Denitrogenative Dismantling of Heteroaromatics by Nucleophilic Substitution Reactions with Diazomethyl Compounds

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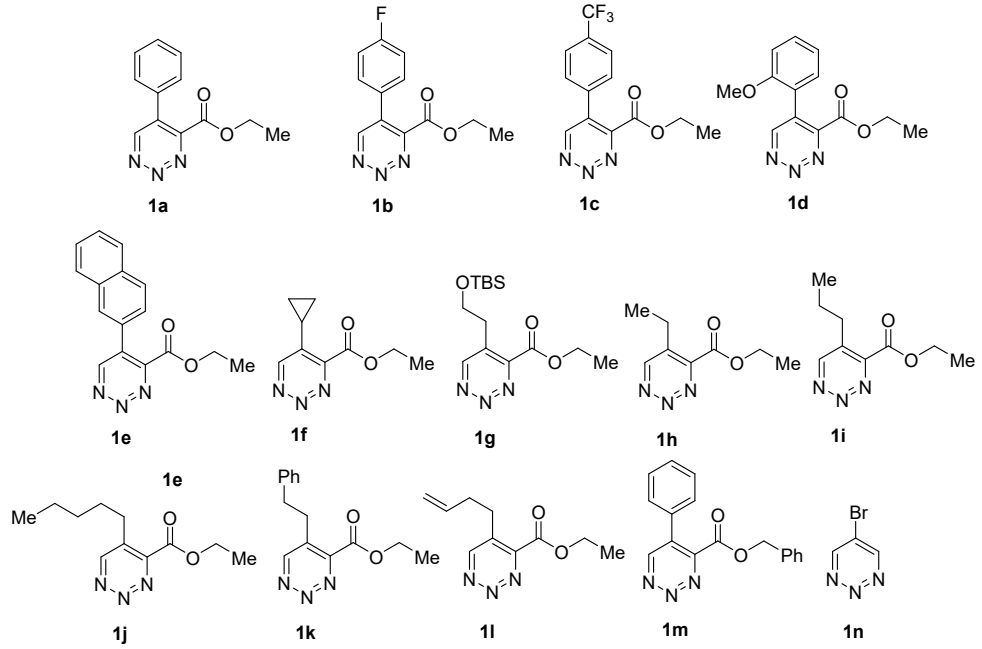
1. General conditions

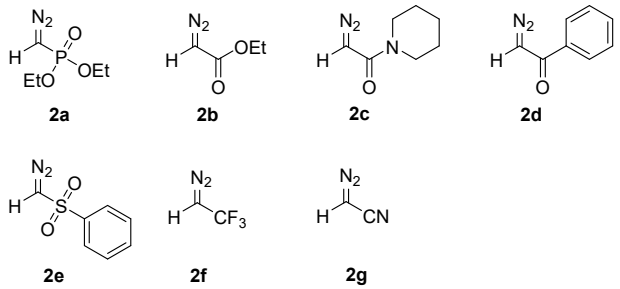
All reactions, unless noted, were performed in oven-dried (150 °C) glassware with magnetic stirring under an atmosphere of air. Analytical thin layer chromatography (TLC) was carried out using EM Science silica gel 60 F254 plates; visualization was accomplished with UV light (254 nm). Column chromatography was performed on CombiFlash® Rf200 and Rf+ purification systems using normal phase disposable columns. NMR spectra were recorded on a on a Bruker spectrometer (500 MHz and 300 MHz) and calibrated using the resonance signal of the residual undeuterated solvent for ^{1}H-NMR [δ_H = 7.26 ppm ($CDCl_3$)] and deuterated solvent for ^{13}C-NMR [δ_C = 77.16 ($CDCl_3$)] as an internal reference at 298 K. Spectra were reported as follows: chemical shift (δ ppm), multiplicity (Mi), coupling constants (Hz), integration and assignment. The peak information was described as: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, m = multiplet, and comp = composite of magnetically non-equivalent protons. ^{13}C-NMR spectra were collected on Bruker instruments (126 MHz and 75 MHz) with complete proton decoupling. High-resolution mass spectra (HRMS) were performed on a Bruker MicroTOFESI mass spectrometer with an ESI resource using CsI or LTQ ESI positive ion calibration solution as the standard. Tetrahydrofuran, dichloromethane, chloroform, and toluene were purified using a JC-Meyer solvent purification system.

Materials: $CsCO_3$, CsOH, CsOAc, ^{t}BuOK, K_2CO_3, DBU (1,8-Diazabicyclo[5.4.0]undec-7-ene) DABCO (1,4-diazabicyclo[2.2.2]octane), DMAP were purchased from Sigma Aldrich, TCI, and Alfa Aesar, and they were used without further purification. All diazomethyl derivatives,[1] triazine 1-oxides,[2,3] and triazine[4] were prepared using literature reported procedures.

1,2,3-triazine used in the manuscript.



Diazomethyl compounds used in the manuscript.



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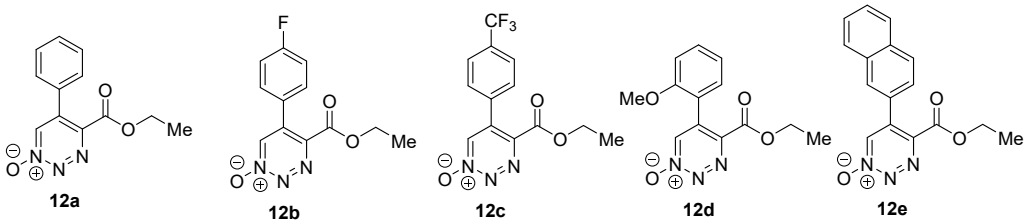
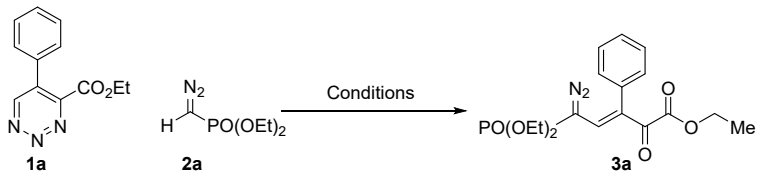


2. Optimization of reaction conditions

Table S1. Study of reaction conditions for diethyl diazomethylphosphonate 2a with ethyl 5-phenyl-1,2,3-triazine-4-carboxylate[a]

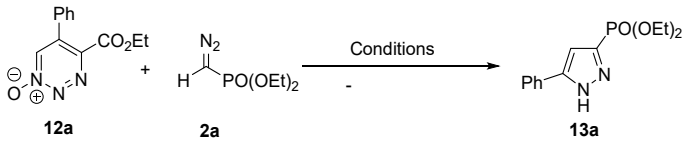


1a 2a 3a

Entry	Conditions	Base (2.0 equiv.)	Yield of **3a** (%)[b]
1	ACN, rt, 2 h	Cs_2CO_3	84 (82)
2	ACN, rt, 4 h	CsOH	66
3	ACN, rt, 6 h	K_2CO_3	32
4	ACN, rt, 4 h	^{t}BuOK	68
5	ACN, rt, 6 h	DABCO	25
6	ACN, rt, 6 h	DBU	38
7	ACN, rt, 6 h	DMAP	30
8[c]	ACN, rt, 12 h	Et_3N	trace
9	THF, rt, 2 h	Cs_2CO_3	71

[a]Reaction conditions: Base was added to a 1.0 mL solution of **1a** (0.1 mmol) and ethyl diazophosphonate **2a** (0.12 mmol) at room temperature and then H_2O was added to quench the reaction. [b]NMR yields. Isolated yield in parenthesis. [c]88% of **1a** was recovered.

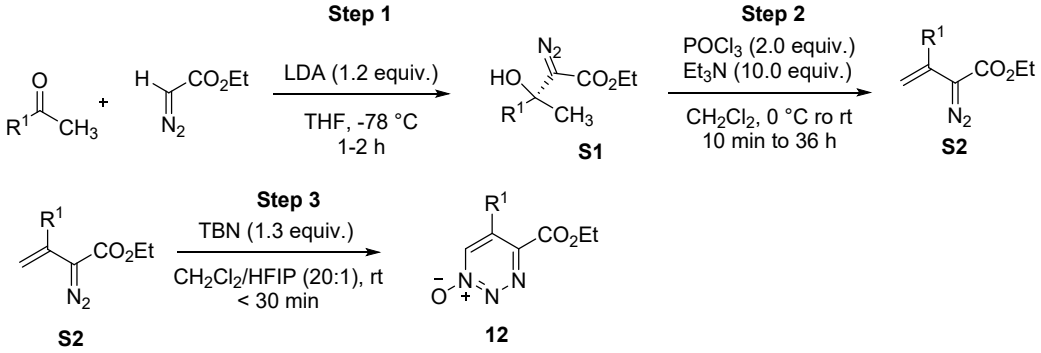
Table S2. Study of reaction conditions for diethyl diazomethylphosphonate 2a with ethyl 5-phenyl-1,2,3-triazine-4-carboxylate-1-oxide[a]



Entry	Conditions	Base (2.0 equiv.)	Yield of **13a** (%)[b]
1	THF, rt, 6 h	Cs_2CO_3	74
2	THF, rt, 6 h	CsOH	54
3	THF, rt, 12 h	CsOAc	NR
4[c]	THF, rt, 12 h	K_2CO_3	41
5	THF, rt, 6 h	*t*BuOK	64
6[d]	THF, rt, 12 h	DABCO	15
7[e]	THF, rt, 12 h	DBU	23
8	ACN, rt, 1 h	Cs_2CO_3	86 (84)
9	DCM, rt, 2 h	Cs_2CO_3	78
10	$CHCl_3$, rt, 2 h	Cs_2CO_3	80

[a]Reaction conditions: Base was added to a solution of **12a** (0.1 mmol) and diazophosphonate **2a** (0.12 mmol) at room temperature. [b]NMR yields. Isolated yield in parenthesis. [c]52% of **12a** was recovered. [d]79% of **12a** was recovered. [e]72% of **12a** was recovered.

3. General procedure for the synthesis of 1,2,3-triazine 1-oxide compounds 12



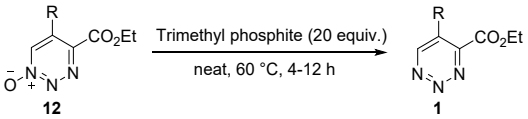
Step 1: Following the reported procedure.[2] To a solution of ketone (10.0 mmol, 1 equiv.) and ethyl diazoacetate (10.0 mmol, 1 equiv.) in 20 mL of dry THF at -78 ℃, was slowly added a solution of freshly prepared LDA (12.0 mmol, 1.2 equiv. 1.0 M in THF) over 30 minutes using a syringe pump. The resulting solution was quenched with water after stirring at -78 ℃ for 1-2 h. The reaction solution was extracted with ethyl acetate (3 x 15 mL), and the combined organic layer was washed with brine and then dried over anhydrous $MgSO_4$. After the solvent was evaporated, the crude product was purified by flash chromatography (% hexanes in ethyl acetate = 2%-10%) to give the *β*-hydroxy diazo **S1** compounds in 45%-83% yield. These compounds are stable at 0 ℃ and could be stored for months.

Step 2: Following the reported procedure.[2] To a solution of the **S1** compound (1.0 mmol, 1 equiv.) and Et_3N (1.4 mL, 10 mmol, 10 equiv.) in 10 mL CH_2Cl_2 at 0 ℃ was slowly added a solution of $POCl_3$ (300 mg, 2.0 mmol, 2 equiv.) in 4 mL of CH_2Cl_2 over 5 min. The reaction

solution was warmed to room temperature, and the progress of the reaction was followed by TLC until consumption of the *β*-hydroxy diazo compound was complete. The reaction solution was quenched with water and extracted with ethyl acetate (3 x 10 mL), and the combined organic layer was dried over anhydrous $MgSO_4$. After the solvent was evaporated, the crude product was purified by flash chromatography (% ethyl acetate in hexanes = 2%-5%) to give the vinyl diazo **S2** compound in 50%-90% yield. These compounds are not stable, slowly undergoing intramolecular cycloaddition to pyrazoles, and were used immediately following their preparation.

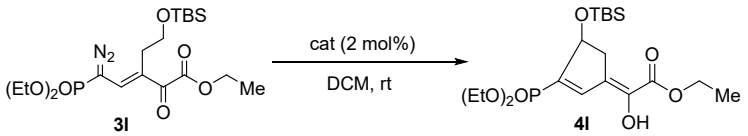
Step 3: Following the reported procedure.[3] ^{t}BuONO (1.3 mmol, 1.3 equiv.) was added to 10 mL solution containing 20:1 v/v DCM:HFIPA (HFIPA = hexafluoroisopropyl alcohol), and the vinyl diazo compound **S2** (1.0 mmol, 1 equiv., 0.1 M in DCM) was added dropwise to the solution over 5 minutes. The reaction solution was stirred at room temperature under air for 1 h. After the solvent was evaporated, the crude product was purified by flash chromatography (% ethyl acetate in hexanes = 20%-50%) to give the 1,2,3-triazine 1-oxide **1`** in 80%-99% yields. These compounds are bench stable and could be stored for months.

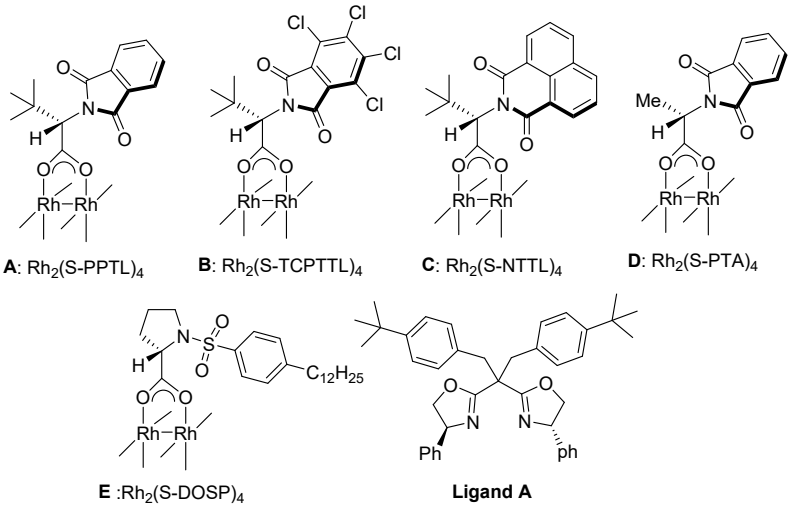
General Procedure for the synthesis of 1,2,3-triazine compound 1



Following the reported procedure.[4] The 1,2,3-triazine 1-oxide **12** (0.1 mmol) was placed in a dry 8 mL vial and triethyl phosphite (2 mmol) was added all at once. The mixture was stirred while heating in an oil bath at 60 ℃ for 4-12 h. The progress of the reaction was followed by TLC until consumption of the triazine 1-oxide compound was complete. Trimethyl phosphite and trimethyl phosphate were removed under reduced pressure in a water bath at 35 ℃, and the residue was purified by flash chromatography (hexane/ethyl acetate, 20-30%) to give the desired 1,2,3-triazine product **1** (85-98%).

4. **Table S3: Screening of chiral Rh(II)-catalyst for the synthesis of ethyl (Z)-2-(4-((tert-butyldimethylsilyl)oxy)-3-(diethoxyphosphoryl)cyclopent-2-en-1-ylidene)-2-hydroxyacetate 4l**[a]



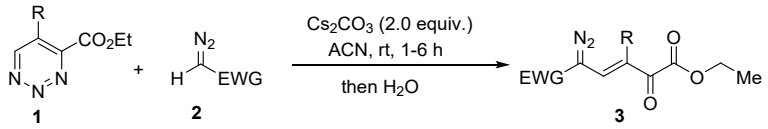


Entry	Catalyst (2.0 mol%)	yield	dr/%ee
1	Rh_2(S-PTTL)$_4$	71	20:1/42
2	Rh_2(S-TCPTTL)$_4$	75	20:1/48
3	Rh_2(S-NTTL)$_4$	68	20:1/40
4	Rh_2(S-PTA)$_4$	70	20:1/22
5	Rh_2(S-DOSP)$_4$	trace	-
6[b]	Cu(MeCN)$_4$PF$_6$/Ligand A	61	20:1/19

[a] Reactions were performed a 0.1 mmol scale by dropwise addition of **3l** in 1.0 mL of DCM (30 min) to Rh(II)-catalyst in 1.0 mL DCM. [b] 2.5 mol% of ligand A was used.

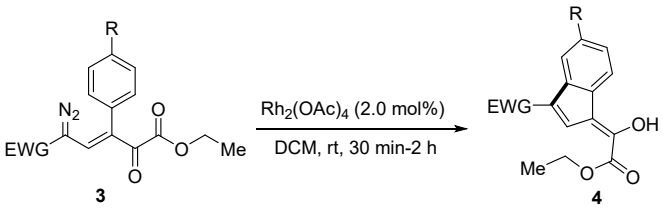
5. General synthetic procedures

General procedure for the synthesis of diazovinylketoester compounds 3 from 1,2,3-triazine 1



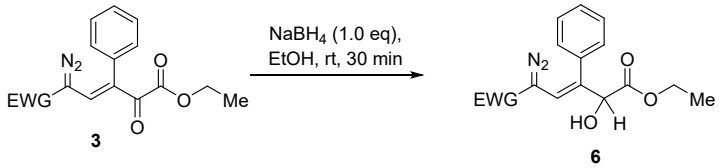
Cs_2CO_3 (0.2 mmol, 65.2 mg) was added in one portion to an acetonitrile solution (1.0 mL) of 1,2,3-triazine derivative **1** (0.1 mmol, 1 equiv.) and diazomethyl compound **2** (0.12 mmol, 1.2 equiv.). The reaction was continued for 1-6 h until the triazine **1** was fully consumed. After the completion of the reaction (monitored by TLC), 2 mL of water was added and stirred for 10 minutes, then the acetonitrile was removed under reduced pressure. The aqueous layer was extracted with ethyl acetate (3 X 5 mL). The combined organic layer was washed with brine solution, then dried over anhydrous $MgSO_4$, filtered, and the solvent was evaporated under reduced pressure. The product mixture was purified by flash chromatography (ethyl acetate in hexanes = 20-50%) to give the diazovinylketoester compound **3** with yields of 63-90%.

General procedure for the synthesis of indene derivatives 4 from diazovinylketoester compounds 3



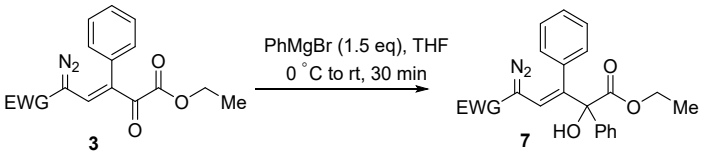
A DCM solution (1.0 mL) of diazovinylketoester **3** (0.1 mmol, 1 equiv.) was added dropwise over 30 minutes to a 1.0 mL solution of DCM containing $Rh_2(OAc)_4$ (0.002 mmol, 0.9 mg) at room temperature in a 7 mL screw capped vial. The reaction was continued for 30 min - 2 h at the same temperature. After the completion of the reaction (monitored by TLC), the volume of DCM was reduced by rotary evaporator. The crude reaction mixture dissolved in a minimal amount of DCM was directly transferred to flash column chromatography for purification (ethyl acetate in hexanes = 30-70%) to give the indene derivative **4** with yields of 72-95%.

Procedure for the synthesis of ethyl (*E*)-5-diazo-5-(Diethoxyphosphoryl)-2-hydroxy-3-phenylpent-3-enoate (6)



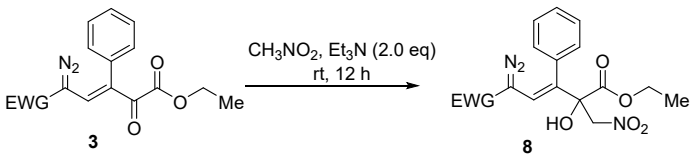
Sodium borohydride ($NaBH_4$) (0.1 mmol, 1.0 equiv.) was added all at once at room temperature to a 1.0 mL ethanol solution of diazovinylketoesters **3** (0.1 mmol). The reaction was stirred for 30 min. After completion of the reaction, the solvent was removed under reduced pressure. Then the reaction was quenched by the addition of 3 ml saturated ammonium chloride solution. The aqueous layer was extracted by ethyl acetate (3 X 3 mL). The combined organic layer was washed with water and brine solution, then dried over anhydrous $MgSO_4$, filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by flash chromatography (ethyl acetate in hexanes = 30-70%) to give compounds **6** in 91-94% yields.

Procedure for the synthesis of ethyl (*E*)-5-diazo-5-(Diethoxyphosphoryl)-2-hydroxy-2,3-diphenylpent-3-enoate (7)



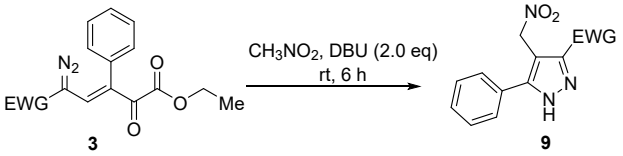
Phenylmagnesium bromide (1 M solution in THF, 0.15 mmol, 1.5 equiv.) was added dropwise to a 1.0 mL THF solution of diazovinylketoesters **3** (0.1 mmol) at 0 °C. After completion of addition the temperature was raised up to room temperature and the reaction was stirred for 30 min. After completion of the reaction, the solvent was removed under reduced pressure. Then the reaction was quenched by the addition of 3 ml saturated ammonium chloride solution. The aqueous layer was extracted by ethyl acetate (3 X 3 mL). The combined organic layer was washed with water and brine solution, then dried over anhydrous $MgSO_4$, filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by flash chromatography (ethyl acetate in hexanes = 30-70%) to give compounds **7** in 85-87% yields.

Procedure for the synthesis of ethyl (*E*)-5-diazo-5-(Diethoxyphosphoryl)-2-hydroxy-2-(nitromethyl)-3-phenylpent-3-enoate (8)



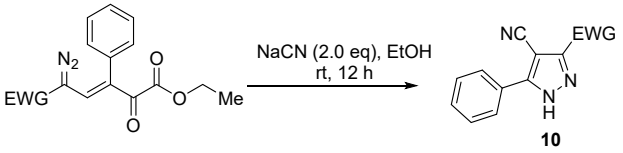
Triethylamine (0.2 mmol, 2.0 equiv.) was added dropwise to a 0.5 mL nitromethane solution of diazovinylketoesters **3** (0.1 mmol) at room temperature. The reaction was continued for 12 h. After completion of the reaction, the nitromethane was removed under reduced pressure. The reaction mixture was transferred to a silica gel column by dissolving this mass in a minimal amount of dichloromethane. Purification by flash chromatography (% ethyl acetate in hexanes = 30-70%) gave compound **8** with good yields (68-72%).

Procedure for the synthesis of 4-nitromethyl substituted pyrazoles (9)



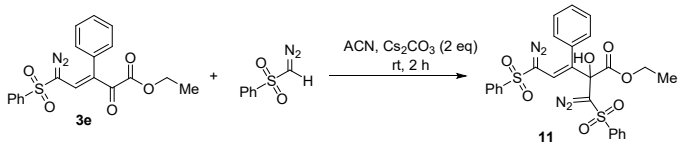
DBU (0.2 mmol, 2.0 equiv.) was added dropwise to a 0.5 mL nitromethane solution of diazovinylketoesters **3** (0.1 mmol) at room temperature. The reaction was continued for 6 h. After completion of the reaction, the nitromethane was removed under reduced pressure. The reaction mixture was transferred to a silica gel column by dissolving this mass in a minimal amount of dichloromethane. Purification by flash chromatography (% ethyl acetate in hexanes = 30-70%) gave compounds **9** with good yields (80-86%).

Procedure for the synthesis of diethyl 4-Cyano substituted pyrazoles (10)



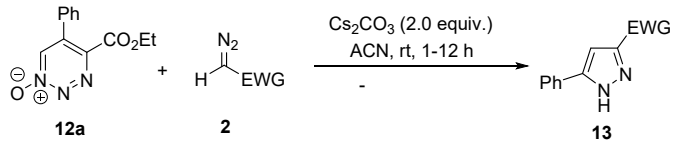
Sodium cyanide (NaCN) (0.2 mmol, 2.0 equiv.) was added all at once at room temperature to a 1.0 mL ethanol solution of diazovinylketoester **3** (0.1 mmol). The reaction was stirred for 12 h. After completion of the reaction, the solvent was removed under reduced pressure. Then the reaction mixture was redissolved in 5 mL ethyl acetate. The organic layer was was washed with water and brine solution, then dried over anhydrous $MgSO_4$, filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by flash chromatography (ethyl acetate in hexanes = 30-70%) to give compound **10** in 81-83% yield.

Procedure for the synthesis of ethyl (*E*)-5-diazo-2-(diazo(phenylsulfonyl)methyl)-2-hydroxy-3-phenyl-5-(phenylsulfonyl)pent-3-enoate (11)



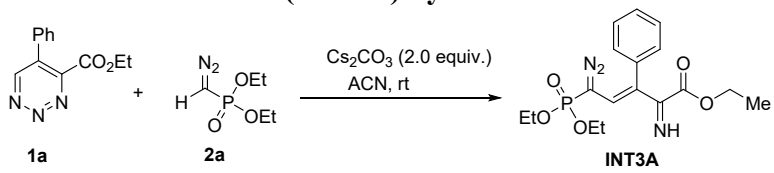
Cs_2CO_3 (0.2 mmol, 65.2 mg) was added in one portion to an acetonitrile solution (1.0 mL) of dizovinylketoester **3e** (0.1 mmol, 1 equiv.) and ((diazomethyl)sulfonyl)benzene (0.12 mmol, 1.2 equiv.). The reaction was continued for 2 h until the dizovinylketoester **3e** was fully consumed. After the completion of the reaction (monitored by TLC), the acetonitrile was removed under reduced pressure and 3 ml of ammonium chloride solution was added. The aqueous layer was extracted with ethyl acetate (3 X 5 mL). The combined organic layer was washed with brine solution, then dried over anhydrous $MgSO_4$, filtered, and the solvent was evaporated under reduced pressure. The product mixture was purified by flash chromatography (ethyl acetate in hexanes = 30-50%) to give the compound **11** with 70% yield.

General procedure for the synthesis of pyrazole derivatives 13 from 1,2,3-triazine 1-oxide 12

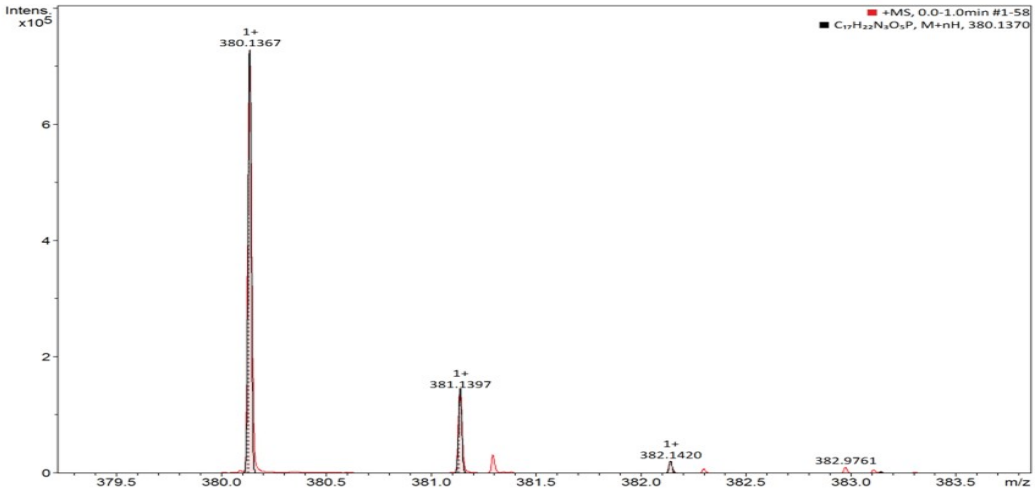


Cs_2CO_3 (0.2 mmol, 2.0 equiv., 65.2 mg) was added in one portion to an acetonitrile solution (1.0 mL) of 1,2,3-triazine 1-oxide **12** (0.1 mmol, 1 equiv.) and diazomethyl compound **2** (0.12 mmol, 1.2 equiv.). The reaction was stirred for 1-12 h until the triazine 1-oxide **12** was fully consumed. After the completion of the reaction (monitored by TLC), the acetonitrile was removed under reduced pressure. 5.0 mL of ethyl acetate was added to the reaction mixture. The organic layer was washed with water and brine solution, then dried over anhydrous $MgSO_4$, filtered, and the solvent was evaporated under reduced pressure. The product mixture was purified by flash chromatography (ethyl acetate in hexanes = 20-60%) to give the pyrazole compounds **13** with yields of 72-88%.

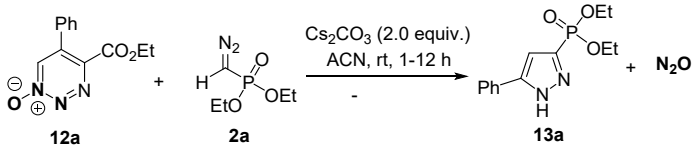
6. Detection of imine intermediate (INT3A) by HRMS



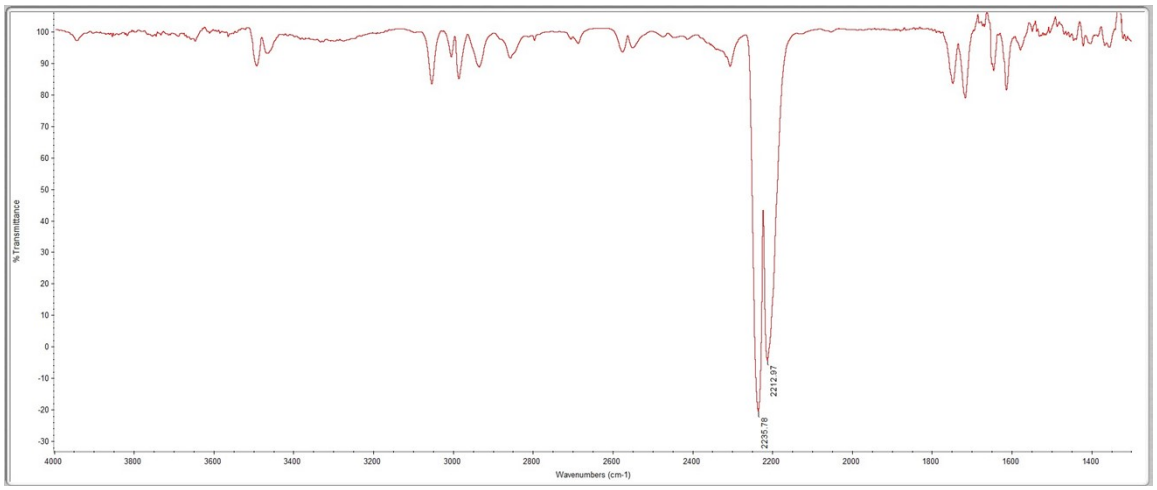
Cs_2CO_3 (0.2 mmol, 65.2 mg) was added in one portion to an acetonitrile solution (1.0 mL) of 1,2,3-triazine derivative **1a** (0.1 mmol, 1 equiv.) and diethyl diazomethylphosphonate **2a** (0.12 mmol, 1.2 equiv.). The resulting solution was stirred for 30 minutes, and a small aliquot of this solution was removed and analyzed by HRMS which detected imine intermediate **INT3A**. HRMS (ESI) calculated for $[M+H]^+$ $C_{17}H_{22}N_3O_5P$ m/z 380.1370, observed: 380.1367.



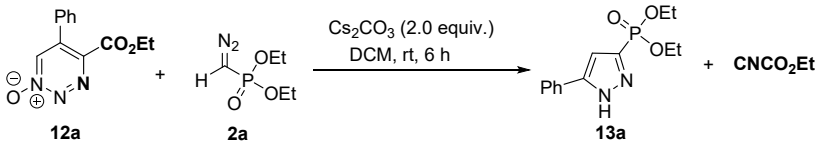
7. Characterization of Nitrous oxide (N_2O) by IR spectroscopy in the reaction between 4-ethylcarboxylato-5-phenyl-1,2,3-triazine 1-oxide (12a) and diethyl diazomethylphosphonate (2a).



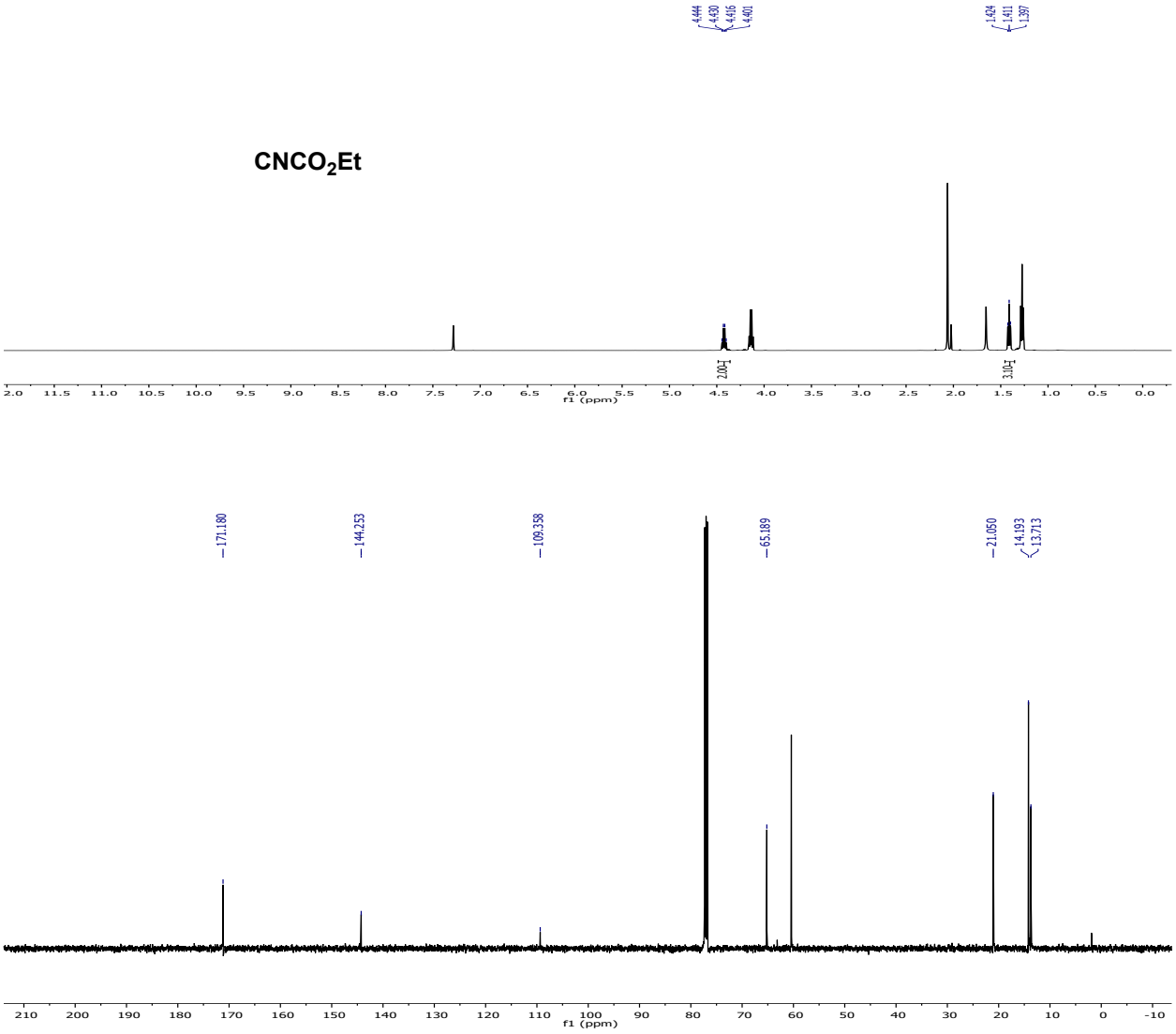
Cs_2CO_3 (2.0 mmol, 65.2 mg) was added in one portion to a DCM solution (10.0 mL, ACN was not used to eliminate solvent signal interference) of 1,2,3-triazine 1-oxide **12a** (1.0 mmol, 1 equiv.) and diethyl diazomethylphosphonate **2a** (1.2 mmol, 1.2 equiv.) in a 20 mL IR gas cell. The resulting solution was stirred for 2 h. After 2 h, the IR spectrum of the evolved gas was recorded again. The obtained IR spectroscopy data was consistent with the literature report for nitrous oxide (N_2O).[5]



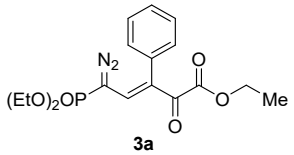
8. Characterization of ethyl cyanoformate in the reaction between 4-ethylcarboxylato-5-phenyl-1,2,3-triazine 1-oxide (12a) and diethyl diazomethylphosphonate (2a).



Cs_2CO_3 (1.0 mmol, 326 mg) was added in one portion to an acetonitrile solution (5.0 mL) of 1,2,3-triazine 1-oxide **12a** (0.5 mmol, 1 equiv.) and diethyl diazomethylphosphonate **2a** (0.6 mmol, 1.2 equiv.). The reaction was continued for 1 h until the triazine 1-oxide **12a** was fully consumed. After the completion of the reaction (monitored by TLC), the acetonitrile was removed under reduced pressure. 5.0 mL of ethyl acetate was added to the reaction mixture. The organic layer was washed with water and brine solution, then dried over anhydrous $MgSO_4$, filtered, and the solvent was evaporated under reduced pressure. Ethyl cyanoformate was isolated by flash chromatography (ethylacetate:hexane = 50 to 100 % ethyl acetate) in 12% yield. The NMR data was consistent with the literature report.[6] **^{1}H NMR** (500 MHz, $CDCl_3$) 4.42 (q, J = 7.0 Hz, 2H), 1.14 (t, J = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.2, 144.4, 109.4, 65.2, 13.7.

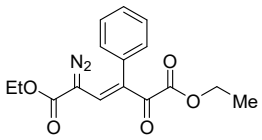


9. Analytical and spectral characterization data for products



3a

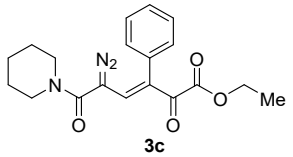
Ethyl (*E*)-5-diazo-5-(Diethoxyphosphoryl)-2-oxo-3-phenylpent-3-enoate, 3a: Yellow liquid (31.2 mg, 82% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 2:1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43 – 7.36 (comp, 3H), 7.27-7.22 (comp, 2H), 6.98 (d, J = 8.0 Hz, 1H), 4.29 (q, J = 7.1 Hz, 2H), 4.25 – 4.15 (comp, 4H), 1.44-1.38 (comp, 6H), 1.29 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 184.8, 164.8, 134.5 (d, $J_{C\text{-}P}$ = 11.1 Hz), 132.3, 130.9, 130.1 (d, $J_{C\text{-}P}$ = 9.3 Hz), 129.25, 128.26, 63.7 (d, $J_{C\text{-}P}$ = 5.5 Hz), 62.1, 16.3 (d, $J_{C\text{-}P}$ = 6.7 Hz), 14.1. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{21}N_2O_6P$ 381.1210; Found: 381.1211.



3b

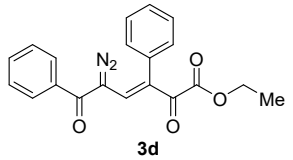
Diethyl (*E*)-5-diazo-2-oxo-3-phenylhex-3-enedioate, 3b: Yellow liquid (21.5 mg, 68% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 5:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.36-7.34 (comp, 3H), 7.24-7.20 (comp, 2H), 4.32-4.30 (comp, 4H), 1.32-1.30 (comp, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 185.4, 164.9, 133.0, 132.2, 130.8, 129.3, 128.7, 128.3, 128.2, 62.5, 62.2, 14.5, 14.2. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{16}N_2O_5$ 339.0951; Found: 339.0951.



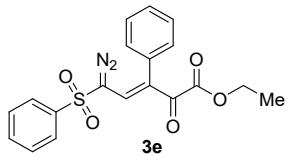
3c

Ethyl (*E*)-5-diazo-2,6-dioxo-3-phenyl-6-(piperidin-1-yl)hex-3-enoate, 3c: Yellow liquid (27.7 mg, 78% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 4:1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44 – 7.34 (comp, 3H), 7.25 (s, 1H), 7.24 – 7.18 (comp, 2H), 4.29 (q, J = 7.1 Hz, 2H), 3.46 – 3.36 (comp, 4H), 1.66-1.65 (comp, 2H), 1.62-1.57 (comp, 4H), 1.30 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 184.9, 164.9, 163.5, 135.2, 132.2, 130.6, 128.9, 128.2, 127.8, 62.0, 47.1, 25.7, 24.4, 14.0. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{21}N_3O_4$ 356.1605; Found: 356.1606.



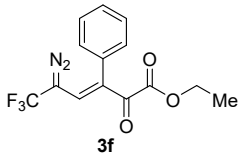
3d

Ethyl (*E*)-5-diazo-2,6-dioxo-3,6-diphenylhex-3-enoate, 3d: Yellow liquid (25.0 mg, 72% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 5:1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.62-7.58 (comp, 3H), 7.54 – 7.51 (comp, 2H), 7.50 (s, 1 H), 7.46-7.44 (comp, 3H), 7.32-7.28 (comp, 2H), 4.25 (q, J = 7.2 Hz, 2H), 1.24 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 187.1, 185.3, 164.6, 136.0, 133.3, 132.6, 132.0, 130.5, 129.3, 128.9, 128.8, 128.4, 127.9, 62.1, 13.9. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{16}N_2O_4$ 349.1183; Found: 349.1182.



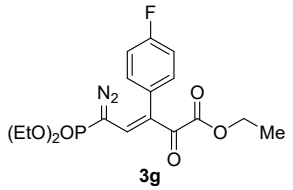
3e

Ethyl (*E*)-5-diazo-2-oxo-3-phenyl-5-(Phenylsulfonyl)pent-3-enoate, 3e: Yellow liquid (30.7 mg, 80% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 5:1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90-7.86 (comp, 2H), 7.76-7.71 (m, 1H), 7.66-7.62 (comp, 2H), 7.41-7.34 (comp, 3H), 7.29 (s, 1H), 7.15-7.09 (comp, 2H), 4.31 (q, J = 7.1 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 184.2, 164.0, 141.8, 134.3, 131.7, 130.4, 130.2, 129.9, 129.7, 129.5, 128.2, 126.8, 62.2, 13.9. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{16}N_2O_5S$ 385.0853; Found: 385.0852.



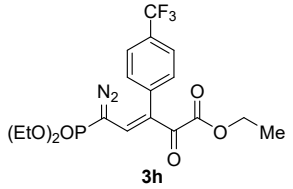
3f

Ethyl (*E*)-5-diazo-6,6,6-trifluoro-2-oxo-3-phenylhex-3-enoate, 3f: Yellow liquid, (21.8 mg, 70% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 5:1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44 – 7.40 (comp, 3H), 7.27 – 7.23 (comp, 2H), 7.07 (s, 1H), 4.28 (q, J = 7.1 Hz, 2H), 1.27 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 184.3, 164.1, 131.7, 130.7, 129.6, 129.4, 128.3, 128.2, 124.2 (q, J_{C-F} = 272 Hz), 62.1, 13.9. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{11}F_3N_2O_3$ 313.0795; Found: 313.0792.



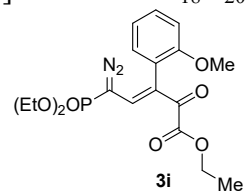
3g

Ethyl (*E*)-5-diazo-5-(Diethoxyphosphoryl)-3-(4-Fluorophenyl)-2-oxopent-3-enoate, 3g: Yellow liquid (35.0 mg, 88% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 3:1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.23 (d, J = 8.4, 2H), 7.10 (d, J = 8.4 Hz, 2H), 6.99 (d, J = 8.1 Hz, 1H), 4.31 (q, J = 7.1 Hz, 2H), 4.19 (comp, 4H), 1.42-1.36 (comp, 6H), 1.31 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 184.5, 164.5, 163.0 (d, $J_{C\text{-}F}$ = 252 Hz), 135.1 (d, $J_{C\text{-}F}$ = 12 Hz), 132.6 (d, $J_{C\text{-}F}$ = 7 Hz), 129.0 (d, $J_{C\text{-}P}$ = 9 Hz), 128.1 (d, $J_{C\text{-}P}$ = 4 Hz), 115.3 (d, $J_{C\text{-}F}$ = 21 Hz), 63.7 (d, $J_{C\text{-}P}$ = 6 Hz), 62.1, 16.2 (d, $J_{C\text{-}P}$ = 6 Hz), 14.0. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{20}FN_2O_6P$ 399.1116; Found: 399.1111.



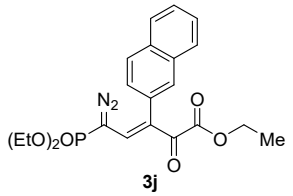
3h

Ethyl (*E*)-5-diazo-5-(Diethoxyphosphoryl)-2-oxo-3-(4-(Trifluoromethyl)phenyl)pent-3-enoate, 3h: Yellow liquid (40.3 mg, 90% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 3:1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.66 (d, J = 7.8 Hz, 2H), 7.37 (d, J = 7.8 Hz, 2H), 7.05 (d, J = 8.2 Hz, 1H), 4.31 (q, J = 7.1 Hz, 2H), 4.21-4.16 (comp, 4H), 1.42-1.36 (comp, 6H), 1.31 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 184.1, 164.2, 135.8, 136.5 (d, $J_{C\text{-}P}$ = 12 Hz), 131.2, 131.0, 128.6 (d, $J_{C\text{-}P}$ = 10 Hz), 125.1 (q, $J_{C\text{-}F}$ = 4 Hz), 123.8 (q, $J_{C\text{-}F}$ = 272 Hz), 63.8 (d, $J_{C\text{-}P}$ = 6.3 Hz), 62.3, 16.2 (d, $J_{C\text{-}P}$ = 6.3 Hz), 14.0. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{20}F_3N_2O_6P$ 449.1084; Found: 449.1072.



3i

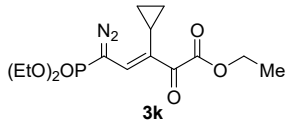
Ethyl (*E*)-5-diazo-5-(Diethoxyphosphoryl)-3-(2-Methoxyphenyl)-2-oxopent-3-enoate, 3i: Yellow liquid (32.8 mg, 80% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 3:1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 1H), 7.16 (dd, J = 7.5, 1.7 Hz, 1H), 7.03 – 6.96 (comp, 2H), 6.91 (d, J = 8.4 Hz, 1H), 4.29 – 4.16 (comp, 6H), 3.80 (s, 3H), 1.42-1.38 (comp, 6H), 1.26 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 184.6, 164.5, 158.0, 133.7 (d, $J_{C\text{-}P}$ = 12 Hz), 132.17, 130.9, 126.5 (d, $J_{C\text{-}P}$ = 10 Hz), 120.7, 120.0, 110.4, 63.5 (d, $J_{C\text{-}P}$ = 6 Hz), 61.8, 55.5, 16.1 (d, $J_{C\text{-}P}$ = 6 Hz), 14.0. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{23}N_2O_7P$ 411.1316; Found: 411.1306.



3j

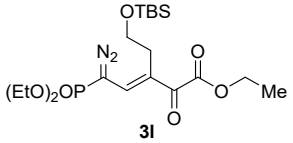
Ethyl (*E*)-5-diazo-5-(Diethoxyphosphoryl)-3-(Naphthalen-2-yl)-2-oxopent-3-enoate, 3j: Yellow liquid (36.1 mg, 84% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 3:1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.94-7.90 (comp, 2H), 7.77 – 7.72 (m, 1H), 7.56-7.52 (comp, 2H), 7.49 (t, J = 7.6 Hz, 1H), 7.39 (d, J = 7.0 Hz, 1H), 7.28 (d, J = 7.0 Hz, 1H), 4.22-4.16 (comp, 6H), 1.40-1.36 (comp, 6H), 1.14 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 184.6, 164.6, 135.8 (d, $J_{C\text{-}P}$ = 12 Hz), 132.9, 132.5, 129.9,

129.7, 129.0, 128.9, 127.8 (d, $J_{C\text{-}P}$ = 10 Hz), 127.0, 126.5, 124.7, 124.5, 63.6 (d, $J_{C\text{-}P}$ = 6 Hz), 61.9, 16.1 (d, $J_{C\text{-}P}$ = 6 Hz), 13.8. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{23}N_2O_6P$ 453.1186; Found: 453.1178.



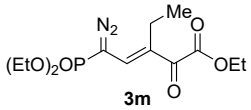
3k

Ethyl (*E*)-3-cyclopropyl-5-diazo-5-(Diethoxyphosphoryl)-2-oxopent-3-enoate, 3k: Yellow liquid (21.7 mg, 63% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 4:1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.70 (d, J = 7.5 Hz, 1H), 4.34 (q, J = 7.1 Hz, 2H), 4.28-4.10 (comp, 4H), 1.53-1.48 (m, 1H), 1.39-1.34 (comp, 9H), 0.95-0.82 (comp, 2H), 0.66-0.62 (comp, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 186.0, 165.1, 135.4 (d, $J_{C\text{-}P}$ = 12 Hz), 129.9 (d, $J_{C\text{-}P}$ = 10 Hz), 63.6 (d, $J_{C\text{-}P}$ = 6.0 Hz), 61.9, 16.2 (d, $J_{C\text{-}P}$ = 6.0 Hz), 14.0, 8.9, 8.0. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{21}N_2O_6P$ 345.1210; Found: 345.1204.



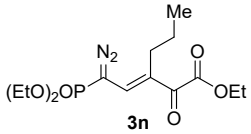
3l

Ethyl (*E*)-3-(2-((tert-butyldimethylsilyl)oxy)ethyl)-5-diazo-5-(diethoxyphosphoryl)-2-oxopent-3-enoate, 3l: Yellow liquid (31.4 mg, 68% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 4:1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.62 (d, J = 8.7 Hz, 1H), 4.35 (q, J = 7.2 Hz, 2H), 4.21 – 4.09 (comp, 4H), 3.68 (t, J = 5.8 Hz, 2H), 2.62 (t, J = 5.8 Hz, 2H), 1.36 (t, J = 7.2 Hz, 9H), 0.86 (s, 9H), 0.01 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 186.6, 164.8, 136.8 (d, $J_{C\text{-}P}$ = 12 Hz), 127.8 (d, $J_{C\text{-}P}$ = 9 Hz), 63.5(d, $J_{C\text{-}P}$ = 6 Hz), 62.0, 60.9, 27.6, 25.9, 18.4, 16.1(d, $J_{C\text{-}P}$ = 6 Hz), 14.1, -5.6. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{35}N_2O_7PSi$ 463.2024; Found: 463.2017.



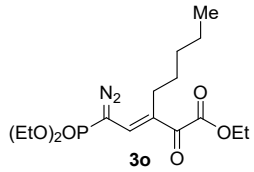
3m

Ethyl (*E*)-5-diazo-5-(Diethoxyphosphoryl)-3-ethyl-2-oxopent-3-enoate, 3m: Yellow liquid (23.2 mg, 70% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 3:1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.49 (d, J = 8.4 Hz, 1H), 4.34 (t, J = 7.3 Hz, 2H), 4.20-4.18 (comp, 4H), 2.42 (q, J = 7.3 Hz, 2H), 1.39-1.36 (comp, 9H), 1.05 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 186.2, 164.7, 133.3 (d, $J_{C\text{-}P}$ = 11.4 Hz), 132.8 (d, $J_{C\text{-}P}$ = 9 Hz), 63.7 (d, $J_{C\text{-}P}$ = 5.6 Hz), 62.0, 17.6, 16.1 (d, $J_{C\text{-}P}$ = 6.1 Hz), 14.3, 14.1. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{21}N_2O_6P$ 333.1210; Found: 333.1214.



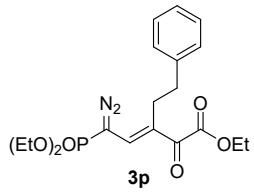
3n

Ethyl (*E*)-3-(2-Diazo-2-(diethoxyphosphoryl)ethylidene)-2-oxohexanoate, 3n: Yellow liquid (24.9 mg, 72% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 3:1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.48 (d, J = 8.5 Hz, 1H), 4.34 (q, J = 7.2 Hz, 2H), 4.19-4.17 (comp, 4H), 2.41 – 2.31 (t, J = 7.5 Hz, 2H), 1.48 – 1.29 (comp, 11H), 0.94 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 186.4, 164.8, 133.6 (d, $J_{C\text{-}P}$ = 11.2 Hz), 131.5 (d, $J_{C\text{-}P}$ = 9 Hz), 63.6 (d, $J_{C\text{-}P}$ = 6 Hz), 62.0, 26.0, 23.0, 16.1 (d, $J_{C\text{-}P}$ = 6 Hz), 14.0, 13.5. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{23}N_2O_6P$ 347.1366; Found: 347.1375.



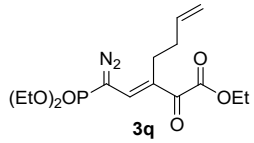
3o

Ethyl (*E*)-3-(2-diazo-2-(diethoxyphosphoryl)ethylidene)-2-oxoheptanoate, 3o: Yellow liquid (27.0 mg, 75% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 4:1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.47 (d, J = 8.4 Hz, 1H), 4.33 (q, J = 7.0 Hz, 2H), 4.23 – 4.10 (comp, 4H), 2.37 (t, J = 7.2 Hz, 2H), 1.39 – 1.30 (comp, 15H), 0.88 (t, J = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 186.4, 164.8, 133.4 (d, $J_{C\text{-}P}$ = 11.6 Hz), 131.8 (d, $J_{C\text{-}P}$ = 9 Hz), 63.7 (d, $J_{C\text{-}P}$ = 5.6 Hz), 62.0, 31.4, 29.6, 24.3, 22.4, 16.1 (d, $J_{C\text{-}P}$ = 6.5 Hz), 14.1, 14.0. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{27}N_2O_6P$ 375.1679; Found: 375.1684.



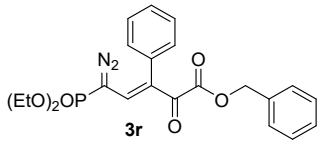
3p

Ethyl (*E*)-5-diazo-5-(Diethoxyphosphoryl)-2-oxo-3-phenethylpent-3-enoate, 3p: Yellow liquid (29.0 mg, 71% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 3:1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32-7.28 (comp, 3H), 7.21 (d, J = 7.5 Hz, 2H), 6.55 (d, J = 8.6 Hz, 1H), 4.39 (q, J = 7.1 Hz, 2H), 4.22 – 4.07 (comp, 4H), 2.77 – 2.67 (comp, 4H), 1.43-135 (comp, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 186.3, 164.7, 140.4, 134.3 (d, $J_{C\text{-}P}$ = 11 Hz), 130.3 (d, $J_{C\text{-}P}$ = 9.7 Hz), 128.6, 128.5, 126.4, 63.6 (d, $J_{C\text{-}P}$ = 6.0 Hz), 62.1, 35.2, 26.7, 16.1 (d, $J_{C\text{-}P}$ = 6.1 Hz), 14.1. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{25}N_2O_6P$ 409.1523; Found: 409.1530.



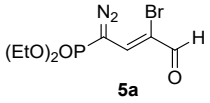
3q

Ethyl (*E*)-3-(2-Diazo-2-(diethoxyphosphoryl)ethylidene)-2-oxohept-6-enoate, 3q: Yellow liquid (25.4 mg, 71% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 3:1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.57 (d, J = 8.6 Hz, 1H), 5.83-5.77 (m, 1H), 5.08 (d, J = 17.0 Hz, 1H), 5.04 (d, J = 10.1 Hz, 1H), 4.37 (q, J = 7.2 Hz, 2H), 4.29 – 4.13 (comp, 4H), 2.51 (t, J = 8.0 Hz, 2H), 2.20-2.16 (comp, 2H), 1.46 – 1.35 (comp, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 186.3, 164.8, 136.49, 134.2 (d, $J_{C\text{-}P}$ = 11.0 Hz), 130.7 (d, $J_{C\text{-}P}$ = 9.3 Hz), 116.2, 63.8 (d, $J_{C\text{-}P}$ = 6.1 Hz), 62.2, 33.5, 23.9, 16.3 (d, $J_{C\text{-}P}$ = 6.8 Hz), 14.2. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{23}N_2O_6P$ 359.1366; Found: 359.1368.



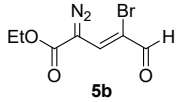
3r

Benzyl (*E*)-5-diazo-5-(Diethoxyphosphoryl)-2-oxo-3-phenylpent-3-enoate, 3r: Yellow liquid (37.6 mg, 85% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 3:1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41 – 7.31 (comp, 8H), 7.25 – 7.21 (comp, 2H), 6.98 (d, J = 8.0 Hz, 1H), 5.23 (s, 2H), 4.18-4.14 (comp, 4H), 1.38 (comp, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 184.2, 164.5, 134.6, 134.5 (d, $J_{C\text{-}P}$ = 11 Hz), 132.1, 130.7, 129.8 (d, $J_{C\text{-}P}$ = 9.5 Hz), 129.1, 128.7, 128.6, 128.6, 128.1, 67.5, 63.6 (d, $J_{C\text{-}P}$ = 6.3 Hz), 16.2 (d, $J_{C\text{-}P}$ = 6.7 Hz). **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{23}N_2O_6P$ 443.1366; Found: 443.1383.



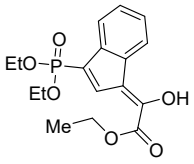
5a

Diethyl (*Z*)-(3-bromo-1-diazo-4-oxobut-2-en-1-yl)phosphonate, 5a: Yellow liquid (22.7 mg, 73% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 3:1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.14 (s, 1H), 6.91 (d, J = 8.5 Hz, 1H), 4.50 – 4.07 (comp, 4H), 1.40 (t, J = 7.1 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 183.91, 136.9 (d, $J_{C\text{-}P}$ = 14 Hz), 119.0 (d, $J_{C\text{-}P}$ = 9 Hz), 63.9 (d, $J_{C\text{-}P}$ = 6 Hz), 16.2 (d, $J_{C\text{-}P}$ = 6 Hz). **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_8H_{12}{}^{79}BrN_2O_4P$ 332.9610; Found: 332.9605; **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_8H_{12}{}^{81}BrN_2O_4P$ 334.9590; Found: 334.9585.



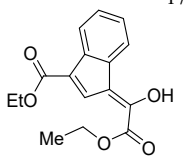
5b

Ethyl (*Z*)-4-bromo-2-diazo-5-oxopent-3-enoate, 5b: Yellow solid (15.1 mg, 61% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 4:1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.20 (s, 1H), 7.36 (s, 1H), 4.37 (q, J = 7.1 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 184.1, 162.6, 134.9, 117.5, 62.8, 14.4. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_7H_7{}^{79}BrN_2O_3$ 268.9532; Found: 268.9534; **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_7H_7{}^{81}BrN_2O_3$ 270.9512; Found: 270.9514.



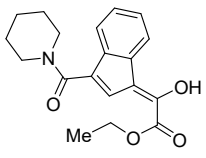
4a

Ethyl (*Z*)-2-(3-(Diethoxyphosphoryl)-1*H*-inden-1-ylidene)-2-hydroxyacetate, 4a: Yellow liquid (33.5 mg, 95% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 1:1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.16-8.12 (m, 1H), 7.98 (d, J = 10.0 Hz, 1H), 7.62 (dd, J = 6.9, 1.4 Hz, 1H), 7.36 – 7.29 (comp, 2H), 4.56 (q, J = 7.1 Hz, 2H), 4.25 – 4.10 (comp, 4H), 1.51 (t, J = 7.1 Hz, 3H), 1.38-1.34 (comp, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.9, 143.1, 140.2 (d, $J_{C\text{-}P}$ = 13 Hz), 139.8 (d, $J_{C\text{-}P}$ = 15 Hz), 135.3 (d, $J_{C\text{-}P}$ = 12 Hz), 131.5 (d, $J_{C\text{-}P}$ = 197 Hz), 128.3, 126.3, 123.3, 123.1, 121.9, 64.2, 62.0 (d, $J_{C\text{-}P}$ = 6 Hz), 16.4 (d, $J_{C\text{-}P}$ = 6 Hz), 14.2. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{21}O_6P$ 353.1149; Found: 353.1146.



4b

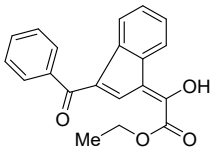
Ethyl (*Z*)-1-(2-Ethoxy-1-hydroxy-2-oxoethylidene)-1*H*-indene-3-carboxylate, 4b: Yellow solid (26.5 mg, 92% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 1:1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.13 (d, J = 7.5 Hz, 1H), 8.06 (s, 1H), 8.00 (d, J = 7.5 Hz, 1H), 7.36-7.34 (m, 1H), 7.32-7.29 (m, 1H), 4.58 (q, J = 7.1 Hz, 2H), 4.41 (q, J = 7.1 Hz, 2H), 1.54 (t, J = 7.1 Hz, 3H), 1.45 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.0, 164.6, 143.2, 138.9, 135.7, 135.1, 133.3, 128.3, 126.2, 126.2, 122.8, 122.5, 64.2, 60.5, 14.4, 14.2. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{16}O_5$ 289.1071; Found: 289.1068.



4c

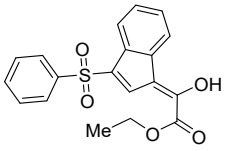
Ethyl (*Z*)-2-hydroxy-2-(3-(Piperidine-1-carbonyl)-1*H*-inden-1-ylidene)acetate, 4c: Yellow solid, (30.8 mg, 94% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 1:1. **^{1}H NMR** (500 MHz, $CDCl_3$) 8.14-8.12 (m, 1H), 7.36-7.34 (m, 1

H), 7.34 (s, 1H), 7.32-7.27 (comp, 2H), 4.51 (q, J = 7.0 Hz, 2H), 3.78-3.75 (comp, 2H), 3.47-3.43 (comp, 2H), 1.71-1.61 (comp, 6H), 1.48 (t, J = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.1, 165.3, 141.3, 140.2, 138.7, 134.9, 128.1, 126.5, 126.4, 126.3, 123.6, 120.6, 63.8, 48.3, 42.8, 26.8, 25.7, 24.6, 14.2. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{21}NO_4$ 328.1543; Found: 328.1541.



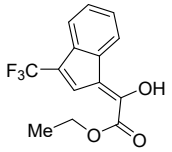
4d

Ethyl (*Z*)-2-(3-Benzoyl-1*H*-inden-1-ylidene)-2-hydroxyacetate, 4d: Yellow solid (28.8 mg, 90% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 1:1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.17 (d, J = 7.4 Hz, 1H), 8.08 (d, J = 7.4 Hz, 1H), 7.94-7.90 (comp, 2H), 7.81 (s, 1H), 7.61 (t, J = 7.4 Hz, 1H), 7.54-7.50 (comp, 2H), 7.38-7.34 (comp, 2H), 4.47 (q, J = 7.1 Hz, 2H), 1.37 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 192.9, 164.8, 143.5, 139.8, 139.1, 138.0, 135.0, 132.2, 129.2, 128.7, 128.5, 128.2, 126.7, 126.2, 123.6, 123.2, 64.0, 13.9. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{16}O_4$ 321.1121; Found: 321.1115.



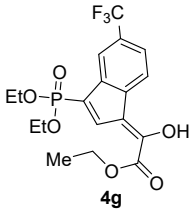
4e

Ethyl (*Z*)-2-hydroxy-2-(3-(Phenylsulfonyl)-1*H*-inden-1-ylidene)acetate, 4e: Yellow solid (33.1 mg, 93% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 1:1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.14 – 8.06 (comp, 3H), 8.04 (s, 1H), 7.71 – 7.67 (m, 1H), 7.60 (t, J = 7.3 Hz, 1H), 7.56-7.52 (comp, 2H), 7.32-7.29 (comp, 2H), 4.60 (q, J = 7.1 Hz, 2H), 1.53 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.5, 144.9, 141.4, 141.0, 135.7, 134.9, 134.8, 133.3, 129.2, 128.4, 127.6, 127.0, 126.6, 121.2, 121.1, 64.6, 14.2. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{16}O_5S$ 357.0791; Found: 357.0786.



