Accessing Spiropiperidines from Dihydropyridones through Tandem Triflation-Allylation and Ring-Closing Metathesis (RCM)

Naresh Gantasala,[a,b] Corentin Fournet,[c] Myriam Le Roch,[c] Claudia Lalli,[c*] Srihari Pabbaraja,[a,b*] Nicolas Gouault.[c*]

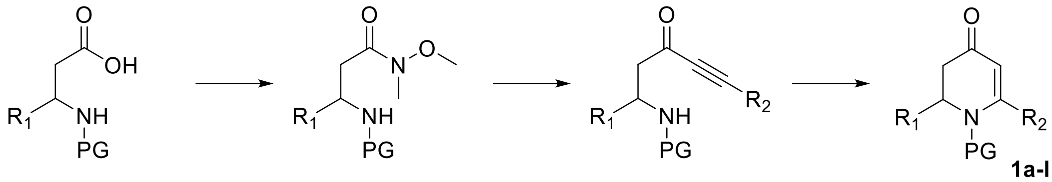
AUTHOR ADDRESS.

[a]CSIR-Indian Institute of Chemical Technology, Uppal Road, Tarnaka, Hyderabad 500007, TS, India.

[b]Academy of Scientific and Innovative Research (AcSIR), Ghazibad 201002, India.

[c]Univ. Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes), UMR 6226, F-35000 Rennes, France.

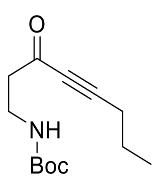
Synthesis of dihydropyridones 1:



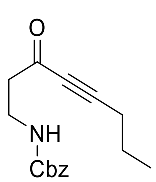
Synthesis of dihydropyridones 1a-l:

Typical procedure for ***N*-protected-β-amino-ynones** synthesis: to a stirred solution of alkyne (8.0 mmol, 4 eq) in THF (6mL) at –78 °C, a 2.5 M solution of BuLi in hexane (7.7 mmol, 3.8 eq) was added dropwise. The solution was stirred for 1h. Then, a solution of Weinreb amide (2.0 mmol, 1 eq) in THF (10 mL) was dropwise added at -78 °C and stirred for 15 min at the same temperature then at –50 °C during 1h. The mixture was then allowed to warm to –5 °C and, after 1.5 h, the reaction was quenched by addition of a 1M NaH_2PO_4 solution (60 mL). The aqueous phase was diluted by addition of 25 mL of NaH_2PO_4 (1M) and 50 mL of water, then extracted with EtOAc (3 x 40 mL). The combined organic layers were washed with brine, then dried over Na_2SO_4 and evaporated *in vacuo*. Purification of the residue by flash chromatography (silica, CH_2Cl_2/EtOAc 95/5) yielded pure amino-ynone intermediate.

Typical procedure for the gold-catalyzed cyclization (**1a-l**): to the amino ynone (2.0 mmol, 1eq) in 1,2-dichoroethane (9 mL) at room temperature under Argon atmosphere was added PPh_3AuCl (49 mg, 0.1 mmol, 5 mol%) and $AgSbF_6$ (34 mg, 0.1 mmol, 5 mol%). After the resulting mixture was stirred at room temperature for 1 h, Et_2O (5 mL) was added and the resulting mixture was filtered through Celite®. After removal of solvents under reduced pressure, the crude product was purified by silica gel column chromatography using a mixture of cyclohexane and ethyl acetate (70/30) as an eluant to give **1**.

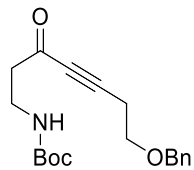


Yield: 84%. Clear oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.93 (bs, NH), 3.41 (dd, *J* = 12.0, 6.0 Hz, 2H), 2.78 (t, *J* = 6.0 Hz, 2H), 2.35 (t, *J* = 7.0 Hz, 2H), 1.61(sext., *J* = 7.0 Hz, 2H), 1.43 (s, 9H), 1.02(t, *J* = 7.0 Hz, 3H); HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{13}H_{21}NO_3Na$ 262.1414, found 262.1416.

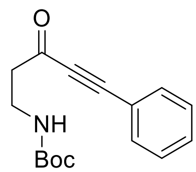


Yield: 88%. Clear oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.25 (m, 5H), 5.26 (bs, NH), 5.10 (s, 2H), 3.49 (q, *J* = 5.9 Hz, 2H), 2.82 (t, *J* = 5.8 Hz, 2H), 2.35 (t, *J* = 7.3 Hz, 2H), 1.61(sext., *J* = 7.3 Hz, 2H), 1.02(t,

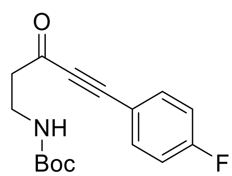
J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.5, 156.3, 136.5, 128.5, 128.1, 128.0, 95.5, 80.8, 66.7, 45.4, 35.6, 21.2, 20.9, 13.5; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{16}H_{19}NO_3Na$ 296.1257, found 296.1259.



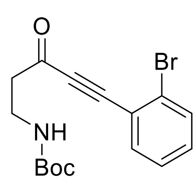
Yield: 90%. Clear oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-7.27 (m, 5H), 4.95 (bs, NH), 4.56 (s, 2H), 3.63 (t, J = 6.7 Hz, 2H), 3.40 (q, J = 6.0 Hz, 2H), 2.77 (t, J = 6.0 Hz, 2H), 2.67 (t, J = 6.7 Hz, 2H), 1.43 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.6, 155.8, 137.7, 128.6, 127.95, 127.8, 92.0, 81.3, 79.4, 73.2, 67.1, 45.6, 35.2, 28.5, 20.6; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{19}H_{25}NO_4Na$ 354.1676, found 354.1677.



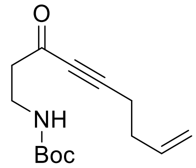
Yield: 90%. Clear oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59-7.39 (m, 5H), 4.98 (bs, 1H), 3.48 (q, J = 5.8 Hz, 2H), 2.93 (t, J = 5.8 Hz, 3H), 1.43 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 186.6, 155.7, 133.1, 130.8, 128.6, 119.6, 91.7, 87.6, 79.4, 45.6, 35.2, 28.4; HRMS (EI, m/z) $[M - tBuO]^+$ Calcd. for $C_{12}H_{10}NO_2$: 200.0711, found: 200.0709; IR (ATR) 3350, 2198, 1694, 1665 cm^{-1}.

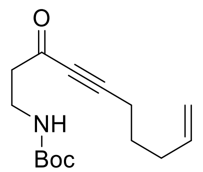


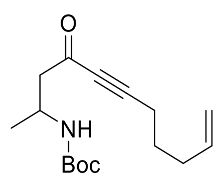
Yield: 96%. Clear oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61-7.55 (m, 2H), 7.12-7.06 (m, 2H), 4.95 (bs, 1H), 3.48 (q, J = 6.0 Hz, 2H), 2.92 (t, J = 6.0 Hz, 3H), 1.43 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 186.5, 164.2 (d, $^1J_{CF}$ = 254.2 Hz), 155.9, 135.6 (d, $^3J_{CF}$ = 9.0 Hz), 116.3 (d, $^2J_{CF}$ = 47.0 Hz), 115.9, 90.6, 87.8, 79.6, 45.7, 35.3, 28.5.

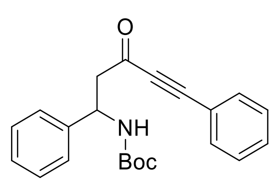


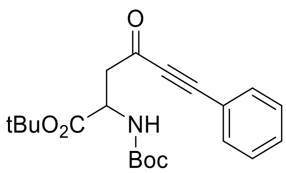
Yield: 97%. Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67-7.55 (m, 2H), 7.38-7.27 (m, 2H), 4.99 (bs, NH), 3.51 (q, J = 5.9 Hz, 2H), 2.96 (t, J = 5.9 Hz, 2H), 1.43 (s, 9H); HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{16}H_{18}NO_3{}^{79}BrNa$ 374.0362, found 374.0362.

 Yield: 84%. Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.82 (ddt, *J* = 16.7, 10.2, 6.5 Hz, 1H), 5.16-5.04 (m, 2H), 4.93 (brs, 1H), 3.40 (q, *J* = 6.0 Hz, 2H), 2.77 (t, *J* = 5.8 Hz, 2H), 2.50-2.42 (m, 2H), 2.37-2.27 (m, 2H), 1.42 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.9, 155.9, 135.9, 116.7, 94.5, 81.1, 79.5, 45.7, 35.3, 31.8, 28.5, 18.9; HRMS (ESI, m/z) $[M+Na]^+$ Calcd for $C_{14}H_{21}NO_3Na$ 274.1414, found 274.1413.

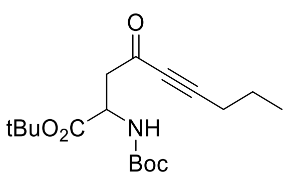
 Yield: 92%. pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.76 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.10-4.98 (m, 2H), 4.93 (brs, 1H), 3.40 (q, *J* = 6.0 Hz, 2H), 2.78 (t, *J* = 5.8 Hz, 2H), 2.37 (t, *J* = 7.2 Hz, 2H), 2.16 (qm, *J* = 7.2 Hz, 2H), 1.67 (quint, *J* = 7.2 Hz, 2H), 1.42 (s, 9H); ^{13}C NMR (75 MHz, CDCl3) δ 186.9, 155.9, 137.2, 116.0, 95.1, 81.0, 79.5, 45.7, 35.3, 32.8, 28.5, 26.9, 18.4.

 Yield: 78%. Clear oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.79 (ddt, *J* = 17.0, 10.2, 6.6 Hz, 1H), 5.10-4.97 (m, 2H), 4.77 (brs, 1H), 4.17-4.03 (m, 1H), 2.81 (dd, *J* = 16.3, 5.5 Hz, 1H), 2.66 (dd, *J* = 16.3, 6.5 Hz, 1H), 2.38 (t, *J* = 7.1 Hz, 2H), 2.16 (q, *J* = 7.1 Hz, 2H), 1.68 (quint., *J* = 7.1 Hz, 2H), 1.43 (s, 9H), 1.22 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, CDCl3) δ 186.2, 155.1, 137.2, 116.0, 94.9, 81.3, 79.5, 51.5, 43.5, 32.9, 28.5, 26.9, 20.7, 18.4; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{16}H_{25}NO_3Na$ 302.1727, found 302.1729.

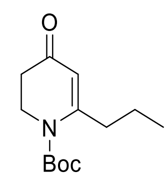
 Yield: 97%. Clear oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59-7.54 (m, 2H), 7.49-7.24 (m, 8H), 5.38-5.20 (m, 2H), 3.28-3.11 (m, 2H), 1.41 (s, 9H); ^{13}C NMR (75 MHz, CDCl3) δ 185.1, 155.1, 141.2, 133.3, 131.0, 128.9, 128.7, 127.7, 126.5, 119.8, 92.2, 87.8, 79.9, 51.3, 28.5.



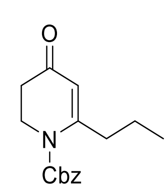
Yield: 89%. Light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60-7.56 (m, 2H), 7.49-7.37 (m, 3H), 5.42 (d, *J* = 8.3 Hz, 1H), 4.51 (dt, *J* = 8.3, 4.6 Hz, 1H), 3.33 (dd, *J* = 17.9, 4.6 Hz, 1H), 3.18 (dd, *J* = 17.9, 4.6 Hz, 1H), 1.46 (bs, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.7, 169.8, 155.5, 133.2, 131.0, 128.7, 119.6, 92.0, 87.4, 82.5, 79.9, 50.2, 47.5, 28.3, 27.9; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{21}H_{28}NO_5$ 374.1968, found 374.1967; IR (DRA) 3368, 2974, 1715, 1669, 1489, 1154 cm^{-1}.



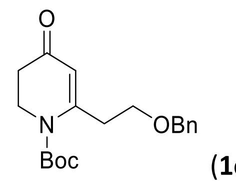
Yield: 95%. Clear oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.38 (d, *J* = 8.6 Hz, 1H), 4.42 (dt, *J* = 8.6, 4.6 Hz, 1H), 3.20 (dd, *J* = 17.8, 4.6 Hz, 1H), 3.01 (dd, *J* = 17.8, 4.6 Hz, 1H), 2.35 (t, *J* = 7.1 Hz, 2H), 1.62 (sext., *J* = 7.1 Hz, 2H), 1.44 (s, 18H), 1.00 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 183.9, 168.9, 154.5, 94.7, 81.3, 79.6, 78.8, 49.0, 46.5, 27.3, 26.8, 20.1, 19.9, 12.5; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{18}H_{29}NO_5Na$ 362.1943, found 362.1946; IR (DRA) 3366, 1716, 1675, 1495, 1366 cm^{-1}.

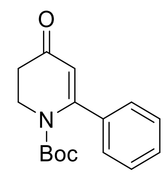


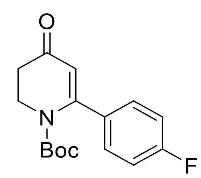
(**1a**): Yield: 85%; clear oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.37 (s, 1H), 3.99 (t, *J* = 6.7 Hz, 2H), 2.65 (t, *J* = 7.3 Hz, 2H), 2.46 (t, *J* = 6.7 Hz, 2H), 1.56-1.48 (m, 2H), 1.52 (s, 9H), 0.93(t, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 194.9, 161.5, 152.1, 112.3, 83.0, 46.7, 37.7, 37.3, 28.1, 21.3, 13.7; HRMS (ESI, m/z) $[M+Na]^+$ Calcd for $C_{13}H_{21}NO_3Na$ 262.1414, found 262.1415.

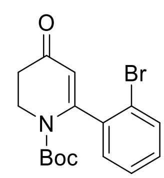


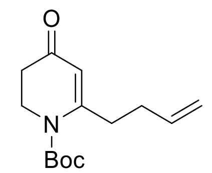
(**1b**): Yield: 88%; clear oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.46-7.36 (m, 5H), 5.42 (s, 1H), 5.23 (s, 2H), 4.08 (t, *J* = 6.6 Hz, 2H), 2.65 (t, *J* = 7.3 Hz, 2H), 2.49 (t, *J* = 6.6 Hz, 2H), 1.47 (sext., *J* = 7.3 Hz, 2H), 0.86 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 194.7, 161.3, 153.1, 135.2, 128.8, 128.6, 128.2, 113.1, 100.0, 68.9, 46.8, 37.5, 37.3, 21.4, 13.8; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{16}H_{19}NO_3Na$ 296.1257, found 296.1259.


(**1c**): Yield: 69%; clear oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.34-7.26 (m, 5H), 5.45 (s, 1H), 4.50 (s, 2H), 3.99 (t, *J* = 6.7 Hz, 2H), 3.61 (t, *J* = 6.4 Hz, 2H), 3.01 (t, *J* = 6.4 Hz, 2H), 2.48 (t, *J* = 6.7 Hz, 2H), 1.49 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 194.6, 158.4, 152.0, 138.1, 128.5, 127.8, 127.7, 113.5, 83.1, 73.1, 67.8, 46.6, 37.4, 36.0, 28.1; HRMS (ESI, m/z) $[M+Na]^+$ Calcd for $C_{19}H_{25}NO_4Na$ 354.1676, found 354.1679.

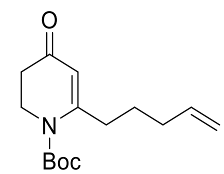

(**1d**): Yield: 85%; white solid, mp: 118-119 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.46-7.36 (m, 5H), 5.64 (s, 1H), 4.24 (t, *J* = 6.7 Hz, 2H), 2.63 (t, *J* = 6.7 Hz, 2H), 1.09 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 194.4, 157.3, 151.9, 137.5, 129.4, 127.9, 126.1, 112.8, 81.9, 45.9, 37.6, 26.9; HRMS (ESI, m/z) $[M+Na]^+$ Calcd for $C_{16}H_{19}NO_3Na$ 296.1263, found 296.1262; IR (DRA) 1712, 1665, 1590 cm^{-1}.


(**1e**): Yield: 85%; yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.45-7.36 (m, 2H), 7.13-7.05 (m, 2H), 5.61 (s, 1H), 4.22 (t, *J* = 6.6 Hz, 2H), 2.62 (t, *J* = 6.6 Hz, 2H), 1.14 (s, 9H).

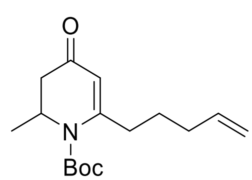

(**1f**): Yield: 77%; yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.58 (d, *J* = 6.7 Hz, 1H), 7.45-7.17 (m, 3H), 5.37 (s, 1H), 4.25 (bs, 2H), 2.66 (dd, *J* = 6.7, 6.4 Hz, 2H), 1.12 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 194.8, 156.3, 151.7, 139.2, 132.7, 130.4, 129.9, 127.7, 121.0, 113.9, 82.8, 45.5, 37.6, 27.6; HRMS (ESI, m/z) $[M+Na]^+$ Calcd for $C_{16}H_{18}NO_3{}^{79}BrNa$ 374.0362, found 374.0362.



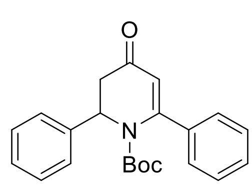
(**1g**): Yield: 95%; CLEAR oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.76 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.37 (s, 1H), 5.07-4.97 (m, 2H), 3.99 (tm, J = 6.7 Hz, 2H), 2.83-2.74 (m, 2H), 2.47 (tm, *J* = 6.7 Hz, 2H), 2.30-2.19 (m, 2H), 1.53 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.9, 160.7, 152.1, 136.8, 116.0, 112.8, 83.2, 46.6, 37.4, 35.2, 32.2, 28.2; HRMS (ESI, m/z) $[M+Na]^+$ Calcd for $C_{14}H_{21}NO_3Na$ 274.1414, found 274.1413.



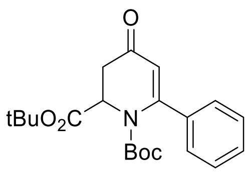
(**1h**): Yield: 75%; clear oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.82-5.72 (m, 1H), 5.39 (s, 1H), 5.06-4.98 (m, 2H), 4.00 (t, *J* = 6.8 Hz, 2H), 2.70 (t, *J* = 7.2 Hz, 2H), 2.48 (t, *J* = 6.8 Hz, 2H), 2.13-2.03 (m, 2H), 1.59 (quint., *J* = 7.2 Hz, 2H), 1.53 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 194.9, 161.5, 152.1, 137.8, 115.5, 112.5, 83.2, 46.8, 37.4, 35.3, 33.3, 28.8, 27.3.



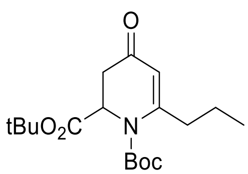
(**1i**): Yield: 76%; clear oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.84-5.71 (m, 1H), 5.38 (s, 1H), 5.06-4.98 (m, 2H), 4.83-4.74 (m, 1H), 3.11-3.01 (m, 1H), 2.82 (dd, *J* = 17.0, 6.2 Hz, 1H), 2.35-2.25 (m, 2H), 2.22-2.02 (m, 2H), 1.53 (s, 9H), 1.25 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 193.8, 158.4, 137.8, 115.5, 111.2, 83.0, 52.2, 42.8, 35.4, 33.3, 28.2, 27.2, 16.6; HRMS (ESI, m/z) $[M+Na]^+$ Calcd for $C_{16}H_{25}NO_3Na$ 302.1727, found 302.1730.



(**1j**): Yield: 80%; clear oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.50-7.43 (m, 2H), 7.38-7.27 (m, 6H), 7.26-7.21 (m, 2H), 6.10-6.6.05 (m, 1H), 5.58 (d, *J* = 1.2 Hz, 1H), 3.19 (dd, *J* = 17.5, 5.7 Hz, 1H), 3.07 (ddd, *J* = 17.5, 1.8, 1.2 Hz, 1H), 1.12 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 194.1, 155.0, 153.4, 138.5, 138.4, 129.8, 128.5, 128.4, 127.9, 127.2, 126.2, 113.8, 82.9, 57.0, 40.8, 27.5.



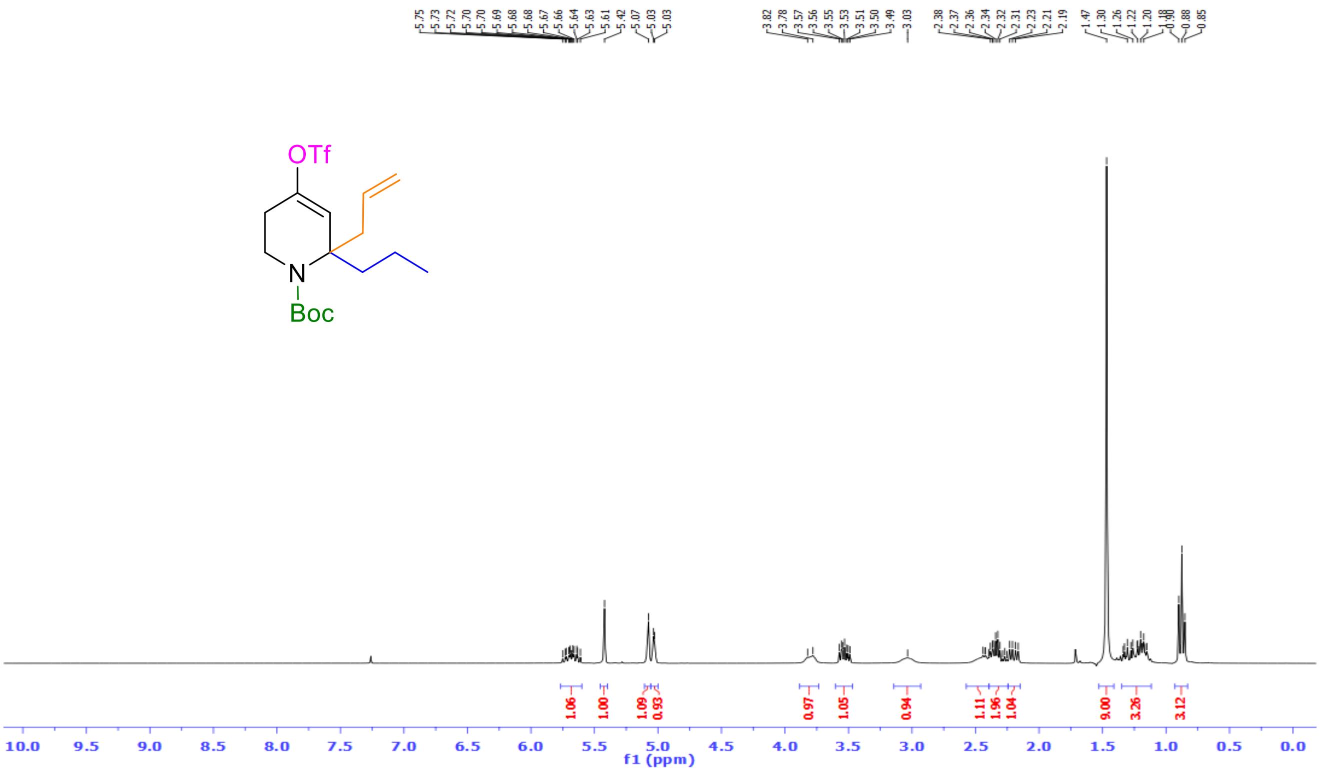
(**1k**): Yield: 90%; clear oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.58-7.48 (m, 2H), 7.45-7.35 (m, 3H), 5.58 (d, *J* = 1.0 Hz, 1H), 5.41 (dd, *J* = 6.2, 2.0 Hz, 1H), 3.07 (ddd, *J* = 17.5, 1.9, 1.3 Hz, 1H), 2.92 (dd, *J* = 17.5, 6.2 Hz, 1H), 1.45 (s, 9H), 1.08 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 192.7, 168.9, 157.2, 152.4, 138.0, 130.1, 128.4, 127.1, 113.2, 83.4, 83.2, 58.2, 40.1, 28.1, 27.5; HRMS (ESI, m/z) $[M+H]^+$ Calcd for $C_{21}H_{28}NO_5$ 374.1968, found 374.1967; IR (DRA) 2971, 1723, 1679, 1385 cm^{-1}.



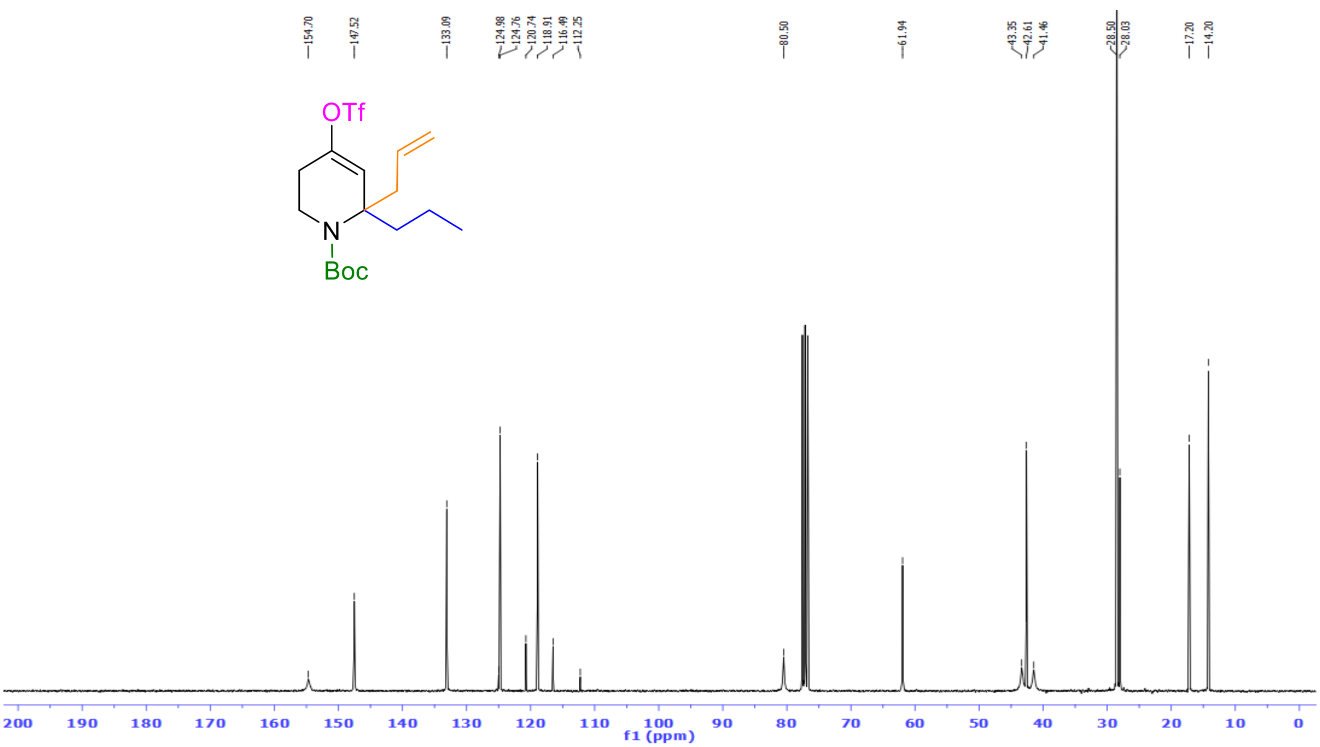
(**1l**): Yield: 88%; light yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.30 (s, 1H), 5.16 (dd, *J* = 6.5, 2.1 Hz, 1H), 2.99-2.86 (m, 2H), 2.74 (dd, *J* = 17.3, 6.5 Hz, 1H), 2.46-2.36 (m, 1H), 1.59 (sext., *J* = 7.5 Hz, 2H), 1.51 (s, 9H), 1.40 (s, 9H), 0.96 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 192.1, 168.8, 161.0, 151.9, 111.3, 83.7, 82.9, 58.5, 38.7, 38.2, 28.2, 28.0, 21.6, 14.1; HRMS (ESI, m/z) $[M+Na]^+$ Calcd for $C_{18}H_{29}NO_5Na$ 362.1943, found 362.1943; IR (DRA) 2975, 1727, 1668, 1310 cm^{-1}.

