Electronic Supplementary Material (ESI) for ChemComm.

Regio- and Diastereoselective Synthesis of Unsymmetrical 1,4-Diketone-Derived (*Z*)-Monosilyl Enol Ethers via Siloxyallylpotassium Intermediates

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Supporting Information

Table of Contents

1. Instrumentation and Materials

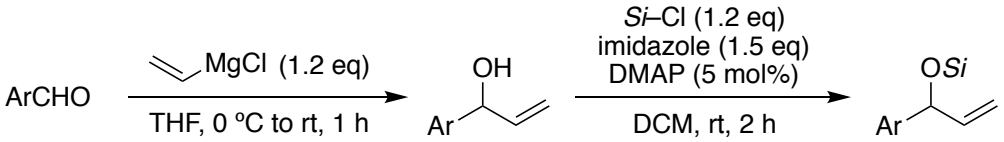
NMR spectra were recorded on JEOL JNM-ECA500 and JNM-ECA600 spectrometers (500 MHz for ^{1}H NMR, 126 MHz for ^{13}C NMR, and 565 MHz for ^{19}F NMR). Tetramethylsilane (TMS) served as internal standard (δ = 0) for ^{1}H NMR, and $CDCl_3$ served as internal standard (δ = 77.16) for ^{13}C NMR. $CF_3C_6H_5$ sealed in a glass capillary was used as an external internal standard (δ = –63.72) for ^{19}F NMR. Multiplicities are indicated as: br (broad), s (singlet), d (doublet), t (triplet), q (quartet), sept (septet), 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. 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. Amino-functionalized silica gel (NH DM1020, Fuji Silysia) was used for purification of **3ga**. 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.

Unless otherwise noted, all chemicals were purchased from commercial suppliers and used as received. (Trimethylsilyl)methylpotassium ($TMSCH_2K$) and (trimethylsilyl)methylsodium ($TMSCH_2Na$) were prepared according to previously reported procedure[1] and stored in an argon-filled glovebox. Hexamethylphosphoramide was purchased from Tokyo Chemical Industry; the bulk of the material was stored in an argon-filled glovebox, and small portions were removed from the glovebox in glass vials and stored in the air. *sec*-Butyllithium (1.2 M in cyclohexane/*n*-hexane) and *tert*-butyllithium (1.6 M in *n*-pentane) were purchased from Kanto Chemical. Tetrahydrofuran (dehydrated, stabilizer free) was purchased from Kanto Chemical and stored in an argon-filled glovebox.

2. Experimental Details

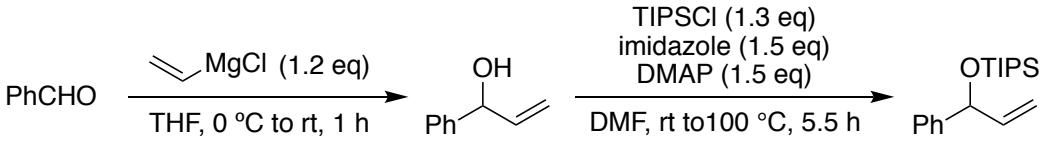
2.1. Synthesis of Allyloxysilanes 1

2.1.1. Synthesis of **1a**, **1a'**, and **1b**–**1j**



To a solution of aldehyde (6 mmol) in THF (12 mL) was slowly added vinylmagnesium chloride (1.38 M in THF, 5.22 mL, 7.2 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 crude allylic alcohol was dissolved in DCM (15 mL), and to the flask were added silyl chloride (7.2 mmol), imidazole (9 mmol), and DMAP (0.3 mmol) at room temperature. After stirring for 2 h, the mixture was diluted with 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 flash chromatography on silica gel (hexane/EtOAc) to give the corresponding allyloxysilane.

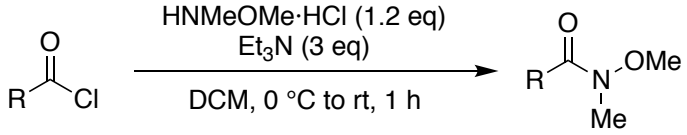
2.1.2. Synthesis of **1a"**



1a"

To a solution of benzaldehyde (0.51 mL, 5 mmol) in THF (10 mL) was slowly added vinylmagnesium chloride (1.38 M in THF, 4.35 mL, 6 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 crude allylic alcohol was dissolved in DMF (12 mL), and to the flask were added TIPSCl (1.38 mL, 6.5 mmol), imidazole (511 mg, 7.5 mmol), and DMAP (916 mg, 7.5 mmol) at room temperature. The reaction mixture was heated at 100 °C for 5.5 h. The mixture was diluted with H_2O and extracted with hexane. The organic layer was combined, washed with brine, 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 **1a"** as a colorless oil.

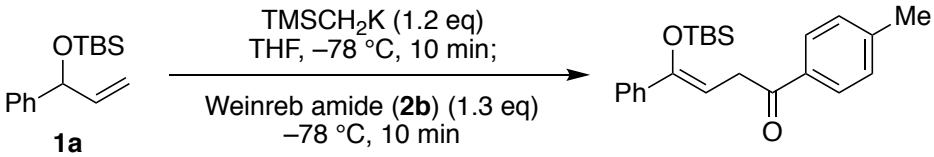
2.2. Synthesis of Weinreb Amides 2



2

To a solution of *N,O*-dimethylhydroxyamine hydrochloride (585 mg, 6 mmol) in DCM (12 mL) was added Et_3N (2.09 mL, 15 mmol) followed by dropwise addition of acyl chloride (5 mmol) at 0 °C. 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 flash chromatography on silica gel or Kugelrohr distillation to give the corresponding Weinreb amide.

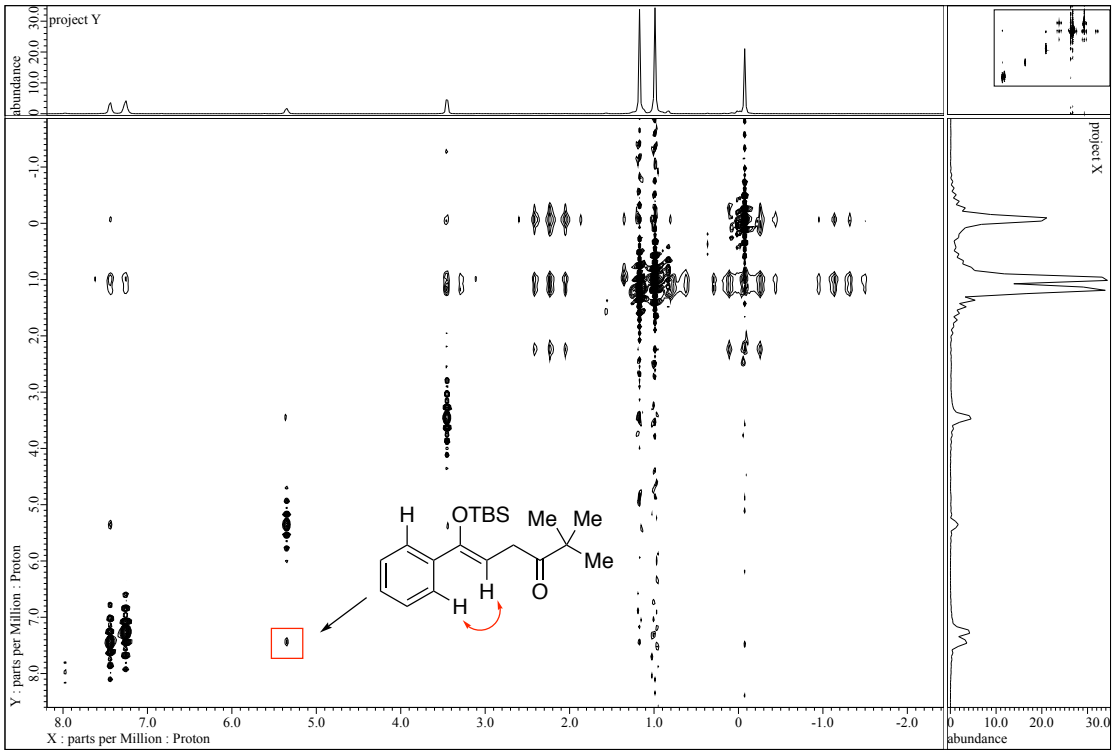
2.3. General Procedure for the Synthesis of 3-Functionalized Silyl Enol Ethers



1a **3ab**

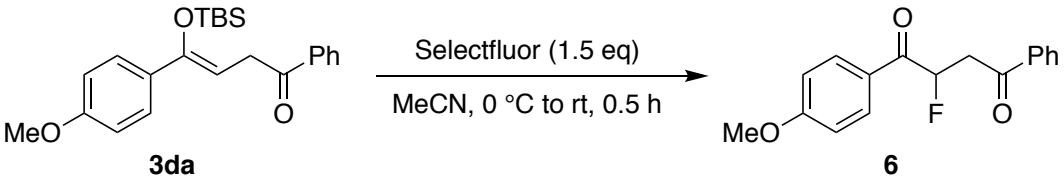
Synthesis of **3ab** is representative: In a glovebox, an oven-dried vial equipped with a magnetic stir bar was charged with $TMSCH_2K$ (37.9 mg, 0.30 mmol). The vial was sealed with a rubber septum and removed from the glovebox. The vial was cooled to –78 °C, and cold THF (2 mL, –78 °C) was added. To the vial was added allyloxysilane **1a** (62.1 mg, 0.25 mmol) via microsyringe at –78 °C, and the mixture was stirred for 10 min. Subsequently, Weinreb amide **2b** (58.2 mg, 0.325 mmol) dissolved in THF (1 mL) was added 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 residue was purified by flash chromatography on silica gel (hexane/EtOAc = 50:1) to give **3ab** (72.1 mg, 79% yield) as a white solid.

2.4. Determination of Z Configuration of 3am by NOESY Analysis



2.5. Procedure for the Transformation of the Products

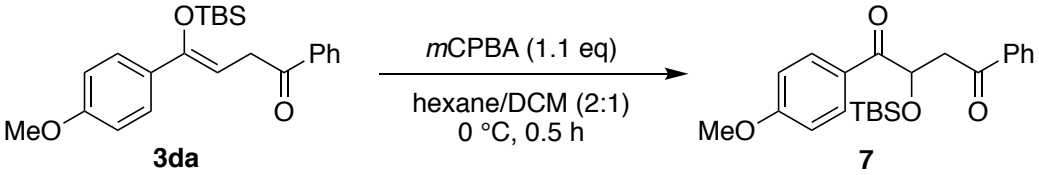
2.5.1. Procedure for the fluorination of **3da**



3da **6**

Selectfluor (26.6 mg, 0.075 mmol) was dissolved in MeCN (0.75 mL), and **3da** (19.1 mg, 0.050 mmol) was added at 0 °C. The reaction mixture was warmed to room temperature and stirred for 0.5 h. The reaction was quenched by saturated aq. $NaHCO_3$ solution and extracted with hexane/EtOAc (5/1). The organic layer was combined, dried over Na_2SO_4, and concentrated under reduced pressure. The crude solid was washed with hexane three times and dried in vacuo to give **6** (10.4 mg, 73%) as a white solid.

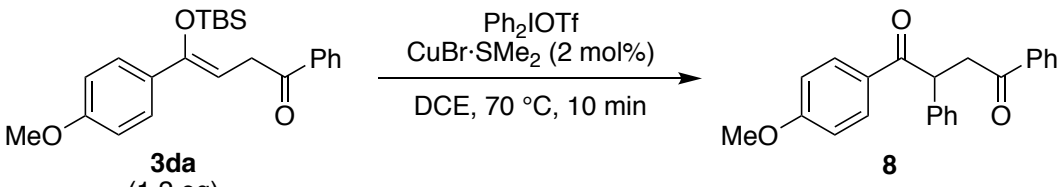
2.5.2. Procedure for the Rubottom oxidation of **3da**



3da **7**

To a solution of **3da** (95.7 mg, 0.25 mmol) in hexane (2 mL) and DCM (1 mL) was added *m*CPBA (contains ca. 30% H_2O, 67.8 mg, 0.275 mmol) at 0 °C, and the mixture was stirred for 0.5 h. The reaction was quenched by saturated aq. $NaHCO_3$ solution and extracted with hexane/EtOAc (5/1). 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 = 7:1) to give **7** (89.0 mg, 89%) as a colorless viscous oil.

2.5.3. Procedure for the synthesis of **8**[2]

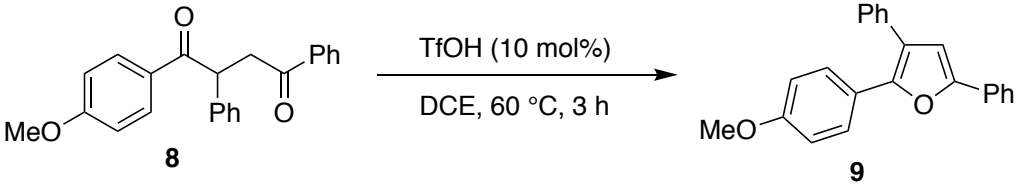


3da (1.2 eq) **8**

An oven-dried vial was charged with $CuBr{\cdot}SMe_2$ (1.0 mg, 5.0 μmol), diphenyliodonium triflate (107.5 mg, 0.25 mmol), and **3da** (114.8 mg, 0.30 mmol), and the vial was flushed with argon and sealed with a rubber septum. To the vial was added DCE (2.5 mL), and the mixture was heated at 70 °C for 10 min. The reaction was quenched by saturated aq. $NaHCO_3$ 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 = 6:1) to give **8** (70.9 mg, 82%) as a pale yellow viscous oil.

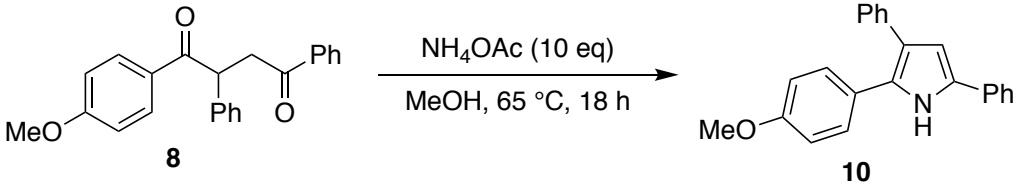
2.5.4. Procedure for the synthesis of **9**



8 **9**

1,4-Diketone **8** (70.9 mg, 0.206 mmol) was dissolved in DCE (3 mL), and triflic acid (1.81 μL, 0.0206 mmol) was added at room temperature. The mixture was heated at 60 °C for 3 h. The reaction was quenched by saturated aq. $NaHCO_3$ 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 = 9:1) to give **9** (46.5 mg, 57% in two steps from **3da**) as a colorless viscous oil.

2.5.5. Procedure for the synthesis of **10**



8 **10**

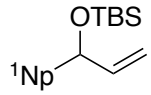
1,4-Diketone **8** (70.9 mg, 0.206 mmol) was dissolved in MeOH (3 mL), and NH_4OAc (159 mg, 2.06 mmol) was added at room temperature. The mixture was heated at 65 °C overnight. The reaction was quenched by saturated aq. $NaHCO_3$ solution and extracted with hexane/EtOAc (5/1). The organic layer was combined, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexane/EtOAc = 7:1) to give **10** (55.6 mg, 68% in two steps from **3da**) as a colorless amorphous solid.

3. Characterization Data

1a,[3] **1a'**,[4] **1a''**,[5] **1b**,[4] **4**,[6] **8**,[7] **9**,[8] and **10**[9] were reported in the literatures.

3.1. Characterization Data for New Allyloxysilanes

***tert*-Butyldimethyl((1-(naphthalen-1-yl)allyl)oxy)silane (1c)**



Colorless oil.

R_f: 0.72 (hexane/EtOAc = 20:1).

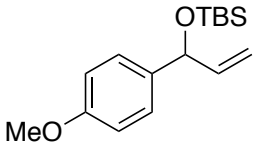
IR (ATR): 3060, 2955, 2929, 2891, 2856, 1640, 1598, 1511, 1472, 1462, 1361, 1335, 1252, 1228, 1168, 1128, 1030, 1005 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.19–8.17 (m, 1H), 7.86–7.84 (m, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 7.5 Hz, 1H), 7.49–7.44 (m, 3H), 6.11 (ddd, *J* = 17.0, 10.5, 5.0 Hz, 1H), 5.82 (br d, *J* = 5.0 Hz, 1H), 5.36 (app. dt, *J* = 17.0, 1.5 Hz, 1H), 5.09 (app. dt, *J* = 10.5, 1.5 Hz, 1H), 0.91 (s, 9H), 0.09 (s, 3H), –0.08 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 141.1, 139.4, 134.0, 130.4, 128.9, 128.0, 125.7, 125.6, 125.5, 124.3, 124.2, 113.9, 74.1, 26.0, 18.5, –4.68, –4.72 ppm.

HRMS (ESI): *m/z* calcd. for $C_{19}H_{26}OSiNa$ $[M+Na]^+$: 321.1645, found: 321.1666.

***tert*-Butyl((1-(4-methoxyphenyl)allyl)oxy)dimethylsilane (1d)**



Colorless oil.

R_f: 0.63 (hexane/EtOAc = 20:1).

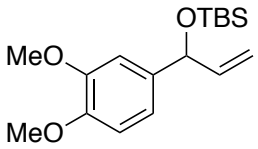
IR (ATR): 2955, 2930, 2897, 2856, 2836, 1640, 1611, 1587, 1509, 1471, 1463, 1442, 1302, 1246, 1171, 1126, 1034, 1006 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.25–7.23 (m, 2H), 6.87–6.84 (m, 2H), 5.90 (ddd, *J* = 17.0, 10.5, 6.0 Hz, 1H), 5.25 (app. dt, *J* = 17.0, 2.0 Hz, 1H), 5.12 (br d, *J* = 6.0 Hz, 1H), 5.04 (app. dt, *J* = 10.5, 1.5 Hz, 1H), 3.79 (s, 3H), 0.91 (s, 9H), 0.07 (s, 3H), –0.02 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 158.8, 142.1, 136.1, 127.3, 113.7, 113.1, 75.6, 55.4, 26.0, 18.5, –4.5, –4.7 ppm.

HRMS (ESI): *m/z* calcd. for $C_{16}H_{27}O_2Si$ $[M+H]^+$: 279.1775, found: 279.1790.

***tert*-Butyl((1-(3,4-dimethoxyphenyl)allyl)oxy)dimethylsilane (1e)**



Colorless oil.

R_f: 0.59 (hexane/EtOAc = 5:1).

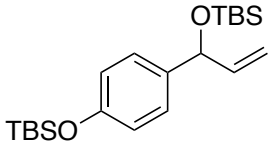
IR (ATR): 2954, 2931, 2898, 2856, 2835, 1640, 1606, 1594, 1512, 1463, 1417, 1361, 1253, 1187, 1132, 1073, 1029, 1006 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.92 (d, *J* = 2.0 Hz, 1H), 6.84 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 5.92 (ddd, *J* = 17.0, 10.0, 6.0 Hz, 1H), 5.27 (app. dt, *J* = 17.0, 1.5 Hz, 1H), 5.12 (br d, *J* = 6.0 Hz, 1H), 5.06 (d, *J* = 10.0 Hz, 1H), 3.874 (s, 3H), 3.867 (s, 3H), 0.92 (s, 9H), 0.08 (s, 3H), 0.00 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 148.9, 148.1, 141.9, 136.6, 118.2, 113.3, 110.8, 109.3, 75.7, 56.0, 55.9, 26.0, 18.5, –4.5, –4.7 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{17}H_{28}O_3SiNa$ $[M+Na]^+$: 331.1700, found: 331.1714.

tert-Butyl(4-(1-((*tert*-butyldimethylsilyl)oxy)allyl)phenoxy)dimethylsilane (1f)



Yellow oil.

R_f: 0.53 (hexane).

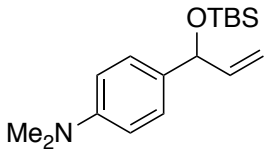
IR (ATR): 2956, 2930, 2891, 2858, 1641, 1607, 1508, 1472, 1463, 1390, 1362, 1251, 1197, 1166, 1126, 1072, 1032, 1006 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.22–7.20 (m, 2H), 6.82–6.81 (m, 2H), 5.94 (ddd, *J* = 16.5, 10.5, 6.0 Hz, 1H), 5.29 (app. dt, *J* = 16.5, 1.5 Hz, 1H), 5.14 (br d, *J* = 6.0 Hz, 1H), 5.08 (dd, *J* = 10.5, 1.5 Hz, 1H), 1.01 (s, 9H), 0.94 (s, 9H), 0.22 (s, 6H), 0.10 (s, 3H), 0.01 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 154.8, 142.0, 136.7, 127.3, 119.9, 113.2, 75.7, 26.0, 25.9, 18.5, 18.3, –4.3 (two signals merged), –4.5, –4.6 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{21}H_{38}O_2Si_2Na$ $[M+Na]^+$: 401.2303, found: 401.2296.

4-(1-((*tert*-Butyldimethylsilyl)oxy)allyl)-*N*,*N*-dimethylaniline (1g)



Colorless oil.

R_f: 0.53 (hexane/EtOAc = 20:1).

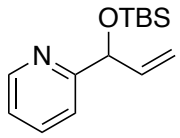
IR (ATR): 2955, 2928, 2886, 2855, 2804, 1640, 1615, 1568, 1520, 1472, 1462, 1346, 1250, 1183, 1113, 1061, 1031, 1005 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.19–7.18 (m, 2H), 6.70 (d, *J* = 9.0 Hz, 2H), 5.91 (ddd, *J* = 17.5, 10.0, 5.5 Hz, 1H), 5.24 (app. dt, *J* = 17.5, 1.5 Hz, 1H), 5.09 (br d, *J* = 5.5 Hz, 1H), 5.02 (app. dt, *J* = 10.0, 1.5 Hz, 1H), 2.93 (s, 6H), 0.91 (s, 9H), 0.06 (s, 3H), –0.02 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 150.0, 142.3, 131.9, 127.1, 112.7, 112.5, 75.7, 40.9, 26.1, 18.5, –4.5, –4.6 ppm.

HRMS (ESI): *m/z* calcd. for $C_{17}H_{29}NOSiNa$ $[M+Na]^+$: 314.1911, found: 314.1932.

2-(1-((*tert*-Butyldimethylsilyl)oxy)allyl)pyridine (1h)



Yellow oil.

R_f: 0.38 (hexane/EtOAc = 20:1).

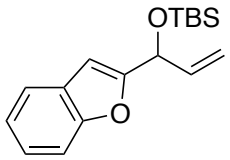
IR (ATR): 3060, 3012, 2955, 2930, 2890, 2857, 1642, 1590, 1571, 1471, 1435, 1361, 1347, 1253, 1138, 1101, 1075, 1006 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.47 (dd, *J* = 5.5, 1.5 Hz, 1H), 7.63 (app. td, *J* = 8.0, 1.5 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.09 (dd, *J* = 7.5, 5.5 Hz, 1H), 6.01 (ddd, *J* = 17.5, 10.5, 5.0 Hz, 1H), 5.38 (app. dt, *J* = 17.5, 1.5 Hz, 1H), 5.28 (d, *J* = 5.0 Hz, 1H), 5.08 (d, *J* = 10.5 Hz, 1H), 0.90 (s, 9H), 0.07 (s, 3H), –0.01 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 163.3, 148.6, 140.3, 136.8, 122.0, 120.1, 114.0, 77.0, 25.9, 18.4, –4.7, –4.9 ppm.

HRMS (ESI): *m/z* calcd. for $C_{14}H_{23}NOSiNa$ $[M+Na]^+$: 272.1441, found: 272.1443.

((1-(Benzofuran-2-yl)allyl)oxy)(*tert*-butyl)dimethylsilane (1i)



Colorless oil.

R_f: 0.72 (hexane/EtOAc = 20:1).

IR (ATR): 3085, 3064, 3035, 2955, 2929, 2886, 2857, 1644, 1600, 1585, 1472, 1462, 1454, 1361, 1253, 1152, 1101, 1006 cm^{-1}.

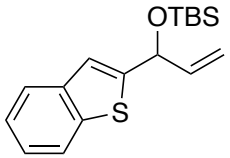
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.52 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.24 (app. td,

J = 8.0, 1.0 Hz, 1H), 7.19 (app. td, *J* = 7.5, 1.0 Hz, 1H), 6.59 (s, 1H), 6.09 (ddd, *J* = 17.0, 10.5, 5.5 Hz, 1H), 5.46 (app. dt, *J* = 17.0, 1.5 Hz, 1H), 5.33–5.32 (m, 1H), 5.25 (app. dt, *J* = 10.5, 1.5 Hz, 1H), 0.94 (s, 9H), 0.14 (s, 3H), 0.09 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 159.0, 155.1, 137.8, 128.4, 124.0, 122.8, 121.1, 115.8, 111.3, 102.7, 70.2, 25.9, 18.6, –4.7, –4.8 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{17}H_{25}O_2Si$ $[M+H]^+$: 289.1612, found: 289.1618.

((1-(Benzo[*b*]thiophen-2-yl)allyl)oxy)(*tert*-butyl)dimethylsilane (1j)



Yellow oil.

R_f: 0.45 (hexane/EtOAc = 60:1).

IR (ATR): 3061, 2955, 2929, 2885, 2856, 1641, 1472, 1459, 1436, 1398, 1361, 1251, 1140, 1114, 1074, 1030, 1005 cm^{-1}.

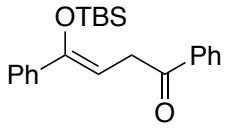
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.76 (d, *J* = 7.5 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.28 (app. t, *J* = 7.5 Hz, 1H), 7.23 (app. t, *J* = 8.0 Hz, 1H), 7.07 (s, 1H), 6.07–6.00 (m, 1H), 5.45 (d, *J* = 6.0 Hz, 1H), 5.37 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.17 (dd, *J* = 10.5, 1.5 Hz, 1H), 0.95 (s, 9H), 0.12 (s, 3H), 0.10 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 150.0, 140.4, 139.9, 139.8, 124.2, 123.9, 123.5, 122.5, 119.5, 114.9, 72.9, 26.0, 18.5, –4.5, –4.8 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{17}H_{24}OSSiNa$ $[M+Na]^+$: 327.1209, found: 327.1214.

3.2. Characterization Data for the Products

(*Z*)-4-((*tert*-Butyldimethylsilyl)oxy)-1,4-diphenylbut-3-en-1-one (3aa)



Yield: 72.4 mg, 82% yield, colorless oil.

R_f: 0.40 (hexane/EtOAc = 30:1).

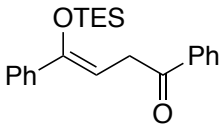
IR (ATR): 3062, 2955, 2930, 2886, 2858, 1686, 1649, 1599, 1581, 1492, 1472, 1447, 1390, 1319, 1255, 1204, 1102, 1050 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.03–8.02 (m, 2H), 7.56 (t, *J* = 7.0 Hz, 1H), 7.49–7.45 (m, 4H), 7.31–7.25 (m, 3H), 5.48 (t, *J* = 6.5 Hz, 1H), 3.92 (d, *J* = 6.5 Hz, 2H), 1.02 (s, 9H), –0.03 (s, 6H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 198.4, 151.6, 139.1, 136.9, 133.2, 128.7, 128.4, 128.1 (two signals merged), 126.3, 103.7, 37.0, 26.0, 18.5, –3.8 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{22}H_{28}O_2SiNa$ [M+Na]$^+$: 375.1751, found: 375.1748.

(*Z*)-1,4-Diphenyl-4-((triethylsilyl)oxy)but-3-en-1-one (3aa')



Yield: 56.8 mg, 64% yield, colorless oil.

R_f: 0.25 (hexane/EtOAc = 60:1).

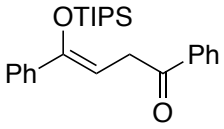
IR (ATR): 3064, 2955, 2911, 2876, 1686, 1654, 1594, 1579, 1491, 1447, 1397, 1352, 1319, 1223, 1179, 1105, 1074, 1002 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.04–8.02 (m, 2H), 7.56 (tt, *J* = 7.0, 1.5 Hz, 1H), 7.50–7.45 (m, 4H), 7.32–7.25 (m, 3H), 5.48 (t, *J* = 7.0 Hz, 1H), 3.93 (d, *J* = 7.0 Hz, 2H), 0.94 (t, *J* = 8.0 Hz, 9H), 0.62 (q, *J* = 8.0 Hz, 6H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 198.5, 151.9, 139.1, 136.9, 133.2, 128.7, 128.4, 128.2, 128.1, 126.0, 103.1, 36.9, 6.8, 5.5 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{22}H_{28}O_2SiNa$ [M+Na]$^+$: 375.1751, found: 375.1722.

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



Yield: 56.5 mg, 64% yield, colorless oil.

R_f: 0.32 (hexane/EtOAc = 60:1).

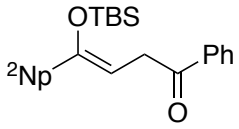
IR (ATR): 2938, 2922, 2888, 2865, 1686, 1649, 1598, 1581, 1462, 1446, 1349, 1306, 1260, 1207, 1115, 1059, 1014 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.03–8.02 (m, 2H), 7.57–7.53 (m, 1H), 7.50–7.45 (m, 4H), 7.31–7.25 (m, 3H), 5.36 (t, *J* = 7.0 Hz, 1H), 3.96 (d, *J* = 7.0 Hz, 2H), 1.13–1.05 (m, 21H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 198.4, 152.6, 139.8, 136.9, 133.1, 128.7, 128.4, 128.1 (two signals merged), 126.4, 103.1, 37.1, 18.0, 13.7 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{25}H_{34}O_2SiNa$ [M+Na]$^+$: 417.2220, found: 417.2249.

(*Z*)-4-((*tert*-Butyldimethylsilyl)oxy)-4-(naphthalen-2-yl)-1-phenylbut-3-en-1-one (3ba)



Yield: 82.3 mg, 82% yield, white solid.

R_f: 0.24 (hexane/EtOAc = 50:1).

IR (ATR): 2948, 2924, 2883, 2853, 1685, 1637, 1596, 1579, 1508, 1471, 1448, 1407, 1357, 1310, 1253, 1206, 1130, 1051 cm^{-1}.

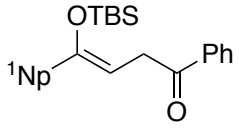
^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.08–8.06 (m, 2H), 7.98 (s, 1H), 7.85–7.78 (m, 3H), 7.65 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.51–7.45 (m, 4H), 5.69 (t, *J* = 6.5 Hz, 1H), 4.01 (d, *J* = 6.5 Hz, 2H), 1.08 (s, 9H), 0.01 (s, 6H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 198.4, 151.5, 136.9, 136.5, 133.19, 133.15, 128.7 (two signals merged), 128.4, 128.3, 127.7 (two signals merged), 126.3, 126.1, 125.0, 124.4, 104.3, 37.0, 26.0, 18.5, –3.8 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{26}H_{30}O_2SiNa$ $[M+Na]^+$: 425.1907, found: 425.1906.

M.p.: 74–75 °C.

(*Z*)-4-((*tert*-Butyldimethylsilyl)oxy)-4-(naphthalen-1-yl)-1-phenylbut-3-en-1-one (3ca)



Yield: 80.6 mg, 79% yield, brown solid.

R_f: 0.25 (hexane/EtOAc = 50:1).

IR (ATR): 2950, 2927, 2883, 2853, 1678, 1646, 1598, 1578, 1448, 1318, 1288, 1255, 1183, 1122, 1058, 1025 cm^{-1}.

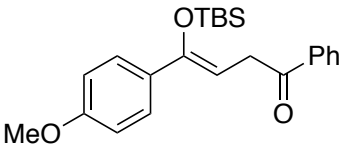
^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.23–8.22 (m, 1H), 8.13–8.11 (m, 2H), 7.83–7.79 (m, 2H), 7.61–7.58 (m, 1H), 7.53–7.45 (m, 5H), 7.41 (dd, *J* = 8.0, 7.0 Hz, 1H), 5.32 (t, *J* = 6.5 Hz, 1H), 4.05 (d, *J* = 6.5 Hz, 2H), 0.92 (s, 9H), –0.30 (s, 6H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 198.7, 151.6, 137.3, 136.9, 133.6, 133.1, 131.7, 128.8, 128.7, 128.5, 128.2, 126.7, 126.6, 126.1, 125.9, 125.1, 106.2, 36.8, 25.8, 18.4, –4.5 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{26}H_{30}O_2SiNa$ $[M+Na]^+$: 425.1907, found: 425.1904.

M.p.: 72–73 °C.

(*Z*)-4-((*tert*-Butyldimethylsilyl)oxy)-4-(4-methoxyphenyl)-1-phenylbut-3-en-1-one (3da)



Yield: 79.1 mg, 83% yield, orange solid.

