Supporting Information for

Divergent Synthesis of Oxindolylidene Acetates and Spirooxindolopyrrolidones from Arynes

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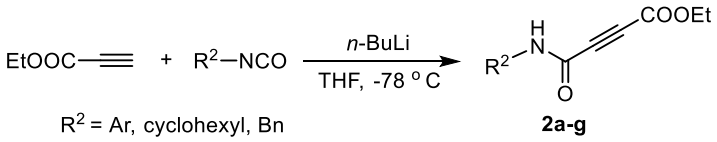
1. General Information:

All reagents and solvents were used as received from commercial sources unless and otherwise noted. THF and dimethoxy ethane (DME) was distilled over benzophenone-ketyl under an atmosphere of argon. All experiments were carried out under Argon atmosphere. *o*-Silyl aryl triflates **1** were synthesized by known procedure[1]. Carbamoylpropiolates **2** were easily prepared usning reported procedure[2]. Pre-coated plates (silica gel 60 PF254, 0.25 mm or 0.5 mm) were utilized for Thin Layer Chromatography (TLC). Column chromatographic purifications were carried out on flash silica-gel (240-400 mesh) using petroleum ether and ethyl acetate as eluents. The ^{1}H, ^{13}C, distortionless enhancement by polarization transfer (DEPT)-NMR spectra were recorded on 200/400/500 and 50/100/125 MHz NMR spectrometer respectively. Chemical shifts were reported as δ values from standard peaks. The multiplicities of signals are designated by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Coupling constants (*J*) are reported in hertz. All yields refer to isolated yields of compounds estimated to be > 95% pure as determined by ^{1}H-NMR. The dr ratios of the products **4a-d** were determined by ^{1}H NMR spectrum. High-resolution mass spectrometry (HRMS) was performed on a TOF/Q-TOF mass spectrometer.

Note: Few compounds contain grease peak, which could not be eliminated completely. The yields for those compounds are reduced accordingly.

2. Experimental Procedure:

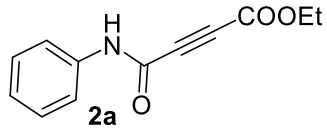
General procedure for the preparation of carbamoylpropiolates:[2]



Ethyl propiolate (1.0 equiv) was dissolved in THF and the solution was cooled to –78 ^{o}C, followed by the slow addition of *n*-BuLi (1.2 equiv, 1.5 M in hexane). The mixture was stirred for 30 min and a solution of the corresponding isocyanate (300 mg, 1.0 equiv) in THF was added drop-wise. The reaction mixture was then stirred for 2 h at –78 ^{o}C and acetic acid was added to quench the reaction. The reaction mixture was allowed to warm to room temperature, water was added and the aqueous layer was extracted three times with ethyl acetate. The combined organic extract was dried over anhydrous Na_2SO_4 and removal of solvent gave a residue that was subjected to flash column chromatography on silica-gel using ethyl acetate:petroleum ether (1:5) as eluent to afford the corresponding compounds.

Characterization data of carbamoylpropiolates:

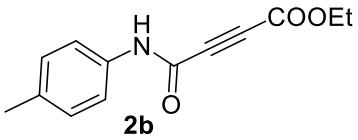
Ethyl 4-oxo-4-(phenylamino)but-2-ynoate (2a)



Reaction time: 2.0 h; R*f*: 0.5 (1:4, EtOAc:Pet. Ether); yellow oil; 294 mg, 54% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (bs, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.28 (t, *J* = 7.3 Hz, 2H), 7.10 (t, *J* = 7.3 Hz, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 1.27 (t, *J* = 7 Hz, 3H). Known compound[2]

Ethyl 4-oxo-4-(p-tolylamino)but-2-ynoate (2b)

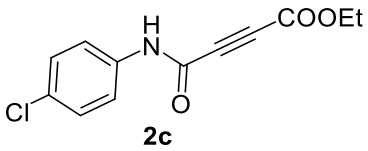


2b

Reaction time: 2.0 h; R*f*: 0.5 (1:4, EtOAc:Pet. Ether); yellow solid; mp 101–102 ^{o}C; 260 mg, 50% yield.

^{1}H NMR (200 MHz, $CDCl_3$) δ 7.60 (bs, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 2H), 4.24 (q, *J* = 7.2 Hz, 2H), 2.26 (s, 3H), 1.27 (t, *J* = 7 Hz, 3H). Known compound[2]

Ethyl 4-((4-chlorophenyl) amino)-4-oxobut-2-ynoate (2c)



2c

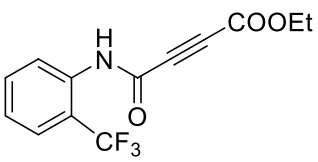
Reaction time: 2.0 h; R*f*: 0.5 (1:4, EtOAc:Pet. Ether); yellow solid; mp 106–108 ^{o}C; 226 mg, 46% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (bs, 1H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 4.24 (q, *J* = 7.3 Hz, 2H), 1.27 (t, *J* = 7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 148.2, 135.1, 130.7, 129.3, 121.3, 76.9, 74.8, 63.2, 13.9.

ESI HRMS: calcd for $C_{12}H_{10}NO_3Cl$ $[M+H]^+$: 252.0422, found: 252.0429.

Ethyl 4-oxo-4-((2-(trifluoromethyl)phenyl)amino)but-2-ynoate (2d)



2d

Reaction time: 2.0 h; R*f*: 0.5 (1:4, EtOAc:Pet. Ether); yellow solid; mp 116–118 ^{o}C; 243 mg,

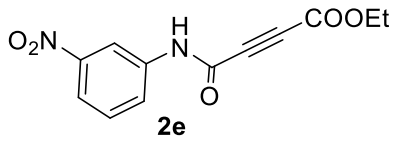
53% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 7.9 Hz, 1H), 7.69 (bs, 1H), 7.59 (d, J = 7.9 Hz, 1H), 7.52 (t, J = 7.9 Hz, 1H), 7.25 (t, J = 7.6 Hz, 1H), 4.26 (q, J = 7.3 Hz, 2H), 1.29 (t, J = 7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 151.9, 148.6, 133.3, 133.1, 126.3 (q, J^3 = 5.39 Hz), 125.9, 124.9, 123.1 (q, J^1 = 272.81 Hz), 122.3, 76.3, 75.3, 63.2, 13.9.

ESI HRMS: calcd for $C_{13}H_{10}NO_3F_3$ $[M+H]^+$: 286.0686 , found: 286.0680.

Ethyl 4-((3-nitrophenyl)amino)-4-oxobut-2-ynoate (2e)



2e

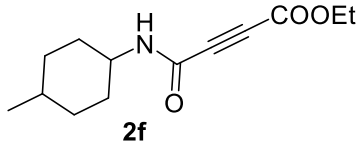
Reaction time: 2.0 h; R*f*: 0.5 (1:4, EtOAc:Pet. Ether); yellow solid; mp 99–101 ^oC; 168 mg, 35% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.35 (bs, 1H), 7.94 (t, J = 9.5 Hz, 2H), 7.47 (t, J = 8.2 Hz, 1H), 4.26 (q, J = 6.9 Hz, 2H), 1.28 (t, J = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 148.6, 148.5, 137.8, 130.2, 125.7, 120, 114.9, 76.5, 75.2, 63.5, 13.8.

ESI HRMS: calcd for $C_{12}H_{10}N_2O_5$ $[M+Na]^+$: 285.0482 , found: 285.0480.

Ethyl 4-((4-methylcyclohexyl)amino)-4-oxobut-2-ynoate (2f)



2f

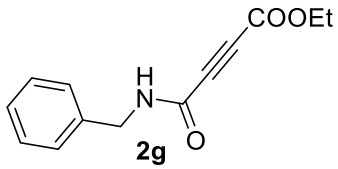
Reaction time: 2.0 h; R*f*: 0.5 (1:4, EtOAc:Pet. Ether); white solid; mp 96–98 ^oC; 245 mg, 48% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.93 (d, J = 5.4 Hz, 1H), 4.19 (q, J = 7.3 Hz, 2 H), 3.71–3.64 (m, 1H), 1.91–1.87 (m, 2H), 1.66–1.61 (m, 2H), 1.29–1.21 (m, 4H), 1.15–1.02 (m, 2H), 1.01–0.88 (m, 2H), 0.80 (d, J = 6.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 149.9, 77.4, 73.5, 62.8, 49.5, 33.5, 32.5, 31.7, 22, 13.9.

ESI HRMS: calcd for $C_{13}H_{19}NO_3$ $[M+H]^+$: 238.1438 , found: 238.1440.

Ethyl 4-((4-benzylphenyl) amino)-4-oxobut-2-ynoate (2g)



2g

Reaction time: 2.0 h; R*f*: 0.5 (1:4, EtOAc:Pet. Ether); thick oil; 224 mg, 43% yield.

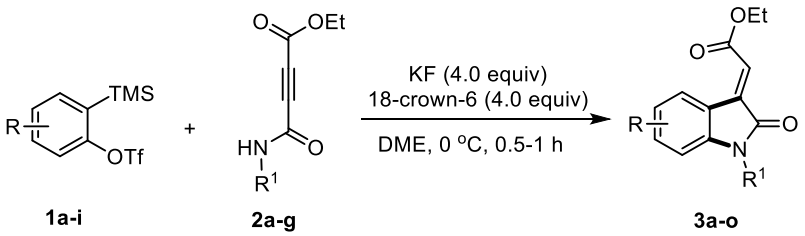
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29–7.23 (m, 3H), 7.20 (d, J = 7.3 Hz, 2H), 6.47 (bs, 1H), 4.41 (d, J = 6.1 Hz, 2H), 4.18 (q, J = 7.3 Hz, 2H), 1.23 (t, J = 7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 152.2, 150.6, 136.4, 128.8, 127.9, 127.2, 76.9, 74.2, 62.9, 44, 13.8.

ESI HRMS: calcd for $C_{13}H_{13}NO_3$ $[M+H]^+$: 232.0968, found: 232.0970.

General experimental procedure for the preparation of compounds 3a-i and 3j-o:

All the reactions were performed on 25 mg of carbamoylpropiolates.

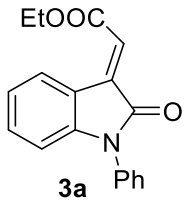


To a flame dried two-neck round-bottom flask containing KF (4.0 equiv) and 18-crown-6 ether (4.0 equiv), *o*-silyl aryl triflate **1** (3.0 equiv) in DME was added at room temperature. The solution was cooled to 0 ^{o}C and carbamoylpropiolate **2** (25 mg, 1.0 equiv) in DME was added drop-wise under argon atmosphere. The reaction mixture was stirred at 0 ^{o}C and the progress was monitored by TLC. After completion of the reaction, water was added. The aqueous layer was extracted with ethyl acetate. The combined organic extract was dried over anhydrous Na_2SO_4 and removal of solvent gave a residue that was subjected to flash column chromatography on silica-gel using ethyl acetate:petroleum ether to afford corresponding compounds.

Characterization data for oxindolylidene acetates:

All reactions were performed on 25 mg scale of carbamoylpropiolates.

Ethyl (E)-2-(2-oxo-1-phenylindolin-3-ylidene) acetate (3a)[3]



3a

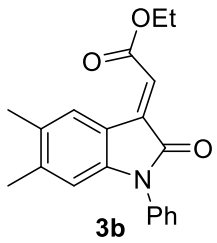
Reaction time: 0.5 h; R*f*: 0.5 (1:10, EtOAc:Pet. Ether); orange solid; mp 106–108 ^{o}C; 24.6 mg, 73% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 7.7 Hz, 1H), 7.51–7.43 (m, 2H), 7.38–7.32 (m, 3H), 7.27–7.24 (m, 1H), 7.07–7.00 (m, 1H), 6.94 (s, 1H), 6.72 (d, *J* = 7.96 Hz, 1H), 4.29 (q, *J* = 7 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167, 165.6, 145.9, 137.6, 133.9, 132.3, 129.7, 128.9, 128.3, 126.6, 123.3, 123.1, 119.9, 109.5, 61.2, 14.2.

LC-MS (M+H): 294. Known compound[3]

Ethyl (E)-2-(5,6-dimethyl-2-oxo-1-phenylindolin-3-ylidene)acetate (3b).



3b

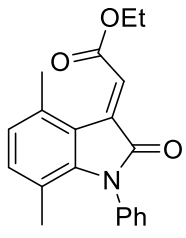
Reaction time: 0.5 h; R*f*: 0.4 (1:10, EtOAc:Pet. Ether); yellow solid; mp 118–119 ^oC; 22.5 mg, 61% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.48–7.44 (m, 2H), 7.36–7.32 (m, 3H), 6.84 (s, 1H), 6.51 (s, 1H), 4.28 (q, *J* = 7.32 Hz, 2H), 2.21 (s, 3H), 2.16 (s, 3H), 1.32 (t, *J* = 7 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 165.9, 144.3, 142, 138, 134.2, 131.3, 129.8, 129.6, 128.1, 126.6, 121.3, 117.6, 110.8, 61.1, 20.8, 19.5, 14.2.

ESI HRMS: calcd for $C_{20}H_{19}NO_3$ $[M+H]^+$: 322.1438, found: 322.1440.

Ethyl (E)-2-(4,7-dimethyl-2-oxo-1-phenylindolin-3-ylidene)acetate (3c)



3c

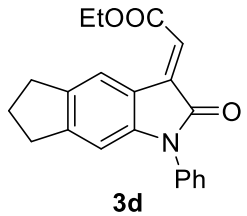
Reaction time: 1 h; R*f*: 0.5 (1:10, EtOAc:Pet. Ether); yellow solid; mp 130–131 ^oC; 21.4 mg, 58% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.34 (m, 3H), 7.24 (d, *J* = 7.3 Hz, 2H), 6.85 (d, *J* = 7.9 Hz, 1H), 6.76 (s, 1H), 6.71 (d, *J* = 7.9 Hz, 1H), 4.29 (q, *J* = 7.3 Hz, 2H), 2.40 (s, 3H), 1.57 (s, 3H), 1.28 (t, *J* = 7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167, 166.2, 141.9, 136.4, 134.3, 133.3, 132.3, 129.2, 128.7, 128.6, 125.8, 125.3, 119.2, 118.5, 61.8, 20.5, 18.6, 14.

ESI HRMS: calcd for $C_{20}H_{19}NO_3$ $[M+H]^+$: 322.1438, found: 322.1441.

Ethyl (E)-2-(2-oxo-1-phenyl-1,5,6,7-tetrahydrocyclopenta[f]indol-3(2H)-ylidene) acetate (3d)



3d

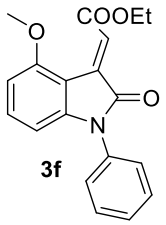
Reaction time: 1 h; R*f*: 0.5 (1:10, EtOAc:Pet. Ether); yellow solid; mp 188–190 ^oC; 17.6 mg, 46% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.48–7.44 (m, 2H), 7.36–7.32 (m, 3H), 6.85 (s, 1H), 6.58 (s, 1H), 4.27 (q, *J* = 6.9 Hz, 2H), 2.86–2.75 (m, 4H), 2.01 (quint, *J* = 7.3 Hz, 2H), 1.31 (t, *J* = 7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 166, 149.7, 145.1, 139, 138.2, 134.2, 129.7, 128.1, 126.7, 124.8, 121.2, 118.3, 106, 61, 33.7, 32.3, 25.4, 14.2.

ESI HRMS: calcd for $C_{21}H_{19}NO_3$ $[M+H]^+$: 334.1438, found: 334.1441.

Ethyl (E)-2-(4-methoxy-2-oxo-1-phenylindolin-3-ylidene) acetate (3f)



3f

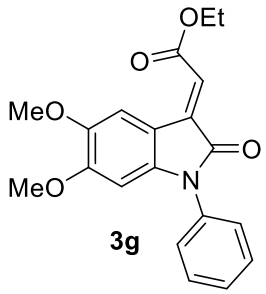
Reaction time: 1 h; R*f*: 0.4 (1:10, EtOAc:Pet. Ether); thick oil; 16.7 mg, 45% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.42 (m, 2H), 7.35–7.31 (m, 3H), 7.15 (t, *J* = 8.2 Hz, 1H), 6.99 (s, 1H), 6.53 (d, *J* = 8.5 Hz, 1H), 6.35 (d, *J* = 7.9 Hz, 1H), 4.30 (q, *J* = 7.3 Hz, 2H), 3.82 (s, 3H), 1.31 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 167.1, 156.6, 145.9, 134.2, 132.5, 129.6, 128.9, 128.2, 126.7, 123.9, 107.9, 106.1, 102.8, 61, 55.6, 14.2.

ESI HRMS: calcd for $C_{19}H_{17}NO_4$ $[M+H]^+$: 324.1230, found: 324.1231.

Ethyl (E)-2-(5,6-dimethoxy-2-oxo-1-phenylindolin-3-ylidene)acetate (3g)



3g

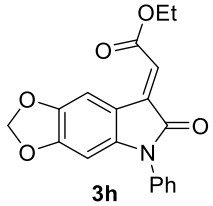
Reaction time: 1 h; R*f*: 0.4 (1: 9, EtOAc:Pet.Ether); yellow solid; mp 118–119 ^oC; 20.7 mg, 51% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.49–7.45 (m, 2H), 7.37–7.33 (m, 3H), 6.76 (s, 1H), 6.28 (s, 1H), 4.26 (q, *J* = 6.7 Hz, 2H), 3.88 (s, 3H), 3.75 (s, 3H), 1.31 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 166.2, 153, 144.9, 141.8, 138, 134.1, 129.8, 128.2, 126.5, 119.6, 112.6, 111.4, 94.2, 61, 56.5, 56.2, 14.2.

ESI HRMS: calcd for $C_{20}H_{19}NO_5$ $[M+H]^+$: 354.1336, found: 354.1338.

Ethyl(E)-2-(6-oxo-5-phenyl-5,6-dihydro-7H-[1,3]dioxolo[4,5-f]indol-7-ylidene)acetate (3h)



3h

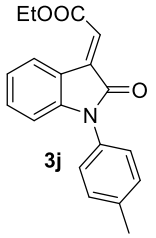
Reaction time: 0.5 h; R*f*: 0.2 (1:9, EtOAc:Pet. Ether); Red solid; mp 166–168 ^oC; 27.2 mg, 70% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.47–7.43 (m, 2H), 7.36 –7.29 (m, 3H), 6.76 (s, 1H), 6.27 (s, 1H), 5.90 (s, 2H), 4.25 (q, *J* = 7.3 Hz, 2H), 1.30 (t, *J* = 7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 166, 151.1, 143.6, 143.1, 137.7, 133.9, 129.7, 128.3, 126.6, 120, 112.4, 109.3, 101.7, 92.8, 61.1, 14.2.

ESI HRMS: calcd for $C_{19}H_{15}NO_5$ $[M+H]^+$: 338.1023, found: 338.1026.

Ethyl (E)-2-(2-oxo-1-(p-tolyl)indolin-3-ylidene)acetate (3j)



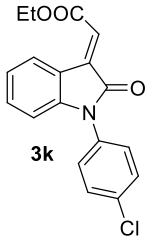
Reaction time: 0.5 h; R*f*: 0.5 (1:9, EtOAc:Pet. Ether); yellow solid; mp 100–102 ^oC; 20.1 mg, 57% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 7.9 Hz, 1H), 7.26–7.23 (m, 2H), 7.21–7.18 (m, 3H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.92 (s, 1H), 6.68 (d, *J* = 7.9 Hz, 1H), 4.28 (q, *J* = 6.9 Hz, 2H), 2.35 (s, 3H), 1.31 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167, 165.7, 146.2, 138.3, 137.7, 132.3, 131.2, 130.3, 128.9, 126.4, 123.1, 122.9, 119.8, 109.4, 61.2, 21.2, 14.2.

ESI HRMS: Calcd for $C_{19}H_{17}NO_3$ $[M+H]^+$: 308.1281, found: 308.1275.

Ethyl (E)-2-(1-(4-chlorophenyl)-2-oxoindolin-3-ylidene) acetate (3k)



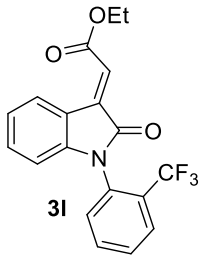
Reaction time: 0.5 h; R*f*: 0.4 (1:9, EtOAc:Pet. Ether); yellow solid; mp 139–140 ^oC; 20.3 mg, 54% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 7.9 Hz, 1H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.93 (s, 1H), 6.71 (d, *J* = 7.9 Hz, 1H), 4.29 (q, *J* = 6.8 Hz, 2H), 1.32 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 165.5, 145.4, 137.3, 134, 132.5, 132.4, 129.9, 129.1, 127.9, 123.5, 123.4, 119.9, 109.3, 61.3, 14.2.

ESI HRMS: calcd for $C_{18}H_{14}NClO_3$ $[M+ Na]^+$: 350.0554, found: 350.0554.

Ethyl (E)-2-(2-oxo-1-(2-(trifluoromethyl)phenyl)indolin-3-ylidene)acetate (3l)



3l

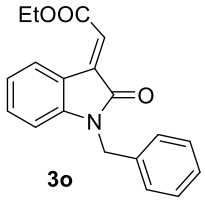
Reaction time: 0.5 h; R*f*: 0.5 (1:9, EtOAc:Pet. Ether); yellow solid; mp 116–118 ^oC; 24.9 mg, 60% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 7.3 Hz, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.70– 7.66 (m, 1H), 7.60–7.56 (m, 1H), 7.32 (d, *J* = 7.3 Hz, 1H), 7.22–7.19 (m, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.92 (s, 1H)), 6.27 (d, *J* = 7.9 Hz, 1H), 4.29 (q, *J* = 7 Hz, 2H), 1.32 (t, *J* = 7 Hz, 3H).

^{13}C NMR (400 MHz, $CDCl_3$) δ 167.5, 165.6, 146.7, 137.2, 133.8, 132.4, 131.3, 130 (q, J^2 = 31.4 Hz), 129.9, 129.4, 128.8, 128 (q, J^3 = 4.7 Hz), 123.4, 123.3, 122.8 (q, J^1 = 273.4 Hz), 119.8, 109.6, 61.3, 14.2.

ESI HRMS m/z: calcd for $C_{19}H_{14}NO_3F_3$ $[M+H]^+$: 362.0999, found: 362.0991

Ethyl (E)-2-(1-benzyl-2-oxoindolin-3-ylidene) acetate (3o).[3]



3o

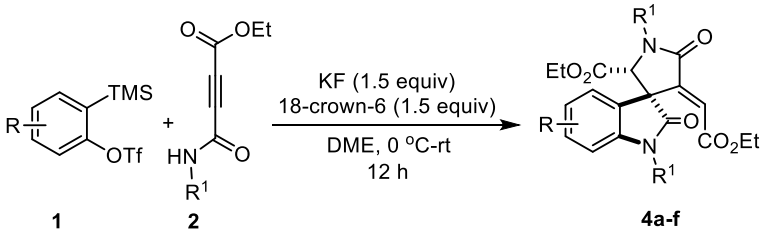
Reaction time: 1 h; R*f*: 0.4 (1:9, EtOAc: Pet. Ether); thick oil; 16.2 mg, 46% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 7.9 Hz, 1H), 7.26–7.17 (m, 6H), 6.96 (t, J = 7.6 Hz, 1H), 6.91 (s, 1H), 6.62 (d, J = 7.9 Hz, 1H), 4.87 (s, 2H), 4.27 (q, J = 7.5 Hz, 2H), 1.31 (t, J = 7.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 165.7, 145.1, 137.7, 135.4, 132.3, 128.8, 127.7, 127.2, 122.9, 122.8, 122.2, 120, 109.1, 61.2, 43.9, 14.2.

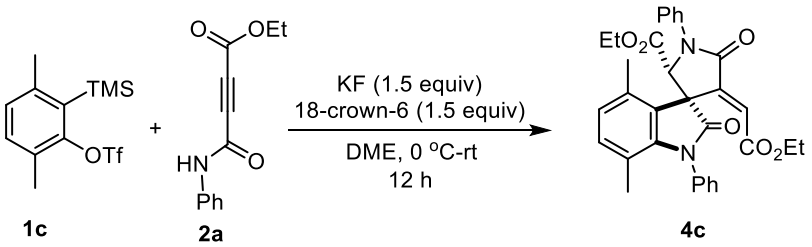
ESI HRMS: calcd for $C_{19}H_{17}NO_3$ $[M+ H]^+$: 308.1281, found: 308.1275.

General experimental procedure for the synthesis of spirooxindolopyrrolidones 4a-f:



To a flame dried two-neck round-bottom flask containing KF (1.5 equiv) and 18-crown-6 ether (1.5 equiv), *o*-silyl aryl triflate **1** (1.0 equiv) in DME (0.5 mL) was added at room temperature. The solution was cooled to 0 ^{o}C and carbamoylpropiolate **2** (25 mg, 3.0 equiv) in DME (0.5 mL) was added drop-wise under argon atmosphere. The reaction mixture was allowed to attain room temperature and stirred until 12 h. The progress of the reaction was monitored by TLC. After completion of the reaction, solvent was removed on rotary evaporator and the crude product was purified by flash silica gel column using a gradient of ethyl acetate:petroleum to afford corresponding products **4a-f** in good yields.

Representative experimental procedure at 1 mmol scale for the synthesis of the compound 4c:

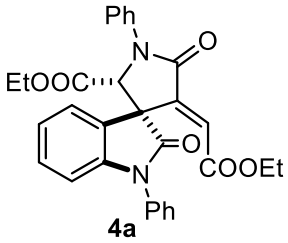


To a flame dried two-neck round-bottom flask containing KF (87 mg, 1.5 mmol, 1.5 equiv) and 18-crown-6 ether (396 mg, 1.5 mmol, 1.5 equiv), *o*-silyl aryl triflate **1c** (326 mg, 1 mmol, 1.0 equiv) in DME (10 mL) was added at room temperature. The solution was cooled to 0 ^{o}C and carbamoylpropiolate **2a** (651 mg, 3.0 mmol, 3.0 equiv) in DME (10 mL) was added drop-wise under argon atmosphere. The reaction mixture was allowed to attain room

temperature and stirred until 12 h. The progress of the reaction was monitored by TLC. After completion of the reaction, solvent was removed on rotary evaporator and the crude product was purified by flash silica gel column using a gradient of ethyl acetate:petroleum (1:10) to afford the corresponding product **4c** in 37% (200 mg) yield.

Characterization data of spirooxindolopyrrolidones:

Ethyl (E)-4'-(2-ethoxy-2-oxoethylidene)-2,5'-dioxo-1,1'-diphenylspiro[indoline-3,3'-pyrrolidine]-2'-carboxylate (4a).



4a

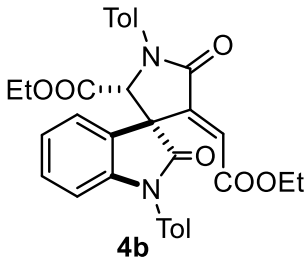
Reaction time: 12 h; R*f*: 0.5 (1:4, EtOAc: Pet. Ether); yellow thick oil; 10.2 mg, 52%; dr 20:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53–7.48 (m, 6H), 7.41–7.40 (m, 1H), 7.36 (t, *J* = 8 Hz, 2H), 7.22–7.19 (m, 1H), 7.15 (t, *J* = 7.7 Hz, 1H), 7.02 (d, *J* = 7.4 Hz, 1H), 6.95 (s, 1H), 6.92 (t, *J* = 7.7 Hz, 1H), 6.71 (d, *J* = 8 Hz, 1H), 5.30 (s, 1H), 4.0–3.89 (m, 2H), 3.68–3.61 (m, 1H), 3.52–3.47 (m, 1H), 1.07 (t, *J* = 7. 1 Hz, 3H), 0.74 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 174.1, 166.5, 164.8, 163.8, 145.9, 145.8, 137.5, 134.5, 129.7, 129.4, 129.1, 128.5, 127.1, 126.7, 126.4, 124.5, 124.3, 122.9, 122.5, 109, 68, 61.7, 61.1, 53.9, 13.9, 13.5.

ESI HRMS: calcd for $C_{30}H_{26}N_2O_6$ $[M+H]^+$: 511.1864, found: 511.1857.

Ethyl (E)-4'-(2-ethoxy-2-oxoethylidene)-2,5'-dioxo-1,1'-di-p-tolylspiro[indoline-3,3'-pyrrolidine]-2'-carboxylate (4b).



4b

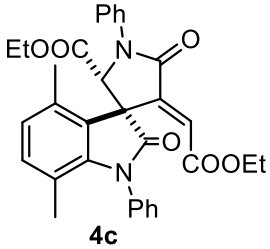
Reaction time: 12 h; R*f*: 0.5 (1:4, EtOAc:Pet. Ether); thick oil; 8.1 mg, 42%; dr 17:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.35 (m, 4H), 7.30 (d, *J* = 8 Hz, 2H), 7.16–7.11 (m, 4H), 7.0 (d, *J* = 7.6 Hz, 1H), 6.93 (s, 1H), 6.68 (d, *J* = 8 Hz, 1H) 5.26 (s, 1H), 4.0–3.86 (m, 2H), 3.67–3.60 (m, 1H), 3.52–3.44 (m, 1H), 2.38 (s, 3H), 2.28 (s, 3H), 1.06 (t, *J* = 7 Hz, 3H), 0.74 (t, *J* = 7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 166.6, 164.8, 163.8, 146.1, 145.9, 138.5, 136.7, 134.9, 131.8, 130.3, 129.7, 129.5, 129.3, 127.6, 126.9, 126.4, 124.3, 122.7, 122.6, 113, 109, 68, 61.6, 61, 53.9, 21.3, 21, 13.8, 13.5.

ESI HRMS: calcd for $C_{32}H_{30}N_2O_6$ $[M+H]^+$: 539.2177, found: 539.2179.

Ethyl (E)-4'-(2-ethoxy-2-oxoethylidene)-4,7-dimethyl-2,5'-dioxo 1,1'diphenylspiro [indoline-3,3'-pyrrolidine]-2'-carboxylate (4c).



4c

Reaction time: 12 h; R*f*: 0.5 (1:4, EtOAc: Pet. Ether); mp 91–93 ^{o}C; 7.2 mg, 35%; dr 7:1.

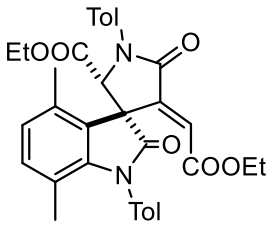
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.7 Hz, 1H), 7.54 (d, *J* =7.6 Hz, 1H), 7.43–7.39 (m, 3H), 7.38–7.33 (m, 2H), 7.32 –7.28 (m, 1H), 7.21–7.18 (m, 2H), 7.01 (s, 1H), 6.84 (d, *J* =

8 Hz, 1H), 6.66 (d, *J* = 7.6 Hz, 1H), 4.94 (s, 1H), 4.07–3.93 (m, 4H), 2.06 (s, 3H), 1.62 (s, 3H), 1.12 (t, *J* = 7 Hz, 3H), 1.0 (t, *J* = 7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 168.1, 165.1, 163.9, 145.7, 142.2, 137.4, 137.1, 132.7, 130.3, 129.5, 129.2, 129.1, 128.9, 128.8, 126.5, 125.5, 125.2, 121.5, 118.2, 68.6, 62.5, 61, 54.7, 18.7, 18.4, 13.9, 13.7.

ESI HRMS: calcd for $C_{32}H_{30}N_2O_6$ $[M+H]^+$: 539.2177, found: 539.2177.

Ethyl (E)-4'-(2-ethoxy-2-oxoethylidene)-4,7-dimethyl-2,5'-dioxo-1,1'-di-p-tolylspiro [indoline-3,3'-pyrrolidine]-2'-carboxylate (4d).



4d

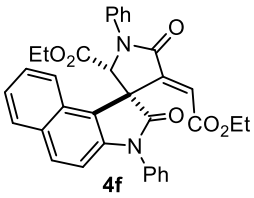
Reaction time: 12 h; R*f*: 0.5 (1:4 EtOAc: Pet. Ether); thick oil; 6.6 mg, 32%; dr 7:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.48 (m, 1H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.26–7.20 (m, 1H), 7.18–7.13 (m, 4H), 6.99 (s, 1H), 6.83 (d, *J* = 7.9 Hz, 1H), 6.66 (d, *J* = 7.9 Hz, 1H), 4.89 (s, 1H), 4.06–3.94 (m, 4H), 2.35 (s, 3H), 2.28 (s, 3H), 2.05 (s, 3H), 1.64 (s, 3H), 1.11 (t, *J* = 7 Hz, 3H), 1.02 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 168.2, 165.1, 163.9, 145.9, 142.3, 138.7, 136.4, 134.8, 134.4, 132.6, 130.3, 130.3, 129.9, 129.8, 129.7, 129.5, 129.2, 128.8, 125.3, 124.9, 121.5, 118.1, 68.7, 62.4, 60.9, 54.7, 21.3, 21, 18.7, 18.3, 13.9, 13.8.

ESI HRMS: calcd for $C_{34}H_{34}N_2O_6$ $[M+H]^+$: 567.2490, found: 567.2491.

Ethyl (1R,E)-4'-(2-ethoxy-2-oxoethylidene)-2,5'-dioxo-1',3-diphenyl-2,3-dihydrospiro [benzo[e]indole-1,3'-pyrrolidine]-2'-carboxylate (4f).



4f

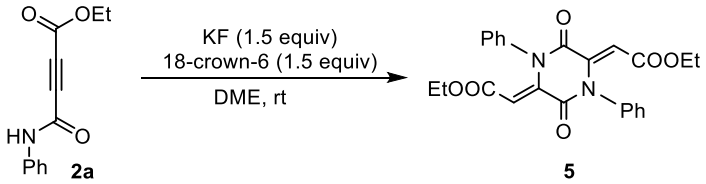
Reaction time: 12 h; R*f*: 0.5 (1:4, EtOAc:Pet. Ether); thick oil; 7.9 mg, 37%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.75 (m, 2 H), 7.72–7.67 (m, 1H), 7.58–7.49 (m, 10H), 7.40–7.33 (m, 7H), 7.31–7.26 (m, 2H), 7.23 (d, *J* = 7.3 Hz, 1H), 7.08 (s, 1H), 7.07–7.04 (m, 1H), 7.01 (d, *J* = 6.1 Hz, 1H), 5.14 (s, 1H), 4.04–3.91 (m, 4H), 3.87–3.76 (m, 1H), 3.55–3.47 (m, 1H), 3.23–3.17 (m, 1H), 1.04–0.94 (m, 6H), 0.50 (t, *J* = 7.0 Hz, 1H), 0.39 (t, *J* = 7.0 Hz, 1H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 167.8, 165.2, 163.7, 146.2, 143.3, 137.4, 134.5, 131.1, 130.7, 130.4, 130.1, 129.8, 129.7, 129.2, 129.1. 128.6, 128.4, 127.5, 127.2, 126.9, 127.3, 127.2, 126.9, 125.7, 123.9, 122.9, 122.5, 121.1, 110.8, 68.7, 68.4, 62.4, 60.9, 55.3, 13.8, 13.7.

ESI HRMS: calcd for $C_{34}H_{28}N_2O_6$ $[M+H]^+$: 561.2020, found: 561.2014.

Dimerization product 5 from carbamoylpropiolate 2a:



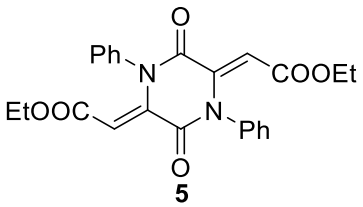
2a **5**

To a flame dried two-neck round-bottom flask containing KF (10.0 mg, 1.5 equiv) and 18-crown-6 ether (45 mg, 1.5 equiv), carbamoylpropiolate **2a** (25 mg, 1.0 equiv) in DME was added drop-wise under argon atmosphere at room temperature. The reaction mixture was allowed to stir at room temperature for 30 minutes. After complete consumption of **2a**, the

solvent was removed on rotary evaporator and the crude product was purified by flash silica gel column using a gradient of ethyl acetate:petroleum to afford compound **5** in 25% yield.

Characterization of dimer 5:

Diethyl 2,2'-(3,6-dioxo-1,4-diphenylpiperazine-2,5-diylidene)(2Z,2'Z)-diacetate



5

R*f*: 0.2 (1:4, EtOAc:Pet. Ether); thick oil; 12.5 mg, 25%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 –7.49 (m, 2H), 7.46–7.42 (m, 1H), 7.40–7.35 (m, 2H), 7.32–7.26 (m, 3H), 7.25–7.22 (m, 2H), 6.52 (s, 1H), 5.30 (s, 1H), 4.14 (q, *J* = 7 Hz, 2H), 3.48 (q, *J* = 7.2 Hz, 2H), 1.19 (t, *J* = 7.2 Hz, 3H), 0.97 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 164, 157.1, 155.3, 136.7, 136, 135.7, 135, 130.5, 129.7, 128.9, 128.7, 128.2, 128, 114.6, 112.4, 61.6, 61.1, 13.8, 13.7.

ESI HRMS: calcd for $C_{24}H_{22}N_2O_6$ $[M+ Na]^+$: 457.1370, found: 457.1367.

3. References:

(1) (a) Sato, Y.; Tamura, T.; Kinbara, A.; Morib, M. *Adv. Synth. Catal*. **2007**, *349*, 647.

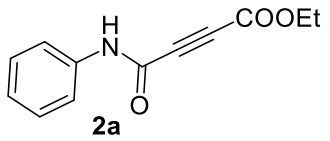
(b) Peña, D.; Cobas, A.; Pérez, D.; Guitián, E. *Synthesis* **2002**, *10*, 1454.

(2) Katritzky, A. R.; Zhang, Y.; Singh, S. K.; Steel, P. J. *ARKIVOC* **2003**, *xv*, 47.

