Supporting information for:

A new mild synthetic route to N-arylated pyridazinones from aryldiazonium salts

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Table of contents

General considerations

Unless otherwise noted, potassium 2-furyltrifluoroborate **2** and anilines were obtained from commercial suppliers and used without further purification. Aryldiazonium salts **3** were prepared according to literature procedures by diazotitation of the appropriate aniline.[1] The salts could be stored for several weeks at -20ºC. EtOAc was removed under reduced pressure with a rotary evaporator. Reaction mixtures were chromatographed on silica gel (230-400 mesh) using a gradient solvent system as the eluent.

IR spectra were recorded on a FT-IR Bruker Platinum-ATR Alpha spectrophotometer using a Reflection ATR System.

All 1D and 2D ^{1}H and ^{13}C NMR spectra were recorded on a 400 or 300 MHz NMR spectrometers at 298K using $CDCl_3$ as a deuterated solvent. Chemical shifts (δ) for ^{1}H and ^{13}C NMR were referenced to internal solvent resonances and reported relative to $SiMe_4$.

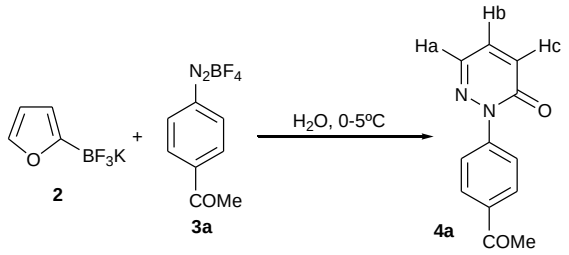
GC-MS analyses were performed on an Agilent 7890A gas equipped with an HP-5 capillary column interfaced with an Agilent 5975C mass spectrometer. The electron ionization (EI) source was set at 70 eV.

Electrospray mass spectrometry analyses were recorded on an Esquire 6000 Ion Trap Mass Spectrometer (Bruker) equipped with an electrospray ion source. The instrument was operated in the negative ESI(-) ion mode.

High resolution mass spectra (HRMS) were recorded on a Bruker MicrOTOF-Q IITM instrument using ESI as ionization sources. Samples were introduced into the mass spectrometer ion source by direct infusion using a syringe pump and were externally calibrated using sodium formate. The instrument was operated in the positive ion mode.

Preparation and characterization data for pyridazinones derivatives 4

Synthesis of 2-(4-acetylphenyl)pyridazin-3(*2H)*-one, **4a**. General procedure



Potassium 2-furantrifluoroborate **2** (89 mg, 0.51 mmol, 1.2 equiv.) was dissolved in H_2O (6 mL) and magnetically stirred in a light-protected round-bottom flask at 0-5 ºC. The diazonium salt **3a** (100 mg, 0.43 mmol, 1 equiv.) was dissolved in H_2O (4 mL) and added slowly to the previous mixture. The progress of the reaction was monitored by testing the formation of azo-coupling between **3a** and 2-naphthol. The reaction mixture was extracted with EtOAc (4 x 10 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography through silica gel using hexane/EtOAc (3:7) as eluent to afford **4a** (60 mg, 66% yield) as a light yellow solid. M.p. 170-173 ºC; IR(ATR): ν (cm^{-1}) 3043 (arC-H), 1670 (C=O, ring); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ (ppm) 2.64 (s, 3H, COMe), 7.07 (dd, $^3J_{H,H}$ = 9.6 Hz, $^4J_{H,H}$ = 1.7 Hz, Hc), 7.27 (dd, $^3J_{H,H}$ = 9.6 Hz, $^3J_{H,H}$ = 3.8 Hz, Hb), 7.80 (d, $^3J_{H,H}$ = 8.7 Hz, 2H), 7.94 (dd, $^3J_{H,H}$ = 3.8 Hz, $^4J_{H,H}$ = 1.7 Hz, Ha), 8.07 (d, $^3J_{H,H}$ = 8.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ (ppm) 26.8, 125.2, 128.9, 131.3, 131.5, 136.3, 137.1, 145.0, 159.9, 197.1; EI-MS (*m/z*, %): 214 (M^+, 46), 199 (M-CH_3, 100), 171 (M-$COCH_3$, 33); Anal. Calcd. (%) for $C_{12}H_{10}N_2O_2$ (214.07): C, 67.28%; H, 4.71%; N, 13.08%. Found: C, 66.77%; H, 4.80%; N, 12.59%.

2-(4-nitrophenyl)pyridazin-3(*2H)*-one, 4b

Orange solid. M.p. 199-201 ºC (Lit.[2] 204-206ºC). IR(ATR): ν (cm^{-1}) 2922 (arC-H), 1669 (C=O), 1511/1493 (ν_{as} NO_2), 1337/1392 (ν_s, NO_2); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ (ppm) 7.09 (dd, $^3J_{H,H}$ = 9.6 Hz, $^4J_{H,H}$ = 1.8 Hz, Hc), 7.29 (dd, $^3J_{H,H}$ = 9.6 Hz, $^3J_{H,H}$ = 3.9 Hz, Hb), 7.95 (d, $J_{H,H}$ = 9.3 Hz, 2H + Ha), 8.34 (d, $^3J_{H,H}$ = 9.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ (ppm) 124.1, 125.7, 131.5, 131.8, 137.5, 146.2, 146.7, 159.8; EI-MS (*m/z*, %): 217 (M, 100), 189 (M-CO, 9).

2-(2-nitrophenyl)pyridazin-3(*2H)*-one, 4c

Orange solid. M.p. 103-105 ºC. IR(ATR): ν (cm^{-1}) 2952 (arC-H), 1660 (C=O), 1523 (NO_2); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ (ppm) 7.04 (dd, $^3J_{H,H}$ = 9.5 Hz, $^4J_{H,H}$ = 1.5 Hz, Hc), 7.31 (dd, $^3J_{H,H}$ = 9.5 Hz, $^3J_{H,H}$ = 3.9 Hz, Hb), 7.61 (m, 2H), 7.77 (td, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,H}$ = 1.5 Hz, 1H), 7.92 (dd, $^3J_{H,H}$ = 3.9 Hz, $^4J_{H,H}$ = 1.5 Hz, Ha), 8.11 (dd, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,H}$ = 1.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ (ppm) 125.1, 129.2, 129.8. 130.9, 132.1, 133.9, 134.7, 136.3, 137.5, 159.8; EI-MS (*m/z*, %): 217 (M, 1), 171 (M-NO_2), 65 (10); HRMS calcd. for $[C_{10}H_7N_3O_3 + Na]^+$: 240.0385. Found: 240.0379.

2-(4-iodophenyl)pyridazin-3(*2H)*-one, 4d

Light brown solid. M.p. 126-128 ºC. IR(ATR): ν (cm^{-1}) 2921 (arC-H), 1657 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ (ppm) 7.05 (dd, $^3J_{H,H}$ = 9.6 Hz, $^4J_{H,H}$ = 1.8 Hz, Hc), 7.25 (dd, $^3J_{H,H}$ = 9.6 Hz, $^3J_{H,H}$ = 3.6 Hz, Hb), 7.41 (d, $^3J_{H,H}$ = 9.0 Hz, 2H), 7.81 (d, $^3J_{H,H}$ = 9.0 Hz, 2H), 7.90 (dd, $^3J_{H,H}$ = 3.6 Hz, $^4J_{H,H}$ = 1.8 Hz, Ha); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ (ppm) 93.6, 127.0, 131.2, 131.4, 136.9, 137.9, 141.1, 159.9; EI-MS (*m/z*, %): 298 (M, 100), 270 (M-N_2, 21), 203 (29), 171 (M-I, 6), 76 (51); HRMS calcd. for $[C_{10}H_7IN_2O + H]^+$: 298.9681. Found: 298.9677.

2-(4-fluorophenyl)pyridazin-3(*2H)*-one, 4e

Light yellow solid. M.p. 135-138 ºC. IR(ATR): ν (cm^{-1}) 3060 (arC-H), 1675 (C=O), 1507 (arC-F); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ (ppm) 7.08 (dd, $^3J_{H,H}$ = 9.6 Hz, $^4J_{H,H}$ = 1.8 Hz, Hc), 7.15-7.21 (m, 2H), 7.28 (dd, $^3J_{H,H}$ = 9.6 Hz, $^3J_{H,H}$ = 3.9 Hz, Hb), 7.60-7.65 (m, 2H), 7.92 (dd, $^3J_{H,H}$ = 3.9 Hz, $^4J_{H,H}$ = 1.8 Hz, Ha); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ (ppm) 115.7 ($J_{C\text{-}F}$ = 23 Hz), 127.1, 127.3, 131.3, 131.4, 136.8, 160.1, 162.0 ($J_{C\text{-}F}$ = 247 Hz); EI-MS (*m/z*, %): 190 (M, 100), 162 (M-CO, 35), 95 (78); HRMS calcd. for $[C_{10}H_7FN_2O + Na]^+$: 213.0440. Found: 213.0439.

2-phenylpyridazin-3(*2H*)-one, 4f

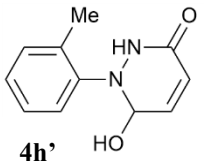
Yellow solid. M.p. 110-112 ºC (Lit.[3] 106-108ºC). IR(ATR): ν (cm^{-1}) 3025 (arC-H), 1654 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ (ppm) 7.07 (dd, $^3J_{H,H}$ = 9.5 Hz, $^4J_{H,H}$ = 1.8 Hz, Hc), 7.25 (dd, $^3J_{H,H}$ = 9.6 Hz, $^3J_{H,H}$ = 3.6 Hz, Hb), 7.40-7.64 (m, 5H), 7.90 (dd, $^3J_{H,H}$ = 3.6 Hz, $^4J_{H,H}$ = 1.8 Hz, Ha); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ (ppm) 125.3, 128.4, 128.8, 131.2, 131.3, 136.7, 141.5, 160.1; EI-MS (*m/z*, %): 172 (M, 100), 144 (M-CO, 35), 77 (75).

2-(4-methylphenyl)pyridazin-3(*2H*)-one, 4g.

Brown solid. M.p. 94-96 ºC (Lit.[4] 97-99 ºC). IR(ATR): ν (cm^{-1}) 3016 (CH_3), 2920 (arC-H), 1654 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ (ppm) 2.40 (s, CH_3), 7.05 (dd, $^3J_{H,H}$ = 9.6 Hz, $^4J_{H,H}$ = 1.7 Hz, Hc), 7.24 (dd, $^3J_{H,H}$ = 9.6 Hz, $^3J_{H,H}$ = 3.8 Hz, Hb), 7.28 (d, $^3J_{H,H}$ = 8.4 Hz, 2H), 7.47 (d, $^3J_{H,H}$ = 8.4 Hz, 2H), 7.88 (dd, $^3J_{H,H}$ = 3.8 Hz, $^4J_{H,H}$ = 1.7 Hz, Ha); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ (ppm) 21.2, 125.1, 129.4, 131.1, 131.2, 136.5, 138.4, 139.0, 160.2; EI-MS (*m/z*, %): 186 (M, 100), 158 (M-N_2, 27), 130 (M-CON_2, 13), 91 (57).

2-(2-methylphenyl)pyridazin-3(*2H*)-one, 4h

This compound suffers a hydration at the end of the reaction giving 4h' together with **4h**.

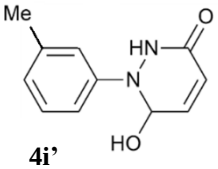


4h'

Orange oil. IR(ATR) (4h + 4h'): ν (cm^{-1}) 3199 (OH), 1661 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ (ppm) 2.16 (s, CH_3, 4j), 2.25 (s, 3H, 4h'), 3.38 (br. singlet, OH, 4h'), 5.52 (s, 1H, 4h'), 5.88 (s, NH, 4h'), 6.28 (d, $^3J_{H,H}$ = 6.4 Hz, 1H, 4h'), 6.66 (d, $^3J_{H,H}$ = 7.6 Hz, 1H, 4h'), 6.84 (dt, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,H}$ = 1.2 Hz, 1H, 4h'), 6.98 (dd, $^3J_{H,H}$ = 6.4 Hz, $^3J_{H,H}$ = 1.2 Hz, 1H, 4h'), 7.07 (dd, $^3J_{H,H}$ = 9.6 Hz, $^4J_{H,H}$ = 1.5 Hz, Hc, 4h), 7.26-7.35 (m, (Hb + 4H), 4h + 2H, 4h'), 7.90 (dd, $^3J_{H,H}$ = 3.6 Hz, $^4J_{H,H}$ = 1.5 Hz, Ha, 4h); EI-MS (*m/z*, %) (4h): 186 (M, 86), 169 (M-OH, 100), 91 (47). ESI-MS (*m/z*) (4h'): 202.9 ($[M-H]^+$).

2-(3-methylphenyl)pyridazin-3(*2H*)-one, 4i

This compound suffers a hydration at the end of the reaction giving traces of 4i' which were identified by mass spectrometry.



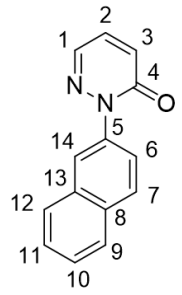
4i'

Brown oil. IR(ATR): ν (cm^{-1}) 1665 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 2.41 (s, CH_3), 7.04 (dd, $^3J_{H,H}$ = 9.4 Hz, $^4J_{H,H}$ = 1.6 Hz, Hc), 7.21 (m, 1H), 7.22 (dd, $^3J_{H,H}$ = 9.4 Hz, $^4J_{H,H}$ = 3.6 Hz, Hb), 7.34-7.41 (m, 3H), 7.87 (dd, $^3J_{H,H}$ = 3.6 Hz, $^4J_{H,H}$ = 1.6 Hz, Ha); EI-MS (*m/z*, %): 186 (M, 100), 158 (M-N_2, 27), 130 (M-CON_2, 16), 91 (61), 65 (33). ESI-MS (*m/z*) (4i'): 202.9 ($[M-H]^+$).

2-(4-methoxyphenyl)pyridazin-3(*2H*)-one, 4j

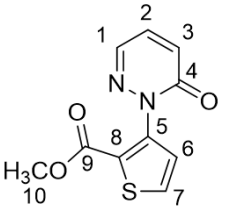
Brown solid. M.p. 97-100 ºC (Lit.[5] 148-150ºC). IR(ATR): ν (cm^{-1}) 2921 (arC-H), 1661 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ (ppm) 3.85 (s, OCH_3), 6.99 (d, $^3J_{H,H}$ = 9.0 Hz, 2H), 7.06 (dd, $^3J_{H,H}$ = 9.3 Hz, $^4J_{H,H}$ = 1.8 Hz, Hc), 7.24 (dd, $^3J_{H,H}$ = 9.3 Hz, $^3J_{H,H}$ = 3.6 Hz, Hb), 7.52 (d, $^3J_{H,H}$ = 9.0 Hz, 2H), 7.88 (dd, $^3J_{H,H}$ = 3.6 Hz, $^4J_{H,H}$ = 1.8 Hz, Ha); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ (ppm) 55.6, 114.0, 126.5, 131.0, 131.2, 134.5, 136.5, 159.3, 160.3; EI-MS (*m/z*, %): 202 (M, 100), 187 (M-CH_3, 10), 174 (M-CO, 10), 77 (27).

2-(naphthalen-2-yl)pyridazin-3(2*H*)-one, 4k



Dark red oil. IR(ATR): ν (cm^{-1}) 2922 (arC-H), 1665 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ (ppm) 7.11 (dd, $^3J_{H,H}$ = 9.6 Hz, $^4J_{H,H}$ = 1.7 Hz, H_3), 7.29 (dd, $^3J_{H,H}$ = 9.6 Hz, $^3J_{H,H}$ = 3.6 Hz, H_2), 7.51-7.54 (m, 2H), 7.71 (dd, $^3J_{H,H}$ = 8.8 Hz, $^4J_{H,H}$ = 2.1 Hz, H_6), 7.87-7.91 (m, 2H), 7.94 (d, $^3J_{H,H}$ = 8.8 Hz, H_7), 7.95 (dd, $^3J_{H,H}$ = 3.6 Hz, $^4J_{H,H}$ = 1.7 Hz, H_1), 8.13 (d, $^4J_{H,H}$ = 2.1 Hz, H_{14}); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ (ppm) 123.2, 124.1, 126.6, 126.8, 127.7, 128.4, 128.6, 131.2, 131.4, 132.8, 133.1, 136.8, 139.0, 160.3; HRMS calcd. for $[C_{14}H_{10}IN_2O + H]^+$: 223.0871. Found: 223.0863.

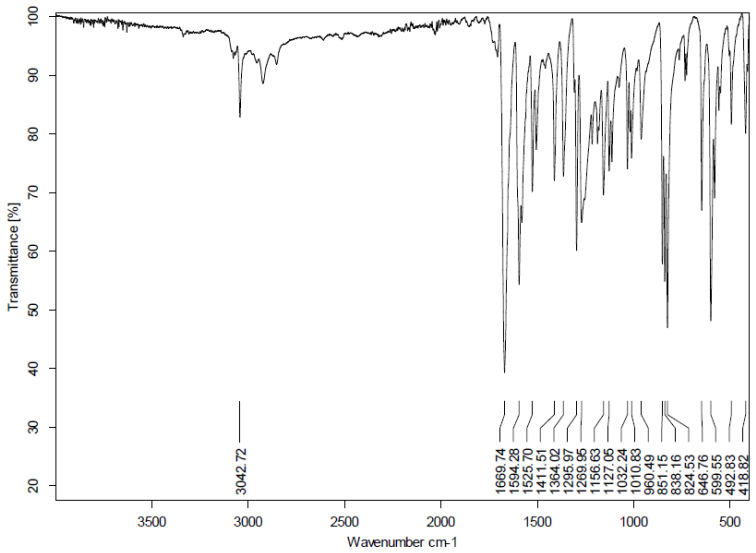
2-(2-(methoxycarbonyl)thiophene-3-yl)pyridazin-3(2*H*)-one, 4l

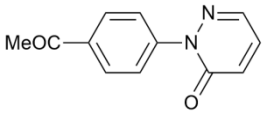


Brown oil. IR(ATR): ν (cm^{-1}) 1716 (CO_2Me), 1668 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 3.79 (s, 3H, CO_2Me), 7.04 (dd, $^3J_{H,H}$ = 9.6 Hz, $^4J_{H,H}$ = 1.6 Hz, H_3), 7.18 (d, $^3J_{H,H}$ = 5.2 Hz, H_7), 7.27 (dd, $^3J_{H,H}$ = 9.6 Hz, $^4J_{H,H}$ = 4.0 Hz, H_2), 7.59 (d, $^3J_{H,H}$ = 5.2 Hz, H_6), 7.87 (dd, $^3J_{H,H}$ = 4.0 Hz, $^4J_{H,H}$ = 1.6 Hz, H_1); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ (ppm) 52.3, 126.7, 127.2, 130.3, 130.9, 131.7, 136.6, 142.7, 160.0, 160.5; EI-MS (*m/z*, %): 236 (M, 78), 205 (38), 177 (100); HRMS calcd. for $[C_{10}H_8N_2O_3S + Na]^+$: 259.0148. Found: 259.0144.

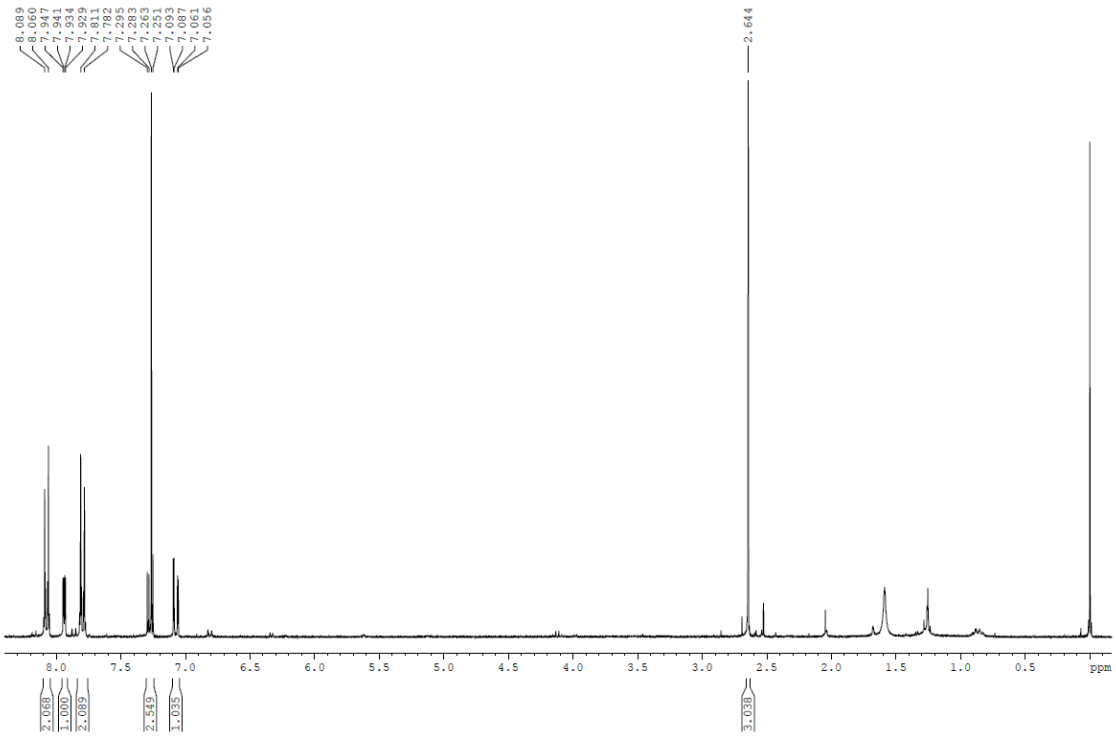
Spectra of pyridazinone derivatives 4

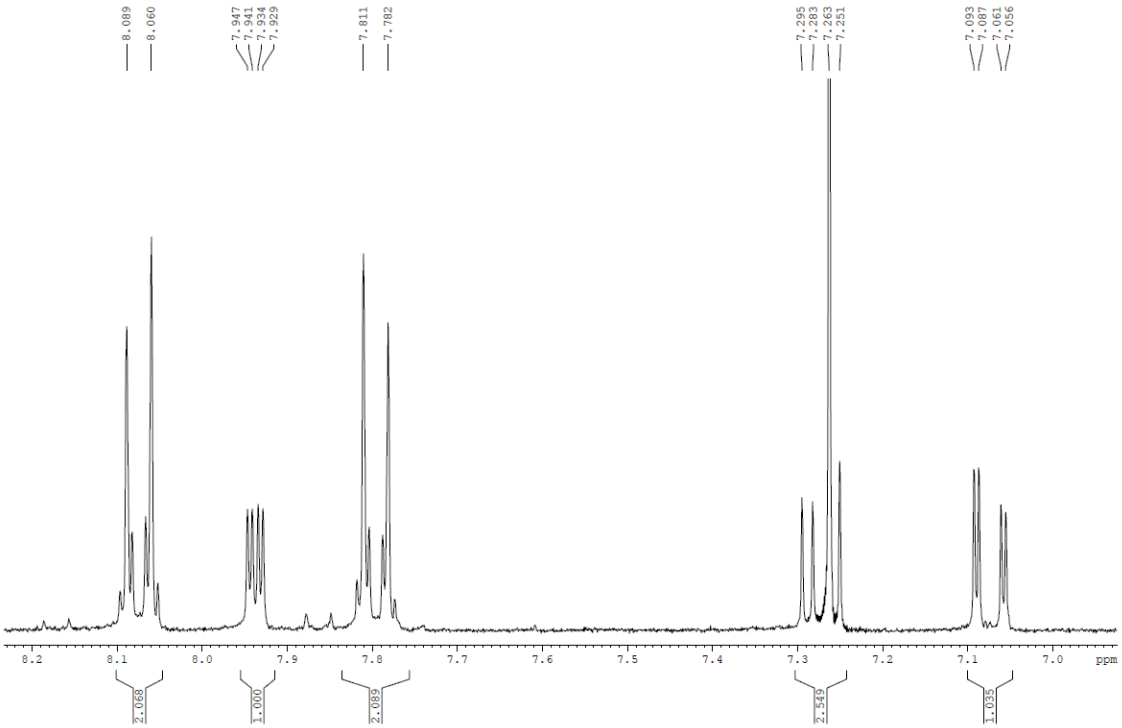
IR (ATR) of compound 4a



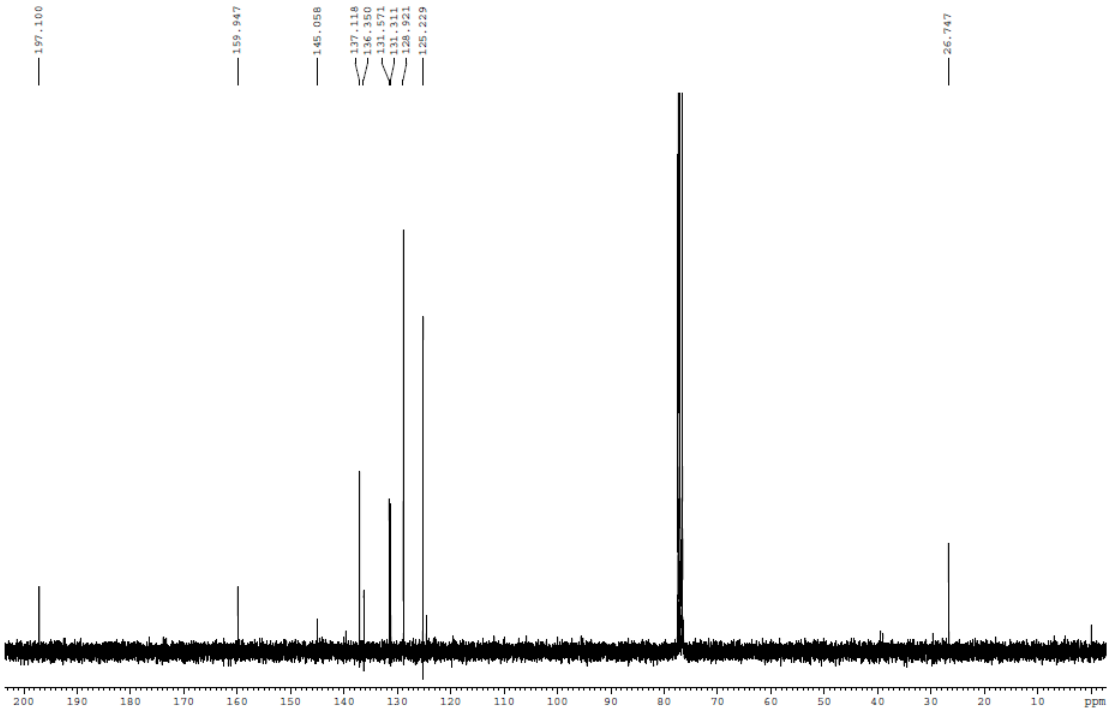


^{1}H NMR ($CDCl_3$, 300 MHz) of compound 4a

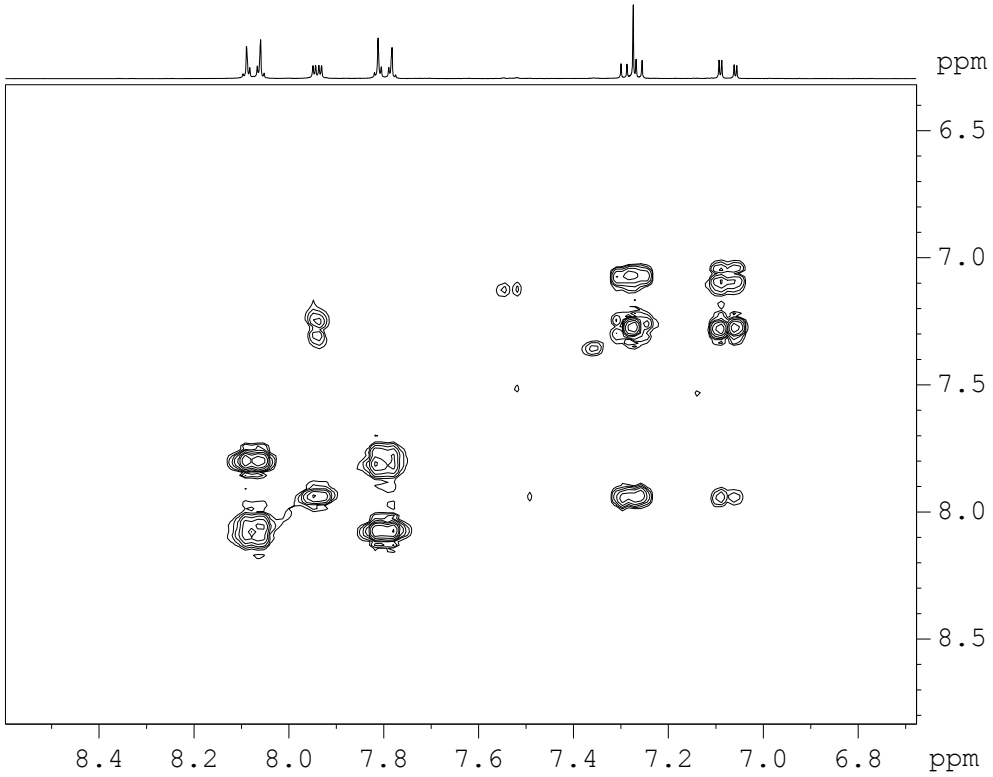




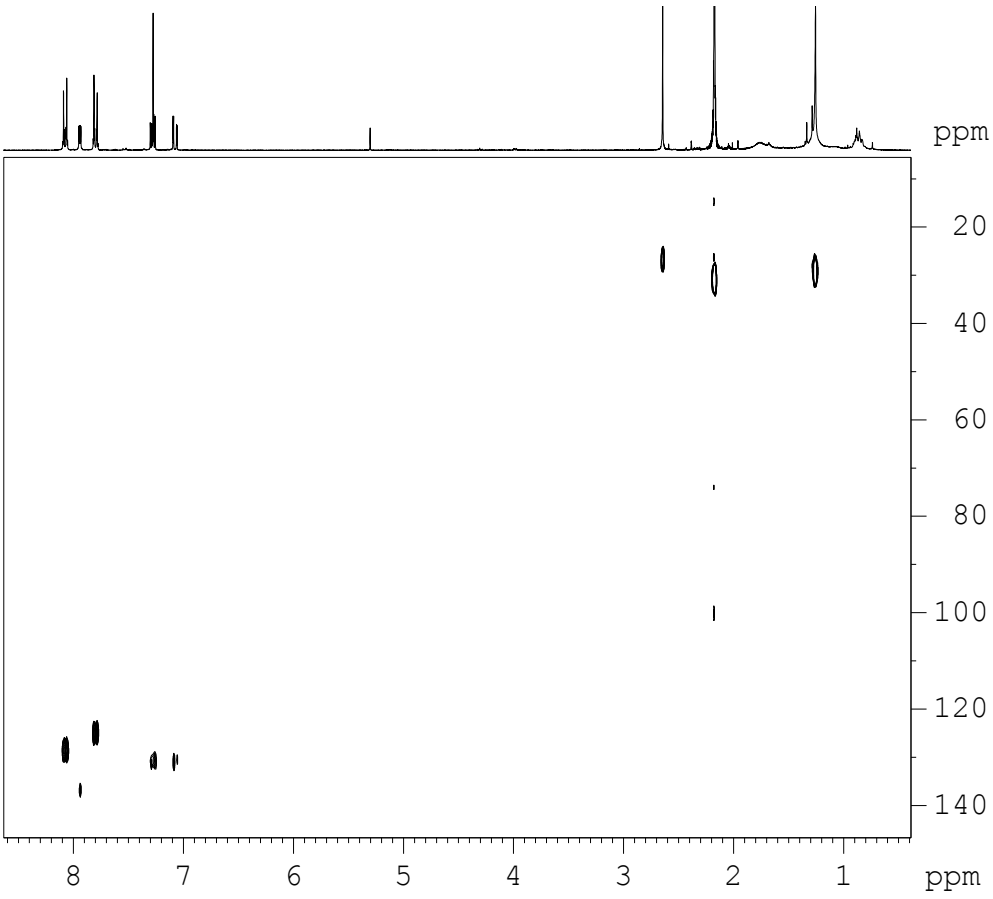
^{13}C NMR ($CDCl_3$, 75 MHz) of compound 4a



