Supporting Information

Design of a Brønsted Acid with Two Different Acidic Sites: Synthesis and Application of Aryl Phosphinic Acid-Phosphoric Acid as a Brønsted Acid Catalyst

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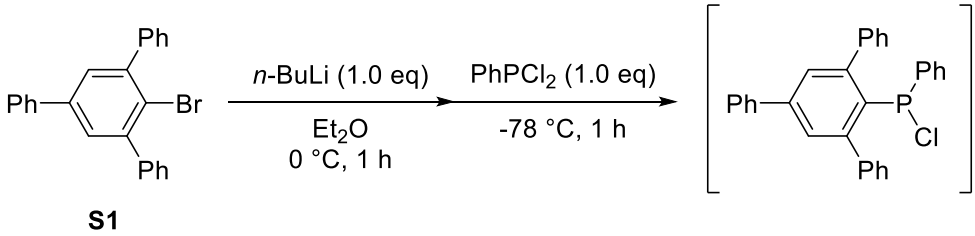
1. General information

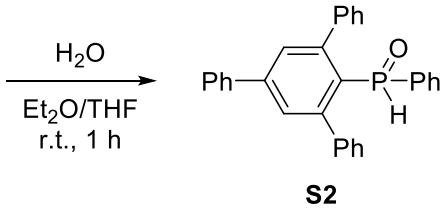
General Information: ^{1}H NMR spectra were recorded on a JEOL ECA-600 (600.2 MHz) spectrometer. Chemical shifts are reported in ppm from the solvent resonance or tetramethylsilane (TMS) as the internal standard ($CDCl_3$: 7.26 ppm referenced to TMS, DMSO-d_6: 2.49 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), and coupling constants (Hz). ^{13}C NMR spectra were recorded on a JEOL ECA-600 (150.9 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard ($CDCl_3$: 77.0 ppm, DMSO-d_6: 39.52 ppm). ^{31}P NMR spectra were recorded on JEOL ECA-600 (243.0 MHz) spectrometer. Infrared spectra were recorded on a Jasco FT/IR-4100 spectrometer in ATR mode. Flash column chromatography was performed on silica gel 60 N (Merck: 0.040-0.063 mm, 230-400 mesh ASTM). High resolution mass spectra analysis was performed on a Bruker Daltonics solariX 9.4T FT-ICR-MS spectrometer at the Instrumental Analysis Center for Chemistry, Graduate School of Science, Tohoku University or a JEOL JMS-777V at Institute for Molecular Science. Melting points were determined using a Yanaco micro melting point apparatus MP-J3 and are uncorrected.

Unless otherwise noted, all reactions were carried out under an atmosphere of standard grade nitrogen gas (oxygen <10 ppm) in flame-dried glassware with magnetic stirring. All substrates were purified by column chromatography or distillation prior to use. Dichloromethane (CH_2Cl_2), diethyl ether (Et_2O), toluene and tetrahydrofuran (THF) were supplied from Kanto Chemical Co., Inc. as “Dehydrated solvent system”. Other solvents were supplied from Wako Pure Chemical Industries Ltd. as dehydrated solvents. Reagents were purchased from commercial suppliers and used without further purification. The other simple chemicals were used as such.

2. Synthesis of aryl phosphinic acid-phosphoric acid

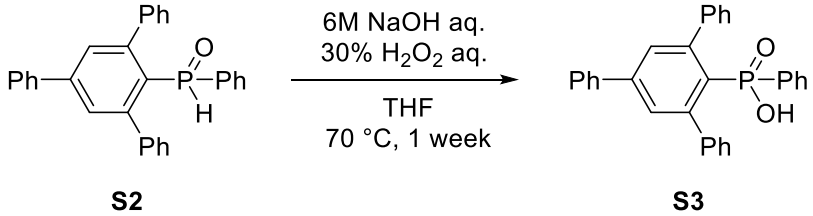
2-1. Synthesis of model aryl phosphinic acid based on reported protocol.[1,2]





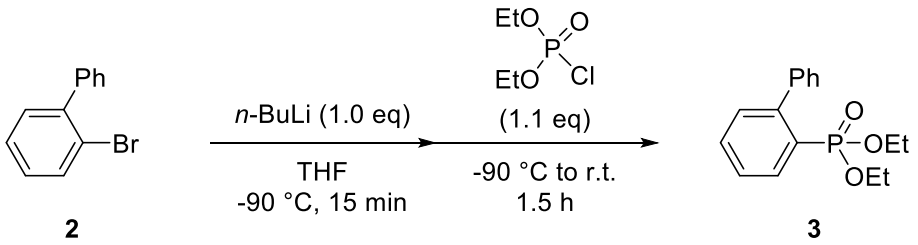
A flame-dried 30-mL two-neck round-bottomed flask equipped with a teflon-coated magnetic stirring bar and rubber septum was charged with **S1** (194.2 mg, 0.5 mmol). The flask was evacuated then backfilled with nitrogen. After Et_2O (2.0 mL) was added to the flask, the flask was cooled to 0 °C. To the solution was added *n*-BuLi (1.65 M in *n*-hexane, 0.33 mL, 0.55 mmol) dropwise at 0 °C and stirred at this temperature for 1 h. Then, dichlorophenylphosphine (68 μL, 0.5 mmol) was added to this solution at -78 °C and stirred for 1 h at the same temperature. After the reaction was warmed to room temperature, THF (5.0 mL) was added to this reaction mixture.

To the reaction mixture was added water (2.0 mL) and stirred for 1 h at room temperature. The product was extracted with CH_2Cl_2 (10 mL×3). The combined extracts were washed with water (5 mL), dried over Na_2SO_4, and concentrated under reduced pressure after filtration. The residual crude was chromatographed on silica gel using a mixture of hexane and EtOAc (4:1-1:1) to give **S2** (72% yield, 2 steps, 154.7 mg) as a white powder.

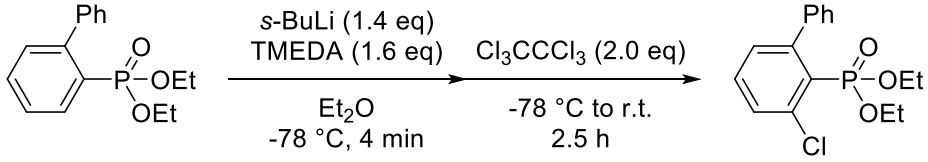


To a solution of **S2** (193.7 mg, 0.45 mmol) in THF (0.5 mL) was added 6M NaOH solution (2.0 mL) and 30% H_2O_2 aq. (0.6 mL) at room temperature. The reaction mixture was stirred at 70 °C for 1 week. After cooling to room temperature, 6 M HCl aq. (5.0 mL) was added. The precipitation was filtrated and washed with CH_2Cl_2 (1.0 mL×3) to give **S3** (13% yield, 25.7 mg) as a pale yellow powder.

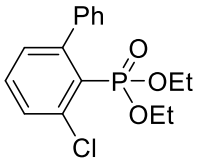
2-2. Synthesis of aryl phosphinic acid based on new synthetic route.



A flame-dried 100-mL two-neck round-bottomed flask equipped with a teflon-coated magnetic stirring bar and rubber septum was charged with **2** (1.67 mL, 10 mmol). The flask was evacuated then backfilled with nitrogen. After THF (30 mL) was added to the flask, the flask was cooled to -90 °C. To the solution was added *n*-BuLi (1.55 M in *n*-hexane, 6.45 mL, 10 mmol) dropwise and stirred at this temperature for 15 min. Then, diethyl chlorophosphate (1.59 mL, 11 mmol) was quickly added to this solution and stirred for 30 min at the same temperature. After the reaction was warmed to room temperature, the reaction was quenched with saturated NH_4Cl aq. (20 mL) and extracted with EtOAc (20mL ×3). The combined extracts were washed with brine (10 mL), dried over Na_2SO_4, and concentrated under reduced pressure after filtration. The residual crude was purified by silica gel column chromatography (hexane:EtOAc 4:1- EtOAc only) to give the product (90% yield, 2.60 g) as a colorless oil. Spectra data of **3** were in agreement with reported data[3].



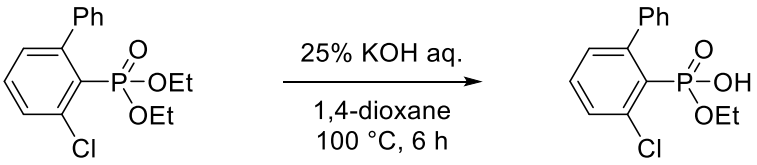
A flame-dried 200-mL three-neck round-bottom flask equipped with a teflon-coated magnetic stirring bar and rubber septum was charged with **3** (2.60 g, 9.0 mmol). The flask was evacuated then backfilled with nitrogen. After Et_2O (30 mL) and TMEDA (2.17 mL, 14.4 mmol) was added to the flask, the flask was cooled to -78 °C. To the solution was added *s*-BuLi (1.02 M in cyclohexane, 12.35 mL, 12.6 mmol) at -78 °C. After being stirred for 4 min, hexachloroethane (4.26 g, 18 mmol) was added at -78 °C in one portion and the resulting solution was stirred for further 30 min at the same temperature. After the reaction was warmed to room temperature, the reaction was quenched with saturated NH_4Cl aq. (20 mL) and extracted with EtOAc (20 mL×3). The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure after filtration. The residual crude product was purified by column chromatography on silica gel (hexane:EtOAc 4:1-2:1 as eluent) to afford the product (76% yield, 2.214 g) as a white solid.



4

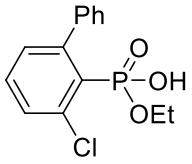
diethyl (3-chloro-[1,1'-biphenyl]-2-yl)phosphonate (4)

White solid; mp: 64-67 °C; TLC Rf = 0.37 (hexane:EtOAc 1:1); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.47 (ddd, 1H, J = 7.8, 4.8, 0.6 Hz), 7.33-7.40 (m, 6H), 7.18 (ddd, 1H, J = 7.8, 4.8, 1.2 Hz), 3.93-4.00 (m, 2H), 3.72-3.79 (m, 2H), 1.10 (t, 6H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 150.9 Hz) δ 149.2 (d, $J_{C\text{-}P}$ = 7.2 Hz), 142.5 (d, $J_{C\text{-}P}$ = 4.4 Hz), 138.5 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.6, 130.3 (d, $J_{C\text{-}P}$ = 14.3 Hz), 130.1 (d, $J_{C\text{-}P}$ = 10.1 Hz), 128.8 (2C), 127.6 (2C), 127.3, 126.2 (d, $J_{C\text{-}P}$ = 192.1 Hz), 61.9 (d, 2C, $J_{C\text{-}P}$ = 7.2 Hz), 15.9 (d, 2C, $J_{C\text{-}P}$ = 5.7 Hz); ^{31}P NMR ($CDCl_3$, 243.0 MHz) δ 14.08; IR (ATR) 3060, 3030, 2982, 2930, 2908, 1577, 1552, 1494, 1477, 1438, 1391, 1367, 1249, 1187, 1163, 1146, 1130, 1060, 1023, 971 cm^{-1}; HRMS (ESI) Exact Mass Calcd for $C_{16}H_{19}ClO_3P$ $(M+H)^+$: 325.0755, Found: 325.0755.



4 **5**

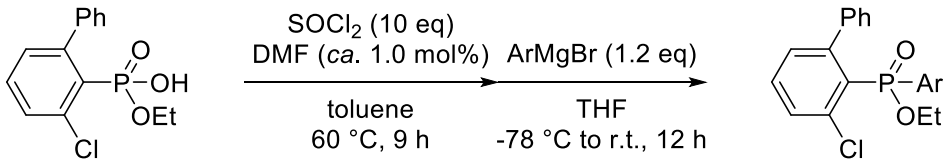
To a solution of **4** (5.918 g, 18 mmol) in 1,4-dioxane (18 mL) was added aqueous 25% KOH solution (2 mL) at room temperature. The reaction mixture was stirred at 100 °C for 6 h. After cooling to room temperature, 6 M HCl aq. (10 mL) was added. Then, aqueous layer was extracted with CH_2Cl_2 (30 mLx3), and the combined extracts were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure after filtration. The residual crude product was chromatographed on silica gel (dichloromethane: methanol 20:1-4:1 as eluent) to afford **5** as a white solid (98% yield, 5.276 g).



5

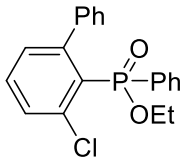
ethyl hydrogen (3-chloro-[1,1'-biphenyl]-2-yl)phosphonate (5)

White solid; mp: 153-155 °C; TLC Rf = 0.46 (dichloromethane:methanol 4:1); ^{1}H NMR (DMSO-d_6, 600 MHz) δ 12.11 (br, 1H), 7.49-7.54 (m, 2H), 7.30-7.37 (m, 5H), 7.19 (ddd, 1H, J = 7.2, 4.2, 1.2 Hz), 3.51-3.56 (m, 2H), 0.84 (t, 3H, J = 7.2 Hz); ^{13}C NMR (DMSO-d_6, 150.9 Hz) δ 148.2 (d, $J_{C\text{-}P}$ = 7.2 Hz), 142.5 (d, $J_{C\text{-}P}$ = 4.2 Hz), 137.1, 131.7, 130.5 (d, $J_{C\text{-}P}$ = 11.5 Hz), 129.9 (d, $J_{C\text{-}P}$ = 8.8 Hz), 128.7 (2C), 128.3 (d, $J_{C\text{-}P}$ = 185.0 Hz), 127.4 (2C), 127.0, 60.1 (d, $J_{C\text{-}P}$ = 5.7 Hz), 15.7 (d, $J_{C\text{-}P}$ = 7.2 Hz); ^{31}P NMR (DMSO-d_6, 243.0 MHz) δ 10.26; IR (ATR) 3057, 3028, 2982, 2930, 2906, 1577, 1552, 1496, 1438, 1392, 1210, 1188, 1132, 1100, 1041, 992, 958 cm^{-1}; HRMS (ESI) Exact Mass Calcd for $C_{14}H_{15}ClO_3P$ $(M+H)^+$: 297.0442, Found: 297.0442.



5 **6**

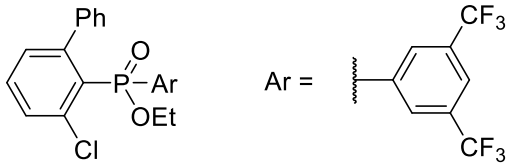
To a mixture of **5** (2.908 g, 9.8 mmol) and *N, N*-dimethylformamide (10 μL) in toluene (10 mL) was added thionyl chloride (7.2 mL, 98 mmol) at room temperature. The mixture was heated to 60 °C, and stirred at this temperature for 9 h. Then, volatiles were removed *in vacuo*, and residues were used without purification. To the solution of residues in THF (30 mL) was added phenyl magnesium bromide (1.1 M in THF, 9.8 mL, 10.8 mmol) at -78 °C. After being stirred for 30 min at this temperature, the reaction mixture was allowed to warm to room temperature and stirred for 12 h. The resulting mixture was cooled in an ice bath and quenched with saturated NH_4Cl aq. (30 mL). The product was extracted with EtOAc (30 mLx3) and combined organic layer was washed with water (10 mL) and brine (10 mL). The combined extracts were dried over Na_2SO_4 and concentrated under reduced pressure after filtration. The crude product was purified by silica gel column chromatography (ethyl acetate:hexane 1:3-1:1 as eluent) to afford **6a** (96% yield, 3.373 g).



6a

ethyl (3-chloro-[1,1'-biphenyl]-2-yl)(phenyl)phosphinate (6a)

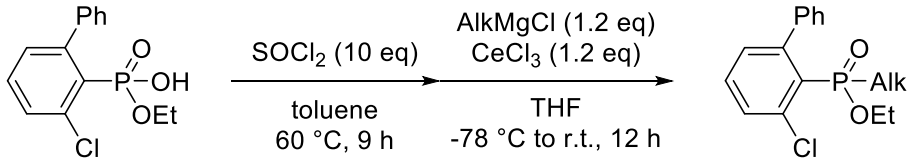
9.8 mmol scale, 96% yield, 3.373 g; white solid; mp: 132-133 °C; TLC Rf = 0.39 (hexane:EtOAc 1:1); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.62-7.65 (m, 2H), 7.43-7.46 (m, 1H), 7.30-7.42 (m, 9H), 7.21 (ddd, 1H, J = 7.2, 3.6, 1.8 Hz), 3.56-3.61 (m, 2H), 0.77 (t, 3H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 150.9 Hz) δ 149.6 (d, $J_{C\text{-}P}$ = 5.7 Hz), 142.5 (d, $J_{C\text{-}P}$ = 2.9 Hz), 138.5 (d, $J_{C\text{-}P}$ = 5.7 Hz), 133.4 (d, $J_{C\text{-}P}$ = 138.7 Hz), 131.7, 131.5 (2C), 131.4, 130.5 (d, $J_{C\text{-}P}$ = 11.6 Hz), 130.1 (d, $J_{C\text{-}P}$ = 8.6 Hz), 129.6 (br), 128.7 (d, $J_{C\text{-}P}$ = 138.7 Hz), 128.0 (d, $J_{C\text{-}P}$ = 14.5 Hz, 2C), 127.5 (br), 127.1, 60.2 (d, $J_{C\text{-}P}$ = 5.7 Hz), 15.5 (d, $J_{C\text{-}P}$ = 7.2 Hz), two peaks for aromatic carbon were not found probably due to overlapping; ^{31}P NMR ($CDCl_3$, 243.0 MHz) δ 30.0; IR (ATR) 3056, 3025, 2981, 2937, 2899, 1576, 1551, 1438, 1392, 1228, 1186, 1159, 1143, 1129, 1115, 1097, 1049, 1033, 998, 958 cm^{-1}; HRMS (ESI) Exact Mass Calcd for $C_{20}H_{18}ClNaO_2P$ $(M+Na)^+$: 379.0625, Found: 379.0625.



6b

ethyl (3,5-bis(trifluoromethyl)phenyl)(3-chloro-[1,1'-biphenyl]-2-yl)phosphinate (6b)

1.0 mmol scale, 76% yield, 361.2 mg; colorless oil; TLC Rf = 0.46 (hexane:EtOAc 2:1); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.92 (d, 2H, J = 12.0 Hz), 7.83 (s, 1H), 7.45-7.50 (m, 2H), 7.30-7.33 (brm, 2H), 7.23 (t, 1H, J = 7.2 Hz), 7.18-7.20 (m, 1H), 7.12 (br, 1H), 6.99 (br, 1H) 3.73-3.90 (m, 2H), 0.99 (t, 3H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 150.9 Hz) δ 149.4 (d, $J_{C\text{-}P}$ = 10.1 Hz), 141.2 (d, $J_{C\text{-}P}$ = 4.3 Hz), 138.4 (d, $J_{C\text{-}P}$ = 2.9 Hz), 137.2 (d, $J_{C\text{-}P}$ = 137.2 Hz), 132.5, 131.5 (br), 131.3 (dq, $J_{C\text{-}P}$, $J_{C\text{-}F}$ = 33.3, 14.5 Hz), 130.5$_4$ (d, $J_{C\text{-}P}$ = 11.5 Hz), 130.4$_8$ (d, $J_{C\text{-}P}$ = 8.8 Hz), 129.5, 129.0, 127.9$_5$, 127.9$_0$ (2C), 127.6 (d, $J_{C\text{-}P}$ = 145.9 Hz), 124.9 (d, $J_{C\text{-}P}$ = 2.9 Hz), 122.8 (q, 2C, $J_{C\text{-}F}$ = 273.1 Hz), 61.5 (d, $J_{C\text{-}P}$ = 5.8 Hz), 15.7 (d, $J_{C\text{-}P}$ = 7.2 Hz), one peak for aromatic carbon was not found probably due to overlapping; ^{31}P NMR ($CDCl_3$, 243.0 MHz) δ 26.52; ^{19}F NMR ($CDCl_3$, 564.7 MHz) δ -62.84 (s); IR (ATR) 3059, 3030, 2984, 2933, 2903, 1620, 1577, 1552, 1438, 1393, 1362, 1276, 1238, 1183, 1127, 1027, 959, 903, 843, 836 cm^{-1}; HRMS (ESI) Exact Mass Calcd for $C_{22}H_{16}ClNaF_6O_2P$ $(M+Na)^+$: 515.0373, Found: 515.0372.

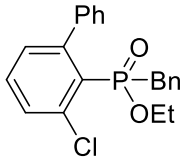


5 **6**

Alk: alkyl group

To a solution of **5** (296.7 mg, 1.0 mmol) in toluene (1.0 mL) was added thionyl chloride (0.72 mL, 10 mmol) at room temperature. The mixture was heated to 60 °C, and stirred at this temperature for 9 h. Then, volatiles were removed *in vacuo*, and residues were used without purification. To the solution of residues in THF (5.0 mL) was added freshly prepared $CeCl_3$-AlkMgCl reagent (Preparation method was shown below) at –78 °C. After being stirred at –78 °C for 30 min, the reaction mixture was allowed to warm to room temperature and stirred for 12 h. The resulting mixture was cooled in an ice bath and quenched with saturated NH_4Cl aq. (10 mL). The product was extracted with EtOAc (10 mL x3) and combined organic layer was washed with water (10 mL) and brine (10 mL). The combined extracts were dried over Na_2SO_4 and concentrated under reduced pressure after filtration. The crude product was purified by silica gel column chromatography (hexane:EtOAc 4:1-2:1) to afford **6c** (80% yield, 296.8 mg).

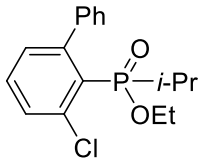
Preparation of $CeCl_3$-AlkMgCl reagent.[4] A flame dried flask equipped with a magnetic stirring bar and rubber septum was charged with $CeCl_3 \cdot 7H_2O$ (447.1 mg, 1.2 mmol) and evacuated to <0.1 mmHg. After gradual warming to 100 °C over 1 h, the flask was heated at 100 °C/<0.1 mmHg for 2 h with intermittent shaking, provided cerium(III) chloride monohydrate ($CeCl_3 \cdot H_2O$). Then, the cerium(III) chloride monohydrate was gradually warmed to 150 °C over 30 min under reduced pressure (<0.1 mmHg) without stirring. Heating at 150 °C/<0.1 mmHg for 3 h with gentle stirring afforded a fine, white powder of anhydrous cerium(III) chloride. After introduction of nitrogen into the flask, the resulting anhydrous cerium(III) chloride was cooled to room temperature. To this anhydrous cerium(III) chloride was added THF (5.0 mL) at 0 °C. After being stirred at room temperature for 2 h, the mixture was cooled to -40 °C. To this solution was added THF solution of AlkMgCl (1.2 eq) at -40 °C. After being stirred at this temperature for 2 h, the mixture was cooled to -78 °C.