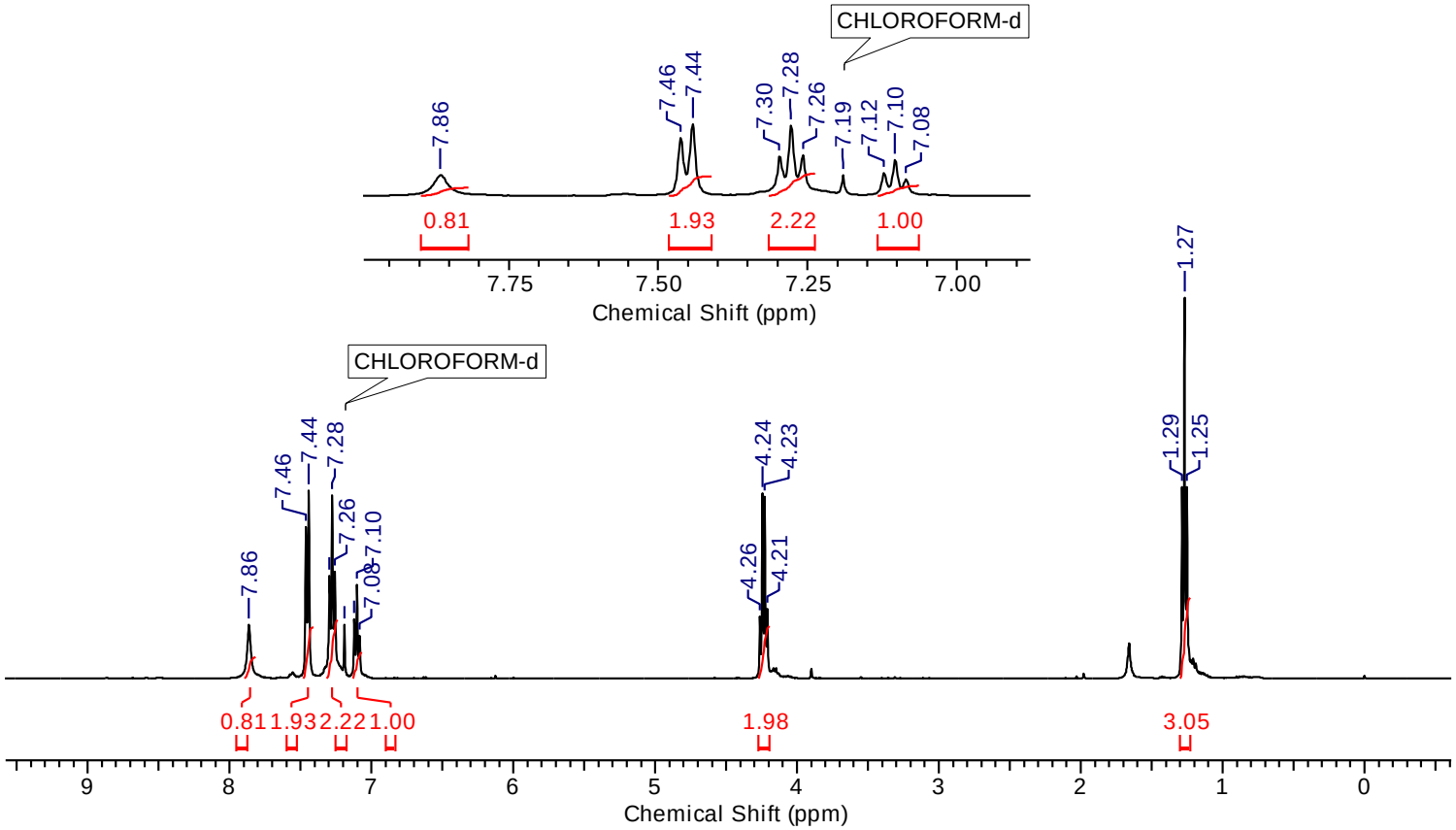
(3) Palumbo, C.; Mazzeo, G.; Mazziotta, A.; Gambacorta, A.; Loreto, M. A.; Migliorini, A.; Superchi, S.; Tofani, D.; Gasperi, T. *Org. Lett.* **2011**, *13*, 6248.

4. Copies of ^{1}H, ^{13}C and HRMS:

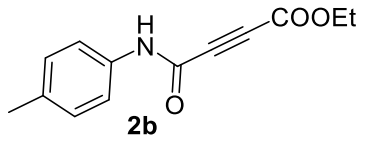
^{1}H NMR 400 MHz



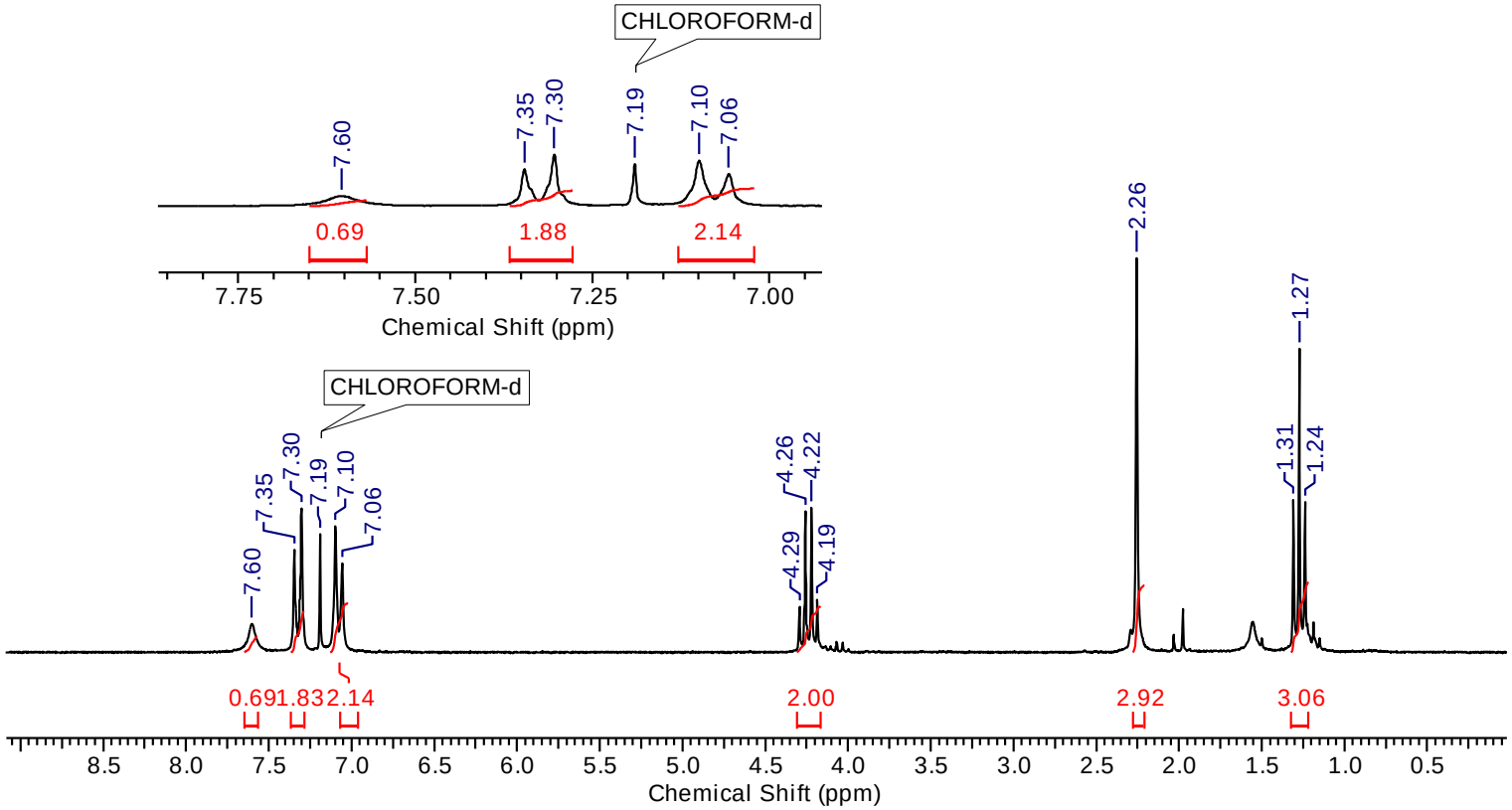
2a



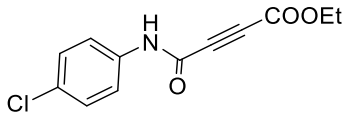
^{1}H NMR 200 MHz



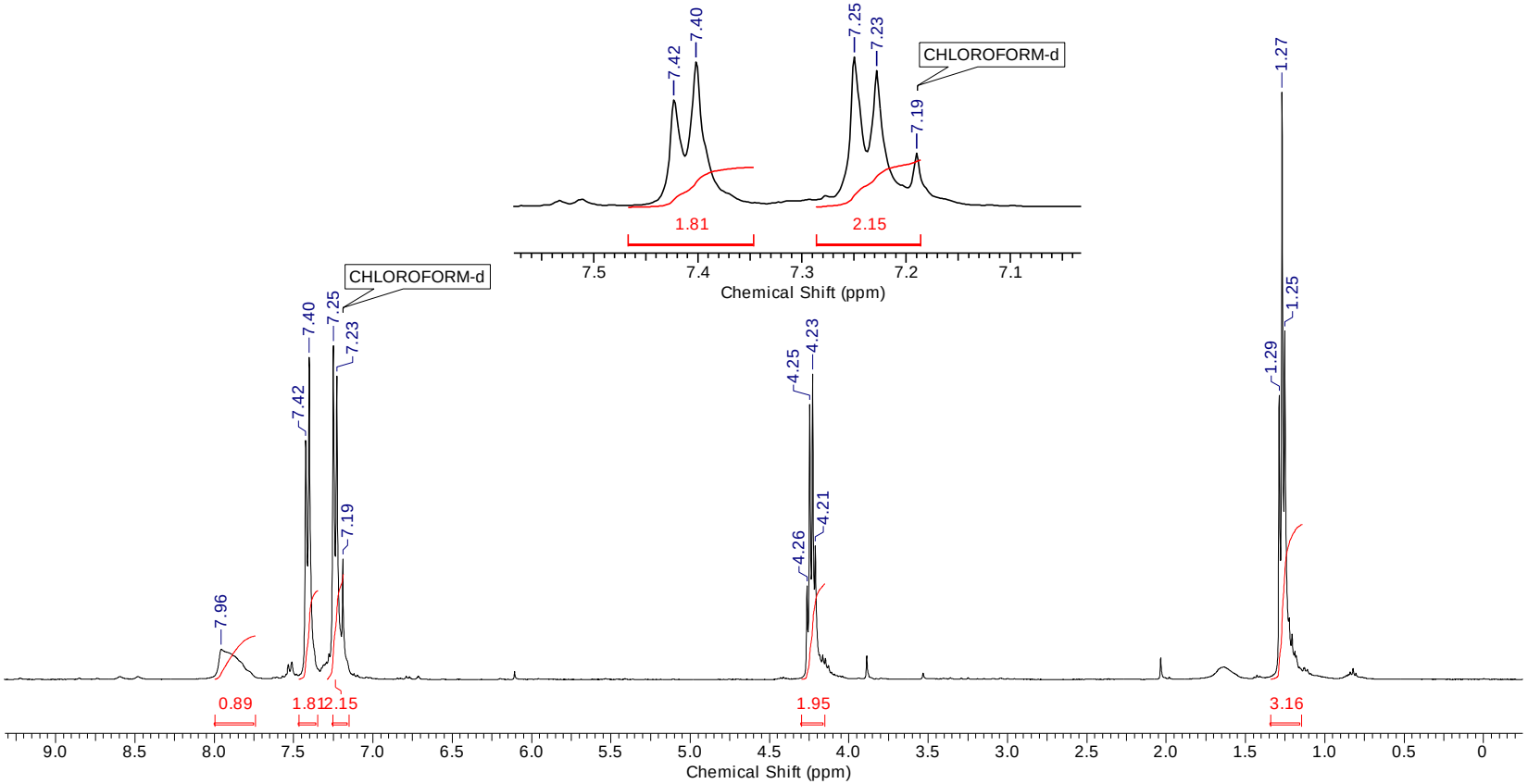
2b



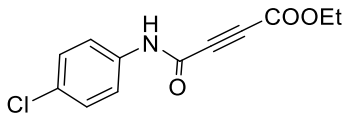
^{1}H NMR 400 MHz



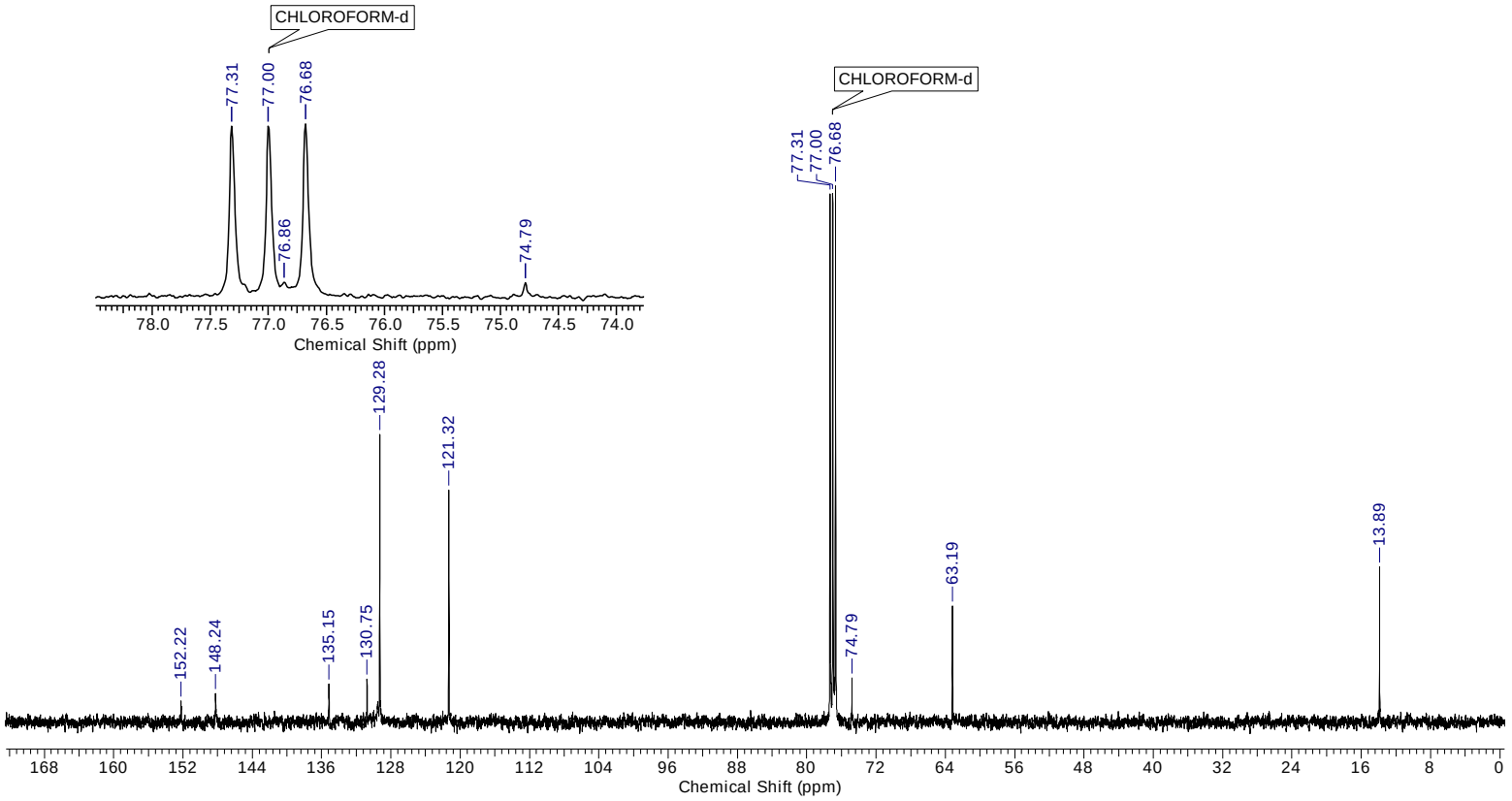
2c



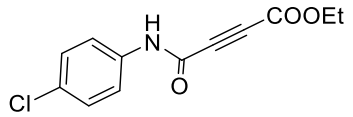
^{13}C NMR 100MHz



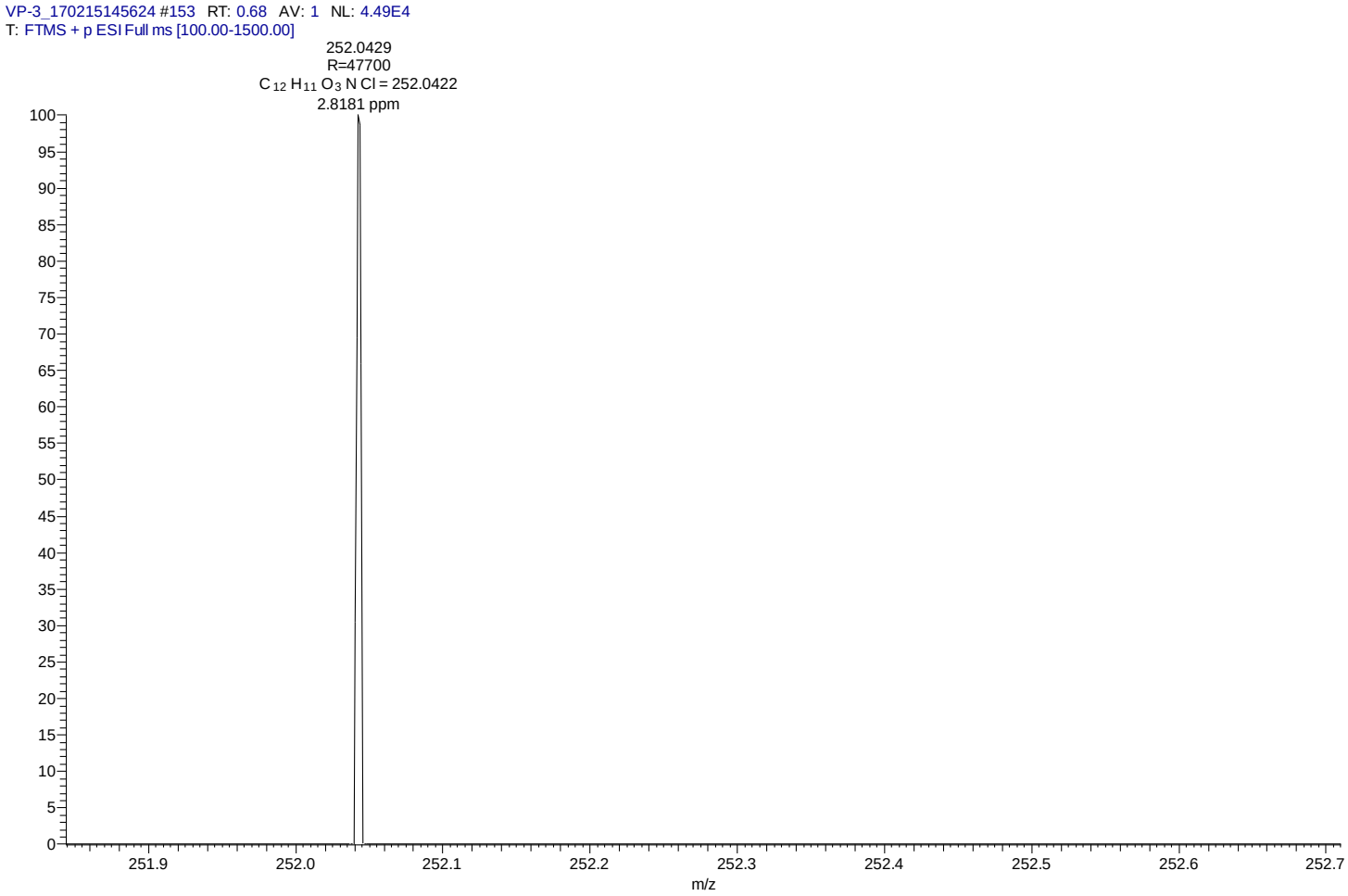
2c



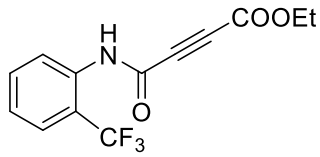
HRMS (ESI-TOF)



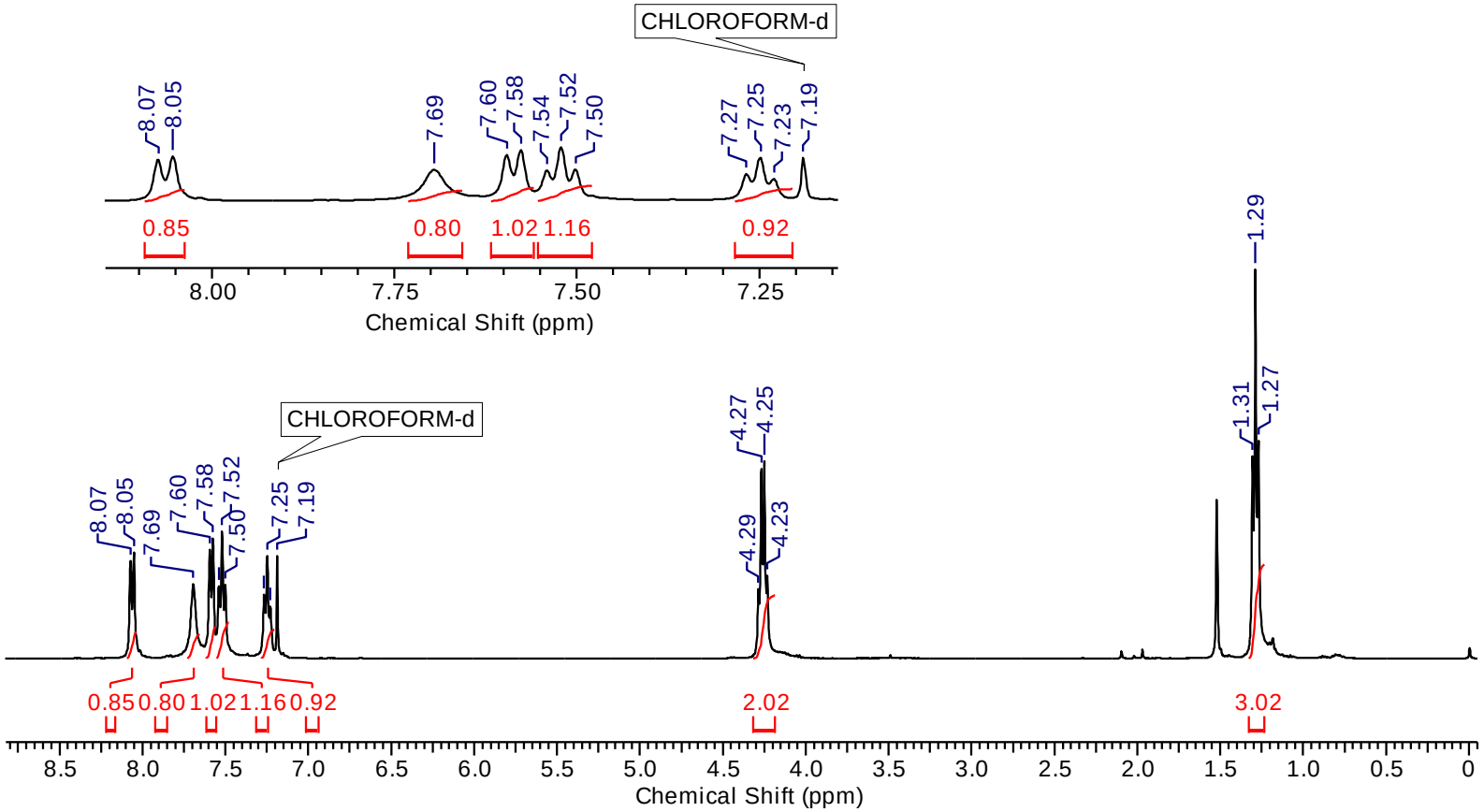
2c



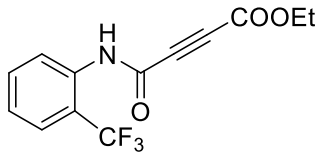
^{1}H NMR 400 MHz



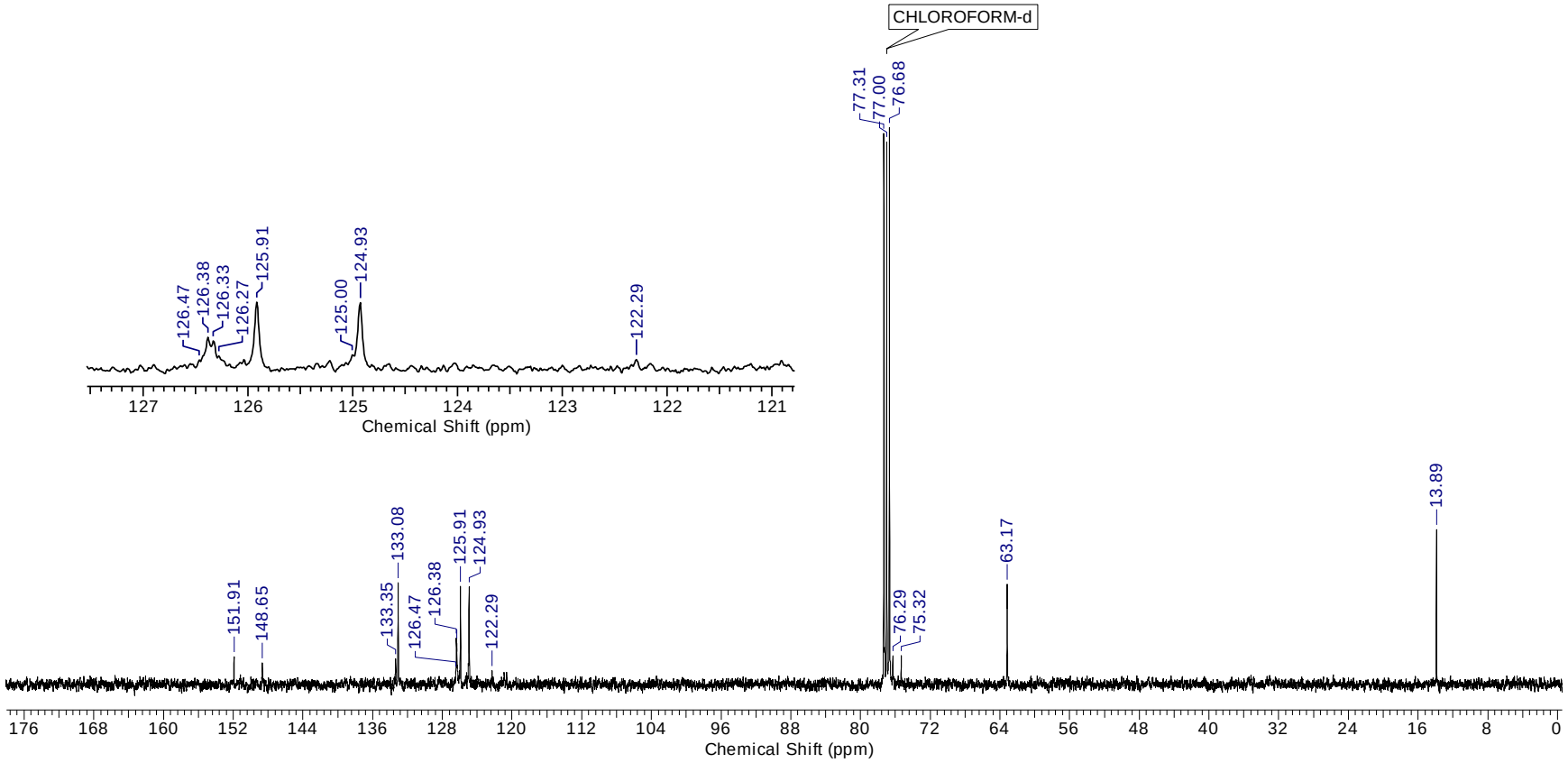
2d



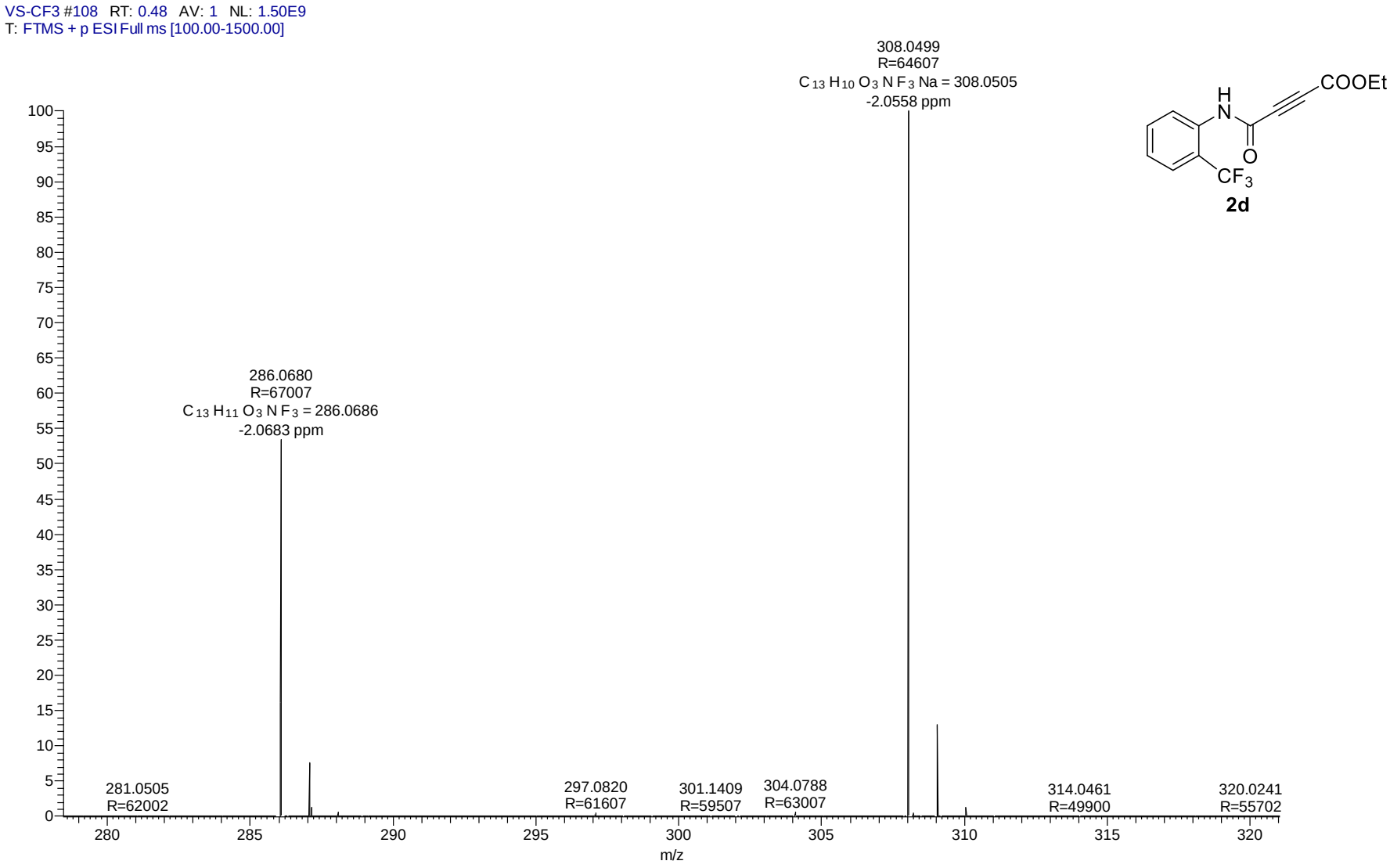
^{13}C NMR 100MHz



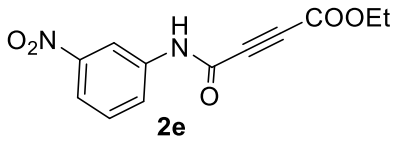
2d



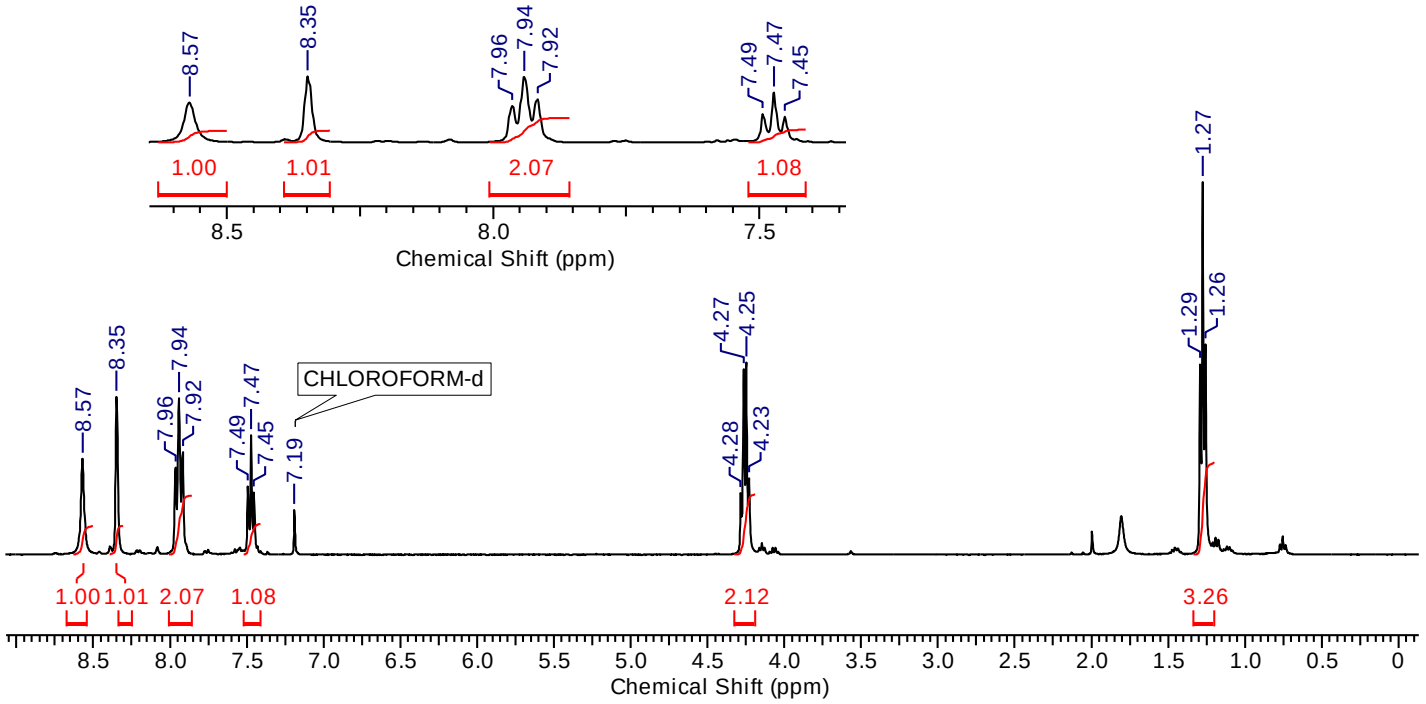
HRMS (ESI-TOF)


VS-CF3 #108 RT: 0.48 AV: 1 NL: 1.50E9
T: FTMS + p ESI Full ms [100.00-1500.00]
308.0499
R=64607
C 13 H 10 O 3 N F 3 Na = 308.0505
-2.0558 ppm
286.0680
R=67007
C 13 H 11 O 3 N F 3 = 286.0686
-2.0683 ppm
281.0505
R=62002
297.0820
R=61607
301.1409
R=59507
304.0788
R=63007
314.0461
R=49900
320.0241
R=55702
m/z
COOEt
H
N
O
CF3
2d

