 86% yield.

¹H NMR (400 MHz, Chloroform-d) δ 8.77 (s, 1H), 8.13 (s, 1H), 8.00 (d, $J = 9.0$ Hz, 1H), 7.89 (d, $J = 7.9$ Hz, 1H), 7.65 (d, $J = 8.3$ Hz, 1H), 7.45 – 7.30 (m, 3H), 7.24 – 7.17 (m, 2H), 4.66 – 4.42 (m, 3H), 3.20 (s, 3H), 1.47 (t, $J = 7.0$ Hz, 3H), 1.10 (d, $J = 6.0$ Hz, 3H), 1.06 (d, $J = 6.0$ Hz, 3H).

¹³C NMR (101 MHz, Chloroform-d) δ 166.1, 153.3, 141.8, 141.4, 140.1, 135.6, 133.7, 131.0, 130.7, 128.8, 128.2, 127.6, 127.4, 126.2, 124.8, 124.6, 124.2, 123.8, 120.5, 116.1, 113.5, 110.6, 72.0, 61.7, 30.4, 22.5, 22.2, 14.5.

HRMS (ESI+) Calcd. For $C_{28}H_{26}BrN_2O_3^+$ ($[M+H]^+$): 517.1121, found: 517.1116.

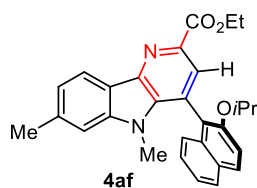


Ethyl 4-(2-isopropoxynaphthalen-1-yl)-5,9-dimethyl-5H-pyrido[3,2-b]indole-2-carboxylate: White solid; 99% yield.

¹H NMR (400 MHz, Chloroform-d) δ 8.09 (s, 1H), 7.97 (d, $J = 9.1$ Hz, 1H), 7.87 (d, $J = 8.1$ Hz, 1H), 7.46 – 7.44 (m, 1H), 7.42 – 7.33 (m, 2H), 7.31 – 7.27 (m, 1H), 7.21 – 7.13 (m, 3H), 4.61 – 4.44 (m, 3H), 3.26 (s, 3H), 3.19 (s, 3H), 1.46 (t, $J = 7.1$ Hz, 3H), 1.09 (d, $J = 6.1$ Hz, 3H), 1.06 (d, $J = 6.0$ Hz, 3H).

¹³C NMR (101 MHz, Chloroform-d) δ 166.5, 153.3, 144.0, 143.5, 139.3, 136.0, 135.1, 133.9, 130.4, 128.8, 128.1, 127.8, 127.2, 126.2, 125.1, 125.0, 124.2, 122.1, 121.4, 120.4, 116.3, 106.2, 72.0, 61.3, 30.2, 22.5, 22.2, 19.5, 14.4.

HRMS (ESI+) Calcd. For $C_{29}H_{29}N_2O_3^+$ ($[M+H]^+$): 453.2173, found: 453.2167.

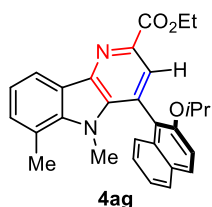


Ethyl 4-(2-isopropoxynaphthalen-1-yl)-5,7-dimethyl-5H-pyrido[3,2-b]indole-2-carboxylate: White solid; 92% yield.

¹H NMR (400 MHz, Chloroform-d) δ 8.51 (d, $J = 8.0$ Hz, 1H), 8.08 (s, 1H), 7.98 (d, $J = 9.1$ Hz, 1H), 7.88 (d, $J = 8.0$ Hz, 1H), 7.43 – 7.28 (m, 3H), 7.21 (d, $J = 8.5$ Hz, 2H), 7.13 (s, 1H), 4.62 – 4.46 (m, 3H), 3.18 (s, 3H), 2.56 (s, 3H), 1.47 (t, $J = 7.1$ Hz, 3H), 1.10 (d, $J = 6.1$ Hz, 3H), 1.06 (d, $J = 6.0$ Hz, 3H).

¹³C NMR (101 MHz, Chloroform-d) δ 166.4, 153.3, 143.8, 142.9, 139.3, 139.0, 135.3, 133.8, 130.5, 128.8, 128.1, 127.2, 126.6, 125.4, 125.0, 124.2, 122.1, 121.7, 121.2, 119.8, 116.3, 109.2, 72.0, 61.5, 30.1, 22.5, 22.4, 22.2, 14.5.

HRMS (ESI+) Calcd. For $C_{29}H_{29}N_2O_3^+$ ($[M+H]^+$): 453.2173, found: 453.2170.

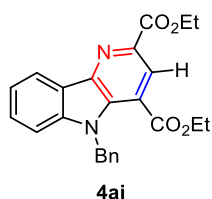


Ethyl 4-(2-isopropoxynaphthalen-1-yl)-5,6-dimethyl-5H-pyrido[3,2-b]indole-2-carboxylate: White solid; 89% yield.

¹H NMR (400 MHz, Chloroform-d) δ 8.51 (d, $J = 7.2$ Hz, 1H), 8.09 (s, 1H), 7.97 (d, $J = 9.1$ Hz, 1H), 7.88 (d, $J = 7.8$ Hz, 1H), 7.43 – 7.19 (m, 6H), 4.67 – 4.45 (m, 3H), 3.49 (s, 3H), 2.71 (s, 3H), 1.46 (t, $J = 7.1$ Hz, 3H), 1.14 (d, $J = 6.0$ Hz, 3H), 1.08 (d, $J = 6.0$ Hz, 3H).

¹³C NMR (101 MHz, Chloroform-d) δ 166.3, 153.1, 143.1, 142.3, 139.6, 136.1, 133.6, 131.9, 130.4, 128.8, 128.1, 127.3, 127.0, 126.1, 125.0, 124.2, 123.3, 121.4, 121.0, 120.7, 120.0, 116.2, 71.9, 61.5, 33.6, 22.5, 22.2, 20.6, 14.5.

HRMS (ESI+) Calcd. For C₂₉H₂₉N₂O₃⁺ ([M+H]⁺): 453.2173, found: 453.2170.



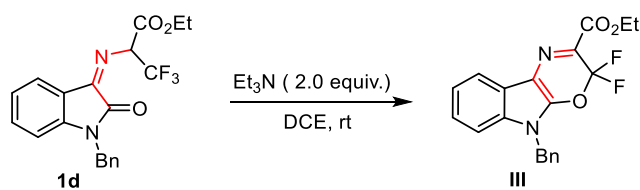
Diethyl 5-benzyl-5H-pyrido[3,2-b]indole-2,4-dicarboxylate: It was obtained through the Diels-Alder reaction between the intermediate **III** with methyl propiolate. Yellow solid; 93% yield.

¹H NMR (400 MHz, Chloroform-d) δ 8.65 – 8.54 (m, 1H), 8.44 (s, 1H), 7.66 – 7.55 (m, 1H), 7.47 (d, $J = 8.3$ Hz, 1H), 7.45 – 7.39 (m, 1H), 7.23 – 7.16 (m, 3H), 6.95 – 6.88 (m, 2H), 5.82 (s, 2H), 4.54 (q, $J = 7.1$ Hz, 2H), 4.25 (q, $J = 7.2$ Hz, 2H), 1.50 (t, $J = 7.1$ Hz, 3H), 1.21 (t, $J = 7.2$ Hz, 3H).

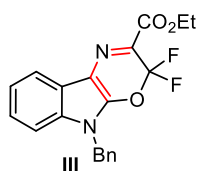
¹³C NMR (101 MHz, Chloroform-d) δ 165.9, 165.5, 145.3, 144.0, 139.4, 136.4, 131.9, 129.6, 128.8, 127.5, 126.1, 122.2, 122.2, 122.1, 121.9, 121.7, 110.1, 62.3, 61.9, 48.6, 14.5, 13.9.

HRMS (ESI+) Calcd. For C₂₄H₂₃N₂O₄⁺ ([M+H]⁺): 403.1651, found: 403.1641.

4. General procedure for synthesis of intermediate III



In a 25 mL nitrogen-filled dry Schlenk tube, isatin-activated ketoimine ester **1d** (0.2 mmol), Et₃N (0.4 mmol) and degassed DCE (2 mL) were added. The reaction was stirred for 12 h at room temperature 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 compound **III**.



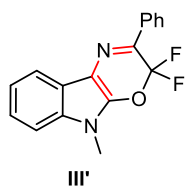
Ethyl 5-benzyl-3,3-difluoro-3,5-dihydro-[1,4]oxazino[2,3-b]indole-2-carboxylate: Green solid; 99% yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.95 (d, $J = 7.7$ Hz, 1H), 7.37 – 7.27 (m, 4H), 7.26 – 7.20 (m, 4H), 5.31 (s, 2H), 4.47 (q, $J = 7.1$ Hz, 2H), 1.44 (t, $J = 7.1$ Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 161.0, 140.3, 134.5, 132.5, 129.2, 128.5 (t, $J = 29.8$ Hz), 128.4, 127.1, 123.5, 123.2, 121.8, 118.4, 117.7 (t, $J = 269.7$ Hz), 110.6, 107.6, 62.1, 45.8, 14.3.

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -47.10.

HRMS (ESI+) Calcd. For C₂₀H₁₇F₂N₂O₃⁺ ([M+H]⁺): 371.1202, found: 371.1196.



3,3-difluoro-5-methyl-2-phenyl-3,5-dihydro-[1,4]oxazino[2,3-b]indole: It was obtained through using ethyl (*Z*)-2-((1-methyl-2-oxoindolin-3-ylidene)amino)-2-phenylacetate as the substrate. Yellow solid; 75% yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.06 – 8.00 (m, 2H), 7.91 – 7.85 (m, 1H), 7.48 – 7.41

(m, 3H), 7.30 – 7.21 (m, 3H), 3.68 (s, 3H).

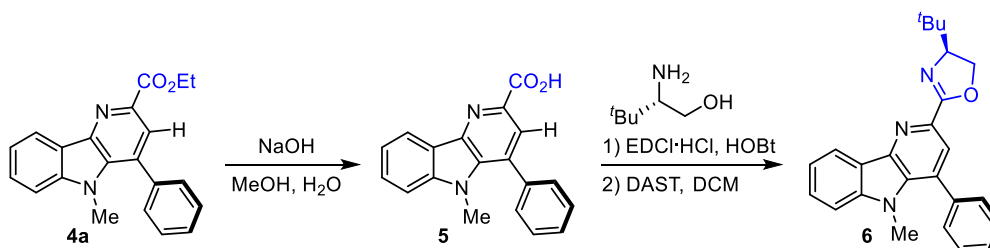
^{13}C NMR (101 MHz, Chloroform-d) δ 139.5 (t, J = 29.4 Hz), 138.3, 133.1, 132.1, 129.9, 128.6, 127.4, 122.0, 121.8, 118.3 (t, J = 267.8 Hz), 117.5, 109.4, 106.5, 27.81.

^{19}F NMR (376 MHz, Chloroform-d) δ -49.70.

HRMS (ESI+) Calcd. For $\text{C}_{17}\text{H}_{13}\text{F}_2\text{N}_2\text{O}^+$ ($[\text{M}+\text{H}]^+$): 299.0990, found: 299.0981.

5. Synthetic application

(a) General procedure for synthesis of Py-box-type ligand **6**

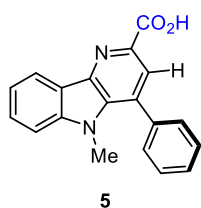


Compound **6** was synthesized according to reported procedure.⁴

Step 1, To a stirred suspension of **4a** (1 mmol) was added methanol (10 mL). Aqueous sodium hydroxide solution (3 mL, 1 M) was added dropwise at 0 °C. The heterogeneous mixture was immersed in a preheated oil bath (50 °C) and was stirred until the full consumption of the starting material was detected by thin layer chromatography (TLC). The mixture was concentrated under vacuum to remove methanol, and was adjusted to pH 6-7 with hydrochloric acid, from which the acid (intermediate **5**) was precipitated, the heterogeneous mixture was filtered, and the intermediate **5** was collected and dried as a white solid in 66% yield.

Step 2, To a dried Schlenk flask charged with **5** (1 mmol) and the chiral amino alcohol (1 mmol), was added anhydrous dichloromethane (5 mL) for dissolution. Hydroxybenzotriazole (HOBt) (175 mg, 1.3 mmol) and *N*-(3-(dimethyl amino)propyl)-*N'*-ethylcarbodiimide hydrochloride (EDCI·HCl) (0.25 g, 1.3 mmol) were then added while the reaction flask was in an ice bath. The mixture was allowed to gradually warm to room temperature, and it was stirred overnight until full consumption of the acid detected by TLC. The mixture was quenched by the addition of a saturated aqueous solution of NaHCO_3 (20 mL) and separated. The water phase was extracted with dichloromethane (10 mL \times 3), and the combined organic phase was sequentially washed with water (10 mL \times 2) and saturated aqueous NaCl (10 mL), dried over anhydrous sodium sulfate, and concentrated under vacuum. Purification by silica gel column

chromatography with hexane/EtOAc (2:1, v/v) as the eluent gave the amide intermediate. To a Schlenk tube charged the amide intermediate (1 mmol) was added anhydrous DCM (5.0 mL) under N₂ atmosphere. Diethylaminosulfur trifluoride (DAST) (160 mg, 1mmol) was added dropwise at -78 °C. The reaction mixture was stirred at -78 °C until the full consumption of the starting material was detected by TLC. The mixture was quenched by the addition of a saturated aqueous solution of NaHCO₃ (10 mL) and separated. The water phase was extracted with dichloromethane (10 mL × 3), and the combined organic phase was sequentially washed with water (10 mL × 2) and saturated aqueous NaCl (10 mL), dried over anhydrous sodium sulfate, and concentrated under vacuum, which was purified by silica gel column chromatography with PE/EA (2:1, v/v) as the eluent to give the chiral ligand **6** as a white solid in 52% yield.

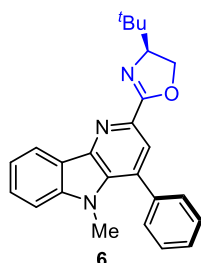


5-methyl-4-phenyl-5H-pyrido[3,2-b]indole-2-carboxylic acid: White solid; 66% yield.

¹H NMR (400 MHz, Chloroform-d) δ 8.41 (d, *J* = 7.8 Hz, 1H), 8.19 (s, 1H), 7.72 – 7.63 (m, 1H), 7.58 – 7.38 (m, 7H), 3.49 (s, 3H).

¹³C NMR (101 MHz, Chloroform-d) δ 165.3, 143.9, 141.3, 137.3, 136.7, 134.4, 133.8, 129.4, 129.3, 128.9, 128.5, 122.4, 121.3, 121.3, 121.05, 109.7, 32.7.

HRMS (ESI+) Calcd. For C₁₉H₁₅N₂O₂⁺ ([M+H]⁺): 303.1128, found: 303.1126.



(S)-4-(tert-butyl)-2-(5-methyl-4-phenyl-5H-pyrido[3,2-b]indol-2-yl)-4,5-dihydrooxazole:

White solid; 52% yield.

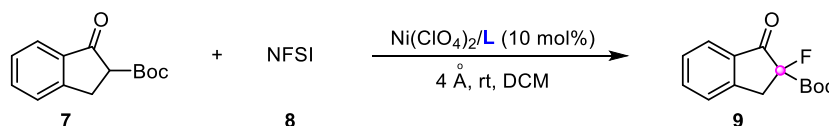
¹H NMR (400 MHz, Chloroform-d) δ 8.57 (d, *J* = 7.8 Hz, 1H), 8.14 (s, 1H), 7.61 – 7.55 (m, 1H), 7.55 – 7.46 (m, 5H), 7.42 – 7.32 (m, 2H), 4.55 (t, *J* = 9.4 Hz, 1H), 4.40 (t, *J* = 8.4 Hz, 1H),

4.16 (dd, $J = 10.1, 8.1$ Hz, 1H), 3.44 (s, 3H), 1.00 (s, 9H).

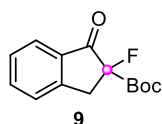
^{13}C NMR (101 MHz, Chloroform- d) δ 163.5, 143.3, 142.6, 138.3, 137.4, 132.9, 132.6, 129.6, 128.5, 128.3, 128.3, 123.1, 122.0, 121.9, 120.4, 109.1, 76.3, 69.4, 34.1, 32.5, 26.0.

HRMS (ESI+) Calcd. For $\text{C}_{25}\text{H}_{26}\text{N}_3\text{O}^+$ ($[\text{M}+\text{H}]^+$): 384.2070, found: 384.2063.

(b) General procedure for synthesis of compound **9**



Compound **9** was synthesized according to reported procedure.⁵ In a 25 mL dry Schlenk tube, ligand **6** (or *t*Bu-Pyrbox) (0.02 mmol), $\text{Ni}(\text{ClO}_4)_2$ (0.02 mmol), 50 mg 4 Å MS and DCM (1 mL) were added and stirred for 1 h at room temperature. Indanone **7** and NFSI was then added, and the reaction was stirred 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 product **9** as a colorless oil in 84% yield and 60% ee (10% ee using *t*Bu-Pybox as the ligand).



Tert-butyl 2-fluoro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate: Colorless oil; 84% yield and 60% ee (91% yield and 10% ee if *t*Bu-Pybox was used); $[\alpha]_{\text{D}}^{25} = -1.8$ (c 0.45, CHCl_3).

HPLC conditions: Chiralpak AD-H, isopropanol/hexane = 10:90, flow: 1.0 mL/min, $\lambda = 254$ nm, $t_{(\text{minor})} = 5.8$ min, $t_{(\text{major})} = 6.3$ min.

^1H NMR (400 MHz, Chloroform- d) δ 7.83 (d, $J = 7.7$ Hz, 1H), 7.75 – 7.62 (m, 1H), 7.54 – 7.40 (m, 2H), 3.73 (dd, $J = 17.5, 10.8$ Hz, 1H), 3.40 (dd, $J = 22.9, 17.5$ Hz, 1H), 1.43 (s, 9H).

^{13}C NMR (101 MHz, Chloroform- d) δ 195.8 (d, $J = 18.4$ Hz), 166.3 (d, $J = 27.3$ Hz), 151.0 (d, $J = 4.2$ Hz), 136.5, 133.6, 128.5, 126.5, 125.5, 94.4 (d, $J = 201.7$ Hz), 84.2, 38.3 (d, $J = 24.1$ Hz), 27.8.

^{19}F NMR (376 MHz, Chloroform- d) δ -163.94 – 164.03 (m).

HRMS (ESI+) Calcd. For $\text{C}_{14}\text{H}_{15}\text{FO}_3\text{Na}^+$ ($[\text{M}+\text{Na}]^+$): 273.0897, found: 273.0893.

6. Photophysical data

a) Absorption and emission spectra.

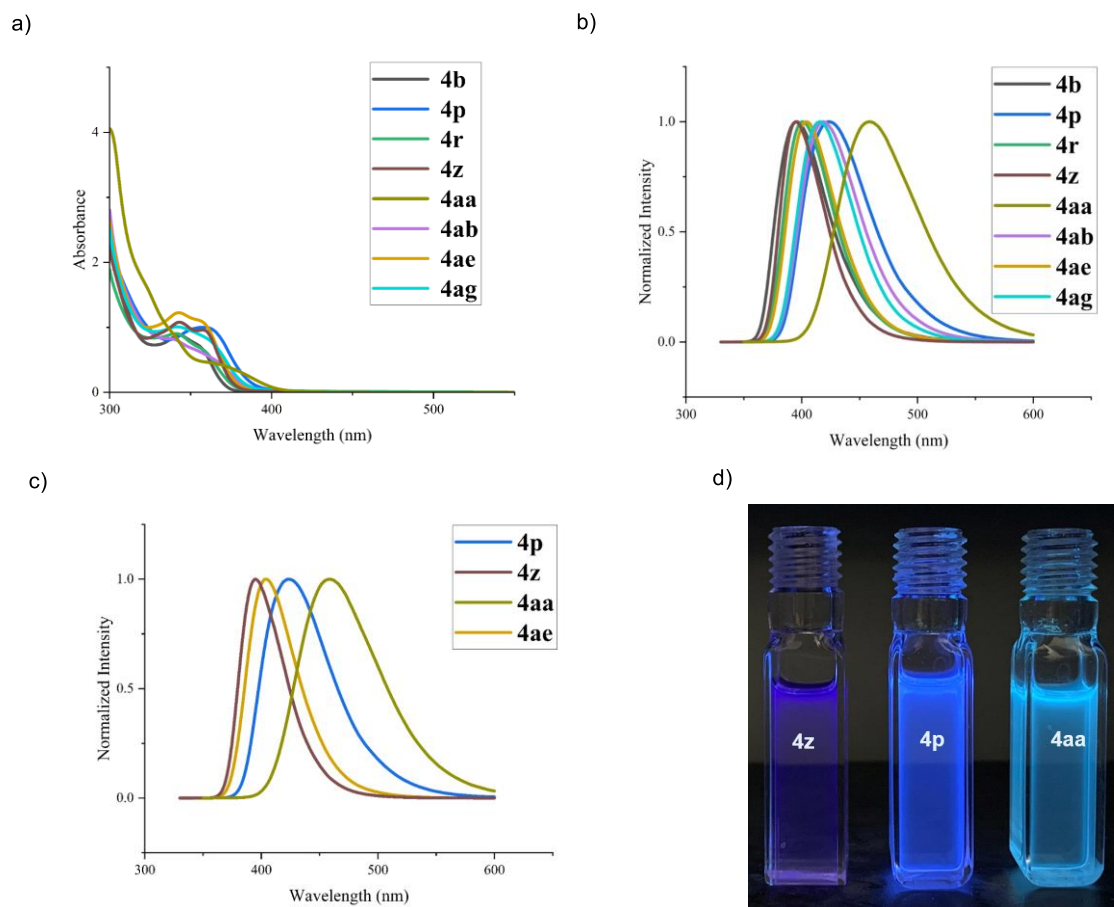


Figure S1. Compounds **4** was dissolved in DCM and diluted to 5×10^{-5} M. a) UV-Vis absorption spectra (slits: 0.5 nm). b) Fluorescence spectra ($\lambda_{\text{ex}} = 365$ nm, slits: 1 nm). c) Fluorescence spectra of **4p**, **4z**, **4aa** and **4ae**. d) Photographs of δ -carboline derivatives under irradiation with UV light ($\lambda_{\text{ex}} = 365$ nm) in DCM.

b) Emission spectra of metal ion recognition

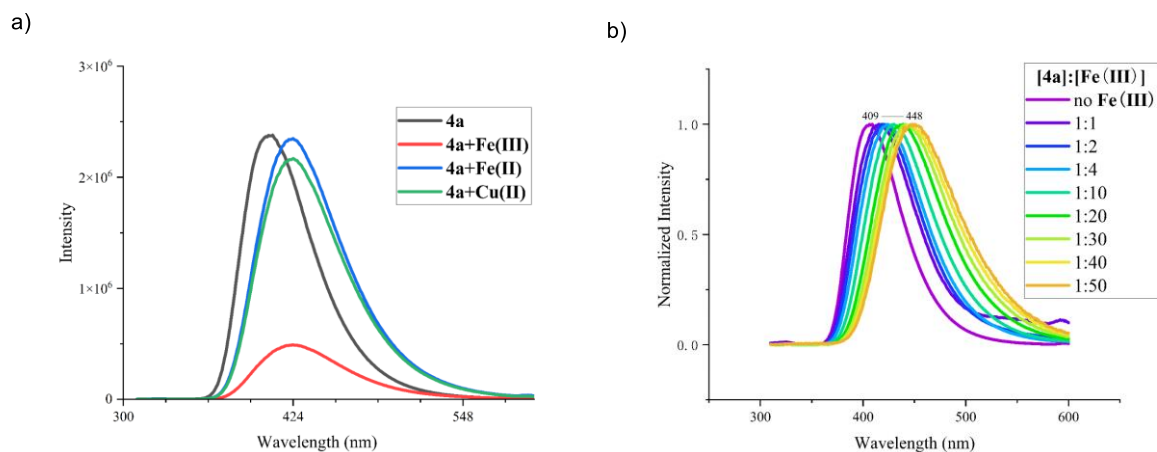


Figure S2. Fluorescence spectra ($\lambda_{\text{ex}} = 365$ nm, slits: 1 nm). a) The samples were prepared by mixing **4a** (50

μL , 5×10^{-3} M in CH_3CN) and metal precursors ($200 \mu\text{L}$, 5×10^{-3} M in CH_3CN) and diluted to 5 mL at 25 °C. b) The samples were prepared by mixing 1, 2, 4, 10, 20, 30, 40 and 50 equiv. of $\text{Fe}(\text{OTf})_3$ with **4a** ($50 \mu\text{L}$, 5×10^{-3} M in CH_3CN) and diluted to 5 mL.

7. X-ray Structure of **4a** and **III**

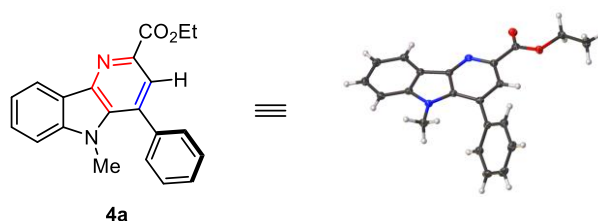


Figure S1. X-ray Structure of **4a**.

To a 10 mL oven-dried glass sample bottle was added 50 mg pure **4a** with DCM to get clear solution, then petroleum ether was slowly added to become muddy. The mixture solution was sealed with filter paper to slowly grow crystals at room temperature. Crystal data for **4a**: $\text{C}_{21}\text{H}_{18}\text{N}_2\text{O}_2$, $M_r = 330.37$, $T = 100$ K, orthorhombic, space group P -1, $a = 8.0404(2)$, $b = 9.2472(3)$, $c = 11.6115(4)$ Å, $V = 812.47(5)$ Å³, $Z = 2$. CCDC 2163875 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.

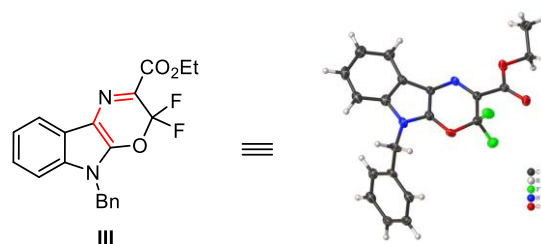


Figure S2. X-ray Structure of **III**.

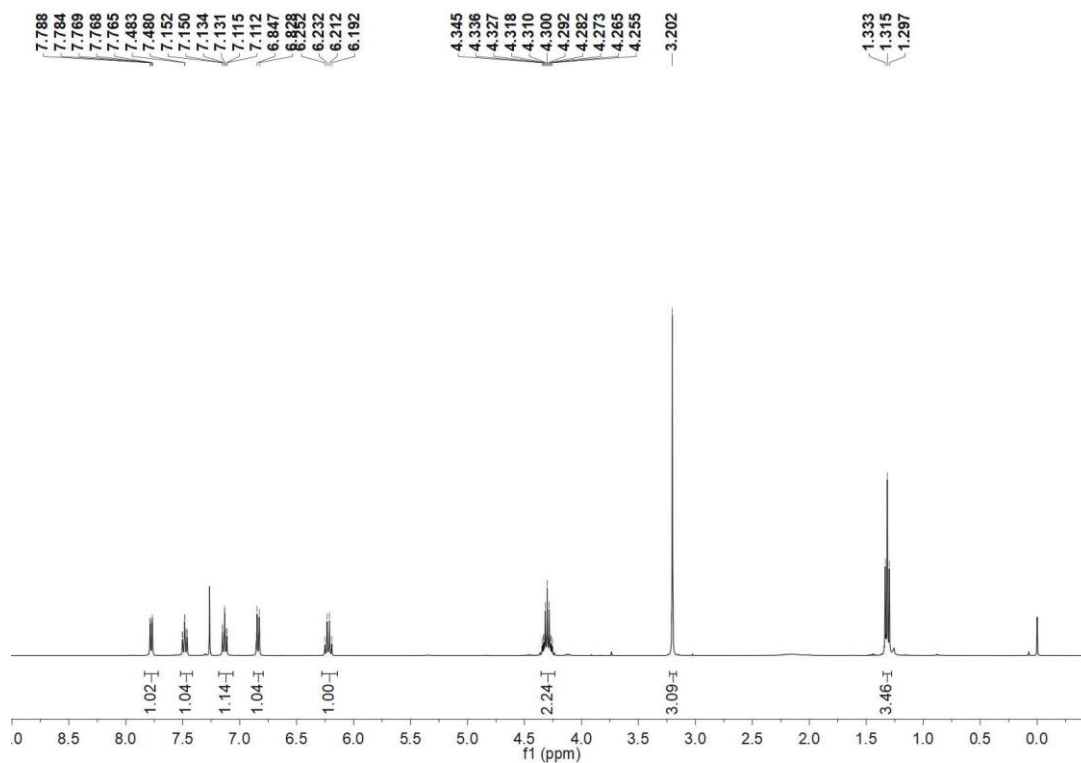
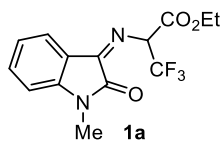
To a 10 mL oven-dried glass sample bottle was added 50 mg pure **III** with DCM to get clear solution, then petroleum ether was slowly added to become muddy. The mixture solution was sealed with filter paper to slowly grow crystals at room temperature. Crystal data for **III**: $\text{C}_{20}\text{H}_{16}\text{F}_2\text{N}_2\text{O}_3$, $M_r = 370.35$, $T = 100$ K, orthorhombic, space group P -1, $a = 108.139(6)$, $b = 90.02(2)$, $c = 107.606(2)$ Å, $V = 3403.1(4)$ Å³, $Z = 8$. CCDC 2163876 contains the

supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.

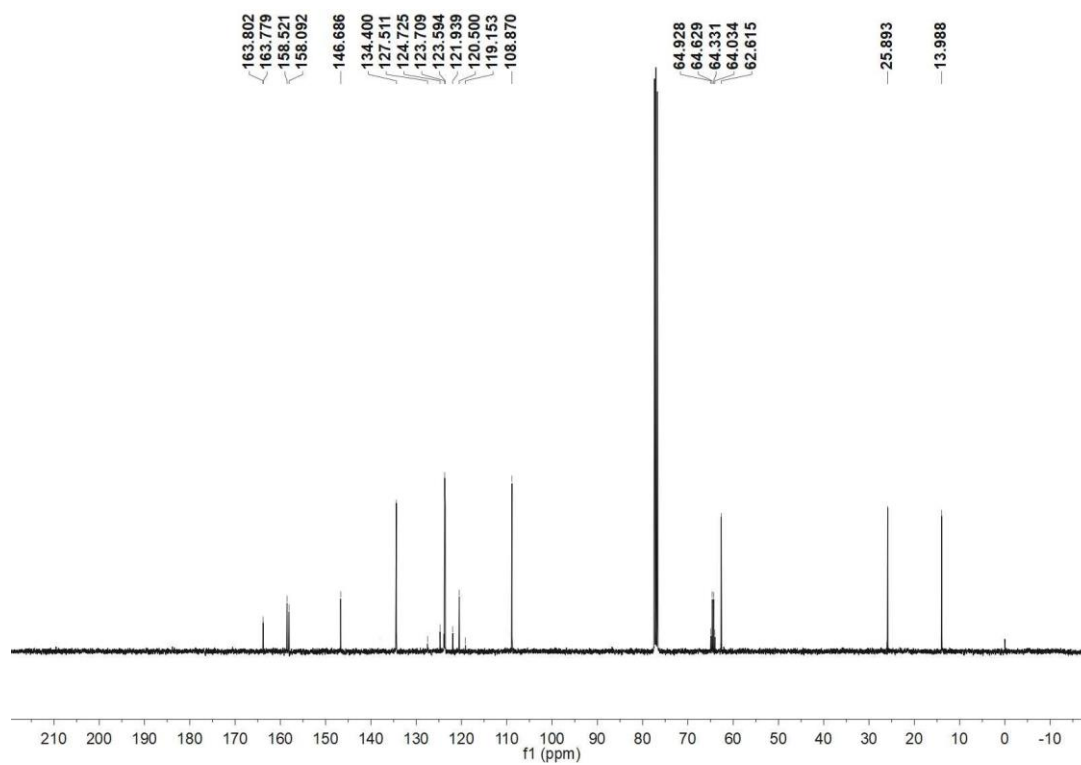
8. Reference

1. N. Kaila, K. Janz, A. Huang, A. Moretto, S. DeBernardo, P. W. Bedard, S. Tam, V. Clerin, J. C. Keith, D. H. H. Tsao, N. Sushkova, G. D. Shaw, R. T. Camphausen, R. G. Schaub, Q. Wang, *J. Med. Chem.* **2007**, *50*, 40-64.
2. Q. Ni, X. Wang, D. Zeng, Q. Wu, X. Song, *Org. Lett.* **2021**, *23*, 2273-2278.
3. X.-S. Sun, X.-H. Wang, H.-Y. Tao, L. Wei, C.-J. Wang, *Chem. Sci.* **2020**, *11*, 10984-10990.
4. J. Lai, W. Li, S. Wei, S. Li, *Org. Chem. Front.* **2020**, *7*, 2263-2268.
5. K. Shibatomi, Y. Tsuzuki, S.-i. Nakata, Y. Sumikawa, S. Iwasa, *Synlett.* **2007**, *2007*, 551.

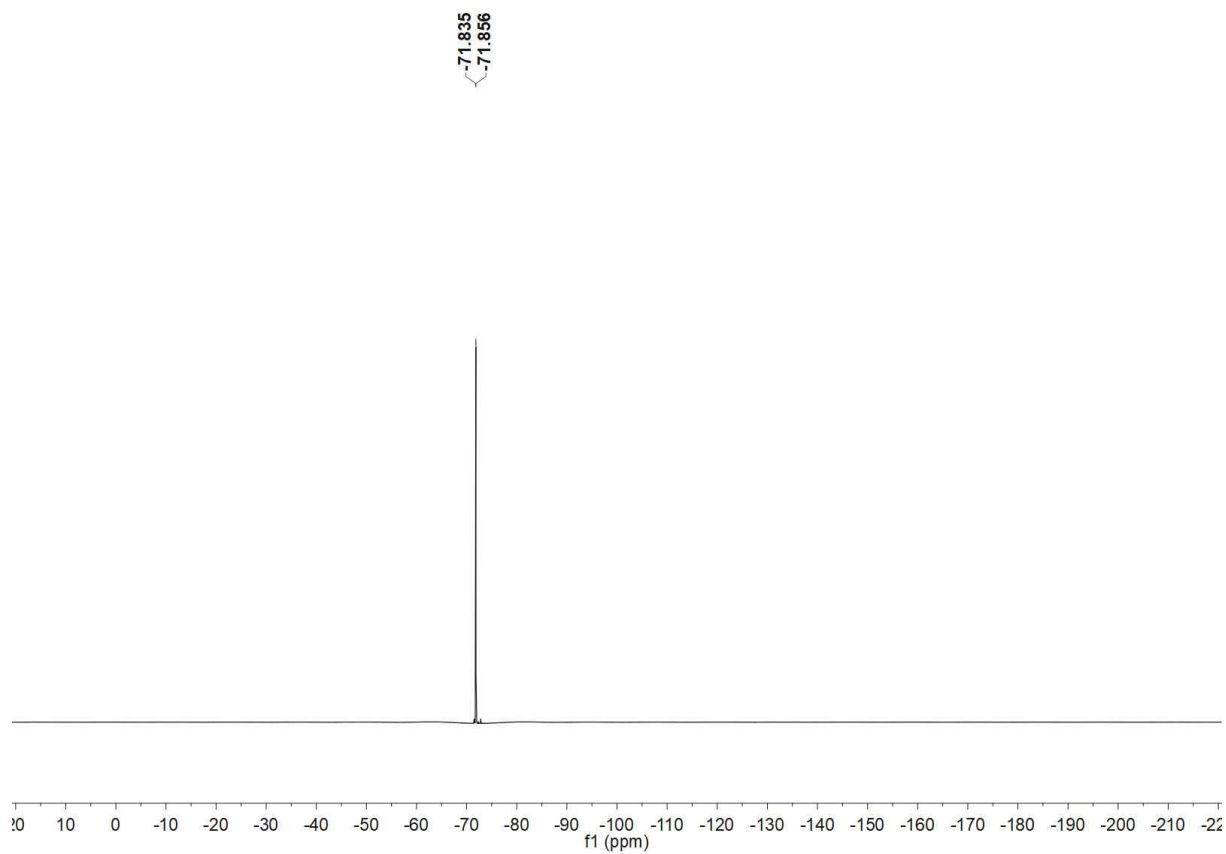
9. NMR and HPLC spectra



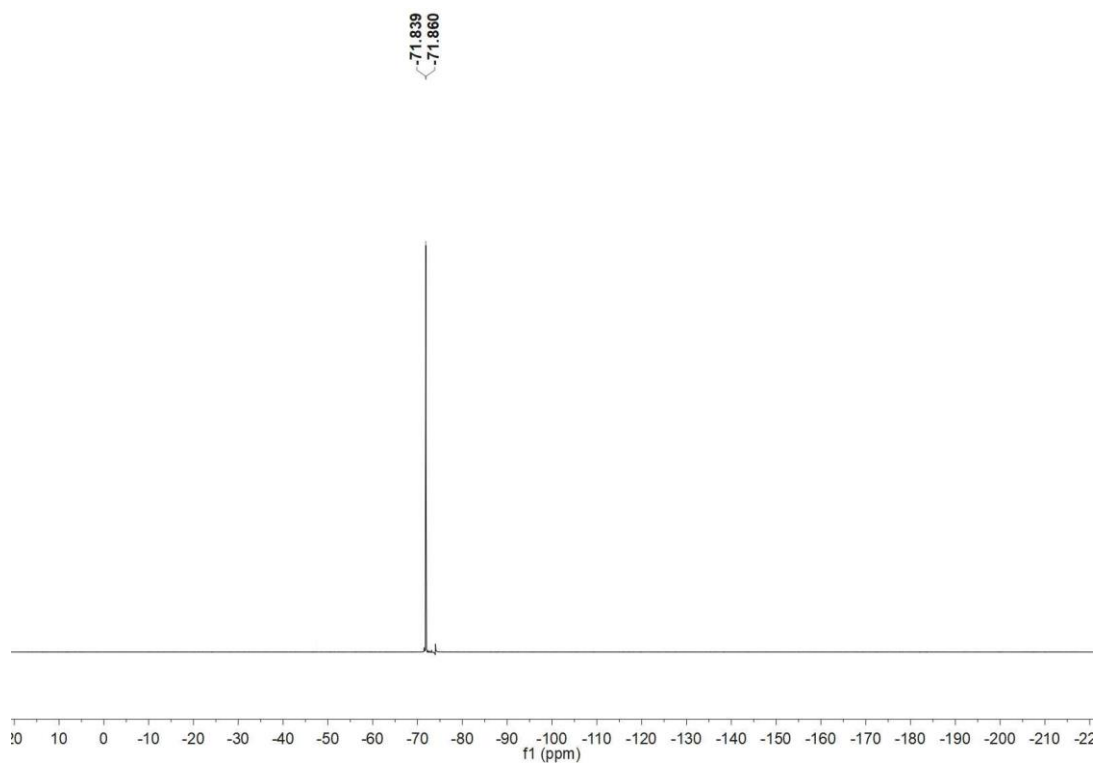
¹H NMR (400 MHz, Chloroform-d)



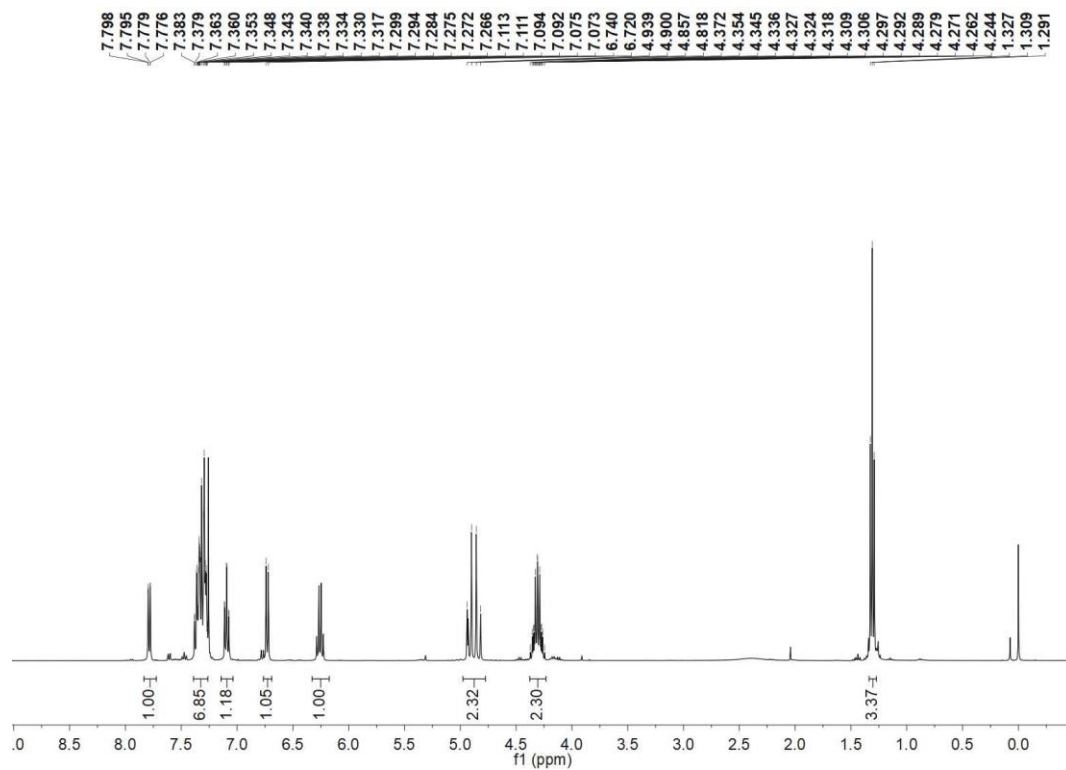
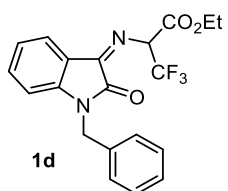
¹³C NMR (101 MHz, Chloroform-d)



