Electronic Supplementary Material (ESI) for Chemical Science.

Asymmetric β-arylation of cyclopropanols enabled by photoredox and nickel dual catalysis

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General techniques and chemicals

Unless otherwise noted, all the reactions for the preparation of the substrates were performed in oven-dried glassware under nitrogen atmosphere with freshly distilled solvents. The catalytic reactions were performed under nitrogen atmosphere. The solvents were purified by distillation from calcium hydride unless otherwise noted. All other commercial reagents were used without further purification unless otherwise indicated. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker 400 MHz spectrometer (ADVNCE III) using chloroform-*d* ($CDCl_3$), methanol-*d4* (CD_3OD) and dimethyl sulphoxide-*d6* (DMSO-*d6*) as the internal standard. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26), carbon (chloroform δ 77.1), proton (methanol δ 3.31), carbon (methanol δ 49.0) or tetramethylsilane (TMS δ 0.00) was used as a reference. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz) and integration. The enantiomeric ratio (er) was determined by HPLC analysis on Agilent 1260 Infinity II Prime using Daicel CHIRALPAK® column IA-U, IB-U, IC-U or LC-20AD/T LPGE KIT using Daicel CHIRALPAK® column IA-3, IB-3, IC-3. X-ray diffraction analyses were carried out on a microcrystalline powder using a Rigaku Oxford Diffraction XtaLAB Synergy-S diffractometer using Cu radiation ($\lambda = 1.54184$ Å). If not specially mentioned, flash column chromatography was performed using 200-300 silica gel purchased from Yaitai Chemicals (China). High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer using ESI (electrospray ionization) as ionization method. Optical rotations were recorded on an AUTOPOL II digital polarimeter at 589 nm and are recorded as $[\alpha]_D^T$ (concentration in grams/100 mL solvent).

The LEDs reaction machine was purchased from Beijing Strongerscience Co., Ltd., the LEDs emits blue light with a spectral output centered at 465 nm (**Figure 1**).

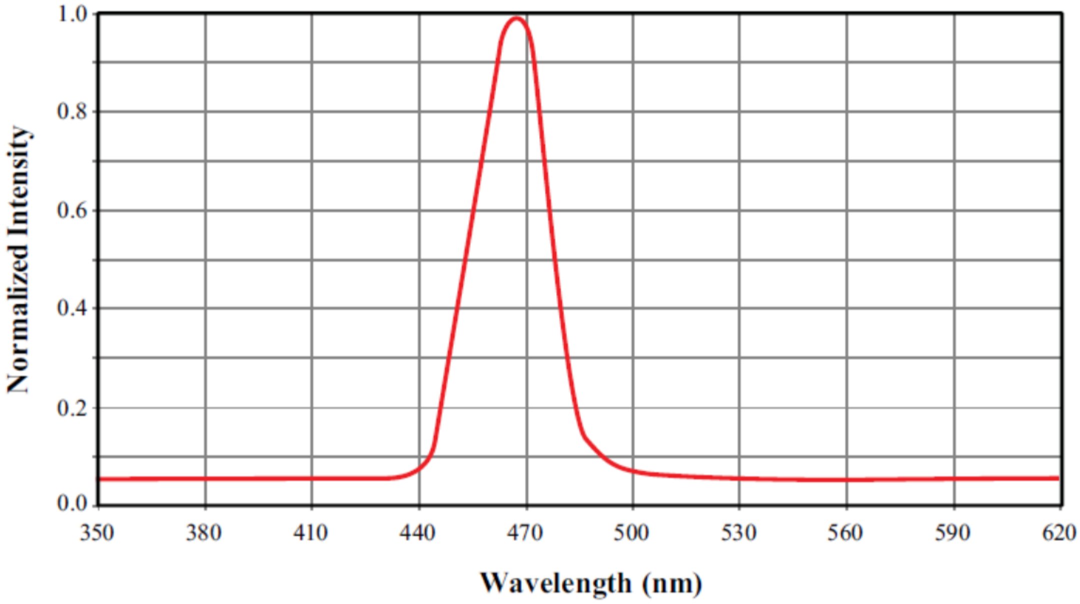


Figure S1: Spectral intensity distribution of LEDs

The reactions were stirred by IKA® RCT basic stirrer, cooled by ethanol circulator bath (**Figure 2**).

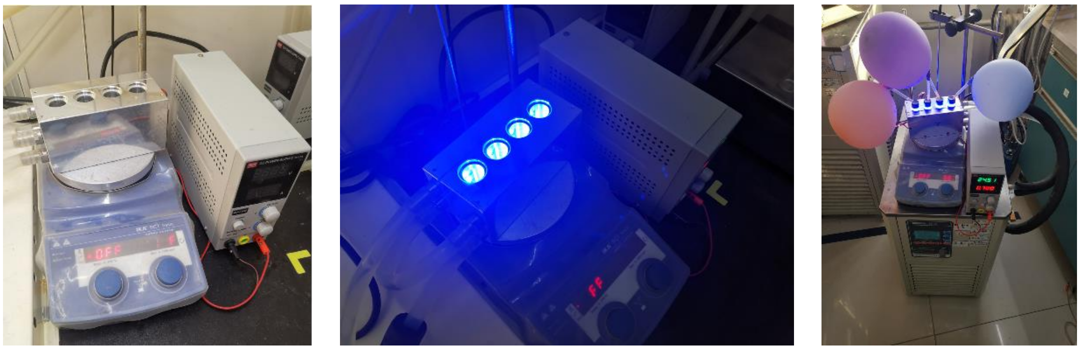
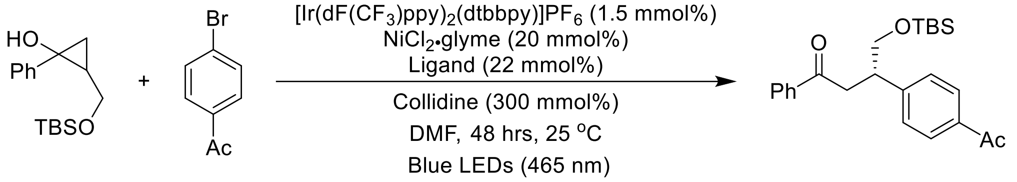
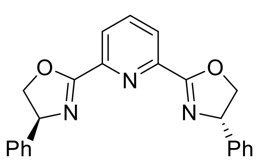
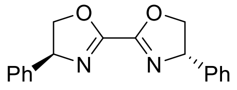
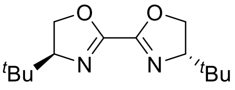
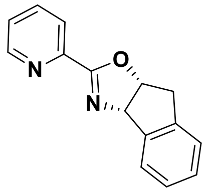
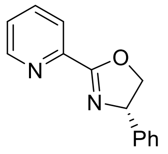
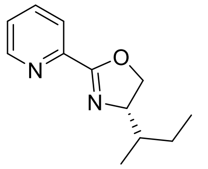
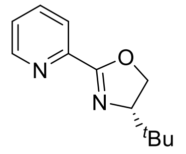
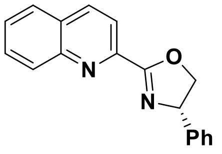


Figure S2: Appearance of Blue LEDs reaction System.

Optimization of reaction conditions

Table S1. Preliminary investigation of chiral ligands. [a]

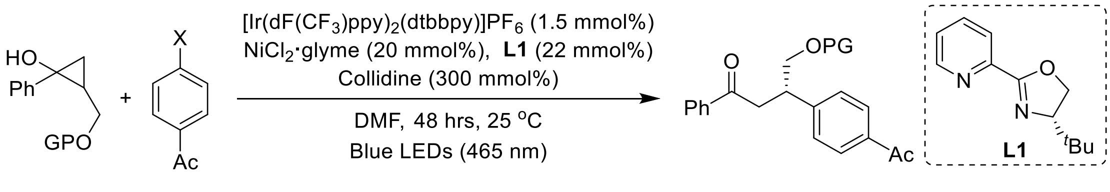


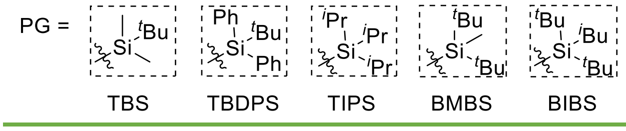
 **NP**	 14% yield, 55:45 er	 **NP**	 9% yield, 55:45 er
 65% yield, 52:48 er	 54% yield, 53:47 er	 68% yield, 81:19 er	 **NP**

[a] Unless otherwise indicated, all reactions were performed with Ir cat (1.5 mmol%), NiCl₂·glyme (20 mmol%), chiral ligand (22 mmol%), collidine (300 mmol%), cyclopropanol (0.30 mmol) and 4-bromoacetophenone (0.10 mmol) in DMF (5 mL) at 25 °C with blue LEDs irradiation under nitrogen atmosphere. NP: No product.

After screening a series of chiral ligands, reactions with chiral Py-(oxazoline) ligands gave better enantioselectivities.

Table S2. Investigation of aryl electrophiles and silyl protection groups. [a]



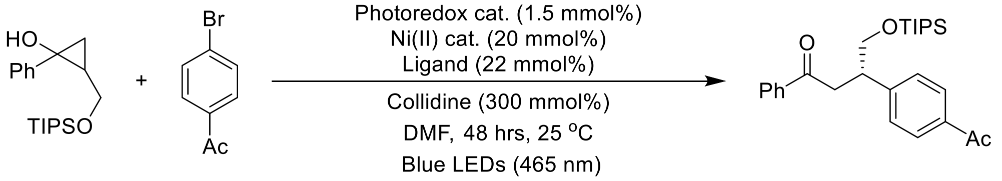


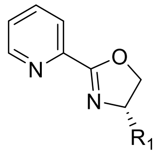
Entry.	PG	X	Yield (%)[b]	er[c]
1	TBS	Cl	0	-
2	TBS	Br	68	81:19
3	TBS	I	13	81:19

4	TBS	OTf	5	52:48
5	TBS	$B(OH)_2$	0	-
6	TBS	BPin	0	-
7	TBDPS	Br	63	80:20
8	TIPS	Br	71	84:16
9	BMBS	Br	51	83.5:16.5
10	BIBS	Br	50	81:19

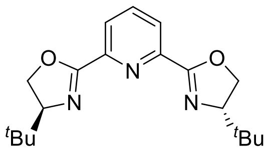
[a] Unless otherwise indicated, all reactions were performed with Ir cat (1.5 mmol%), $NiCl_2$·glyme (20 mmol%), **L1** (22 mmol%), collidine (300 mmol%), cyclopropanols (0.30 mmol) and electrophiles (0.10 mmol) in DMF (5 mL) at 25 °C with blue LEDs irradiation under nitrogen atmosphere. [b] Isolated yield. [c] Determined by HPLC analysis.

Table S3. Investigation of Ni(II) catalysts, ligands and photoredox catalysts. [a]

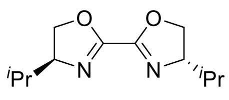




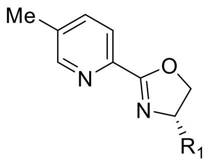
L1: R_1 = ^{t}Bu
L2: R_1 = Ph



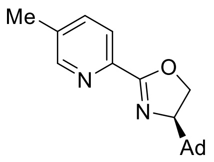
L3



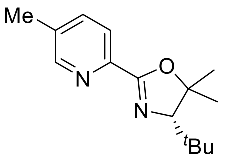
L4



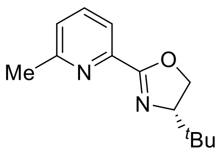
L5: R_1 = ^{t}Bu
L6: R_1 = Ad



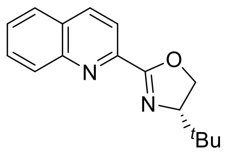
L7



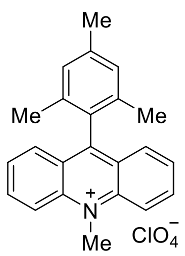
L8



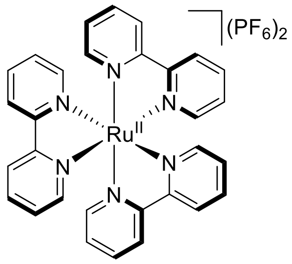
L9



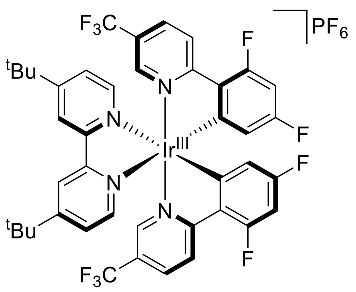
L10



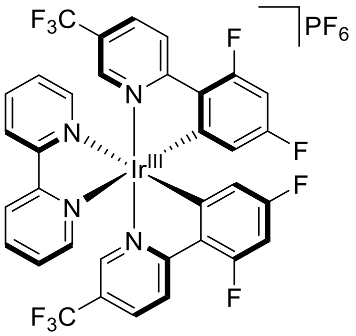
N-Me Mes-Acr^+·ClO_4^- (**Acr-1**)
$E_{1/2}$ $^*Acr^+/Acr^\cdot$ = +2.08 V
$E_{1/2}$ $Acr^+/Acr^\cdot$ = -0.55 V



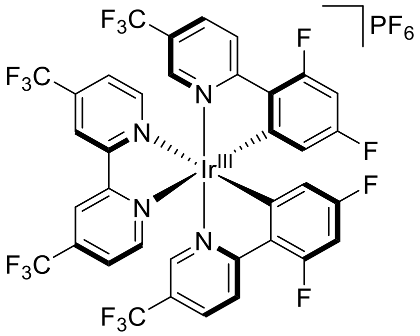
$[Ru(bpy)_3](PF_6)_2$ (**Ru-1**)
$E_{1/2}$ $^*Ru^{II}/Ru^{I}$ = +0.77 V
$E_{1/2}$ Ru^{II}/Ru^{I} = -1.33 V



$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (**Ir-1**)
$E_{1/2}$ $^*Ir^{III}/Ir^{II}$ = +1.21 V
$E_{1/2}$ Ir^{III}/Ir^{II} = -1.37 V



[Ir(dF(CF$_3$)ppy)$_2$(bpy)]PF$_6$ (**Ir-2**)
$E_{1/2}$ *Ir^{III}/Ir^{II} = +1.32 V
$E_{1/2}$ Ir^{III}/Ir^{II} = -1.37 V



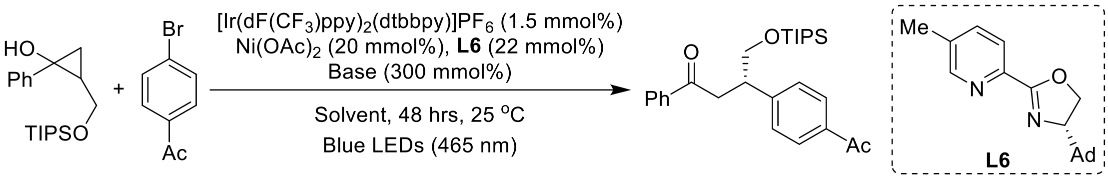
[Ir(dF(CF$_3$)ppy)$_2$(4,4'-d(CF$_3$)bpy)]PF$_6$ (**Ir-3**)
$E_{1/2}$ *Ir^{III}/Ir^{II} = +1.27 V
$E_{1/2}$ Ir^{III}/Ir^{II} = -1.07 V

Entry	Ligands	Ni(II) cat.	Photoredox cat.	Yields (%)[b]	er[c]
1	**L1**	$NiCl_2$·glyme	**Ir-1**	71	84:16
2	**L1**	$NiBr_2$·glyme	**Ir-1**	58	87:13
3	**L1**	NiI_2	**Ir-1**	0	-
4	**L1**	$Ni(OAc)_2$	**Ir-1**	80	88:12
5	**L1**	$Ni(acac)_2$	**Ir-1**	44	82:18
6	**L1**	$Ni(PPh_3)_2Cl_2$	**Ir-1**	0	-
7	**L2**	$Ni(OAc)_2$	**Ir-1**	70	55:45
8	**L3**	$Ni(OAc)_2$	**Ir-1**	0	-
9	**L4**	$Ni(OAc)_2$	**Ir-1**	20	60:40
10	**L5**	$Ni(OAc)_2$	**Ir-1**	77	90:10
11	**L6**	$Ni(OAc)_2$	**Ir-1**	75	93:7
12	**L7**	$Ni(OAc)_2$	**Ir-1**	73	7:93
13	**L8**	$Ni(OAc)_2$	**Ir-1**	58	79:21
14	**L9**	$Ni(OAc)_2$	**Ir-1**	11	92:8
15	**L10**	$Ni(OAc)_2$	**Ir-1**	0	-
16	**L6**	$NiCl_2$·glyme	**Ir-1**	64	87:13
17	**L6**	$NiBr_2$·glyme	**Ir-1**	47	90:10
18	**L6**	$Ni(OAc)_2$	**Acr-1**	0	-
19	**L6**	$Ni(OAc)_2$	**Ru-1**	0	-
20	**L6**	$Ni(OAc)_2$	**Ir-2**	31	92:8
21	**L6**	$Ni(OAc)_2$	**Ir-3**	9	79:21

[a] Unless otherwise indicated, all reactions were performed with Ir cat (1.5 mmol%), nickel catalysts (20 mmol%), chiral ligand (22 mmol%), collidine (300 mmol%), cyclopropanol (0.30 mmol) and 4-bromoacetophenone (0.10 mmol) in DMF (5 mL) at 25 °C with blue LEDs irradiation under nitrogen atmosphere. [b] Isolated yield. [c] Determined by HPLC analysis. Ad: Adamantyl. For **Acr-1**, **Ru-1**, **Ir-1** and **Ir-2**, potentials measured in V vs SCE in MeCN; for **Ir-3**, potentials measured in V vs FC^+/FC in MeCN. [1]

After investigation of photocatalysts, nickel salts and chiral ligands, $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$, $Ni(OAc)_2$ and Py-(oxazoline) ligand **L6** were optimal for this reaction.

Table S4. Investigation of solvents and bases. [a]

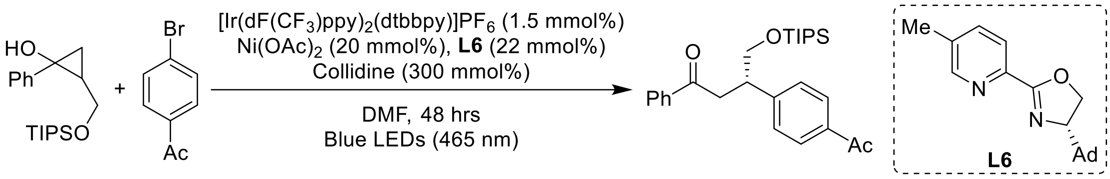


Entry.	Solvent	base	Yield (%)[b]	er[c]
1	DCE	collidine	0	-
2	DMF	collidine	75	93:7
3	DMA	collidine	71	88:12
4	DMSO	collidine	62	75:25
5	DMPU	collidine	0	-
6	DMF	pyridine	20	93.5:6.5
7	DMF	lutidine	64	93:7
8	DMF	$P^nBu_3Et^+(EtO)_2POO^-$	67	87:13

[a] Unless otherwise indicated, all reactions were performed with Ir cat (1.5 mmol%), $Ni(OAc)_2$ (20 mmol%), **L6** (22 mmol%), base (300 mmol%), cyclopropanol (0.30 mmol) and 4-bromoacetophenone (0.10 mmol) in solvent (5 mL) at 25 °C with blue LEDs irradiation under nitrogen atmosphere. [b] Isolated yield. [c] Determined by HPLC analysis.

Reactions with DMF as the solvent and collidine as the base gave the best result.

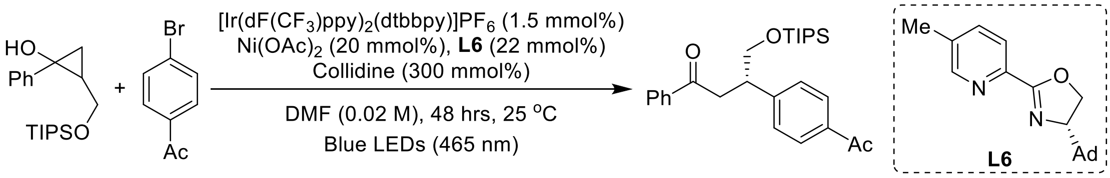
Table S5. Investigation of equivalents of cyclopropanol, reaction concentration and temperature. [a]



Entry.	Cyclopropanol (eq.)	DMF	Temp. (°C)	Yield (%)[b]	er[c]
1	2.5	5 mL	25 °C	60	93:7
2	3.0	5 mL	25 °C	75	93:7
3	3.5	5 mL	25 °C	76	93:7
4	3.0	2.5 mL	25 °C	61	92:8
5	3.0	7.5 mL	25 °C	77	93:7
6	3.0	5 mL	35 °C	77	91:9
7	3.0	5 mL	10 °C	31	90:10

[a] Unless otherwise indicated, all reactions were performed with Ir cat (1.5 mmol%), Ni(OAc)$_2$ (20 mmol%), **L6** (22 mmol%), collidine (300 mmol%), cyclopropanol and 4-bromoacetophenone (0.10 mmol) in DMF at 25 °C with blue LEDs irradiation under nitrogen atmosphere. [b] Isolated yield. [c] Determined by HPLC analysis.

Table S6. Control experiments. [a]



Entry.	Variations from the standard conditions	Yield (%)[b]	er[c]
1	no change	77	93:7
2	no Ir. catalyst	0	-
3	no Ni(OAc)$_2$	0	-
4	no ligand	0	-
5	no base	0	-
6	no light	0	-

[a] Unless otherwise indicated, all reactions were performed with Ir cat (1.5 mmol%), Ni(OAc)$_2$ (20 mmol%), **L6** (22 mmol%), collidine (300 mmol%), cyclopropanol (0.30 mmol) and 4-bromoacetophenone (0.10 mmol) in DMF (5 mL) at 25 °C with blue LEDs irradiation under nitrogen atmosphere. [b] Isolated yield. [c] Determined by HPLC analysis.

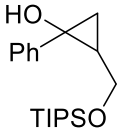
General procedure for the preparation of cyclopropanols

The β-oxy silyl ether ketone **S1** was prepared following literature reported. [2]

The cyclopropanols (**1**) was produced *via* Simmons–Smith sequence. [3]

General Procedure 1 (**GP1**): To a stirred solution of ketone **S1** (10.0 mmol, 1.0 eq.) and Et_3N (12.0 mmol, 1.2 eq.) in anhydrous DCM (20 mL) was added TMSOTf (11.0 mmol, 1.1 eq.) dropwise at 0 °C under nitrogen, then stirred at room temperature for 4 h. The reaction was cooled to 0 °C, quenched by saturated aq. $NaHCO_3$ (10 mL), extracted with DCM (20 mL×2). The combined organic layer was washed by brine, dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and got crude silyl enol ether **S2**, which can be used to next step without further purification. The solution of **S2** in anhydrous DCM (20 mL) was cooled to 0 °C under nitrogen, then added CH_2I_2 (12.0 mmol, 1.2 eq.) and Et_2Zn (1 M in hexane, 12.0 mmol, 1.2 eq.) during 15 mins. The reaction was stirred at room temperature for 6 h. The reaction was cooled to 0 °C, quenched by saturated aq. $NaHCO_3$ (10 mL) and extracted with DCM (20 mL×2). The combined organic layer was washed by brine, dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and got crude TMS-protected cyclopropanol **S3**, which was used in next step without further purification. The solution of TMS-protected cyclopropanol **S3** in methanol (10 mL) was cooled to 0°C under nitrogen, then added K_2CO_3 (1.0 mmol, 0.1 eq.) in one portion and stirred at 0°C for 1 h. The reaction was quenched with water (20 mL), extracted with DCM (20 mL×2). The combined organic layer was washed by brine, dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel and gave desired product **1**. Notably, the *trans*-cyclopropanols **1** were isolated as major isomers following this procedure and used for the corresponding asymmetric transformations.

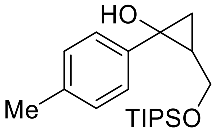
1-phenyl-2-(((triisopropylsilyl)oxy)methyl)cyclopropan-1-ol (1a)



Following general procedure **GP 1**, got product **1a** (2.2 g, dr > 20:1) as pale-yellow oil in 53% yield over three steps.

^{1}H NMR (400 MHz, CDCl$_3$) *δ* 1.03 – 1.15 (m, 21H), 1.21 – 1.27 (m, 2H), 1.46 – 1.57 (m, 1H), 3.53 (s, 1H), 3.94 (dd, *J* = 10.7, 7.6 Hz, 1H), 4.33 (dd, *J* = 10.7, 4.9 Hz, 1H), 7.21 (dt, *J* = 8.6, 4.3 Hz, 1H), 7.32 (d, *J* = 4.3 Hz, 4H); ^{13}C NMR (100 MHz, CDCl$_3$) *δ* 12.0, 18.1, 21.0, 28.8, 59.7, 63.6, 124.5, 126.3, 128.3, 144.6.

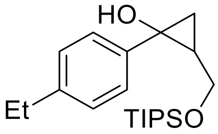
1-(p-tolyl)-2-(((triisopropylsilyl)oxy)methyl)cyclopropan-1-ol (1b)



Following general procedure **GP 1**, got product **1b** (5.0 g, dr > 20:1) as colorless oil in 47% yield over three steps.

^{1}H NMR (400 MHz, CDCl$_3$) δ 1.04 – 1.15 (m, 21H), 1.17 – 1.22 (m, 2H), 1.45 – 1.52 (m, 1H), 2.33 (s, 3H), 3.44 (s, 1H), 3.92 (dd, *J* = 10.7, 7.7 Hz, 1H), 4.30 (dd, *J* = 10.7, 5.0 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 12.0, 18.1, 20.7, 21.1, 28.5, 59.6, 63.6, 124.7, 129.0, 136.0, 141.6.

1-(4-ethylphenyl)-2-(((triisopropylsilyl)oxy)methyl)cyclopropan-1-ol (1c)

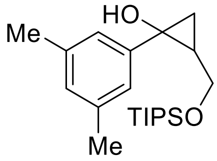


Following general procedure **GP 1**, got product **1c** (1.0 g, dr > 20:1) as pale-yellow oil in 47% yield over three steps.

^{1}H NMR (400 MHz, CDCl$_3$) *δ* 1.04 – 1.14 (m, 21H), 1.17 (d, *J* = 1.9 Hz, 2H), 1.23 (t, *J* = 7.6 Hz, 3H), 1.45 – 1.54 (m, 1H), 2.63 (q, *J* = 7.6 Hz, 2H), 3.38 (s, 1H), 3.93 (dd, *J* = 10.7, 7.7 Hz, 1H), 4.30 (dd, *J* = 10.7, 5.0 Hz, 1H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.25 (d,

J = 7.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.0, 15.7, 18.1, 20.6, 28.49, 28.52, 59.7, 63.6, 124.9, 127.8, 141.9, 142.4.

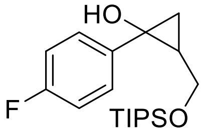
1-(3,5-dimethylphenyl)-2-(((triisopropylsilyl)oxy)methyl)cyclopropan-1-ol (1d)



Following general procedure **GP 1**, got product **1d** (2.7 g, dr > 20:1) as colorless oil in 45% yield over three steps.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04 – 1.15 (m, 21H), 1.18 (d, J = 3.2 Hz, 1H), 1.20 (s, 1H), 1.45 – 1.54 (m, 1H), 2.30 (s, 6H), 3.46 (s, 1H), 3.94 (dd, J = 10.6, 7.5 Hz, 1H), 4.29 (dd, J = 10.7, 4.9 Hz, 1H), 6.85 (s, 1H), 6.95 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 12.0, 18.1, 20.6, 21.4, 28.5, 59.7, 63.5, 122.6, 128.0, 137.8, 144.48.

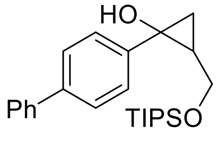
1-(4-fluorophenyl)-2-(((triisopropylsilyl)oxy)methyl)cyclopropan-1-ol (1e)



Following general procedure **GP1**, got product **1e** (1.9 g, dr > 20:1) as light-yellow oil in 69% yield over three steps.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.03 – 1.15 (m, 21H), 1.16 – 1.20 (m, 1H), 1.23 (t, J = 6.3 Hz, 1H), 1.42 – 1.51 (m, 1H), 3.58 (s, 1H), 3.93 (dd, J = 10.7, 7.6 Hz, 1H), 4.32 (dd, J = 10.7, 4.8 Hz, 1H), 6.99 (t, J = 8.7 Hz, 2H), 7.29 (dd, J = 8.8, 5.3 Hz, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 12.0, 18.1, 20.6, 28.5, 59.4, 63.5, 115.1 (d, C-F, $^2J_{C-F}$ = 21.3 Hz), 126.5 (d, C-F, $^3J_{C-F}$ = 8.1 Hz), 140.3 (d, C-F, $^4J_{C-F}$ = 3.1 Hz), 161.7 (d, C-F, $^1J_{C-F}$ = 244.4 Hz).

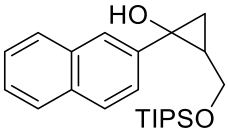
1-([1,1'-biphenyl]-4-yl)-2-(((triisopropylsilyl)oxy)methyl)cyclopropan-1-ol (1f)



Following general procedure **GP 1**, got product **1f** (2.0 g, dr = 10:1) as white waxy solid (m.p. = 37-38 °C) in 46% yield over three steps.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.03 – 1.14 (m, 21H), 1.14- 1.17 (m, 1H), 1.26 – 1.29 (m, 1H), 1.52 – 1.58 (m, 1H), 3.64 (s, 1H), 3.96 (dd, J = 10.7, 7.5 Hz, 1H), 4.33 (dd, J = 10.7, 4.8 Hz, 1H), 7.31 (t, J = 7.3 Hz, 1H), 7.30 – 7.43 (m, 4H),7.54 – 7.59 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 12.0, 18.1, 21.2, 29.0, 59.5, 63.6, 124.9, 127.1, 127.1, 127.2, 128.8, 139.2, 141.0, 143.9.

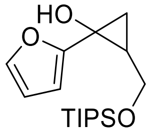
1-(naphthalen-2-yl)-2-(((triisopropylsilyl)oxy)methyl)cyclopropan-1-ol (1g)



Following general procedure **GP 1**, got product **1g** (1.8 g, dr = 10:1) as white waxy solid (m.p. = 41-42 °C) in 57% yield over three steps.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05 – 1.11 (m, 21H), 1.31 – 1.36 (m, 2H), 1.58 – 1.66 (m, 1H), 3.67 (s, 1H), 3.99 (dd, J = 10.7, 7.5 Hz, 1H), 4.36 (dd, J = 10.7, 4.9 Hz, 1H), 7.34 (dd, J = 8.6, 1.6 Hz, 1H), 7.39 – 7.48 (m, 2H), 7.78 – 7.81 (m, 3H), 7.86 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.0, 18.1, 21.0, 28.8, 59.9, 63.6, 123.1, 123.2, 125.5, 126.1, 127.6, 127.9, 128.1, 132.2, 133.4, 142.0.

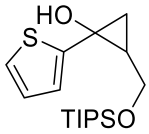
1-(furan-2-yl)-2-(((triisopropylsilyl)oxy)methyl)cyclopropan-1-ol (1h)



Following general procedure **GP 1**, got product **1h** (1.1 g, dr > 20:1) as light-yellow oil in 21% yield over three steps.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04 – 1.13 (m, 21H), 1.15 (d, J = 3.4 Hz, 1H), 1.27 (dd, J = 9.6, 5.7 Hz, 1H), 1.54 – 1.63 (m, 1H), 3.57 (s, 1H), 3.88 (dd, J = 10.8, 7.8 Hz, 1H), 4.27 (dd, J = 10.8, 5.0 Hz, 1H), 6.22 (d, J = 3.2 Hz, 1H), 6.31 (dd, J = 2.9, 2.0 Hz, 1H), 7.27 – 7.33 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.0, 18.0, 18.8, 26.5, 55.6, 63.2, 104.5, 110.4, 141.2, 156.8.

1-(thiophen-2-yl)-2-(((triisopropylsilyl)oxy)methyl)cyclopropan-1-ol (1i)

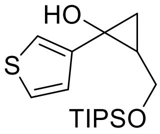


Following general procedure **GP 1**, got product **1i** (1.1 g, dr > 20:1) as light-yellow oil in 32% yield over three steps.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.06 – 1.15 (m, 21H), 1.24 – 1.31 (m, 2H), 1.51 – 1.61 (m, 1H), 3.71 (s, 1H), 3.89 (dd, J = 10.8, 7.7 Hz, 1H), 4.31 (dd, J = 10.8, 4.9 Hz, 1H), 6.83 (dd, J = 3.6, 1.2 Hz, 1H), 6.93 (dd, J = 5.0, 3.5 Hz, 1H), 7.16 (dd, J = 5.0, 1.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 12.0, 18.1, 22.0, 29.7, 57.4, 63.4, 121.6, 123.7, 126.8, 150.0.

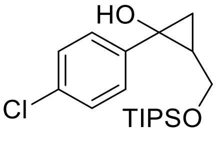
1-(thiophen-3-yl)-2-(((triisopropylsilyl)oxy)methyl)cyclopropan-1-ol (1j)



Following general procedure **GP 1**, got product **1j** (1.1 g, dr > 20:1) as light-yellow oil in 27% yield over three steps.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.02 – 1.15 (m, 21H), 1.16 – 1.20 (m, 1H), 1.20 – 1.24 (m, 1H), 1.42 – 1.53 (m, 1H), 3.60 (s, 1H), 3.92 (dd, J = 10.7, 7.4 Hz, 1H), 4.29 (dd, J = 10.7, 4.9 Hz, 1H), 6.84 (d, J = 5.0 Hz, 1H), 7.15 (d, J = 2.9 Hz, 1H), 7.23 – 7.28 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.9, 18.1, 20.8, 28.5, 58.0, 63.4, 118.6, 124.6, 125.9, 146.7.