NMR Spectroscopic Data:

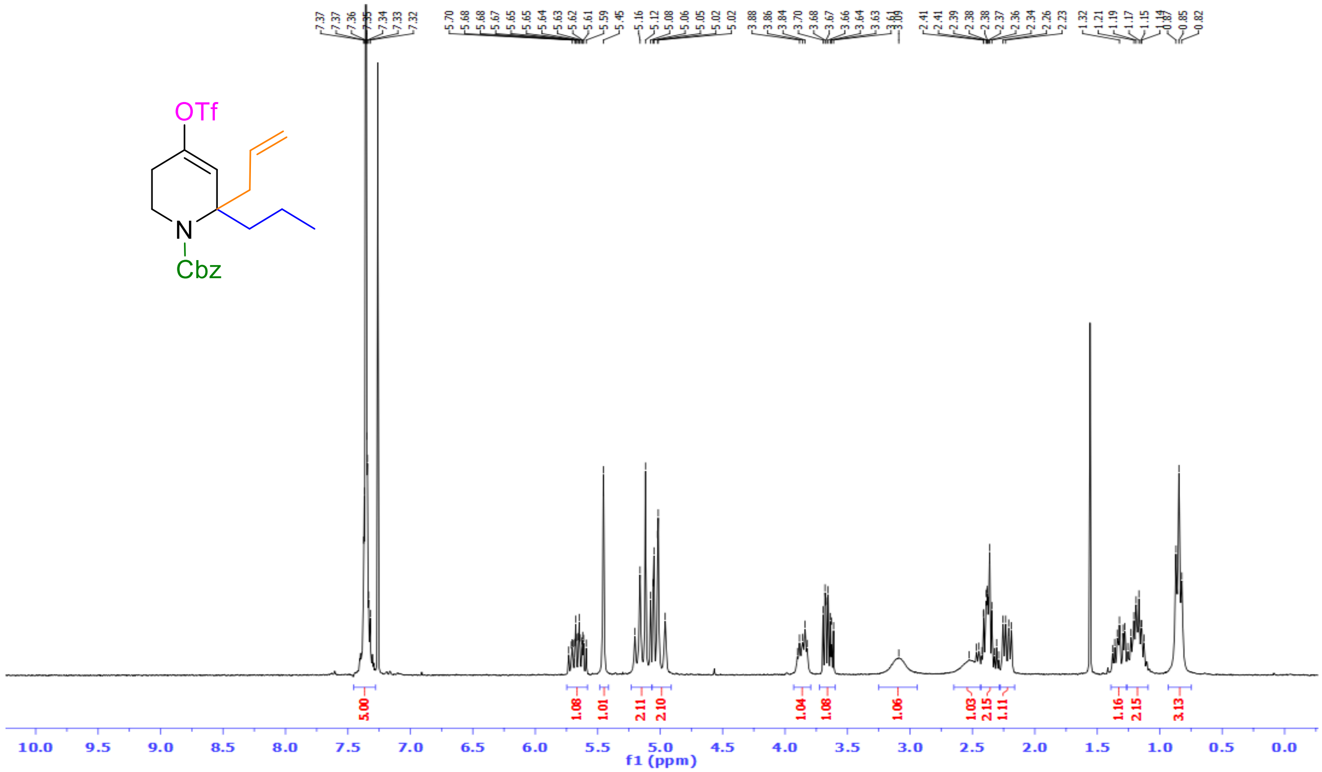
1H NMR of **2a** (300 MHz, $CDCl_3$)



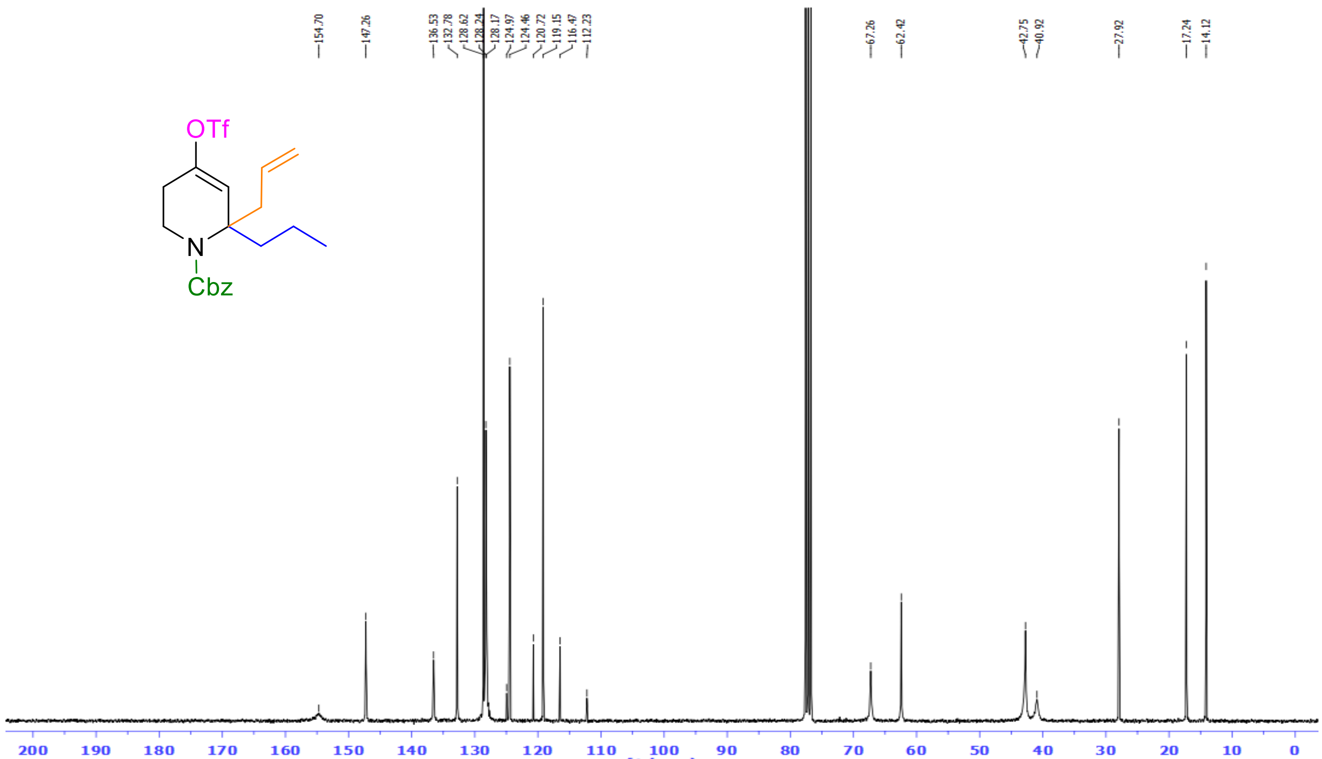
^{13}C NMR of **2a** (75 MHz, $CDCl_3$)



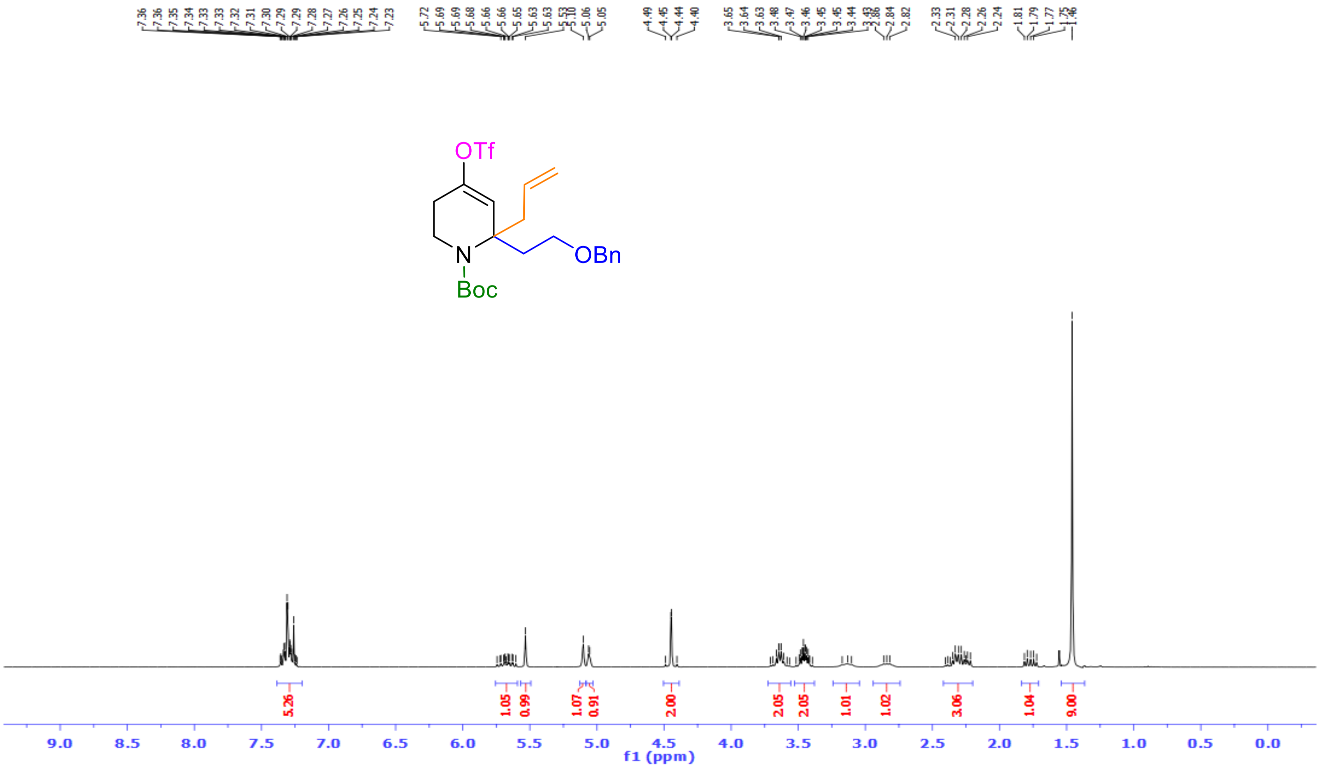
^{1}H NMR of **2b** (300 MHz, $CDCl_3$)



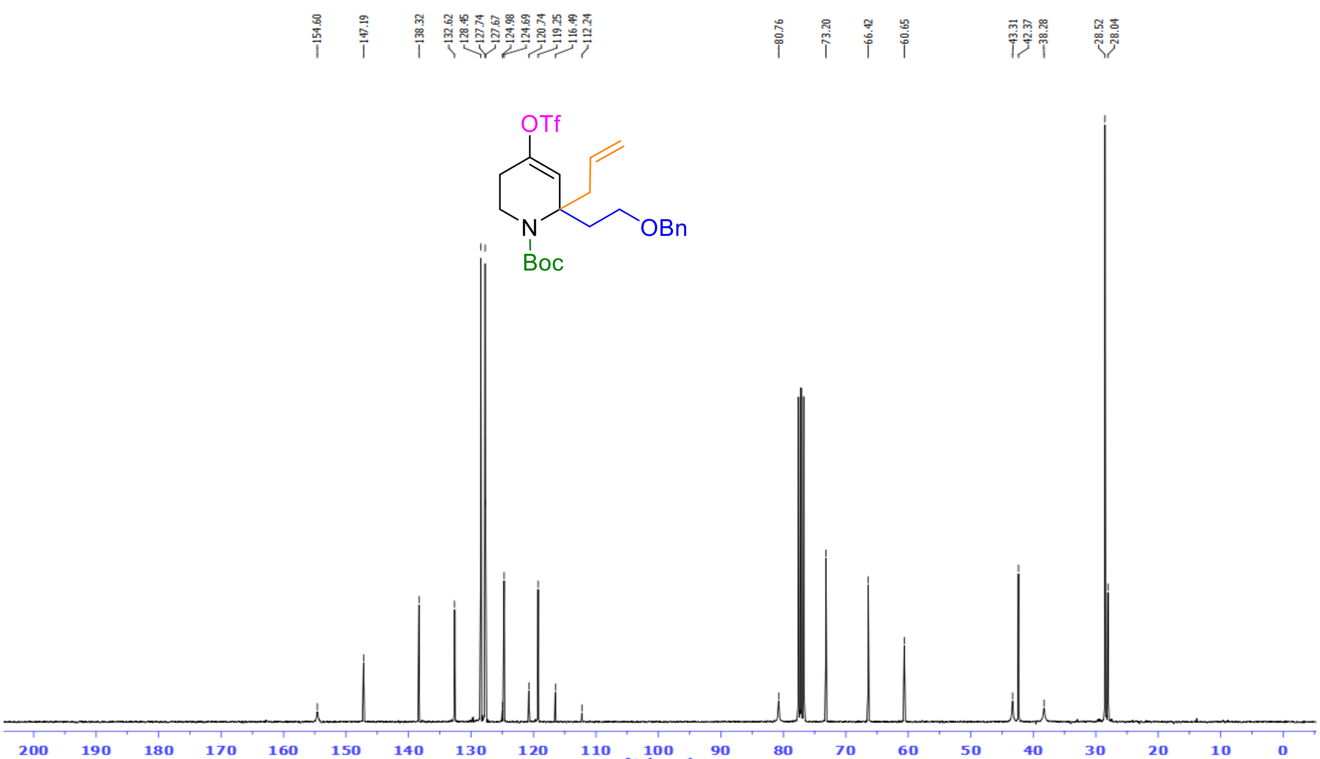
^{13}C NMR of **2b** (75 MHz, $CDCl_3$)



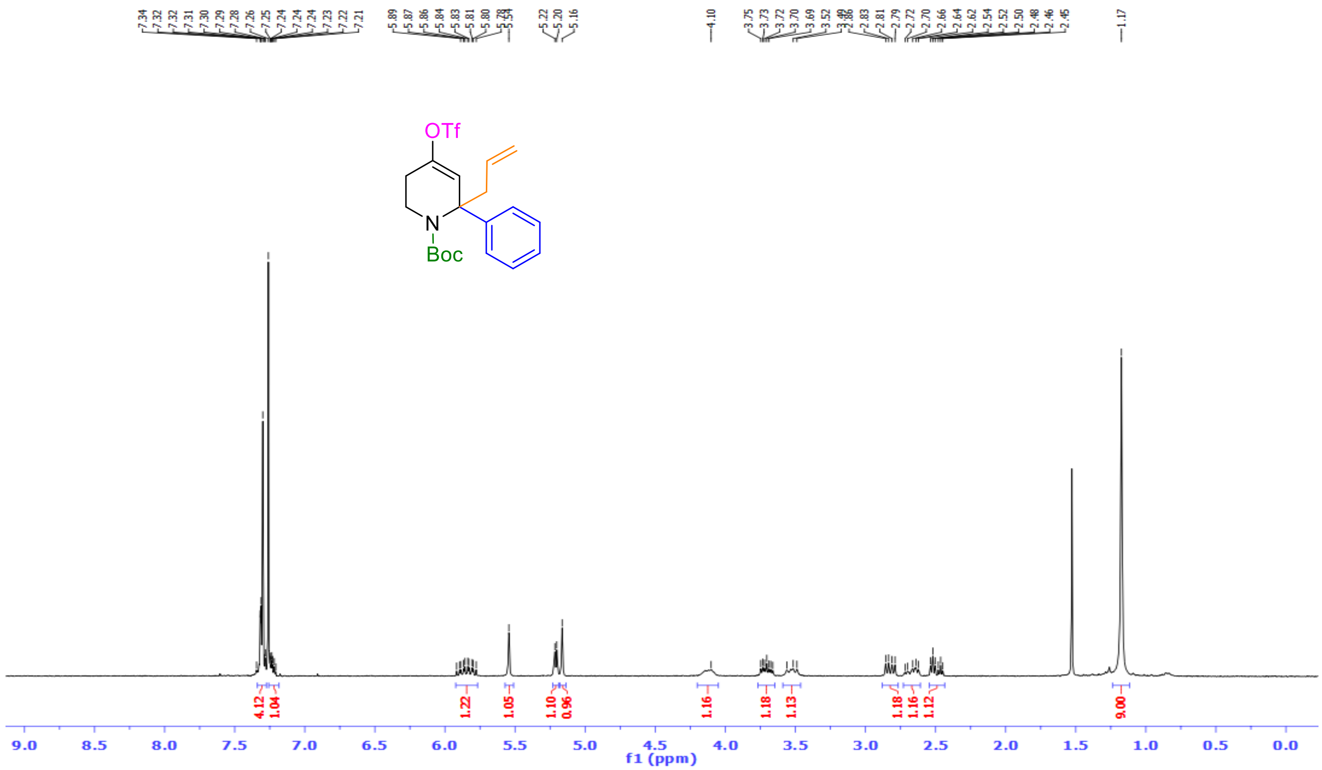
^{1}H NMR of **2c** (300 MHz, $CDCl_3$)



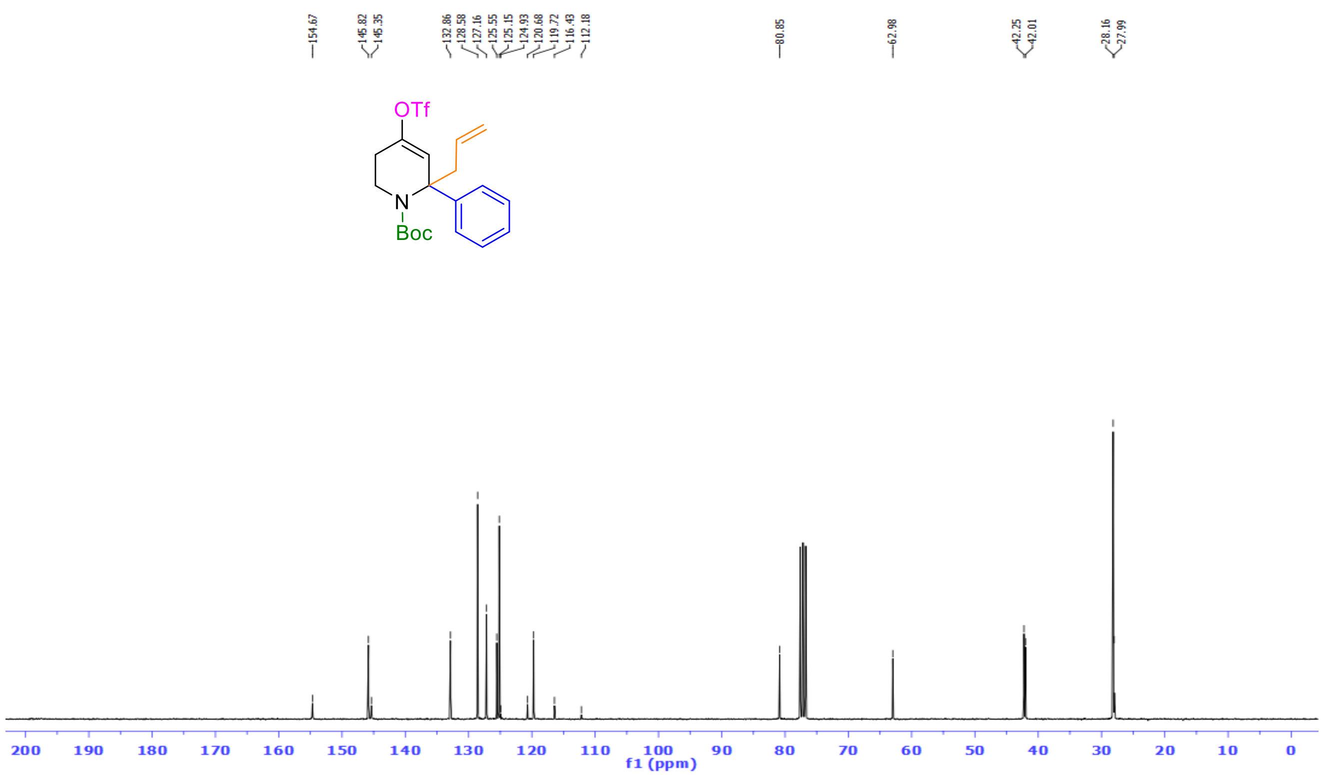
^{13}C NMR of **2c** (75 MHz, $CDCl_3$)



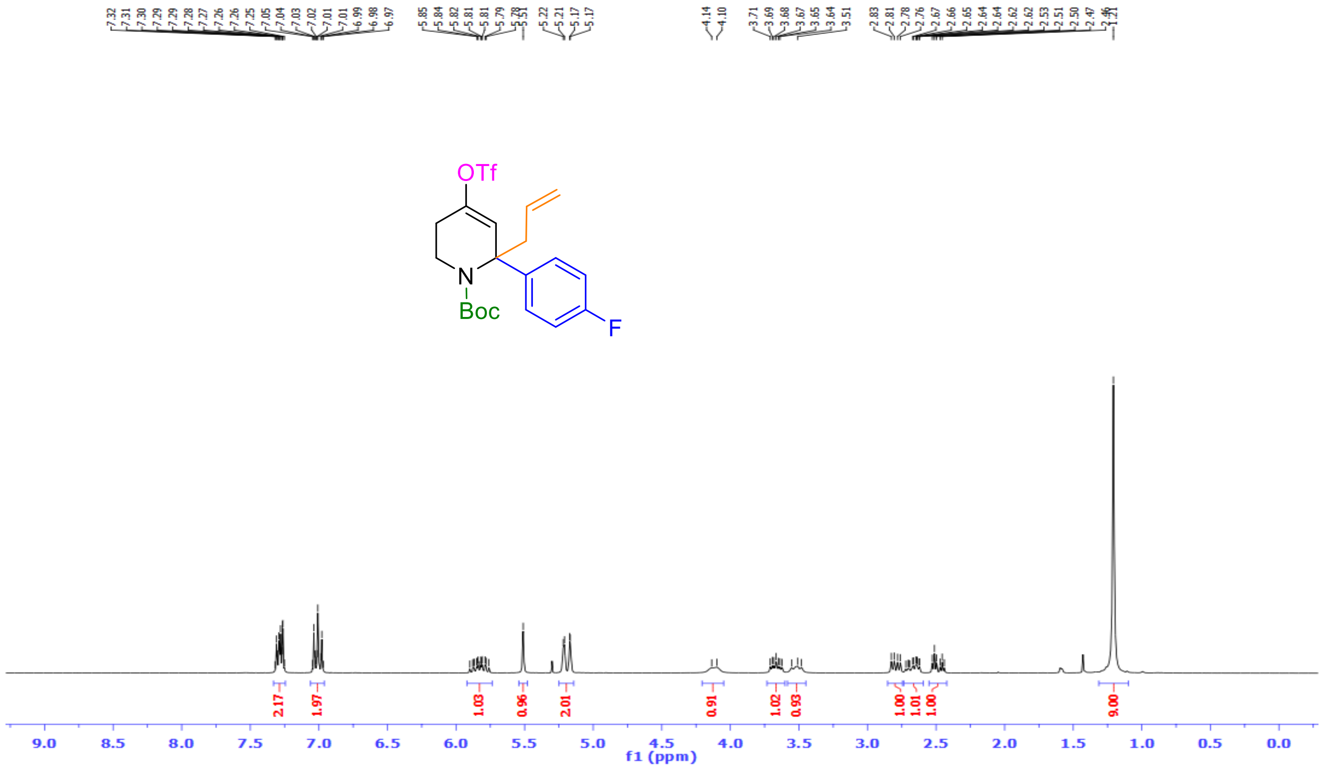
^{1}H NMR of **2d** (300 MHz, $CDCl_3$)



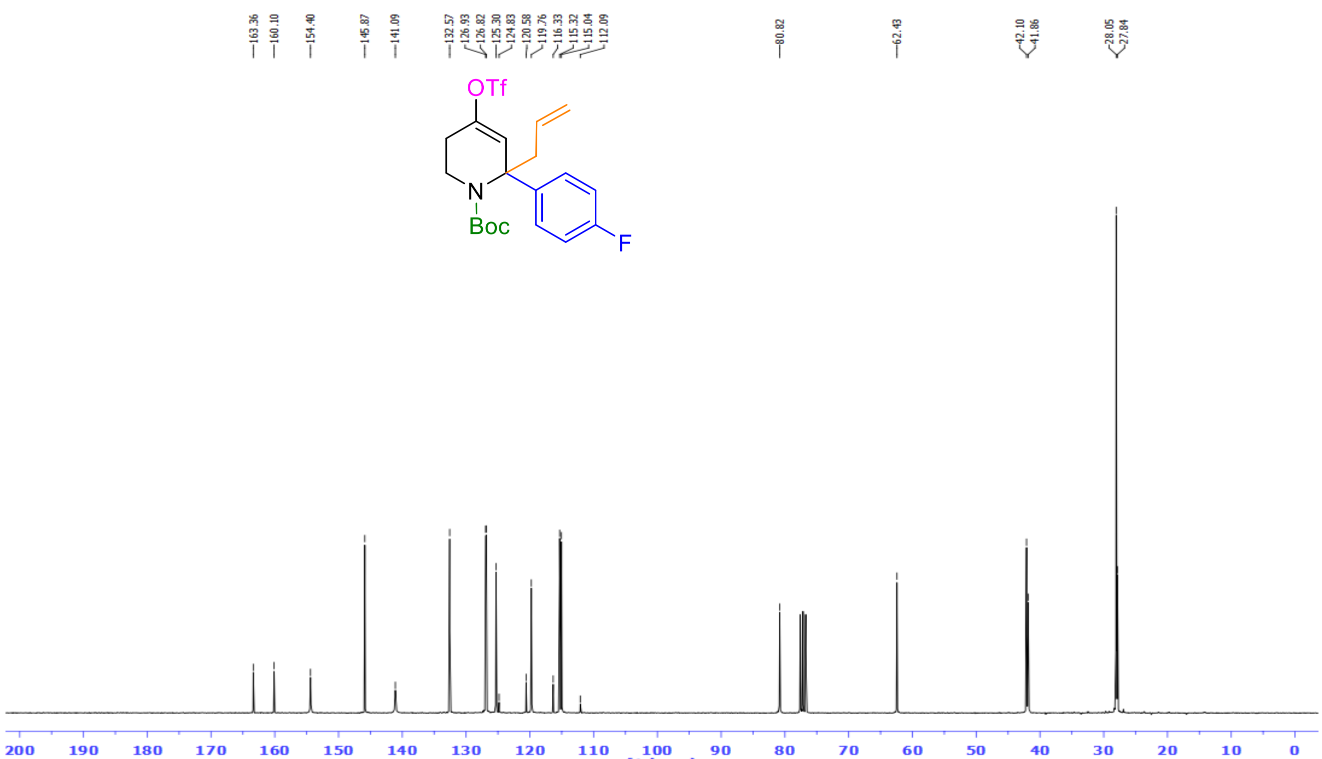
^{13}C NMR of **2d** (75 MHz, $CDCl_3$)