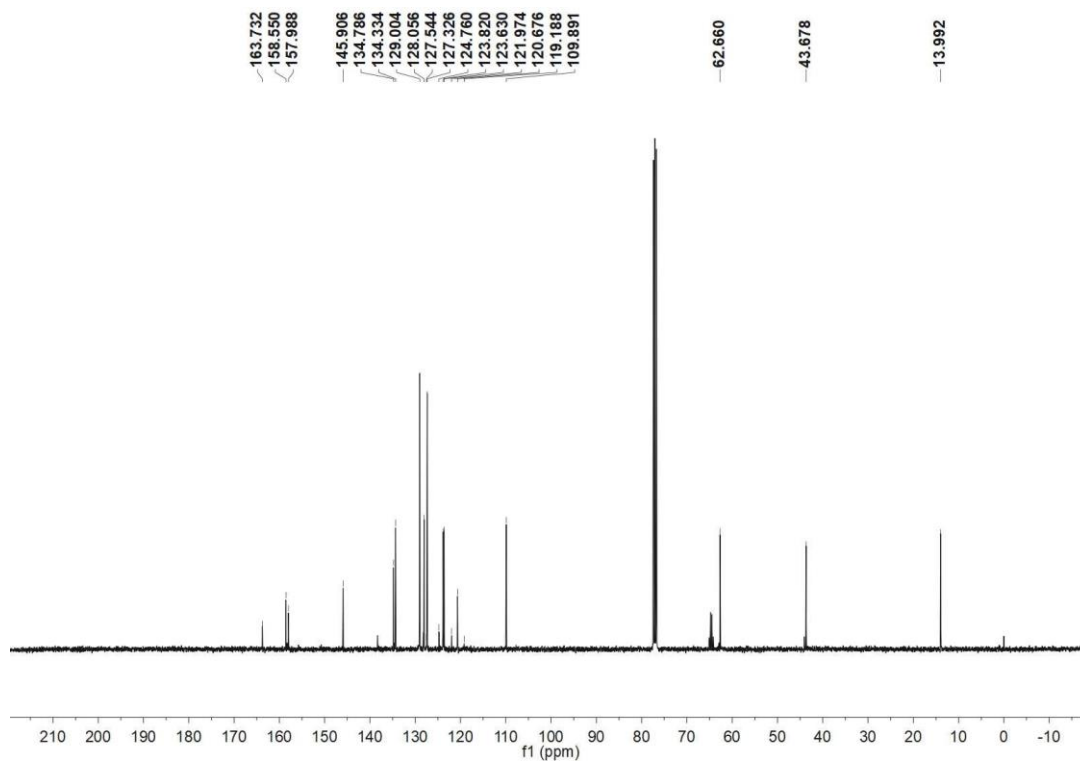
^{19}F NMR (376 MHz, Chloroform-d)