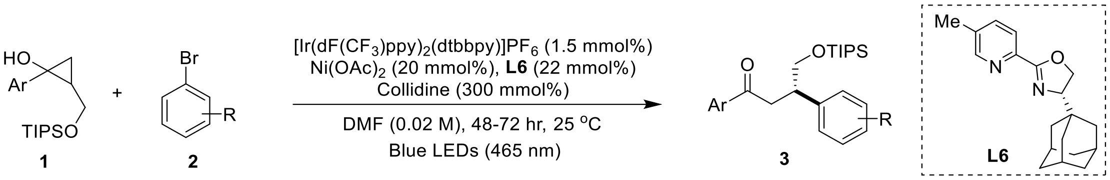
1-(4-chlorophenyl)-2-(((triisopropylsilyl)oxy)methyl)cyclopropan-1-ol (1k)



Following general procedure **GP 1**, got product **1k** (2.7 g, dr > 20:1) as light-yellow oil in 56% yield over three steps.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.02 – 1.17 (m, 21H), 1.17 – 1.22 (m, 1H), 1.27 (t, J = 6.4 Hz, 1H), 1.41 – 1.55 (m, 1H), 3.67 (s, 1H), 3.93 (dd, J = 10.8, 7.5 Hz, 1H), 4.33 (dd, *J* = 10.8, 4.8 Hz, 1H), 7.20 – 7.33 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.9, 18.0, 21.2, 29.0, 59.2, 63.5, 125.8, 128.4, 132.0, 143.4.

General procedure for asymmetric β-arylation of cyclopropanols

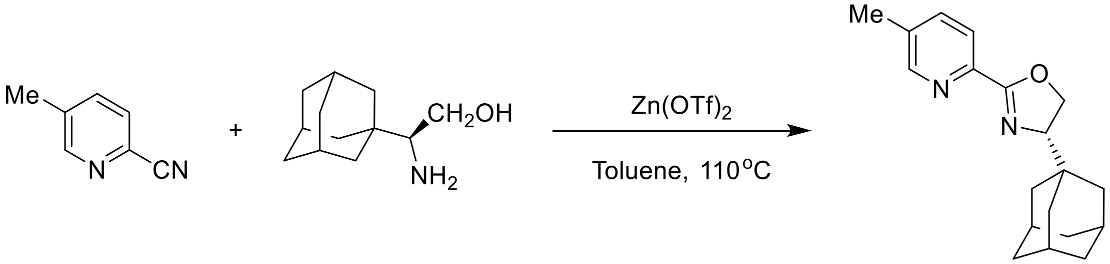


General Procedure 2 (**GP 2**): To a 10 mL vial equipped with a stir bar was added [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (1.7 mg, 1.5 μmol, 1.5 mmol%), Nickel(II) acetate (3.6 mg, 20 μmol, 20 mmol%), **L6** (6.6 mg, 22 μmol, 22 mmol%) and aryl bromide **2** (0.1 mmol). The vial was sealed, evacuated and backfilled with nitrogen three times, then anhydrous DMF (5mL) was injected under nitrogen protection, stirred at room temperature for 10 min. Cyclopropanol **1** (0.3 mmol) and collidine (36.5 mg, 0.3 mmol) was injected *via* micro syringe respectively. After degassing the reaction mixture with Freeze-Pump-Thaw methods for three cycles, it was stirred and irradiated with the corresponding blue LEDs photoreactor at 25 °C (cooled by ethanol circulator bath) for 48~72 h. The reaction mixture was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (petroleum ether /ethyl acetate = 100:1 to 20:1 as the eluent) to give the product **3**.

Procedure for preparation of L6

(S)-2-(adamantan-1-yl)-2-aminoethan-1-ol was synthesized following literature reported method. [4]

L6 was prepared as following according to literature reported. [5]

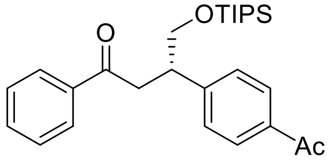


L6

To a 100 mL two-necked round bottomed flask equipped with reflux condenser was added 5-methylpicolinonitrile (1.0 g, 8.46 mmol), (S)-2-(adamantan-1-yl)-2-aminoethan-1-ol (1.8 g, 9.31 mmol) and anhydrous toluene (35 mL), then anhydrous zinc triflate (0.31 g, 0.85 mmol) was added under nitrogen protection. The reaction mixture was heated to reflux and stirred at this temperature for 24 h. Cooled the reaction to room temperature, dilute the mixture with EtOAc (30 mL) and washed with saturated aq. $NaHCO_3$ solution (30mL). The organic layer was separated and the aqueous layer was extracted the with EtOAc (30 mL×2). Combined of the organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure, the residue was purified by column chromatography on silica gel (dichloromethane /methanol = 100:1 to 20:1 as the eluent) to give the product (1.6 g) as a white solid in 64% yield. The white solid was recrystallized from ethanol to give **L6** (1.4 g) in 88% yield.

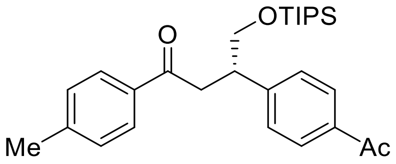
White solid, m.p. 142-143 °C; $[\alpha]_D^{20.0}$ = -78.8 (0.1, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.48 (d, *J* = 12.0 Hz, 3H), 1.68 – 1.74 (m, 9H), 2.00 (s, 3H), 2.39 (s, 3H), 3.94 (t, *J* = 9.2 Hz, 1H), 4.35 (t, *J* = 8.8 Hz, 1H), 4.49 (t, *J* = 8.8 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 8.53 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 18.6, 28.3, 35.8, 37.2, 38.6, 67.8, 76.6, 123.5, 135.5, 137.0, 144.4, 150.2, 162.4; HRMS (ESI-quadrupole) m/z calcd. for $C_{19}H_{25}N_2O$ $[M+H]^+$: 297.1961, found: 297.1962.

(*S*)-3-(4-acetylphenyl)-1-phenyl-4-((triisopropylsilyl)oxy)butan-1-one (3a)



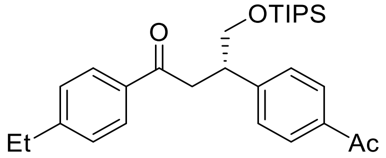
Colorless oil; 33 mg, 75% yield; 93:7 er; $[\alpha]_D^{20.0}$ = -13.9 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 70/30, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 7.0 min, t (minor) = 12.6 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 0.97 – 1.08 (m, 21H), 2.57 (s, 3H), 3.60 – 3.74 (m, 2H), 3.31 (dd, *J* = 6.8, 16.0 Hz, 1H), 3.94 (dd, *J* = 9.7, 5.0 Hz, 1H), 3.85 (dd, *J* = 6.3, 9.7 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.88 (d, *J* = 8.3 Hz, 2H), 7.94 (d, *J* = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 12.0, 18.0, 26.6, 40.5, 44.0, 67.0, 128.1, 128.4, 128.5, 128.6, 133.1, 135.7, 137.1, 148.3, 197.9, 198.6; HRMS (ESI- quadrupole) m/z calcd. for $C_{27}H_{39}O_3Si$ $[M+H]^+$: 439.2663, found: 439.2667.

(*S*)-3-(4-acetylphenyl)-1-(*p*-tolyl)-4-((triisopropylsilyl)oxy)butan-1-one (3b)



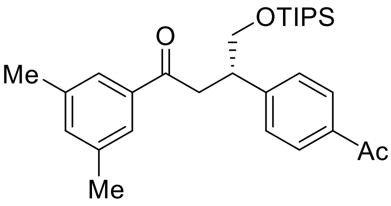
Colorless oil; 35 mg, 77% yield; 93:7 er; $[\alpha]_D^{20.0}$ = -15.9 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 70/30, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 5.6 min, t (minor) = 9.1 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 0.97 – 1.08 (m, 21H), 2.40 (s, 3H), 2.56 (s, 3H), 3.28 (dd, *J* = 10.0, 18.8Hz, 1H), 3.60 – 3.69 (m, 2H), 3.84 (dd, *J* = 6.2, 9.7 Hz, 1H), 3.93 (dd, *J* = 5.0, 9.7 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.84 (d, *J* = 8.1 Hz, 2H), 7.87 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 12.0, 18.0, 21.7, 26.6, 40.3, 44.0, 67.0, 128.2, 128.4, 128.5, 129.3, 134.6, 135.6, 143.9, 148.4, 197.9, 198.3; HRMS (ESI-quadrupole) m/z calcd. for $C_{28}H_{41}O_3Si$ $[M+H]^+$: 453.2819, found: 453.2822.

(*S*)-3-(4-acetylphenyl)-1-(4-ethylphenyl)-4-((triisopropylsilyl)oxy)butan-1-one (3c)



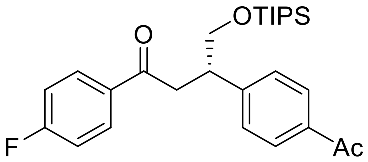
Colorless oil; 33 mg, 70% yield; 93:7 er; $[\alpha]_D^{20.0}$ = -14.5 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 70/30, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 6.4 min, t (minor) = 12.8 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 0.94 – 1.09 (m, 21H), 1.25 (t, *J* = 7.6 Hz, 3H), 2.57 (s, 3H), 2.70 (q, *J* = 7.6 Hz, 2H), 3.30 (dd, *J* = 10.0, 18.8 Hz, 1H), 3.61 – 3.72 (m, 2H), 3.84 (dd, *J* = 6.2, 9.6 Hz, 1H), 3.93 (dd, *J* = 4.8, 9.6 Hz, 1H), 7.26 (d, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 12.0, 15.3, 18.0, 26.6, 29.0, 40.3, 44.0, 67.1, 128.1, 128.3, 128.4, 128.5, 134.8, 135.6, 148.4, 150.1, 197.9, 198.3; HRMS (ESI- quadrupole) m/z calcd. for $C_{29}H_{43}O_3Si$ $[M+H]^+$: 467.2976, found: 467.2971.

(*S*)-3-(4-acetylphenyl)-1-(3,5-dimethylphenyl)-4-((triisopropylsilyl)oxy)butan-1-one (3d)



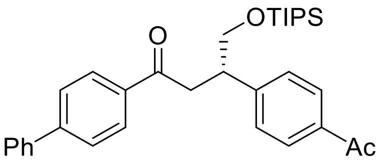
Colorless oil; 32 mg, 68% yield; 91:9 er; $[\alpha]_D^{20.0}$ = -7.2 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IC-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 95/5, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 7.1 min, t (minor) = 8.4 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 0.97 – 1.08 (m, 21H), 2.35 (s, 6H), 2.57 (s, 3H), 3.20– 3.31 (m, 1H), 3.60 – 3.70 (m, 2H), 3.85 (dd, *J* = 6.2, 9.8 Hz, 1H), 3.93 (dd, *J* = 4.9, 9.7, Hz, 1H), 7.18 (s, 1H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.54 (s, 2H), 7.87 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.0, 18.0, 21.3, 26.6, 40.6, 44.1, 67.1, 125.9, 128.4, 128.5, 134.8, 135.7, 137.2, 138.3, 148.4, 197.9, 199.1; HRMS (ESI- quadrupole) m/z calcd. for $C_{29}H_{43}O_3Si$ [M+H]$^+$: 467.2976, found: 467.2976.

(*S*)-3-(4-acetylphenyl)-1-(4-fluorophenyl)-4-((triisopropylsilyl)oxy)butan-1-one (3e)



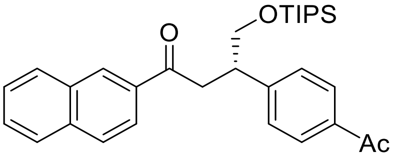
Colorless oil; 28 mg, 60% yield; 93:7 er; $[\alpha]_D^{20.0}$ = -8.1 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 70/30, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 5.8 min, t (minor) = 7.3 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 0.98 – 1.09 (m, 21H), 2.57 (s, 3H), 3.27 (dd, *J* = 6.8, 16.0 Hz, 1H), 3.60 – 3.71 (m, 2H), 3.84 (dd, *J* = 6.2, 9.7 Hz, 1H), 3.94 (dd, *J* = 4.7, 9.7 Hz, 1H), 7.11 (t, *J* = 8.6 Hz, 2H), 7.39(d, *J* = 8.0 Hz, 2H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.97 (dd, *J* = 5.5, 8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*, 12.0, 18.0, 26.6, 40.3, 44.0, 67.0, 115.7, (d, C-F, $^2J_{C\text{-}F}$ = 21.7 Hz), 128.3, 128.5, 130.7 (d, C-F, $^3J_{C\text{-}F}$ = 9.2 Hz,), 133.5 (d, C-F, $^4J_{C\text{-}F}$ = 2.8 Hz), 135.7, 148.1, 165.80 (d, C-F, $^1J_{C\text{-}F}$ = 253.3 Hz), 197.0, 197.8; HRMS (ESI-quadrupole) m/z calcd. for $C_{27}H_{38}FO_3Si$ [M+H]$^+$: 457.2569, found: 457.2568.

(*S*)-1-([1,1'-biphenyl]-4-yl)-3-(4-acetylphenyl)-4-((triisopropylsilyl)oxy)butan-1-one (3f)



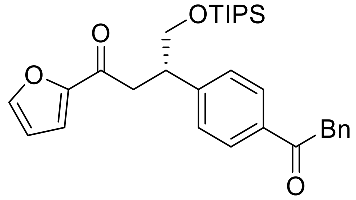
Colorless oil; 27 mg, 52% yield; 90:10 er; $[\alpha]_D^{20.0}$ = -13.5 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 70/30, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 8.2 min, t (minor) = 13.8 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 0.99 –1.09 (m, 21H), 2.57 (s, 3H), 3.34 (dd, *J* = 7.1, 16.0, Hz, 1H), 3.70 (m, 2H), 3.87 (dd, *J* = 6.2, 9.7, Hz, 1H), 3.96 (dd, *J* = 4.9, 9.7 Hz, 1H), 7.40 – 7.45 (m, 3H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.62 (d, *J* = 7.2 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.89 (d, *J* = 8.2 Hz, 2H), 8.02 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 12.0, 18.0, 26.7, 40.5, 44.0, 67.1, 127.3, 127.4, 128.3, 128.4, 128.5, 128.7, 129.0, 135.7, 135.8, 139.9, 145.8, 148.3, 197.9, 198.3; HRMS (ESI-quadrupole) m/z calcd. for $C_{33}H_{43}O3Si$ $[M+H]^+$: 515.2976, found: 515.2978.

(*S*)-3-(4-acetylphenyl)-1-(naphthalen-2-yl)-4-((triisopropylsilyl)oxy)butan-1-one (3g)



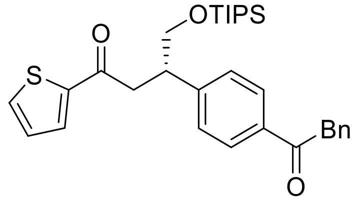
Colorless oil; 24 mg, 50% yield; 90:10 er; $[\alpha]_D^{20.0}$ = -11.7 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 70/30, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 15.6 min, t (minor) = 18.7 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 0.99 – 1.08 (m, 21H), 2.56 (s, 3H), 3.43 (dd, *J* = 7.9, 16.8 Hz, 1H), 3.68 – 3.74 (m, 1H), 3.84 (dd, *J* = 5.8, 16.8, Hz, 1H), 3.90 (dd, *J* = 6.6, 9.6, Hz, 1H), 3.99 (dd, *J* = 5.2, 9.7, Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.53 – 7.61 (m, 2H), 7.88 (t, *J* = 8.1 Hz, 4H), 7.94 (d, *J* = 7.9 Hz, 1H), 7.99 (d, *J* = 8.6 Hz, 1H), 8.47 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 12.0, 18.0, 26.6, 40.5, 44.1, 67.1, 123.9, 126.8, 127.8, 128.4, 128.5, 129.6, 129.8, 132.6, 134.4, 135.6, 135.7, 148.3, 197.9, 198.6; HRMS (ESI- quadrupole) m/z calcd. for $C_{31}H_{41}O_3Si$ $[M+H]^+$: 489.2819, found: 489.2822.

(*S*)-1-(furan-2-yl)-3-(4-(2-phenylacetyl)phenyl)-4-((triisopropylsilyl)oxy)butan-1-one (3h)



Colorless oil; 29 mg, 58% yield; 89:11 er; $[\alpha]_D^{20.0}$ = -8.4 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 80/20, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 7.6 min, t (minor) = 8.8 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 – 1.11 (m, 21H), 3.17 (dd, *J* = 7.8, 16.5 Hz, 1H), 3.48 (dd, *J* = 6.4, 16.5 Hz, 1H), 3.62 (m, 1H), 3.82 (dd, *J* = 6.5, 9.7 Hz, 1H), 3.90 (dd, *J* = 5.3, 9.7 Hz, 1H), 4.24 (s, 2H), 6.50 (dd, *J* = 1.7, 3.6 Hz, 1H), 7.15 (d, *J* = 3.5 Hz, 1H), 7.21 – 7.27 (m, 3H), 7.28 – 7.34 (m, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 7.54 (d, *J* = 1.5 Hz, 1H), 7.93 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.0, 18.0, 40.3, 43.7, 45.5, 67.0, 112.3, 117.0, 126.9, 128.4, 128.7, 128.8, 129.5, 134.7, 135.2, 146.3, 148.1, 152.9, 187.8, 197.3; HRMS (ESI- quadrupole) m/z calcd. for $C_{31}H_{41}O_4Si$ [M+H]$^+$: 505.2769, found: 505.2773.

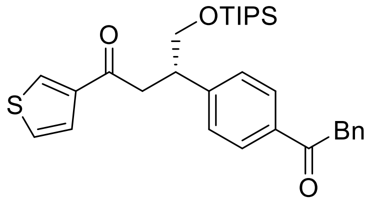
(*S*)-3-(4-(2-phenylacetyl)phenyl)-1-(thiophen-2-yl)-4-((triisopropylsilyl)oxy)butan-1-one (3i)



Colorless oil; 29 mg, 56% yield; 88:12 er; $[\alpha]_D^{20.0}$ = -9.7 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 90/10, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 13.1 min, t (minor) = 14.1 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 – 1.10 (m, 21H), 3.24 (dd, *J* = 6.8, 11.2 Hz, 1H), 3.55 – 3.66 (m, 2H), 3.83 (dd, *J* = 6.1, 9.7 Hz, 1H), 3.92 (dd, *J* = 4.7, 9.7 Hz, 1H), 4.24 (s, 2H), 7.11 (t, *J* = 3.6 Hz, 1H), 7.21 – 7.27 (m, 3H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.38 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 3.9 Hz, 1H), 7.72 (d, *J* = 2.8 Hz, 1H), 7.93 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.0, 18.0, 41.2, 44.1, 45.5, 66.9, 126.9, 128.1, 128.4, 128.7, 128.8, 129.5, 131.9, 133.7, 134.7, 135.2, 144.4, 148.1, 191.5, 197.3; HRMS (ESI- quadrupole) m/z calcd. for $C_{31}H_{41}O_3SSi$ [M+H]$^+$: 521.2540, found: 521.2545.

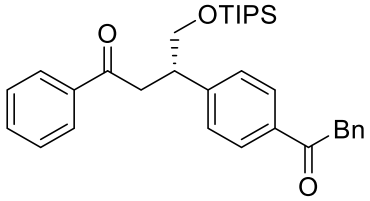
(*S*)-3-(4-(2-phenylacetyl)phenyl)-1-(thiophen-3-yl)-4-((triisopropylsilyl)oxy)-

butan-1-one (3j)



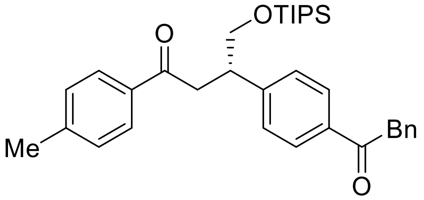
Colorless oil; 29 mg, 55% yield; 91:9 er; $[\alpha]_D^{20.0}$ = -8.1 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 90/10, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 15.6 min, t (minor) = 18.7 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 0.97 – 1.08 (m, 21H), 3.21 (dd, *J* = 6.8, 16.0 Hz, 1H), 3.53 – 3.68 (m, 2H), 3.82 (dd, *J* = 6.2, 9.7 Hz, 1H), 3.91 (dd, *J* = 5.0, 9.7 Hz, 1H), 4.24 (s, 2H), 7.22 – 7.26 (m, 3H), 7.27 – 7.34 (m, 3H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 5.1 Hz, 1H), 7.93 (d, *J* = 8.3 Hz, 2H), 8.04 (d, *J* = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 12.0, 18.0, 41.7, 43.9, 45.5, 67.0, 126.4, 126.9, 127.0, 128.4, 128.7, 128.8, 129.5, 132.0, 134.8, 135.1, 142.4, 148.3, 192.9, 197.3; HRMS (ESI- quadrupole) m/z calcd. for $C_{31}H_{41}O_3SSi$ [M+H]$^+$: 521.2540, found: 521.2542.

(*S*)-1-phenyl-3-(4-(2-phenylacetyl)phenyl)-4-((triisopropylsilyl)oxy)butan-1-one (3k)



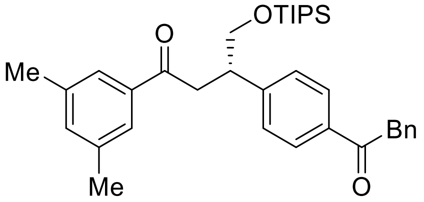
Colorless oil; 36 mg, 71% yield; 92:8 er; $[\alpha]_D^{20.0}$ = -10.1 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 90/10, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 13.0 min, t (minor) = 14.3 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 0.95 – 1.08 (m, 21H), 3.30 (dd, *J* = 6.8, 16.0 Hz, 1H), 3.59 – 3.74 (m, 2H), 3.83 (dd, *J* = 6.3, 9.6 Hz, 1H), 3.92 (dd, *J* = 4.8, 9.7 Hz, 1H), 4.24 (s, 2H), 7.21 – 7.27 (m, 3H), 7.31 (t, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.3 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 12.0, 18.0, 40.4, 43.9, 45.5, 67.0, 126.9, 128.1, 128.5, 128.6, 128.7, 128.8, 129.5, 133.2, 134.8, 135.1, 137.1, 148.4, 197.3, 198.7. HRMS (ESI- quadrupole) m/z calcd. for $C_{33}H_{43}O_3Si$ [M+H]$^+$: 515.2976, found: 515.2976.

(*S*)-3-(4-(2-phenylacetyl)phenyl)-1-(*p*-tolyl)-4-((triisopropylsilyl)oxy)butan-1-one (3l)



Colorless oil; 39 mg, 73% yield; 93:7 er; $[\alpha]_D^{20.0}$ = -9.8 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 70/30, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 8.6 min, t (minor) = 13.2 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 – 1.06 (m, 21H), 2.40 (s, 3H), 3.27 (dd, J = 10.0, 18.8 Hz, 1H), 3.58 – 3.69 (m, 2H), 3.83 (dd, J = 6.2, 9.6 Hz, 1H), 3.92 (dd, J = 4.9, 9.6 Hz, 1H), 4.24 (s, 2H), 7.20 – 7.26 (m, 5H), 7.31 (t, J = 7.6 Hz, 2H), 7.37 (d, J = 8.1 Hz, 2H), 7.84 (d, J = 8.1 Hz, 2H), 7.93 (d, J = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.0, 18.0, 21.7, 40.3, 44.0, 45.5, 67.0, 126.9, 128.2, 128.5, 128.7, 128.8, 129.3, 129.5, 134.6, 134.8, 135.1, 143.9, 148.5, 197.3, 198.3; HRMS (ESI- quadrupole) m/z calcd. for $C_{34}H_{45}O_3Si$ $[M+H]^+$: 529.3132, found: 529.3133.

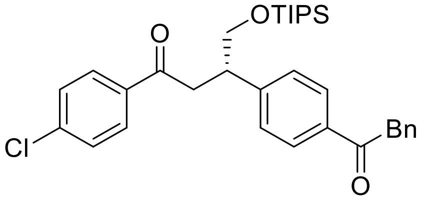
(*S*)-1-(3,5-dimethylphenyl)-3-(4-(2-phenylacetyl)phenyl)-4-((triisopropylsilyl)-oxy)butan-1-one (3m)



Colorless oil; 41 mg, 75% yield; 91:9 er; $[\alpha]_D^{20.0}$ = -11.7 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IC-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 80/20, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 10.8 min, t (minor) = 12.5 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.07 – 0.96 (m, 21H), 2.34 (s, 6H), 3.31 – 3.19 (m, 1H), 3.70 – 3.57 (m, 2H), 3.87 – 3.80 (m, 1H), 3.96 – 3.88 (m, 1H), 4.24 (s, 2H), 7.17 (s, 1H), 7.27 – 7.21 (m, 3H), 7.34 – 7.28 (m, 2H), 7.38 (d, J = 8.3 Hz, 2H), 7.53 (s, 2H), 7.93 (d, J = 8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.0, 18.0, 21.3, 40.5, 44.0, 45.5, 67.1, 125.9, 126.9, 128.5, 128.7, 128.8, 129.5, 134.7, 134.8, 135.1, 137.3, 138.3, 148.5, 197.3, 199.0; HRMS (ESI- quadrupole) m/z calcd. for $C_{35}H_{47}O_3Si$ $[M+H]^+$: 543.3289, found:

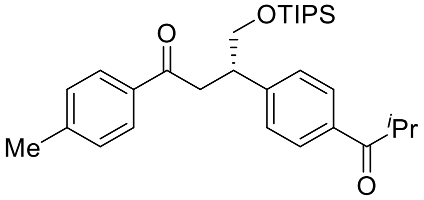
543.3290.

(*S*)-1-(4-chlorophenyl)-3-(4-(2-phenylacetyl)phenyl)-4-((triisopropylsilyl)oxy)-butan-1-one (3n)



Colorless oil; 36 mg, 65% yield; 92:8 er; $[\alpha]_D^{20.0}$ = -7.7 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 80/20, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 10.1 min, t (minor) = 12.7 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 – 1.05 (m, 21H), 3.25 (dd, *J* = 6.4, 16.4 Hz,1H), 3.63 (m, 2H), 3.83 (dd, *J* = 6.3, 9.7, Hz, 1H), 3.92 (dd, *J* = 4.8, 9.6, Hz, 1H), 4.24 (s, 2H), 7.25 (m, 3H), 7.31 (t, *J* = 6.8 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.87 (d, *J* = 8.6 Hz, 2H), 7.93 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.0, 18.0, 40.4, 43.9, 45.5, 66.9, 126.9, 128.4, 128.7, 128.9, 129.0, 129.5, 129.6, 134.7, 135.2, 135.4, 139.6, 148.1, 197.3, 197.4; HRMS (ESI- quadrupole) m/z calcd. for $C_{33}H_{12}ClO_3Si$ $[M+H]^+$: 549.2586, found: 549.2585.

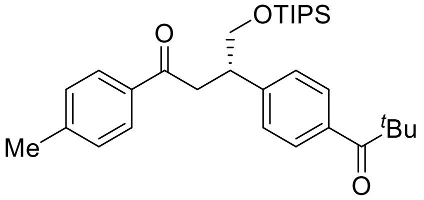
(*S*)-3-(4-isobutyrylphenyl)-1-(*p*-tolyl)-4-((triisopropylsilyl)oxy)butan-1-one (3o)



Colorless oil; 40 mg, 83% yield; 92:8 er; $[\alpha]_D^{20.0}$ = -10.4 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 70/30, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 5.4 min, t (minor) = 8.7 min]; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 0.97 – 1.07 (m, 21H), 1.18 (s, 3H), 1.20 (s, 3H), 2.40 (s, 3H), 3.29 (dd, *J* = 9.6, 18.8 Hz, 1H), 3.48 – 3.56 (m, 1H), 3.59 – 3.69 (m, 2H), 3.84 (dd, *J* = 6.2, 9.6 Hz, 1H), 3.93 (dd, *J* = 4.9, 9.7 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.87 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.0, 18.0, 19.2, 19.3, 21.7, 35.3, 40.3, 44.0, 67.1, 128.2, 128.4, 128.5, 129.3, 134.6, 134.7, 143.9, 148.1, 198.4, 204.2; HRMS (ESI- quadrupole) m/z calcd. for $C_{30}H_{45}O_3Si$

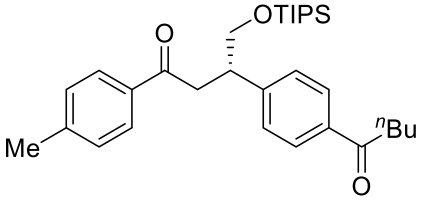
$[M+H]^+$: 481.3132, found: 481.3131.

(*S*)-3-(4-pivaloylphenyl)-1-(p-tolyl)-4-((triisopropylsilyl)oxy)butan-1-one (3p)



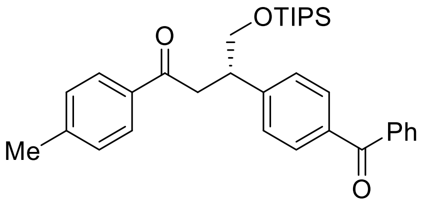
Colorless oil; 37 mg, 76% yield; 94:6 er; $[\alpha]_D^{20.0}$ = -9.8 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 90/10, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 6.2 min, t (minor) = 11.2 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 – 1.04 (m, 21H), 1.33 (s, 9H), 2.40 (s, 3H), 3.22 – 3.32 (m, 1H), 3.58 – 3.68 (m, 2H), 3.83 (dd, *J* = 6.3, 9.6 Hz, 1H), 3.92 (dd, *J* = 4.9, 9.7 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.85 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.0, 18.0, 21.7, 28.2, 40.3, 43.8, 44.2, 67.2, 127.8, 128.2, 128.3, 129.3, 134.7, 136.6, 143.8, 146.0, 198.5, 208.5; HRMS (ESI- quadrupole) m/z calcd. for $C_{31}H_{47}O_3Si$ $[M+H]^+$: 495.3289, found: 495.3287.

(*S*)-3-(4-pentanoylphenyl)-1-(*p*-tolyl) -4-((triisopropylsilyl)oxy)butan-1-one (3q)



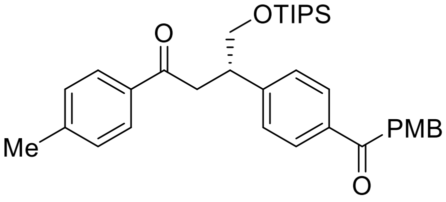
Colorless oil; 41 mg, 83% yield; 95:5 er; $[\alpha]_D^{20.0}$ = -12.1 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 90/10, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 9.0 min, t (minor) = 17.6 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (t, *J* = 7.3 Hz, 3H), 0.97 – 1.05 (d, *J* = 5.9 Hz, 21H), 1.38 (dt, *J* = 7.4, 14.7 Hz, 2H), 1.70 (dt, *J* = 7.4, 14.7 Hz, 2H), 2.40 (s, 3H), 2.92 (t, *J* = 7.4 Hz, 2H), 3.28 (dd, *J* = 10.0, 19.2 Hz, 1H), 3.59 – 3.70 (m, 2H), 3.84 (dd, *J* = 6.2, 9.7 Hz, 1H), 3.93 (dd, *J* = 4.9, 9.7 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.0, 14.0, 18.0, 21.7, 22.6, 26.7, 38.4, 40.3, 44.0, 67.1, 128.2, 128.3, 129.3, 134.7, 135.6, 143.9, 148.1, 198.3, 200.3; HRMS (ESI- quadrupole) m/z calcd. for $C_{31}H_{47}O_3Si$ $[M+H]^+$: 495.3289, found: 495.3292.

(*S*)-3-(4-benzoylphenyl)-1-(*p*-tolyl)-4-((triisopropylsilyl)oxy)butan-1-one (3r)



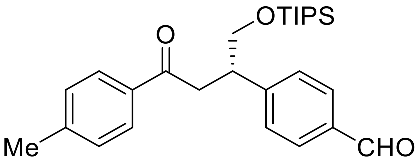
Colorless oil; 39 mg, 75% yield; 92:8 er; $[\alpha]_D^{20.0}$ = -9.1 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 70/30, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 5.4 min, t (minor) = 9.7 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 0.97 – 1.10 (m, 21H), 2.40 (s, 3H), 3.32 (dd, *J* = 9.4, 18.5 Hz, 1H), 3.63 – 3.71 (m, 2H), 3.87 (dd, *J* = 6.1, 9.6 Hz, 1H), 3.96 (dd, *J* = 4.9, 9.7 Hz, 1H), 7.25 (d, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.77 (d, *J* = 7.1 Hz, 2H), 7.86 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 12.0, 18.0, 21.7, 40.3, 44.0, 67.2, 128.1, 128.3, 129.3, 130.1, 130.3, 132.3, 134.7, 135.9, 137.9, 143.9, 147.8, 196.5, 198.4; HRMS (ESI- quadrupole) m/z calcd. for $C_{33}H_{43}O_3Si$ $[M+H]^+$: 515.2976, found: 515.2971.

(*S*)-3-(4-(4-methoxybenzoyl)phenyl)-1-(*p*-tolyl)-4-((triisopropylsilyl)oxy)butan-1-one (3s)



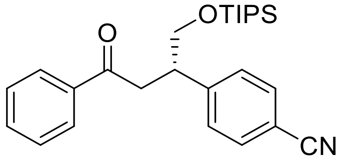
Colorless oil; 41 mg, 75% yield; 94:6 er; $[\alpha]_D^{20.0}$ = -14.2 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 60/40, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 6.9 min, t (minor) = 15.5 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 0.97 – 1.06 (m, 21H), 2.40 (s, 3H), 3.31 (dd, *J* = 9.6, 18.4 Hz, 1H), 3.61 – 3.73 (m, 2H), 3.84 – 3.91 (m, 4H), 3.96 (dd, *J* = 4.9, 9.7 Hz, 1H), 6.94 (d, *J* = 8.8 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.68 (d, *J* = 8.1 Hz, 2H), 7.79 (d, *J* = 8.8 Hz, 2H), 7.86 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 12.0, 18.1, 21.7, 40.4, 44.0, 55.6, 67.2, 113.6, 128.0, 128.3, 129.3, 130.0, 130.5, 132.6, 134.8, 136.6, 143.9, 147.2, 163.2, 195.4, 198.4; HRMS (ESI- quadrupole) m/z calcd. for $C_{34}H_{45}O_4Si$ $[M+H]^+$: 545.3082, found: 545.3080.

