Supporting information

Rhodium (III) catalyzed olefination and deuteration of tetrahydrocarbazole

Wan Peng, Qiaohong Liu, Fucheng Yin, Cunjian Shi, Limei Ji, Lailiang Qu, Cheng Wang, Heng Luo, Lingyi Kong* and Xiaobing Wang*

Jiangsu Key Laboatory of Bioactive Natural Product Research and State Key Laboratory of Natural Medicines, School of Traditional Chinese Pharmacy, China Pharmaceutical University, 24 Tong Jia Xiang, Nanjing 210009, People's Republic of China

**Corresponding Authors*

Tel/Fax: +86-25-83271405;

E-mail: xbwang@cpu.edu.cn (Xiaobing Wang); cpu_lykong@126.com (Lingyi Kong)

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1. General Information

Unless otherwise noted, all materials were gained from commercial sources without further purification. Solvents were available from Sigma-Aldrich, Alfa-Aesar, and Acros and used directly without further purification. Before running reactions all heating plates were allowed to warm to the desired temperature for at least 15 minutes to allow for sufficient equilibration.

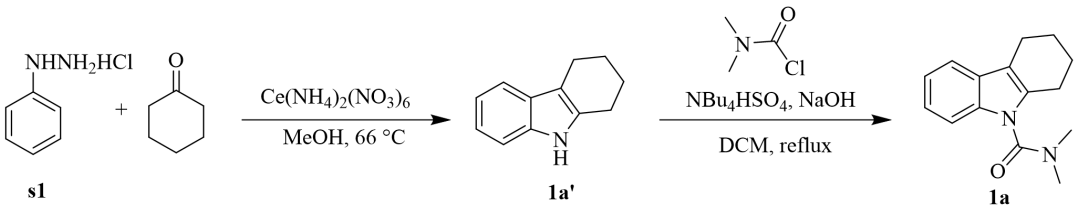
All isolated compounds were characterized by ^{1}H NMR, ^{13}C NMR spectroscopy. Copies of the ^{1}H NMR, ^{13}C NMR could be noted in the supporting information. ^{1}H NMR spectra were recorded either on a Bruker AVANCE AV-500 spectrometer (500 MHz for ^{1}H, 125 MHz for ^{13}C) or Bruker AVANCE AV-500 spectrometer (600 MHz for ^{1}H, 150 MHz for ^{13}C). All ^{1}H NMR experiments were reported in units, parts per million (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm) in the deuterated solvent, unless otherwise stated. All ^{13}C NMR spectra were reported in ppm relative to $CDCl_3$ (77.23 ppm), unless otherwise stated.

High-resolution electrospray ionization (HRESI) mass spectra were carried out using an Agilent 6520B Q-TOF mass spectrometer (Agilent Technologies, Santa Clara, CA, USA).

2. Experimental section

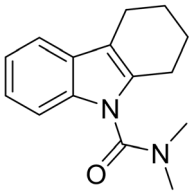
2.1 Preparation and characterization of substrates

2.1.1 Procedure for the preparation of template substrates



s1 **1a'** **1a**

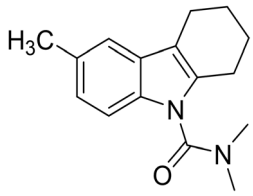
To a solution of **s1** (1.0 g, 6.9 mmol) and cylohexanone (6.9 mmol) in MeOH (40 mL) in a round bottom flask were added $Ce(NH_4)_2(NO_3)_6$ (1.4 mmol). Then the reaction mixture was heated to 66 °C until the reaction completed as judged by TLC. The reaction mixture was quenched with H_2O and extracted with ethyl acetate (three times). The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuum. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (15:1) as eluents to afford the product **1a'**.[1] The product was used in the next step without further purification. A 100 mL flask was charged with **s1** (1.1 g, 6.4 mmol), NBu_4HSO_4 (0.64 mmol) and NaOH (16 mmol). The flask was then fitted with a reflux condenser and flushed with argon. Dry CH_2Cl_2 (20 mL) and dimethylcarbamylchloride (9.6 mmol) were added to the flask and the resulting solution was refluxed overnight. The reaction was quenched with saturated NH_4Cl solution. The organic layer was separated, and the aqueous phase was extracted with CH_2Cl_2. The organics were combined, dried over $MgSO_4$, concentrated and the residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (10:1) as eluents.[2]



***N,N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (1a)**

Faint yellow solid, m.p. 73-74 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.44 (d, J = 7.7 Hz, 1H), 7.23 (d, J = 8.1 Hz, 1H), 7.18 (t, J = 7.5 Hz, 1H), 7.13 (t, J = 7.3 Hz, 1H), 3.04 (s, 6H), 2.79 (s, 2H), 2.68 (t, J = 6.0 Hz, 2H), 1.94-1.84 (m, 4H); **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 154.6, 135.3, 134.9, 128.6, 122.1, 120.7, 118.0, 113.8, 111.3, 77.2, 37.9, 23.0, 22.9, 22.7, 20.8; **HRMS** calcd. for $C_{15}H_{19}N_2O$ $[M+H]^+$: 243.1492, found: 243.1491.

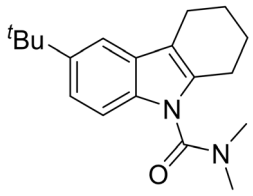
The spectroscopic data are in accordance with those reported.[3]



***N,N*,6-trimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (1b)**

Yellow oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.22 (d, J = 1.6 Hz, 1H), 7.11 (d, J = 8.2 Hz, 1H), 7.00 (dd, J = 8.4, 1.6 Hz, 1H), 3.04 (s, 6H), 2.78 (s, 2H), 2.66-2.64 (m, 2H), 2.44 (s, 3H), 1.93-1.82 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 154.8, 135.6, 133.3, 130.1, 128.9, 123.5, 118.0, 113.6, 111.2, 77.2, 38.0, 23.2, 23.1, 22.8, 21.4, 20.9; **HRMS** calcd. for $C_{14}H_{17}N_2O$ $[M+H]^+$: 257.1648, found: 257.1651.

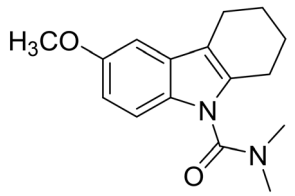
The spectroscopic data are in accordance with those reported.[3]



6-(*tert*-butyl)-*N,N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (1c)

White solid, m.p. 106-108 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.41 (d, J = 1.9 Hz, 1H), 7.25 (dd, J = 8.6, 1.9 Hz, 1H), 7.16 (d, J = 8.6 Hz, 1H), 3.05 (s, 6H), 2.79 (t, J = 5.6

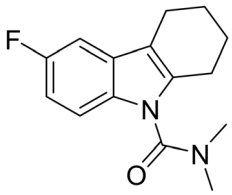
Hz, 2H), 2.69 (td, J = 5.8, 2.0 Hz, 2H), 2.08-1.70 (m, 4H), 1.38 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 154.8, 143.8, 135.5, 133.1, 128.4, 120.1, 114.0, 113.9, 111.0, 77.2, 37.9, 34.5, 31.8, 23.1, 23.1, 22.8, 20.9; **HRMS** calcd. for $C_{19}H_{27}N_2O$ $[M+H]^+$: 299.2118, found: 299.2120.



6-methoxy-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (1d)

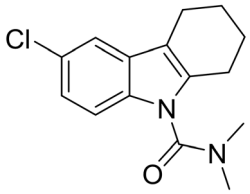
Yellow oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.18 (d, J = 8.8 Hz, 1H), 6.94 (s, 1H), 6.86 (d, J = 8.6 Hz, 1H), 3.90 (s, 3H), 3.09 (s, 6H), 2.84 (s, 2H), 2.69 (s, 2H), 2.03-1.84 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 154.8, 154.7, 136.2, 129.9, 129.2, 113.7, 112.0, 111.0, 100.7, 77.2, 55.7, 37.9, 23.1, 23.0, 22.7, 20.9; **HRMS** calcd. for $C_{16}H_{21}N_2O_2$ $[M+H]^+$: 273.1595, found: 273.1594.

The spectroscopic data are in accordance with those reported.[3]



6-fluoro-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (1e)

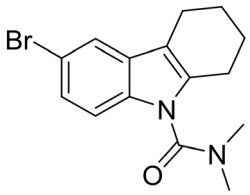
Faint yellow oil; **^{1}H NMR** (600 MHz, $CDCl_3$ δ 7.14 (dd, J = 8.8, 4.3 Hz, 1H), 7.07 (dd, J = 9.1, 2.5 Hz, 1H), 6.90 (td, J = 9.0, 2.6 Hz, 1H), 3.04 (s, 6H), 2.78 (s, 2H), 2.63 (tt, J = 5.9, 1.8 Hz, 2H), 1.98-1.82 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 158.8 (d, J = 235.5 Hz), 154.8, 137.6, 131.8, 129.7 (d, J = 9.0 Hz), 114.2 (d, J = 4.5 Hz), 112.3 (d, J = 10.5 Hz), 110.2 (d, J = 25.5 Hz), 103.9 (d, J = 24.0 Hz), 77.2, 38.3, 23.5, 23.3, 23.0, 21.2; **HRMS** calcd. for $C_{15}H_{18}FN_2O$ $[M+H]^+$: 261.1398, found: 261.1399.



6-chloro-*N,N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (1f)

Faint yellow oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 (s, 1H), 7.13 (s, 2H), 3.03 (s, 6H), 2.78 (t, J = 5.5 Hz, 2H), 2.64 (td, J = 5.9, 1.8 Hz, 2H), 1.98-1.80 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 154.1, 136.8, 133.3, 129.7, 126.3, 122.1, 117.7, 113.3, 112.2, 77.2, 37.8, 22.9, 22.9, 22.5, 20.6; **HRMS** calcd. for $C_{15}H_{18}ClN_2O$ $[M+H]^+$: 277.1102, found: 277.1102.

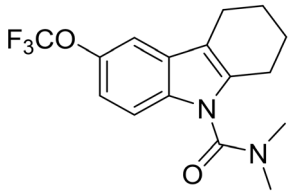
The spectroscopic data are in accordance with those reported.[3]



6-bromo-*N,N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (1g)

Faint yellow oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 (d, J = 1.9 Hz, 1H), 7.25 (dd, J = 8.8, 2.5 Hz, 1H), 7.09 (d, J = 8.6 Hz, 1H), 3.02 (s, 6H), 2.77 (s, 2H), 2.63 (t, J = 5.6 Hz, 2H), 1.91-1.83 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 154.0, 136.6, 133.5, 130.2, 124.7, 120.7, 113.9, 113.2, 112.6, 77.2, 37.8, 22.8, 22.8, 22.5, 20.6; **HRMS** calcd. for $C_{15}H_{18}BrN_2O$ $[M+H]^+$: 321.0597, found: 321.0597.

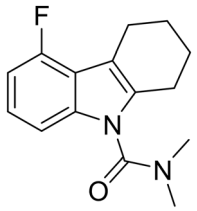
The spectroscopic data are in accordance with those reported.[3]



***N,N*-dimethyl-6-(trifluoromethoxy)-1,2,3,4-tetrahydro-9*H*-carbazole-9-carbo xamide (1h)**

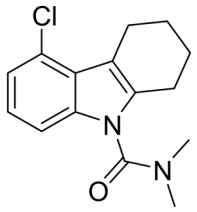
Faint yellow solid, m.p. 73-74 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.27 (d, J = 2.2 Hz, 1H), 7.20 (d, J = 8.7 Hz, 1H), 7.04 (dd, J = 8.8, 2.3 Hz, 1H), 3.04 (s, 6H), 2.78 (s, 2H),

2.71-2.58 (m, 2H), 1.97-1.82 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 154.6, 144.2, 137.8, 133.7, 129.5, 122.2, 116.1, 114.4, 112.2, 111.1, 77.2, 38.3, 23.4, 23.4, 23.0, 21.2; **HRMS** calcd. for $C_{16}H_{18}F_3N_2O_2$ $[M+H]^+$: 327.1315, found: 327.1316.



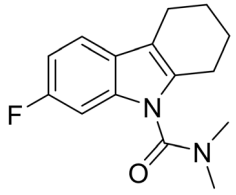
5-fluoro-*N,N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (1i)

Faint yellow oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.33 (dd, J = 8.5, 5.4 Hz, 1H), 6.95 (dd, J = 9.9, 2.3 Hz, 1H), 6.89 (td, J = 9.0, 2.3 Hz, 1H), 3.05 (s, 6H), 2.76 (s, 2H), 2.65 (td, J = 5.9, 2.0 Hz, 2H), 1.91-1.84 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 160.0 (d, J = 236.2 Hz), 154.2, 135.5 (d, J = 5.0 Hz), 135.0 (d, J = 12.5 Hz), 125.0, 118.4 (d, J = 10.0 Hz), 113.6, 108.8 (d, J = 23.8 Hz), 98.5 (d, J = 26.2 Hz), 77.2, 37.8, 22.9, 22.6, 20.7; **HRMS** calcd. for $C_{15}H_{18}FN_2O$ $[M+H]^+$: 261.1398, found: 261.1400.



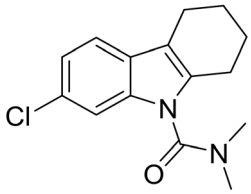
5-chloro-*N,N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (1j)

Faint yellow oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.33 (d, J = 8.3 Hz, 1H), 7.22 (d, J = 1.8 Hz, 1H), 7.10 (dd, J = 8.3, 1.8 Hz, 1H), 3.04 (s, 6H), 2.76 (s, 2H), 2.65 (tt, J = 5.8, 1.8 Hz, 2H), 1.95-1.79 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 154.0, 136.0, 135.3, 128.0, 127.1, 121.2, 118.8, 113.7, 111.4, 77.2, 37.9, 22.9, 22.9, 22.5, 20.7; **HRMS** calcd. for $C_{15}H_{18}ClN_2O$ $[M+H]^+$: 277.1102, found: 277.1102.



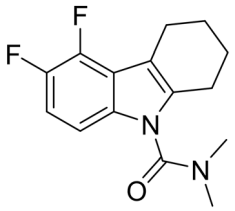
7-fluoro-*N,N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (1k)

Faint yellow solid; m.p. 101-102 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.06 (td, J = 8.0, 5.1 Hz, 1H), 6.99 (d, J = 8.2 Hz, 1H), 6.77 (ddd, J = 10.4, 7.9, 0.8 Hz, 1H), 3.03 (s, 6H), 2.87 (t, J = 5.5 Hz, 2H), 2.76 (s, 2H), 1.96-1.80 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 156.6 (d, J = 244.5 Hz), 154.1, 137.3 (d, J = 12.0 Hz), 134.9, 122.5 (d, J = 7.5 Hz), 117.0 (d, J = 19.5 Hz), 111.8, 107.3, 106.2 (d, J = 19.5 Hz), 77.2, 37.8, 22.8, 22.8, 22.6, 22.3; **HRMS** calcd. for $C_{15}H_{18}FN_2O$ $[M+H]^+$: 261.1398, found: 261.1397.



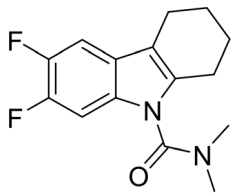
7-chloro-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (1l)

Faint yellow solid; m.p. 90-91 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.10 (d, J = 7.1 Hz, 1H), 7.06-7.03 (m, 2H), 3.11-2.95 (m, 8H), 2.75 (s, 2H), 1.93-1.81 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 153.8, 136.0, 135.9, 126.0, 125.6, 122.5, 121.3, 113.4, 109.6, 77.2, 37.7, 22.9, 22.9, 22.4; **HRMS** calcd. for $C_{15}H_{18}ClN_2O$ $[M+H]^+$: 277.1102, found: 277.1101.



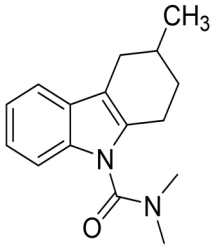
5,6-difluoro-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (1m)

White solid, m.p. 78-79 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.95 (ddd, J = 10.7, 8.9, 7.4 Hz, 1H), 6.88 (dd, J = 8.8, 3.3 Hz, 1H), 3.03 (s, 6H), 2.89-2.84 (m, 2H), 2.75 (s, 2H), 1.88-1.85 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 153.8, 145.0 (dd, J = 227.5, 3.8 Hz), 143.4 (dd, J = 243.8, 12.5 Hz), 136.6, 132.7, 118.4 (d, J = 16.2 Hz), 112.2, 111.0 (d, J = 21.2 Hz), 106.4, 77.2, 37.7, 22.9, 22.6, 22.4, 22.1; **HRMS** calcd. for $C_{15}H_{17}F_2N_2O$ $[M+H]^+$: 279.1303, found: 279.1301.



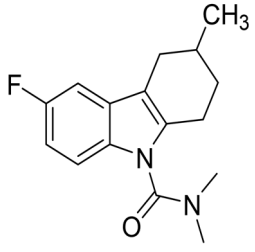
6,7-difluoro-*N,N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (1n)

Yellow solid, m.p. 71-72 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.15 (dd, J = 10.4, 7.7 Hz, 1H), 7.05 (dd, J = 10.8, 6.6 Hz, 1H), 3.03 (s, 6H), 2.75 (d, J = 7.3 Hz, 2H), 2.68-2.55 (m, 2H), 1.89-1.85 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 154.1, 147.7 (dd, J = 240.0, 15.0 Hz), 146.8 (dd, J = 238.5, 15.0 Hz), 136.7, 130.0 (d, J = 9.0 Hz), 124.0 (d, J = 7.5 Hz), 113.6, 105.0 (d, J = 18.0 Hz), 100.1 (d, J = 24.0 Hz), 77.2, 37.9, 23.0, 22.8, 22.5, 20.7; **HRMS** calcd. $C_{15}H_{17}F_2N_2O$ $[M+H]^+$: 279.1303, found: 279.1304.



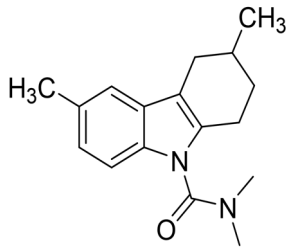
***N,N*,3-trimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (1o)**

Yellow solid, m.p. 60-61 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.43 (d, J = 7.5 Hz, 1H), 7.23 (d, J = 8.1 Hz, 1H), 7.20-7.16 (m, 1H), 7.14 (td, J = 7.4, 1.2 Hz, 1H), 3.06 (s, 3H), 3.03 (s, 3H), 2.83 (d, J = 5.3 Hz, 2H), 2.82-2.79 (m, 1H), 2.28-2.23 (m, 1H), 2.02-1.90 (m, 2H), 1.58-1.51 (m, 1H), 1.14 (d, J = 6.5 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 154.6, 135.2, 135.1, 128.5, 122.1, 120.7, 118.0, 113.7, 111.4, 77.2, 38.0, 37.7, 31.3, 29.2, 29.0, 22.6, 21.6; **HRMS** calcd. for $C_{16}H_{21}N_2O$ $[M+H]^+$: 257.1648, found: 257.1647.



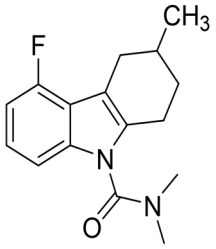
6-fluoro-*N*,*N*,3-trimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (1p)

Faint yellow solid, m.p. 80-81 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.14 (dd, J = 8.8, 4.3 Hz, 1H), 7.06 (dd, J = 9.1, 2.5 Hz, 1H), 6.90 (td, J = 9.0, 2.6 Hz, 1H), 3.04 (s, 3H), 3.02 (s, 3H), 2.81 (s, 2H), 2.79-2.71 (m, 1H), 2.23-2.18 (m, 1H), 2.01-1.86 (m, 2H), 1.56-1.49 (m, 1H), 1.13 (d, J = 6.5 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 158.5 (d, J = 235.5 Hz), 154.5, 137.0, 131.7, 129.2 (d, J = 10.5 Hz), 113.8, 112.0 (d, J = 9.0 Hz), 109.9 (d, J = 25.5 Hz), 103.6 (d, J = 24.0 Hz), 77.2, 38.1, 37.8, 31.2, 29.2, 29.1, 22.8, 21.6; **HRMS** calcd. for $C_{16}H_{20}FN_2O$ $[M+H]^+$: 275.1554, found: 275.1555.



***N*,*N*,3,6-tetramethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (1q)**

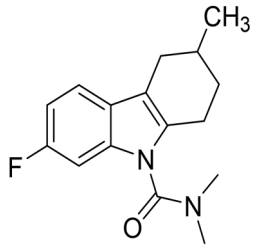
Faint yellow oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.22-7.20 (m, 1H), 7.10 (d, J = 8.3 Hz, 1H), 7.02-6.98 (m, 1H), 3.04 (s, 3H), 3.02 (s, 3H), 2.84-2.79 (m, 2H), 2.81-2.76 (m, 1H), 2.43 (s, 3H), 2.24-2.19 (m, 1H), 2.00-1.91 (m, 2H), 1.55-1.49 (m, 1H), 1.13 (d, J = 6.5 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 155.2, 135.7, 133.9, 130.5, 129.1, 123.8, 118.4, 113.9, 111.5, 77.2, 38.6, 38.1, 31.7, 29.7, 29.5, 23.1, 22.0, 21.7; **HRMS** calcd. for $C_{17}H_{23}N_2O$ $[M+H]^+$: 271.1805, found: 271.1806.



5-fluoro-*N*,*N*,3-trimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (1r)

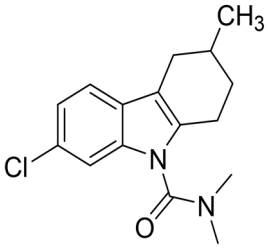
Faint yellow solid, m.p. 70-71 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31 (dd, J = 8.5, 5.4 Hz, 1H), 6.95 (dd, J = 9.9, 2.3 Hz, 1H), 6.89 (ddd, J = 9.5, 8.6, 2.3 Hz, 1H), 3.05 (s, 3H), 3.03 (s, 3H), 2.79 (d, J = 5.3 Hz, 2H), 2.76 (d, J = 5.1 Hz, 1H), 2.33-2.16 (m,

1H), 2.03-1.88 (m, 2H), 1.57-1.47 (m, 1H), 1.13 (d, J = 6.5 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 160.0 (d, J = 237.5 Hz), 154.2, 135.3, 135.2, 124.8, 118.4 (d, J = 10.0 Hz), 113.5, 108.8 (d, J = 23.8 Hz), 98.5 (d, J = 27.5 Hz), 77.2, 37.9, 37.6, 31.1, 29.1, 28.9, 22.5, 21.4; **HRMS** calcd. for $C_{16}H_{20}FN_2O$ $[M+H]^+$: 275.1554, found: 275.1555.



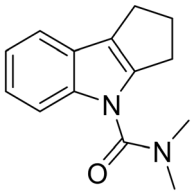
7-fluoro-*N*,*N*,3-trimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (1s)

Faint yellow oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.11 (td, J = 8.0, 5.1 Hz, 1H), 7.03 (d, J = 8.1 Hz, 1H), 6.81 (dd, J = 10.5, 7.8 Hz, 1H), 3.14-3.02 (m, 7H), 2.84 (s, 2H), 2.58-2.38 (m, 1H), 2.10-1.92 (m, 2H), 1.65-1.60 (m, 1H), 1.18 (d, J = 6.5 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 156.6 (d, J = 245.0 Hz), 154.1, 137.5 (d, J = 12.5 Hz), 134.7, 122.4 (d, J = 7.5 Hz), 116.9 (d, J = 20.0 Hz), 111.7, 107.3, 106.2, 77.2, 37.6, 30.8, 30.6, 29.1, 22.4, 21.4; **HRMS** calcd. for $C_{16}H_{20}FN_2O$ $[M+H]^+$: 275.1554, found: 275.1555.



7-chloro-*N*,*N*,3-trimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (1t)

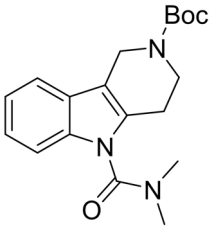
Faint yellow solid, m.p. 89-90 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.10 (dd, J = 7.3, 1.7 Hz, 1H), 7.08-7.02 (m, 2H), 3.38-3.24 (m, 1H), 3.03 (s, 3H), 3.01 (s, 3H), 2.78 (s, 2H), 2.57-2.46 (m, 1H), 1.99-1.86 (m, 2H), 1.55-1.44 (m, 1H), 1.14 (d, J = 6.6 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 153.9, 136.3, 135.8, 126.0, 125.5, 122.5, 121.4, 113.4, 109.7, 77.2, 37.7, 31.3, 30.6, 29.3, 22.6, 21.6; **HRMS** calcd. for $C_{16}H_{20}ClN_2O$ $[M+H]^+$: 291.1259, found: 291.1257.



***N,N*-dimethyl-2,3-dihydrocyclopenta[b]indole-4(1*H*)-carboxamide (1u)**

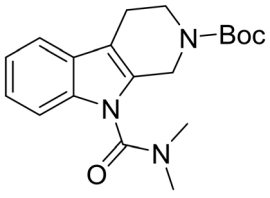
Faint yellow solid, m.p. 96-97 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41 (dd, J = 7.3, 1.6 Hz, 1H), 7.39-7.35 (m, 1H), 7.22 -7.12 (m, 2H), 3.07 (s, 6H), 2.97 (ddd, J = 7.8, 5.1, 1.7 Hz, 2H), 2.81 (ddt, J = 7.4, 5.4, 1.8 Hz, 2H), 2.53 (p, J = 7.2 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 155.5, 145.2, 140.4, 126.3, 123.4, 122.2, 121.7, 119.2, 113.4, 77.2, 38.6, 28.4, 27.0, 24.6; **HRMS** calcd. for $C_{14}H_{17}N_2O$ $[M+H]^+$: 229.1335, found: 229.1336.

The spectroscopic data are in accordance with those reported.[3]



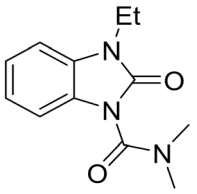
***tert*-butyl 5-(dimethylcarbamoyl)-1,3,4,5-tetrahydro-2*H*-pyrido[4,3-b]indole-2-carboxylate (1v)**

Faint yellow oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43 (d, J = 7.7 Hz, 1H), 7.30-7.26 (m, 1H), 7.25-7.20 (m, 1H), 7.17 (t, J = 7.2 Hz, 1H), 4.62 (s, 2H), 3.79 (s, 2H), 3.06 (s, 6H), 2.91 (s, 2H), 1.50 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 155.5, 154.6, 135.7, 126.8, 123.3, 121.7, 118.4, 112.2, 100.4, 80.4, 77.2, 40.9, 38.4, 28.9, 23.9; **HRMS** calcd. for $C_{19}H_{25}N_3NaO_3$ $[M+Na]^+$: 366.1788, found: 366.1788.



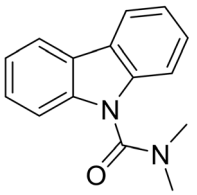
***tert*-butyl 9-(dimethylcarbamoyl)-1,3,4,9-tetrahydro-2*H*-pyrido[3,4-*b*]indole-2-carboxylate** (**1w**)

Faint yellow oil; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.49 (d, J = 7.7 Hz, 1H), 7.33 (d, J = 8.1 Hz, 1H), 7.27-7.20 (m, 1H), 7.16 (t, J = 7.4 Hz, 1H), 4.60 (s, 2H), 3.68 (t, J = 5.7 Hz, 2H), 2.98 (s, 6H), 2.70 (t, J = 5.8 Hz, 2H), 1.43 (s, 9H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ 154.2, 153.0, 134.6, 131.9, 127.1, 122.9, 121.0, 118.3, 111.9, 79.3, 41.4, 39.5, 37.6, 28.0; **HRMS** calcd. for $C_{19}H_{25}N_3NaO_3$ $[M+Na]^+$: 366.1788, found: 366.1786.



3-ethyl-*N*,*N*-dimethyl-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazole-1-carboxamide (1x)

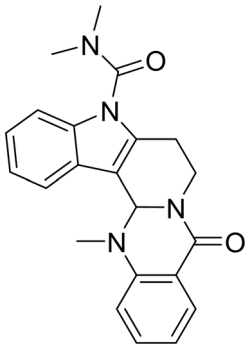
White solid, m.p. 63-64 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33 (dd, J = 7.8, 1.3 Hz, 1H), 7.16 (td, J = 7.7, 1.3 Hz, 1H), 7.11 (td, J = 7.7, 1.3 Hz, 1H), 7.01 (dd, J = 7.7, 1.2 Hz, 1H), 3.92 (q, J = 7.2 Hz, 2H), 3.17 (s, 6H), 1.35 (t, J = 7.3 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 151.2, 150.7, 129.3, 127.1, 122.6, 121.5, 111.8, 107.5, 77.2, 38.3, 35.7, 13.0; **HRMS** calcd. for $C_{12}H_{16}N_3O_2$ $[M+H]^+$: 234.1237, found: 234.1236.



***N*,*N*-dimethyl-9*H*-carbazole-9-carboxamide (1y)**

Faint yellow solid, m.p. 138-139 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.06 (d, J = 7.8 Hz, 2H), 7.59 (d, J = 8.3 Hz, 2H), 7.48 (ddd, J = 8.3, 7.1, 1.3 Hz, 2H), 7.38-7.30 (m, 2H), 3.10 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 155.1, 138.9, 126.8, 124.6, 121.7, 120.5, 112.9, 77.2, 38.3; **HRMS** calcd. for $C_{15}H_{15}N_2O$ $[M+H]^+$: 239.1179, found: 239.1180.

The spectroscopic data are in accordance with those reported.[5]



***N,N*,14-trimethyl-9-oxo-6,9,14,14a-tetrahydroindolo[3',2':3,4]pyrido[2,1-*b*] quinazoline-5(7*H*)-carboxamide (4)**

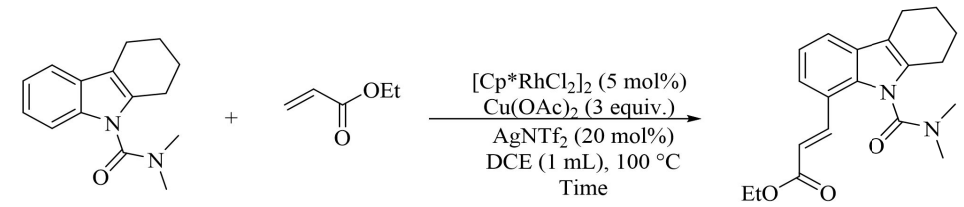
Yellow solid, m.p. 218-220 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.11 (dd, J = 7.9, 1.5 Hz, 1H), 7.62 (d, J = 7.8 Hz, 1H), 7.48 (td, J = 7.7, 1.5 Hz, 1H), 7.36 (dd, J = 8.4, 2.5 Hz, 2H), 7.30-7.24 (m, 1H), 7.22-7.16 (m, 1H), 7.10 (d, J = 7.9 Hz, 1H), 6.16 (s, 1H), 5.07-4.89 (m, 1H), 3.38-3.28 (m, 1H), 3.22 (s, 3H), 3.09 (s, 3H), 3.04-2.93 (m, 2H), 2.58 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 164.8, 153.6, 150.6, 136.0, 133.0, 129.9, 128.8, 126.8, 124.3, 123.8, 123.3, 122.4, 121.5, 119.4, 117.6, 111.6, 77.2, 68.6, 39.4, 38.0, 37.1, 29.3, 20.2; **HRMS** calcd. for $C_{22}H_{23}N_4O_2$ $[M+H]^+$: 375.1816, found: 375.1816.

References

1 Y. Xie, Y. Zhao, B. Qian, L. Yang, C. Xia and H. Huang, *Angew Chem Int Ed.*, 2011, **50**, 5682.
2 L. Ye, S. H. Cai, D. X. Wang, Y. Q. Wang, L. J. Lai, C. Feng and T. P. Loh, *Org Lett.*, 2017, **19**, 6164.
3 Y. Nakano and D. W. Lupton, *Chem Commun.*, 2014, **50**, 1757.
4 Compounds **1u'**, **1v', 1w', 1x', 1y', 4'** are obtained from commercial sources.
5 X.-F. H. P. Cao, H. Ding, H. M. Ge, H. Q. Li, B. F. Ruan and H. Li. Zhu, *Chem. Biodiv.*, 2007, **4**, 881.

2.2 Optimization Studies

Table S1. Screening of time [a]

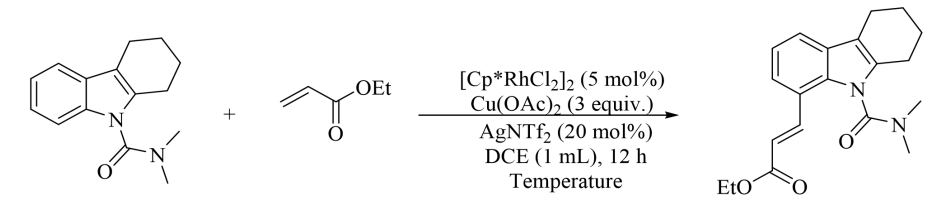


1a (0.1 mmol, 1 equiv.) **2** (5 equiv.) **3a**

entry	time (h)	yield [a] (%)
1	36	80
2	24	74
3	12	86
4	6	67

[a] Data were obtained by ^{1}H NMR analysis with CH_2Br_2 as reference.

Table S2. Screening of temperature [a]



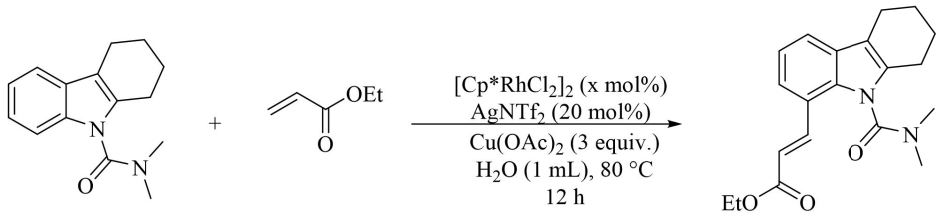
1a (0.1 mmol, 1 equiv.) **2** (5 equiv.) **3a**

entry	temperature (ºC)	yield [a] (%)
1	100	86
2	80	93
3	40	26

[a] Data were obtained by ^{1}H NMR analysis with CH_2Br_2 as reference.

After completing the conditional screening, it was later found that the reaction can also be carried out in water with a yield of 90%. Therefore, the reaction conditions were further optimized.

Table S3. Screening of catalyst amount [a]

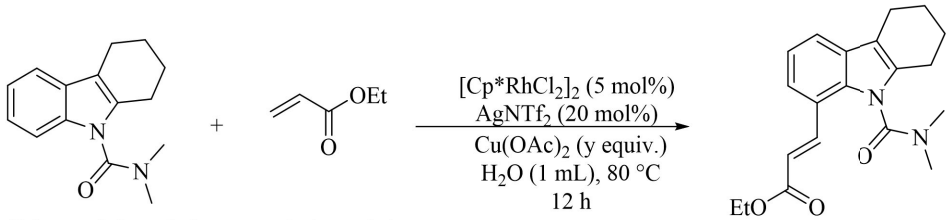


1a (0.1 mmol, 1 equiv.) **2** (5 equiv.) **3a**

entry	x	yield [a] (%)
1	5	96
2	4	92
3	2.5	64
4	1	24

[a] Data were obtained by ^{1}H NMR analysis with CH_2Br_2 as reference.

Table S4. Screening of oxidant amount [a]

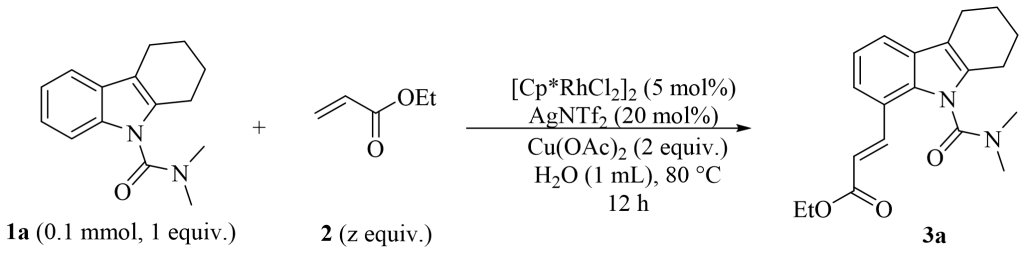


1a (0.1 mmol, 1 equiv.) **2** (5 equiv.) **3a**

entry	y	yield [a] (%)
1	3	96
2	2	84
3	1	40

[a] Data were obtained by ^{1}H NMR analysis with CH_2Br_2 as reference.

Table S5. Screening of olefinated reagent amount [a]

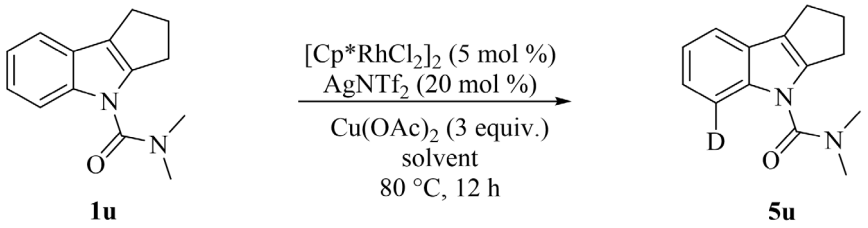


1a (0.1 mmol, 1 equiv.) **2** (z equiv.) **3a**

entry	z	yield [a] (%)
1	5	96
2	3	92
3	2	86

[a] Data were obtained by ^{1}H NMR analysis with CH_2Br_2 as reference.

Table S6. Optimization of deuterium conditions [a]

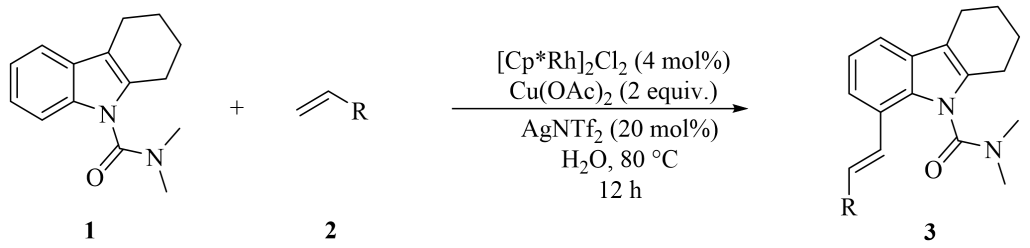


1u **5u**

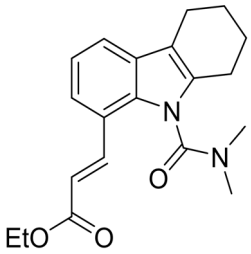
entry	solvent	deuterium incorporation (%) [b]	yield (%) [c]
1	D_2O	99	90
2	[D_4]-methanol	75	86
3	[D_1]-TFA	0	Trace
4	$CDCl_3$	--	95

[a] **1u** (0.1 mmol, 1 equiv.), $[Cp^*RhCl_2]_2$ (5 mol%), $AgNTf_2$ (20 mol%), $Cu(OAc)_2$ (3 equiv.), D_2O (0.5 mL), 80 °C, 12 h. [b] Deuterium incorporation at the aromatic position was determined by ^{1}H NMR spectroscopy. [c] Data are reported as isolated yields.

2.3 The general procedure for rhodium-catalyzed olefination



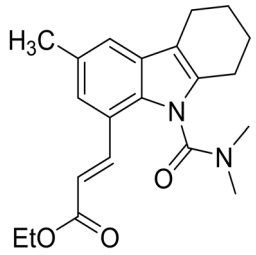
An oven-dried screw cap reaction tube was charged with a magnetic stir-bar, substrate (0.1 mmol, 1.0 equiv.), olefin (0.2 mmol, 2.0 equiv.), $[Cp^*RhCl_2]_2$ (0.004 mmol, 4 mol%), $Cu(OAc)_2$ (0.2 mmol, 2.0 equiv.), and $AgNTf_2$ (0.02 mmol, 20 mol%) were taken. Subsequently, H_2O (1 mL) was added and the reaction mixture was stirred vigorously at 80 °C for 12 h. The reaction mixture was then diluted with EtOAc and filtered through celite pad. After evaporation of the solvent, the crude mixture was purified by preparative Thin-Layer Chromatography (petroleum ether/ethyl acetate = 3:1).



ethyl (*E*)-3-(9-(dimethylcarbamoyl)-2,3,4,9-tetrahydro-1*H*-carbazol-8-yl)acrylate (3a)

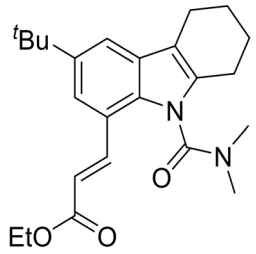
Yellow oil, 28 mg, 84% yield; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.96 (d, J = 15.6 Hz, 1H), 7.47 (d, J = 7.7 Hz, 1H), 7.36 (d, J = 7.5 Hz, 1H), 7.13 (t, J = 7.6 Hz, 1H), 6.41 (d, J = 15.6 Hz, 1H), 4.27 (q, J = 7.2 Hz, 2H), 3.19 (s, 3H), 2.94-2.81 (m, 1H), 2.75-2.65 (m, 2H), 2.60 (s, 3H), 2.58-2.46 (m, 1H), 1.98-1.89 (m, 2H), 1.89-1.82 (m, 2H), 1.34 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.9, 154.9, 140.2, 135.3, 133.3, 129.4, 121.1, 120.8, 120.3, 119.4, 119.2, 112.7, 77.2, 60.6, 38.0, 36.6,

23.0, 22.9, 22.2, 20.8, 14.5; **HRMS** calcd. for $C_{20}H_{25}N_2O_3$ $[M+H]^+$: 341.1860, found: 341.1860.



ethyl(*E*)-3-(9-(dimethylcarbamoyl)-6-methyl-2,3,4,9-tetrahydro-1*H*-carbazol-8-yl)acrylate (3b)

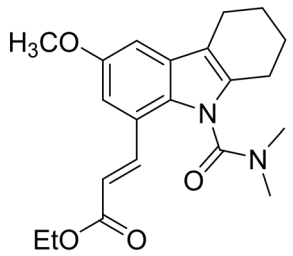
Yellow oil, 29 mg, 80% yield; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92 (d, J = 15.6 Hz, 1H), 7.27 (s, 1H), 7.20 (s, 1H), 6.40 (d, J = 15.6 Hz, 1H), 4.46-4.17 (m, 2H), 3.18 (s, 3H), 2.93-2.80 (m, 1H), 2.65 (d, J = 5.3 Hz, 2H), 2.59 (s, 3H), 2.55-2.46 (m, 1H), 2.43 (s, 3H), 1.94-1.89 (m, 2H), 1.87-1.83 (m, 2H), 1.34 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.7, 154.8, 140.0, 135.2, 131.5, 129.9, 129.5, 122.0, 120.3, 118.8, 118.7, 112.0, 77.2, 60.3, 37.7, 36.3, 22.8, 22.7, 22.0, 21.1, 20.6, 14.3; **HRMS** calcd. for $C_{21}H_{27}N_2O_3$ $[M+H]^+$: 355.2016, found: 355.2014.



ethyl *(E)*-3-(6-*(tert*-butyl)-9-(dimethylcarbamoyl)-2,3,4,9-tetrahydro-1*H*-carbazol-8-yl)acrylate (3c)

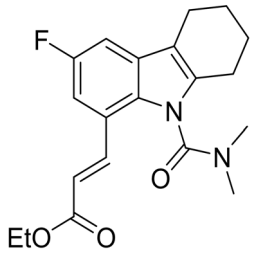
Yellow oil, 29 mg, 79% yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.95 (d, J = 15.6 Hz, 1H), 7.46 (d, J = 1.8 Hz, 1H), 7.41 (d, J = 1.8 Hz, 1H), 6.42 (d, J = 15.6 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 3.18 (s, 3H), 2.89-2.79 (m, 1H), 2.73-2.67 (m, 2H), 2.64 (s, 3H), 2.55-2.48 (m, 1H), 1.97-1.88 (m, 2H), 1.88-1.82 (m, 2H), 1.38 (s, 9H), 1.35 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.8, 154.9, 143.7, 140.6, 135.3, 131.5, 129.2, 118.8, 118.6, 118.5, 116.6, 112.5, 77.2, 60.4, 37.9, 36.4, 34.6, 31.8, 22.9, 22.7,

22.1, 20.7, 14.3; **HRMS** calcd. for $C_{24}H_{33}N_2O_3$ $[M+H]^+$: 397.2486, found: 397.2486.



ethyl (*E*)-3-(9-(dimethylcarbamoyl)-6-methoxy-2,3,4,9-tetrahydro-1*H*-carbazol-8-yl)acrylate (3d)

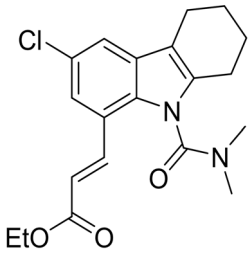
Yellow oil, 30 mg, 83% yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.90 (d, J = 15.6 Hz, 1H), 7.11-6.85 (m, 2H), 6.39 (d, J = 15.6 Hz, 1H), 4.27 (q, J = 7.2, 2H), 3.86 (s, 3H), 3.17 (s, 3H), 2.89-2.81 (m, 1H), 2.66-2.62 (m, 2H), 2.61 (s, 3H), 2.54-2.47 (m, 1H), 1.96-1.88 (m, 2H), 1.88-1.83 (m, 2H), 1.34 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.6, 154.8, 154.5, 139.7, 136.1, 130.2, 128.6, 119.7, 119.4, 112.3, 108.8, 103.6, 77.2, 60.4, 55.9, 37.8, 36.4, 22.8, 22.7, 22.2, 20.7, 14.3; **HRMS** calcd. for $C_{21}H_{26}N_2NaO_4$ $[M+Na]^+$: 393.1785 found: 393.1783.



ethyl (*E*)-3-(9-(dimethylcarbamoyl)-6-fluoro-2,3,4,9-tetrahydro-1*H*-carbazol-8-yl)acrylate (3e)

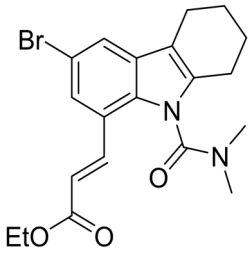
Yellow oil, 26 mg, 74% yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.88 (dd, J = 15.6 Hz, 1H), 7.12 (dd, J = 8.6, 2.5 Hz, 1H), 7.09 (dd, J = 10.0, 2.5 Hz, 1H), 6.39 (d, J = 15.6 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 3.19 (s, 3H), 2.89-2.81 (m, 1H), 2.63 (s, 5H), 2.55-2.48 (m, 1H), 1.98-1.89 (m, 2H), 1.89-1.82 (m, 2H), 1.35 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.5, 158.2 (d, J = 235.0 Hz), 154.7, 139.0, 137.3, 130.4 (d, J = 10.0 Hz), 130.0, 120.5, 120.0 (d, J = 8.8 Hz), 112.9 (d, J = 5.0 Hz), 108.1 (d, J = 26.2 Hz), 105.8 (d, J = 23.8 Hz), 77.2, 60.8, 38.0, 36.7, 23.0, 22.8, 22.3, 20.8, 14.5;

^{19}F NMR (471 MHz, $CDCl_3$) δ -123.2; **HRMS** calcd. for $C_{20}H_{24}FN_2O_3$ $[M+H]^+$: 359.1765 found: 359.1758.



ethyl (*E*)-3-(6-chloro-9-(dimethylcarbamoyl)-2,3,4,9-tetrahydro-1*H*-carbazol-8-yl)acrylate (3f)

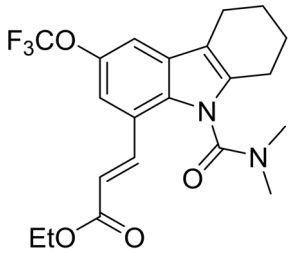
Yellow oil, 25 mg, 68% yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.86 (d, J = 15.6 Hz, 1H), 7.42 (d, J = 1.9 Hz, 1H), 7.31 (d, J = 1.9 Hz, 1H), 6.40 (d, J = 15.6 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 3.18 (s, 3H), 2.95-2.81 (m, 1H), 2.63 (d, J = 5.6 Hz, 2H), 2.60 (s, 3H), 2.55-2.45 (m, 1H), 2.00-1.89 (m, 2H), 1.89-1.81 (m, 2H), 1.34 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.3, 154.2, 138.6, 136.7, 131.4, 130.4, 126.4, 120.4, 120.4, 120.1, 119.4, 112.2, 77.2, 60.6, 37.8, 36.5, 22.7, 22.5, 22.0, 20.5, 14.3; **HRMS** calcd. for $C_{20}H_{24}ClN_2O_3$ $[M+H]^+$: 375.1470, found: 375.1469.



ethyl (*E*)-3-(6-bromo-9-(dimethylcarbamoyl)-2,3,4,9-tetrahydro-1*H*-carbazol-8-yl)acrylate (3g)

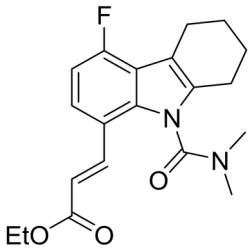
Yellow oil, 22 mg, 54% yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.85 (d, J = 15.6 Hz, 1H), 7.57 (d, J = 1.8 Hz, 1H), 7.44 (d, J = 1.8 Hz, 1H), 6.40 (d, J = 15.6 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.18 (s, 3H), 2.92-2.81 (m, 1H), 2.63 (t, J = 5.8 Hz, 2H), 2.59 (s, 3H), 2.56-2.46 (m, 1H), 1.99-1.88 (m, 2H), 1.88-1.79 (m, 2H), 1.34 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.3, 154.1, 138.5, 136.5, 131.7, 130.9, 123.1, 122.4, 120.6, 120.4, 113.8, 112.1, 77.2, 60.6, 37.8, 36.5, 22.7, 22.5, 22.0, 20.5, 14.3;

HRMS calcd. for $C_{20}H_{24}BrN2O_3$ $[M+H]^+$: 419.0965, found: 419.0967.



ethyl (*E*)-3-(9-(dimethylcarbamoyl)-6-(trifluoromethoxy)-2,3,4,9-tetrahydro-1*H*-carbazol-8-yl)acrylate (3h)

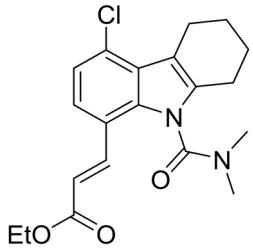
Yellow oil, 27 mg, 65% yield; **^{1}H NMR** (500 MHz, $CDCl_3$) δ ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 15.6 Hz, 1H), 7.31 (d, *J* = 2.2 Hz, 1H), 7.22-7.19 (m, 1H), 6.41 (d, *J* = 15.6 Hz, 1H), 4.27 (q, *J* = 7.0 Hz, 2H), 3.20 (s, 3H), 2.87-2.83 (m, 1H), 2.65 (s, 5H), 2.55-2.49 (m, 1H), 1.93-1.91 (m, 2H), 1.89-1.87 (m, 2H), 1.35 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.2, 154.1, 143.5, 138.5, 137.2, 131.3, 129.9, 121.6, 120.7, 119.8, 113.9, 112.8, 112.3, 77.2, 60.6, 37.8, 36.5, 22.7, 22.5, 22.0, 20.5, 14.2; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -58.0;**HRMS** calcd. for $C_{21}H_{24}F_3N_2O_4$ $[M+H]^+$: 425.1683, found: 425.1682.



ethyl (*E*)-3-(9-(dimethylcarbamoyl)-5-fluoro-2,3,4,9-tetrahydro-1*H*-carbazol-8-yl)acrylate (3i)

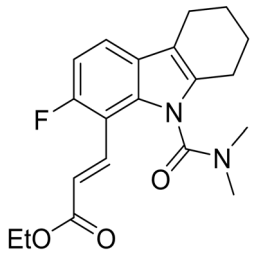
Yellow solid, 23 mg, 65% yield, m.p. 110-111 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 16.0 Hz, 1H), 7.35 (dd, *J* = 8.5, 4.9 Hz, 1H), 6.94 (dd, *J* = 11.6, 8.5 Hz, 1H), 6.58 (d, *J* = 16.0 Hz, 1H), 4.27 (qd, *J* = 7.2, 2.7 Hz, 2H), 3.18 (s, 3H), 2.85-2.79 (m, 1H), 2.68 (s, 3H), 2.67-2.63 (m, 2H), 2.55-2.48 (m, 1H), 1.95-1.88 (m, 2H), 1.88-1.82 (m, 2H), 1.35 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.1, 158.5 (d, *J* = 246.0 Hz), 154.6, 135.6, 133.7, 133.6 (d, *J* = 7.5 Hz), 125.8, 123.6 (d, *J* = 12.0 Hz),

120.1, 112.7, 109.5 (d, J = 25.5 Hz), 107.7 (d, J = 18.0 Hz), 77.2, 60.7, 38.0, 36.6, 22.9, 22.8, 22.2, 20.7, 14.5; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -119.6;**HRMS** calcd. for $C_{20}H_{24}FN_2O_3$ $[M+H]^+$: 359.1765, found: 359.1757.



ethyl (*E*)-3-(5-chloro-9-(dimethylcarbamoyl)-2,3,4,9-tetrahydro-1*H*-carbazol-8-yl)acrylate (3j)

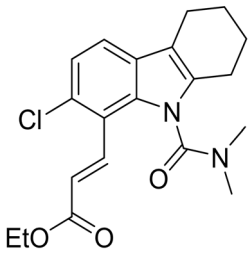
Yellow oil, 20 mg, 53% yield; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.86 (d, J = 16.2 Hz, 1H), 7.33 (d, J = 8.3 Hz, 1H), 7.19 (d, J = 8.3 Hz, 1H), 6.26 (d, J = 16.3 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 3.04 (s, 3H), 2.78 (dd, J = 14.2, 8.8 Hz, 1H), 2.69 (s, 3H), 2.68-2.61 (m, 2H), 2.57-2.47 (m, 1H), 1.92-1.83 (m, 4H), 1.35 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.2, 153.9, 138.0, 136.0, 133.8, 128.1, 127.3, 124.7, 122.3, 119.1, 118.5, 112.8, 77.2, 60.6, 37.8, 36.1, 22.7, 22.6, 22.2, 20.5, 14.3; **HRMS** calcd. for $C_{20}H_{24}ClN_2O_3$ $[M+H]^+$: 375.1470, found: 375.1469.



ethyl (*E*)-3-(9-(dimethylcarbamoyl)-7-fluoro-2,3,4,9-tetrahydro-1*H*-carbazol-8-yl)acrylate (3k)

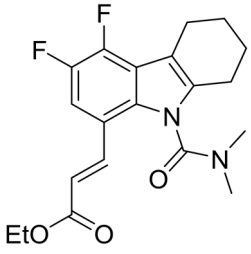
Yellow oil, 17 mg, 47% yield; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.87 (d, J = 15.6 Hz, 1H), 7.28 (d, J = 4.9 Hz, 1H), 6.78 (dd, J = 10.0, 8.3 Hz, 1H), 6.34 (d, J = 15.6 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.20 (s, 3H), 2.87 (d, J = 5.9 Hz, 2H), 2.61 (s, 3H), 2.46-2.50 (m, 2H), 1.96-1.88 (m, 2H), 1.86 (dd, J = 7.9, 4.4 Hz, 2H), 1.34 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.6, 157.9 (d, J = 250.0 Hz), 154.0, 139.0,

135.2 (d, J = 12.5 Hz), 134.7, 121.7 (d, J = 7.5 Hz), 118.6, 117.4 (d, J = 21.2 Hz), 115.7, 110.7, 106.6 (d, J = 20.0 Hz), 77.2, 60.4, 37.7, 36.4, 22.7, 22.4, 22.0, 21.9, 14.3; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -121.2;**HRMS** calcd. for $C_{20}H_{24}FN_2O_3$ $[M+H]^+$: 359.1765, found: 359.1763.



ethyl (*E*)-3-(7-chloro-9-(dimethylcarbamoyl)-2,3,4,9-tetrahydro-1*H*-carbazol-8-yl)acrylate (3l)

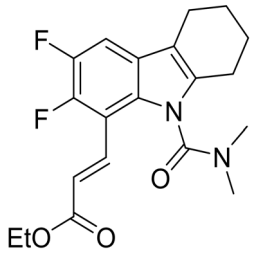
Yellow oil, 15 mg, 39% yield; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.88 (d, J = 15.6 Hz, 1H), 7.23 (d, J = 8.1 Hz, 1H), 7.07 (d, J = 8.1 Hz, 1H), 6.37 (d, J = 15.6 Hz, 1H), 4.26 (q, J = 7.0 Hz, 2H), 3.19 (s, 3H), 3.09-3.01 (m, 2H), 2.90-2.79 (m, 1H), 2.59 (s, 3H), 2.54-2.44 (m, 1H), 1.96-1.81 (m, 4H), 1.34 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.5, 154.1, 139.0, 135.9, 133.8, 128.2, 126.2, 121.6, 121.3, 119.5, 117.9, 112.5, 77.2, 60.5, 37.7, 36.5, 22.9, 22.8, 22.2, 22.1, 14.3; **HRMS** calcd. for $C_{20}H_{24}ClN_2O_3$ $[M+H]^+$: 375.1470, found: 375.1470.



ethyl (*E*)-3-(9-(dimethylcarbamoyl)-5,7-difluoro-2,3,4,9-tetrahydro-1*H*-carbazol-8-yl)acrylate (3m)

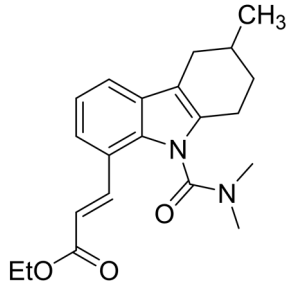
Yellow oil, 22 mg, 59% yield; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (d, J = 15.5 Hz, 1H), 7.16 (dd, J = 11.6, 7.3 Hz, 1H), 6.31 (d, J = 15.5 Hz, 1H), 4.26 (q, J = 6.9 Hz, 2H), 3.19 (s, 3H), 2.90-2.83 (m, 2H), 2.83-2.76 (m, 1H), 2.63 (s, 3H), 2.55-2.43 (m, 1H), 1.97-1.79 (m, 4H), 1.34 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ

166.2, 153.8, 144.9 (d, J = 237.5 Hz), 144.6 (d, J = 251.2 Hz), 137.9, 136.5, 130.5 (d, J = 10.0 Hz), 129.8, 119.8, 114.8, 111.2, 109.4 (d, J = 21.2 Hz), 77.2, 60.5, 37.7, 36.5, 22.6, 22.2, 21.9, 21.8, 14.2; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -147.3 (d, J = 23.5 Hz), -150.1 (d, J = 18.8 Hz); **HRMS** calcd. for $C_{20}H_{23}F_2N_2O_3$ $[M+H]^+$: 377.1671, found: 377.1669.



ethyl (*E*)-3-(9-(dimethylcarbamoyl)-5,6-difluoro-2,3,4,9-tetrahydro-1*H*-carbazol-8-yl)acrylate (3n)

Faint yellow solid, 26 mg, 69% yield, m.p. 118-120 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.69 (d, J = 16.1 Hz, 1H), 7.19 (dd, J = 9.8, 7.5 Hz, 1H), 6.59 (dd, J = 16.1, 1.2 Hz, 1H), 4.28 (qd, J = 7.1, 1.4 Hz, 2H), 3.17 (s, 3H), 2.86-2.76 (m, 1H), 2.69 (s, 3H), 2.65-2.57 (m, 2H), 2.54-2.45 (m, 1H), 1.94-1.88 (m, 2H), 1.88-1.81 (m, 2H), 1.35 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.0, 154.5, 147.4 (d, J = 238.8 Hz), 146.8 (d, J = 262.5 Hz), 137.1, 133.2, 129.2, 125.0 (d, J = 12.5 Hz), 124.5, 113.1, 109.4 (d, J = 13.8 Hz), 106.6 (d, J = 18.8 Hz), 77.2, 61.1, 38.3, 36.9, 23.1, 23.0, 22.5, 21.0, 14.8; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -144.0 (d, J = 23.5 Hz), -145.7 (d, J = 23.5 Hz); **HRMS** calcd. for $C_{20}H_{23}F_2N_2O_3$ $[M+H]^+$: 377.1671, found: 377.1670.



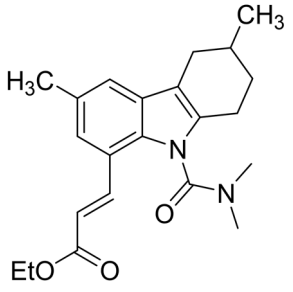
ethyl (*E*)-3-(9-(dimethylcarbamoyl)-3-methyl-2,3,4,9-tetrahydro-1*H*-carbazol-8-yl)acrylate (3o)

Faint yellow oil, 29 mg, 83% yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.95 (dd, J = 15.6,

1.4 Hz, 1H), 7.47 (d, *J* = 7.7 Hz, 1H), 7.36 (d, *J* = 7.5 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.41 (dd, *J* = 15.6, 5.9 Hz, 1H), 4.47-4.18 (m, 2H), 3.19 (s, 3H), 2.97-2.86 (m, 1H), 2.86-2.74 (m, 1H), 2.63 (s, 1H), 2.56 (s, 2H), 2.56-2.51 (m, 1H), 2.32-2.21 (m, 1H), 2.05-1.90 (m, 2H), 1.61-1.50 (m, 1H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.14 (dd, *J* = 6.5, 1.6 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) *δ* 167.1, 155.3, 140.4, 135.3, 133.9, 133.6, 129.6, 121.3, 120.5, 119.7, 119.5, 112.7, 77.2, 60.8, 38.2, 36.9, 31.5, 29.6, 29.4, 22.3, 21.9, 14.7; **HRMS** calcd. for $C_{21}H_{27}N_2O_3$ $[M+H]^+$: 355.2016, found: 355.2013.

ethyl (*E*)-3-(9-(dimethylcarbamoyl)-6-fluoro-3-methyl-2,3,4,9-tetrahydro-1*H*-carbazol-8-yl)acrylate (3p)

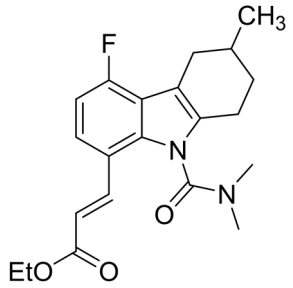
Yellow solid, 28 mg, 75% yield, m.p. 123-124 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) *δ* 7.86 (d, *J* = 15.5 Hz, 1H), 7.12-7.01 (m, 2H), 6.36 (dd, *J* = 14.7, 6.2 Hz, 1H), 4.36-4.18 (m, 2H), 3.16 (s, 3H), 2.90-2.80 (m, 1H), 2.76-2.68 (m, 1H), 2.63 (s, 3H), 2.54-2.48 (m, 1H), 2.26-2.13 (m, 1H), 2.04-1.85 (m, 2H), 1.61-1.46 (m, 1H), 1.32 (td, *J* = 7.1, 2.0 Hz, 3H), 1.10 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) *δ* 166.2, 157.9 (d, *J* = 235.5 Hz), 154.4, 138.6 (d, *J* = 10.5 Hz), 136.7, 130.1, 129.9, 120.1, 119.7 (d, *J* = 9.0 Hz), 112.3, 107.7 (d, *J* = 27.0 Hz), 105.5 (d, *J* = 22.5 Hz), 77.2, 60.4, 37.7, 36.3, 30.8, 29.0, 28.8, 21.8, 21.4, 14.2; **^{19}F NMR** (471 MHz, $CDCl_3$) *δ* -123.2; **HRMS** calcd. for $C_{21}H_{26}FN_2O_3$ $[M+H]^+$: 373.1922, found: 373.1921.



ethyl (*E*)-3-(9-(dimethylcarbamoyl)-3,6-dimethyl-2,3,4,9-tetrahydro-1*H*-car

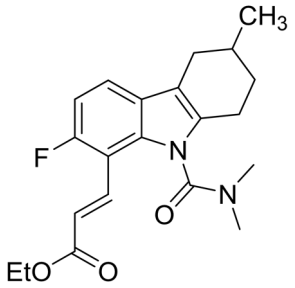
bazol-8-yl) acrylate (3q)

Yellow oil, 29 mg, 80% yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.92 (d, J = 15.6 Hz, 1H), 7.26 (s, 1H), 7.19 (s, 1H), 6.40 (dd, J = 15.6, 5.7 Hz, 1H), 4.31-4.22 (m, 2H), 3.17 (s, 3H), 2.95-2.84 (m, 1H), 2.81-2.75 (m, 1H), 2.59 (s, 3H), 2.54-2.48 (m, 1H), 2.44 (s, 3H), 2.27-2.18 (m, 1H), 2.03-1.90 (m, 2H), 1.59 (s, 1H), 1.34 (t, J = 7.2 Hz, 3H), 1.13 (d, J = 6.6 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.9, 155.2, 140.3, 135.3, 132.2, 131.9, 130.2, 129.7, 122.2, 120.5, 119.0, 112.3, 77.2, 60.5, 38.0, 36.6, 31.3, 29.4, 29.2, 22.2, 21.7, 21.3, 14.5; **HRMS** calcd. for $C_{22}H_{29}N_2O_3$ $[M+H]^+$: 369.2173, found: 369.2175.



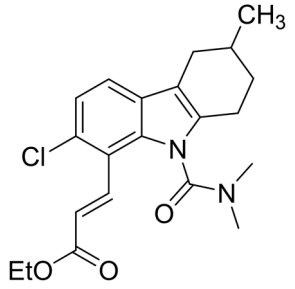
ethyl (*E*)-3-(9-(dimethylcarbamoyl)-5-fluoro-3-methyl-2,3,4,9-tetrahydro-1*H*-carbazol-8-yl)acrylate (3r)

Yellow oil, 25 mg, 68% yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.72 (d, J = 16.0 Hz, 1H), 7.33 (ddd, J = 8.3, 5.0, 3.2 Hz, 1H), 6.93 (dd, J = 11.6, 8.5 Hz, 1H), 6.57 (ddd, J = 16.0, 12.4, 1.3 Hz, 1H), 4.38-4.19 (m, 2H), 3.17 (s, 3H), 2.89-2.81 (m, 1H), 2.80-2.74 (m, 1H), 2.66 (s, 3H), 2.58-2.48 (m, 1H), 2.29-2.15 (m, 1H), 2.02-1.87 (m, 2H), 1.64-1.49 (m, 1H), 1.34 (t, J = 7.1 Hz, 3H), 1.12 (dd, J = 6.6, 2.6 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.9, 158.2 (d, J = 244.5 Hz), 154.4, 135.1, 133.8, 133.4, 125.5, 123.4, 119.9, 112.5, 109.2 (d, J = 25.5 Hz), 107.5 (d, J = 36.0 Hz), 77.2, 60.5, 37.8, 36.4, 30.9, 29.2, 28.9, 21.8, 21.4, 14.3; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -119.6;**HRMS** calcd. for $C_{21}H_{26}FN_2O_3$ $[M+H]^+$: 373.1922, found: 373.1924.



ethyl(*E*)-3-(9-(dimethylcarbamoyl)-7-fluoro-3-methyl-2,3,4,9-tetrahydro-1*H*-carbazol-8-yl)acrylate (3s)

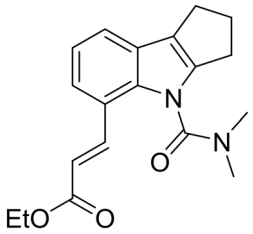
Yellow oil, 20 mg, 54% yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.87 (d, J = 15.4 Hz, 1H), 7.27 (d, J = 5.2 Hz, 1H), 6.77 (dd, J = 9.9, 8.3 Hz, 1H), 6.33 (dd, J = 15.6, 6.3 Hz, 1H), 4.36-4.16 (m, 2H), 3.19 (s, 3H), 3.02 (s, 1H), 2.94-2.82 (m, 1H), 2.60 (s, 3H), 2.56-2.48 (m, 1H), 2.49-2.34 (m, 1H), 2.07-1.85 (m, 2H), 1.62-1.46 (m, 1H), 1.34 (t, J = 7.1 Hz, 3H), 1.12 (dd, J = 6.6, 2.3 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.6, 157.9 (d, J = 250.5 Hz), 154.1, 139.0, 135.6 (d, J = 12.0 Hz), 134.6, 121.7 (d, J = 9.0 Hz), 118.6, 117.3 (d, J = 21.0 Hz), 115.7, 110.7, 106.7 (d, J = 19.5 Hz), 77.2, 60.4, 37.8, 36.5, 30.3, 29.3, 29.0, 21.8, 21.4, 14.3; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -121.2;**HRMS** calcd. for $C_{21}H_{26}FN_2O_3$ $[M+H]^+$: 373.1922, found: 373.1919.



ethyl (*E*)-3-(7-chloro-9-(dimethylcarbamoyl)-3-methyl-2,3,4,9-tetrahydro-1*H*-carbazol-8-yl)acrylate (3t)

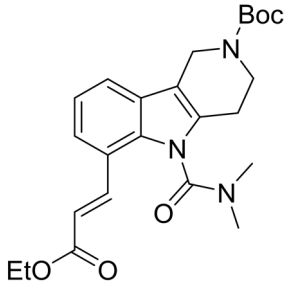
Yellow oil, 19 mg, 48% yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.88 (dd, J = 15.6, 2.2 Hz, 1H), 7.22 (d, J = 8.5 Hz, 1H), 7.06 (d, J = 8.1 Hz, 1H), 6.37 (dd, J = 15.5, 6.6 Hz, 1H), 4.43-4.19 (m, 2H), 3.28 (ddt, J = 15.5, 10.1, 5.0 Hz, 1H), 3.18 (d, J = 7.3 Hz, 3H), 2.92-2.81 (m, 1H), 2.66-2.47 (m, 5H), 2.02-1.85 (m, 2H), 1.53 (dtd, J = 24.4, 12.3, 11.6, 5.5 Hz, 1H), 1.34 (t, J = 7.1 Hz, 3H), 1.14 (dd, J = 6.7, 2.5 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.5, 154.1, 139.0, 135.7, 134.2, 128.1, 126.1, 121.6,

121.2, 119.5, 118.0, 112.5, 77.2, 60.4, 37.7, 36.5, 31.1, 30.2, 29.4, 21.9, 21.4, 14.3; **HRMS** calcd. for $C_{21}H_{26}ClN_2O_3$ $[M+H]^+$: 389.1626, found: 389.1625.



ethyl (*E*)-3-(4-(dimethylcarbamoyl)-1,2,3,4-tetrahydrocyclopenta[*b*]indol-5-yl) acrylate (3u)

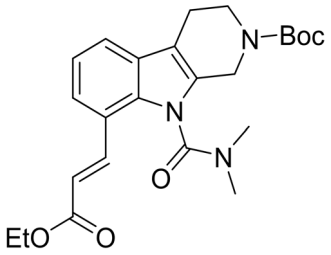
Faint yellow oil, 29 mg, 90% yield; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.94 (d, J = 15.7 Hz, 1H), 7.44 (d, J = 7.8 Hz, 1H), 7.35 (d, J = 7.5 Hz, 1H), 7.15 (t, J = 7.7 Hz, 1H), 6.40 (d, J = 15.7 Hz, 1H), 4.27 (q, J = 7.2 Hz, 2H), 3.23-3.07 (m, 3H), 3.03-2.92 (m, 2H), 2.85-2.79 (m, 3H), 2.75 (s, 2H), 2.55 (p, J = 7.1 Hz, 2H), 1.34 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.6, 154.8, 145.2, 140.2, 138.2, 126.5, 121.8, 121.3, 120.8, 120.8, 120.5, 118.8, 77.2, 60.3, 28.0, 25.7, 24.3, 14.3; **HRMS** calcd. for $C_{19}H_{23}N_2O_3$ $[M+H]^+$: 327.1703, found: 327.1704.



***tert*-butyl (*E*)-5-(dimethylcarbamoyl)-6-(3-ethoxy-3-oxoprop-1-en-1-yl)-1,3,4,5-tetrahydro-2*H*-pyrido[4,3-b]indole-2-carboxylate (3v)**

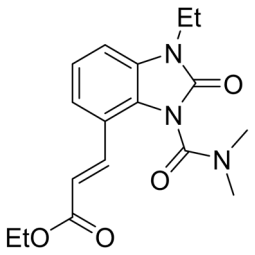
Yellow oil, 29 mg, 67% yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.93 (d, J = 15.6 Hz, 1H), 7.47 (d, J = 7.7 Hz, 1H), 7.40 (d, J = 7.5 Hz, 1H), 7.17 (t, J = 7.7 Hz, 1H), 6.42 (d, J = 15.5 Hz, 1H), 4.78-4.61 (m, 1H), 4.60-4.48 (m, 1H), 4.27 (q, J = 7.1 Hz, 2H), 3.95 (s, 1H), 3.67 (s, 1H), 3.19 (s, 3H), 3.02-2.88 (m, 1H), 2.71-2.57 (m, 4H), 1.50 (s, 9H), 1.34 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.5, 154.9, 154.1, 139.6, 133.3, 126.9, 121.5, 121.2, 120.1, 119.8, 119.6, 119.5, 80.1, 77.2, 60.5, 40.3,

37.9, 36.5, 29.6, 28.4, 14.3; **HRMS** calcd. for $C_{24}H_{31}N_3NaO_5$ [M+Na]$^+$: 464.2156, found: 464.2156.



***tert*-butyl (*E*)-9-(dimethylcarbamoyl)-8-(3-ethoxy-3-oxoprop-1-en-1-yl)-1,3,4,9-tetrahydro-2*H*-pyrido[3,4-*b*]indole-2-carboxylate (3w)**

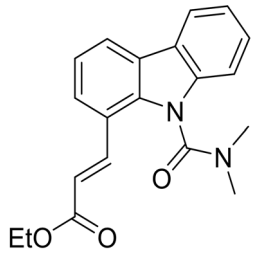
Faint yellow oil, 31 mg, 70% yield; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.93 (d, J = 15.6 Hz, 1H), 7.49 (d, J = 7.7 Hz, 1H), 7.40 (d, J = 7.5 Hz, 1H), 7.17 (t, J = 7.7 Hz, 1H), 6.42 (d, J = 15.6 Hz, 1H), 4.70 (s, 1H), 4.50 (s, 1H), 4.27 (q, J = 6.8 Hz, 2H), 4.19 – 4.00 (m, 1H), 3.95 – 3.55 (m, 1H), 3.17 (s, 3H), 2.77 (d, J = 7.0 Hz, 2H), 2.61 (s, 3H), 1.49 (s, 9H), 1.34 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.7, 155.2, 154.1, 139.9, 133.5, 128.7, 122.0, 121.4, 120.5, 120.1, 119.7, 80.4, 77.2, 60.7, 41.2, 38.2, 36.7, 29.8, 28.6, 14.5; **HRMS** calcd. for $C_{24}H_{31}N_3NaO_5$ [M+Na]$^+$: 464.2156, found: 464.2158.



ethyl (*E*)-3-(3-(dimethylcarbamoyl)-1-ethyl-2-oxo-2,3-dihydro-1*H*-benzo[d]imidazole-4-yl)acrylate (3x)

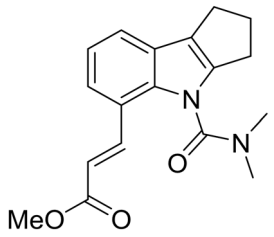
Faint yellow oil, 29 mg, 88% yield; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.72 (dd, J = 15.8, 2.5 Hz, 1H), 7.30-7.26 (m, 1H), 7.16 (td, J = 8.0, 2.4 Hz, 1H), 6.99 (dd, J = 7.9, 2.4 Hz, 1H), 6.33 (dd, J = 15.5, 2.5 Hz, 1H), 4.25 (q, J = 7.2 Hz, 2H), 3.91 (qt, J = 7.8, 3.9 Hz, 2H), 3.23 (s, 3H), 3.15 (s, 3H), 1.39-1.29 (m, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.5, 151.8, 151.7, 138.6, 131.2, 126.2, 123.2, 120.5, 120.3, 119.4, 109.0,

77.2, 60.7, 38.5, 37.1, 36.3, 14.4, 13.4; **HRMS** calcd. for $C_{17}H_{22}N_3O_4$ $[M+H]^+$: 332.1605, found: 332.1602.



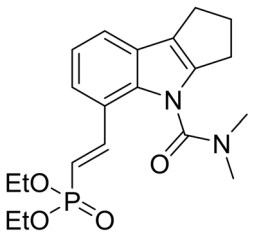
ethyl (*E*)-3-(9-(dimethylcarbamoyl)-9*H*-carbazol-1-yl)acrylate (3y)

Faint yellow solid, 30 mg, 90% yield, m.p. 146-147 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.14-7.89 (m, 3H), 7.63 (d, J = 7.6 Hz, 1H), 7.51-7.44 (m, 2H), 7.35-7.29 (m, 2H), 6.46 (d, J = 15.6 Hz, 1H), 4.30 (qd, J = 7.2, 2.1 Hz, 2H), 3.29 (s, 3H), 2.81 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.7, 154.8, 140.0, 139.3, 137.2, 127.2, 125.6, 125.3, 123.7, 122.2, 121.7, 121.7, 120.5, 120.2, 119.7, 111.1, 77.2, 60.7, 38.2, 36.8, 14.5; **HRMS** calcd. for $C_{20}H_{21}N_2O_3$ $[M+H]^+$: 337.1547, found: 337.1549.