6c

ethyl benzyl(3-chloro-[1,1'-biphenyl]-2-yl)phosphinate (6c)

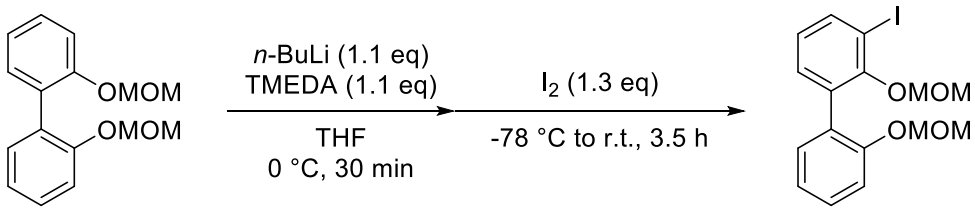
1.0 mmol scale, 80% yield, 296.8 mg; colorless oil; TLC Rf = 0.59 (hexane:EtOAc 1:1); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.48 (ddd, 1H, *J* = 7.8, 4.8, 1.2 Hz), 7.40 (dt, 1H, *J* = 7.8, 1.2 Hz), 7.27-7.38 (m, 8H), 7.23-7.25 (m, 2H), 7.19 (ddd, 1H, *J* = 7.8, 4.2, 1.2 Hz), 5.01 (dd, 1H, *J* = 11.4, 8.4 Hz), 4.60 (dd, 1H, *J* = 11.4, 9.6 Hz), 3.76-3.82 (m, 1H), 3.62-3.68 (m, 1H), 0.96 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 150.9 Hz) δ 149.2 (d, $J_{C\text{-}P}$ = 7.2 Hz), 142.4 (d, $J_{C\text{-}P}$ = 2.9 Hz), 138.4 (d, $J_{C\text{-}P}$ = 4.2 Hz), 136.2 (d, $J_{C\text{-}P}$ = 5.7 Hz), 131.7, 130.3 (d, $J_{C\text{-}P}$ = 13.0 Hz), 130.1 (d, $J_{C\text{-}P}$ = 10.1 Hz), 128.7 (2C), 128.3 (2C), 128.1, 128.0 (2C), 127.6 (2C), 127.3, 126.1 (d, $J_{C\text{-}P}$ = 192.2 Hz), 67.4 (d, $J_{C\text{-}P}$ = 5.9 Hz), 61.9 (d, $J_{C\text{-}P}$ = 5.7 Hz), 15.7 (d, $J_{C\text{-}P}$ = 5.7 Hz); ^{31}P NMR ($CDCl_3$, 243.0 MHz) δ 14.54; IR (ATR) 3467, 3059, 3029, 2980, 2935, 2903, 1951, 1879, 1812, 1576, 1552, 1496, 1438, 1250, 1187, 1130, 1055, 998, 965 cm^{-1}; HRMS (ESI) Exact Mass Calcd for $C_{21}H_{20}ClKO_2P$ $(M+K)^+$: 409.0521, Found: 409.0730.



6d

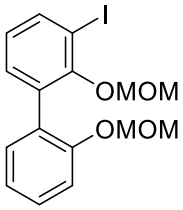
ethyl (3-chloro-[1,1'-biphenyl]-2-yl)(isopropyl)phosphinate (6d)

1.0 mmol scale, 45% yield, 144.8 mg; colorless oil; TLC Rf = 0.40 (hexane:EtOAc 1:1); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.46 (ddd, 1H, *J* = 7.8, 4.8, 1.2 Hz), 7.33-7.39 (m, 6H), 7.17 (ddd, 1H, *J* = 7.2, 4.8, 1.2 Hz), 4.63-4.70 (m, 1H), 3.92-3.99 (m, 1H), 3.66-3.73 (m, 1H), 1.22 (d, 3H, *J* = 6.0 Hz), 1.15 (d, 3H, *J* = 6.0 Hz), 1.06 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 150.9 Hz) δ 149.1 (d, $J_{C\text{-}P}$ = 7.1 Hz), 142.6 (d, $J_{C\text{-}P}$ = 2.9 Hz), 138.5 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.5, 130.3 (d, $J_{C\text{-}P}$ = 13.0 Hz), 130.1 (d, $J_{C\text{-}P}$ = 10.1 Hz), 129.0 (br), 127.4 (br), 127.2, 126.7 (d, $J_{C\text{-}P}$ = 190.7 Hz), 71.0 (d, $J_{C\text{-}P}$ = 5.9 Hz), 61.8 (d, $J_{C\text{-}P}$ = 7.2 Hz), 23.8 (d, $J_{C\text{-}P}$ = 2.9 Hz), 23.5 (d, $J_{C\text{-}P}$ = 5.7 Hz), 15.9 (d, $J_{C\text{-}P}$ = 7.2 Hz); ^{31}P NMR ($CDCl_3$, 243.0 MHz) δ 12.83; IR (ATR) 3058, 3027, 2979, 2933, 1576, 1552, 1495, 1467, 1437, 1386, 1374, 1250, 1186, 1145, 1130, 1105, 1052, 1039, 1039, 1022, 984, 890 cm^{-1}; HRMS (ESI) Exact Mass Calcd for $C_{17}H_{20}ClKO_2P$ $(M+K)^+$: 361.0521, Found: 361.0730.



S4 **S5**

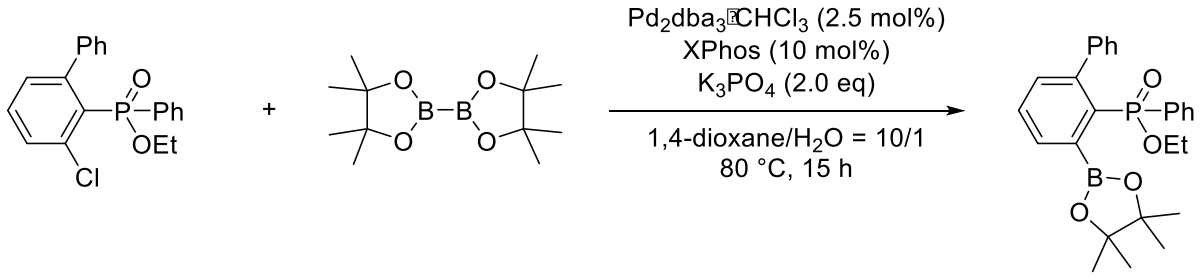
To a solution of **S4** (2.74 g, 10 mmol) in THF (30 mL) was added TMEDA (1.66 mL, 11 mmol) and *n*-BuLi (6.75 mL, 11 mmol) at 0 °C in this order. After being stirred for 30 min at this temperature, the reaction mixture was cooled to -78 °C and solid iodine (3.3 g, 13 mmol) was added. The mixture was stirred for 30 min at this temperature, and warmed to room temperature, and stirred for 3h at this temperature. Then, the reaction mixture was quenched with saturated Na_2SO_3 aq. (20 mL). The aqueous layer was extracted with EtOAc (20 mLx3) and combined organic layer was washed with water (20 mL) and brine (20 mL). The combined extracts were dried over Na_2SO_4 and concentrated under reduced pressure after filtration. The crude product was purified by silica gel column chromatography (hexane:EtOAc 50:1-10:1 as eluent) to afford product (76% yield, 3.04 g) as a white waxy solid.



S5

3-iodo-2,2'-bis(methoxymethoxy)-1,1'-biphenyl (S5)

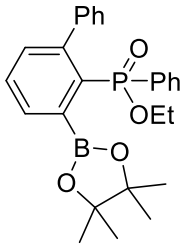
White waxy solid; mp: 48-49 °C; TLC Rf = 0.67 (hexane:EtOAc 4:1); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.81 (dd, 1H, *J* = 8.4, 1.2 Hz), 7.31 (dt, 1H, *J* = 7.8, 1.2 Hz), 7.27-7.29 (m, 2H), 7.19 (d, 1H, *J* = 8.4 Hz), 7.06 (dt, 1H, *J* = 7.2, 0.6 Hz), 6.90 (t, 1H, *J* = 7.2 Hz), 5.11 (s, 2H) 4.71 (s, 2H), 3.37 (s, 3H), 3.05 (s, 3H); ^{13}C NMR ($CDCl_3$, 150.9 Hz) δ 154.6, 154.5, 138.7, 133.5, 132.1, 131.5, 129.1, 128.5, 125.6, 121.7, 115.2, 99.3, 94.8, 92.7, 57.2, 56.0; IR (ATR) 3059, 2955, 2903, 2825, 1601, 1582, 1557, 1496, 1456, 1442, 1426, 1393, 1309, 1272, 1229, 1199, 1153, 1114, 1079, 995, 948 cm^{-1}; HRMS (ESI) Exact Mass Calcd for $C_{16}H_{17}INaO_4$ $(M+Na)^+$: 423.0064, Found: 423.0064.



6a **7a**

To a mixture of **6a** (356.8 mg, 1.0 mmol), bis(pinacolato)diboron (355.5 mg, 1.4 mmol), XPhos (47.7 mg, 0.1 mmol) and K_3PO_4 (424.5 mg, 2.0 mmol) under nitrogen atmosphere was added 1,4-dioxane (5.0 mL), H_2O (0.5 mL) and $Pd_2dba_3 \cdot CHCl_3$ (25.9 mg, 0.025 mmol). After evacuated and refilled with nitrogen twice, the reaction mixture was warmed to 80 °C and stirred for 15 h. After the resulting mixture was cooled to room temperature, the residue was filtrated through a pad of Celite. The filtrate was diluted with EtOAc (30 mL), and washed with water (10 mL) and brine (10 mL), and dried over Na_2SO_4. The combined organic layer was concentrated under reduced pressure after filtration. The crude product was

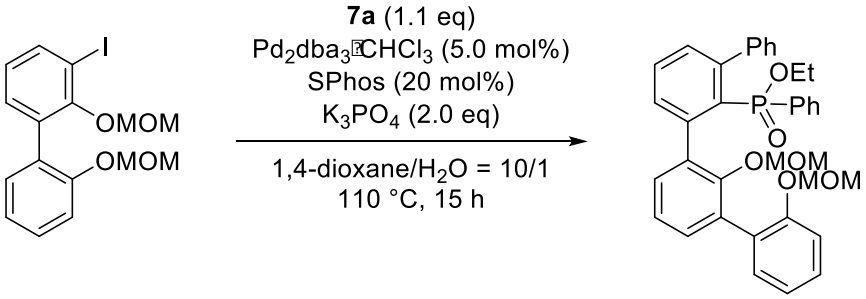
purified by silica gel column chromatography (hexane:EtOAc 4:1-1:1 as eluent) to give **7a** as a semi-solid (82% yield, 367.2 mg).



7a

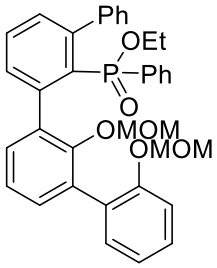
ethyl phenyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[1,1'-biphenyl]-2-yl)phosphinate (7a)

Semi-solid; TLC Rf = 0.45 (hexane:EtOAc 1:1); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.73 (ddd, 1H, *J* = 7.8, 1.8, 1.2 Hz), 7.57 (dt, 1H, *J* = 7.8, 1.2 Hz), 7.40 (t, 1H, *J* = 7.8 Hz), 7.29-7.33 (m, 2H), 7.27 (t, 1H, *J* = 7.2 Hz), 7.13-7.21 (m, 5H), 6.88-6.89 (m, 2H), 4.28-4.34 (m, 1H), 3.98-4.04 (m, 1H), 1.40 (a pair of singlet, 12H), 1.35 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 150.9 Hz) δ 144.0 (d, $J_{C\text{-}P}$ = 13.0 Hz), 140.2 (d, $J_{C\text{-}P}$ = 4.4 Hz), 132.9, 132.5 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.9 (d, 2C, $J_{C\text{-}P}$ = 11.6 Hz), 130.2, 130.1, 129.5 (d, $J_{C\text{-}P}$ = 11.6 Hz), 129.1 (d, $J_{C\text{-}P}$ = 122.8 Hz), 129.0 (2C), 127.9 (d, 2C, $J_{C\text{-}P}$ = 14.5 Hz), 127.7 (d, $J_{C\text{-}P}$ = 147.7 Hz), 127.6 (2C), 127.4, 81.3 (2C), 62.9 (d, $J_{C\text{-}P}$ = 5.9 Hz), 25.6 (2C), 25.4 (2C), 16.0 (d, $J_{C\text{-}P}$ = 7.2 Hz); ^{31}P NMR ($CDCl_3$, 243.0 MHz) δ 46.85; IR (ATR) 3054, 2972, 2928, 1593, 1570, 1479, 1455, 1440, 1384, 1372, 1362, 1336, 1300, 1232, 1147, 1122, 1090, 1038, 1019, 963, 874 cm^{-1}; HRMS (ESI) Exact Mass Calcd for $C_{26}H_{30}BNaO_4P$ $(M+Na)^+$: 471.1867, Found: 471.1867.



S5 **S6**

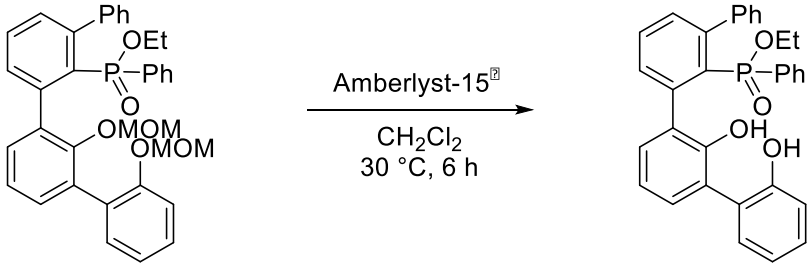
To a mixture of **S5** (333.2 mg, 0.83 mmol), **7a** (407.9 mg, 0.91 mmol), SPhos (68.1 mg, 0.17 mmol) and K_3PO_4 (352.4 mg, 1.66 mmol) under nitrogen atmosphere was added 1,4-dioxane (5.0 mL), H_2O (0.5 mL) and $Pd_2dba_3 \cdot CHCl_3$ (43.5 mg, 0.04 mmol). After evacuated and refilled with nitrogen twice, the reaction mixture was warmed to 110 °C and stirred for 15 h. After the resulting mixture was cooled to room temperature, the residue was filtrated through a pad of Celite. The filtrate was diluted with EtOAc (30 mL), and washed with water (10 mL) and brine (10 mL), and dried over Na_2SO_4. The combined organic layer was concentrated under reduced pressure after filtration. The crude product was used for the following reaction after short-path chromatography on silica gel. Analytical sample of **S6** was purified by column chromatography on silica gel (hexane:EtOAc 4:1-1:1).



S6

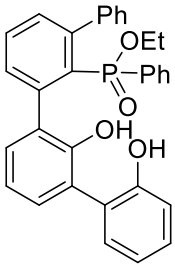
ethyl (2'',2'''-bis(methoxymethoxy)-[1,1':3',1'':3'',1'''-quaterphenyl]-2'-yl)(phenyl)phosphinate (S6)

White powder; mp: 51-54 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.65-7.70 (m, 2.40H, mixture of diastereomer), 7.48-7.52 (m, 1.15H, mixture of diastereomer), 7.45 (dd, 0.15H, *J* = 6.0, 3.6 Hz), 7.40 (d, 0.86H, *J* = 7.2 Hz), 7.27-7.34 (m, 3.00H, mixture of diastereomer), 7.19-7.25 (m, 2.42H, mixture of diastereomer), 6.95-7.16 (m, 8.42H, mixture of diastereomer), 6.81 (br, 0.86H), 6.50 (br, 0.85H), 5.14-5.20 (m, 2.06H, mixture of diastereomer), 4.72 (d, 0.86H, *J* = 5.4 Hz), 4.58 (d, 0.85H, *J* = 6.0 Hz), 4.24 (s, 0.24H), 3.41-3.42 (a pair of singlet, 3.05H, mixture of diastereomer), 3.21-3.39 (m, 2.05H, mixture of diastereomer), 2.72 (s, 2.54H), 2.71 (s, 0.45H), 0.58-0.63 (m, 3.00H, mixture of diastereomer); ^{13}C NMR ($CDCl_3$, 150.9 Hz) δ 154.9, 151.9, 150.9, 148.2, 148.1, 144.2, 144.1, 141.6, 141.5, 137.3, 134.0, 133.3, 133.2, 132.5, 131.9, 131.7, 131.6, 131.5, 131.4, 131.0, 130.9, 130.7, 130.6, 130.3, 130.2, 130.1, 130.0, 129.8, 128.6, 128.5, 128.4, 127.9, 127.4, 127.3, 127.2, 126.9, 126.8, 123.4, 122.9, 121.7, 115.4, 115.2, 98.3, 98.1, 94.9, 59.5, 59.4, 56.0, 55.9, 15.2, 15.1; ^{31}P NMR ($CDCl_3$, 243.0 MHz) δ 32.63, 31.75; IR (ATR) 3458, 3058, 3024, 2979, 2930, 2899, 2824, 1581, 1561, 1496, 1439, 1389, 1227, 1155, 1116, 1071, 1034, 998, 962, 858 cm^{-1}; HRMS (ESI) Exact Mass Calcd for $C_{36}H_{35}NaO_6P$ $(M+Na)^+$: 617.2063, Found: 617.2063.



S6 **8a**

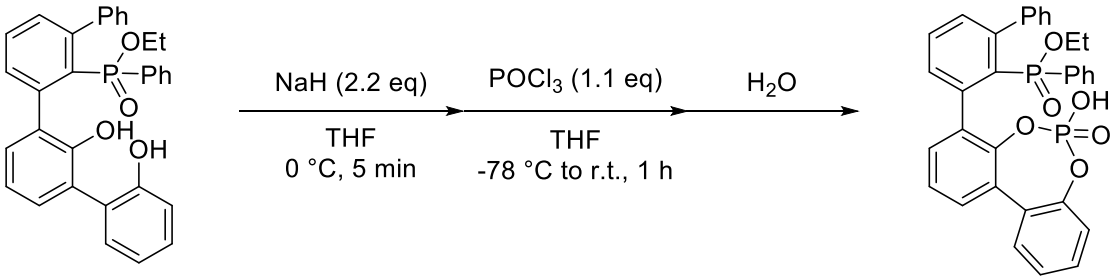
S6 was dissolved in CH_2Cl_2 (5.7 mL) and Amberlyst-15® (57 mg) was added at room temperature. The resulting mixture was stirred at 30 °C for 5 h. After filtration of the reaction mixture, the organic layer was concentrated under reduced pressure. The crude product was chromatographed on silica gel using a mixture of hexane and EtOAc (4:1-3:1) to give **8a** (57% yield, 2 steps, 237.8 mg) as a white powder.



8a

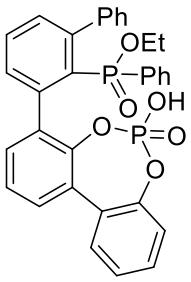
ethyl (2'',2'''-dihydroxy-[1,1':3',1'':3'',1'''-quaterphenyl]-2'-yl)(phenyl)phosphinate (8a)

White powder; mp: 87-89 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.91 (br, 0.28H), 7.75 (br, 0.28H), 7.62 (m, 1.03H, mixture of diastereomer), 7.55 (br, 0.75H), 7.35-7.50 (m, 4.97H, mixture of diastereomer), 7.27-7.32 (m, 3.35H, mixture of diastereomer), 7.22-7.25$_5$ (m, 1.09H, mixture of diastereomer), 6.99-7.20 (m, 8.04H, mixture of diastereomer), 6.92 (br, 0.25H), 6.88 (br, 0.23H), 6.56 (t, 0.75H, *J* = 7.8 Hz), 6.30 (dd, 0.73H, *J* = 7.8, 1.8 Hz), 3.19-3.39 (m, 2.00H, O*CH*$_2$CH$_3$, mixture of diastereomer), 0.60 (t, 0.74H, *J* = 7.2 Hz), 0.50 (t, 2.24H, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 150.9 Hz) δ 154.5, 154.1, 149.9, 149.1, 147.3$_3$, 147.2$_9$, 143.6, 143.5, 143.4$_1$, 143.3$_9$, 141.5, 134.3, 132.4, 132.2, 131.8, 131.6, 131.5, 131.4$_4$, 131.3$_6$, 131.2$_2$, 131.1$_6$, 131.1, 130.8, 130.7, 130.6, 130.5, 130.3, 129.9, 129.1$_4$, 129.0$_5$, 128.2, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.2, 127.0, 126.5, 122.3, 122.2, 120.7, 120.6, 118.1, 117.9, 60.4$_4$, 60.4$_1$, 60.3$_2$, 60.2$_8$, 15.2$_2$, 15.1$_7$, 15.0$_8$, 15.0$_3$; ^{31}P NMR ($CDCl_3$, 243.0 MHz) δ 37.64, 35.00 ; IR (ATR) 3237, 3056, 2979, 2930, 2898, 2862, 2718, 2591, 1601, 1583, 1564, 1508, 1457, 1438, 1390, 1291, 1231, 1182, 1132, 1114, 1071, 1033, 960, 843 cm^{-1}; HRMS (ESI) Exact Mass Calcd for $C_{32}H_{27}NaO_4P$ $(M+Na)^+$: 529.1539, Found: 529.1539.



8a **10a**

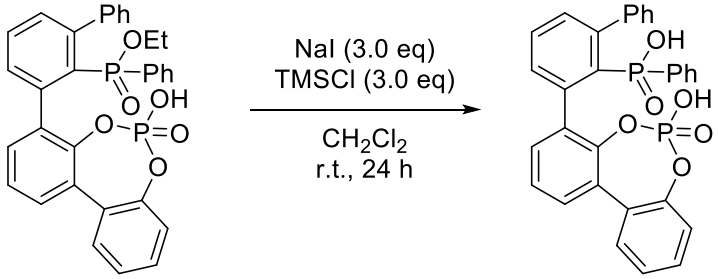
8a (152 mg, 0.3 mmol) was dissolved in THF (3.0 mL) and NaH (60% dispersion in mineral oil, 26.4 mg, 0.66 mmol) added at 0 °C. The resulting mixture was stirred at this temperature for 5 min, and then phosphoryl chloride (31 μL, 0.33 mmol) was added at -78 °C. The resulting mixture was stirred at this temperature for 5 min, and then warmed to room temperature. After being stirred for 6 h, the mixture was quenched with H_2O (1.0 mL) at 0 °C, acidified with 6 M HCl aq. (5.0 mL), and extracted with CH_2Cl_2 (10 mL×3). The combined organic extracts were concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (hexane:EtOAc 1:1 to EtOAc:MeOH 10:1-3:1 as eluent) to give the product as a white powder (89% yield, 152.1 mg).



10a

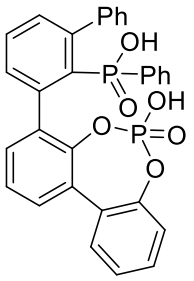
ethyl(3-(6-hydroxy-6-oxidodibenzo[d,f][1,3,2]dioxaphosphepin-4-yl)-[1,1'-biphenyl]-2-yl)(phenyl)phosphinate (10a)

White powder; mp: 170-173 °C; ^{1}H NMR (DMSO-d_6, 600 MHz) δ 7.87 (br, 0.44H,), 7.74 (br, 0.56H), 7.58-7.63 (m, 2.15H, mixture of diastereomer), 7.50 (m, 0.80H, mixture of diastereomer), 7.44-7.47 (m, 2.34H, mixture of diastereomer), 7.28-7.42 (m, 5.38H, mixture of diastereomer), 7.22 (m, 0.85H, mixture of diastereomer), 7.15-7.18 (m, 1.76H, mixture of diastereomer), 7.01-7.04 (m, 1.36H, mixture of diastereomer), 6.94-6.96 (m, 2.68H, mixture of diastereomer), 6.87-6.90 (m, 1.34H, mixture of diastereomer), 6.53 (br, 0.41H), 2.94-3.05 (m, 2.00H, O*CH*$_2$CH$_3$, mixture of diastereomer), 0.37-0.41 (m, 2.92H, OCH$_2$*CH*$_3$, mixture of diastereomer); ^{13}C NMR (DMSO-d_6, 150.9 Hz) δ 148.16, 148.11, 147.90, 147.84, 147.25, 147.21, 147.07, 146.98, 144.90, 144.84, 144.66, 144.61, 143.09, 143.07, 141.61, 141.58, 141.41, 141.33, 141.10, 141.06, 135.90, 133.84, 133.25, 133.01, 132.37, 132.23, 131.95, 131.71, 131.63, 131.53, 131.47, 131.17, 131.07, 130.87, 130.79, 130.74, 130.67, 130.56, 130.51, 130.40, 130.13, 130.08, 129.94, 129.69, 129.60, 129.49, 128.98, 128.60, 128.36, 127.42, 127.33, 127.18, 127.09, 126.91, 126.81, 125.92, 125.42, 124.51, 124.25, 121.44, 120.94, 58.87, 58.85, 14.98, 14.96, 14.93, 14.91; ^{31}P NMR (DMSO-d_6, 243.0 MHz) δ 32.49, 32.08, 1.57, 1.16; IR (ATR) 3417, 3057, 3026, 2982, 2925, 2898, 2854, 1722, 1565, 1494, 1458, 1439, 1429, 1394, 1288, 1265, 1196, 1159, 1133, 1115, 1075, 1023, 1011, 962, 916, 814, 801 cm^{-1}; HRMS (ESI) Exact Mass Calcd for $C_{32}H_{25}O_6P_2$ $(M-H)^-$: 567.1132, Found: 567.1131.



