Supporting Information

Electrochemically Dehydrogenative C-H/P-H Cross-Coupling: Effective Synthesis of Phosphonated Quinoxalin-2(1*H*)-ones and Xanthenes

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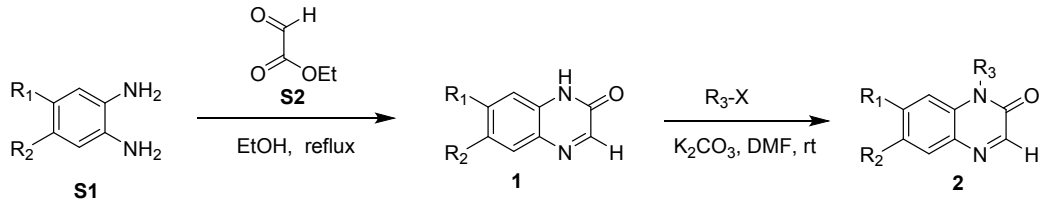
Contents

Typical procedure for the synthesis of Quinoxalin-2(1*H*)-one



To a stirred solution of 1,2-phenylenediamines **S1** (5 mmol, 1.0 equiv) in ethanol (40 mL) was added ethyl glyoxalate **S2** (6 mmol, 1.2 equiv). After complete addition, the resultant reaction mixture was stirred at 80 °C until the raw material disappears and gave quinoxalin-2(1*H*)-one **1**. For alkylation, the corresponding halogenoalkane (1.6 equiv.) was added to a suspension of quinoxalinone (1.0 equiv.) and potassium carbonate (1.2 equiv.) in DMF (16 mL). The mixture was stirred at room temperature until the raw material disappears (as monitored by TLC). After complete reaction, ammonium chloride saturated solution (5 ml) was added to the reaction system, and then added ethyl acetate (10 mL) and water (10 mL) to extract the reaction system. The residue was purified by column chromatography on silica gel to afford the alkylated quinoxalinone **2.**[1]

Cyclic voltammograms

1) The CV for the electrochemical oxidative phosphonation of quinoxaline-2(1*H*)-ones.

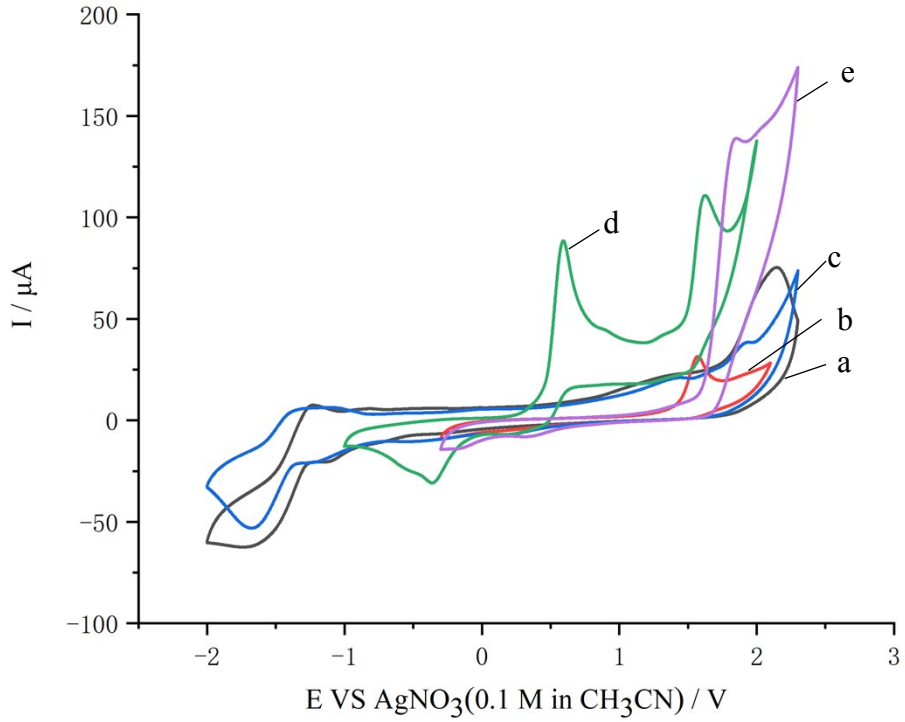


Figure 1. Cyclic voltammograms of 0.1 M $LiClO_4$ and related compounds in CH_3CN using Pt working electrode, Pt wire, and $Ag/AgNO_3$ (0.1 M in CH_3CN) as counter and reference electrode at 100 mV/s scan rate. (a) blank (b) **1a** (5.0 mmol/L), (c) **2a** (5.0 mmol/L), (d) **4aa** (5.0 mmol/L), (e) **3aa** (5.0 mmol).

2) The CV for the electrochemical oxidative phosphonation of quinoxaline-2(1*H*)-ones.

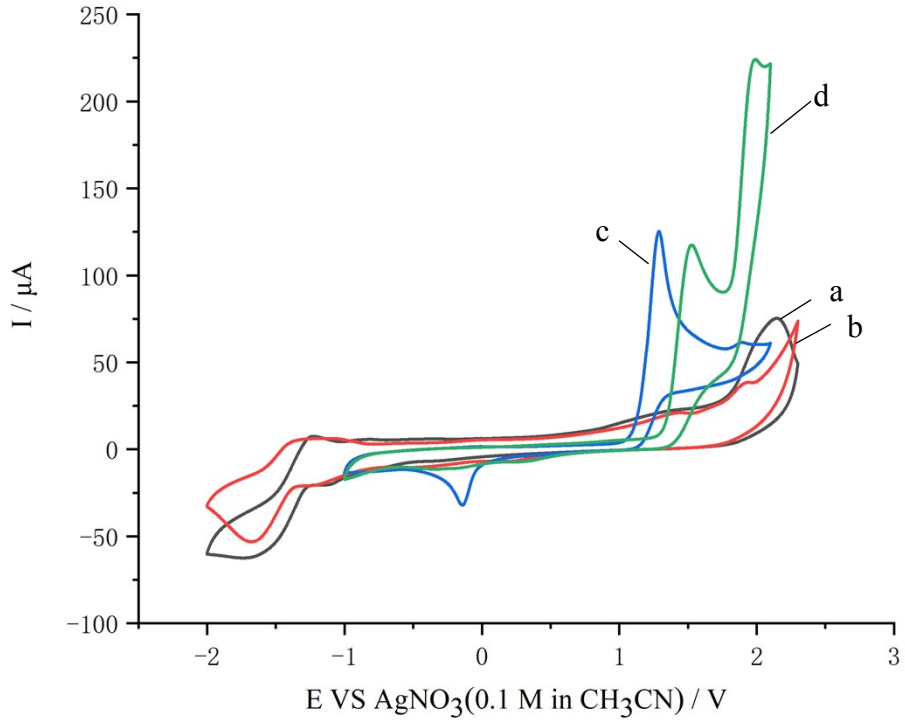
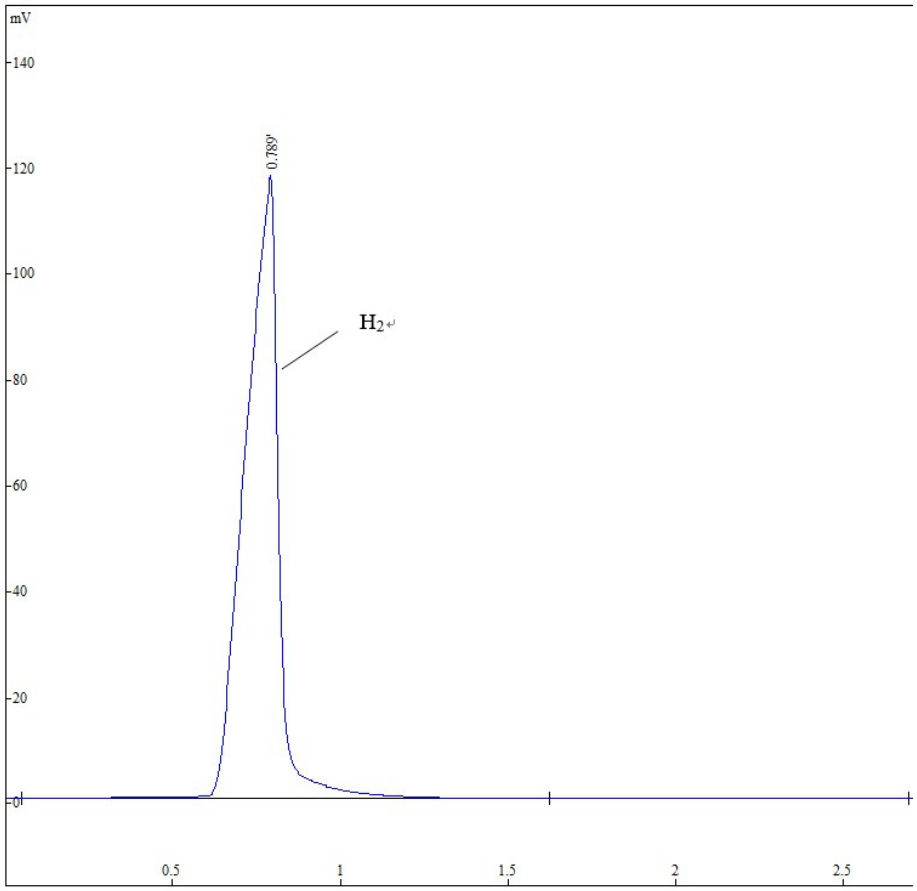
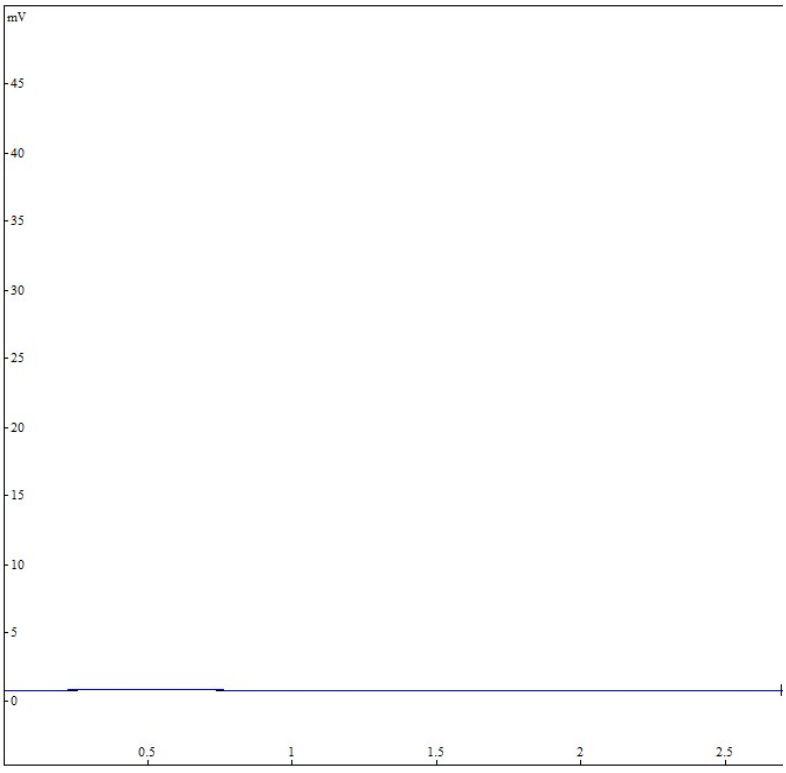


Figure 2. Cyclic voltammograms of 0.1 M $LiClO_4$ and related compounds in CH_3CN using Pt working electrode, Pt wire, and $Ag/AgNO_3$ (0.1 M in CH_3CN) as counter and reference electrode at 100 mV/s scan rate. (a) blank (b) **2a** (5.0 mmol/L), (c) **4** (5.0 mmol/L), (d) **5a** (5.0 mmol/L).

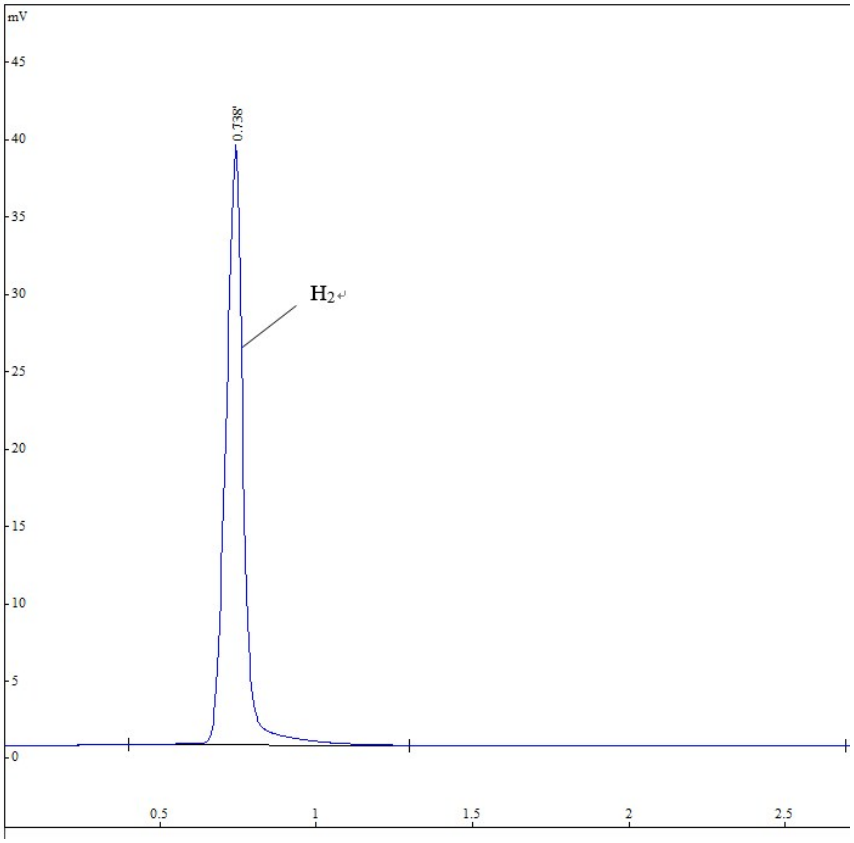
GC detection test of H_2



(a). GC of H_2 standard sample



(b). GC of the atmosphere (before electrolysis)

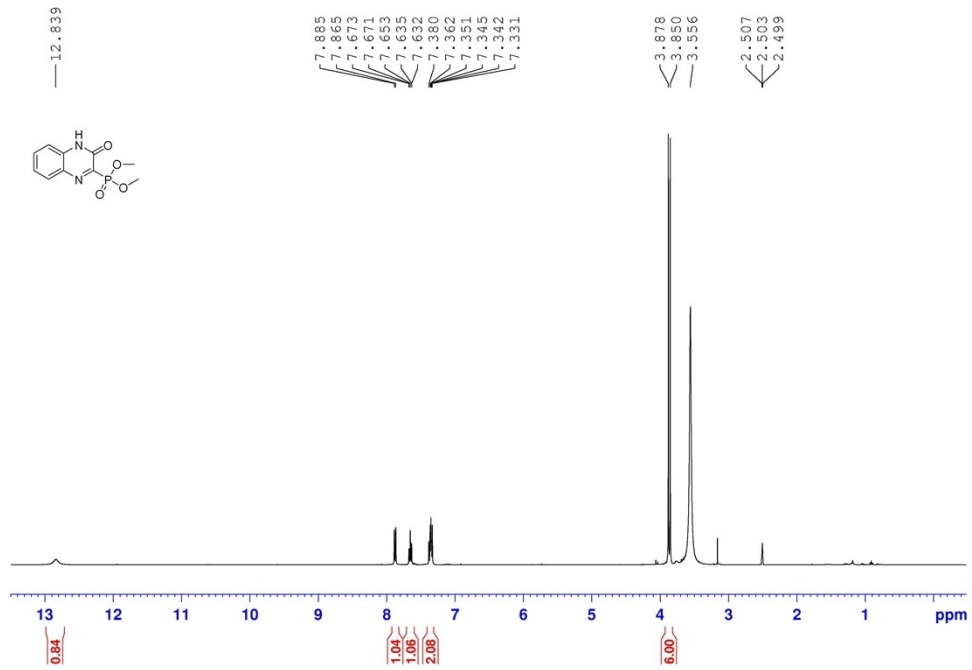


(c). (b). GC of the atmosphere (during electrolysis)

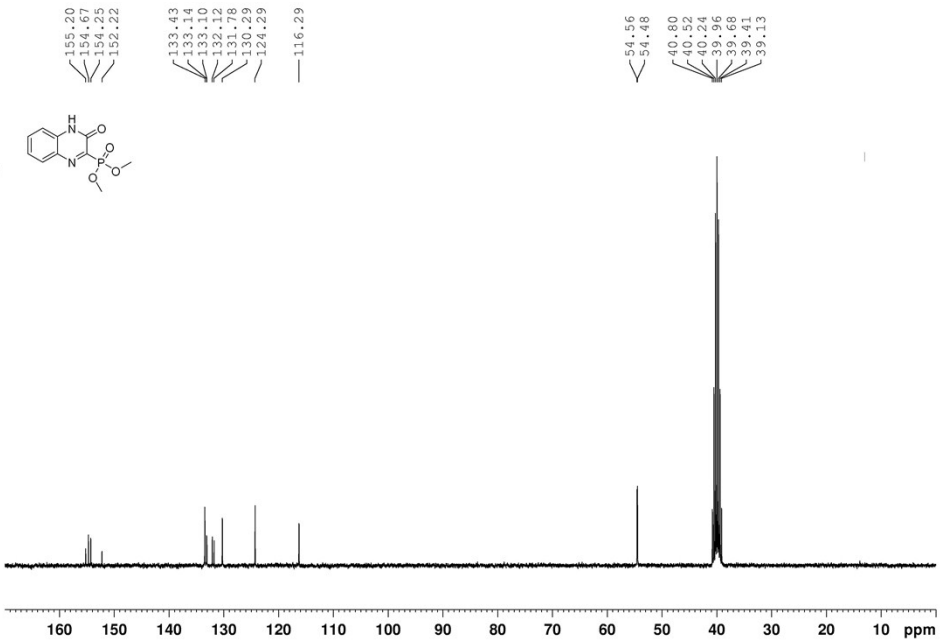
Figure 3. GC detection test of H_2

Spectra of prepared compounds

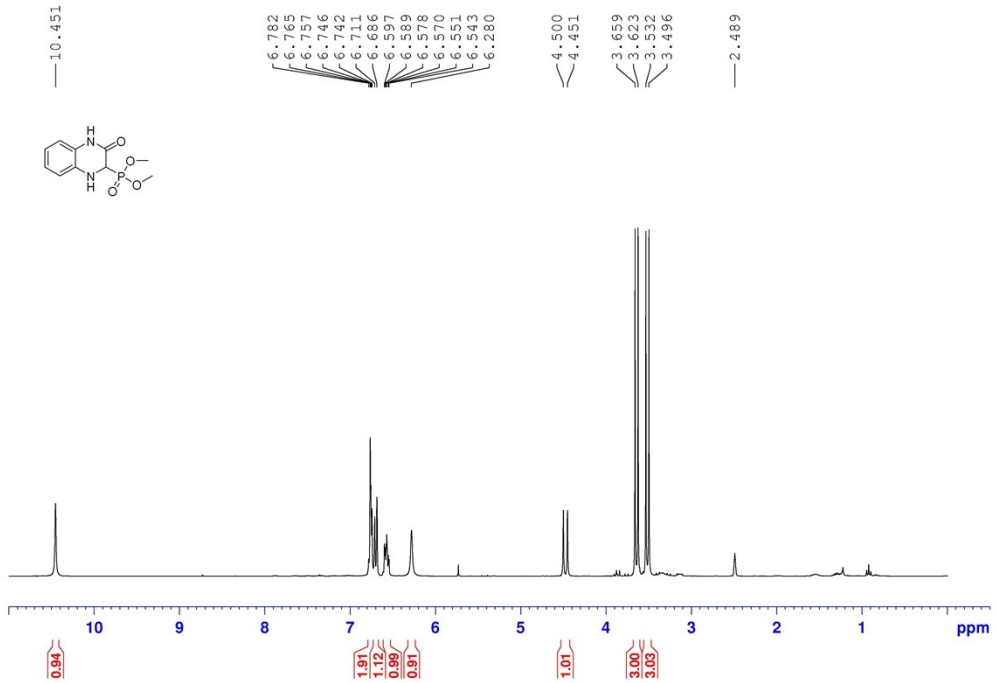
^{1}H NMR spectra of Dimethyl (3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3aa)[2]