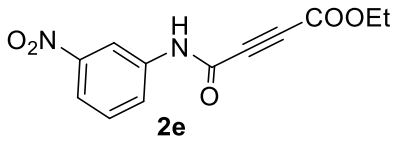
^{1}H NMR 400 MHz



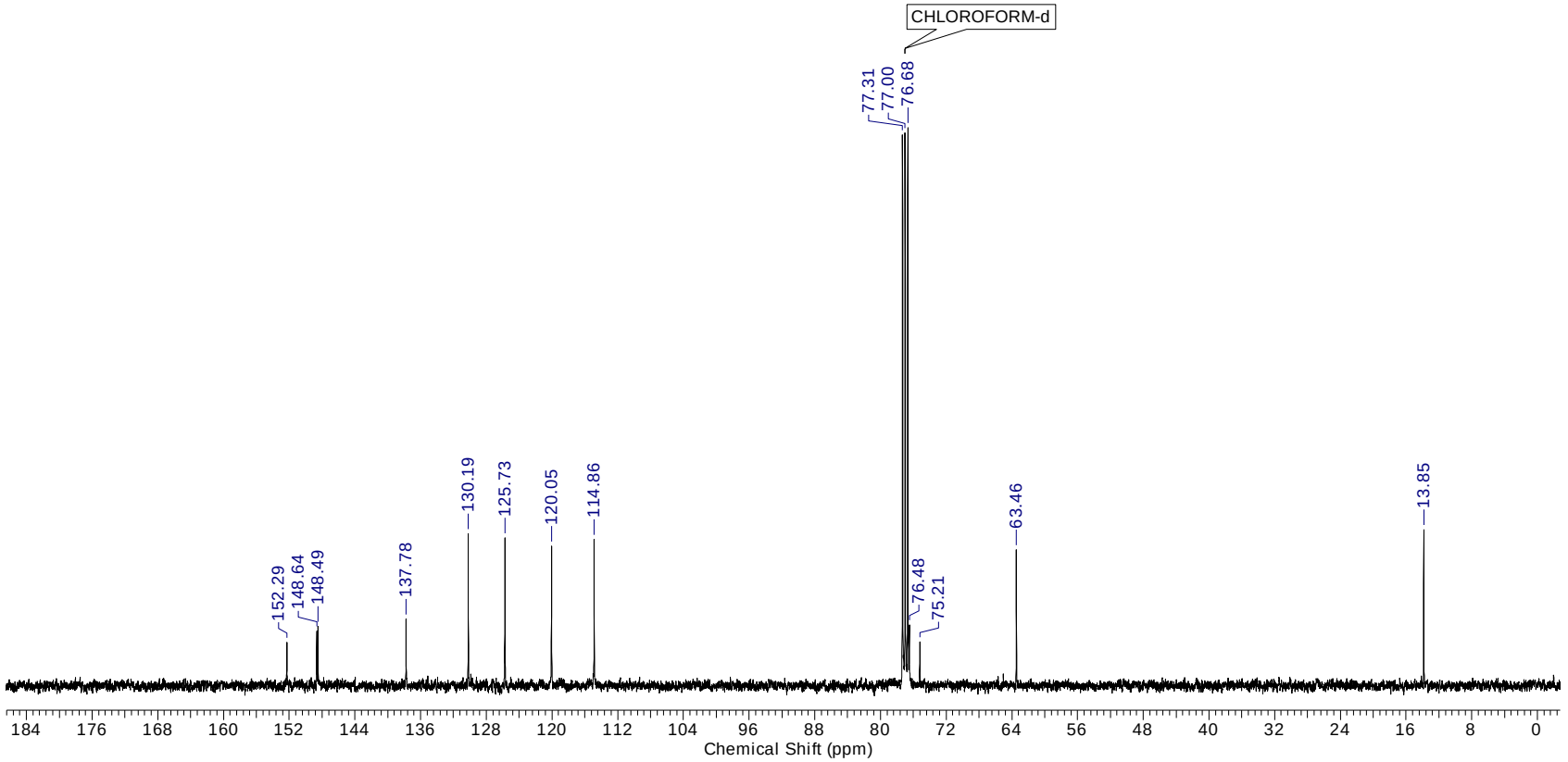
2e



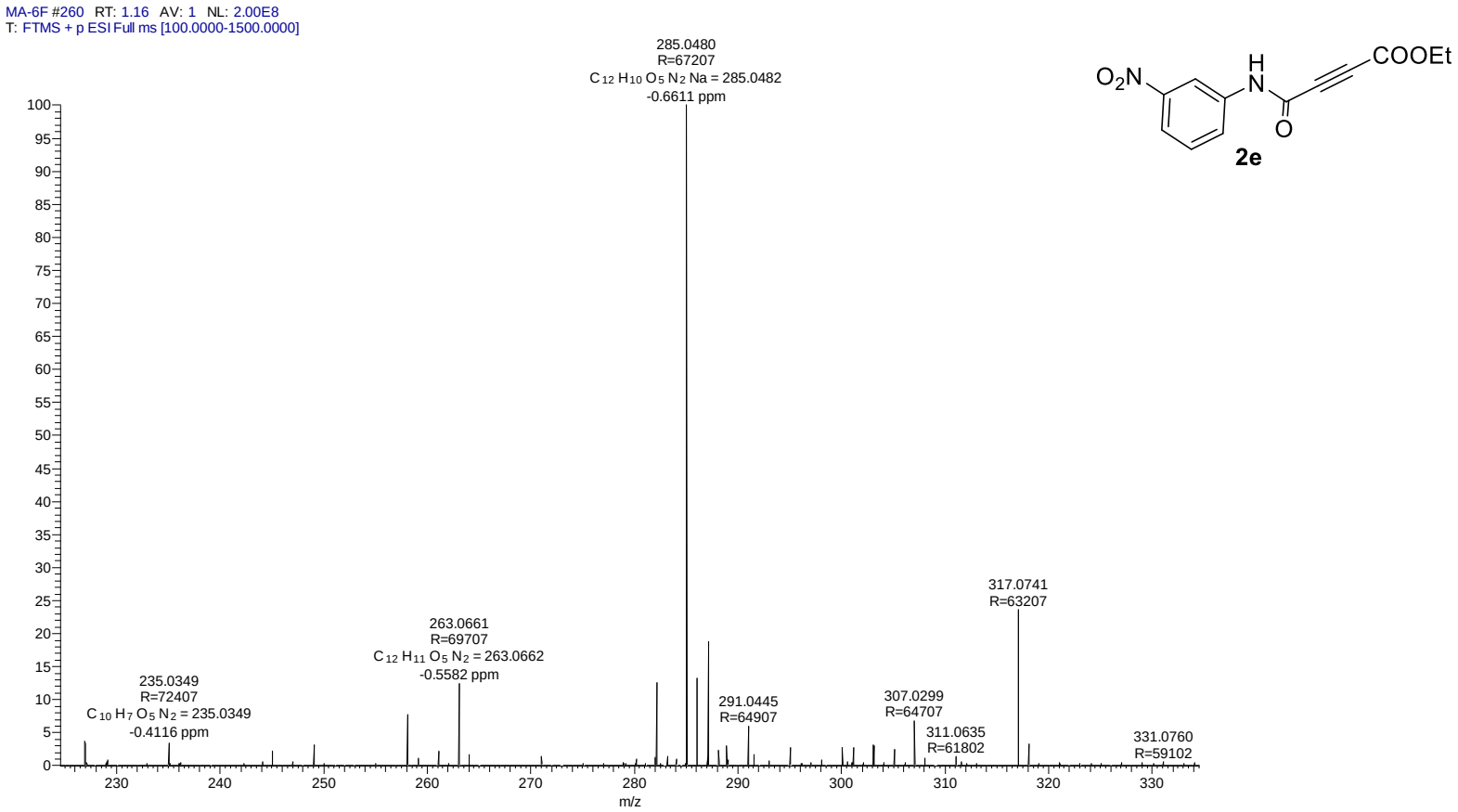
^{13}C NMR 100MHz



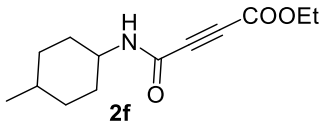
2e



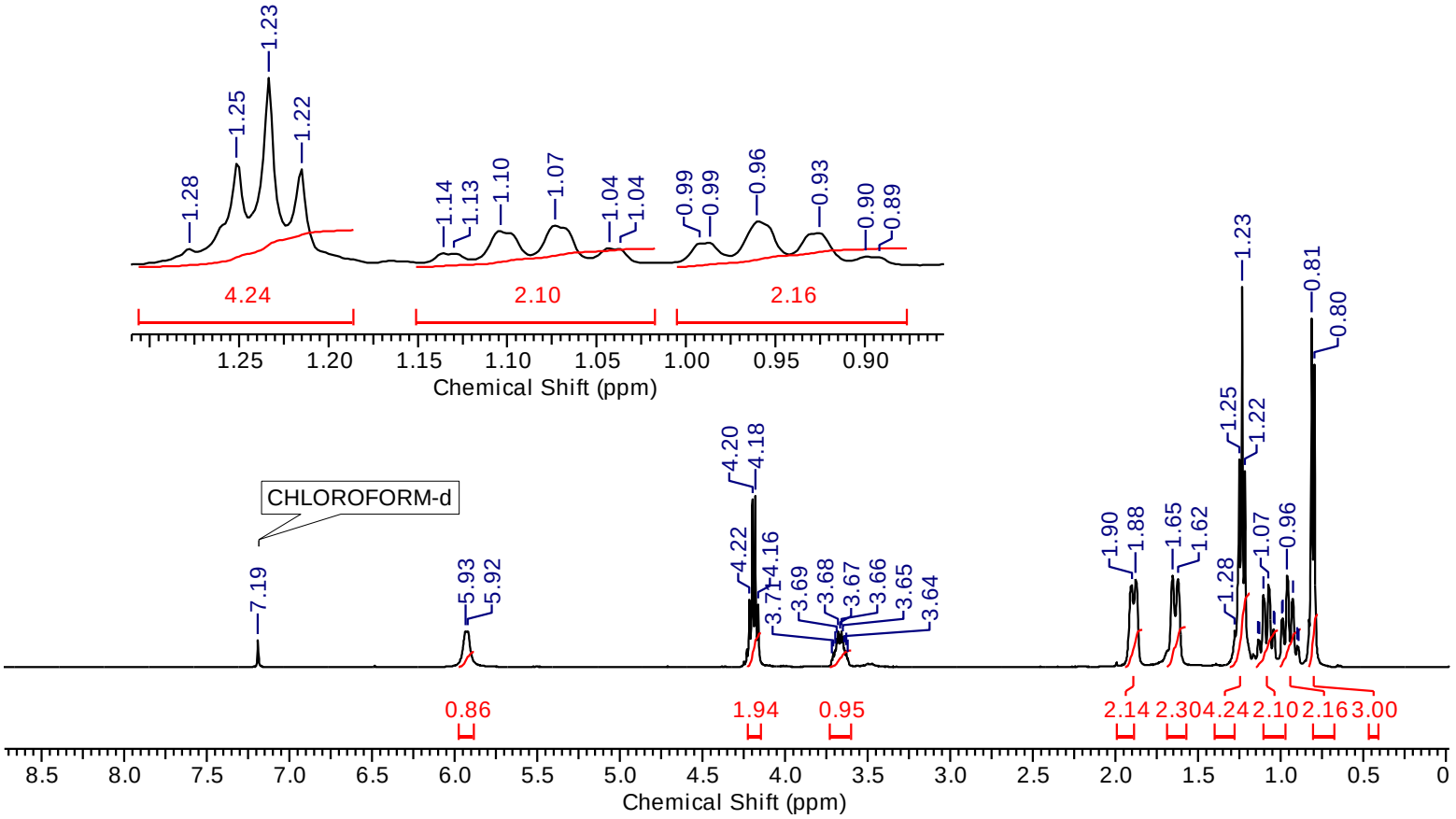
HRMS (ESI-TOF)


MA-6F #260 RT: 1.16 AV: 1 NL: 2.00E8
T: FTMS + p ESI Full ms [100.0000-1500.0000]
285.0480
R=67207
C 12 H 10 O 5 N 2 Na = 285.0482
-0.6611 ppm
263.0661
R=69707
C 12 H 11 O 5 N 2 = 263.0662
-0.5582 ppm
235.0349
R=72407
C 10 H 7 O 5 N 2 = 235.0349
-0.4116 ppm
291.0445
R=64907
307.0299
R=64707
311.0635
R=61802
317.0741
R=63207
331.0760
R=59102
m/z
O2N
H
N
O
COOEt
2e

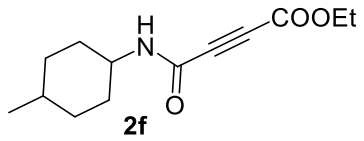
^{1}H NMR 400 MHz



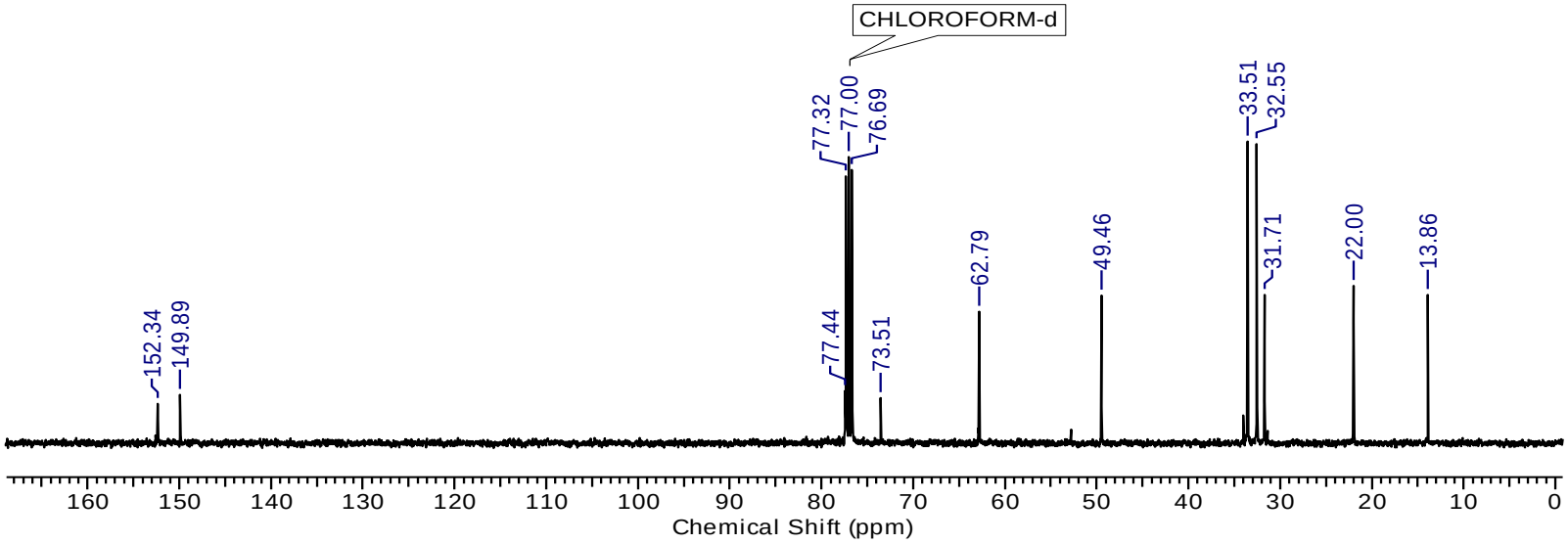
2f



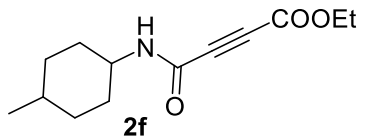
^{13}C NMR 100MHz



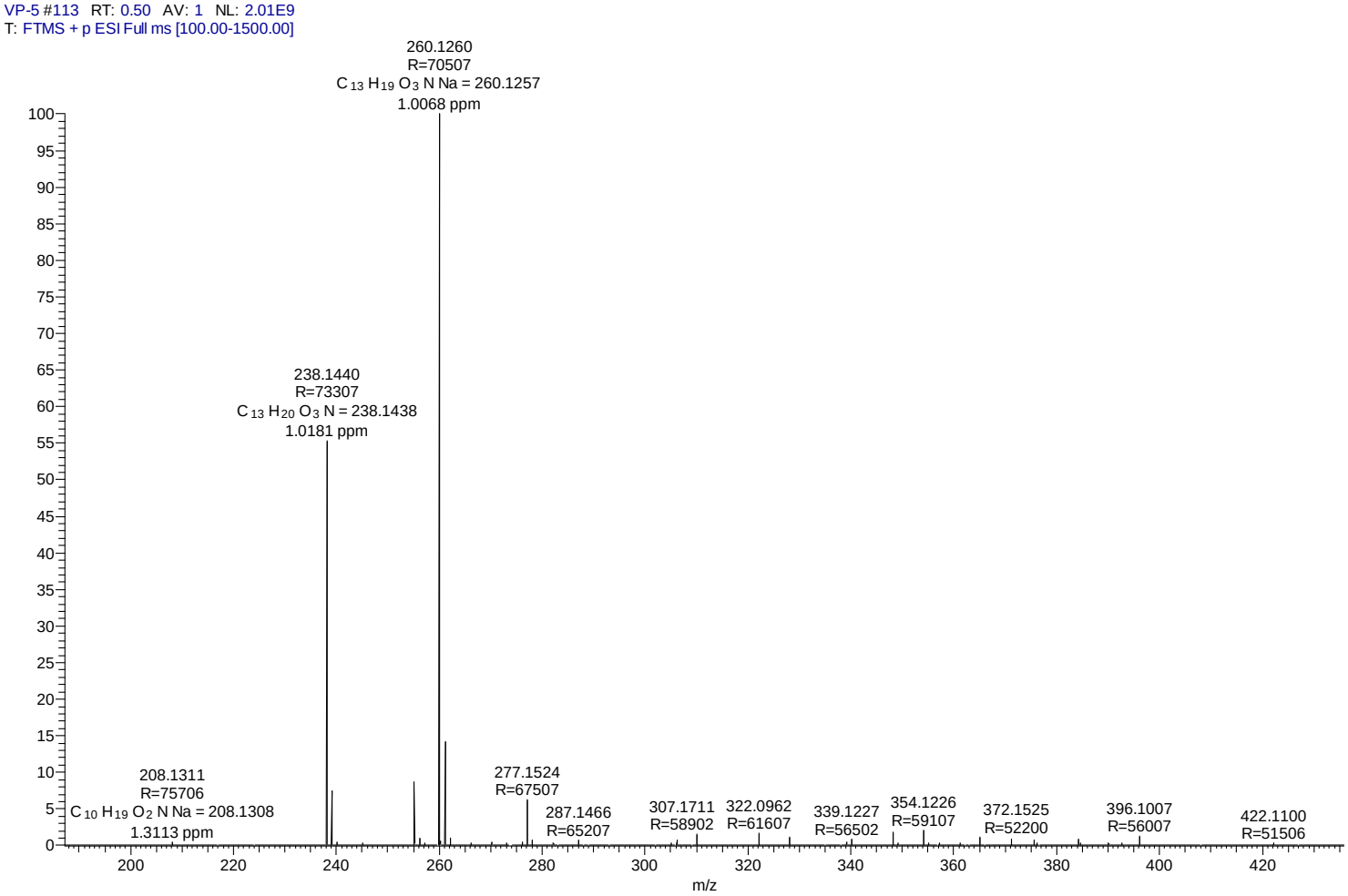
2f



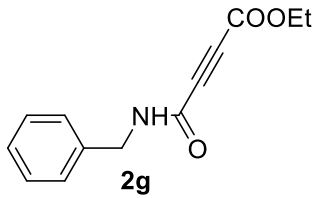
HRMS (ESI-TOF)

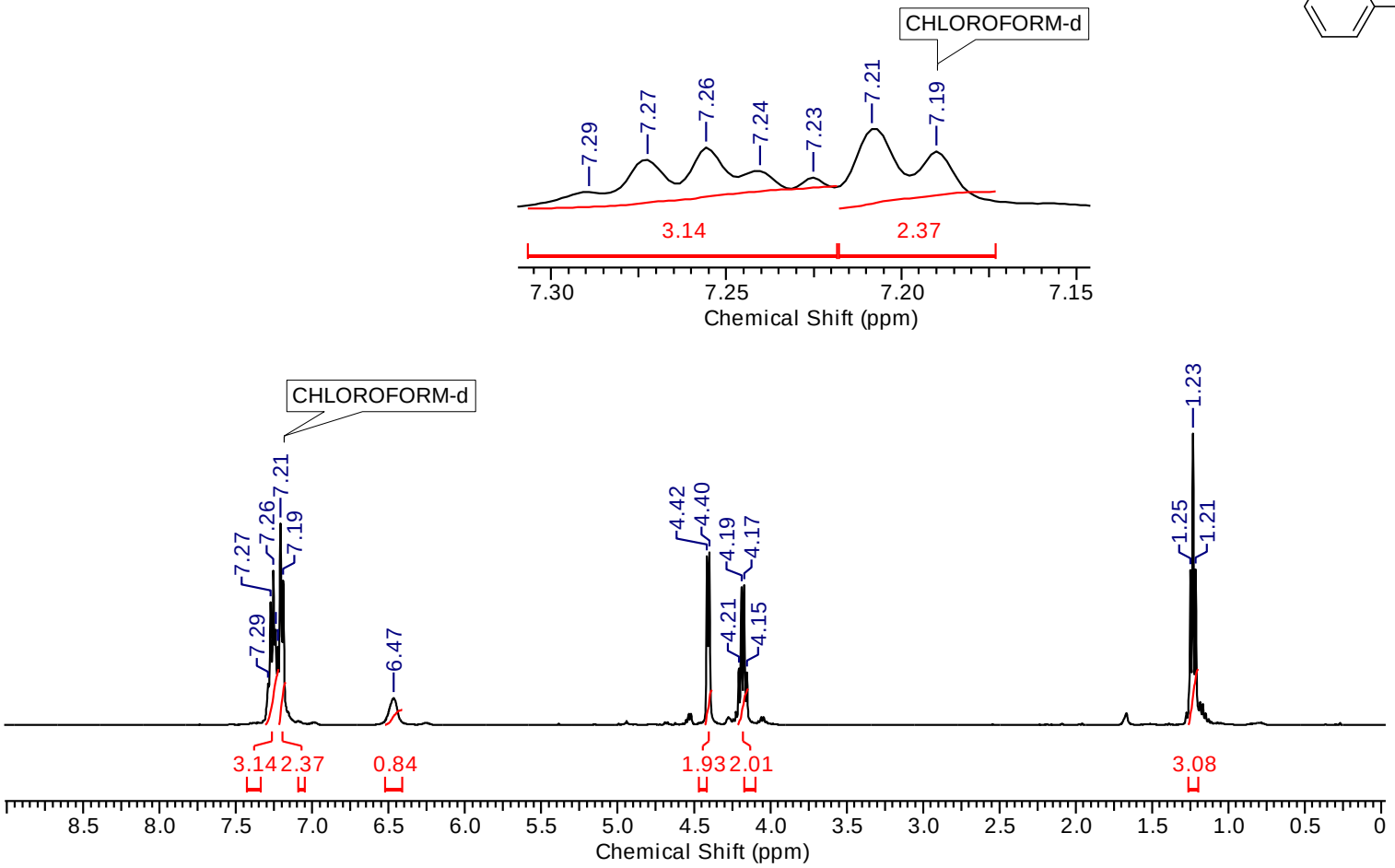


2f

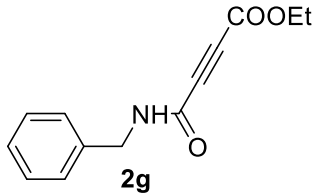


^{1}H NMR 400 MHz

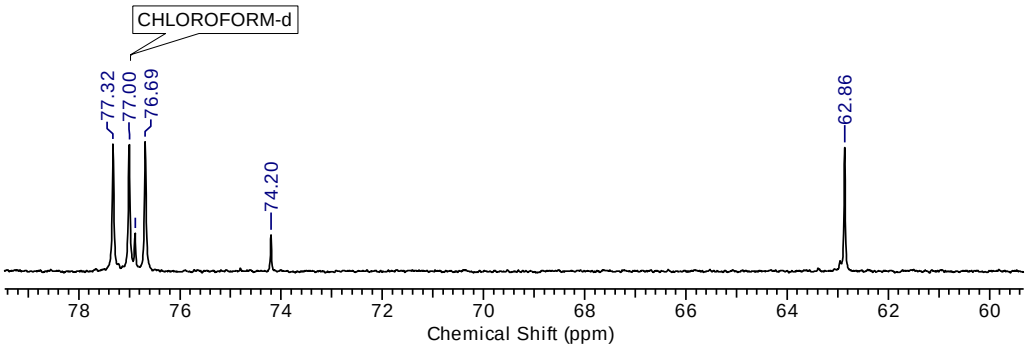


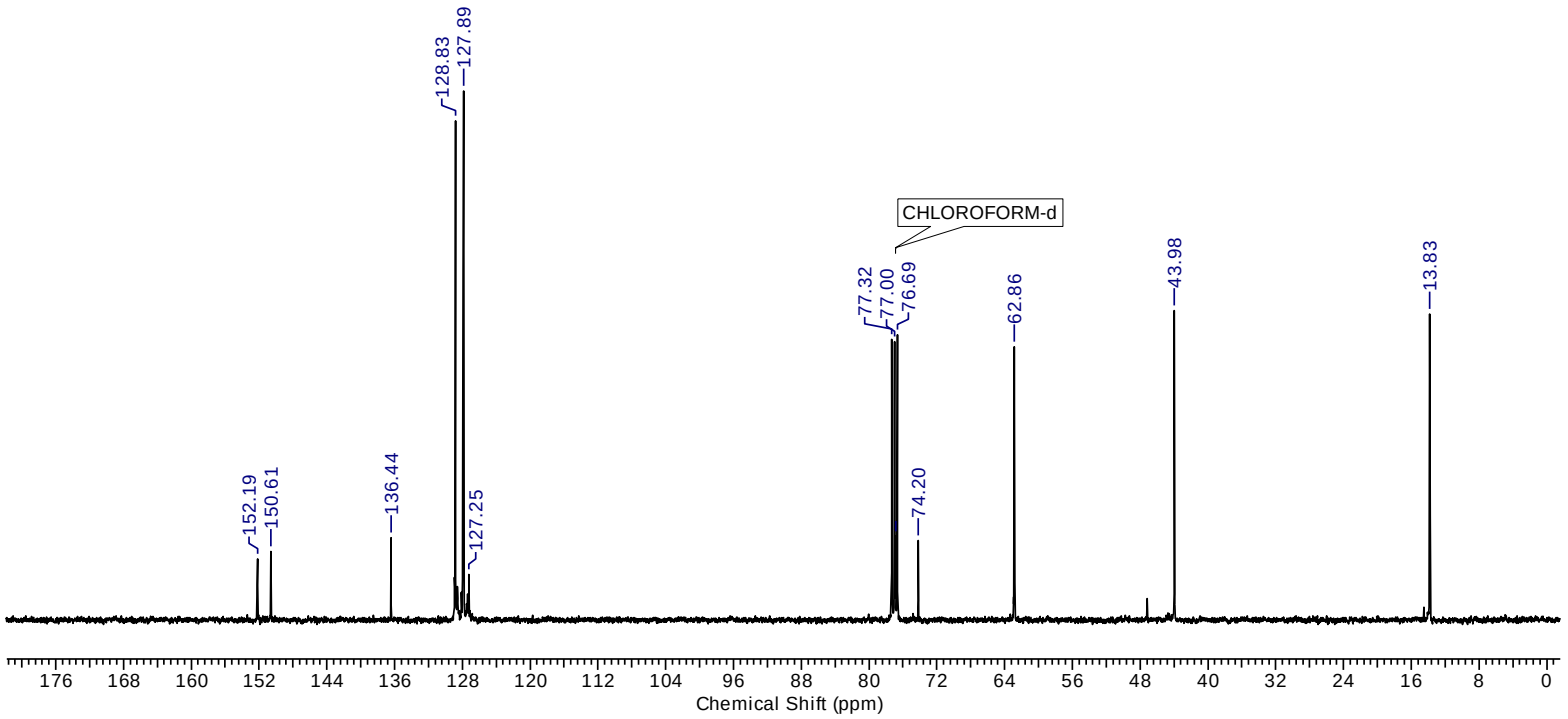


^{13} C NMR 100MHz

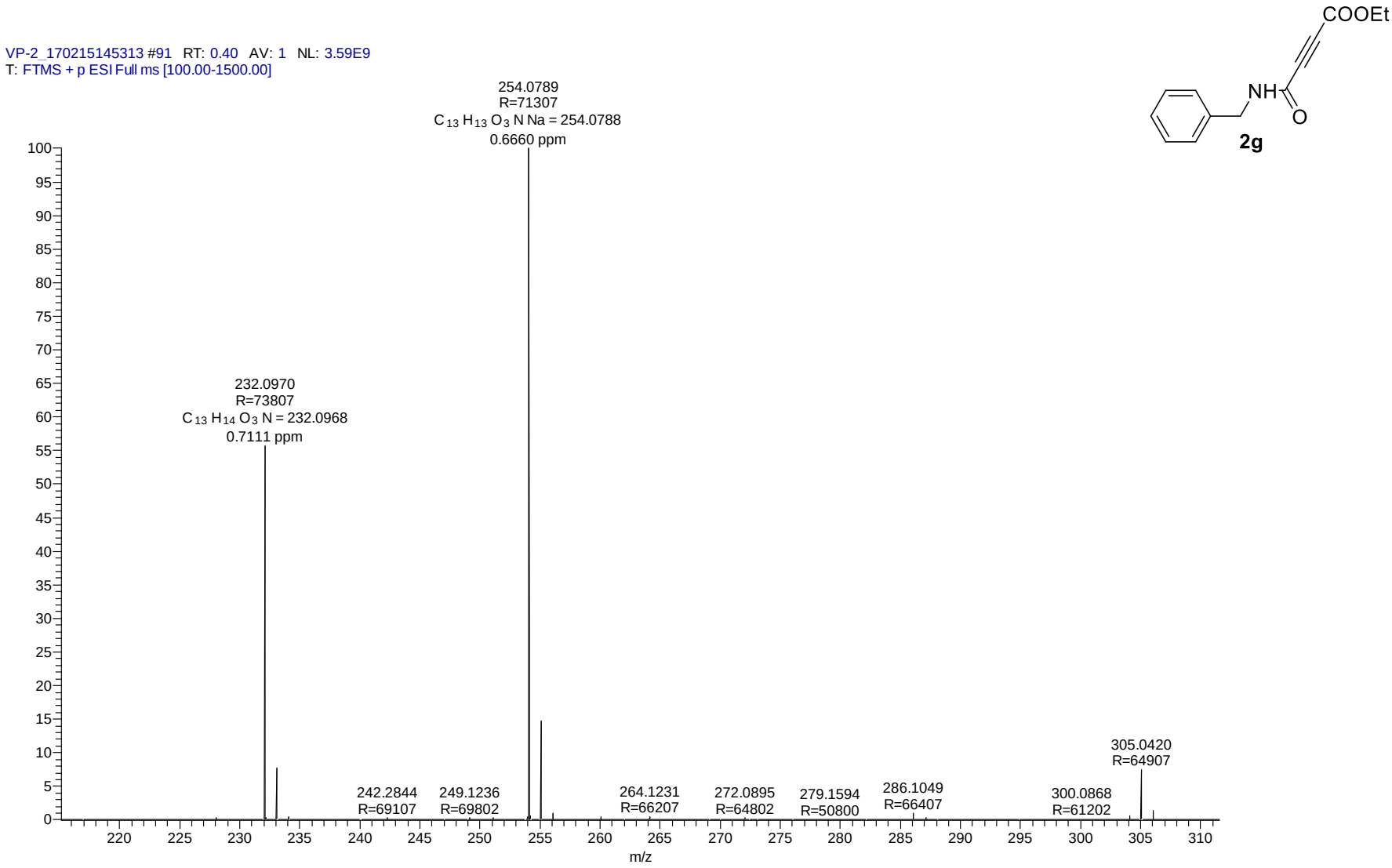


2g

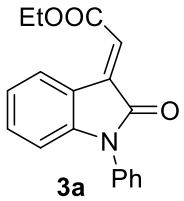




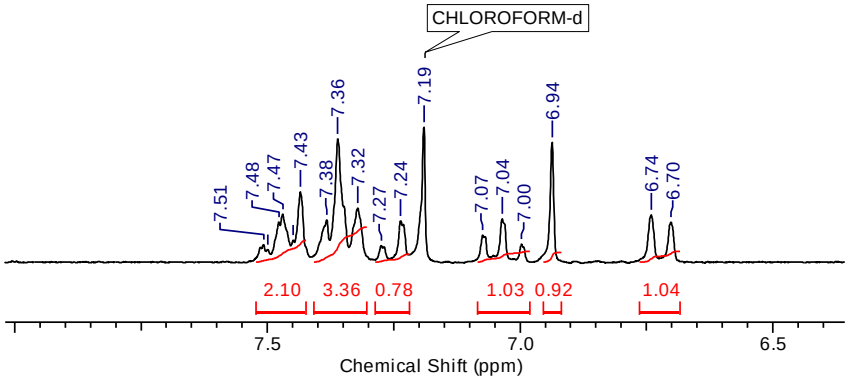
HRMS (ESI-TOF)

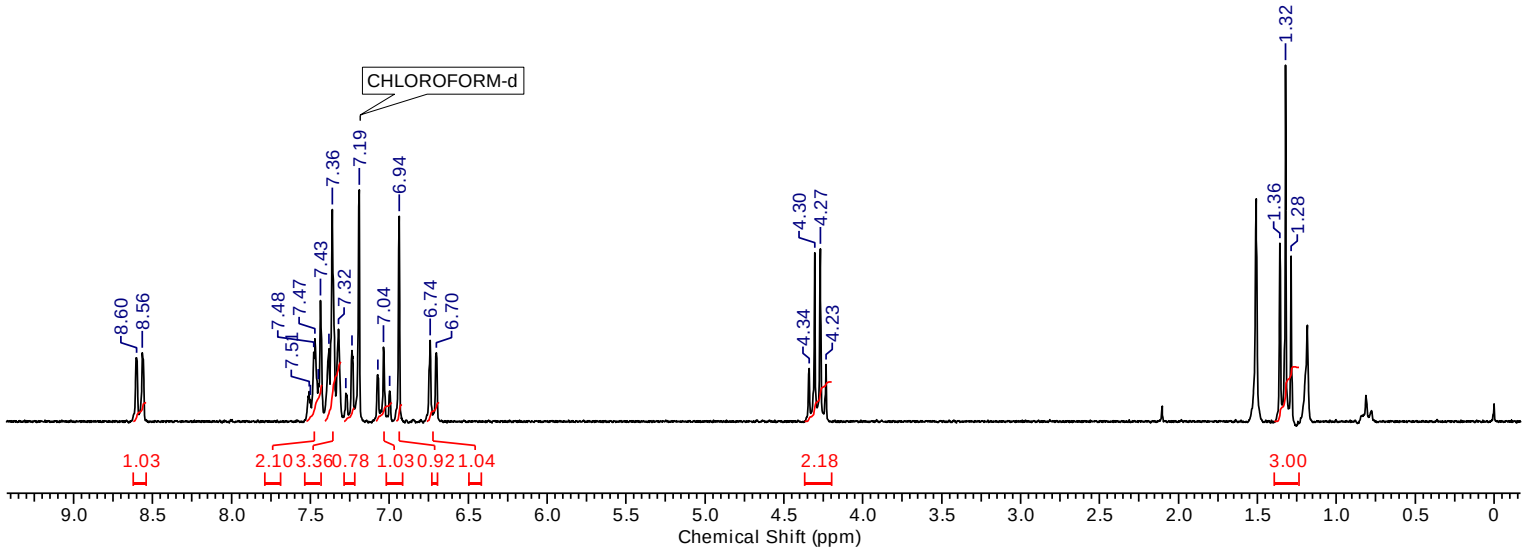

VP-2_170215145313 #91 RT: 0.40 AV: 1 NL: 3.59E9
T: FTMS + p ESI Full ms [100.00-1500.00]
254.0789
R=71307
C 13 H 13 O 3 N Na = 254.0788
0.6660 ppm
232.0970
R=73807
C 13 H 14 O 3 N = 232.0968
0.7111 ppm
242.2844
R=69107
249.1236
R=69802
264.1231
R=66207
272.0895
R=64802
279.1594
R=50800
286.1049
R=66407
300.0868
R=61202
305.0420
R=64907
m/z
COOEt
NH
O
2g