4f

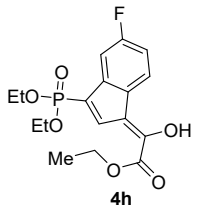
Ethyl (*Z*)-2-hydroxy-2-(3-(Trifluoromethyl)-1*H*-inden-1-ylidene)acetate, 4f: Yellow solid (26.1 mg, 91% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 2:1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.16 – 8.12 (m, 1H), 7.62 (q, J = 2.0 Hz, 1H), 7.54 – 7.44 (m, 1H), 7.35 – 7.30 (comp, 2H), 4.54 (q, J = 7.2 Hz, 2H), 1.50 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.8, 143.0, 136.8, 134.9, 132.2 (q, J_{C-F} = 34 Hz), 128.5 (q, J_{C-F} = 6 Hz), 128.3, 126.8, 126.6, 122.8 (q, J_{C-F} = 270 Hz), 121.8, 120.5, 64.2, 14.2. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{11}F_3O_3$ 285.0733; Found: 285.0711.



4g

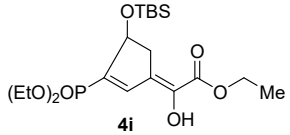
Ethyl (*Z*)-2-(3-(Diethoxyphosphoryl)-5-(Trifluoromethyl)-1*H*-inden-1-ylidene)-2-hydroxyacetate, 4g: Yellow liquid (38.7 mg, 92% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 1:1. **^{1}H NMR** (500 MHz, $CDCl_3$)

δ 8.21 (d, J = 8.0 Hz, 1H), 8.05 (d, J = 9.9 Hz, 1H), 7.84 (s, 1H), 7.53 (d, J = 8.0 Hz, 1H), 4.55 (q, J = 7.1 Hz, 2H), 4.26 – 4.08 (comp, 4H), 1.49 (t, J = 7.1 Hz, 3H), 1.37-1.33 (comp, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.6, 145.0, 141.0 (d, J_{C-P} = 15 Hz), 140.5 (d, J_{C-P} = 11 Hz), 138.5 (d, J_{C-P} = 11 Hz), 130.1 (q, J_{C-F} = 32 Hz), 130.0 (d, J_{C-P} = 200 Hz), 126.2, 126.7 (q, J_{C-F} = 273 Hz), 123.4 (d, J_{C-P} = 11 Hz), 122.0 (d, J_{C-P} = 21 Hz), 118.6 (q, J_{C-F} = 4.2 Hz), 64.7, 62.4 (d, J_{C-P} = 5.2 Hz), 16.5 (d, J_{C-P} = 6.5 Hz), 14.5. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{20}F_3O_6P$ 421.1022; Found: 421.1026.



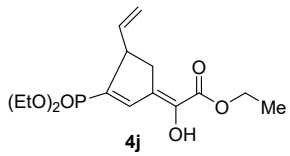
4h

Ethyl (*Z*)-2-(3-(Diethoxyphosphoryl)-5-fluoro-1*H*-inden-1-ylidene)-2-hydroxyacetate, 4h: Yellow liquid (33.3 mg, 91% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 1:1. **^{1}H NMR** (500 MHz, $CDCl_3$) 8.07-8.04 (m, 1H), 8.00 (d, J = 9.0 Hz, 1H), 7.30 (d, J = 8.0 Hz, 1H), 6.94 (t, J = 8.0 Hz, 1H), 4.51 (q, J = 7.2 Hz, 2H), 4.23 – 4.08 (comp, 4H), 1.46 (t, J = 7.2 Hz, 3H), 1.36-1.33 (comp, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.8, 163.2 (d, J_{C-F} = 247 Hz), 143.6, 142.3 (dd, J = 13.4, 3.7 Hz), 141.5 (d, J_{C-F} = 15 Hz), 131.3 (d, J_{C-P} = 11.5 Hz), 129.8 (d, J_{C-P} = 200 Hz), 127.4 (d, J_{C-P} = 9.2 Hz), 122.4 (d, J_{C-P} = 21.3 Hz), 112.9 (d, J_{C-F} = 22.8 Hz), 109.5 (d, J_{C-F} = 25 Hz), 64.3, 62.3 (d, J_{C-P} = 5.3 Hz), 16.5 (d, J_{C-P} = 6.8 Hz), 14.3. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{20}FO_6P$ 371.1054; Found: 371.1058.



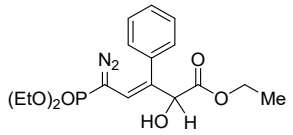
4i

Ethyl (*Z*)-2-(4-((tert-butyldimethylsilyl)oxy)-3-(diethoxyphosphoryl)cyclopent-2-en-1-ylidene)-2-hydroxyacetate, 4i: light yellow liquid, (35.2 mg, 81% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 1:1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97 (dd, J = 21.4, 17.3 Hz, 1H), 5.93 (dd, J = 6.9, 2.2 Hz, 1H), 5.61 (t, J = 17.3 Hz, 1H), 4.43 – 4.25 (comp, 2H), 4.12 (comp, J = 7.2, 1.6 Hz, 4H), 3.05 (dd, J = 16.8, 6.9 Hz, 1H), 2.72 (dd, J = 16.8, 2.2 Hz, 1H), 1.41 – 1.30 (comp, 9H), 0.89 (s, 9H), 0.16 (s, 3H), 0.14 (s, 3H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.8, 144.7, 139.6 (d, J_{C-P} = 7.9 Hz), 121.4 (d, J_{C-P} = 27.6 Hz), 116.3 (d, J_{C-P} = 193 Hz), 99.4, 61.9 (d, J_{C-P} = 8 Hz), 61.5, 39.9, 25.6, 17.8, 16.4 (d, J_{C-P} = 6.3 Hz), 14.1, -4.36, -5.16. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{35}O_7PSi$ 435.1962; Found: 435.1949.



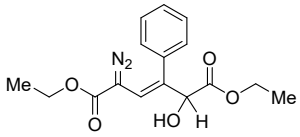
4j

Ethyl (*Z*)-2-(3-(Diethoxyphosphoryl)-4-vinylcyclopent-2-en-1-ylidene)-2-hydroxyacetate, 4j: , (23.8 mg, 72% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 1:1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.63 (d, J = 10.5 Hz, 1H), 6.02 (s, 1H), 5.80-5.73 (m, 1H), 5.19 (d, J = 17.0 Hz, 1H), 5.08 (d, J = 9.9 Hz, 1H), 4.39 (t, J = 7.1 2H), 4.13 (comp, 4H), 3.73-3.67 (m, 1H), 3.10 (dd, J = 18.6, 7.7 Hz, 1H), 2.65 (d, J = 18.6, 1H), 1.41 (t, J = 7.1 Hz, 3H), 1.35 (comp, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.4, 143.6 (d, J_{C-P} = 17 Hz), 141.7 (d, J_{C-P} = 190 Hz), 138.9, 135.1, 131.9 (d, J_{C-P} = 26 Hz), 115.4, 62.6, 61.8 (d, J_{C-P} = 5 Hz), 49.4 (d, J_{C-P} = 11 Hz), 35.9 (d, J_{C-P} = 10 Hz), 16.4 (d, J_{C-P} = 6.5 Hz), 14.3. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{23}O_6P$ 331.1305; Found: 331.1312.



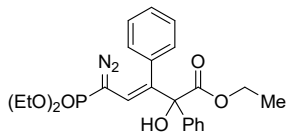
6a

Ethyl (*E*)-5-diazo-5-(Diethoxyphosphoryl)-2-hydroxy-3-phenylpent-3-enoate, 6a: yellow liquid, (34.8 mg, 91% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 2:1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36-7.30 (comp, 3H), 7.21 (d, J = 6.8 Hz, 2H), 5.70 (d, J = 6.3 Hz, 1H), 4.88 (d, J = 5.1 Hz, 1H), 4.22-4.10 (comp, 6H), 3.25 (d, J = 5.1 Hz, 1H), 1.49 – 1.35 (comp, 6H), 1.20 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.9, 134.6, 133.4 (d, $J_{C\text{-}P}$ = 10 Hz), 129.6, 128.3, 128.0, 115.6 (d, $J_{C\text{-}P}$ = 11 Hz), 76.0, 62.9 (d, $J_{C\text{-}P}$ = 8 Hz), 62.1, 16.2 (d, $J_{C\text{-}P}$ = 6.6 Hz), 14.0. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{23}N_2O_6P$ 405.1186; Found: 405.1182.



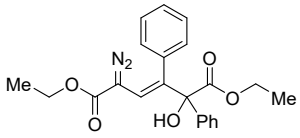
6b

Diethyl (*E*)-5-diazo-2-hydroxy-3-phenylhex-3-enedioate, 6b: yellow liquid, (29.9 mg, 94% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 4:1. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.36-7.32 (comp, 3H), 7.23 – 7.18 (comp, 2H), 6.19 (s, 1H), 4.92 (s, 1H), 4.28 (q, J = 7.1 Hz, 2H), 4.19 (q, J = 7.1 Hz, 2H), 1.29 (t, J = 7.1 Hz, 3H), 1.21 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 173.0, 173.0, 134.7, 131.9, 129.6, 128.3, 128.0, 115.1, 76.0, 62.1, 61.4,14.4, 14.0. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{18}N_2O_5$ 341.1108; Found: 341.1104.



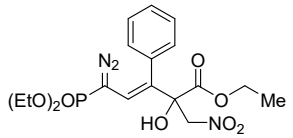
7a

Ethyl (*E*)-5-diazo-5-(Diethoxyphosphoryl)-2-hydroxy-2,3-diphenylpent-3-enoate, 7a: White solid, (39.0 mg, 85% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 2:1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.75 (d, J = 7.3 Hz, 2H), 7.42 – 7.29 (comp, 8H), 5.28 (d, J = 6.6 Hz, 1H), 4.16 (s, 1H), 4.13 – 3.97 (comp, 6H), 1.30 (t, J = 7.1 Hz, 3H), 1.24 (t, J = 7.1 Hz, 3H), 1.14 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.8, 139.2, 138.1 (d, $J_{C\text{-}P}$ = 6.6 Hz), 136.2, 130.4, 128.1 (d, $J_{C\text{-}P}$ = 10 Hz), 128.0, 127.9, 127.8, 127.5, 116.1 (d, $J_{C\text{-}P}$ = 12 Hz), 82.3, 62.9, 62.8 (d, $J_{C\text{-}P}$ = 6 Hz), 16.1 (d, $J_{C\text{-}P}$ = 8 Hz), 13.8. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{27}N_2O_6P$ 481.1499; Found: 481.1501.



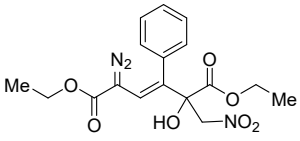
7b

Diethyl (*E*)-5-diazo-2-hydroxy-2,3-diphenylhex-3-enedioate, 7b: yellow liquid, (34.3 mg, 87% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 4:1. **^{1}H NMR** (300 MHz, $CDCl_3$) δ δ 7.82 – 7.74 (comp, 2H), 7.45 – 7.29 (comp, 8H), 5.85 (s, 1H), 4.20 – 4.10 (comp, 5H), 1.21 (t, J = 7.1 Hz, 3H), 1.17 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 173.8, 165.8, 139.0, 136.5, 136.2, 130.5, 128.2, 128.1, 127.9, 127.7, 127.5, 115.7, 82.2, 62.8, 61.26, 14.31, 13.83. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{22}N_2O_5$ 417.1421; Found: 417.1413.



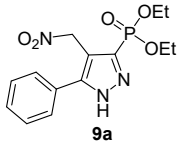
8a

Ethyl (*E*)-5-diazo-5-(Diethoxyphosphoryl)-2-hydroxy-2-(nitromethyl)-3-phenylpent-3-enoate, 8a: yellow liquid, (31.8 mg, 72% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 2:1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32-7.35 (comp, 3H), 7.19 – 7.08 (comp, 2H), 5.98 (d, J = 7.1 Hz, 1H), 4.98 (d, J = 13.8, 1H), 4.69 (d, J = 13.8 Hz, 1H), 4.34 – 4.10 (comp, 6H), 4.08 (s, 1H), 1.40-1.36 (comp, 6H), 1.22 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.3, 134.2, 131.3 (d, J_{C-P} = 10 Hz), 130.8, 129.1, 128.3, 128.1, 116.3 (d, J_{C-P} = 12 Hz), 79.4, 63.2, 63.1 (d, J_{C-P} = 6 Hz), 16.2 (d, J_{C-P} = 10.6 Hz), 13.8. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{24}N_3O_8P$ 464.1193; Found: 464.1192.



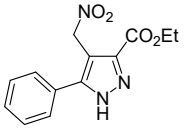
8b

Diethyl (*E*)-5-diazo-2-hydroxy-2-(Nitromethyl)-3-phenylhex-3-enedioate, 8b: yellow liquid, (25.6 mg, 68% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 3:1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44 – 7.32 (comp, 3H), 7.14 (d, J = 7.2 Hz, 2H), 6.44 (s, 1H), 5.01 (d, J = 13.9 Hz, 1H), 4.71 (d, J = 13.9 Hz, 1H), 4.43 – 4.19 (comp, 4H), 4.08 (s, 1H), 1.29 – 1.23 (comp, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 171.2, 165.3, 134.1, 130.6, 130.0, 129.1, 128.2, 115.7, 79.4, 63.2, 61.6, 14.4, 13.8. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{19}N_3O_7$ 400.1115; Found: 400.1108.



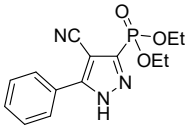
9a

Diethyl (4-(Nitromethyl)-5-phenyl-1H-pyrazol-3-yl)phosphonate, 9a: colorless liquid, (29.2 mg, 86% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 2:1. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.51-7.49 (comp, 5H), 5.65 (s, 2H), 4.30 – 4.15 (m, 4H), 1.37 (t, J = 7.1 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 148.6, 129.5, 129.2, 128.92, 128.8, 128.1, 125.8, 112.66 (d, J_{C-P} = 20 Hz), 68.8, 63.3 (d, J_{C-P} = 5.4 Hz), 16.12 (d, J_{C-P} = 6.5 Hz). **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{18}N_3O_5P$ 362.0876; Found: 362.0870.



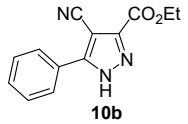
9b

Ethyl 4-(nitromethyl)-5-phenyl-1*H*-pyrazole-3-carboxylate, 9b: white solid, (22.0 mg, 80% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 3:1. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.55-7.51 (comp, 5H), 5.69 (s, 2H), 4.45 (q, J = 7.1 Hz, 2H), 1.42 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 160.7, 148.5, 146.1, 140.1, 129.8, 129.3, 128.1, 109.8, 68.9, 61.7, 14.0. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{13}N_3O_4$ 298.0798; Found: 298.0796.



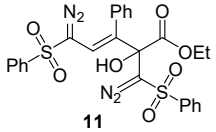
10a

Diethyl (4-Cyano-5-phenyl-1*H*-pyrazol-3-yl)phosphonate, 10a: white solid, (24.7 mg, 81% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 2:1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01 (d, J = 7.3 Hz, 2H), 7.60 – 7.44 (comp, 3H), 4.40-4.30 (comp, 4H), 1.47-1.43 (comp, 6H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 153.4, 130.0, 129.1, 128.9 (d, $J_{C\text{-}P}$ = 5 Hz), 126.9, 126.4 (d, $J_{C\text{-}P}$ = 140 Hz), 113.4, 93.8 (d, $J_{C\text{-}P}$ = 16 Hz), 64.4 (d, $J_{C\text{-}P}$ = 6.4 Hz), 16.2 (d, $J_{C\text{-}P}$ = 6.7 Hz). **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{16}N_3O_3P$ 306.1002; Found: 306.1001.



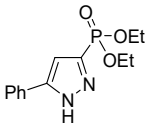
10b

Ethyl 4-cyano-5-phenyl-1*H*-pyrazole-3-carboxylate, 10b: white solid, (20.0 mg, 83% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 2:1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 – 7.87 (comp, 2H), 7.57-7.54 (comp, 3H), 4.53 (q, J = 7.1 Hz, 2H), 1.49 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 165.8, 148.1, 130.6, 129.5, 129.3, 126.9, 126.8, 112.9, 62.6, 14.0. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{11}N_3O_2$ 264.0743; Found: 264.0740.



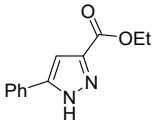
11

Ethyl (*E*)-5-diazo-2-(Diazo(phenylsulfonyl)methyl)-2-hydroxy-3-phenyl-5-(phenylsulfonyl)pent-3-enoate, 11: yellow liquid, (40.2 mg, 71% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 5:1. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.00 – 7.89 (comp, 2H), 7.78 – 7.73 (m, 1H), 7.72 – 7.69 (comp, 2H), 7.64 – 7.55 (comp, 5H), 7.46 – 7.39 (comp, 3H), 7.35 (dd, J = 8.3, 6.7 Hz, 2H), 6.74 (s, 1H), 4.14 – 4.01 (m, 2H), 2.96 (br s, 1H), 0.94 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.5, 145.5, 142.8, 137.9, 137.1, 134.6, 134.1, 133.7, 130.0, 129.3, 129.1, 128.8, 128.6, 128.3, 109.4, 74.7, 63.2, 13.3. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{22}N_4O_7S_2$ 589.0822; Found: 589.0825.



13a

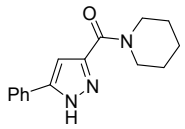
Diethyl (5-Phenyl-1*H*-pyrazol-3-yl)phosphonate, 13a:[7] White solid, (23.5 mg, 84% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 2:1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92 – 7.79 (comp, 2H), 7.46-7.44 (comp, 2H), 7.40 – 7.35 (m, 1H), 7.03 (s, 1H), 4.37 – 4.12 (comp, 4H), 1.41-1.37 (comp, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.9, 131.3, 129.1 (d, $J_{C\text{-}P}$ = 180 Hz), 129.0, 128.5, 125.9, 108.8 (d, $J_{C\text{-}P}$ = 20 Hz), 63.2 (d, $J_{C\text{-}P}$ = 5.3 Hz), 16.4 (d, $J_{C\text{-}P}$ = 7 Hz). **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{17}N_2O_3P$ 281.1050; Found: 281.1048.



13b

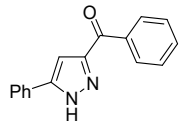
Ethyl 5-phenyl-1*H*-pyrazole-3-carboxylate, 13b: White solid (15.6 mg, 72% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 3:1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.76 (d, J = 7.6 Hz, 2H), 7.46-7.3 (comp, 2H), 7.38 (m, 1H), 7.13 (s, 1H),

4.43 (q, J = 7.2 Hz, 2H), 1.42 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.4, 150.6, 138.6, 131.3, 129.1, 128.8, 125.8, 105.8, 61.6, 14.5. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{12}N_2O_2$ 217.0972; Found: 217.0967.



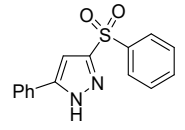
13c

(5-phenyl-1*H*-pyrazol-3-yl)(piperidin-1-yl)methanone, 13c: White solid (21.0 mg, 82% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 3:1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.77 (d, J = 7.6 Hz, 2H), 7.44-7.40 (comp, 3H), 6.83 (s, 1H), 3.85-3.82 (comp, 4H), 1.82 – 1.58 (comp, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.8, 149.3, 141.2, 131.5, 129.0, 128.6, 125.8, 103.9, 48.2, 43.9, 26.8, 25.8, 24.7. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{17}N_3O$ 256.1444; Found: 256.1442.



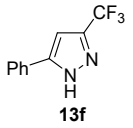
13d

Phenyl(5-phenyl-1*H*-pyrazol-3-yl)methanone, 13d: White solid (18.4 mg, 74% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 4:1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 11.26 (s, 1H), 8.09 (d, J = 7.6 Hz, 2H), 7.80 (d, J = 7.6 Hz, 2H), 7.66-7.64 (m, 1H), 7.56-7.54 (comp, 2H), 7.46-7.44 (comp, 2H), 7.39-7.37 (m, 1H), 7.14 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 185.7, 151.0, 137.2, 133.3, 131.4, 130.3, 129.6, 129.1, 128.8, 126.9, 125.9, 107.2. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{12}N_2O_2$ 249.1022; Found: 249.1018.



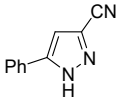
13e

5-phenyl-3-(Phenylsulfonyl)-1*H*-pyrazole, 13e: White solid, (22.7 mg, 80% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 3:1. **^{1}H NMR** (500 MHz, $CDCl_3$) 8.03 (d, J = 7.7 Hz, 2H), 7.56-7.52 (comp, 3H), 7.46-7.42 (comp, 5H), 7.01 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 152.9, 146.1, 140.7, 133.8, 129.7, 129.4, 129.4, 128.0, 127.9, 125.9, 104.0. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{12}N_2O_2S$ 285.0692; Found: 285.0688.



13f

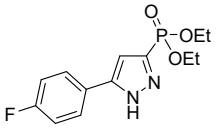
5-phenyl-3-(Trifluoromethyl)-1H-pyrazole, 13f: White solid (14.9 mg, 70% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 3:1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.61-7.56 (comp, 2H), 7.50-7.42 (comp, 3H), 6.80 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.9, 129.5, 129.4, 128.0, 125.7, 124.8, 121.1 (q, J_{C-F} = 270 Hz), 101.3. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{10}H_7F_3N_2$ 213.0634; Found: 213.0635.



13g

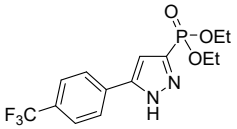
5-phenyl-1*H*-pyrazole-3-carbonitrile, 13g: White solid (13.2 mg, 78% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 3:1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 12.01 (br s, 1H), 7.68 – 7.56 (comp, 2H), 7.56 – 7.41 (comp, 3H), 6.92 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 145.1, 129.8, 129.4, 127.2, 125.9, 125.6, 113.6, 107.8. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{10}H_7N_3$ 170.0713; Found: 170.0710.



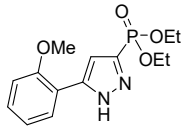
13h

Diethyl (5-(4-Fluorophenyl)-1H-pyrazol-3-yl)phosphonate, 13h:[7] White solid (25.9 mg, 87% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 3:1. **^{1}H NMR** (500 MHz, $CDCl_3$) 7.82 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 8.4 Hz, 2H), 6.97 (s, 1H), 4.37 – 4.12 (comp, 4H), 1.41-1.38 (comp, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.8 (d, $J_{C\text{-}F}$ = 247 Hz), 150.1, 128.8 (d, $J_{C\text{-}P}$ = 161 Hz), 127.9, 127.6 (d, $J_{C\text{-}F}$ = 8.0 Hz), 115.8 (d, $J_{C\text{-}F}$ = 21 Hz), 108.5 (d, $J_{C\text{-}P}$ = 20 Hz), 63.2 (d, $J_{C\text{-}P}$ = 5.3 Hz), 16.3 (d, $J_{C\text{-}P}$ = 6.5 Hz). **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{16}FN_2O_3P$ 299.0955; Found: 299.0951.



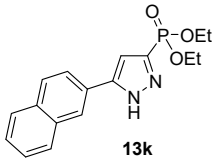
13i

Diethyl (5-(4-(Trifluoromethyl)phenyl)-1*H*-pyrazol-3-yl)phosphonate, 13i:[7] White solid (30.6 mg, 88% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 3:1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 8.0 Hz, 2H), 7.08 (s, 1H), 4.37 – 4.14 (comp, 4H), 1.40 (t, J = 7.1 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.2, 135.3, 133.8 (d, $J_{C\text{-}P}$ = 215 Hz), 130.1 (q, $J_{C\text{-}F}$ = 32 Hz), 126.0, 125.8 (q, $J_{C\text{-}F}$ = 4.1 Hz), 124.1 (q, $J_{C\text{-}F}$ = 173 Hz), 109.1 (d, $J_{C\text{-}P}$ = 20 Hz), 63.3 (d, $J_{C\text{-}P}$ = 5.2 Hz), 16.3 (d, $J_{C\text{-}P}$ = 6.3 Hz). **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{16}F_3N_2O_3P$ 349.0923; Found: 309.0917.



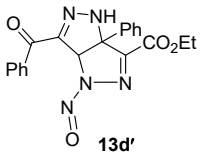
13j

Diethyl (5-(2-Methoxyphenyl)-1H-pyrazol-3-yl)phosphonate, 13j:[7] White solid (25.4 mg, 82% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 3:1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.69 (d, J = 7.8 Hz, 1H), 7.35 (t, J = 7.8 Hz, 1H), 7.11 (s, 1H), 7.10 – 7.01 (comp, 2H), 4.28 – 4.13 (comp, 4H), 4.01 (s, 3H), 1.38-1.34 (comp, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.8, 142.5, 141.3 (d, $J_{C\text{-}P}$ = 182 Hz), 129.9, 128.1, 121.7, 120.5, 116.7, 108.6 (d, $J_{C\text{-}P}$ = 21 Hz), 62.6 (d, $J_{C\text{-}P}$ = 5.3 Hz), 55.9, 16.3 (d, $J_{C\text{-}P}$ = 6.1 Hz). **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{19}N_2O_4P$ 311.1155; Found: 311.1145.



13k

Diethyl (5-(Naphthalen-2-yl)-1*H*-pyrazol-3-yl)phosphonate, 13k: White solid (28.0 mg, 85% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 2:1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.37 – 8.19 (m, 1H), 7.92 (d, J = 7.8 Hz, 2H), 7.65 (d, J = 7.8 Hz, 1H), 7.55-7.52 (comp, 3H), 7.04 (s, 1H), 4.28-4.26 (comp, 4H), 1.42-1.38 (comp, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.6, 136.9 (d, $J_{C\text{-}P}$ = 220 Hz), 133.8, 131.2, 129.3, 128.5, 128.4, 127.4, 126.8, 126.2, 125.4, 125.3, 112.2 (d, $J_{C\text{-}P}$ = 21 Hz), 63.0 (d, $J_{C\text{-}P}$ = 5.5 Hz), 16.3 (d, $J_{C\text{-}P}$ = 6.8 Hz). **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{19}N_2O_3P$ 331.1206; Found: 331.1200.



Ethyl 6-benzoyl-1-nitroso-3a-phenyl-1,3a,4,6a-tetrahydropyrazolo[4,3-c]pyrazole-3-carboxylate, 13d': White solid, (16.8 mg, 43% yield) 0.1 mmol scale reaction. Flash column chromatography conditions: hexane:ethyl acetate = 2:1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.7 Hz, 2H), 7.78 (s, 1H), 7.61-7.59 (m, 1H), 7.47-7.42 (comp, 5H), 7.19 (d, *J* = 7.0 Hz, 2H), 6.32 (s, 1H), 4.39 (t, *J* = 7.0 Hz, 2H), 1.37 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 185.6, 160.5, 151.3, 142.2, 135.9, 134.6, 133.2, 130.0, 129.8, 129.7, 128.3, 124.9, 81.8, 74.2, 63.3, 14.0. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{70}H_{17}N_5O_4$ 414.1173; Found: 414.1173.

10. Crystallographic data

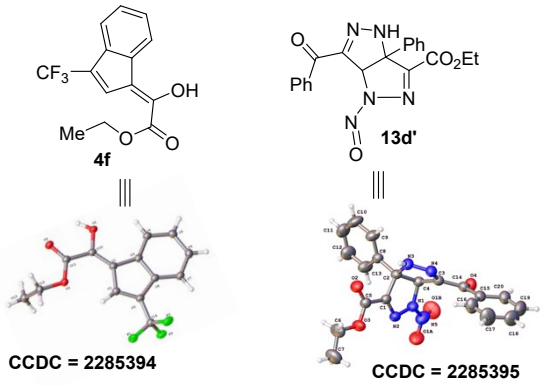


Figure S1. ORTEP drawing of **4f, 13d'** showing thermal ellipsoids at the 50% probability level.

Single crystals of $C_{20}H_{16}N_5O_4$(**13d'**) were prepared by slow evaporation of ethylacetate/hexane (5:1) solution. A suitable dark yellow plate-like crystal, with dimensions of 0.233 mm × 0.135 mm × 0.082 mm, was mounted in paratone oil onto a nylon loop. Single crystals of $C_{14}H_{11}F_3O_3$(**4f**) were prepared by slow evaporation of a ethylacetate/hexane (5:1) solution. A suitable dark yellow plate-like crystal, with dimensions of 0.119 mm × 0.103 mm × 0.091 mm, was mounted in paratone oil onto a nylon loop. All data were collected at 100.0(1) K and 298(1) K for compounds 1 and 2 respectively, using a XtaLAB Synergy/ Dualflex, HyPix fitted with CuKα radiation (λ = 1.54184 Å). Data collection and unit cell refinement were performed using *CrysAlisPro* software.[8] The total number of data were measured in the 9.1° < 2θ < 144.7° and 9.6° < 2θ < 151.6° for compounds (**13d'**) and (**4f**) respectively, using ω scans. Data processing and absorption correction, giving minimum and maximum transmission factors (0.470, 1.000 for compound (**13d'**), 0.649, 1.00 for compound (**4f**)) were accomplished with *CrysAlisPro*[9] and *SCALE3 ABSPACK*[10] respectively. The structure, using Olex2,[11] was solved with the ShelXT[12] structure solution program using direct methods and refined (on F^2) with the ShelXL refinement package using full-matrix, least-squares techniques. All non-hydrogen

atoms were refined with anisotropic displacement parameters. All carbon bound hydrogen atom positions were determined by geometry and refined by a riding model. The oxygen bound H atom, H1 on compound 2, was determine by electron density map.

Table S4: Crystallographic data and structure refinement for **4f and 13d'**

Compound number	**13d'**	**4f**
Identification code	Hpd630(1)	Hpd718(2)
Empirical formula	$C_{20}H_{16}N_5O_4$	$C_{14}H_{11}F_3O_3$
Formula weight	390.38	284.23
Crystal system	Monoclinic	Triclinic
Space group	*P2₁/n*	*P-1*
a (Å)	10.4348(2)	7.1427(3)
b (Å)	9.9373(2)	9.1744(4)
c (Å)	18.8362(3)	9.7896(4)
α (°)	90	97.571(3)
β (°)	99.256(2)	107.127(4)
γ (°)	90	95.412(4)
Volume (Å^3)	1927.76(6)	601.69(5)
Z	4	2
ρ (calc.)	1.345	1.569
λ	1.54184	1.54184
Temp. (K)	100.0(1)	100.0(1)
F(000)	812	292
μ (mm^{-1})	0.807	1.220
T_{min}, T_{max}	0.470, 1.000	0.649, 1.000
$2\theta_{range}$ (°)	9.1 to 144.7	9.6 to 151.6
Reflections collected	18614	9968
Independent reflections	3713 [R(int) = 0.0435]	2315 [R(int) = 0.0275]

Completeness	99.9%	98.8%
Data / restraints / parameters	3713 / 1 / 275	2315 / 0 / 185
Observed data [I > 2σ(I)]	3170	2023
wR(F^2 all data)	0.1211	0.1034
R(*F* obsd data)	0.0510	0.0365
Goodness-of-fit on F^2	1.01	1.06
largest diff. peak and hole (e Å^{-3})	0.64 / -0.21	0.28 / -0.24

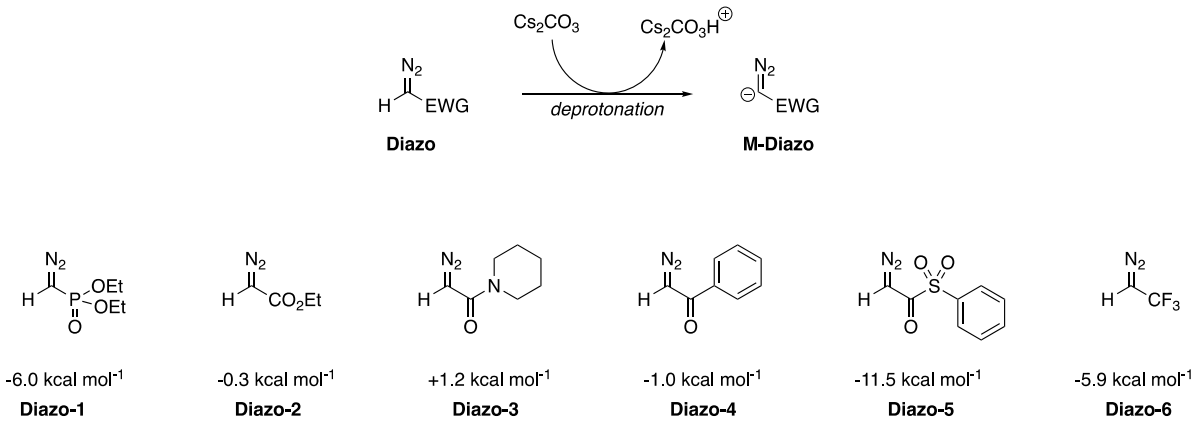
$wR_2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$

$R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$

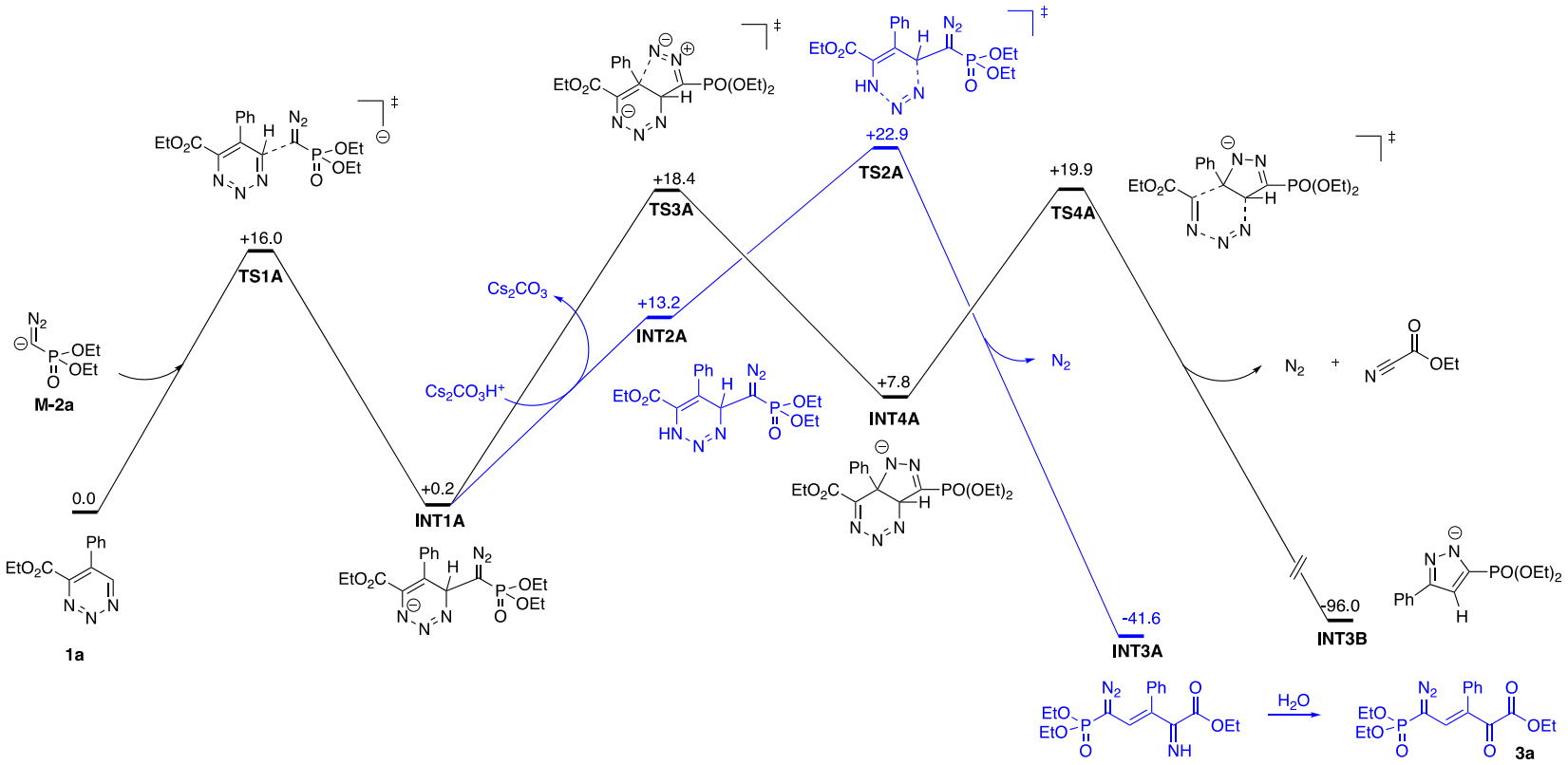
11. Computational Details

All the calculations were performed with the Gaussian 16 program.[13] Structure optimization was performed usi5g the B3LYP functional,[14] with Grimme's dispersion correction (denoted B3LYP-D3BJ)[14] and the def2-svp basis set[16] for all atoms. Furthermore, we have also considered the solvent effects in acetonitrile (ε = 35.688) using the SMD solvation model,[17] for all structure optimizations. Harmonic vibrational frequencies were calculated at the same level for all stationary points to confirm them as a local minima or transition structures. Key transition-state structures were confirmed to connect corresponding reactants and products by intrinsic reaction coordinate (IRC) calculations.[18] To improve the calculation accuracy, single point calculations were performed using the M06-2X[19] functional and the def2-tzvpp basis set[16] for all atoms. Furthermore, we have also considered the solvent effects in acetonitrile (ε = 35.688) using the SMD solvation model,[17] for all single-point energy calculations. The CYL View software was employed to show the 3D structures of the studied species.[20]

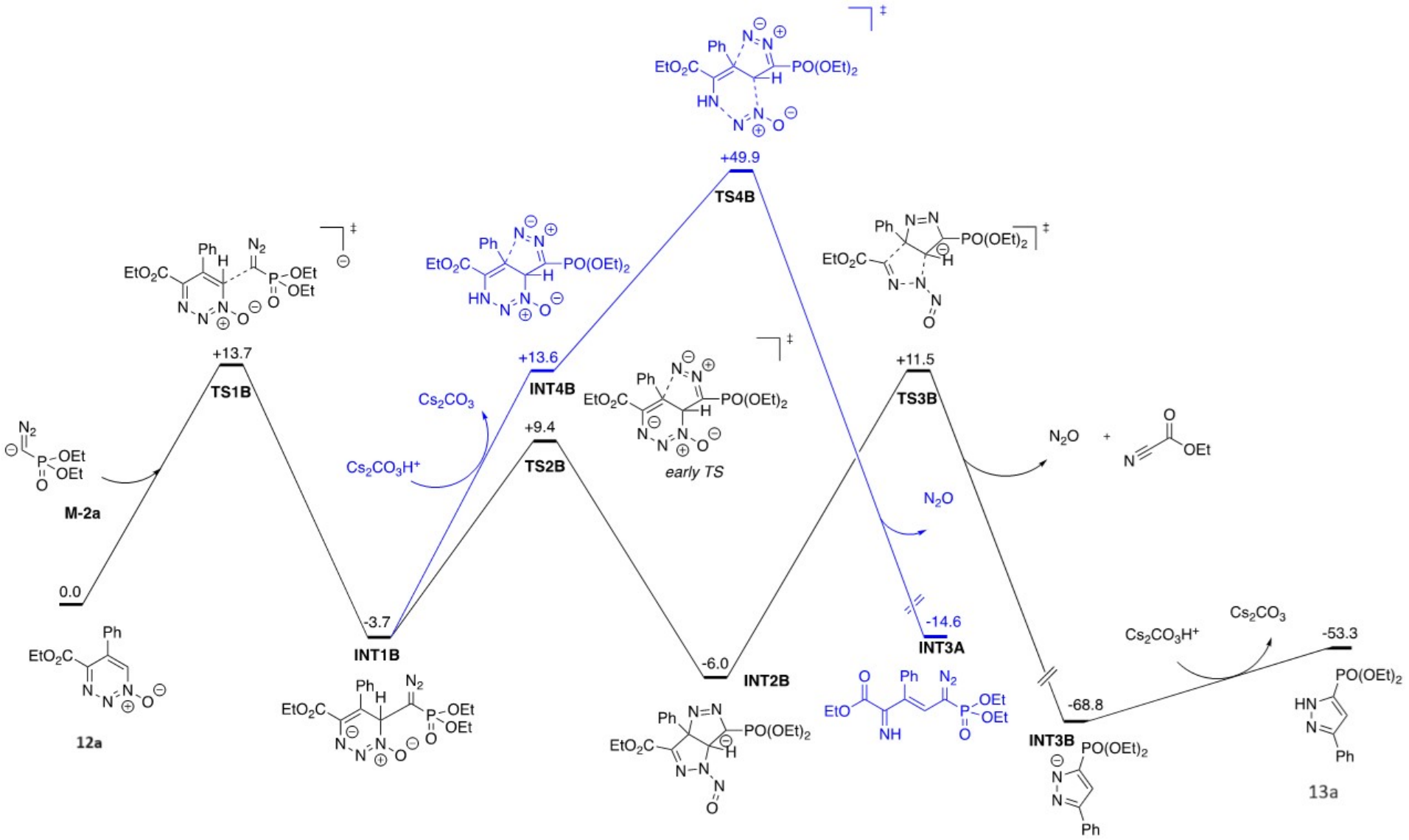
12. Schemes of Computed Reaction Pathways



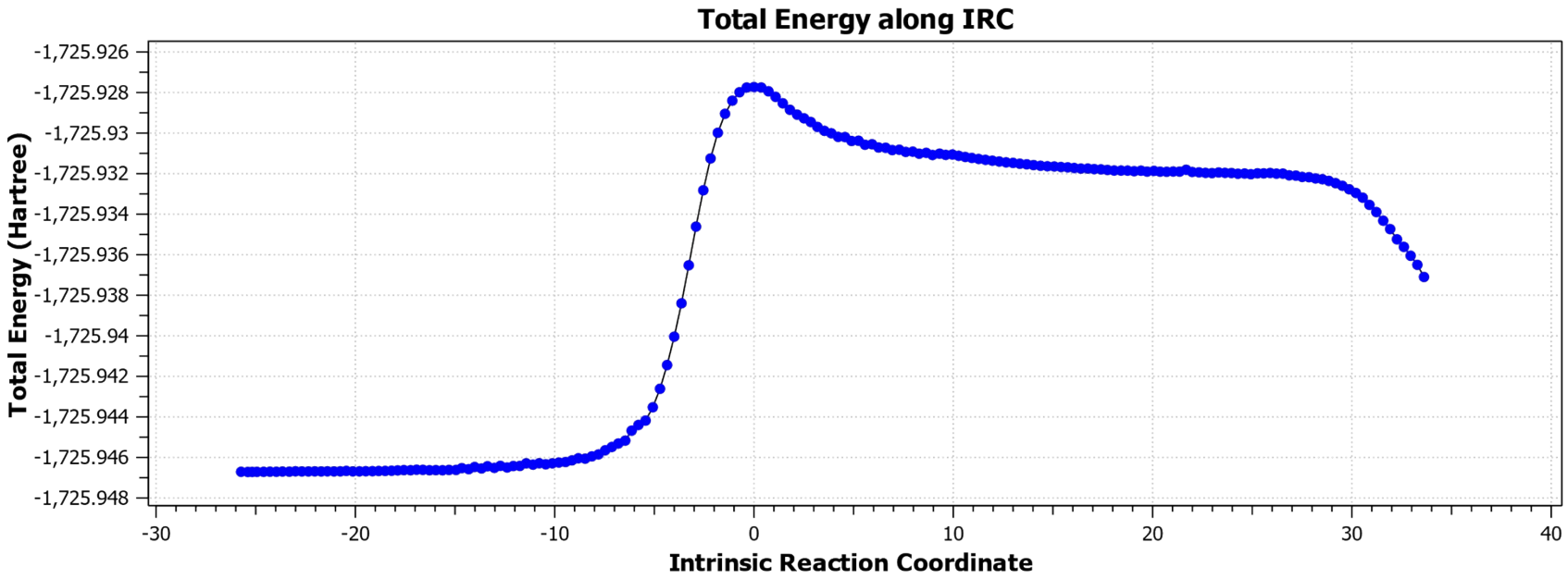
Scheme S1: Calculated deprotonations of diazoalkanes.

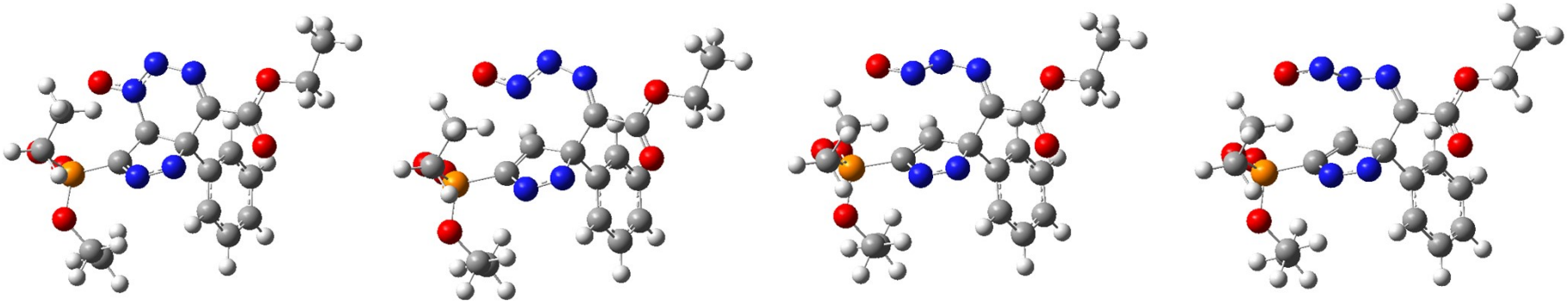


Scheme S2: Calculated reaction pathway for 1,2,3-triazines.



Scheme S3: Calculated reaction pathway for 1,2,3-triazine-1-oxides.





N = -20 N = 0 N = 20 N = 34

Scheme S4: Calculated IRC path for early TS **TS2B**.

13. Computed Energies of all Stationary Points

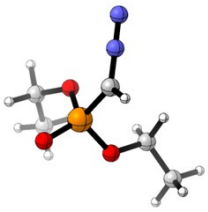
Table S5. Calculated Energies of all Stationary Points for Reaction Pathways.

Thermal correction to Gibbs free energies (***TCG***, in Hartree), thermal correction to enthalpies (***TCH***, in Hartree), sum of electronic and thermal free energies (***G***, in Hartree), sum of electronic and thermal enthalpies (***H***, in Hartree), at the B3LYP-D3BJ / def2-2svp level in acetonitrile, single point energies in acetonitrile computed at the M06-2X / def2-tzvpp level (E_{sol}, in Hartree).

Name	*TCG* / Hartree	*TCH* / Hartree	*G* / Hartree	*H* / Hartree	E_{sol} /Hartree
Diazo-1 (2a)	0.127403	0.185823	-873.11362	-873.0552	-873.720577
M-Diazo-1 (M-2a)	0.118013	0.174116	-872.621872	-872.565769	-873.228643
Diazo-2	0.070423	0.113981	-415.590093	-415.546535	-415.948776
M-Diazo-2	0.058984	0.101872	-415.090436	-415.047548	-415.446412
Diazo-3	0.146936	0.194035	-512.333293	-512.286194	-512.797417
M-Diazo-3	0.134515	0.181699	-511.830778	-511.783593	-512.291582
Diazo-4	0.089625	0.13505	-492.732448	-492.687022	-493.13561
M-Diazo-4	0.078213	0.122871	-492.235725	-492.191067	-492.634361
Diazo-5	0.093447	0.147958	-1041.070743	-1041.016232	-1041.74839
M-Diazo-5	0.080548	0.13556	-1040.592923	-1040.537911	-1041.262276
Diazo-6	0.006329	0.045464	-485.418766	-485.379631	-485.825539
M-Diazo-6	-0.004711	0.033331	-484.927077	-484.889035	-485.332487
Cs_2CO_3	-0.022673	0.024011	-304.123531	-304.076847	-304.194111
$Cs_2CO_3H^+$	-0.012686	0.036619	-304.629116	-304.579812	-304.695565
1a	0.1715	0.231266	-777.875861	-777.816095	-778.544918
TS1A	0.312654	0.406292	-1650.486889	-1650.393251	-1651.771204
INT1A	0.313259	0.407984	-1650.506565	-1650.41184	-1651.796996
INT2A	0.328331	0.422164	-1650.99044	-1650.896607	-1652.282738
TS2A	0.324822	0.418491	-1650.971828	-1650.878159	-1652.263793
N_2	-0.012758	0.008987	-109.447723	-109.425978	-109.530115
INT3A	0.316546	0.408978	-1541.611439	-1541.519007	-1542.815454
TS3A	0.314678	0.405553	-1650.484648	-1650.393772	-1651.769359
INT4A	0.316736	0.407132	-1650.49415	-1650.403755	-1651.788406
TS4A	0.313308	0.404499	-1650.476036	-1650.384845	-1651.765685
10a	0.176001	0.236448	-852.992702	-852.932255	-853.722719
TS1B	0.318022	0.411818	-1725.609757	-1725.515961	-1726.953635
INT1B	0.319483	0.413519	-1725.631384	-1725.537348	-1726.982725
TS2B	0.320275	0.410708	-1725.607454	-1725.517021	-1726.962595
INT2B	0.317709	0.411781	-1725.629072	-1725.535001	-1726.984656
TS3B	0.314571	0.409473	-1725.602857	-1725.507955	-1726.953549
Byproduct-1	0.062588	0.112634	-544.74381	-544.693764	-545.195046
Byproduct-2	0.056258	0.097029	-360.310076	-360.269304	-360.620405
N_2O	-0.006772	0.014433	-184.527158	-184.505953	-184.666414
INT3B	0.225909	0.296536	-1180.87231	-1180.801683	-1181.755828
11a	0.240094	0.310791	-1181.350878	-1181.28018	-1182.236711
INT4B	0.333087	0.427743	-1726.108566	-1726.01391	-1727.460105
TS4B	0.329245	0.423335	-1726.057412	-1725.963322	-1727.398612

14. 3D Structures and Coordinates of all Stationary Points

Diazo-1 (2a)



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O -0.28228100 -0.78526100 2.10544900

C 1.53553500 1.29491100 -0.64261900

C 2.81866800 2.05962200 -0.41311800

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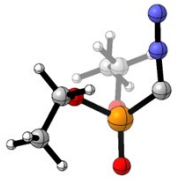
M-Diazo-1 (M-2a)



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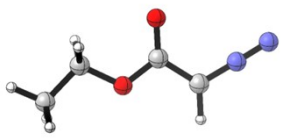
C -0.02248600 1.31913100 1.18539100

Diazo-2



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O	-0.37912500	1.39506800	-0.00012800
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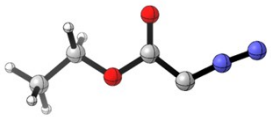
H	-1.14915600	-1.88171900	0.00056200

M-Diazo-2

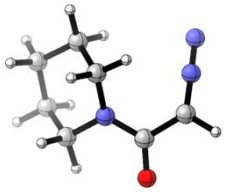


Charge: -1

Spin: 1

N	-2.52658400	-0.36047800	-0.00002100
N	-3.64750400	-0.07179600	0.00051800
C	-1.33353700	-0.80996700	-0.00065900
C	-0.26485200	0.15882200	-0.00024900
O	-0.33718700	1.38662700	-0.00055800
O	0.96145700	-0.45776200	0.00040800
C	2.10378600	0.39436800	0.00074800
C	3.34118400	-0.47859000	-0.00035100
H	2.08121500	1.05350800	0.88622000
H	2.08062500	1.05504100	-0.88352800
H	4.24766100	0.14753600	-0.00003900
H	3.36798200	-1.12523200	0.89167100
H	3.36748200	-1.12364400	-0.89353700

Diazo-3

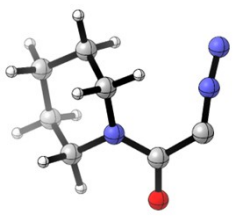


Charge: 0

Spin: 1

N	-2.24504900	-0.98995900	-0.27245600
N	-2.18210300	-2.07666700	-0.60487600
C	-2.29210300	0.25153500	0.10754200
H	-3.28665900	0.69602800	0.16827300
C	-1.09890900	1.13630000	0.11088200
O	-1.25564600	2.32739900	-0.15223900
C	1.33679200	1.34893400	0.07815400
C	0.38608400	-0.67860600	1.05750700
C	2.27031800	0.51530600	-0.80444500
H	1.84544100	1.60825200	1.02568200
H	1.04079200	2.28432700	-0.41017700
C	1.27203900	-1.58152800	0.19914300
H	0.91346600	-0.44816800	2.00228900
H	-0.55122400	-1.16738400	1.34250400
C	2.56686800	-0.85069200	-0.17567700
H	3.20427900	1.07549400	-0.97517500
H	1.78917100	0.37460800	-1.78827600
H	1.49275500	-2.51004900	0.75021400
H	0.71879000	-1.86301900	-0.71384100
H	3.17314300	-1.46582400	-0.86034400
H	3.17022200	-0.70348200	0.73848500
N	0.12550300	0.58841700	0.37728100

M-Diazo-3

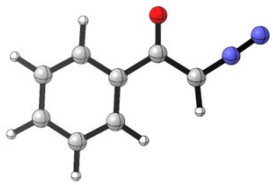


Charge: -1

Spin: 1

N	-2.34057800	-0.80452100	-0.23050200
N	-2.49789200	-1.91859900	-0.53917900
C	-2.29801200	0.41464300	0.09996500
C	-1.06668900	1.19993900	0.08404900
O	-1.06251400	2.40453300	-0.21065400
C	1.40172500	1.26288000	0.18125400
C	0.30145000	-0.73226000	1.02550900
C	2.27503000	0.42787400	-0.76282200
H	1.93951900	1.41778300	1.13837100
H	1.17403200	2.24901800	-0.23938100
C	1.11739300	-1.64844500	0.10906500
H	0.84381000	-0.61804400	1.98589800
H	-0.67206800	-1.17042100	1.26327400
C	2.46388800	-0.99823100	-0.23176600
H	3.25183100	0.92190600	-0.90093800
H	1.78503000	0.39241100	-1.75223700
H	1.27057900	-2.62588000	0.59693500
H	0.53629700	-1.82905900	-0.81201900
H	3.01921900	-1.61207600	-0.96048000
H	3.08169900	-0.96026100	0.68453100
N	0.13867800	0.58597100	0.43393100

Diazo-4

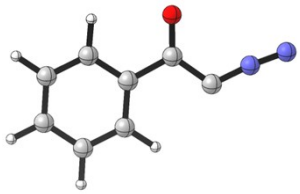


Charge: 0

Spin: 1

N	3.14238800	0.46656200	0.00022600
N	4.23275900	0.16744200	0.00010400
C	1.86377900	0.74440600	0.00031000
H	1.60638400	1.80184800	0.00087800
C	0.94973700	-0.39591100	-0.00017300
O	1.37064800	-1.55019800	-0.00061200
C	-0.52200500	-0.10311600	-0.00004900
C	-1.05953800	1.19528600	-0.00026600
C	-1.39639100	-1.20401900	0.00026800
C	-2.44335100	1.38470300	-0.00023200
H	-0.41025900	2.07163400	-0.00051200
C	-2.77723800	-1.01397400	0.00033500
H	-0.96669200	-2.20702100	0.00044000
C	-3.30446100	0.28285500	0.00006400
H	-2.85040900	2.39860000	-0.00044500
H	-3.44670400	-1.87769500	0.00058400
H	-4.38672400	0.43480300	0.00009500

M-Diazo-4



Charge: -1

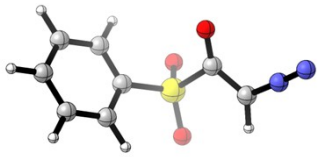
Spin: 1

N	3.13652400	-0.47211500	0.00008000
N	4.29014600	-0.39643000	-0.00059000
C	1.87905300	-0.68519300	0.00050300
C	0.98433200	0.44566200	0.00028800
O	1.32711000	1.64215600	0.00010800
C	-0.49528200	0.12219500	0.00012800
C	-1.41471500	1.18446600	-0.00004100
C	-0.98799000	-1.19307500	-0.00000200
C	-2.78975700	0.94207000	-0.00015400
H	-1.01821500	2.20156600	-0.00011100
C	-2.36312300	-1.44012300	-0.00002700
H	-0.27539600	-2.02008700	-0.00013700
C	-3.26933700	-0.37311500	-0.00011600
H	-3.49254000	1.77985000	-0.00044200

H -2.73114000 -2.46970600 0.00011700

H -4.34536500 -0.56638000 -0.00018800

Diazo-5



Charge: 0

Spin: 1

N -3.58368400 -1.01737700 0.16839200

N -4.41479900 -1.71360400 -0.13247600

C -2.58560300 -0.21521100 0.47700600

H -2.64581600 0.32682300 1.42067700

C -1.49910300 -0.11559100 -0.44479300

O -1.29893100 -0.66975600 -1.49777300

S -0.22166800 1.16465000 0.15178000

O -0.17500900 2.20535900 -0.89226400

O -0.53018300 1.52508900 1.55181000

C 1.29978800 0.23153600 0.10547400

C 2.03523500 0.20026300 -1.08222800

C 1.69615300 -0.46767800 1.24918200

C 3.20689900 -0.55823100 -1.11954400

H 1.69642100 0.76365100 -1.95248400

C 2.87131800 -1.21953300 1.19575200

H 1.09830900 -0.41627800 2.16055300

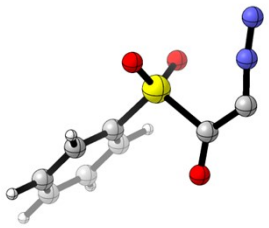
C 3.62161200 -1.26498500 0.01499900

H 3.79910100 -0.59530100 -2.03659300

H 3.20349000 -1.76922400 2.07925000

H 4.53975500 -1.85616100 -0.02056600

M-Diazo-5



Charge: -1

Spin: 1

N 3.43915600 0.21610200 -0.00114300

N 4.19111600 -0.65265700 0.00063900

C 2.74059800 1.28927800 -0.00332200

C 1.34222200 1.28375600 -0.00251500

O 0.50929700 2.16800100 -0.00368100

S 0.59566700 -0.53570900 0.00151000

O 0.96172900 -1.20956500 -1.27102000

O 0.96120800 -1.20311600 1.27758000

C -1.18626000 -0.28016300 0.00057300

C -1.85632900 -0.17169900 -1.21975700

C -1.85672200 -0.16594200 1.22015200

C -3.23465600 0.05590500 -1.21486200

H -1.30188400 -0.27199500 -2.15449500

C -3.23504600 0.06162300 1.21375200

H -1.30253800 -0.26179400 2.15550400

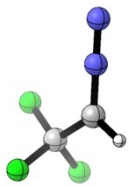
C -3.92147400 0.17338300 -0.00093400

H -3.77490500 0.13968000 -2.16094100

H -3.77556400 0.14989300 2.15927200

H -4.99954800 0.35203100 -0.00152900

Diazo-6



Charge: 0

Spin: 1

N 1.69015200 -0.25869100 0.00371400

N 2.70732600 0.24573900 0.00018400

C 0.53203400 -0.84069400 0.00367500

H 0.49297600 -1.93034300 0.02912400

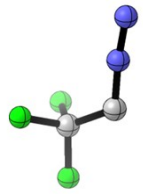
C -0.69786800 -0.01169600 -0.00120500

F -1.51330800 -0.32139900 -1.03136800

F -1.44228000 -0.18416200 1.11383300

F -0.40889100 1.29837700 -0.09037900

M-Diazo-6



Charge: -1

Spin: 1

N 1.67065800 -0.26442900 0.00058000

N 2.74153100 0.17939200 -0.00028600

C 0.55788400 -0.88030600 0.00217900

C -0.64862200 -0.07499000 -0.00009600

F -1.77446600 -0.83734000 0.00153100

F -0.79873900 0.77254600 1.08094300

F -0.79800600 0.76779800 -1.08409100

Cs_2CO_3

Charge: 0

Spin: 1

C 0.00001200 1.26382100 0.00025600

O 1.12190800 1.89351900 0.07606100

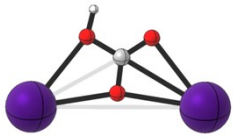
O -1.12184800 1.89347600 -0.07633600

O -0.00001400 -0.05037900 0.00104500

Cs -2.89825700 -0.34068500 0.00422000

Cs 2.89824900 -0.34069400 -0.00436000

$Cs_2CO_3H^+$



Charge: +1

Spin: 1

C 0.11303200 1.32778100 0.00258000

O 1.15882500 2.00303900 -0.00238800

O -1.09234000 2.03543300 0.00017500

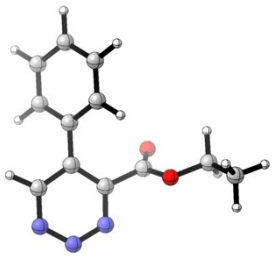
O -0.02930300 0.08314800 0.00927600

Cs -3.02239000 -0.40186100 -0.00065700

Cs 3.02034700 -0.39666300 -0.00054400

H -0.86329300 2.97919300 -0.00594300

1a



Charge: 0

Spin: 1

C 0.67377300 1.05384200 0.16595400

C -0.70289700 1.12613900 -0.09816000

C -1.13838000 2.42778100 -0.37838900

H -2.18818300 2.63702700 -0.60299300

C -1.61455500 -0.03279700 -0.11580300

C -1.20636300 -1.25637100 -0.67849500

C -2.91566900 0.08128100 0.40581500

C -2.07835000 -2.34413800 -0.70780600

H -0.21374600 -1.35056000 -1.12378600

C -3.78199500 -1.01266600 0.38190100

H -3.24175700 1.02245500 0.85330800

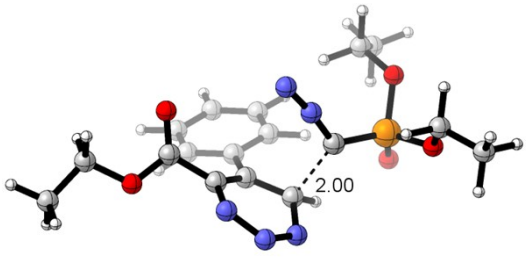
C -3.36614900 -2.22687400 -0.17366200

H -1.75250800 -3.28603800 -1.15506100

H -4.78595000 -0.91657100 0.80182600

H -4.04664300 -3.08154400 -0.19357200
C 1.34692700 -0.20380500 0.66102500
O 0.98957900 -0.77790500 1.66209500
O 2.36344000 -0.55619100 -0.11189200
C 3.11581800 -1.73266300 0.28314600
C 4.18777800 -1.96578600 -0.75310900
H 2.41705900 -2.58016700 0.35713700
H 3.53739200 -1.55196000 1.28388800
H 4.77648800 -2.85373800 -0.47528300
H 3.74633300 -2.14079200 -1.74670800
H 4.87043300 -1.10407400 -0.81683700
N 1.46931200 2.12778400 0.09716700
N 0.97706700 3.31189000 -0.19045300
N -0.31247700 3.47390900 -0.41214900