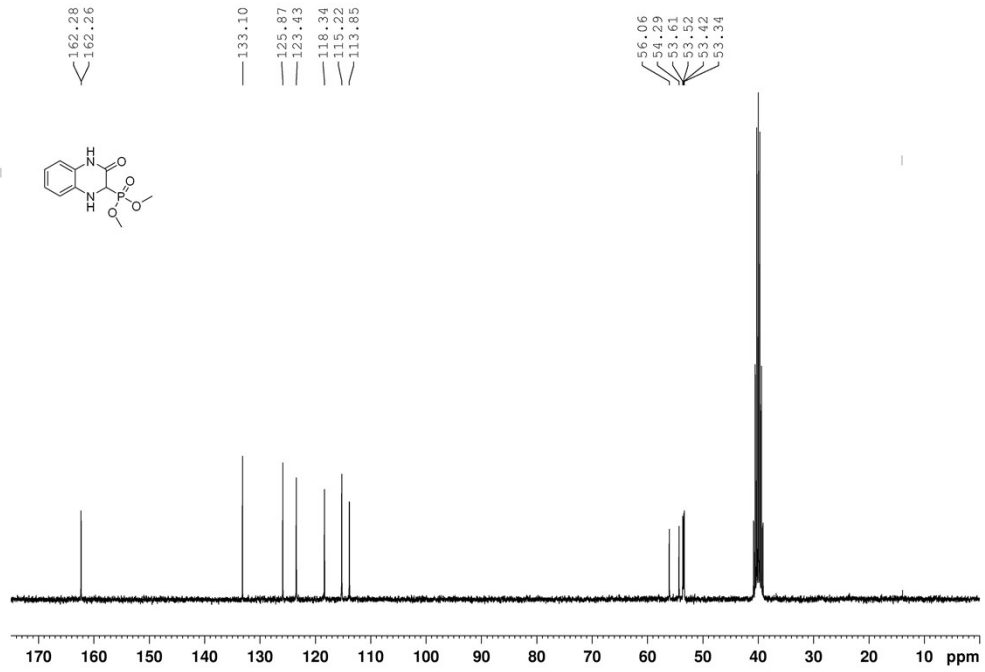
^{13}C NMR spectra of Dimethyl (3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3aa)[2]



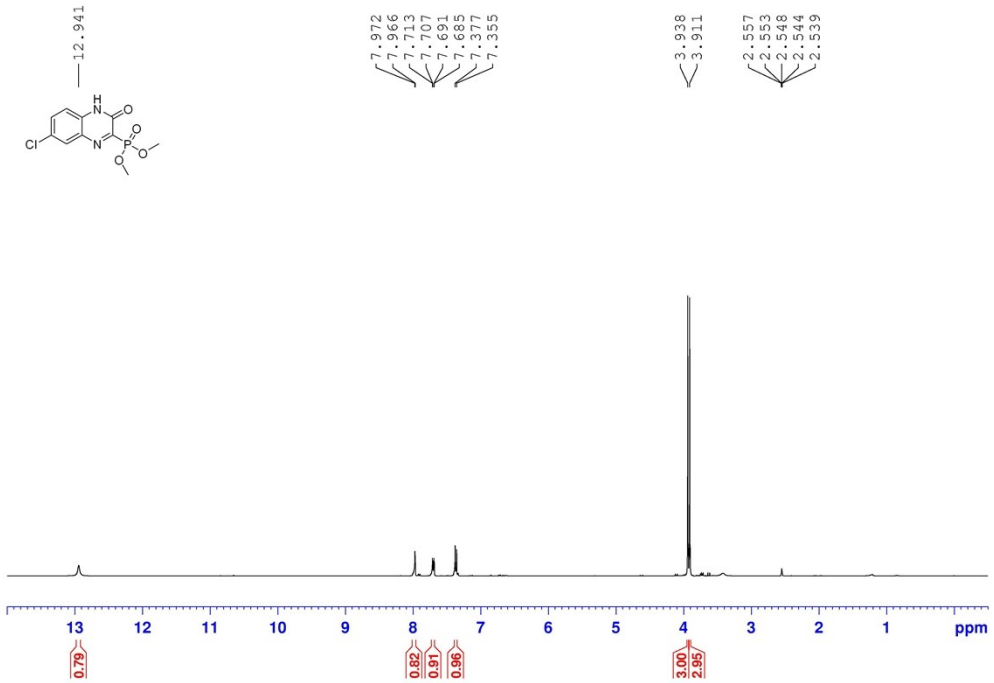
^{1}H NMR spectra of Dimethyl (3-oxo-1,2,3,4-tetrahydroquinoxalin-2-yl)phosphonate (4aa)[2]



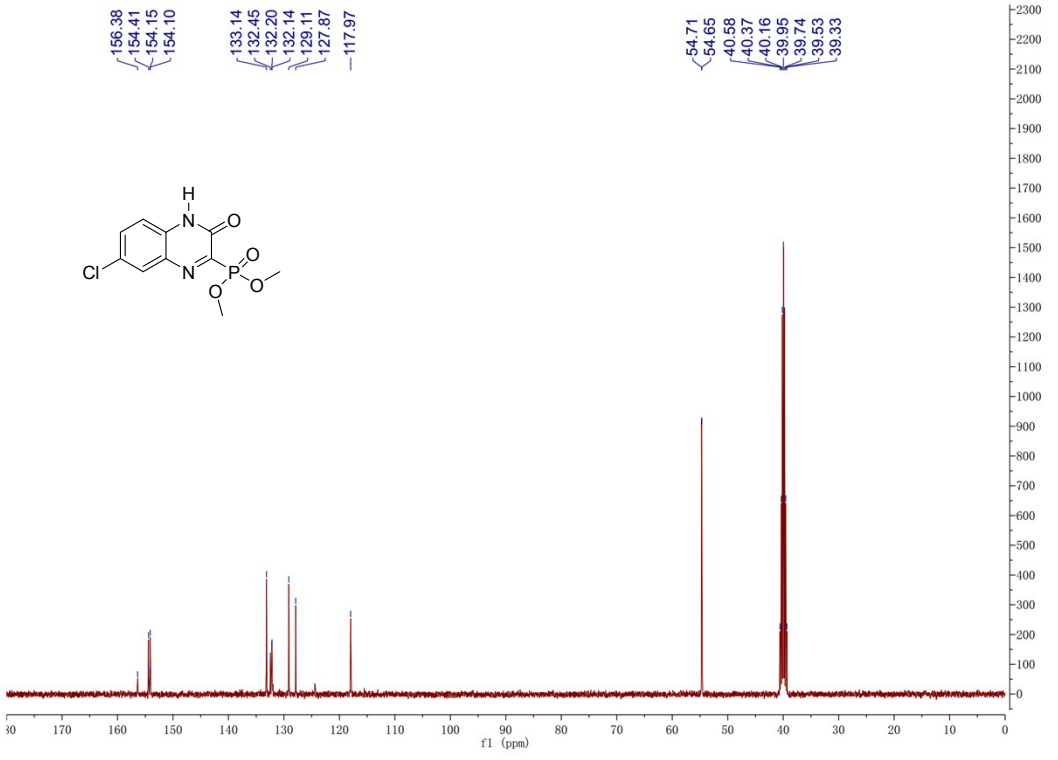
^{13}C NMR spectra of Dimethyl (3-oxo-1,2,3,4-tetrahydroquinoxalin-2-yl)phosphonate (4aa)[2]



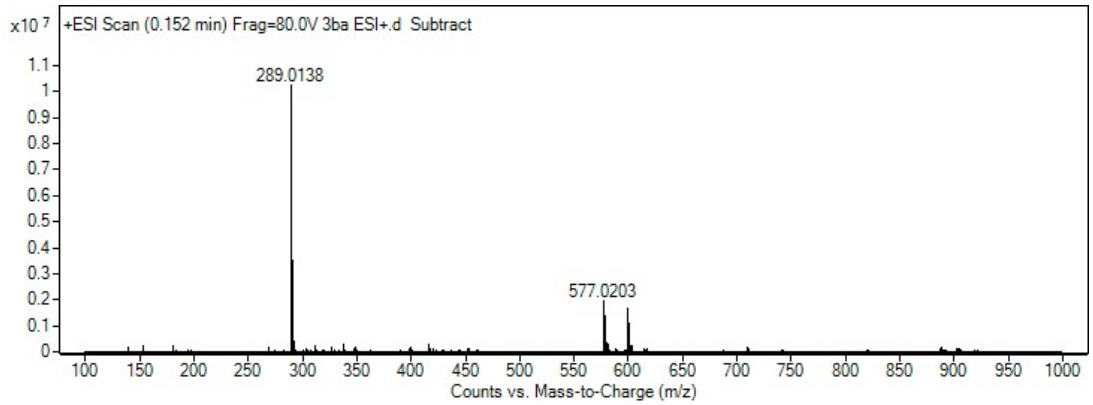
^{1}H NMR spectra of Dimethyl (7-chloro-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3ba)



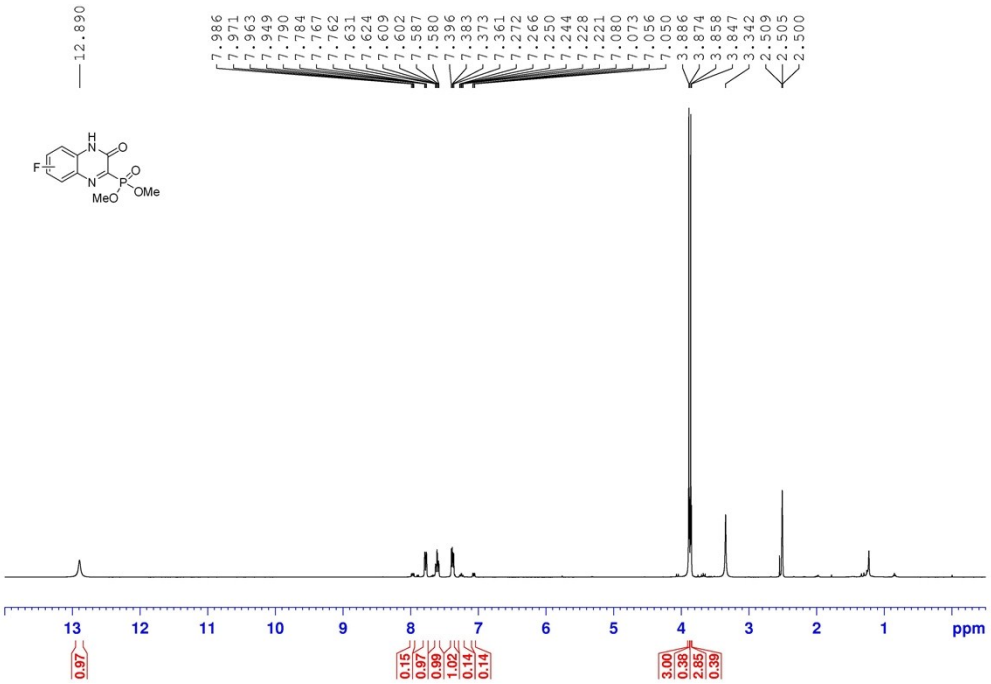
^{13}C NMR spectra of Dimethyl (7-chloro-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3ba)



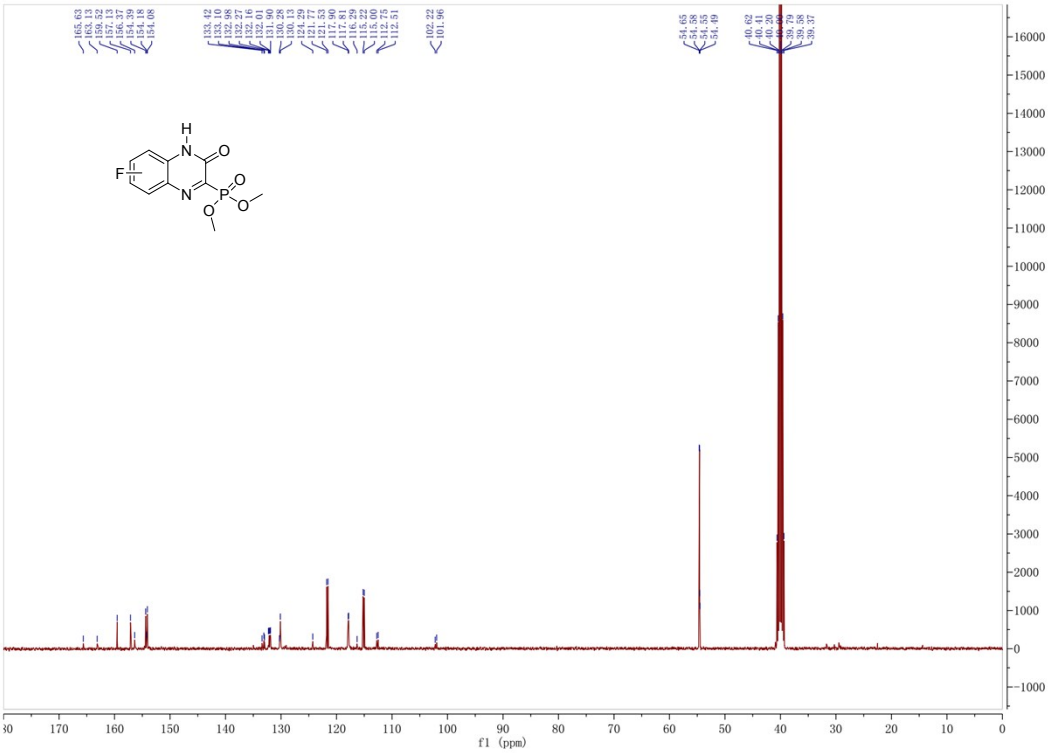
HRMS spectra of Dimethyl (7-chloro-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3ba)



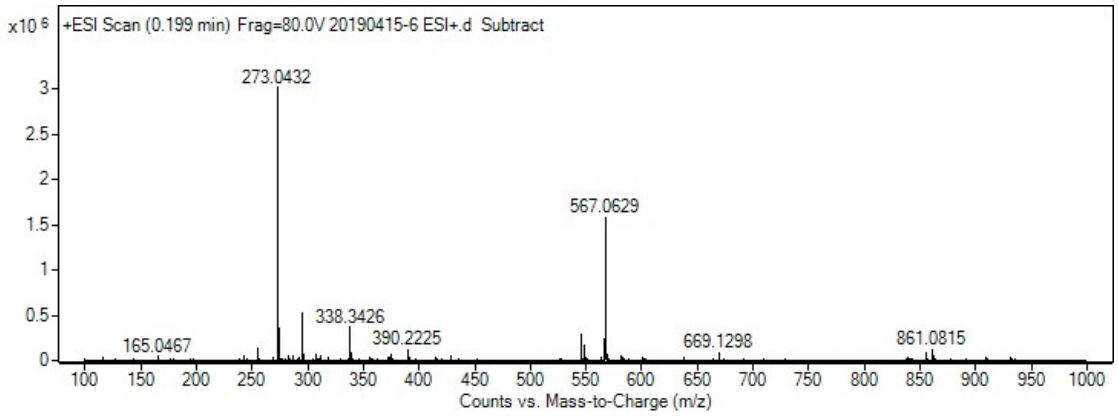
^{1}H NMR spectra of Dimethyl (6-fluoro-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3ca) and dimethyl (7-fluoro-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3ca')



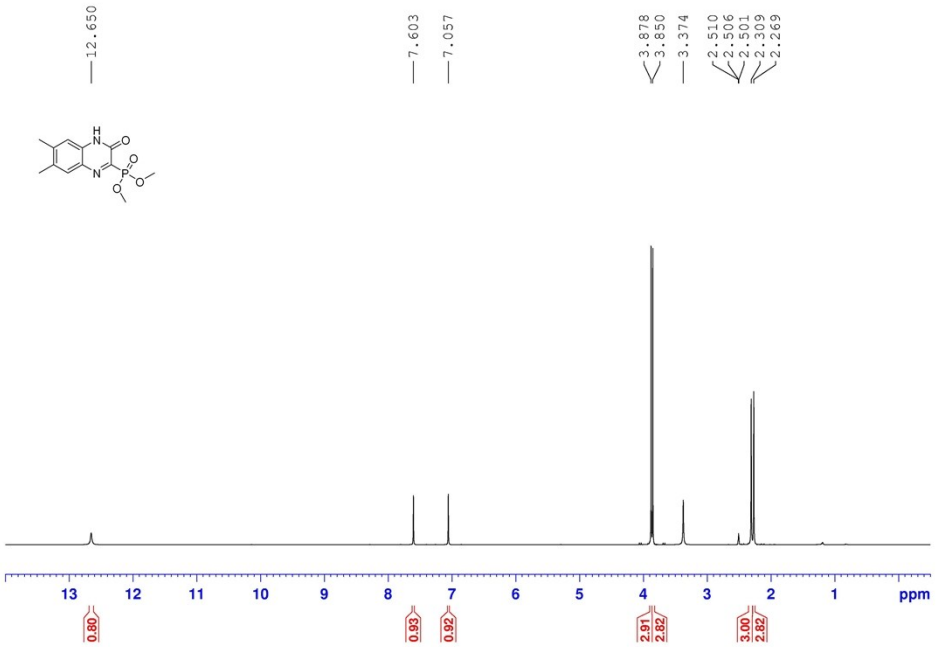
^{13}C NMR spectra of Dimethyl (6-fluoro-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3ca) and dimethyl (7-fluoro-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3ca')



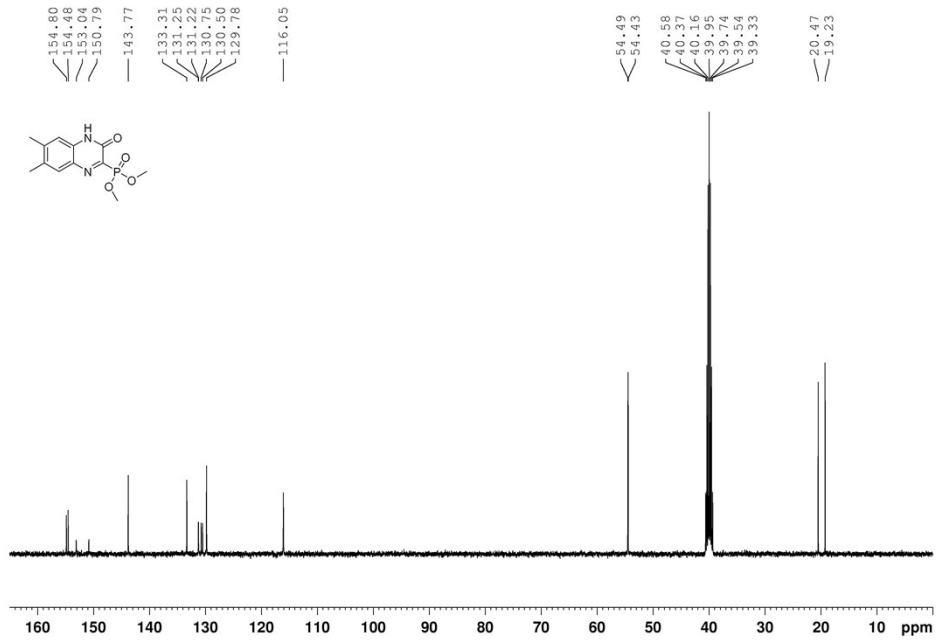
HRMS spectra of Dimethyl (6-fluoro-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3ca) and dimethyl (7-fluoro-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3ca')



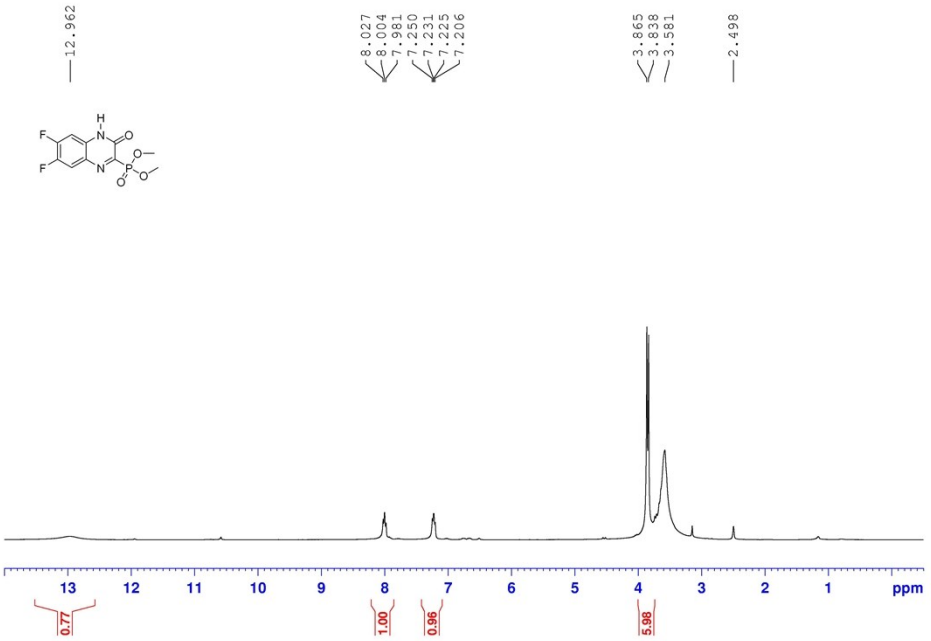
^{1}H NMR spectra of Dimethyl (6,7-dimethyl-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3da)[2]



