Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

One-Pot Synthesis of 3-Functionalized (*Z*)-Silyl Enol Ethers from 1-Arylallylic Alcohols by *C*,*O*-Difunctionalization of Dipotassio α,β-Dianion Intermediates

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Supporting Information

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1. Instrumentation and Materials

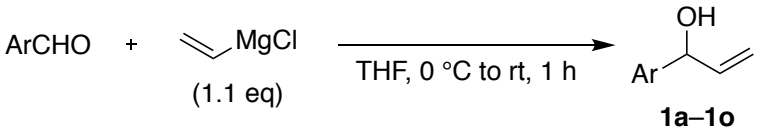
NMR spectra were recorded on JEOL JNM-ECX400P, JNM-ECA500, and JNM-ECA600 spectrometers (400 and 500 MHz for ^{1}H NMR, 101, 126, and 151 MHz for ^{13}C NMR, 565 MHz for ^{19}F NMR, and 202 MHz for ^{31}P NMR). Tetramethylsilane (TMS) served as internal standard (δ = 0) for ^{1}H NMR, and $CDCl_3$ served as internal standard (δ = 77.16) for ^{13}C NMR. $CF_3C_6H_5$ sealed in a glass capillary was used as an external internal standard (δ = –63.72) for ^{19}F NMR. 85% H_3PO_4 sealed in a glass capillary was used as an external internal standard (δ = 0) for ^{31}P NMR. Multiplicities are indicated as: br (broad), s (singlet), d (doublet), t (triplet), q (quartet), or m (multiplet). Coupling constants (*J*) are reported in Hertz (Hz). IR spectra were taken with a Perkin-Elmer spectrum 400. High-resolution mass spectra (HRMS) were recorded on a Waters Xevo Q-Tof mass spectrometer and a Thermo Fisher Scientific Exactive Plus. Melting points were determined with a Yanaco micro melting point apparatus Model MP-J3. Preparative HPLC was performed with a Yamazen EPCLC-AI-580S equipped with Fuji Silysia CHROMATOREX Q-PACK SI 30. Analytical thin-layer chromatography (TLC) was performed on Merck aluminium sheets precoated with silica gel 60 F254. The TLC plates were visualized with UV light (254 nm), anisaldehyde, $KMnO_4$, and phosphomolybdic acid. The reactions at cryogenic temperatures were performed with Techno Sigma UCR-150N.

Unless otherwise noted, all chemicals were purchased from commercial suppliers and used as received. (Trimethylsilyl)methylpotassium ($TMSCH_2K$), *N*-benzylideneaniline, *N*-methoxy-*N*-methylbenzamide, and phenyl *P*,*P*-diphenylphosphinate were prepared according to previously reported procedure.[1] Benzaldehyde was purified by Kugelrohr distillation prior to use. Silyl chlorides were purchased from commercial suppliers and stored in an argon-filled glovebox. Tetrahydrofuran (dehydrated, stabilizer free) was purchased from Kanto Chemical and stored in an argon-filled glovebox.

2. Experimental Details

2.1. Synthesis of Allylic Alcohols and Their Derivatives

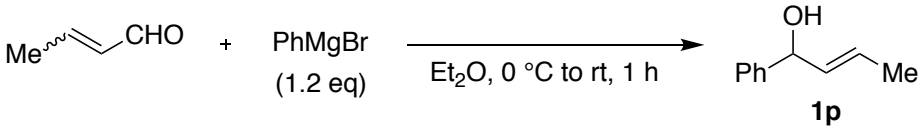
2.1.1. Synthesis of allylic alcohols **1a**–**1o**



1a–**1o**

To a solution of aldehyde (5 mmol) in THF (10 mL) was slowly added vinylmagnesium chloride (1.40 M in THF, 3.93 mL, 5.5 mmol) under argon at 0 °C. The reaction mixture was warmed to room temperature and stirred for 1 h. The reaction was quenched by saturated aq. NH_4Cl solution and extracted with Et_2O. The organic layer was combined, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexane/EtOAc) to give the corresponding allylic alcohol.

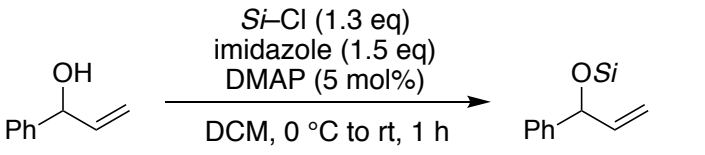
2.1.2. Synthesis of allylic alcohol **1p**



1p

Phenylmagnesium bromide (1 M in Et_2O, 6.0 mL, 6 mmol) was slowly added to a solution of crotonaldehyde (0.41 mL, 5 mmol) in Et_2O (10 mL) under argon at 0 °C. The reaction mixture was warmed to room temperature and stirred for 1 h. The reaction was quenched by saturated aq. NH_4Cl solution and extracted with Et_2O. The organic layer was combined, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexane/EtOAc = 10:1) to give (*E*)-**1p**.

2.1.3. Synthesis of allyloxysilanes **1a**-TES and **1a**-TBS



1a

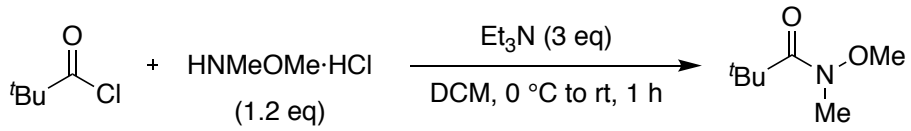
1a-TES (*Si* = TES)
1a-TBS (*Si* = TBS)

To a solution of **1a** (403 mg, 3 mmol) in DCM (8 mL) were added silyl chloride (3.9 mmol), imidazole (306 mg, 4.5 mmol), and DMAP (18 mg, 0.15 mmol) at room temperature. After stirring for 1 h, the reaction was quenched by H_2O and extracted with hexane/EtOAc (10:1). The organic layer was combined, dried over Na_2SO_4, and concentrated under reduced pressure. The residue

was purified by flash chromatography on silica gel (hexane/EtOAc) to give the corresponding allyloxysilane.

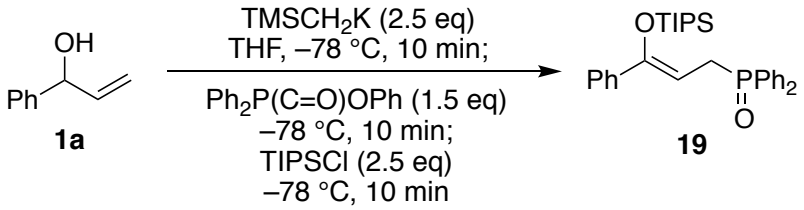
2.2. Synthesis of Electrophiles

2.2.1. Synthesis of *N*-methoxy-*N*-methylpivalamide



To a solution of *N*,*O*-dimethylhydroxylamine hydrochloride (1.17 g, 12 mmol) in DCM (24 mL) was added dropwise triethylamine (4.18 mL, 30 mmol) at 0 °C. Subsequently, pivaloyl chloride (1.22 mL, 10 mmol) was added, and the mixture was warmed to room temperature and stirred for 1 h. The reaction was quenched by H_2O and extracted with DCM. The organic layer was combined, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by Kugelrohr distillation to give *N*-methoxy-*N*-methylpivalamide.

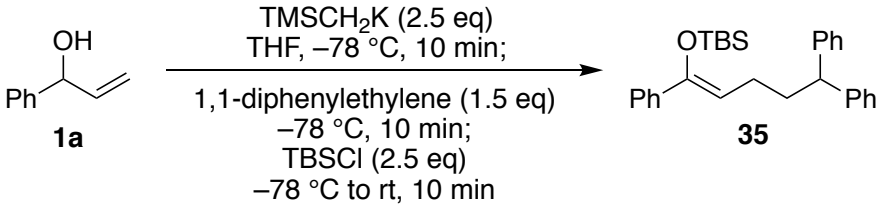
2.3. General Procedure for the Synthesis of 3-Functionalized (*Z*)-Silyl Enol Ethers



Synthesis of **19** is representative: In a glovebox, an oven-dried vial equipped with a magnetic stir bar was charged with $TMSCH_2K$ (78.9 mg, 0.625 mmol). The vial was sealed with a rubber septum and removed from the glovebox. The vial was cooled to –78 °C, and cold THF (2 mL, –78 °C) was added. Allylic alcohol **1a** (33.6 mg, 0.25 mmol) was added via microsyringe, and the mixture was stirred at –78 °C for 10 min. Subsequently, phenyl *P*,*P*-diphenylphosphinate (110.4 mg, 0.375 mmol) dissolved in THF (1 mL) was added at –78 °C. After stirring for 10 min, TIPSCl (132.4 μL, 0.625 mmol) was added via microsyringe, and the mixture was stirred at –78 °C for an additional 10 min. The reaction was quenched by saturated aq. NH_4Cl solution and extracted with EtOAc three times. The organic layer was combined, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (DCM/MeOH = 97:3) to give **19** (91.2 mg, 74% yield) as a colorless oil.

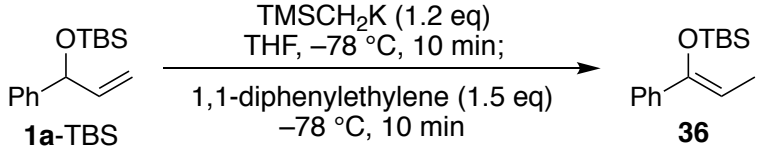
2.4. Procedure for Control Experiments

2.4.1. Procedure for the reaction of dipotassio dianion **A** with 1,1-diphenylethylene



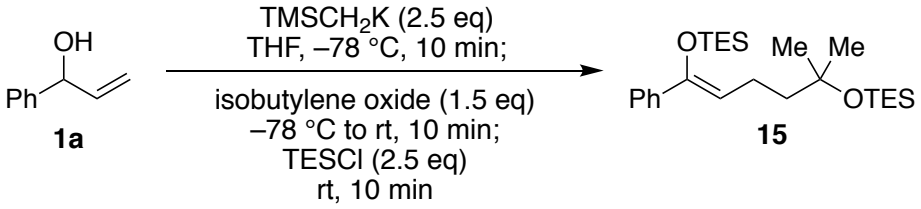
In a glovebox, an oven-dried vial equipped with a magnetic stir bar was charged with $TMSCH_2K$ (78.9 mg, 0.625 mmol). The vial was sealed with a rubber septum and removed from the glovebox. The vial was cooled to –78 °C, and cold THF (3 mL, –78 °C) was added. Allylic alcohol **1a** (33.6 mg, 0.25 mmol) was added via microsyringe, and the mixture was stirred at –78 °C for 10 min. Subsequently, 1,1-diphenylethylene (65.6 μL, 0.375 mmol) was added via microsyringe at –78 °C. After stirring for 10 min, TBSCl (94.2 mg, 0.625 mmol) dissolved in THF (1 mL) was added, and the mixture was stirred at –78 °C for an additional 10 min. The reaction was quenched by saturated aq. NH_4Cl solution and extracted with EtOAc three times. The organic layer was combined, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexane/EtOAc = 99:1) to give **35** (78.5 mg, 73% yield) as a colorless oil.

2.4.2. Procedure for the reaction of siloxyallylpotassium **B** with 1,1-diphenylethylene



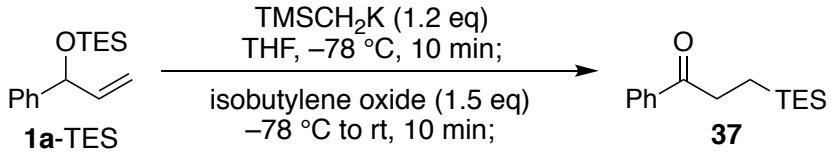
In a glovebox, an oven-dried vial equipped with a magnetic stir bar was charged with $TMSCH_2K$ (37.9 mg, 0.30 mmol). The vial was sealed with a rubber septum and removed from the glovebox. The vial was cooled to –78 °C, and cold THF (3 mL, –78 °C) was added. Allyloxysilane **1a**-TBS (62.1 mg, 0.25 mmol) was added via microsyringe, and the mixture was stirred at –78 °C for 10 min. Subsequently, 1,1-diphenylethylene (65.6 μL, 0.375 mmol) was added via microsyringe at –78 °C, and the mixture was stirred at this temperature for an additional 10 min. The reaction was quenched by saturated aq. NH_4Cl solution and extracted with EtOAc three times. The organic layer was combined, dried over Na_2SO_4, and concentrated under reduced pressure. The yield of **36** was determined by ^1H NMR analysis of the crude reaction mixture using dibenzyl ether as internal standard.

2.4.3. Procedure for the reaction of dipotassio dianion **A** with isobutylene oxide



In a glovebox, an oven-dried vial equipped with a magnetic stir bar was charged with $TMSCH_2K$ (78.9 mg, 0.625 mmol). The vial was sealed with a rubber septum and removed from the glovebox. The vial was cooled to –78 °C, and cold THF (3 mL, –78 °C) was added. Allylic alcohol **1a** (33.6 mg, 0.25 mmol) was added via microsyringe, and the mixture was stirred at –78 °C for 10 min. Isobutylene oxide (33.8 μL, 0.375 mmol) was added via microsyringe at –78 °C, and the vial was warmed to room temperature with a water bath and stirred for 10 min. Subsequently, TESCl (104.7 μL, 0.625 mmol) was added via microsyringe at room temperature, and the mixture was stirred for an additional 10 min. The reaction was quenched by saturated aq. NH_4Cl solution and extracted with EtOAc three times. The organic layer was combined, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexane/EtOAc = 99:1) to give **15** (66.5 mg, 61% yield) as a colorless oil.

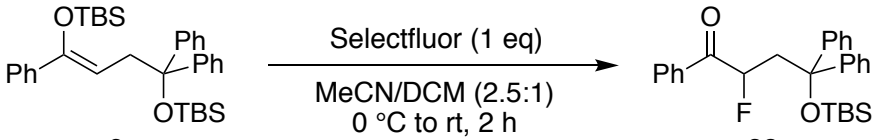
2.4.4. Procedure for the reaction of siloxyallylpotassium **C** with isobutylene oxide



In a glovebox, an oven-dried vial equipped with a magnetic stir bar was charged with $TMSCH_2K$ (37.9 mg, 0.30 mmol). The vial was sealed with a rubber septum and removed from the glovebox. The vial was cooled to –78 °C, and cold THF (2 mL, –78 °C) was added. To the vial was added allyloxysilane **1a**-TES (62.1 mg, 0.25 mmol) dissolved in THF (1 mL), and the mixture was stirred at –78 °C for 10 min. Subsequently, isobutylene oxide (33.8 μL, 0.375 mmol) was added via microsyringe at –78 °C, and the mixture was warmed to room temperature with a water bath and stirred for an additional 10 min. The reaction was quenched by saturated aq. NH_4Cl solution and extracted with EtOAc three times. The organic layer was combined, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexane/EtOAc = 49:1) to give **37** (48.5 mg, 78% yield) as a colorless oil.

2.5. Procedure for the Transformations of the Product (Scheme 6)

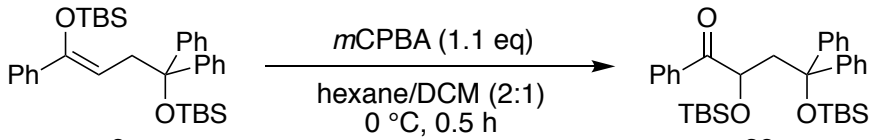
2.5.1. Procedure for the reaction of **6** with Selectfluor



6 **38**

Silyl enol ether **6** (54.5 mg, 0.10 mmol) was dissolved in MeCN (1 mL) and DCM (0.4 mL). To the vial was added Selectfluor (35.4 mg, 0.10 mmol) at 0 °C, and the mixture was stirred at 0 °C for 1 h and at room temperature for an additional 1 h. The reaction was quenched by saturated aq. $NaHCO_3$ solution and extracted with hexane/EtOAc (5:1) three times. The organic layer was combined, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexane/EtOAc = 49:1) to give **38** (43.7 mg, 97% yield) as a colorless oil.

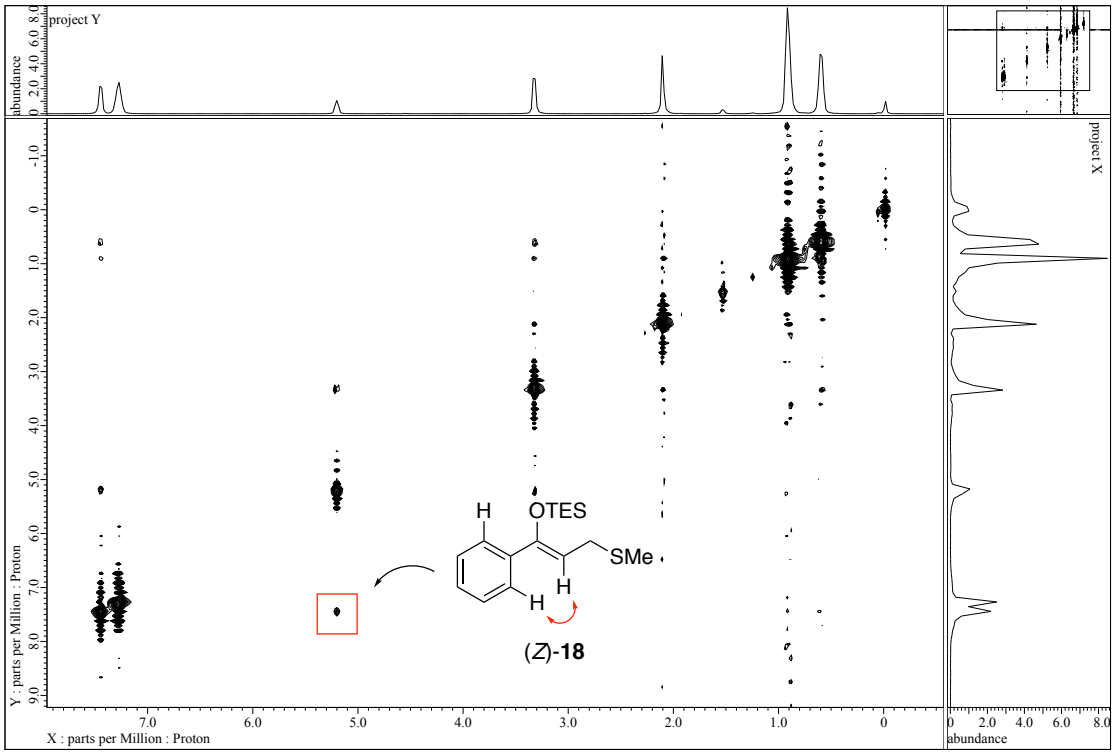
2.5.2. Procedure for the reaction of **6** with *m*CPBA



6 **39**

Silyl enol ether **6** (54.5 mg, 0.10 mmol) was dissolved in hexane (1 mL) and DCM (0.5 mL). To the vial was added *m*CPBA (contains ca. 30% water, 27.1 mg, 0.11 mmol) at 0 °C, and the mixture was stirred at 0 °C for 0.5 h. The reaction was quenched by saturated aq. $NaHCO_3$ solution and extracted with hexane/EtOAc (5:1) three times. The organic layer was combined, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexane/EtOAc = 49:1) to give **39** (40.6 mg, 72% yield) as a colorless oil.

2.6. Determination of *Z*-Configuration of 18 by NOESY

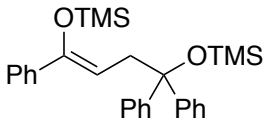


3. Characterization Data

Allylic alcohols, 1-phenylprop-2-en-1-ol (**1a**), 1-(naphthalen-2-yl)prop-2-en-1-ol (**1b**), 1-(naphthalen-1-yl)prop-2-en-1-ol (**1c**), 1-(4-(dimethylamino)phenyl)prop-2-en-1-ol (**1e**), 1-(4-methoxyphenyl)prop-2-en-1-ol (**1f**), 1-(2-methoxyphenyl)prop-2-en-1-ol (**1g**), 1-(3,4-dimethoxyphenyl)prop-2-en-1-ol (**1h**), 1-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)prop-2-en-1-ol (**1i**), 1-(4-fluorophenyl)prop-2-en-1-ol (**1j**), and (*E*)-1-phenylbut-2-en-1-ol (**1p**) were reported in our previous study.[1] Allylic alcohols and their ethers, triethyl((1-phenylallyl)oxy)silane (**1a**-TES),[2] *tert*-butyldimethyl((1-phenylallyl)oxy)silane (**1a**-TBS),[3] 1-(*p*-tolyl)prop-2-en-1-ol (**1d**),[4] 1-(benzofuran-2-yl)prop-2-en-1-ol (**1l**),[5] 1-(pyridin-2-yl)prop-2-en-1-ol (**1m**),[6] 1-(pyridin-3-yl)prop-2-en-1-ol (**1n**),[7] and silyl enol ether **36**[8] were reported in the literatures.

Characterization Data for the Products

(*Z*)-2,2,9,9-Tetramethyl-4,7,7-triphenyl-3,8-dioxa-2,9-disiladec-4-ene (2)



Yield: 74.7 mg, 65% yield, white solid.

R_f: 0.29 (hexane/EtOAc = 50:1).

IR (ATR): 3059, 3024, 2956, 2896, 1649, 1599, 1492, 1446, 1344, 1286, 1250, 1070, 1021 cm^{-1}.

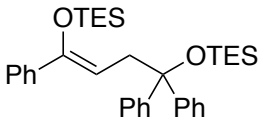
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.26–7.24 (m, 4H), 7.17–7.04 (m, 11H), 5.03 (t, J = 6.0 Hz, 1H), 3.13 (d, J = 6.0 Hz, 2H), –0.03 (s, 9H), –0.20 (s, 9H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 150.3, 148.0, 139.4, 128.1, 127.9, 127.5, 127.1, 126.7, 125.6, 106.9, 80.7, 38.6, 2.0, 0.9 ppm.

HRMS (ESI): *m/z* calcd. for $C_{28}H_{36}O_2Si_2Na$ $[M+Na]^+$: 483.2146, found: 483.2148.

M.p.: 35–36 °C.

(*Z*)-3,3,10,10-Tetraethyl-5,8,8-triphenyl-4,9-dioxa-3,10-disiladodec-5-ene (3)



Yield: 93.1 mg, 68% yield, colorless oil.

R_f: 0.28 (hexane/EtOAc = 50:1).

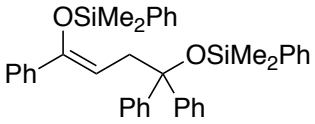
IR (ATR): 3059, 3025, 2955, 2909, 2876, 1649, 1600, 1492, 1458, 1456, 1413, 1345, 1286, 1238, 1069 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.37 (d, *J* = 7.5 Hz, 4H), 7.28–7.17 (m, 11H), 5.06 (t, *J* = 6.0 Hz, 1H), 3.26 (d, *J* = 6.0 Hz, 2H), 0.91 (t, *J* = 8.0 Hz, 9H), 0.84 (t, *J* = 8.0 Hz, 9H), 0.56 (q, *J* = 8.0 Hz, 6H), 0.41 (q, *J* = 8.0 Hz, 6H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 150.5, 148.2, 139.9, 128.0, 127.8, 127.4, 127.3, 126.7, 125.7, 106.8, 80.5, 38.7, 7.3, 6.9, 6.4, 5.6 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{34}H_{48}O_2Si_2Na$ $[M+Na]^+$: 567.3085, found: 567.3103.

(*Z*)-2,9-Dimethyl-2,4,7,7,9-pentaphenyl-3,8-dioxa-2,9-disiladec-4-ene (4)



Yield: 98.2 mg, 67% yield, pale yellow solid.

R_f: 0.28 (hexane/EtOAc = 50:1).

IR (ATR): 3067, 3024, 2962, 2948, 1645, 1491, 1445, 1428, 1250, 1118, 1067 cm^{-1}.

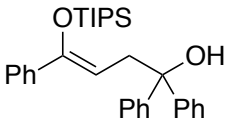
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.62–7.60 (m, 2H), 7.49–7.39 (m, 5H), 7.33–7.12 (m, 18H), 5.17 (t, *J* = 6.5 Hz, 1H), 3.00 (d, *J* = 6.5 Hz, 2H), 0.30 (s, 6H), 0.06 (s, 6H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 150.1, 147.6, 139.8, 139.0, 138.1, 133.6, 133.5, 129.9, 129.1, 128.1, 128.0, 127.8, 127.7, 127.4, 127.0, 126.7, 125.4, 107.0, 81.0, 38.7, 0.6, –1.0 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{38}H_{40}O_2Si_2Na$ $[M+Na]^+$: 607.2459, found: 607.2463.

M.p.: 39–41 °C.

(*Z*)-1,1,4-Triphenyl-4-((triisopropylsilyl)oxy)but-3-en-1-ol (5)



Yield: 77.6 mg, 66% yield, white solid.

R_f: 0.13 (hexane/EtOAc = 50:1).

IR (ATR): 3559, 3026, 2937, 2862, 1638, 1491, 1445, 1343, 1280, 1114, 1058 cm^{-1}.

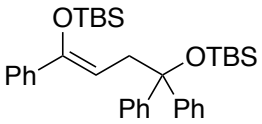
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.39 (d, *J* = 8.0 Hz, 4H), 7.30–7.29 (m, 2H), 7.22 (app. t, *J* = 7.5 Hz, 4H), 7.17–7.11 (m, 5H), 4.85–4.82 (m, 1H), 3.17–3.16 (m, 2H), 2.66 (br d, *J* = 3.0 Hz, 1H), 1.01–0.95 (m, 21H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 154.3, 147.2, 139.9, 128.2 (two signals merged), 128.1, 126.8, 126.5, 126.3, 104.9, 78.4, 39.4, 18.0, 13.6 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{31}H_{40}O_2SiNa$ $[M+Na]^+$: 495.2690, found: 495.2689.

M.p.: 76–77 °C.

(*Z*)-2,2,3,3,10,10,11,11-Octamethyl-5,8,8-triphenyl-4,9-dioxa-3,10-disiladodec-5-ene (6)



Yield: 93.4 mg, 69% yield, white solid.

R_f: 0.22 (hexane/EtOAc = 50:1).

IR (ATR): 3059, 2953, 2930, 2891, 2856, 1655, 1599, 1491, 1472, 1445, 1354, 1253, 1100, 1068 cm^{-1}.

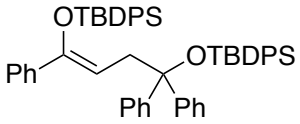
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.39 (d, *J* = 7.0 Hz, 4H), 7.29–7.18 (m, 11H), 5.02 (t, *J* = 6.5 Hz, 1H), 3.28 (d, *J* = 6.5 Hz, 2H), 1.04 (s, 9H), 0.95 (s, 9H), –0.06 (s, 6H), –0.23 (s, 6H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 150.3, 147.8, 139.9, 127.9, 127.7, 127.6, 127.4, 126.8, 126.1, 107.5, 80.7, 38.7, 26.3, 26.1, 18.9, 18.5, –2.9, –3.7 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{34}H_{48}O_2Si_2Na$ $[M+Na]^+$: 567.3085, found: 567.3086.

M.p.: 85–86 °C.

(*Z*)-2,2,11,11-Tetramethyl-3,3,5,8,8,10,10-heptaphenyl-4,9-dioxa-3,10-disiladodec-5-ene (7)



Yield: 89.7 mg, 45% yield, white solid.

R_f: 0.33 (hexane/EtOAc = 50:1).

IR (ATR): 3051, 2957, 2930, 2856, 1653, 1590, 1492, 1472, 1445, 1427, 1360, 1279, 1104, 1060 cm^{-1}.

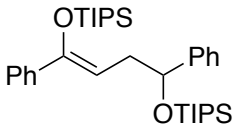
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.53 (d, *J* = 8.0 Hz, 4H), 7.38–7.33 (m, 6H), 7.29–7.23 (m, 6H), 7.11 (t, *J* = 7.5 Hz, 4H), 7.08–7.02 (m, 7H), 6.97 (t, *J* = 7.5 Hz, 4H), 6.90–6.88 (m, 4H), 4.97 (t, *J* = 6.0 Hz, 1H), 2.80 (d, *J* = 6.0 Hz, 2H), 0.94 (s, 9H), 0.93 (s, 9H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 150.6, 146.8, 139.6, 136.2, 135.7, 134.7, 133.8, 129.6, 129.0, 127.7 (two signals merged), 127.6, 127.4, 127.2, 127.1, 126.5, 126.4, 107.5, 82.2, 39.4, 27.6, 27.0, 20.03, 19.97 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{54}H_{56}O_2Si_2Na$ $[M+Na]^+$: 815.3711, found: 815.3716.

M.p.: 130–131 °C.

(Z)-3,3,10,10-Tetraisopropyl-2,11-dimethyl-5,8-diphenyl-4,9-dioxa-3,10-disiladodec-5-ene (8)



Yield: 83.1 mg, 60% yield, colorless oil.

R_f: 0.34 (hexane/EtOAc = 50:1).

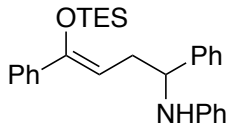
IR (ATR): 2944, 2891, 2866, 1649, 1600, 1492, 1463, 1341, 1279, 1092, 1056 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.36–7.33 (m, 4H), 7.30–7.19 (m, 6H), 4.96 (t, *J* = 6.5 Hz, 1H), 4.85 (t, *J* = 6.5 Hz, 1H), 2.78–2.73 (m, 1H), 2.62 (ddd, *J* = 15.0, 6.5, 6.5 Hz, 1H), 1.03–0.94 (m, 42H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 151.4, 145.7, 140.6, 128.0, 127.9, 127.5, 127.0, 126.3, 126.2, 106.9, 75.2, 38.0, 18.2, 18.1, 18.0, 13.6, 12.5 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{34}H_{56}O_2Si_2Na$ $[M+Na]^+$: 575.3711, found: 575.3721.

(*Z*)-*N*-(1,4-Diphenyl-4-((triethylsilyl)oxy)but-3-en-1-yl)aniline (9)



Yield: 65.2 mg, 61% yield, pale pink solid.

R_f: 0.32 (hexane/EtOAc = 50:1).

IR (ATR): 3401, 3052, 3027, 2957, 2875, 1648, 1599, 1503, 1450, 1421, 1346, 1316, 1267, 1012 cm^{-1}.

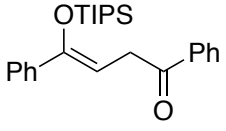
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.48–7.45 (m, 4H), 7.38–7.25 (m, 6H), 7.09 (app. t, *J* = 7.5 Hz, 2H), 6.64 (t, *J* = 7.5 Hz, 1H), 6.50 (d, *J* = 8.0 Hz, 2H), 5.19 (t, *J* = 7.5 Hz, 1H), 4.67 (br s, 1H), 4.41 (dd, *J* = 8.5, 4.5 Hz, 1H), 2.78 (app. dt, *J* = 15.0, 8.0 Hz, 1H), 2.65 (ddd, *J* = 15.0, 7.0, 4.5 Hz, 1H), 0.98 (t, *J* = 8.0 Hz, 9H), 0.65 (q, *J* = 8.0 Hz, 6H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 152.7, 148.0, 144.3, 139.2, 129.1, 128.7, 128.2, 128.1, 127.0, 126.4, 126.0, 117.0, 113.3, 106.8, 59.1, 35.8, 6.8, 5.5 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{28}H_{36}ONSi$ $[M+H]^+$: 430.2561, found: 430.2565.

M.p.: 32–33 °C.

(*Z*)-1,4-Diphenyl-4-((triisopropylsilyl)oxy)but-3-en-1-one (10)



Yield: 55.3 mg, 56% yield, colorless oil.

R_f: 0.27 (hexane/EtOAc = 50:1).

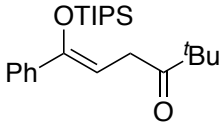
IR (ATR): 3059, 2945, 2866, 1686, 1599, 1581, 1464, 1448, 1276 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.03 (d, *J* = 7.0 Hz, 2H), 7.56 (t, *J* = 7.0 Hz, 1H), 7.50–7.45 (m, 4H), 7.32–7.25 (m, 3H), 5.37 (t, *J* = 7.0 Hz, 1H), 3.97 (d, *J* = 7.0 Hz, 2H), 1.13–1.03 (m, 21H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 198.4, 152.6, 139.7, 136.8, 133.1, 128.7, 128.4, 128.1 (two signals merged), 126.4, 103.1, 37.1, 18.0, 13.6 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{25}H_{35}O_2Si$ $[M+H]^+$: 395.2401, found: 395.2397.

(*Z*)-2,2-Dimethyl-6-phenyl-6-((triisopropylsilyl)oxy)hex-5-en-3-one (11)



Yield: 70.5 mg, 75% yield, colorless oil.

R_f: 0.28 (hexane/EtOAc = 50:1).

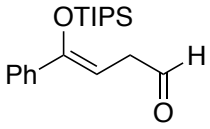
IR (ATR): 2946, 2867, 1709, 1650, 1492, 1464, 1446, 1340, 1276, 1114, 1069 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.47–7.45 (m, 2H), 7.30–7.25 (m, 3H), 5.26 (t, *J* = 6.5 Hz, 1H), 3.51 (d, *J* = 6.5 Hz, 2H), 1.18 (s, 9H), 1.09–1.02 (m, 21H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 213.9, 152.1, 139.8, 128.0, 127.9, 126.3, 103.4, 44.3, 34.7, 26.7, 18.0, 13.6 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{23}H_{39}O_2Si$ $[M+H]^+$: 375.2714, found: 375.2704.

(*Z*)-4-Phenyl-4-((triisopropylsilyl)oxy)but-3-enal (12)



Yield: 32.1 mg, 40% yield, colorless oil.

R_f: 0.20 (hexane/EtOAc = 10:1).

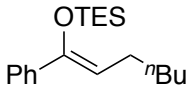
IR (ATR): 2945, 2892, 2867, 1702, 1649, 1492, 1464, 1447, 1336, 1279, 1058 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.74 (t, *J* = 1.5 Hz, 1H), 7.48–7.46 (m, 2H), 7.33–7.28 (m, 3H), 5.14 (t, *J* = 6.0 Hz, 1H), 3.37 (dd, *J* = 6.0, 1.5 Hz, 2H), 1.08–1.00 (m, 21H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 200.3, 154.5, 139.5, 128.4, 128.2, 126.5, 99.5, 41.7, 18.0, 13.6 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{19}H_{31}O_2Si$ $[M+H]^+$: 319.2088, found: 319.2087.

(*Z*)-Triethyl((1-phenylhept-1-en-1-yl)oxy)silane (13)



Yield: 31.2 mg, 41% yield, colorless oil.

R_f: 0.67 (hexane).

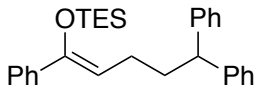
IR (ATR): 2955, 2916, 2876, 2855, 1648, 1600, 1492, 1458, 1446, 1330, 1278, 1081, 1004 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.46–7.44 (m, 2H), 7.30–7.26 (m, 2H), 7.24–7.21 (m, 1H), 5.13 (t, *J* = 7.5 Hz, 1H), 2.20 (app. q, *J* = 7.5 Hz, 2H), 1.45–1.39 (m, 2H), 1.37–1.32 (m, 4H), 0.95–0.89 (m, 12H), 0.60 (q, *J* = 8.0 Hz, 6H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 149.4, 139.9, 128.1, 127.4, 125.7, 111.7, 31.9, 29.6, 26.3, 22.8, 14.2, 6.9, 5.5 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{19}H_{33}OSi$ $[M+H]^+$: 305.2295, found: 305.2318.

(*Z*)-Triethyl((1,5,5-triphenylpent-1-en-1-yl)oxy)silane (14)



Yield: 60.5 mg, 56% yield, colorless oil.

R_f: 0.20 (hexane).

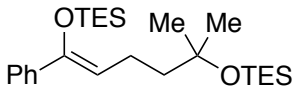
IR (ATR): 3060, 3025, 2955, 2875, 1647, 1599, 1493, 1449, 1412, 1325, 1278, 1103, 1051, 1003 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.42 (d, *J* = 7.5 Hz, 2H), 7.28–7.20 (m, 11H), 7.17–7.14 (m, 2H), 5.14 (app. br s, 1H), 3.95 (app. br s, 1H), 2.18–2.16 (m, 4H), 0.84–0.80 (m, 9H), 0.49–0.44 (m, 6H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 149.9, 145.2, 139.7, 128.5, 128.1 (two signals merged), 127.5, 126.2, 125.7, 110.7, 51.3, 35.8, 24.9, 6.8, 5.4 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{29}H_{36}OSiNa$ $[M+Na]^+$: 451.2428, found: 451.2424.

(*Z*)-3,3,11,11-Tetraethyl-9,9-dimethyl-5-phenyl-4,10-dioxa-3,11-disilatridec-5-ene (15)



Yield: 66.5 mg, 61% yield, colorless oil.

R_f: 0.38 (hexane/EtOAc = 50:1).

IR (ATR): 2956, 2911, 2876, 1648, 1600, 1493, 1458, 1413, 1363, 1329, 1236, 1145, 1052, 1004 cm^{-1}.