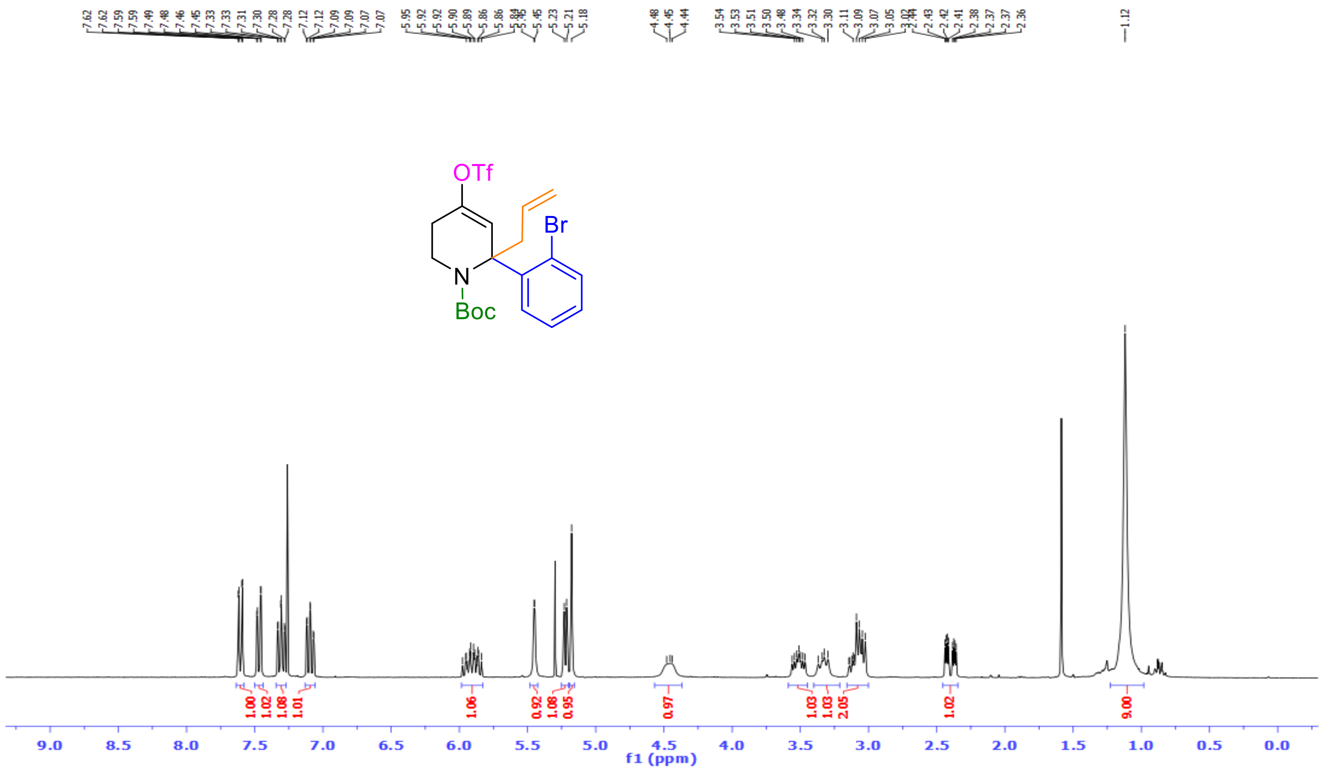
[1]H NMR of **2e** (300 MHz, $CDCl_3$)



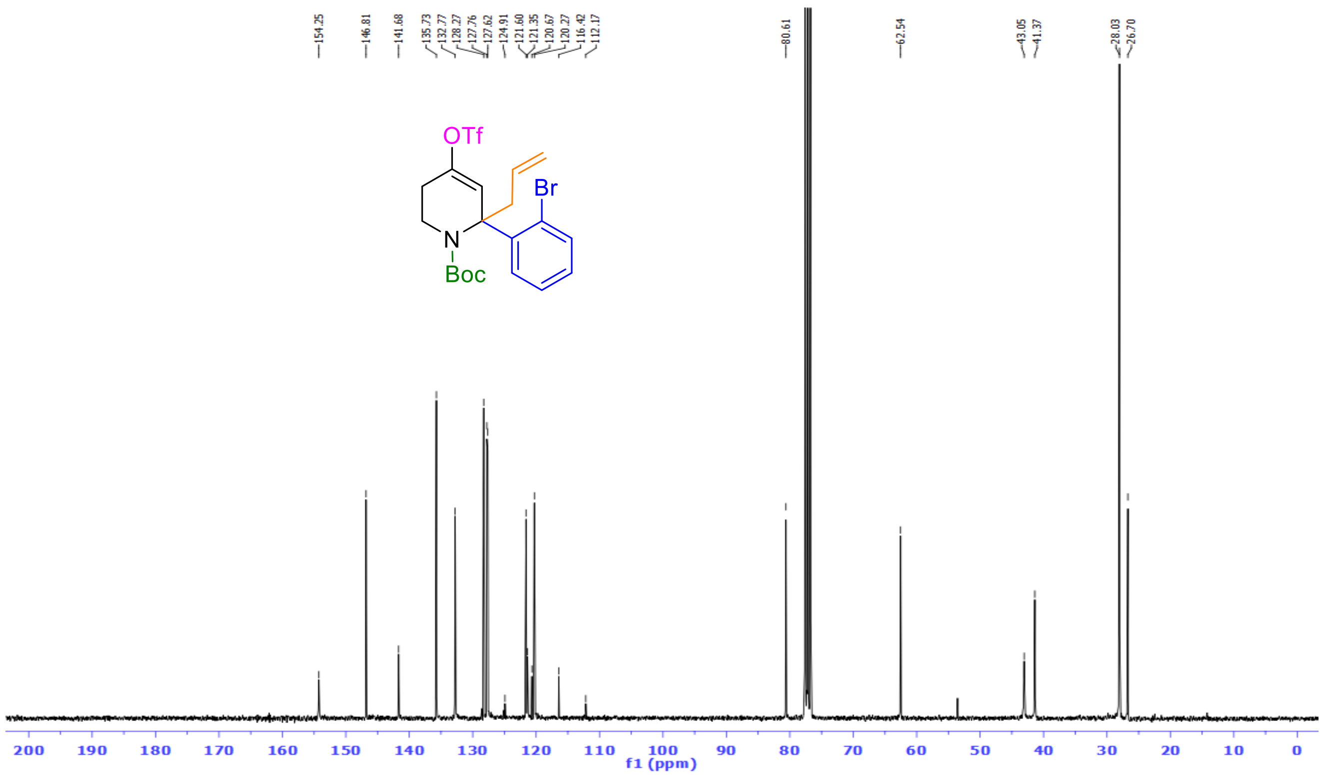
[13]C NMR of **2e** (75 MHz, $CDCl_3$)



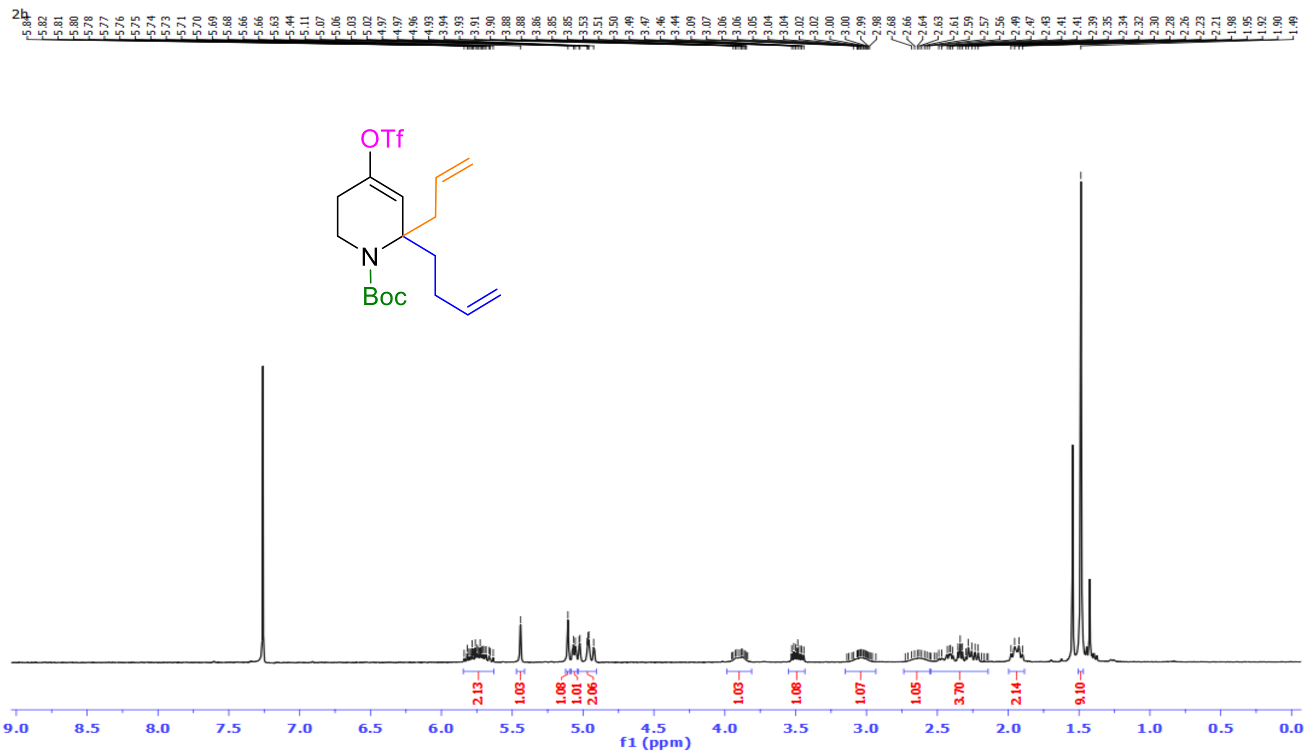
[1]H NMR of **2f** (300 MHz, $CDCl_3$)



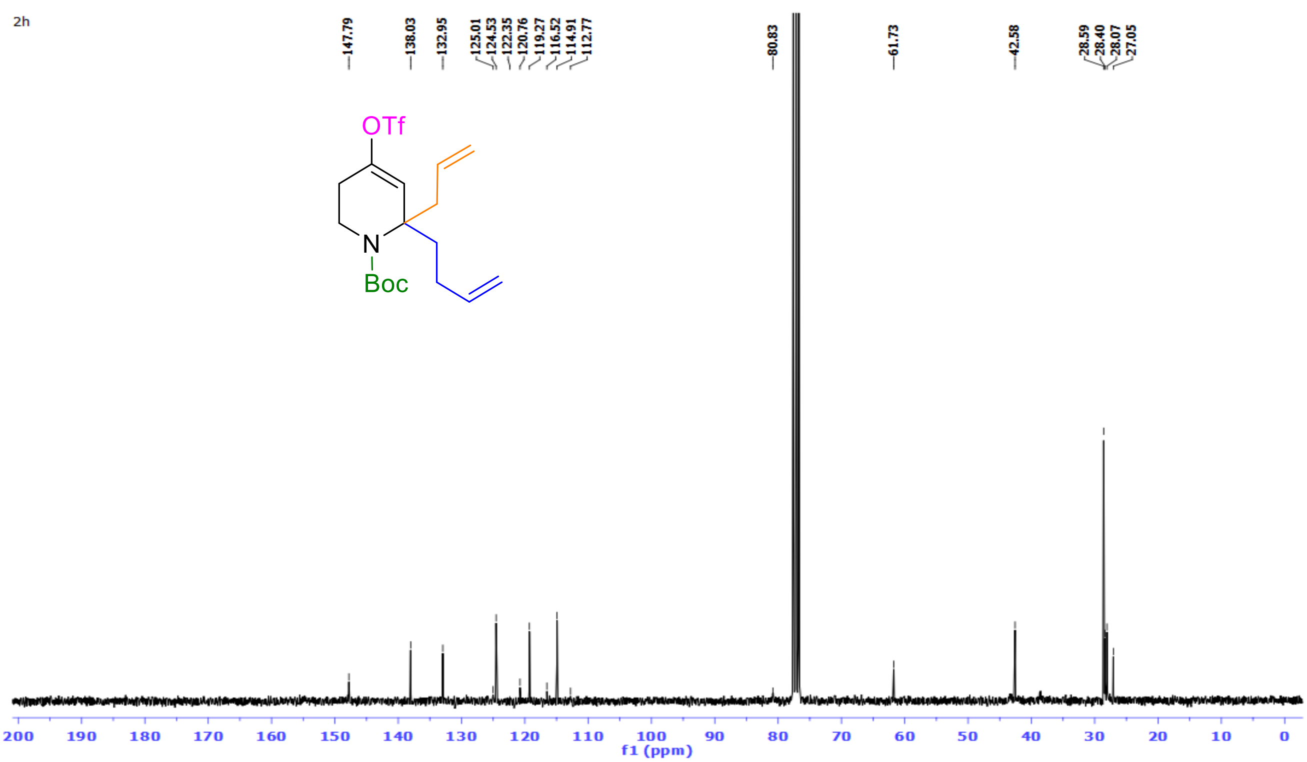
[13]C NMR of **2f** (75 MHz, $CDCl_3$)



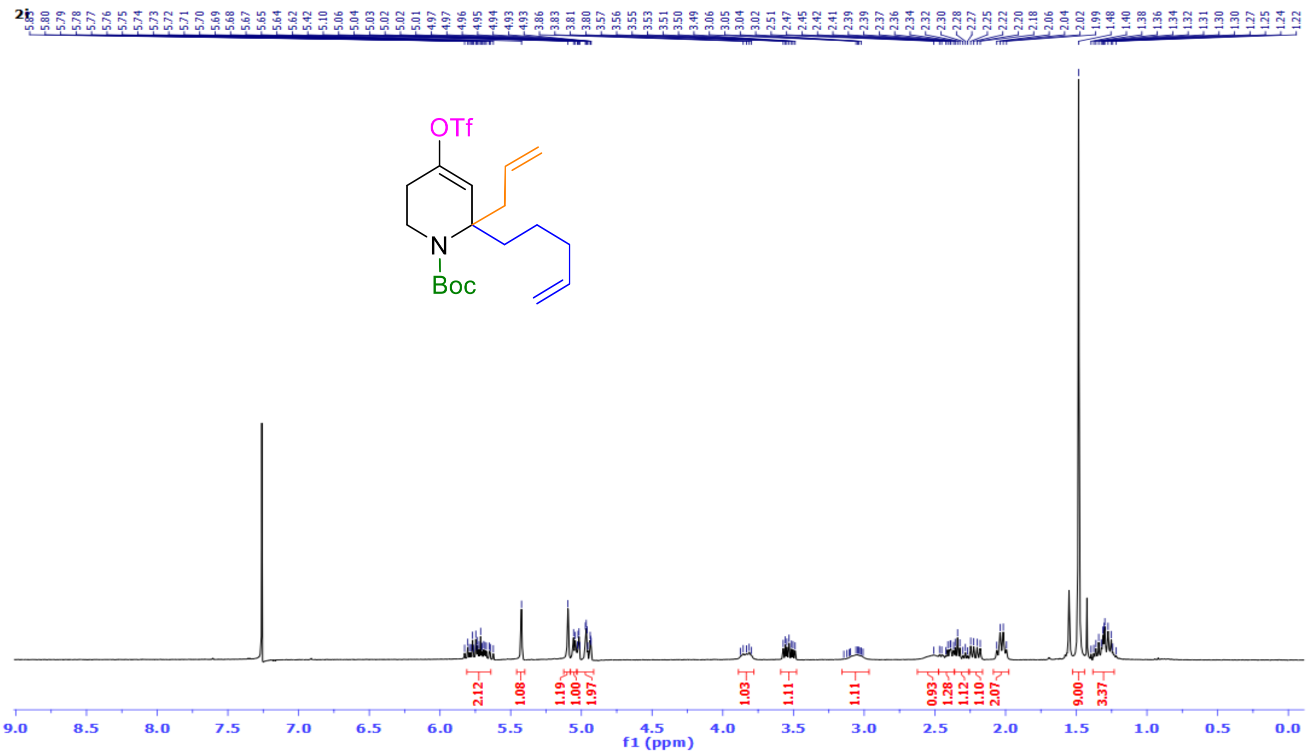
^{1}H NMR of **2g** (300 MHz, $CDCl_3$)



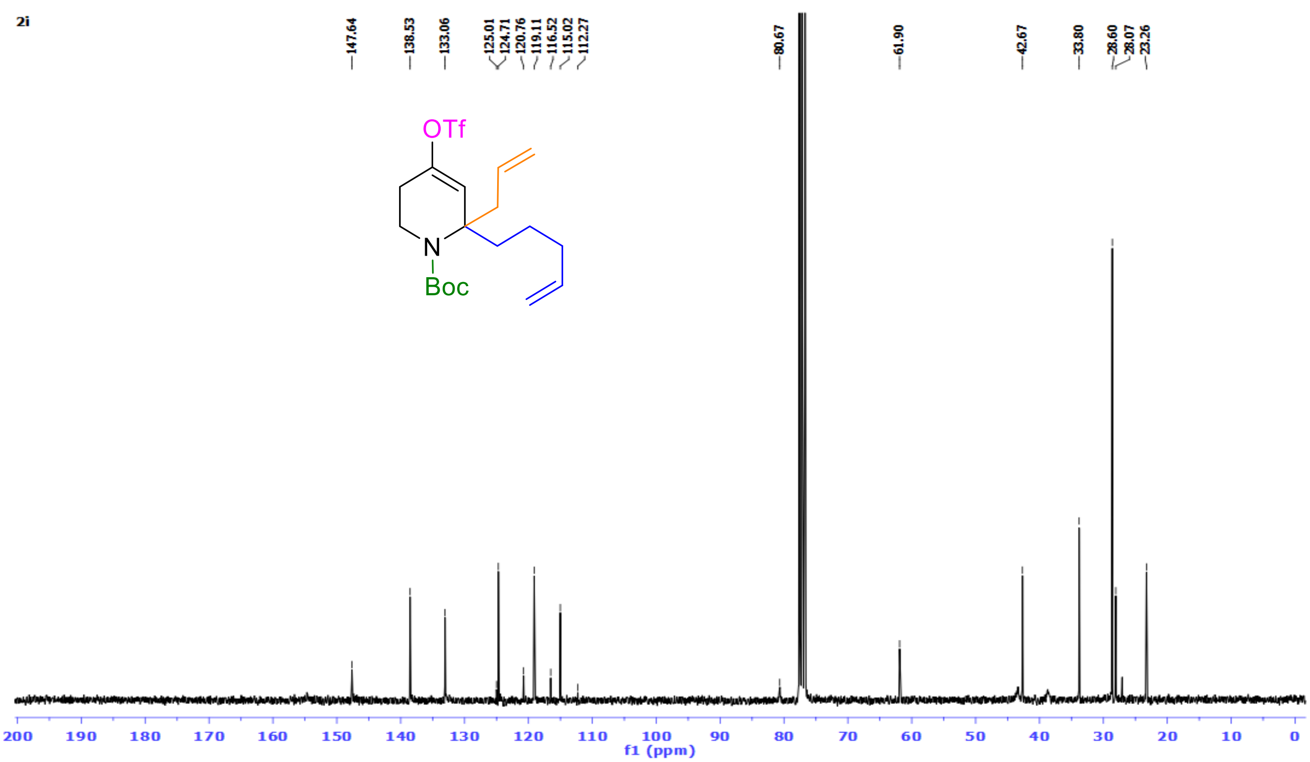
^{13}C NMR of **2g** (75 MHz, $CDCl_3$)



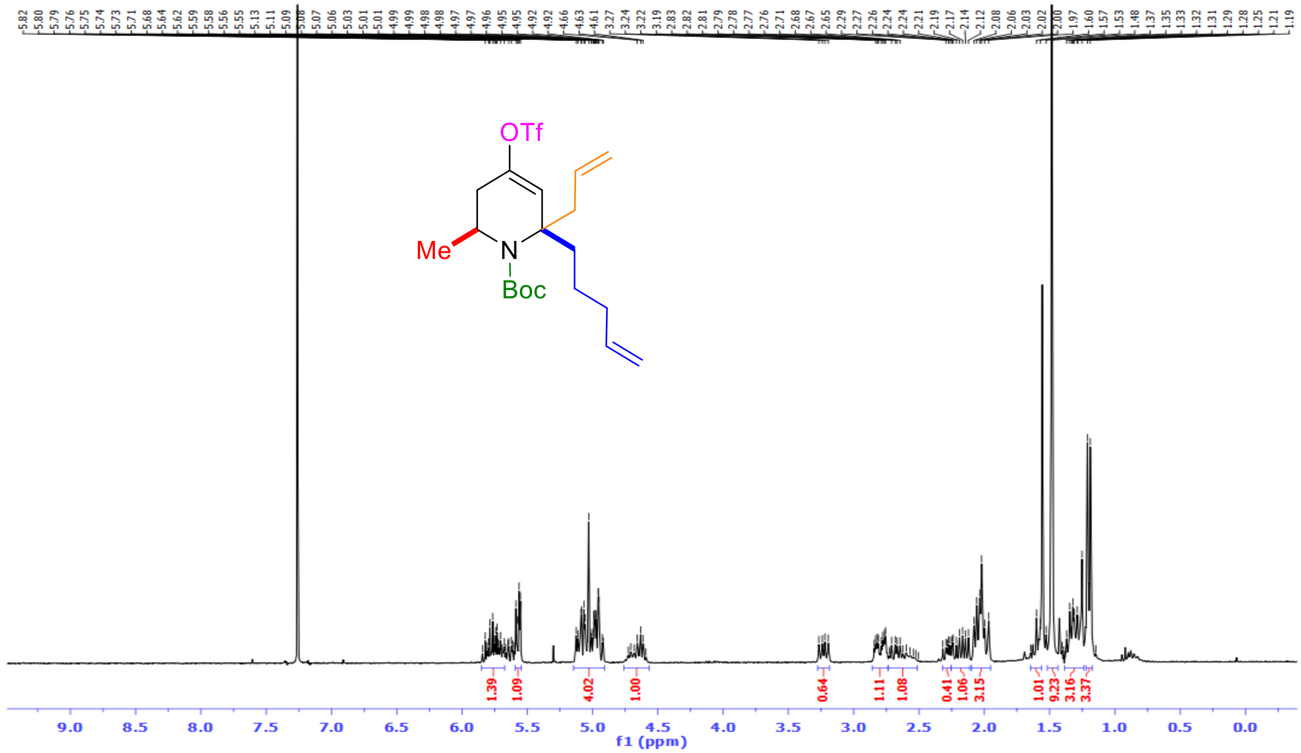
^{1}H NMR of **2h** (300 MHz, $CDCl_3$)



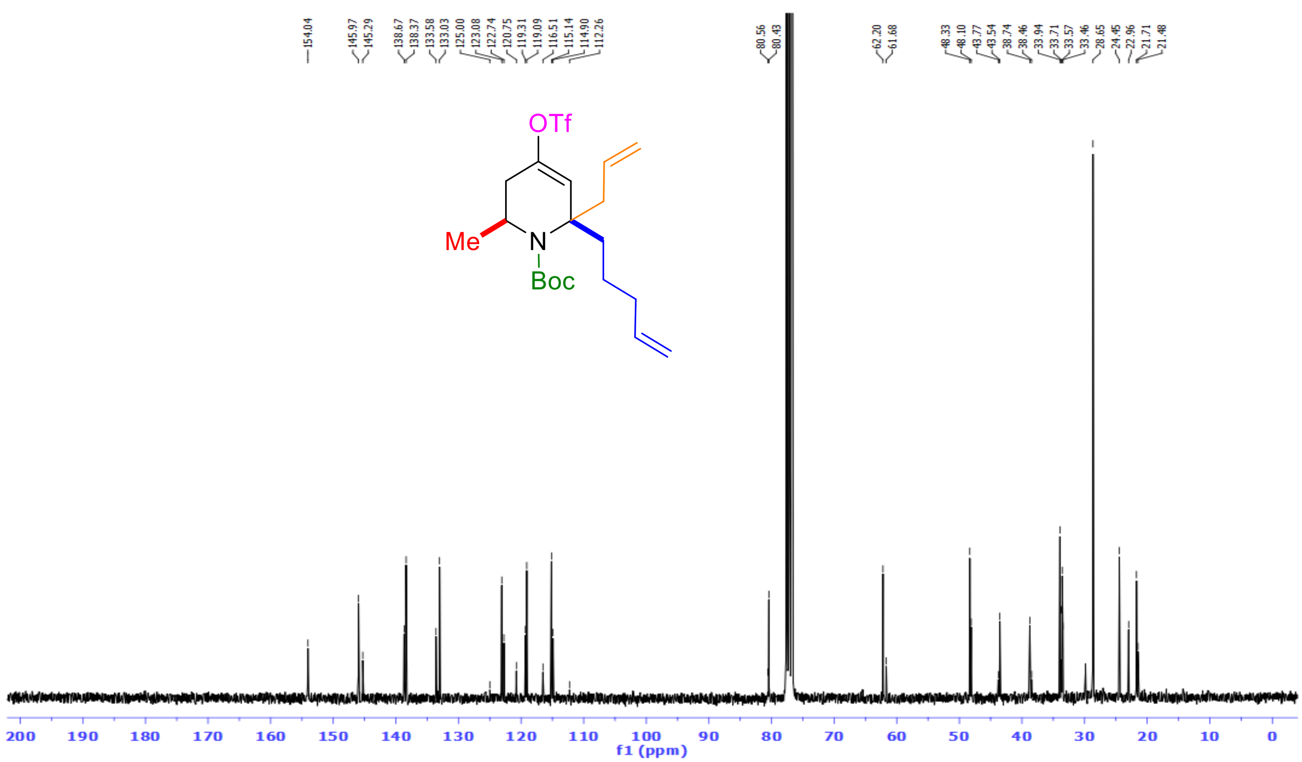
^{13}C NMR of **2h** (75 MHz, $CDCl_3$)