TS1A



Charge: -1

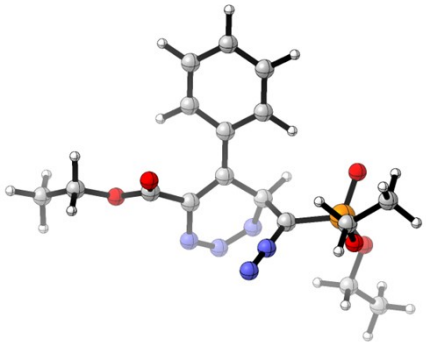
Spin: 1

C 2.01312800 -1.12861200 0.26810900
C 1.15184100 -0.17063300 0.79716500
C 0.00410200 -0.74247500 1.43194600
H -0.67045600 -0.10803200 2.00846900
C 1.33354300 1.28849400 0.70187100
C 2.61586300 1.86862100 0.61608100
C 0.21576500 2.14705100 0.73529400
C 2.77190700 3.25075100 0.51730700
H 3.50553400 1.23896800 0.66431900
C 0.37502400 3.53055500 0.63286700
H -0.78663700 1.73356000 0.84196400
C 1.65110800 4.08930300 0.51423300
H 3.77645500 3.67656600 0.45451400
H -0.50802900 4.17390500 0.64766300
H 1.77439600 5.17225000 0.43488500
C 3.14344600 -0.80770600 -0.67675200
O 3.00111300 -0.28182300 -1.75582300
O 4.31856100 -1.20526100 -0.18470100
C 5.48150900 -0.99471800 -1.01683100
C 6.68962500 -1.49395600 -0.26057600
H 5.55573100 0.07886100 -1.25169400
H 5.33605000 -1.53478800 -1.96549700
H 7.59322800 -1.34972300 -0.87312200
H 6.82072500 -0.94249700 0.68379700
H 6.59543100 -2.56680000 -0.03011500
N 1.89068000 -2.44975100 0.53145500
N 0.97726700 -2.84718000 1.40268500
N 0.07554500 -2.04205000 1.87916200
P -2.99702800 -0.00349700 0.30618000
O -4.18164700 -1.09968600 0.43593300
O -3.53373900 0.81221600 -1.00587200
O -2.91597100 0.79995600 1.56946600
C -4.45589700 -2.02862000 -0.62400900
C -5.36829700 -3.11173000 -0.09392400
H -3.50668200 -2.45903100 -0.98905700
H -4.92370500 -1.48718600 -1.46312200
H -5.60187900 -3.83088900 -0.89506100
H -4.88680400 -3.65649400 0.73369100
H -6.31421700 -2.68343300 0.27436800
C -2.81138900 1.95235700 -1.50545100
C -3.22020600 3.22741200 -0.79409900
H -3.04449200 2.00622300 -2.57994400
H -1.72568300 1.78377300 -1.41489900
H -2.68032900 4.08747900 -1.22177000
H -4.30163900 3.40509300 -0.90807500
H -2.99213900 3.16323700 0.28001900
N -0.94612900 -0.79097800 -1.23954900

N -0.29073300 -0.80195900 -2.19004300

C -1.50980200 -0.79748900 -0.10690500

INT1A



Charge: -1

Spin: 1

C -1.84615500 -0.94422900 -0.11329500

C -1.09992500 0.08024200 -0.65619900

C 0.25793200 -0.37710600 -1.07786400

H 0.70455600 0.30825000 -1.81051300

C -1.50297800 1.48202500 -0.78612400

C -2.85786100 1.85928400 -0.93047300

C -0.53276200 2.51099000 -0.79112400

C -3.22891300 3.19906500 -1.03248400

H -3.62737600 1.08725500 -0.99539700

C -0.90819900 3.85184100 -0.90466100

H 0.52639500 2.26299600 -0.68938400

C -2.25630900 4.20716000 -1.01753500

H -4.28515700 3.45917000 -1.14362300

H -0.13727200 4.62746900 -0.89900000

H -2.54717300 5.25707000 -1.10451700

C -3.05449500 -0.70487700 0.74252800

O -3.07109300 0.02593200 1.71055600

O -4.11673500 -1.41674200 0.34309500

C -5.31270000 -1.30331000 1.13838100

C -6.37512200 -2.17325000 0.50759600

H -5.61713600 -0.24490700 1.17499600

H -5.08526200 -1.61625800 2.17011400

H -7.30390800 -2.11113100 1.09602700

H -6.59489800 -1.84506300 -0.52071600

H -6.05491900 -3.22673000 0.47667600

N -1.53380100 -2.27051200 -0.27734100

N -0.64162800 -2.55748900 -1.22493000

N 0.15994100 -1.70097700 -1.73665600

P 2.90876600 0.29166700 -0.14074300

O 3.79377700 -0.72465000 -1.01888200

O 3.59798900 0.15567900 1.31629900

O 2.88793600 1.65132000 -0.75591900

C 3.75063600 -2.15482600 -0.81039600

C 4.83517200 -2.78877000 -1.64939700

H 2.75258500 -2.51714200 -1.10458200

H 3.89781700 -2.37228200 0.26029700

H 4.81008000 -3.88257400 -1.52229200

H 4.68667500 -2.55989800 -2.71658000

H 5.83022200 -2.42550100 -1.34771200

C 3.27195900 1.09285800 2.37065100

C 4.23344000 2.26164100 2.37017200

H 3.33242900 0.51614900 3.30539200

H 2.23047800 1.43746600 2.25677100

H 4.00214800 2.93734300 3.20927600

H 5.27238400 1.91268100 2.48015500

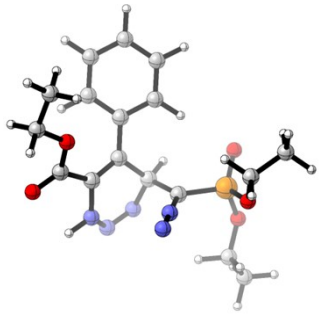
H 4.14794400 2.82605900 1.42940400

N 1.03020300 -1.03671700 1.17863100

N 0.80154200 -1.54842500 2.17115600

C 1.28946700 -0.42189000 0.06841400

INT2A

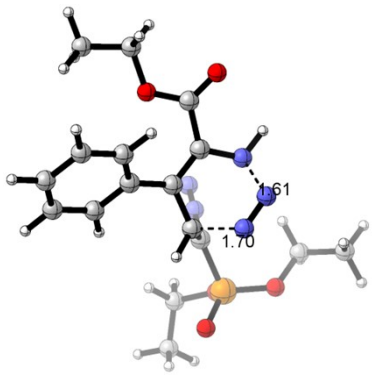


Charge: 0

Spin: 1

C -1.60672900 -1.59787100 -0.17421700
C -1.07995900 -0.48805300 -0.76362200
C 0.37706400 -0.64640200 -1.11864000
H 0.66620400 0.06468100 -1.90058000
C -1.77667700 0.76531100 -1.09346700
C -3.11372600 0.77262200 -1.53849600
C -1.08791000 1.99272900 -1.01349200
C -3.75504100 1.97073600 -1.84822700
H -3.64741100 -0.17094400 -1.66392000
C -1.73464700 3.19151700 -1.32218900
H -0.03954000 2.01511500 -0.70909900
C -3.07109500 3.18719100 -1.73203800
H -4.79146500 1.95538700 -2.19429000
H -1.18763400 4.13428900 -1.24351600
H -3.57517900 4.12577500 -1.97546000
C -2.91197300 -1.78437500 0.52413600
O -3.40186500 -2.88348100 0.69113000
O -3.41585000 -0.65286200 0.99463300
C -4.71119500 -0.70946200 1.63373900
C -5.08830000 0.69824000 2.02906400
H -4.64408100 -1.38080600 2.50382500
H -5.43109800 -1.14723300 0.92447600
H -6.07012200 0.68846600 2.52715200
H -4.35028700 1.12214600 2.72798300
H -5.15273900 1.35323900 1.14647800
N -0.85998000 -2.77432200 -0.21522900
N 0.08529000 -2.98672500 -1.15324200
N 0.65555600 -2.00345800 -1.67540900
P 2.73146300 0.71171600 -0.13792800
O 3.93274800 -0.14459600 -0.76634700
O 3.23640600 0.94125600 1.37647500
O 2.42711800 1.91601000 -0.96177400
C 4.29791000 -1.45394600 -0.27204200
C 5.47800600 -1.94946900 -1.07353600
H 3.43169000 -2.12677300 -0.38334200
H 4.54271400 -1.37755100 0.79954000
H 5.76940900 -2.95127900 -0.72075800
H 5.22213100 -2.01789600 -2.14256600
H 6.34155300 -1.27543500 -0.96063500
C 2.56232800 1.88122600 2.25183600
C 3.16769900 3.26233900 2.13019400
H 2.68272700 1.47034000 3.26465400
H 1.48411600 1.89707300 2.02122100
H 2.67624900 3.94789000 2.83899200
H 4.24470700 3.23808500 2.35918700
H 3.03159500 3.65307500 1.11056000
N 1.10247900 -0.90279100 1.21509600
N 0.92535700 -1.33736400 2.24963600
C 1.31246300 -0.36672500 0.04877700
H -1.31416700 -3.62502600 0.11344500

TS2A



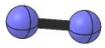
Charge: 0

Spin: 1

C -1.31375500 -1.25055400 0.06696700
C -1.09561200 0.05115900 -0.37075700
C 0.26288200 0.35243300 -0.78082200
H 0.37897100 1.22463000 -1.42858800
C -2.16993100 1.00482400 -0.72827300
C -3.33712700 0.59283300 -1.39890700
C -2.02092400 2.36862800 -0.41664000

C -4.34013100 1.50991400 -1.71353600
H -3.45062900 -0.45288500 -1.69345000
C -3.02331300 3.28787200 -0.73540200
H -1.11884100 2.70424300 0.10098100
C -4.18939800 2.86080400 -1.37839900
H -5.23926500 1.17127600 -2.23433600
H -2.89500900 4.34161000 -0.47546500
H -4.97469200 3.57898500 -1.62684300
C -2.65279400 -1.79914100 0.47287300
O -3.00095600 -2.93464400 0.22862600
O -3.35930400 -0.92278000 1.17680800
C -4.71269500 -1.28313300 1.53064100
C -5.34719400 -0.08565000 2.19687800
H -4.68148300 -2.16049600 2.19554400
H -5.24662800 -1.57504200 0.61262100
H -6.38089500 -0.33070200 2.48620800
H -4.79288900 0.20096800 3.10435800
H -5.37315600 0.77731100 1.51335800
N -0.29710500 -2.13555100 -0.01411700
N 0.42545900 -2.04661100 -1.59567500
N 0.65771000 -0.95362100 -1.93461900
P 3.07519800 0.56425200 -0.34308000
O 3.66998600 -0.81558600 -0.90614000
O 3.88037100 0.72599400 1.04399900
O 3.15191100 1.65670200 -1.34892600
C 3.61722500 -2.05597500 -0.16452600
C 3.95319100 -3.18637500 -1.10803000
H 2.60749100 -2.18964600 0.25727600
H 4.33277000 -1.99472800 0.67053000
H 3.93862300 -4.14136800 -0.55961600
H 3.21629800 -3.24182700 -1.92418800
H 4.95532800 -3.05019700 -1.54382900
C 3.77934100 1.94373300 1.82584900
C 4.82892100 2.94782100 1.40248200
H 3.91377500 1.62863600 2.87053900
H 2.76399700 2.36258700 1.72709500
H 4.76818800 3.84172900 2.04369800
H 5.83942200 2.52011600 1.49691300
H 4.67052500 3.25360500 0.35734400
N 1.17839600 -0.16063200 1.40092500
N 1.00329700 -0.49810000 2.46827500
C 1.38415900 0.25053300 0.18203200
H -0.60730700 -3.10681800 0.07302400

N_2

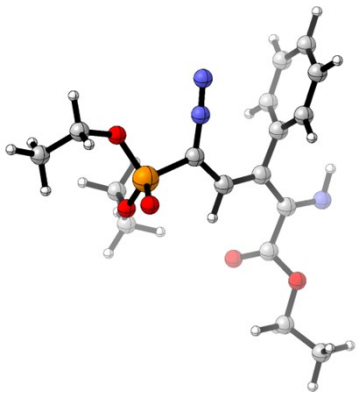


Charge: 0

Spin: 1

N 0.00000000 0.00000000 0.54998200
N 0.00000000 0.00000000 -0.54998200

INT3A



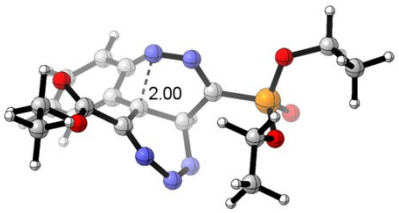
Charge: 0

Spin: 1

P -2.34037300 -0.91509500 0.70728200
O -2.05029100 -2.03340400 -0.41523800
O -3.65933100 -0.09827100 0.26844700
O -2.36522600 -1.52864500 2.06116000
C -2.06610100 -1.74005200 -1.83322700
C -1.01282500 -2.57998000 -2.51779100
H -1.87815400 -0.66587300 -1.99344800

H	-3.07645800	-1.96639200	-2.20792900
H	-1.04783200	-2.39842000	-3.60398600
H	-0.00604100	-2.32742600	-2.15195700
H	-1.19428000	-3.65230100	-2.34217500
C	-4.97108300	-0.48087400	0.75317200
C	-5.51815800	-1.67584500	0.00162400
H	-5.59733200	0.40983800	0.60407000
H	-4.90226400	-0.68270500	1.83322500
H	-6.54327000	-1.88838600	0.34493500
H	-5.55015100	-1.47863400	-1.08131800
H	-4.90704600	-2.57472300	0.17958400
N	-1.51188800	1.59251300	0.35169200
N	-1.96131000	2.63080200	0.33274000
C	-1.08519900	0.34959300	0.38578500
C	0.28909300	-0.04215500	0.17929400
C	1.37326700	0.74507500	-0.06072400
H	0.42307200	-1.12460800	0.20702600
C	1.24715600	2.23106800	-0.10787900
C	1.02384500	2.88564700	-1.32994100
C	1.29436100	2.98525300	1.07548700
C	0.82197500	4.26730400	-1.36375800
H	0.98770500	2.30116500	-2.25238100
C	1.09358700	4.36729800	1.04064200
H	1.46803600	2.47806200	2.02754200
C	0.85003300	5.00924500	-0.17791600
H	0.63415800	4.76623800	-2.31771100
H	1.11909500	4.94403500	1.96845400
H	0.68419700	6.08911100	-0.20409100
C	2.71931500	0.18285600	-0.26451900
C	2.87940100	-1.32696700	-0.33057800
O	2.20221200	-2.04886100	-1.03156200
O	3.86864800	-1.75493500	0.44311600
C	4.15905200	-3.17263300	0.41687500
C	5.28780600	-3.43223700	1.38546200
H	4.42513300	-3.45485800	-0.61378400
H	3.24508400	-3.72334500	0.68904400
H	5.53285500	-4.50570700	1.38401900
H	6.19101800	-2.87057500	1.09980600
H	5.00378300	-3.14397000	2.40977800
N	3.79283900	0.86309900	-0.43896900
H	3.57556500	1.86834500	-0.42561400

TS3A



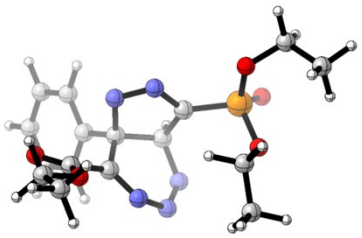
Charge: -1

Spin: 1

C	-1.46263800	-0.76779400	-0.41388400
C	-1.28599900	0.64947600	-0.22941100
C	0.04244600	1.07957000	-0.81826200
H	0.06434400	2.15451600	-1.04998500
C	-2.38856800	1.63440600	-0.14887900
C	-3.63513100	1.40651200	-0.75813800
C	-2.17685900	2.86323500	0.50338100
C	-4.64385300	2.37025400	-0.70395300
H	-3.81069900	0.46723400	-1.28654400
C	-3.18440300	3.82863200	0.55652200
H	-1.21594600	3.05174200	0.98762000
C	-4.42395900	3.58545100	-0.04540900
H	-5.60564600	2.17473000	-1.18550300
H	-3.00252300	4.77423800	1.07399300
H	-5.21350400	4.34016500	-0.00462800
C	-2.46608900	-1.51588600	0.42289800
O	-3.28473900	-0.98497900	1.14094700
O	-2.35260900	-2.84004100	0.29252800
C	-3.25366100	-3.64595800	1.07517800
C	-2.95047400	-5.09729800	0.78387900

H	-4.28993600	-3.38132900	0.80985700
H	-3.11488900	-3.40319400	2.14107600
H	-3.62449500	-5.74124300	1.37012700
H	-3.09666300	-5.32470000	-0.28389300
H	-1.91224100	-5.34568900	1.05512900
N	-0.66794100	-1.48266900	-1.19047900
N	0.00138600	-0.81149000	-2.18552200
N	0.31415100	0.39825000	-2.08830900
P	2.85666900	0.88664100	-0.10194100
O	3.29358100	-0.43751200	-0.95311100
O	3.51460300	0.67904000	1.37048500
O	3.32298900	2.08960600	-0.85606600
C	2.94967700	-1.76189700	-0.52239300
C	2.94016600	-2.67990600	-1.72513900
H	1.95686600	-1.75087500	-0.04143900
H	3.68512500	-2.09551600	0.22916200
H	2.70177000	-3.70865000	-1.41047100
H	2.17907100	-2.35151300	-2.44944700
H	3.92333400	-2.68864000	-2.22269100
C	4.88103400	1.06655000	1.60845500
C	5.86397200	-0.00437200	1.17532700
H	4.95034400	1.24944500	2.69138800
H	5.08130100	2.01661300	1.08710100
H	6.88916700	0.30351200	1.43795800
H	5.65145100	-0.95978700	1.68074500
H	5.82029200	-0.16678400	0.08756200
N	0.59105200	0.46697300	1.39590700
N	-0.59412500	0.34065700	1.62391800
C	1.13953500	0.76488200	0.23401600

INT4A



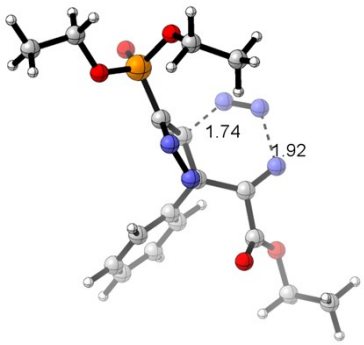
Charge: -1

Spin: 1

C	-1.39642500	0.82047000	0.50639300
C	-1.33196700	-0.56914600	-0.06646200
C	-0.10699400	-1.25621200	0.58761600
H	-0.19491800	-2.35380400	0.58462300
C	-2.59369500	-1.38655400	-0.07459000
C	-3.37925000	-1.47524500	1.08405900
C	-2.96295400	-2.11940600	-1.20918000
C	-4.51869700	-2.28274600	1.10705700
H	-3.09199500	-0.90736100	1.97333600
C	-4.10329900	-2.92823400	-1.18730300
H	-2.35261500	-2.03656600	-2.11040700
C	-4.88490600	-3.01208900	-0.03030100
H	-5.12434200	-2.34262000	2.01511500
H	-4.38486500	-3.49347500	-2.07975000
H	-5.77789300	-3.64220100	-0.01446100
C	-2.21046200	1.82902500	-0.25521700
O	-3.29620200	1.58246900	-0.73269900
O	-1.62442800	3.02507200	-0.29766300
C	-2.33914300	4.07846000	-0.97613500
C	-1.49528300	5.32956400	-0.90835000
H	-3.31744800	4.21460900	-0.48817800
H	-2.52699800	3.76544500	-2.01563100
H	-2.01566400	6.15457100	-1.41936300
H	-1.31512500	5.62817200	0.13641500
H	-0.52242200	5.17628800	-1.40151200
N	-0.62936900	1.23104000	1.46516700
N	-0.15468400	0.25120700	2.36571600

N	0.10754600	-0.90311100	1.99655700
P	2.69790500	-1.13366500	-0.08612300
O	3.18687600	-0.10524700	1.08403600
O	3.40739400	-0.60290100	-1.44609700
O	3.06096900	-2.52100600	0.33491200
C	3.00213300	1.31426400	0.97075600
C	2.95311300	1.91305900	2.35922300
H	2.06577400	1.52658300	0.42713700
H	3.83562200	1.73503500	0.38390900
H	2.83811100	3.00681000	2.29225600
H	2.10074600	1.50682300	2.92509800
H	3.87967700	1.69492000	2.91427700
C	4.72889700	-1.05751500	-1.79502800
C	5.81074100	-0.30057100	-1.04885100
H	4.81517200	-0.90004400	-2.88057000
H	4.80056700	-2.13930400	-1.59785700
H	6.80302400	-0.63328100	-1.39439900
H	5.72827100	0.78284900	-1.22961200
H	5.74570600	-0.48045100	0.03525900
N	0.46254900	-0.27665600	-1.45775400
N	-0.83122700	-0.13990500	-1.43948900
C	0.99193900	-0.80098100	-0.36620900

TS4A



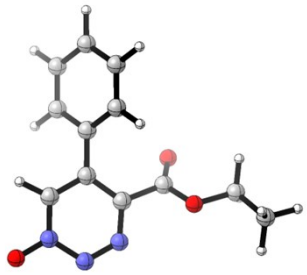
Charge: -1

Spin: 1

C	-1.92624500	1.10729100	0.15353400
C	-0.83970600	-0.03226900	0.00010400
C	0.31717600	0.00147600	0.97584200
H	0.25015600	-0.61847700	1.87098500
C	-1.54251000	-1.38054200	0.12746800
C	-2.35440500	-1.63587900	1.24339100
C	-1.38445700	-2.37768200	-0.84273200
C	-3.00350900	-2.86568800	1.38265800
H	-2.48279300	-0.86621300	2.00874700
C	-2.03043100	-3.60902500	-0.70121100
H	-0.76017300	-2.17323500	-1.71313800
C	-2.84373400	-3.85748300	0.40946000
H	-3.63546900	-3.04895100	2.25544100
H	-1.89988000	-4.37847900	-1.46669600
H	-3.35127500	-4.81948900	0.51621400
C	-3.25243600	0.76655700	-0.51832700
O	-3.34892600	0.39573700	-1.66405800
O	-4.28142000	0.97204200	0.30586600
C	-5.60912500	0.74054600	-0.21840400
C	-6.12596000	1.94978900	-0.97130300
H	-6.22127600	0.52859200	0.66890600
H	-5.58743900	-0.15353000	-0.85848300
H	-7.16655800	1.77073000	-1.28614500
H	-6.10776400	2.84670100	-0.33224600
H	-5.52305700	2.14419200	-1.87103700
N	-1.80962100	2.24448000	0.64574900
N	-0.13491500	2.48550600	1.56375700
N	0.49199100	1.53417600	1.77438200
P	3.13510700	-0.03039800	0.61001900
O	3.74260100	1.47671000	0.41398400
O	3.91020500	-0.88833400	-0.53927200
O	3.37626200	-0.46119700	2.01999900
C	3.61603300	2.18292300	-0.83265700
C	2.48361500	3.19131900	-0.79221700
H	3.46996100	1.46874500	-1.65936300
H	4.58050800	2.69008000	-0.99554600
H	2.50671500	3.81119100	-1.70356200

H 1.50372700 2.69572500 -0.74299400
H 2.58546000 3.85622000 0.08009800
C 5.34767700 -0.94559000 -0.51795100
C 5.79298700 -2.19495300 -1.24475200
H 5.70126600 -0.95379600 0.52669600
H 5.75115900 -0.04060600 -1.00369200
H 6.89324000 -2.24979300 -1.26189300
H 5.40609900 -3.09662400 -0.74398600
H 5.42986200 -2.19194200 -2.28498800
N 1.06380800 0.09653500 -1.19879900
N -0.21340600 0.15343200 -1.33831100
C 1.46438800 -0.09472900 0.08489800

10a

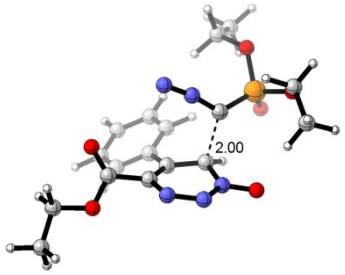


Charge: 0

Spin: 1

C 0.65388000 0.73415200 0.15909300
C -0.75212800 0.74345600 -0.00799200
C -1.31734300 1.99455400 -0.17182300
H -2.37950500 2.17726800 -0.33240200
C -1.60367600 -0.46339800 -0.06825500
C -1.20858400 -1.57592900 -0.83199000
C -2.83862200 -0.49073600 0.60156600
C -2.03384900 -2.69637500 -0.91723800
H -0.26515800 -1.55422700 -1.38113800
C -3.65556100 -1.62026300 0.52363100
H -3.14852100 0.36621200 1.20352000
C -3.25591000 -2.72410300 -0.23549600
H -1.72290200 -3.55206500 -1.52109400
H -4.60708500 -1.63758500 1.06006200
H -3.89750300 -3.60634700 -0.29847000
C 1.42837500 -0.50162900 0.52269600
O 1.01038800 -1.33747600 1.29139400
O 2.61399100 -0.54025900 -0.07302100
C 3.47608100 -1.65636000 0.25384600
C 4.74469500 -1.51260400 -0.55177300
H 2.94094700 -2.59021000 0.02135500
H 3.66942300 -1.64120600 1.33786300
H 5.42171400 -2.34969400 -0.32107500
H 4.53072800 -1.52853100 -1.63198500
H 5.26263600 -0.57146900 -0.30937100
N 1.35794100 1.86434300 0.10585100
N 0.82588400 3.03392600 -0.05457500
N -0.53416500 3.11890900 -0.17128100
O -1.02144800 4.25061200 -0.29897500

TS1B



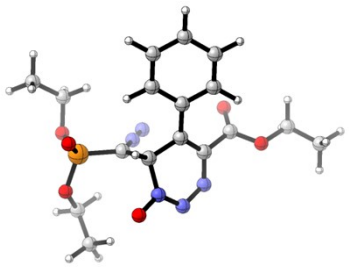
Charge: -1

Spin: 1

C 2.11937100 -0.90692400 0.12384100
C 1.14149200 -0.04764600 0.66366800
C -0.01840300 -0.69598900 1.13160400
H -0.75840700 -0.20378700 1.75956000
C 1.24535400 1.42120300 0.75935400
C 2.48880500 2.06200800 0.92780800
C 0.08197600 2.21641500 0.73441300
C 2.56890200 3.45085100 1.02406700
H 3.40154900 1.47098900 1.01837400

C	0.16631000	3.60702700	0.82413500
H	-0.89916800	1.74959700	0.65104700
C	1.40920100	4.23238300	0.96101500
H	3.54377000	3.92609500	1.15889600
H	-0.74973300	4.20237300	0.78858100
H	1.47489300	5.32087300	1.03270600
C	3.29281400	-0.42542600	-0.68672600
O	3.21660500	0.39536100	-1.57218600
O	4.42391300	-1.03400500	-0.32722300
C	5.61140000	-0.70073300	-1.07854400
C	6.76402900	-1.48307800	-0.49491500
H	5.77579200	0.38650900	-1.01361000
H	5.43884200	-0.94848200	-2.13786700
H	7.68613200	-1.25078900	-1.05013600
H	6.92273400	-1.22219700	0.56335700
H	6.58130200	-2.56689600	-0.56511900
N	2.03520600	-2.23626000	0.22695700
N	1.03941000	-2.81896100	0.85881700
N	0.05201100	-2.07349700	1.34136900
P	-3.06087700	-0.05430600	0.06754600
O	-4.10492500	-1.27611100	0.21347500
O	-3.76753100	0.78472400	-1.14709100
O	-2.97729000	0.70338000	1.36146800
C	-4.11743300	-2.40549700	-0.67685800
C	-3.66514100	-3.64823100	0.06146900
H	-3.46734300	-2.20918400	-1.54494500
H	-5.15024500	-2.50796100	-1.04731100
H	-3.67362400	-4.51713600	-0.61690800
H	-2.64809000	-3.50986600	0.46099700
H	-4.33926700	-3.86415800	0.90652000
C	-3.25730400	2.08404700	-1.50197700
C	-3.90319600	3.18141400	-0.67877000
H	-3.47616700	2.21042200	-2.57356500
H	-2.16083400	2.10886400	-1.38857000
H	-3.52322100	4.16572800	-0.99762800
H	-4.99737500	3.17297400	-0.80911000
H	-3.67823600	3.04157600	0.38876200
N	-0.87193300	-0.25682400	-1.48649300
N	-0.10533200	0.07462300	-2.28619600
C	-1.54486300	-0.67824600	-0.50491100
O	-0.88271700	-2.64159800	1.95775200

INT1B



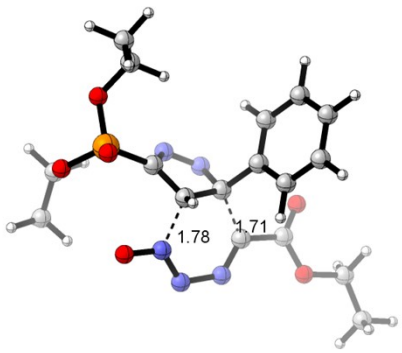
Charge: -1

Spin: 1

C	-1.86854500	-0.91703300	-0.09293800
C	-1.09207600	0.08780500	-0.65640500
C	0.28964700	-0.35552800	-0.99612100
H	0.73147000	0.20626200	-1.82790500
C	-1.44308100	1.49643200	-0.78512000
C	-2.78872500	1.93475800	-0.84254600
C	-0.43508100	2.48752800	-0.88303400
C	-3.10693000	3.28698600	-0.94616800
H	-3.59610000	1.20010800	-0.84228900
C	-0.75956700	3.84067000	-0.99964600
H	0.61738800	2.19900100	-0.85263500
C	-2.09541100	4.25418100	-1.02232200
H	-4.15686100	3.58968700	-0.98813800
H	0.04355700	4.57970900	-1.06757800
H	-2.34735900	5.31385600	-1.11012600
C	-3.04486600	-0.62717900	0.79800400
O	-2.98316700	0.05844200	1.79539000
O	-4.16076800	-1.24114800	0.39093800
C	-5.33349300	-1.07850900	1.21497400

C -6.46878100 -1.83175700 0.56207900
H -5.55374400 -0.00318600 1.30961300
H -5.11283600 -1.46134000 2.22417800
H -7.38000200 -1.73049000 1.17207000
H -6.68012500 -1.43423200 -0.44323900
H -6.23054700 -2.90329800 0.47120900
N -1.59154400 -2.23591400 -0.18769400
N -0.60836000 -2.62631900 -1.00466600
N 0.21677900 -1.75569200 -1.49098000
P 3.02749600 0.10227300 -0.14203000
O 3.84865500 -1.26122900 -0.33049700
O 3.57090800 0.59484200 1.30317600
O 3.21893000 1.02983000 -1.29414900
C 3.62049400 -2.45357500 0.45240700
C 3.38481000 -3.62358100 -0.47695400
H 2.75654400 -2.30962800 1.12039700
H 4.51025700 -2.60032000 1.08502500
H 3.20687700 -4.53761300 0.11247400
H 2.51402000 -3.42535600 -1.12189200
H 4.26469000 -3.79315100 -1.11872800
C 3.23431000 1.90906900 1.80615000
C 4.25122500 2.93914100 1.36238800
H 3.21247500 1.80665300 2.90117900
H 2.21921300 2.18905400 1.47716400
H 4.00370800 3.92100300 1.79695800
H 5.26291200 2.65672300 1.69423200
H 4.25221400 3.02883600 0.26572400
N 0.87647300 -0.33735200 1.37455500
N 0.45431000 -0.37416700 2.43009500
C 1.30617100 -0.25797100 0.15382600
O 1.09489200 -2.08934800 -2.34833800

TS2B



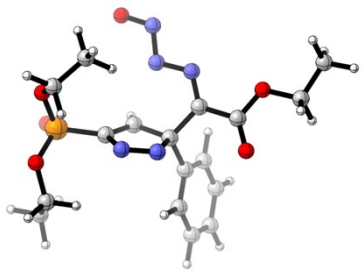
Charge: -1

Spin: 1

C 1.95798300 -0.74108700 0.25925900
C 0.74172000 0.14907000 0.02399600
C -0.49294500 -0.12144100 0.84040400
H -0.58070200 0.09542400 1.90196900
C 1.05857700 1.64190900 0.23478200
C 1.76715300 2.02136500 1.38178900
C 0.58797800 2.62886300 -0.63969300
C 2.01765400 3.37138100 1.64422100
H 2.12634200 1.25655800 2.07511500
C 0.83312500 3.97826800 -0.37306000
H 0.03786400 2.34230000 -1.53660400
C 1.55115100 4.35529200 0.76718000
H 2.57673700 3.65366700 2.53998200
H 0.46369000 4.73984500 -1.06464600
H 1.74467000 5.41129100 0.97138300
C 3.16587400 -0.35512600 -0.54927400
O 3.19050400 0.59068900 -1.30981200
O 4.21612500 -1.15763500 -0.35140100
C 5.41220300 -0.84527200 -1.08854100
C 6.46832600 -1.85731400 -0.70882500
H 5.72458900 0.18346600 -0.84620700
H 5.18633400 -0.87409900 -2.16681500
H 7.39936000 -1.64525500 -1.25742200
H 6.68547300 -1.81521500 0.37024600
H 6.14410700 -2.87957300 -0.96012500

N	2.09326500	-1.78023300	1.01533200
N	1.16486500	-2.35481700	1.81395000
N	-0.06138700	-2.17237200	1.41708500
P	-3.26796200	-0.27712900	0.27813800
O	-3.79467200	-1.76626500	-0.04538800
O	-3.98546600	0.53961200	-0.93182400
O	-3.63069600	0.13435900	1.66309100
C	-3.43903500	-2.47722800	-1.24872500
C	-2.25092300	-3.39157100	-1.02533800
H	-3.24236000	-1.76062900	-2.06189300
H	-4.33285900	-3.05777900	-1.52432800
H	-2.09153500	-4.00851700	-1.92499700
H	-1.32990400	-2.82517300	-0.82637300
H	-2.42928600	-4.05822700	-0.16834500
C	-3.54241900	1.83909700	-1.36933100
C	-3.50546400	2.87731000	-0.26452100
H	-4.25838000	2.13093100	-2.15193800
H	-2.55345100	1.73555200	-1.84474100
H	-2.74442200	2.63815100	0.49339000
H	-3.25801100	3.85995300	-0.69725900
H	-4.48232700	2.95160000	0.23845700
N	-1.00061400	-0.24273700	-1.36145900
N	0.25756500	-0.10256700	-1.37674200
C	-1.52758200	-0.16509600	-0.06701300
O	-0.96612500	-2.69060600	2.07634000

INT2B



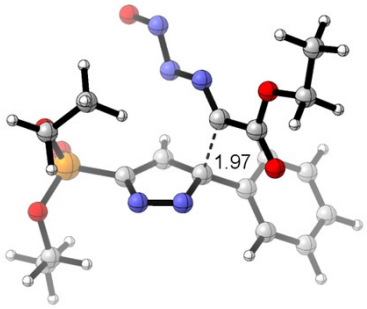
Charge: -1

Spin: 1

C	1.84273900	-0.61566100	0.02007900
C	0.69180100	0.39474300	-0.09601900
C	-0.51195800	0.08062400	0.75378600
H	-0.54909600	0.15887800	1.83538100
C	1.14100600	1.82243900	0.24468700
C	1.88923000	2.03854300	1.40970900
C	0.76030600	2.91672100	-0.54062700
C	2.26508400	3.33264900	1.77772300
H	2.18222300	1.18840800	2.03091800
C	1.13525300	4.21141300	-0.16961200
H	0.18064400	2.75535400	-1.45025800
C	1.89005500	4.42473200	0.98795100
H	2.85233800	3.48765300	2.68640400
H	0.83759900	5.05816200	-0.79346000
H	2.18422500	5.43751400	1.27437800
C	3.12315100	-0.27295100	-0.64830400
O	3.27106300	0.70020900	-1.36102300
O	4.10395200	-1.14749300	-0.38753800
C	5.37458200	-0.89597000	-1.01482900
C	6.32688500	-1.98919800	-0.58827200
H	5.73332700	0.10081700	-0.71084000
H	5.23761100	-0.87597700	-2.10817000
H	7.31190500	-1.82495700	-1.05250300
H	6.45673000	-1.99487200	0.50556000
H	5.95770500	-2.97869600	-0.90114200
N	1.71869100	-1.76161700	0.60406300
N	0.52513900	-2.05653100	1.10479200
N	0.54469500	-3.25909200	1.67261800
P	-3.27372400	-0.29329500	0.29481400
O	-3.63272600	-1.82771900	-0.04346400
O	-4.12666000	0.46042700	-0.86106500
O	-3.60593500	0.03390800	1.70949700
C	-3.21799500	-2.47156900	-1.26854200
C	-1.97780800	-3.31093100	-1.04202200
H	-3.05019700	-1.71438000	-2.05075300

H -4.06878600 -3.09502100 -1.58335700
H -1.72219700 -3.85280800 -1.96720500
H -1.11789500 -2.68972700 -0.75167400
H -2.14348600 -4.04559800 -0.23943600
C -3.91713200 1.84455700 -1.20726600
C -4.20231400 2.79780500 -0.06353100
H -4.60009400 2.02863800 -2.04956500
H -2.88751000 1.96966100 -1.58085400
H -3.48496900 2.66630200 0.76030000
H -4.12645200 3.83569600 -0.42561400
H -5.21718200 2.63981800 0.33421400
N -1.09082100 0.08503600 -1.44255500
N 0.14966500 0.31408800 -1.48434900
C -1.56254000 -0.00050200 -0.11353700
O -0.52147500 -3.58849500 2.19174600

TS3B



Charge: -1

Spin: 1

C 1.62448000 -0.65334500 0.11719600
C 0.52044600 0.97182100 -0.06464800
C -0.67218200 0.70529800 0.74527300
H -0.77235700 0.82083000 1.81795900
C 1.45295600 2.08548800 0.28869000
C 1.98491100 2.16356600 1.58567400
C 1.78192200 3.07671800 -0.64630400
C 2.83150500 3.21576300 1.94081200
H 1.74083200 1.38690300 2.31497800
C 2.63008900 4.12808100 -0.28932100
H 1.37310600 3.01112500 -1.65513500
C 3.15790300 4.20292900 1.00393100
H 3.24089700 3.26309400 2.95317600
H 2.87977900 4.89490200 -1.02737700
H 3.82107900 5.02627100 1.28099200
C 2.80964300 -0.62091800 -0.77028000
O 3.09965400 0.28976100 -1.51214200
O 3.53701100 -1.73877300 -0.63842500
C 4.73336200 -1.82710700 -1.43997600
C 5.39807300 -3.14836200 -1.13204400
H 5.38608500 -0.97259000 -1.20006100
H 4.45636200 -1.74466800 -2.50318500
H 6.31821500 -3.24620100 -1.72904500
H 5.66817000 -3.21566900 -0.06639200
H 4.73411300 -3.99175400 -1.37893500
N 1.33080400 -1.55320200 0.93580600
N 0.29085200 -1.58816000 1.74567800
N 0.28217100 -2.74893900 2.41262700
P -3.28377900 -0.22286900 0.19503300
O -3.30177600 -1.82308800 0.00427700
O -4.19534300 0.22792300 -1.06843400
O -3.76366700 0.15625700 1.55316000
C -2.81088000 -2.48908500 -1.17894300
C -1.41564500 -3.03619100 -0.95735500
H -2.83647500 -1.79754900 -2.03559600
H -3.52513500 -3.30175900 -1.38156000
H -1.12389400 -3.66285700 -1.81568100
H -0.67767400 -2.22784800 -0.85866600
H -1.37891200 -3.65244300 -0.04591900
C -4.25957700 1.59282600 -1.52946400
C -4.91843600 2.52206300 -0.52921100
H -4.83920100 1.54722400 -2.46318900
H -3.24358800 1.93554500 -1.78546400
H -4.32152800 2.61104500 0.39066900

H -5.02471300 3.52473800 -0.97364300

H -5.92010900 2.15416000 -0.25570700

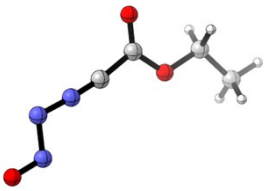
N -1.10867000 0.42084100 -1.46405900

N 0.10907600 0.81400200 -1.43044900

C -1.63603800 0.36260700 -0.16383400

O -0.66377800 -2.85510100 3.18830200

Byproduct-1



Charge: 0

Spin: 1

C 0.39395700 -0.54749200 -0.00230300

C -1.04367000 -0.82708500 -0.00037600

O -1.46057000 -1.95824500 0.00164400

O -1.73283900 0.29523700 -0.00162300

C -3.18794100 0.18128900 0.00050800

C -3.75655700 1.57769400 0.00039500

H -3.48129300 -0.39096400 0.89340000

H -3.48372800 -0.39200700 -0.89091300

H -4.85573700 1.51658600 0.00157800

H -3.44000100 2.13505700 0.89547900

H -3.44190200 2.13407100 -0.89597600

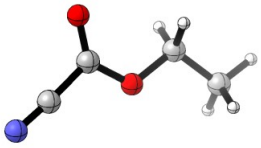
N 1.55604900 -0.48033400 -0.00000200

N 2.82612000 -0.48696200 -0.00085200

N 3.30292100 0.82544700 0.00143400

O 4.50244700 0.87347800 0.00035700

Byproduct-2



Charge: 0

Spin: 1

C -1.91355500 -0.42213900 0.00012700

C -0.69705700 0.41817700 -0.00002500

O -0.75820900 1.62038800 0.00078000

O 0.38092300 -0.33727600 -0.00136500

C 1.67078500 0.34458000 -0.00098500

C 2.74803600 -0.71049700 0.00113600

H 1.71221900 0.98912600 0.88984700

H 1.71365400 0.98686800 -0.89340300

H 3.73246500 -0.21772700 0.00160900

H 2.67909300 -1.34622400 0.89735200

H 2.68089300 -1.34806400 -0.89391100

N -2.90704100 -1.01565700 0.00023800

N_2O

Charge: 0

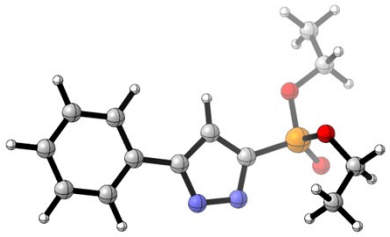
Spin: 1

N -0.00932700 1.18353900 0.00000000

N 0.00000000 0.06723800 0.00000000

O 0.00816100 -1.09443000 0.00000000

INT3B



Charge: -1

Spin: 1

C -1.72686700 0.29240200 0.28150000

C -0.58022900 -0.47255500 -0.01182800

C 0.47197200 0.33637400 0.45441900

N -1.35205200 1.46400800 0.86935700

H -0.51093200 -1.45417100 -0.47418200

N -0.02191800 1.49340200 0.97781100

C -3.14128000 -0.02654500 0.04207400

C -3.53047100 -1.22908400 -0.58272700

C -4.15683400 0.87059400 0.43466400

C -4.87777900 -1.52173200 -0.80487500

H -2.76702000 -1.94352800 -0.89905800

C -5.50263700 0.57674200 0.21190300

H -3.86614800 1.80410000 0.91935700

C -5.87406800 -0.62179000 -0.40941000

H -5.15205100 -2.46167100 -1.29179300

H -6.27014400 1.28951400 0.52651200

H -6.92824700 -0.85179500 -0.58361700

P 2.22350800 0.06598600 0.38497800

O 2.28791300 -1.51149700 0.02232800

O 2.79645700 0.70657900 -1.01004000

O 3.03034000 0.50792800 1.56609100

C 3.56374500 -2.12909500 -0.22902100

C 3.45646600 -3.60632700 0.07484100

H 4.33188400 -1.65382800 0.40342800

H 3.83789000 -1.95587300 -1.28299000

H 4.41688700 -4.10397700 -0.13415500

H 3.20193500 -3.76951200 1.13408600

H 2.67932700 -4.07866700 -0.54716700

C 3.43156000 1.99505500 -1.01403000

C 2.42098700 3.12480300 -1.07980700

H 4.08840700 2.00046100 -1.89774600

H 4.06357100 2.08736900 -0.11638900

H 2.94293300 4.09423400 -1.13205000

H 1.78098400 3.02580400 -1.97149900

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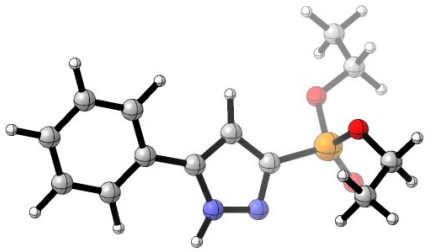
11a



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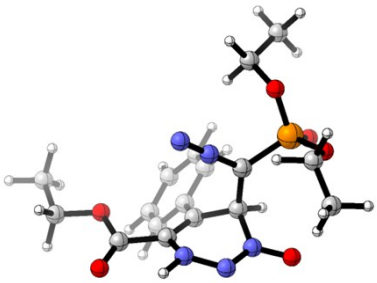
INT4B



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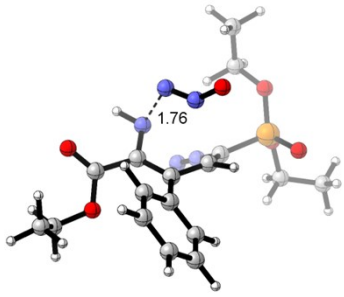
TS4B



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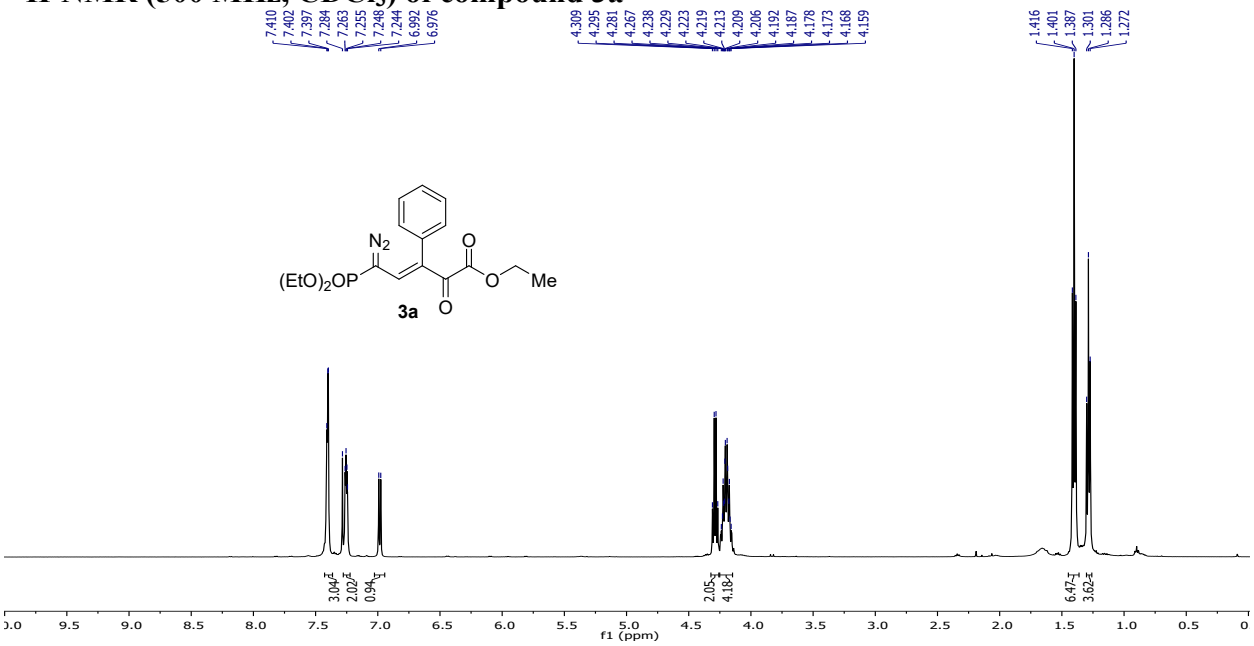
15. References

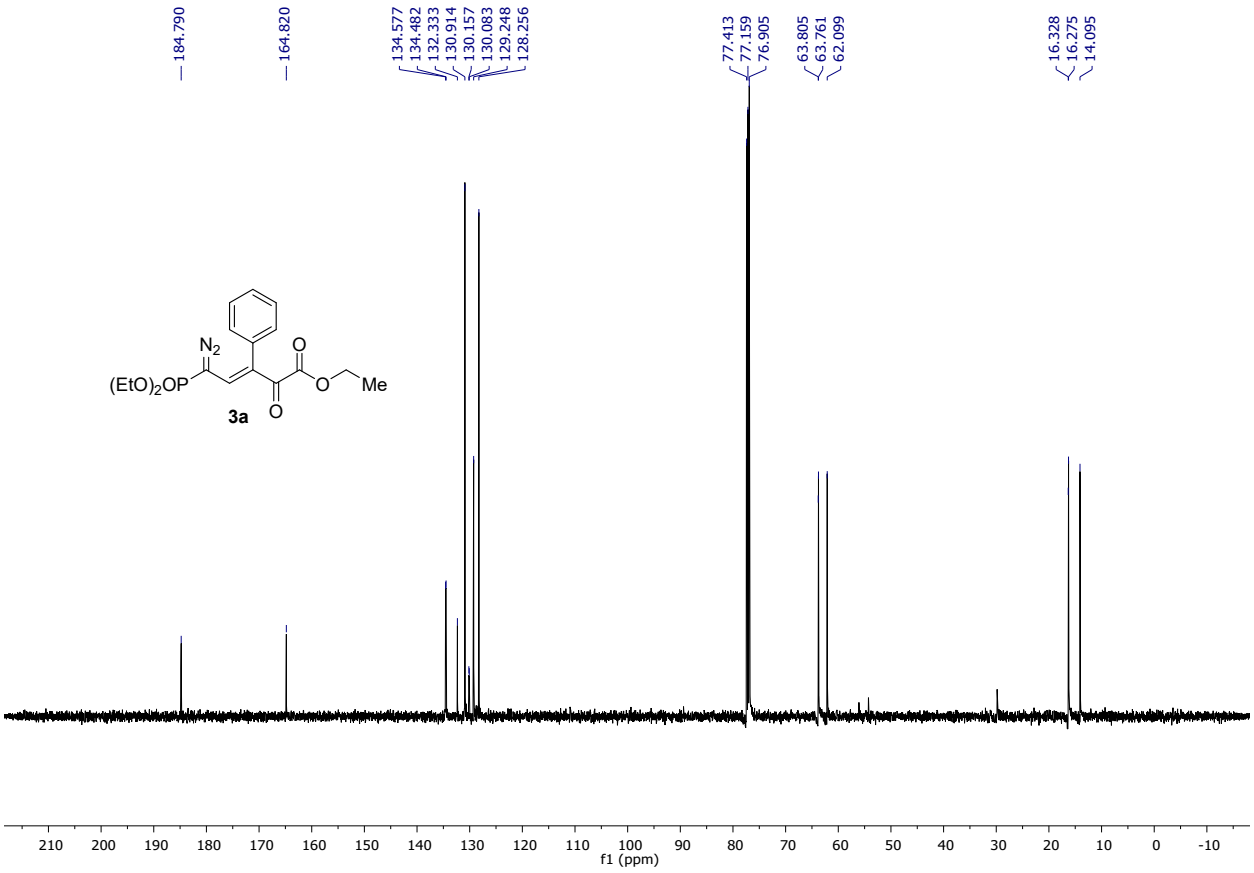
1. G. Pisella, A. Gagnebin, J. Waser, Three-Component Reaction for the Synthesis of Highly Functionalized Propargyl Ethers *Chem. Eur. J.* **2020**, *26*,10199–10204.
2. (a) A. Padwa, Y. S. Kulkarni, Z. J. Zhang, *J. Org. Chem*. **1990**, *55*, 4144-4153. (b) H. M. L. Davis, P. W. Hougland, W. R. Cantrell Jr. *Synth Commun*. **1992**, *22*, 971-978. (c) H. M. L. Davies, B. H. Hu, E. Saikali, P. R. Bruzinski, *J. Org. Chem.***1994**, *59*, 4535-4541. (d) M. P. Doyle, M. Yan, W. H. Hu, *J. Am. Chem. Soc.* **2003**, *125*, 46924693. (e) V. V. Pagar, A. M. Jadhav, R. S. Liu, *J. Am. Chem. Soc.* **2011**, *133*, 20728-20731. (f) H. F. Zheng, K. Y. Dong, D. Wherritt, H. Arman, M. P. Doyle, *Angew. Chem. Int. Ed.* **2020**, *59*, 13613-13617.
3. L. De Angelis, H. Zheng, M.T. Perz, H. Arman, M.P. Doyle, *Org. Lett.* **2021**, *23*, 6542-6546.
4. G. Rivera, L. De Angelis, A. Al-Sayyed, S. Biswas, H. D. Arman, M. P. Doyle, *Org. Lett.* **2022**, *24*, 6543–6547.
5. Nitrous oxide. NISTWeb. National Institute of Standards and Technology. https://webbook.nist.gov/cgi/cbook.cgi?ID=C10024972&Type=IR-SPEC&Index=1.
6. F. M. Betzler, T. M. Klapötke, S. M. Sproll, *Eur. J. Org. Chem.* **2013**, 509–514.
7. R. Kumar, D. Verma, S. M. Mobin, I. N. N. Namboothiri, *Org.Lett*., **2012**, 14, 4070-4073.
8. CrysAlisPro 1.171.40.63a (Rigaku Oxford Diffraction, 2019)
9. SCALE3 ABSPACK -An Oxford Diffraction program(1.0.4,gui:1.0.3) (C) 2005 Oxford Diffraction Ltd.
10. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339.
11. G. M. Sheldrick, *Acta Cryst.* **2015**, *A71*, 3.
12. G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112.
13. M. J. Frisch, *et al. Gaussian 16, Revision C.01*, Gaussian, Inc., Wallingford CT, **2019**.
14. A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648-5652.
15. S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104.
16. F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys*. **2005**, *7* 3297-3305.
17. A. V. Marenich, C. J. Cramer, D . G. Truhlar, *J. Phys. Chem. B* **2009**, *113*, 6378−6396.
18. (a) K. Fukui, *J. Phys. Chem*. **1970**, *74*, 4161−4163. (b) K. Fukui, *Acc. Chem. Res*. **1981**, *14*, 363−368.
19. Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215-41.
20. CYLview20; C. Y. Legault, Universitéde Sherbrooke, **2020**, (http://www.cylview.org).

16. NMR spectra

^{1}H-NMR (500 MHz, $CDCl_3$) of compound 3a



^{13}C-NMR (126 MHz, $CDCl_3$) of compound 3a



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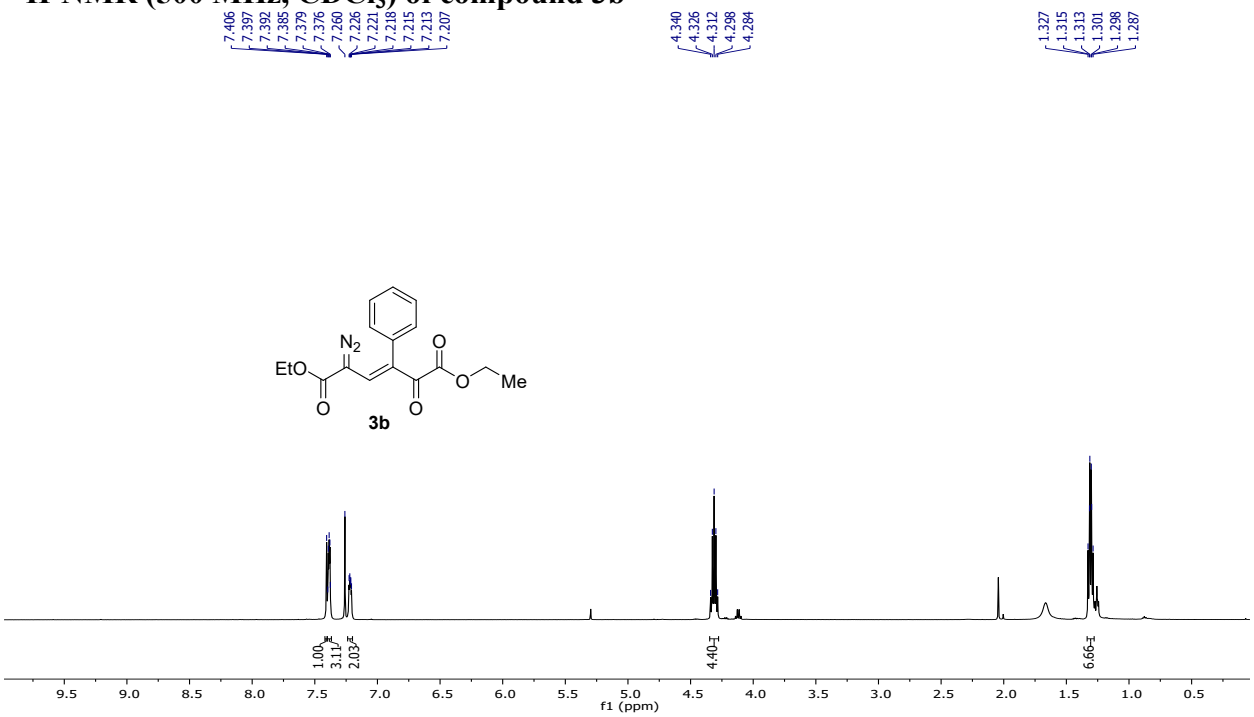

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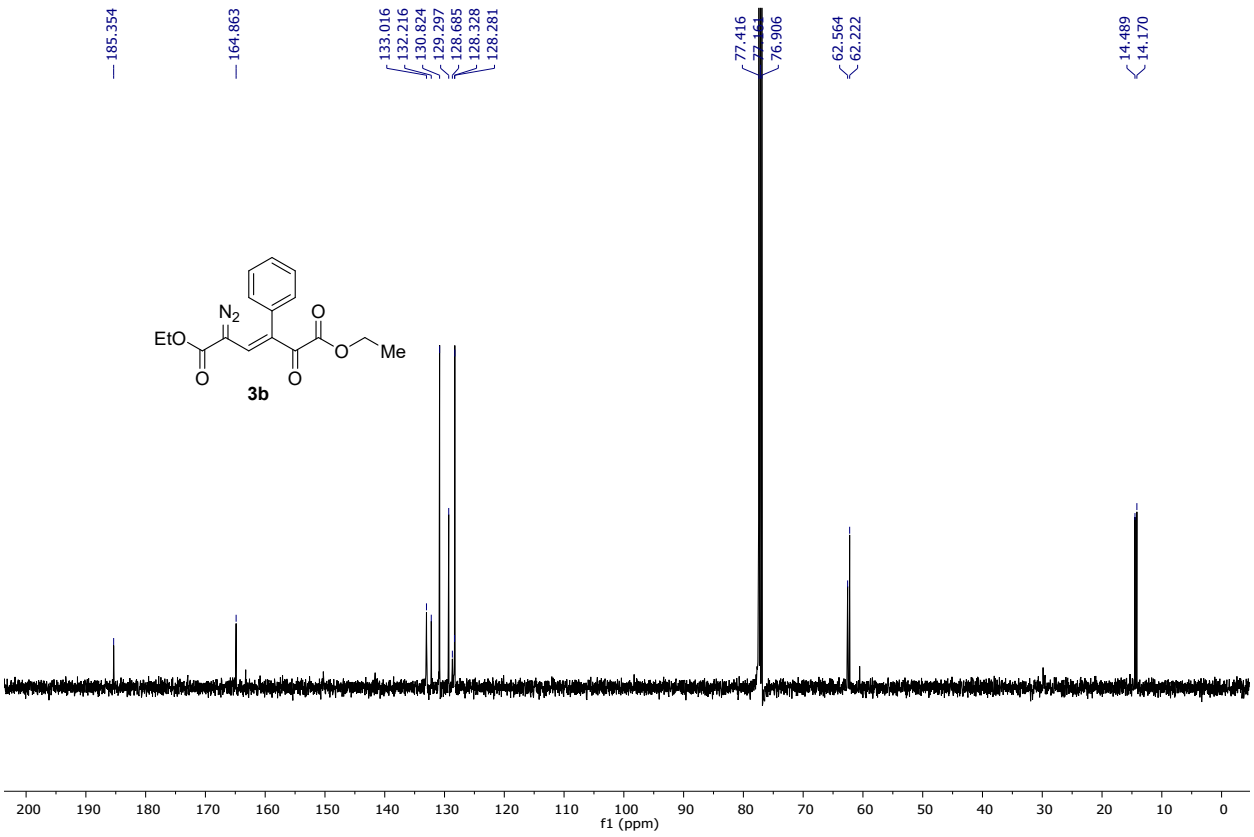

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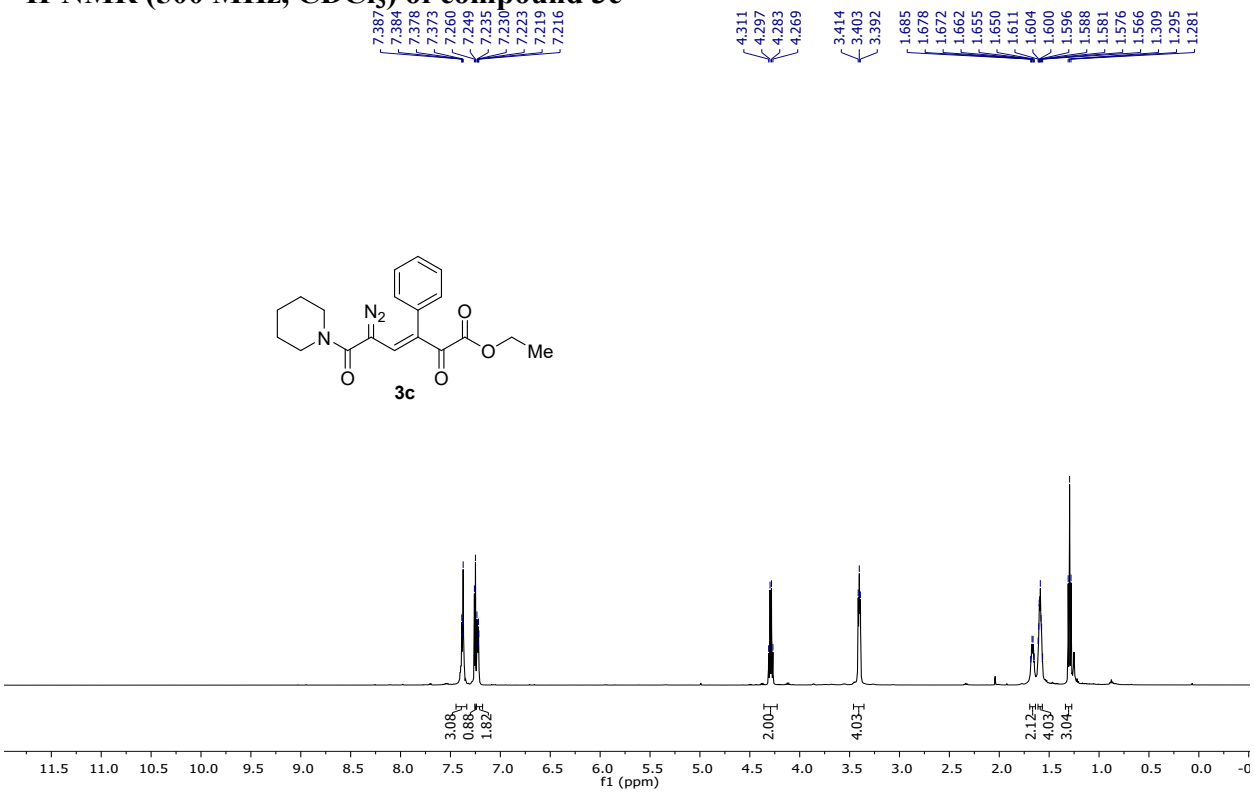