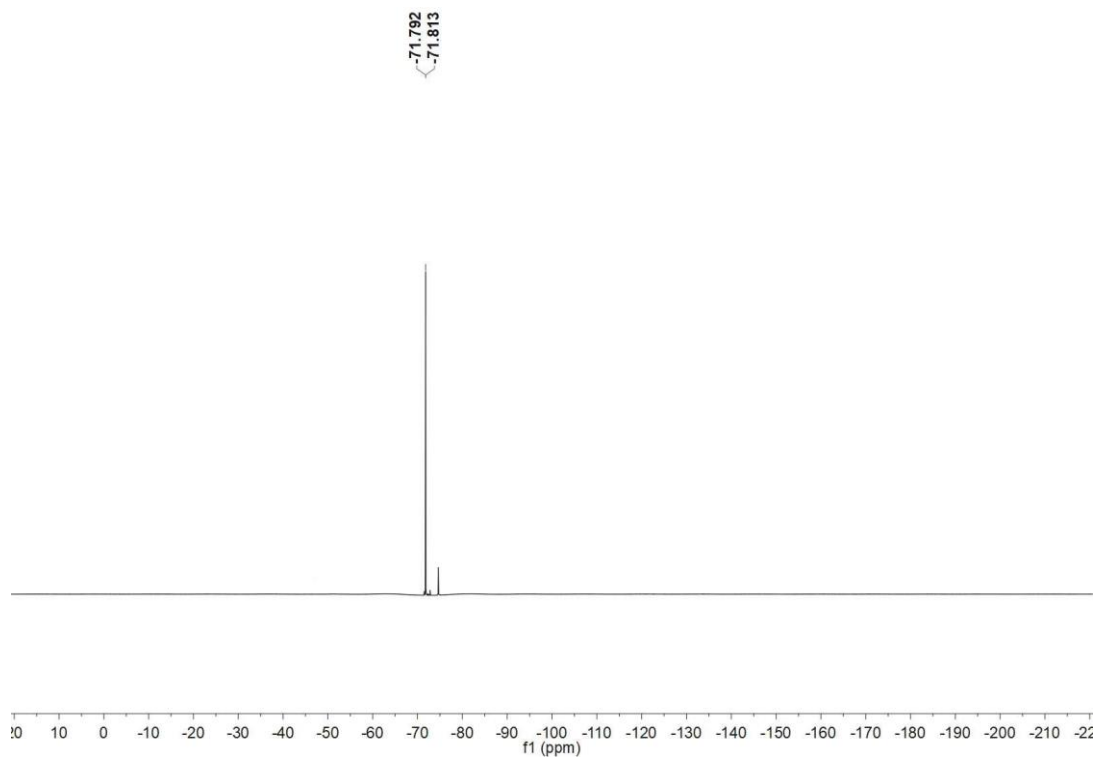
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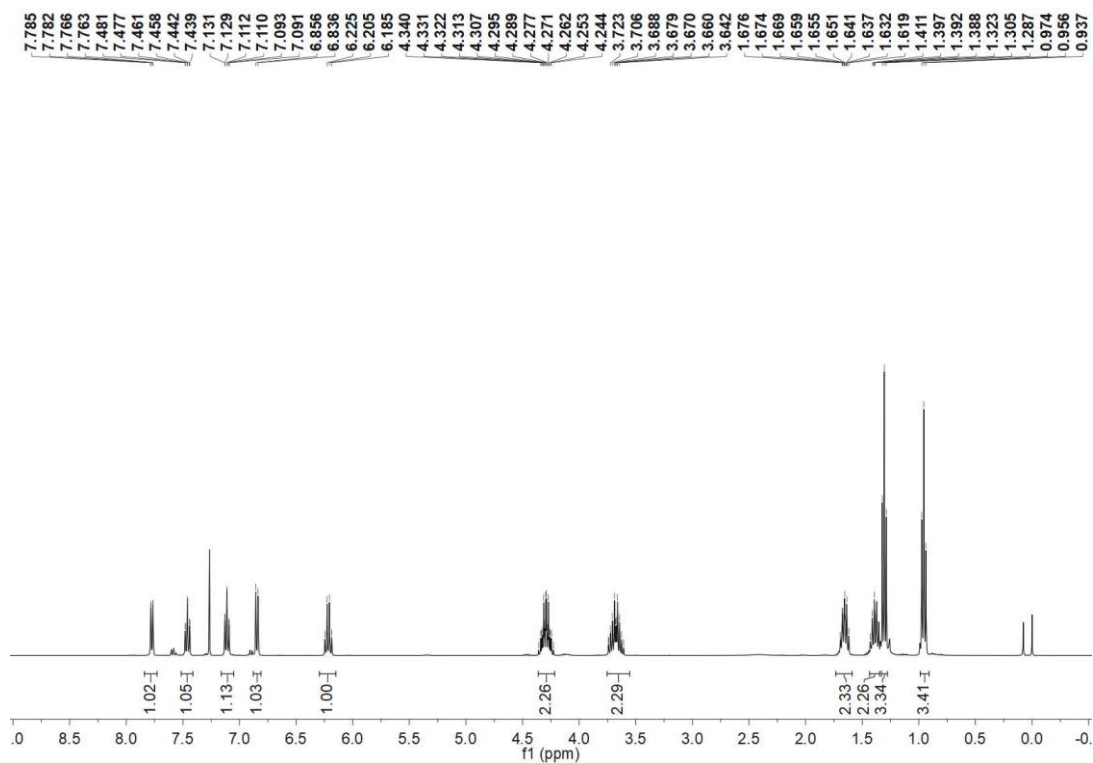
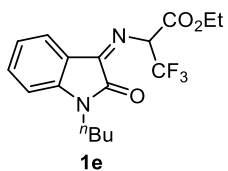
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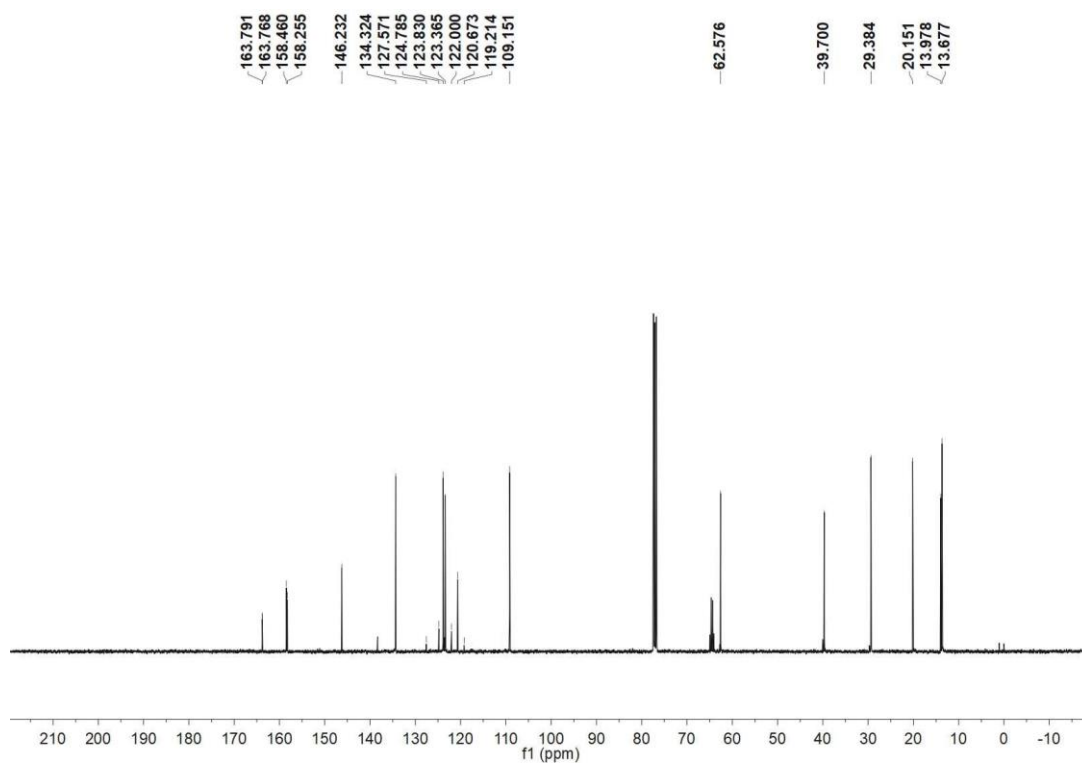
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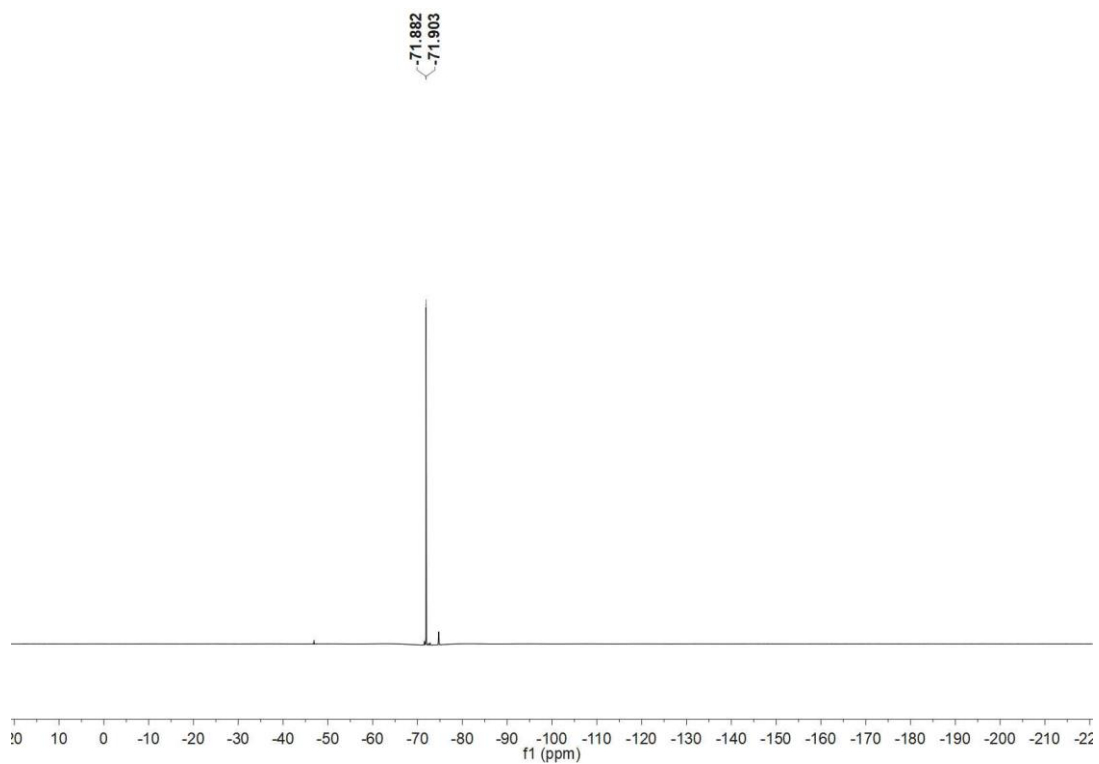
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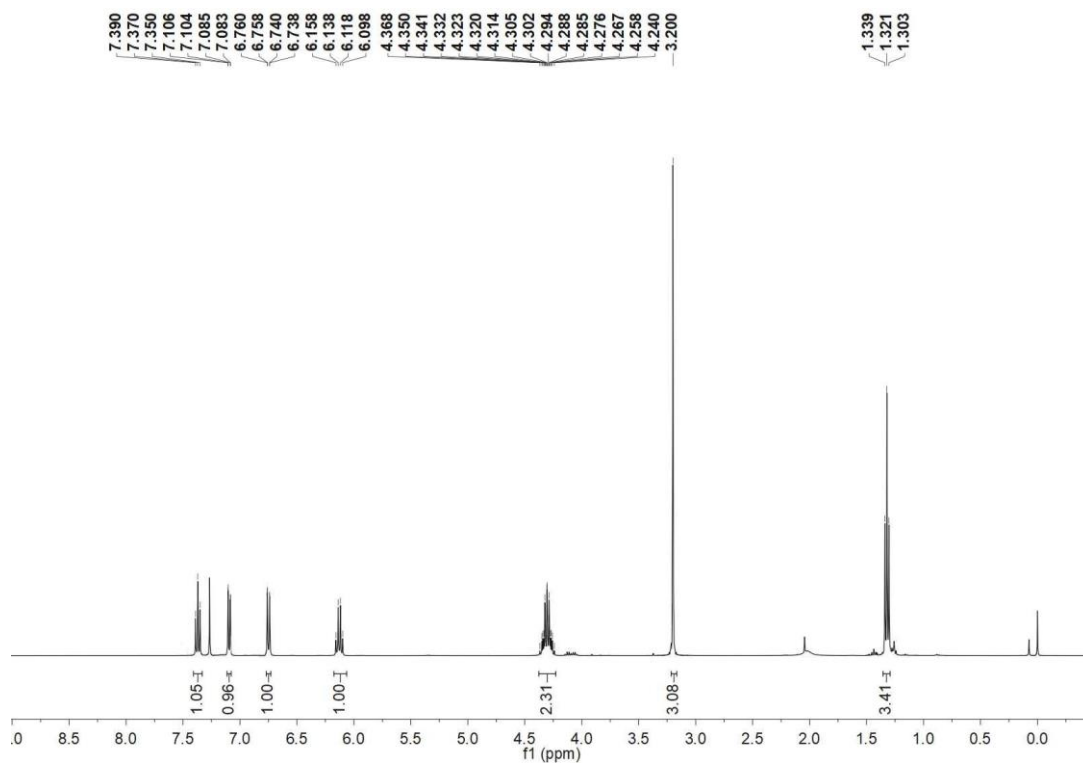
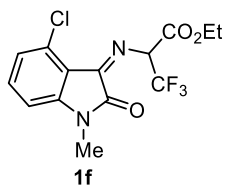
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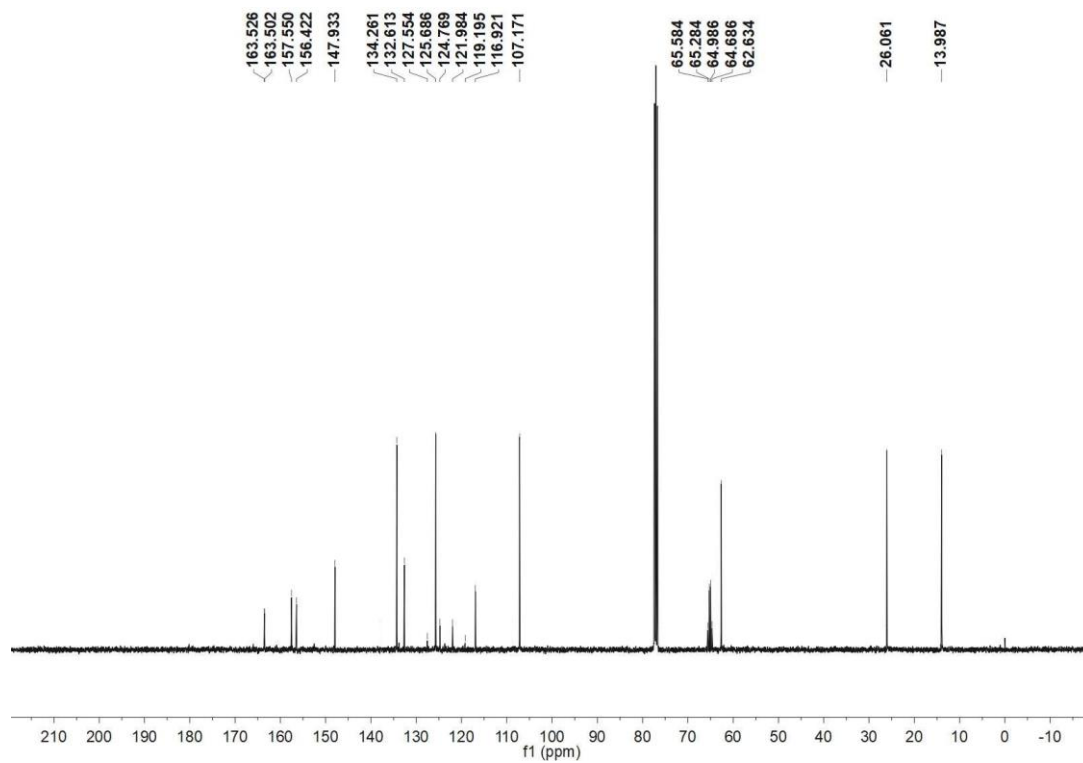
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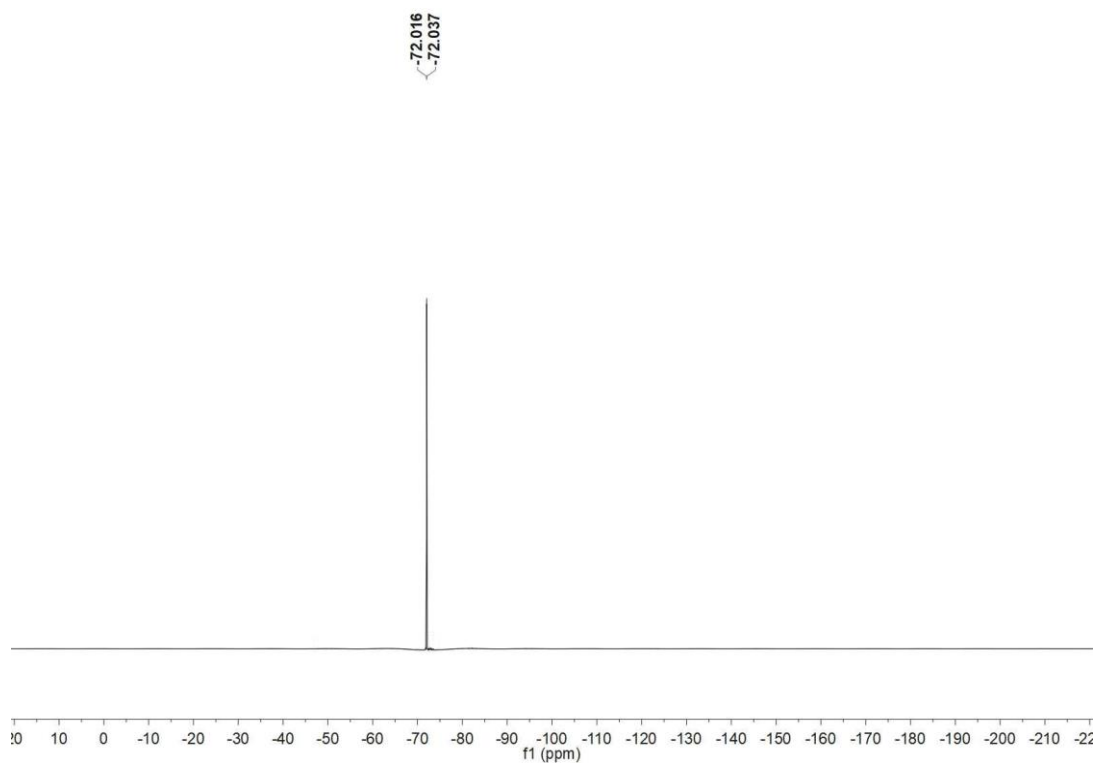
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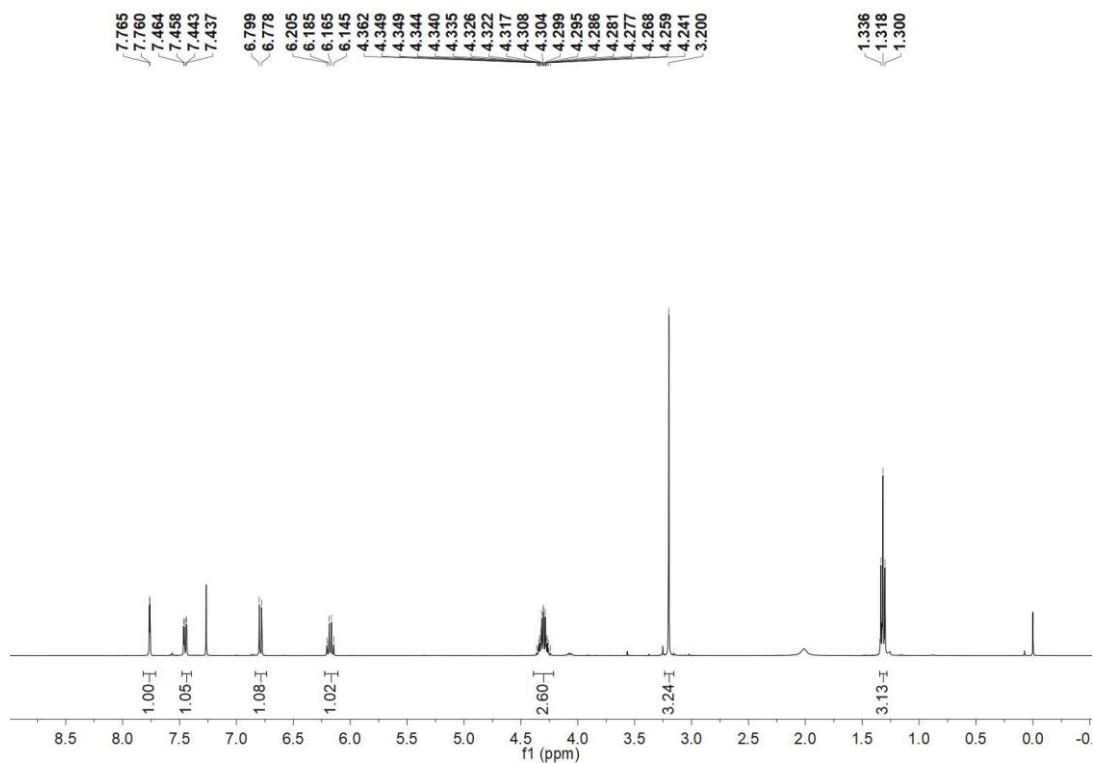
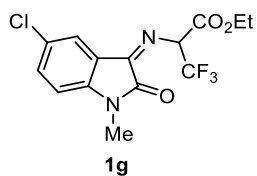
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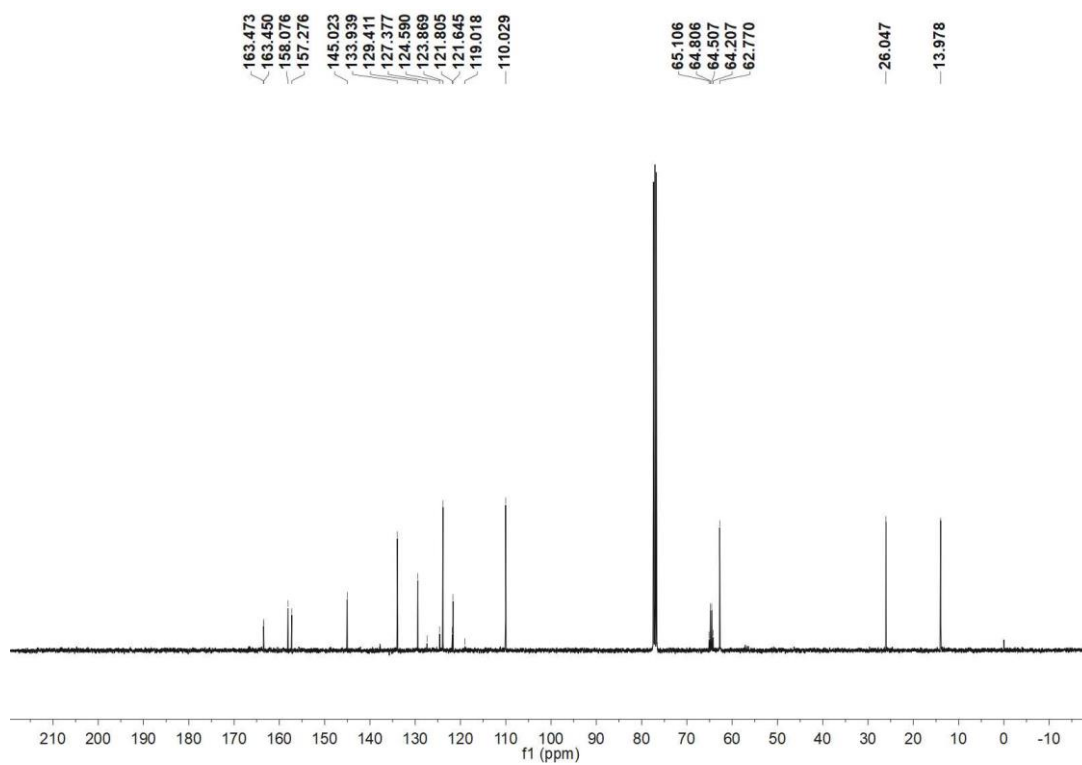
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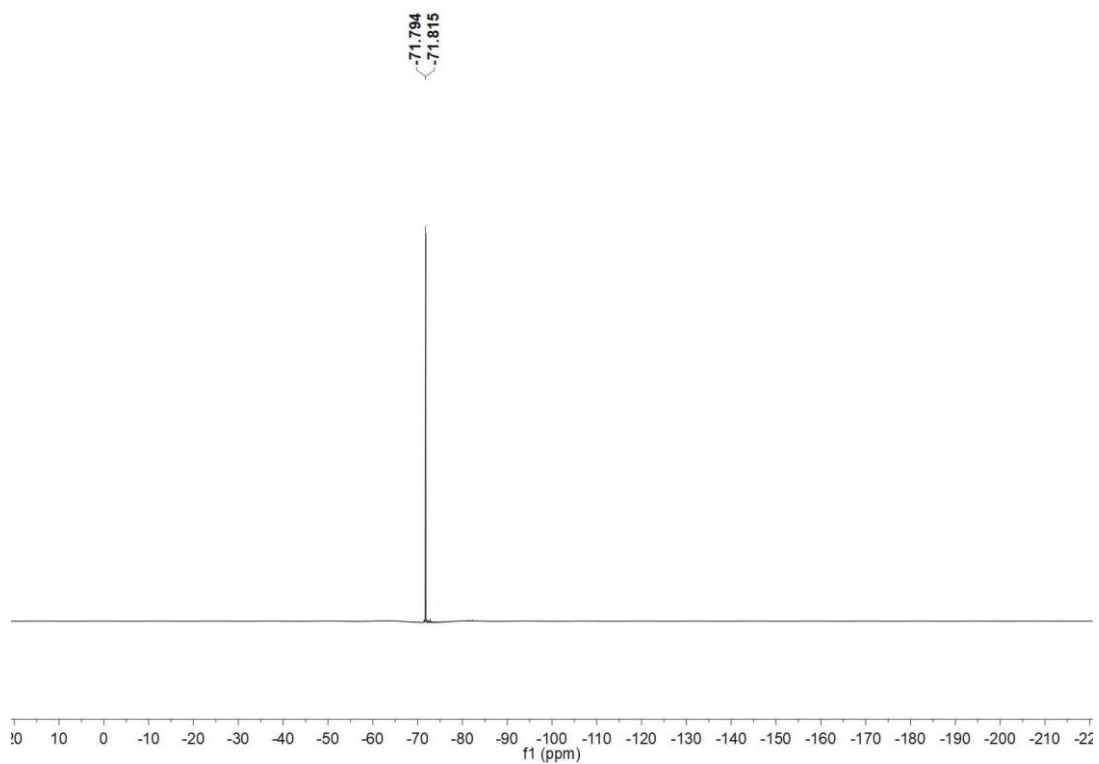
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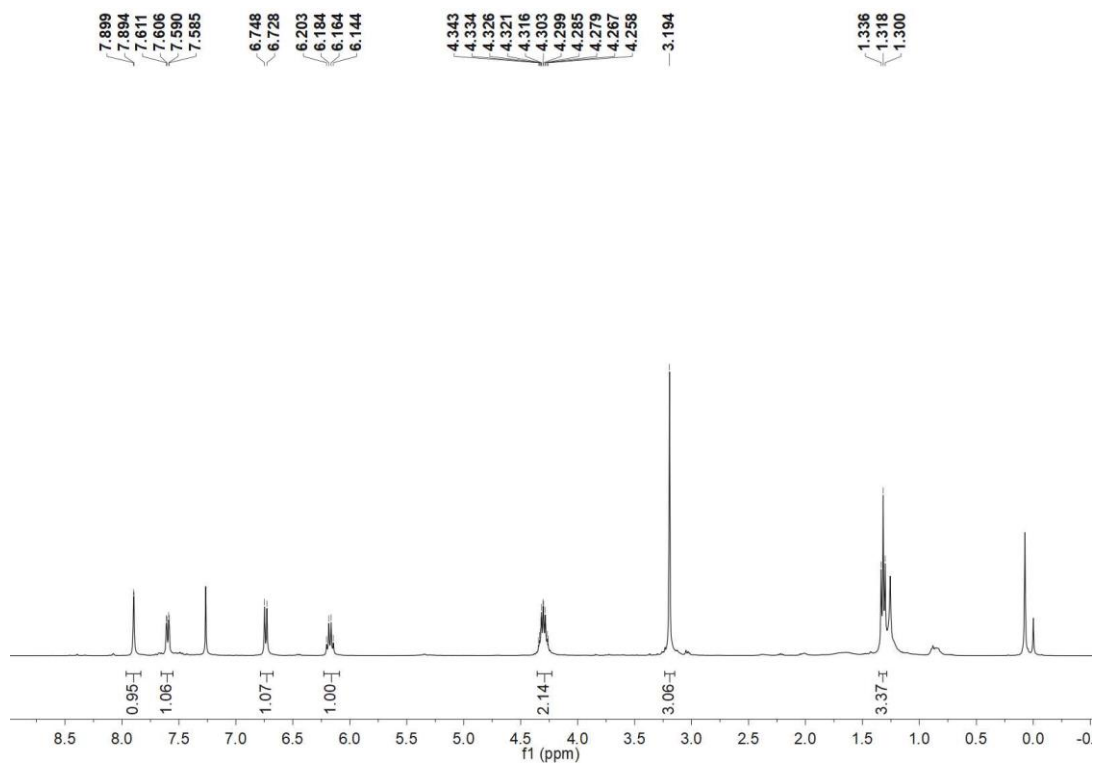
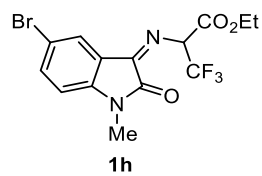
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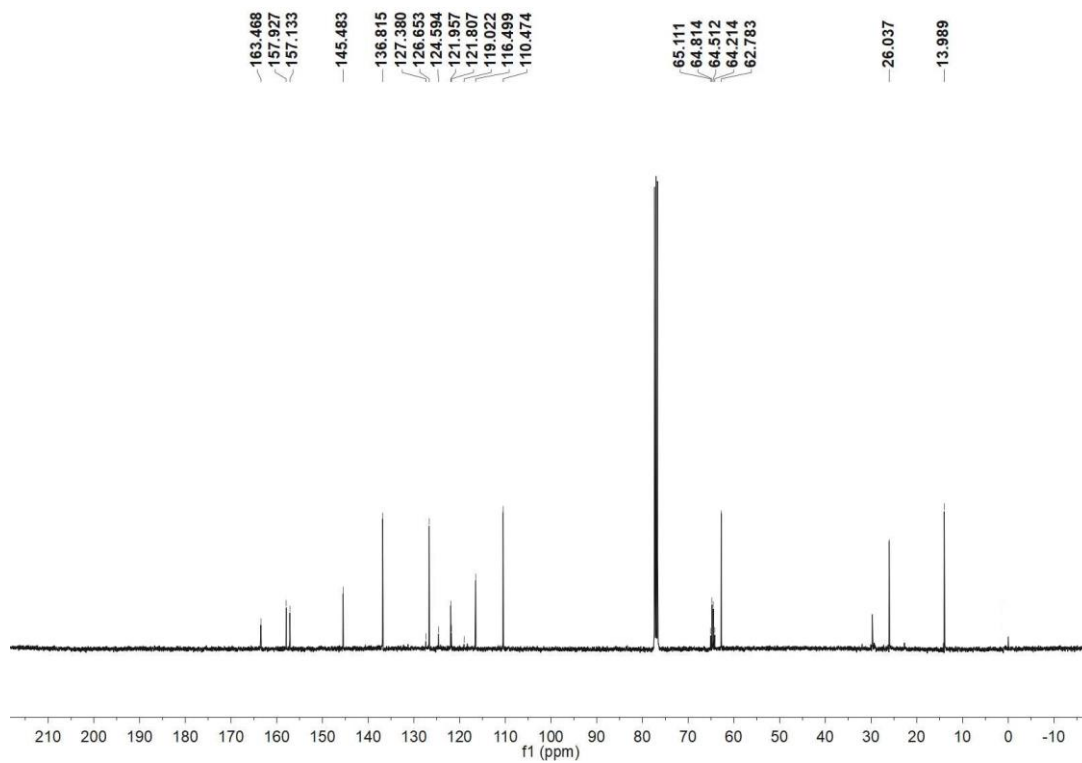
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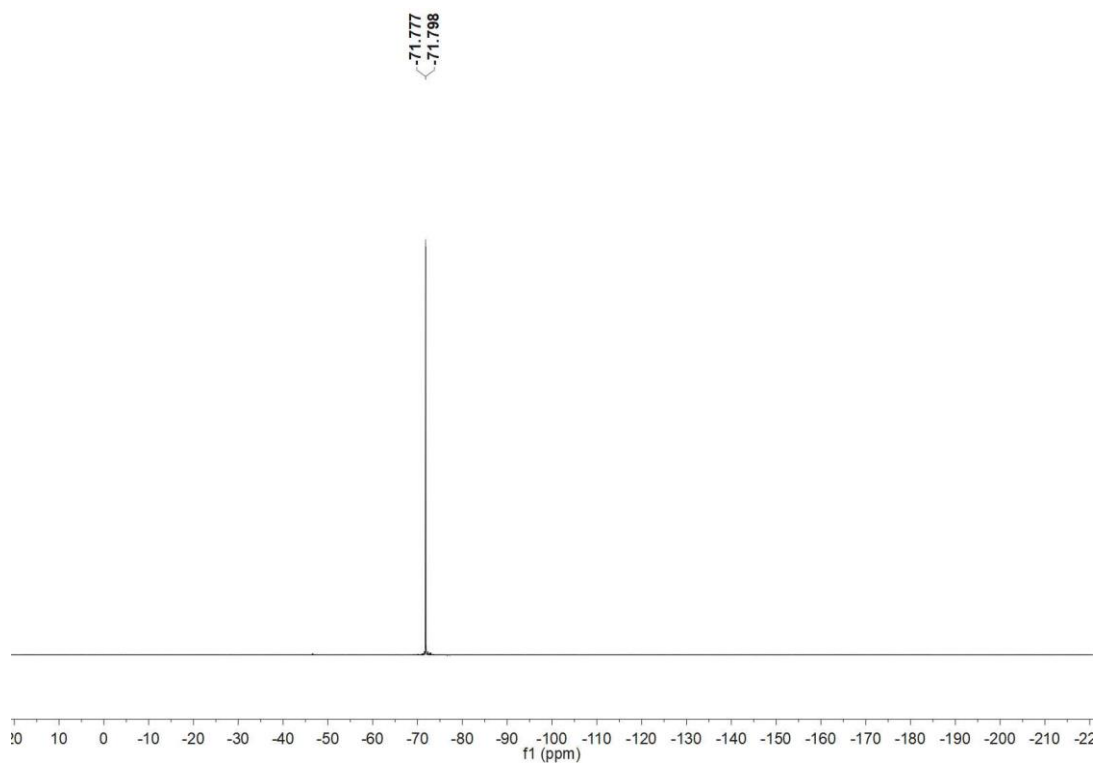
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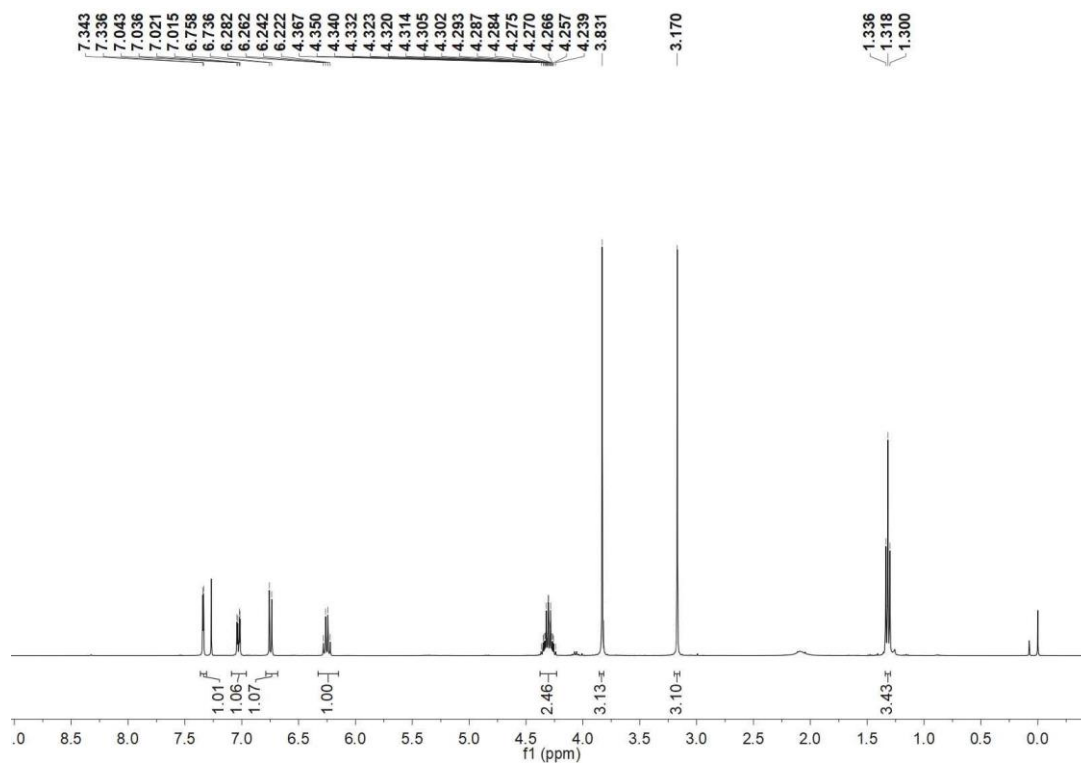
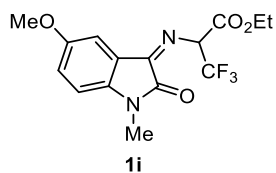
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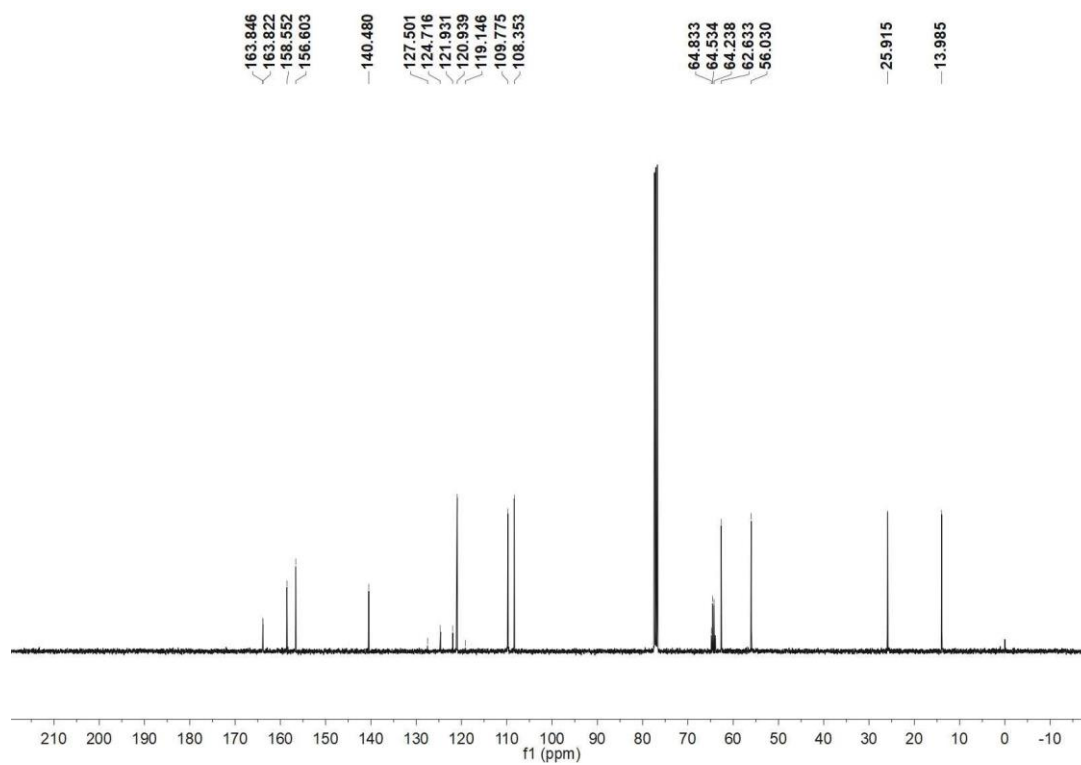
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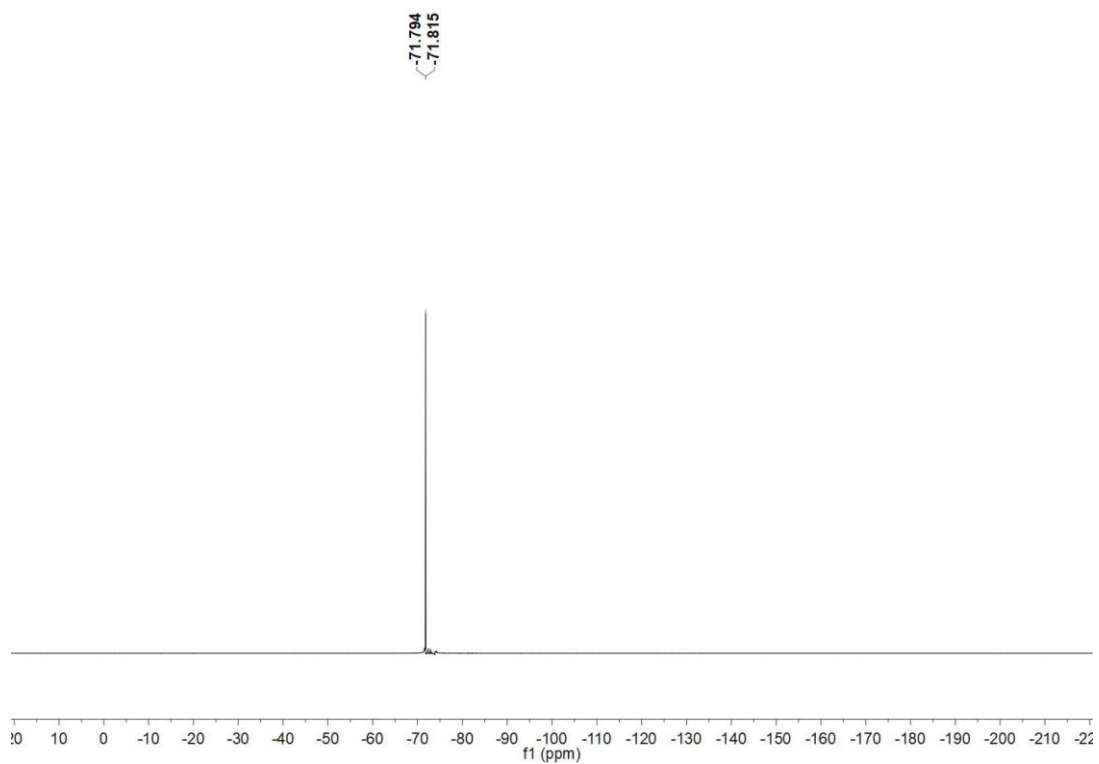
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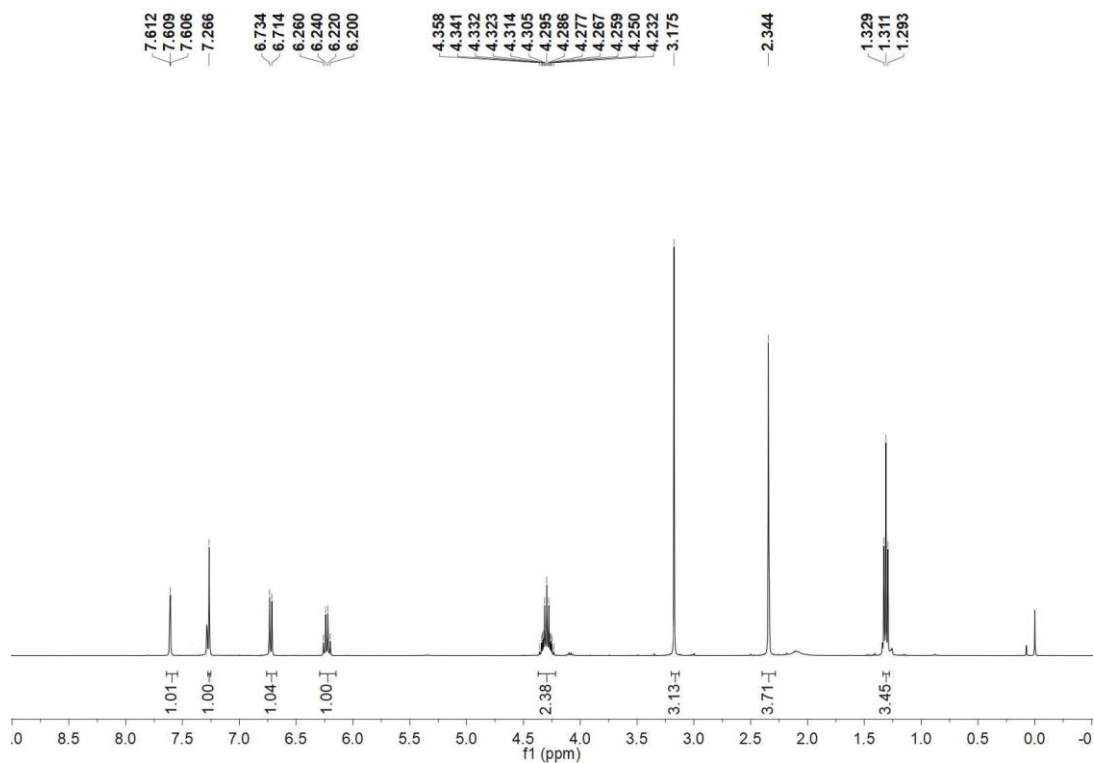
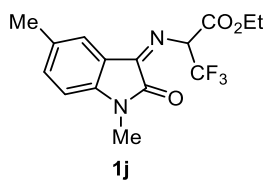
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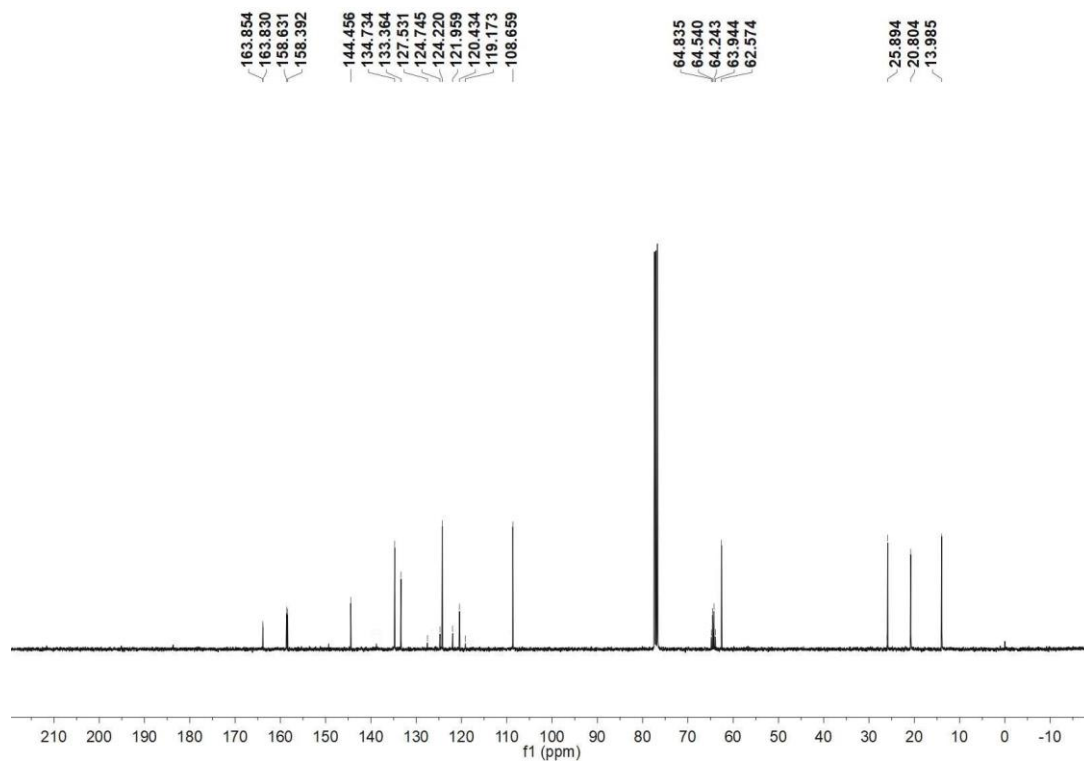
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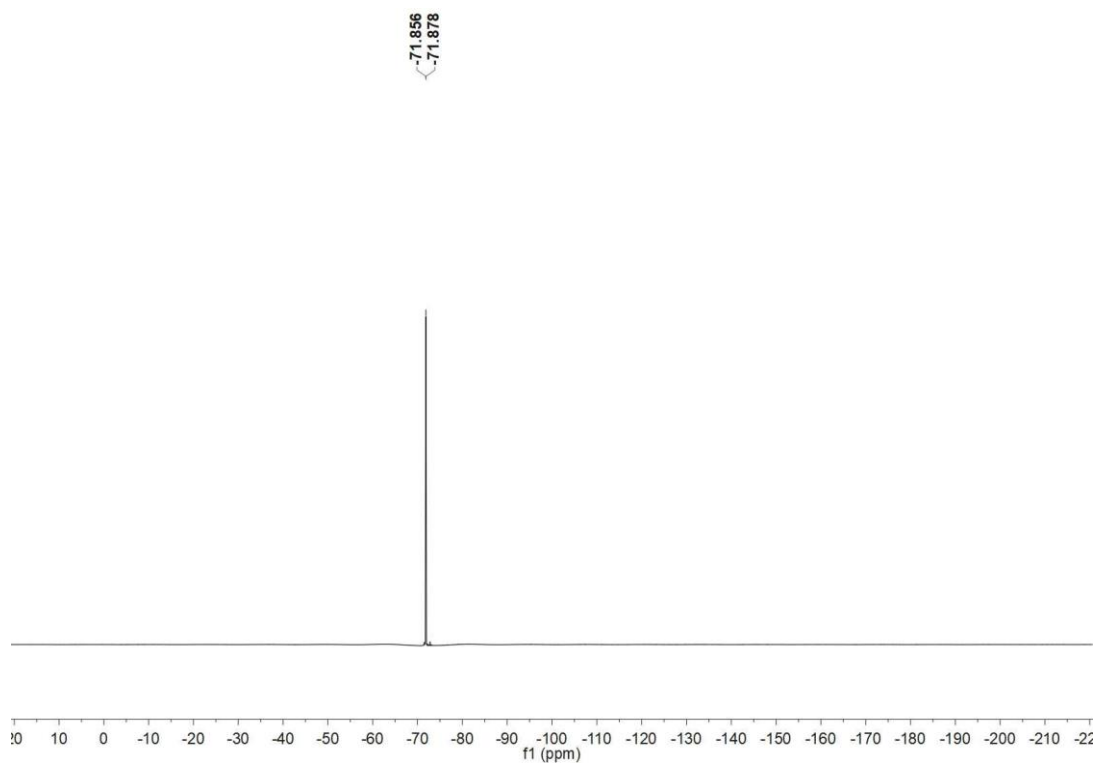
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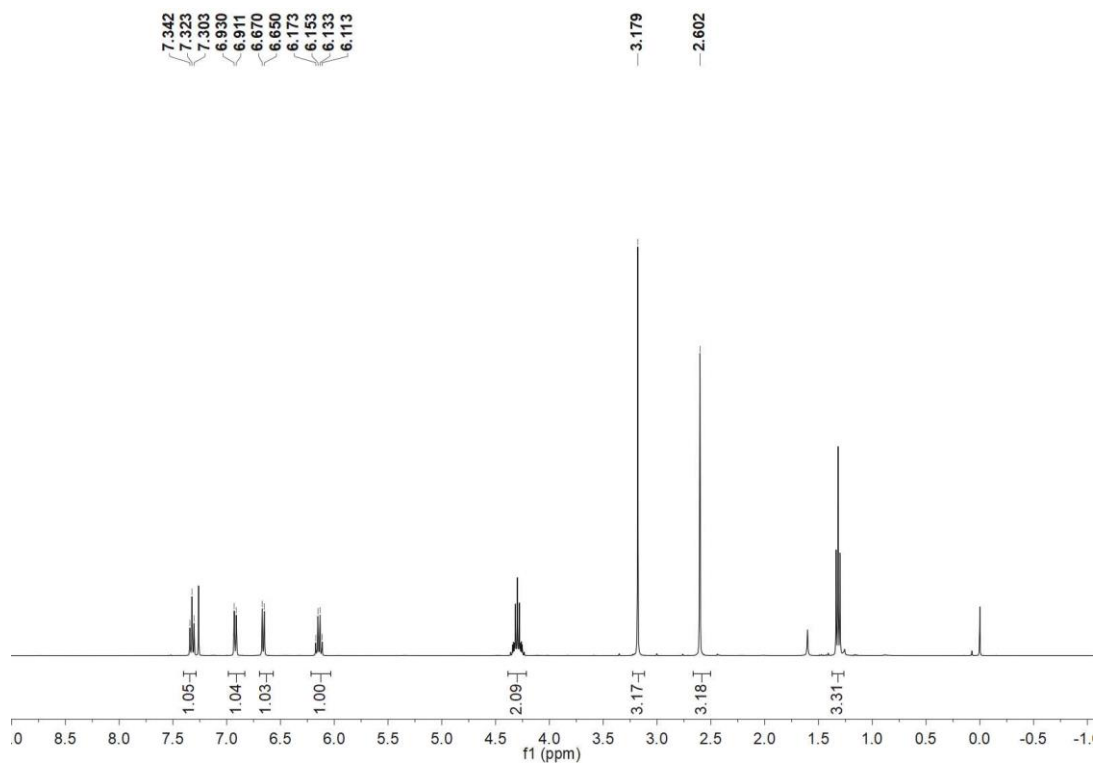
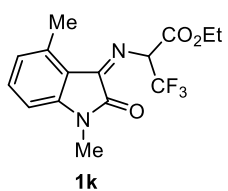
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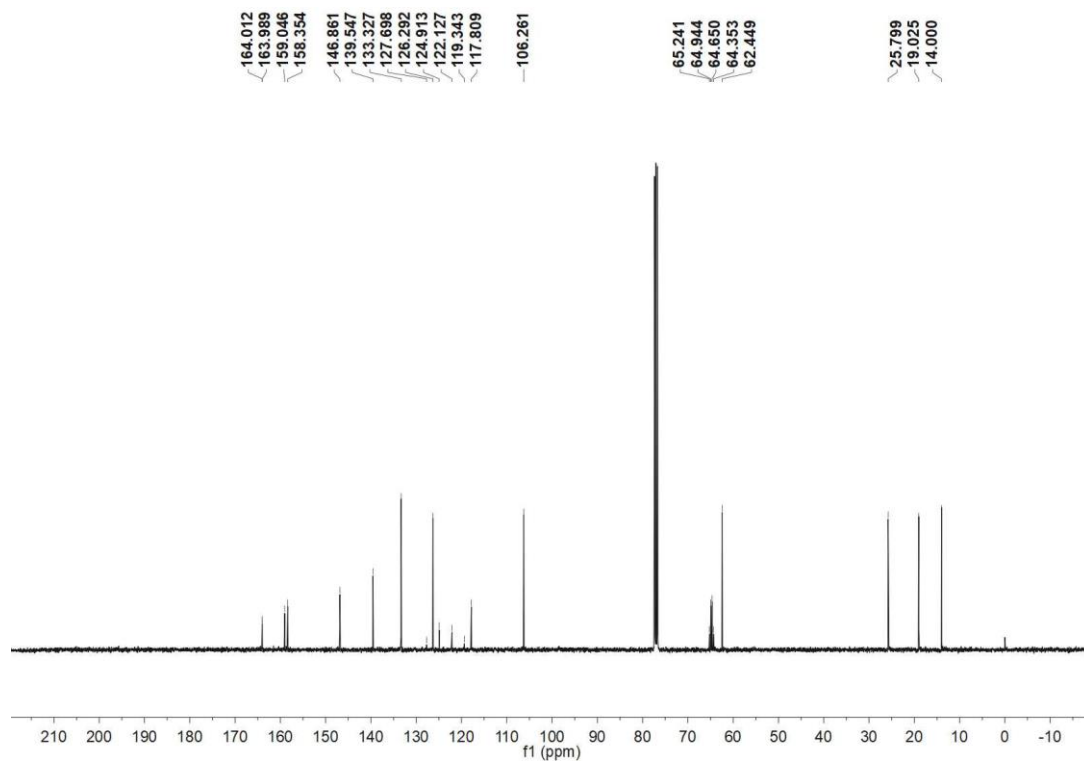
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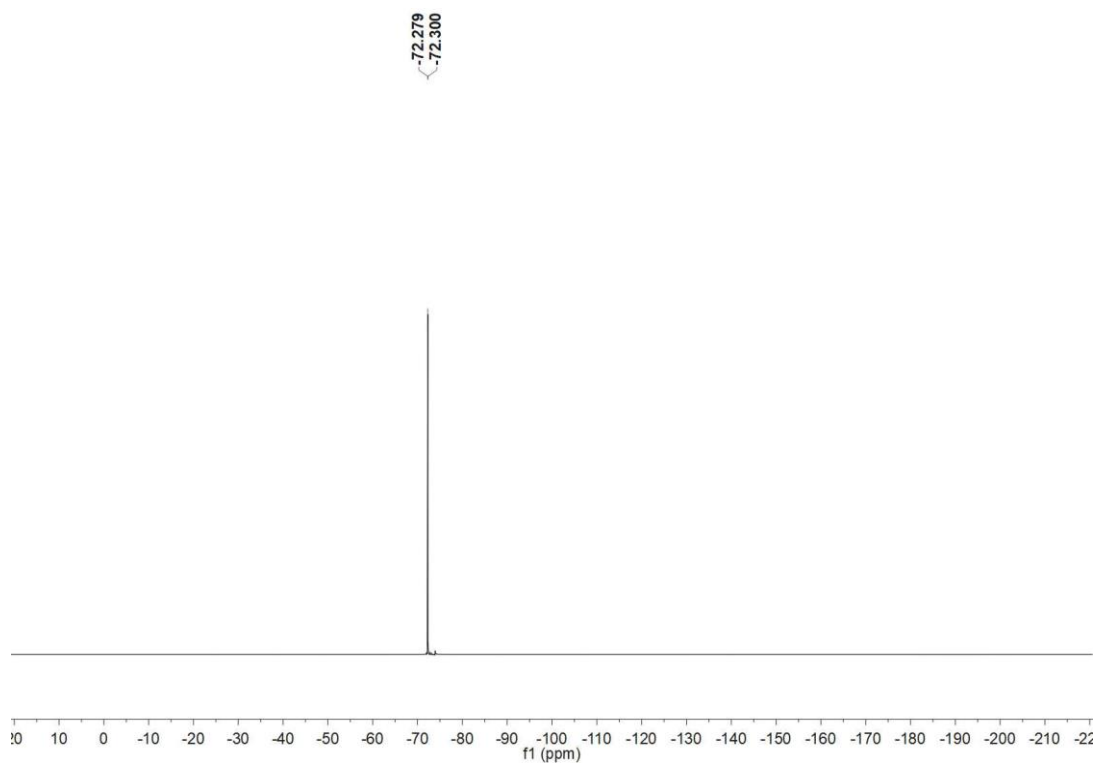
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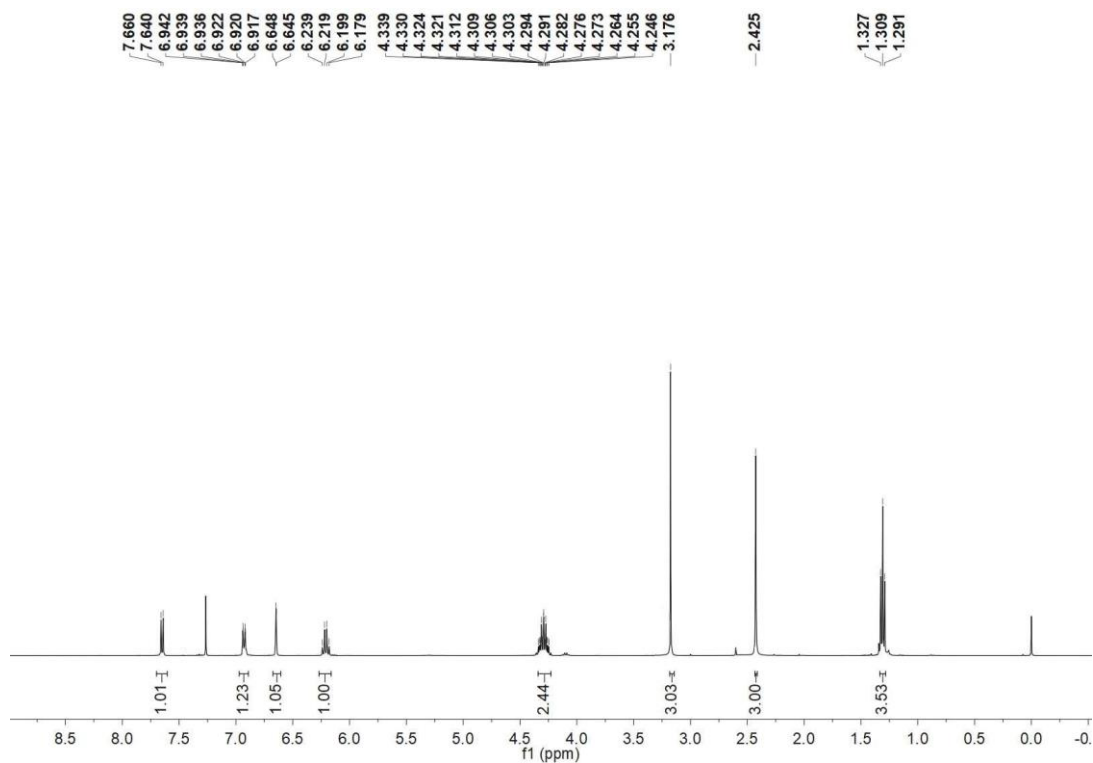
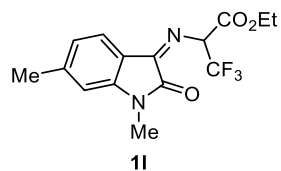
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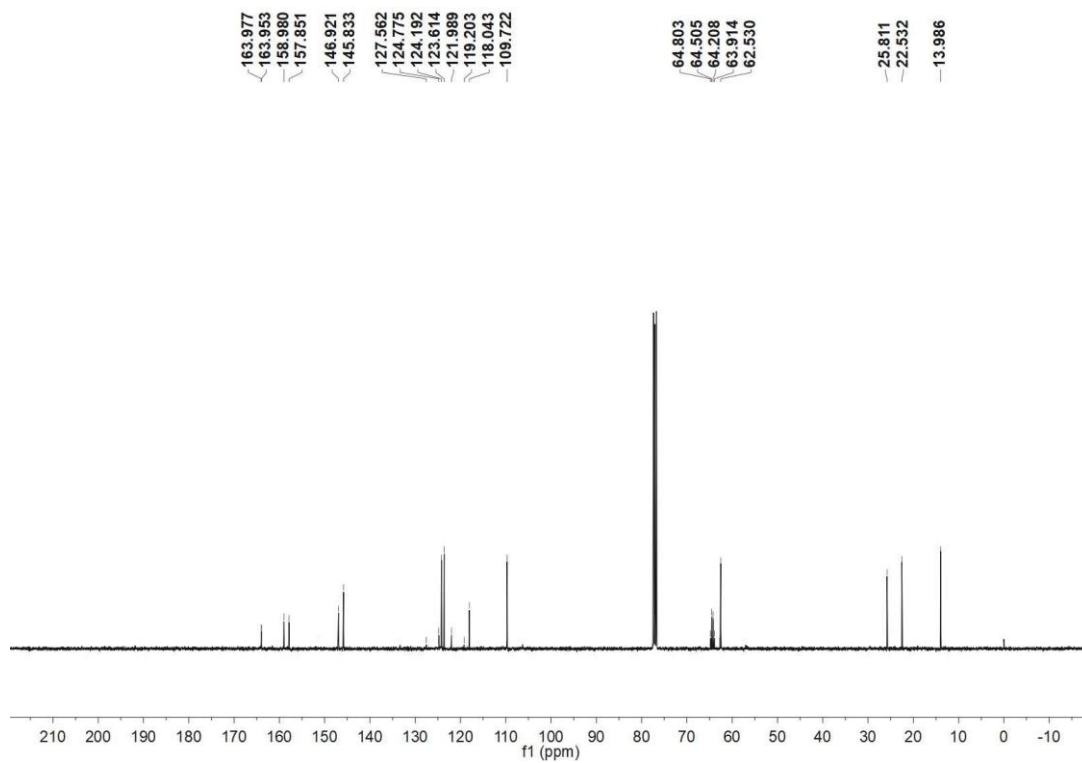
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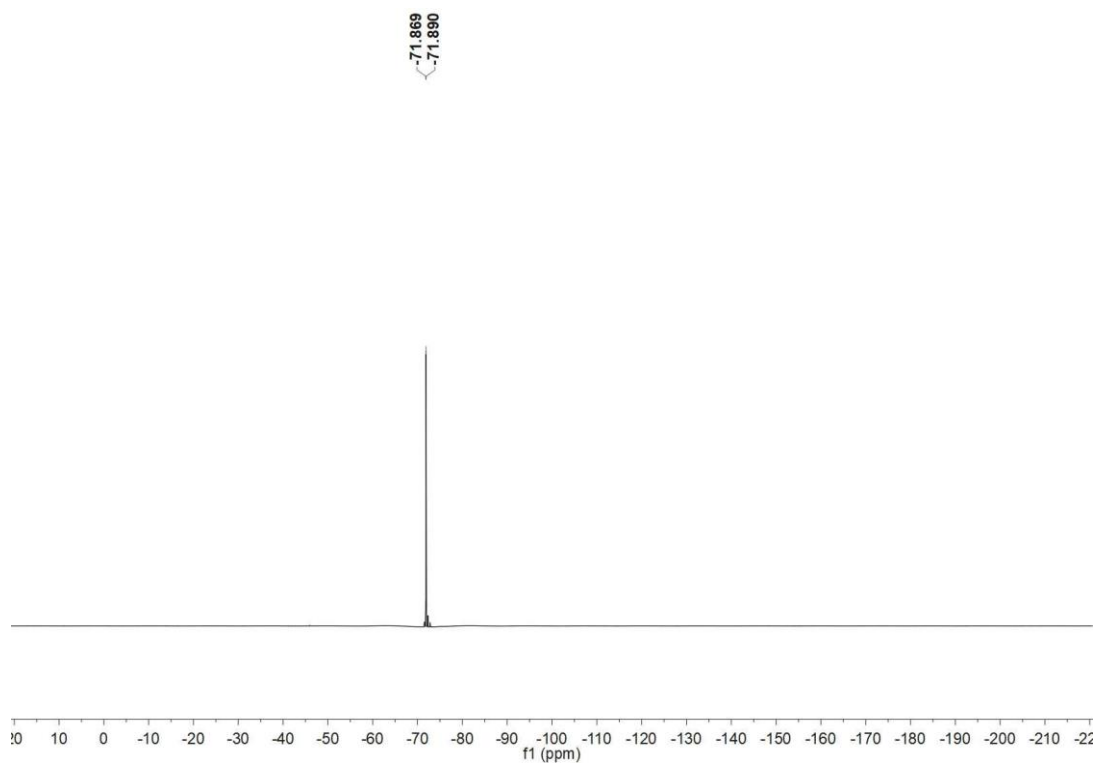
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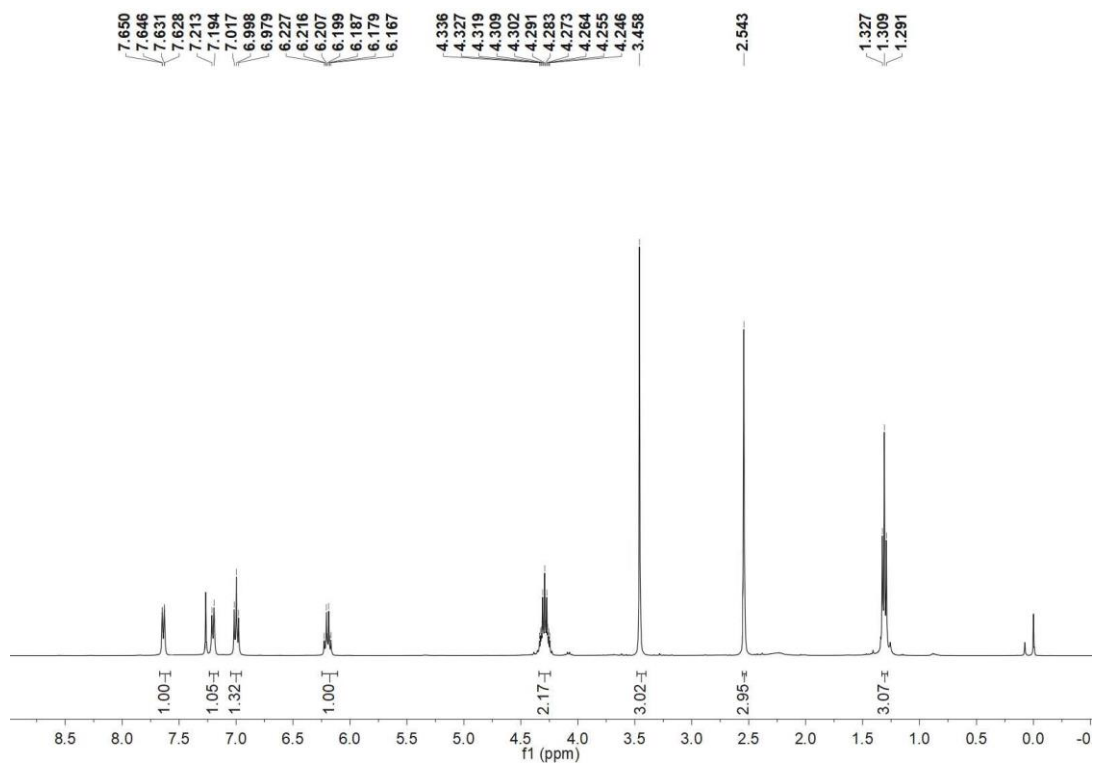
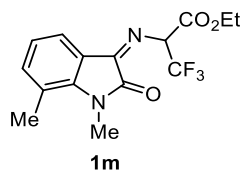
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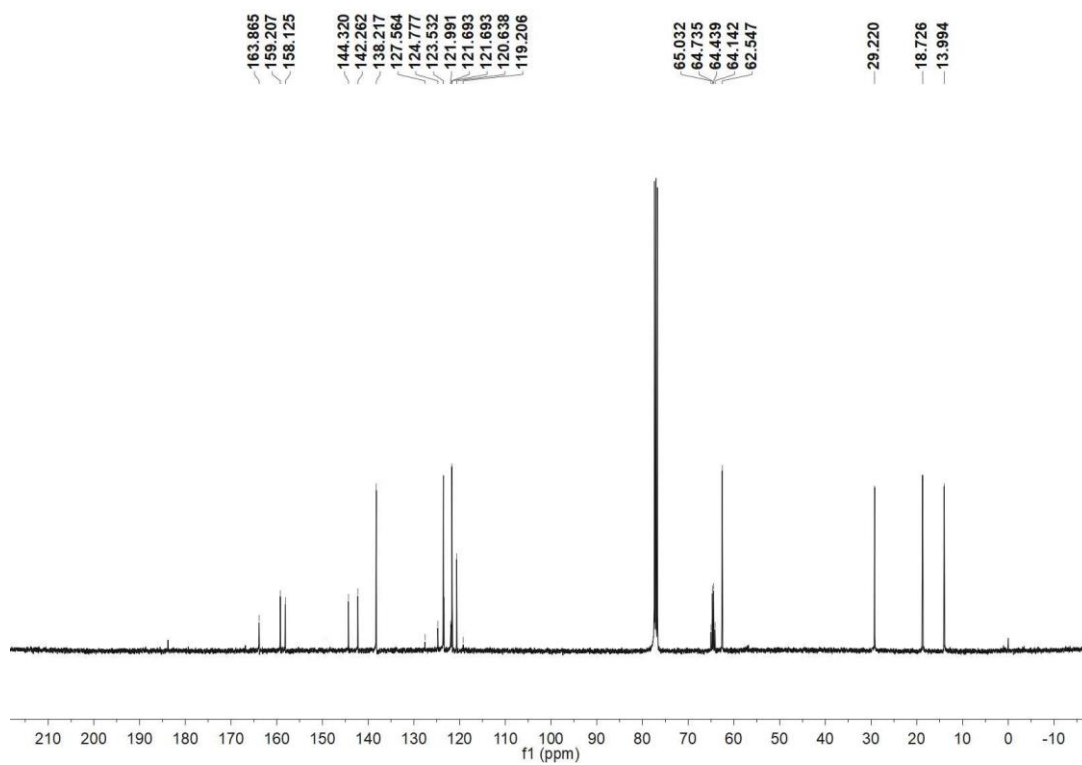
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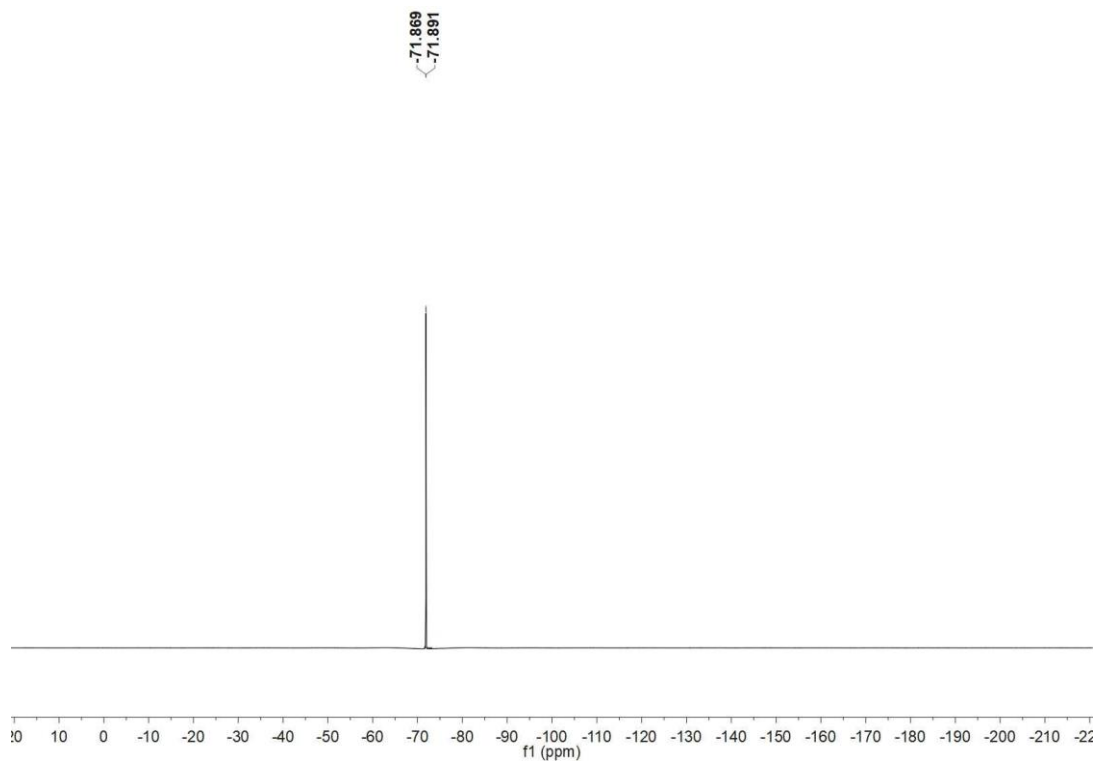
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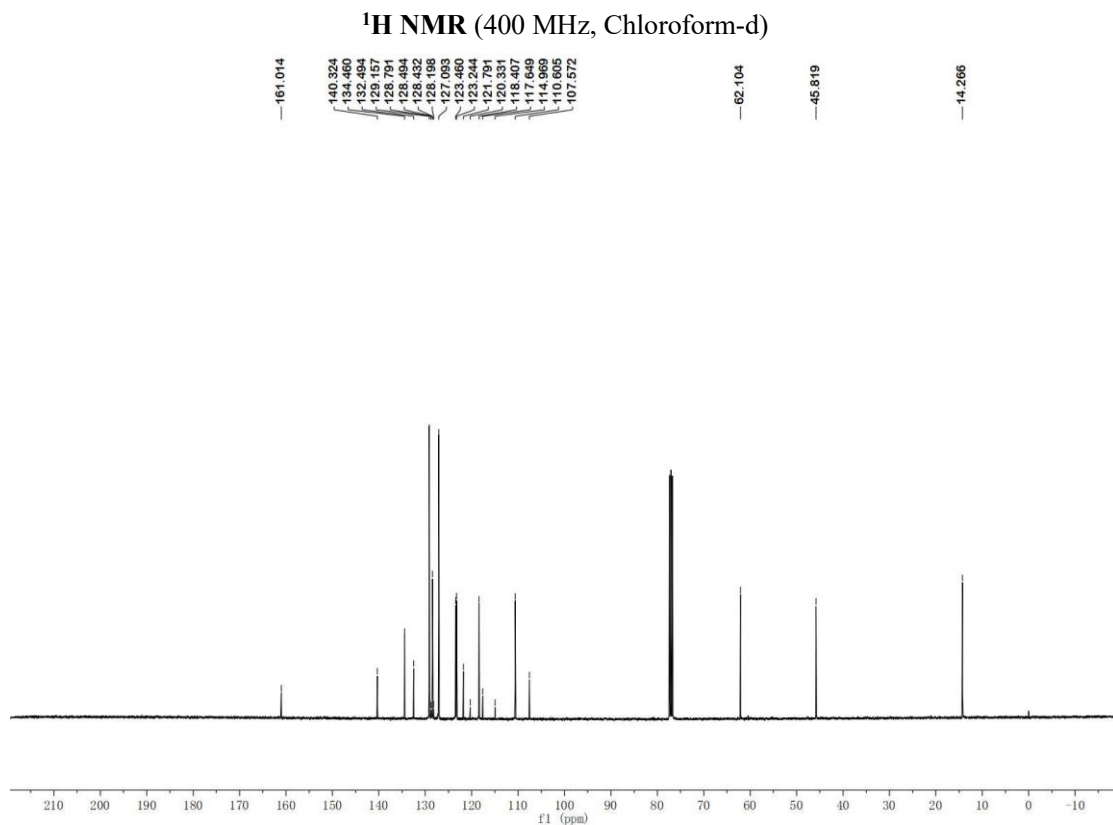
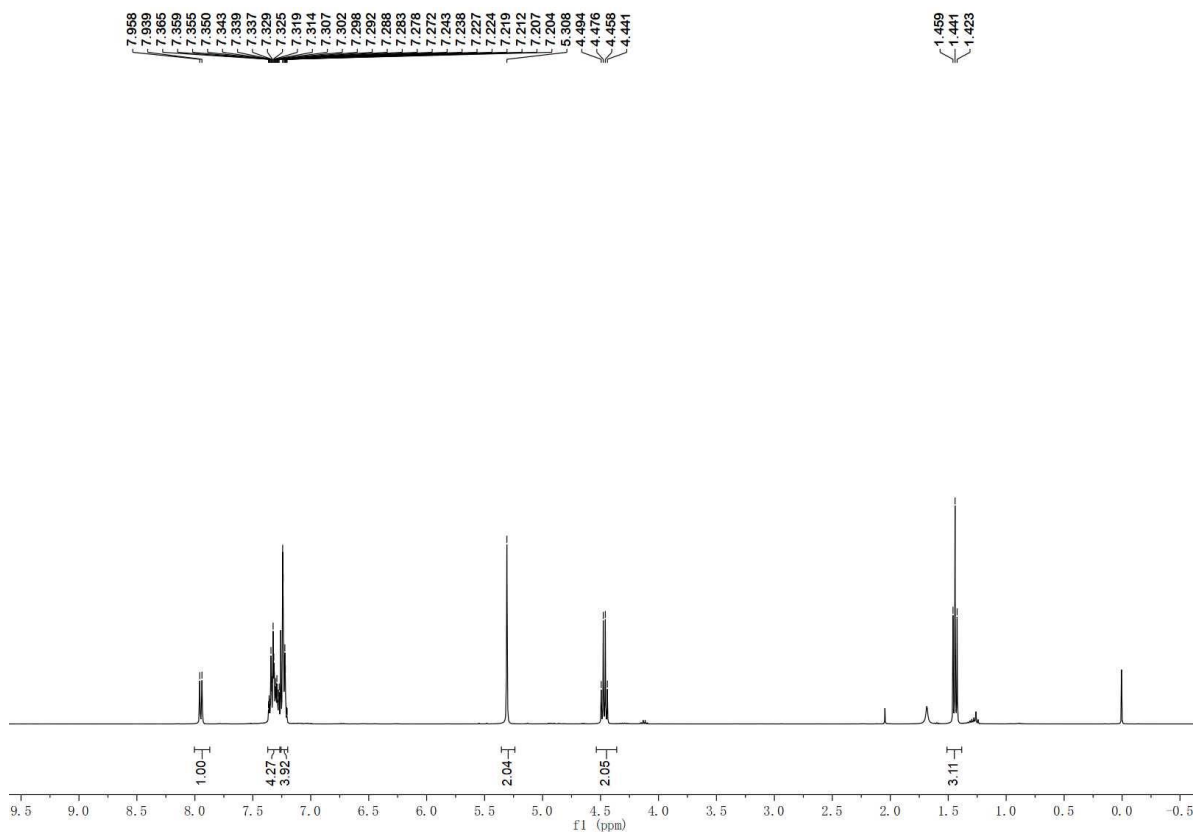
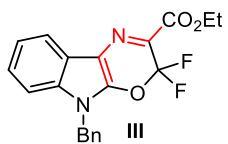
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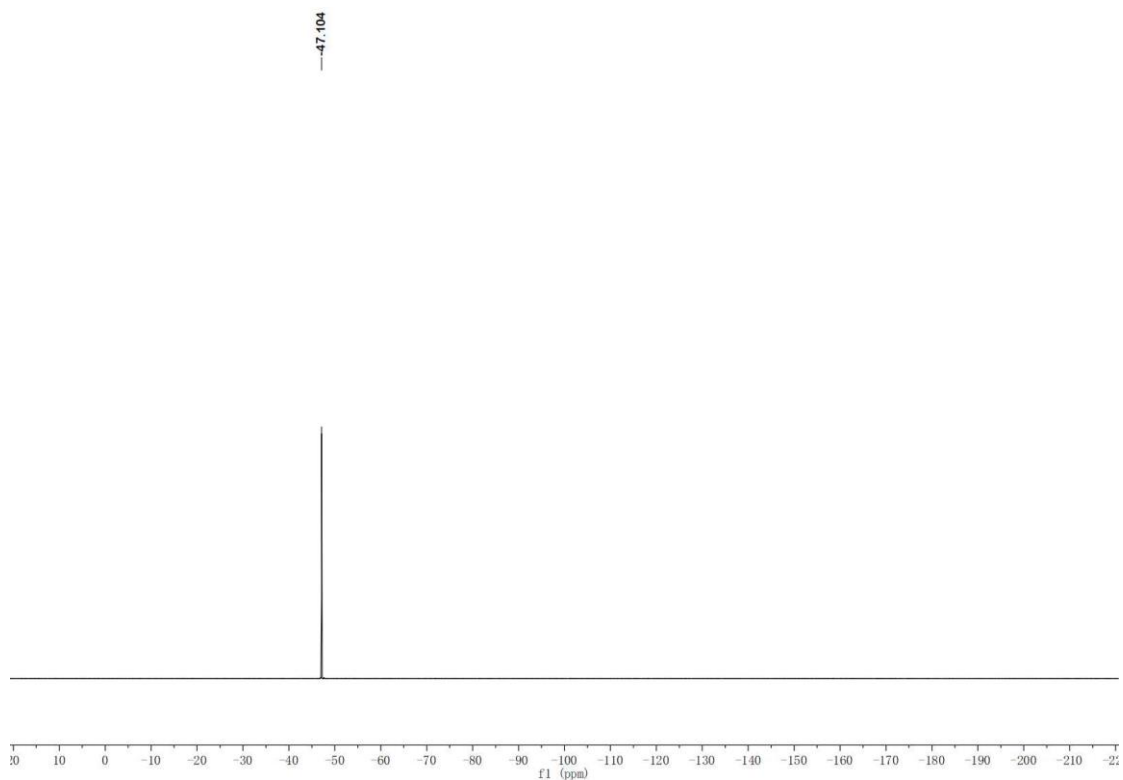