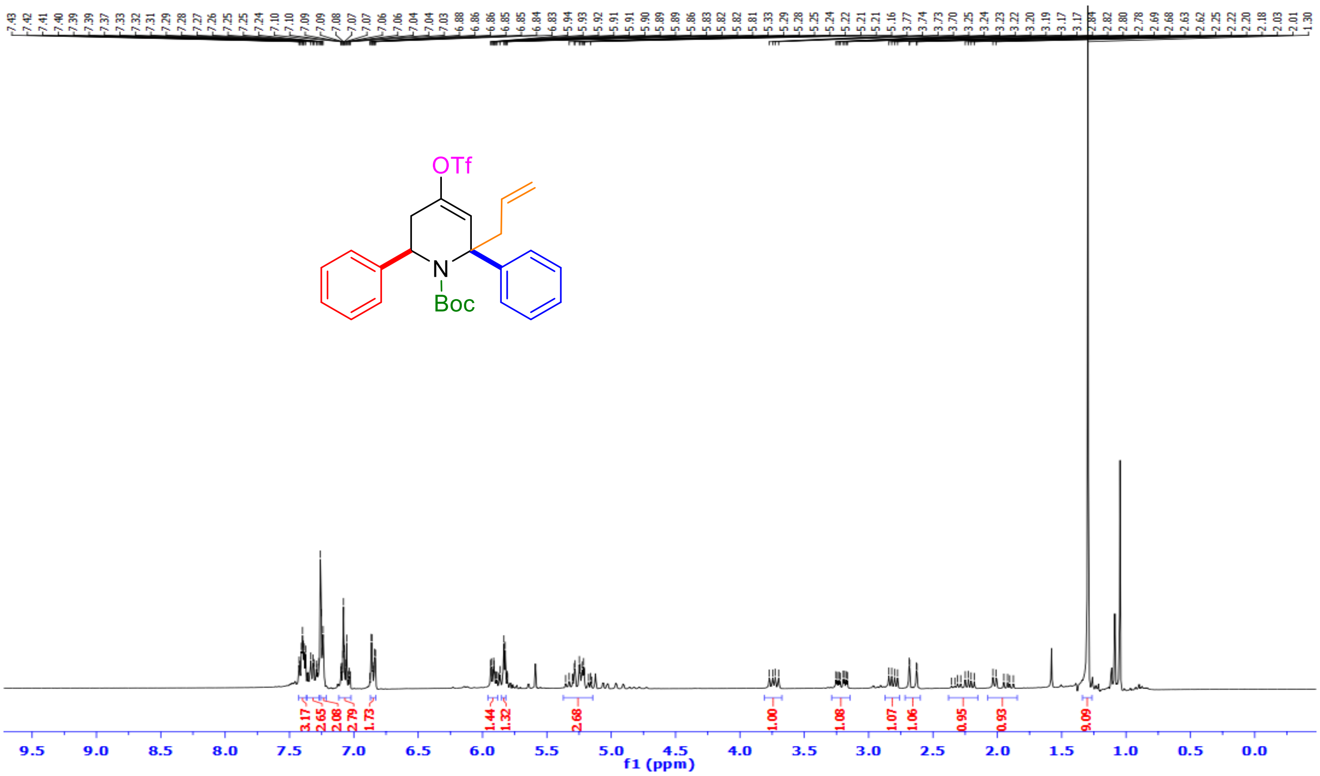
^{1}H NMR of **2i** (300 MHz, $CDCl_3$)



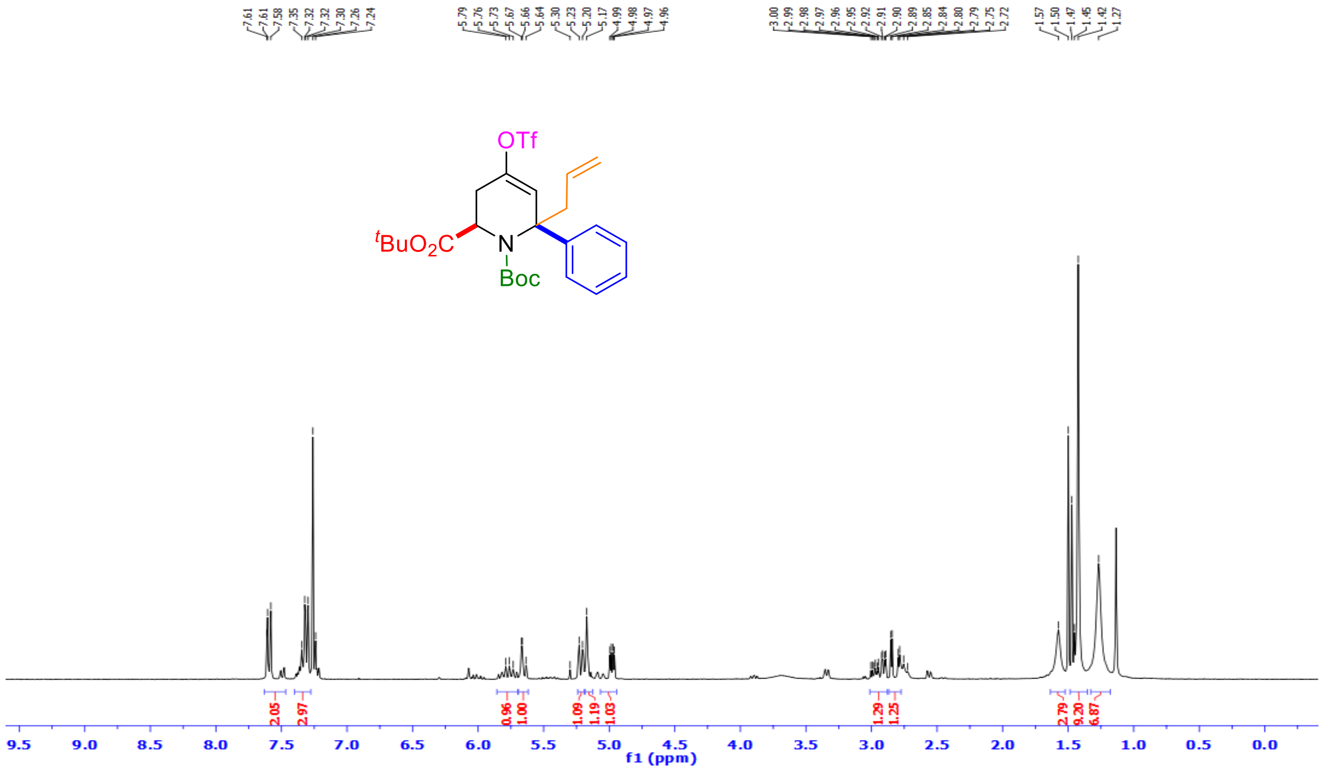
^{13}C NMR of **2i** (75 MHz, $CDCl_3$)



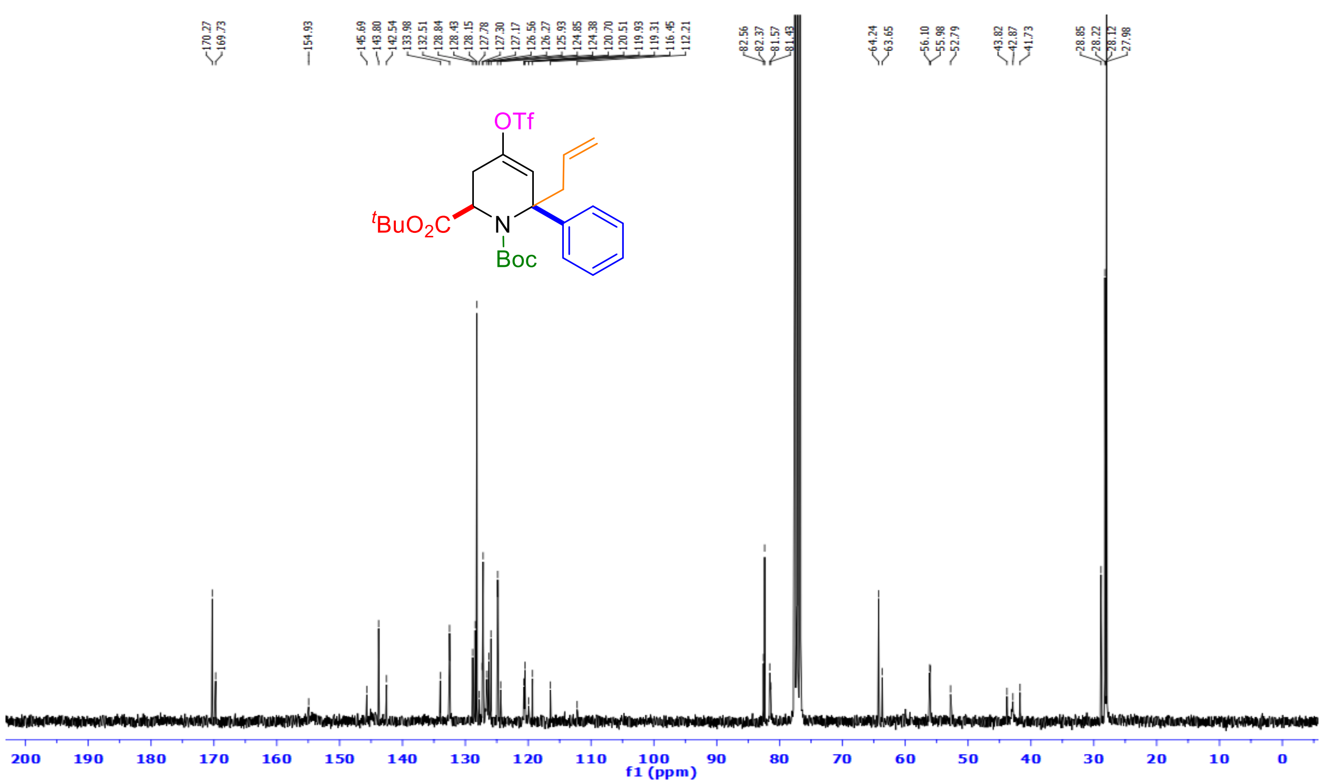
[1]H NMR of **2j** (300 MHz, $CDCl_3$)



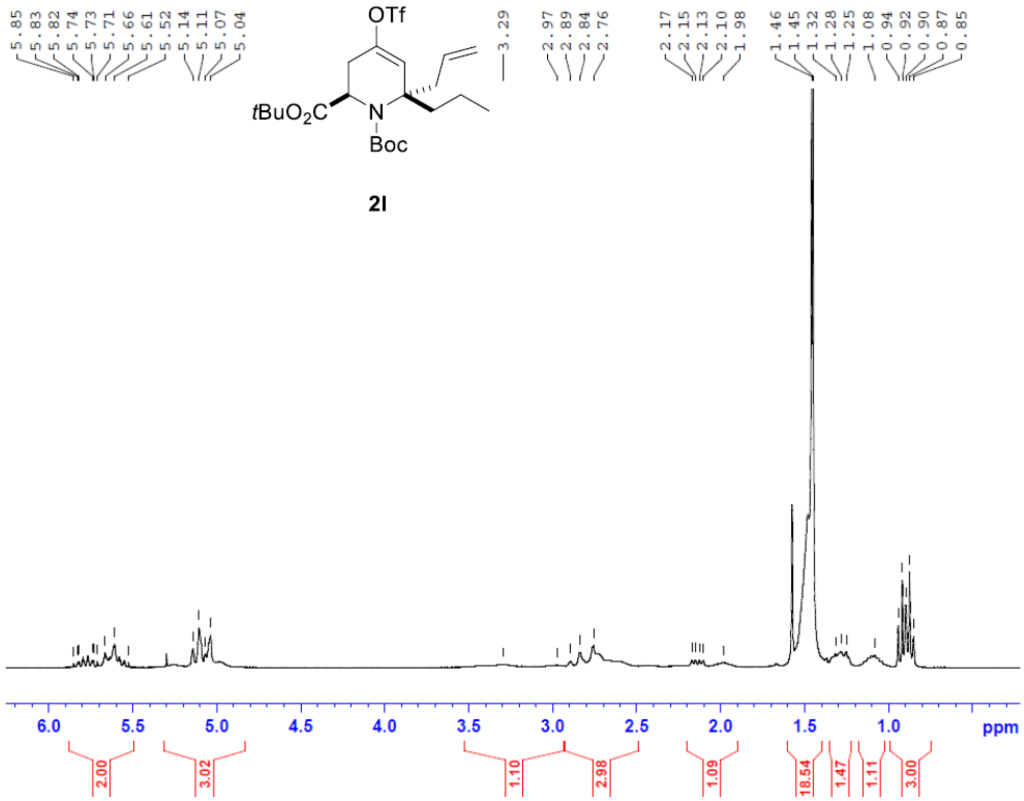
[1]H NMR of **2k** (300 MHz, $CDCl_3$)



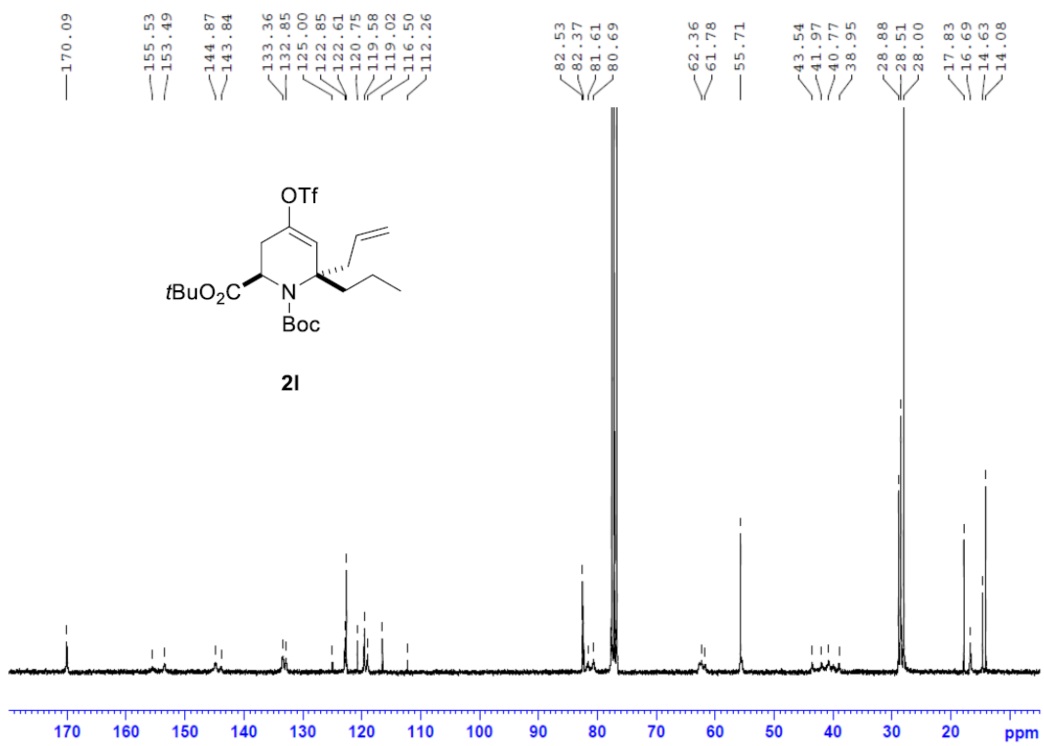
[13]C NMR of **2k** (75 MHz, $CDCl_3$)



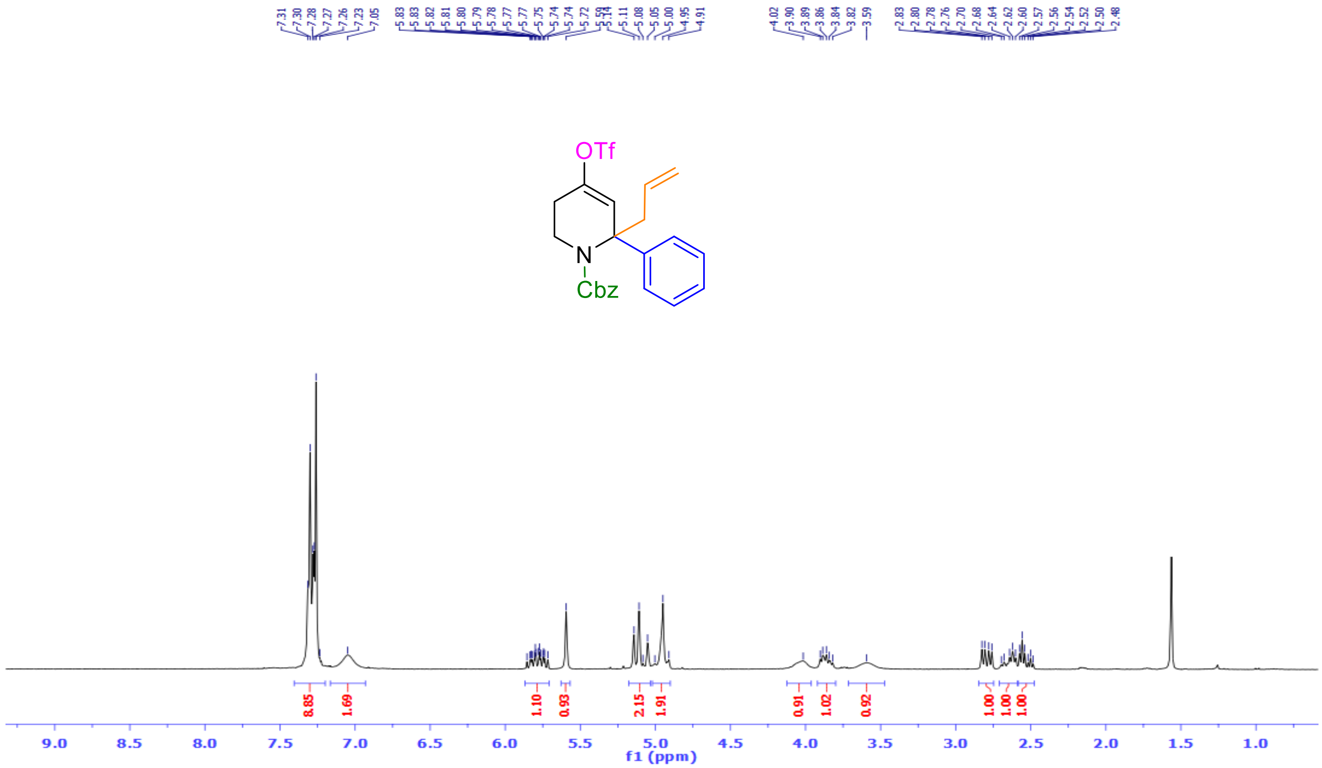
[1]H NMR of **2l** (300 MHz, $CDCl_3$)



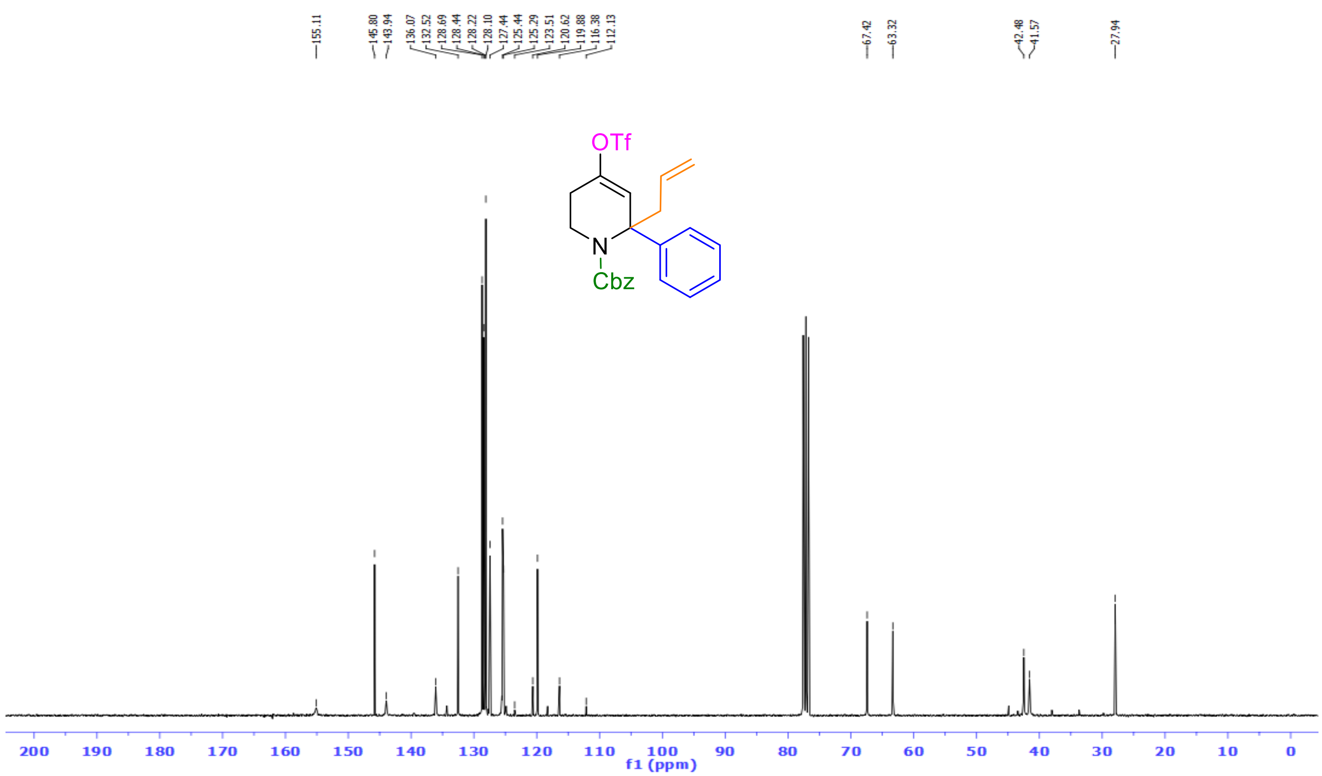
[13]C NMR of **2l** (300 MHz, $CDCl_3$)



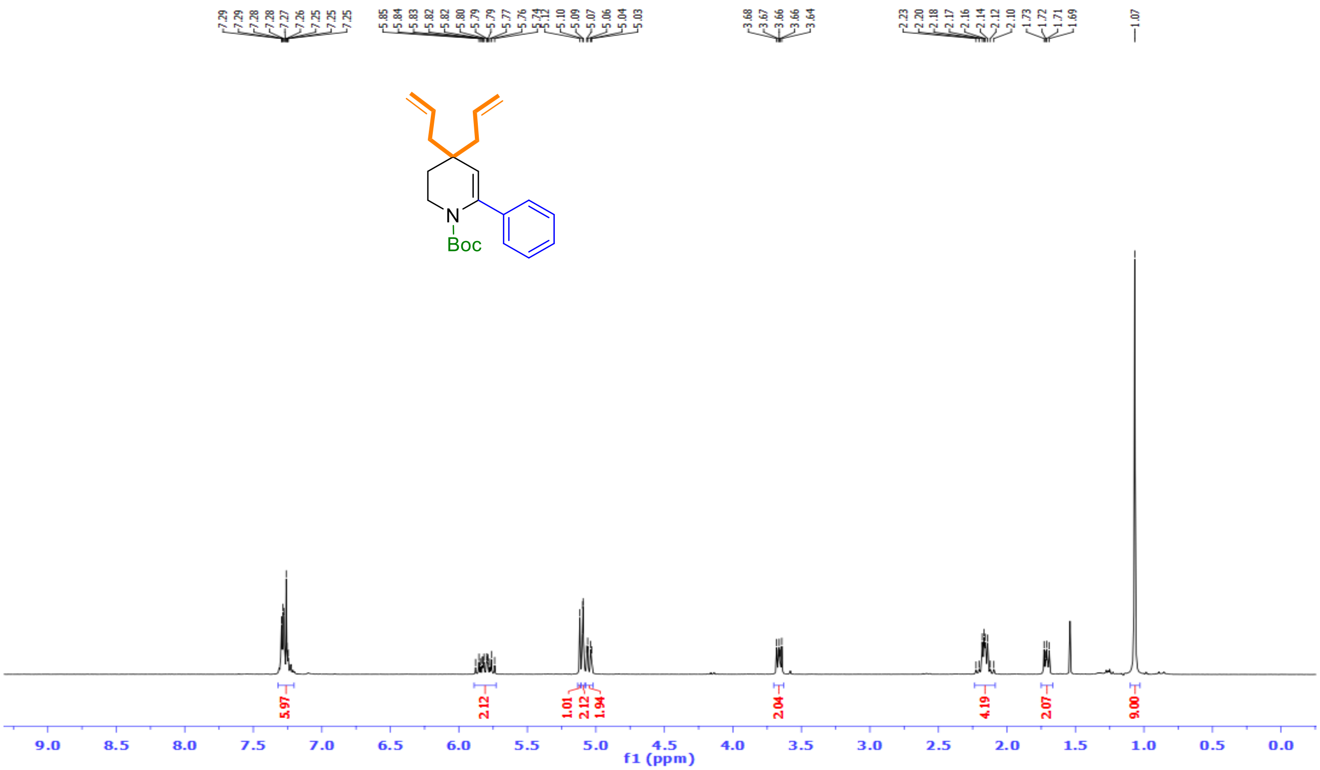
[1]H NMR of **2m** (300 MHz, $CDCl_3$)