R_f: 0.21 (hexane/EtOAc = 50:1).

IR (ATR): 2949, 2927, 2894, 1727, 1686, 1638, 1604, 1578, 1509, 1447, 1346, 1308, 1249, 1200, 1106, 1051, 1005 cm^{-1}.

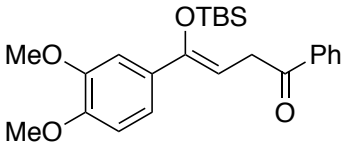
^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.03 (dd, *J* = 8.5, 1.0 Hz, 2H), 7.57–7.54 (m, 1H), 7.47 (app. t, *J* = 7.5 Hz, 2H), 7.41 (d, *J* = 9.0 Hz, 2H), 6.83 (d, *J* = 9.0 Hz, 2H), 5.37 (t, *J* = 7.0 Hz, 1H), 3.90 (d, *J* = 7.0 Hz, 2H), 3.81 (s, 3H), 1.02 (s, 9H), –0.03 (s, 6H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 198.6, 159.6, 151.3, 136.9, 133.1, 131.8, 128.7, 128.4, 127.6, 113.4, 102.2, 55.4, 37.0, 26.0, 18.5, –3.8 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{23}H_{30}O_3SiNa$ $[M+Na]^+$: 405.1856, found: 405.1853.

M.p.: 73–74 °C.

(*Z*)-4-((*tert*-Butyldimethylsilyl)oxy)-4-(3,4-dimethoxyphenyl)-1-phenylbut-3-en-1-one (3ea)



Yield: 79.4 mg, 77% yield, brown oil.

R_f: 0.22 (hexane/EtOAc = 10:1).

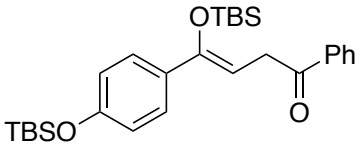
IR (ATR): 2957, 2928, 2894, 2858, 1688, 1654, 1600, 1582, 1513, 1460, 1327, 1268, 1209, 1167, 1140, 1108, 1054, 1020 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.02 (dd, *J* = 8.0, 1.0 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.47 (app. t, *J* = 7.5 Hz, 2H), 7.06 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.02 (d, *J* = 2.5 Hz, 1H), 6.80 (d, *J* = 8.5 Hz, 1H), 5.41 (t, *J* = 6.5 Hz, 1H), 3.90 (d, *J* = 6.5 Hz, 2H), 3.89 (s, 3H), 3.88 (s, 3H), 1.02 (s, 9H), –0.01 (s, 6H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 198.5, 151.3, 149.0, 148.4, 136.9, 133.1, 132.1, 128.7, 128.3, 118.8, 110.6, 109.5, 102.3, 56.0, 55.9, 36.9, 26.0, 18.5, –3.8 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{24}H_{33}O_4Si$ $[M+H]^+$: 413.2143, found: 413.2150.

(*Z*)-4-((*tert*-Butyldimethylsilyl)oxy)-4-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)-1-phenylbut-3-en-1-one (3fa)



Yield: 86.3 mg, 71% yield, colorless oil.

R_f: 0.26 (hexane/EtOAc = 60:1).

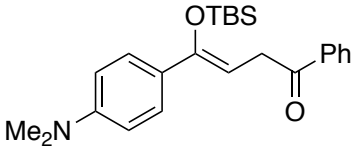
IR (ATR): 2955, 2930, 2887, 1686, 1649, 1605, 1582, 1507, 1472, 1449, 1362, 1305, 1253, 1167, 1100, 1050, 1005 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.04–8.02 (m, 2H), 7.57–7.54 (m, 1H), 7.47 (app. t, *J* = 7.5 Hz, 2H), 7.36–7.34 (m, 2H), 6.79–6.76 (m, 2H), 5.37 (t, *J* = 7.0 Hz, 1H), 3.90 (d, *J* = 7.0 Hz, 2H), 1.02 (s, 9H), 0.98 (s, 9H), 0.19 (s, 6H), –0.03 (s, 6H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 198.6, 155.7, 151.5, 136.9, 133.1, 132.5, 128.7, 128.4, 127.6, 119.7, 102.2, 37.0, 26.0, 25.8, 18.5, 18.4, –3.9, –4.3 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{28}H_{43}O_3Si_2$ $[M+H]^+$: 483.2745, found: 483.2736.

(*Z*)-4-((*tert*-Butyldimethylsilyl)oxy)-4-(4-(dimethylamino)phenyl)-1-phenylbut-3-en-1-one (3ga)



Yield: 43.4 mg, 44% yield, white solid.

R_f: 0.25 (hexane/EtOAc = 30:1).

IR (ATR): 2950, 2922, 2886, 2858, 1686, 1637, 1607, 1522, 1445, 1359, 1321, 1256, 1207, 1048, 1002 cm^{-1}.

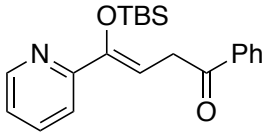
^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.03 (d, *J* = 7.5 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.45 (app. t, *J* = 7.5 Hz, 2H), 7.36 (d, *J* = 9.0 Hz, 2H), 6.64 (d, *J* = 9.0 Hz, 2H), 5.31 (t, *J* = 7.0 Hz, 1H), 3.89 (d, *J* = 7.0 Hz, 2H), 2.95 (s, 6H), 1.03 (s, 9H), –0.01 (s, 6H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 198.9, 151.8, 150.4, 137.0, 133.0, 128.6, 128.4, 127.2 (two signals merged), 111.7, 100.6, 40.6, 37.3, 26.1, 18.5, –3.7 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{24}H_{34}NO_2Si$ $[M+H]^+$: 396.2353, found: 396.2362.

M.p.: 96–97 °C.

(*Z*)-4-((*tert*-Butyldimethylsilyl)oxy)-1-phenyl-4-(pyridin-2-yl)but-3-en-1-one (3ha)



Yield: 41.1 mg, 47% yield, yellow oil.

R_f: 0.24 (hexane/EtOAc = 10:1).

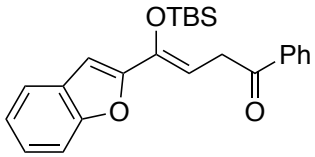
IR (ATR): 3062, 2955, 2929, 2893, 2857, 1685, 1648, 1598, 1584, 1567, 1471, 1448, 1347, 1324, 1254, 1205, 1118, 1055 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.53 (d, *J* = 4.5 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 2H), 7.64 (ddd, *J* = 7.5, 7.5, 1.5 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 7.5 Hz, 1H), 7.46 (app. t, *J* = 7.5 Hz, 2H), 7.15 (dd, *J* = 7.5, 5.0 Hz, 1H), 6.12 (t, *J* = 6.5 Hz, 1H), 3.96 (d, *J* = 6.5 Hz, 2H), 1.05 (s, 9H), 0.07 (s, 6H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 198.0, 155.7, 150.3, 148.9, 136.8, 136.3, 133.2, 128.7, 128.4, 122.7, 120.2, 106.2, 37.0, 26.1, 18.7, –3.6 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{21}H_{28}NO_2Si$ $[M+H]^+$: 354.1884, found: 354.1891.

(*Z*)-4-(Benzofuran-2-yl)-4-((*tert*-butyldimethylsilyl)oxy)-1-phenylbut-3-en-1-one (3ia)



Yield: 82.7 mg, 84% yield, yellow oil.

R_f: 0.40 (hexane/EtOAc = 30:1).

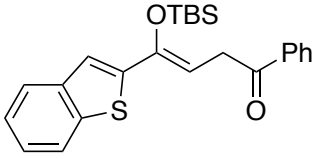
IR (ATR): 3065, 2953, 2930, 2892, 2857, 1685, 1655, 1596, 1560, 1472, 1447, 1408, 1358, 1302, 1256, 1159, 1115, 1051 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.80–7.78 (m, 2H), 7.35–7.32 (m, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.25 (app. t, *J* = 7.5 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.04–7.01 (m, 1H), 6.98–6.95 (m, 1H), 6.49 (s, 1H), 5.79 (t, *J* = 7.0 Hz, 1H), 3.73 (d, *J* = 7.0 Hz, 2H), 0.86 (s, 9H), –0.05 (s, 6H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 197.6, 154.7, 153.8, 142.6, 136.7, 133.3, 128.8, 128.6, 128.4, 124.6, 123.0, 121.2, 111.2, 105.1, 103.2, 36.5, 26.0, 18.6, –3.7 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{24}H_{28}O_3SiNa$ $[M+Na]^+$: 415.1700, found: 415.1704.

(*Z*)-4-(Benzo[*b*]thiophen-2-yl)-4-((*tert*-butyldimethylsilyl)oxy)-1-phenylbut-3-en-1-one (3ja)



Yield: 78.4 mg, 77% yield, yellow oil.

R_f: 0.30 (hexane/EtOAc = 60:1).

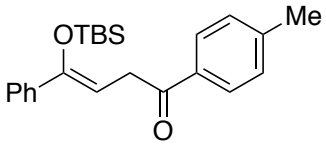
IR (ATR): 3060, 2954, 2927, 2854, 1682, 1632, 1596, 1579, 1522, 1471, 1436, 1339, 1254, 1178, 1129, 1081, 1025, 1001 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.03–8.02 (m, 2H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.71 (d, *J* = 7.0 Hz, 1H), 7.58 (app. t, *J* = 7.5 Hz, 1H), 7.49 (app. t, *J* = 7.5 Hz, 2H), 7.34–7.30 (m, 3H), 5.72 (t, *J* = 7.0 Hz, 1H), 3.94 (d, *J* = 7.0 Hz, 2H), 1.09 (s, 9H), 0.15 (s, 6H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 197.7, 146.1, 142.6, 139.8, 139.4, 136.8, 133.3, 128.8, 128.3, 124.7, 124.5, 123.7, 122.3, 120.8, 105.7, 36.9, 26.1, 18.6, –3.6 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{24}H_{29}O_2SSi$ $[M+H]^+$: 409.1652, found: 409.1657.

(*Z*)-4-((*tert*-Butyldimethylsilyl)oxy)-4-phenyl-1-(*p*-tolyl)but-3-en-1-one (3ab)



Yield: 72.1 mg, 79% yield, white solid.

R_f: 0.24 (hexane/EtOAc = 50:1).

IR (ATR): 2956, 2927, 2855, 1683, 1655, 1607, 1470, 1445, 1402, 1342, 1316, 1258, 1176, 1107, 1049, 1025 cm^{-1}.

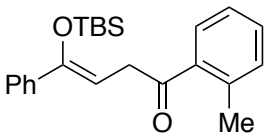
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.49–7.47 (m, 2H), 7.31–7.25 (m, 5H), 5.48 (t, *J* = 6.5 Hz, 1H), 3.89 (d, *J* = 6.5 Hz, 2H), 2.40 (s, 3H), 1.02 (s, 9H), –0.04 (s, 6H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 198.1, 151.4, 143.9, 139.2, 134.4, 129.4, 128.5, 128.1, 128.0, 126.2, 103.9, 36.9, 26.0, 21.8, 18.5, –3.9 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{23}H_{31}O_2Si$ $[M+H]^+$: 367.2088, found: 367.2087.

M.p.: 73–74 °C.

(*Z*)-4-((*tert*-Butyldimethylsilyl)oxy)-4-phenyl-1-(*o*-tolyl)but-3-en-1-one (3ac)



Yield: 49.1 mg, 54% yield, colorless oil.

R_f: 0.31 (hexane/EtOAc = 50:1).

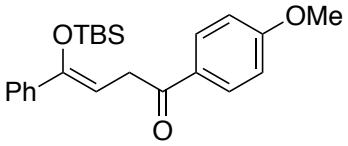
IR (ATR): 3061, 3024, 2955, 2930, 2892, 2857, 1686, 1653, 1601, 1571, 1492, 1472, 1446, 1337, 1305, 1255, 1103, 1026 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.75–7.74 (m, 1H), 7.48–7.47 (m, 2H), 7.38–7.35 (m, 1H), 7.31–7.23 (m, 5H), 5.45 (t, *J* = 6.5 Hz, 1H), 3.84 (d, *J* = 6.5 Hz, 2H), 2.52 (s, 3H), 1.00 (s, 9H), –0.05 (s, 6H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 202.3, 151.6, 139.2, 138.5, 137.7, 132.1, 131.4, 128.8, 128.1, 128.0, 126.3, 125.8, 103.8, 39.6, 26.0, 21.6, 18.4, –3.9 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{23}H_{31}O_2Si$ $[M+H]^+$: 367.2088, found: 367.2103.

(*Z*)-4-((*tert*-Butyldimethylsilyl)oxy)-1-(4-methoxyphenyl)-4-phenylbut-3-en-1-one (3ad)



Yield: 71.8 mg, 75% yield, colorless oil.

R_f: 0.21 (hexane/EtOAc = 30:1).

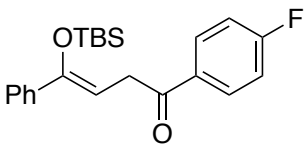
IR (ATR): 2959, 2924, 2894, 2857, 1671, 1648, 1599, 1574, 1509, 1461, 1420, 1351, 1306, 1259, 1210, 1172, 1108, 1024 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.01 (d, *J* = 9.0 Hz, 2H), 7.49–7.47 (m, 2H), 7.29 (app. t, *J* = 7.5 Hz, 2H), 7.26–7.23 (m, 1H), 6.93 (d, *J* = 9.0 Hz, 2H), 5.47 (t, *J* = 7.0 Hz, 1H), 3.87–3.86 (m, 5H), 1.02 (s, 9H), –0.03 (s, 6H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 197.1, 163.5, 151.3, 139.2, 130.6, 130.0, 128.1, 128.0, 126.2, 113.8, 104.1, 55.5, 36.8, 26.0, 18.5, –3.9 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{23}H_{31}O_3Si$ $[M+H]^+$: 383.2037, found: 383.2026.

(*Z*)-4-((*tert*-Butyldimethylsilyl)oxy)-1-(4-fluorophenyl)-4-phenylbut-3-en-1-one (3ae)



Yield: 75.6 mg, 82% yield, colorless oil.

R_f: 0.25 (hexane/EtOAc = 50:1).

IR (ATR): 2956, 2930, 2886, 2859, 1687, 1637, 1607, 1522, 1445, 1359, 1321, 1256, 1207, 1048, 1002 cm^{-1}.

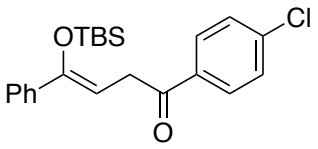
^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.07–8.04 (m, 2H), 7.48–7.47 (m, 2H), 7.31–7.24 (m, 3H), 7.14–7.10 (m, 2H), 5.44 (t, *J* = 7.0 Hz, 1H), 3.87 (d, *J* = 7.0 Hz, 2H), 1.02 (s, 9H), –0.03 (s, 6H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 196.8, 165.8 (d, $J_{C–F}$ = 254.8 Hz), 151.7, 139.0, 133.2, 131.0(d, $J_{C–F}$ = 9.7 Hz), 128.1 (two signals merged), 126.2, 115.8 (d, $J_{C–F}$ = 21.5 Hz), 103.5, 37.0, 26.0, 18.4, –3.9 ppm.

^{19}F NMR ($CDCl_3$, 565 MHz): δ –106.35 – –106.40 (m) ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{22}H_{28}FO_2Si$ $[M+H]^+$: 371.1837, found: 371.1829.

(*Z*)-4-((*tert*-Butyldimethylsilyl)oxy)-1-(4-chlorophenyl)-4-phenylbut-3-en-1-one (3af)



Yield: 82.1 mg, 85% yield, colorless oil.

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

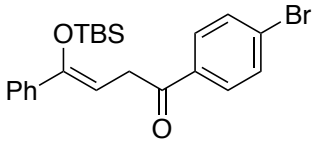
IR (ATR): 2956, 2929, 2894, 2858, 1695, 1660, 1586, 1571, 1471, 1399, 1336, 1316, 1275, 1258, 1209, 1088, 1042, 1013 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.98–7.95 (m, 2H), 7.48–7.46 (m, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.31–7.25 (m, 3H), 5.42 (t, *J* = 7.0 Hz, 1H), 3.87 (d, *J* = 7.0 Hz, 2H), 1.02 (s, 9H), –0.04 (s, 6H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 197.2, 151.8, 139.6, 139.0, 135.1, 129.8, 129.0, 128.2, 128.1, 126.2, 103.4, 37.1, 26.0, 18.4, –3.9 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{22}H_{28}ClO_2Si$ $[M+H]^+$: 387.1542, found: 387.1528.

(*Z*)-1-(4-Bromophenyl)-4-((*tert*-butyldimethylsilyl)oxy)-4-phenylbut-3-en-1-one (3ag)



Yield: 90.0 mg, 83% yield, colorless oil.

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

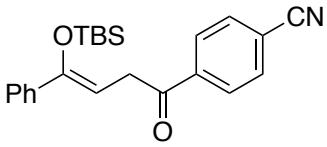
IR (ATR): 2952, 2931, 2892, 2856, 1696, 1656, 1581, 1491, 1470, 1445, 1397, 1335, 1312, 1256, 1209, 1099, 1042, 1010 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.88 (d, *J* = 8.5 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 7.0 Hz, 2H), 7.30–7.23 (m, 3H), 5.40 (t, *J* = 6.5 Hz, 1H), 3.85 (d, *J* = 6.5 Hz, 2H), 1.01 (s, 9H), –0.05 (s, 6H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 197.4, 151.8, 139.0, 135.5, 132.0, 129.9, 128.3, 128.2, 128.1, 126.2, 103.3, 37.1, 26.0, 18.4, –3.9 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{22}H_{28}BrO_2Si$ $[M+H]^+$: 431.1036, found: 431.1031.

(*Z*)-4-(4-((*tert*-Butyldimethylsilyl)oxy)-4-phenylbut-3-enoyl)benzonitrile (3ah)



Yield: 64.5 mg, 68% yield, pale yellow solid.

R_f: 0.42 (hexane/EtOAc = 10:1).

IR (ATR): 2956, 2928, 2890, 2856, 1699, 1660, 1604, 1563, 1490, 1471, 1403, 1338, 1319, 1254, 1211, 1190, 1103, 1043 cm^{-1}.

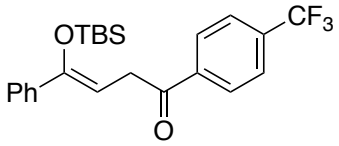
^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.11 (d, *J* = 8.5 Hz, 2H), 7.77 (d, *J* = 8.5 Hz, 2H), 7.47–7.44 (m, 2H), 7.33–7.28 (m, 3H), 5.37 (t, *J* = 7.0 Hz, 1H), 3.90 (d, *J* = 7.0 Hz, 2H), 1.02 (s, 9H), –0.04 (s, 6H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 197.2, 152.4, 139.7, 138.8, 132.6, 128.8, 128.4, 128.2, 126.3, 118.1, 116.4, 102.6, 37.4, 26.0, 18.5, –3.8 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{23}H_{27}NO_2SiNa$ $[M+Na]^+$: 400.1703, found: 400.1730.

M.p.: 92–93 °C.

(*Z*)-4-((*tert*-Butyldimethylsilyl)oxy)-4-phenyl-1-(4-(trifluoromethyl)phenyl)but-3-en-1-one (3ai)



Yield: 79.3 mg, 75% yield, colorless viscous oil.

R_f: 0.36 (hexane/EtOAc = 50:1).

IR (ATR): 2959, 2953, 2929, 2900, 2884, 2858, 1698, 1660, 1600, 1580, 1492, 1471, 1409, 1313, 1256, 1209, 1130, 1043 cm^{-1}.

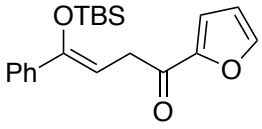
^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.13 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 7.5 Hz, 2H), 7.32–7.25 (m, 3H), 5.42 (t, *J* = 7.0 Hz, 1H), 3.92 (d, *J* = 7.0 Hz, 2H), 1.03 (s, 9H), –0.03 (s, 6H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 197.5, 152.2, 139.4, 138.9, 134.4 (q, J_{C-F} = 32.8 Hz), 128.7, 128.3, 128.2, 126.3, 125.8, 123.8 (q, J_{C-F} = 274.1 Hz), 102.9, 37.4, 26.0, 18.5, –3.9 ppm.

^{19}F NMR ($CDCl_3$, 565 MHz): δ –64.1 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{23}H_{28}F_3O_2Si$ $[M+H]^+$: 421.1805, found: 421.1831.

(*Z*)-4-((*tert*-Butyldimethylsilyl)oxy)-1-(furan-2-yl)-4-phenylbut-3-en-1-one (3aj)



Yield: 71.0 mg, 83% yield, colorless viscous oil.

R_f: 0.45 (hexane/EtOAc = 10:1).

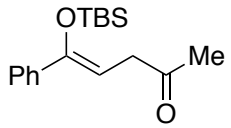
IR (ATR): 3061, 2955, 2930, 2886, 2858, 1678, 1649, 1600, 1569, 1492, 1467, 1446, 1391, 1317, 1255, 1156, 1054, 1012 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.59 (d, *J* = 1.5 Hz, 1H), 7.48–7.46 (m, 2H), 7.32–7.24 (m, 4H), 6.53 (dd, *J* = 3.5, 1.5 Hz, 1H), 5.45 (t, *J* = 7.0 Hz, 1H), 3.78 (d, *J* = 7.0 Hz, 2H), 1.01 (s, 9H), –0.04 (s, 6H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 187.4, 152.6, 151.9, 146.5, 139.1, 128.1 (two signals merged), 126.3, 117.4, 112.3, 102.9, 36.6, 26.0, 18.5, –3.9 ppm.

HRMS (ESI): *m/z* calcd. for $C_{20}H_{26}O_3SiNa$ $[M+Na]^+$: 365.1543, found: 365.1556.

(*Z*)-5-((*tert*-Butyldimethylsilyl)oxy)-5-phenylpent-4-en-2-one (3ak)



Yield: 42.4 mg, 58% yield, colorless oil.

R_f: 0.21 (hexane/EtOAc = 50:1).

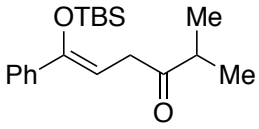
IR (ATR): 2955, 2930, 2887, 2858, 1717, 1649, 1600, 1492, 1473, 1446, 1337, 1279, 1254, 1156, 1109, 1049, 1006 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.45 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.32–7.25 (m, 3H), 5.29 (t, *J* = 7.0 Hz, 1H), 3.33 (d, *J* = 7.0 Hz, 2H), 2.19 (s, 3H), 0.99 (s, 9H), –0.07 (s, 6H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 207.3, 152.1, 139.1, 128.1 (two signals merged), 126.3, 103.0, 41.5, 29.6, 25.9, 18.4, –3.9 ppm.

HRMS (ESI): *m/z* calcd. for $C_{17}H_{27}O_2Si$ $[M+Na]^+$: 291.1775, found: 291.1787.

(*Z*)-6-((*tert*-Butyldimethylsilyl)oxy)-2-methyl-6-phenylhex-5-en-3-one (3al)



Yield: 57.1 mg, 72% yield, colorless oil.

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

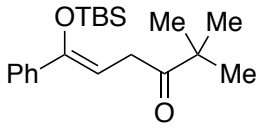
IR (ATR): 2957, 2931, 2891, 2858, 1713, 1649, 1600, 1492, 1464, 1446, 1384, 1332, 1282, 1255, 1111, 1066, 1028, 1005 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.45 (d, *J* = 6.5 Hz, 2H), 7.31–7.24 (m, 3H), 5.32 (t, *J* = 6.5 Hz, 1H), 3.39 (d, *J* = 6.5 Hz, 2H), 2.71 (sept, *J* = 6.5 Hz, 1H), 1.12 (d, *J* = 6.5 Hz, 6H), 0.99 (s, 9H), –0.07 (s, 6H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 212.9, 151.7, 139.2, 128.1, 128.0, 126.3, 103.4, 40.5, 38.4, 26.0, 18.5, 18.4, –3.9 ppm.

HRMS (ESI): *m/z* calcd. for $C_{19}H_{31}O_2Si$ $[M+H]^+$: 319.2088, found: 319.2086.

(*Z*)-6-((*tert*-Butyldimethylsilyl)oxy)-2,2-dimethyl-6-phenylhex-5-en-3-one (3am)



Yield: 54.0 mg, 65% yield, colorless oil.

R_f: 0.39 (hexane/EtOAc = 50:1).

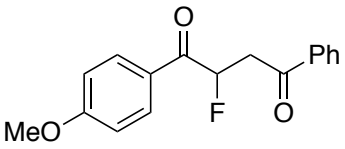
IR (ATR): 2957, 2930, 2902, 2859, 1708, 1650, 1600, 1492, 1474, 1446, 1392, 1363, 1303, 1256, 1111, 1071, 1042, 1027 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.42 (d, J = 8.0 Hz, 2H), 7.30–7.24 (m, 3H), 5.37 (t, J = 7.0 Hz, 1H), 3.47 (d, J = 7.0 Hz, 2H), 1.18 (s, 9H), 1.00 (s, 9H), –0.06 (s, 6H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 213.9, 151.2, 139.2, 128.0, 127.9, 126.2, 104.0, 44.3, 34.7, 26.7, 26.0, 18.4, –3.9 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{20}H_{32}O_2SiNa$ $[M+Na]^+$: 355.2064, found: 355.2074.

2-Fluoro-1-(4-methoxyphenyl)-4-phenylbutane-1,4-dione (6)



Yield: 10.4 mg, 73% yield, white solid.

R_f: 0.31 (hexane/EtOAc = 5:1).

IR (ATR): 2977, 1689, 1678, 1604, 1595, 1510, 1453, 1320, 1268, 1172 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.06 (d, J = 8.5 Hz, 2H), 8.01–7.99 (m, 2H), 7.61 (t, J = 7.5 Hz, 1H), 7.49 (app. t, J = 7.5 Hz, 2H), 6.99–6.96 (m, 2H), 6.32 (ddd, J = 47.5, 6.5, 5.5 Hz, 1H), 3.89 (s, 3H), 3.72–3.70 (m, 1H), 3.67–3.66 (m, 1H) ppm.

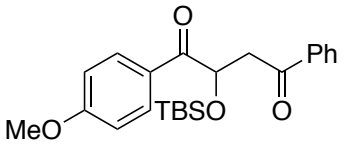
^{13}C NMR ($CDCl_3$, 126 MHz): δ 195.7 (d, $J_{C–F}$ = 4.8 Hz, 1H), 193.7 (d, $J_{C–F}$ = 19.3 Hz, 1H), 164.3, 136.4, 133.8, 131.8 (d, $J_{C–F}$ = 4.9 Hz, 1H), 128.9, 128.4, 127.3, 114.2, 89.1 (d, $J_{C–F}$ = 180.3 Hz, 1H), 55.7, 40.5 (d, $J_{C–F}$ = 21.7 Hz, 1H) ppm.

^{19}F NMR ($CDCl_3$, 565 MHz): δ –187.4 – –187.6 (m) ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{17}H_{16}FO_3$ $[M+H]^+$: 287.1078, found: 287.1078.

M.p.: 76–77 °C.

2-((*tert*-Butyldimethylsilyl)oxy)-1-(4-methoxyphenyl)-4-phenylbutane-1,4-dione (7)



Yield: 89.0 mg, 89% yield, colorless viscous oil.

R_f: 0.44 (hexane/EtOAc = 5:1).

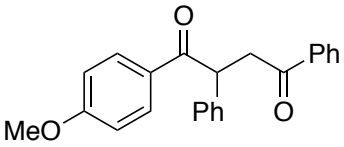
IR (ATR): 2947, 2934, 2927, 2916, 2854, 1691, 1683, 1600, 1574, 1512, 1464, 1449, 1421, 1317, 1254, 1177, 1133, 1029 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.10–8.07 (m, 2H), 7.98–7.97 (m, 2H), 7.58–7.55 (m, 1H), 7.46 (app. t, *J* = 7.5 Hz, 2H), 6.97–6.94 (m, 2H), 5.67 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.87 (s, 3H), 3.55 (dd, *J* = 16.0, 8.0 Hz, 1H), 3.24 (dd, *J* = 16.0, 4.0 Hz, 1H), 0.79 (s, 9H), 0.03 (s, 3H), –0.02 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 198.2, 197.6, 163.8, 137.1, 133.4, 131.4, 128.7, 128.5, 127.7, 114.0, 72.4, 55.6, 44.1, 25.7, 18.3, –4.6, –5.0 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{23}H_{31}O_4Si$ $[M+H]^+$: 399.1986, found: 399.1960.

1-(4-Methoxyphenyl)-2,4-diphenylbutane-1,4-dione (8)



Yield: 70.9 mg, 82% yield, pale yellow viscous oil.

R_f: 0.34 (hexane/EtOAc = 5:1).

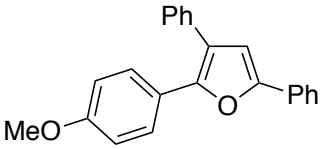
IR (ATR): 3061, 3027, 3005, 2955, 2933, 2909, 2840, 1670, 1597, 1575, 1510, 1493, 1419, 1320, 1249, 1166, 1076, 1028 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.04–8.01 (m, 2H), 7.98–7.96 (m, 2H), 7.53 (t, *J* = 7.0 Hz, 1H), 7.42 (app. t, *J* = 7.5 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.29 (app. t, *J* = 7.5 Hz, 2H), 7.21 (t, *J* = 7.5 Hz, 1H), 6.88–6.85 (m, 2H), 5.29 (dd, *J* = 10.0, 4.0 Hz, 1H), 4.19 (dd, *J* = 17.5, 10.0 Hz, 1H), 3.79 (s, 3H), 3.26 (dd, *J* = 17.5, 4.0 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 198.3, 197.4, 163.4, 139.3, 136.7, 133.3, 131.4, 129.5, 129.2, 128.6, 128.3 (two signals merged), 127.4, 113.8, 55.5, 48.5, 43.9 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{23}H_{20}O_3Na$ $[M+Na]^+$: 367.1305, found: 367.1307.

2-(4-Methoxyphenyl)-3,5-diphenylfuran (9)



Yield: 46.5 mg, 57% yield in two steps, colorless viscous oil.

R_f: 0.59 (hexane/EtOAc = 5:1).

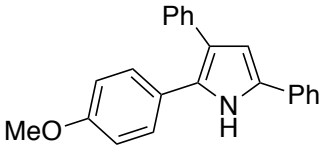
IR (ATR): 3055, 3030, 3001, 2955, 2932, 2835, 1607, 1570, 1509, 1489, 1462, 1419, 1389, 1299, 1247, 1175, 1111, 1027 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.75–7.72 (m, 2H), 7.55–7.52 (m, 2H), 7.46–7.44 (m, 2H), 7.41–7.35 (m, 4H), 7.31–7.24 (m, 2H), 6.86–6.83 (m, 2H), 6.79 (s, 1H), 3.80 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 159.3, 152.2, 148.2, 134.6, 130.8, 128.84, 128.76 (two signals merged), 127.8, 127.4, 127.2, 124.1, 123.8, 123.2, 114.0, 109.4, 55.4 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{23}H_{18}O_2Na$ $[M+Na]^+$: 349.1199, found: 349.1178.

2-(4-Methoxyphenyl)-3,5-diphenyl-1*H*-pyrrole (10)



Yield: 55.6 mg, 68% yield in two steps, colorless amorphous solid.

R_f: 0.44 (hexane/EtOAc = 5:1).

IR (ATR): 3425, 3061, 3049, 3020, 2997, 2954, 2933, 2834, 1602, 1566, 1509, 1489, 1437, 1244, 1173, 1107, 1053, 1025 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.31 (br s, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.39–7.36 (m, 4H), 7.32–7.26 (m, 4H), 7.23–7.17 (m, 2H), 6.86 (d, *J* = 8.0 Hz, 2H), 6.68 (d, *J* = 3.0 Hz, 1H), 3.79 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 158.9, 136.6, 132.4, 131.8, 129.5, 129.1 (two signals merged), 128.44, 128.40, 126.5, 125.9, 125.8, 123.8, 123.1, 114.3, 108.4, 55.4 ppm.

HRMS (ESI): *m*/*z* calcd. for $C_{23}H_{19}NONa$ $[M+Na]^+$: 348.1359, found: 348.1357.

M.p.: 50–51 °C.