10a **11a**

To a solution of **10a** (152.1 mg, 0.27 mmol) in CH_2Cl_2 (2.7 mL) was added NaI (120.5 mg, 0.8 mmol) and TMSCl (102 μL, 0.8 mmol) at room temperature. The resulting mixture was stirred at this temperature for 24 h. The reaction mixture was diluted with water (2.0 mL) and acidified with 6 M HCl aq. (5.0 mL). The aqueous layer was extracted with CH_2Cl_2 (10 mL×5). The combined organic extracts were concentrated under reduced pressure. The crude product was purified by silica gel using a mixture of CH_2Cl_2 and MeOH (20:1-10:1). After evaporation of solvent, the residue was dissolved in EtOH (10 mL) and 12 M HCl aq. (2.0 mL) was added at room temperature. After being stirred for 1 h, the aqueous layer was extracted with CH_2Cl_2 (10 mL×3). The combined organic extracts were concentrated under reduced pressure. The residue was purified by Silica gel 60 extra pure (Catalogue No. 107754 Merck KgaA) column chromatography (hexane:Et_2O 4:1- Et_2O only) to give **11a** (51% yiled, 73.9 mg) as a pale yellow solid.



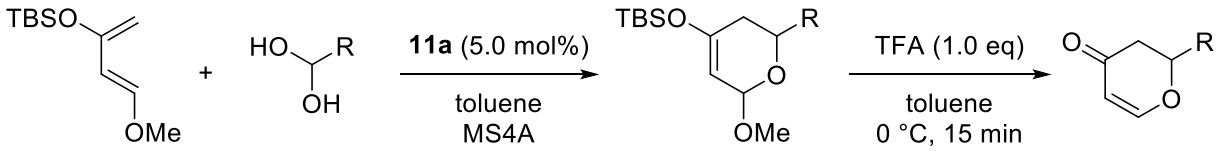
11a

(3-(6-hydroxy-6-oxidodibenzo[d,f][1,3,2]dioxaphosphepin-4-yl)-[1,1'-biphenyl]-2-yl)(phenyl)phosphinic acid (11a)

Pale yellow solid; mp: 233 °C (**11a** was decomposed at melting point.); ^{1}H NMR (DMSO-d_6, 600 MHz) δ 7.62 (d, 1H, *J* = 7.2 Hz), 7.53 (d, 1H, *J* = 7.2 Hz), 7.47 (m, 2H), 7.41 (dd, 1H *J* = 8.4, 7.2 Hz), 7.31 (m, 2H), 7.24 (d, 1H, *J* = 6.6 Hz), 7.06-7.10 (m, 8H), 6.90 (br, 4H); ^{13}C NMR (DMSO-d_6, 150.9 Hz) δ 150.12, 150.06, 146.83, 146.78, 145.47, 142.79, 142.76, 141.87, 137.94, 137.05, 136.51, 134.33, 133.50, 132.08, 130.83, 130.78, 130.61, 130.07, 130.03, 129.82, 129.26, 129.16, 128.47, 126.67, 126.58, 126.45, 124.38, 123.86, 121.40, 121.38; ^{31}P NMR (DMSO-d_6, 243.0 MHz) δ 22.82, 3.06; IR (ATR) 3054, 2972, 2928, 1593, 1570, 1479, 1455, 1440, 1384, 1372, 1362, 1336, 1300, 1232, 1147, 1122, 1090, 1038, 1019, 963, 874 cm^{-1}; HRMS (ESI) Exact Mass Calcd for $C_{30}H_{21}O_6P_2$ $(M-H)^-$: 539.0819, Found: 539.0817.

3. Aryl phosphinic acid-phosphoric acid catalyzed hetero Diels－Alder reaction

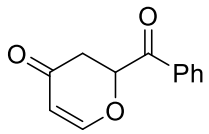
3-1. Procedure for **11a** catalyzed hetero Diels－Alder reaction.



12 (1.5 eq) **13** (1.0 eq) **14**

A dried test tube equipped with a teflon-coated magnetic stirring bar was charged with **11a** (5.0 mol%, 2.7 mg, 0.005 mmol), **13** (1.0 eq, 0.1 mmol) and MS4A (50 mg). Toluene (0.5 mL) was added at room temperature and the resulting mixture was cooled to the reaction temperature. And then, **12** (1.5 eq, 32.2 mg, 0.15 mmol) was added at the reaction temperature. After being stirred at this temperature for 24 or 48 h, the resulting mixture was directly charged on silica gel, and eluted with hexane/EtOAc (20/1-10/1). The obtained Diels-Alder product was dissolved in toluene (1.0 mL) and TFA (1.0 eq, 0.1 mmol, 7.7 μL) was added at 0 °C. The resulting mixture was stirred at this temperature for 15 min. The reaction mixture was quenched with sat. $NaHCO_3$ aq. (*ca*. 5.0 mL) and the aqueous layer was extracted with CH_2Cl_2 (10 mL×3). The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure after filtration. The residual crude product was chromatographed on silica gel using a mixture of hexane and EtOAc as eluent to give **14**.

3-2. Product data of hetero Diels－Alder reaction.

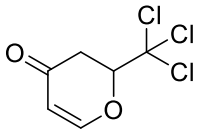


14a

The reaction was conducted at -20 °C for 48 h. Purification by silica gel column chromatography with elution by hexane:EtOAc (4:1-2:1) provided as a colorless oil.

2-benzoyl-2,3-dihydro-4H-pyran-4-one (14a)

82% yield, 16.6 mg; colorless oil; TLC Rf = 0.29 (hexane:EtOAc 2:1); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.97 (dd, 2H, *J* = 8.4, 1.2 Hz), 7.65 (ddd, 1H, *J* = 7.8, 1.8, 1.2 Hz), 7.52 (m, 2H), 7.41 (d, 1H, *J* = 6.0 Hz), 5.81 (dd, 1H, *J* = 11.4, 4.2 Hz), 5.51 (dd, 1H, *J* = 6.0, 1.2 Hz), 2.98 (dd, 1H, *J* = 17.4, 11.4 Hz) 2.82 (ddd, 1H, *J* = 17.4, 4.2, 1.2 Hz); ^{13}C NMR ($CDCl_3$, 150.9 Hz) δ 193.0, 190.0, 161.6, 134.3, 133.7, 129.0 (2C), 128.9 (2C), 107.9, 78.9, 38.0; IR (ATR) 3066, 2922, 2853, 1673, 1595, 1449, 1401, 1331, 1275, 1221, 1205, 1182, 1040, 1000, 957, 938, 859 cm^{-1}; HRMS (FAB) Exact Mass Calcd for $C_{12}H_{11}O_3$ $(M+H)^+$: 203.0703, Found: 203.0704.



14b

The reaction was conducted at 10 °C for 24 h. Purification by silica gel column chromatogwraphy with elution by hexane:EtOAc (5:1-3:1) provided as a white solid.

2-(trichloromethyl)-2,3-dihydro-4H-pyran-4-one (14b)

81% yield, 17.3 mg; white solid; mp: 105-107 °C; TLC Rf = 0.39 (hexane:EtOAc 4:1); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.45 (dd, 1H, *J* = 6.0, 2.4 Hz), 5.56 (m, 1H), 4.81 (ddd, 1H, *J* = 13.8, 3.6, 1.8 Hz), 2.92-3.04 (m, 2H); ^{13}C NMR ($CDCl_3$, 150.9 Hz) δ 189.3, 161.2, 107.8, 97.4, 86.1, 37.9; IR (ATR) 3074, 3061, 2924, 2633, 1687, 1663, 1595, 1403, 1340, 1279, 1259, 1181, 1109, 1060, 1042, 1004, 922, 863, 824, 807 cm^{-1}; HRMS (FAB) Exact Mass Calcd for $C_6H_6O_2$ $(M+H)^+$: 214.9428, Found: 214.9429.

References

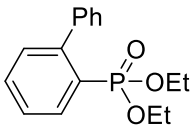
[1] E. Rivard, A. D. Sutton, J. C. Fettinger and P. P. Power, *Inorganica Chemica Acta*, *2007*, **360**, 1278.

[2] J. P. Abell and H. Yamamoto, *J. Am. Chem. Soc.*, *2009*, **131**, 15118.

[3] I. Bonnaventure and A. Charette, *J. Org. Chem.*, *2008*, **73**, 6330.

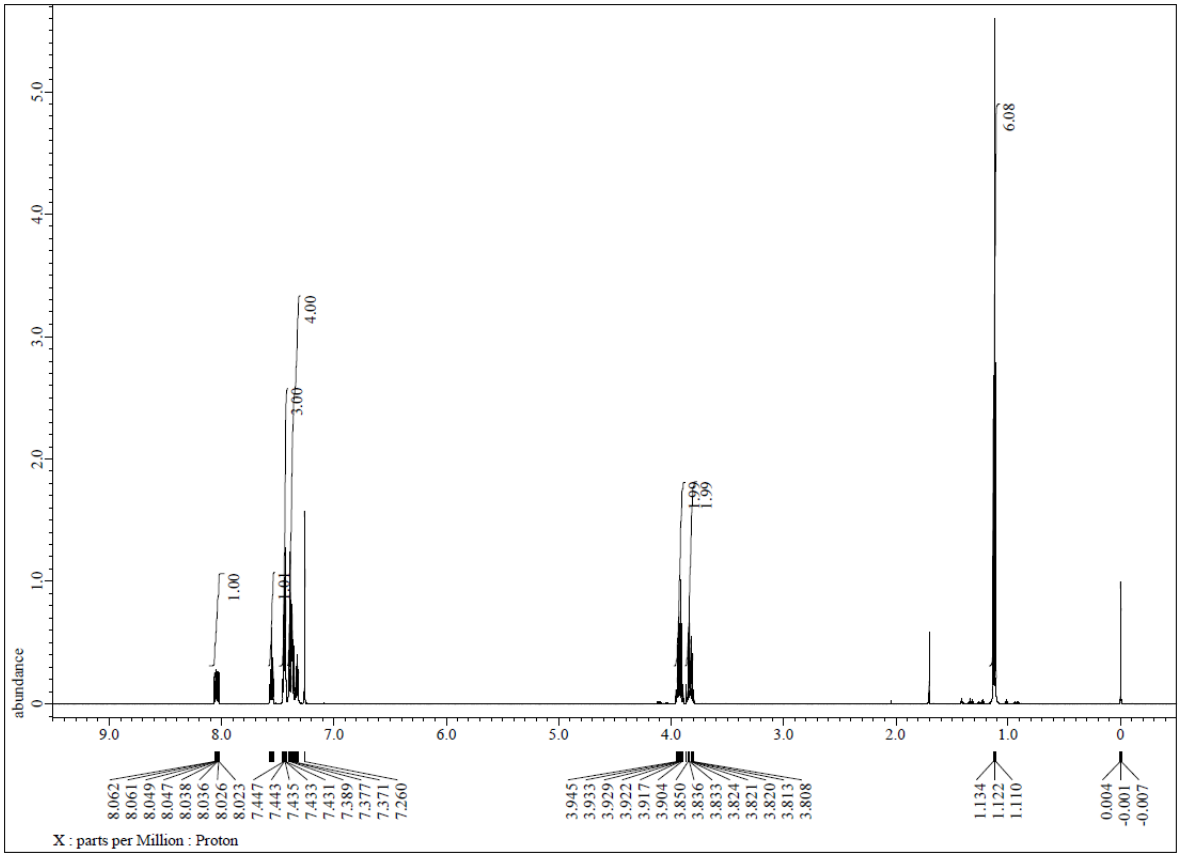
[4] N. Takeda and T. Imamoto, *Org. Synth.*, *1999*, **76**, 228.

4. Spectrum data

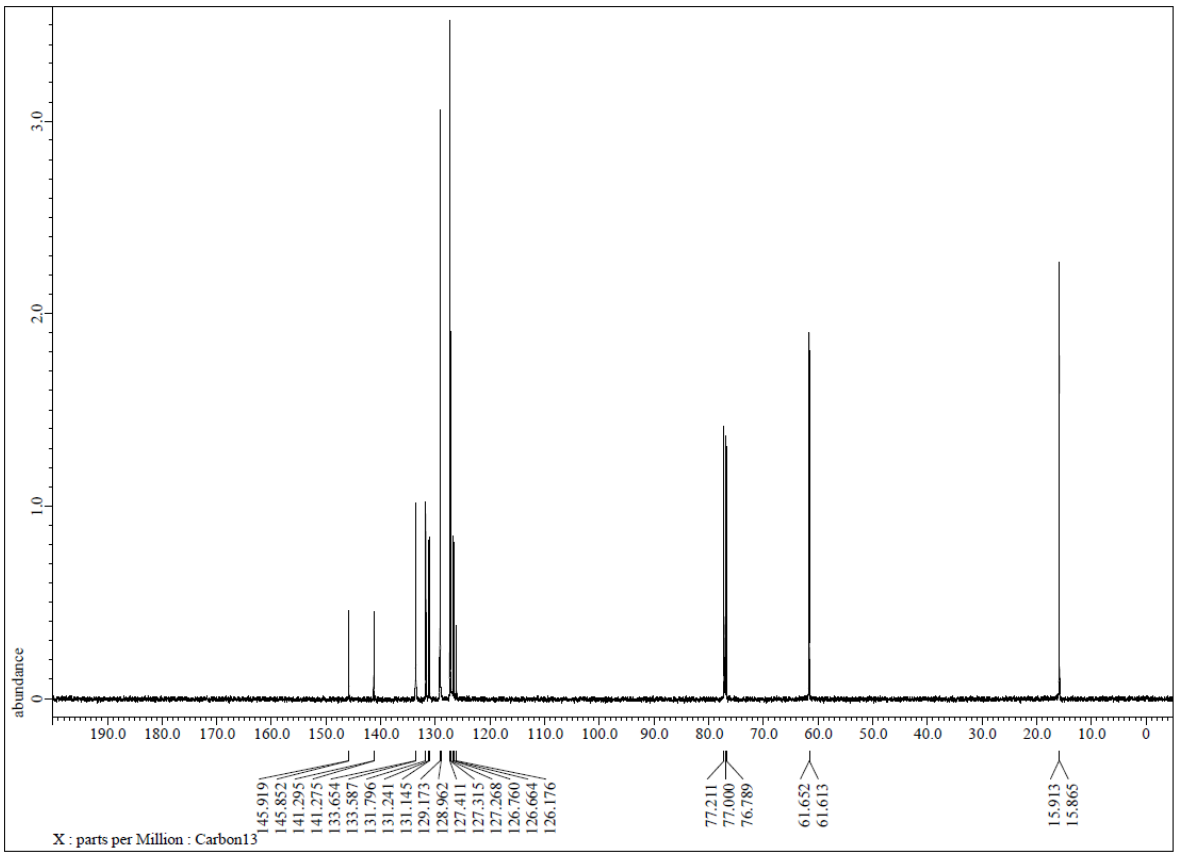


3

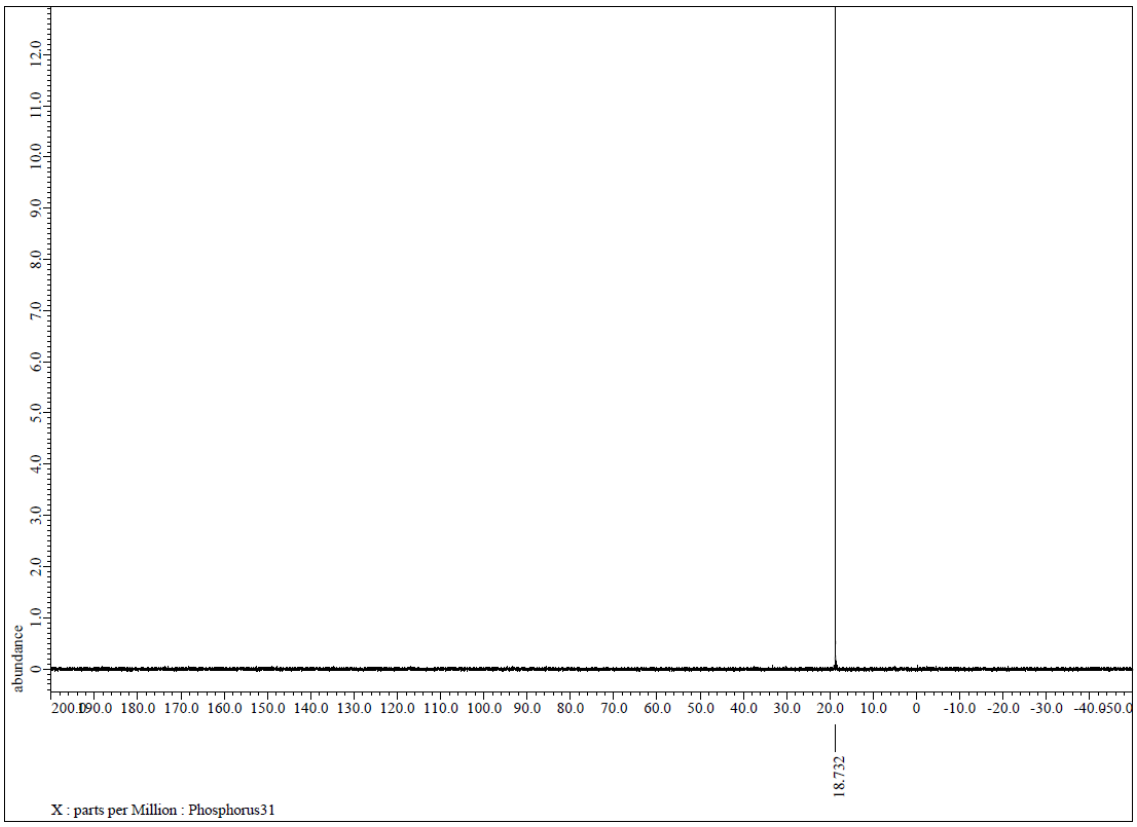
^{1}H NMR ($CDCl_3$)

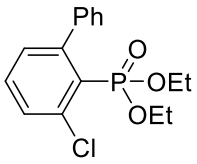


^{13}C NMR ($CDCl_3$)



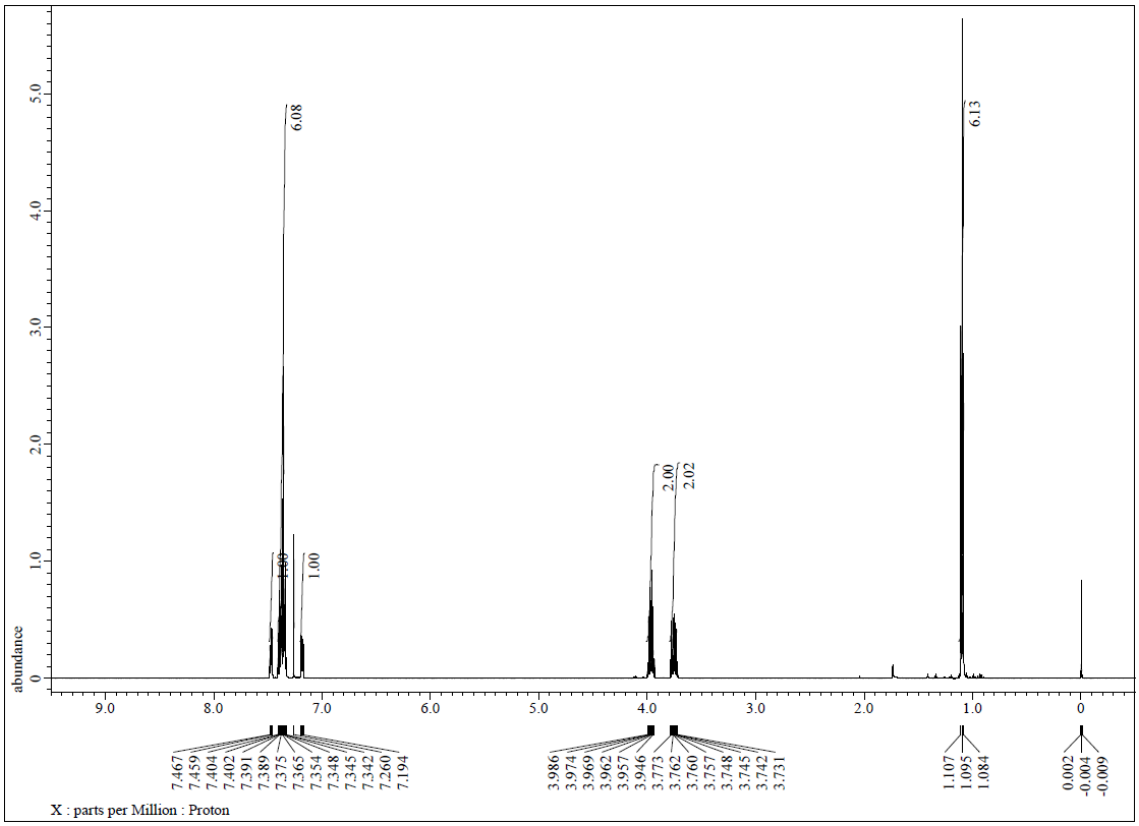
^{31}P NMR ($CDCl_3$)





4

^{1}H NMR ($CDCl_3$)



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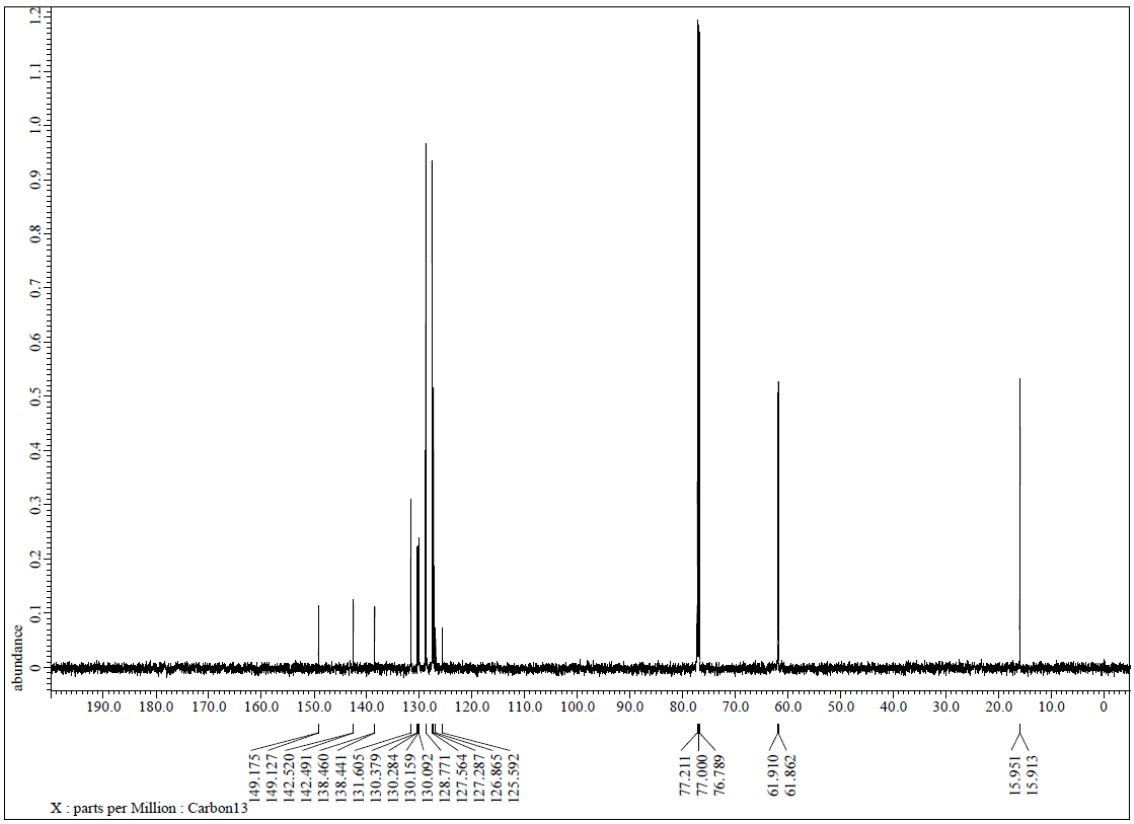