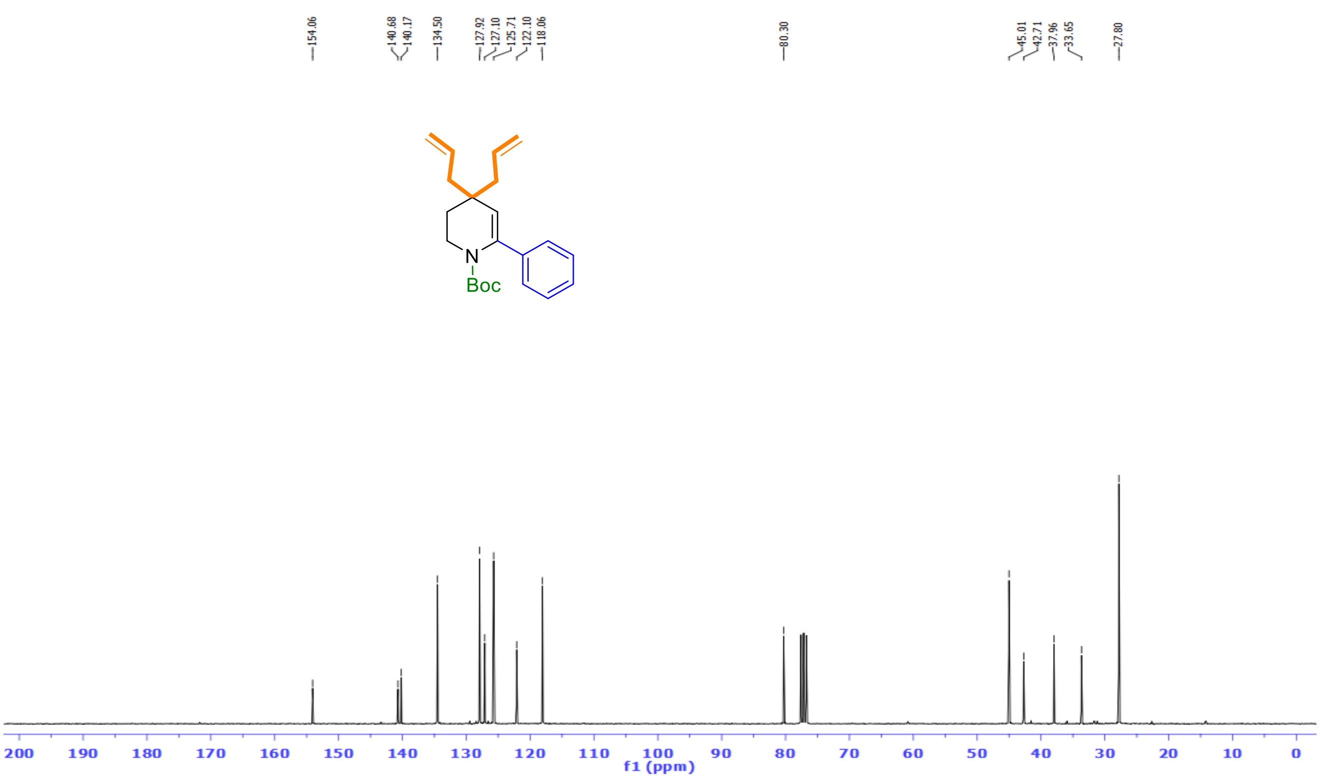
[13]C NMR of **2m** (75 MHz, $CDCl_3$)



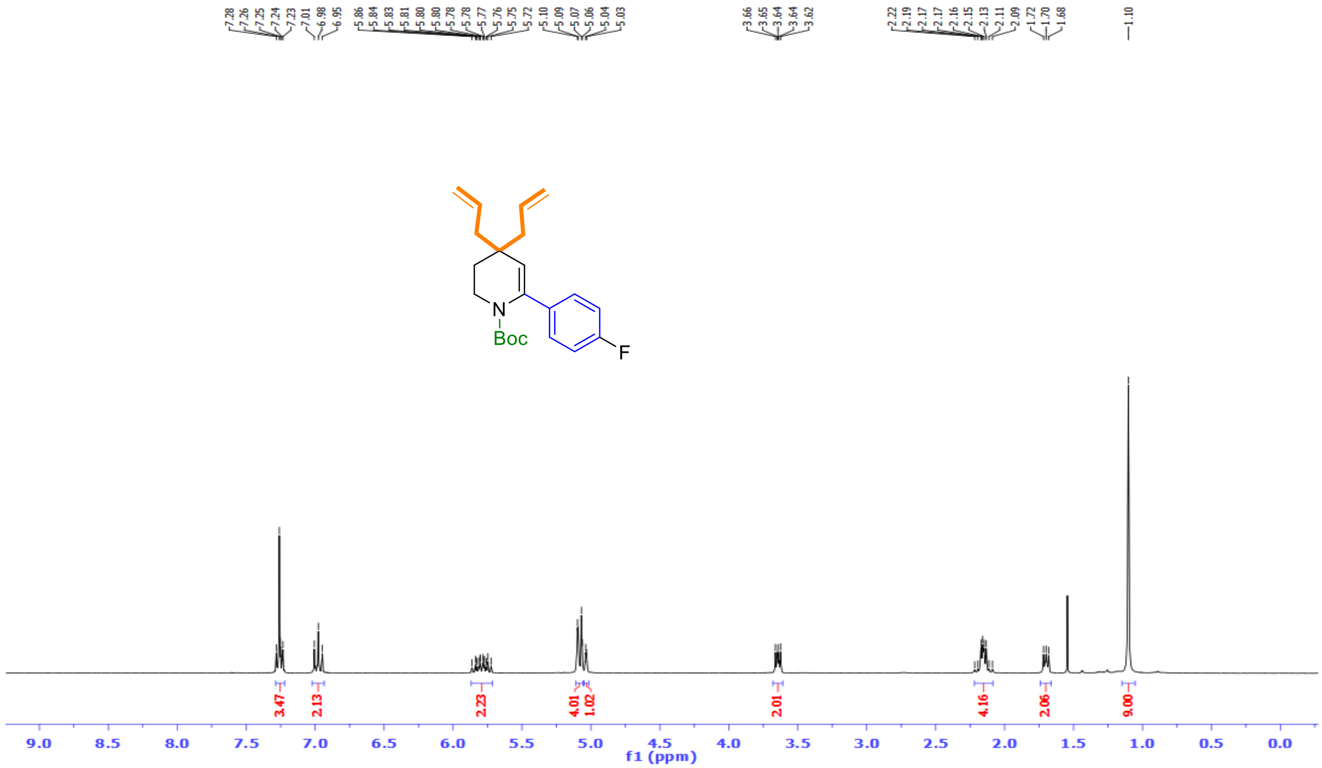
^{1}H NMR of **3d** (300 MHz, $CDCl_3$)



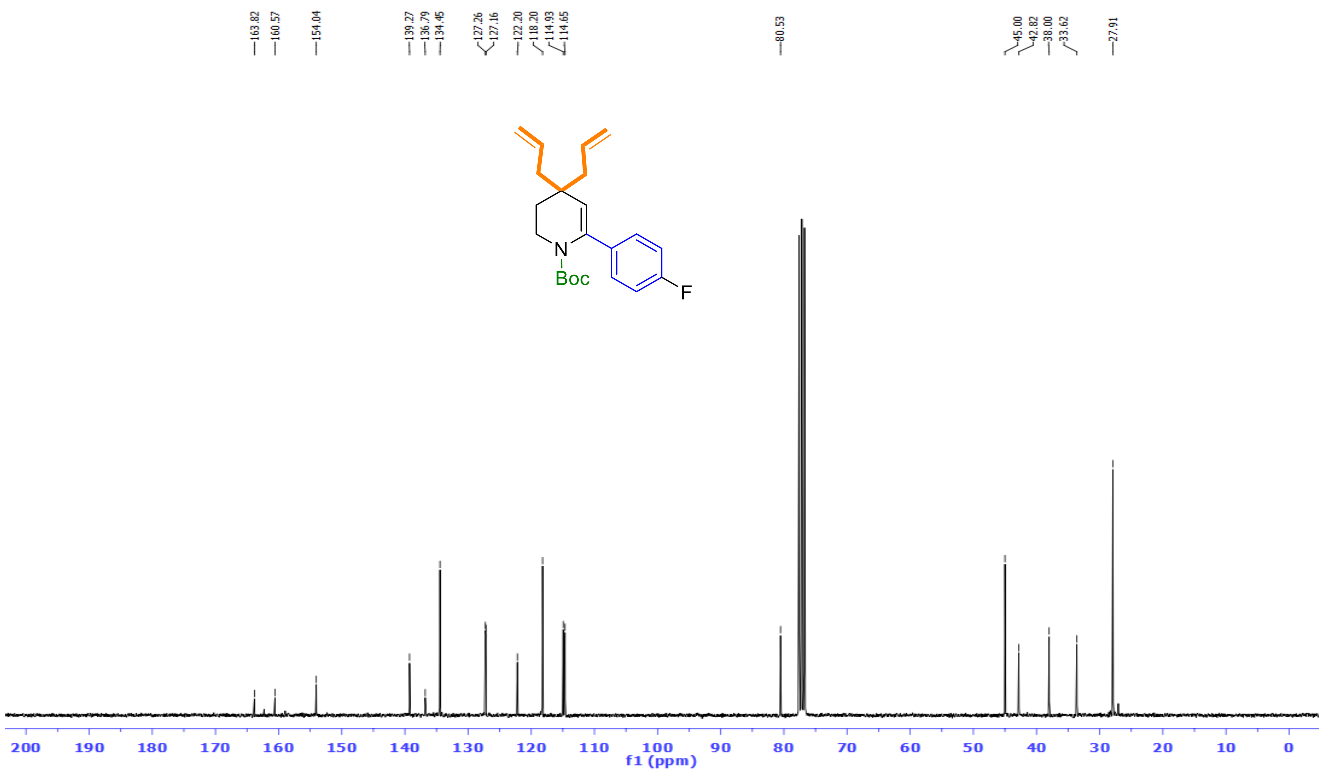
^{13}C NMR of **3d** (75 MHz, $CDCl_3$)



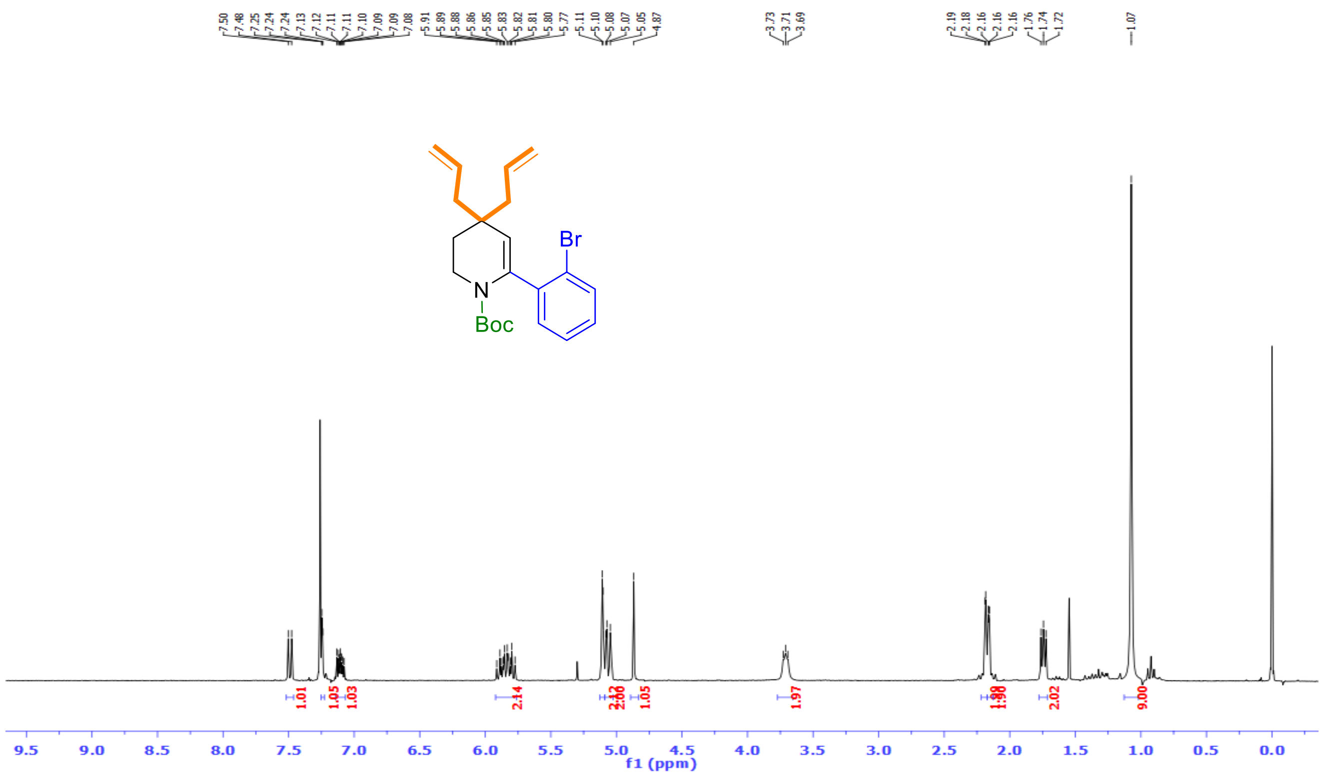
[1]H NMR of **3e** (300 MHz, $CDCl_3$)



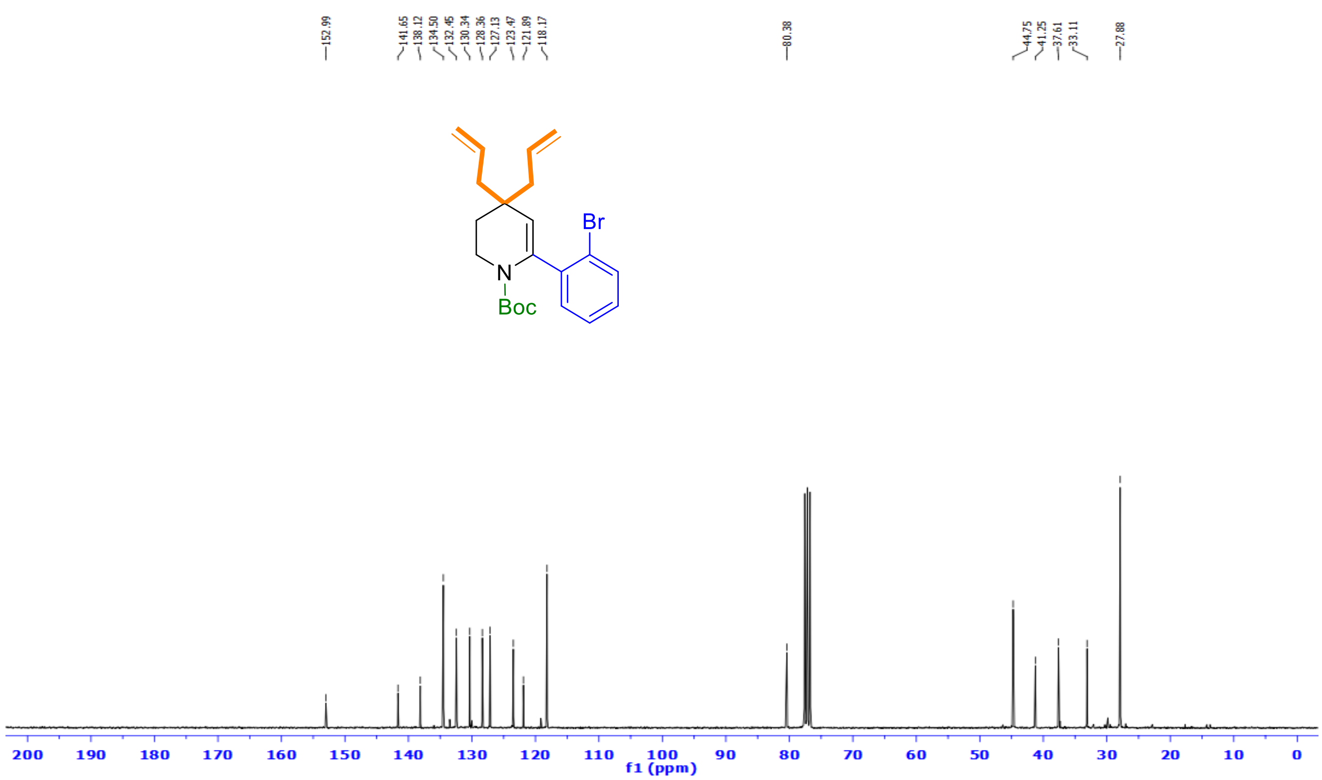
[13]C NMR of **3e** (75 MHz, $CDCl_3$)



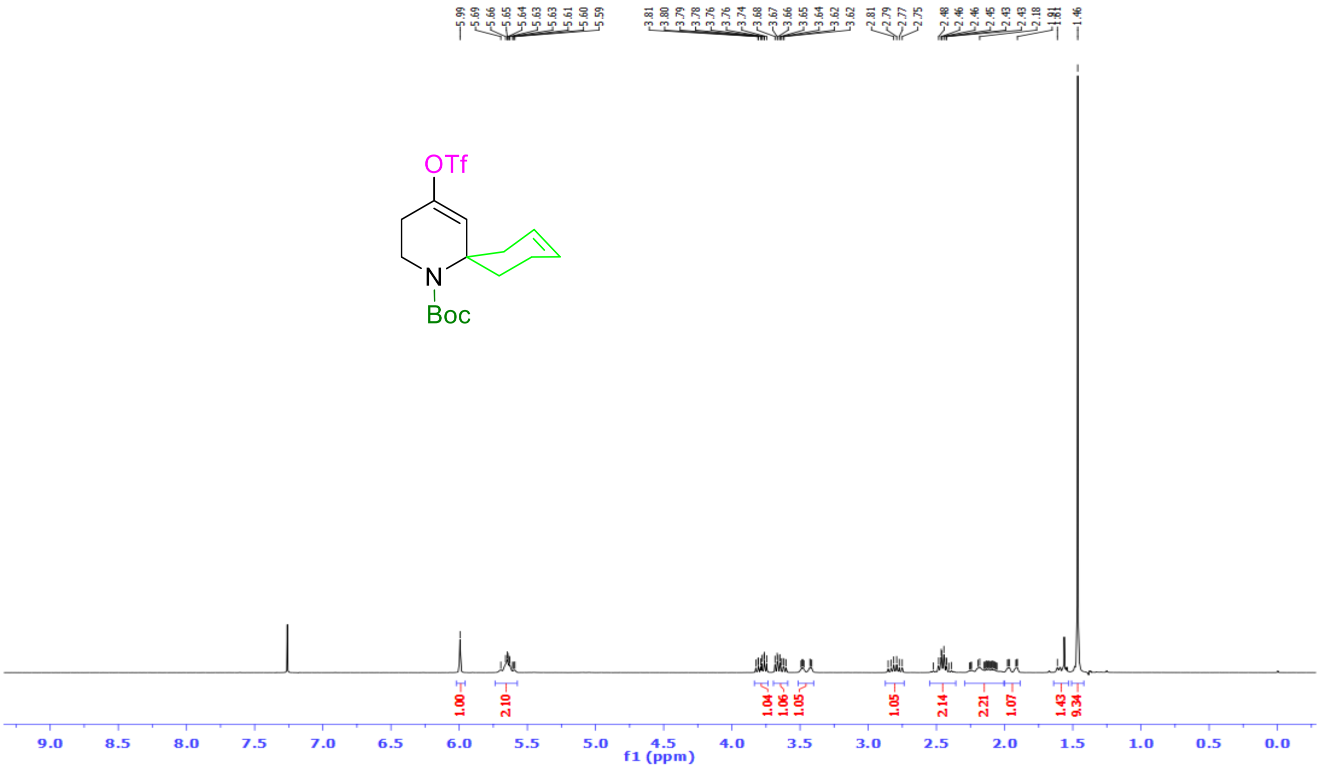
^{1}H NMR of **3f** (300 MHz, $CDCl_3$)



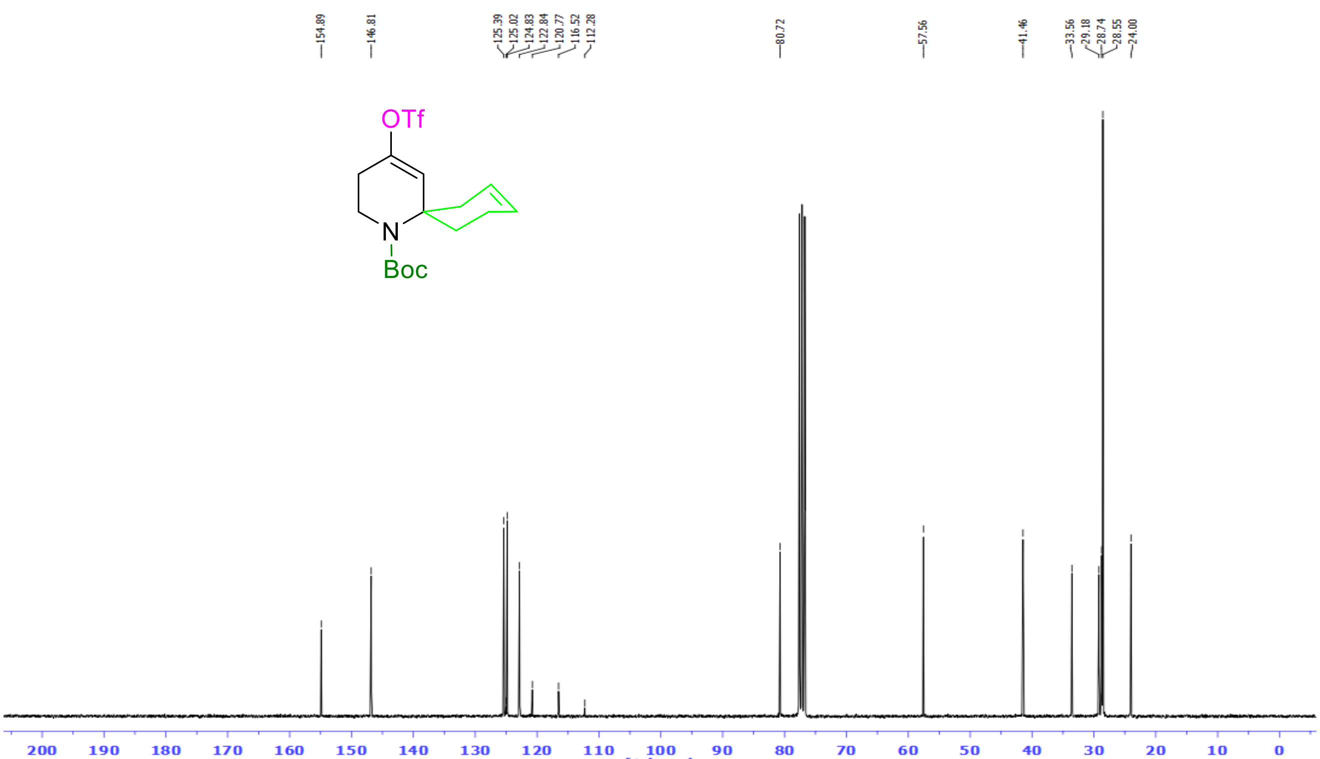
^{13}C NMR of **3f** (75 MHz, $CDCl_3$)



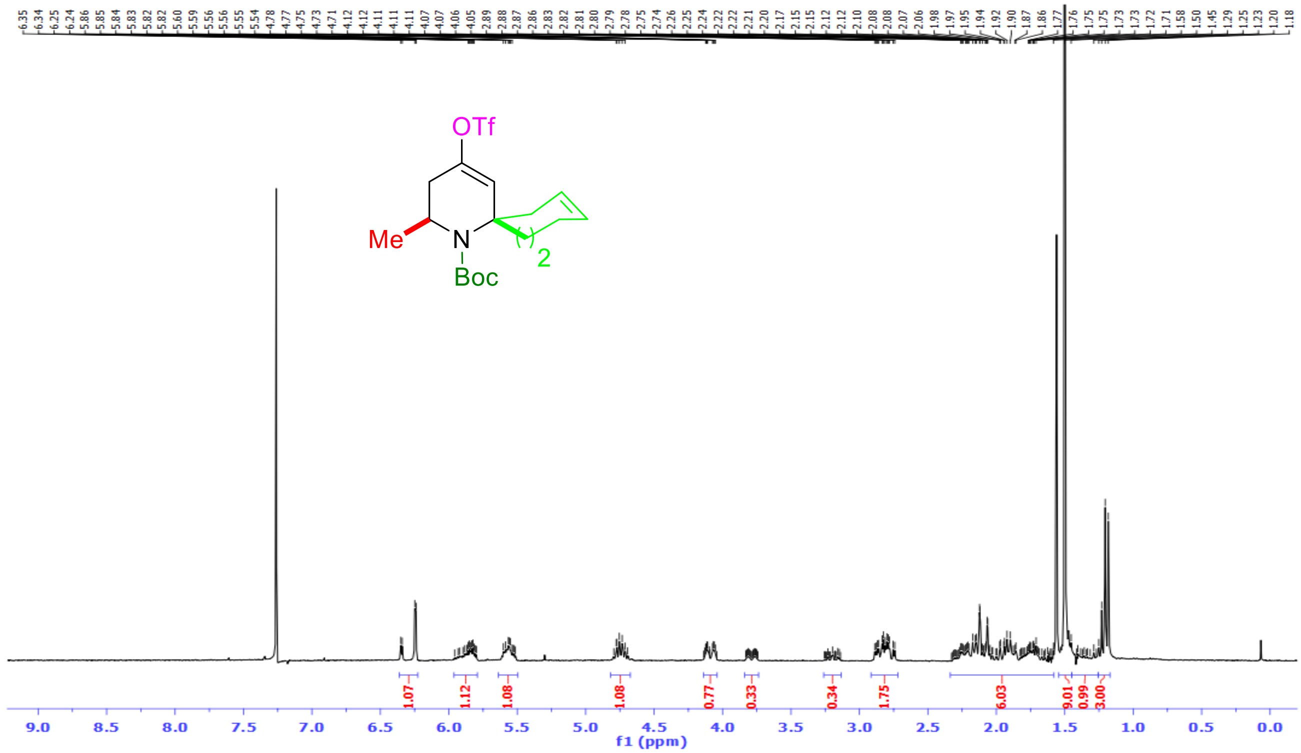
^{1}H NMR of **4a** (300 MHz, $CDCl_3$)



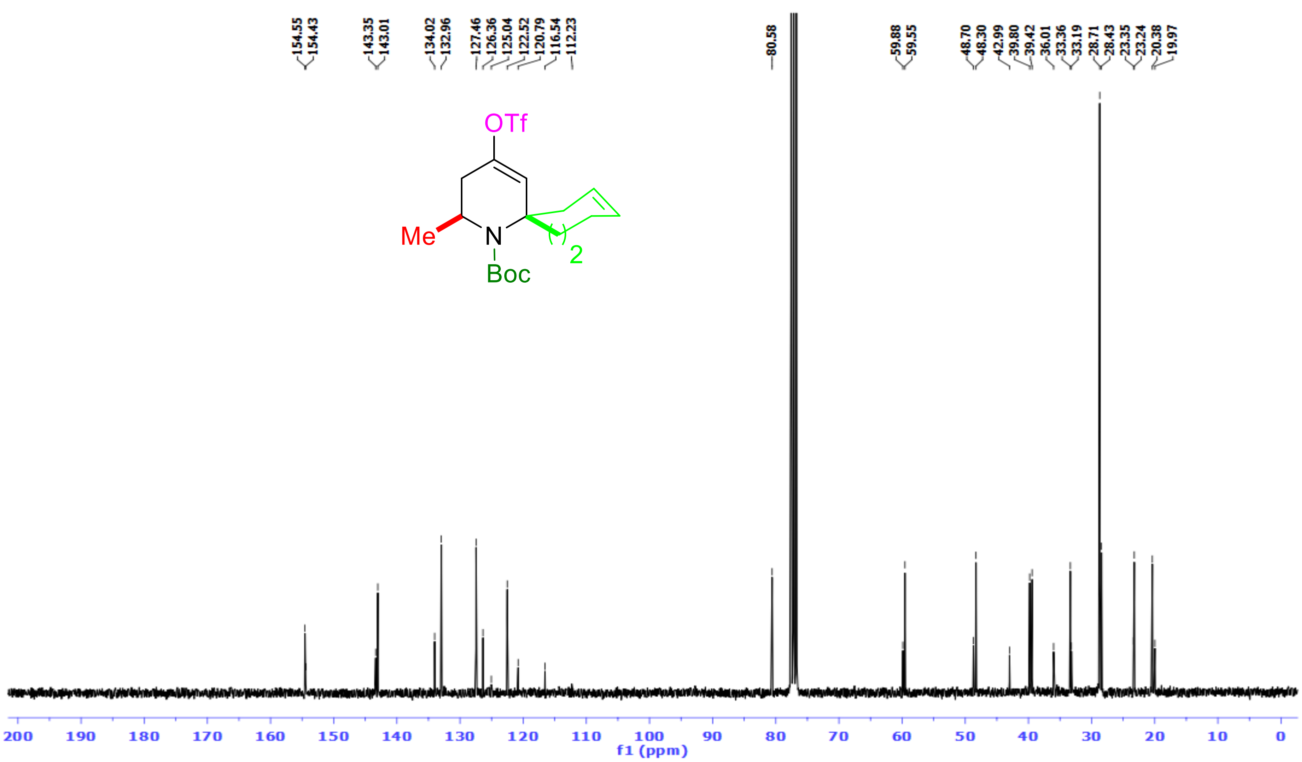
^{13}C NMR of **4a** (75 MHz, $CDCl_3$)