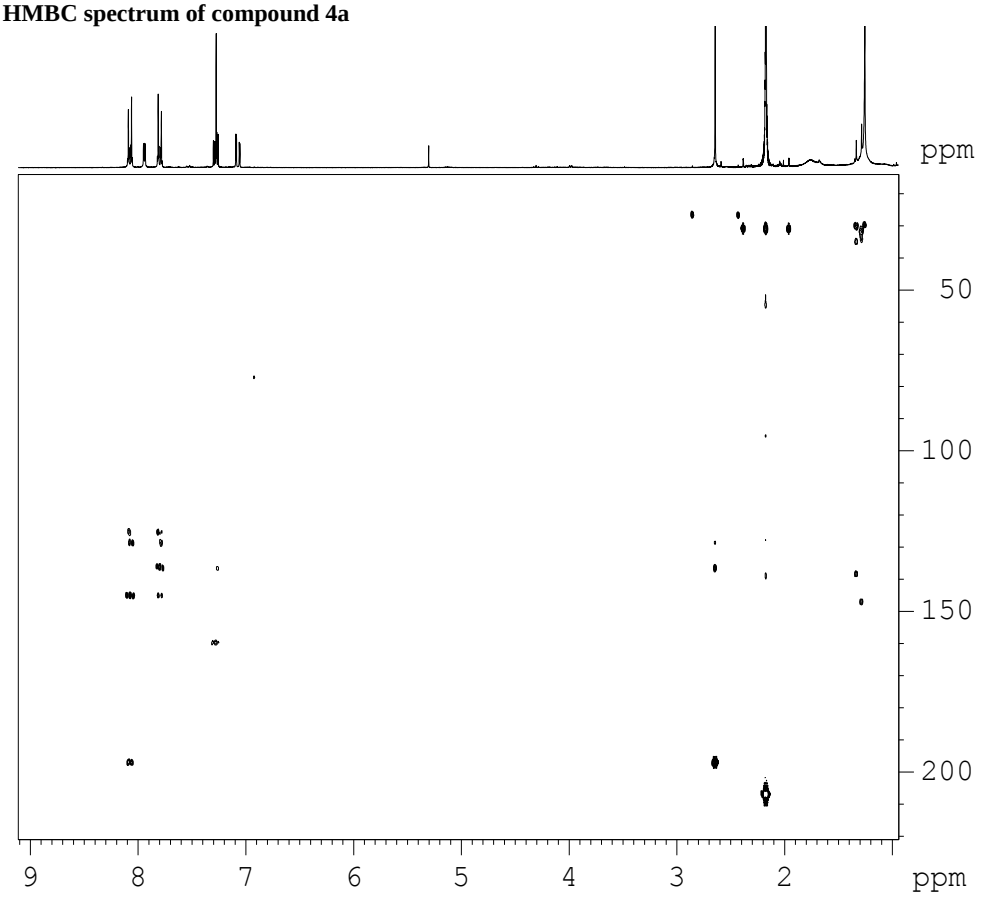
^{1}H-^{1}H COSY spectrum of compound 4a



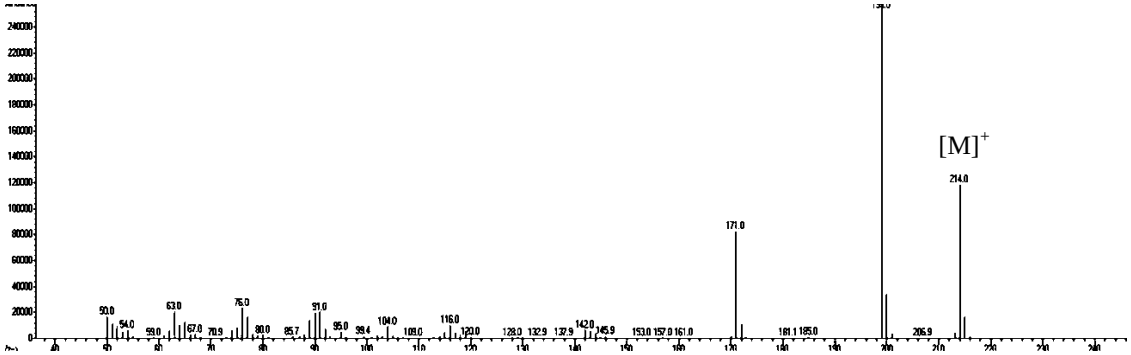
^{1}H-^{13}C HSQC spectrum of compound 4a



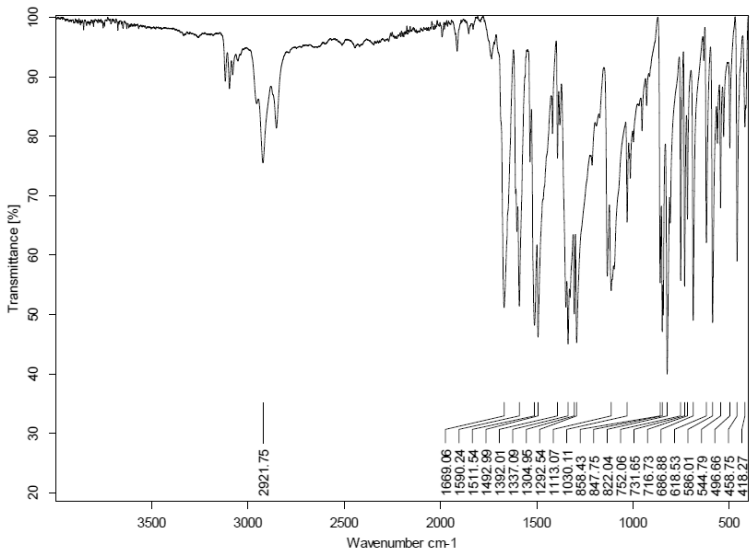
^{1}H-^{13}C HMBC spectrum of compound 4a

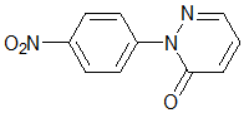


EI-MS (*m/z*) of compound 4a

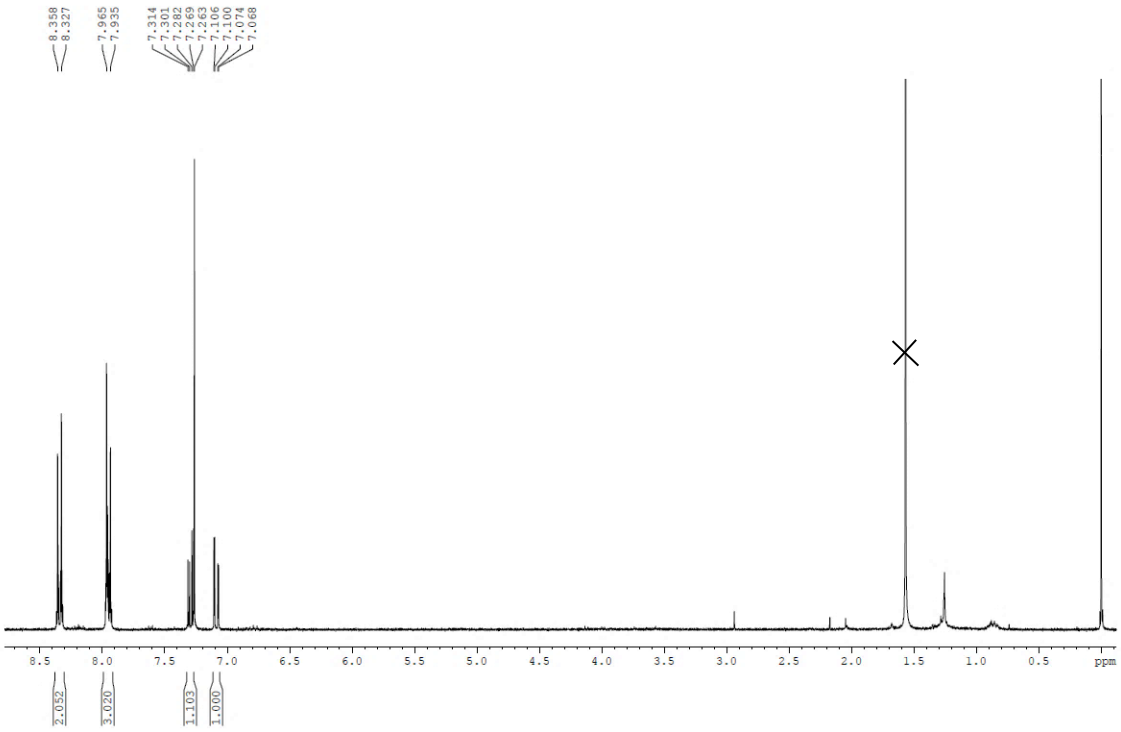


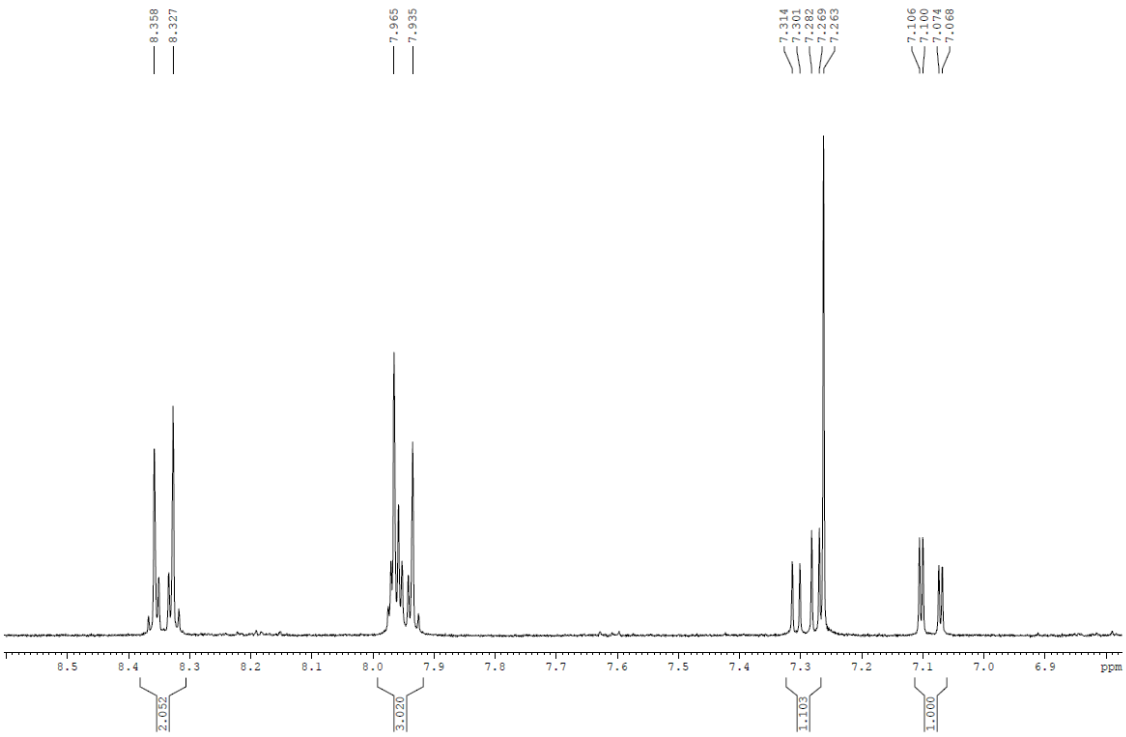
IR (ATR) of compound 4b



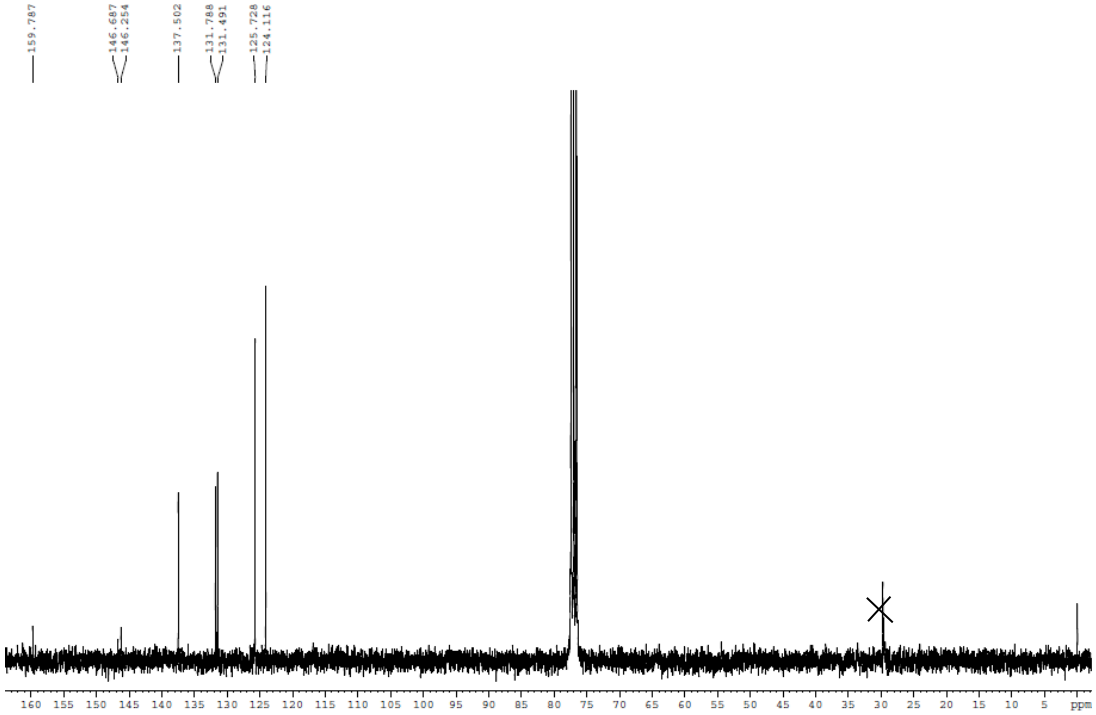


^{1}H NMR ($CDCl_3$, 300 MHz) of compound 4b

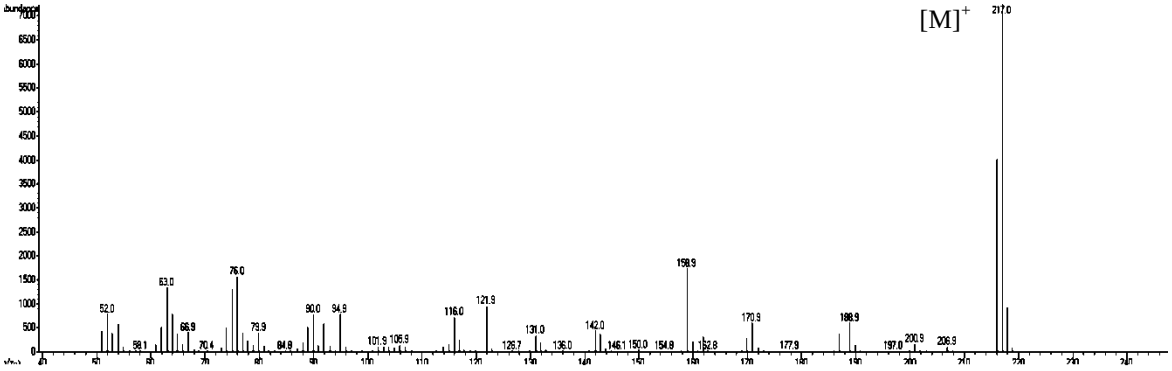




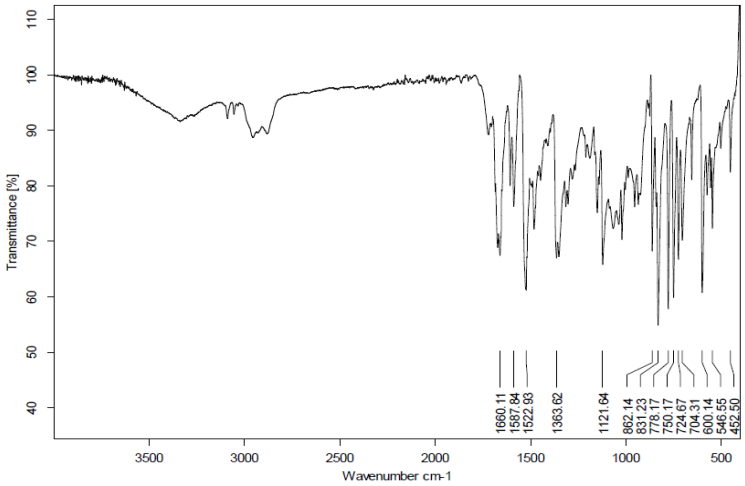
^{13}C NMR ($CDCl_3$, 75 MHz) of compound 4b