4. References

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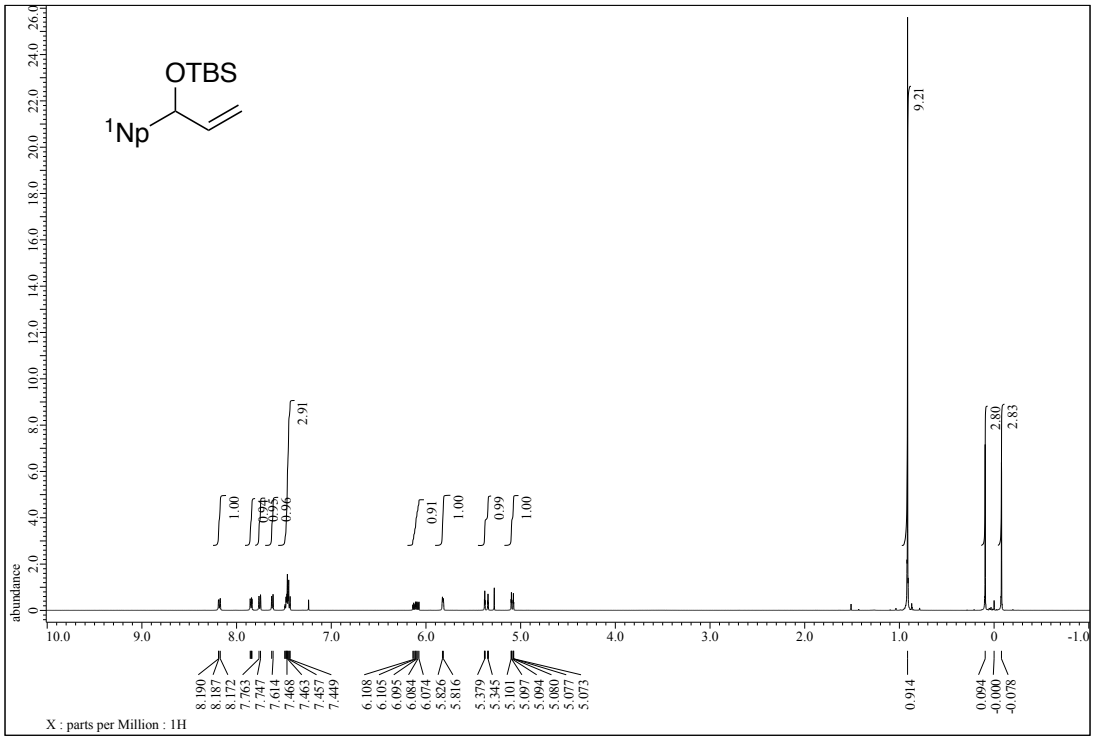
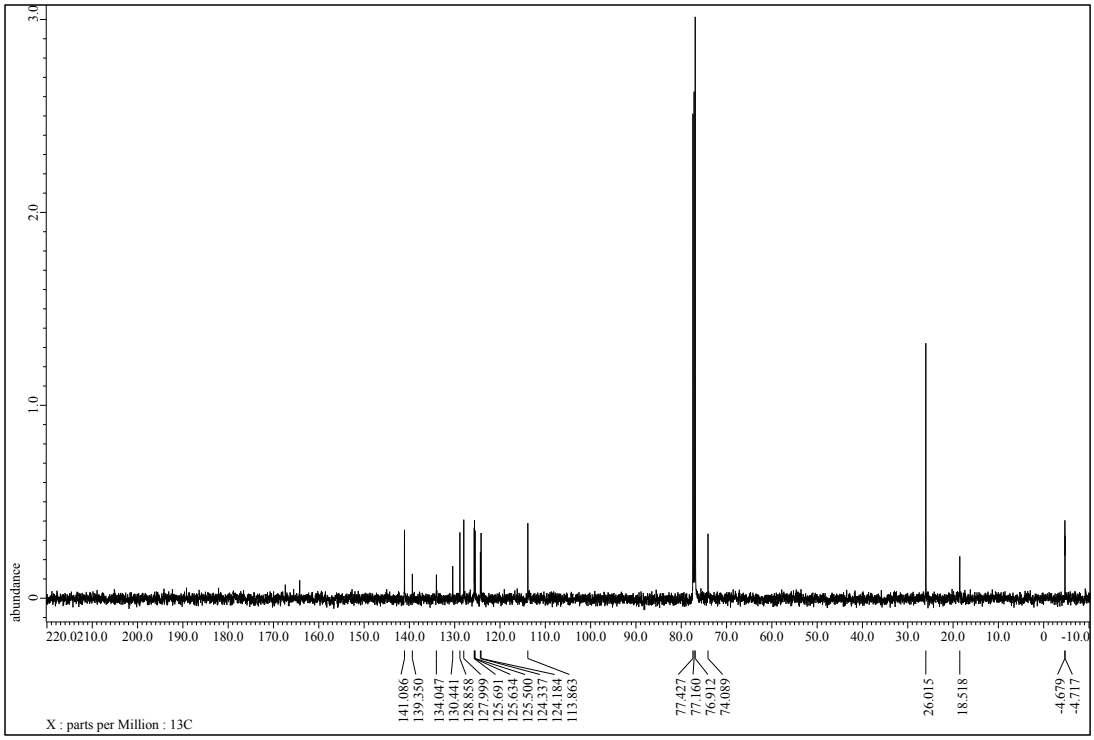
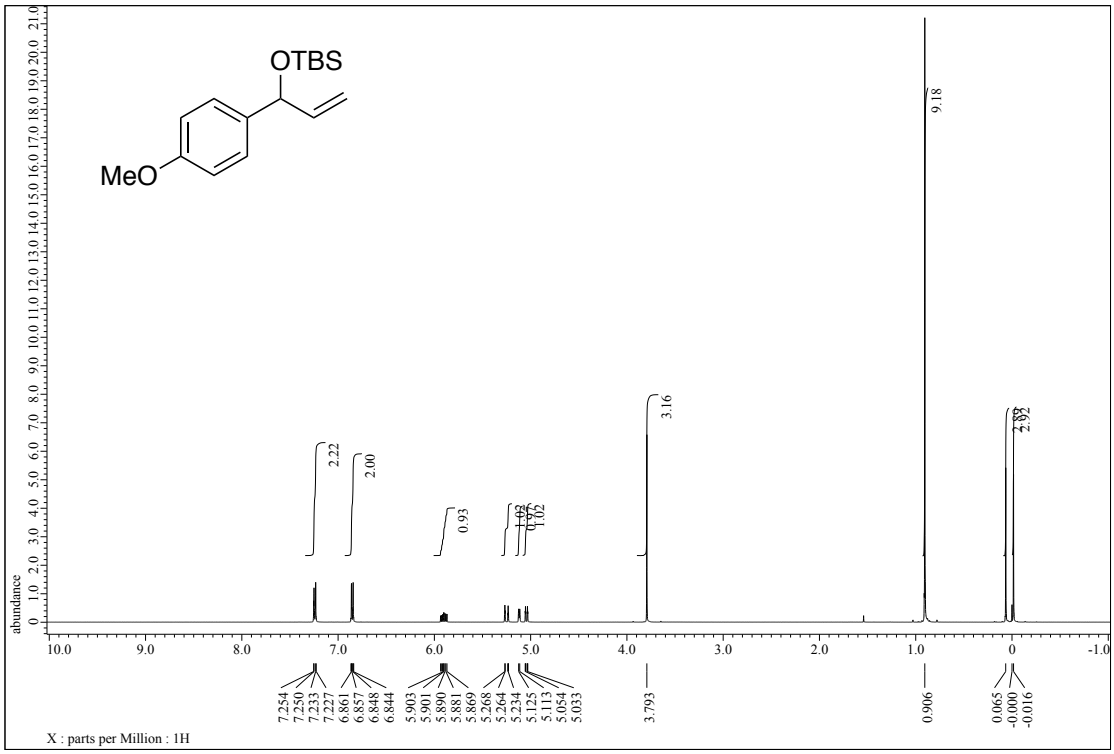
5. ^{1}H, ^{13}C, and ^{19}F NMR Spectra