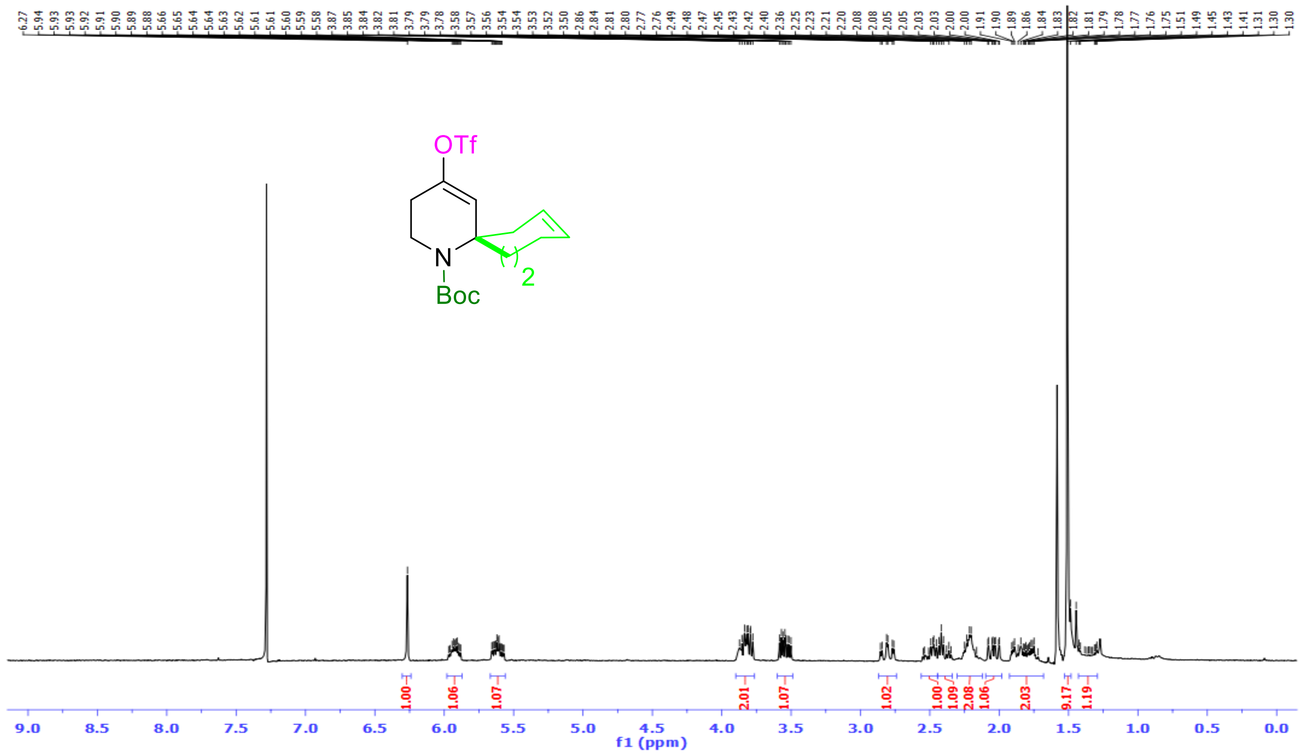
^{1}H NMR of **4b** (300 MHz, $CDCl_3$)



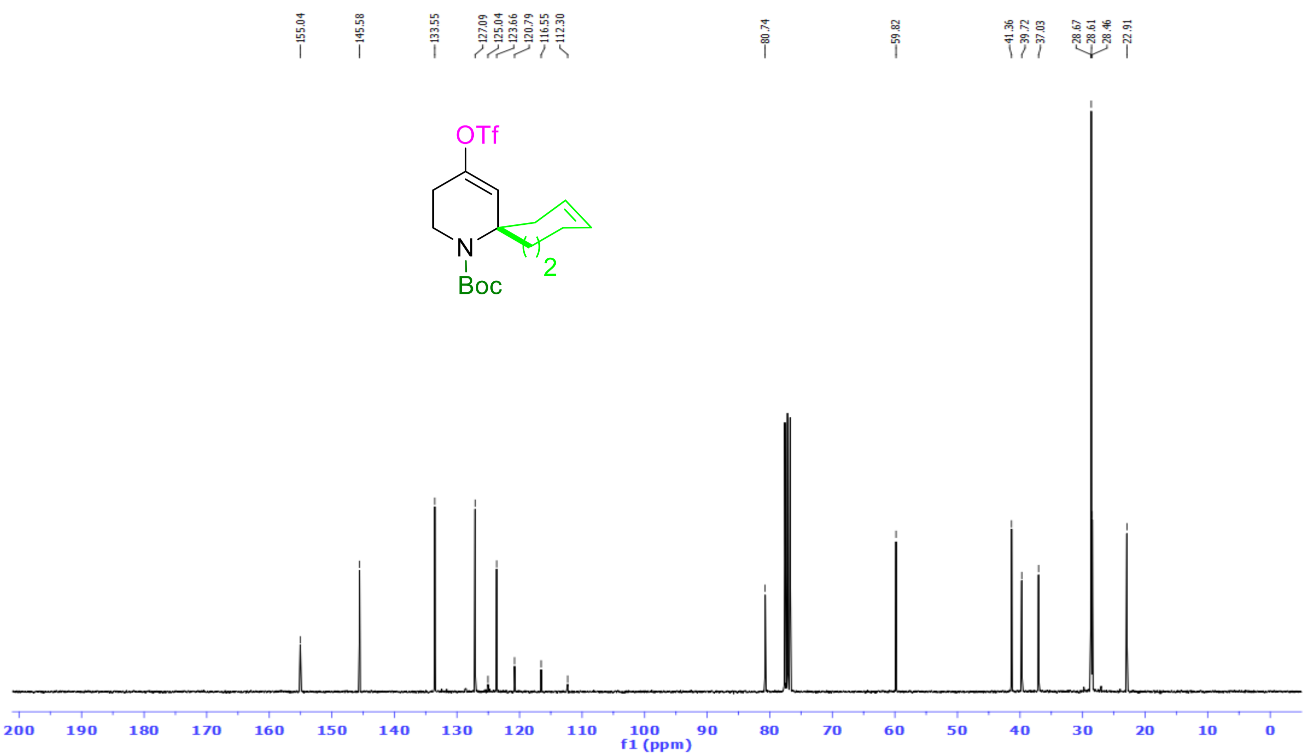
^{13}C NMR of **4b** (75 MHz, $CDCl_3$)



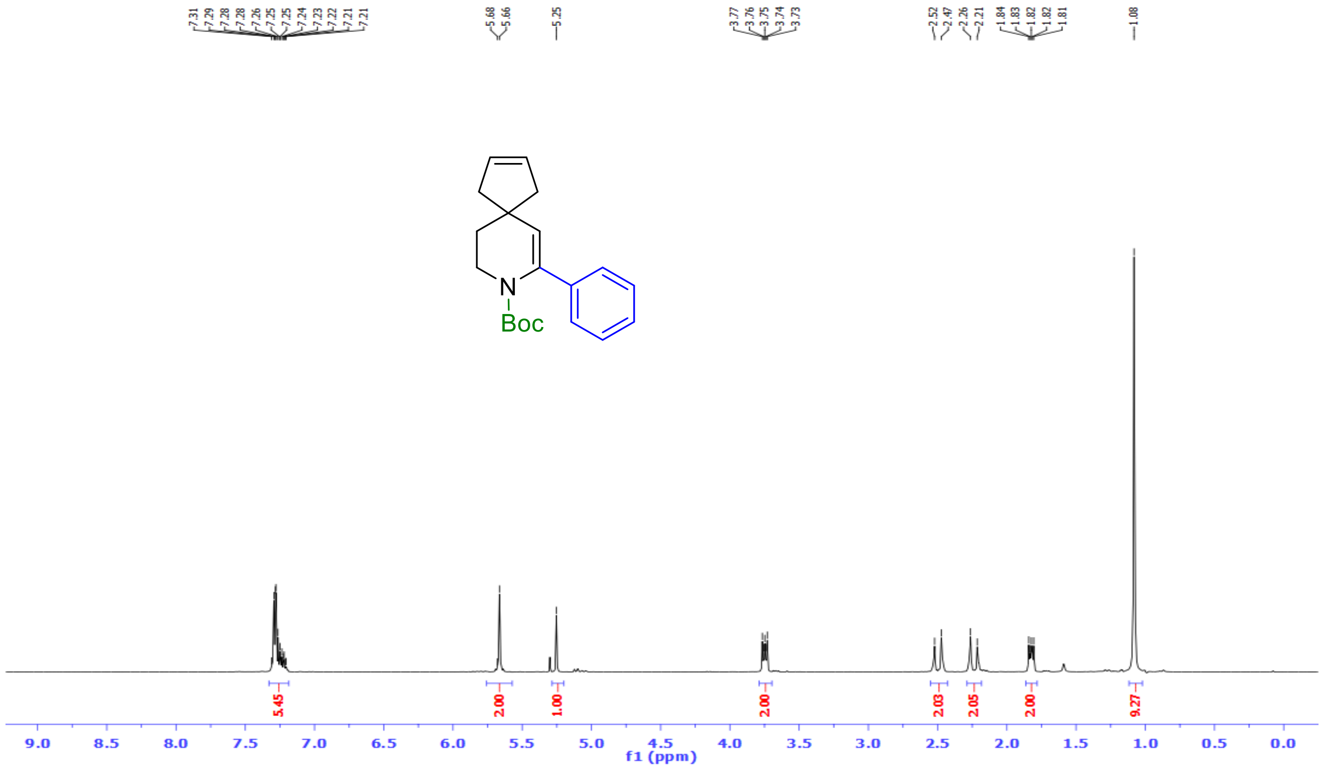
[1]H NMR of **4c** (300 MHz, $CDCl_3$)



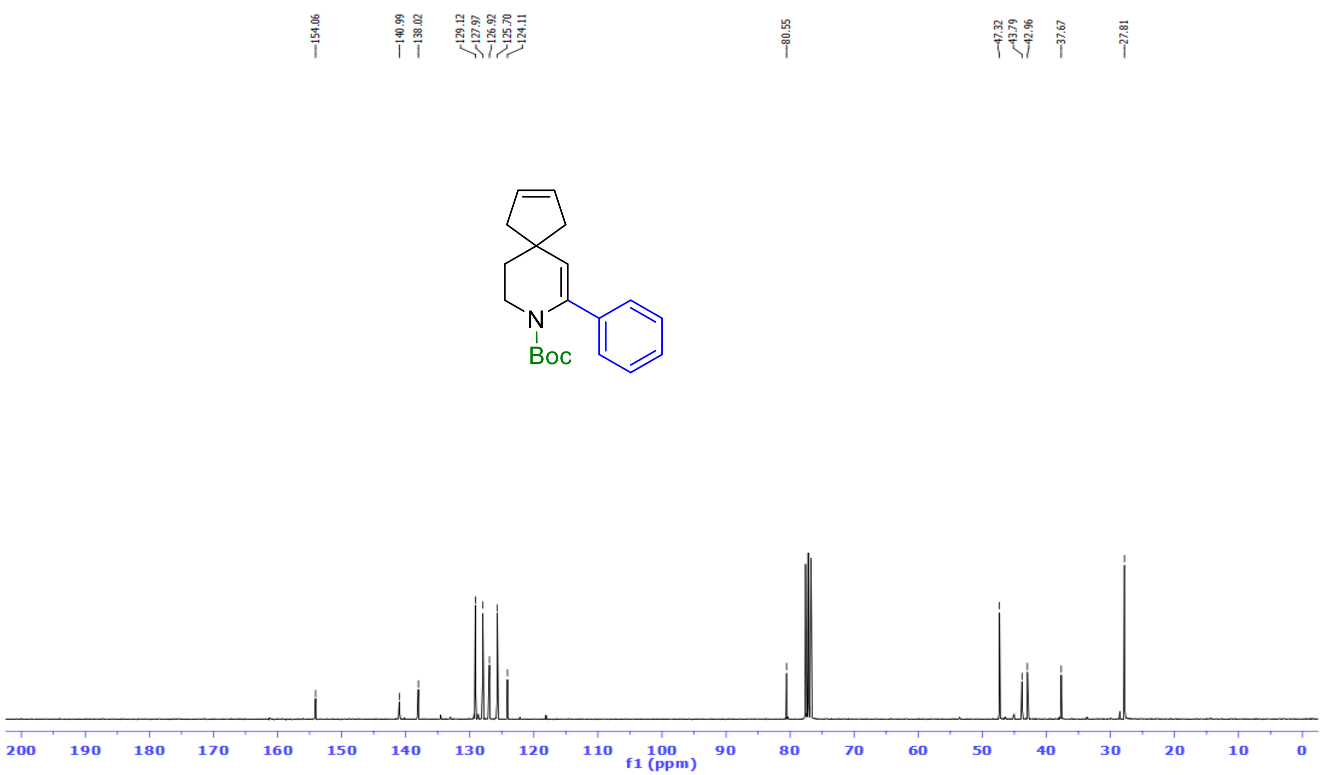
[13]C NMR of **4c** (75 MHz, $CDCl_3$)



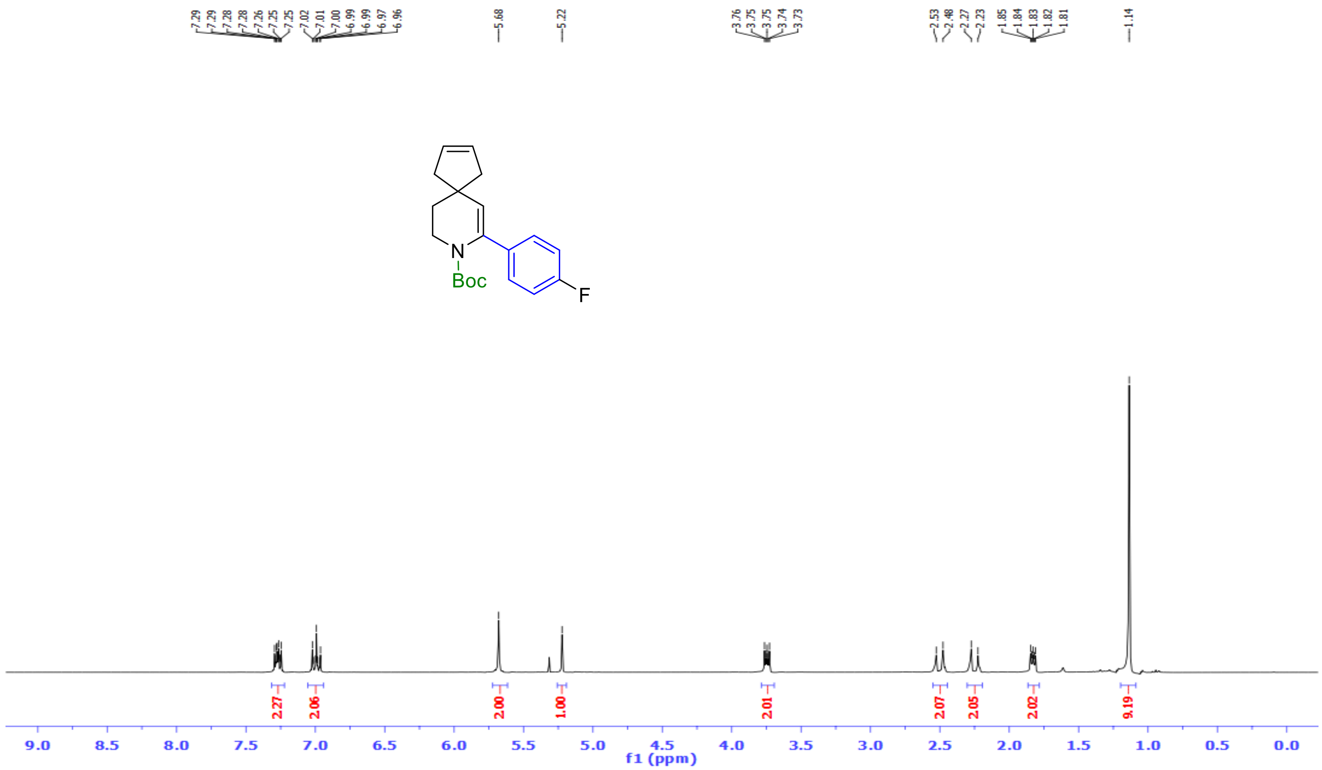
[1]H NMR of **5d** (300 MHz, $CDCl_3$)



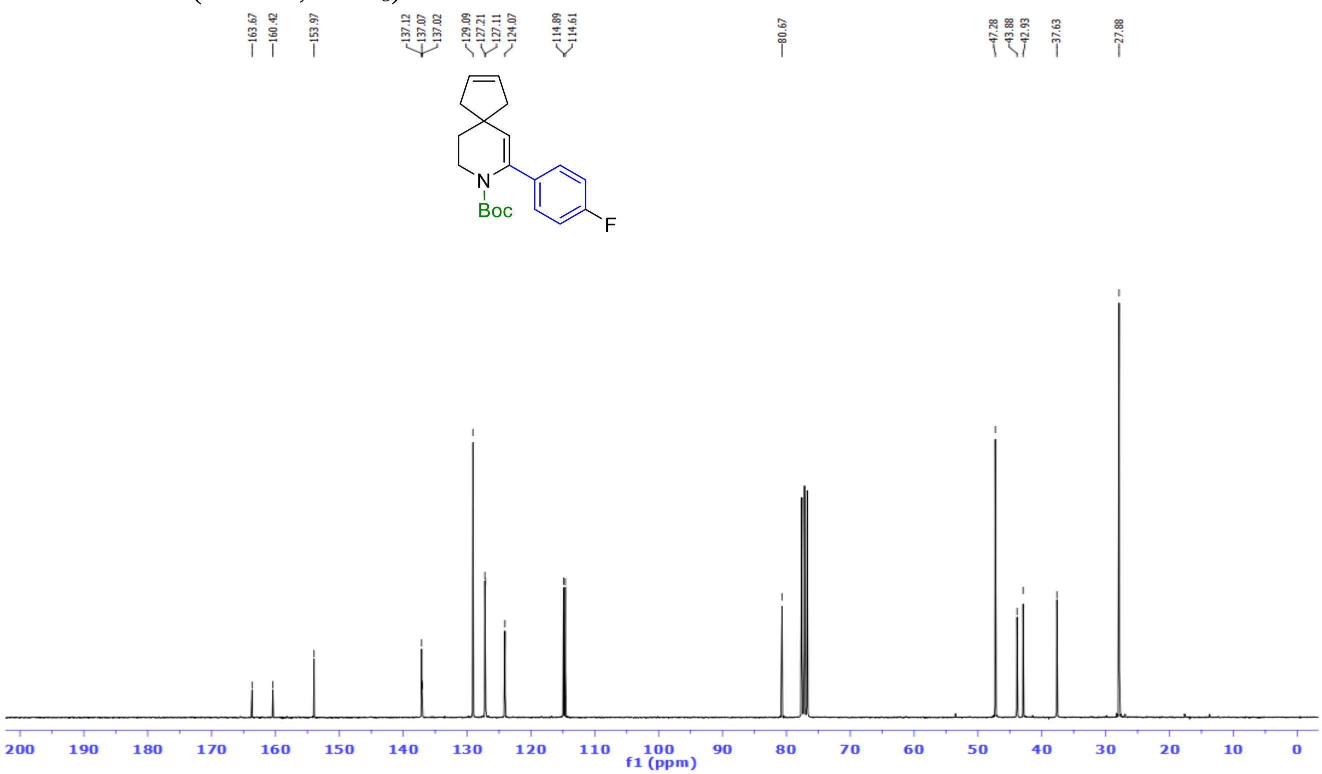
[13]C NMR of **5d** (75 MHz, $CDCl_3$)



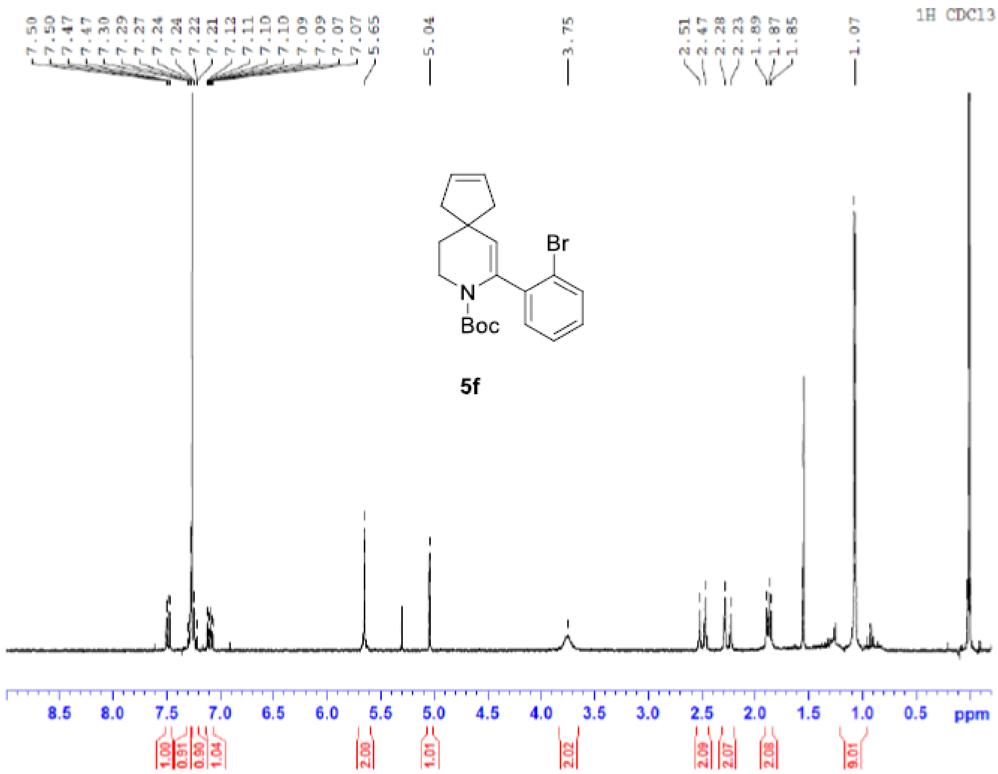
[1]H NMR of **5e** (300 MHz, $CDCl_3$)



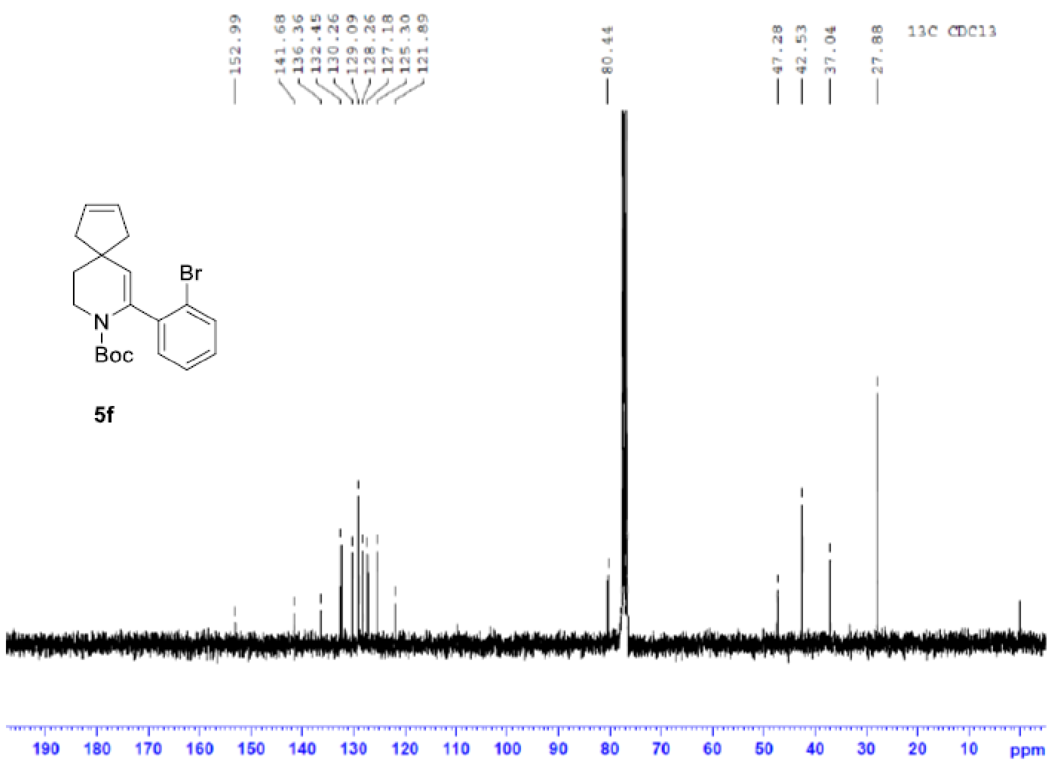
[13]C NMR of **5e** (75 MHz, $CDCl_3$)