^{1}H NMR 400 MHz

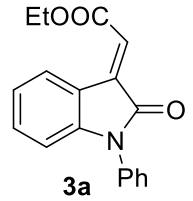


3a

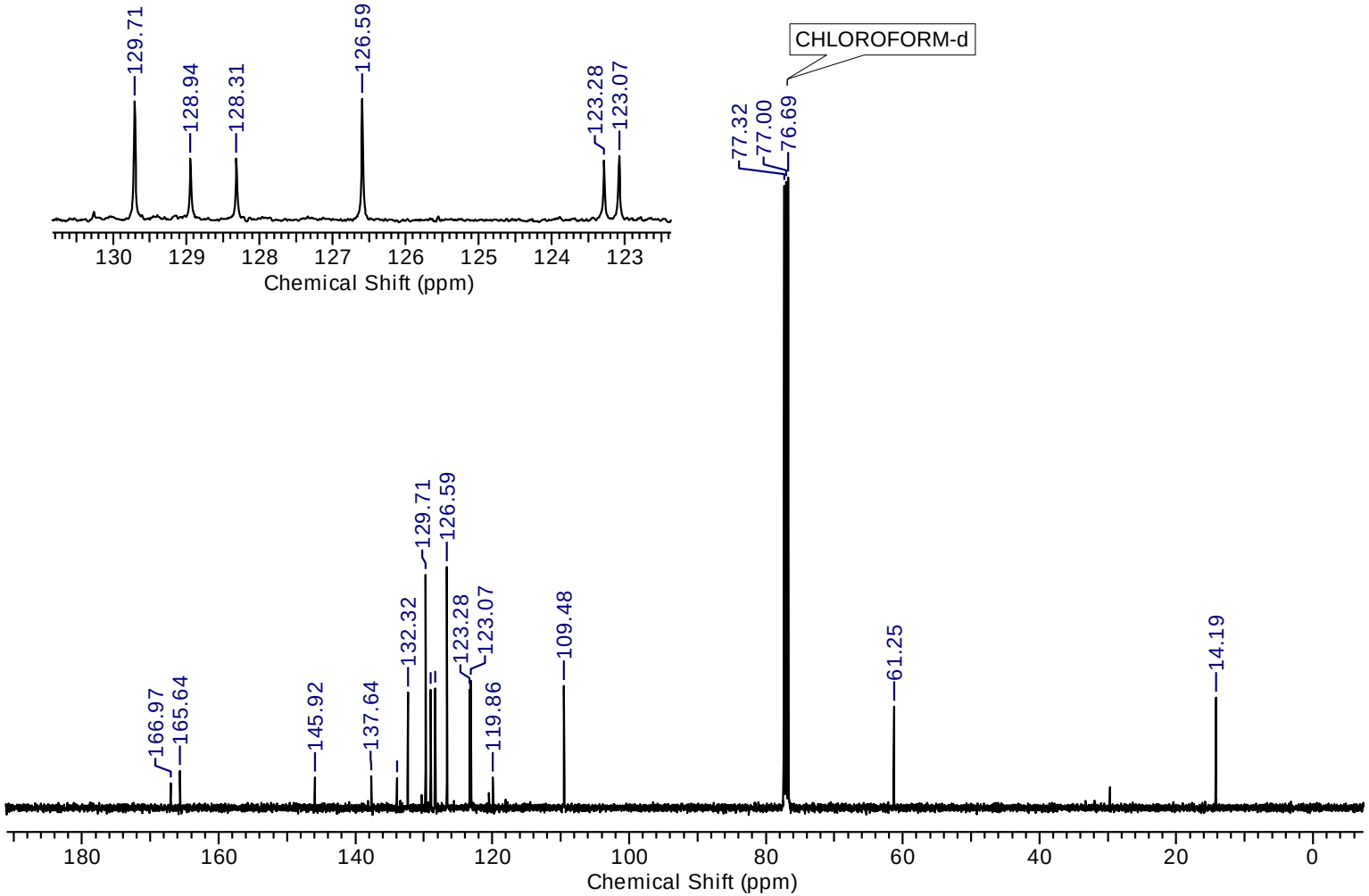




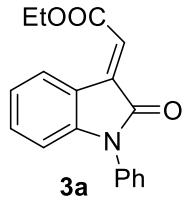
^{13}C NMR 100 MHz



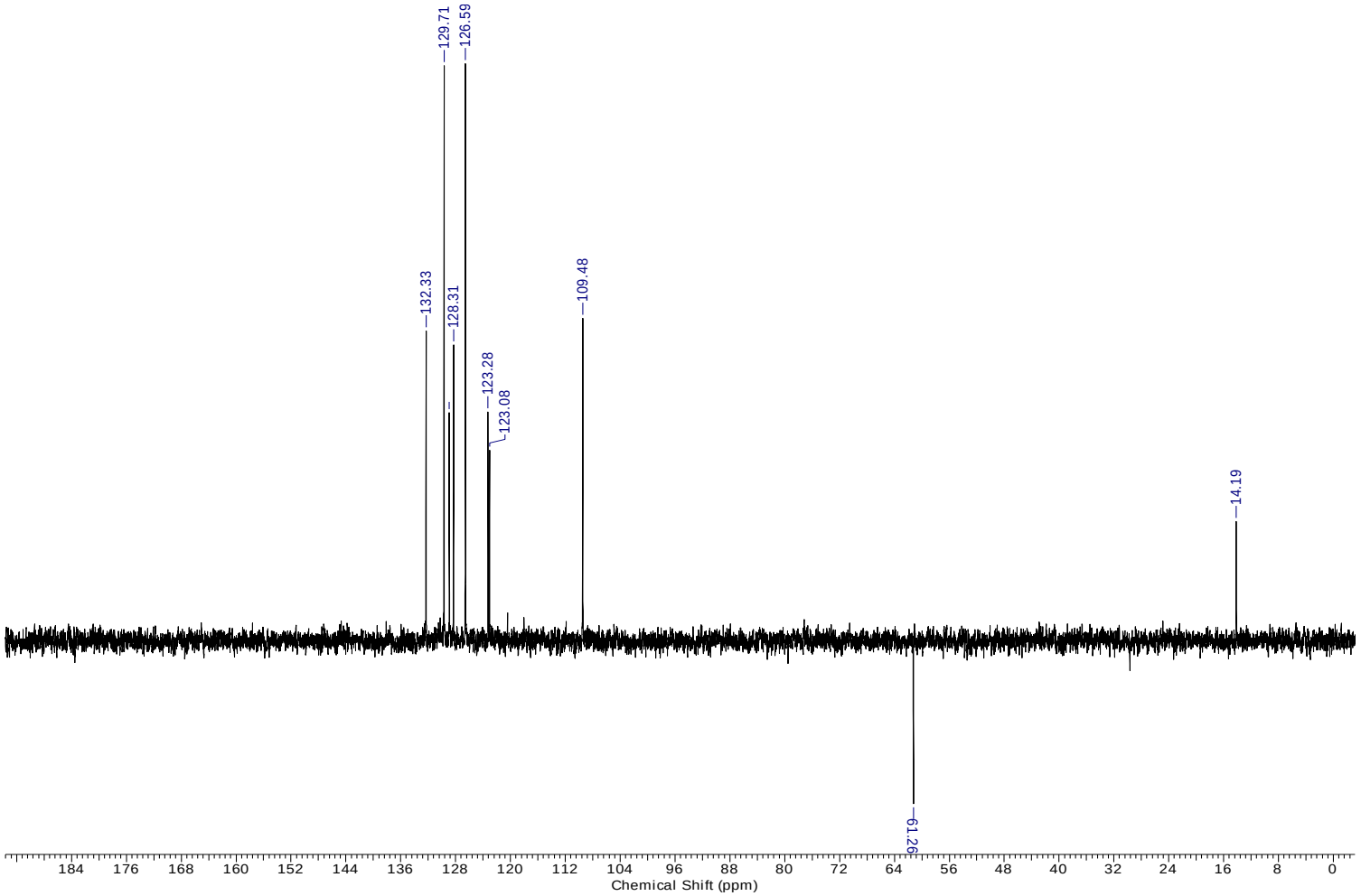
3a



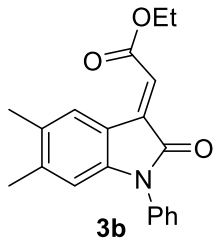
DEPT NMR 100 MHz



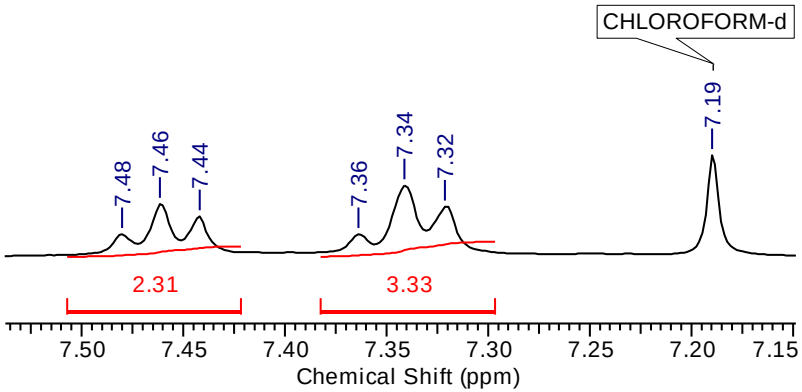
3a

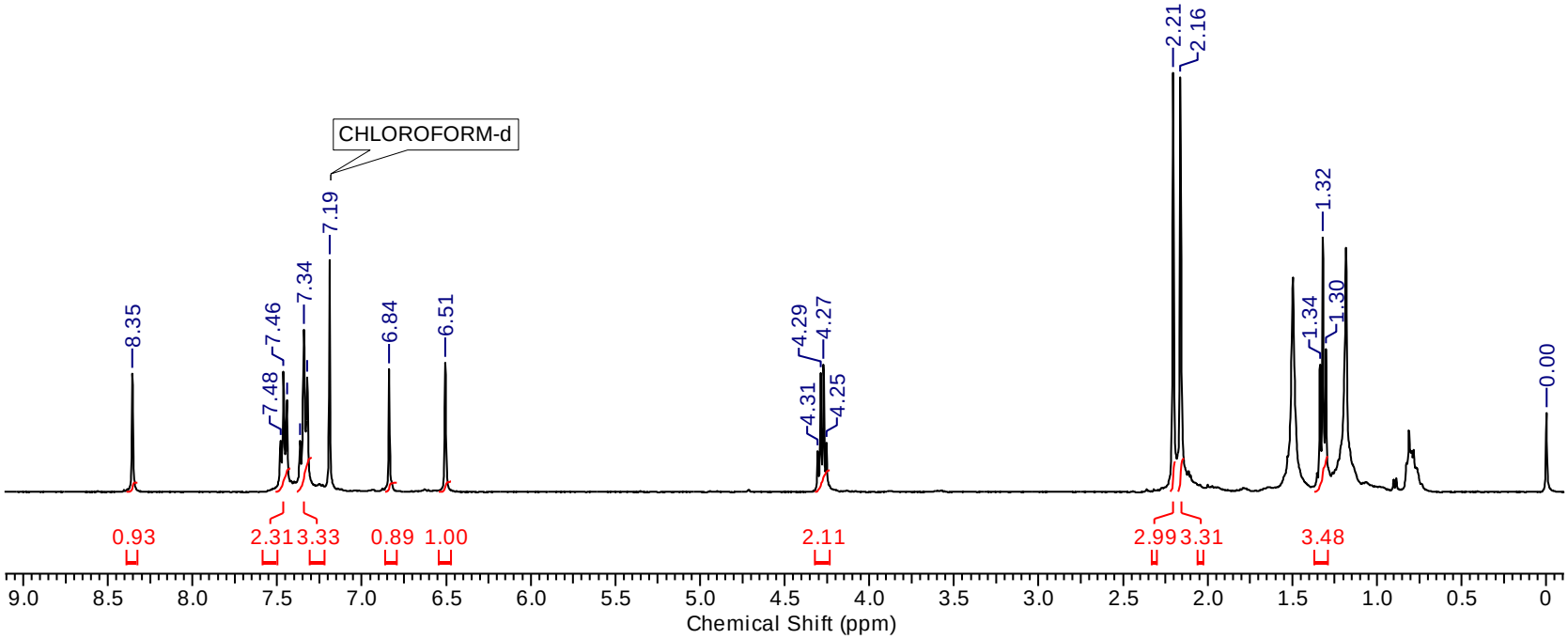


^{1}H NMR 400 MHz

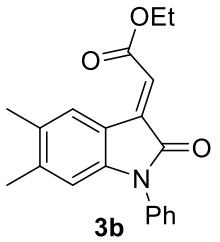


3b

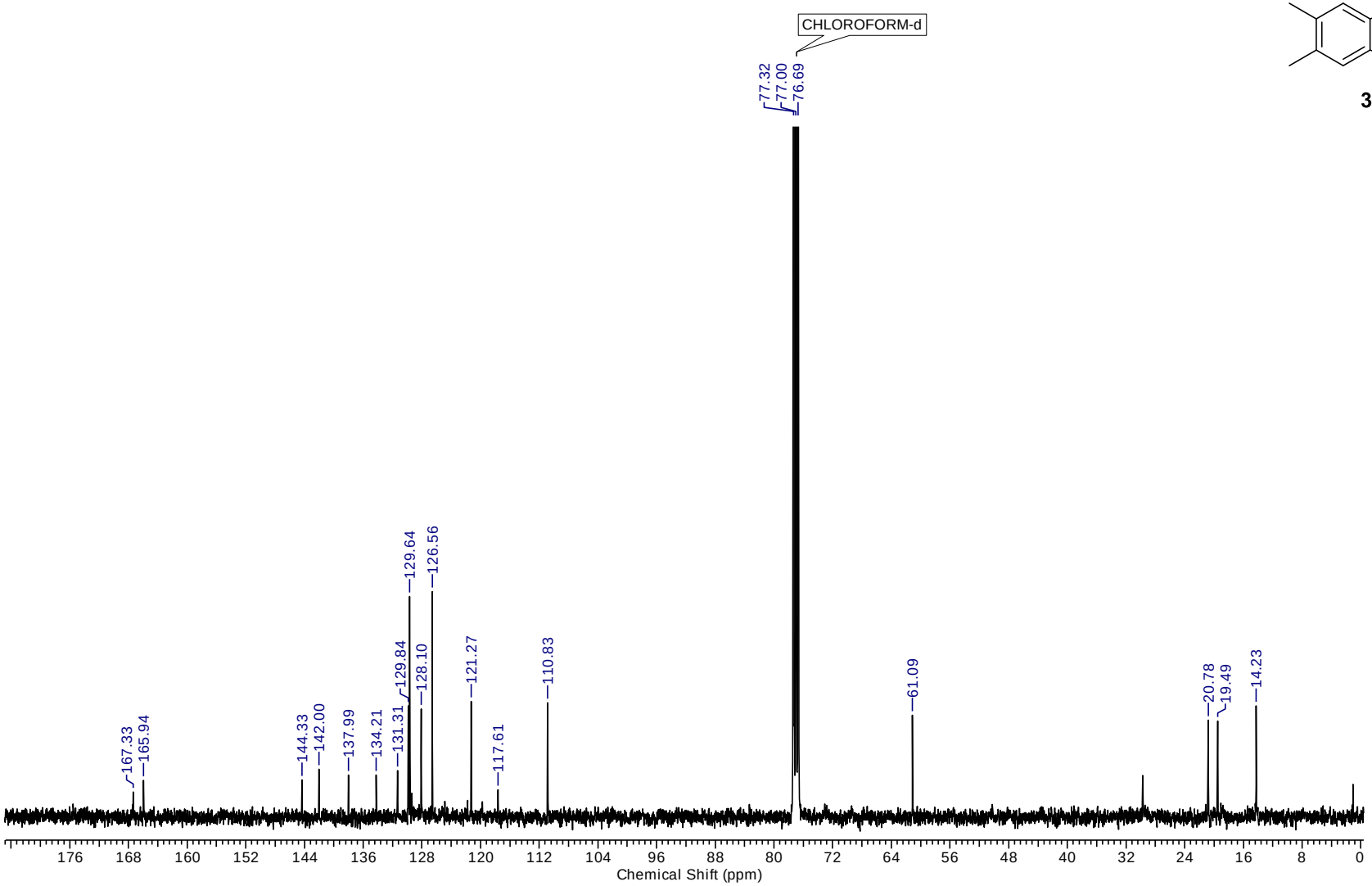




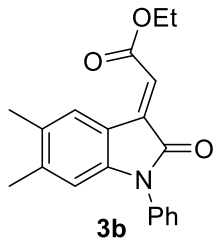
^{13}C NMR 100 MHz



3b

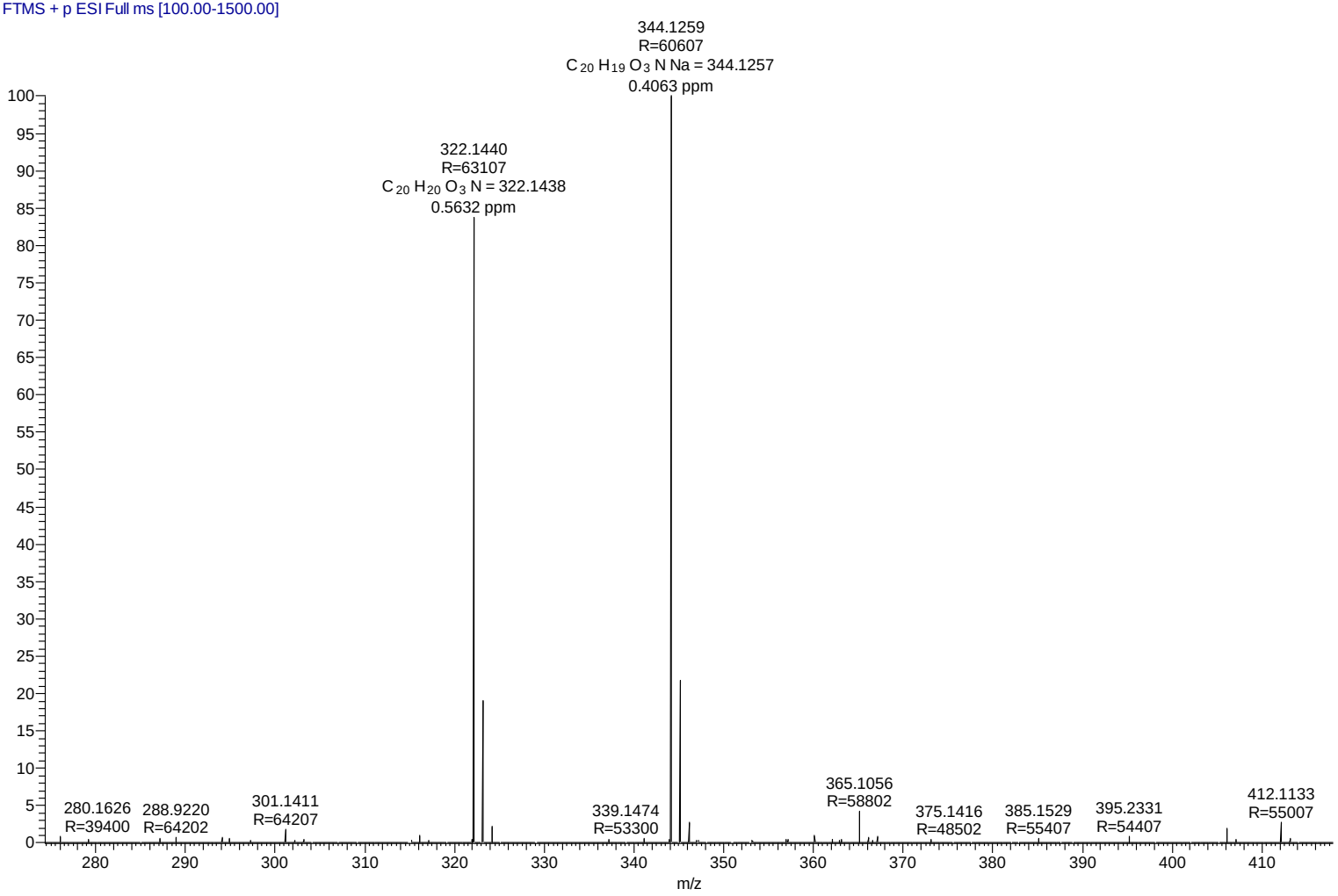


HRMS (ESI-TOF)

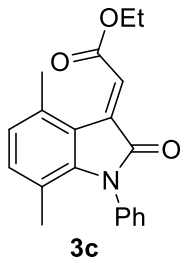


3b

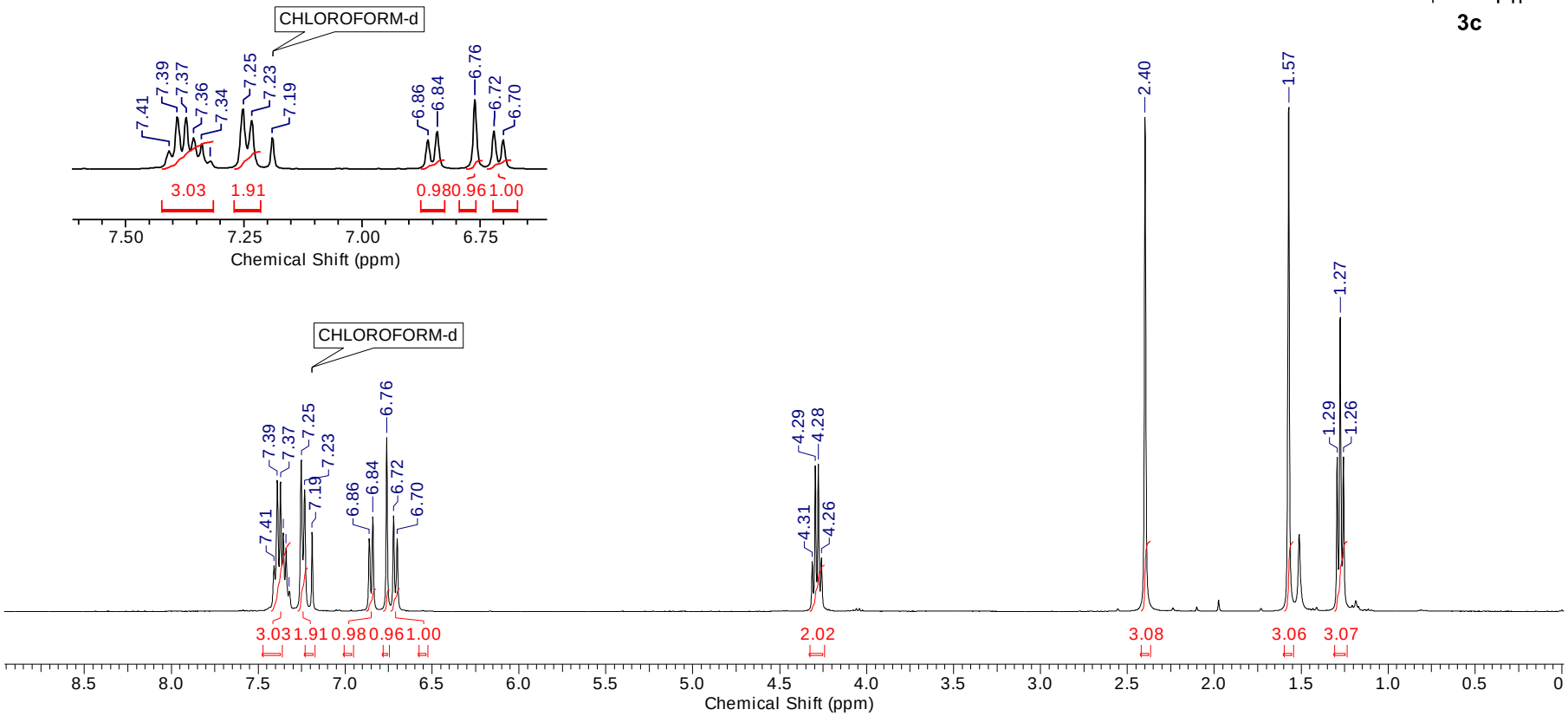
VP-6 #167 RT: 0.74 AV: 1 NL: 4.09E8
T: FTMS + p ESI Full ms [100.00-1500.00]



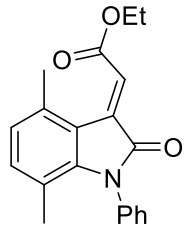
^{1}H NMR 400 MHz



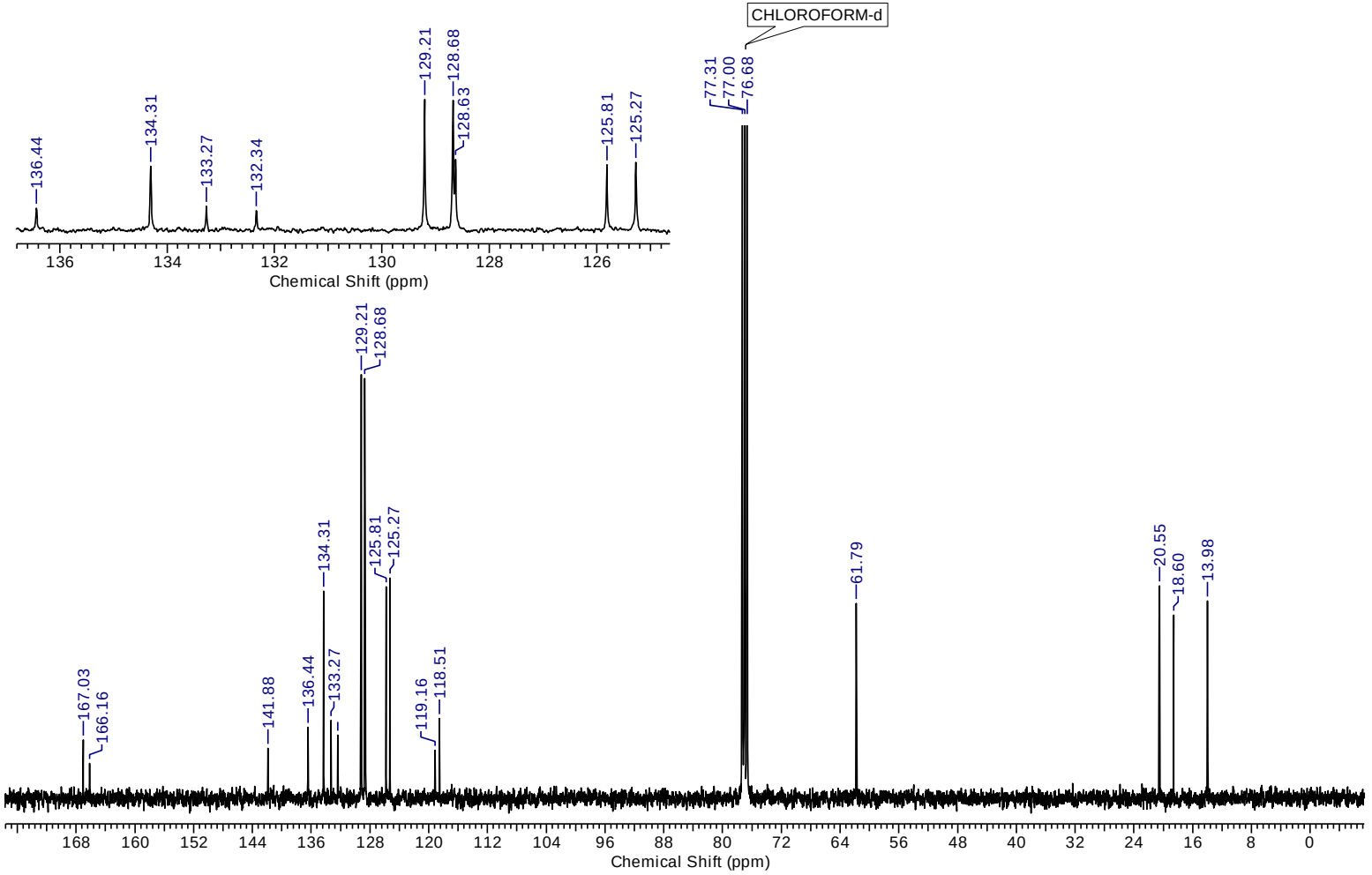
3c



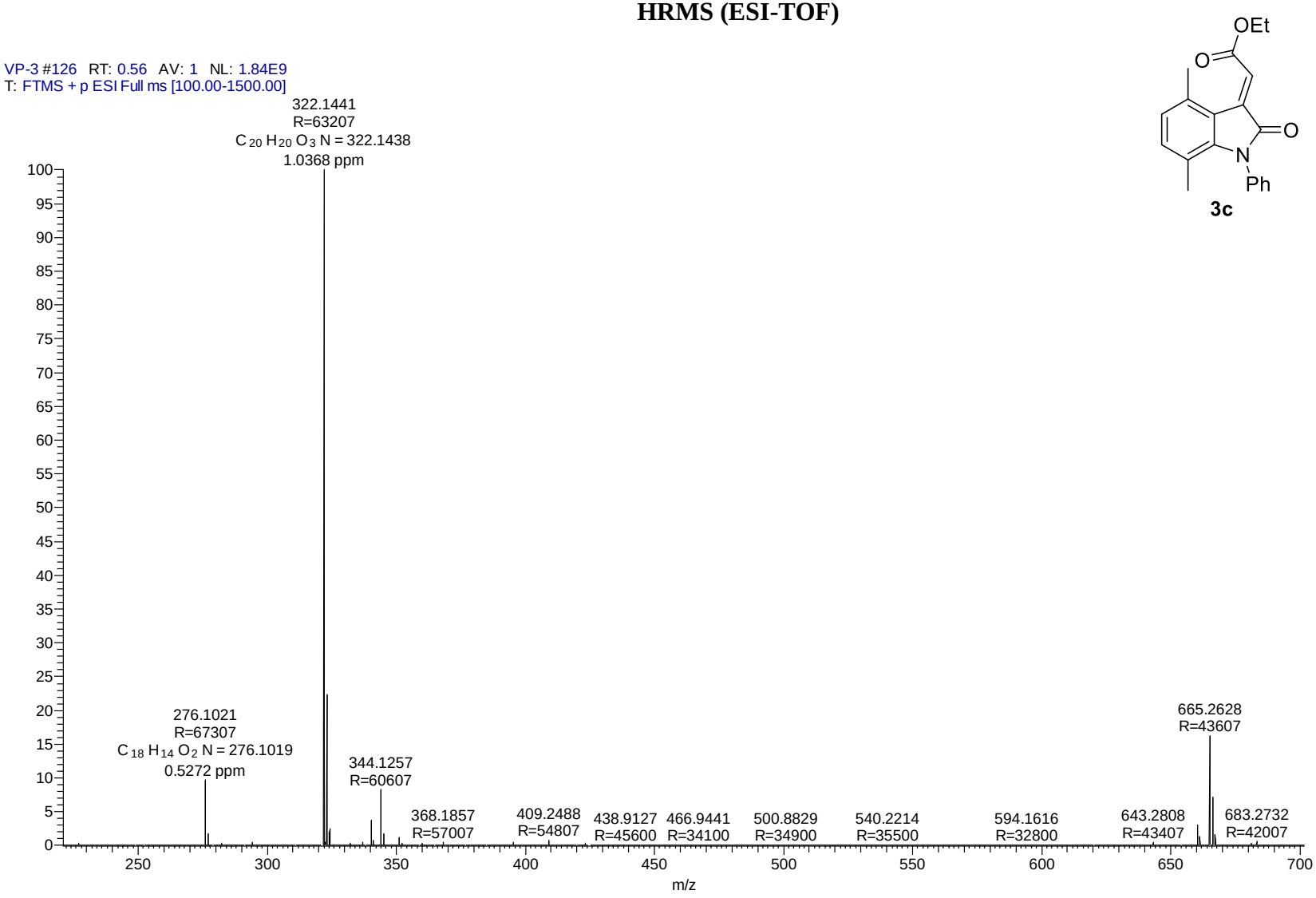
^{13}C NMR 100 MHz



3c

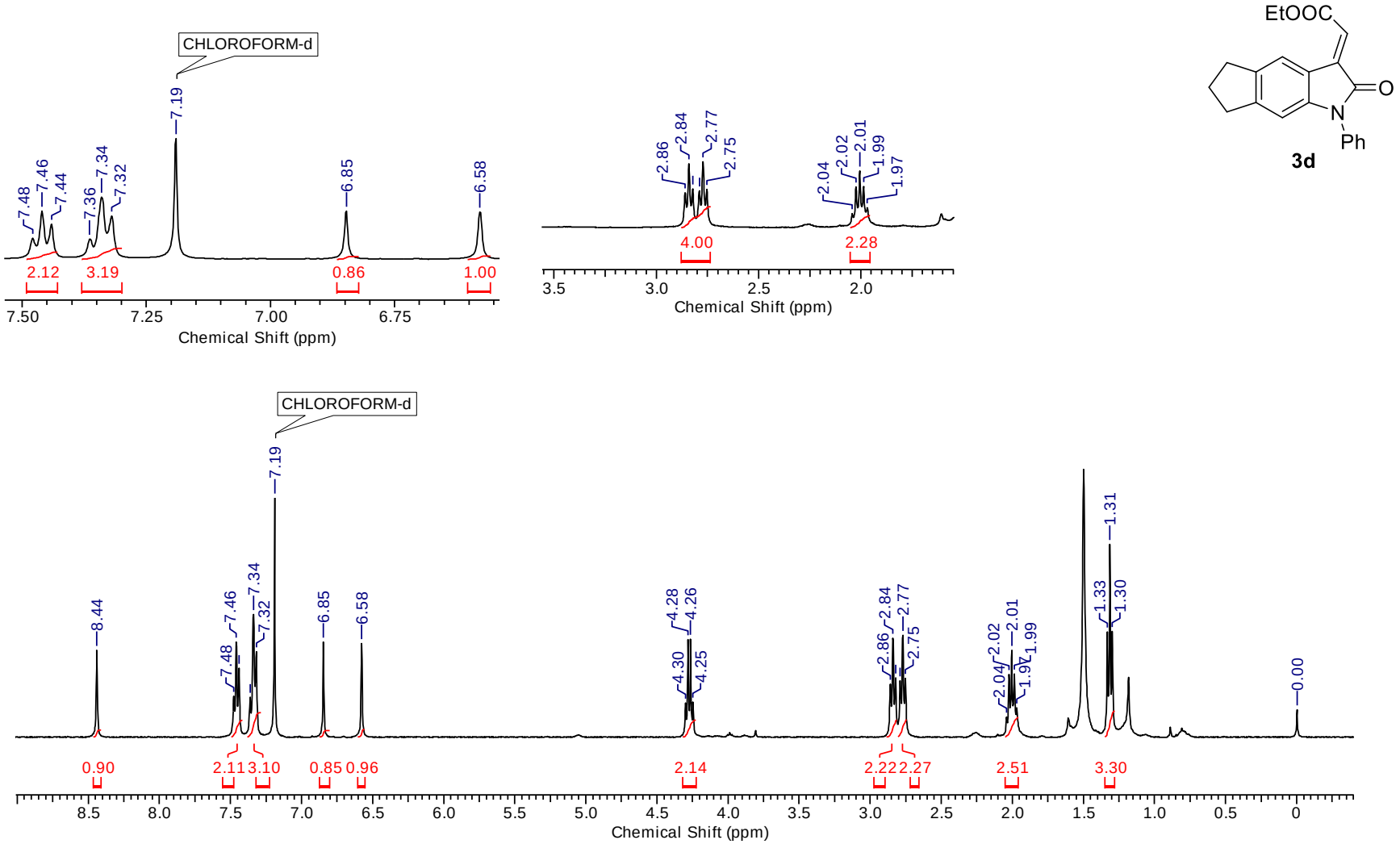


HRMS (ESI-TOF)

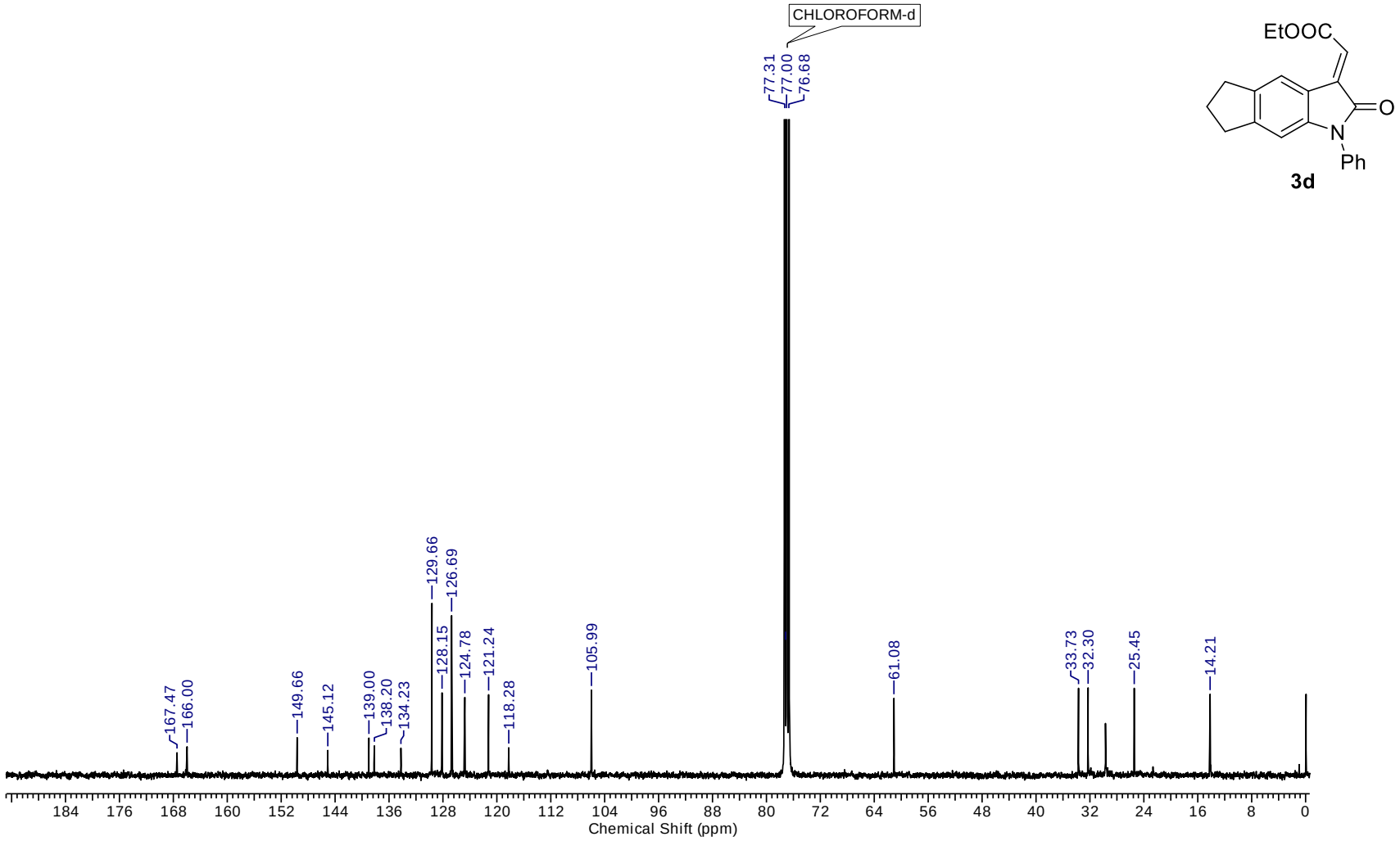


3c

^{1}H NMR 400 MHz

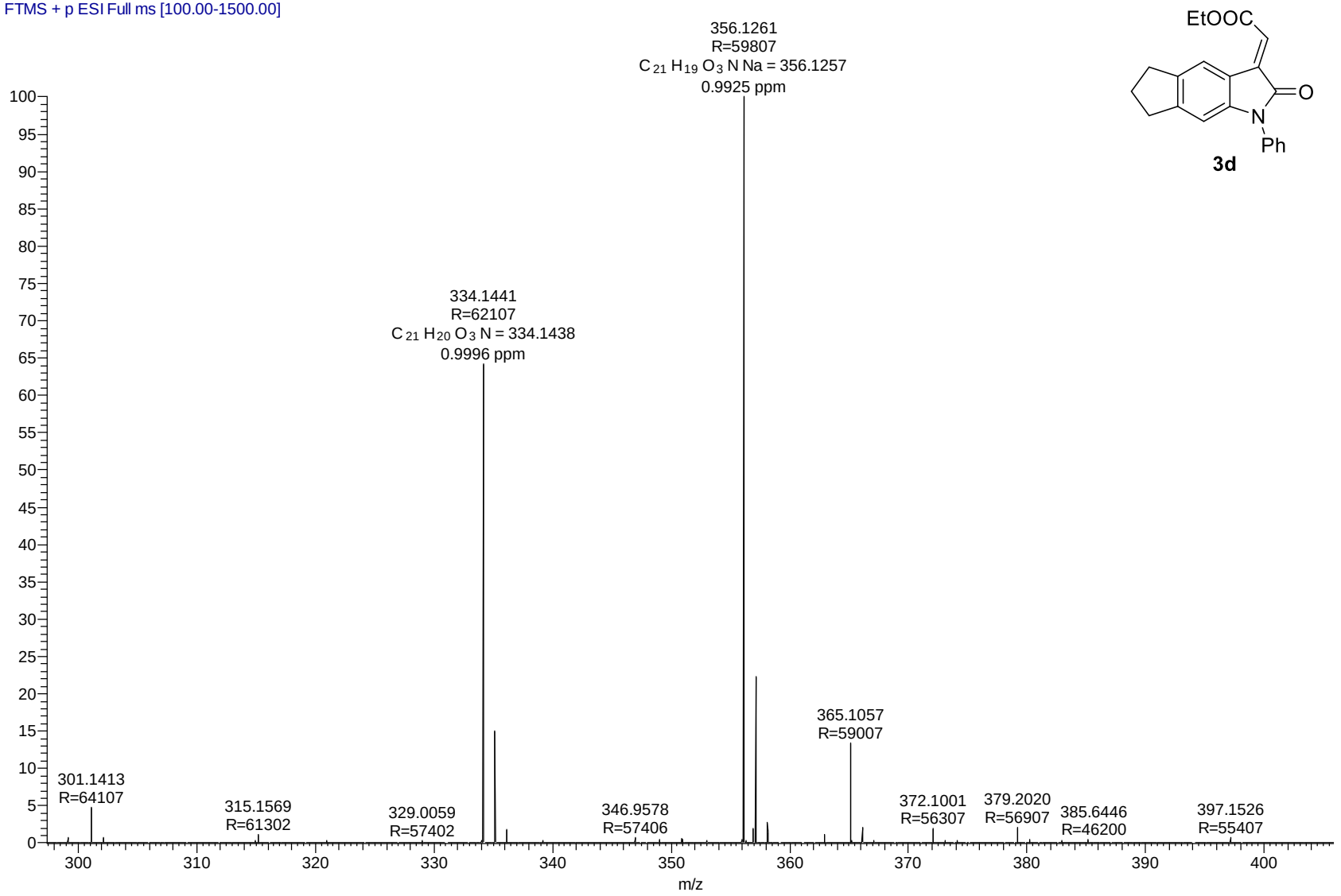


^{13}C NMR 100 MHz



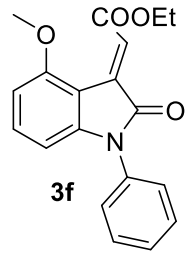
HRMS (ESI-TOF)

VP-3_170215143725 #202 RT: 0.90 AV: 1 NL: 1.58E8
T: FTMS + p ESI Full ms [100.00-1500.00]