(*S*)-3-(4-formylphenyl)-1-(*p*-tolyl)-4-((triisopropylsilyl)oxy)butan-1-one (3t)



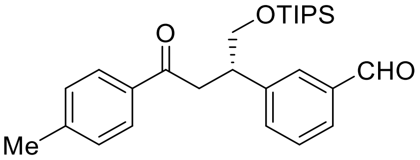
Colorless oil; 29 mg, 65% yield; 92:8 er; $[\alpha]_D^{20.0}$ = -15.1 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 85/15, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 7.0 min, t (minor) = 8.9 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 0.94 – 1.07 (m, 21H), 2.40 (s, 3H), 3.30 (dd, *J* = 9.4, 18.6, Hz, 1H), 3.59 – 3.71 (m, 2H), 3.86 (dd, *J* = 5.9, 9.7 Hz, 1H), 3.94 (dd, *J* = 5.0, 9.7 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.80 (d, *J* = 8.1 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 2H), 9.96 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 12.0, 18.0, 21.7, 40.2, 44.1, 67.0, 128.2, 128.9, 129.4, 129.9, 134.6, 135.1, 144.0, 150.2, 192.1, 198.2; HRMS (ESI- quadrupole) m/z calcd. for $C_{27}H_{39}O_3Si$ $[M+H]^+$: 439.2663, found: 439.2661.

(*S*)-1-phenyl-3-(4-cyanophenyl)-4-((triisopropylsilyl)oxy)butan-1-one (3u)



Colorless oil; 24 mg, 56% yield; 91:9 er; $[\alpha]_D^{20.0}$ = -10.2 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 90/10, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 6.3 min, t (minor) = 8.2 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 0.94 – 1.10 (m, 21H), 3.31 (dd, *J* = 9.6, 18.8 Hz, 1H), 3.59 – 3.71 (m, 2H), 3.85 (dd, *J* = 5.6, 9.8 Hz, 1H), 3.93 (dd, *J* = 5.1, 9.8 Hz, 1H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 3H), 7.93 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 11.9, 18.0, 40.2, 43.8, 66.8, 110.4, 119.1, 128.1, 128.7, 129.0, 132.2, 133.3, 136.9, 148.4, 198.3; HRMS (ESI- quadrupole) m/z calcd. for $C_{26}H_{36}NO_2Si$ $[M+H]^+$: 422.2510, found: 422.2510.

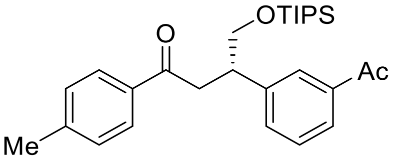
(*S*)-3-(3-formylphenyl)-1-(*p*-tolyl)-4-((triisopropylsilyl)oxy)butan-1-one (3v)



Colorless oil; 24 mg, 55% yield; 95:5 er; $[\alpha]_D^{20.0}$ = -13.2 (0.1, CH_2Cl_2); [Daicel

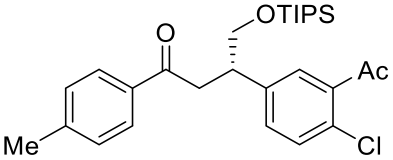
CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 90/10, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 7.7 min, t (minor) = 17.9 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 0.95 – 1.05 (m, 21H), 2.40 (s, 3H), 3.30 (dd, *J* = 9.6, 18.8 Hz, 1H), 3.62 – 3.72 (m, 2H), 3.86 (dd, *J* = 5.9, 9.6 Hz, 1H), 3.94 (dd, *J* = 5.0, 9.7 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.82 (s, 1H), 7.85 (d, *J* = 8.1 Hz, 2H), 9.98 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 12.0, 18.0, 21.7, 40.4, 43.6, 67.2, 128.2, 128.3, 129.0, 129.1, 129.4, 134.6, 134.8, 136.5, 143.9, 144.0, 192.5, 198.3; HRMS (ESI- quadrupole) m/z calcd. for $C_{27}H_{39}O_3Si$ $[M+H]^+$: 439.2663, found: 439.2663.

(*S*)-3-(3-acetylphenyl)-1-(*p*-tolyl)-4-((triisopropylsilyl)oxy)butan-1-one (3w)



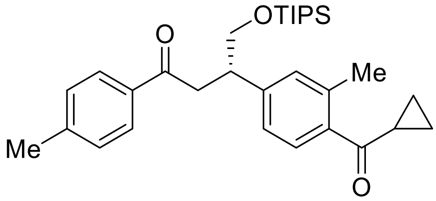
Colorless oil; 27 mg, 63% yield; 95:5 er; $[\alpha]_D^{20.0}$ = -13.6 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 90/10, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 5.9 min, t (minor) = 13.1 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 0.97 – 1.06 (m, 21H), 2.40 (s, 3H), 2.58 (s, 3H), 3.23 – 3.35 (m, 1H), 3.60 – 3.72 (m, 2H), 3.85 (dd, *J* = 6.2, 9.6 Hz, 1H), 3.93 (dd, *J* = 4.9, 9.6 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.78 (d, *J* = 7.7 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 2H), 7.89 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 12.0, 18.0, 21.7, 26.7, 40.4, 43.8, 67.2, 126.8, 127.7, 128.3, 128.5, 129.3, 133.3, 134.7, 137.2, 143.3, 143.9, 198.3, 198.4; HRMS (ESI- quadrupole) m/z calcd. for $C_{28}H_{41}O_3Si$ $[M+H]^+$: 453.2819, found: 453.2819.

(*S*)-3-(3-acetyl-4-chlorophenyl)-1-(*p*-tolyl)-4-((triisopropylsilyl)oxy)butan-1-one (3x)



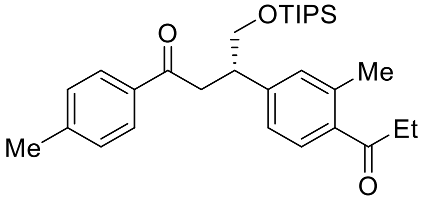
Colorless oil; 31 mg, 63% yield; 94:6 er; $[\alpha]_D^{20.0}$ = -15.1 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 90/10, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 6.7 min, t (minor) = 13.0 min]; ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.97 – 1.07 (m, 21H), 2.40 (s, 3H), 2.62 (s, 3H), 3.22 (dd, J = 6.8, 16.0 Hz, 1H), 3.54 – 3.67 (m, 2H), 3.81 (dd, J = 5.9, 9.7 Hz, 1H), 3.90 (dd, J = 5.0, 9.6 Hz, 1H), 7.24 (d, J = 8.0 Hz, 2H), 7.28 – 7.37 (m, 2H), 7.48 (d, J = 1.9 Hz, 1H), 7.83 (d, J = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 12.0, 18.0, 21.7, 30.8, 40.3, 43.2, 67.0, 128.2, 129.0, 129.3, 129.4, 130.5, 132.1, 134.6, 138.9, 142.1, 144.0, 198.1, 200.7; HRMS (ESI- quadrupole) m/z calcd. for $C_{28}H_{39}ClO_3Si$ [M+H]$^+$: 487.2430, found: 487.2433.

(*S*)-3-(4-(cyclopropanecarbonyl)-3-methylphenyl)-1-(*p*-tolyl)-4-((triisopropylsilyl)oxy)butan-1-one (3y)



Colorless oil; 36 mg, 76% yield; 94:6 er; $[\alpha]_D^{20.0}$ = -9.6 (0.1, CH$_2$Cl$_2$); [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 90/10, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 6.0 min, t (minor) = 11.6 min]; ^{1}H NMR (400 MHz, CDCl$_3$) δ ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.97 – 1.04 (m, 21H), 1.05 – 1.08 (m, 2H), 1.18 – 1.21 (m, 2H), 2.38 – 2.41 (m, 1H), 2.40 (s, 3H), 2.45 (s, 3H), 3.26 (dd, J = 7.7, 16.6 Hz, 1H), 3.52 – 3.61 (m, 1H), 3.67 (dd, J = 5.7, 16.7 Hz, 1H), 3.81 (dd, J = 6.9, 9.5 Hz, 1H), 3.92 (dd, J = 4.9, 9.5 Hz, 1H), 7.14 – 7.21 (m, 2H), 7.24 (d, J = 8.9 Hz, 2H), 7.65 (d, J = 7.9 Hz, 1H), 7.86 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 11.8, 12.0, 18.1, 20.5, 21.0, 21.7, 40.4, 43.8, 67.2, 125.3, 128.3, 128.8, 129.3, 131.4, 134.8, 137.3, 137.9, 143.8, 145.8, 198.5, 204.8; HRMS (ESI- quadrupole) m/z calcd. for $C_{31}H_{45}O_3Si$ [M+H]$^+$: 493.3132, found: 493.3129.

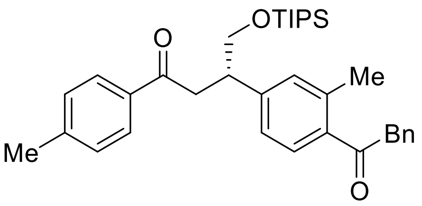
(*S*)-3-(3-methyl-4-propionylphenyl)-1-(*p*-tolyl)-4-((triisopropylsilyl)oxy)butan-1-one (3z)



Colorless oil; 35 mg, 72% yield; 94:6 er; $[\alpha]_D^{20.0}$ = -10.1 (0.1, CH$_2$Cl$_2$); [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 90/10, v = 1.0

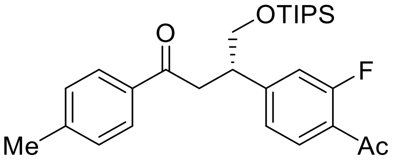
mL·min^{-1}, λ = 254 nm, t (major) = 5.9 min, t (minor) = 9.8 min]; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 0.98 – 1.08 (m, 21H), 1.17 (t, *J* = 7.3 Hz, 3H), 2.40 (s, 3H), 2.47 (s, 3H), 2.88 (q, *J* = 7.2 Hz, 2H), 3.26 (dd, *J* = 7.7, 16.7 Hz, 1H), 3.53 – 3.60 (m, *J* = 6.2 Hz, 1H), 3.66 (dd, *J* = 5.8, 16.7 Hz, 1H), 3.81 (dd, *J* = 6.8, 9.6 Hz, 1H), 3.91 (dd, *J* = 5.1, 9.6 Hz, 1H), 7.17 (d, *J* = 6.5 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 8.5, 12.0, 18.0, 21.6, 21.7, 34.5, 40.3, 43.8, 67.1, 125.4, 128.3, 128.8, 129.3, 131.8, 134.7, 136.1, 138.4, 143.8, 146.2, 198.5, 204.5; HRMS (ESI- quadrupole) m/z calcd. for $C_{30}H_{45}O_3Si$ [M+H]$^+$: 481.3132, found: 481.3133.

(*S*)-3-(3-methyl-4-(2-phenylacetyl)phenyl)-1-(*p*-tolyl)-4-((triisopropylsilyl)oxy)-butan-1-one (za)



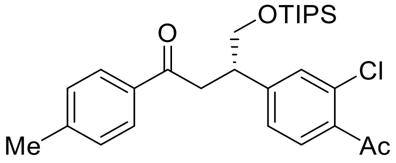
Colorless oil; 39 mg, 72% yield; 95:5 er; $[\alpha]_D^{20.0}$ = -12.9 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 90/10, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 9.8 min, t (minor) = 15.6 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 0.96 – 1.06 (m, 21H), 2.40 (s, 3H), 2.44 (s, 3H), 3.25 (dd, *J* = 7.5, 16.6 Hz, 1H), 3.52 – 3.60 (m, 1H), 3.64 (dd, *J* = 5.9, 16.6 Hz, 1H), 3.81 (dd, *J* = 6.5, 9.7 Hz, 1H), 3.91 (dd, *J* = 5.1, 9.7 Hz, 1H), 4.18 (s, 2H), 7.14 – 7.21 (m, 3H), 7.23 (d, *J* = 9.2 Hz, 4H), 7.30 (t，*J* = 6.8 Hz, 2H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 12.0, 18.0, 21.7, 21.8, 40.3, 43.8, 48.2, 67.1, 125.4, 126.8, 128.3, 128.6, 129.2, 129.3, 129.6, 132.0, 134.7, 134.8, 135.6, 139.2, 143.9, 146.6, 198.4, 200.8; HRMS (ESI- quadrupole) m/z calcd. for $C_{35}H_{47}O_3Si$ [M+H]$^+$: 543.3289, found: 543.3286.

(*S*)-3-(4-acetyl-3-fluorophenyl)-1-(*p*-tolyl)-4-((triisopropylsilyl)oxy)butan-1-one (3zb)



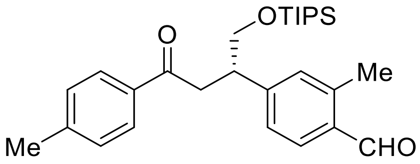
Colorless oil; 32 mg, 69% yield; 92:8 er; $[\alpha]_{D}^{20.0}$ = -21.5 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 90/10, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 5.8 min, t (minor) = 8.5 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 – 1.07 (m, 21H), 2.40 (s, 3H), 2.60 (d, *J* = 4.5 Hz, 3H), 3.27 (dd, *J* = 9.6, 18.7 Hz, 1H), 3.62 (m, 2H), 3.84 (dd, *J* = 5.6, 9.6 Hz, 1H), 3.93 (dd, *J* = 4.7, 9.6 Hz, 1H), 7.10 (d, *J* = 12.4 Hz, 1H), 7.15 (d, *J* = 8.1 Hz, 1H), 7.25 (d, *J* = 8.1 Hz, 2H), 7.79 (t, *J* = 7.9 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.0, 18.0, 21.7, 31.4 (d, C-F, J_{C-F} = 7.4 Hz), 40.1, 43.6, 66.8, 116.4 (d, C-F, $^{2}J_{C-F}$ = 24.0 Hz), 123.9 (d, C-F, $^{2}J_{C-F}$ = 12.9 Hz), 124.2 (d, $^{4}J_{C-F}$ = 2.9 Hz), 128.2, 129.4, 130.5 (d, $^{3}J_{C-F}$ = 2.9 Hz), 134.6, 144.1, 151.2 (d, C-F, $^{3}J_{C-F}$ = 8.4 Hz), 162.3 (d, C-F, $^{1}J_{C-F}$ = 254.9 Hz), 195.7, 197.9; HRMS (ESI- quadrupole) m/z calcd. for $C_{28}H_{40}FO_3Si$ $[M+H]^+$: 471.2725, found: 471.2720.

(*S*)-3-(4-acetyl-3-chlorophenyl)-1-(*p*-tolyl)-4-((triisopropylsilyl)oxy)butan-1-one (3zc)



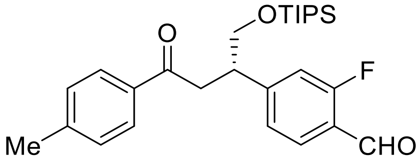
Colorless oil; 35 mg, 71% yield; 91:9 er; $[\alpha]_{D}^{20.0}$ = -16.7 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 90/10, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 5.7 min, t (minor) = 8.3 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 – 1.07 (m, 21H), 2.41 (s, 3H), 2.62 (s, 3H), 3.20 – 3.32 (dd, *J* = 6.4, 16.0 Hz, 1H), 3.54 – 3.67 (m, 2H), 3.83 (dd, *J* = 5.4, 9.7 Hz, 1H), 3.92 (dd, *J* = 4.6, 9.5 Hz, 1H), 7.25 (d, *J* = 9.0 Hz, 3H), 7.39 (s, 1H), 7.51 (d, *J* = 7.9 Hz, 1H), 7.85 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.0, 18.0, 21.7, 30.7, 40.1, 43.3, 66.8, 126.9, 128.2, 129.4, 129.8, 130.5, 131.6, 134.6, 137.0, 144.1, 148.0, 197.9, 200.0; HRMS (ESI- quadrupole) m/z calcd. for $C_{28}H_{40}ClO_3Si$ $[M+H]^+$: 487.2430, found: 487.2433.

(*S*)-3-(3-methyl-4-formylphenyl)-1-(*p*-tolyl)-4-((triisopropylsilyl)oxy)butan-1-one (3zd)



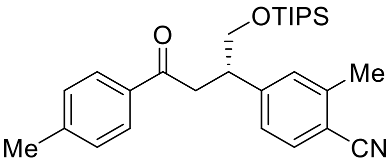
Colorless oil; 30 mg, 66% yield; 94:6 er; $[\alpha]_D^{20.0}$ = -12.9 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 90/10, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 6.1 min, t (minor) = 8.8 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 – 1.06 (m, 21H), 2.40 (s, 3H), 2.63 (s, 3H), 3.28 (dd, *J* = 7.1, 16.3 Hz, 1H), 3.56 – 3.69 (m, 2H), 3.84 (dd, *J* = 6.1, 9.7 Hz, 1H), 3.93 (dd, *J* = 5.0, 9.6 Hz, 1H), 7.20 (s, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 2H), 10.20 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.0, 18.0, 19.7, 21.7, 40.2, 44.0, 67.0, 126.1, 128.3, 129.3, 131.8, 132.4, 132.9, 134.6, 140.6, 144.0, 149.2, 192.5, 198.2; HRMS (ESI- quadrupole) m/z calcd. for $C_{28}H_{41}O_3Si$ [M+H]$^+$: 453.2819, found: 453.2821.

(*S*)-3-(3-fluoro-4-formylphenyl)-1-(*p*-tolyl)-4-((triisopropylsilyl)oxy)butan-1-one (3ze)



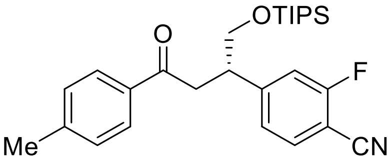
Colorless oil; 23 mg, 51% yield; 88:12 er; $[\alpha]_D^{20.0}$ = -7.2 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 90/10, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 5.9 min, t (minor) = 8.5 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 – 1.08 (m, 21H), 2.41 (s, 3H), 3.29 (dd, *J* = 9.6, 19.2 Hz, 1H), 3.59 – 3.67 (m, 2H), 3.86 (dd, *J* = 5.4, 9.7 Hz, 1H), 3.94 (dd, *J* = 5.0, 9.8 Hz, 1H), 7.14 (d, *J* = 11.6 Hz, 1H), 7.21 (d, *J* = 8.0, 1H), 7.25 (d, *J* = 8.3, 2H), 7.78 (t, *J* = 7.6 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 2H), 10.30 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.0, 18.0, 21.7, 40.0, 43.9, 66.7, 116.2 (d, C-F, $^2J_{C-F}$ = 20.6 Hz), 122.6 (d, C-F, $^3J_{C-F}$ = 8.1 Hz), 124.6 (d, C-F, $^3J_{C-F}$ = 3.1 Hz), 128.2, 128.6 (d, C-F, $^4J_{C-F}$ = 2.3 Hz), 129.4, 134.5, 144.2, 153.2 (d, C-F, $^2J_{C-F}$ = 8.4 Hz), 164.7 (d, C-F, $^1J_{C-F}$ = 258.5 Hz), 187.0 (d, C-F, J_{C-F} = 6.2 Hz), 197.7; HRMS (ESI- quadrupole) m/z calcd. for $C_{27}H_{38}FO_3Si$ [M+H]$^+$: 457.2569, found: 457.2568.

(*S*)-3-(4-cyano-3-methylphenyl)-1-(*p*-tolyl)-4-((triisopropylsilyl)oxy)butan-1-one (3zf)



Colorless oil; 28 mg, 63% yield; 94.5:5.5 er; $[\alpha]_D^{20.0}$ = -12.5 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 70/30, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 4.4 min, t (minor) = 5.9 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 0.96 – 1.04 (m, 21H), 2.41 (s, 3H), 2.50 (s, 3H), 3.26 (dd, *J* = 6.8, 16.0 Hz, 1H), 3.53 – 3.66 (m, 2H), 3.82 (dd, *J* = 5.8, 9.7 Hz, 1H), 3.90 (dd, *J* = 5.0, 9.6 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 7.22 – 7.27 (m, 3H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 12.0, 18.0, 20.6, 21.7, 40.0, 43.8, 66.9, 110.8, 118.4, 126.1, 128.2, 129.4, 130.3, 132.5, 134.5, 141.8, 144.1, 148.3, 198.0; HRMS (ESI- quadrupole) m/z calcd. for $C_{28}H_{40}NO_2Si$ $[M+H]^+$: 450.2823, found: 450.2827.

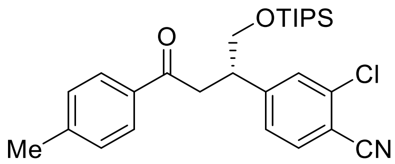
(*S*)-3-(4-cyano-3-fluorophenyl)-1-(*p*-tolyl)-4-((triisopropylsilyl)oxy)butan-1-one (3zg)



Colorless oil; 26 mg, 57% yield; 92:8 er; $[\alpha]_D^{20.0}$ = -9.5 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 90/10, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 6.6 min, t (minor) = 11.0 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 0.96 – 1.07 (m, 21H), 2.41 (s, 3H), 3.28 (dd, *J* = 7.2, 16.4 Hz, 1H), 3.54 – 3.67 (m, 2H), 3.85 (dd, *J* = 5.2, 9.7 Hz, 1H), 3.93 (dd, *J* = 5.1, 9.7 Hz, 1H), 7.20 (dd, *J* = 6.0, 7.9 Hz, 2H), 7.25 (d, *J* = 7.6 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 11.9, 18.0, 21.7, 39.9, 43.7, 66.6, 99.3 (d, C-F, $^2J_{C\text{-}F}$ = 15.5 Hz), 114.2, 116.2 (d, C-F, $^2J_{C\text{-}F}$ = 19.5 Hz), 124.9 (d, C-F, $^3J_{C\text{-}F}$ = 3.3 Hz), 128.2, 129.4, 133.1, 134.3, 144.3, 152.0 (d, C-F, $^3J_{C\text{-}F}$ = 7.6 Hz), 163.1 (d, C-F, $^1J_{C\text{-}F}$ = 258.4 Hz), 197.4; HRMS (ESI- quadrupole) m/z calcd. for $C_{27}H_{37}FNO_2Si$ $[M+H]^+$: 454.2572, found: 454.2574.

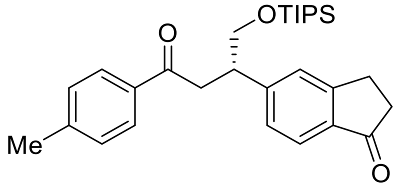
(*S*)-3-(4-cyano-3-chlorophenyl)-1-(*p*-tolyl)-4-((triisopropylsilyl)oxy)butan-1-one

(3zh)



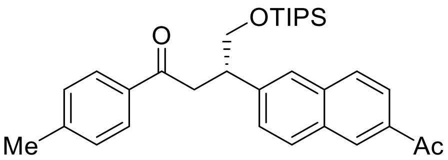
Colorless oil; 23 mg, 50% yield; 88:12 er; $[\alpha]_D^{20.0}$ = -8.1 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 90/10, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 6.6 min, t (minor) = 10.5 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 0.97 – 1.08 (m, 21H), 2.41 (s, 3H), 3.28 (dd, *J* = 9.6, 19.2 Hz, 1H), 3.53 – 3.65 (m, 2H), 3.85 (dd, *J* = 4.9, 9.7 Hz, 1H), 3.92 (dd, *J* = 5.0, 9.7 Hz, 1H), 7.25 (d, *J* = 7.4 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.50 (s, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 11.9, 18.0, 21.7, 39.8, 43.5, 66.6, 111.3, 116.2, 127.3, 128.2, 129.4, 129.9, 133.7, 134.3, 136.6, 144.3, 150.5, 197.4; HRMS (ESI- quadrupole) m/z calcd. for $C_{27}H_{37}ClNO_2Si$ $[M+H]^+$: 470.2277, found: 470.2275.

(*S*)-5-(4-oxo-4-(*p*-tolyl)-1-((triisopropylsilyl)oxy)butan-2-yl)-2,3-dihydro-1H-inden-1-one (3zi)



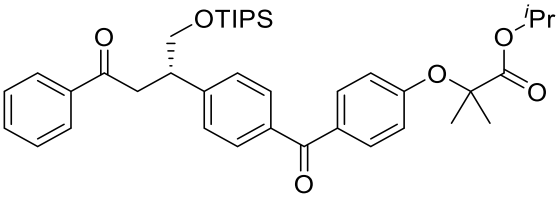
Colorless oil; 37 mg, 80% yield; 94:6 er; $[\alpha]_D^{20.0}$ = -11.3 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 90/10, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 10.3 min, t (minor) = 18.5 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 0.97 – 1.09 (m, 21H), 2.40 (s, 3H), 2.66 (t, *J* = 5.6 Hz, 2H), 3.09 (t, *J* = 5.6 Hz, 2H), 3.31 (dd, *J* = 10.0, 18.4, Hz, 1H), 3.62 – 3.71 (m, 2H), 3.85 (dd, *J* = 6.2, 9.6 Hz, 1H), 3.94 (dd, *J* = 4.9, 9.7 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 1H), 7.41 (s, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 12.0, 18.0, 21.7, 25.8, 36.5, 40.4, 44.3, 67.1, 123.7, 126.4, 127.5, 128.2, 129.3, 134.6, 135.8, 144.0, 150.3, 155.5, 198.2, 206.7; HRMS (ESI- quadrupole) m/z calcd. for $C_{29}H_{41}O_3Si$ $[M+H]^+$: 465.2819, found: 465.2821.

(*S*)-3-(6-acetylnaphthalen-2-yl)-1-(*p*-tolyl)-4-((triisopropylsilyl)oxy)butan-1-one (3zj)



Colorless oil; 28 mg, 56% yield; 94:6 er; $[\alpha]_D^{20.0}$ = -11.8 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 90/10, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 10.5 min, t (minor) = 17.0 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 – 1.08 (m, 21H), 2.40 (s, 3H), 2.71 (s, 3H), 3.38 (dd, J = 9.2, 18.4 Hz, 1H), 3.71 – 3.81 (m, 2H), 3.93 (dd, J = 6.1, 9.7 Hz, 1H), 4.02 (dd, J = 4.6, 9.7 Hz, 1H), 7.24 (d, J = 8.0 Hz, 2H), 7.53 (dd, J = 1.7, 8.5 Hz, 1H), 7.77 (d, J = 1.6 Hz, 1H), 7.81 (d, J = 8.6 Hz, 1H), 7.88 (t, J = 8.7 Hz, 3H), 7.99 (dd, J = 1.8, 8.6 Hz, 1H), 8.41 (d, J = 1.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.0, 18.0, 21.7, 26.7, 40.6, 44.2, 67.2, 124.0, 126.5, 127.8, 128.2, 128.3, 129.3, 129.6, 130.0, 131.5, 134.2, 134.7, 135.8, 143.4, 143.9, 198.2, 198.5; HRMS (ESI- quadrupole) m/z calcd. for $C_{32}H_{43}O_3Si$ [M+H]$^+$: 503.2976, found: 503.2978.

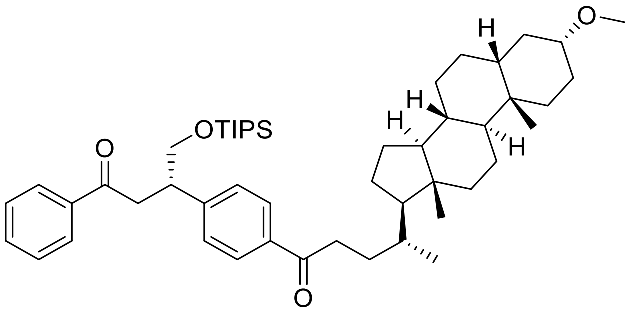
isopropyl (S)-2-methyl-2-(4-(4-(4-oxo-4-phenyl-1-((triisopropylsilyl)oxy)butan-2-yl)benzoyl)phenoxy)propanoate (3zk)



White solid, m.p. = 48-49 ºC; 45 mg, 70% yield; 94:6 er; $[\alpha]_D^{20.0}$ = -7.9 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 90/10, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 8.8 min, t (minor) = 15.9 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 – 1.08 (m, 21H), 1.20 (d, J = 6.3 Hz, 6H), 1.65 (s, 6H), 3.28 – 3.41 (m, 1H), 3.62 – 3.75 (m, 2H), 3.87 (dd, J = 6.0, 10.0 Hz, 1H), 3.96 (dd, J = 4.7, 9.7 Hz, 1H), 5.05 – 5.12 (m, 1H), 6.85 (d, J = 8.8 Hz, 2H), 7.39 (d, J = 8.1 Hz, 2H), 7.45 (t, J = 7.6 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.67 (d, J = 8.1 Hz, 2H), 7.72 (d, J = 8.8 Hz, 2H), 7.96 (d, J = 7.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.0, 18.0, 21.6, 25.4, 25.5, 40.5, 44.0, 67.2, 69.4, 79.4, 117.2, 128.0, 128.1, 128.6, 130.0, 130.9, 132.0, 133.1, 136.5, 137.2, 147.1, 159.5, 173.3, 195.3, 198.8; HRMS (ESI- quadrupole) m/z calcd.

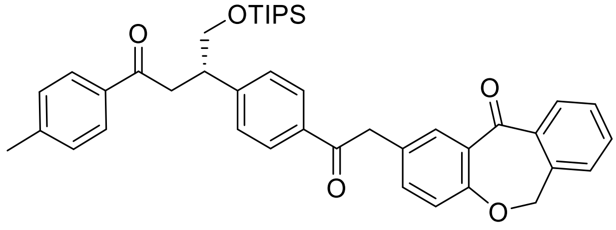
for $C_{39}H_{53}O_6Si$ $[M+H]^+$: 645.3606, found: 645.3603.

(*R*)-4-((3*R*,5*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-methoxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)-1-(4-((S)-4-oxo-4-phenyl-1-((triisopropylsilyl)oxy)butan-2-yl)phenyl)pentan-1-one (3zl)



Colorless oil; 49 mg, 63% yield; 94:6 er; $[\alpha]_D^{20.0}$ = -20.8 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 85/15, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 11.1 min, t (minor) = 12.3 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.64 (s, 3H), 0.80 – 0.92 (m, 5H), 0.96 – 1.07 (m, 21H), 1.09 – 1.15 (m, 5H), 1.18 – 1.33 (m, 7H), 1.34 – 1.51 (m, 7H), 1.63 – 1.97 (m, 8H), 2.77 – 2.89 (m, 1H), 2.90 – 3.01 (m, 1H), 3.13 – 3.19 (m, 1H), 3.26 – 3.34 (m, 1H), 3.35 (s, 3H), 3.60 – 3.76 (m, 2H), 3.80 – 3.88 (m, 1H), 3.94 (dd, J = 9.6, 4.5 Hz, 1H), 7.38 (d, J = 8.0 Hz, 2H), 7.44 (t, J = 7.5 Hz, 2H), 7.55 (t, J = 7.3 Hz, 1H), 7.87 (d, J = 8.0 Hz, 2H), 7.94 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.0, 12.2, 18.0, 18.7, 20.9, 23.5, 24.3, 26.5, 26.9, 27.4, 28.3, 30.7, 32.9, 35.0, 35.4, 35.5, 35.6, 36.0, 40.3, 40.4, 40.5, 42.2, 42.9, 44.0, 55.6, 56.1, 56.6, 67.1, 80.5, 128.1, 128.3, 128.4, 128.7, 133.1, 135.7, 137.1, 148.0, 198.8, 200.9. HRMS (ESI- quadrupole) m/z calcd. for $C_{50}H_{77}O_4Si$ $[M+H]^+$: 769.5586, found: 769.5582.

(*S*)-2-(2-oxo-2-(4-(4-oxo-4-(p-tolyl)-1-((triisopropylsilyl)oxy)butan-2-yl)phenyl)ethyl)dibenzo[b,e]oxepin-11(6H)-one (3zm)

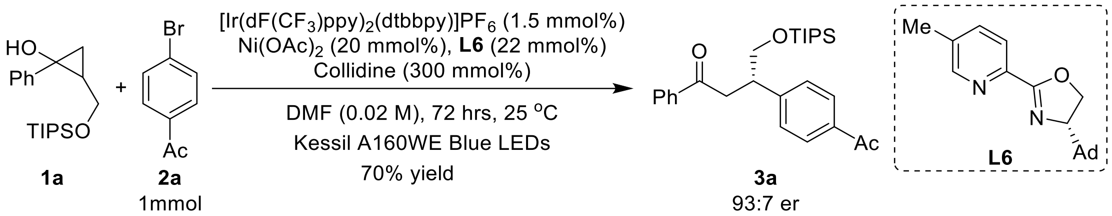


Light-yellow amorphous foam; 44 mg, 68% yield; 95:5 er; $[\alpha]_D^{20.0}$ = -12.0 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 60/40, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 19.4 min, t (minor) = 32.2 min]; ^{1}H NMR (400

MHz, $CDCl_3$) δ 0.95 – 1.08 (m, 21H), 2.40 (s, 3H), 3.28 (dd, J = 9.6, 18.8 Hz, 1H), 3.58 – 3.73 (m, 2H), 3.84 (dd, J = 6.1, 9.6 Hz, 1H), 3.93 (dd, J = 4.9, 9.7 Hz, 1H), 4.27 (s, 2H), 5.18 (s, 2H), 7.02 (d, J = 8.4 Hz, 1H), 7.24 (d, J = 8.0 Hz, 2H), 7.38 (m, 4H), 7.46 (t, J = 7.1 Hz, 1H), 7.55 (t, J = 7.8 Hz, 1H), 7.84 (d, J = 8.1 Hz, 2H), 7.89 (d, J = 7.5 Hz, 1H), 7.94 (d, J = 8.2 Hz, 2H), 8.11 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.0, 18.0, 21.7, 40.3, 44.0, 44.3, 67.0, 73.7, 121.1, 125.3, 127.8, 128.2, 128.5, 128.6, 128.7, 129.2, 129.3, 129.6, 132.7, 132.8, 134.6, 134.9, 135.7, 136.7, 140.6, 143.9, 148.8, 160.4, 190.9, 197.0, 198.3; HRMS (ESI- quadrupole) m/z calcd. for $C_{42}H_{49}O_5Si$ $[M+H]^+$: 661.3344, found: 661.3345.