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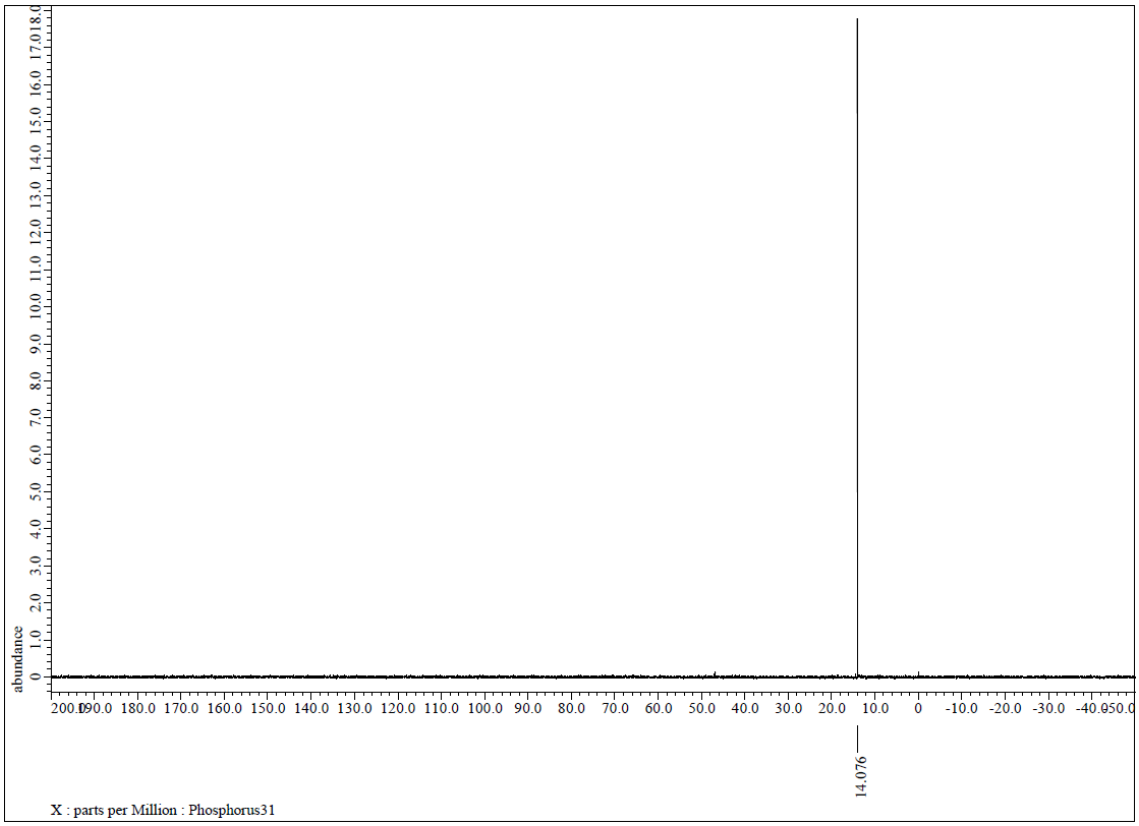
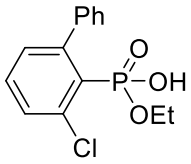
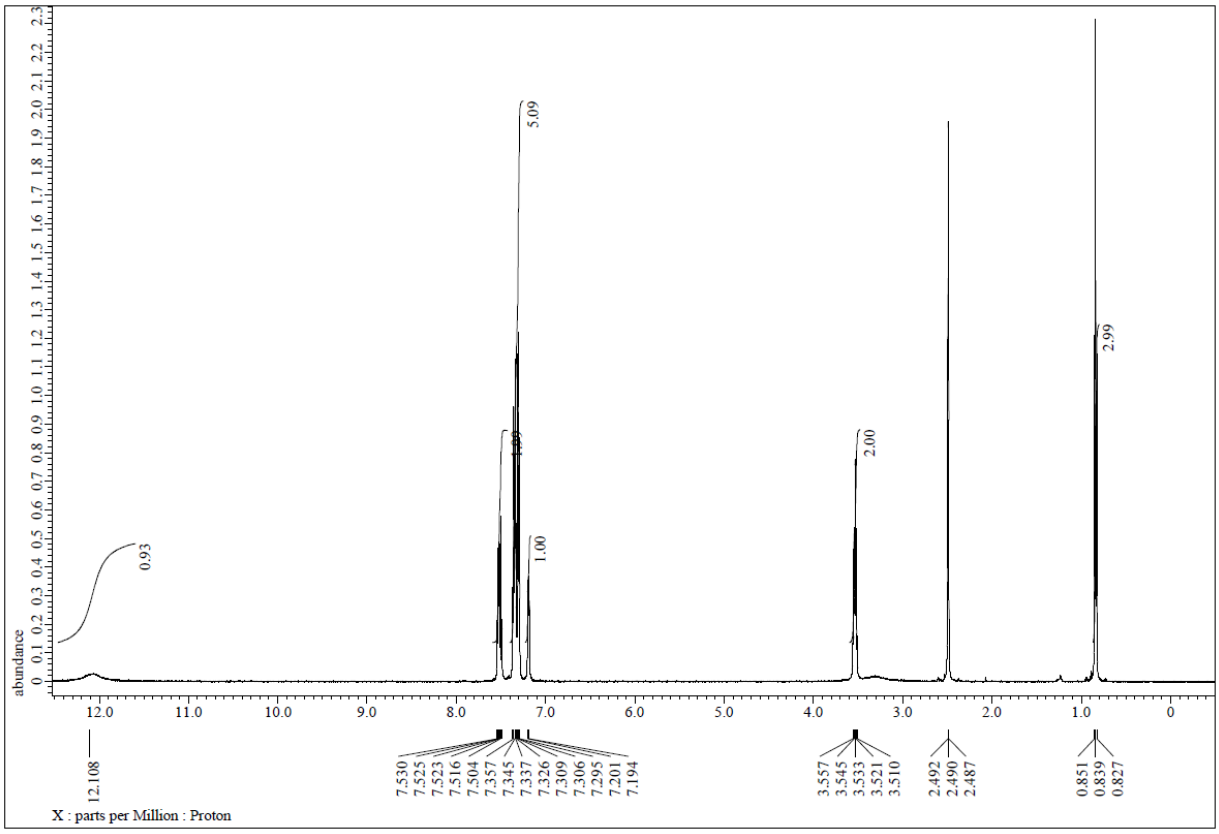




5

^{1}H NMR (DMSO-d_6)



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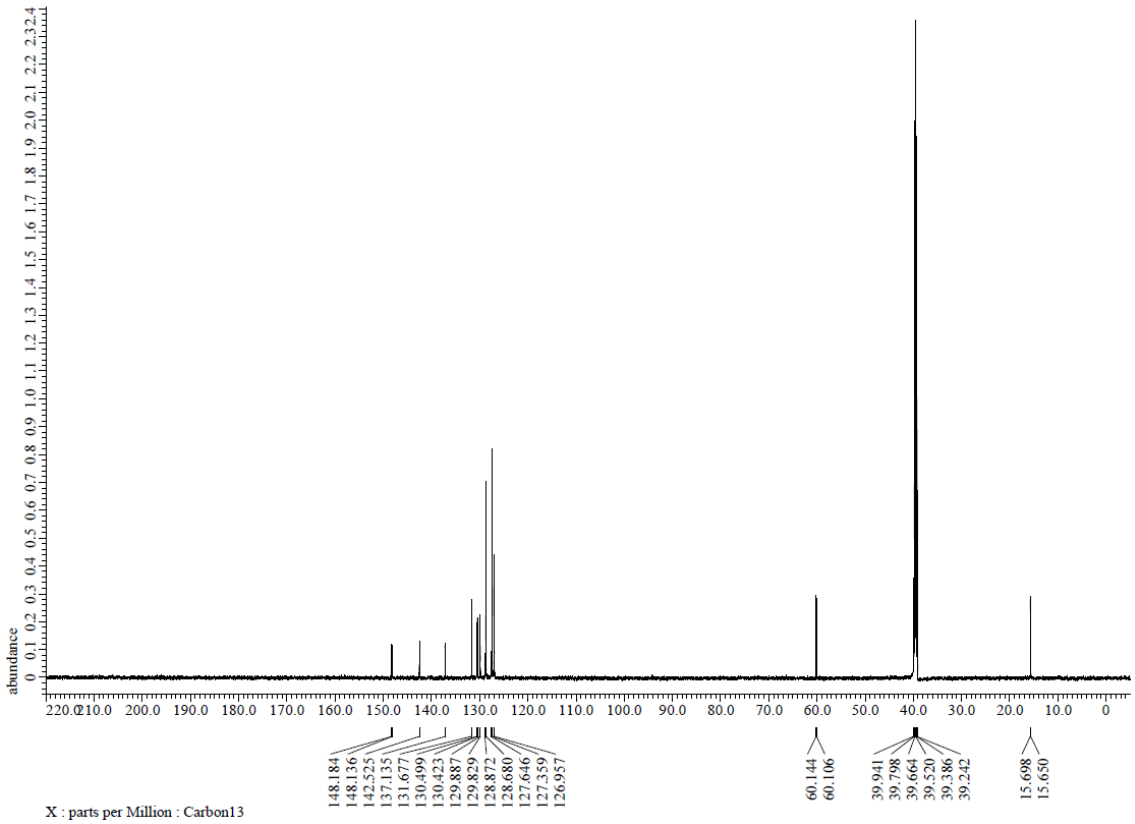

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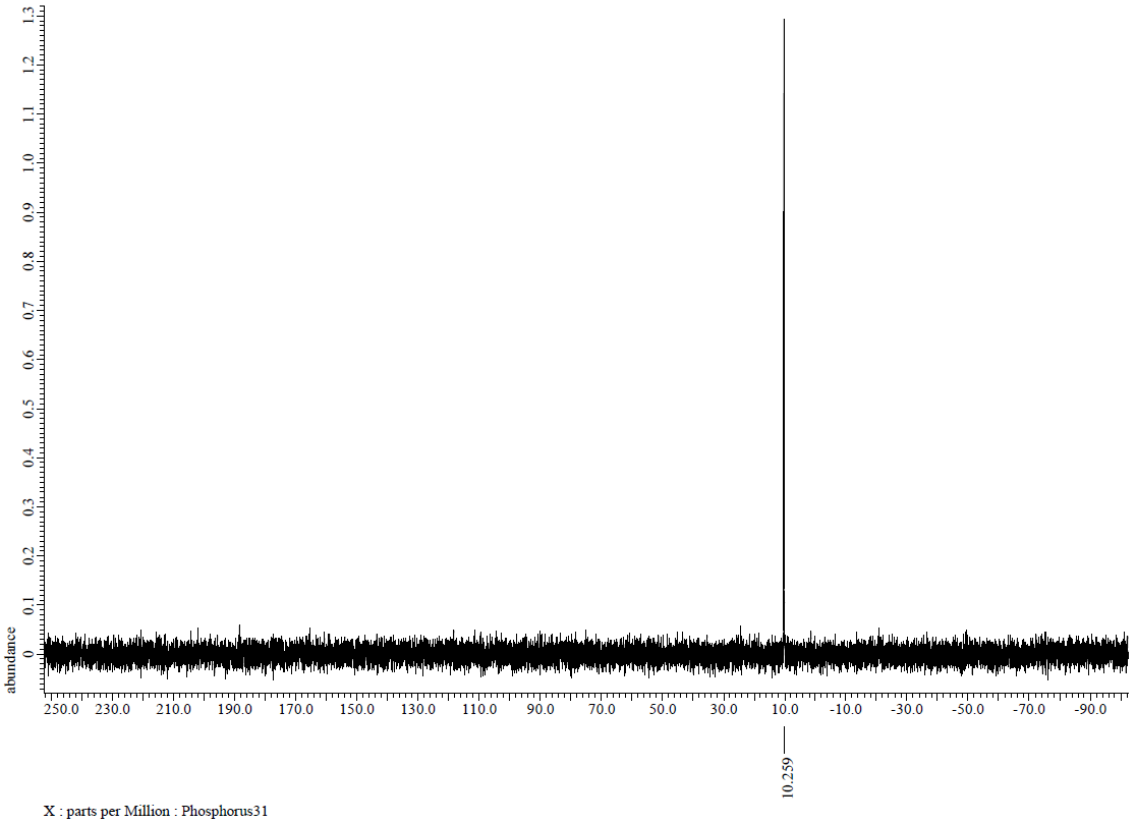
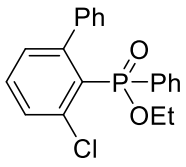
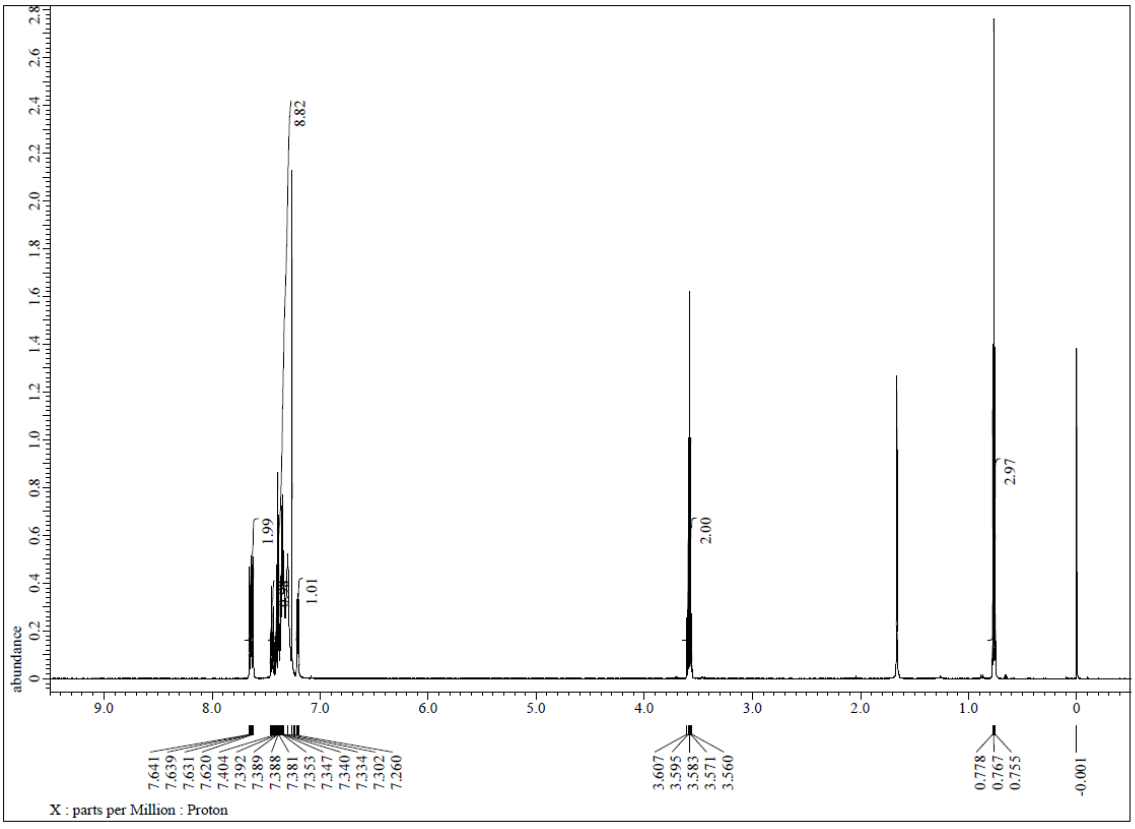




6a

^{1}H NMR ($CDCl_3$)



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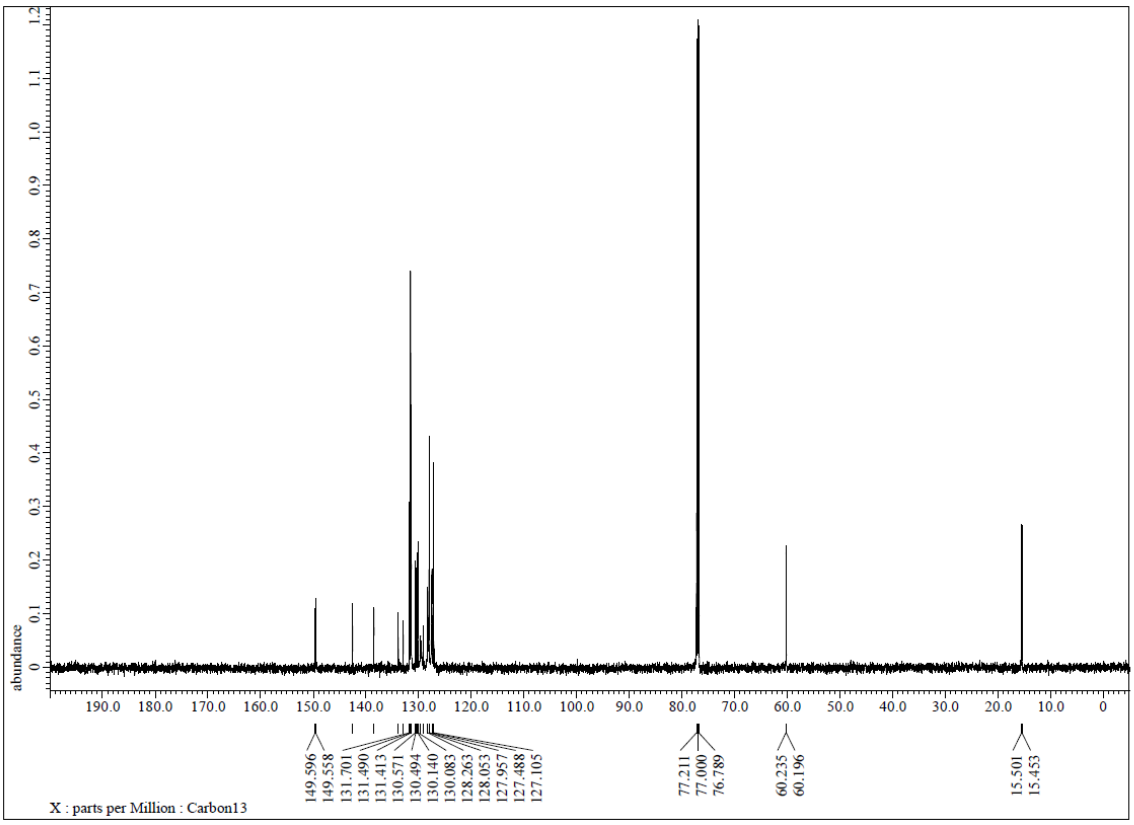

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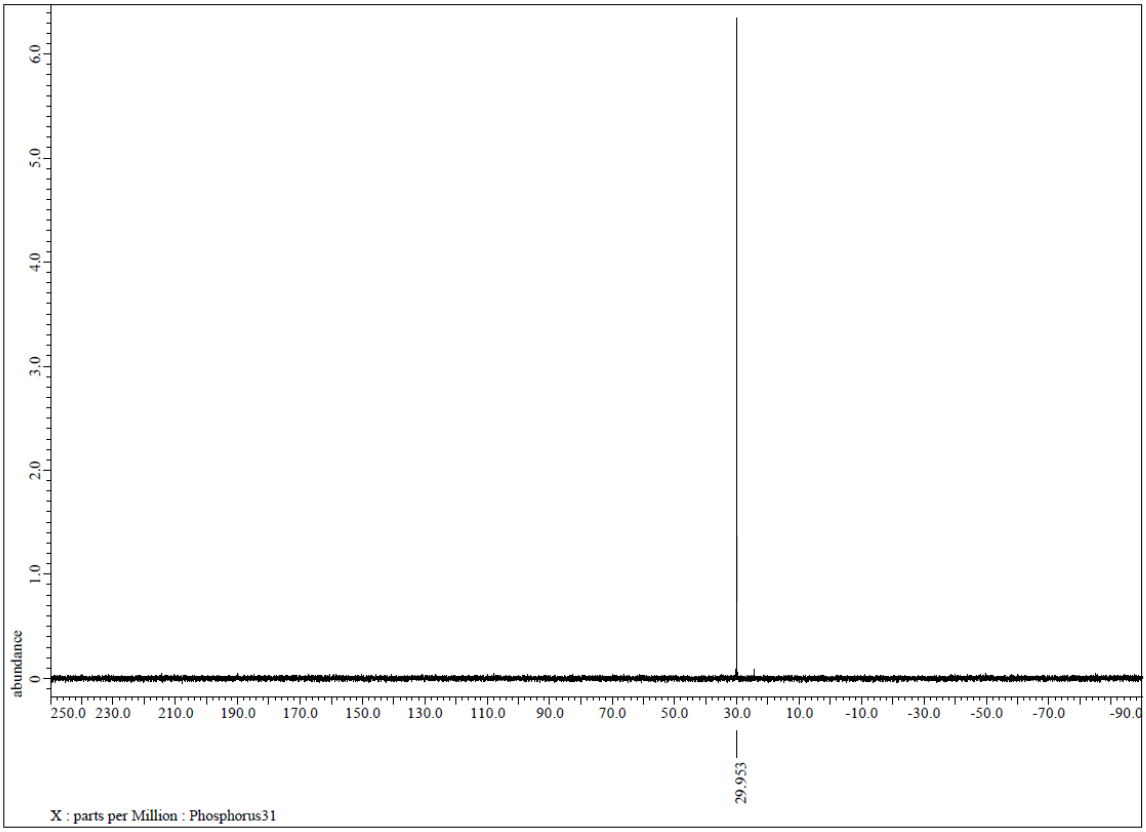

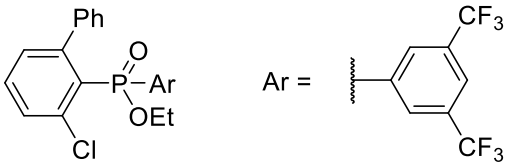

6b

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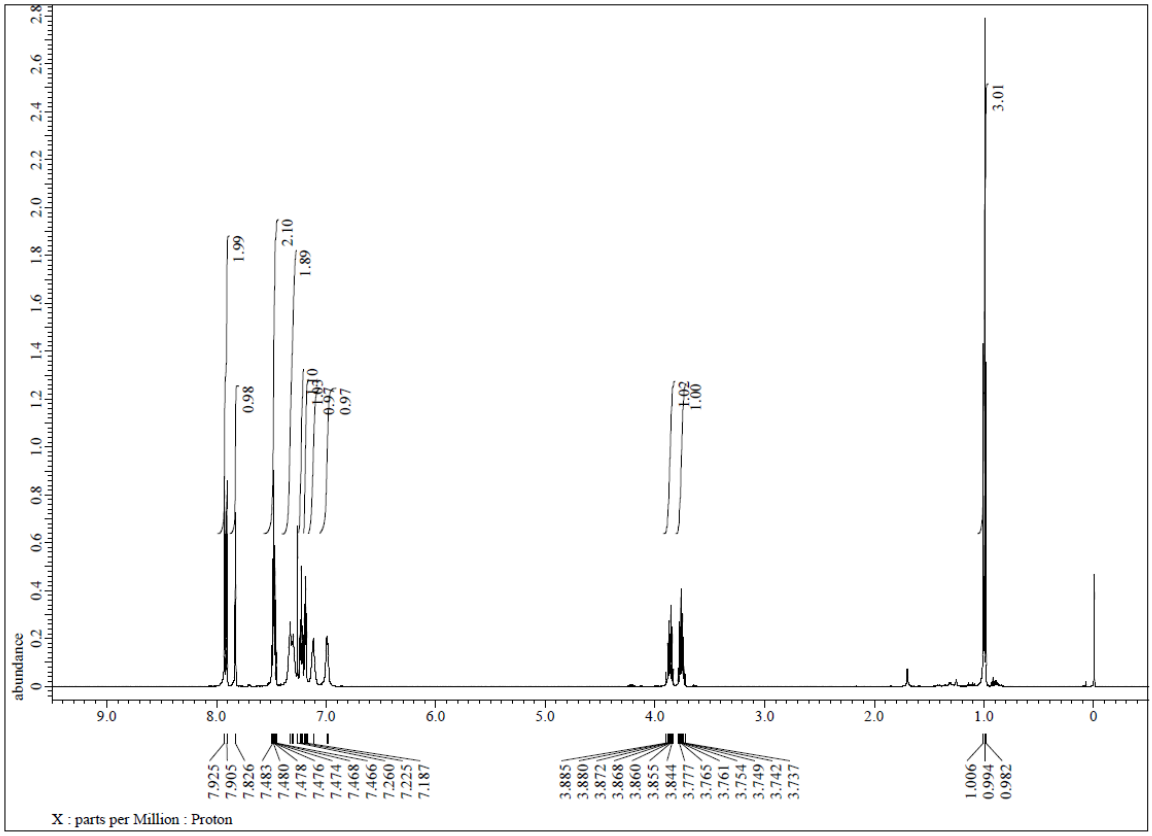