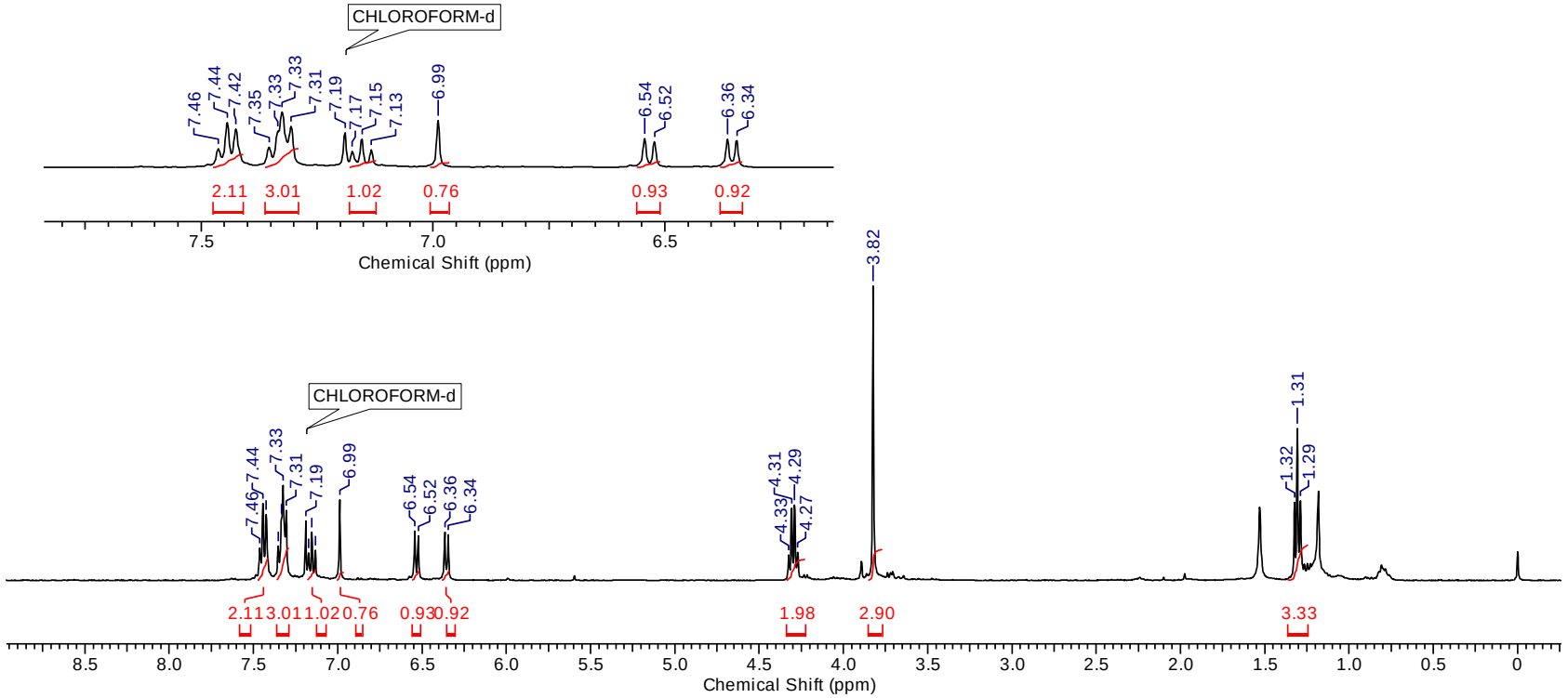


3d

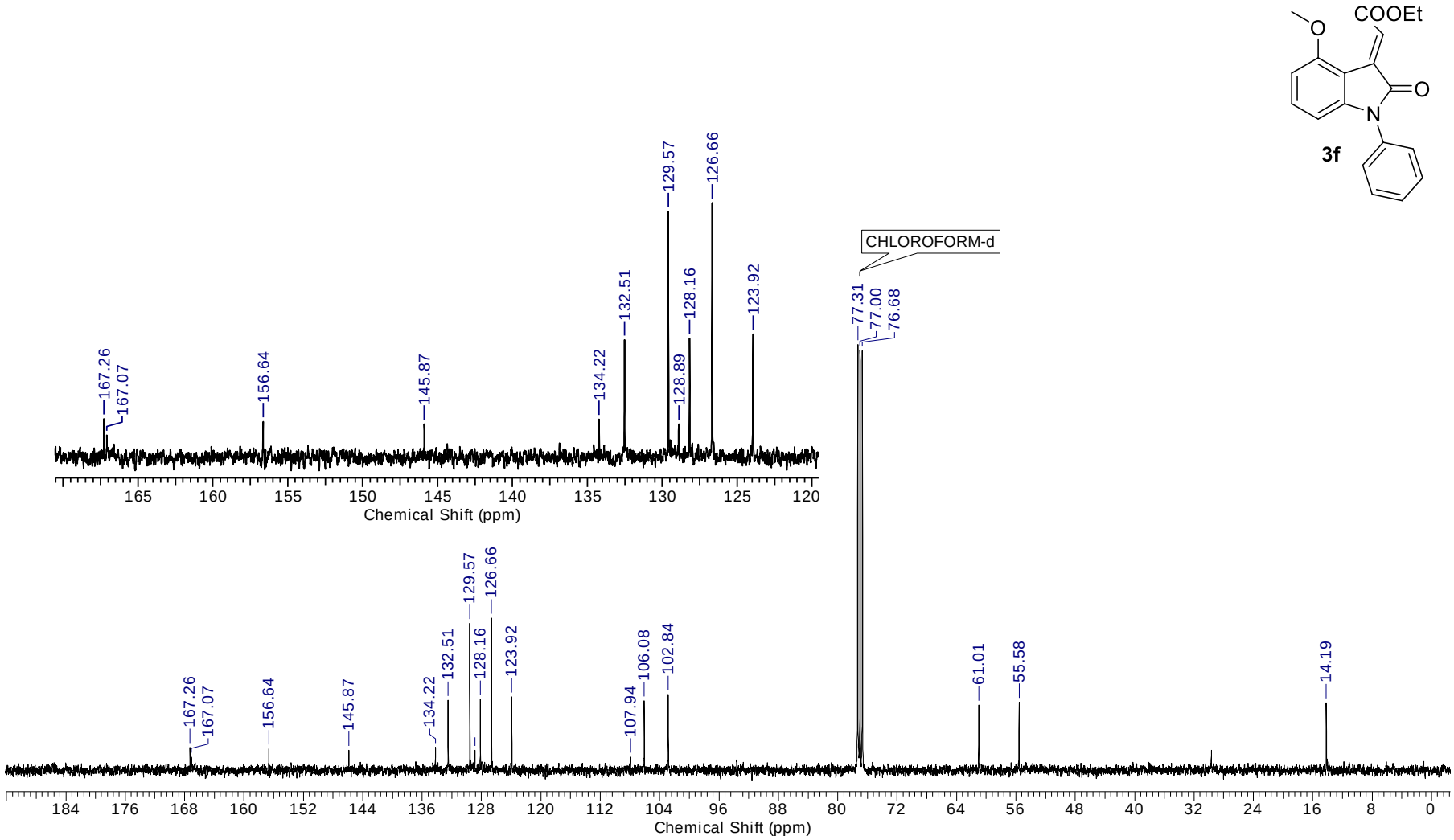
^{1}H NMR 400 MHz



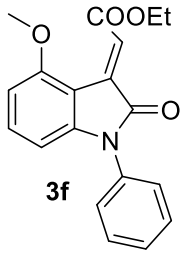
3f

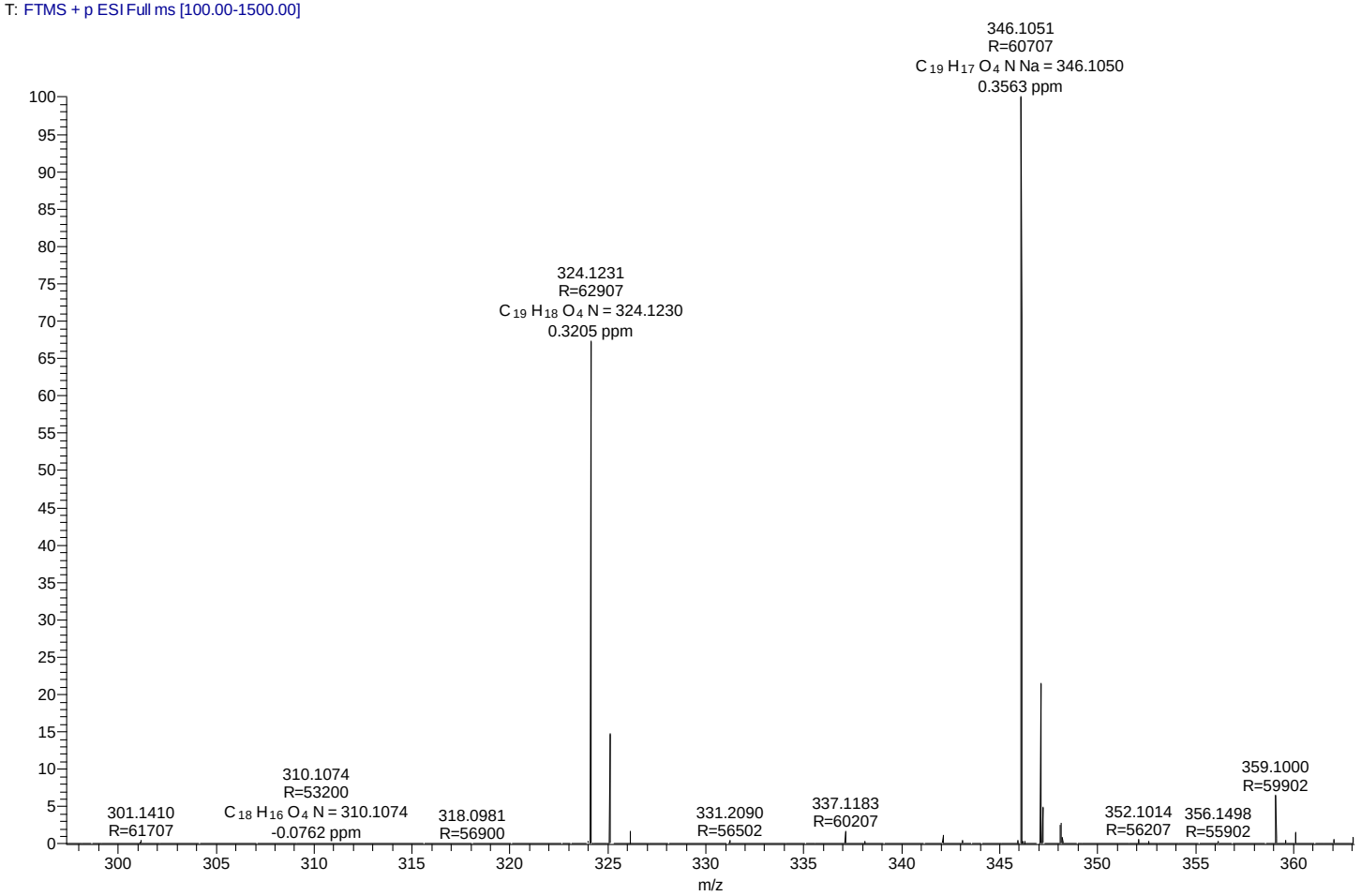


^{13}C NMR 100 MHz

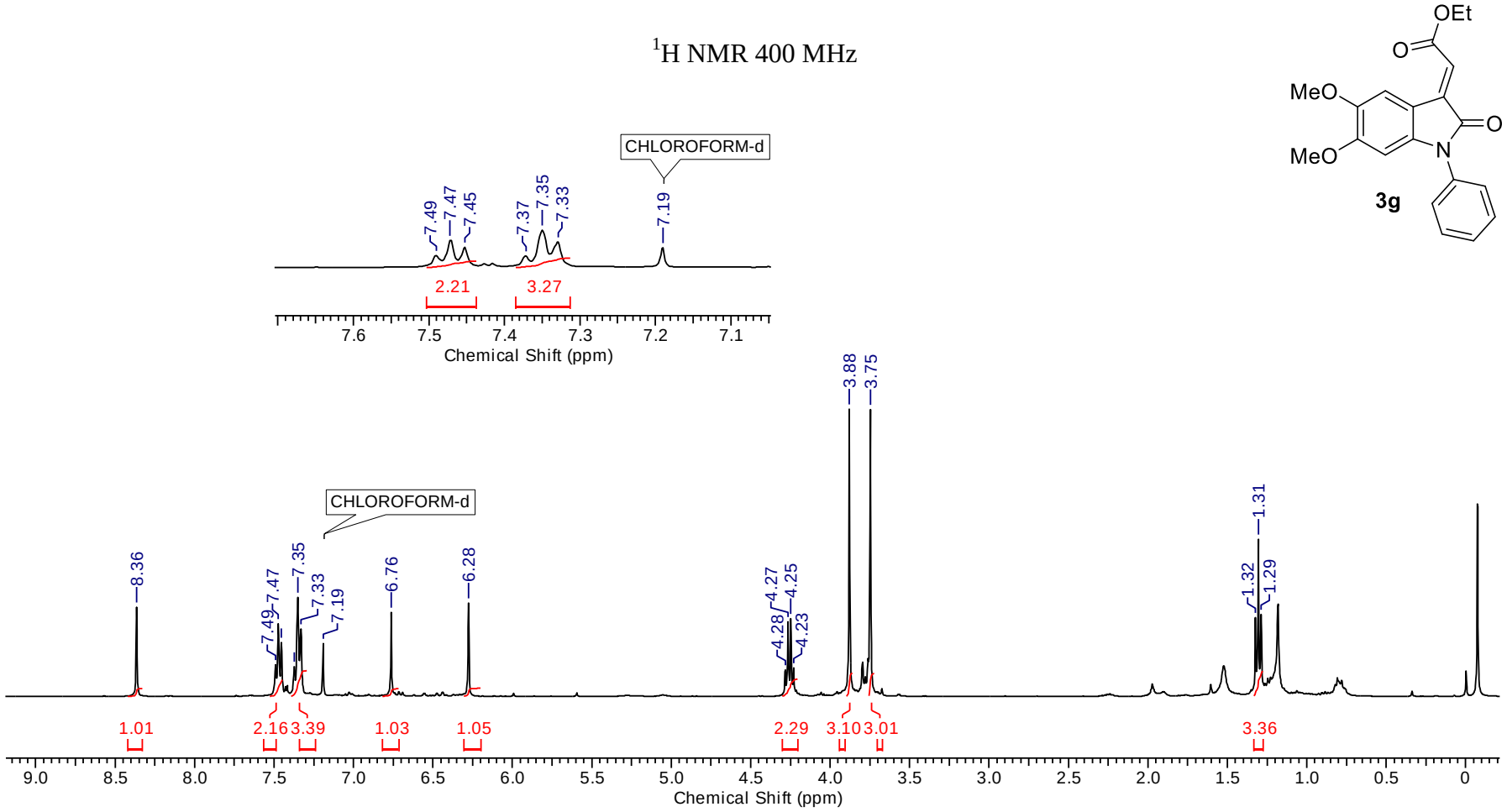


HRMS (ESI-TOF)

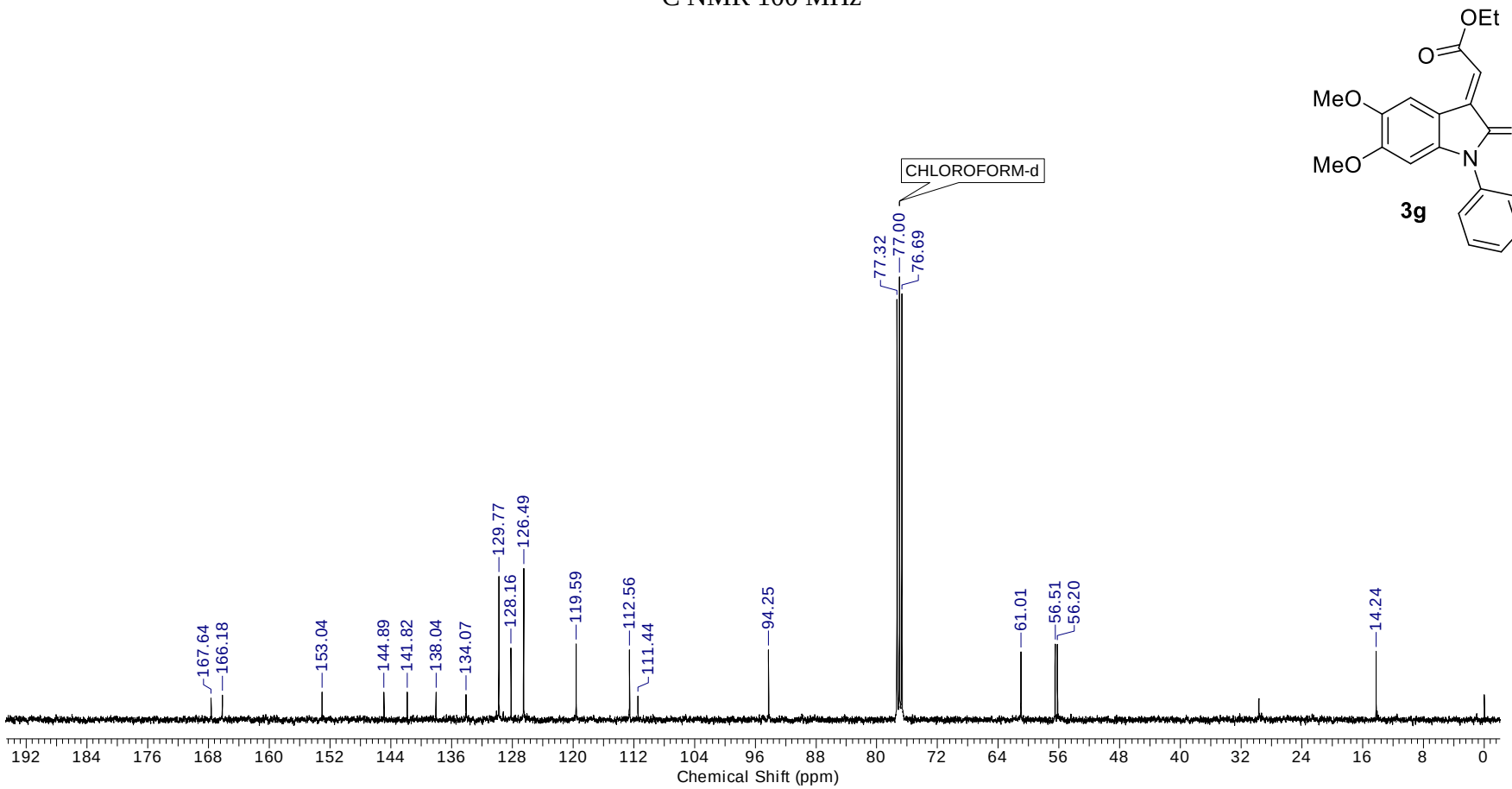

COOEt
O
O
N
3f


VP-8 #108 RT: 0.48 AV: 1 NL: 7.25E8
T: FTMS + p ESI Full ms [100.00-1500.00]
346.1051
R=60707
C19 H17 O4 N Na = 346.1050
0.3563 ppm
324.1231
R=62907
C19 H18 O4 N = 324.1230
0.3205 ppm
310.1074
R=53200
C18 H16 O4 N = 310.1074
-0.0762 ppm
301.1410
R=61707
318.0981
R=56900
331.2090
R=56502
337.1183
R=60207
352.1014
R=56207
356.1498
R=55902
359.1000
R=59902
m/z

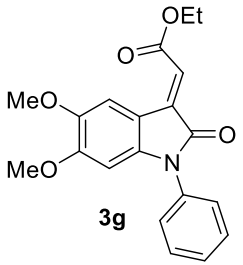
^{1}H NMR 400 MHz



^{13}C NMR 100 MHz

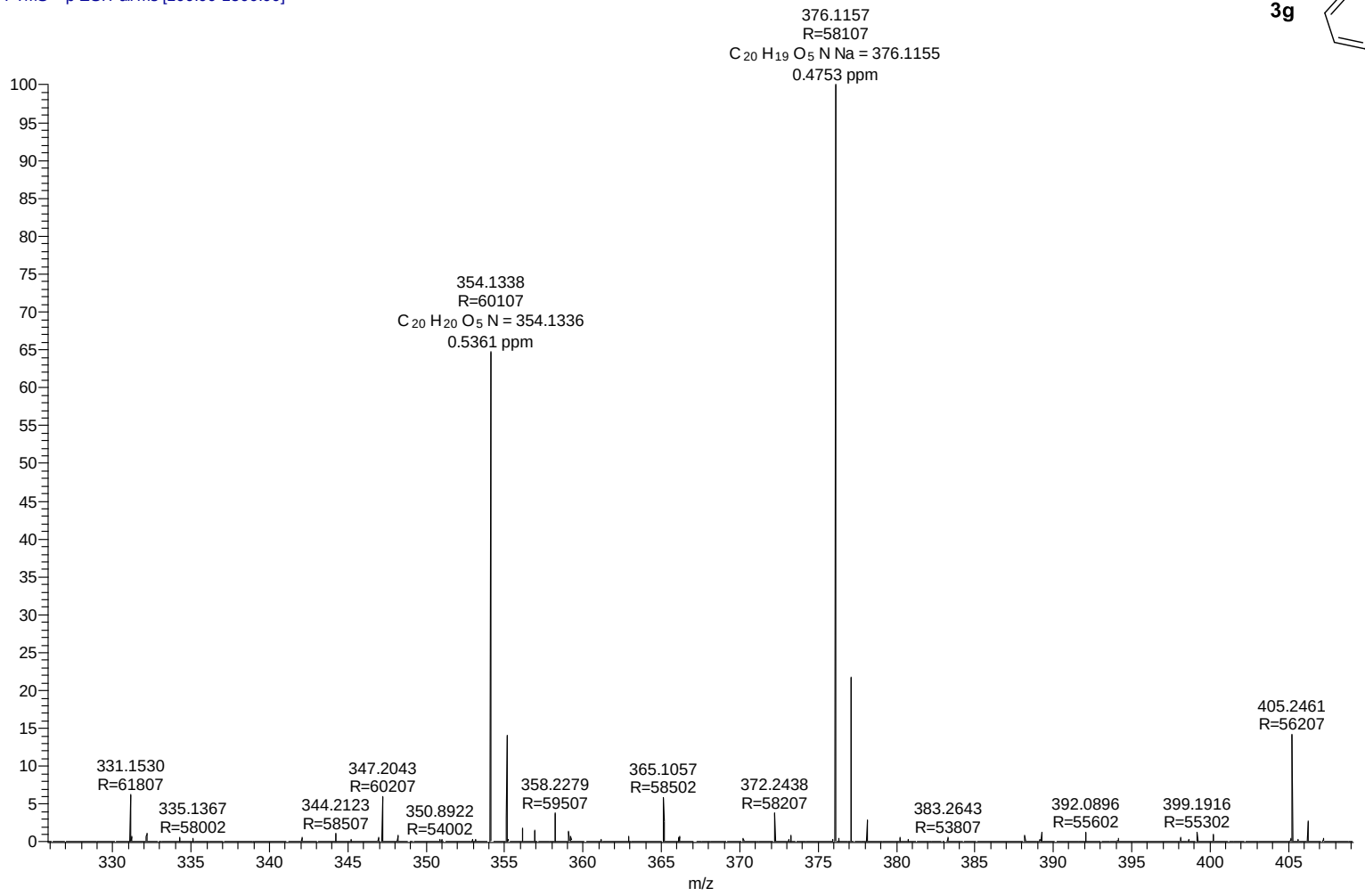


HRMS (ESI-TOF)

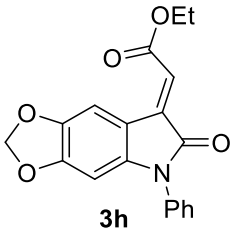


3g

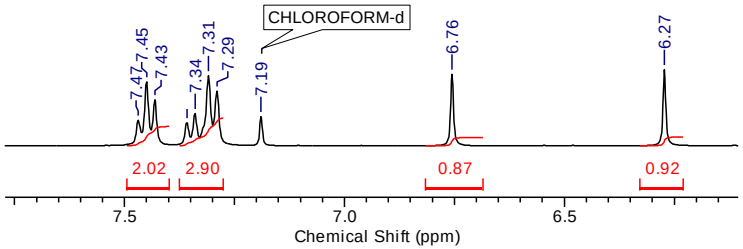
VP-7 #121 RT: 0.54 AV: 1 NL: 2.00E8
T: FTMS + p ESI Full ms [100.00-1500.00]

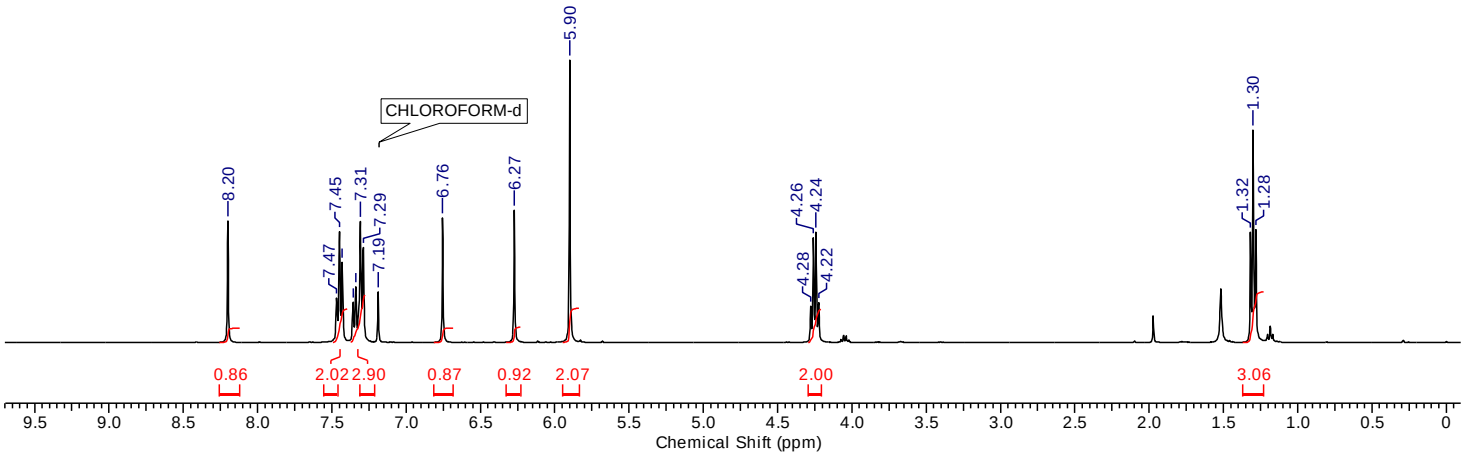


^{1}H NMR 400 MHz

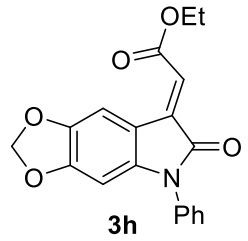


3h

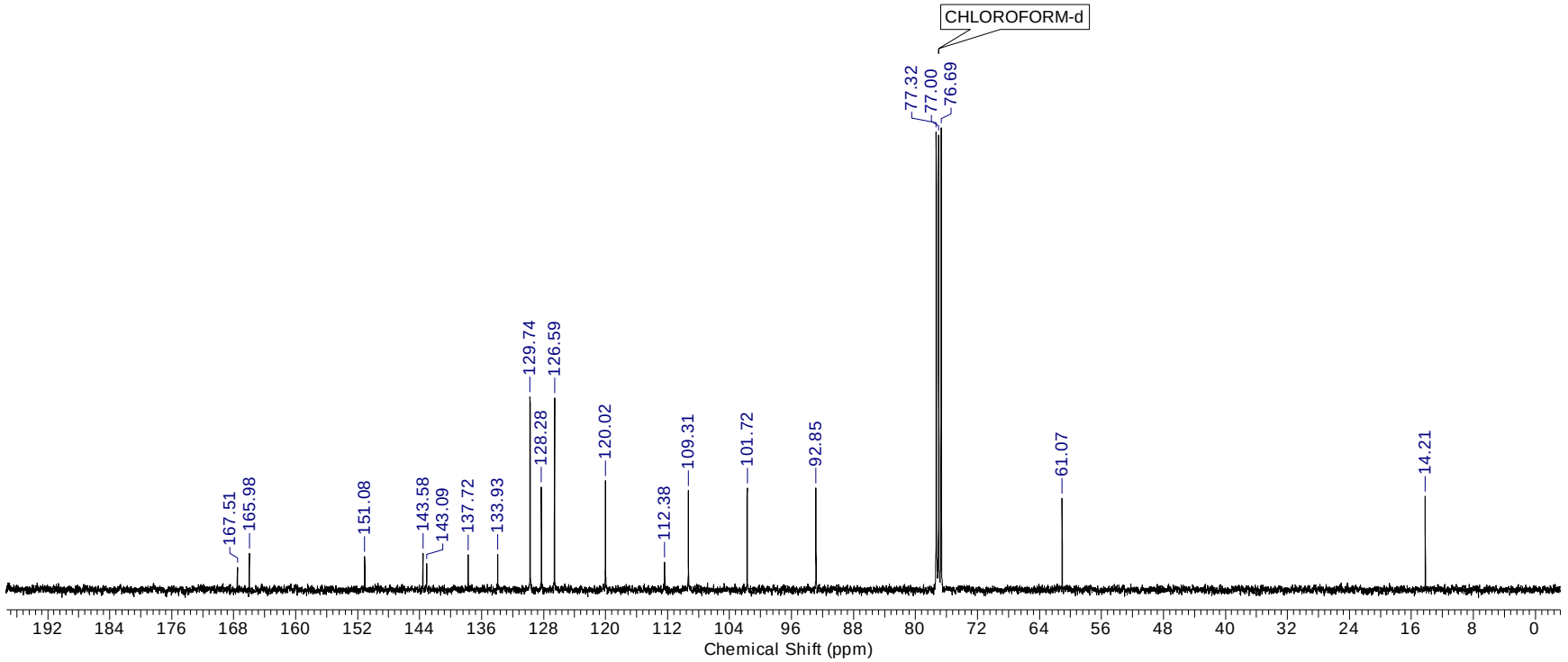




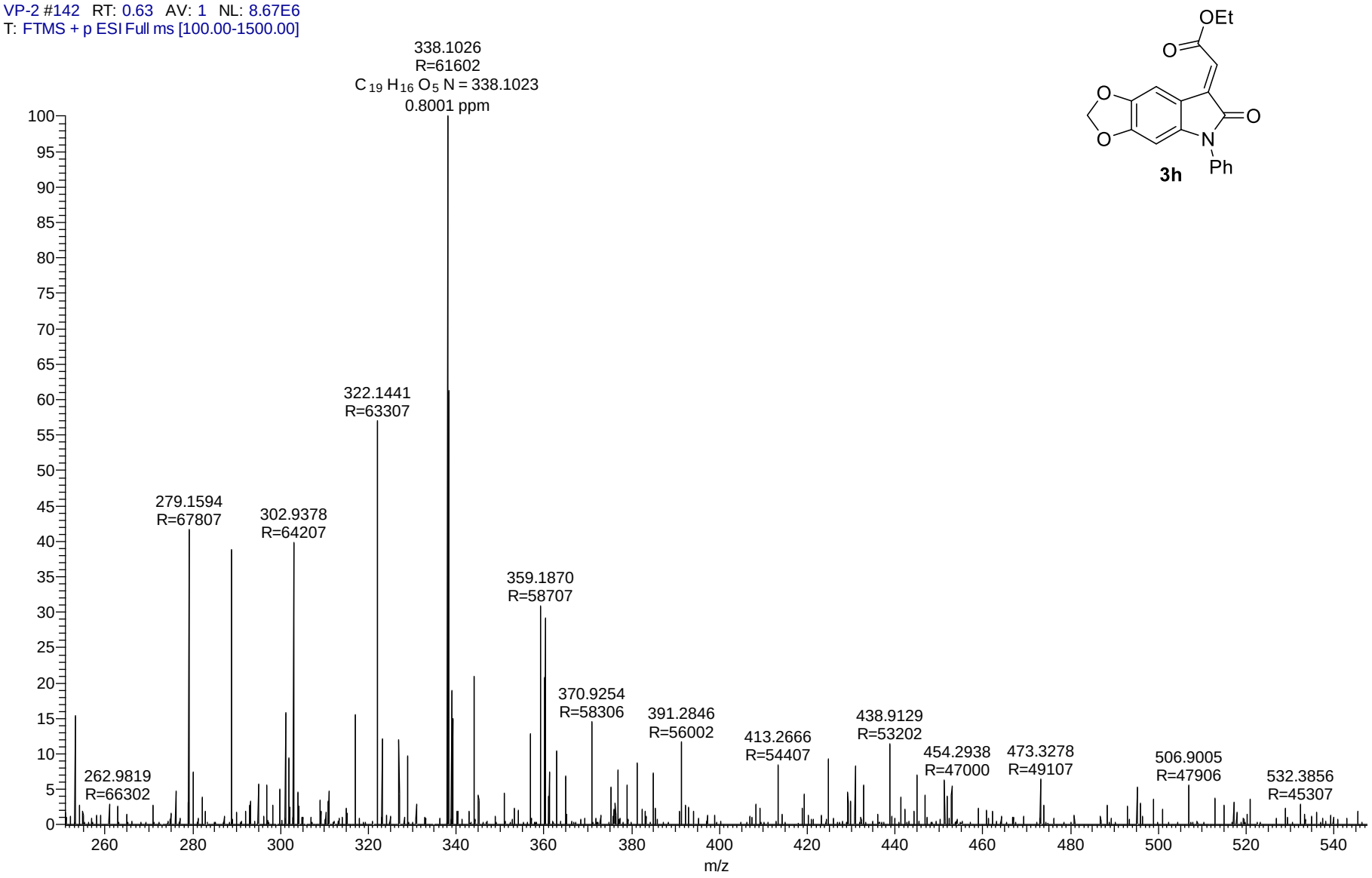
^{13}C NMR 100 MHz



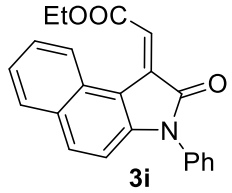
3h



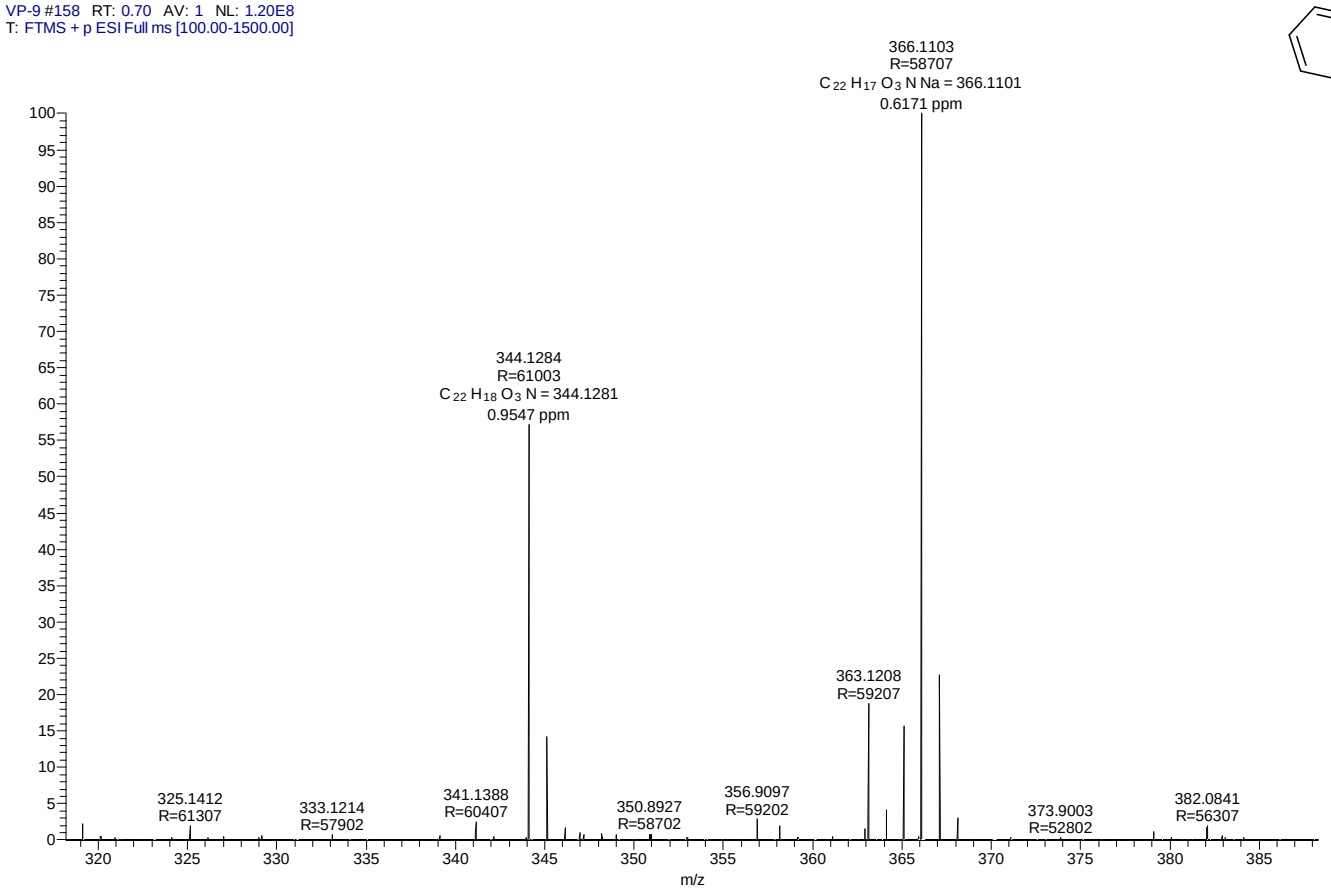
HRMS (ESI-TOF)


VP-2 #142 RT: 0.63 AV: 1 NL: 8.67E6
T: FTMS + p ESI Full ms [100.00-1500.00]
338.1026
R=61602
C 19 H 16 O 5 N = 338.1023
0.8001 ppm
322.1441
R=63307
279.1594
R=67807
302.9378
R=64207
359.1870
R=58707
370.9254
R=58306
391.2846
R=56002
413.2666
R=54407
438.9129
R=53202
454.2938
R=47000
473.3278
R=49107
506.9005
R=47906
532.3856
R=45307
262.9819
R=66302
m/z
OEt
O
O
O
O
N
Ph
3h

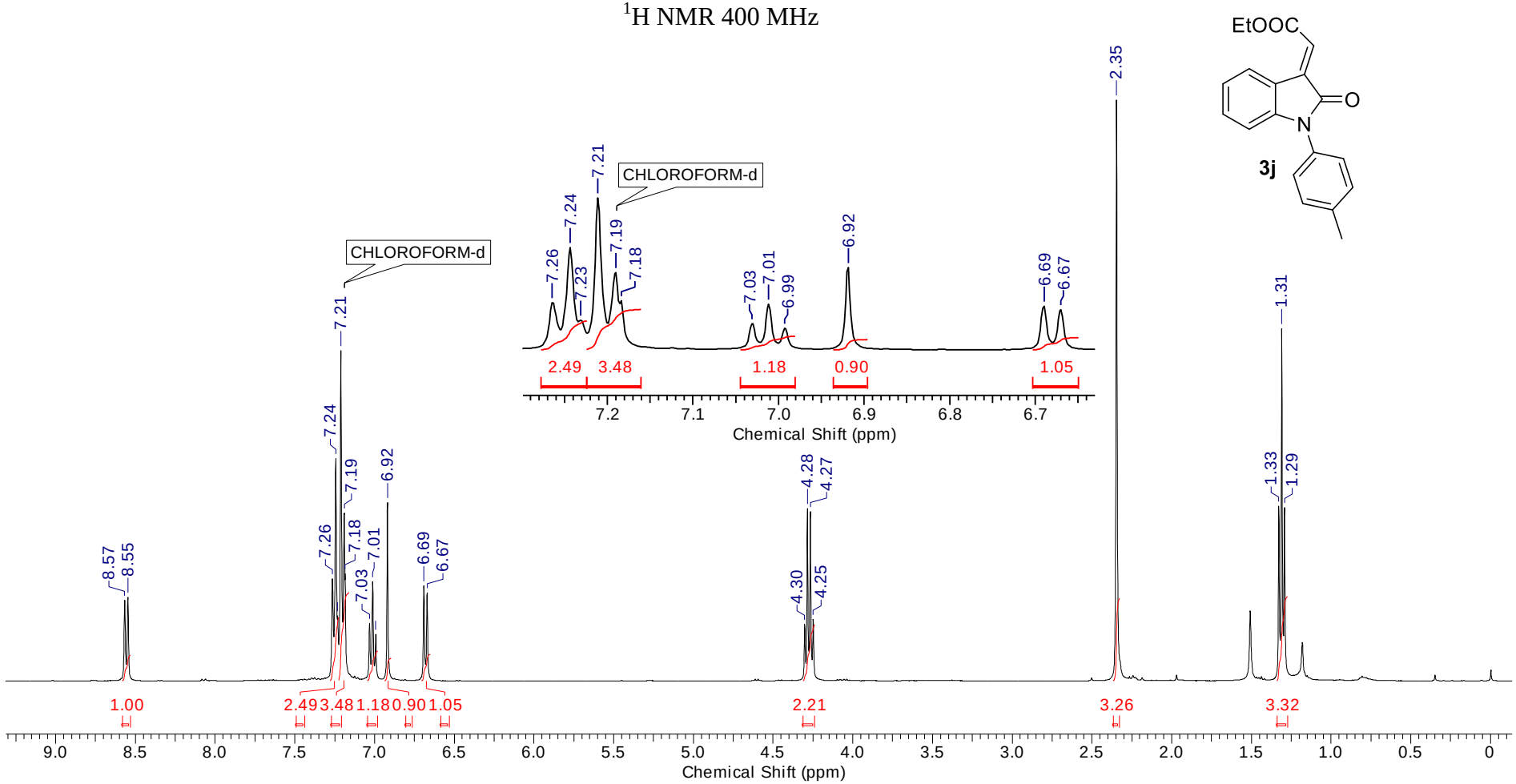
HRMS (ESI-TOF)