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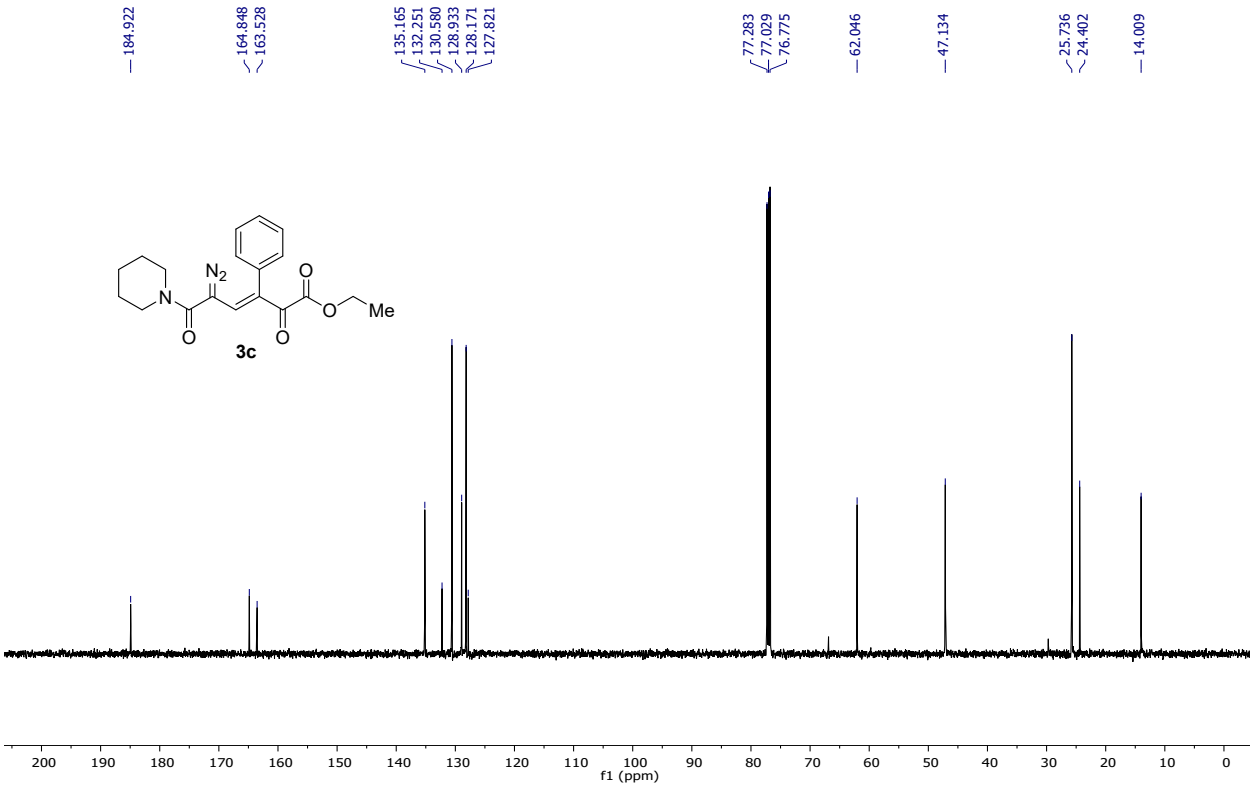

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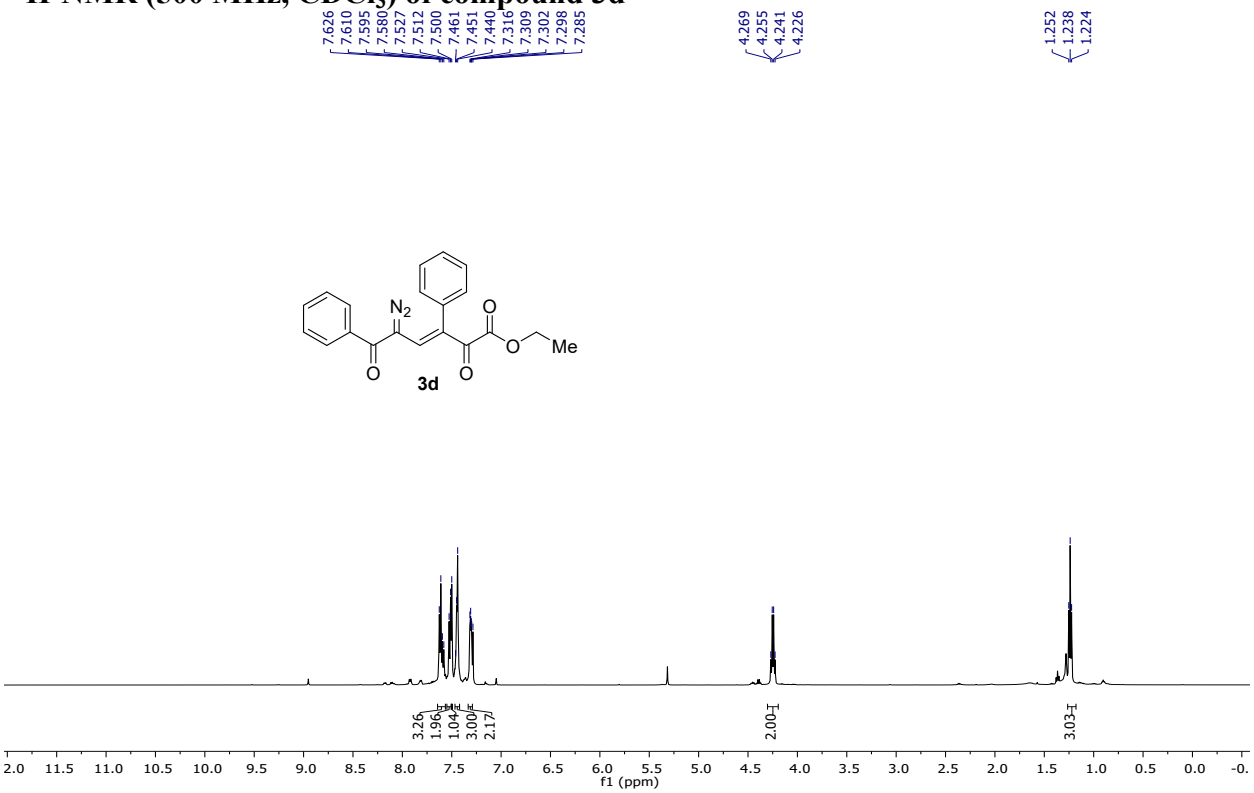

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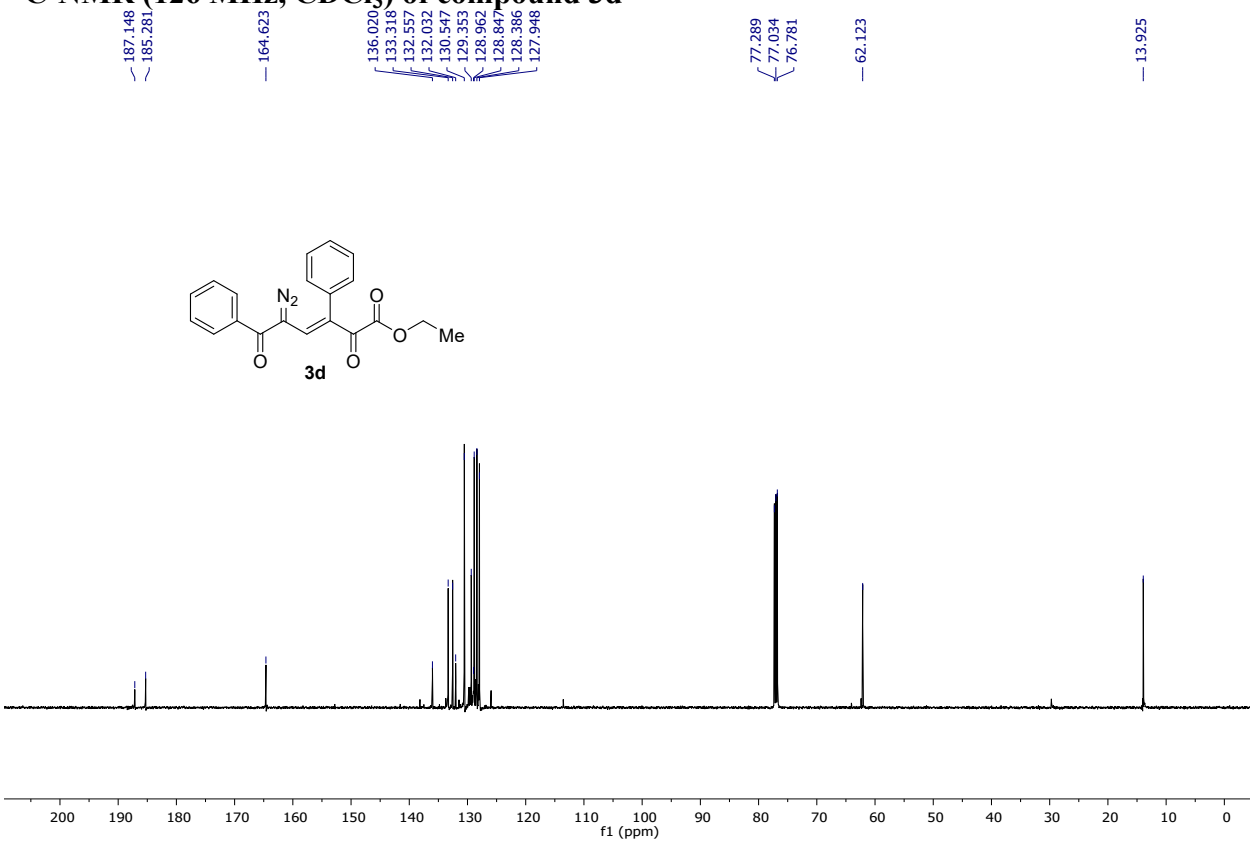

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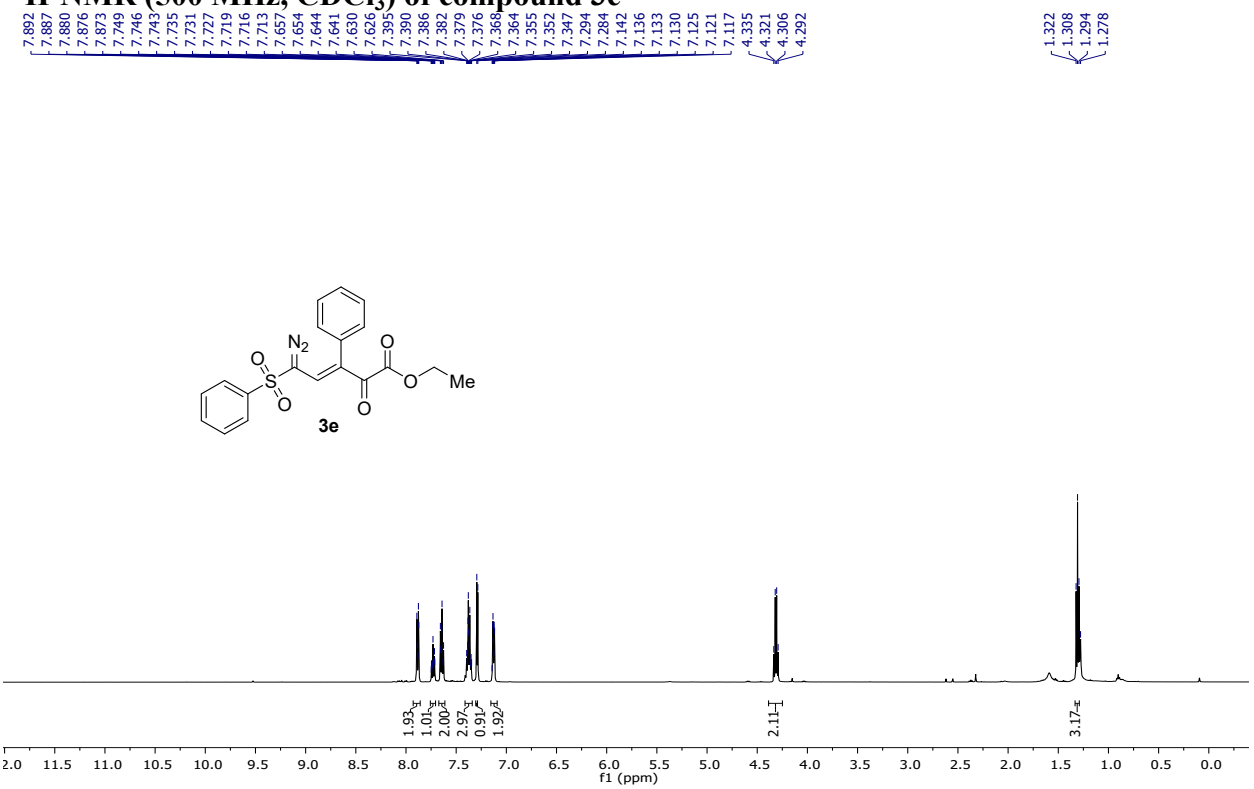

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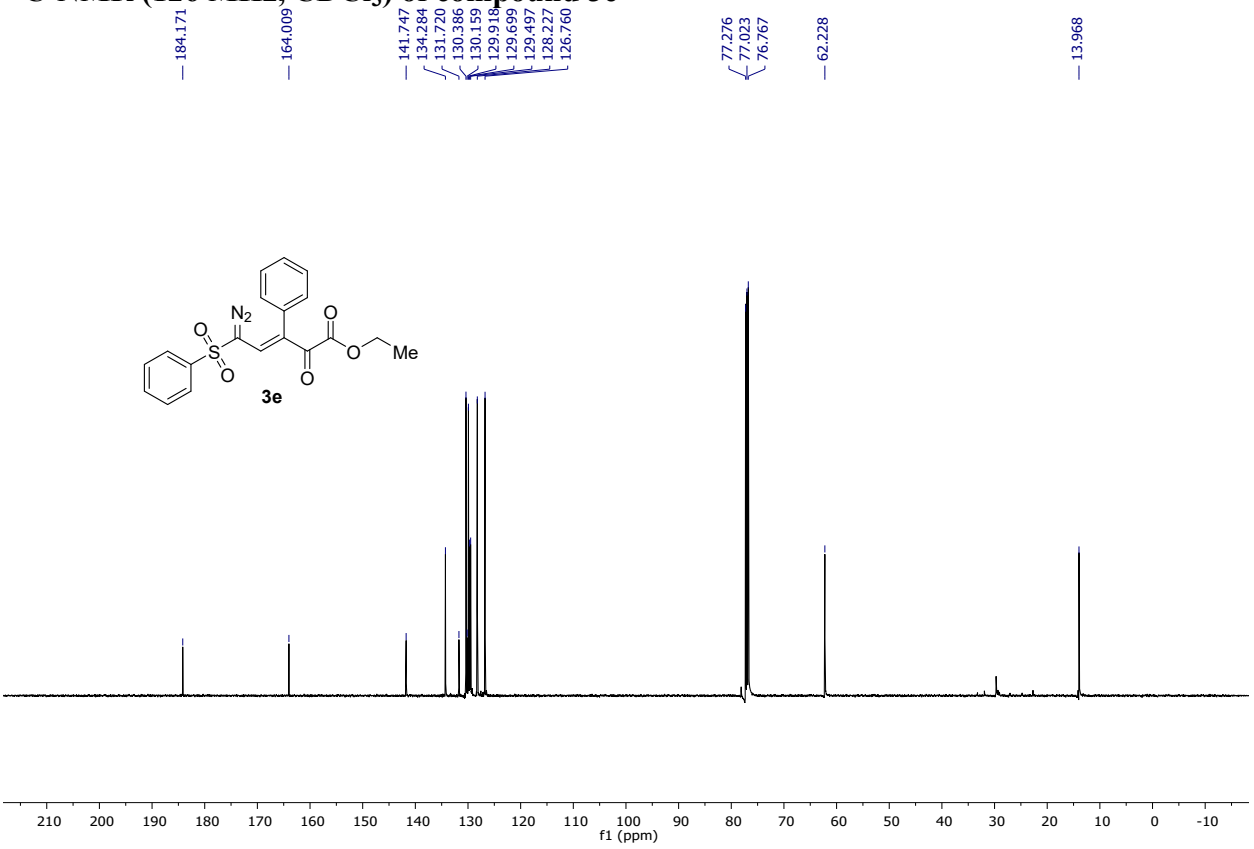

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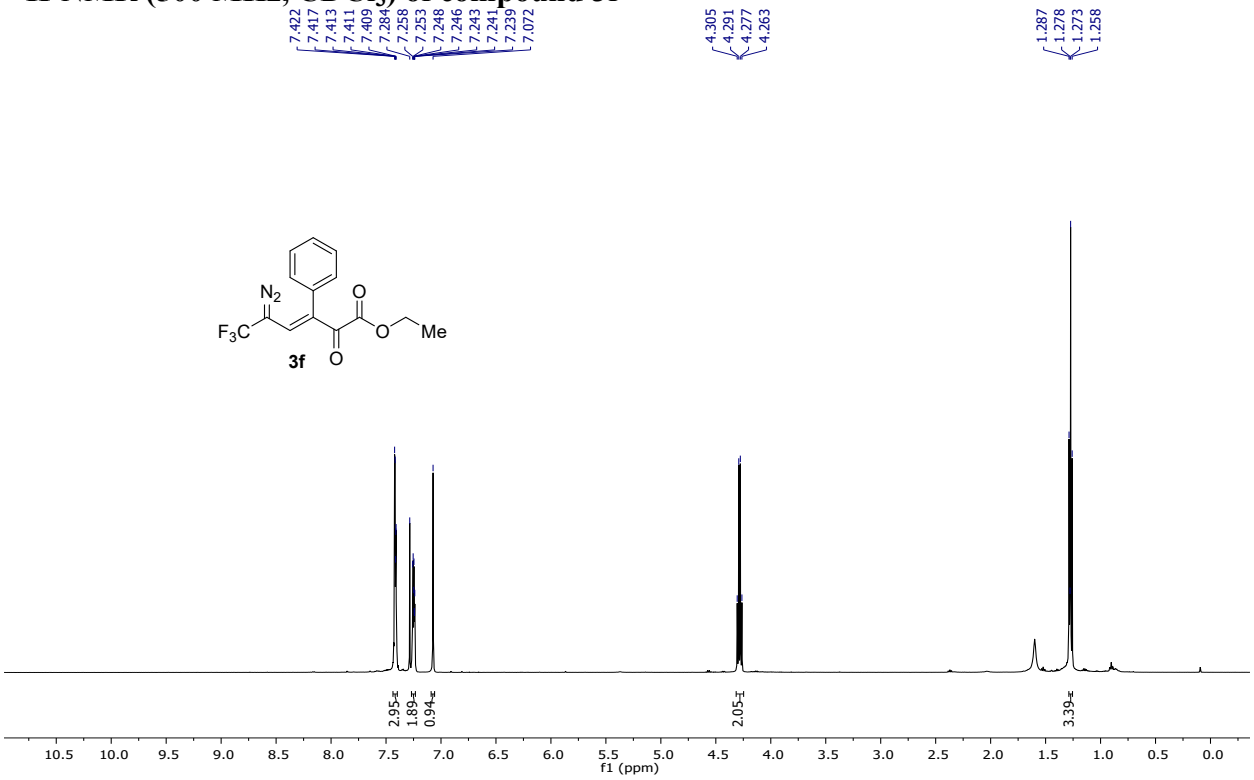

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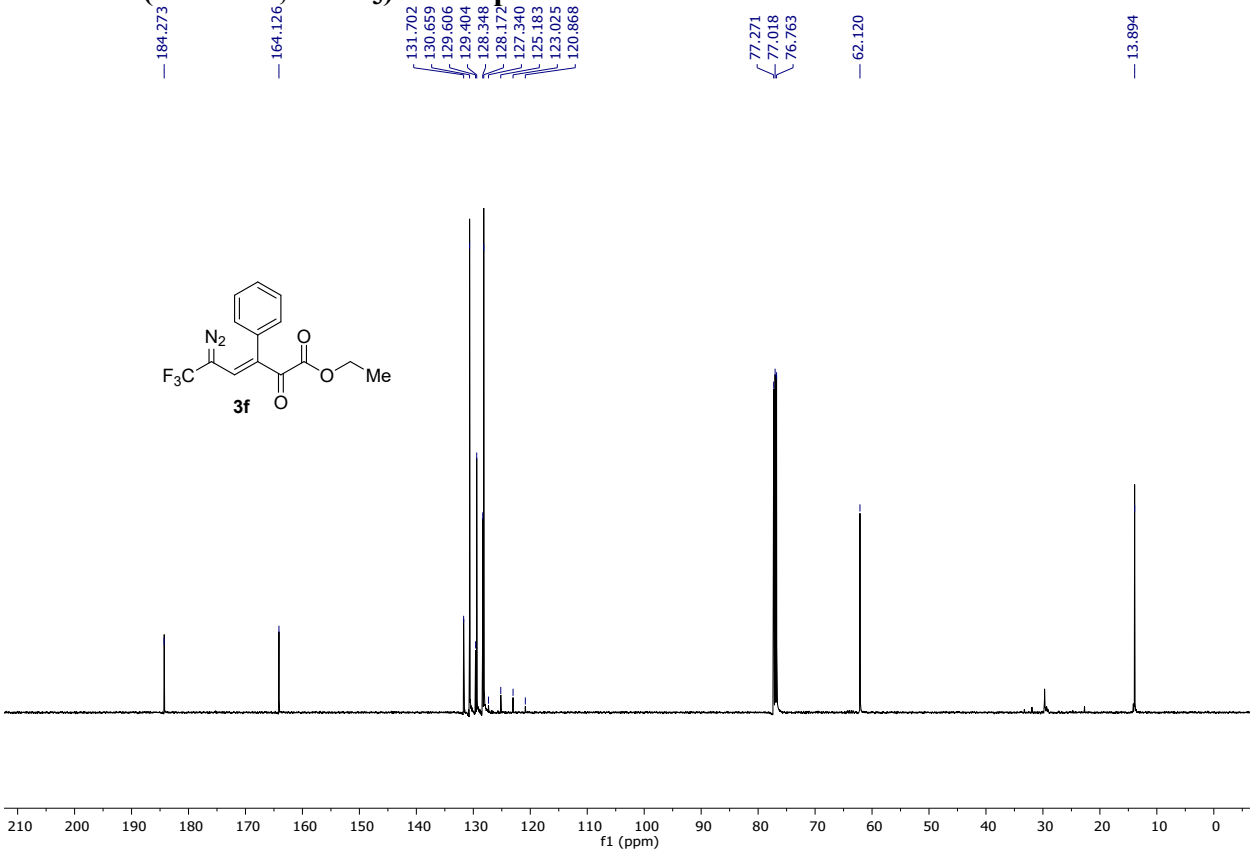

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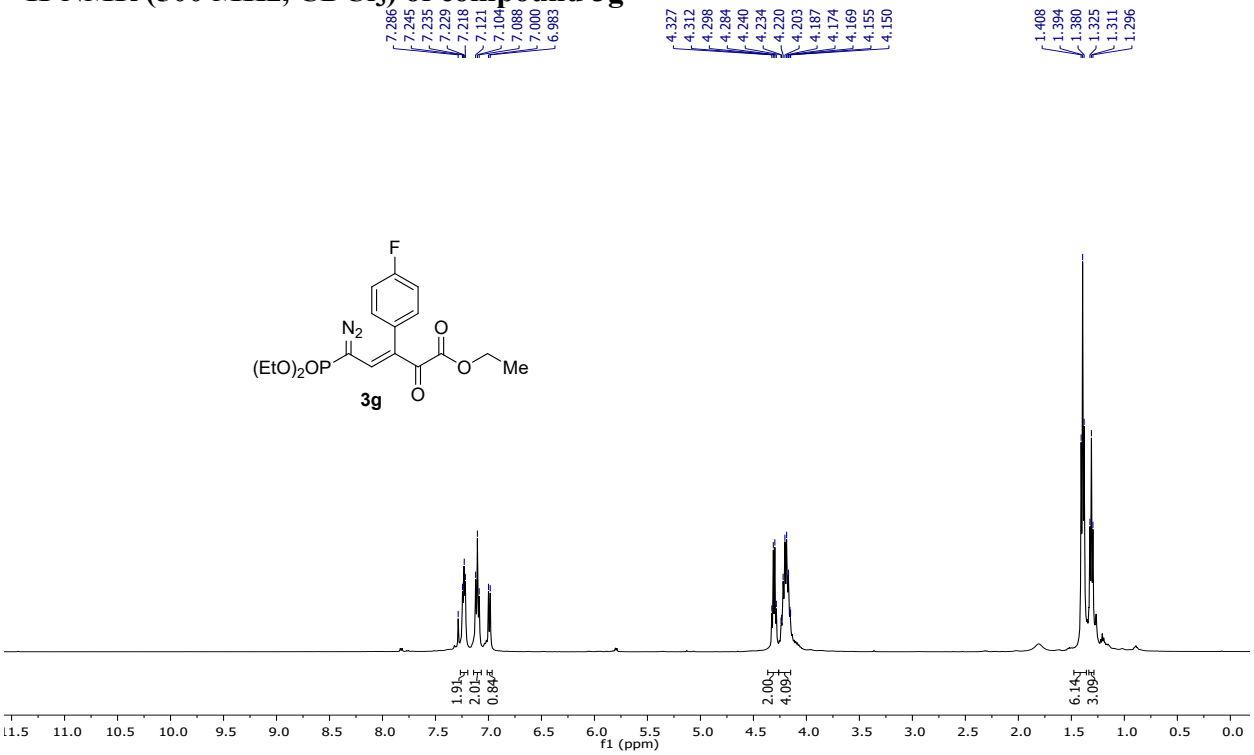

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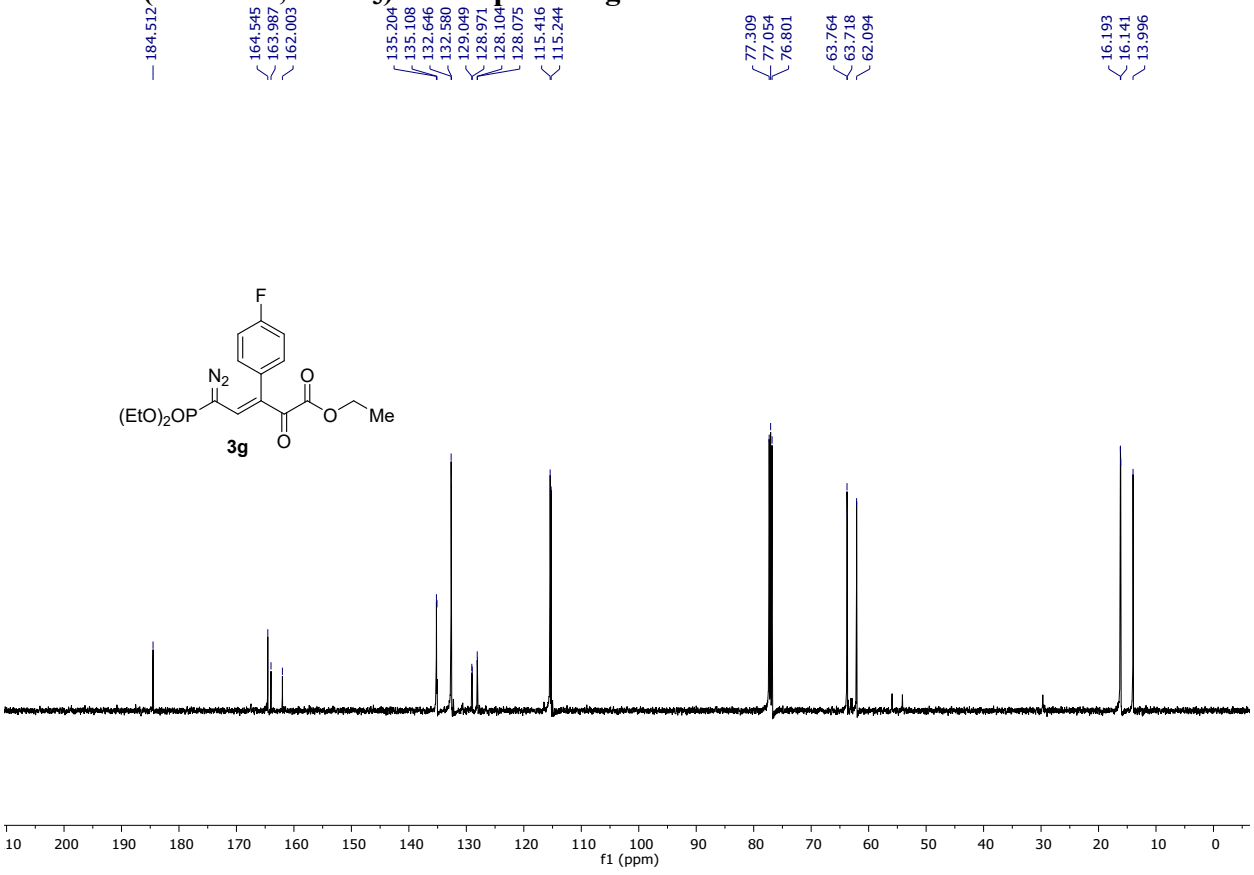

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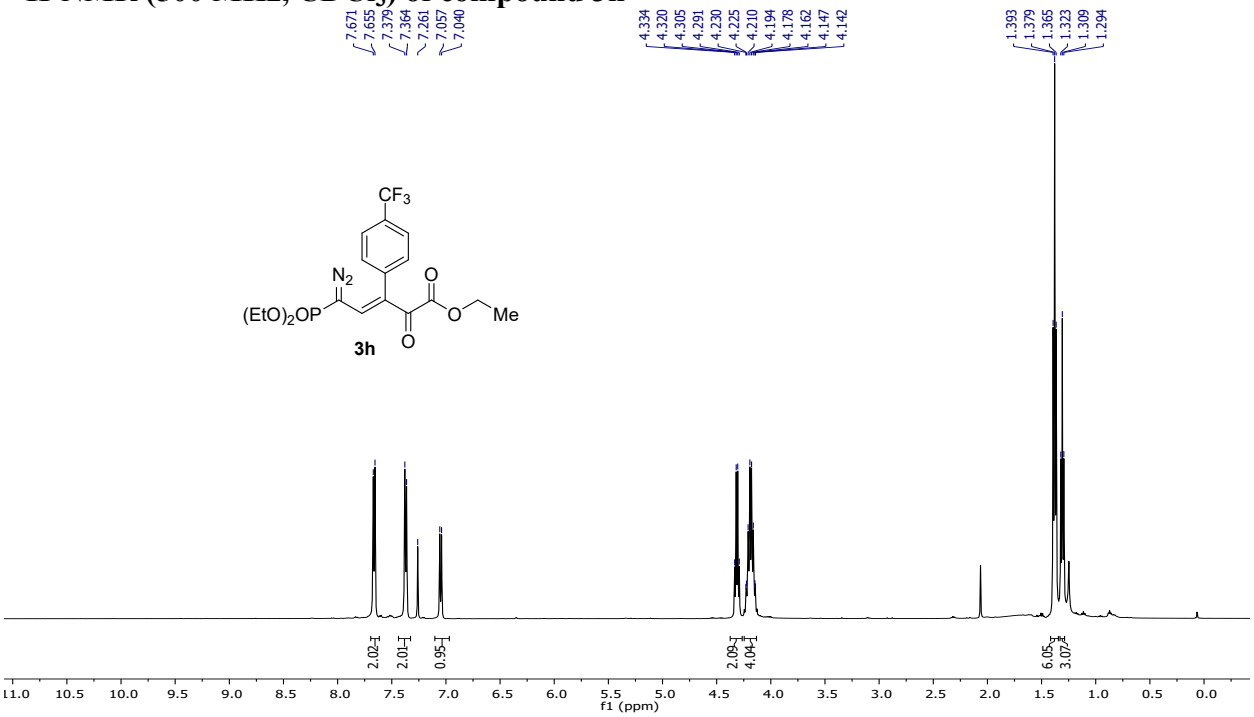

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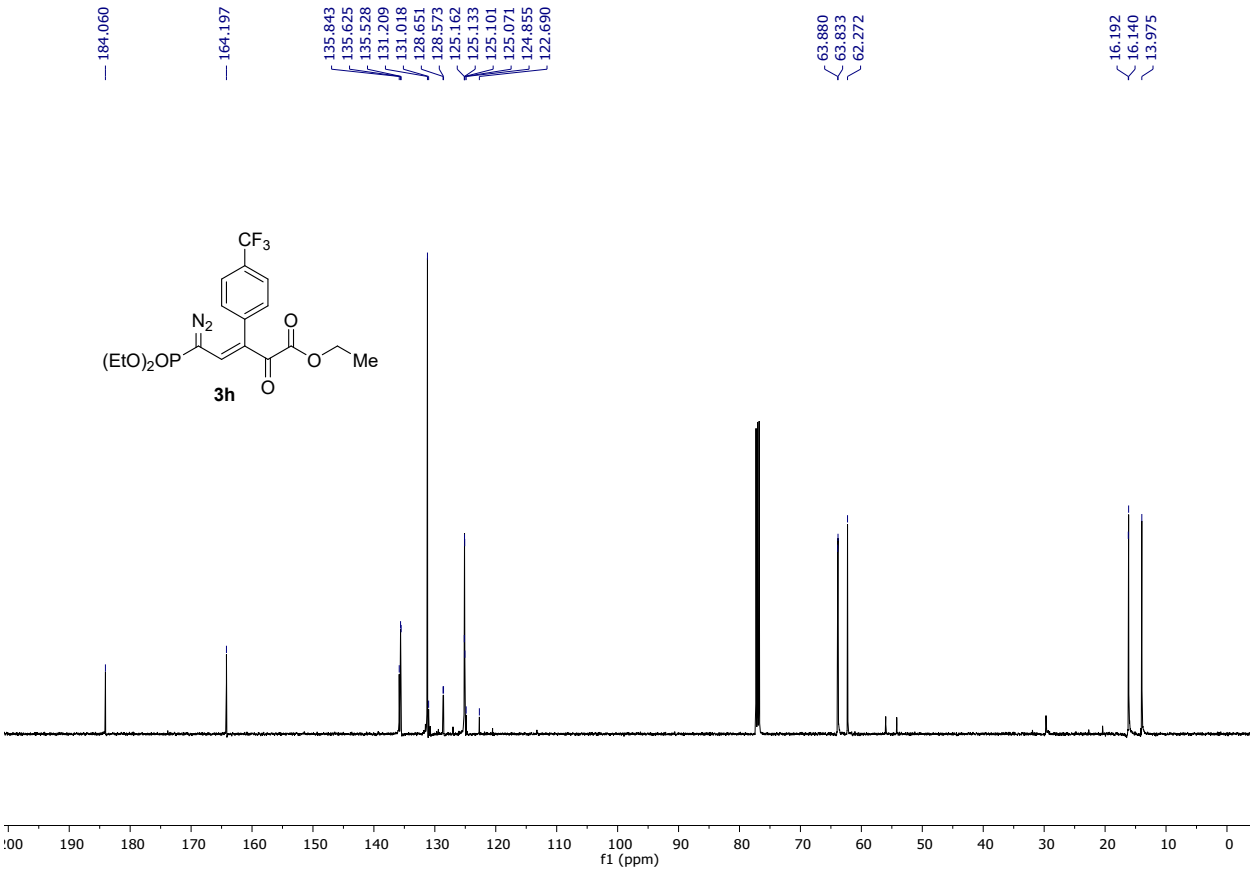

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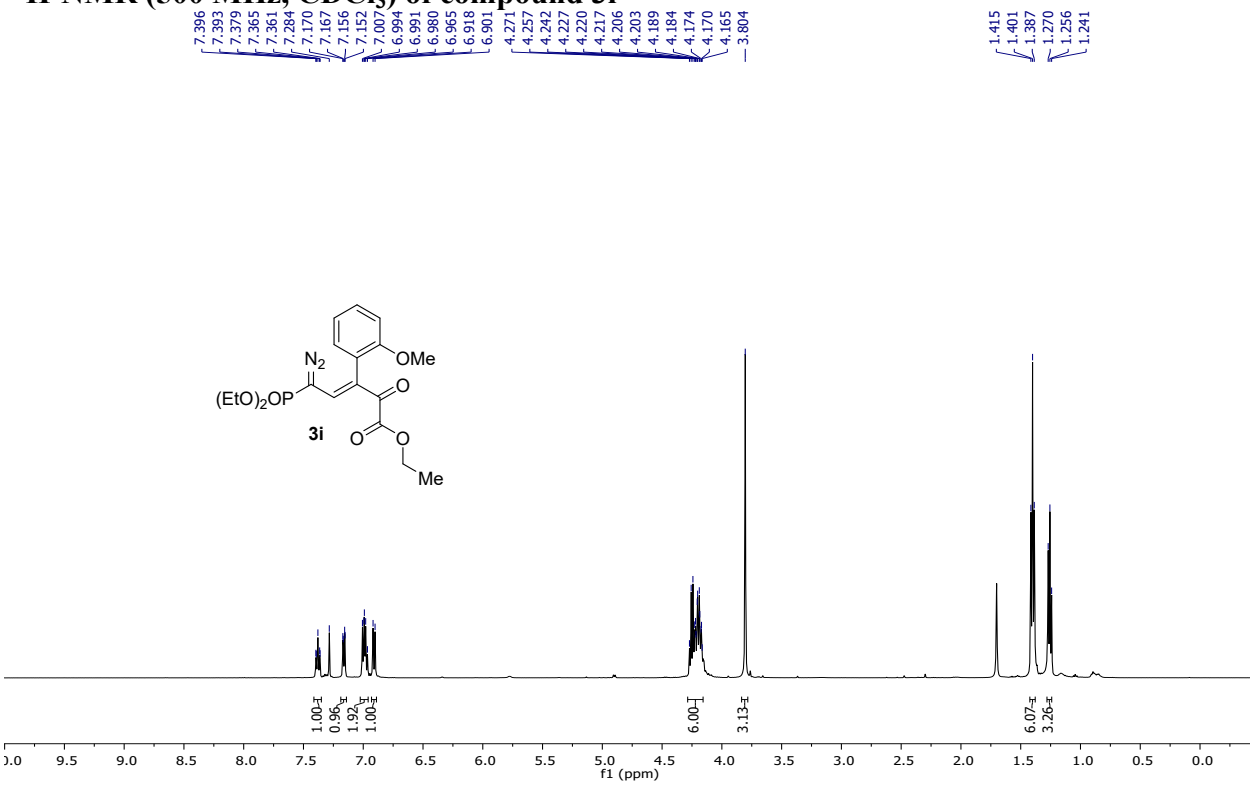

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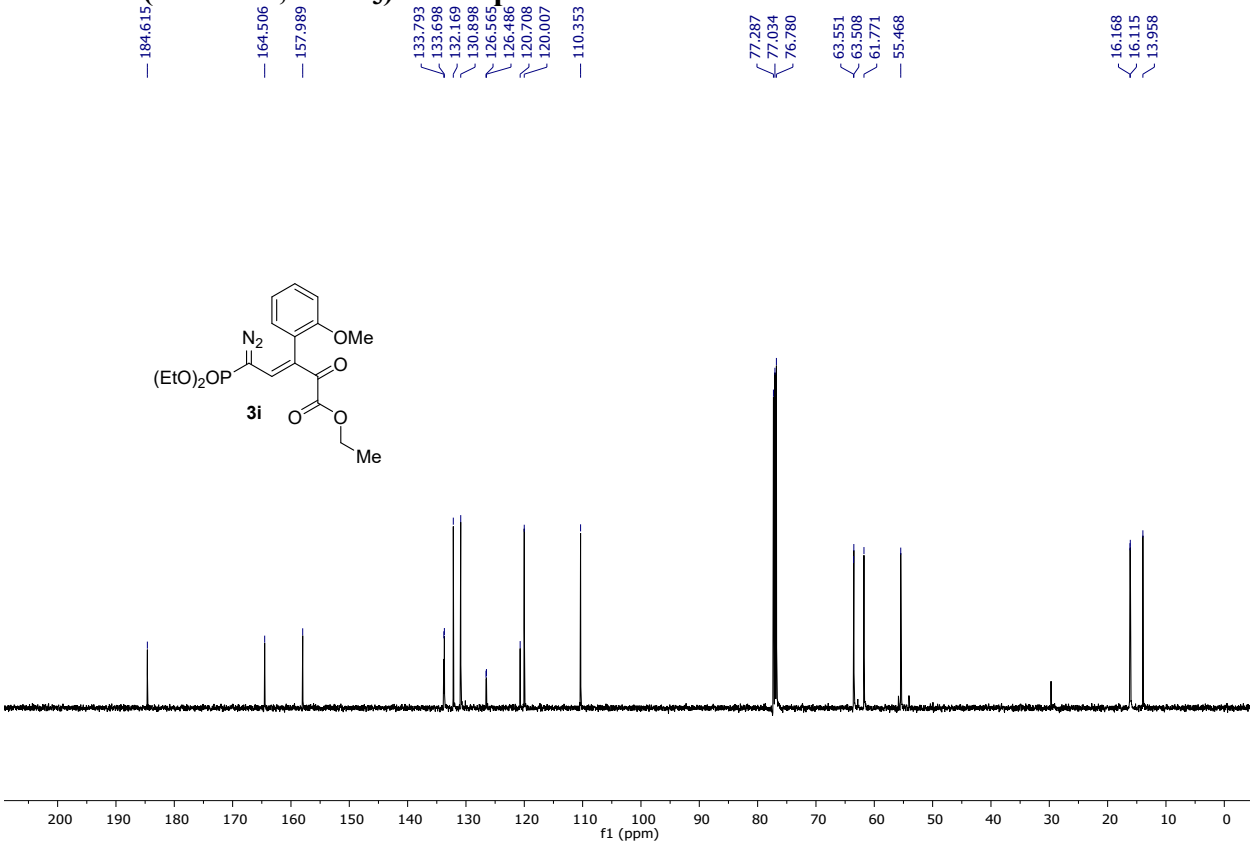

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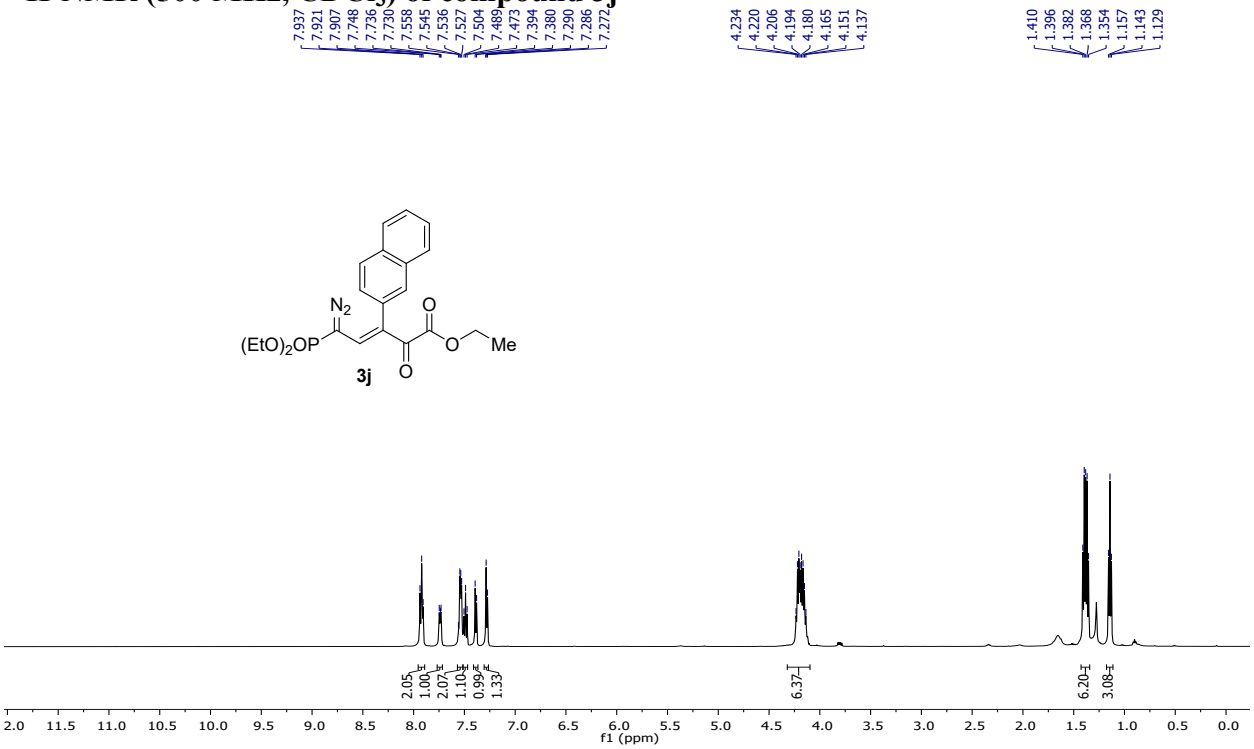

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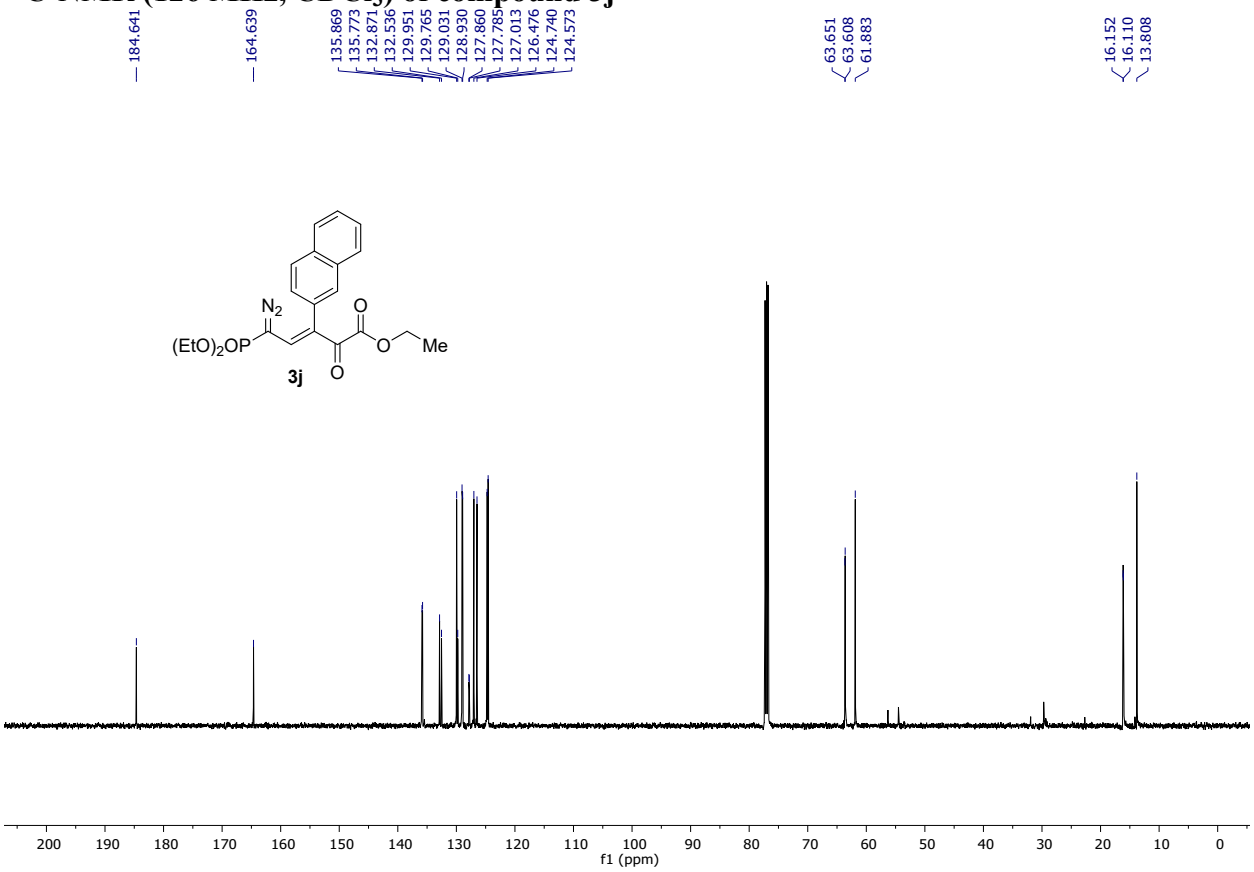

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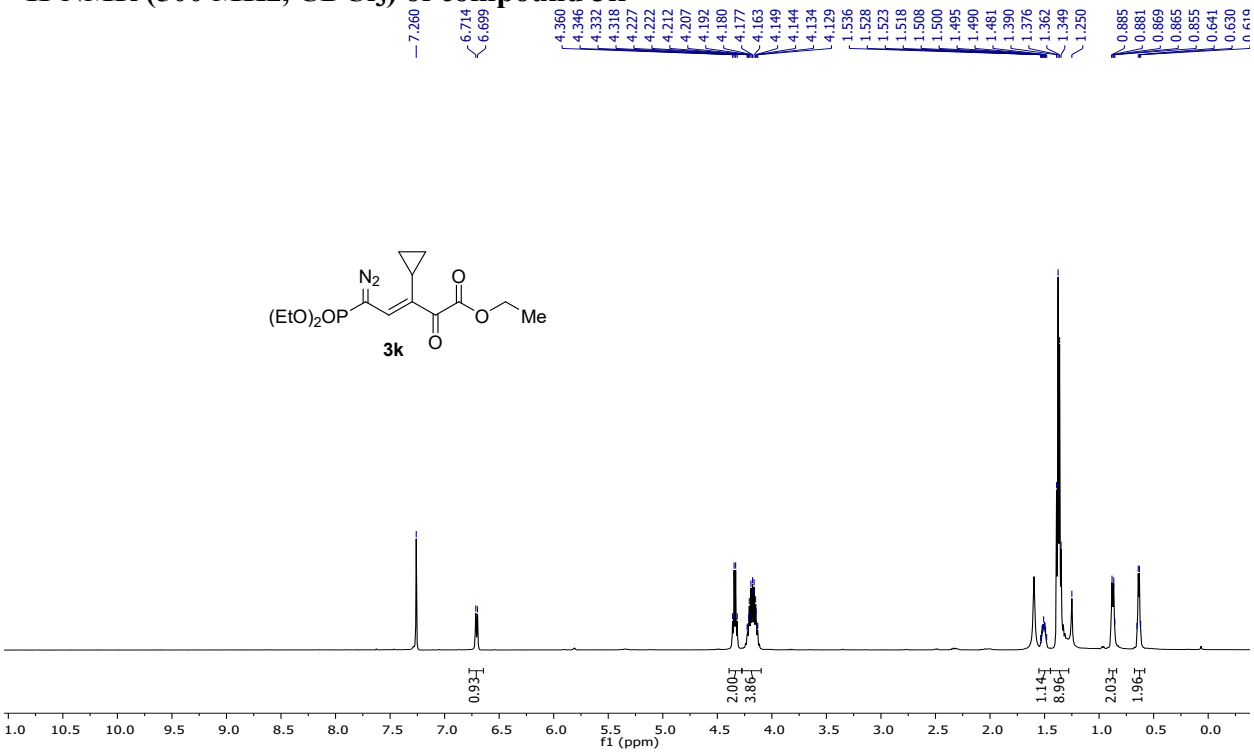

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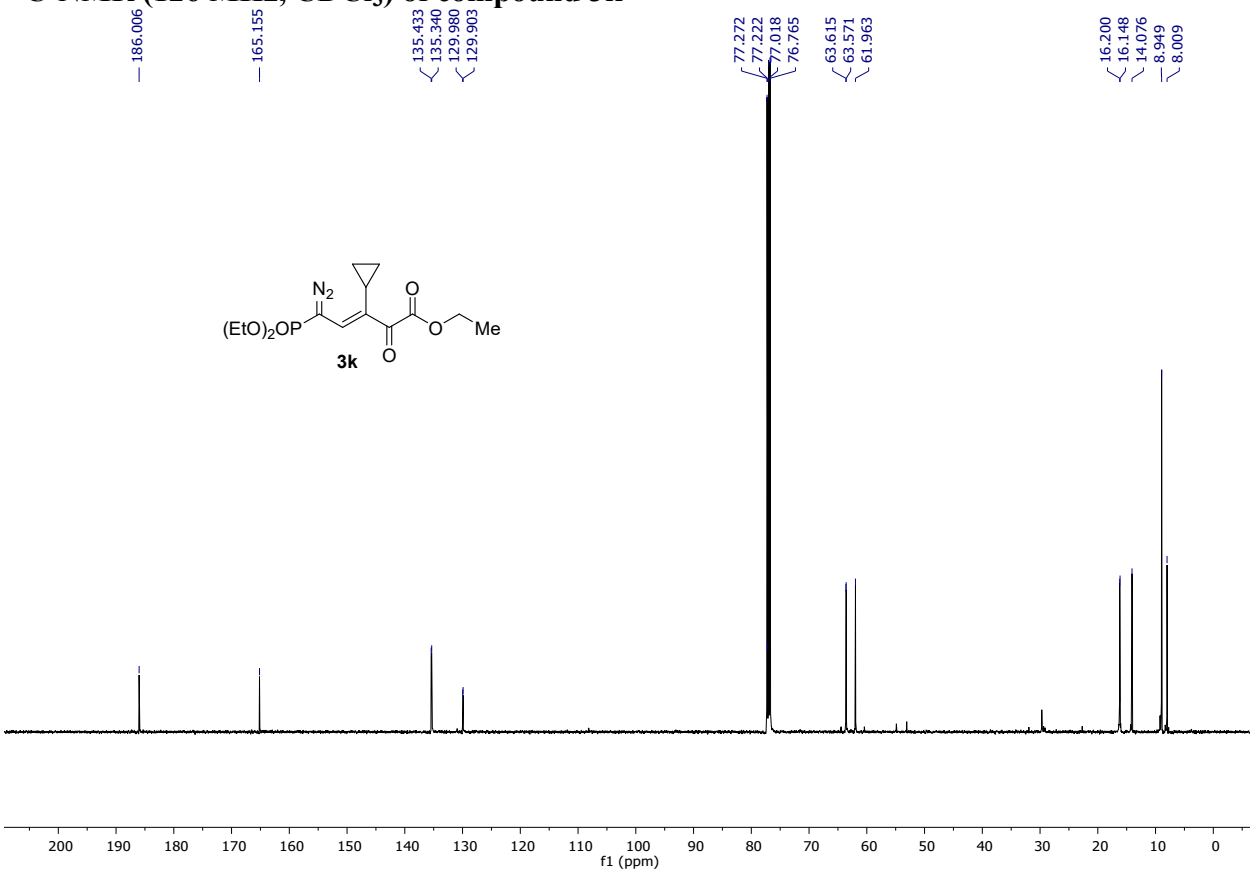

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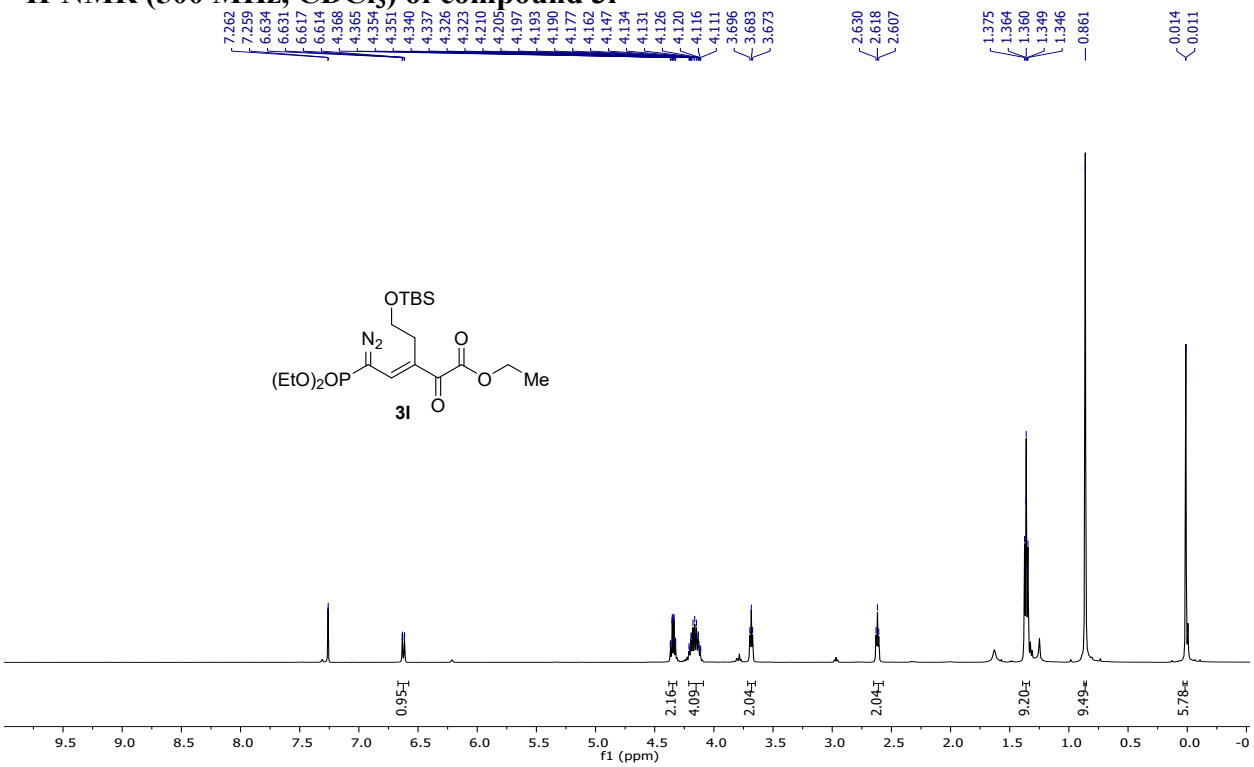

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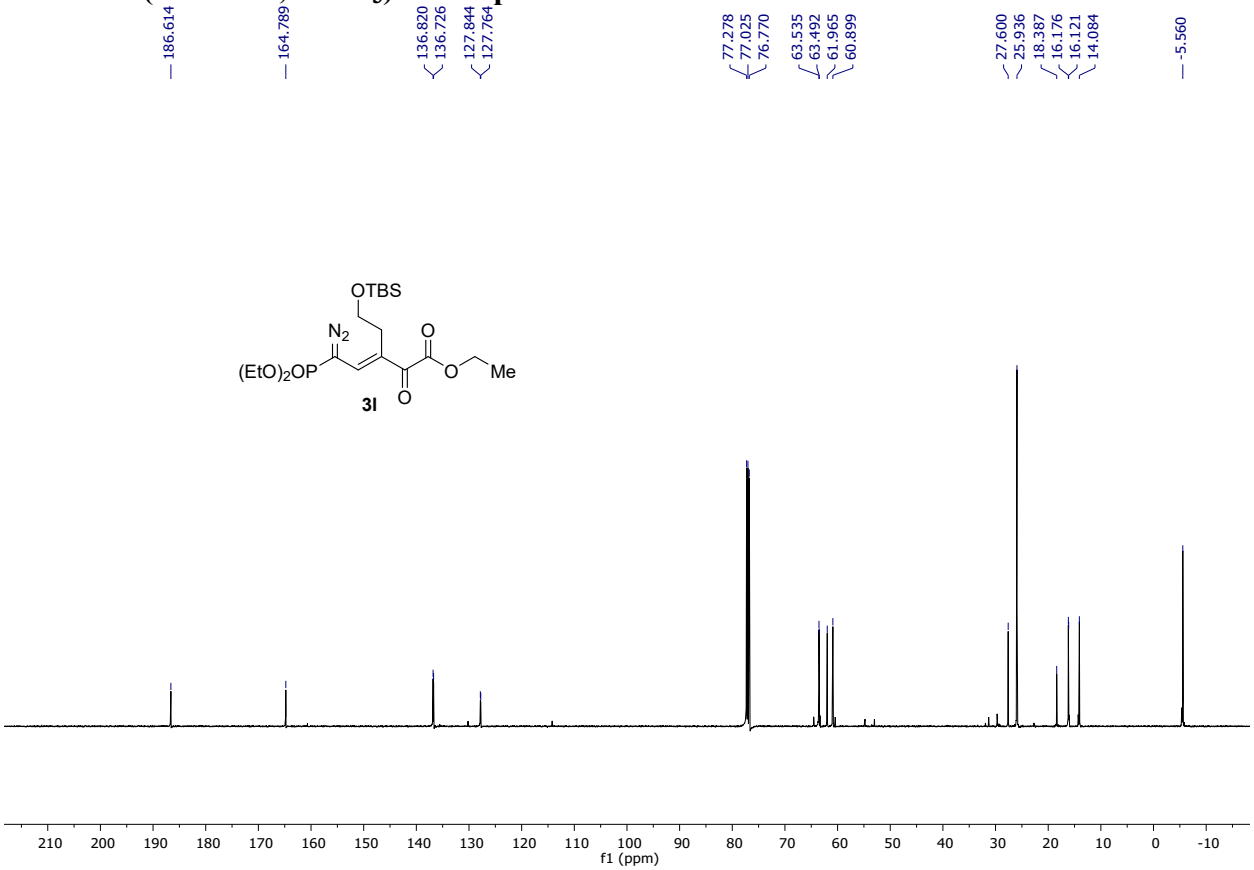
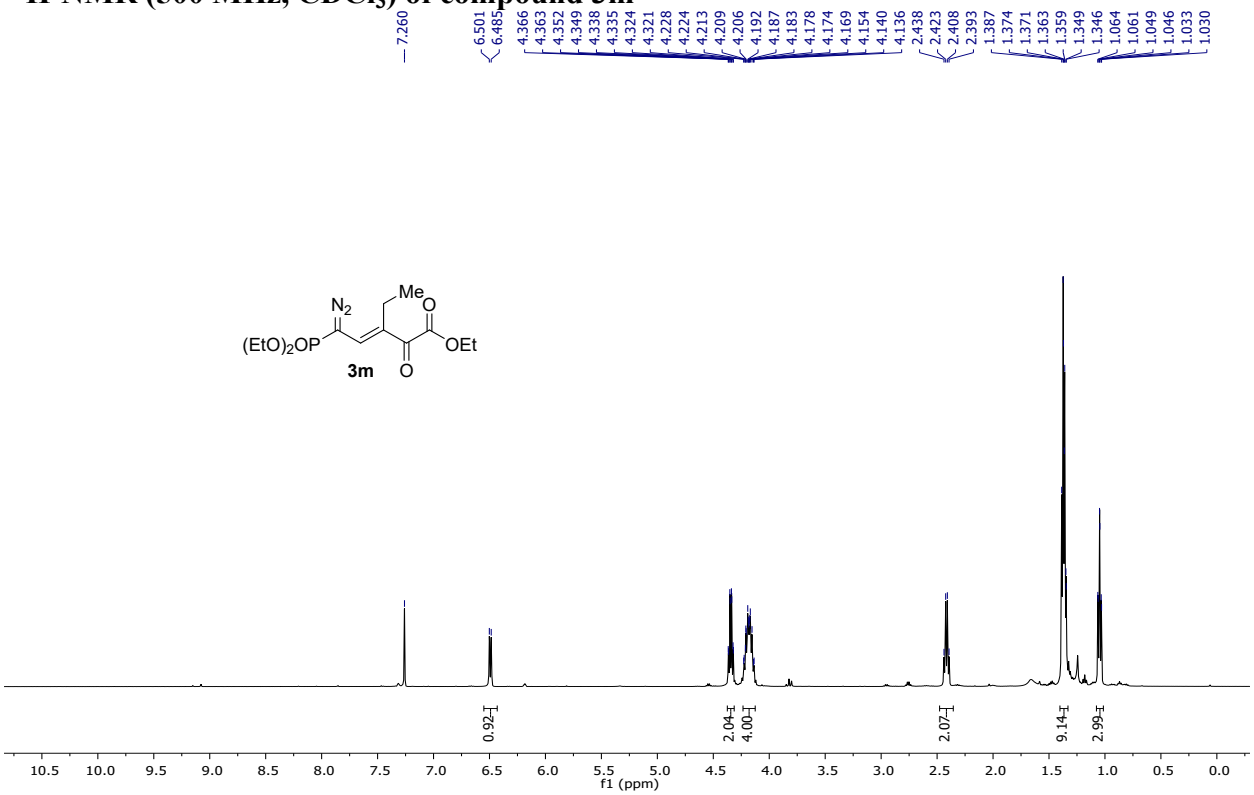
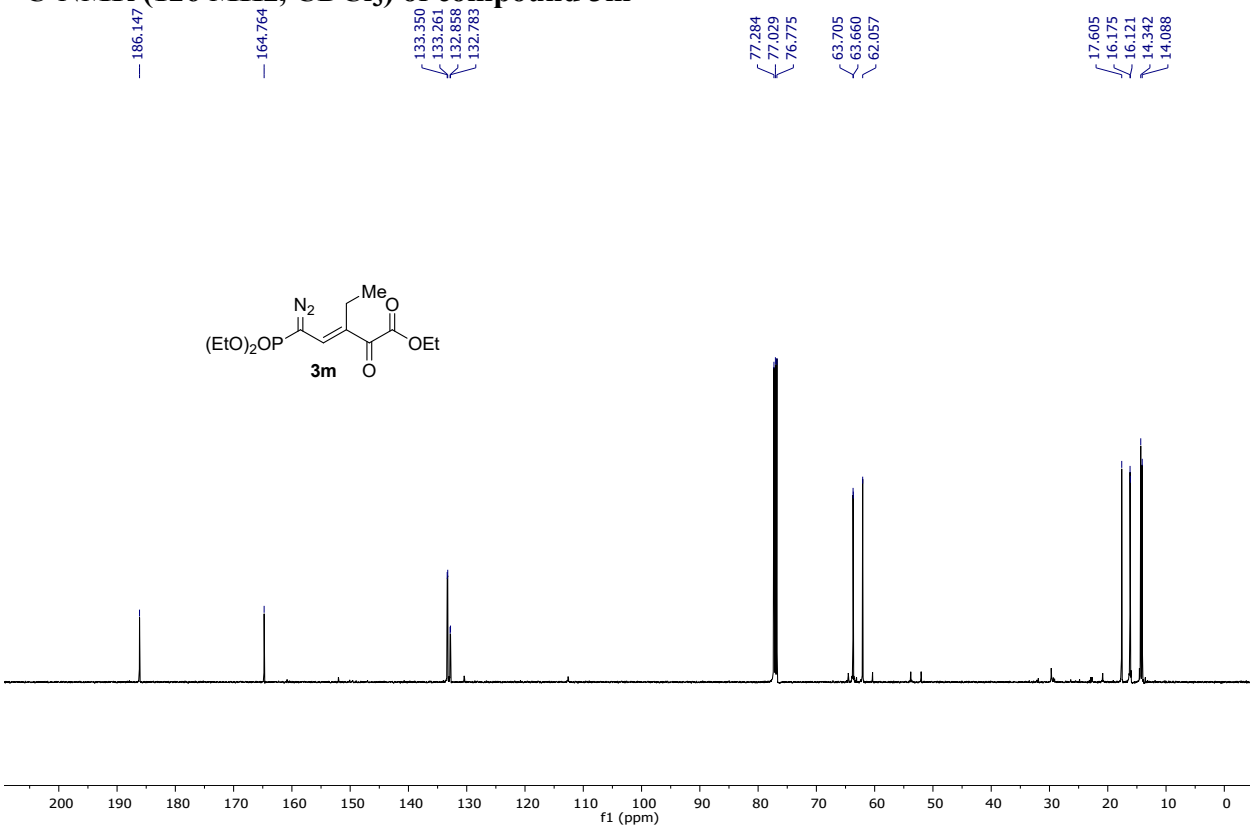