¹³C NMR (101 MHz, Chloroform-d)

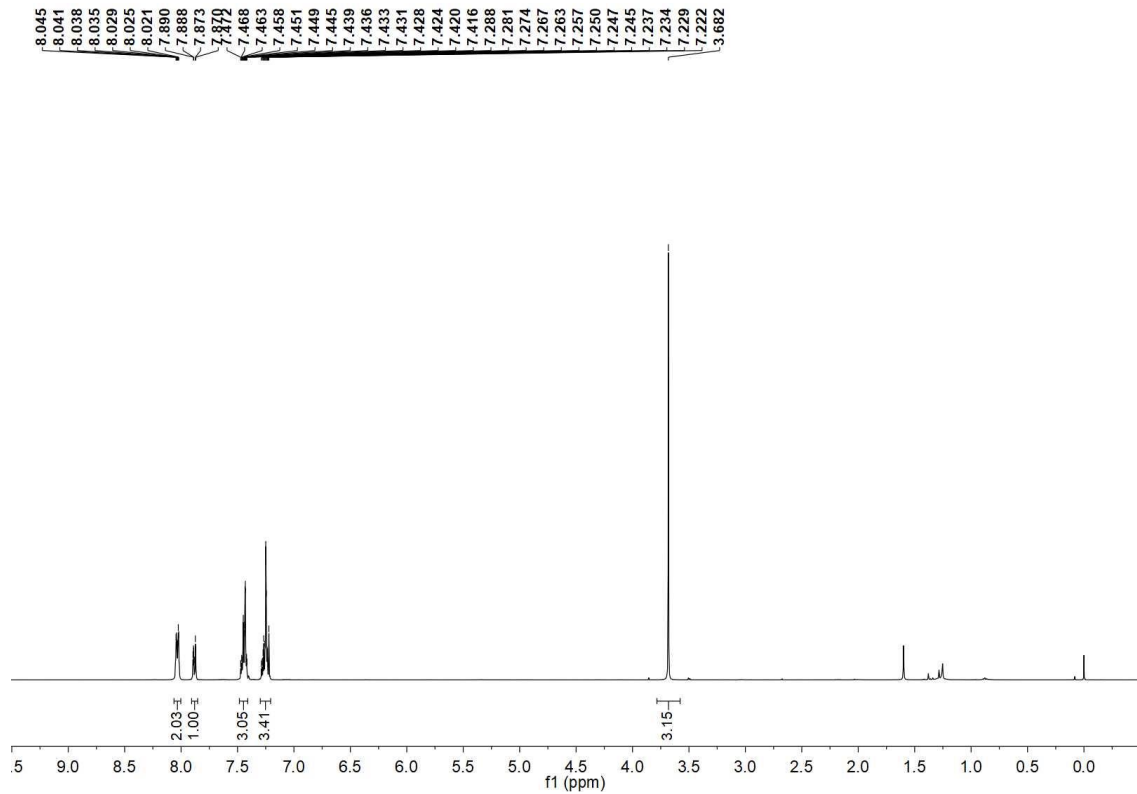
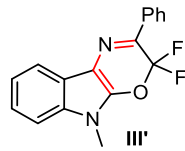


^{19}F NMR (376 MHz, Chloroform-d)

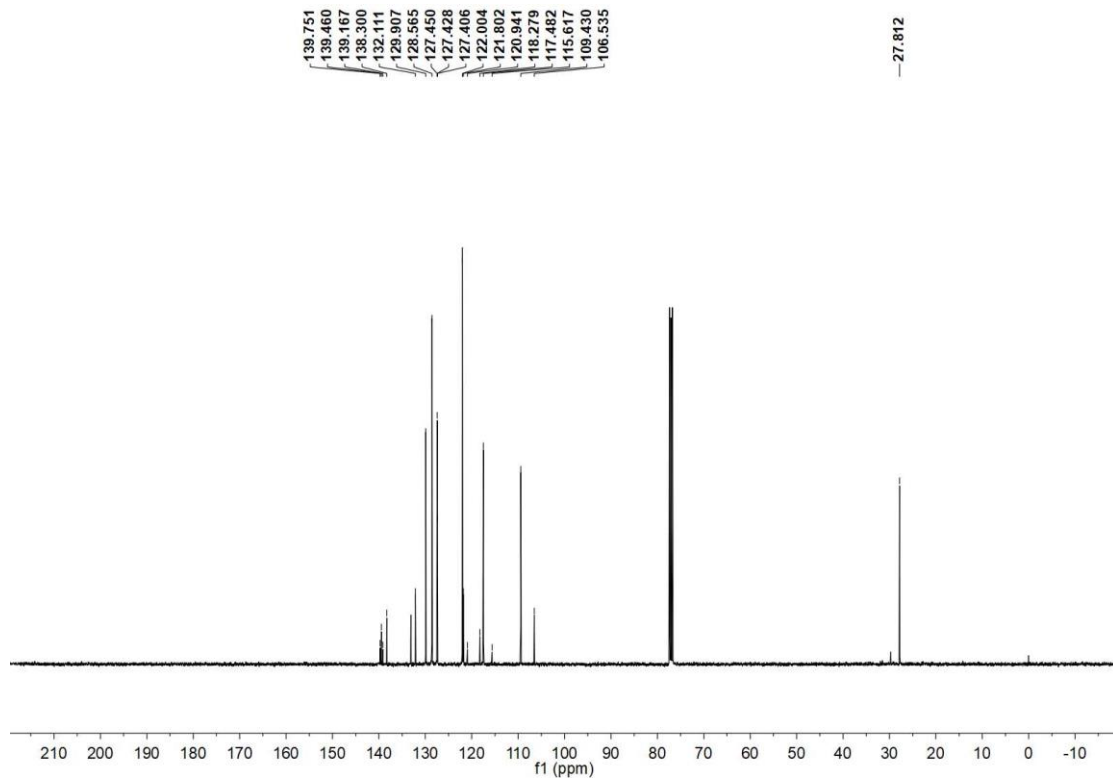




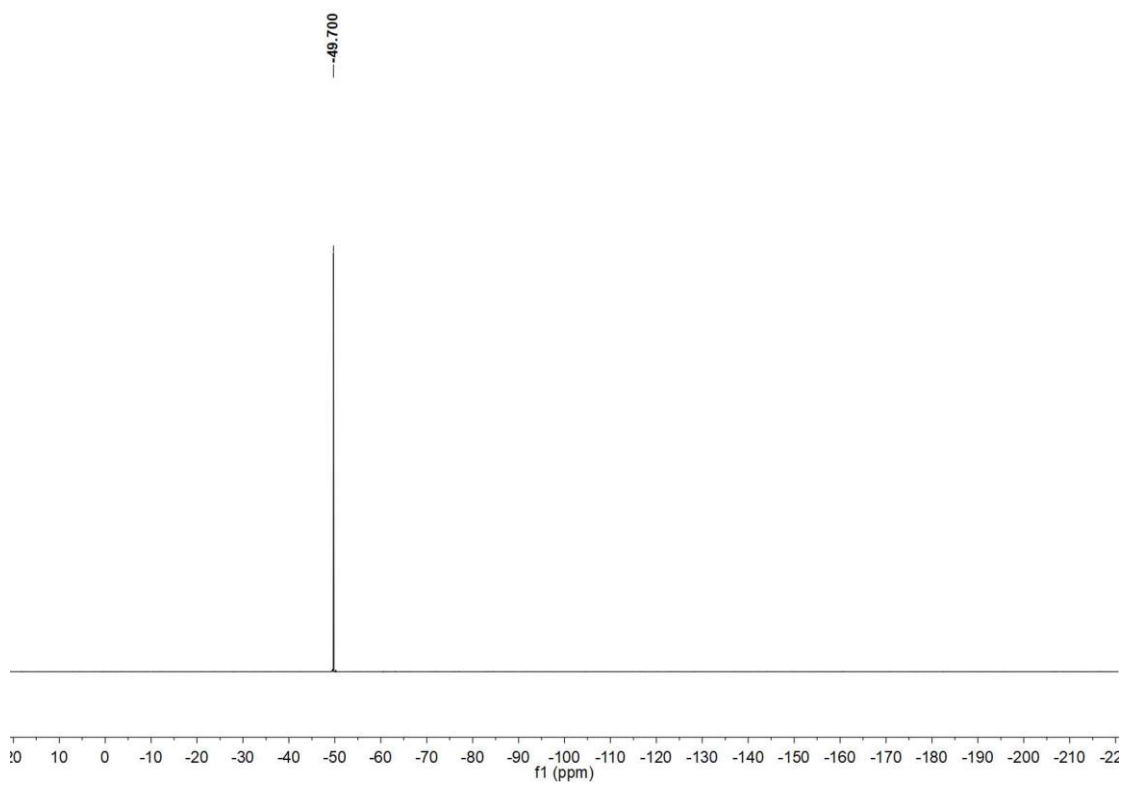
^{19}F NMR (376 MHz, Chloroform-d)



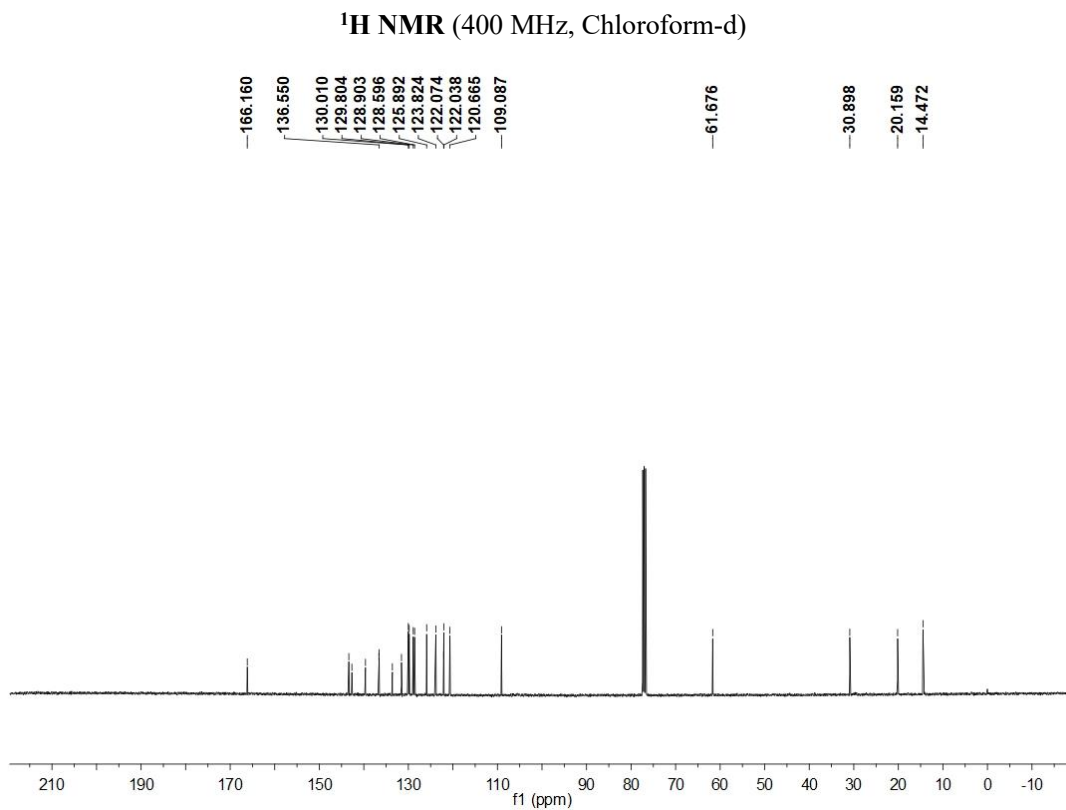
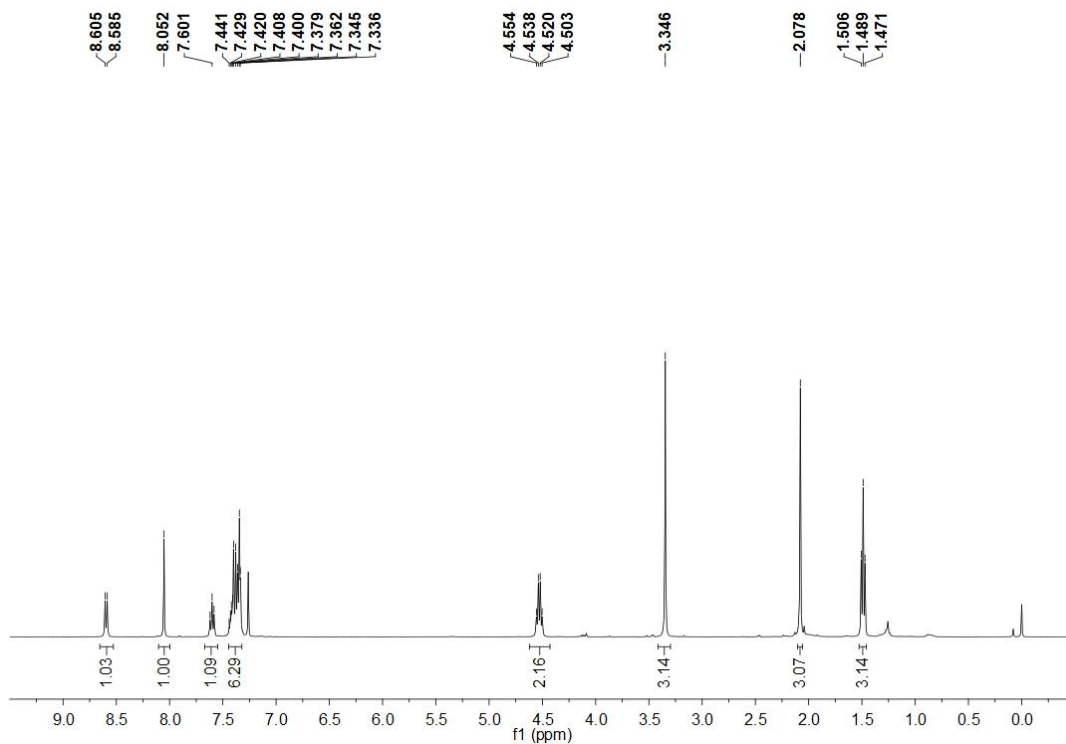
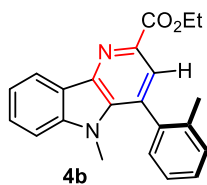
¹H NMR (400 MHz, Chloroform-d)

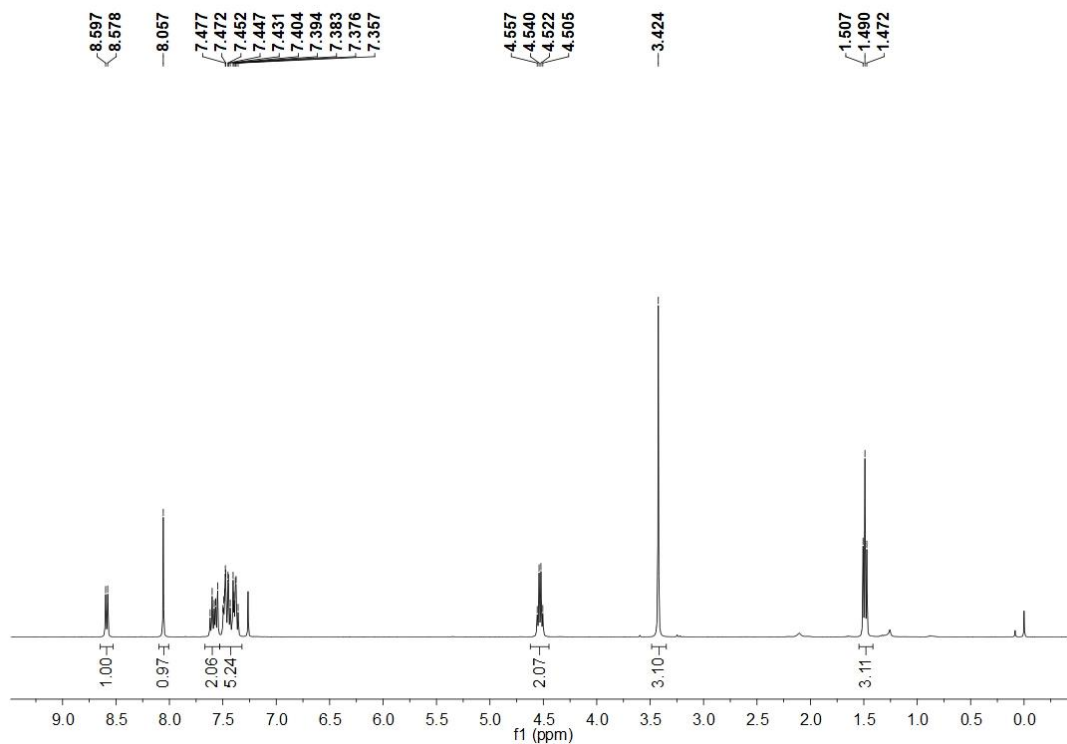
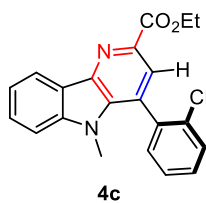


¹³C NMR (101 MHz, Chloroform-d)

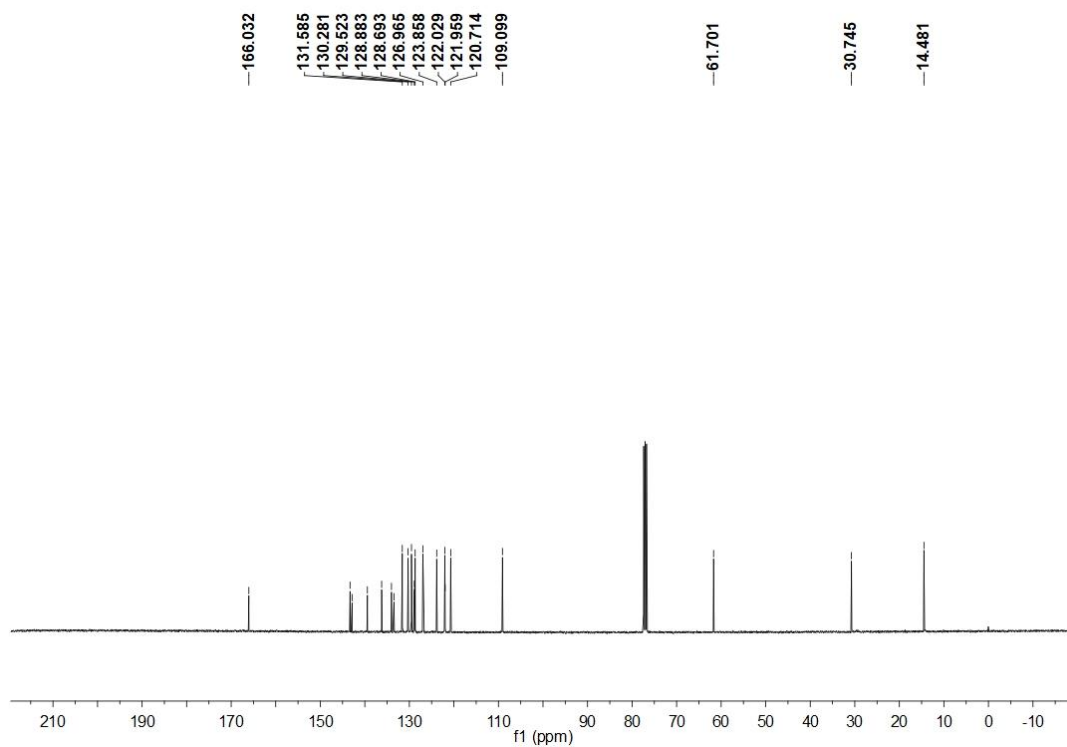


^{19}F NMR (376 MHz, Chloroform-d)

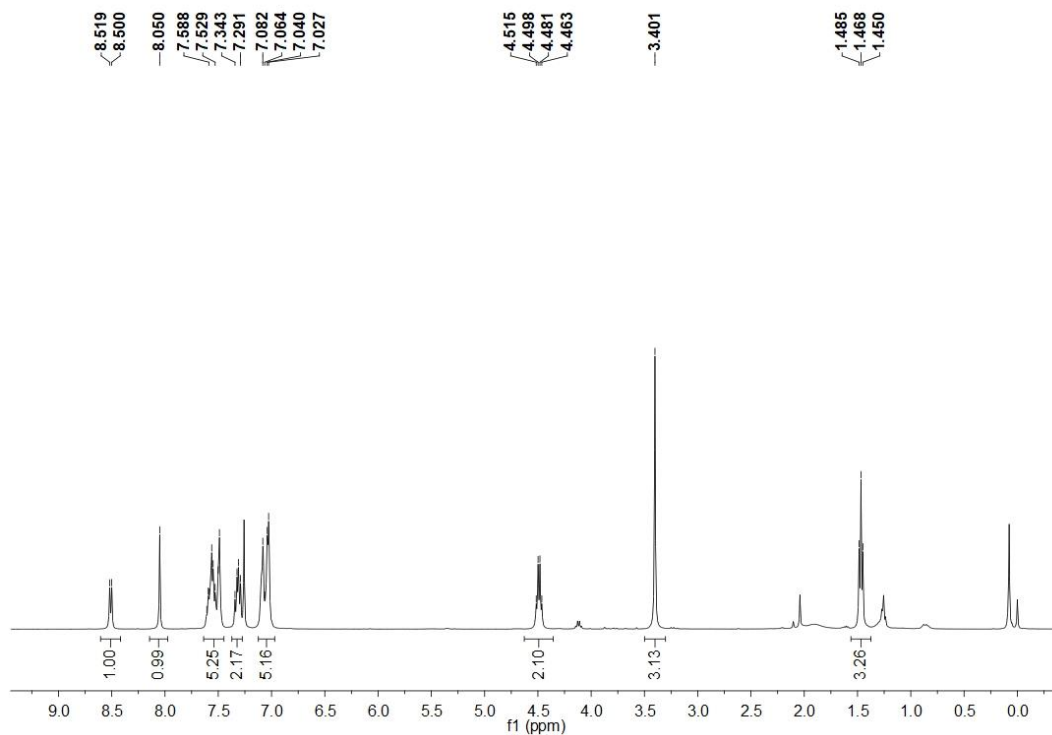
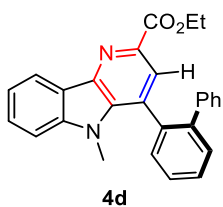




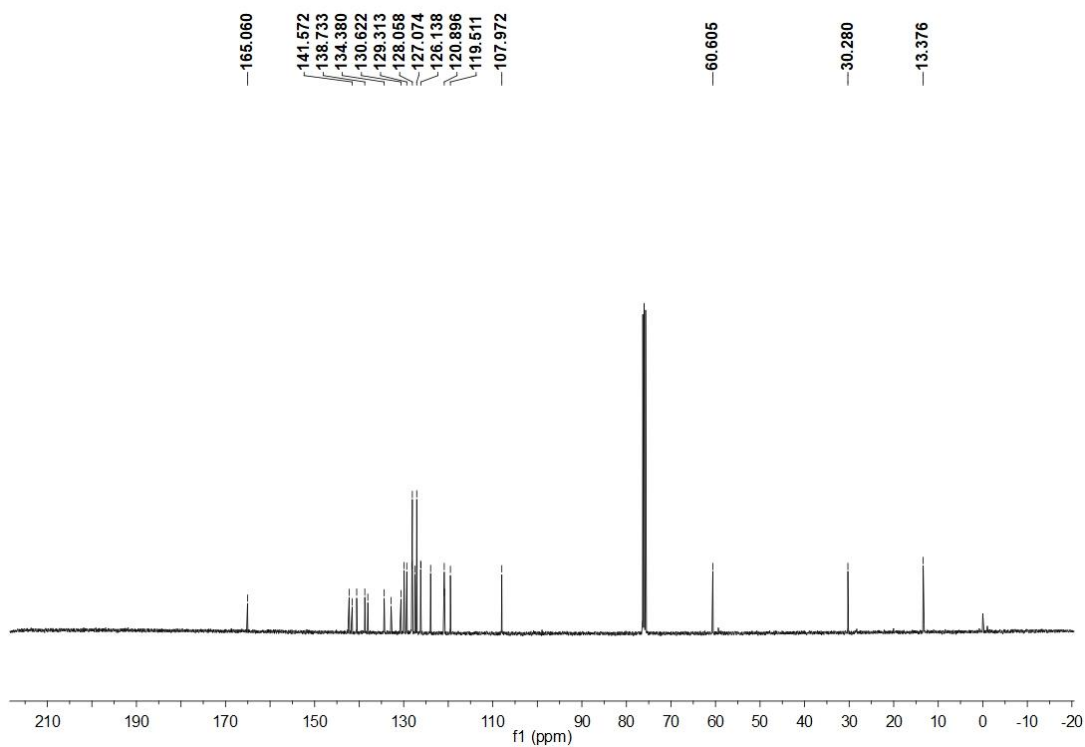
¹H NMR (400 MHz, Chloroform-d)



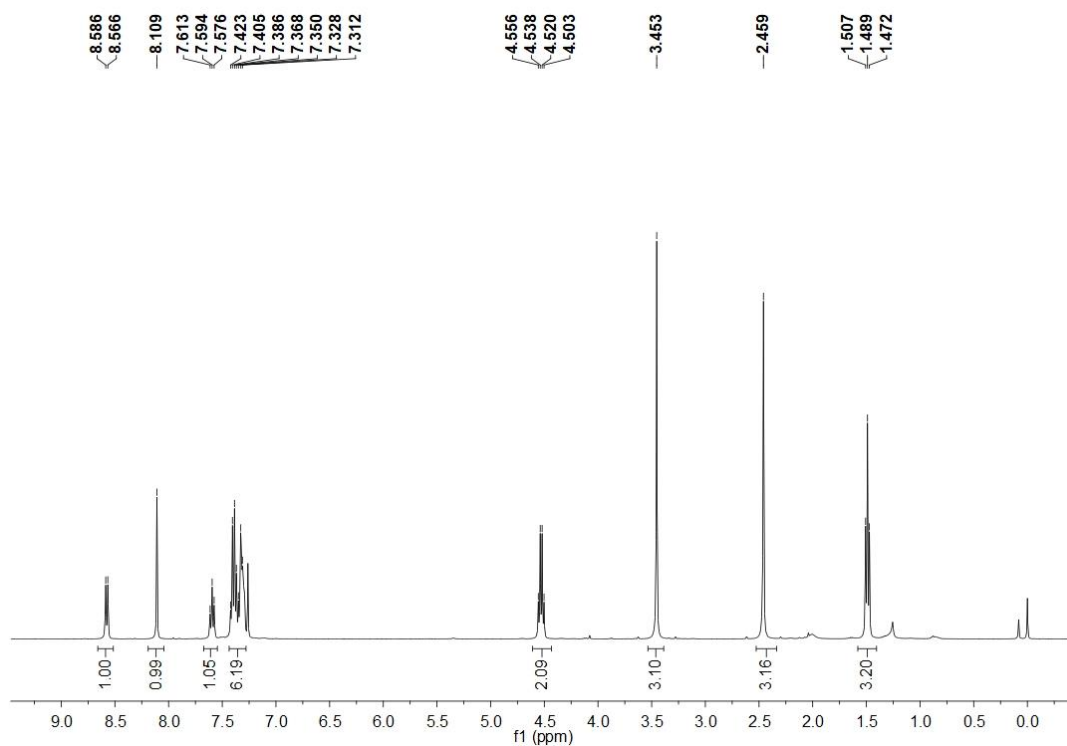
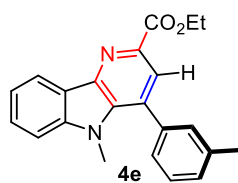
¹³C NMR (101 MHz, Chloroform-d)



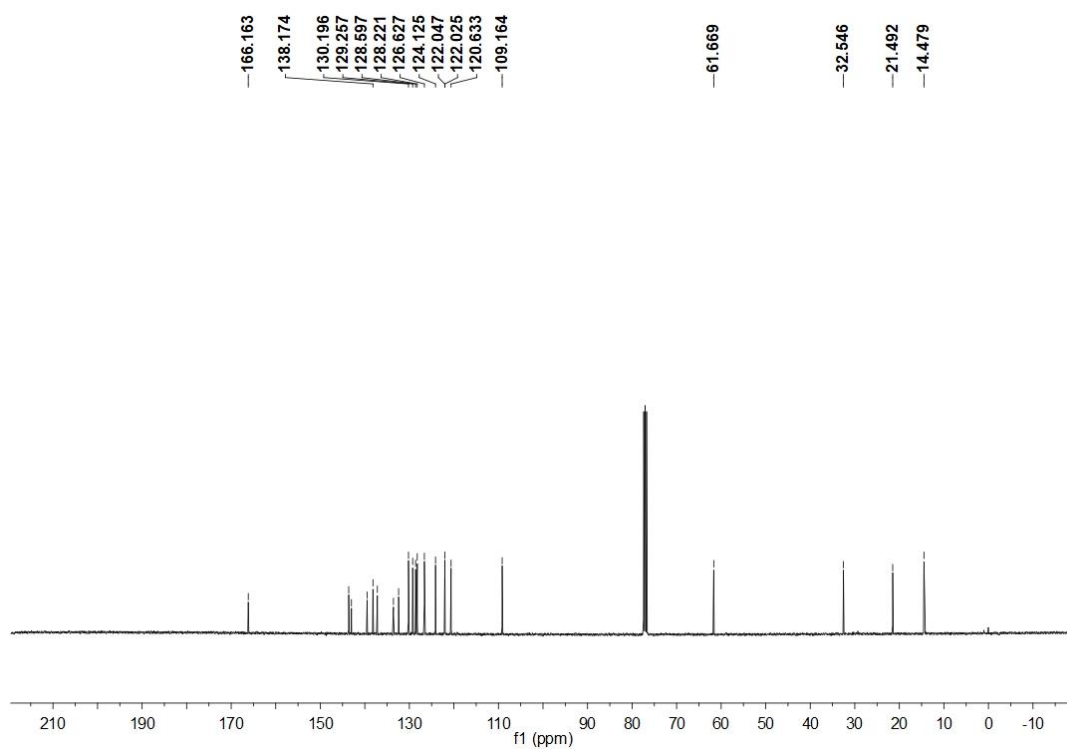
¹H NMR (400 MHz, Chloroform-d)



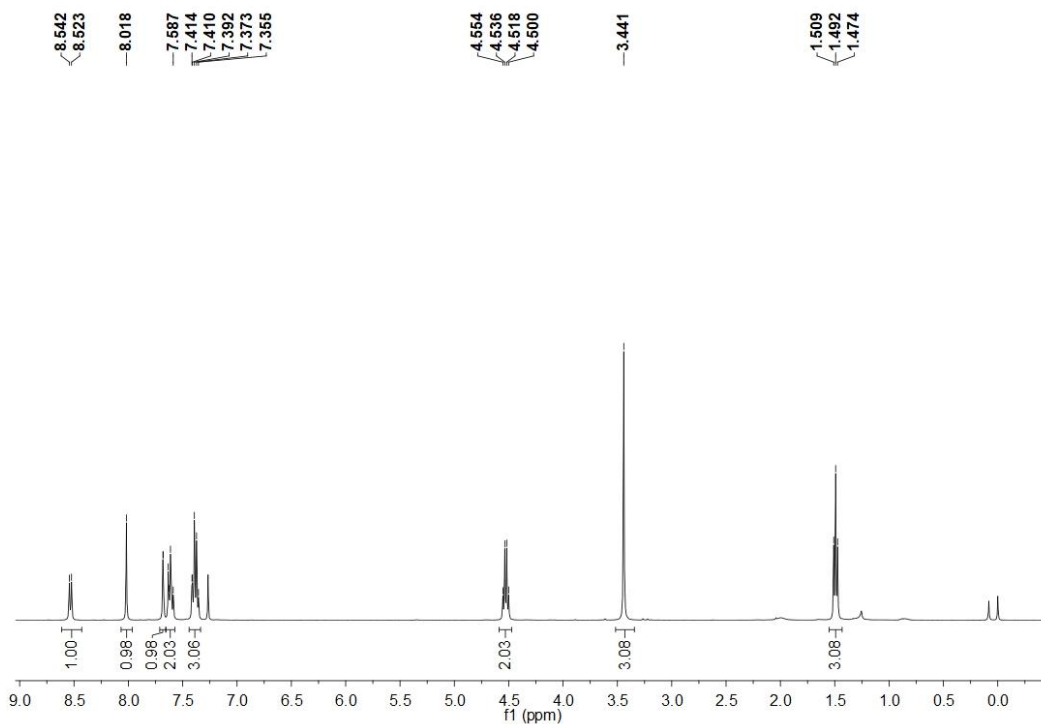
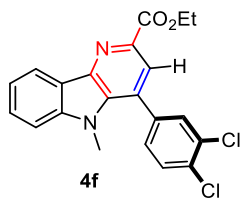
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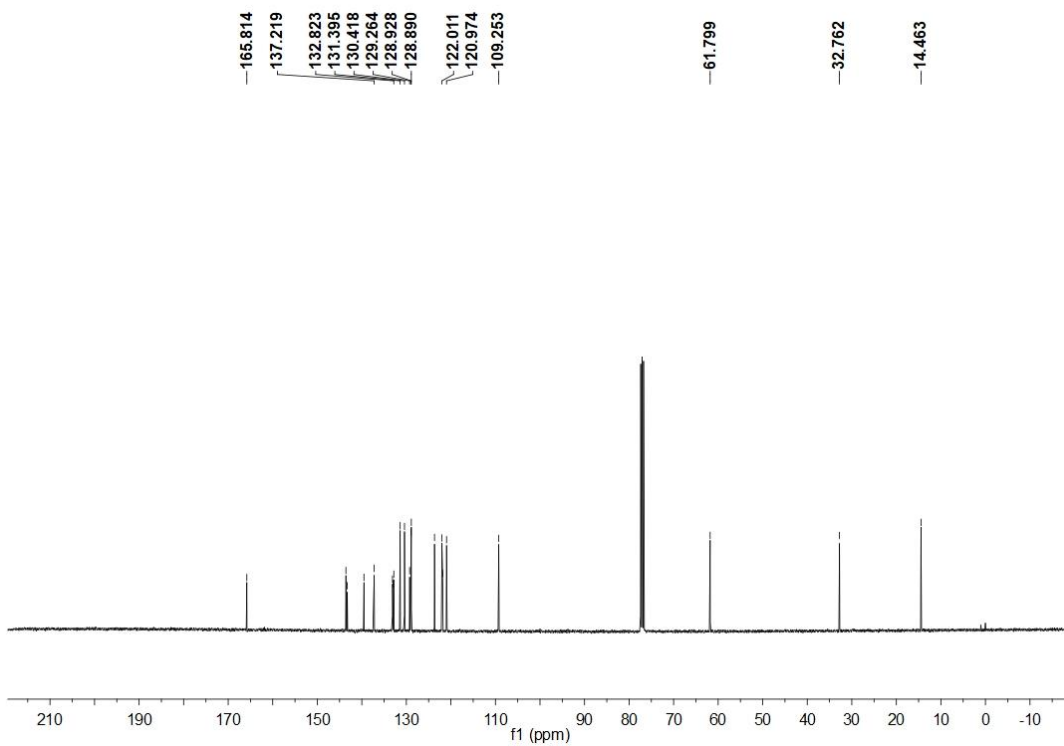
¹H NMR (400 MHz, Chloroform-d)



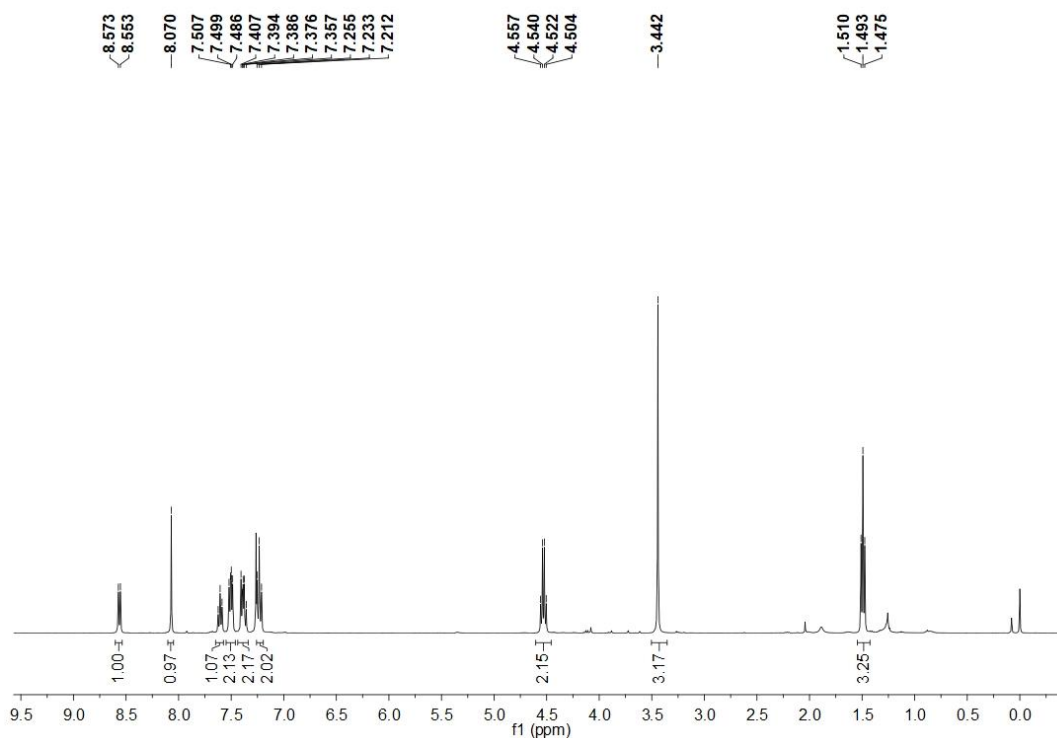
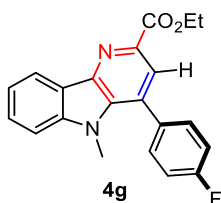
¹³C NMR (101 MHz, Chloroform-d)