^{13}C NMR spectra of Dimethyl (6,7-dimethyl-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3da)[2]



^{1}H NMR spectra of Dimethyl (6,7-difluoro-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3ea)



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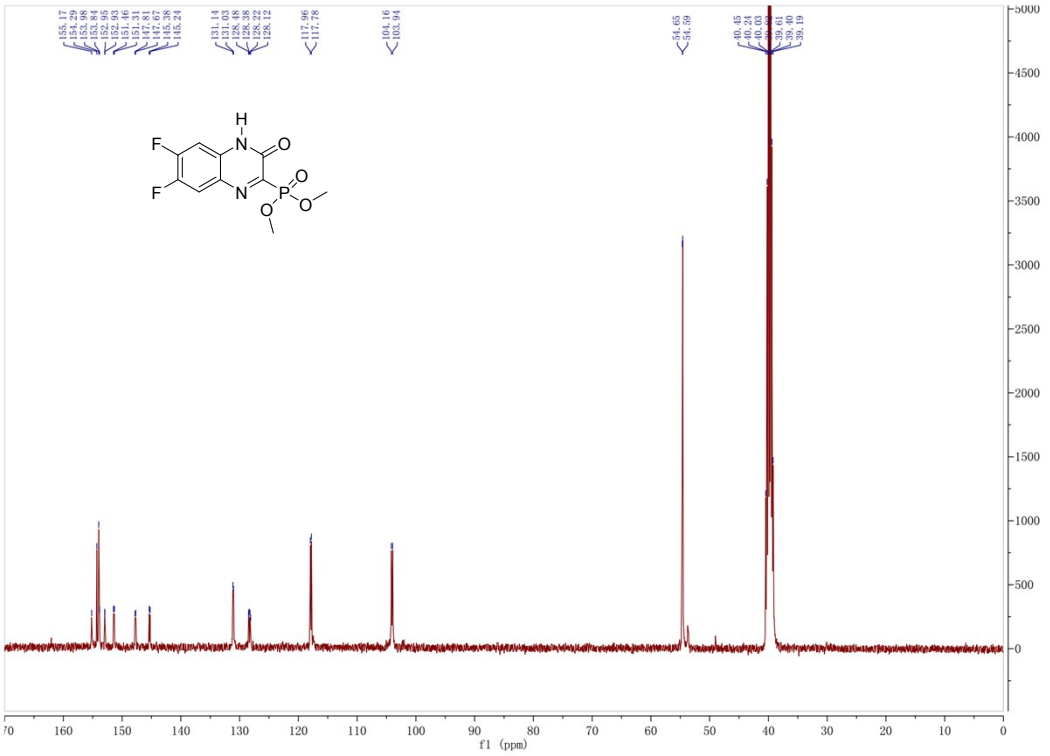

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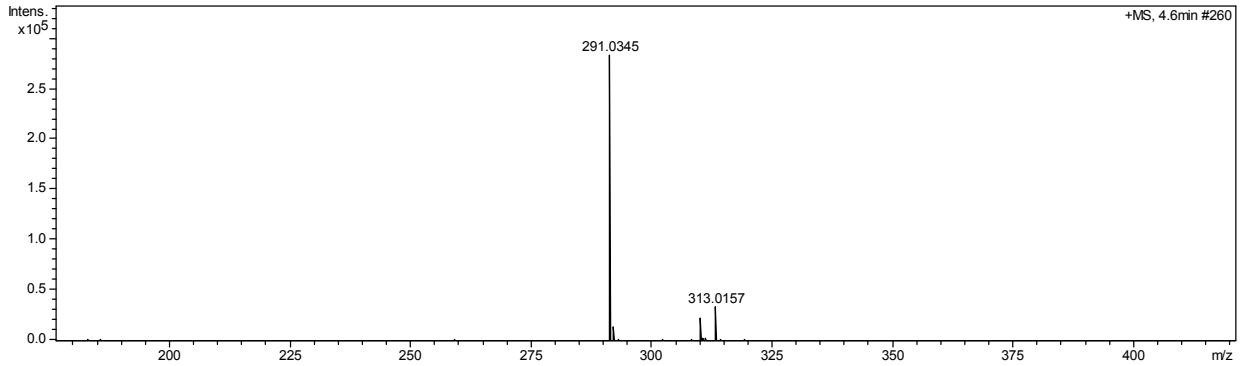
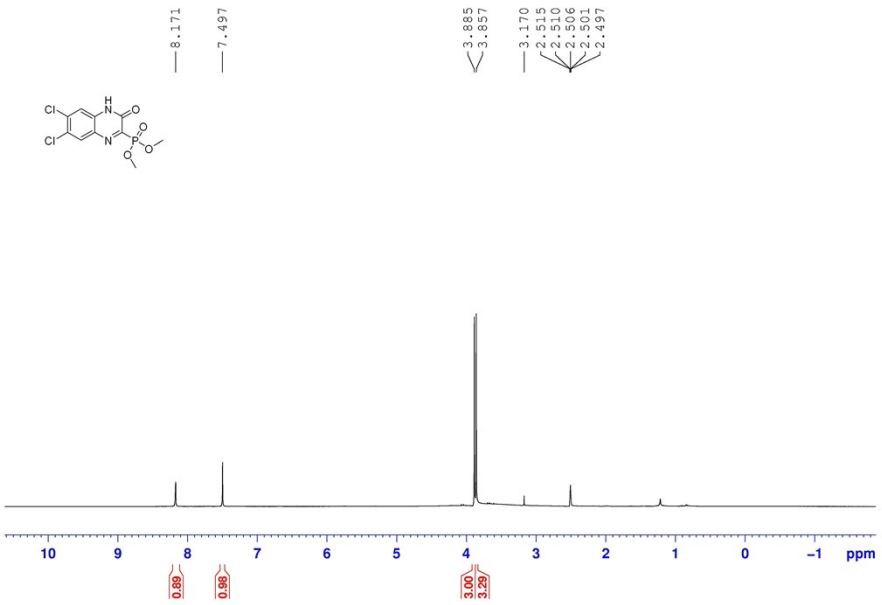
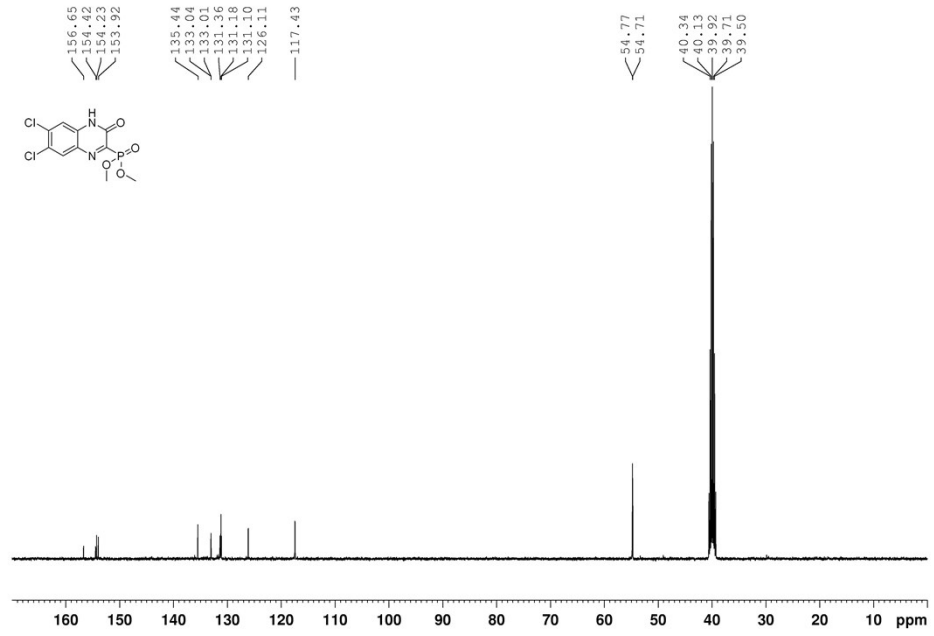


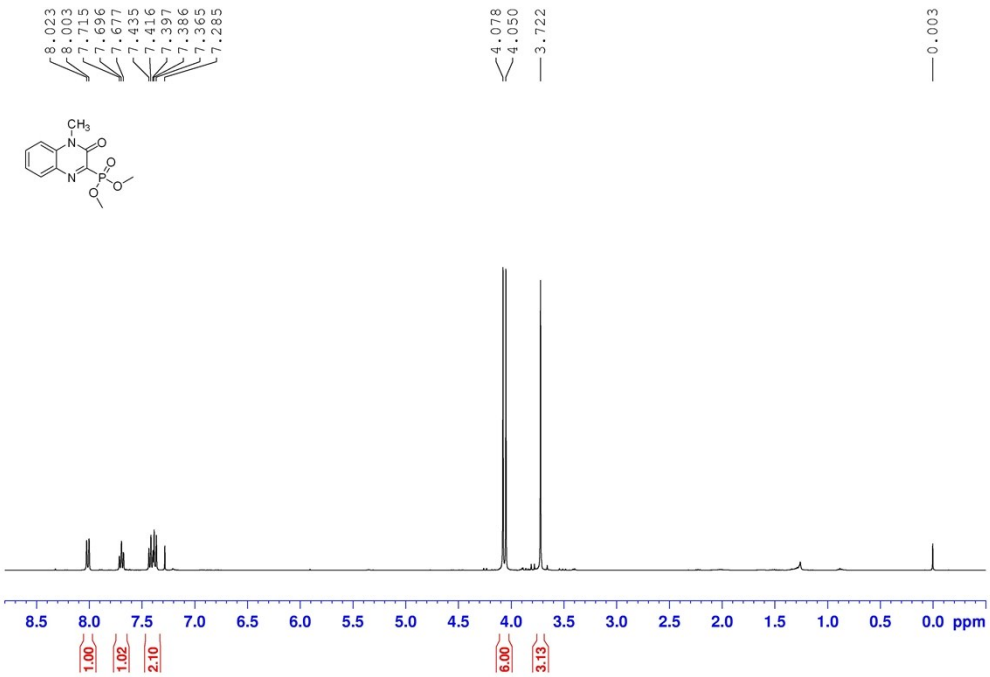
^{1}H NMR spectra of Dimethyl (6,7-dichloro-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3fa)[2]



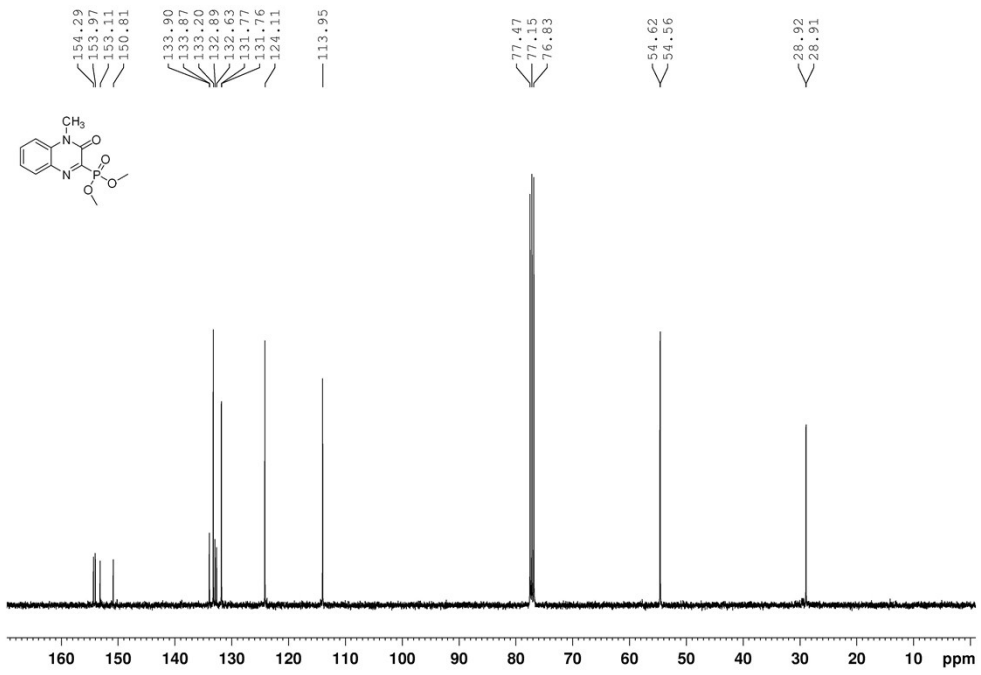
^{13}C NMR spectra of Dimethyl (6,7-dichloro-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3fa)[2]



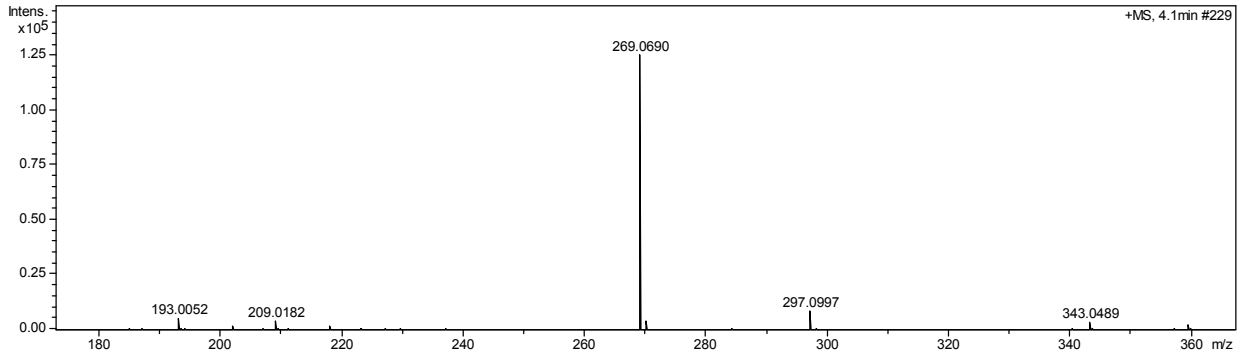
^{1}H NMR spectra of Dimethyl (4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3ga)



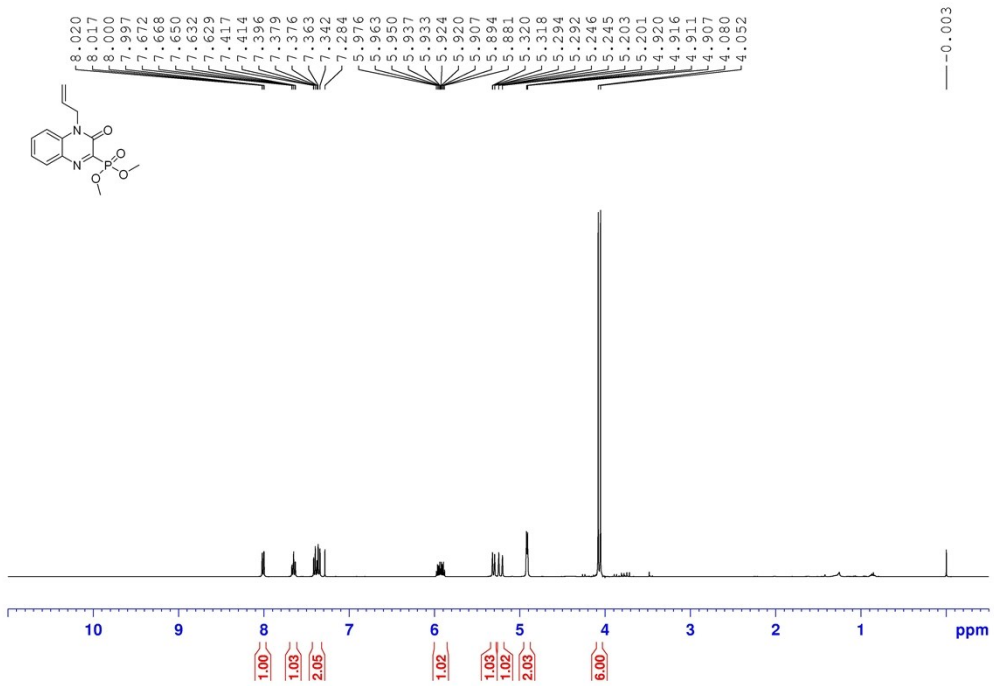
^{13}C NMR spectra of Dimethyl (4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3ga)



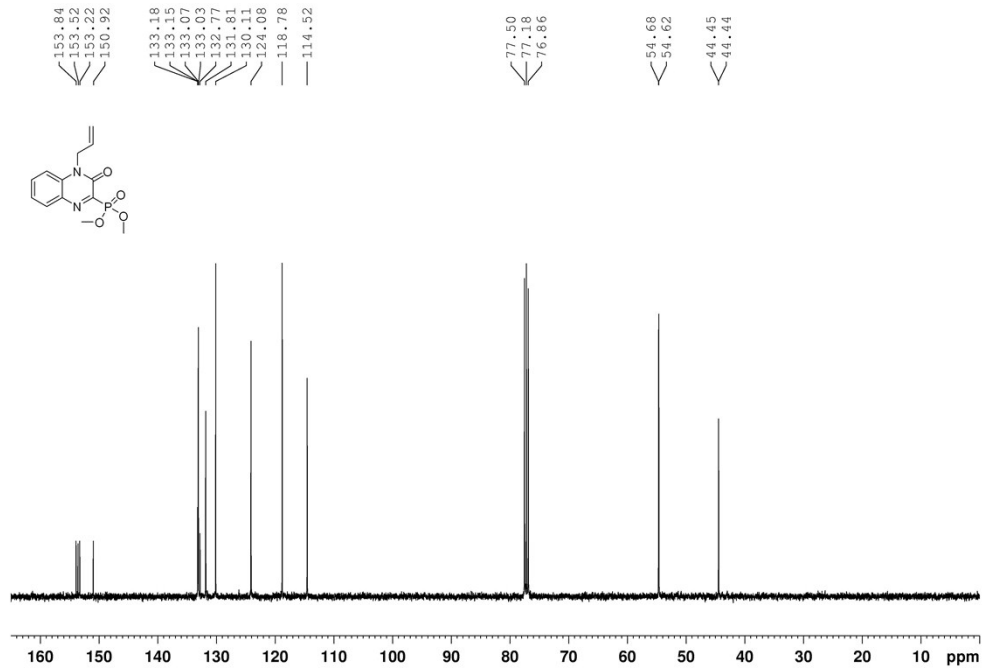
HRMS spectra of Dimethyl (4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3ga)



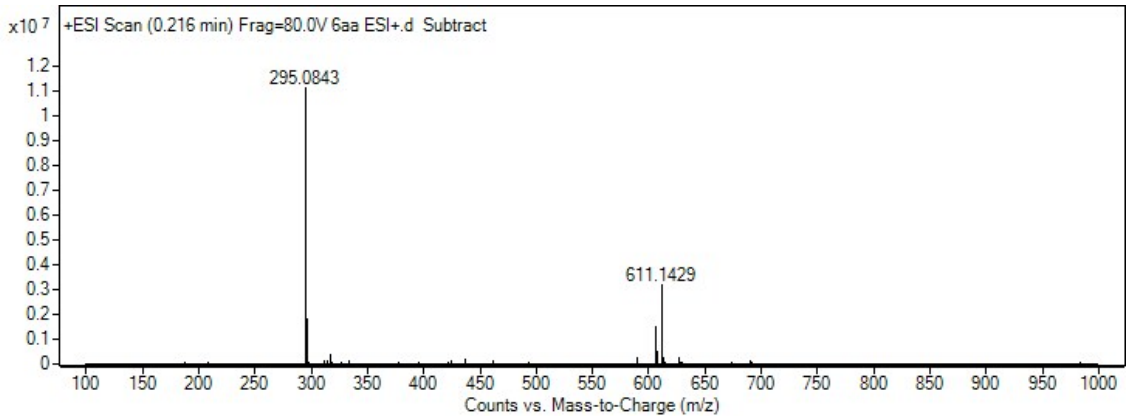
^{1}H NMR spectra of Dimethyl (4-allyl-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3ha)