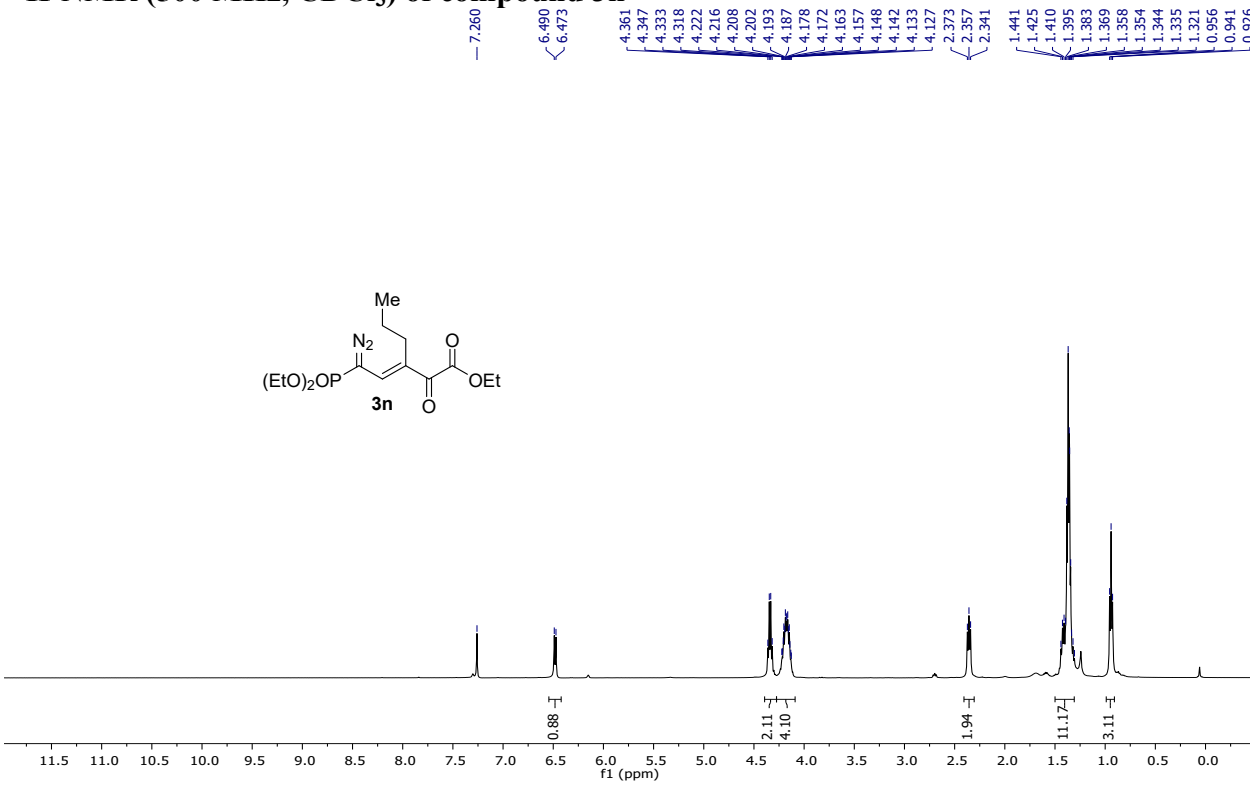
^{1}H-NMR (500 MHz, $CDCl_3$) of compound 3m



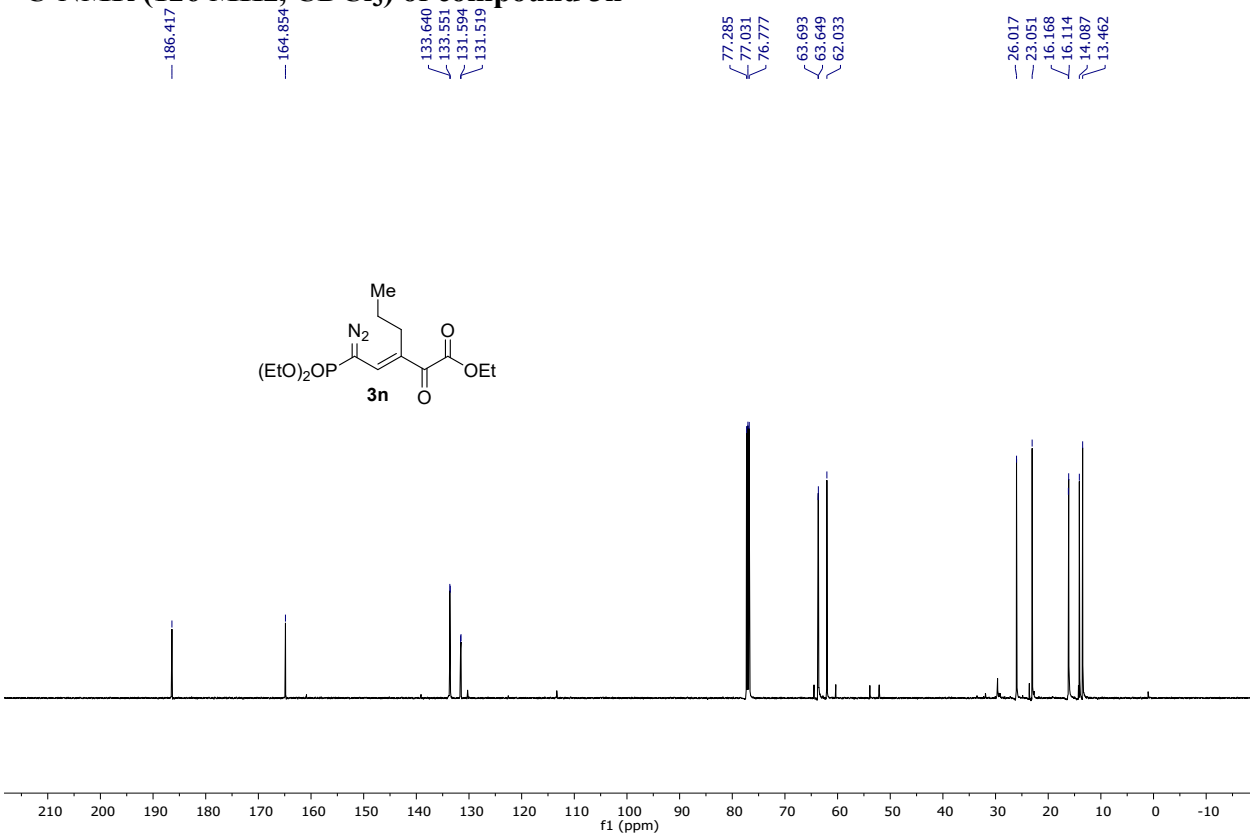
^{13}C-NMR (126 MHz, $CDCl_3$) of compound 3m



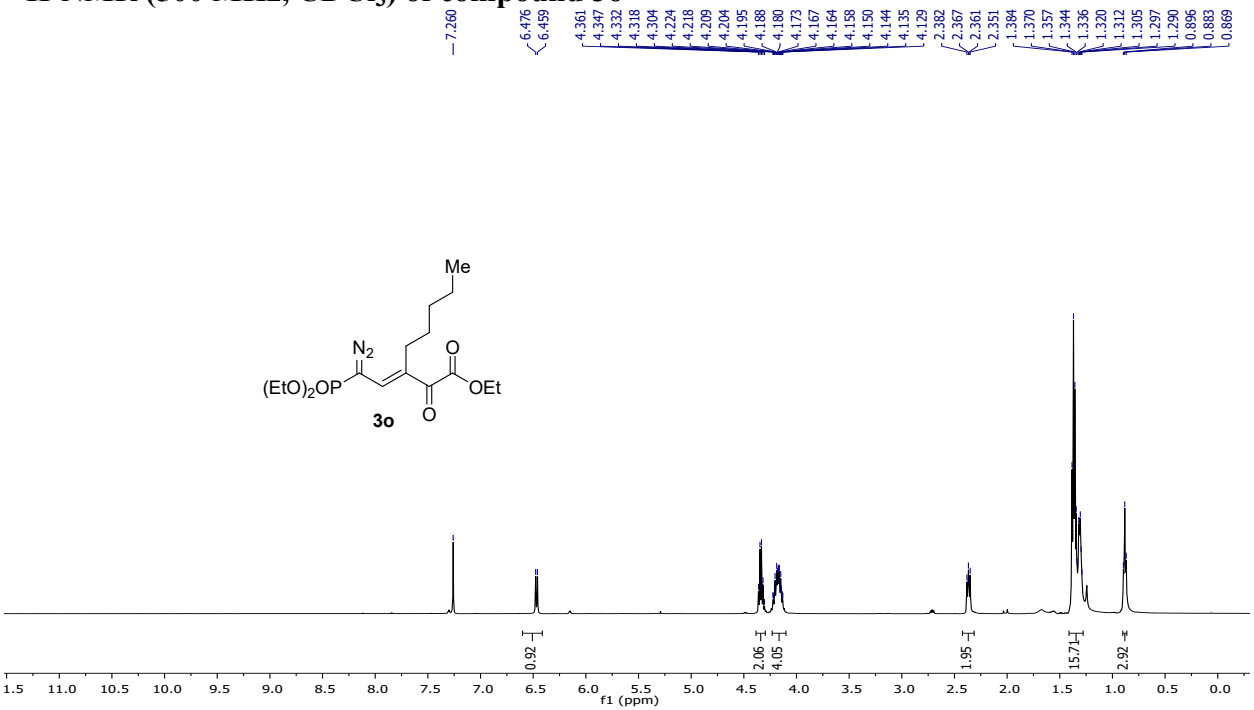
^{1}H-NMR (500 MHz, $CDCl_3$) of compound 3n



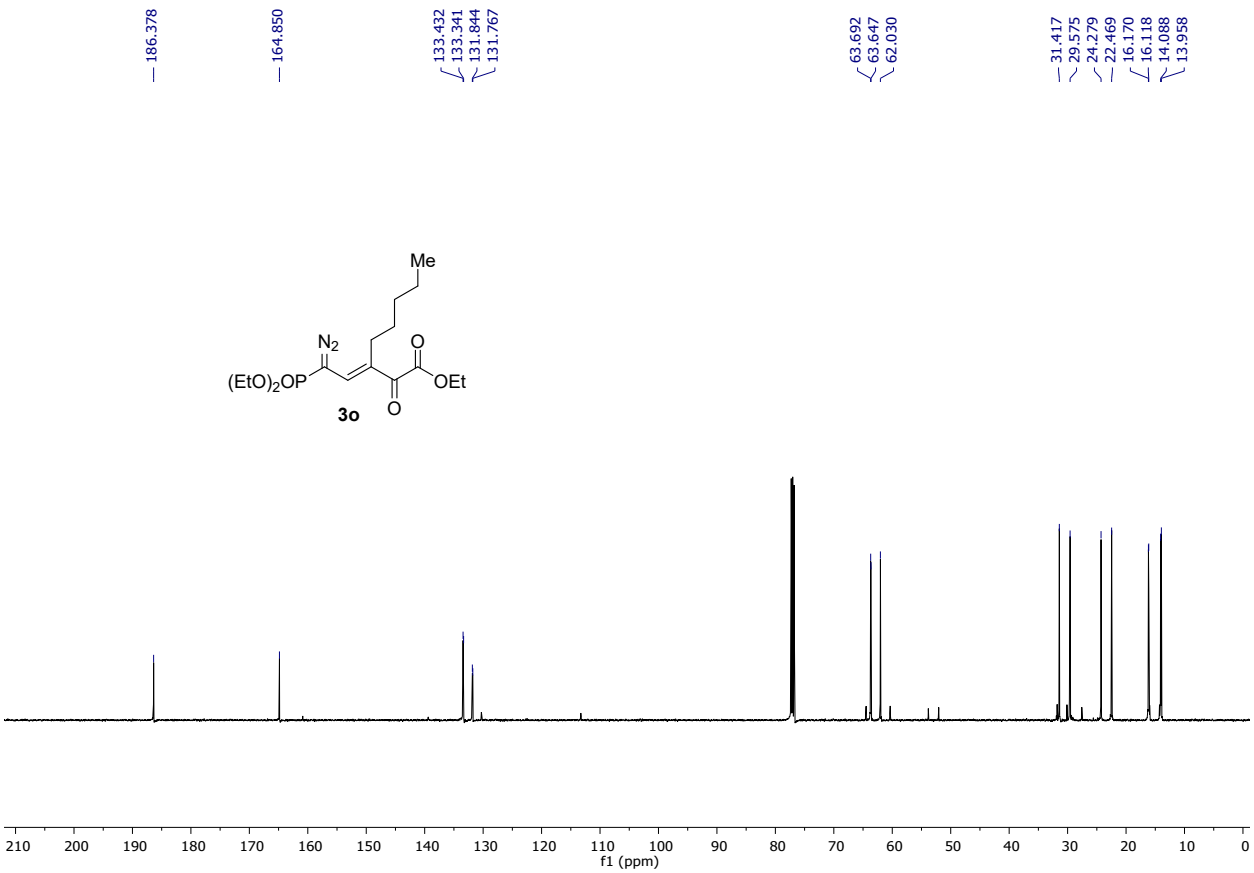
^{13}C-NMR (126 MHz, $CDCl_3$) of compound 3n



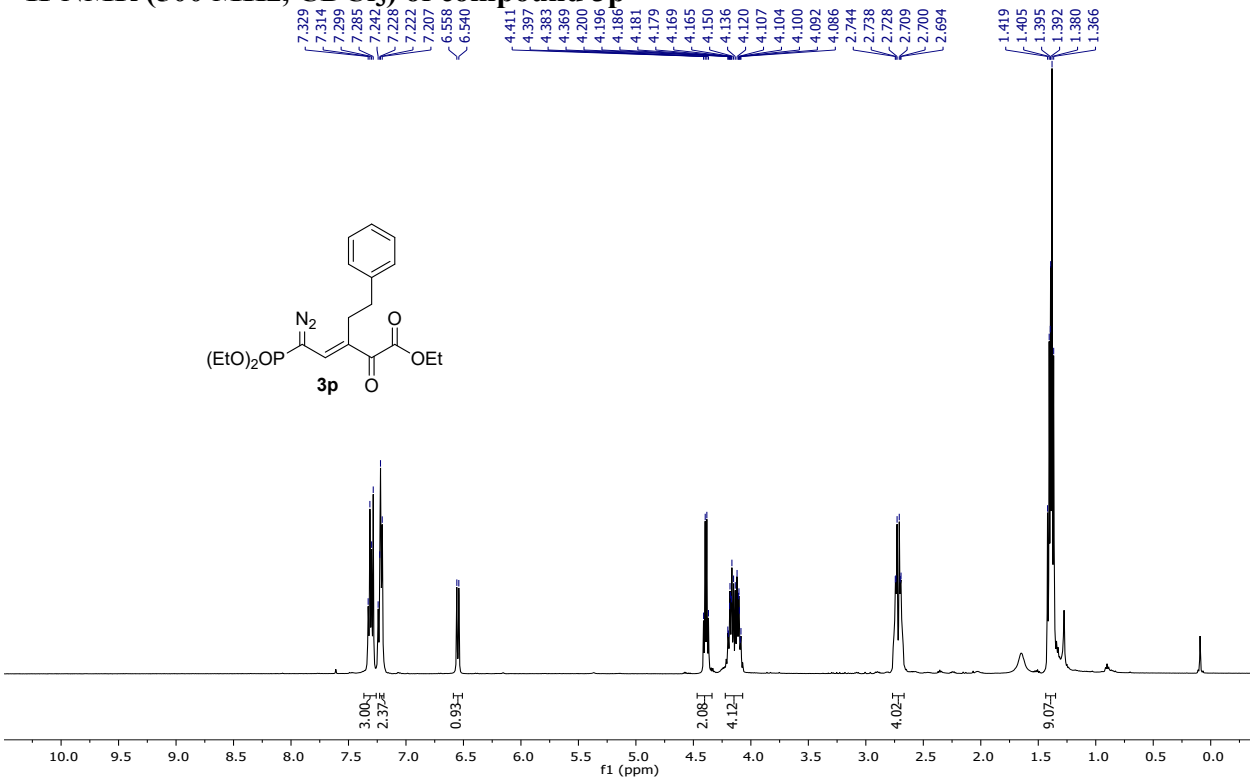
^{1}H-NMR (500 MHz, $CDCl_3$) of compound 3o



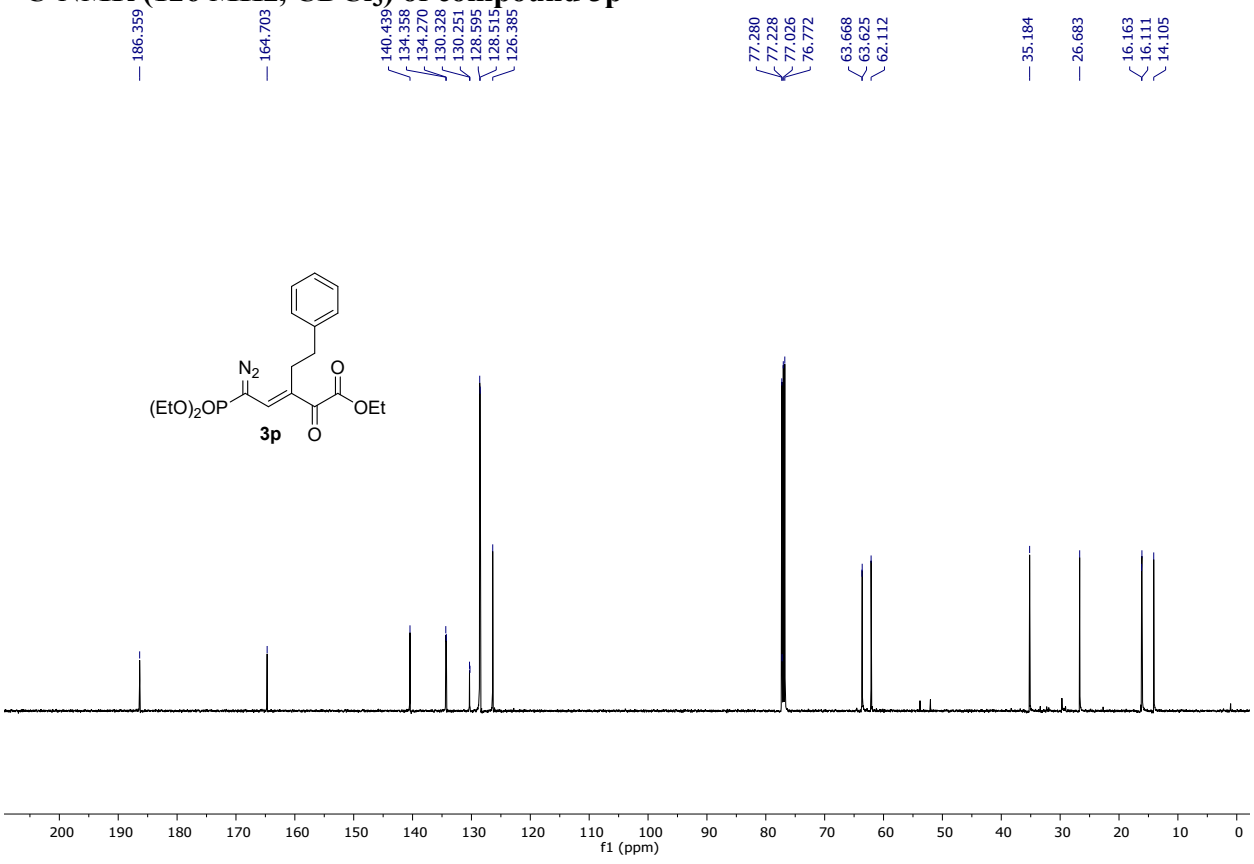
^{13}C-NMR (126 MHz, $CDCl_3$) of compound 3o



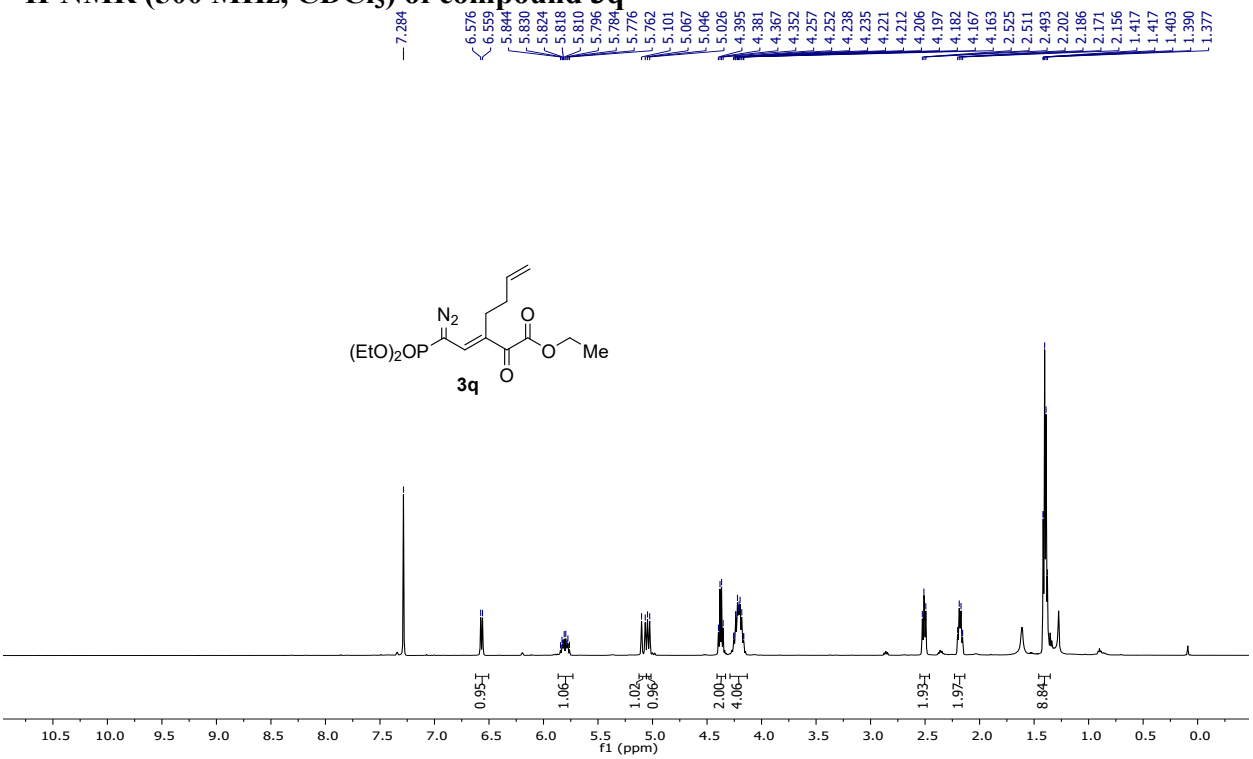
^{1}H-NMR (500 MHz, $CDCl_3$) of compound 3p



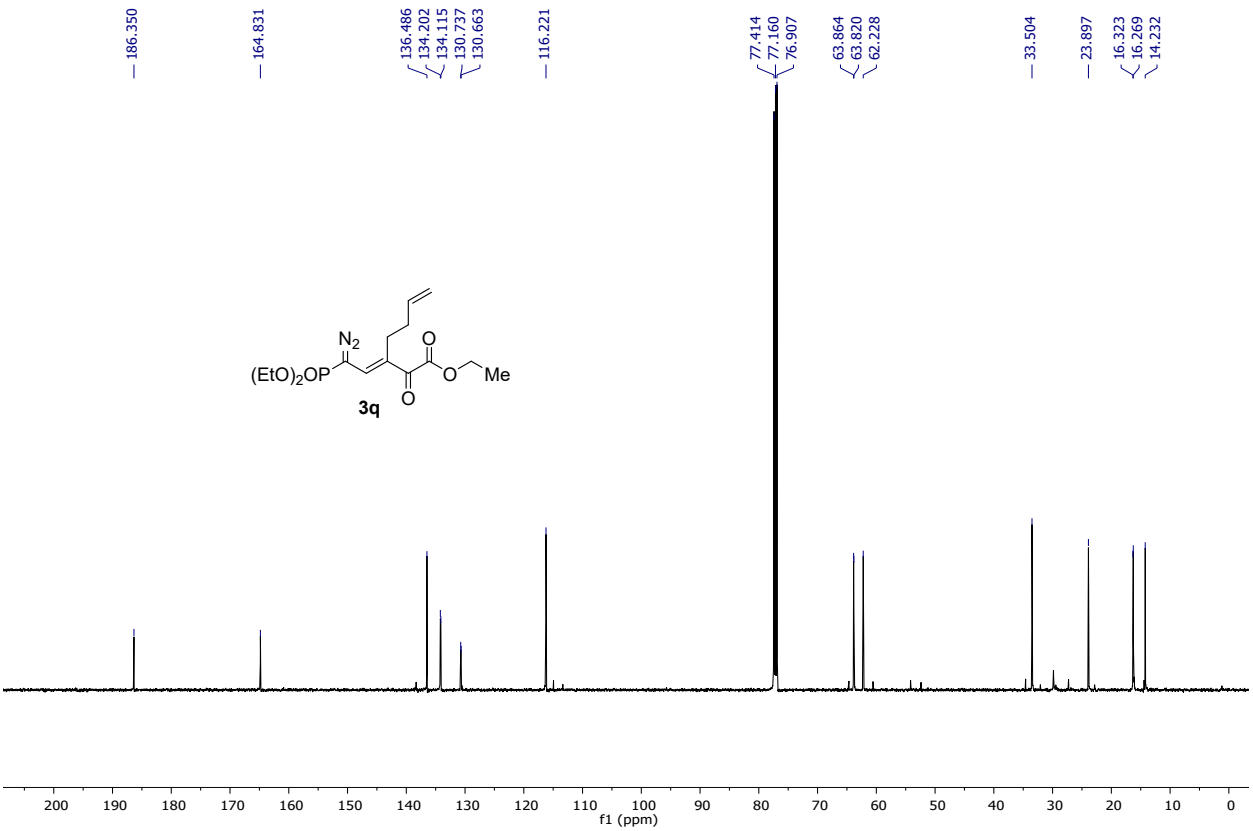
^{13}C-NMR (126 MHz, $CDCl_3$) of compound 3p



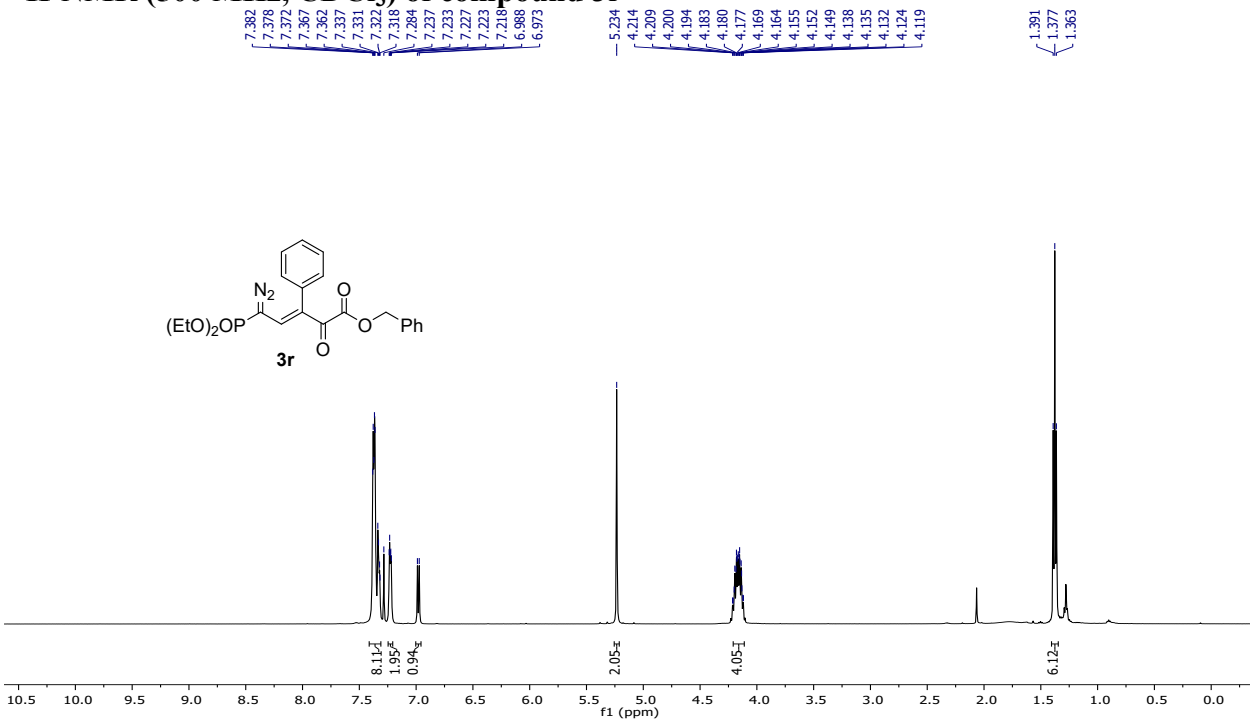
^{1}H-NMR (500 MHz, $CDCl_3$) of compound 3q



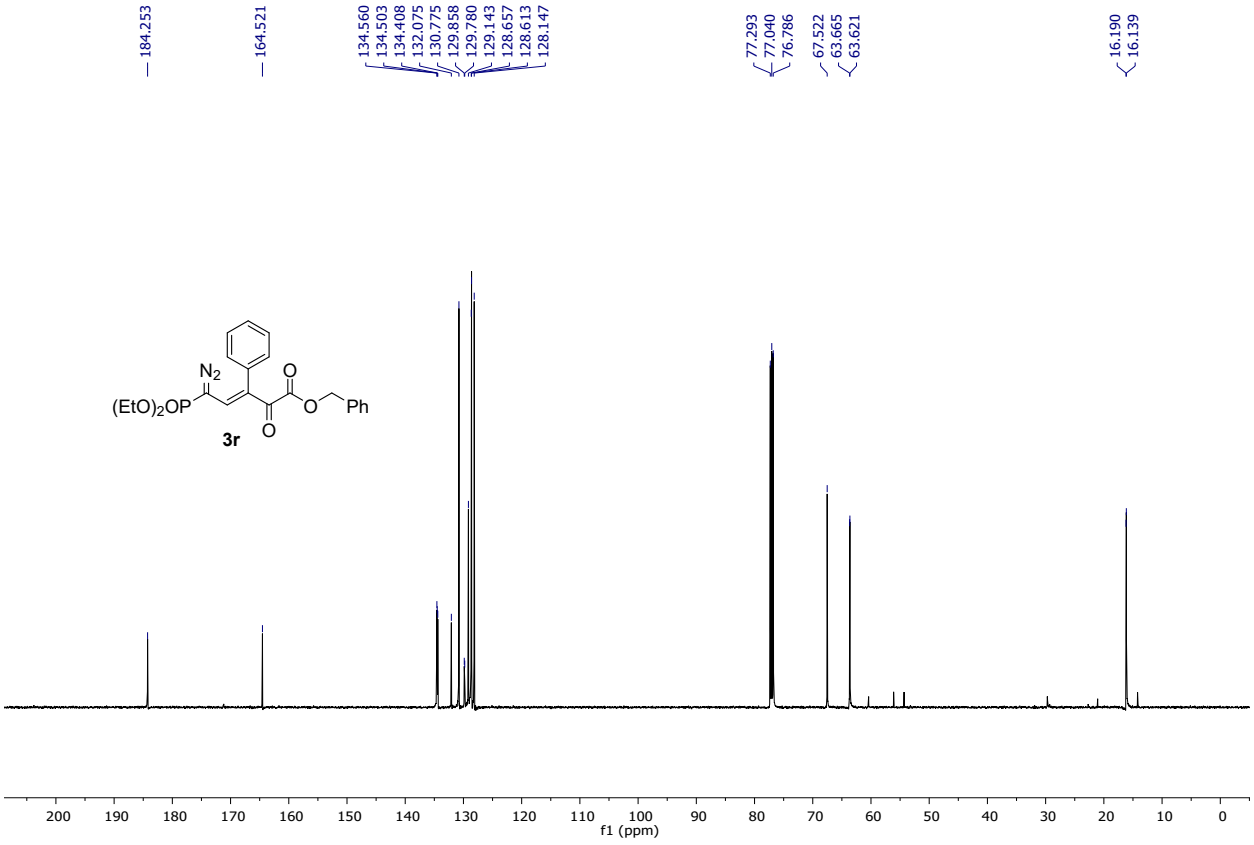
^{13}C-NMR (126 MHz, $CDCl_3$) of compound 3q



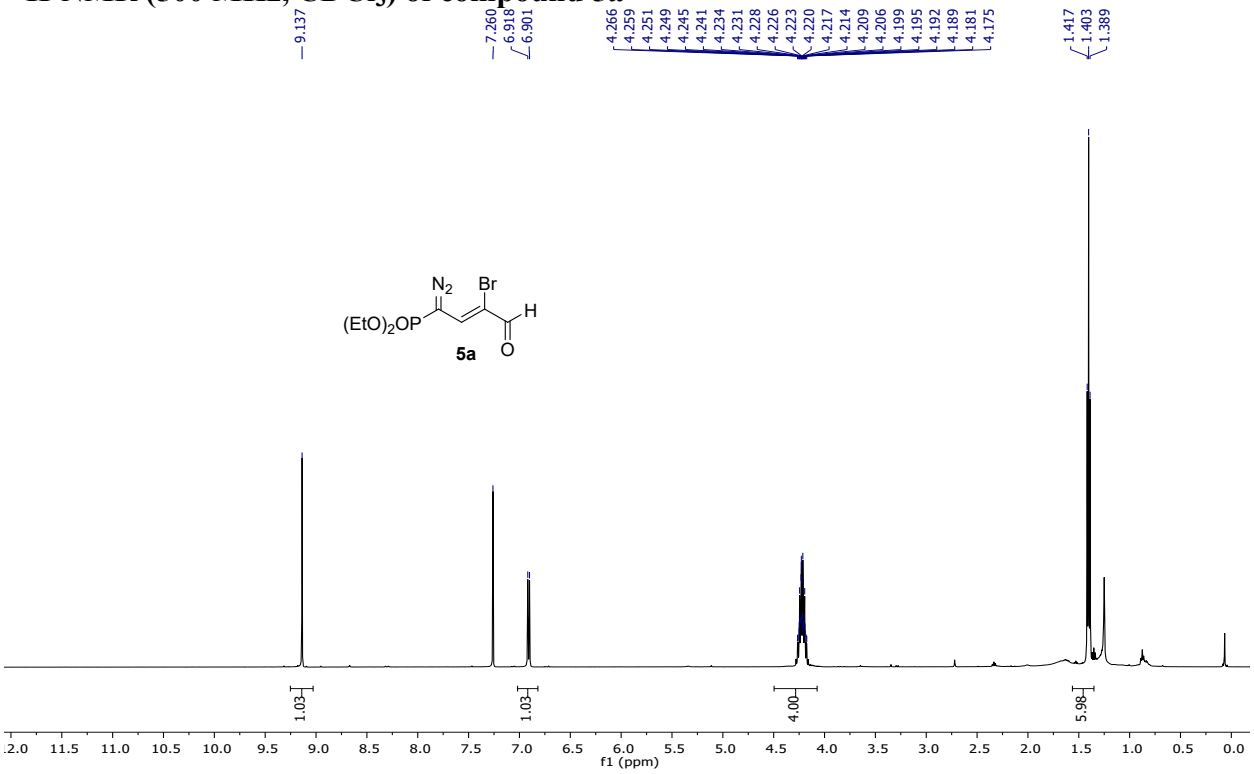
^{1}H-NMR (500 MHz, $CDCl_3$) of compound 3r



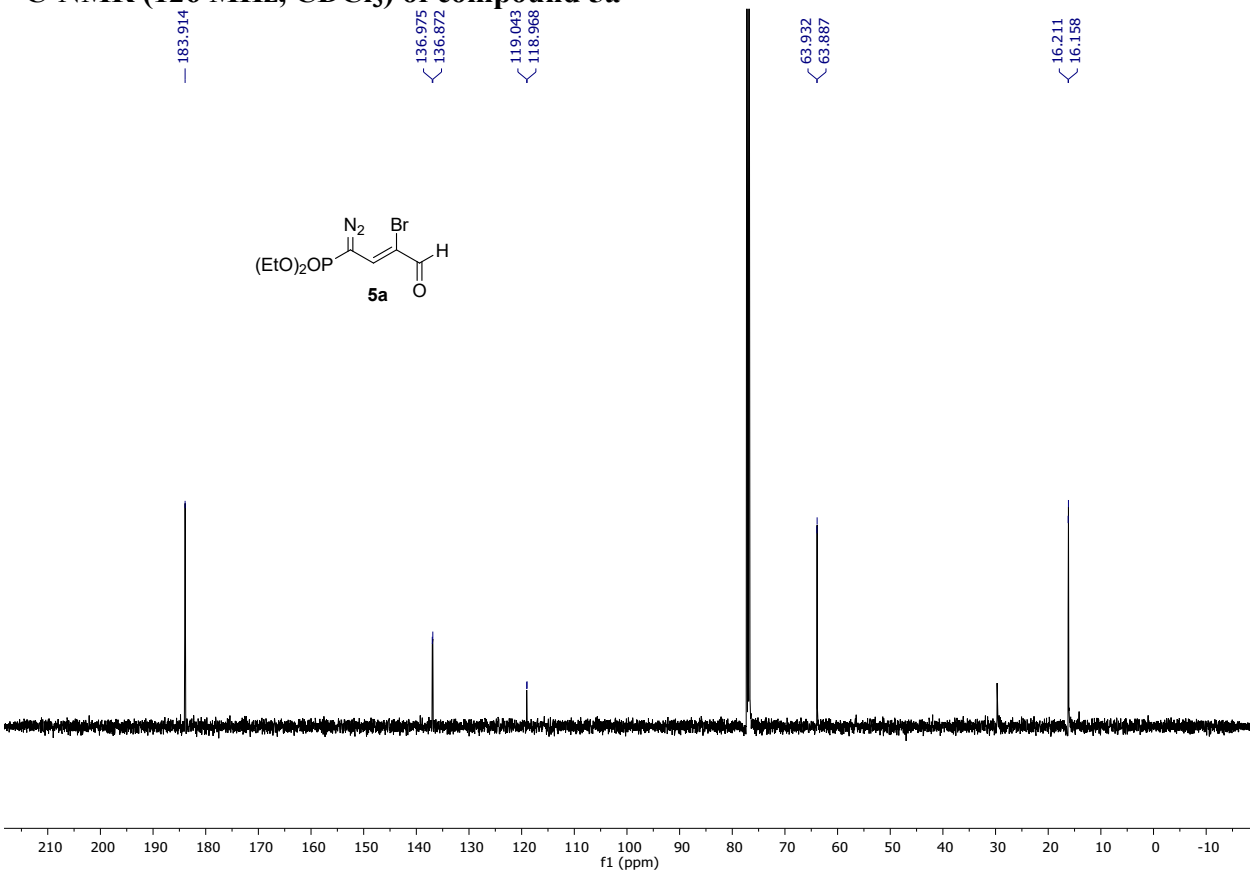
^{13}C-NMR (126 MHz, $CDCl_3$) of compound 3r



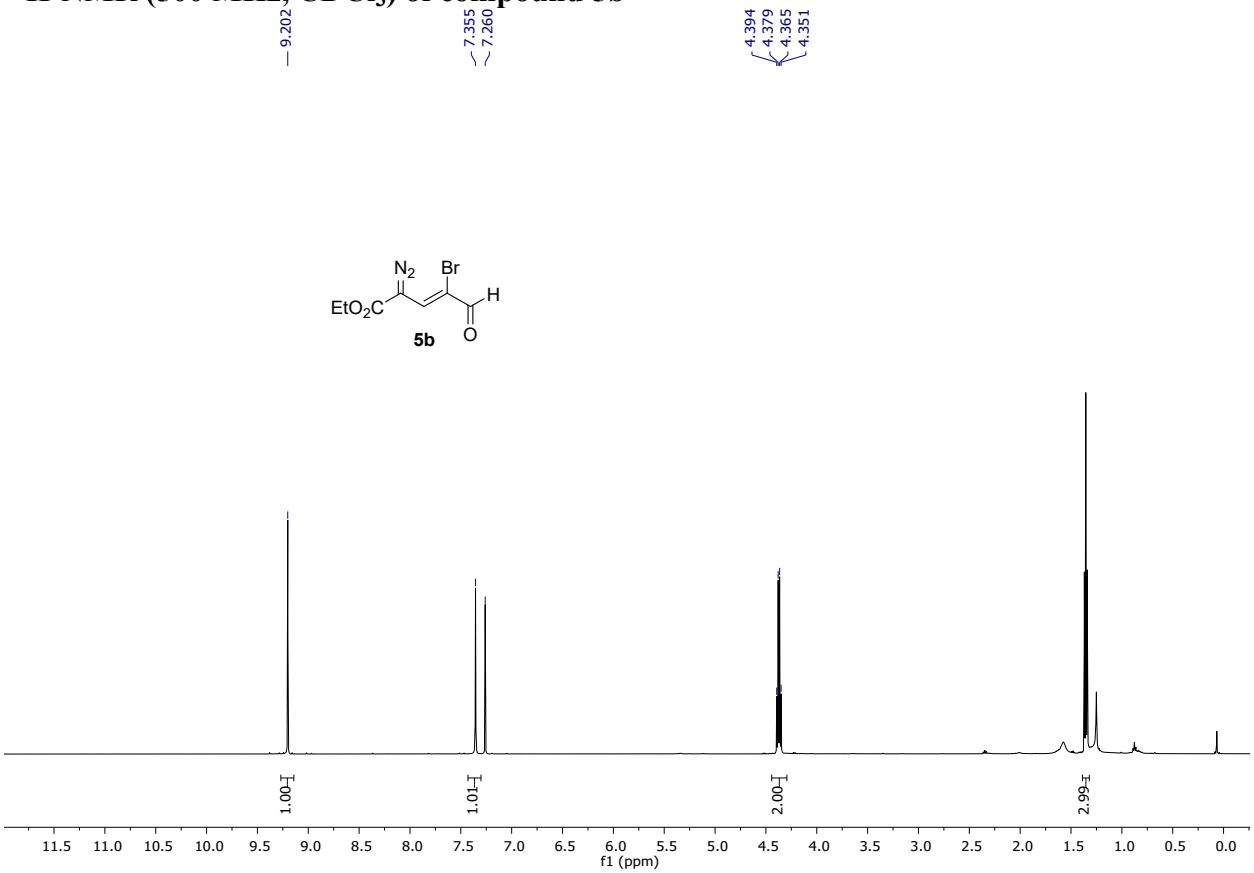
^{1}H-NMR (500 MHz, $CDCl_3$) of compound 5a



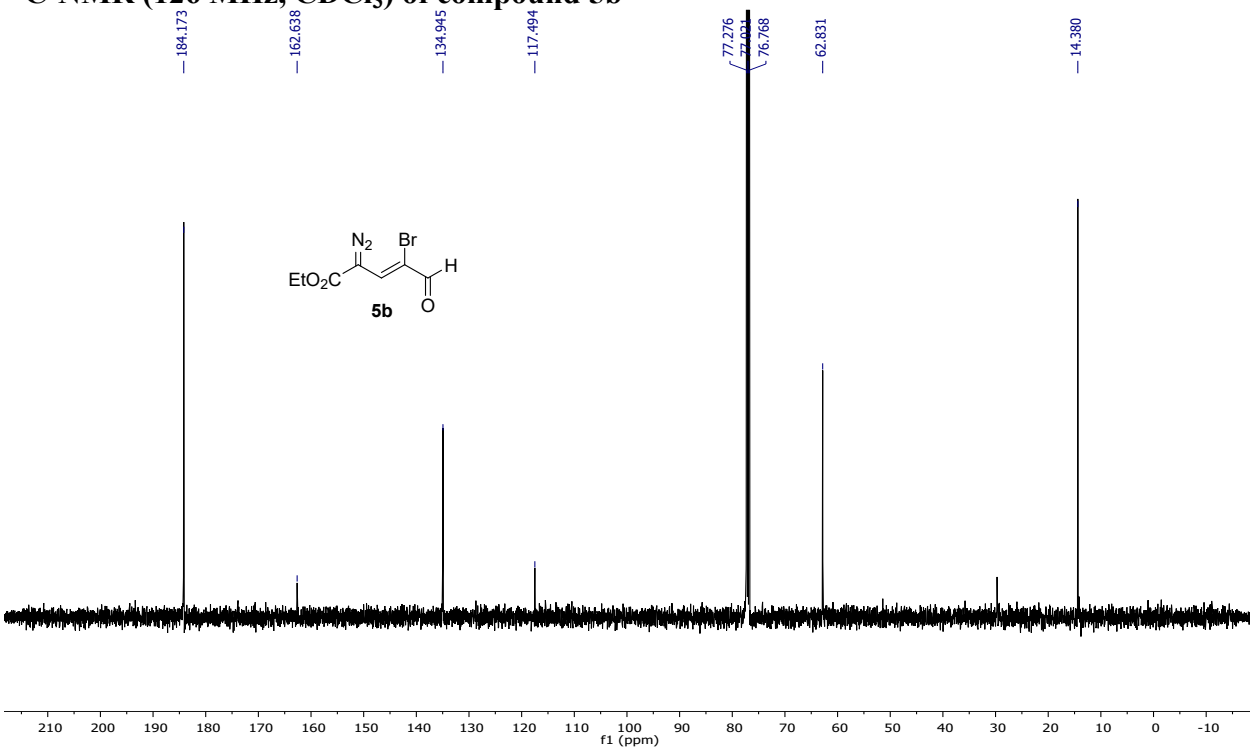
^{13}C-NMR (126 MHz, $CDCl_3$) of compound 5a



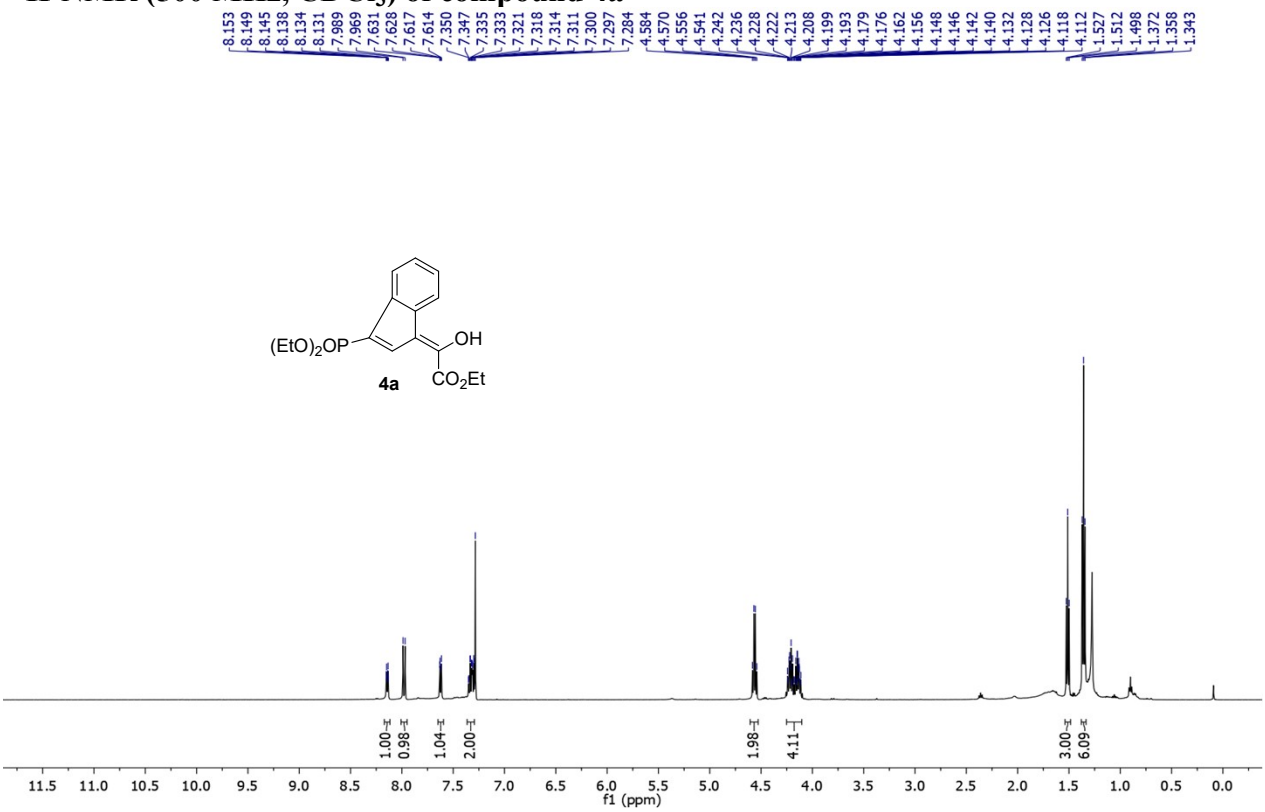
^{1}H-NMR (500 MHz, $CDCl_3$) of compound 5b



^{13}C-NMR (126 MHz, $CDCl_3$) of compound 5b



^{1}H-NMR (500 MHz, $CDCl_3$) of compound 4a



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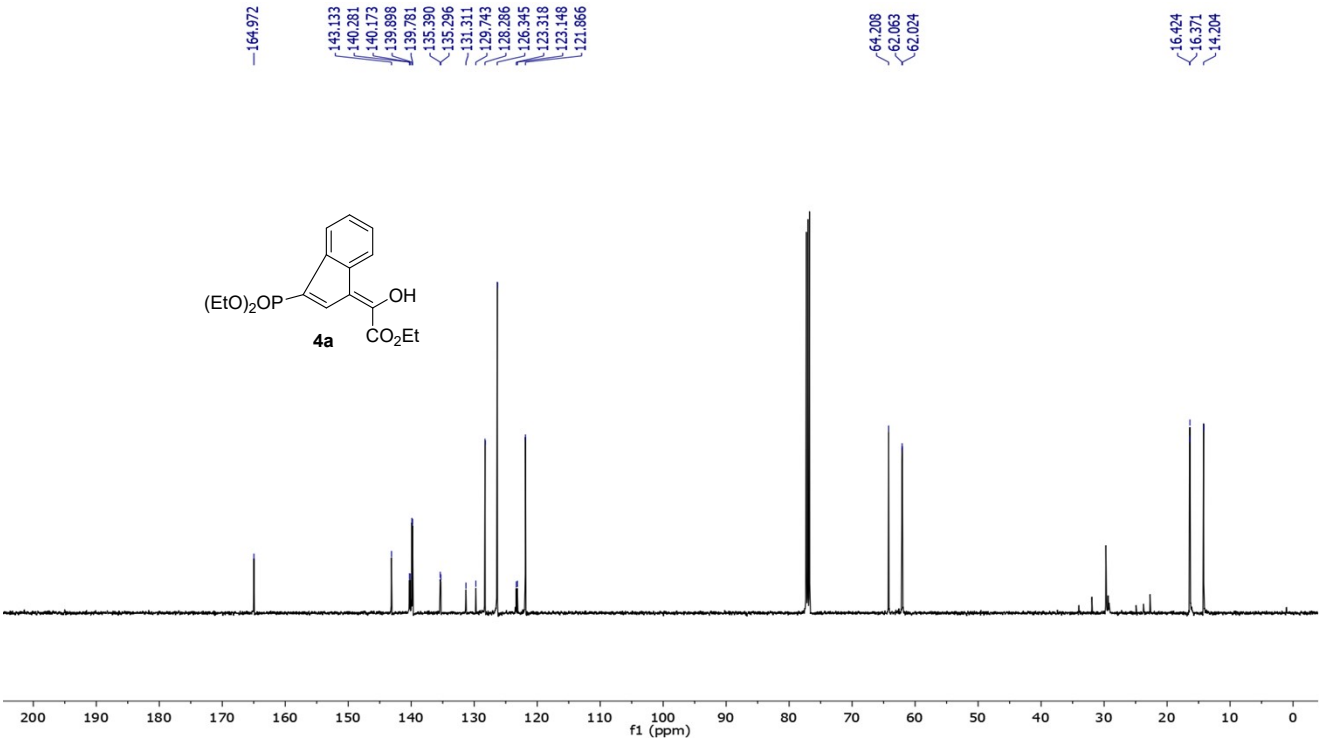
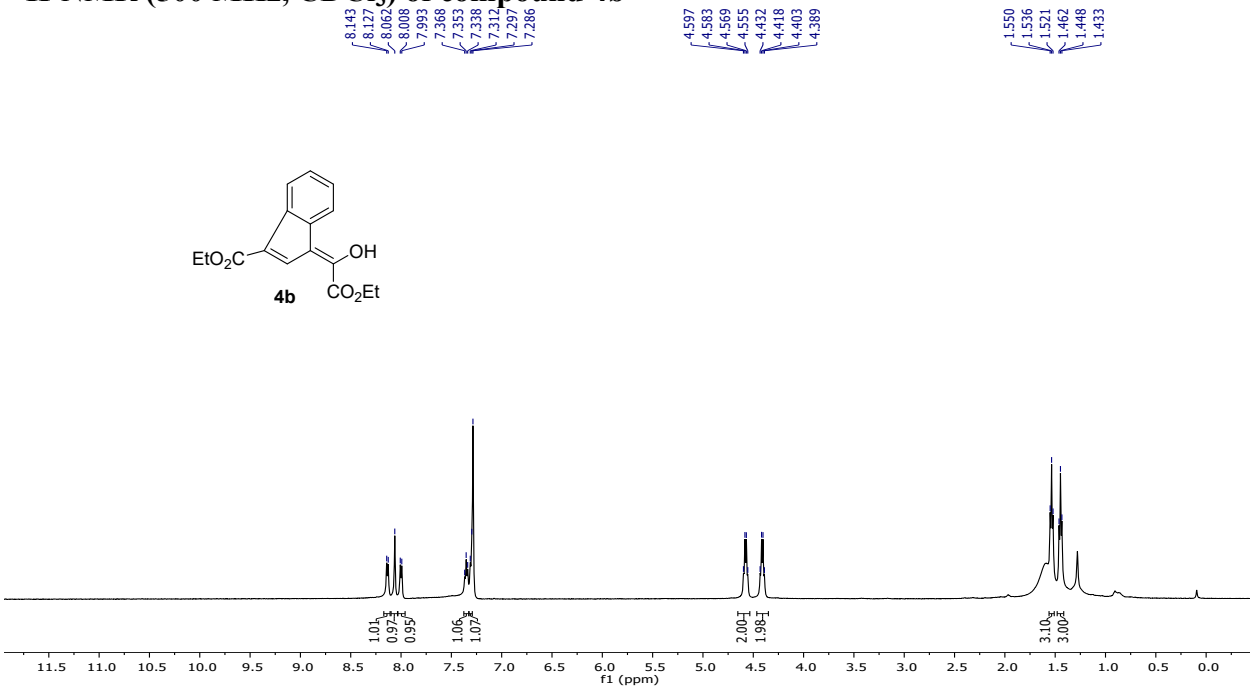
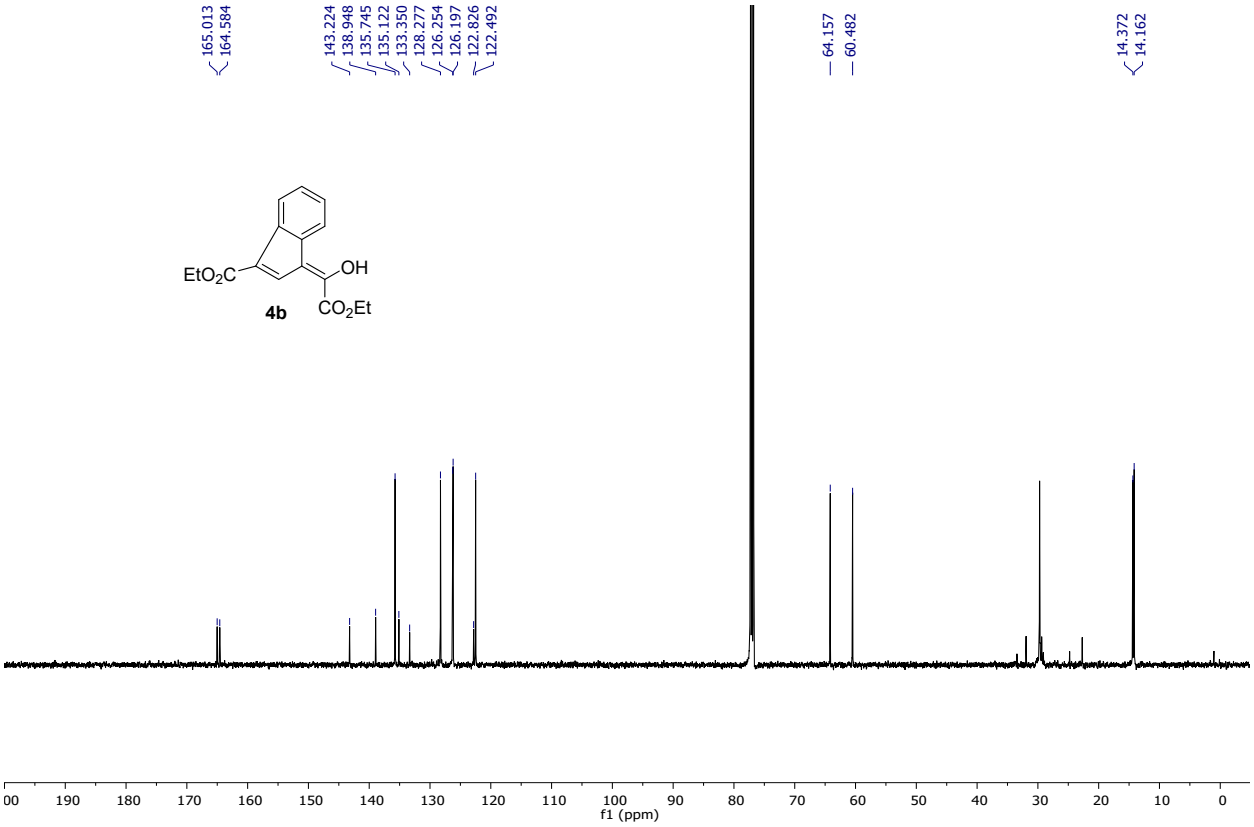


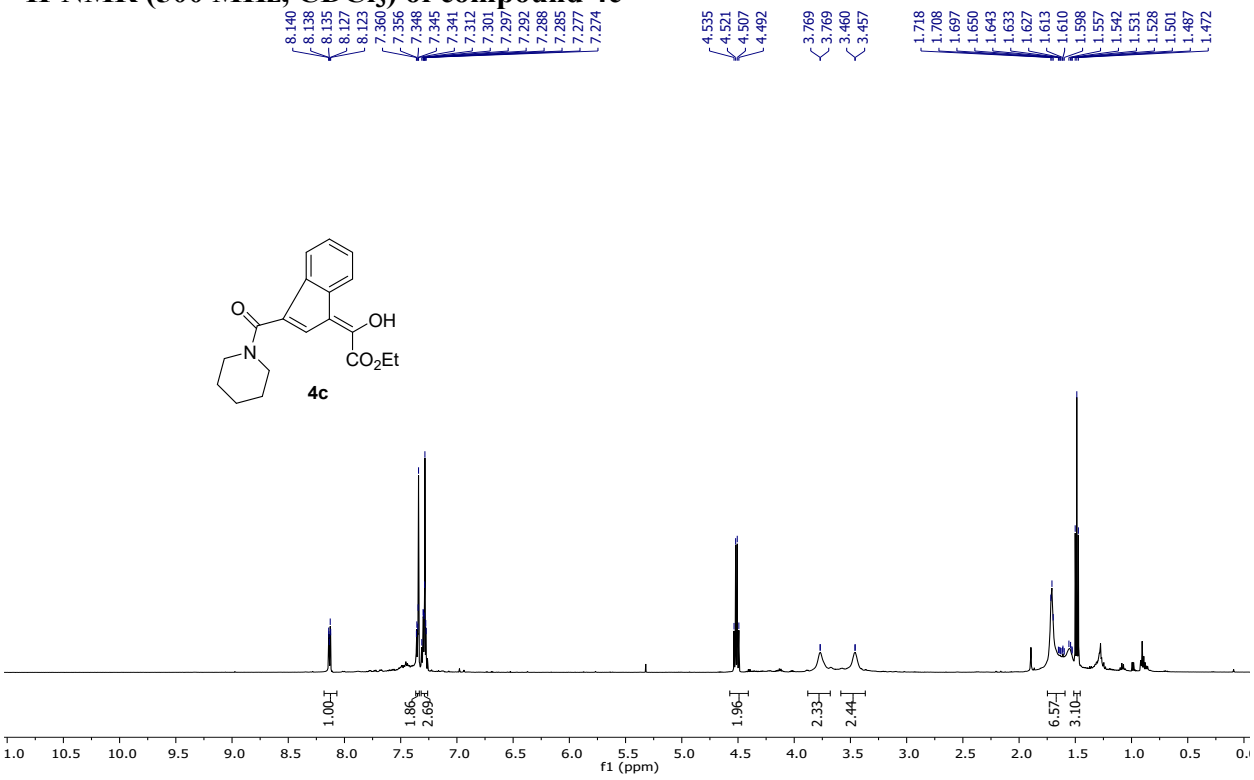
^{1}H-NMR (500 MHz, $CDCl_3$) of compound 4b