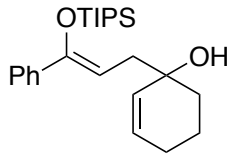
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.45 (dd, *J* = 7.0, 1.0 Hz, 2H), 7.28 (app. t, *J* = 6.5 Hz, 2H), 7.22 (tt, *J* = 6.5, 1.0 Hz, 1H), 5.10 (t, *J* = 6.0 Hz, 1H), 2.31–2.27 (m, 2H), 1.56–1.53 (m, 2H), 1.24 (s, 6H),

0.96 (t, *J* = 6.5 Hz, 9H), 0.93 (t, *J* = 6.5 Hz, 9H), 0.61 (q, *J* = 6.5 Hz, 6H), 0.58 (q, *J* = 6.5 Hz, 6H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 149.3, 139.9, 128.1, 127.4, 125.6, 112.0, 73.4, 45.0, 30.0, 21.5, 7.3, 6.93, 6.87, 5.5 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{25}H_{46}O_2Si_2Na$ $[M+Na]^+$: 457.2929, found: 457.2938.

(*Z*)-1-(3-Phenyl-3-((triisopropylsilyl)oxy)allyl)cyclohex-2-en-1-ol (16)



Yield: 56.2 mg, 58% yield, colorless oil.

R_f: 0.20 (hexane/EtOAc = 10:1).

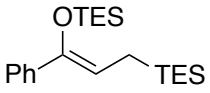
IR (ATR): 3354, 3022, 2943, 2866, 1646, 1600, 1492, 1464, 1446, 1390, 1335, 1279, 1066 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.46 (d, *J* = 6.5 Hz, 2H), 7.30–7.23 (m, 3H), 5.80 (dt, *J* = 10.0, 4.0 Hz, 1H), 5.68 (d, *J* = 10.0 Hz, 1H), 5.07 (t, *J* = 7.5 Hz, 1H), 2.58 (dd, *J* = 14.0, 8.0 Hz, 1H), 2.41 (dd, *J* = 14.0, 6.5 Hz, 1H), 2.06–2.01 (m, 1H), 1.96–1.89 (m, 1H), 1.87 (br s, 1H), 1.78–1.63 (m, 4H), 1.08–1.02 (m, 21H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 153.0, 140.2, 132.7, 130.1, 128.0, 127.8, 126.4, 105.5, 70.3, 39.0, 35.9, 25.4, 19.2, 18.0, 13.6 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{24}H_{38}O_2SiNa$ $[M+Na]^+$: 409.2533, found: 409.2532.

(*Z*)-Triethyl(3-phenyl-3-((triethylsilyl)oxy)allyl)silane (17)



Yield: 80.3 mg, 89% yield, colorless oil.

R_f: 0.80 (hexane).

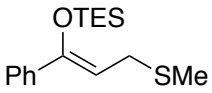
IR (ATR): 2952, 2909, 2876, 1638, 1599, 1492, 1458, 1414, 1325, 1273, 1086, 1005 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.41 (d, *J* = 7.5 Hz, 2H), 7.26 (app. t, *J* = 7.5 Hz, 2H), 7.19 (t, *J* = 7.5 Hz, 1H), 5.14 (t, *J* = 8.5 Hz, 1H), 1.62 (d, *J* = 8.5 Hz, 2H), 0.95 (t, *J* = 8.0 Hz, 9H), 0.93 (t, *J* = 8.0 Hz, 9H), 0.61 (q, *J* = 8.0 Hz, 6H), 0.55 (q, *J* = 8.0 Hz, 6H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 148.2, 140.4, 128.0, 126.9, 125.5, 107.4, 11.6, 7.6, 6.9, 5.7, 3.7 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{21}H_{39}OSi_2$ $[M+H]^+$: 363.2534, found: 363.2543.

(*Z*)-Triethyl((3-(methylthio)-1-phenylprop-1-en-1-yl)oxy)silane (18)



Yield: 58.8 mg, 80% yield, colorless oil.

R_f: 0.35 (hexane/EtOAc = 50:1).

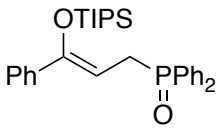
IR (ATR): 3059, 2956, 2913, 2876, 1639, 1600, 1492, 1458, 1446, 1413, 1330, 1273, 1102, 1003 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.46 (d, *J* = 7.0 Hz, 2H), 7.32–7.25 (m, 3H), 5.22 (t, *J* = 8.0 Hz, 1H), 3.34 (d, *J* = 8.0 Hz, 2H), 2.11 (s, 3H), 0.92 (t, *J* = 8.0 Hz, 9H), 0.61 (q, *J* = 8.0 Hz, 6H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 152.2, 139.1, 128.2, 128.1, 125.9, 107.0, 29.8, 15.0, 6.8, 5.5 ppm.

HRMS (ESI): *m/z* calcd. for $C_{16}H_{27}OSSi$ $[M+H]^+$: 295.1546, found: 295.1555.

(*Z*)-Diphenyl(3-phenyl-3-((triisopropylsilyl)oxy)allyl)phosphine oxide (19)



Yield: 91.2 mg, 74% yield, colorless oil.

R_f: 0.38 (DCM/MeOH = 32:1).

IR (ATR): 3058, 2945, 2867, 1642, 1592, 1491, 1464, 1437, 1390, 1331, 1275, 1204, 1099 cm^{-1}.

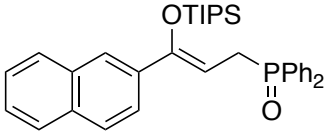
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.78–7.74 (m, 4H), 7.52–7.49 (m, 2H), 7.46–7.42 (m, 4H), 7.33–7.31 (m, 2H), 7.27–7.24 (m, 3H), 5.11 (dt, *J* = 7.5, 7.0 Hz, 1H), 3.34 (dd, *J* = 15.5, 7.5 Hz, 2H), 1.05–0.97 (m, 21H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 153.8 (d, J_{C-P} = 12.0 Hz), 139.5, 133.0 (d, J_{C-P} = 98.5 Hz), 131.8, 131.2 (d, J_{C-P} = 9.6 Hz), 128.5 (d, J_{C-P} = 9.7 Hz), 128.2, 128.0, 126.3, 99.5 (d, J_{C-P} = 7.2 Hz), 29.2 (d, J_{C-P} = 72.2 Hz), 17.9, 13.5 ppm.

^{31}P NMR ($CDCl_3$, 202 MHz): δ 31.2 ppm.

HRMS (ESI): *m/z* calcd. for $C_{30}H_{40}O_2PSi$ $[M+H]^+$: 491.2530, found: 491.2530.

(*Z*)-(3-(Naphthalen-2-yl)-3-((triisopropylsilyl)oxy)allyl)diphenylphosphine oxide (20)



Yield: 80.6 mg, 60% yield, light brown solid.

R_f: 0.35 (DCM/MeOH = 32:1).

IR (ATR): 3059, 2944, 2923, 2862, 1639, 1593, 1504, 1461, 1436, 1353, 1317, 1277, 1259, 1224, 1189, 1103 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.81–7.76 (m, 7H), 7.72 (d, *J* = 8.5 Hz, 1H), 7.52–7.49 (m, 2H), 7.46–7.42 (m, 7H), 5.27 (dt, *J* = 7.5, 7.5 Hz, 1H), 3.40 (dd, *J* = 15.5, 7.5 Hz, 2H), 1.09–0.96 (m, 21H) ppm.

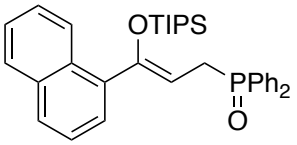
^{13}C NMR ($CDCl_3$, 126 MHz): δ 153.8 (d, J_{C-P} = 12.0 Hz), 136.8, 133.2, 133.01 (d, J_{C-P} = 98.5 Hz), 133.00, 131.8, 131.2 (d, J_{C-P} = 9.6 Hz), 128.6 (d, J_{C-P} = 12.1 Hz), 128.3, 127.7 (two signals merged), 126.3, 126.2, 125.0, 124.5, 100.2 (d, J_{C-P} = 7.2 Hz), 29.5 (d, J_{C-P} = 72.2 Hz), 18.0, 13.6, ppm.

^{31}P NMR ($CDCl_3$, 202 MHz): δ 31.9 ppm.

HRMS (ESI): *m/z* calcd. for $C_{34}H_{42}O_2PSi$ $[M+H]^+$: 541.2686, found: 541.2666.

M.p.: 91–92 °C.

(*Z*)-(3-(Naphthalen-1-yl)-3-((triisopropylsilyl)oxy)allyl)diphenylphosphine oxide (21)



Yield: 73.2 mg, 54% yield, yellow oil.

R_f: 0.30 (DCM/MeOH = 32:1).

IR (ATR): 3058, 2944, 2866, 1649, 1592, 1508, 1463, 1437, 1390, 1312, 1247, 1193, 1116 cm^{-1}.

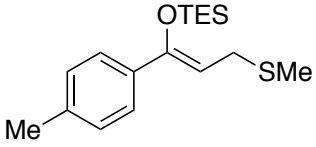
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.86–7.82 (m, 4H), 7.76–7.72 (m, 2H), 7.59–7.54 (m, 3H), 7.50–7.46 (m, 4H), 7.41–7.38 (m, 1H), 7.34–7.31 (m, 2H), 7.30–7.26 (m, 1H), 5.08 (dt, *J* = 6.5, 7.5 Hz, 1H), 3.48 (dd, *J* = 15.0, 7.5 Hz, 2H), 0.90–0.81 (m, 21H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 153.0 (d, J_{C-P} = 12.0 Hz), 137.5, 133.4, 133.1 (d, J_{C-P} = 96.1 Hz), 131.8, 131.6, 131.3 (d, J_{C-P} = 9.7 Hz), 128.8, 128.6 (d, J_{C-P} = 12.0 Hz), 128.0, 126.7, 126.3, 125.9, 125.8, 125.0, 101.9 (d, J_{C-P} = 7.2 Hz), 29.0 (d, J_{C-P} = 72.2 Hz), 17.8, 13.1 ppm.

^{31}P NMR ($CDCl_3$, 202 MHz): δ 31.1 ppm.

HRMS (ESI): *m/z* calcd. for $C_{34}H_{42}O_2PSi$ $[M+H]^+$: 541.2686, found: 541.2709.

(*Z*)-Triethyl((3-(methylthio)-1-(*p*-tolyl)prop-1-en-1-yl)oxy)silane (22)



Yield: 58.1 mg, 75% yield, colorless oil.

R_f: 0.30 (hexane/EtOAc = 50:1).

IR (ATR): 2955, 2914, 2876, 1639, 1509, 1458, 1412, 1326, 1274, 1239, 1101, 1004 cm^{-1}.

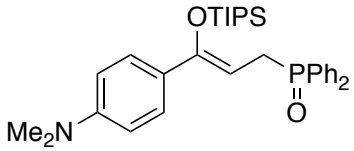
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.35 (d, *J* = 7.5 Hz, 2H), 7.11 (d, *J* = 7.5 Hz, 2H), 5.17 (t, *J* = 8.5 Hz,

1H), 3.32 (d, J = 8.5 Hz, 2H), 2.34 (s, 3H), 2.10 (s, 3H), 0.93 (t, J = 8.0 Hz, 9H), 0.61 (q, J = 8.0 Hz, 6H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 152.2, 137.9, 136.3, 128.9, 125.8, 106.2, 29.8, 21.3, 15.0, 6.8, 5.5 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{17}H_{29}OSSi$ $[M+H]^+$: 309.1703, found: 309.1702.

(*Z*)-(3-(4-(Dimethylamino)phenyl)-3-((triisopropylsilyl)oxy)allyl)diphenylphosphine oxide (23)



Yield: 84.4 mg, 63% yield, yellow solid.

R_f: 0.37 (DCM/MeOH = 32:1).

IR (ATR): 2961, 2943, 2865, 1636, 1611, 1523, 1436, 1358, 1324, 1276, 1261, 1187, 1095 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.78–7.74 (m, 4H), 7.50–7.47 (m, 2H), 7.44–7.41 (m, 4H), 7.20 (d, J = 8.5 Hz, 2H), 6.59 (d, J = 8.5 Hz, 2H), 4.94 (dt, J = 7.5, 7.5 Hz, 1H), 3.32 (dd, J = 15.5, 7.5 Hz, 2H), 2.92 (s, 6H), 1.07–0.95 (m, 21H) ppm.

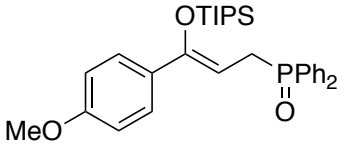
^{13}C NMR ($CDCl_3$, 126 MHz): δ 154.1 (d, J_{C-P} = 12.0 Hz), 150.4, 133.2 (d, J_{C-P} = 98.7 Hz), 131.6, 131.3 (d, J_{C-P} = 9.7 Hz), 128.5 (d, J_{C-P} = 12.0 Hz), 127.7, 127.3, 111.6, 96.6 (d, J_{C-P} = 7.2 Hz), 40.5, 29.3 (d, J_{C-P} = 72.1 Hz), 18.0, 13.6 ppm.

^{31}P NMR ($CDCl_3$, 202 MHz): δ 31.5 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{32}H_{44}NO_2PSiNa$ $[M+Na]^+$: 556.2771, found: 556.2790.

M.p.: 121–122 °C.

(*Z*)-(3-(4-Methoxyphenyl)-3-((triisopropylsilyl)oxy)allyl)diphenylphosphine oxide (24)



Yield: 80.7 mg, 62% yield, pale yellow solid.

R_f: 0.30 (DCM/MeOH = 32:1).

IR (ATR): 2958, 2945, 2866, 1644, 1607, 1511, 1461, 1436, 1335, 1276, 1248, 1197, 1099, 1016 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.78–7.74 (m, 4H), 7.52–7.48 (m, 2H), 7.45–7.42 (m, 4H), 7.26–7.23 (m, 2H), 6.79–6.77 (m, 2H), 5.01 (dt, J = 7.5, 7.0 Hz, 1H), 3.78 (s, 3H), 3.32 (dd, J = 15.0, 7.0 Hz, 2H), 1.04–0.97 (m, 21H) ppm.

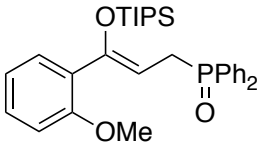
^{13}C NMR ($CDCl_3$, 126 MHz): δ 159.6, 153.5 (d, $J_{C–P}$ = 12.0 Hz), 133.1 (d, $J_{C–P}$ = 98.5 Hz), 132.3, 131.7, 131.2 (d, $J_{C–P}$ = 9.6 Hz), 128.5 (d, $J_{C–P}$ = 12.1 Hz), 127.6, 113.4, 98.1 (d, $J_{C–P}$ = 7.2 Hz), 55.3, 29.2 (d, $J_{C–P}$ = 72.2 Hz), 17.9, 13.6 ppm.

^{31}P NMR ($CDCl_3$, 202 MHz): δ 31.4 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{31}H_{42}O_3PSi$ $[M+H]^+$: 521.2635, found: 521.2607.

M.p.: 106–107 °C.

(*Z*)-(3-(2-Methoxyphenyl)-3-((triisopropylsilyl)oxy)allyl)diphenylphosphine oxide (25)



Yield: 73.5 mg, 56% yield, colorless oil.

R_f: 0.30 (DCM/MeOH = 32:1).

IR (ATR): 3058, 2944, 2866, 1649, 1598, 1579, 1490, 1463, 1436, 1326, 1258, 1119, 1093, 1024 cm^{-1}.

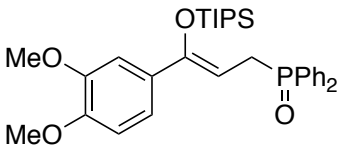
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.83–7.80 (m, 4H), 7.51–7.48 (m, 2H), 7.45–7.42 (m, 4H), 7.23–7.19 (m, 1H), 7.14 (dd, *J* = 7.0, 1.5 Hz, 1H), 6.83 (app. t, *J* = 7.0 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 4.93 (dt, *J* = 7.0, 7.5 Hz, 1H), 3.69 (s, 3H), 3.37 (dd, *J* = 16.0, 7.5 Hz, 2H), 0.99–0.95 (m, 21H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 157.1, 150.1 (d, $J_{C–P}$ = 12.0 Hz), 133.3 (d, $J_{C–P}$ = 98.5 Hz), 131.6, 131.4 (d, $J_{C–P}$ = 9.6 Hz), 130.1, 129.5, 128.7, 128.4 (d, $J_{C–P}$ = 12.0 Hz), 119.9, 110.7, 101.2 (d, $J_{C–P}$ = 7.2 Hz), 55.0, 29.0 (d, $J_{C–P}$ = 72.2 Hz), 17.9, 13.2 ppm.

^{31}P NMR ($CDCl_3$, 202 MHz): δ 31.5 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{31}H_{42}O_3PSi$ $[M+H]^+$: 521.2635, found: 521.2610.

(*Z*)-(3-(3,4-Dimethoxyphenyl)-3-((triisopropylsilyl)oxy)allyl)diphenylphosphine oxide (26)



Yield: 64.2 mg, 47% yield, yellow oil.

R_f: 0.25 (DCM/MeOH = 32:1).

IR (ATR): 3058, 2945, 2866, 1642, 1603, 1583, 1513, 1463, 1437, 1411, 1339, 1313, 1267, 1219, 1098, 1026 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.78–7.74 (m, 4H), 7.52–7.49 (m, 2H), 7.46–7.43 (m, 4H), 6.90 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.84 (d, *J* = 2.0 Hz, 1H), 6.75 (d, *J* = 8.5 Hz, 1H), 5.06 (dt, *J* = 7.5, 7.5 Hz, 1H),

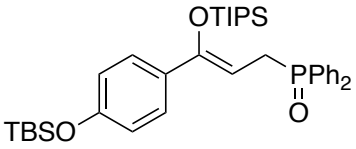
3.86 (s, 3H), 3.84 (s, 3H), 3.32 (dd, J = 15.5, 7.5 Hz, 2H), 1.06–1.00 (m, 21H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 153.6 (d, J_{C-P} = 12.0 Hz), 149.1, 148.4, 133.1 (d, J_{C-P} = 98.5 Hz), 132.5, 131.7, 131.2 (d, J_{C-P} = 9.6 Hz), 128.5 (d, J_{C-P} = 12.1 Hz), 118.9, 110.6, 109.6, 98.3 (d, J_{C-P} = 7.2 Hz), 55.95, 55.85, 29.2 (d, J_{C-P} = 72.2 Hz), 18.0, 13.6 ppm.

^{31}P NMR ($CDCl_3$, 202 MHz): δ 31.2 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{32}H_{44}O_4PSi$ $[M+H]^+$: 551.2741, found: 551.2729.

(*Z*)-(3-(4-((*tert*-Butyldimethylsilyl)oxy)phenyl)-3-((triisopropylsilyl)oxy)allyl)diphenylphosphine oxide (27)



Yield: 76.1 mg, 49% yield, colorless oil.

R_f: 0.31 (DCM/MeOH = 32:1).

IR (ATR): 3058, 2946, 2930, 2865, 1644, 1605, 1506, 1463, 1437, 1390, 1362, 1327, 1275, 1259, 1098 cm^{-1}.

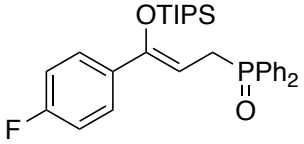
^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.78–7.74 (m, 4H), 7.52–7.49 (m, 2H), 7.46–7.42 (m, 4H), 7.17 (d, J = 9.0 Hz, 2H), 6.72 (d, J = 9.0 Hz, 2H), 5.01 (dt, J = 7.5, 7.5 Hz, 1H), 3.31 (dd, J = 15.0, 7.5 Hz, 2H), 1.07–0.92 (m, 30H), 0.17 (s, 6H) ppm.

^{13}C NMR ($CDCl_3$, 151 MHz): δ 155.8, 153.7 (d, J_{C-P} = 12.1 Hz), 133.1 (d, J_{C-P} = 98.5 Hz), 133.0 (d, J_{C-P} = 2.1 Hz), 131.7 (d, J_{C-P} = 2.1 Hz), 131.2 (d, J_{C-P} = 9.1 Hz), 128.5 (d, J_{C-P} = 12.1 Hz), 127.7, 119.7, 98.1 (d, J_{C-P} = 6.9 Hz), 29.2 (d, J_{C-P} = 72.3 Hz), 25.8, 18.3, 18.0, 13.5, –4.3 ppm.

^{31}P NMR ($CDCl_3$, 202 MHz): δ 32.1 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{36}H_{54}O_3PSi_2$ $[M+H]^+$: 621.3344, found: 621.3345.

(*Z*)-(3-(4-Fluorophenyl)-3-((triisopropylsilyl)oxy)allyl)diphenylphosphine oxide (28)



Yield: 63.1 mg, 50% yield, colorless oil.

R_f: 0.36 (DCM/MeOH = 32:1).

IR (ATR): 3058, 2945, 2903, 2867, 1646, 1604, 1507, 1464, 1437, 1330, 1275, 1222, 1204, 1098 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.76 (dd, J = 11.5, 8.0 Hz, 4H), 7.51 (t, J = 7.5 Hz, 2H), 7.46–7.43 (m, 4H), 7.29 (dd, J = 8.0, 5.0 Hz, 2H), 6.94 (app. t, J = 8.0 Hz, 2H), 5.07 (dt, J = 7.5, 7.5 Hz, 1H),

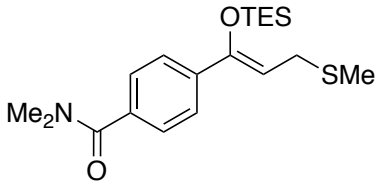
3.31 (dd, J = 15.5, 7.5 Hz, 2H), 1.03–0.97 (m, 21H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 162.7 (d, $J_{C–F}$ = 250.0 Hz), 152.8 (d, $J_{C–P}$ = 12.0 Hz), 135.7, 133.0 (d, $J_{C–P}$ = 98.5 Hz), 131.8, 131.1 (d, $J_{C–P}$ = 9.6 Hz), 128.6 (d, $J_{C–P}$ = 12.1 Hz), 128.0 (d, $J_{C–F}$ = 7.3 Hz), 115.0 (d, $J_{C–F}$ = 21.5 Hz), 99.5 (d, $J_{C–P}$ = 7.2 Hz), 29.2 (d, $J_{C–P}$ = 72.1 Hz), 17.9, 13.5 ppm.

^{31}P NMR ($CDCl_3$, 202 MHz): δ 31.8 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{30}H_{39}FO_2PSi$ $[M+H]^+$: 509.2435, found: 509.2429.

(*Z*)-*N*,*N*-Dimethyl-4-(3-(methylthio)-1-((triethylsilyl)oxy)prop-1-en-1-yl)benzamide (29)



Yield: 40.1 mg, 44% yield, light yellow oil.

R_f: 0.32 (hexane/EtOAc = 1:2).

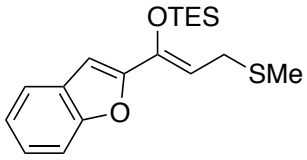
IR (ATR): 2954, 2914, 2876, 1633, 1512, 1489, 1457, 1390, 1330, 1269, 1239, 1220, 1102, 1079, 1031, 1004 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35 (d, J = 8.5 Hz, 2H), 7.38 (d, J = 8.5 Hz, 2H), 5.28 (t, J = 8.0 Hz, 1H), 3.33 (d, J = 8.0 Hz, 2H), 3.11 (br s, 3H), 2.99 (br s, 3H), 2.12 (s, 3H), 0.93 (t, J = 8.0 Hz, 9H), 0.62 (q, J = 8.0 Hz, 6H) ppm.

^{13}C NMR ($CDCl_3$, 101 MHz): δ 171.4, 151.4, 140.3, 135.8, 127.2, 125.7, 108.1, 39.7, 35.5, 29.7, 15.1, 6.8, 5.4 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{19}H_{32}NO_2SSi$ $[M+H]^+$: 366.1918, found: 366.1927.

(*Z*)-((1-(Benzofuran-2-yl)-3-(methylthio)prop-1-en-1-yl)oxy)triethylsilane (30)



Yield: 49.9 mg, 60% yield, yellow oil.

R_f: 0.30 (hexane/EtOAc = 50:1).

IR (ATR): 2956, 2914, 2876, 1642, 1560, 1451, 1413, 1356, 1255, 1099, 1005 cm^{-1}.

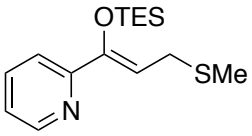
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.54 (d, J = 7.5 Hz, 1H), 7.43 (d, J = 8.5 Hz, 1H), 7.27 (app. t, J = 7.5 Hz, 1H), 7.21 (app. t, J = 7.5 Hz, 1H), 6.70 (s, 1H), 5.72 (t, J = 8.0 Hz, 1H), 3.35 (d, J = 8.0 Hz, 2H), 2.13 (s, 3H), 1.02 (d, J = 8.0 Hz, 9H), 0.78 (q, J = 8.0 Hz, 6H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 154.8, 154.1, 143.0, 128.7, 124.7, 123.0, 121.2, 111.2, 108.4,

103.0, 29.1, 15.1, 6.9, 5.5 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{18}H_{27}O_2SSi$ $[M+H]^+$: 335.1496, found: 335.1525.

(*Z*)-2-(3-(Methylthio)-1-((triethylsilyl)oxy)prop-1-en-1-yl)pyridine (31)



Yield: 37.4 mg, 51% yield, brown oil.

R_f: 0.40 (hexane/EtOAc = 10:1).

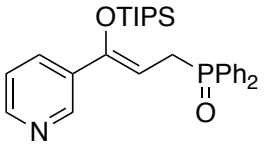
IR (ATR): 2954, 2912, 2876, 1641, 1584, 1567, 1467, 1431, 1379, 1333, 1278, 1238, 1155, 1112, 1088, 1067, 1004 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.54 (d, *J* = 5.0 Hz, 1H), 7.11 (app. t, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 7.5 Hz, 1H), 7.16 (dd, *J* = 7.5, 5.0 Hz, 1H), 5.93 (d, *J* = 8.0 Hz, 1H), 3.37 (d, *J* = 8.0 Hz, 2H), 2.12 (s, 3H), 0.95 (t, *J* = 8.0 Hz, 9H), 0.70 (q, *J* = 8.0 Hz, 6H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 155.6, 150.5, 148.9, 136.3, 122.6, 119.7, 109.2, 29.5, 15.1, 6.9, 5.7 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{15}H_{26}NOSSi$ $[M+H]^+$: 296.1499, found: 296.1499.

(*Z*)-Diphenyl(3-(pyridin-3-yl)-3-((triisopropylsilyl)oxy)allyl)phosphine oxide (32)



Yield: 66.4 mg, 54% yield, light brown solid.

R_f: 0.27 (DCM/MeOH = 19:1).

IR (ATR): 3051, 2943, 2866, 1642, 1460, 1437, 1417, 1338, 1277, 1181, 1118, 1107 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.57 (d, *J* = 1.5 Hz, 1H), 8.49 (dd, *J* = 4.5, 1.5 Hz, 1H), 7.78–7.74 (m, 4H), 7.60 (app. dt, *J* = 8.0, 1.5 Hz, 1H), 7.54–7.51 (m, 2H), 7.48–7.44 (m, 4H), 7.20 (dd, *J* = 8.0, 4.5 Hz, 1H), 5.17 (dt, *J* = 7.5, 7.5 Hz, 1H), 3.34 (dd, *J* = 15.0, 7.5 Hz, 2H), 1.04–0.97 (m, 21H) ppm.

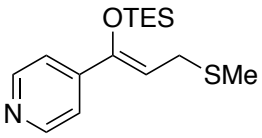
^{13}C NMR ($CDCl_3$, 126 MHz): δ 151.0 (d, J_{C-P} = 14.5 Hz), 149.3, 147.5, 135.1, 133.5, 132.8 (d, J_{C-P} = 98.5 Hz), 131.9, 131.1 (d, J_{C-P} = 9.7 Hz), 128.6 (d, J_{C-P} = 12.0 Hz), 123.0, 101.5 (d, J_{C-P} = 7.2 Hz), 29.2 (d, J_{C-P} = 69.8 Hz), 17.9, 13.5 ppm.

^{31}P NMR ($CDCl_3$, 202 MHz): δ 31.6 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{29}H_{38}NO_2PSiNa$ $[M+Na]^+$: 514.2302, found: 514.2320.

M.p.: 77–78 °C.

(*Z*)-4-(3-(Methylthio)-1-((triethylsilyl)oxy)prop-1-en-1-yl)pyridine (33)



Yield: 38.4 mg, 52% yield, yellow oil.

R_f: 0.38 (hexane/EtOAc = 5:1).

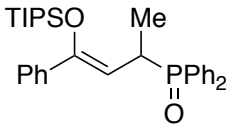
IR (ATR): 2956, 2913, 2877, 1637, 1593, 1547, 1475, 1458, 1409, 1338, 1315, 1275, 1239, 1107, 1032, 1004 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.57 (app. s, 2H), 7.36 (d, *J* = 4.5 Hz, 2H), 5.47 (t, *J* = 7.5 Hz, 1H), 3.33 (d, *J* = 7.5 Hz, 2H), 2.11 (s, 3H), 0.93 (t, *J* = 8.0 Hz, 9H), 0.65 (q, *J* = 8.0 Hz, 6H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 150.0, 149.6, 146.2, 120.0, 110.4, 29.6, 15.2, 6.8, 5.4 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{15}H_{25}NOSSiNa$ $[M+Na]^+$: 318.1318, found: 318.1325.

(*Z*)-Diphenyl(4-phenyl-4-((triisopropylsilyl)oxy)but-3-en-2-yl)phosphine oxide (34)



Yield: 76.8 mg, 61% yield, white solid.

R_f: 0.27 (DCM/MeOH = 32:1).

IR (ATR): 3058, 2962, 2945, 2926, 2866, 1637, 1591, 1460, 1436, 1339, 1278, 1189, 1117, 1065 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.87–7.83 (m, 2H), 7.80–7.76 (m, 2H), 7.53–7.42 (m, 4H), 7.38–7.35 (m, 2H), 7.26–7.23 (m, 5H), 5.06 (dd, *J* = 11.0, 7.0 Hz, 1H), 3.81–3.73 (m, 1H), 1.34 (dd, *J* = 16.0, 7.5 Hz, 3H), 1.03–0.97 (m, 21H) ppm.

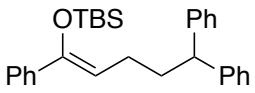
^{13}C NMR ($CDCl_3$, 126 MHz): δ 152.3 (d, J_{C-P} = 12.0 Hz), 139.6, 132.68 (d, J_{C-P} = 98.5 Hz), 132.66 (d, J_{C-P} = 93.7 Hz), 131.6 (two signals merged), 131.4 (d, J_{C-P} = 9.6 Hz), 131.3 (d, J_{C-P} = 9.6 Hz), 128.6 (d, J_{C-P} = 12.0 Hz), 128.13, 128.12 (d, J_{C-P} = 12.0 Hz), 128.0, 126.5, 107.2 (d, J_{C-P} = 4.8 Hz), 32.0 (d, J_{C-P} = 72.1 Hz), 18.0, 17.9, 13.9, 13.6 ppm.

^{31}P NMR ($CDCl_3$, 202 MHz): δ 35.0 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{31}H_{42}O_2PSi$ $[M+H]^+$: 505.2686, found: 505.2688.

M.p.: 61–62 °C.

(*Z*)-*tert*-Butyldimethyl((1,5,5-triphenylpent-1-en-1-yl)oxy)silane (35)



Yield: 78.5 mg, 73% yield, colorless oil.

R_f: 0.17 (hexane).

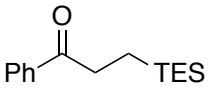
IR (ATR): 3059, 3026, 2956, 2929, 2857, 1648, 1600, 1492, 1472, 1462, 1447, 1278, 1255 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.42–7.40 (m, 2H), 7.28–7.20 (m, 11H), 7.17–7.14 (m, 2H), 5.11 (t, *J* = 6.5 Hz, 1H), 3.94 (t, *J* = 6.5 Hz, 1H), 2.16–2.15 (m, 4H), 0.87 (s, 9H), –0.17 (s, 6H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 149.8, 145.2, 139.9, 128.5, 128.1, 128.0, 127.5, 126.2, 126.0, 111.3, 51.3, 35.8, 25.9, 25.0, 18.4, –4.0 ppm.

HRMS (ESI): *m/z* calcd. for $C_{29}H_{37}OSi$ $[M+H]^+$: 429.2608, found: 429.2618.

1-Phenyl-3-(triethylsilyl)propan-1-one (37)



Yield: 48.5 mg, 78% yield, colorless oil.

R_f: 0.32 (hexane/EtOAc = 50:1).

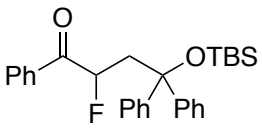
IR (ATR): 2951, 2908, 2874, 1685, 1599, 1581, 1449, 1415, 1226 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.95 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.57–7.54 (m, 1H), 7.46 (app. t, *J* = 8.0 Hz, 2H), 2.95–2.92 (m, 2H), 0.98–0.92 (m, 11H), 0.58 (q, *J* = 8.0 Hz, 6H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 201.5, 136.9, 133.0, 128.7, 128.2, 33.2, 7.6, 5.9, 3.4 ppm.

HRMS (ESI): *m/z* calcd. for $C_{15}H_{25}OSi$ $[M+H]^+$: 249.1669, found: 249.1686.

4-((*tert*-Butyldimethylsilyl)oxy)-2-fluoro-1,4,4-triphenylbutan-1-one (38)



Yield: 43.7 mg, 97% yield, colorless oil.

R_f: 0.26 (hexane/EtOAc = 50:1).

IR (ATR): 3059, 3027, 2955, 2929, 2886, 2856, 1698, 1598, 1580, 1493, 1472, 1462, 1447, 1256, 1120, 1103, 1067 cm^{-1}.

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.52–7.49 (m, 1H), 7.36–7.33 (m, 6H), 7.31–7.22 (m, 6H), 5.65 (ddd, *J* = 48.5, 7.0, 3.0 Hz, 1H), 3.08–2.96 (m, 2H), 0.97 (s, 9H), –0.20 (s, 3H), –0.42 (s, 3H) ppm.

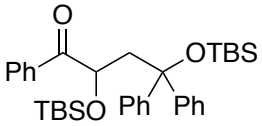
^{13}C NMR ($CDCl_3$, 151 MHz): δ 196.2 (d, $J_{C–F}$ = 19.6 Hz), 146.5, 146.4, 134.3, 133.6, 129.0 (d, $J_{C–F}$ = 4.2 Hz), 128.6, 128.1, 128.0, 127.8, 127.7, 127.6, 127.4, 89.7 (d, $J_{C–F}$ = 181.4 Hz), 79.6, 43.1

(d, J_{C-F} = 19.6 Hz), 26.4, 18.9, –2.7, –3.0 ppm.

^{19}F NMR ($CDCl_3$, 565 MHz): δ –183.5 – –183.6 (m) ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{28}H_{34}FO_2Si$ $[M+H]^+$: 449.2307, found: 449.2313.

2,4-Bis((*tert*-butyldimethylsilyl)oxy)-1,4,4-triphenylbutan-1-one (39)



Yield: 40.6 mg, 72% yield, colorless oil.

R_f: 0.29 (hexane/EtOAc = 50:1).

IR (ATR): 3059, 3027, 2956, 2929, 2885, 2856, 1686, 1598, 1493, 1472, 1463, 1447, 1253, 1100, 1064 cm^{-1}.

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.48–7.45 (m, 1H), 7.36–7.31 (m, 4H), 7.30–7.27 (m, 2H), 7.26–7.23 (m, 1H), 7.20–7.19 (m, 2H), 7.06–7.05 (m, 3H), 4.98 (dd, *J* = 7.0, 3.5 Hz, 1H), 3.22 (dd, *J* = 14.5, 7.0 Hz, 1H), 2.87 (dd, *J* = 14.5, 3.5 Hz, 1H), 0.93 (s, 9H), 0.75 (s, 9H), –0.207 (s, 3H), –0.214 (s, 3H), –0.30 (s, 3H), –0.41 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 151 MHz): δ 198.5, 146.9, 146.0, 134.9, 132.7, 129.4, 128.3, 128.1, 128.0, 127.9, 127.6, 127.3, 127.2, 79.8, 72.9, 47.2, 26.4, 25.8, 18.9, 18.1, –2.8, –3.0, –4.0, –4.6 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{34}H_{48}O_3Si_2Na$ $[M+Na]^+$: 583.3034, found: 583.3042.