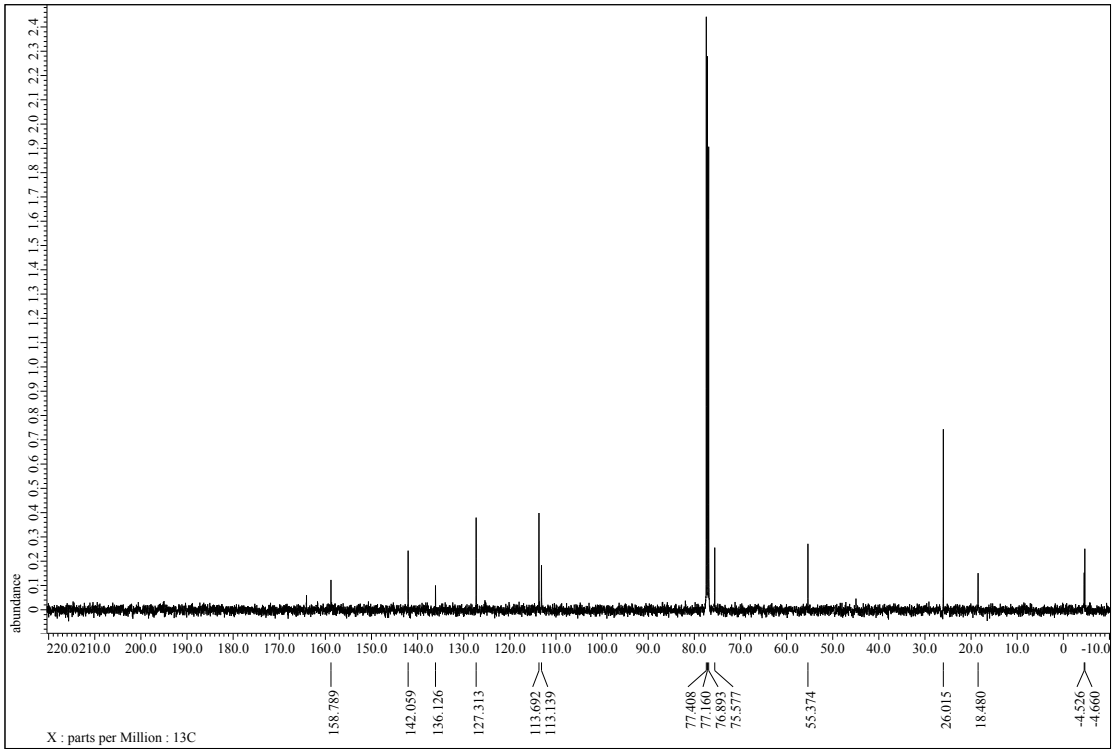
^{1}H and ^{13}C NMR spectra of **1c**



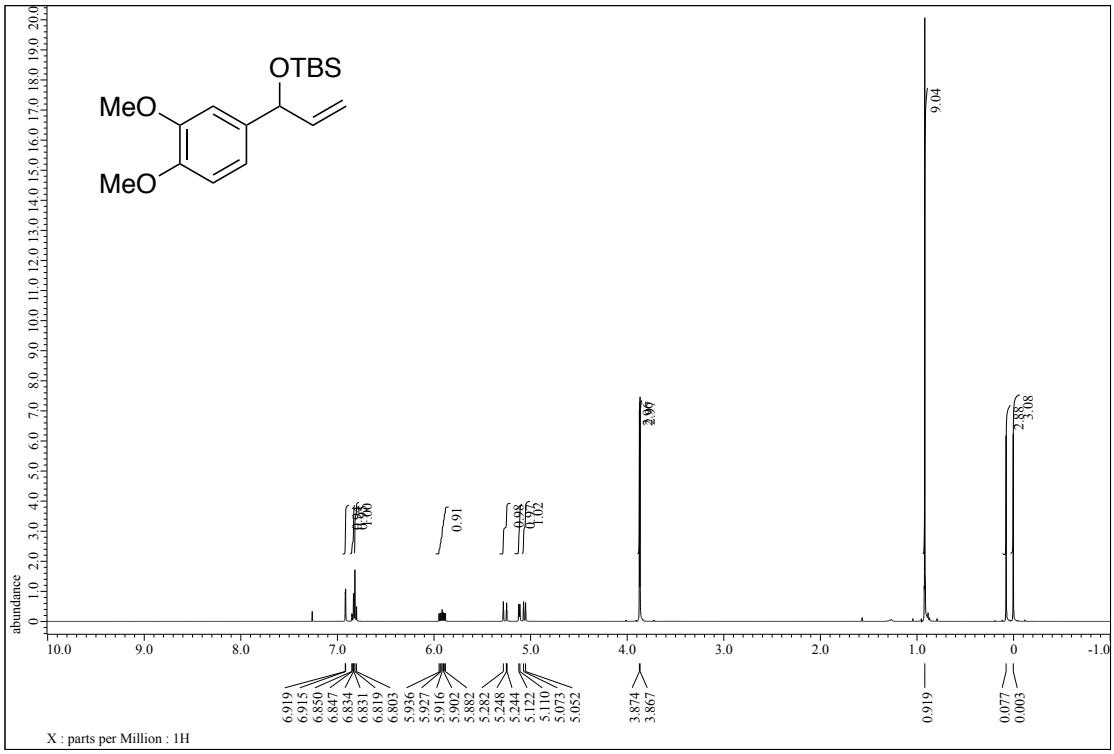


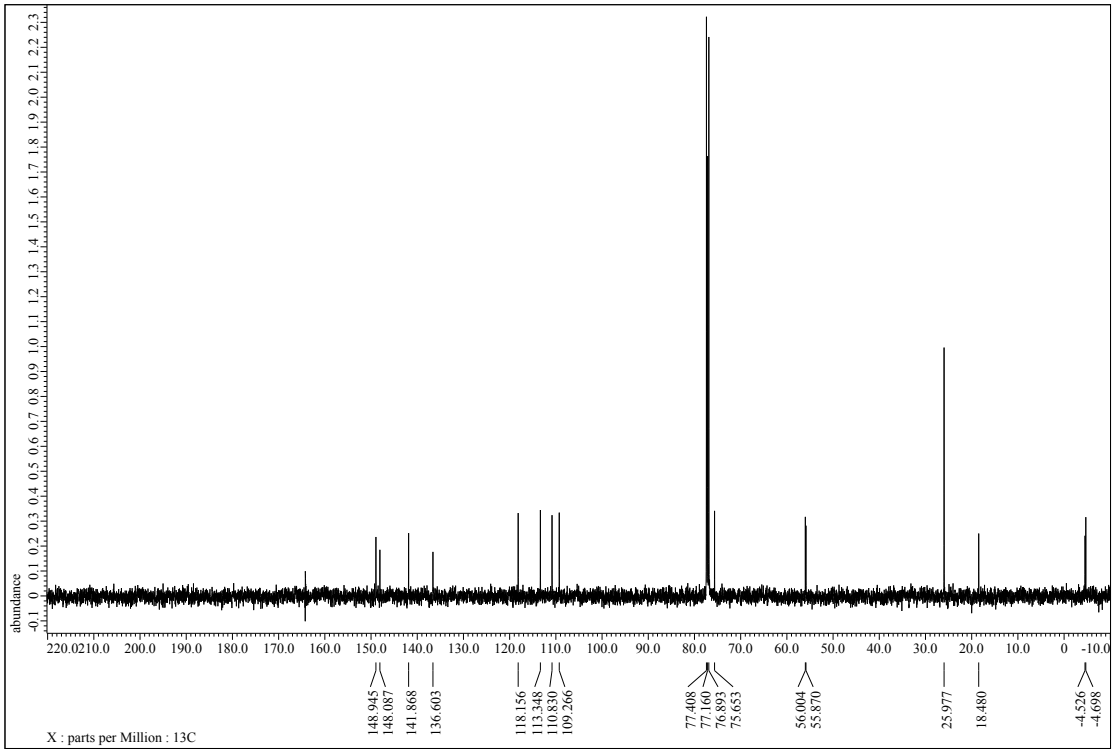
^{1}H and ^{13}C NMR spectra of **1d**



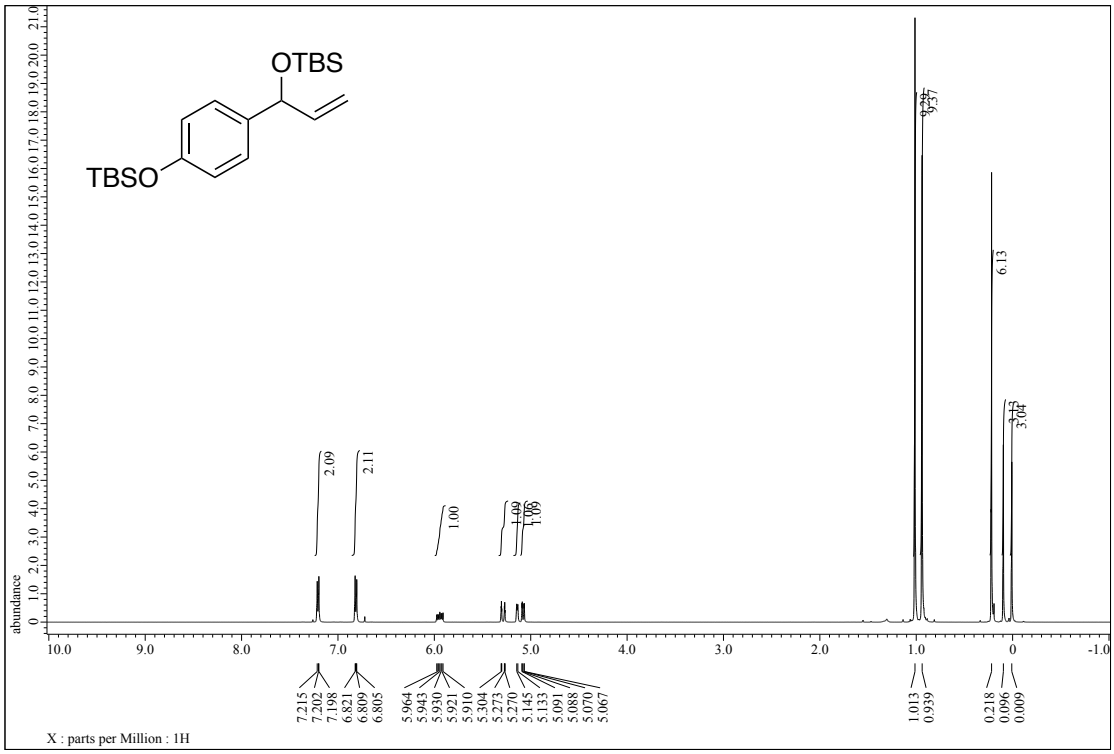


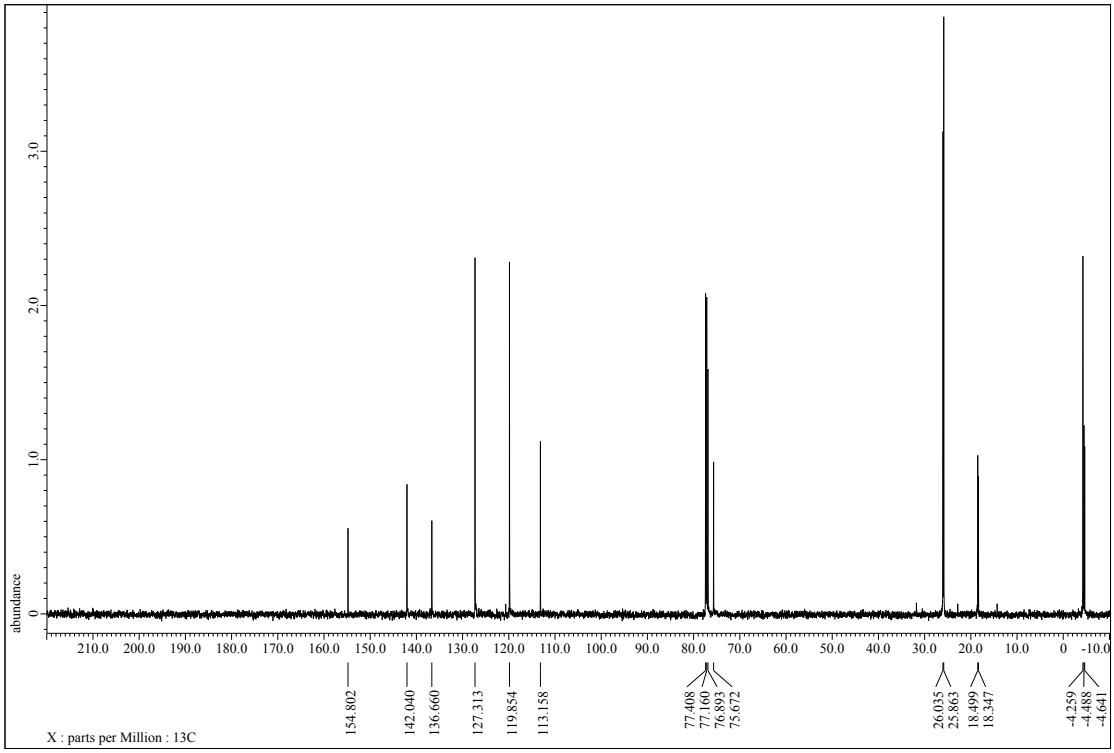
^{1}H and ^{13}C NMR spectra of **1e**



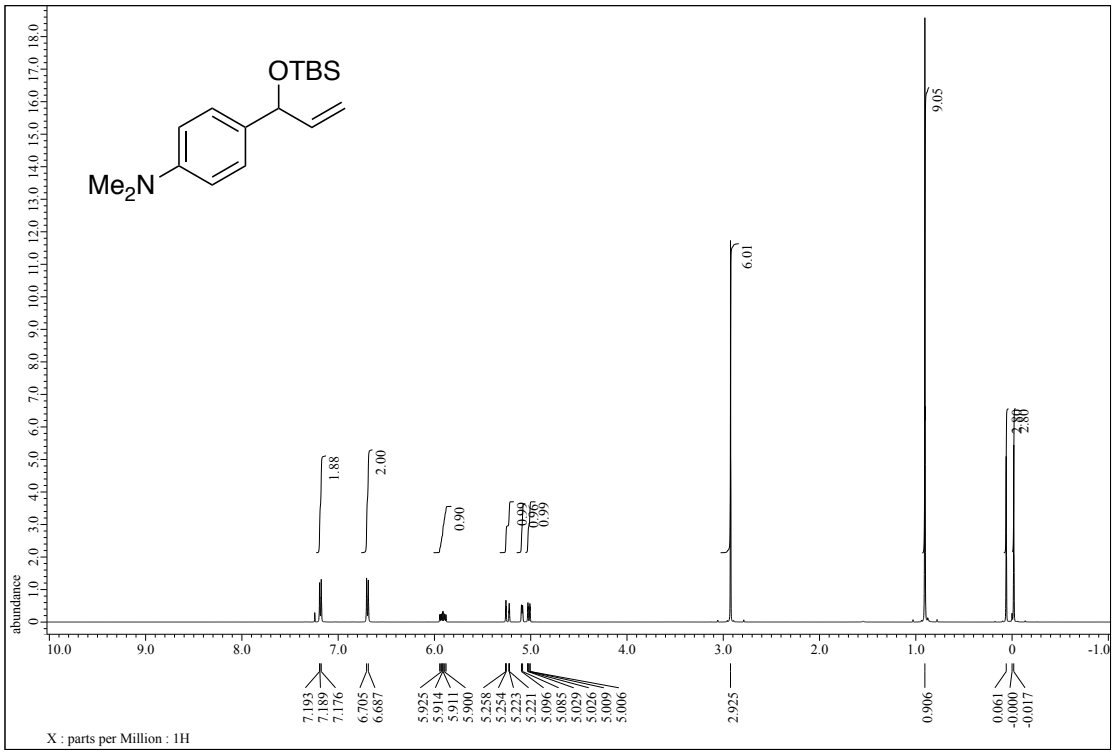


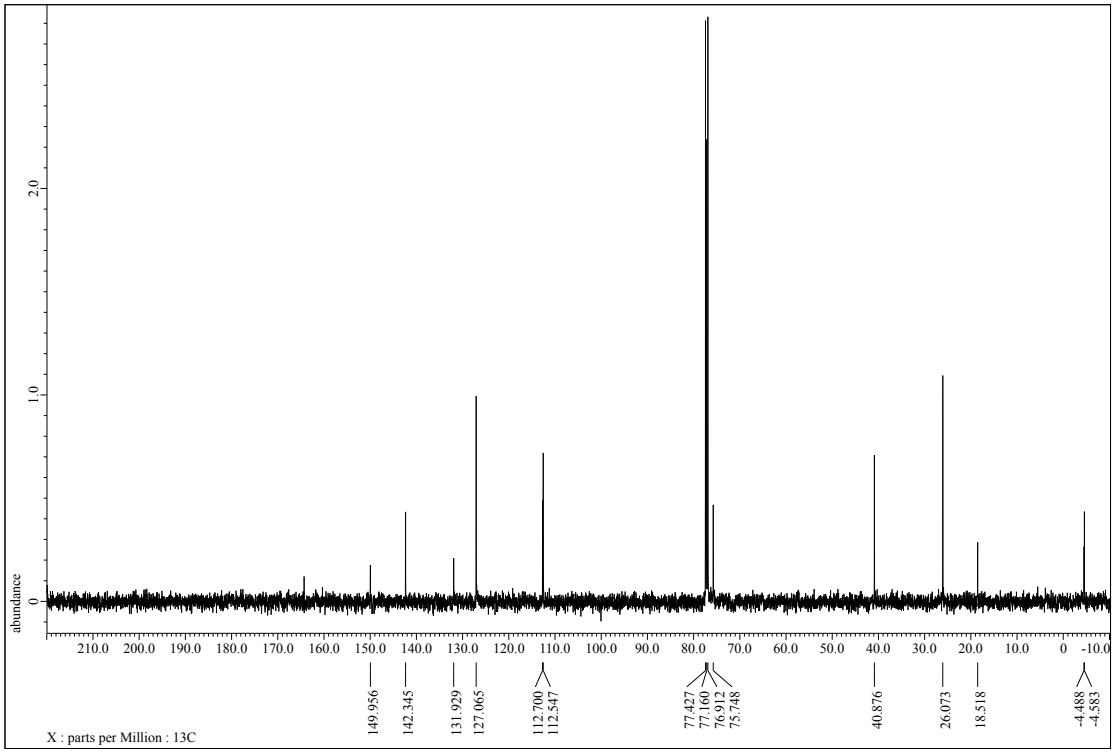
^{1}H and ^{13}C NMR spectra of **1f**



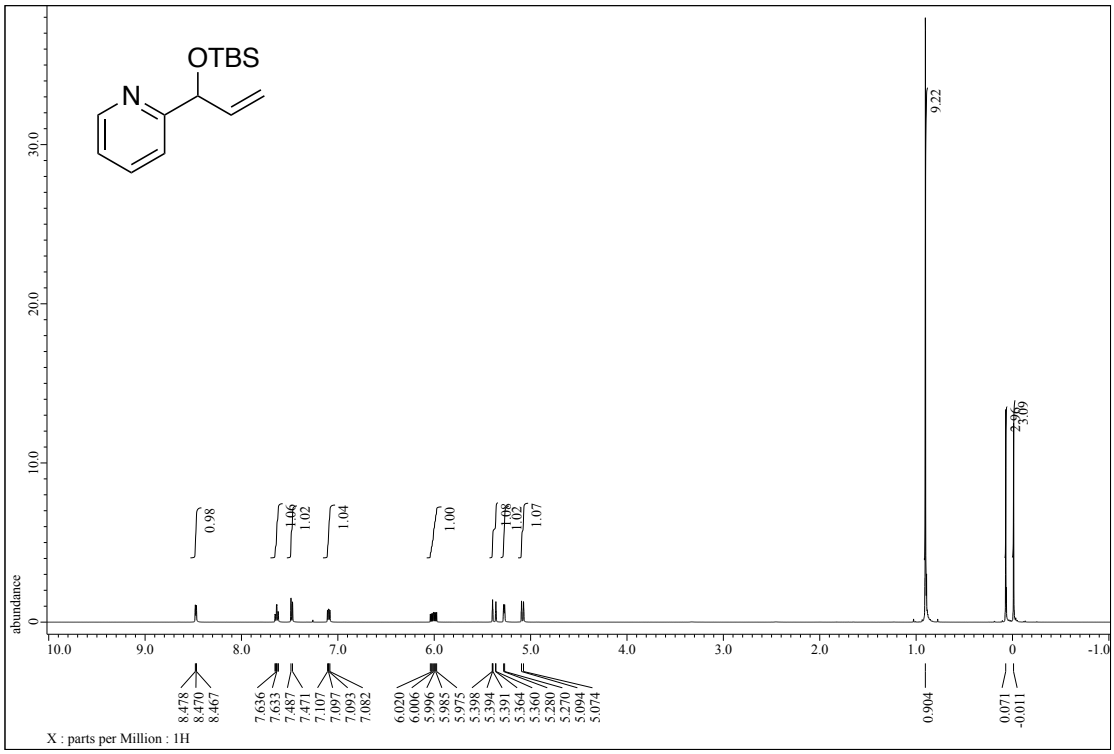


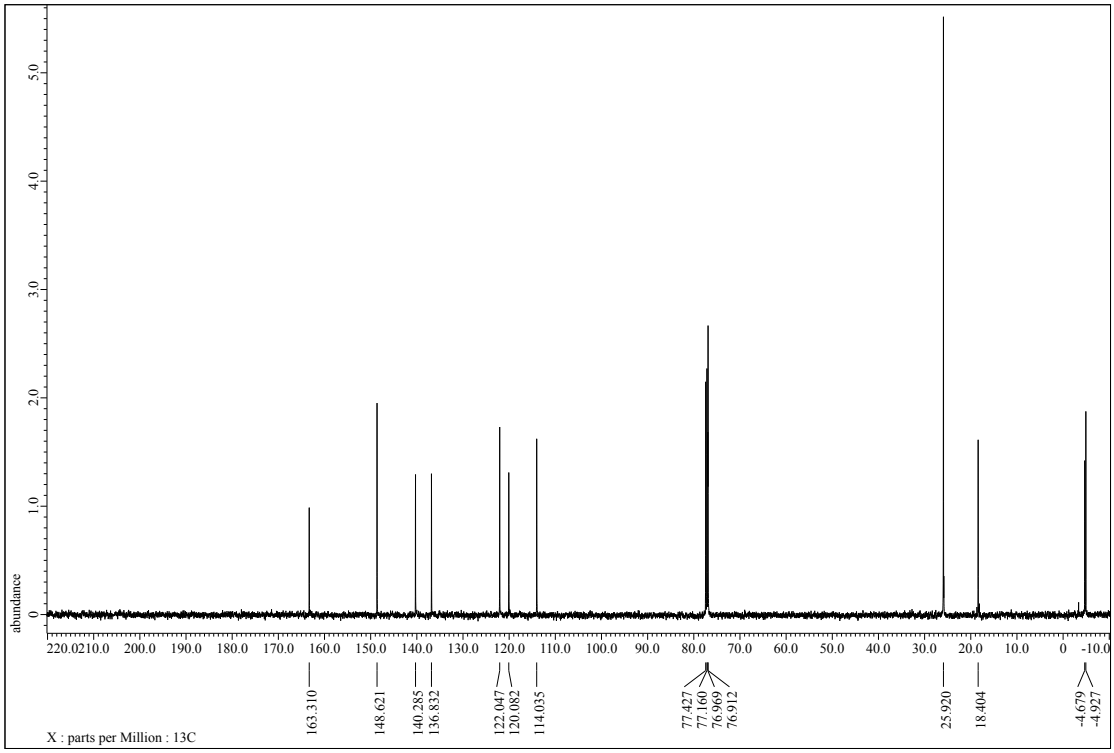
^{1}H and ^{13}C NMR spectra of **1g**



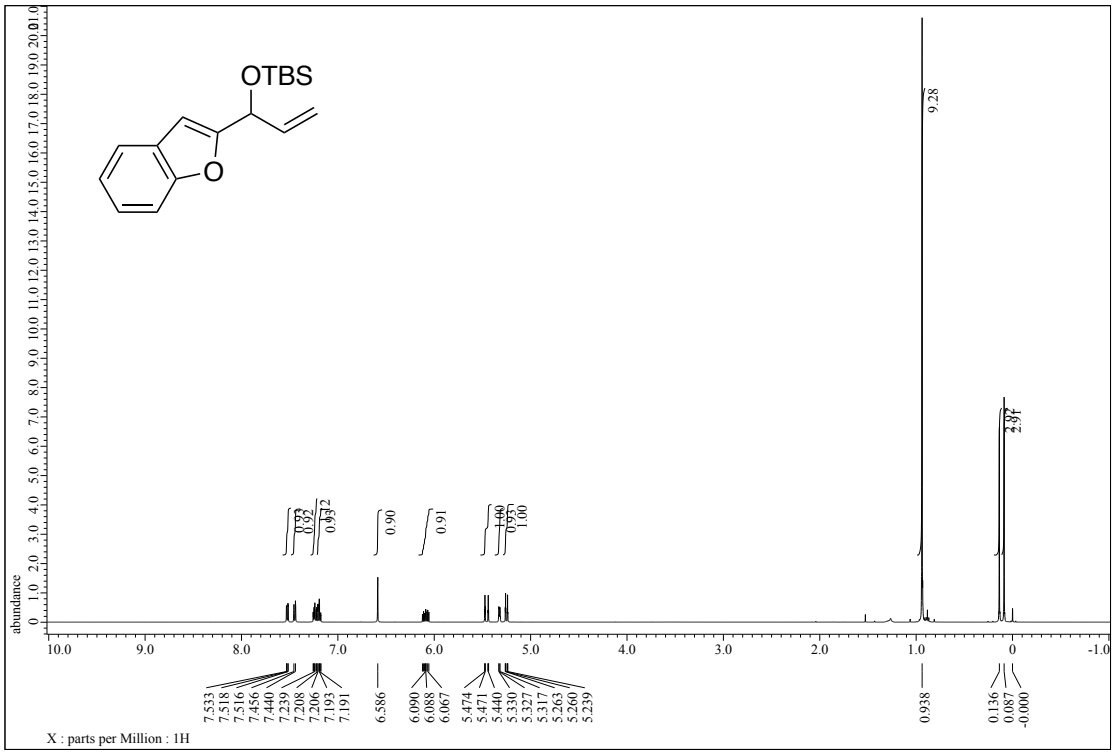


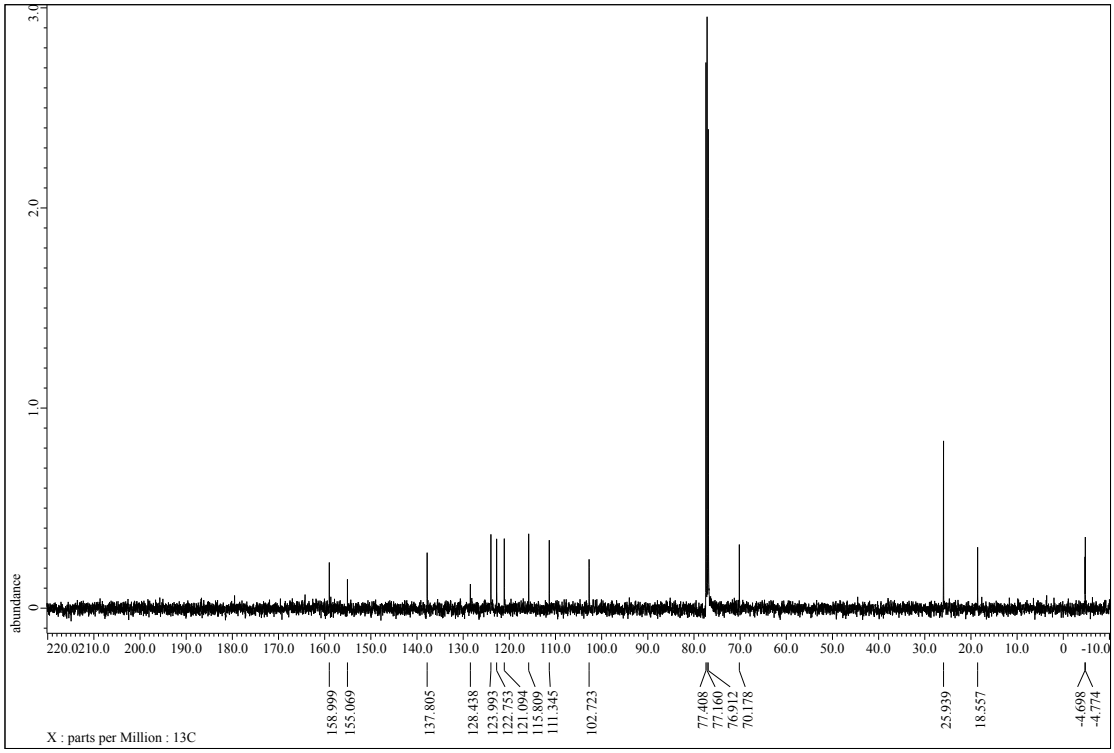
^{1}H and ^{13}C NMR spectra of **1h**



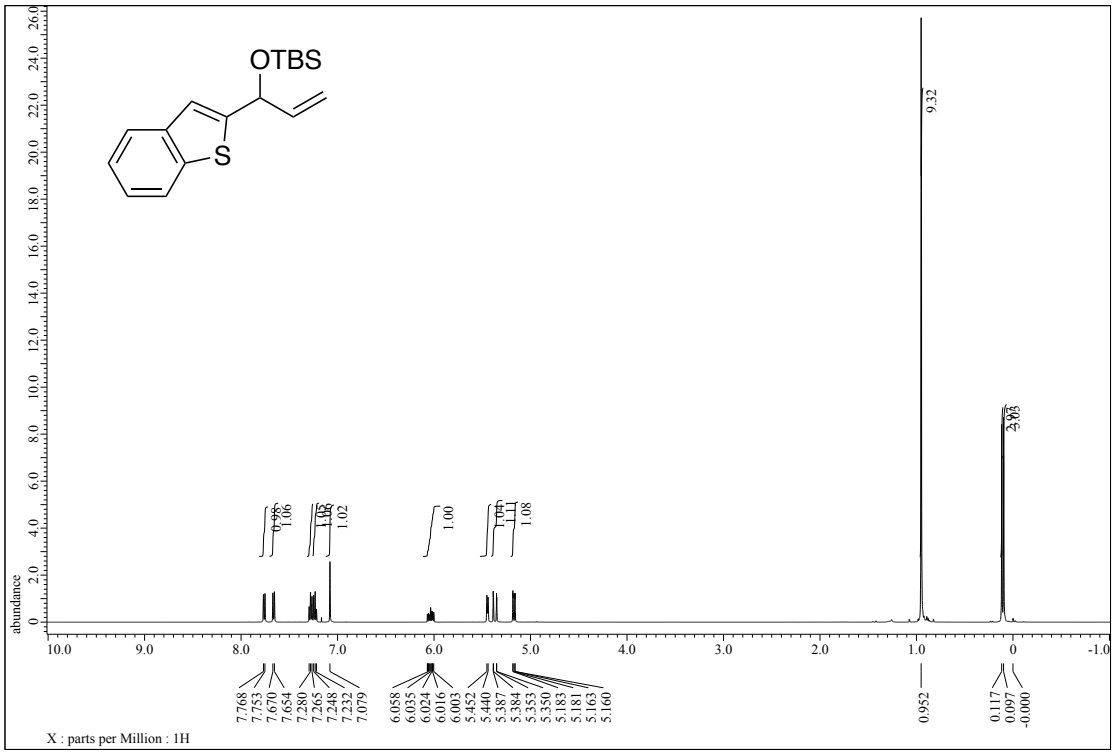


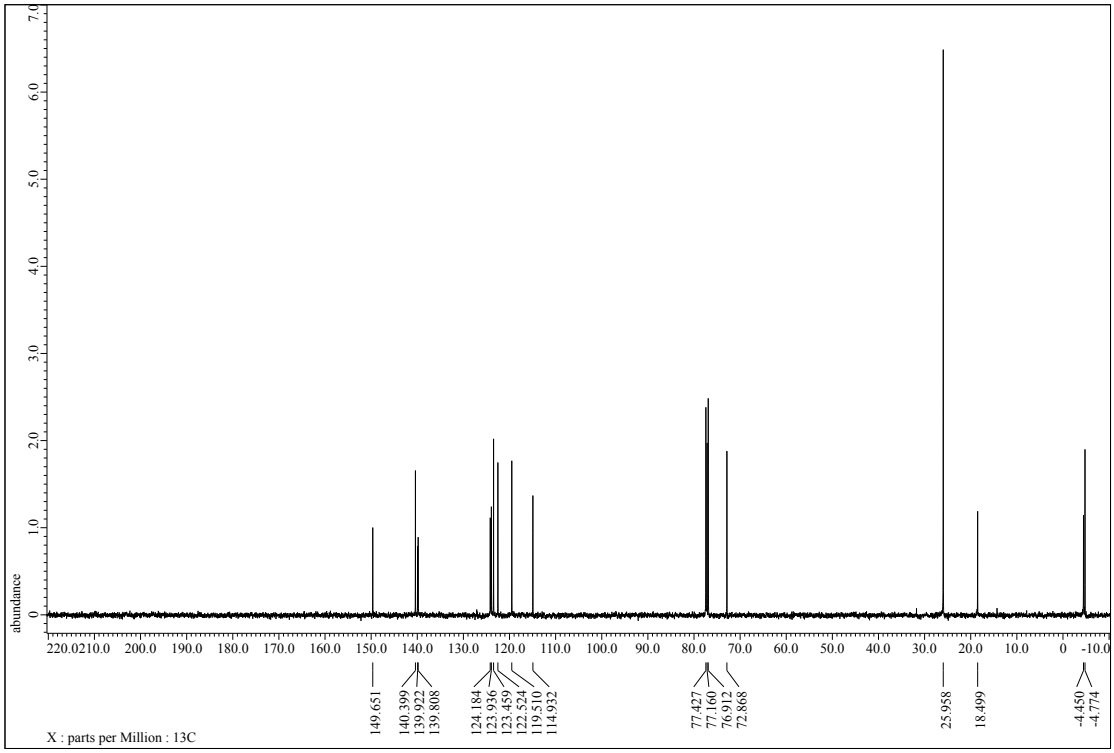
^{1}H and ^{13}C NMR spectra of **1i**



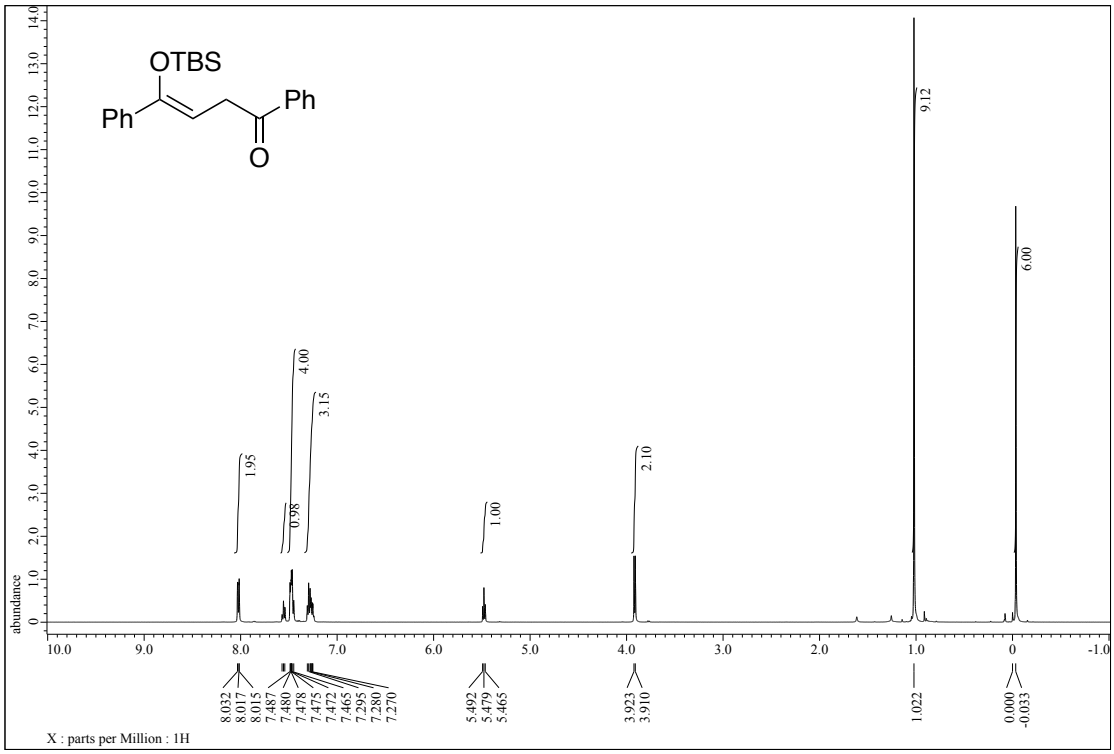


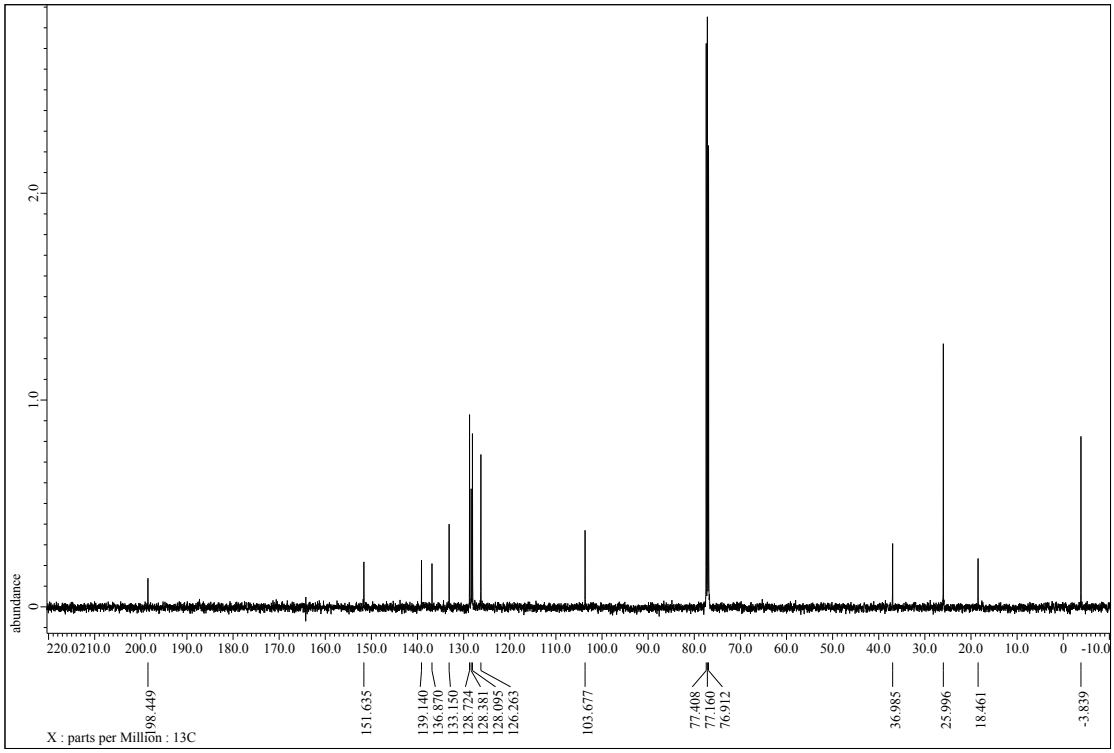
^{1}H and ^{13}C NMR spectra of **1j**



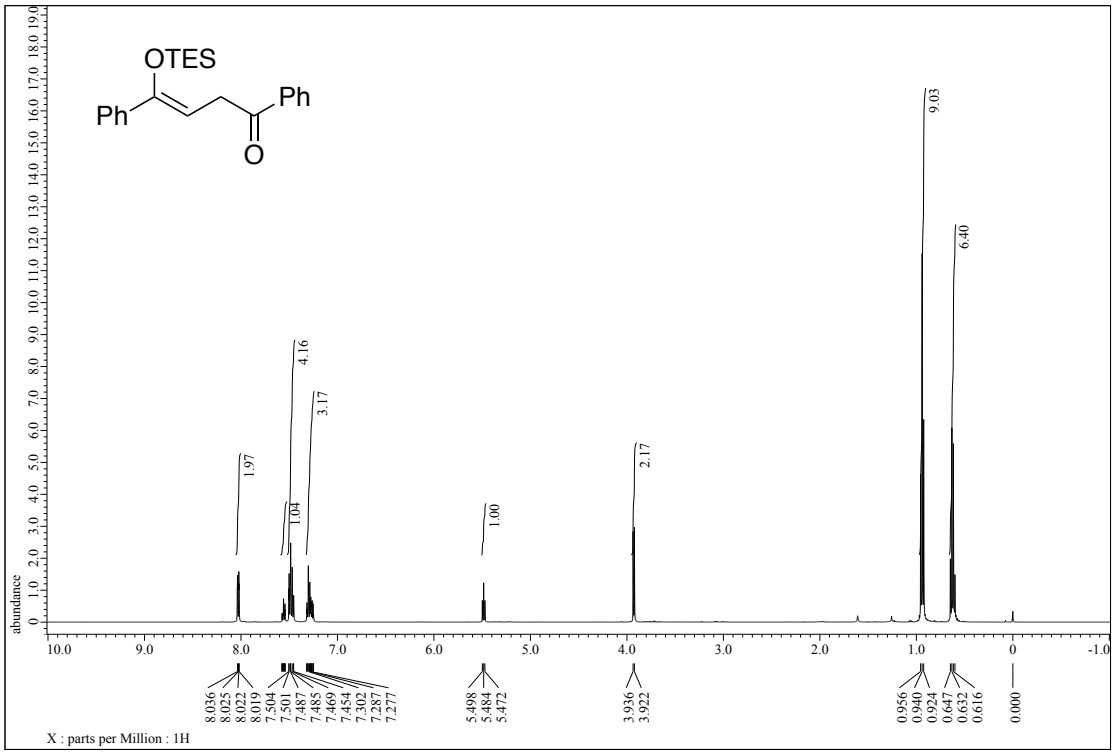


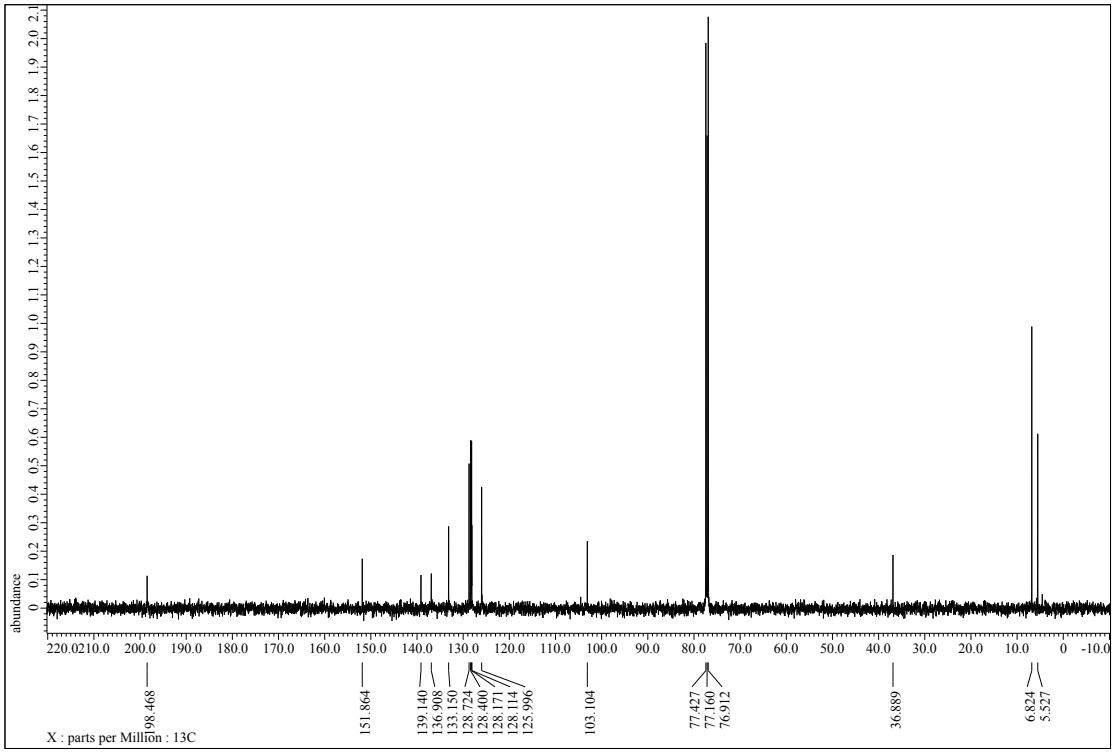
^{1}H and ^{13}C NMR spectra of **3aa**



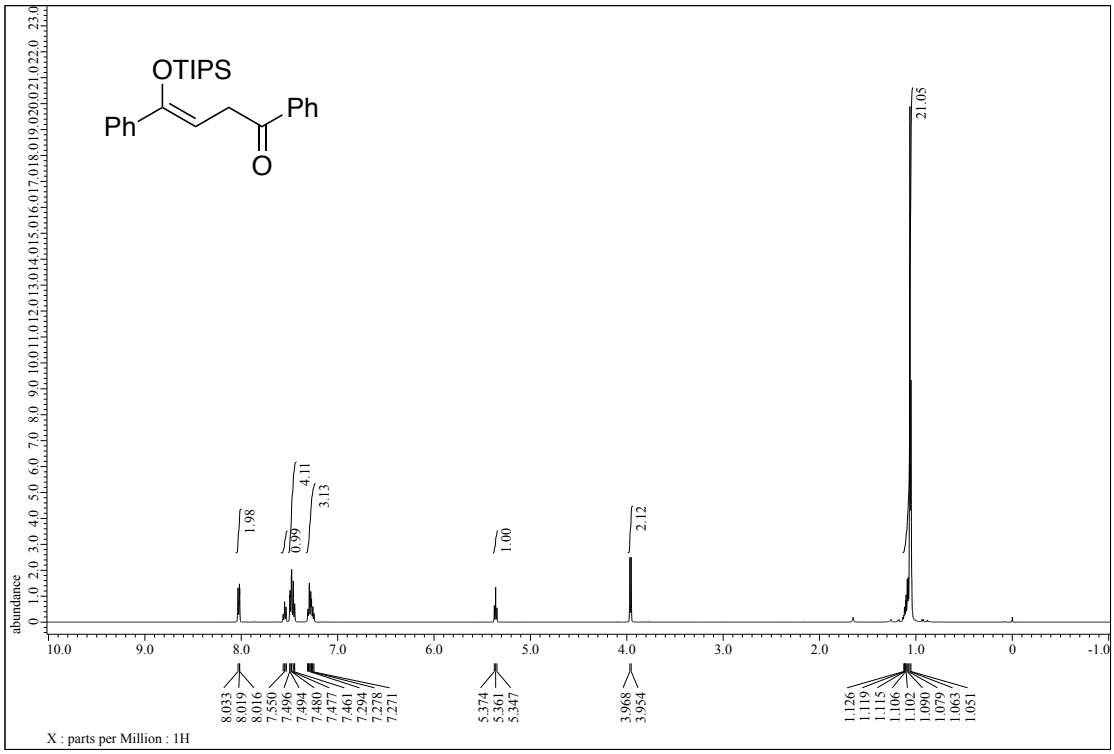


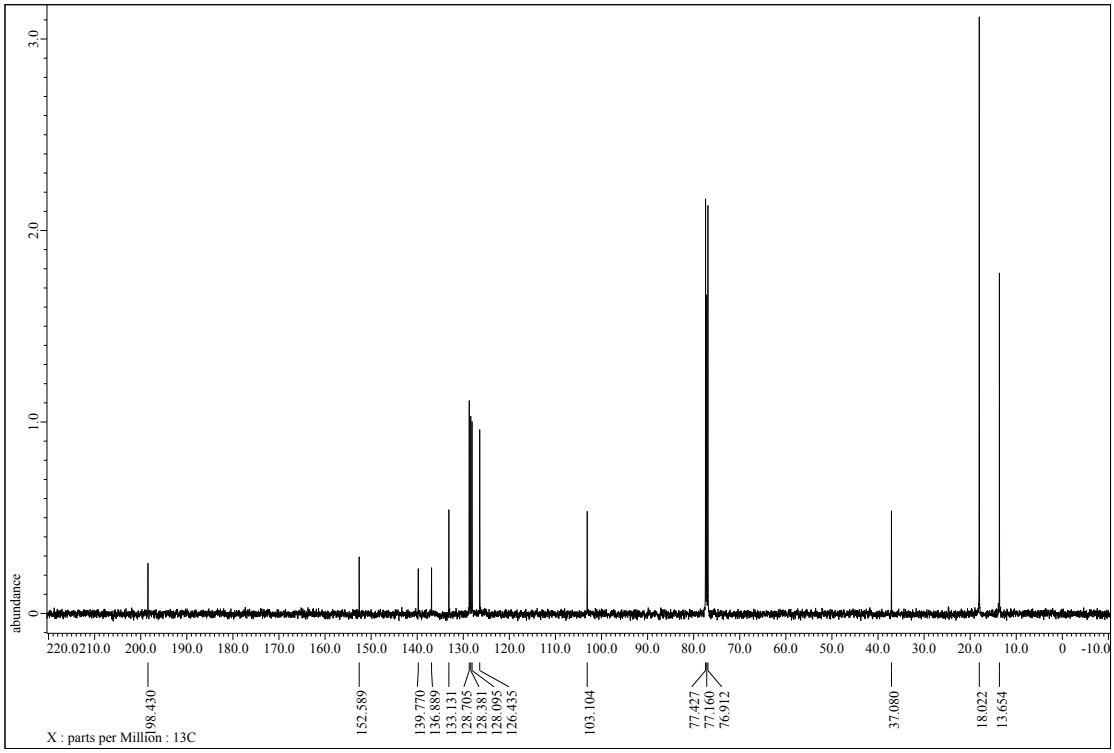
^{1}H and ^{13}C NMR spectra of **3aa'**



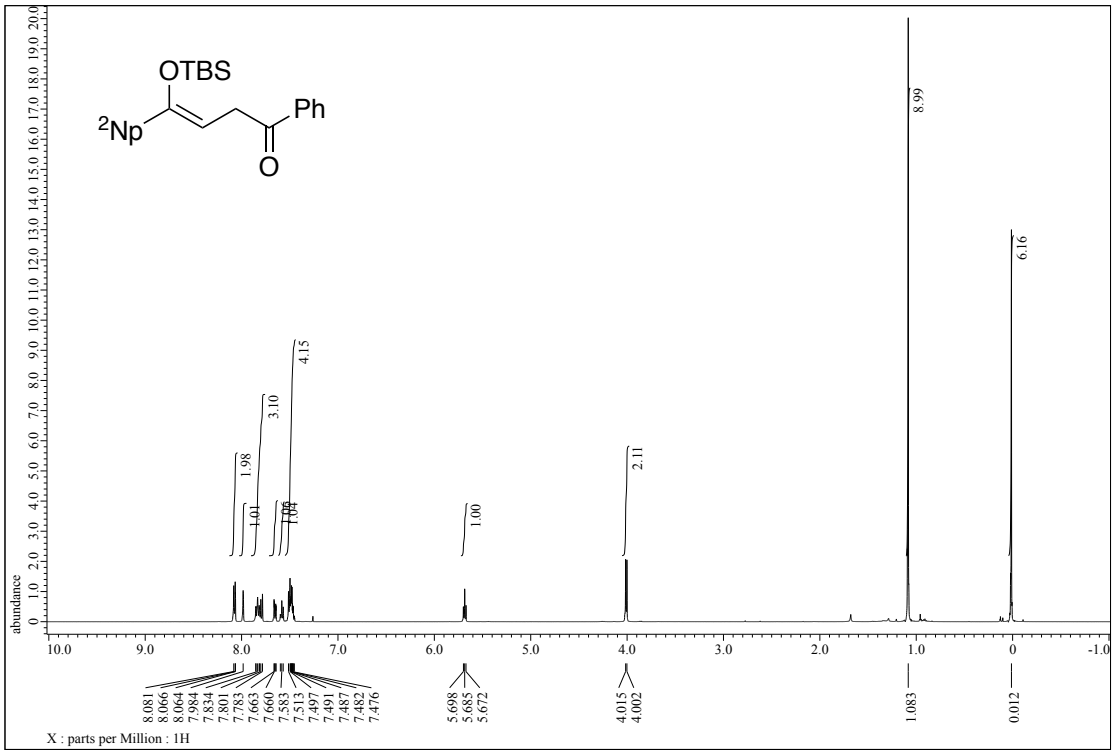


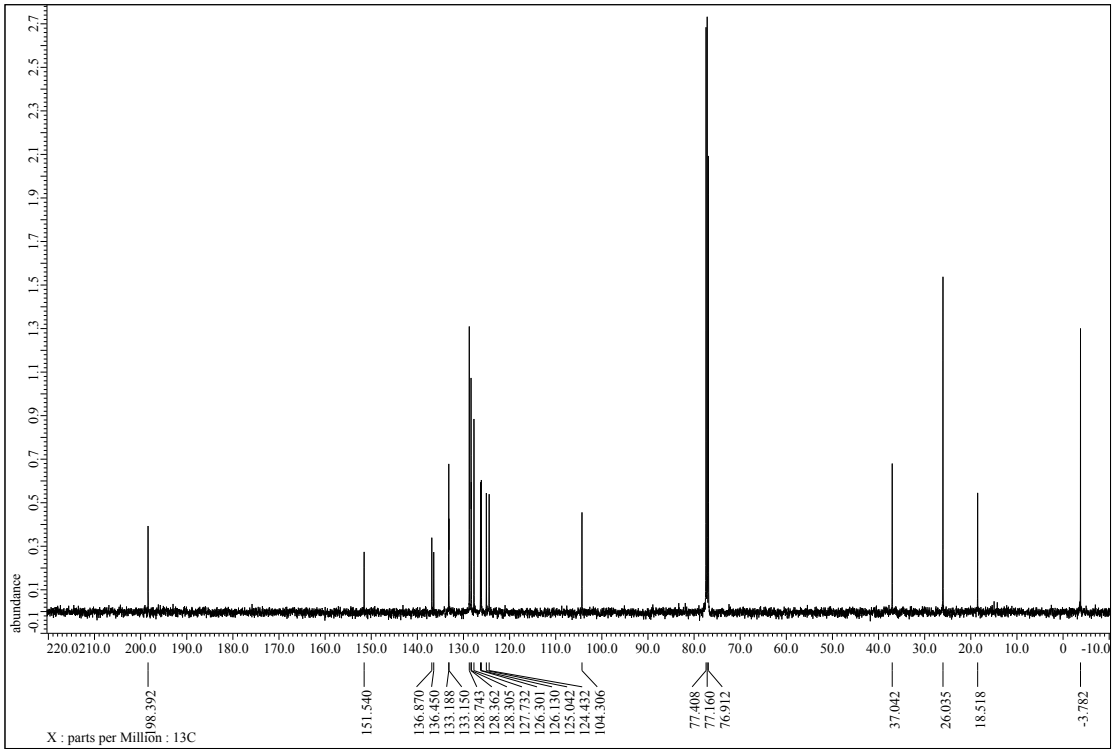
^{1}H and ^{13}C NMR spectra of **3aa"**