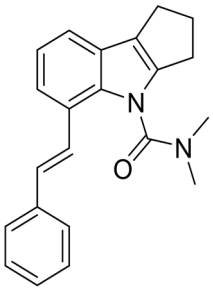
methyl (*E*)-3-(4-(dimethylcarbamoyl)-1,2,3,4-tetrahydrocyclopenta[*b*]indol-5-yl) acrylate (3aa)

Yellow solid, 28 mg, 89% yield, m.p. 101-102 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.96 (d, J = 15.6 Hz, 1H), 7.44 (d, J = 7.7 Hz, 1H), 7.34 (d, J = 7.5 Hz, 1H), 7.15 (t, J = 7.6 Hz, 1H), 6.40 (d, J = 15.7 Hz, 1H), 3.80 (s, 3H), 3.24-2.63 (m, 10H), 2.54 (p, J = 7.1 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.3, 155.0, 145.4, 140.8, 138.4, 126.7, 122.0, 121.5, 121.1, 121.0, 120.6, 118.6, 77.2, 51.8, 38.2, 36.7, 28.2, 26.0, 24.5; **HRMS** calcd. for $C_{18}H_{21}N_2O_3$ $[M+H]^+$: 313.1547, found: 313.1547.



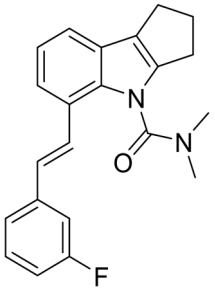
diethyl(*E*)-(2-(4-(dimethylcarbamoyl)-1,2,3,4-tetrahydrocyclopenta[*b*]indol-5-yl) vinyl)phos phonate (3ab)

Yellow oil, 21 mg, 54% yield; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.69 (dd, J = 22.4, 17.2 Hz, 1H), 7.43 (d, J = 7.7 Hz, 1H), 7.30 (d, J = 7.5 Hz, 1H), 7.15 (t, J = 7.7 Hz, 1H), 6.21 (dd, J = 19.2, 17.1 Hz, 1H), 4.15 (p, J = 7.2 Hz, 4H), 3.25-2.66 (m, 10H), 2.54 (q, J = 7.1 Hz, 2H), 1.36 (t, J = 7.1 Hz, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 154.8, 145.1, 144.4, 137.9, 126.5, 121.8, 121.3, 120.7, 120.6, 115.4, 114.2, 77.2, 61.9, 61.9, 38.2, 36.4, 27.9, 25.7, 24.3, 16.4, 16.3; **HRMS** calcd. for $C_{20}H_{28}N_2O_4P$ $[M+H]^+$: 391.1776, found: 391.1779.



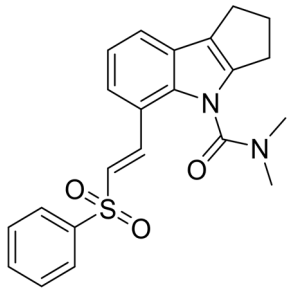
(*E*)-*N*,*N*-dimethyl-5-styryl-2,3-dihydrocyclopenta[*b*]indole-4(1*H*)-carboxamide (3ac)

Yellow oil, 19 mg, 57% yield; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.52 (d, J = 7.6 Hz, 2H), 7.41 (d, J = 16.0 Hz, 1H), 7.36 (q, J = 8.0, 7.5 Hz, 4H), 7.27 (d, J = 7.3 Hz, 1H), 7.17 (t, J = 7.7 Hz, 1H), 7.03 (d, J = 16.0 Hz, 1H), 3.18-2.68 (m, 8H), 2.64-2.49 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 155.7, 145.0, 138.2, 137.7, 130.3, 129.1, 128.0, 126.8, 126.4, 124.7, 124.3, 122.0, 121.8, 120.6, 118.9, 77.2, 38.3, 37.1, 28.5, 26.2, 24.8; **HRMS** calcd. for $C_{22}H_{23}N_2O$ $[M+H]^+$: 331.1085, found: 331.1082.



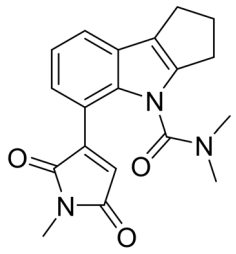
(*E*)-5-(3-fluorostyryl)-*N*,*N*-dimethyl-2,3-dihydrocyclopenta[*b*]indole-4(1*H*)-carbo xamide (3ad)

Yellow oil, 18 mg, 51% yield; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41 (d, J = 15.9 Hz, 1H), 7.37 (d, J = 7.9 Hz, 1H), 7.32 (dd, J = 6.7, 3.8 Hz, 2H), 7.29 (d, J = 9.9 Hz, 1H), 7.21-7.18 (m, 1H), 7.16 (d, J = 7.6 Hz, 1H), 7.01-6.93 (m, 2H), 3.01 (s, 4H), 2.84 (t, J = 7.1 Hz, 3H), 2.62 (s, 2H), 2.55 (p, J = 7.3 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 163.4 (d, J = 243.8 Hz), 155.4, 144.9, 139.9 (d, J = 7.5 Hz), 138.0, 130.3 (d, J = 8.8 Hz), 128.9, 126.3, 126.0, 123.6, 122.4, 121.9, 121.6, 120.5, 119.0, 114.5 (d, J = 21.2 Hz), 113.0 (d, J = 21.2 Hz), 28.2, 26.0, 24.6; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -113.3;**HRMS** calcd. for $C_{22}H_{22}FN_2O$ $[M+H]^+$: 349.1711, found: 349.1712.



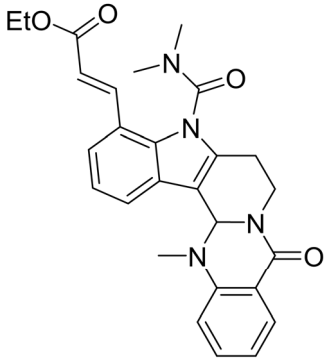
(*E*)-*N*,*N*-dimethyl-5-(2-(phenylsulfonyl)vinyl)-2,3-dihydrocyclopenta[*b*]indole-4(1 *H)*-carboxamide (3ae)

Yellow solid, 18 mg, 47% yield, m.p. 102-104 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.05-7.93 (m, 3H), 7.64-7.58 (m, 1H), 7.55 (dd, J = 8.3, 6.8 Hz, 2H), 7.46 (d, J = 7.7 Hz, 1H), 7.25-7.21 (m, 1H), 7.12 (t, J = 7.7 Hz, 1H), 6.81 (d, J = 15.0 Hz, 1H), 3.25 (s, 3H), 2.87 (s, 4H), 2.85-2.78 (m, 3H), 2.62-2.48 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 154.7, 145.5, 140.5, 138.9, 138.4, 133.2, 129.2, 127.7, 127.3, 126.8, 122.0, 121.8, 121.3, 121.0, 118.2, 77.2, 38.2, 36.5, 28.0, 25.8, 24.2; **HRMS** calcd. for $C_{22}H_{23}N_2O_3S$ $[M+H]^+$: 395.1424, found: 395.1423.



***N,N*-dimethyl-5-(1-methyl-2,5-dioxo-2,5-dihydro-1*H*-pyrrol-3-yl)-2,3-dihydro cyclopenta[*b*]indole-4(1*H*)-carboxamide (3af)**

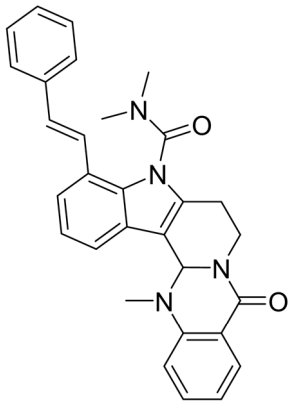
Yellow solid, 14 mg, 43% yield, m.p. 128-130 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.51 (dd, J = 7.1, 1.8 Hz, 1H), 7.24-7.17 (m, 2H), 6.51 (s, 1H), 3.05 (s, 3H), 3.01 (s, 6H), 2.90 (t, J = 7.2 Hz, 2H), 2.83 (t, J = 7.0 Hz, 2H), 2.53 (p, J = 7.1 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.0, 170.8, 155.6, 148.0, 144.9, 137.5, 127.4, 124.7, 123.6, 122.5, 121.5, 121.4, 115.3, 77.2, 28.0, 27.0, 24.1, 23.6; **HRMS** calcd. for $C_{19}H_{20}N_3O_3$ $[M+H]^+$: 338.1499, found: 338.1500.



ethyl (*E*)-3-(5-(dimethylcarbamoyl)-14-methyl-9-oxo-5,6,7,9,14,14a-hexahydro indolo[3',2':3,4] pyrido[2,1-*b*]quinazolin-4-yl)acrylate (4a)

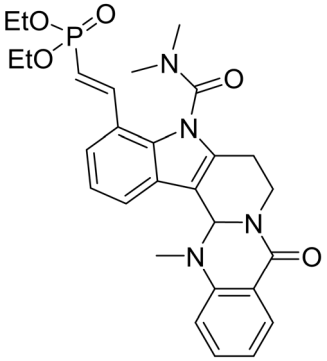
Yellow solid, 23 mg, 49% yield, m.p. 221-222 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.6 (d, J = 15.8 Hz, 1H), 7.6 (d, J = 7.8 Hz, 1H), 7.4 (t, J = 7.8 Hz, 1H), 7.4-7.3 (m, 2H), 7.3-7.3 (m, 1H), 7.3-7.2 (m, 1H), 7.1 (d, J = 8.1 Hz, 1H), 6.2 (d, J = 15.9 Hz, 1H), 6.1 (s, 1H), 4.9 (ddd, J = 12.9, 5.4, 2.1 Hz, 1H), 4.5-4.2 (m, 2H), 3.3 (ddd, J = 12.9, 11.2, 4.3 Hz, 1H), 3.1 (s, 3H), 3.1 (d, J = 2.7 Hz, 3H), 3.0-3.0 (m, 1H), 2.9 (tdd, J = 10.5, 5.6, 1.8 Hz, 1H), 2.5 (s, 3H), 1.3 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.0, 163.9, 153.7, 152.0, 145.6, 138.4, 136.4, 132.4, 126.7, 124.6, 124.5, 124.0,

122.4, 121.8, 120.1, 119.6, 118.3, 118.1, 111.9, 77.2, 67.2, 60.6, 39.0, 37.3, 37.0, 29.5, 20.4, 14.5; **HRMS** calcd. for $C_{27}H_{29}N_4O_4$ $[M+H]^+$: 473.2183, found: 473.2184.



(*E*)-*N*,*N*,14-trimethyl-9-oxo-4-styryl-6,9,14,14a-tetrahydroindolo[3',2':3,4] pyrido[2,1-*b*]quinazoline-5(7*H*)-carboxamide (4b)

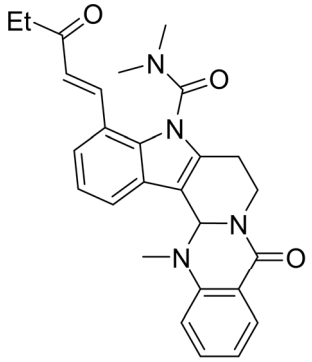
Faint yellow solid, 20 mg, 43% yield, m.p. 216-217 °C **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.2 (d, J = 16.2 Hz, 1H), 7.7-7.5 (m, 3H), 7.5 (d, J = 7.6 Hz, 1H), 7.4 (t, J = 7.8 Hz, 1H), 7.3 (t, J = 6.9 Hz, 4H), 7.2 (d, J = 7.8, 3.5 Hz, 2H), 7.1-7.0 (m, 2H), 6.1 (s, 1H), 4.9 (ddd, J = 12.9, 5.5, 2.1 Hz, 1H), 3.4 (ddd, J = 12.8, 11.1, 4.3 Hz, 1H), 3.2 (s, 3H), 3.1 (s, 3H), 3.1-3.0 (m, 1H), 3.0-2.9 (m, 1H), 2.4 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 164.4, 153.5, 152.0, 140.9, 137.7, 136.2, 132.0, 130.2, 129.9, 129.2, 129.1, 128.5, 127.4, 126.9, 126.5, 124.3, 123.0, 122.1, 121.5, 119.4, 117.7, 111.7, 66.8, 38.5, 37.1, 36.7, 29.3, 20.3; **HRMS** calcd. for $C_{30}H_{29}N_4O_2$ $[M+H]^+$: 477.2285, found: 477.2285.



diethyl (*E*)-(2-(5-(dimethylcarbamoyl)-14-methyl-9-oxo-5,6,7,9,14,14a-hexahydroindolo[3',2':3,4]pyrido[2,1-*b*]quinazolin-4-yl)vinyl)phosphonate (4c)

Faint yellow solid, 25 mg, 47% yield, m.p. 226-227 °C; **^{1}H NMR** (600 MHz, $CDCl_3$)

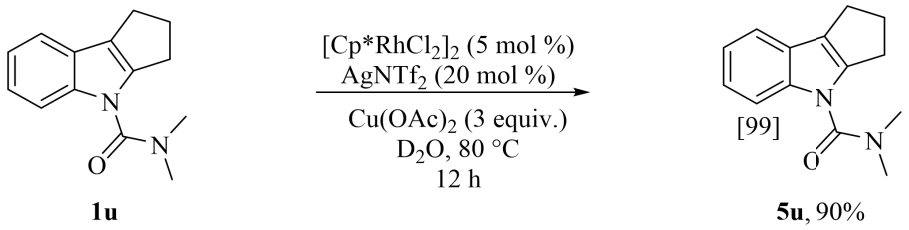
δ 8.3 (dd, J = 22.2, 17.5 Hz, 1H), 7.6 (d, J = 7.8 Hz, 1H), 7.4 (t, J = 7.8 Hz, 1H), 7.4-7.3 (m, 2H), 7.3 (d, J = 7.6 Hz, 1H), 7.2 (d, J = 7.9 Hz, 1H), 7.1-7.1 (m, 1H), 6.2-6.1 (m, 1H), 6.1 (s, 1H), 4.9 (ddd, J = 12.9, 5.4, 1.9 Hz, 1H), 4.2 (qd, J = 7.3, 3.0 Hz, 4H), 3.3 (ddd, J = 12.9, 11.3, 4.3 Hz, 1H), 3.1 (s, 3H), 3.1 (s, 3H), 3.0 (ddd, J = 14.0, 4.2, 2.1 Hz, 1H), 2.9 (dddd, J = 16.0, 11.4, 5.5, 1.7 Hz, 1H), 2.4 (s, 3H), 1.4 (td, J = 7.1, 5.0 Hz, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 163.5, 153.4, 151.7, 149.1, 138.6, 138.5, 136.1, 132.1, 126.4, 124.4, 124.0, 123.6, 121.6, 119.4, 117.8, 115.9, 114.6, 111.7, 77.2, 66.9, 62.0, 61.9, 38.7, 37.0, 36.7, 29.2, 20.2, 16.4, 16.3; **HRMS** calcd. for $C_{28}H_{33}N_4NaO_5P$ $[M+Na]^+$: 559.2081, found: 559.2075.



(*E*)-*N*,*N*,14-trimethyl-9-oxo-4-(3-oxopent-1-en-1-yl)-6,9,14,14a-tetrahydro indolo[3',2':3,4]pyrido[2,1-*b*]quinazoline-5(7*H*)-carboxamide (4d)

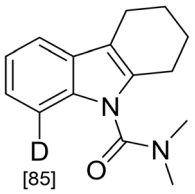
Yellow solid, 17 mg, 37% yield, m.p. 223-224 °C;**^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.57 (d, J = 16.4 Hz, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.43 (t, J = 7.8 Hz, 1H), 7.38-7.30 (m, 3H), 7.27-7.23 (m, 1H), 7.14 (dd, J = 8.0, 1.1 Hz, 1H), 6.49 (d, J = 16.4 Hz, 1H), 6.11 (s, 1H), 4.86 (ddd, J = 12.9, 5.4, 2.0 Hz, 1H), 3.35 (ddd, J = 12.9, 11.2, 4.3 Hz, 1H), 3.16 (s, 3H), 3.11 (s, 3H), 3.03 (ddt, J = 15.8, 4.1, 1.8 Hz, 1H), 2.96-2.90 (m, 1H), 2.90-2.85 (m, 1H), 2.85-2.78 (m, 1H), 2.47 (s, 3H), 1.19 (t, J = 7.3 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 202.5, 164.4, 153.9, 152.3, 144.1, 138.7, 136.6, 132.7, 130.3, 129.1, 126.9, 124.9, 124.5, 124.1, 122.5, 122.1, 119.9, 118.3, 112.2, 77.2, 67.4, 39.2, 37.5, 37.2, 32.7, 29.7, 20.7, 8.7; **HRMS** calcd. for $C_{27}H_{29}N_4O_3$ $[M+H]^+$: 457.2234, found: 457.2236.

2.4 The general procedure for rhodium-catalyzed deuteration



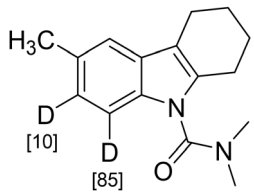
1u **5u**, 90%

An oven-dried screw cap reaction tube was charged with a magnetic stir-bar, substrate (0.1 mmol, 1.0 equiv.), $[Cp^*RhCl_2]_2$ (0.005 mmol, 5 mol%), $Cu(OAc)_2$ (0.3 mmol, 3.0 equiv.), and $AgNTf_2$ (0.02 mmol, 20 mol%) were taken. Subsequently, D_2O (0.5 mL) was added and the reaction mixture was stirred vigorously at 80 °C for 12 h. The reaction mixture was then diluted with EtOAc and filtered through celite pad. After evaporation of the solvent, the crude mixture was purified by preparative Thin-Layer Chromatography (petroleum ether/ethyl acetate = 3:1).



***N, N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide-8-*d* (5a)**

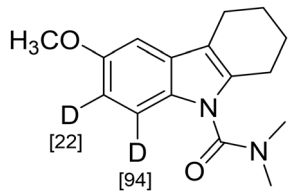
Faint yellow solid, 21 mg, 88% yield; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44 (d, J = 7.6 Hz, 1H), 7.23 (d, J = 8.1 Hz, 0.15H), 7.19 (d, J = 7.1 Hz, 1H), 7.14 (t, J = 7.4 Hz, 1H), 3.05 (s, 6H), 2.80 (t, J = 5.5 Hz, 2H), 2.73-2.63 (m, 2H), 1.96-1.83 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 154.5, 135.2, 134.9, 128.5, 122.1, 120.6, 117.9, 113.7, 111.2, 77.2, 37.8, 23.0, 22.9, 22.6, 20.8; **HRMS** calcd. for $C_{15}H_{18}DN_2O$ $[M+H]^+$: 244.1555, found: 244.1551.



***N,N*,6-trimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide-7,8-d_2 (5b)**

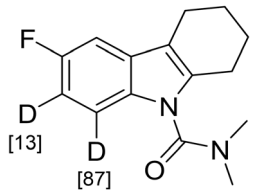
Yellow oil, 21 mg, 83% yield; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.22 (d, J = 1.5 Hz, 1H), 7.11 (d, J = 8.4 Hz, 0.15H), 7.00 (d, J = 1.6 Hz, 0.90H), 3.04 (s, 6H), 2.78 (s, 2H),

2.65 (td, J = 5.9, 2.0 Hz, 2H), 2.44 (s, 3H), 1.96-1.80 (m, 4H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 153.5, 135.1, 132.9, 129.2, 128.0, 123.4, 117.8, 112.3, 111.0, 39.5, 37.3, 22.6, 22.4, 22.4, 21.0, 20.4; **HRMS** calcd. for $C_{16}H_{20}DN_2O$ $[M+H]^+$: 258.1711, found: 258.1712.



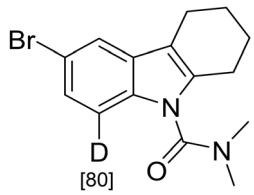
6-methoxy-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide-7,8-d_2 (5d)

Yellow oil, 22 mg, 80% yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.12 (d, J = 8.8 Hz, 0.06H), 6.89 (d, J = 2.5 Hz, 1H), 6.81 (d, J = 2.5 Hz, 0.78H), 3.85 (s, 3H), 3.03 (s, 6H), 2.79 (s, 2H), 2.70-2.58 (m, 2H), 1.95-1.77 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 154.8, 154.7, 136.2, 129.8, 129.3, 113.7, 110.9, 100.7, 100.7, 77.2, 55.7, 37.9, 23.1, 23.0, 22.7, 20.9; **HRMS** calcd. for $C_{16}H_{19}DN_2O_2$ $[M+H]^+$: 274.1660, found: 274.1655.



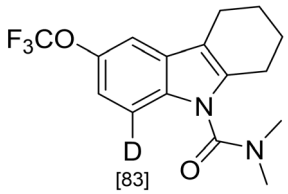
6-fluoro-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide-7,8-d_2 (5e)

Faint yellow oil, 22 mg, 85% yield; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.14 (dd, J = 8.9, 4.3 Hz, 0.13 H), 7.07 (dd, J = 9.1, 2.3 Hz, 1H), 6.90 (dd, J = 9.2, 2.6 Hz, 0.87 H), 3.03 (s, 6H), 2.78 (s, 2H), 2.67-2.57 (m, 2H), 1.94-1.80 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 158.4 (d, J = 235.0 Hz), 154.3, 137.1, 131.3, 129.3 (d, J = 10.0 Hz), 113.8, 111.8 (d, J = 8.8 Hz), 109.6 (d, J = 26.2 Hz), 103.4 (d, J = 23.8 Hz), 77.2, 37.8, 23.0, 22.9, 22.5, 20.7; **HRMS** calcd. for $C_{15}H_{17}DFN_2O$ $[M+H]^+$: 262.1460, found: 262.1459.



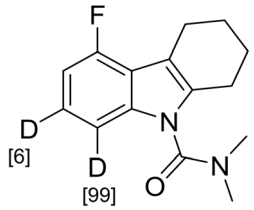
6-bromo-*N,N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide-8-*d* (5g)

Faint yellow oil, 24 mg, 76% yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.55 (d, J = 2.0 Hz, 1H), 7.25 (d, J = 1.9 Hz, 1H), 7.09 (d, J = 8.6 Hz, 0.20H), 3.02 (s, 6H), 2.78 (s, 2H), 2.69-2.58 (m, 2H), 1.94-1.77 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 154.1, 136.7, 133.5, 130.3, 124.8, 120.8, 113.9, 113.3, 112.6, 77.2, 37.8, 22.9, 22.8, 22.5, 20.6; **HRMS** calcd. for $C_{15}H_{17}DBrN_2O$ $[M+H]^+$: 322.0660, found: 322.0652.



***N,N*-dimethyl-6-(trifluoromethoxy)-1,2,3,4-tetrahydro-9*H*-carbazole-9-carbo xamide-8-*d* (5h)**

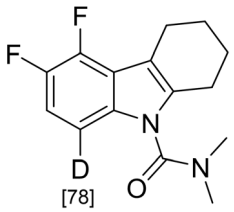
Faint yellow oil, 26 mg, 79% yield; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.41 (d, J = 2.3 Hz, 1H), 7.38–7.34 (m, 0.17H), 7.12 (d, J = 2.3 Hz, 1H), 2.96 (s, 6H), 2.70 (d, J = 6.0 Hz, 2H), 2.63 (t, J = 5.9 Hz, 2H), 1.87–1.75 (m, 4H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ 153.3, 143.2, 137.9, 133.4, 130.1, 128.8, 119.8, 115.7, 113.3, 110.9, 39.5, 37.8, 22.9, 22.8, 22.7, 20.7; **HRMS** calcd. for $C_{16}H_{17}DF_3N_2O_2$ $[M+H]^+$: 328.1378, found: 328.1377.



5-fluoro-*N,N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide-7,8-d_2 (5i)

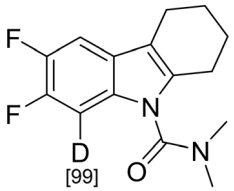
Yellow oil, 21 mg, 82% yield; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32 (dd, J = 8.6, 5.4

Hz, 1H), 6.89 (t, *J* = 9.0 Hz, 0.94H), 3.04 (s, 6H), 2.76 (s, 2H), 2.69-2.60 (m, 2H), 1.94-1.79 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 159.9 (d, *J* = 236.2 Hz), 154.2, 135.5, 134.9 (d, *J* = 11.2 Hz) 125.0, 118.4 (d, *J* = 11.0 Hz), 113.6, 108.8 (d, *J* = 23.8 Hz), 98.2 (q, *J* = 25.6 Hz), 77.2, 37.8, 22.9, 22.9, 22.5, 20.7; **HRMS** calcd. for $C_{15}H_{17}DFN_2O$ $[M+H]^+$: 262.1460, found: 262.1457.



5,6-difluoro-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide-8-*d* (5m)

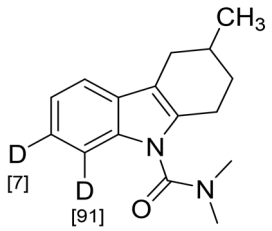
Faint yellow solid, 22 mg, 78% yield; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.94 (dd, *J* = 10.8, 7.4 Hz, 1H), 6.88 (dd, *J* = 8.9, 3.4 Hz, 0.22H), 3.02 (s, 6H), 2.89-2.81 (m, 2H), 2.74 (s, 2H), 1.94-1.77 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 153.8, 145.0 (dd, *J* = 231.2, 7.5 Hz), 143.3 (dd, *J* = 245.0, 12.5 Hz), 136.6, 132.5 (d, *J* = 8.8 Hz), 118.3 (d, *J* = 17.5 Hz), 112.1, 110.9 (d, *J* = 21.2 Hz), 106.4 (q, *J* = 3.8 Hz), 77.2, 37.7, 22.9, 22.6, 22.4, 22.0; **HRMS** calcd. for $C_{15}H_{16}DF_2N_2O$ $[M+H]^+$: 280.1366, found: 280.1360.



6,7-difluoro-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide-8-*d* (5n)

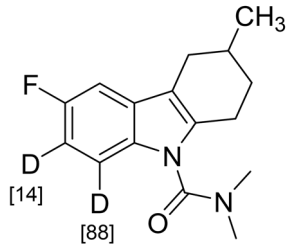
Faint yellow solid, 23 mg, 81% yield; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.19 (dd, *J* = 10.4, 7.7 Hz, 1H), 3.08 (s, 6H), 2.80 (s, 2H), 2.68-2.59 (m, 2H), 1.97-1.87 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 154.0, 147.6 (dd, *J* = 238.8, 15.0 Hz), 146.7 (dd, *J* = 238.1, 15.0 Hz), 136.7, 129.9 (d, *J* = 10.0 Hz), 123.9 (d, *J* = 6.2 Hz), 113.6, 104.9 (d, *J* = 18.8 Hz), 99.8 (d, *J* = 9.5 Hz), 77.2, 37.8, 23.0, 22.7, 22.4, 20.7; **HRMS** calcd. for

$C_{15}H_{16}DF_2N_2O$ $[M+H]^+$: 280.1366, found: 280.1362.



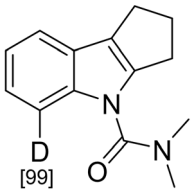
***N,N*,3-trimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide-7,8-d_2 (5o)**

Yellow oil, 23 mg, 91% yield; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43 (dd, J = 7.7, 1.4 Hz, 1H), 7.23 (dd, J = 8.1, 1.5 Hz, 0.09H), 7.19 (d, J = 7.6 Hz, 1H), 7.14 (t, J = 7.4 Hz, 1H), 3.06 (s, 3H), 3.03 (s, 3H), 2.84 (d, J = 5.6 Hz, 2H), 2.81 (d, J = 5.3 Hz, 1H), 2.33-2.20 (m, 1H), 2.02-1.90 (m, 2H), 1.65-1.48 (m, 1H), 1.14 (d, J = 6.5 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 155.1, 135.6, 135.5, 128.9, 122.5, 121.1, 118.4, 114.2, 111.8, 77.2, 38.5, 38.2, 31.7, 29.7, 29.5, 23.1, 22.0; **HRMS** calcd. for $C_{16}H_{20}DN_2O$ $[M+H]^+$: 258.1711, found: 258.1703.



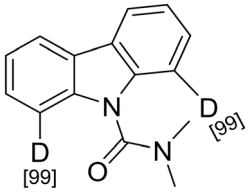
6-fluoro-*N,N*,3-trimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide-7,8-d_2 (5p)

Yellow solid, 22 mg, 81% yield; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.18-7.13 (m, 0.12H), 7.06 (dd, J = 9.1, 2.5 Hz, 1H), 6.90 (dd, J = 9.3, 2.6 Hz, 1H), 3.04 (s, 3H), 3.02 (s, 3H), 2.81 (s, 2H), 2.79-2.71 (m, 1H), 2.26-2.16 (m, 1H), 2.00-1.91 (m, 2H), 1.58-1.48 (m, 1H), 1.13 (d, J = 6.5 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 158.4 (d, J = 235.0 Hz), 154.4, 136.9, 131.5, 129.2, 129.1, 113.7, 109.6 (d, J = 25.0 Hz), 103.4 (d, J = 23.8 Hz), 77.2, 38.0, 37.7, 31.1, 29.1, 29.0, 22.7, 21.5; **HRMS** calcd. for $C_{16}H_{19}DFN_2O$ $[M+H]^+$: 276.1617, found: 276.1611.



***N,N*-dimethyl-2,3-dihydrocyclopenta[*b*]indole-4(1*H*)-carboxamide-5-*d* (5u)**

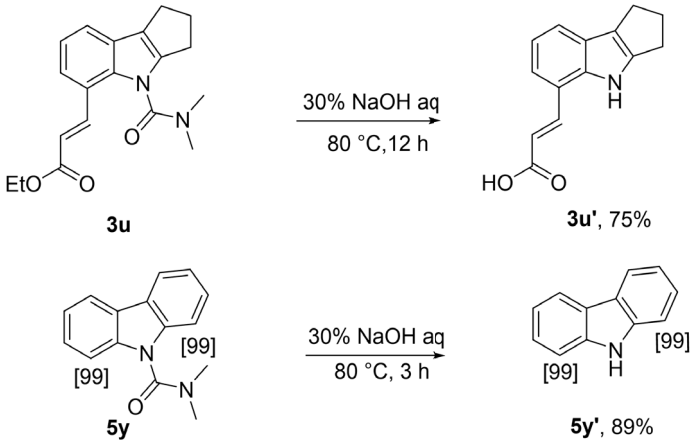
Yellow solid, 20 mg, 90% yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.41 (dd, J = 7.5, 1.5 Hz, 1H), 7.20-7.12 (m, 2H), 3.06 (s, 6H), 3.00-2.94 (m, 2H), 2.83-2.76 (m, 2H), 2.53 (p, J = 7.2 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 155.0, 144.8, 139.9, 125.8, 123.0, 121.7, 121.2, 118.8, 113.0, 77.2, 38.2, 27.9, 26.6, 24.1; **HRMS** calcd. for $C_{14}H_{16}DN_2O$ $[M+H]^+$: 230.1398, found: 230.1398.



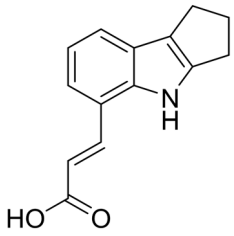
***N,N*-dimethyl-9*H*-carbazole-9-carboxamide-1,8-*d*$_2$ (5y)**

Yellow oil, 22 mg, 94% yield; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.05 (dd, J = 7.8, 1.2 Hz, 2H), 7.47 (dd, J = 7.2, 1.2 Hz, 2H), 7.31 (t, J = 7.5 Hz, 2H), 3.12 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 154.8, 138.5, 126.3, 124.3, 121.4, 120.1, 112.3, 77.2, 38.0; **HRMS** calcd. for $C_{15}H_{13}D_2N_2O$ $[M+H]^+$: 241.1304, found: 241.1301.

2.5 The utility of this method - removal of template



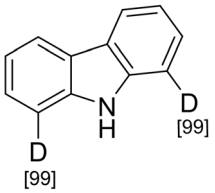
A sealable tube with a magnetic stir bar was charged with **3u** and **5y** (0.25 mmol), EtOH (2.8 mL) and 30% sodium hydroxide solution (0.9 mL). The tube was then capped and the mixture was stirred at 80 °C. The mixture was then stirred at 80 ºC for 3-12 h, then the solution was cooled to ambient temperature, concentration, acidified to pH = 5-6 using 1N HCl, and extracted with ethyl acetate for 3 times. The combined organic phases were dried over anhydrous $MgSO_4$. The solvent was concentrated and the residue was purified by preparative Thin-Layer Chromatography (petroleum ether/ethyl acetate = 2:1) to provide the desired products.



(*E*)-3-(1,2,3,4-tetrahydrocyclopenta[*b*]indol-5-yl)acrylic acid (3u')

Yellow solid, 43 mg, 75% yield, m.p. 150-151 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.09 (d, J = 15.9 Hz, 1H), 7.49 (d, J = 7.8 Hz, 1H), 7.33 (d, J = 7.6 Hz, 1H), 7.11 (t, J = 7.7 Hz, 1H), 6.49 (d, J = 16.0 Hz, 1H), 2.90 (t, J = 7.2 Hz, 2H), 2.86-2.79 (m, 2H), 2.55 (p, J = 7.2 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 172.0, 144.6, 143.6, 139.5, 125.7, 121.5, 121.0, 120.4, 119.6, 117.8, 116.3, 77.2, 28.6, 25.8,

24.3; **HRMS** calcd. for $C_{14}H_{12}NO_2$ $[M-H]^-$: 226.0874, found: 226.0876.

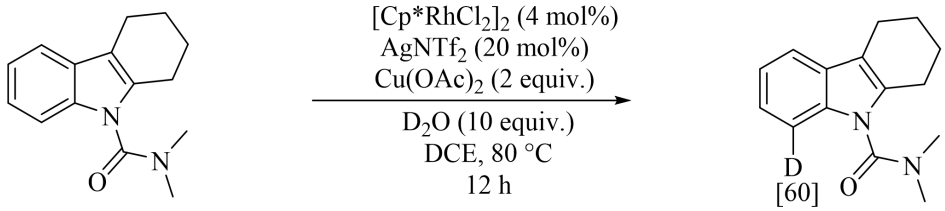


9*H*-carbazole-1,8-d2 (5y')

White solid, 38 mg, 89% yield; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.15-8.07 (m, 2H), 8.05 (s, 1H), 7.43 (d, J = 7.2 Hz, 2H), 7.25 (s, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 139.3, 125.6, 123.2, 120.2, 119.3, 110.4, 77.2; **HRMS** calcd. for $C_{12}H_6D_2N$ $[M-H]^-$: 168.0788, found: 168.0787.

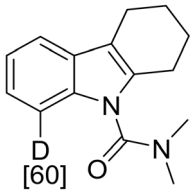
2.6. Mechanistic Studies

2.6.1 H/D exchange experiment

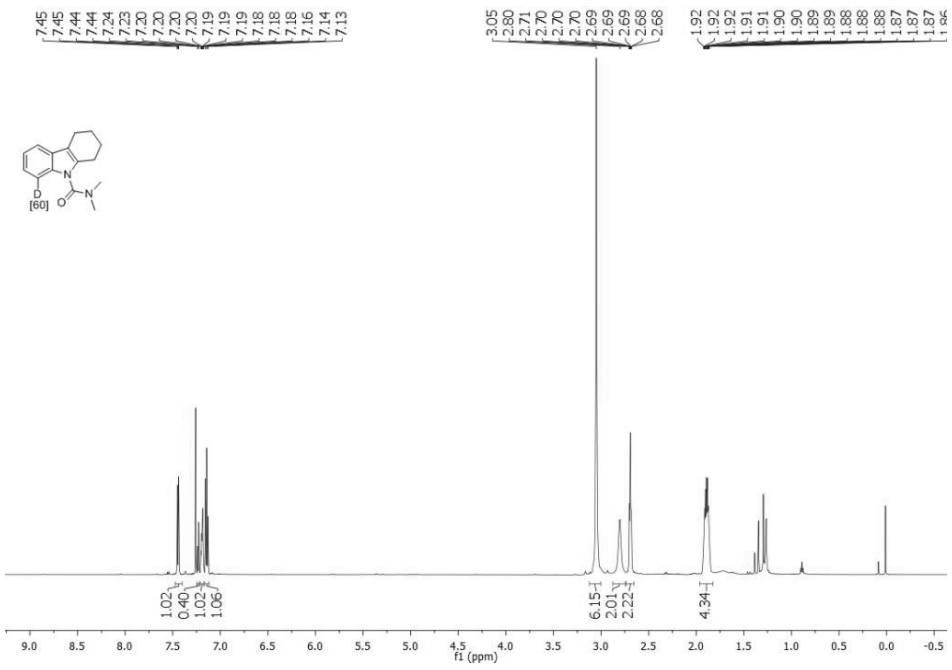


1a

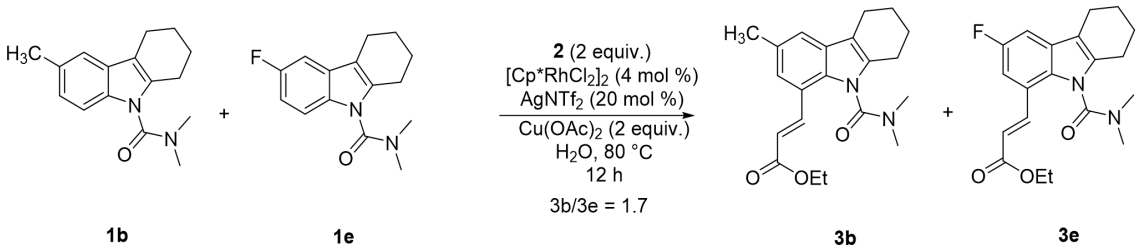
An oven-dried screw cap reaction tube was charged with a magnetic stir-bar, substrate (0.1 mmol, 1.0 equiv.), D_2O (0.3 mL), $[Cp^*RhCl_2]_2$ (0.004 mmol, 4 mol%), $Cu(OAc)_2$ (0.2 mmol, 2.0 equiv.), $AgNTf_2$ (0.02 mmol, 20 mol%) and DCE (0.7 mL) were taken. The reaction mixture was stirred vigorously at 80 °C for 12 h. The reaction mixture was then diluted with EtOAc and filtered through celite pad. After evaporation of the solvent, the crude mixture was purified by preparative Thin-Layer Chromatography (petroleum ether/ethyl acetate = 3:1).



Faint yellow oil, 21 mg, 87% yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.45 (dd, J = 7.7, 1.3 Hz, 1H), 7.23 (d, J = 8.1 Hz, 0.40H), 7.21-7.17 (m, 1H), 7.14 (t, J = 7.4 Hz, 1H), 3.05 (s, 6H), 2.80 (s, 2H), 2.69 (tt, J = 5.7, 1.9 Hz, 2H), 1.96-1.82 (m, 4H).

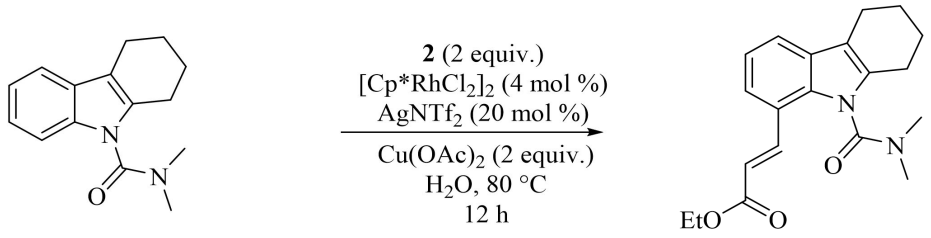


2.6.2 Intermolecular competitive experiments



The mixture of **1b** (0.1 mmol, 1 equiv.) & **1e** (0.1 mmol, 1 equiv.), ethyl acrylate (**2**, 0.2 mmol, 2 equiv.), $[Cp^*RhCl_2]_2$ (0.004 mmol, 4 mol%), $AgNTf_2$ (0.2 mmol, 20 mol%), $Cu(OAc)_2$ (0.2 mmol, 2.0 equiv.) and H_2O (1 mL) were added into the tube and sealed. The reaction mixture was vigorously stirred at 80 ºC for 12 h. Then, the reaction mixture was then diluted with EtOAc and filtered through celite pad. After evaporation of the solvent, the crude mixture was purified by preparative Thin-Layer Chromatography (TLC).

2.6.3 Radical trapping experiments



1a **3a**, 82%

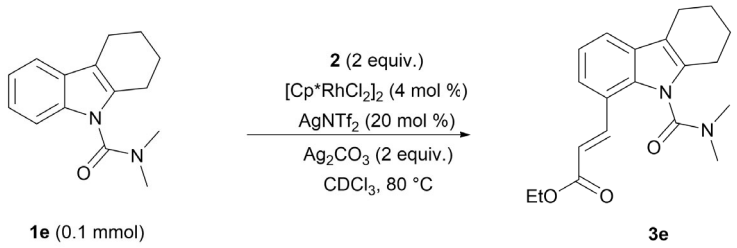
An oven-dried screw cap reaction tube was charged with a magnetic stir-bar, **1a** (0.1 mmol, 1.0 equiv.), **2** (0.2 mmol, 2.0 equiv.), $[Cp^*RhCl_2]_2$ (0.004 mmol, 4 mol%), $Cu(OAc)_2$ (0.2 mmol, 2.0 equiv.), $AgNTf_2$ (0.02 mmol, 20 mol%) and different proportions of free radical scavenger were taken. Subsequently, H_2O (1 mL) was added and the reaction mixture was stirred vigorously at 80 °C for 12 h. The reaction mixture was then diluted with EtOAc and filtered through celite pad. After evaporation of the solvent, NMR yields of **3a** were measured with an internal standard of CH_2Br_2 (0.1 mmol).

2.6.4 NMR studies:

2.6.4.1 Real-time on-line ^{1}H NMR momitoring of substrate-Rh-NaOAc interaction

In a clean NMR tube the substrate **1e** (1 equiv.) was added to 500 µl of $CDCl_3$. The ^{1}H NMR and ^{19}F NMR of **1e** was recorded. Then $[Cp^*RhCl_2]_2$ (0.25 equiv.) was added and put for sonication for 30 min at 80 °C. The ^{1}H NMR and ^{19}F NMR of the reaction mixture was recorded. Then NaOAc (4 equiv.) was added and put for sonication for 30 min at 80 °C. The ^{1}H NMR and ^{19}F NMR of the reaction mixture was recorded.

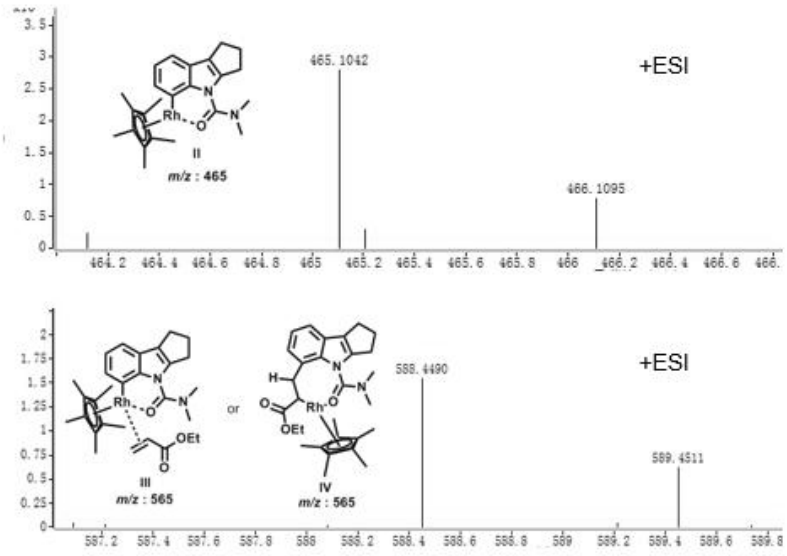
2.6.4.2 C-H olefination monitored by ^{1}H NMR and ^{19}F NMR spectroscopy



An oven-dried screw cap reaction tube was charged with a magnetic stir-bar, **1a** (0.1 mmol, 1.0 equiv.), **2** (0.2 mmol, 2.0 equiv.), $[Cp^*RhCl_2]_2$ (0.004 mmol, 4 mol%), Ag_2CO_3 (0.2 mmol, 2.0 equiv.), $AgNTf_2$ (0.02 mmol, 20 mol%) and different proportions of free radical scavenger were taken. Subsequently, $CDCl_3$ (1 mL) was added and the reaction mixture was stirred vigorously at 80 °C. The ^{1}H NMR and ^{19}F NMR of the reaction mixture was recorded at 0 h, 1.5 h, 2.5 h, 3.5 h, 6 h.

2.6.5 ESI-MS studies:

2.6.5.1 ESI-MS study to detect the monomeric Rh-substrate complex II



An oven-dried screw cap reaction tube was charged with a magnetic stir-bar, **1u**

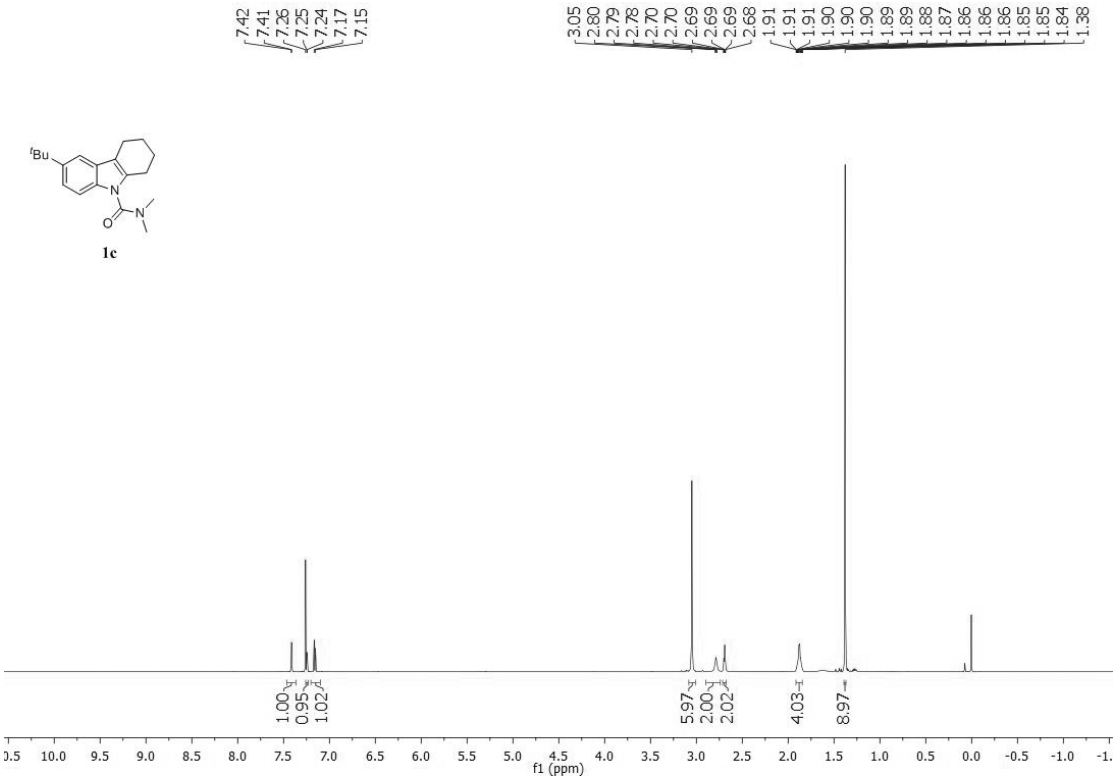
(0.1 mmol, 1 equiv.), $[Cp^*RhCl_2]_2$ (0.1 mmol, 1 equiv.), and NaOAc (0.3 mmol, 3 equiv.) were taken. Subsequently, DCE (1 mL) was added and the reaction mixture was stirred at 80 °C for 12 h. After evaporation of the solvent, ESI-MS analysis of the mixture was undertaken.

2.6.5.2 ESI-MS study to detect the monomeric Rh-substrate-olefin complex III or IV

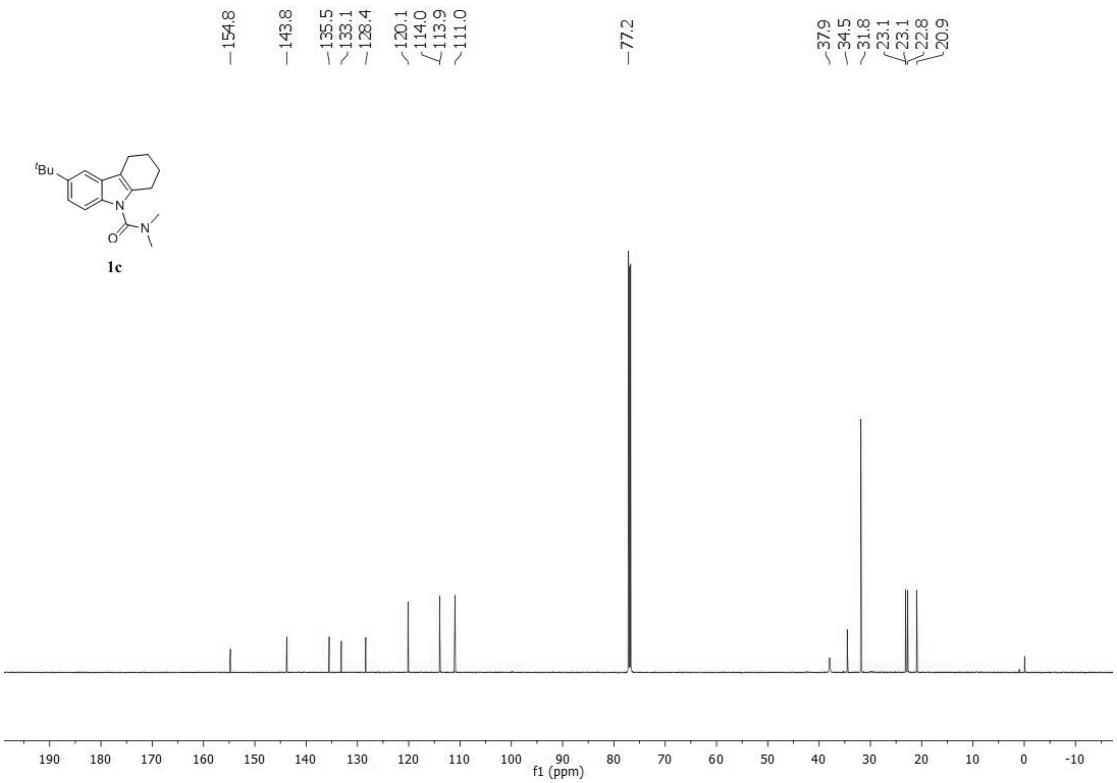
An oven-dried screw cap reaction tube was charged with a magnetic stir-bar, **1u** (0.1 mmol, 1 equiv.), $[Cp^*RhCl_2]_2$ (0.1 mmol, 1 equiv.), NaOAc (0.3 mmol, 3 equiv.) and **2** (0.2 mmol, 2 equiv.) were taken. Subsequently, DCE (1 mL) was added and the reaction mixture was stirred at 80 °C for 12 h. After evaporation of the solvent, ESI-MS analysis of the mixture was undertaken.

3. Spectra for new compounds

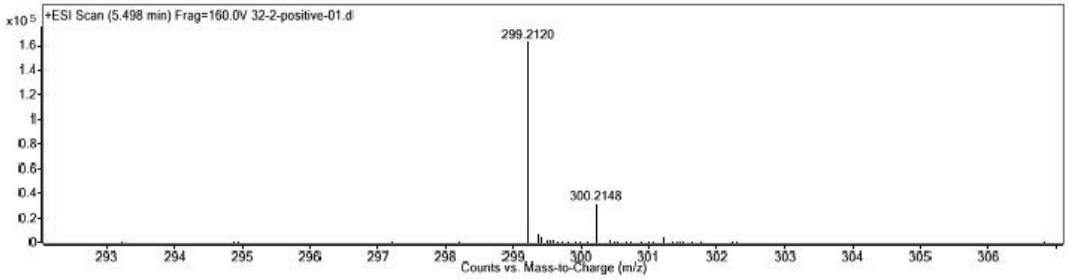
^{1}H NMR spectra of compound **1c**



^{13}C NMR spectra of compound **1c**



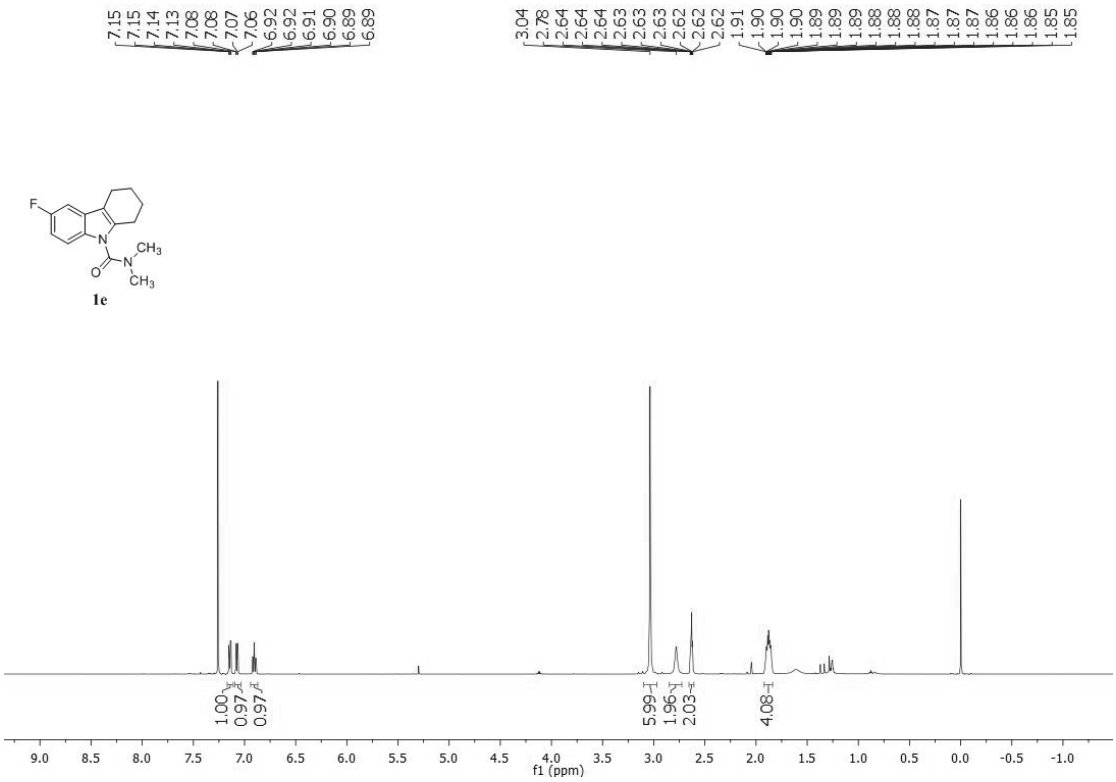
HRMS spectrum of compound **1c**



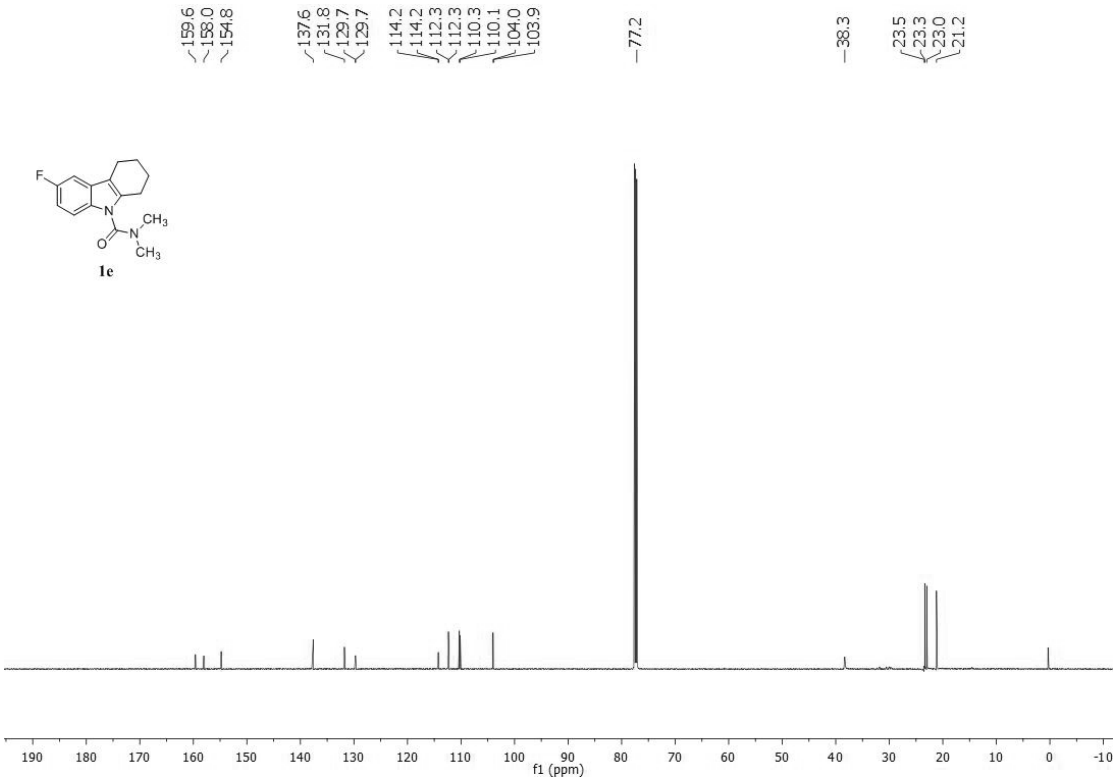
Elemental Composition Calculator

Target m/z:	299.2120	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C19H27N2O		299.2118		-0.85	

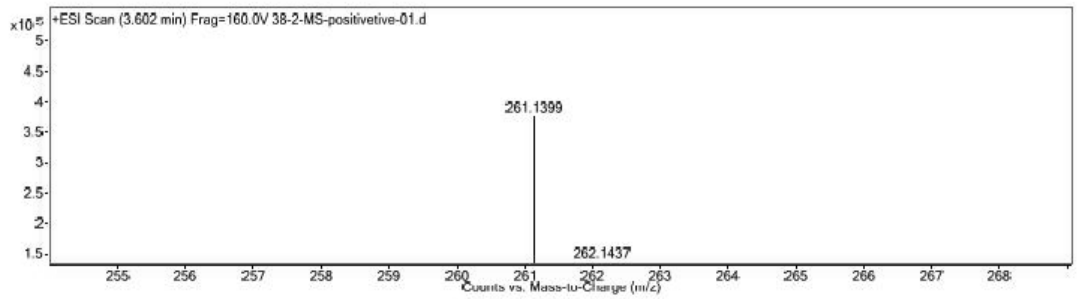
^{1}H NMR spectra of compound **1e**



^{13}C NMR spectra of compound **1e**



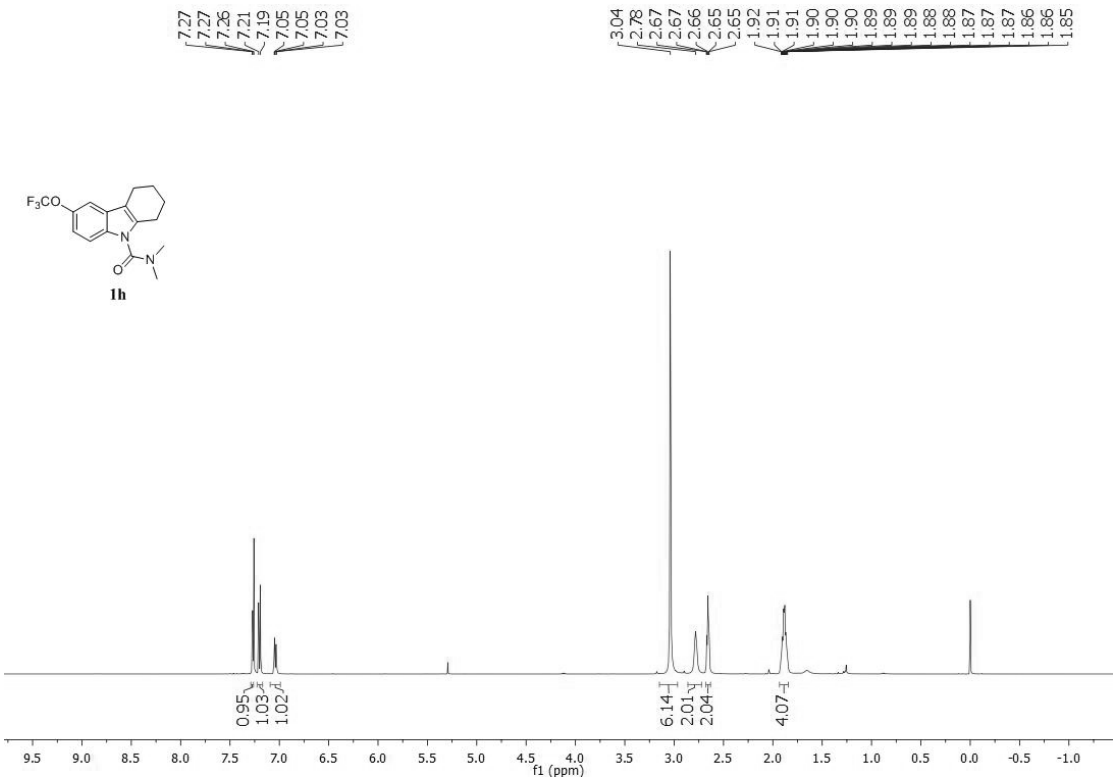
HRMS spectrum of compound **1e**



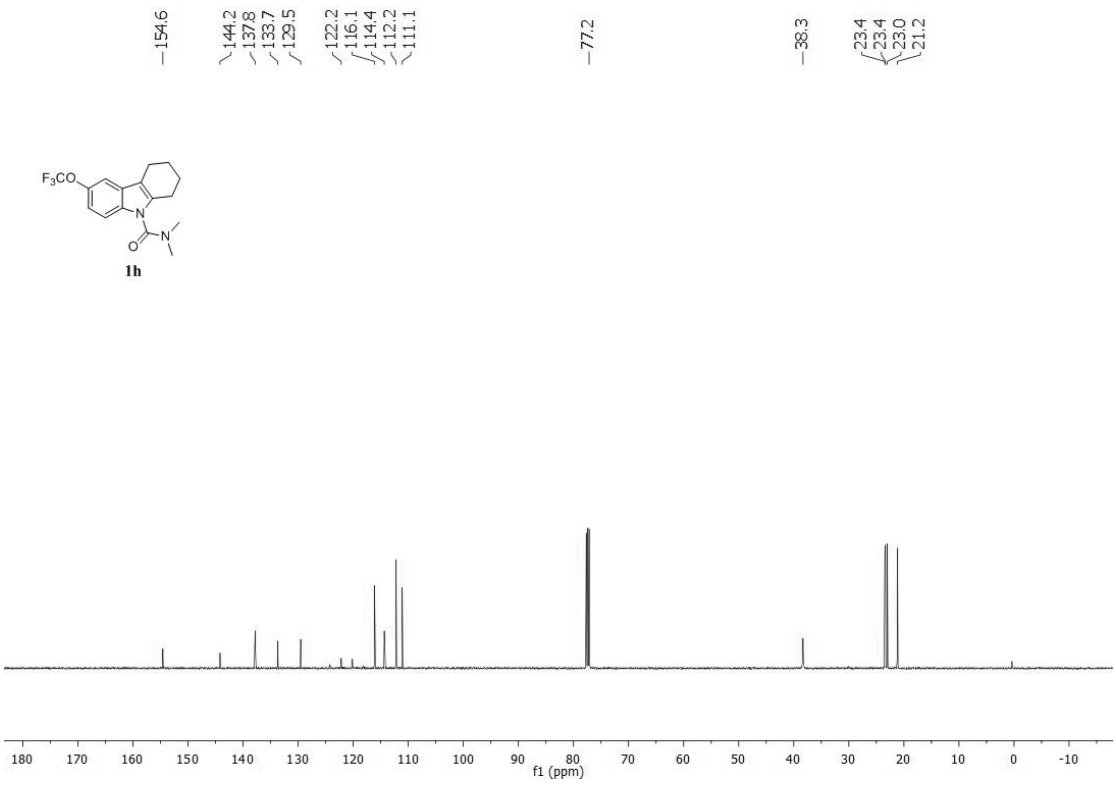
Elemental Composition Calculator

Target m/z:	261.1399	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5); F(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C15H18FN2O		261.1398		-0.42	

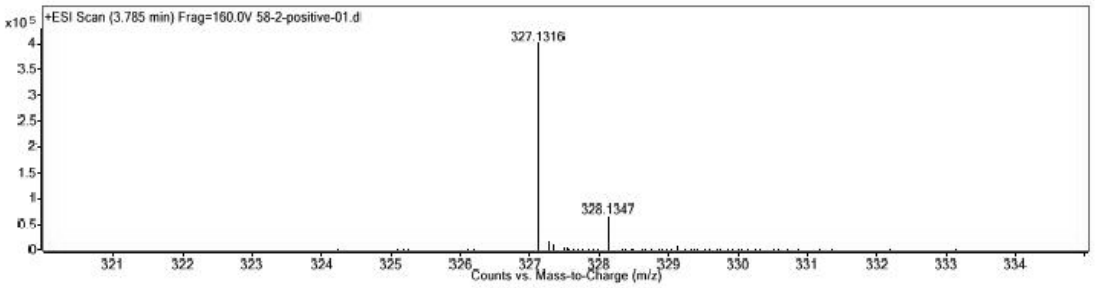
^{1}H NMR spectra of compound **1h**



^{13}C NMR spectra of compound **1h**



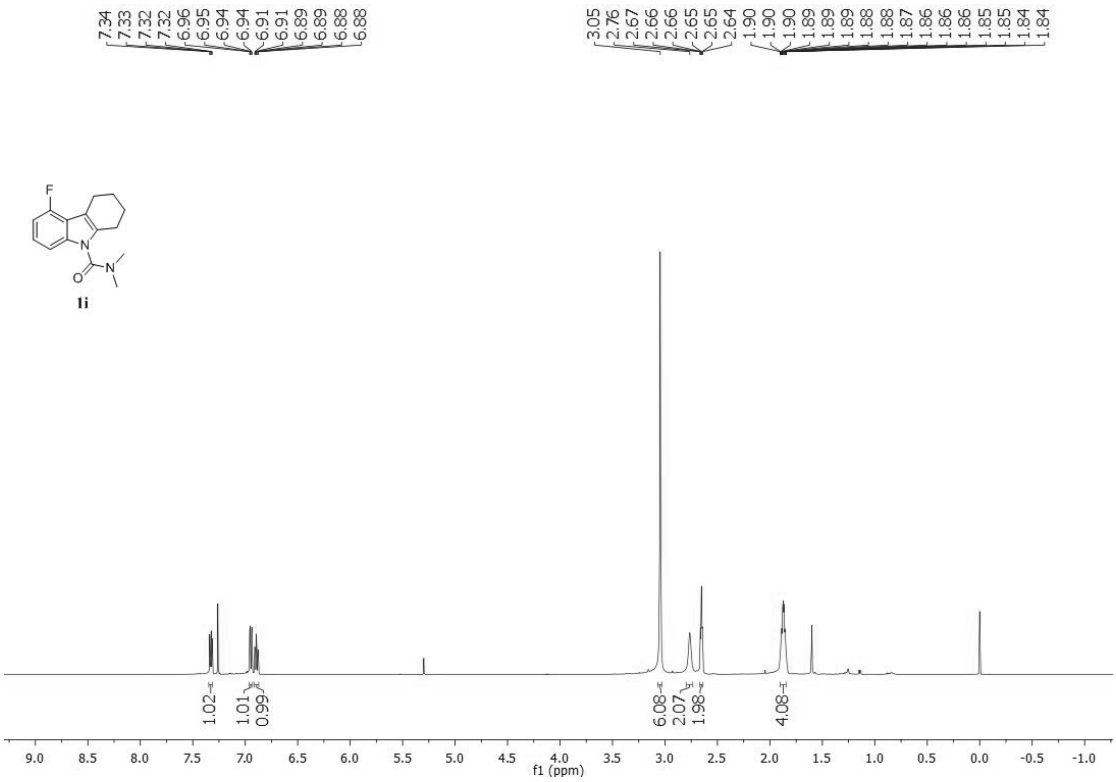
HRMS spectrum of compound **1h**



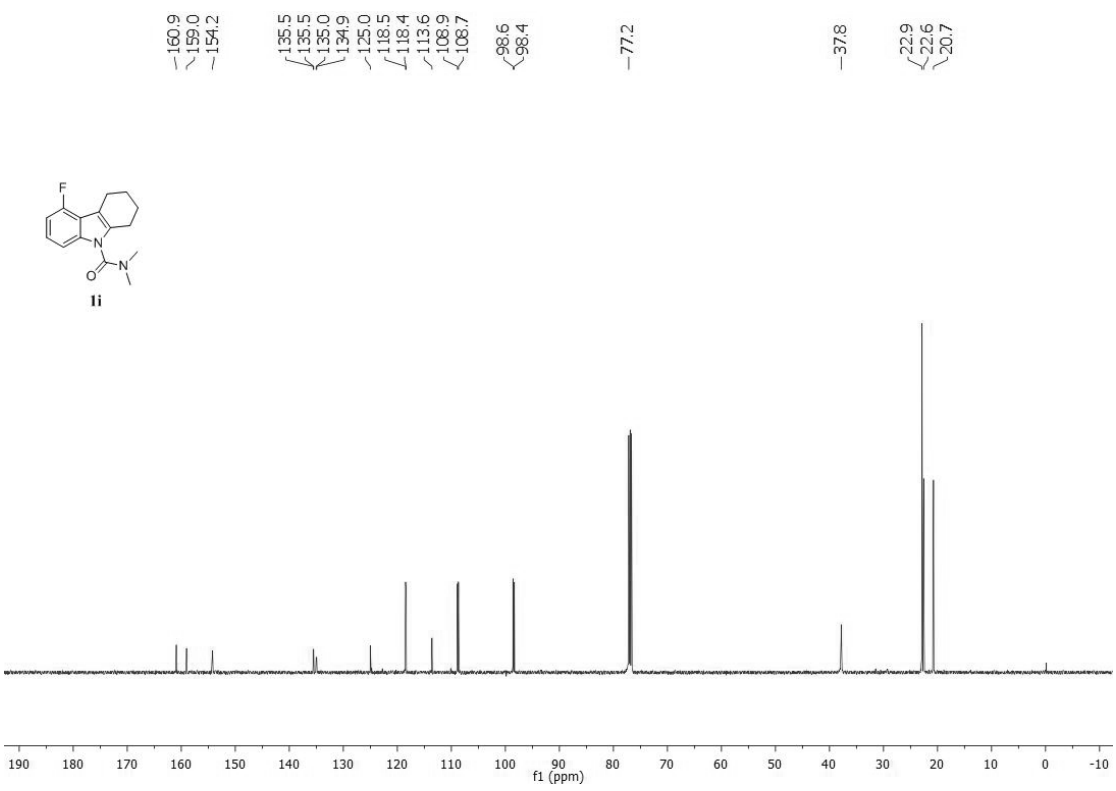
Elemental Composition Calculator

Target m/z:	327.1316	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5); F(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C16H18F3N2O2		327.1315		-0.25	

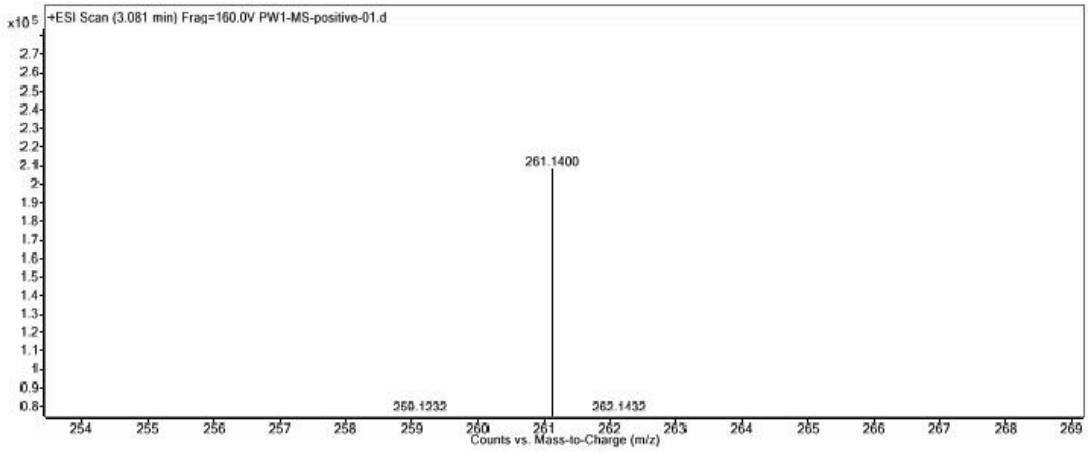
^{1}H NMR spectra of compound **1i**



^{13}C NMR spectra of compound **1i**



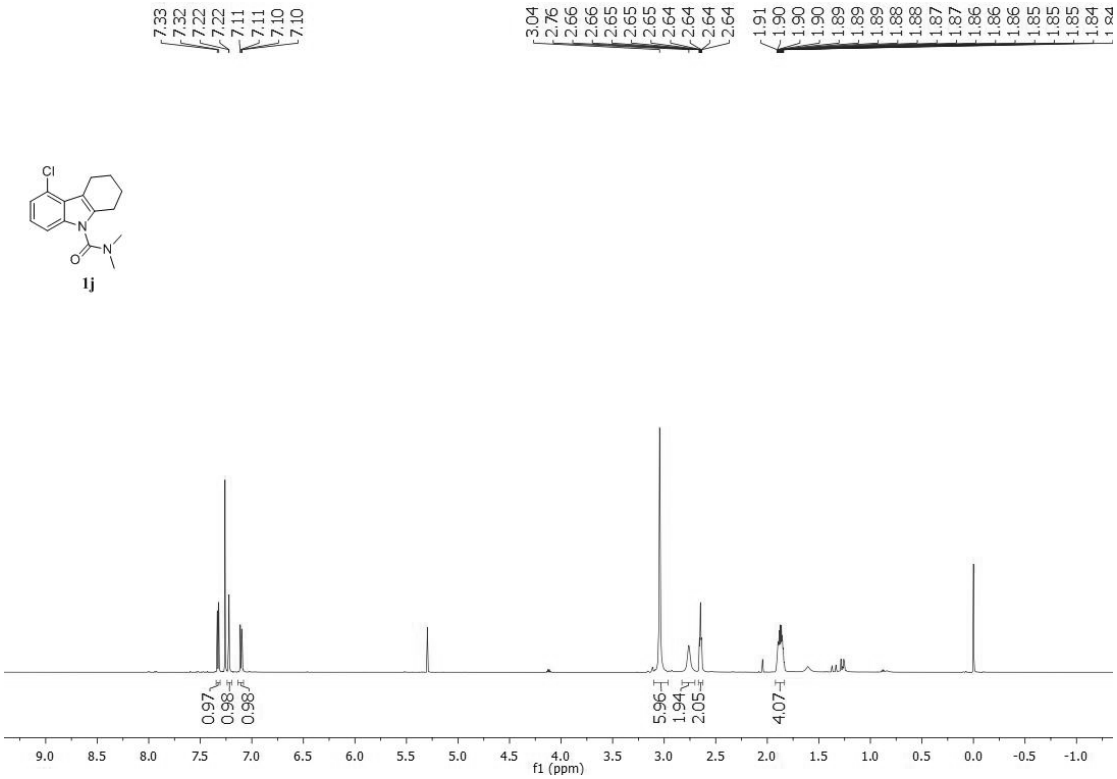
HRMS spectrum of compound **1i**



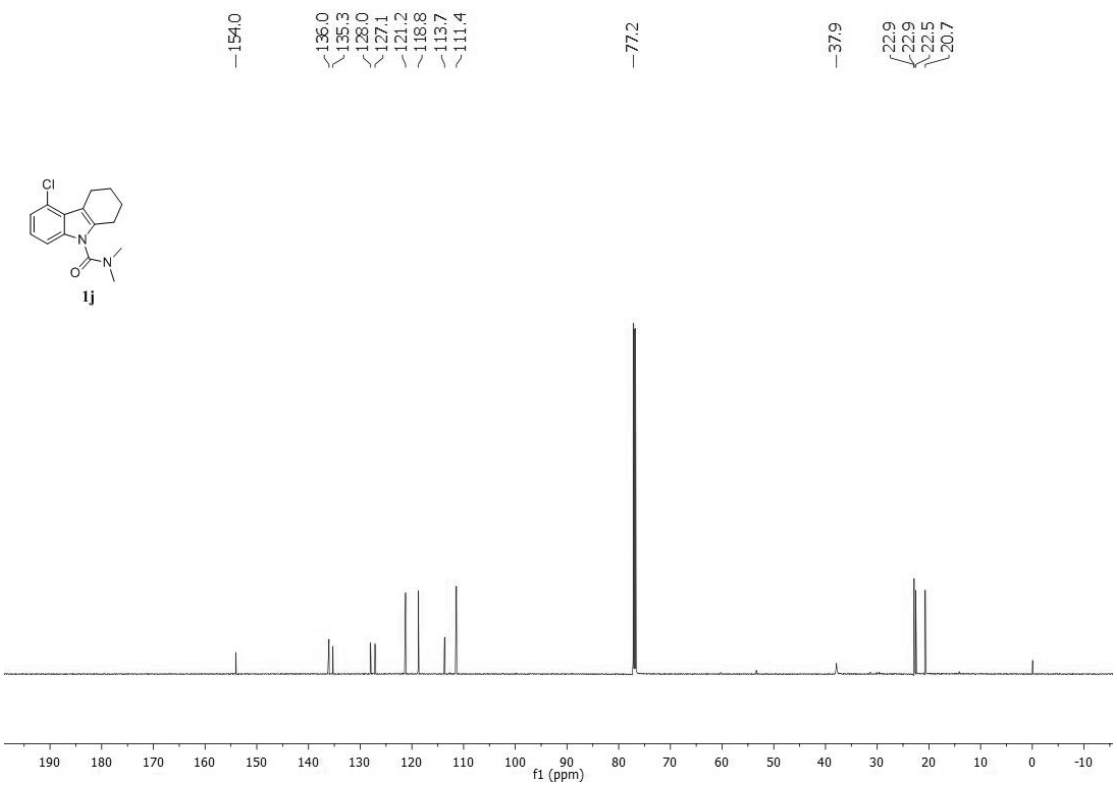
Elemental Composition Calculator

Target m/z:	261.1400	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30); F (0-5); N (0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C15H18FN2O		261.1398		-0.85	