Derivatization of chiral β-aryl ketones

Large-scale experiment



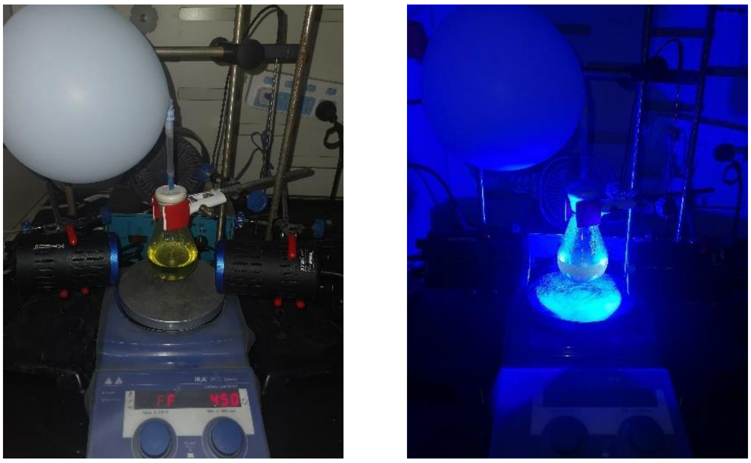
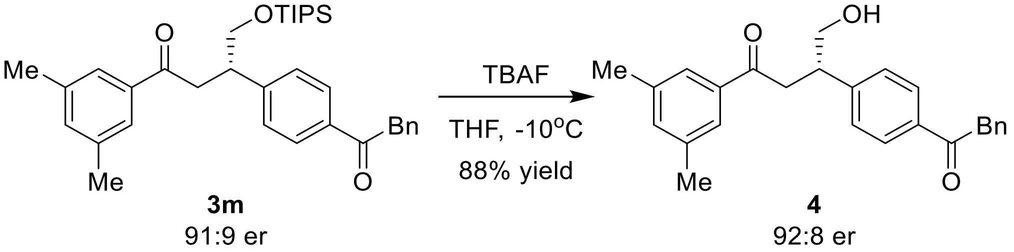


Figure S3: Set-up for large scale reaction under blue LEDs irradiation.

To a 100 mL round bottomed flask was added [Ir(dFCF$_3$ppy)$_2$dtbbpy]PF$_6$ (16.9 mg, 0.015 mmol, 1.5 mmol%), Nickel(II) acetate (35.5 mg, 0.2 mmol, 20 mmol%), **L6** (65.5 mg, 0.22 mmol, 22 mmol%), followed by **2a** (200 mg, 1 mmol). The reaction flask was sealed, evacuated and backfilled with nitrogen three times, then degassed DMF (50 mL) was injected under nitrogen protection, stirred at room temperature for 30 min. Cyclopropanol **1a** (0.97 g, 3 mmol) and collidine (0.365 g, 0.4 mL, 3 mmol) was injected *via* syringe respectively. The reaction mixture was degassed by Freeze-Pump-Thaw methods for three cycles, then stirred under nitrogen atmosphere with the irradiated of two Kessil® A160WE blue LED lamps (5 cm away from reaction flask) at room temperature (cooled by fan) for 72 h. The reaction mixture was poured into water (150 mL), then added EA (30 mL) to the mixture, stirred for 20 min. The organic layer was separated and the aqueous layer was extracted with EA (20 mL×2). Combined of the organic layer was washed by brine, dried over anhydrous Na$_2$SO$_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (petroleum ether /ethyl acetate = 100:1 to 20:1 as the eluent) to afford **3a.**

Colorless oil; 308 mg, 70% yield; 93:7 er; $[\alpha]_D^{20.0}$ = -12.0 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 70/30, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 7.0 min, t (minor) = 12.4 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 0.95 – 1.08 (m, 21H), 2.57 (s, 3H), 3.31 (dd, *J* = 15.9, 5.7 Hz, 1H), 3.58 – 3.76 (m, 2H), 3.81 – 3.90 (m, 1H), 3.91 – 3.99 (m, 1H), 7.39 (d, *J* = 7.0 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.88 (d, *J* = 6.9 Hz, 2H), 7.94 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 12.0, 18.0, 26.6, 40.5, 44.0, 67.1, 128.1, 128.4, 128.5, 128.7, 133.1, 135.7, 137.1, 148.3, 197.9, 198.7; HRMS (ESI- quadrupole) m/z calcd. for $C_{27}H_{39}O_3Si$ $[M+H]^+$: 439.2663, found: 439.2666.

Deprotection of TIPS

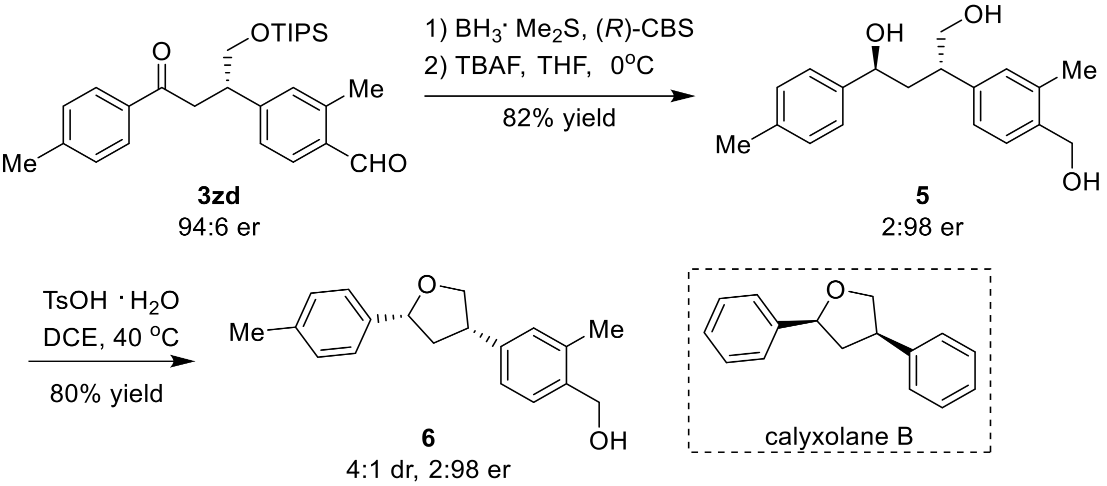


To a solution of **3m** (30 mg, 0.05 mmol) in anhydrous THF (2 mL) was added TBAF (78 μL, 0.08 mmol, 1.5 eq., 1M in THF) at -10 °C. The reaction was stirred at -10 °C for 2 hrs. After that, the reaction mixture was concentrated under reduced pressure, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1 to 2:1 as the eluent) quickly to afford product **4** (19 mg, 88% yield) as amorphous foam (Note: Product **4** should be stored at -20 °C).

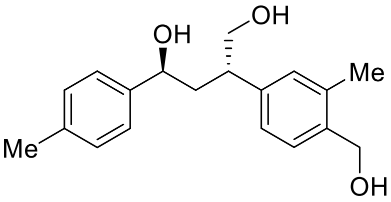
(*S*)-1-(3,5-dimethylphenyl)-4-hydroxy-3-(4-(2-phenylacetyl)phenyl)butan-1-one (4)

Amorphous foam; 19 mg, 88% yield; 92:8 er; $[\alpha]_D^{20.0}$ = -14.4 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 60/40, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 13.5 min, t (minor) = 18.2 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 2.35 (s, 6H), 3.36 (dd, *J* = 6.7, 17.3 Hz, 1H), 3.47 (dd, *J* = 6.9, 17.3 Hz, 1H), 3.62 – 3.72 (m, 1H), 3.80 – 3.92 (m, 2H), 4.25 (s, 2H), 7.19 (s, 1H), 7.22 – 7.28 (m, 3H), 7.32 (t, *J* = 6.7 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.54 (s, 2H), 7.98 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 41.1, 43.5, 45.6, 66.7, 126.0, 127.0, 128.3, 128.8, 129.2, 129.5, 134.6, 135.0, 135.4, 136.9, 138.4, 147.9, 197.2, 199.0; HRMS (ESI- quadrupole) m/z calcd. for $C_{26}H_{27}O_3$ $[M+H]^+$: 387.1955, found: 387.1951.

Synthesis of *ent*-calyxolane B analog



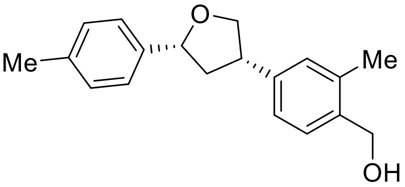
(1*S*,3*S*)-3-(4-(hydroxymethyl)-3-methylphenyl)-1-(*p*-tolyl)butane-1,4-diol (5)



To a solution of (*R*)-CBS (7.4 mg, 0.026 mmol) in anhydrous THF (2 mL) was added $BH_3{\cdot}Me_2S$ (133μL, 0.266 mmol, 4.0 eq., 2M in THF) at 0°C with nitrogen protection, stirred for a while. To the mixture was added a solution of **3zd** (30.0 mg, 0.066 mmol) in anhydrous THF (1 mL) slowly. After the addition, the reaction was allowed to stirred at room temperature for 3 h. The reaction was cooled to 0°C, added methanol (1 mL) slowly, followed by brine (10 mL). The mixture was extracted by EA (10 mL×2). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4. The organic layer was concentrated to dryness and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1 to 2:1 as the eluent) to afford the intermediate (26.5 mg) as colorless oil. The intermediate (26.5 mg, 0.058 mmol) was dissolved in anhydrous THF (2 mL), then TBAF (87 μL, 0.087 mmol, 1.5 eq., 1M in THF) was added to the reaction at 0°C, stirred at 0°C for 30 min. The reaction mixture was concentrated to dryness and the residue was purified by column chromatography on silica gel (dichloromethane/methanol = 100:1 to 20:1 as the eluent) to afford **5** (16 mg, 82% yield) as a white solid.

White solid, m.p. = 138-139°C; 16 mg, 82% yield; 2:98 er; $[\alpha]_D^{20.0}$ = +76.1 (0.1, methanol); [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 80/20, v = 1.0 mL·min^{-1}, λ = 210 nm, t (major) = 12.7 min, t (minor) = 11.4 min]; ^{1}H NMR (400 MHz, CD_3OD) δ 2.07 – 2.25 (m, 2H), 2.32 (s, 3H), 2.33 (s, 3H), 2.40 –2.50 (m, 1H), 3.57 (d, *J* = 6.7 Hz, 2H), 4.34 (dd, *J* = 8.9, 5.6 Hz, 1H), 4.60 (s, 2H), 6.97 (d, *J* = 5.4 Hz, 2H), 7.07 – 7.17 (m, 4H), 7.28 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, CD_3OD) δ 18.9, 21.2, 42.1, 46.0, 63.2, 68.1, 73.2, 126.7, 127.7, 129.1, 129.9, 131.0, 137.3, 138.3, 138.5, 142.4, 143.1; HRMS (ESI- quadrupole) m/z calcd. for $C_{19}H_{24}O_3Na$ $[M+Na]^+$: 323.1618, found: 323.1619.

(2-methyl-4-((3*S*,5*R*)-5-(p-tolyl)tetrahydrofuran-3-yl)phenyl)methanol (6) [6]

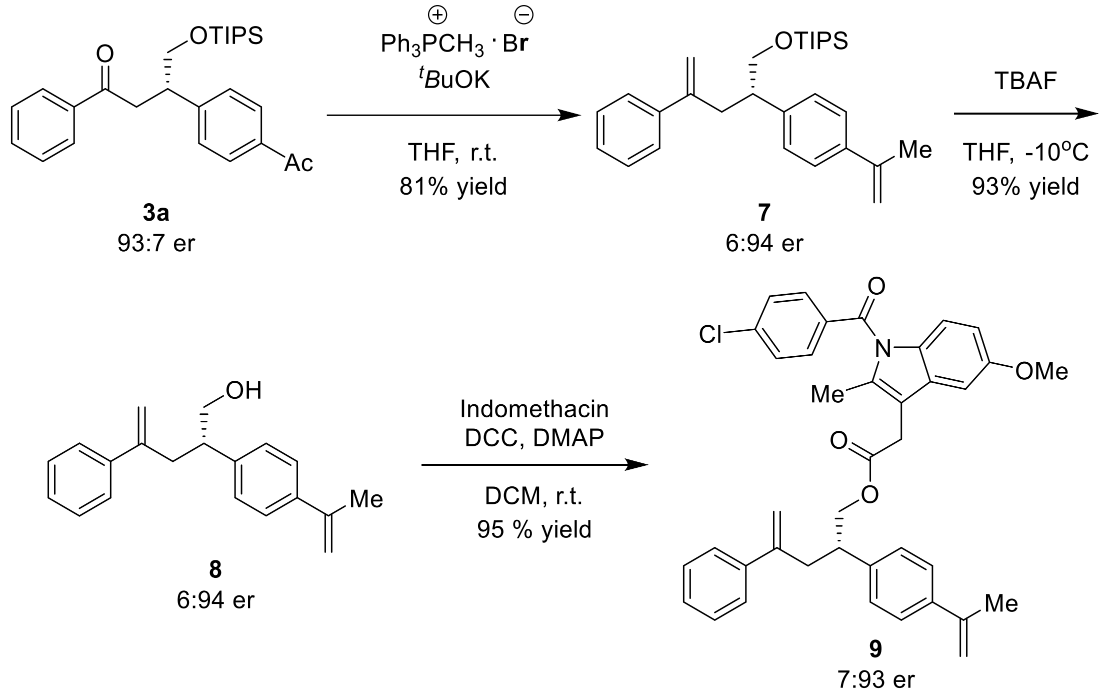


To a solution of **5** (16 mg, 0.05 mmol) in anhydrous 1,2-dichloroethane (2 mL) was added *p*-toluenesulfonic acid monohydrate (1.0 mg, 0.005 mmol, 0.1 eq.). The reaction was allowed to stirred at 40°C for 12 h before quenched by brine (10 mL). The organic layer was separated and the aqueous layer was extracted with DCM (10 mL×2). The combined organic layer was washed by brine, dried over anhydrous Na_2SO_4. The organic layer was concentrated and the crude product was purified by column chromatography on silica gel (petroleum ether / ethyl acetate = 5:1 as the eluent) to afford product **6** (12 mg, dr 4:1, totally 80% yield) as amorphous foam.

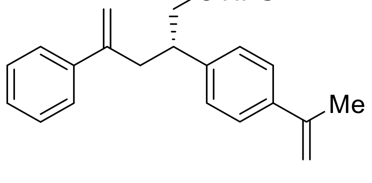
Amorphous foam; 12 mg, 80% yield; 2:98 er (*major isomer*); $[\alpha]_D^{20.0}$ = +27.2 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 90/10, v = 1.0 mL·min^{-1}, λ = 210 nm, t (major) = 16.9 min, t (minor) = 15.1 min]; *major isomer:* ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.66 (s, 1H), 1.95 – 2.03 (m, 1H), 2.34 (s, 3H), 2.35 (s, 3H), 2.67 – 2.74 (m, 1H), 3.54 – 3.65 (m, 1H), 3.98 (t, *J* = 8.4 Hz, 1H), 4.32 (t,

J = 8.2 Hz, 1H), 4.66 (s, 2H), 5.03 (dd, J = 5.7, 10.1 Hz, 1H), 7.07 – 7.12 (m, 2H), 7.17 (d, J = 7.8 Hz, 2H), 7.24 – 7.28 (m, 1H), 7.30 (d, J = 7.1 Hz, 2H); *minor isomer:* ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.63 (s, 1H), 2.25 – 2.30 (m, 1H), 2.34 (s, 3H), 2.35 (s, 3H), 2.40 – 2.48 (m, 1H), 3.46 – 3.52 (m, 1H), 3.91 (t, J = 8.2 Hz, 1H), 4.43 (t, J = 7.9 Hz, 1H), 4.66 (s, 2H), 5.19 (t, 1H), 7.10 (dd, J = 13.2, 5.5 Hz, 2H), 7.17 (d, J = 7.8 Hz, 2H), 7.28 – 7.24 (m, 1H), 7.30 (d, J = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 18.7, 18.8, 21.1, 21.2, 42.8, 43.7, 44.2, 45.8, 63.3, 63.4, 75.1, 80.6, 81.8, 124.9, 125.0, 125.6, 125.8, 128.1, 129.1, 129.2, 129.4, 129.5, 130.0, 136.6, 137.1, 137.2, 138.5, 139.6, 140.6, 141.4; HRMS (ESI- quadrupole) m/z calcd. for $C_{20}H_{19}BrNO_3$ [M+H]$^+$: 283.1693, found: 283.1689.

Synthesis of indomethacin ester (9)



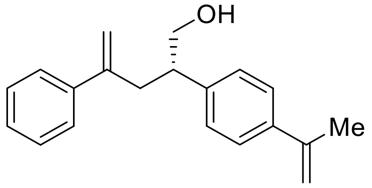
(*S*)-triisopropyl((4-phenyl-2-(4-(prop-1-en-2-yl)phenyl)pent-4-en-1-yl)oxy)silane (7)



To a suspension of methyltriphenylphosphonium bromide (200.0 mg, 0.56 mmol) in anhydrous THF (2 mL) was added *t*-BuOK (63 mg, 0.56 mmol) at 0°C with nitrogen protection, then the reaction was stirred at ambient temperature for 2 h to form a bright yellow suspension. The witting reagent was cooled to 0°C, then a solution of compound **3a** (80 mg, 0.18 mmol) in anhydrous THF (1 mL) was added *via* syringe at 0°C. After the addition, the reaction was allowed to stirred at room temperature for 2 h. The reaction was quenched by water (5 mL) and extracted with EA (10 mL×2). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4. The organic layer was concentrated to dryness and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1 as the eluent) to afford product **7** as colorless oil.

Colorless oil; 64 mg, 81% yield; 6:94 er; $[\alpha]_D^{20.0}$ = +57.1 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane, v = 0.1 mL·min^{-1}, λ = 254 nm, t (major) = 36.7 min, t (minor) = 35.3 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 0.98 – 1.07 (m, 21H), 2.13 (s, 3H), 2.68 (dd, *J* = 9.1, 14.2 Hz, 1H), 2.88 (dt, *J* = 5.7, 12.8, Hz, 1H), 3.33 (dd, *J* = 5.4, 14.2, Hz, 1H), 3.71 – 3.87 (m, 2H), 4.89 (s, 1H), 5.03 (s, 1H), 5.18 (s, 1H), 5.34 (s, 1H), 7.06 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 4.0 Hz, 1H), 7.27 (d, *J* = 5.6 Hz, 1H), 7.33 (d, *J* = 9.0 Hz, 2H), 7.37 (d, *J* = 4.0 Hz, 2H), 7.39 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 12.1, 18.1, 21.9, 37.9, 46.7, 67.5, 111.7, 114.3, 125.2, 126.5, 127.4, 128.1, 128.3, 139.1, 141.0, 142.0, 143.2, 146.6; HRMS (ESI- quadrupole) m/z calcd. for $C_{29}H_{43}OSi$ $[M+H]^+$: 435.3078, found: 435.3074.

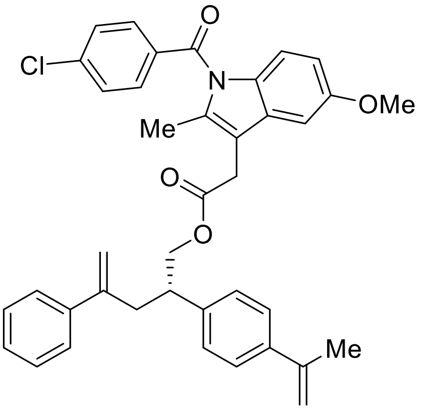
(*S*)-4-phenyl-2-(4-(prop-1-en-2-yl)phenyl)pent-4-en-1-ol (8)



To a solution of compound **7** (62.0 mg, 0.143 mmol) in anhydrous THF (2 mL) was added TBAF (210 μL, 0.21 mmol, 1.5 eq., 1M in THF) at -10°C, then stirred the reaction at 0°C for 2 h. The reaction mixture was concentrated and the residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate = 50:1 to 10:1 as the eluent) to afford **8** (37 mg, 93% yield) as colorless oil.

Colorless oil; 37 mg, 93% yield; 6:94 er; $[\alpha]_D^{20.0}$ = +70.4 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 90/10, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 7.8 min, t (minor) = 6.3 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 1.32 (s, 1H), 2.16 (s, 3H), 2.82 (dd, *J* = 12.4, 5.7 Hz, 1H), 2.88 – 3.08 (m, 2H), 3.73 – 3.81 (m, 2H), 5.01 (s, 1H), 5.08 (s, 1H), 5.24 (s, 1H), 5.38 (s, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.27 – 7.41 (m, 5H),7.43 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 21.8, 38.4, 46.1, 66.7, 112.1, 114.6, 125.7, 126.4, 127.6, 127.9, 128.5, 139.7, 140.8, 141.3, 142.9, 146.3; HRMS (ESI- quadrupole) m/z calcd. for $C_{20}H_{23}O$ $[M+H]^+$: 279.1743, found: 279.1741.

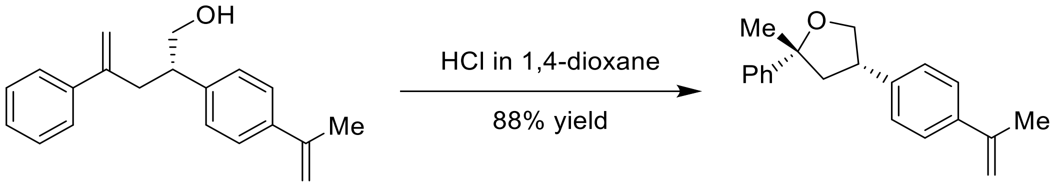
Indomethacin (*S*)-4-phenyl-2-(4-(prop-1-en-2-yl)phenyl)pent-4-en-1-yl ester (9)



To a mixture of compound **8** (18 mg, 0.065 mmol) and indomethacin (27.8 mg, 0.078 mmol) in anhydrous DCM (2 mL) was added DMAP (1.6 mg, 0.013 mmol) and DCC (18.7 mg, 0.09 mmol) at 0°C with nitrogen protection, then the reaction was stirred at ambient temperature for 4 h. The reaction mixture was concentrated and the crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1 as the eluent) to afford **9** (38 mg, 95% yield) as thick yellow oil.

Yellow oil; 38 mg, 95% yield; 7:93 er; $[\alpha]_D^{20.0}$ = +22.3 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 60/40, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 6.9 min, t (minor) = 5.5 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 2.09 (s, 3H), 2.26 (s, 3H), 2.73 (dd, *J* = 7.7, 14.2 Hz, 1H), 2.84 (dd, *J* = 7.2, 14.2 Hz, 1H), 2.96 – 3.03 (m, 1H), 3.59 (s, 2H), 3.77 (s, 3H), 4.17 – 4.31 (m, 2H), 4.86 (s, 1H), 5.03 (s, 1H), 5.17 (s, 1H), 5.32 (s, 1H), 6.67 (dd, *J* = 2.3, 9.0 Hz, 1H), 6.86 – 6.91 (m, 2H), 6.93 (d, *J* = 8.1 Hz, 2H), 7.23 – 7.29 (m, 7H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.59 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.3, 21.7, 30.4, 38.4, 42.4, 55.7, 67.8, 101.3, 111.8, 112.1, 112.6, 115.0, 115.1, 125.4, 126.3, 127.6, 127.7, 128.4, 129.1, 130.7, 130.8, 131.2, 133.9, 135.8, 139.2, 139.4, 140.5, 140.6, 142.7, 145.6, 156.1, 168.2, 170.6; HRMS (ESI- quadrupole) m/z calcd. for $C_{39}H_{37}ClNO_4$ $[M+H]^+$: 618.2406, found: 618.2408.

Synthesis of (2*R*,4*S*)-2-methyl-2-phenyl-4-(4-(prop-1-en-2-yl)phenyl)tetrahydrofuran (10) [7]



8
6:94 er

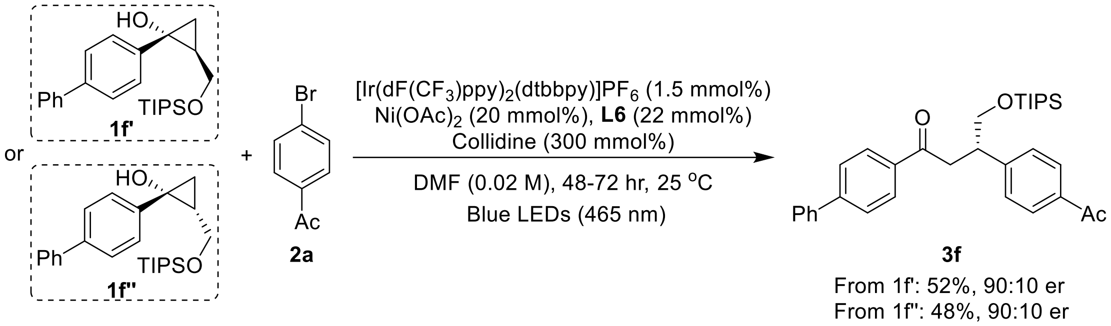
10
2:1 dr

To a solution of compound **8** (16 mg, 0.065 mmol) in anhydrous chloroform (2 mL) was added HCl solution (57 μL, 0.057 mmol, 1.0 eq., 1M in 1,4-dioxane) at 0°C with nitrogen protection. The reaction was stirred for 30 min at room temperature. The reaction mixture was concentrated and the crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1 as the eluent) to afford **10** (14 mg, dr 2:1, totally 88% yield) as yellow viscous oil.

Yellow viscous oil; 14 mg, 88% yield; $[\alpha]_D^{20.0}$ = +10.8 (0.1, CH_2Cl_2); *major isomer:* ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.60 (s, 3H), 2.11 (s, 3H), 2.30 (dd, J = 12.2, 10.8 Hz, 1H), 2.63 (dd, J = 8.0, 12.4 Hz, 1H), 3.60 – 3.74 (m, 1H), 3.81 (m, 1H), 4.38 (t, J = 7.9 Hz, 1H), 5.04 (s, 1H), 5.31 (s, 1H), 7.11 (d, J = 8.2 Hz, 1H), 7.22 – 7.30 (m, 2H), 7.33 – 7.38 (m, 4H), 7.46 (d, J = 7.7 Hz, 2H); *minor isomer*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.65 (s, 3H), 2.13 (s, 3H), 2.18 – 2.20 (m, 1H), 2.71 (dd, J = 12.1, 7.1 Hz, 1H), 3.34 – 3.22 (m, 1H), 3.96 (t, J = 8.6 Hz, 1H), 4.32 (t, J = 8.4 Hz, 1H), 5.05 (s, 1H), 5.34 (s, 1H), 7.11 (d, J = 8.2 Hz, 1H), 7.19 (d, J = 8.2 Hz, 2H), 7.31 – 7.22 (m,1H), 7.43 – 7.38 (m, 3H), 7.46 (d, J = 7.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 21.8, 21.9, 30.3, 30.7, 44.4, 45.6, 48.1, 48.4, 74.0, 74.5, 85.1, 85.6, 112.2, 124.6, 124.8, 125.7, 125.8, 126.6, 126.7, 127.2, 127.4, 128.3, 128.4, 139.6, 139.7, 140.1, 140.9, 142.9, 145.0, 147.7, 149.0; HRMS (ESI- quadrupole) m/z calcd. for $C_{20}H_{22}O$ $[M+H]^+$: 279.1743, found: 279.1739.

Mechanistic studies

(A). Effect of cyclopropanol isomers

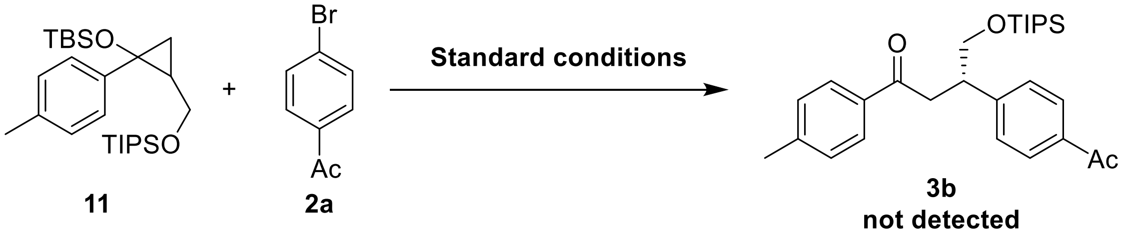


Two experiments were carried out to evaluate the effect of the cyclopropanol isomers. When used *trans*-isomer **1f’** as the starting material, followed the standard reaction conditions, product **3f** was obtained in 52% yield with 90:10 er. [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 70/30, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 8.2 min, t (minor) = 13.8 min];

When used *cis*-isomer **1f”** as the starting material, followed the standard reaction conditions, product **3f** was obtained in 48% yield with 90:10 er. [Daicel CHIRALPAK® IA-3 (4.6 mm x 250mm), *n*-hexane/2-propanol = 70/30, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 8.0 min, t (minor) = 12.9 min];

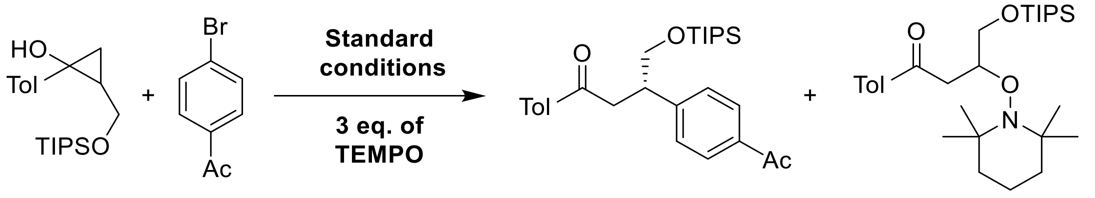
The results showed that both cyclopropanol isomers could provide the product in similar yields with the same enantioselectivity.

(B). Effect of cyclopropanol OH



To a 10 mL vial equipped with a stir bar was added $[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1.7 mg, 1.5 μmol, 1.5 mmol%), Nickel(II) acetate (3.6 mg, 20 μmol, 20 mmol%), **L6** (6.6 mg, 22 μmol, 22 mmol%) and **2a** (20 mg, 0.1 mmol).The vial was sealed, evacuated and backfilled with nitrogen three times, then anhydrous DMF (5mL) was injected under nitrogen protection. The reaction was stirred at room temperature for 10 min. TBSprotected cyclopropanol **11** (135 mg, 0.3 mmol) and collidine (36.5 mg, 0.3 mmol) was injected *via* micro syringe respectively. After degassing the reaction mixture with Freeze-Pump-Thaw methods for three cycles, it was stirred and irradiated with the corresponding blue LEDs photoreactor at 25°C (cooled by ethanol circulator bath) for 48 h. No product **3b** was observed from ^{1}H-NMR of the crude reaction mixture.

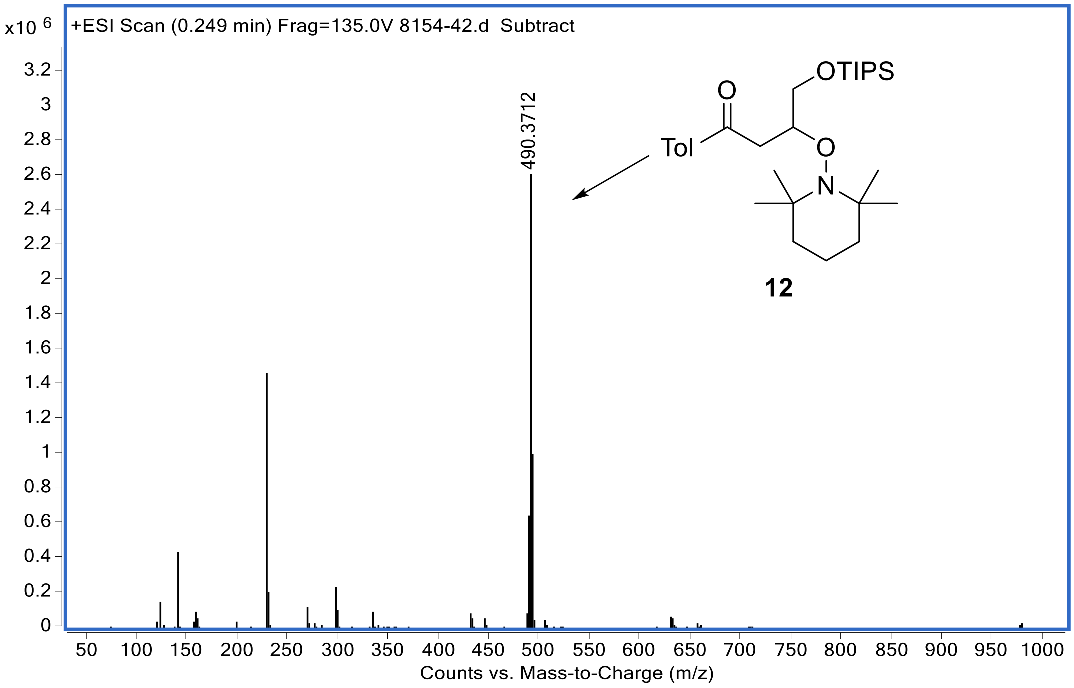
(C) Trapping of the radical intermediate by TEMPO



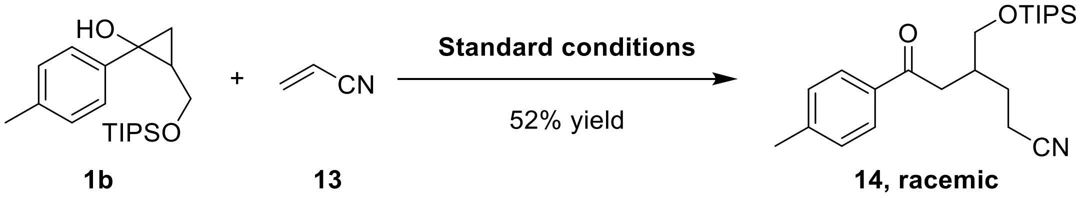
1b **2a** **3b** not detected **12,** detected by HRMS
Found [**13**+H]$^+$: 490.3712

To a 10 mL vial equipped with a stir bar was added [Ir(dFCF$_3$ppy)$_2$dtbbpy]PF$_6$ (1.7 mg, 1.5 µmol, 1.5 mmol%), Nickel(II) acetate (3.6 mg, 20 µmol, 20 mmol%), **L6** (6.6 mg, 22 µmol, 22 mmol%) and **2a** (20 mg, 0.1 mmol) The vial was sealed, evacuated and backfilled with nitrogen three times, then anhydrous DMF (5 mL) was injected under nitrogen protection, stirred at room temperature for 10 min. Cyclopropanol **1b** (100 mg, 0.3 mmol) and collidine (36.5 mg, 0.3 mmol) was injected *via* micro syringe respectively. Then TEMPO (47 mg, 0.3 mmol, 3 equiv.) in anhydrous DMF (1 mL) was injected slowly at -10^{o}C. After degassing the reaction mixture with Freeze-Pump-Thaw methods for three cycles, it was stirred and irradiated with the corresponding blue LEDs photoreactor at 25°C (cooled by ethanol circulator bath) for 48 h. The reaction mixture was poured into ice-water (50 mL), then extracted with DCM (10 mL×2), combined of the organic layer was washed with brine, dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure to give yellow thick oil. The yellow thick oil was analyzed by HRMS.