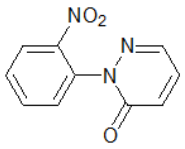


EI-MS (*m/z*) of compound 4b

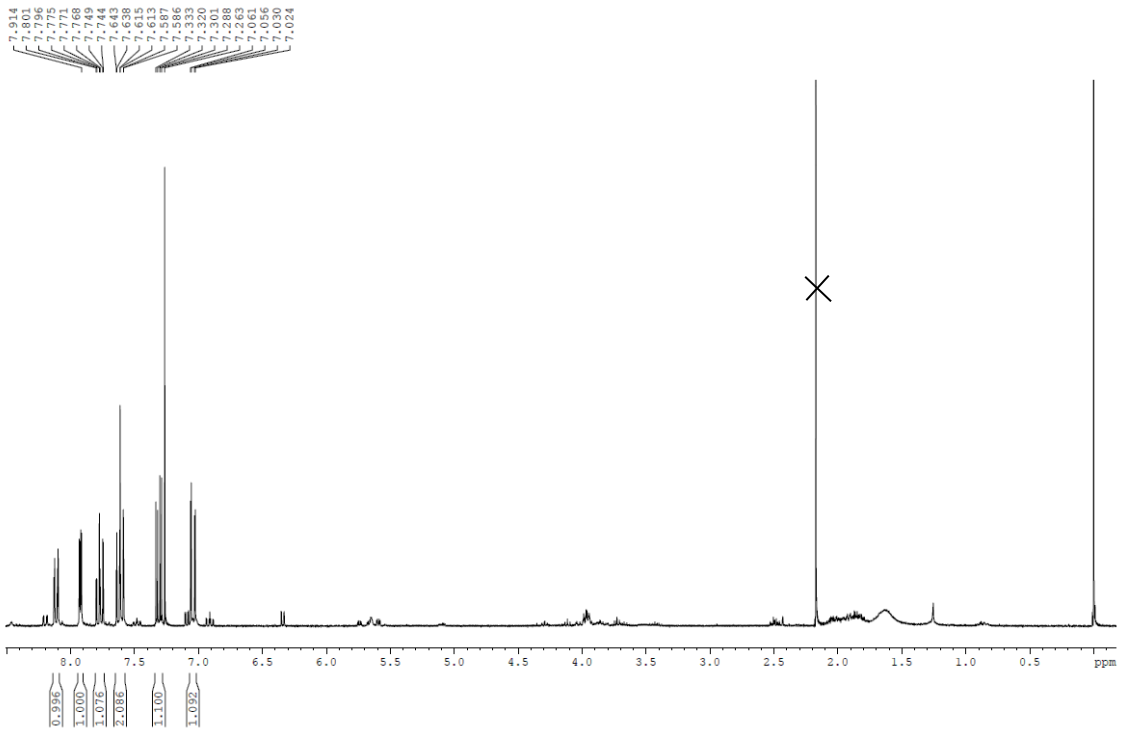


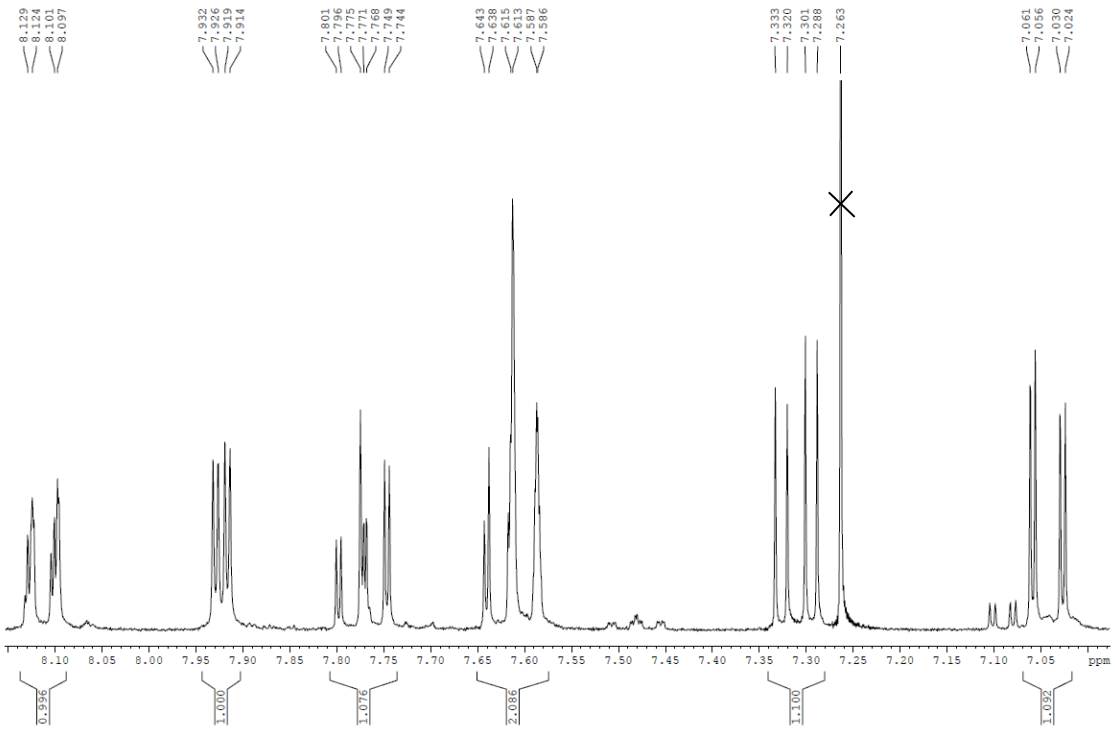
IR (ATR) of compound 4c



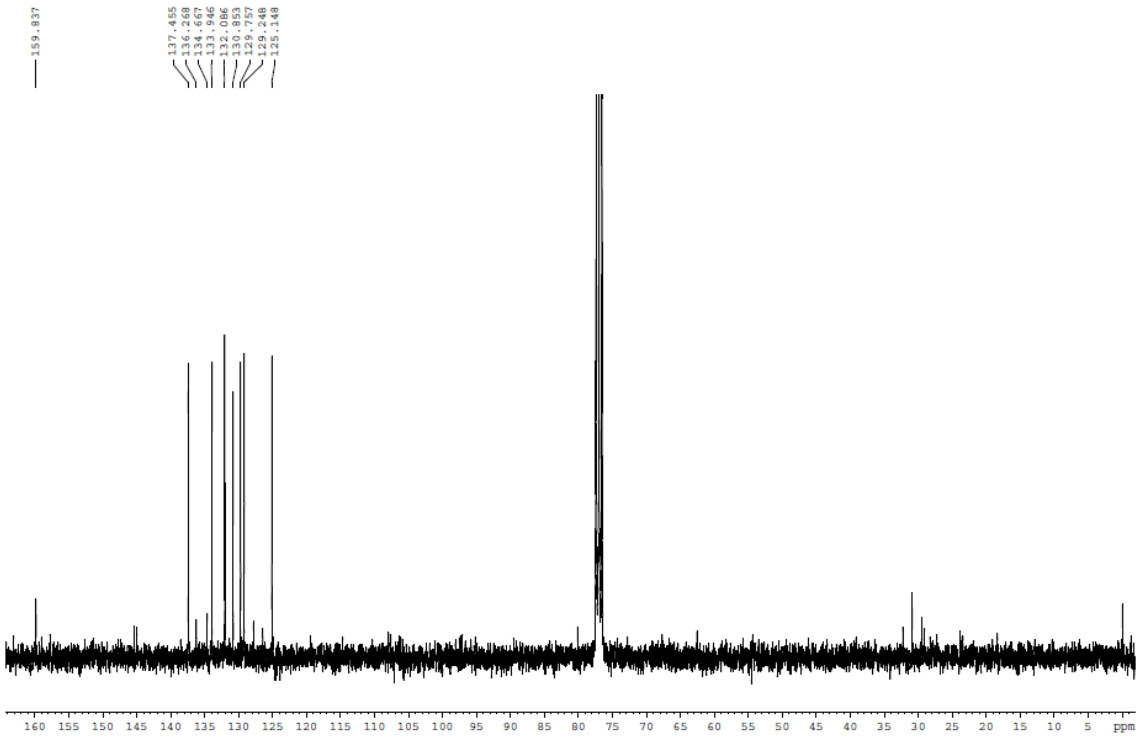


^{1}H NMR ($CDCl_3$, 300 MHz) of compound 4c

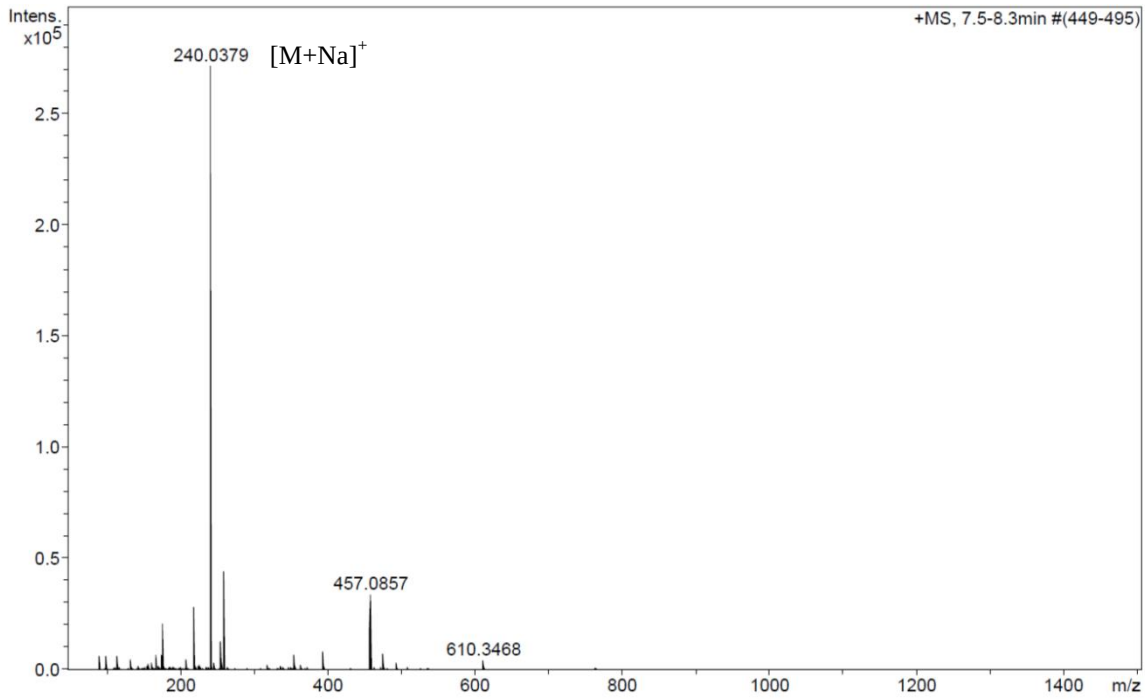




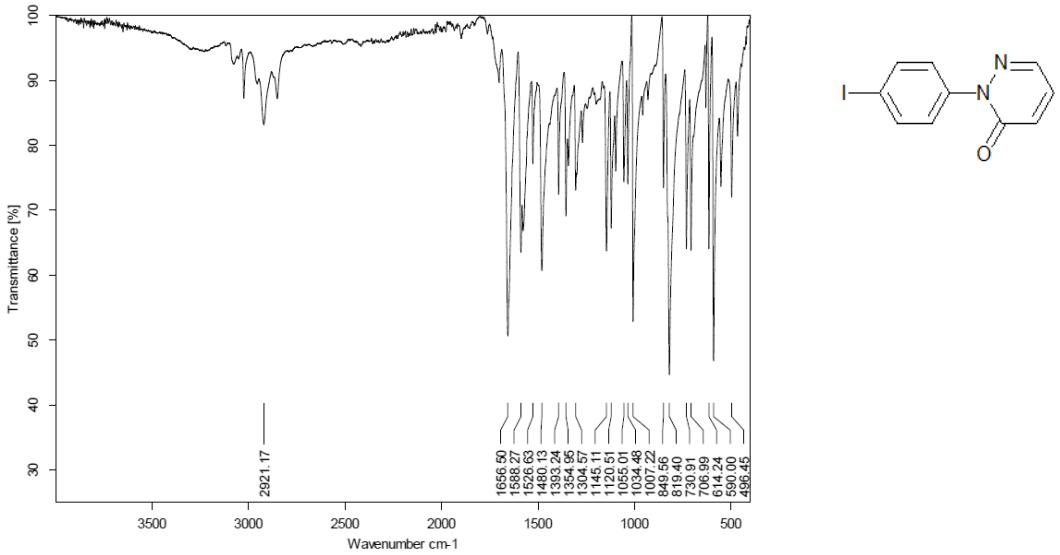
^{13}C NMR ($CDCl_3$, 75 MHz) of compound 4c



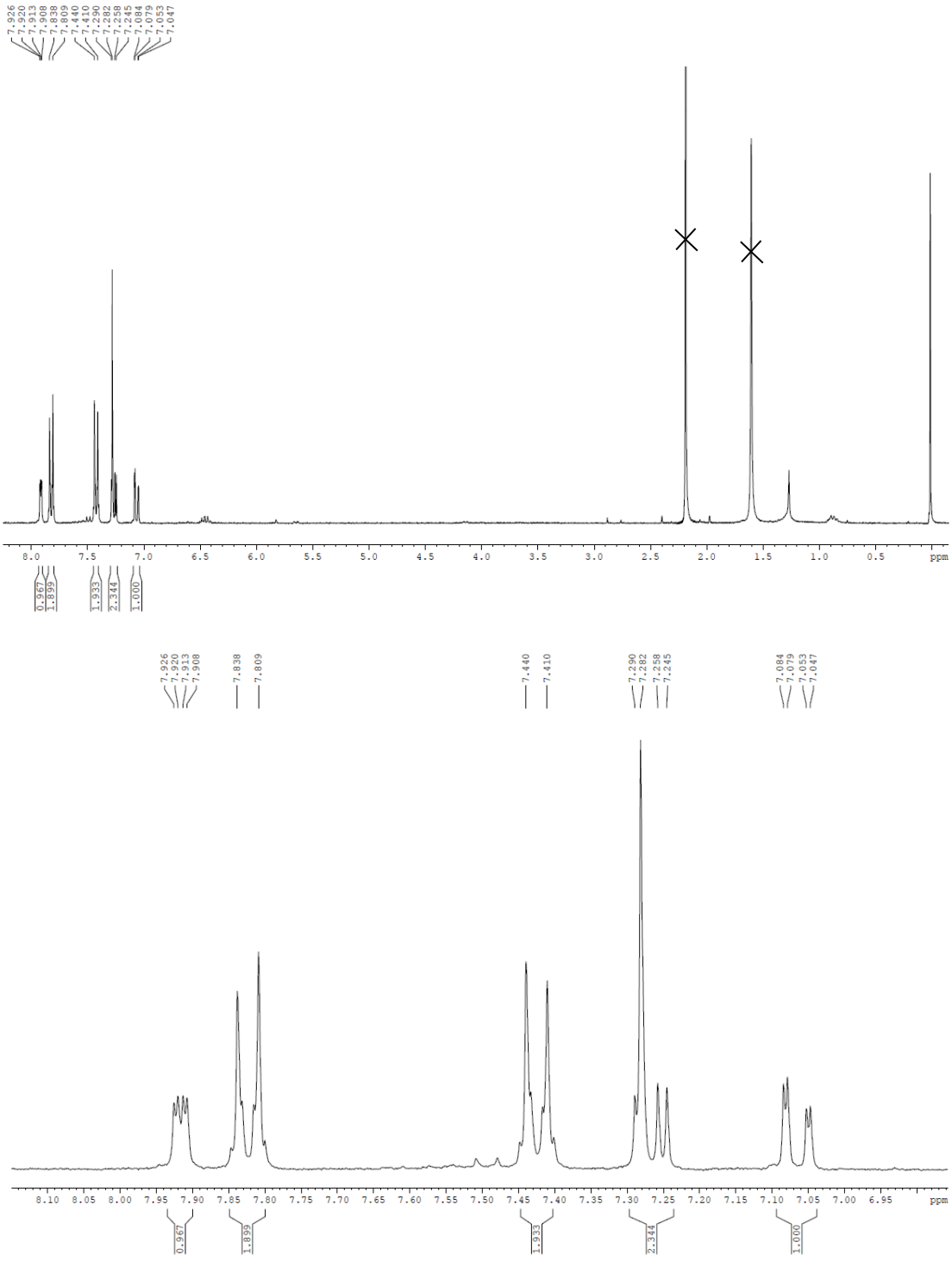
HRMS of compound 4c



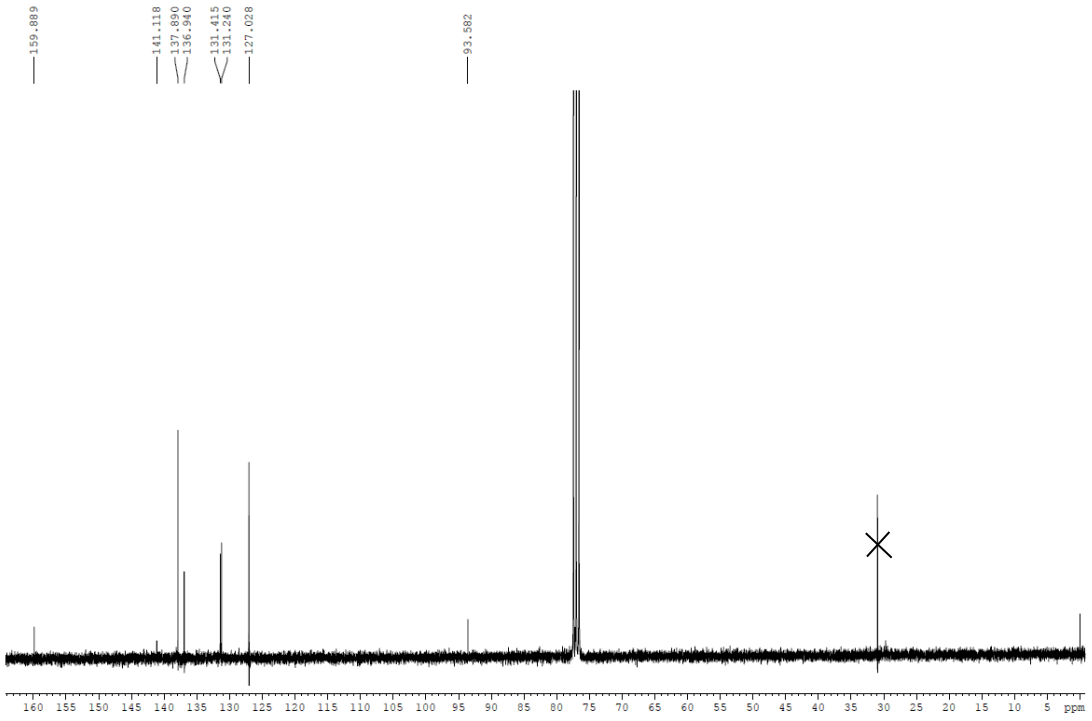
IR (ATR) of compound 4d



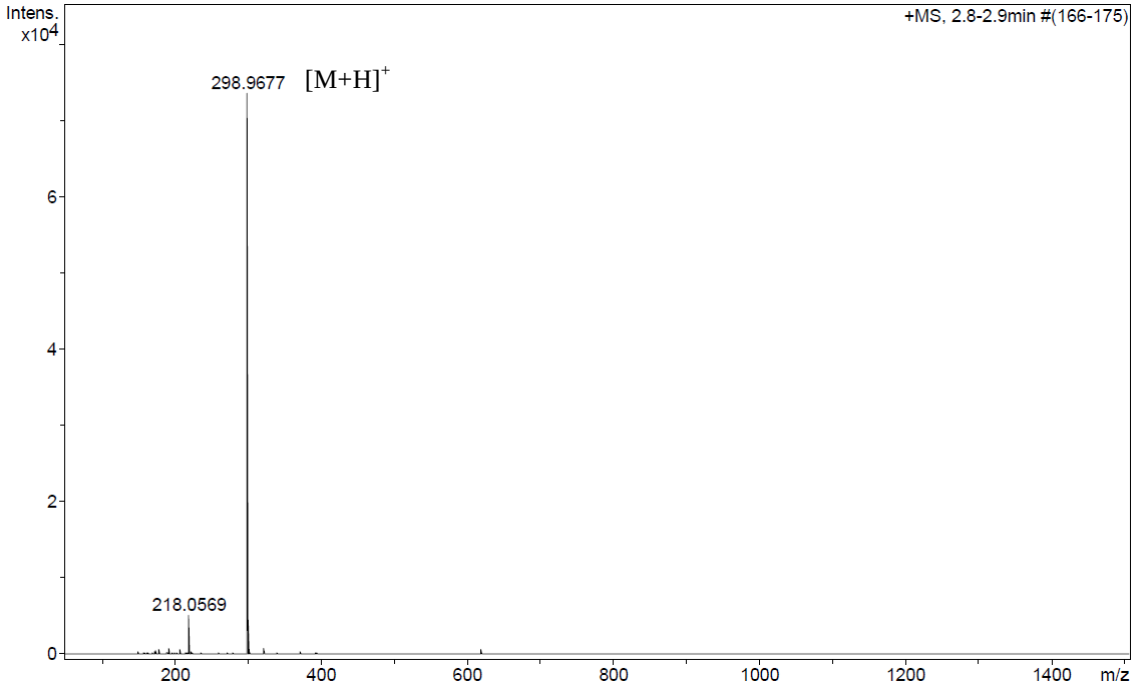
^{1}H NMR ($CDCl_3$, 300 MHz) of compound 4d



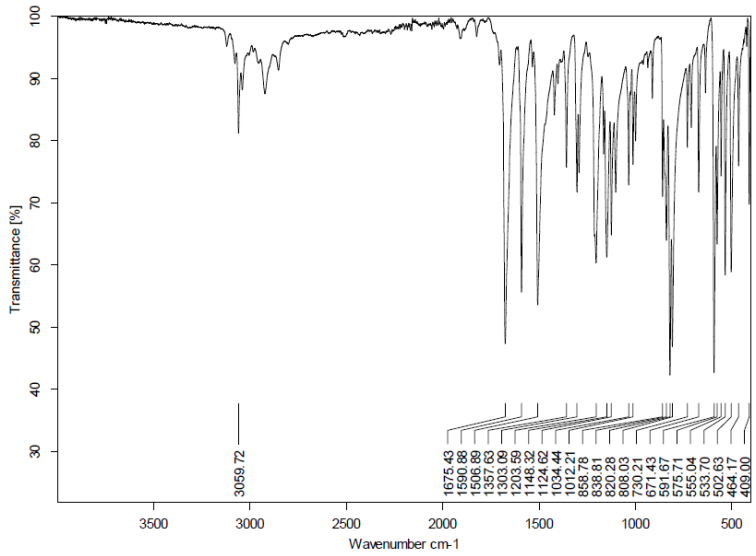
^{13}C NMR ($CDCl_3$, 75 MHz) of compound 4d

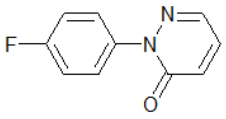


HRMS of compound 4d

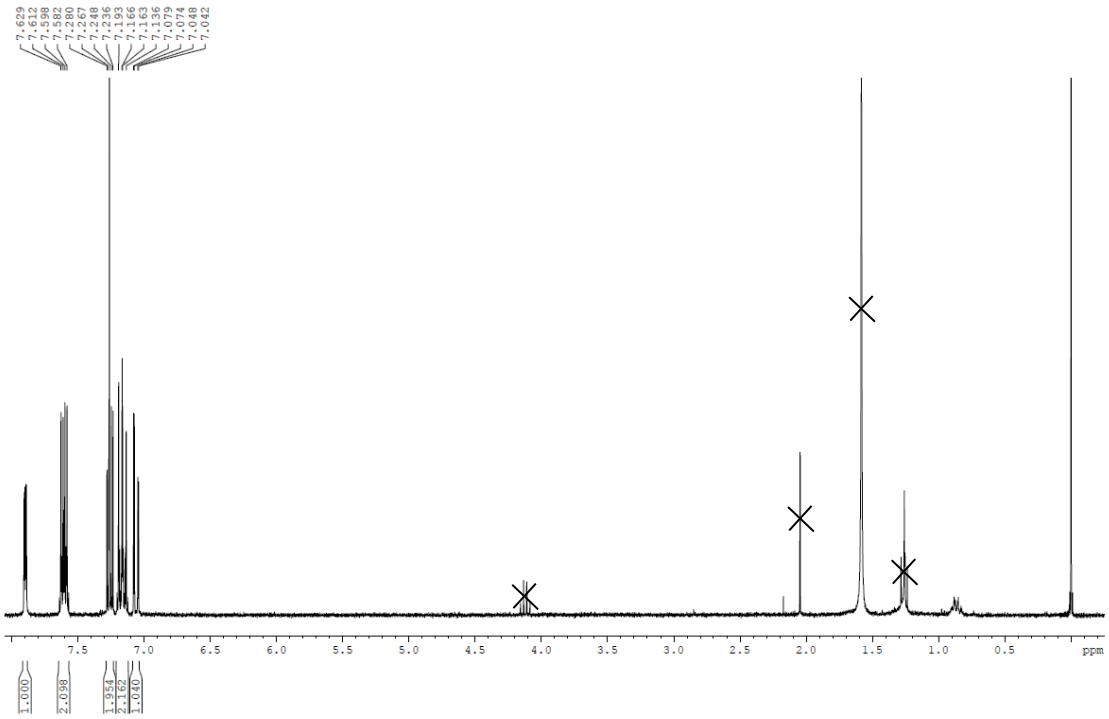


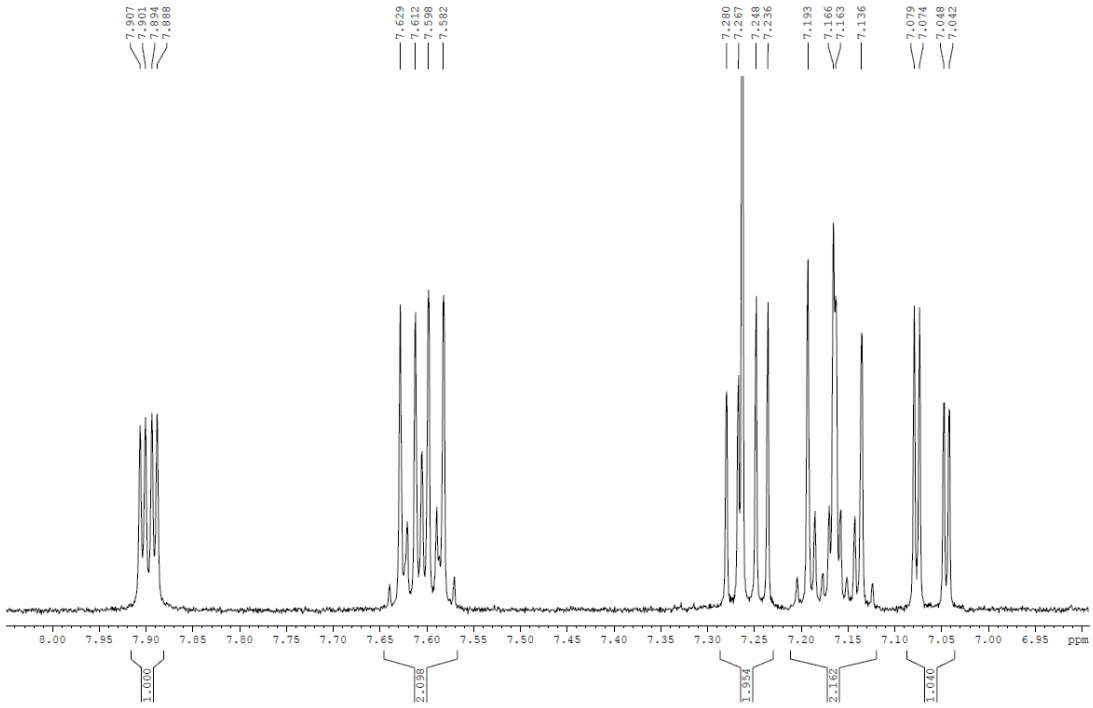
IR (ATR) of compound 4e



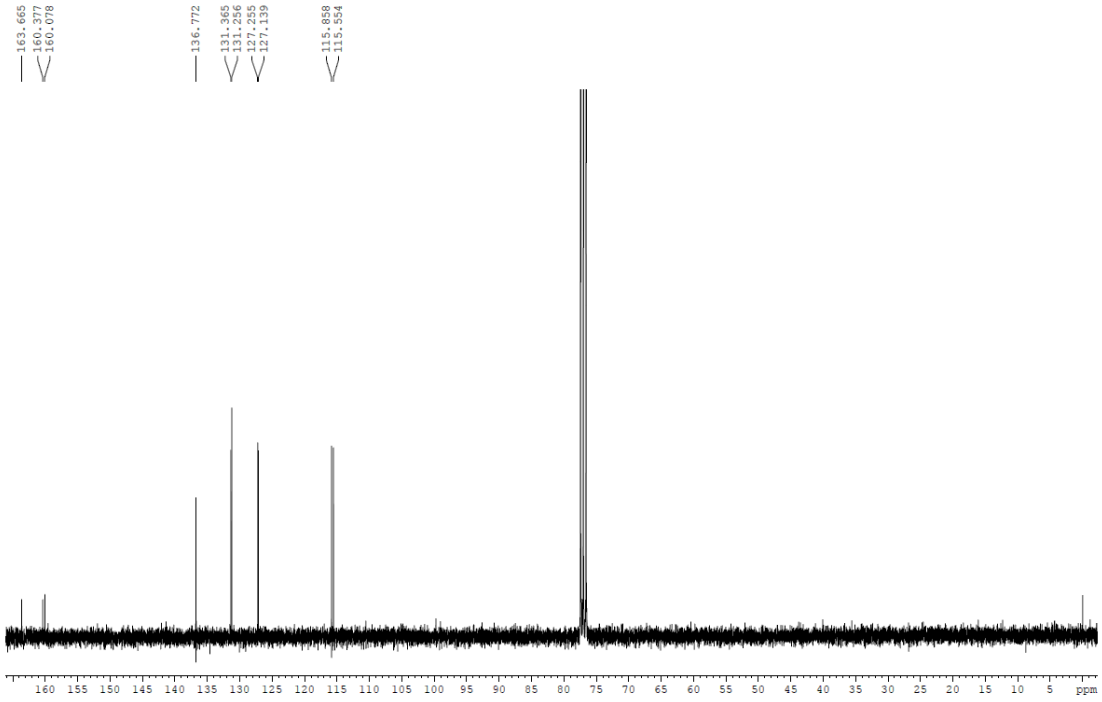


^{1}H NMR ($CDCl_3$, 300 MHz) of compound 4e

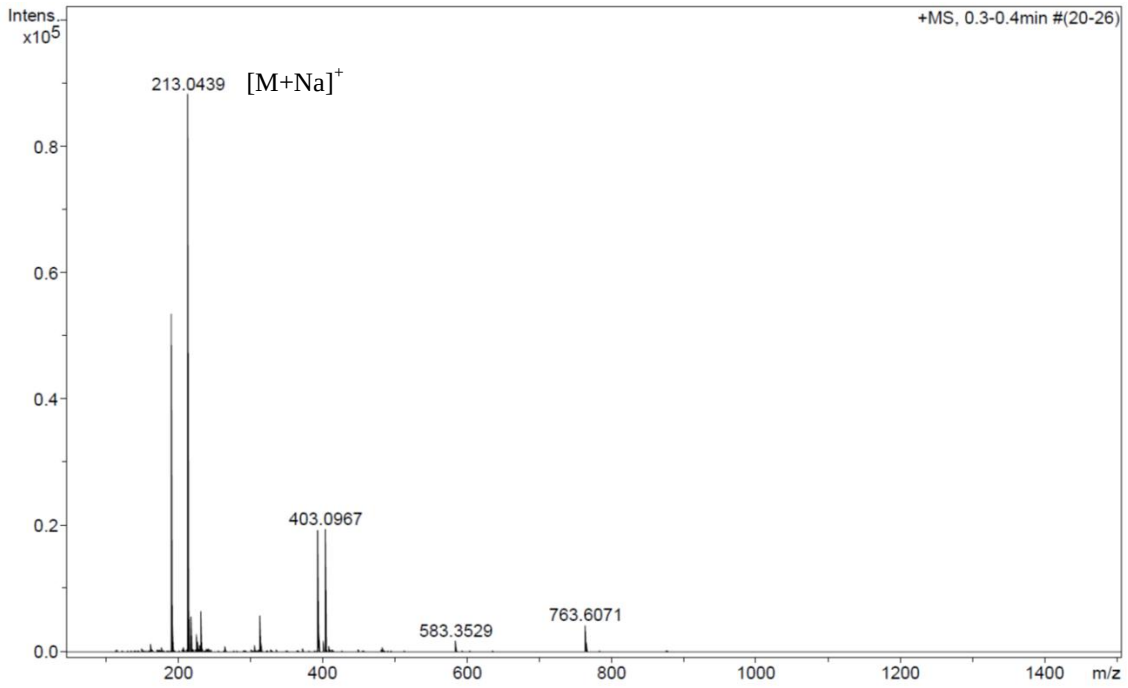




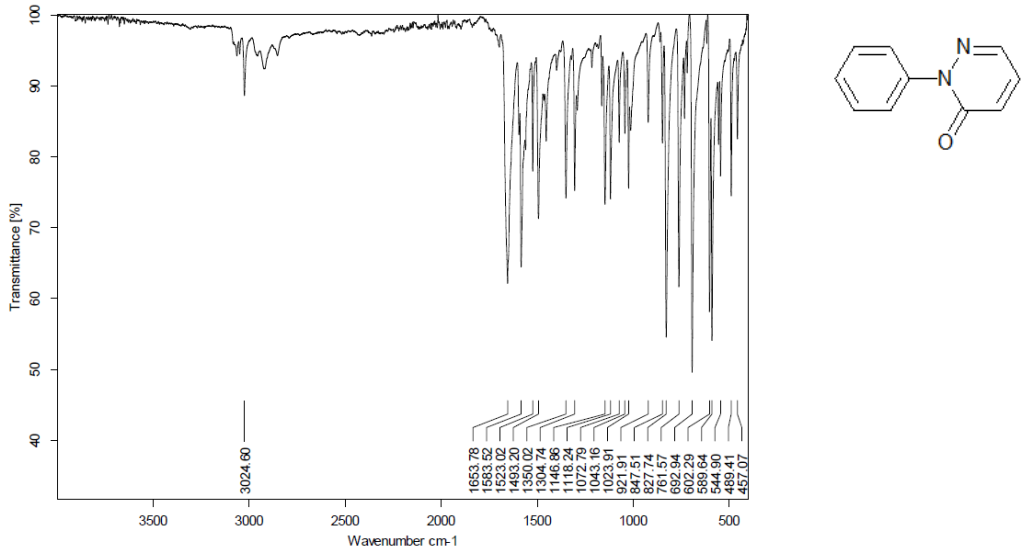
^{13}C NMR ($CDCl_3$, 75 MHz) of compound 4e