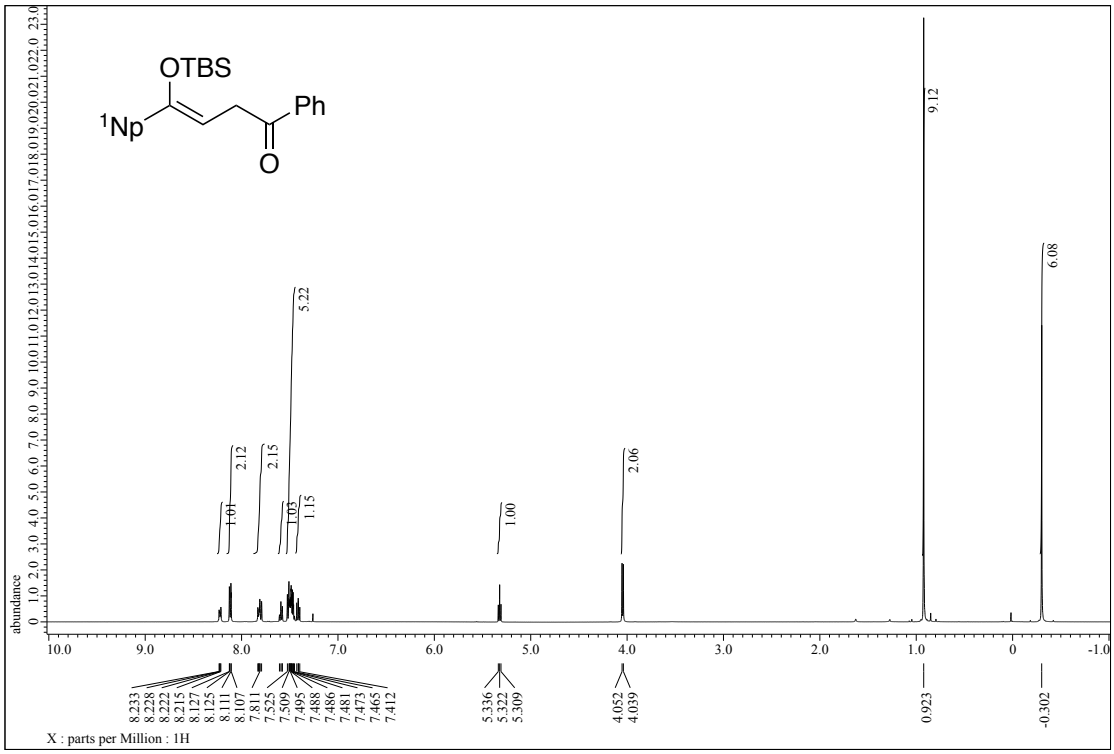


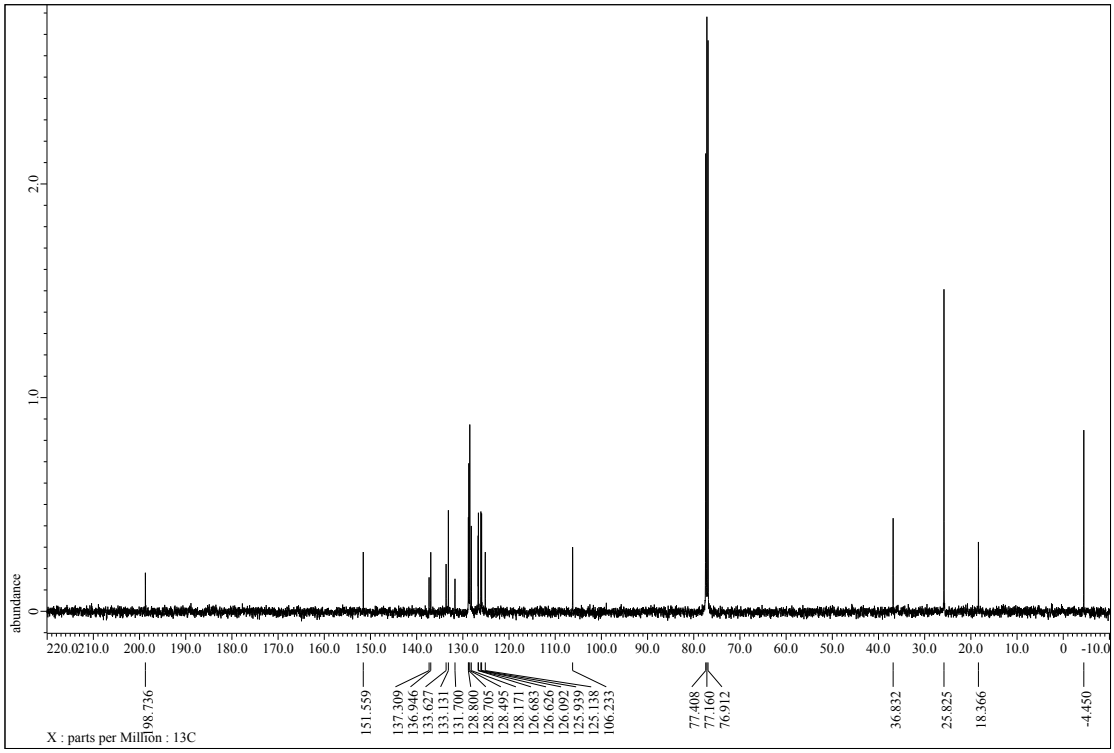
^{1}H and ^{13}C NMR spectra of **3ba**



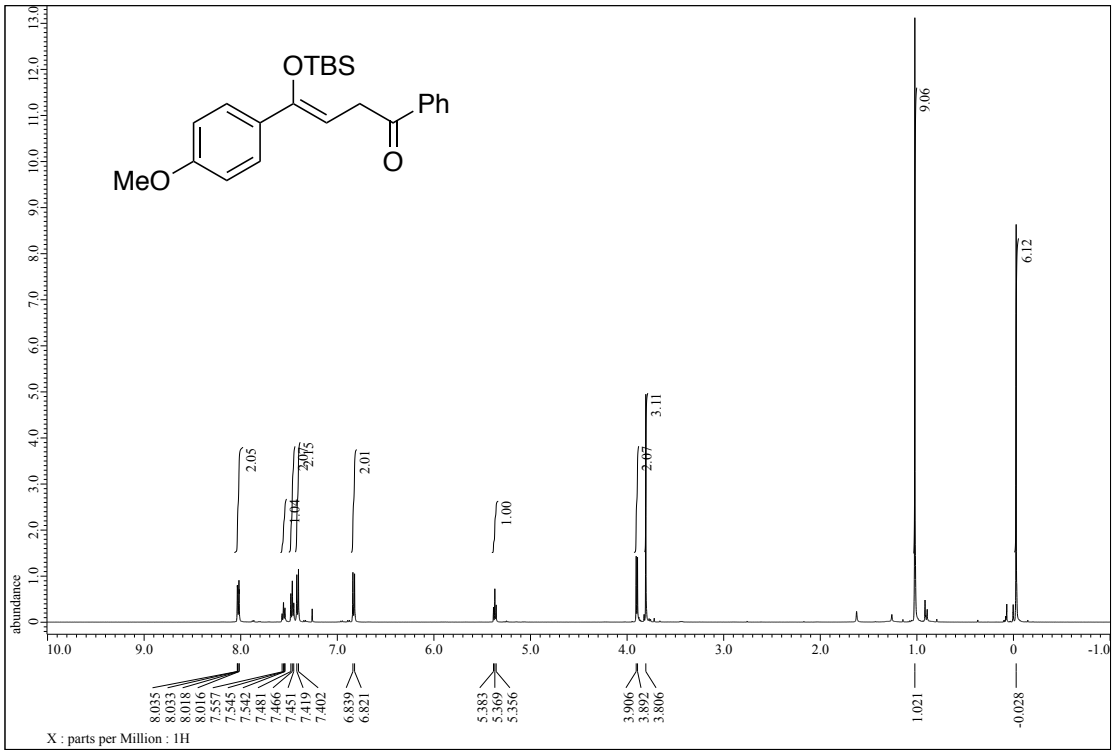


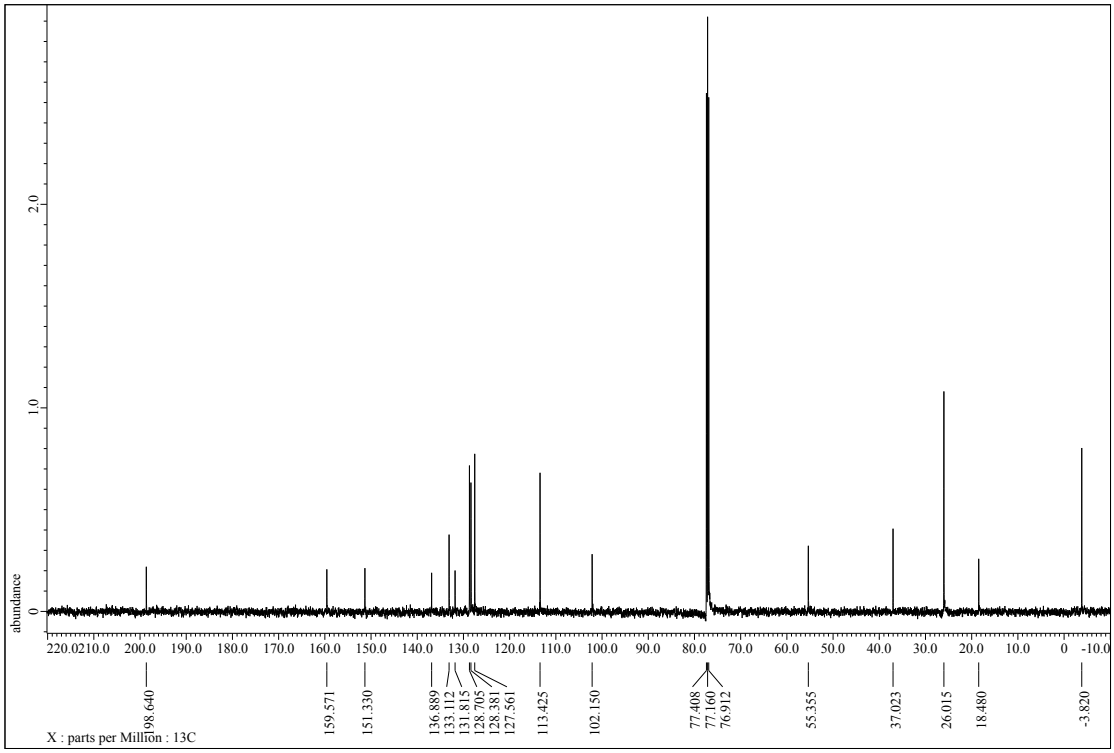
^{1}H and ^{13}C NMR spectra of **3ca**



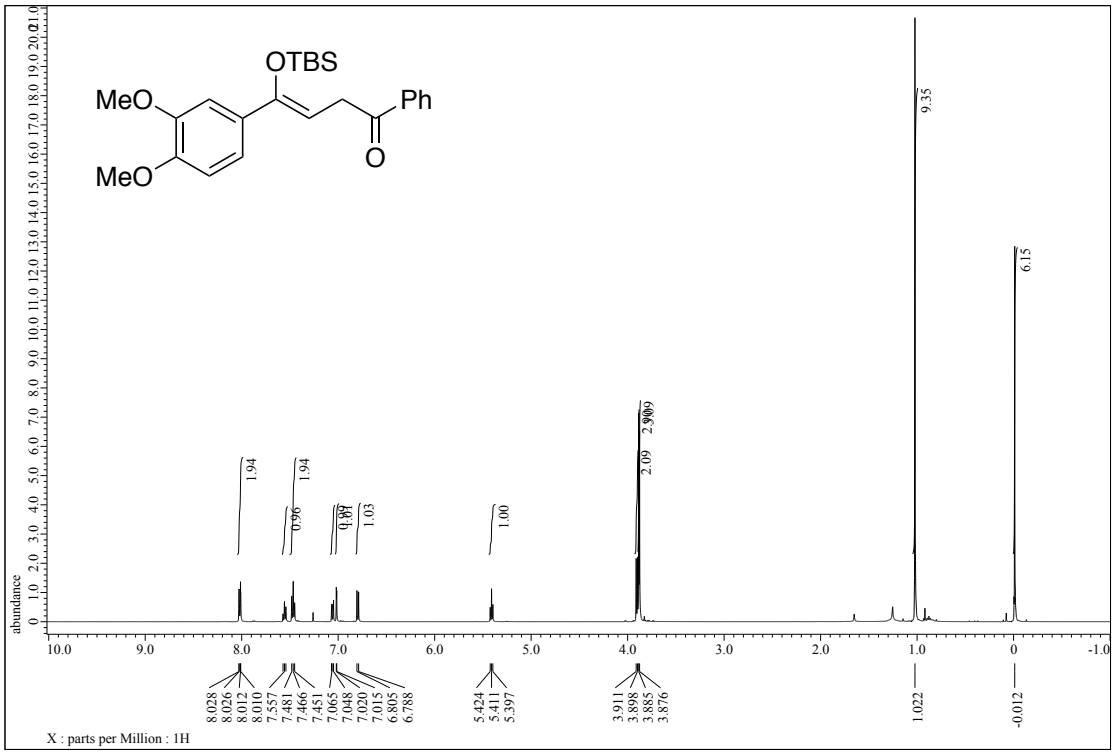


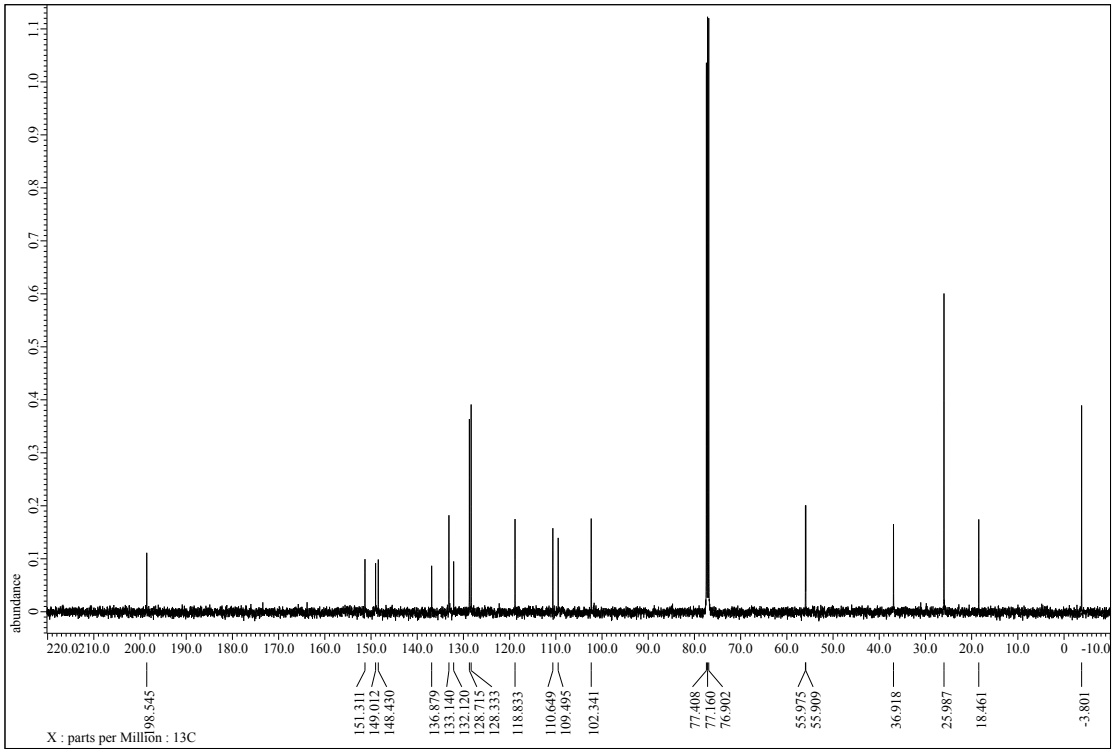
^{1}H and ^{13}C NMR spectra of **3da**



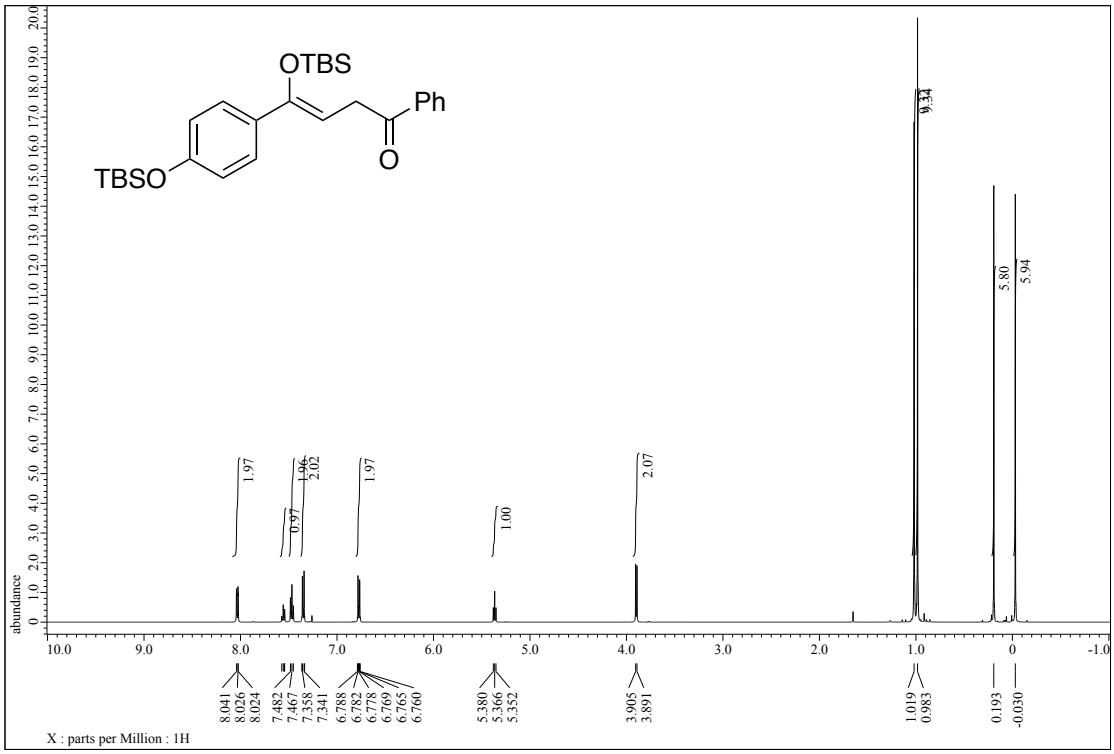


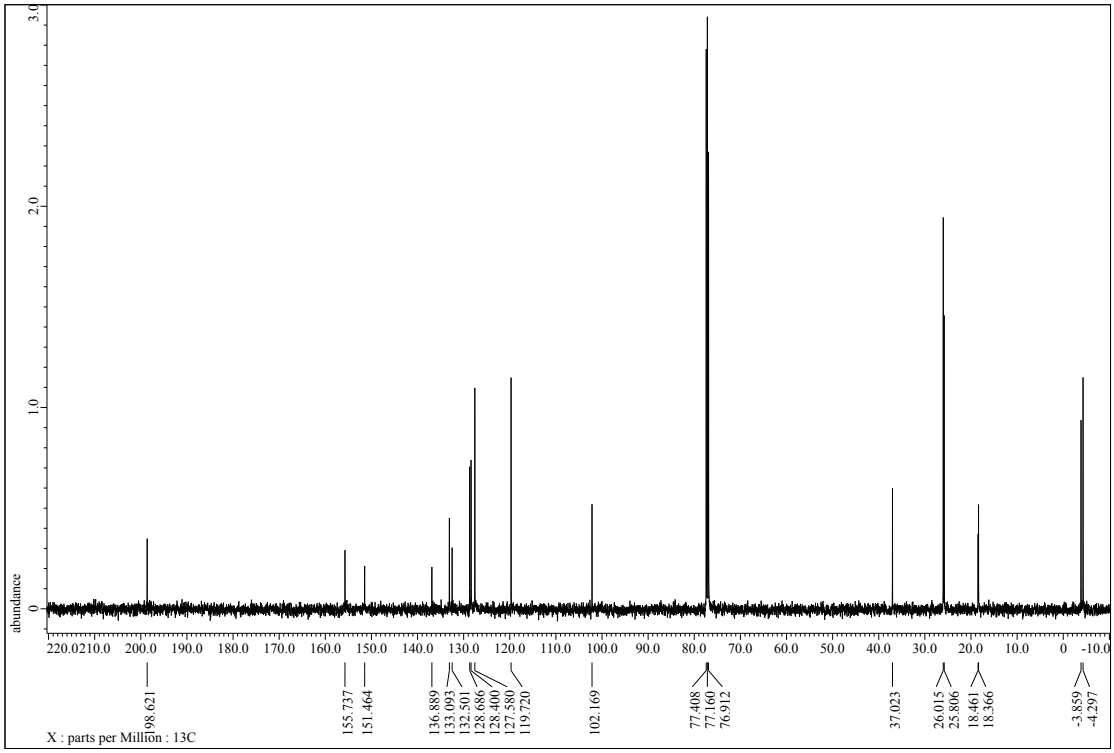
^{1}H and ^{13}C NMR spectra of **3ea**



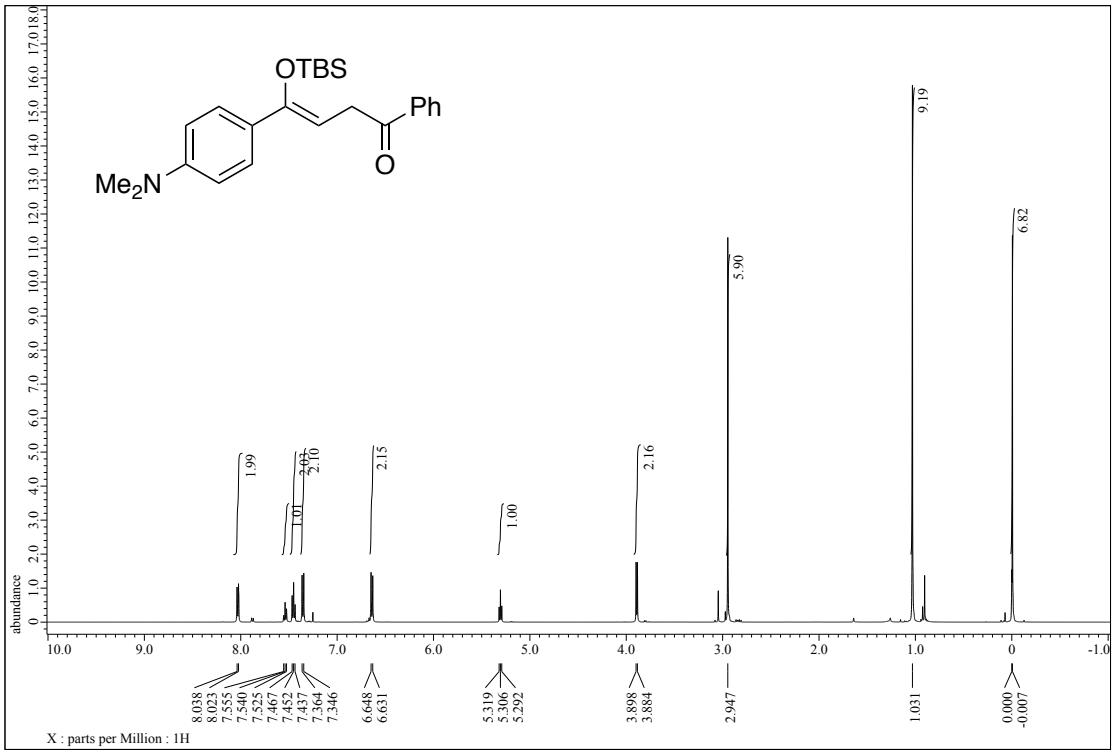


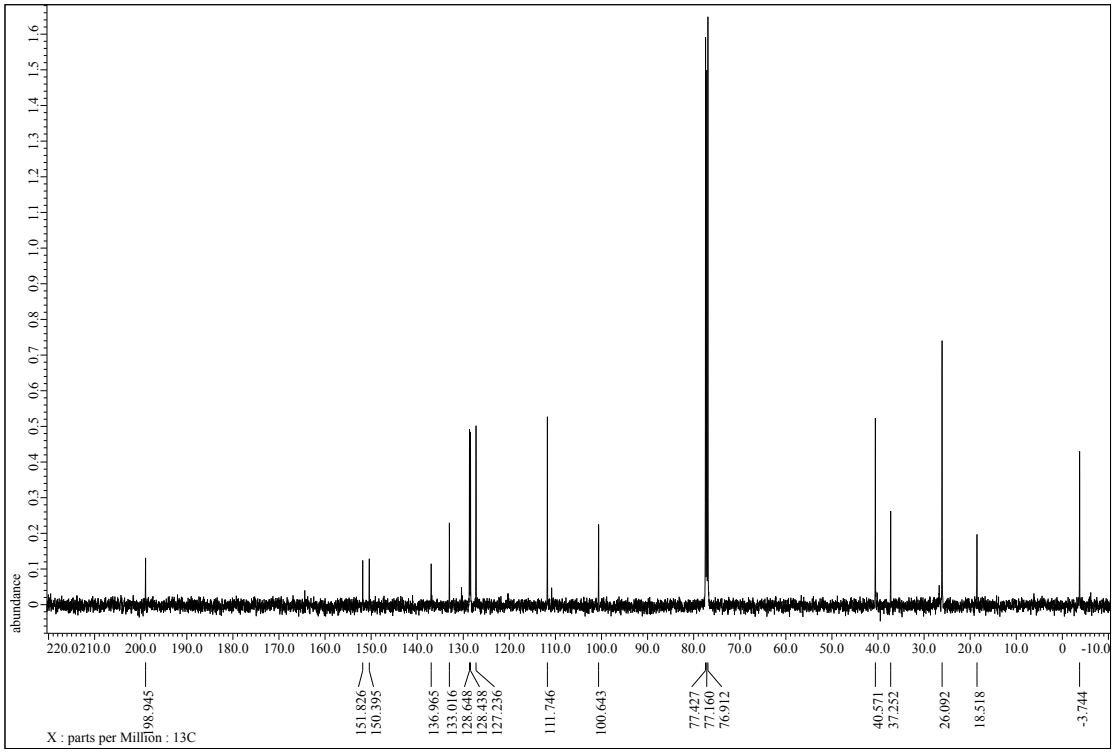
^{1}H and ^{13}C NMR spectra of **3fa**



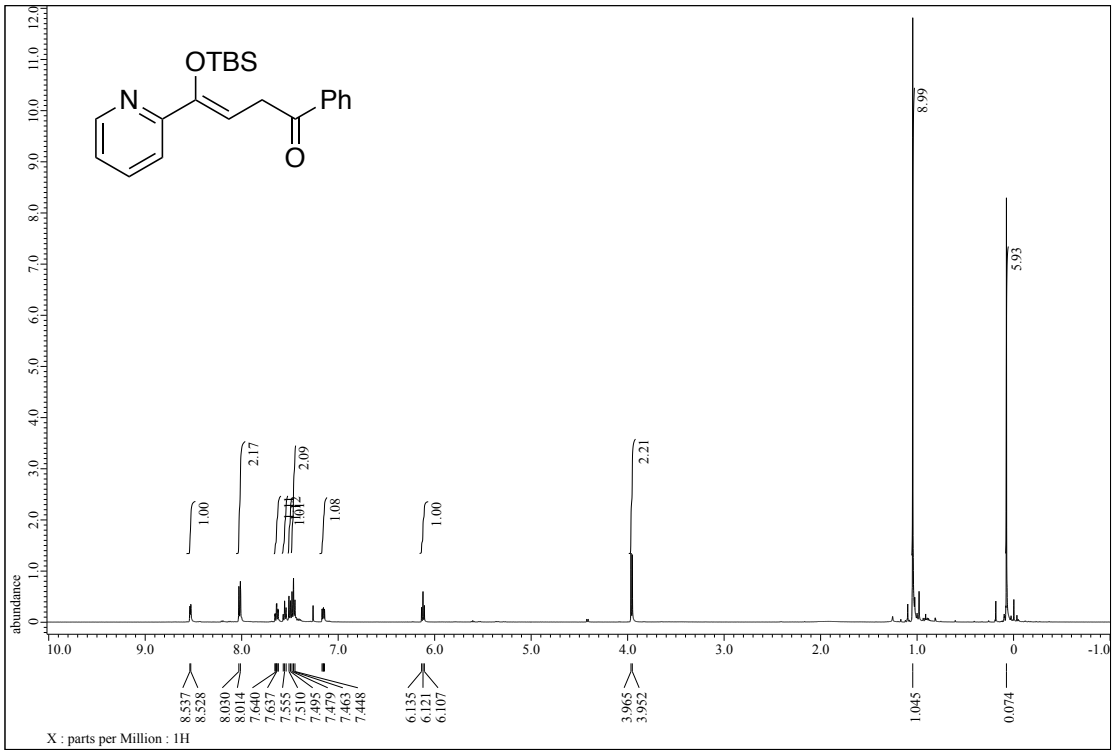


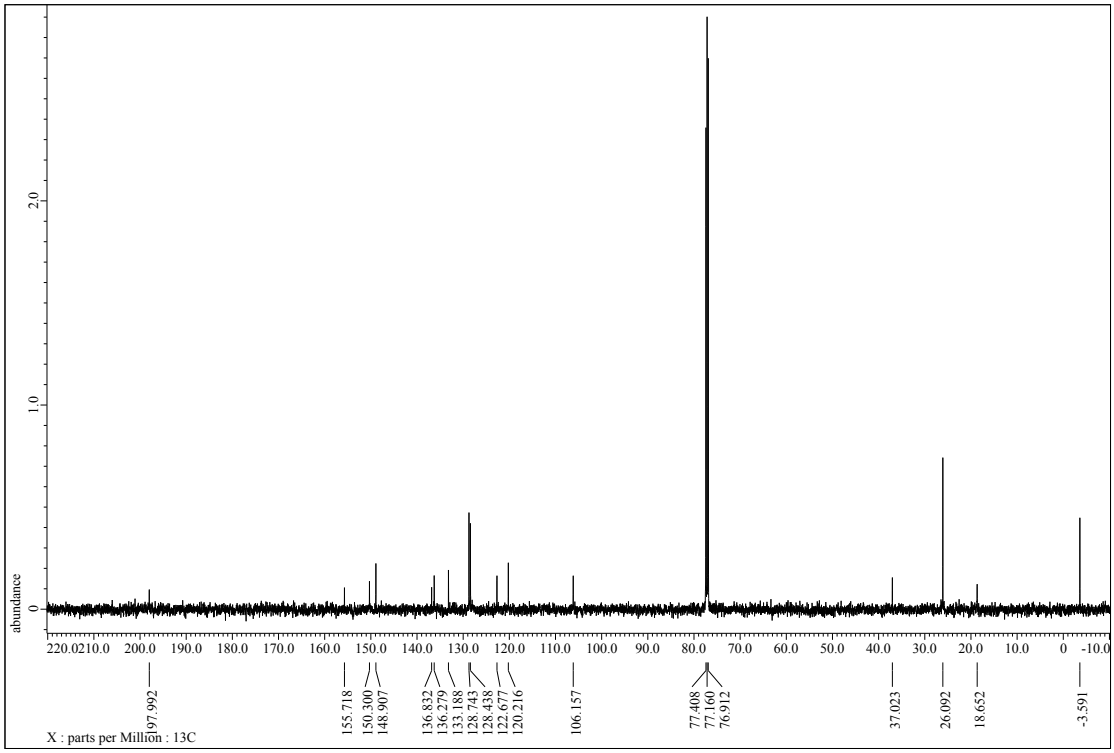
^{1}H and ^{13}C NMR spectra of **3ga**



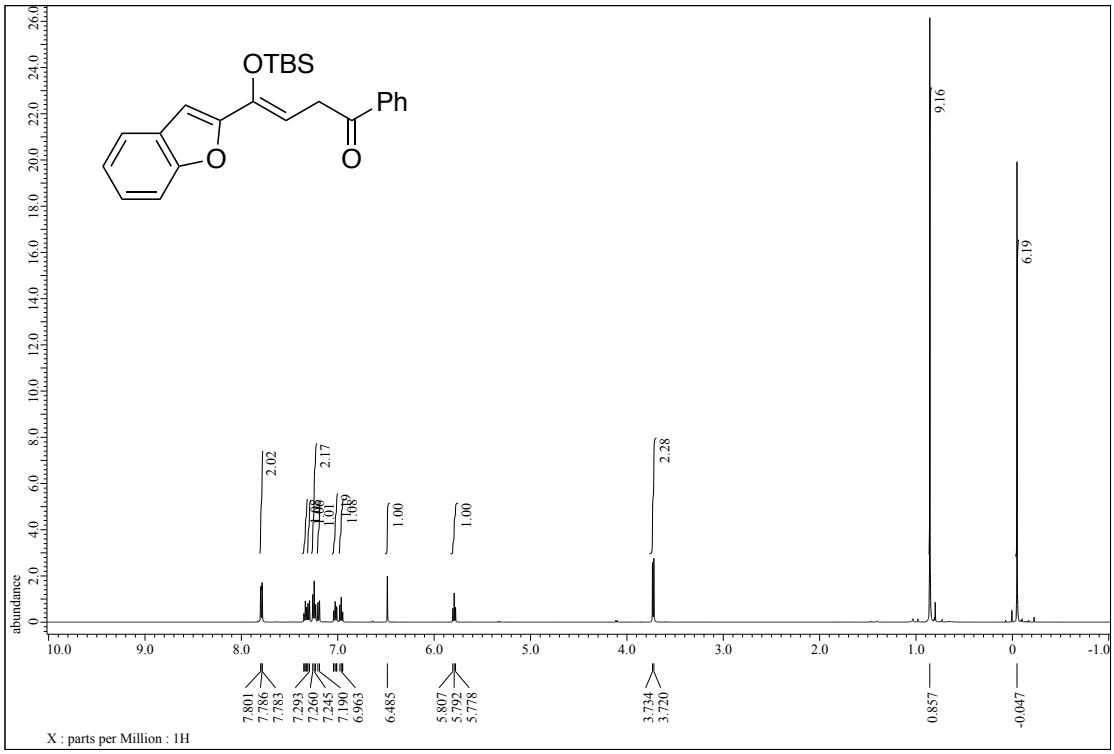


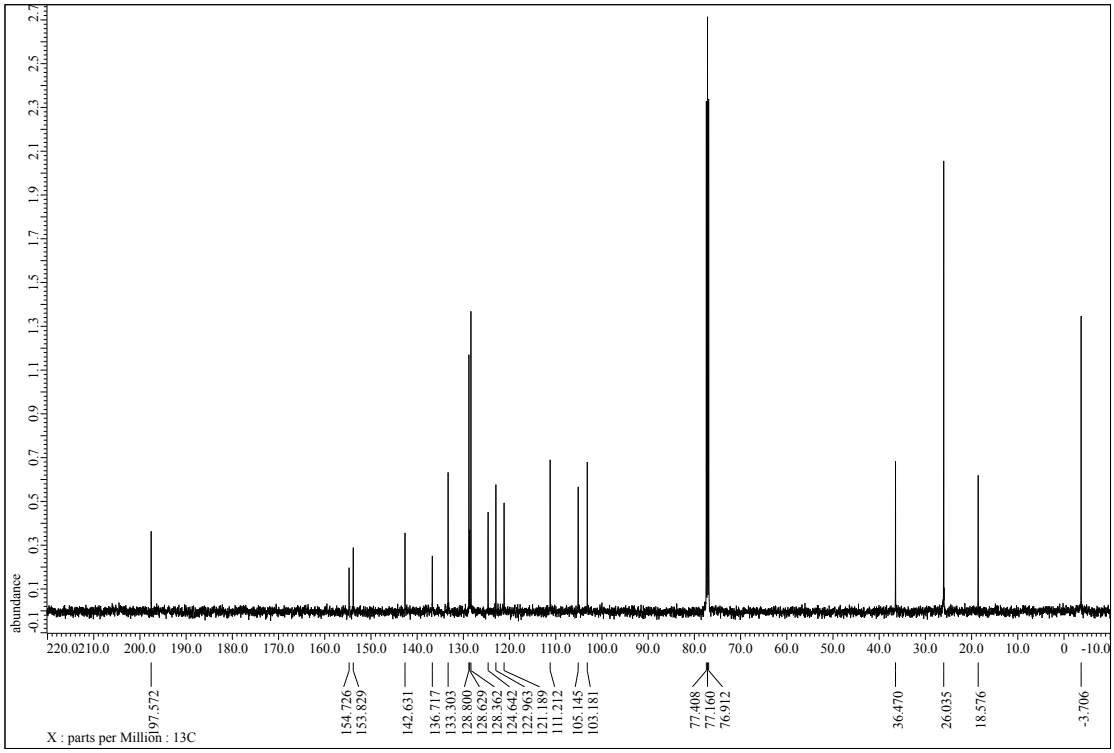