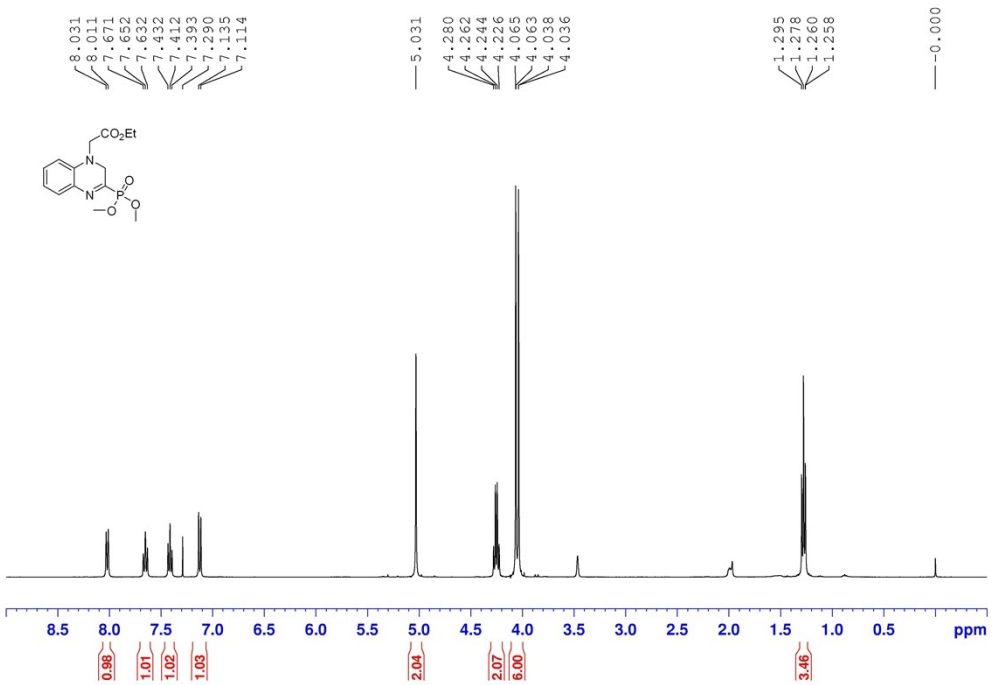
^{13}C NMR spectra of Dimethyl (4-allyl-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3ha)



HRMS spectra of Dimethyl (4-allyl-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3ha)



^{1}H NMR spectra of Ethyl 2-(3-(dimethoxyphosphoryl)-2-oxoquinoxalin-1(2H)-yl)acetate (3ia)[2]



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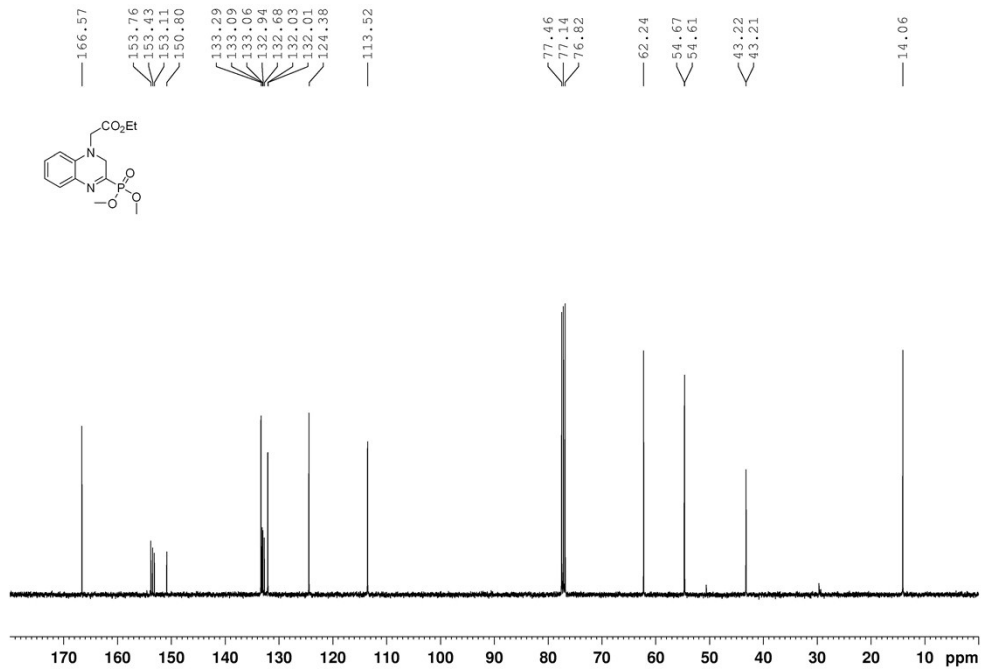
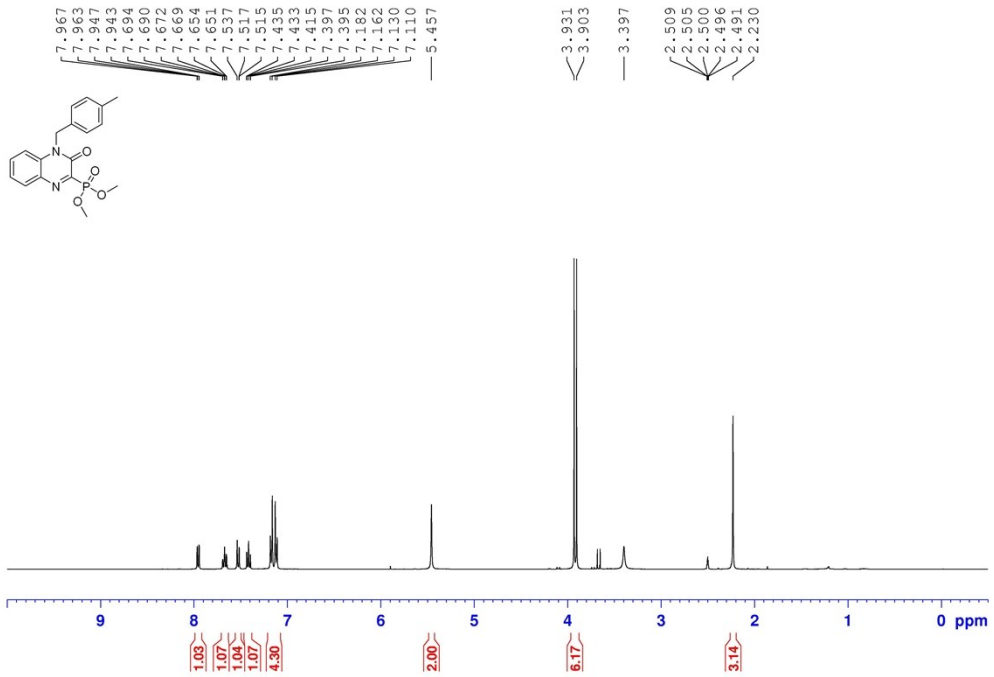


^{1}H NMR spectra of Dimethyl (4-(4-methylbenzyl)-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3ja)



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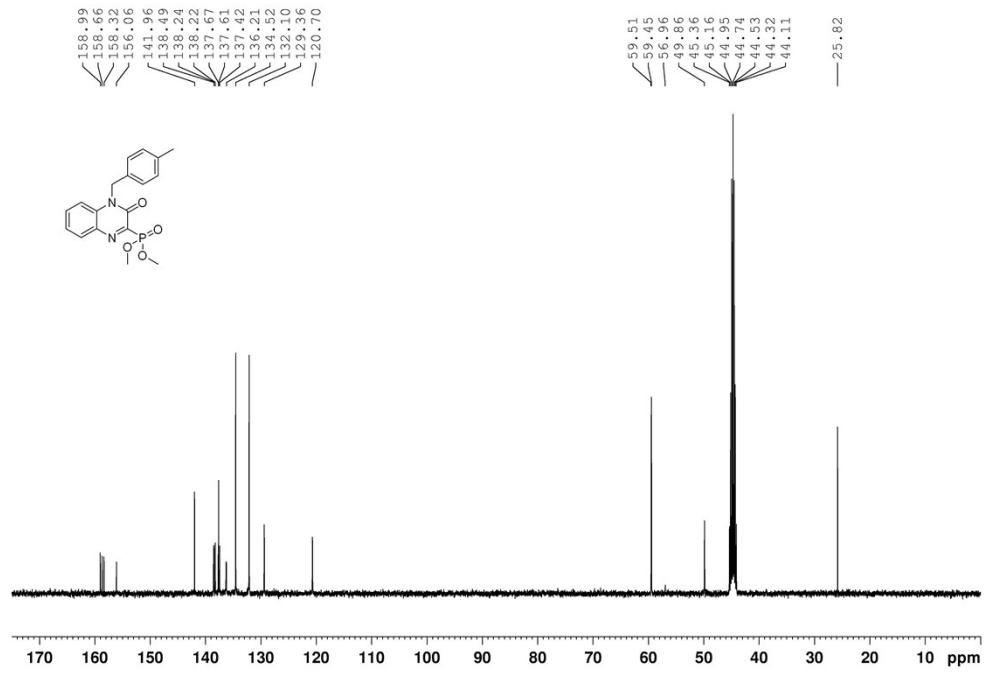

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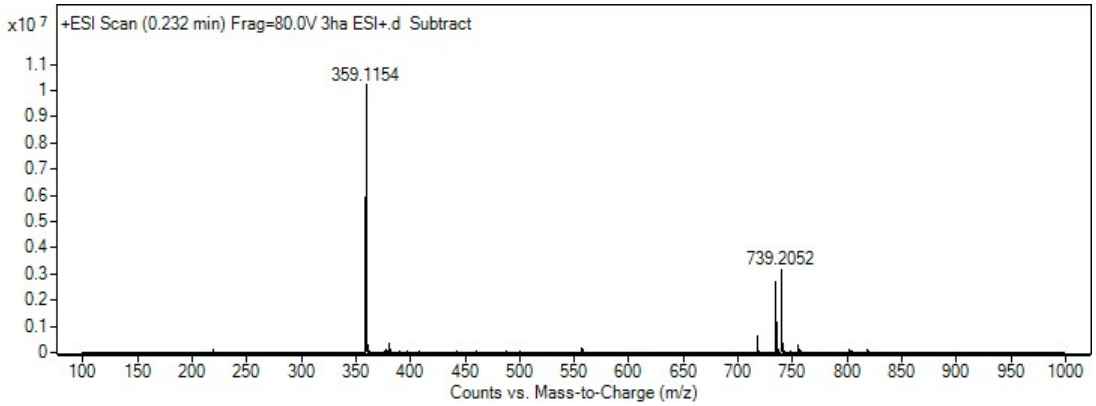
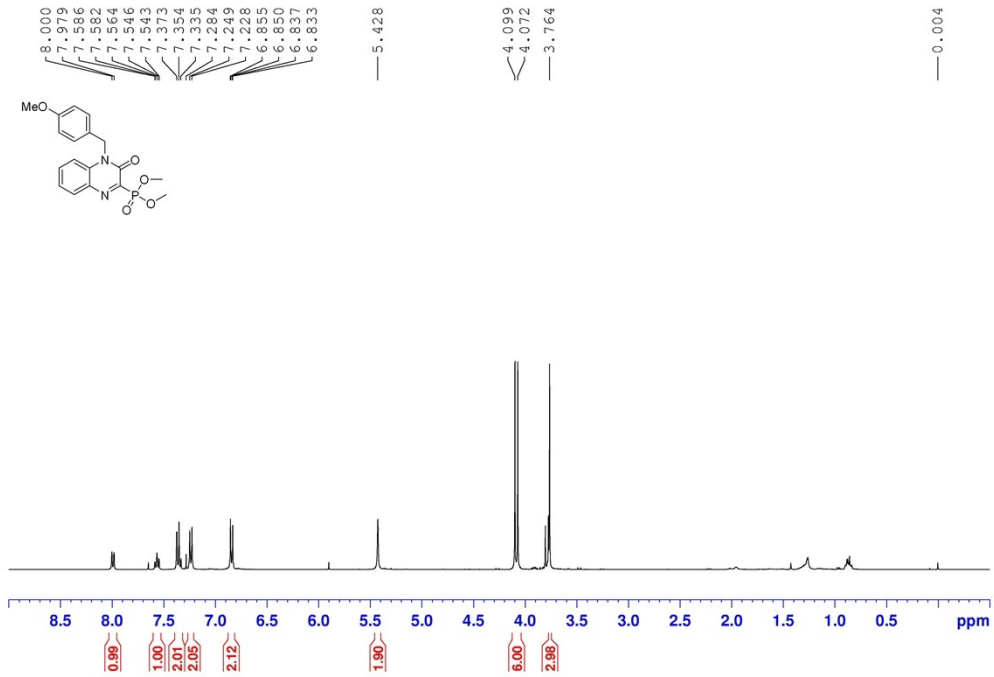


^{1}H NMR spectra of Dimethyl (4-(4-methoxybenzyl)-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3ka)



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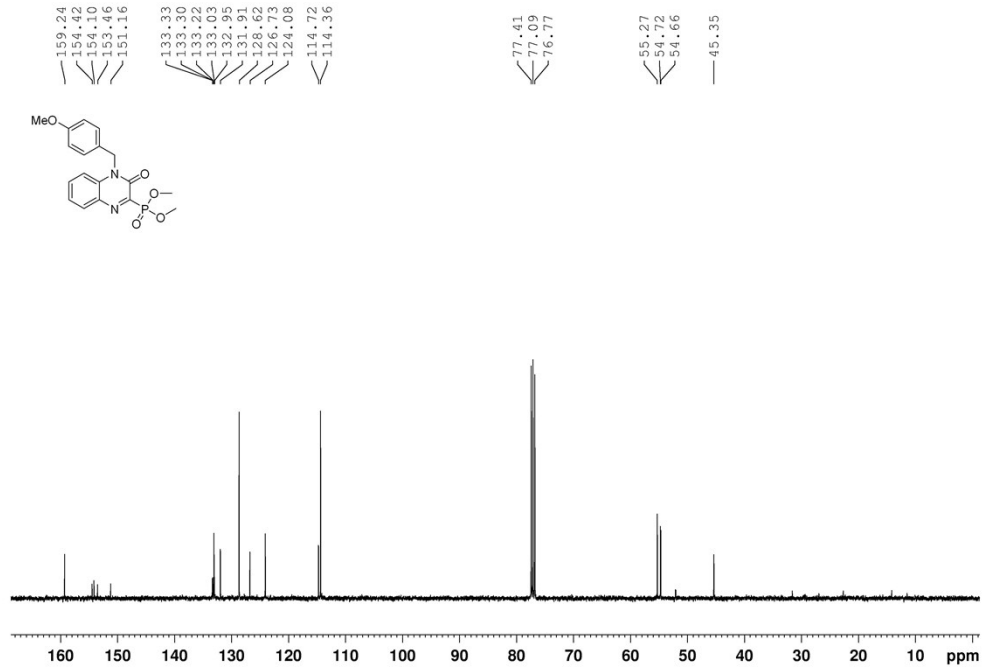

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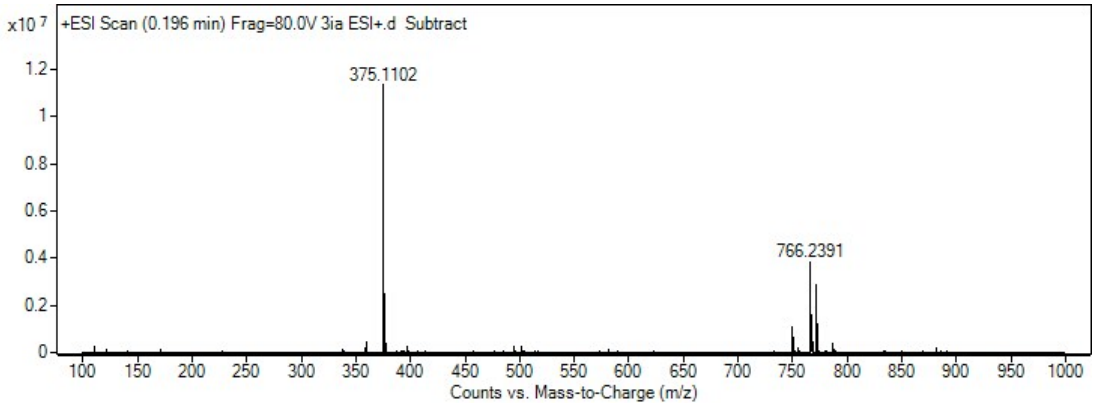
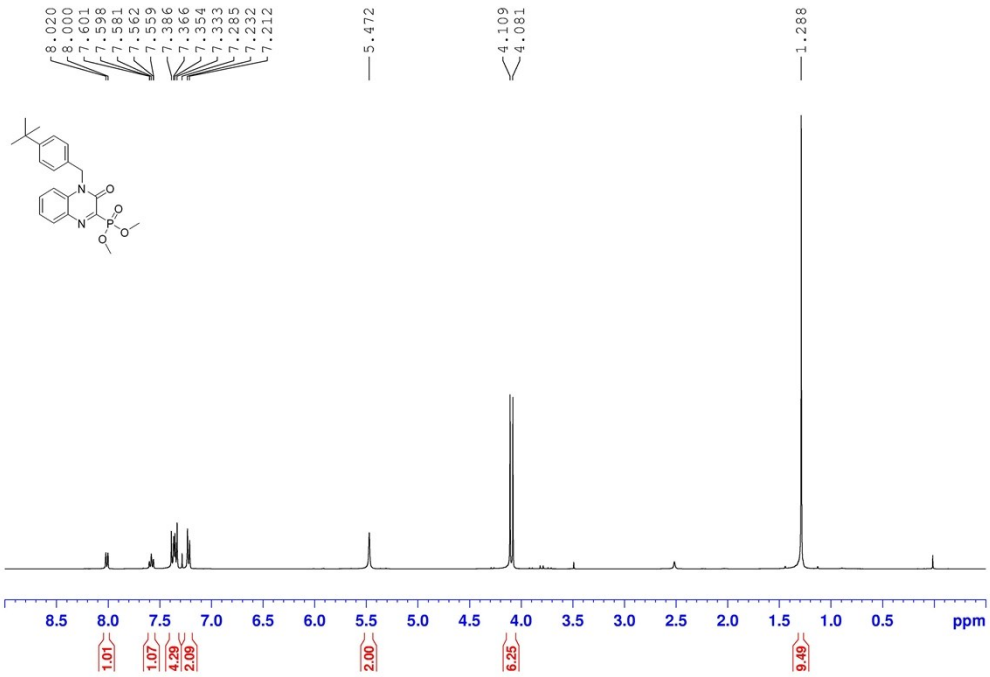
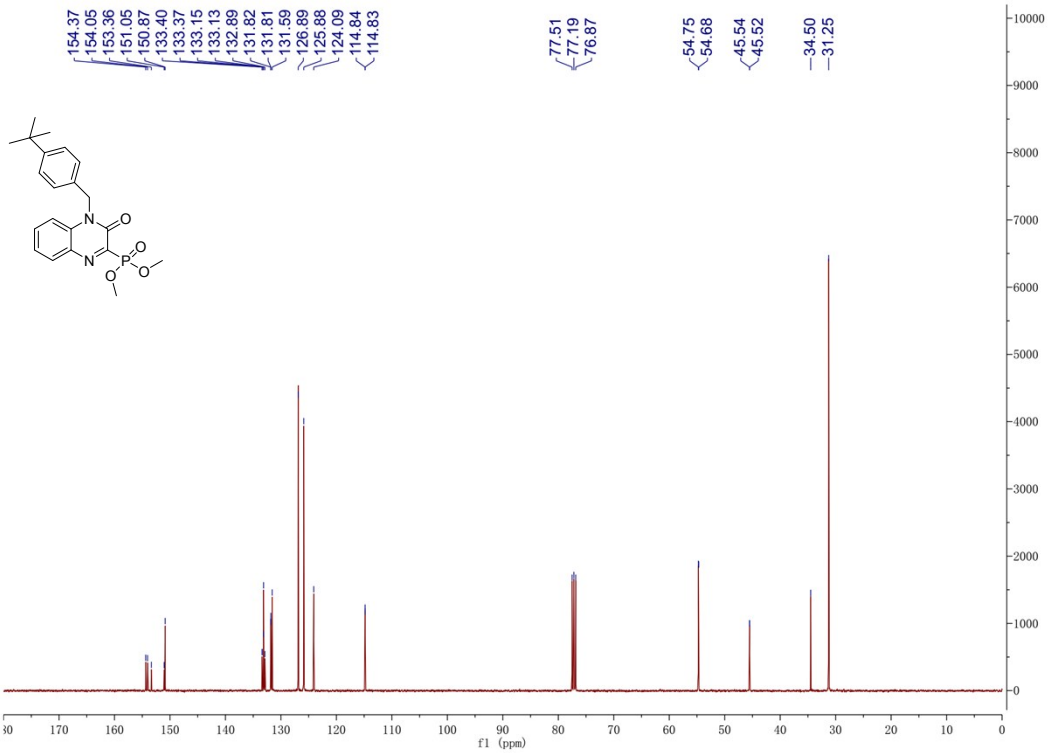


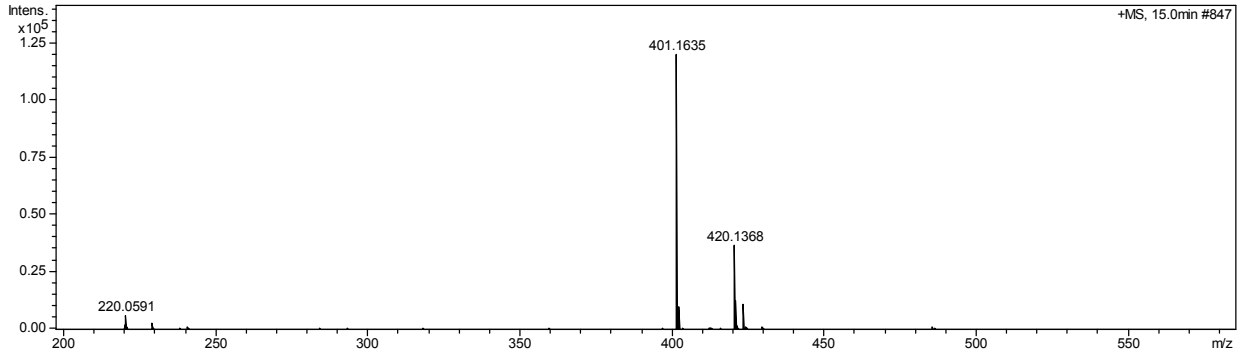
^{1}H NMR spectra of Dimethyl (4-(4-(tert-butyl)benzyl)-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3la)