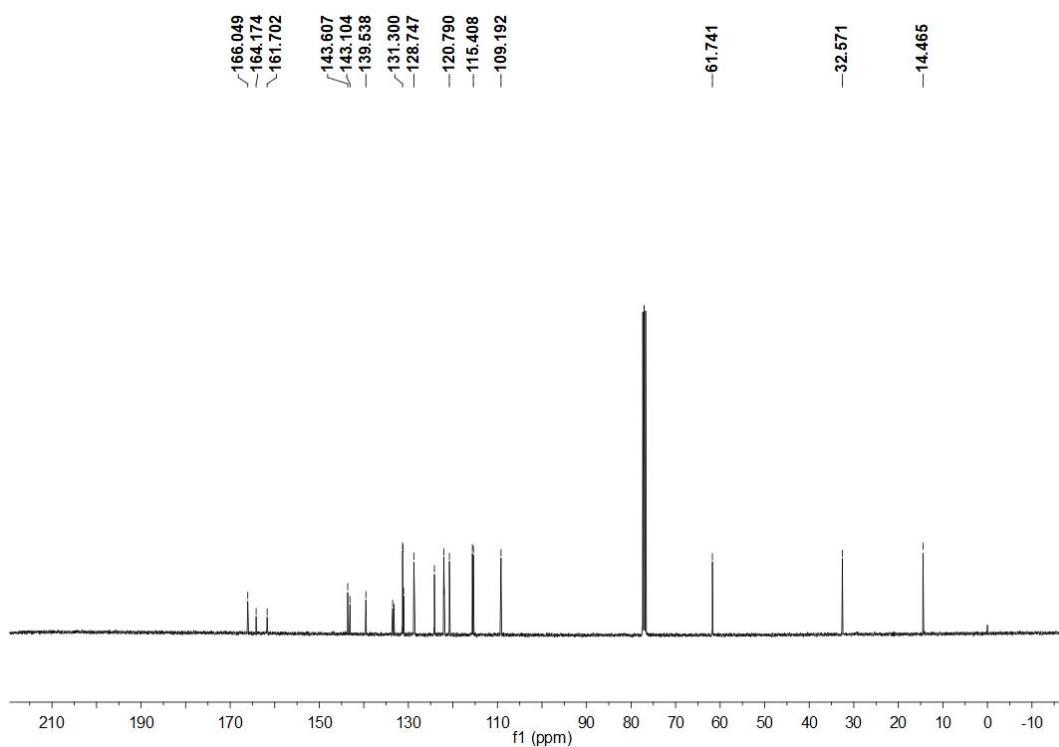
¹H NMR (400 MHz, Chloroform-d)



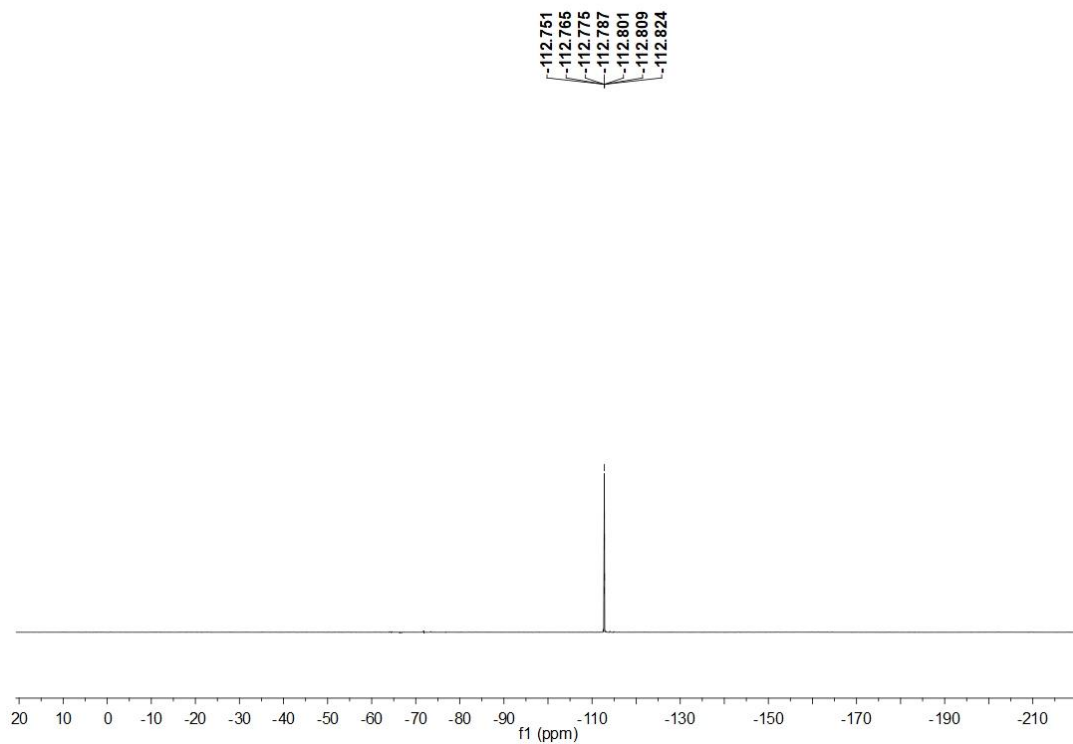
¹³C NMR (101 MHz, Chloroform-d)



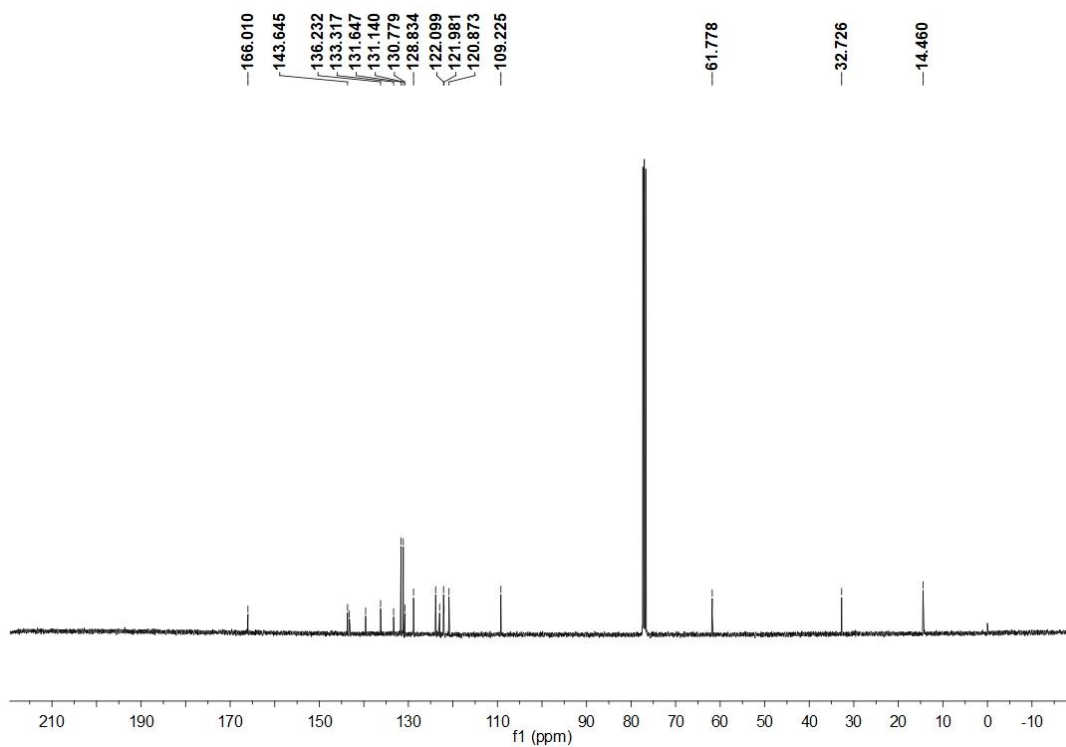
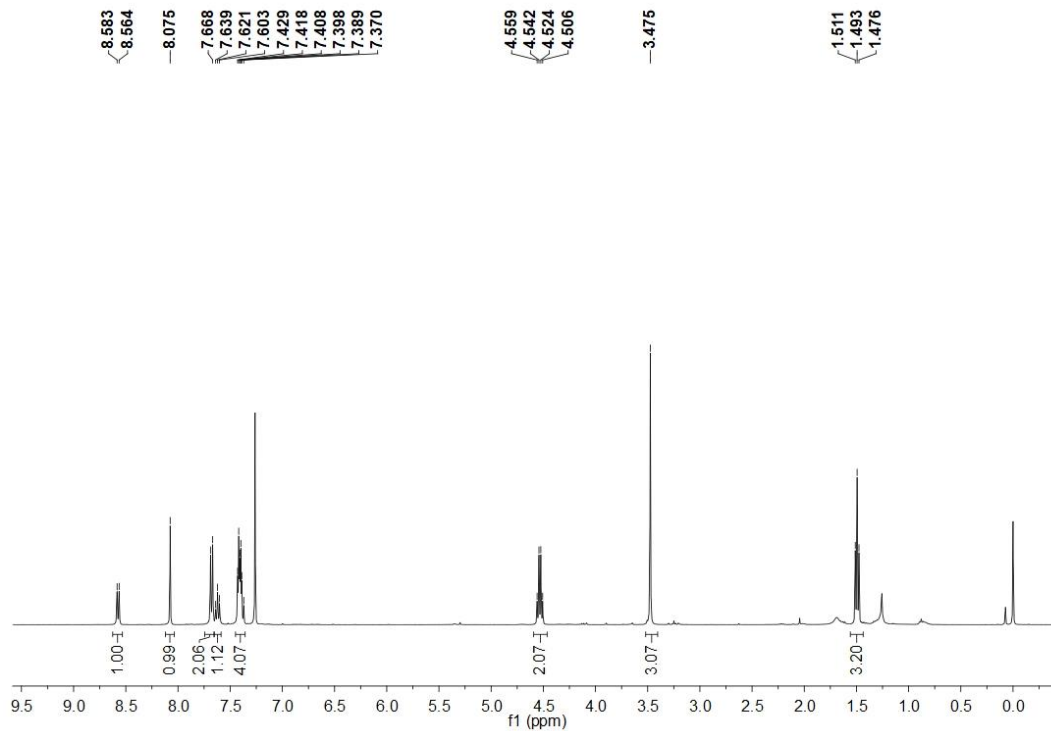
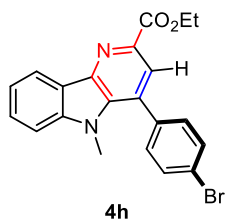
¹H NMR (400 MHz, Chloroform-d)

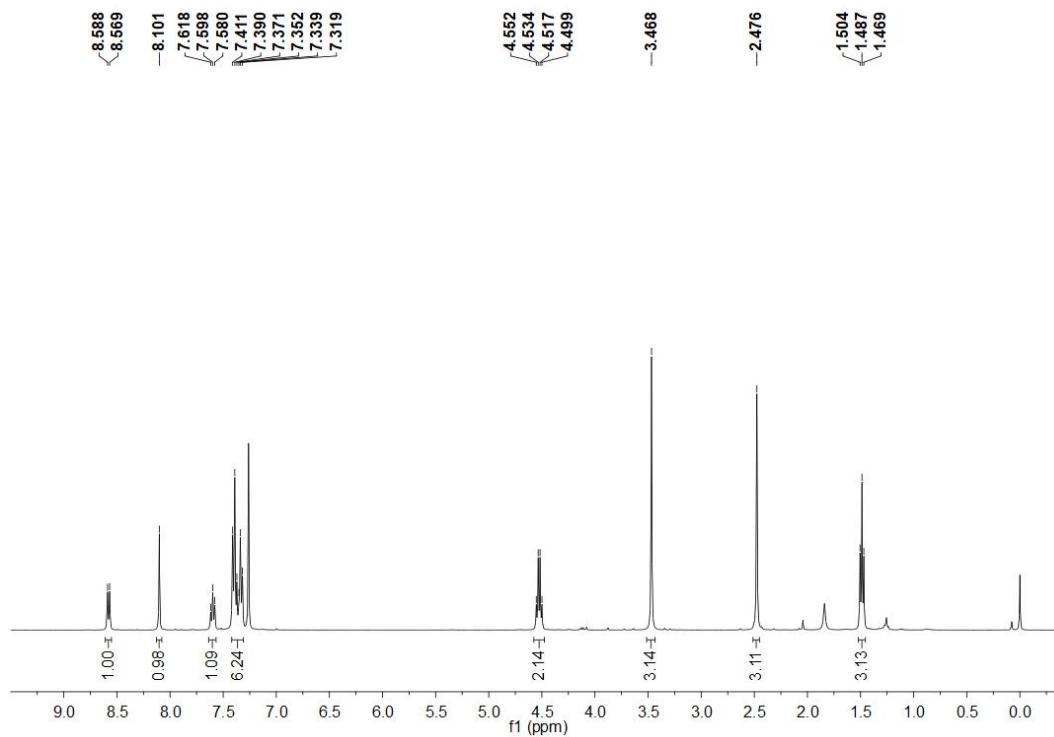
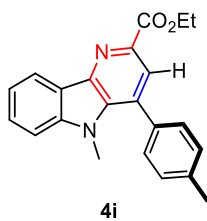


¹³C NMR (101 MHz, Chloroform-d)

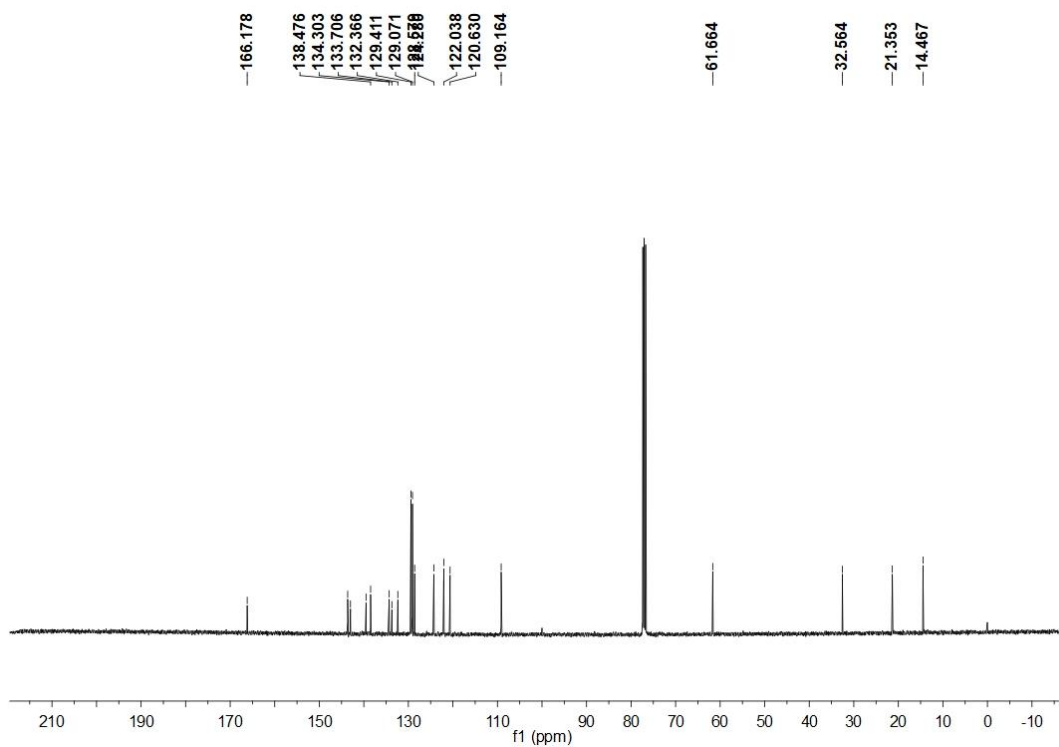


^{19}F NMR (376 MHz, Chloroform-d)

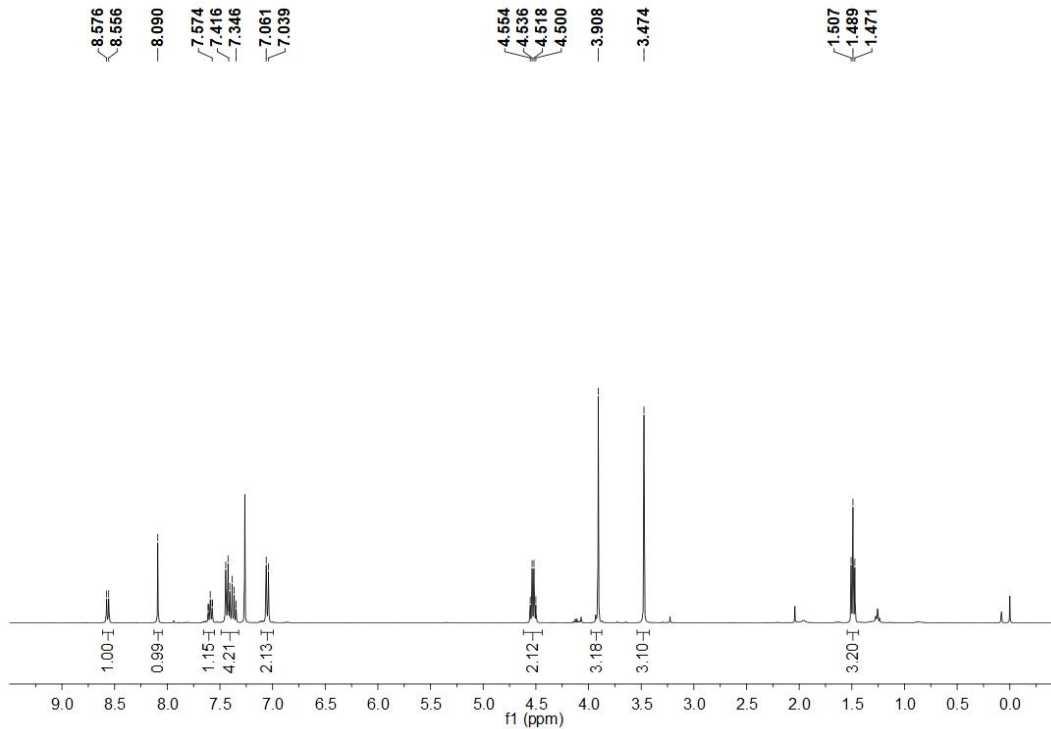
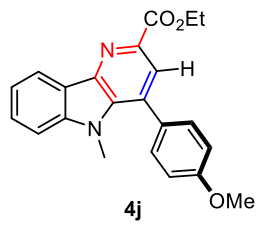




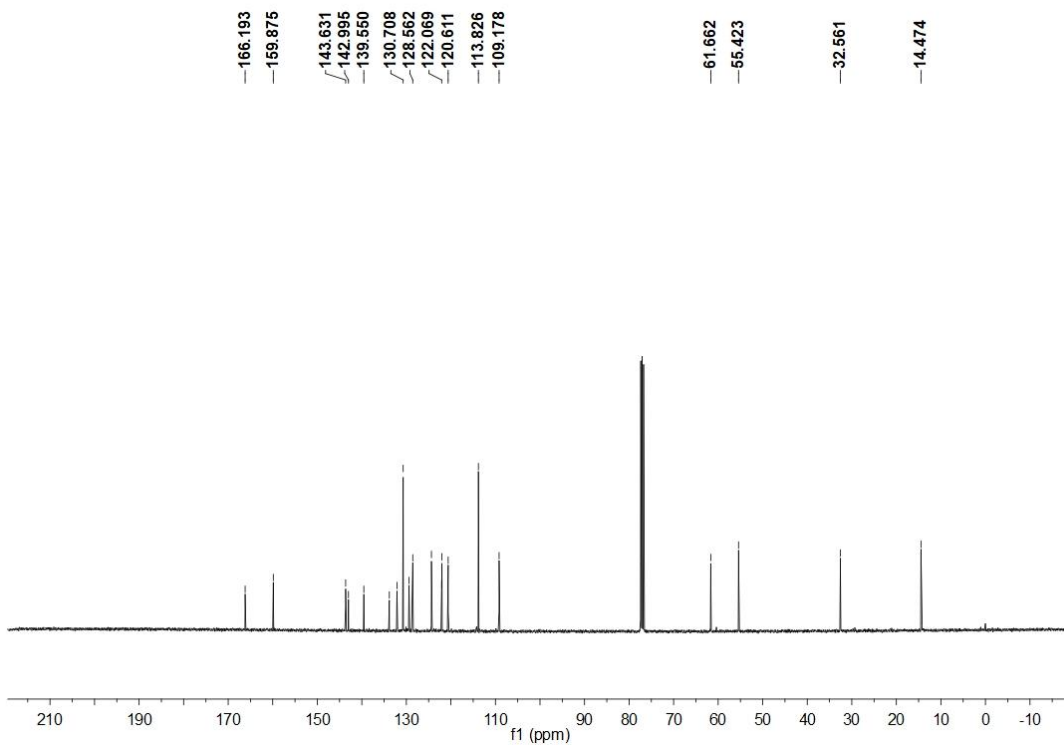
¹H NMR (400 MHz, Chloroform-d)



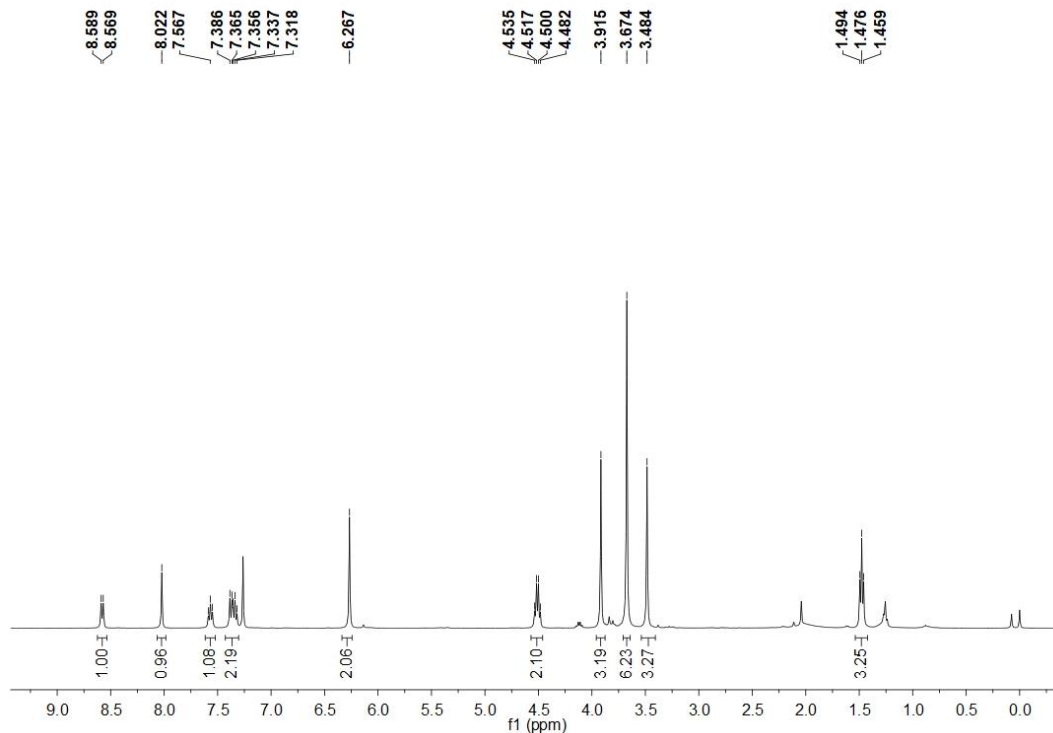
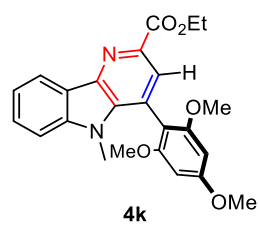
¹³C NMR (101 MHz, Chloroform-d)



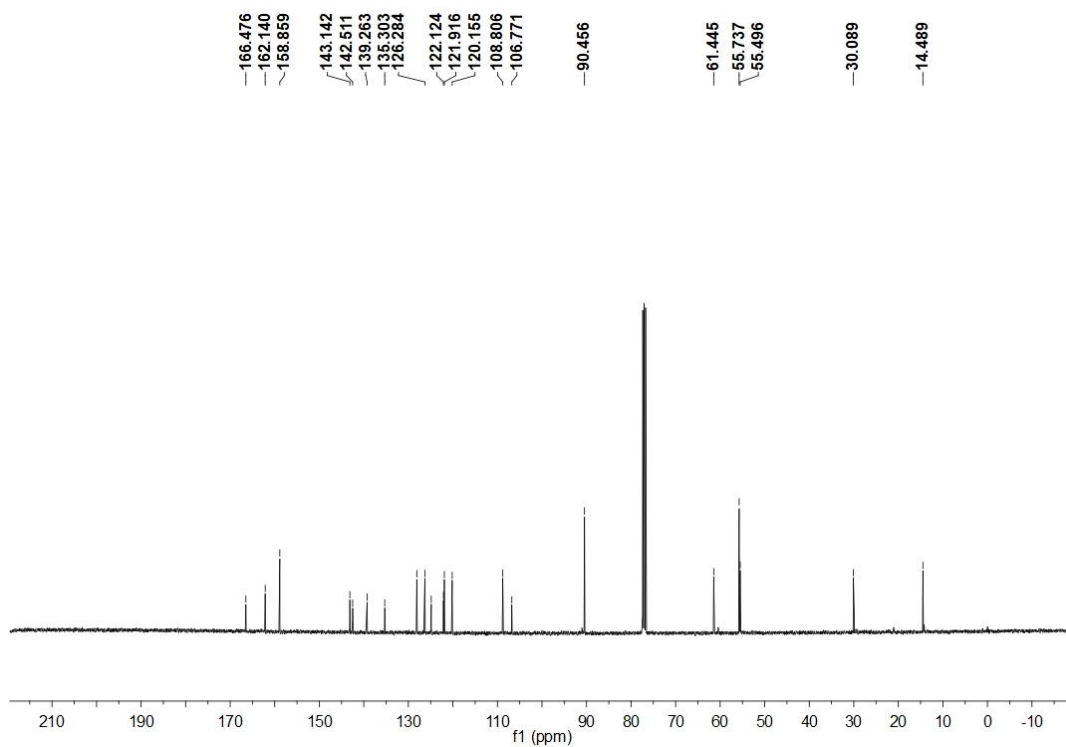
¹H NMR (400 MHz, Chloroform-d)



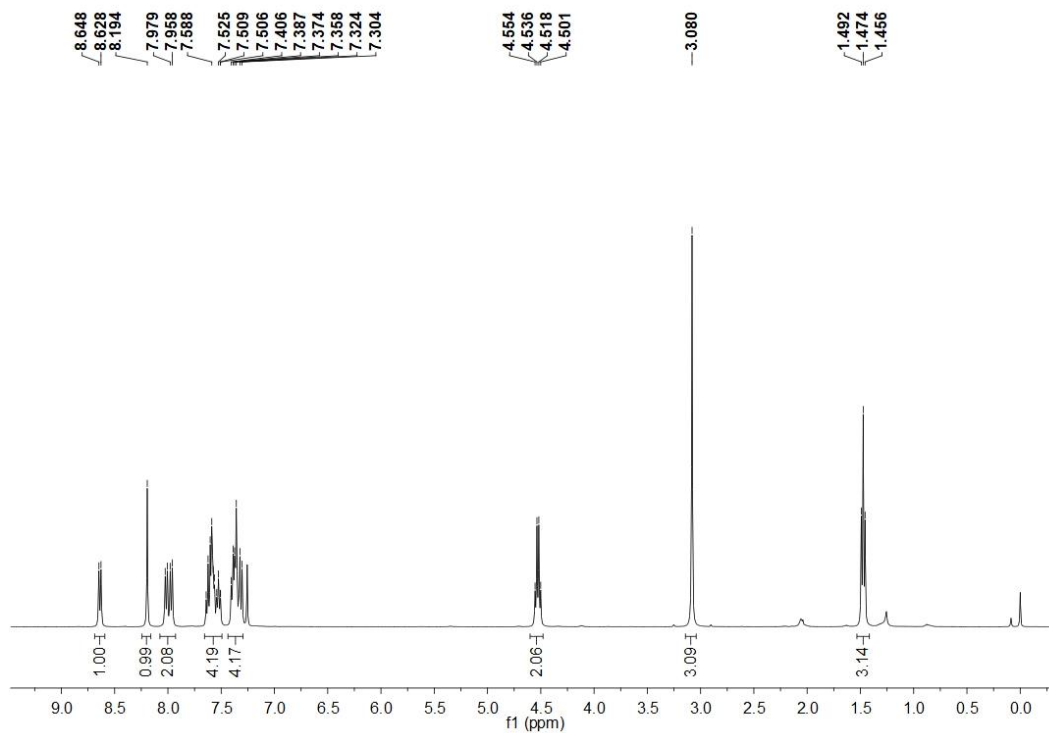
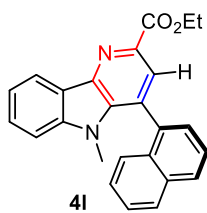
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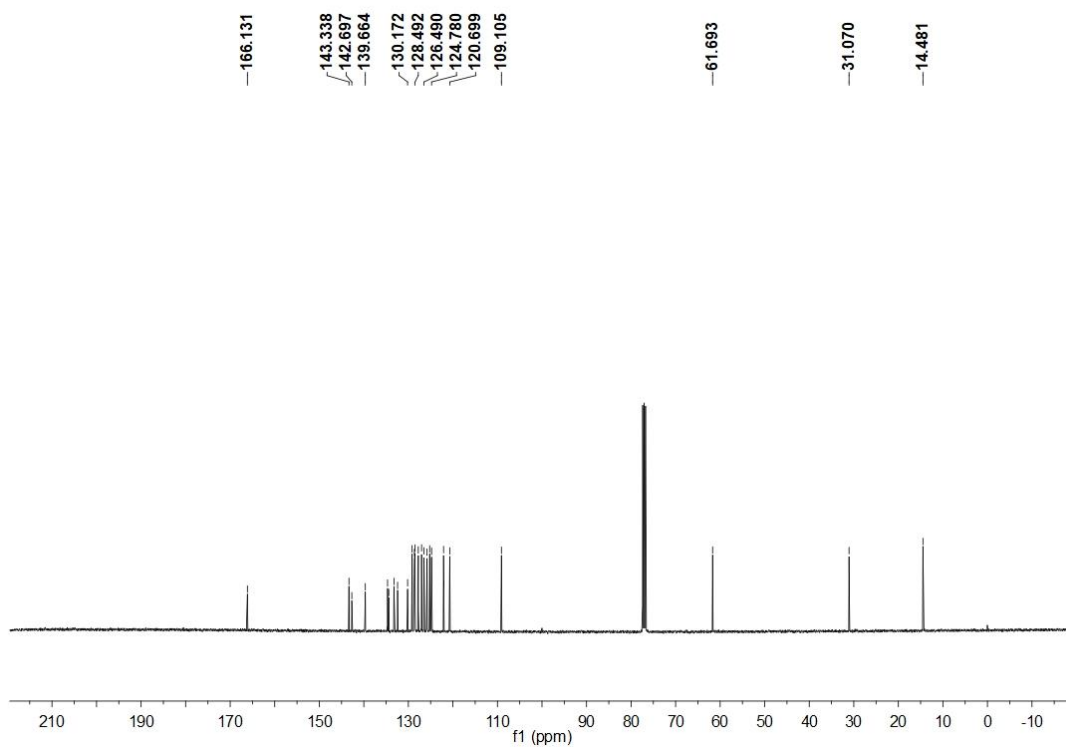
¹H NMR (400 MHz, Chloroform-d)



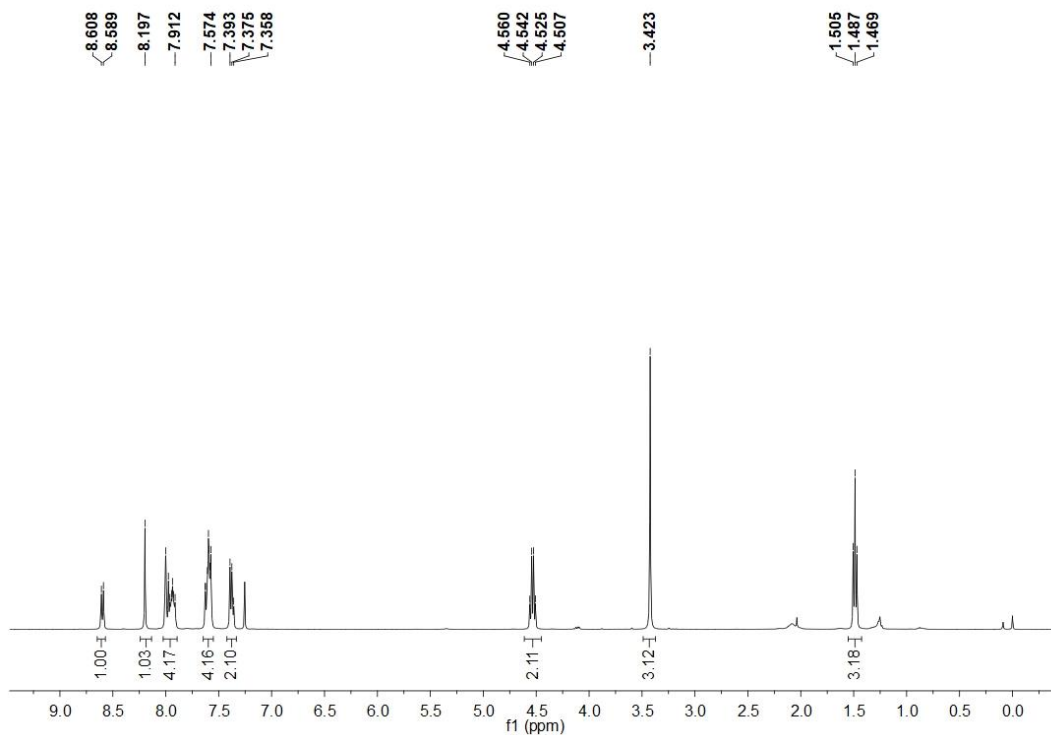
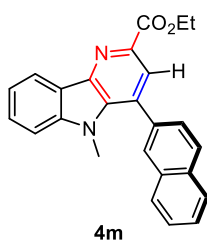
¹³C NMR (101 MHz, Chloroform-d)



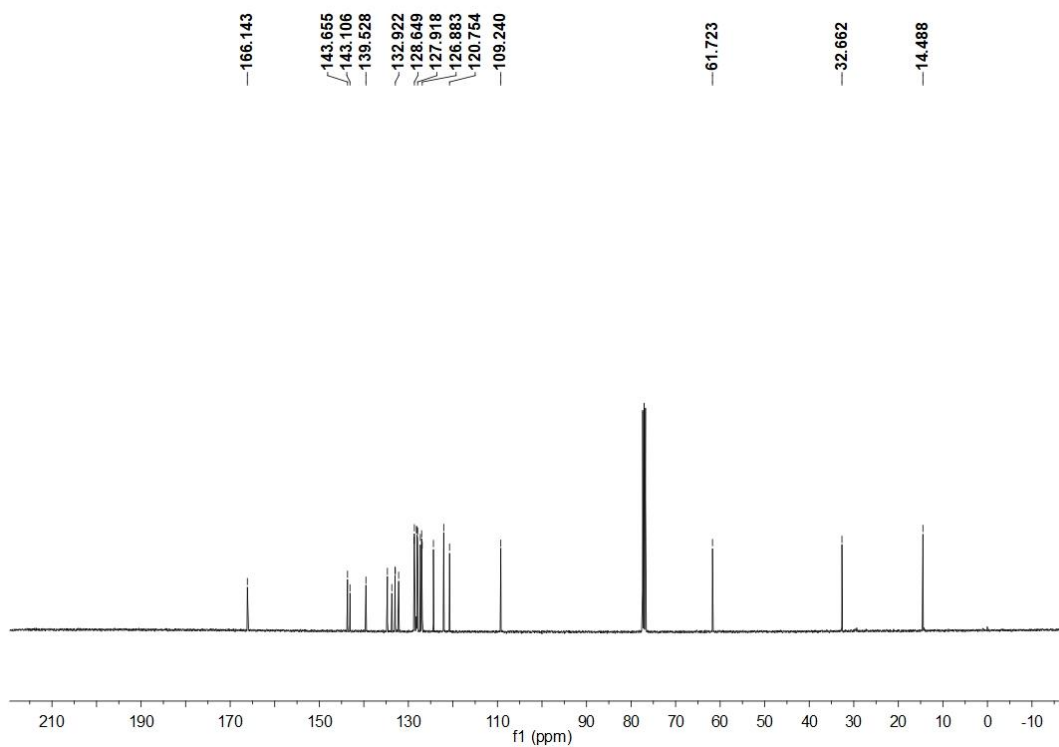
¹H NMR (400 MHz, Chloroform-d)