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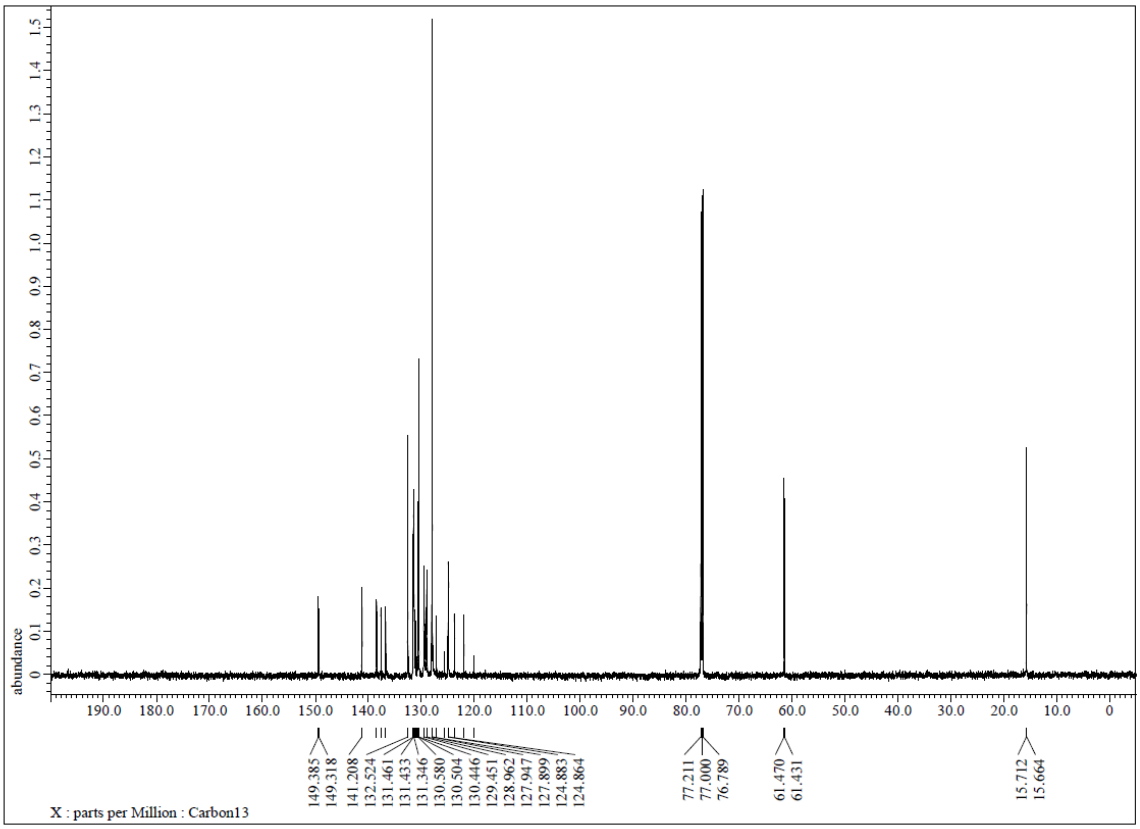

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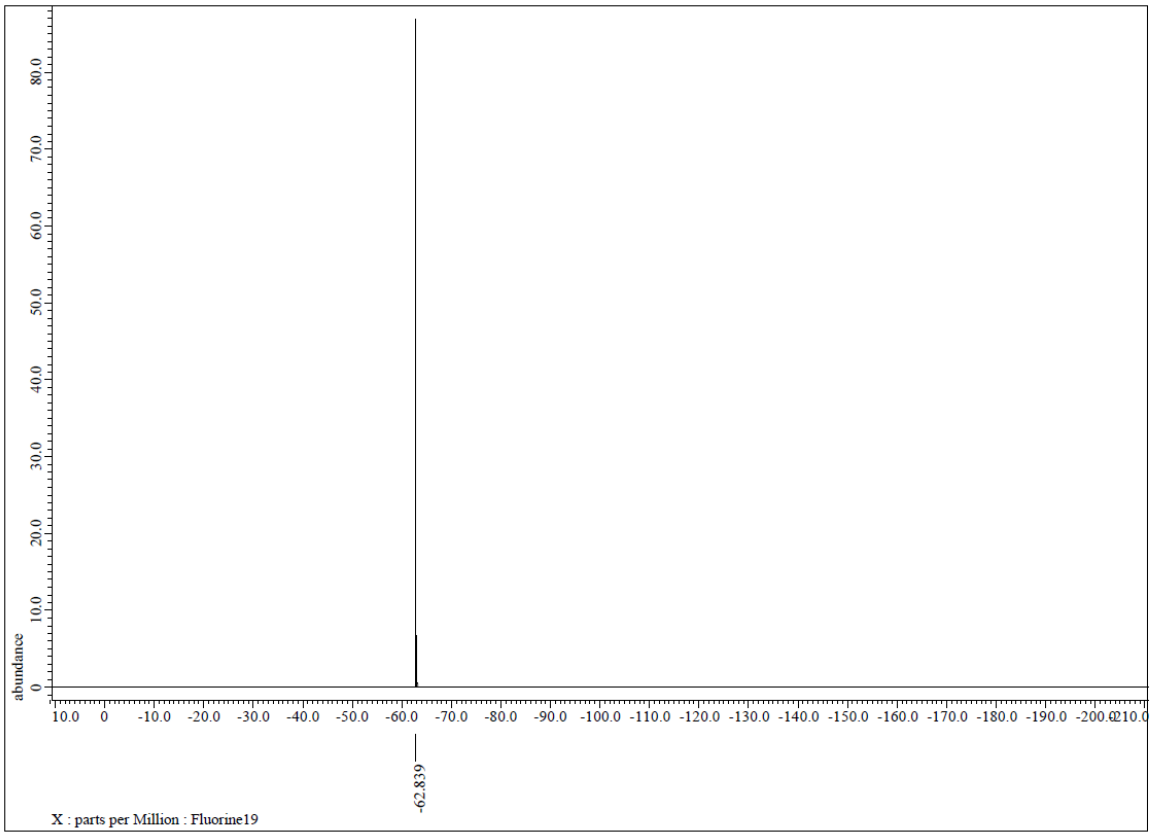
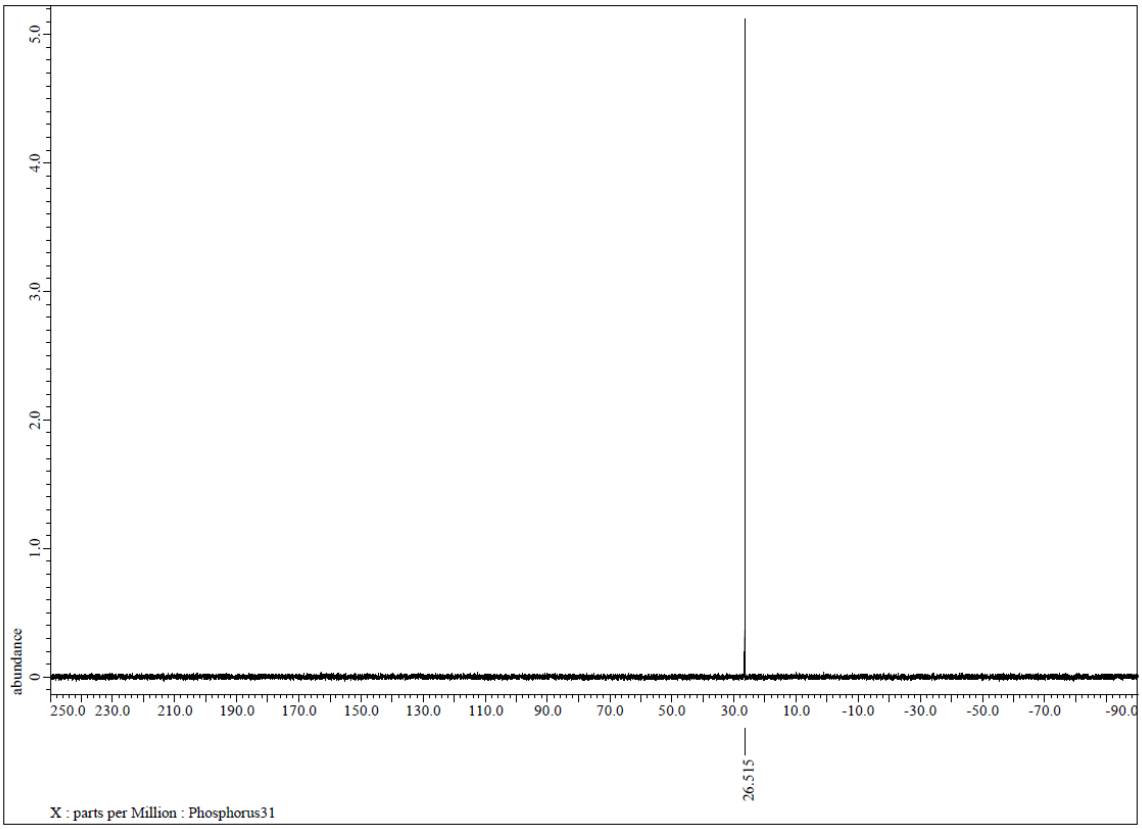
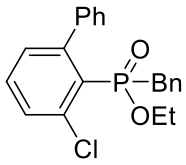


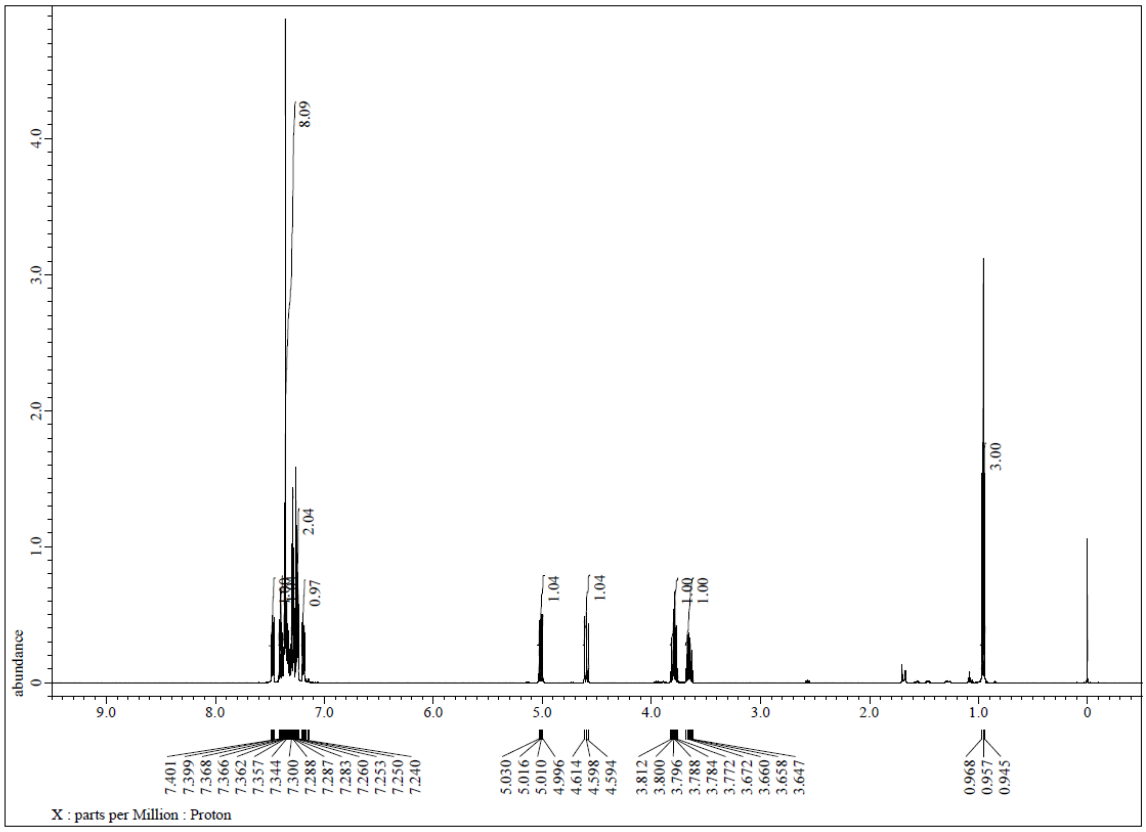
^{19}F NMR ($CDCl_3$)





6c

^{1}H NMR ($CDCl_3$)



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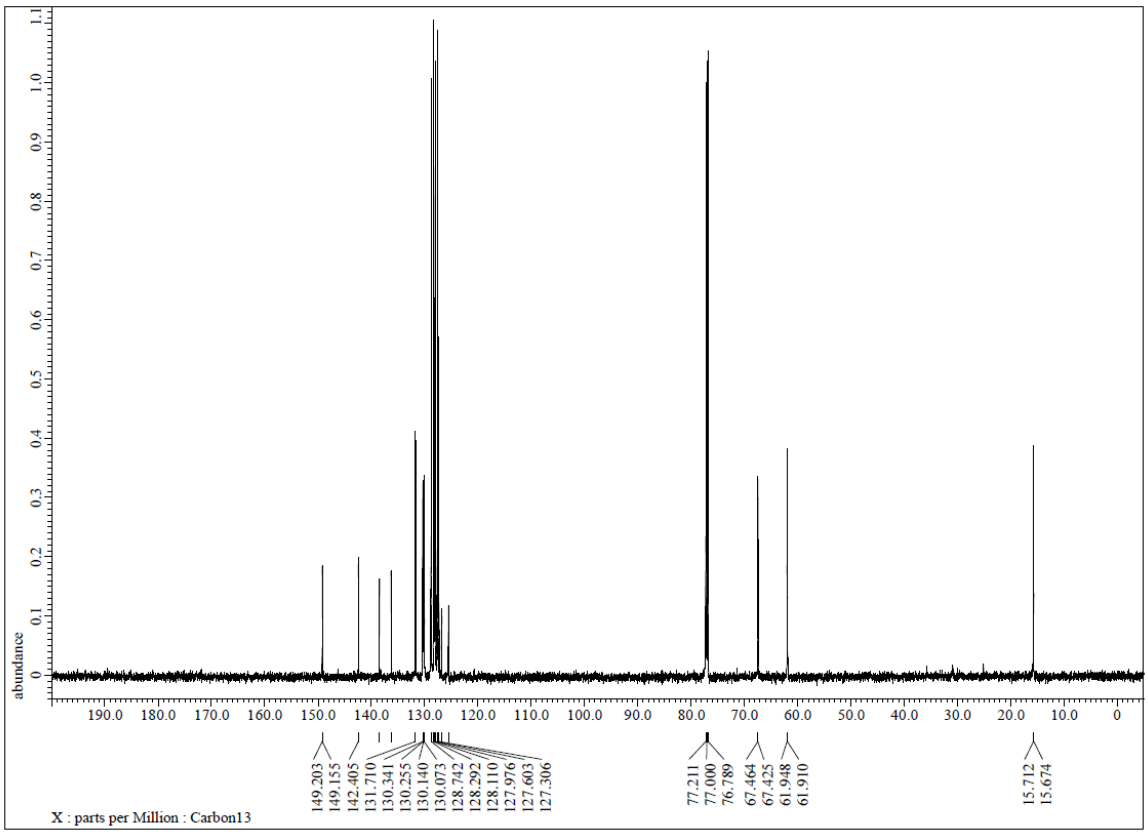

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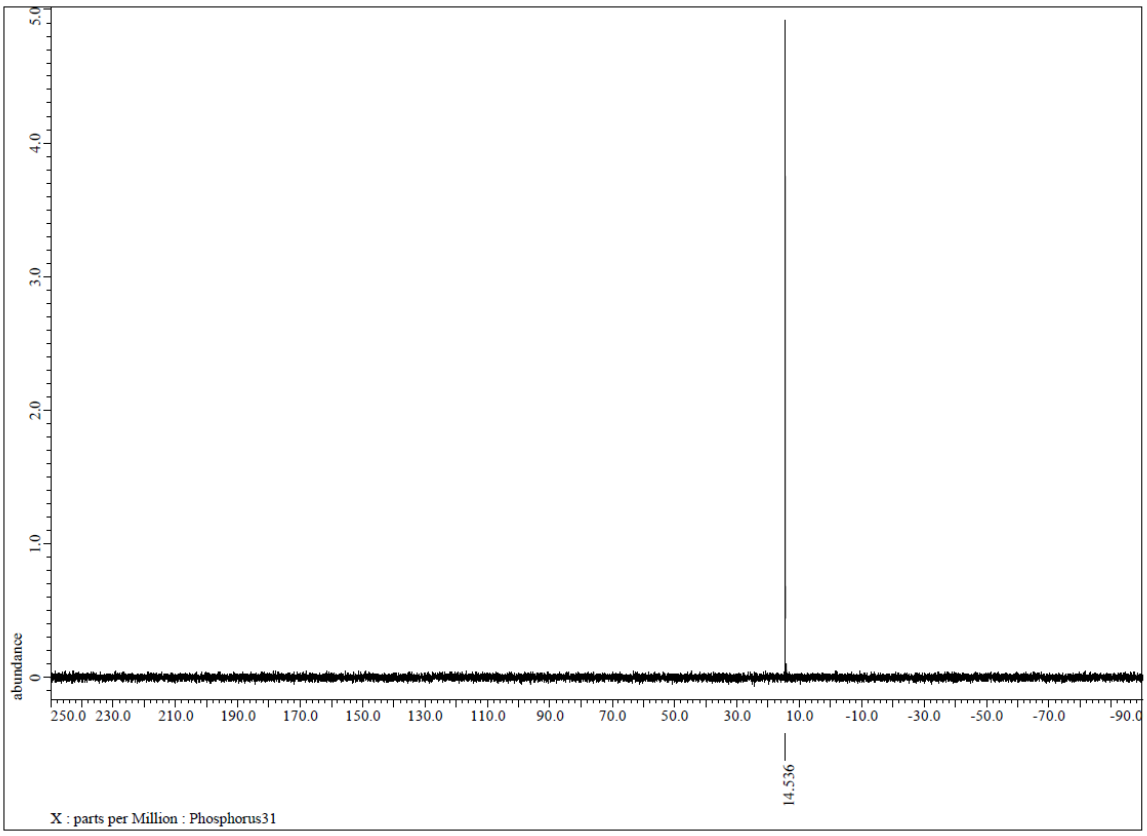

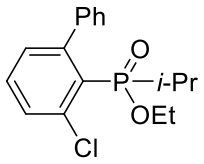

6d

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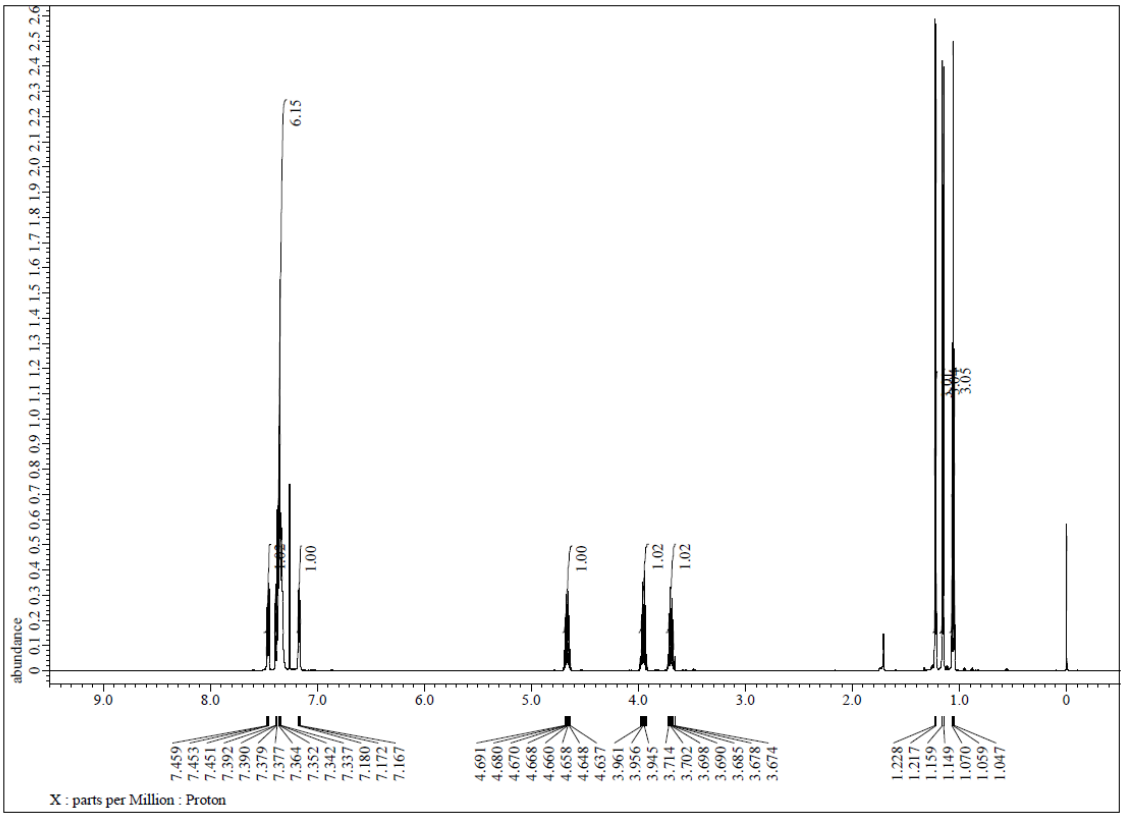