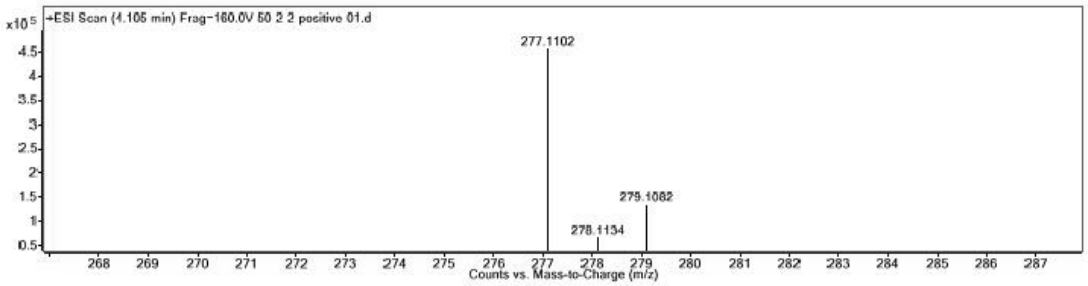
^{1}H NMR spectra of compound **1j**



^{13}C NMR spectra of compound **1j**



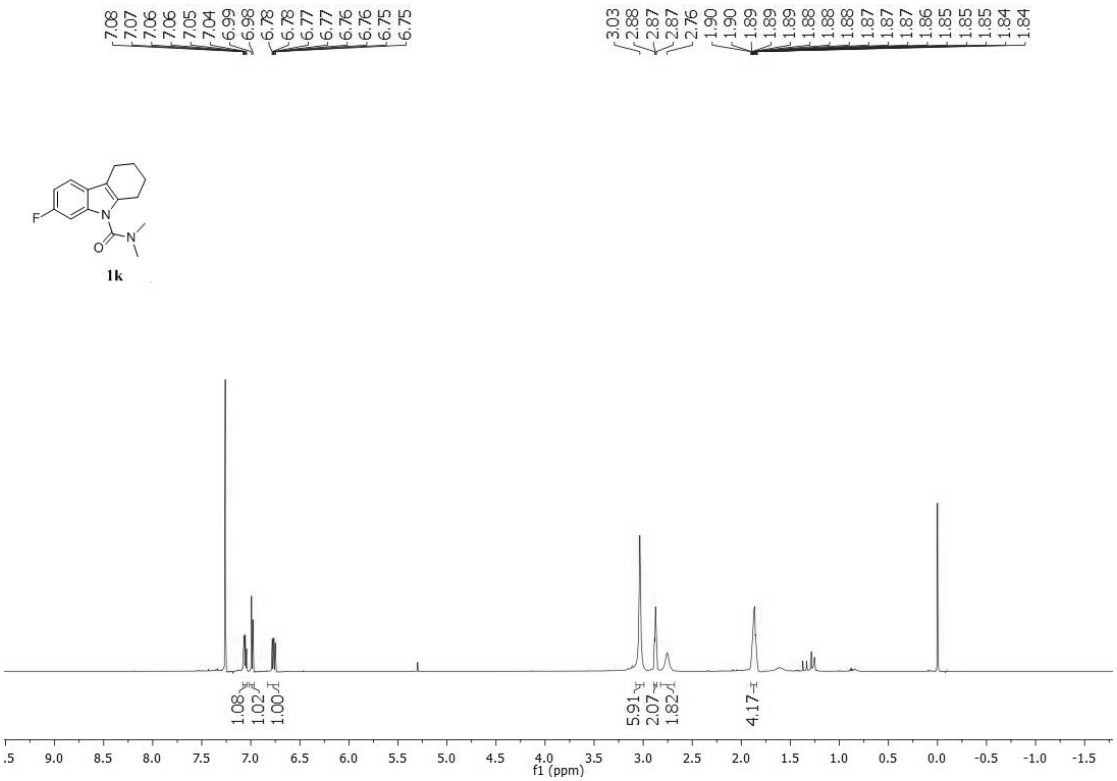
HRMS spectrum of compound **1j**



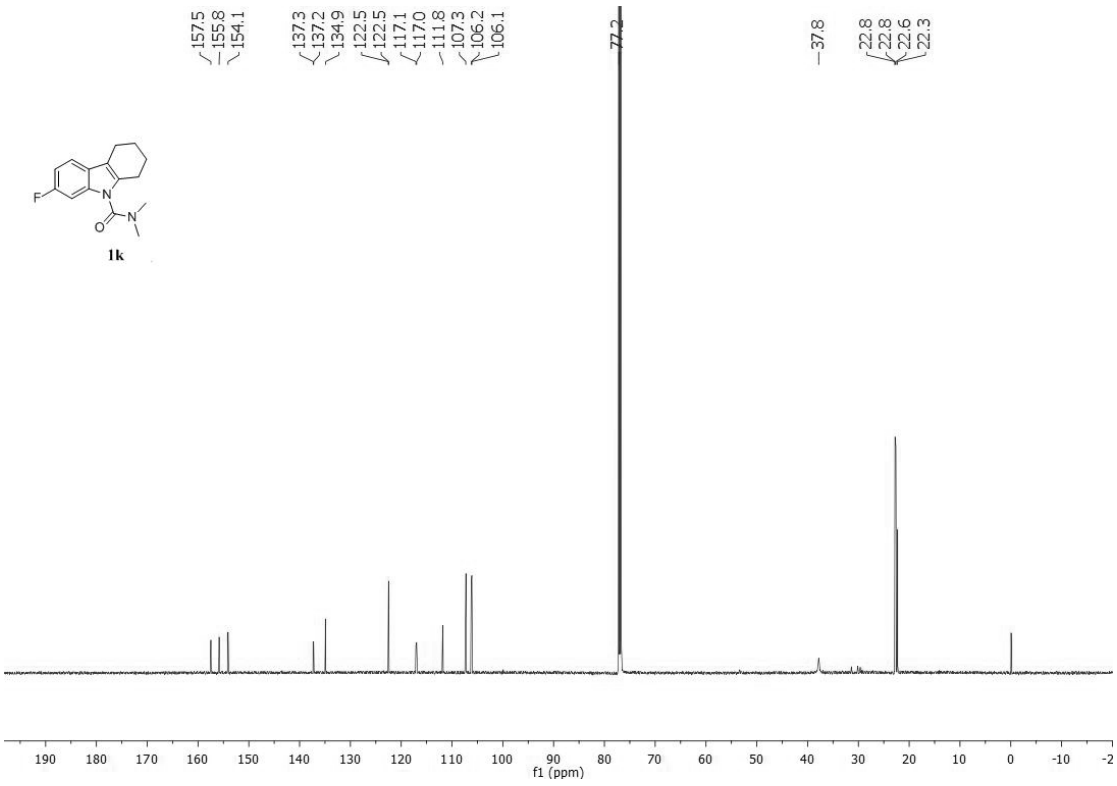
Elemental Composition Calculator

Target m/z:	277.1102	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5) ; Cl(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C15H18ClN2O		277.1102		-0.01	

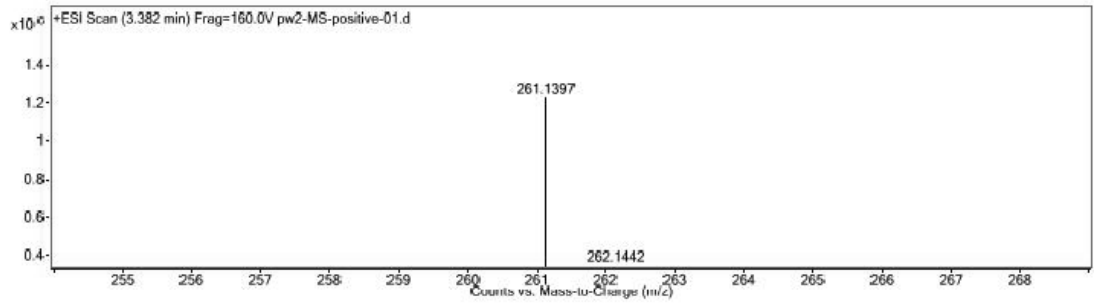
^{1}H NMR spectra of compound **1k**



^{13}C NMR spectra of compound **1k**



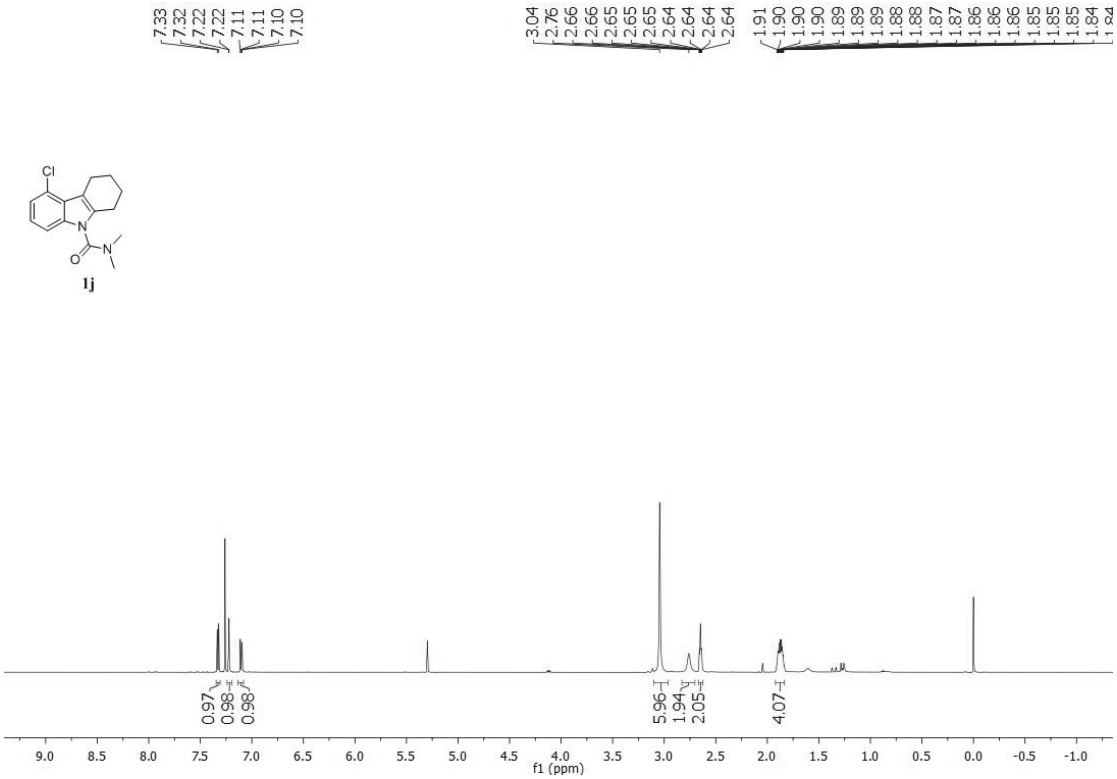
HRMS spectrum of compound **1k**



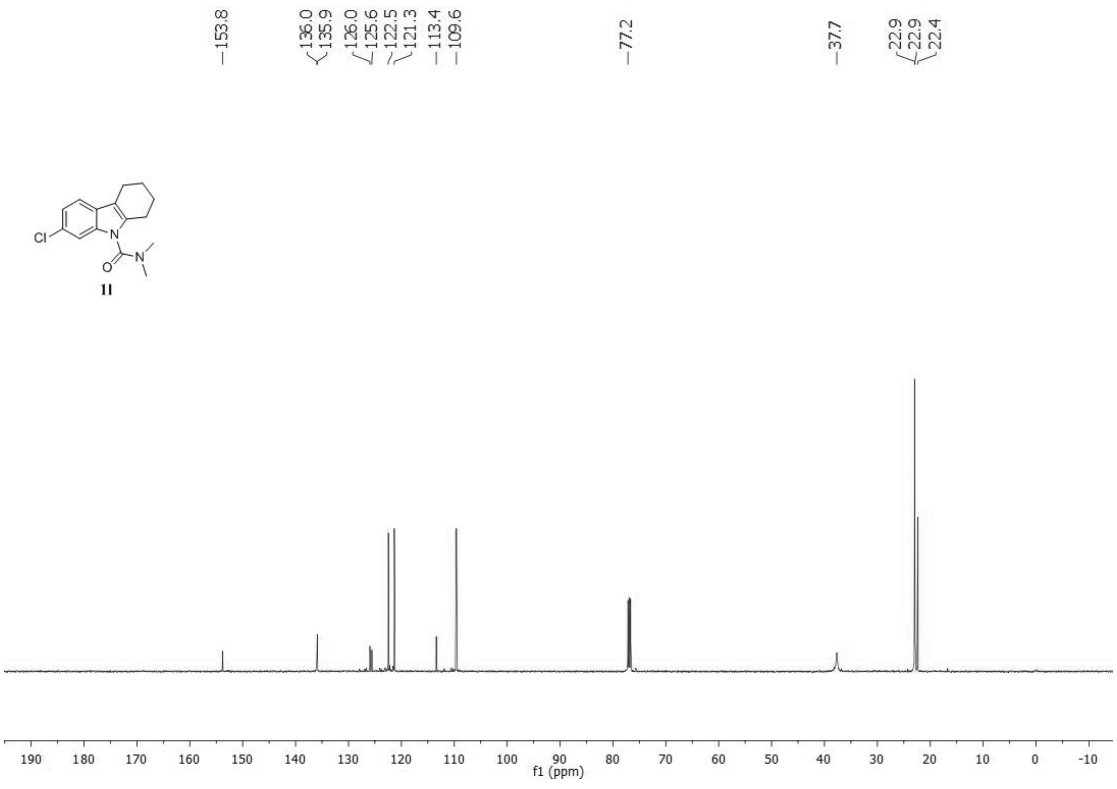
Elemental Composition Calculator

Target m/z:	261.1397	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5) ; F(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C15H18FN2O		261.1398		0.44	

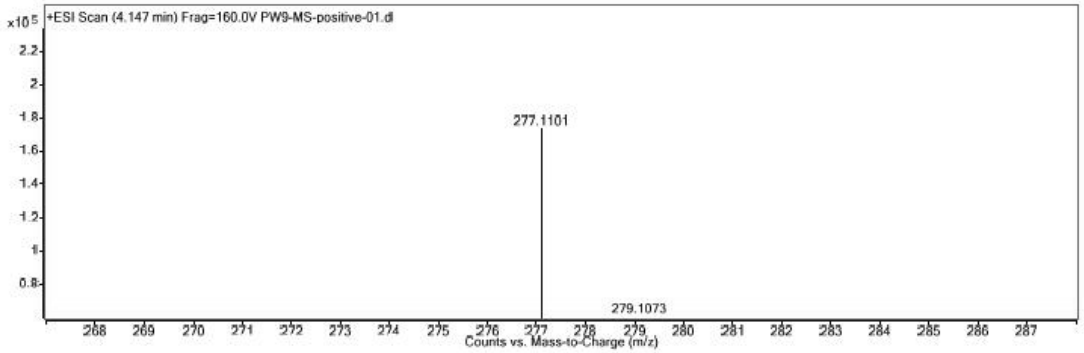
^{1}H NMR spectra of compound **1l**



^{13}C NMR spectra of compound **1l**



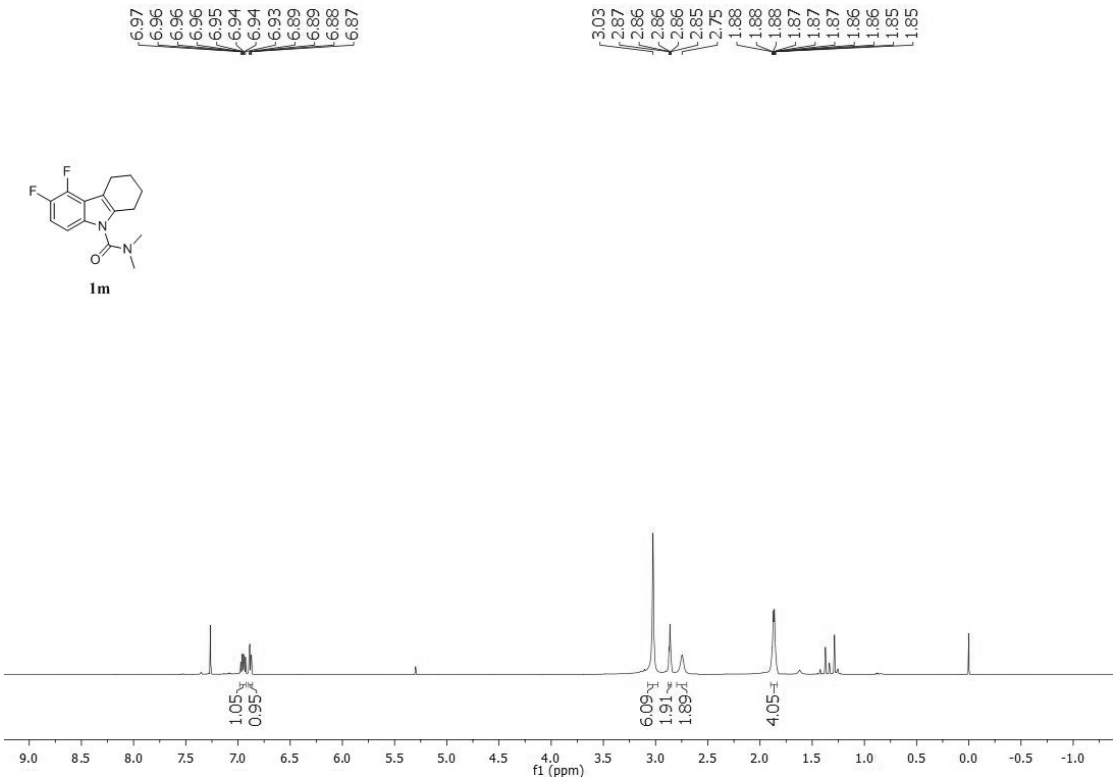
HRMS spectrum of compound **1l**



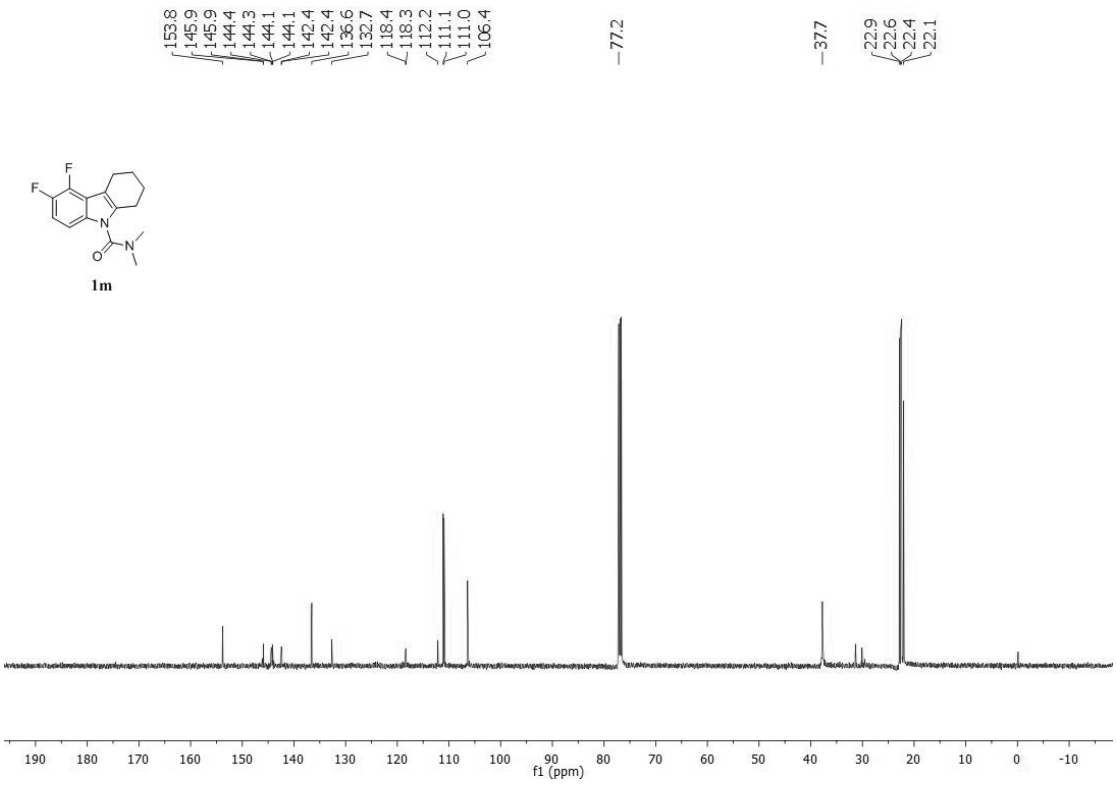
Elemental Composition Calculator

Target m/z:	277.1101	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5) ; Cl(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C15H18ClN2O		277.1102		0.55	

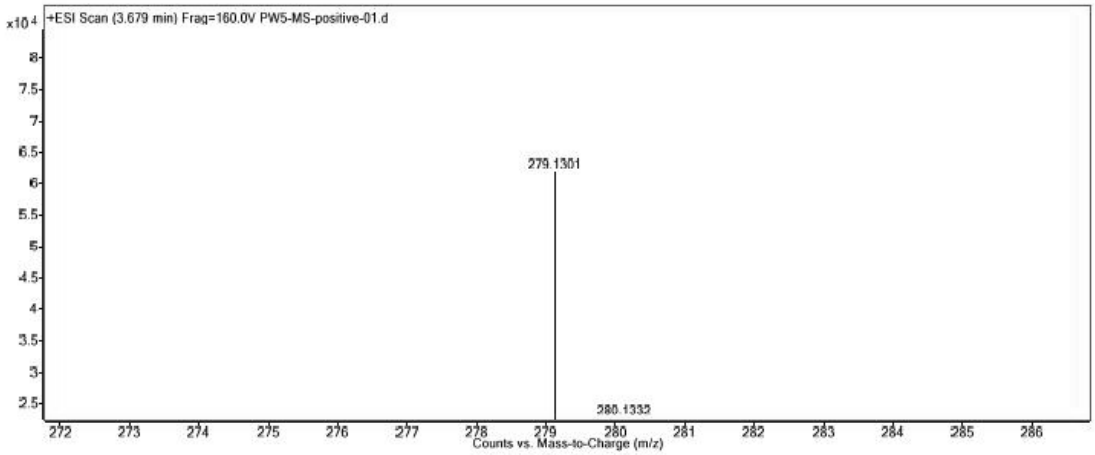
^{1}H NMR spectra of compound **1m**



^{13}C NMR spectra of compound **1m**



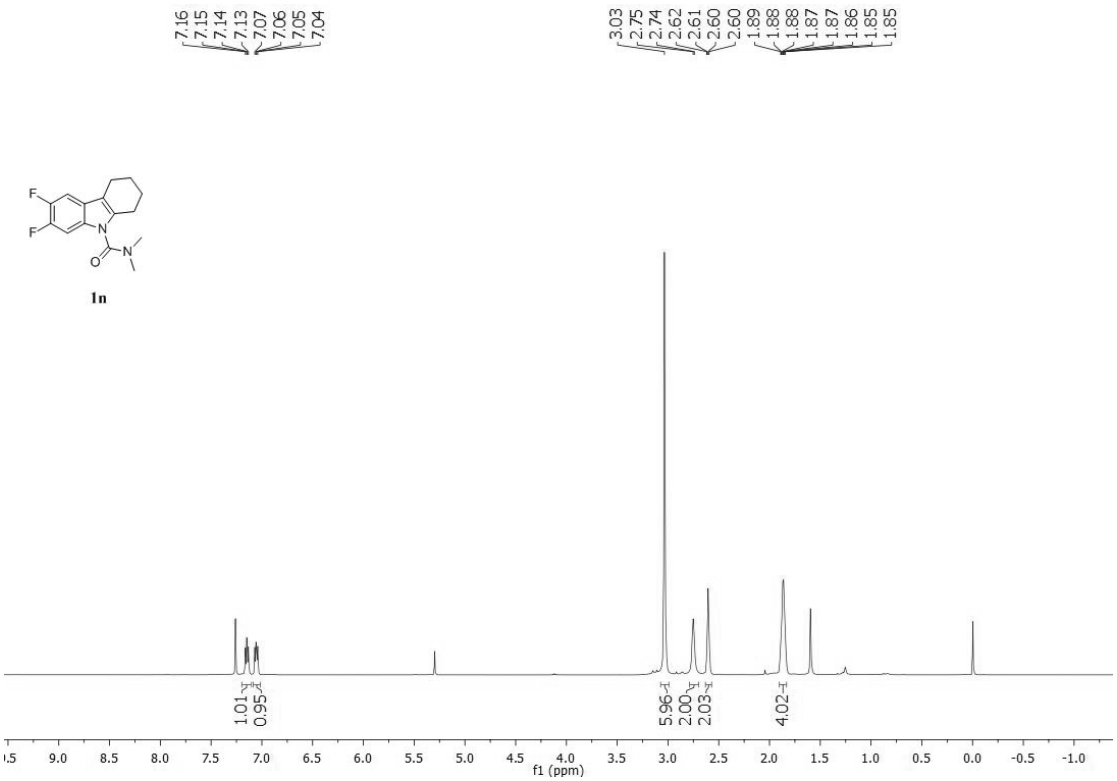
HRMS spectrum of compound **1m**



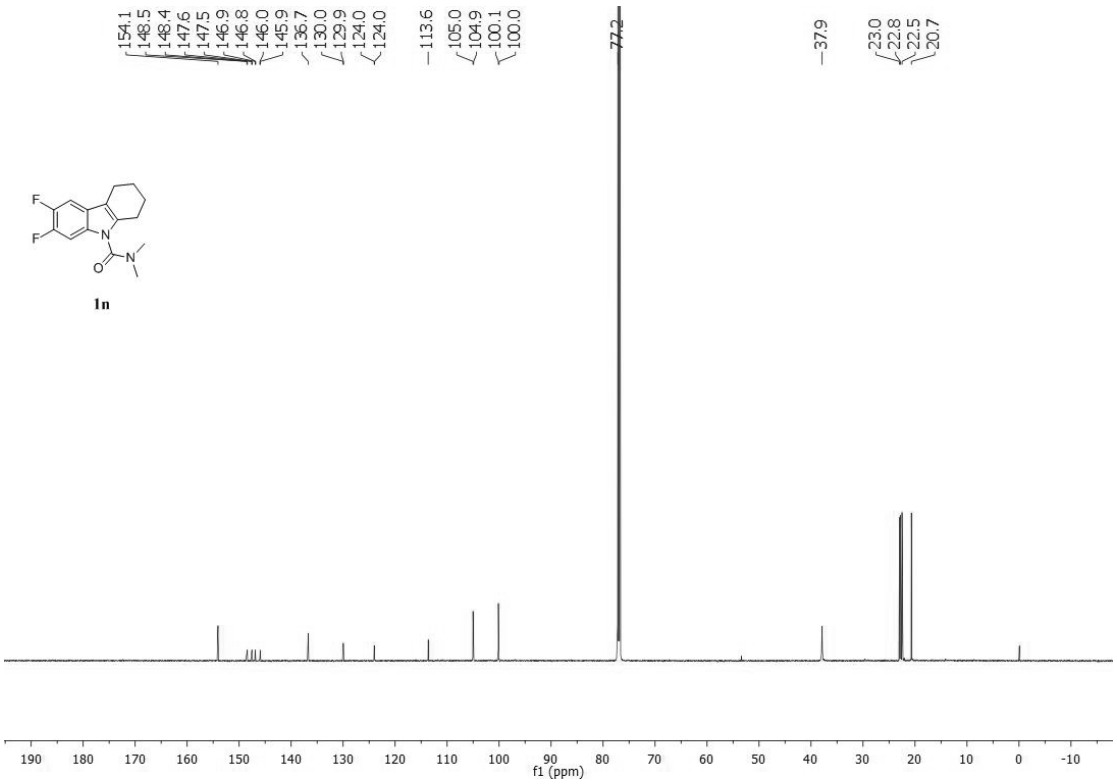
Elemental Composition Calculator

Target m/z:	279.1301	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30); N (0-5) ;F (0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C15H17F2N2O		279.1303		0.76	

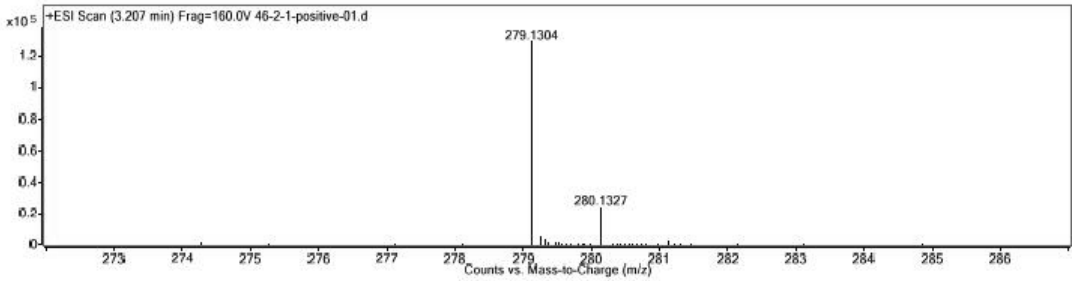
^{1}H NMR spectra of compound **1n**



^{13}C NMR spectra of compound **1n**



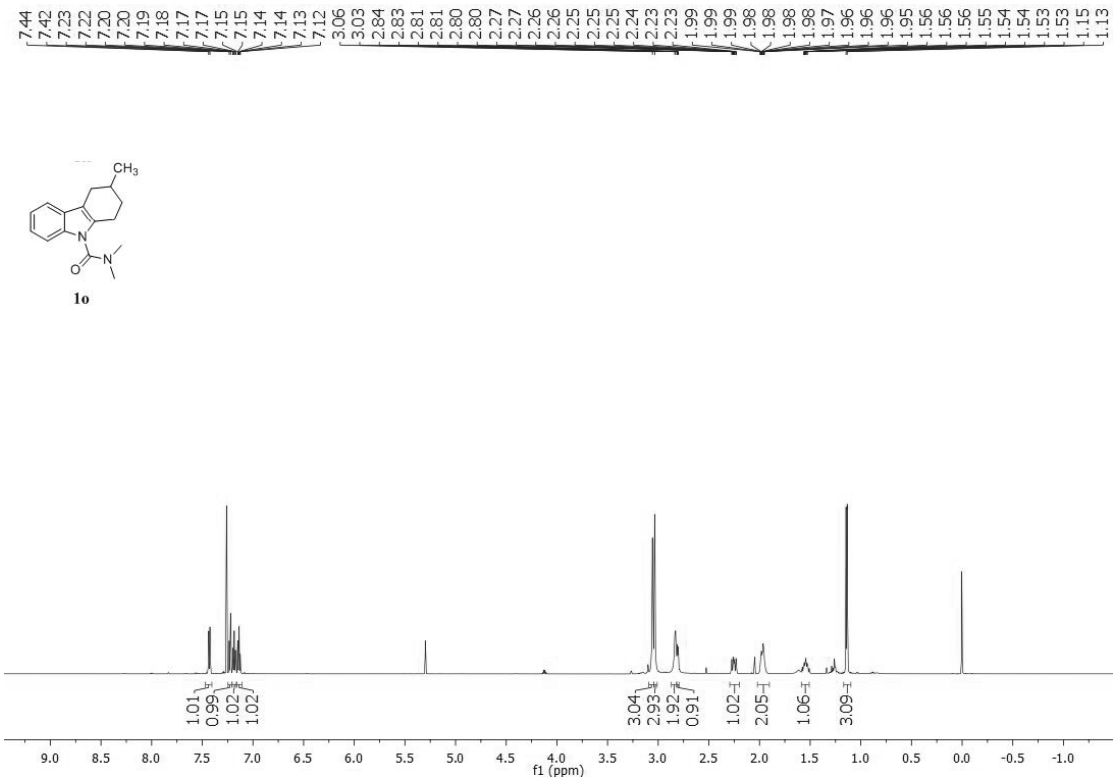
HRMS spectrum of compound **1n**



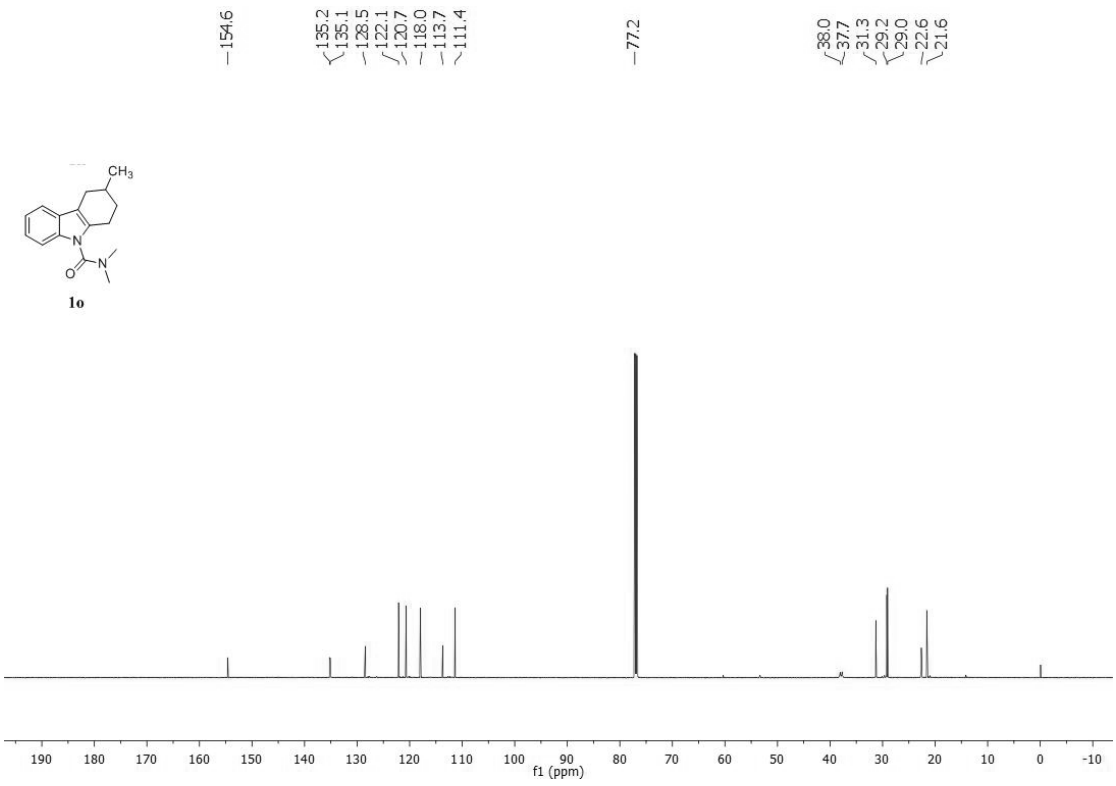
Elemental Composition Calculator

Target m/z:	279.1304	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5); F(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C15H17F2N2O		279.1303		-0.27	

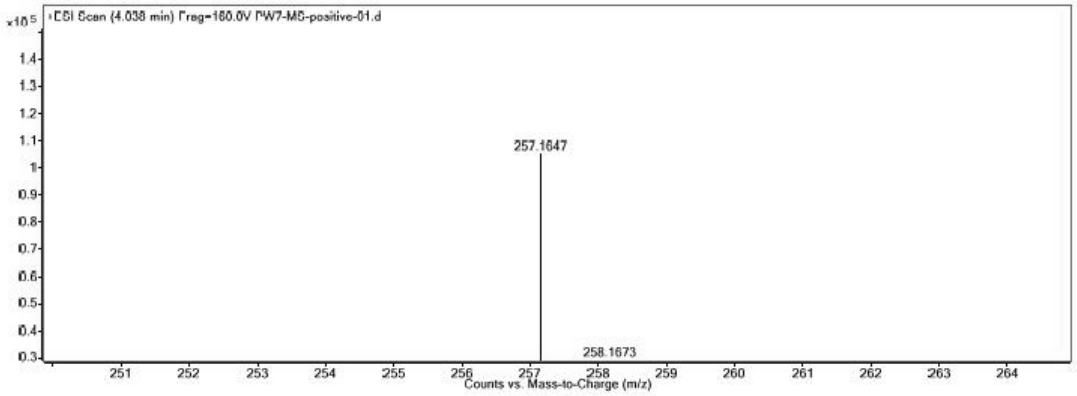
^{1}H NMR spectra of compound **1o**



^{13}C NMR spectra of compound **1o**



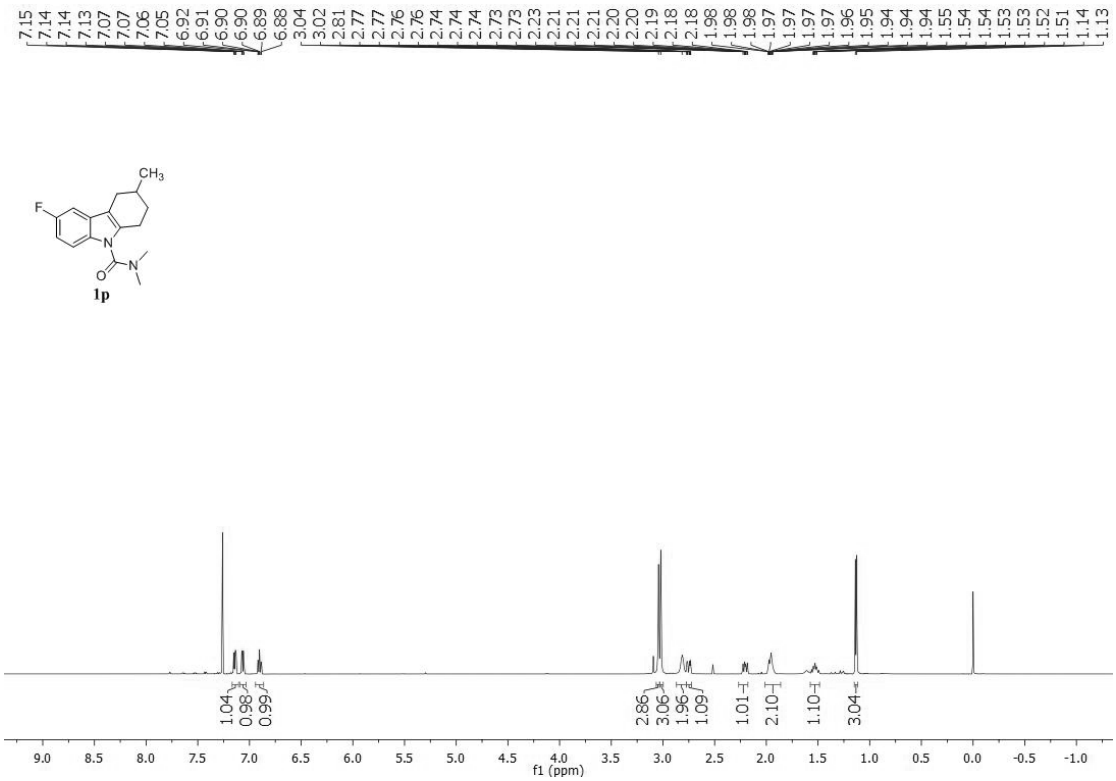
HRMS spectrum of compound **1o**



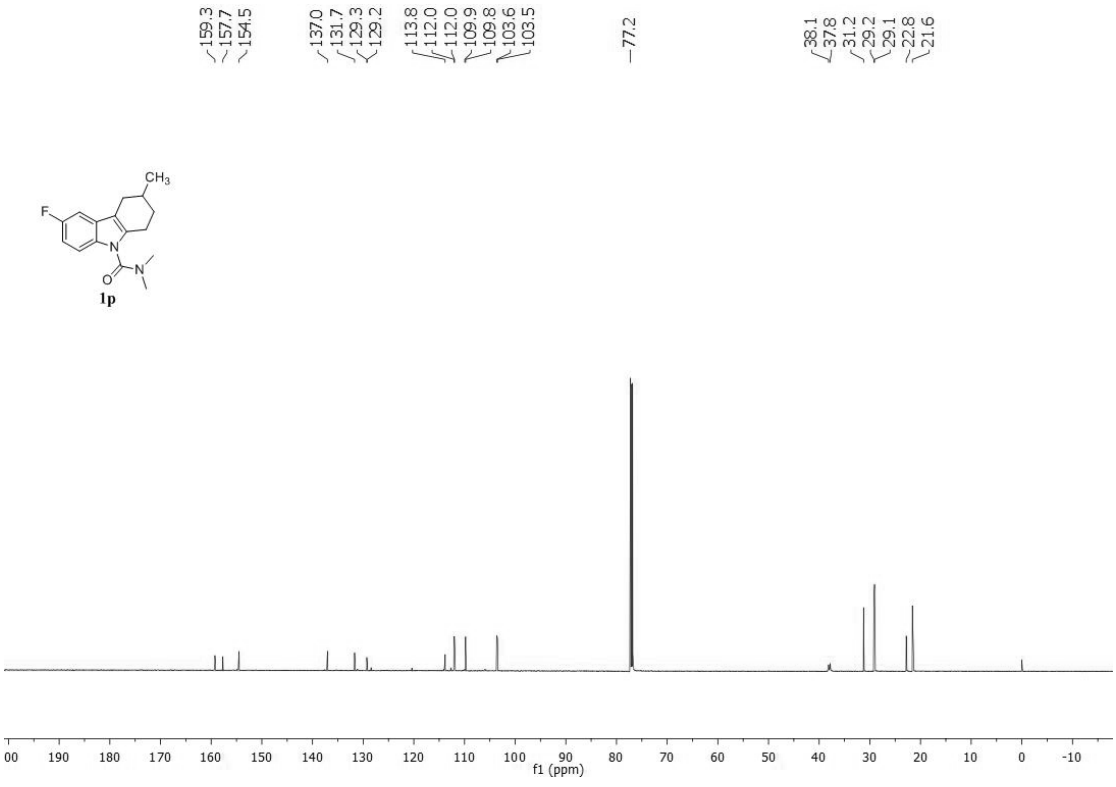
Elemental Composition Calculator

Target m/z:	257.1647	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C16H21N2O		257.1648		0.66	

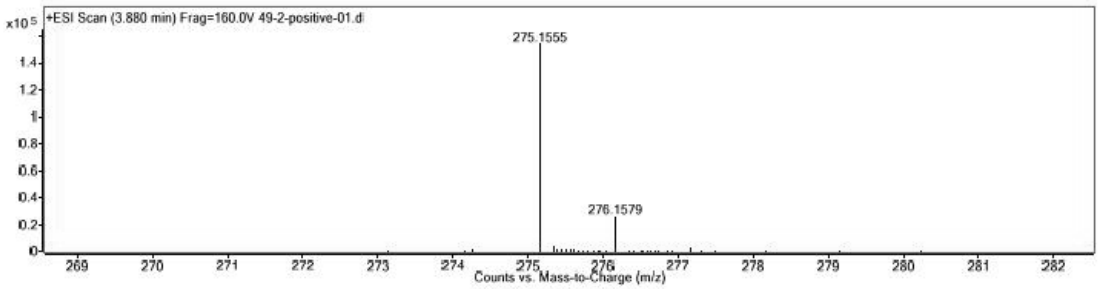
^{1}H NMR spectra of compound **1p**



^{13}C NMR spectra of compound **1p**



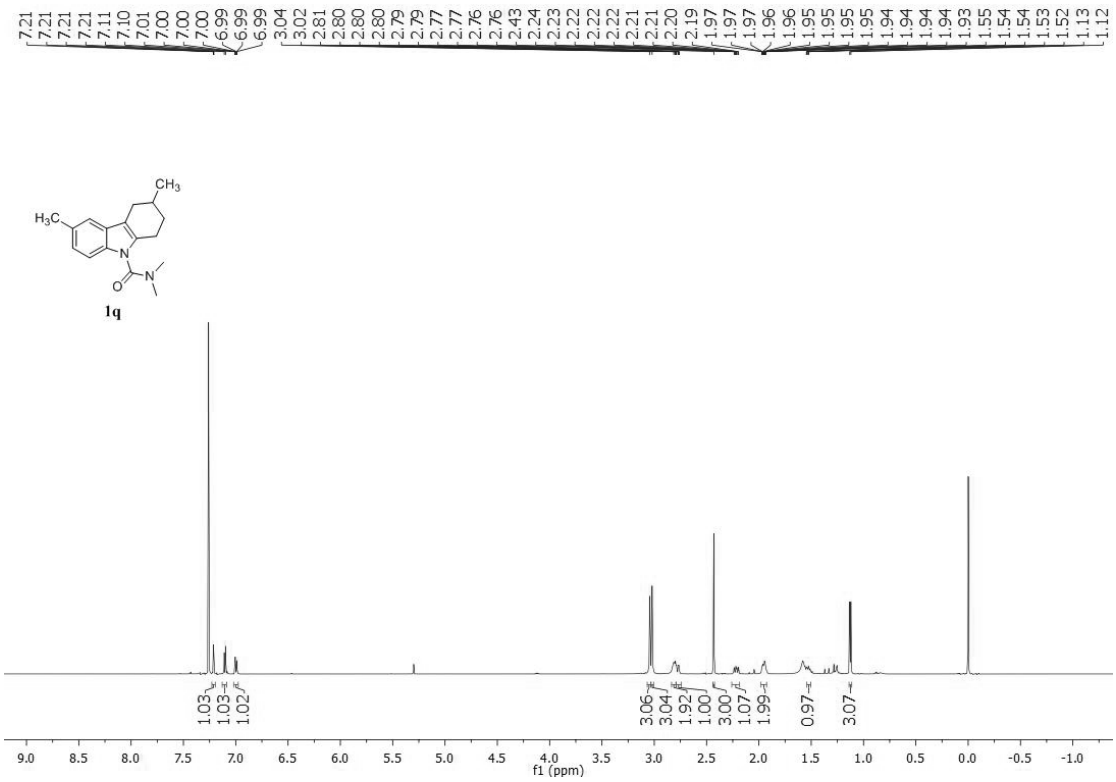
HRMS spectrum of compound **1p**



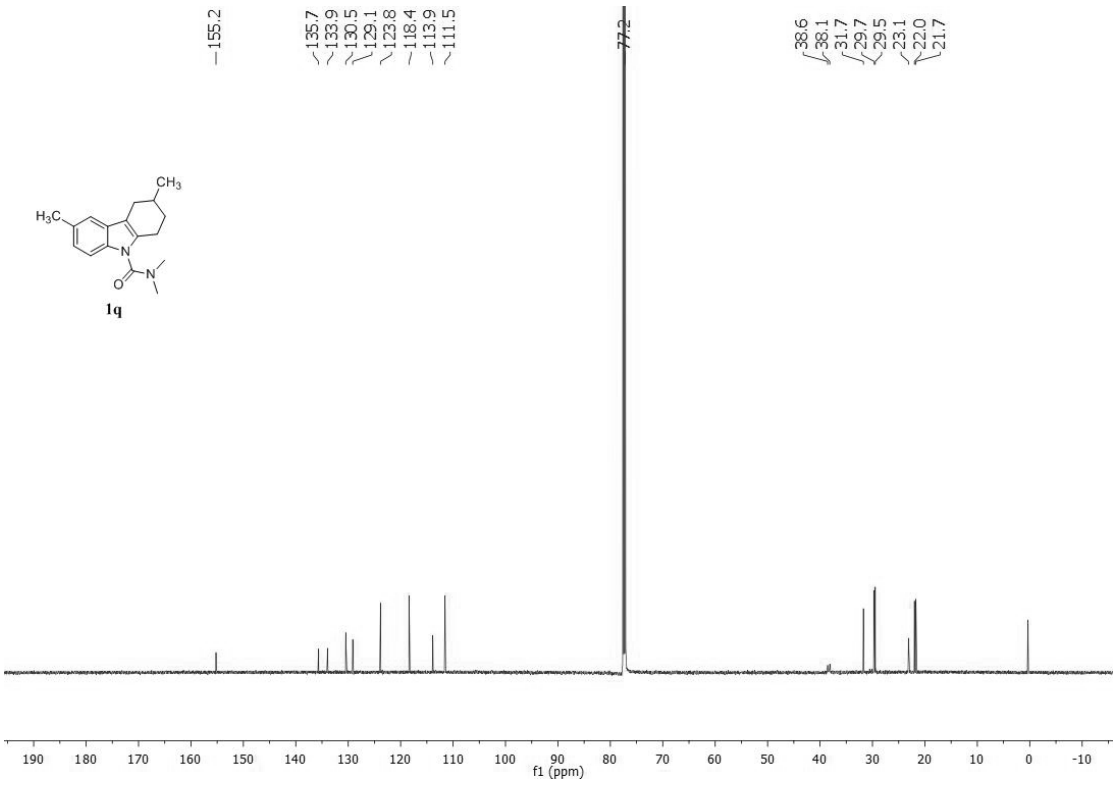
Elemental Composition Calculator

Target m/z:	275.1555	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5); F(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C16H20FN2O		275.1554		-0.12	

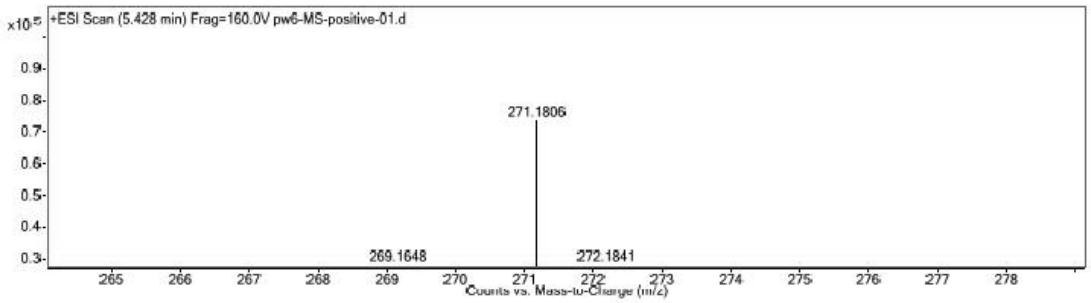
^{1}H NMR spectra of compound **1q**



^{13}C NMR spectra of compound **1q**



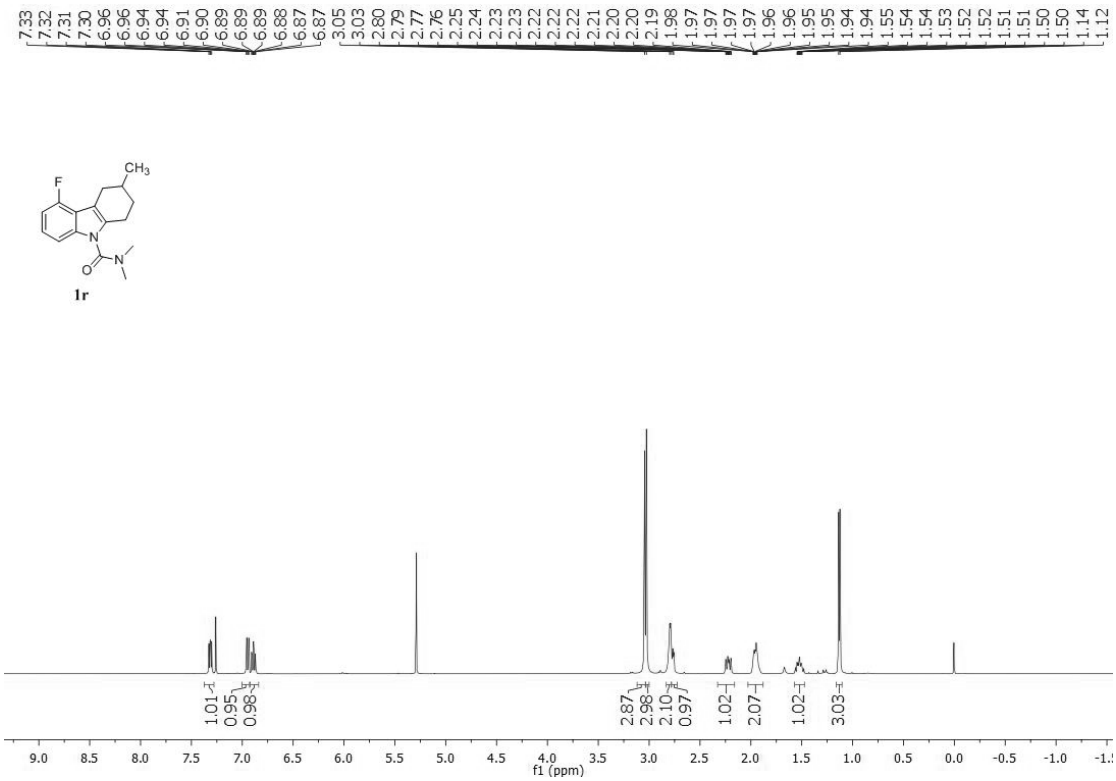
HRMS spectrum of compound **1q**



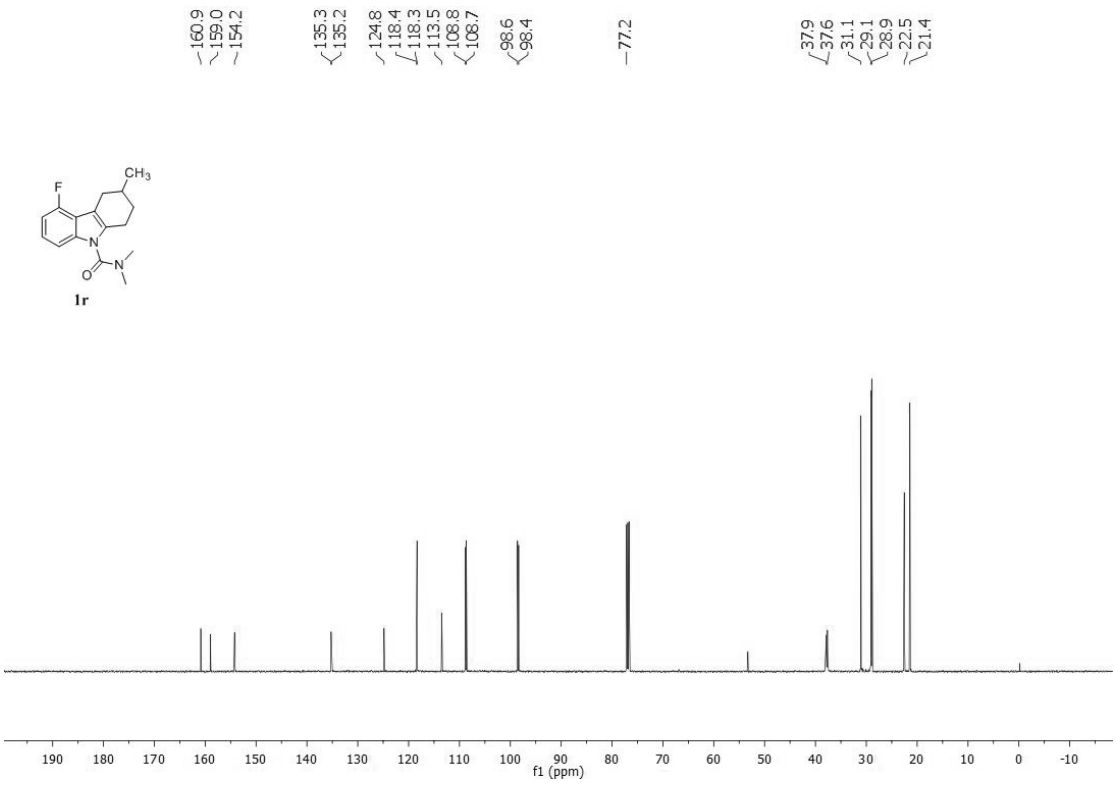
Elemental Composition Calculator

Target m/z:	271.1806	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C17H23N2O		271.1805		-0.47	

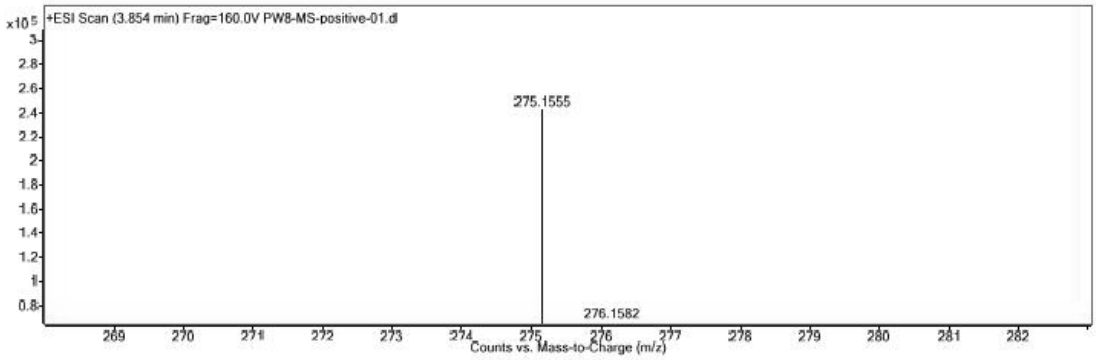
^{1}H NMR spectra of compound **1r**



^{13}C NMR spectra of compound **1r**



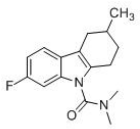
HRMS spectrum of compound **1r**



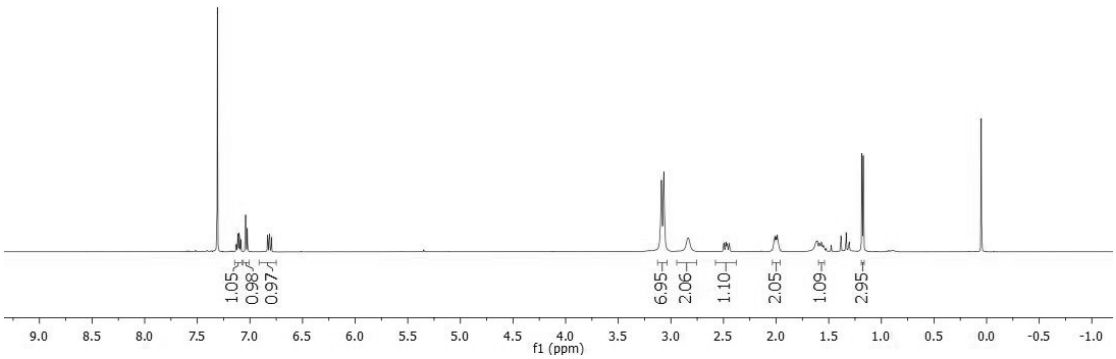
Elemental Composition Calculator

Target m/z:	275.1555	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5) ; F(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C16H20FN2O		275.1554		-0.15	

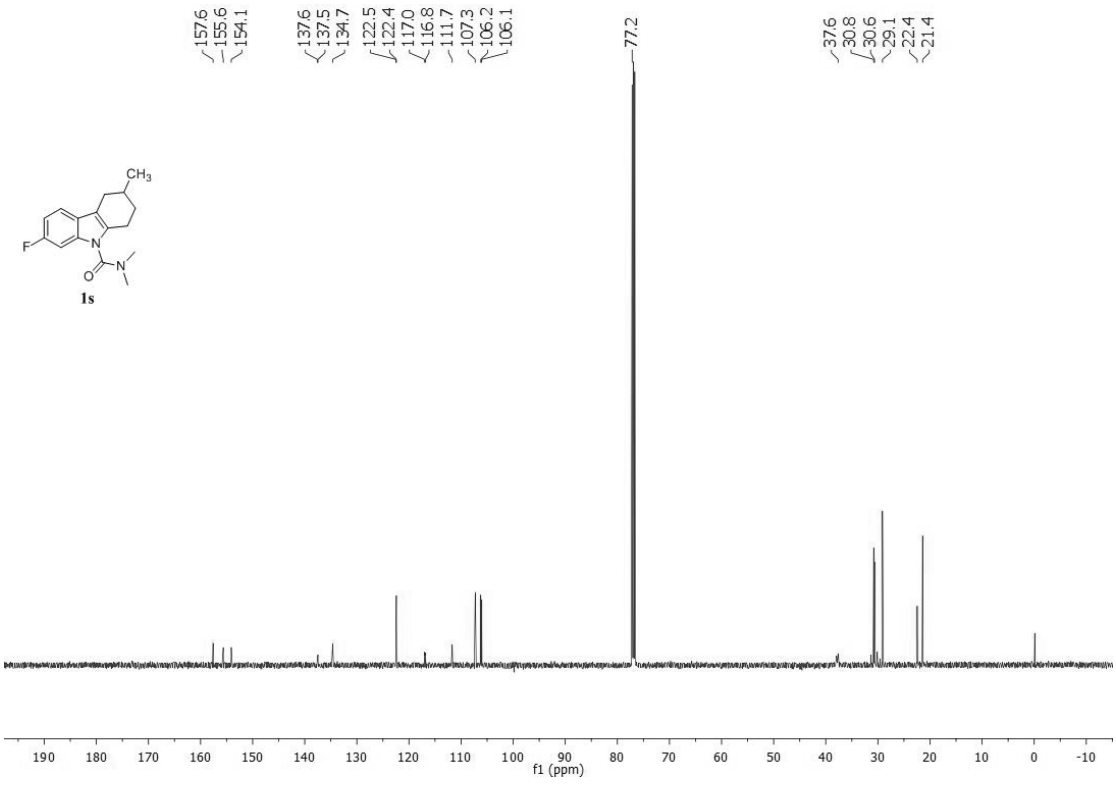
^{1}H NMR spectra of compound **1s**



1s

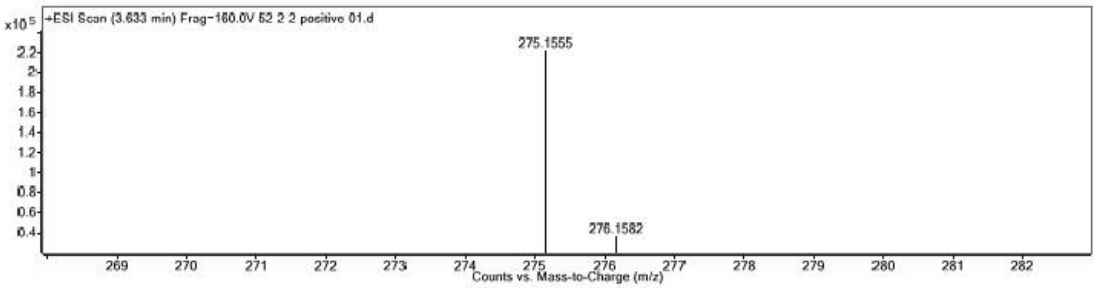


^{13}C NMR spectra of compound **1s**



1s

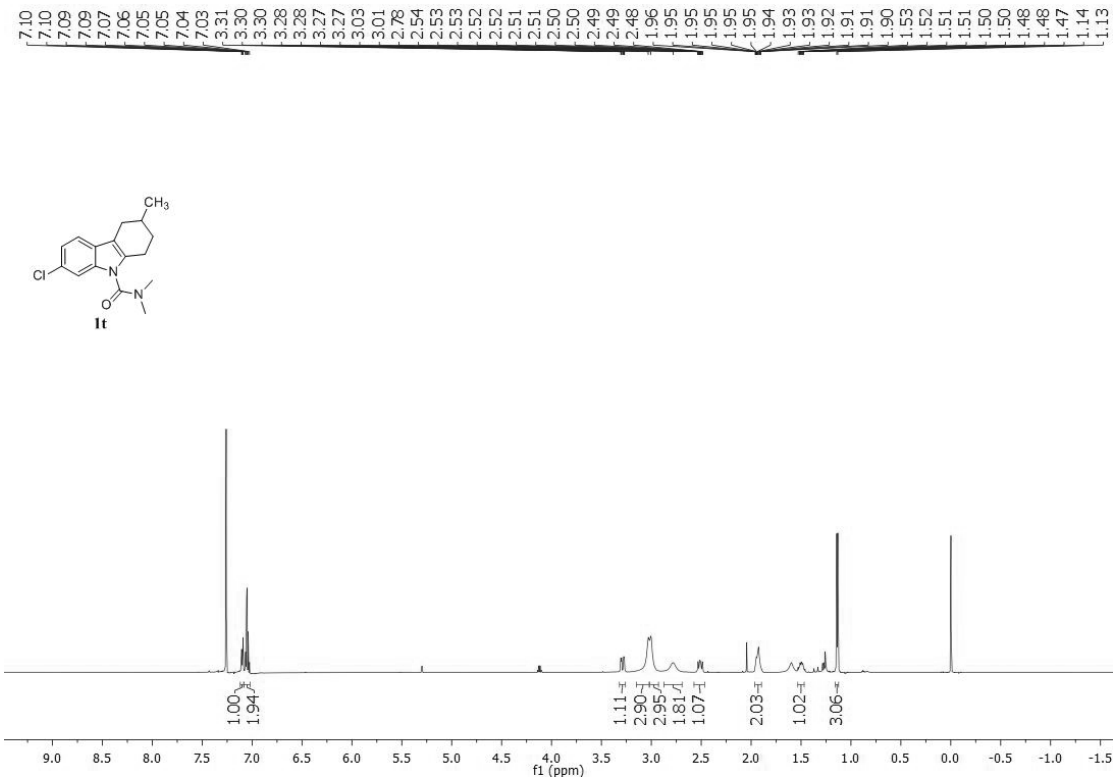
HRMS spectrum of compound **1s**



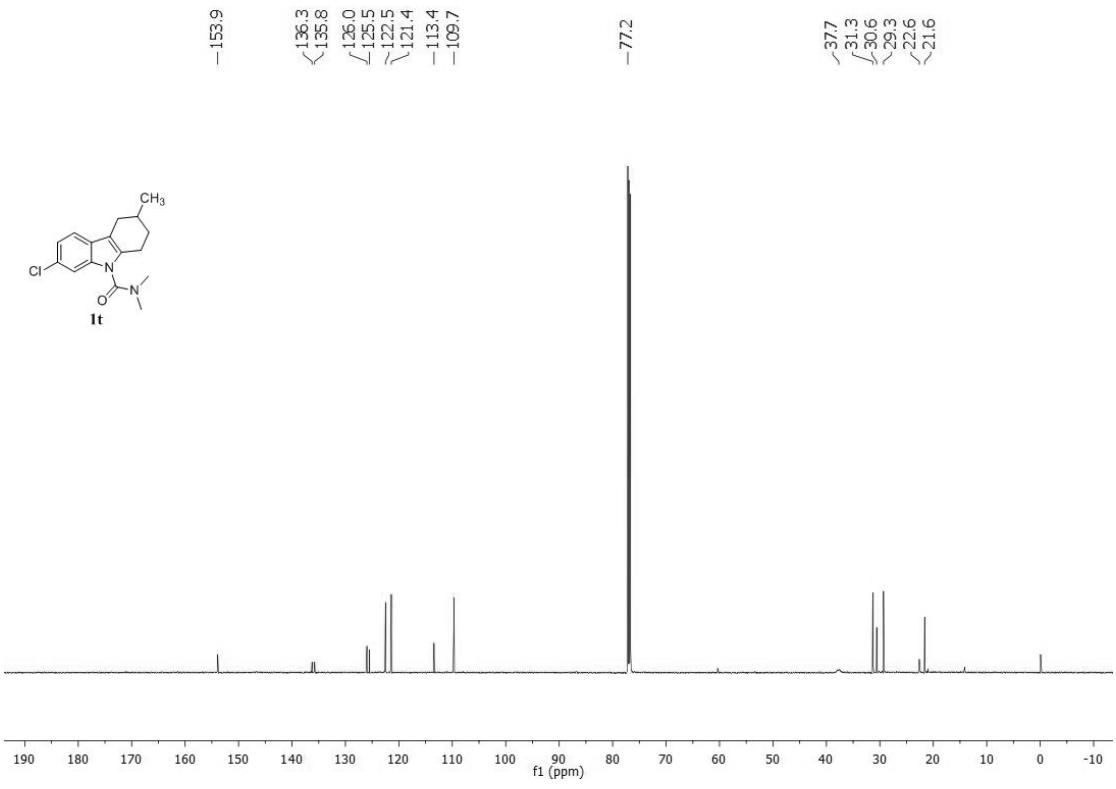
Elemental Composition Calculator

Target m/z:	275.1555	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5); F(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C16H20FN2O		275.1554		-0.24	

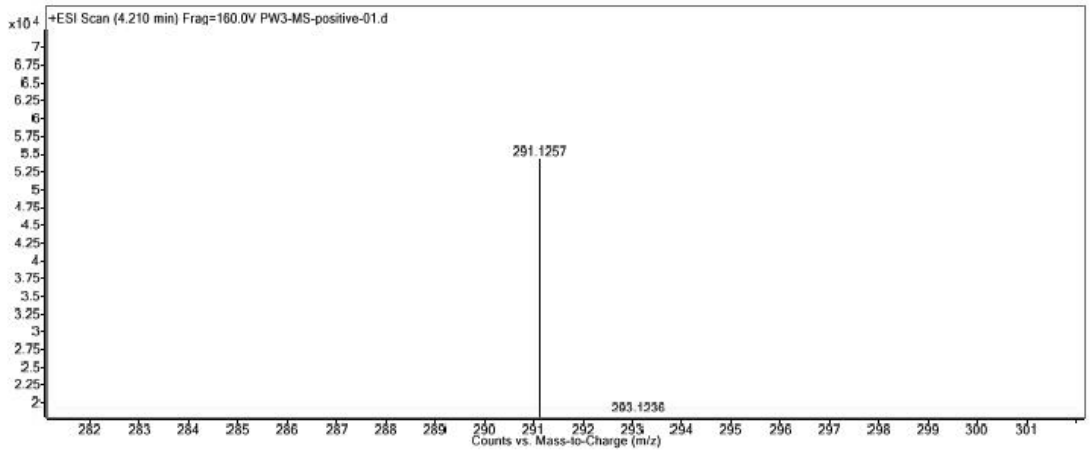
^{1}H NMR spectra of compound **1t**



^{13}C NMR spectra of compound **1t**



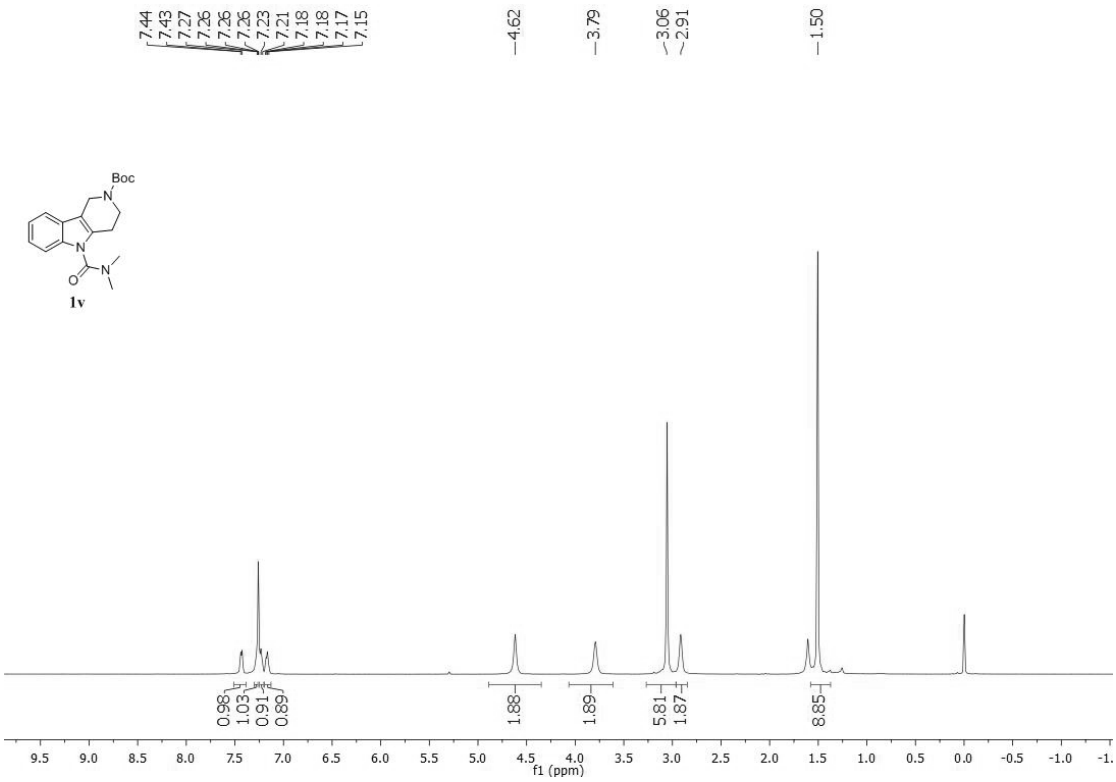
HRMS spectrum of compound **1t**



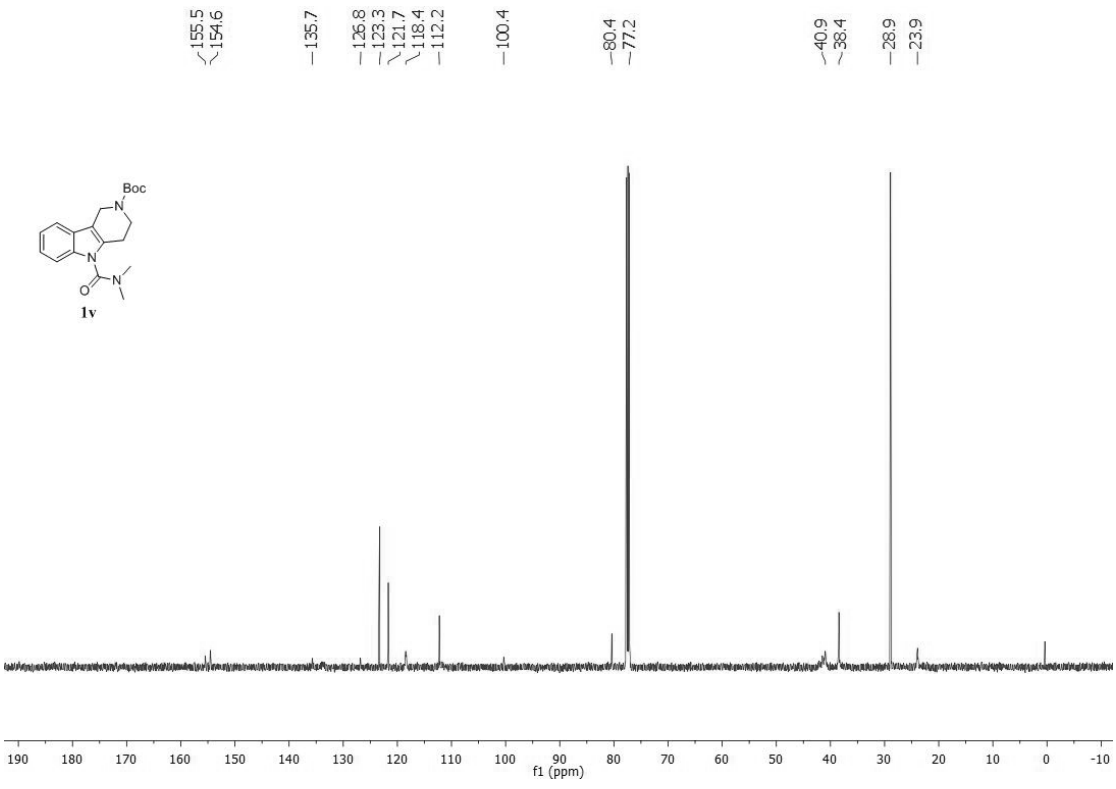
Elemental Composition Calculator

Target m/z:	291.1257	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30); N (0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C16H20ClN2O		291.1259		0.55	