HRMS (ESI- quadrupole) m/z calcd. for $C_{29}H_{52}NO_3Si$ [M+H]$^+$: 490.3711, found: 490.3712.



(D) Trapping of the radical intermediate with acrylonitrile



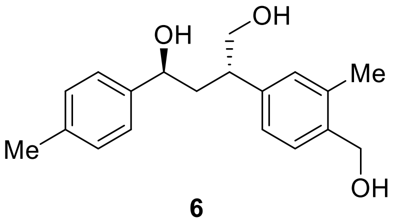
To a 10 mL vial equipped with a stir bar was added [Ir(dFCF$_3$ppy)$_2$dtbbpy]PF$_6$ (1.7 mg, 1.5 μmol, 1.5 mmol%), Nickel(II) acetate (3.6 mg, 20 μmol, 20 mmol%) and **L6** (6.6 mg, 22 μmol, 22 mmol%). The vial was sealed, evacuated and backfilled with nitrogen three times, then anhydrous DMF (5mL) was injected under nitrogen protection, stirred at room temperature for 10 min. Cyclopropanol **1b** (100 mg, 0.3 mmol) and collidine (36.5 mg, 0.3 mmol) was injected *via* micro syringe respectively. After degassing the reaction mixture with Freeze-Pump-Thaw methods for three cycles, compound **13** (5.3 mg, 0.1 mmol) was injected *via* micro syringe. The reaction was stirred and irradiated with the corresponding blue LEDs photoreactor at 25°C (cooled by ethanol circulator bath) for 48 h. The reaction mixture was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1 to 20:1 as the eluent) to give product **14** (20.0 mg, 52% yield) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.03 – 1.10 (m, 21H), 1.76 –1.81 (m, 1H), 1.86 –1.92 (m, 1H), 2.32 – 2.36 (m, 1H), 2.42 (s, 3H), 2.45 – 2.49 (m, 2H), 2.84 (dd, *J* = 17.0, 6.6 Hz, 1H), 3.20 (dd, *J* = 17.0, 6.3 Hz, 1H), 3.73 (d, *J* = 4.6 Hz, 2H), 7.26 (d, *J* = 7.8 Hz, 2H), 7.86 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.0, 15.4, 18.1, 21.7, 27.7, 36.4, 39.8, 65.1, 119.9, 128.2, 129.4, 134.6, 144.1, 198.7.

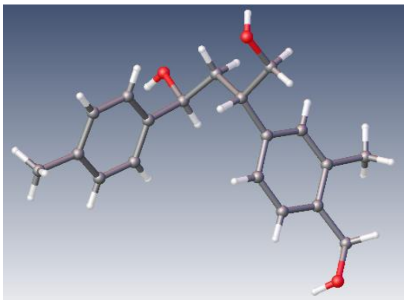
HRMS (ESI- quadrupole) m/z calcd. for $C_{23}H_{38}NO_2Si$ $[M+H]^+$: 388.2666, found: 388.2665.

X-ray Crystallography data

X-ray structure of compound 6



6



CDCC: 2126211

Table S7 Crystal data and structure refinement for Compound 6.

Identification code	Compound **6**
Empirical formula	$C_{19}H_{24}O_3$
Formula weight	300.38
Temperature/K	293.00(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	9.16551(16)
b/Å	10.4822(2)
c/Å	17.5734(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1688.36(6)
Z	4
ρ_{calc}g/cm^3	1.182
μ/mm^{-1}	0.624
F(000)	648.0
Crystal size/mm^3	0.06 × 0.05 × 0.04
Radiation	Cu Kα (λ = 1.54184)

2Θ range for data collection/°	9.826 to 134.15
Index ranges	$-4 \le h \le 10$, $-12 \le k \le 12$, $-19 \le l \le 20$
Reflections collected	8109
Independent reflections	2989 [R_{int} = 0.0365, R_{sigma} = 0.0407]
Data/restraints/parameters	2989/0/204
Goodness-of-fit on F^2	1.098
Final R indexes [I>=2σ (I)]	R_1 = 0.0396, wR_2 = 0.1004
Final R indexes [all data]	R_1 = 0.0422, wR_2 = 0.1025
Largest diff. peak/hole / e Å^{-3}	0.16/-0.23
Flack parameter	-0.04(11)

Table S8 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Compound 6. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	7452.7(16)	3709.5(16)	5073.1(11)	52.6(4)
O2	2001.7(16)	3624.5(15)	4373.7(11)	48.0(4)
O3	4159.3(16)	11061.1(15)	6187.8(10)	48.0(4)
C1	4904.8(19)	6436.7(19)	5437.0(12)	33.9(4)
C2	5442(2)	5231.6(19)	5055.5(12)	35.6(4)
C3	4378(2)	6428(2)	6183.5(13)	41.3(5)
C4	4575(2)	8719(2)	5430.2(12)	37.4(4)
C5	6705(2)	4651(2)	5504.5(14)	42.9(5)
C6	4090.9(19)	8711(2)	6177.7(12)	36.7(4)
C7	4986(2)	7601(2)	5067.5(12)	37.0(4)
C8	3093(3)	6445(3)	2526.2(16)	53.9(6)
C9	3009(2)	4684.7(19)	4413.9(13)	36.6(4)
C10	3446(2)	5083(2)	3618.7(12)	37.8(4)
C11	4242(2)	4232.4(19)	4922.7(13)	36.7(4)
C12	2821(2)	6149(2)	3280.7(15)	46.1(5)

C13	4011(3)	5709(3)	2085.3(14)	50.5(6)
C14	3977(2)	7545(2)	6560.5(13)	42.0(5)
C15	4406(3)	4365(3)	3181.9(15)	52.9(6)
C16	3735(3)	9945(2)	6587.8(14)	47.4(5)
C17	4681(3)	4677(3)	2431.7(16)	58.3(6)
C18	4250(4)	5984(4)	1253.7(17)	72.9(9)
C19	3493(4)	7491(3)	7382.6(17)	67.7(8)

Table S9 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for Compound 6. The Anisotropic displacement factor exponent takes the form: -$2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
O1	49.0(8)	35.8(8)	72.9(12)	8.1(9)	18.0(8)	8.3(6)
O2	45.3(7)	39.6(8)	58.9(10)	9.2(8)	-11.7(7)	-8.5(7)
O3	53.1(8)	35.1(8)	55.9(10)	-5.7(7)	-4.7(7)	1.5(6)
C1	33.3(9)	31.1(9)	37.4(10)	0.8(9)	-1.9(7)	-0.9(7)
C2	37.5(9)	31.3(9)	38.0(10)	0.7(9)	1.9(8)	-0.2(7)
C3	46.6(10)	34.8(11)	42.7(12)	6.6(9)	4.0(8)	-2.3(8)
C4	43.3(9)	30.1(9)	38.7(10)	3.7(9)	-2.5(8)	0.6(8)
C5	39.0(10)	38.1(11)	51.6(12)	1.7(10)	-0.7(9)	4.6(8)
C6	33.1(8)	35.8(10)	41.3(11)	-2.9(9)	-0.9(7)	0.1(7)
C7	43.6(9)	35.8(10)	31.7(10)	2.1(9)	0.9(8)	-0.3(8)
C8	57.8(13)	52.0(14)	52.0(14)	14.6(12)	1.4(11)	3.4(11)
C9	38.9(9)	30.2(9)	40.6(11)	-1.2(9)	0.3(8)	-1.2(7)
C10	36.3(9)	38.8(10)	38.5(10)	-1.3(9)	-3.0(8)	0.4(8)
C11	42.4(10)	30.5(9)	37.3(11)	1.7(8)	-1.4(8)	-1.0(8)
C12	46.1(11)	41.6(11)	50.6(13)	6.8(11)	8.5(9)	7.8(10)
C13	49.6(11)	60.0(14)	41.9(13)	0.3(11)	0.7(10)	-11.5(10)
C14	43.4(10)	42.1(11)	40.6(12)	1.1(9)	7.3(8)	-2.0(9)

C15	60.7(13)	51.6(14)	46.2(13)	-3.3(11)	-1.7(11)	18.1(11)
C16	53.9(12)	40.9(12)	47.4(13)	-5.6(10)	4.4(10)	3.3(9)
C17	61.8(14)	67.1(16)	46.1(13)	-7.9(13)	7.4(11)	11.7(12)
C18	86.6(19)	87(2)	45.1(15)	2.5(15)	8.1(13)	-14.0(17)
C19	96(2)	56.6(16)	50.5(15)	2.3(14)	26.5(14)	1.1(15)

Table S10 Bond Lengths for Compound 6.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C5	1.421(3)	C6	C16	1.516(3)
O2	C9	1.447(2)	C8	C12	1.384(4)
O3	C16	1.419(3)	C8	C13	1.379(4)
C1	C2	1.513(3)	C9	C10	1.512(3)
C1	C3	1.398(3)	C9	C11	1.517(3)
C1	C7	1.385(3)	C10	C12	1.389(3)
C2	C5	1.527(3)	C10	C15	1.389(3)
C2	C11	1.537(3)	C13	C17	1.385(4)
C3	C14	1.395(3)	C13	C18	1.506(4)
C4	C6	1.387(3)	C14	C19	1.512(4)
C4	C7	1.386(3)	C15	C17	1.382(4)
C6	C14	1.399(3)			

Table S11 Bond Angles for Compound 6.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C3	C1	C2	121.53(18)	C10	C9	C11	115.70(17)
C7	C1	C2	120.72(18)	C12	C10	C9	120.54(19)
C7	C1	C3	117.68(19)	C15	C10	C9	121.9(2)
C1	C2	C5	110.51(17)	C15	C10	C12	117.4(2)
C1	C2	C11	113.78(16)	C9	C11	C2	114.19(16)
C5	C2	C11	110.45(17)	C8	C12	C10	121.0(2)
C14	C3	C1	122.1(2)	C8	C13	C17	117.4(2)

C7	C4	C6	121.2(2)	C8	C13	C18	121.8(3)
O1	C5	C2	111.50(19)	C17	C13	C18	120.8(3)
C4	C6	C14	119.0(2)	C3	C14	C6	119.05(19)
C4	C6	C16	120.9(2)	C3	C14	C19	120.0(2)
C14	C6	C16	120.05(19)	C6	C14	C19	120.9(2)
C1	C7	C4	121.01(18)	C17	C15	C10	121.0(2)
C13	C8	C12	121.5(2)	O3	C16	C6	114.12(18)
O2	C9	C10	109.62(18)	C15	C17	C13	121.5(2)
O2	C9	C11	105.32(16)				

Table S12 Torsion Angles for Compound 6.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O2	C9	C10	C12	101.6(2)	C7	C4	C6	C14	-1.9(3)
O2	C9	C10	C15	-74.3(3)	C7	C4	C6	C16	176.07(19)
O2	C9	C11	C2	-179.11(17)	C8	C13	C17	C15	2.2(4)
C1	C2	C5	O1	-165.95(16)	C9	C10	C12	C8	-173.0(2)
C1	C2	C11	C9	60.8(2)	C9	C10	C15	C17	173.7(2)
C1	C3	C14	C6	0.7(3)	C10	C9	C11	C2	59.7(2)
C1	C3	C14	C19	-176.6(2)	C10	C15	C17	C13	-0.3(4)
C2	C1	C3	C14	175.30(19)	C11	C2	C5	O1	67.2(2)
C2	C1	C7	C4	-176.16(17)	C11	C9	C10	C12	-139.5(2)
C3	C1	C2	C5	-59.2(2)	C11	C9	C10	C15	44.6(3)
C3	C1	C2	C11	65.7(2)	C12	C8	C13	C17	-1.5(4)
C3	C1	C7	C4	0.8(3)	C12	C8	C13	C18	176.7(3)
C4	C6	C14	C3	1.1(3)	C12	C10	C15	C17	-2.4(4)
C4	C6	C14	C19	178.3(2)	C13	C8	C12	C10	-1.2(4)
C4	C6	C16	O3	-9.5(3)	C14	C6	C16	O3	168.48(19)
C5	C2	C11	C9	-174.27(17)	C15	C10	C12	C8	3.1(3)
C6	C4	C7	C1	1.0(3)	C16	C6	C14	C3	-176.9(2)

C7	C1	C2	C5	117.7(2)	C16	C6	C14	C19	0.3(3)
C7	C1	C2	C11	-117.4(2)	C18	C13	C17	C15	-176.0(3)
C7	C1	C3	C14	-1.6(3)					

Table S13 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Compound 6.

Atom	***x***	***y***	***z***	**U(eq)**
H1	7249.3	2999.2	5237.34	79
H2	1258.38	3848.8	4151.13	72
H3	3619.28	11164.83	5820.9	72
H2A	5824.3	5474.77	4555.17	43
H3A	4291.12	5652.2	6436.63	50
H4	4625.86	9488.36	5167.69	45
H5A	7382.8	5320.37	5647.07	51
H5B	6330.94	4268.7	5967.79	51
H7	5320.96	7633.94	4568.38	44
H8	2645.96	7155.26	2311.62	65
H9	2518.65	5403.96	4661.88	44
H11A	4679.37	3479.66	4696.73	44
H11B	3838.28	3985.4	5411.15	44
H12	2211.01	6672.59	3565.77	55
H15	4870.25	3664.15	3397.71	63
H16A	2691.56	9978.9	6678.05	57
H16B	4216.14	9940.12	7079.43	57
H17	5331.79	4182.4	2152.72	70
H18A	3620.6	6667.89	1097.29	109
H18B	4033	5234.58	960.89	109
H18C	5248.08	6225.52	1172.57	109
H19A	3387.76	6616.85	7536.01	101

H19B	2574.88	7922.05	7436.24	101
H19C	4210.08	7899.96	7697.53	101

Experimental

Single crystals of **6** ($C_{19}H_{24}O_3$) were crystallized from tetrahydrofuran and *n*-hexane. A suitable crystal was selected and measured on a XtaLAB Synergy, Dualflex, HyPix diffractometer. The crystal was kept at 293.0(2) K during data collection. Using Olex2 [1], the structure was solved with the Unknown [2] structure solution program using Unknown and refined with the Unknown [3] refinement package using Unknown minimisation.

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Crystal structure determination of Compound 6

Crystal Data for $C_{19}H_{24}O_3$ (M =300.38 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 9.16551(16) Å, b = 10.4822(2) Å, c = 17.5734(4) Å, V = 1688.36(6) Å^3, Z = 4, T = 293.00(2) K, μ(Cu Kα) = 0.624 mm^{-1}, *Dcalc* = 1.182 g/cm^3, 8109 reflections measured (9.826° ≤ 2Θ ≤ 134.15°), 2989 unique (R_{int} = 0.0365, R_{sigma} = 0.0407) which were used in all calculations. The final R_1 was 0.0396 (I > 2σ(I)) and $wR_2$was 0.1025 (all data).

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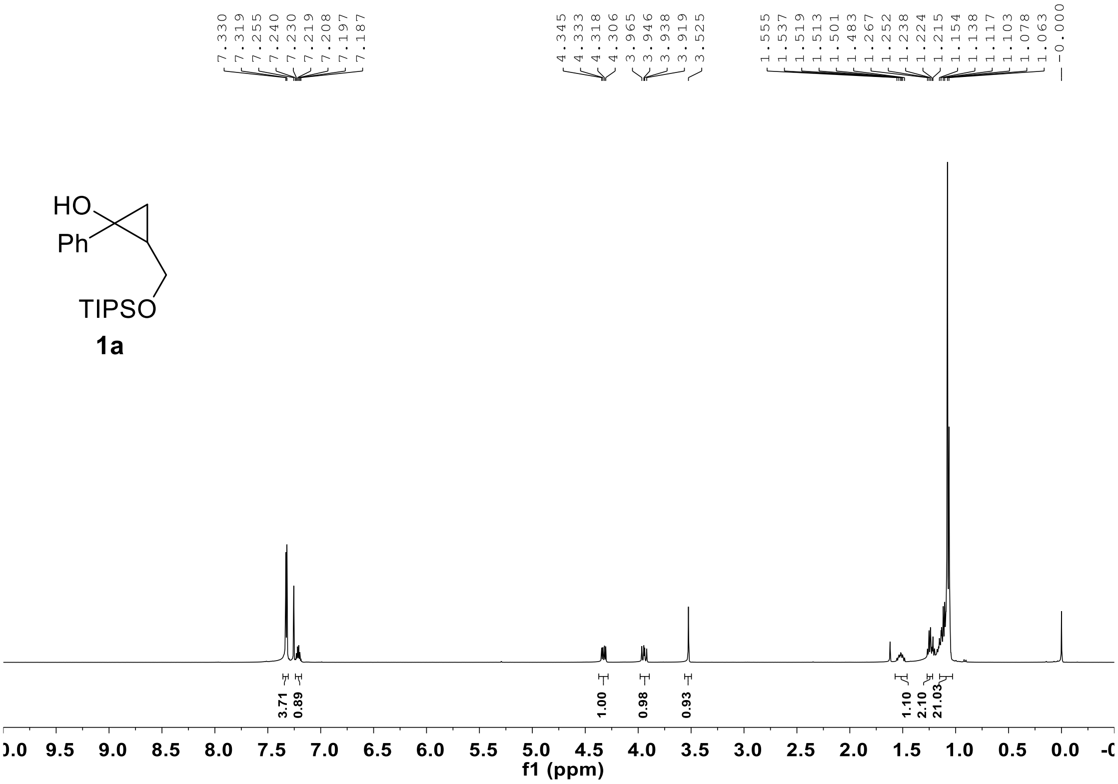
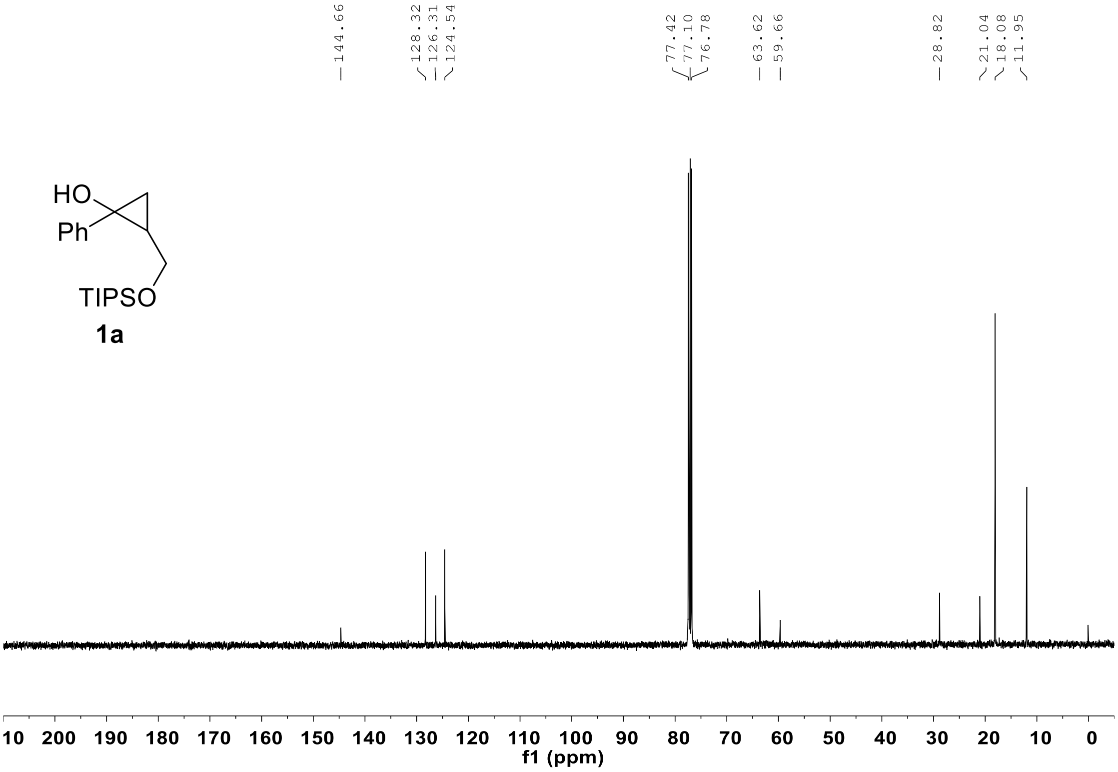
NMR Spectra

1a ^{1}H NMR (400M Hz, $CDCl_3$)



1a ^{13}C NMR (100M Hz, $CDCl_3$)



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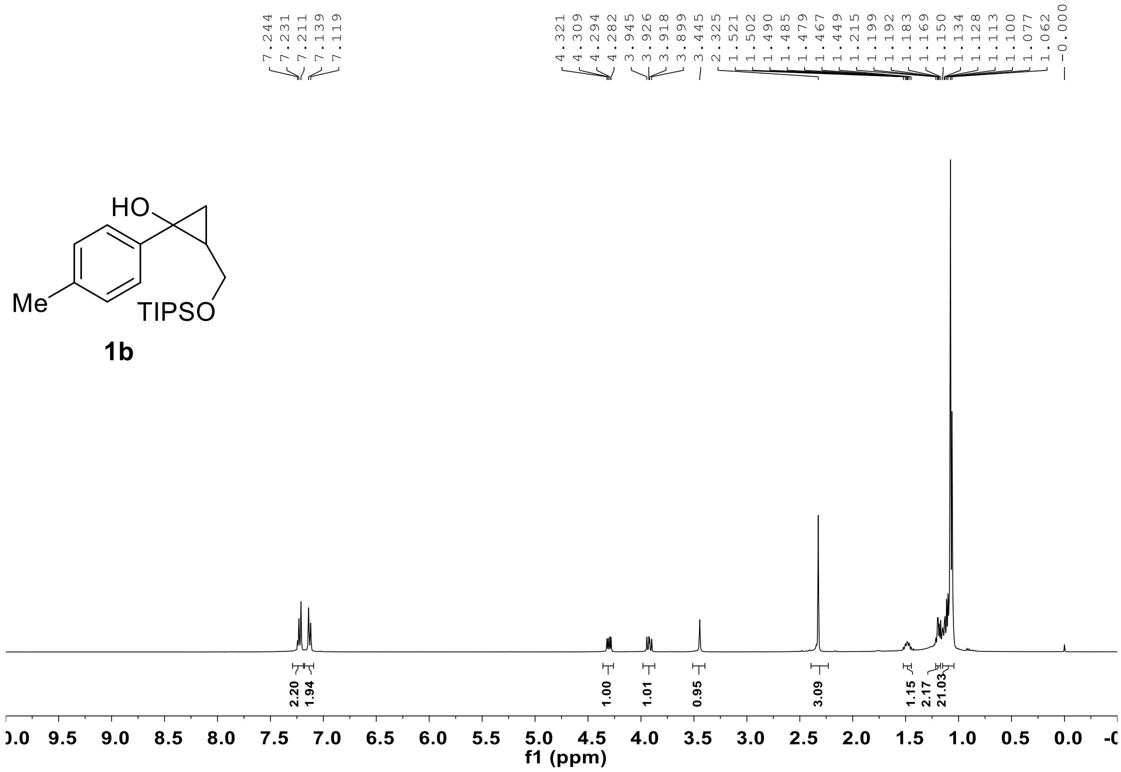

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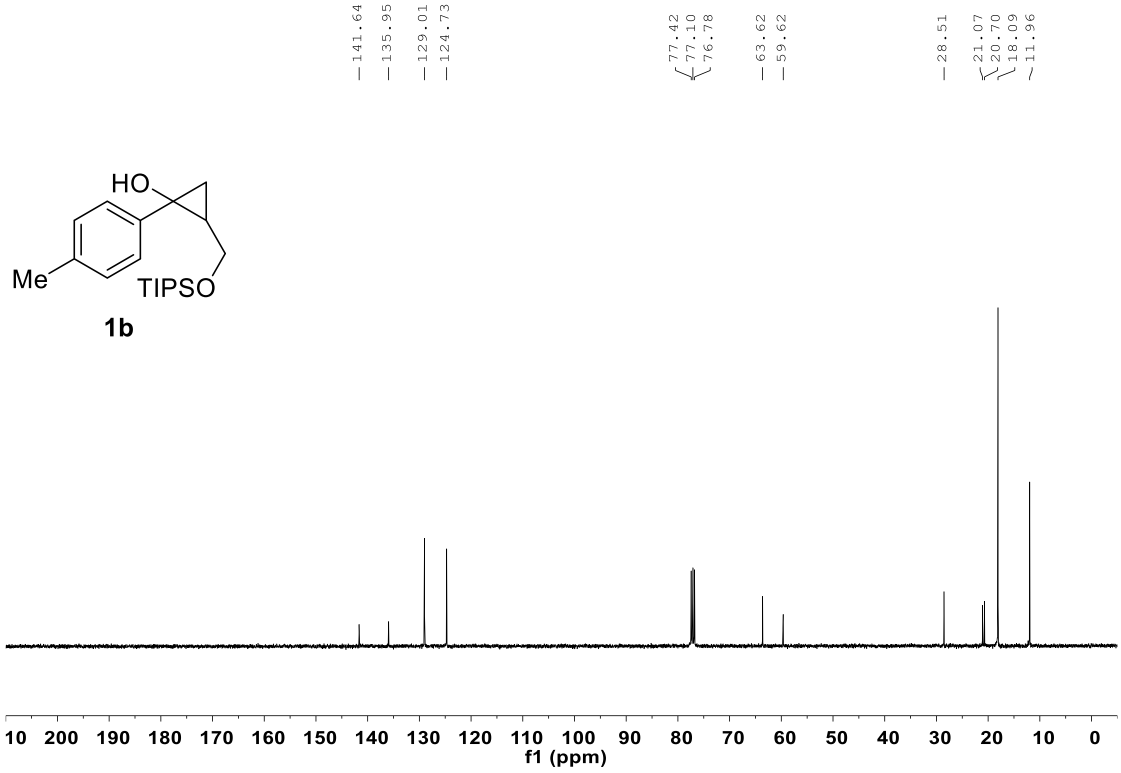
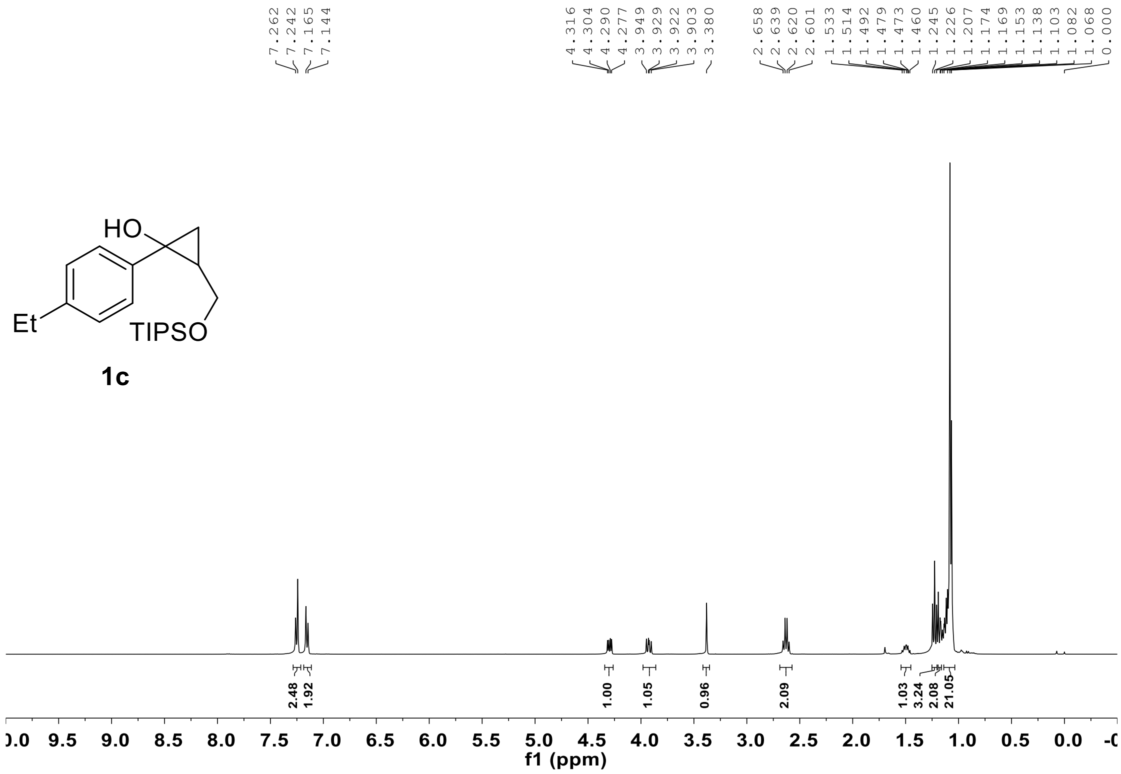


1c ^{1}H NMR (400M Hz, $CDCl_3$)



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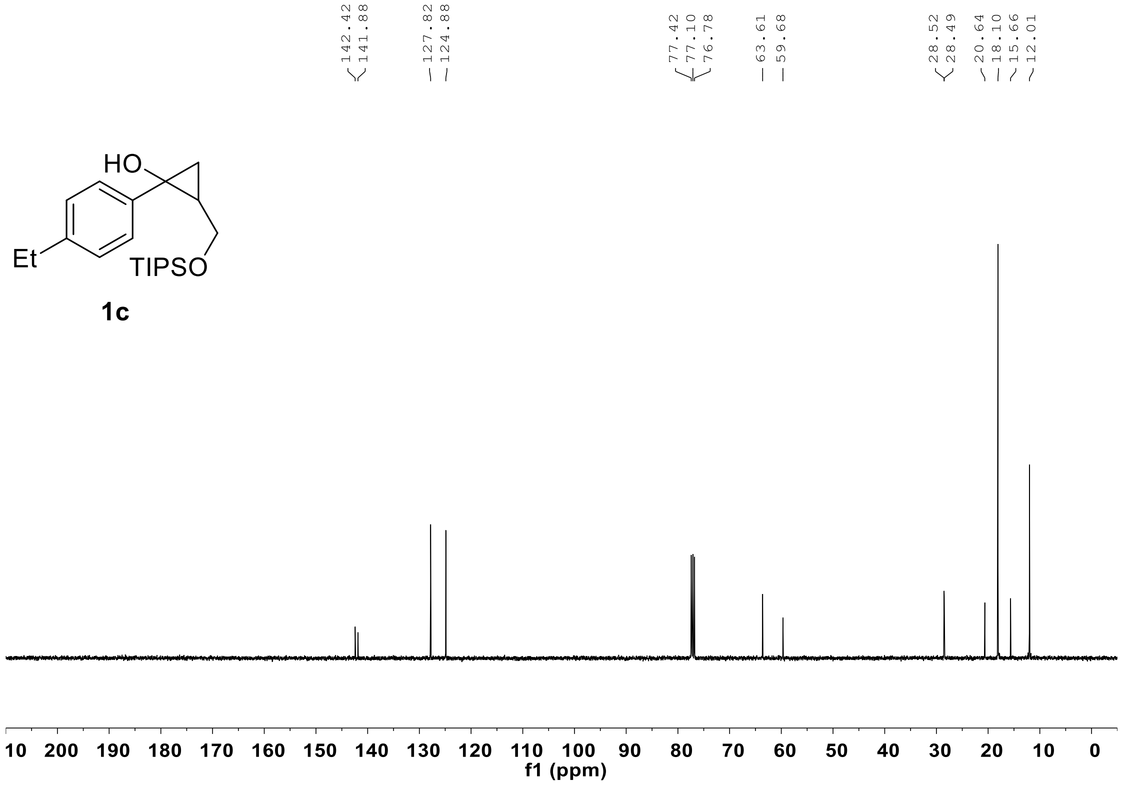