^{1}H and ^{13}C NMR spectra of **3ha**



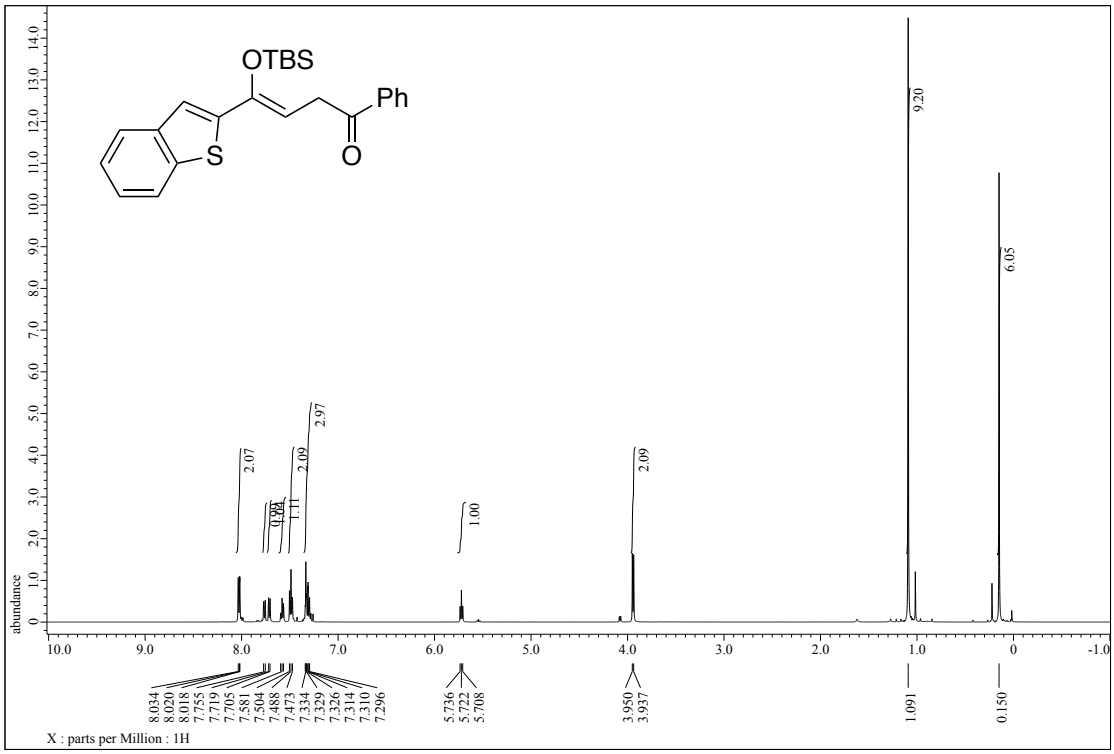


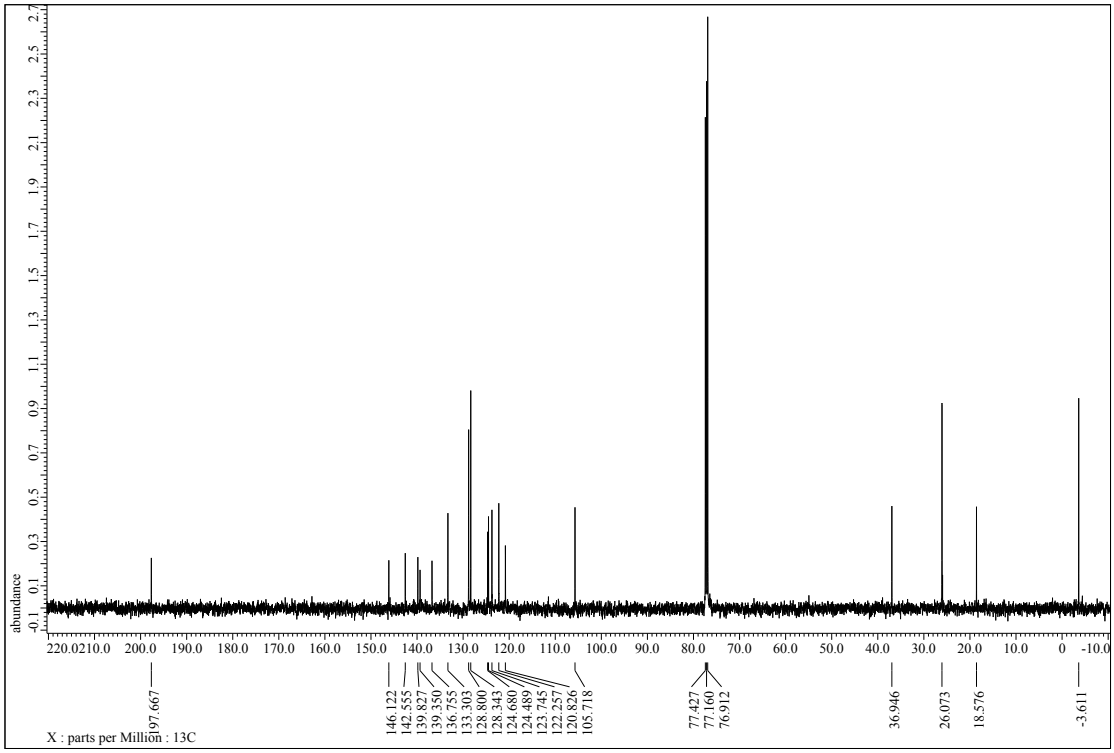
^{1}H and ^{13}C NMR spectra of **3ia**



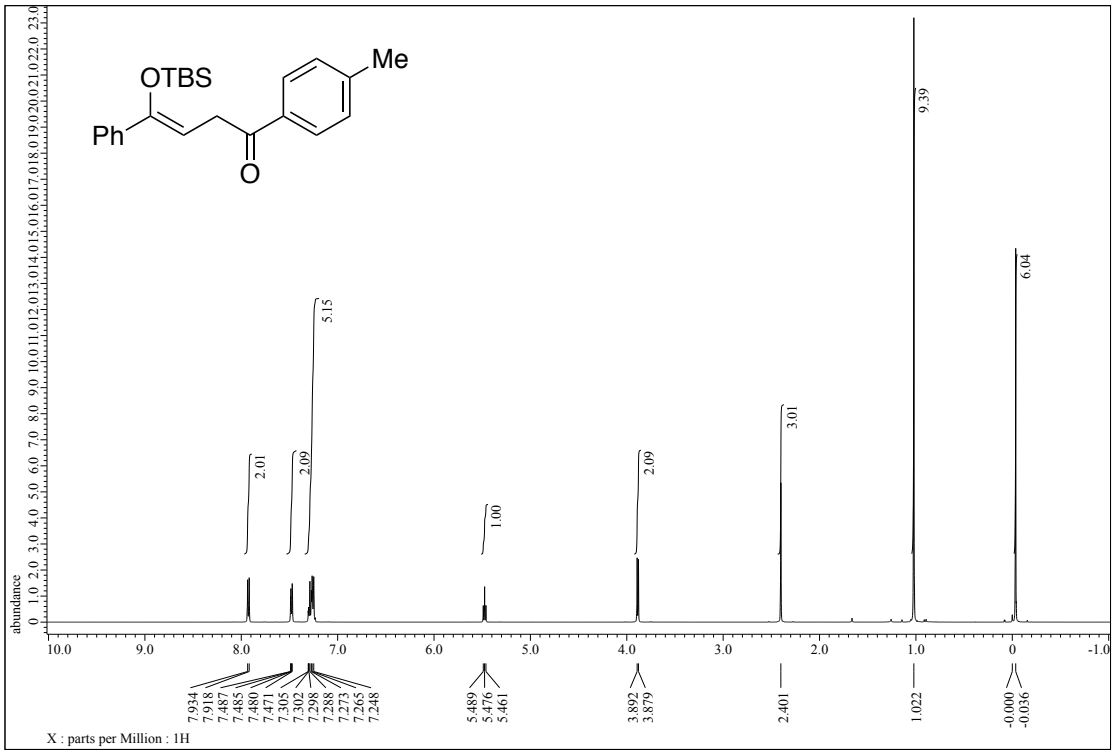


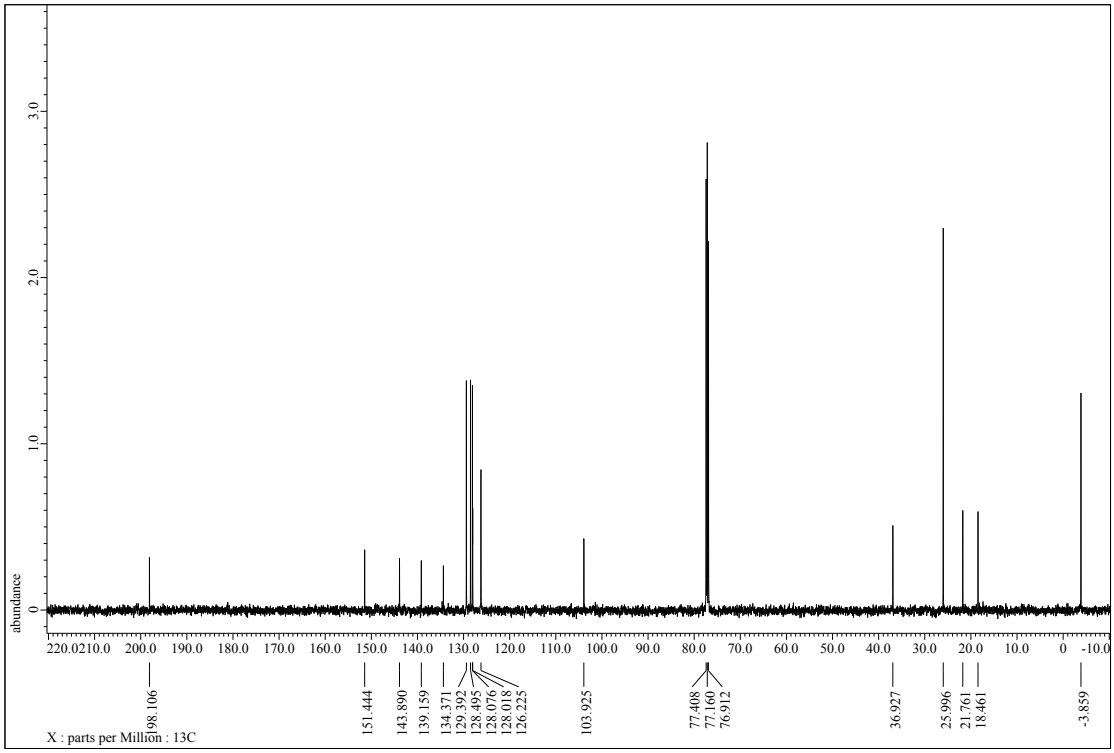
^{1}H and ^{13}C NMR spectra of **3ja**



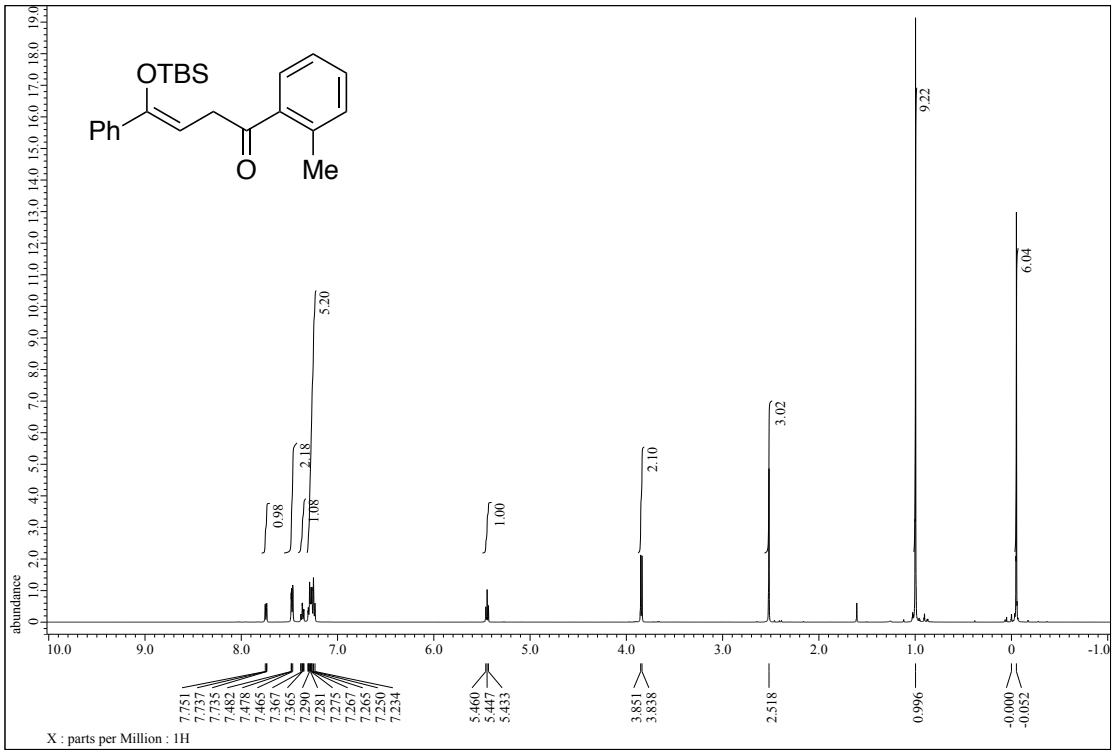


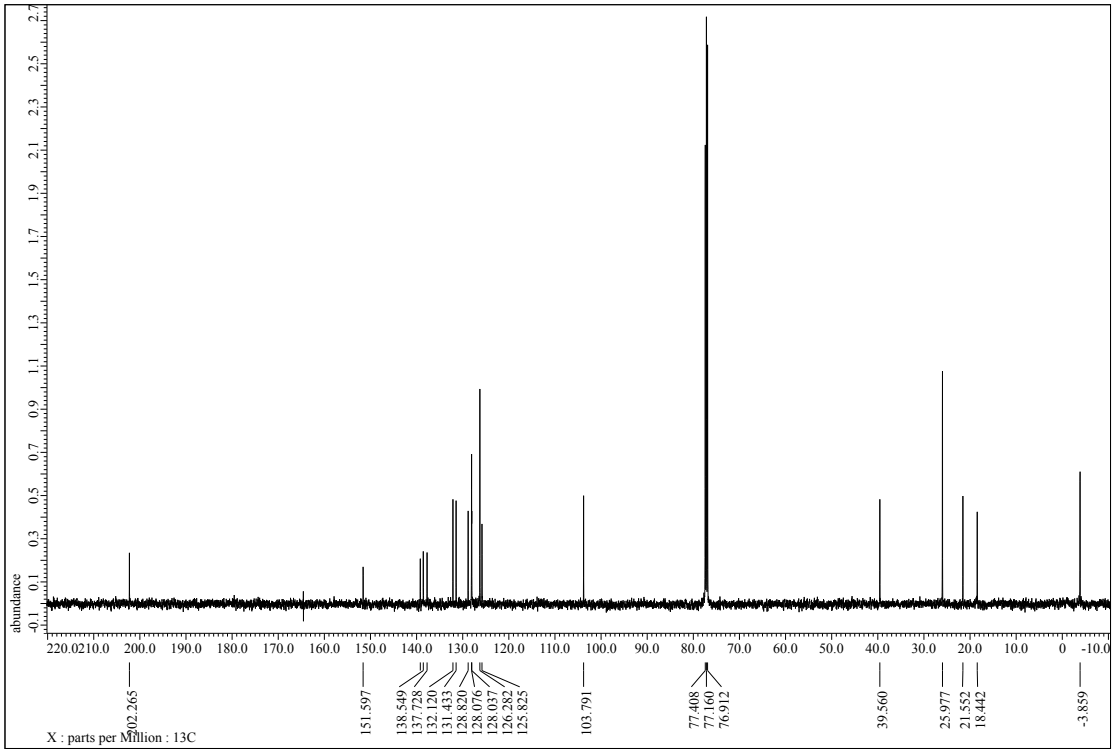
^{1}H and ^{13}C NMR spectra of **3ab**



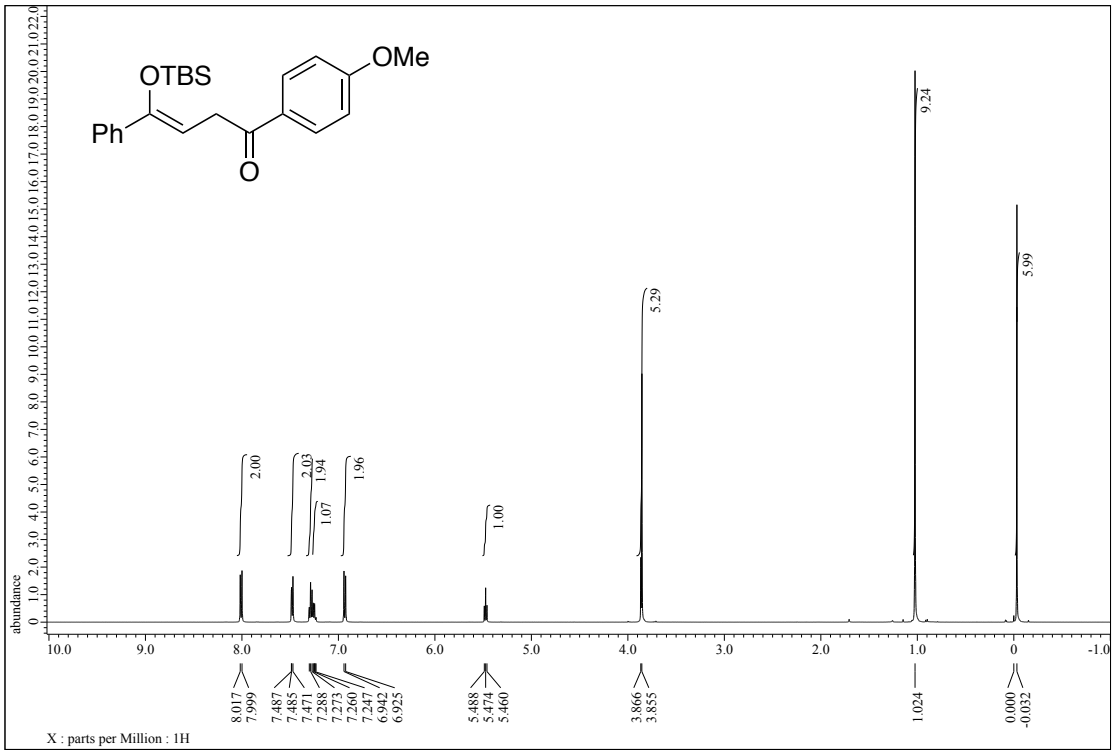


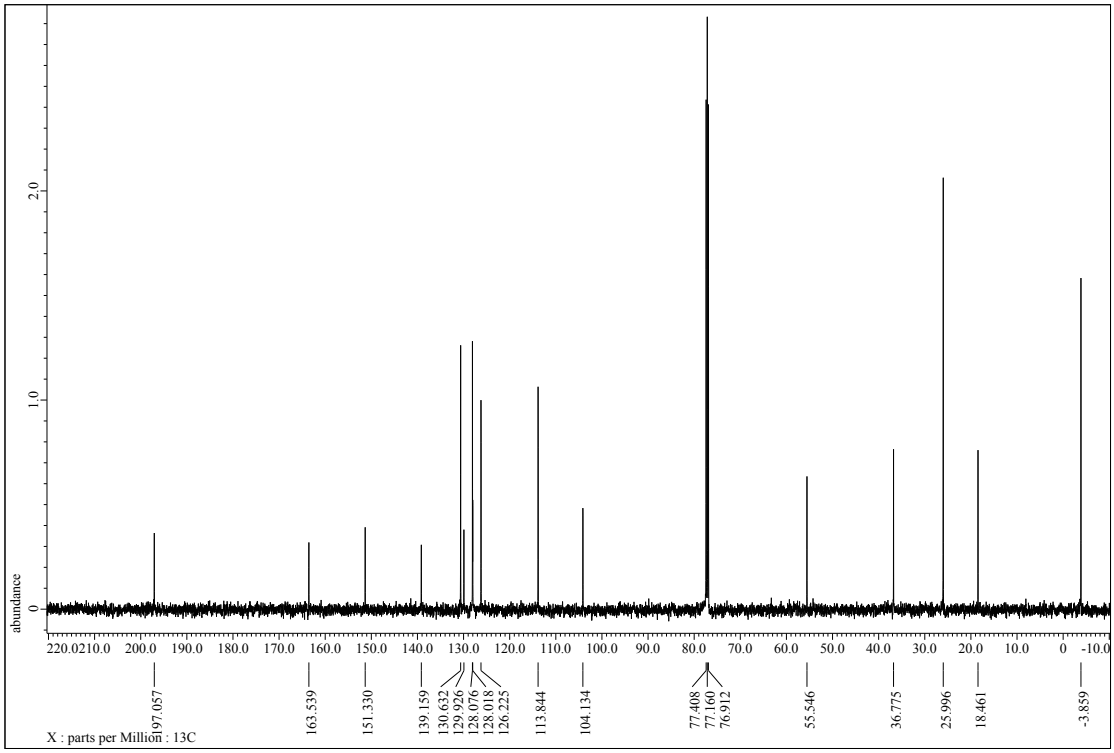
^{1}H and ^{13}C NMR spectra of **3ac**



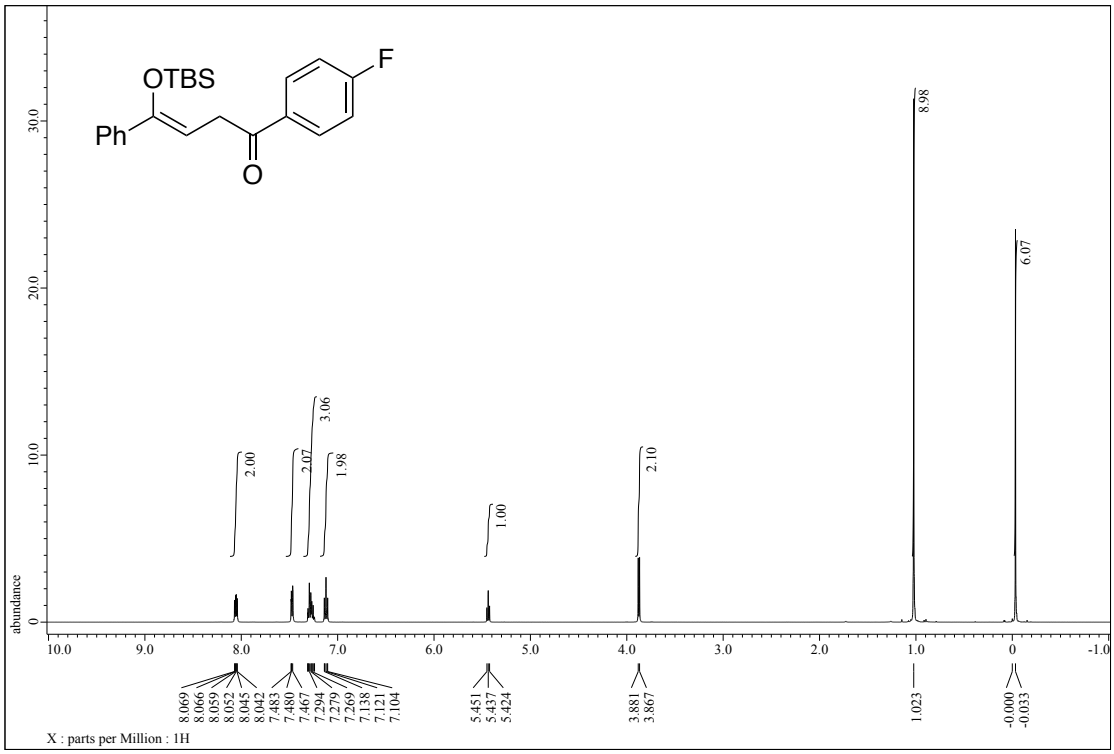


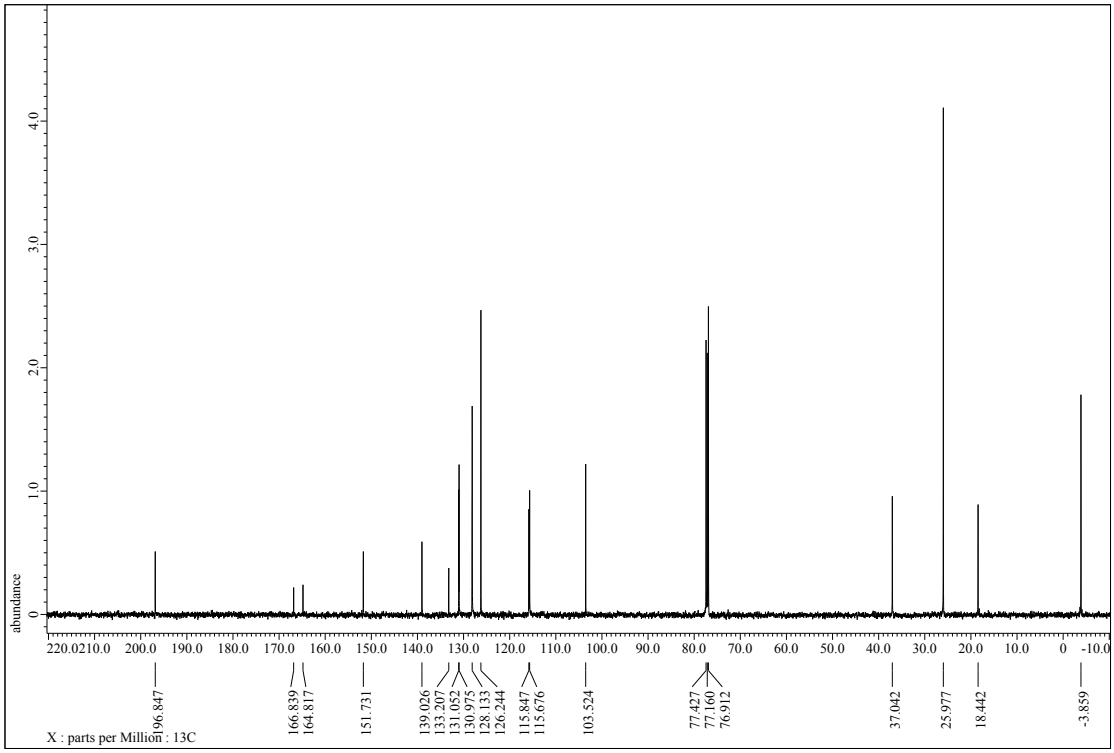
^{1}H and ^{13}C NMR spectra of **3ad**

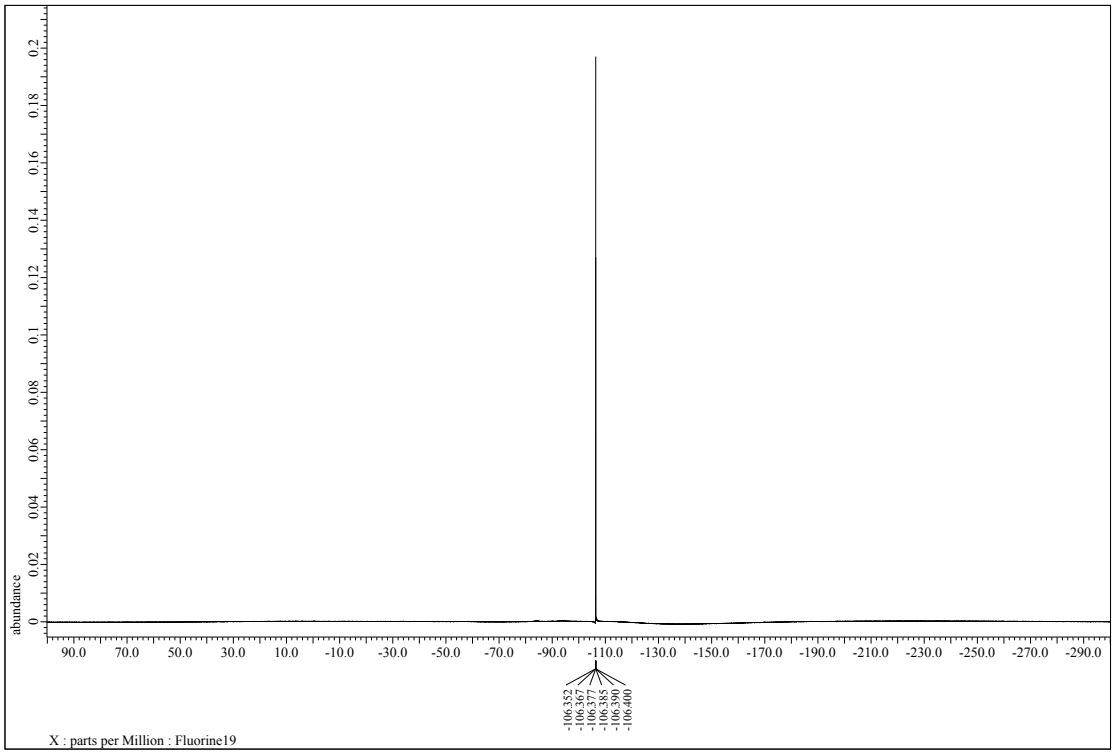




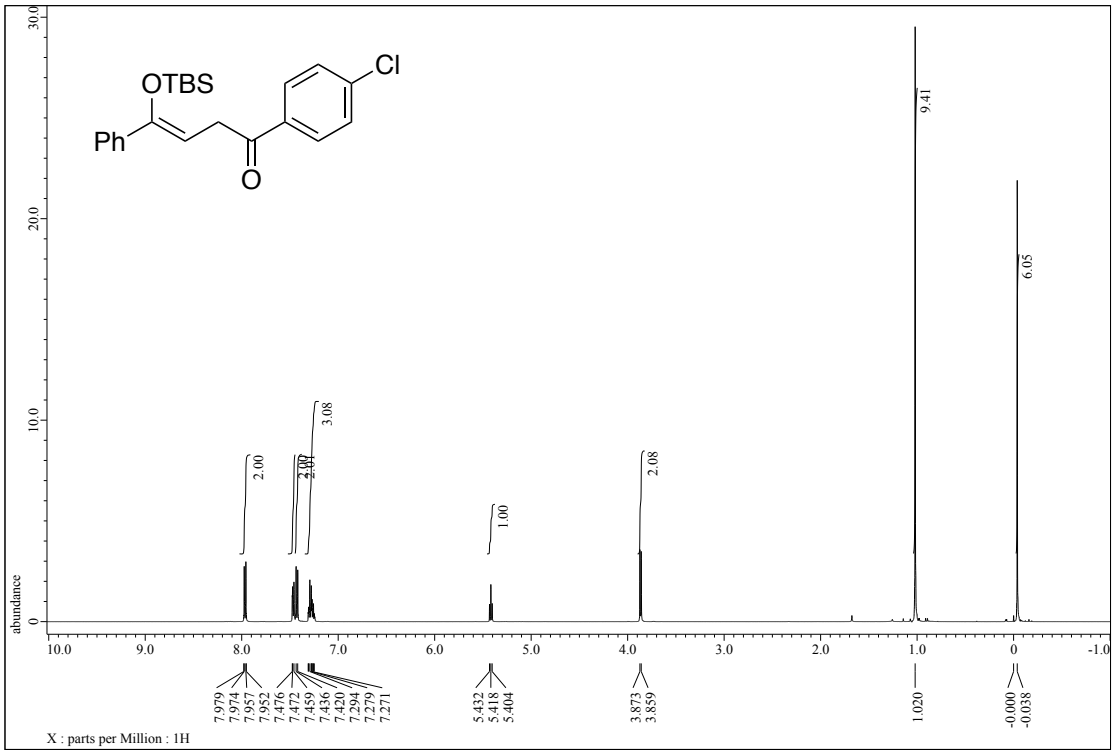
^{1}H, ^{13}C, and ^{19}F NMR spectra of **3ae**