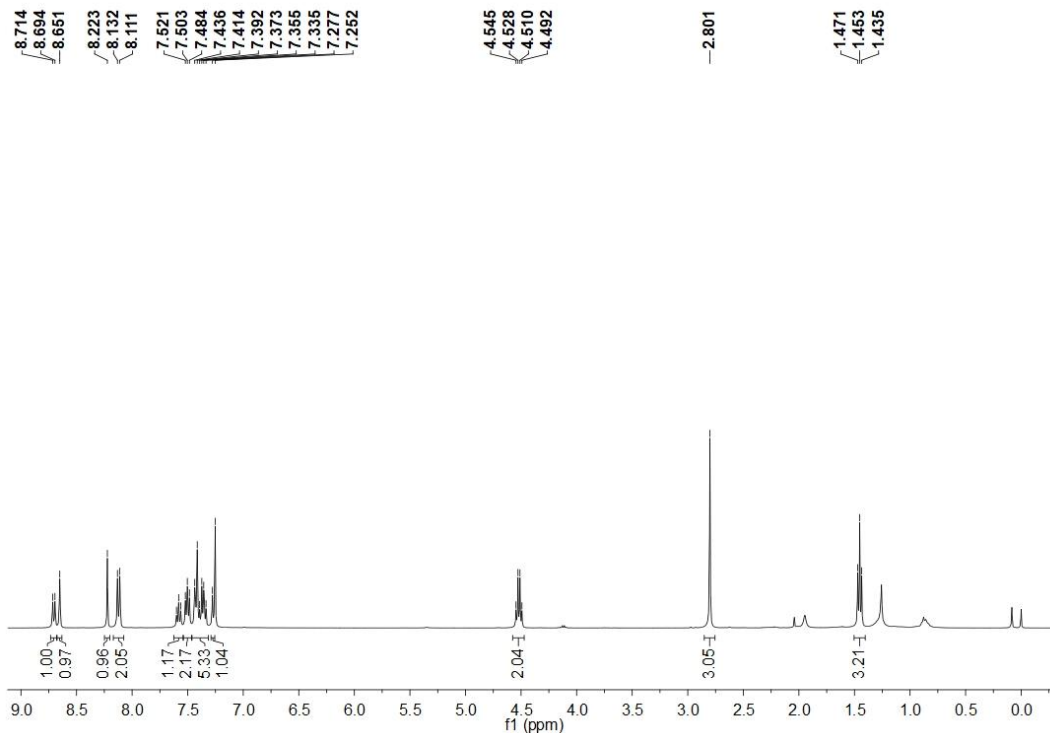
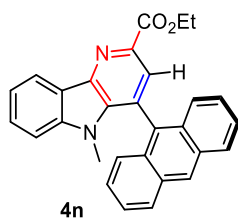
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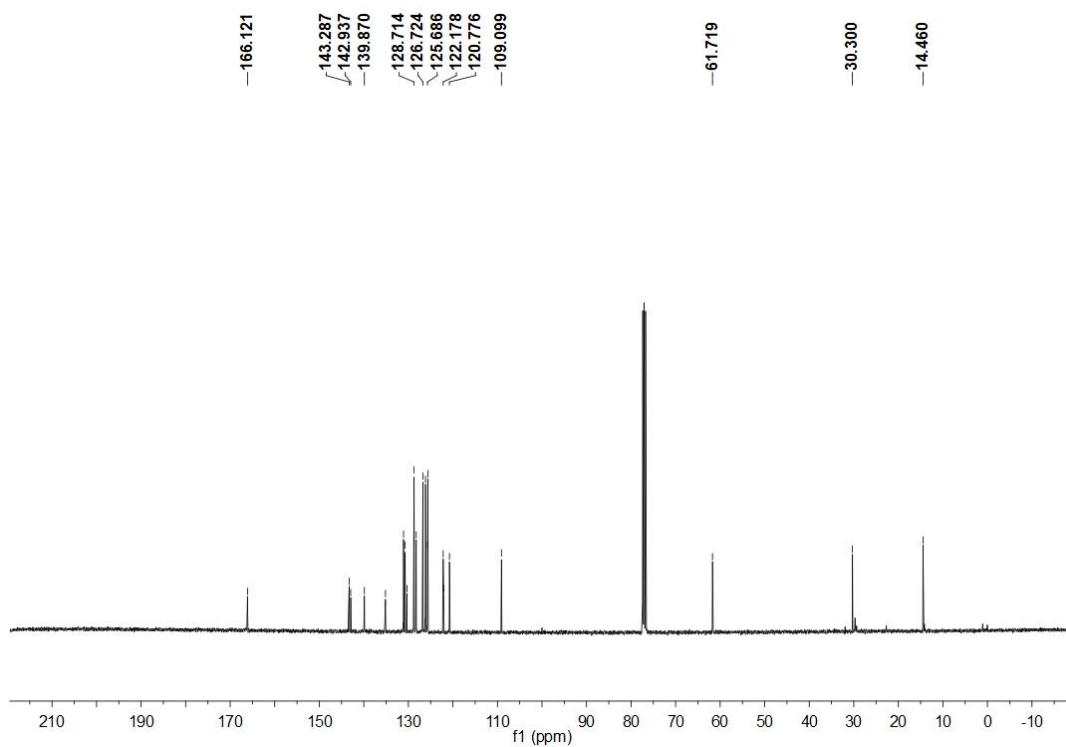
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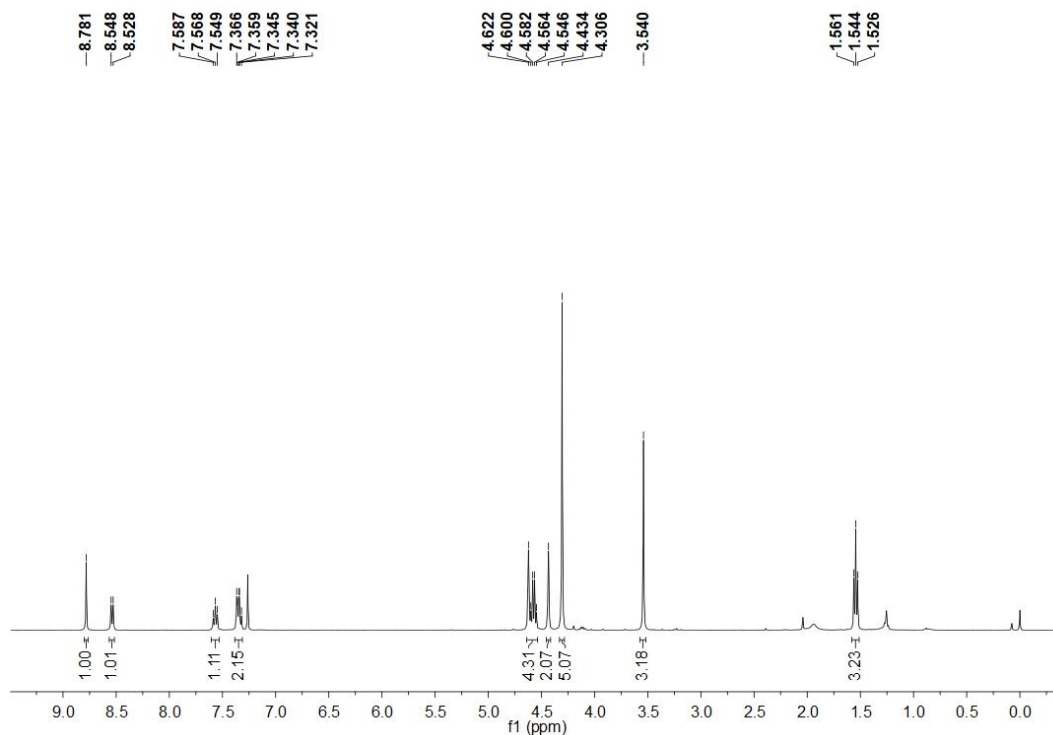
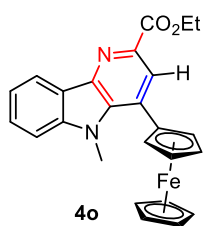
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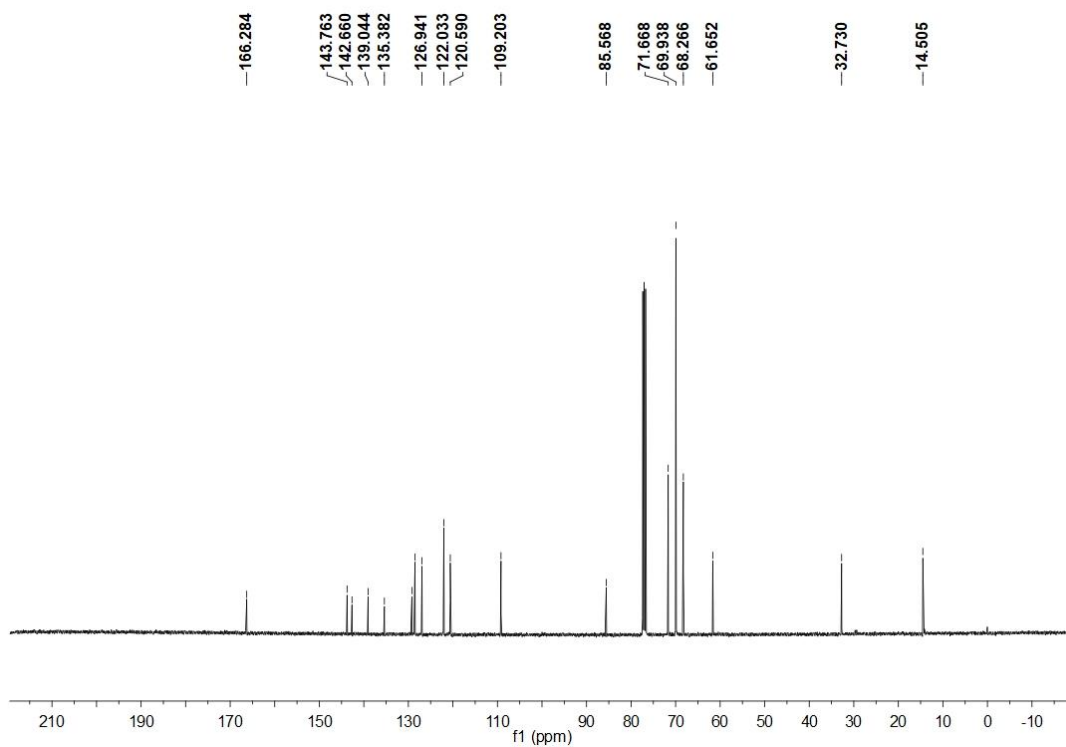
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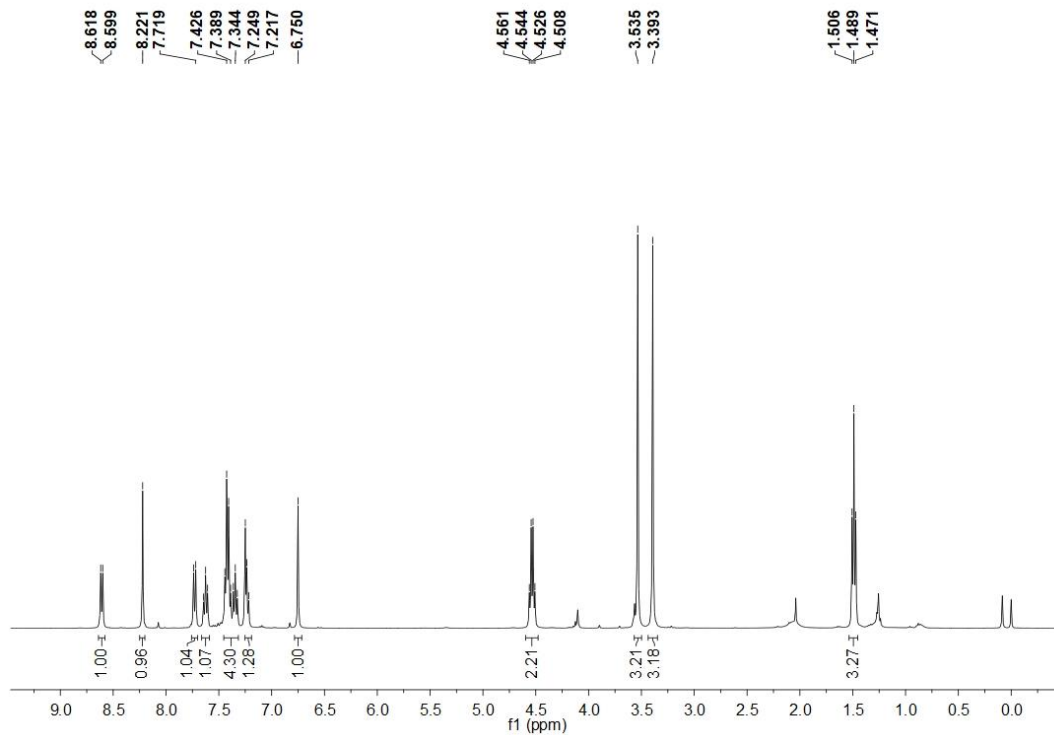
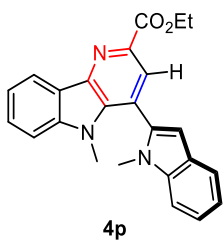
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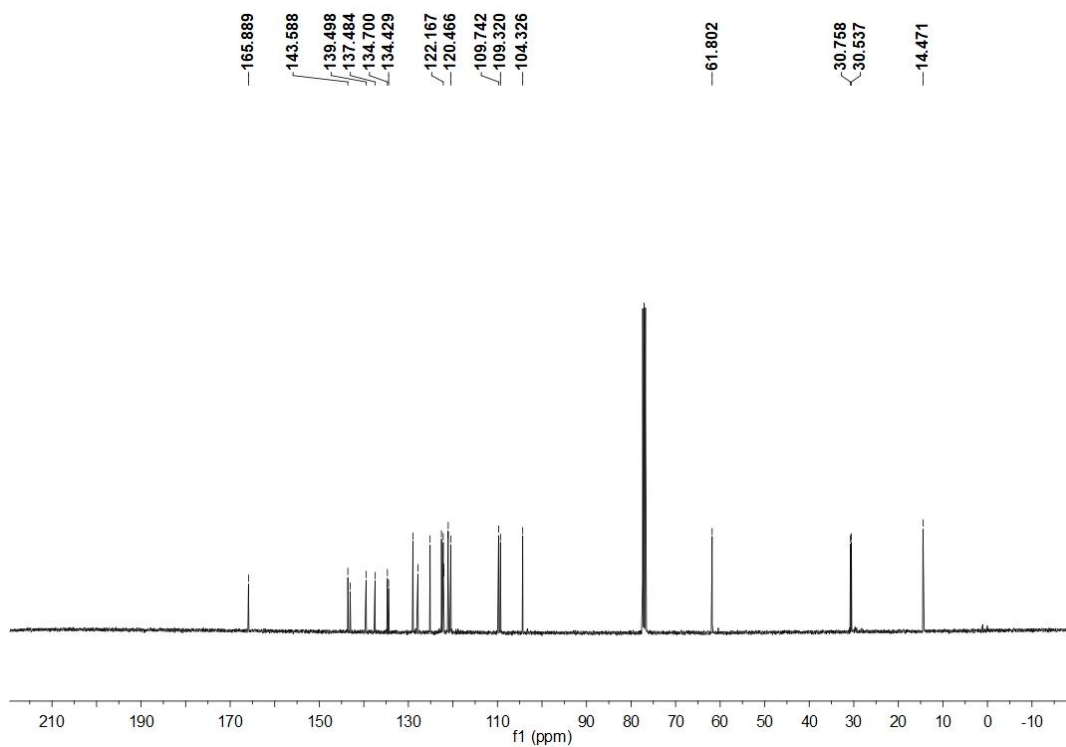
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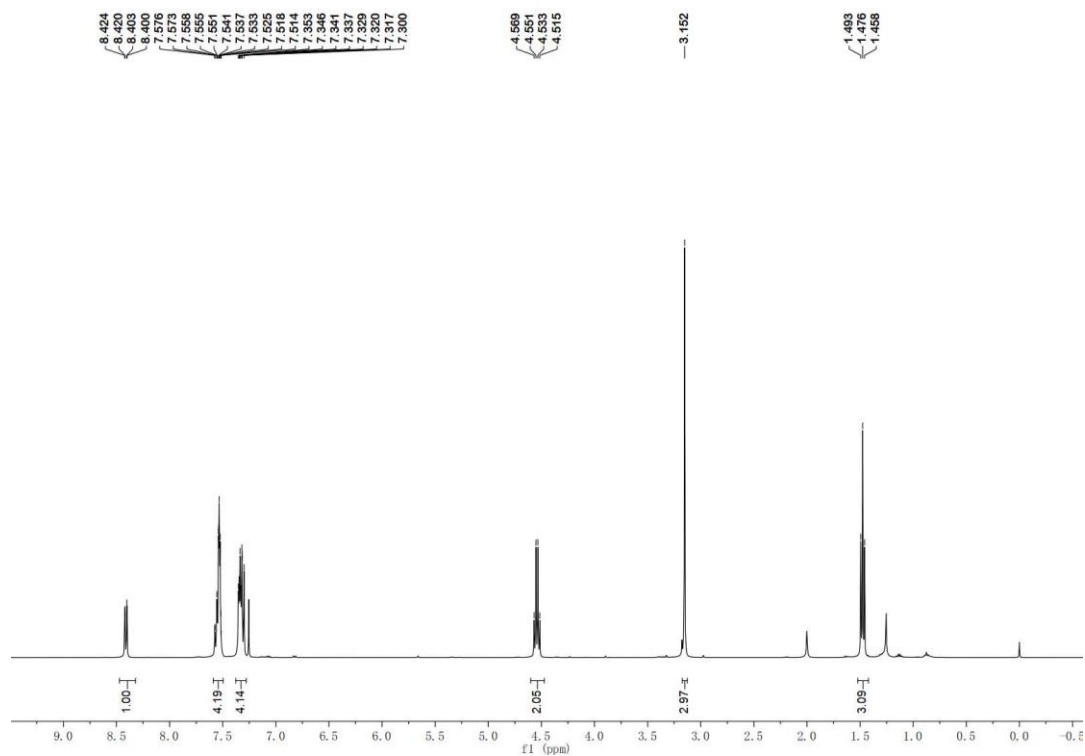
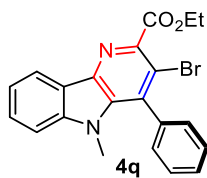
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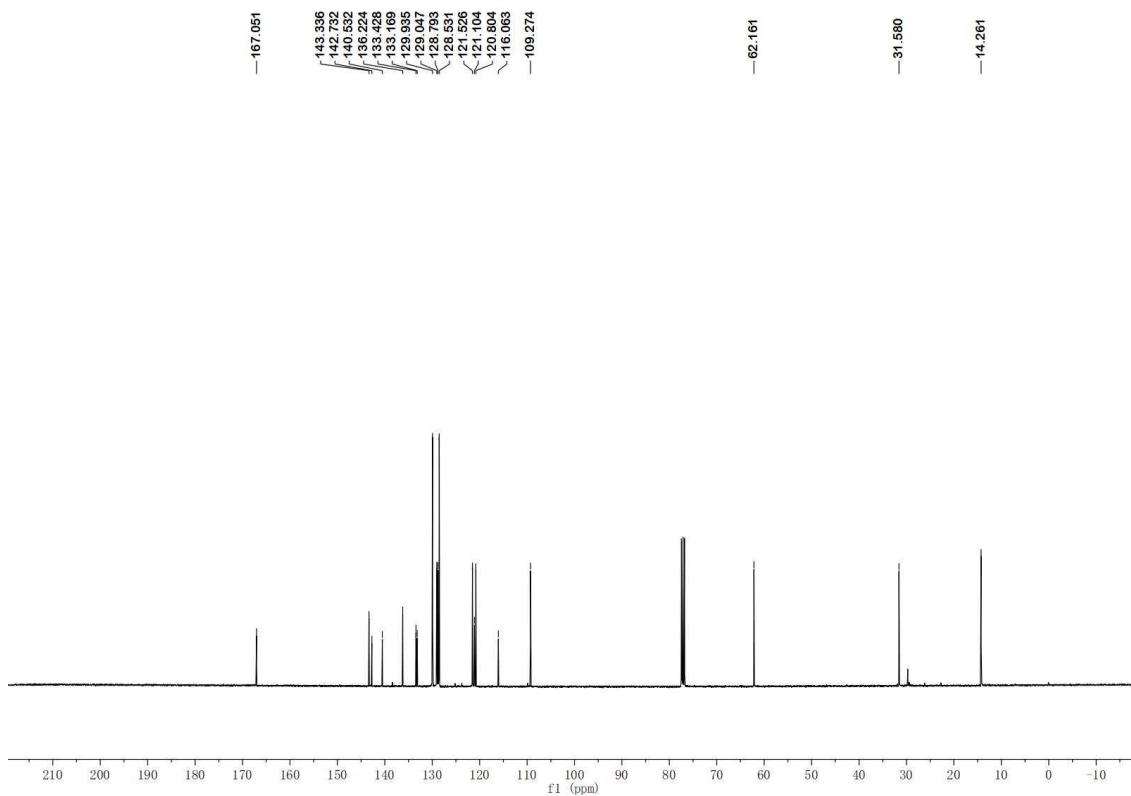
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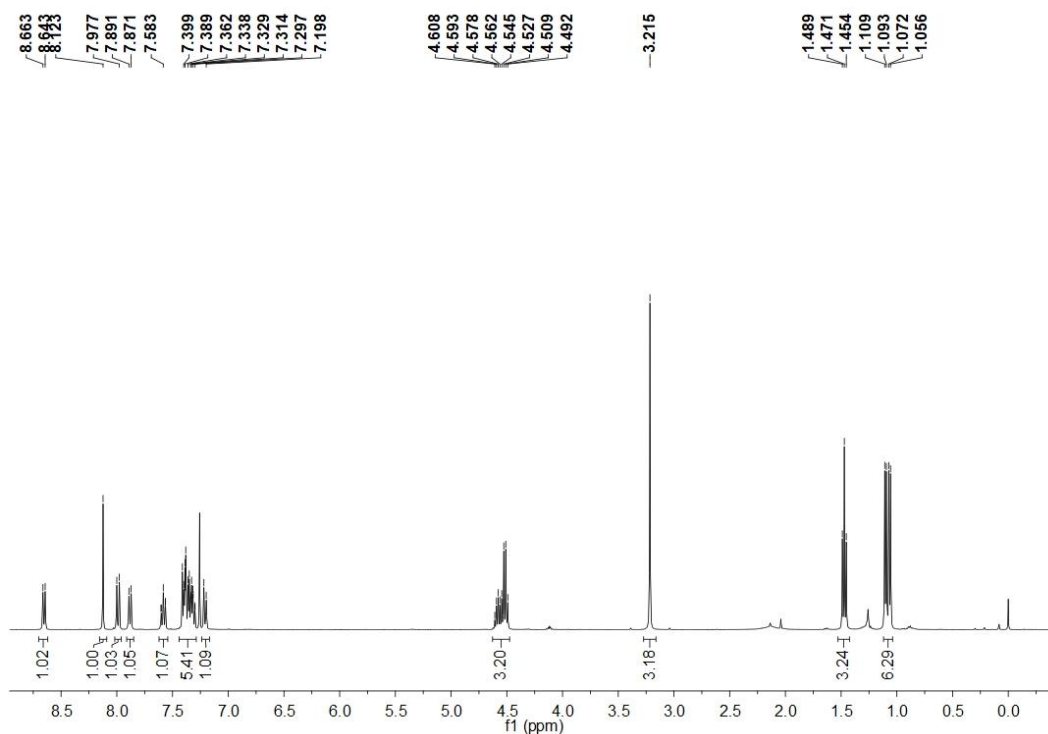
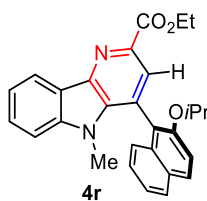
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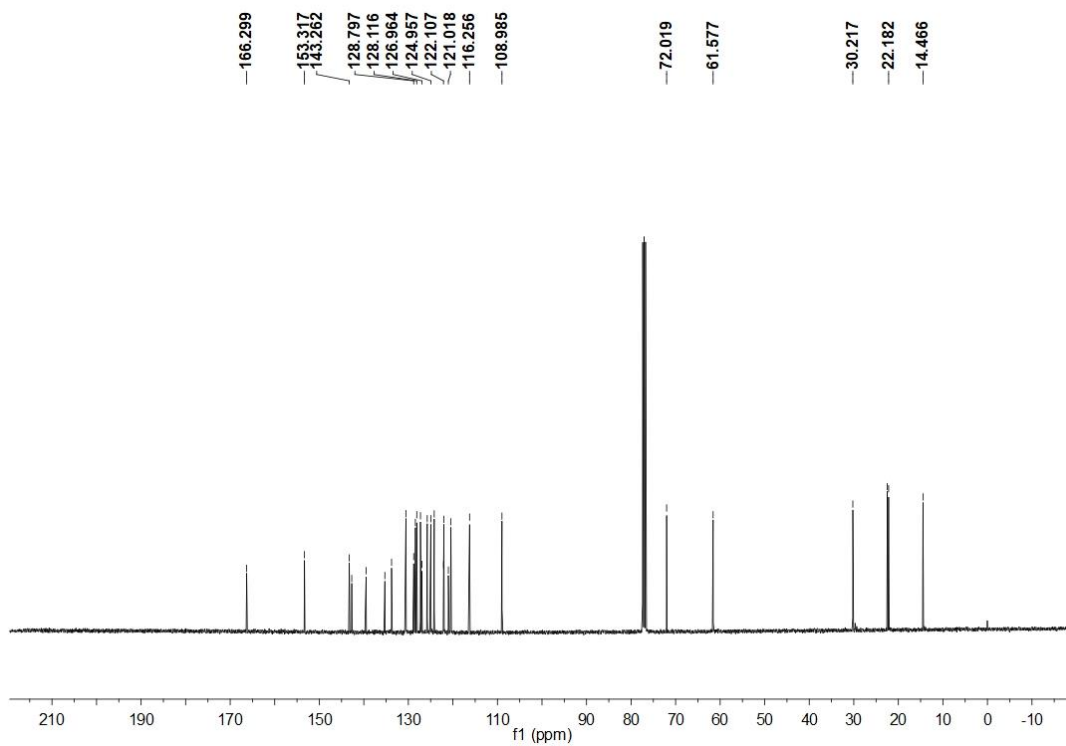
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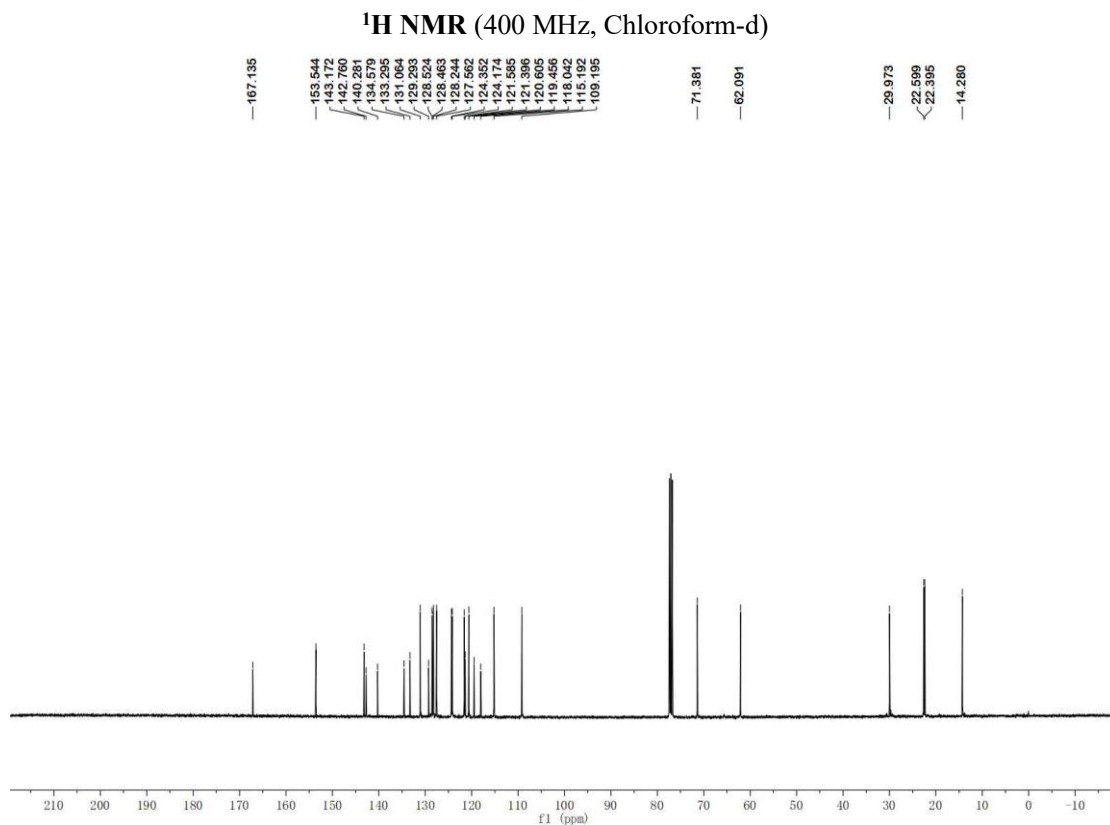
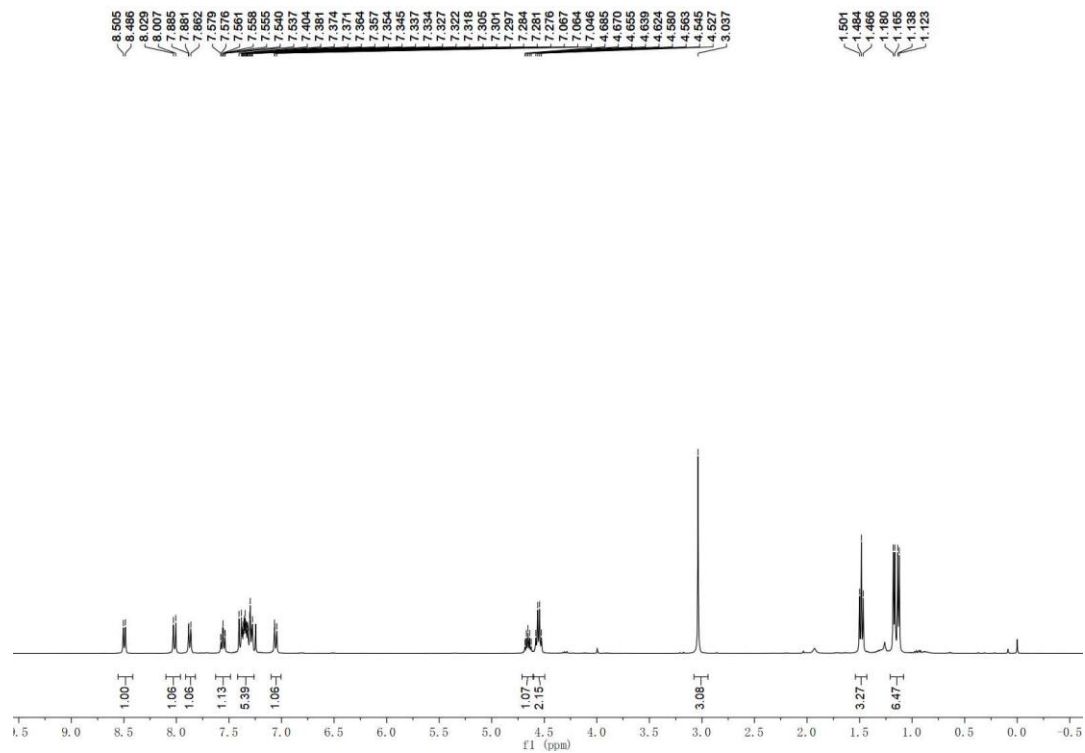
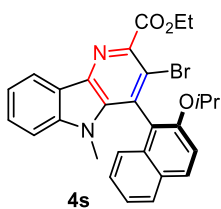
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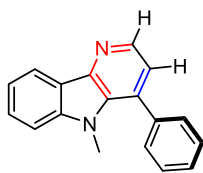


¹H NMR (400 MHz, Chloroform-d)

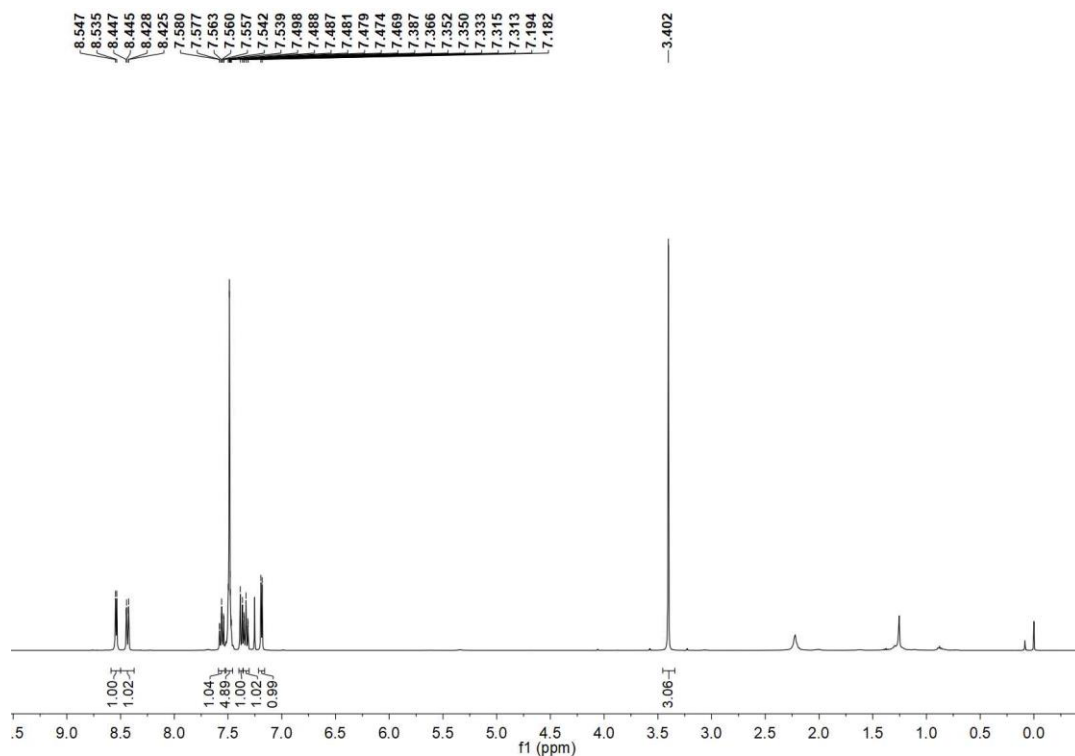


¹³C NMR (101 MHz, Chloroform-d)

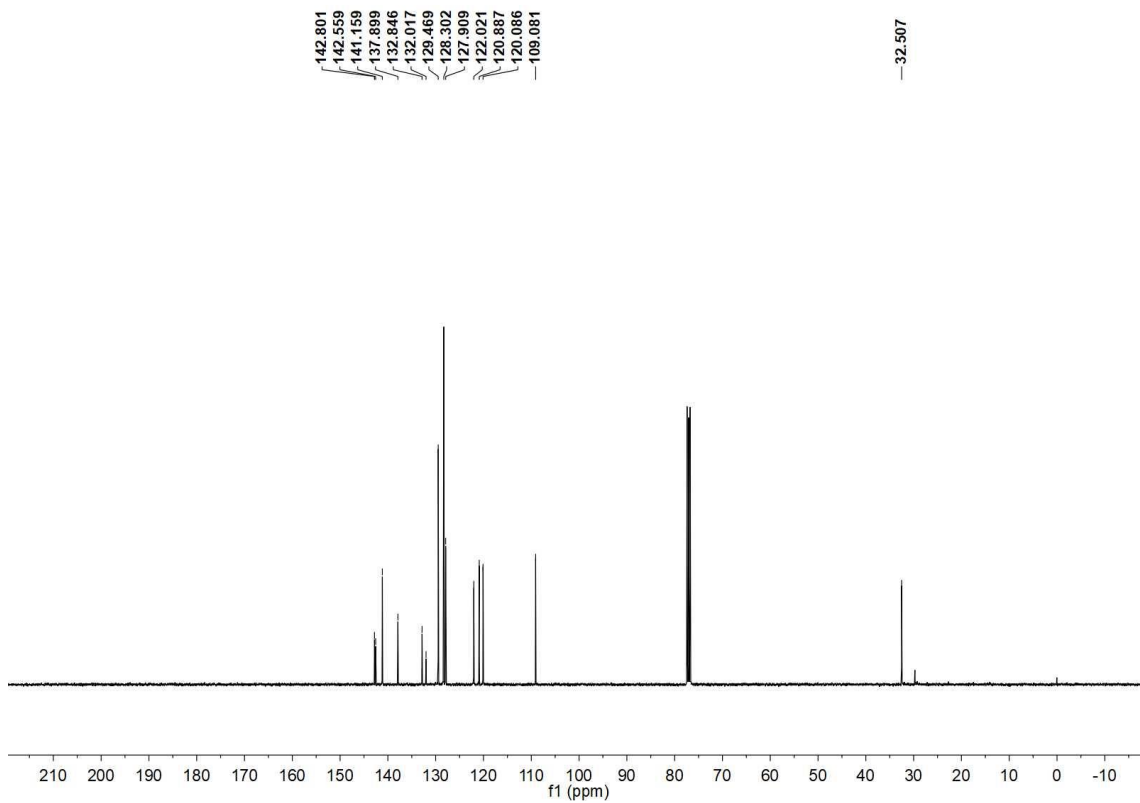




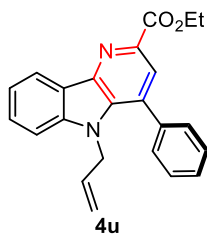
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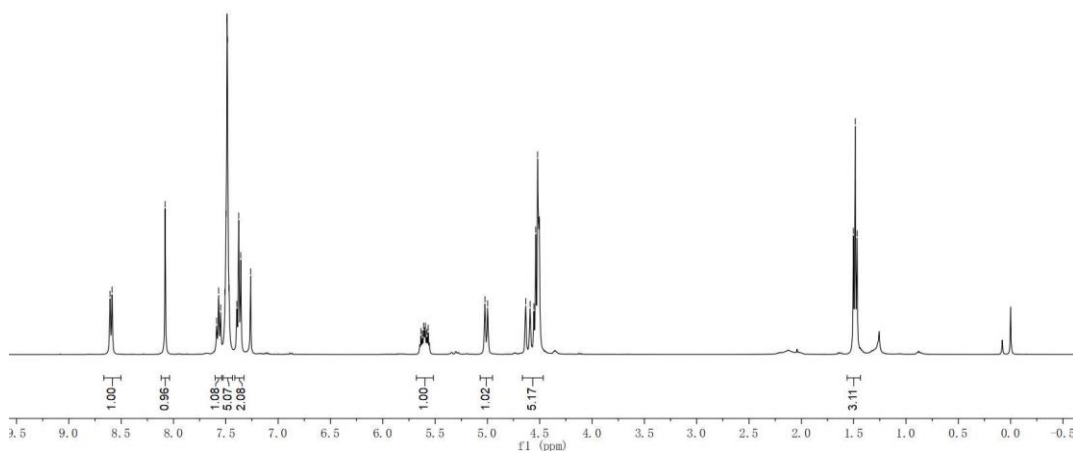
¹H NMR (400 MHz, Chloroform-d)



¹³C NMR (101 MHz, Chloroform-d)

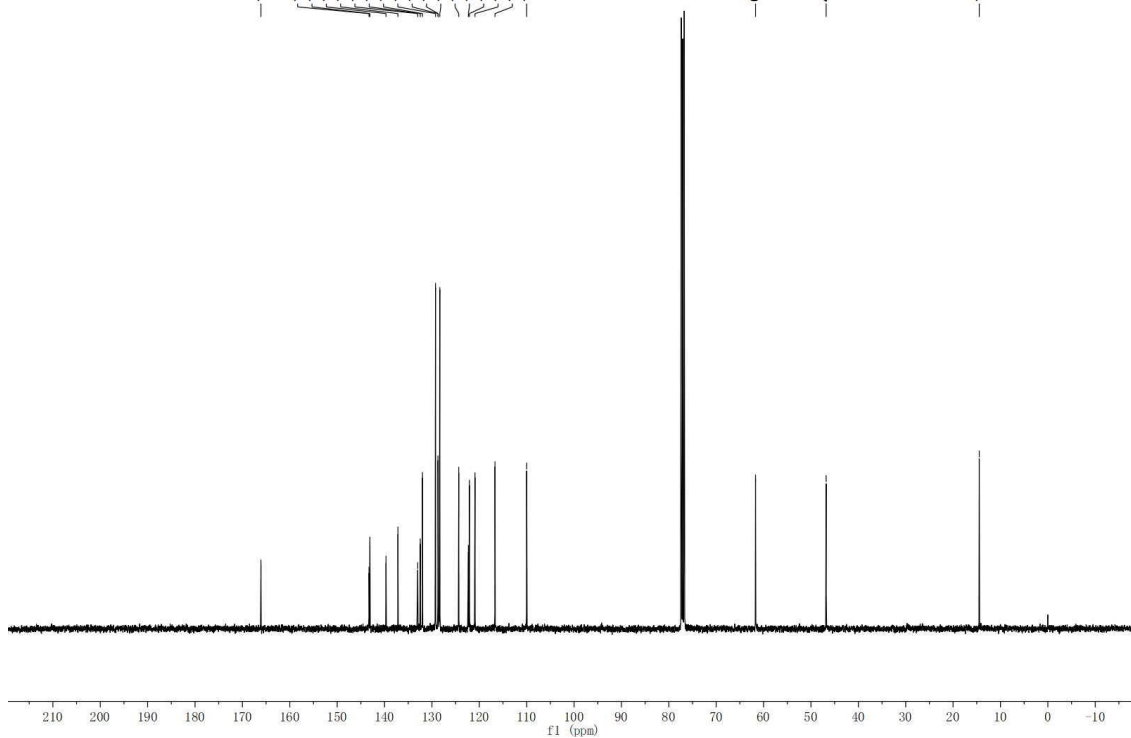


¹H NMR (400 MHz, Chloroform-d) peaks (ppm): 8.606, 8.567, 8.070, 7.568, 7.569, 7.549, 7.508, 7.487, 7.489, 7.468, 7.460, 7.394, 7.377, 7.357, 7.263, 5.635, 5.622, 5.609, 5.603, 5.597, 5.592, 5.579, 5.565, 5.024, 4.998, 4.635, 4.592, 4.566, 4.558, 4.552, 4.511, 4.503, 1.503, 1.485, 1.467.

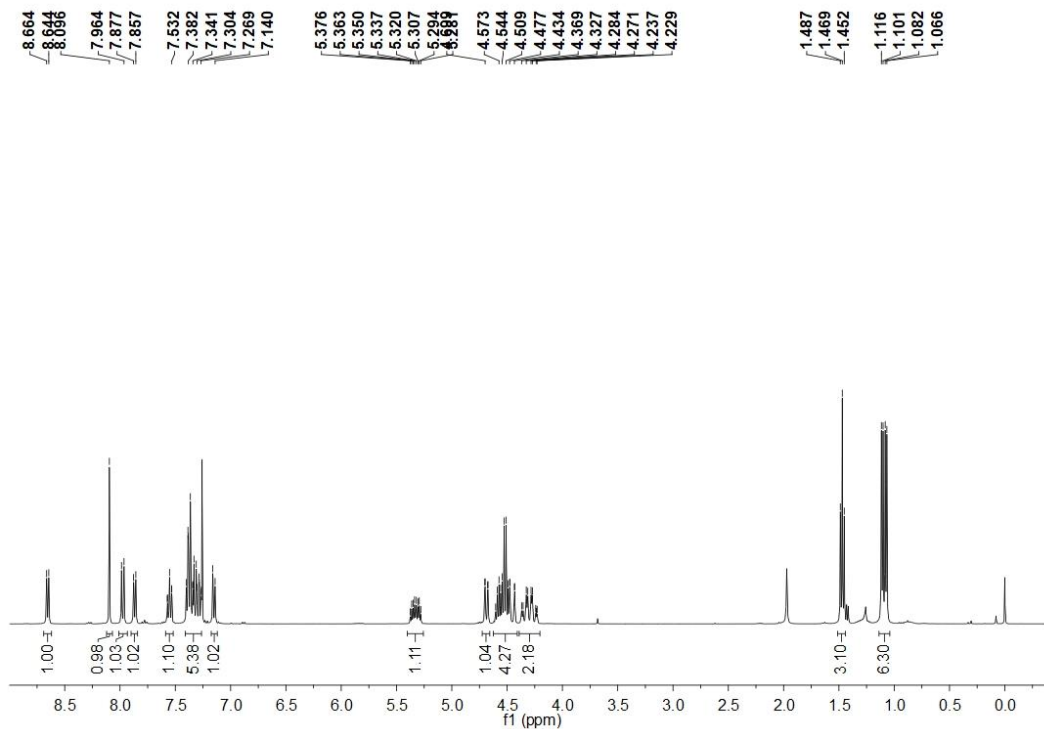
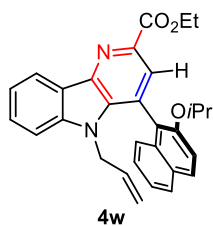


¹H NMR (400 MHz, Chloroform-d)

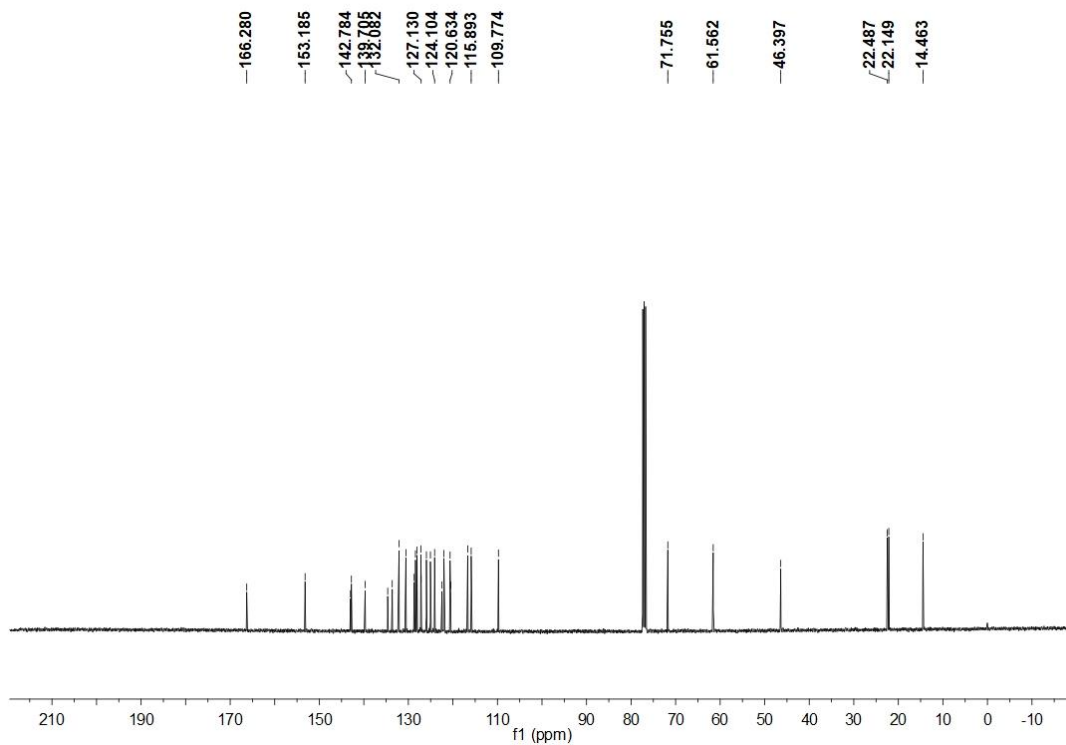
¹³C NMR (101 MHz, Chloroform-d) peaks (ppm): 166.093, 143.284, 143.092, 139.697, 137.178, 132.986, 132.985, 131.995, 129.725, 128.683, 128.339, 124.336, 122.309, 122.092, 120.610, 117.694, 110.007, 61.696, 46.793, 14.475.