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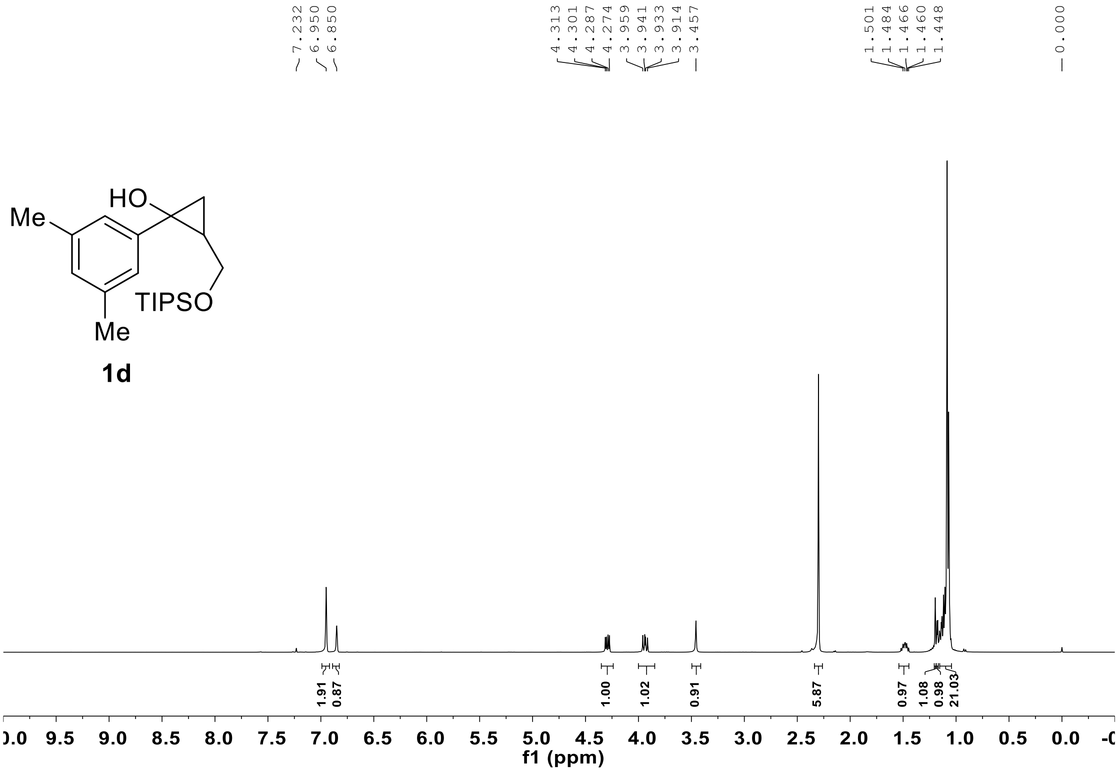
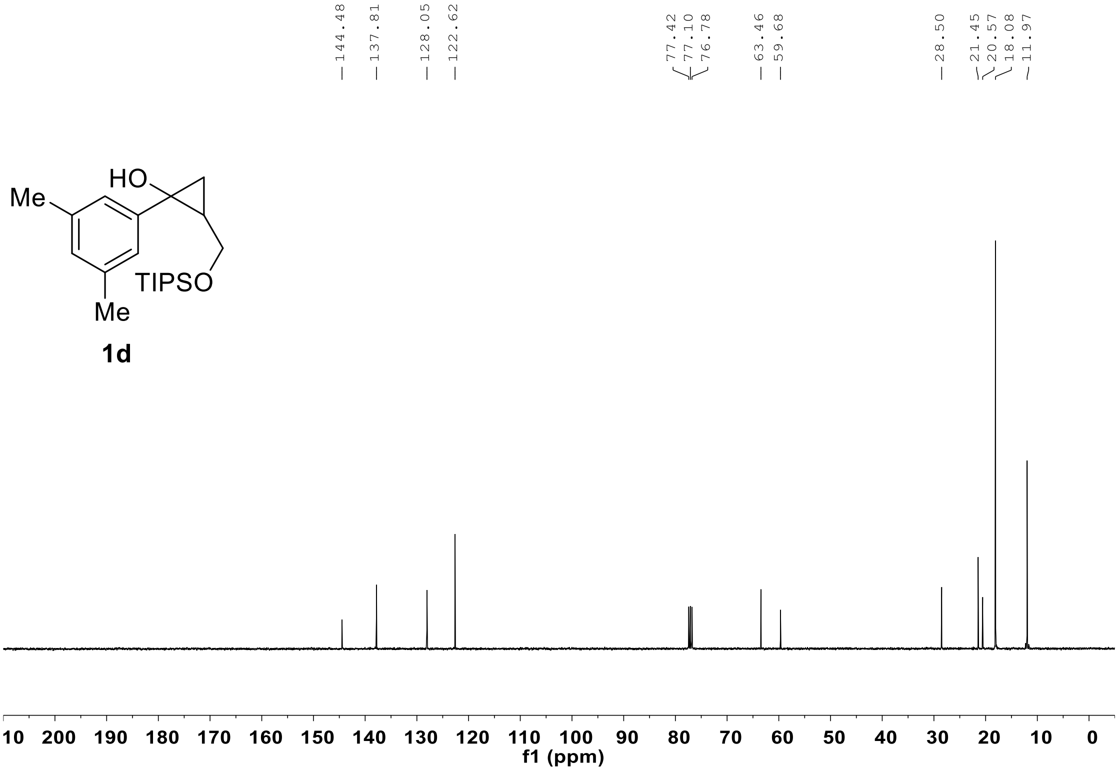
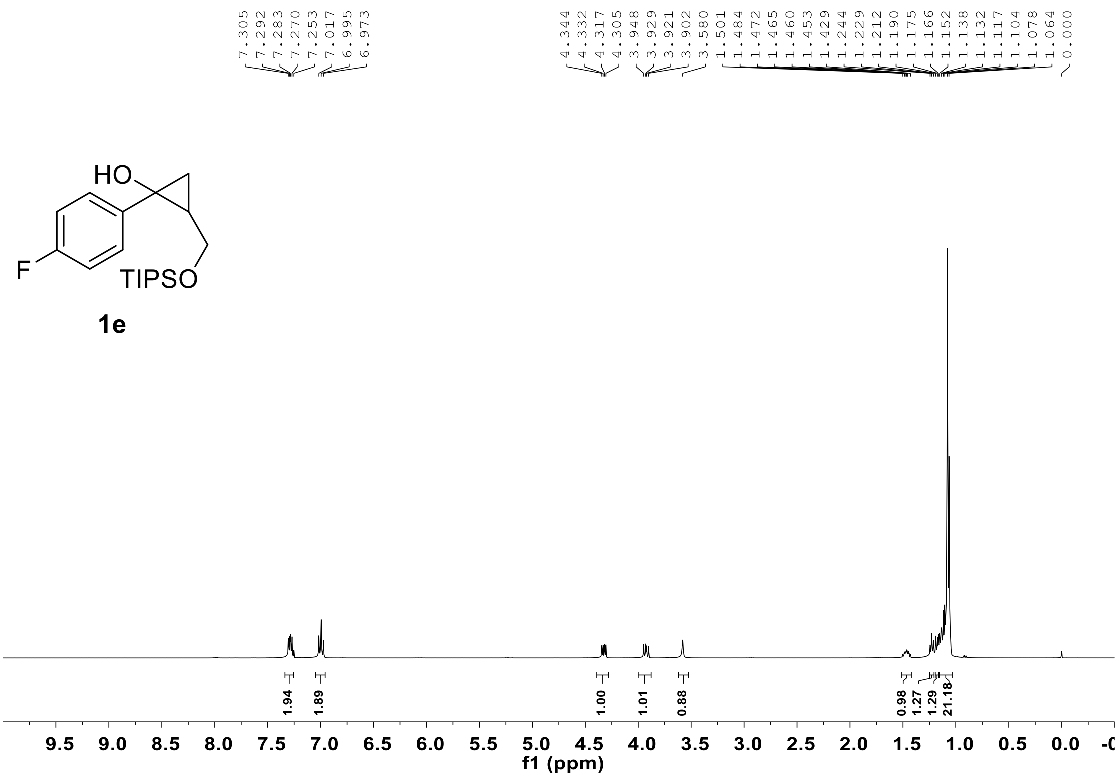


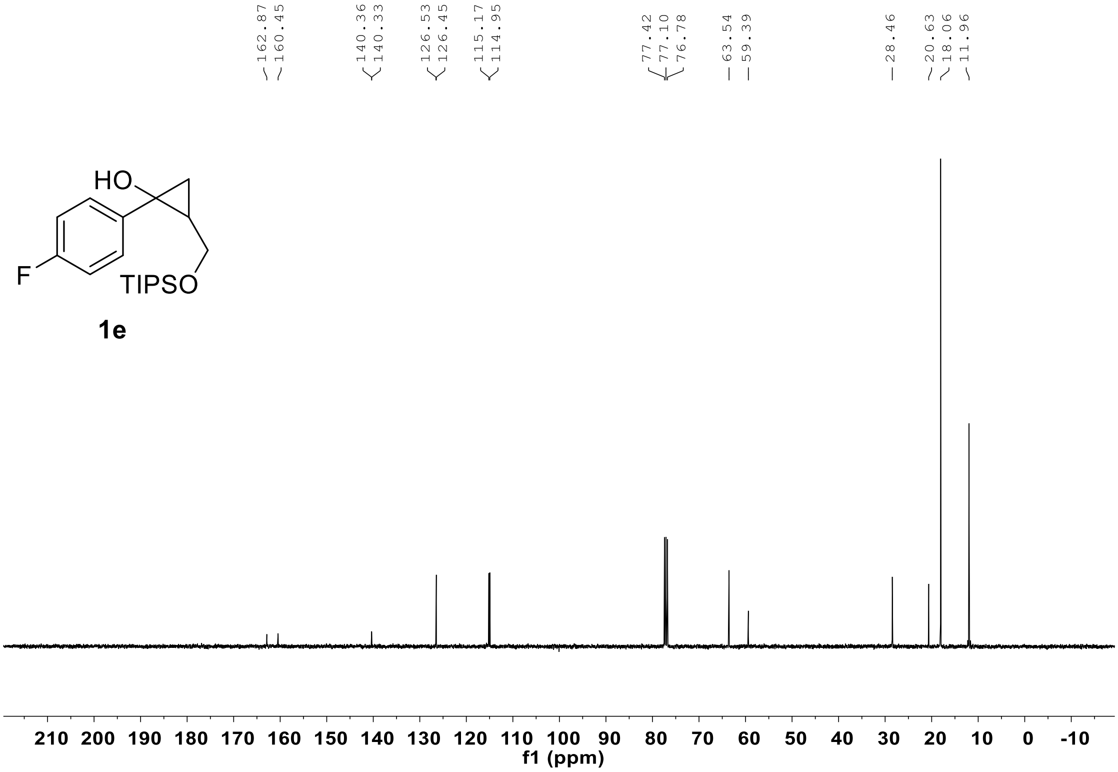
1d ^{13}C NMR (400M Hz, CDCl$_3$)



1e ^{1}H NMR (400M Hz, CDCl$_3$)



1e ^{13}C NMR (400M Hz, CDCl$_3$)



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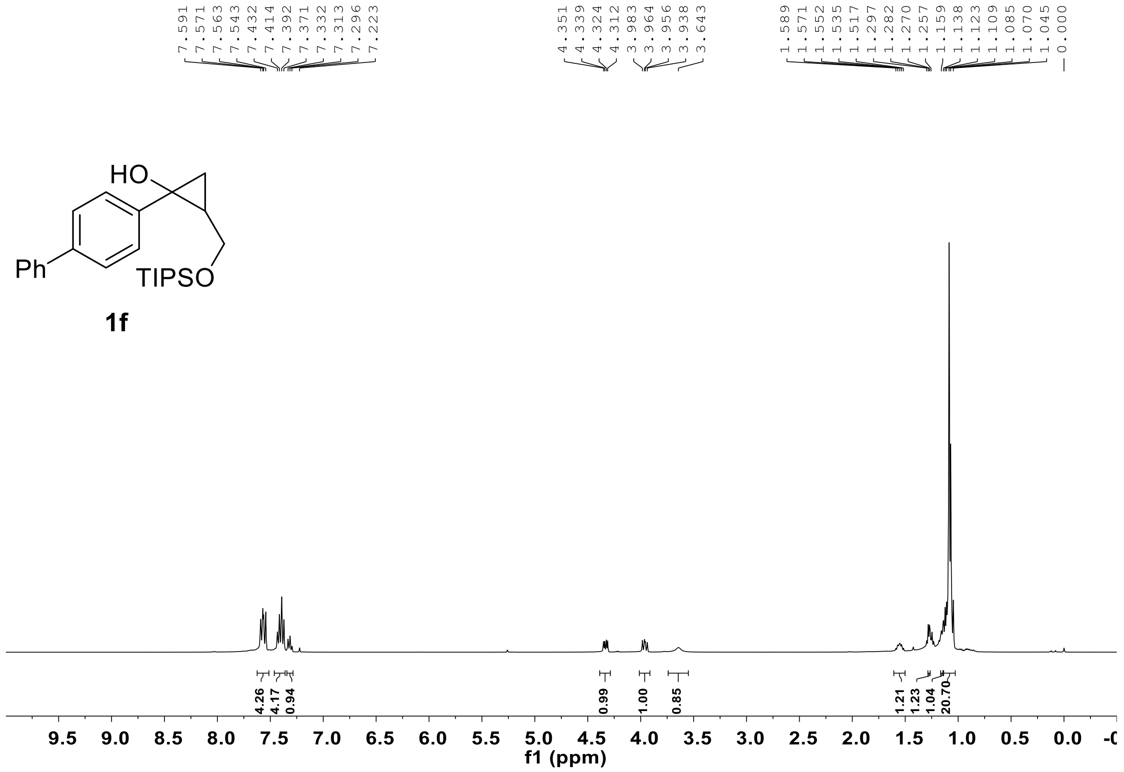
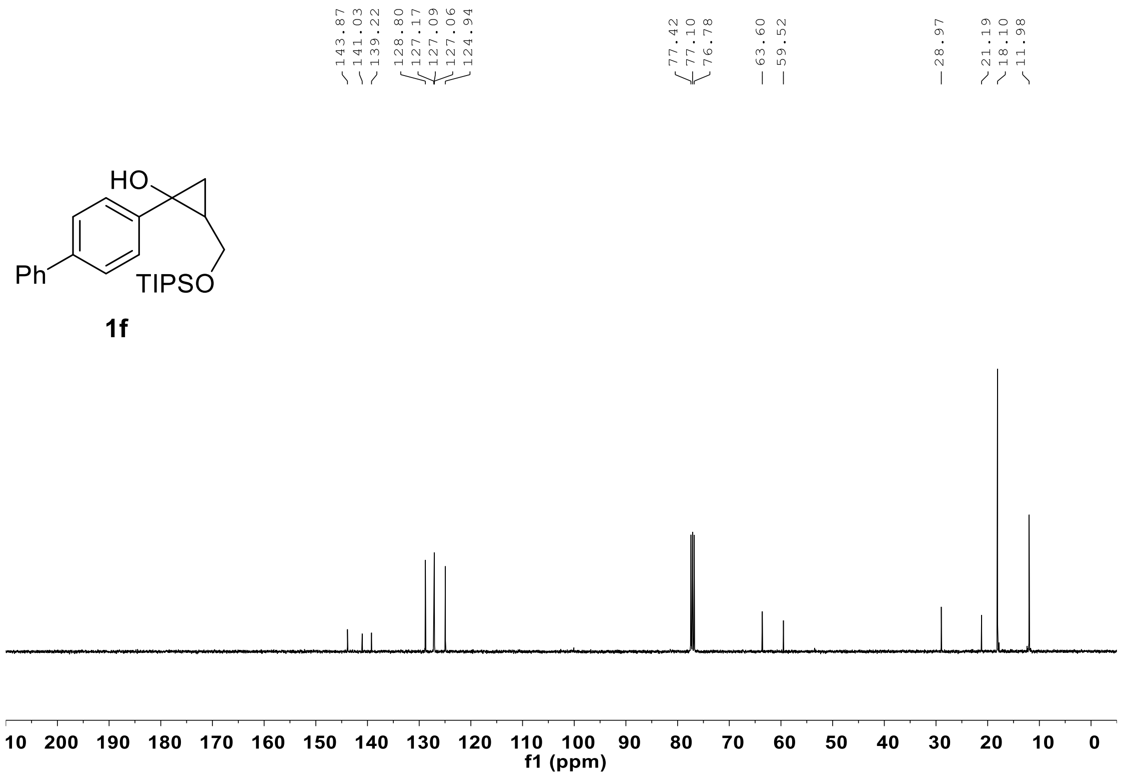


1f ^{13}C NMR (400M Hz, CDCl$_3$)



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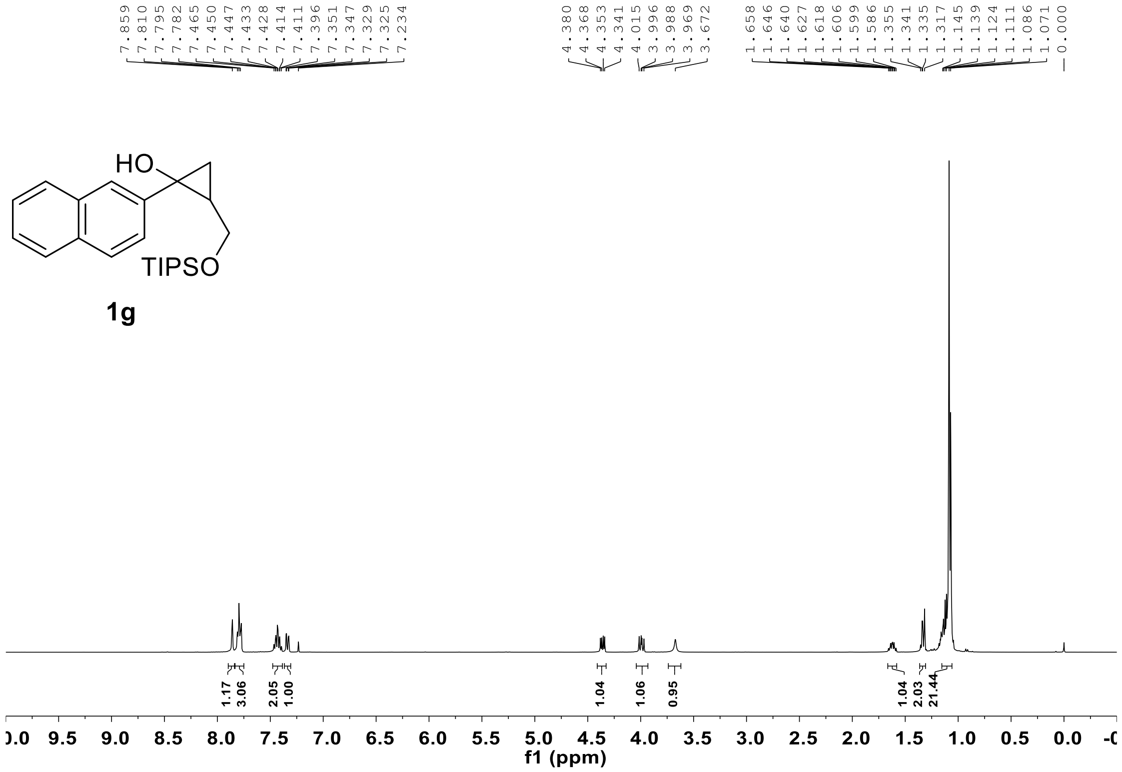

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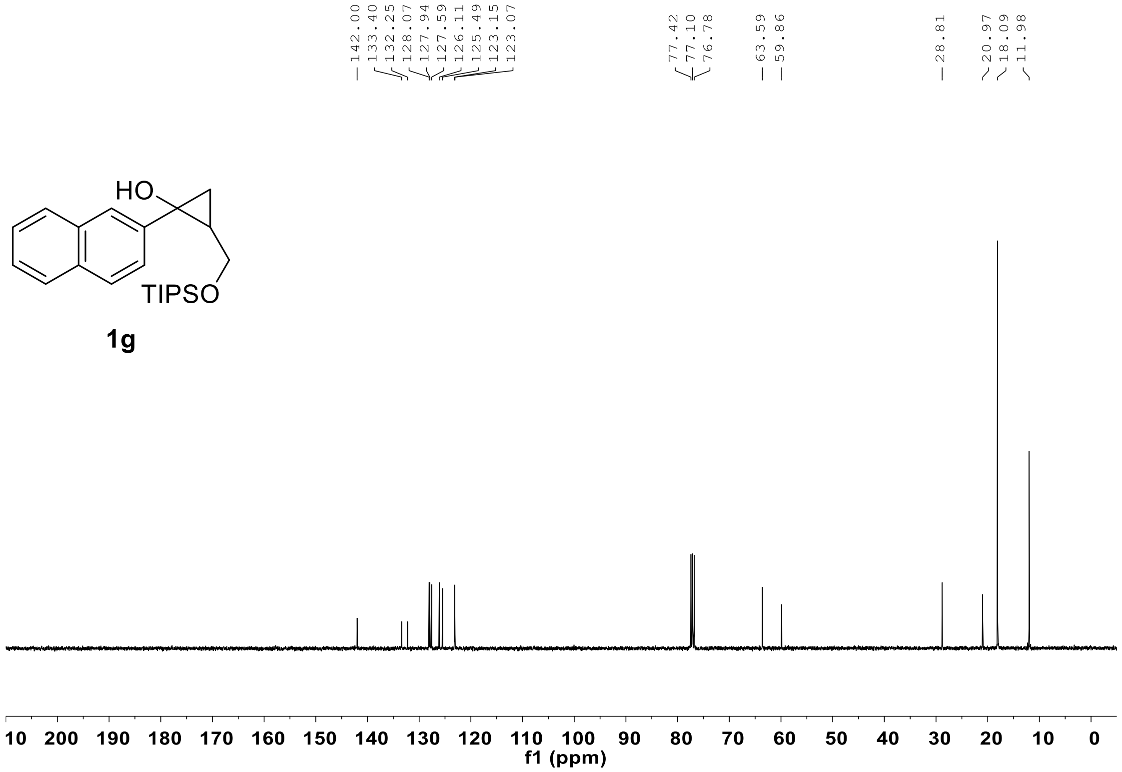

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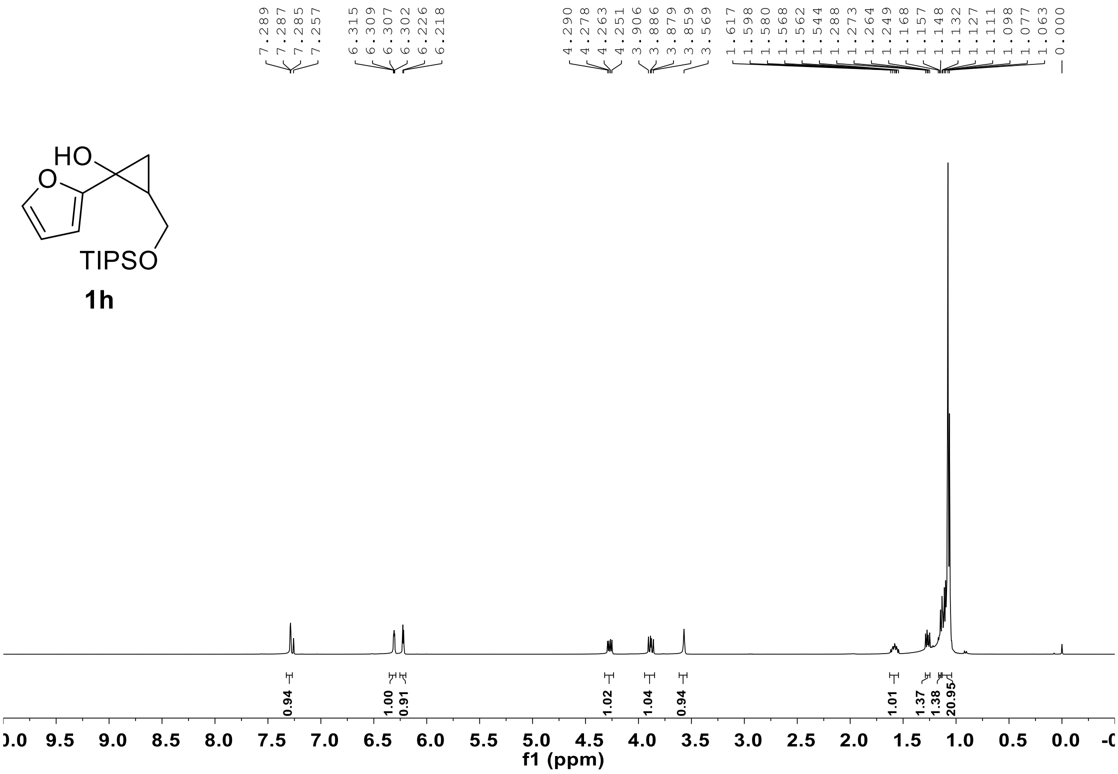

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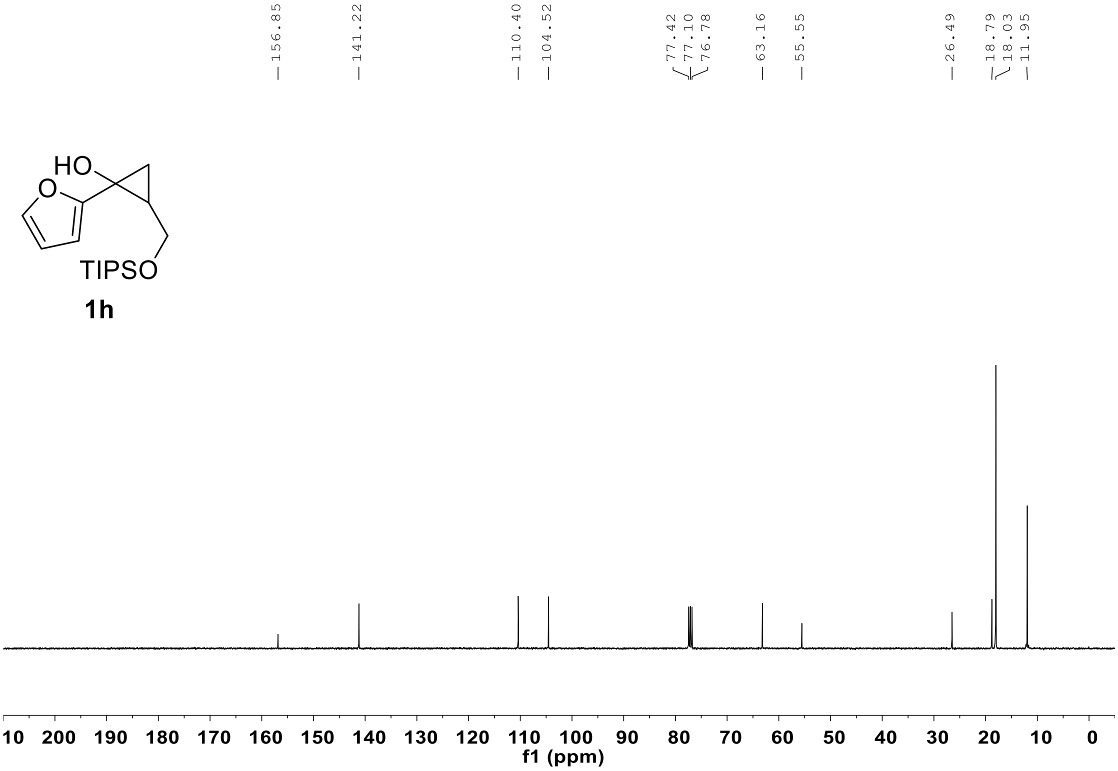

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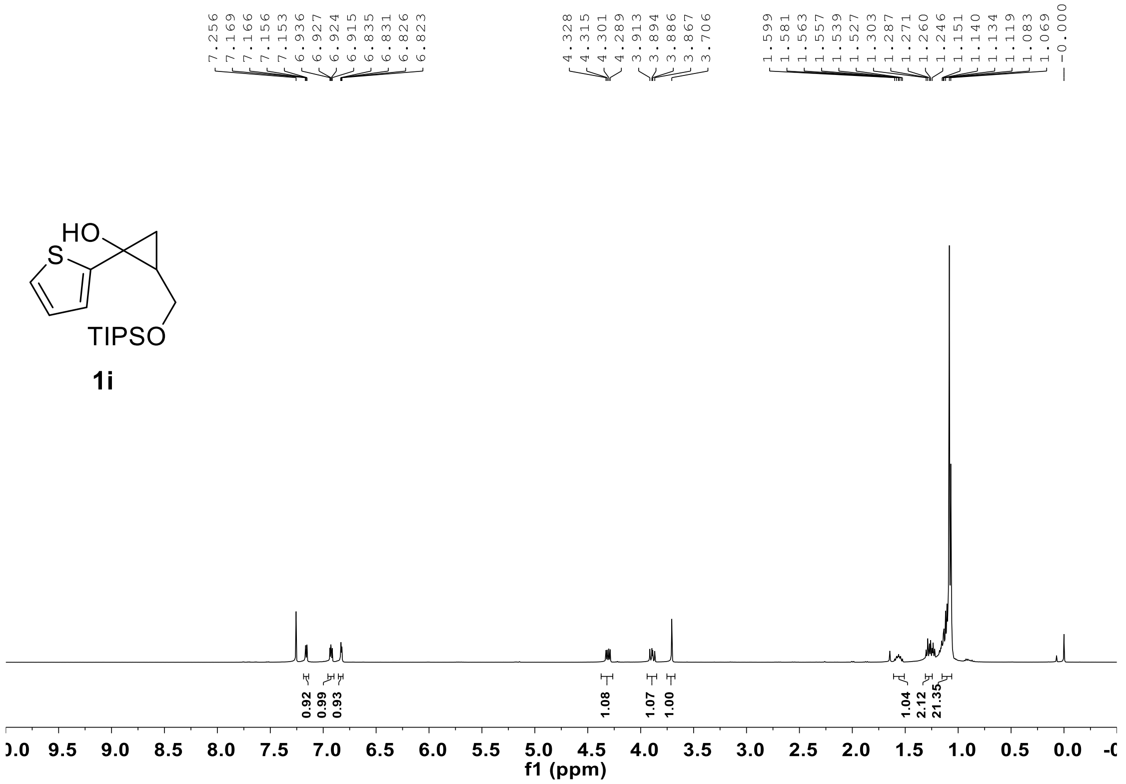

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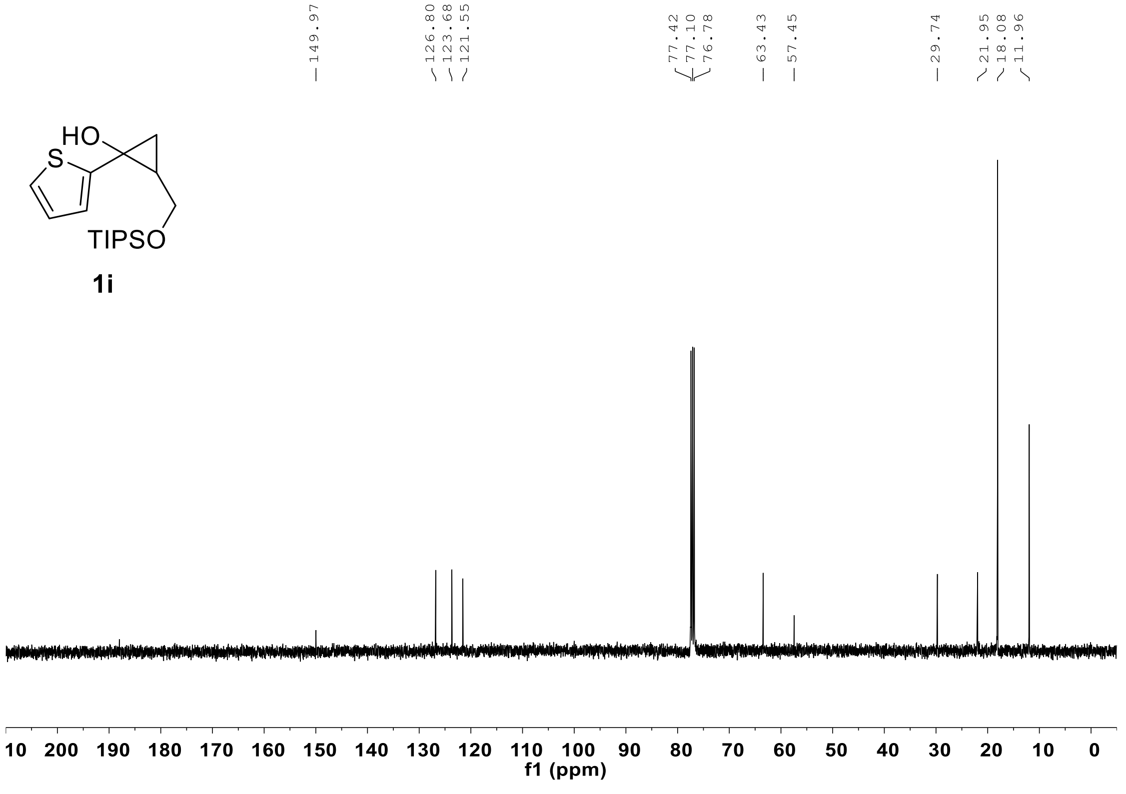

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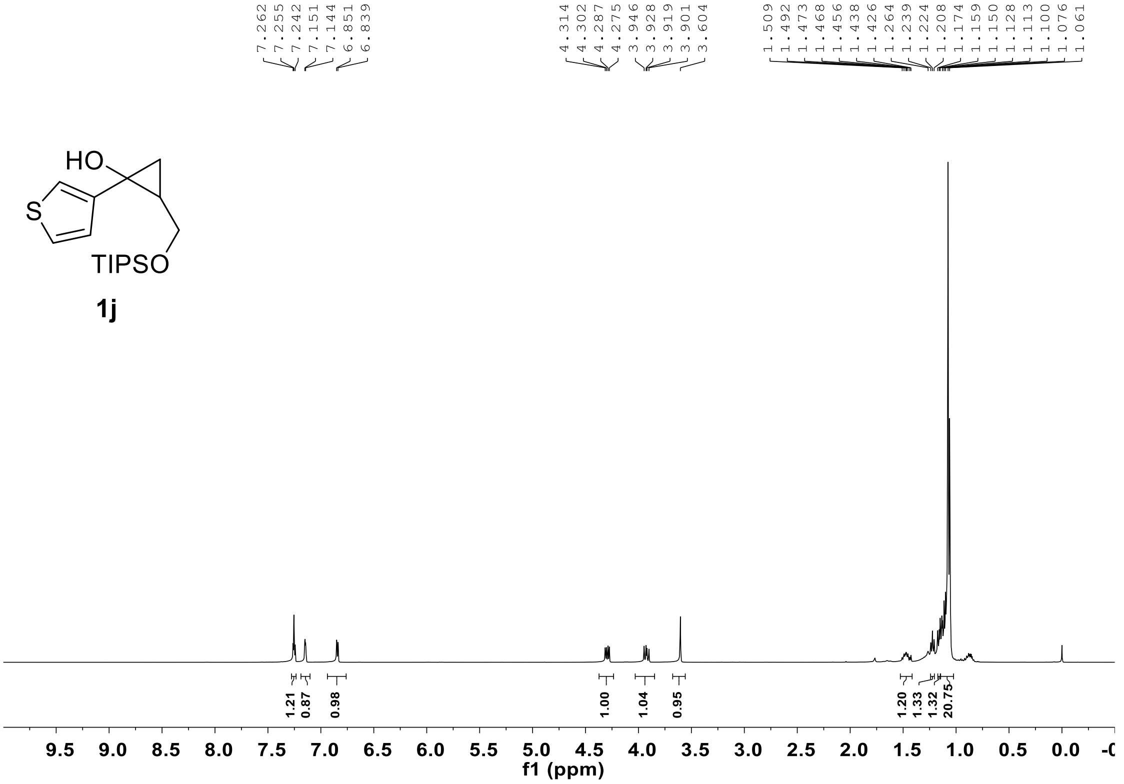