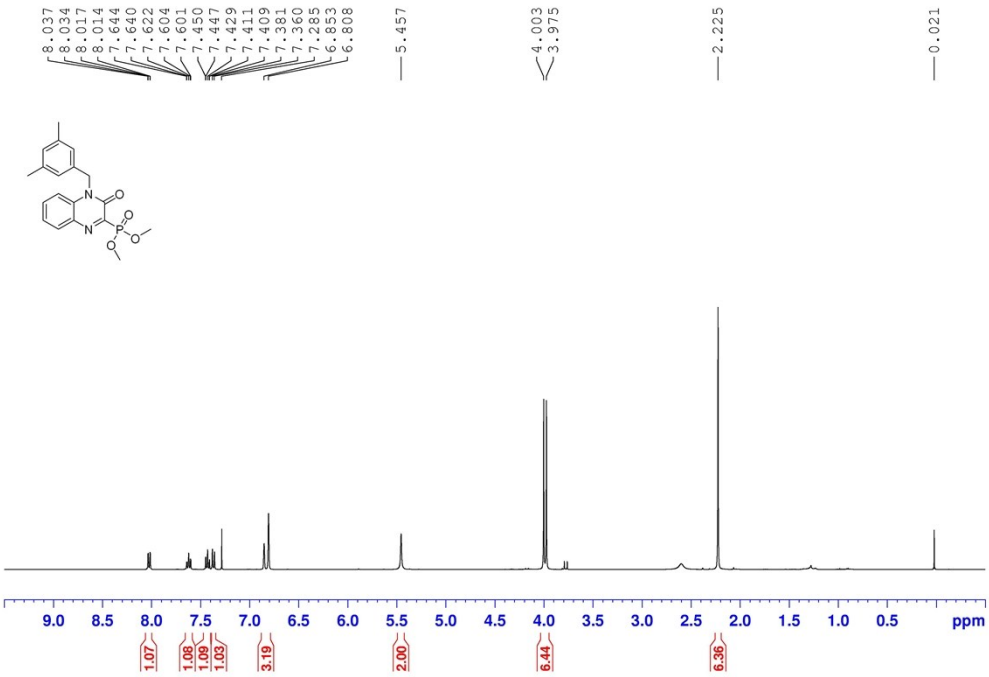
^{13}C NMR spectra of Dimethyl (4-(4-(tert-butyl)benzyl)-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3la)



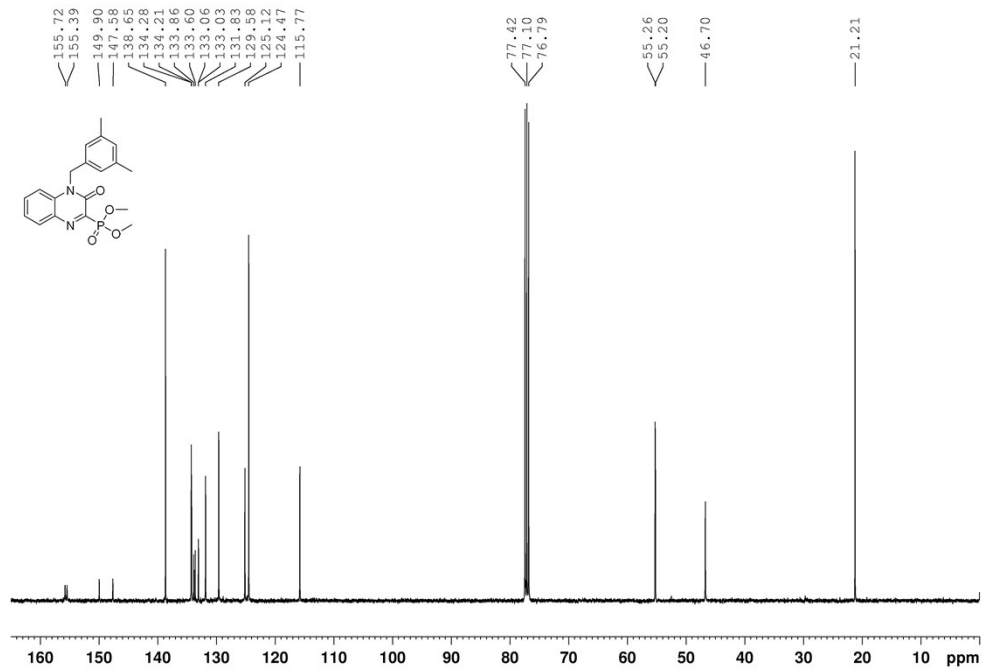
HRMS spectra of Dimethyl (4-(4-(tert-butyl)benzyl)-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3la)



^{1}H NMR spectra of Dimethyl (4-(3,5-dimethylbenzyl)-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3ma)



^{13}C NMR spectra of Dimethyl (4-(3,5-dimethylbenzyl)-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3ma)



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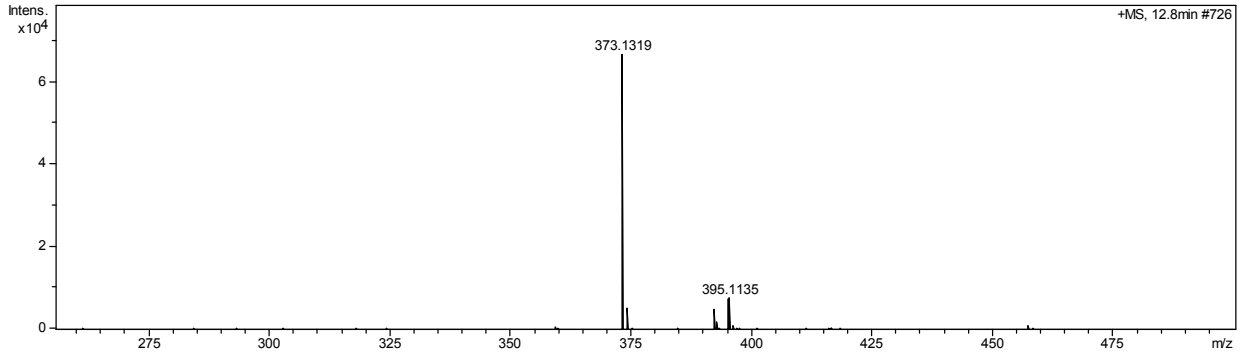
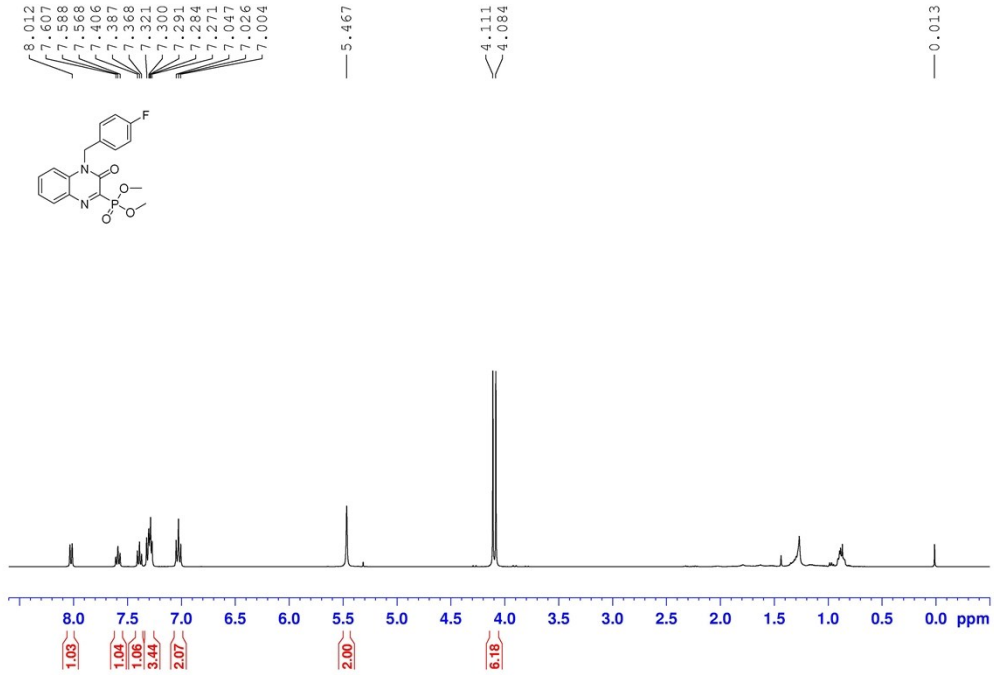
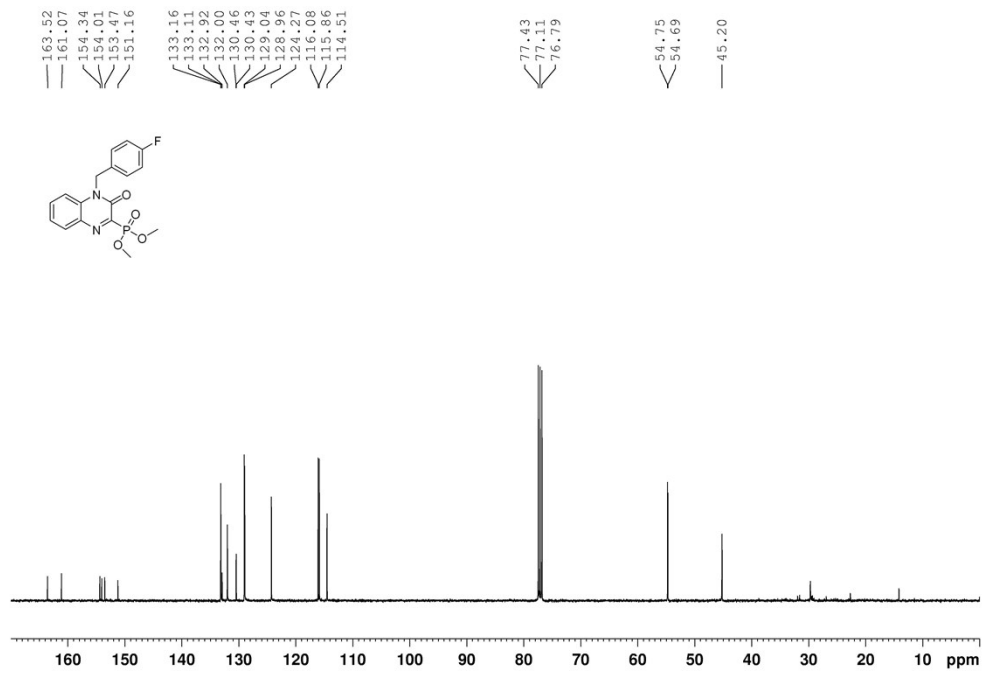


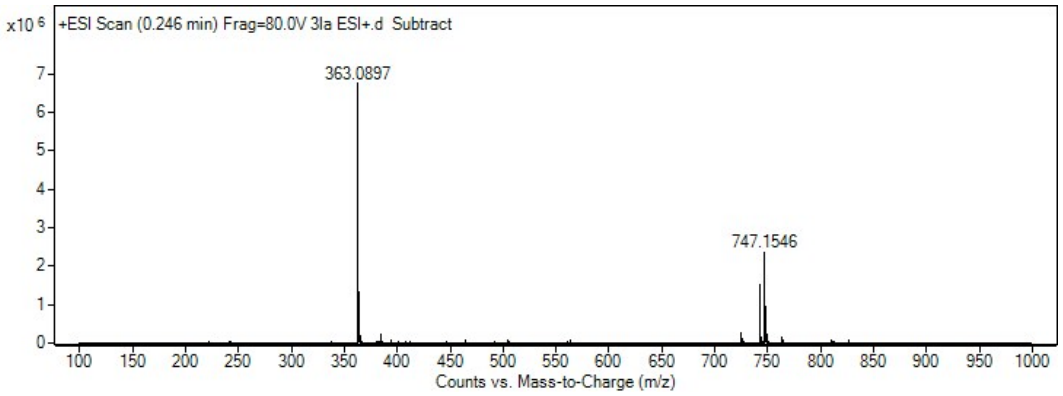
^{1}H NMR spectra of Dimethyl (4-(4-fluorobenzyl)-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3na)



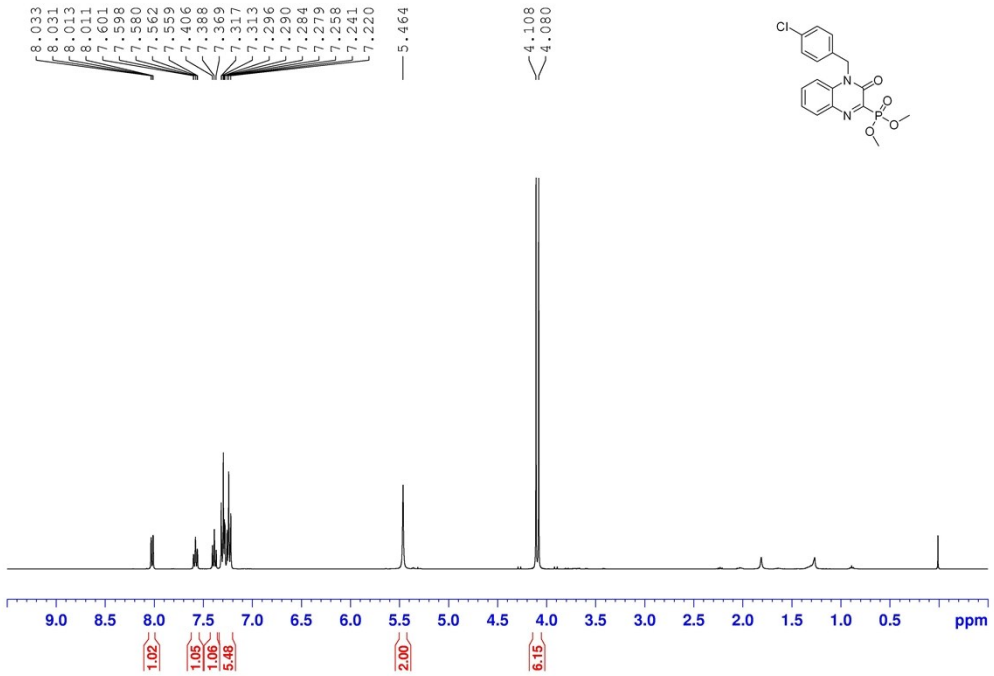
^{13}C NMR spectra of Dimethyl (4-(4-fluorobenzyl)-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3na)



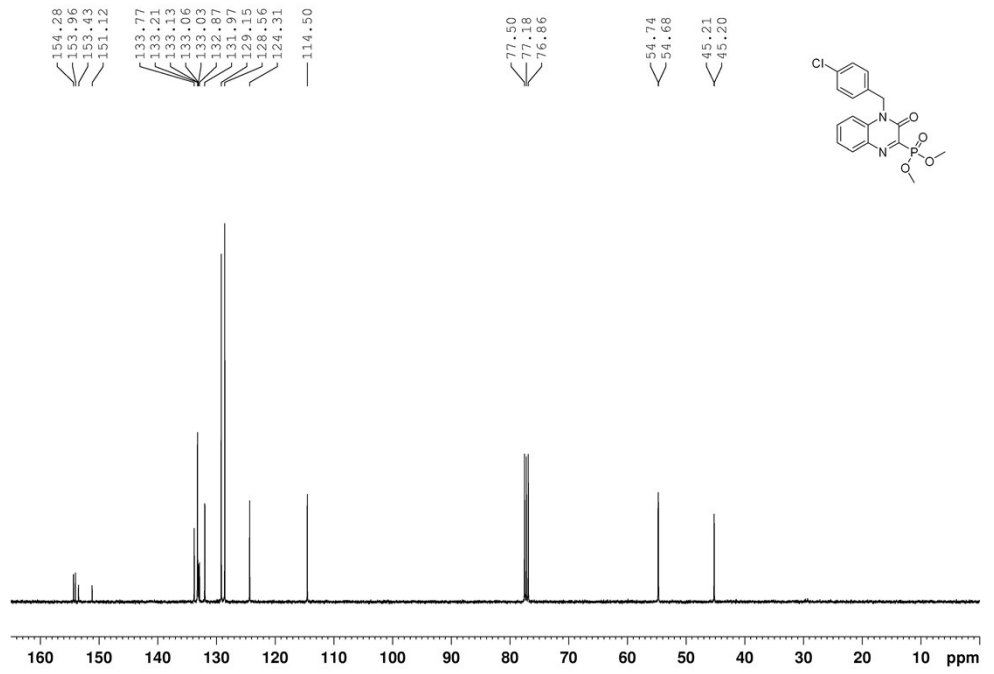
HRMS spectra of Dimethyl (4-(4-fluorobenzyl)-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3na)



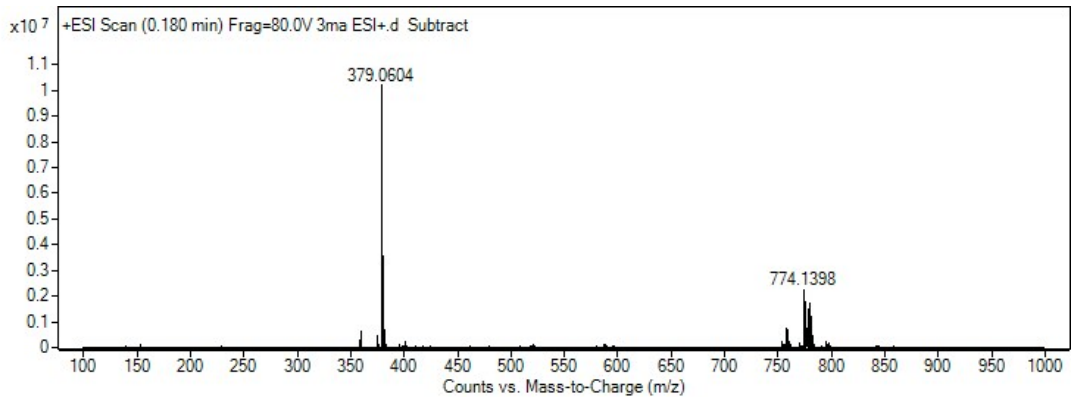
^{1}H NMR spectra of Dimethyl (4-(4-chlorobenzyl)-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3oa)



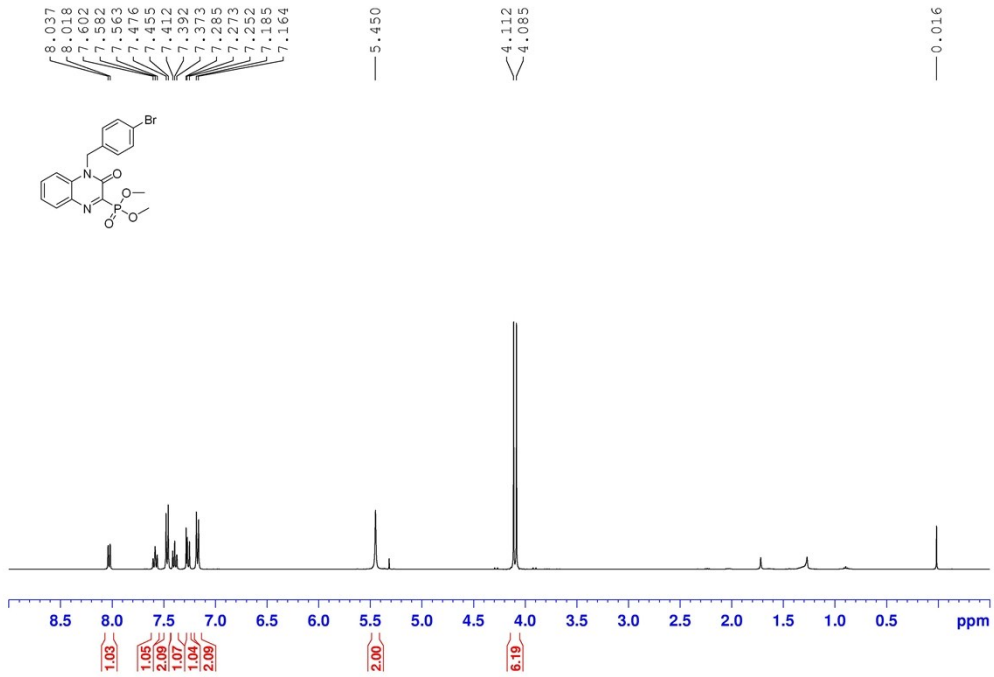
^{13}C NMR spectra of Dimethyl (4-(4-chlorobenzyl)-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3oa)