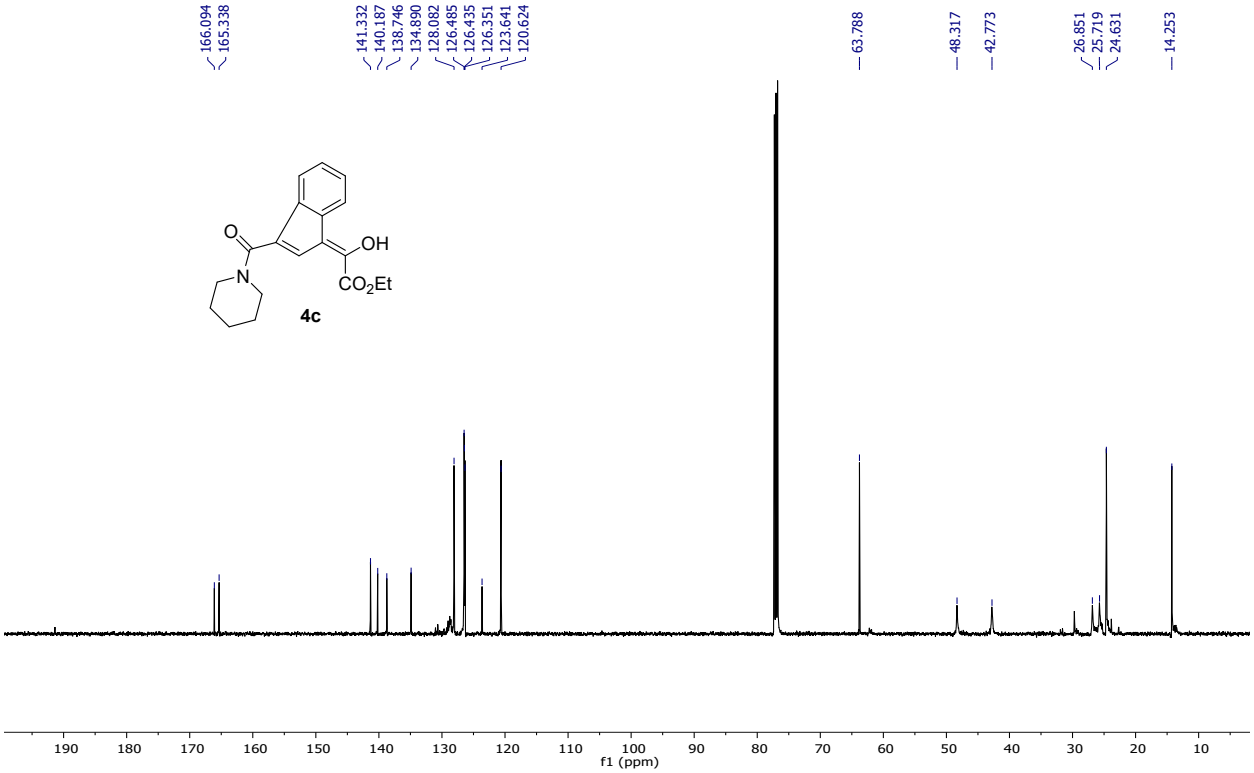
^{13}C-NMR (126 MHz, $CDCl_3$) of compound 4b



^{1}H-NMR (500 MHz, $CDCl_3$) of compound 4c



^{13}C-NMR (126 MHz, $CDCl_3$) of compound 4c



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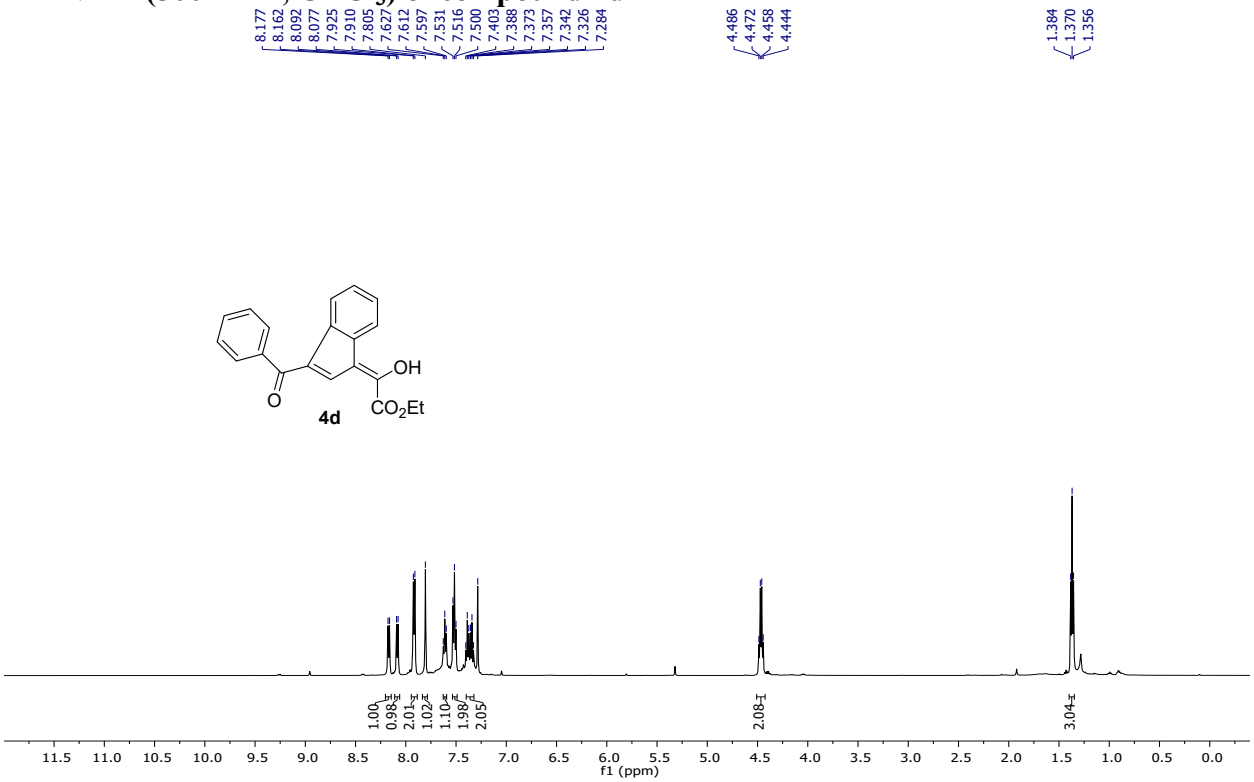

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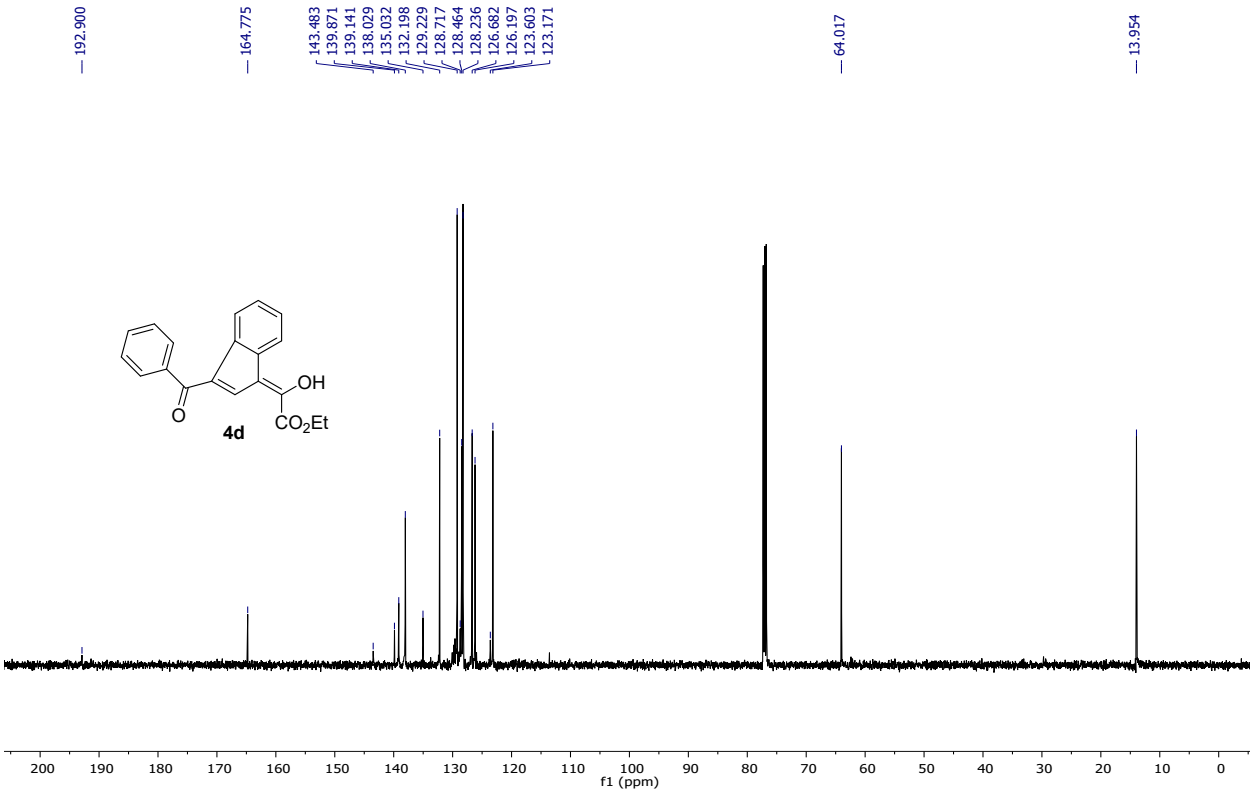
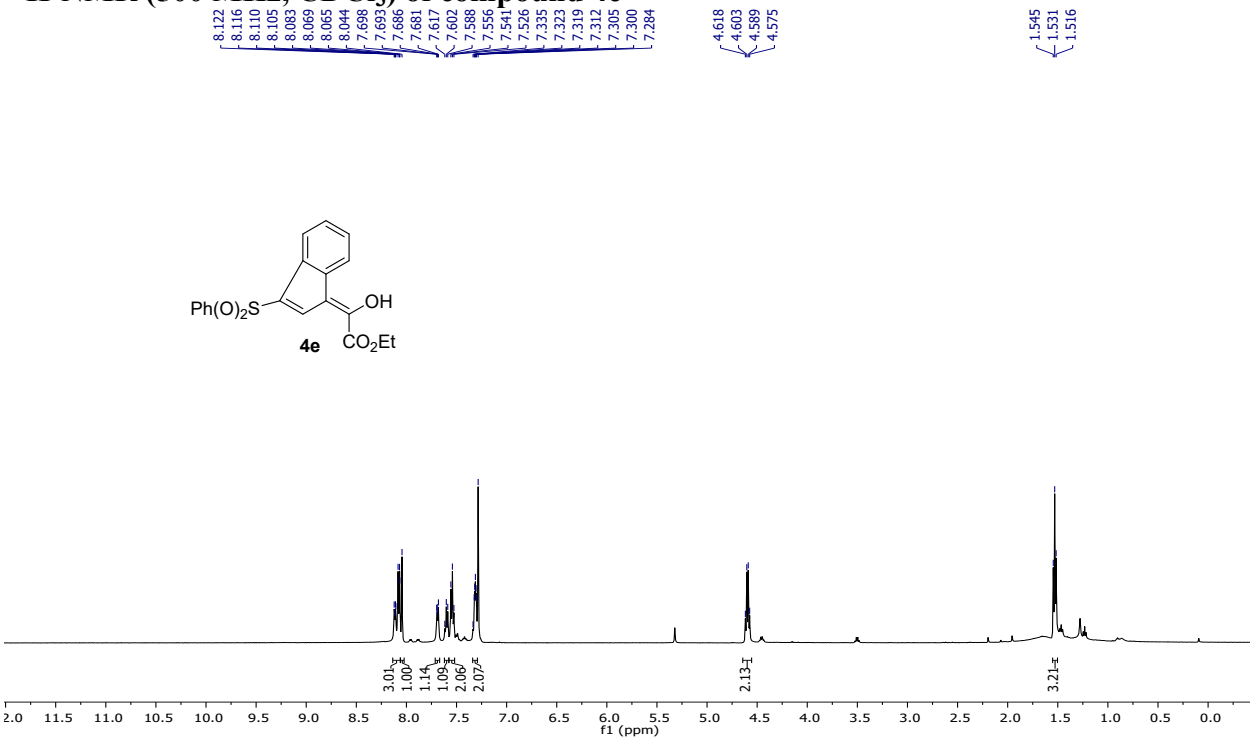
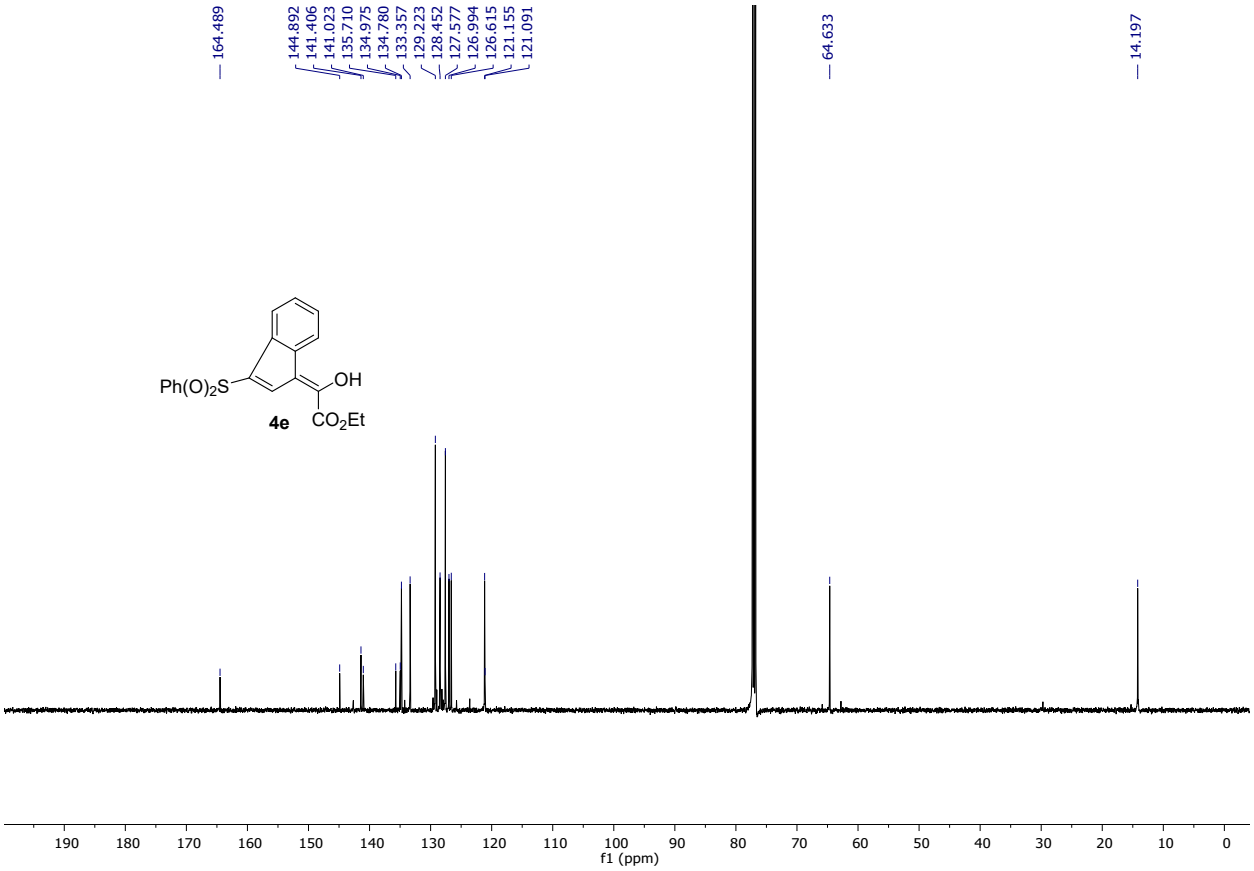


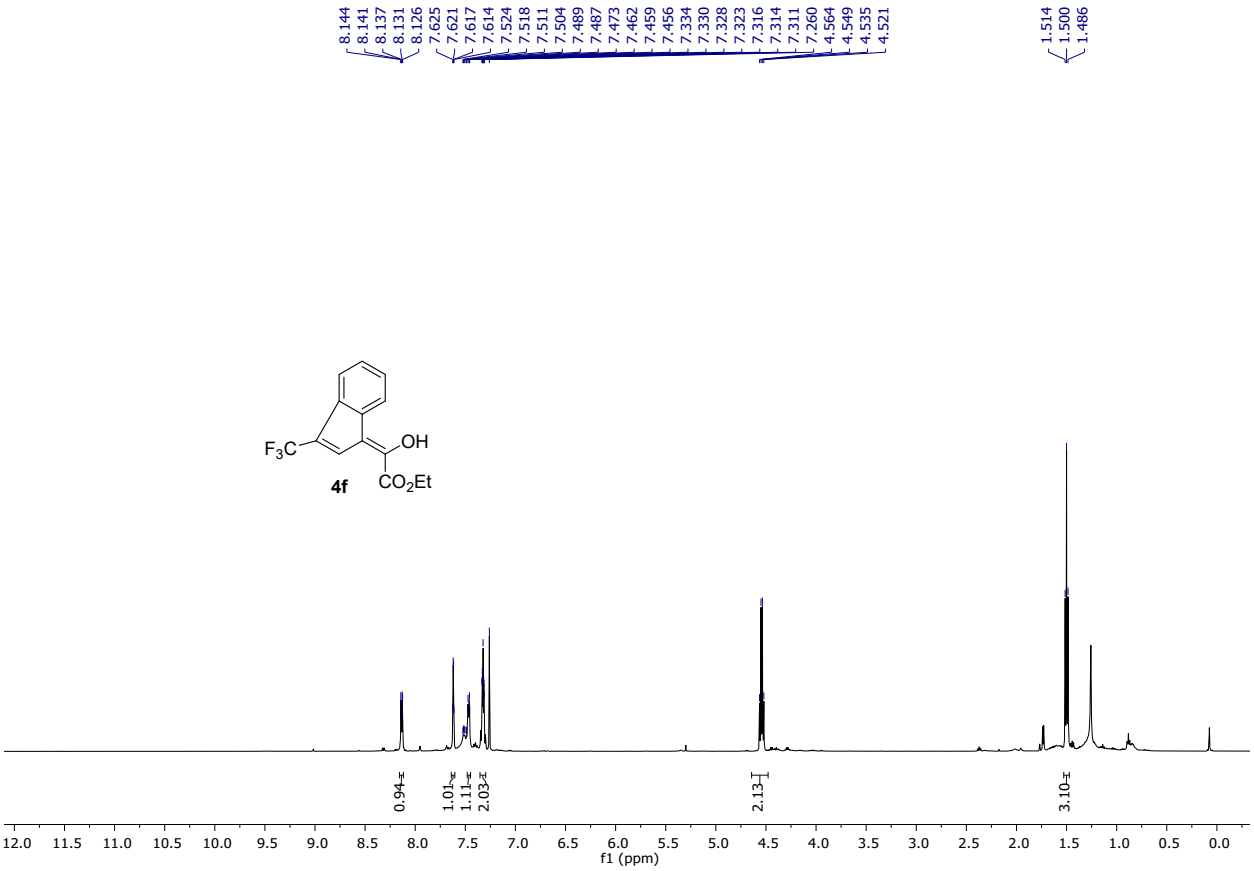
^{1}H-NMR (500 MHz, $CDCl_3$) of compound 4e



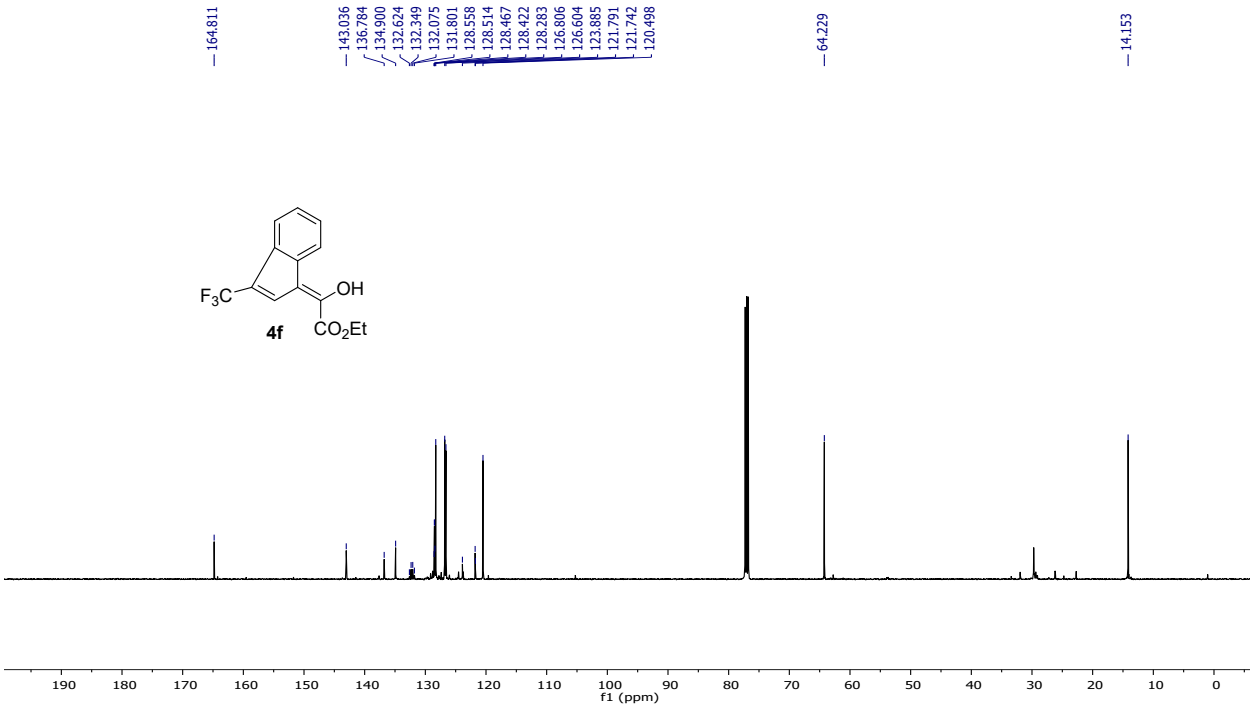
^{13}C-NMR (126 MHz, $CDCl_3$) of compound 4e



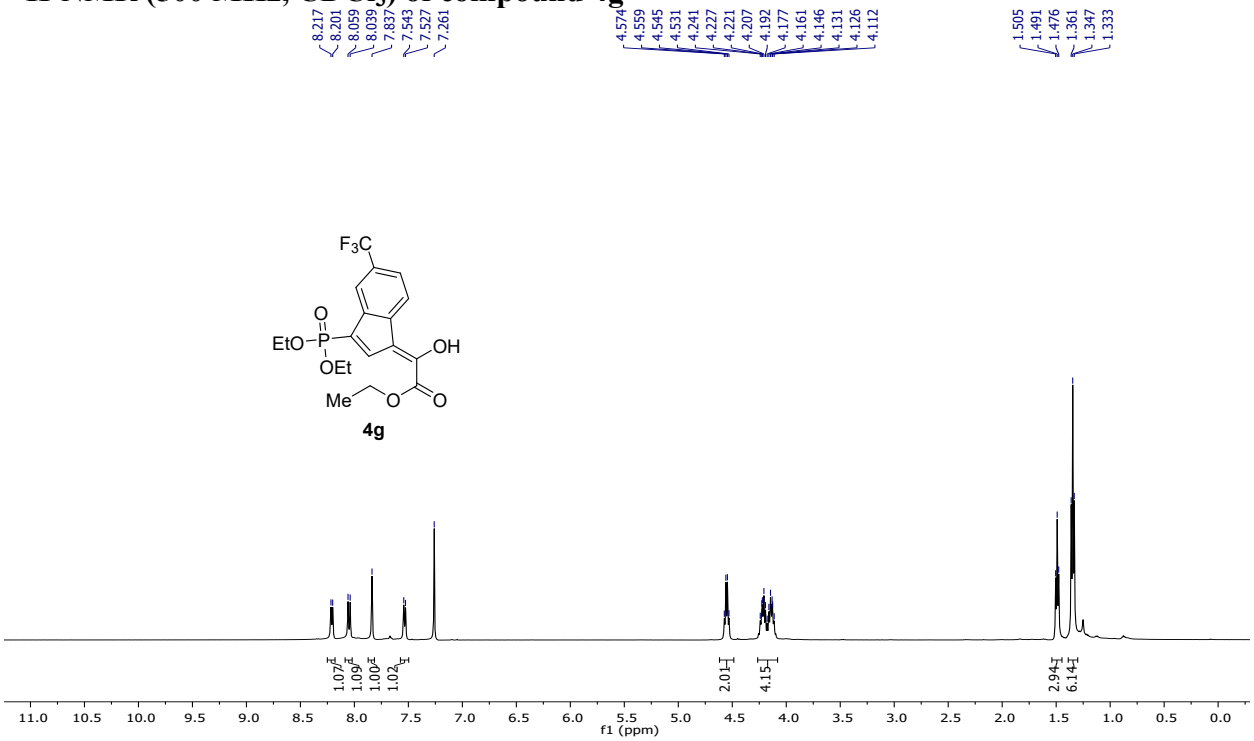
^{1}H-NMR (500 MHz, $CDCl_3$) of compound 4f

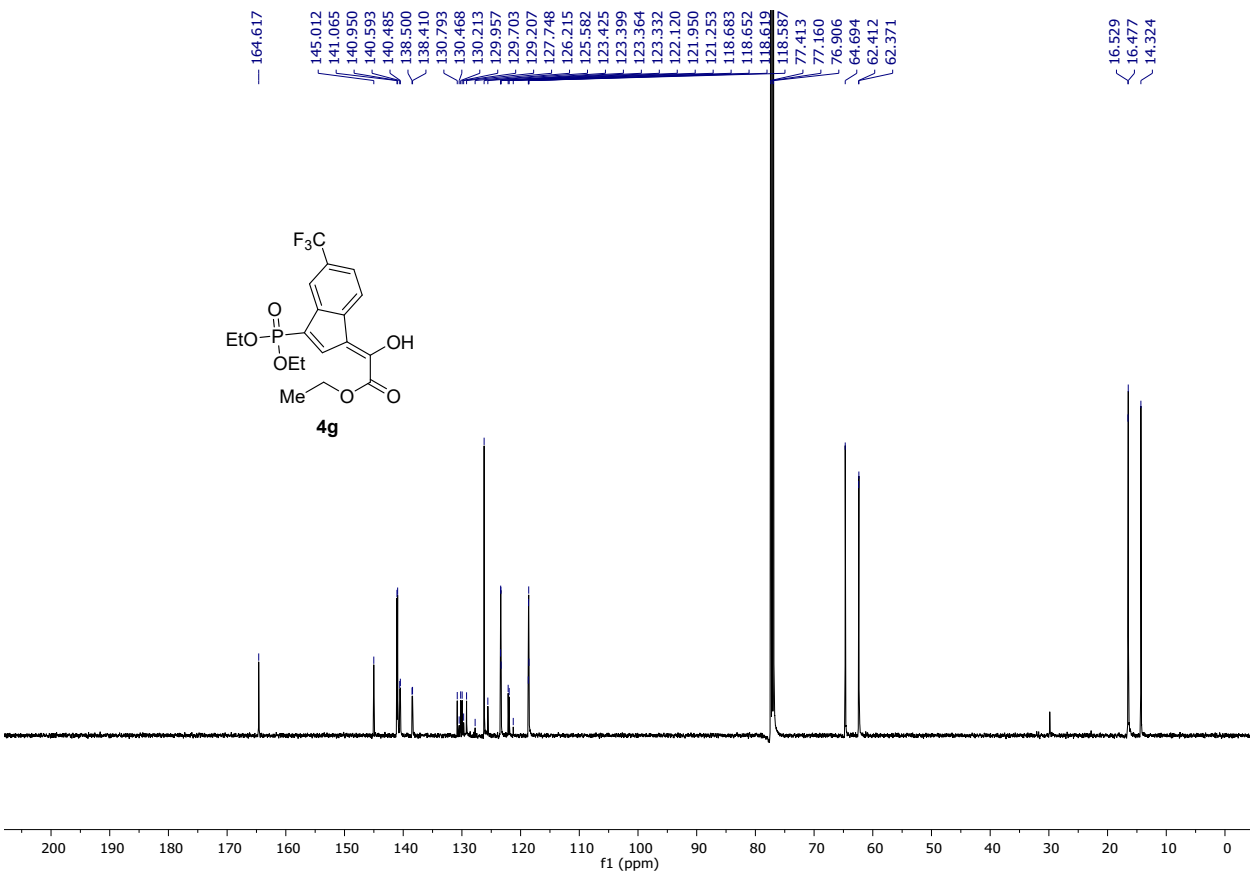


^{13}C-NMR (126 MHz, $CDCl_3$) of compound 4b

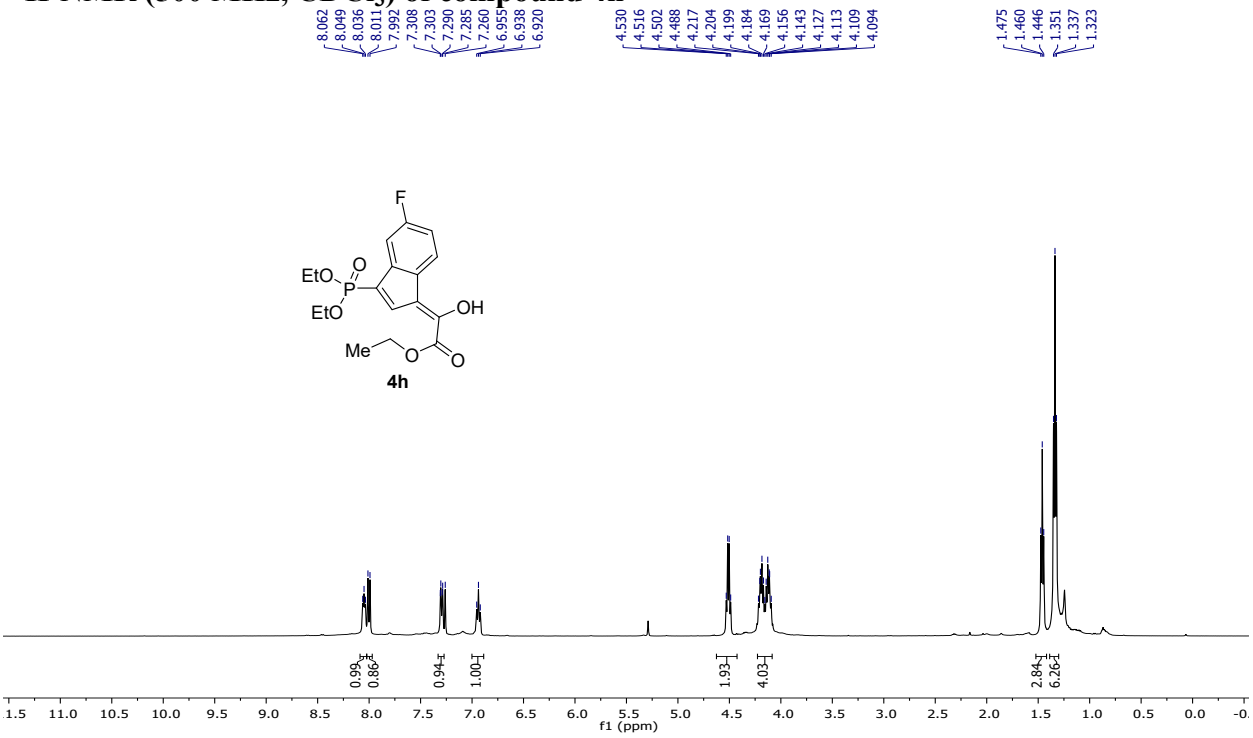


^{1}H-NMR (500 MHz, $CDCl_3$) of compound 4g

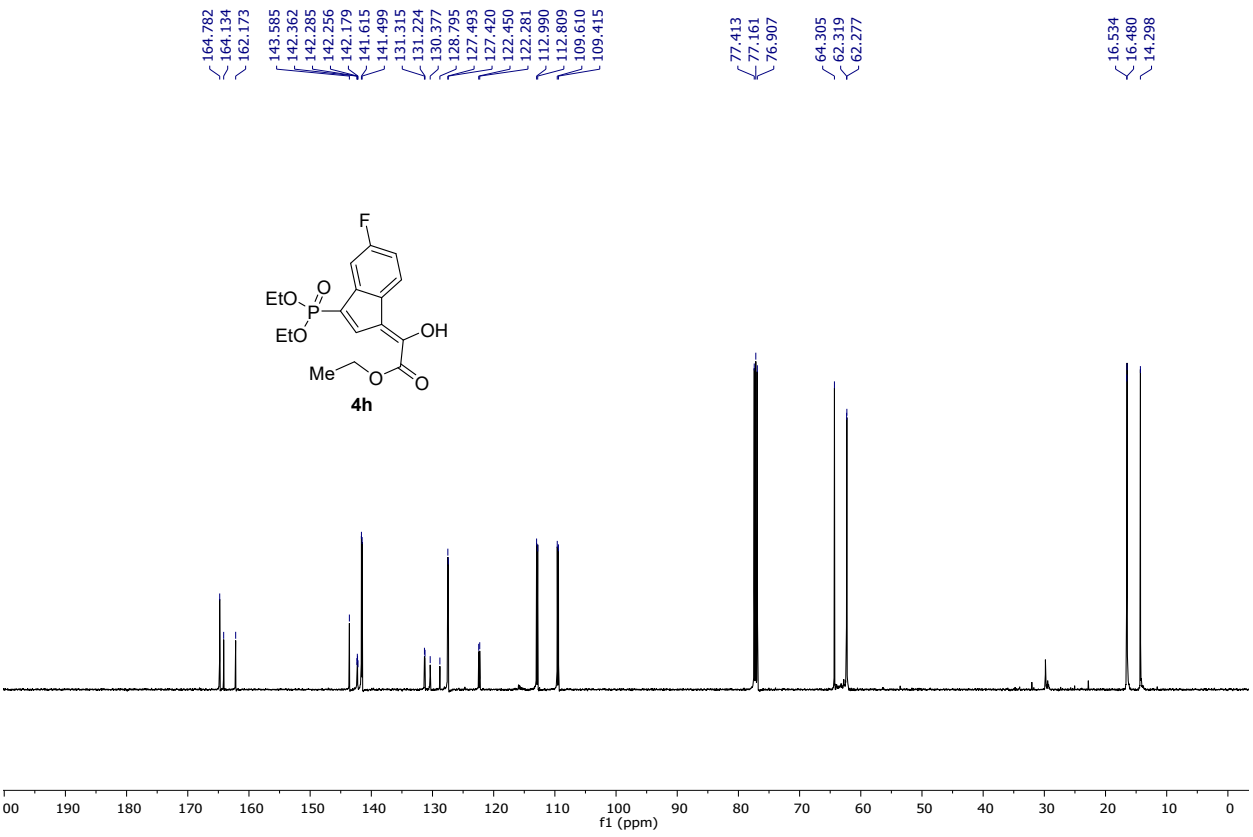




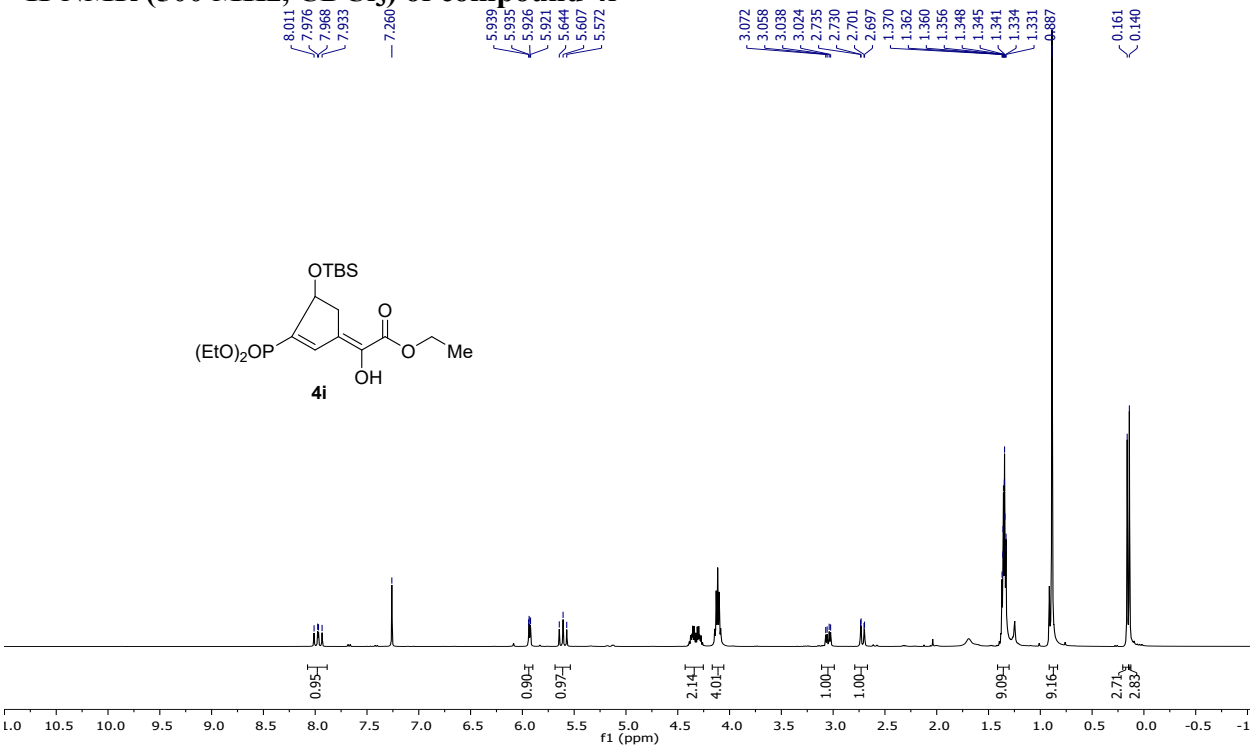
^{1}H-NMR (500 MHz, $CDCl_3$) of compound 4h



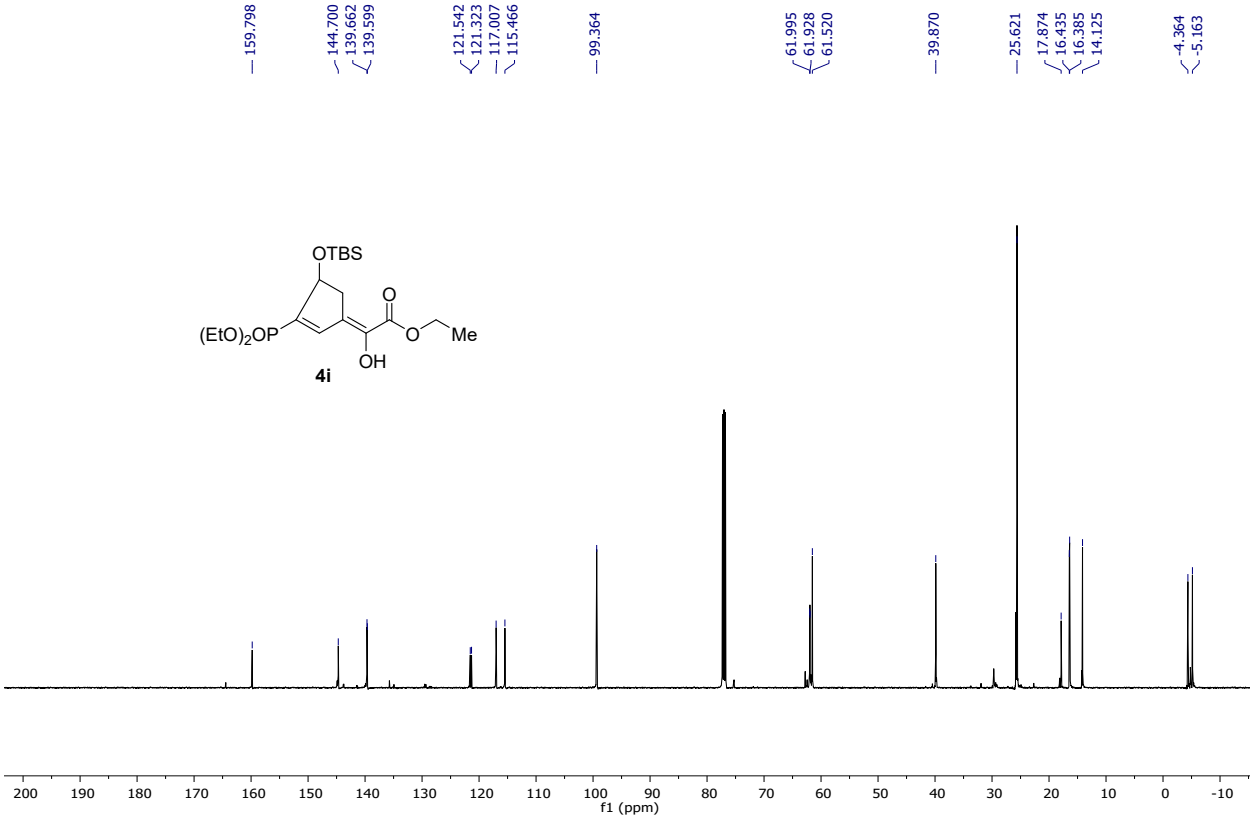
^{13}C-NMR (126 MHz, $CDCl_3$) of compound 4h



^{1}H-NMR (500 MHz, $CDCl_3$) of compound 4i



^{13}C-NMR (126 MHz, $CDCl_3$) of compound 4i



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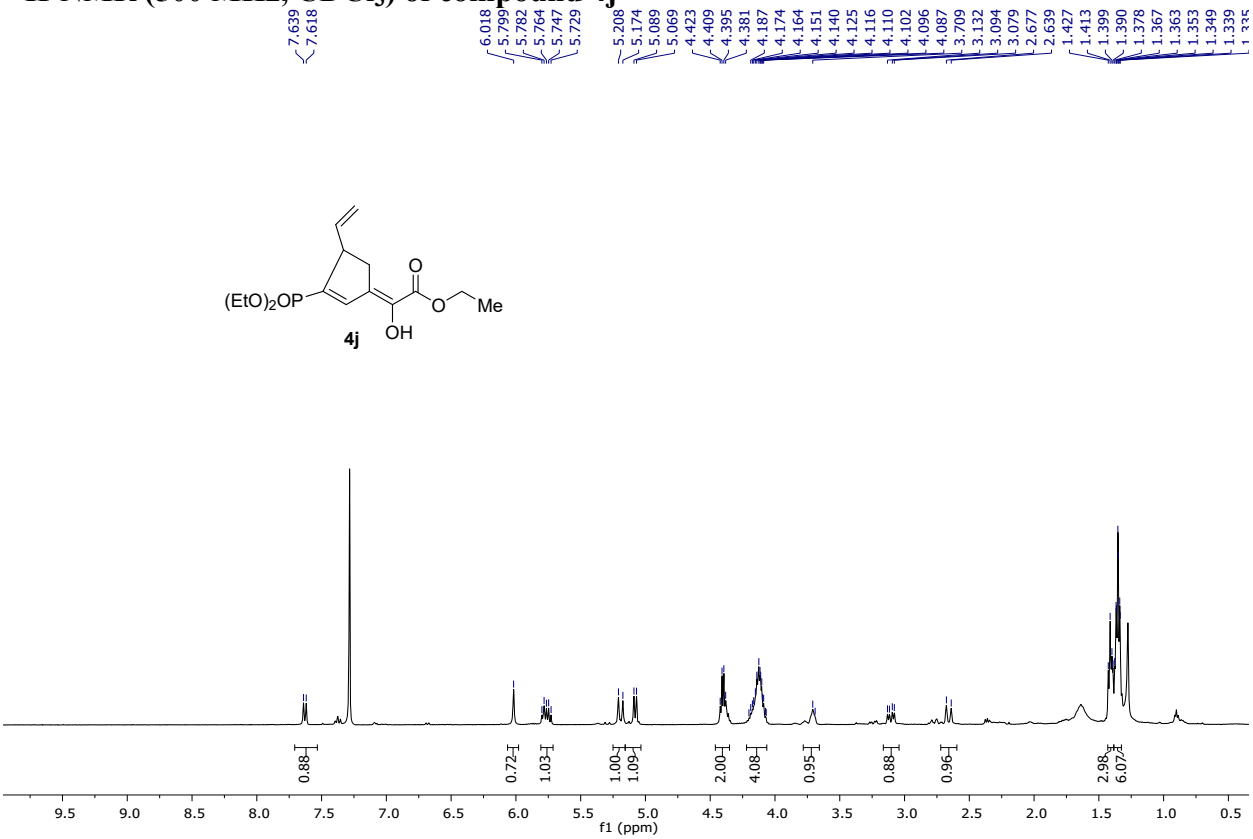

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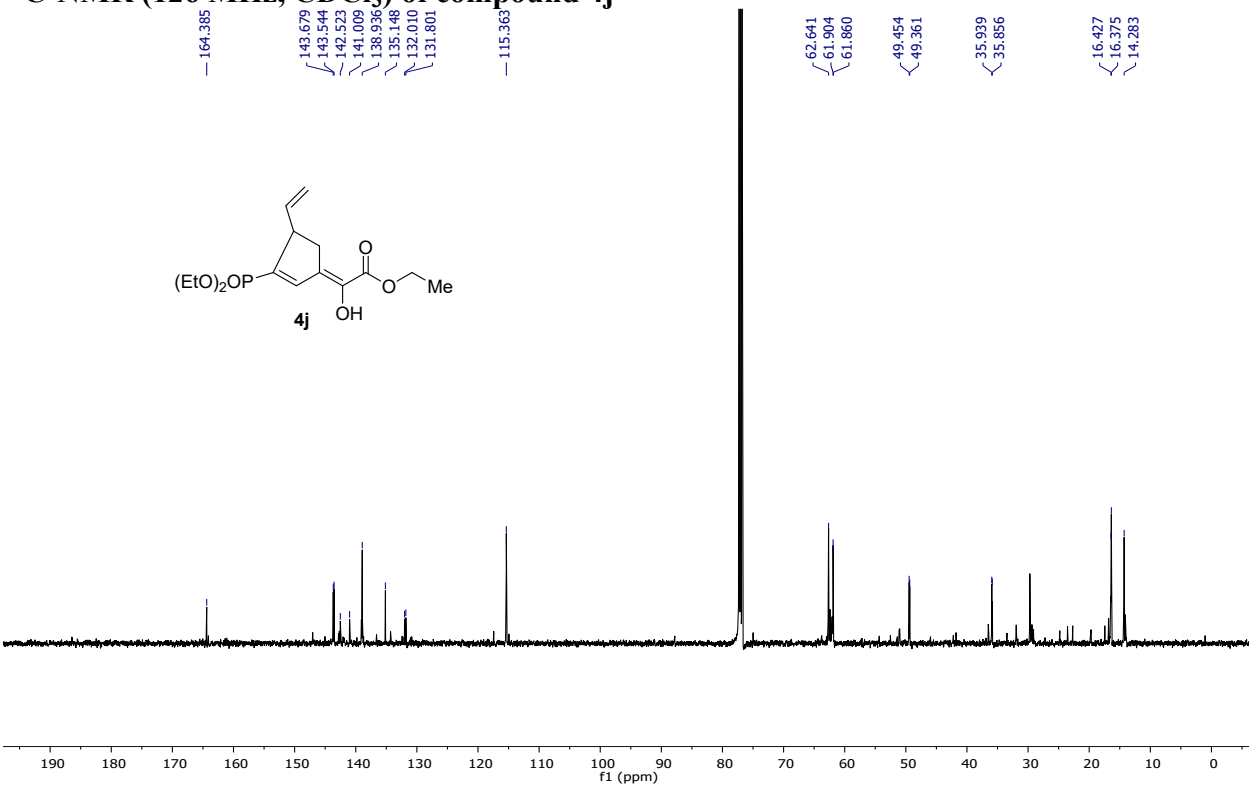
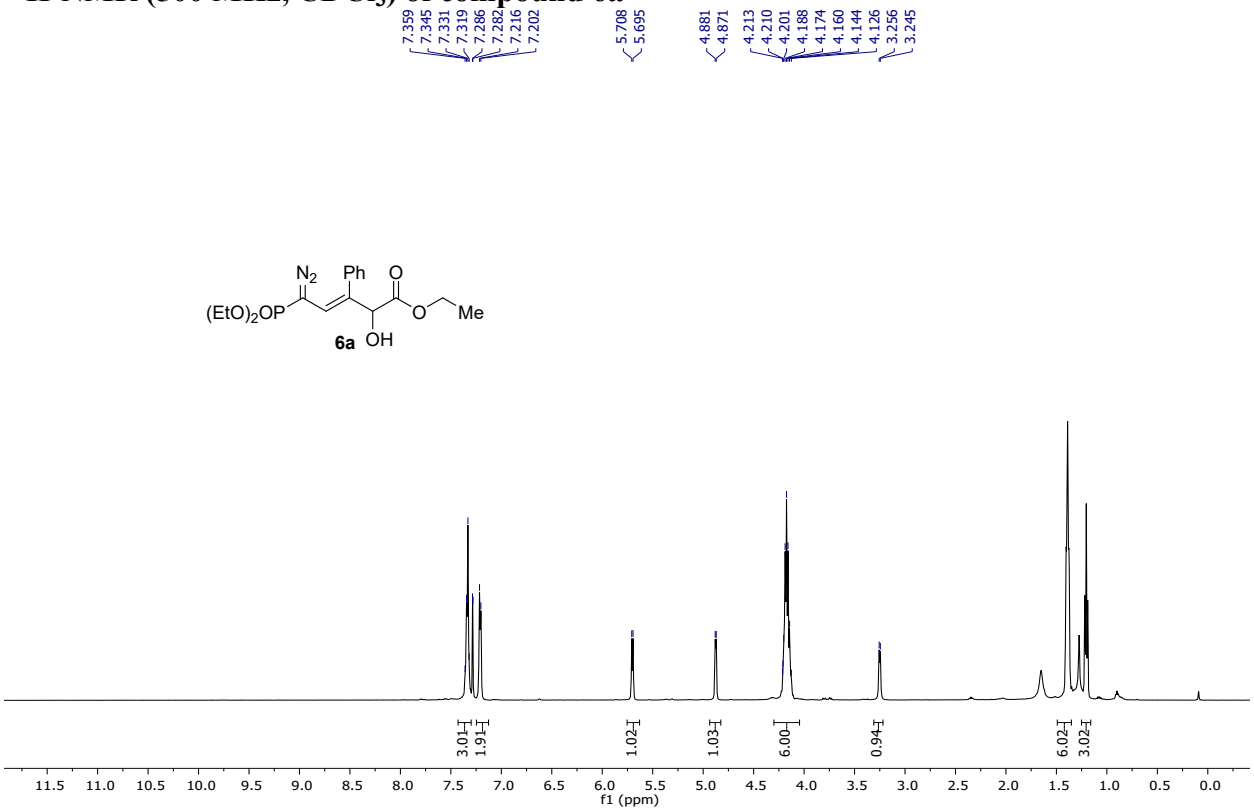
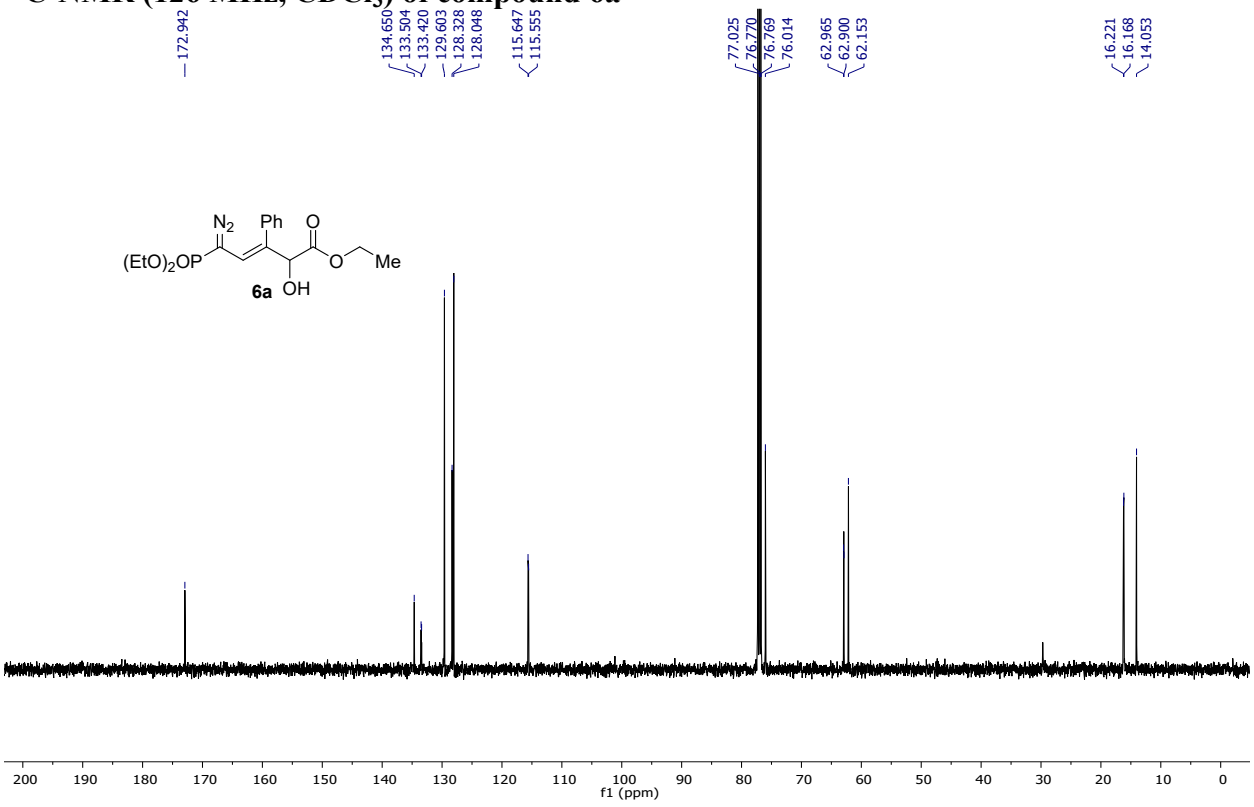


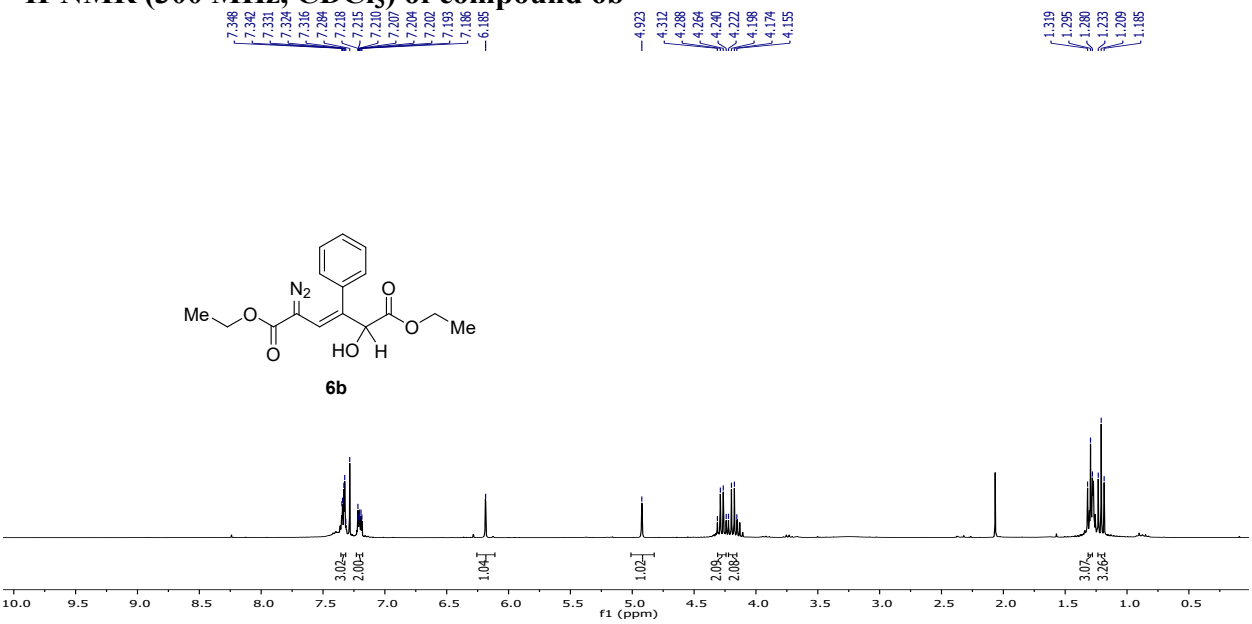
^{1}H-NMR (500 MHz, $CDCl_3$) of compound 6a



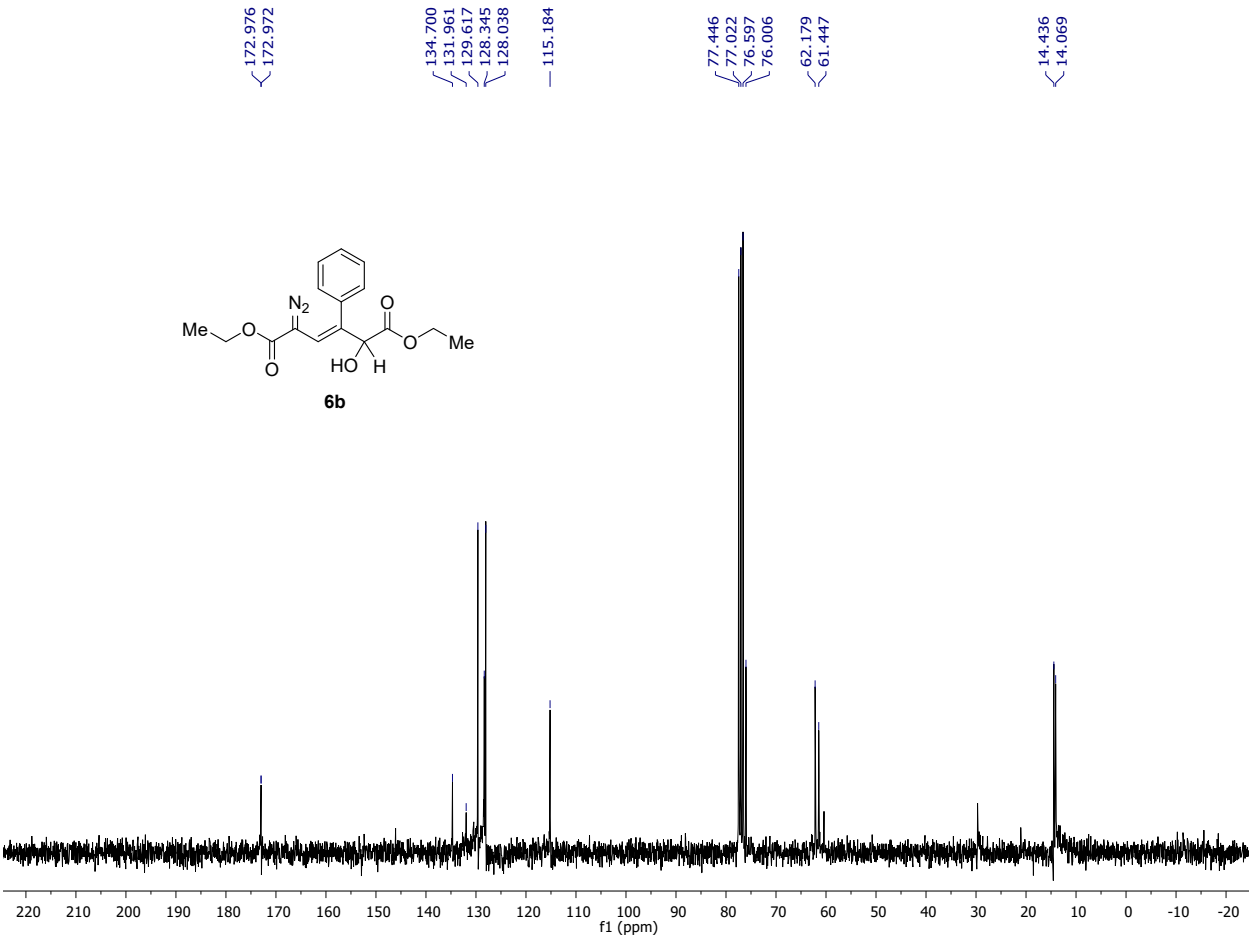
^{13}C-NMR (126 MHz, $CDCl_3$) of compound 6a



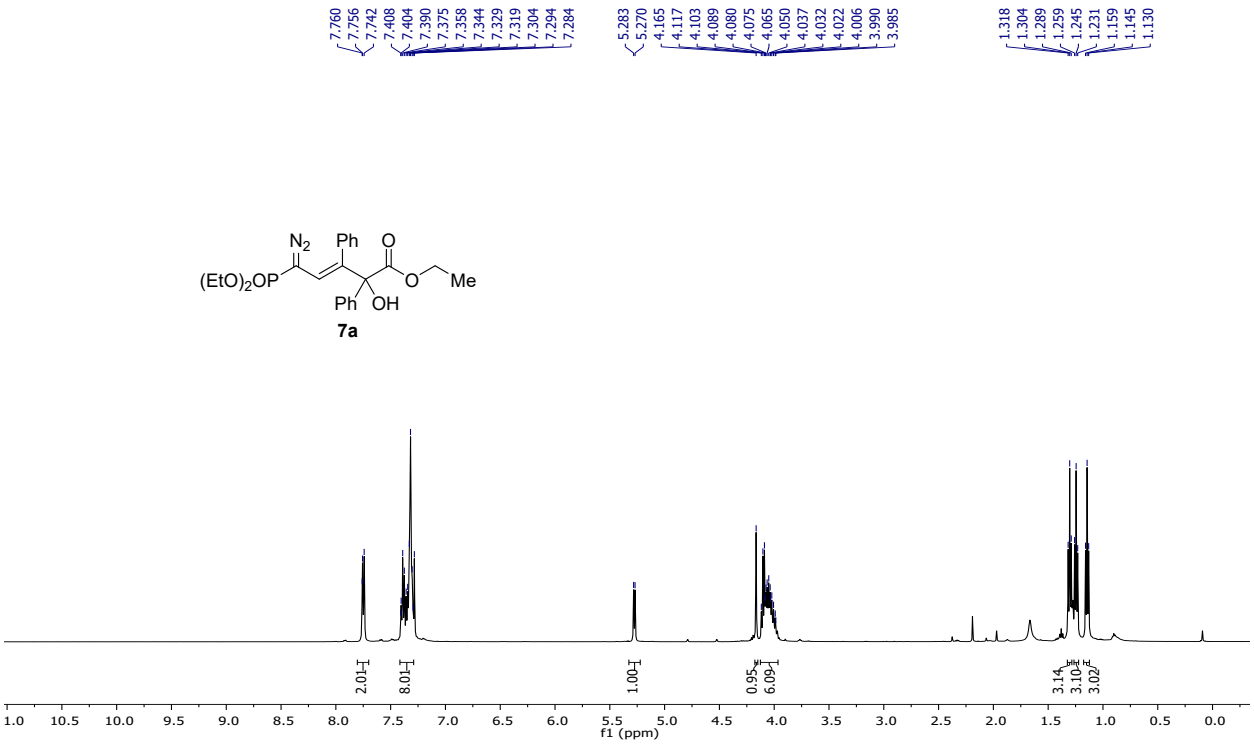
^{1}H-NMR (300 MHz, $CDCl_3$) of compound 6b