4. References

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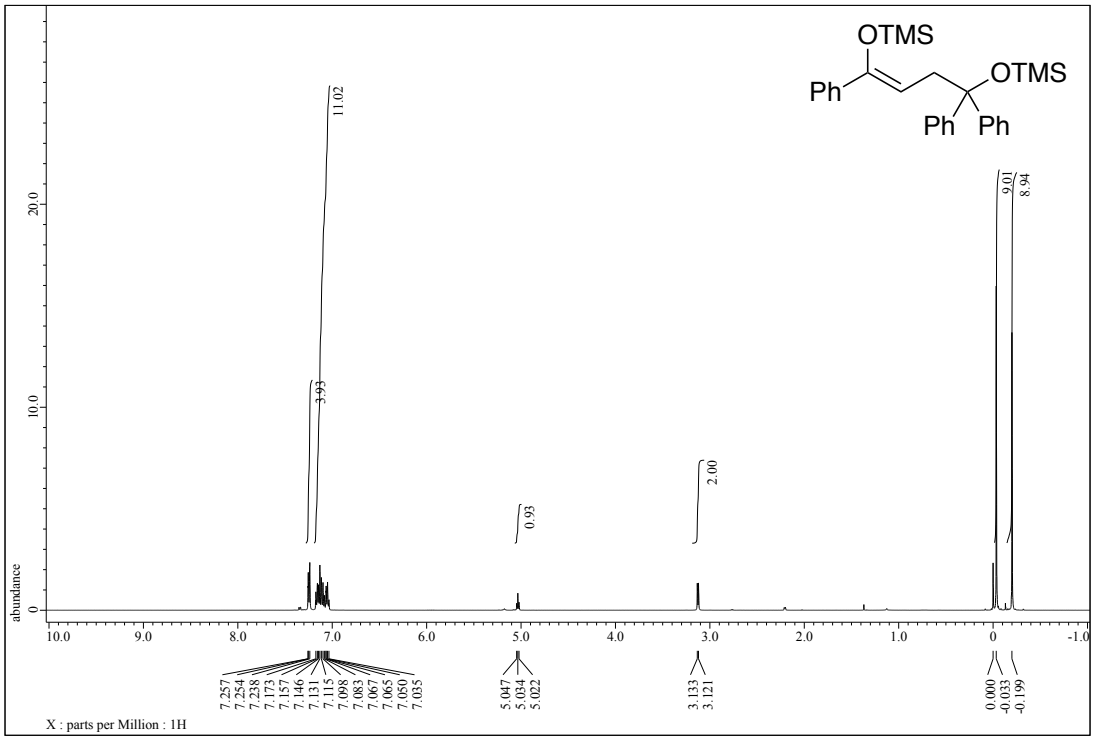
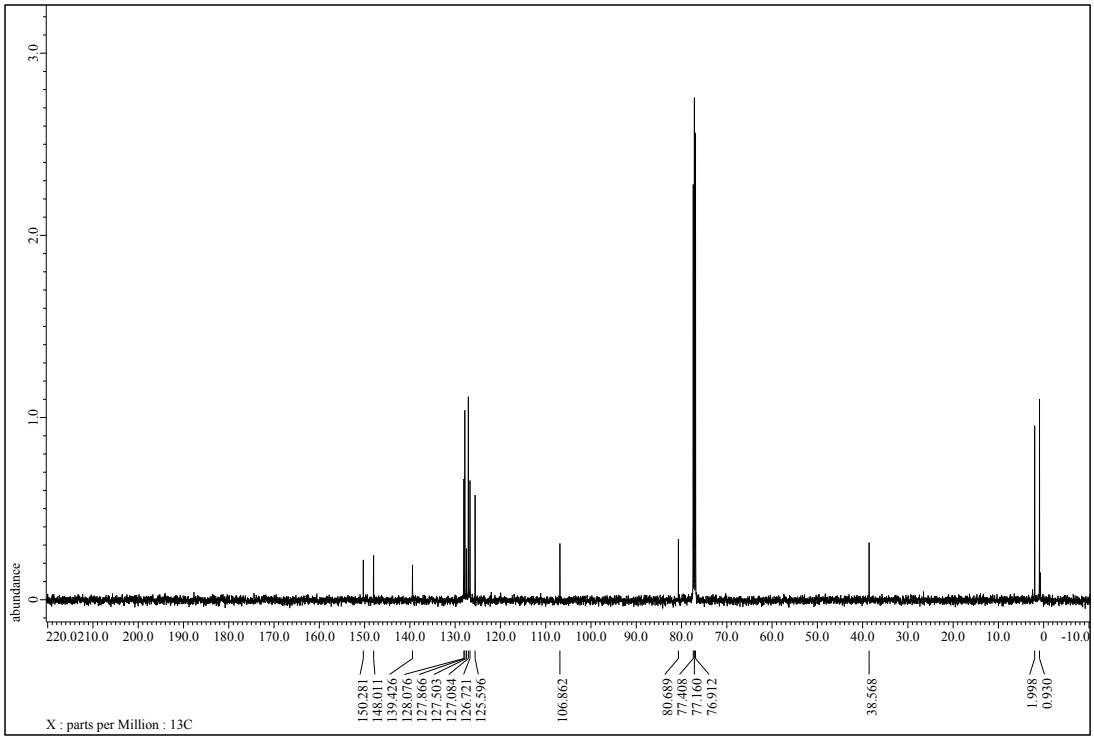
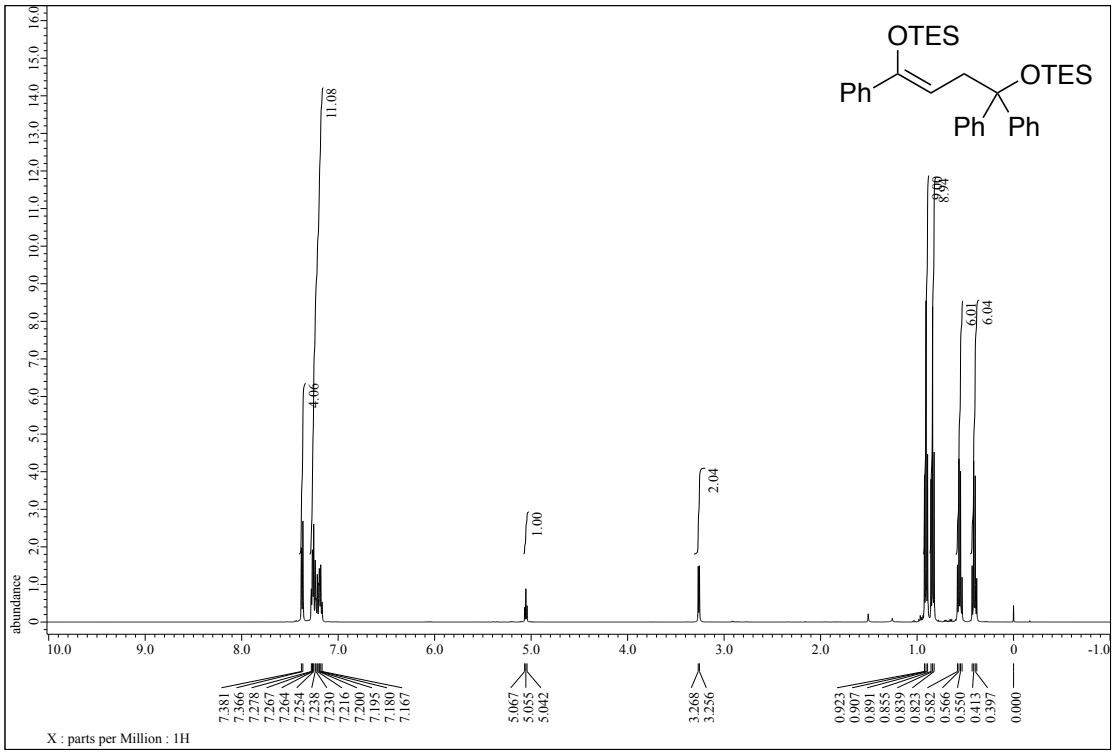
5. ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR Spectra