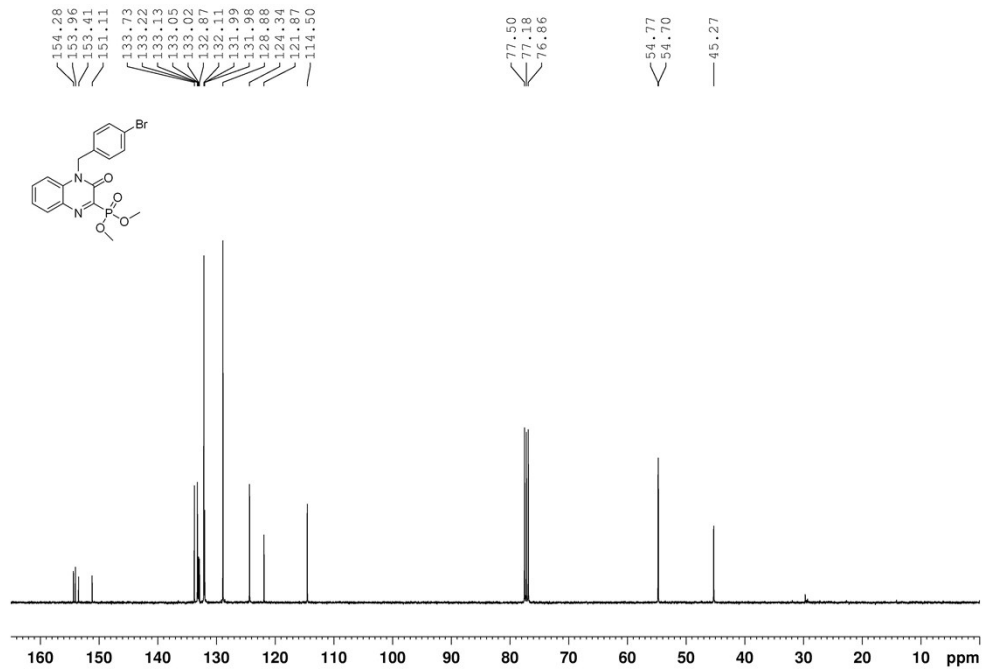
HRMS spectra of Dimethyl (4-(4-chlorobenzyl)-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3oa)



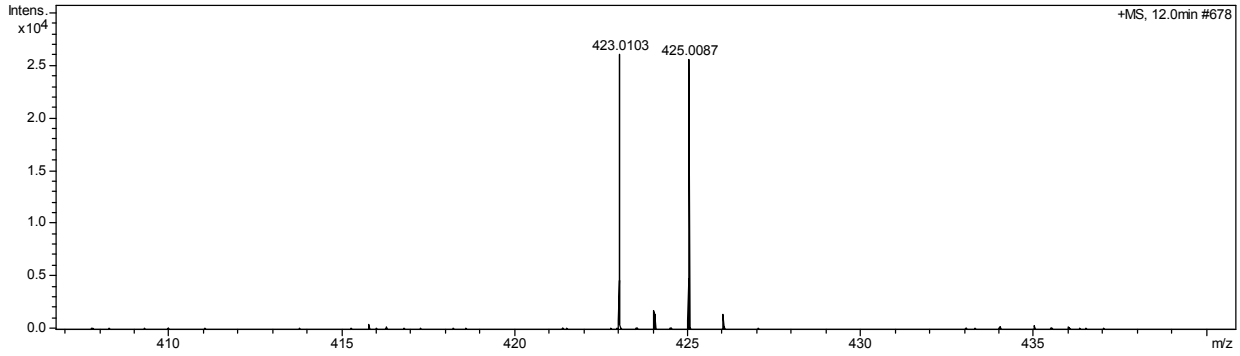
^{1}H NMR spectra of Dimethyl (4-(4-bromobenzyl)-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3pa)



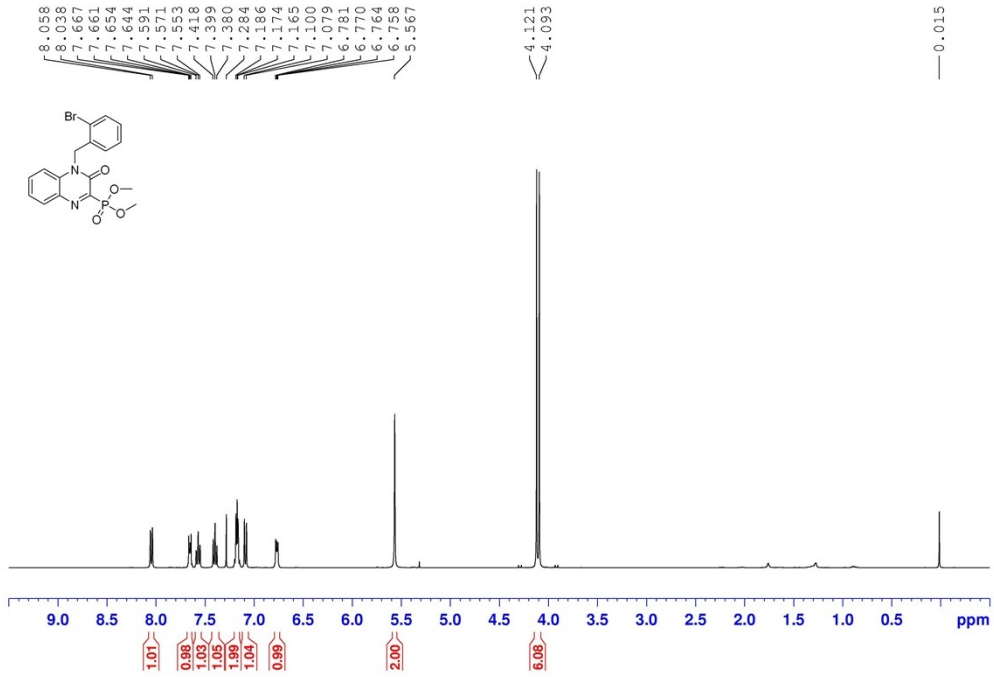
^{13}C NMR spectra of Dimethyl (4-(4-bromobenzyl)-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3pa)



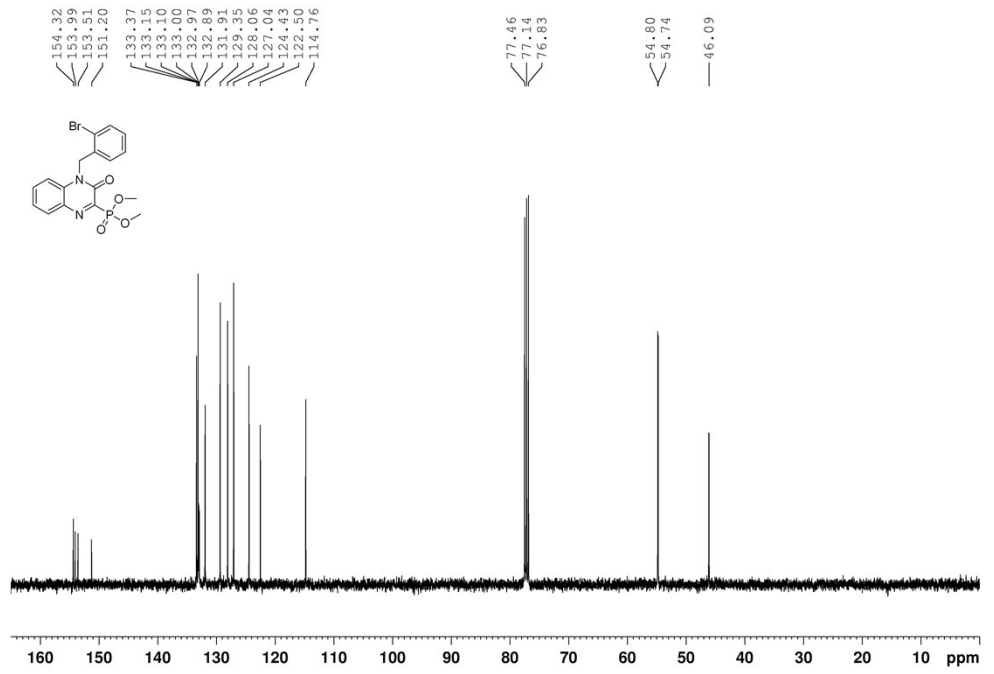
HRMS spectra of Dimethyl (4-(4-bromobenzyl)-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3pa)



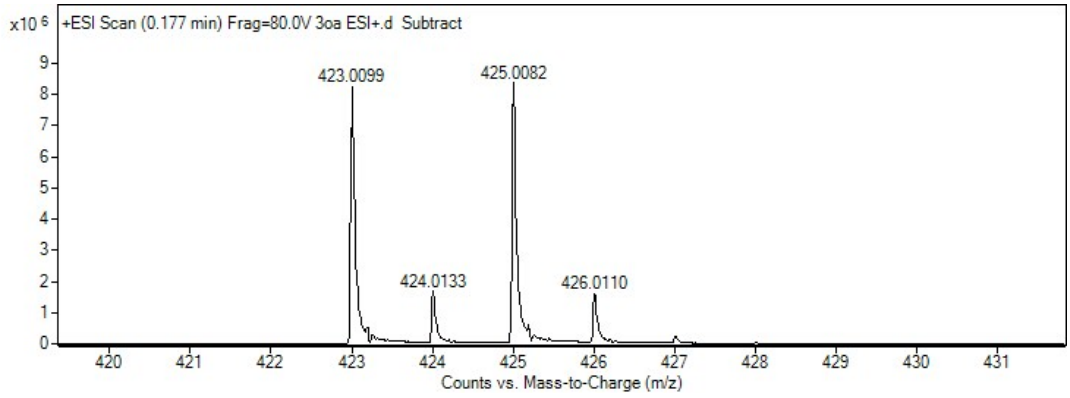
^{1}H NMR spectra of Dimethyl (4-(2-bromobenzyl)-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3qa)



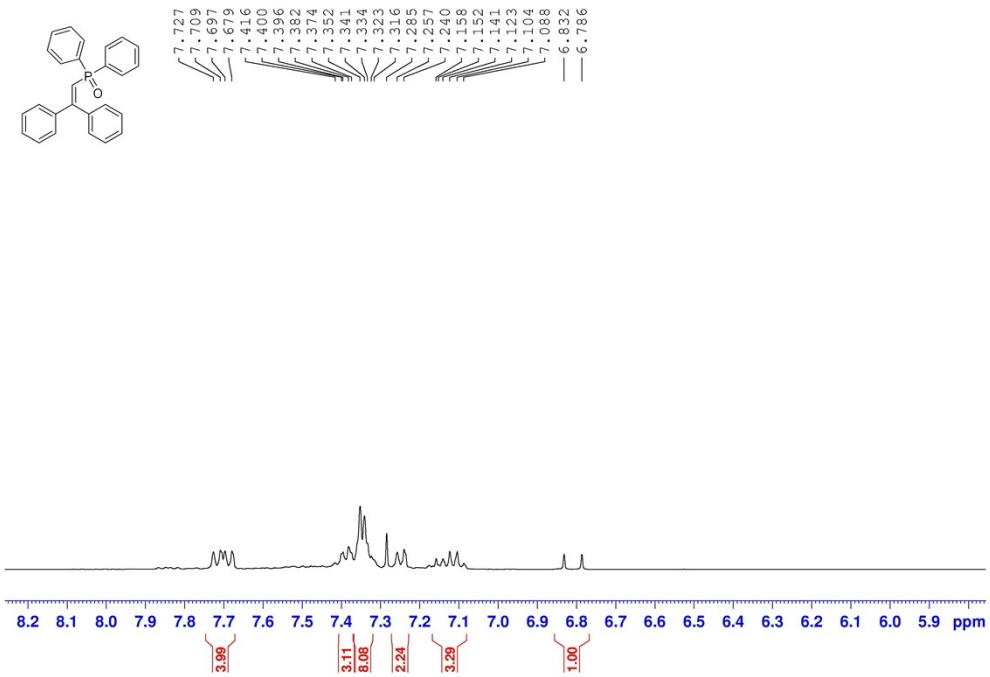
^{13}C NMR spectra of Dimethyl (4-(2-bromobenzyl)-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3qa)



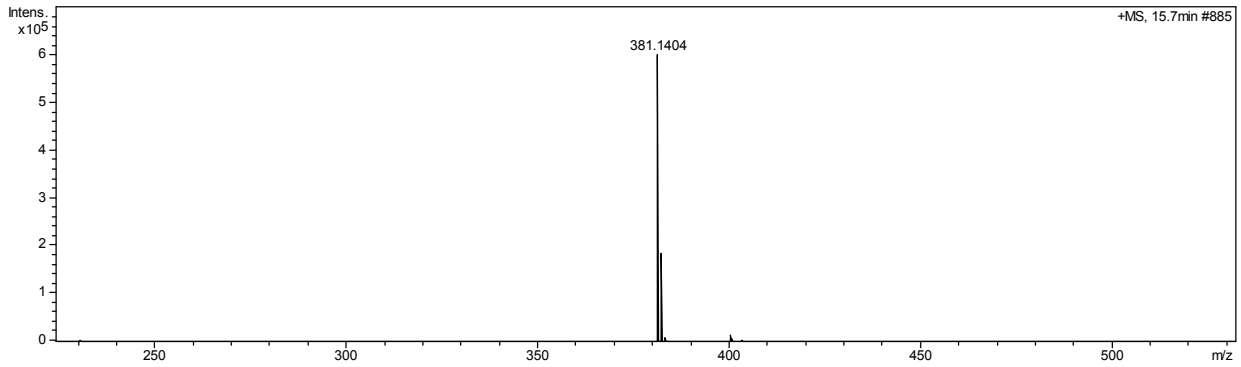
HRMS spectra of Dimethyl (4-(2-bromobenzyl)-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3qa)



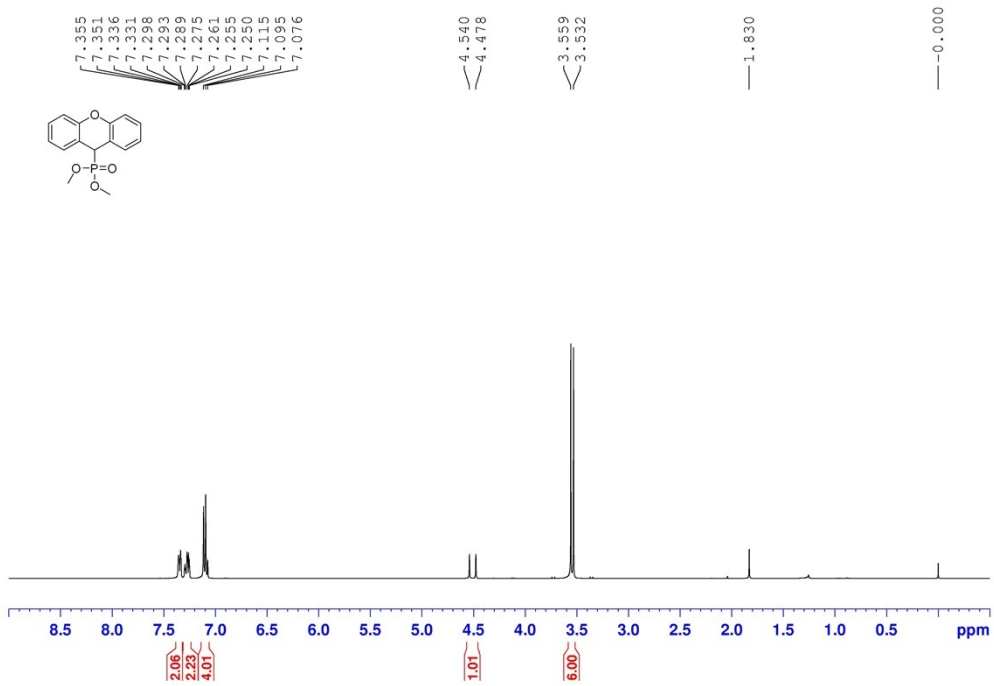
^{1}H NMR spectra of (2,2-diphenylvinyl)diphenylphosphine oxide (3ra)



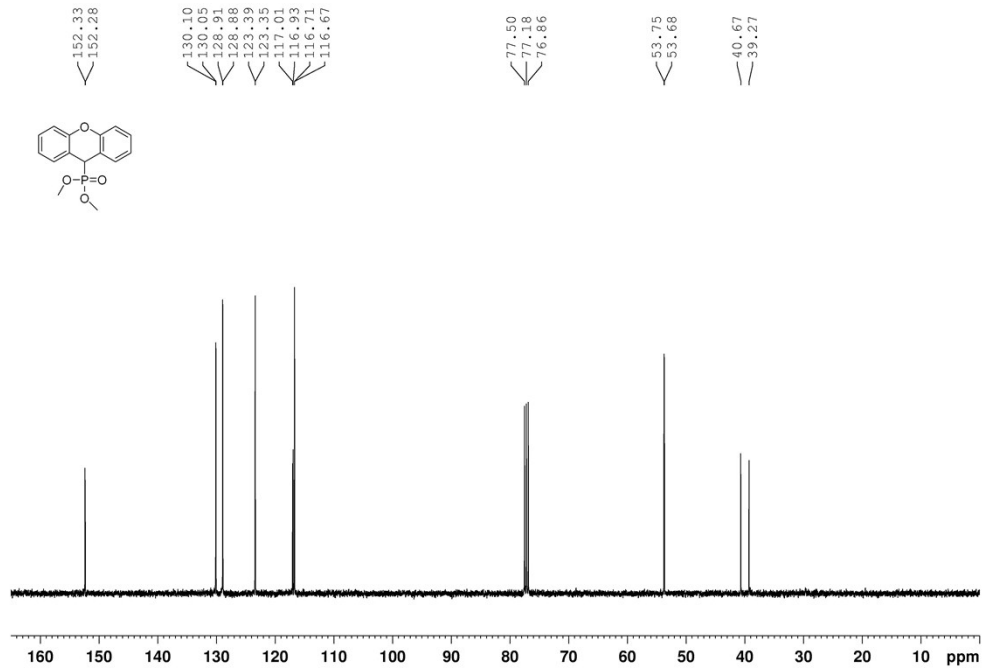
HRMS spectra of (2,2-diphenylvinyl)diphenylphosphine oxide (3ra)



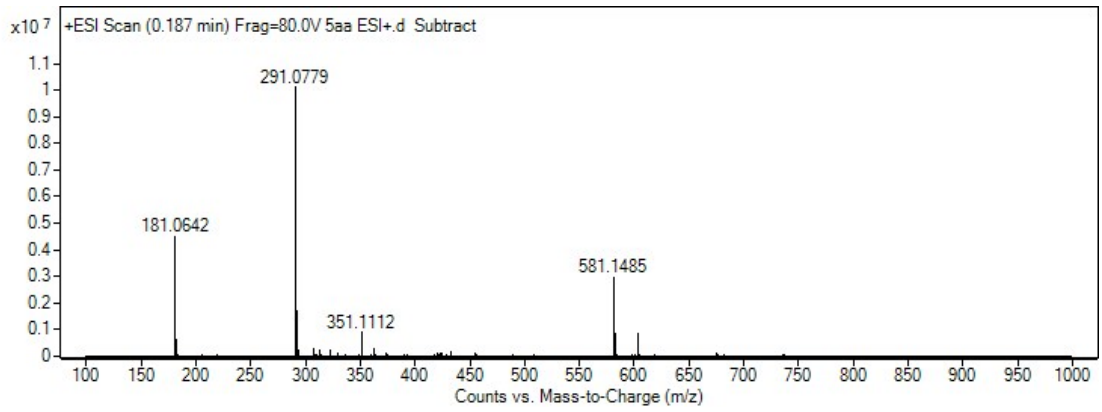
^{1}H NMR spectra of Dimethyl (9H-xanthen-9-yl)phosphonate (3sa)