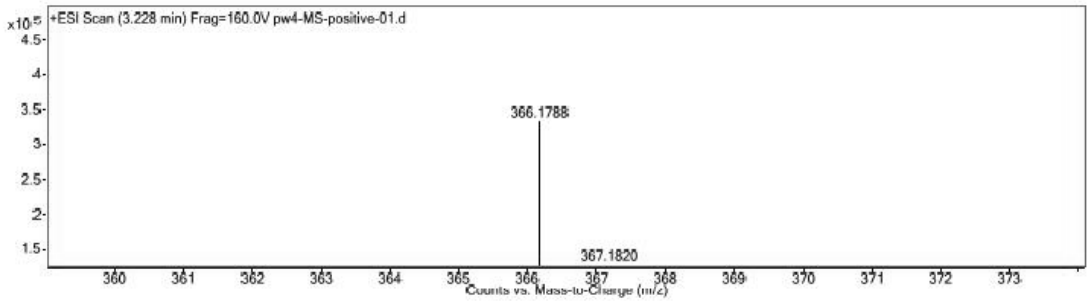
^{1}H NMR spectra of compound **1v**



^{13}C NMR spectra of compound **1v**



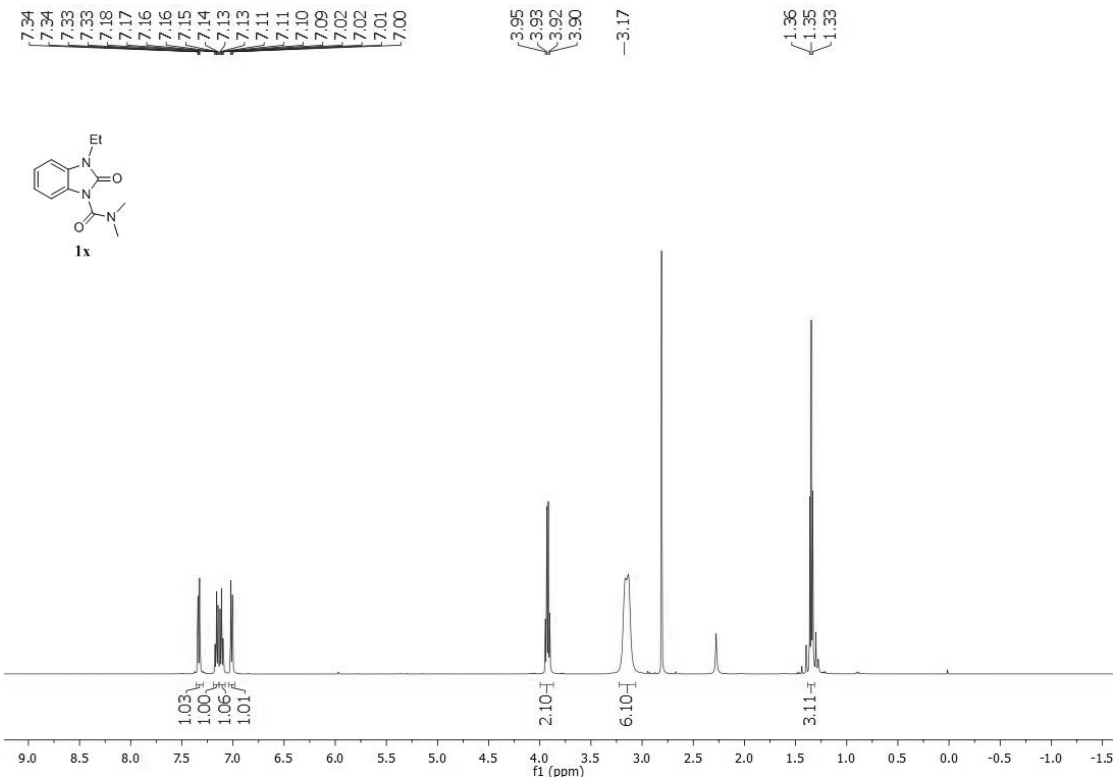
HRMS spectrum of compound **1v**



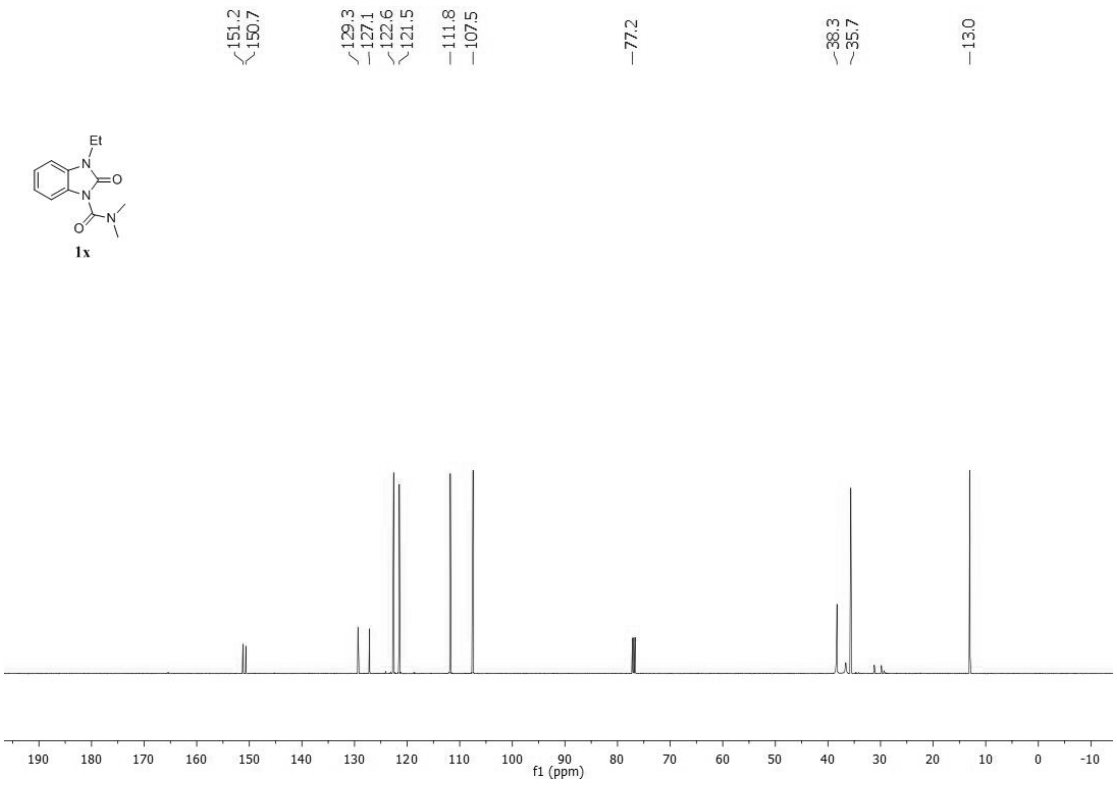
Elemental Composition Calculator

Target m/z:	366.1788	**Result type:**	Positive ions	**Species:**	$[M+Na]^+$
Elements:		C (0-80); H (0-120); O (0-30); N(0-5); Na (0-5)			
Ion Formula		**Calculated m/z**		**PPM Error**	
C19H25N3NaO3		366.1788		0.03	

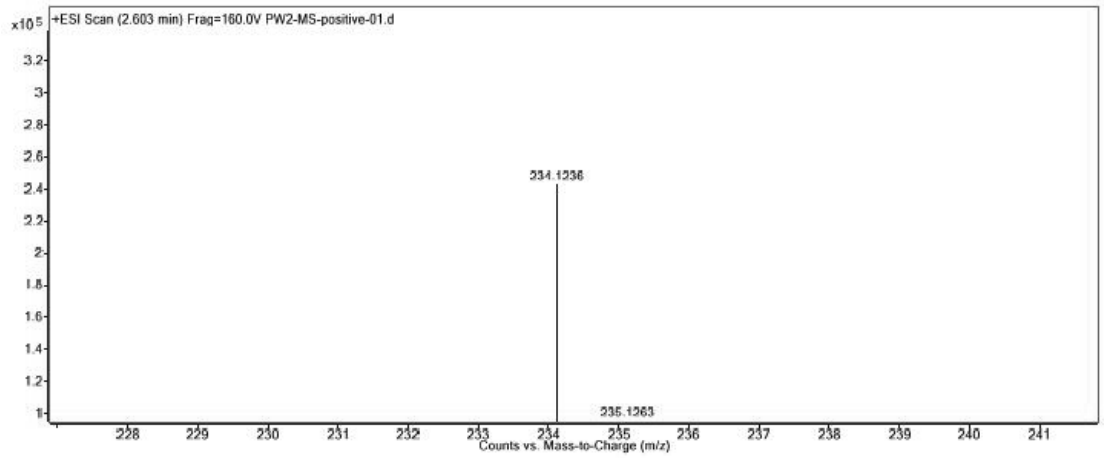
^{1}H NMR spectra of compound **1x**



^{13}C NMR spectra of compound **1x**



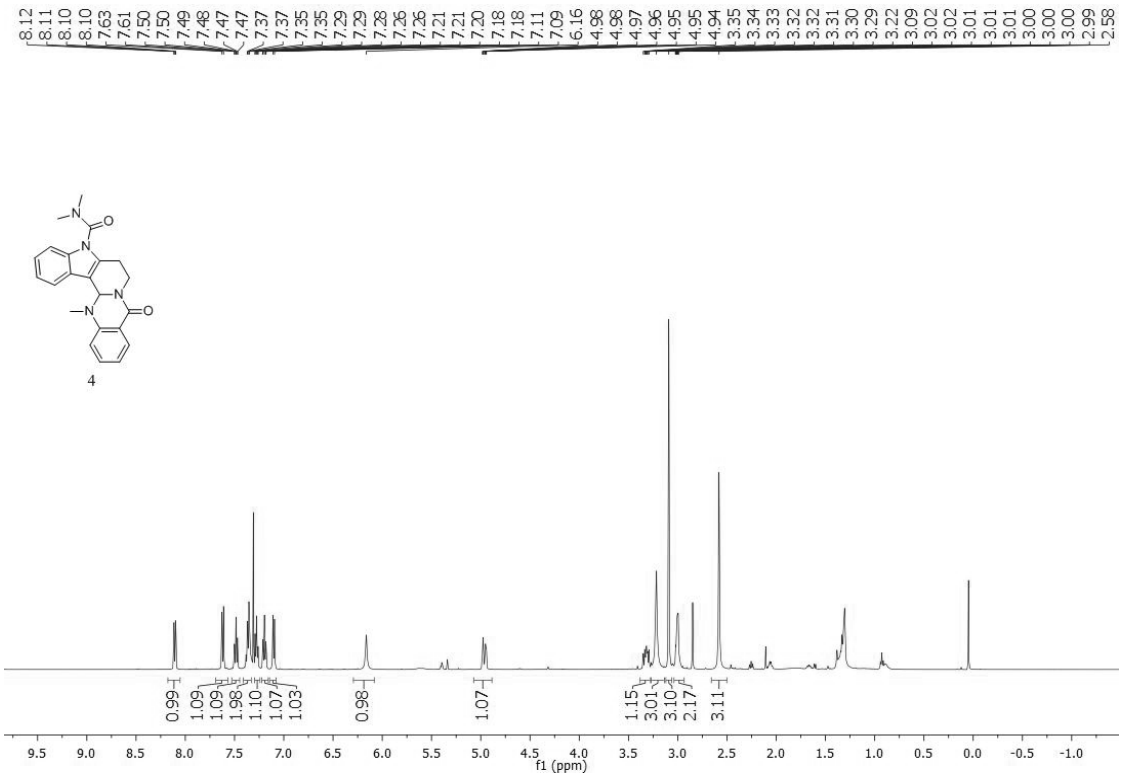
HRMS spectrum of compound **1x**



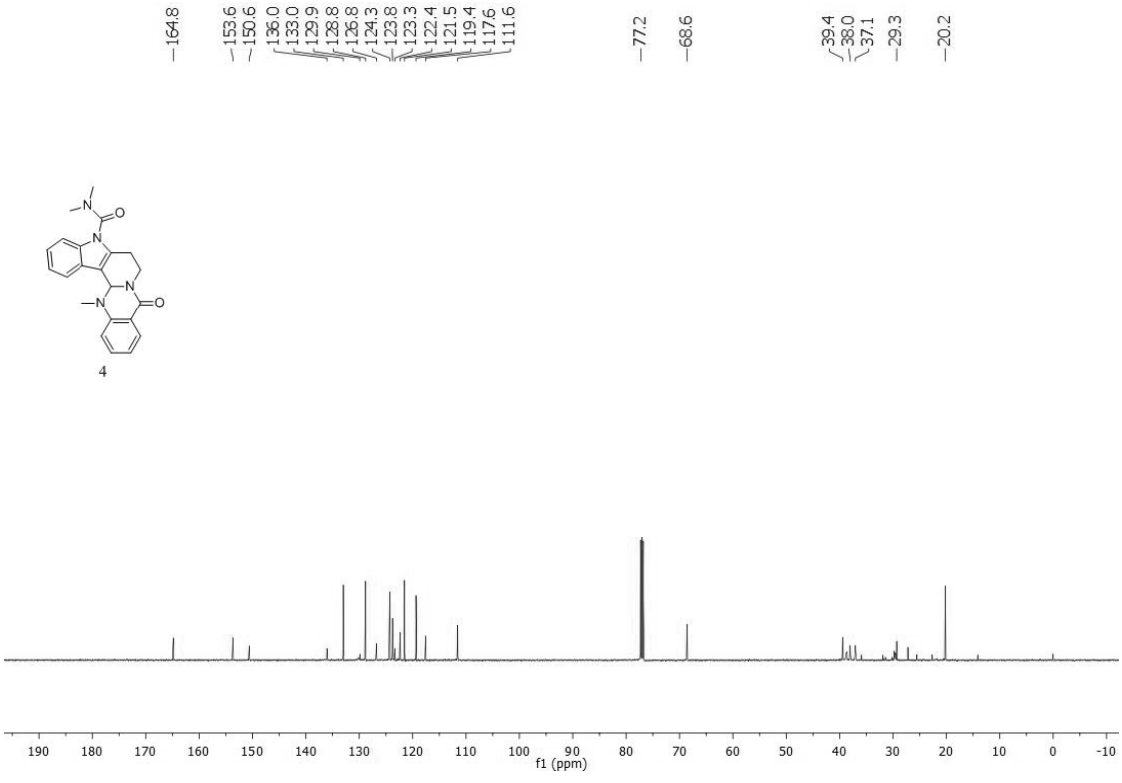
Elemental Composition Calculator

Target m/z:	234.1236	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30); N (0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C12H16N3O2		234.1237		0.45	

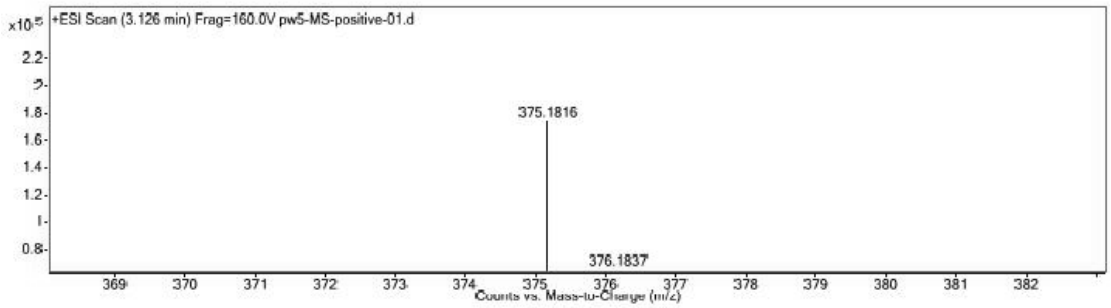
^{1}H NMR spectra of compound **4**



^{13}C NMR spectra of compound **4**



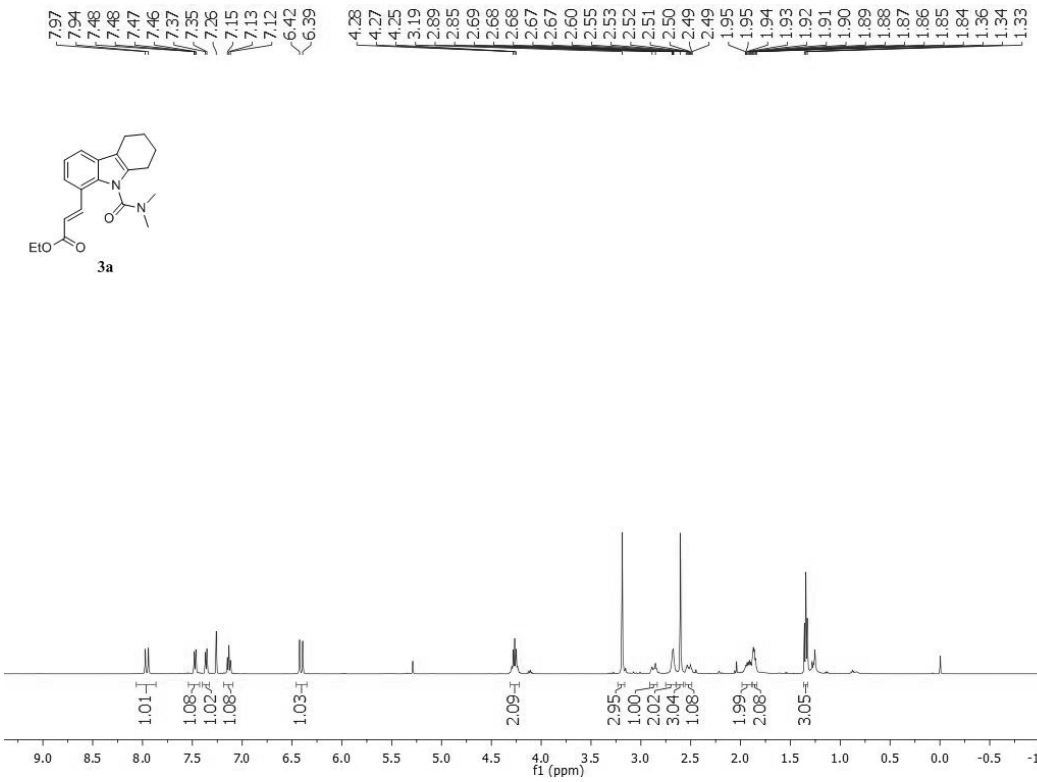
HRMS spectrum of compound **4**



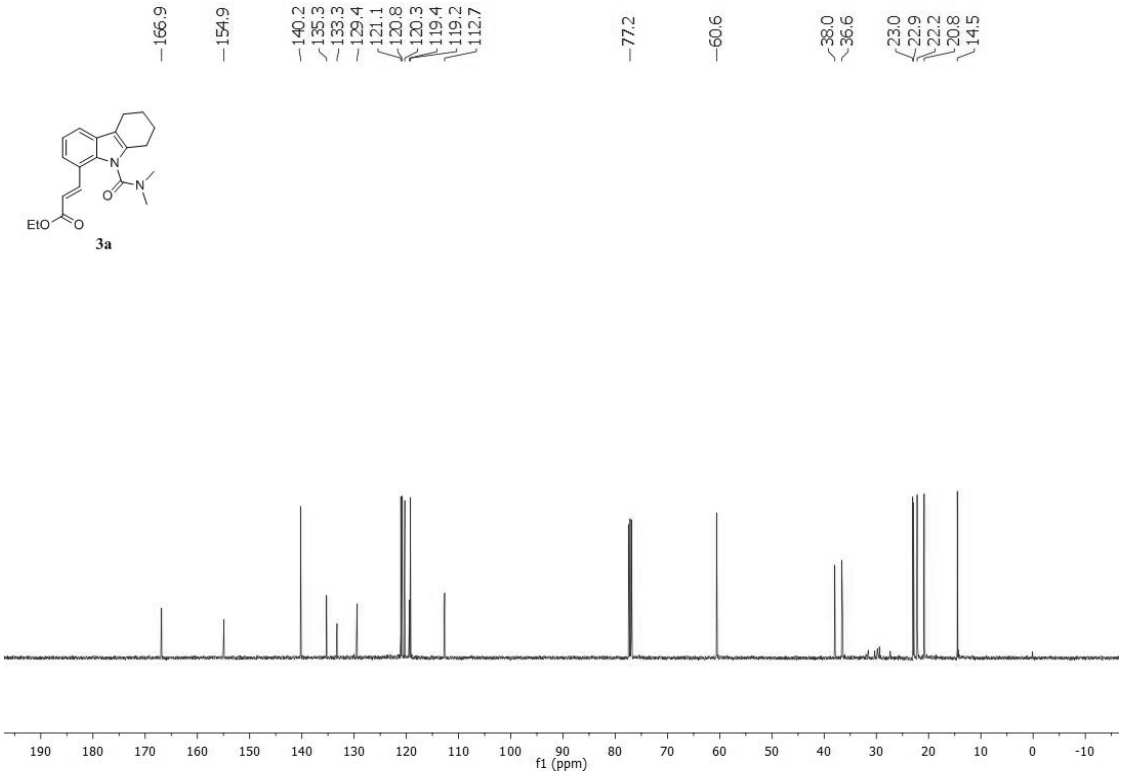
Elemental Composition Calculator

Target m/z:	375.1816	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C22H23N4O2		375.1816		-0.23	

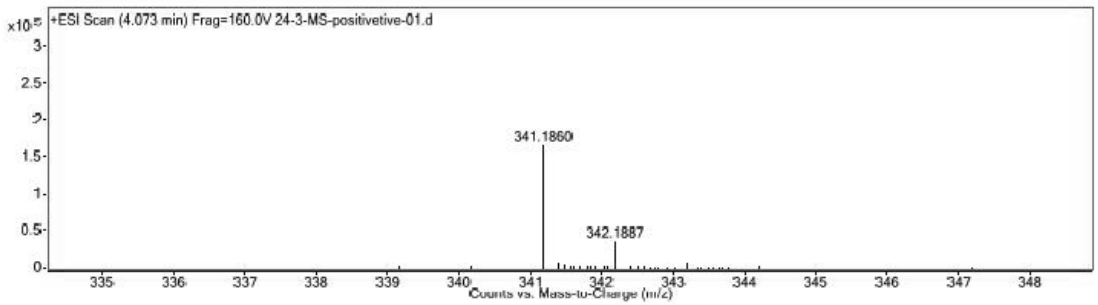
^{1}H NMR spectra of compound **3a**



^{13}C NMR spectra of compound **3a**



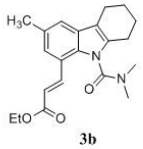
HRMS spectrum of compound **3a**



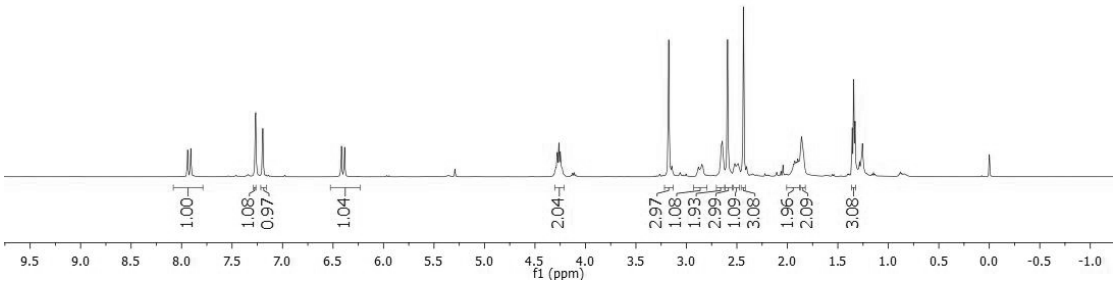
Elemental Composition Calculator

Target m/z:	341.1860	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C20H25N2O3		341.1860		-0.09	

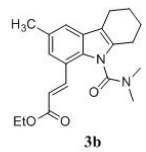
^{1}H NMR spectra of compound **3b**



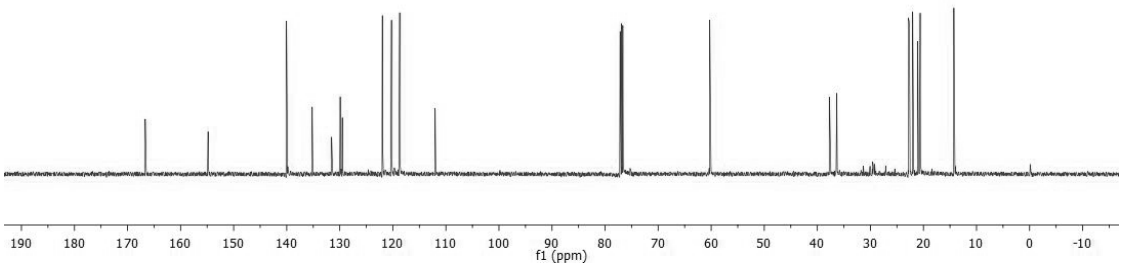
3b



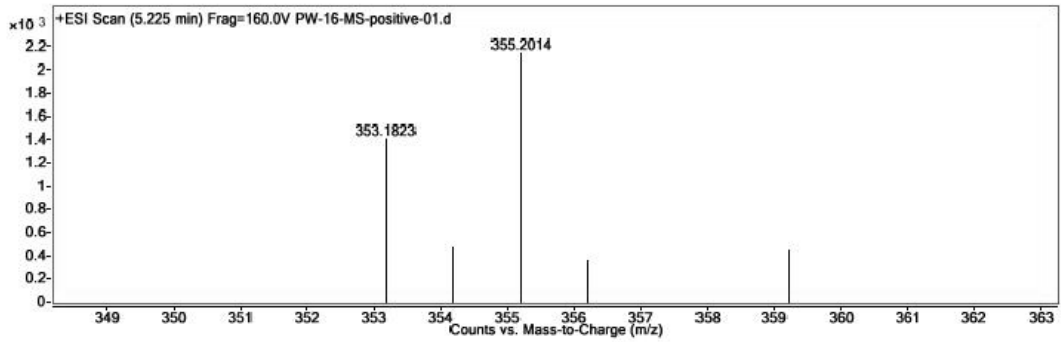
^{13}C NMR spectra of compound **3b**



3b



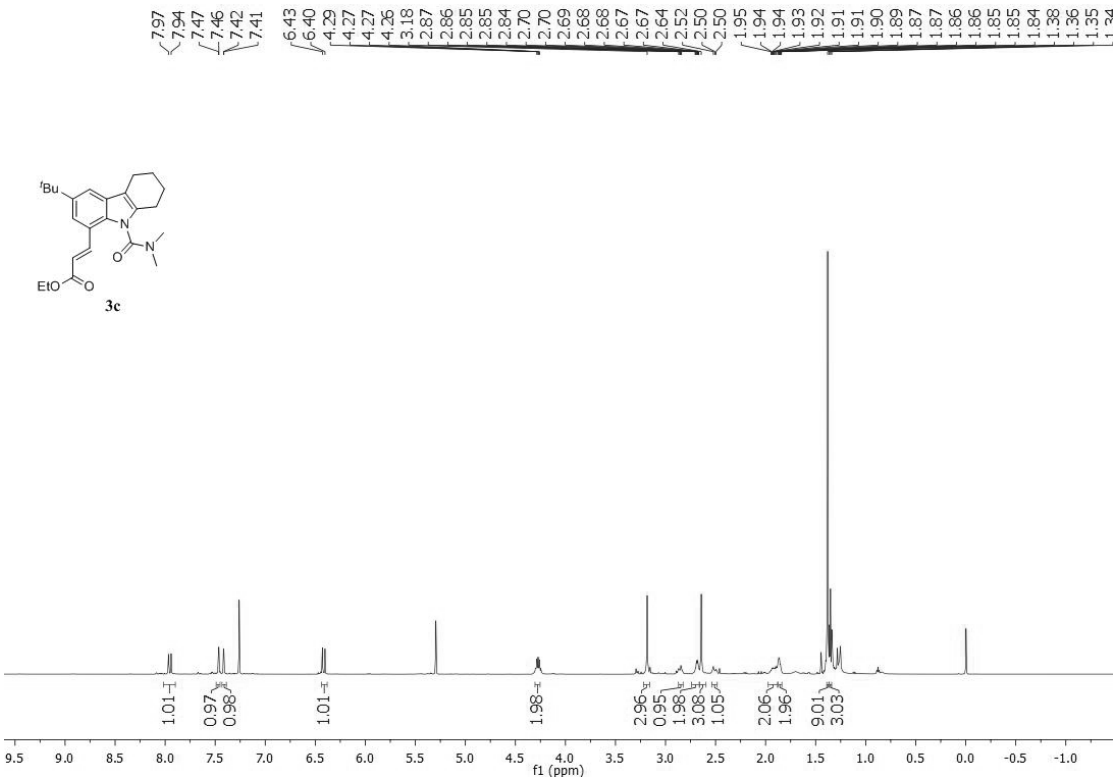
HRMS spectrum of compound **3b**



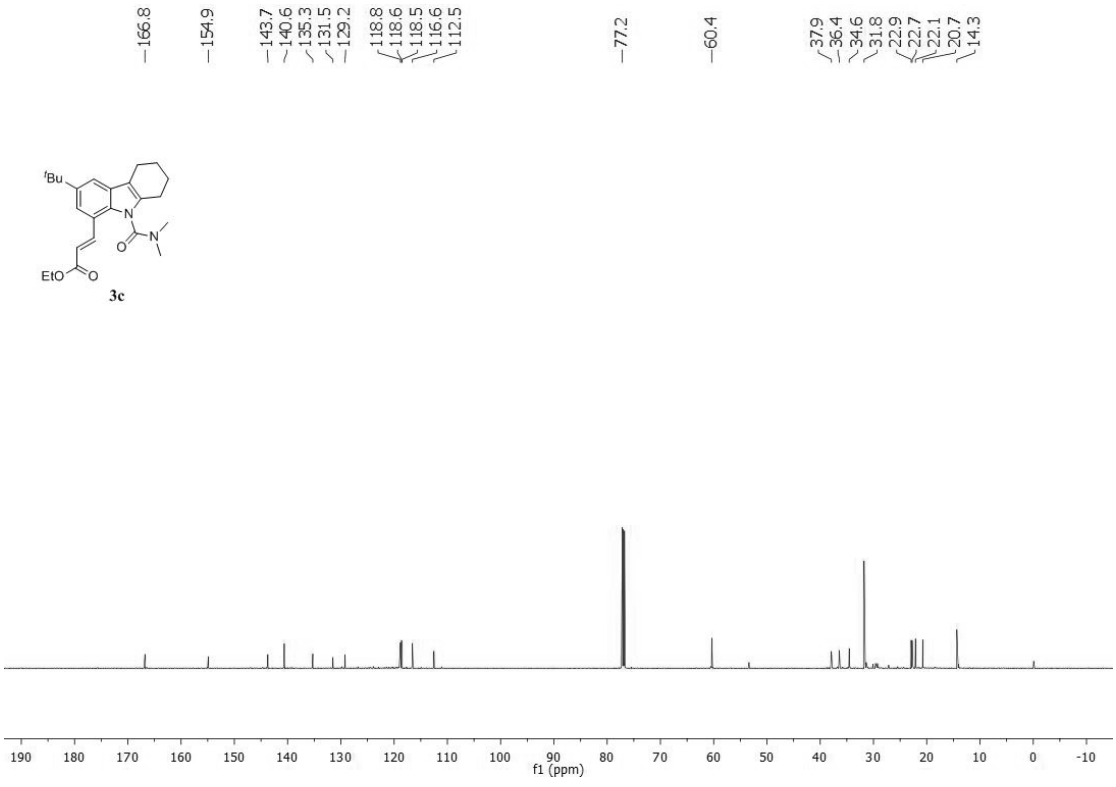
Elemental Composition Calculator

Target m/z:	355.2014	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C21H27N2O3		355.2016		0.71	

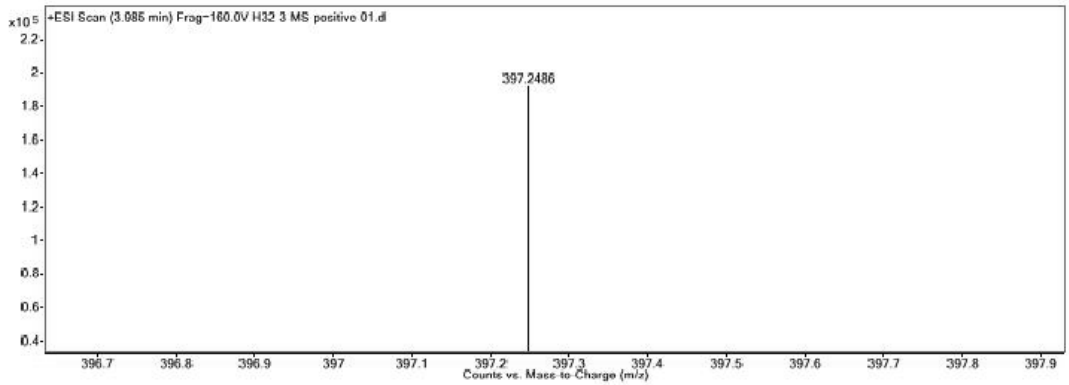
^{1}H NMR spectra of compound **3c**



^{13}C NMR spectra of compound **3c**



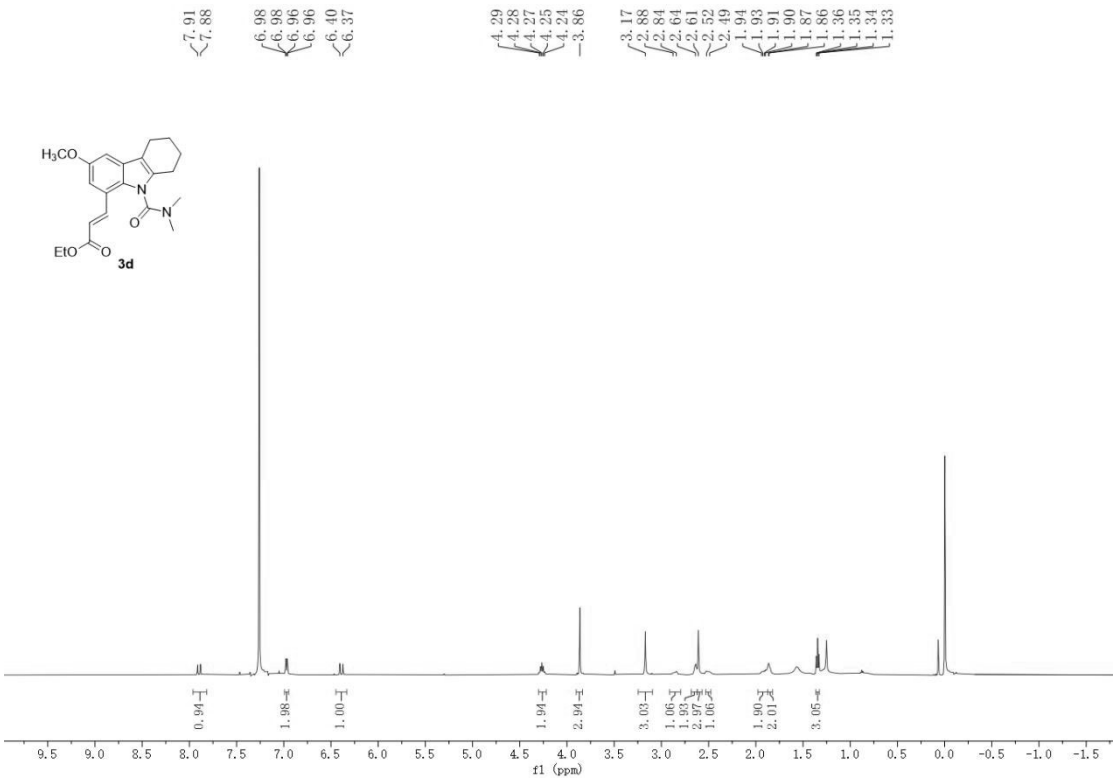
HRMS spectrum of compound **3c**



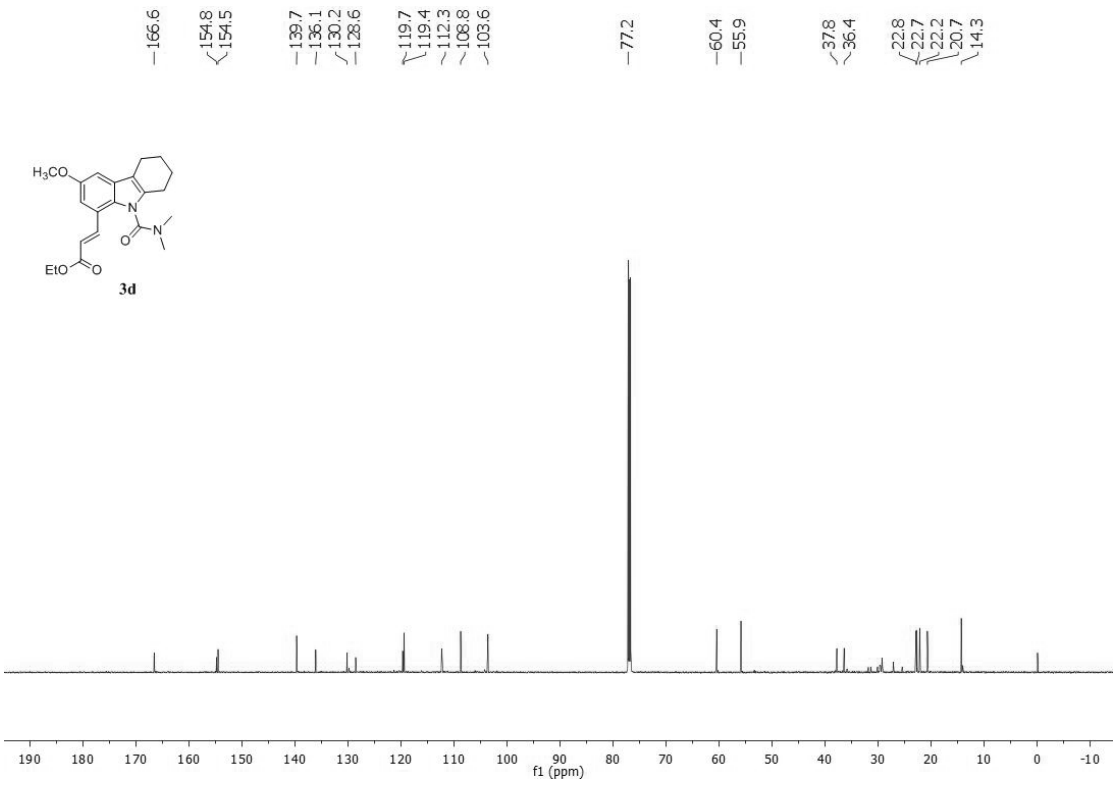
Elemental Composition Calculator

Target m/z:	397.2486	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C24H33N2O3		397.2486		0.02	

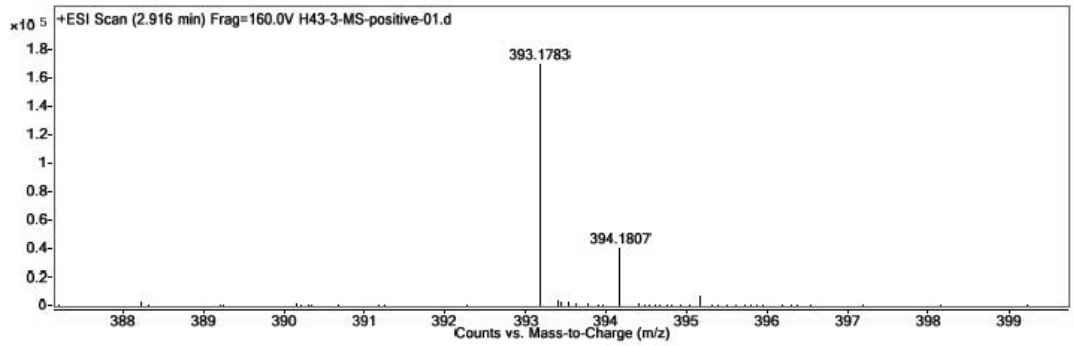
^{1}H NMR spectra of compound **3d**



^{13}C NMR spectra of compound **3d**



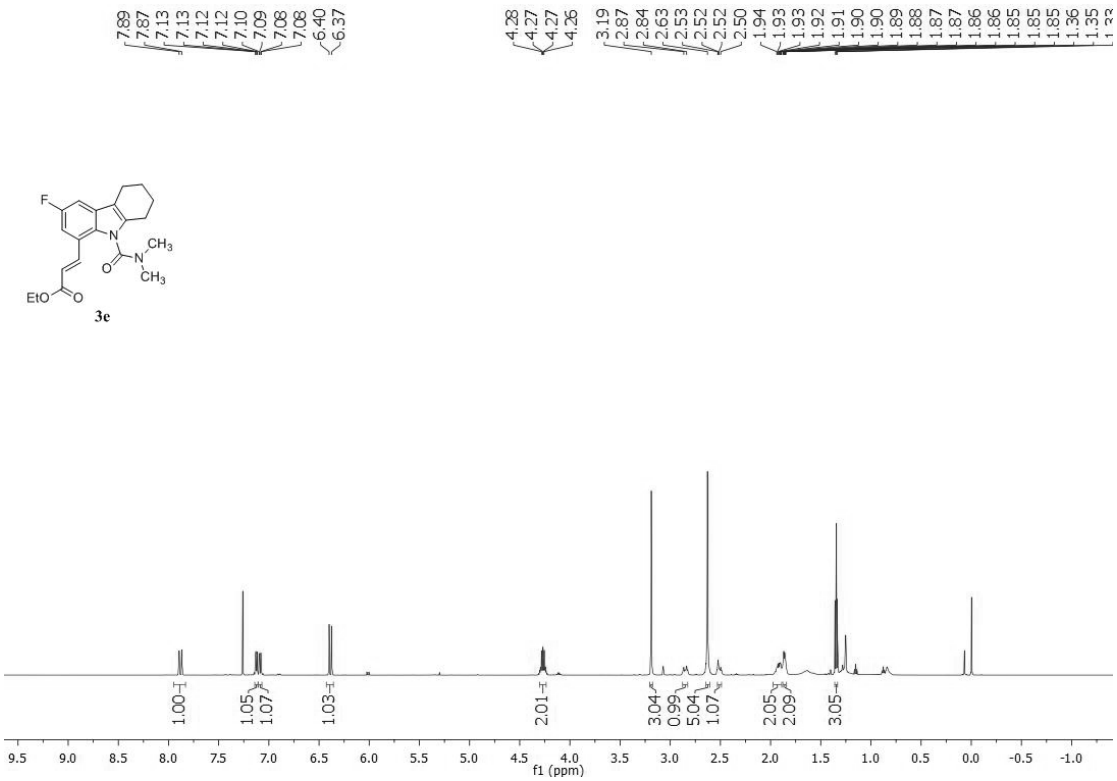
HRMS spectrum of compound **3d**



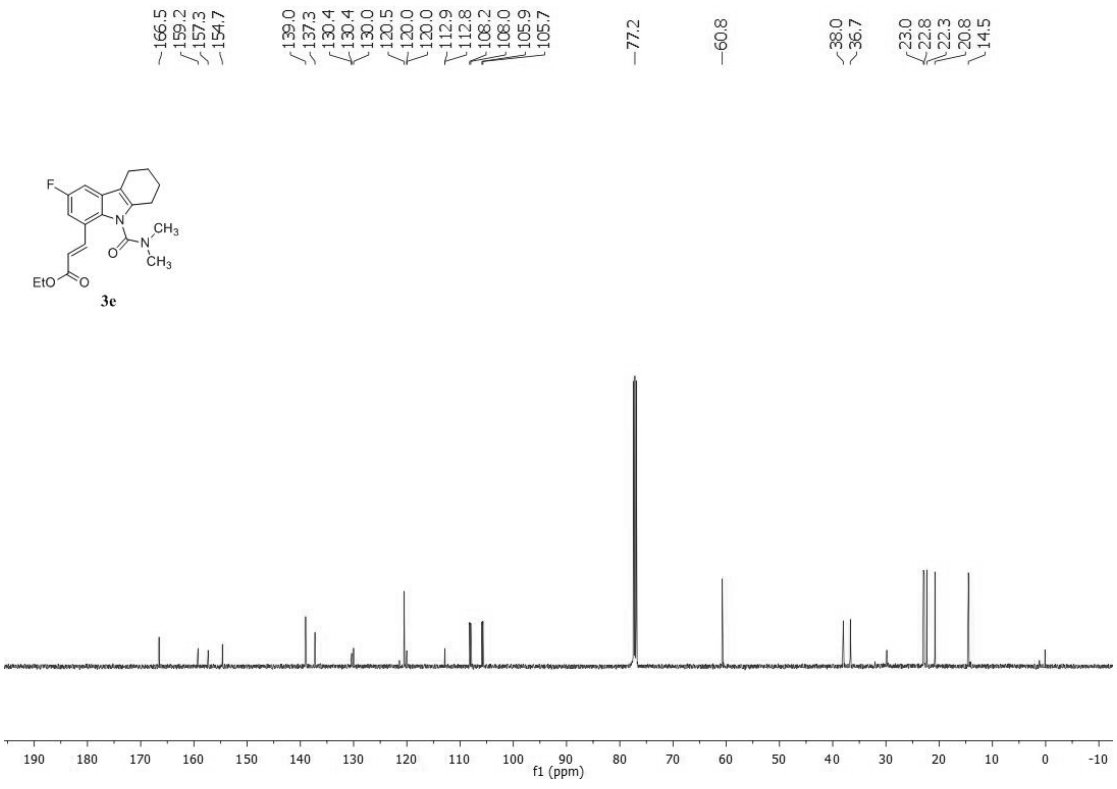
Elemental Composition Calculator

Target m/z:	393.1783	**Result type:**	Positive ions	**Species:**	$[M+Na]^+$
Elements:		C (0-80); H (0-120); O (0-30); N(0-5); Na (0-5)			
Ion Formula		**Calculated m/z**		**PPM Error**	
C21H26N2NaO4		393.1785		0.46	

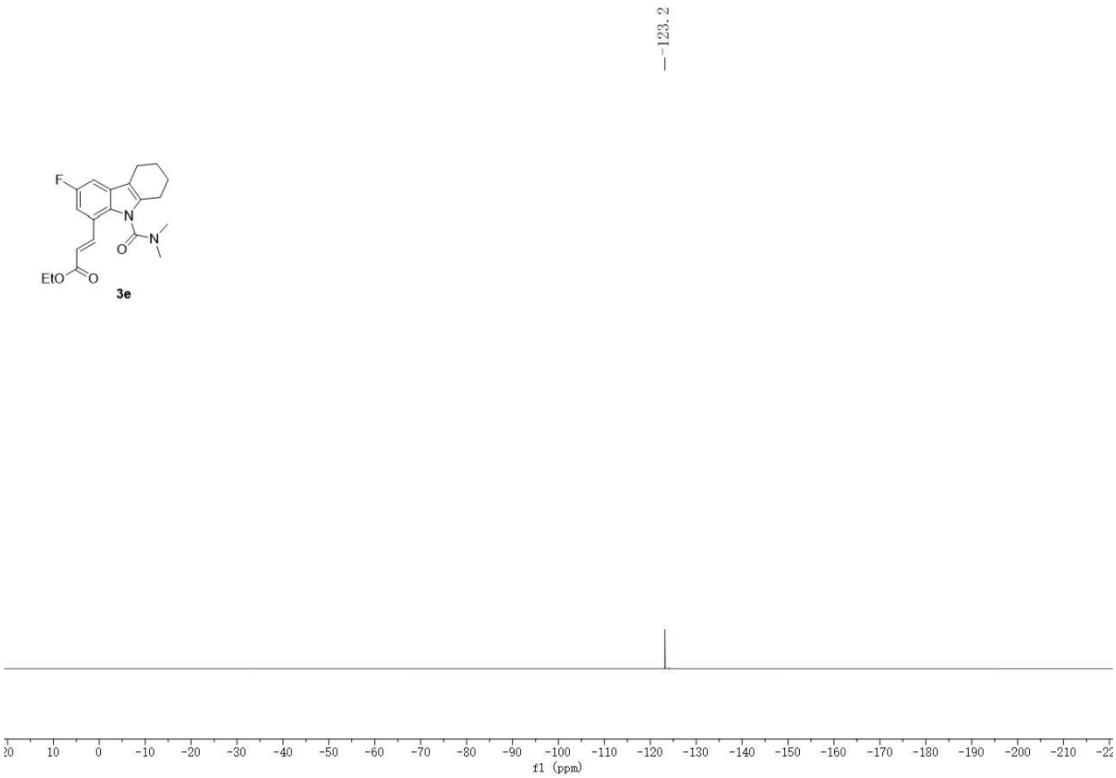
^{1}H NMR spectra of compound **3e**



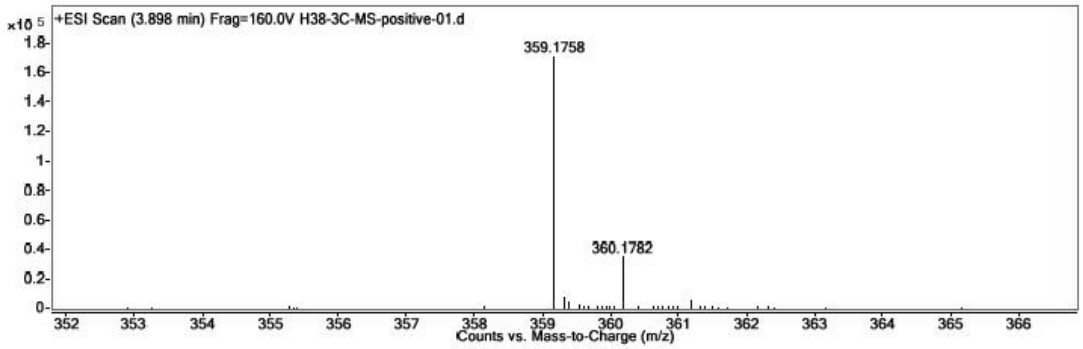
^{13}C NMR spectra of compound **3e**



^{19}F NMR spectra of compound **3e**



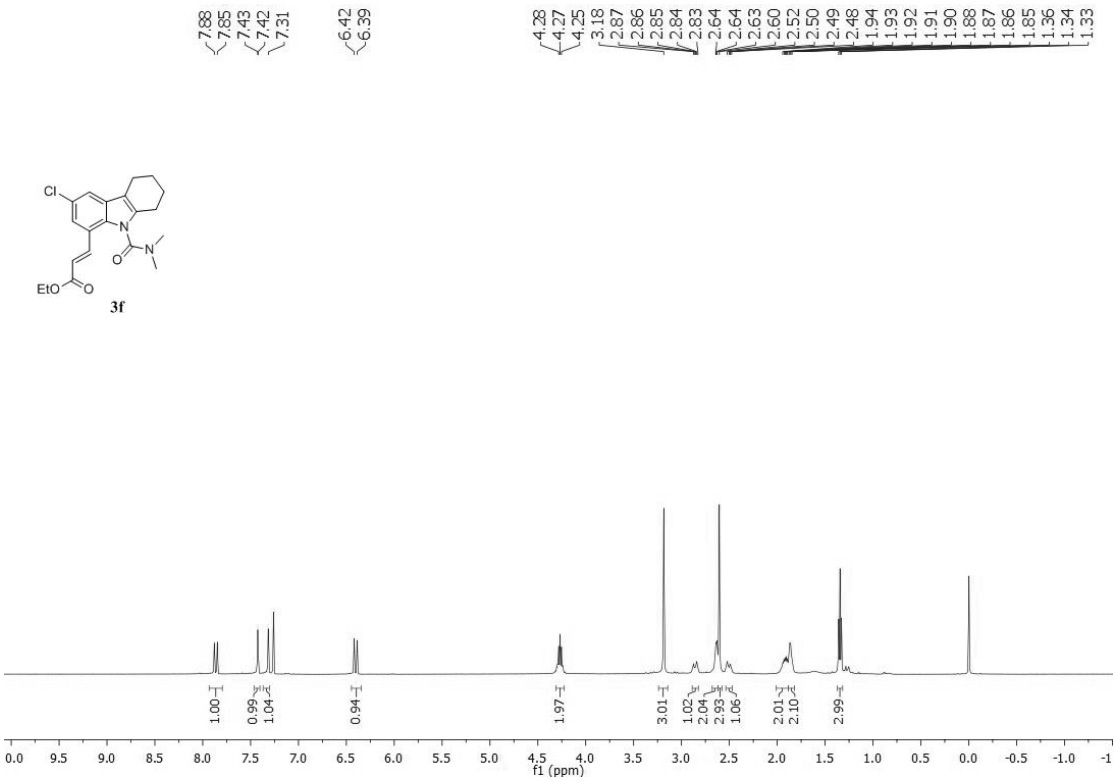
HRMS spectrum of compound **3e**



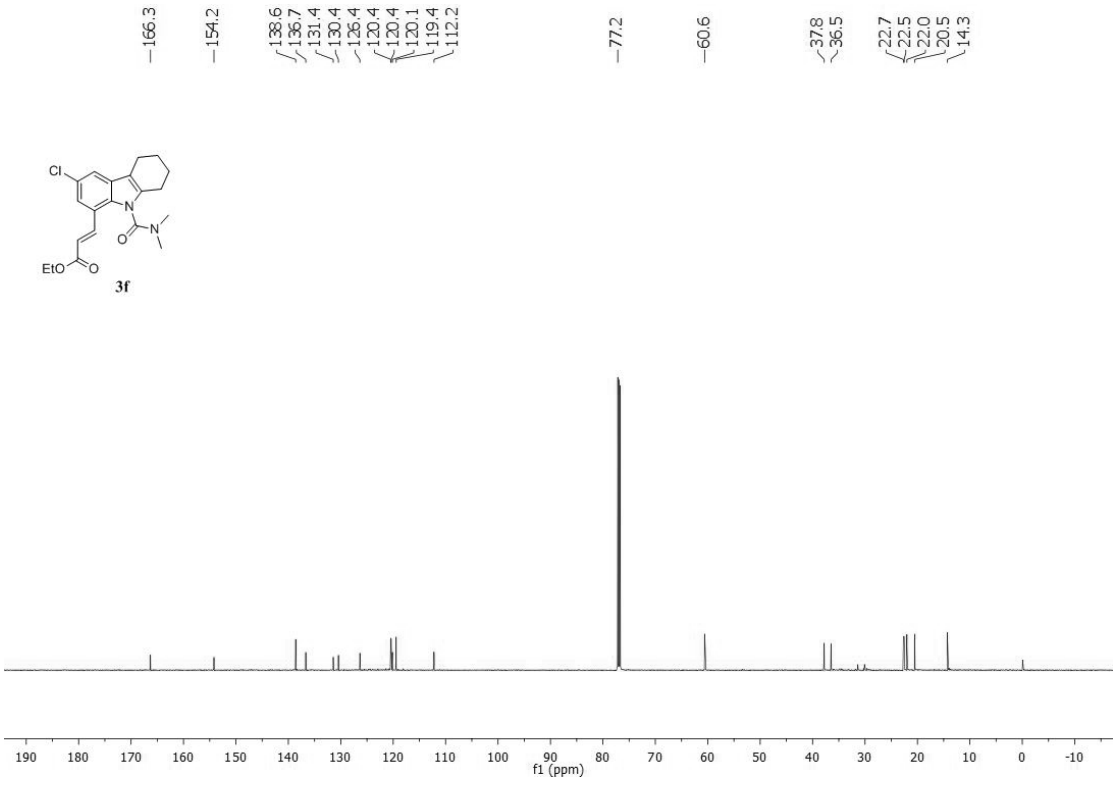
Elemental Composition Calculator

Target m/z:	359.1758	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5) ; F(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C20H24FN2O3		359.1765		2.01	

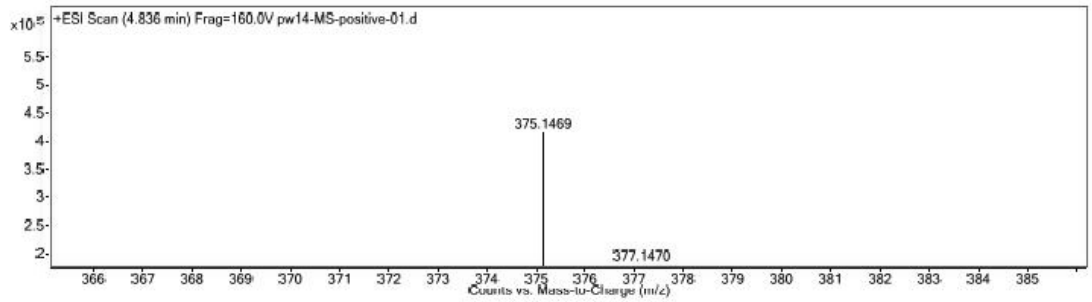
^{1}H NMR spectra of compound **3f**



^{13}C NMR spectra of compound **3f**



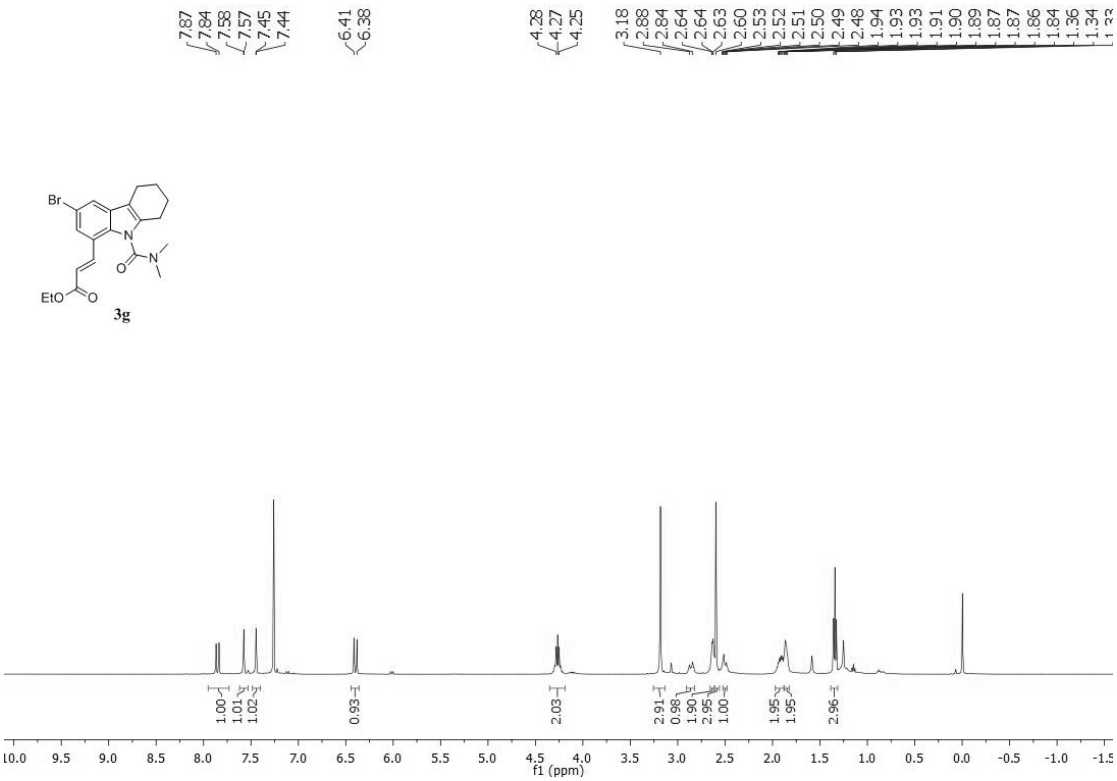
HRMS spectrum of compound **3f**



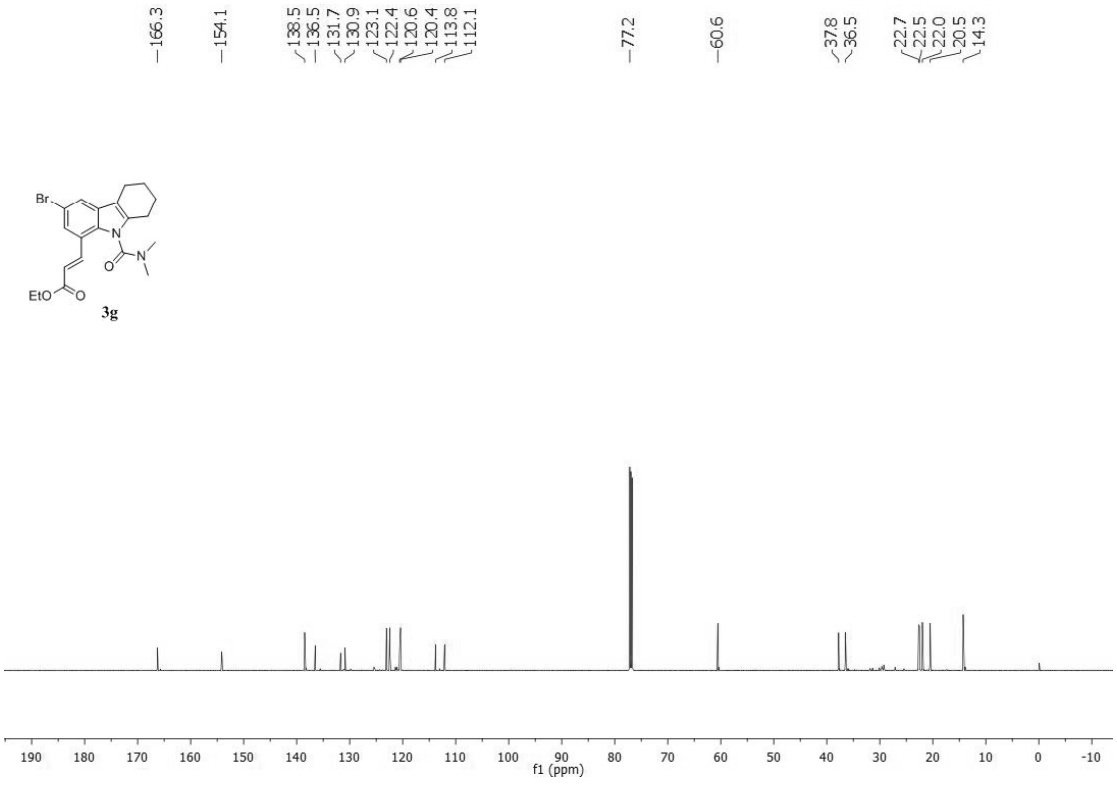
Elemental Composition Calculator

Target m/z:	375.1469	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5) ; Cl(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C20H24ClN2O3		375.1470		0.13	

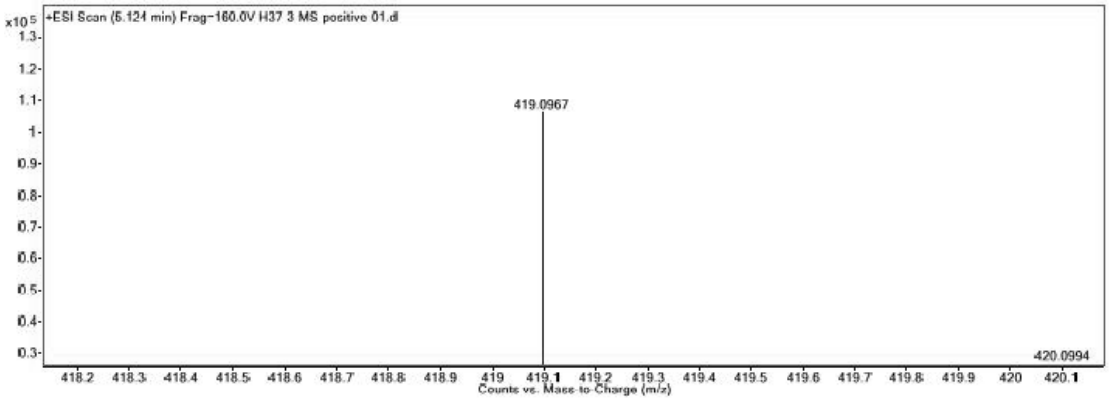
^{1}H NMR spectra of compound **3g**



^{13}C NMR spectra of compound **3g**



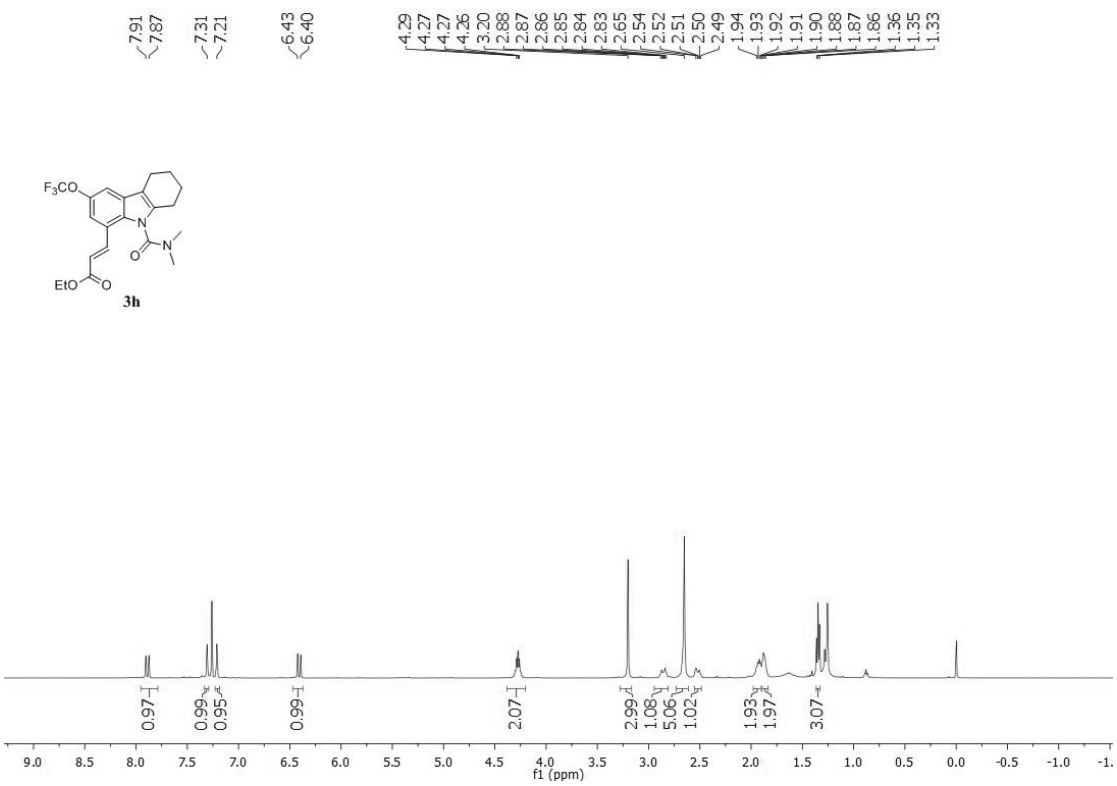
HRMS spectrum of compound **3g**



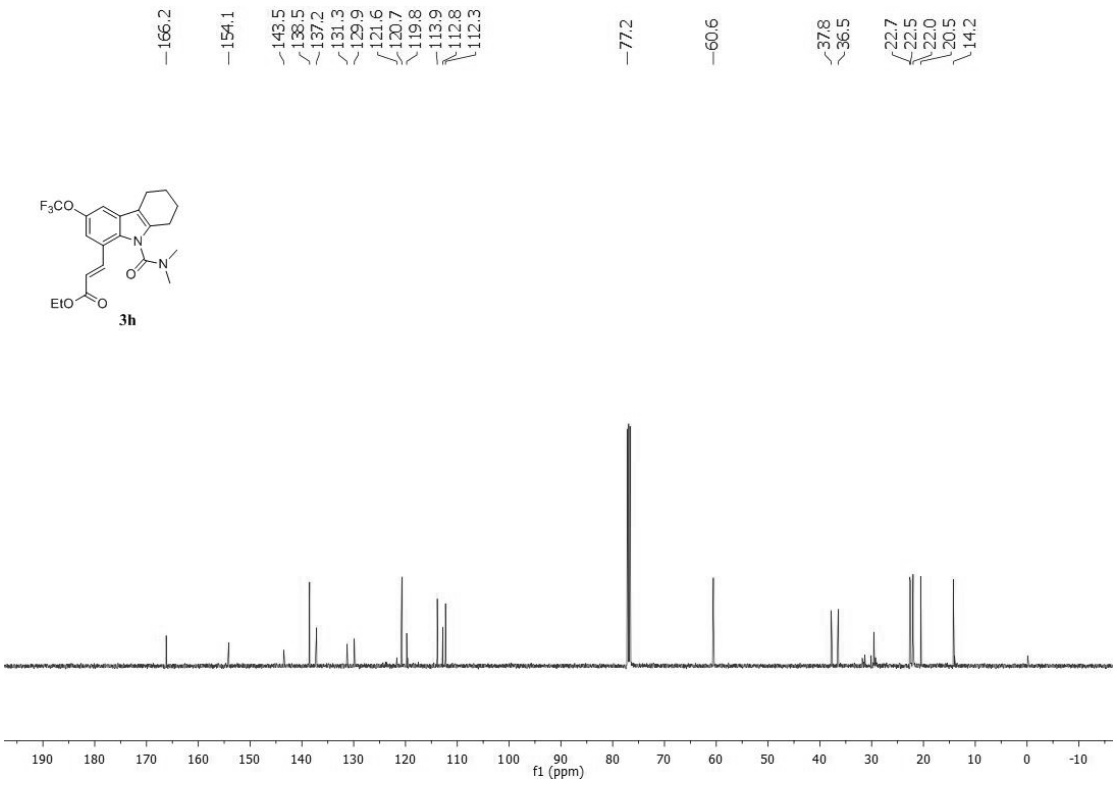
Elemental Composition Calculator

Target m/z:	419.0967	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5) ;Br(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C20H24BrN2O3		419.0965		-0.53	

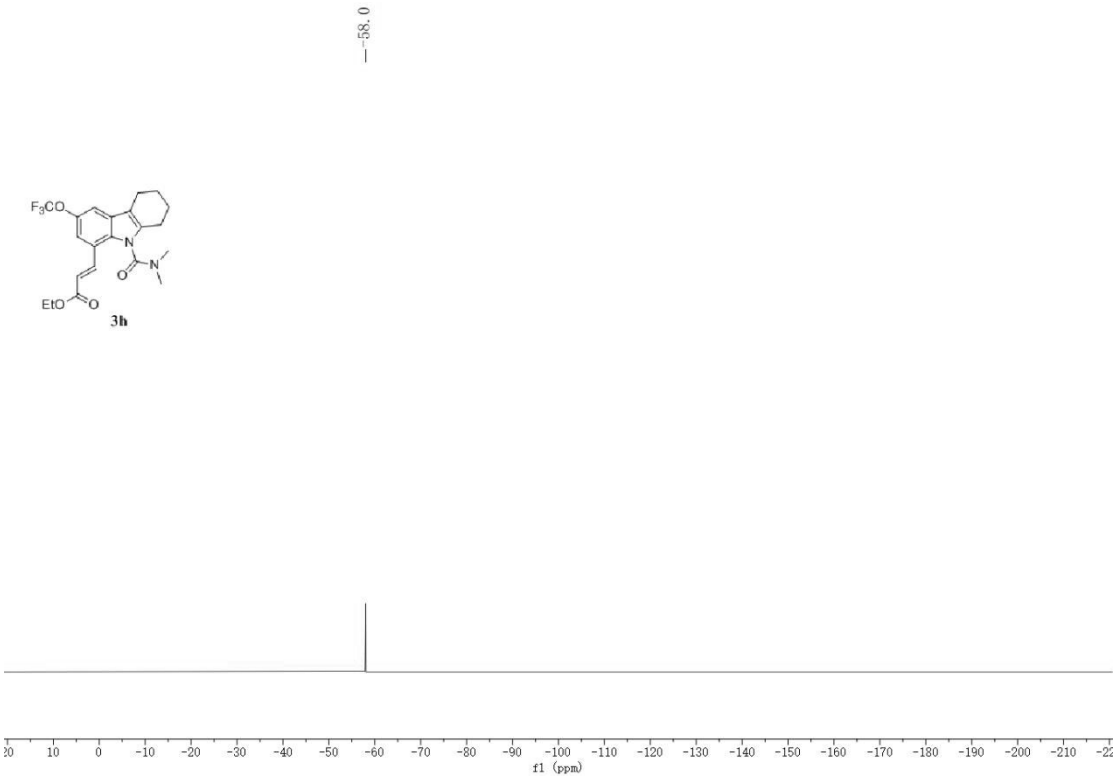
^{1}H NMR spectra of compound **3h**



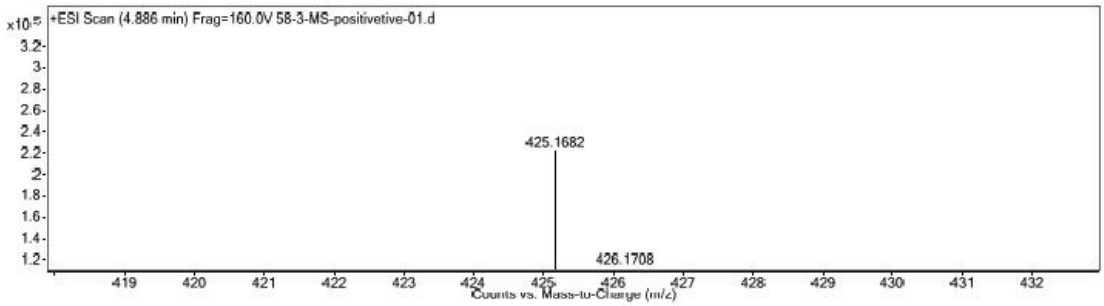
^{13}C NMR spectra of compound **3h**



^{19}F NMR spectra of compound **3h**



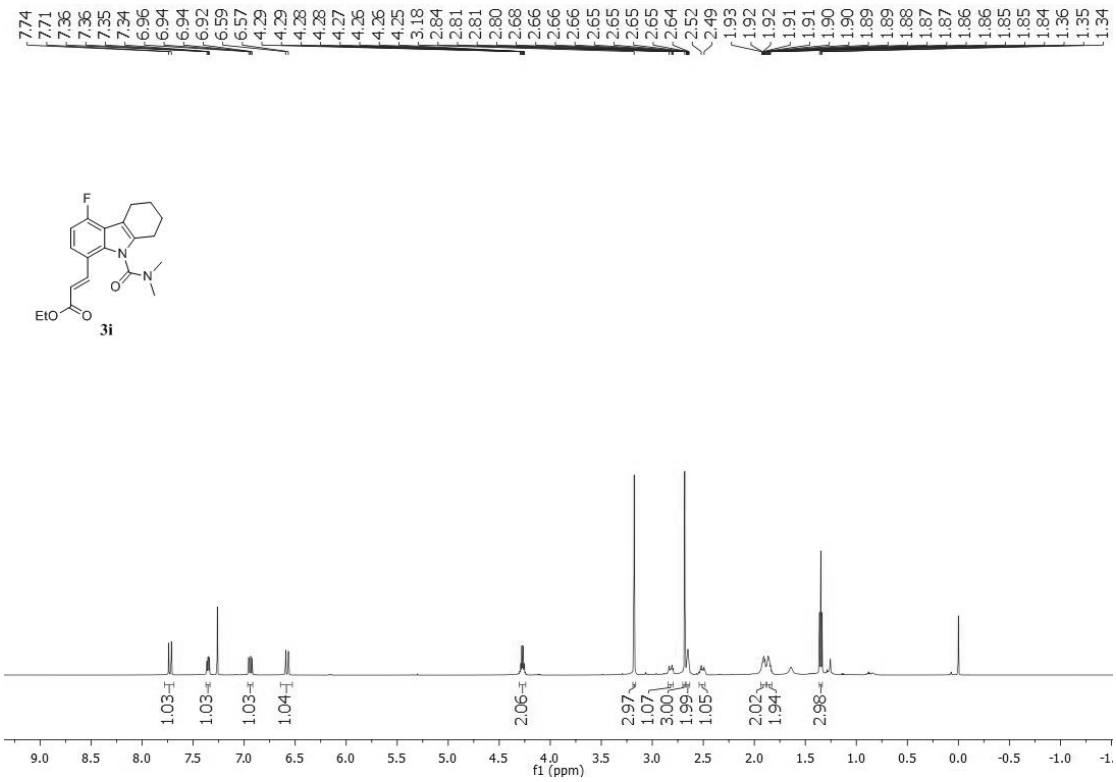
HRMS spectrum of compound **3h**



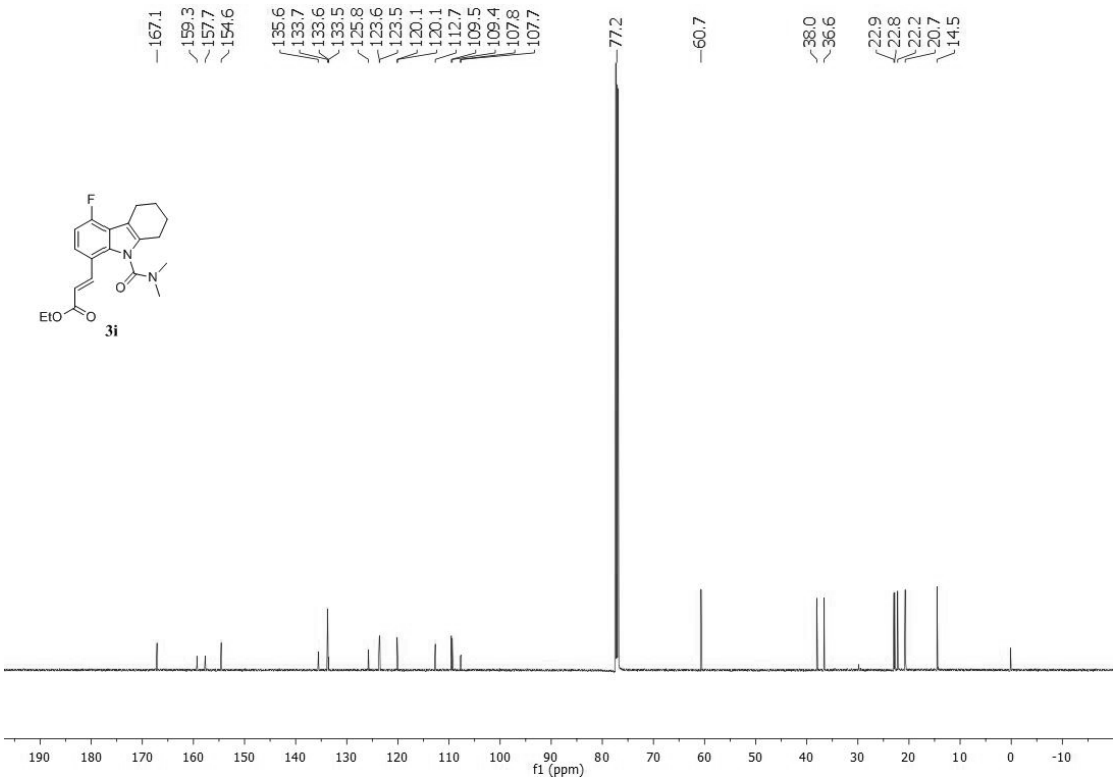
Elemental Composition Calculator

Target m/z:	425.1682	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5) ; F(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C21H24F3N2O4		425.1683		0.11	