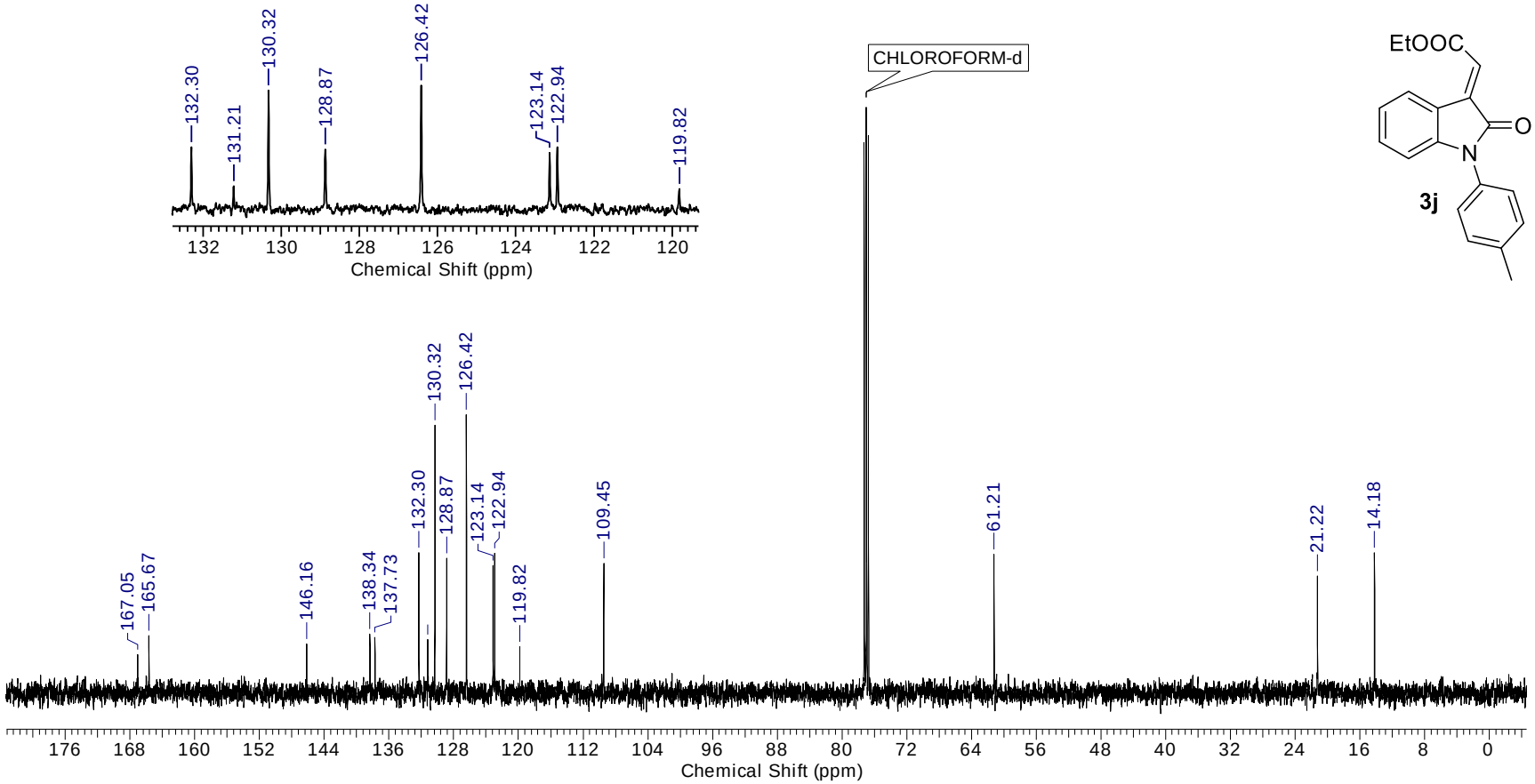
3i



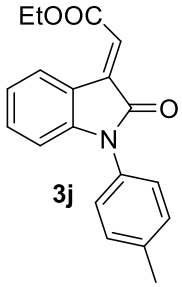
^{1}H NMR 400 MHz



^{13} C NMR 125 MHz

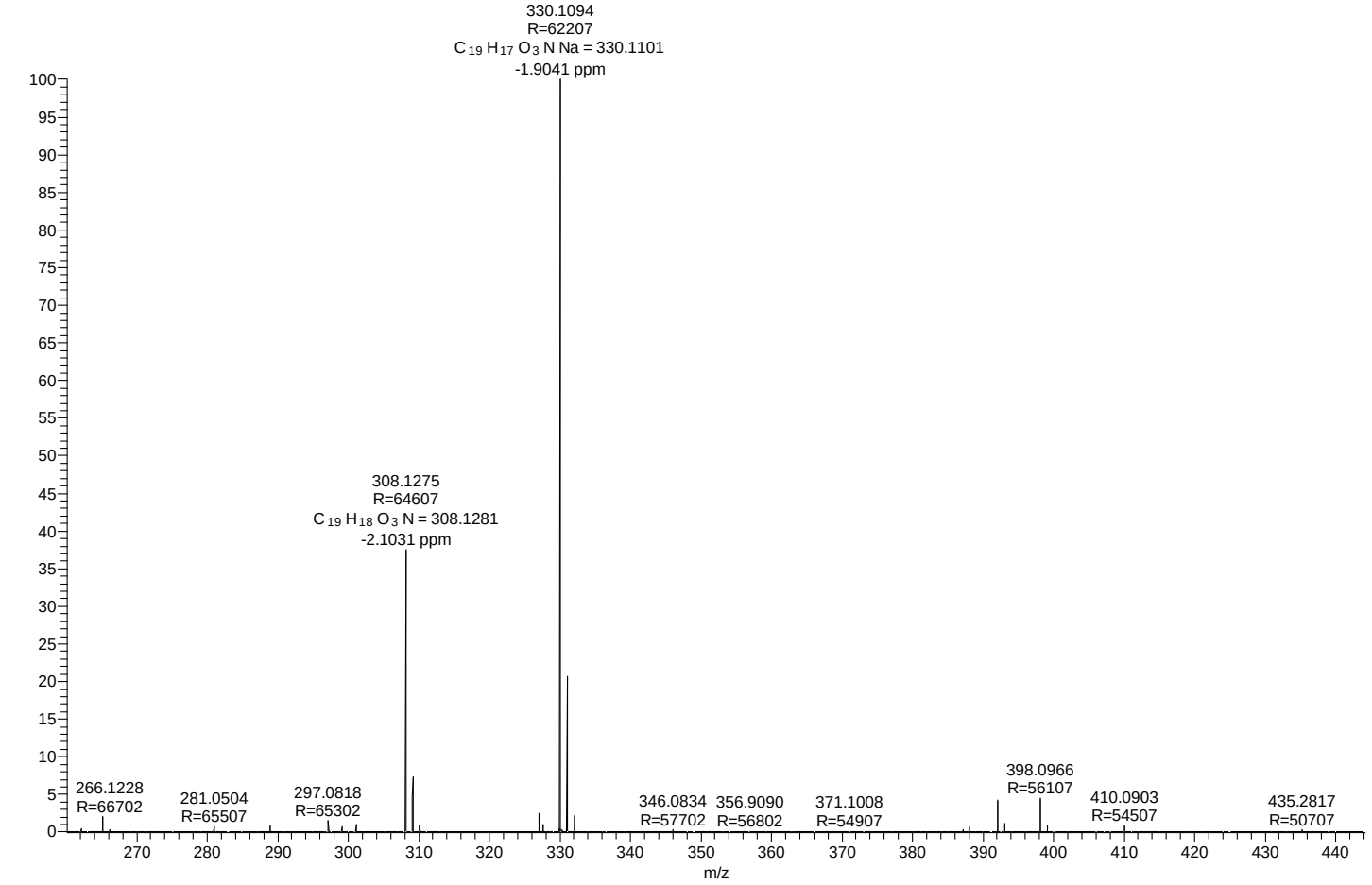


HRMS (ESI-TOF)

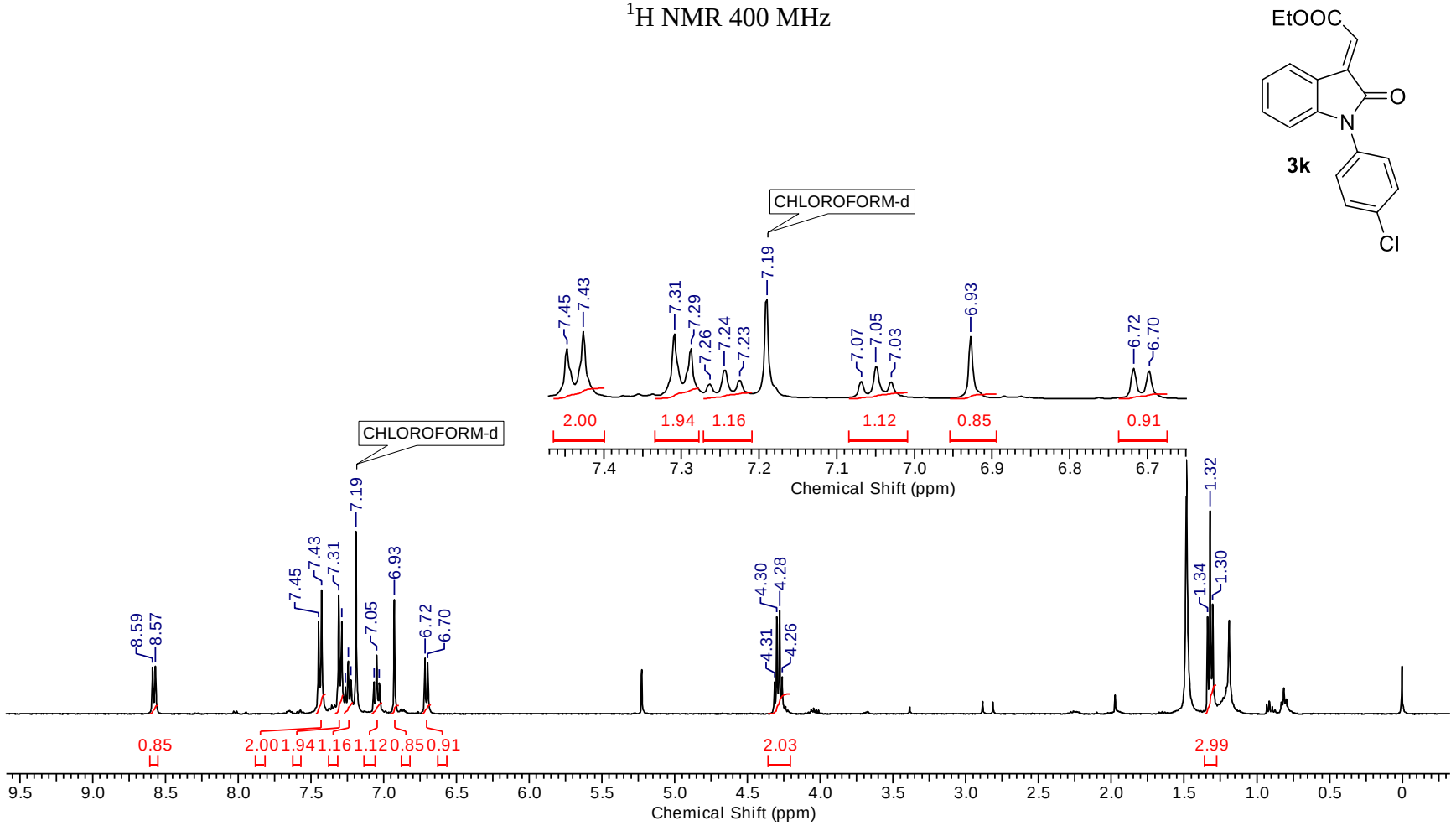


3j

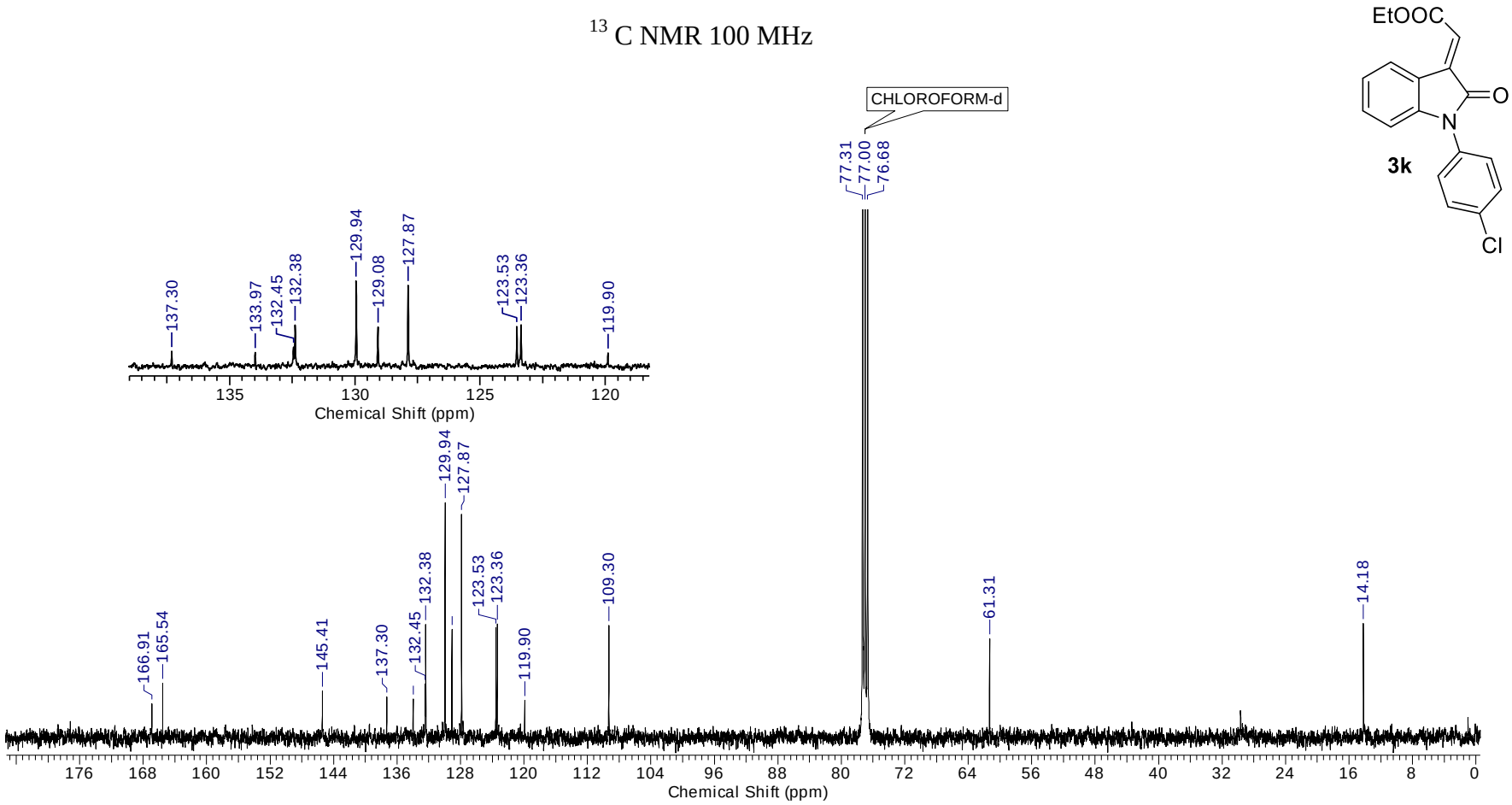
VPP-2 #139 RT: 0.62 AV: 1 NL: 4.71E8
T: FTMS + p ESI Full ms [100.00-1500.00]



^{1}H NMR 400 MHz

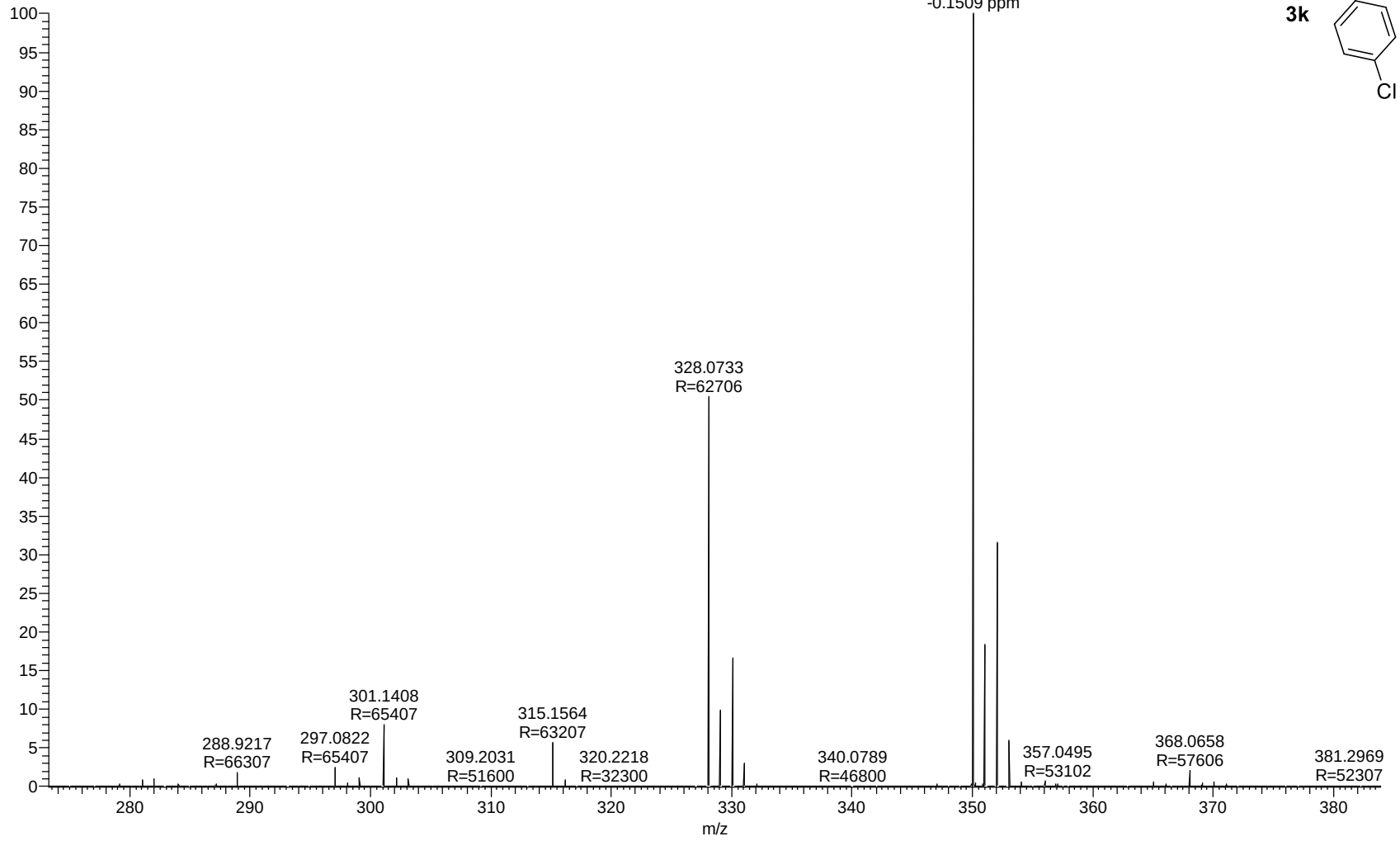


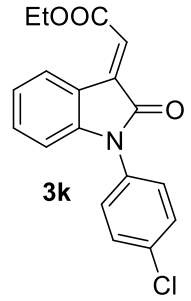
^{13} C NMR 100 MHz



HRMS (ESI-TOF)

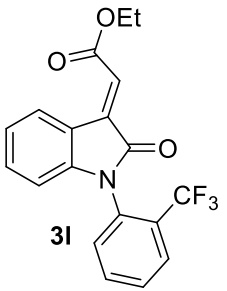
VPP-4_170712162636 #157 RT: 0.70 AV: 1 NL: 2.71E8
T: FTMS + p ESI Full ms [100.00-1500.00]



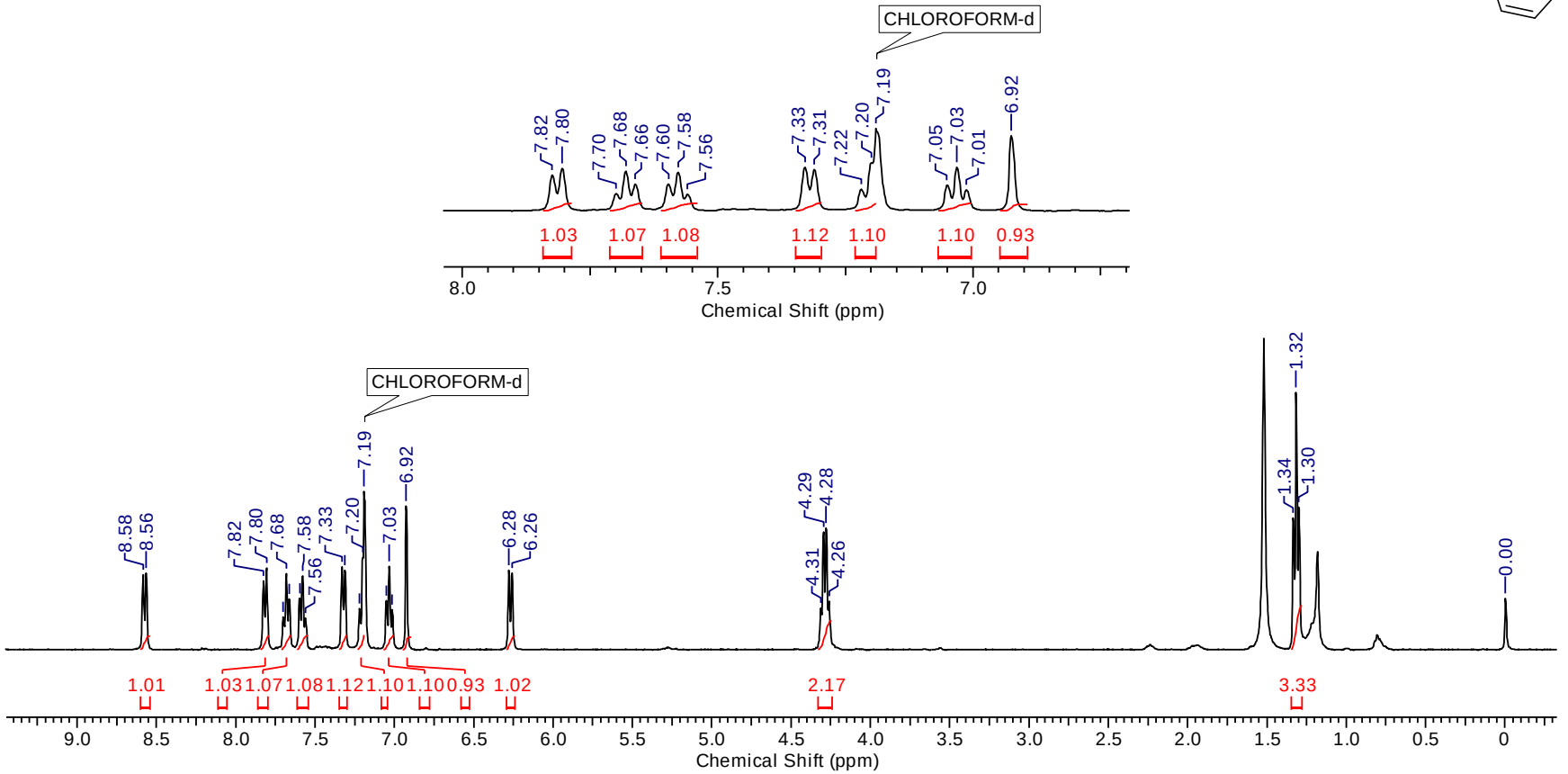


3k

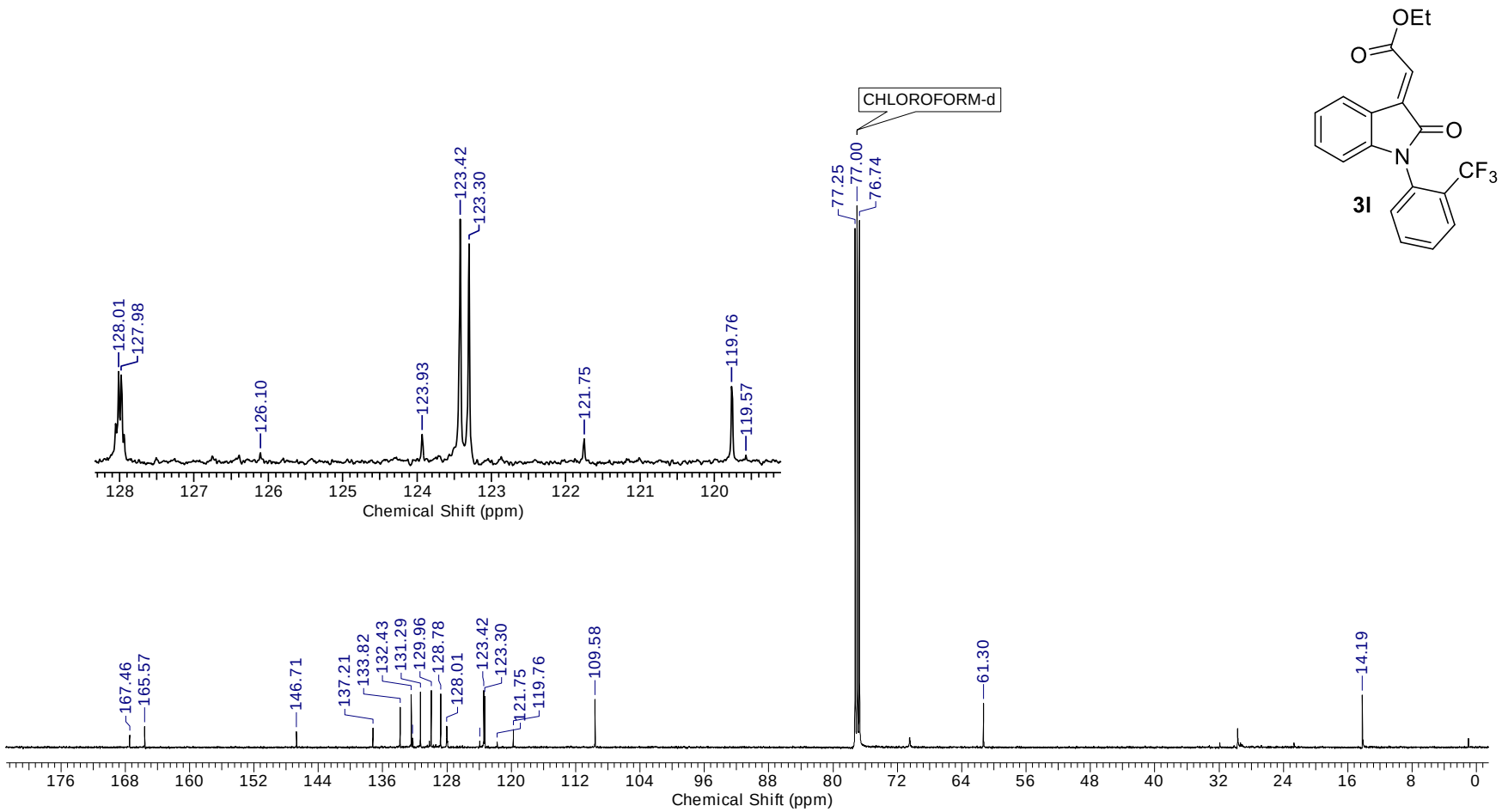
^{1}H NMR 400 MHz



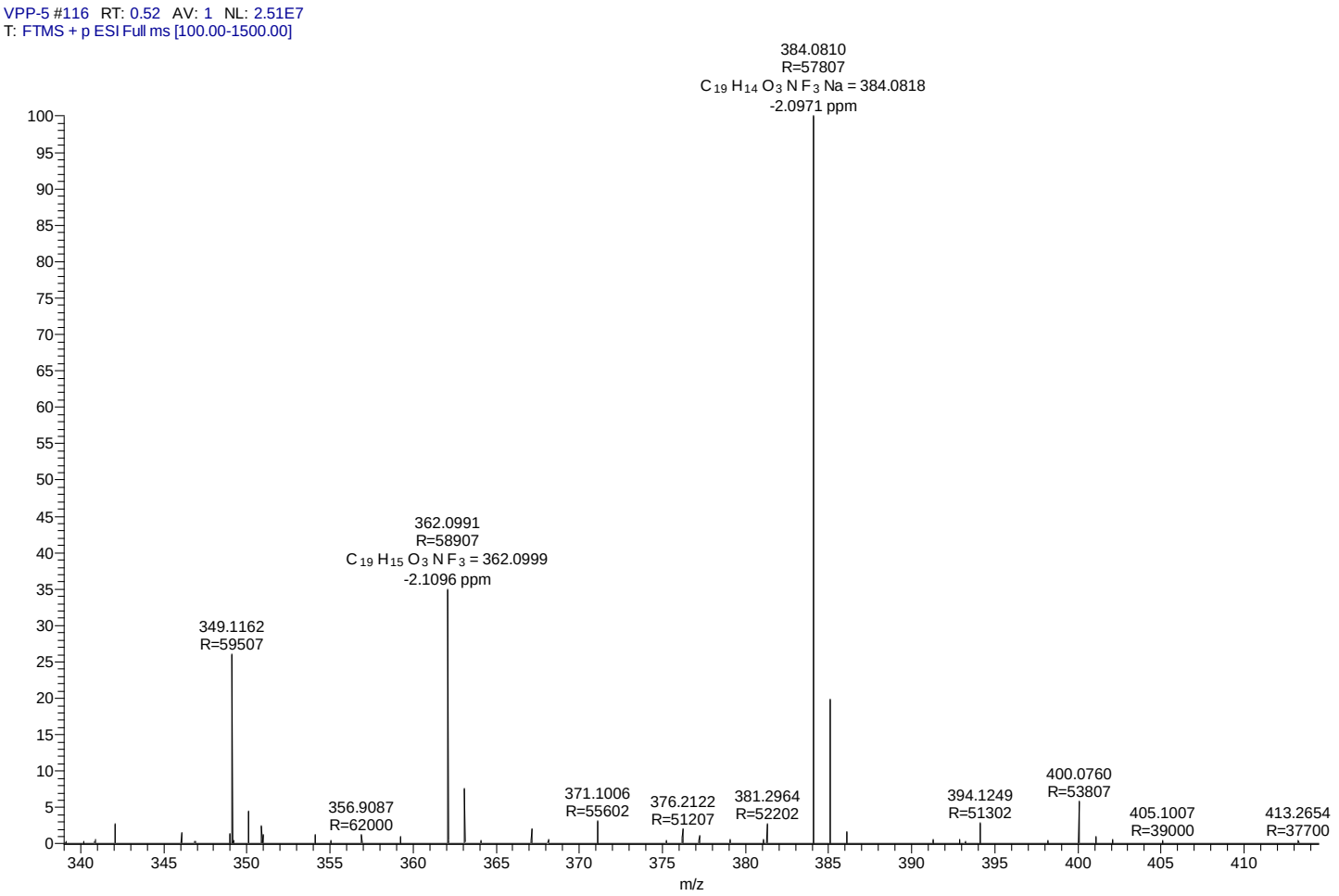
3l

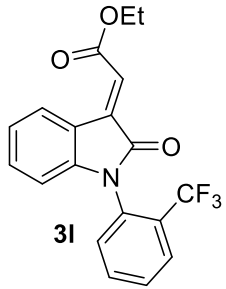


^{13} C NMR 125 MHz

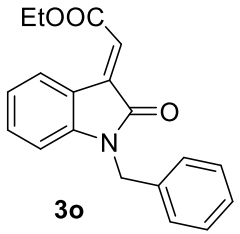


HRMS (ESI-TOF)

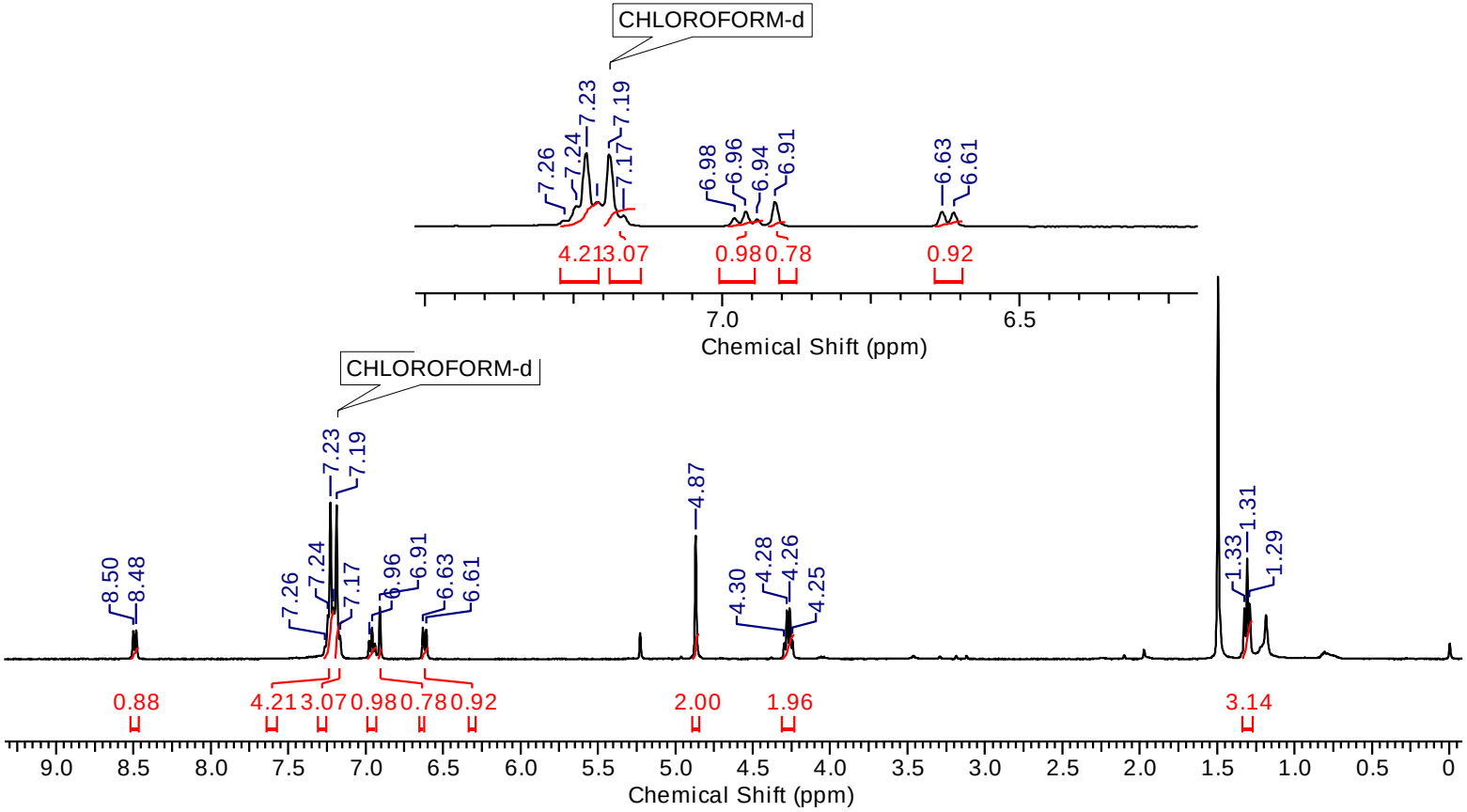

VPP-5 #116 RT: 0.52 AV: 1 NL: 2.51E7
T: FTMS + p ESI Full ms [100.00-1500.00]
384.0810
R=57807
C19 H14 O3 N F3 Na = 384.0818
-2.0971 ppm
362.0991
R=58907
C19 H15 O3 N F3 = 362.0999
-2.1096 ppm
349.1162
R=59507
356.9087
R=62000
371.1006
R=55602
376.2122
R=51207
381.2964
R=52202
394.1249
R=51302
400.0760
R=53807
405.1007
R=39000
413.2654
R=37700
m/z