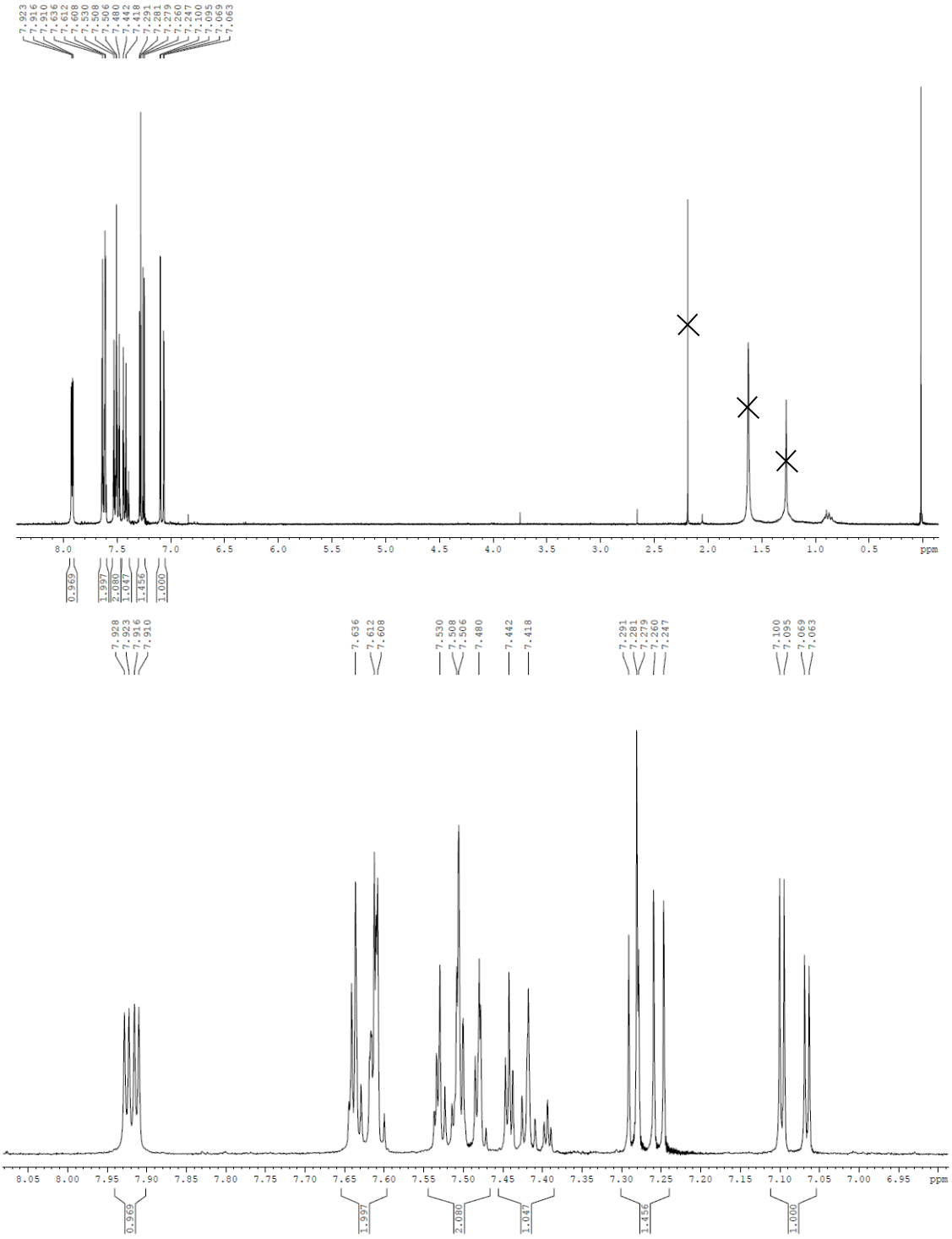
HRMS of compound 4e



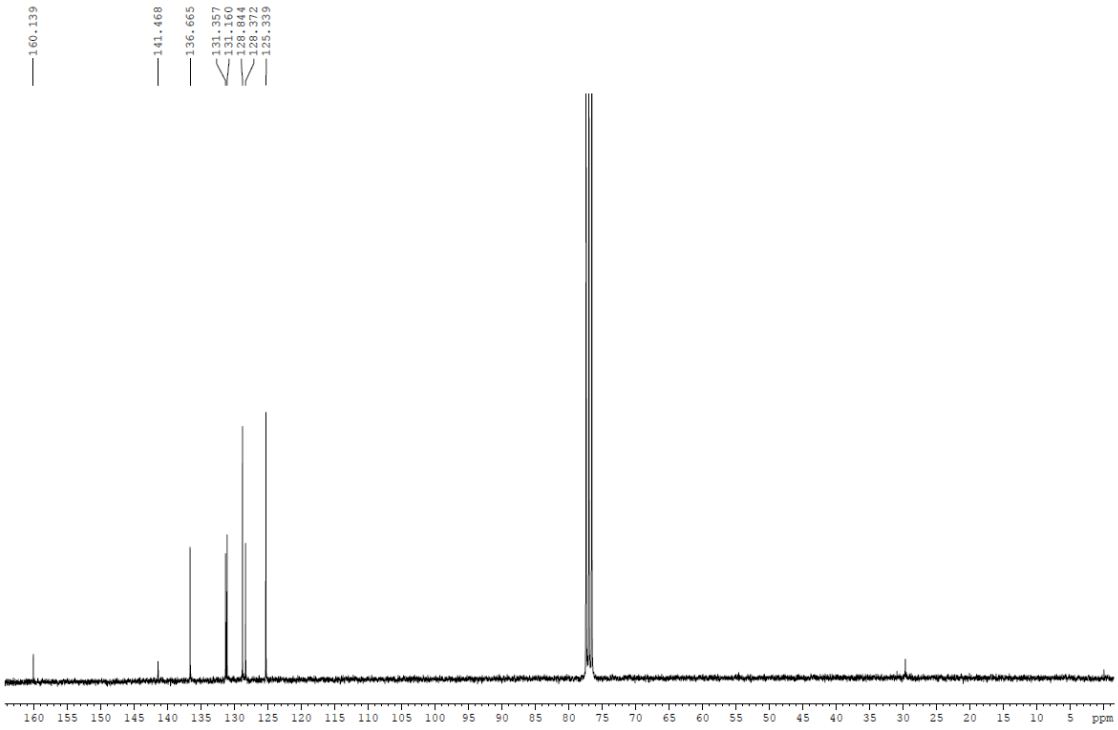
IR (ATR) of compound 4f



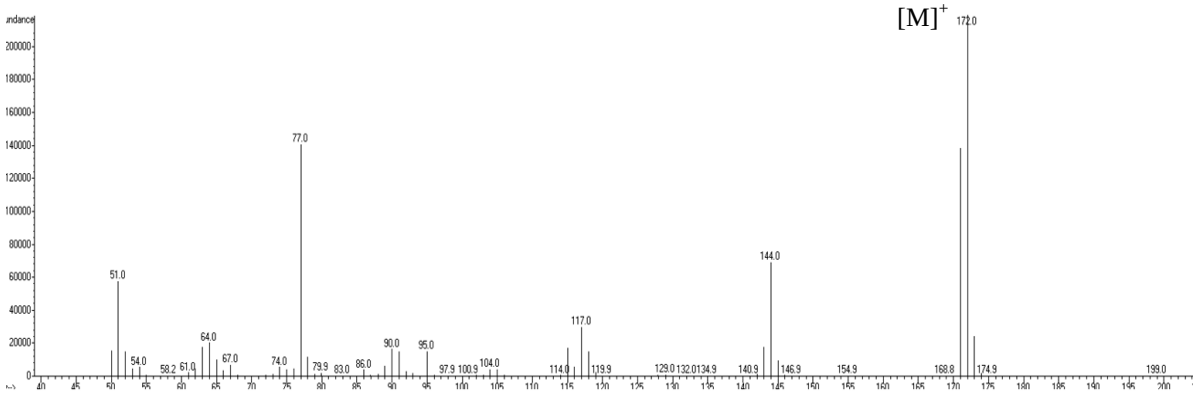
^{1}H NMR ($CDCl_3$, 300 MHz) of compound 4f



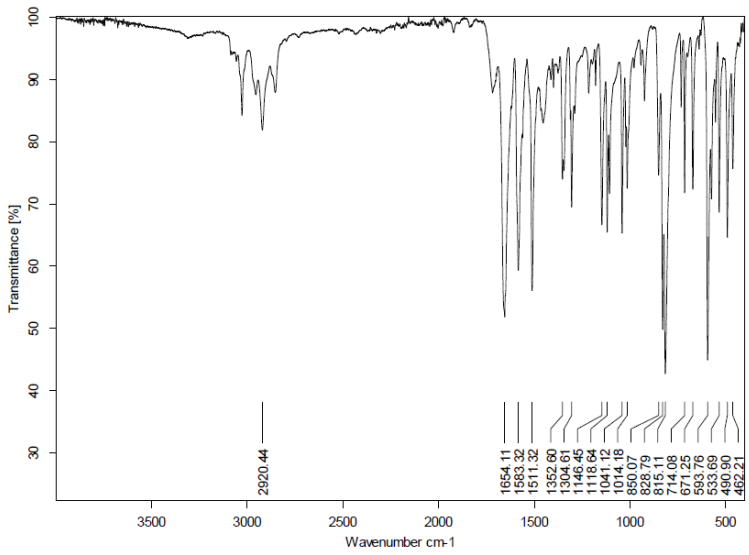
^{13}C NMR ($CDCl_3$, 75 MHz) of compound 4f

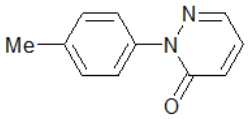


EI-MS (*m/z*) of compound 4f

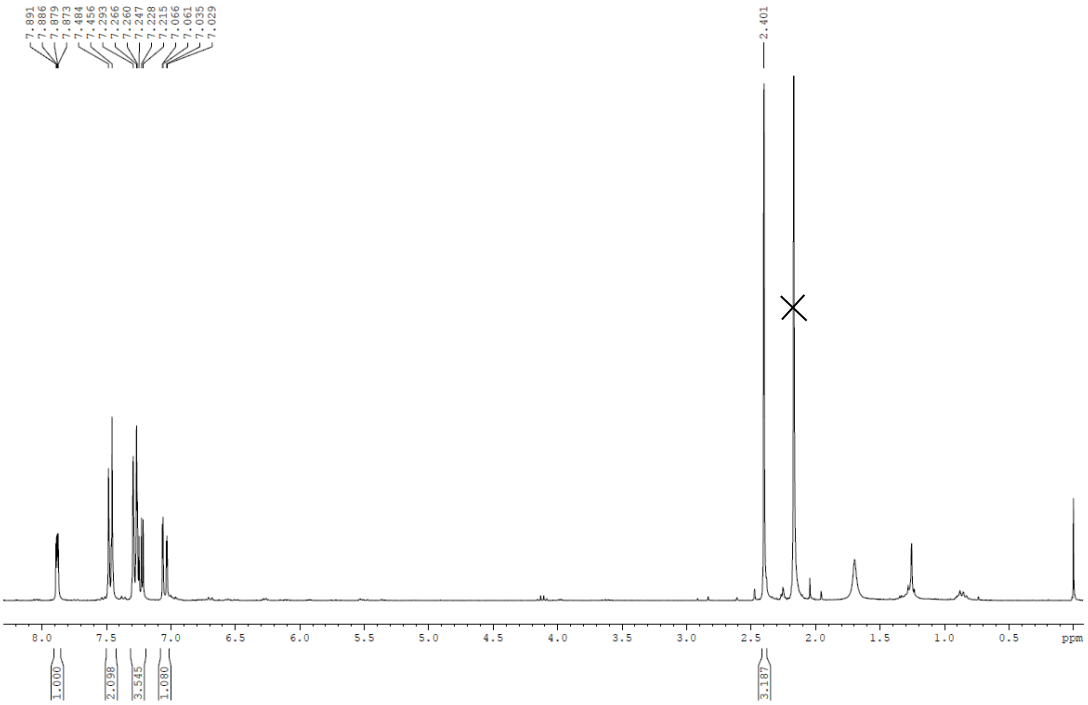


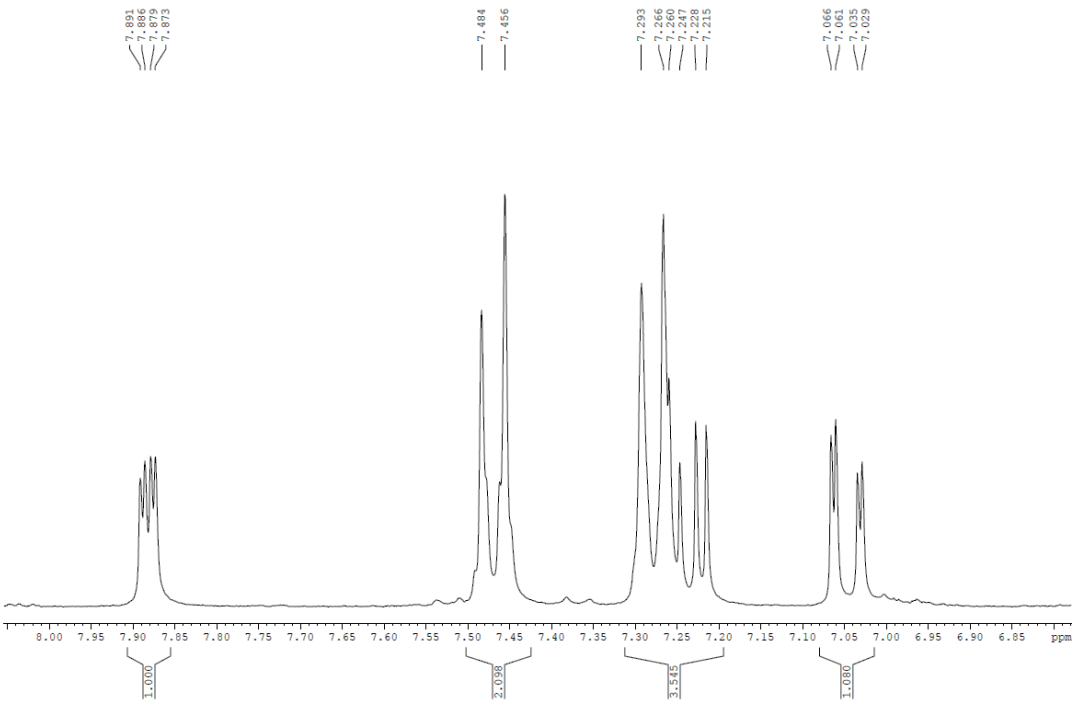
IR (ATR) of compound 4g



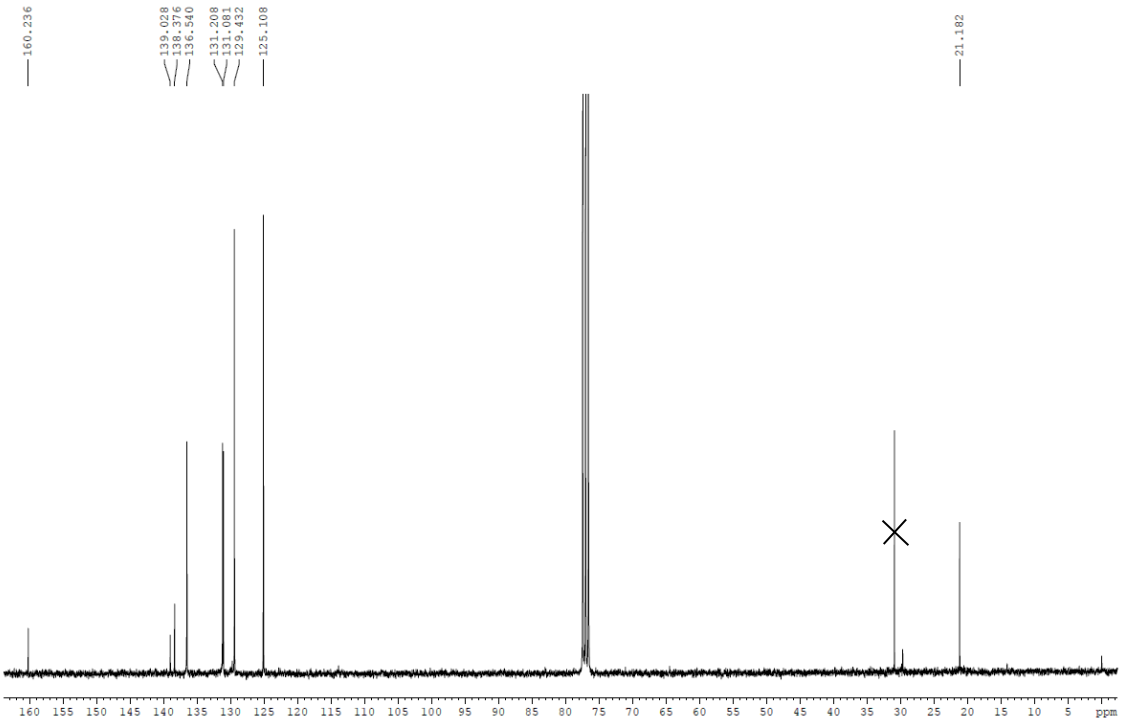


^{1}H NMR ($CDCl_3$, 300 MHz) of compound 4g

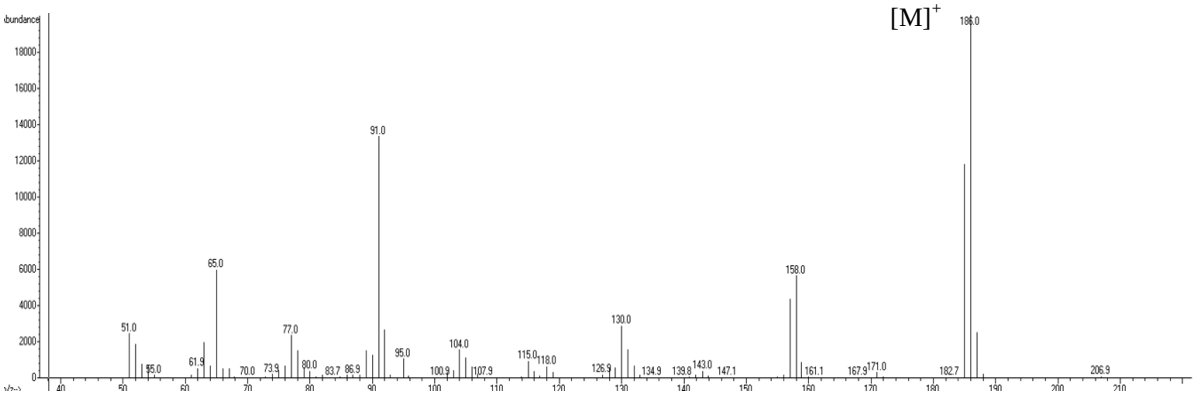




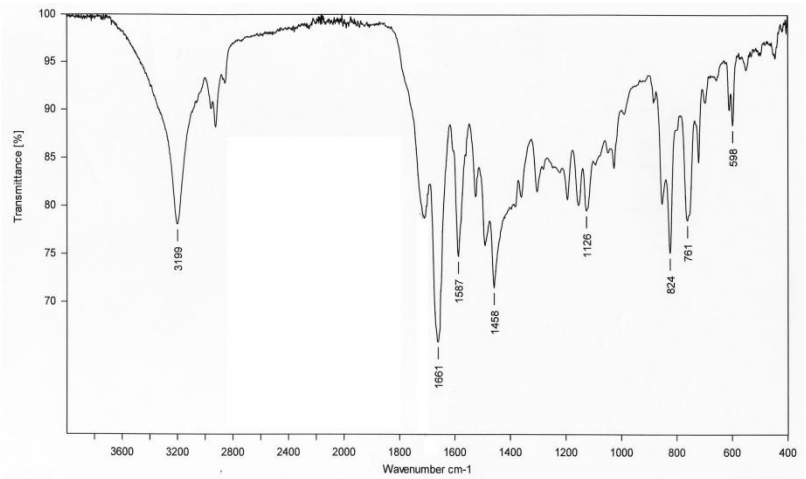
^{13}C NMR ($CDCl_3$, 75 MHz) of compound 4g

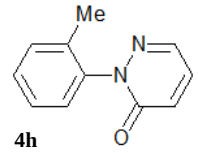


EI-MS (*m/z*) of compound 4g

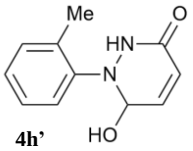


IR (ATR) of compound 4h + 4h'



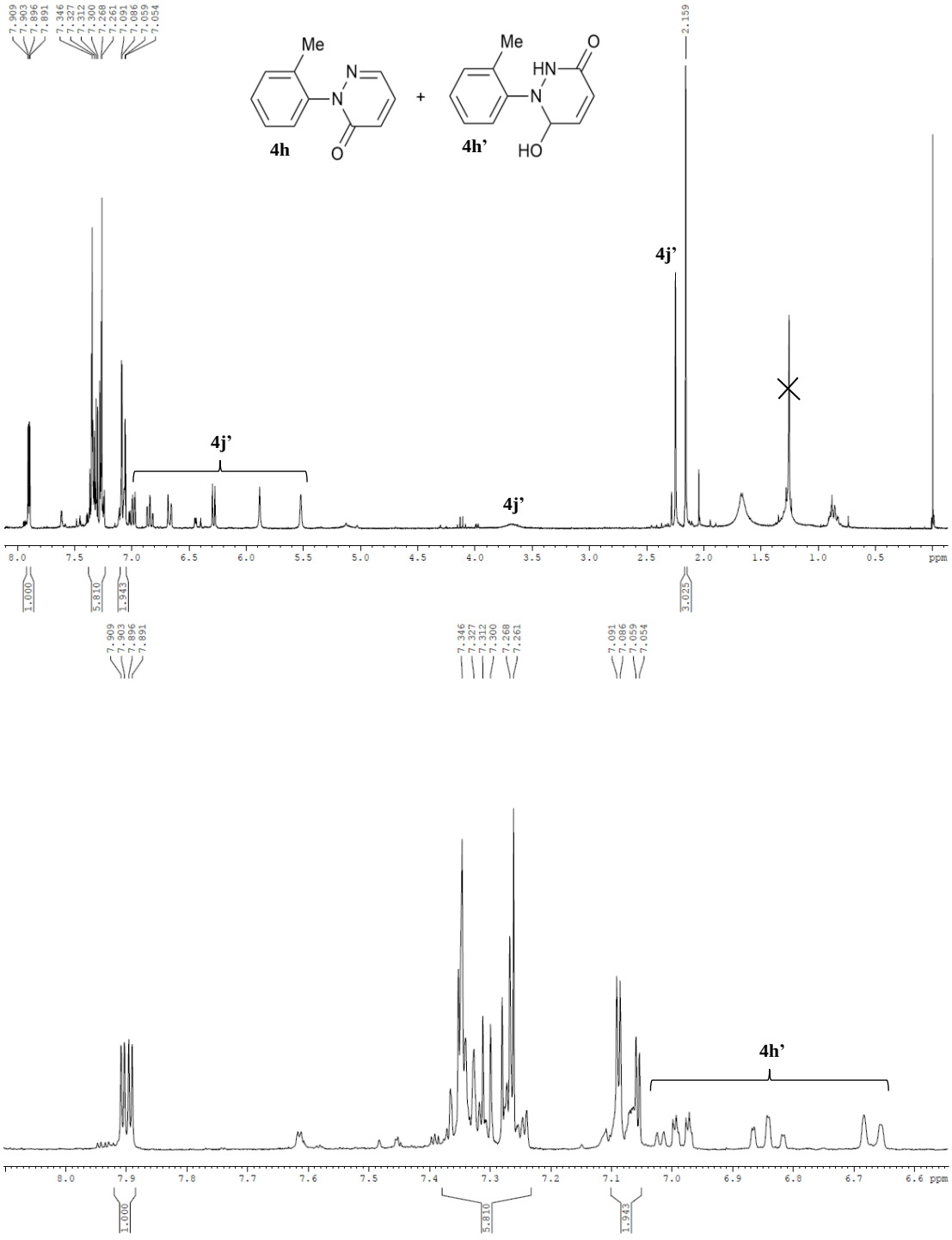


4h

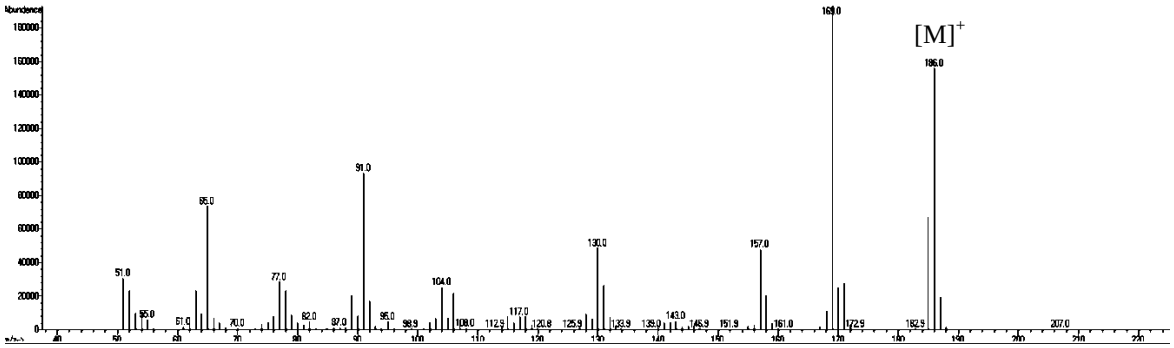


4h'

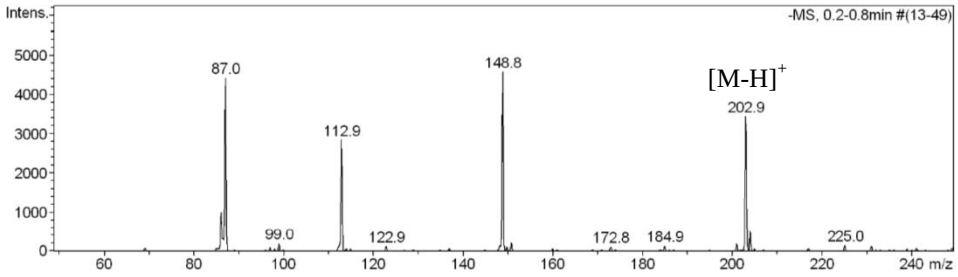
^{1}H NMR ($CDCl_3$, 300 MHz) of compound 4h



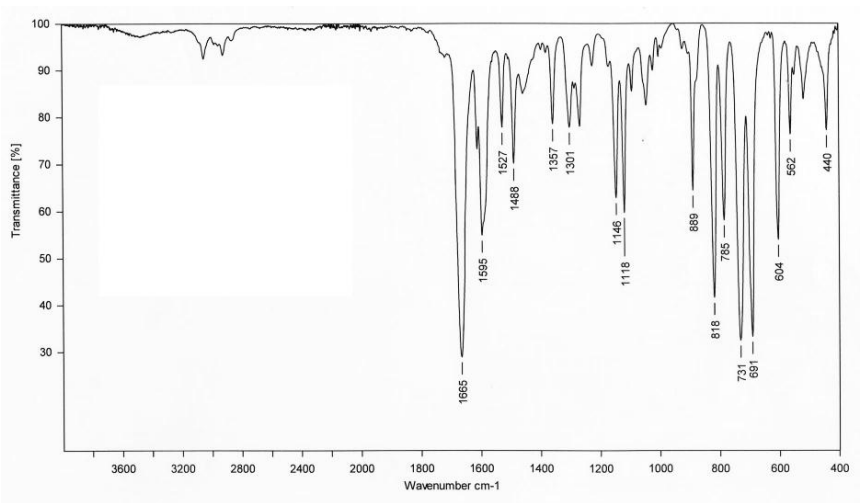
EI-MS (*m/z*) of compound 4h

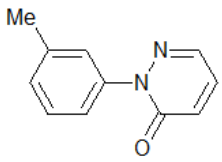


ESI-MS (*m/z*) of compound 4h'