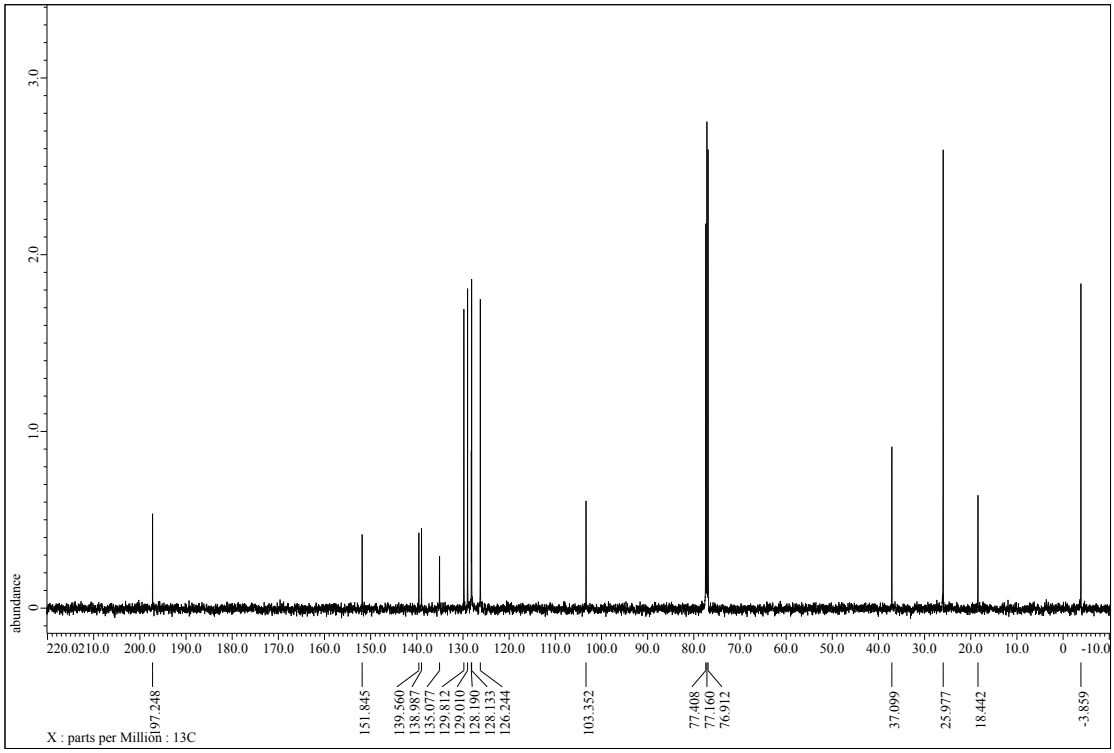




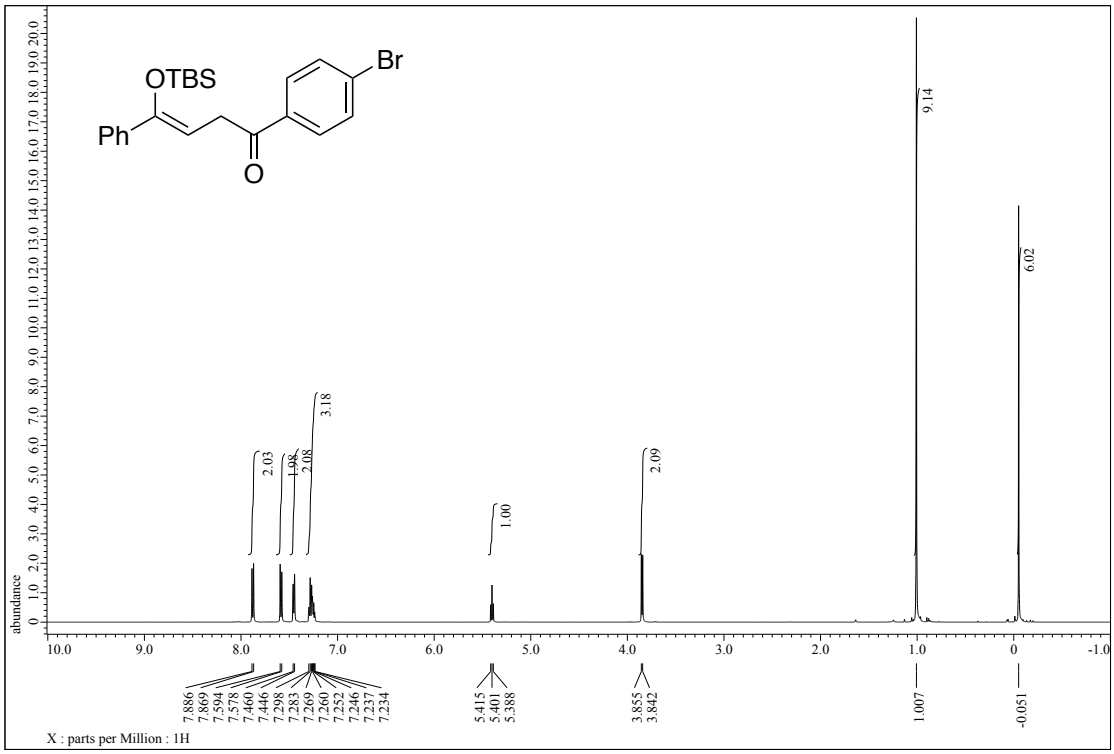

abundance
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
0.18
0.2
90.0
70.0
50.0
30.0
10.0
-10.0
-30.0
-50.0
-70.0
-90.0
-110.0
-130.0
-150.0
-170.0
-190.0
-210.0
-230.0
-250.0
-270.0
-290.0
-106.352
-106.367
-106.377
-106.385
-106.390
-106.397
-106.400
X : parts per Million : Fluorine19

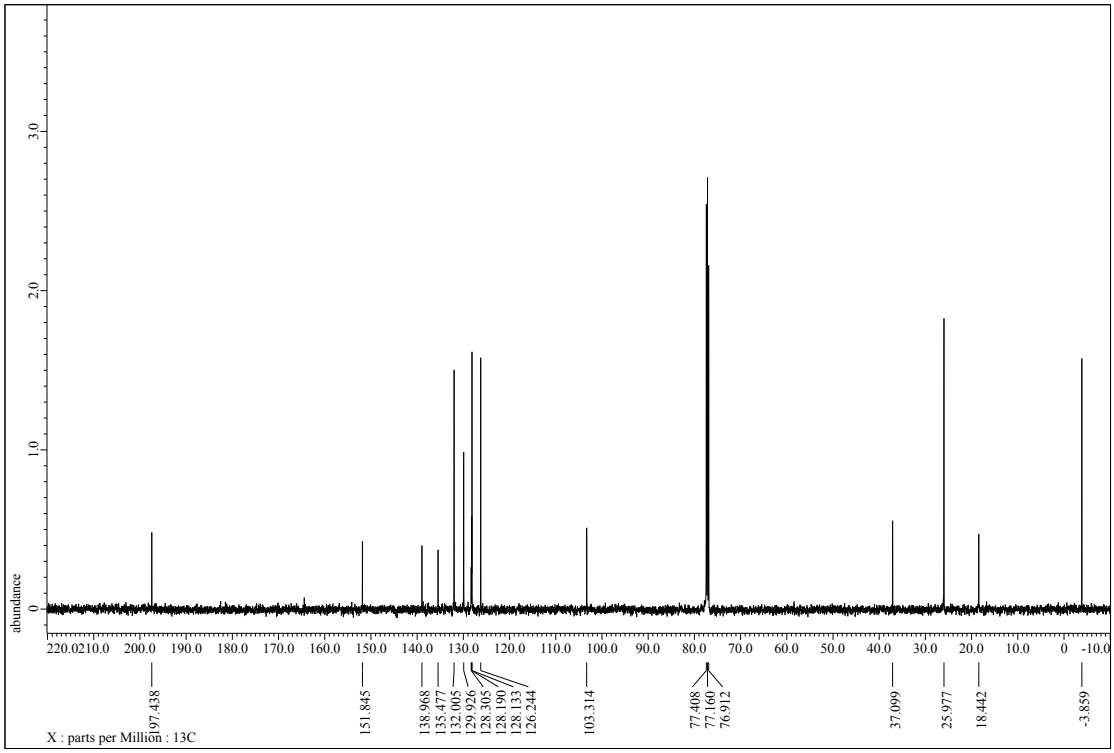
^{1}H and ^{13}C NMR spectra of **3af**



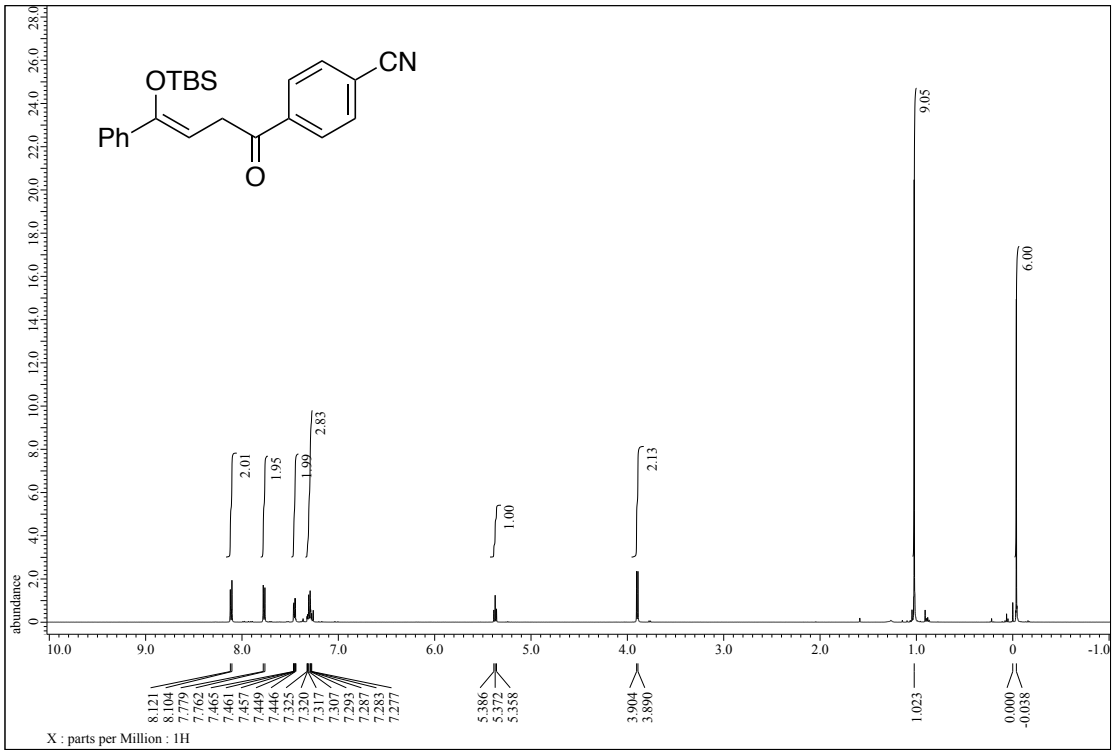


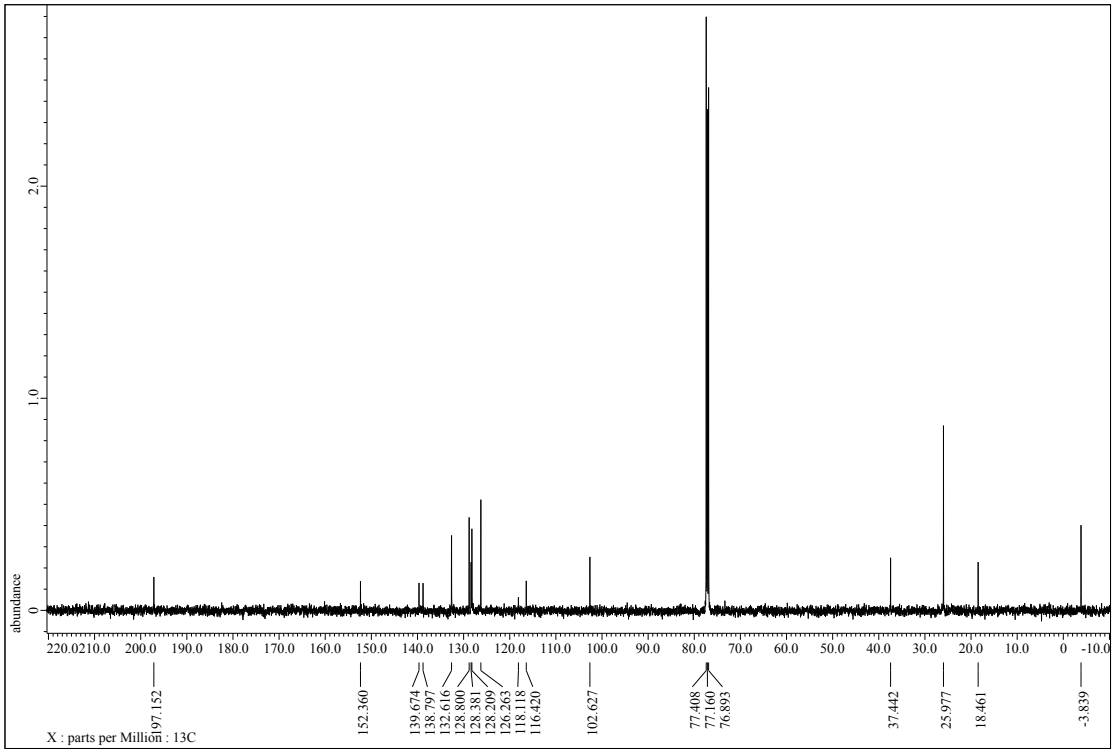
^{1}H and ^{13}C NMR spectra of **3ag**



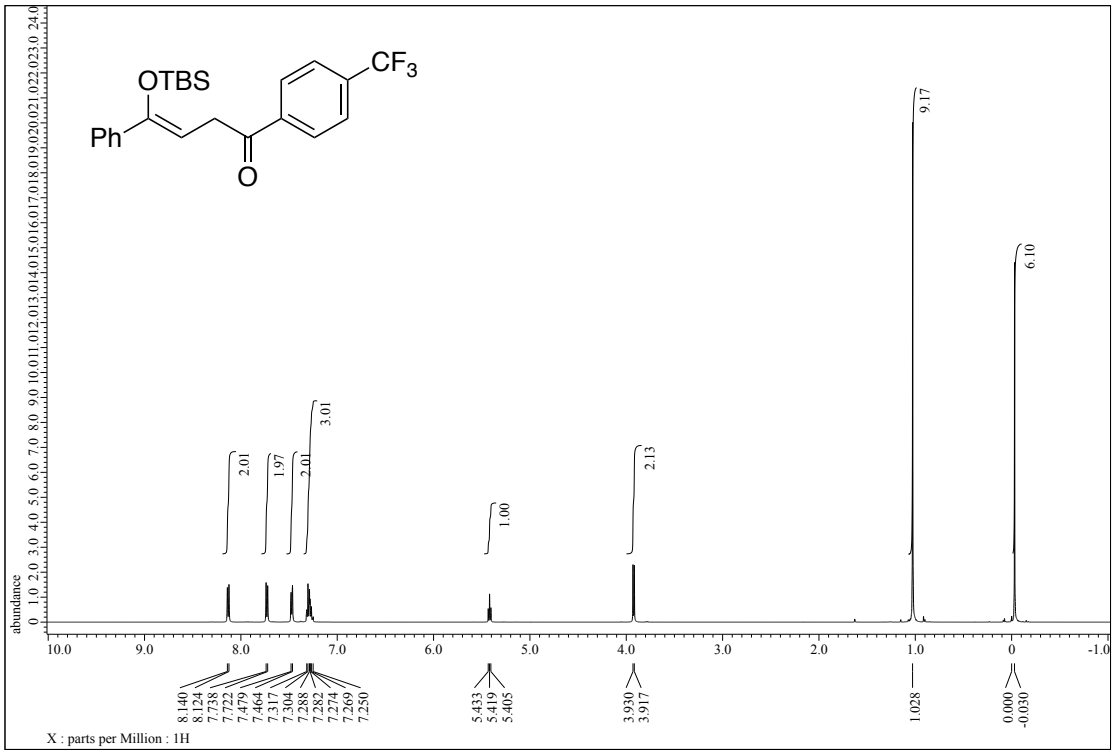


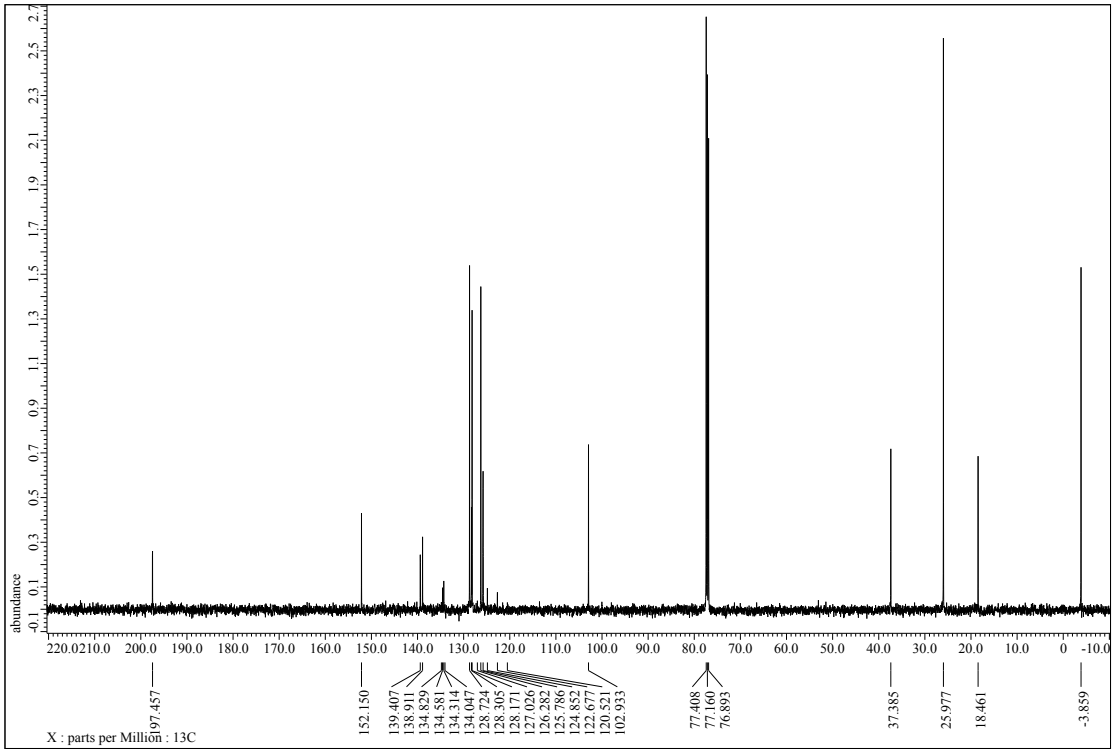
^{1}H and ^{13}C NMR spectra of **3ah**

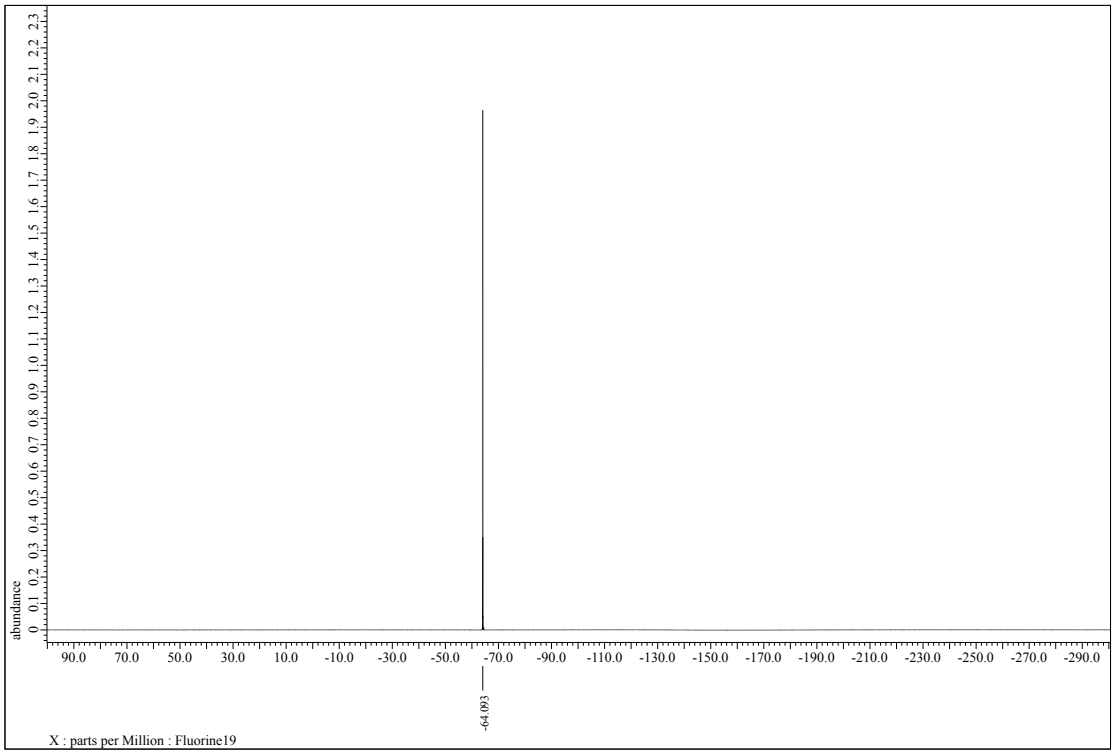




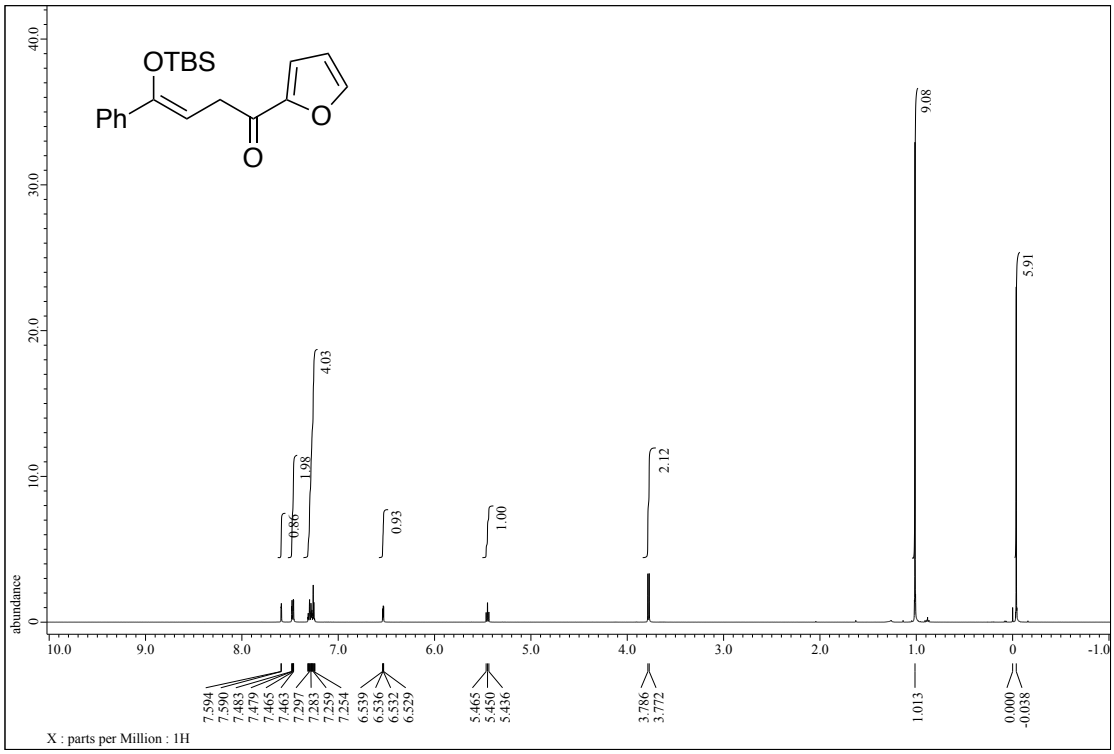
^{1}H and ^{13}C NMR spectra of **3ai**

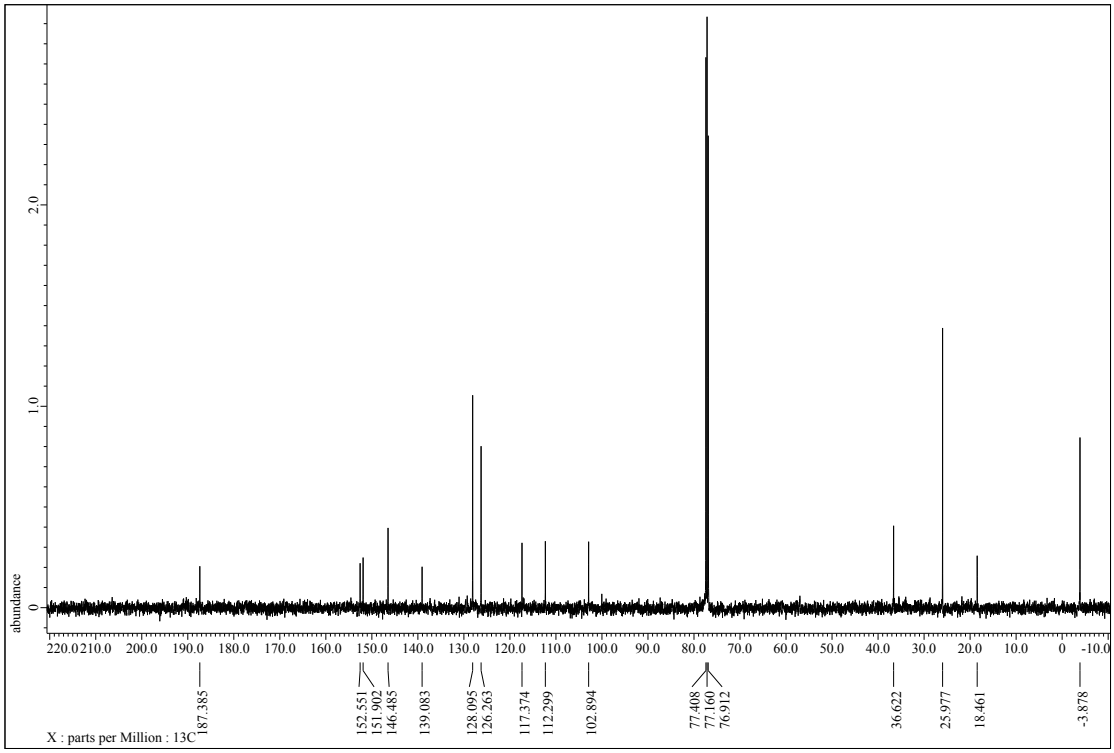




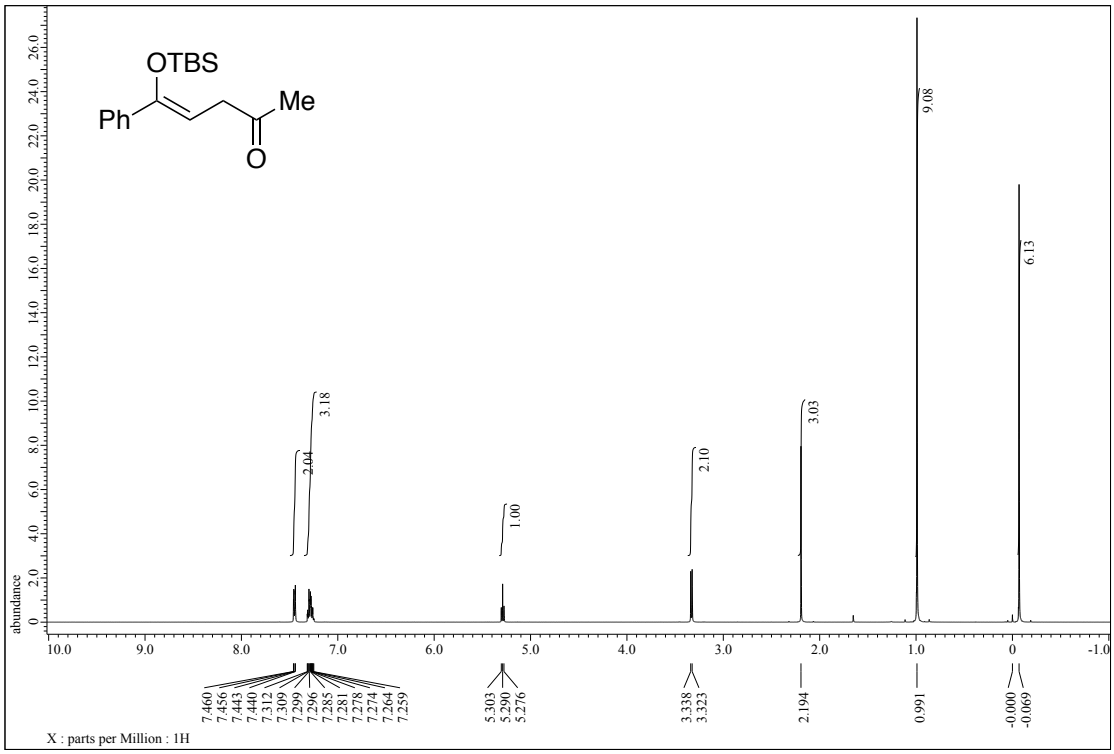

abundance
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0 2.1 2.2 2.3
90.0 70.0 50.0 30.0 10.0 -10.0 -30.0 -50.0 -70.0 -90.0 -110.0 -130.0 -150.0 -170.0 -190.0 -210.0 -230.0 -250.0 -270.0 -290.0
-64.093
X : parts per Million : Fluorine19