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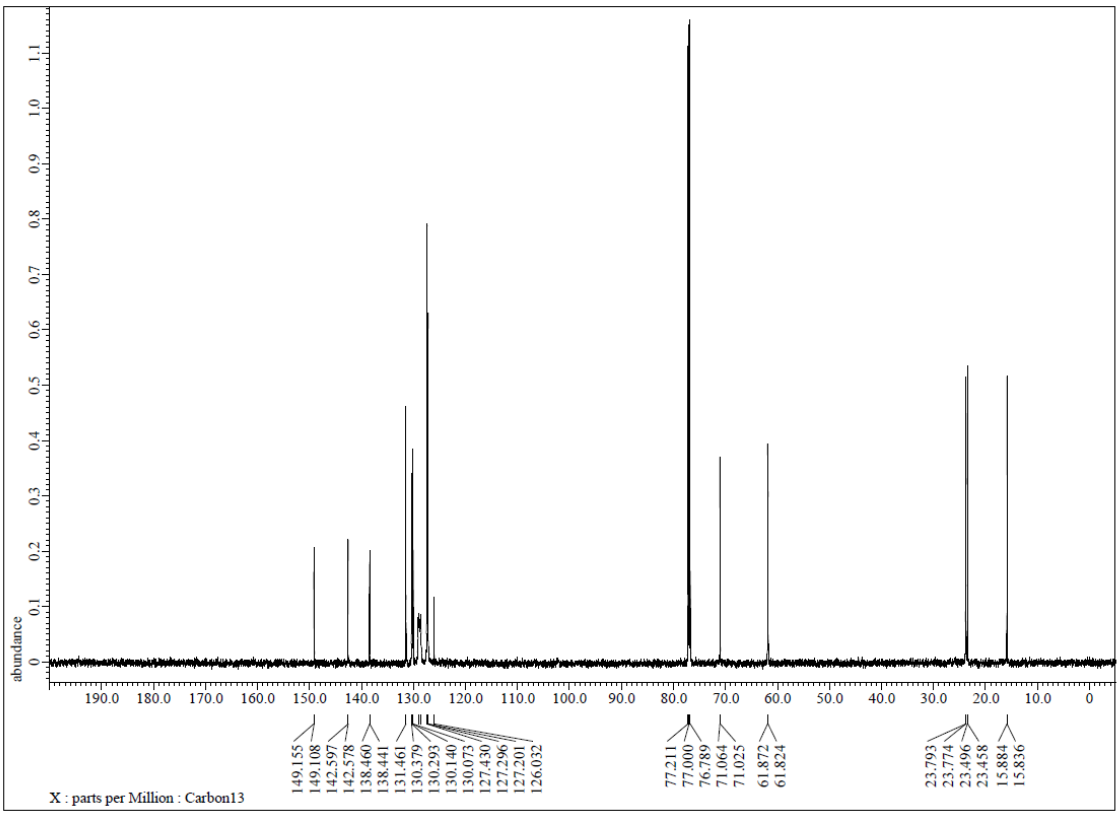
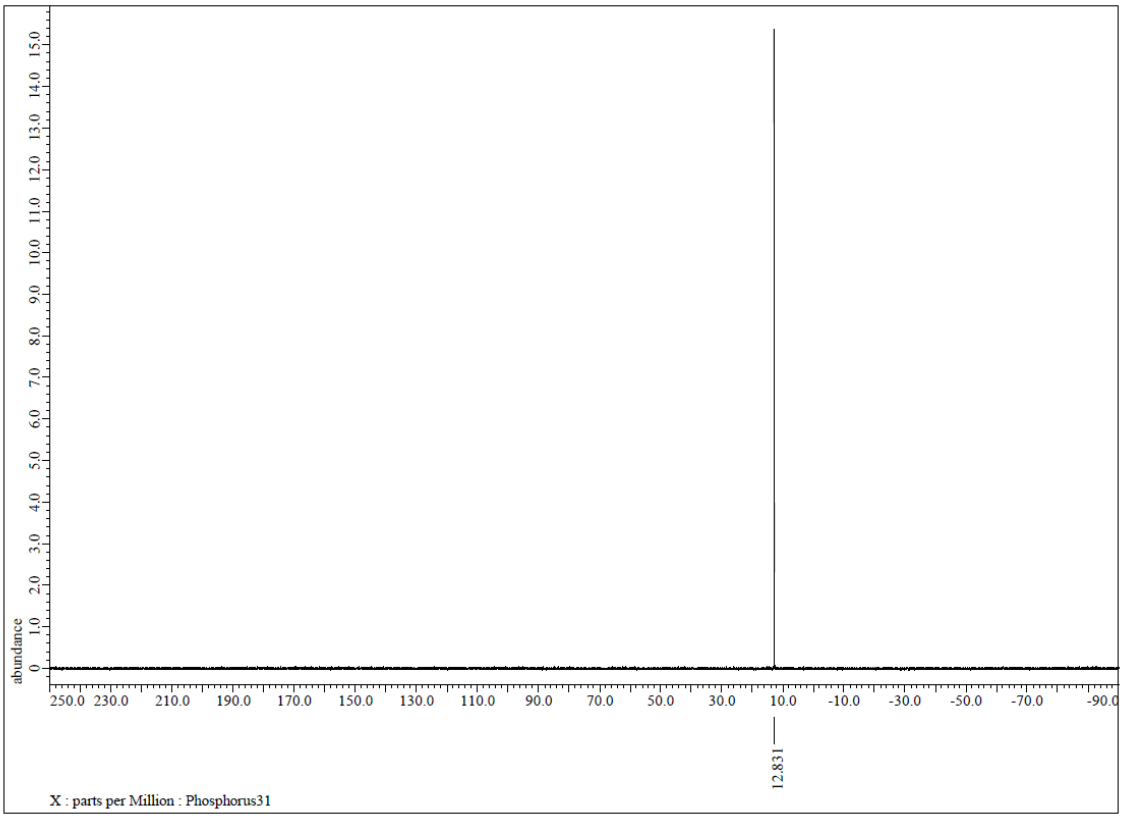
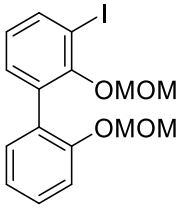


^{31}P NMR ($CDCl_3$)





S5

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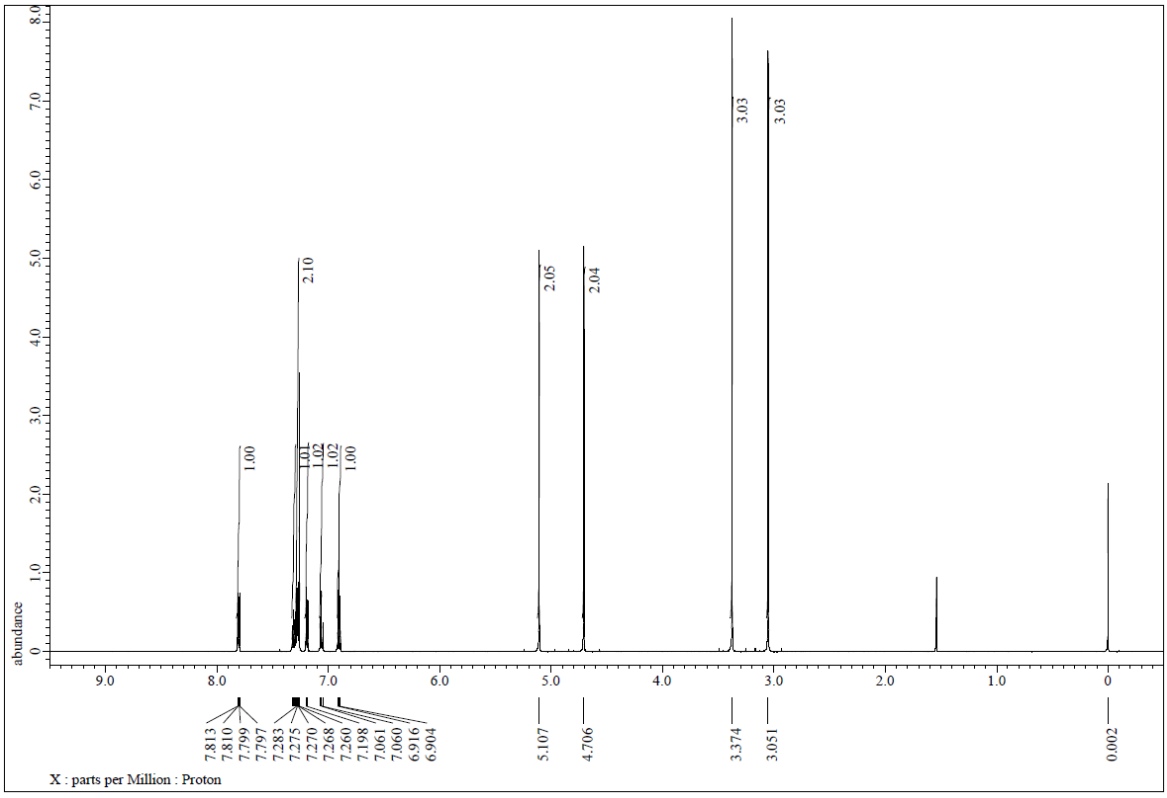

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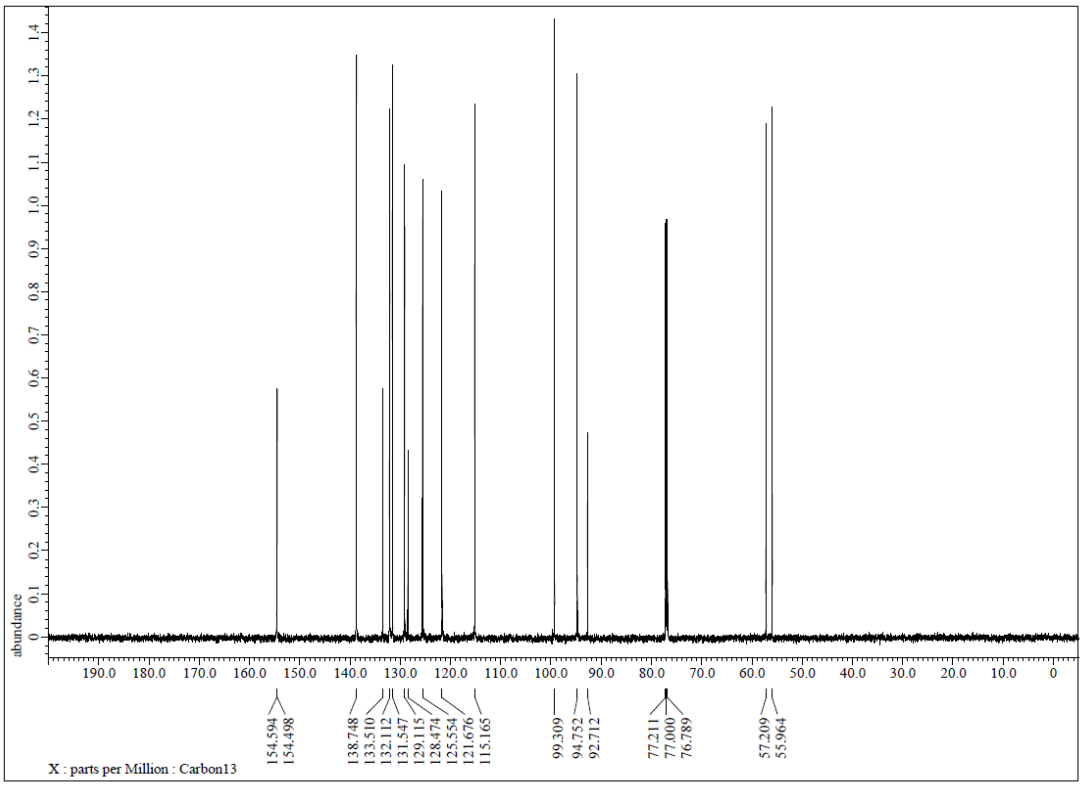
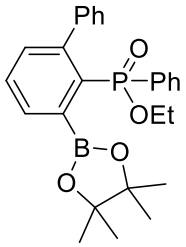
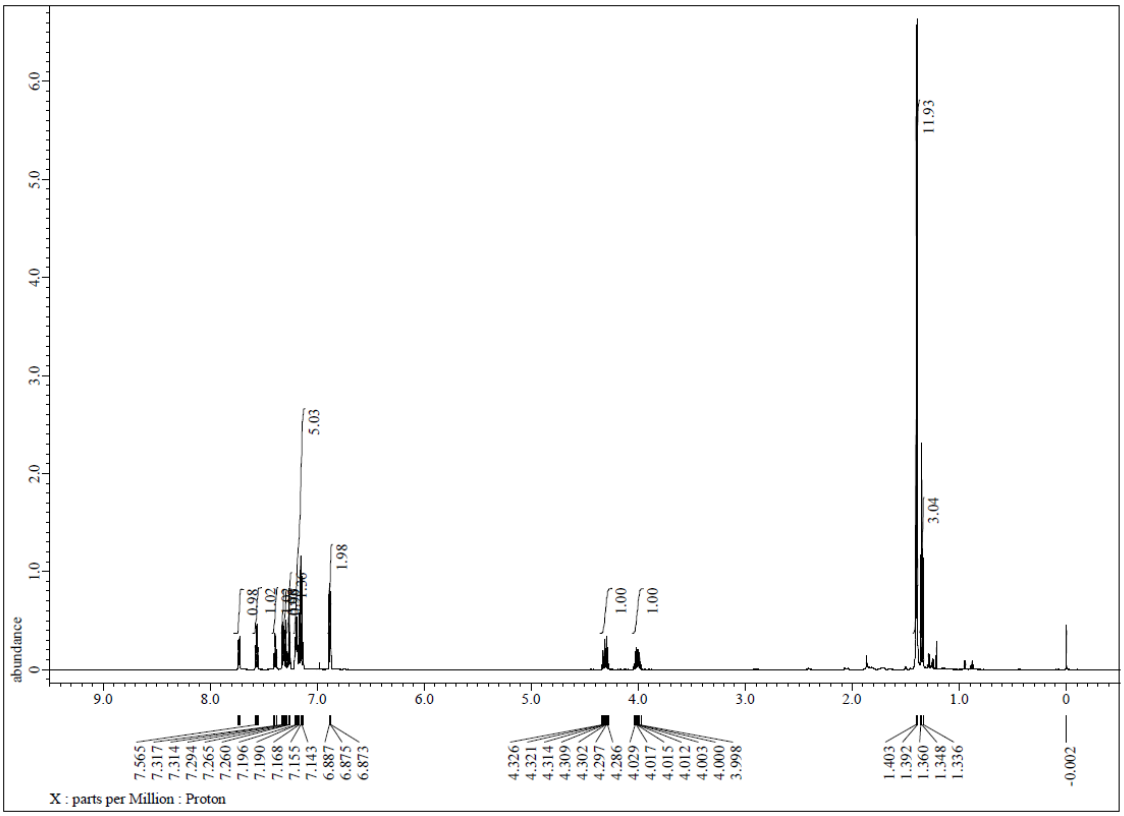




7a

^{1}H NMR ($CDCl_3$)



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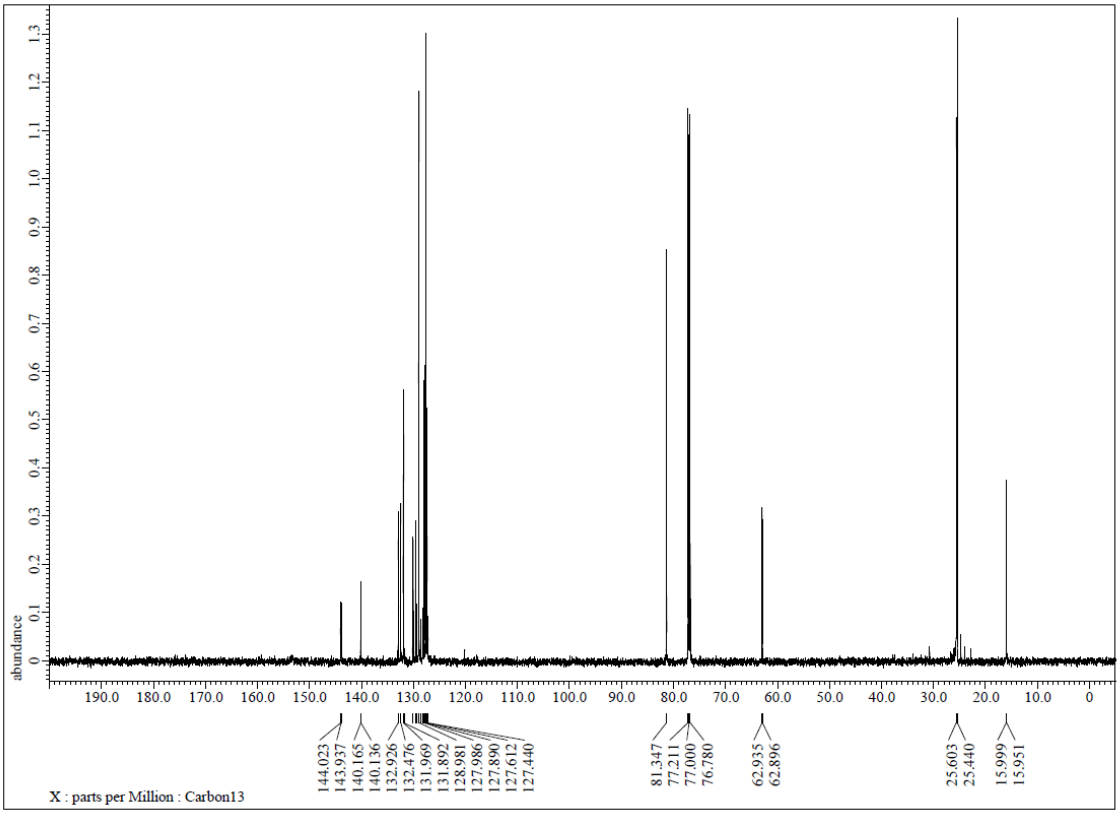
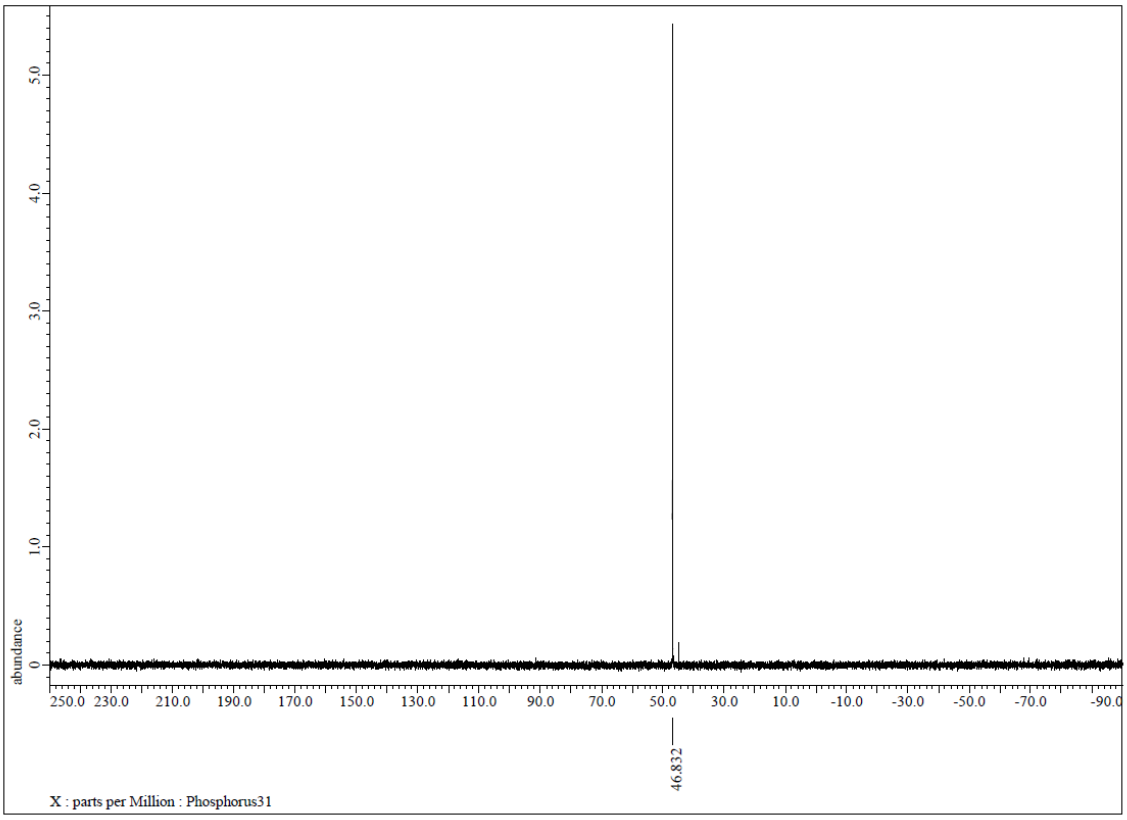
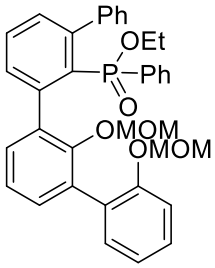


^{31}P NMR ($CDCl_3$)





S6

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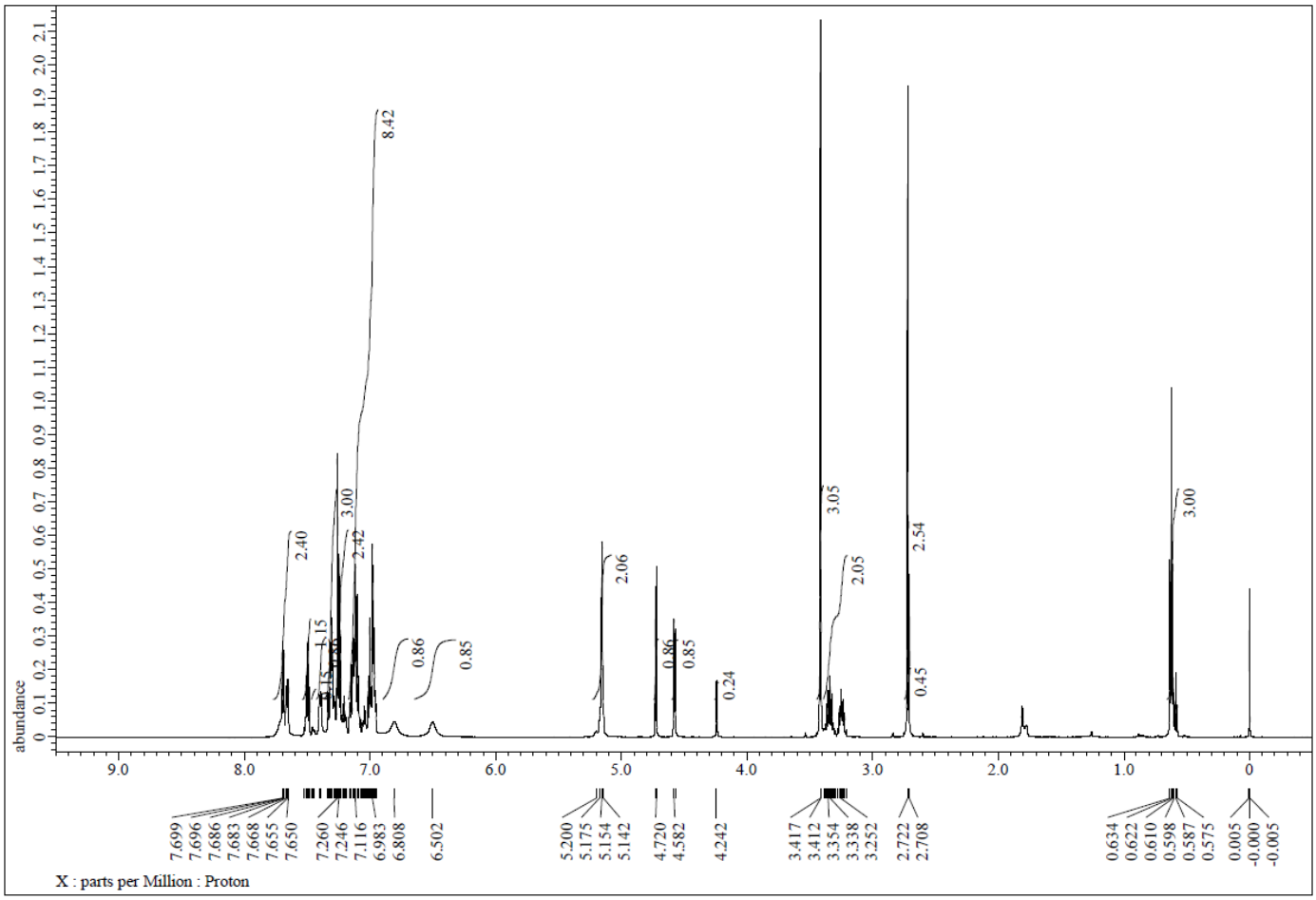