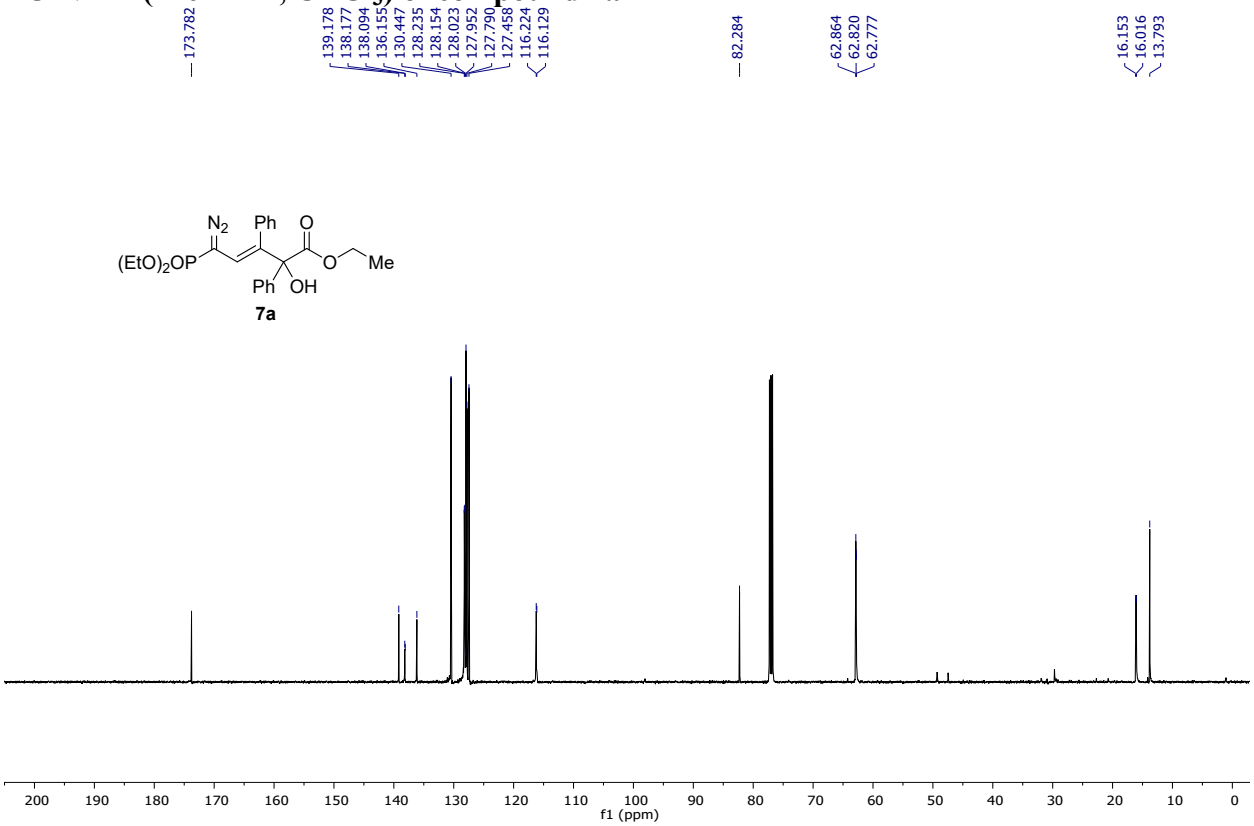
^{13}C-NMR (75 MHz, $CDCl_3$) of compound 6b



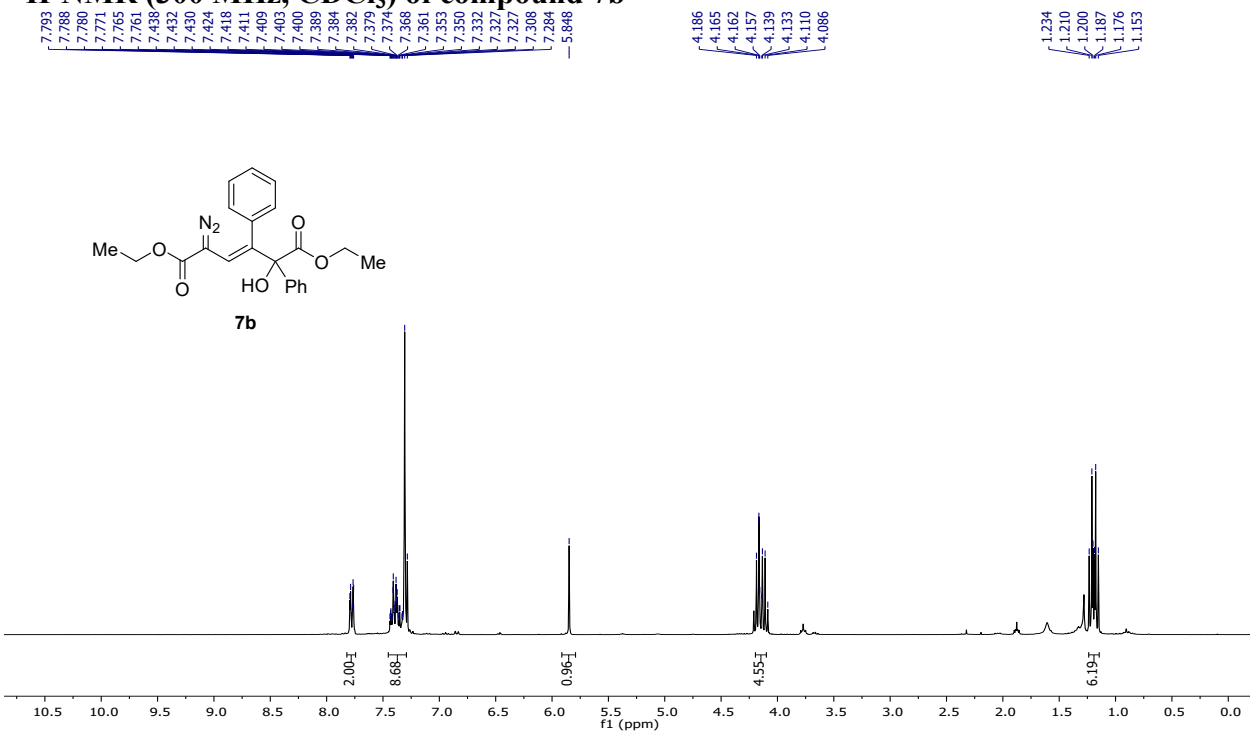
^{1}H-NMR (500 MHz, $CDCl_3$) of compound 7a



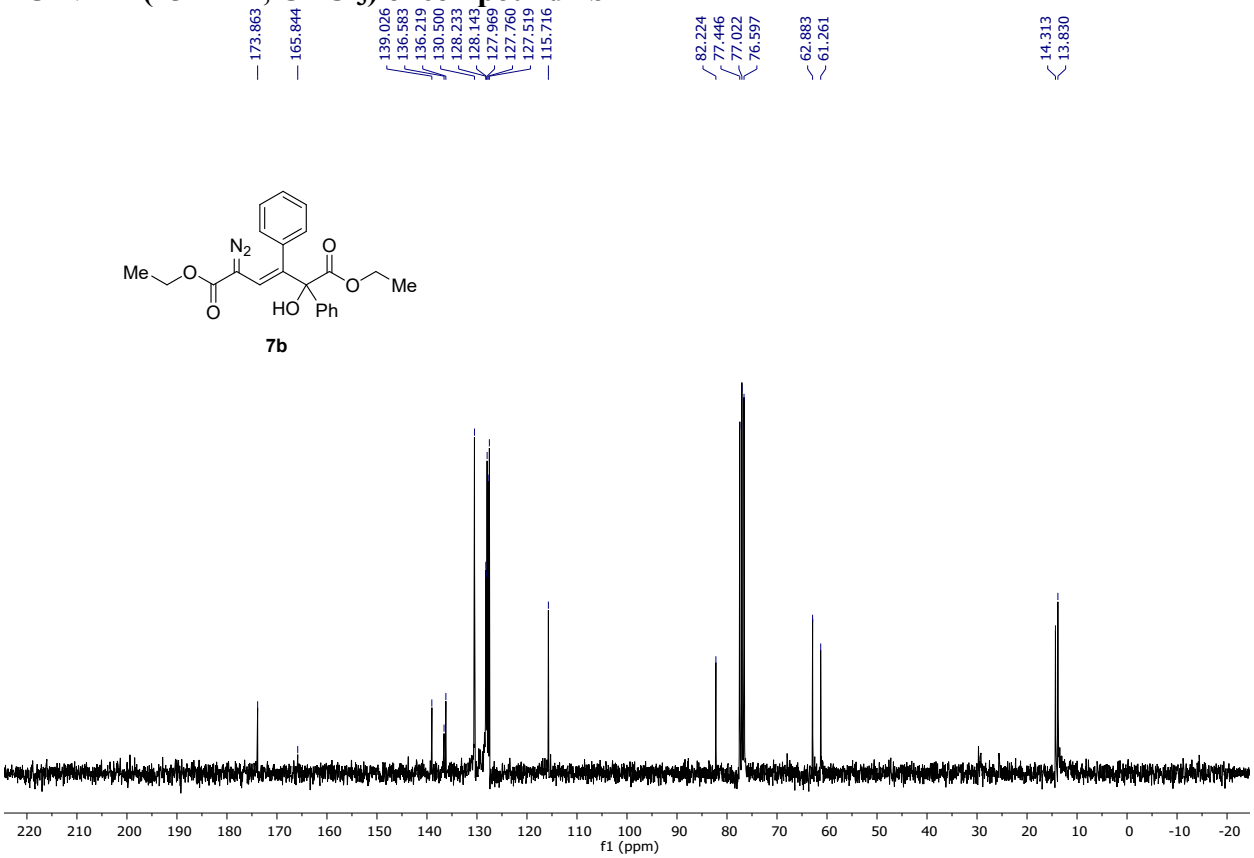
^{13}C-NMR (126 MHz, $CDCl_3$) of compound 7a



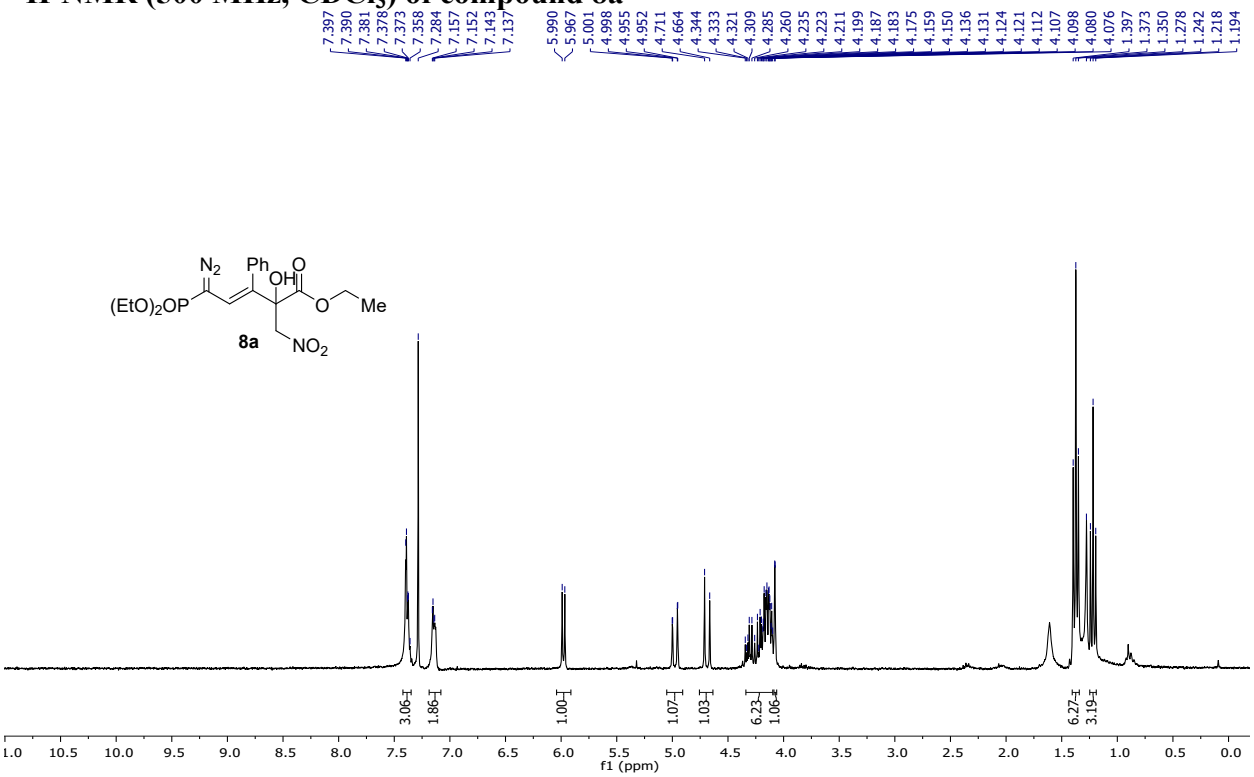
^{1}H-NMR (300 MHz, $CDCl_3$) of compound 7b



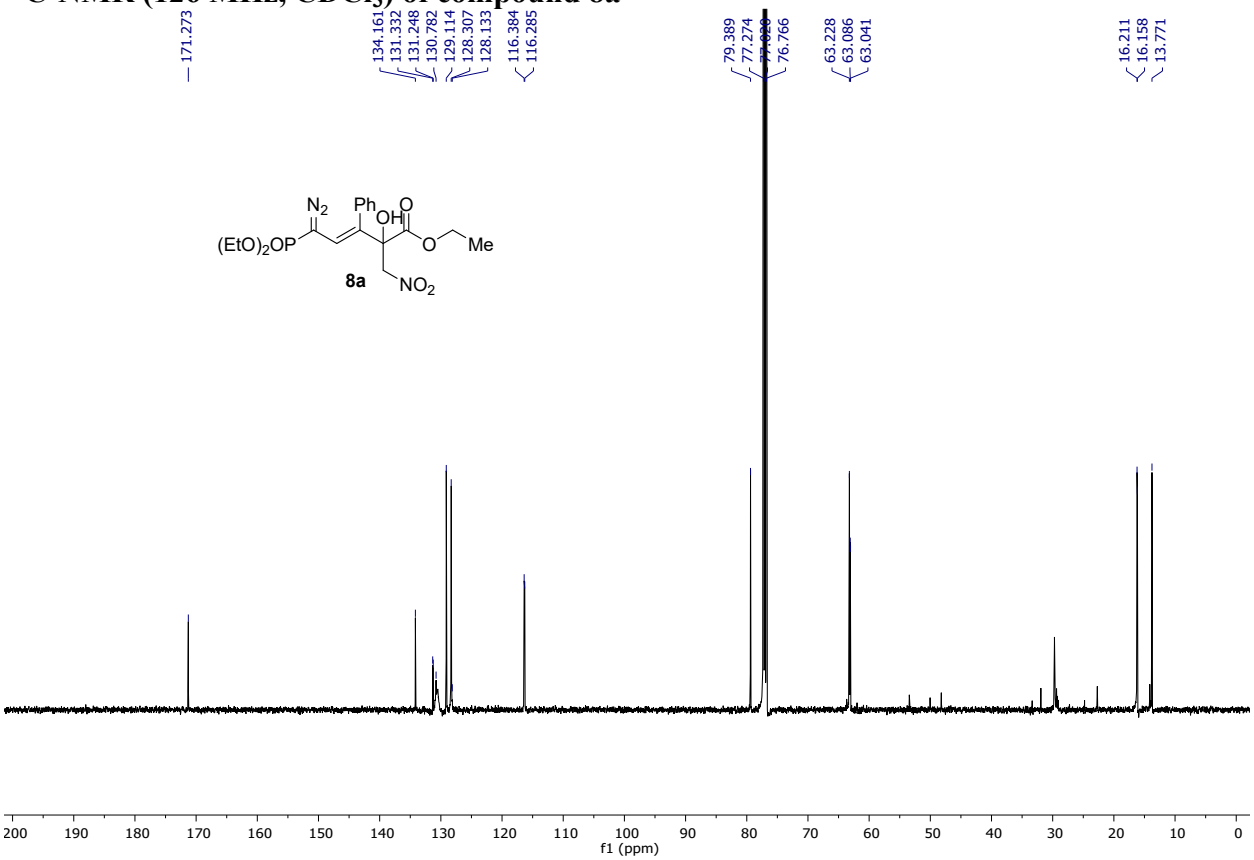
^{13}C-NMR (75 MHz, $CDCl_3$) of compound 7b



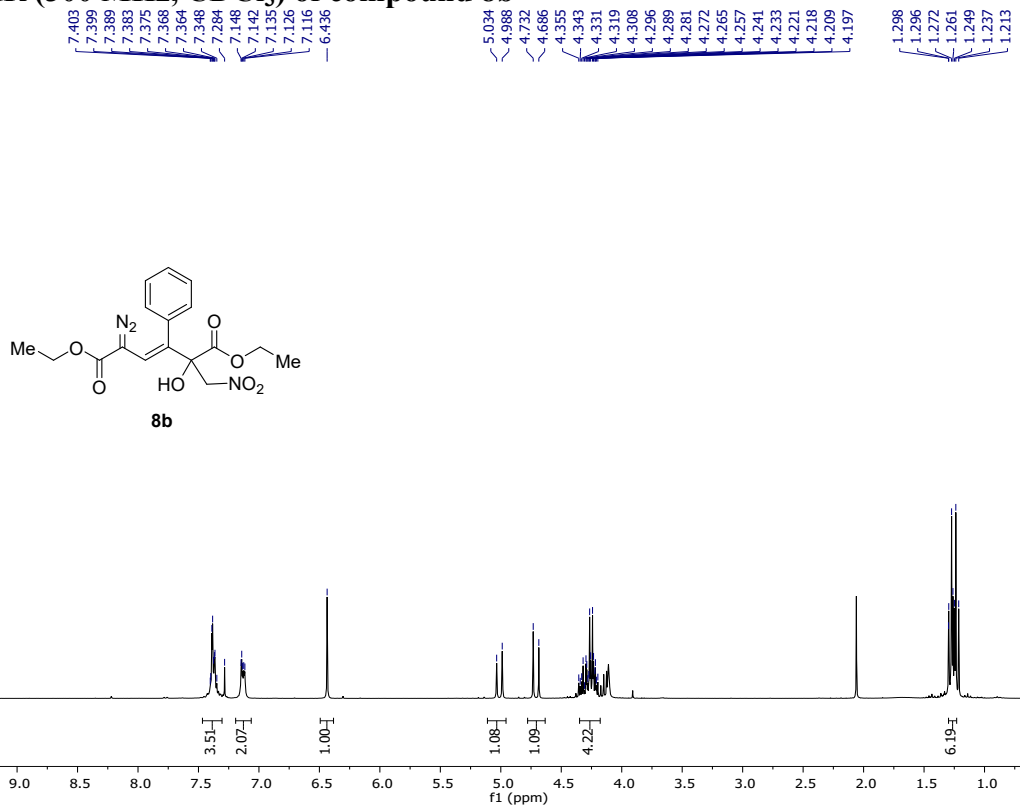
^{1}H-NMR (500 MHz, $CDCl_3$) of compound 8a



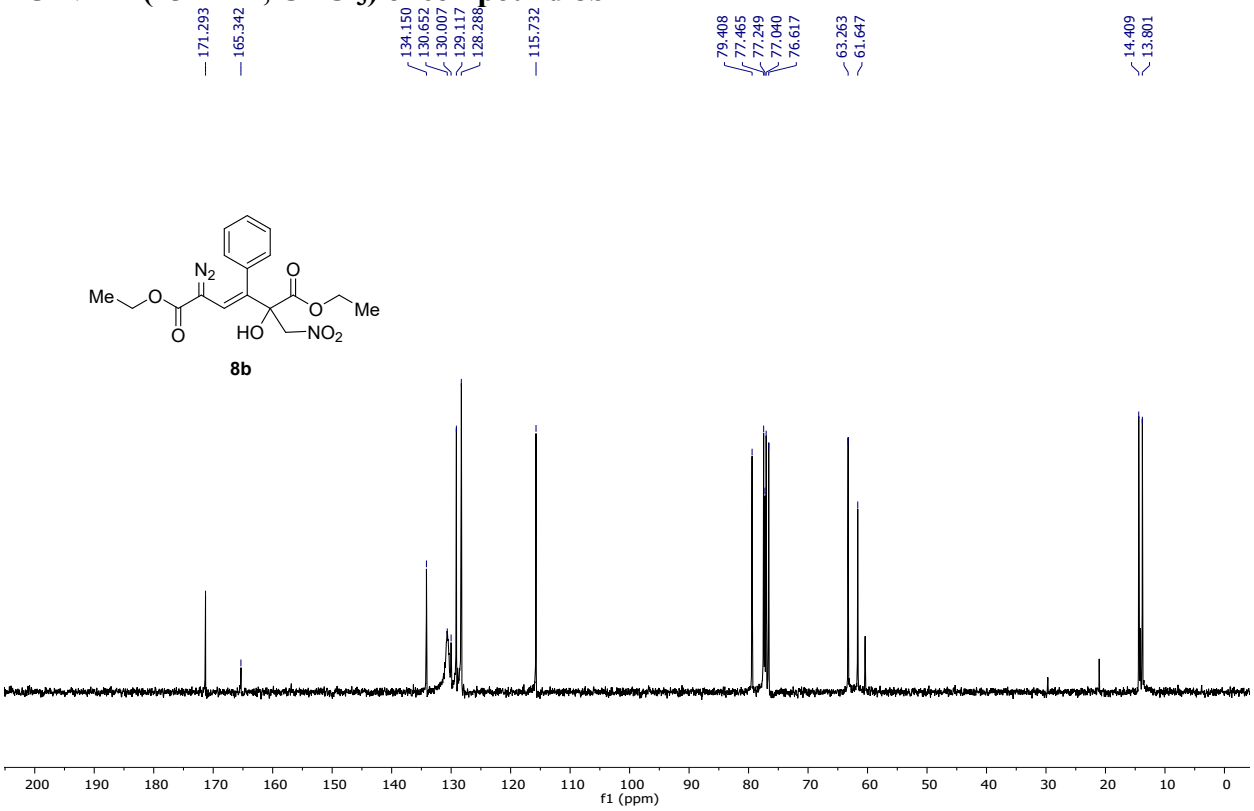
^{13}C-NMR (126 MHz, $CDCl_3$) of compound 8a



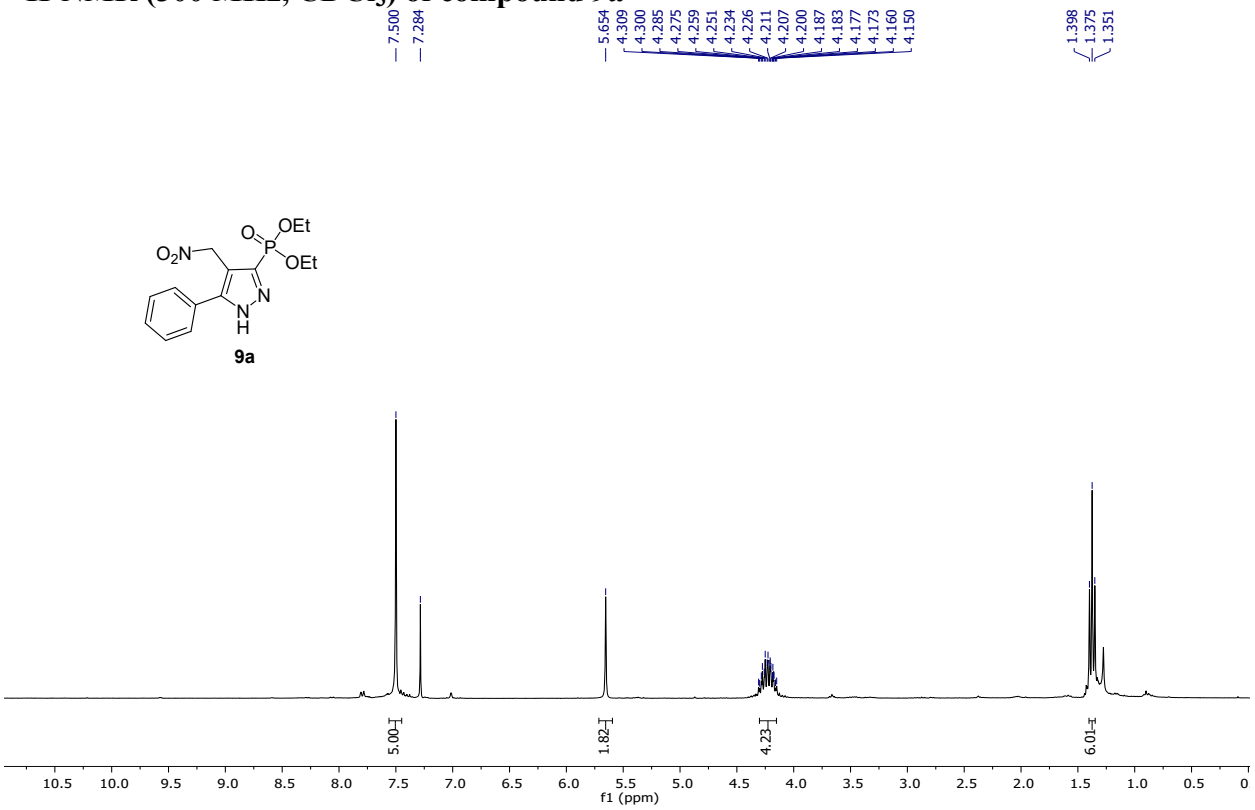
^{1}H-NMR (300 MHz, $CDCl_3$) of compound 8b



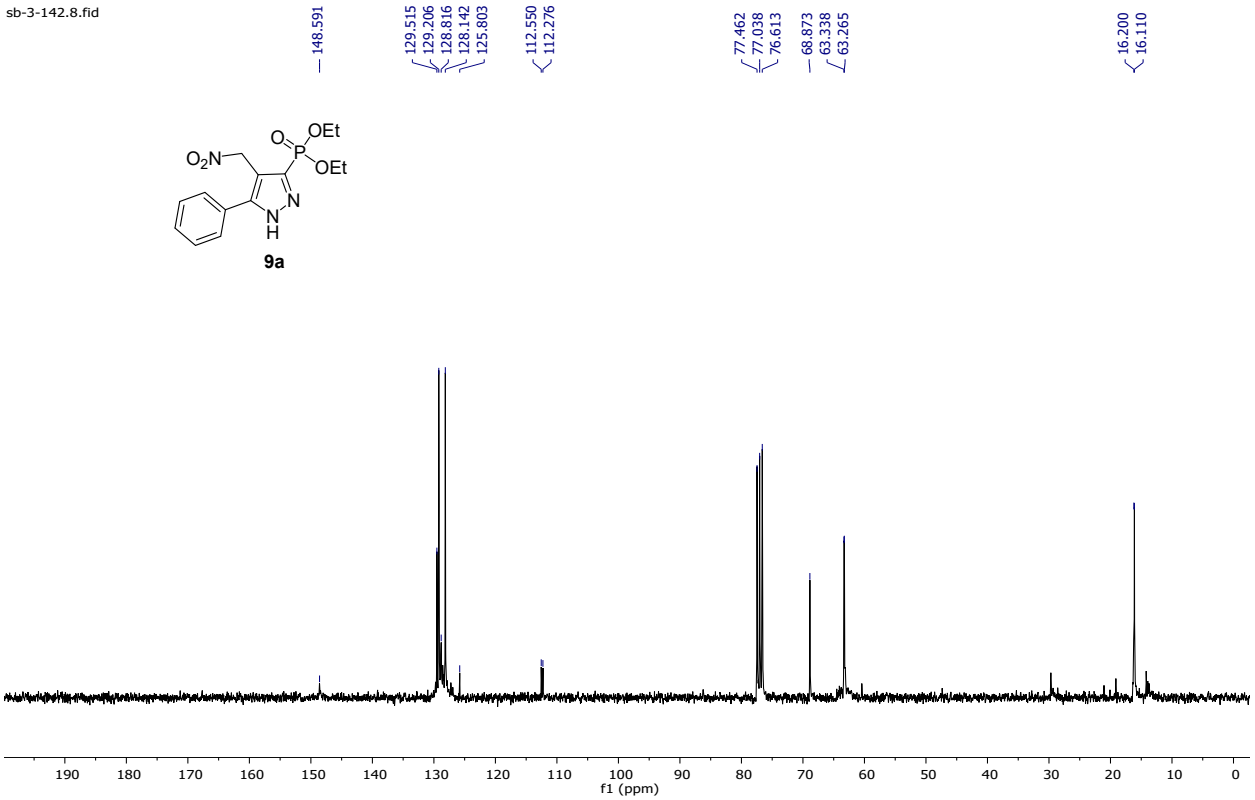
^{13}C-NMR (75 MHz, $CDCl_3$) of compound 8b



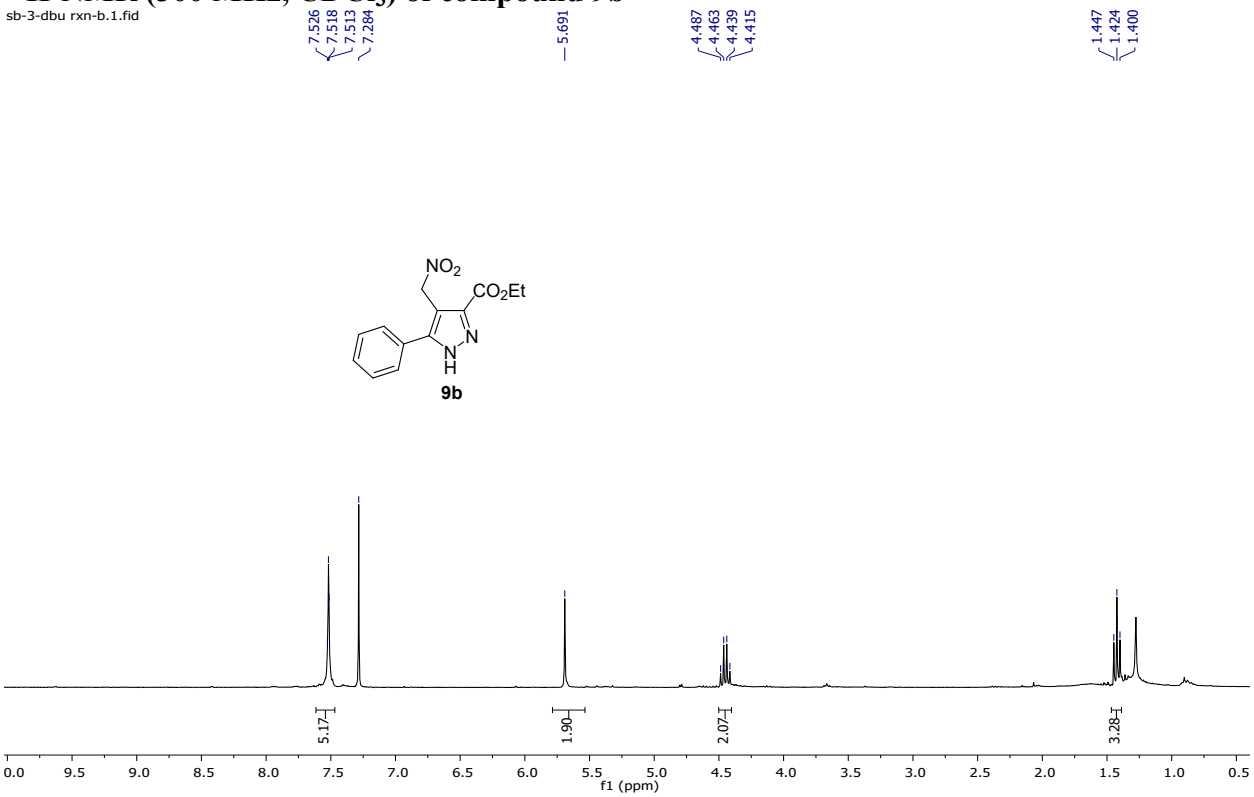
^{1}H-NMR (300 MHz, $CDCl_3$) of compound 9a



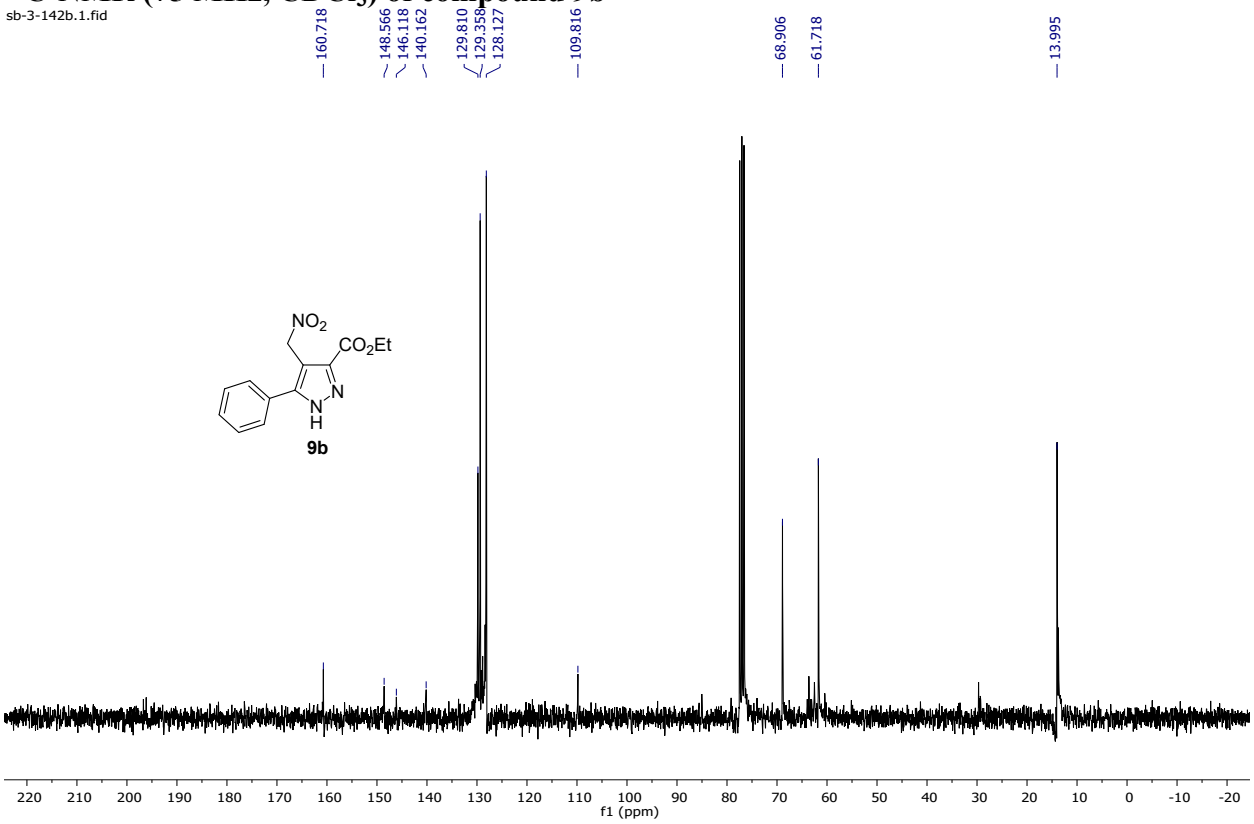
^{13}C-NMR (75 MHz, $CDCl_3$) of compound 9a



^{1}H-NMR (300 MHz, $CDCl_3$) of compound 9b



^{13}C-NMR (75 MHz, $CDCl_3$) of compound 9b



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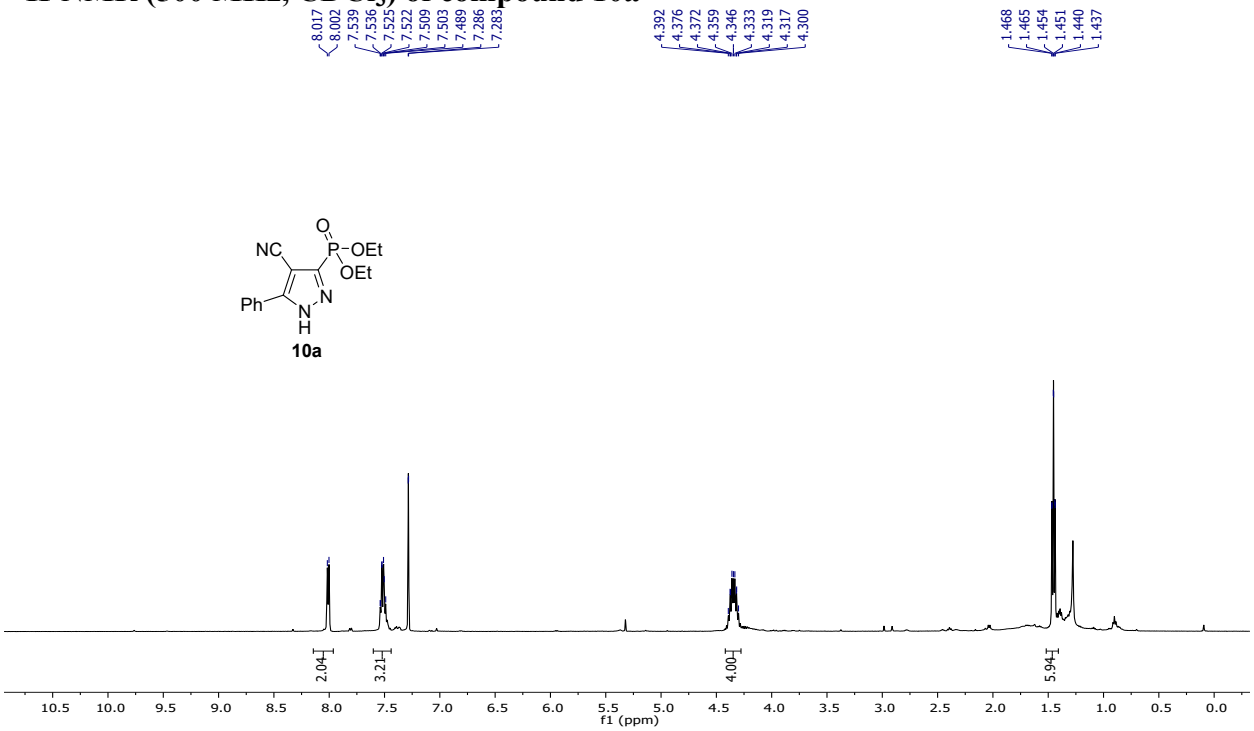
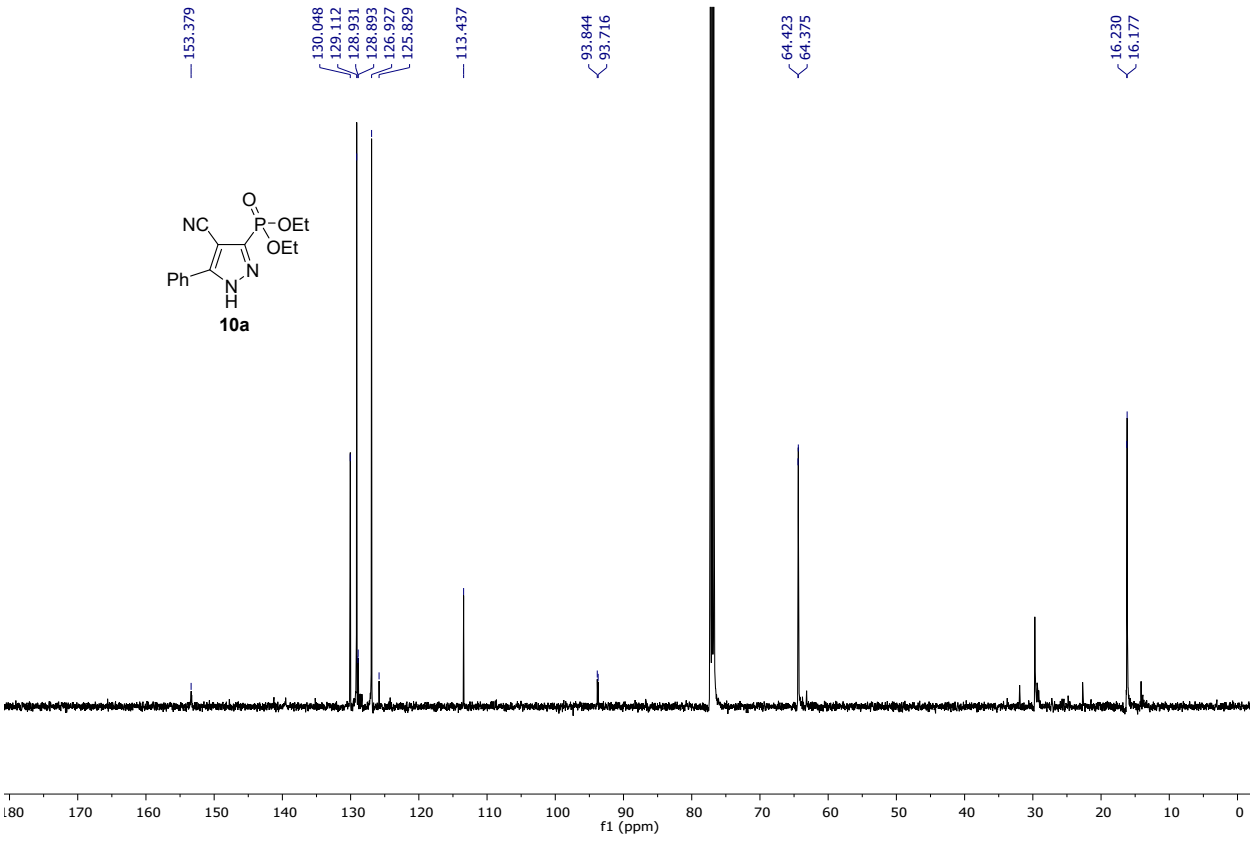


^{13}C-NMR (126 MHz, $CDCl_3$) of compound 10a



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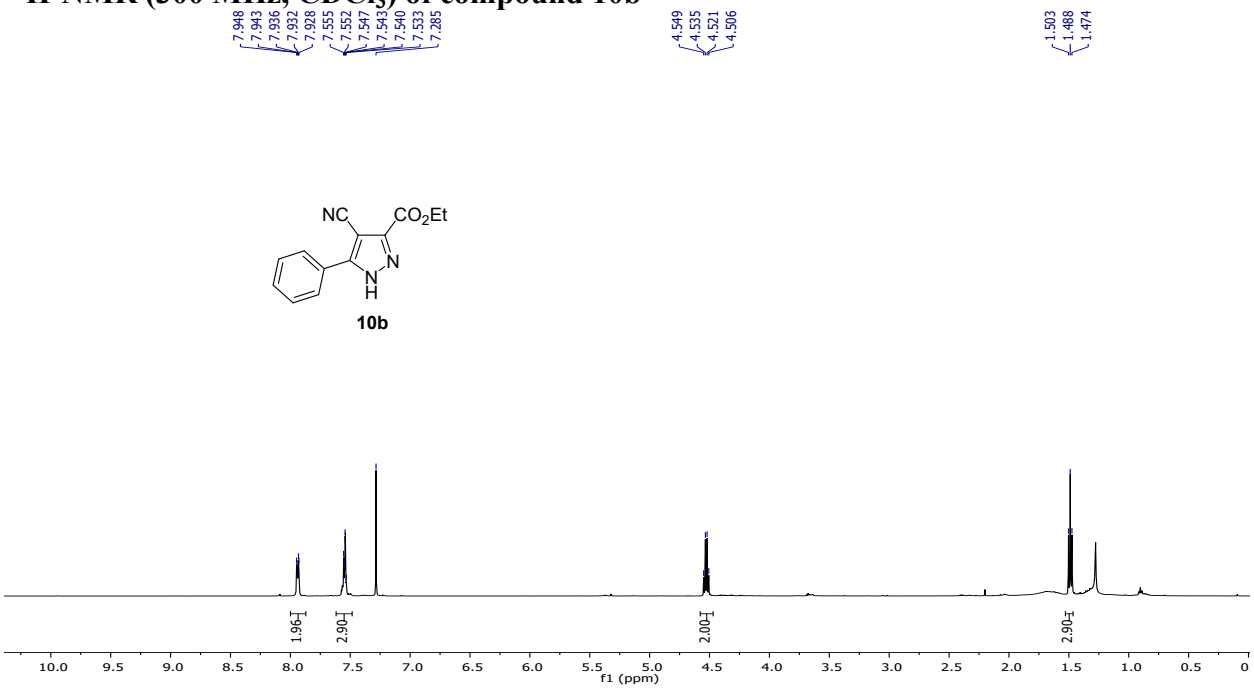
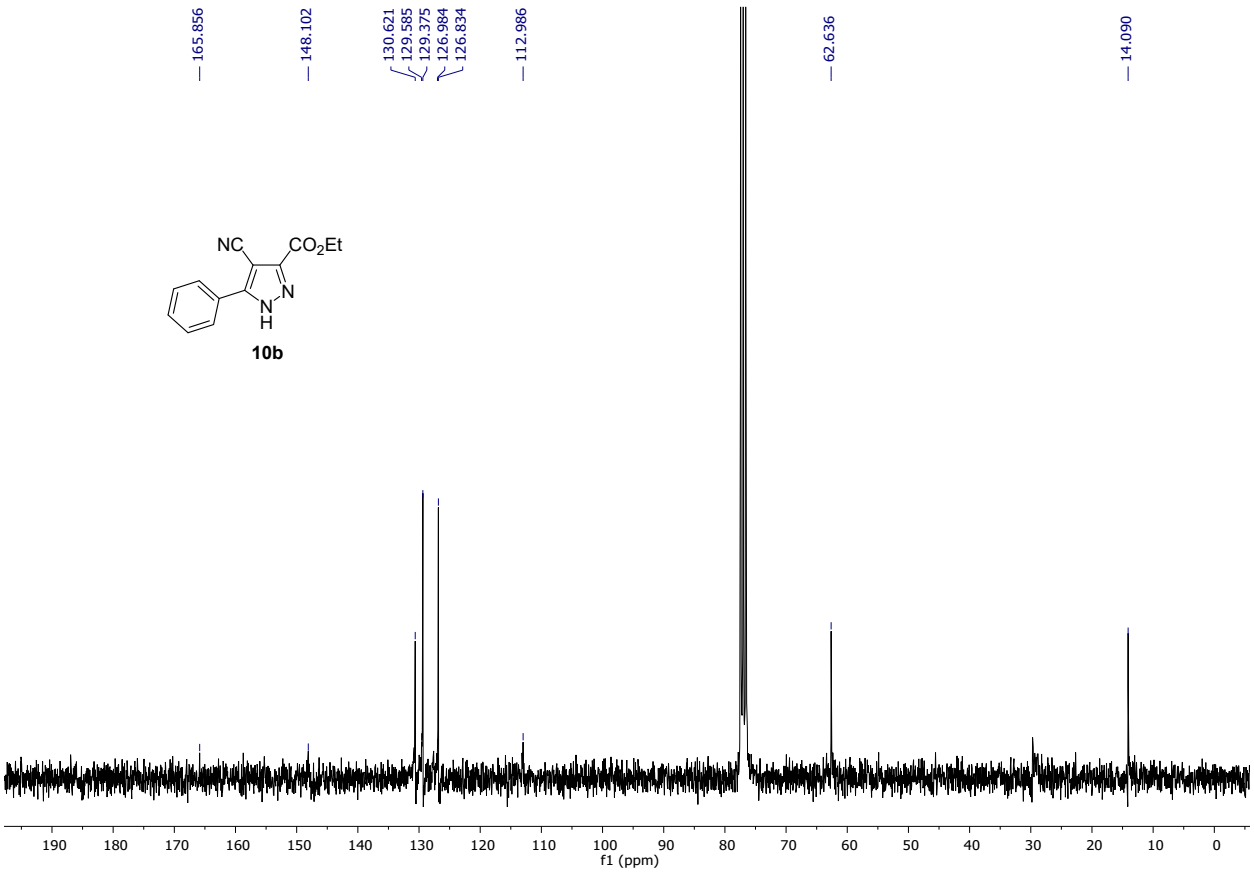
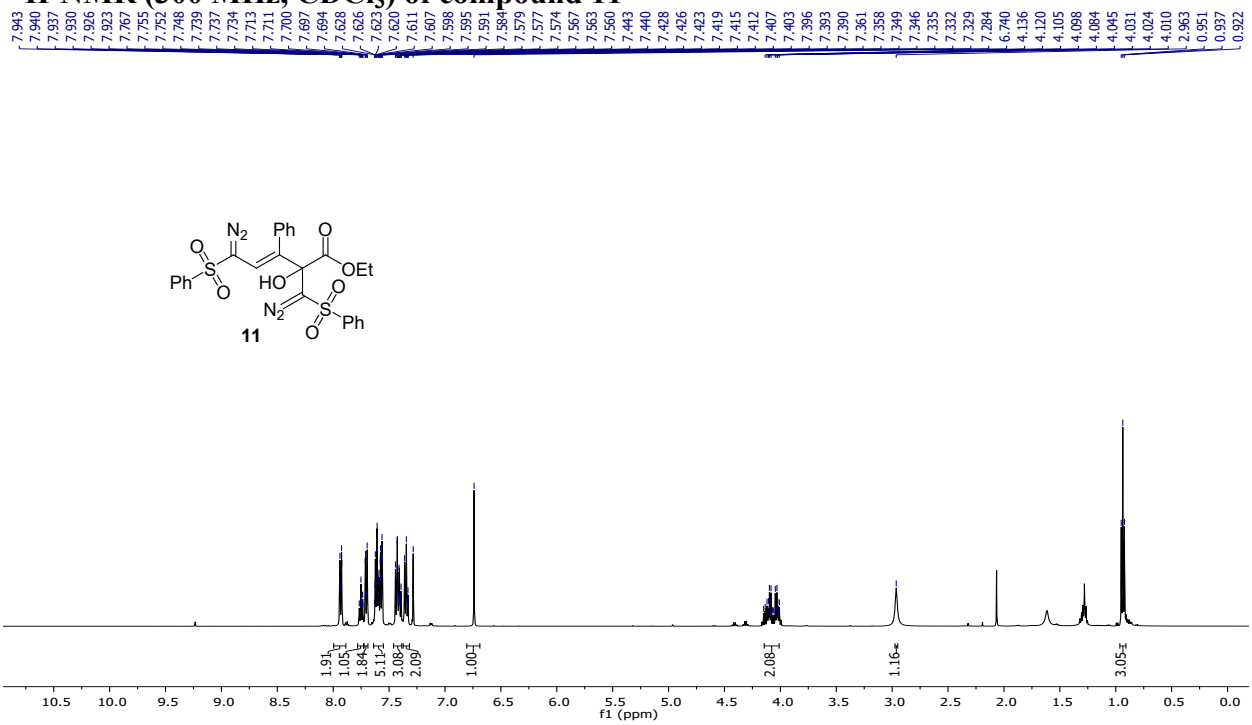


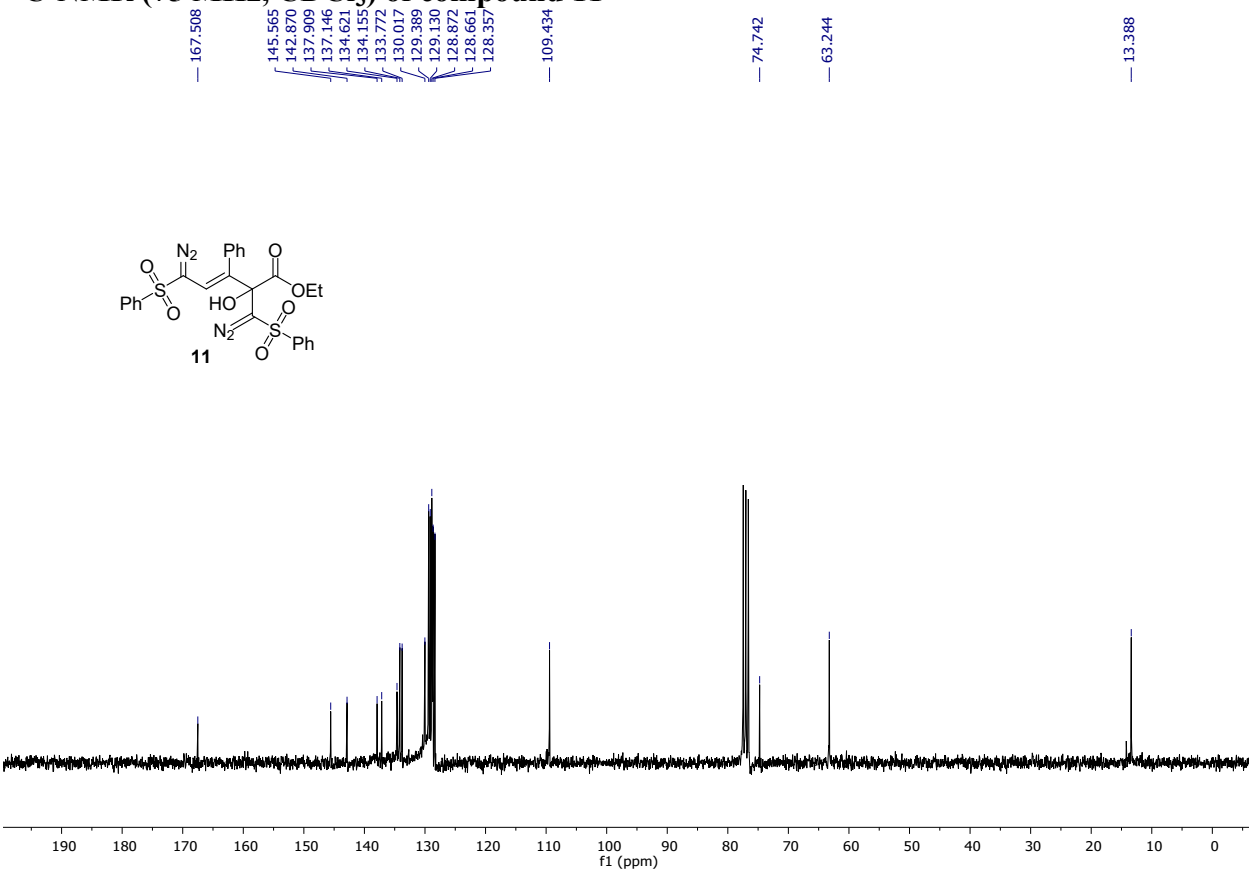
^{13}C-NMR (75 MHz, $CDCl_3$) of compound 10b



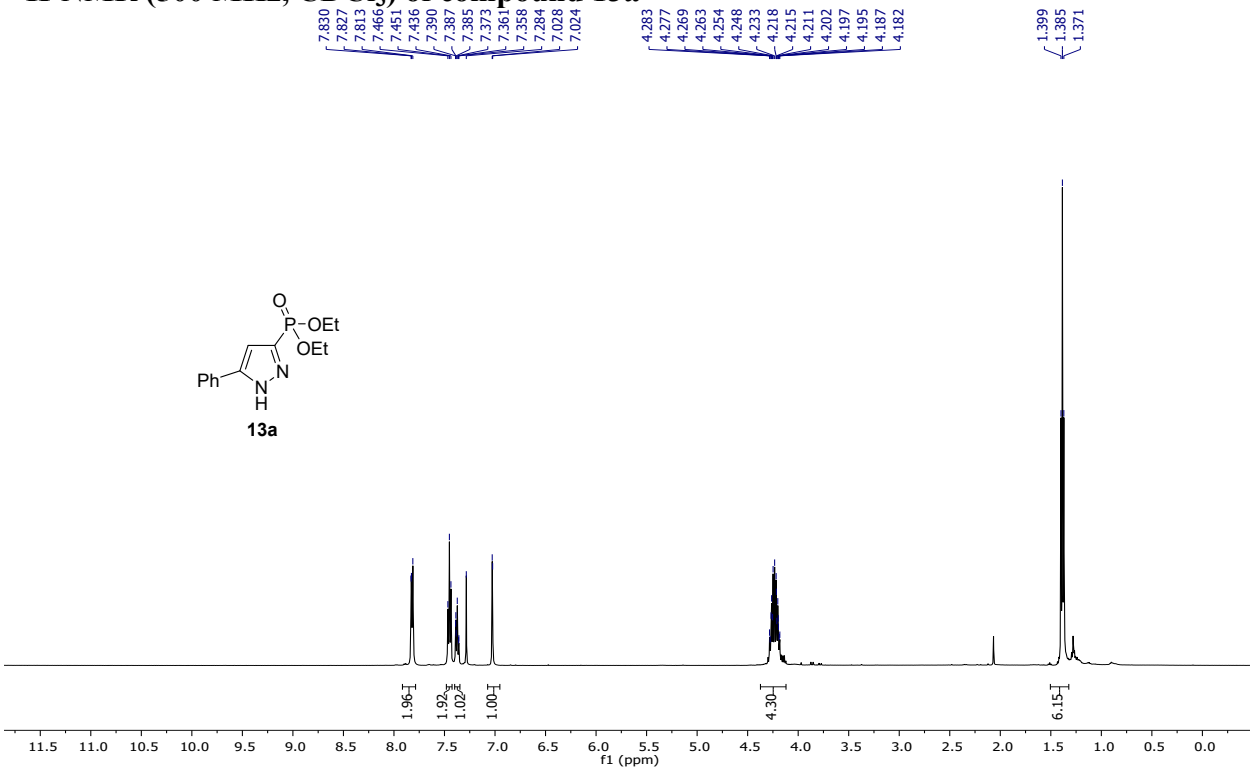
^{1}H-NMR (300 MHz, $CDCl_3$) of compound 11



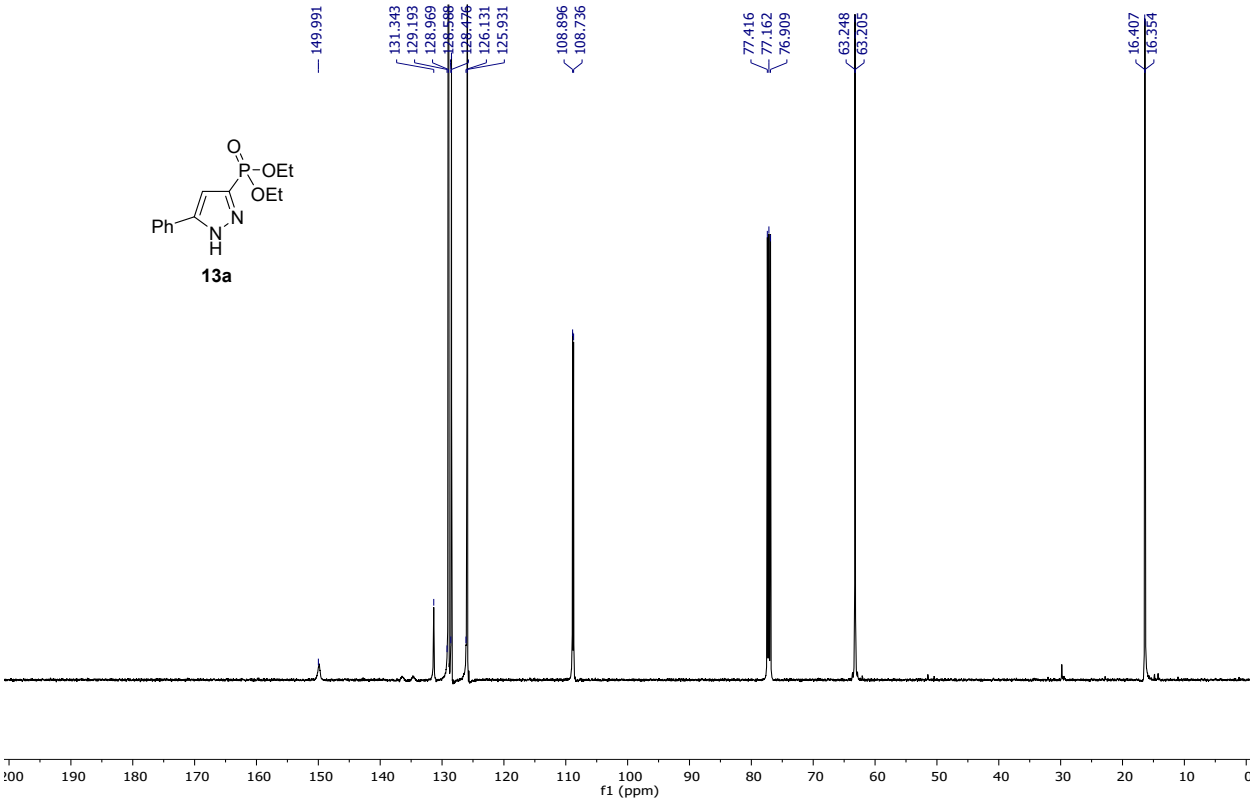
^{13}C-NMR (75 MHz, $CDCl_3$) of compound 11



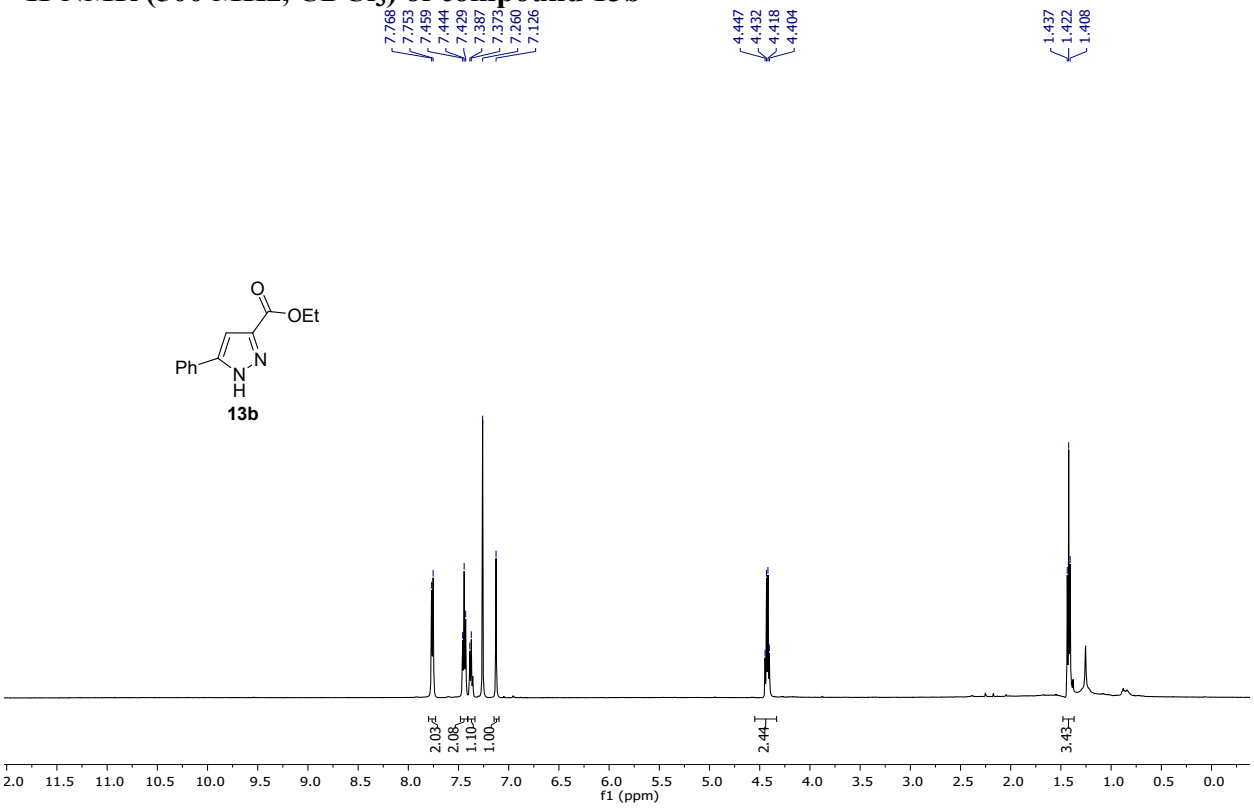
^{1}H-NMR (500 MHz, $CDCl_3$) of compound 13a



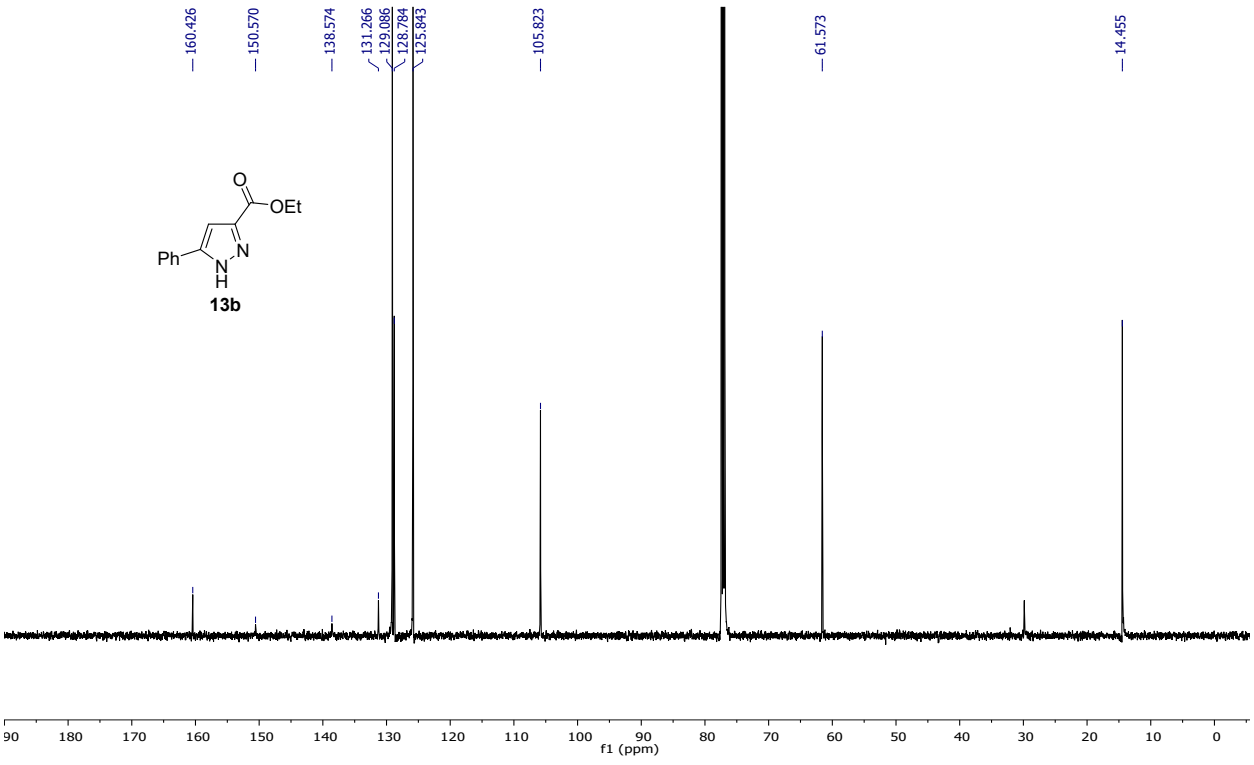
^{13}C-NMR (126 MHz, $CDCl_3$) of compound13a