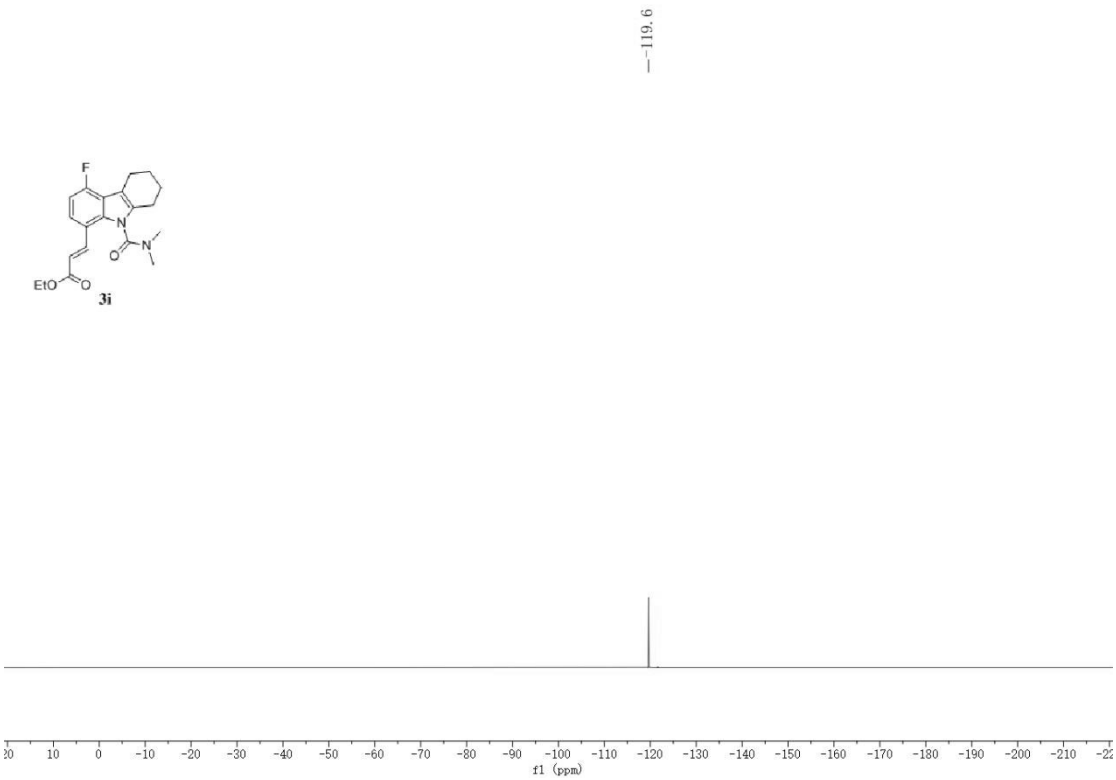
^{1}H NMR spectra of compound **3i**



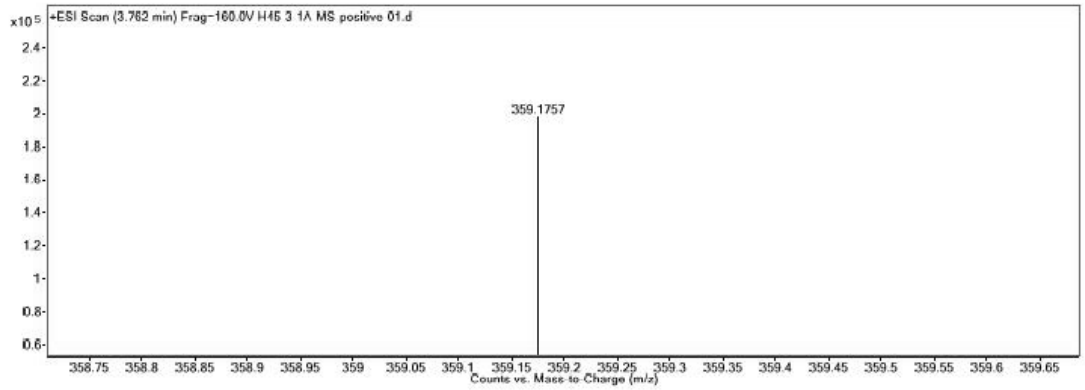
^{13}C NMR spectra of compound **3i**



^{19}F NMR spectra of compound **3i**



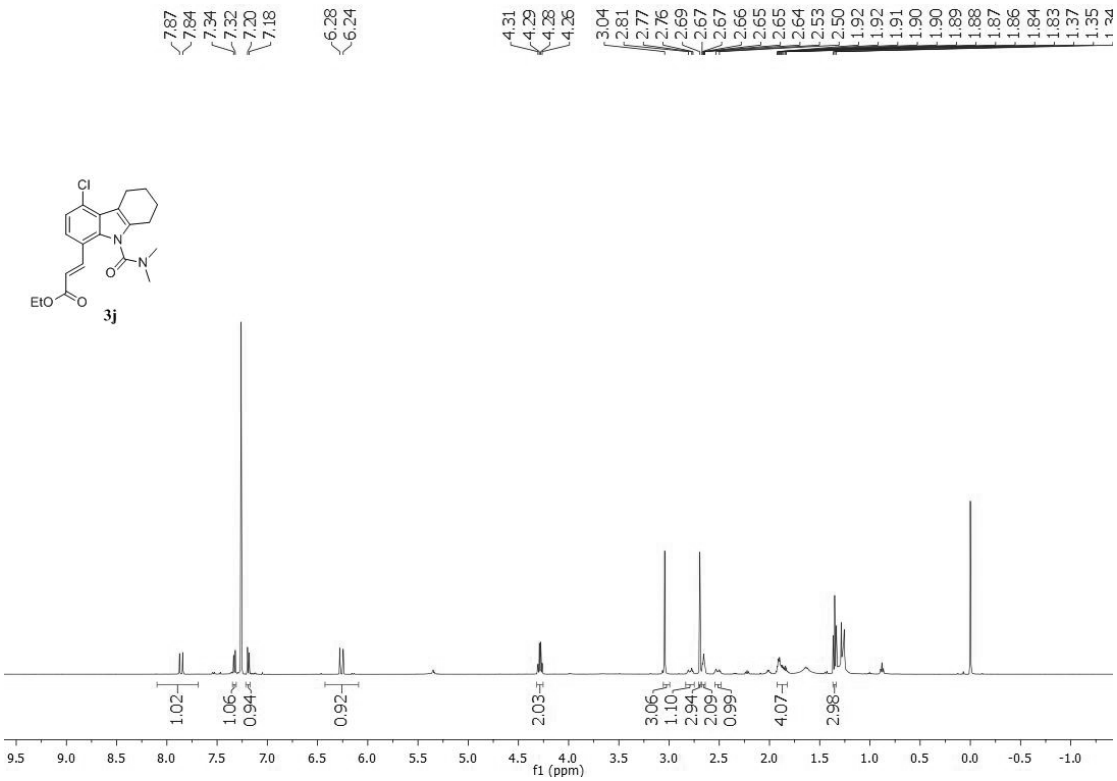
HRMS spectrum of compound **3i**



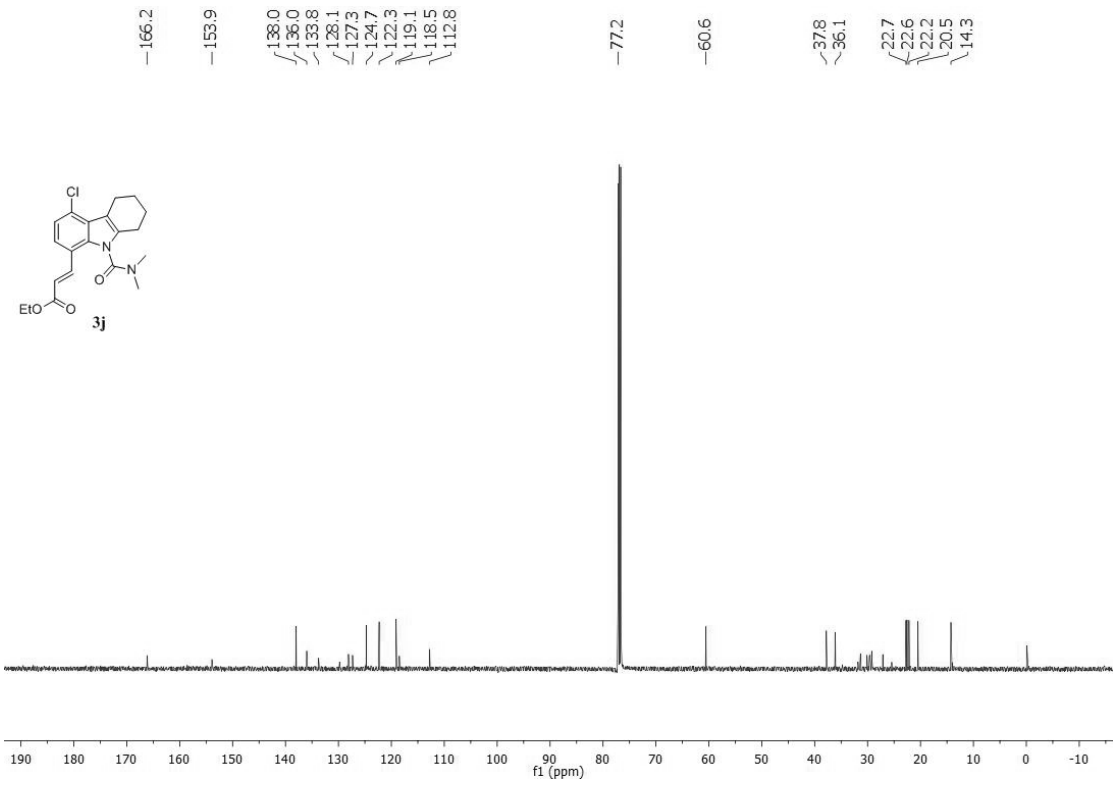
Elemental Composition Calculator

Target m/z:	359.1757	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5) ; F(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C20H24FN2O3		359.1765		2.46	

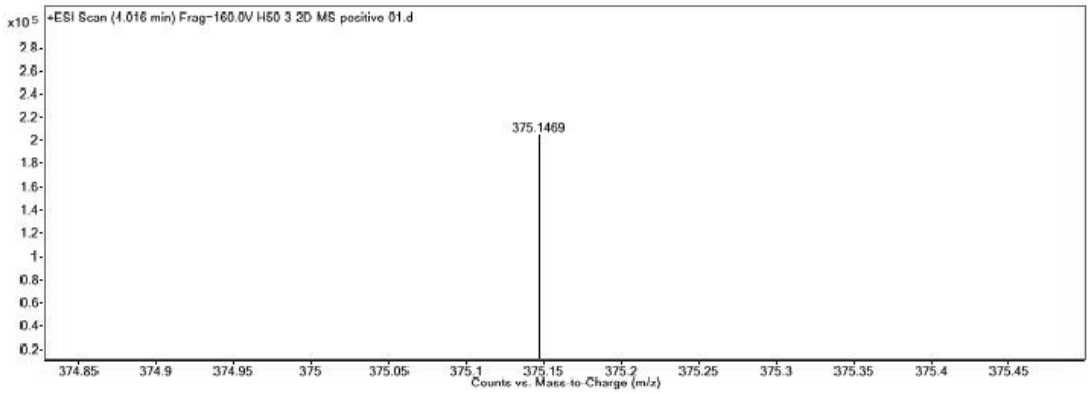
^{1}H NMR spectra of compound **3j**



^{13}C NMR spectra of compound **3j**



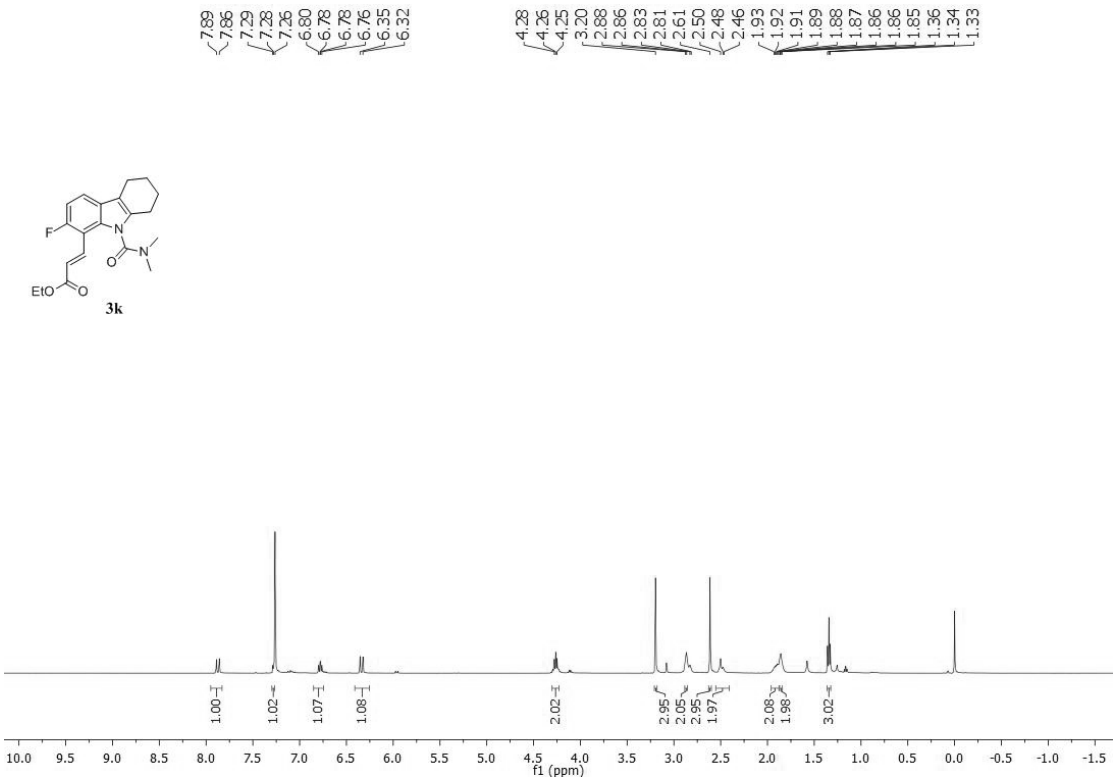
HRMS spectrum of compound **3j**



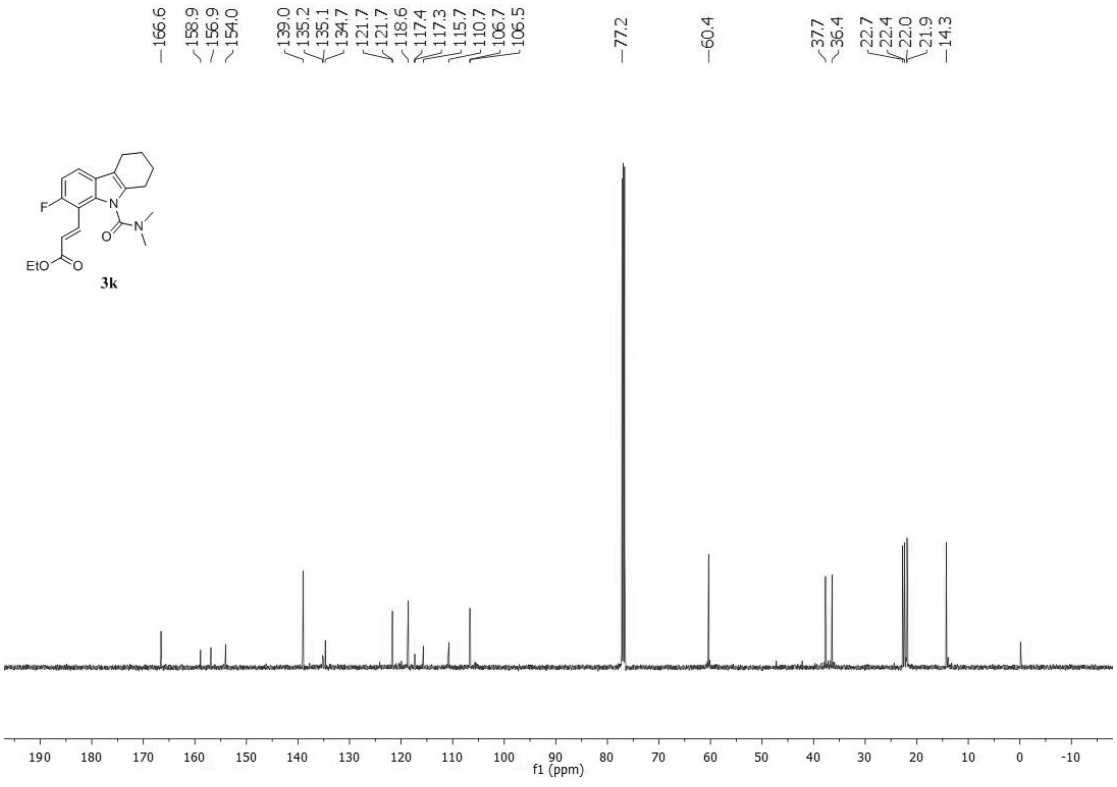
Elemental Composition Calculator

Target m/z:	375.1469	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5) ; Cl(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C20H24ClN2O3		375.1470		0.37	

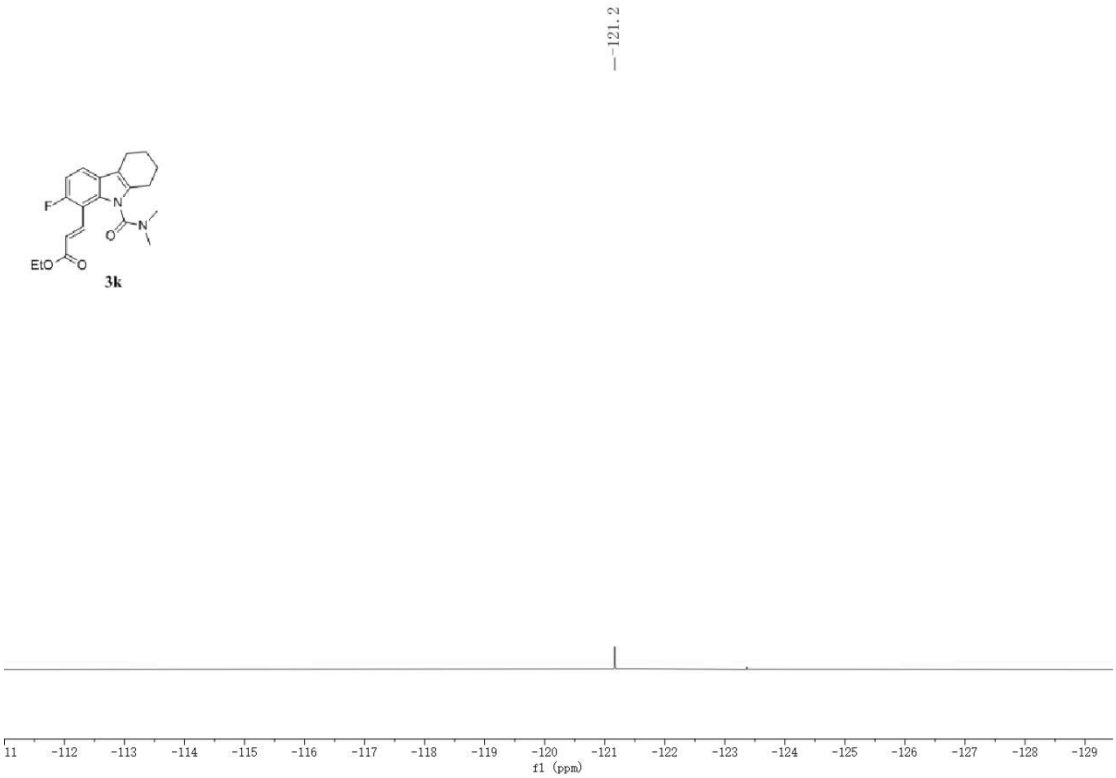
^{1}H NMR spectra of compound **3k**



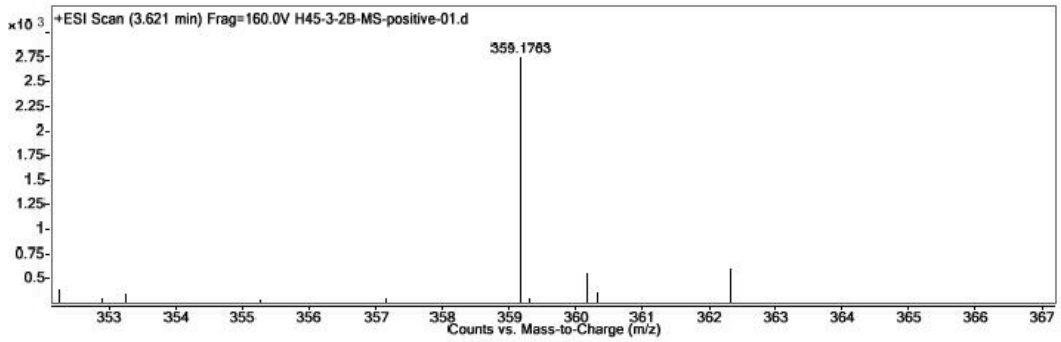
^{13}C NMR spectra of compound **3k**



^{19}F NMR spectra of compound **3k**



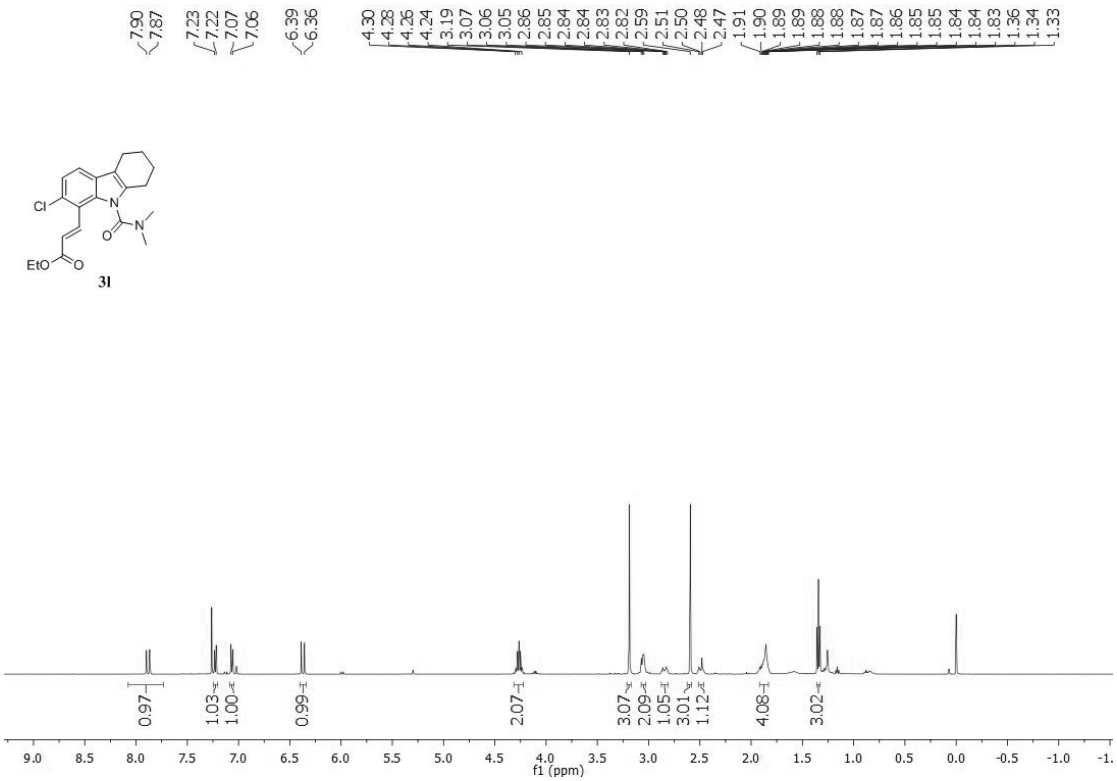
HRMS spectrum of compound **3k**



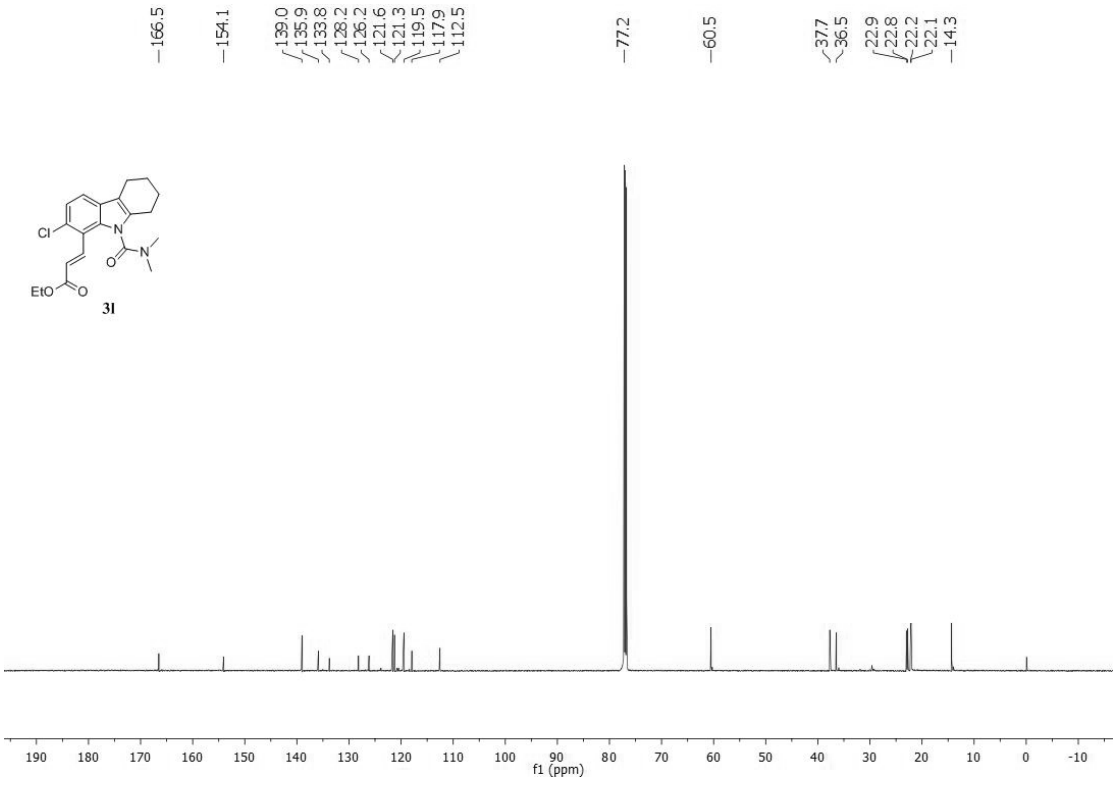
Elemental Composition Calculator

Target m/z:	359.1763	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5) ;F(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C20H24FN2O3		359.1765		0.75	

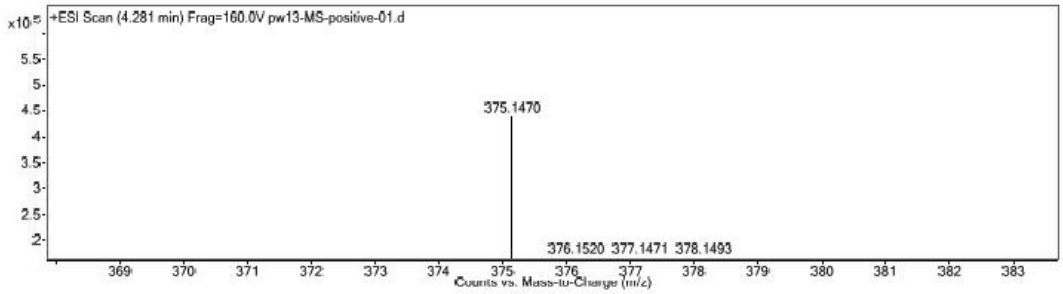
^{1}H NMR spectra of compound **3l**



^{13}C NMR spectra of compound **3l**



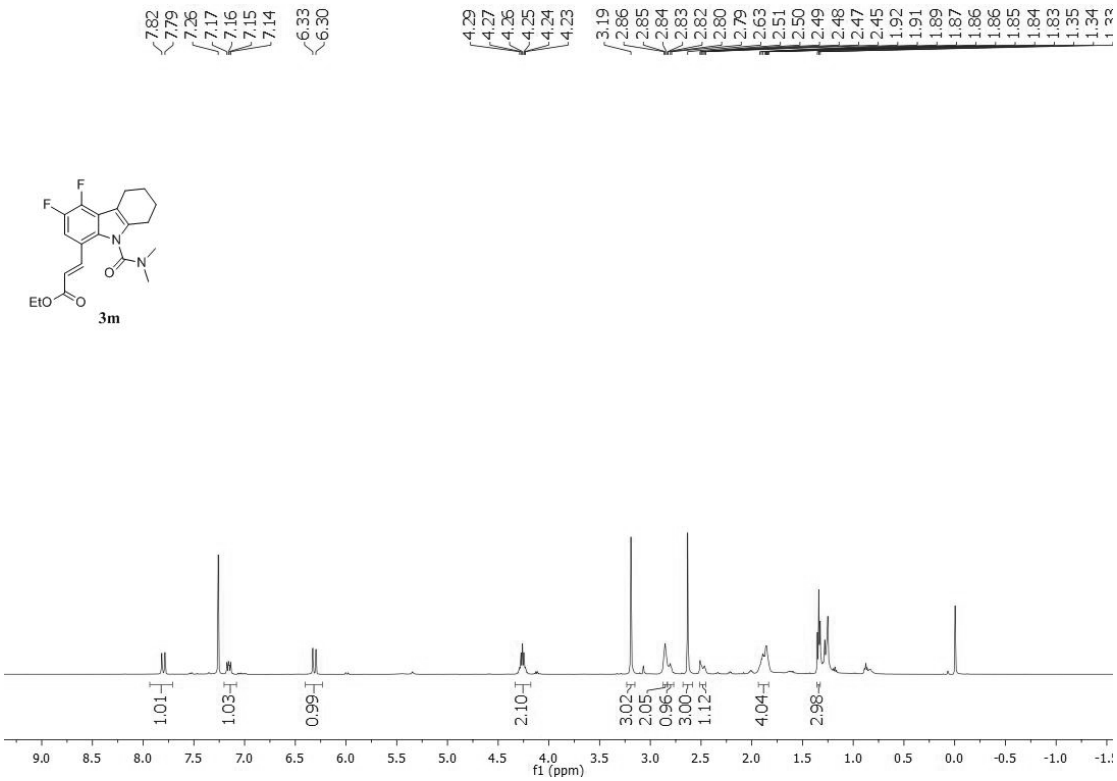
HRMS spectrum of compound **3l**



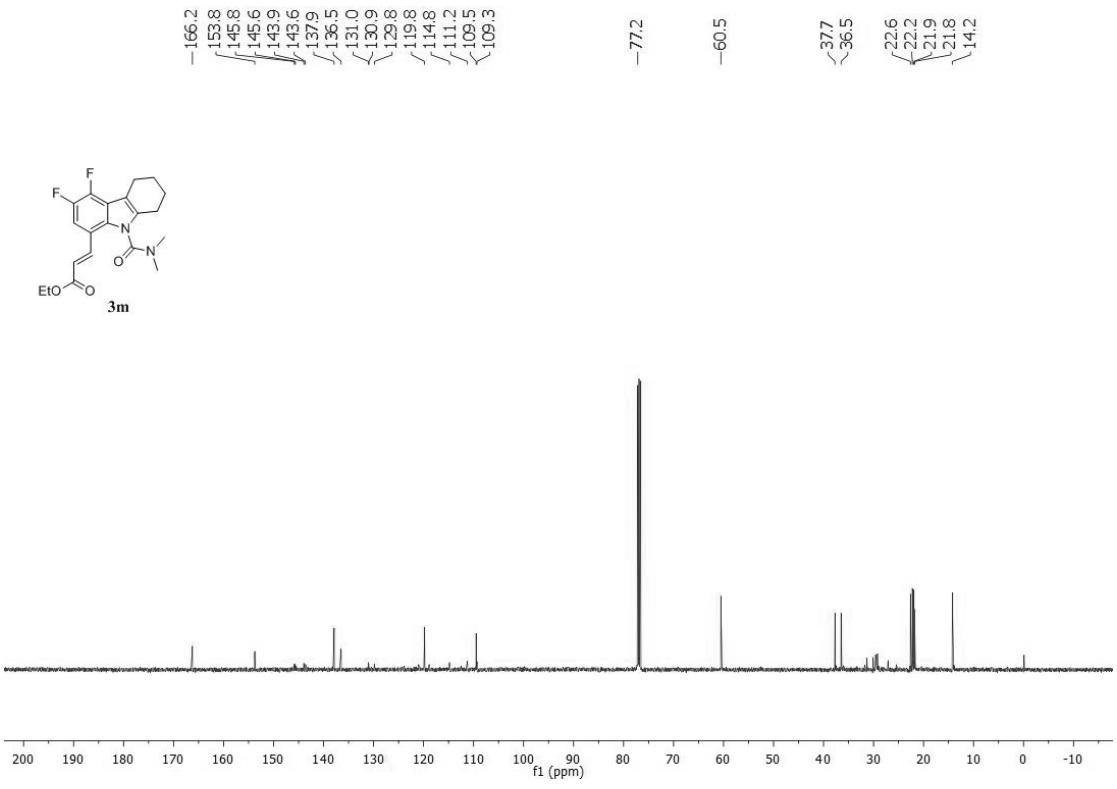
Elemental Composition Calculator

Target m/z:	375.1470	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5) ; Cl(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C20H24ClN2O3		375.1470		-0.11	

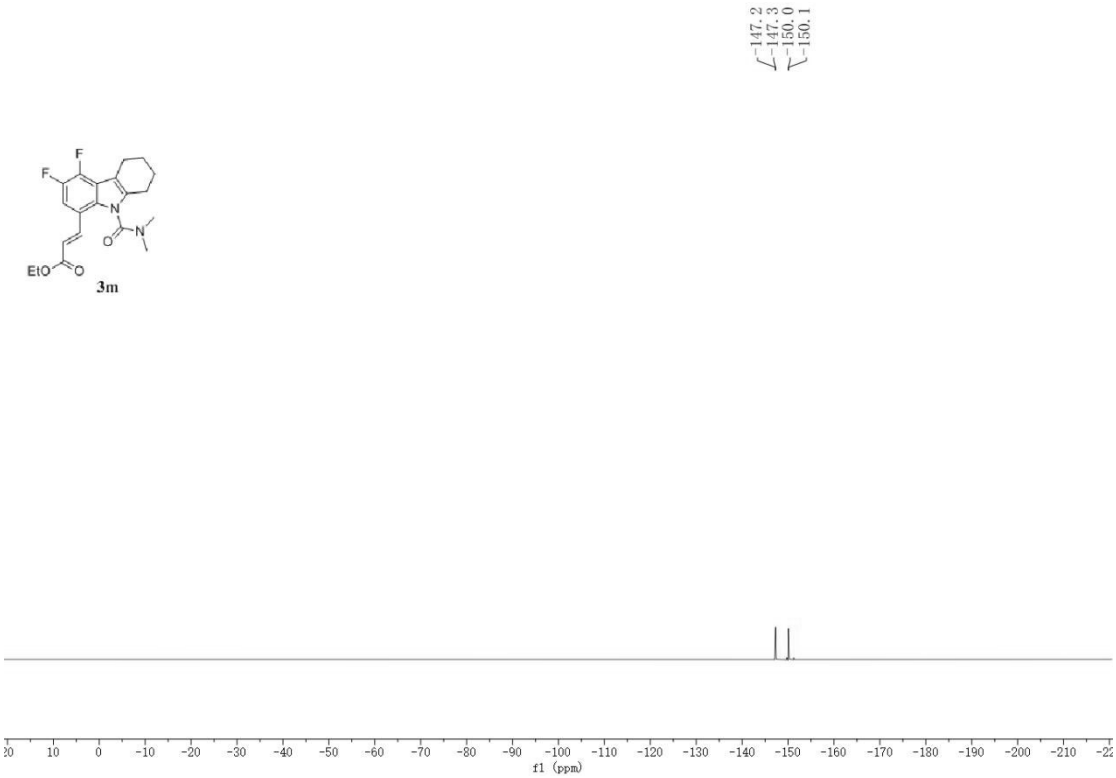
^{1}H NMR spectra of compound **3m**



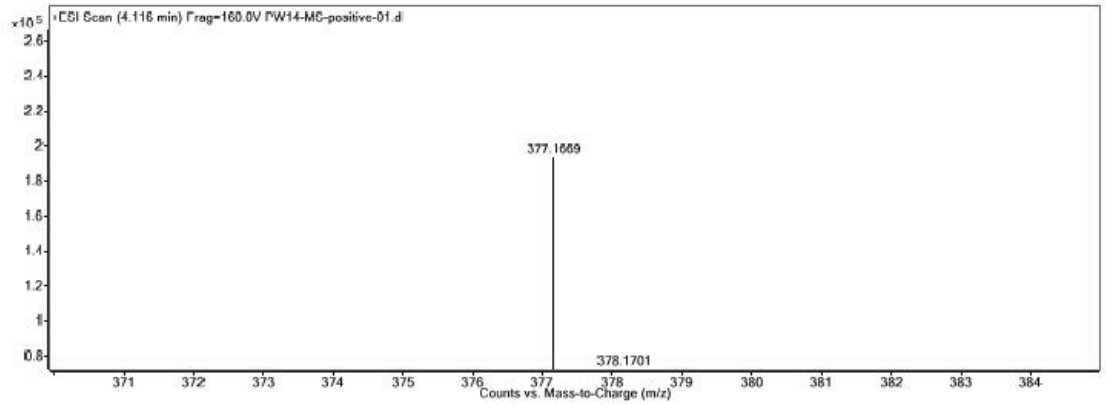
^{13}C NMR spectra of compound **3m**



^{19}F NMR spectra of compound **3m**



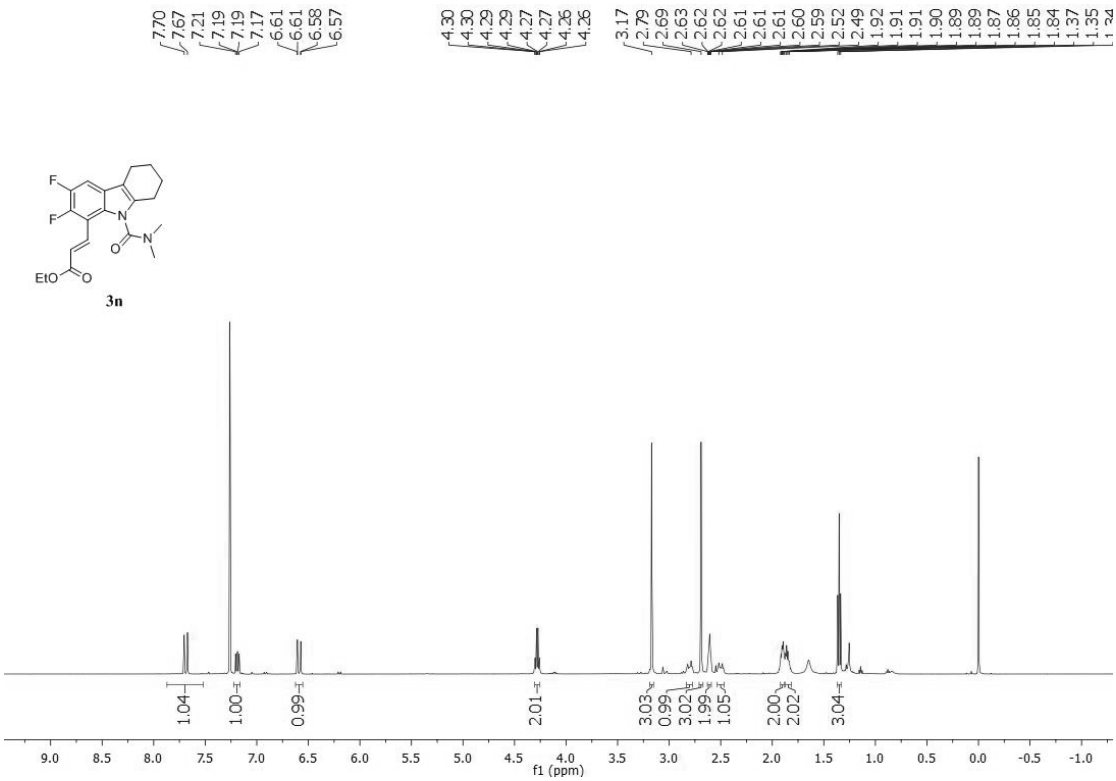
HRMS spectrum of compound **3m**



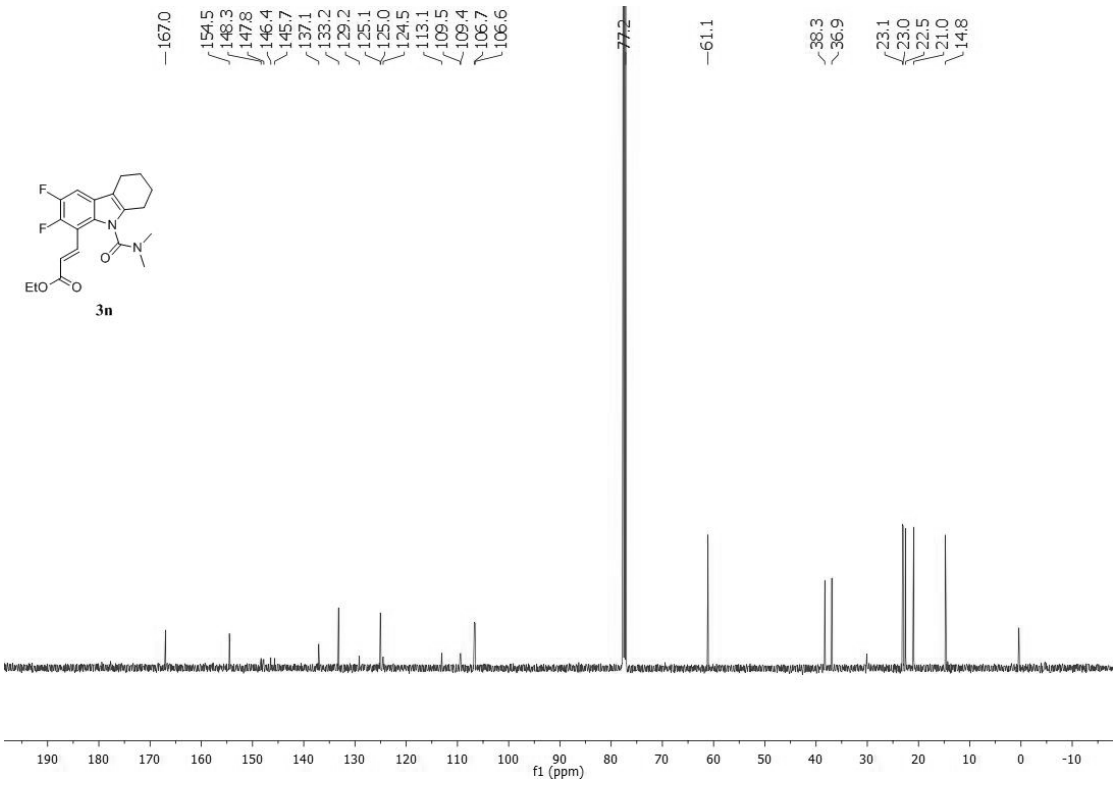
Elemental Composition Calculator

Target m/z:	377.1669	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5) ; F(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C20H23F2N2O3		377.1671		0.48	

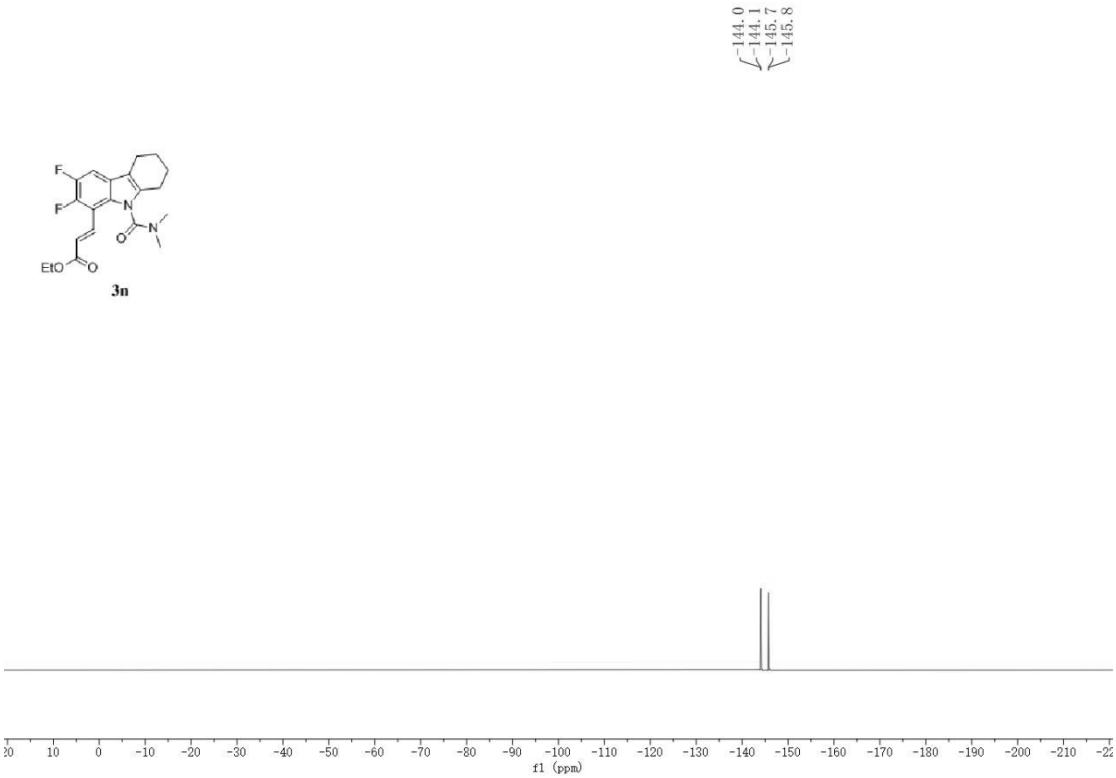
^{1}H NMR spectra of compound **3n**



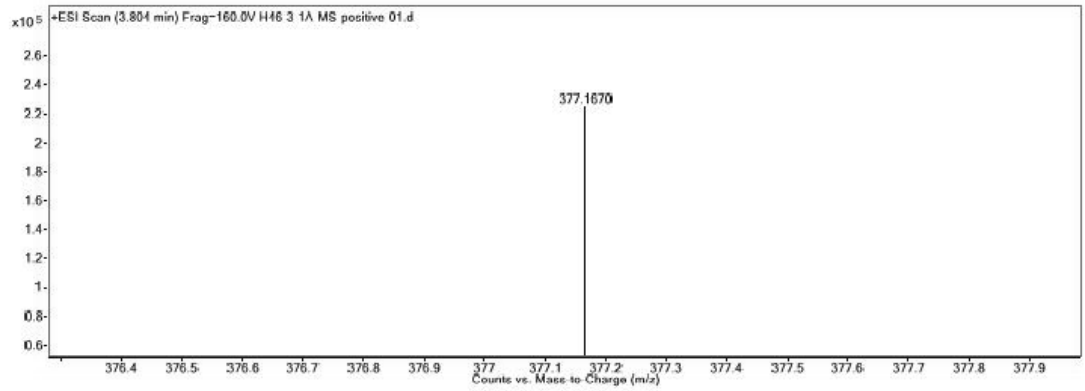
^{13}C NMR spectra of compound **3n**



^{19}F NMR spectra of compound **3n**



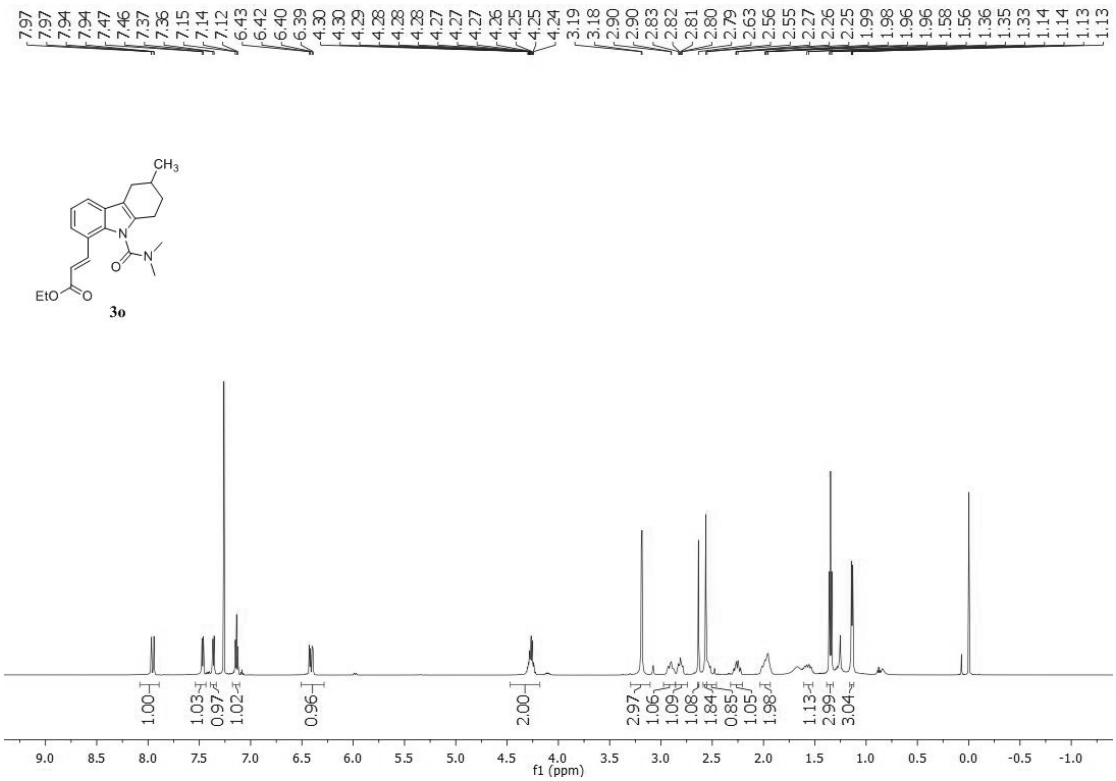
HRMS spectrum of compound **3n**



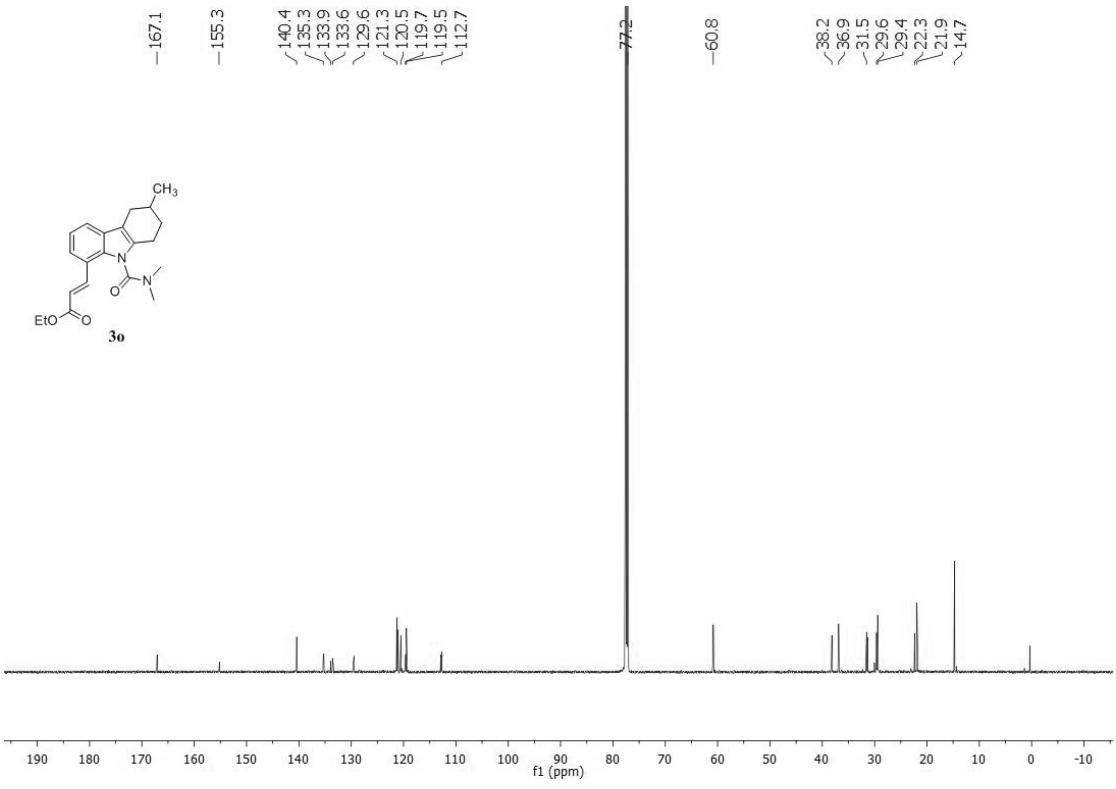
Elemental Composition Calculator

Target m/z:	377.1670	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5) ; F(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C20H23F2N2O3		377.1671		0.31	

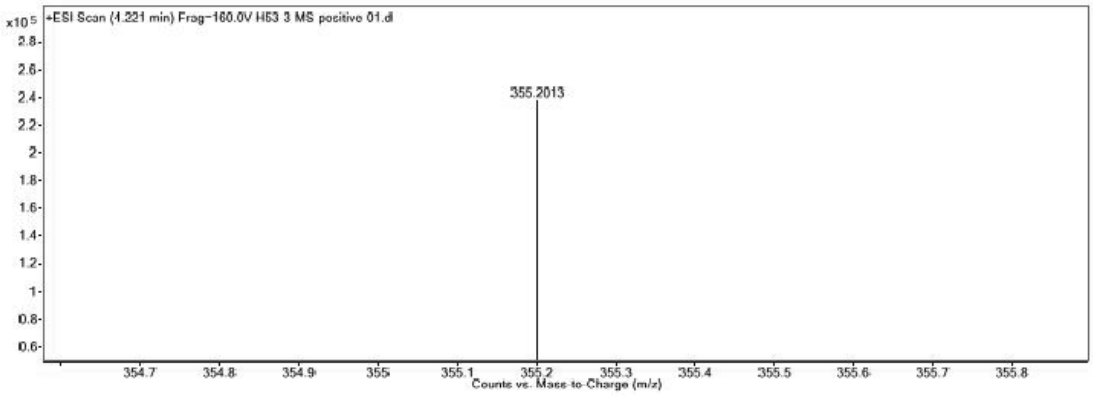
^{1}H NMR spectra of compound **3o**



^{13}C NMR spectra of compound **3o**



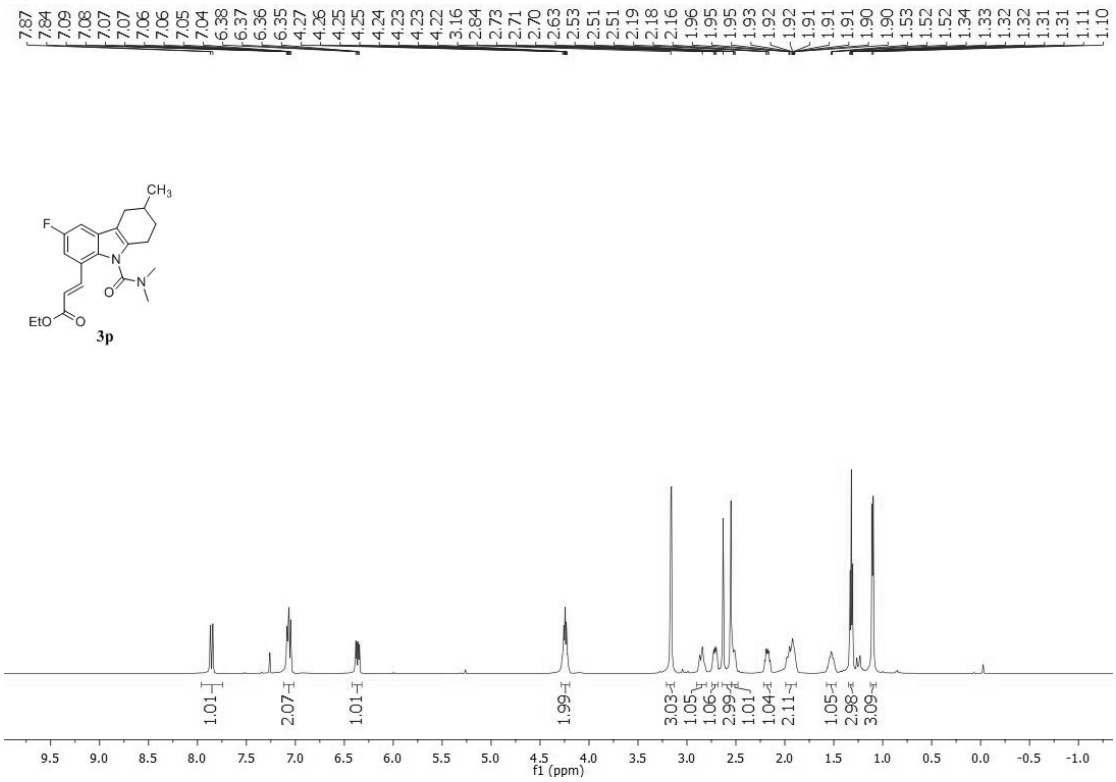
HRMS spectrum of compound **3o**



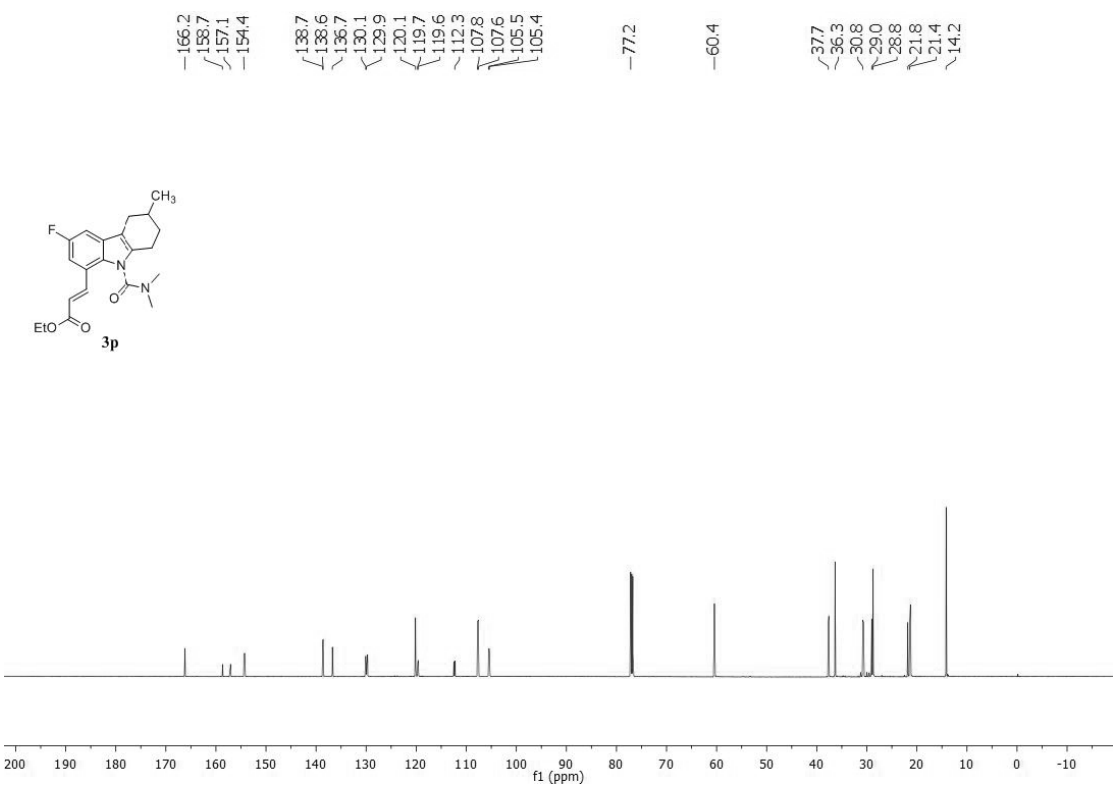
Elemental Composition Calculator

Target m/z:	355.2013	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C21H27N2O3		355.2016		0.95	

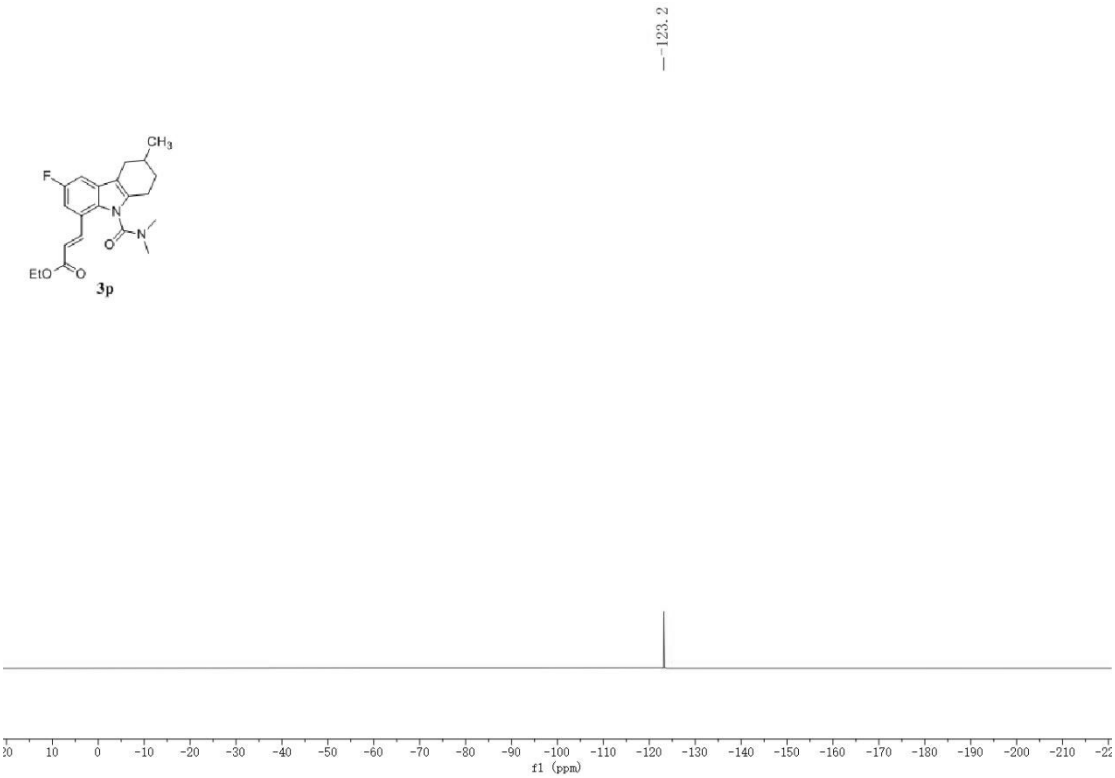
^{1}H NMR spectra of compound **3p**



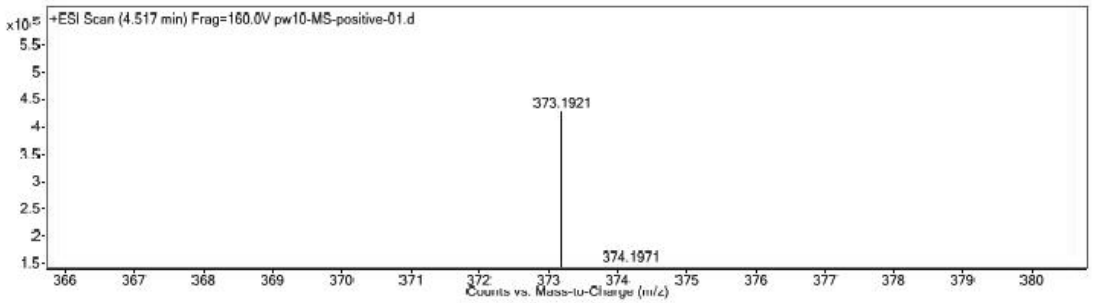
^{13}C NMR spectra of compound **3p**



^{19}F NMR spectra of compound **3p**



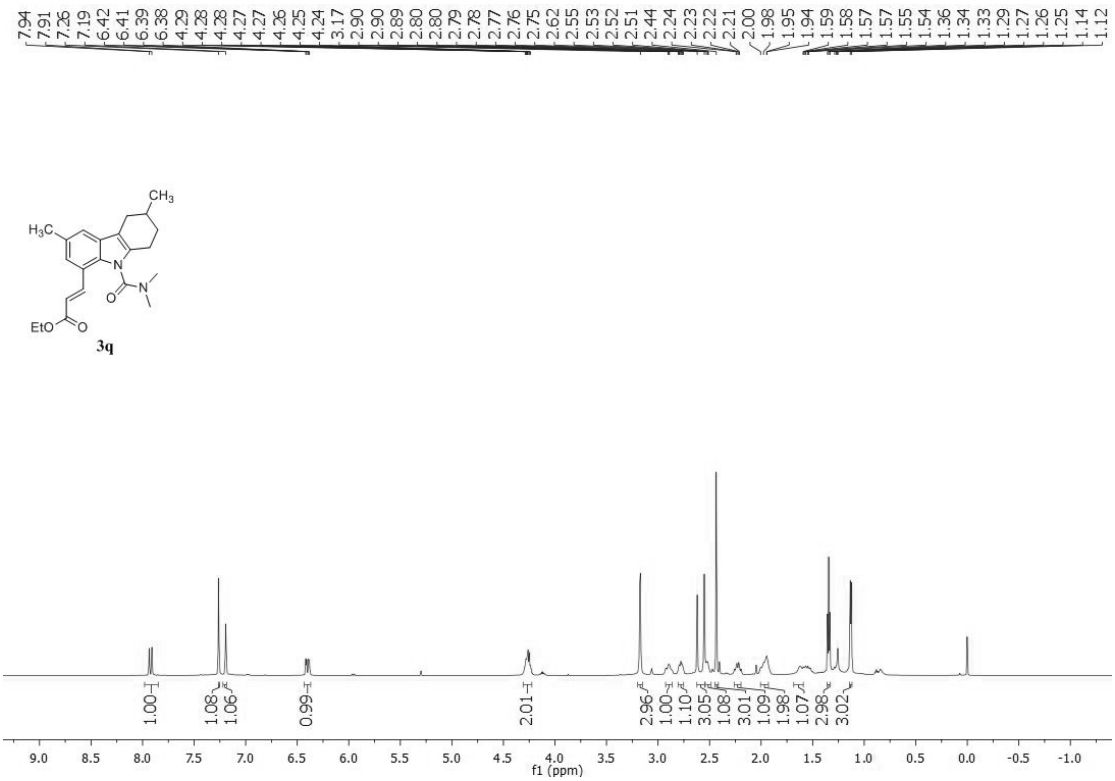
HRMS spectrum of compound **3p**



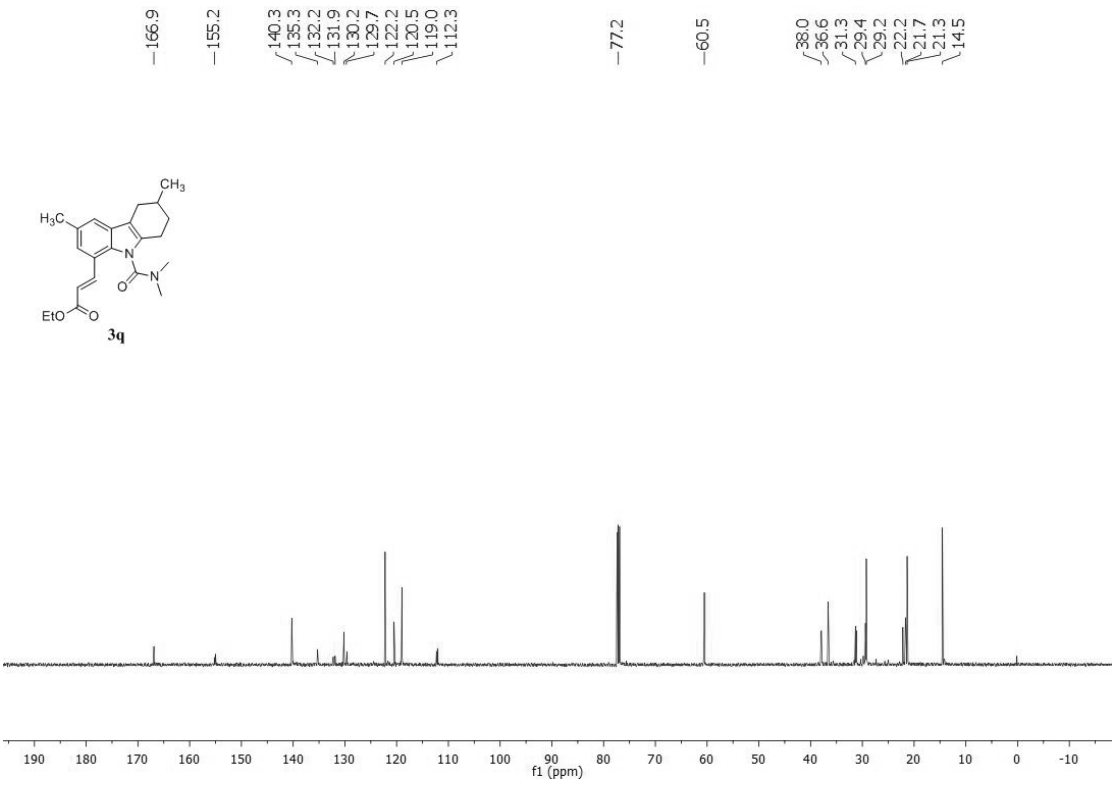
Elemental Composition Calculator

Target m/z:	373.1921	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5) ; F(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C21H26FN2O3		373.1922		0.29	

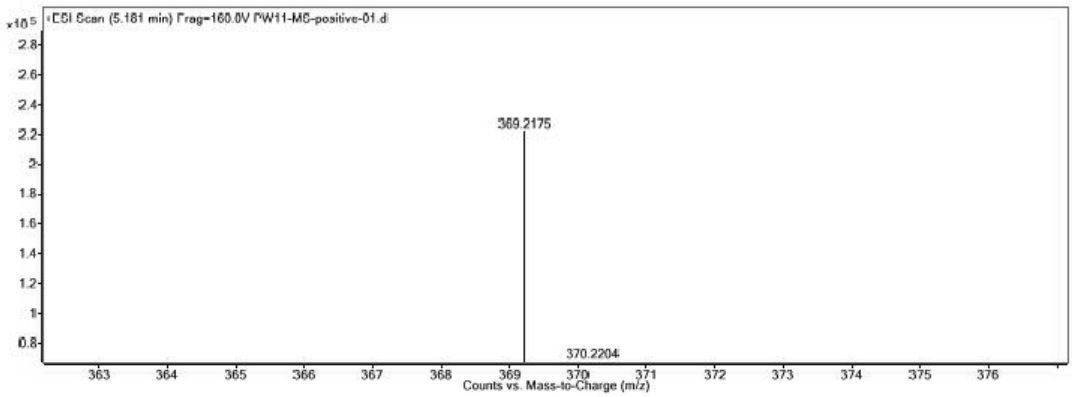
^{1}H NMR spectra of compound **3q**



^{13}C NMR spectra of compound **3q**



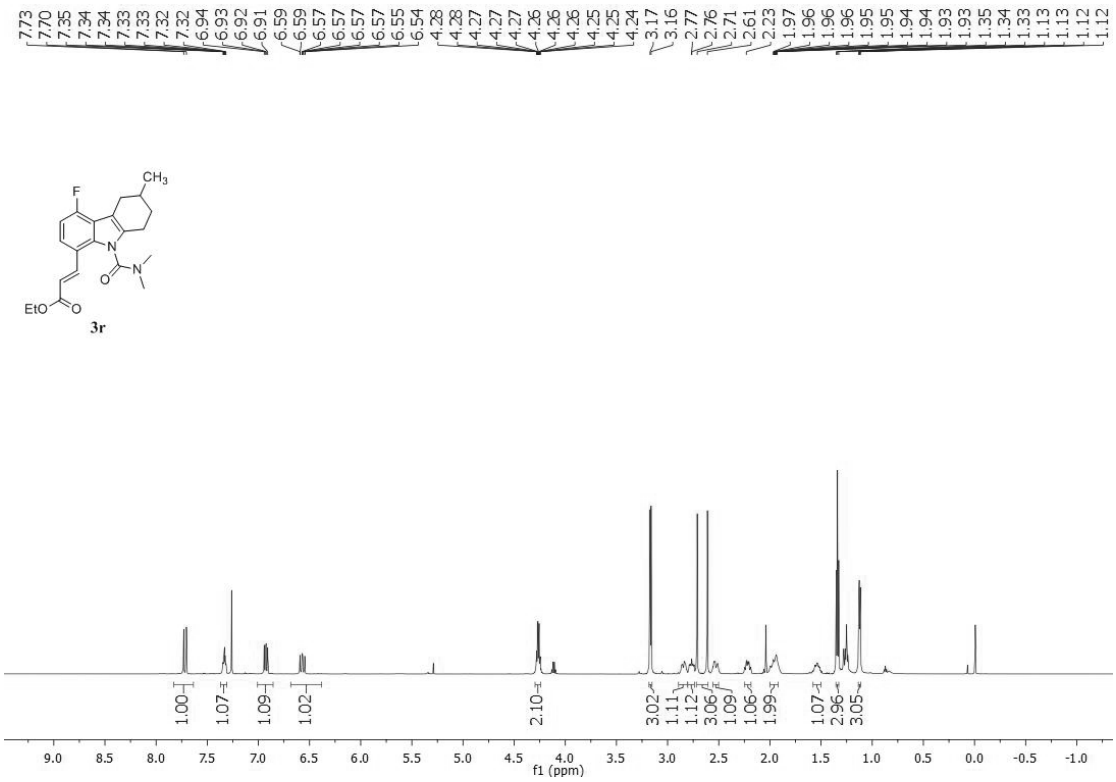
HRMS spectrum of compound **3q**



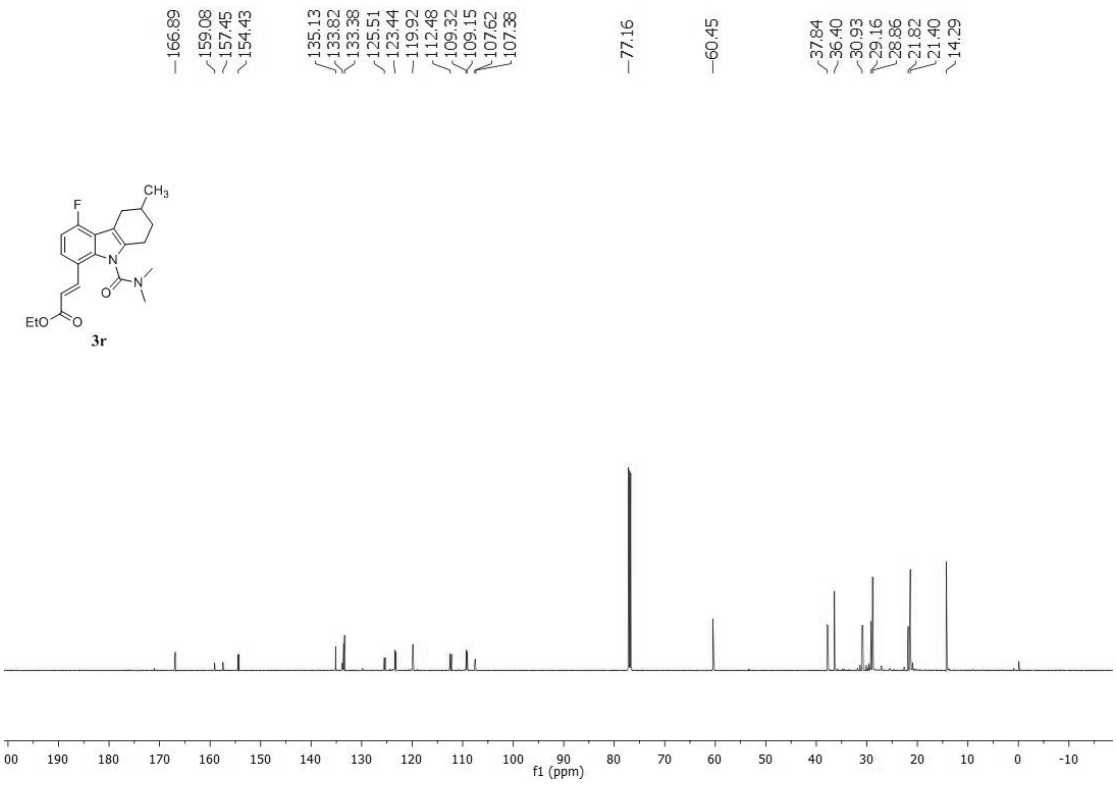
Elemental Composition Calculator

Target m/z:	369.2175	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C22H29N2O3		369.2173		-0.57	