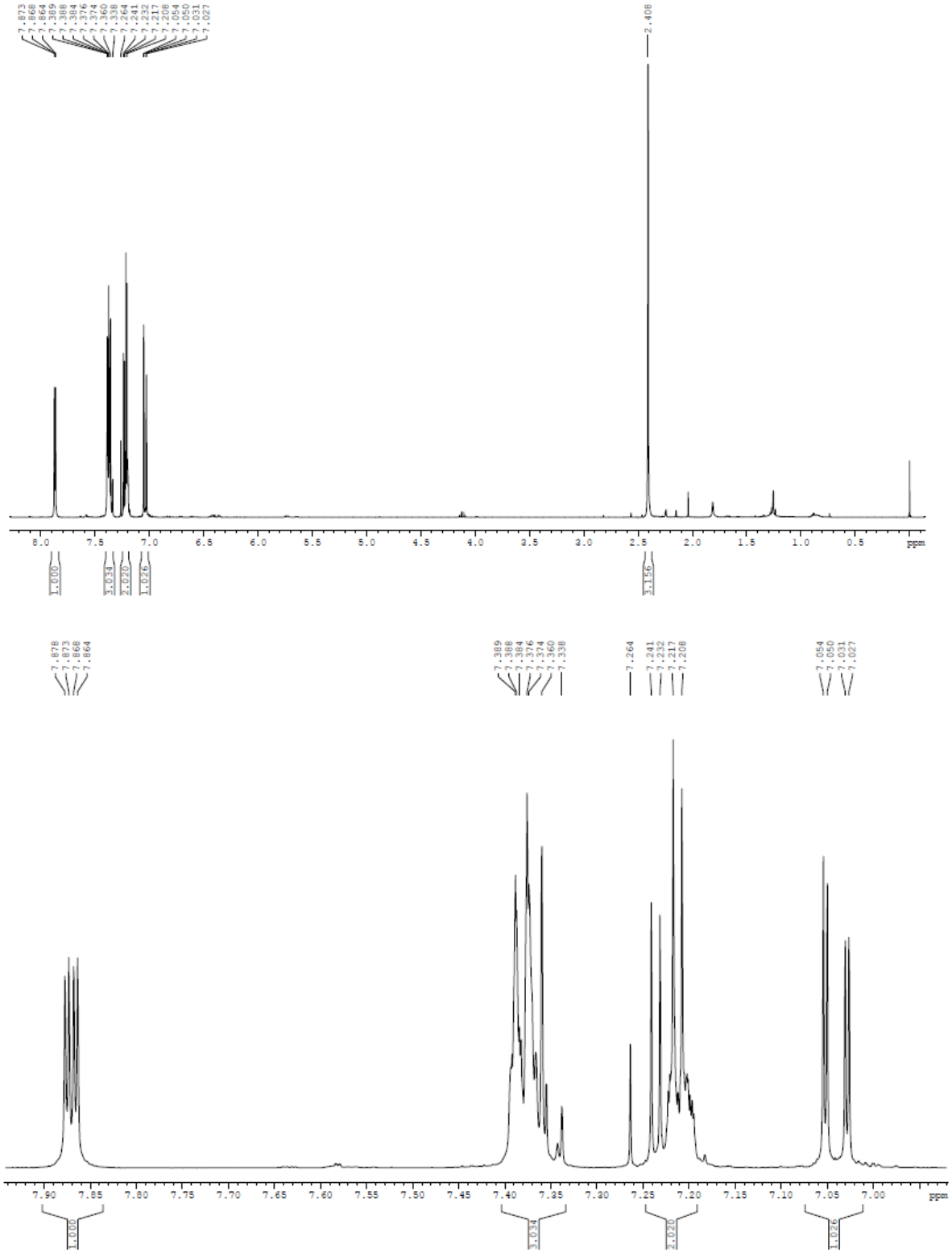


IR (ATR) of compound 4i

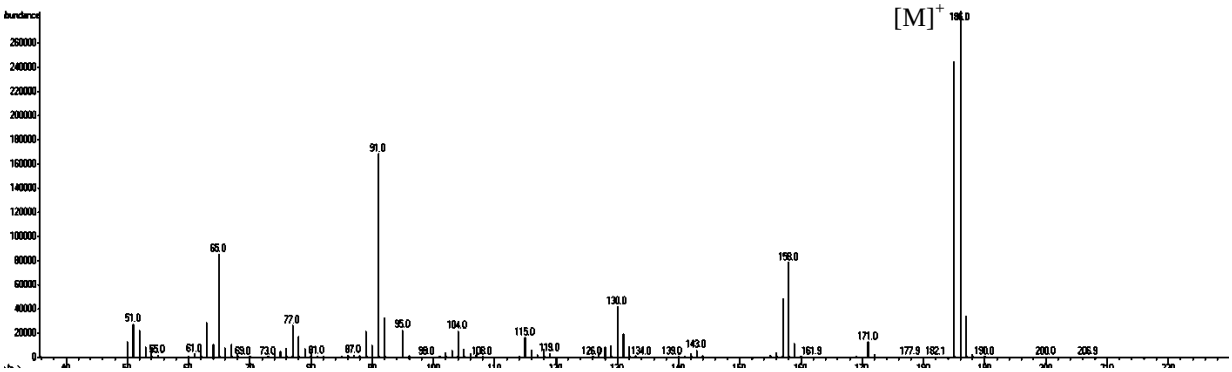




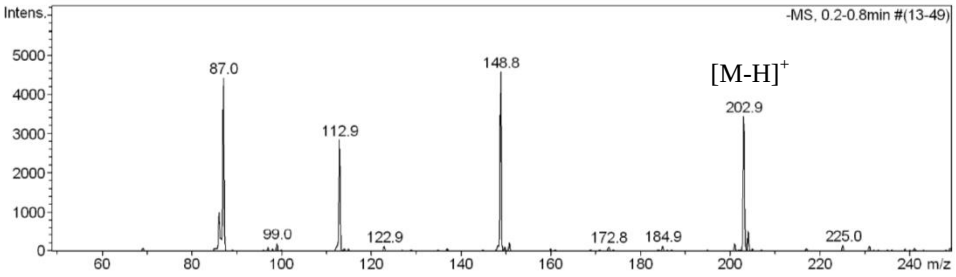
^{1}H NMR ($CDCl_3$, 400 MHz) of compound 4i



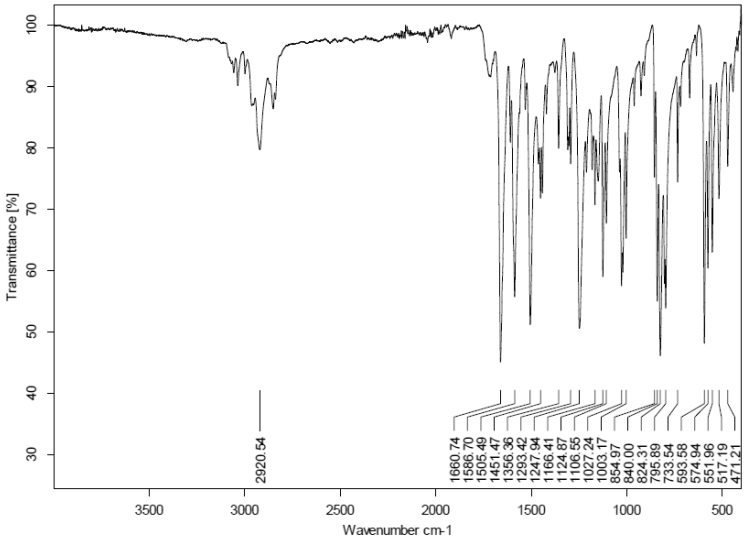
EI-MS (*m/z*) of compound 4i

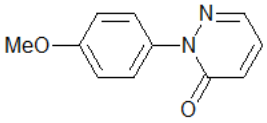


ESI (-)-MS (*m/z*) of compound 4i'

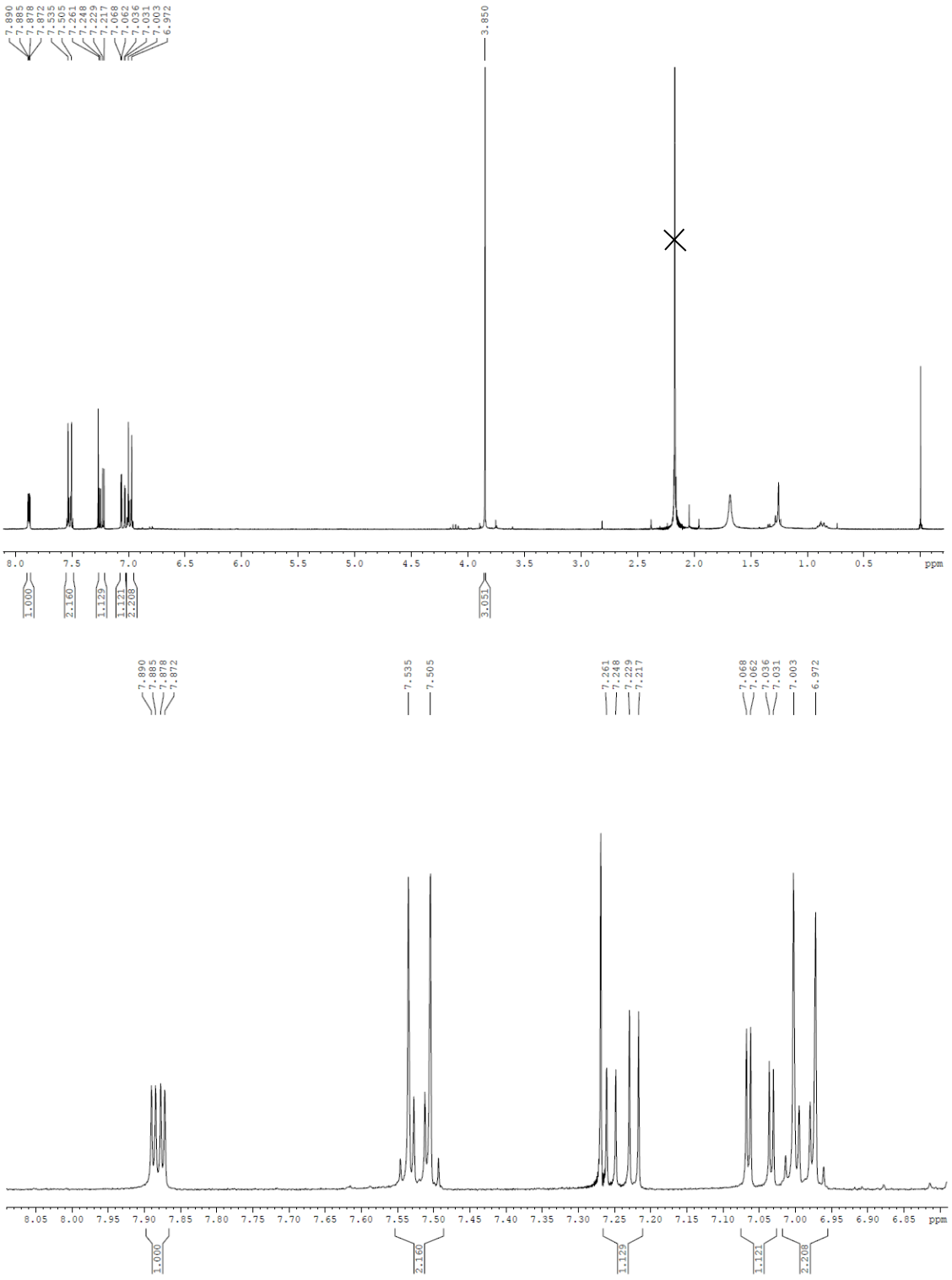


IR (ATR) of compound 4j

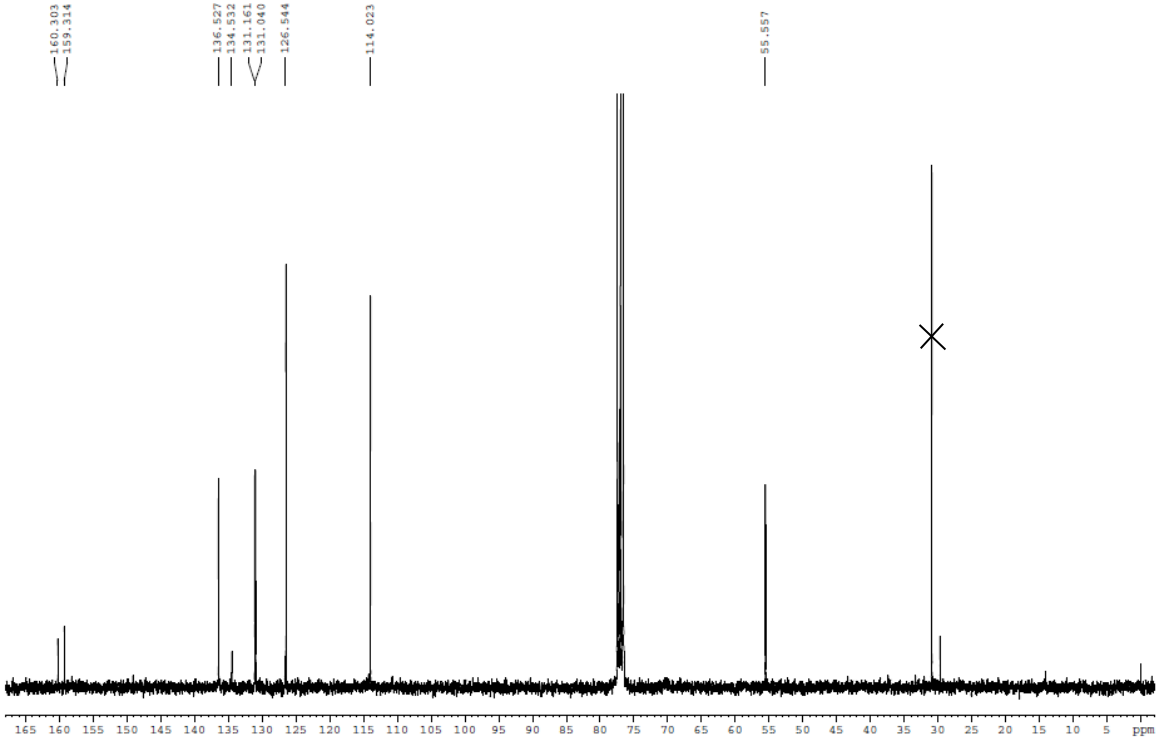




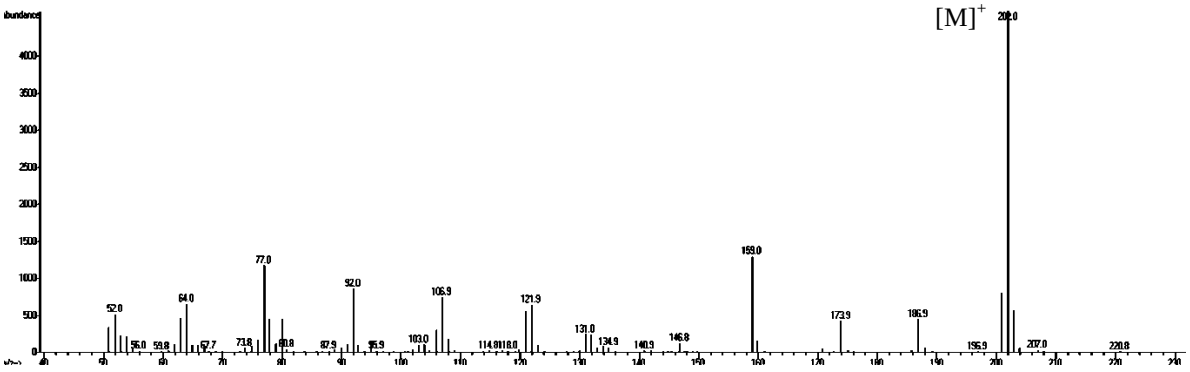
^{1}H NMR ($CDCl_3$, 300 MHz) of compound 4j



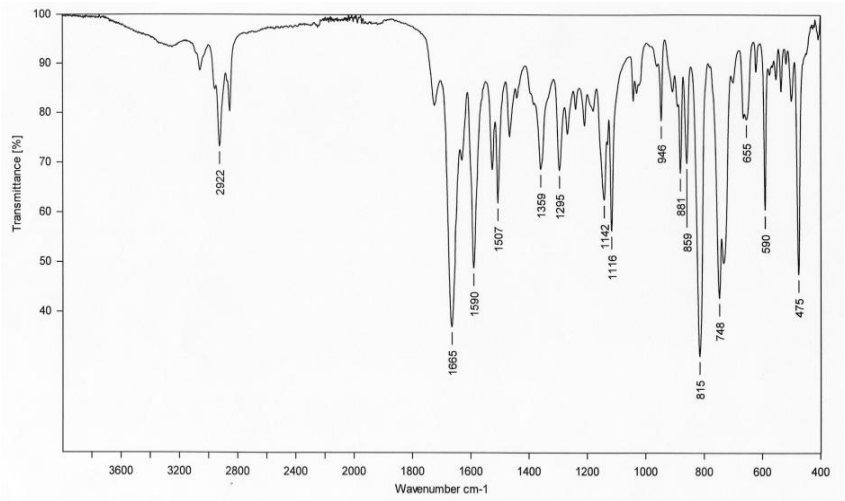
^{13}C NMR ($CDCl_3$, 75 MHz) of compound 4j

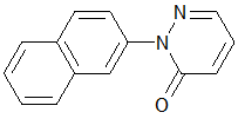


EI-MS (*m/z*) of compound 4j

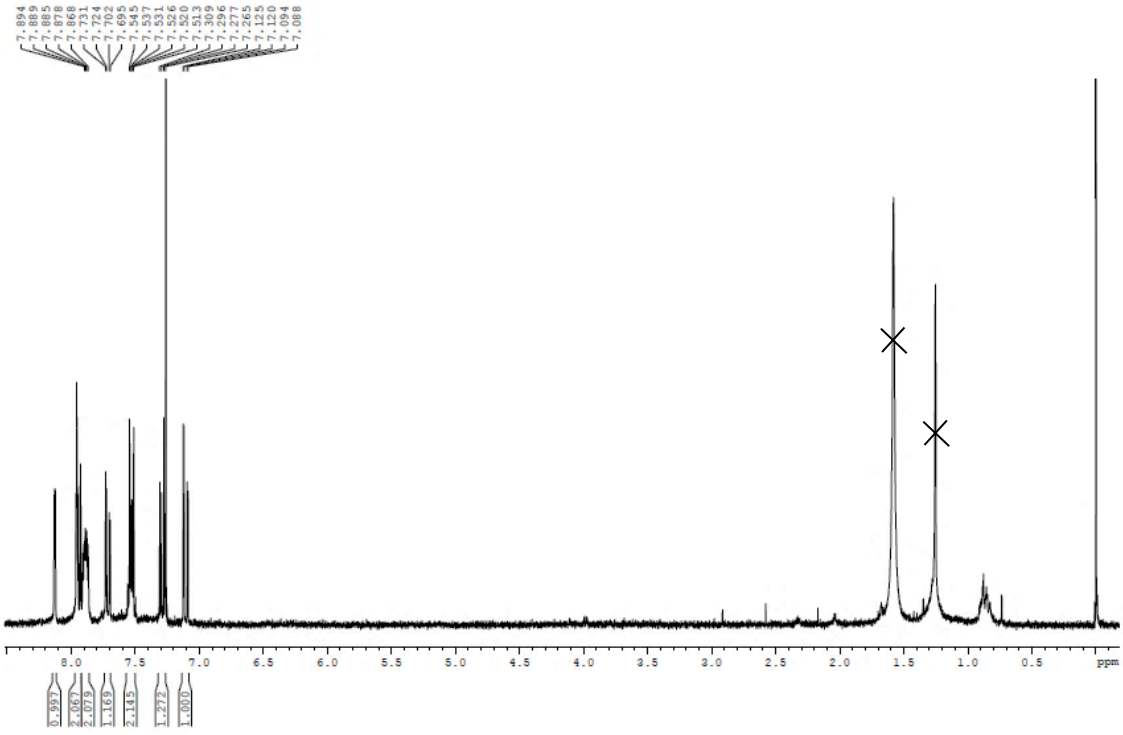


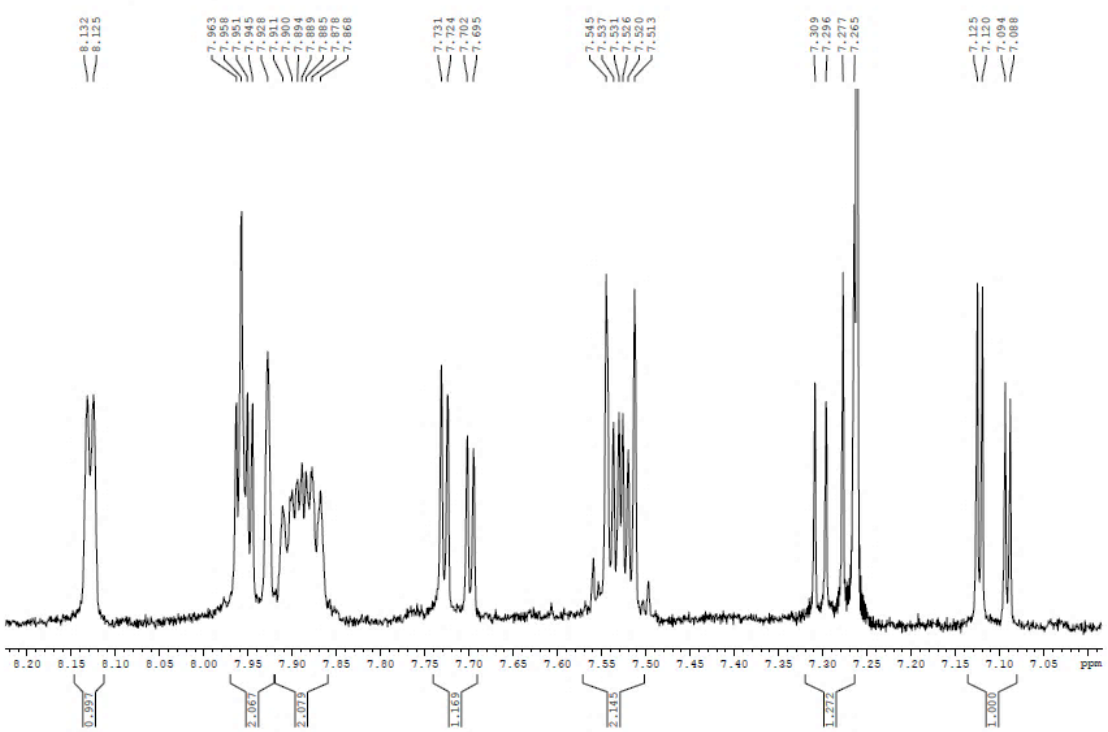
IR (ATR) of compound 4k



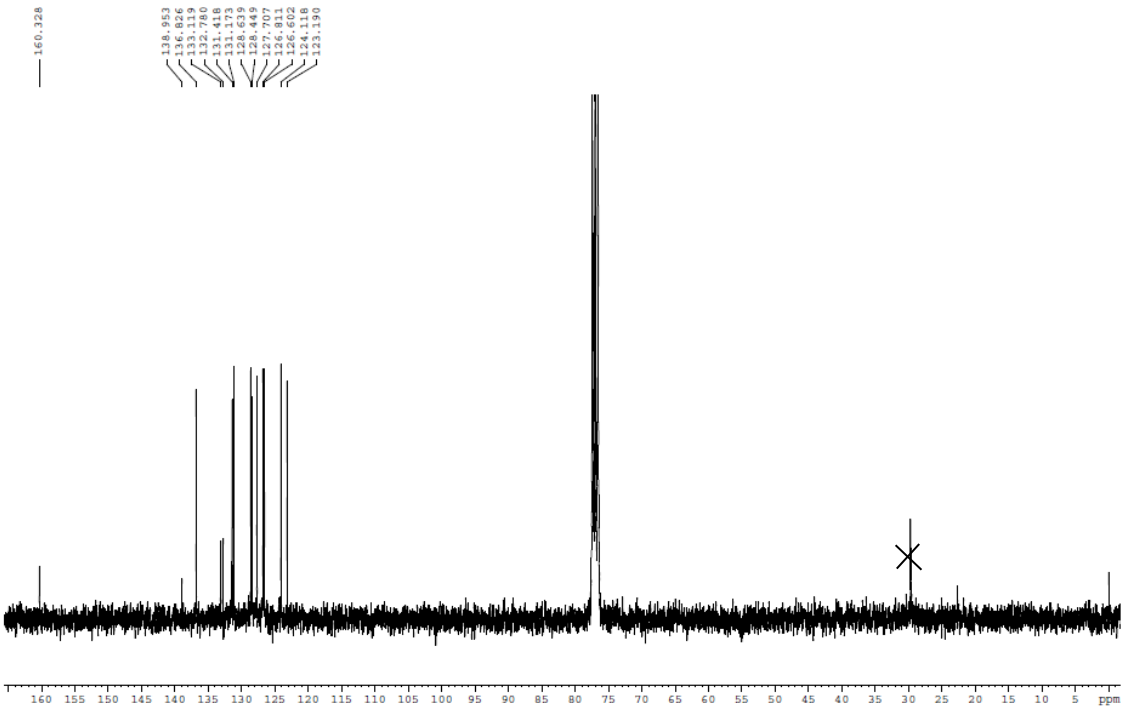


^{1}H NMR ($CDCl_3$, 300 MHz) of compound 4k

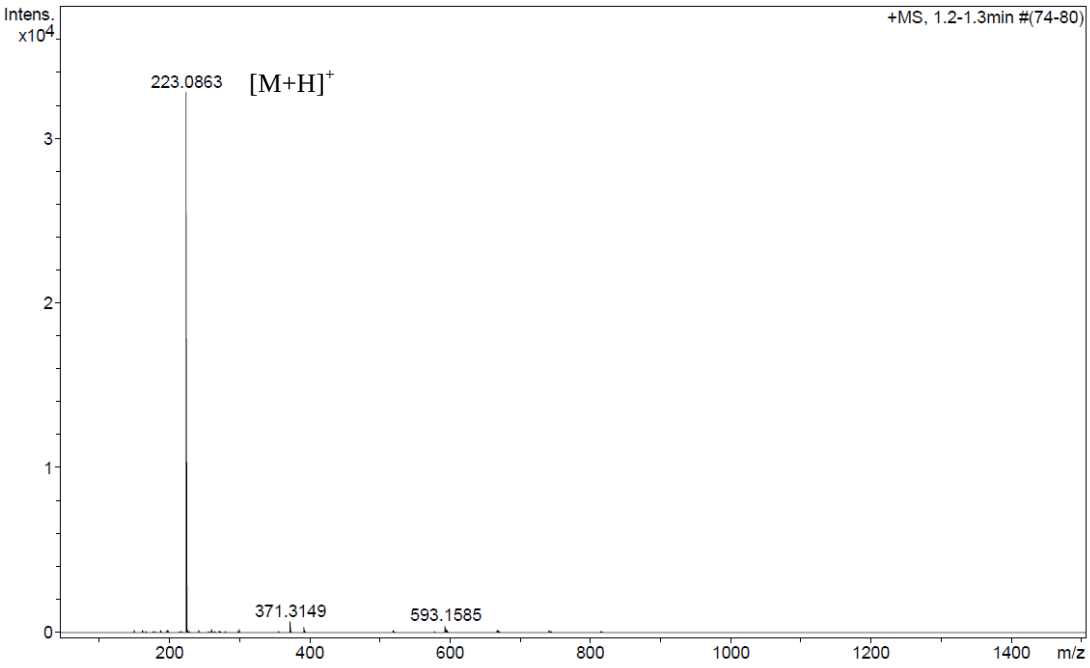




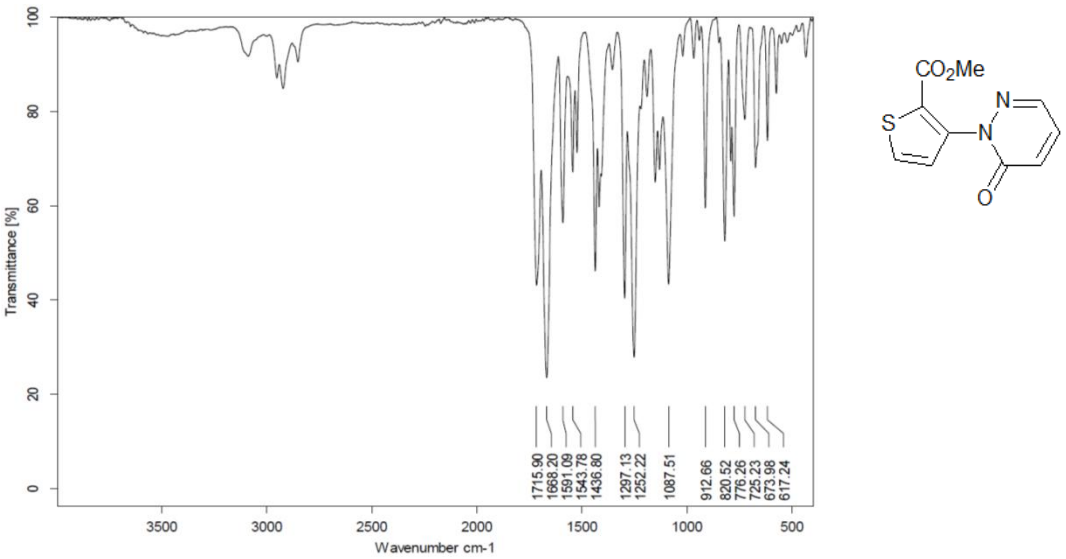
^{13}C NMR ($CDCl_3$, 75 MHz) of compound 4k