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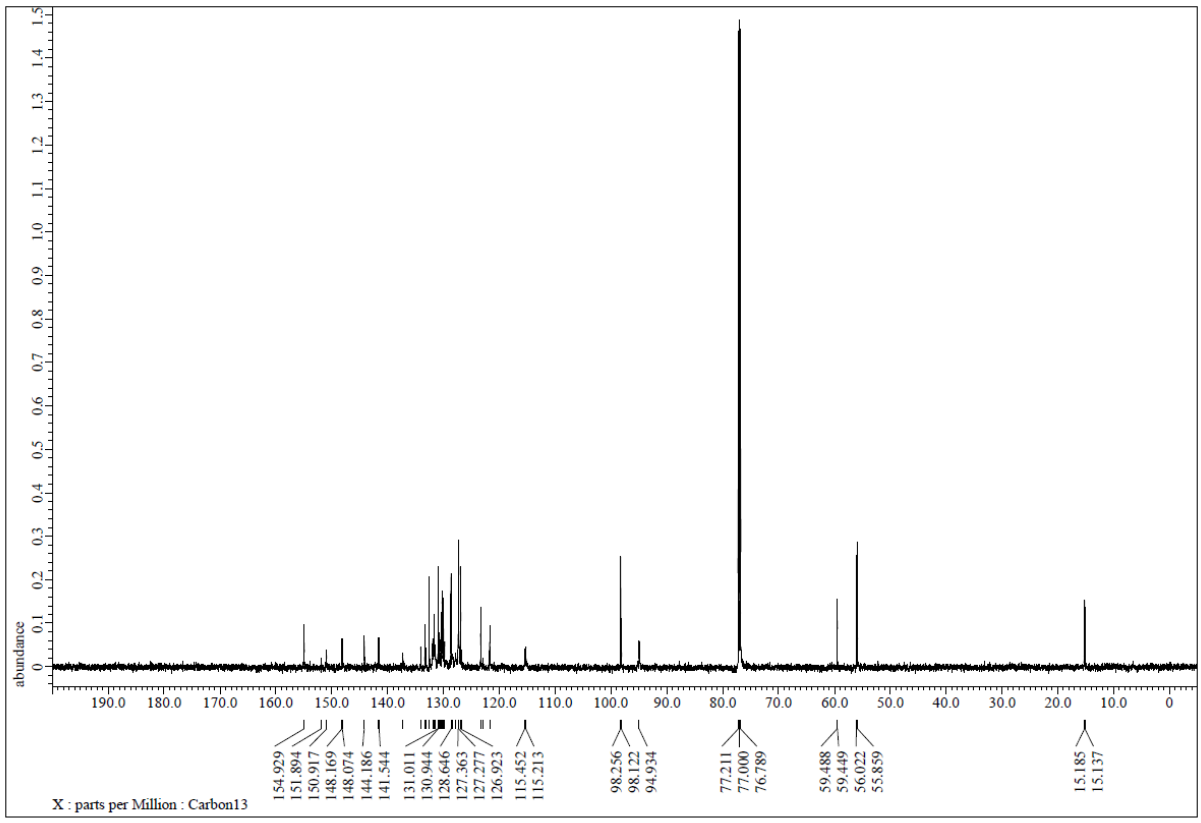

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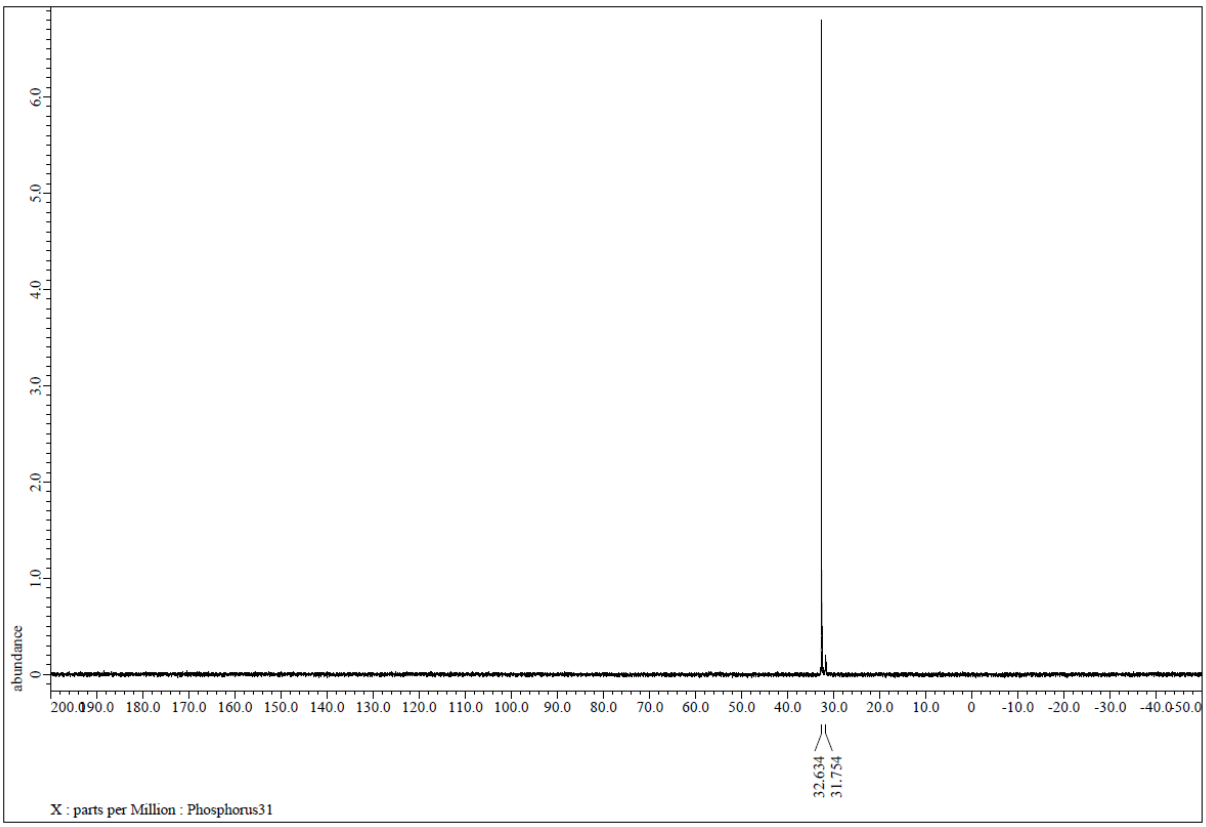
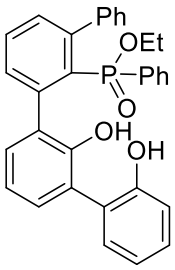
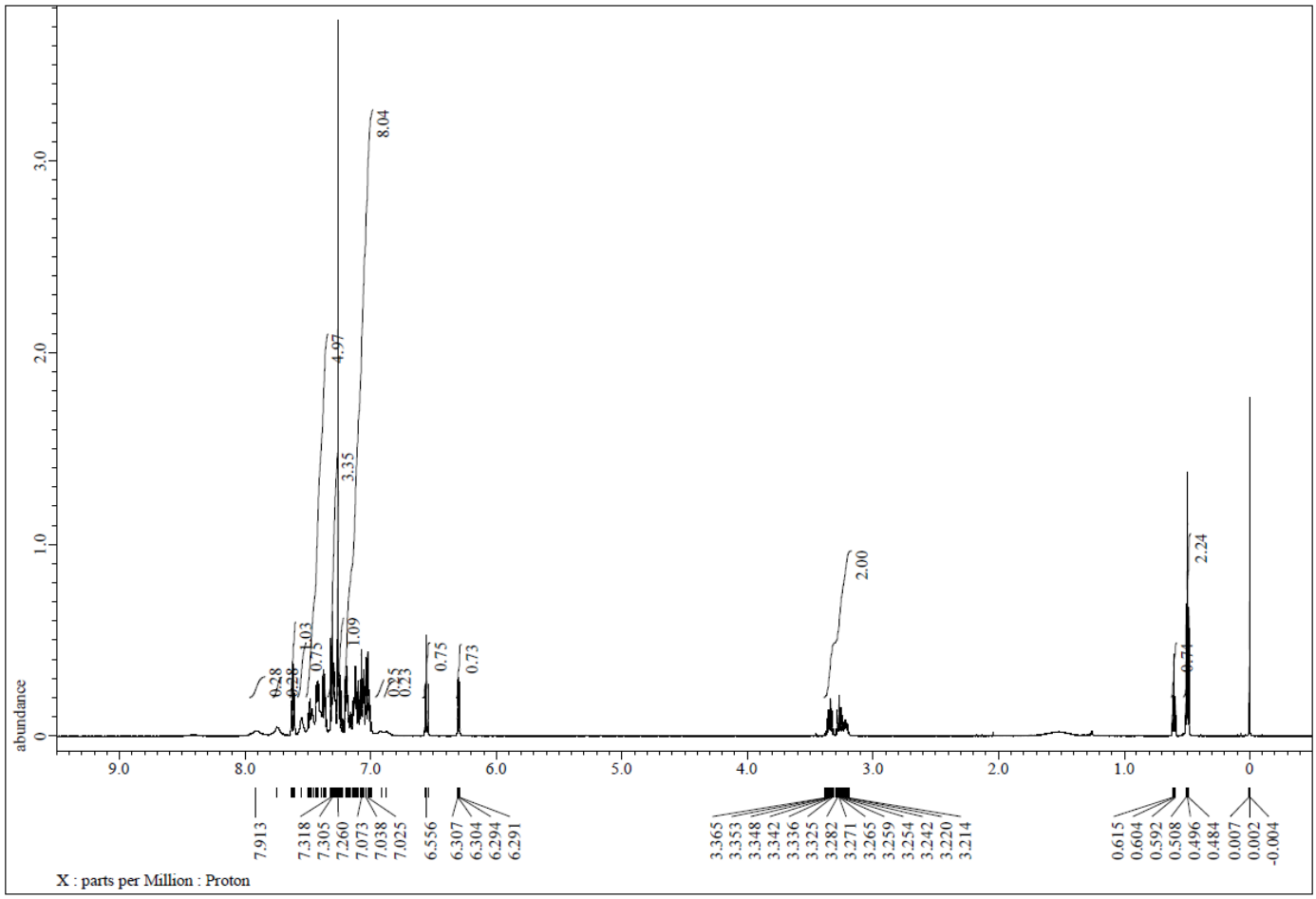


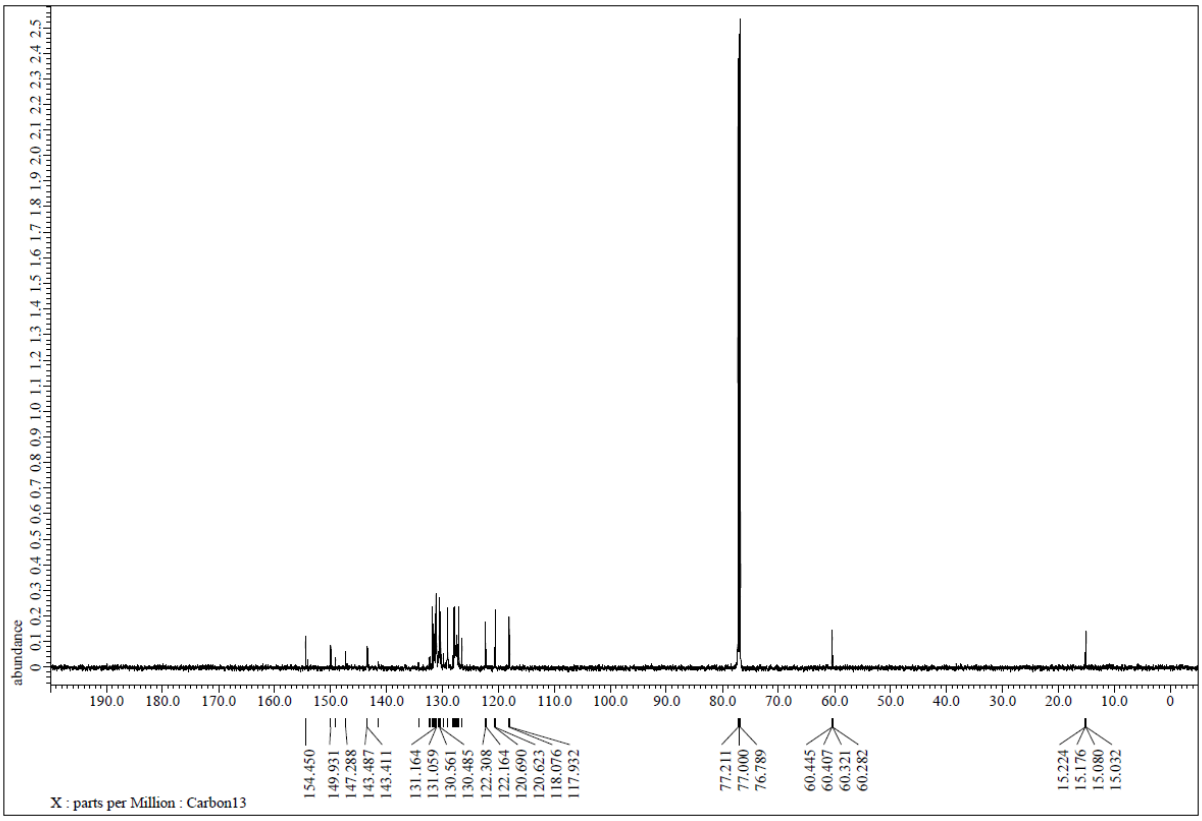


8a

^{1}H NMR ($CDCl_3$)



^{13}C NMR ($CDCl_3$)



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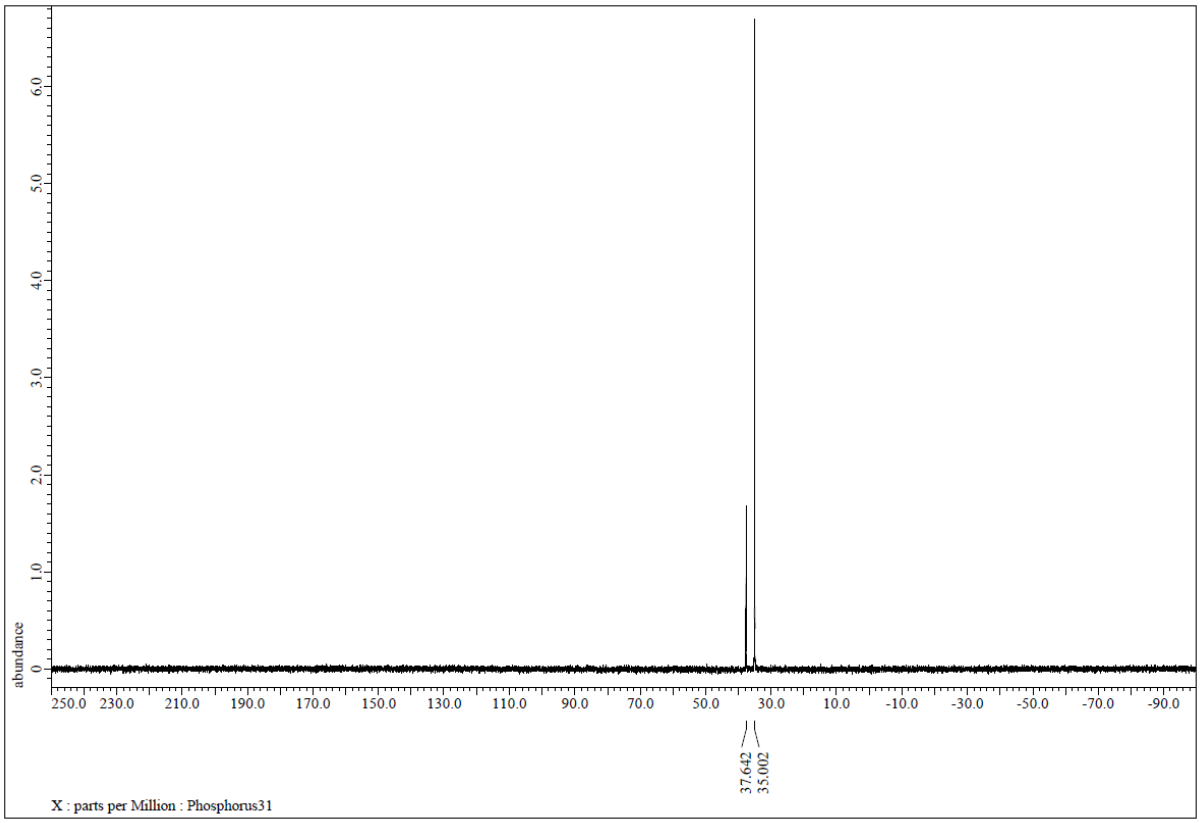
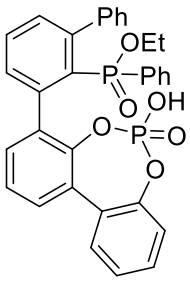
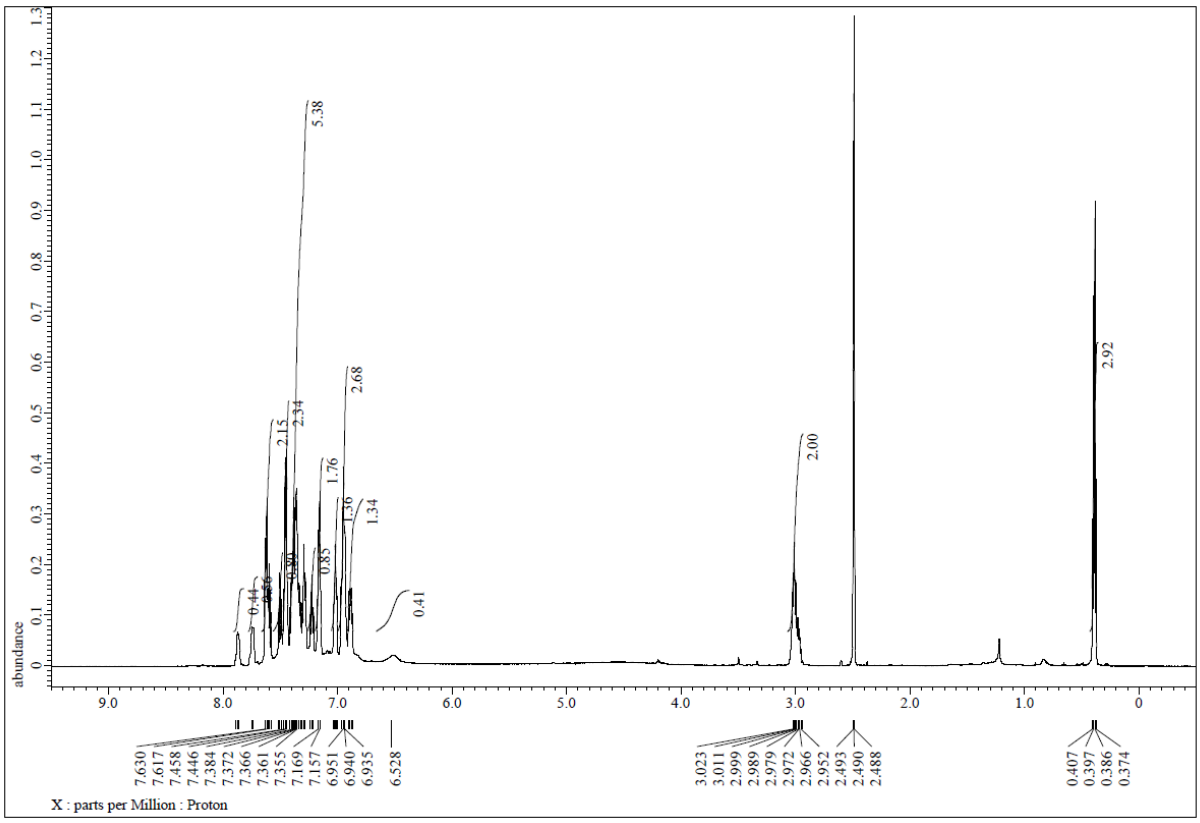


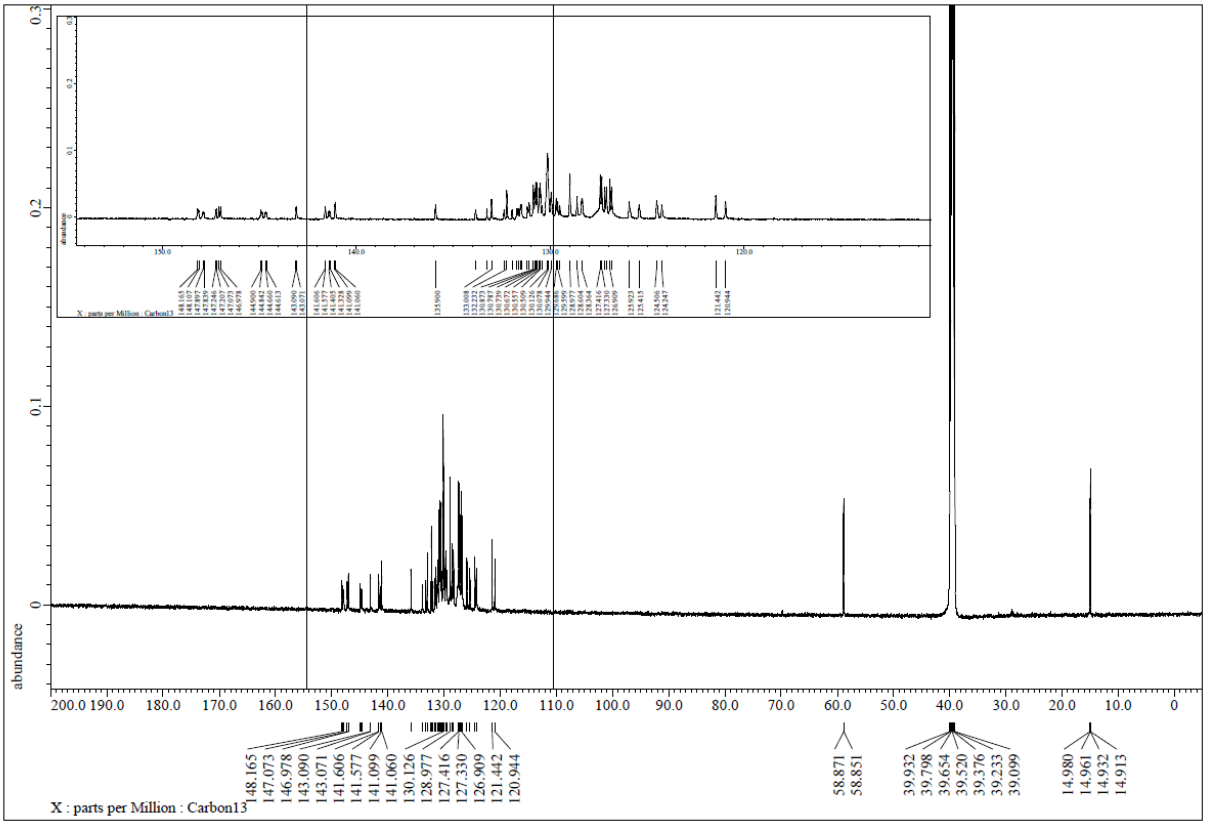


10a

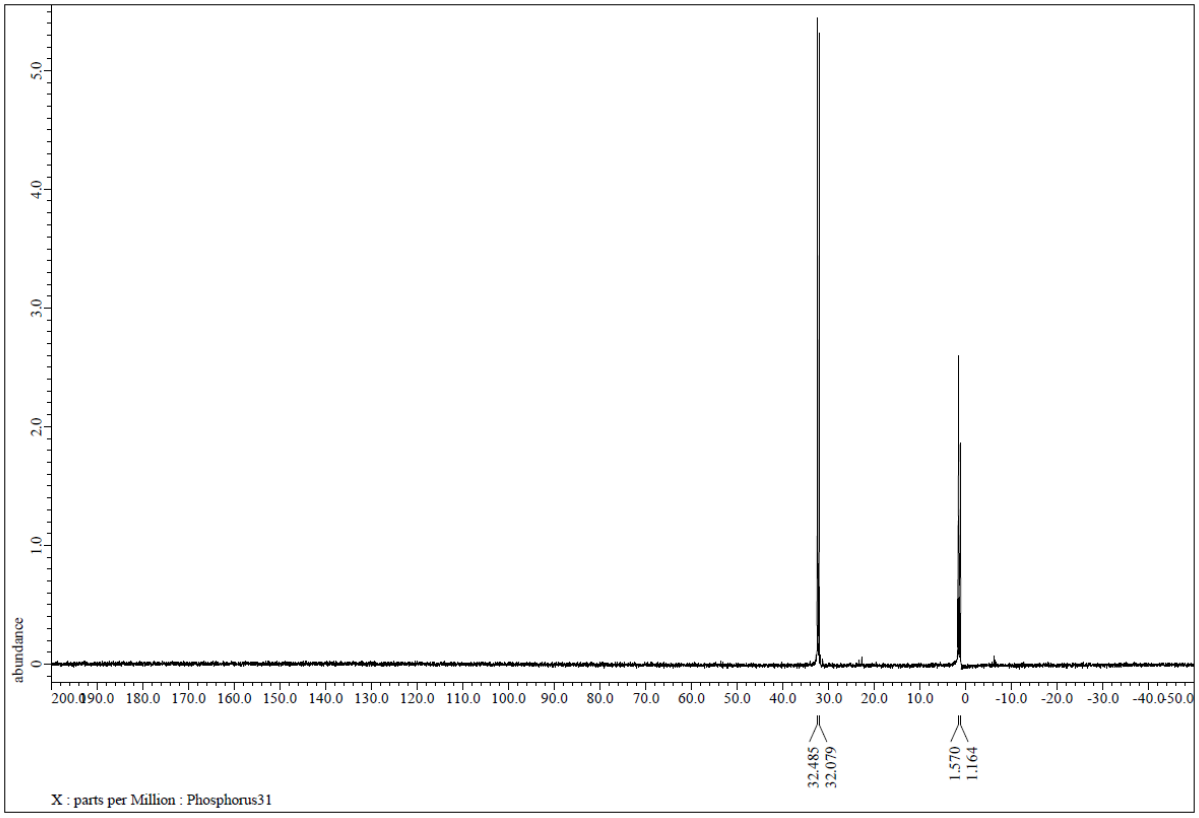
^{1}H NMR (DMSO-d_6)