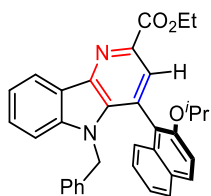
¹³C NMR (101 MHz, Chloroform-d)



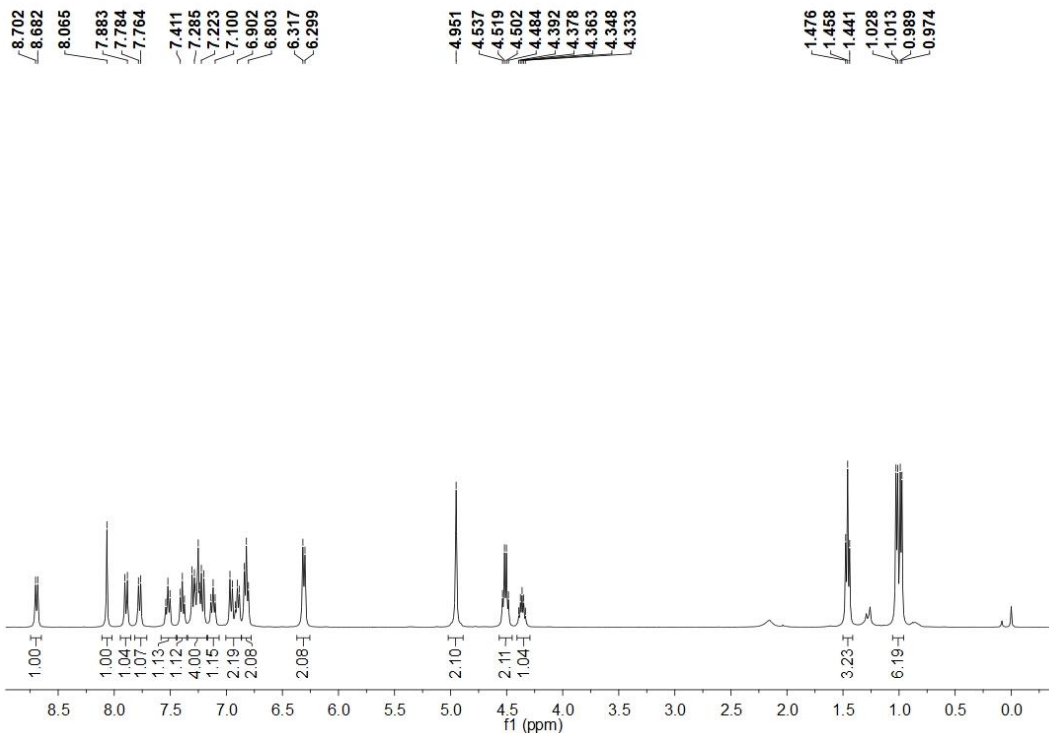
¹H NMR (400 MHz, Chloroform-d)



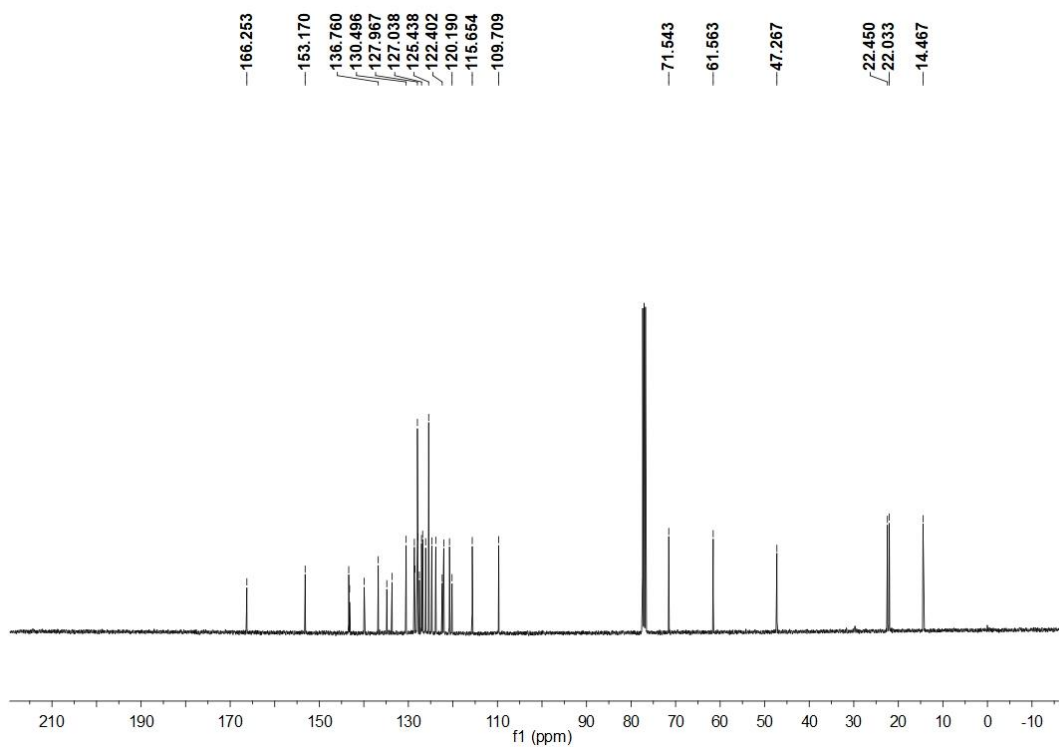
¹³C NMR (101 MHz, Chloroform-d)



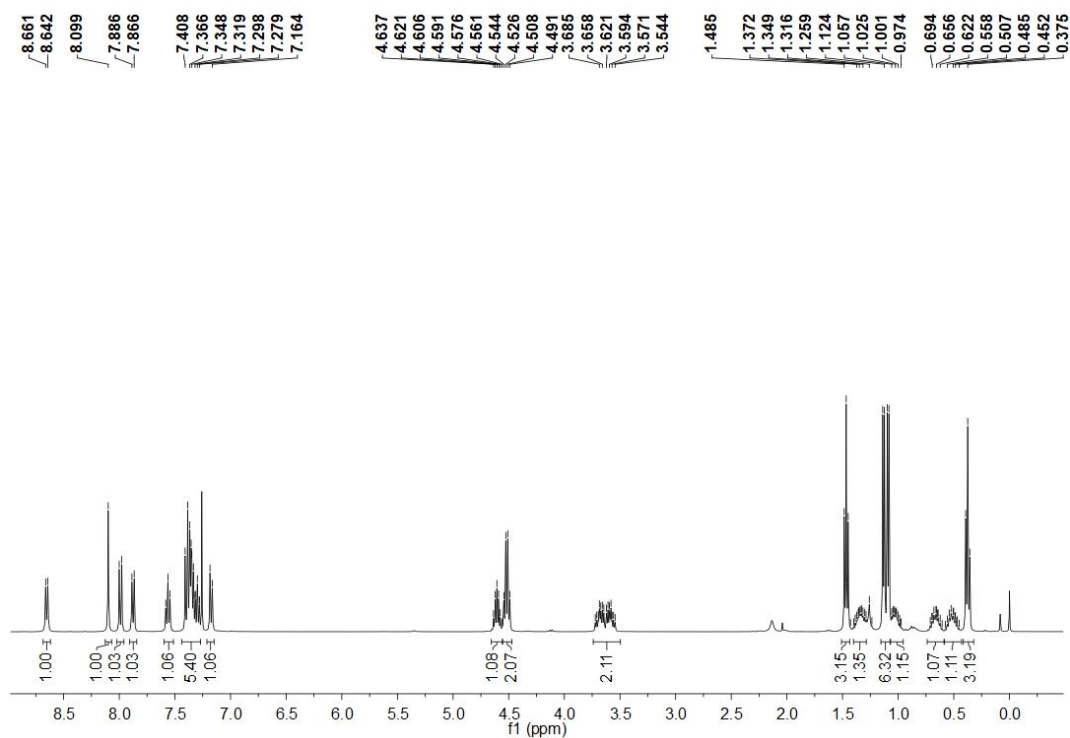
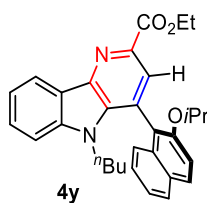
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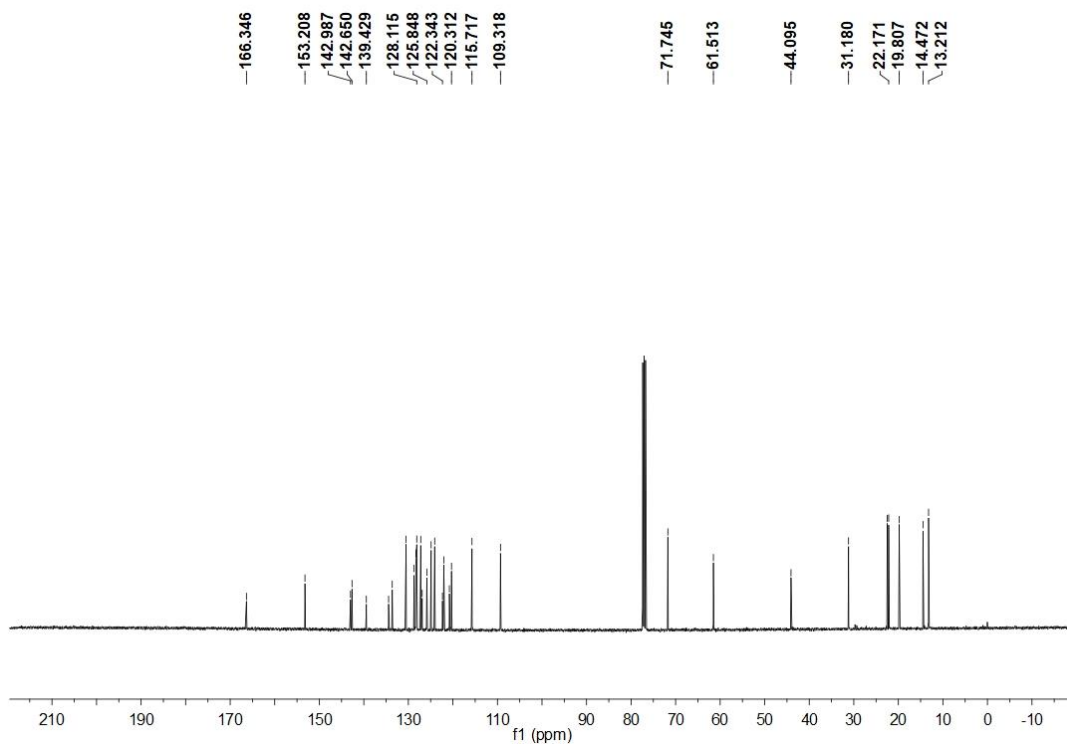
¹H NMR (400 MHz, Chloroform-d)



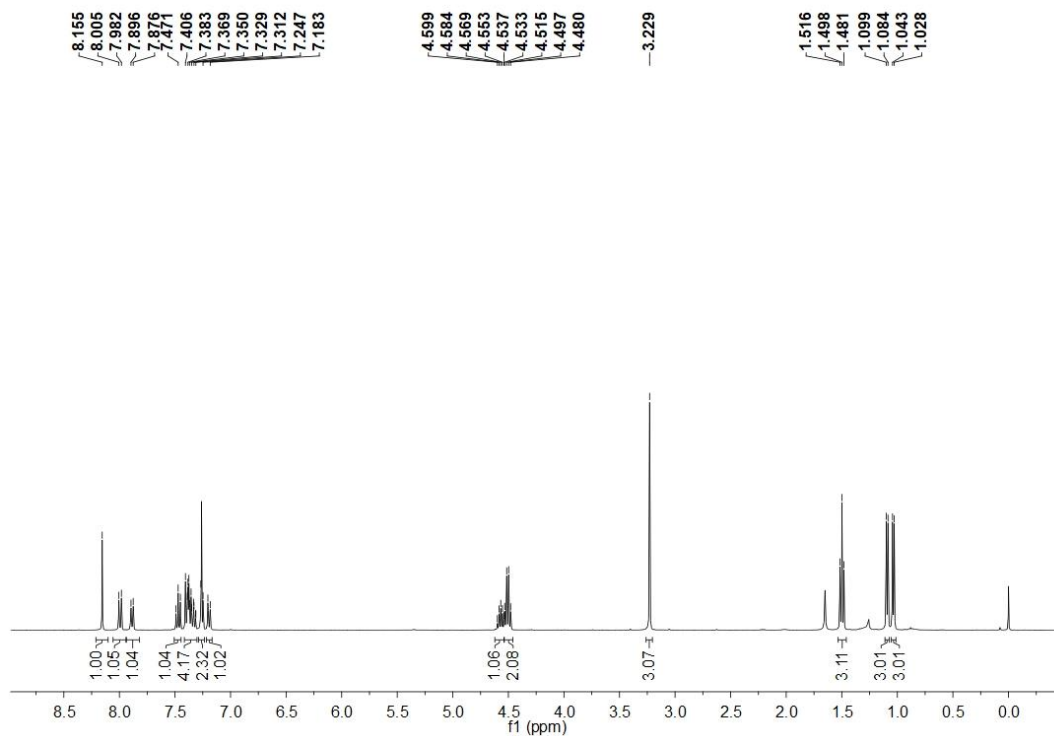
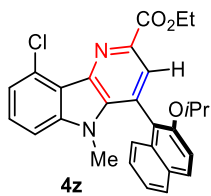
¹³C NMR (101 MHz, Chloroform-d)



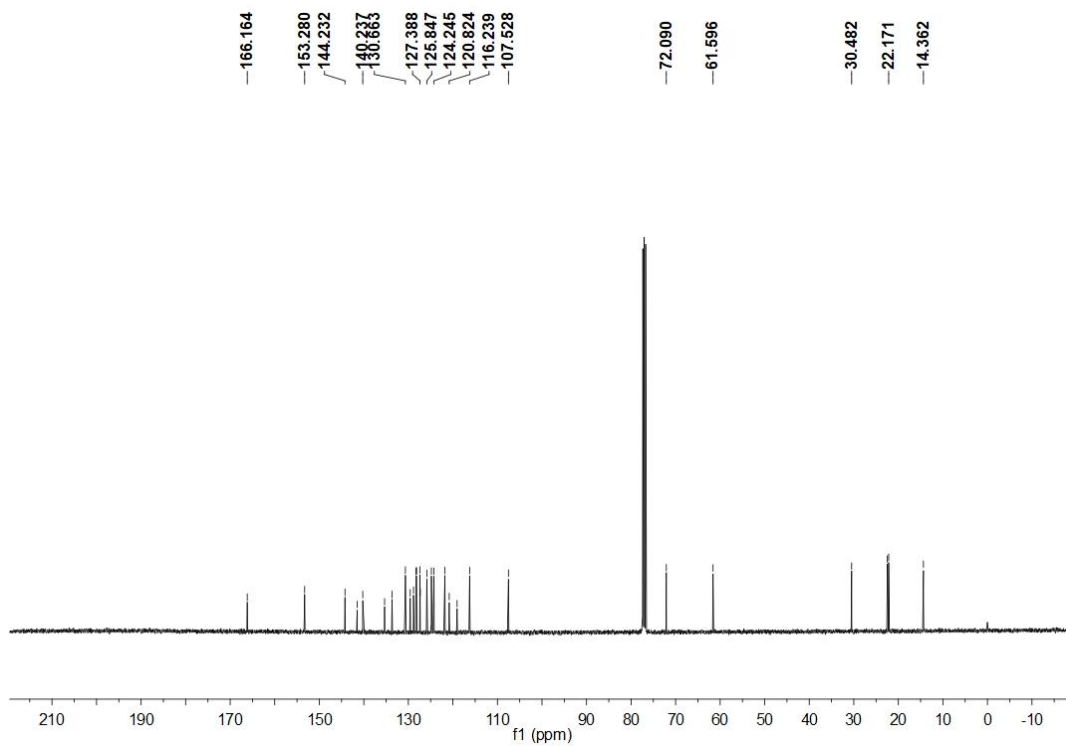
¹H NMR (400 MHz, Chloroform-d)



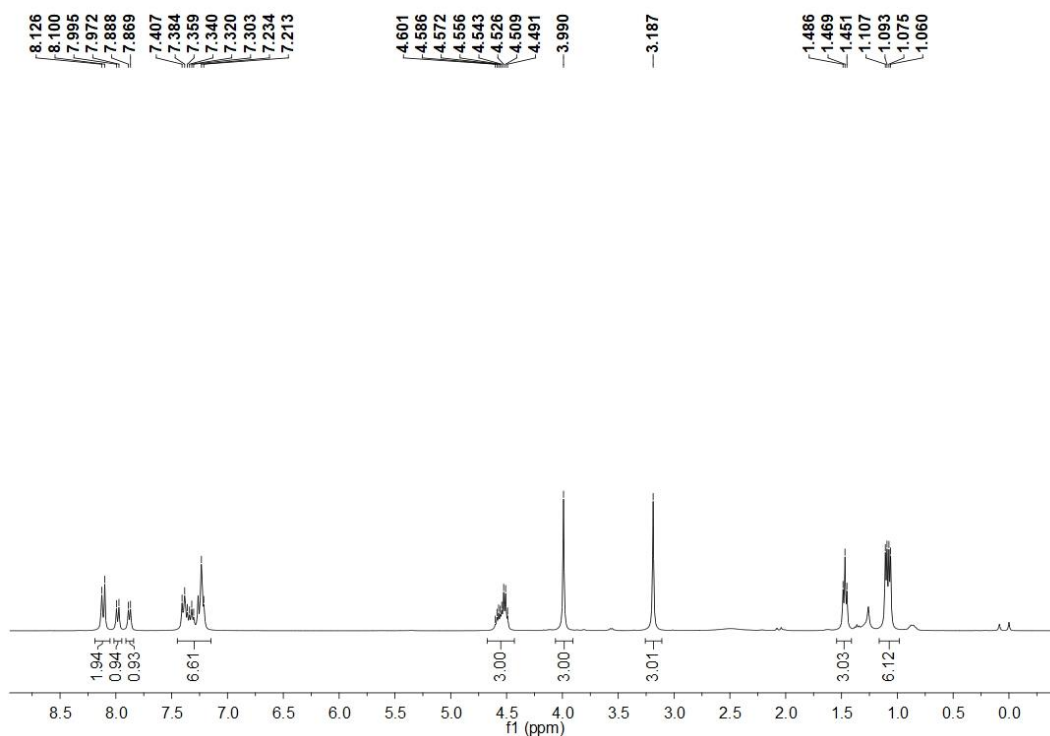
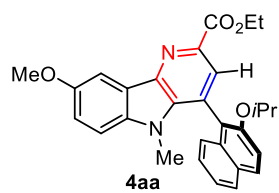
¹³C NMR (101 MHz, Chloroform-d)



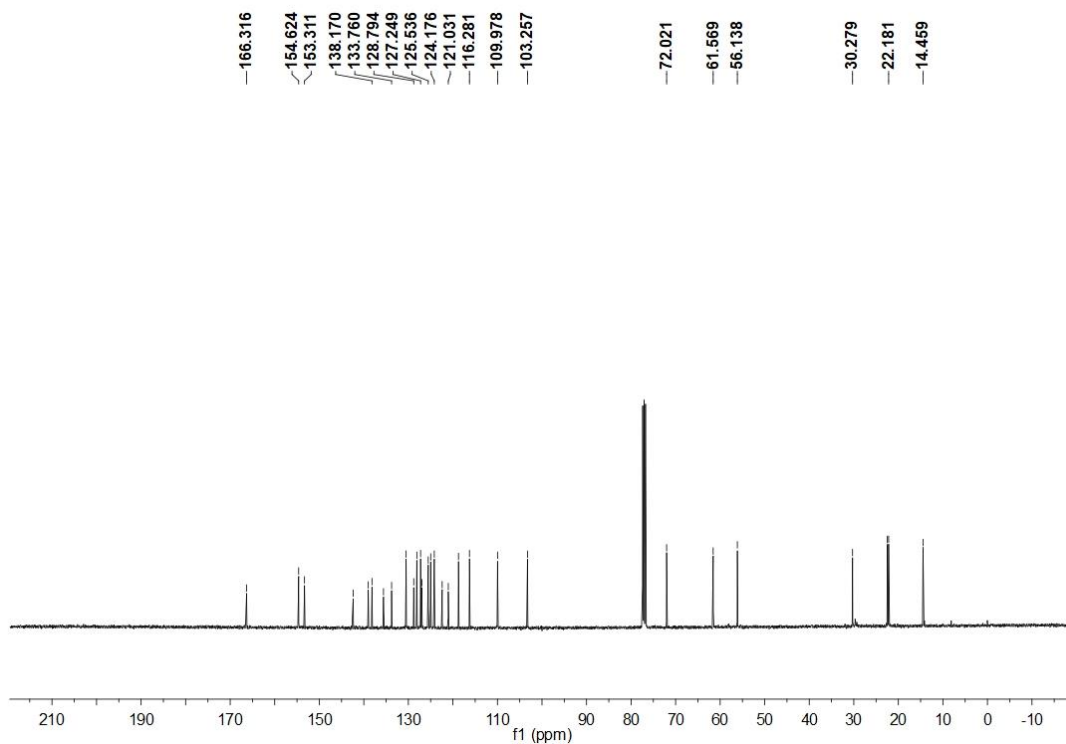
¹H NMR (400 MHz, Chloroform-d)



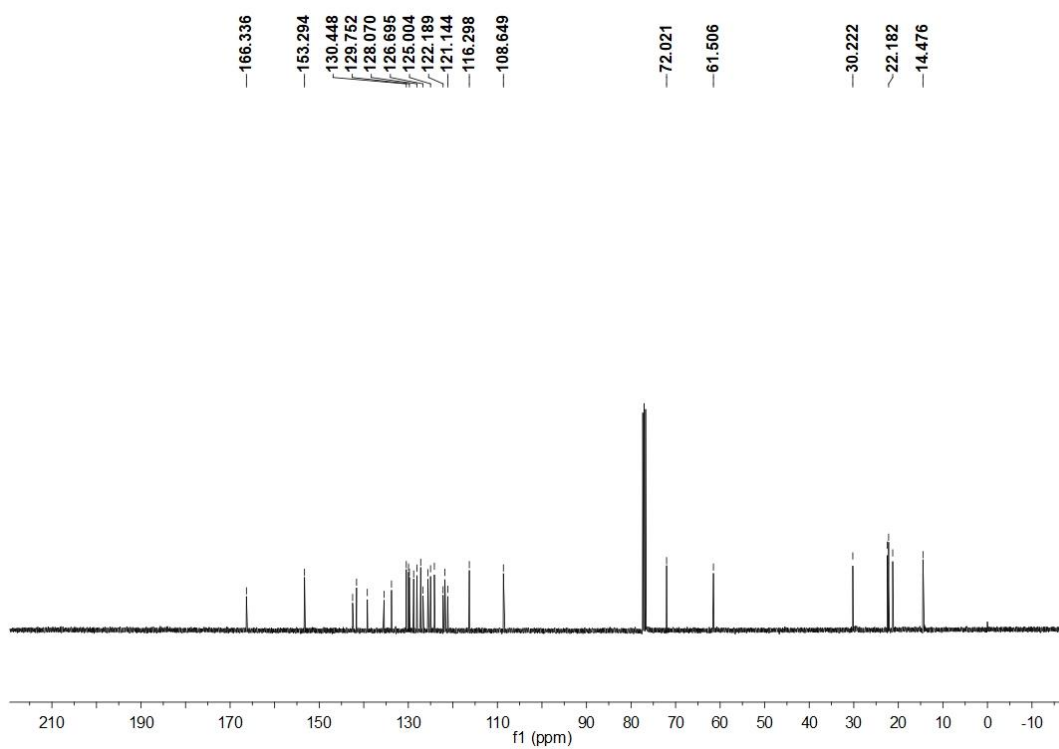
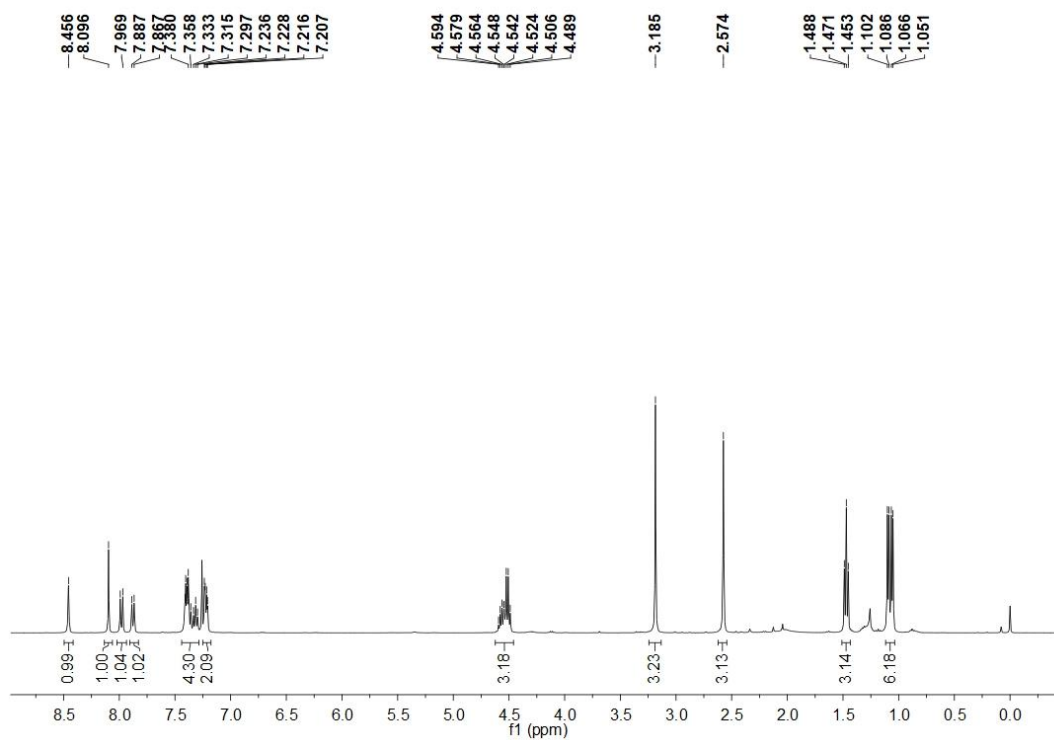
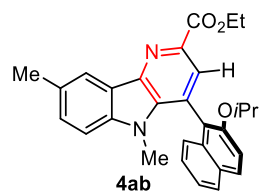
¹³C NMR (101 MHz, Chloroform-d)

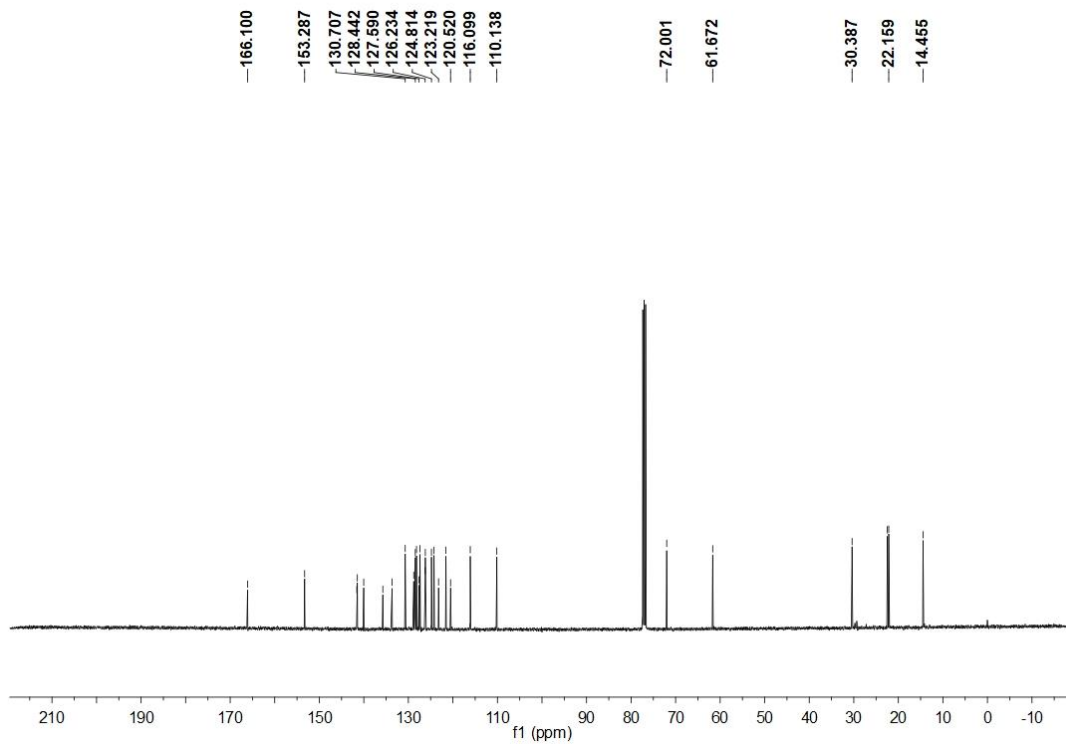
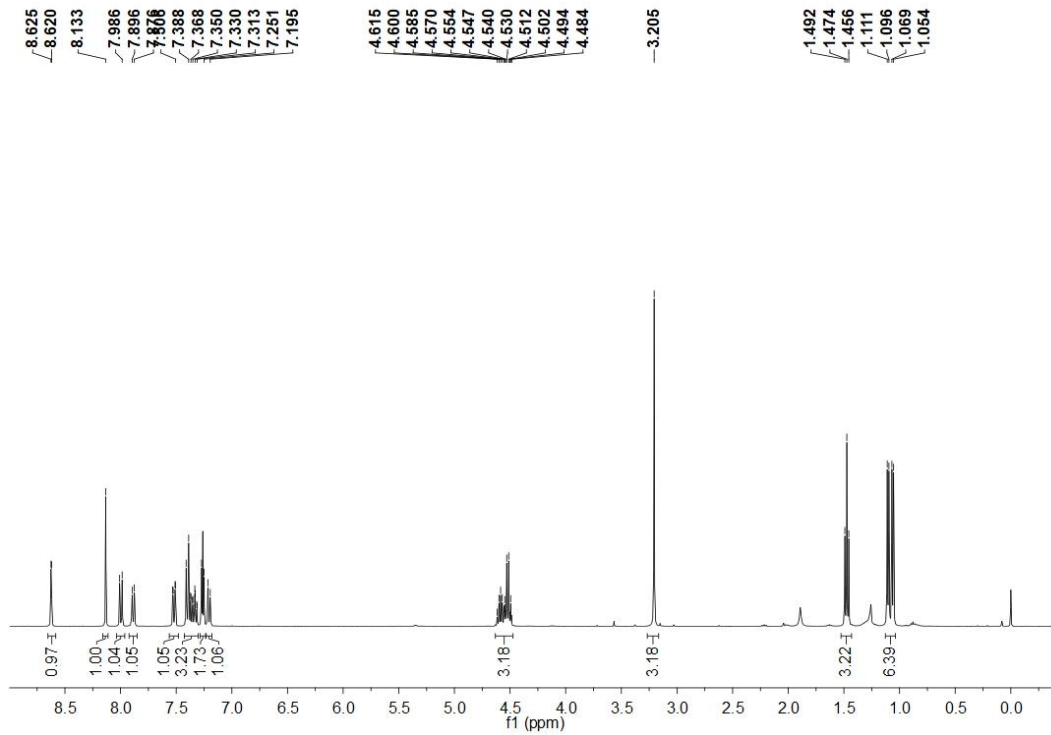
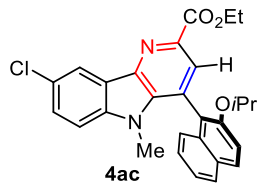


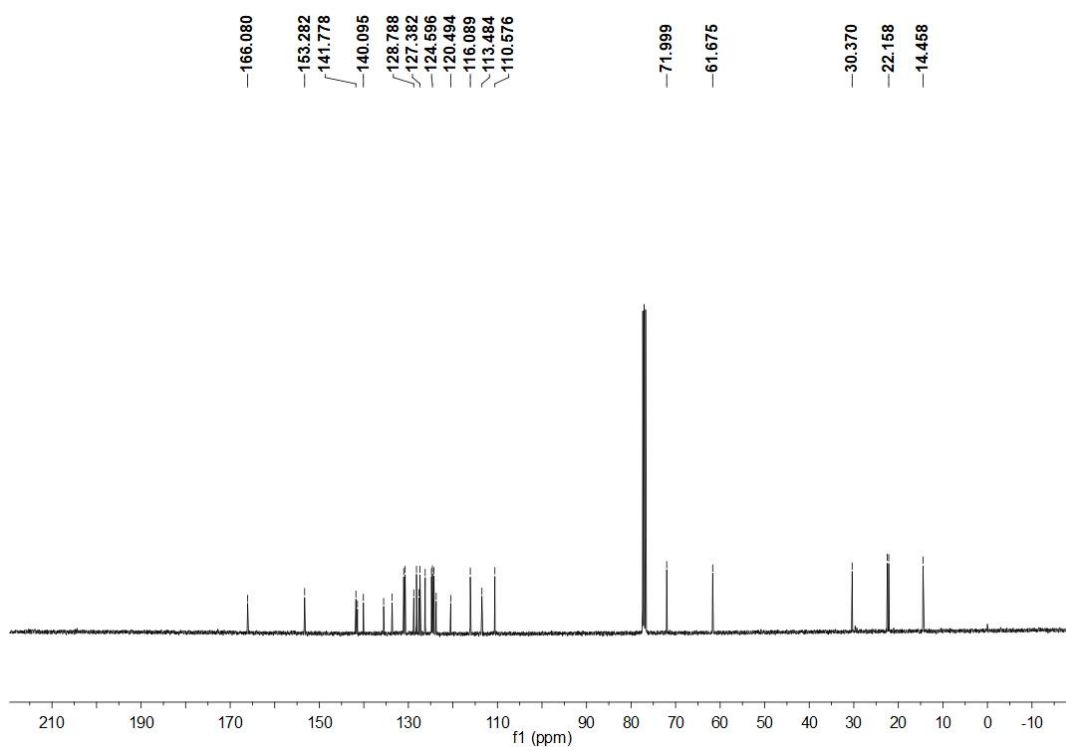
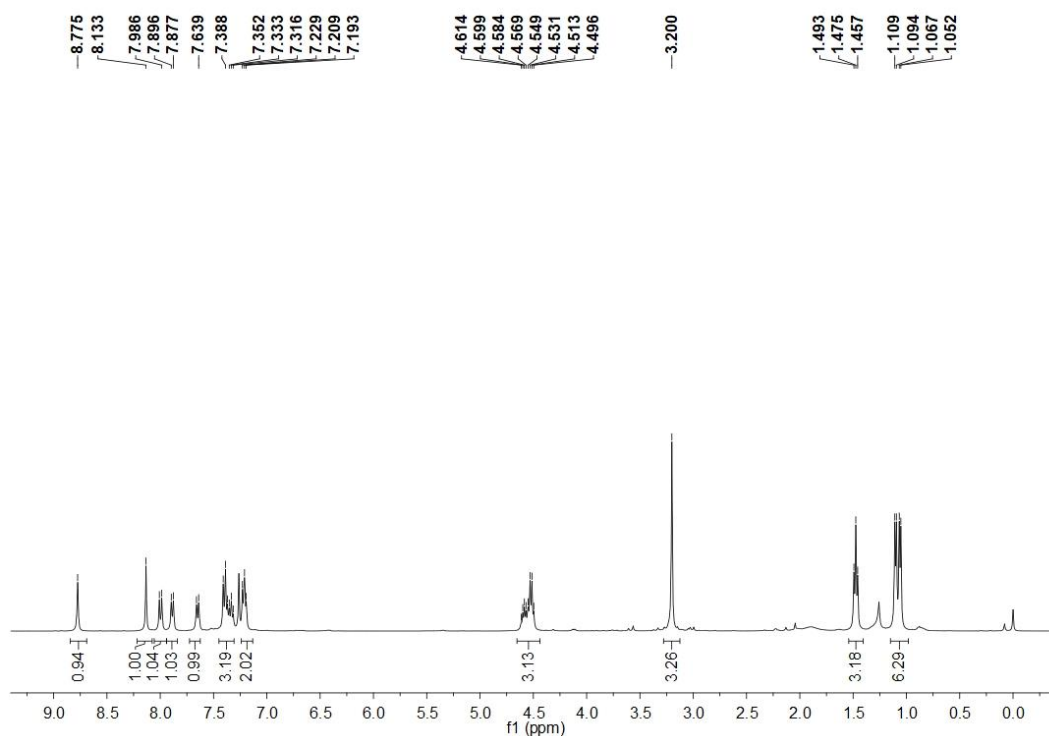
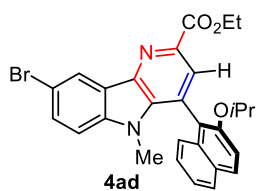
¹H NMR (400 MHz, Chloroform-d)

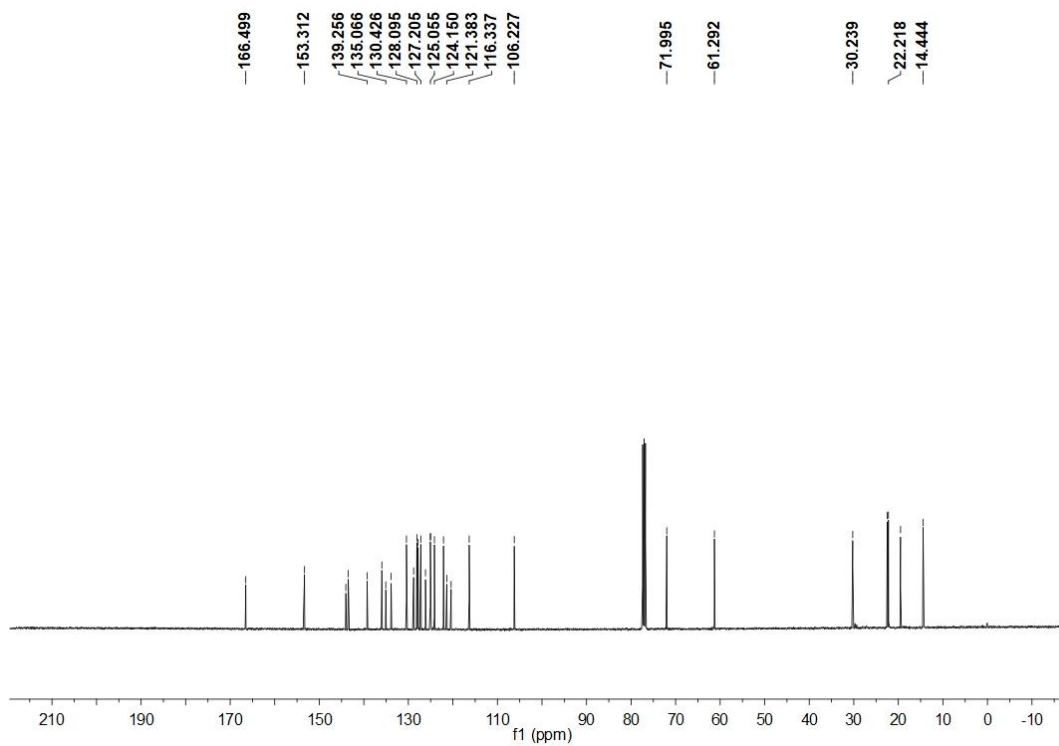
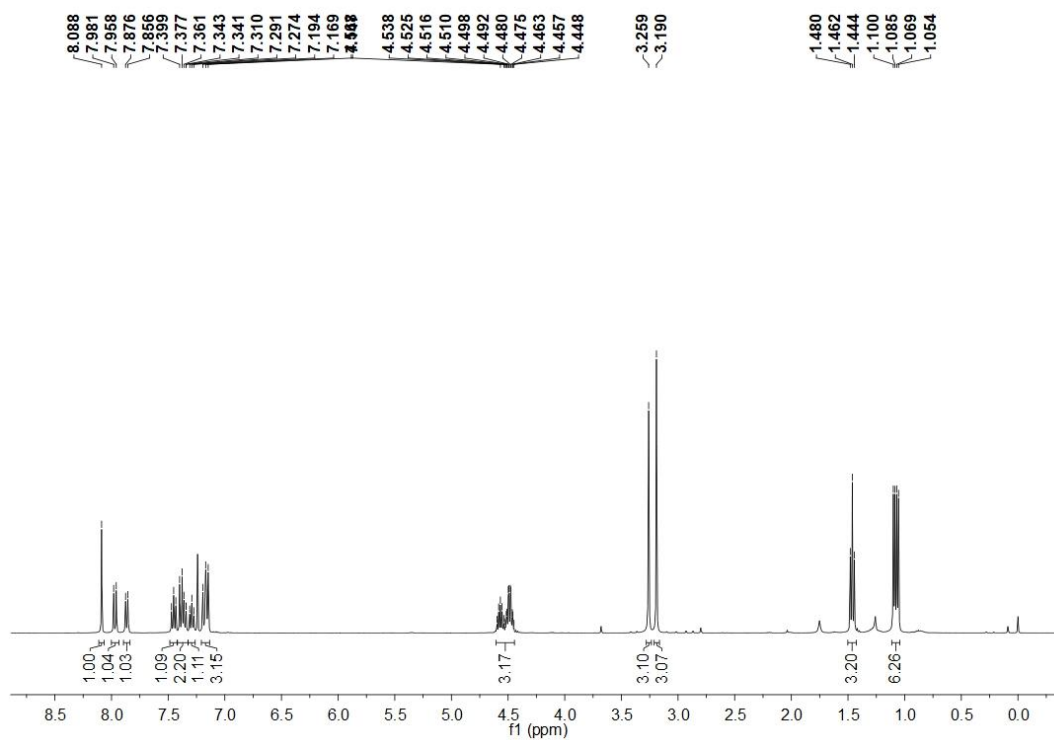
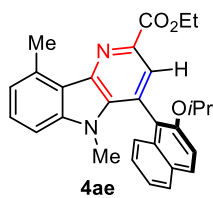


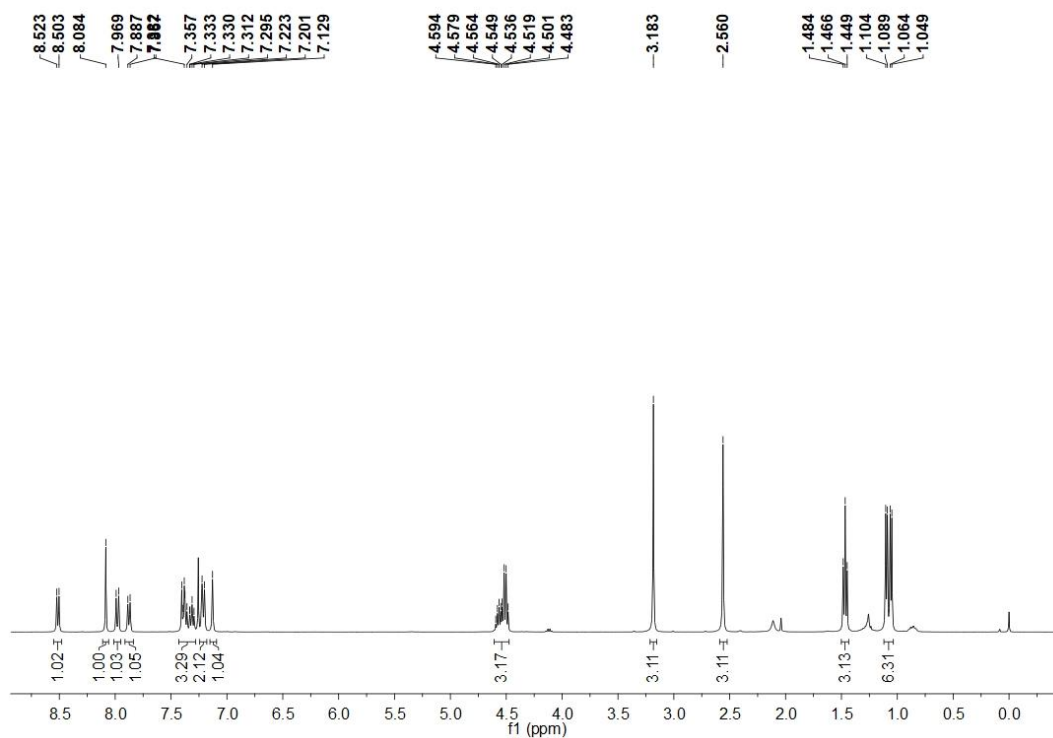
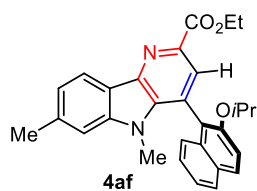
¹³C NMR (101 MHz, Chloroform-d)