OEt
O
O
N
CF3
3l

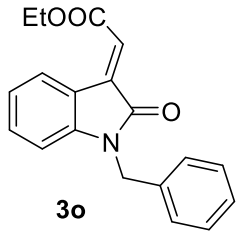
^{1}H NMR 400 MHz



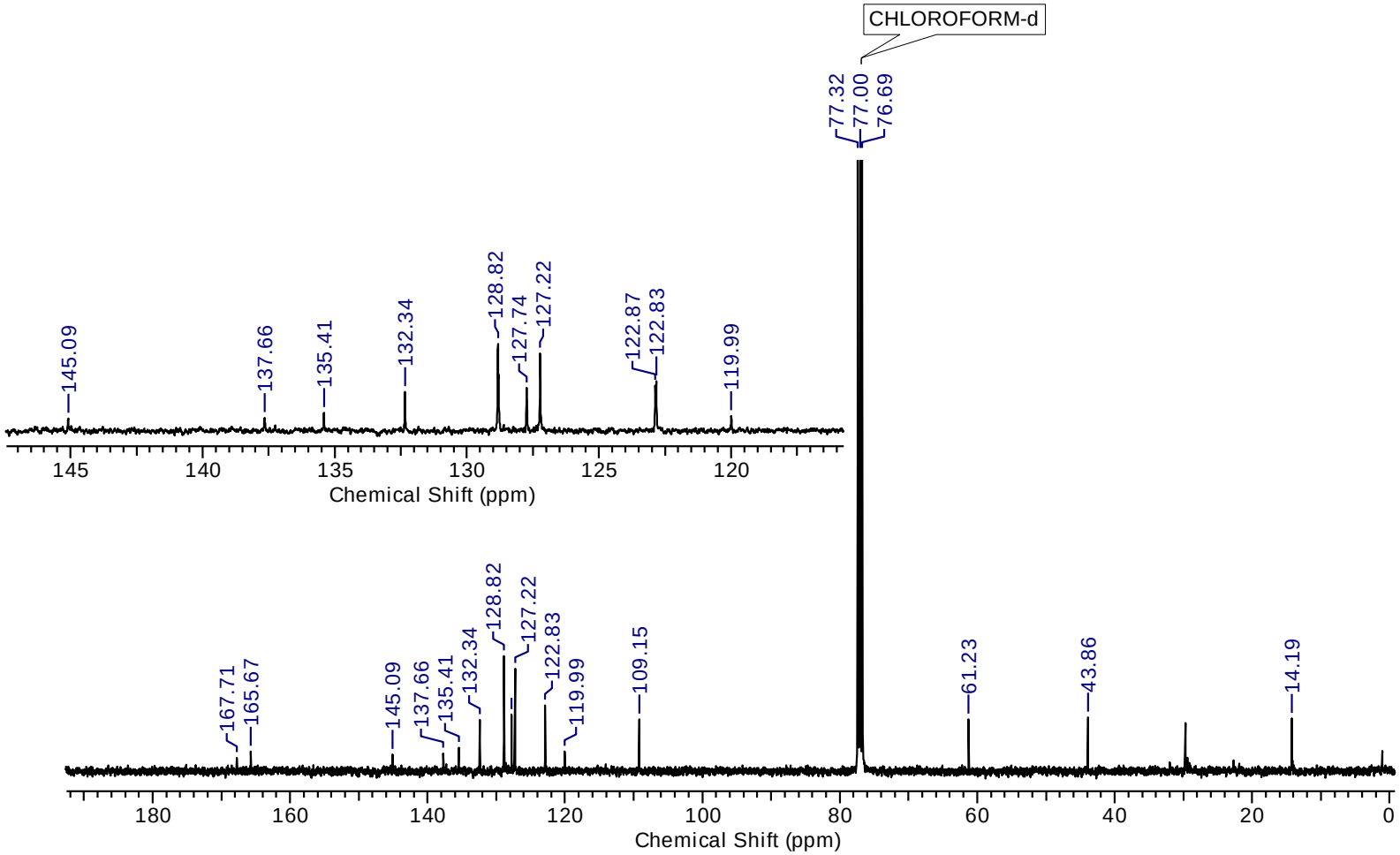
3o



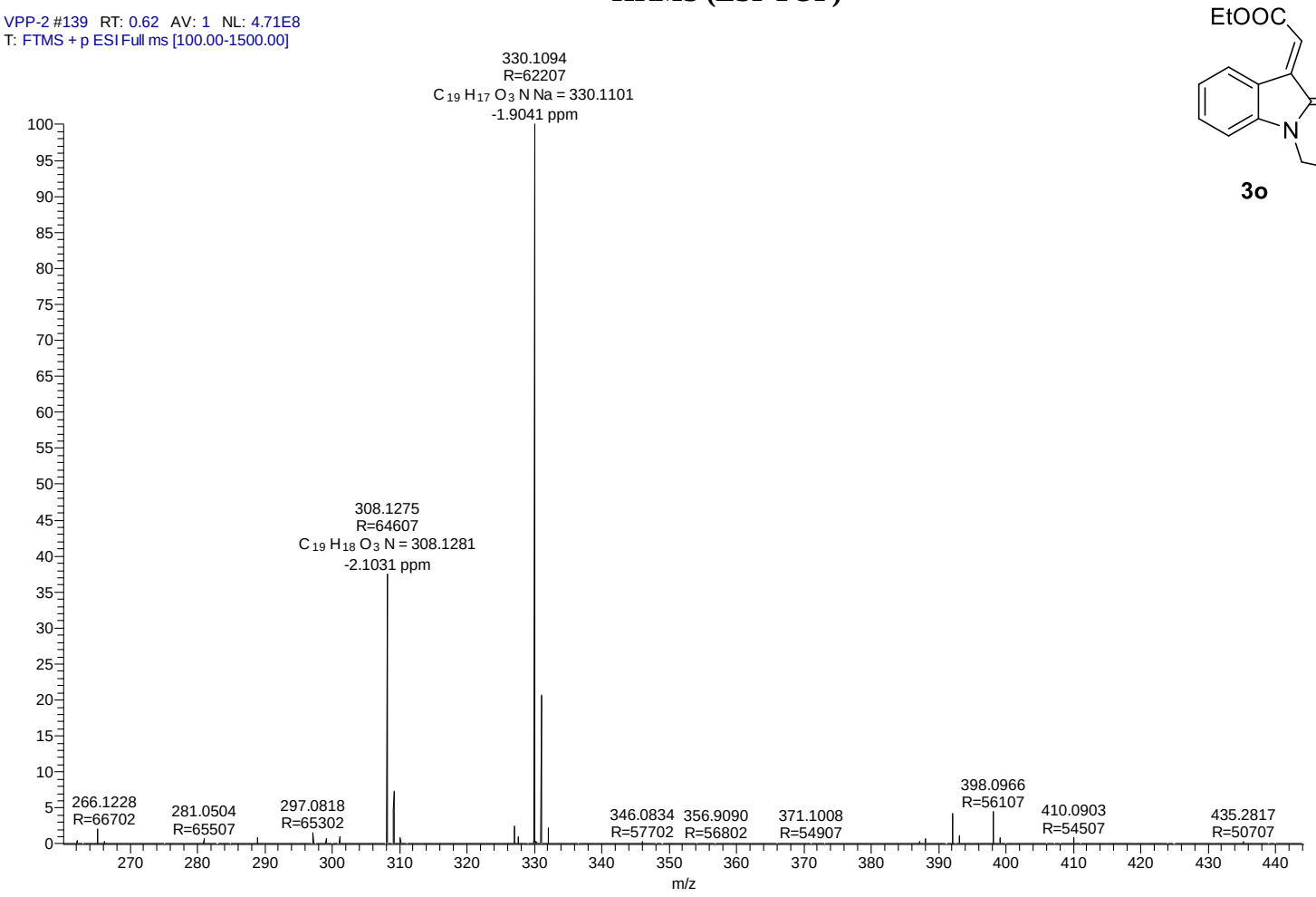
^{13} C NMR 100 MHz



3o

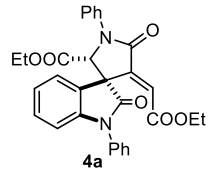


HRMS (ESI-TOF)

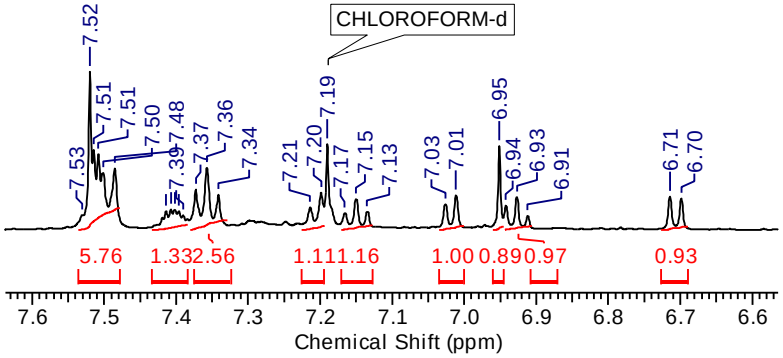


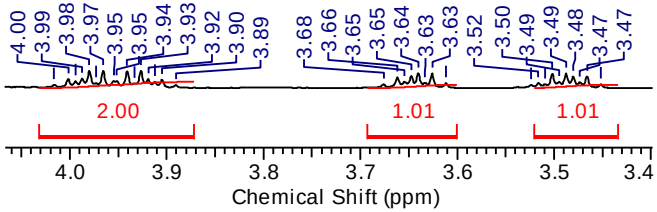
3o

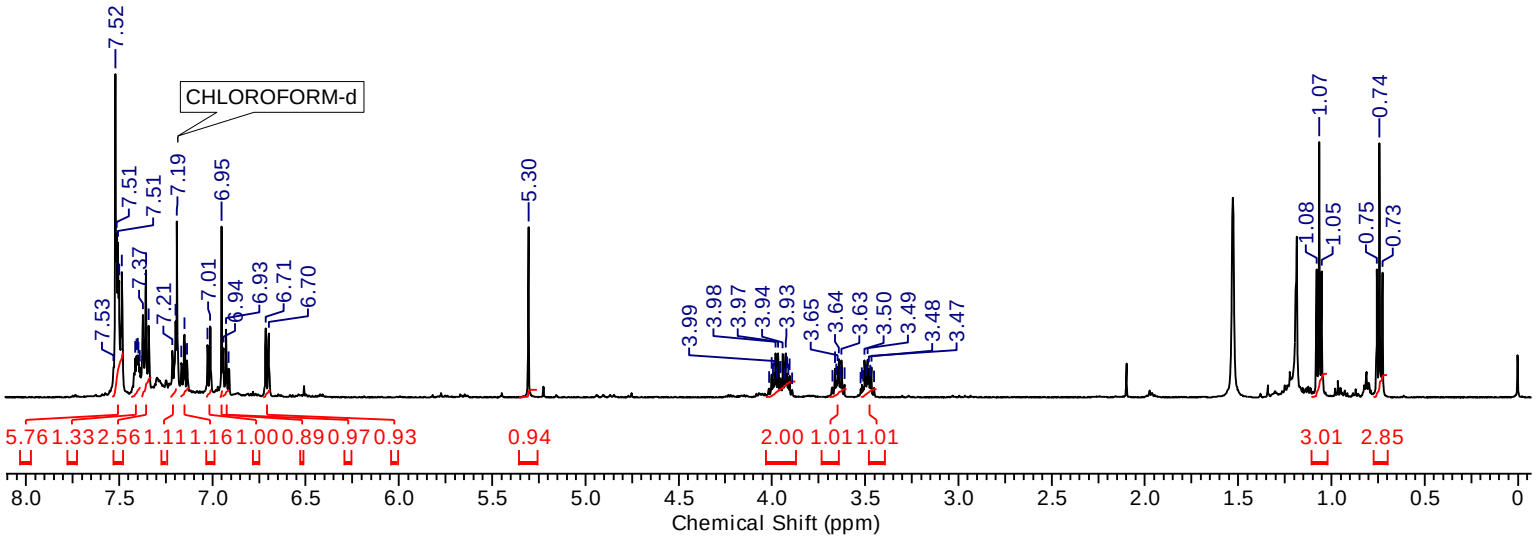
^{1}H NMR 500 MHz



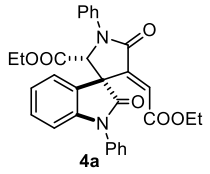
4a

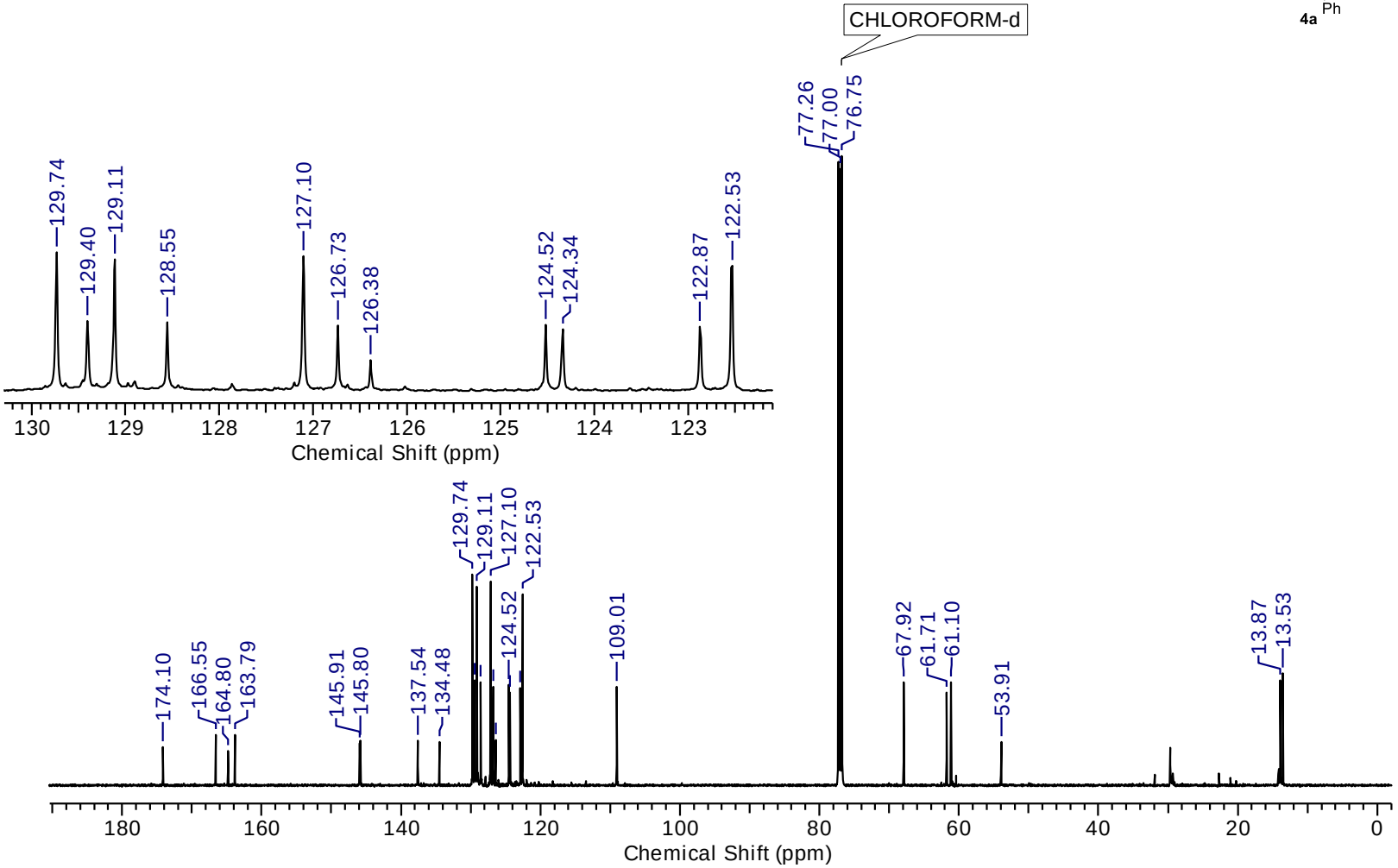




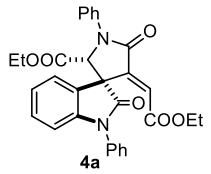


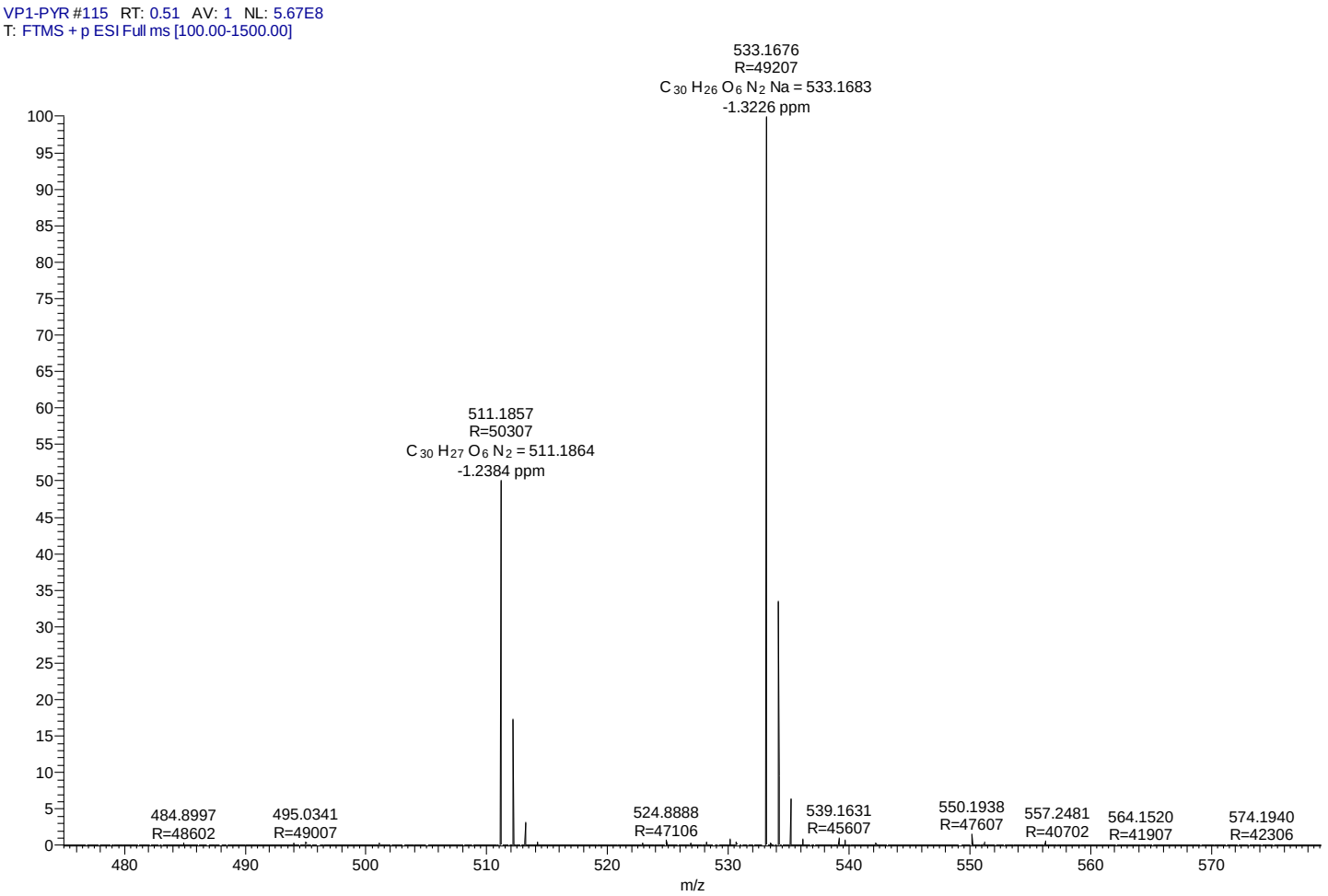
^{13} C NMR 125 MHz



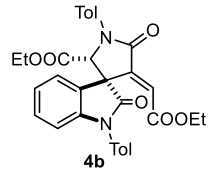


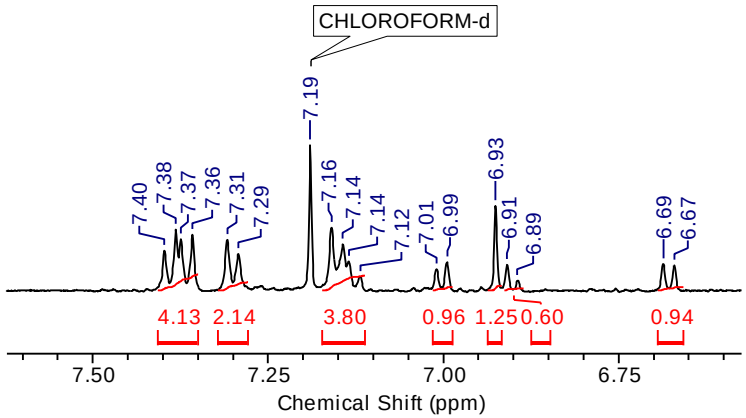
ESI HRMS

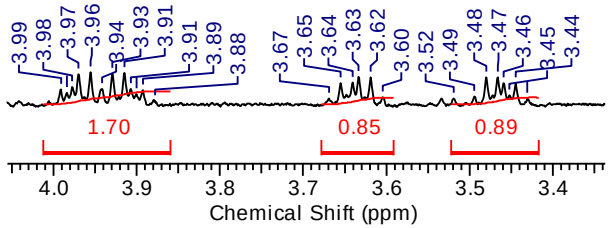

Ph
N
O
EtOOC
O
N
Ph
COOEt
4a

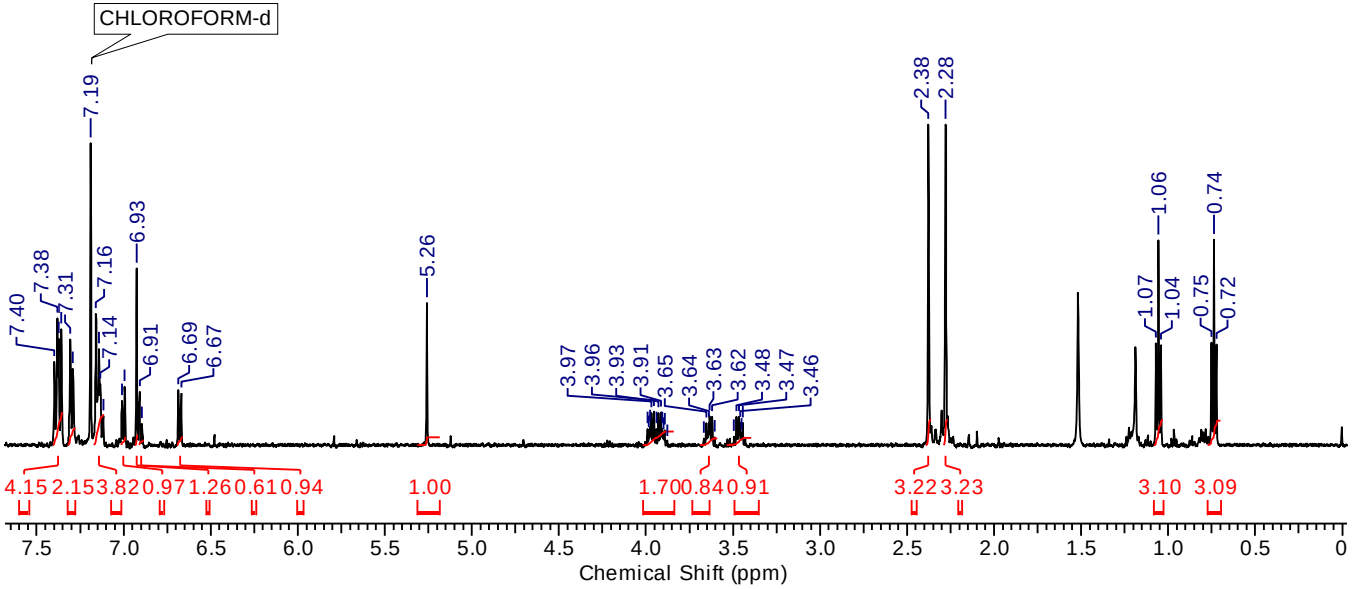

VP1-PYR #115 RT: 0.51 AV: 1 NL: 5.67E8
T: FTMS + p ESI Full ms [100.00-1500.00]
533.1676
R=49207
C30 H26 O6 N2 Na = 533.1683
-1.3226 ppm
511.1857
R=50307
C30 H27 O6 N2 = 511.1864
-1.2384 ppm
484.8997
R=48602
495.0341
R=49007
524.8888
R=47106
539.1631
R=45607
550.1938
R=47607
557.2481
R=40702
564.1520
R=41907
574.1940
R=42306
m/z

^{1}H NMR 400 MHz

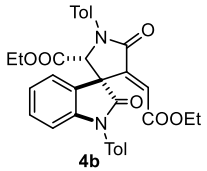


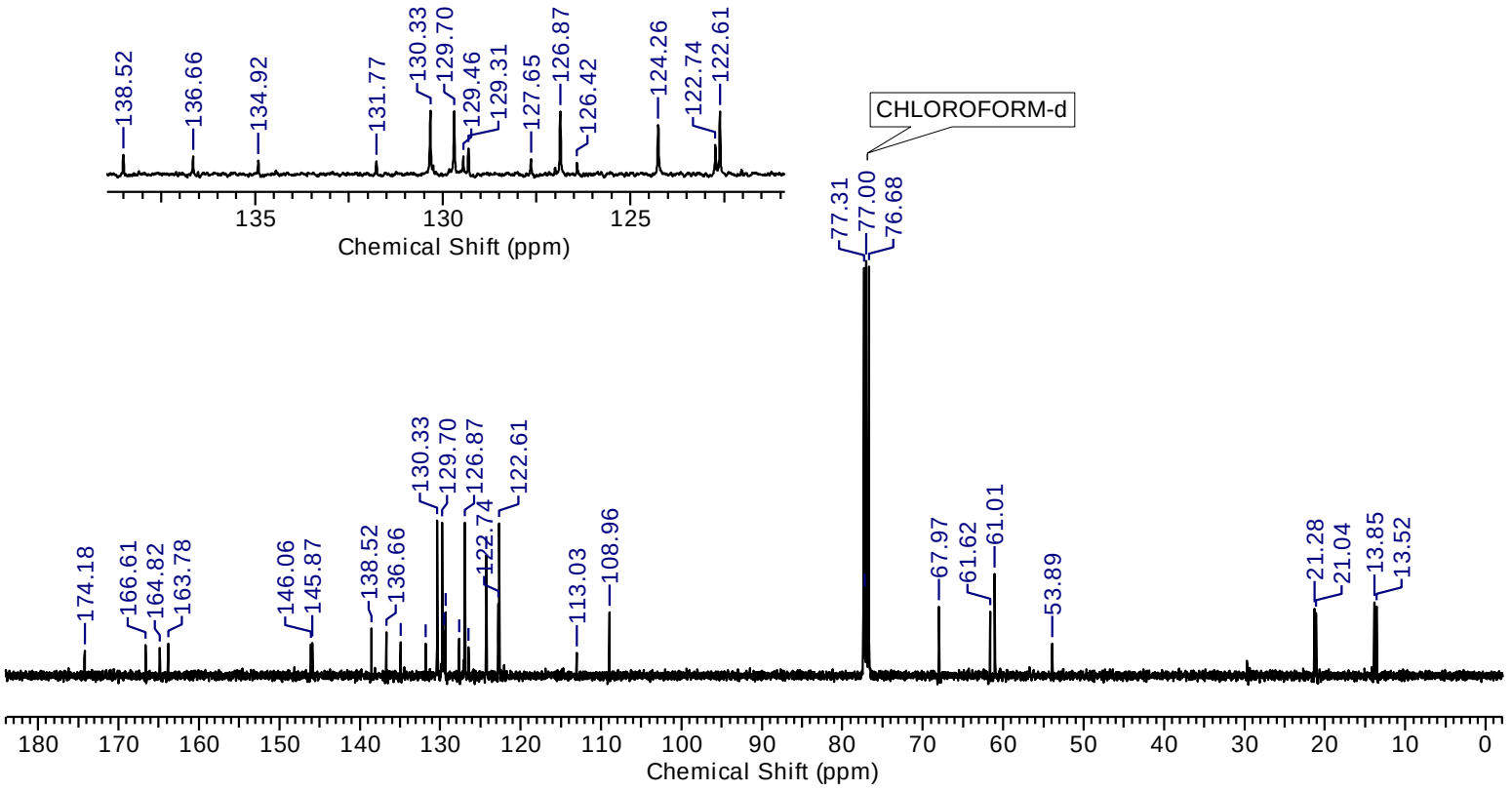




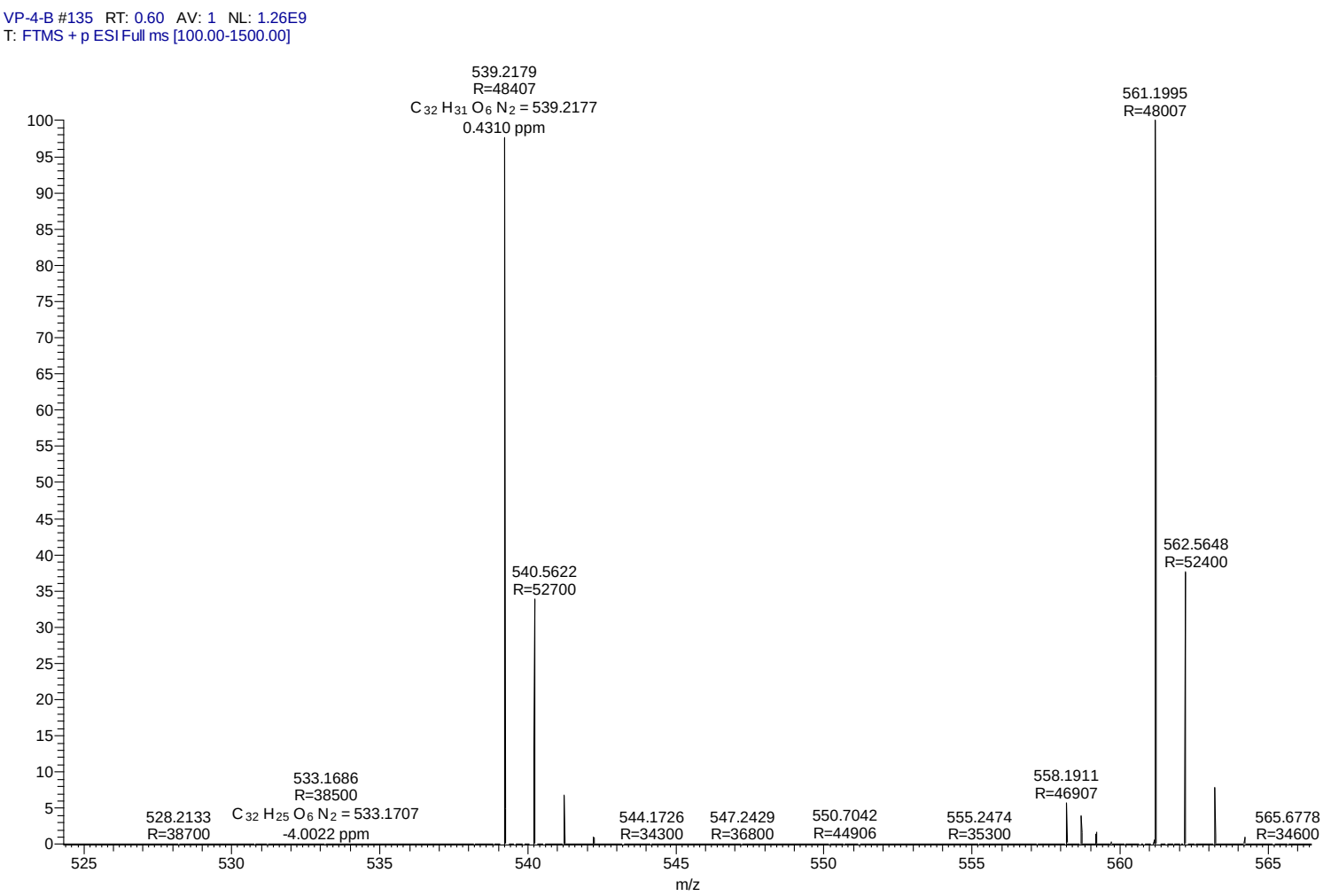


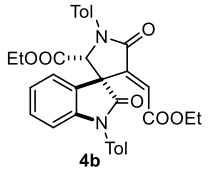
^{13}C NMR 100 MHz





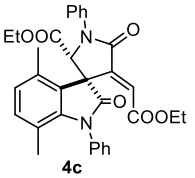
HRMS (ESI-TOF)



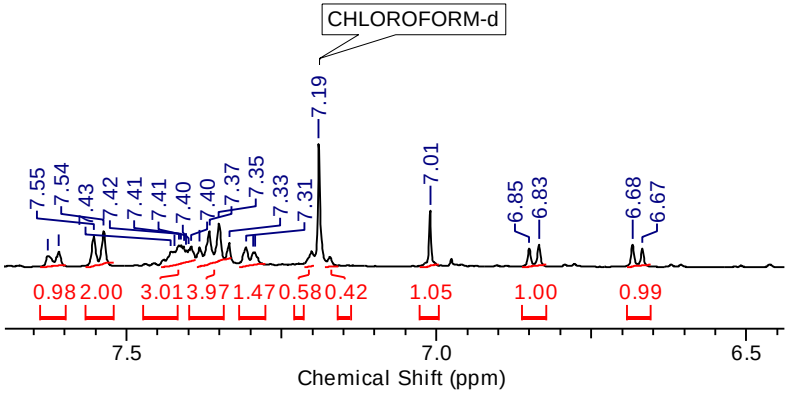


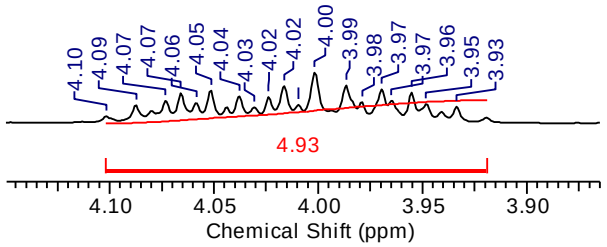
4b

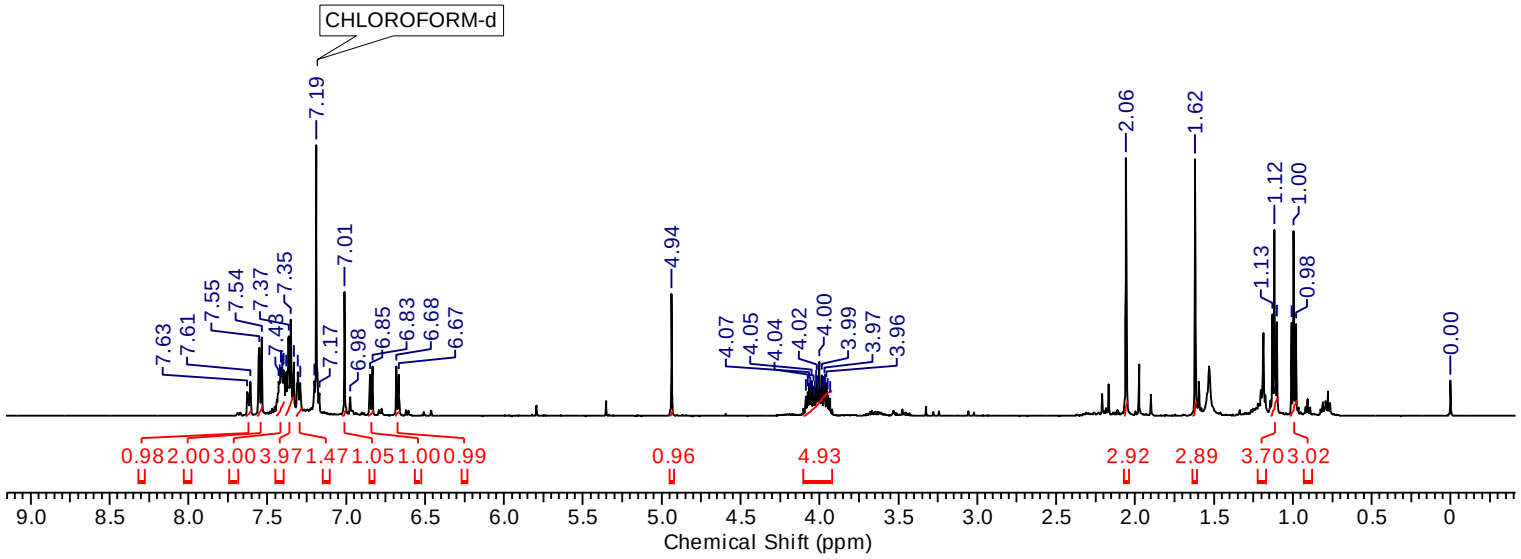
^{1}H NMR 400 MHz



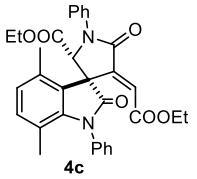
4c



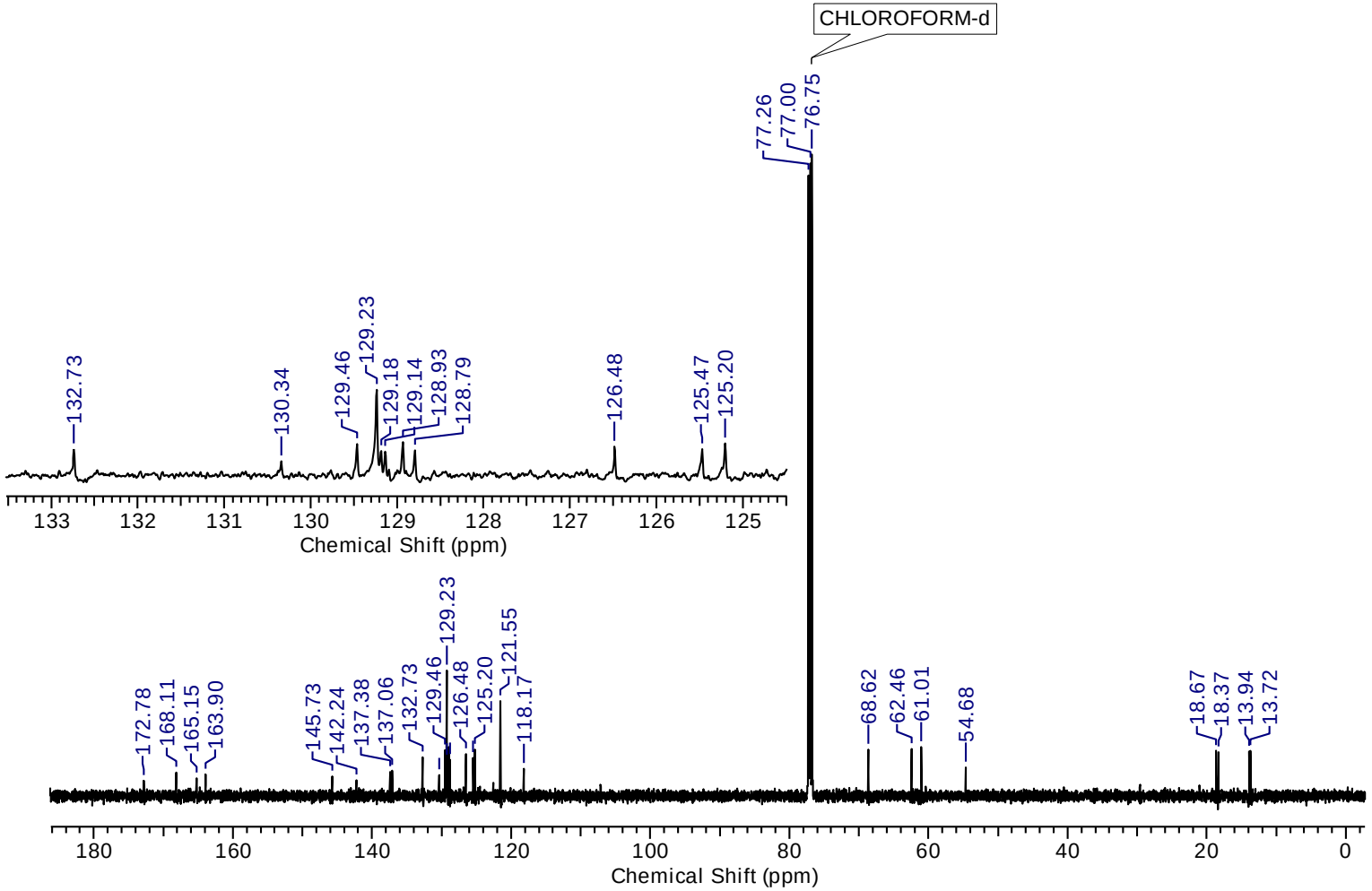




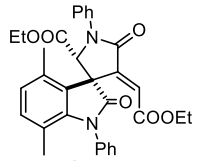
^{13} C NMR 100 MHz



4c

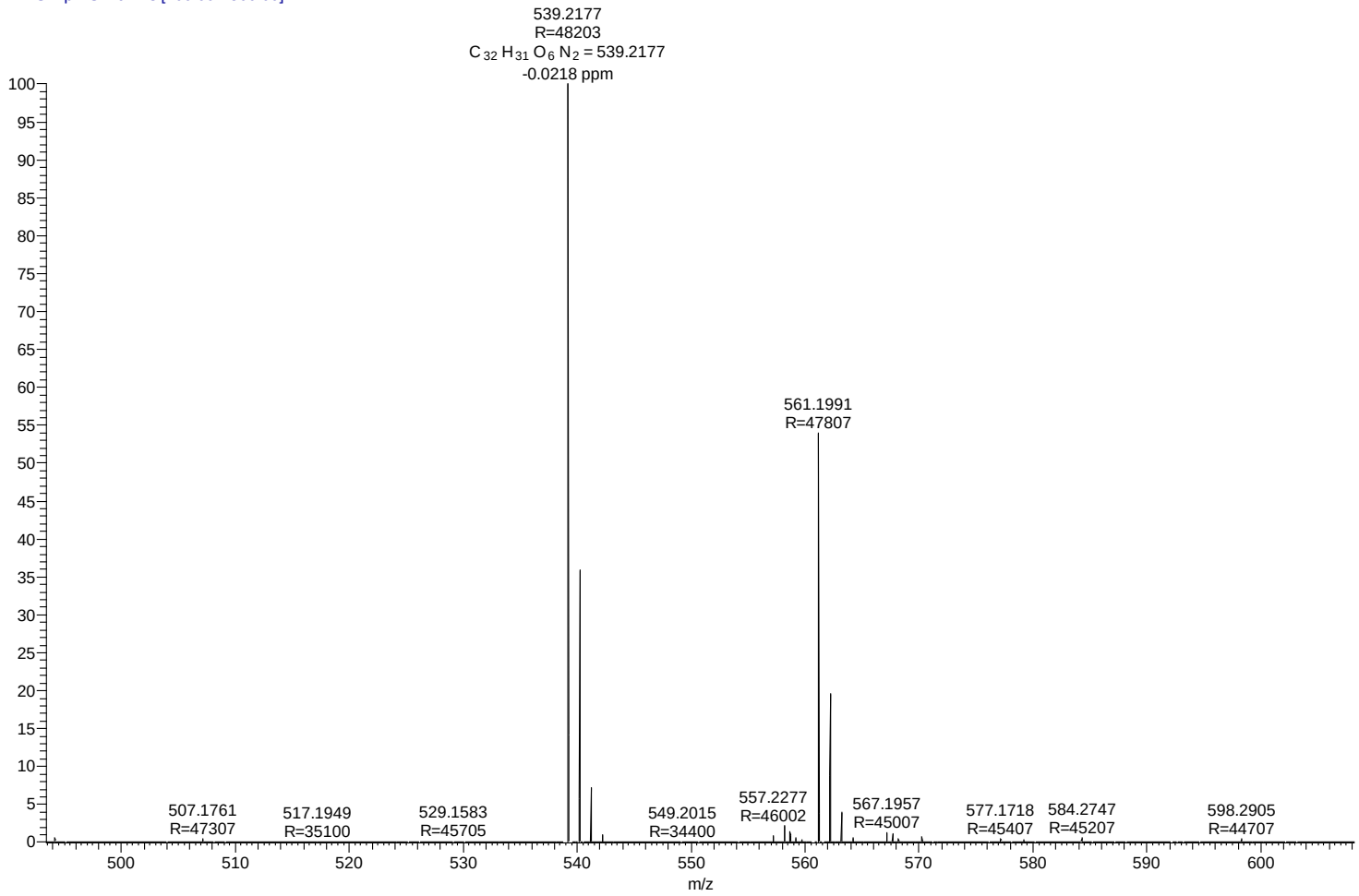


HRMS (ESI-TOF)