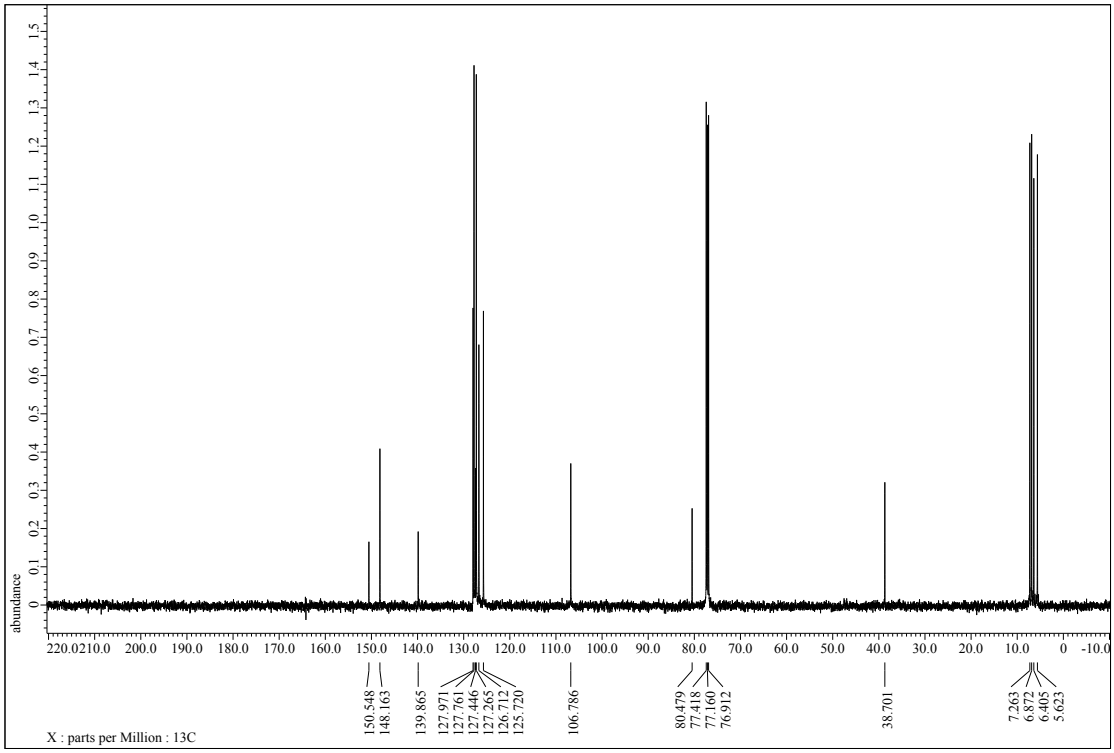
^{1}H and ^{13}C NMR spectra of **2**



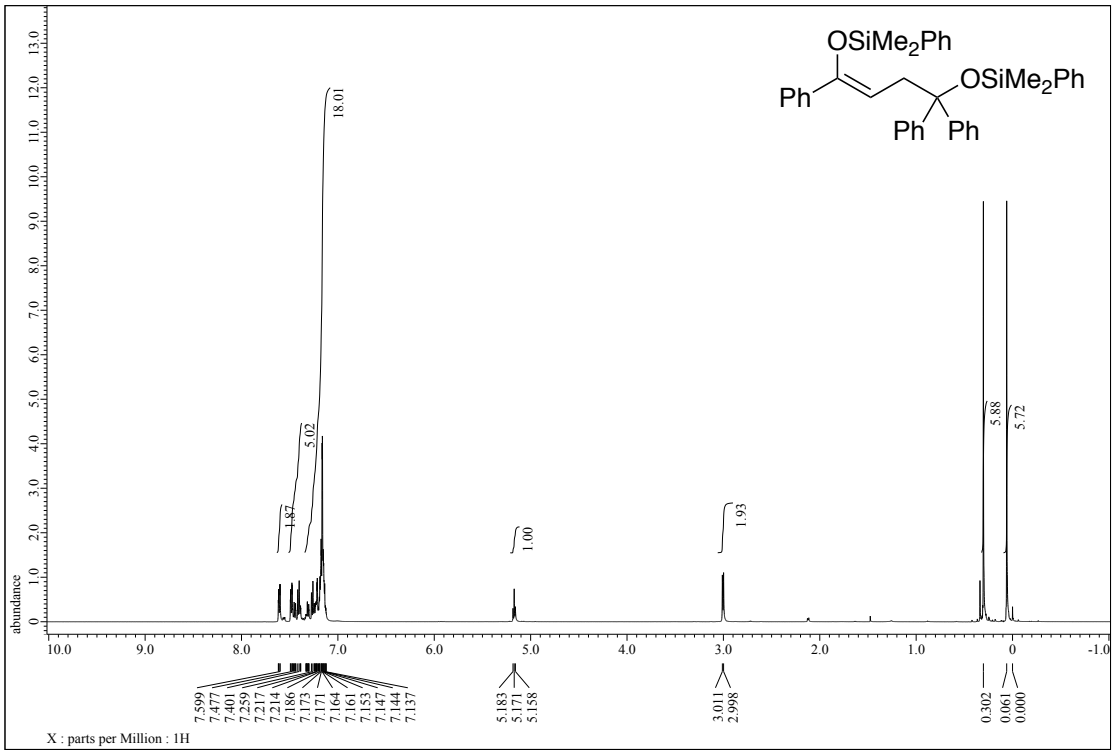


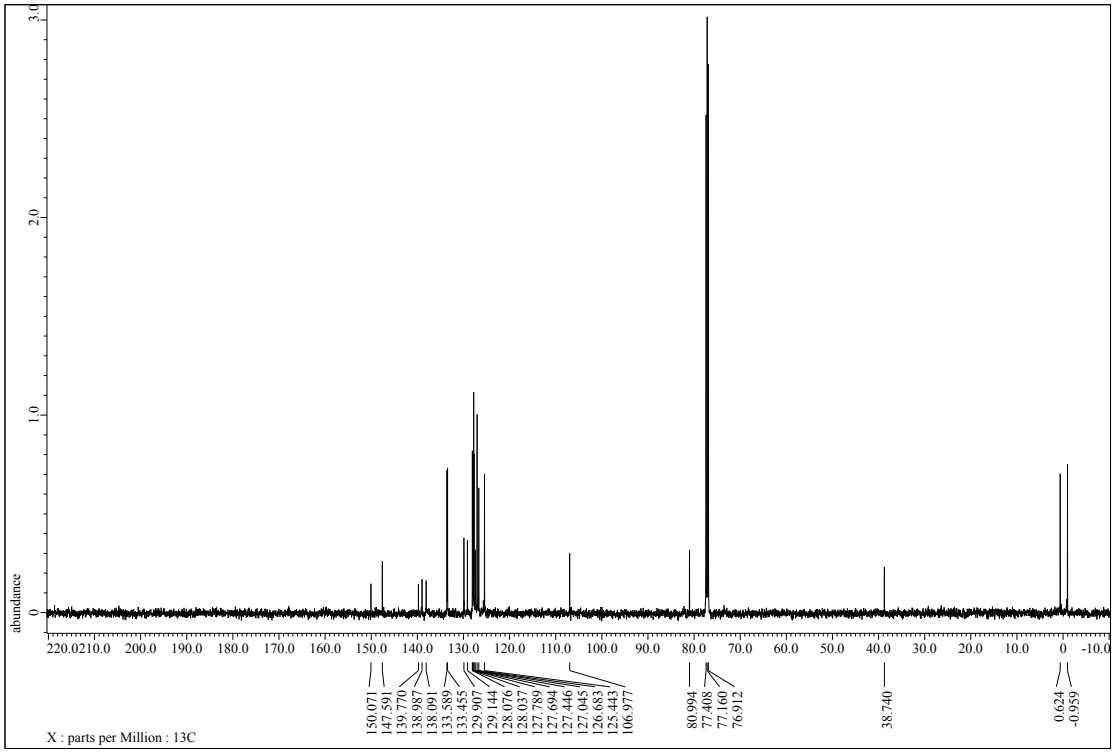
^{1}H and ^{13}C NMR spectra of **3**



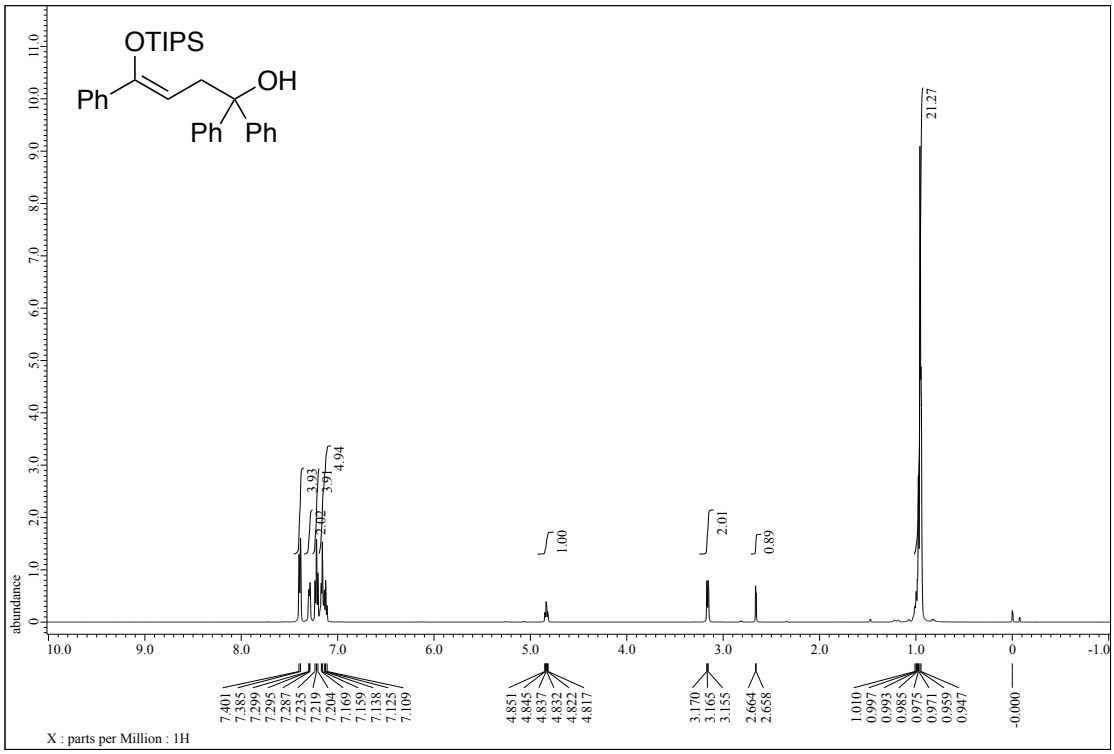


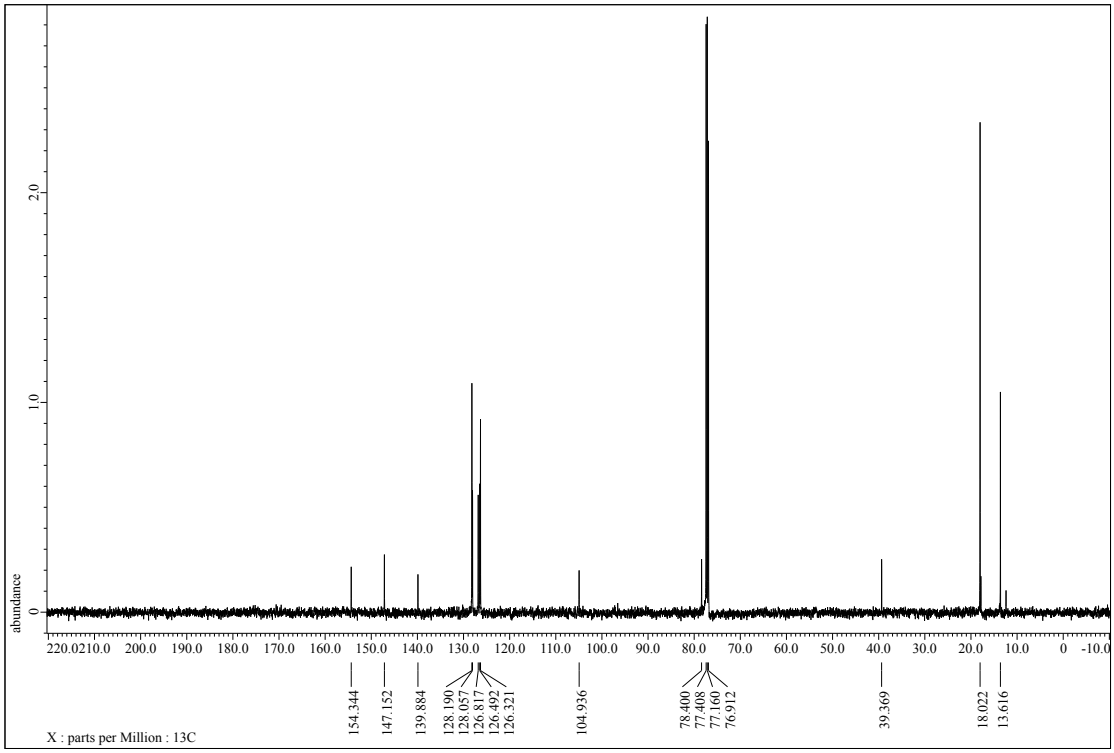
^{1}H and ^{13}C NMR spectra of **4**



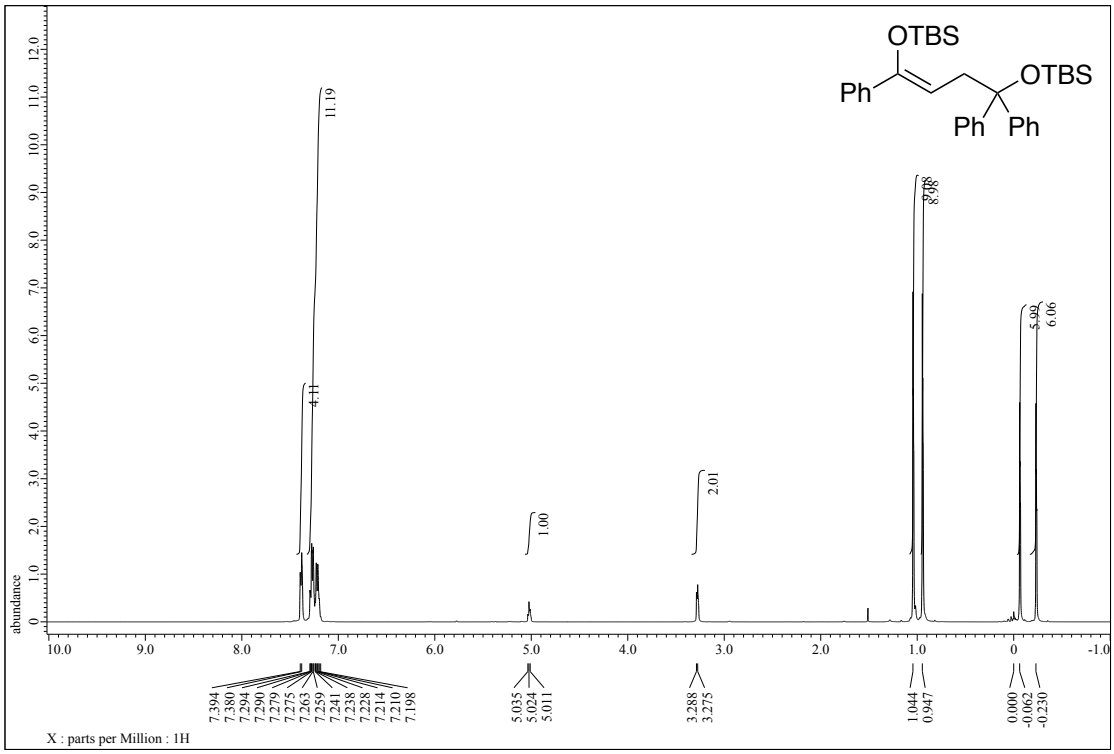


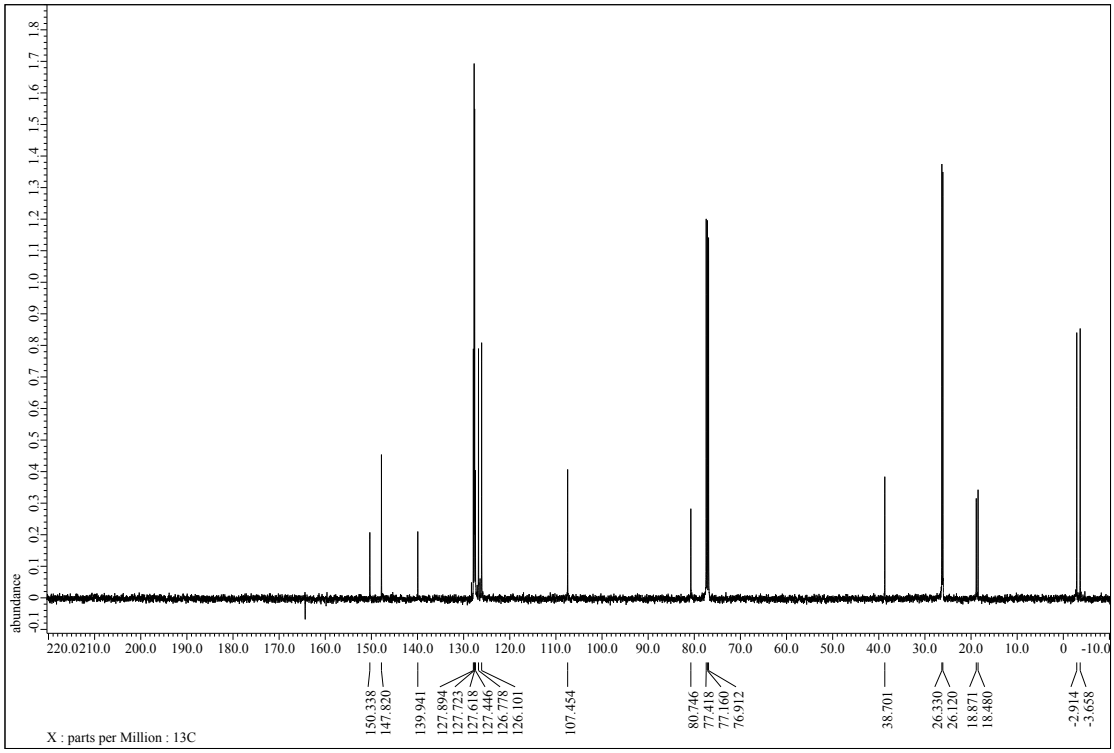
^{1}H and ^{13}C NMR spectra of **5**



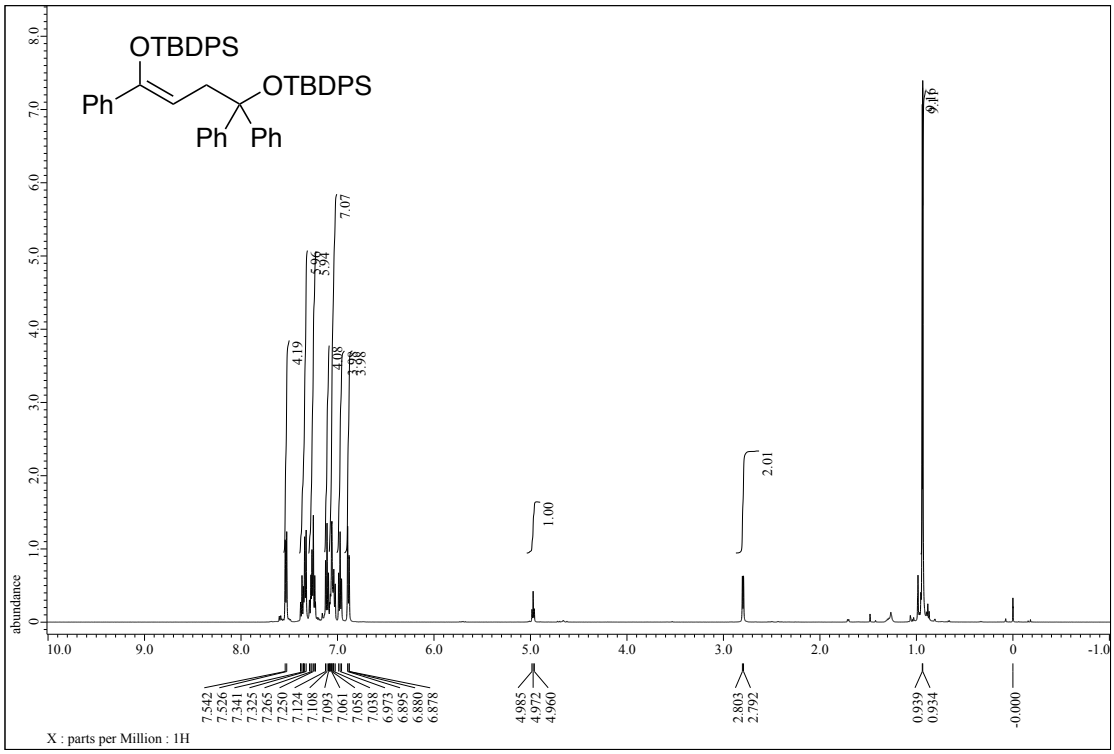


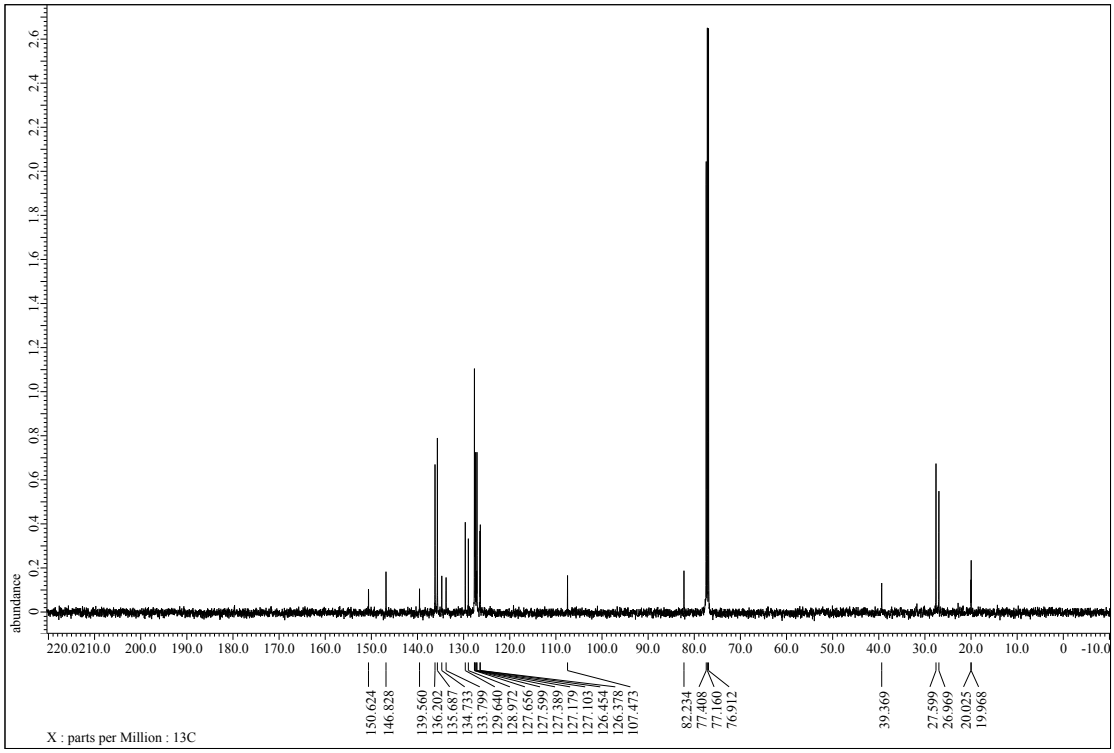
^{1}H and ^{13}C NMR spectra of **6**



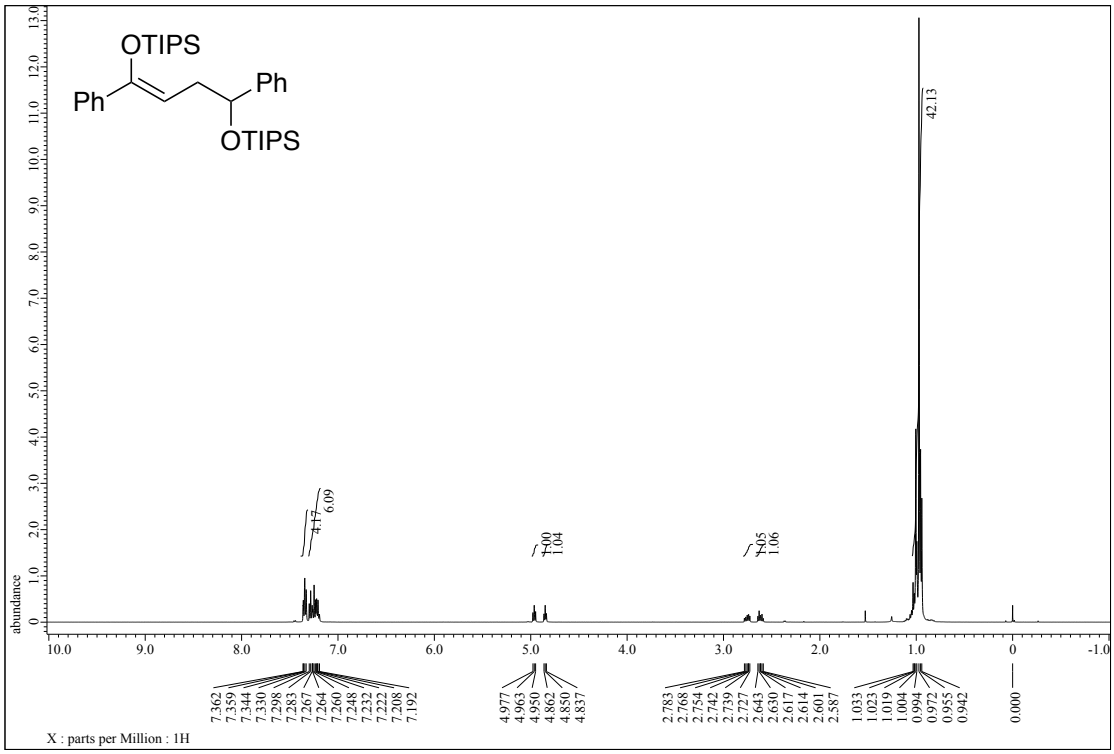


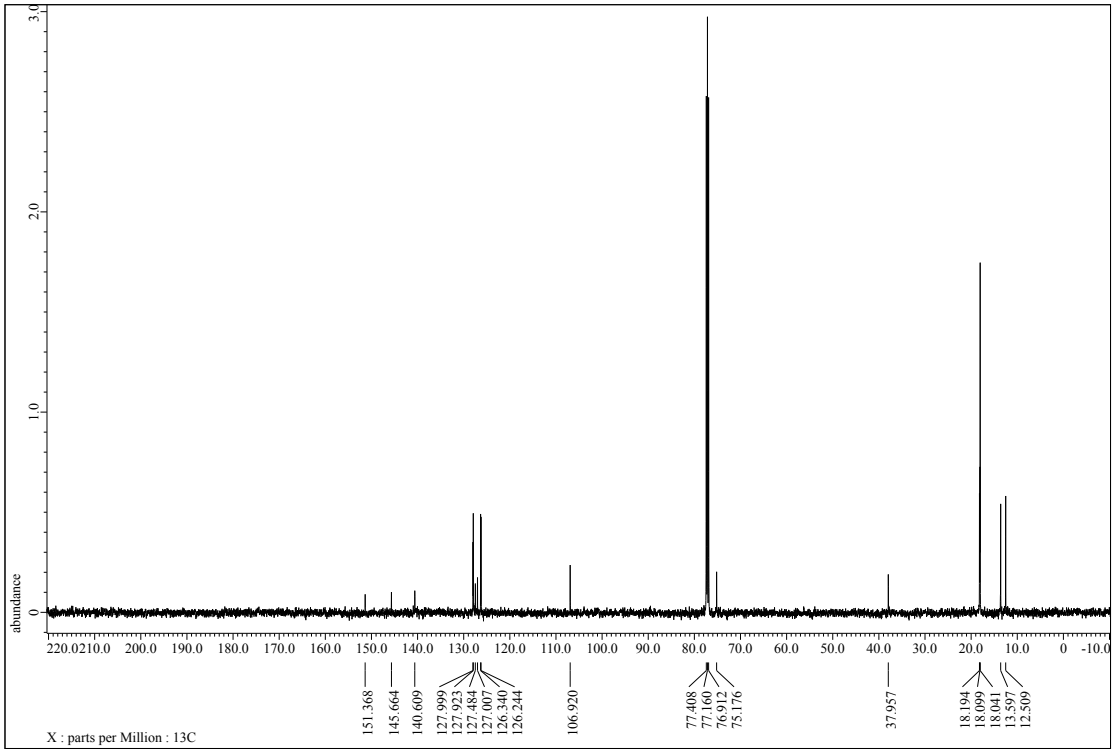
^{1}H and ^{13}C NMR spectra of **7**



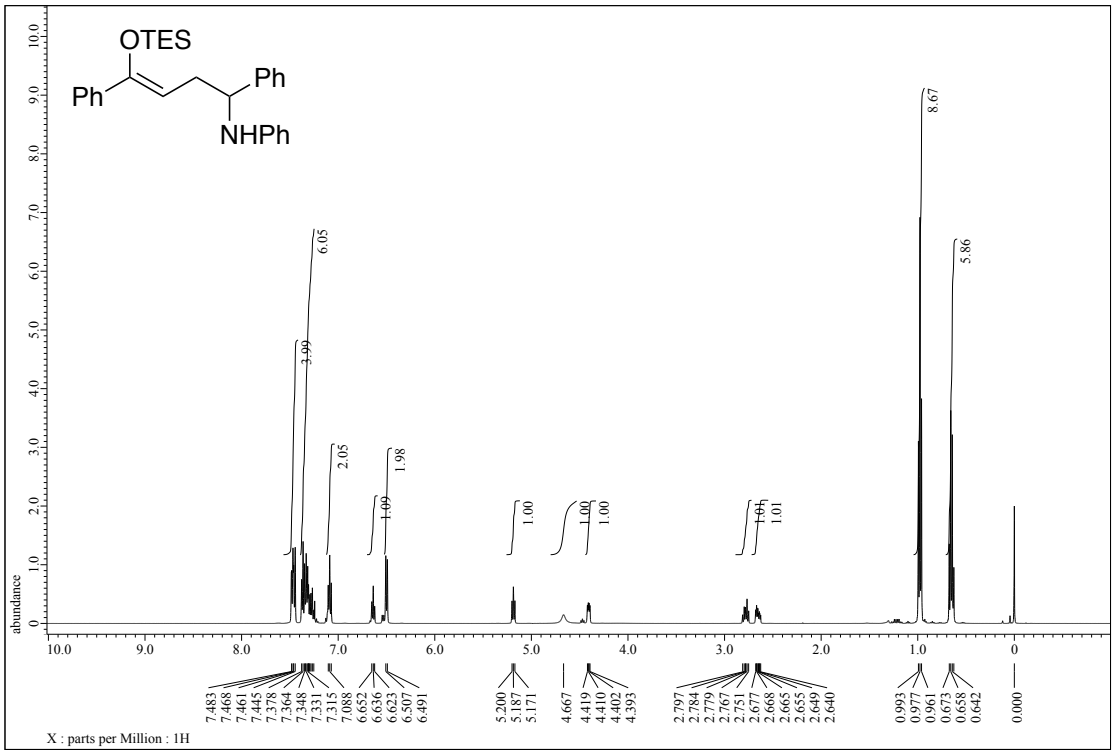


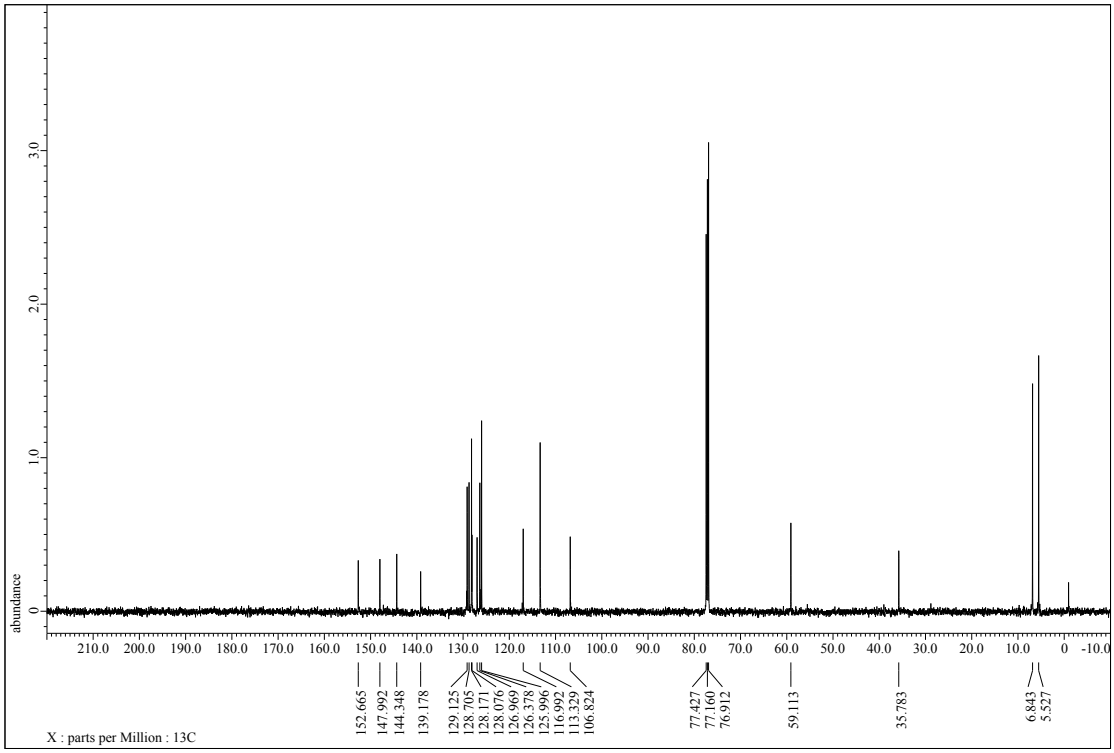
^{1}H and ^{13}C NMR spectra of **8**



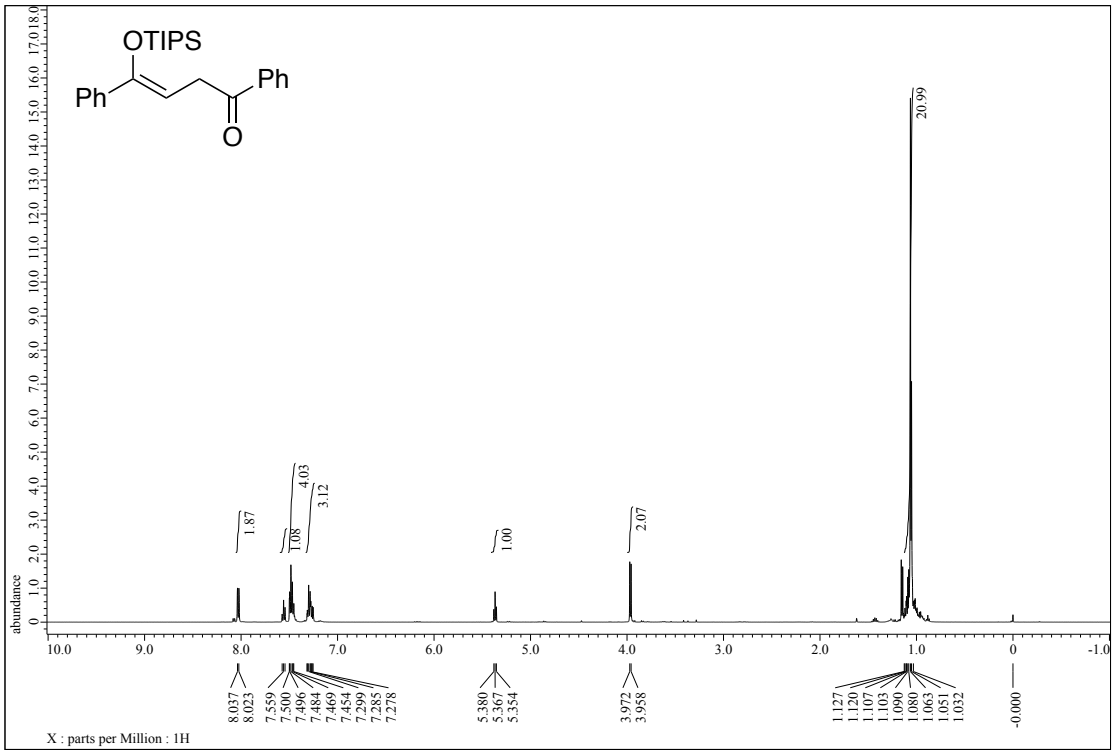


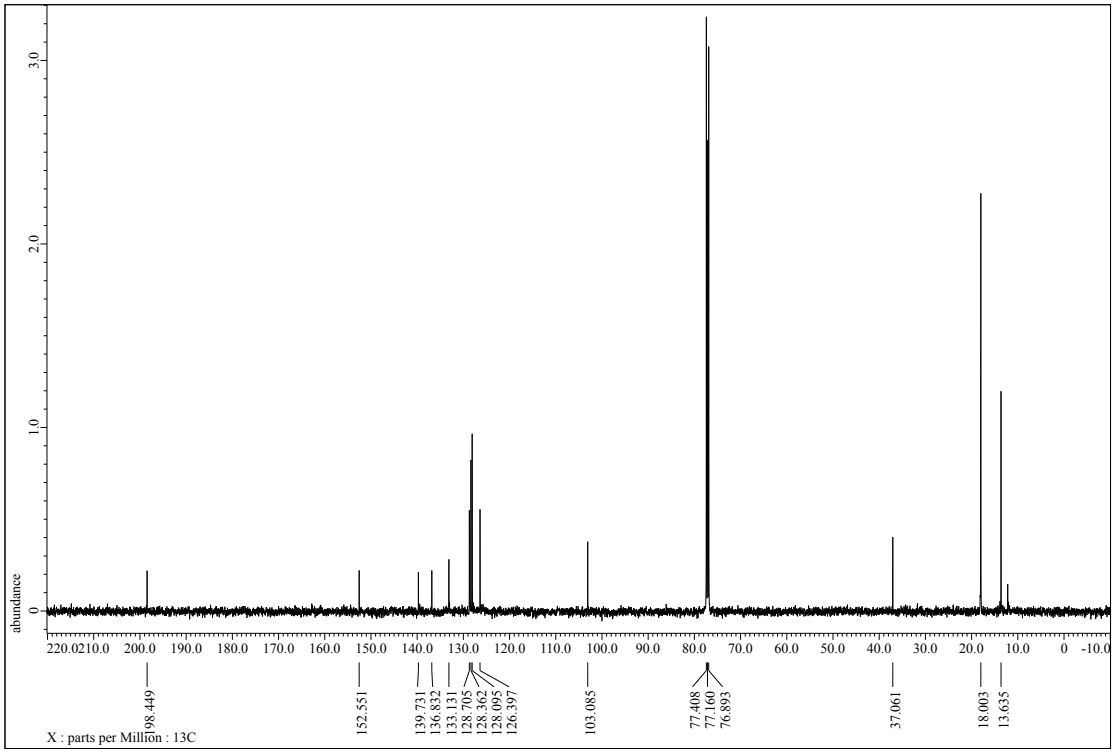
^{1}H and ^{13}C NMR spectra of **9**



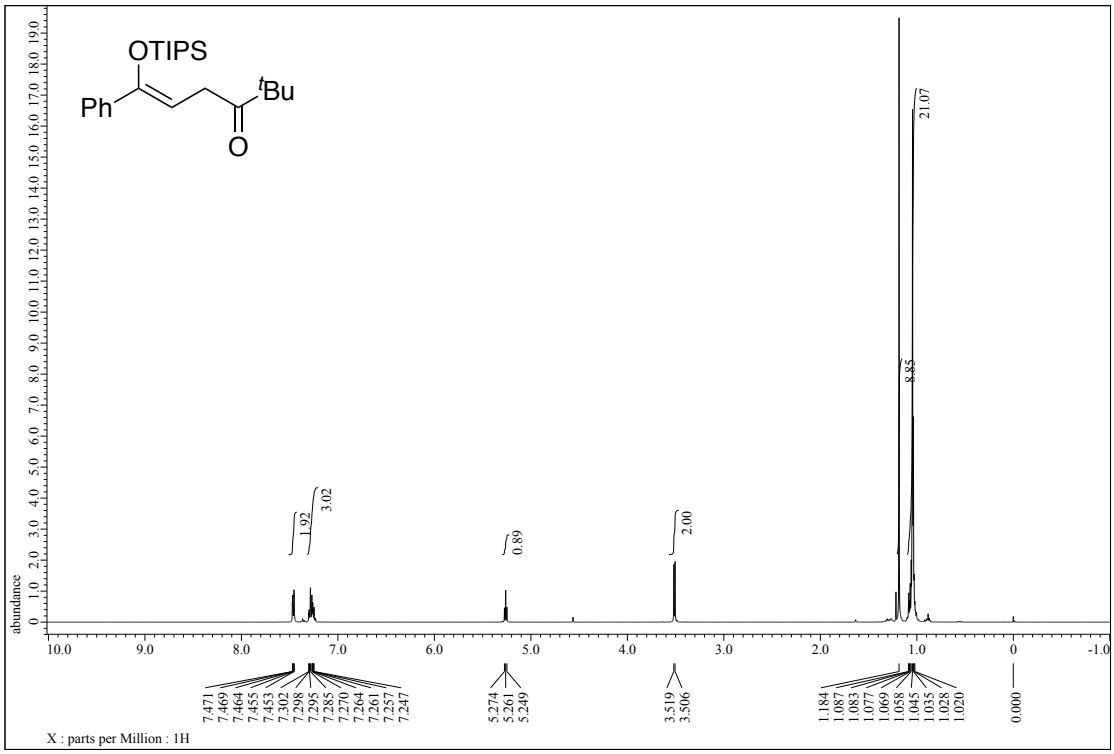


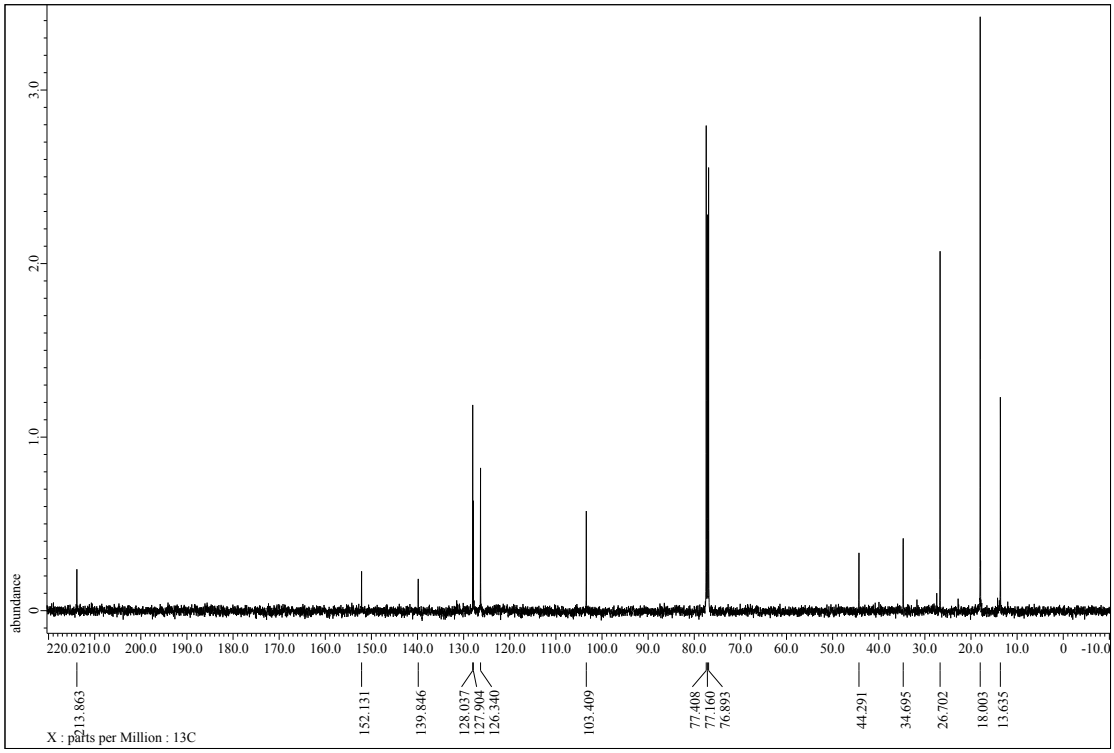
^{1}H and ^{13}C NMR spectra of **10**



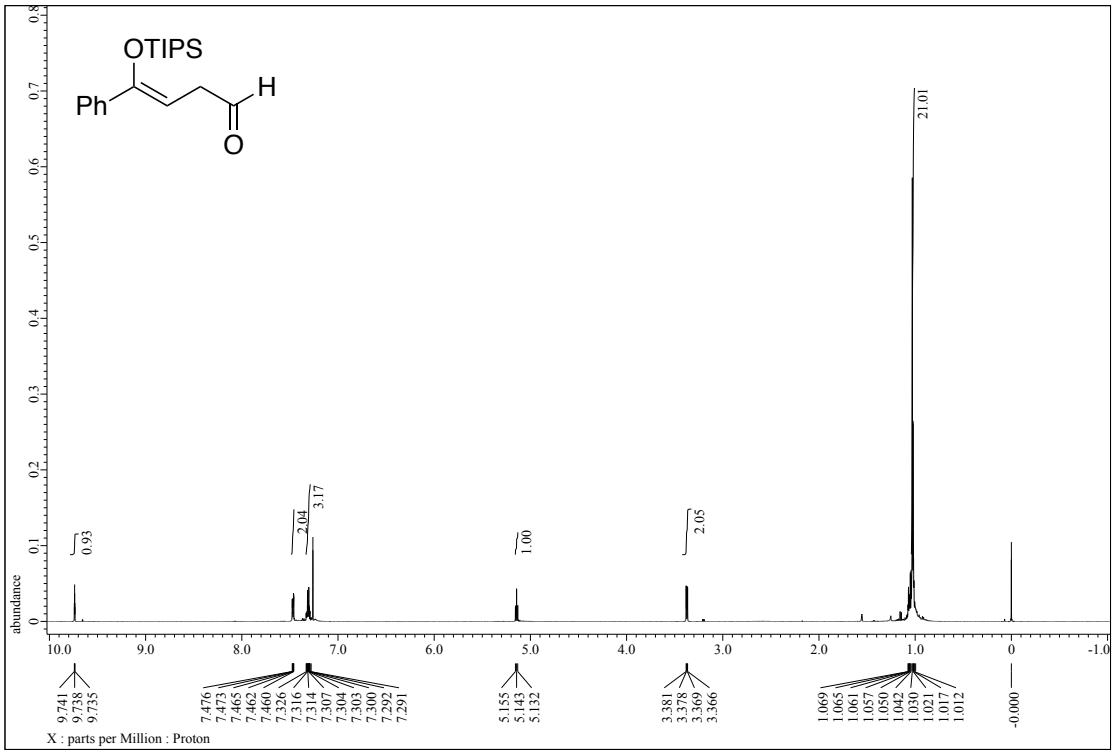


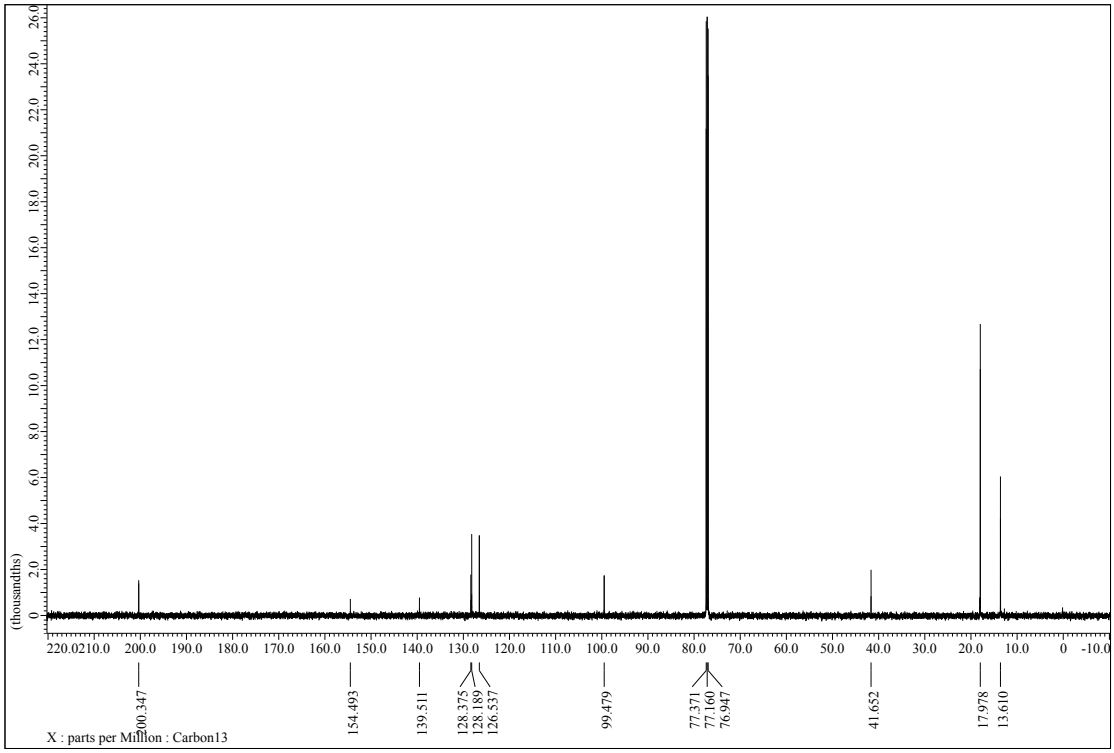
^{1}H and ^{13}C NMR spectra of **11**



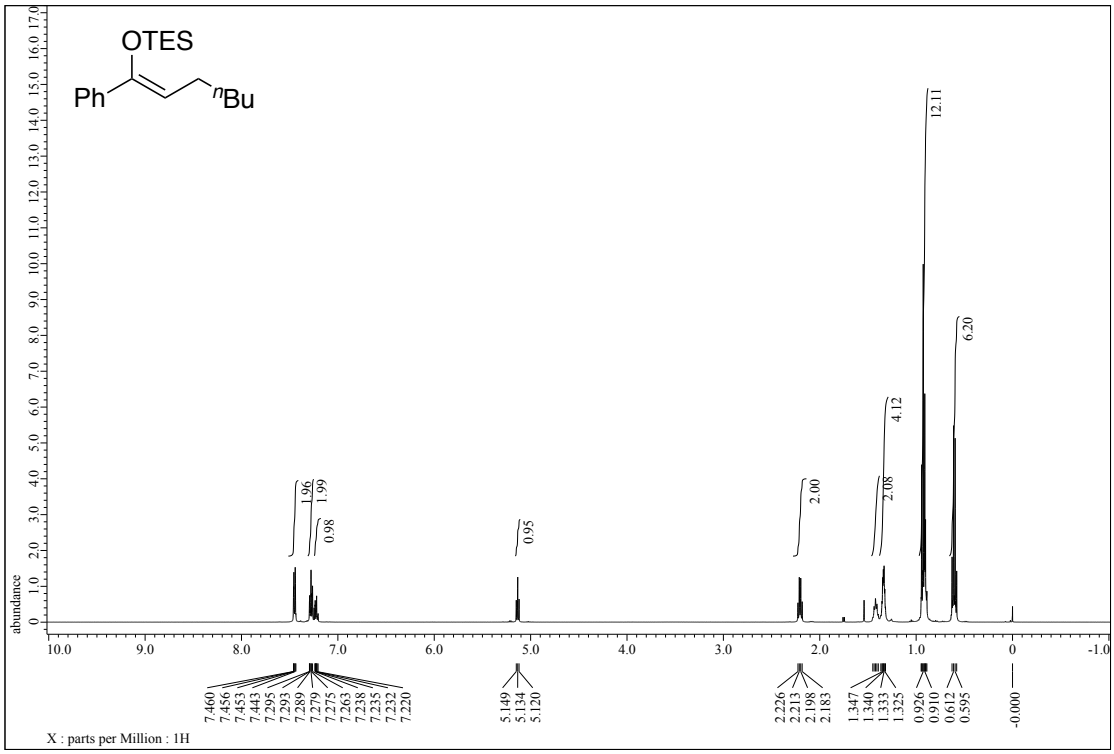


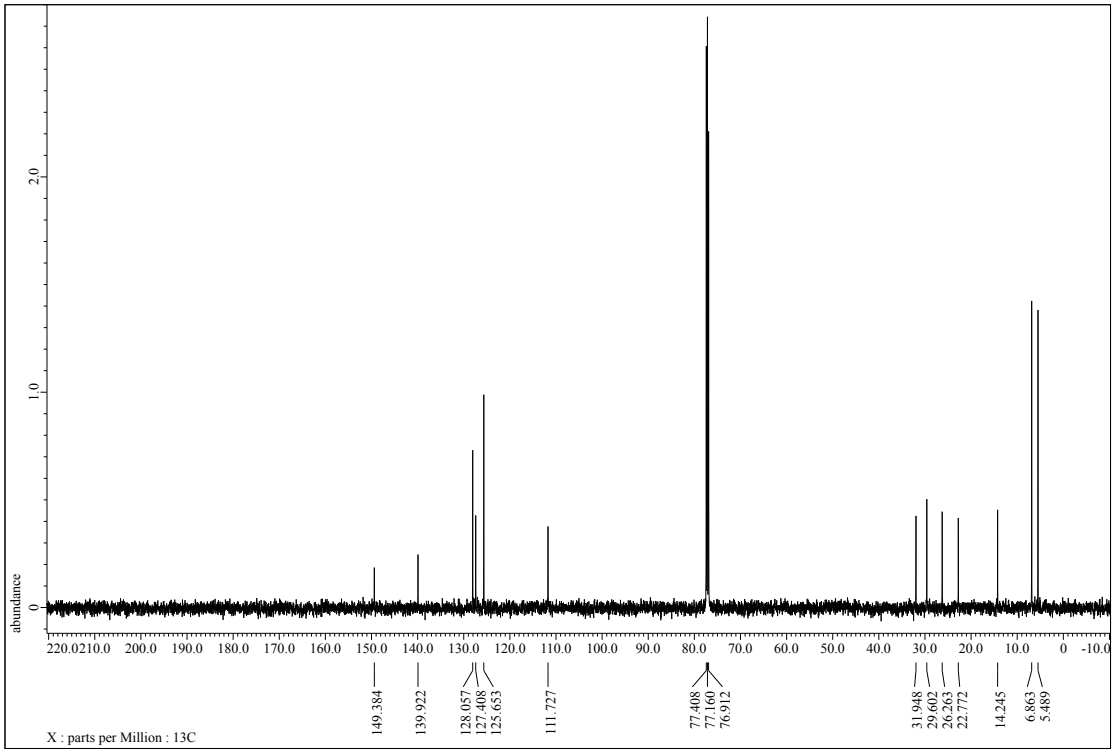
^{1}H and ^{13}C NMR spectra of **12**



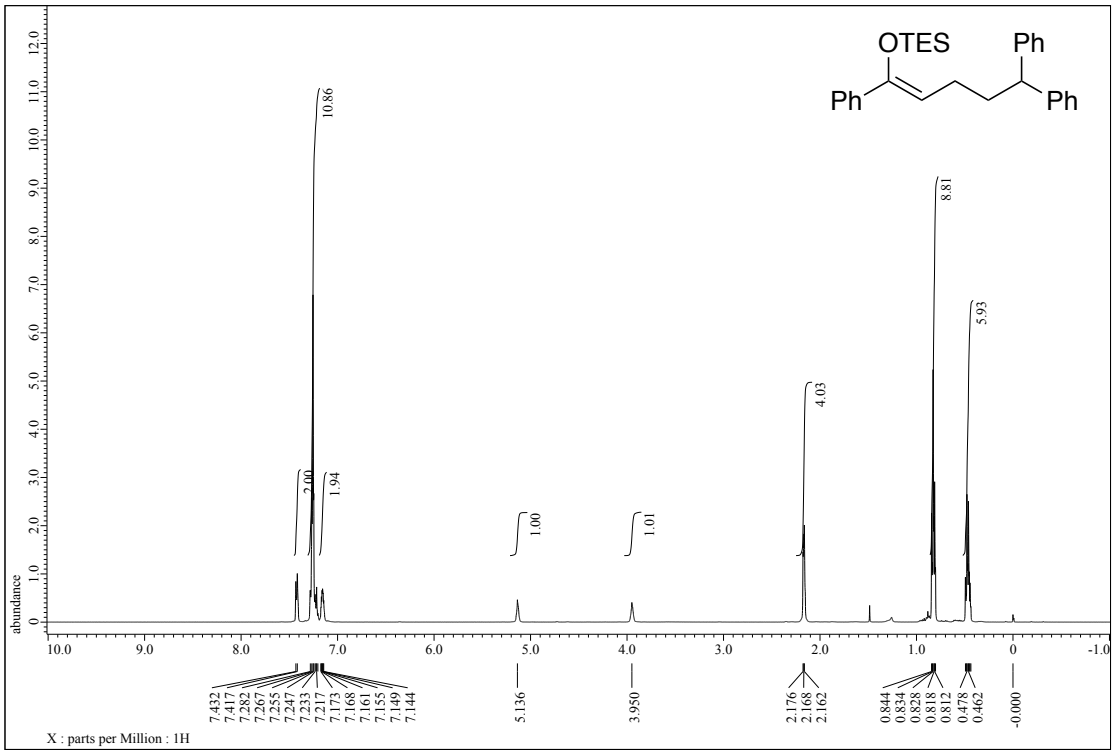


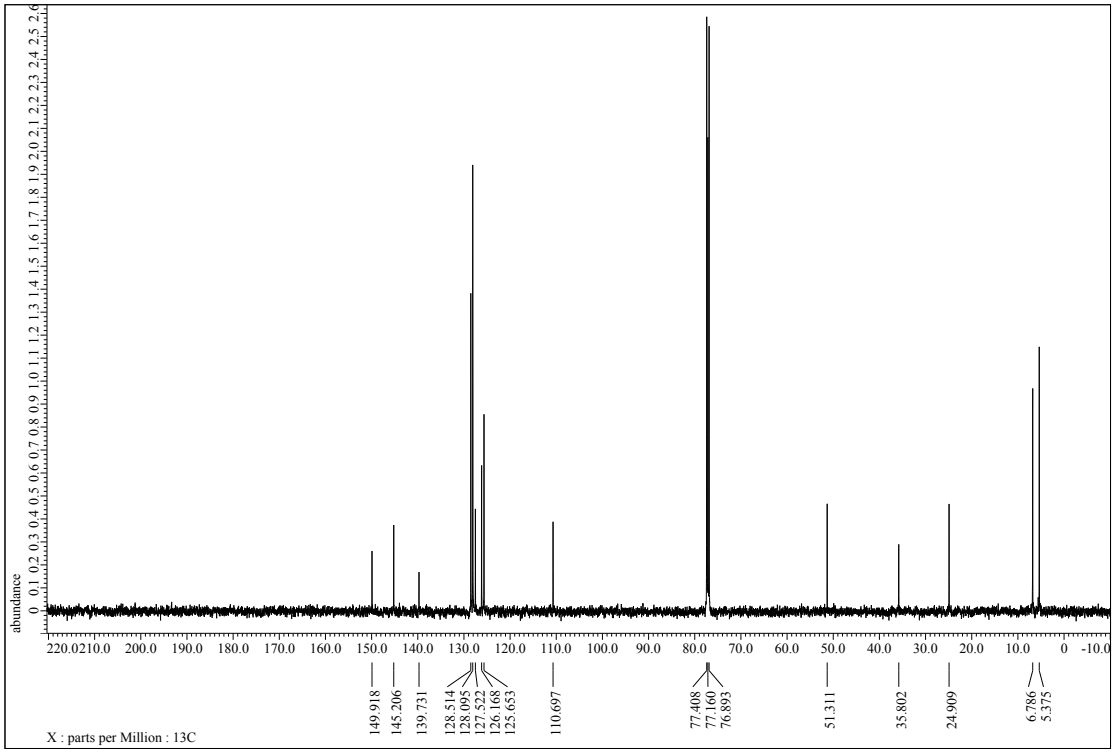