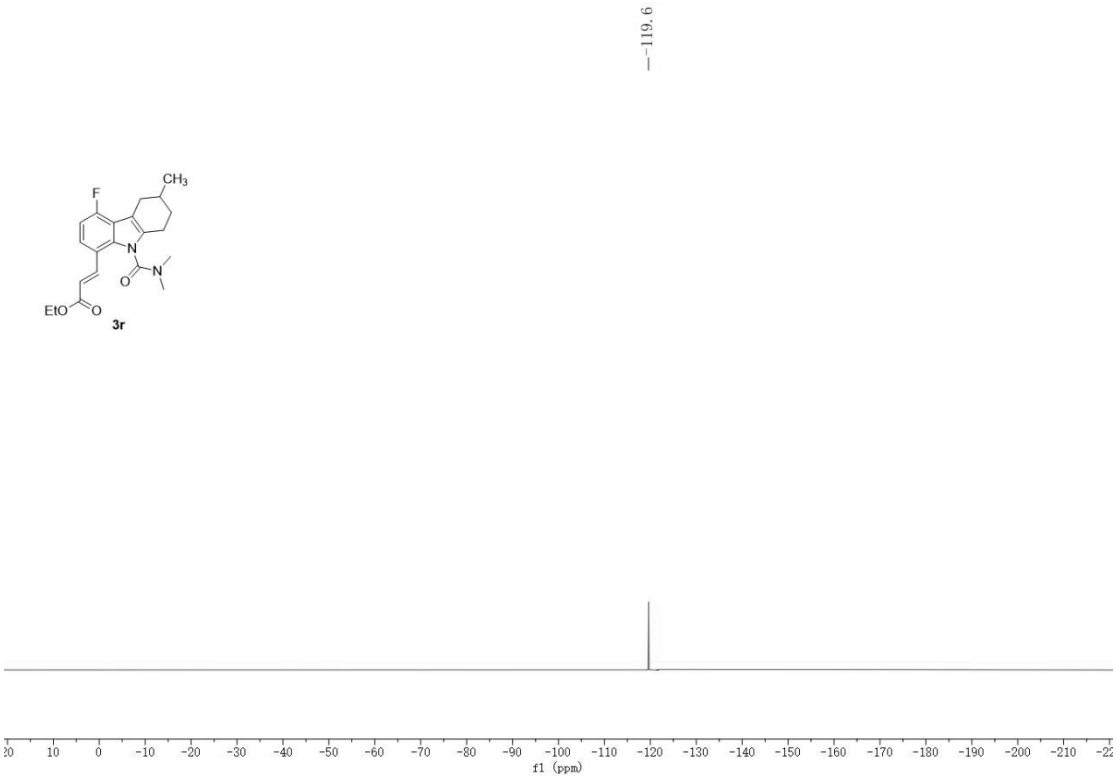
^{1}H NMR spectra of compound **3r**



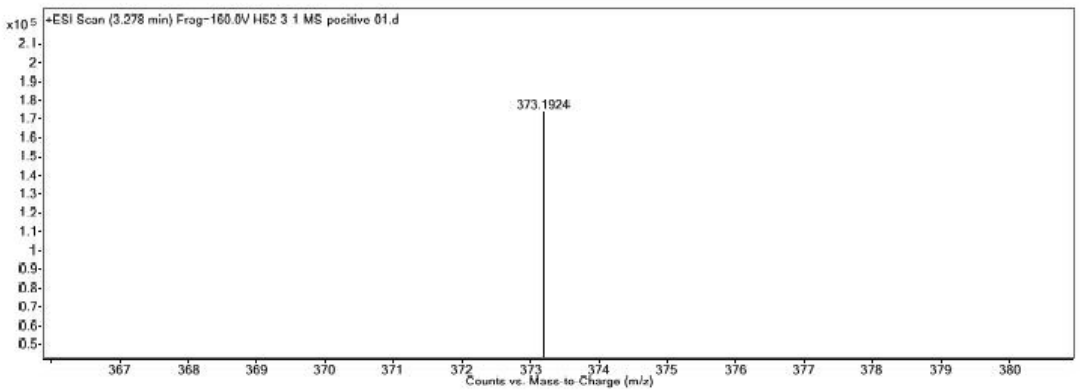
^{13}C NMR spectra of compound **3r**



^{19}F NMR spectra of compound **3r**



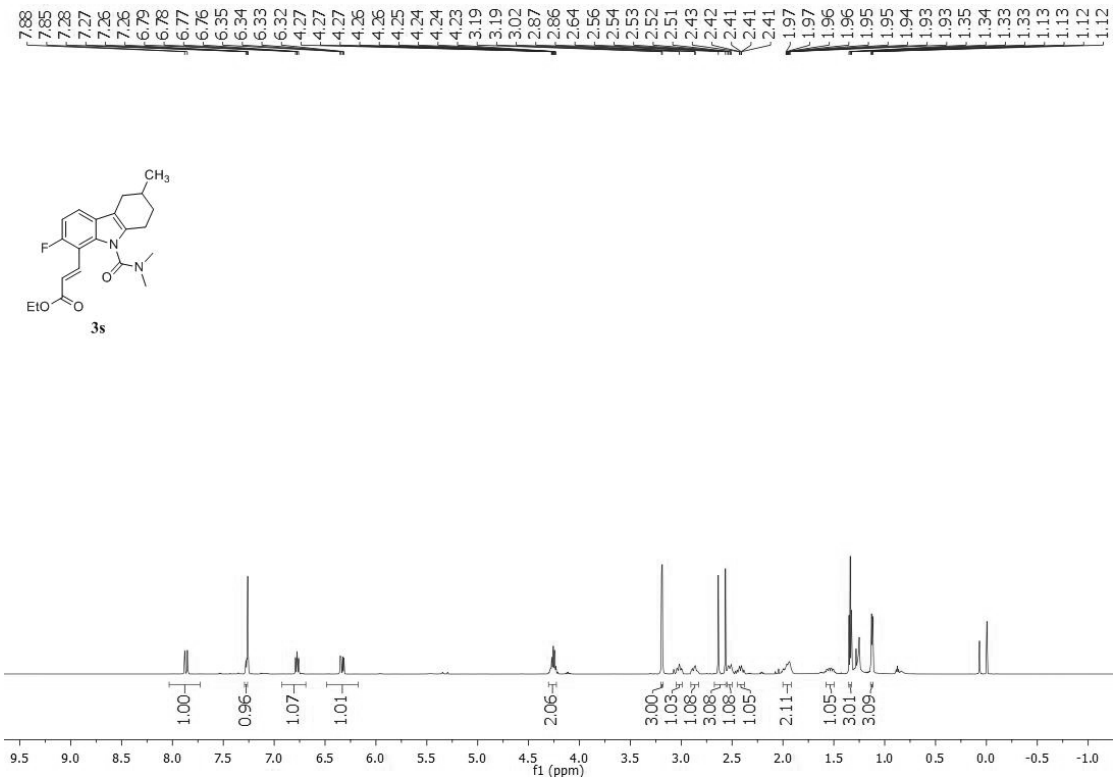
HRMS spectrum of compound **3r**



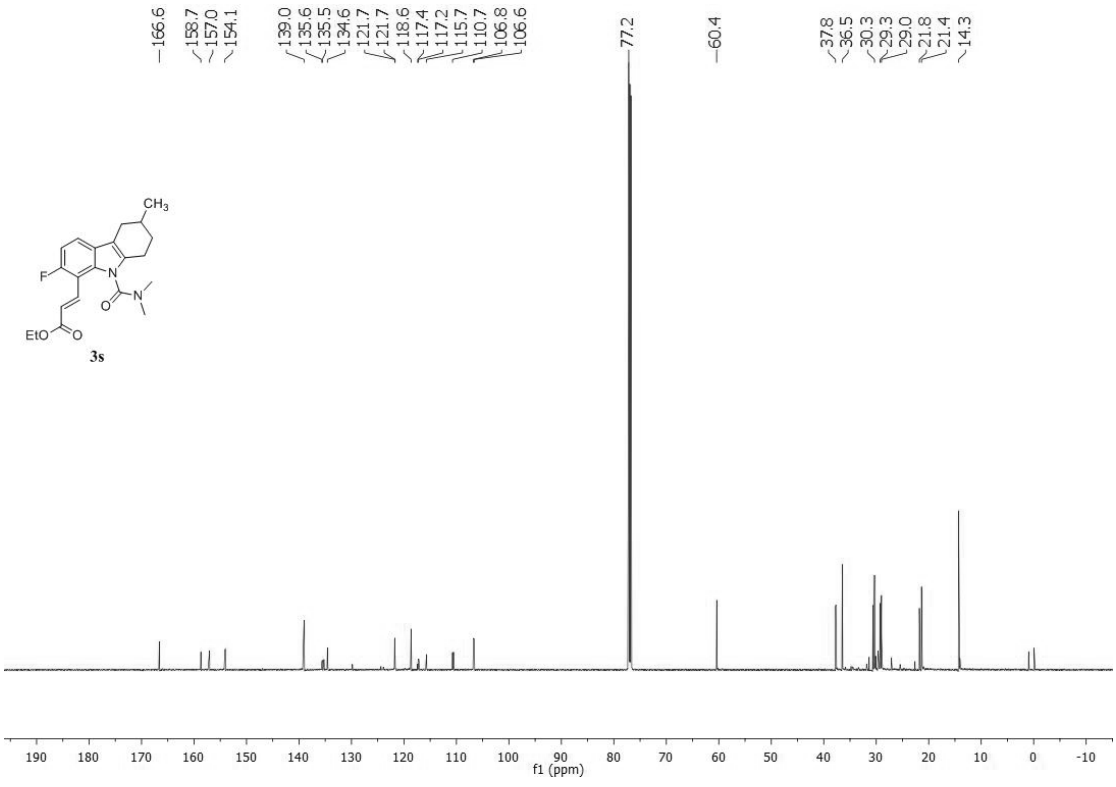
Elemental Composition Calculator

Target m/z:	373.1924	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5) ;F(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C21H26FN2O3		373.1922		-0.6	

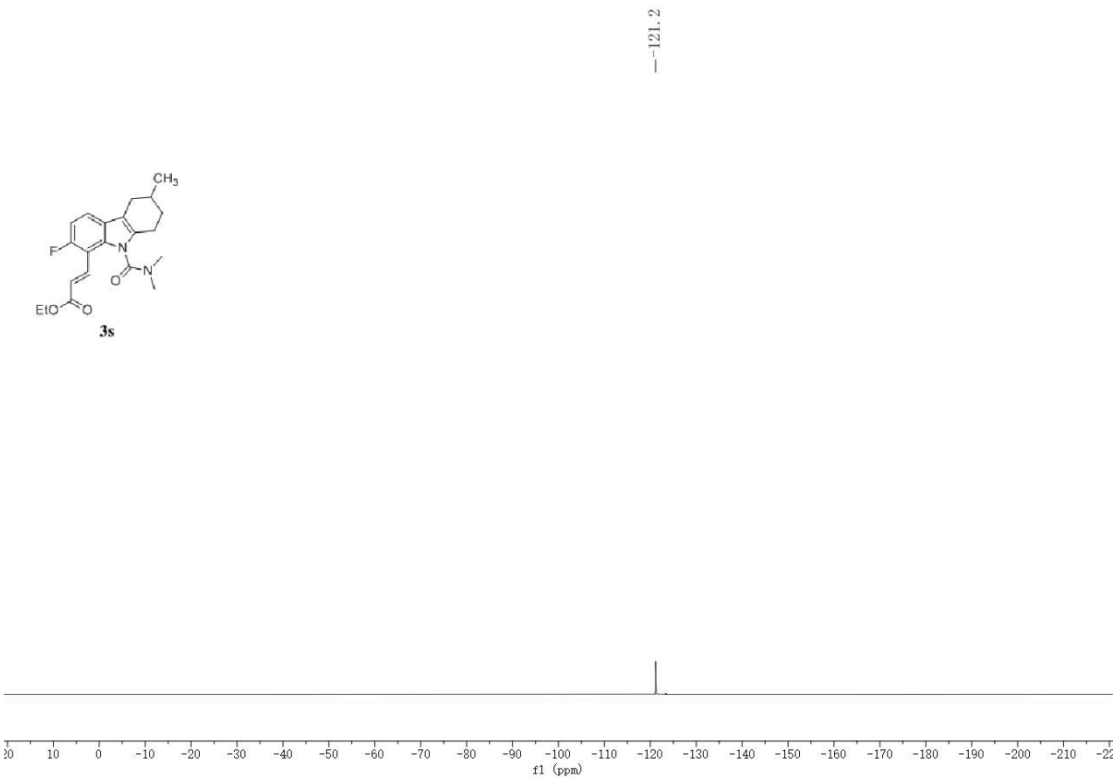
^{1}H NMR spectra of compound **3s**



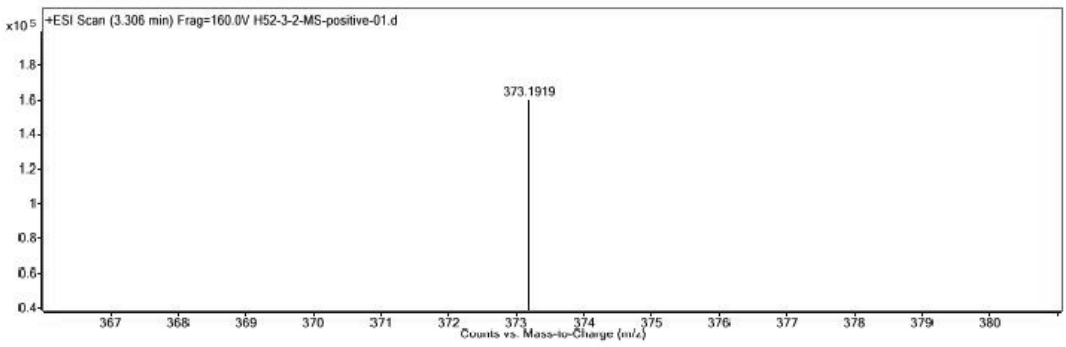
^{13}C NMR spectra of compound **3s**



^{19}F NMR spectra of compound **3s**



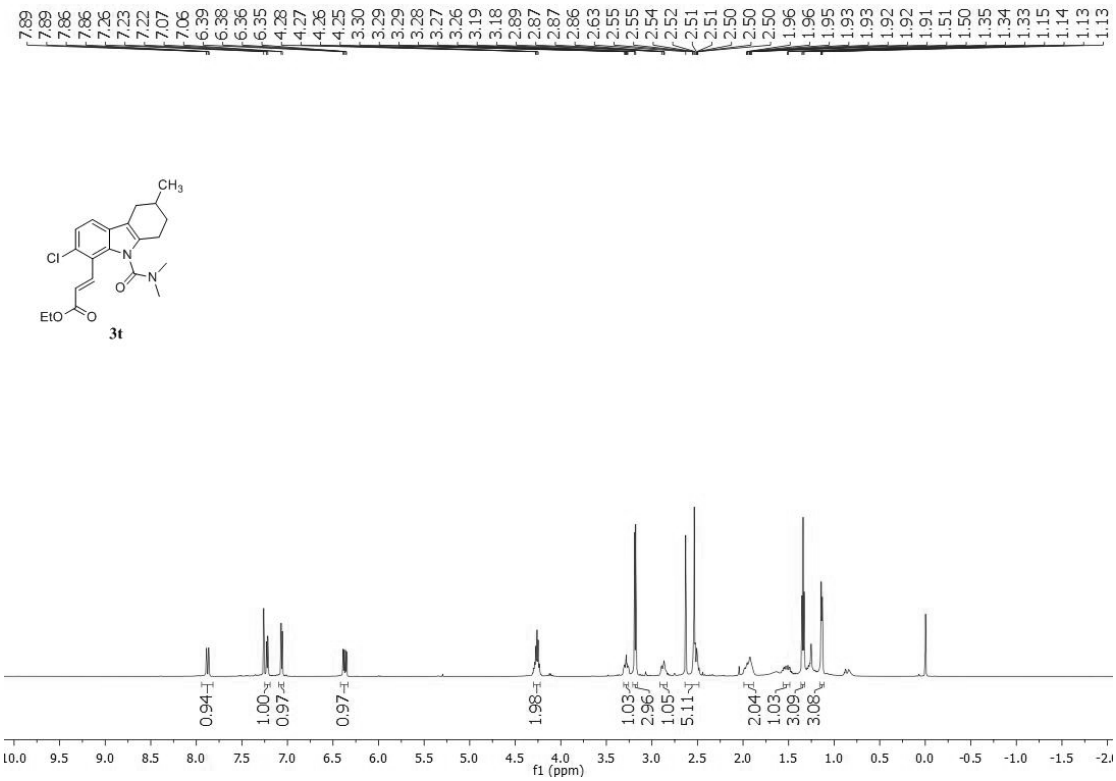
HRMS spectrum of compound **3s**



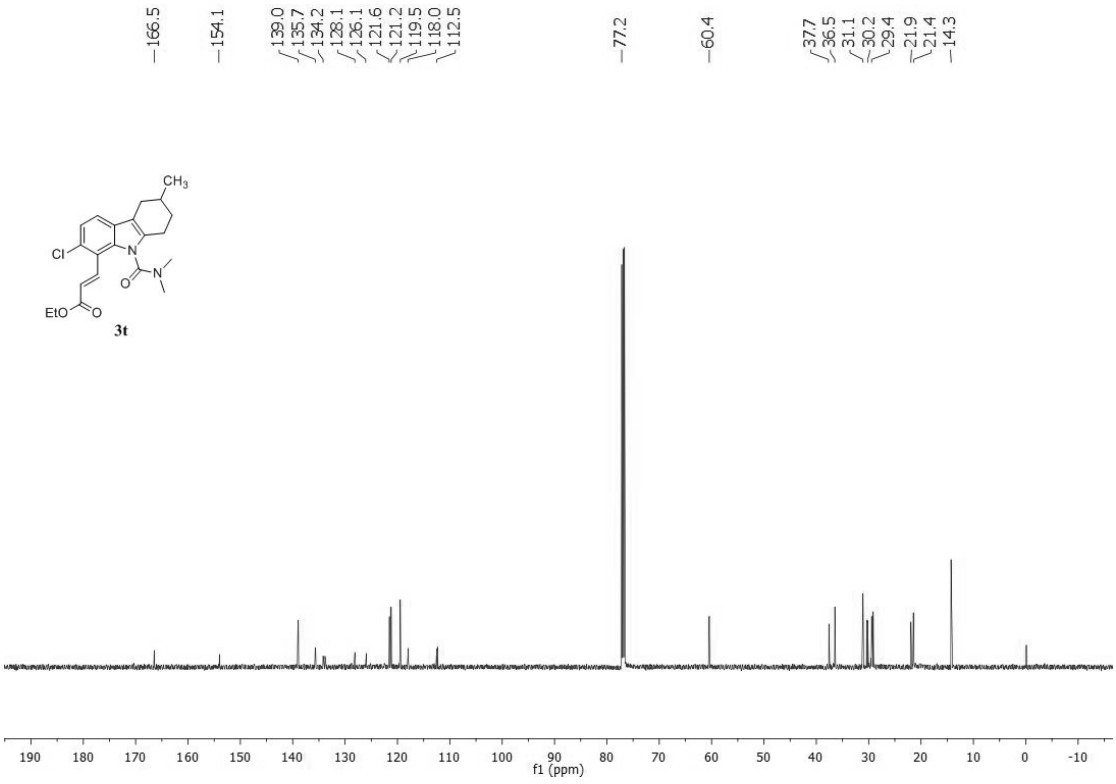
Elemental Composition Calculator

Target m/z:	373.1919	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5) ; F(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C21H26FN2O3		373.1922		0.76	

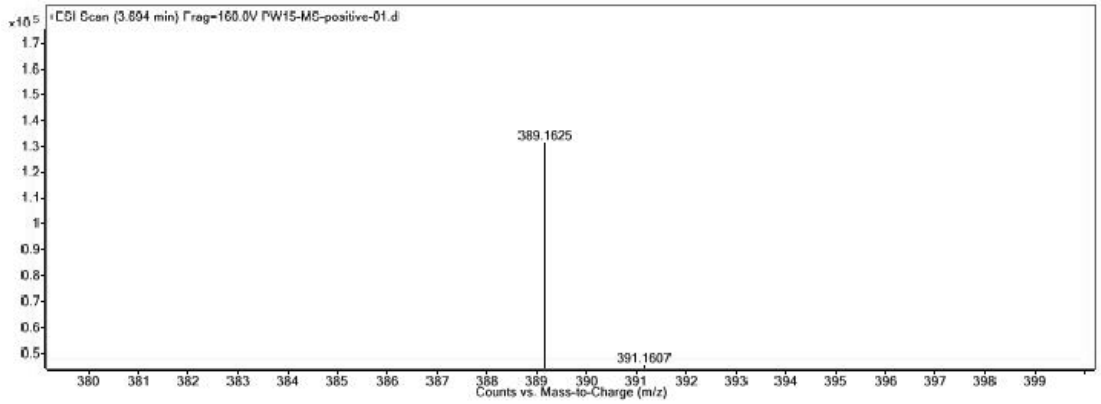
^{1}H NMR spectra of compound **3t**



^{13}C NMR spectra of compound **3t**



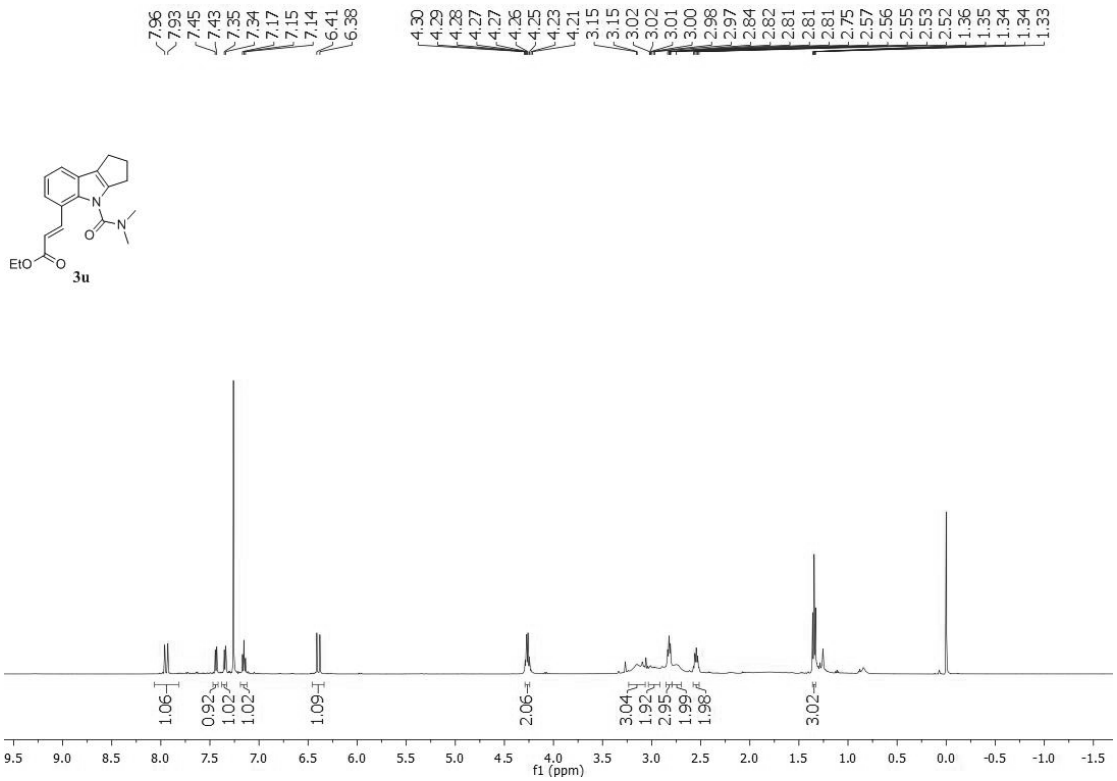
HRMS spectrum of compound **3t**



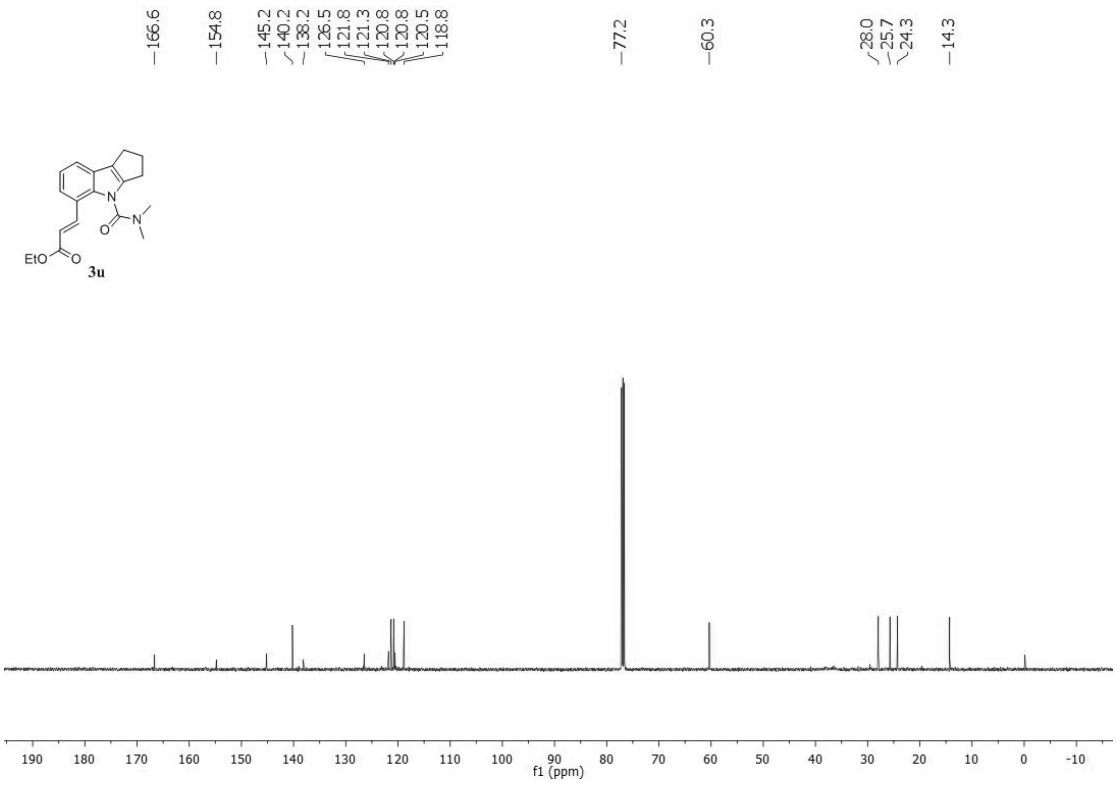
Elemental Composition Calculator

Target m/z:	389.1625	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5) ; Cl(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C21H26ClN2O3		389.1626		0.32	

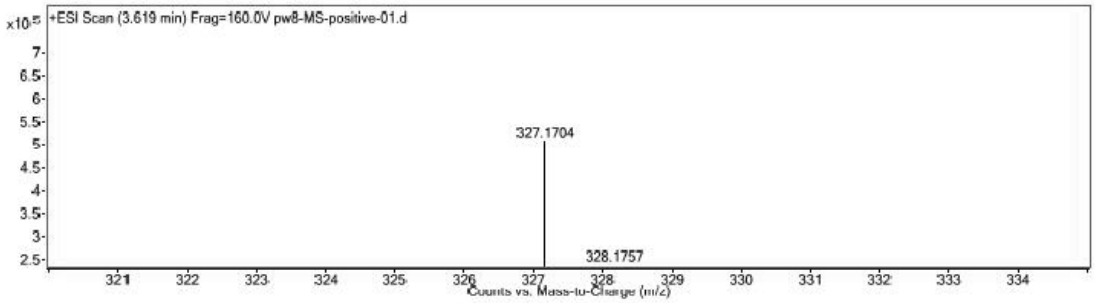
^{1}H NMR spectra of compound **3u**



^{13}C NMR spectra of compound **3u**



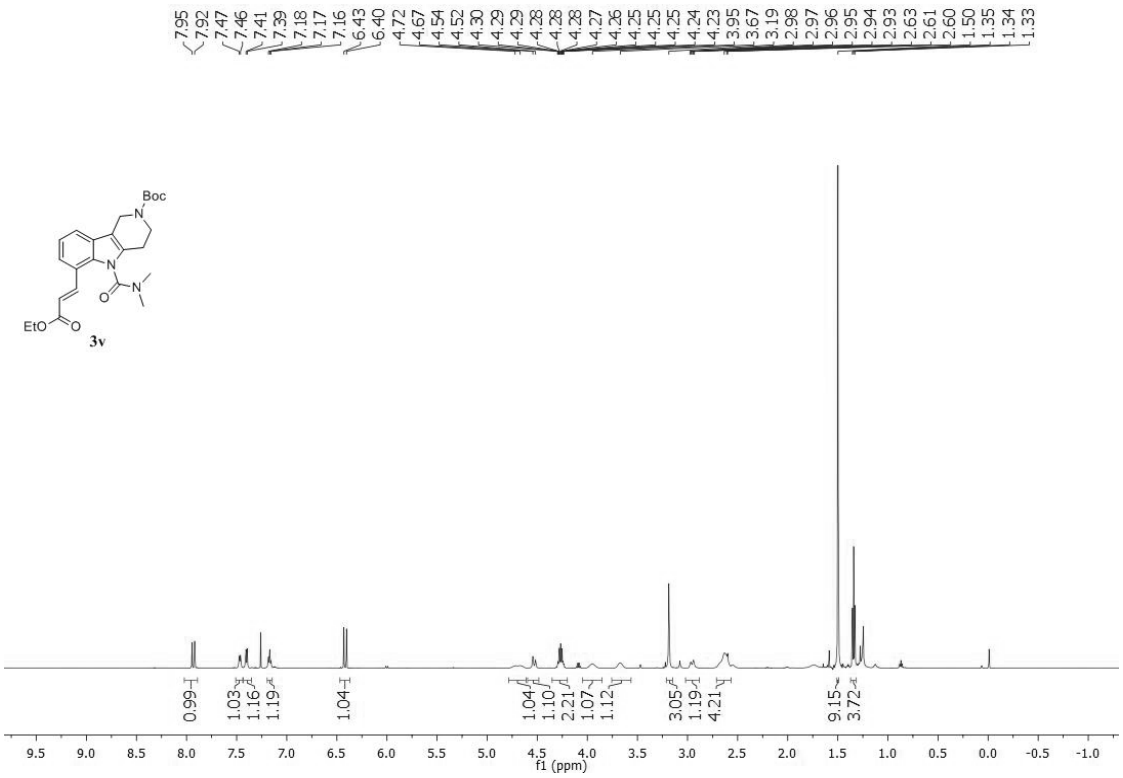
HRMS spectrum of compound **3u**



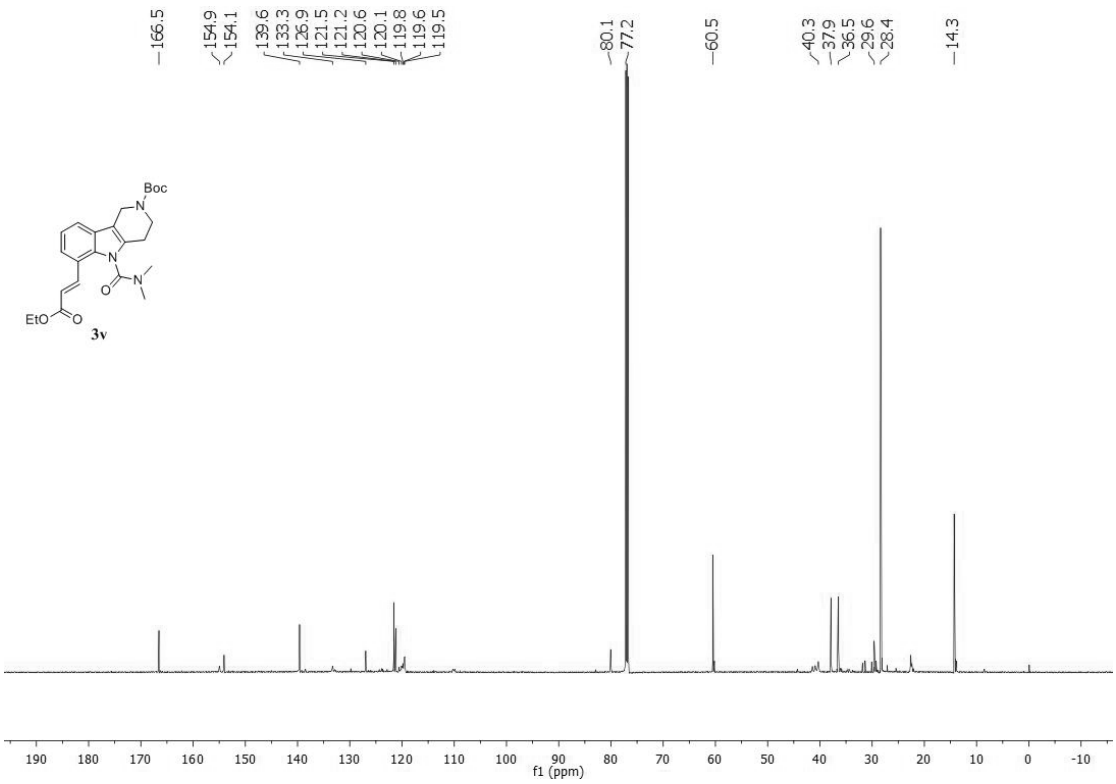
Elemental Composition Calculator

Target m/z:	327.1704	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C19H23N2O3		327.1703		-0.32	

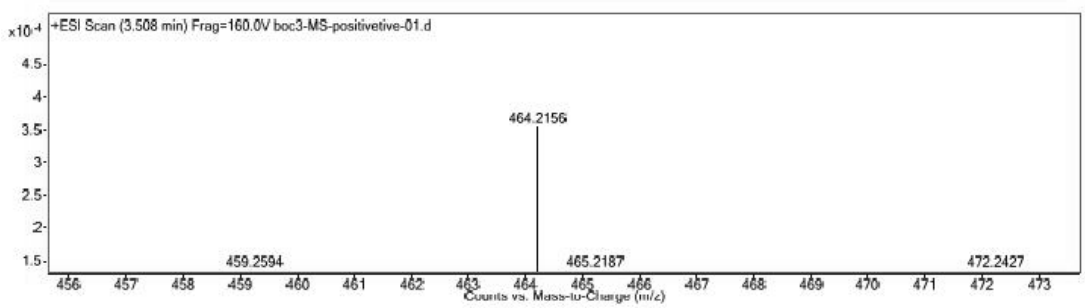
^{1}H NMR spectra of compound **3v**



^{13}C NMR spectra of compound **3v**



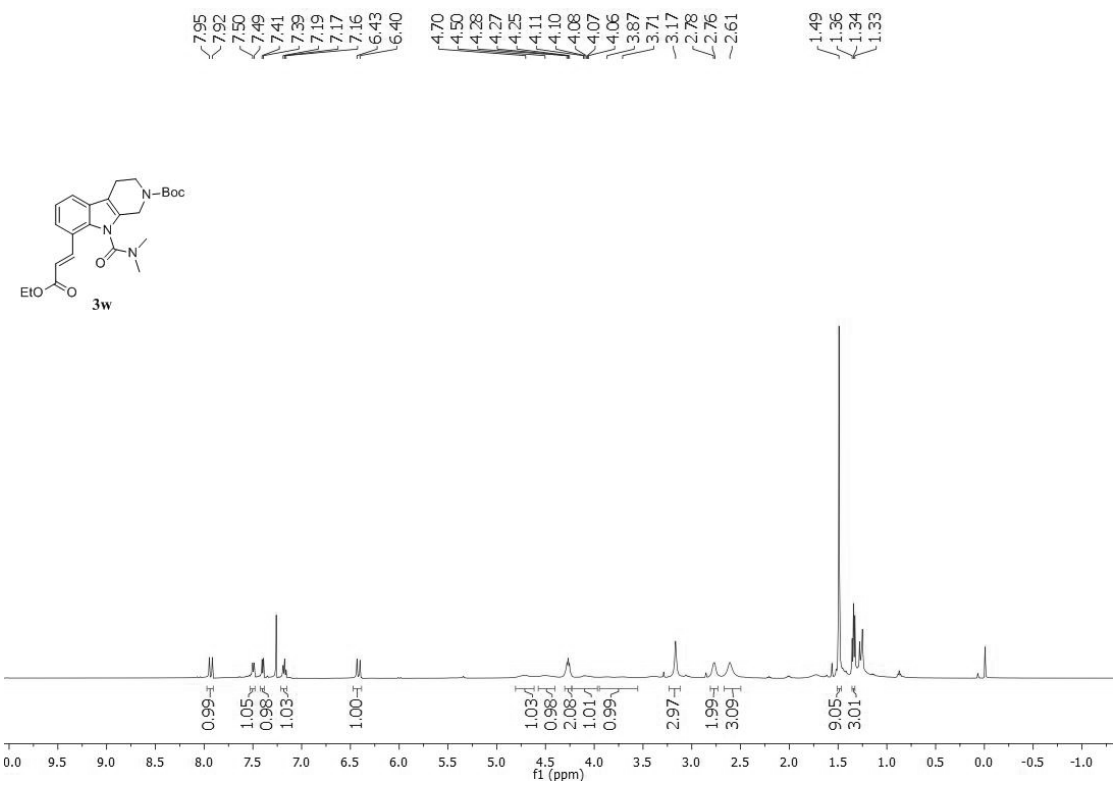
HRMS spectrum of compound **3v**



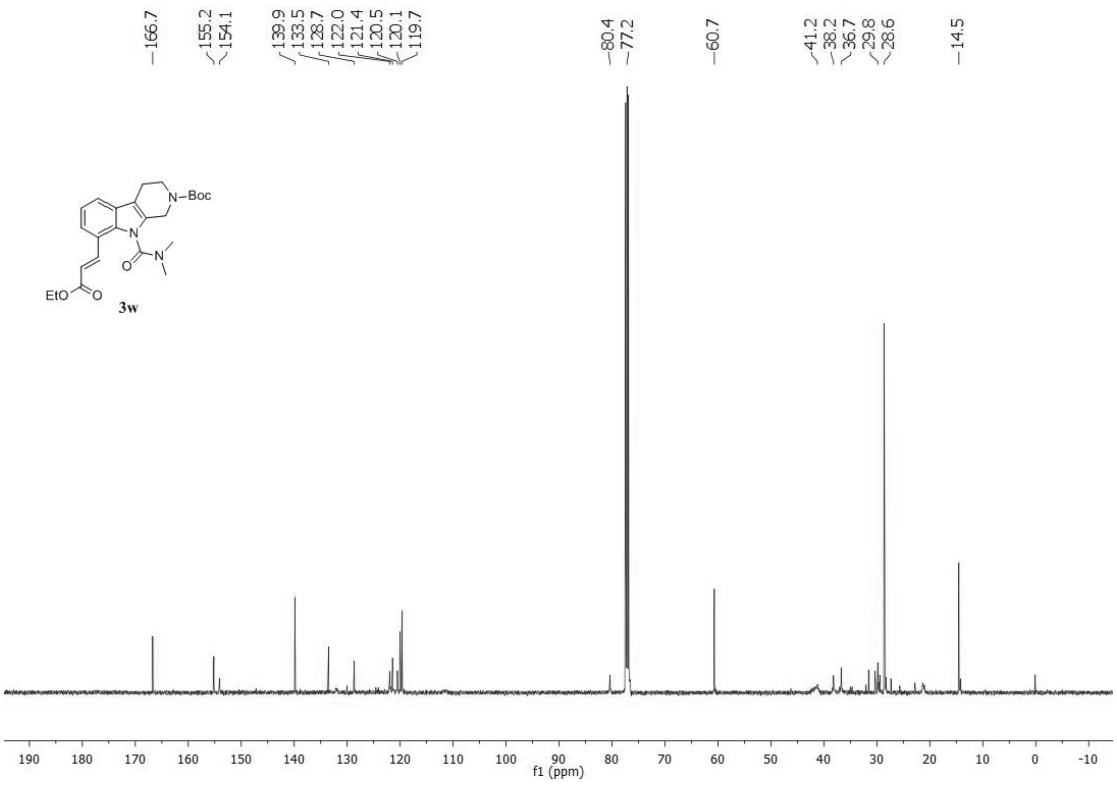
Elemental Composition Calculator

Target m/z:	464.2156	**Result type:**	Positive ions	**Species:**	$[M+Na]^+$
Elements:		C (0-80); H (0-120); O (0-30); N(0-5); Na (0-5)			
Ion Formula		**Calculated m/z**		**PPM Error**	
C24H31N3NaO5		464.2156		-0.07	

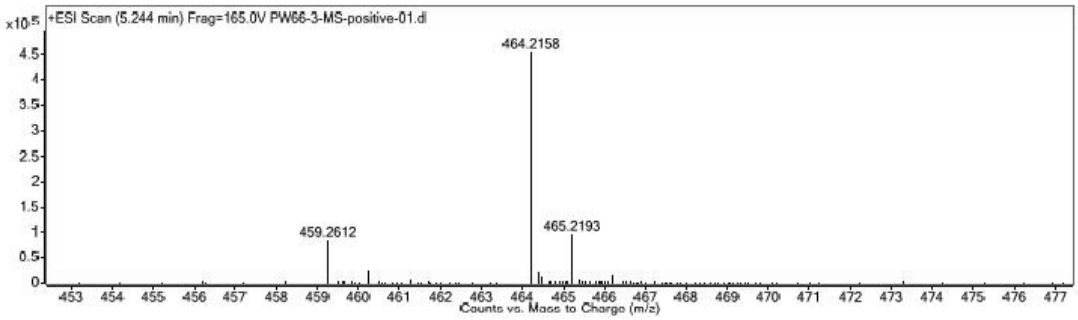
^{1}H NMR spectra of compound **3w**



^{13}C NMR spectra of compound **3w**



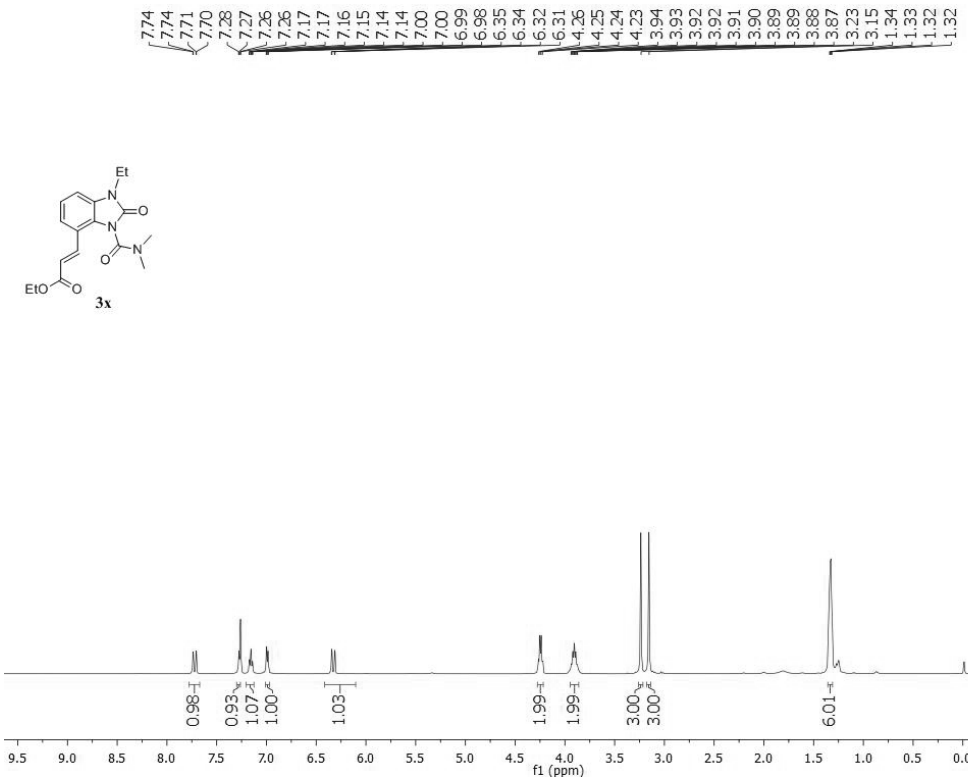
HRMS spectrum of compound **3w**



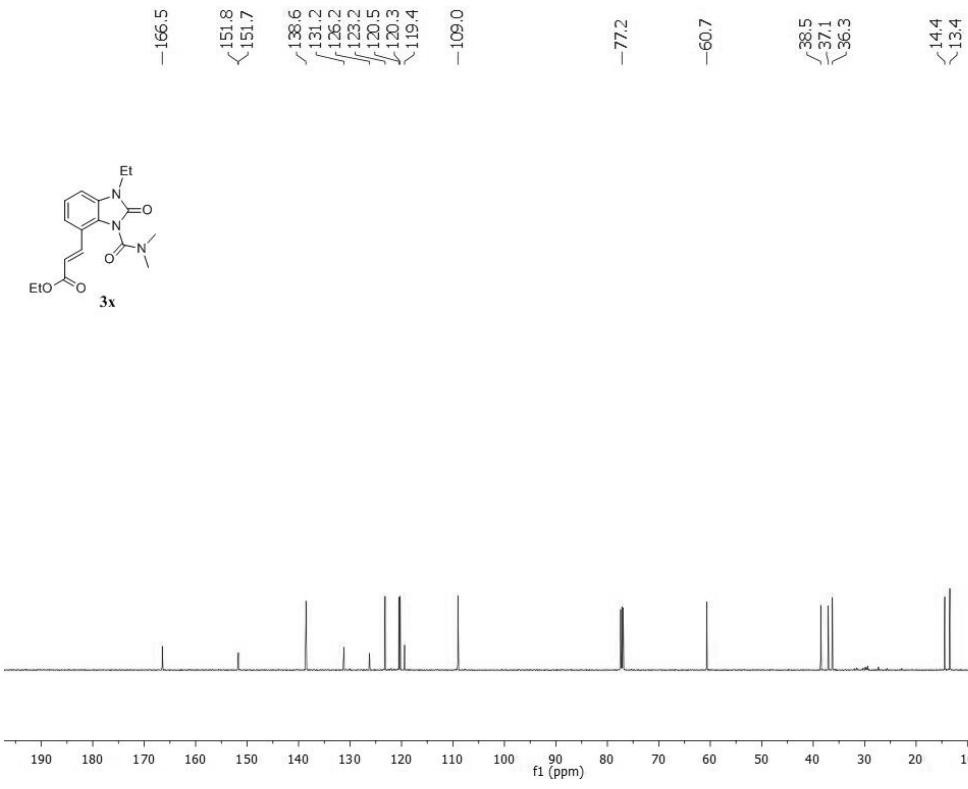
Elemental Composition Calculator

Target m/z:	464.2158	**Result type:**	Positive ions	**Species:**	$[M+Na]^+$
Elements:		C (0-80); H (0-120); O (0-30); N(0-5); Na (0-5)			
Ion Formula		**Calculated m/z**		**PPM Error**	
C24H31N3NaO5		464.2156		-0.44	

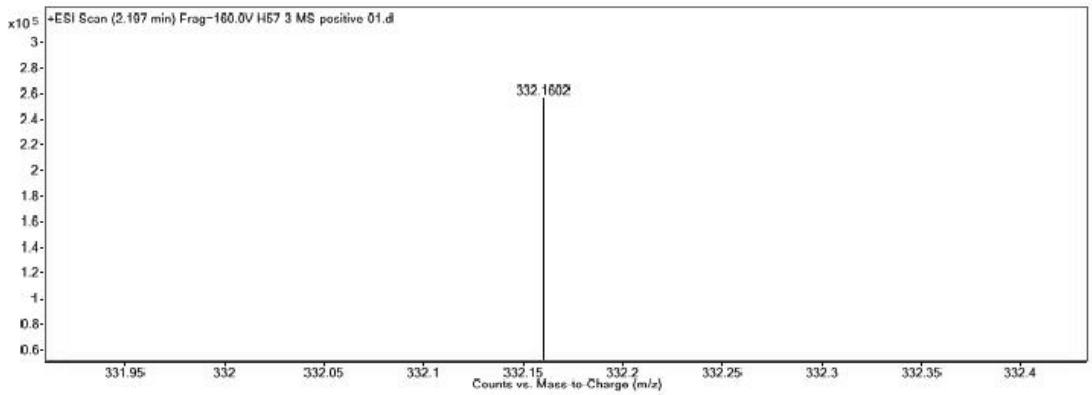
^{1}H NMR spectra of compound **3x**



^{13}C NMR spectra of compound **3x**



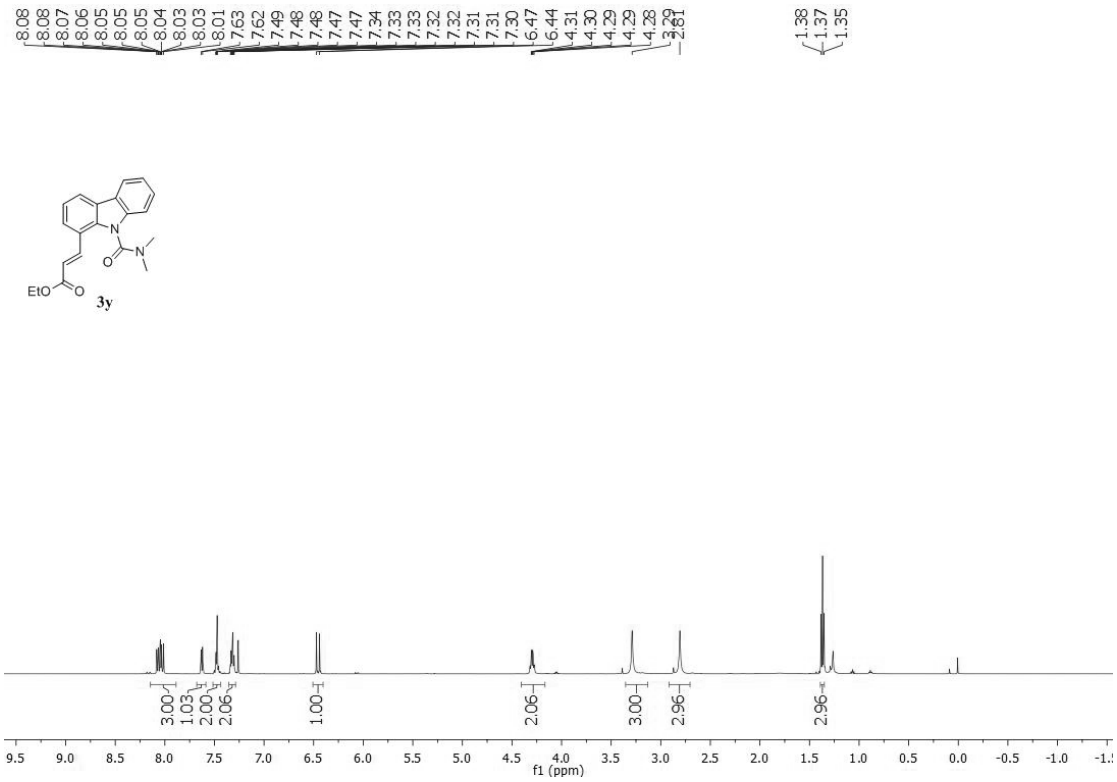
HRMS spectrum of compound **3x**



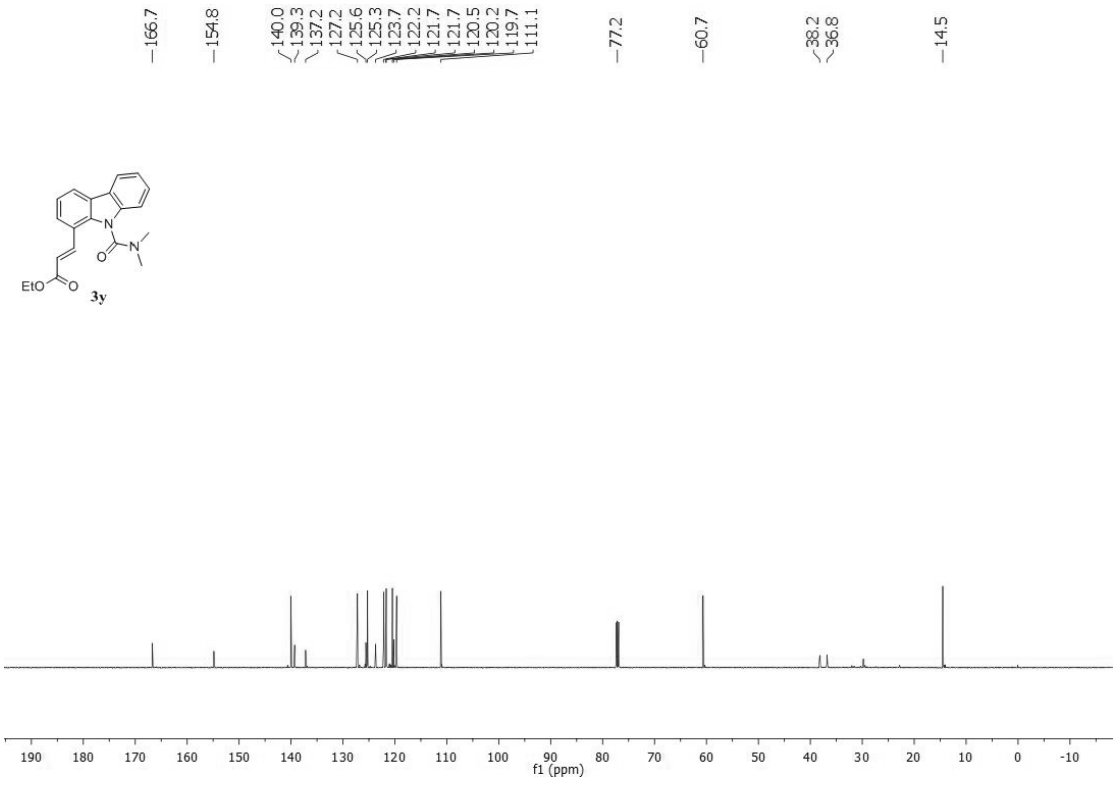
Elemental Composition Calculator

Target m/z:	332.1602	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C17H22N3O4		332.1605		0.88	

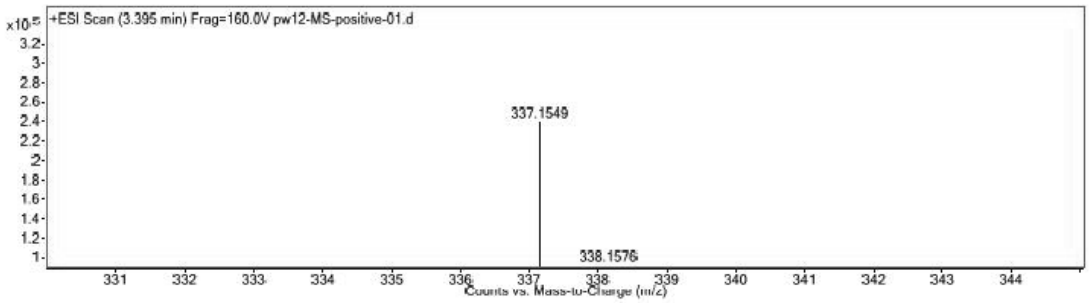
^{1}H NMR spectra of compound **3y**



^{13}C NMR spectra of compound **3y**



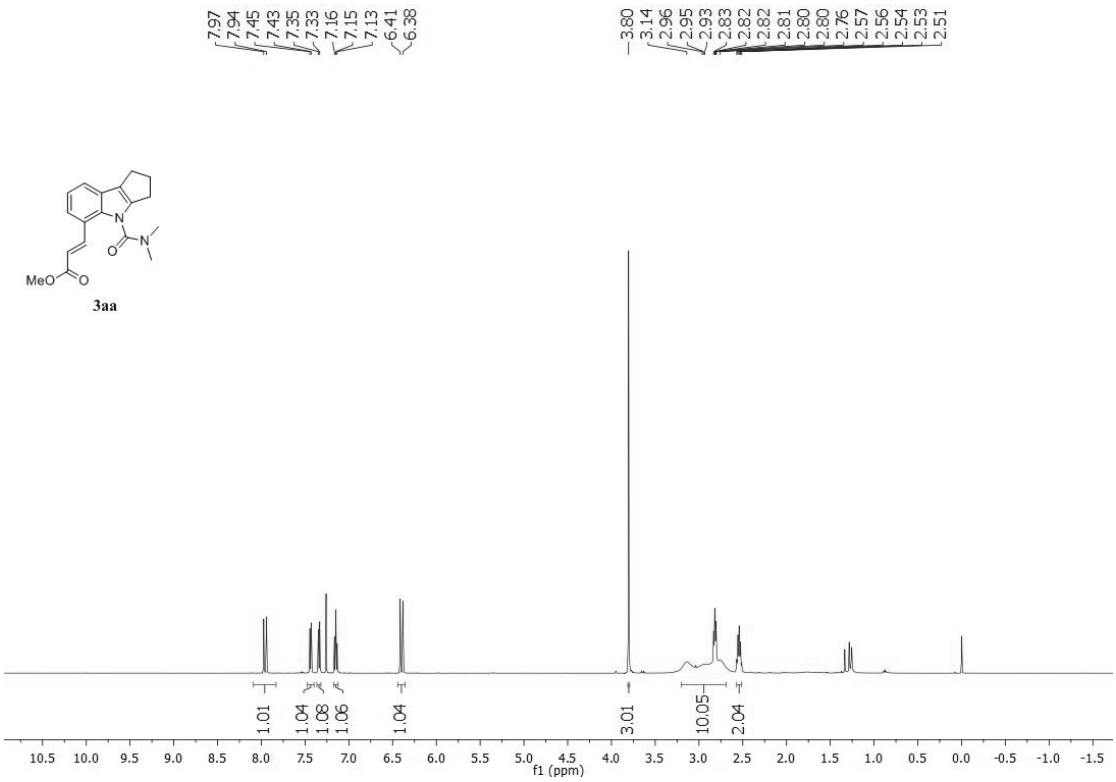
HRMS spectrum of compound **3y**



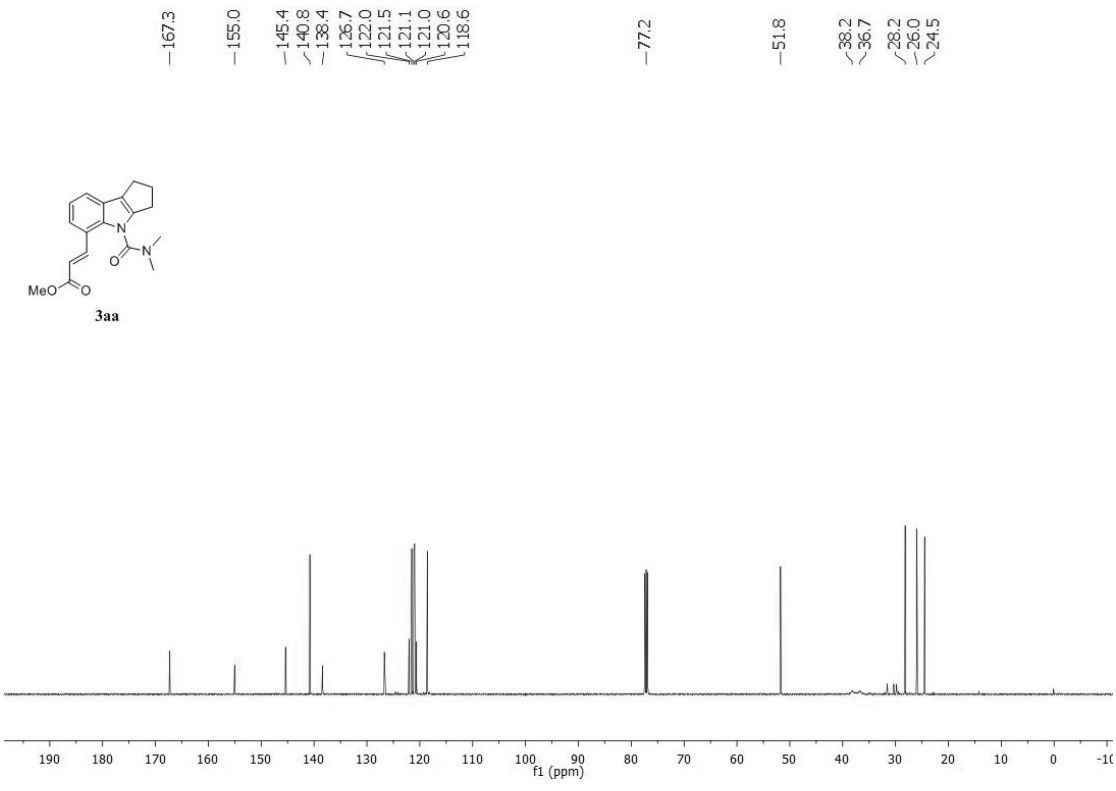
Elemental Composition Calculator

Target m/z:	337.1549	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C20H21N2O3		337.1547		-0.71	

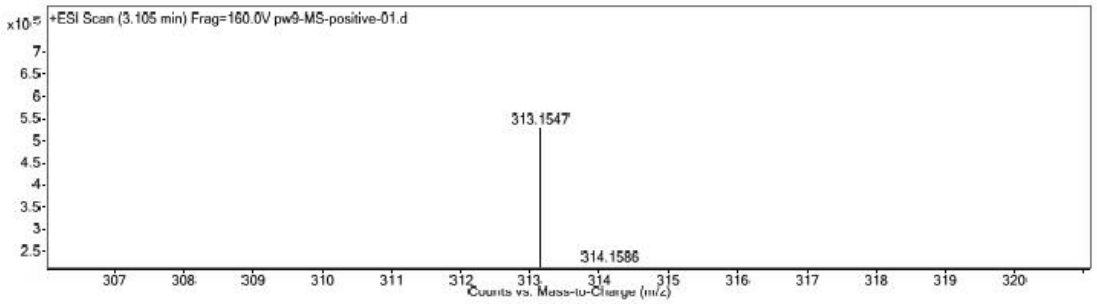
^{1}H NMR spectra of compound **3aa**



^{13}C NMR spectra of compound **3aa**



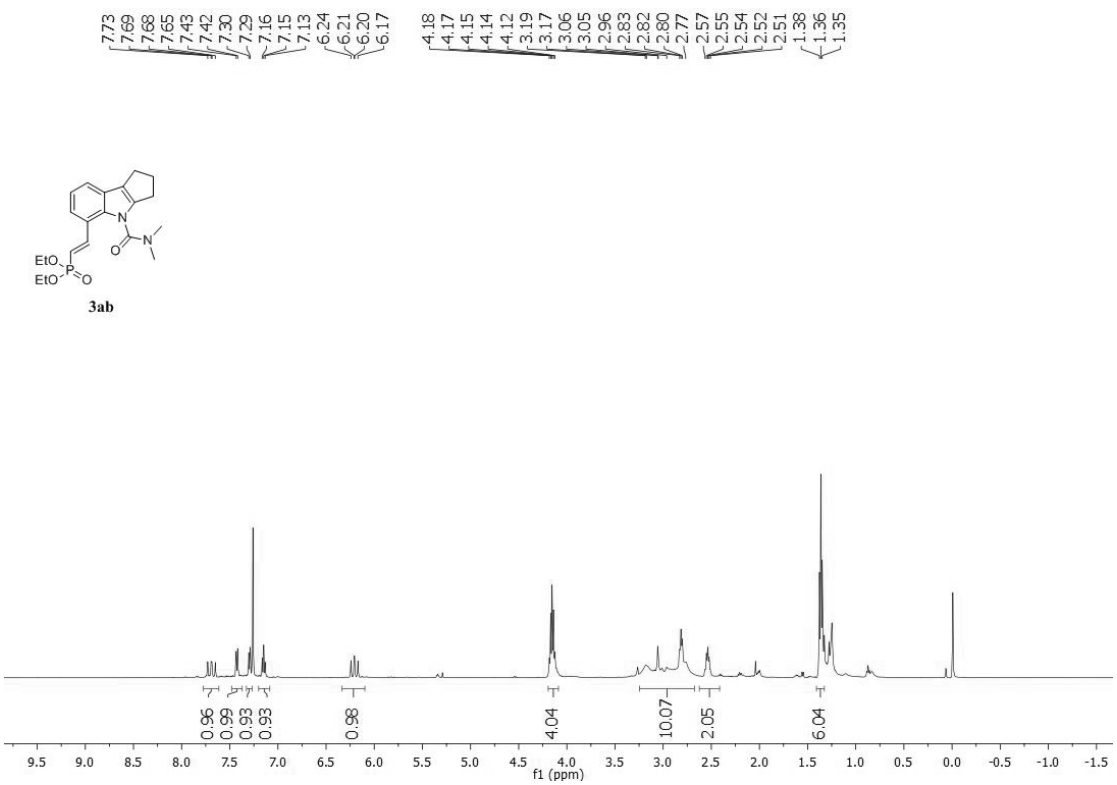
HRMS spectrum of compound **3aa**



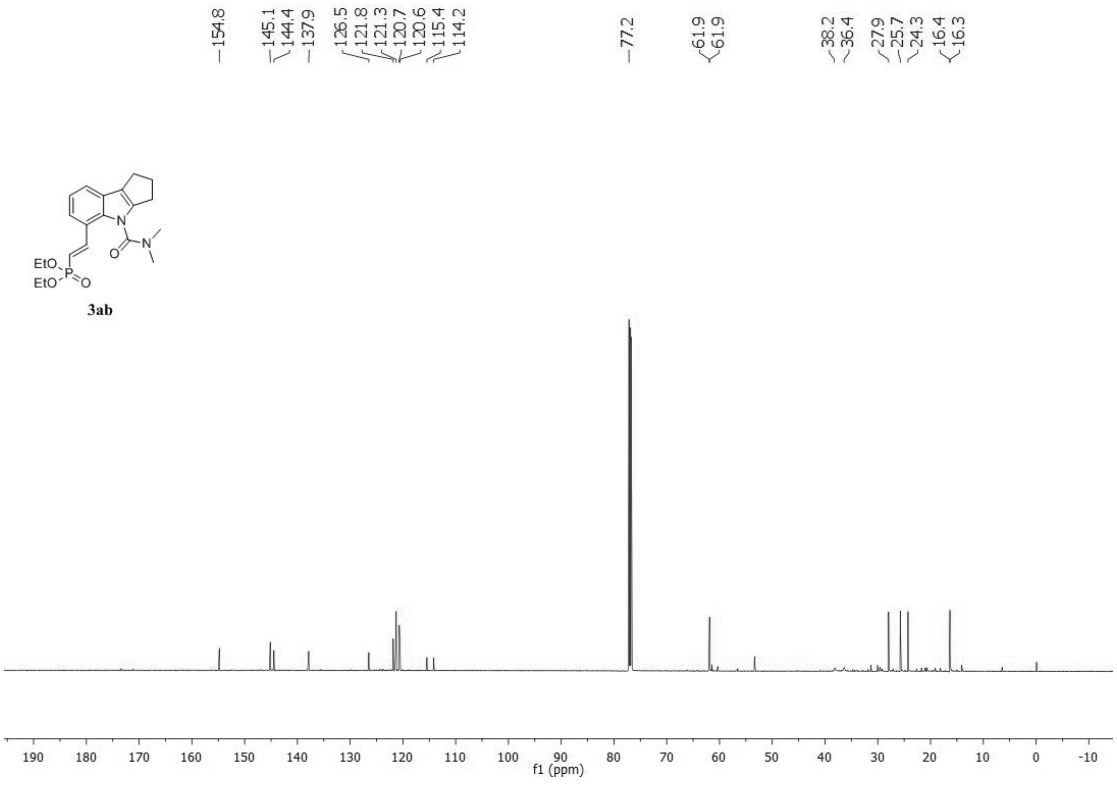
Elemental Composition Calculator

Target m/z:	313.1547	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C18H21N2O3		313.1547		-0.03	

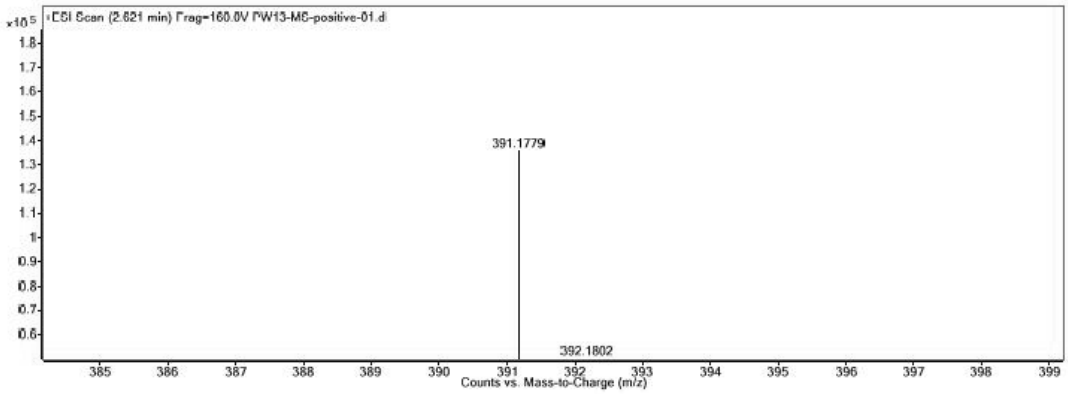
^{1}H NMR spectra of compound **3ab**



^{13}C NMR spectra of compound **3ab**



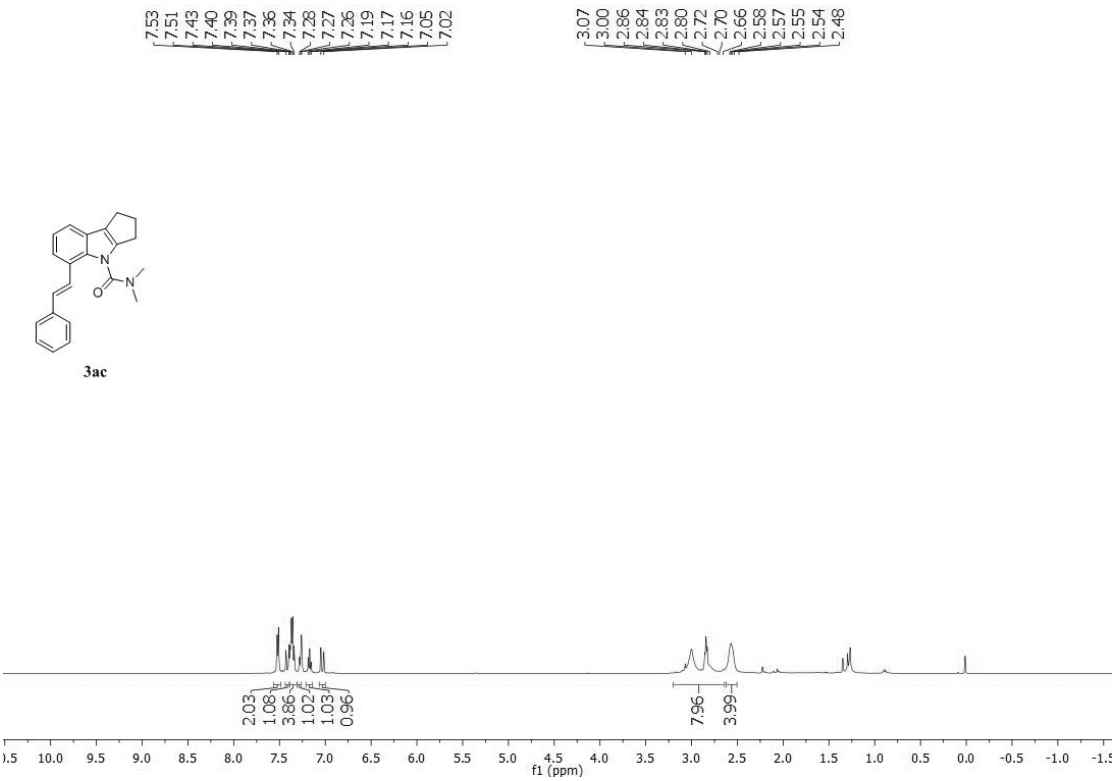
HRMS spectrum of compound **3ab**



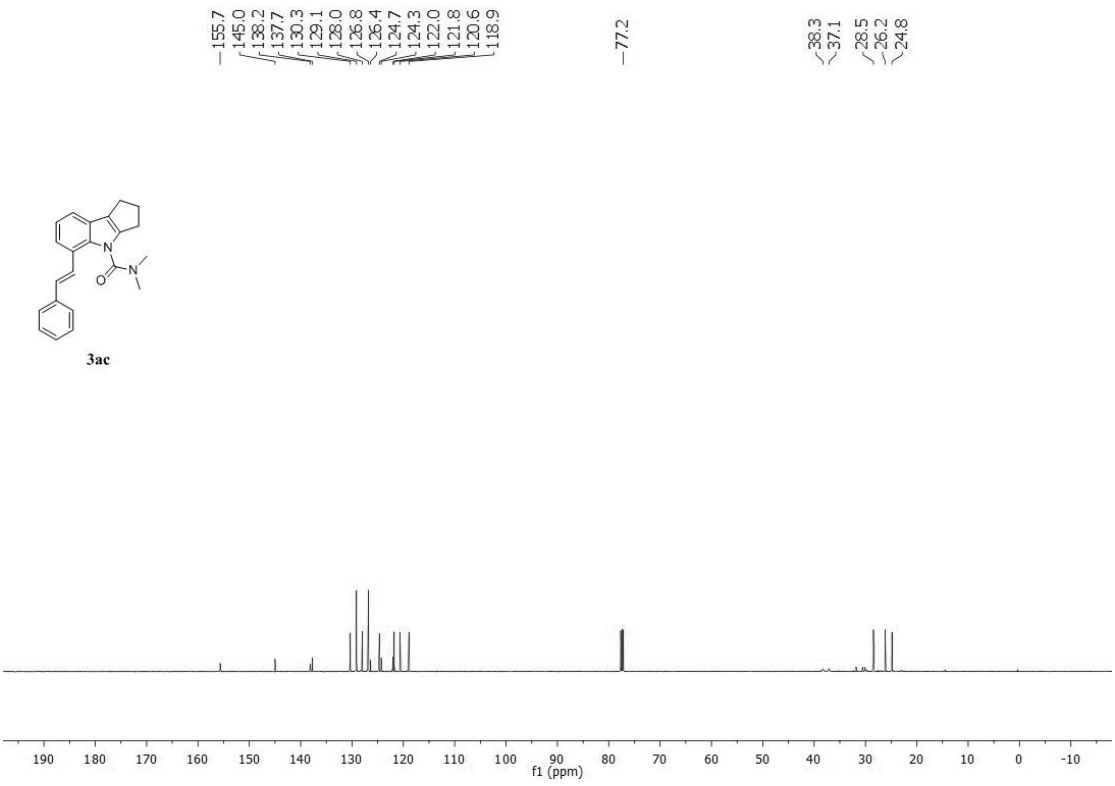
Elemental Composition Calculator

Target m/z:	391.1779	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5) ; P(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C20H28N2O4P		391.1776		0.67	