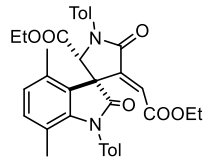


4c

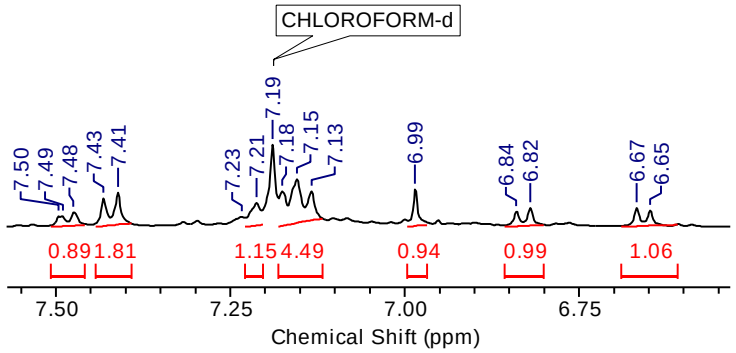
VP-4-C #136 RT: 0.60 AV: 1 NL: 1.54E9
T: FTMS + p ESI Full ms [100.00-1500.00]

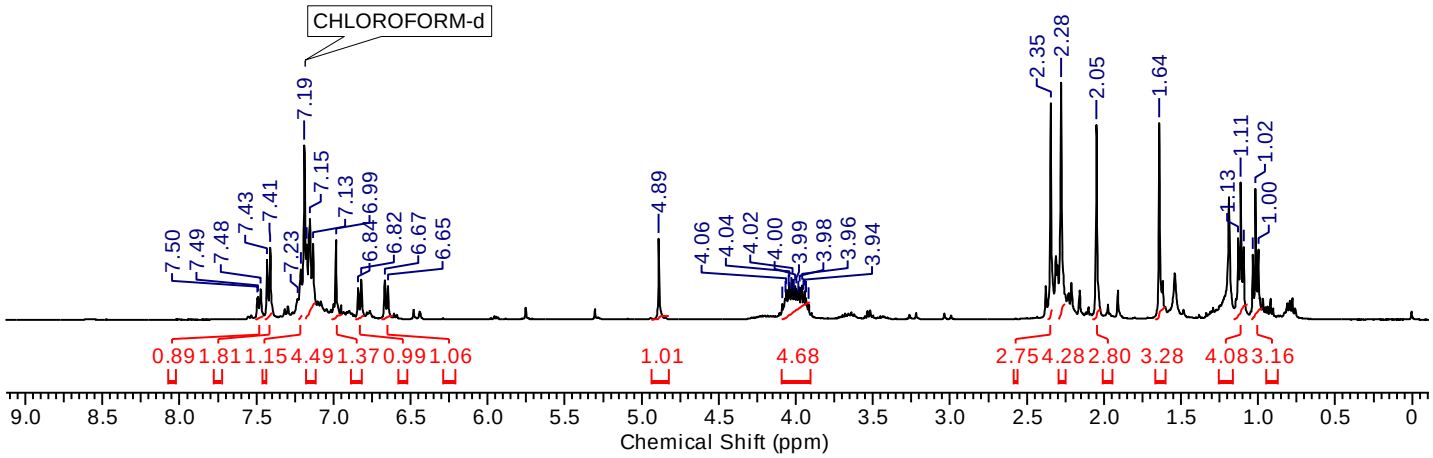


^{1}H NMR 400 MHz

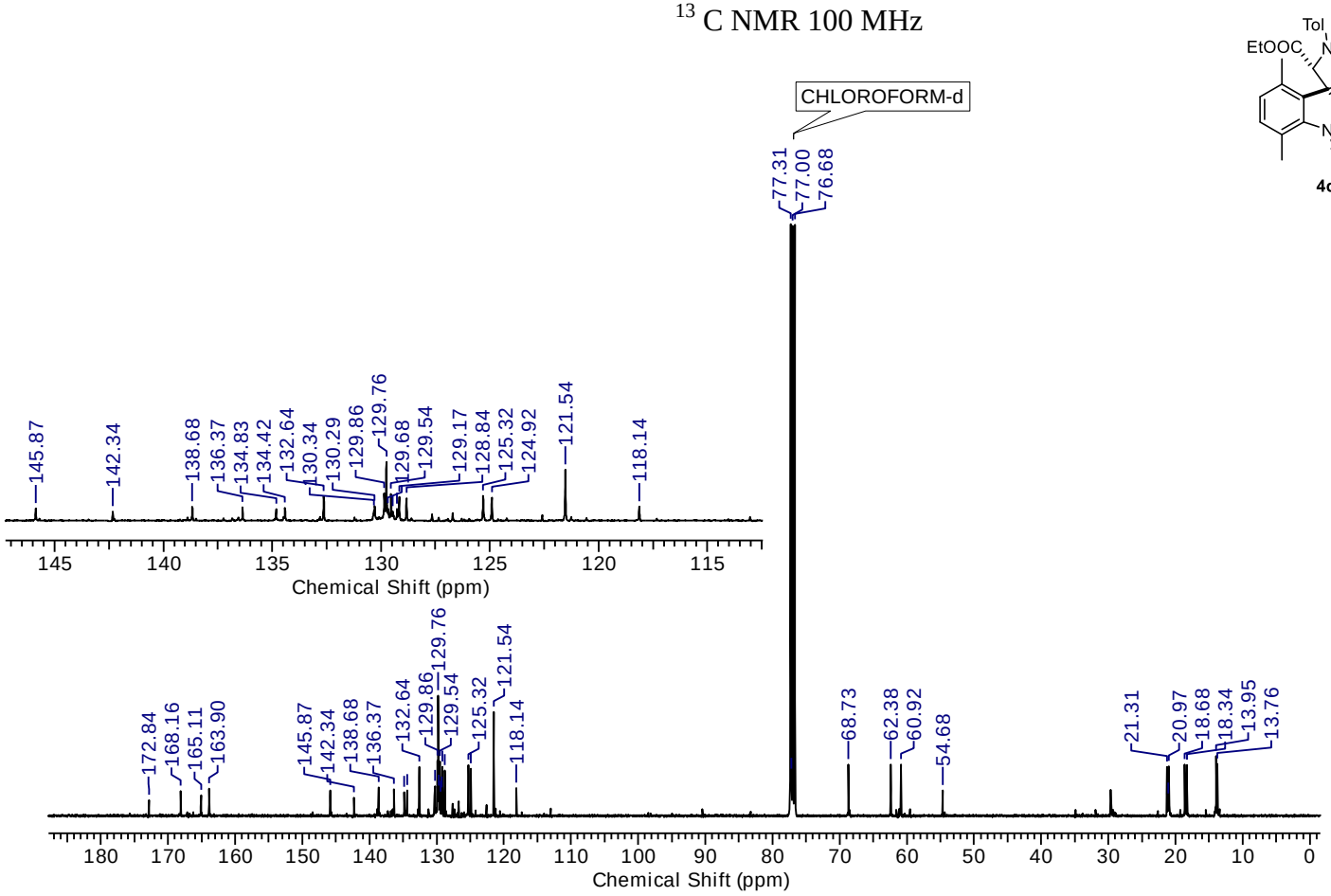


4d

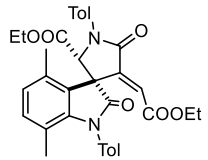




^{13} C NMR 100 MHz

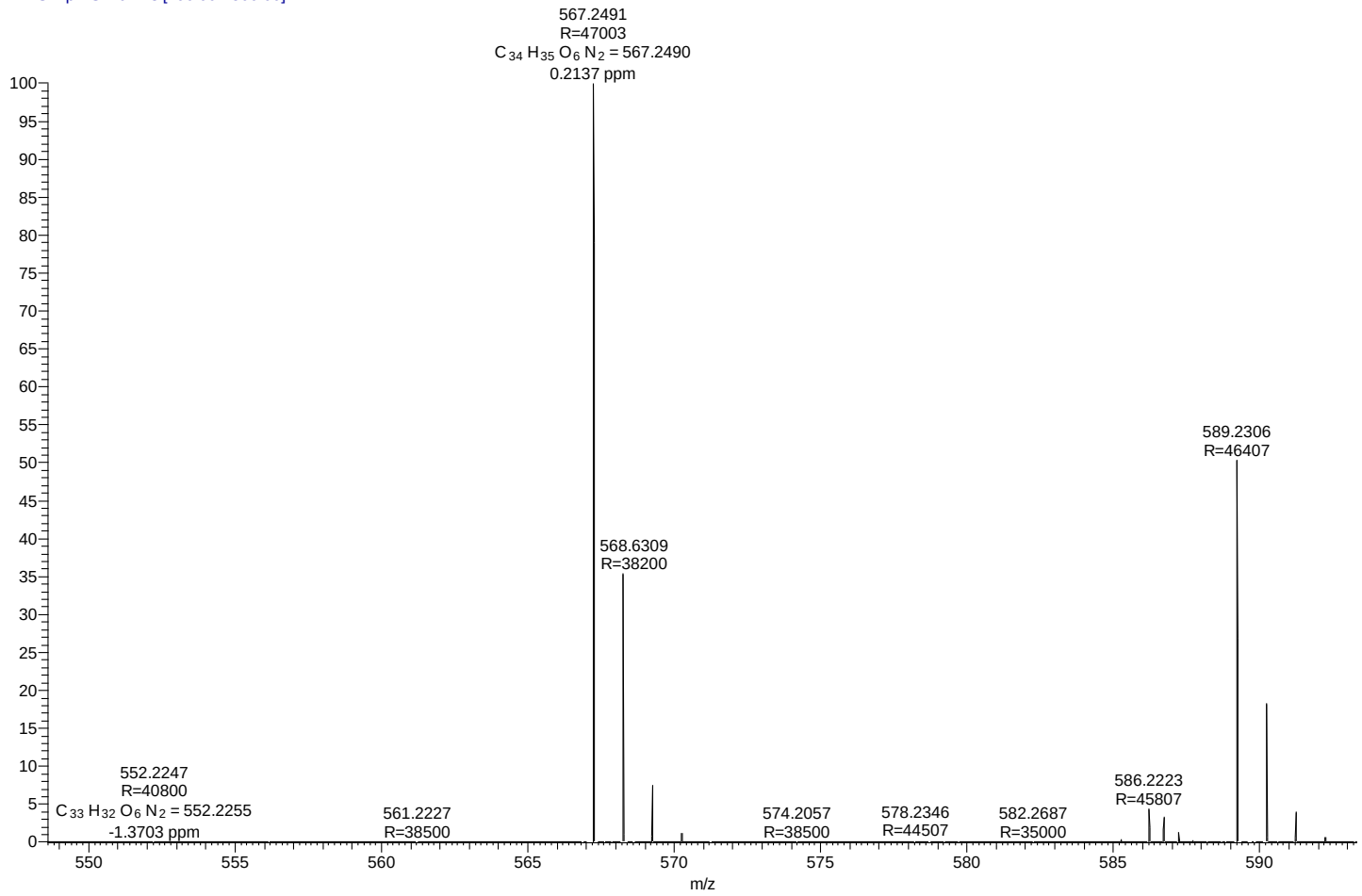


HRMS (ESI-TOF)

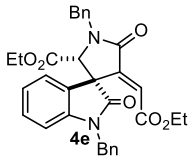


4d

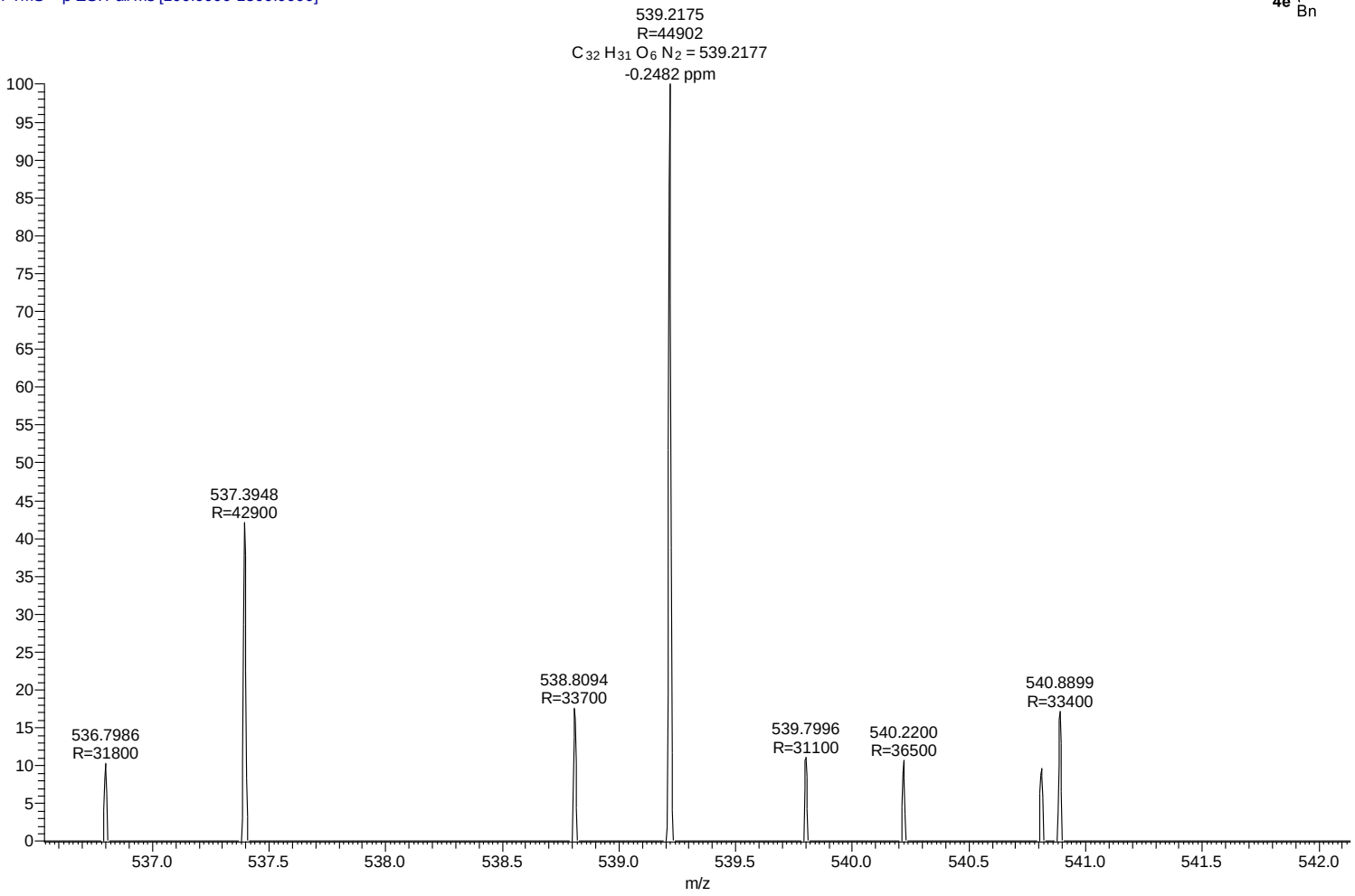
VP-4-D #158 RT: 0.70 AV: 1 NL: 2.11E9
T: FTMS + p ESI Full ms [100.00-1500.00]



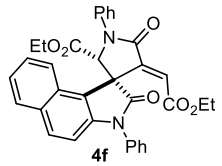
HRMS (ESI-TOF)



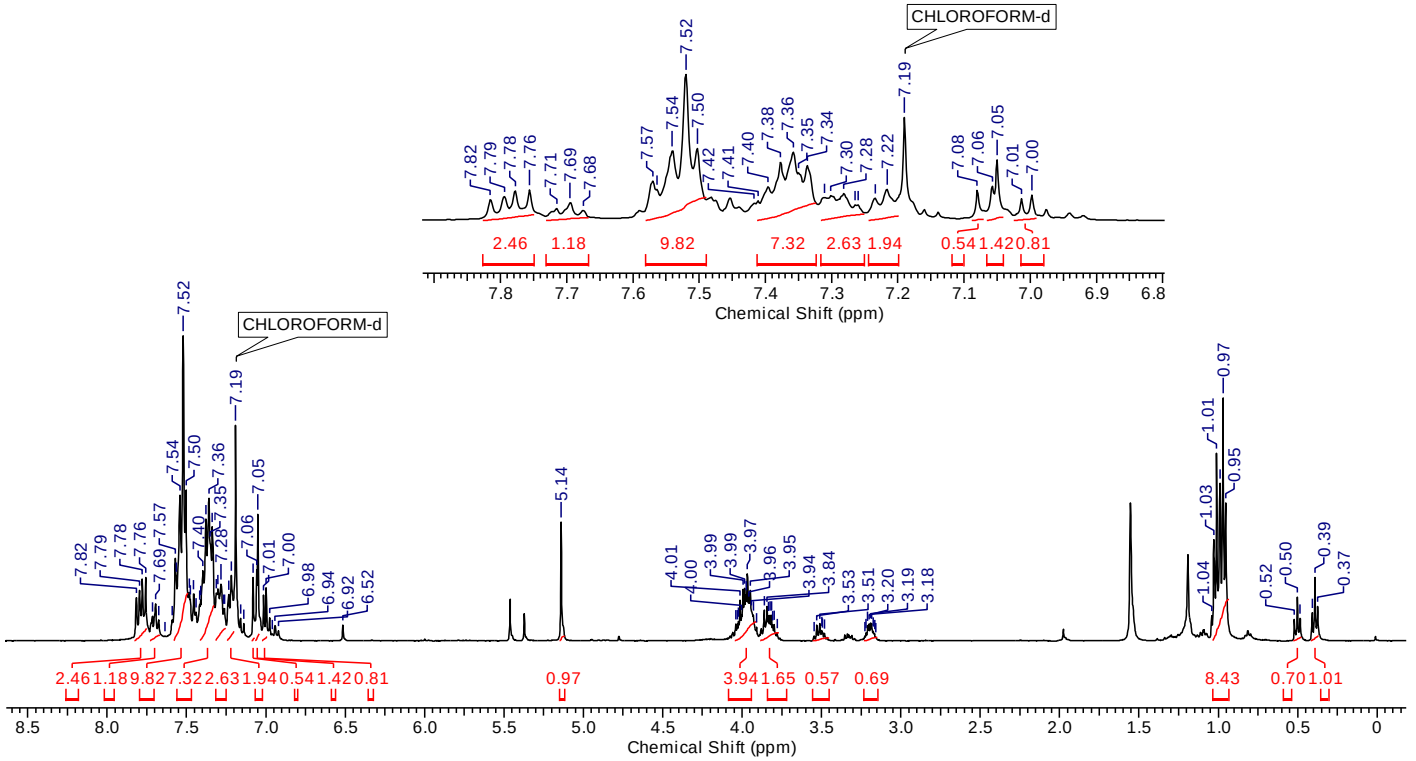
VP-E #280 RT: 1.25 AV: 1 NL: 6.62E4
T: FTMS + p ESI Full ms [100.0000-1500.0000]



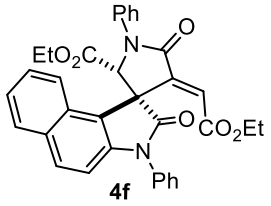
^{1}H NMR 400 MHz



4f



^{13} C NMR 100 MHz



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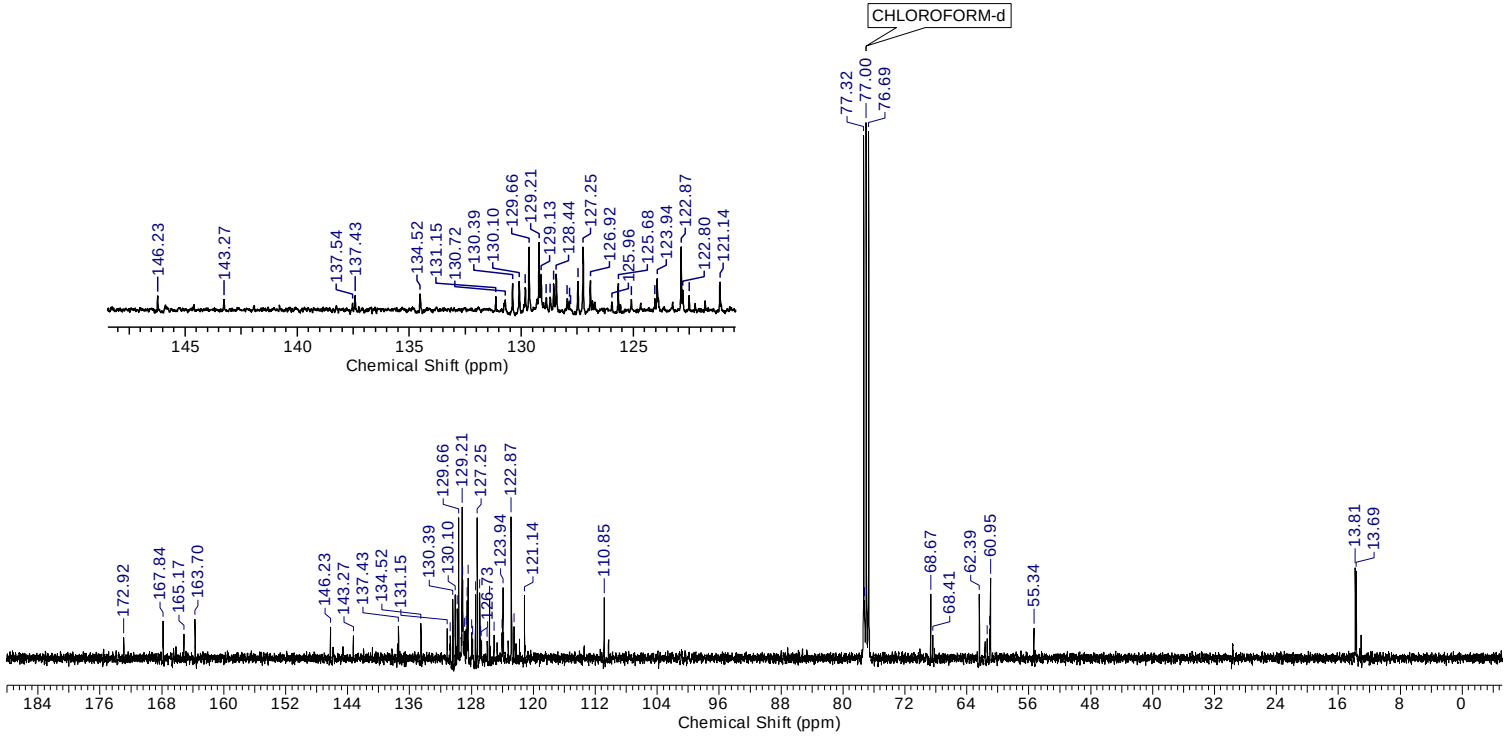
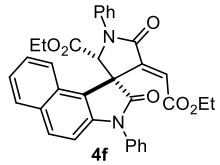


HRMS (ESI-TOF)



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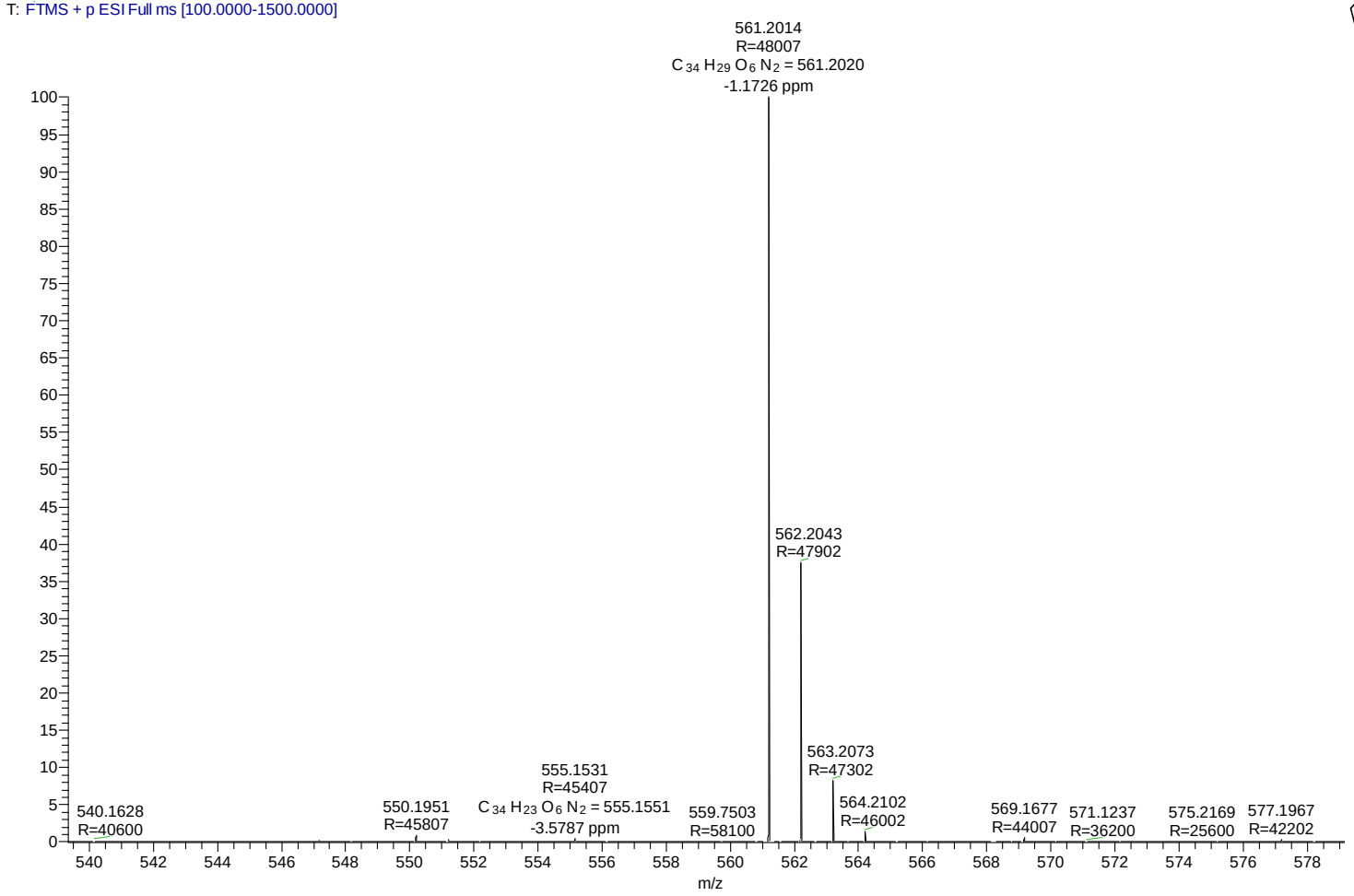
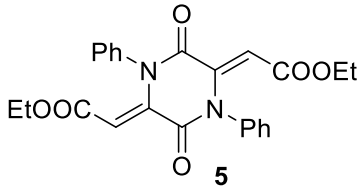
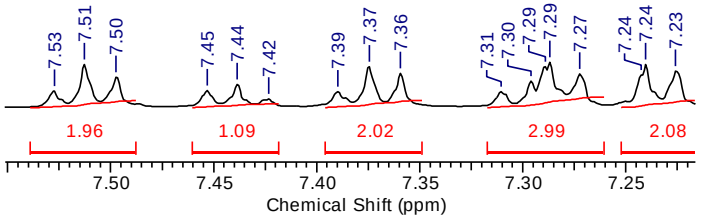
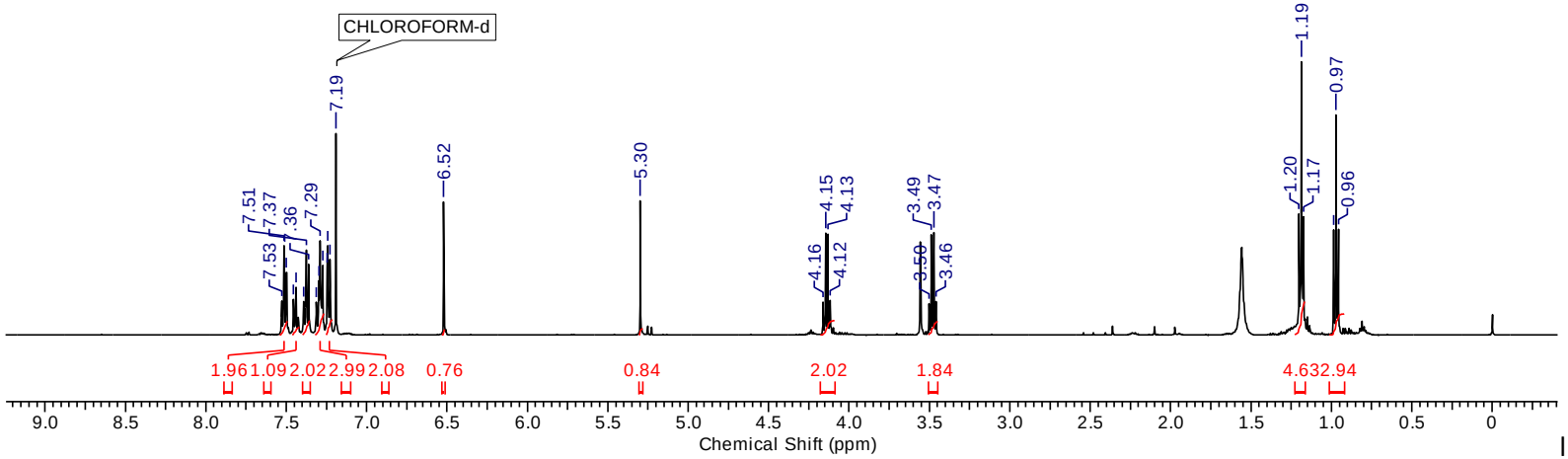


^{1}H NMR 400 MHz

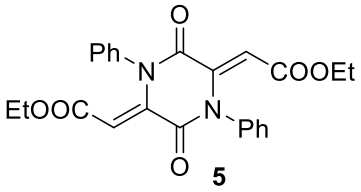


5





^{13} C NMR 100 MHz



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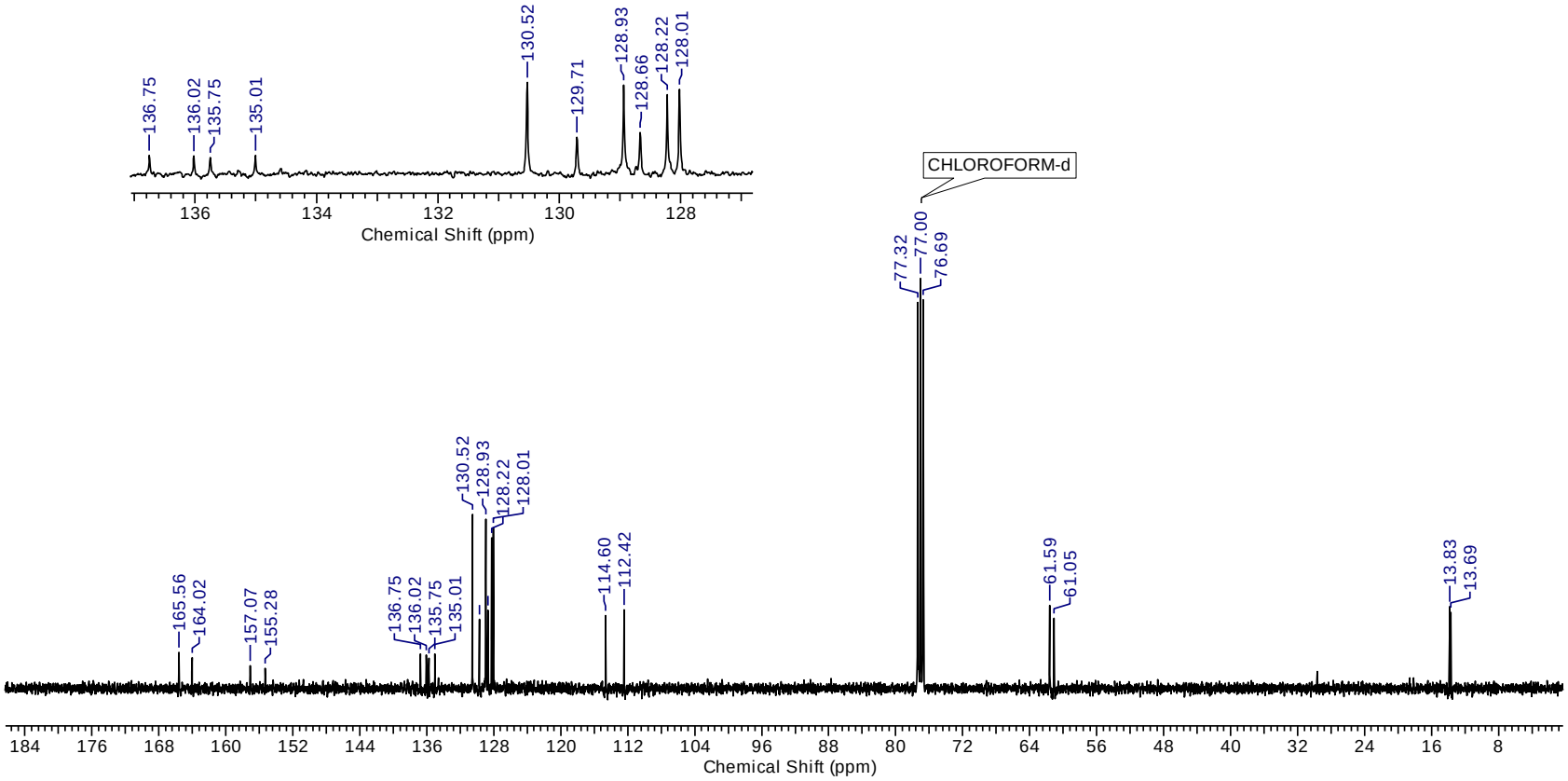
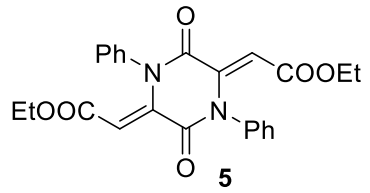


HRMS (ESI-TOF)



5