^{1}H and ^{13}C NMR spectra of **13**



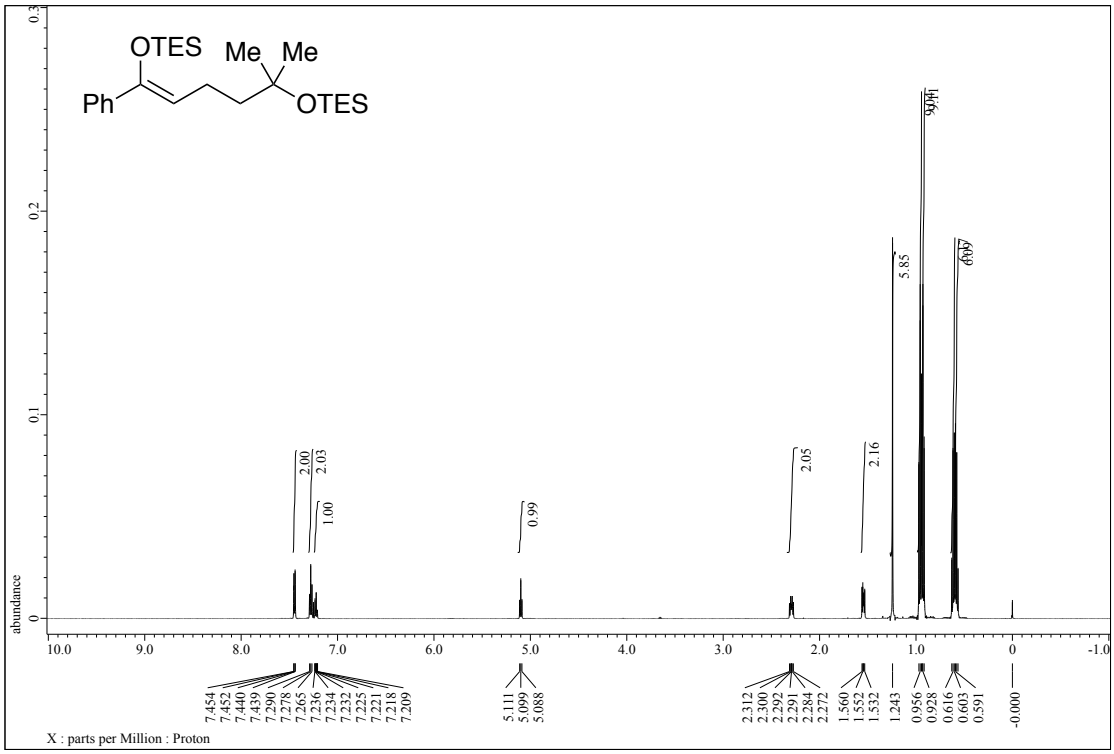


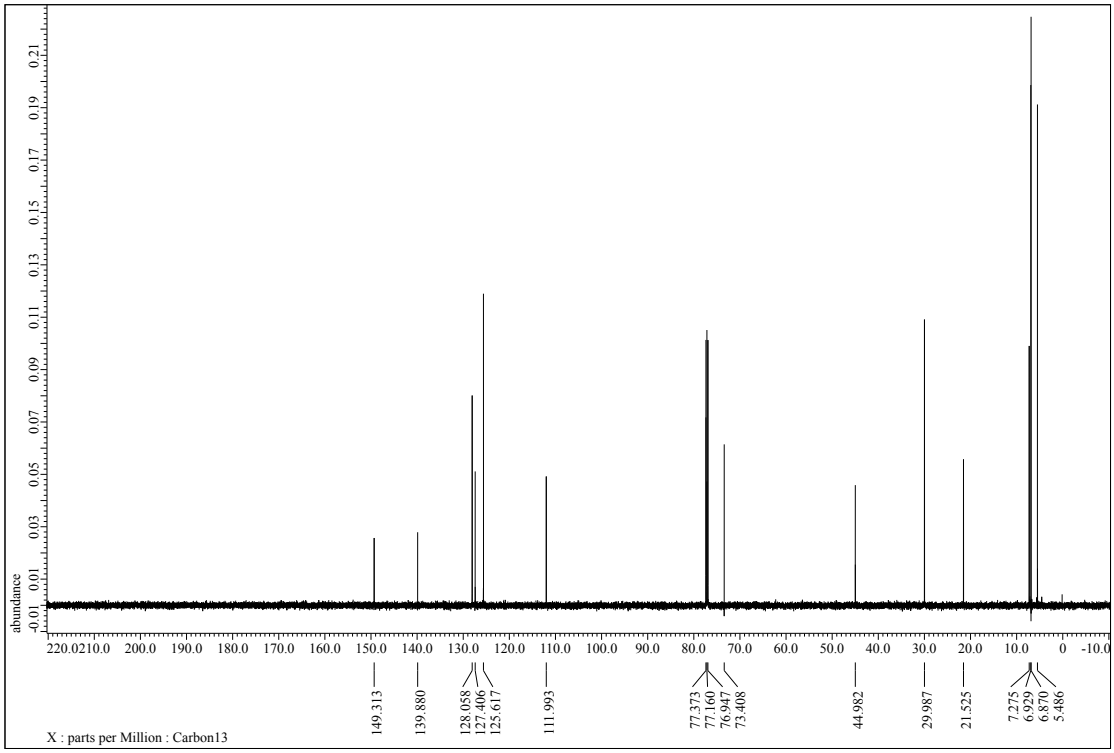
^{1}H and ^{13}C NMR spectra of **14**



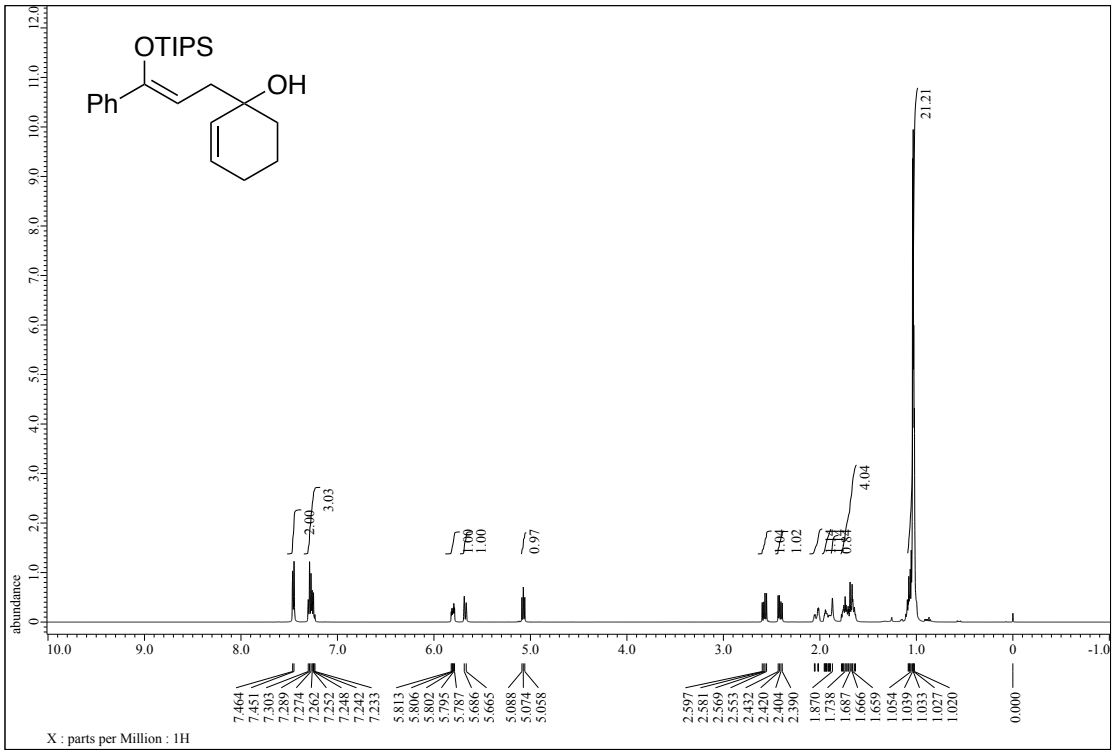


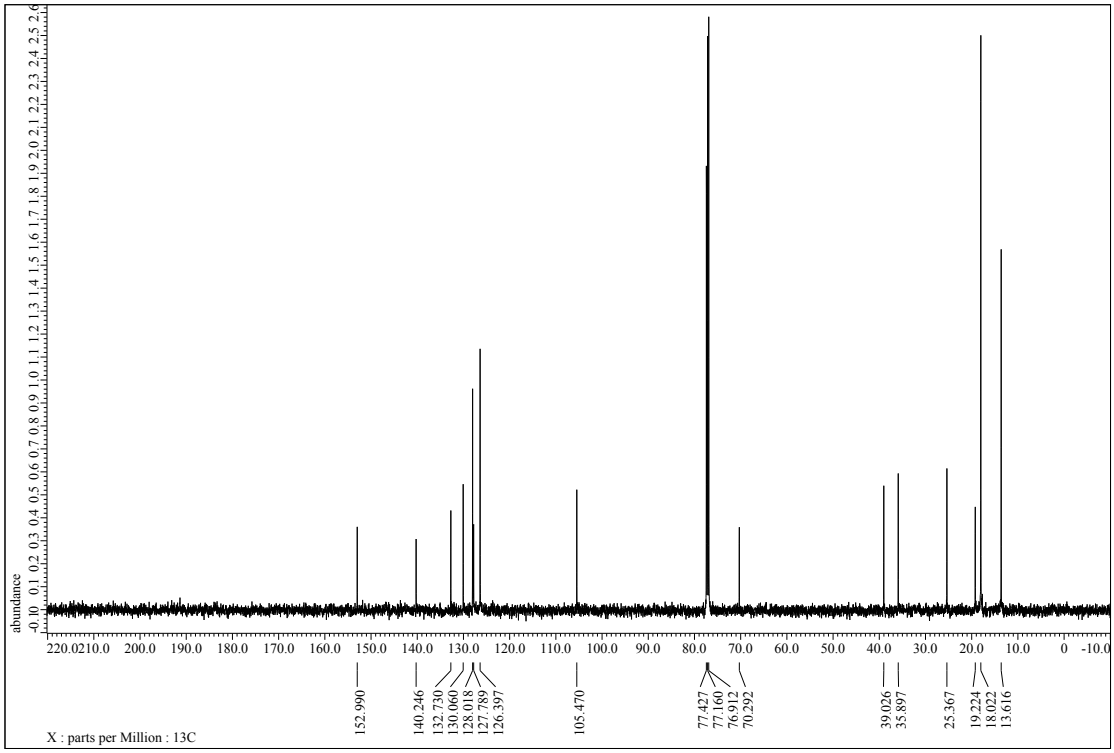
^{1}H and ^{13}C NMR spectra of **15**



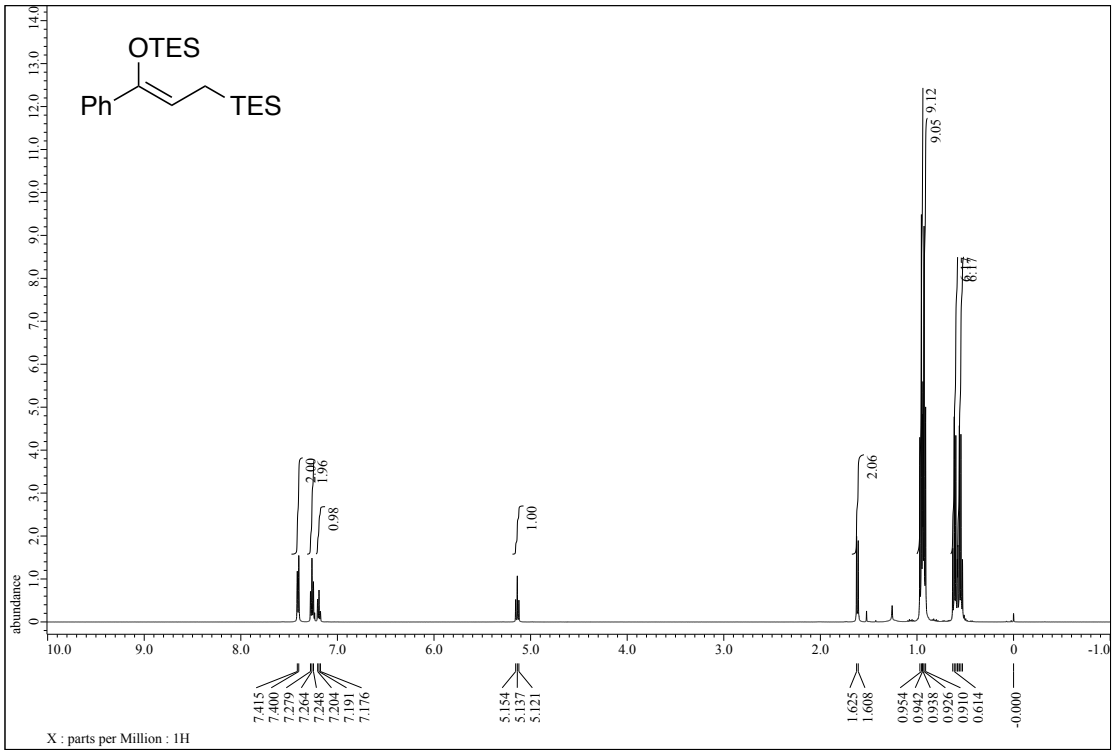


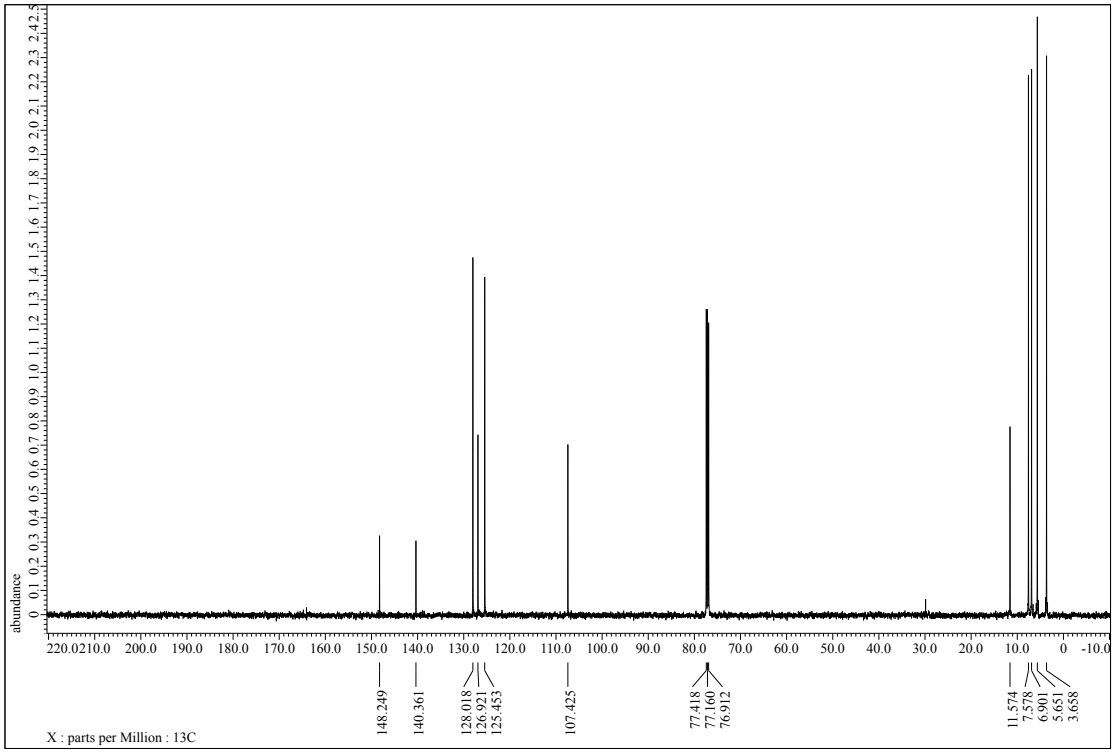
^{1}H and ^{13}C NMR spectra of **16**



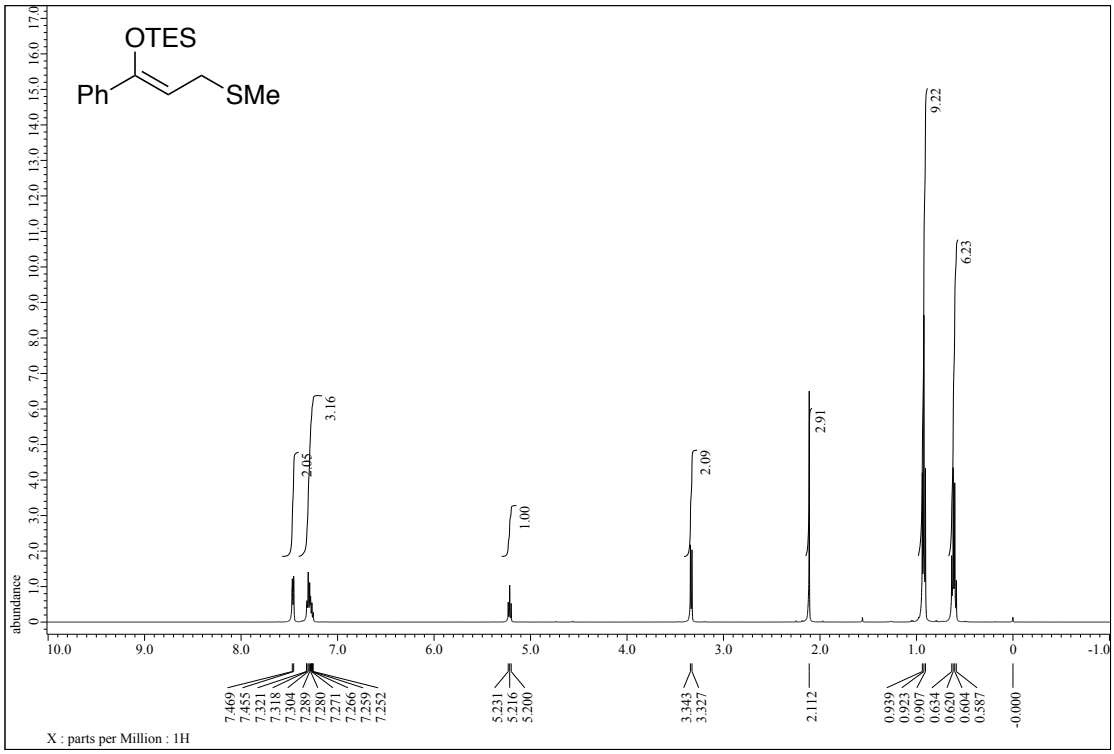


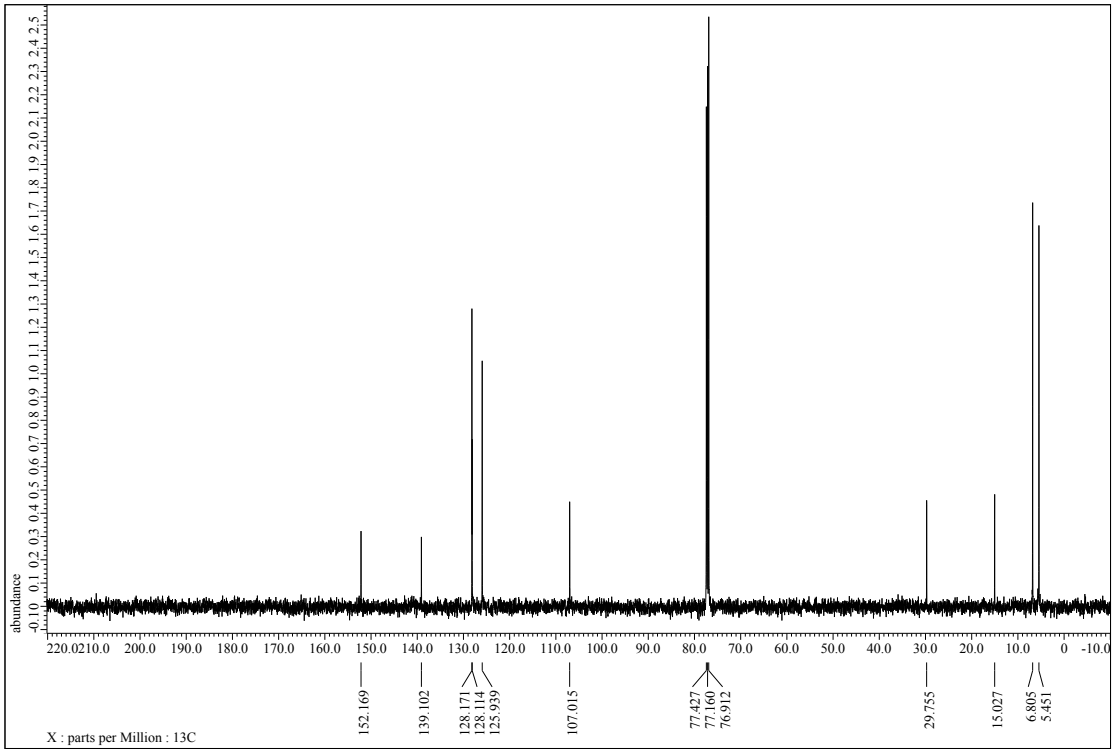
^{1}H and ^{13}C NMR spectra of **17**



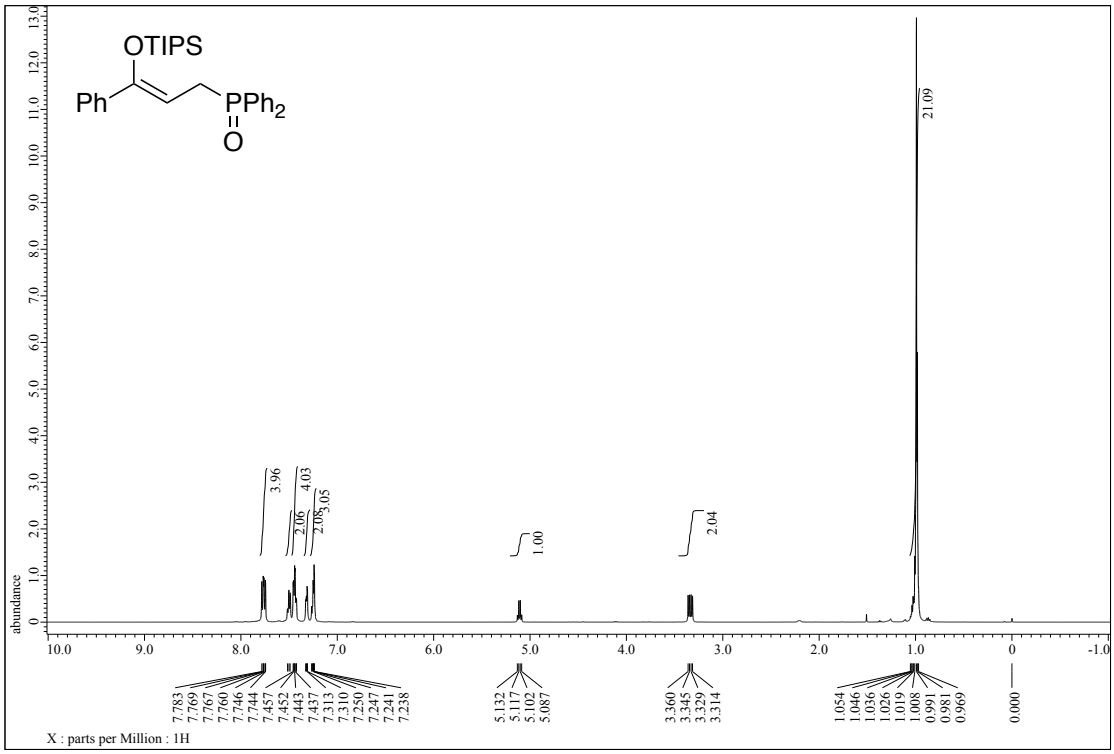


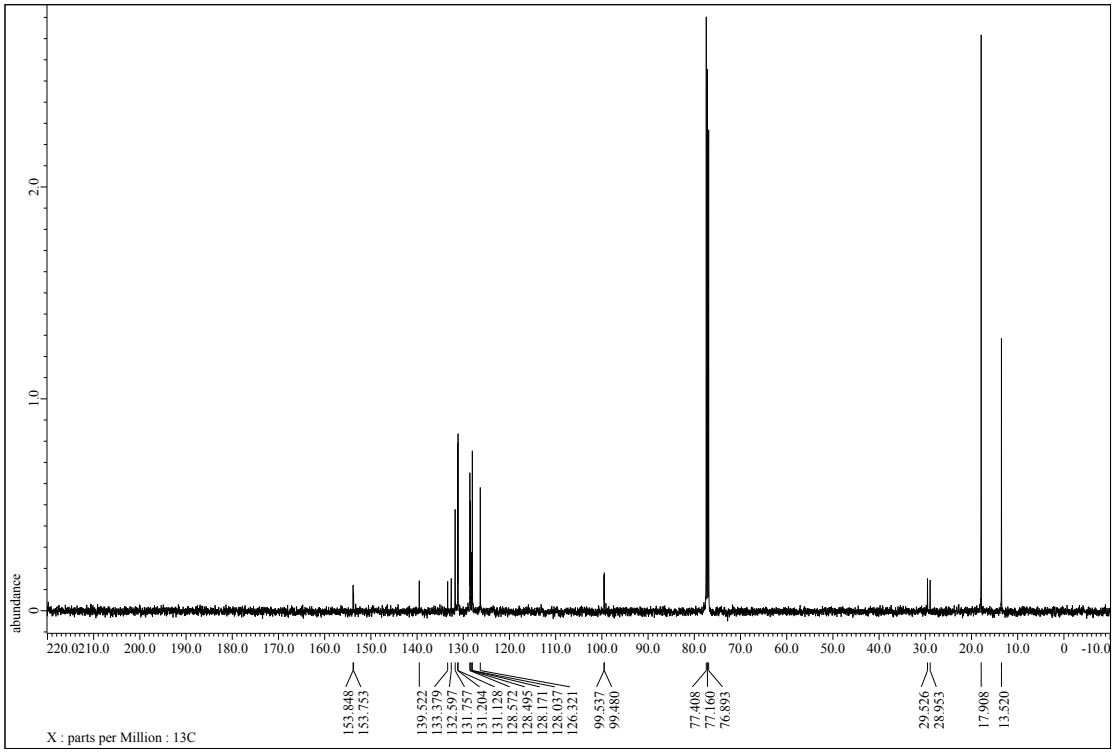
^{1}H and ^{13}C NMR spectra of **18**

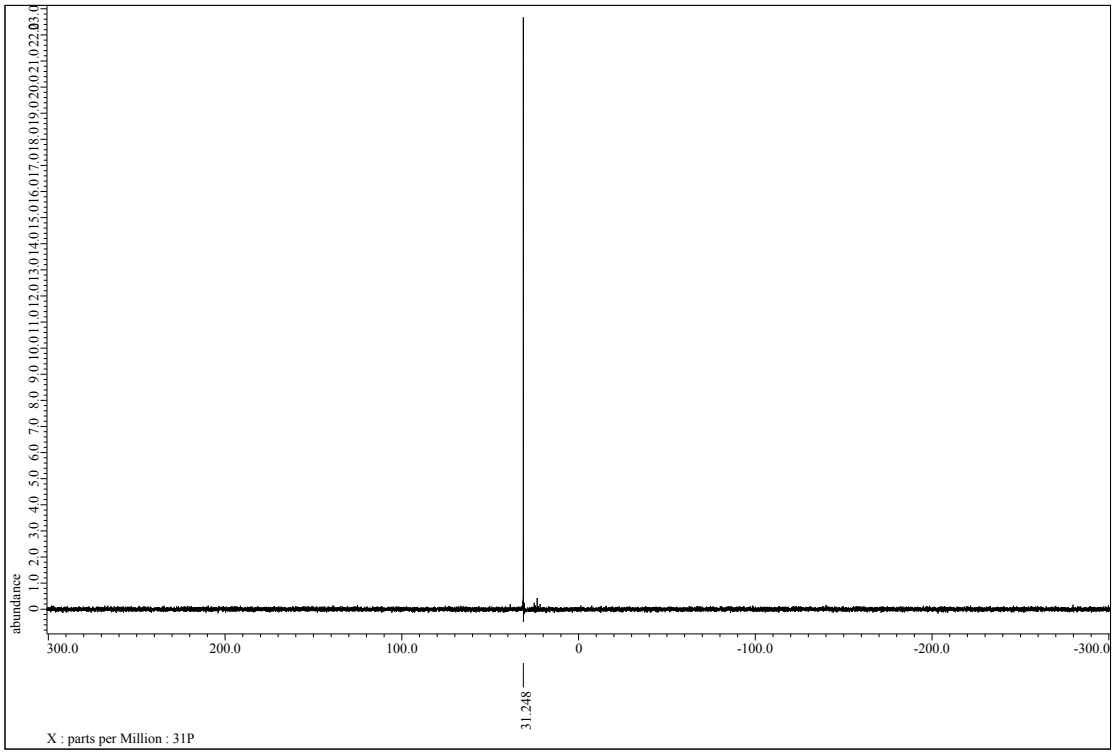




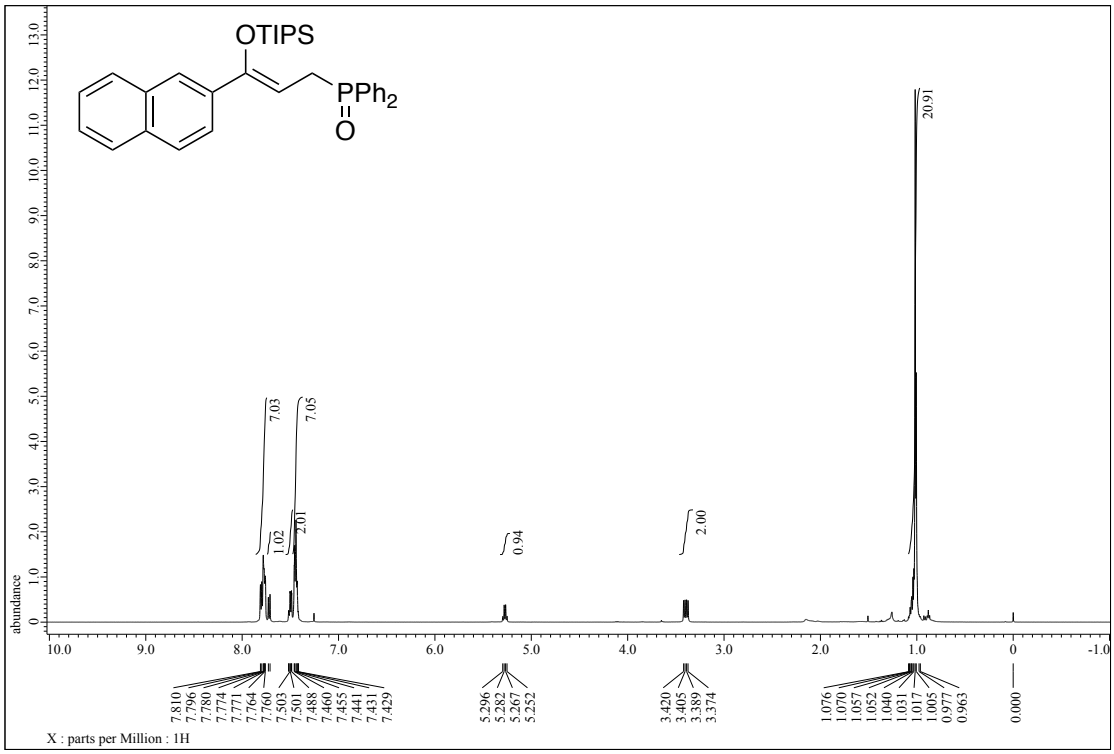
^{1}H, ^{13}C, and ^{31}P NMR spectra of **19**

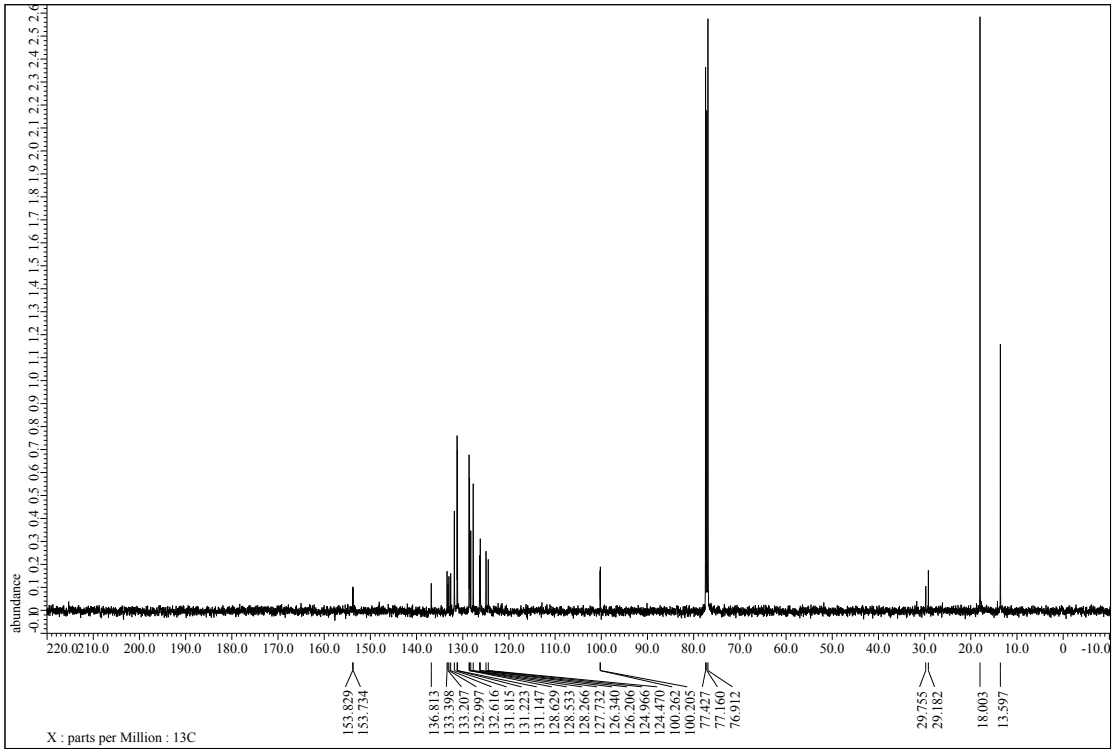


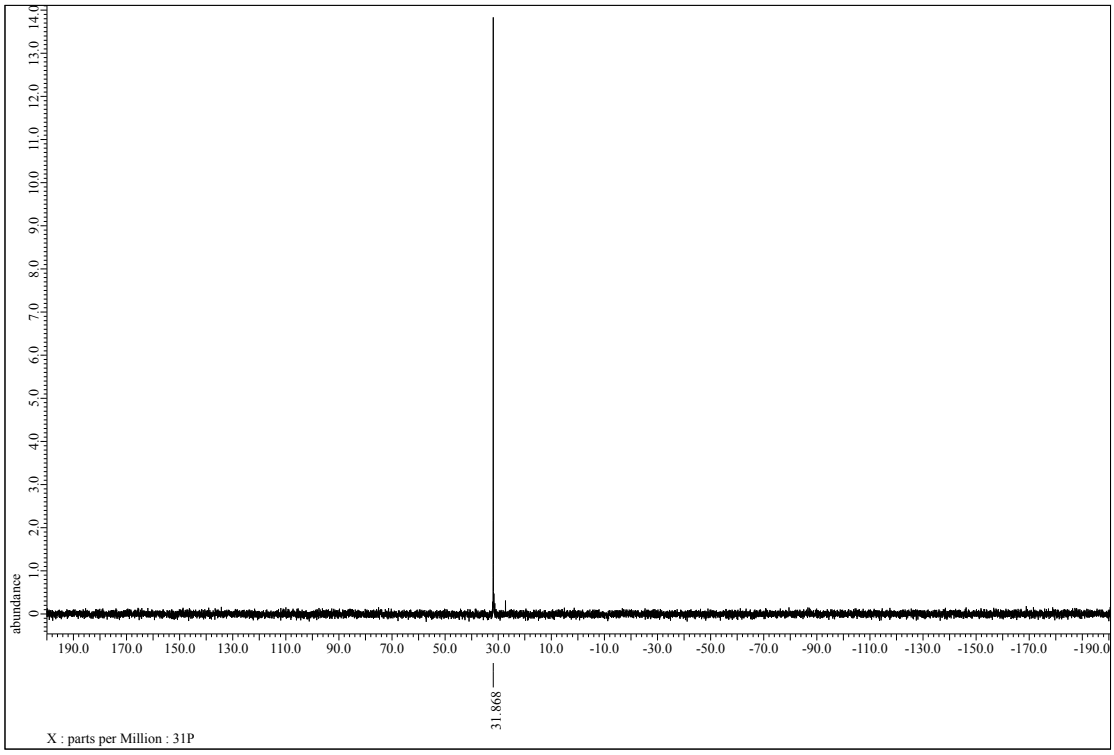



abundance
300.0
200.0
100.0
0
-100.0
-200.0
-300.0
31.248
X : parts per Million : 31P

^{1}H, ^{13}C, and ^{31}P NMR spectra of **20**






abundance
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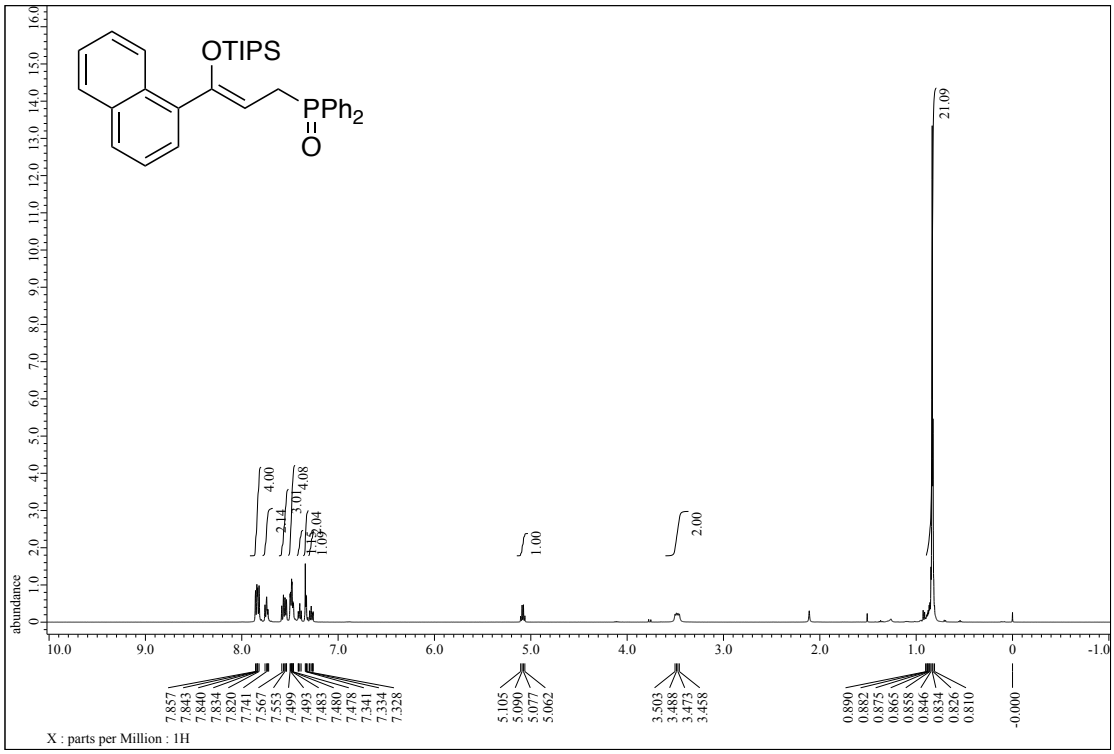
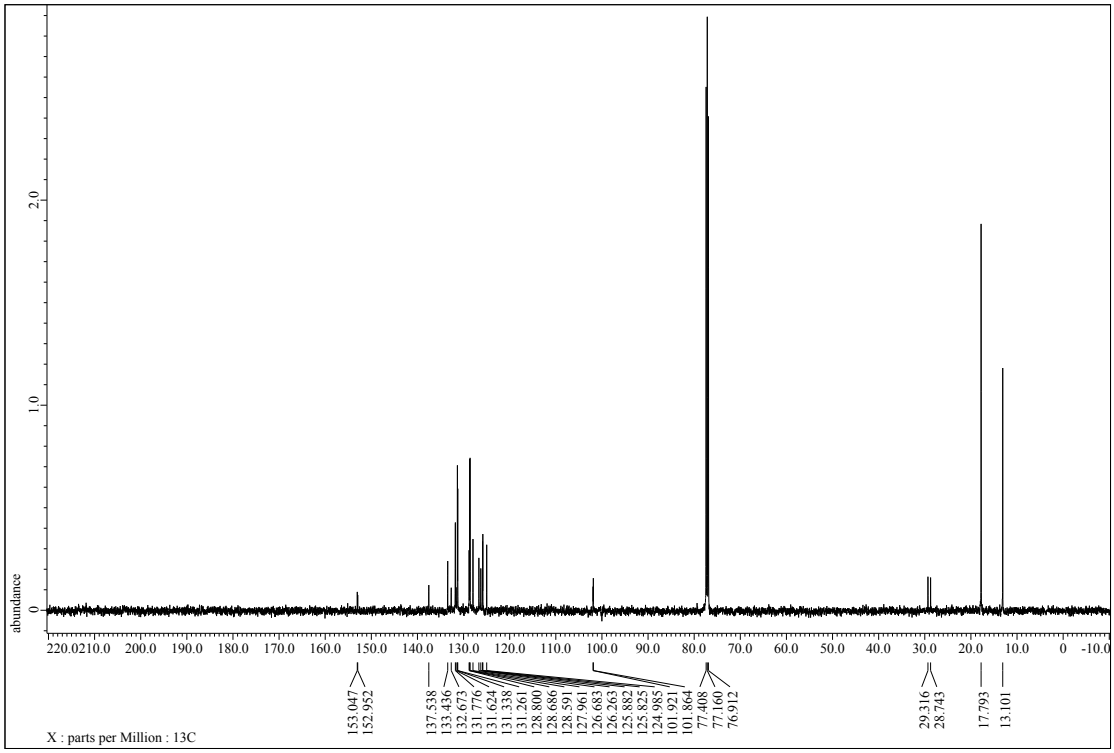
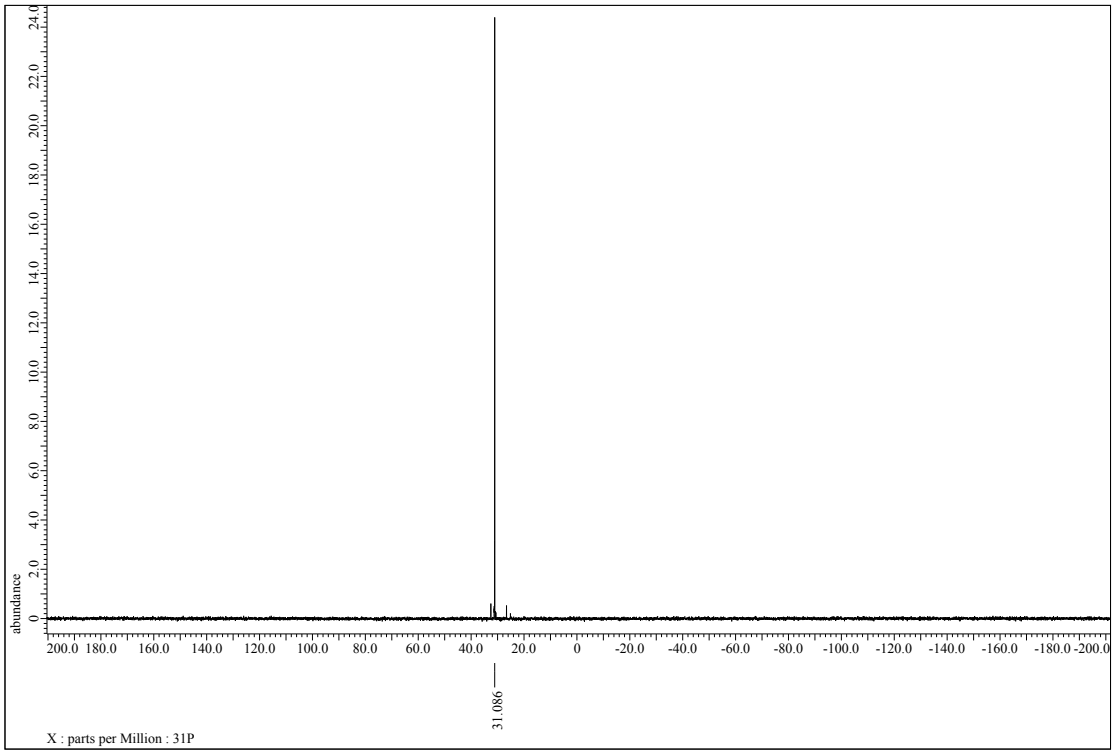
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
190.0
170.0
150.0
130.0
110.0
90.0
70.0
50.0
30.0
10.0
-10.0
-30.0
-50.0
-70.0
-90.0
-110.0
-130.0
-150.0
-170.0
-190.0
31.868
X : parts per Million : 31P