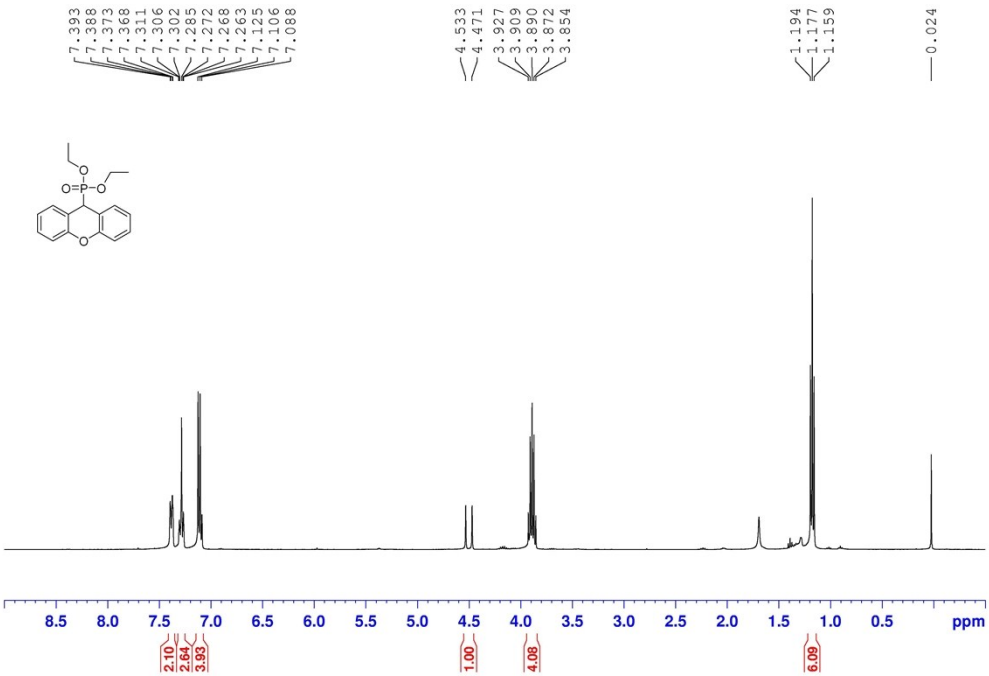
^{13}C NMR spectra of Dimethyl (9H-xanthen-9-yl)phosphonate (3sa)



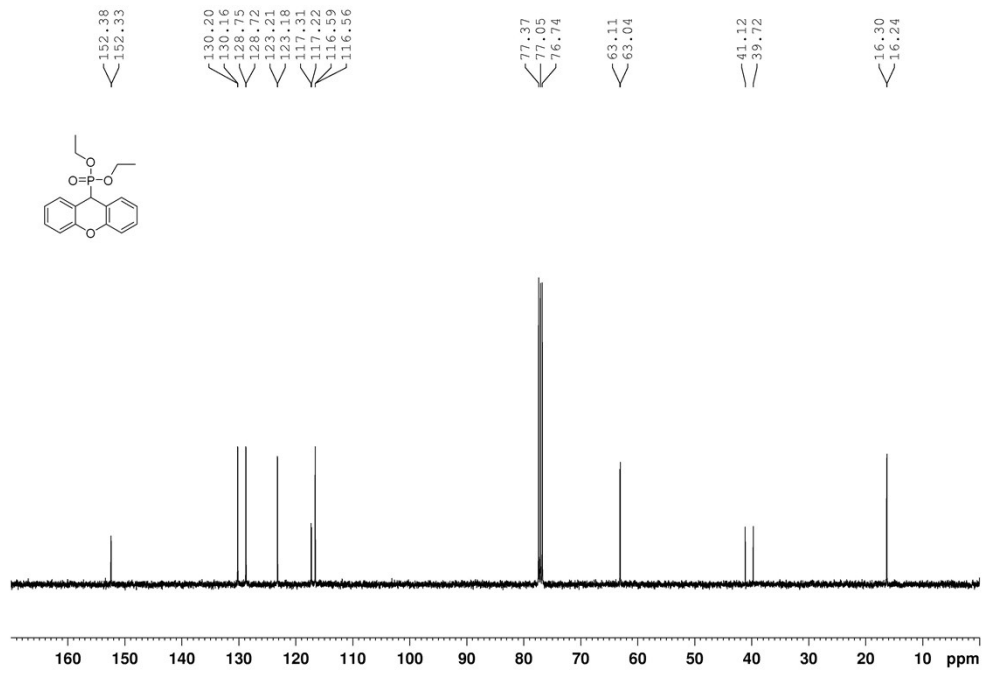
HRMS spectra of (2,2-diphenylvinyl)diphenylphosphine oxide (3ra)



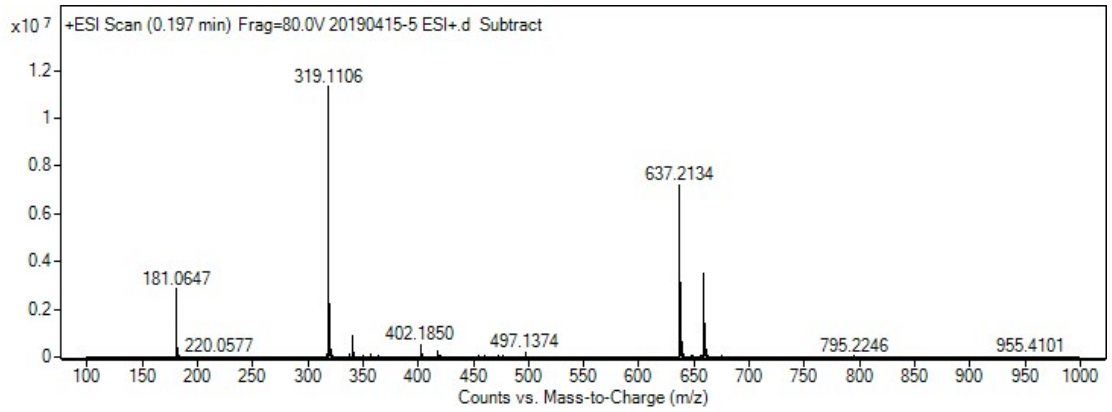
^{1}H NMR spectra of Diethyl (9H-xanthen-9-yl)phosphonate (3ta)



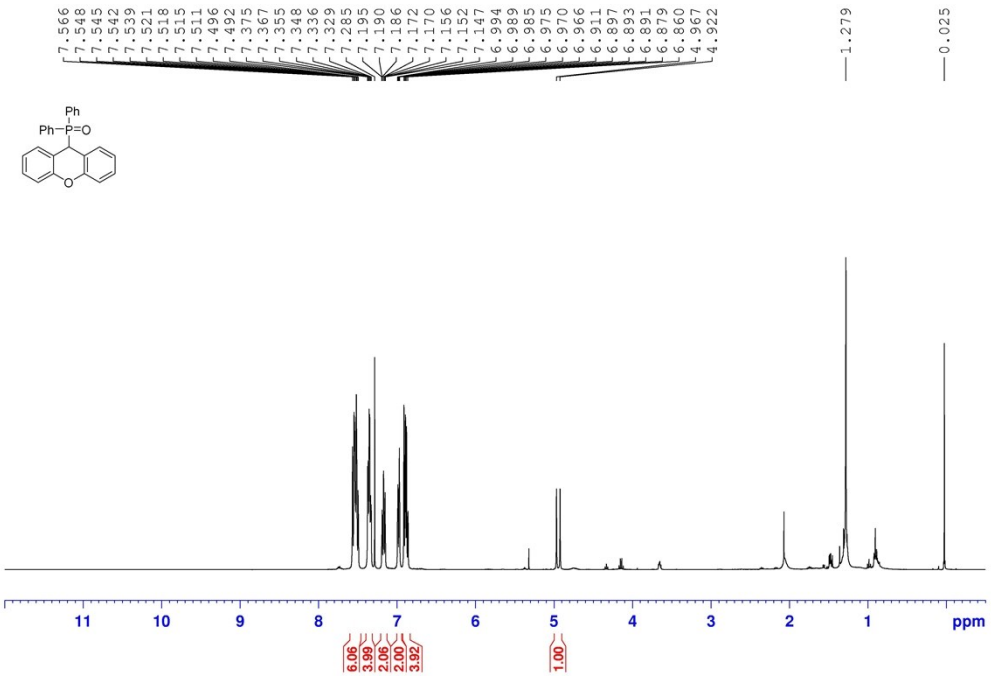
^{1}H NMR spectra of Diethyl (9H-xanthen-9-yl)phosphonate (3ta)



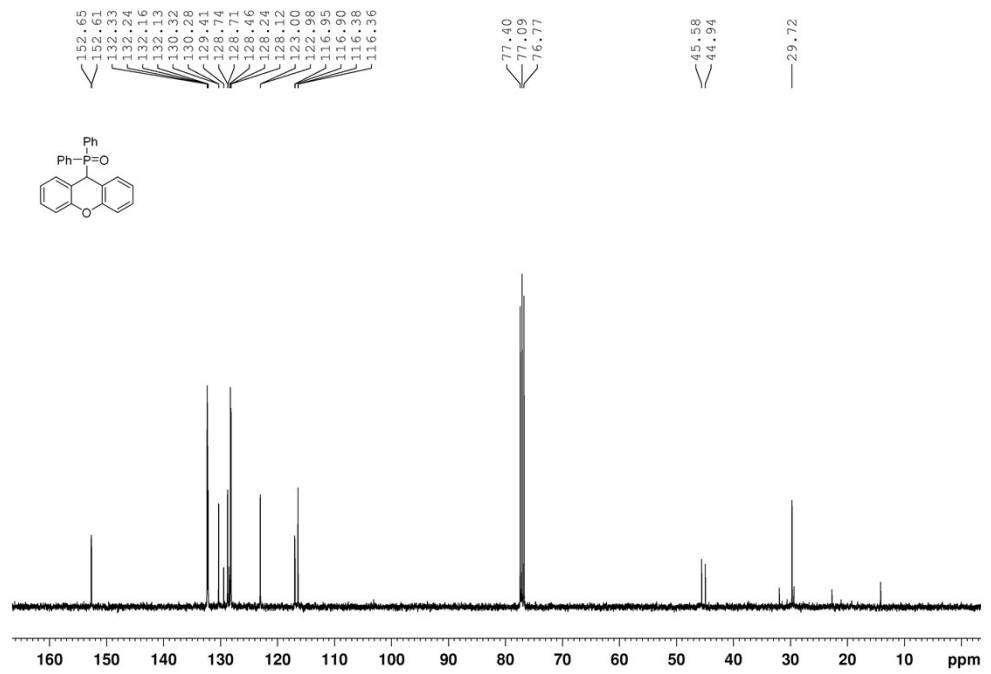
HRMS spectra of Diethyl (9H-xanthen-9-yl)phosphonate (3ta)



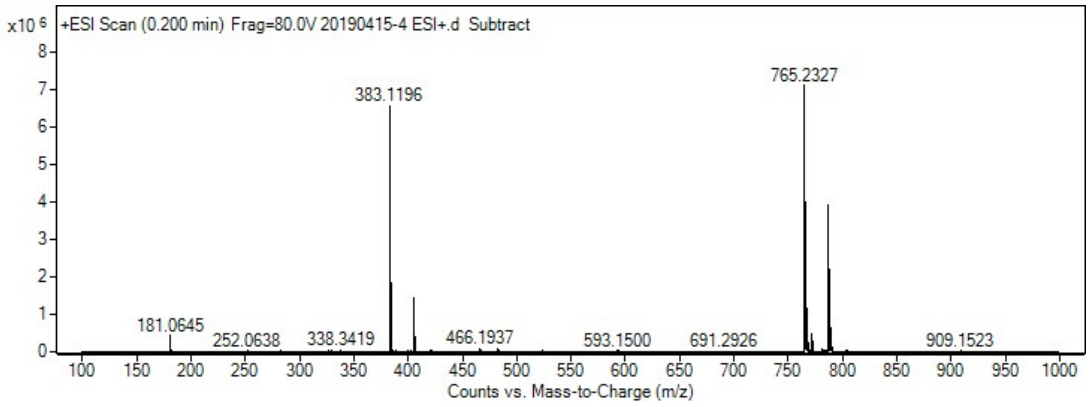
^{1}H NMR spectra of Diphenyl(9H-xanthen-9-yl)phosphine oxide (3ua)



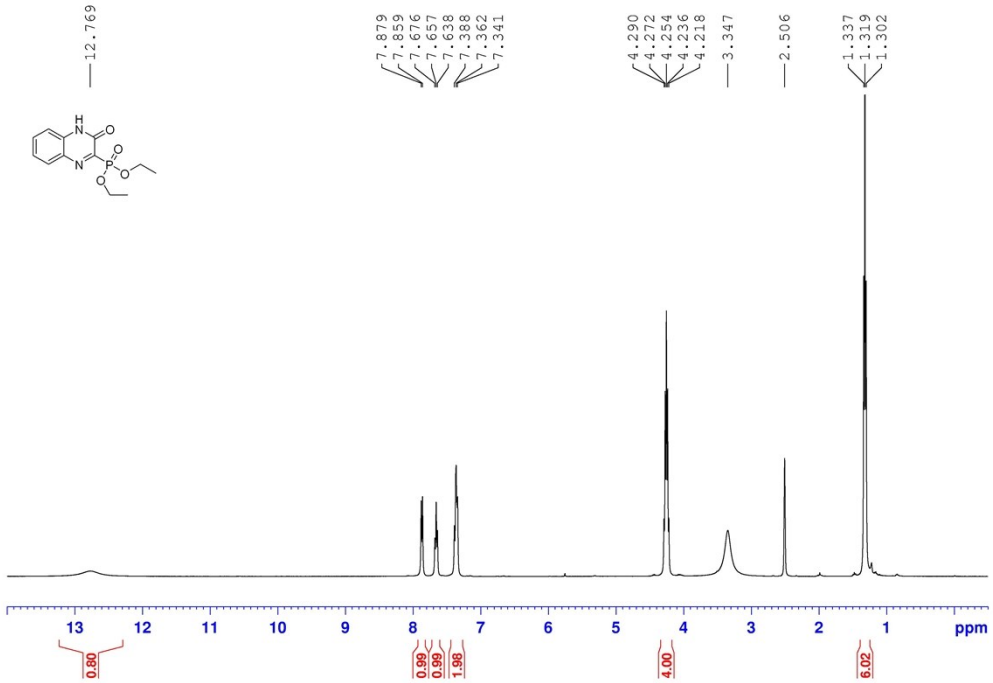
^{13}C NMR spectra of Diphenyl(9H-xanthen-9-yl)phosphine oxide (3ua)



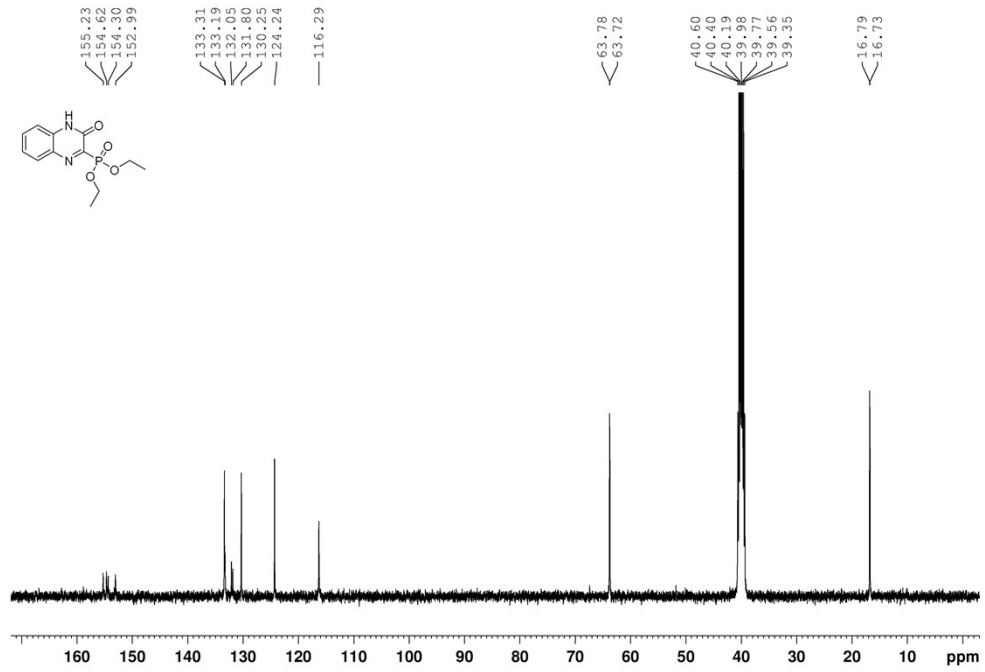
HRMS spectra of Diphenyl(9H-xanthen-9-yl)phosphine oxide (3ua)



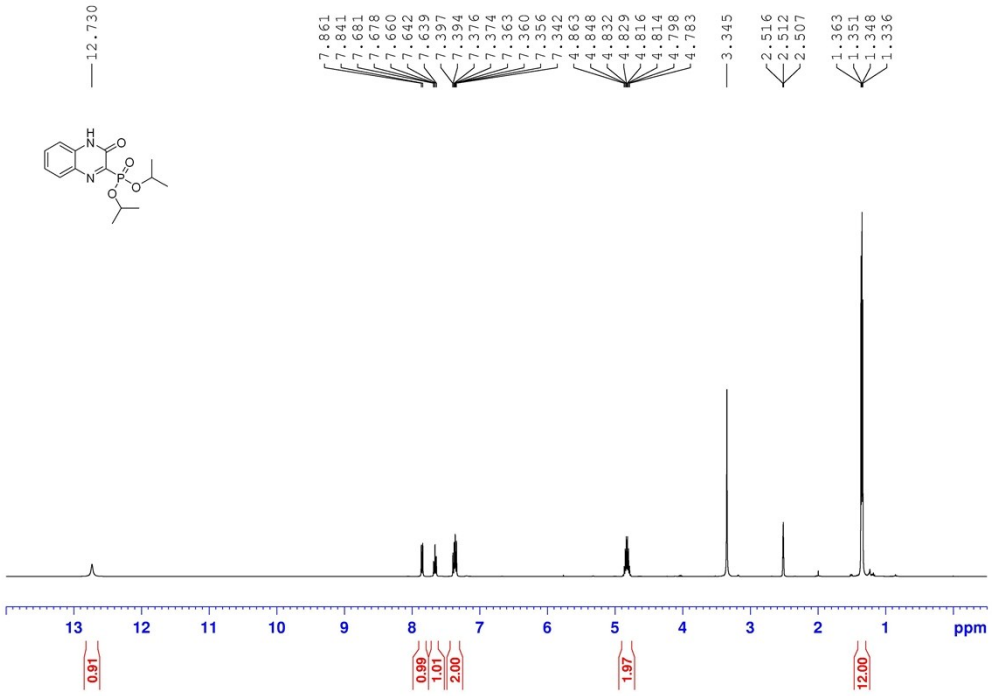
^{1}H NMR spectra of diethyl (3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3ab)[2]



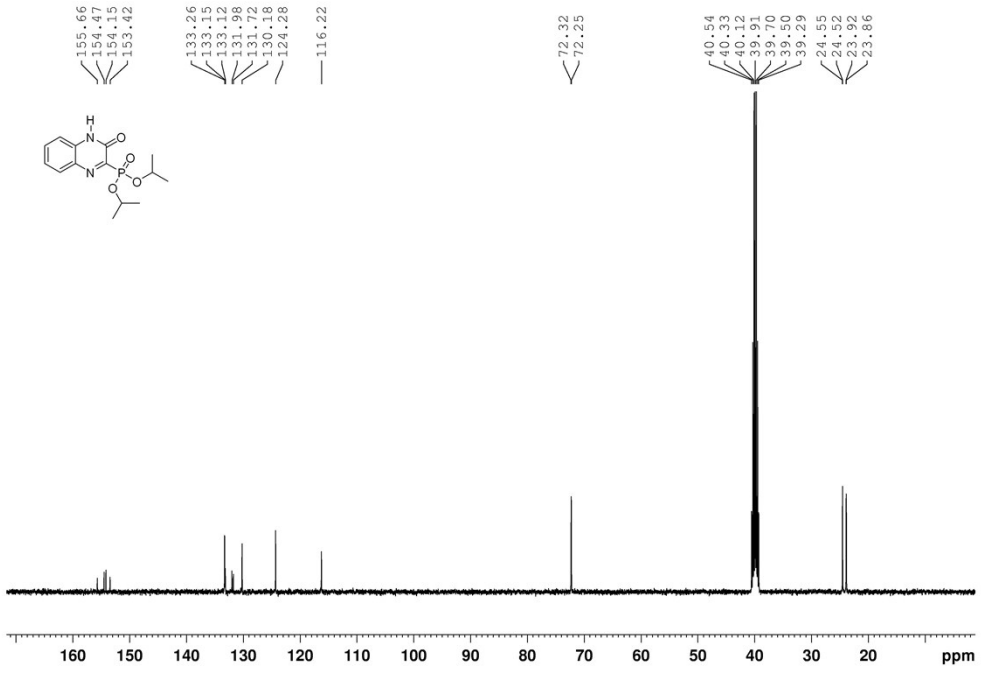
^{13}C NMR spectra of diethyl (3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3ab)[2]