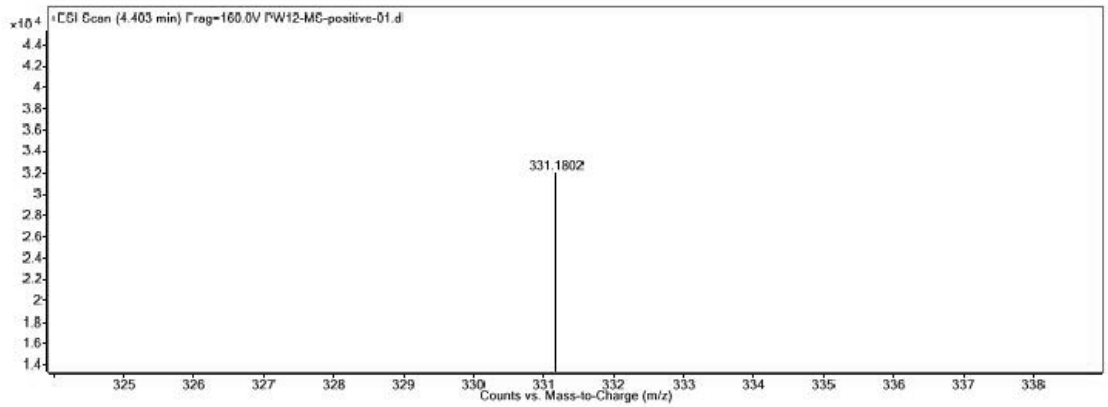
^{1}H NMR spectra of compound **3ac**



^{13}C NMR spectra of compound **3ac**



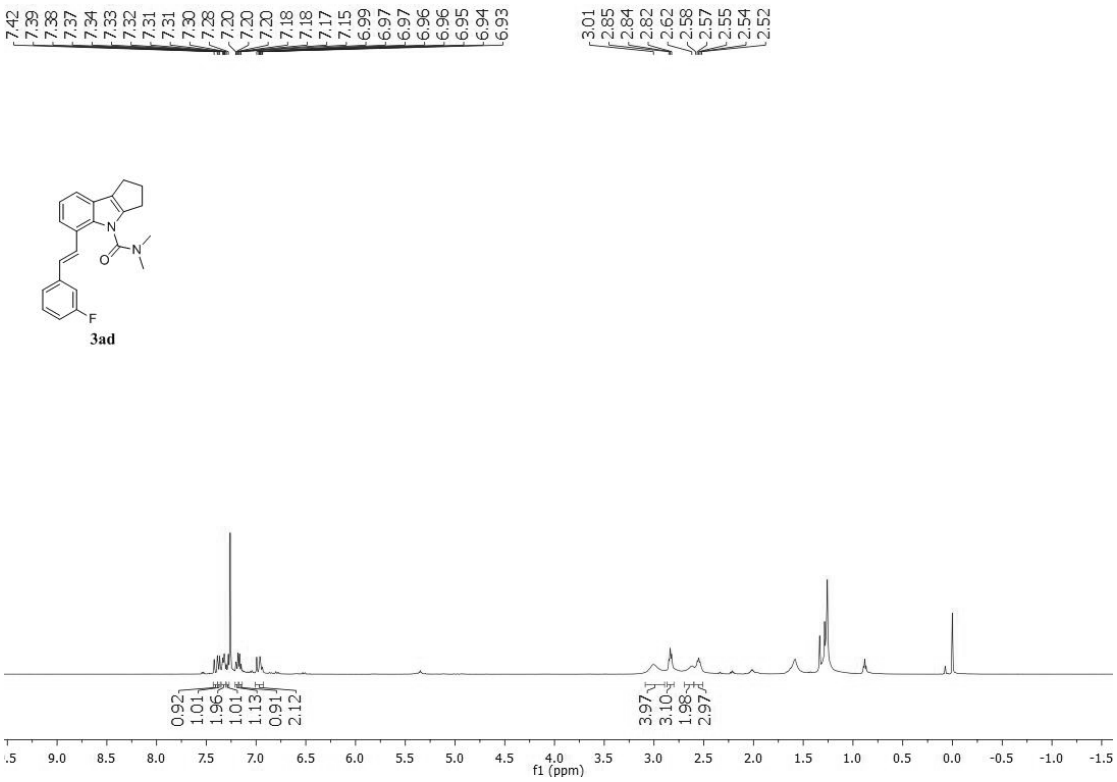
HRMS spectrum of compound **3ac**



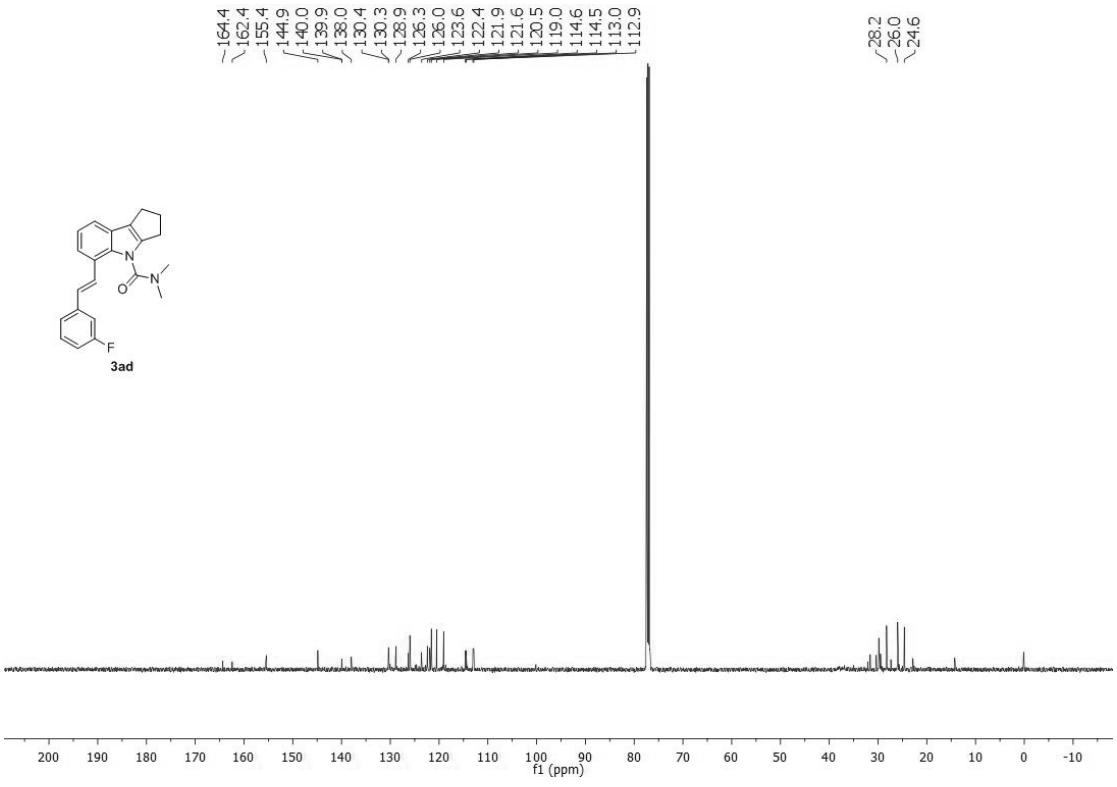
Elemental Composition Calculator

Target m/z:	331.1082	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C22H23N2O		331.1085		0.92	

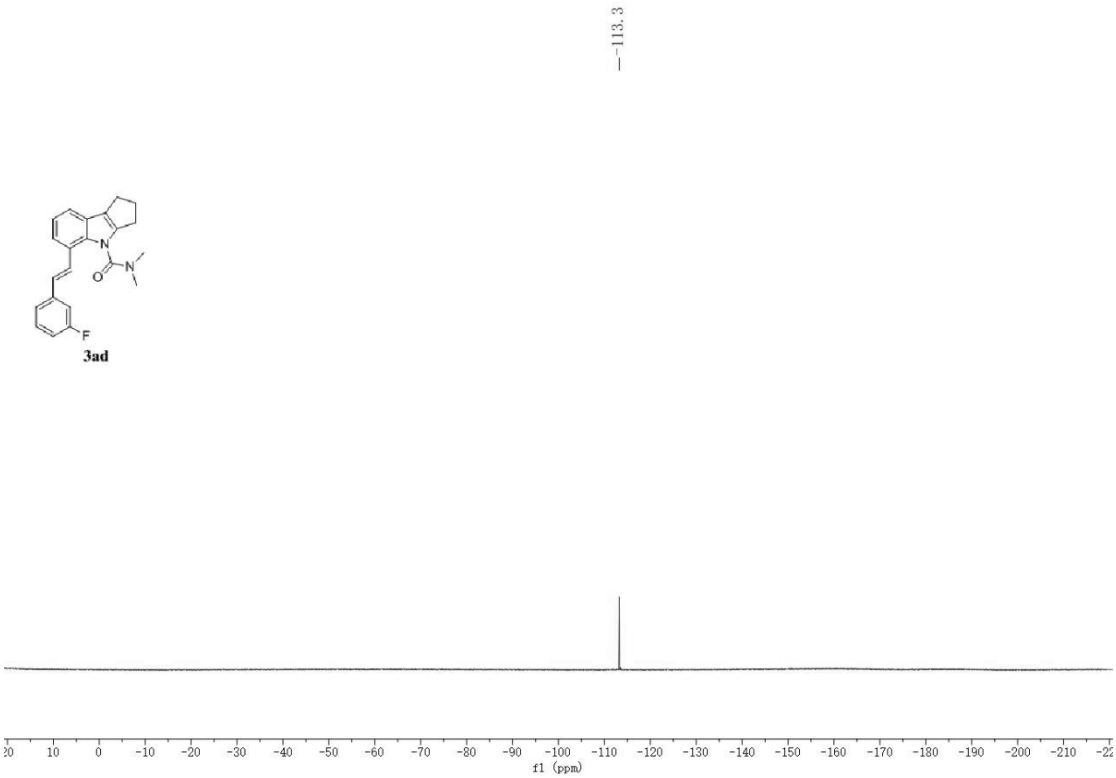
^{1}H NMR spectra of compound **3ad**



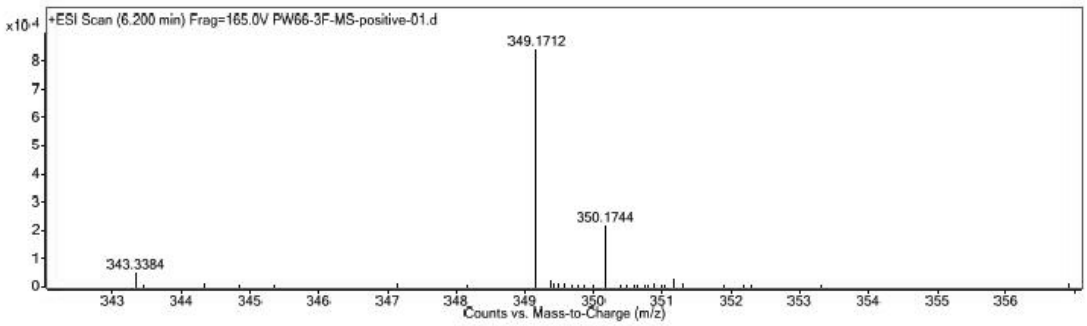
^{13}C NMR spectra of compound **3ad**



^{19}F NMR spectra of compound **3ad**



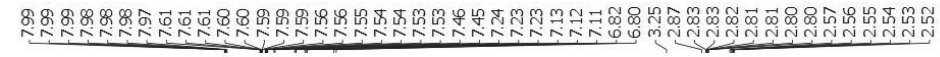
HRMS spectrum of compound **3ad**

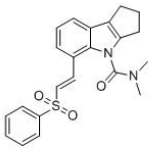


Elemental Composition Calculator

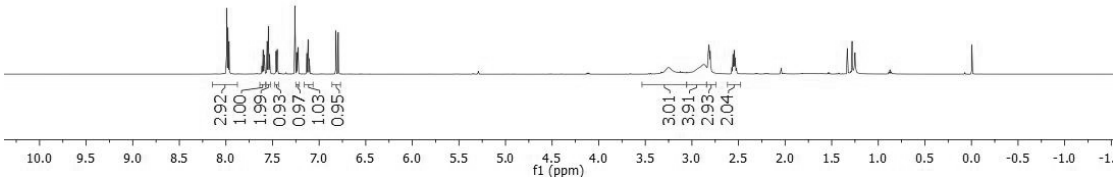
Target m/z:	349.1712	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5) ; F(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C22H22FN2O		349.1711		-0.44	

^{1}H NMR spectra of compound **3ae**

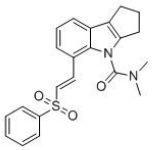




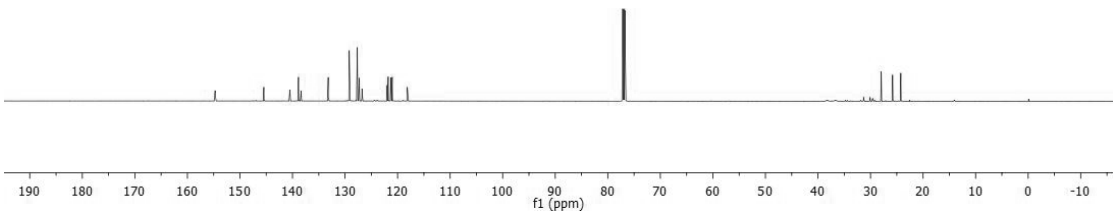
3ae



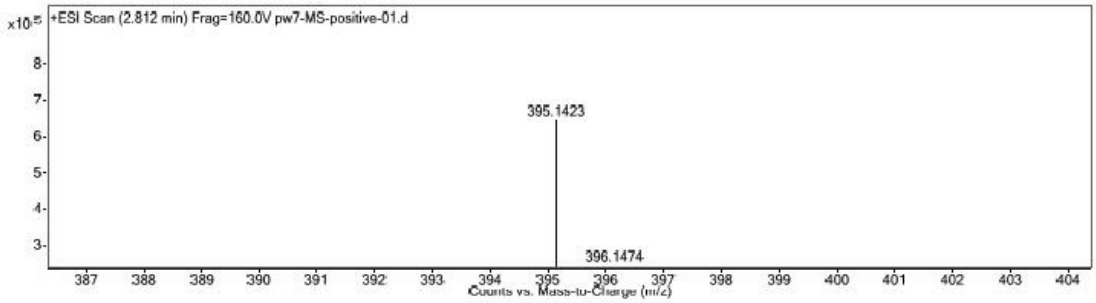
^{13}C NMR spectra of compound **3ae**



3ae



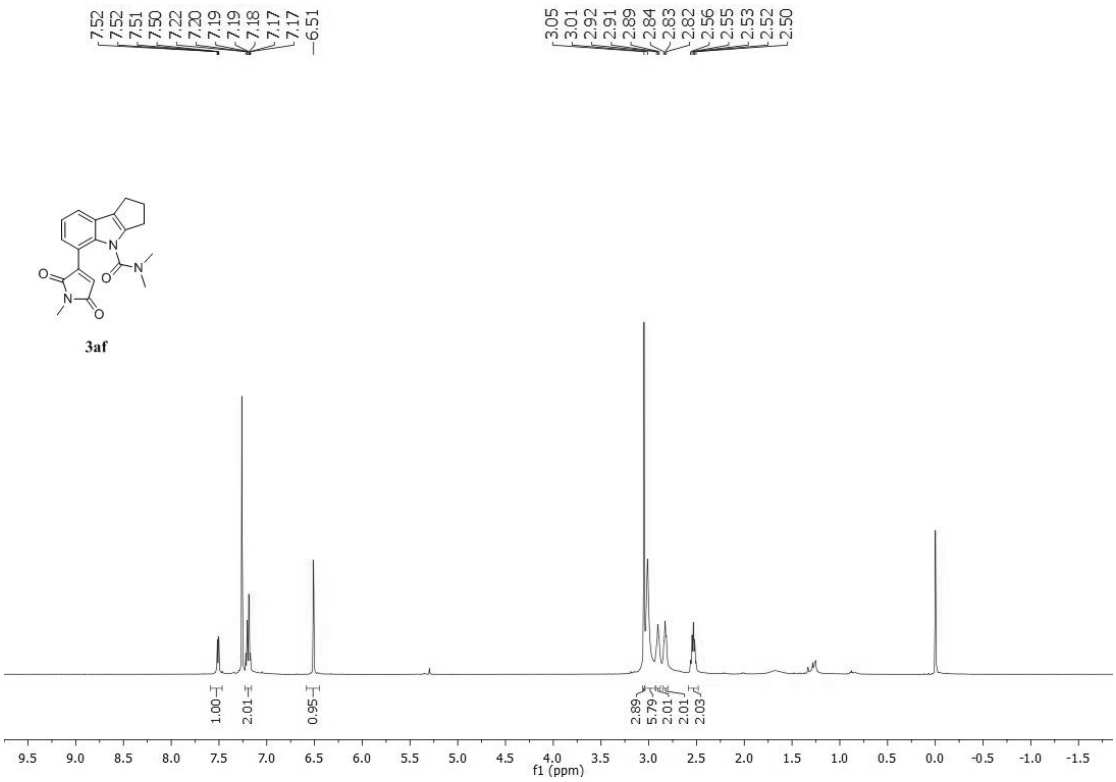
HRMS spectrum of compound **3ae**



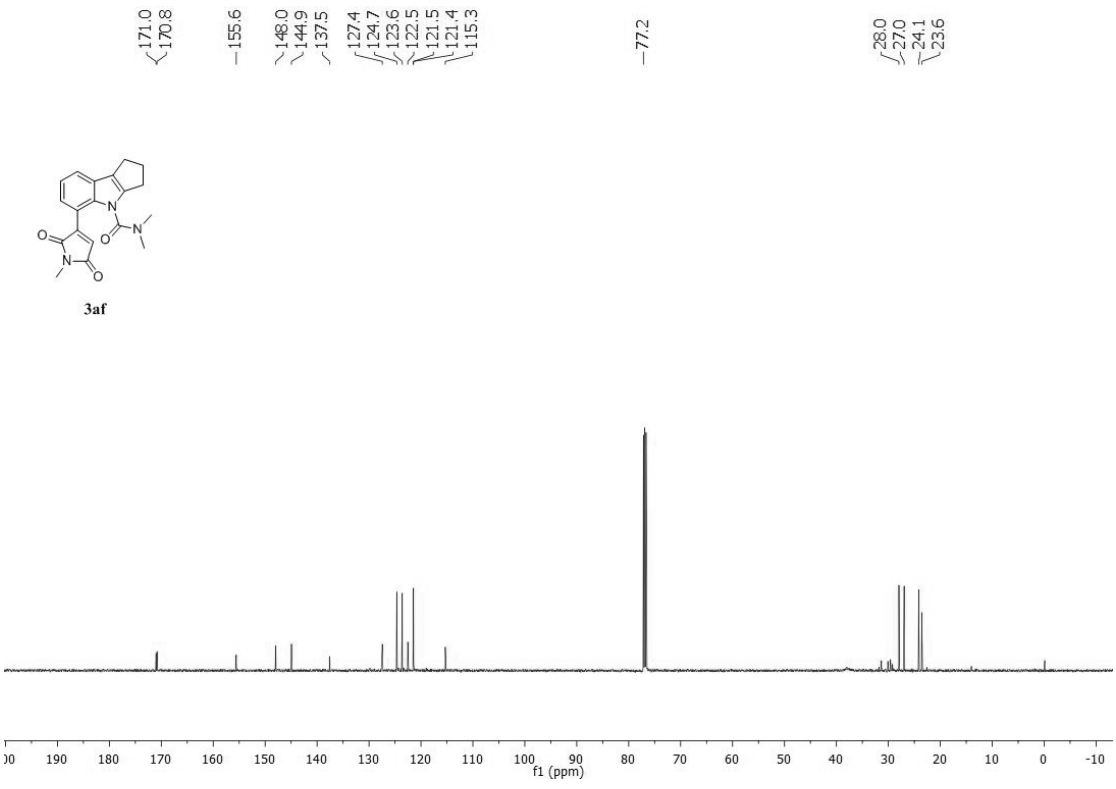
Elemental Composition Calculator

Target m/z:	395.1423	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5) ; S(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C22H23N2O3S		395.1424		0.16	

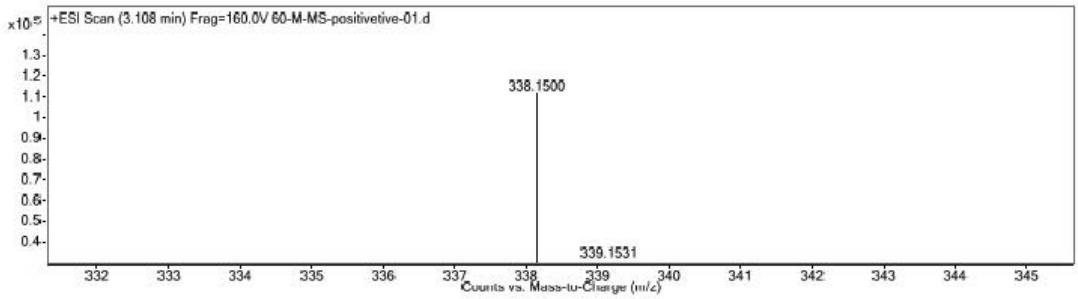
^{1}H NMR spectra of compound **3af**



^{13}C NMR spectra of compound **3af**



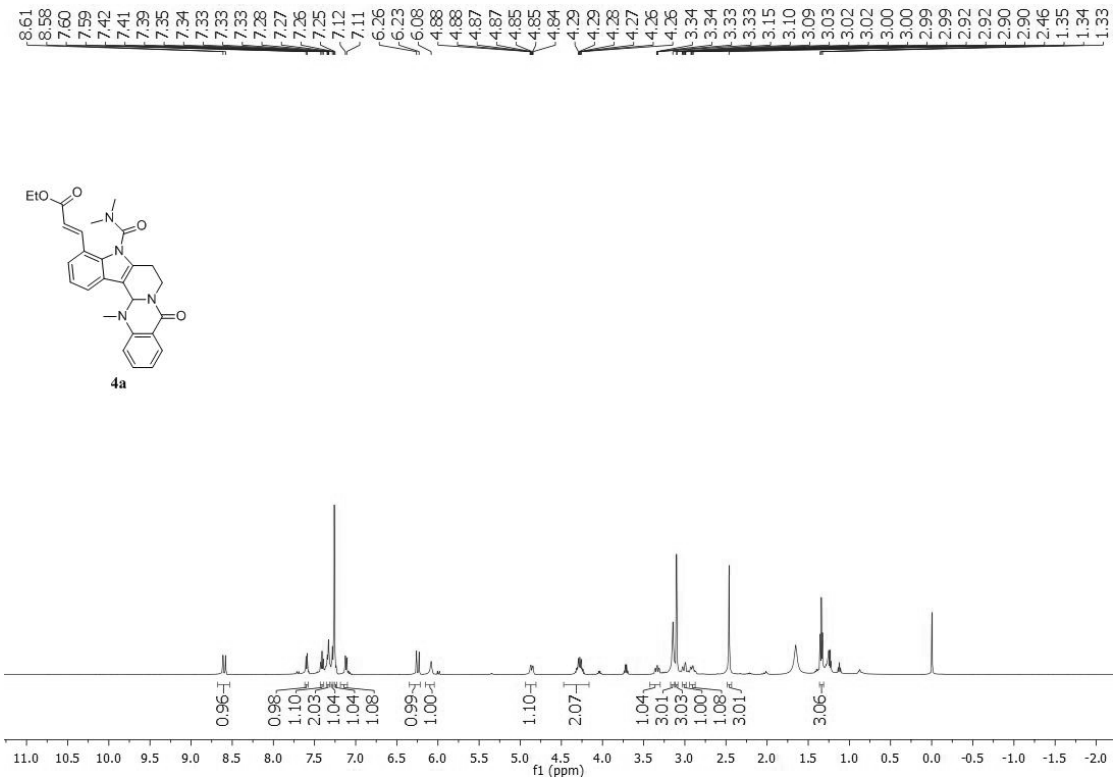
HRMS spectrum of compound **3af**



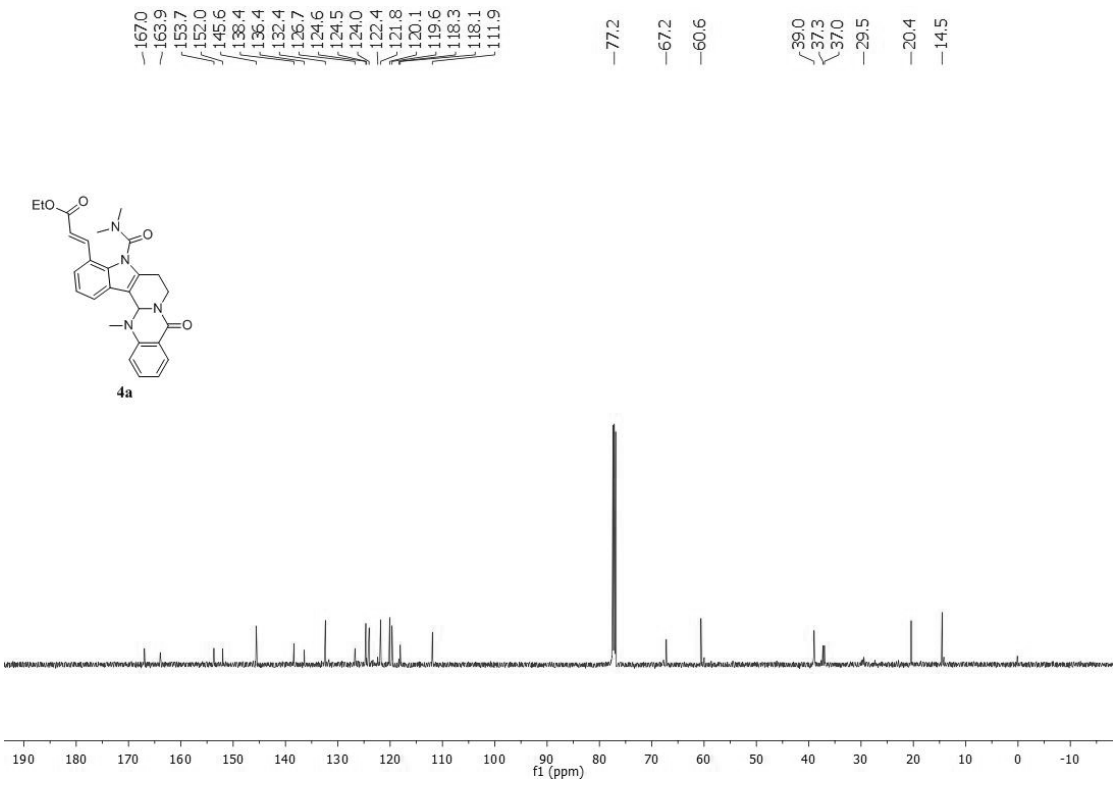
Elemental Composition Calculator

Target m/z:	338.1500	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C19H20N3O3		338.1499		-0.22	

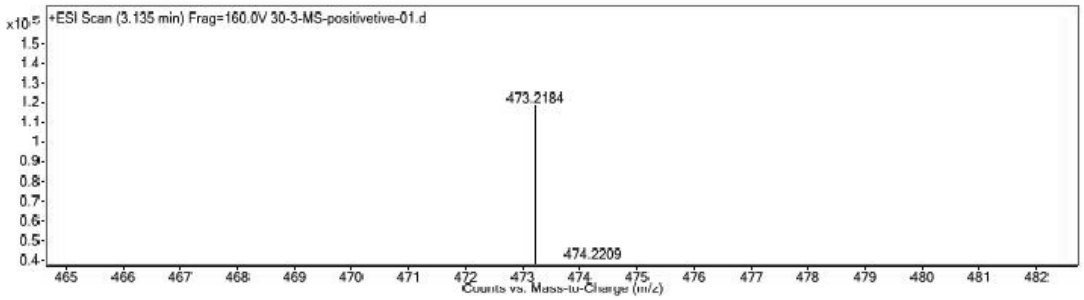
^{1}H NMR spectra of compound **4a**



^{13}C NMR spectra of compound **4a**



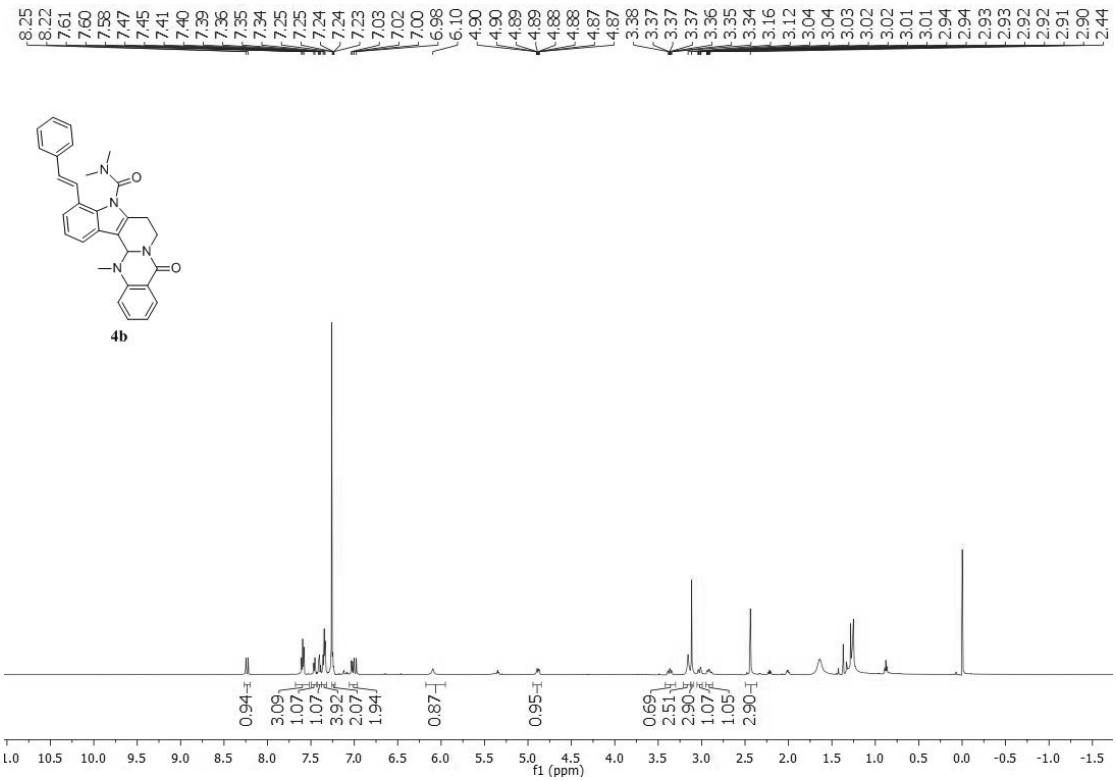
HRMS spectrum of compound **4a**



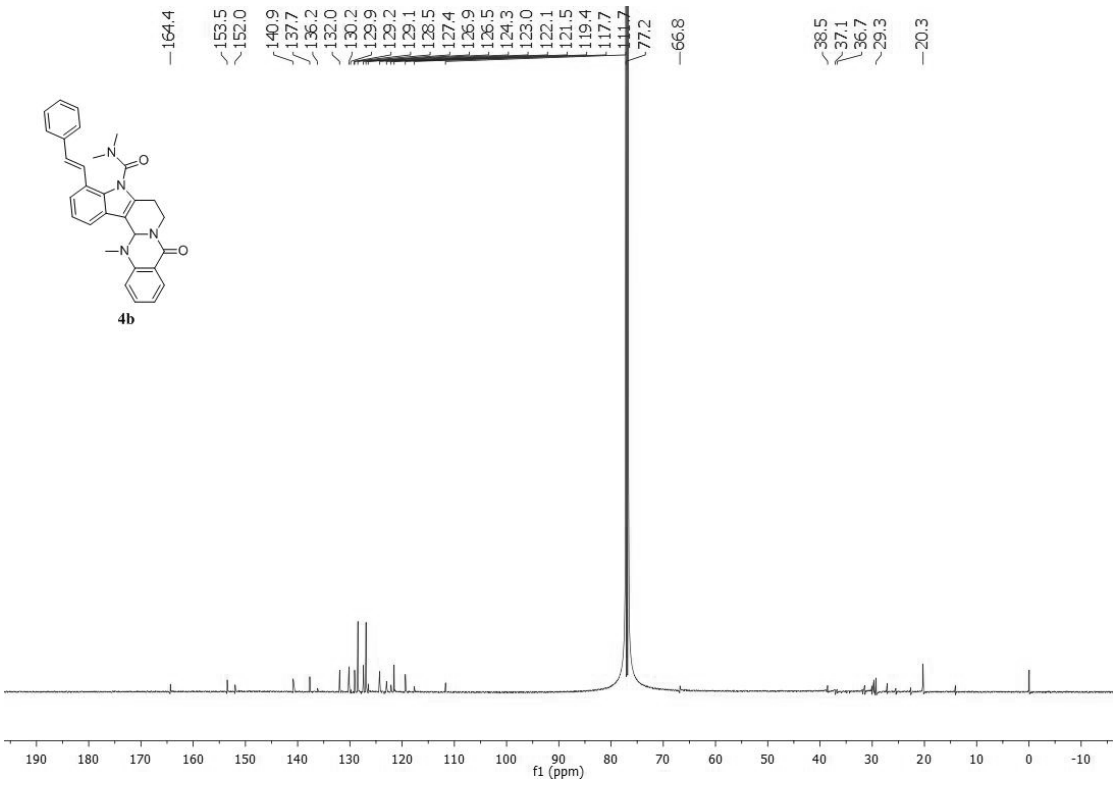
Elemental Composition Calculator

Target m/z:	473.2184	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C27H29N4O4		473.2183		-0.25	

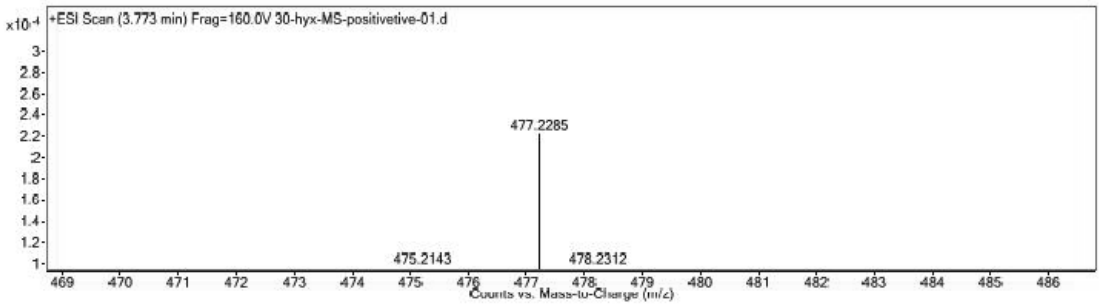
^{1}H NMR spectra of compound **4b**



^{13}C NMR spectra of compound **4b**



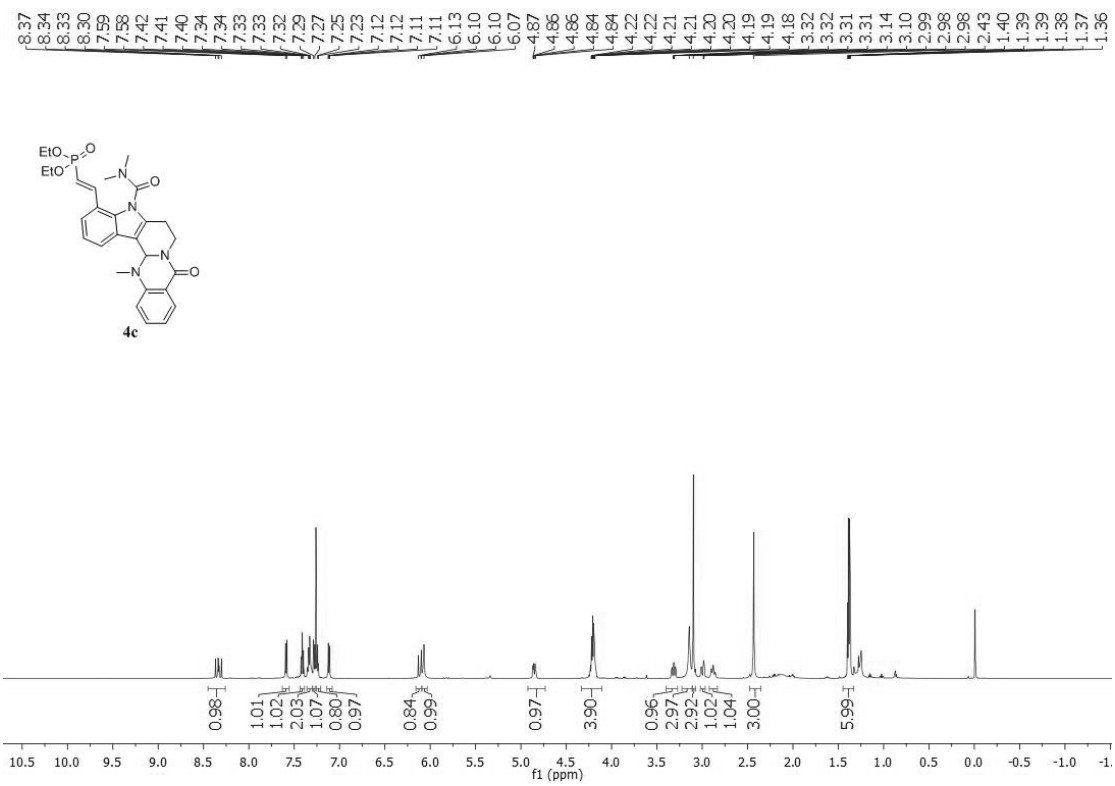
HRMS spectrum of compound **4b**



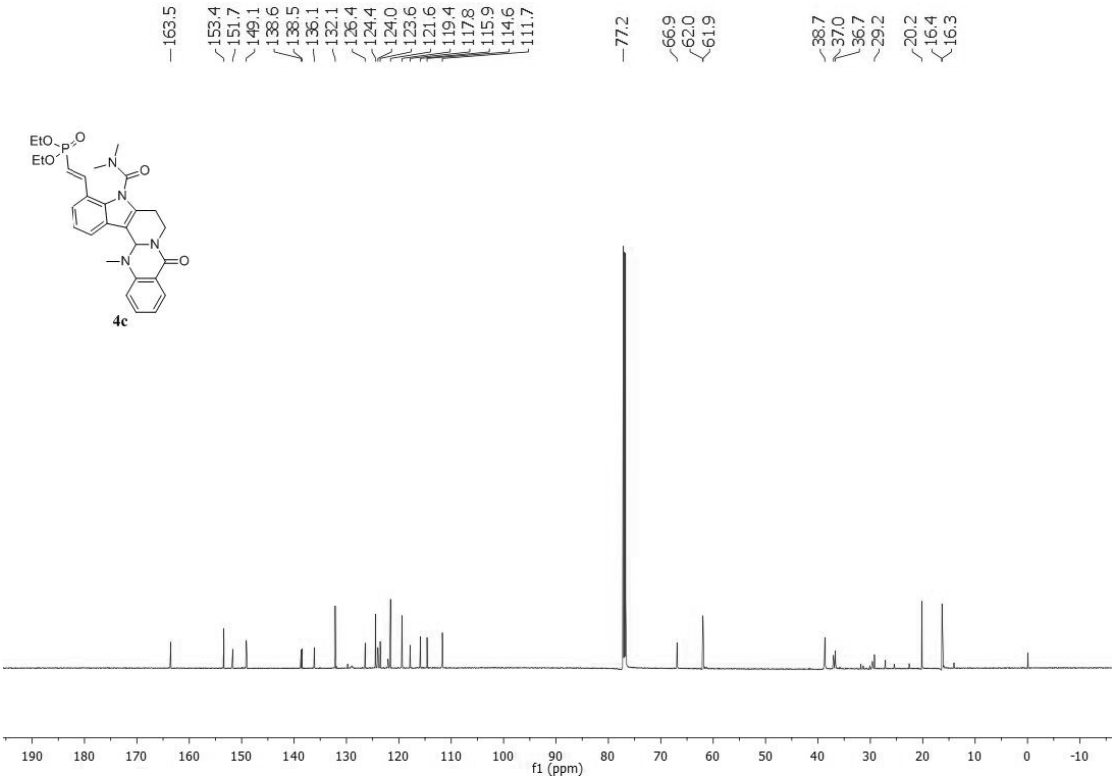
Elemental Composition Calculator

Target m/z:	477.2285	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C30H29N4O2		477.2285		0.07	

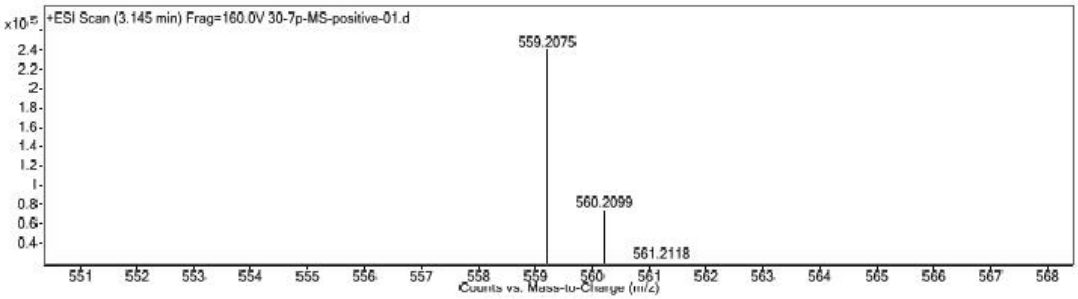
^{1}H NMR spectra of compound **4c**



^{13}C NMR spectra of compound **4c**



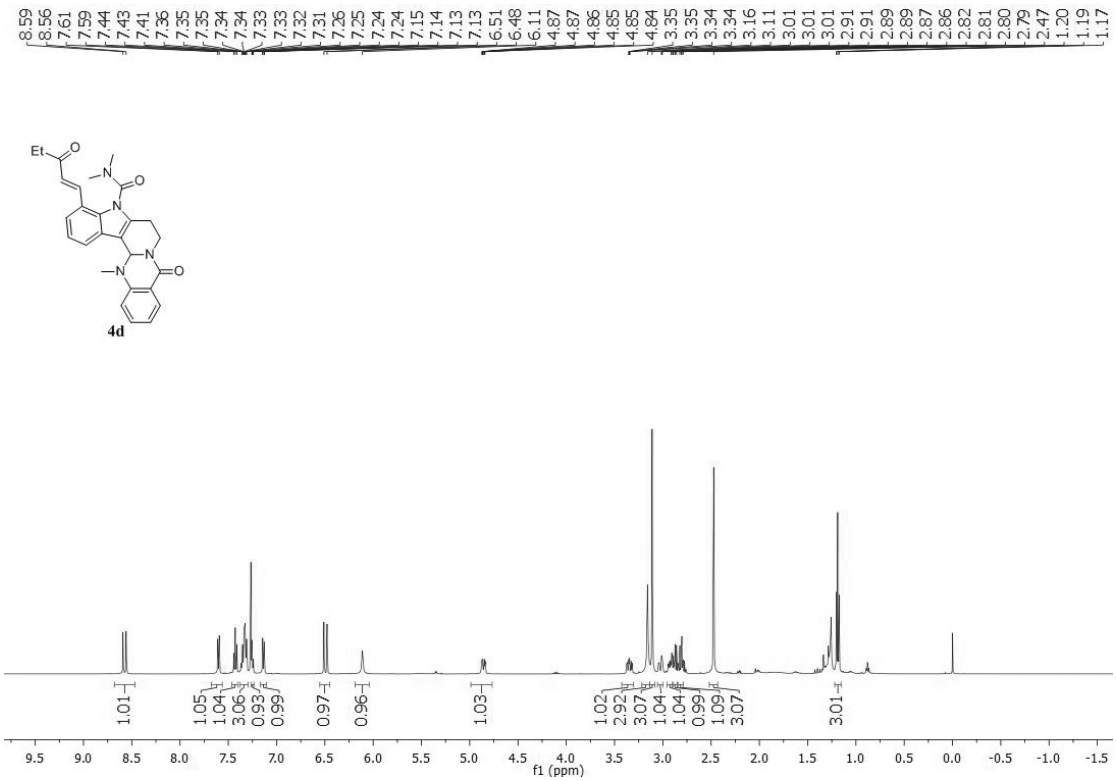
HRMS spectrum of compound **4c**



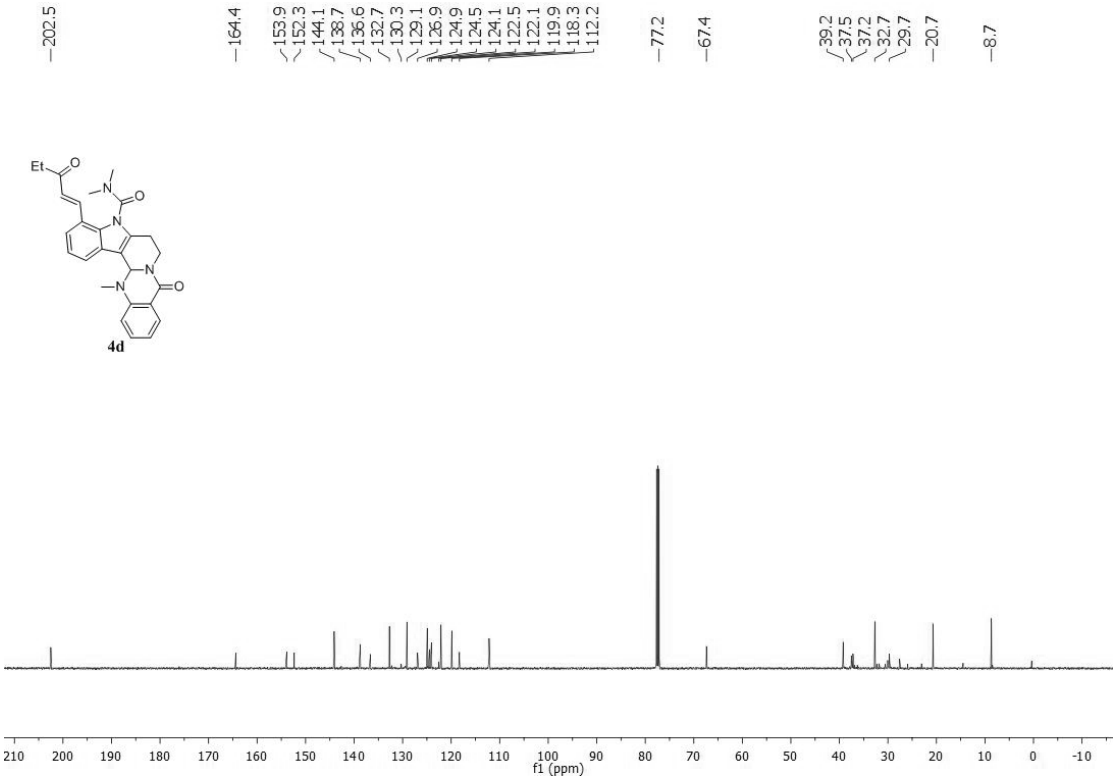
Elemental Composition Calculator

Target m/z:	559.2075	**Result type:**	Positive ions	**Species:**	$[M+Na]^+$
Elements:		C (0-80); H (0-120); O (0-30); N(0-5); Na (0-5) ; P (0-5)			
Ion Formula		**Calculated m/z**		**PPM Error**	
C28H33N4NaO5P		559.2081		1.05	

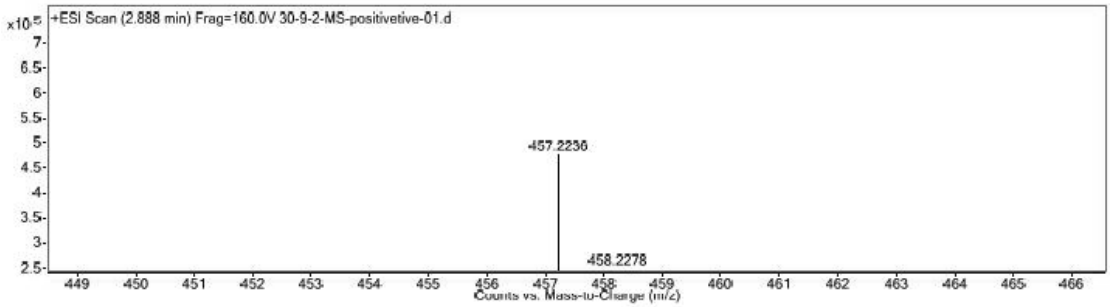
^{1}H NMR spectra of compound **4d**



^{13}C NMR spectra of compound **4d**



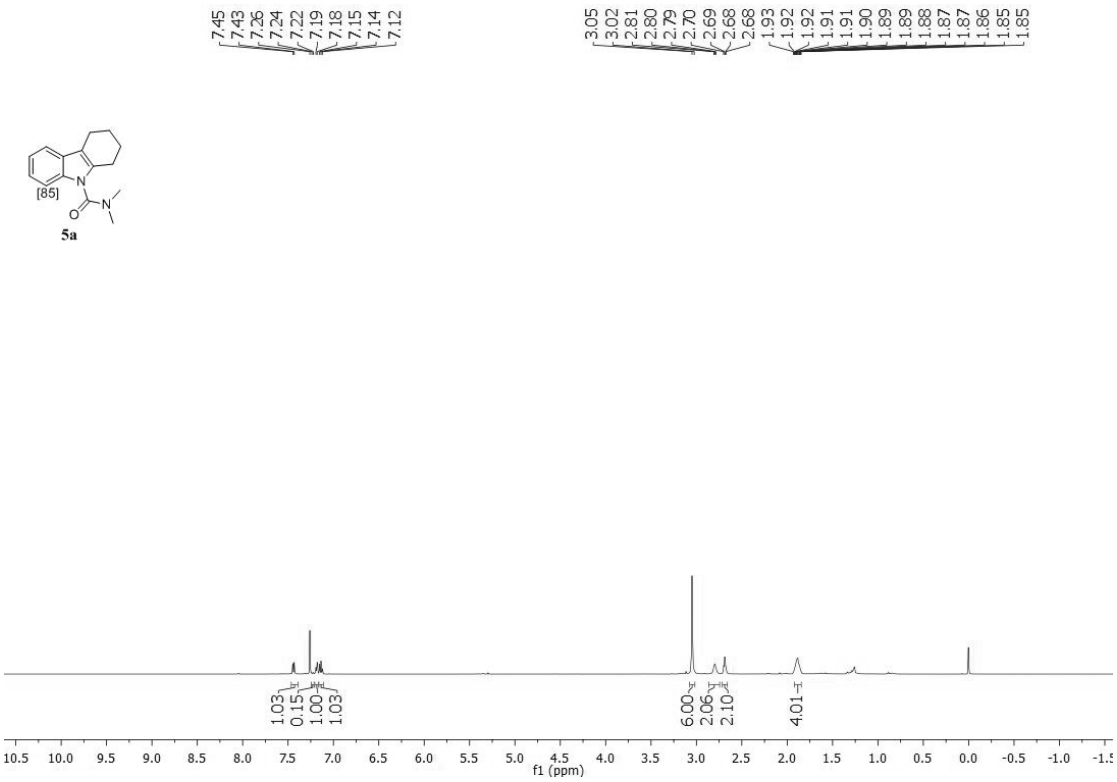
HRMS spectrum of compound **4d**



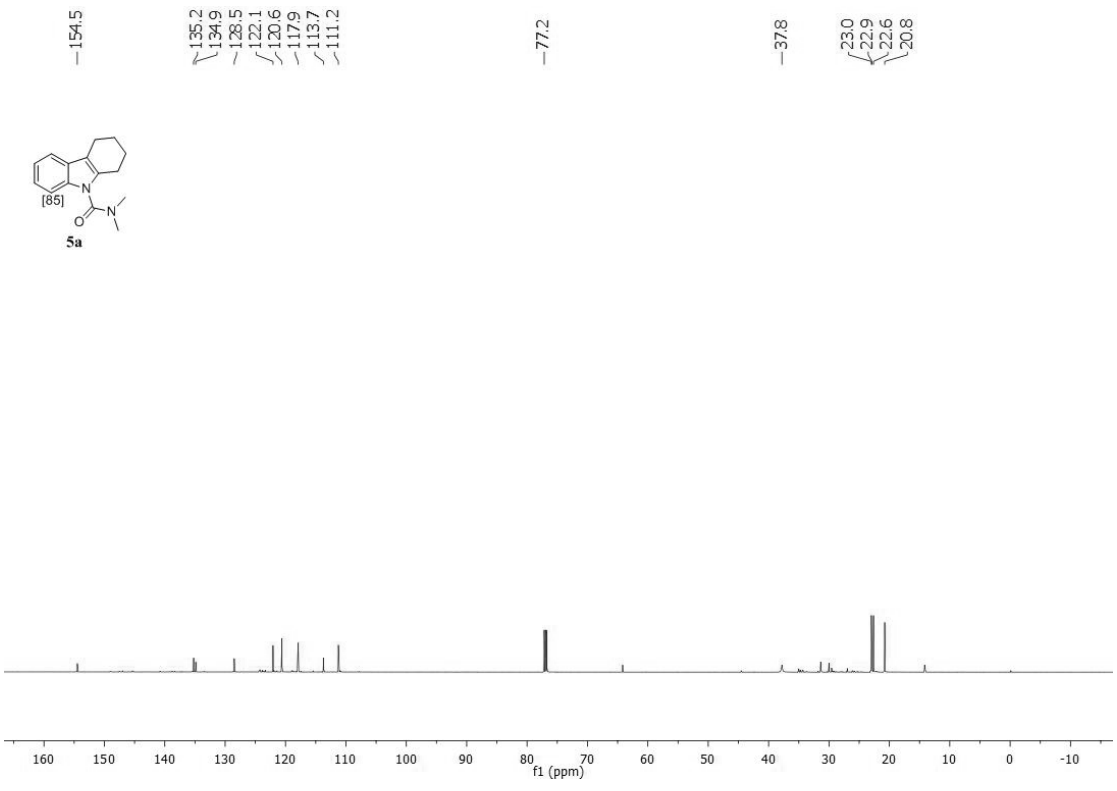
Elemental Composition Calculator

Target m/z:	457.2236	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C27H29N4O3		457.2234		-0.5	

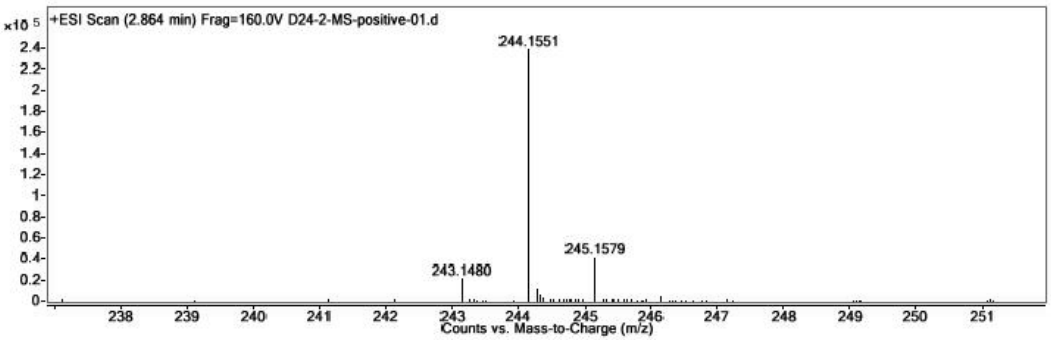
^{1}H NMR spectra of compound **5a**



^{13}C NMR spectra of compound **5a**



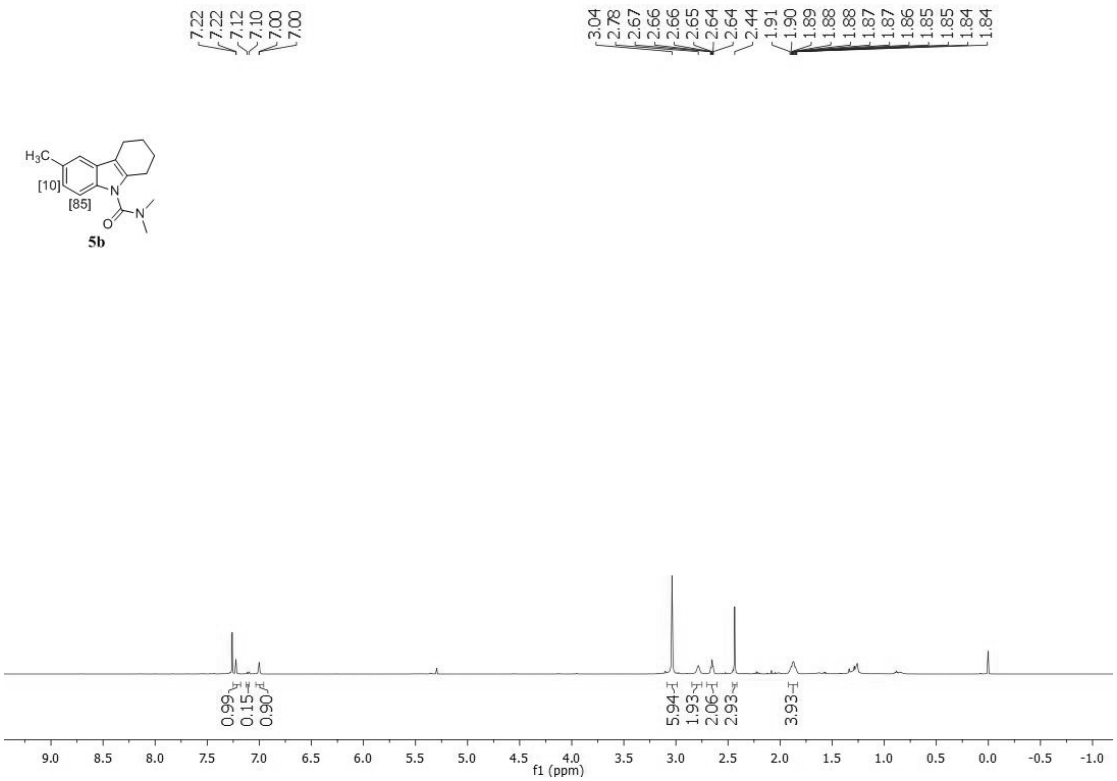
HRMS spectrum of compound **5a**



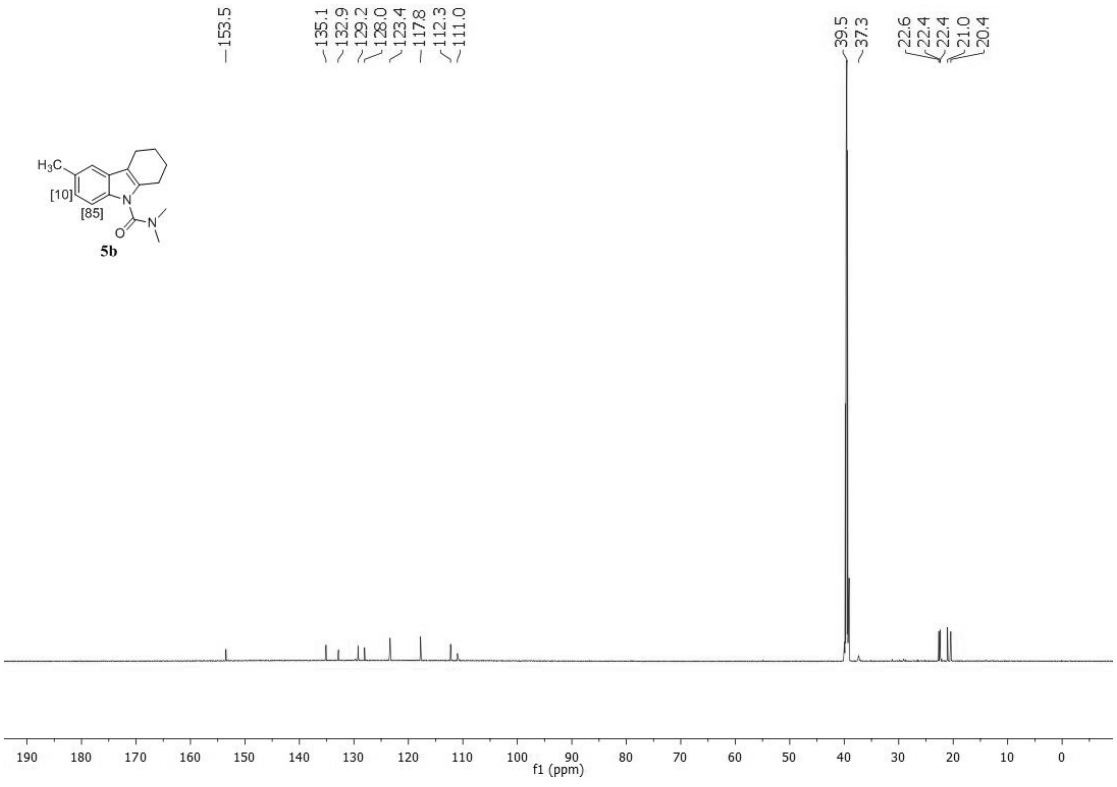
Elemental Composition Calculator

Target m/z:	244.1551	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5) ;D(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C15H18DN2O		244.1555		0.75	

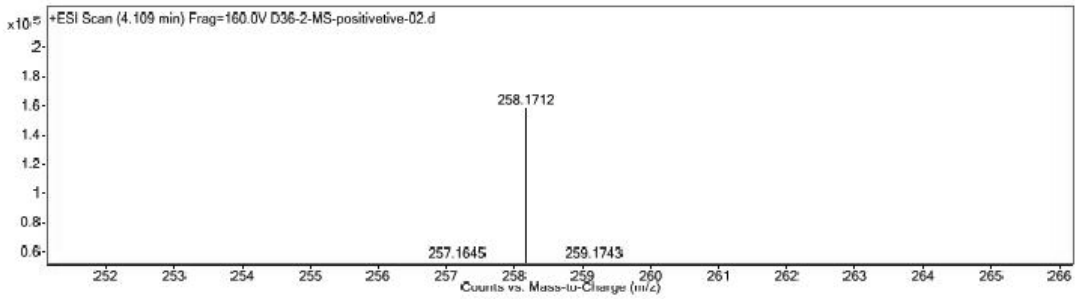
^{1}H NMR spectra of compound **5b**



^{13}C NMR spectra of compound **5b**



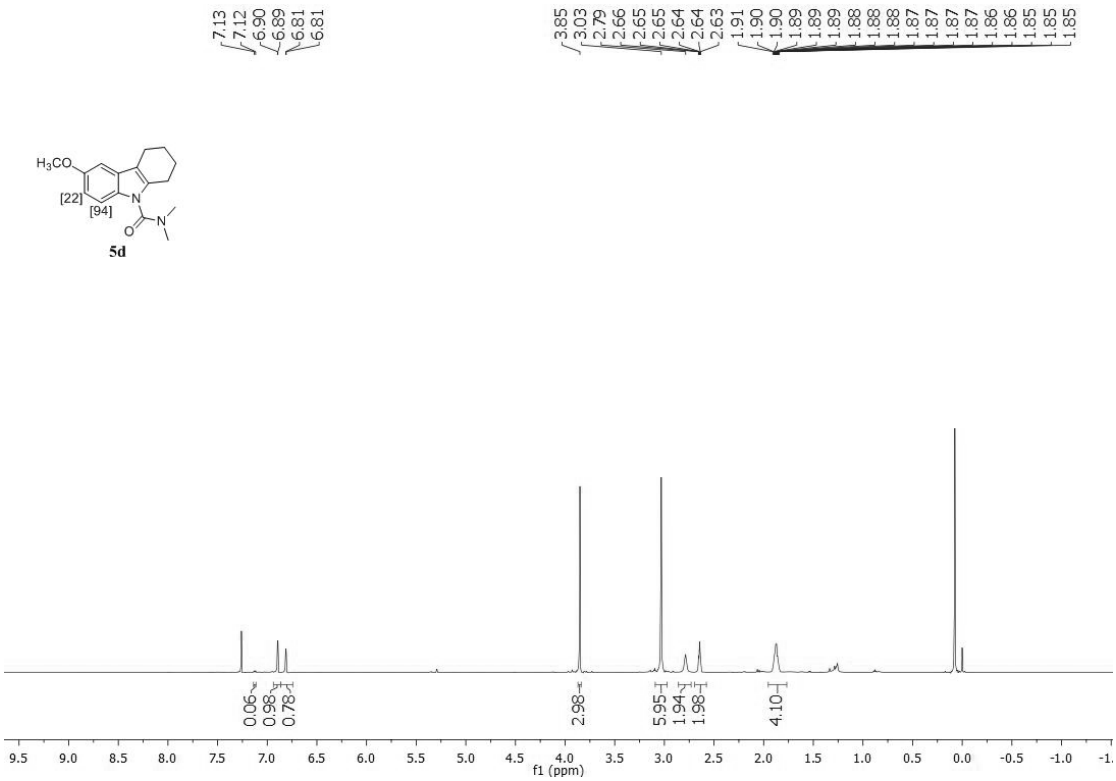
HRMS spectrum of compound **5b**



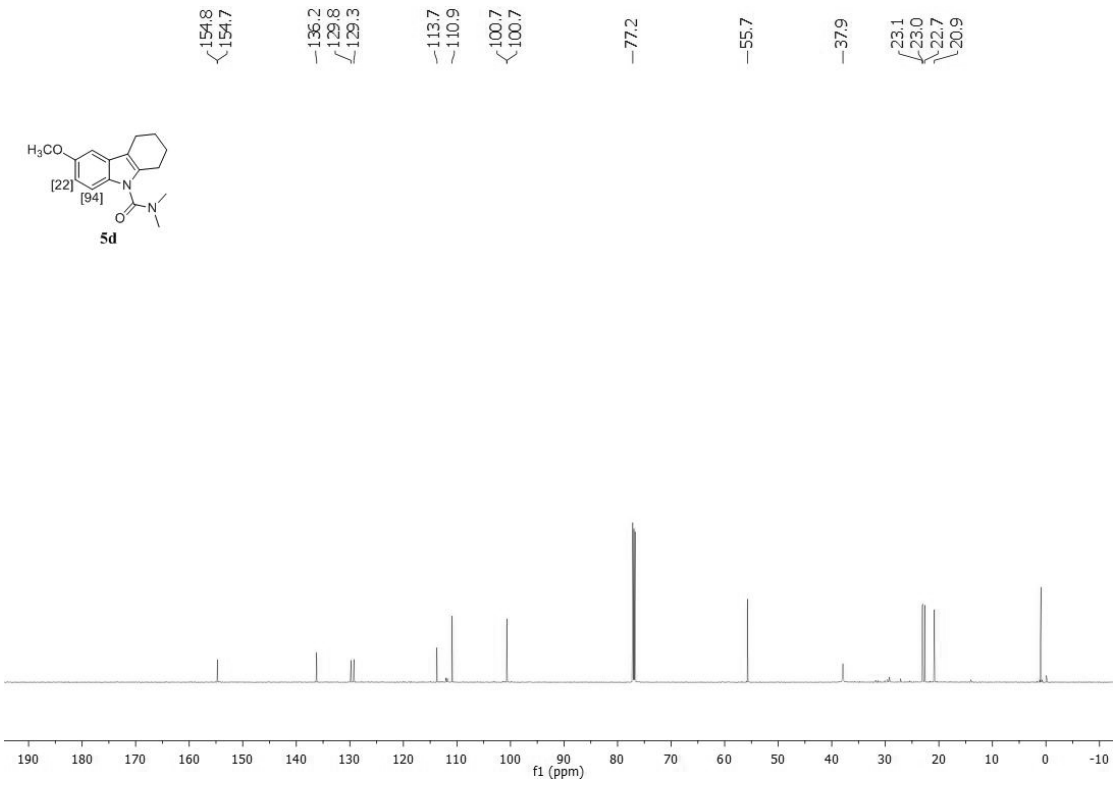
Elemental Composition Calculator

Target m/z:	258.1712	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5); D(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C16H20DN2O		258.1711		-0.22	

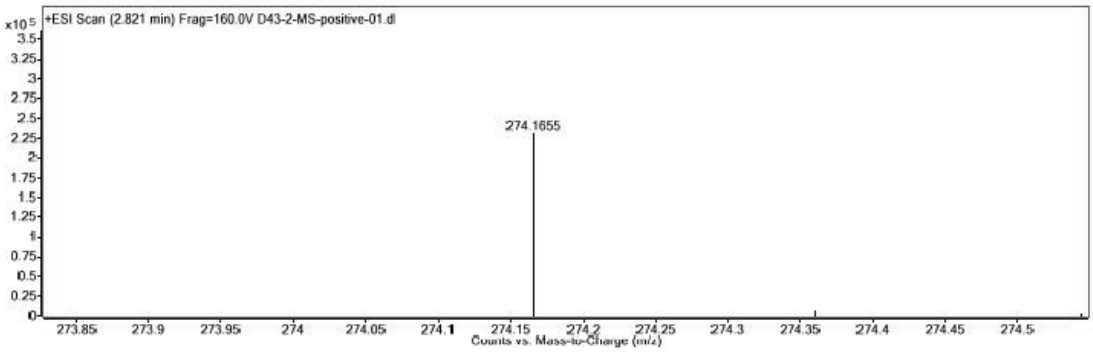
^{1}H NMR spectra of compound **5d**



^{13}C NMR spectra of compound **5d**



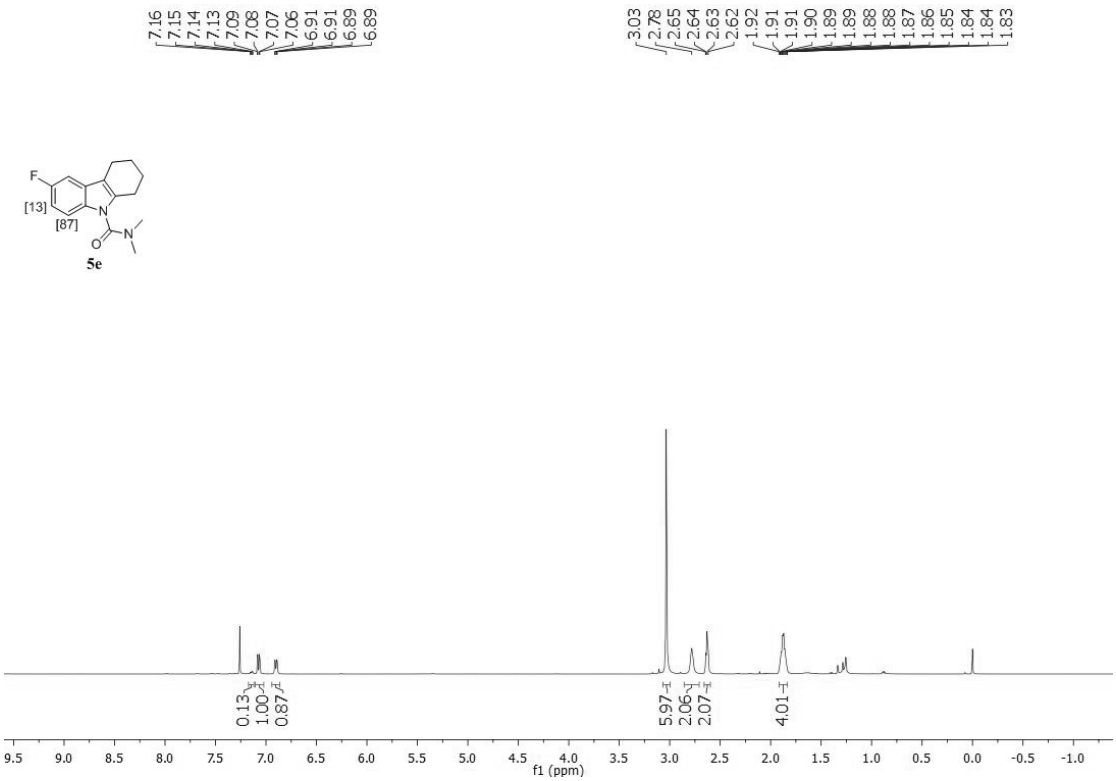
HRMS spectrum of compound **5d**



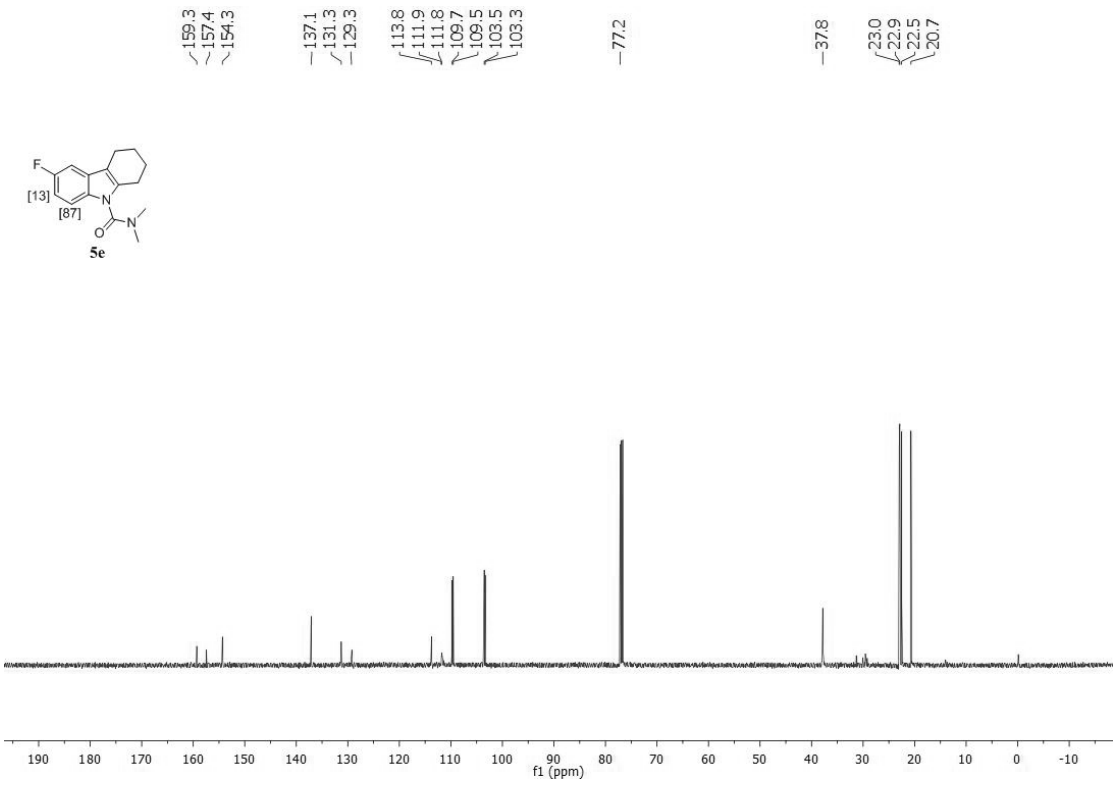
Elemental Composition Calculator

Target m/z:	274.1655	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5) ; D(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C16H19DN2O2		274.1660		1.89	

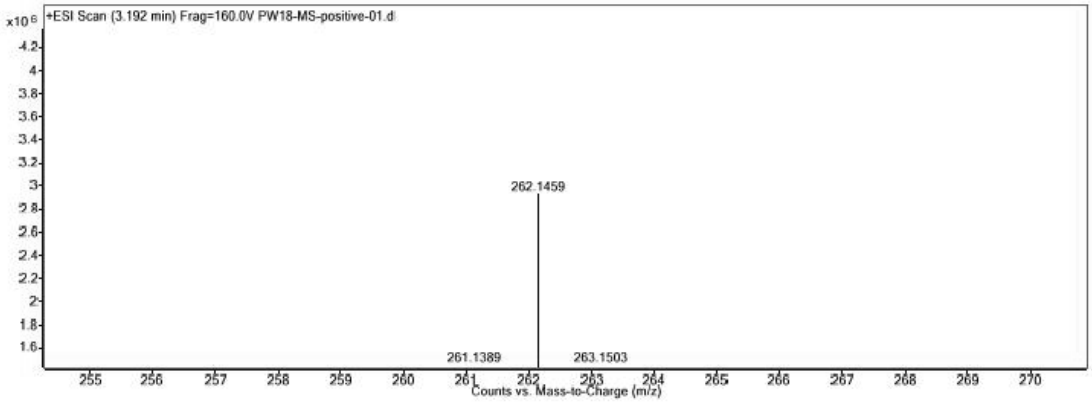
^{1}H NMR spectra of compound **5e**



^{13}C NMR spectra of compound **5e**



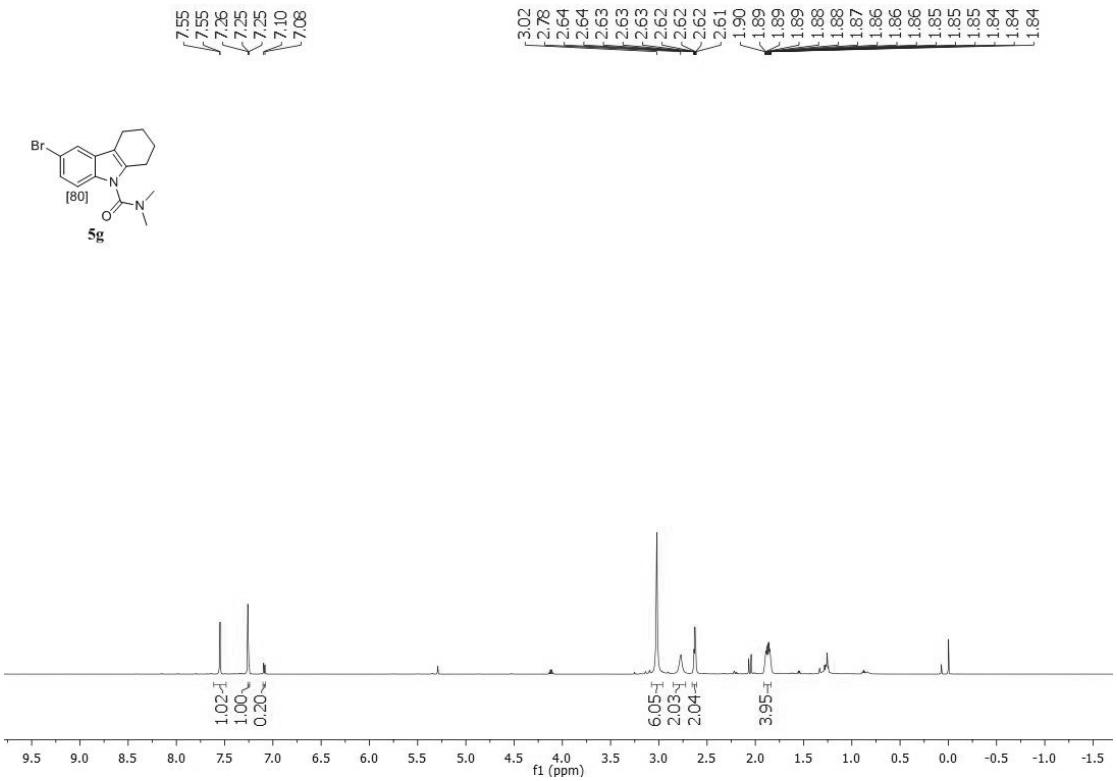
HRMS spectrum of compound **5e**



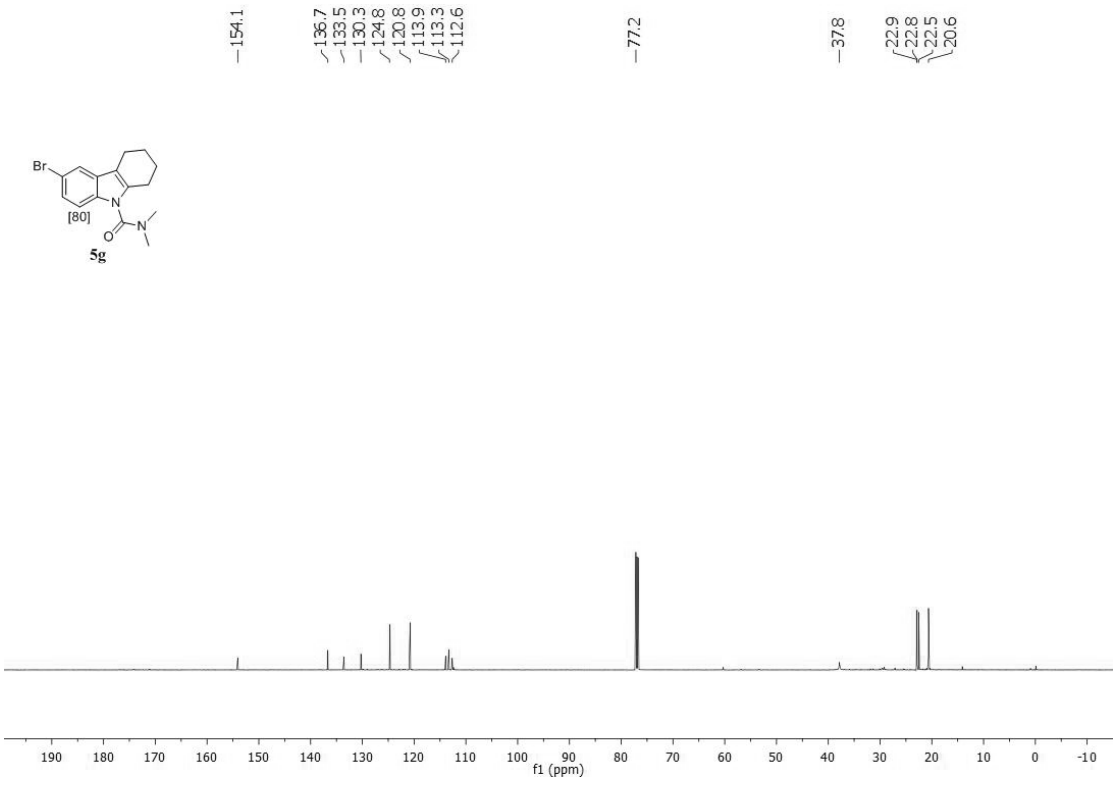
Elemental Composition Calculator

Target m/z:	262.1459	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5) ; D(0-5) ; F(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C15H17DFN2O		262.1460		0.40	