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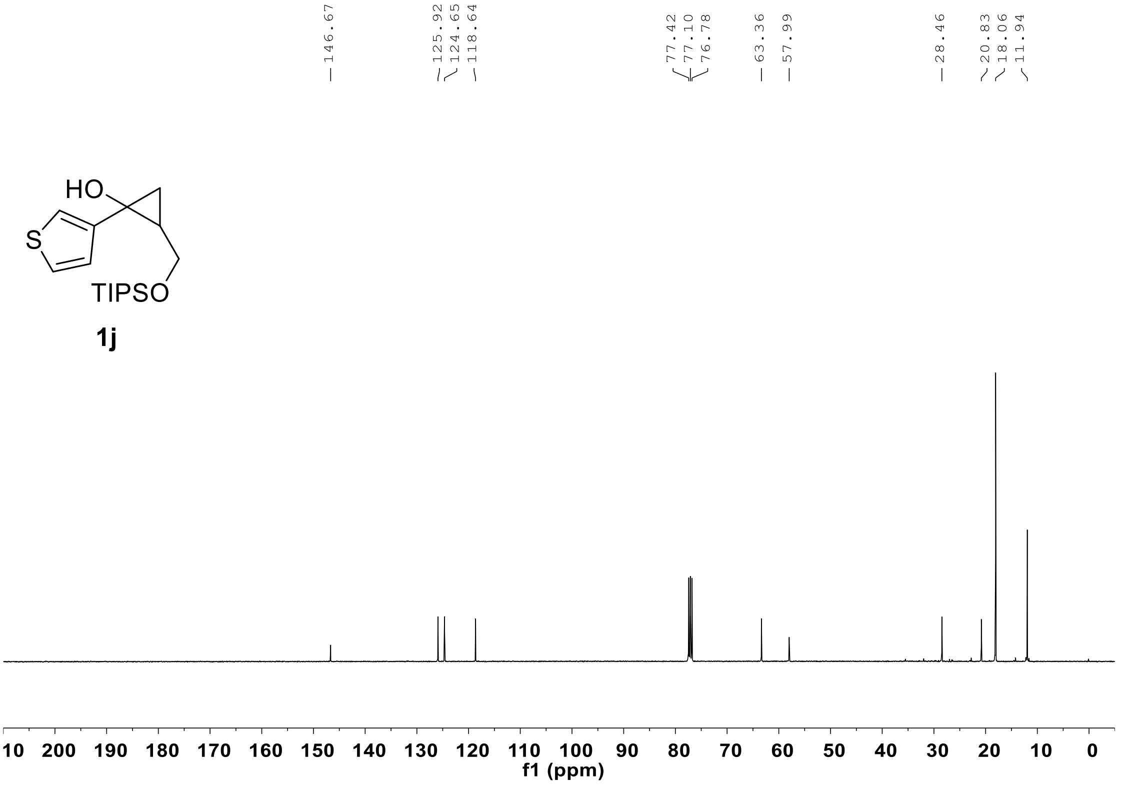

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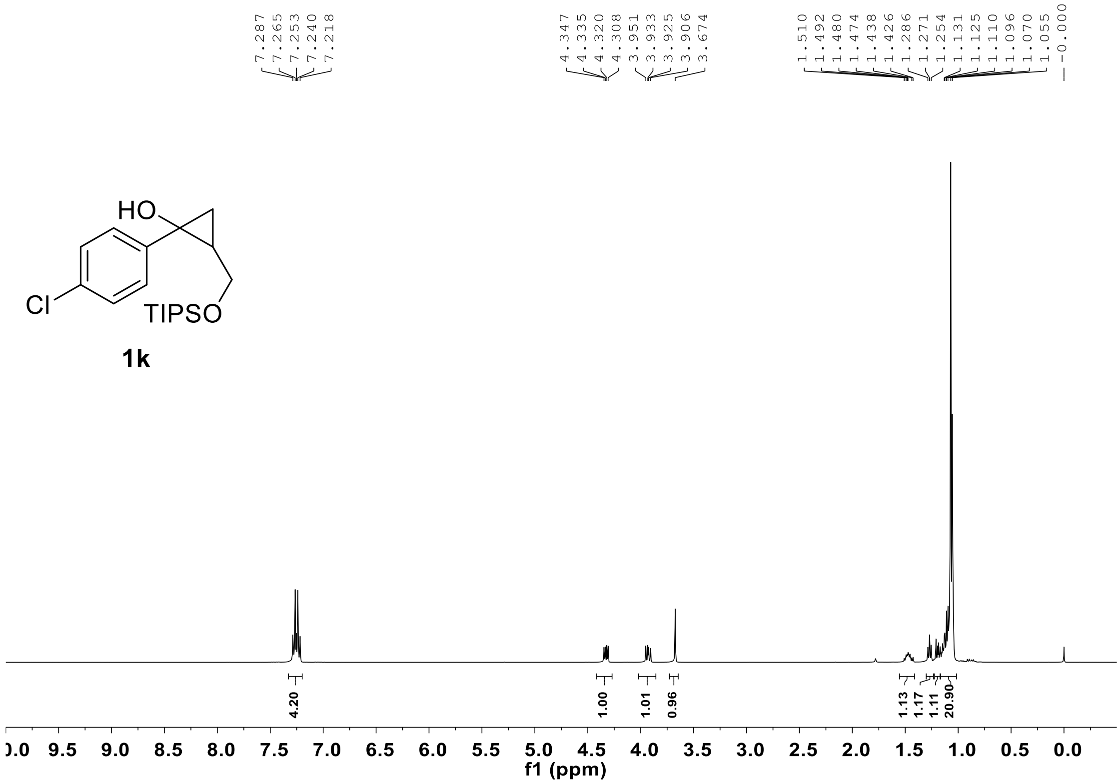

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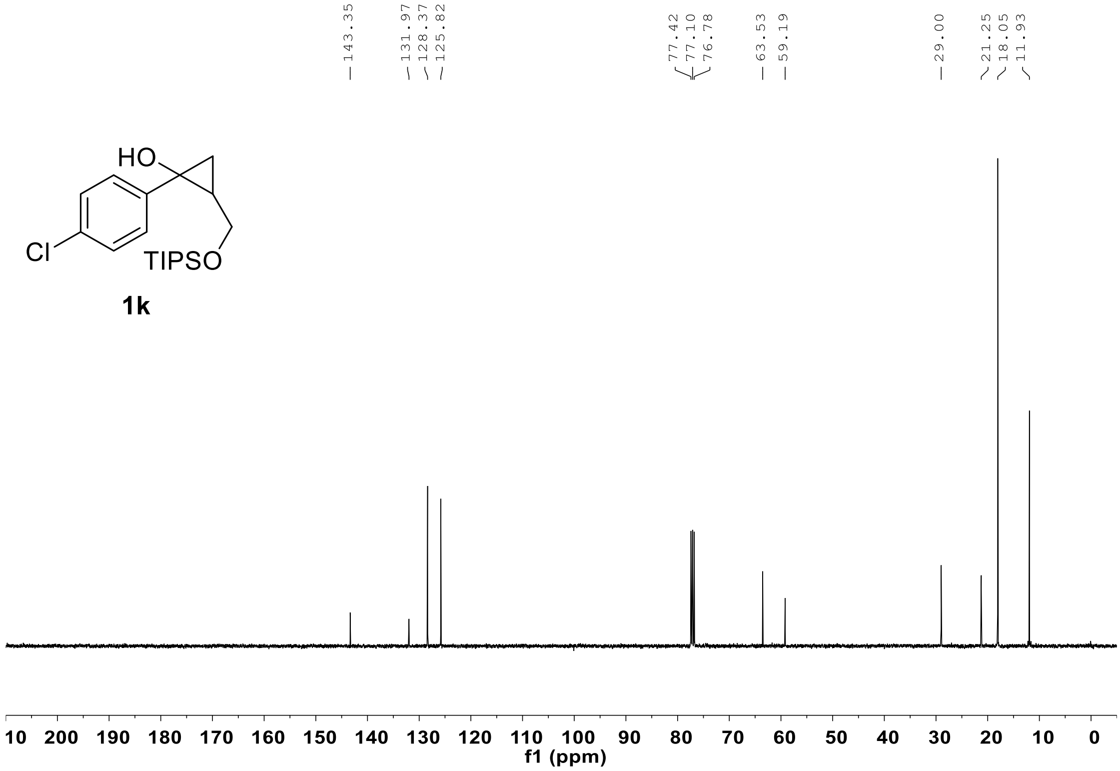
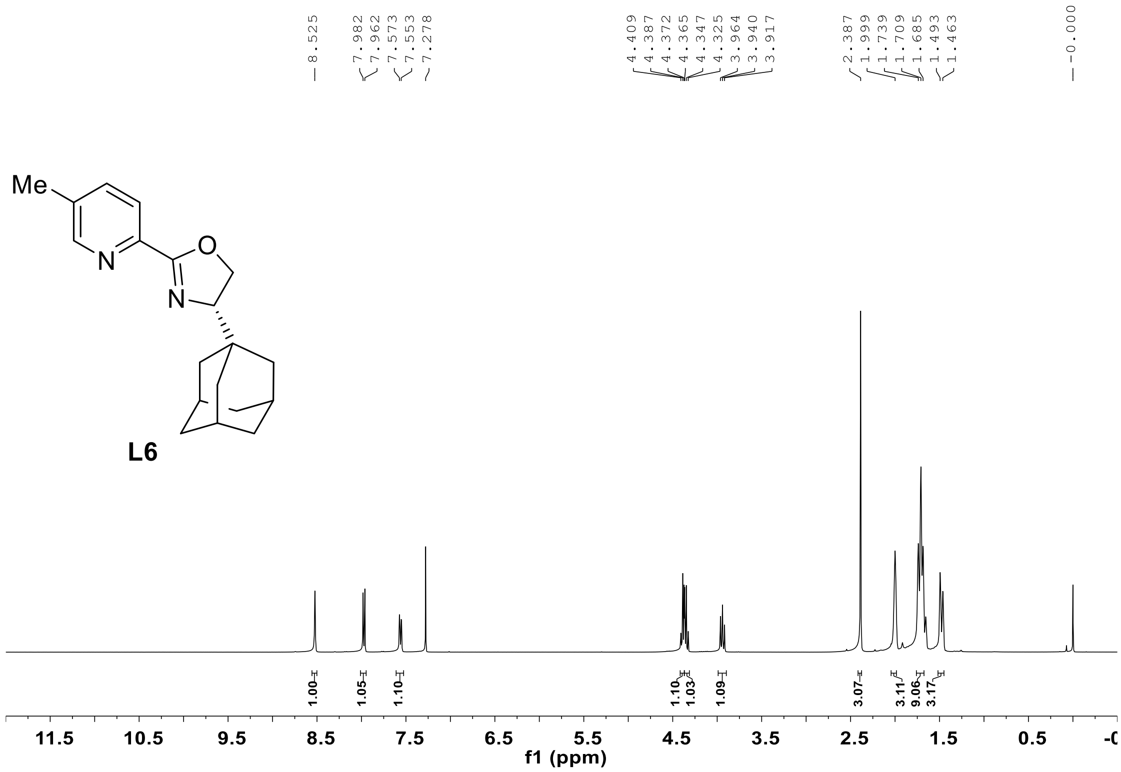
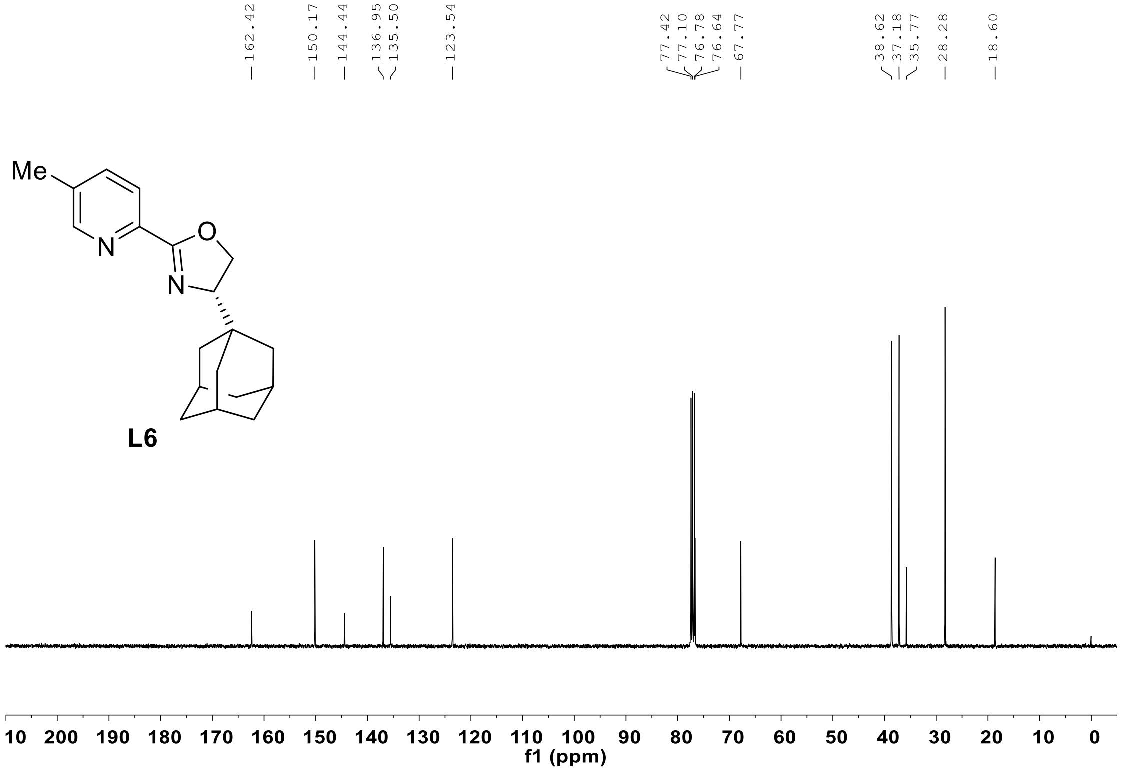


L6 ^{1}H NMR (400M Hz, CDCl$_3$)



L6 ^{13}C NMR (400M Hz, CDCl$_3$)



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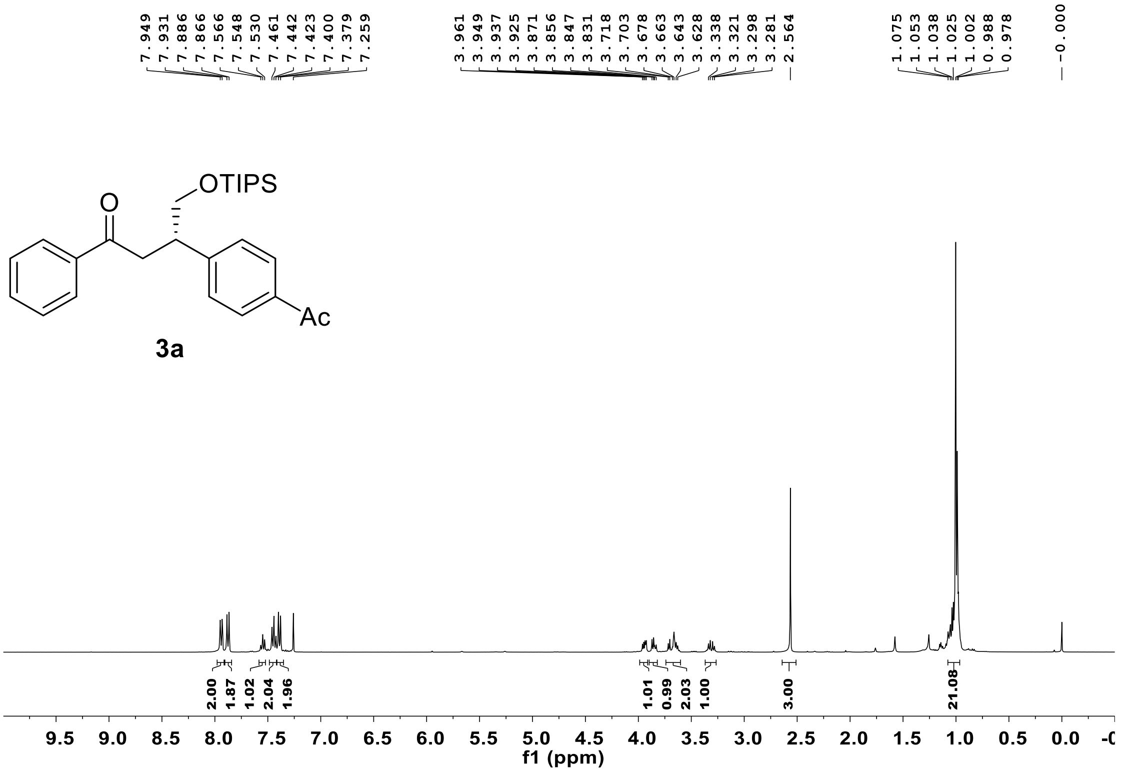

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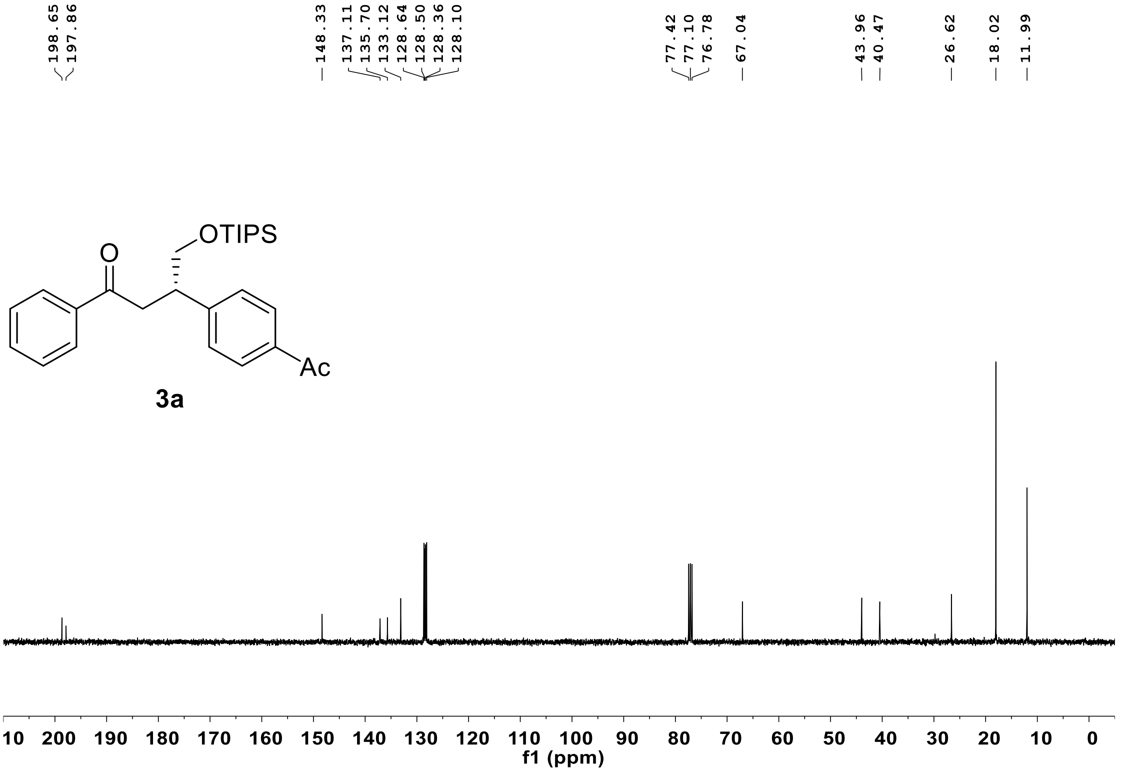

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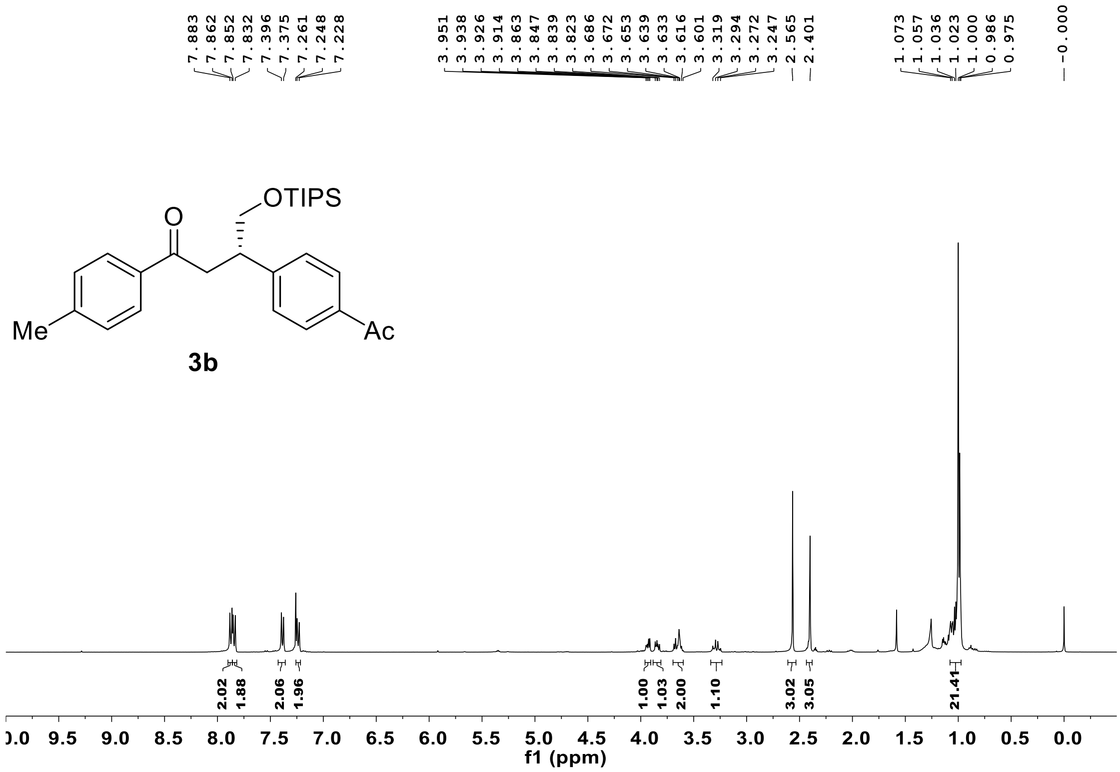

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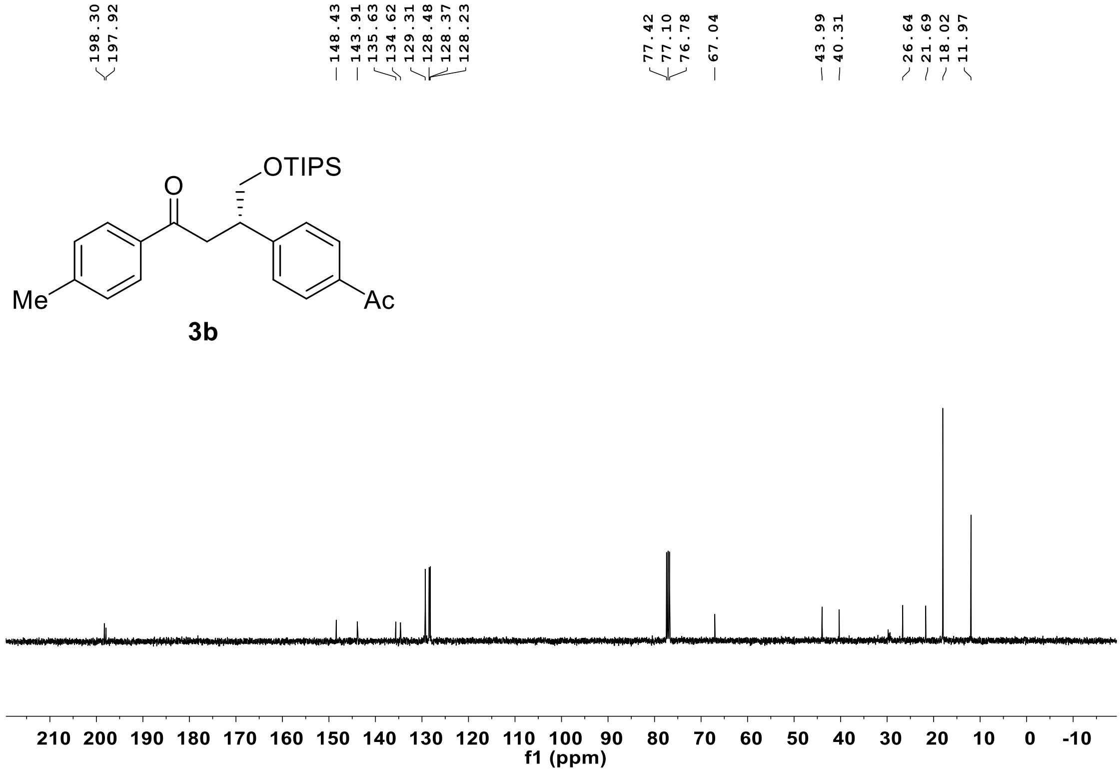

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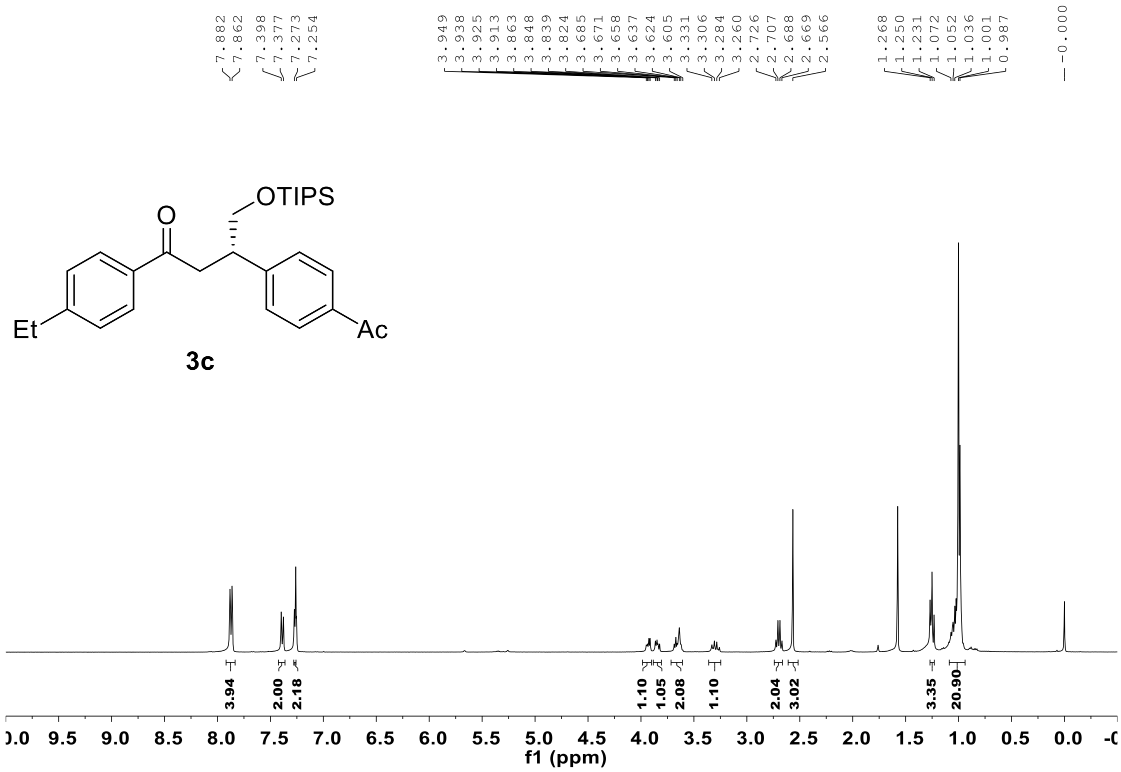

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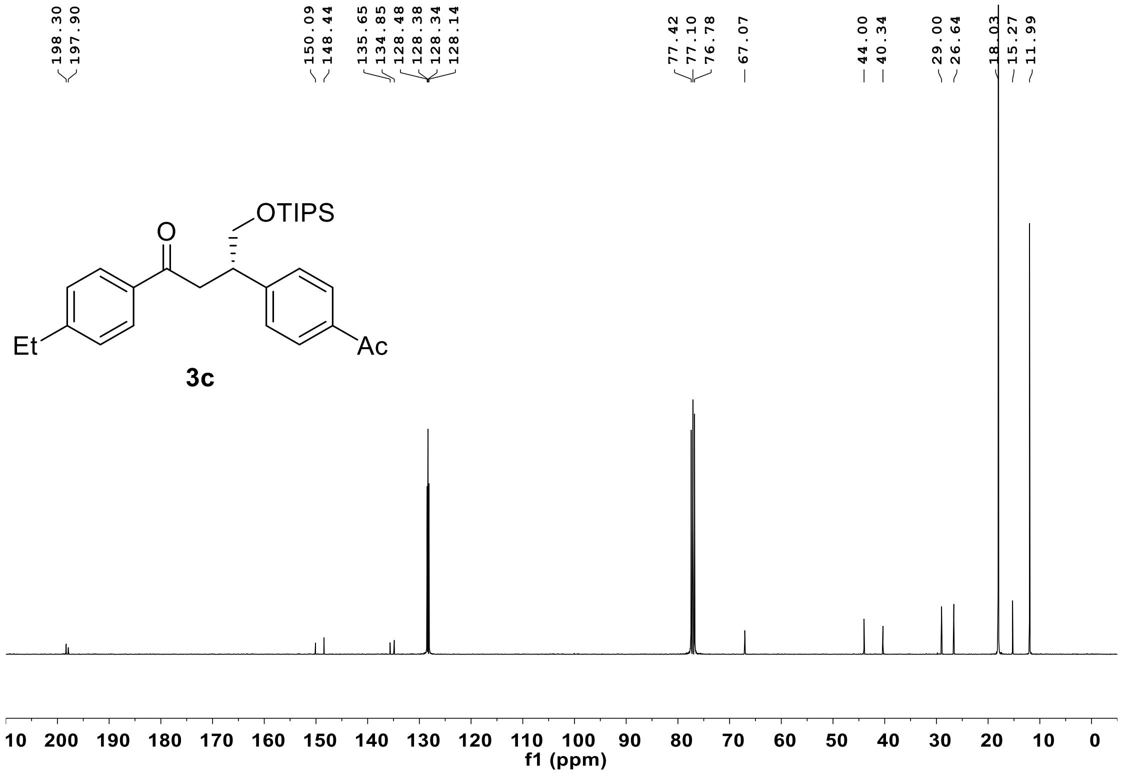

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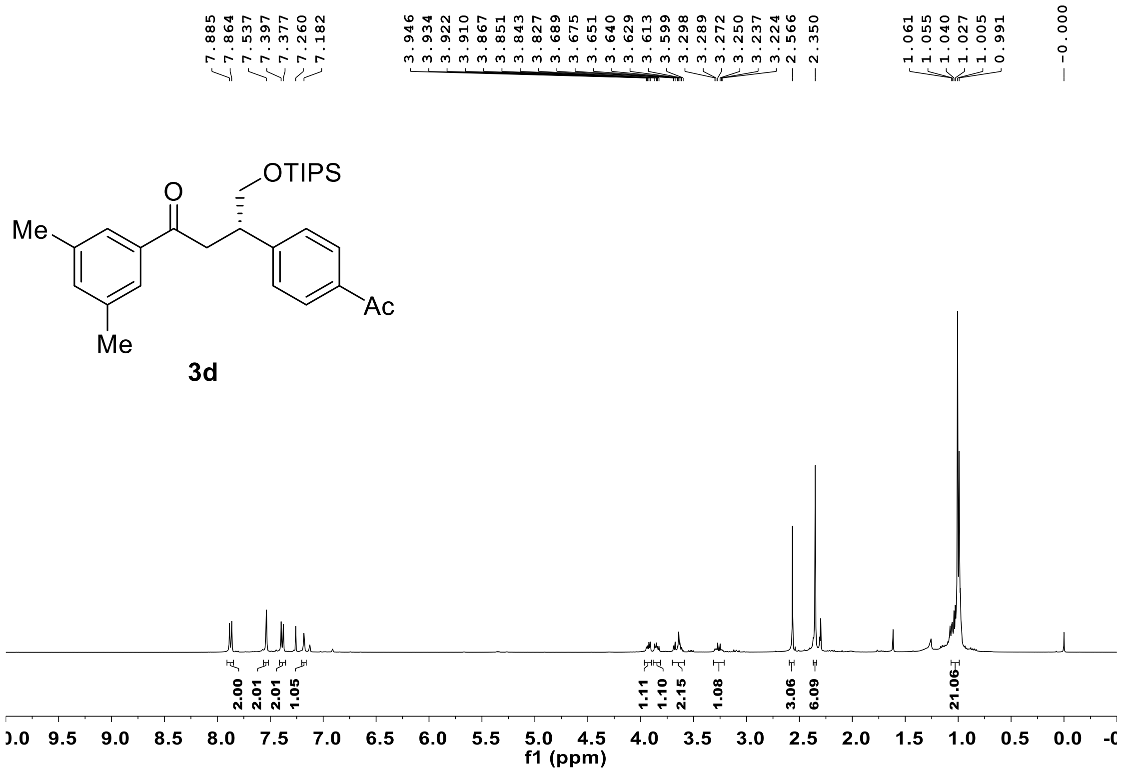