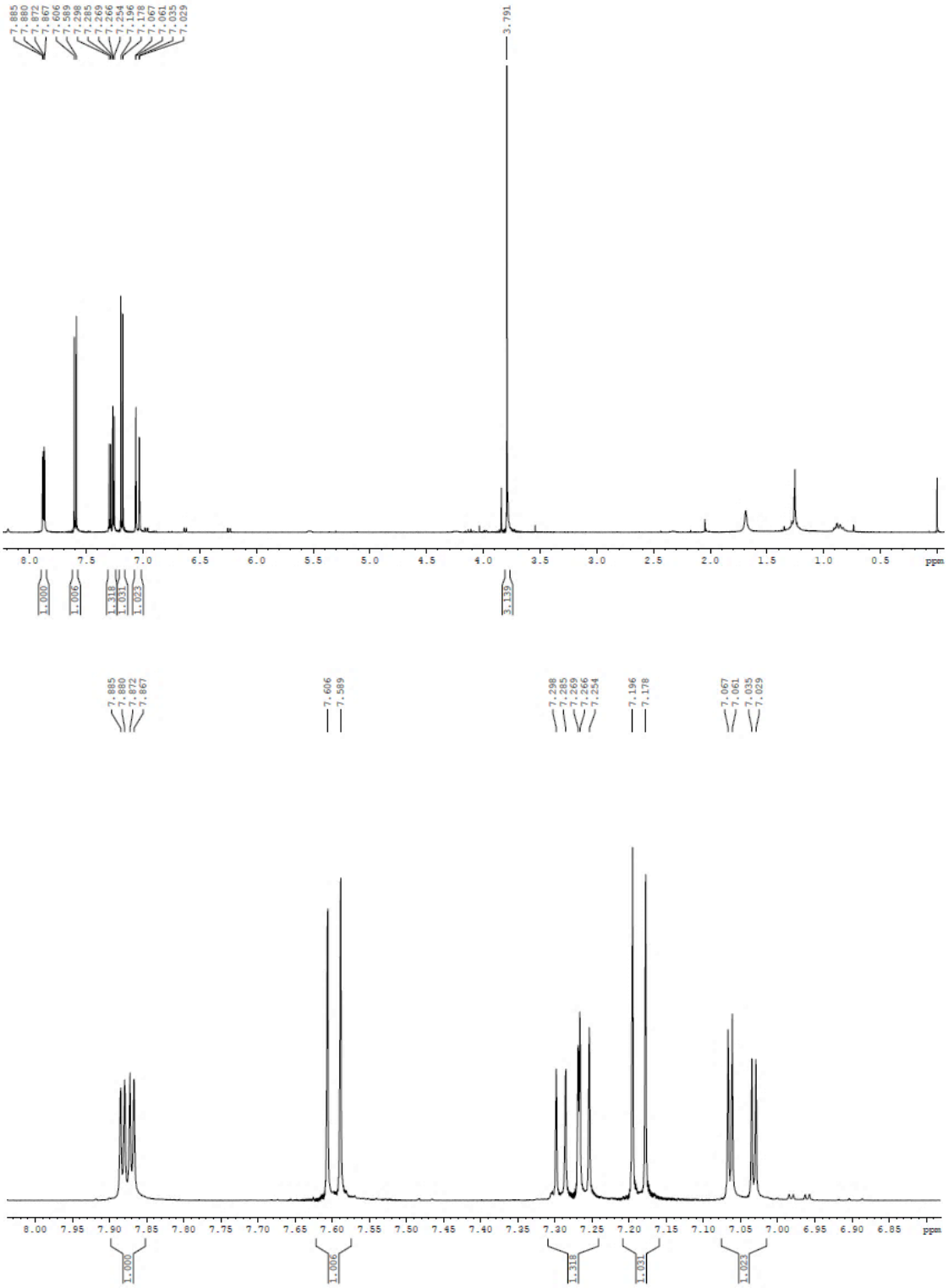
HRMS of compound 4k



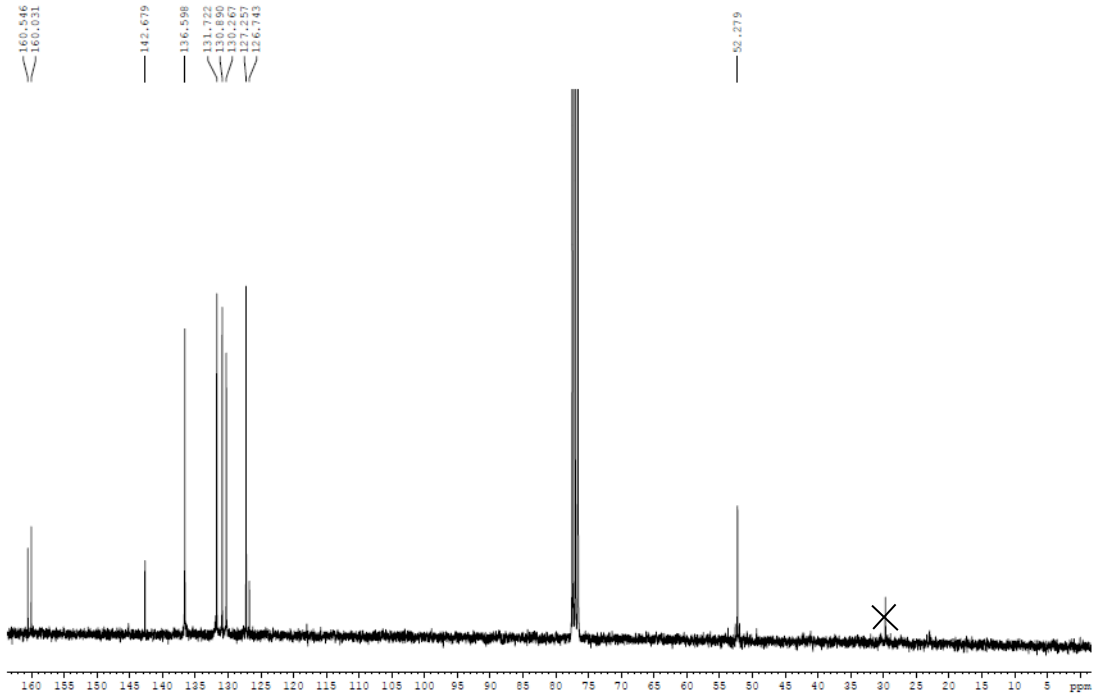
IR (ATR) of compound 4l



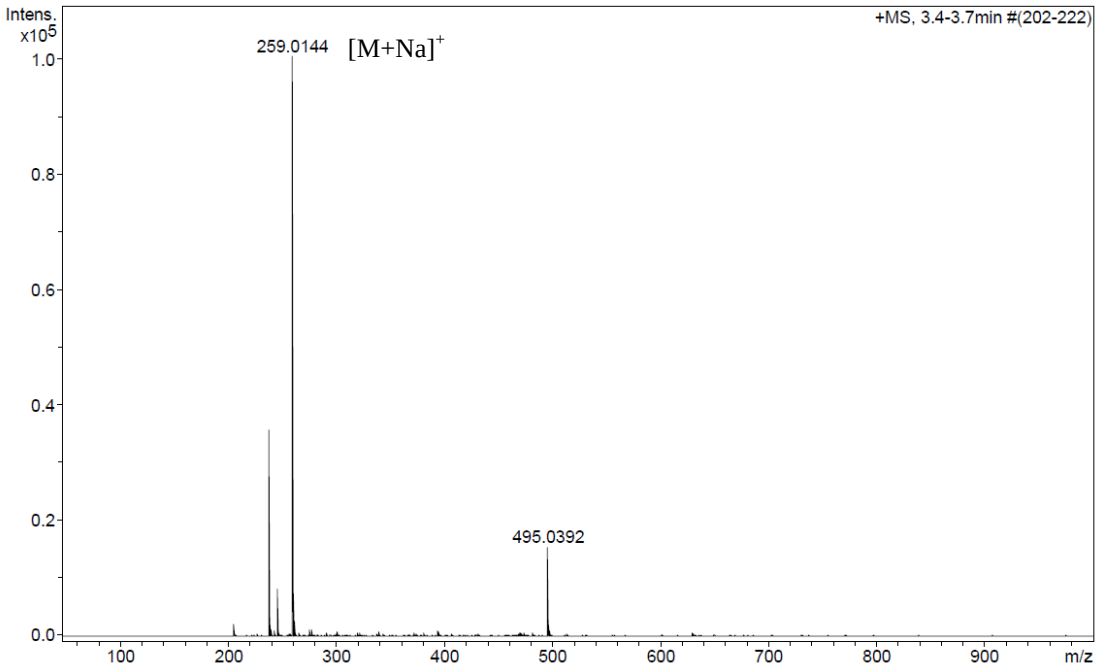
^{1}H NMR ($CDCl_3$, 300 MHz) of compound 4l



^{13}C NMR ($CDCl_3$, 75 MHz) of compound 4l

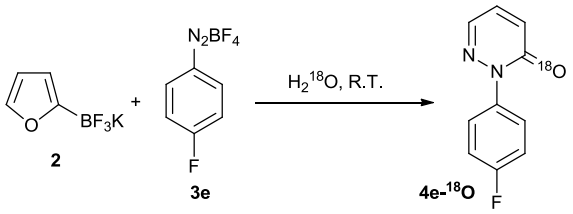


HRMS of compound 4l

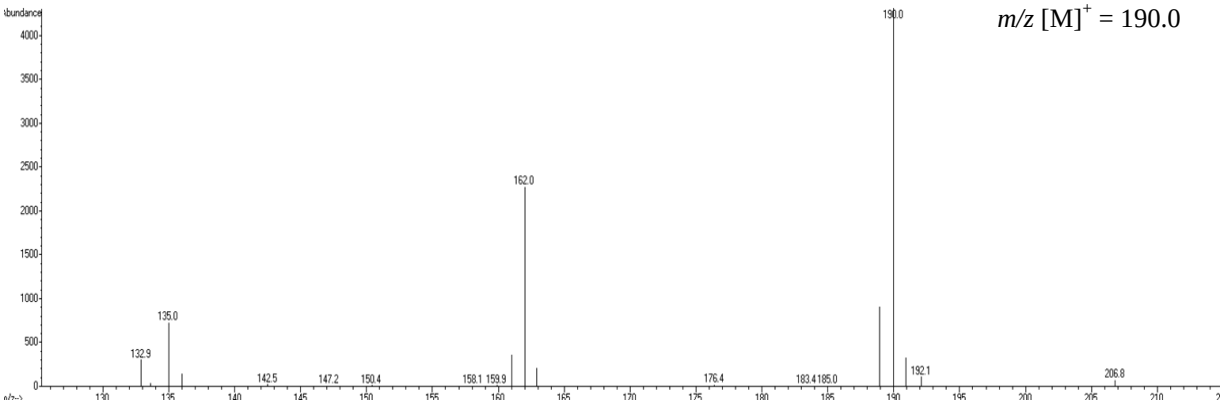


Isotopic experiments for the formation of 4e

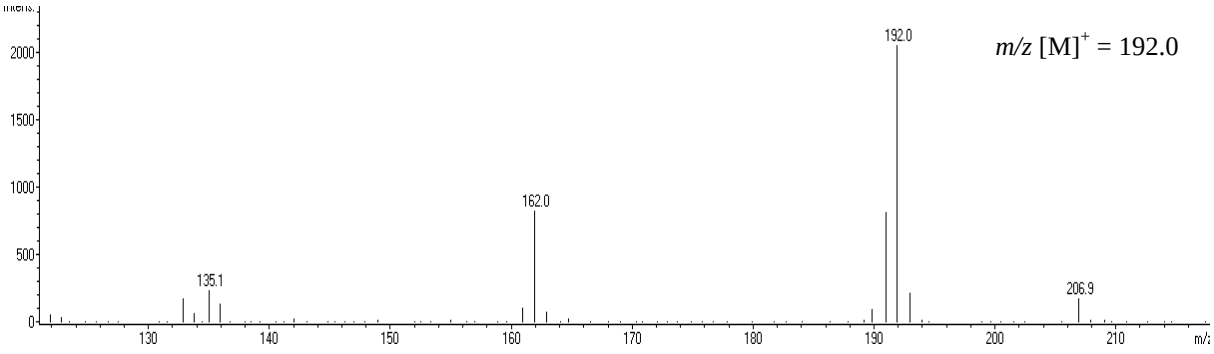
The reaction was carried out following the general procedure but using $H_2{}^{18}O$ 99% as solvent.



EI-MS of compound **4e**



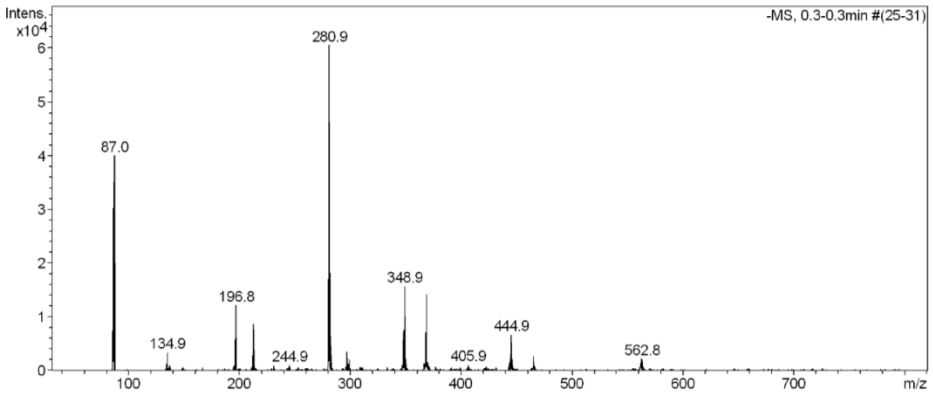
EI-MS of compound **4e-^{18}O**



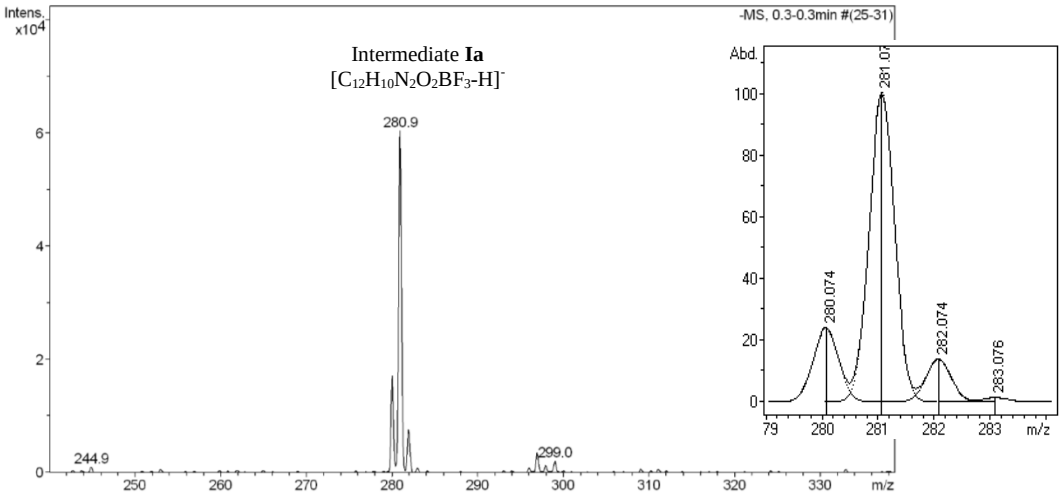
ESI-MS experiments for the detection of reactive intermediates in the formation of 4a

ESI(-) mass spectrum of a solution of **2** and **3a** in H_2O/CH_3CN 7:3

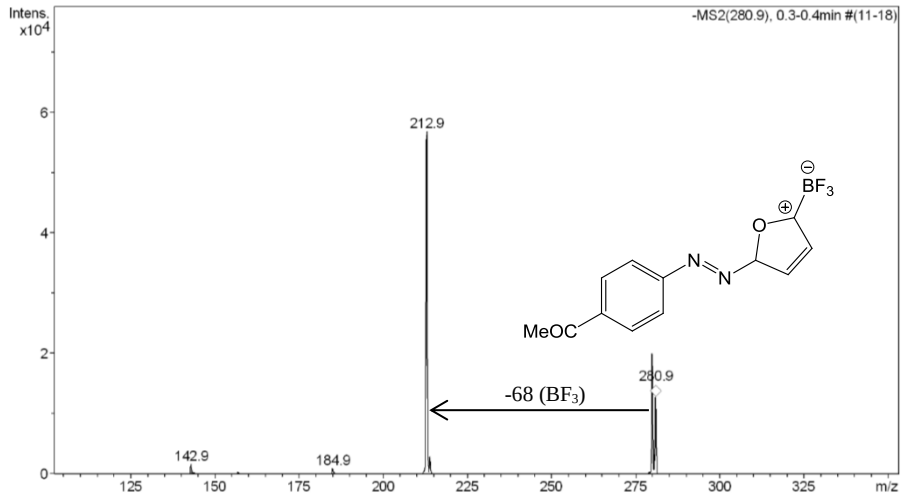
a)



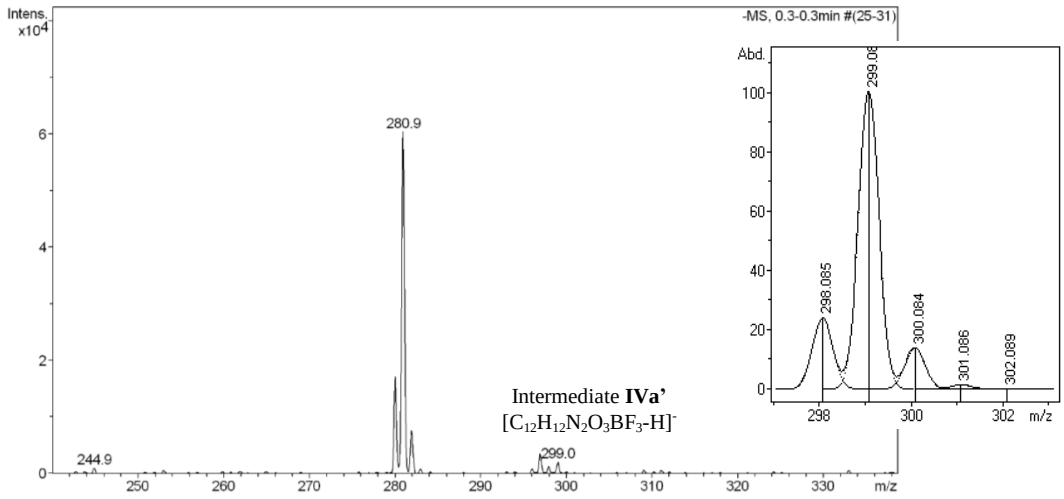
b) Isotope pattern experimentally obtained compared to that calculated for intermediate at *m/z* = 280.9 (Intermediate **Ia**)



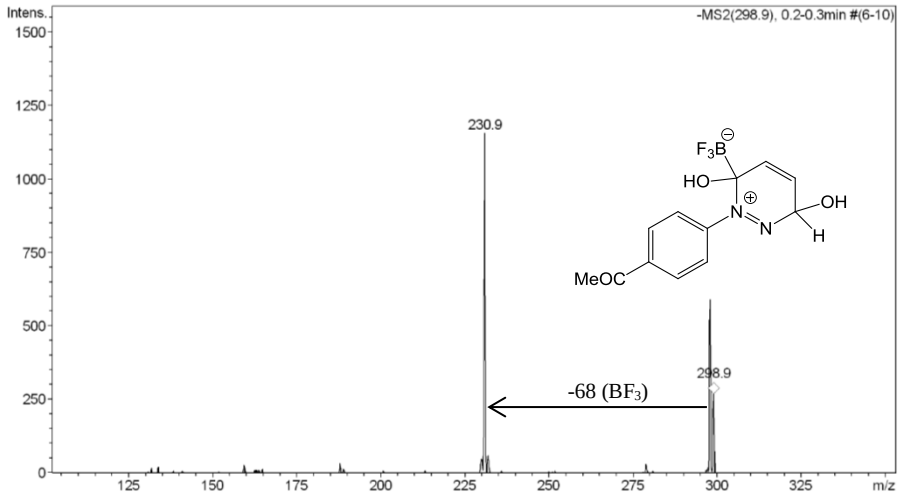
ESI(-) – MS/MS mass spectrum of the ion at *m/z* = 280.9 (Intermediate **Ia**)



c) Isotope pattern experimentally obtained compared to that calculated for intermediate at *m/z* = 299.0 (Intermediate **IV'a**)



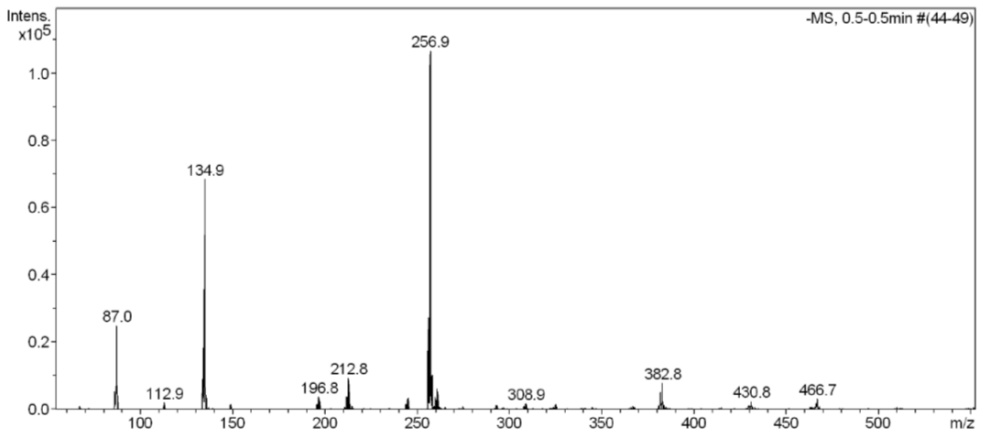
ESI(-) – MS/MS mass spectrum of the ion at *m/z* = 299.0 (Intermediate **IV'a**)



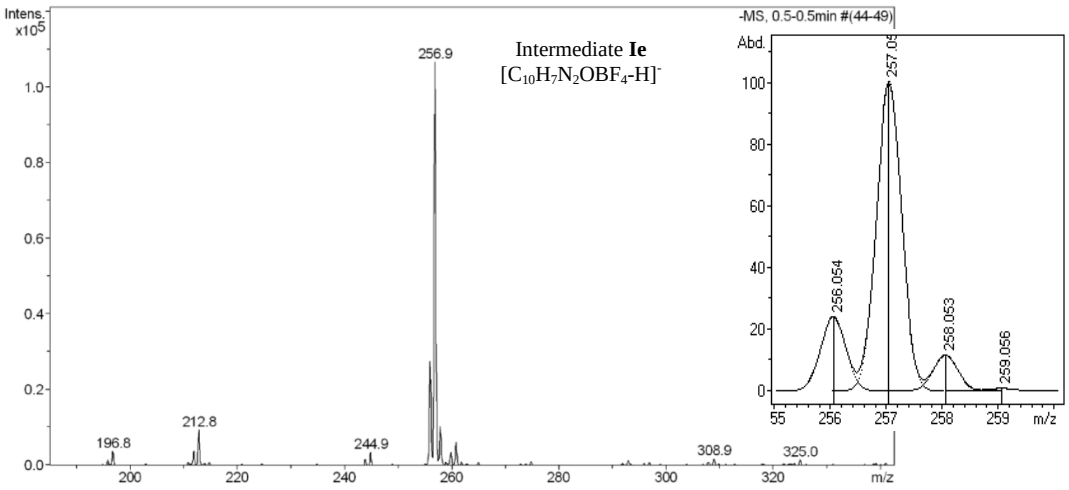
ESI-MS experiments for the detection of reactive intermediates in the formation of 4e

ESI(-) mass spectrum of a solution of **2** and **3e** in H_2O/CH_3CN 7:3

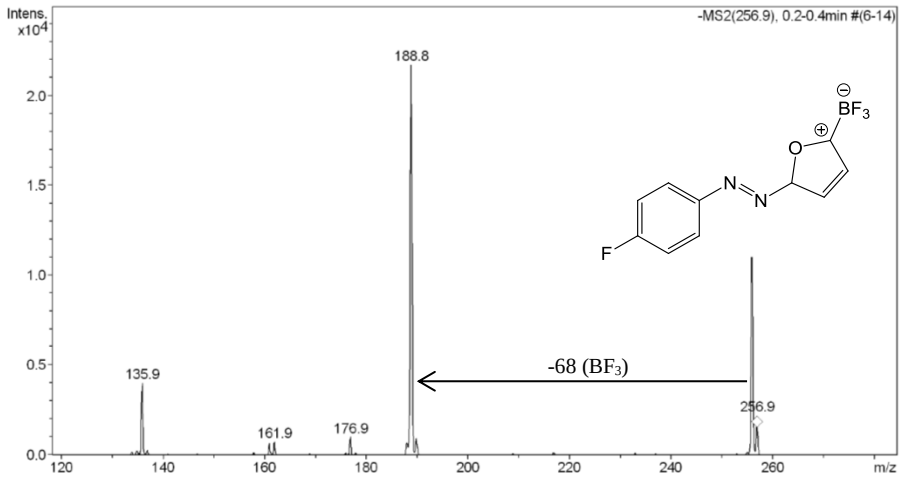
a)



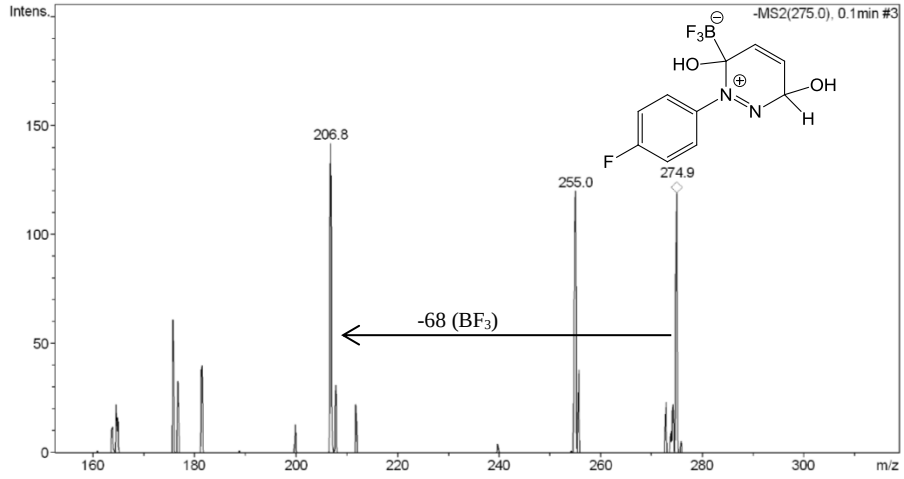
b) Isotope pattern experimentally obtained compared to that calculated for intermediate at *m/z* = 256.9 (Intermediate **Ie**)



ESI(-) – MS/MS mass spectrum of the ion at *m/z* = 256.9 (Intermediate **Ie**)



ESI(-) – MS/MS mass spectrum of the ion at *m/z* = 275.0 (Intermediate **IV'e**)



Computational methods

Geometries of the reactants, intermediates, transition states (TSs), and products at their singlet closed-shell ground state were optimized using the DFT M06-2X hybrid exchange-correlation functional[6] with the Gaussian09[7] program. All geometry optimizations were performed without symmetry constraints with the all-electron 6-31++G(d,p) basis set.[8,9] Analytical Hessians were computed to determine the nature of stationary points (one and zero imaginary frequencies for TSs and minima, respectively) and to calculate unscaled zero-point energies (ZPEs) as well as thermal corrections and entropy effects using the standard statistical-mechanics relationships for an ideal gas.[10] These two latter terms were computed at 298.15 K and 1 atm to provide relative Gibbs energies in gas-phase (ΔG_{298}). Entropy corrections were divided by a factor of 2 to correct for the overestimation suffered by gas-phase entropies when used to determine entropies for reactions in solution.[11-15] Solvation free energies in water calculated with the SMD solvation model[16] at the gas-phase geometries were added to the final Gibbs energies in gas-phase. Standard Gibbs energies in solution refer to a 1 M standard-state concentration for all species. Compared to conventional 1 atm standard state for gas-phase calculations, this requires the introduction of a concentration-change term of 1.89 kcal/mol (in the case of the H_2O molecule, this value is 4.27 kcal/mol).[17,18] Therefore, the final reported Gibbs energies contain electronic energies calculated at the M06-2X/6-31++G(d,p) level together with gas-phase thermal corrections and the entropic term (divided by two) plus solvation Gibbs energies.