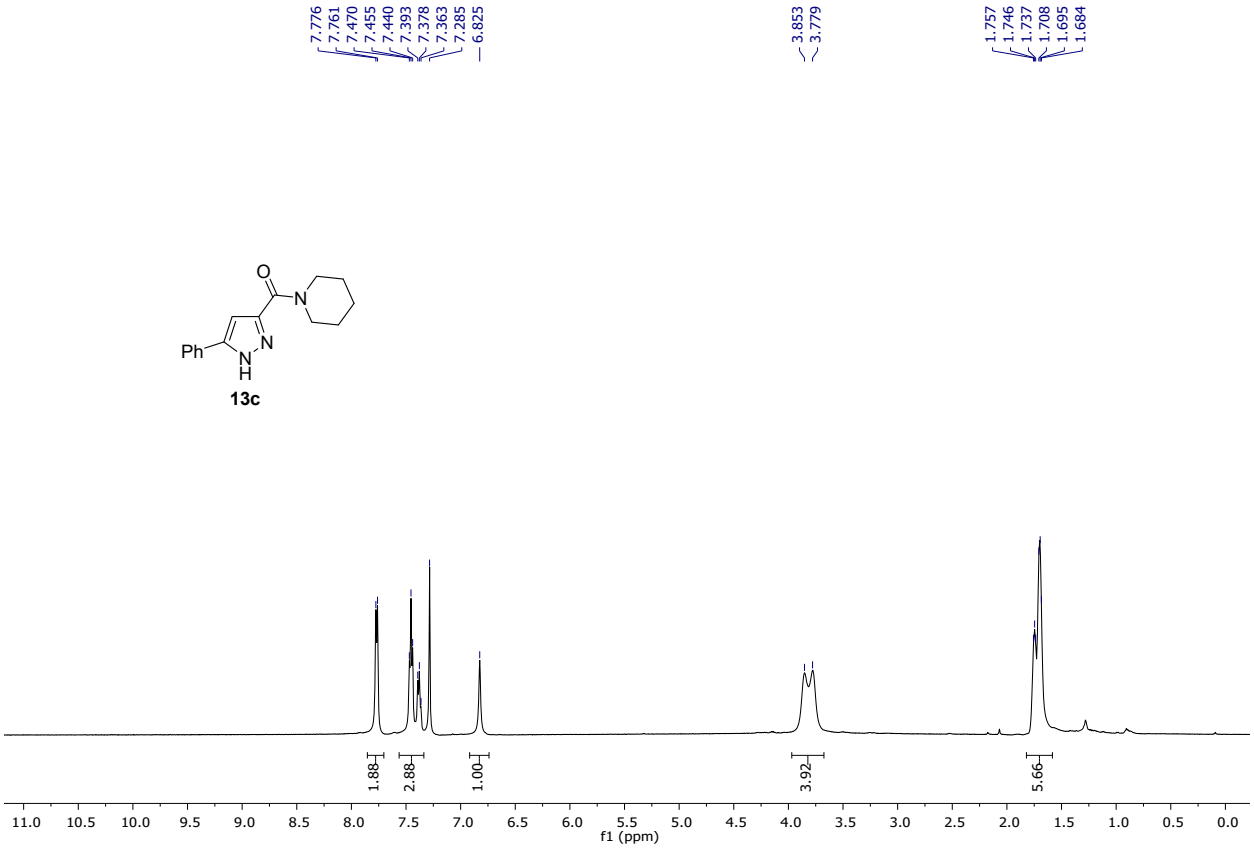
^{1}H-NMR (500 MHz, $CDCl_3$) of compound 13b



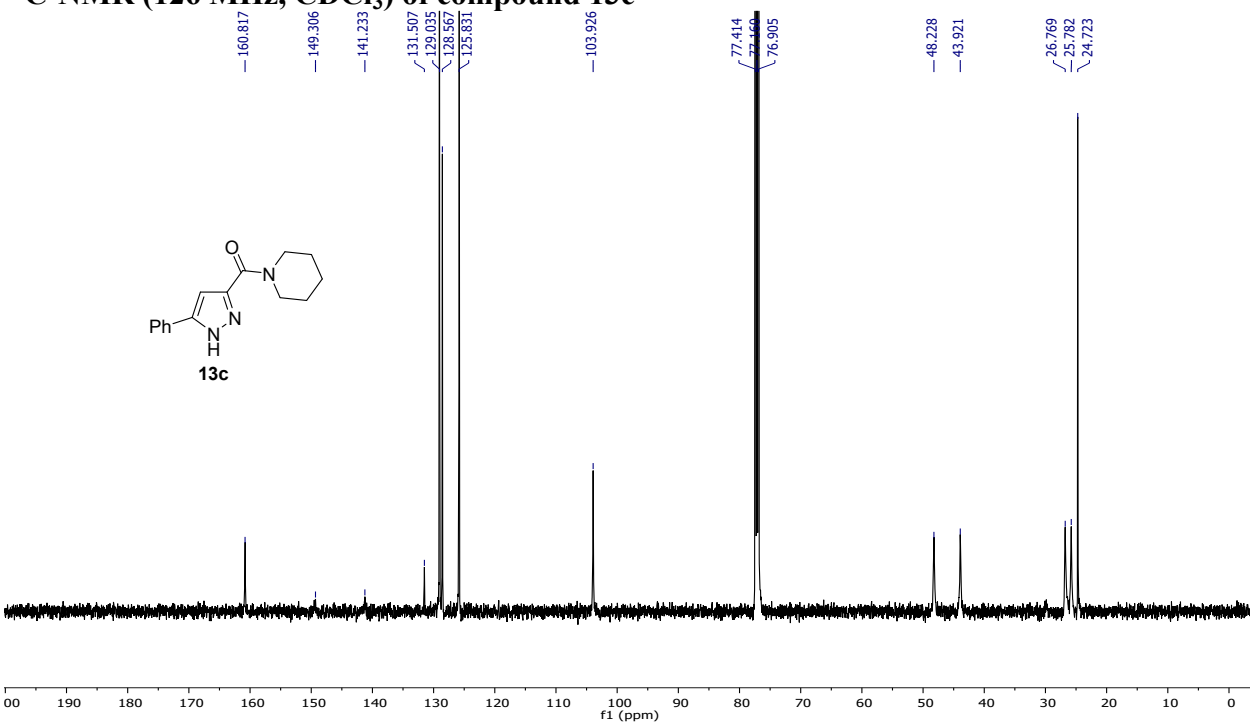
^{13}C-NMR (126 MHz, $CDCl_3$) of compound 13b



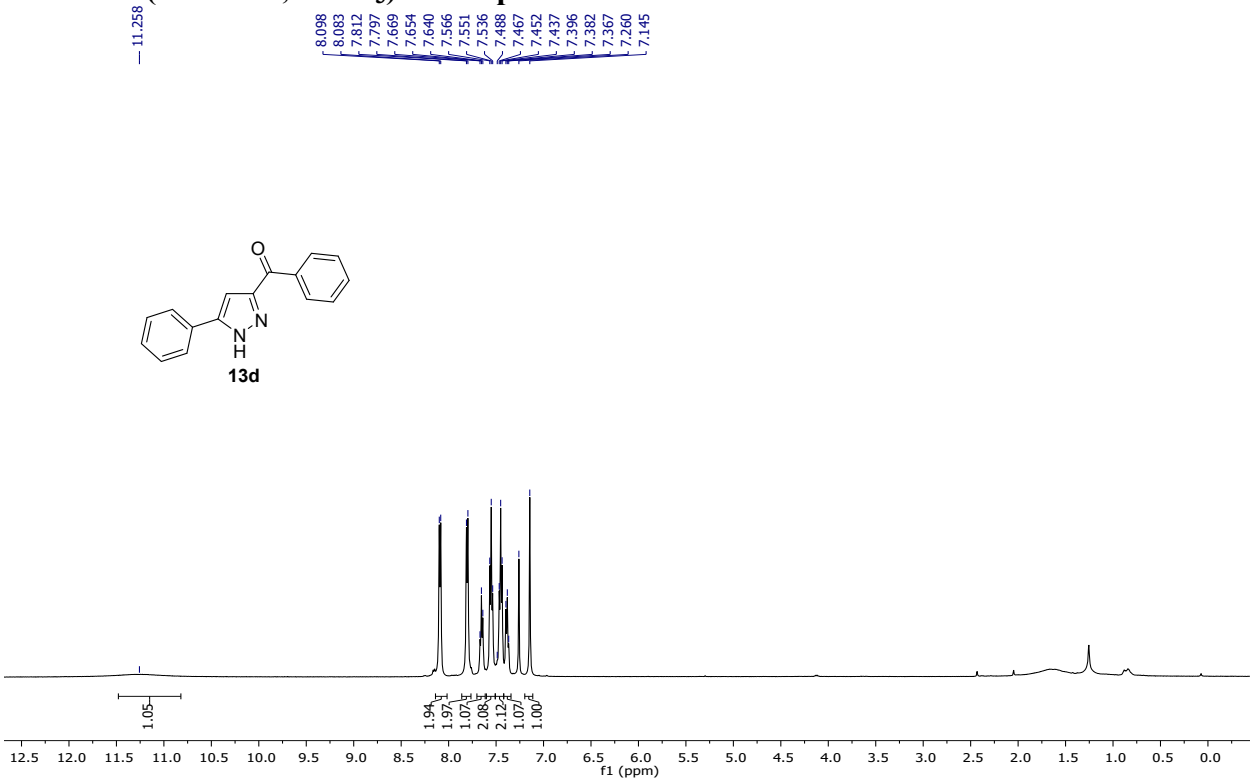
^{1}H-NMR (500 MHz, $CDCl_3$) of compound 13c



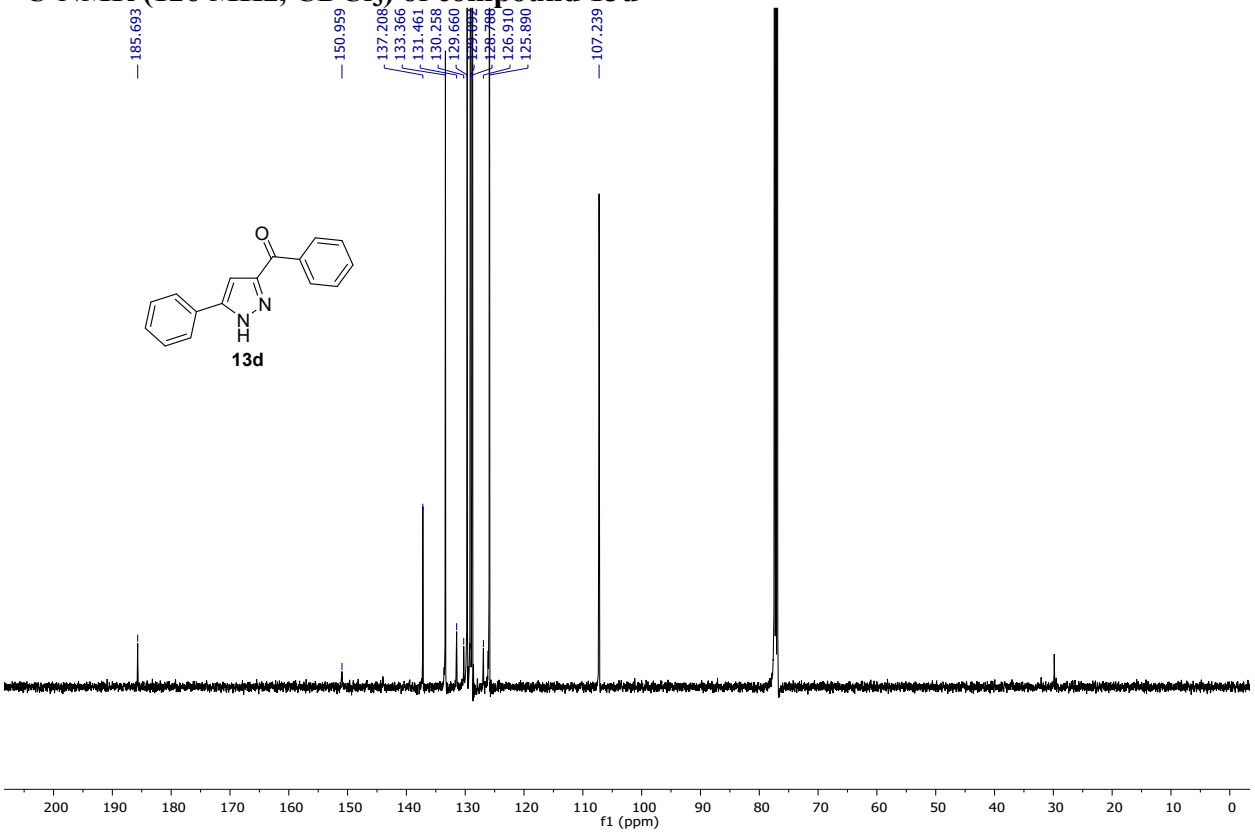
^{13}C-NMR (126 MHz, $CDCl_3$) of compound 13c



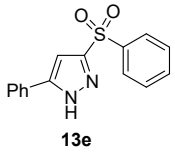
^{1}H-NMR (500 MHz, $CDCl_3$) of compound 13d



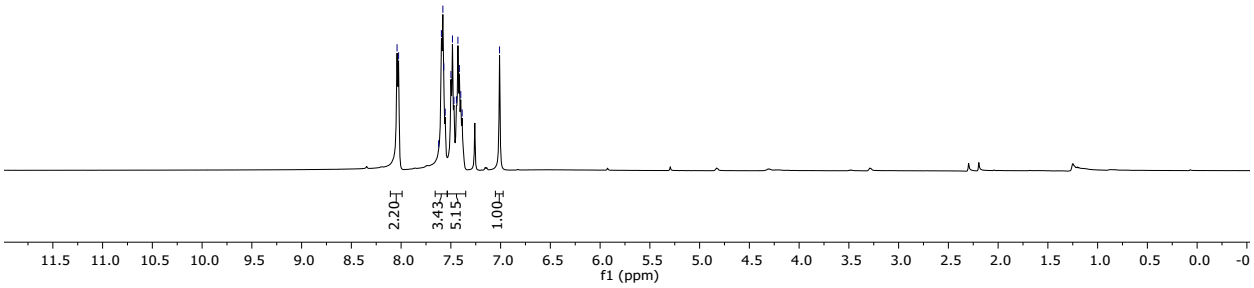
^{13}C-NMR (126 MHz, $CDCl_3$) of compound 13d



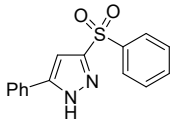
^{1}H-NMR (500 MHz, $CDCl_3$) of compound 13e



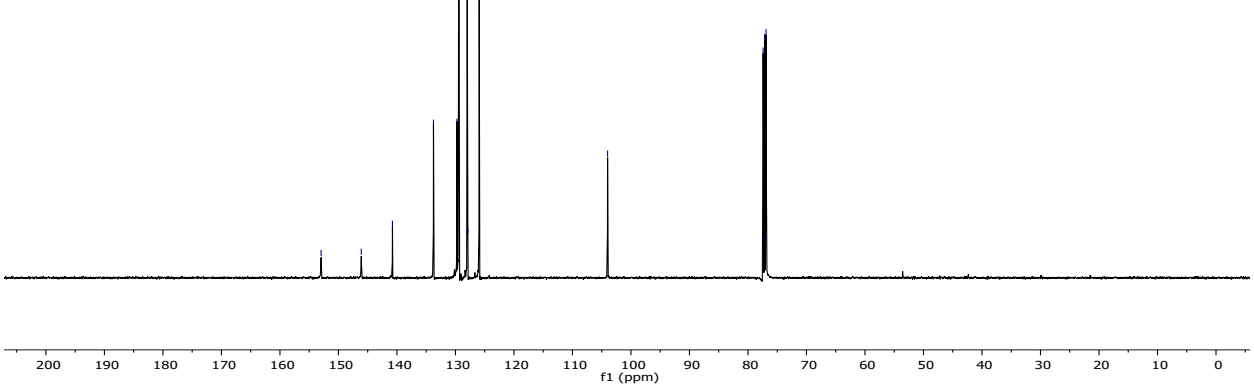
13e



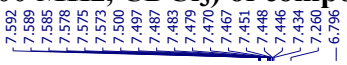
^{13}C-NMR (126 MHz, $CDCl_3$) of compound 13e

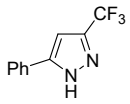


13e

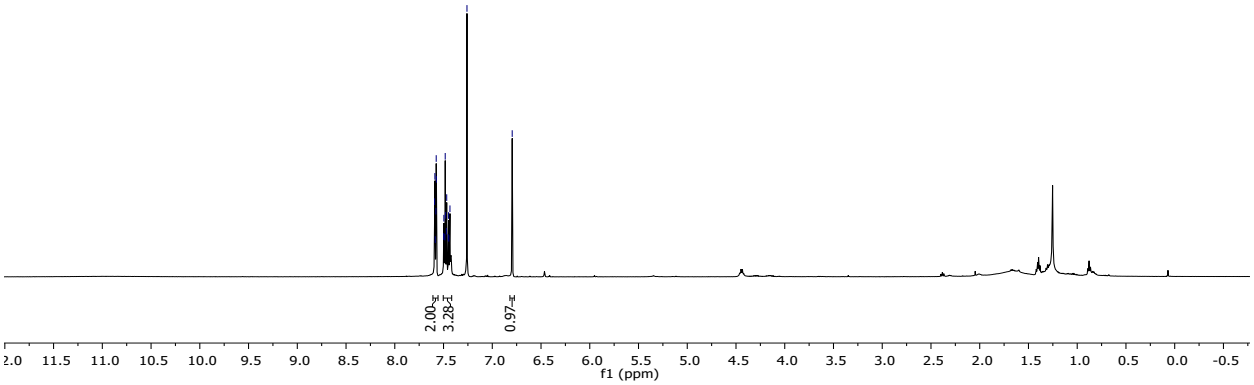


^{1}H-NMR (500 MHz, $CDCl_3$) of compound 13f

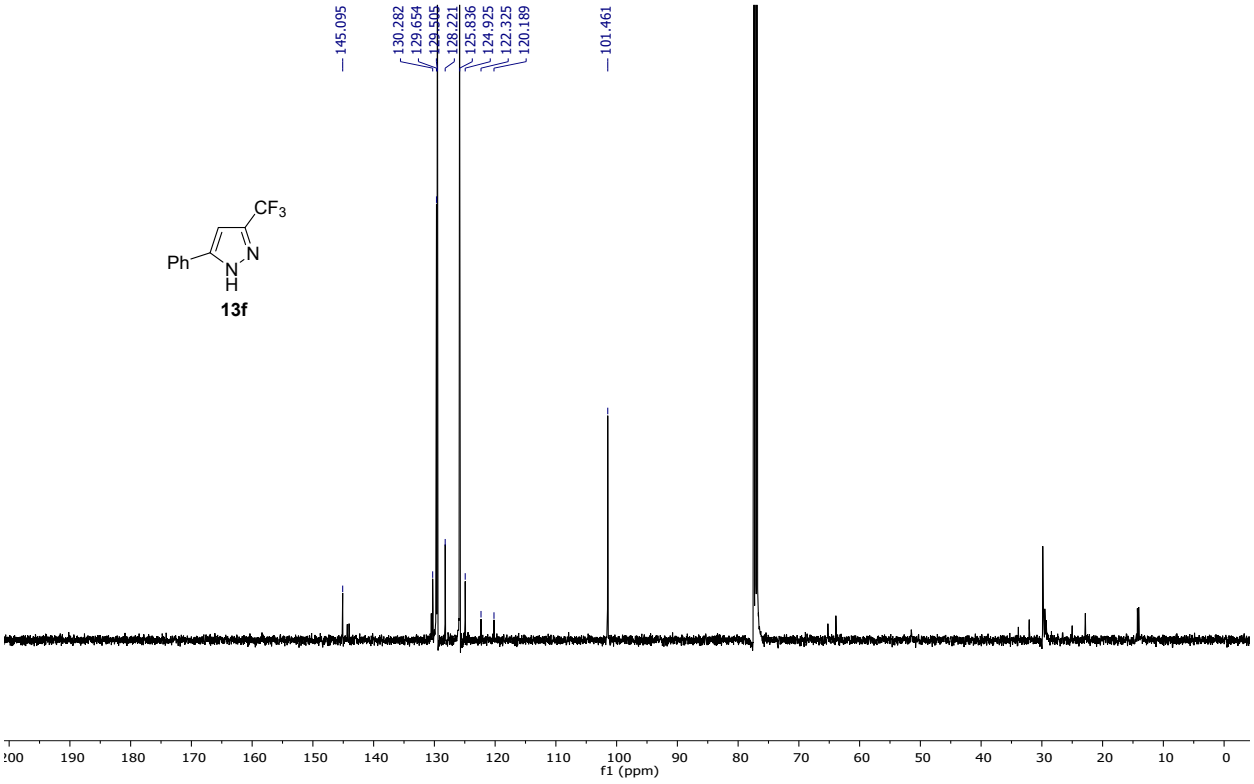




13f

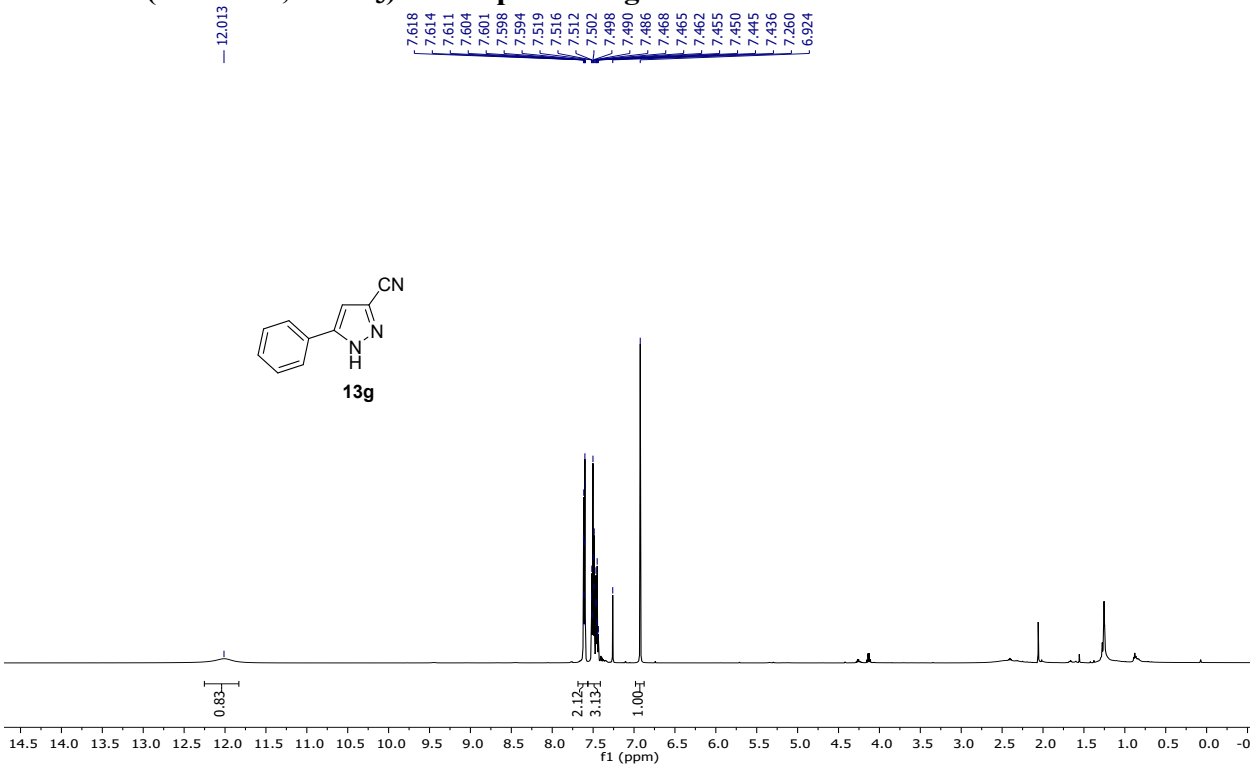


^{13}C-NMR (126 MHz, $CDCl_3$) of compound 13f

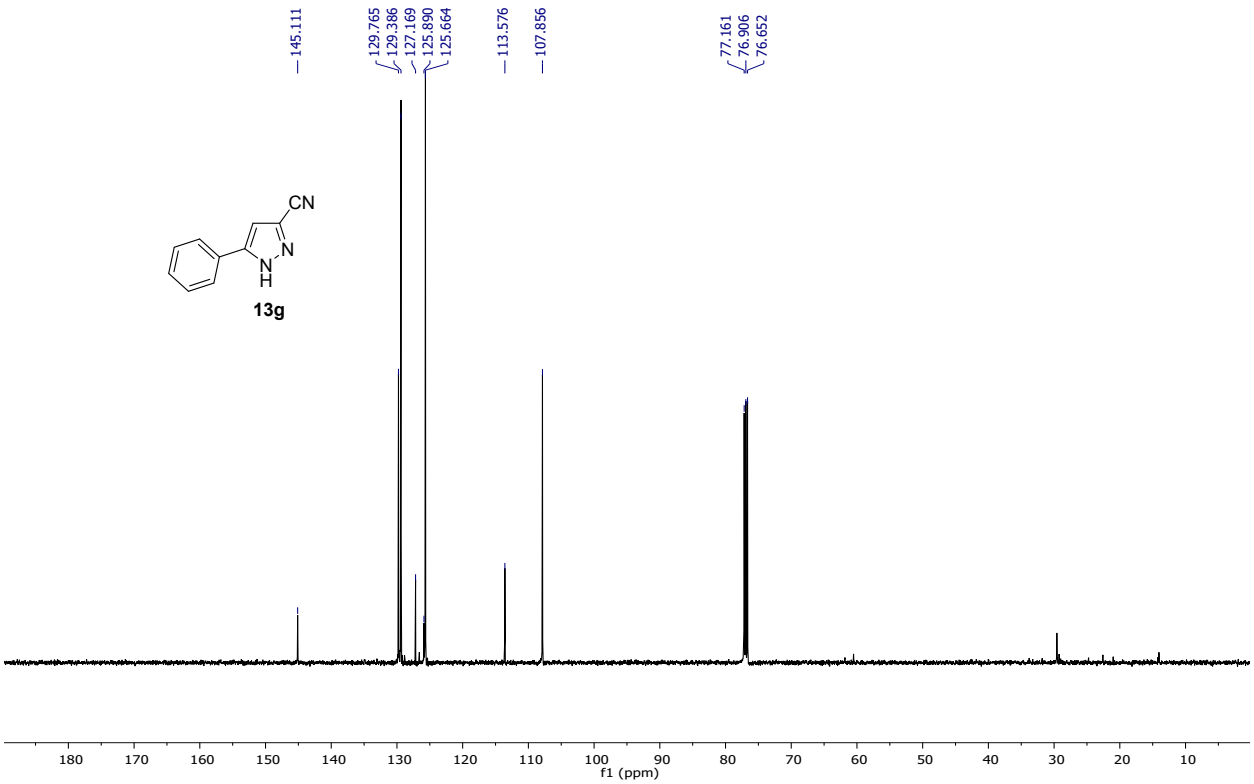


13f

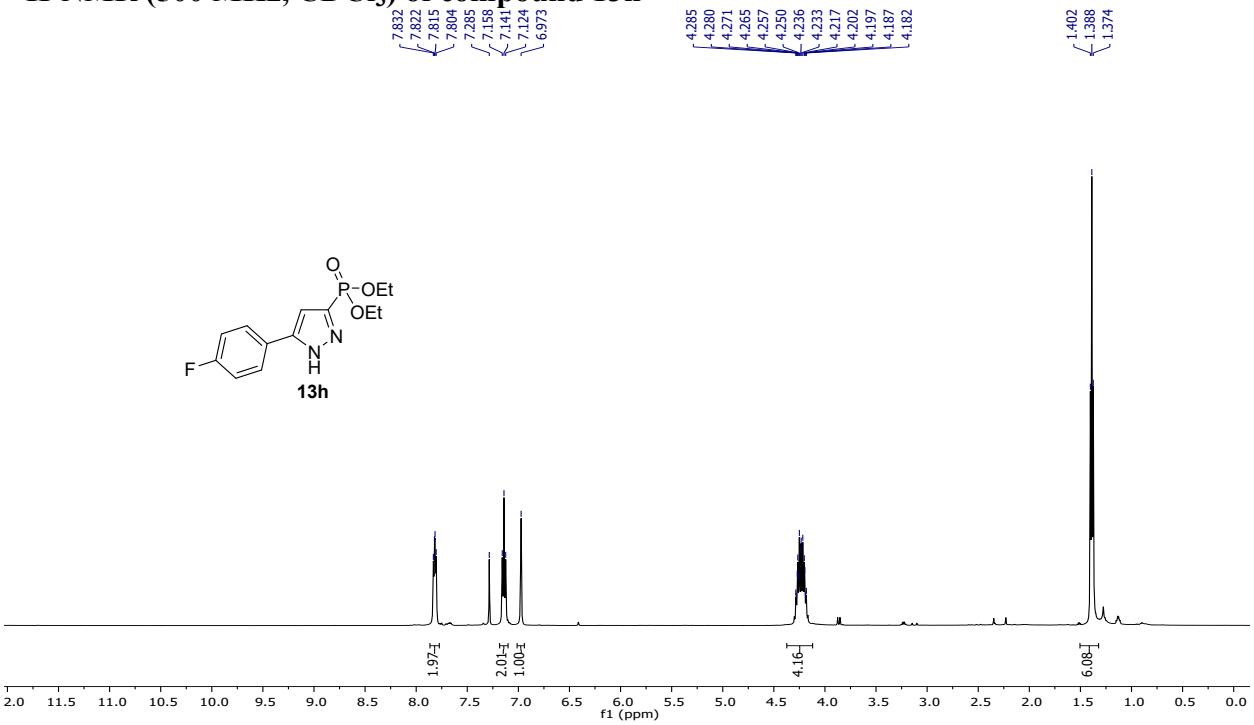
^{1}H-NMR (500 MHz, $CDCl_3$) of compound 13g



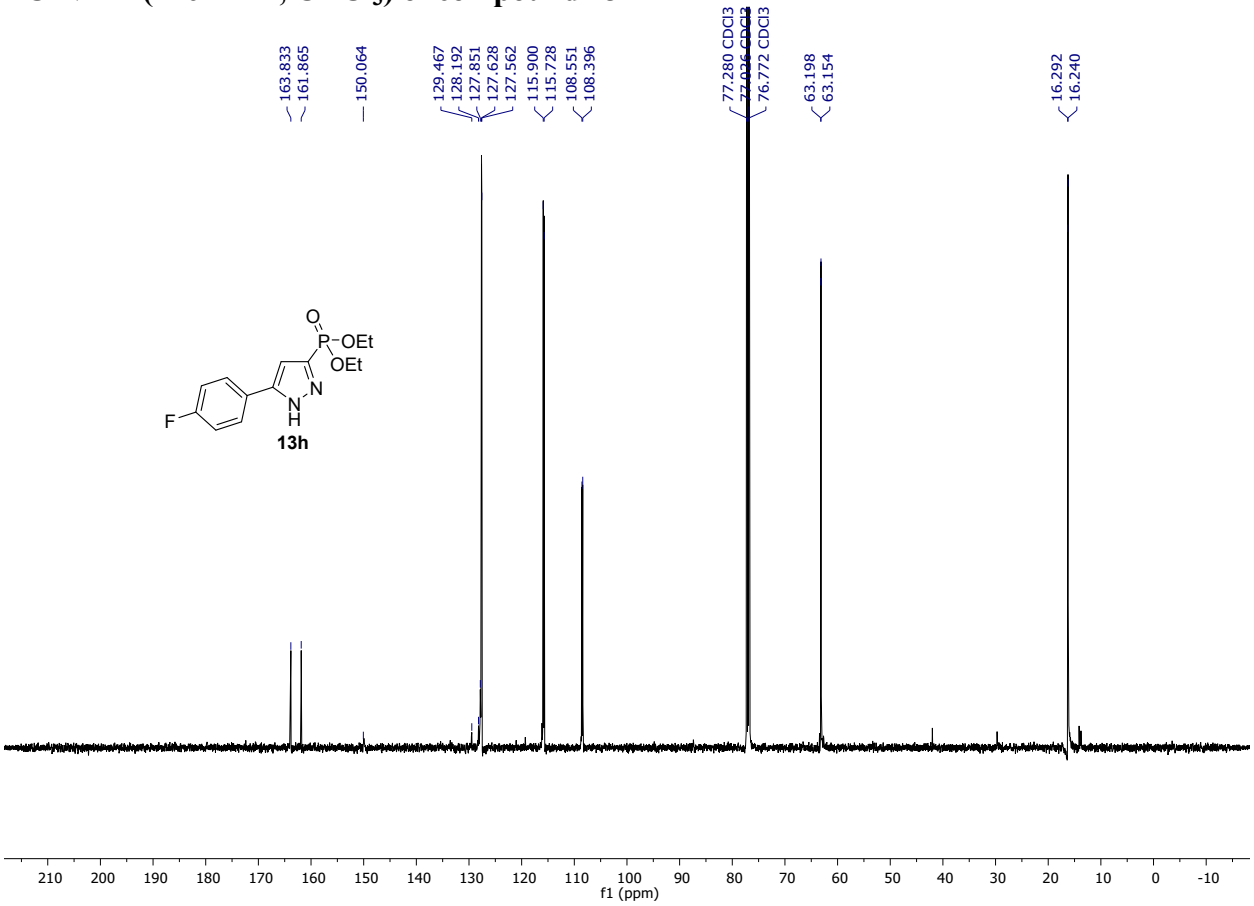
^{13}C-NMR (126 MHz, $CDCl_3$) of compound 13g



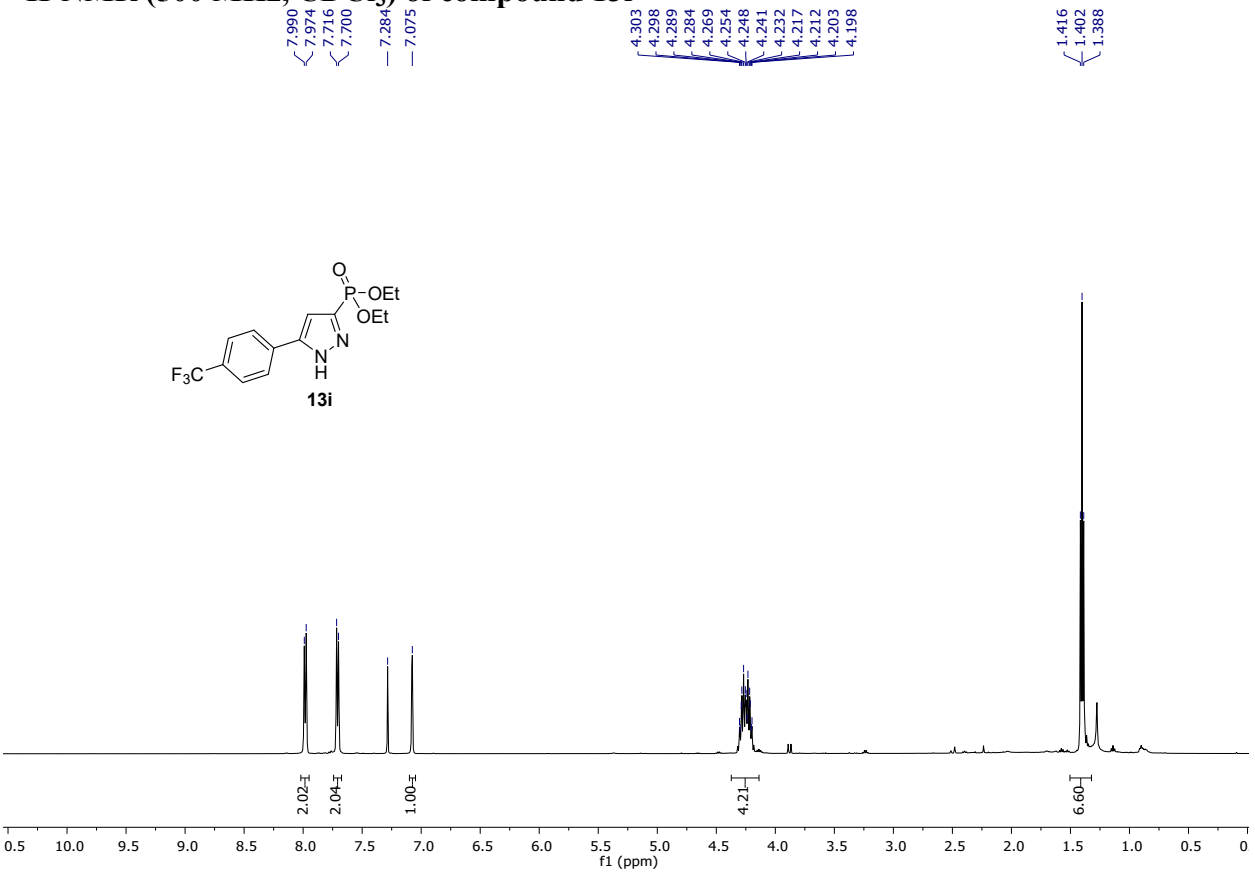
^{1}H-NMR (500 MHz, $CDCl_3$) of compound 13h



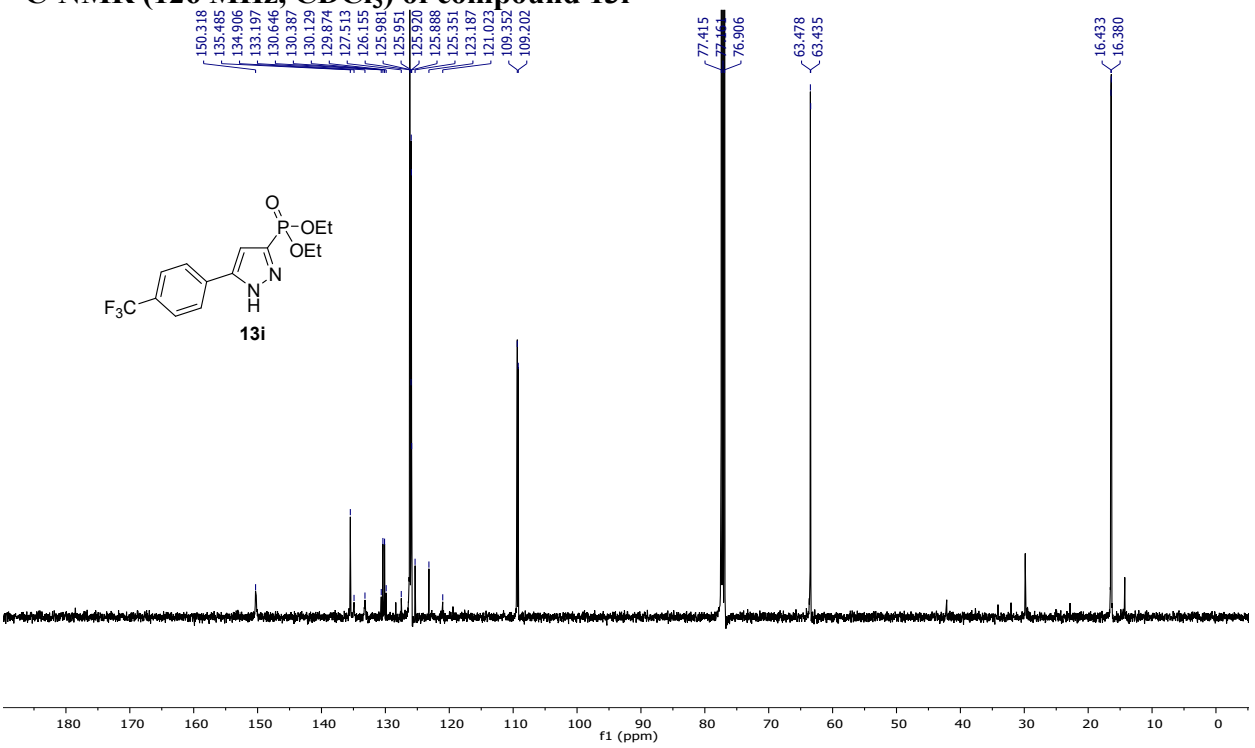
^{13}C-NMR (126 MHz, $CDCl_3$) of compound 13h



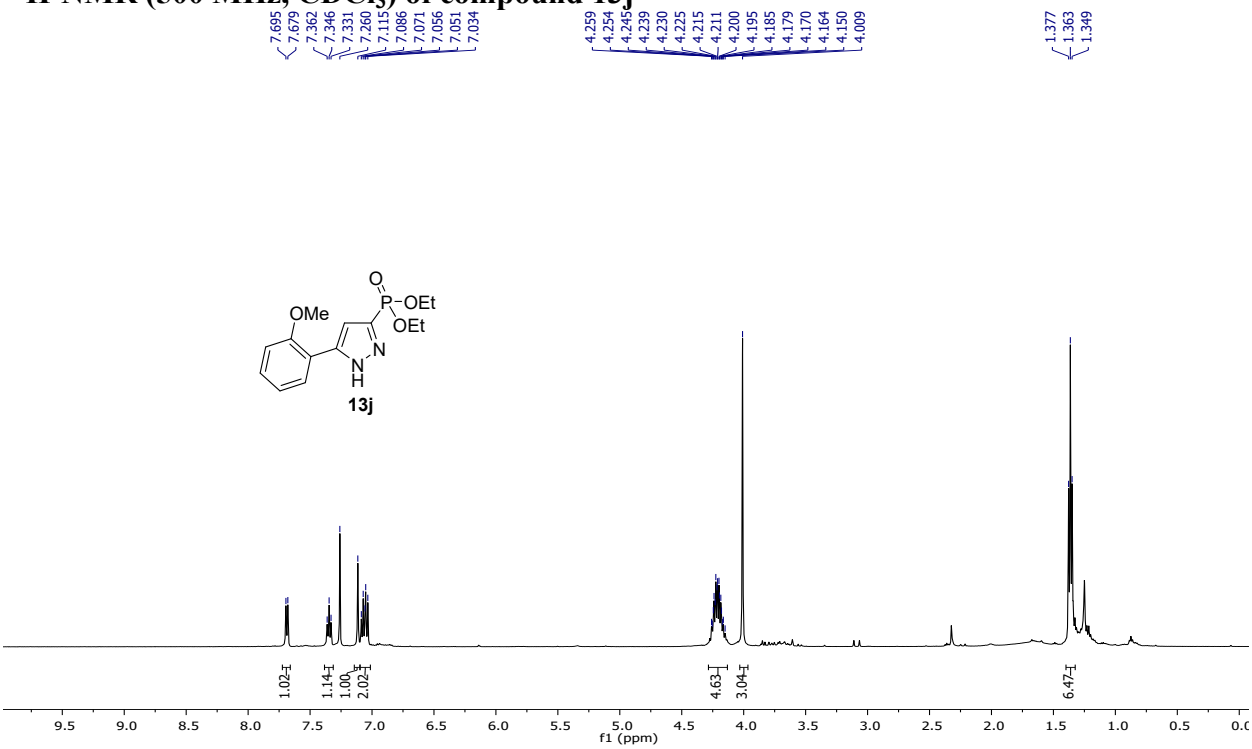
^{1}H-NMR (500 MHz, $CDCl_3$) of compound 13i



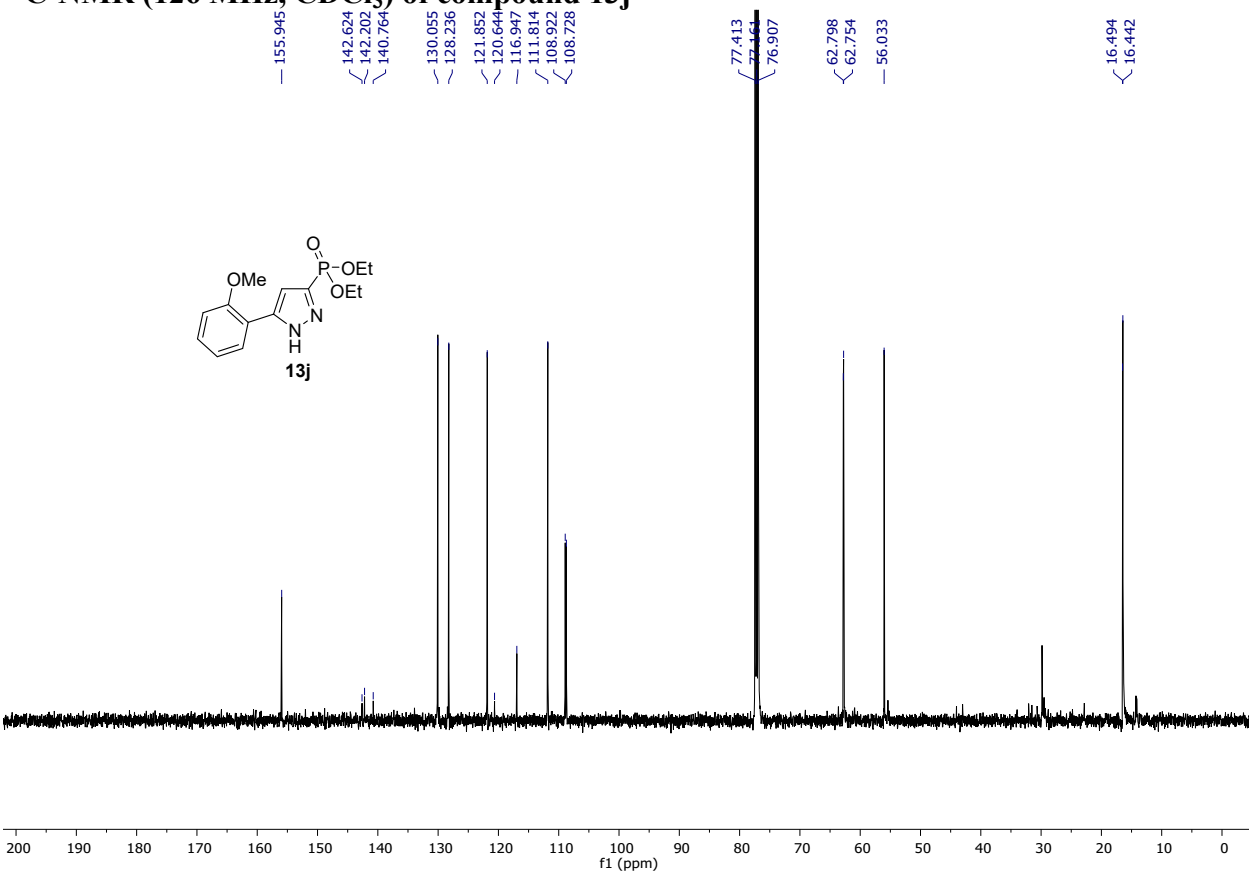
^{13}C-NMR (126 MHz, $CDCl_3$) of compound 13i



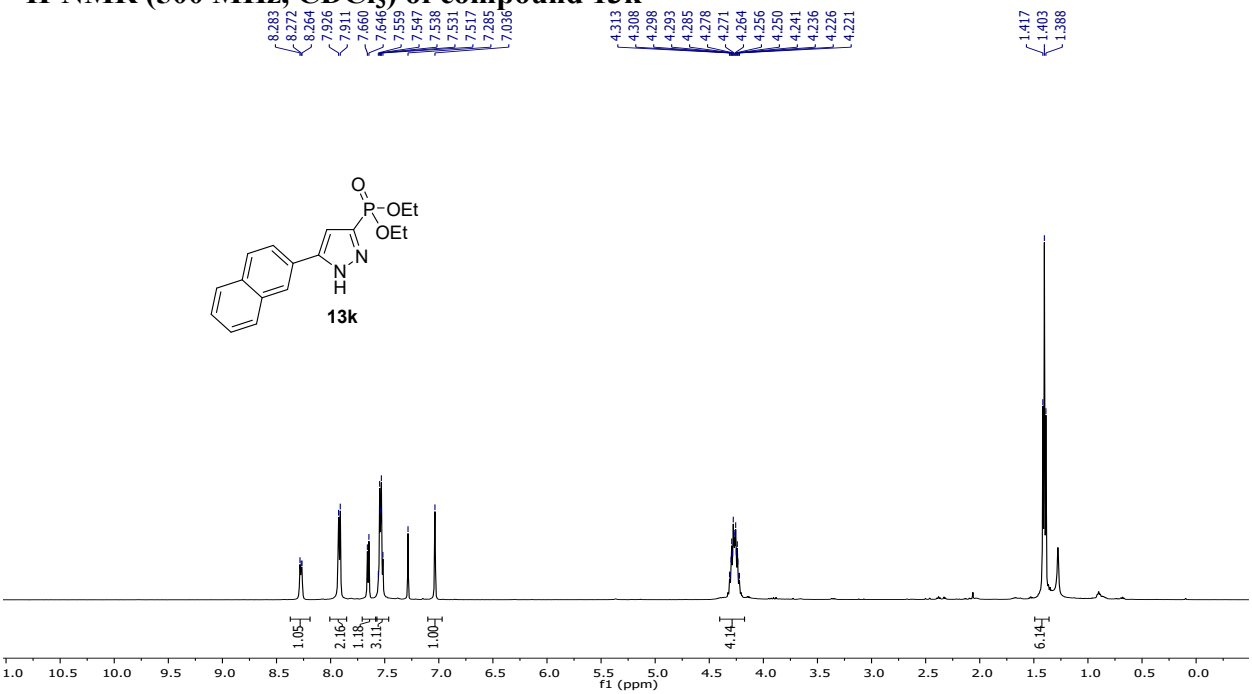
^{1}H-NMR (500 MHz, $CDCl_3$) of compound 13j



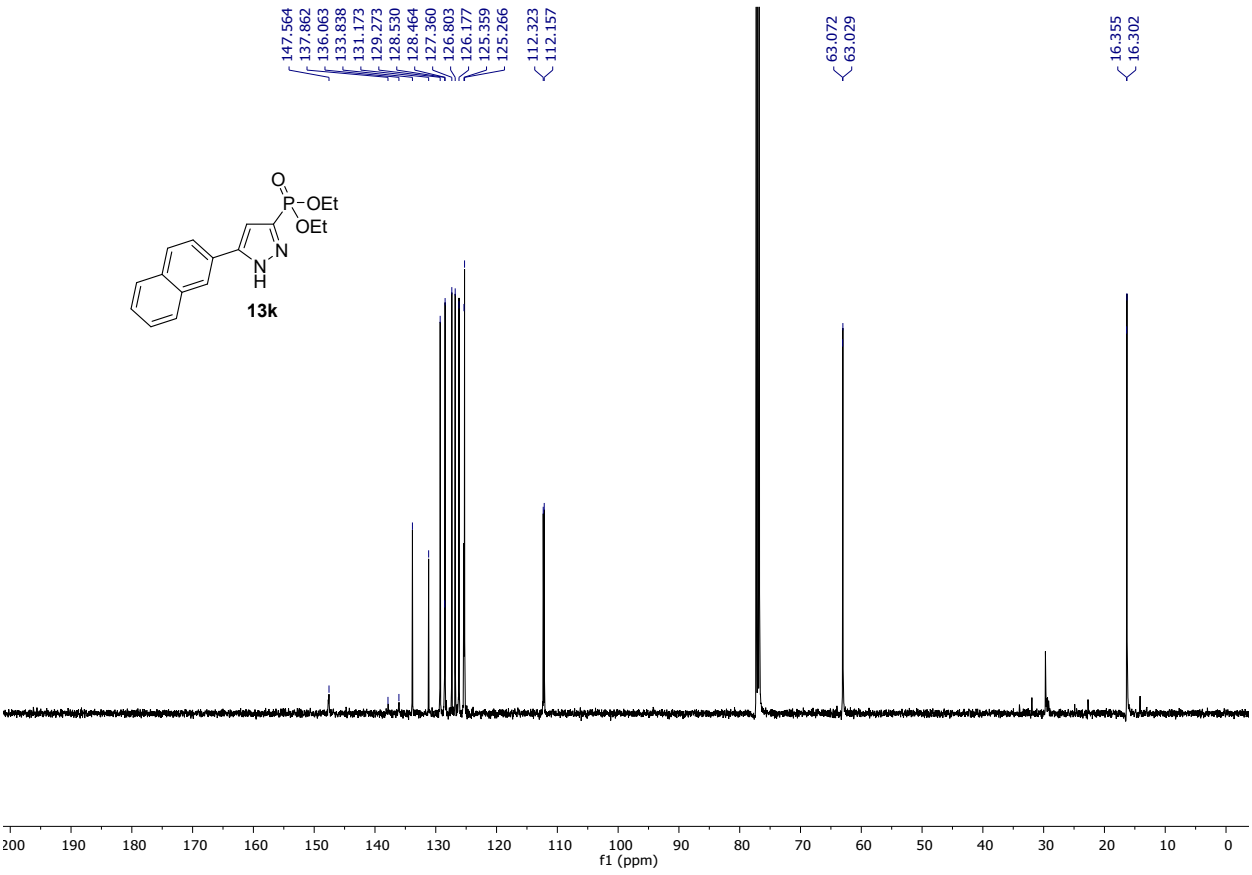
^{13}C-NMR (126 MHz, $CDCl_3$) of compound 13j



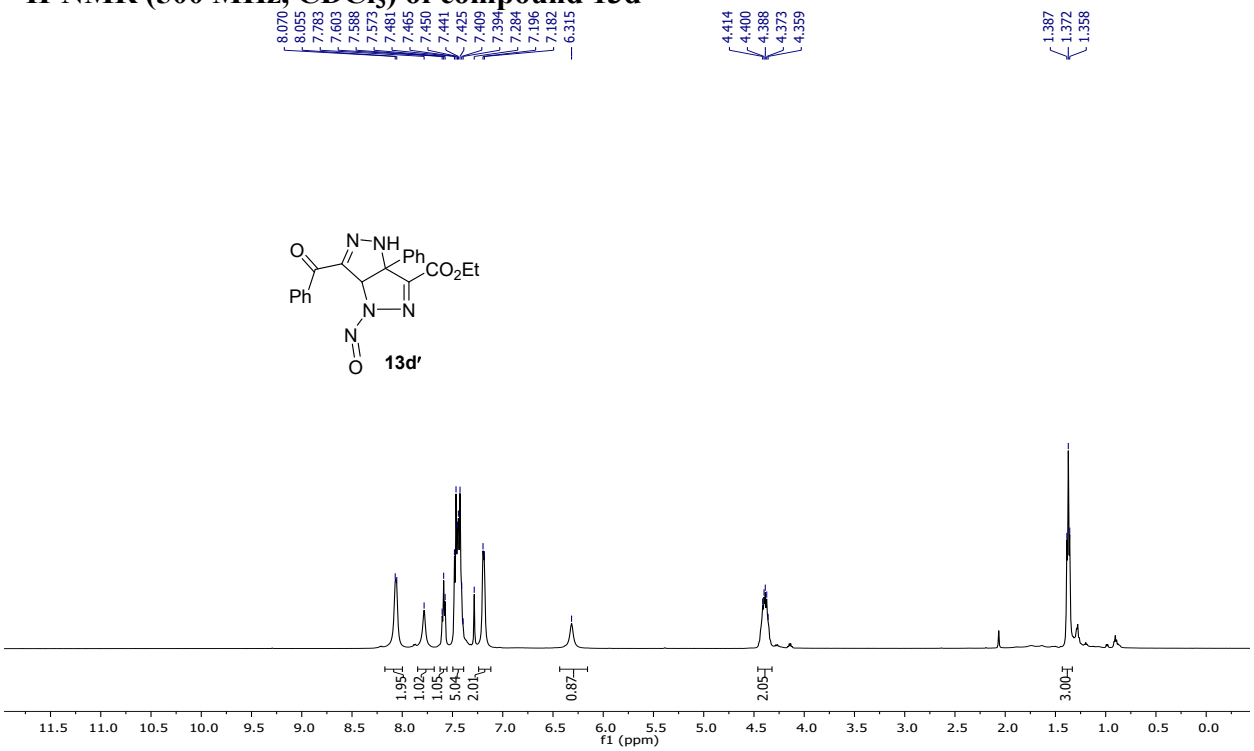
^{1}H-NMR (500 MHz, $CDCl_3$) of compound 13k



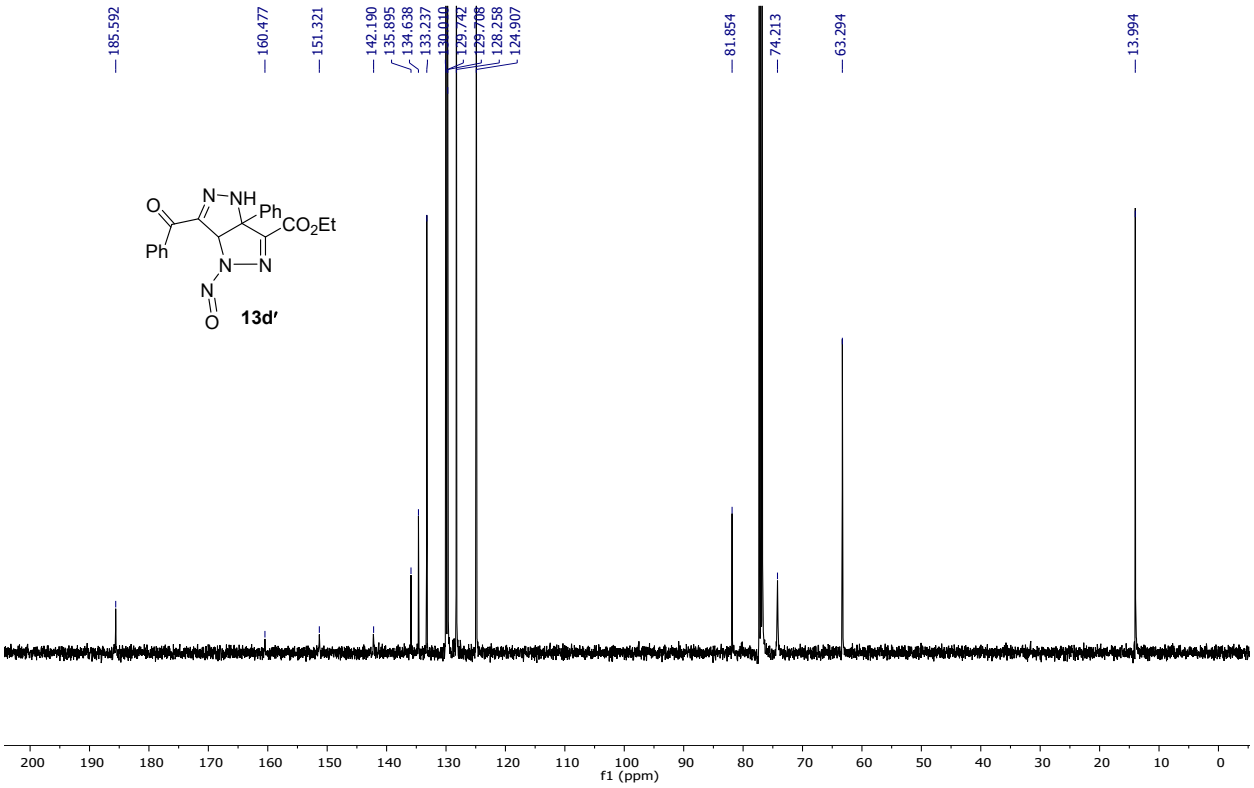
^{13}C-NMR (126 MHz, $CDCl_3$) of compound 13k



^{1}H-NMR (500 MHz, $CDCl_3$) of compound 13d'

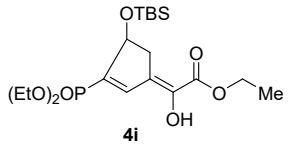


^{13}C-NMR (126 MHz, $CDCl_3$) of compound 13d'

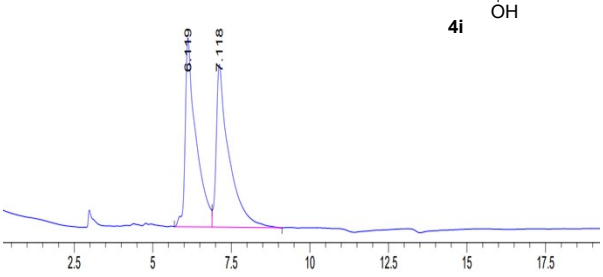


17. HPLC data

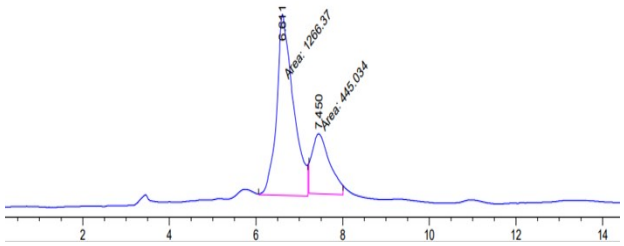
HPLC Chiral assay was conducted on Chiralpak® AD-H column using IPA:nHex (5:95) as an eluent (1 mL/min).



4i

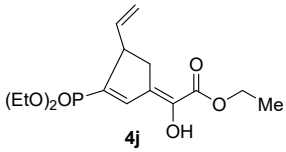


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.119	BV	0.3181	773.19763	32.43999	49.4703
2	7.118	VB	0.3781	789.75708	27.91505	50.5297

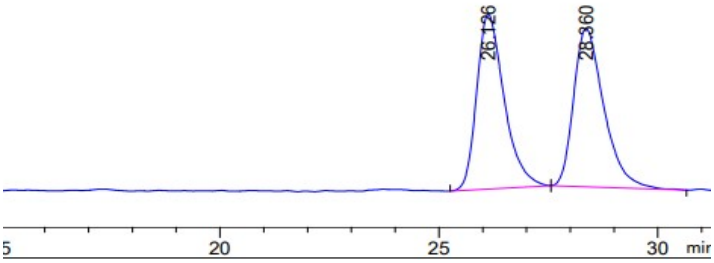


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.611	MM	0.4465	1266.36755	47.26876	73.9959
2	7.450	MM	0.4736	445.03372	15.66075	26.0041

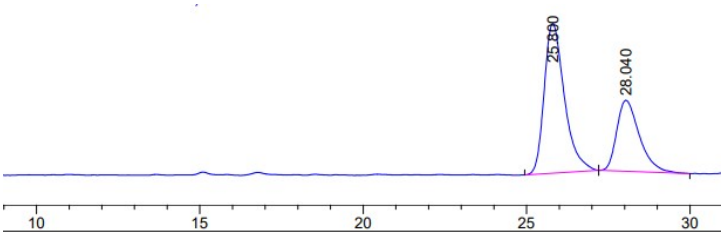
Chiral assay was conducted on Regis (R,R)-whelk-O1 column using IPA:nHex (10:90) as an eluent (1 mL/min).



4j



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.126	BB	0.6632	839.18909	19.22869	50.0409
2	28.360	BB	0.7152	837.81689	17.41827	49.9591



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.800	BB	0.6516	899.08569	20.91094	65.2566
2	28.040	BB	0.7150	478.68472	9.91924	34.7434