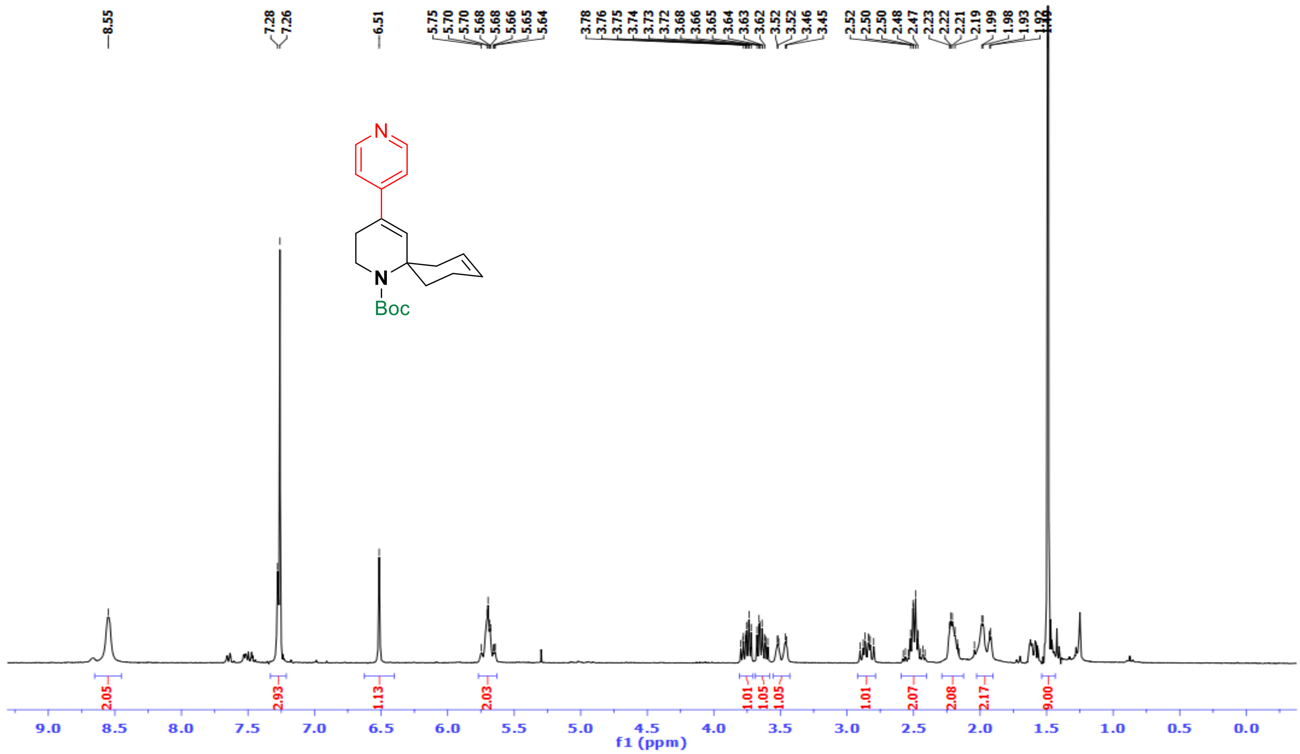
^{1}H NMR of **5f** (300 MHz, $CDCl_3$)



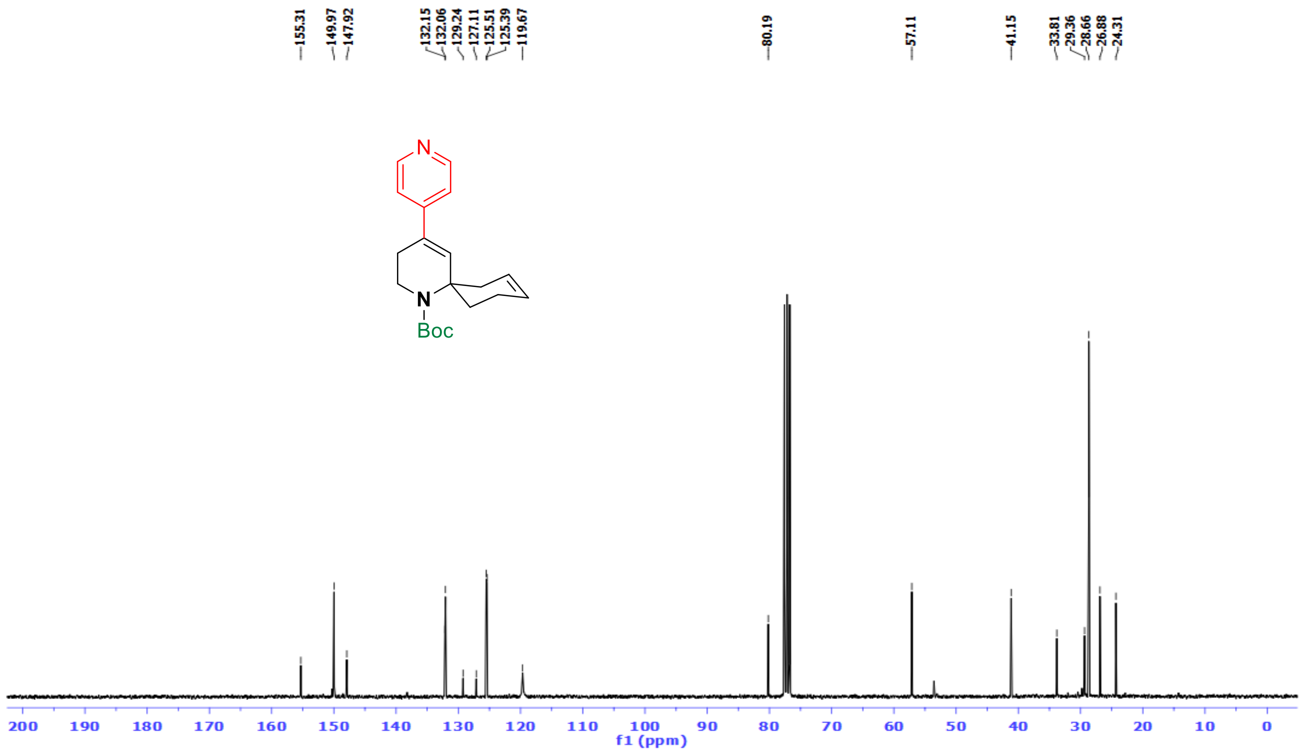
^{13}C NMR of **5f** (75 MHz, $CDCl_3$)



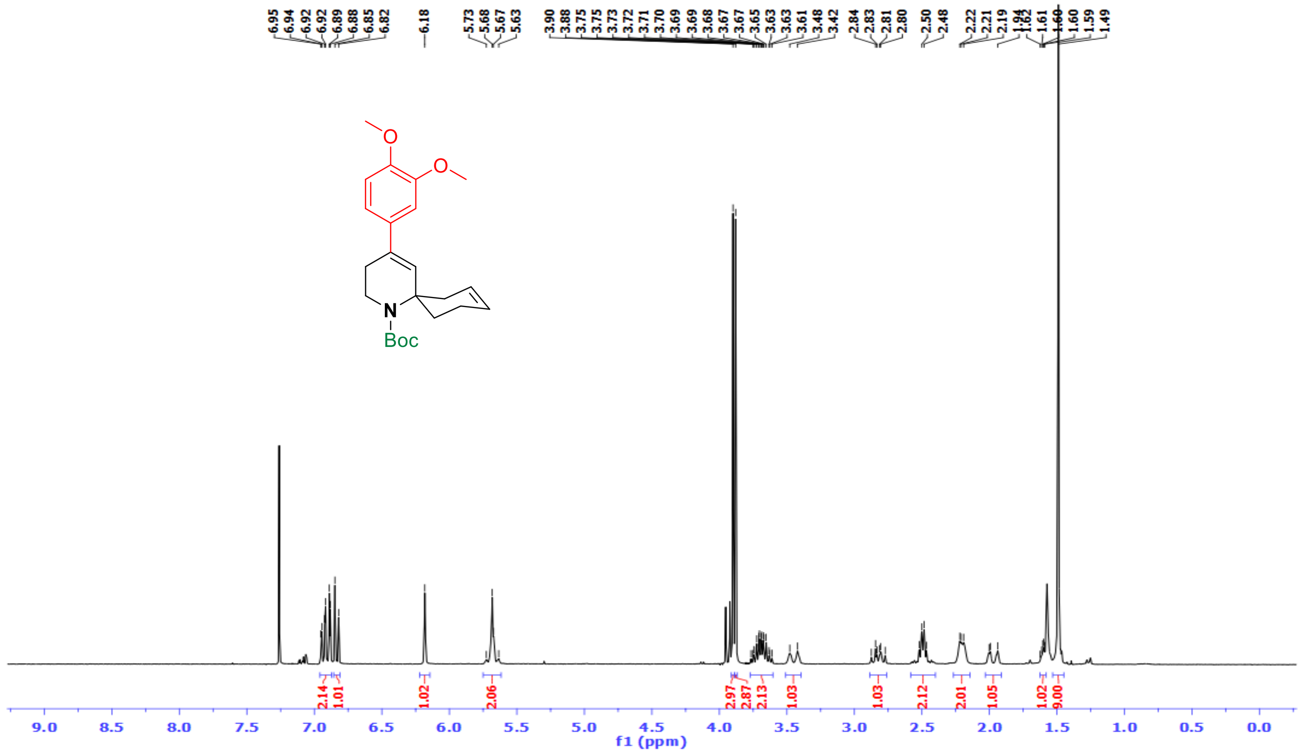
^{1}H NMR of **6a** (300 MHz, $CDCl_3$)



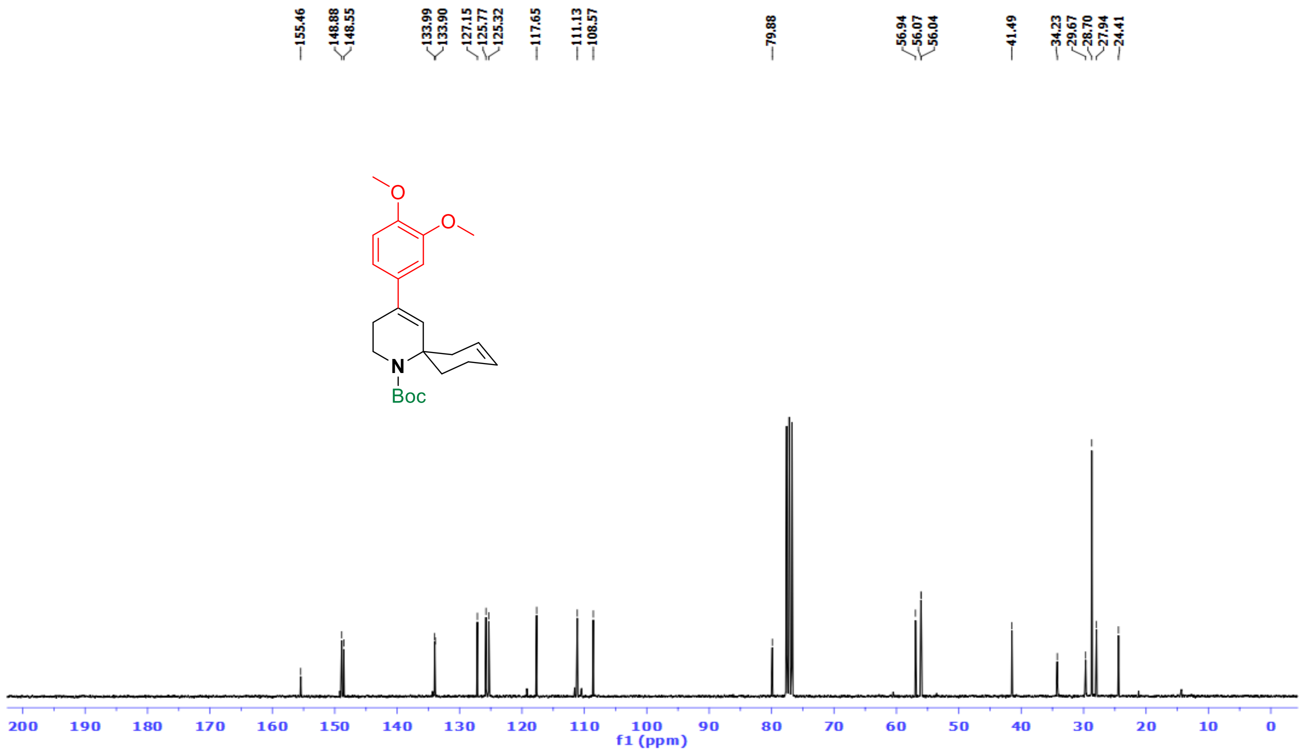
^{13}C NMR of **6a** (75 MHz, $CDCl_3$)



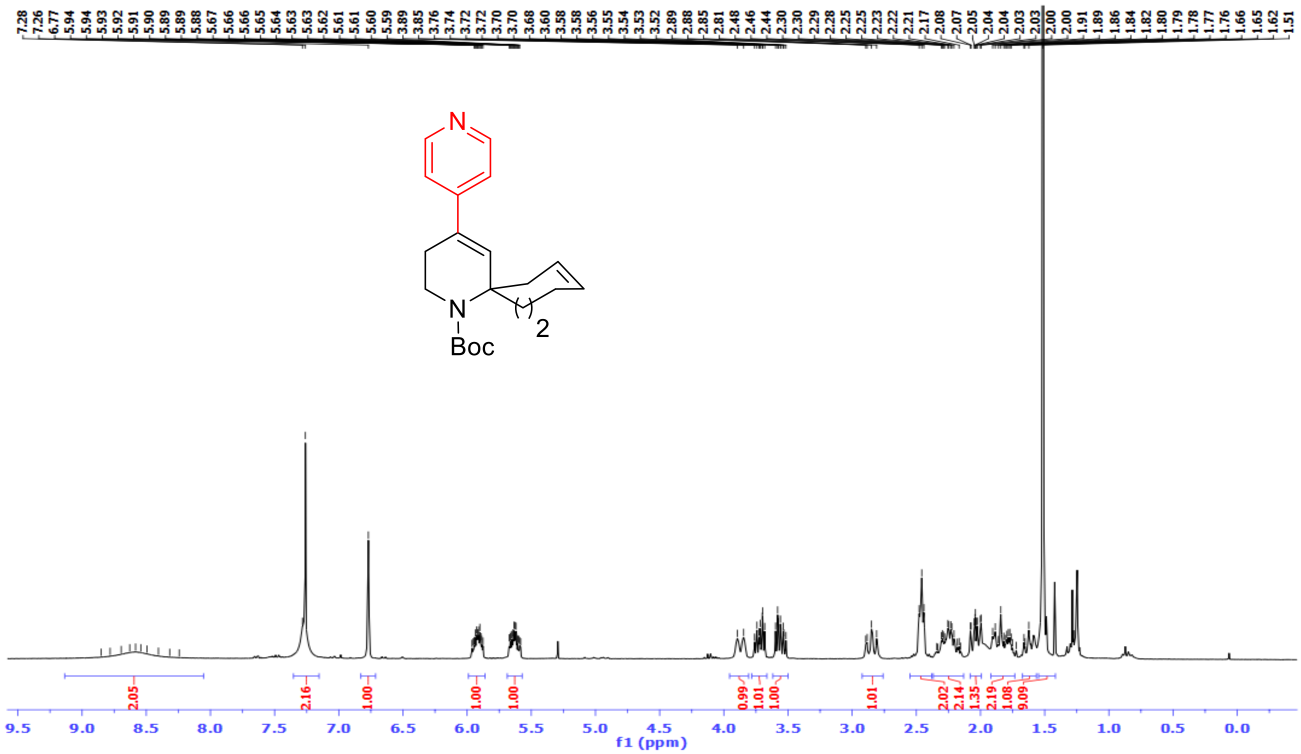
^{1}H NMR of **6b** (300 MHz, $CDCl_3$)



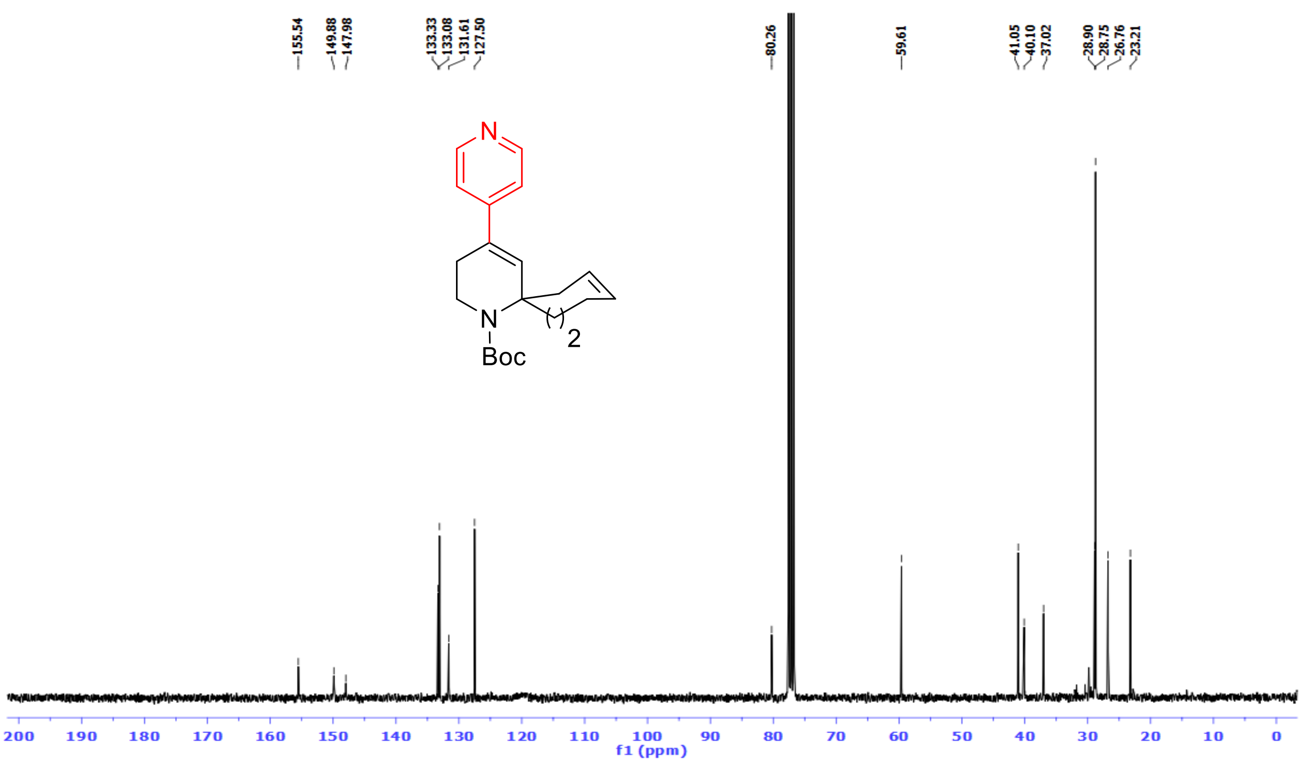
^{13}C NMR of **6b** (75 MHz, $CDCl_3$)



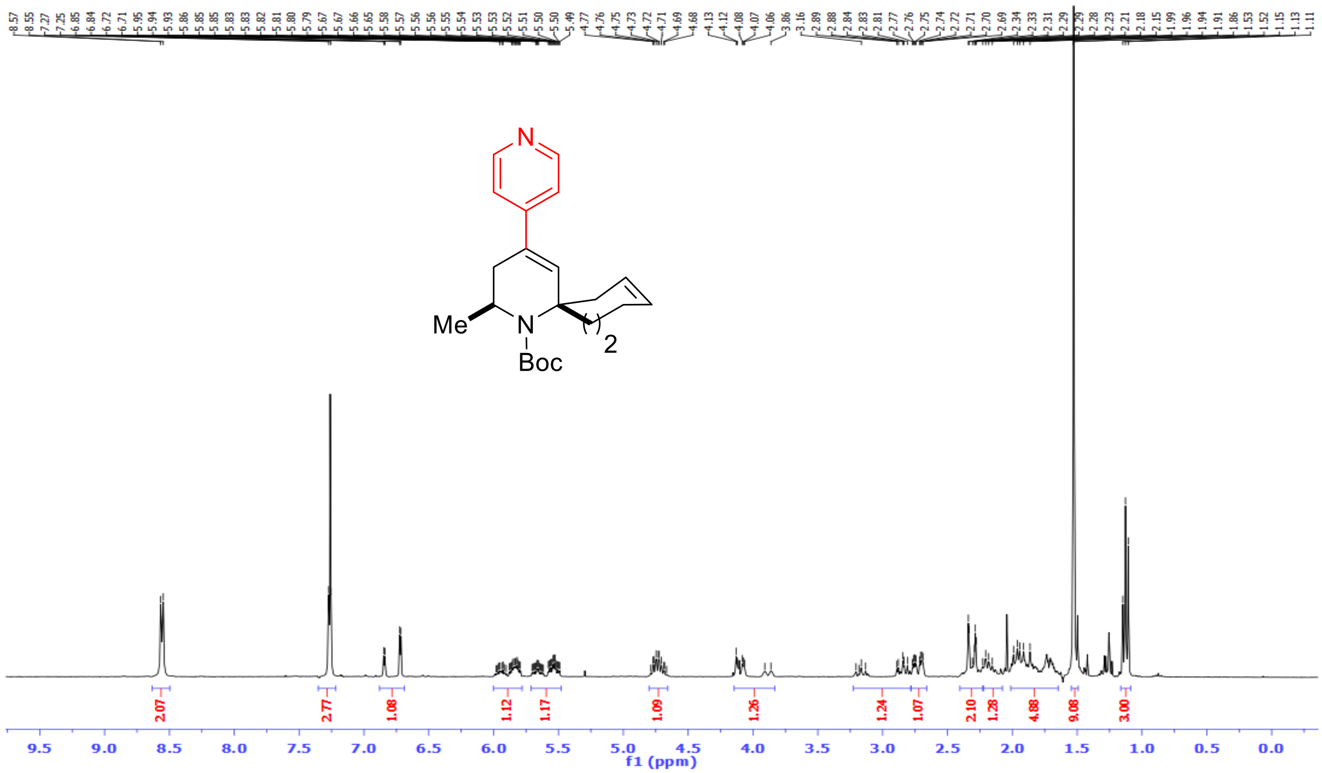
[1]H NMR of **6c** (300 MHz, $CDCl_3$)



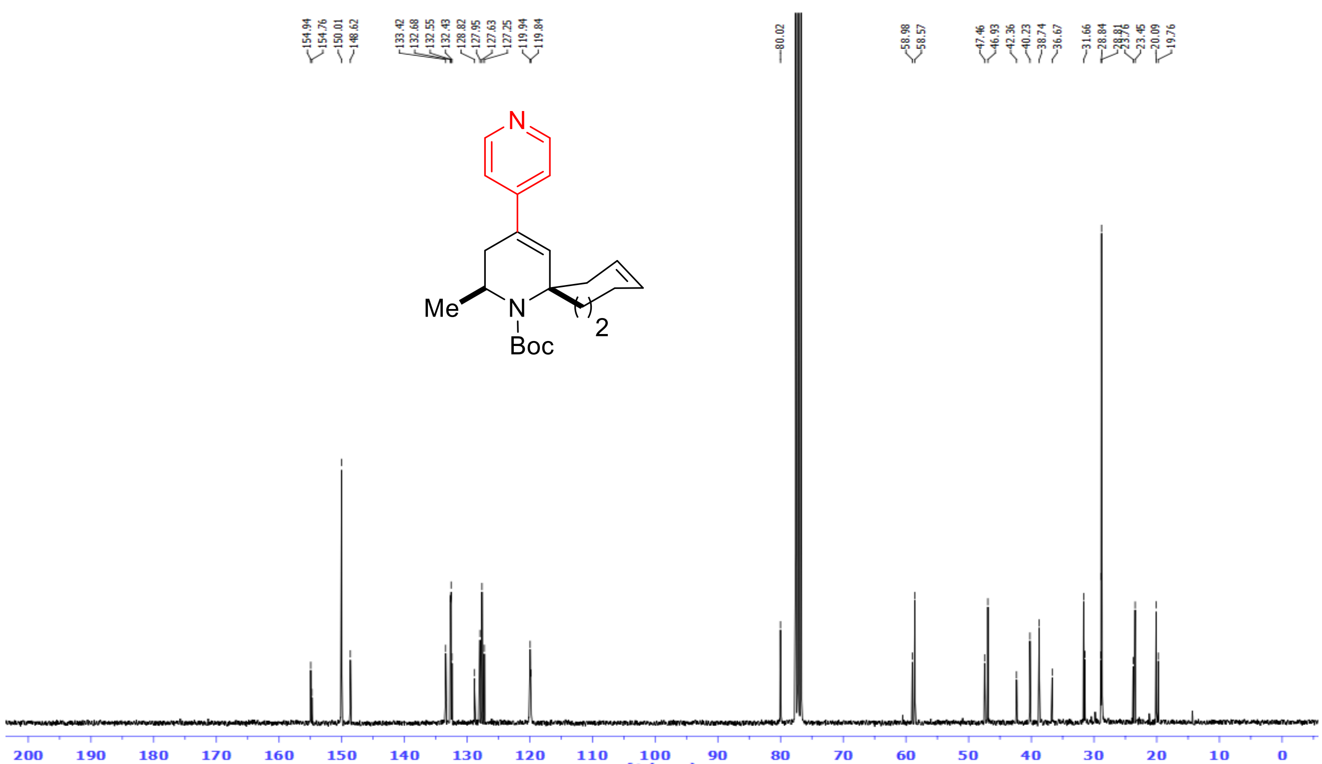
[13]C NMR of **6c** (75 MHz, $CDCl_3$)



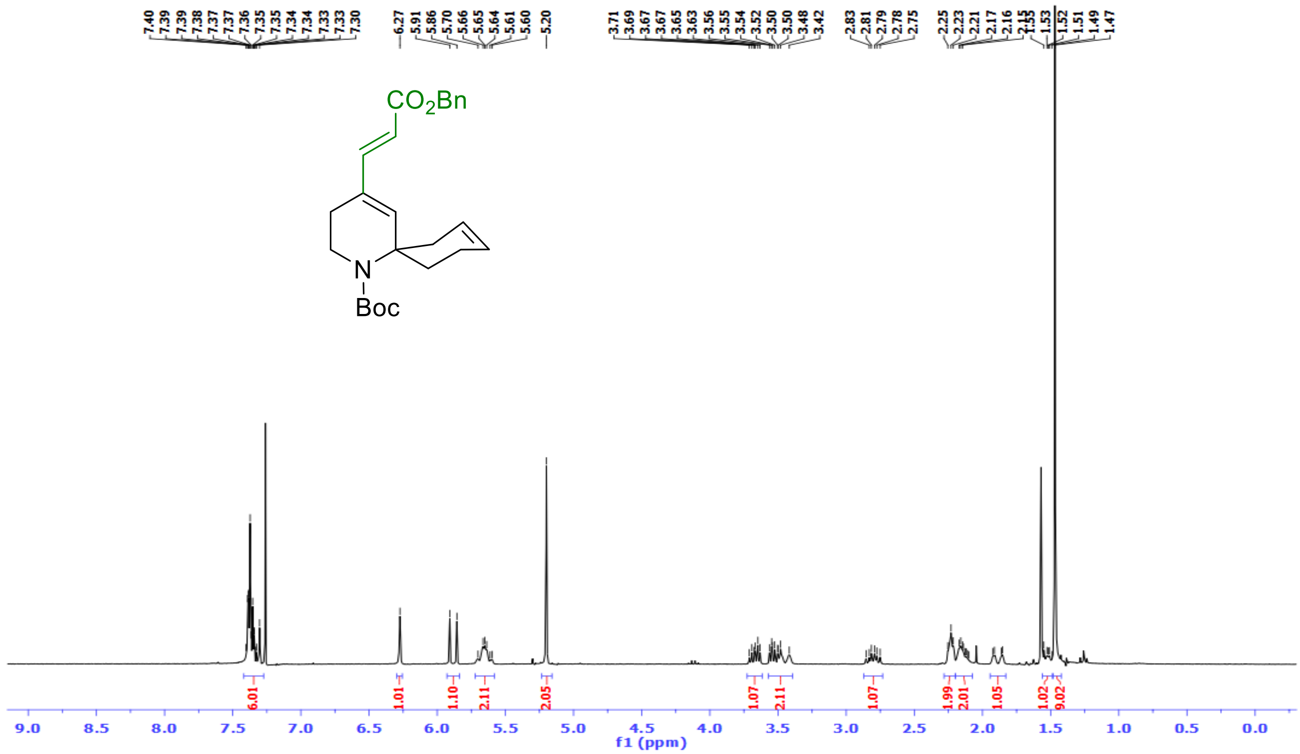
^{1}H NMR of **6d** (300 MHz, $CDCl_3$)