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Table S1. Xyz Cartesian coordinates of all optimized species

BF_3

B	0.000000000	0.000000000	0.000000000
F	0.000000000	1.321024000	0.000000000
F	-1.144040000	-0.660512000	0.000000000
F	1.144040000	-0.660512000	0.000000000

2

C	3.252833000	-0.769491000	-0.000040000
C	3.443333000	0.576426000	-0.000002000
C	2.129310000	1.151128000	-0.000008000
C	1.237583000	0.117775000	0.000002000
H	3.925758000	-1.613079000	-0.000062000
H	4.393350000	1.090304000	0.000000000
H	1.869724000	2.199963000	-0.000007000
O	1.932743000	-1.060745000	0.000029000
B	-0.346429000	0.049950000	0.000015000
F	-0.913185000	-0.623454000	-1.133840000
F	-0.941365000	1.352966000	-0.000020000
K	-3.125654000	-0.044793000	-0.000017000
F	-0.913180000	-0.623395000	1.133901000

H_2O

O	0.000000000	0.000000000	0.115621000
H	0.000000000	0.768758000	-0.462485000
H	0.000000000	-0.768758000	-0.462485000

KBF_4

B	0.928659000	0.000130000	-0.000445000
F	0.367750000	-0.362912000	1.260039000
F	2.285491000	0.004428000	0.001346000
F	0.364002000	1.271830000	-0.318554000
F	0.369873000	-0.914242000	-0.943321000
K	-1.848808000	0.000390000	0.000349000

X=COMe

3a

C	-1.498622000	-0.876845000	-0.519811000
C	-2.533239000	-0.051609000	-0.066974000
C	-2.282314000	1.280645000	0.281821000
C	-1.000481000	1.799451000	0.173226000
C	-0.002671000	0.934890000	-0.280090000
C	-0.199658000	-0.400809000	-0.629075000
H	-1.728617000	-1.906085000	-0.773239000
H	-3.080123000	1.922309000	0.638346000
H	-0.774230000	2.827164000	0.434374000
H	0.644304000	-1.004731000	-0.944440000
N	1.280777000	1.496283000	-0.396616000
N	2.241193000	2.023751000	-0.502867000
C	-3.920867000	-0.652524000	0.032747000
O	-4.102677000	-1.782952000	-0.359452000
C	-5.033129000	0.179820000	0.620404000
H	-5.203759000	1.076881000	0.016315000
H	-5.941444000	-0.420693000	0.640280000
H	-4.781180000	0.500591000	1.636125000
B	3.159606000	-0.681318000	0.258839000
F	2.642907000	-0.686652000	-1.081148000
F	2.029646000	-0.435923000	1.098486000
F	4.021677000	0.414786000	0.373240000
F	3.756940000	-1.874832000	0.560150000

2···3a

C	-3.868438000	-1.351839000	0.129751000
C	-3.524030000	-1.196880000	1.451906000
C	-2.673920000	-0.072876000	1.487556000

C	-2.568553000	0.425007000	0.186773000
H	-3.827854000	-1.835723000	2.268185000
H	-2.203977000	0.374156000	2.352905000
O	-3.342630000	-0.352069000	-0.611656000
B	-1.802672000	1.719004000	-0.485401000
H	-4.525512000	-2.037110000	-0.384451000
N	-0.929505000	-1.520079000	-0.131113000
N	-1.622071000	-2.362983000	-0.401112000
C	0.420011000	-1.060522000	-0.048928000
C	1.371451000	-1.832453000	-0.725242000
C	0.719525000	0.080861000	0.673658000
C	2.691126000	-1.424888000	-0.653363000
H	1.073265000	-2.710485000	-1.287536000
C	2.055542000	0.468454000	0.725391000
H	-0.056842000	0.677908000	1.135061000
C	3.037295000	-0.274054000	0.068798000
H	3.476425000	-1.979333000	-1.155994000
H	2.308772000	1.371506000	1.269114000
C	4.495808000	0.123003000	0.094902000
O	5.318987000	-0.607730000	-0.413226000
C	4.880632000	1.424284000	0.752652000
H	4.348845000	2.261802000	0.290484000
H	4.619814000	1.409471000	1.815752000
H	5.955343000	1.564341000	0.644412000
F	-1.134909000	2.377940000	0.574472000
F	-0.851841000	1.221837000	-1.405915000
F	-2.715854000	2.546858000	-1.108492000

TS(R,I)

C	-3.217253000	-1.880710000	-0.200951000
C	-3.326715000	-1.676448000	1.210680000
C	-2.961131000	-0.376378000	1.419319000
C	-2.740508000	0.218717000	0.133004000
H	-3.506945000	-2.455239000	1.938569000
H	-2.802342000	0.145366000	2.352445000
O	-3.129593000	-0.658664000	-0.797896000
B	-2.272808000	1.750677000	-0.296655000
H	-3.643242000	-2.669486000	-0.805499000
N	-0.836904000	-1.219216000	-0.068970000
N	-1.336613000	-2.247503000	-0.316203000
C	0.549252000	-0.875104000	-0.053040000
C	1.512574000	-1.817457000	-0.431711000
C	0.872052000	0.410851000	0.358342000
C	2.843933000	-1.445246000	-0.386038000
H	1.208890000	-2.808773000	-0.751031000
C	2.219910000	0.764798000	0.395628000
H	0.090586000	1.117339000	0.621541000
C	3.203547000	-0.153289000	0.026910000
H	3.631359000	-2.136393000	-0.667888000
H	2.486537000	1.768894000	0.706998000
C	4.672008000	0.193152000	0.050190000
O	5.492903000	-0.650198000	-0.244540000
C	5.081396000	1.592569000	0.441062000
H	4.635618000	2.327163000	-0.236792000
H	4.740599000	1.825360000	1.454714000
H	6.167324000	1.662765000	0.395197000
F	-1.661904000	2.283924000	0.856603000
F	-1.343058000	1.631904000	-1.331617000
F	-3.393994000	2.470264000	-0.666057000

I

C	-1.945882000	-1.835078000	-0.472106000
C	-2.533225000	-2.146432000	0.869513000
C	-3.391237000	-1.166369000	1.190252000
C	-3.413015000	-0.217632000	0.079847000
H	-2.246168000	-3.016262000	1.446645000
H	-3.990827000	-1.042079000	2.081048000
O	-2.605405000	-0.611607000	-0.846192000

B	-4.299260000	1.208032000	-0.035757000
H	-2.182786000	-2.572580000	-1.245378000
N	-0.099717000	-0.548951000	-0.319459000
N	-0.487721000	-1.719520000	-0.390029000
C	1.312710000	-0.380172000	-0.208350000
C	2.236307000	-1.433247000	-0.222894000
C	1.729462000	0.942985000	-0.085906000
C	3.584965000	-1.142141000	-0.108172000
H	1.887184000	-2.454524000	-0.326441000
C	3.088304000	1.225256000	0.031147000
H	0.980432000	1.728678000	-0.084364000
C	4.019946000	0.185752000	0.020331000
H	4.332422000	-1.928922000	-0.117129000
H	3.410555000	2.256765000	0.126932000
C	5.501036000	0.434825000	0.138888000
O	6.274413000	-0.500528000	0.127866000
C	5.991315000	1.857855000	0.269555000
H	5.692266000	2.449904000	-0.601040000
H	5.564832000	2.332842000	1.158577000
H	7.077669000	1.845069000	0.347438000
F	-5.383969000	1.002111000	0.811632000
F	-3.437676000	2.188089000	0.440661000
F	-4.662065000	1.385768000	-1.353082000

I···H_2O

C	1.815432000	1.911732000	-0.363430000
C	2.308768000	2.057202000	1.059504000
C	2.979437000	0.952295000	1.376903000
C	3.002919000	0.030735000	0.195383000
H	2.085676000	2.913720000	1.681973000
H	3.447337000	0.695565000	2.318358000
O	2.478487000	0.776133000	-0.856523000
B	4.316215000	-0.919628000	-0.187312000
H	2.024996000	2.756385000	-1.022625000
N	-0.054726000	0.608976000	-0.202100000
N	0.333298000	1.773257000	-0.336724000
C	-1.470056000	0.407149000	-0.148724000
C	-2.395553000	1.447203000	-0.289530000
C	-1.888070000	-0.905582000	0.051197000
C	-3.747190000	1.153893000	-0.221288000
H	-2.042926000	2.459491000	-0.450000000
C	-3.249416000	-1.190677000	0.117792000
H	-1.151538000	-1.696887000	0.154563000
C	-4.184176000	-0.163115000	-0.017730000
H	-4.495275000	1.932712000	-0.326782000
H	-3.570503000	-2.215169000	0.273613000
C	-5.668864000	-0.415001000	0.042246000
O	-6.442652000	0.512867000	-0.067447000
C	-6.159034000	-1.830239000	0.238643000
H	-5.804587000	-2.477393000	-0.569780000
H	-5.786177000	-2.239720000	1.182762000
H	-7.248114000	-1.822204000	0.249643000
F	4.934295000	-1.279153000	1.004492000
F	3.720442000	-2.088722000	-0.786818000
F	5.145479000	-0.271331000	-1.066623000
H	1.035228000	-0.594659000	0.151977000
O	1.901353000	-1.035854000	0.490054000
H	2.210203000	-1.795213000	-0.069290000

TS(I,II)

C	1.904796000	1.986805000	-0.248059000
C	2.358254000	1.979314000	1.200318000
C	2.908694000	0.789785000	1.434611000
C	2.880284000	-0.054624000	0.191368000
H	2.204554000	2.805139000	1.882069000
H	3.319536000	0.420091000	2.365689000
O	2.490529000	0.872183000	-0.826481000

B	4.188881000	-0.990558000	-0.221244000
H	2.140319000	2.883422000	-0.824483000
N	-0.018203000	0.746040000	-0.183589000
N	0.403342000	1.903455000	-0.246089000
C	-1.418243000	0.483231000	-0.146068000
C	-2.364585000	1.485240000	-0.375282000
C	-1.785897000	-0.831052000	0.130121000
C	-3.706414000	1.149025000	-0.314465000
H	-2.040378000	2.495403000	-0.598055000
C	-3.138966000	-1.151981000	0.191828000
H	-1.025301000	-1.586033000	0.306620000
C	-4.102133000	-0.166035000	-0.029602000
H	-4.477772000	1.892078000	-0.487421000
H	-3.430458000	-2.173012000	0.413314000
C	-5.581475000	-0.461838000	0.023008000
O	-6.377000000	0.430973000	-0.177309000
C	-6.030490000	-1.870191000	0.328250000
H	-5.640426000	-2.570610000	-0.416842000
H	-5.663669000	-2.187355000	1.309610000
H	-7.119205000	-1.897548000	0.319875000
F	4.715615000	-1.510610000	0.963018000
F	3.621105000	-2.051327000	-0.997261000
F	5.110043000	-0.265017000	-0.944284000
H	0.738807000	-0.178394000	-0.042728000
O	1.736993000	-0.971239000	0.329911000
H	1.985619000	-1.735684000	-0.232078000

II

C	1.911388000	1.965907000	-0.270092000
C	2.349026000	1.961065000	1.183946000
C	2.874069000	0.762166000	1.429199000
C	2.854108000	-0.096349000	0.196210000
H	2.209325000	2.797325000	1.855784000
H	3.273259000	0.395191000	2.366612000
O	2.459953000	0.835142000	-0.836120000
B	4.210332000	-0.968539000	-0.197152000
H	2.161883000	2.856486000	-0.850519000
N	-0.039395000	0.769416000	-0.233030000
N	0.405249000	1.918431000	-0.263811000
C	-1.435112000	0.495412000	-0.176867000
C	-2.385645000	1.505689000	-0.337957000
C	-1.787929000	-0.832126000	0.048526000
C	-3.724483000	1.161146000	-0.261790000
H	-2.068390000	2.526172000	-0.520493000
C	-3.138533000	-1.159313000	0.126577000
H	-1.018704000	-1.588408000	0.175838000
C	-4.108758000	-0.167367000	-0.028061000
H	-4.501975000	1.907818000	-0.383694000
H	-3.422607000	-2.189974000	0.309491000
C	-5.586525000	-0.470181000	0.046767000
O	-6.387243000	0.427755000	-0.101951000
C	-6.024953000	-1.890142000	0.308858000
H	-5.653238000	-2.560330000	-0.472621000
H	-5.632536000	-2.244030000	1.267513000
H	-7.113466000	-1.920117000	0.327440000
F	4.735025000	-1.471340000	0.998463000
F	3.718598000	-2.046207000	-0.993017000
F	5.117759000	-0.191623000	-0.888099000
H	0.649910000	-0.101013000	-0.151611000
O	1.746570000	-1.023251000	0.324056000
H	2.027320000	-1.801444000	-0.195994000

TS(II,III)

C	1.848707000	1.715358000	-0.463369000
C	2.464688000	2.006607000	0.876795000
C	2.986012000	0.887614000	1.372714000
C	2.894994000	-0.277325000	0.445654000
H	2.454376000	2.995773000	1.314504000

H	3.501536000	0.780639000	2.319381000
O	2.083458000	0.355676000	-0.708945000
B	4.328605000	-0.827638000	-0.195088000
H	2.179259000	2.335361000	-1.300625000
N	-0.141471000	0.754236000	-0.415107000
N	0.347073000	1.881578000	-0.352867000
C	-1.527893000	0.497420000	-0.280859000
C	-2.462068000	1.529920000	-0.157262000
C	-1.899937000	-0.843724000	-0.274855000
C	-3.798918000	1.193650000	-0.026459000
H	-2.132339000	2.562935000	-0.165397000
C	-3.247216000	-1.165232000	-0.139325000
H	-1.140455000	-1.614423000	-0.364757000
C	-4.198747000	-0.150758000	-0.015961000
H	-4.562402000	1.958099000	0.072127000
H	-3.544693000	-2.208221000	-0.129900000
C	-5.671980000	-0.445411000	0.133709000
O	-6.458355000	0.472430000	0.229773000
C	-6.126580000	-1.884530000	0.161204000
H	-5.854686000	-2.392830000	-0.769295000
H	-5.652732000	-2.423381000	0.987677000
H	-7.208467000	-1.904684000	0.284594000
F	5.238767000	-0.936324000	0.856837000
F	4.014084000	-2.107335000	-0.712597000
F	4.763282000	0.045222000	-1.182834000
H	0.867833000	0.035097000	-0.585597000
O	2.104023000	-1.292994000	0.939251000
H	2.465950000	-2.113365000	0.563346000

III

C	-1.657097000	-1.269035000	-0.335774000
C	-2.243520000	-1.673889000	0.989643000
C	-3.068168000	-0.755874000	1.481830000
C	-3.362094000	0.403790000	0.601370000
H	-1.990758000	-2.624147000	1.442119000
H	-3.615400000	-0.840244000	2.414199000
O	-2.123016000	0.067999000	-0.551988000
B	-4.725442000	0.360275000	-0.354501000
H	-1.996011000	-1.877290000	-1.178973000
N	0.329694000	-0.221886000	-0.283636000
N	-0.191888000	-1.340557000	-0.278888000
C	1.754189000	-0.181165000	-0.200204000
C	2.558293000	-1.327104000	-0.205172000
C	2.313382000	1.090949000	-0.116771000
C	3.932709000	-1.180589000	-0.119815000
H	2.098754000	-2.306247000	-0.278559000
C	3.696114000	1.227651000	-0.027668000
H	1.660322000	1.957617000	-0.119219000
C	4.511054000	0.094025000	-0.029294000
H	4.589885000	-2.043977000	-0.122636000
H	4.128820000	2.220164000	0.041505000
C	6.012197000	0.185583000	0.059067000
O	6.680513000	-0.827238000	0.056131000
C	6.653231000	1.550734000	0.149677000
H	6.396182000	2.156401000	-0.724952000
H	6.302661000	2.083017000	1.039501000
H	7.733817000	1.424403000	0.202116000
F	-5.801336000	0.145841000	0.498472000
F	-4.773970000	1.648439000	-0.926401000
F	-4.580158000	-0.645609000	-1.299994000
H	-1.345989000	0.658120000	-0.378372000
O	-3.049073000	1.602204000	1.101504000
H	-3.569676000	2.255681000	0.598233000

TS(III,IV)

C	2.815220000	-2.122409000	-0.621444000
C	3.637766000	-0.928172000	-0.980499000
C	3.354965000	0.284612000	-0.506517000

C	2.218084000	0.572901000	0.403911000
H	4.451006000	-1.076975000	-1.682865000
H	3.912129000	1.165496000	-0.816732000
O	3.110452000	-2.503910000	0.710786000
H	3.000272000	-2.951057000	-1.309434000
N	0.935474000	-0.779241000	-0.441970000
N	1.328847000	-1.922732000	-0.662600000
C	-0.485949000	-0.629210000	-0.308956000
C	-1.230222000	-1.623731000	0.333951000
C	-1.081259000	0.518172000	-0.821875000
C	-2.598964000	-1.459219000	0.462246000
H	-0.726883000	-2.495632000	0.736826000
C	-2.461124000	0.657758000	-0.702939000
H	-0.475472000	1.281170000	-1.295989000
C	-3.223123000	-0.319279000	-0.059555000
H	-3.209934000	-2.199275000	0.968364000
H	-2.929877000	1.549272000	-1.105345000
C	-4.713820000	-0.191293000	0.110303000
O	-5.339690000	-1.077938000	0.654809000
C	-5.398766000	1.051913000	-0.406191000
H	-4.983024000	1.945820000	0.069022000
H	-5.251774000	1.151272000	-1.486313000
H	-6.463316000	0.979738000	-0.187054000
H	2.654523000	-3.331366000	0.921214000
B	1.547639000	2.085801000	0.239441000
F	1.342802000	2.291499000	-1.136291000
F	0.377570000	2.206819000	0.964726000
F	2.570797000	2.909026000	0.711729000
O	2.227966000	0.039052000	1.606982000
H	2.826709000	-0.729640000	1.666396000

IV

C	2.843774000	-2.095499000	-0.686935000
C	3.774053000	-0.931486000	-0.787398000
C	3.362601000	0.238023000	-0.310692000
C	1.988725000	0.408348000	0.263617000
H	4.762390000	-1.090538000	-1.204854000
H	3.985544000	1.126135000	-0.291805000
O	2.851893000	-2.733199000	0.558660000
H	3.026833000	-2.863299000	-1.437175000
N	1.046013000	-0.618633000	-0.440124000
N	1.404517000	-1.711124000	-0.883989000
C	-0.398556000	-0.464727000	-0.325050000
C	-1.064340000	-1.469586000	0.377708000
C	-1.061565000	0.608223000	-0.904700000
C	-2.441356000	-1.384815000	0.515368000
H	-0.497575000	-2.286849000	0.813096000
C	-2.445758000	0.664110000	-0.771363000
H	-0.515757000	1.379738000	-1.432074000
C	-3.139084000	-0.318883000	-0.061305000
H	-2.997532000	-2.137015000	1.064581000
H	-2.975355000	1.494282000	-1.225988000
C	-4.635764000	-0.275580000	0.113681000
O	-5.198825000	-1.166526000	0.715028000
C	-5.400384000	0.888224000	-0.470564000
H	-5.037857000	1.834283000	-0.056723000
H	-5.268530000	0.927738000	-1.556532000
H	-6.456657000	0.764180000	-0.235499000
H	2.841150000	-2.054010000	1.255613000
B	1.507974000	2.010262000	0.201128000
F	1.239600000	2.388775000	-1.116314000
F	0.386546000	2.126193000	1.040818000
F	2.581943000	2.721496000	0.723177000
O	1.961167000	-0.060435000	1.593352000
H	1.358998000	0.517317000	2.090860000

IV'

C	2.886512000	-1.609771000	-0.579513000

C	3.553108000	-1.102397000	0.669466000
C	3.005254000	-0.077159000	1.311909000
C	1.742058000	0.537472000	0.811876000
H	4.480398000	-1.578986000	0.968344000
H	3.438384000	0.386279000	2.191368000
O	3.202295000	-2.919687000	-0.910017000
H	3.135713000	-0.988121000	-1.448830000
N	0.937939000	-0.568881000	0.174819000
N	1.406156000	-1.505342000	-0.478555000
C	-0.512228000	-0.445890000	0.159363000
C	-1.239053000	-0.626929000	1.331635000
C	-1.103268000	-0.151103000	-1.060512000
C	-2.621731000	-0.532250000	1.259913000
H	-0.730285000	-0.831271000	2.266318000
C	-2.490434000	-0.040677000	-1.107946000
H	-0.481164000	0.012272000	-1.934745000
C	-3.252371000	-0.236664000	0.045764000
H	-3.237919000	-0.677812000	2.140992000
H	-2.966499000	0.198079000	-2.052953000
C	-4.756267000	-0.135840000	0.039868000
O	-5.378917000	-0.338658000	1.061303000
C	-5.455580000	0.217446000	-1.251467000
H	-5.105793000	1.183160000	-1.629156000
H	-5.248866000	-0.535779000	-2.018462000
H	-6.527669000	0.262810000	-1.064734000
H	3.052560000	-3.492339000	-0.147009000
B	1.980124000	1.686473000	-0.456352000
F	2.050235000	0.987769000	-1.665311000
F	0.831912000	2.487999000	-0.398341000
F	3.126434000	2.390667000	-0.175037000
O	1.011060000	1.092609000	1.848147000
H	0.593139000	1.899444000	1.507389000

TS(IV',V)

C	2.742630000	-1.595948000	-0.449481000
C	3.308765000	-1.379903000	0.930426000
C	2.803232000	-0.333329000	1.597494000
C	1.629061000	0.326744000	1.052896000
H	4.095013000	-2.029065000	1.297440000
H	3.163042000	0.023523000	2.556236000
O	3.092165000	-2.810913000	-1.038346000
H	3.097404000	-0.809680000	-1.136996000
N	0.844315000	-0.518489000	0.300110000
N	1.285438000	-1.518992000	-0.372423000
C	-0.596081000	-0.345791000	0.230754000
C	-1.354046000	-0.311617000	1.398990000
C	-1.174332000	-0.282926000	-1.029361000
C	-2.733309000	-0.213203000	1.288875000
H	-0.867797000	-0.361234000	2.365922000
C	-2.558947000	-0.169741000	-1.123843000
H	-0.542665000	-0.324125000	-1.909619000
C	-3.343364000	-0.136366000	0.031288000
H	-3.363652000	-0.193845000	2.171549000
H	-3.017119000	-0.111398000	-2.105587000
C	-4.843268000	-0.023606000	-0.021465000
O	-5.487977000	0.001179000	1.006848000
C	-5.518691000	0.055986000	-1.371235000
H	-5.169029000	0.932632000	-1.925574000
H	-5.289182000	-0.830670000	-1.970389000
H	-6.594850000	0.125957000	-1.217824000
H	2.574530000	-3.508987000	-0.616245000
B	2.392848000	1.738685000	-0.797709000
F	1.776203000	1.117196000	-1.800416000
F	1.784457000	2.794289000	-0.237840000
F	3.701461000	1.603062000	-0.646048000
O	0.959046000	1.231216000	1.842406000
H	1.006933000	2.111264000	1.445257000

V

C	3.414877000	-1.127569000	-0.537912000
C	4.128008000	0.177375000	-0.657548000
C	3.516132000	1.240838000	-0.086803000
C	2.169244000	1.092852000	0.334581000
H	5.094310000	0.252264000	-1.143561000
H	3.970638000	2.222129000	0.000127000
O	3.651478000	-1.609578000	0.792492000
H	3.778872000	-1.859628000	-1.264873000
N	1.478523000	0.057690000	-0.143143000
N	2.019156000	-0.961976000	-0.818556000
C	0.037544000	0.019445000	-0.081631000
C	-0.568024000	-1.186905000	0.259730000
C	-0.717064000	1.141159000	-0.410976000
C	-1.953489000	-1.263420000	0.293007000
H	0.056564000	-2.043699000	0.482686000
C	-2.104502000	1.051718000	-0.380576000
H	-0.226004000	2.066171000	-0.689900000
C	-2.731987000	-0.146067000	-0.025023000
H	-2.457519000	-2.185991000	0.561537000
H	-2.691993000	1.925116000	-0.643946000
C	-4.227234000	-0.282346000	0.024582000
O	-4.736342000	-1.336496000	0.348396000
C	-5.078133000	0.915695000	-0.334782000
H	-4.861525000	1.756529000	0.331500000
H	-4.872042000	1.241042000	-1.359324000
H	-6.127182000	0.636825000	-0.243271000
H	3.186775000	-2.453292000	0.877973000
O	1.506436000	2.042944000	1.054464000
H	1.980545000	2.200922000	1.880235000

V···H_2O

C	3.121335000	-1.295828000	-0.775430000
C	3.835160000	-0.054682000	-1.182615000
C	3.261549000	1.097825000	-0.765719000
C	1.950663000	1.040647000	-0.221893000
H	4.767591000	-0.087863000	-1.734838000
H	3.723427000	2.074921000	-0.854543000
O	3.419901000	-1.500489000	0.642300000
H	3.454563000	-2.176957000	-1.327952000
N	1.222658000	-0.048880000	-0.483110000
N	1.720137000	-1.177809000	-1.003488000
C	-0.208457000	-0.053941000	-0.309286000
C	-0.807785000	-1.211075000	0.181584000
C	-0.967723000	1.054805000	-0.673622000
C	-2.187794000	-1.250273000	0.327115000
H	-0.184967000	-2.061029000	0.432147000
C	-2.349005000	1.002965000	-0.527117000
H	-0.483368000	1.942198000	-1.063309000
C	-2.969009000	-0.145261000	-0.023710000
H	-2.684404000	-2.134473000	0.712982000
H	-2.938612000	1.867235000	-0.814953000
C	-4.457378000	-0.239889000	0.153732000
O	-4.958906000	-1.252888000	0.598771000
C	-5.311738000	0.947647000	-0.231187000
H	-5.027276000	1.831179000	0.348685000
H	-5.181537000	1.188612000	-1.290837000
H	-6.355187000	0.702606000	-0.036773000
H	2.933967000	-2.290342000	0.920968000
O	1.410288000	2.058326000	0.489120000
H	1.793024000	1.971708000	1.385850000
O	2.825575000	0.664759000	2.396388000
H	3.141327000	-0.080073000	1.846524000
H	3.408106000	0.723788000	3.158494000

TS(V···H_2O,4a)

C	3.109567000	-1.156985000	-0.990432000

C	3.923061000	0.038432000	-1.064452000
C	3.338062000	1.175677000	-0.624156000
C	1.986676000	1.095388000	-0.181965000
H	4.959033000	-0.011986000	-1.380001000
H	3.852509000	2.120792000	-0.497516000
O	3.335146000	-1.421700000	0.906220000
H	3.518132000	-2.092074000	-1.356984000
N	1.256531000	0.055083000	-0.609346000
N	1.785087000	-1.062125000	-1.152465000
C	-0.168947000	0.008085000	-0.412859000
C	-0.748721000	-1.203419000	-0.044784000
C	-0.939709000	1.148416000	-0.621368000
C	-2.125615000	-1.268843000	0.120628000
H	-0.115445000	-2.069535000	0.103811000
C	-2.316562000	1.069714000	-0.451881000
H	-0.466631000	2.082010000	-0.902944000
C	-2.919565000	-0.136490000	-0.080345000
H	-2.609401000	-2.195514000	0.411366000
H	-2.915943000	1.958917000	-0.617650000
C	-4.403611000	-0.263290000	0.116550000
O	-4.891203000	-1.331906000	0.425600000
C	-5.268754000	0.962212000	-0.075036000
H	-5.172490000	1.346449000	-1.095400000
H	-6.305857000	0.689454000	0.116498000
H	-4.964747000	1.759189000	0.610793000
H	3.011430000	-2.306610000	1.119406000
O	1.492712000	1.923362000	0.718636000
H	1.771101000	1.373196000	1.606117000
O	2.286070000	0.283595000	2.346881000
H	2.773931000	-0.495434000	1.752611000
H	2.795960000	0.450261000	3.144475000