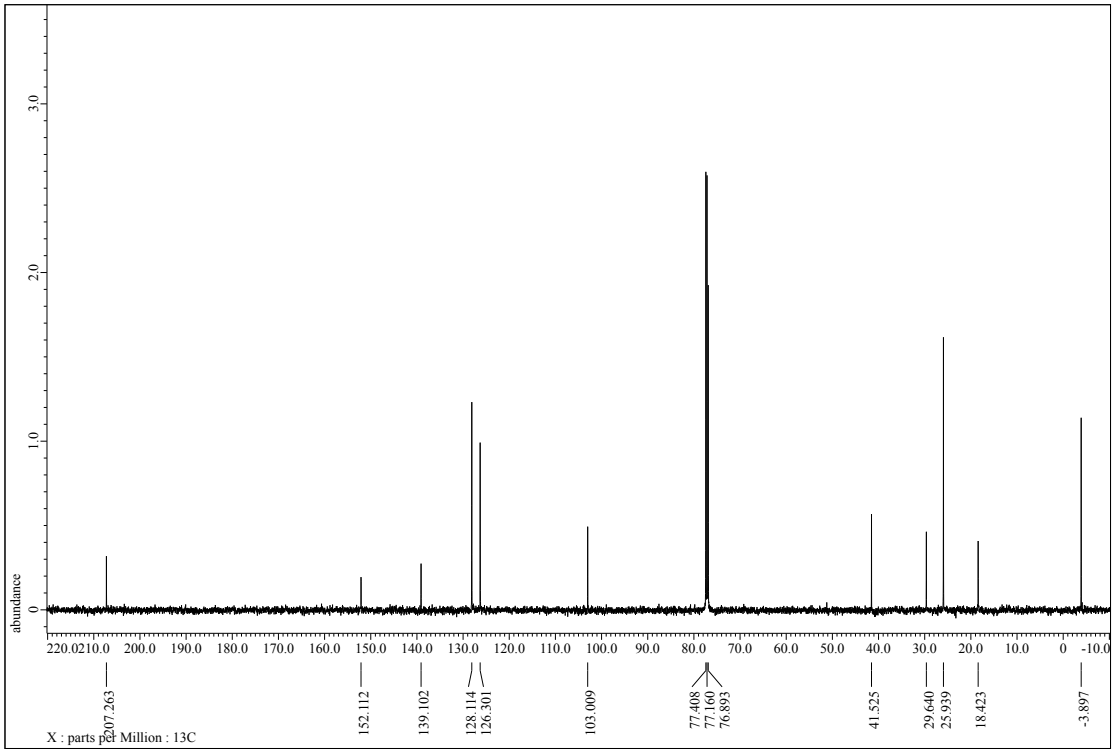
^{1}H and ^{13}C NMR spectra of **3aj**



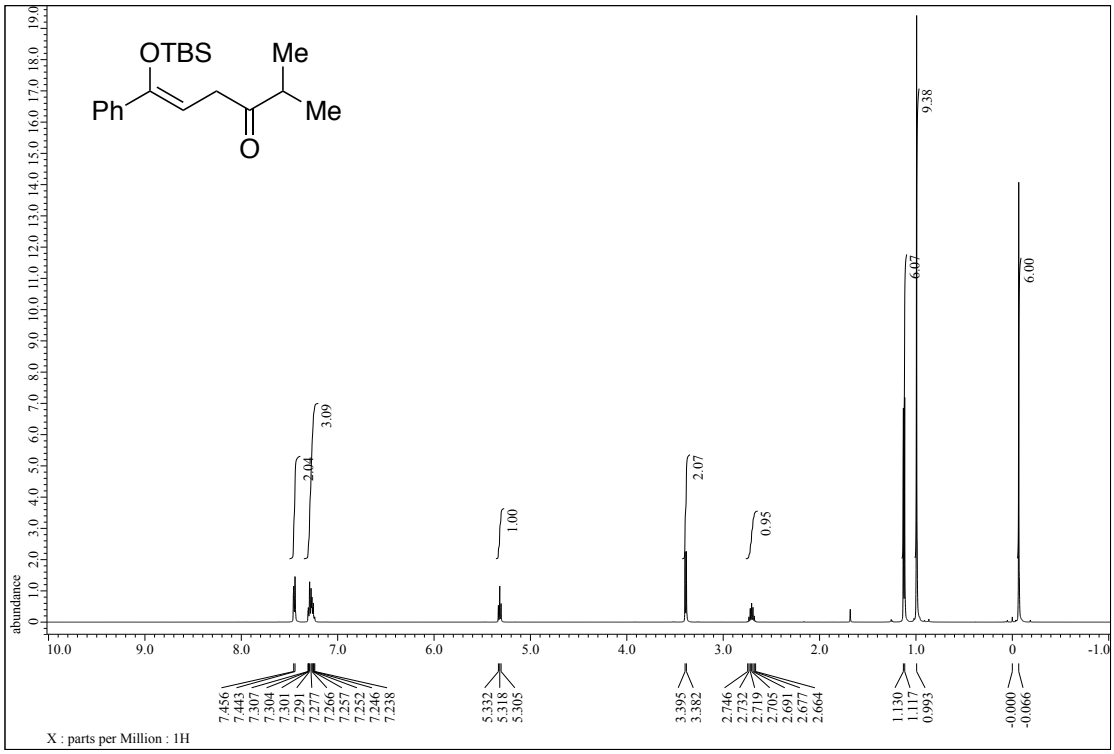


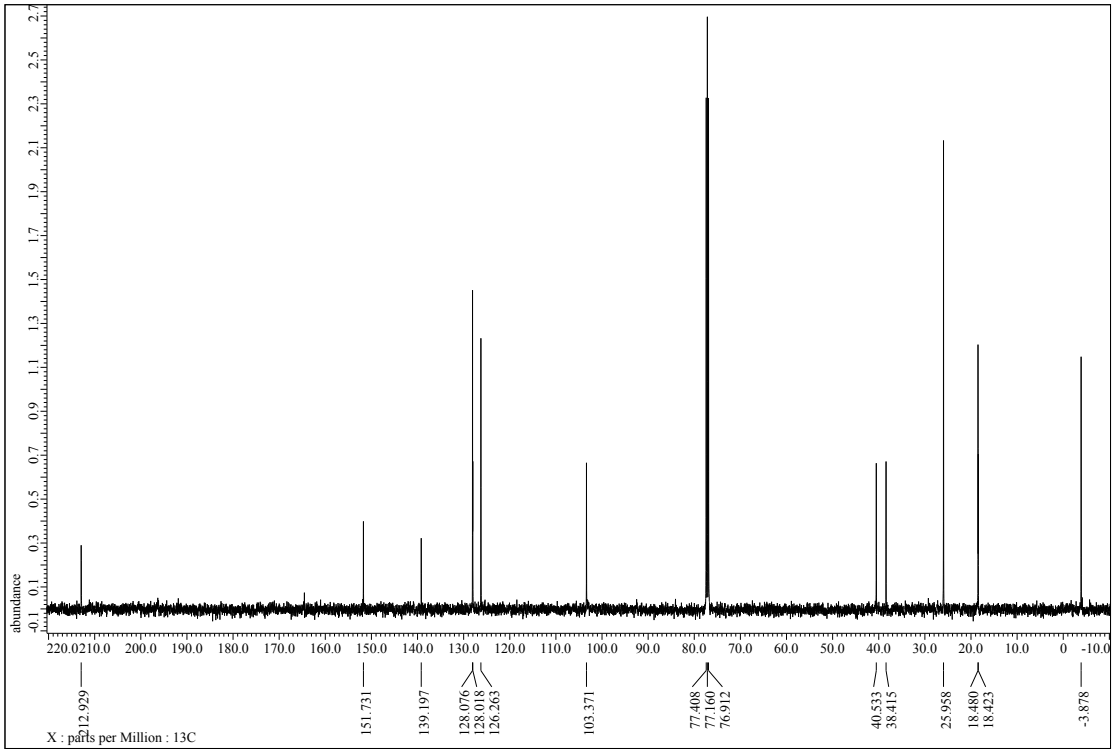
^{1}H and ^{13}C NMR spectra of **3ak**



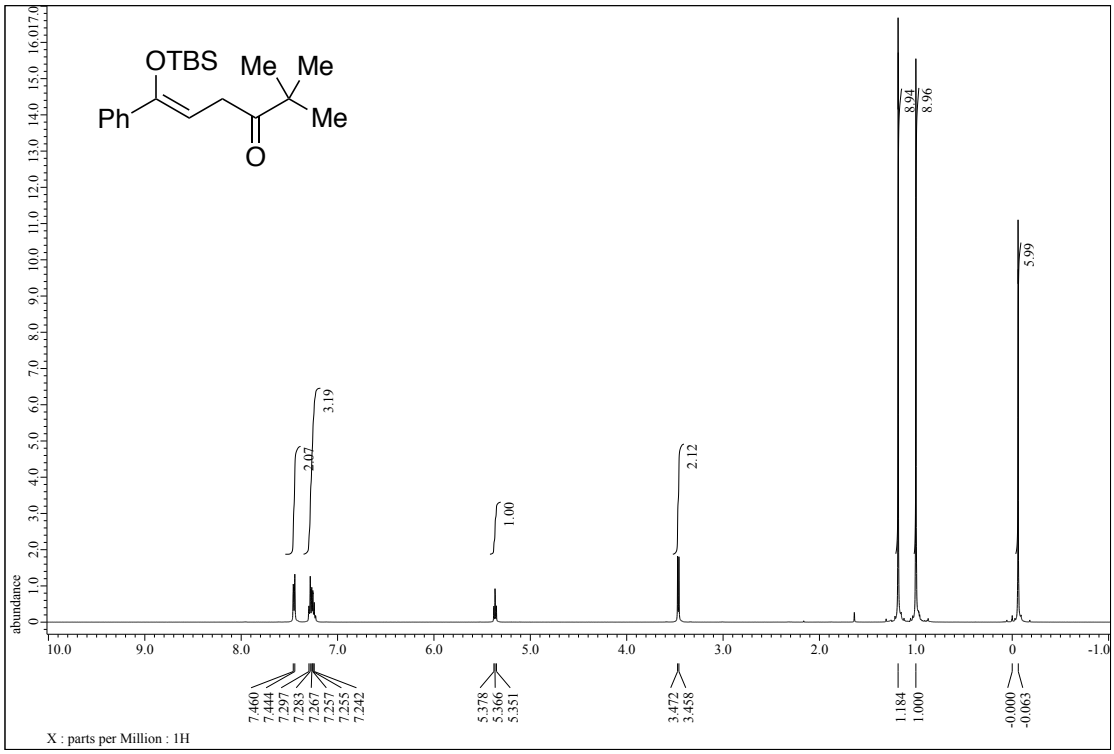


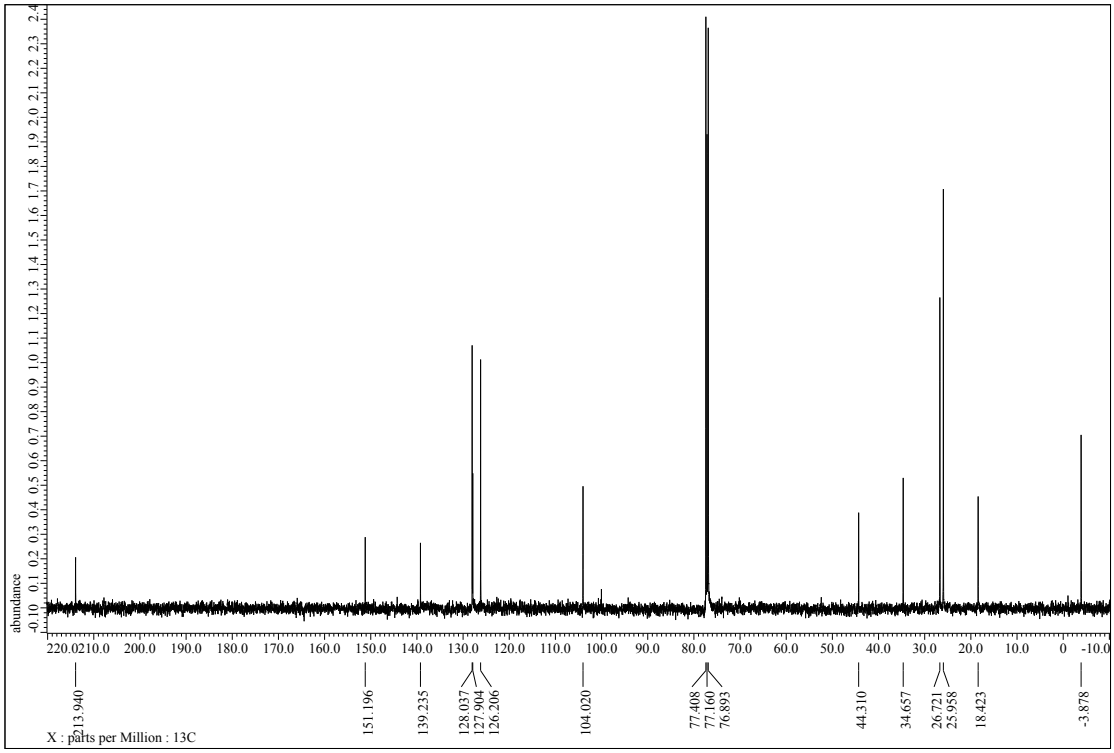
^{1}H and ^{13}C NMR spectra of **3al**



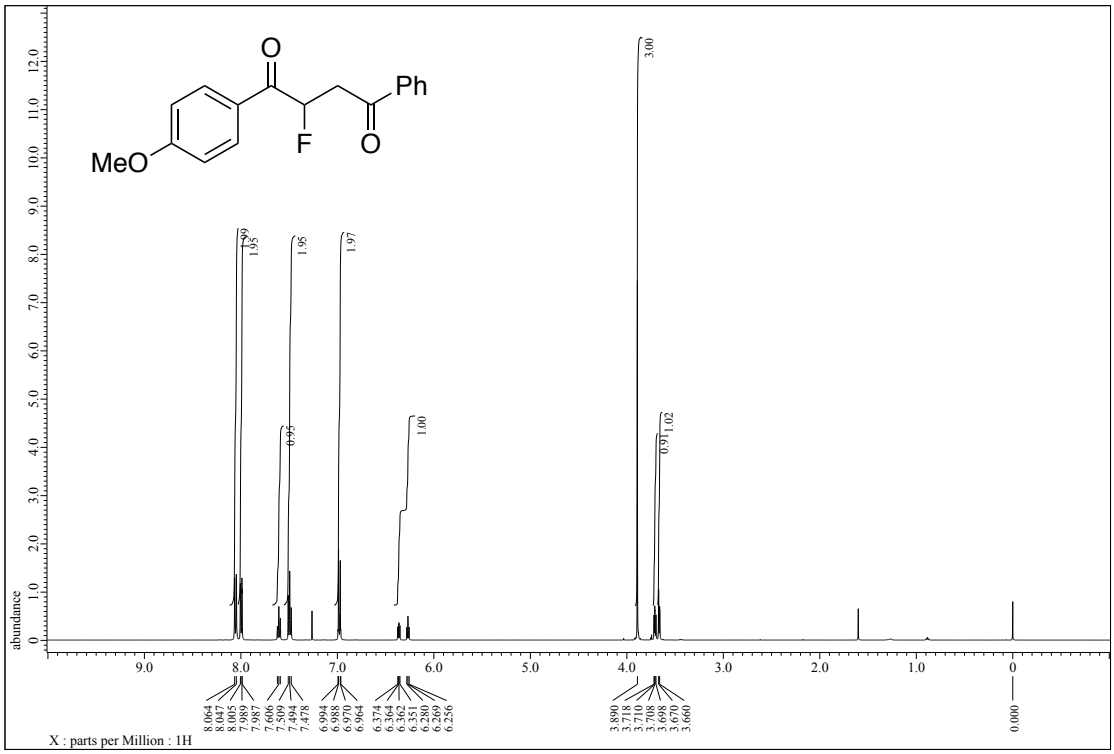


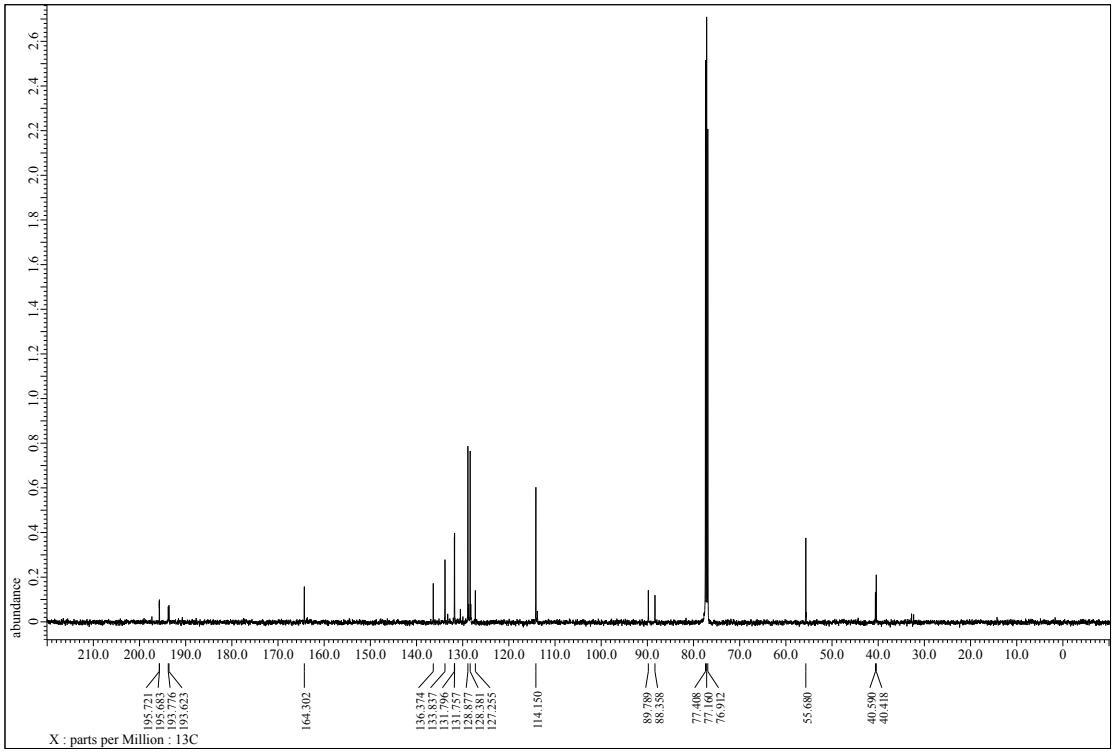
^{1}H and ^{13}C NMR spectra of **3am**

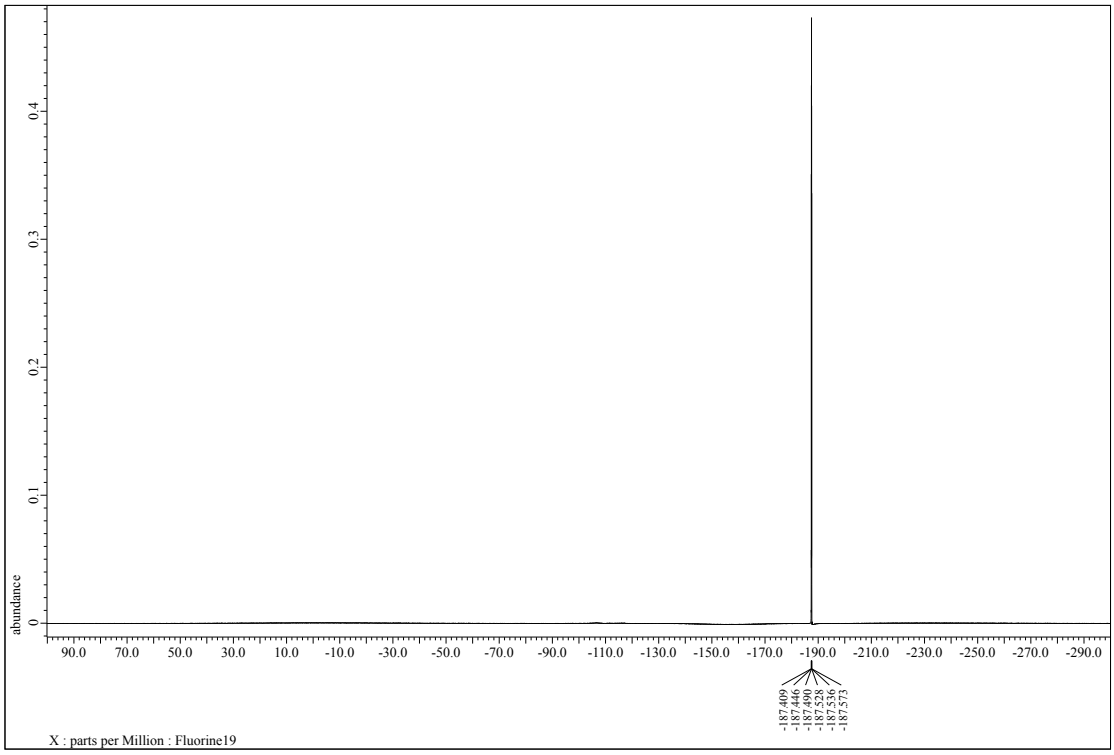




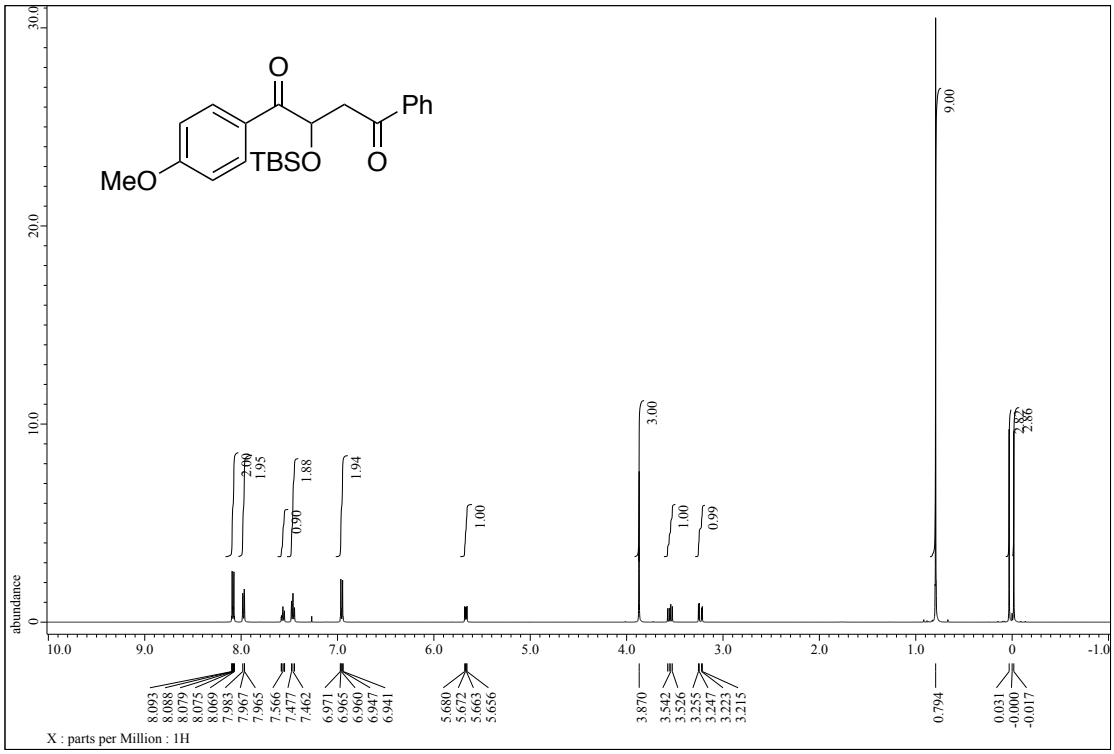
^{1}H, ^{13}C, and ^{19}F NMR spectra of **6**

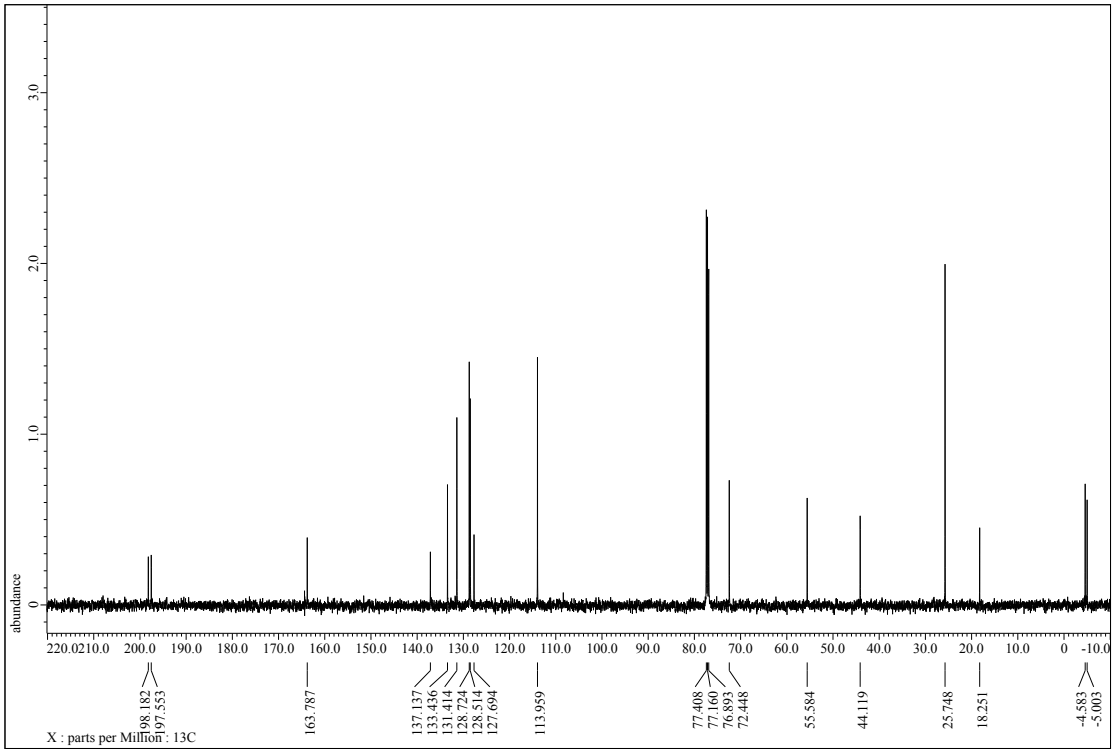




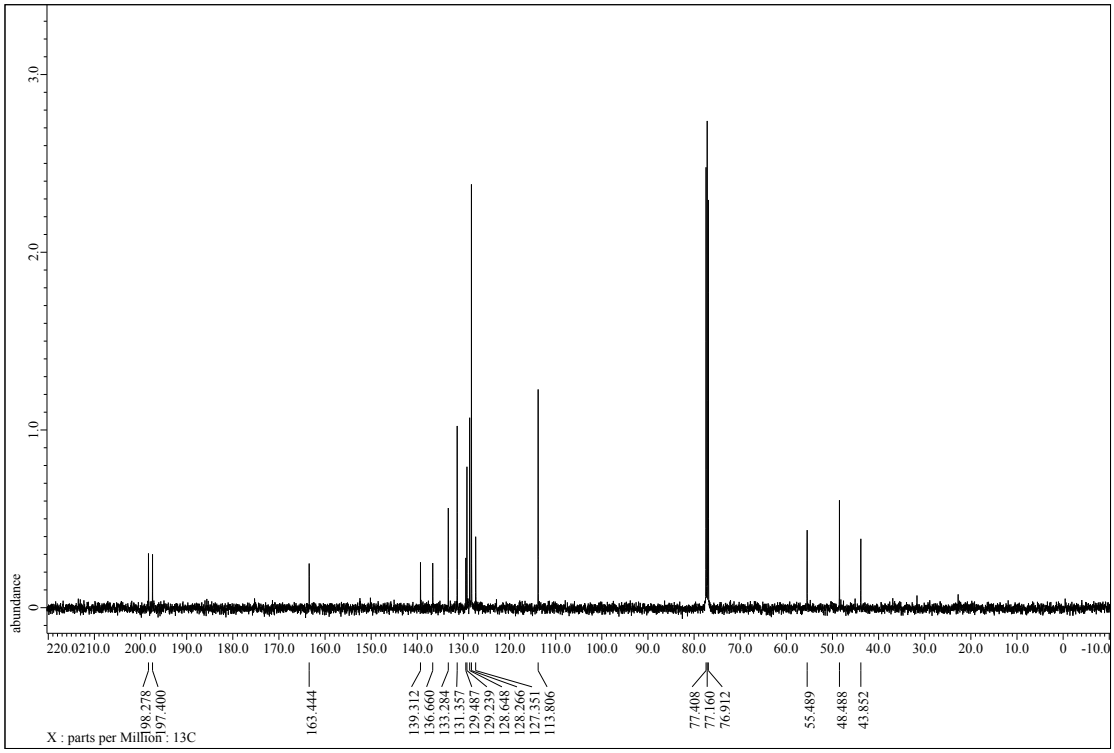

abundance
0
0.1
0.2
0.3
0.4
90.0
70.0
50.0
30.0
10.0
-10.0
-30.0
-50.0
-70.0
-90.0
-110.0
-130.0
-150.0
-170.0
-190.0
-210.0
-230.0
-250.0
-270.0
-290.0
-187.409
-187.446
-187.490
-187.528
-187.536
-187.573
X : parts per Million : Fluorine19

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

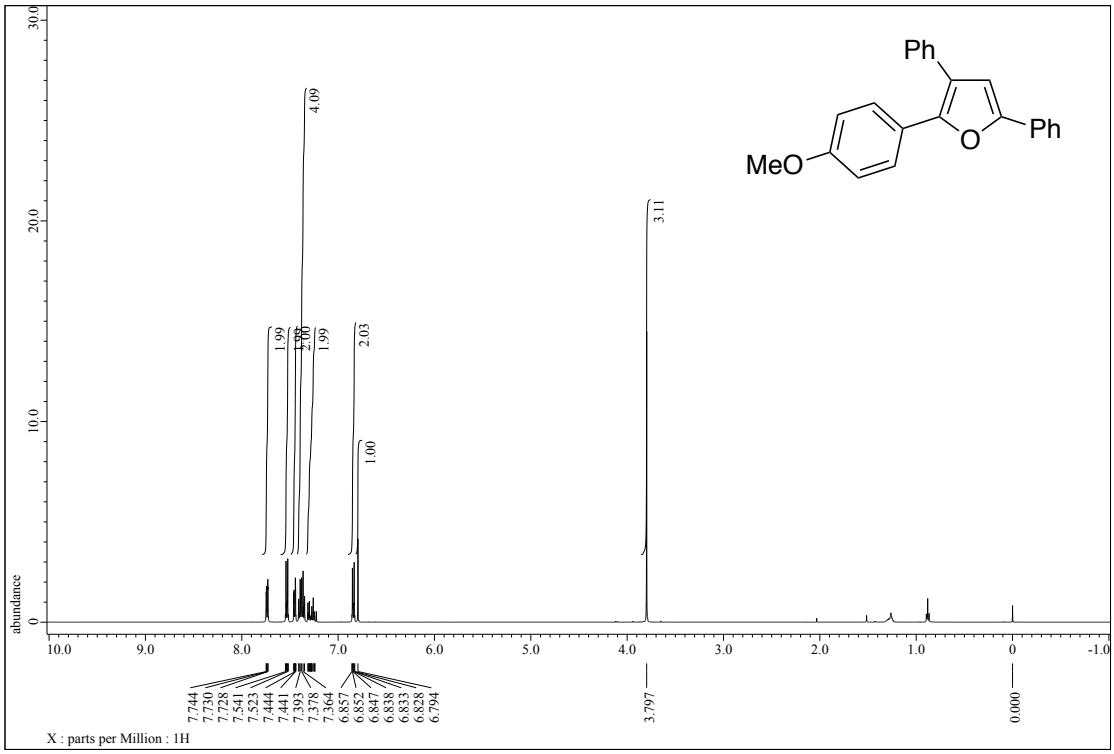


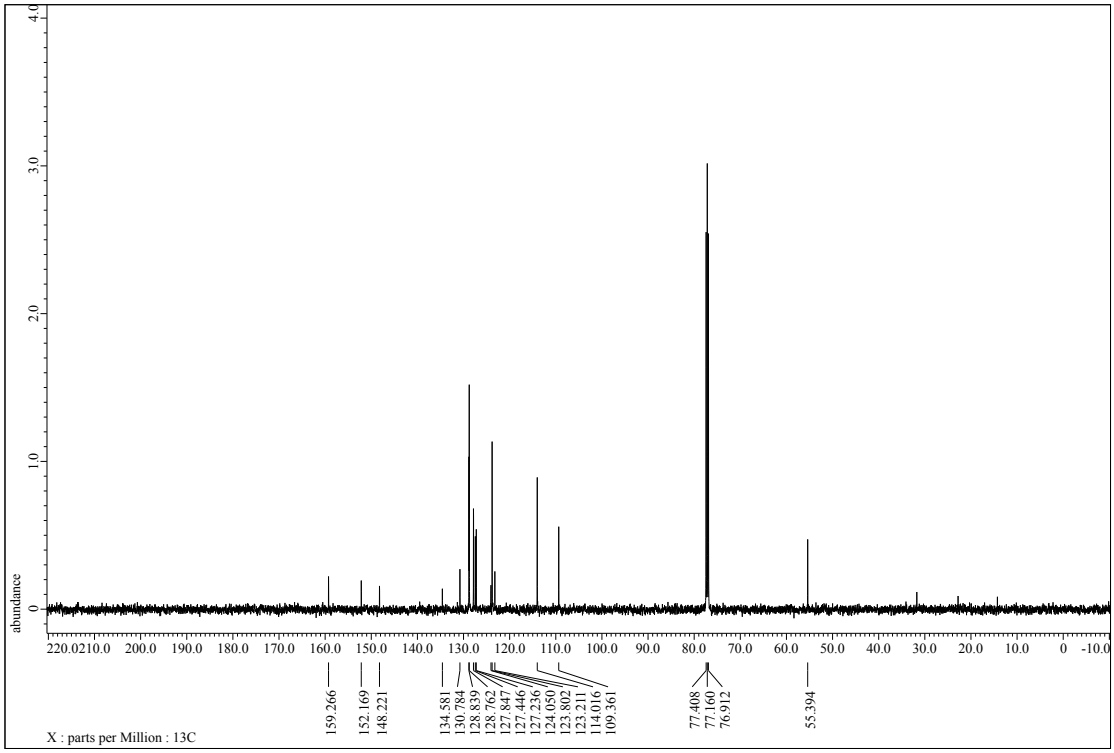


^{1}H and ^{13}C NMR spectra of **8**



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





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