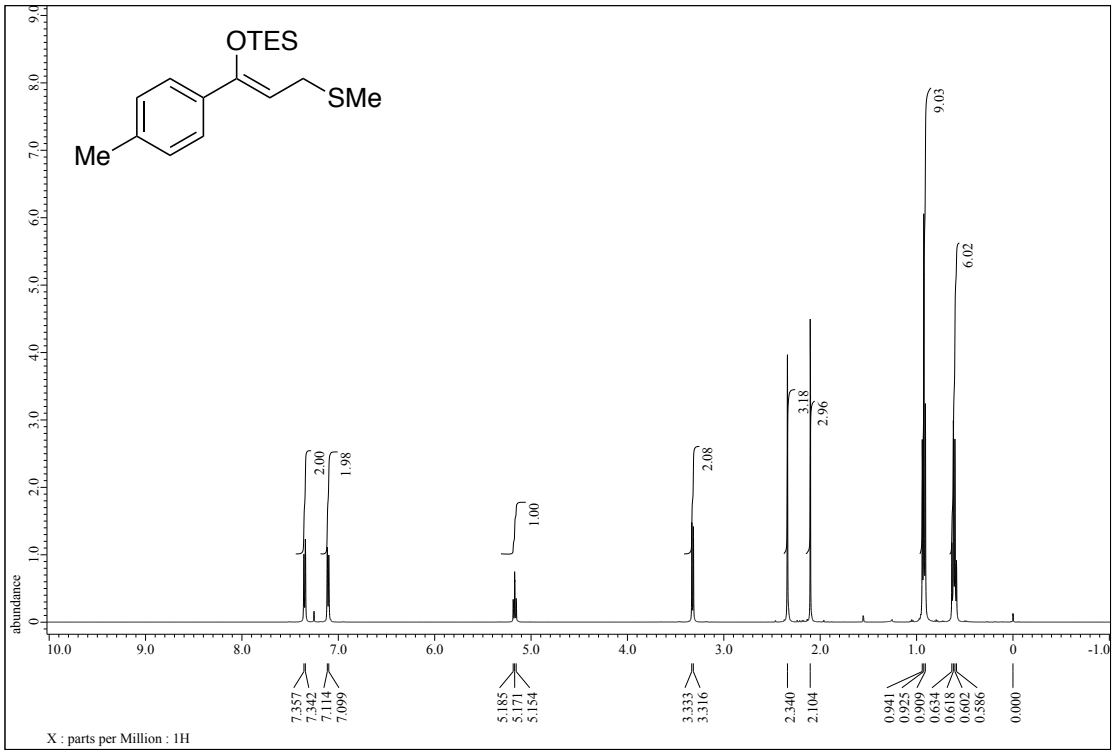
^{1}H, ^{13}C, and ^{31}P NMR spectra of **21**

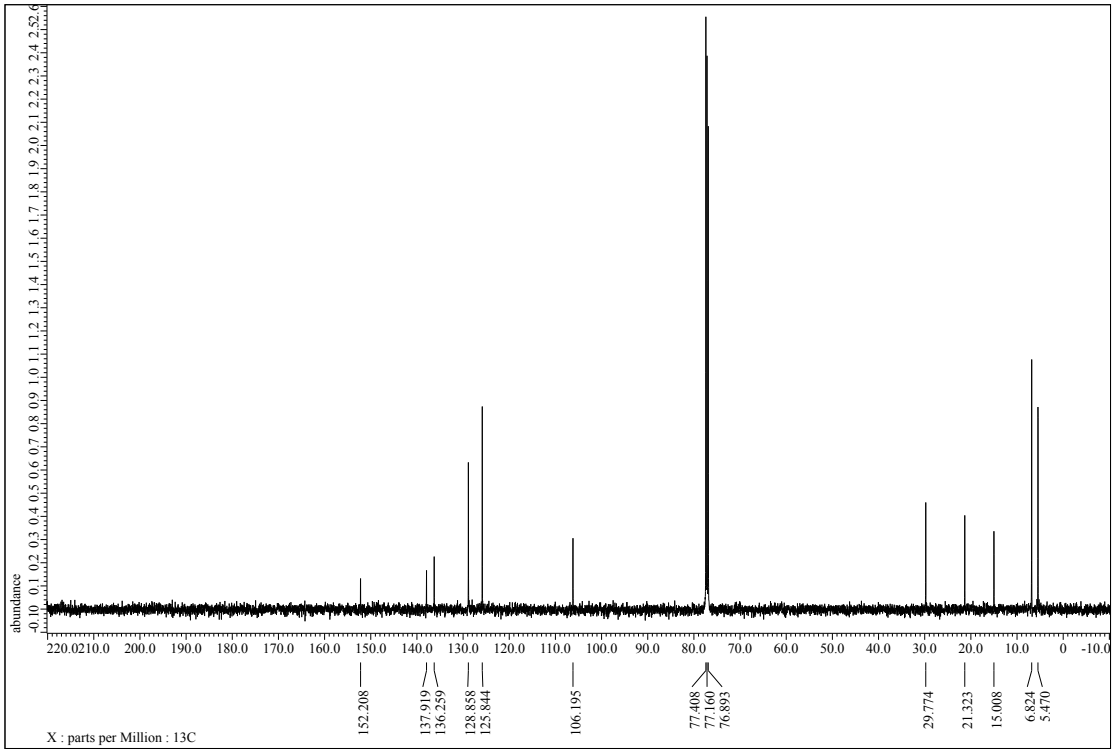




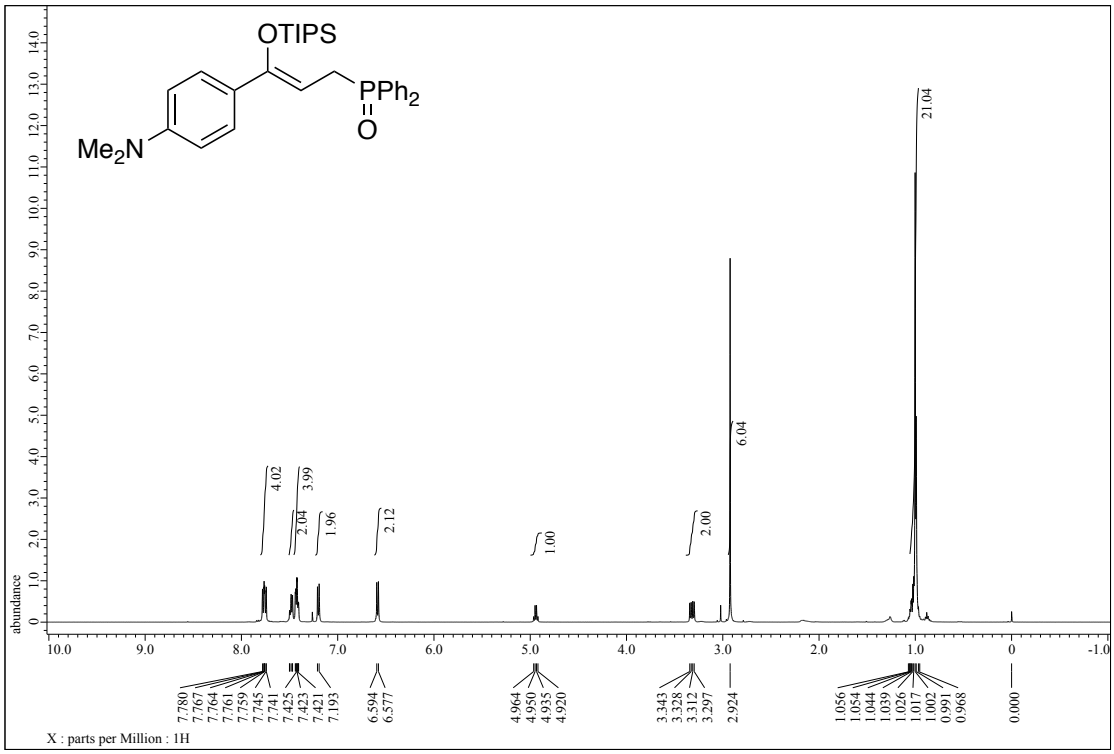

abundance
0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
18.0
20.0
22.0
24.0
200.0 180.0 160.0 140.0 120.0 100.0 80.0 60.0 40.0 20.0 0 -20.0 -40.0 -60.0 -80.0 -100.0 -120.0 -140.0 -160.0 -180.0 -200.0
31.086
X : parts per Million : 31P

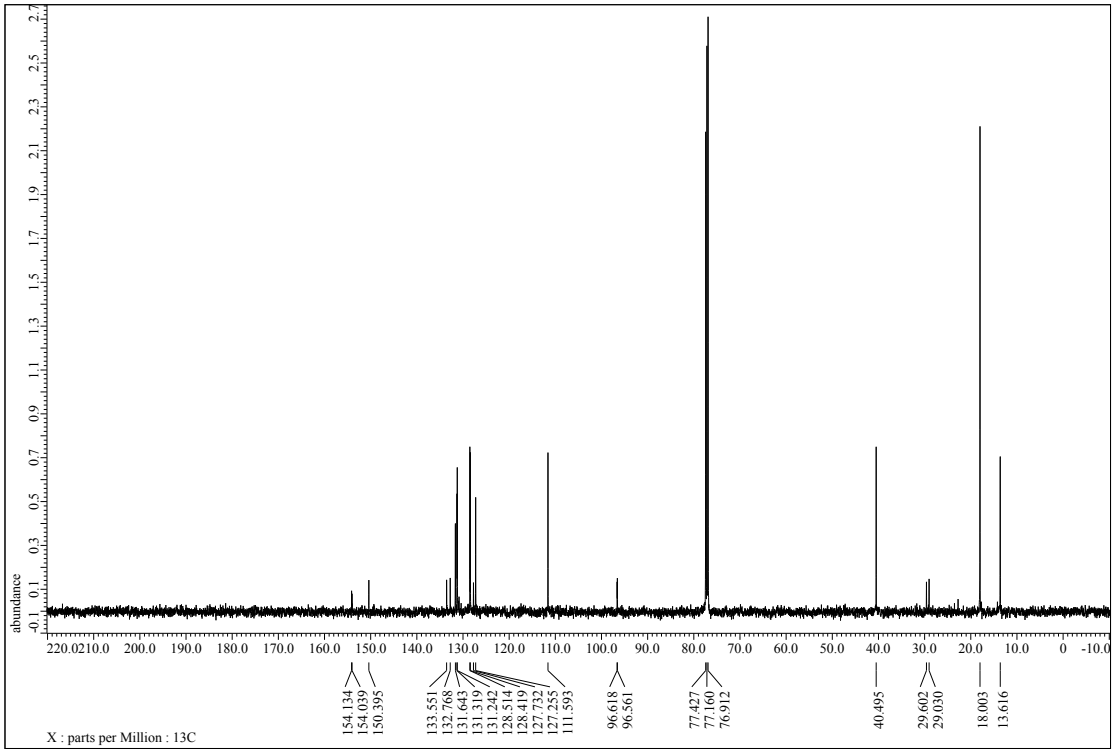
^{1}H and ^{13}C NMR spectra of **22**

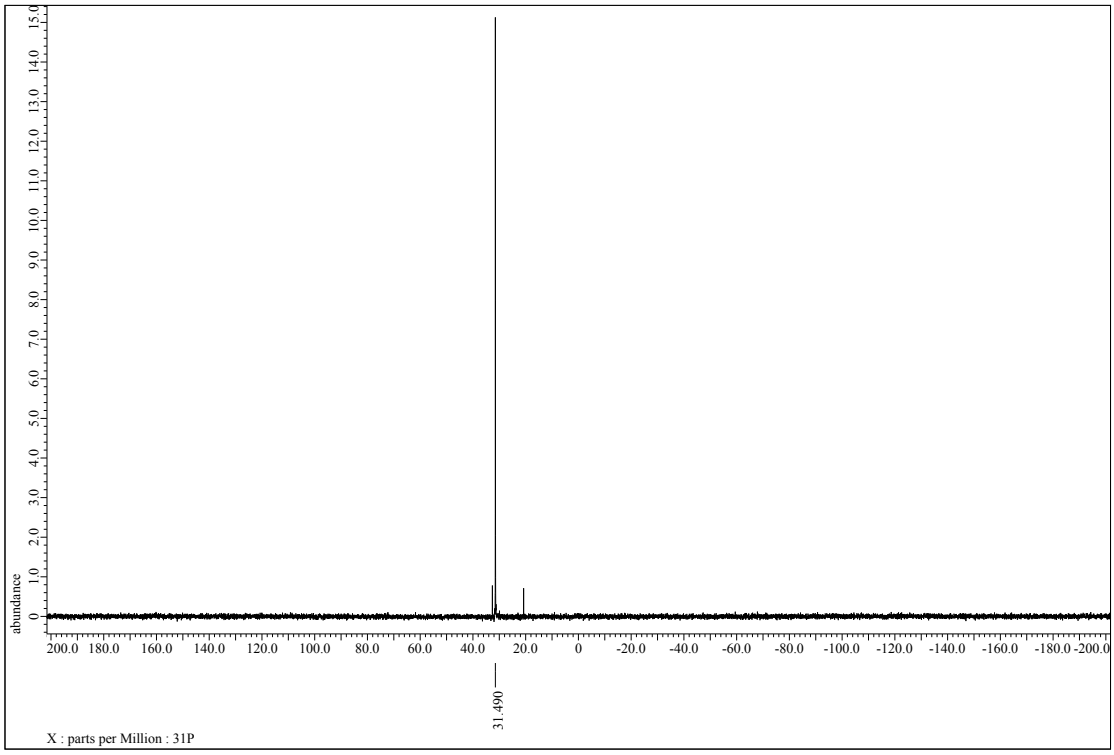




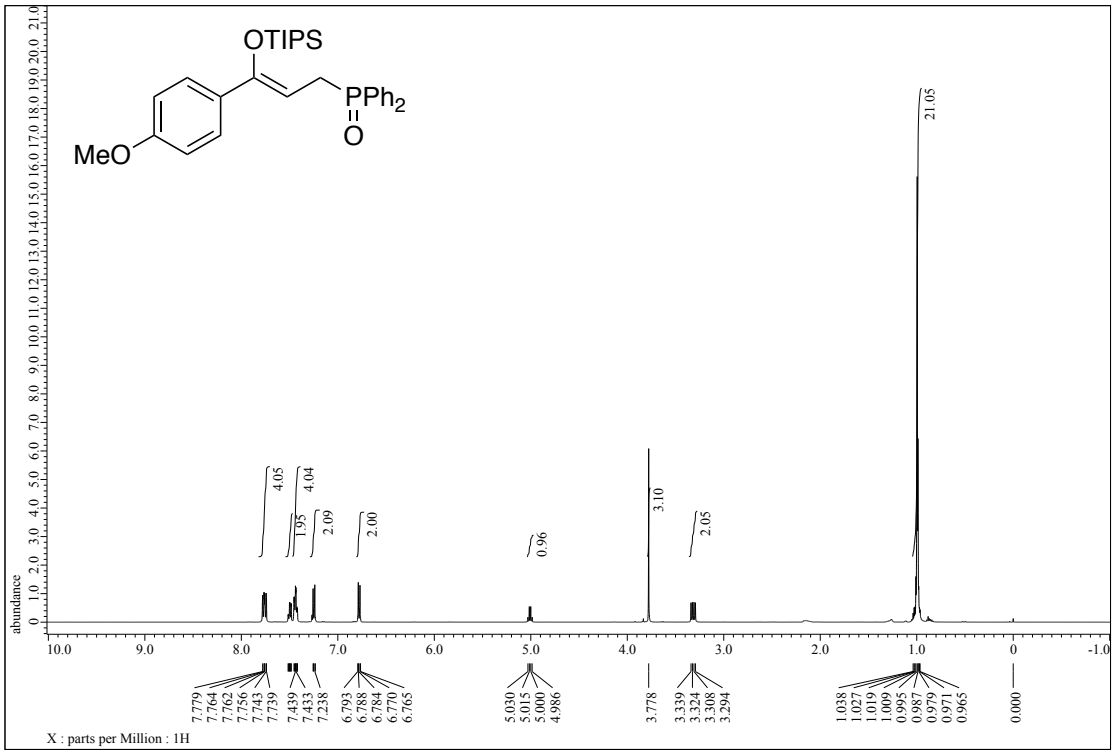
^{1}H, ^{13}C, and ^{31}P NMR spectra of **23**

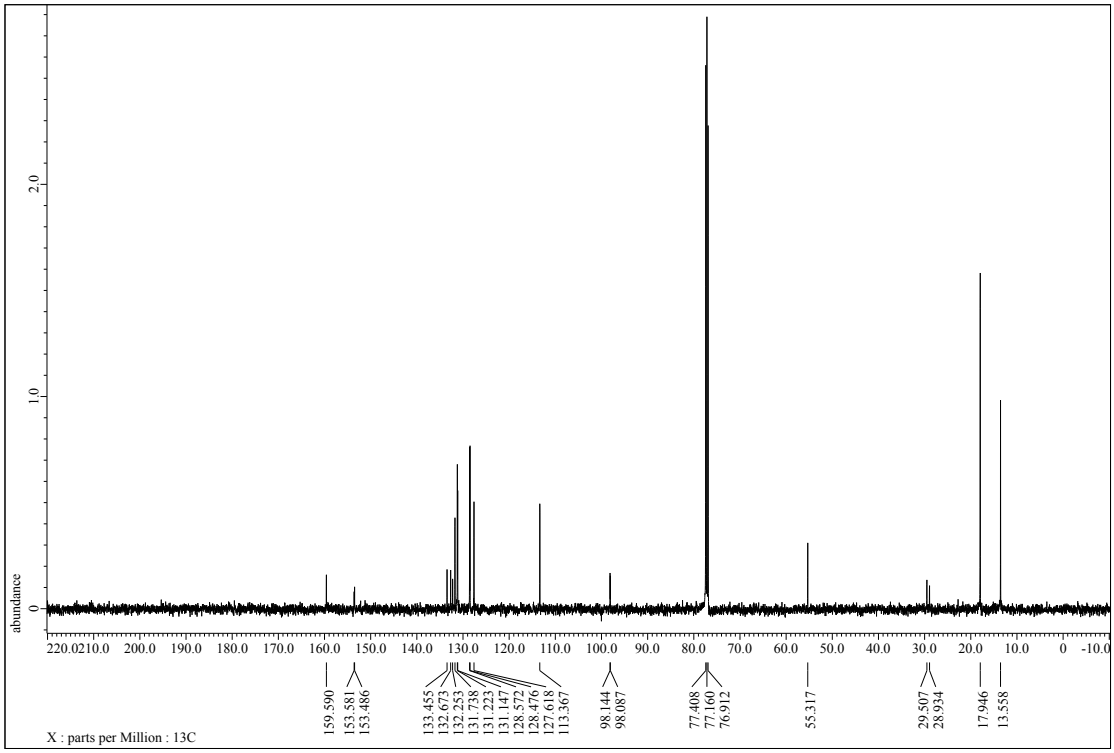


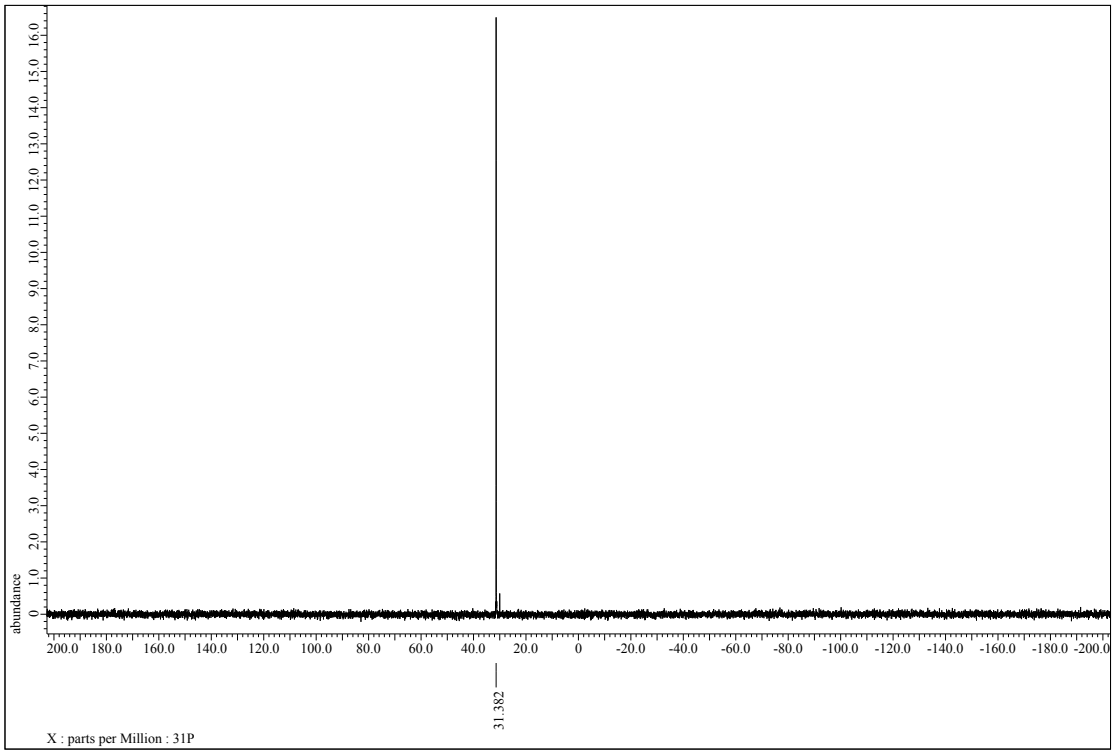



abundance
15.0
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
200.0 180.0 160.0 140.0 120.0 100.0 80.0 60.0 40.0 20.0 0 -20.0 -40.0 -60.0 -80.0 -100.0 -120.0 -140.0 -160.0 -180.0 -200.0
31.490
X : parts per Million : 31P

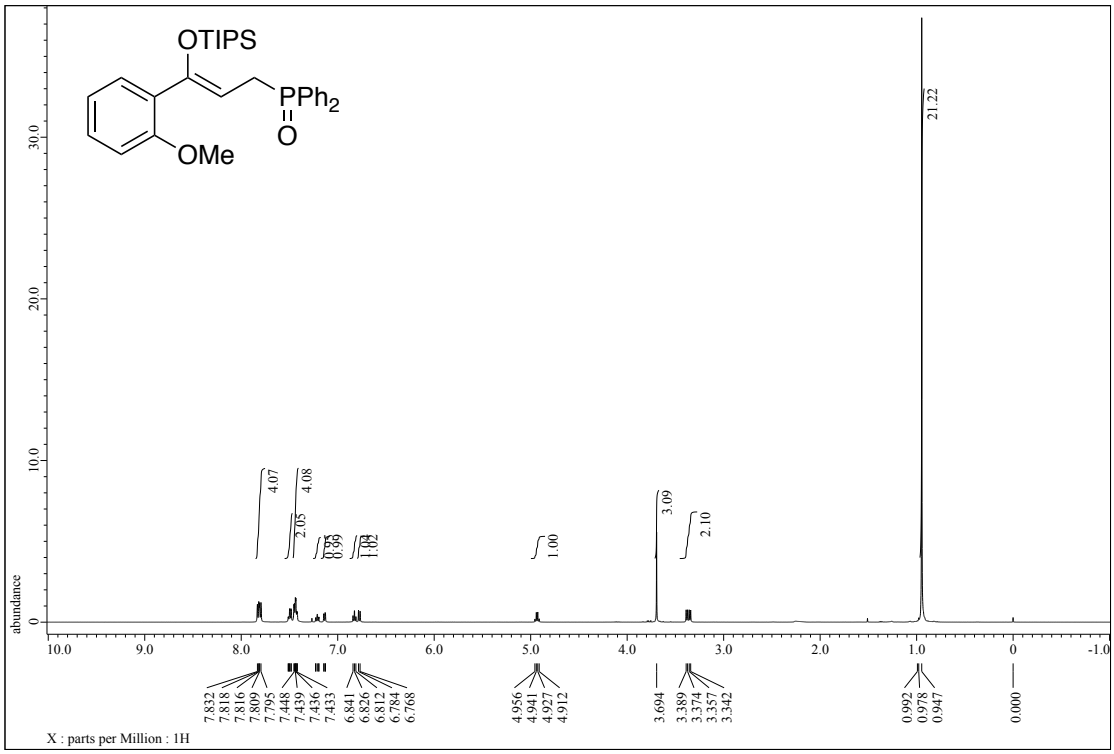
^{1}H, ^{13}C, and ^{31}P NMR spectra of **24**

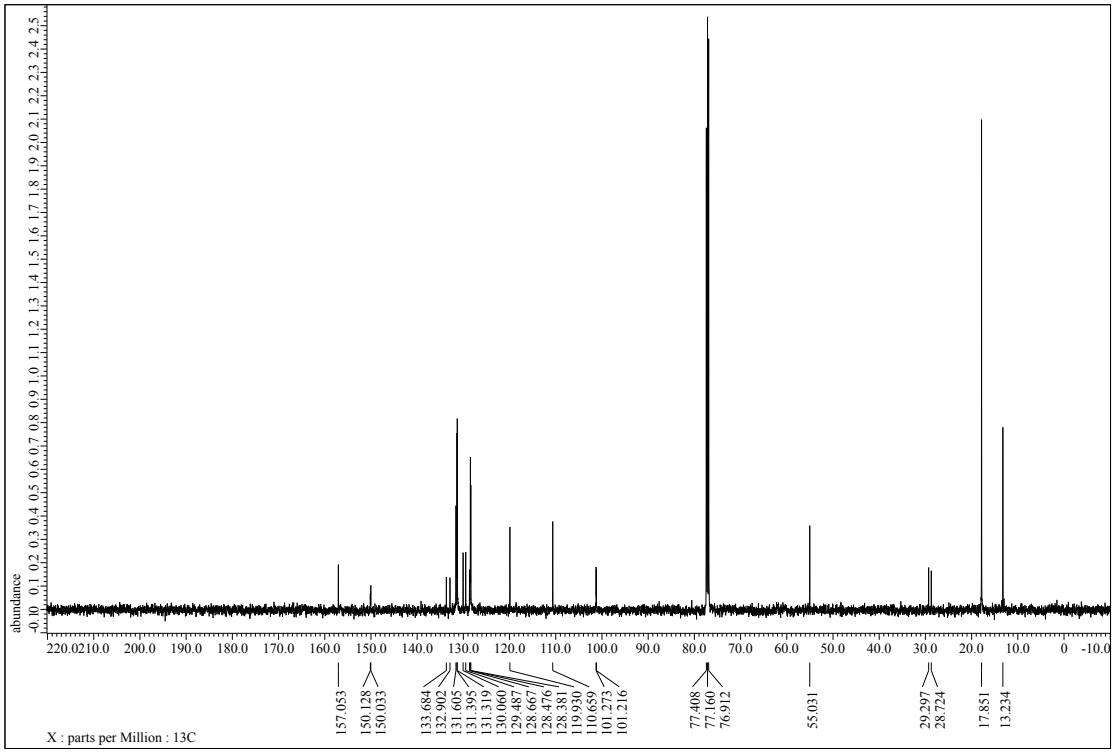


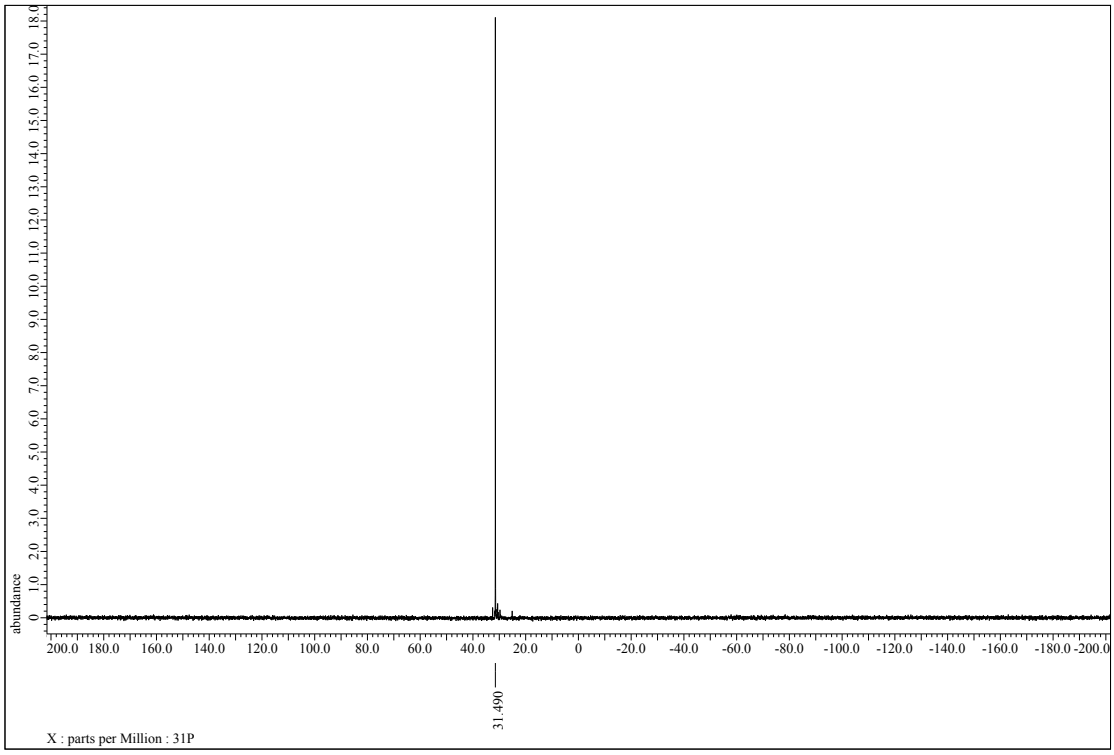



abundance
16.0
15.0
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
200.0 180.0 160.0 140.0 120.0 100.0 80.0 60.0 40.0 20.0 0 -20.0 -40.0 -60.0 -80.0 -100.0 -120.0 -140.0 -160.0 -180.0 -200.0
31.382
X : parts per Million : 31P

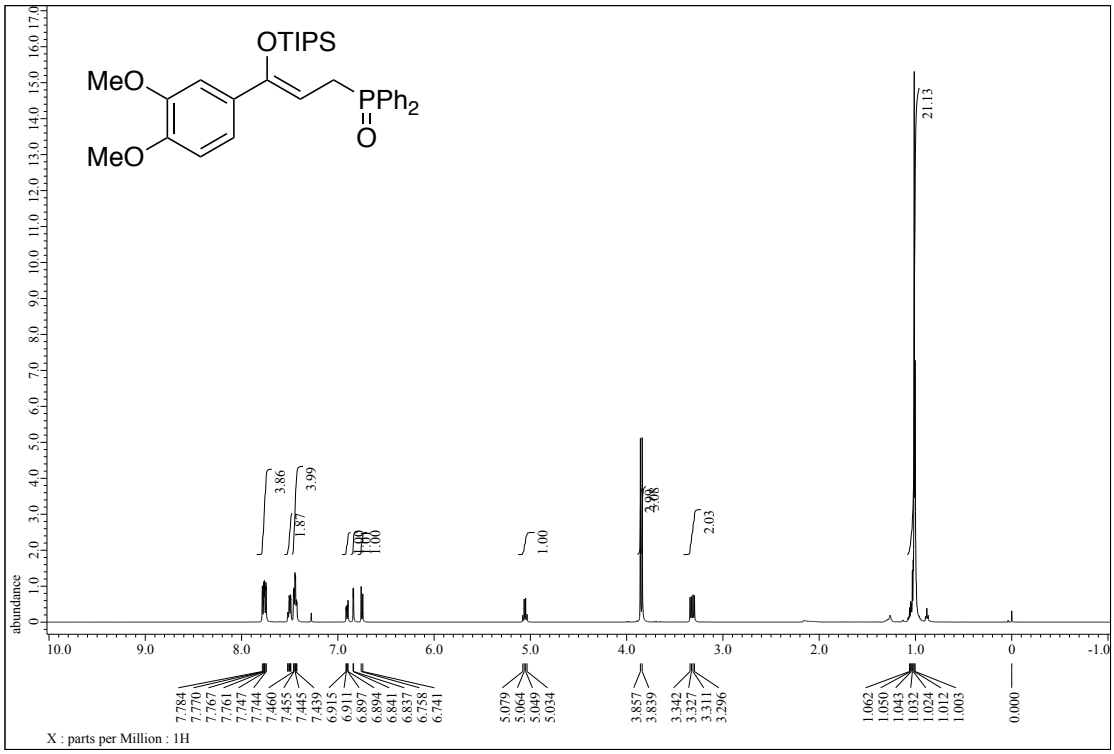
^{1}H, ^{13}C, and ^{31}P NMR spectra of **25**

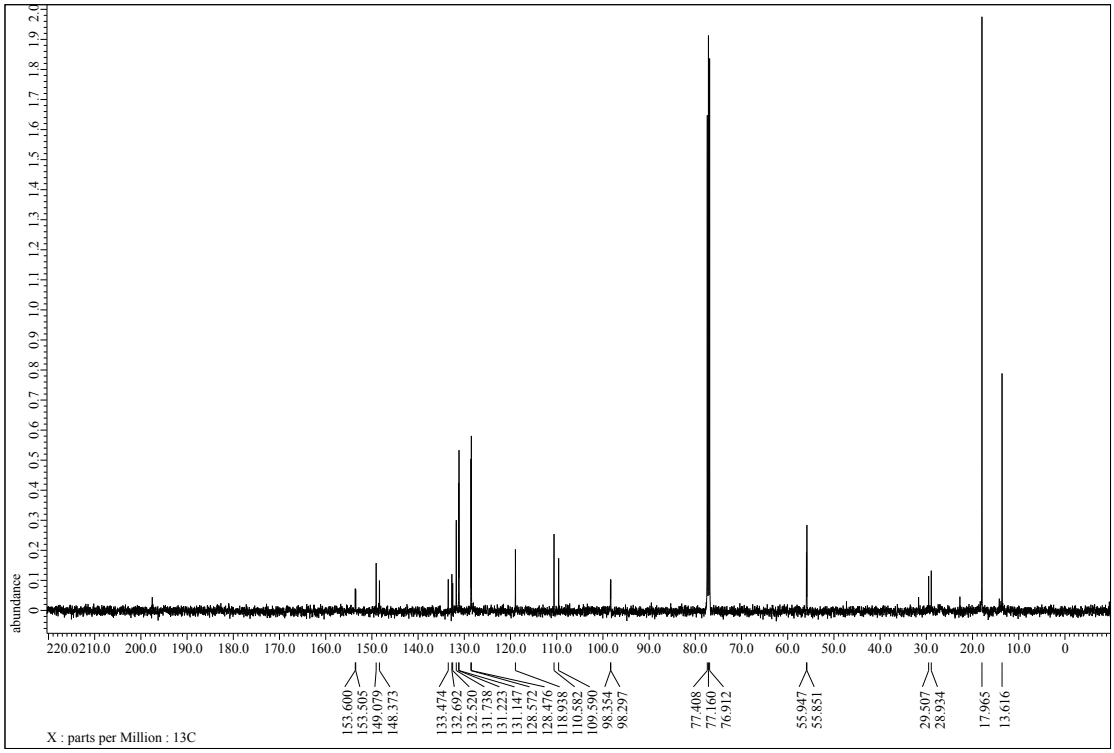


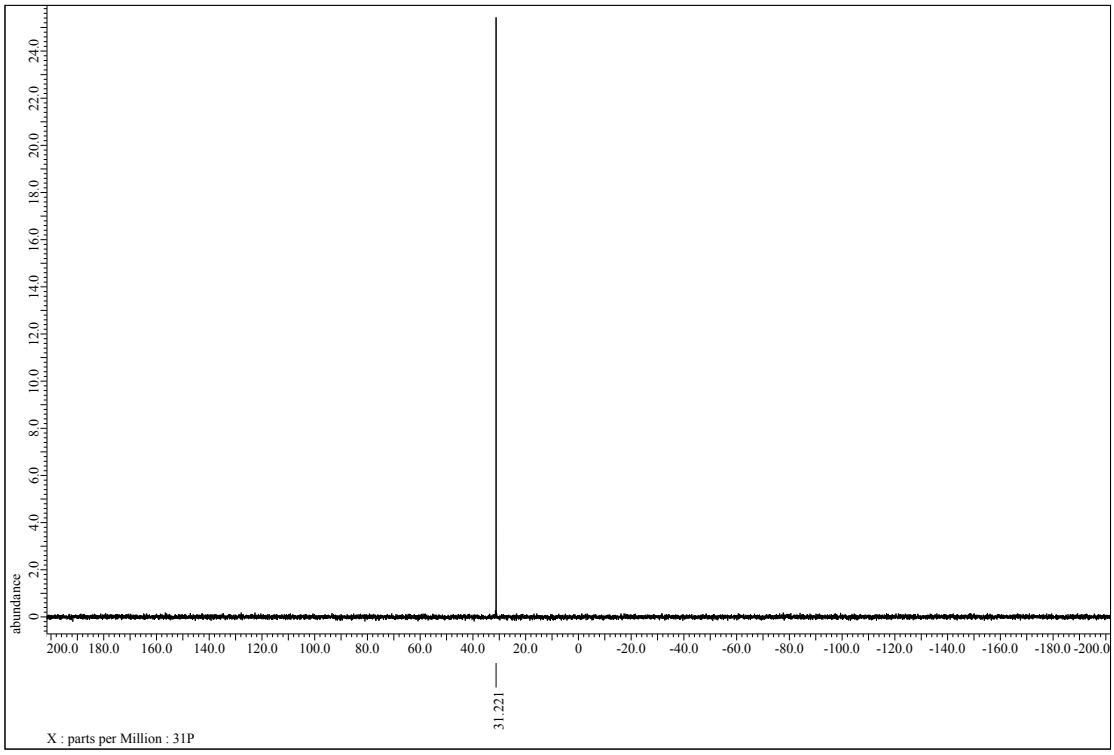



abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
17.0
18.0
200.0 180.0 160.0 140.0 120.0 100.0 80.0 60.0 40.0 20.0 0 -20.0 -40.0 -60.0 -80.0 -100.0 -120.0 -140.0 -160.0 -180.0 -200.0
31.490
X : parts per Million : 31P