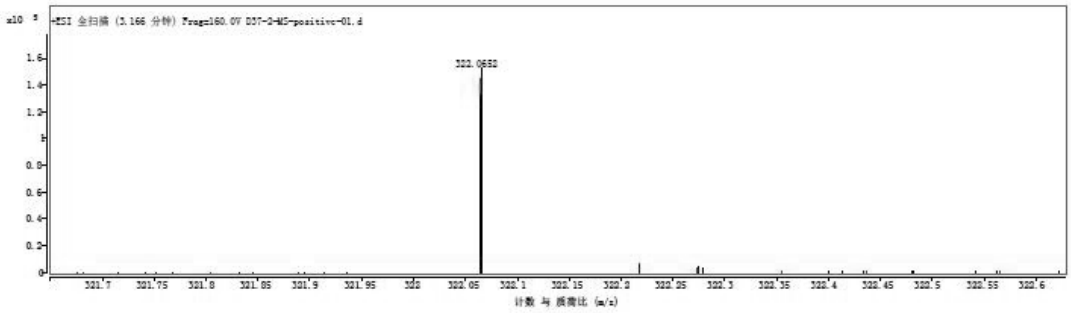
^{1}H NMR spectra of compound **5g**



^{13}C NMR spectra of compound **5g**



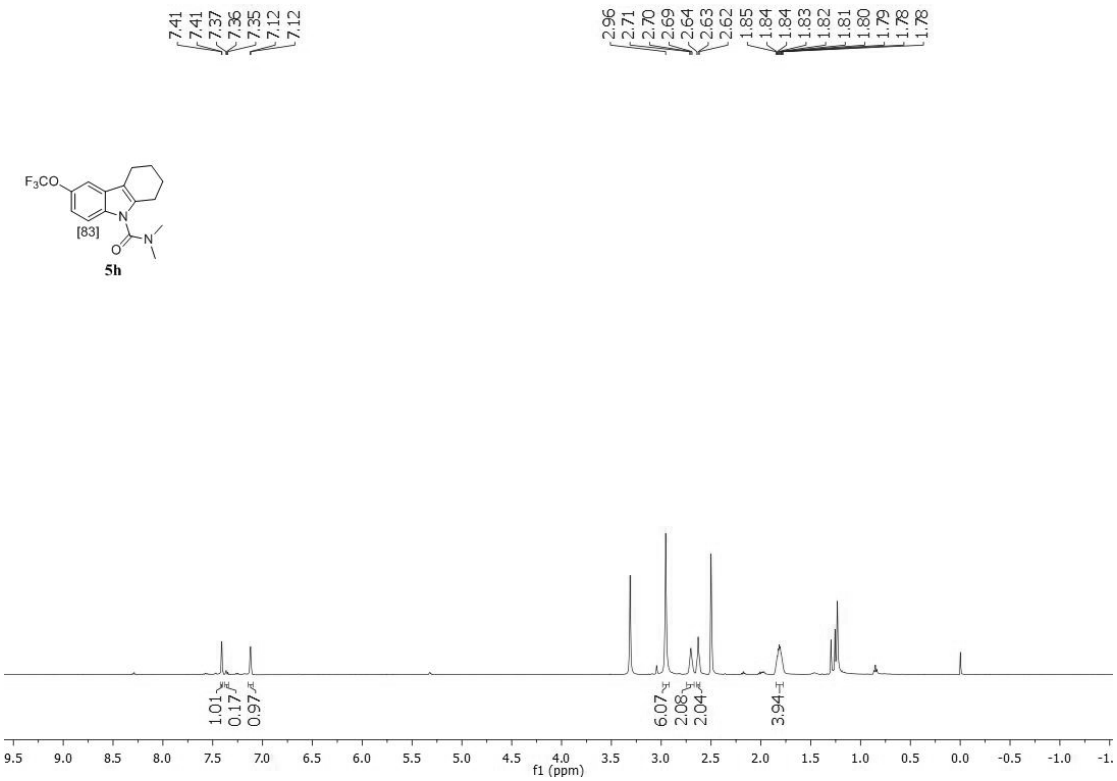
HRMS spectrum of compound **5g**



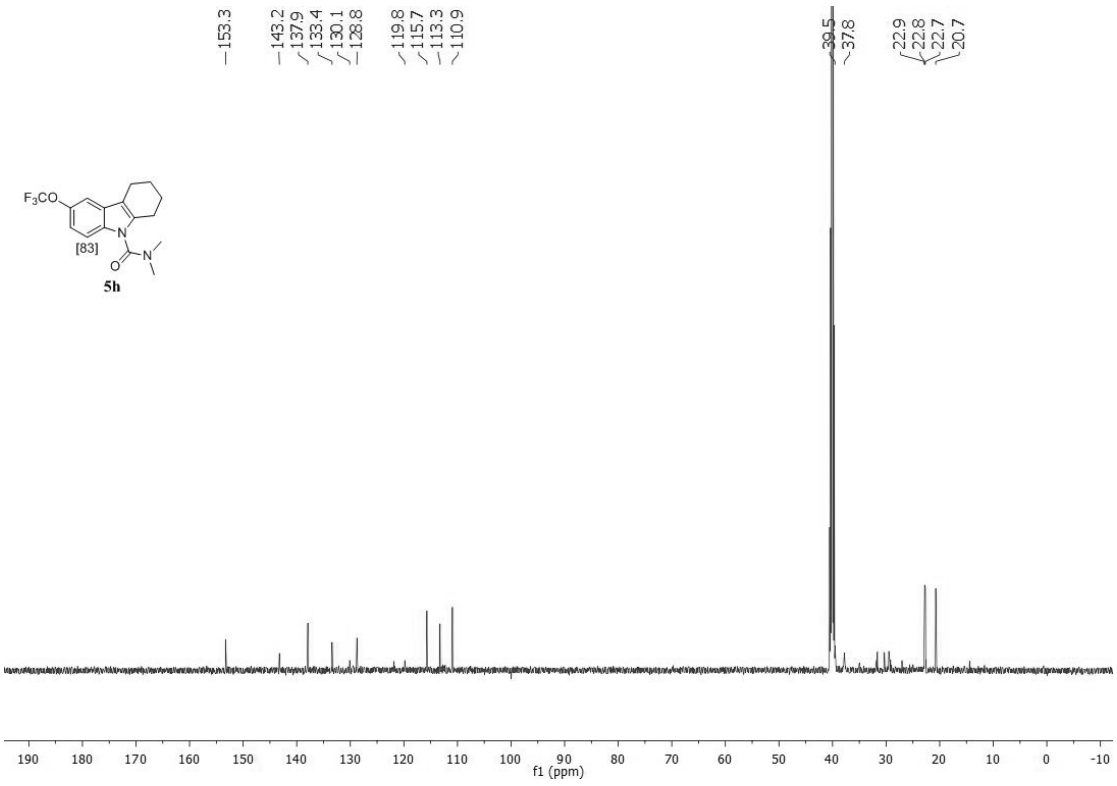
Elemental Composition Calculator

Target m/z:	322.0652	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C28H38NO10		322.066		3.52	

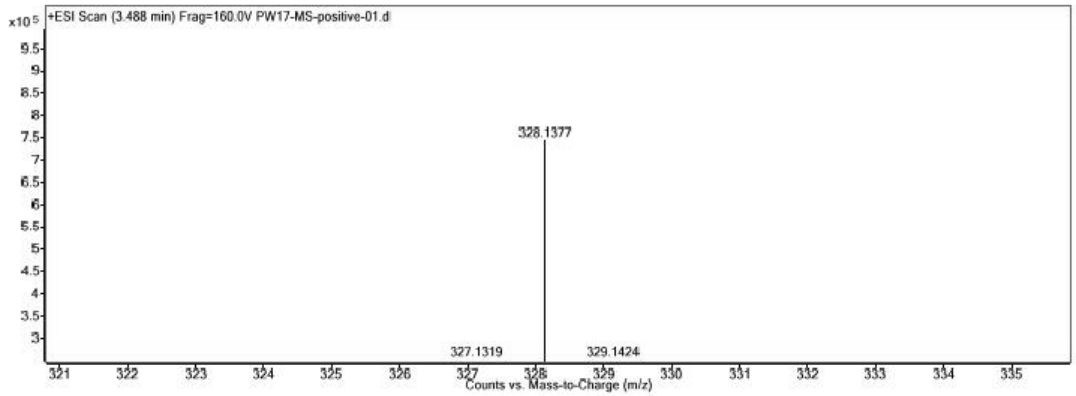
^{1}H NMR spectra of compound **5h**



^{13}C NMR spectra of compound **5h**



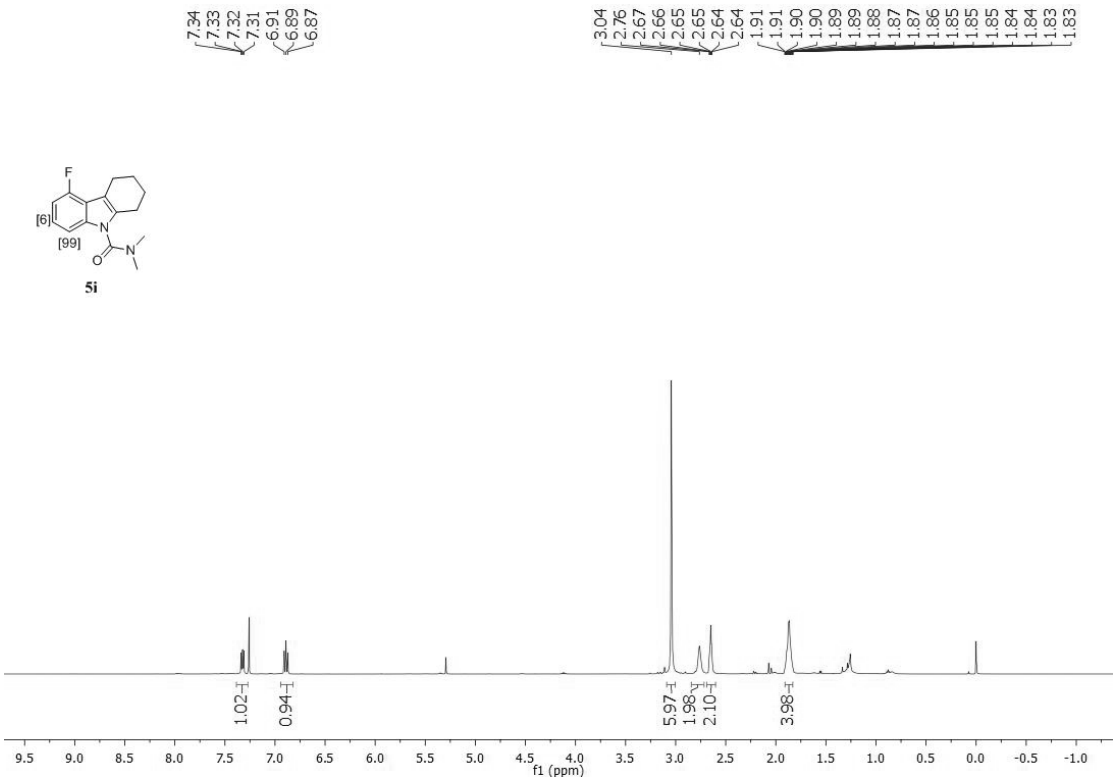
HRMS spectrum of compound **5h**



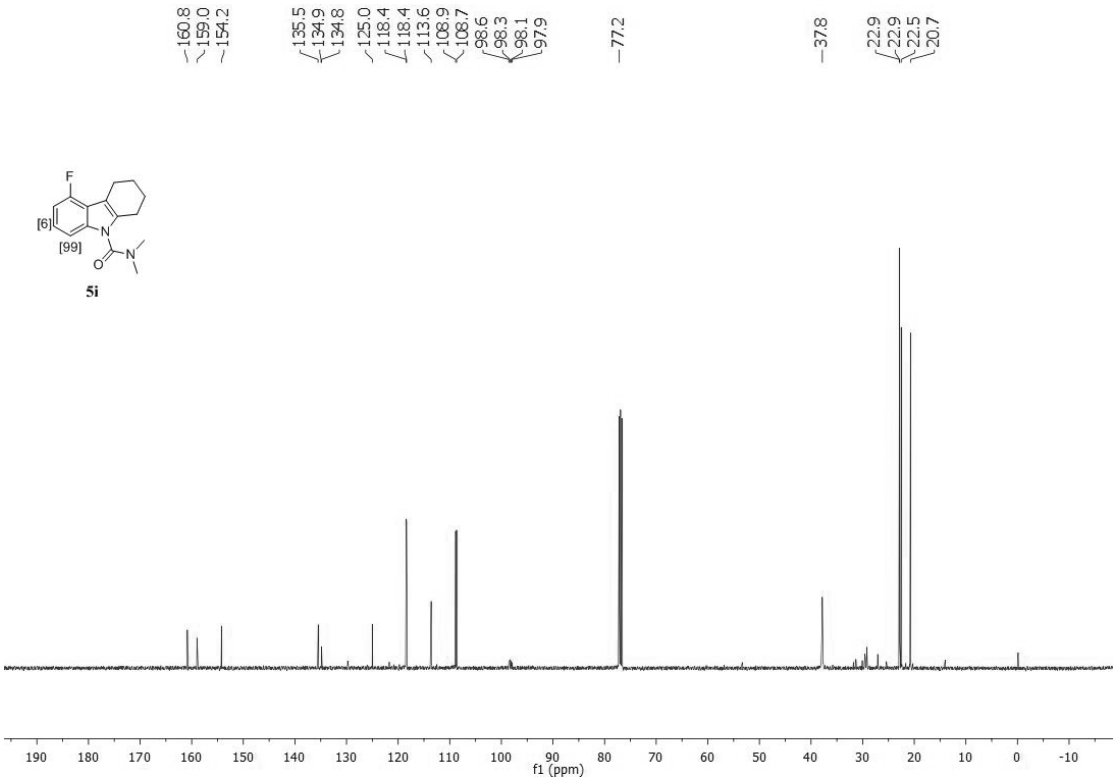
Elemental Composition Calculator

Target m/z:	328.1377	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5) ; D(0-5) ; F(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C16H17DF3N2O2		328.1378		0.14	

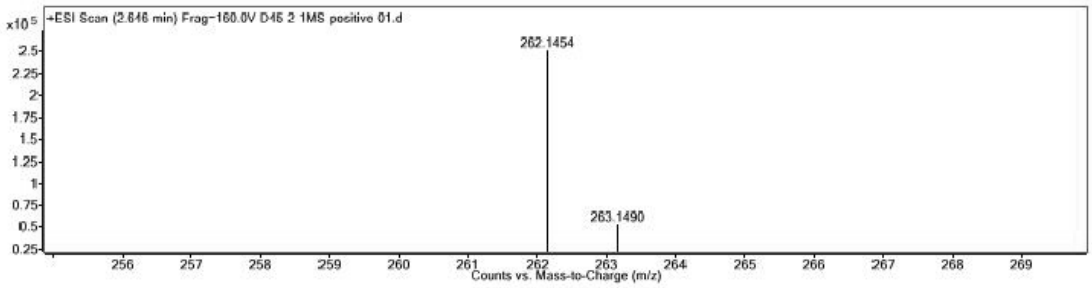
^{1}H NMR spectra of compound **5i**



^{13}C NMR spectra of compound **5i**



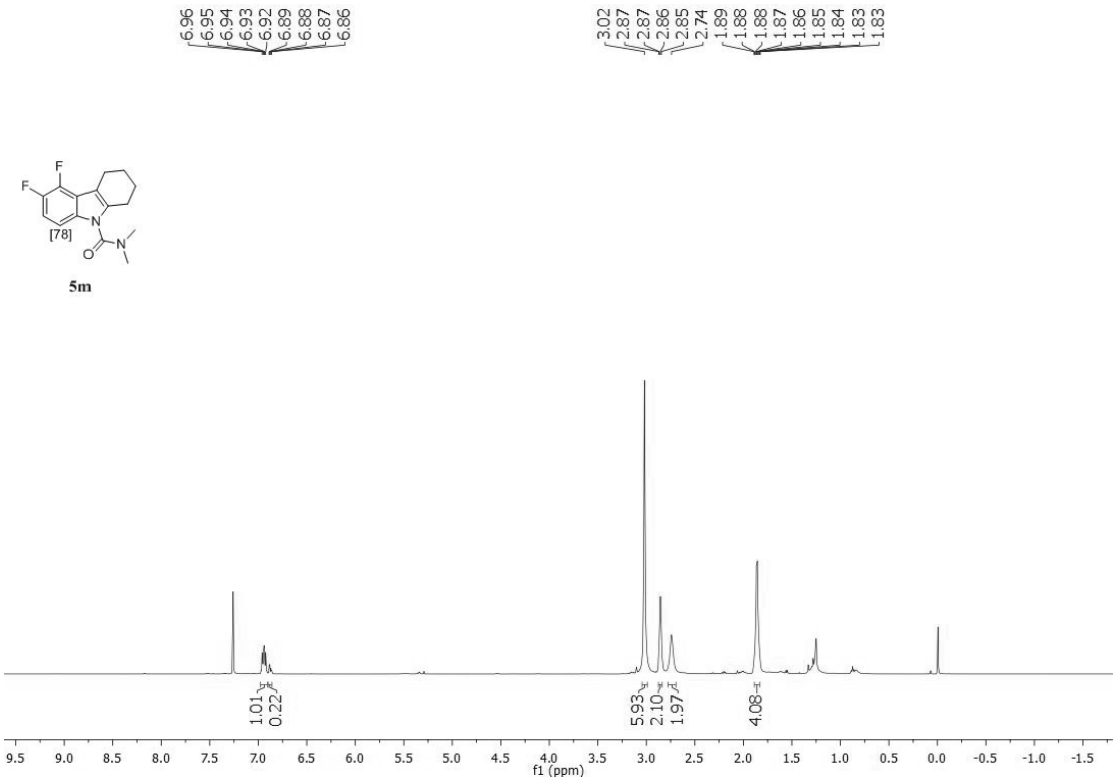
HRMS spectrum of compound **5i**



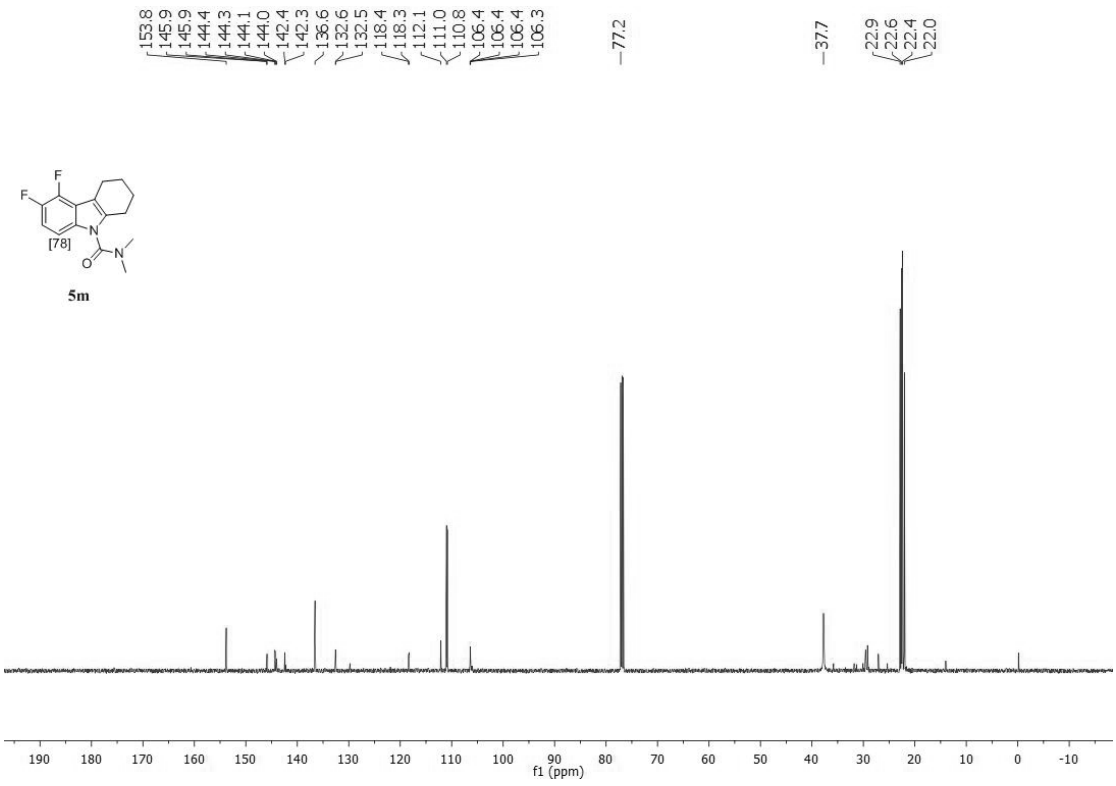
Elemental Composition Calculator

Target m/z:	262.1454	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5) ; D(0-5) ; F(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C15H17DFN2O		262.1460		2.44	

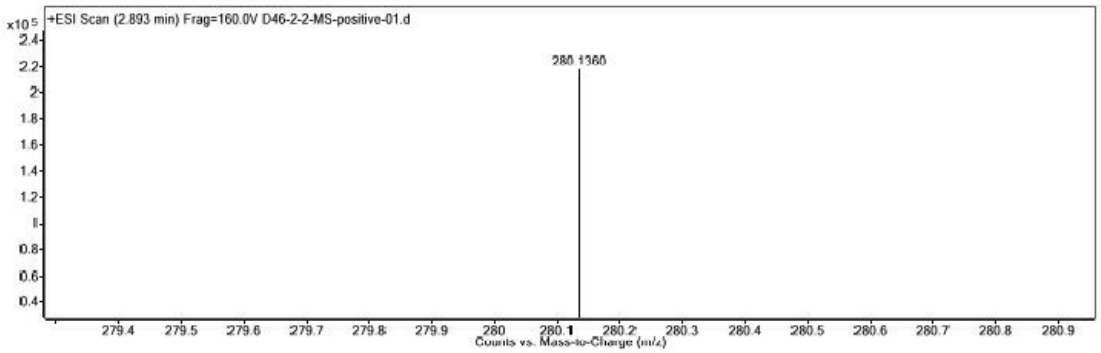
^{1}H NMR spectra of compound **5m**



^{13}C NMR spectra of compound **5m**



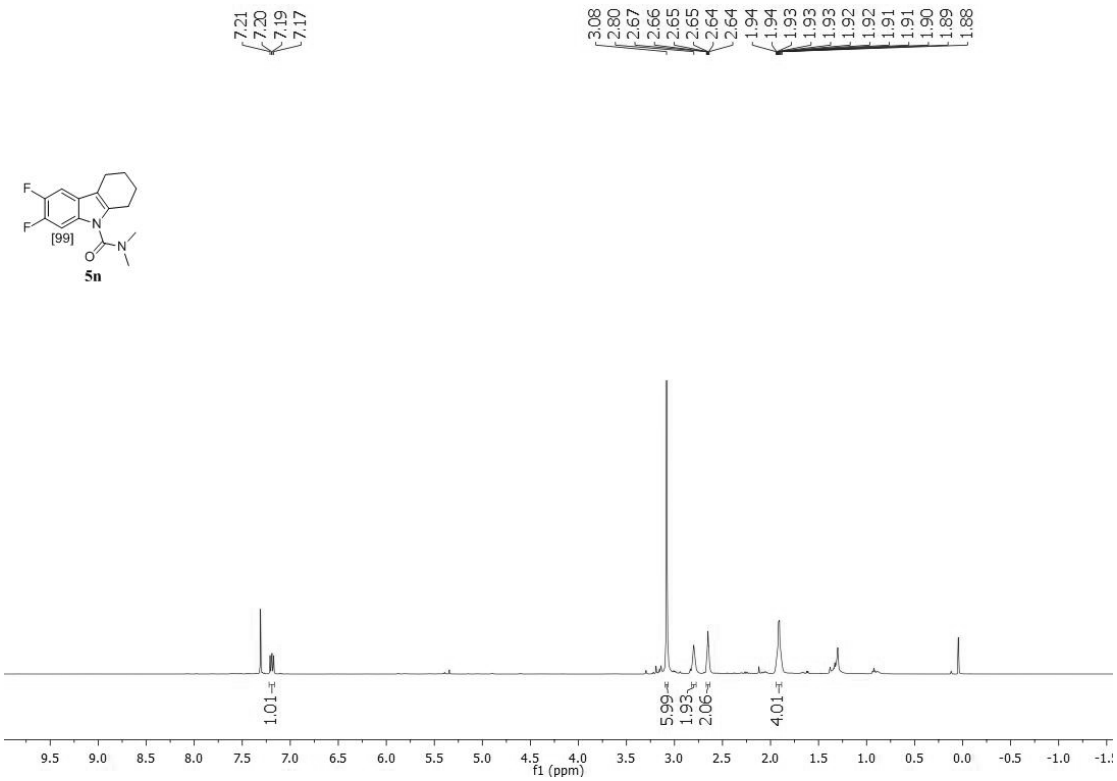
HRMS spectrum of compound **5m**



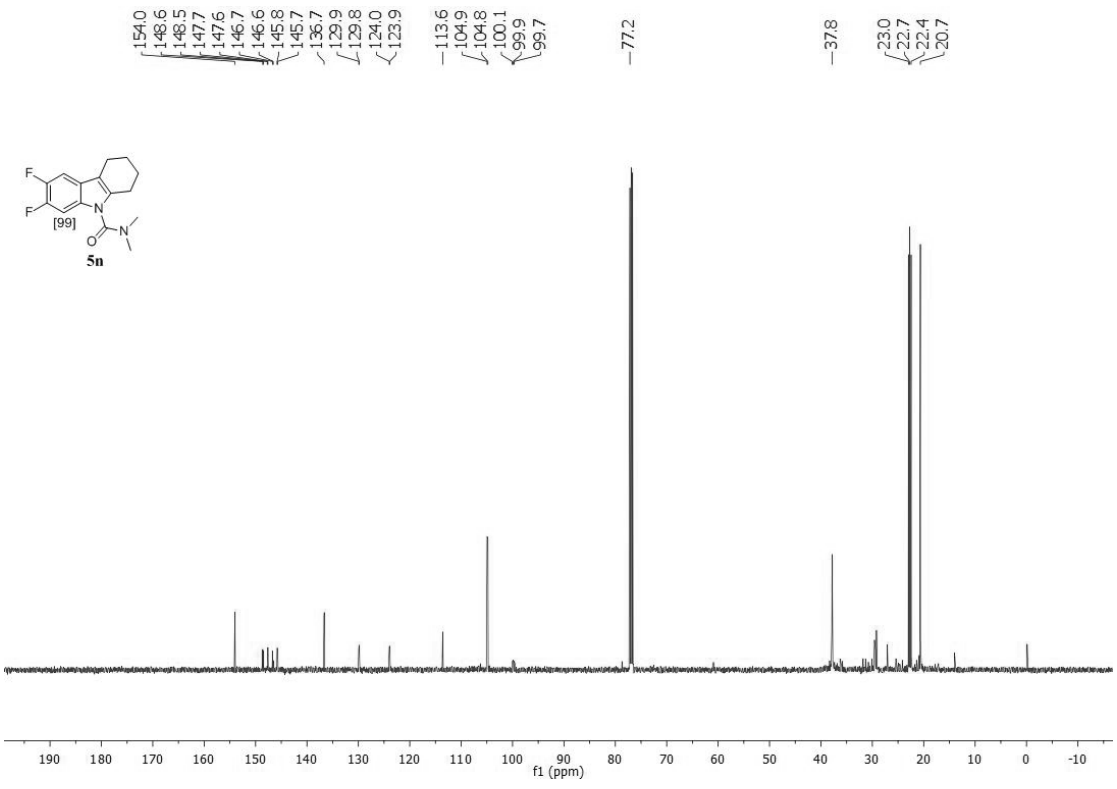
Elemental Composition Calculator

Target m/z:	280.1360	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5) ; D(0-5) ; F(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C15H16DF2N2O		280.1366		2.38	

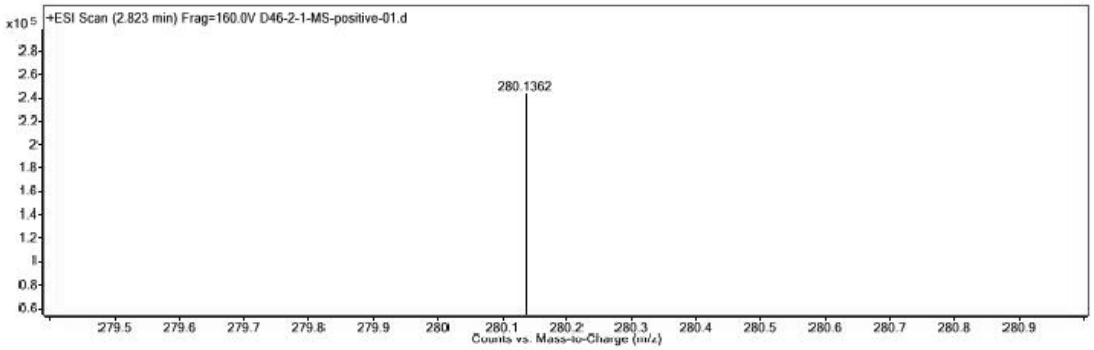
^{1}H NMR spectra of compound **5n**



^{13}C NMR spectra of compound **5n**



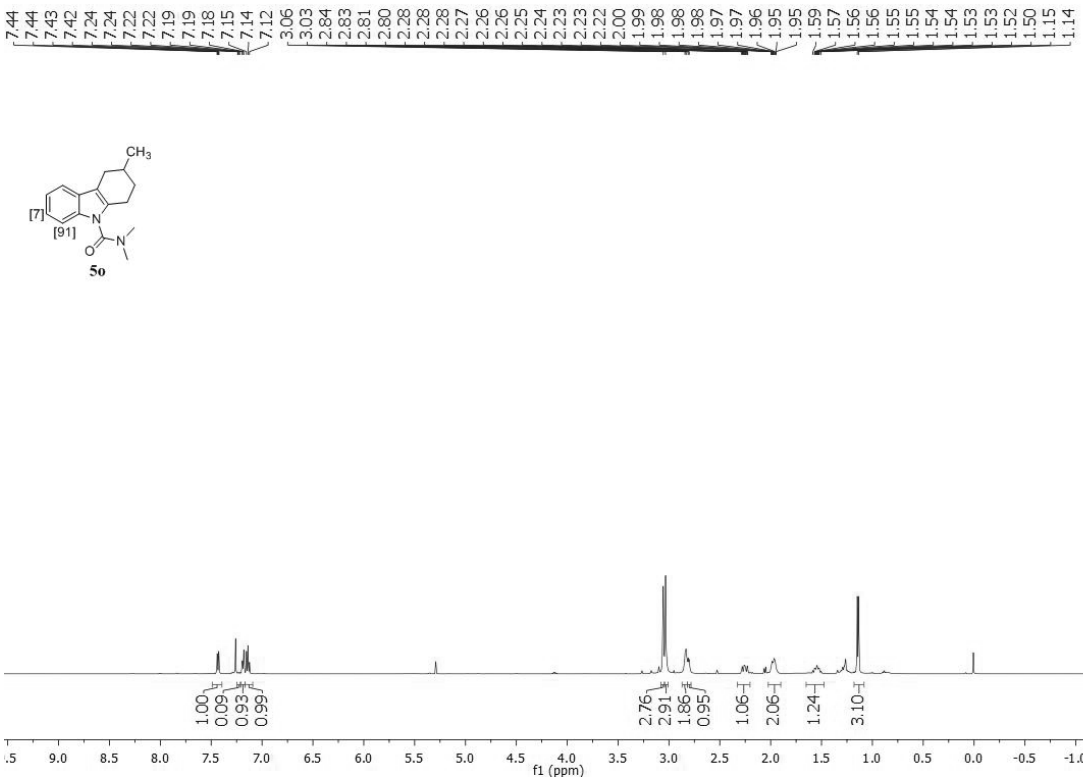
HRMS spectrum of compound **5n**



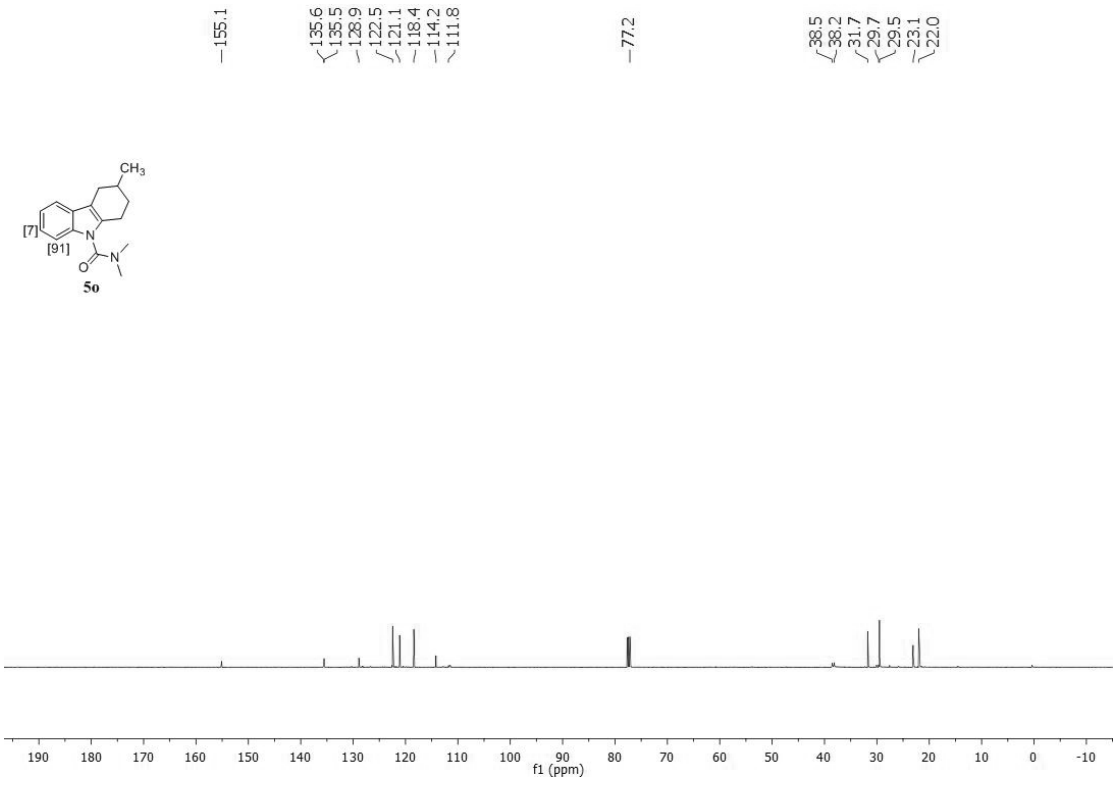
Elemental Composition Calculator

Target m/z:	280.1362	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5) ; D(0-5) ; F(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C15H16DF2N2O		280.1366		1.51	

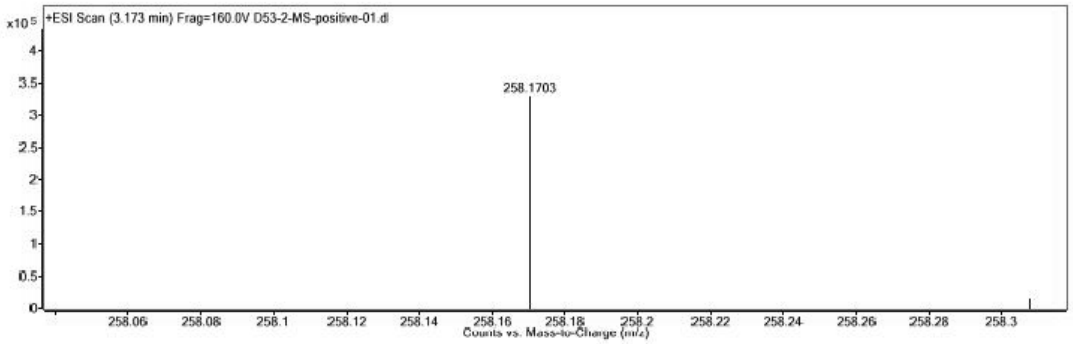
^{1}H NMR spectra of compound **5o**



^{13}C NMR spectra of compound **5o**



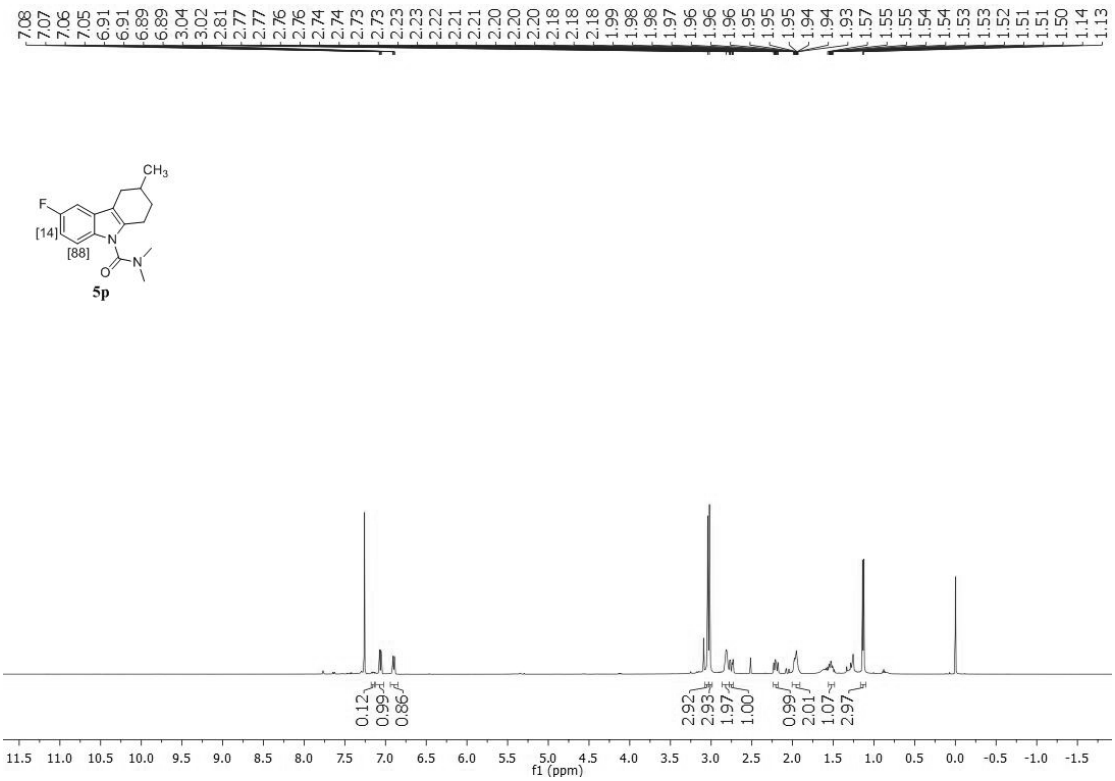
HRMS spectrum of compound **5o**



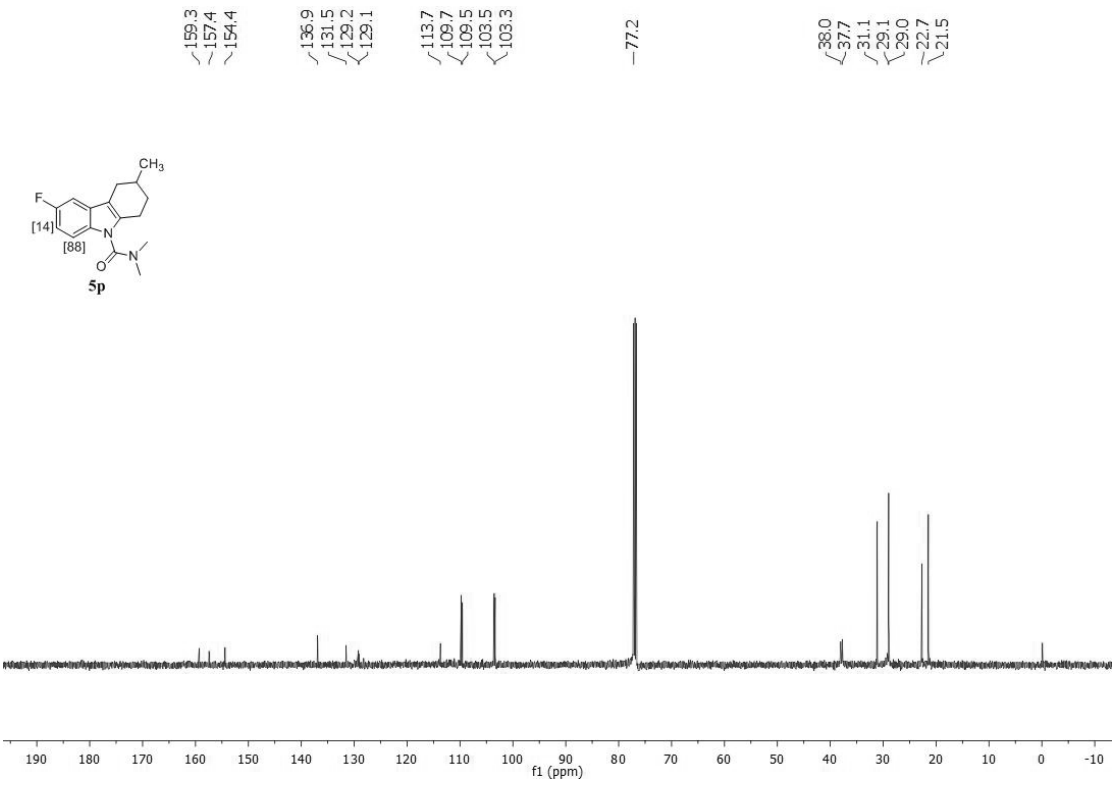
Elemental Composition Calculator

Target m/z:	258.1703	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5) ; D(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C16H20DN2O		258.1711		3.11	

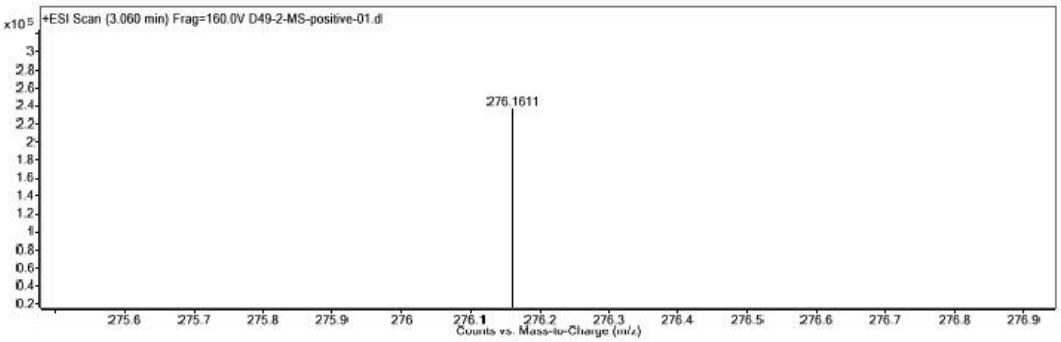
^{1}H NMR spectra of compound **5p**



^{13}C NMR spectra of compound **5p**



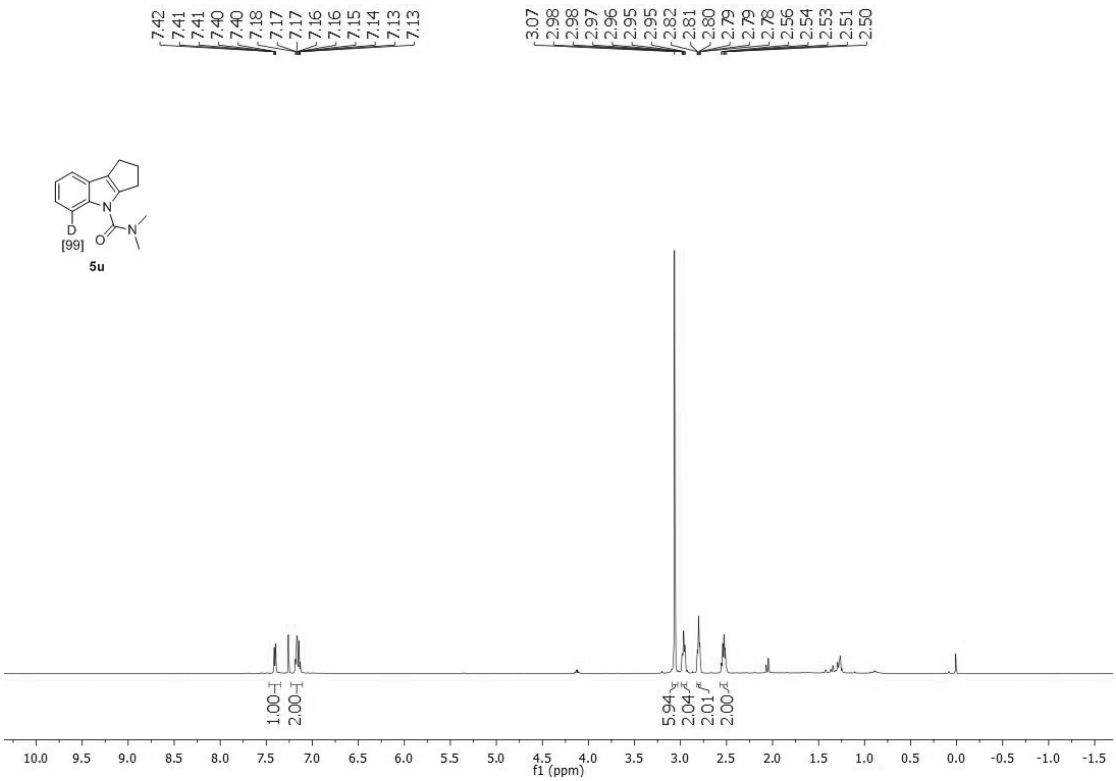
HRMS spectrum of compound **5p**



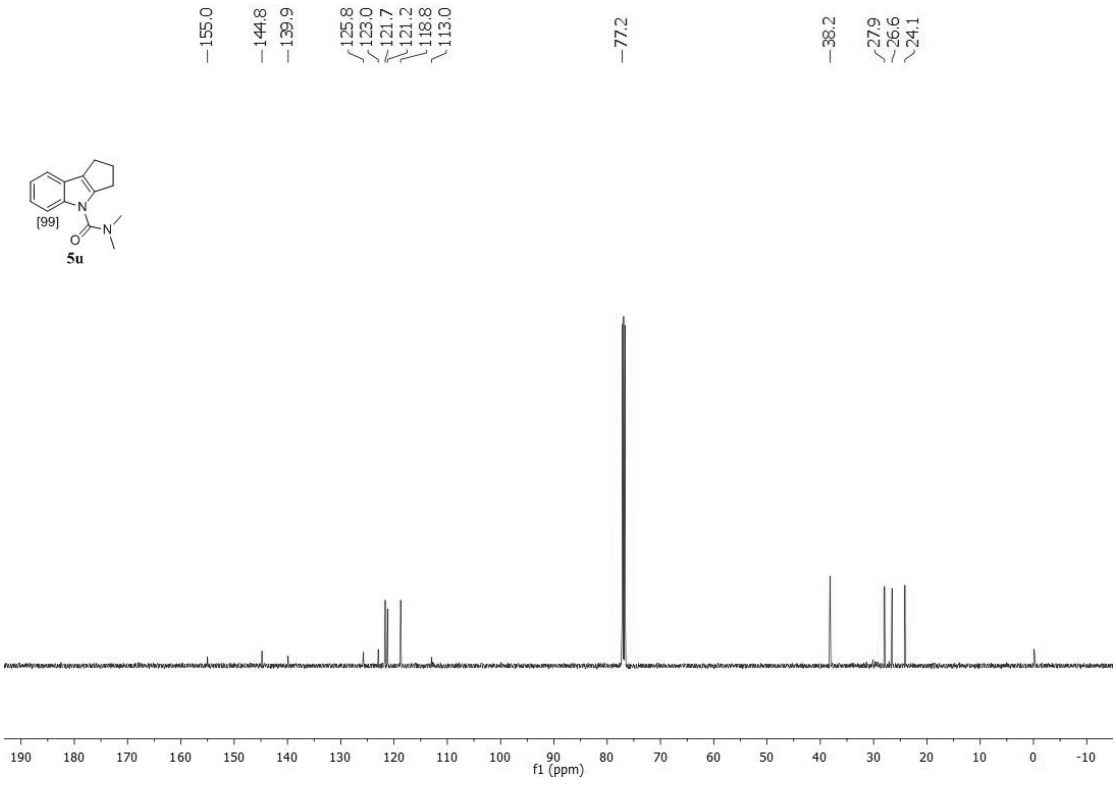
Elemental Composition Calculator

Target m/z:	276.1611	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5) ; D(0-5) ; F(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C16H19DFN2O		276.1617		2.07	

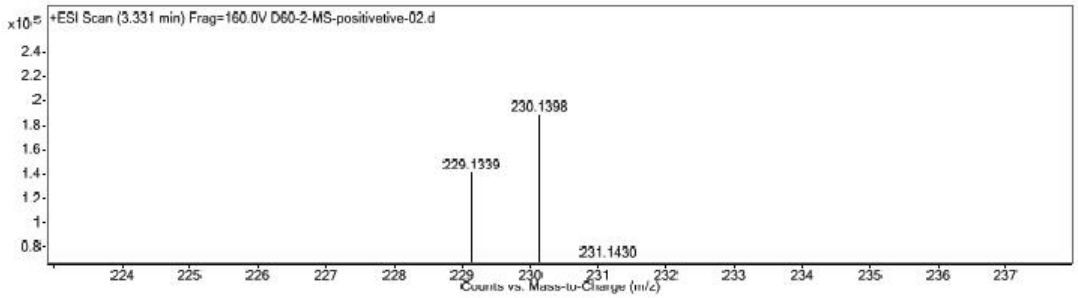
^{1}H NMR spectra of compound **5u**



^{13}C NMR spectra of compound **5u**



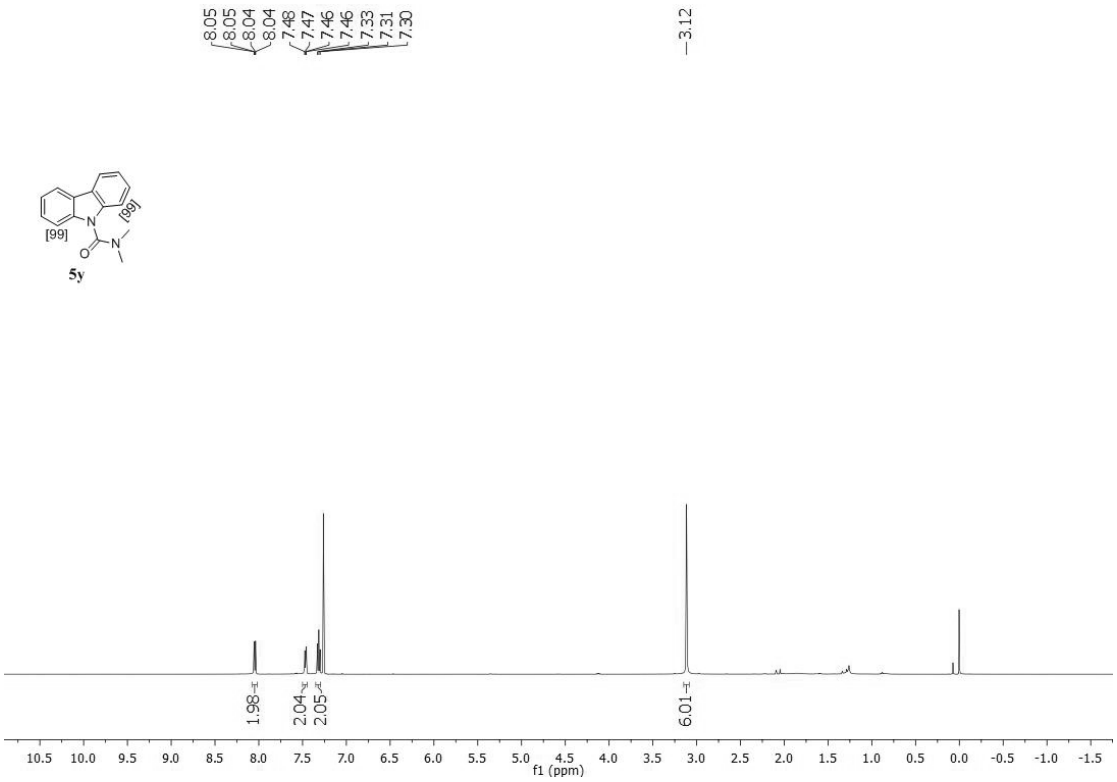
HRMS spectrum of compound **5u**



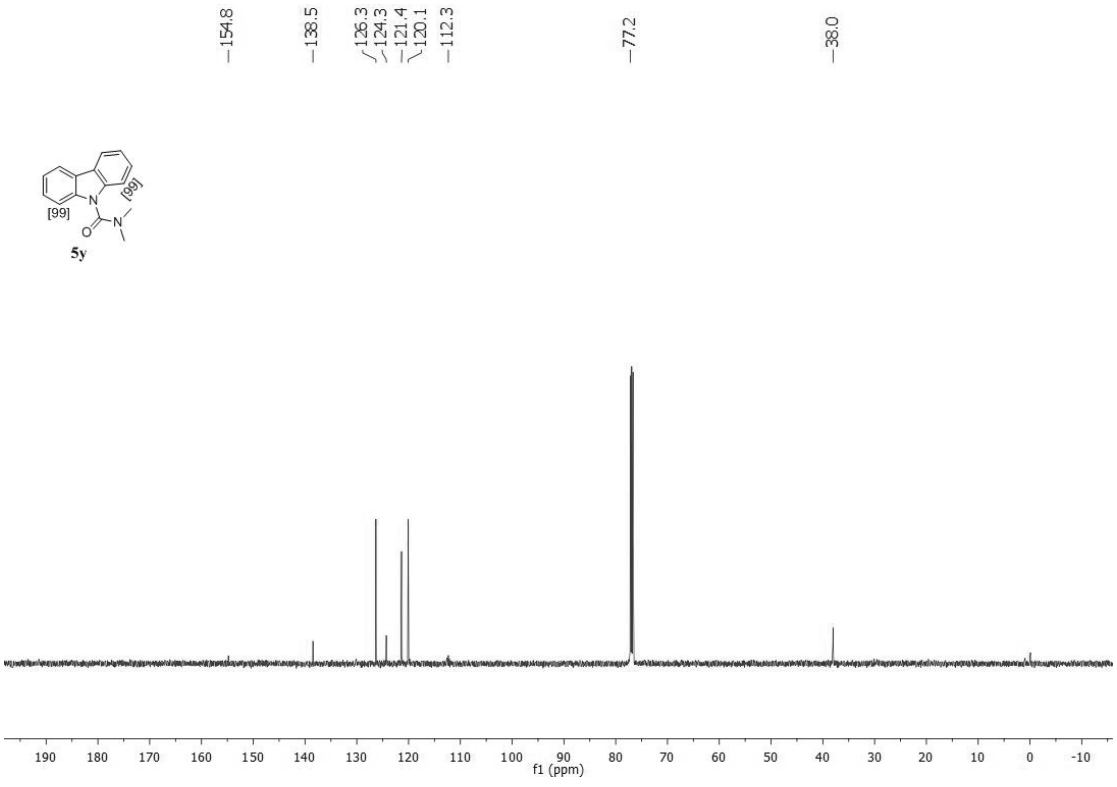
Elemental Composition Calculator

Target m/z:	230.1398	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5); D(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C14H16DN2O		230.1398		0.04	

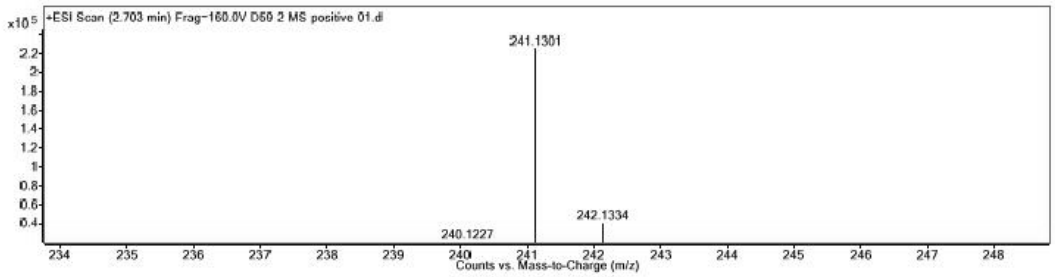
^{1}H NMR spectra of compound **5y**



^{13}C NMR spectra of compound **5y**



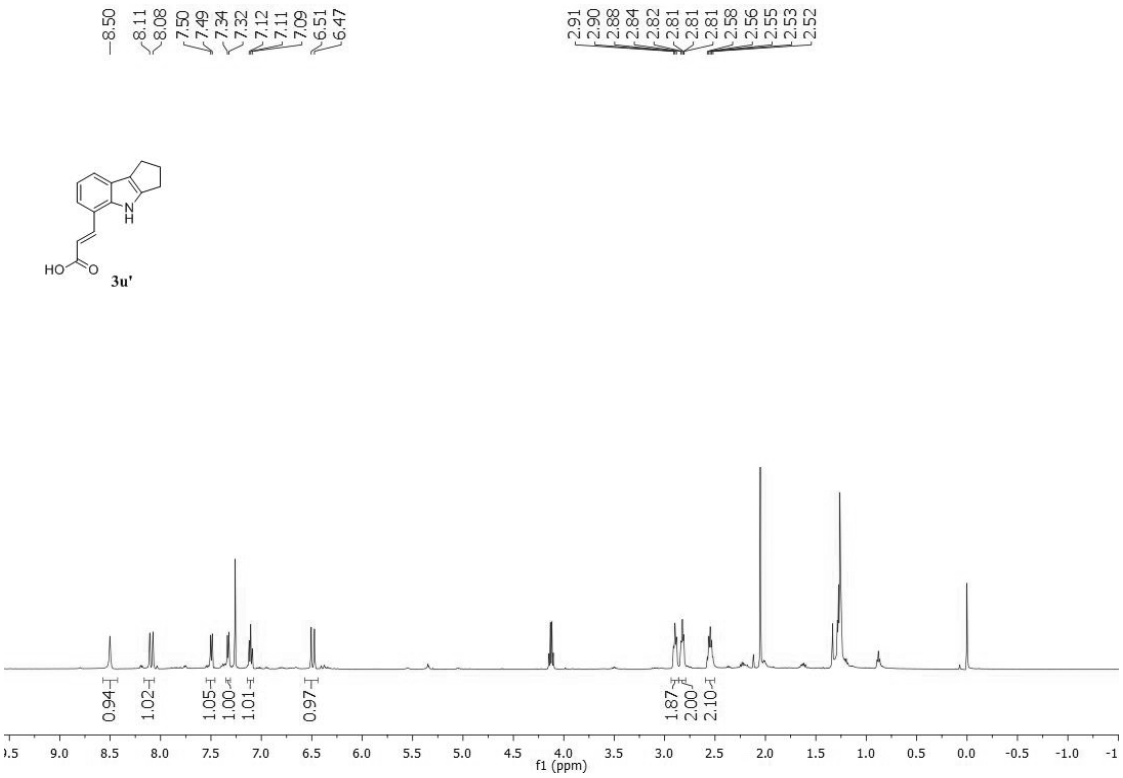
HRMS spectrum of compound **5y**



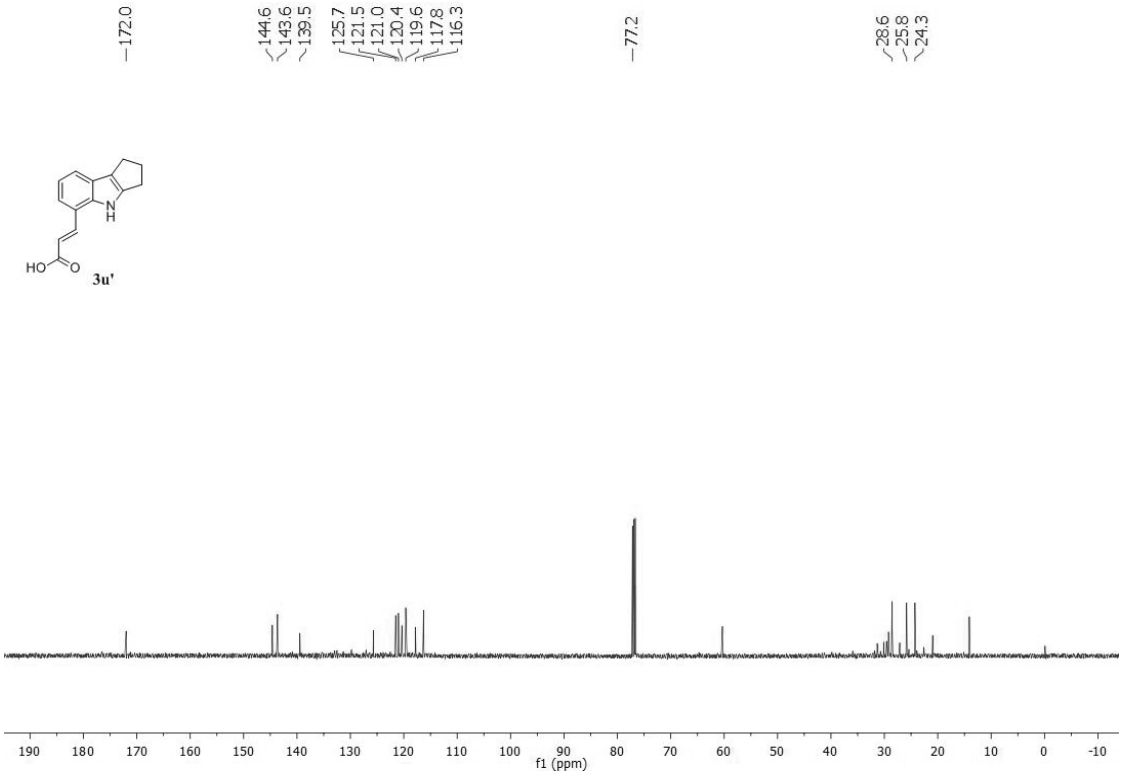
Elemental Composition Calculator

Target m/z:	241.1301	**Result type:**	Positive ions	**Species:**	$[M+H]^+$
Elements:		C (0-80); H (0-120); O (0-30) ; N(0-5) ; D(0-5)			
Ion Formula		**Calcalated m/z**		**PPM Error**	
C15H13D2N2O		241.1304		1..55	

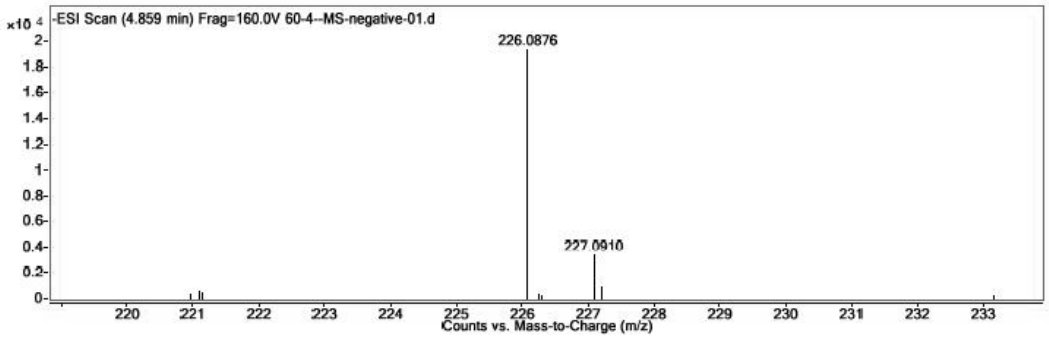
^{1}H NMR spectra of compound **3u'**



^{13}C NMR spectra of compound **3u'**



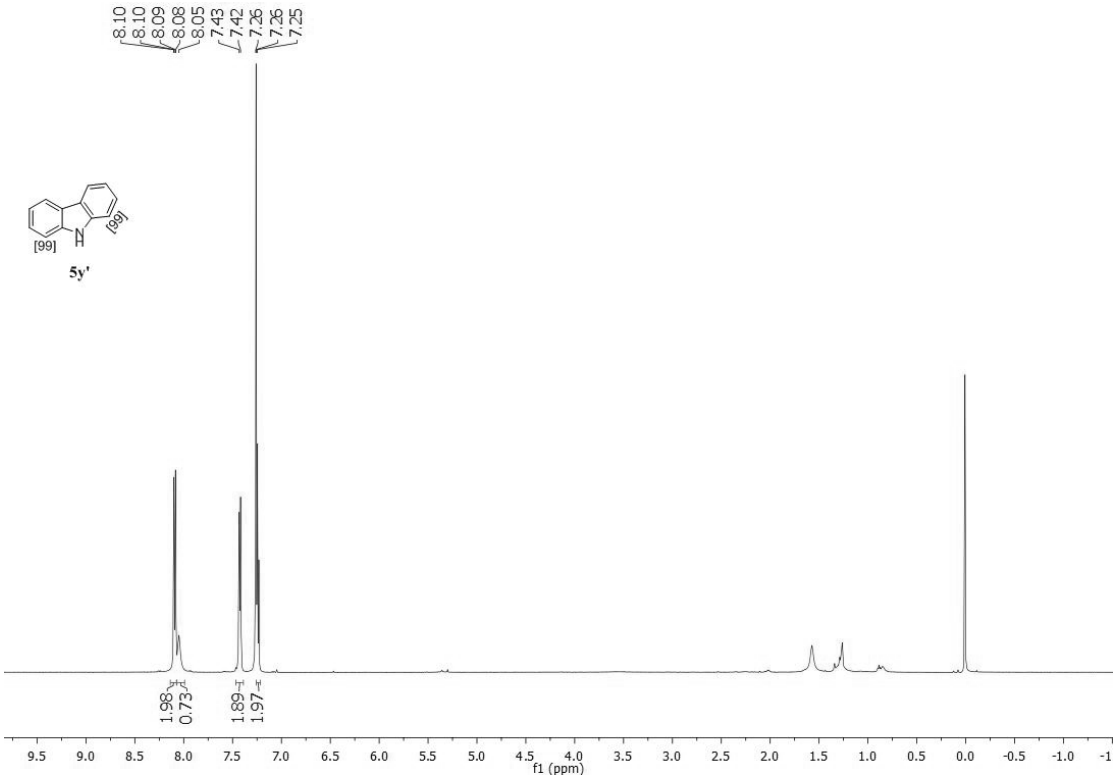
HRMS spectrum of compound **3u'**



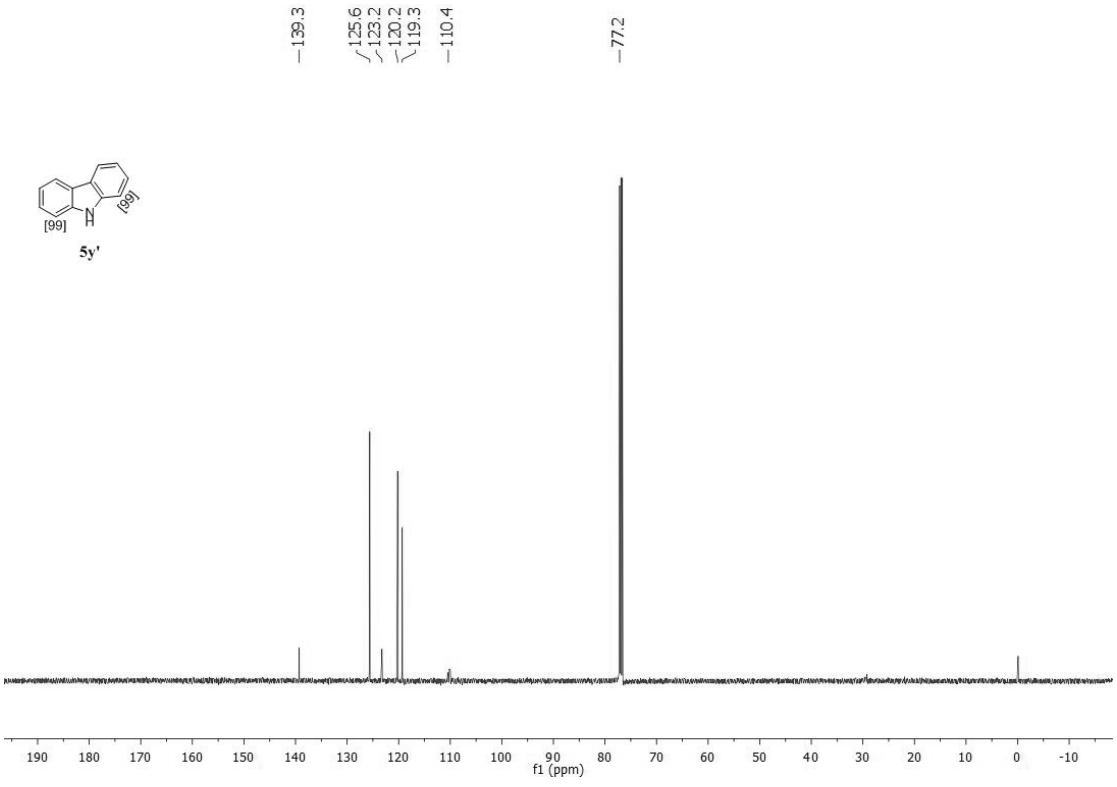
Elemental Composition Calculator

Target m/z:	226.0876	**Result type:**	Negative ions	**Species:**	$[M-H]^-$
Elements:		C (0-80); H (0-120); O (0-30); N(0-5)			
Ion Formula		**Calculated m/z**		**PPM Error**	
C14H12NO2		226.0874		-1.0	

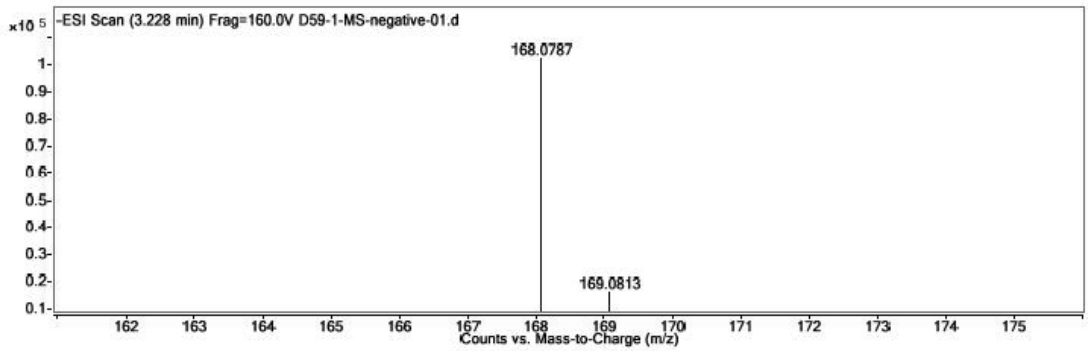
^{1}H NMR spectra of compound **5y'**



^{13}C NMR spectra of compound **5y'**



HRMS spectrum of compound **5y'**



Elemental Composition Calculator

Target m/z:	168.0787	**Result type:**	Negative ions	**Species:**	$[M-H]^-$
Elements:		C (0-80); H (0-120); O (0-30); N(0-5); D(0-5)			
Ion Formula		**Calculated m/z**		**PPM Error**	
C12H6D2N		168.0788		0.32	

4. X-ray Crystallographic Analysis of 3p

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC Number: 2025858.

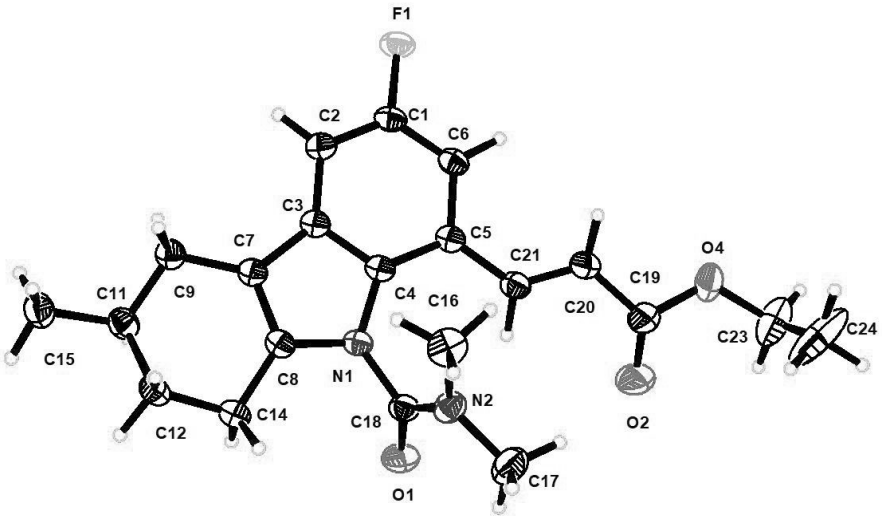


Table S6 Crystal data and structure refinement for **3p**.

Bond precision:	C-C = 0.0027 A		Wavelength=1.54178
Cell:	a = 10.4277 (3)	b = 8.5846 (2)	c= 22.3869 (5)
	alpha=90	beta=98.044 (1)	gamma=90
Temperature:	170 K		
	Calculated	Reported	
Volume	1984.31 (9)	1984.30 (9)	
Space group	P 21/n	P 1 21/n 1	
Hall group	-P 2yn	-P 2yn	
Moiety formula	C21H25FN2O3	C21H25FN2O3	
Sum formula	C21H25FN2O3	C21H25FN2O3	
Mr	372.43	372.43	
Dx,g cm^{-3}	1.247	1.247	
Z	4	4	
Mu (mm^{-1})	0.738	0.738	
F000	792.0	792.0	
F000’	794.53		
h,k,lmax	12, 9, 26	12, 9, 25	
Nref	3257	3203	
Tmin,Tmax	0.876, 0.915	0.647, 0.754	
Tmin’	0.869		

Correction method= # Reported T Limits: Tmin=0.647 Tmax=0.754
AbsCorr = MULTI-SCAN			

Data completeness = 0.983		Theta (max) = 63.675	
R (reflections) = 0.0483 (2738)		wR2 (reflections) = 0.1354 (3203)	
S = 1.040		Npar= 294	