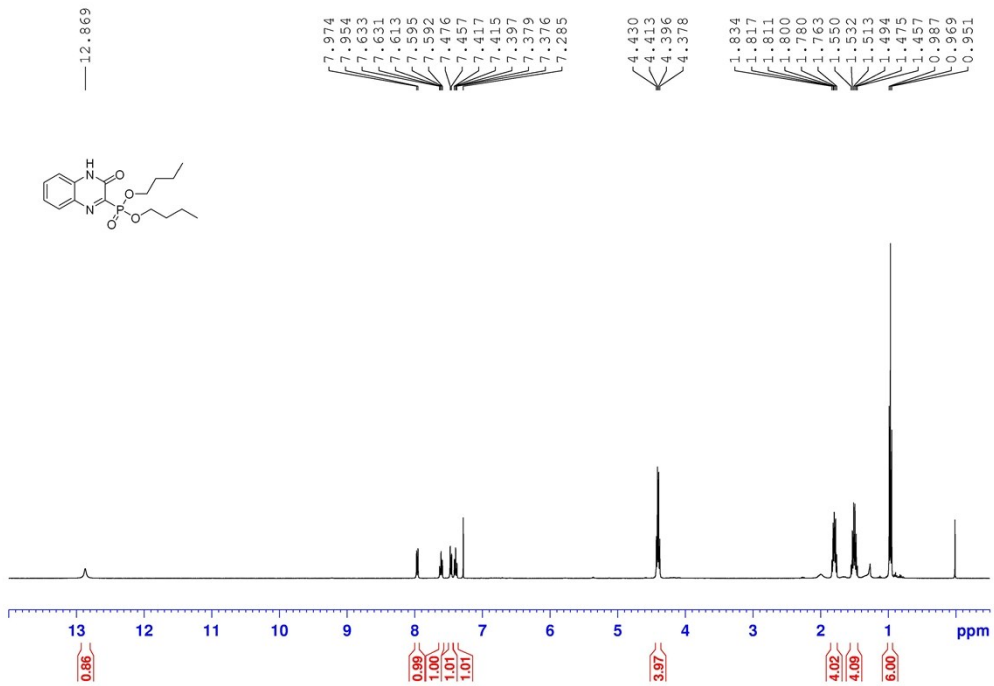
^{1}H NMR spectra of diisopropyl (3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3ac)[2]



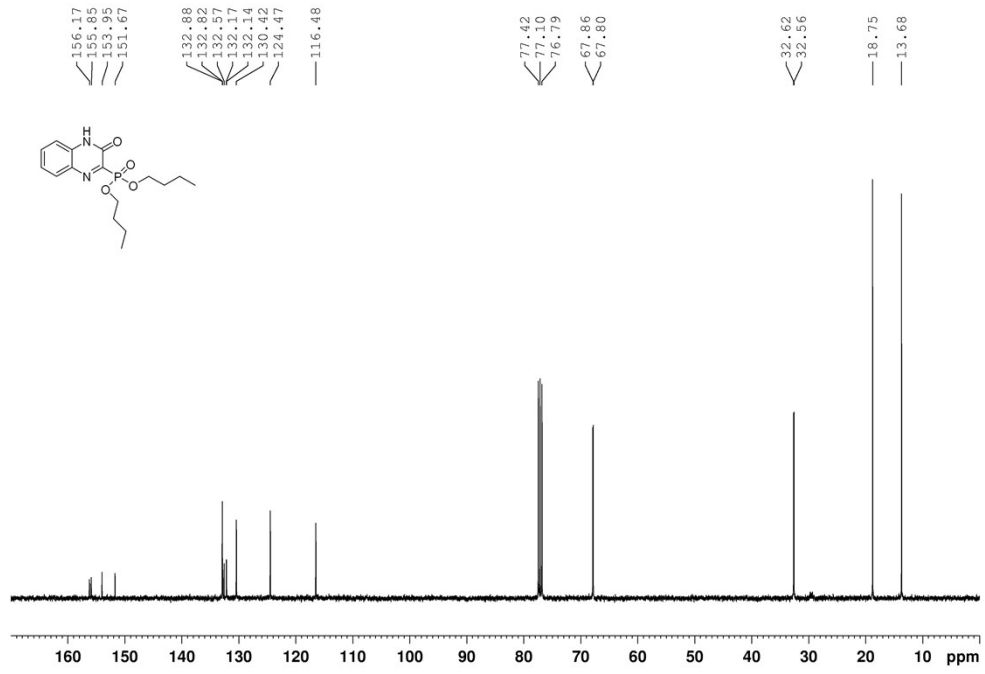
^{13}C NMR spectra of diisopropyl (3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3ac)[2]



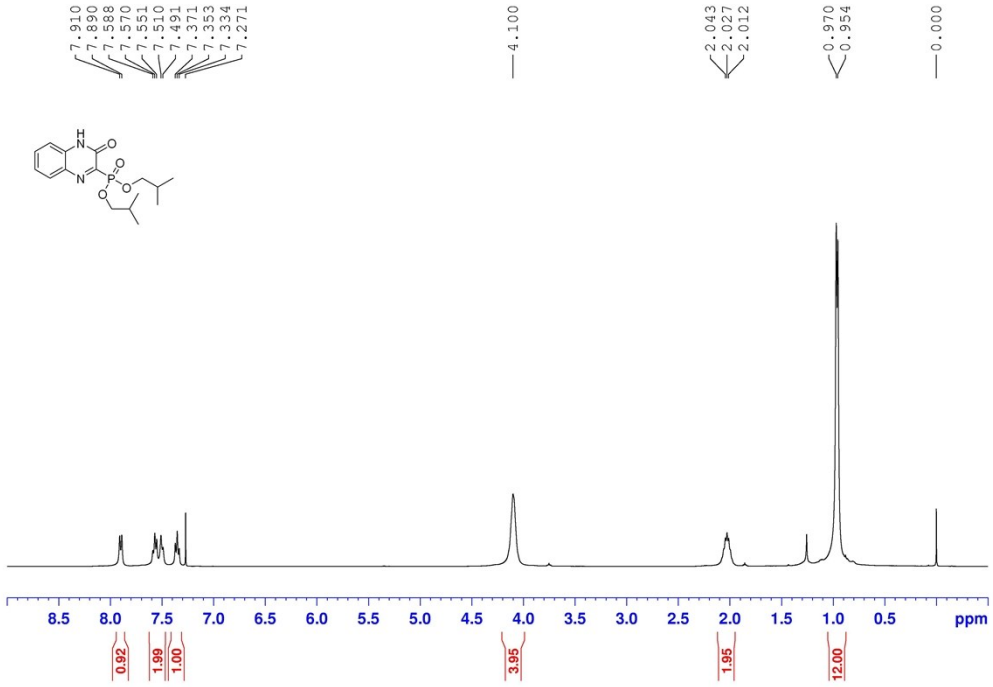
^{1}H NMR spectra of Dibutyl (3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3ad)[2]



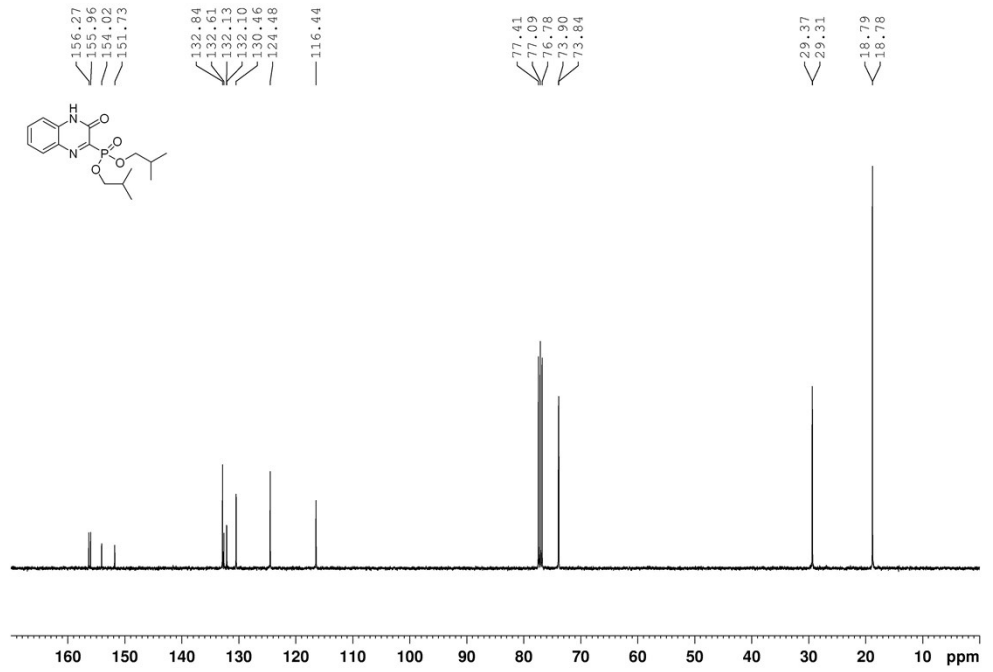
^{13}C NMR spectra of Dibutyl (3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3ad)[2]



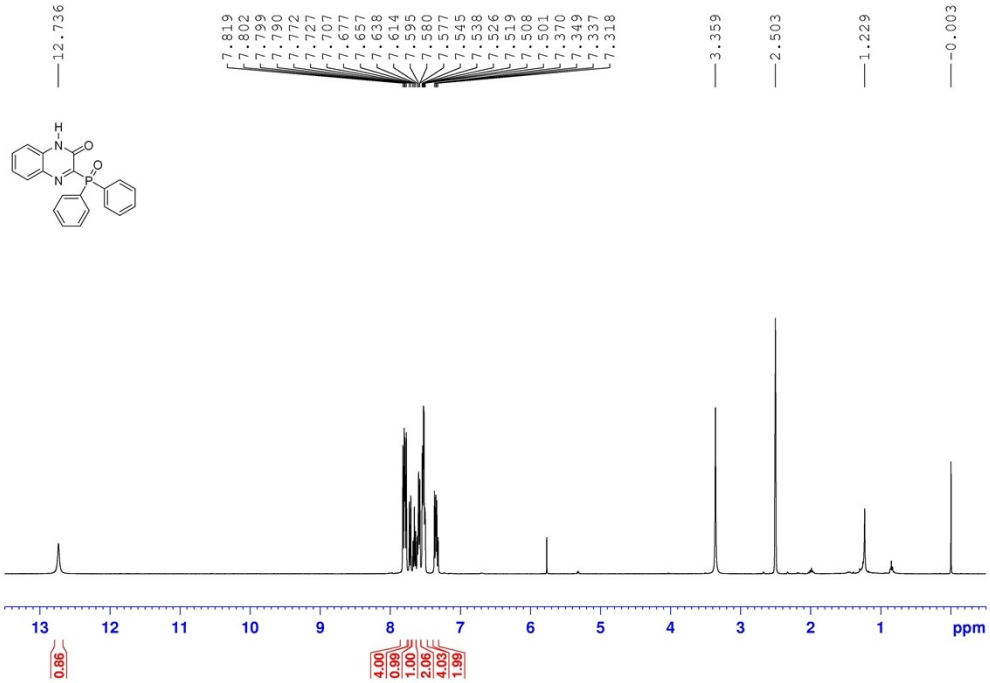
^{1}H NMR spectra of Diisobutyl (3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3ae)[2]



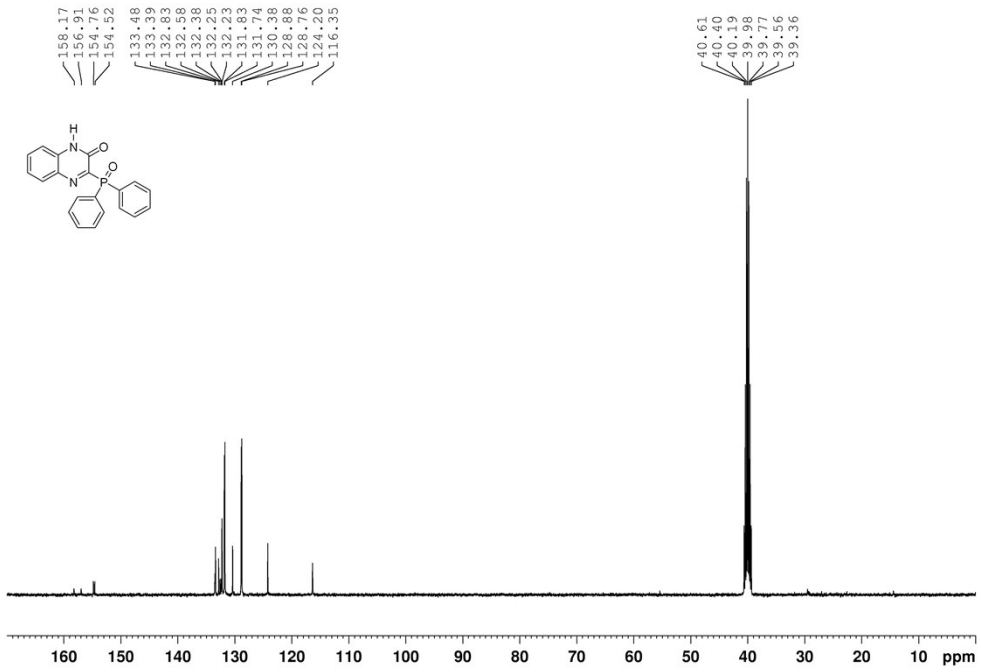
^{13}C NMR spectra of Diisobutyl (3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3ae)[2]



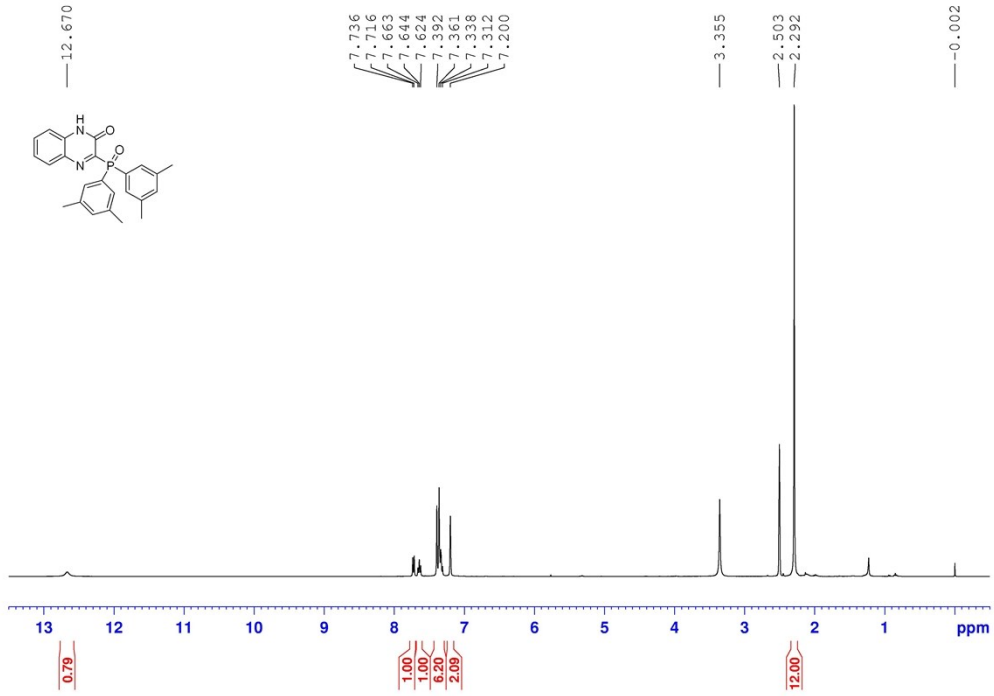
^{1}H NMR spectra of 3-(diphenylphosphoryl)quinoxalin-2(1H)-one (3af)[2]



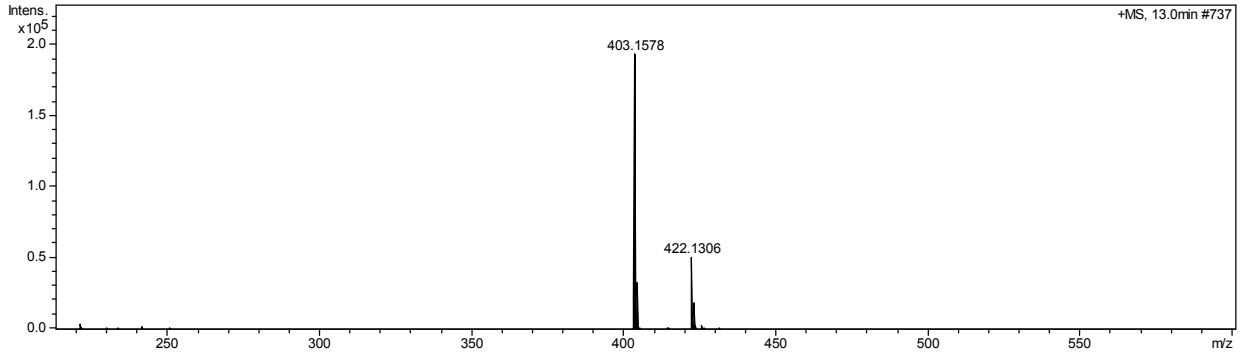
^{13}C NMR spectra of 3-(diphenylphosphoryl)quinoxalin-2(1H)-one (3af)[2]



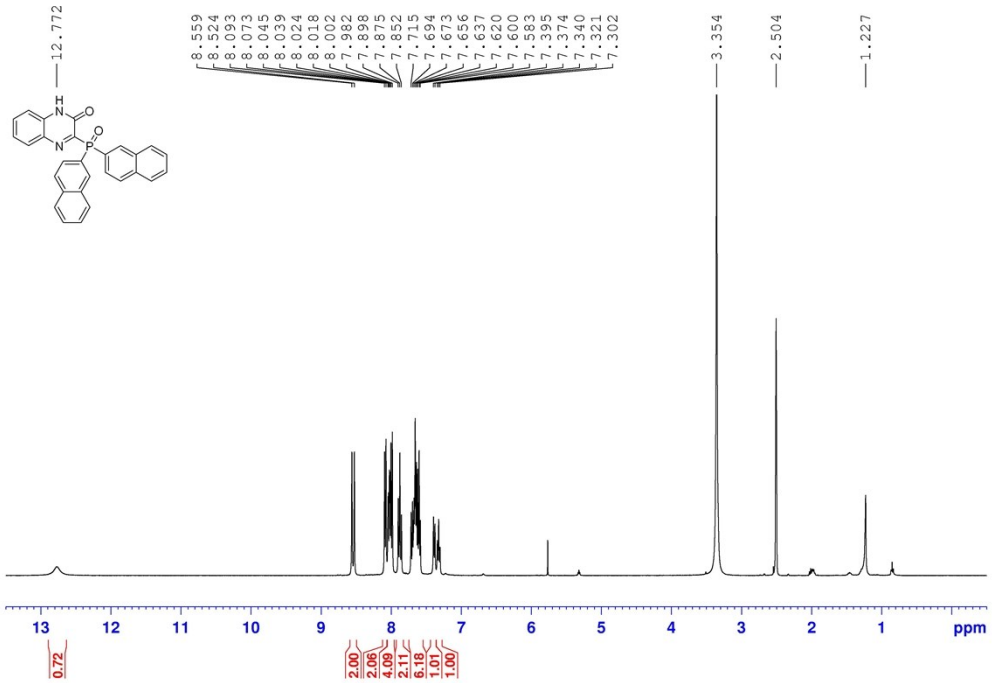
^{1}H NMR spectra of 3-(bis(3,5-dimethylphenyl)phosphoryl)quinoxalin-2(1*H*)-one (3ag)



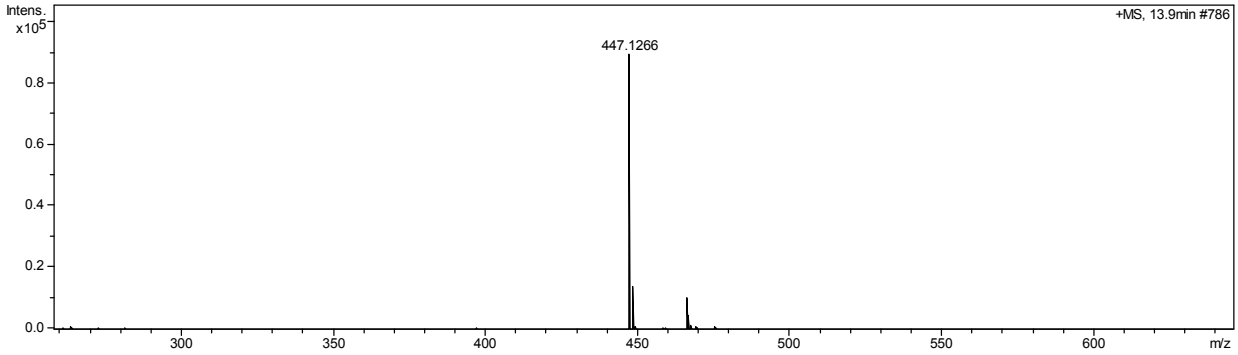
HRMS spectra of 3-(bis(3,5-dimethylphenyl)phosphoryl)quinoxalin-2(1*H*)-one (3ag)



^{1}H NMR spectra of 3-(di(naphthalen-2-yl)phosphoryl)quinoxalin-2(1H)-one (3ah)



HRMS spectra of 3-(di(naphthalen-2-yl)phosphoryl)quinoxalin-2(1H)-one (3ah)



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1. M. Gao, Y. Li, L. J. Xie, R. Chauvinabc, X. L. Cui, *Chem. Commun*., 2016, **52,** 2846.
2. L. Sumunnee, C. Pimpasri, M. Noikham, S. Yotphan, *Org. Biomol. Chem.*, 2018, **16**, 2697.