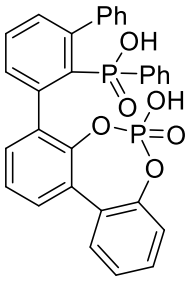


^{13}C NMR (DMSO-d_6)



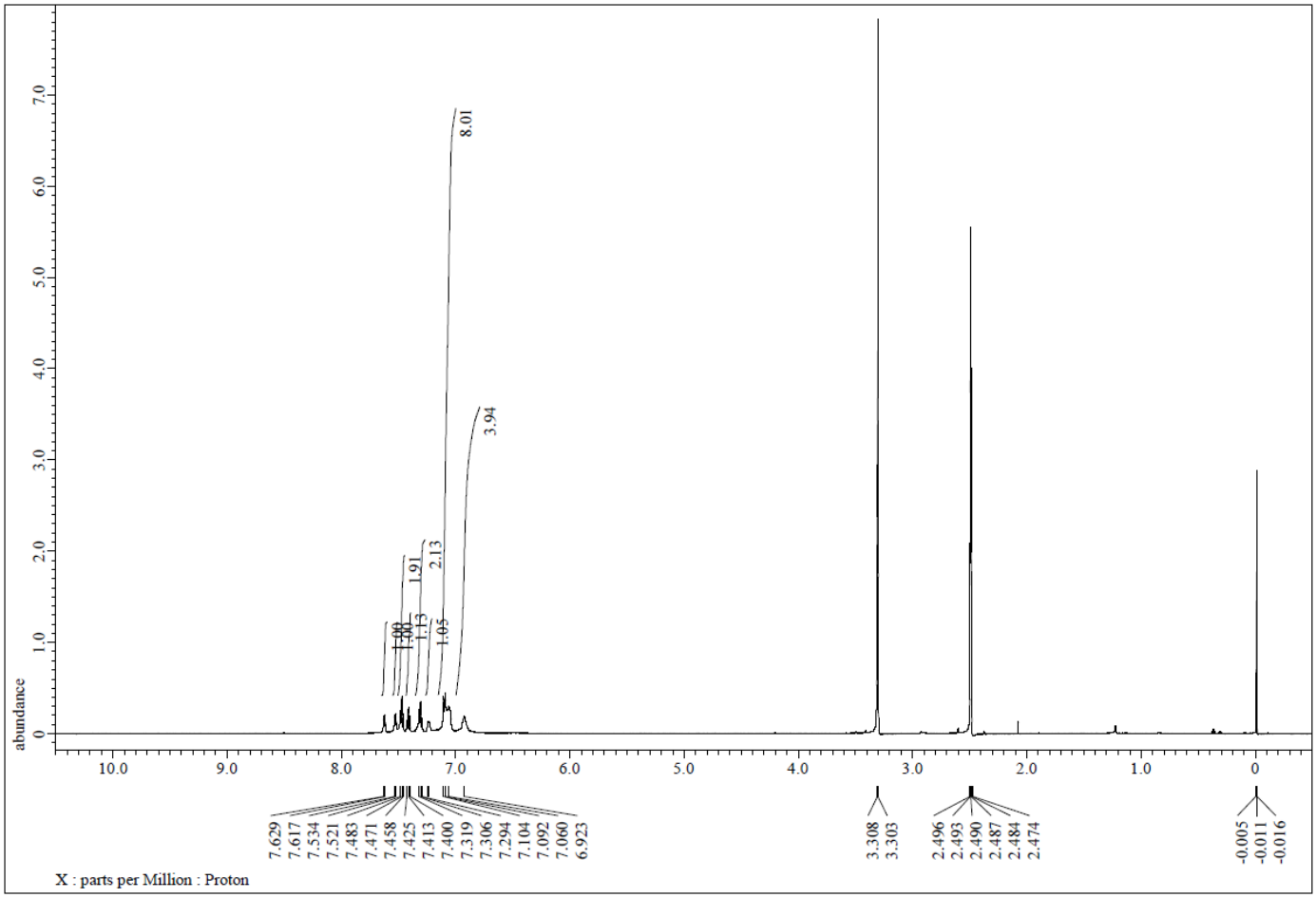
^{31}P NMR (DMSO-d_6)



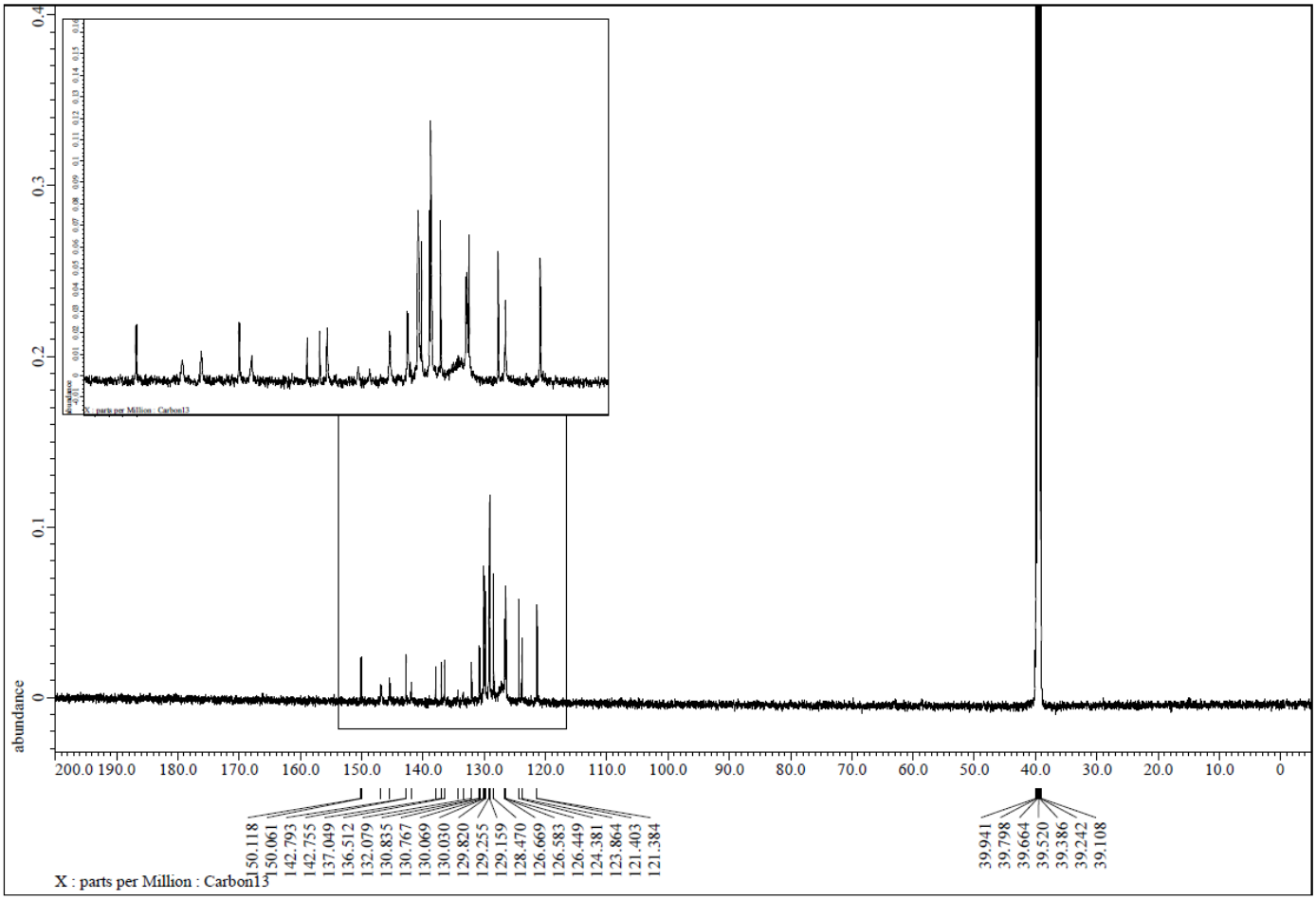


11a

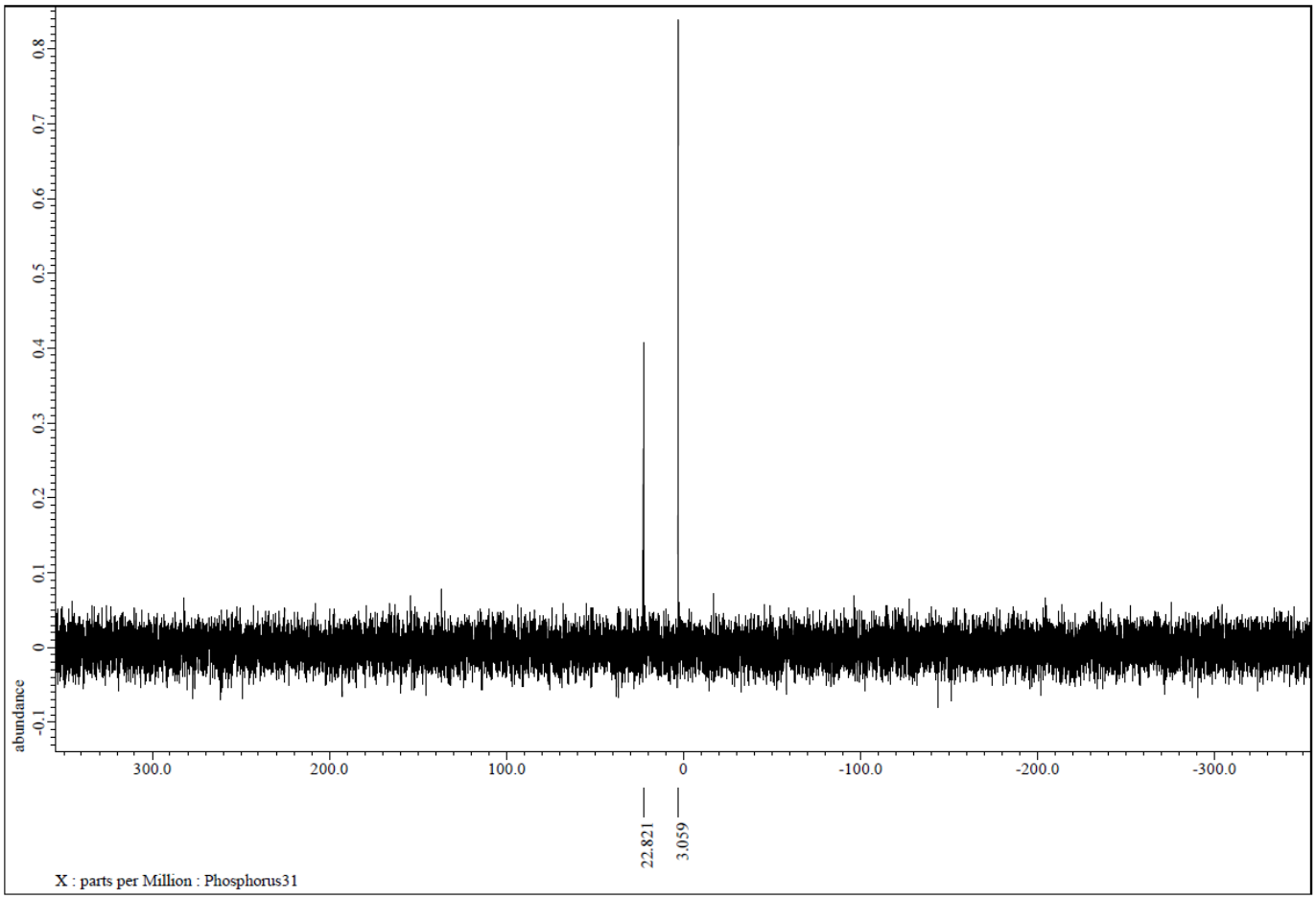
^{1}H NMR (DMSO-d_6)

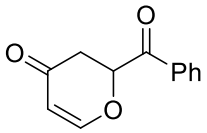


^{13}C NMR (DMSO-d_6)



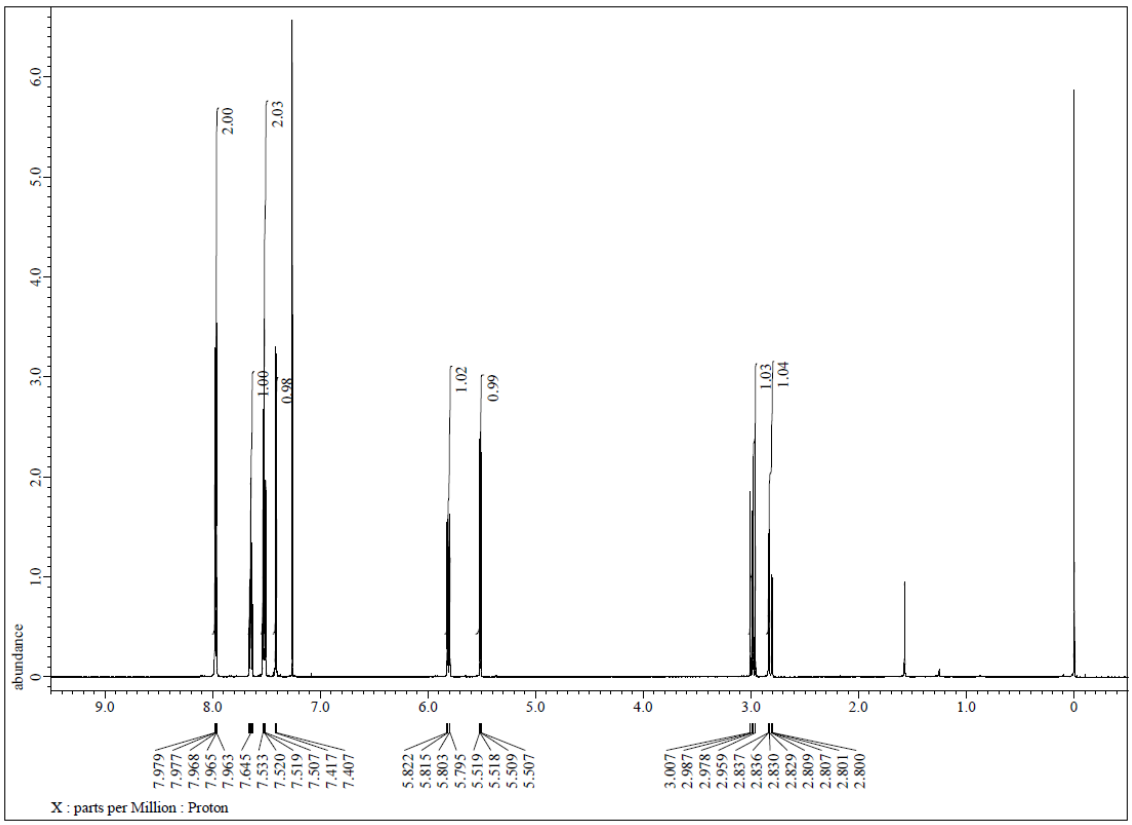
^{31}P NMR (DMSO-d_6)



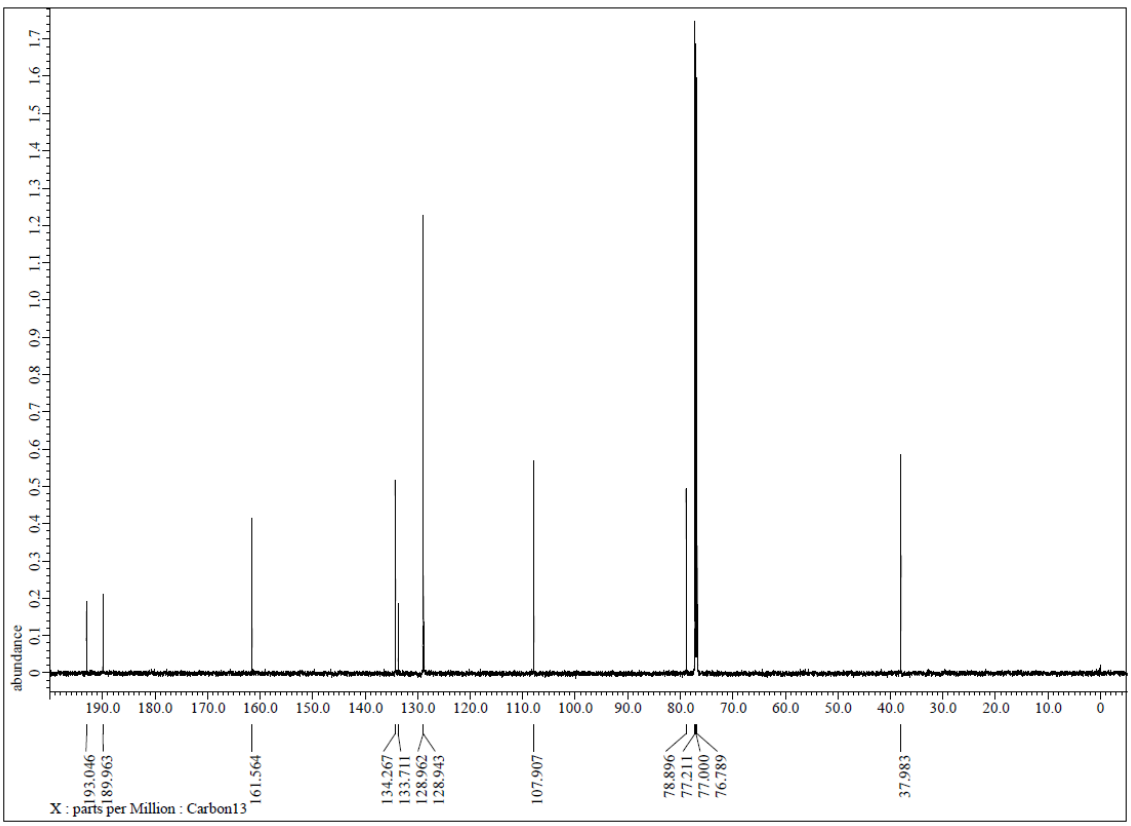


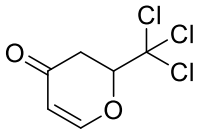
14a

^{1}H NMR ($CDCl_3$)



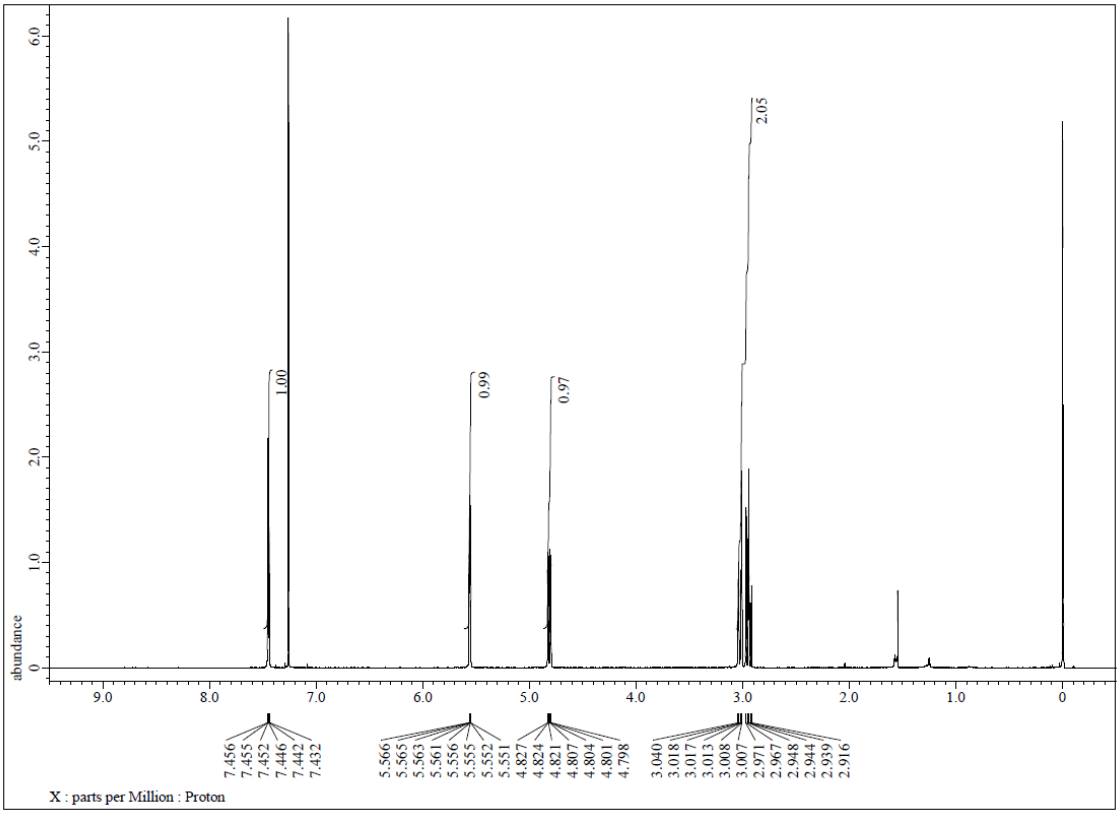
^{13}C NMR ($CDCl_3$)





14b

^{1}H NMR ($CDCl_3$)



^{13}C NMR ($CDCl_3$)