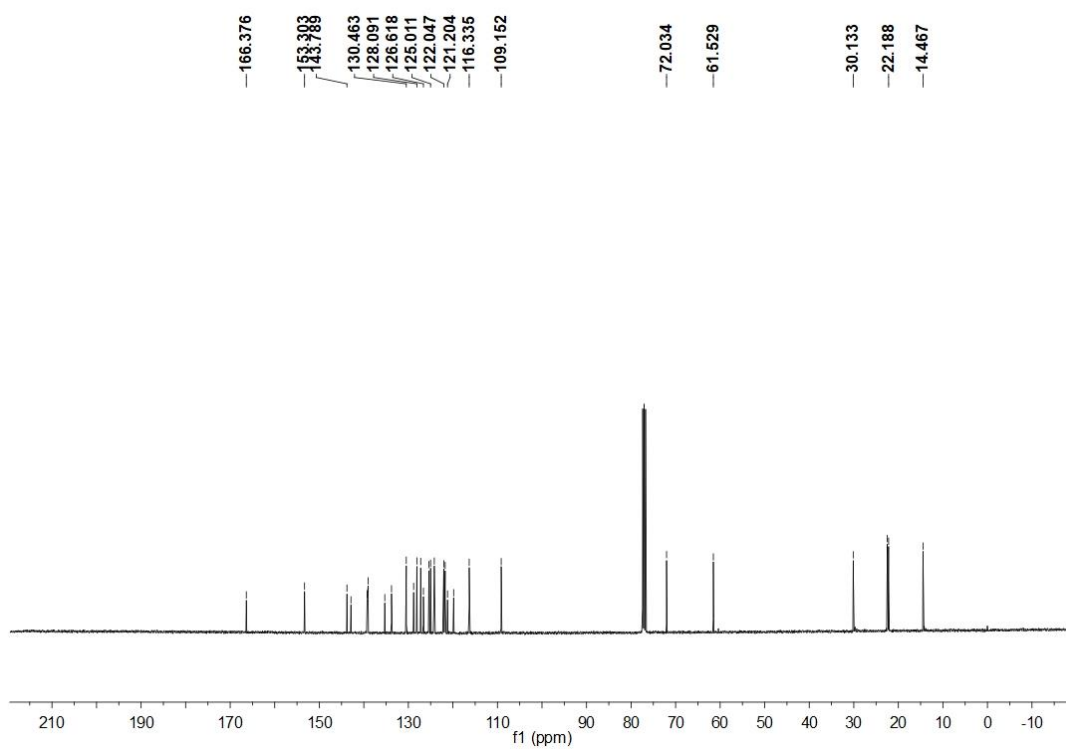




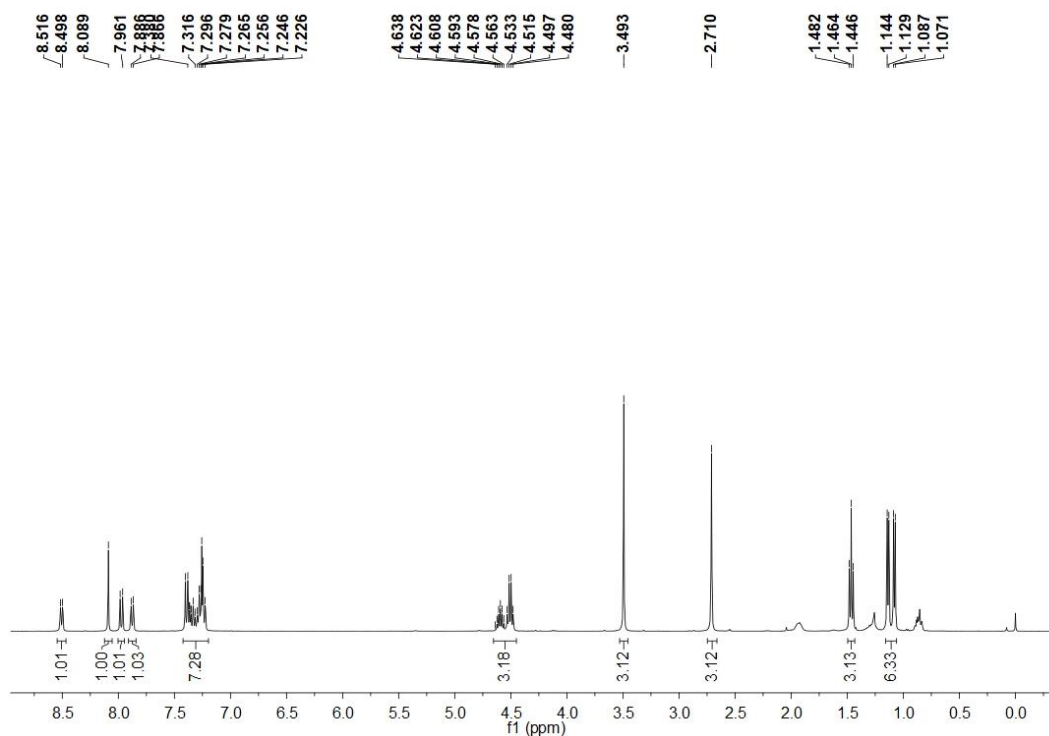
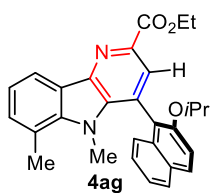




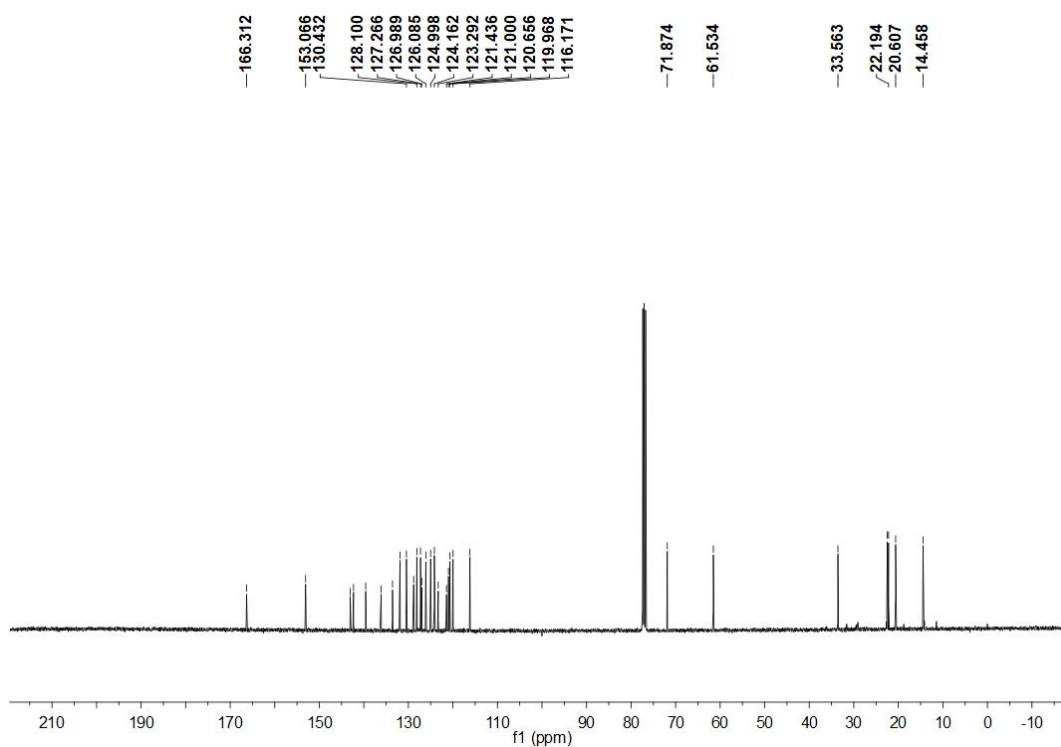
¹H NMR (400 MHz, Chloroform-d)



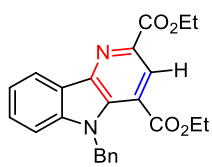
¹³C NMR (101 MHz, Chloroform-d)



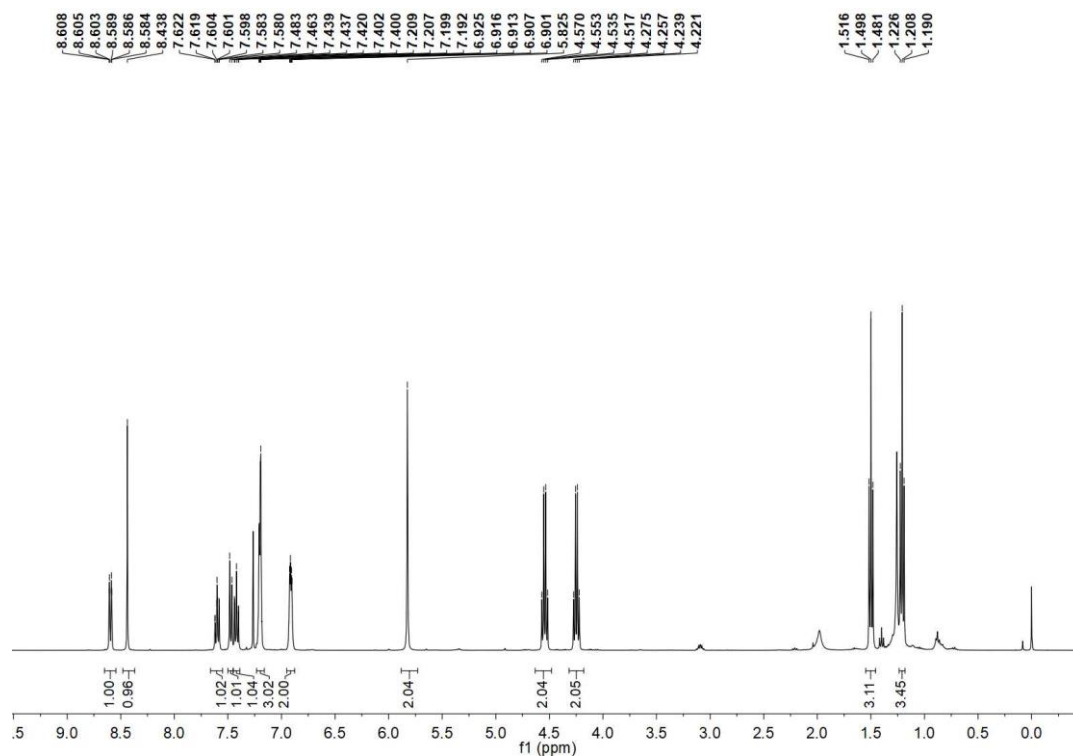
¹H NMR (400 MHz, Chloroform-d)



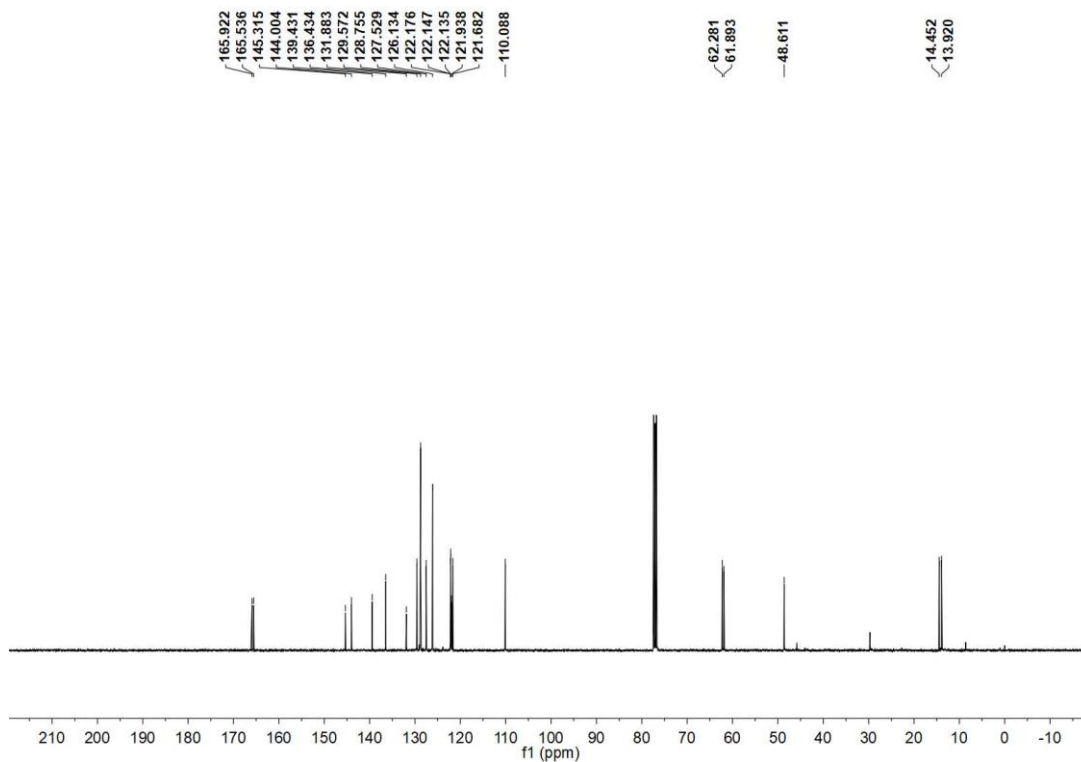
¹³C NMR (101 MHz, Chloroform-d)



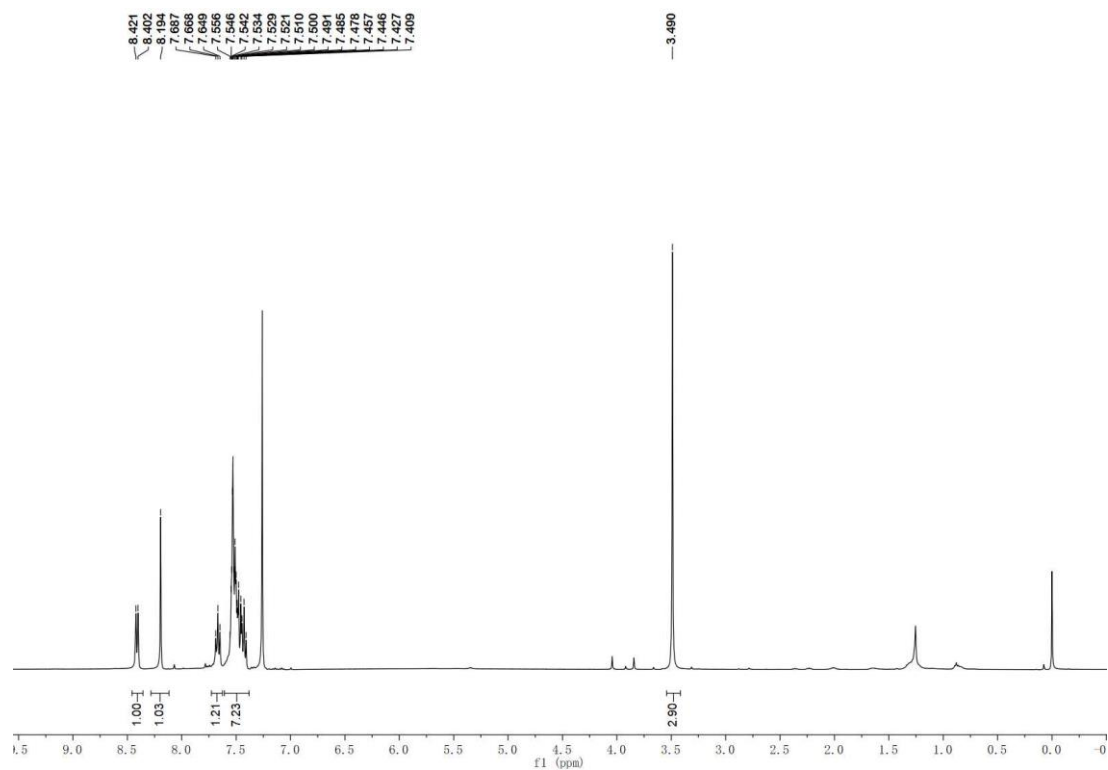
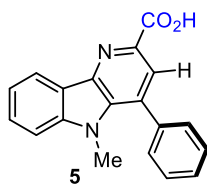
4ai



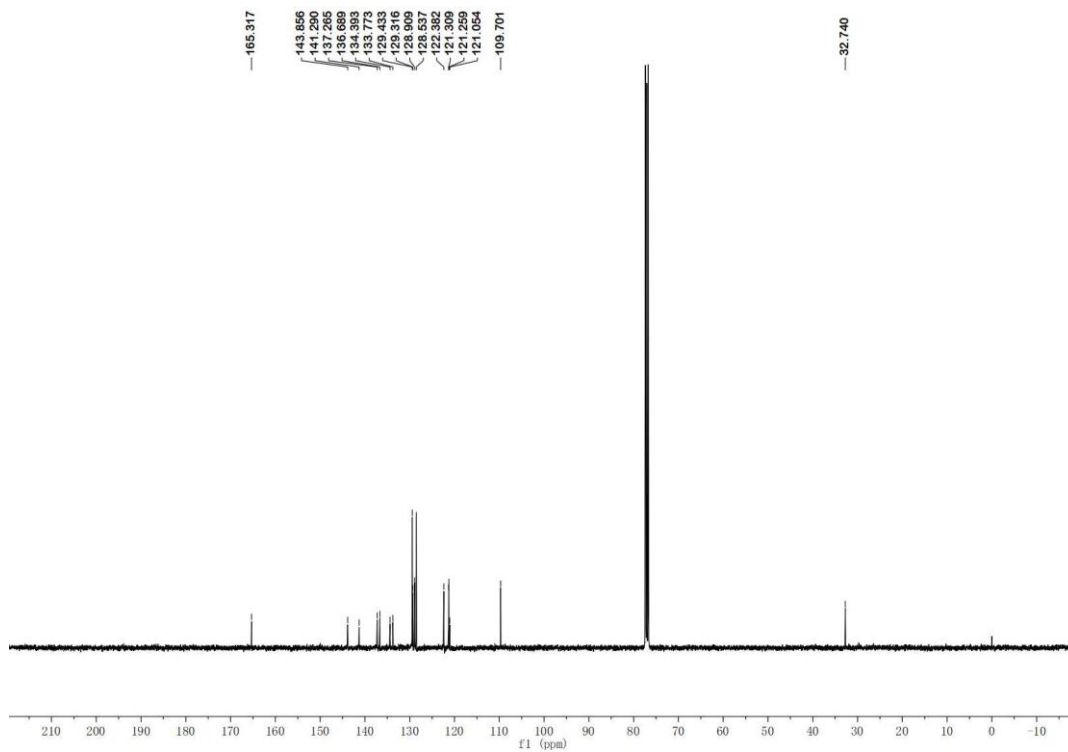
¹H NMR (400 MHz, Chloroform-d)



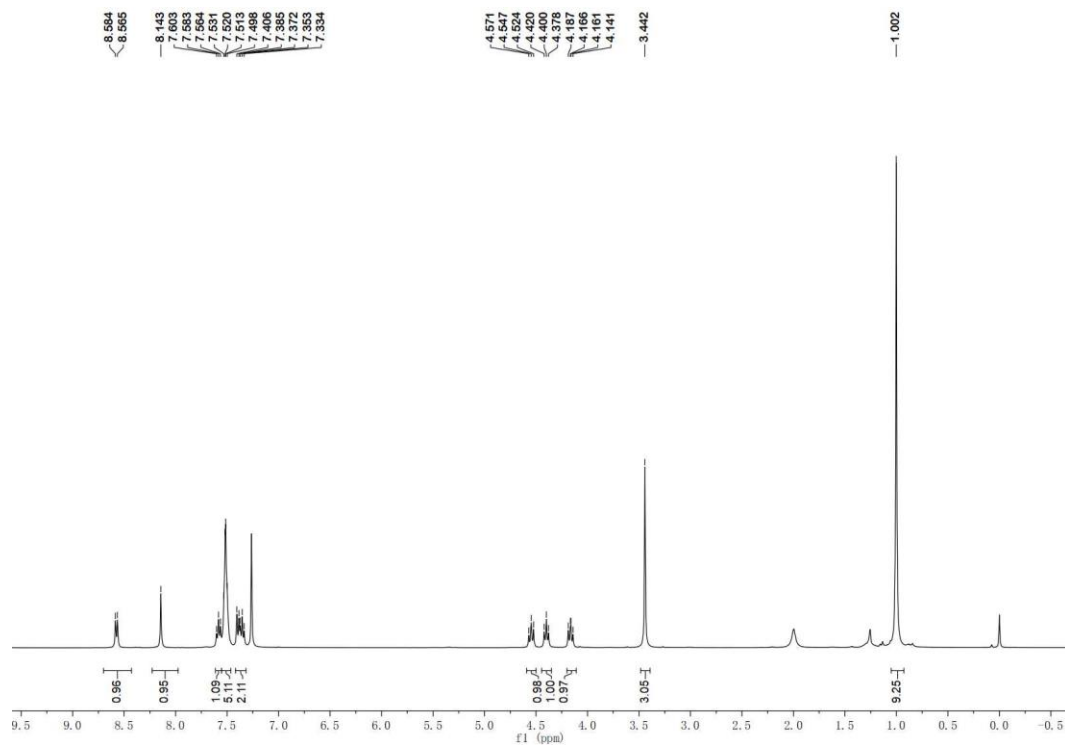
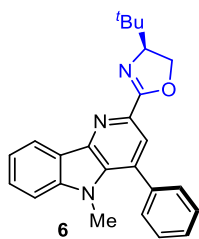
¹³C NMR (101 MHz, Chloroform-d)



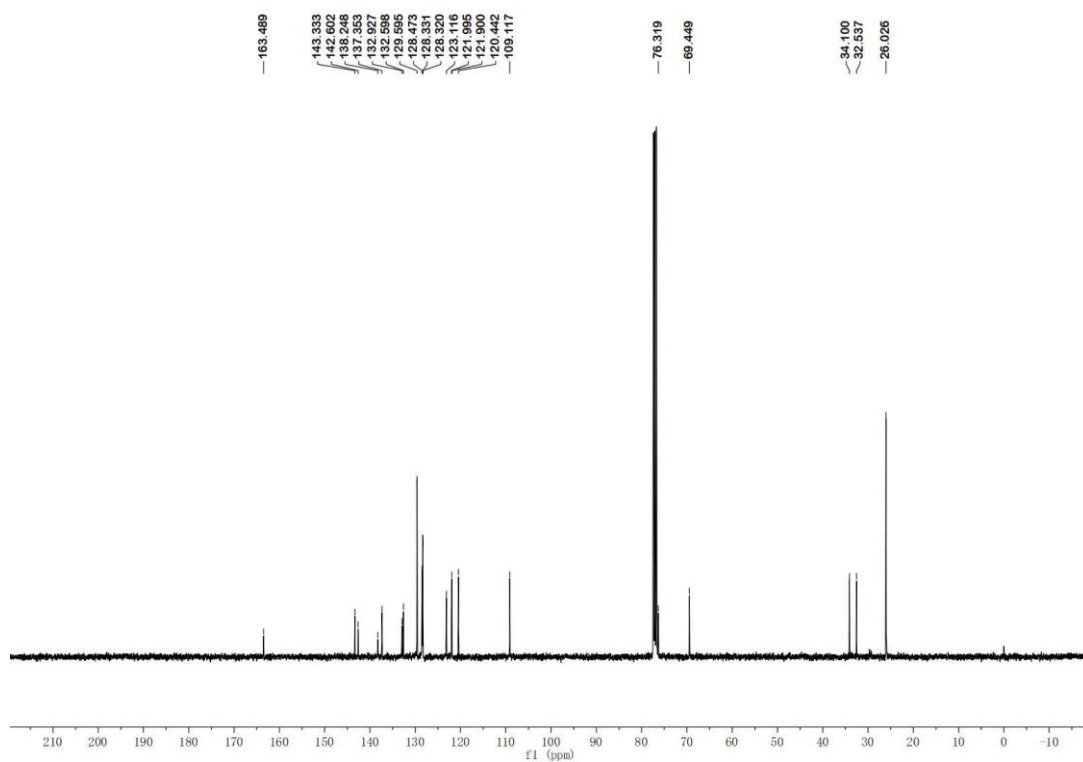
¹H NMR (400 MHz, Chloroform-d)



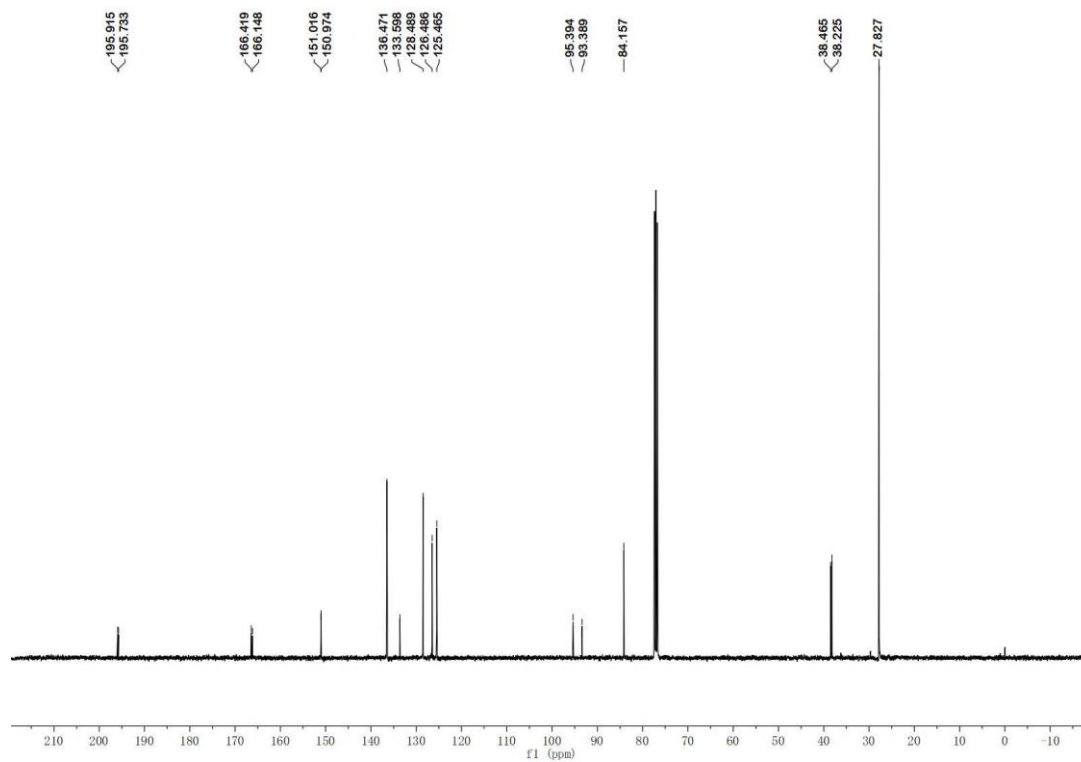
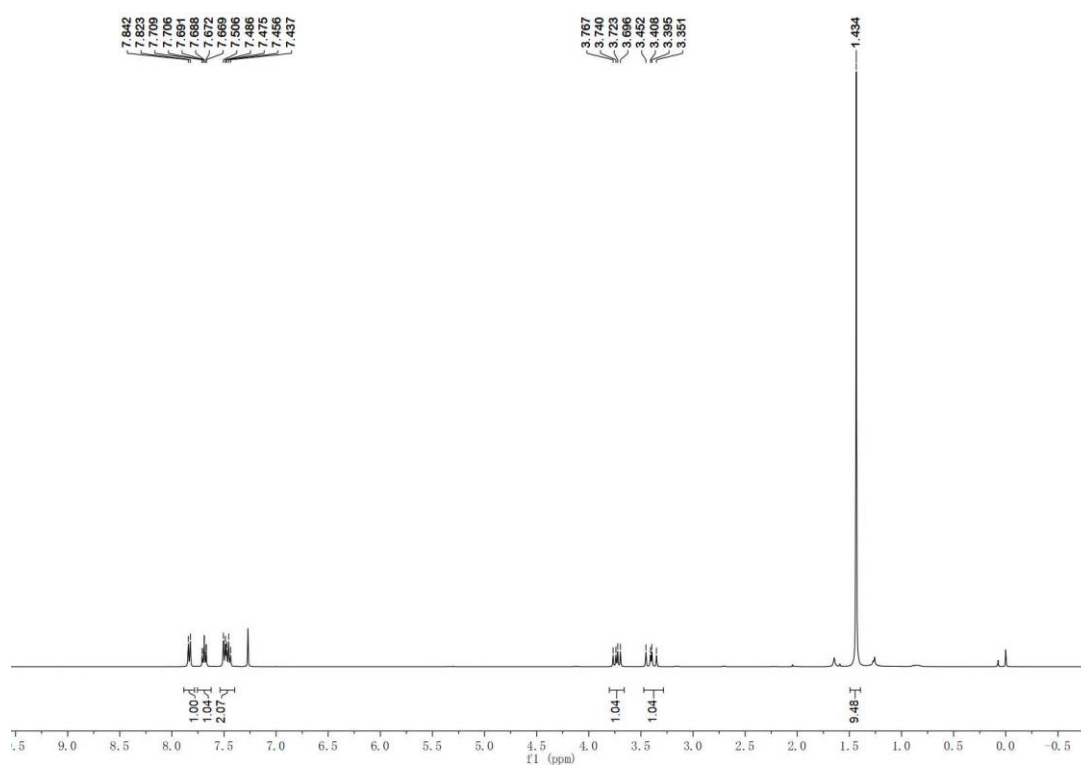
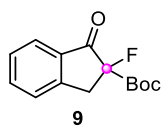
¹³C NMR (101 MHz, Chloroform-d)



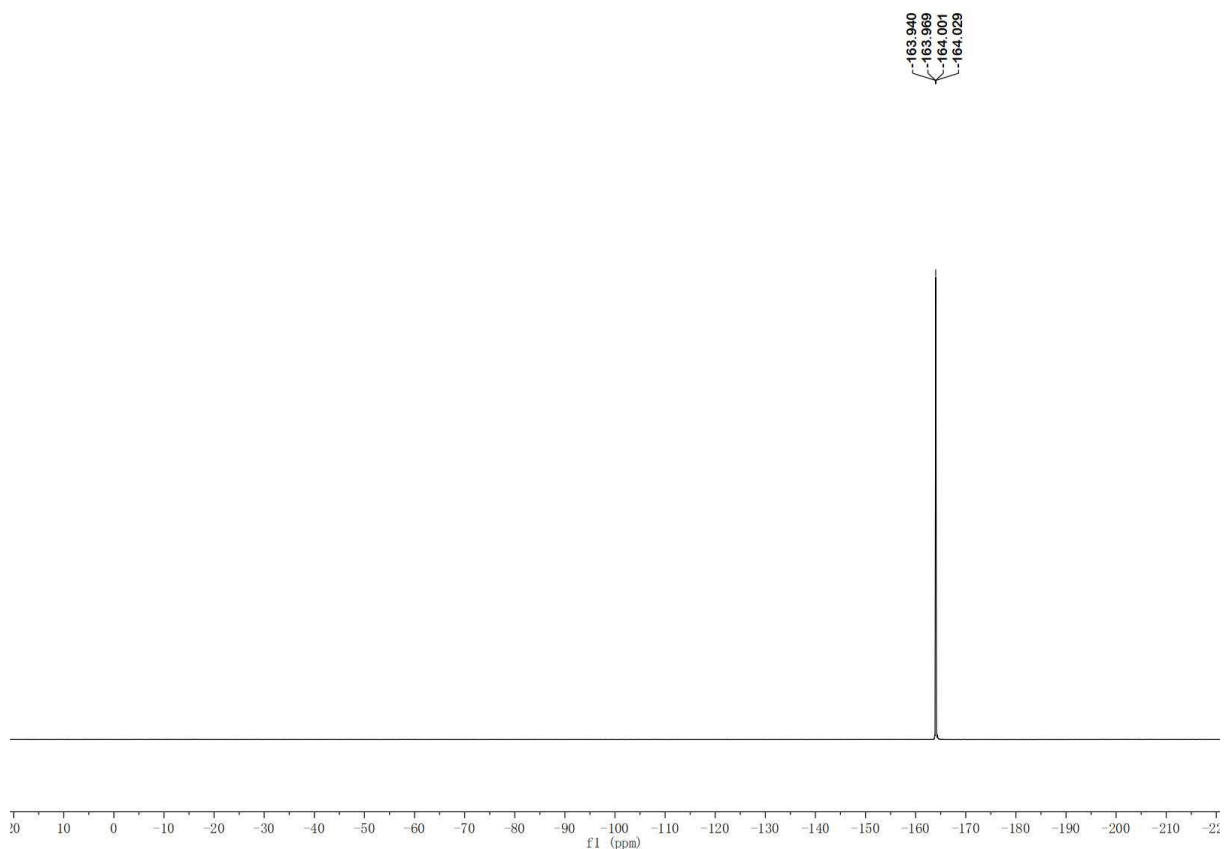
¹H NMR (400 MHz, Chloroform-d)



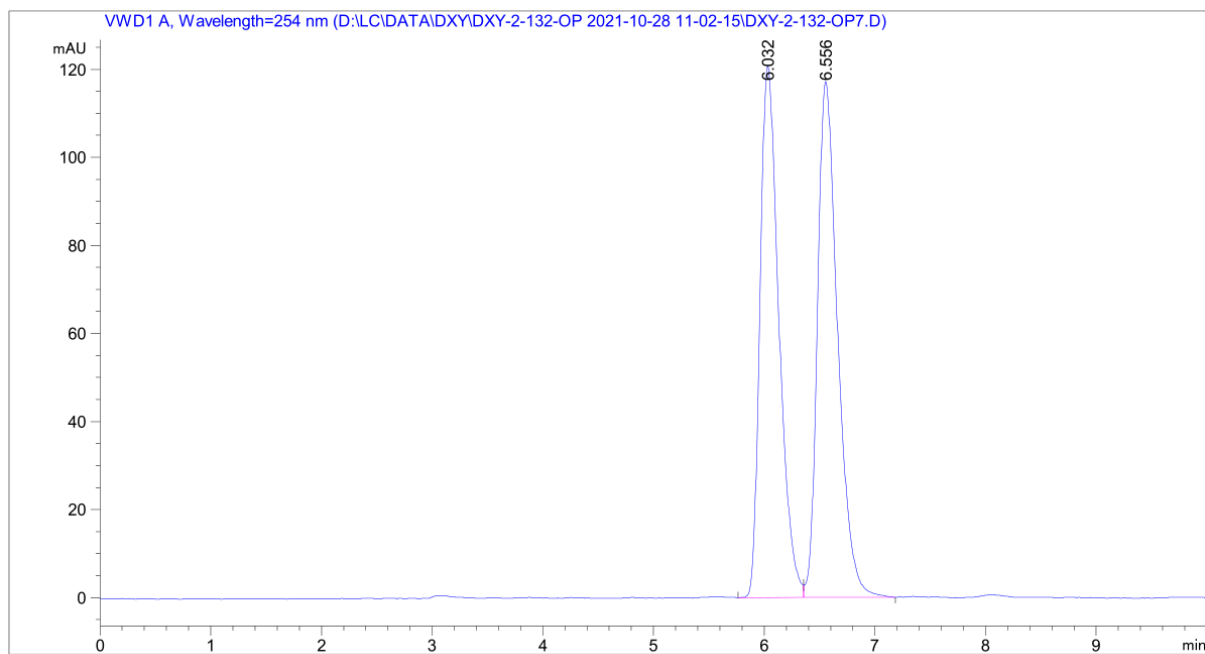
¹³C NMR (101 MHz, Chloroform-d)



¹³C NMR (101 MHz, Chloroform-d)

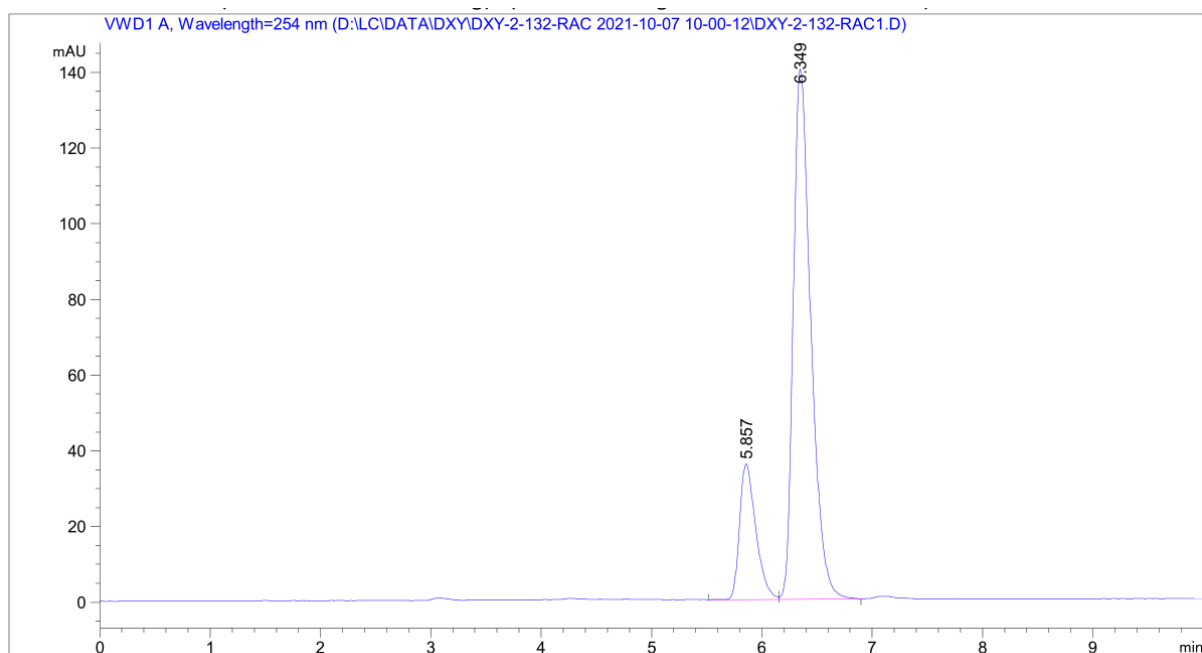


¹⁹F NMR (376 MHz, Chloroform-d)



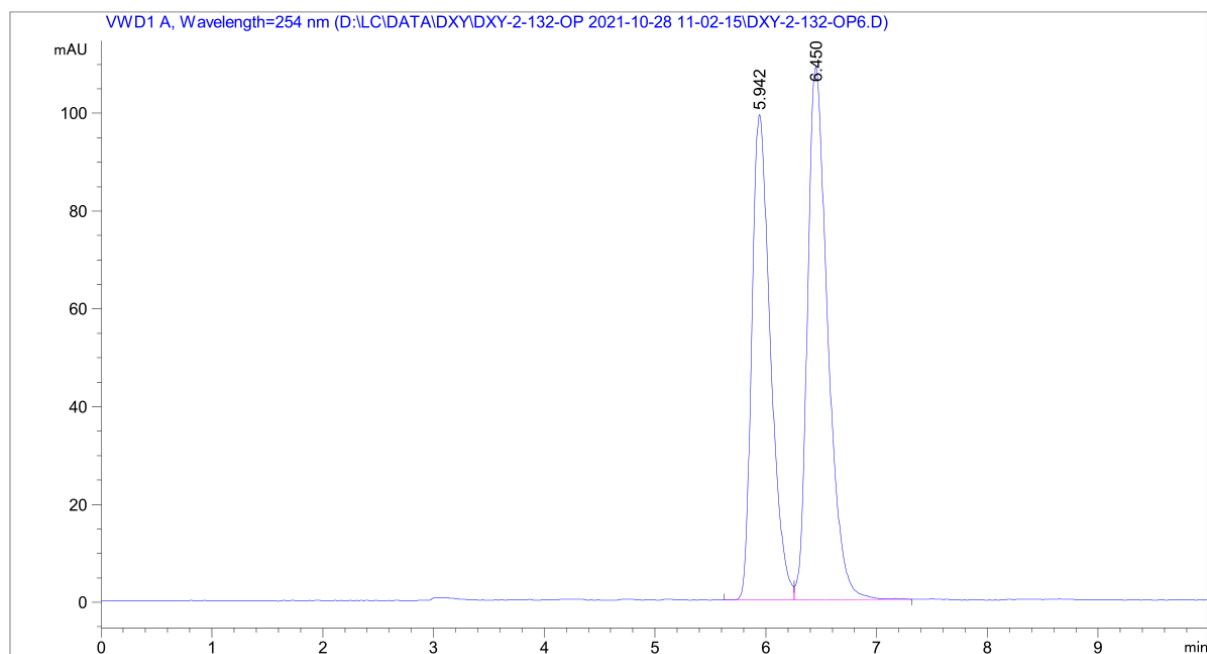
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.032	BV	0.1805	1430.65918	120.71239	49.0712
2	6.556	VB	0.1915	1484.81628	117.20554	50.9288

HPLC chromatogram of compound (*rac*)-9



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.857	BV	0.1560	367.71194	35.86565	19.1706
2	6.349	VB	0.1684	1550.39331	140.08653	80.8294

HPLC chromatogram of chiral compound 9 (ligand 6 was used)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.942	BV	0.1786	1160.30664	99.24376	45.6307
2	6.450	VV R	0.1918	1382.51416	108.87755	54.3693

HPLC chromatogram of chiral compound 9 (Bu-Pyrbox was used)