4a

C	-2.457682000	-0.119541000	-0.002092000
C	-1.735519000	-1.247811000	-0.404425000
C	-0.349226000	-1.240092000	-0.386036000
C	0.328857000	-0.094074000	0.037561000
C	-0.373619000	1.039626000	0.444263000
C	-1.764731000	1.016935000	0.422012000
H	-2.284031000	-2.124447000	-0.733276000
H	0.218071000	-2.112861000	-0.687011000
H	0.157328000	1.927546000	0.759711000
H	-2.303638000	1.902970000	0.742042000
C	-3.956361000	-0.178363000	-0.043870000
O	-4.522267000	-1.189499000	-0.410602000
C	-4.742826000	1.042714000	0.380180000
H	-5.805211000	0.824494000	0.277607000
H	-4.519485000	1.301109000	1.420172000
H	-4.481835000	1.905602000	-0.240222000
C	2.523368000	1.003486000	-0.306509000
C	3.565856000	-1.456278000	0.465557000
C	3.963778000	0.792941000	-0.237764000
C	4.475002000	-0.399783000	0.136137000
H	3.915862000	-2.436692000	0.768812000
H	4.574132000	1.645256000	-0.513565000
H	5.545216000	-0.572047000	0.188989000
N	2.277622000	-1.316492000	0.431620000
N	1.764035000	-0.124678000	0.076330000
O	2.001092000	2.048086000	-0.660522000

X=OMe

3j

C	1.657547000	-1.146620000	0.400716000
C	2.795651000	-0.386145000	0.071507000
C	2.685773000	0.989134000	-0.204275000
C	1.442215000	1.592266000	-0.150763000

C	0.332324000	0.806474000	0.174081000
C	0.409710000	-0.567079000	0.452083000
H	1.785978000	-2.203672000	0.602282000
H	3.551734000	1.585009000	-0.460623000
H	1.327585000	2.650211000	-0.361096000
H	-0.492600000	-1.117096000	0.691681000
N	-0.886727000	1.470228000	0.222684000
N	-1.797731000	2.091132000	0.262930000
O	3.949144000	-1.059056000	0.044013000
C	5.146412000	-0.368993000	-0.291819000
H	5.354166000	0.422639000	0.435278000
H	5.935754000	-1.116973000	-0.254360000
H	5.082157000	0.050042000	-1.301051000
B	-3.023955000	-0.567337000	-0.154556000
F	-2.400133000	-0.526785000	1.137062000
F	-1.952697000	-0.475258000	-1.094914000
F	-3.812764000	0.578360000	-0.282630000
F	-3.728266000	-1.732401000	-0.319506000

2···3j

C	3.520810000	-1.473458000	-0.491013000
C	2.538228000	-1.892511000	-1.336471000
C	1.646086000	-0.776681000	-1.469178000
C	2.140412000	0.245461000	-0.700145000
H	2.478395000	-2.858370000	-1.817995000
H	0.743228000	-0.719594000	-2.062055000
O	3.292569000	-0.194620000	-0.107376000
B	1.538213000	1.675036000	-0.214048000
H	4.422265000	-1.932856000	-0.114619000
N	0.690155000	-0.932157000	1.482713000
N	1.665167000	-1.162971000	1.948517000
C	-0.580534000	-0.749220000	0.960322000
C	-1.144669000	-1.833934000	0.265502000
C	-1.221248000	0.478011000	1.128004000
C	-2.403770000	-1.672483000	-0.256415000
H	-0.584772000	-2.753373000	0.133121000
C	-2.493452000	0.619567000	0.597706000
H	-0.706279000	1.296965000	1.614678000
C	-3.083100000	-0.443522000	-0.098914000
H	-2.892645000	-2.466595000	-0.808282000
H	-2.992575000	1.573995000	0.698047000
O	-4.292894000	-0.389640000	-0.664128000
C	-5.020445000	0.832655000	-0.607851000
H	-5.245109000	1.100885000	0.429233000
H	-4.460583000	1.636901000	-1.094571000
H	-5.946451000	0.646866000	-1.148195000
F	0.240691000	1.813719000	-0.765946000
F	1.379169000	1.586401000	1.222384000
F	2.337794000	2.759509000	-0.518104000

TS(R,I)

C	-2.953581000	-1.852005000	-0.233733000
C	-3.070945000	-1.665434000	1.182123000
C	-2.690694000	-0.374062000	1.411965000
C	-2.461260000	0.238473000	0.135327000
H	-3.259482000	-2.453739000	1.897631000
H	-2.526914000	0.131226000	2.353145000
O	-2.858781000	-0.617425000	-0.809813000
B	-1.994161000	1.780583000	-0.255561000
H	-3.403672000	-2.619423000	-0.848328000
N	-0.578576000	-1.246092000	-0.091787000
N	-1.113839000	-2.258485000	-0.350977000
C	0.798571000	-0.933203000	-0.074997000
C	1.760387000	-1.890145000	-0.438310000
C	1.155357000	0.352773000	0.314544000
C	3.091508000	-1.540905000	-0.401523000
H	1.449503000	-2.884084000	-0.742944000
C	2.501481000	0.702571000	0.350764000

H	0.386996000	1.076251000	0.571419000
C	3.469303000	-0.240583000	-0.009314000
H	3.871067000	-2.243257000	-0.674786000
H	2.774598000	1.707345000	0.646128000
O	4.793561000	-0.001843000	-0.016843000
C	5.246148000	1.297245000	0.331633000
H	4.837987000	2.048254000	-0.352725000
H	4.970675000	1.543748000	1.362570000
H	6.330460000	1.267112000	0.239802000
F	-1.352188000	2.272805000	0.899603000
F	-1.095963000	1.705489000	-1.319876000
F	-3.126226000	2.515203000	-0.565548000

I

C	1.759171000	1.996556000	-0.365031000
C	2.264275000	2.086316000	1.039172000
C	2.990575000	0.988001000	1.297164000
C	3.028820000	0.190246000	0.075850000
H	1.998342000	2.896653000	1.706235000
H	3.480045000	0.686623000	2.212496000
O	2.379229000	0.795221000	-0.860450000
B	3.730642000	-1.319650000	-0.132630000
H	2.055703000	2.814707000	-1.024309000
N	-0.091929000	0.738317000	-0.169338000
N	0.281966000	1.899435000	-0.382918000
C	-1.485512000	0.521050000	-0.131342000
C	-2.456202000	1.522778000	-0.309136000
C	-1.869687000	-0.797393000	0.100528000
C	-3.791838000	1.189711000	-0.244133000
H	-2.145949000	2.544880000	-0.497137000
C	-3.216994000	-1.141253000	0.167960000
H	-1.094922000	-1.547817000	0.225914000
C	-4.180905000	-0.143139000	-0.004279000
H	-4.570110000	1.933404000	-0.376213000
H	-3.496737000	-2.171117000	0.349875000
O	-5.511813000	-0.356006000	0.040654000
C	-5.971927000	-1.674725000	0.280669000
H	-5.638312000	-2.355816000	-0.509938000
H	-5.625829000	-2.039363000	1.254016000
H	-7.059059000	-1.615746000	0.277645000
F	4.833952000	-1.314605000	0.717078000
F	2.741267000	-2.199175000	0.300443000
F	4.064267000	-1.481225000	-1.459276000

I···H_2O

C	1.559978000	1.932570000	-0.359657000
C	2.046988000	2.055642000	1.067420000
C	2.691363000	0.934356000	1.382002000
C	2.702914000	0.020974000	0.193481000
H	1.834823000	2.910220000	1.696510000
H	3.142648000	0.658116000	2.326077000
O	2.210536000	0.790004000	-0.858206000
B	3.992953000	-0.959695000	-0.180857000
H	1.791273000	2.779045000	-1.008831000
N	-0.329154000	0.657860000	-0.199208000
N	0.075759000	1.816920000	-0.350310000
C	-1.733840000	0.456126000	-0.155781000
C	-2.666763000	1.493162000	-0.313700000
C	-2.165355000	-0.849073000	0.055300000
C	-4.013803000	1.207657000	-0.251418000
H	-2.316102000	2.504921000	-0.483305000
C	-3.524510000	-1.145881000	0.121159000
H	-1.434139000	-1.643862000	0.173285000
C	-4.452816000	-0.112054000	-0.031978000
H	-4.763036000	1.982657000	-0.370061000
H	-3.840313000	-2.167779000	0.287998000
O	-5.789684000	-0.276868000	0.013682000
C	-6.297778000	-1.581424000	0.235097000

H	-5.996370000	-2.260168000	-0.570396000
H	-5.958534000	-1.975081000	1.199502000
H	-7.381736000	-1.481345000	0.241929000
F	4.559247000	-1.379691000	1.019227000
F	3.381096000	-2.087447000	-0.835980000
F	4.877013000	-0.312553000	-1.008087000
H	0.710752000	-0.524293000	0.141591000
O	1.571431000	-1.012286000	0.468876000
H	1.847001000	-1.769330000	-0.106182000

TS(I,II)

C	1.632070000	1.988580000	-0.296889000
C	2.095043000	2.018431000	1.146970000
C	2.646040000	0.836425000	1.414497000
C	2.606866000	-0.039137000	0.193220000
H	1.940701000	2.860623000	1.808567000
H	3.056636000	0.489287000	2.354165000
O	2.222672000	0.854168000	-0.845754000
B	3.886980000	-1.021764000	-0.197046000
H	1.880360000	2.864827000	-0.898258000
N	-0.295676000	0.760914000	-0.185389000
N	0.133774000	1.914307000	-0.301753000
C	-1.688087000	0.511395000	-0.153589000
C	-2.639588000	1.517362000	-0.377049000
C	-2.079666000	-0.797023000	0.114152000
C	-3.978141000	1.196033000	-0.323037000
H	-2.313115000	2.528600000	-0.592173000
C	-3.430426000	-1.124474000	0.174534000
H	-1.328908000	-1.562821000	0.288232000
C	-4.384080000	-0.124419000	-0.045088000
H	-4.746052000	1.942376000	-0.493132000
H	-3.721177000	-2.144503000	0.390233000
O	-5.713380000	-0.324410000	-0.014707000
C	-6.193890000	-1.630639000	0.261179000
H	-5.850927000	-2.341051000	-0.498664000
H	-5.873278000	-1.962492000	1.254571000
H	-7.279564000	-1.559283000	0.231697000
F	4.409671000	-1.519893000	0.998311000
F	3.284940000	-2.093355000	-0.935383000
F	4.821456000	-0.346858000	-0.950931000
H	0.487355000	-0.195313000	0.008248000
O	1.442595000	-0.941710000	0.369180000
H	1.669827000	-1.716609000	-0.189377000

II

C	1.641333000	1.957444000	-0.308127000
C	2.084280000	1.975636000	1.143282000
C	2.591901000	0.775174000	1.414928000
C	2.560158000	-0.111240000	0.202448000
H	1.957981000	2.827897000	1.797669000
H	2.985927000	0.423052000	2.360152000
O	2.164784000	0.801703000	-0.849647000
B	3.918732000	-0.983195000	-0.177149000
H	1.914079000	2.828639000	-0.907799000
N	-0.331676000	0.804008000	-0.252716000
N	0.135425000	1.945572000	-0.304215000
C	-1.716208000	0.533849000	-0.192606000
C	-2.675587000	1.547364000	-0.320803000
C	-2.082172000	-0.793930000	0.007543000
C	-4.008491000	1.210703000	-0.240002000
H	-2.361763000	2.572558000	-0.482689000
C	-3.427291000	-1.133716000	0.093883000
H	-1.316168000	-1.557541000	0.112377000
C	-4.394655000	-0.128799000	-0.029072000
H	-4.787123000	1.958784000	-0.337449000
H	-3.704564000	-2.167038000	0.257251000
O	-5.718484000	-0.340936000	0.040177000
C	-6.182419000	-1.663667000	0.267326000

H	-5.877107000	-2.328452000	-0.547571000
H	-5.811310000	-2.047287000	1.223472000
H	-7.268135000	-1.594957000	0.296787000
F	4.446428000	-1.467437000	1.026695000
F	3.437678000	-2.075764000	-0.958259000
F	4.827478000	-0.213154000	-0.876875000
H	0.335337000	-0.058683000	-0.172386000
O	1.457123000	-1.032083000	0.355760000
H	1.736204000	-1.823248000	-0.142719000

TS(II,III)

C	1.563317000	1.705543000	-0.474849000
C	2.210839000	2.015403000	0.845501000
C	2.739158000	0.904922000	1.352317000
C	2.622842000	-0.277994000	0.450912000
H	2.213674000	3.012069000	1.266196000
H	3.274530000	0.814226000	2.289590000
O	1.782160000	0.333525000	-0.693435000
B	4.036149000	-0.842922000	-0.217905000
H	1.896859000	2.297432000	-1.330795000
N	-0.435201000	0.765448000	-0.383975000
N	0.068494000	1.890687000	-0.355401000
C	-1.812655000	0.524507000	-0.243381000
C	-2.746441000	1.562205000	-0.103349000
C	-2.212187000	-0.808560000	-0.245773000
C	-4.080227000	1.244994000	0.030928000
H	-2.410810000	2.593494000	-0.102169000
C	-3.557544000	-1.132296000	-0.108717000
H	-1.464624000	-1.589902000	-0.347087000
C	-4.495043000	-0.101978000	0.029484000
H	-4.837152000	2.013257000	0.141975000
H	-3.858671000	-2.171990000	-0.108896000
O	-5.817918000	-0.294642000	0.168871000
C	-6.312243000	-1.625016000	0.182356000
H	-6.091523000	-2.132605000	-0.762830000
H	-5.886889000	-2.190016000	1.018700000
H	-7.389896000	-1.538980000	0.308882000
F	4.972740000	-0.947399000	0.812030000
F	3.703767000	-2.127033000	-0.714641000
F	4.453458000	0.016103000	-1.225881000
H	0.586516000	0.031568000	-0.546012000
O	1.845055000	-1.282869000	0.985807000
H	2.191250000	-2.110409000	0.611508000

III

C	-1.391369000	-1.305108000	-0.369441000
C	-1.998452000	-1.726036000	0.940900000
C	-2.789995000	-0.788949000	1.451410000
C	-3.019560000	0.399988000	0.589284000
H	-1.782382000	-2.696624000	1.368278000
H	-3.348161000	-0.869247000	2.377222000
O	-1.819567000	0.056500000	-0.542502000
B	-4.395063000	0.435312000	-0.347026000
H	-1.747188000	-1.872251000	-1.233622000
N	0.611762000	-0.296681000	-0.273797000
N	0.071258000	-1.408360000	-0.314012000
C	2.024897000	-0.263982000	-0.185470000
C	2.830822000	-1.414189000	-0.173080000
C	2.603498000	0.998562000	-0.111517000
C	4.200176000	-1.281636000	-0.084126000
H	2.368999000	-2.393208000	-0.236658000
C	3.985730000	1.141054000	-0.019583000
H	1.960573000	1.873226000	-0.123309000
C	4.787307000	-0.004444000	-0.006525000
H	4.853404000	-2.147206000	-0.074536000
H	4.417388000	2.132015000	0.040670000
O	6.133424000	0.010633000	0.076321000
C	6.786770000	1.266548000	0.135056000

H	6.573249000	1.860565000	-0.760440000
H	6.486967000	1.823238000	1.029795000
H	7.851915000	1.046284000	0.182033000
F	-5.472063000	0.229392000	0.507910000
F	-4.410230000	1.741328000	-0.881217000
F	-4.294294000	-0.543868000	-1.327374000
H	-1.014174000	0.608405000	-0.350432000
O	-2.662667000	1.577805000	1.127082000
H	-3.165592000	2.261518000	0.648255000

TS(III,IV)

C	2.612577000	-2.109383000	-0.529126000
C	3.353240000	-0.914691000	-1.040631000
C	3.045869000	0.314979000	-0.625816000
C	1.954588000	0.619274000	0.335539000
H	4.109451000	-1.071184000	-1.803998000
H	3.529223000	1.197284000	-1.038867000
O	2.899441000	-2.383498000	0.843328000
H	2.817207000	-2.995527000	-1.134774000
N	0.684977000	-0.844680000	-0.375837000
N	1.128586000	-1.984637000	-0.535661000
C	-0.725354000	-0.742704000	-0.224903000
C	-1.463080000	-1.812941000	0.308615000
C	-1.358526000	0.432486000	-0.618904000
C	-2.828838000	-1.694368000	0.446703000
H	-0.945903000	-2.711386000	0.626402000
C	-2.740174000	0.544145000	-0.500173000
H	-0.780819000	1.249761000	-1.032522000
C	-3.476691000	-0.513836000	0.039316000
H	-3.426835000	-2.489432000	0.878083000
H	-3.219269000	1.462100000	-0.815709000
O	-4.813612000	-0.494675000	0.219194000
C	-5.517844000	0.686688000	-0.123760000
H	-5.155878000	1.540860000	0.458544000
H	-5.424666000	0.901986000	-1.193962000
H	-6.561169000	0.491882000	0.119523000
H	3.746776000	-2.841298000	0.908631000
B	1.282304000	2.129785000	0.147722000
F	0.985576000	2.293001000	-1.216426000
F	0.170673000	2.305591000	0.948675000
F	2.350454000	2.954718000	0.514705000
O	2.027042000	0.154603000	1.564143000
H	2.607538000	-0.627865000	1.633466000

IV

C	2.671511000	-2.059490000	-0.610191000
C	3.549875000	-0.868562000	-0.811673000
C	3.099203000	0.311375000	-0.401922000
C	1.737613000	0.454975000	0.210934000
H	4.532919000	-1.013210000	-1.246735000
H	3.682299000	1.224399000	-0.458813000
O	2.745650000	-2.620145000	0.671011000
H	2.871525000	-2.864271000	-1.316531000
N	0.814630000	-0.645036000	-0.408657000
N	1.218992000	-1.745806000	-0.800152000
C	-0.620962000	-0.553962000	-0.257721000
C	-1.247240000	-1.630152000	0.383850000
C	-1.352752000	0.521004000	-0.746892000
C	-2.616779000	-1.616701000	0.552070000
H	-0.645033000	-2.450876000	0.760335000
C	-2.735564000	0.520470000	-0.597668000
H	-0.861256000	1.344149000	-1.248292000
C	-3.370352000	-0.540730000	0.057373000
H	-3.131401000	-2.420741000	1.065576000
H	-3.299804000	1.357157000	-0.989372000
O	-4.700090000	-0.616705000	0.265273000
C	-5.512338000	0.454002000	-0.187185000
H	-5.223595000	1.394414000	0.294594000

H	-5.449882000	0.560085000	-1.275750000
H	-6.530955000	0.194736000	0.096327000
H	2.705655000	-1.900755000	1.325228000
B	1.212421000	2.040993000	0.114845000
F	0.873255000	2.375306000	-1.198802000
F	0.130803000	2.168182000	1.005254000
F	2.291680000	2.797586000	0.560508000
O	1.780965000	0.045531000	1.561169000
H	1.164935000	0.613369000	2.052762000

IV'

C	-2.605456000	1.672558000	-0.449231000
C	-3.332418000	1.042970000	0.706356000
C	-2.821108000	-0.055120000	1.251179000
C	-1.543264000	-0.623645000	0.734688000
H	-4.266874000	1.497062000	1.017598000
H	-3.295650000	-0.609632000	2.053098000
O	-2.902406000	3.014955000	-0.650526000
H	-2.819863000	1.152554000	-1.391450000
N	-0.694035000	0.539376000	0.275024000
N	-1.134796000	1.549177000	-0.286314000
C	0.748101000	0.407450000	0.300010000
C	1.435301000	0.268209000	1.507173000
C	1.408809000	0.443560000	-0.918732000
C	2.814916000	0.183039000	1.476754000
H	0.895099000	0.234129000	2.445060000
C	2.796493000	0.333940000	-0.948809000
H	0.834363000	0.524983000	-1.835836000
C	3.501035000	0.207836000	0.252237000
H	3.391449000	0.088969000	2.390128000
H	3.306153000	0.342153000	-1.903767000
O	4.844527000	0.099036000	0.337288000
C	5.592856000	0.106232000	-0.865815000
H	5.312993000	-0.737447000	-1.506228000
H	5.452889000	1.047630000	-1.408826000
H	6.635728000	0.008491000	-0.568425000
H	-2.759688000	3.503986000	0.169810000
B	-1.735625000	-1.607099000	-0.674485000
F	-1.710876000	-0.777506000	-1.798609000
F	-0.620531000	-2.455663000	-0.642111000
F	-2.918759000	-2.298121000	-0.545341000
O	-0.876001000	-1.324961000	1.724501000
H	-0.455718000	-2.090062000	1.299880000

TS(IV',V)

C	-2.485037000	1.599288000	-0.447720000
C	-3.116941000	1.349026000	0.896348000
C	-2.636694000	0.287750000	1.560362000
C	-1.434630000	-0.349601000	1.056613000
H	-3.922367000	1.986332000	1.242066000
H	-3.038723000	-0.094200000	2.492380000
O	-2.813828000	2.828012000	-1.023887000
H	-2.802324000	0.827658000	-1.169822000
N	-0.615610000	0.512789000	0.363850000
N	-1.034689000	1.532787000	-0.298867000
C	0.821246000	0.332774000	0.334210000
C	1.552460000	0.195240000	1.515564000
C	1.449591000	0.369941000	-0.900284000
C	2.929705000	0.093679000	1.443543000
H	1.045296000	0.171837000	2.472355000
C	2.836622000	0.253920000	-0.976428000
H	0.850152000	0.489872000	-1.796199000
C	3.578133000	0.116120000	0.199473000
H	3.533286000	-0.002965000	2.339180000
H	3.315960000	0.276061000	-1.946944000
O	4.926203000	-0.001757000	0.241821000
C	5.633652000	0.029138000	-0.983308000
H	5.333046000	-0.801112000	-1.632592000

H	5.476805000	0.980684000	-1.504043000
H	6.686278000	-0.074745000	-0.723792000
H	-2.289683000	3.510176000	-0.584254000
B	-2.077466000	-1.715983000	-0.911099000
F	-1.407953000	-1.046687000	-1.844696000
F	-1.487921000	-2.778988000	-0.346646000
F	-3.393694000	-1.600476000	-0.830215000
O	-0.811778000	-1.287713000	1.846453000
H	-0.815613000	-2.145361000	1.400953000

V

C	3.192971000	-1.061136000	-0.508467000
C	3.838223000	0.270528000	-0.692928000
C	3.177290000	1.325227000	-0.162229000
C	1.844605000	1.127356000	0.283794000
H	4.794647000	0.371916000	-1.193460000
H	3.580338000	2.331851000	-0.124772000
O	3.470295000	-1.477542000	0.837688000
H	3.584155000	-1.804980000	-1.209108000
N	1.200652000	0.039474000	-0.139713000
N	1.786319000	-0.979328000	-0.774190000
C	-0.235233000	-0.067479000	-0.056357000
C	-0.783725000	-1.286812000	0.339235000
C	-1.055653000	0.991883000	-0.416379000
C	-2.158930000	-1.435076000	0.394577000
H	-0.119696000	-2.106556000	0.587213000
C	-2.441240000	0.847725000	-0.366710000
H	-0.621346000	1.931453000	-0.739116000
C	-2.995009000	-0.368061000	0.043346000
H	-2.613798000	-2.370053000	0.702962000
H	-3.067291000	1.682627000	-0.655630000
O	-4.327516000	-0.610212000	0.129400000
C	-5.215096000	0.427841000	-0.234525000
H	-5.081859000	1.305919000	0.408521000
H	-5.076493000	0.716662000	-1.283076000
H	-6.218282000	0.026126000	-0.097849000
H	3.027452000	-2.327230000	0.969208000
O	1.145155000	2.079617000	0.968592000
H	1.590677000	2.254354000	1.806846000

V···H_2O

C	2.902149000	-1.329008000	-0.621220000
C	3.551884000	-0.129562000	-1.215987000
C	2.929945000	1.043412000	-0.955352000
C	1.633126000	1.005402000	-0.376557000
H	4.476460000	-0.200576000	-1.777926000
H	3.342673000	2.017636000	-1.193628000
O	3.231394000	-1.317594000	0.806283000
H	3.268133000	-2.265154000	-1.048348000
N	0.951271000	-0.139625000	-0.463634000
N	1.492806000	-1.307276000	-0.830465000
C	-0.473501000	-0.180921000	-0.252613000
C	-1.016769000	-1.273378000	0.422190000
C	-1.295472000	0.820328000	-0.751374000
C	-2.385883000	-1.350182000	0.614130000
H	-0.355217000	-2.053393000	0.779758000
C	-2.673833000	0.747625000	-0.562929000
H	-0.865172000	1.660263000	-1.284656000
C	-3.221239000	-0.338943000	0.125181000
H	-2.836585000	-2.185180000	1.139112000
H	-3.301692000	1.535228000	-0.960412000
O	-4.547387000	-0.501402000	0.363939000
C	-5.429830000	0.504043000	-0.092391000
H	-5.196524000	1.472457000	0.365812000
H	-5.393158000	0.597129000	-1.184155000
H	-6.427170000	0.188816000	0.211658000
H	2.762500000	-2.065392000	1.204563000
O	1.061941000	2.091963000	0.198505000

H	1.457580000	2.138925000	1.092191000
O	2.589241000	1.056400000	2.254943000
H	2.917692000	0.255130000	1.799758000
H	3.236971000	1.284596000	2.927133000

TS(V···H_2O,4j)

C	2.880589000	-1.157071000	-0.957396000
C	3.630548000	0.065149000	-1.134163000
C	3.001459000	1.201344000	-0.752487000
C	1.667356000	1.089042000	-0.272535000
H	4.660482000	0.042184000	-1.471519000
H	3.473801000	2.175269000	-0.702218000
O	3.178499000	-1.269875000	0.964797000
H	3.324877000	-2.097493000	-1.263720000
N	0.979972000	-0.013391000	-0.598068000
N	1.548334000	-1.139173000	-1.071586000
C	-0.436442000	-0.109735000	-0.363968000
C	-0.949271000	-1.288720000	0.175689000
C	-1.275886000	0.943977000	-0.695753000
C	-2.312862000	-1.406590000	0.383236000
H	-0.270579000	-2.095659000	0.425740000
C	-2.648395000	0.830029000	-0.488996000
H	-0.863437000	1.857845000	-1.108939000
C	-3.169362000	-0.349556000	0.051698000
H	-2.742033000	-2.308628000	0.805004000
H	-3.290993000	1.659722000	-0.755289000
O	-4.487265000	-0.561524000	0.290924000
C	-5.394848000	0.473165000	-0.032022000
H	-5.366441000	0.703639000	-1.103453000
H	-6.382832000	0.098710000	0.232972000
H	-5.181001000	1.380560000	0.544728000
H	2.916339000	-2.152012000	1.258329000
O	1.146018000	1.969279000	0.567962000
H	1.465008000	1.527690000	1.480100000
O	2.086270000	0.497076000	2.306876000
H	2.587185000	-0.299113000	1.760452000
H	2.625989000	0.749384000	3.061103000

4j

C	-2.734214000	-0.309766000	-0.087785000
C	-1.955289000	-1.376069000	-0.552004000
C	-0.574247000	-1.301144000	-0.502420000
C	0.047084000	-0.160641000	0.013809000
C	-0.720858000	0.899756000	0.478912000
C	-2.113241000	0.828147000	0.429264000
H	-2.456721000	-2.250650000	-0.951830000
H	0.034548000	-2.126937000	-0.852587000
H	-0.242994000	1.789413000	0.867759000
H	-2.692159000	1.667565000	0.794174000
O	-4.079438000	-0.473476000	-0.184346000
C	-4.905346000	0.575498000	0.278728000
H	-5.930579000	0.246146000	0.113687000
H	-4.748116000	0.759633000	1.348185000
H	-4.723407000	1.499853000	-0.282167000
C	2.191084000	1.045590000	-0.258361000
C	3.341991000	-1.386300000	0.443280000
C	3.637901000	0.895795000	-0.198795000
C	4.201910000	-0.284300000	0.142802000
H	3.733484000	-2.358199000	0.722311000
H	4.211659000	1.779715000	-0.452890000
H	5.278906000	-0.410269000	0.190061000
N	2.047084000	-1.301105000	0.408128000
N	1.483041000	-0.128042000	0.079002000
O	1.619920000	2.079520000	-0.569554000