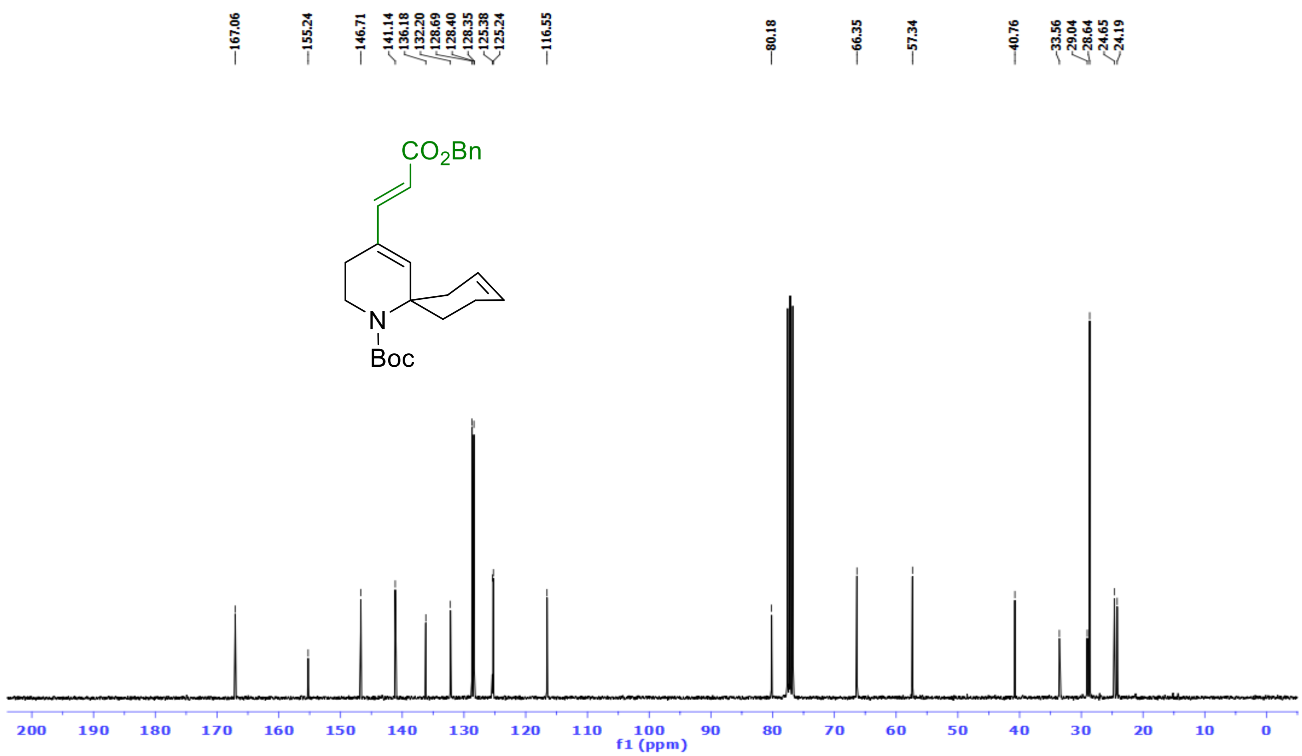
^{13}C NMR of **6d** (75 MHz, $CDCl_3$)



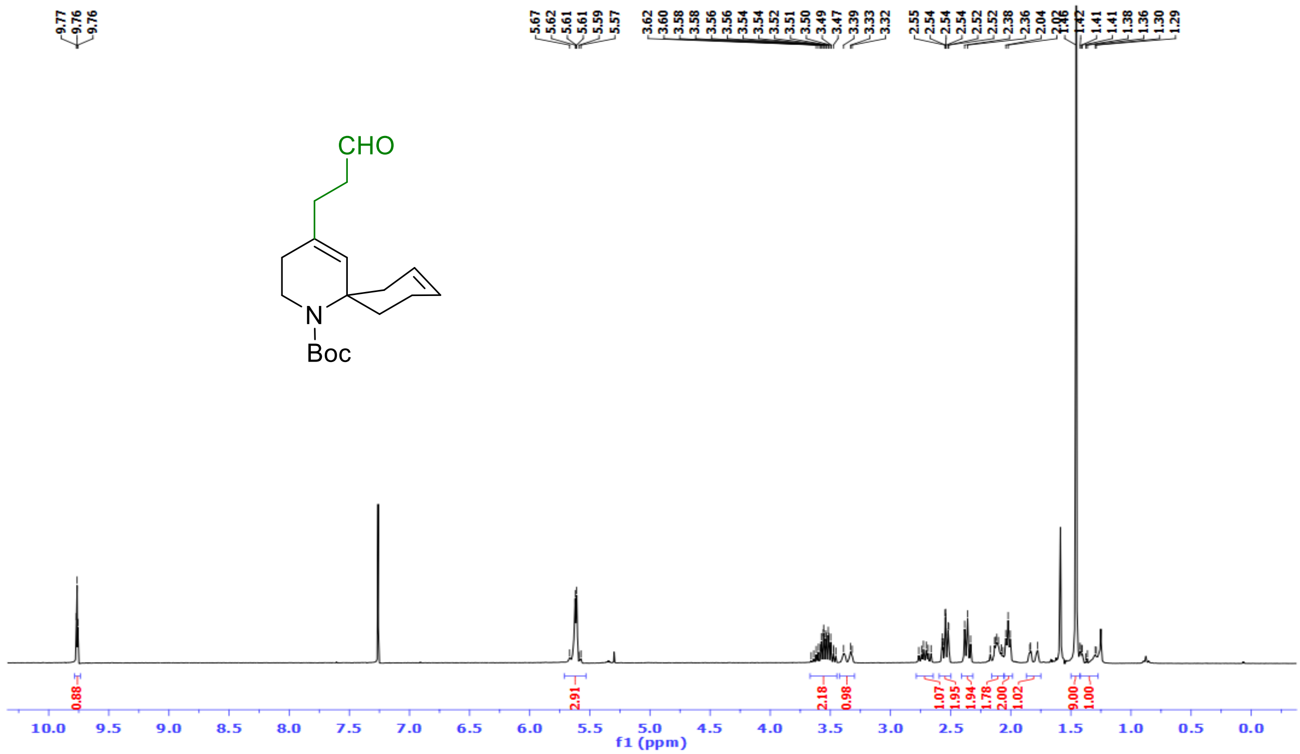
^{1}H NMR of **7a** (300 MHz, $CDCl_3$)



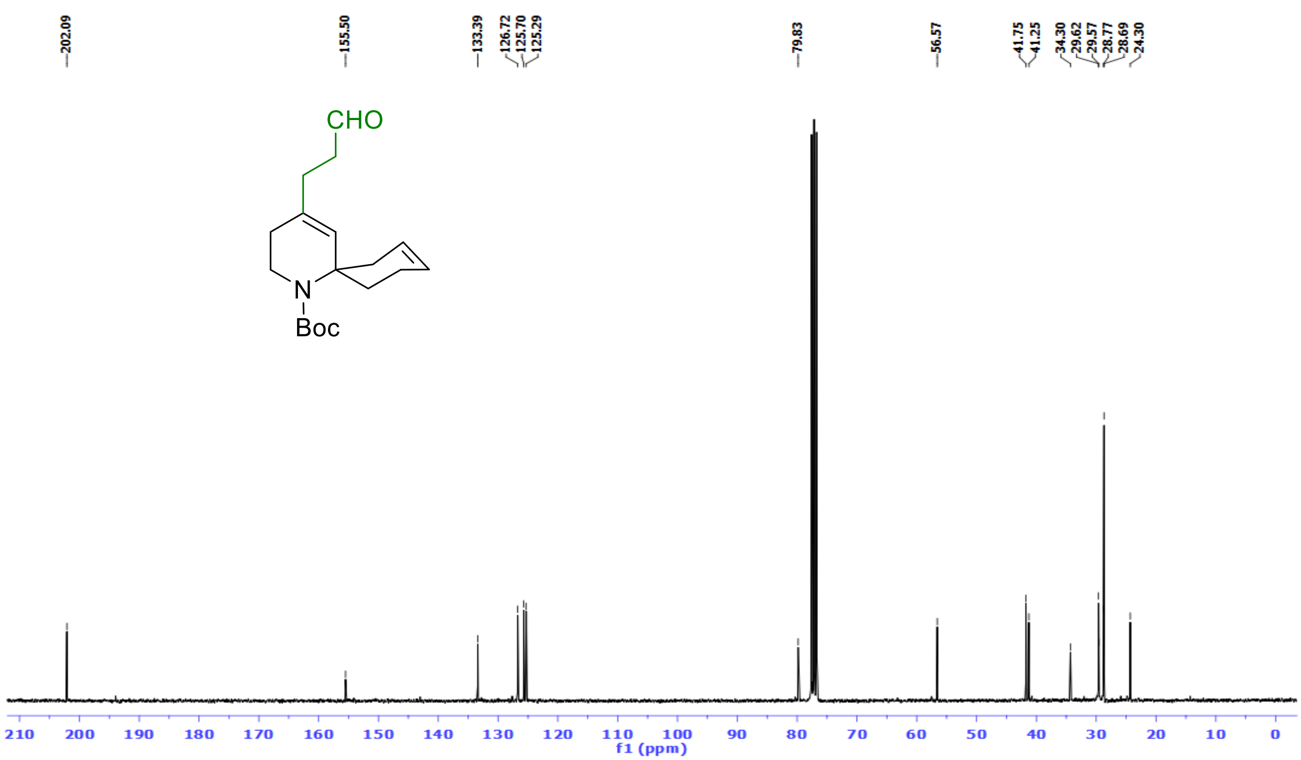
^{13}C NMR of **7a** (75 MHz, $CDCl_3$)



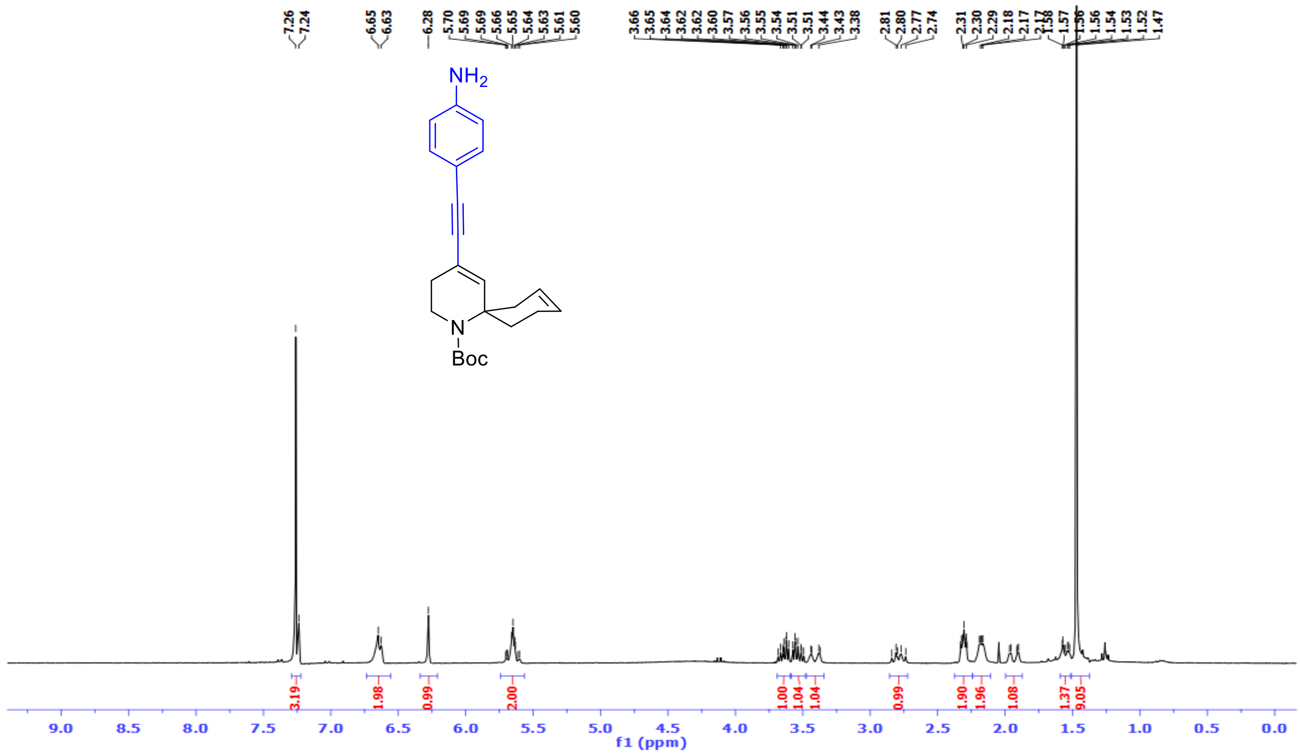
^{1}H NMR of **7b** (300 MHz, $CDCl_3$)



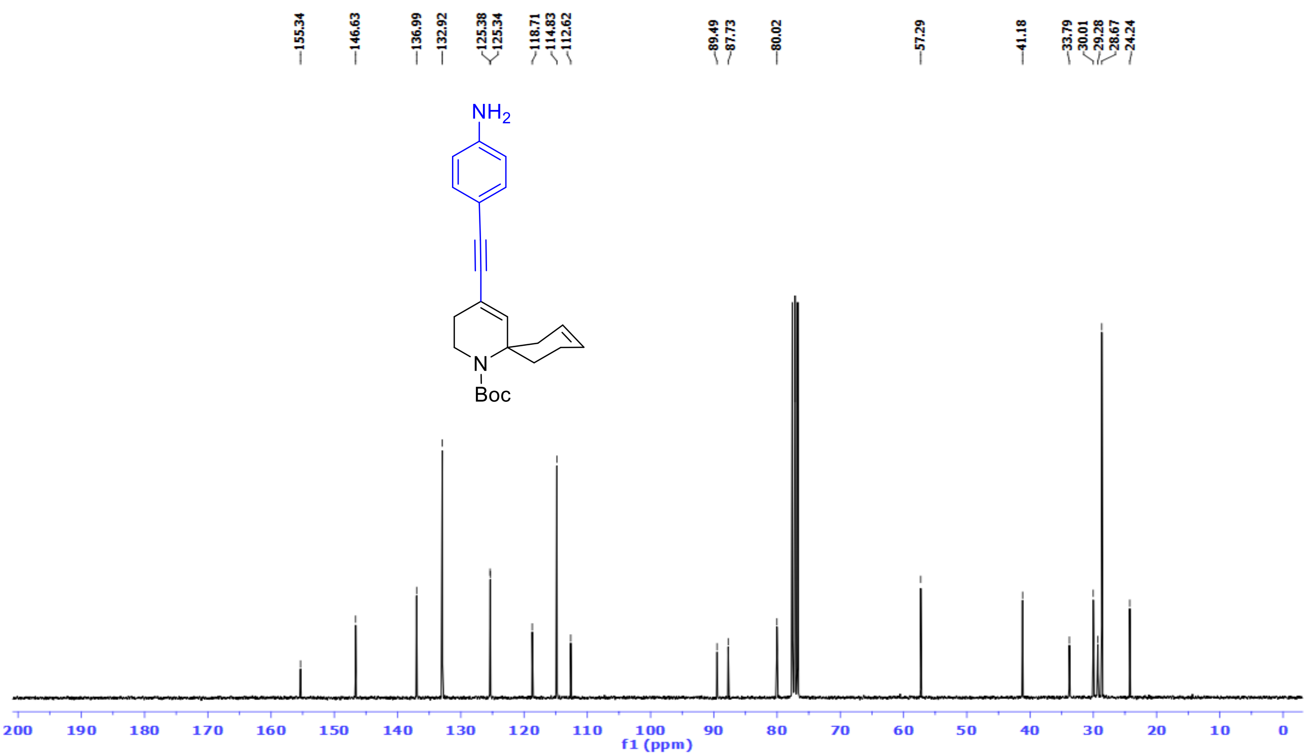
^{13}C NMR of **7b** (75 MHz, $CDCl_3$)



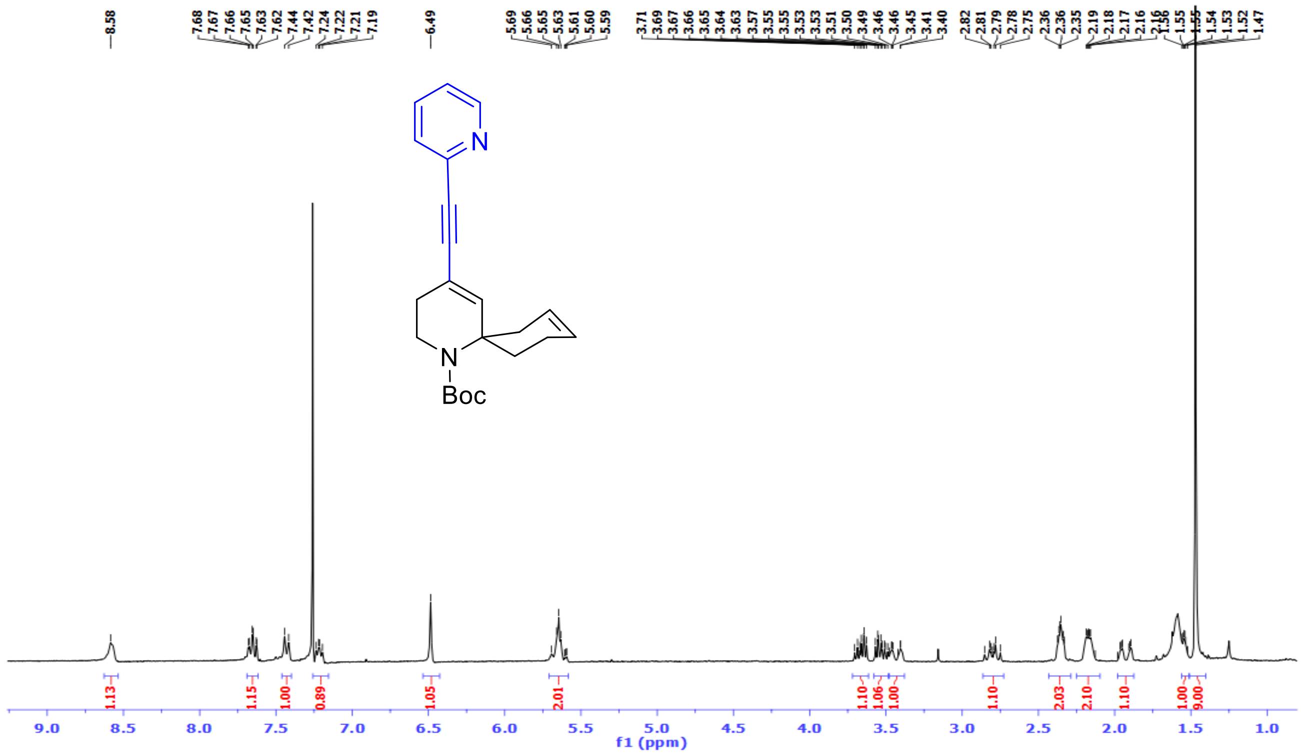
^{1}H NMR of **8a** (300 MHz, $CDCl_3$)



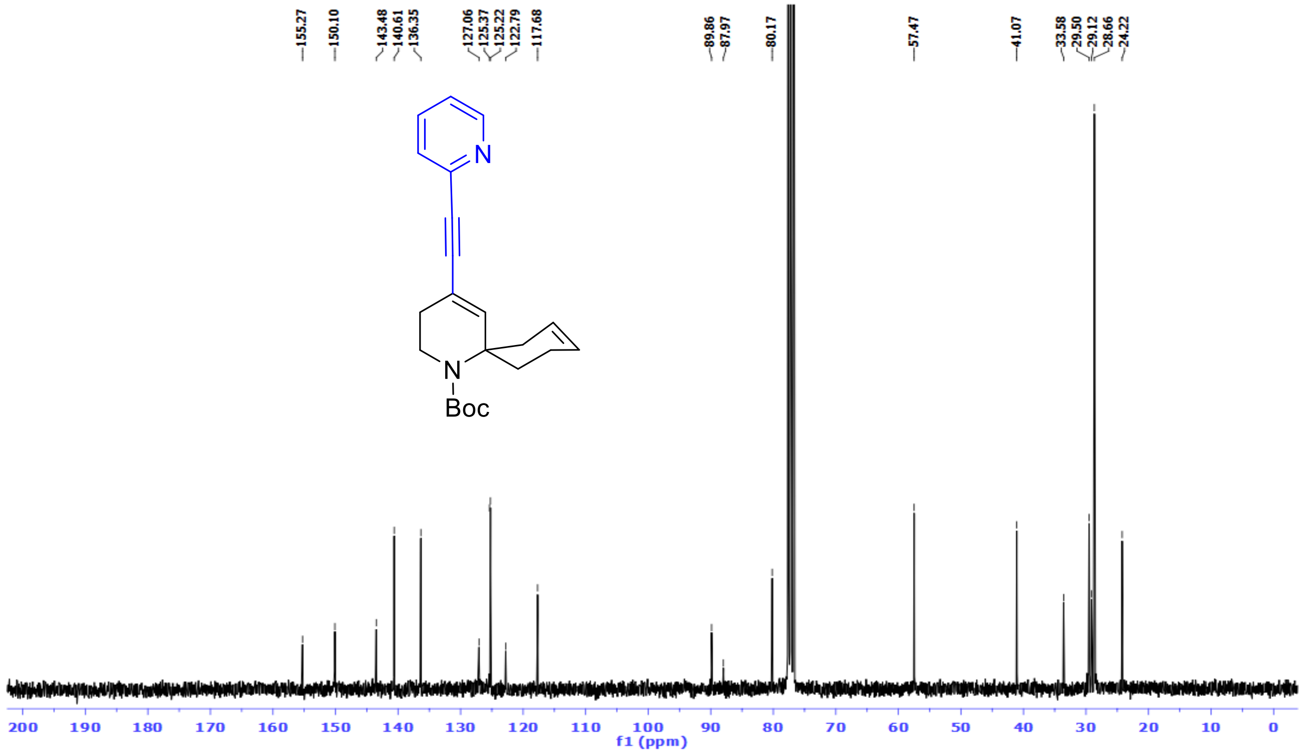
^{13}C NMR of **8a** (75 MHz, $CDCl_3$)



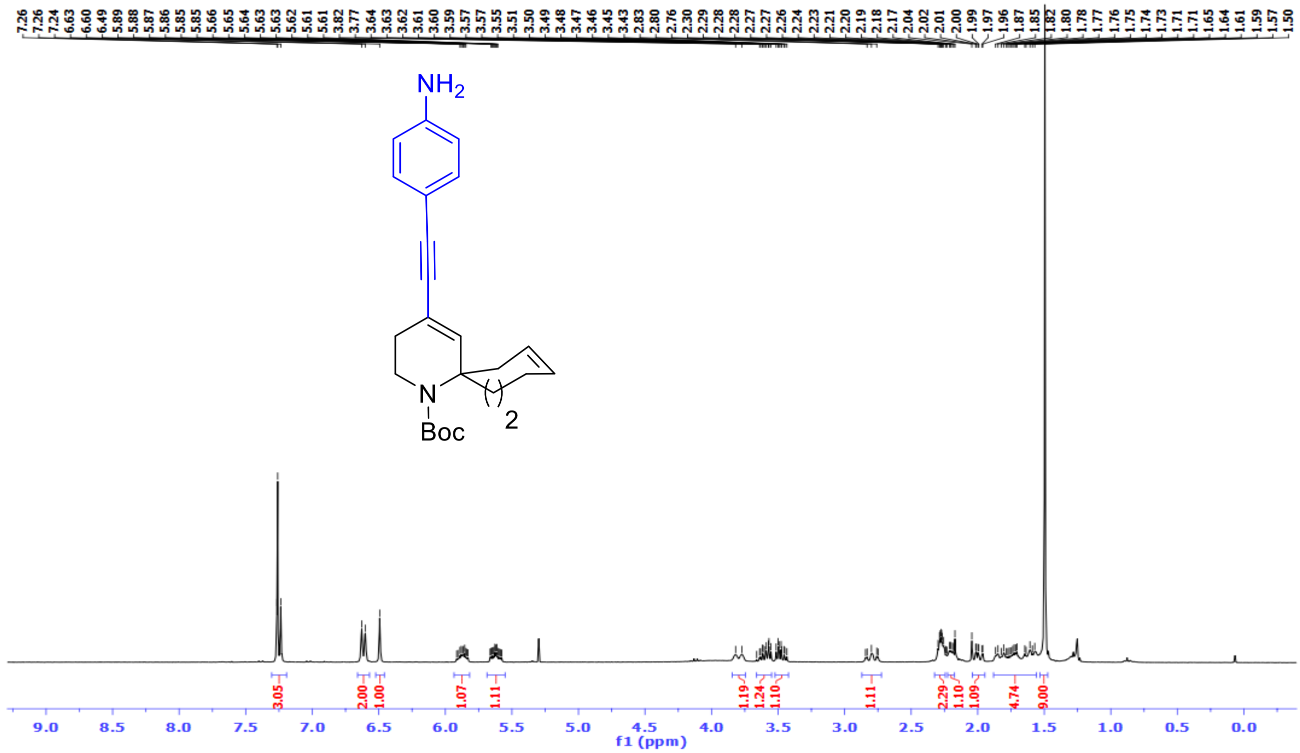
[1]H NMR of **8b** (300 MHz, $CDCl_3$)



[13]C NMR of **8b** (75 MHz, $CDCl_3$)



^{1}H NMR of **8c** (300 MHz, $CDCl_3$)



^{13}C NMR of **8c** (75 MHz, $CDCl_3$)