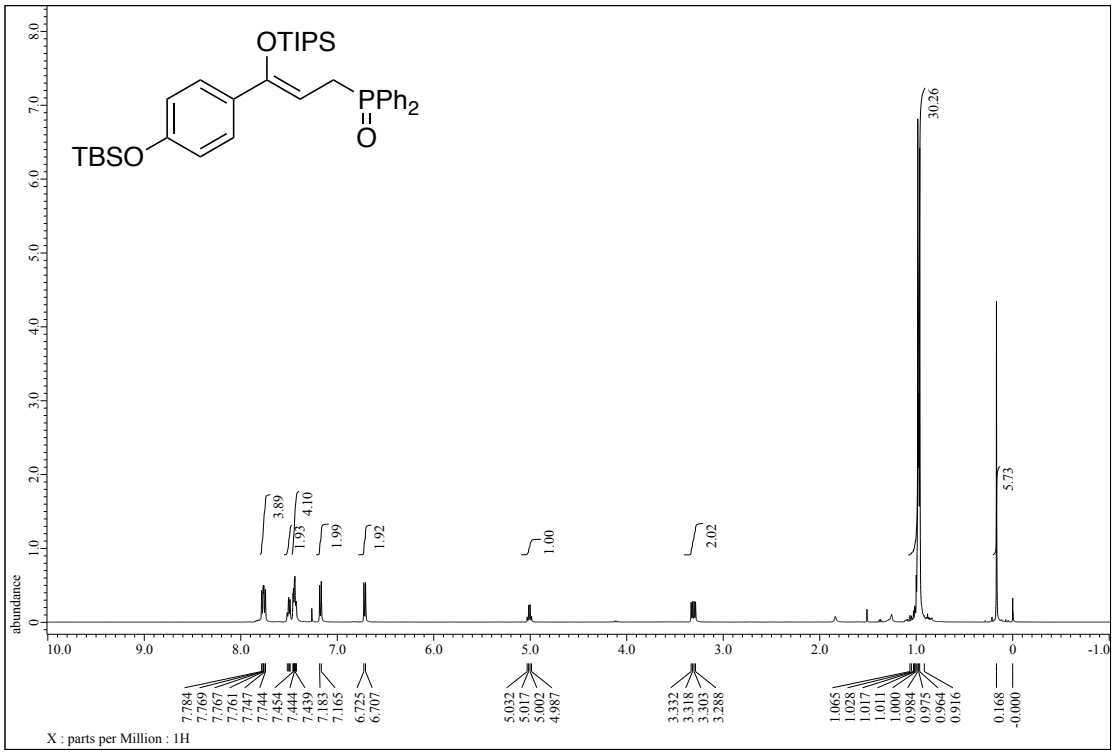
^{1}H, ^{13}C, and ^{31}P NMR spectra of **26**

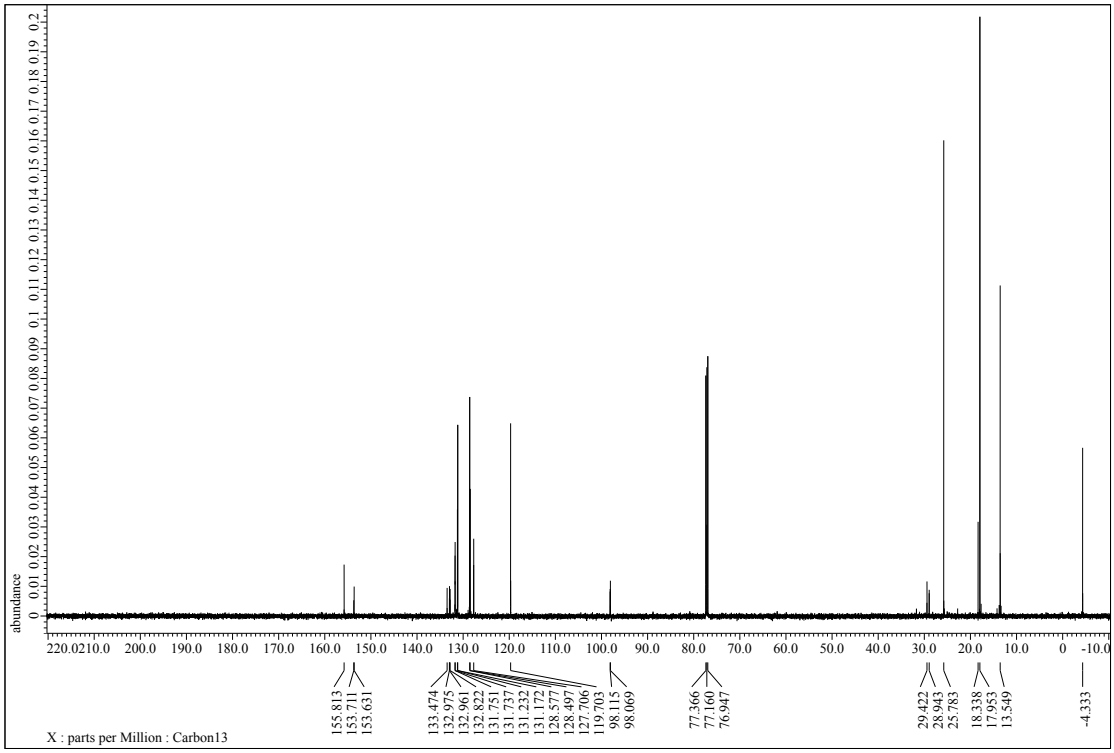


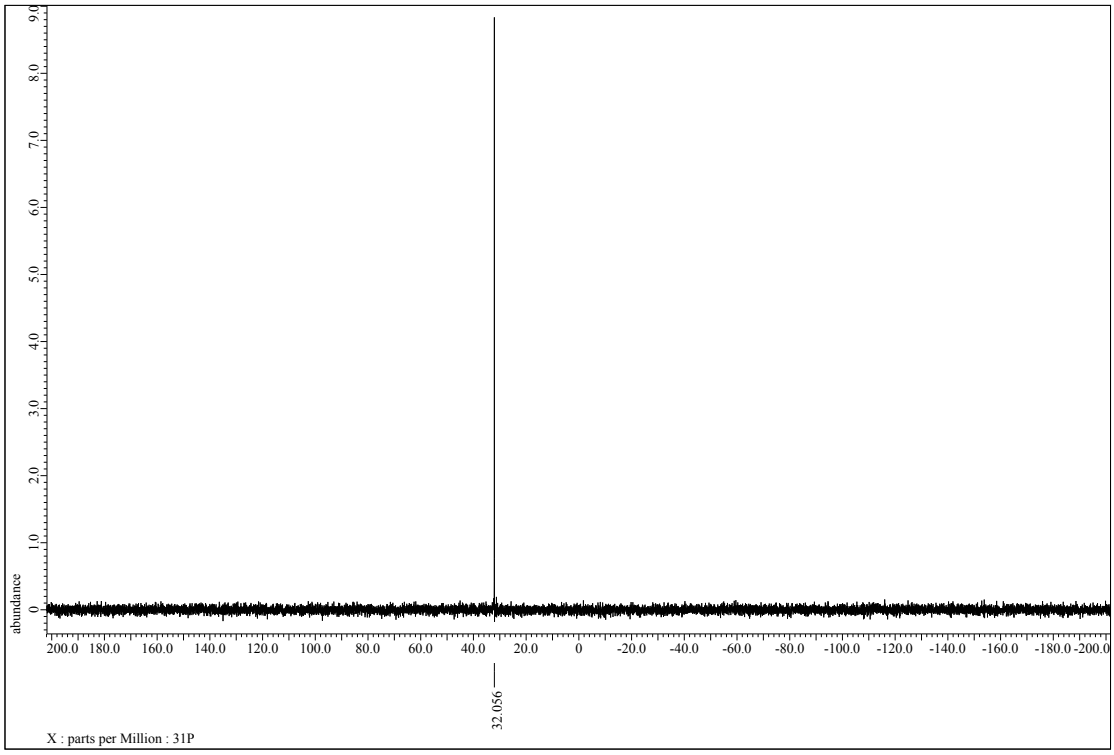



abundance
0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
18.0
20.0
22.0
24.0
200.0 180.0 160.0 140.0 120.0 100.0 80.0 60.0 40.0 20.0 0 -20.0 -40.0 -60.0 -80.0 -100.0 -120.0 -140.0 -160.0 -180.0 -200.0
31.221
X : parts per Million : 31P

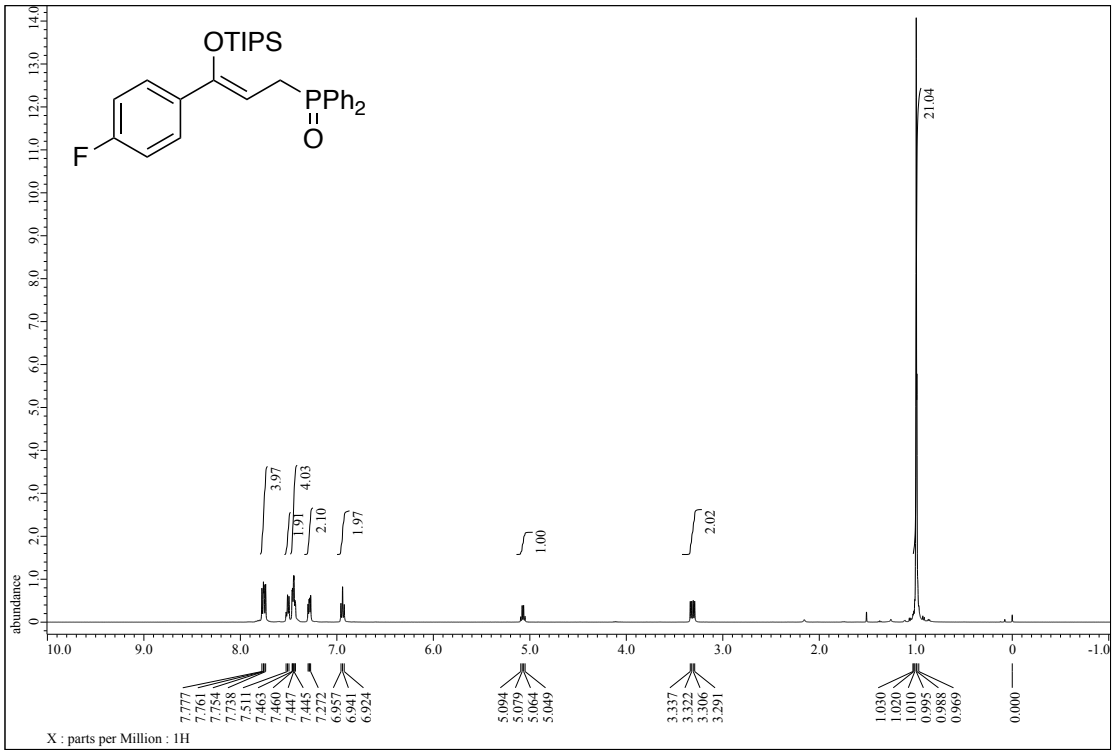
^{1}H, ^{13}C, and ^{31}P NMR spectra of **27**

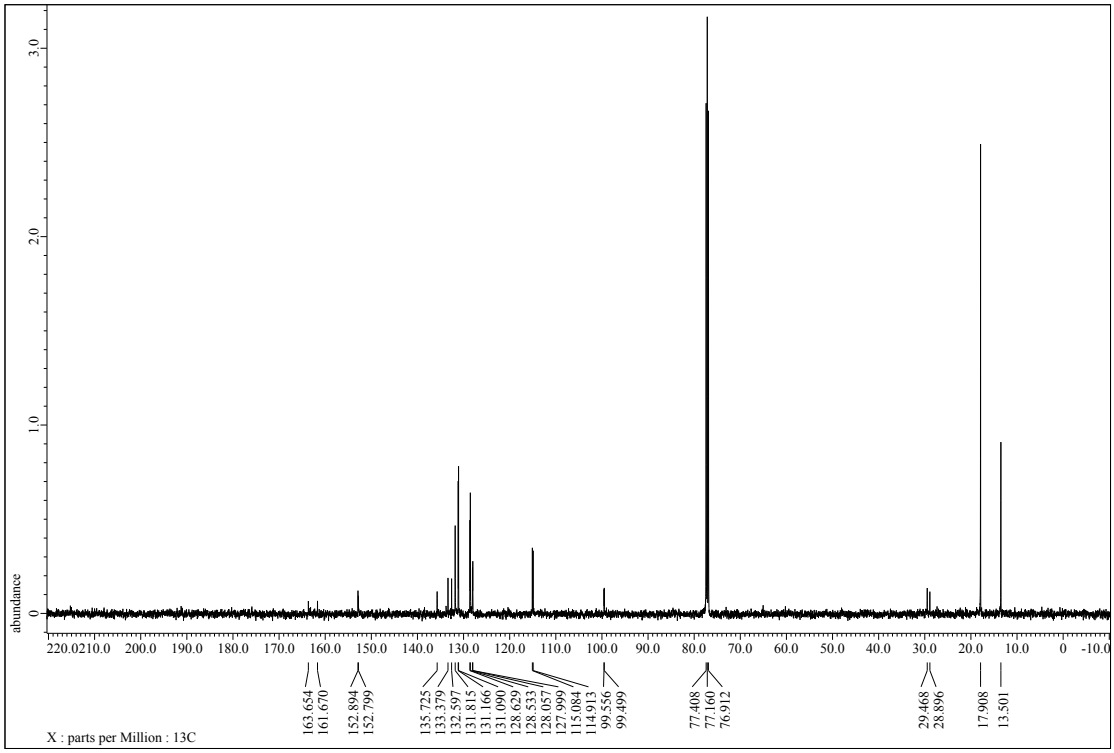


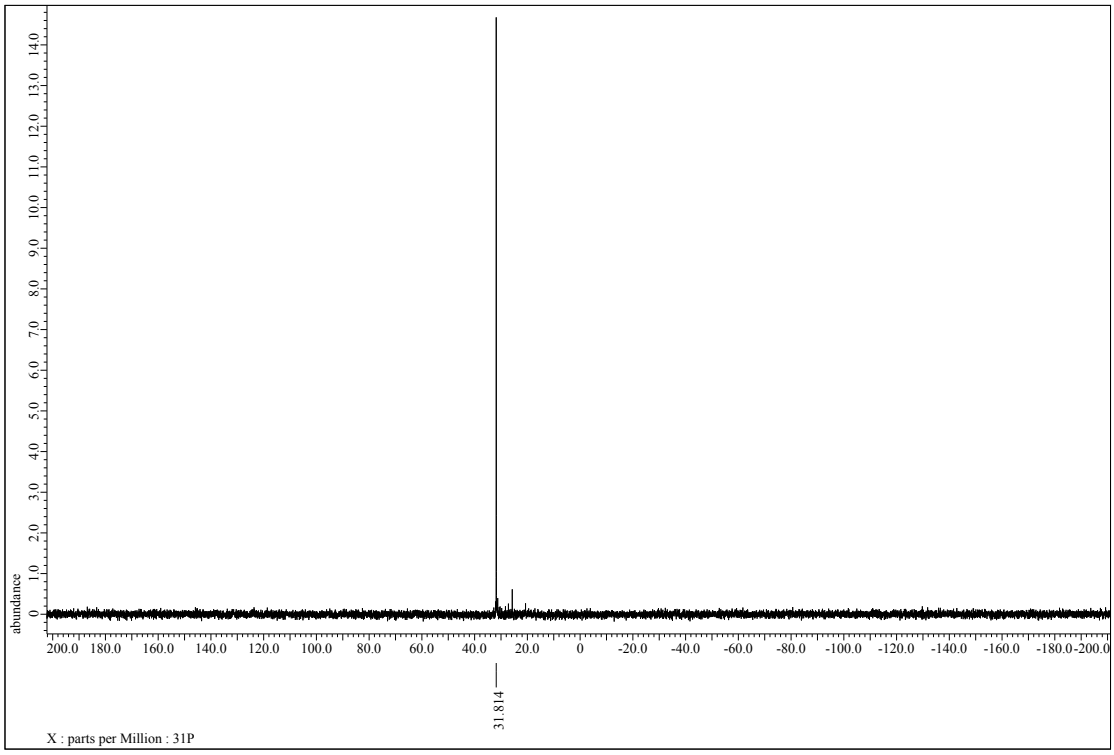



abundance
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
200.0 180.0 160.0 140.0 120.0 100.0 80.0 60.0 40.0 20.0 0 -20.0 -40.0 -60.0 -80.0 -100.0 -120.0 -140.0 -160.0 -180.0 -200.0
32.056
X : parts per Million : 31P

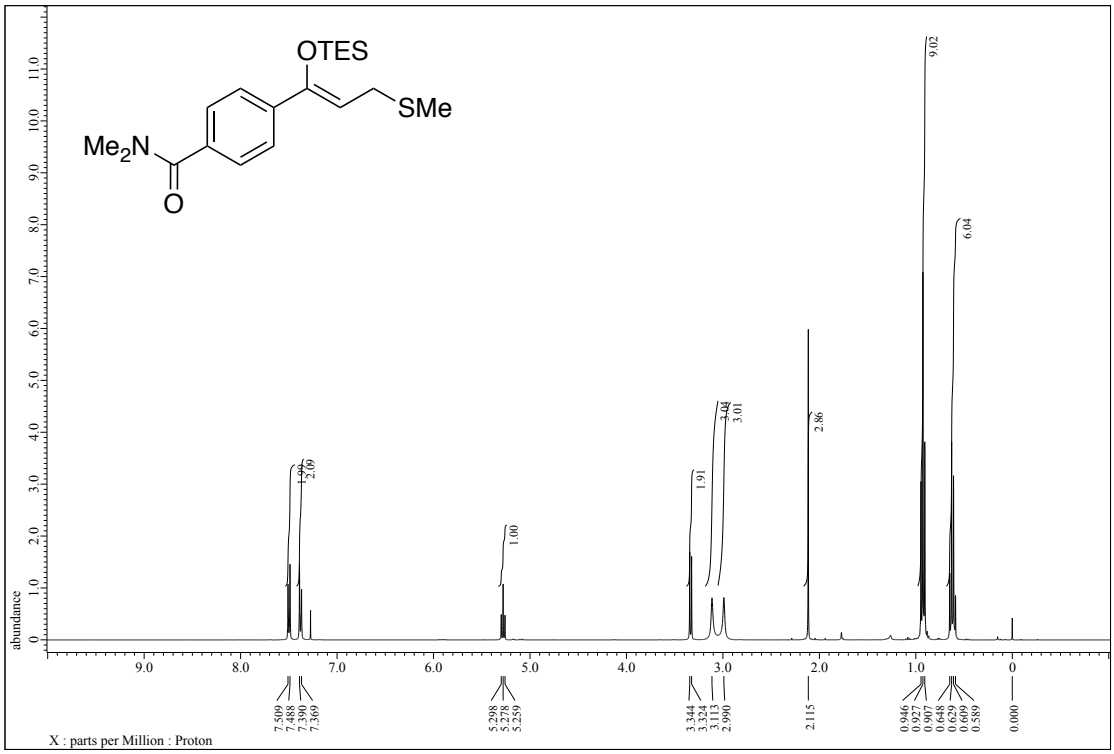
^{1}H, ^{13}C, and ^{31}P NMR spectra of **28**

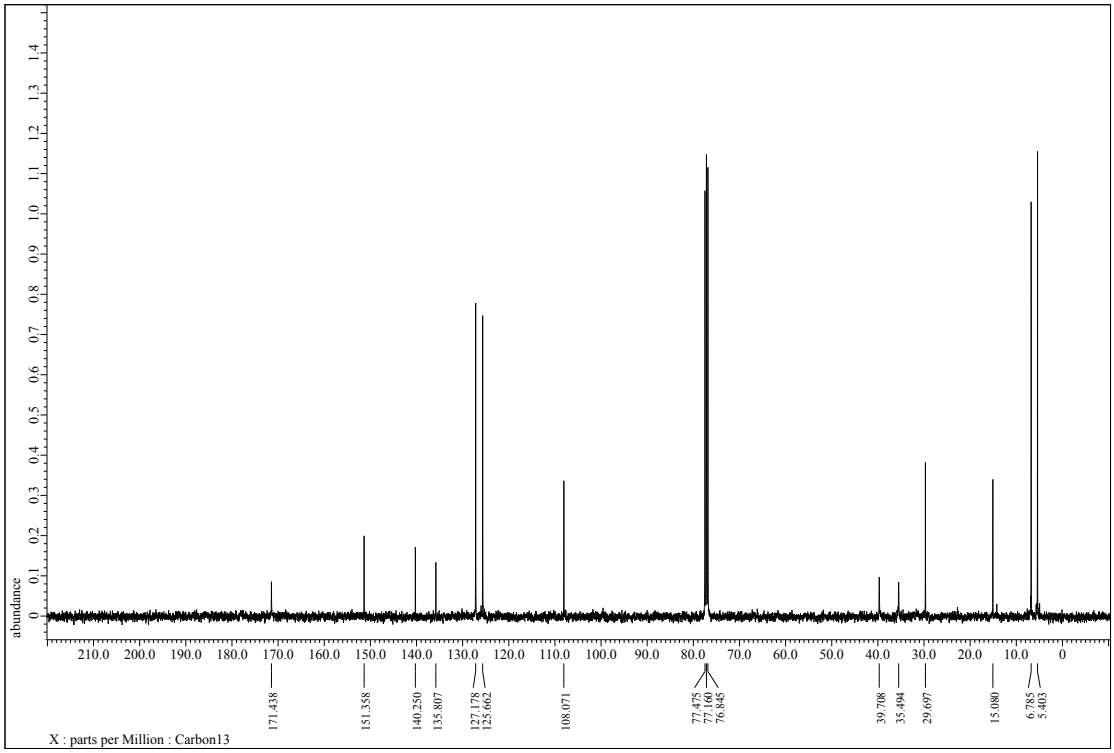




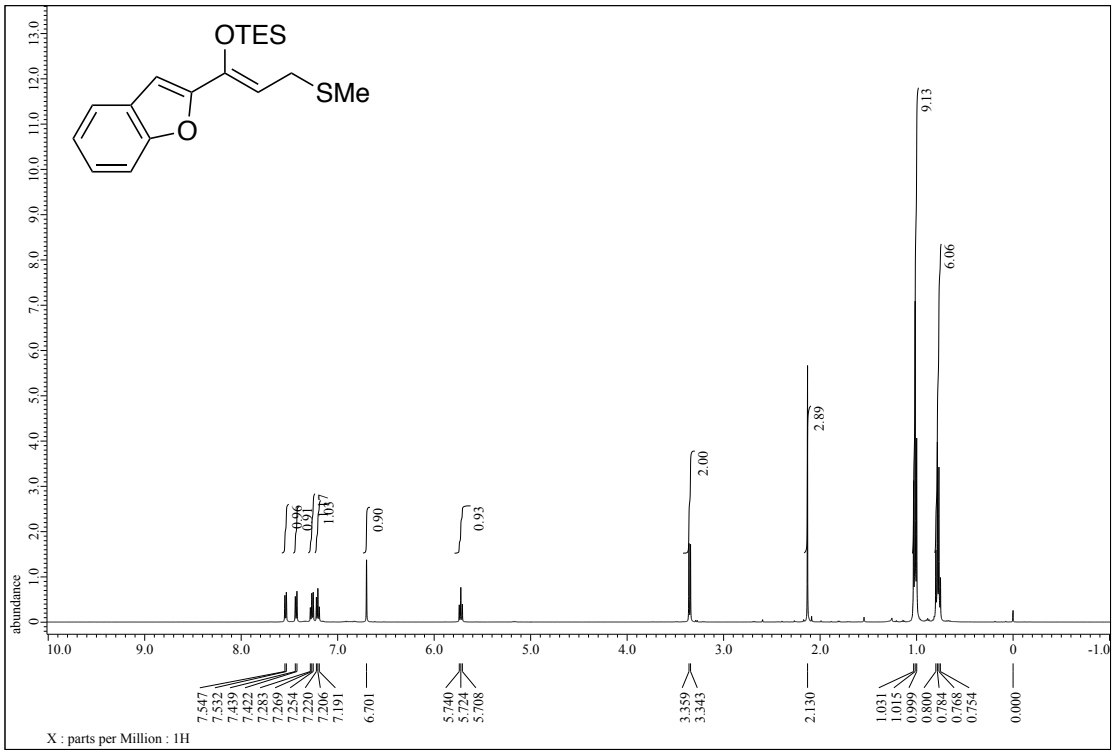

abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
200.0 180.0 160.0 140.0 120.0 100.0 80.0 60.0 40.0 20.0 0 -20.0 -40.0 -60.0 -80.0 -100.0 -120.0 -140.0 -160.0 -180.0 -200.0
31.814
X : parts per Million : 31P

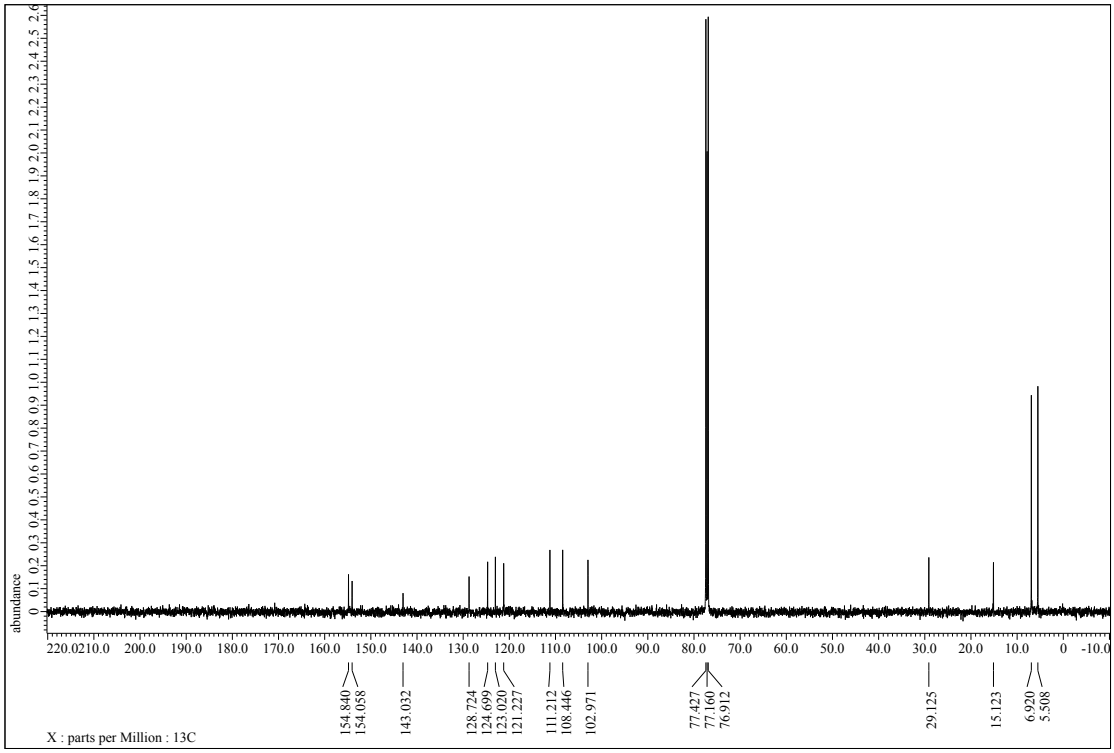
^{1}H and ^{13}C NMR spectra of **29**



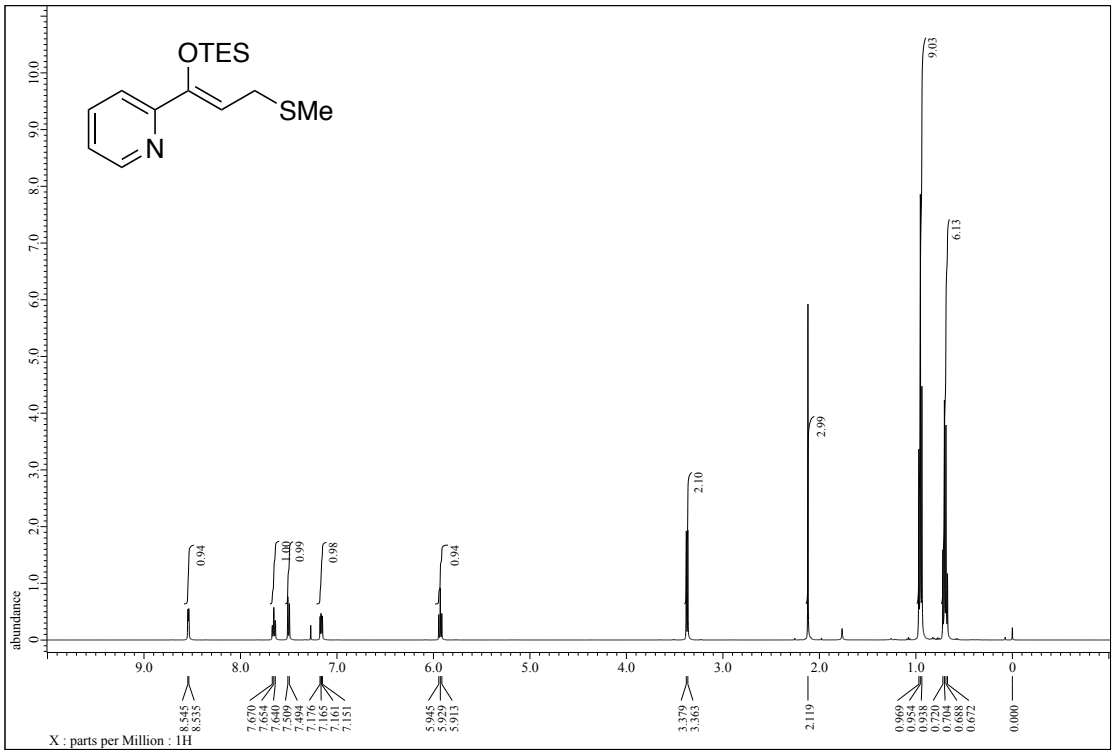


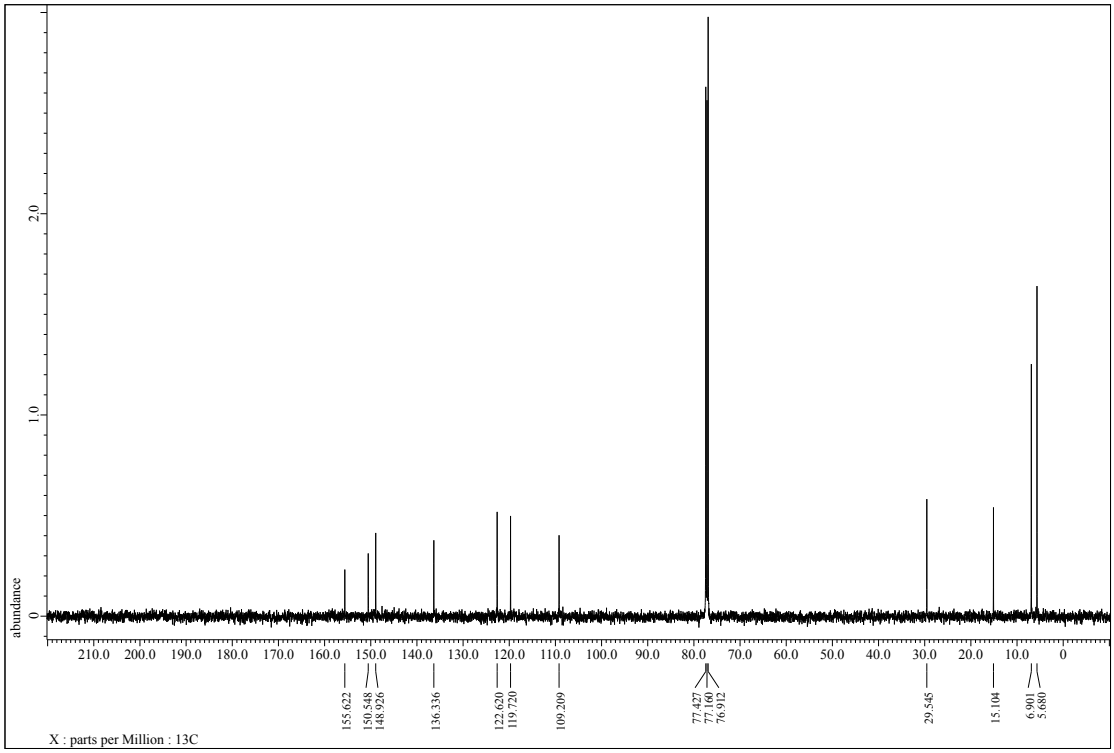
^{1}H and ^{13}C NMR spectra of **30**



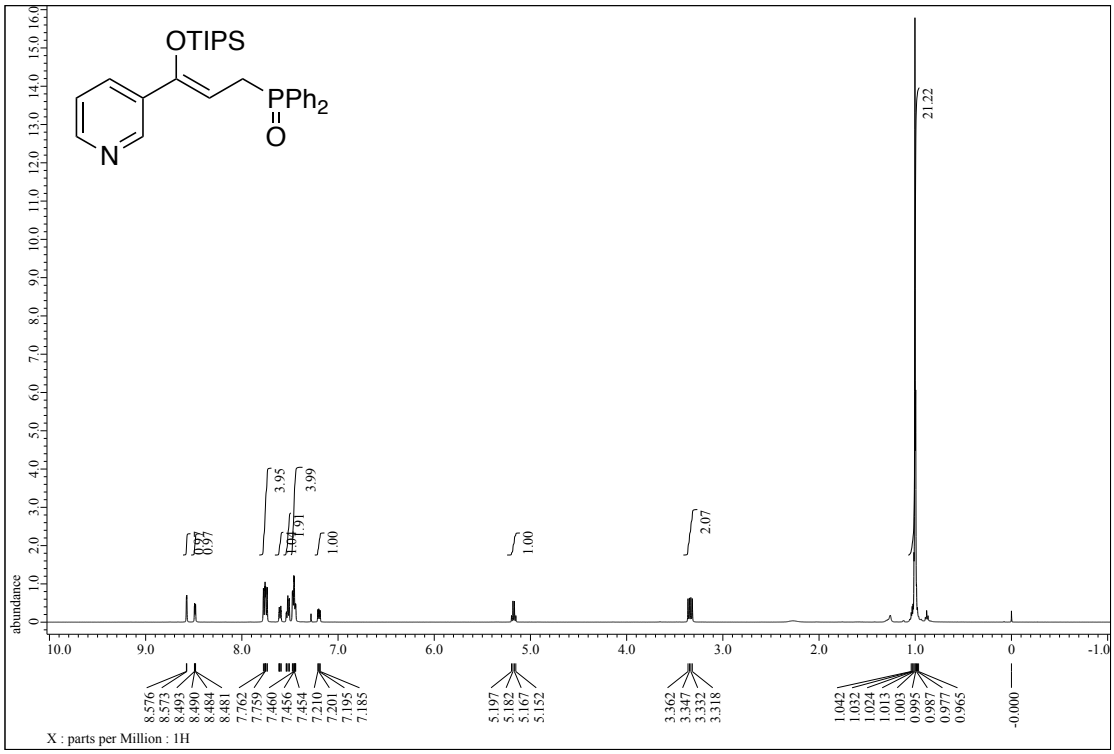


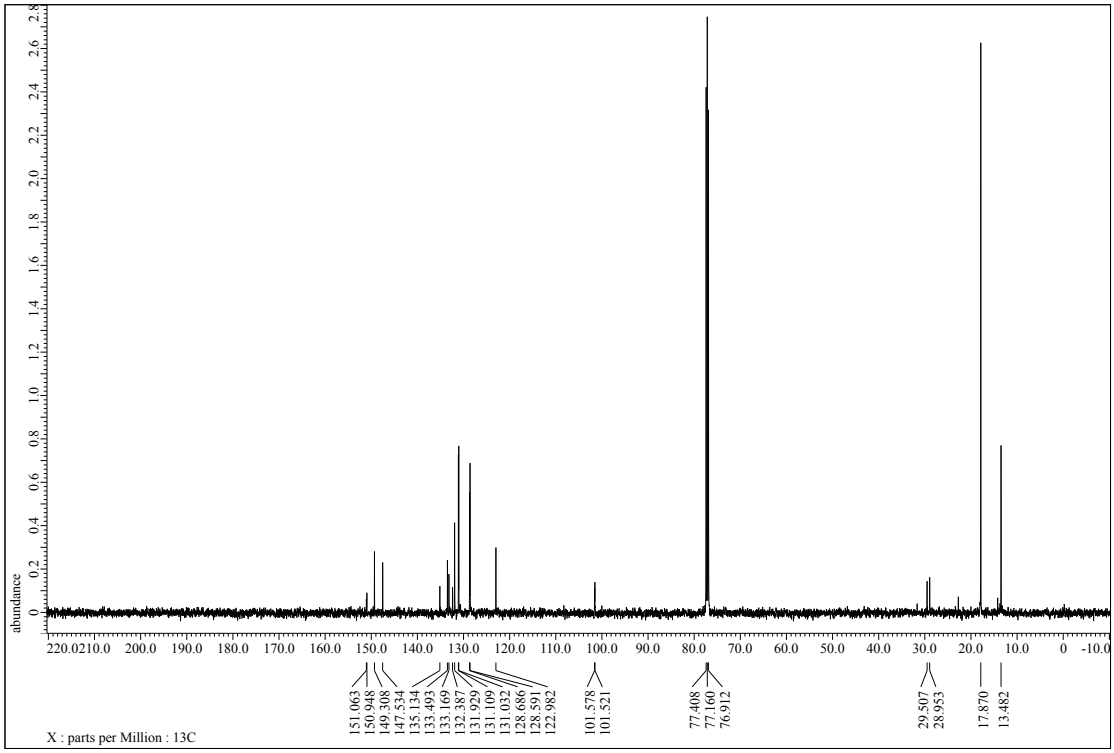
^{1}H and ^{13}C NMR spectra of **31**

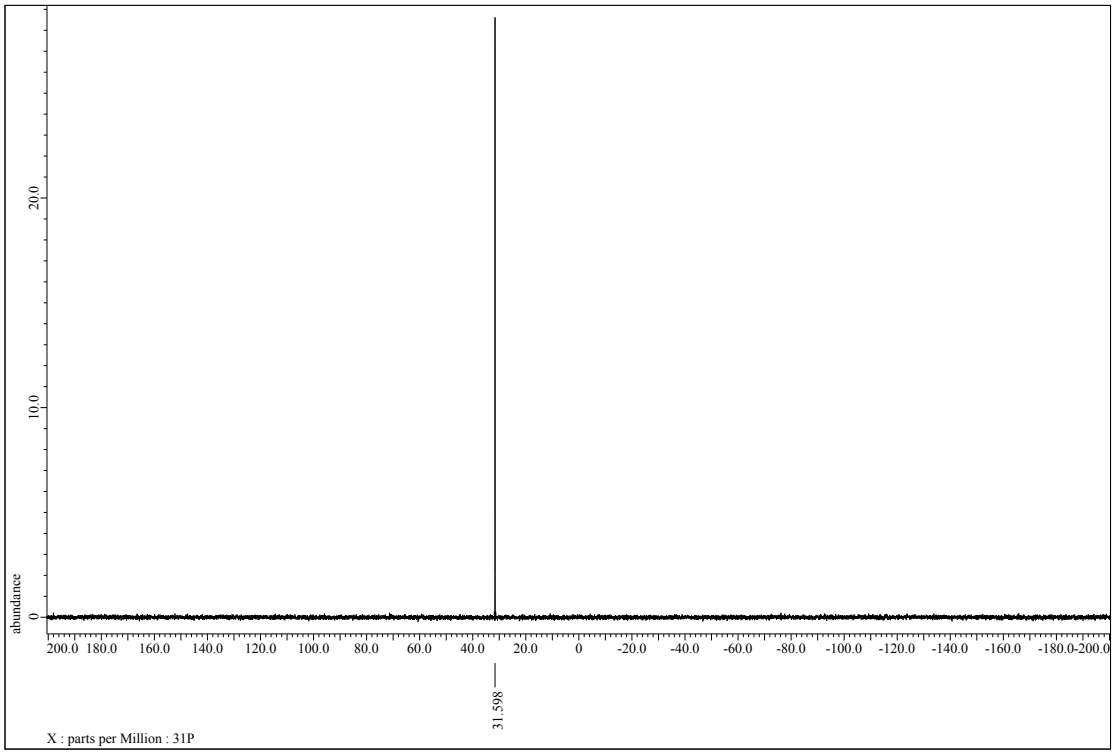




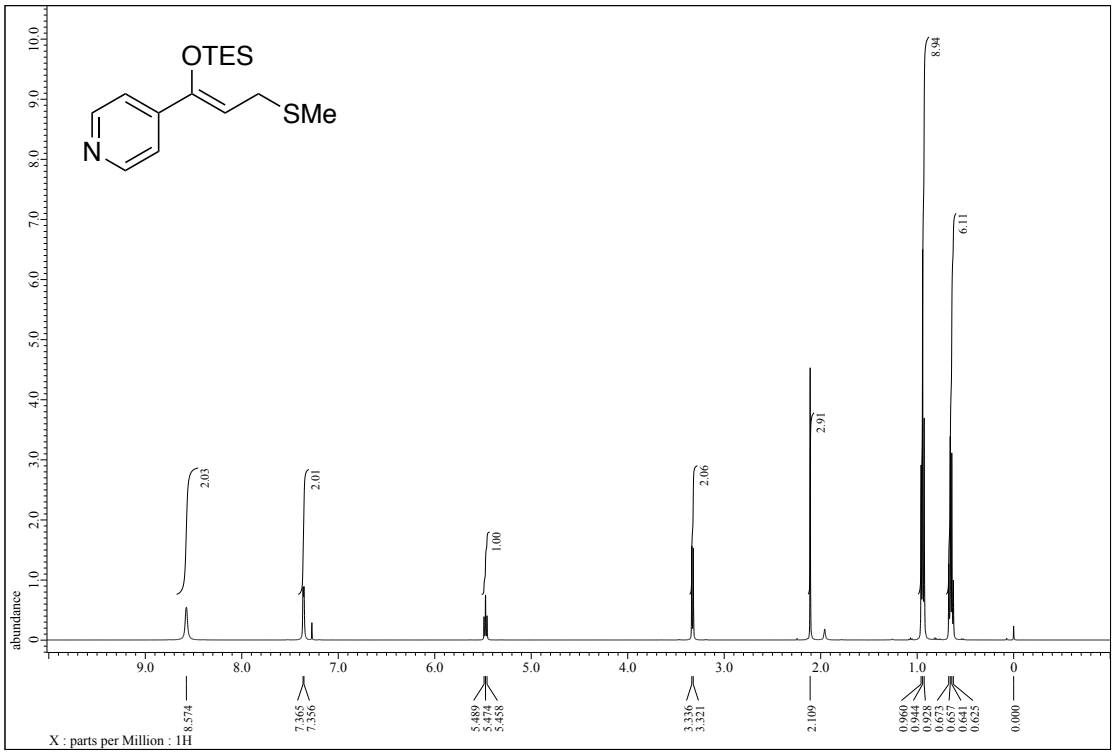
^{1}H, ^{13}C, and ^{31}P NMR spectra of **32**

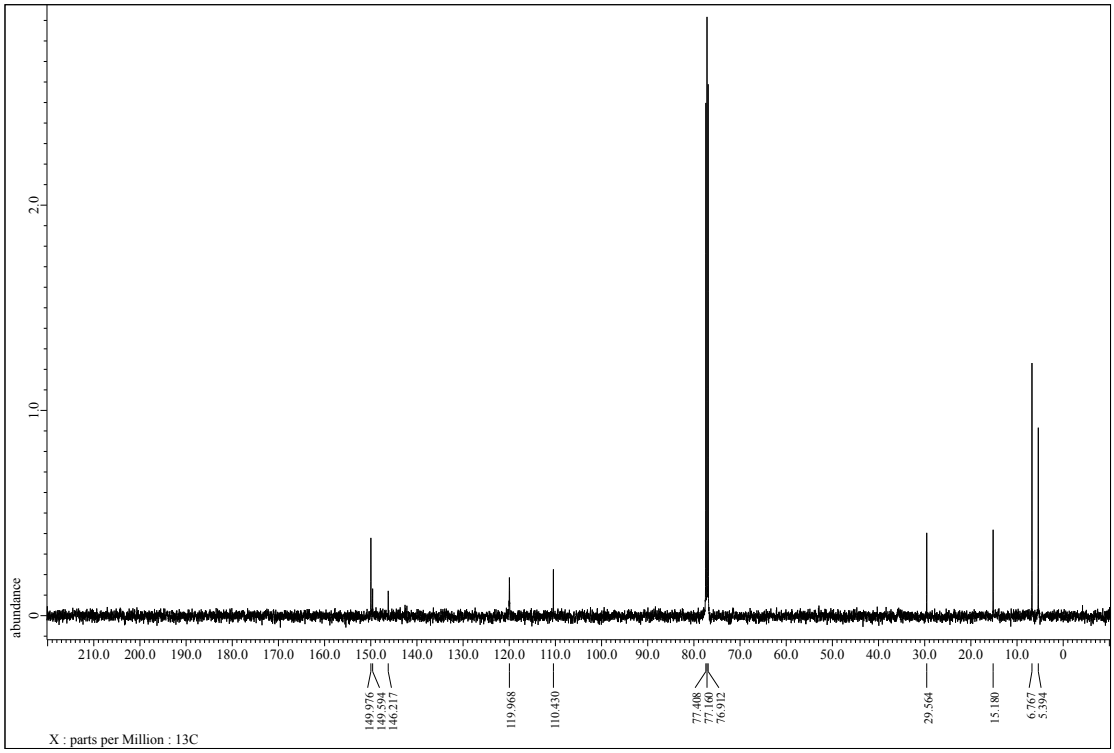




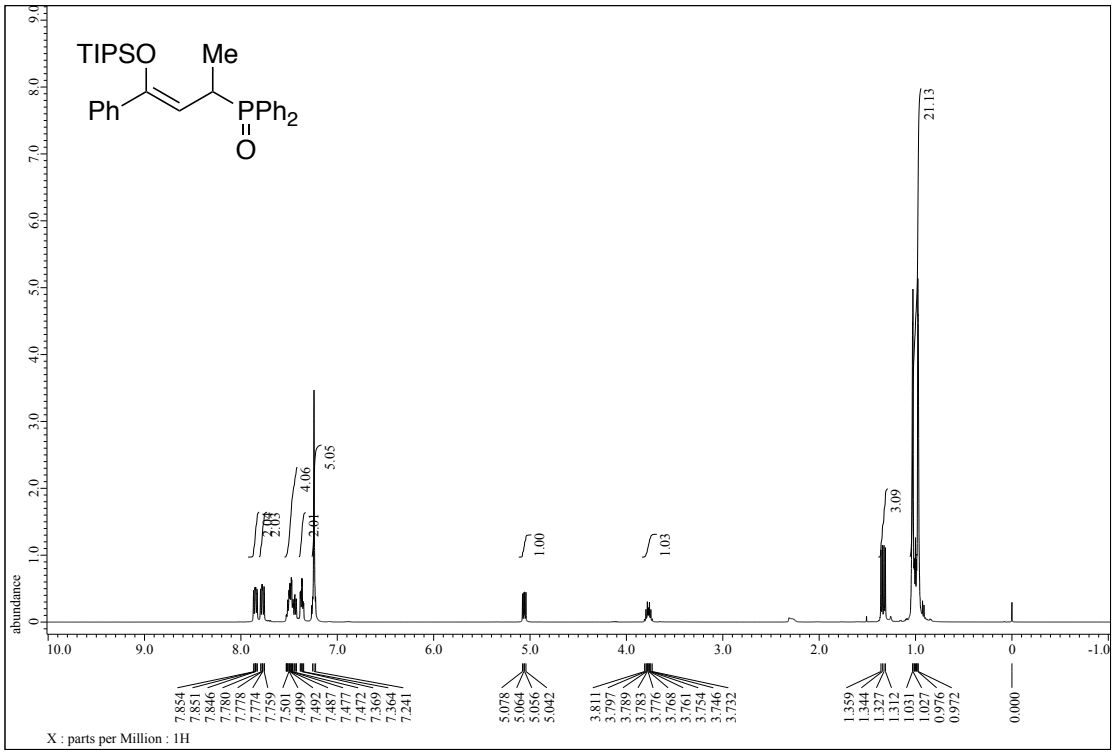

abundance
20.0
10.0
0
200.0 180.0 160.0 140.0 120.0 100.0 80.0 60.0 40.0 20.0 0 -20.0 -40.0 -60.0 -80.0 -100.0 -120.0 -140.0 -160.0 -180.0-200.0
31.598
X : parts per Million : 31P

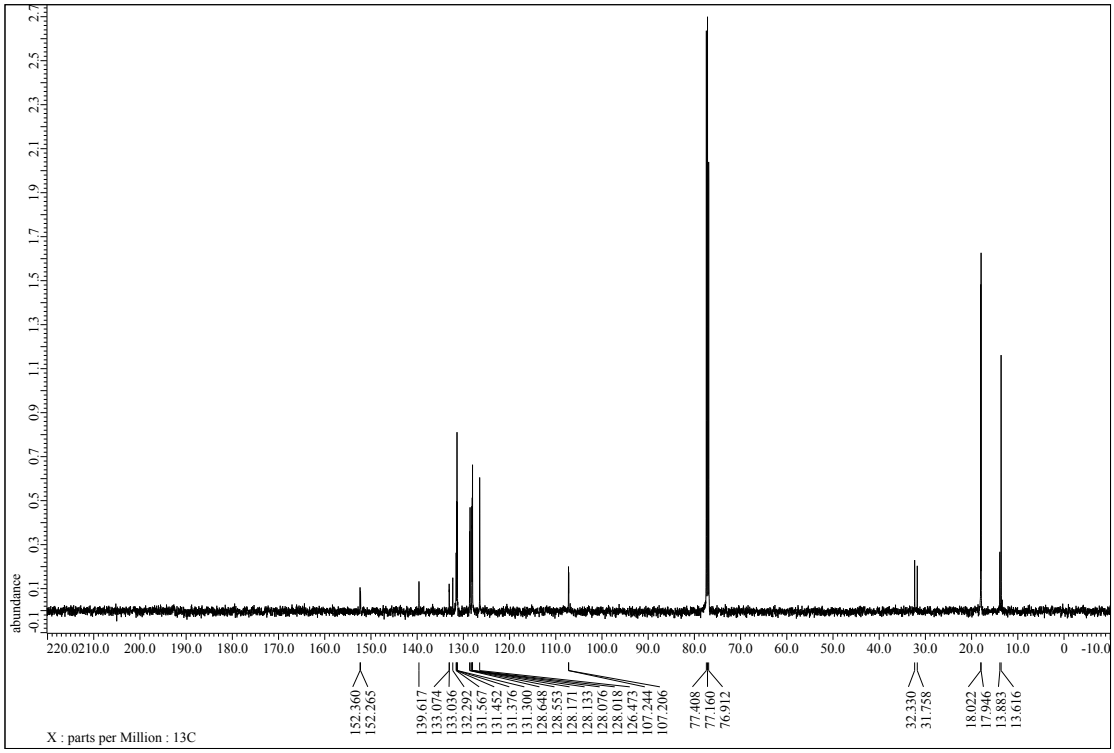
^{1}H and ^{13}C NMR spectra of **33**

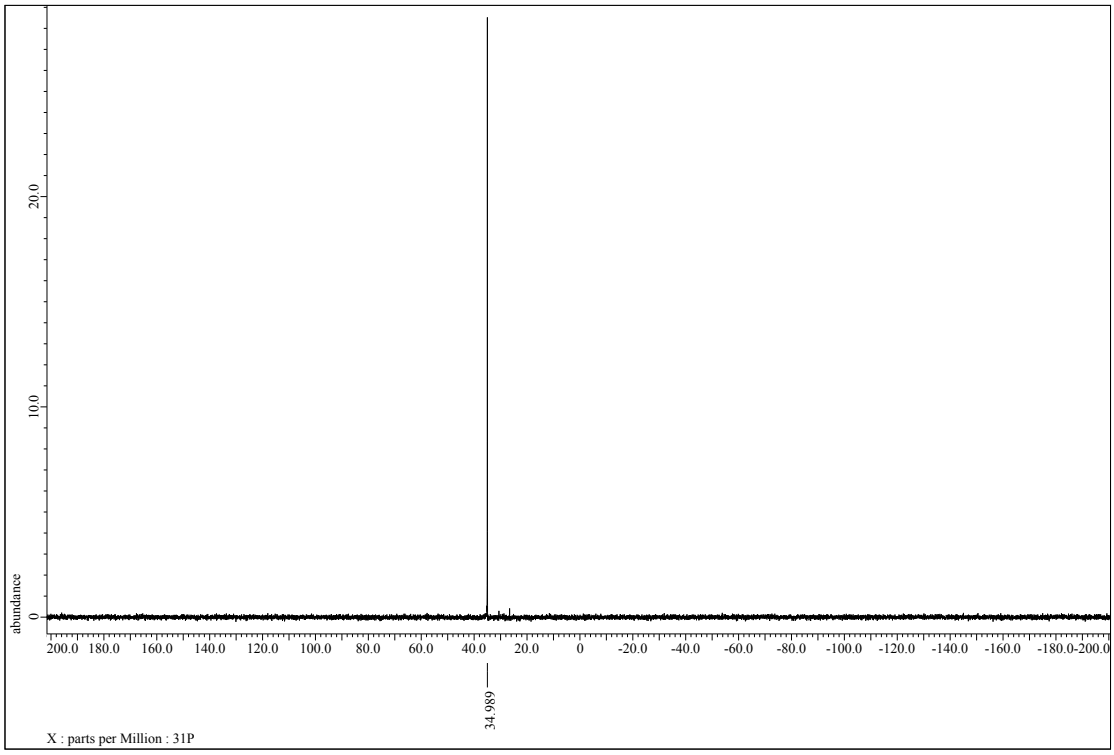




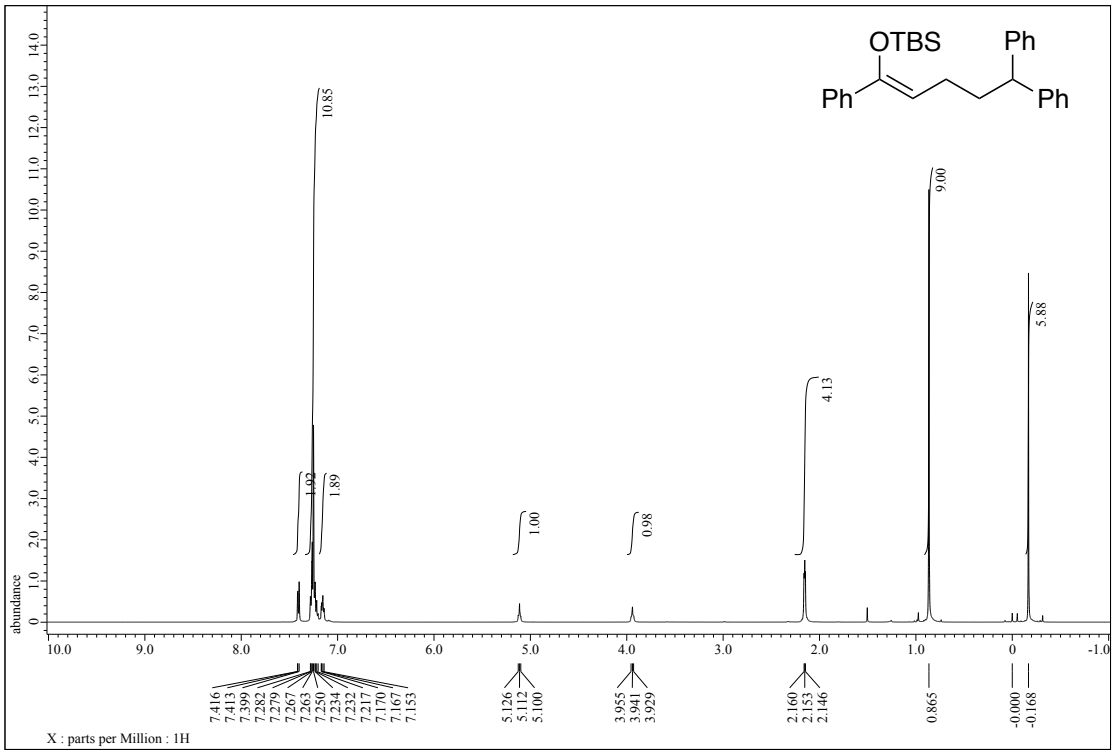
^{1}H, ^{13}C, and ^{31}P NMR spectra of **34**

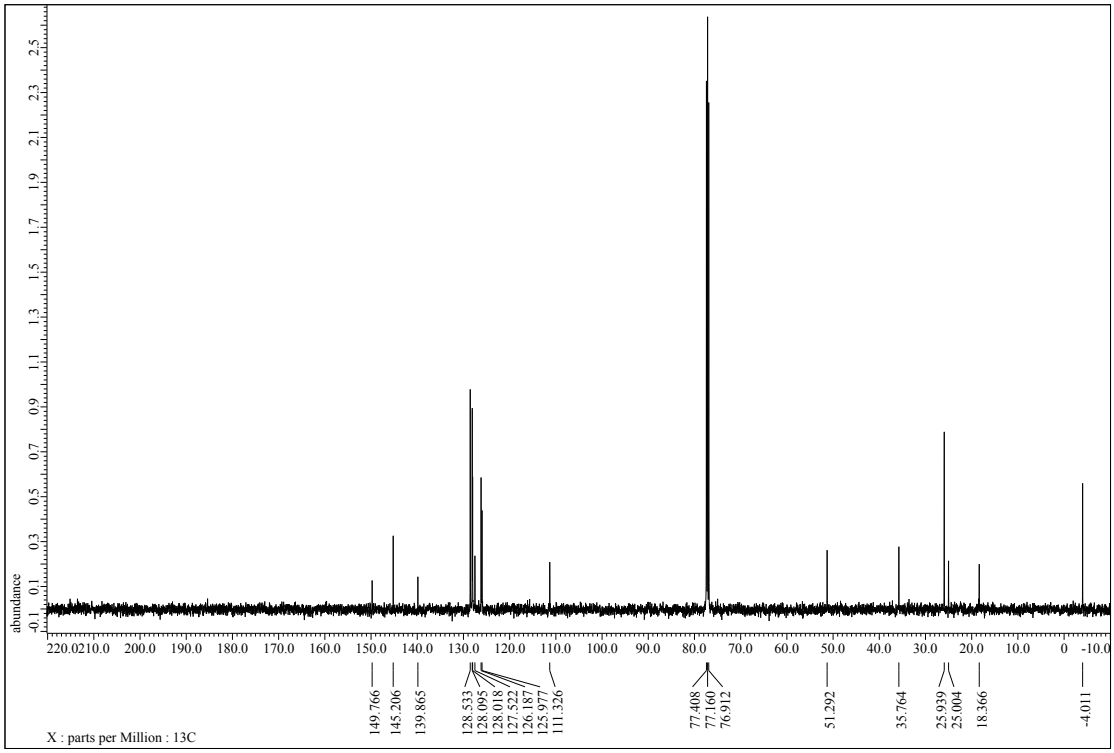




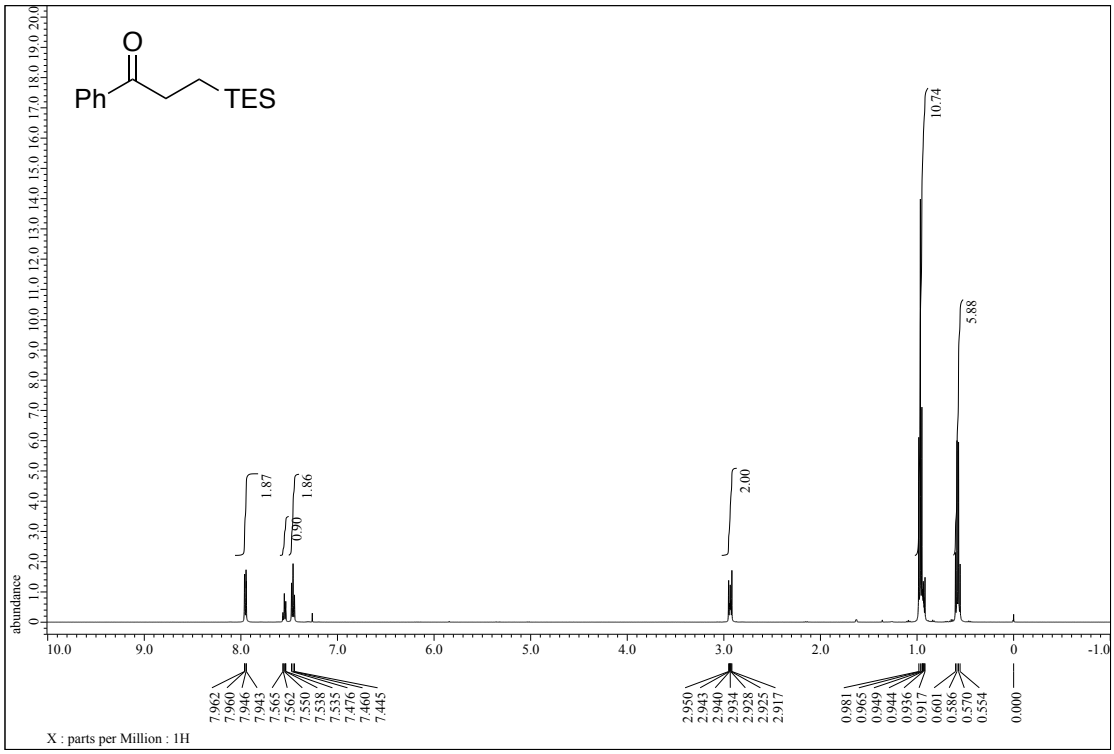

abundance
20.0
10.0
0
200.0 180.0 160.0 140.0 120.0 100.0 80.0 60.0 40.0 20.0 0 -20.0 -40.0 -60.0 -80.0 -100.0 -120.0 -140.0 -160.0 -180.0-200.0
34.989
X : parts per Million : 31P

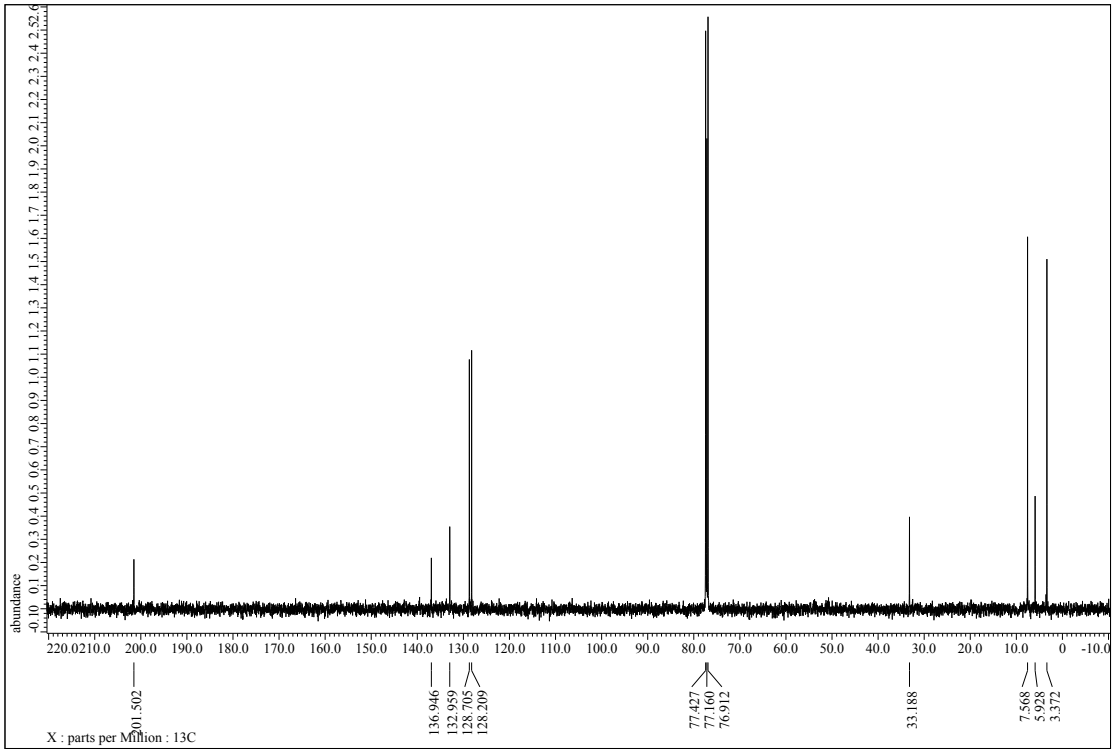
^{1}H and ^{13}C NMR spectra of **35**



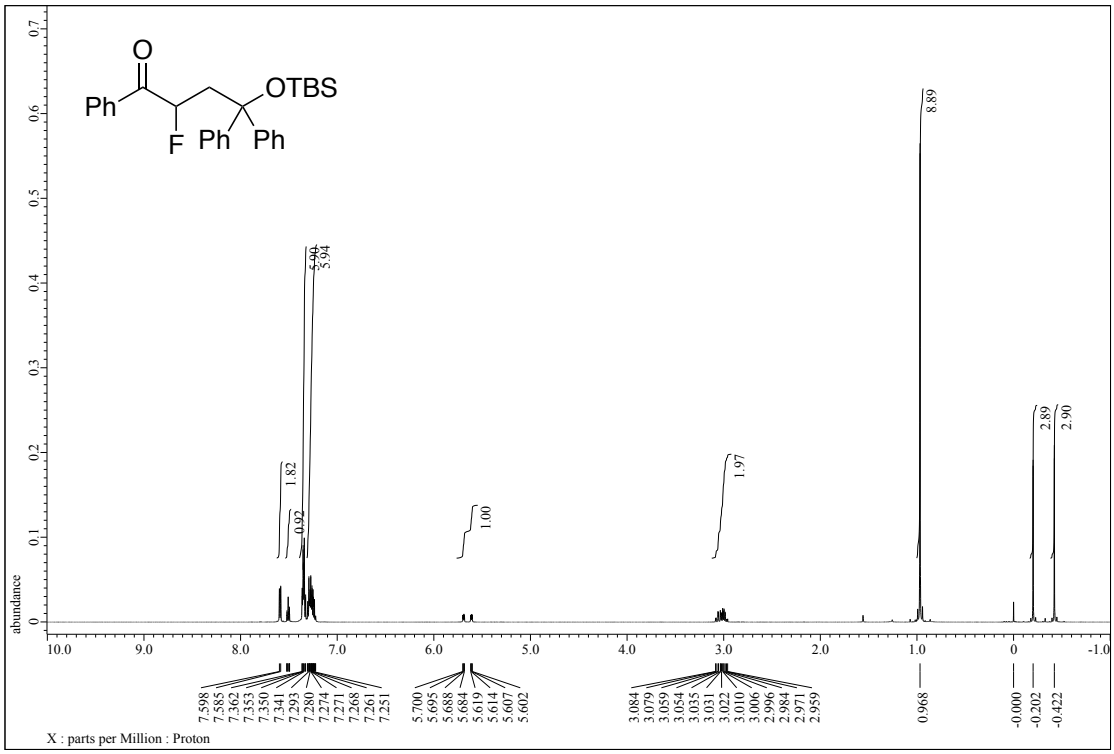


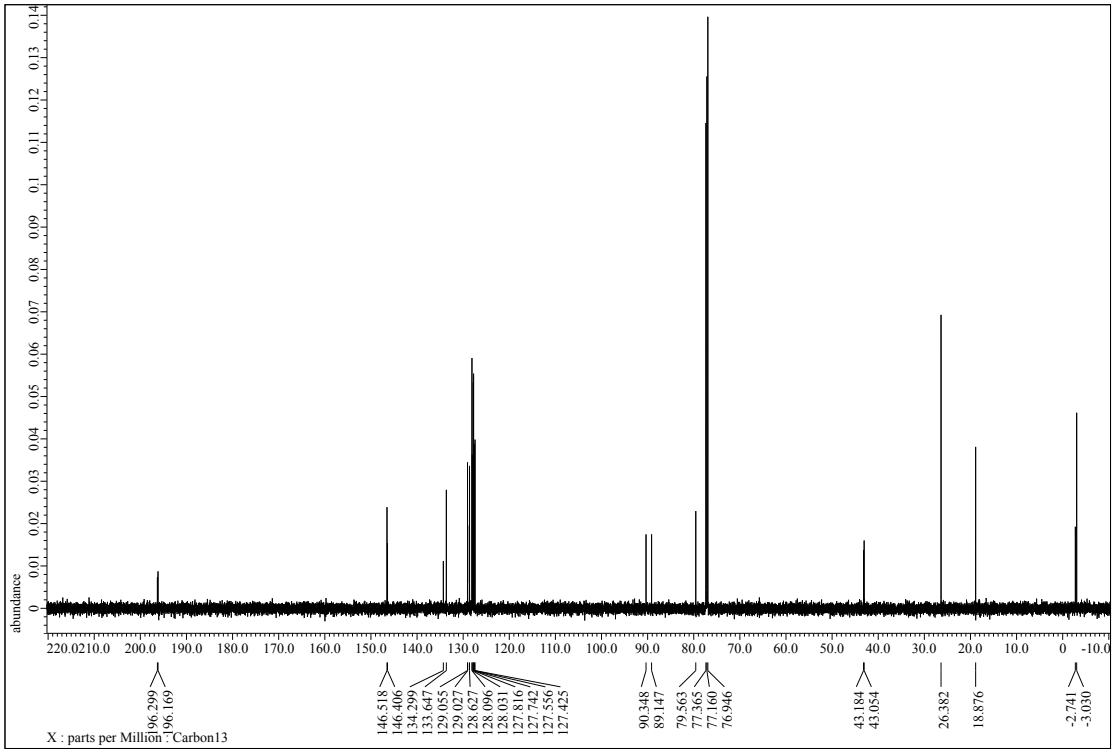
^{1}H and ^{13}C NMR spectra of **37**

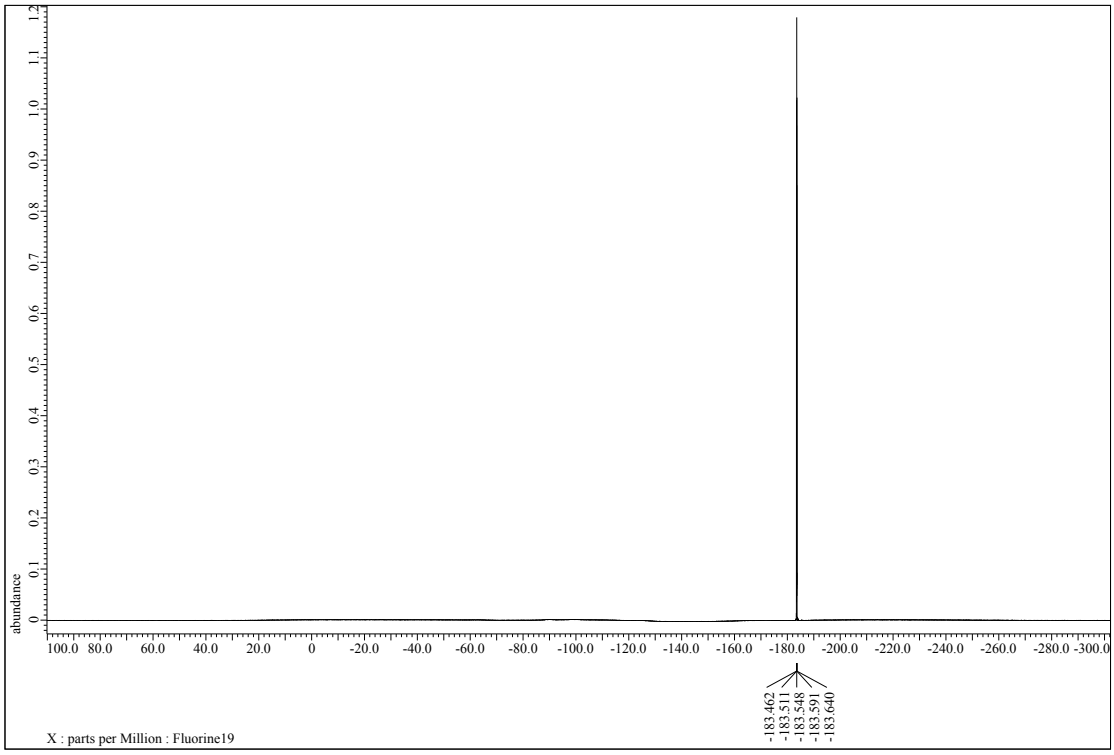




^{1}H, ^{13}C, and ^{19}F NMR spectra of **38**






abundance
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
100.0 80.0 60.0 40.0 20.0 0 -20.0 -40.0 -60.0 -80.0 -100.0 -120.0 -140.0 -160.0 -180.0 -200.0 -220.0 -240.0 -260.0 -280.0 -300.0
-183.462
-183.511
-183.548
-183.591
-183.640
X : parts per Million : Fluorine19

^{1}H and ^{13}C NMR spectra of **39**