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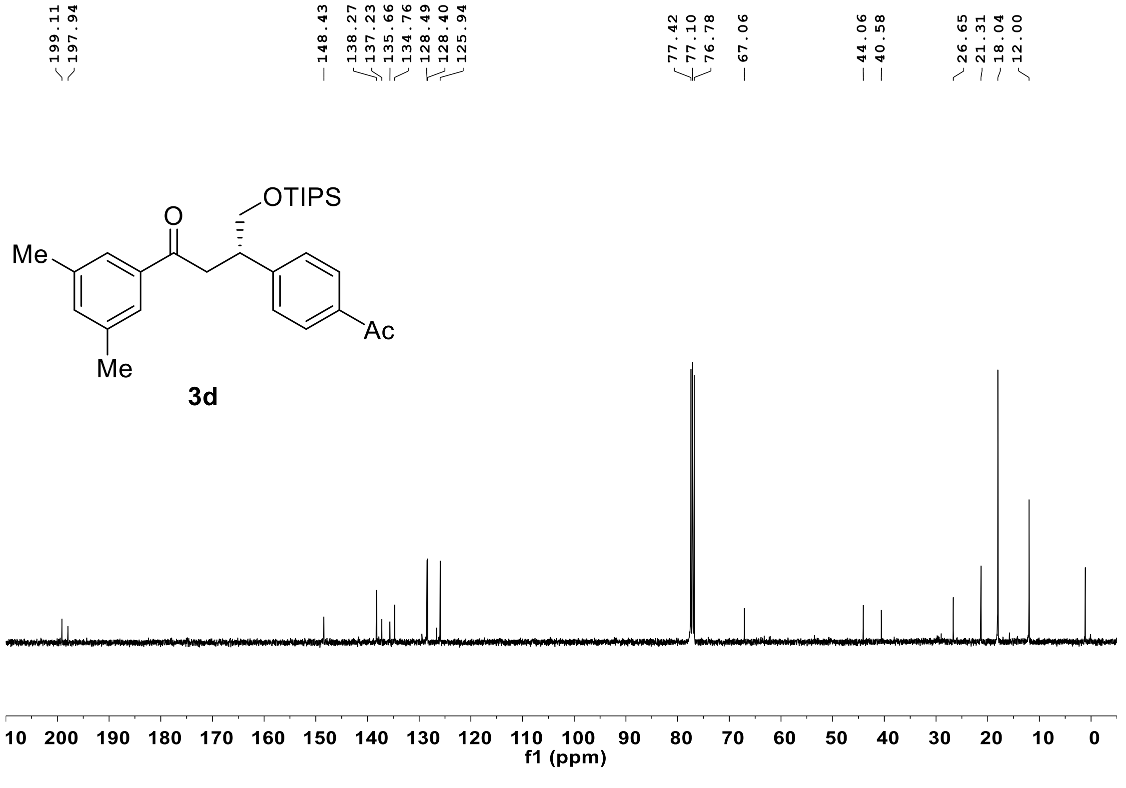

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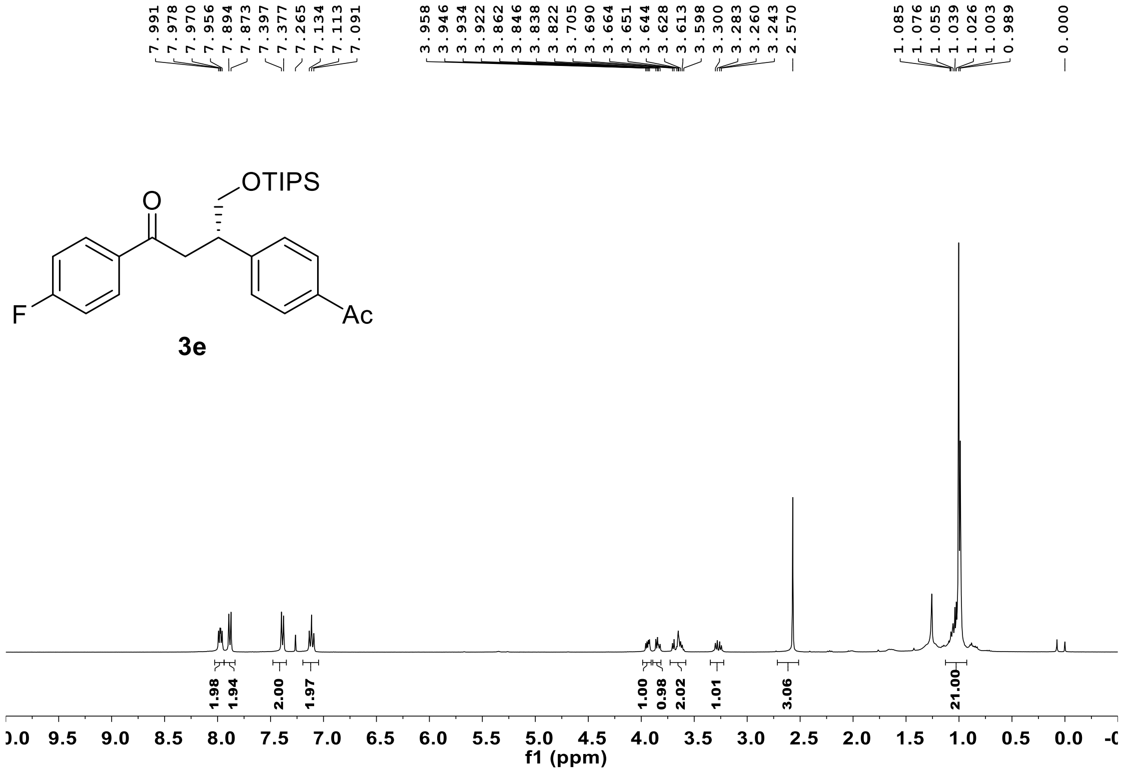

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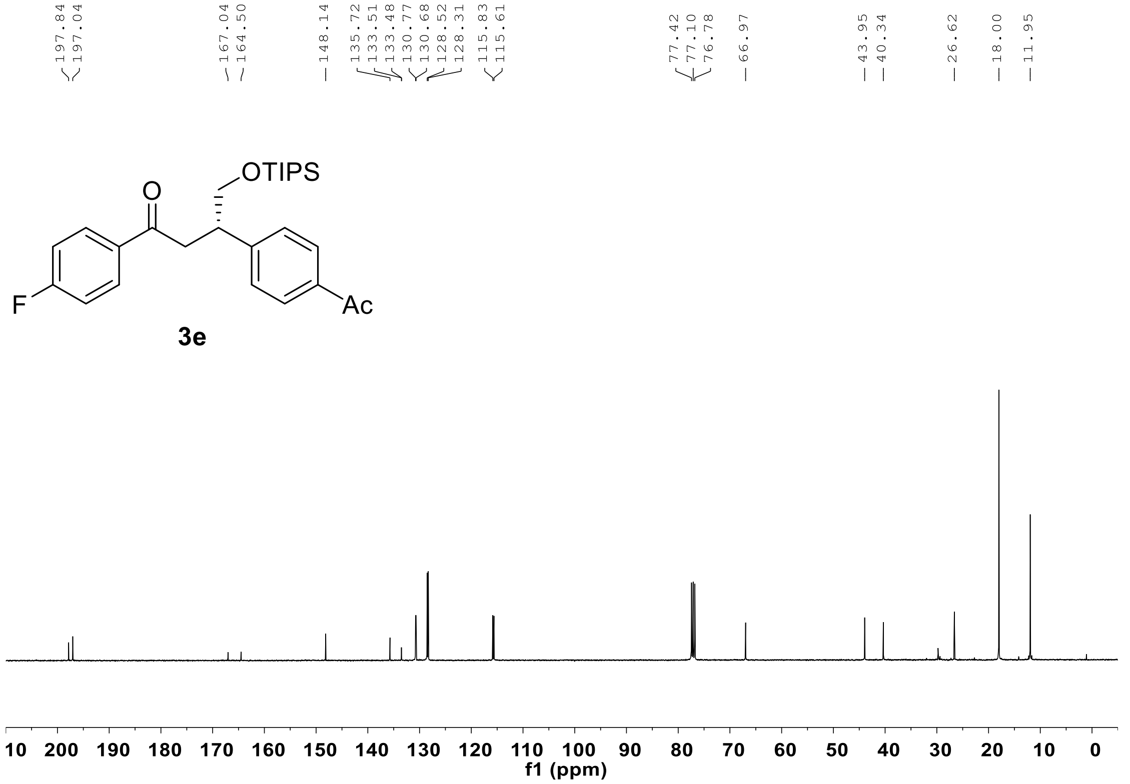

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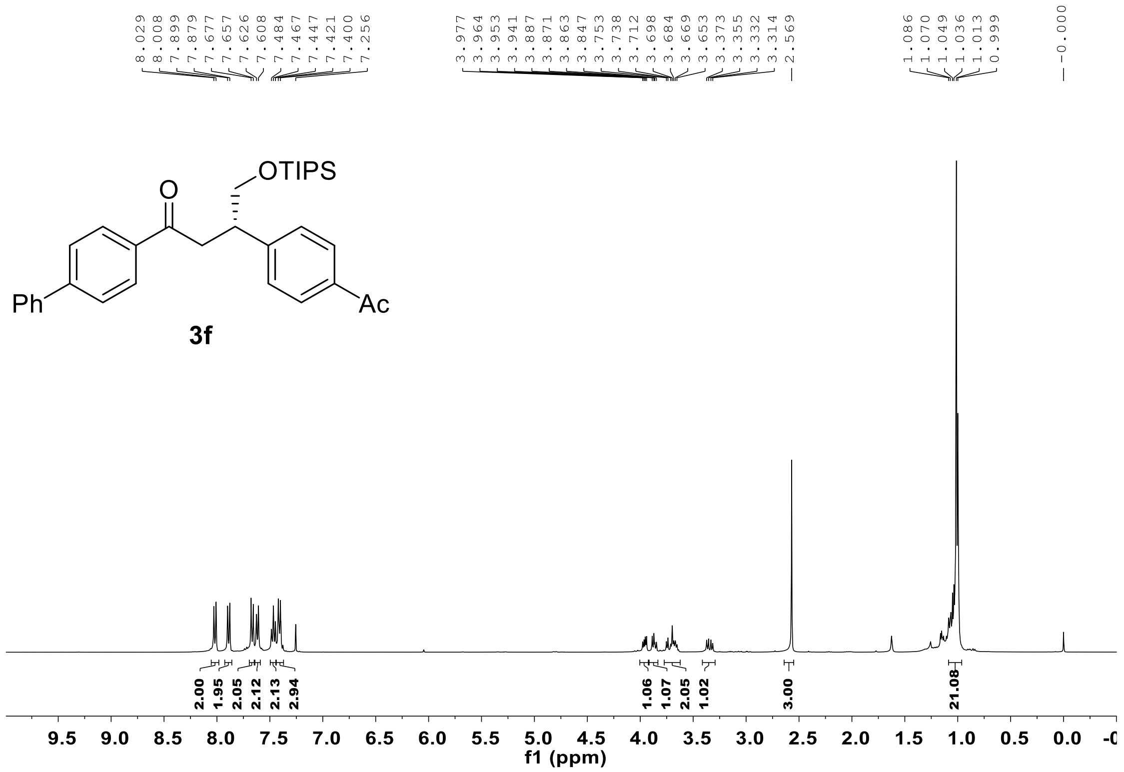

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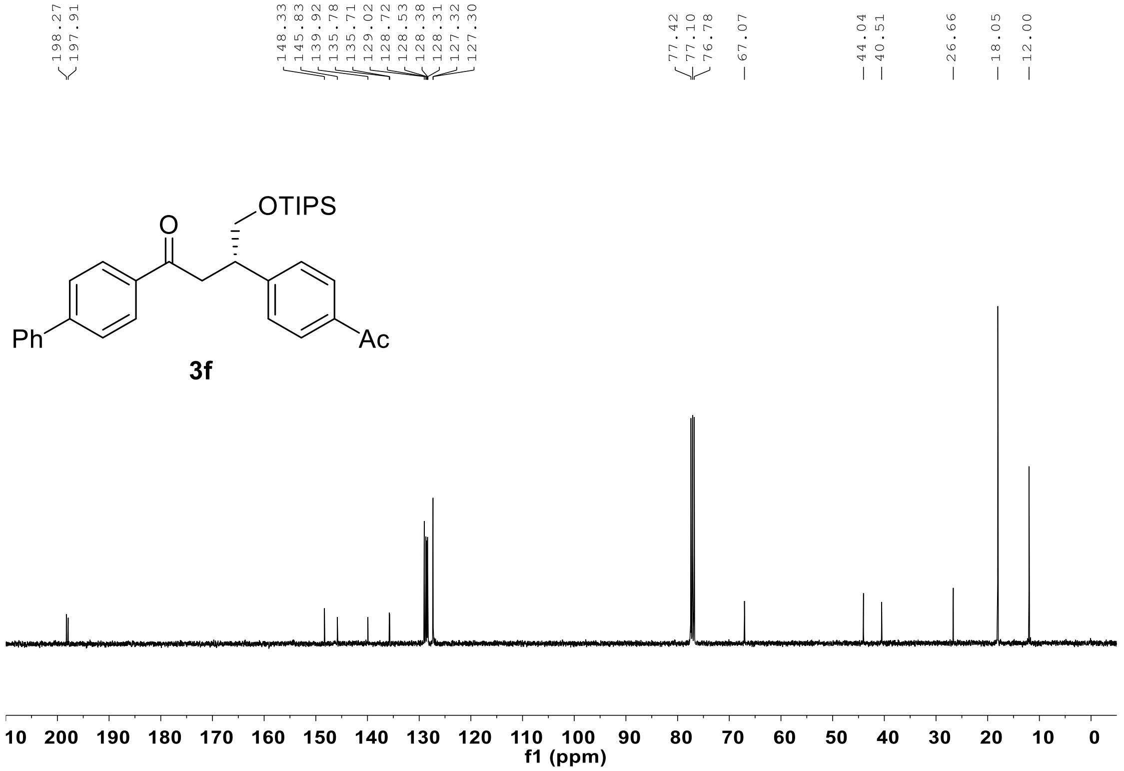

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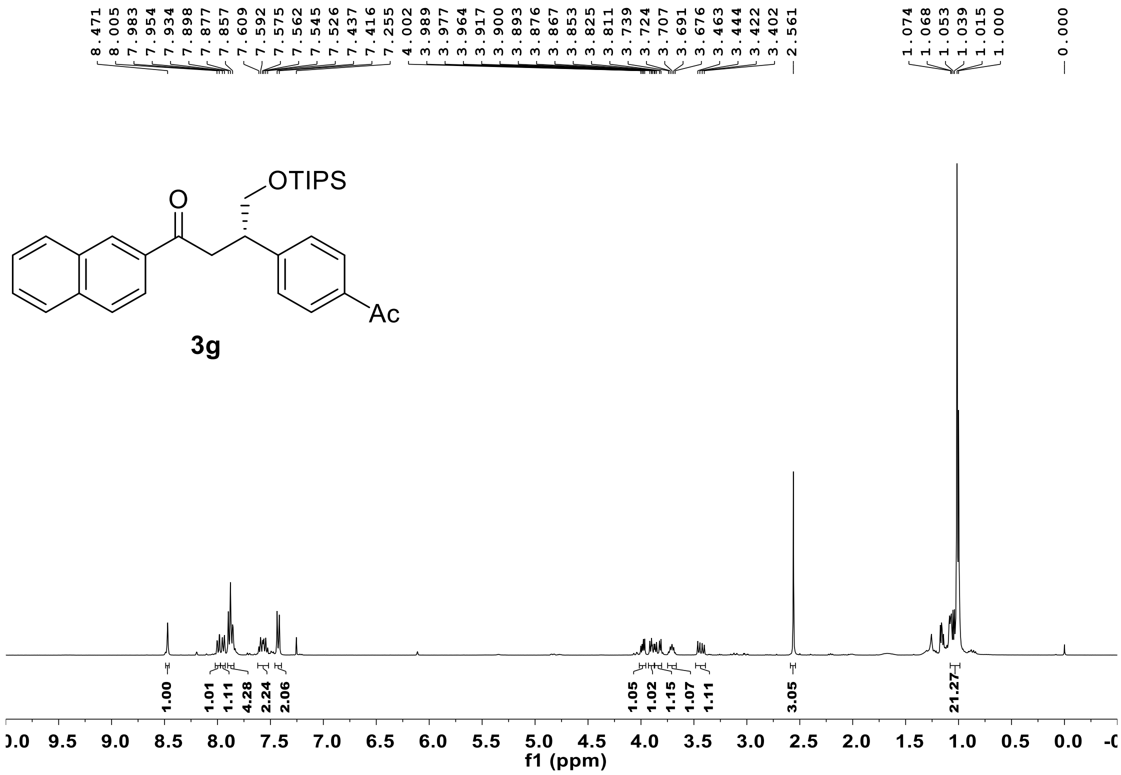

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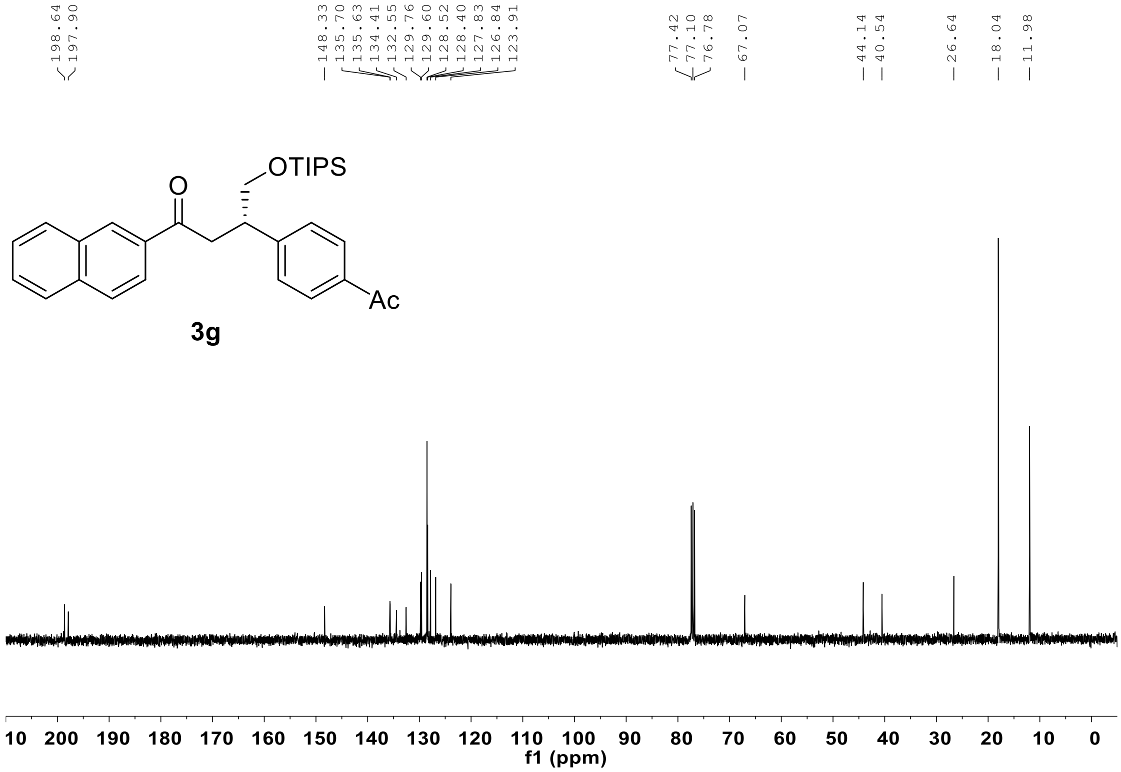

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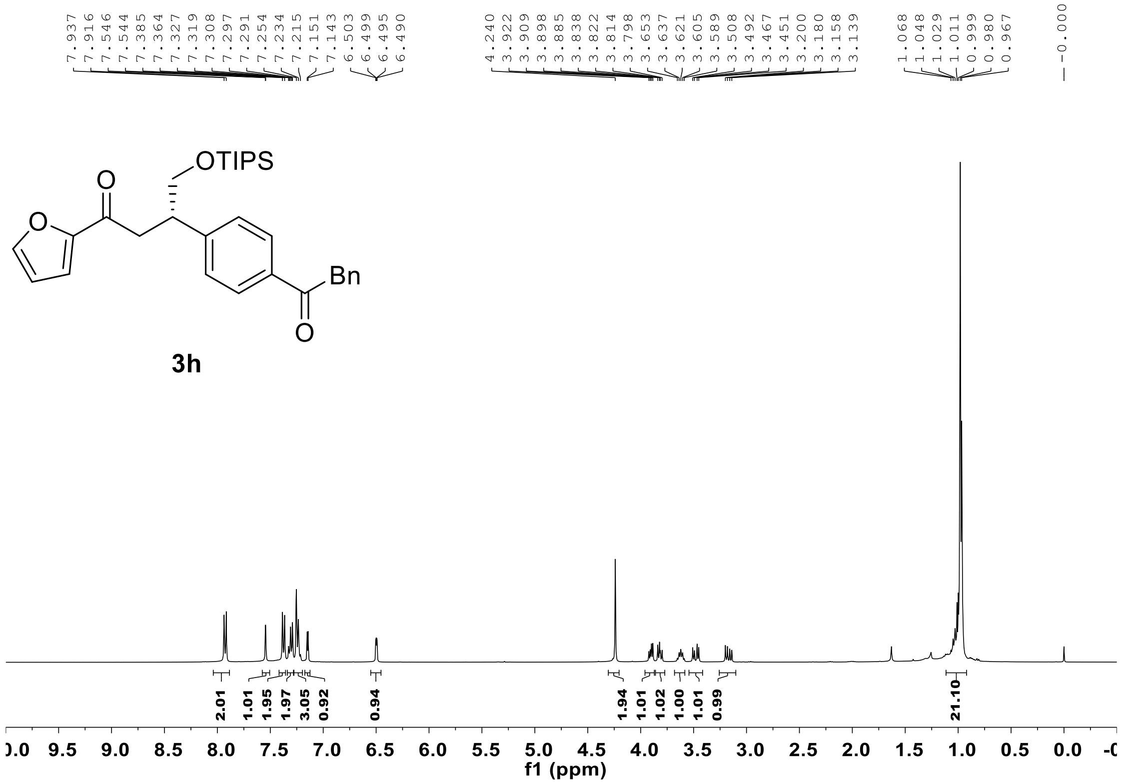

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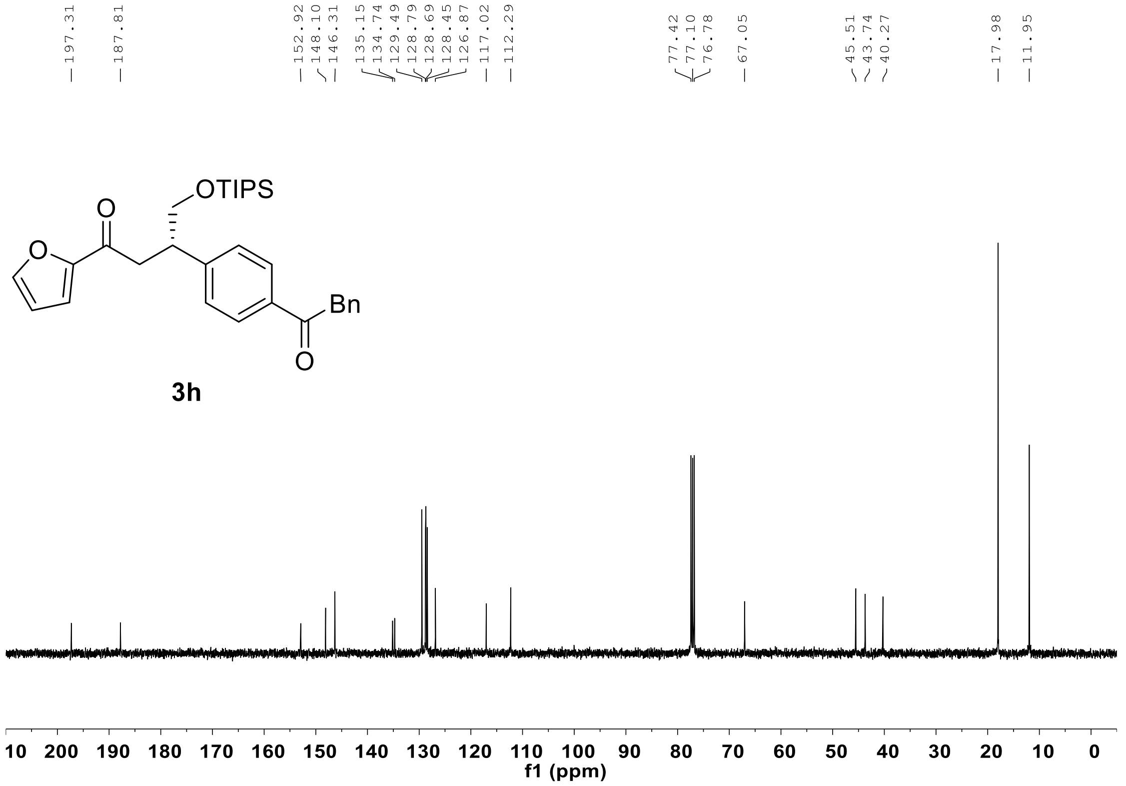

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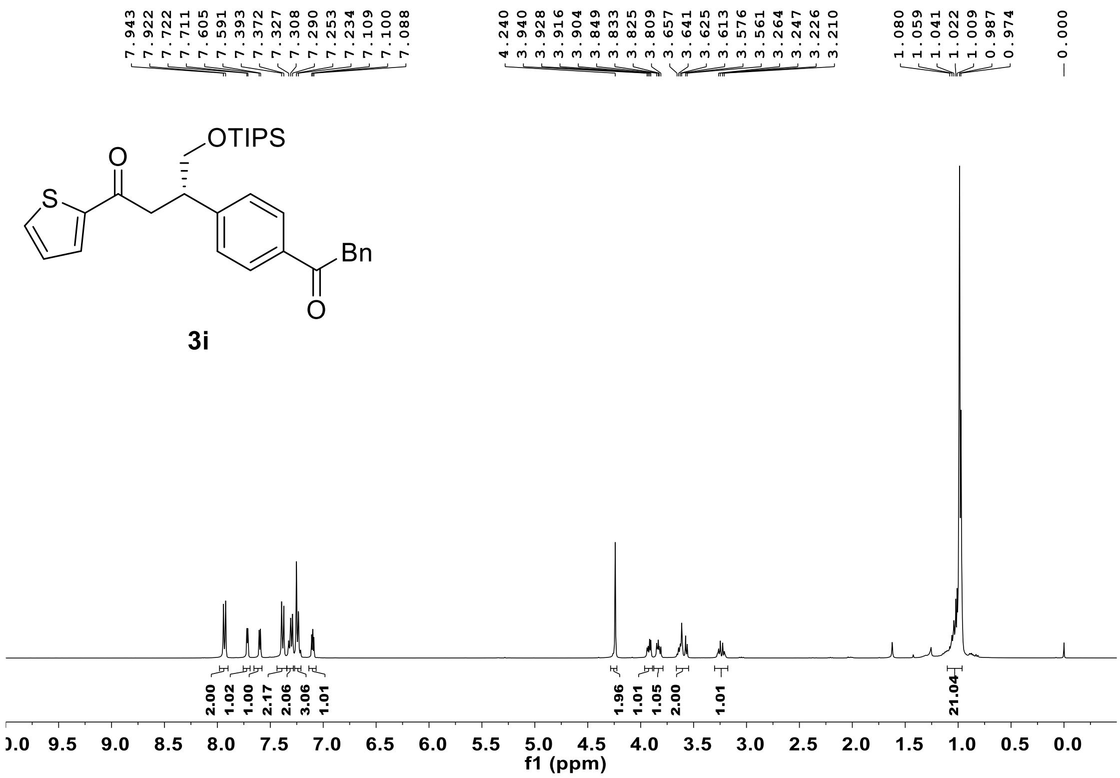
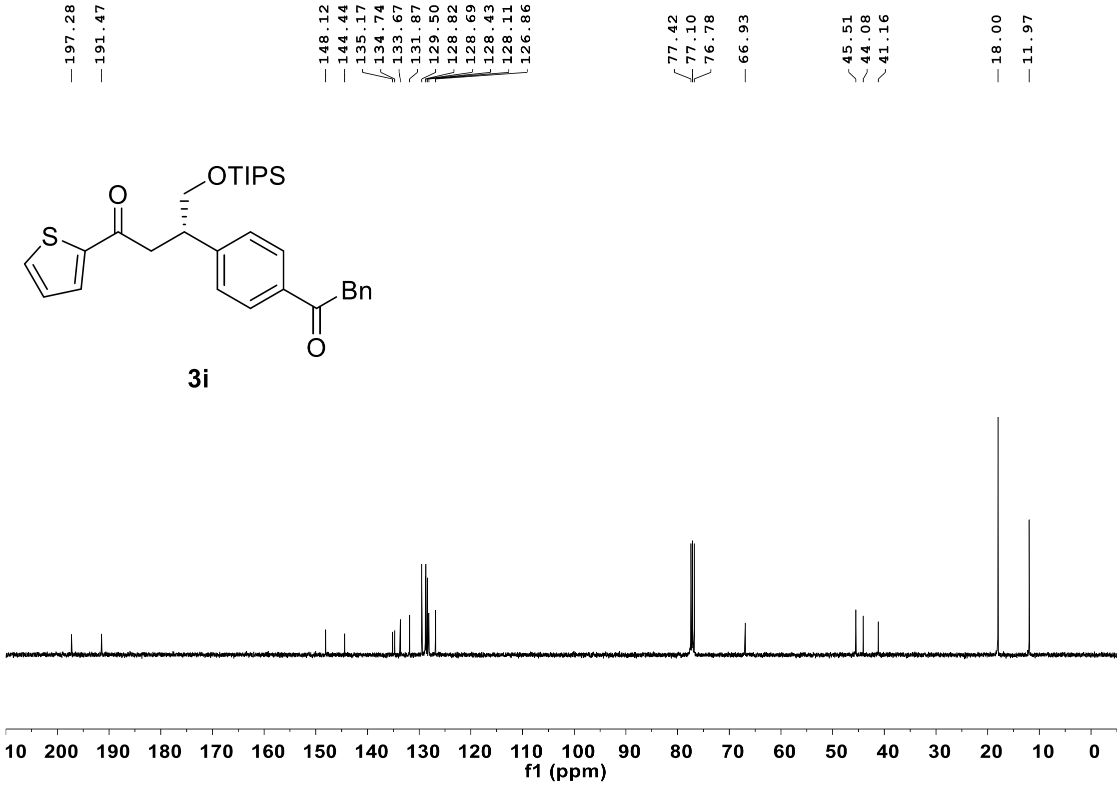
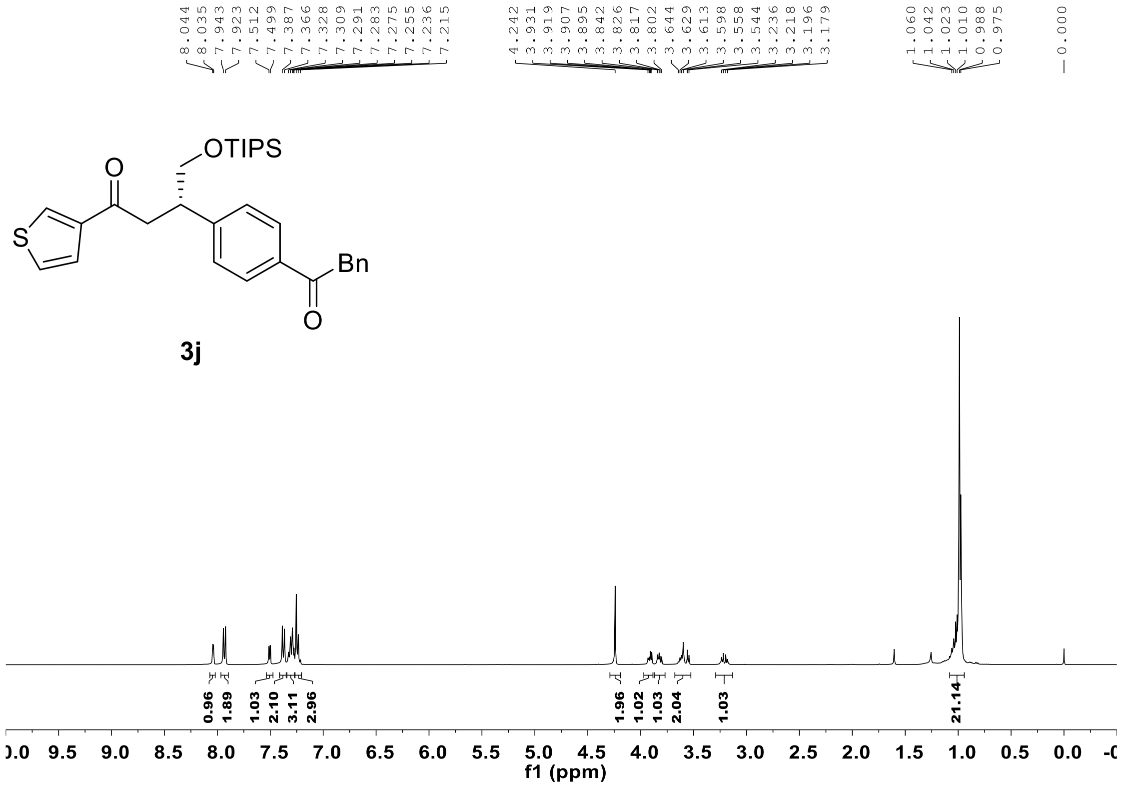


3i ^{13}C NMR (400M Hz, CDCl$_3$)



3j ¹H NMR (400M Hz, $CDCl_3$)



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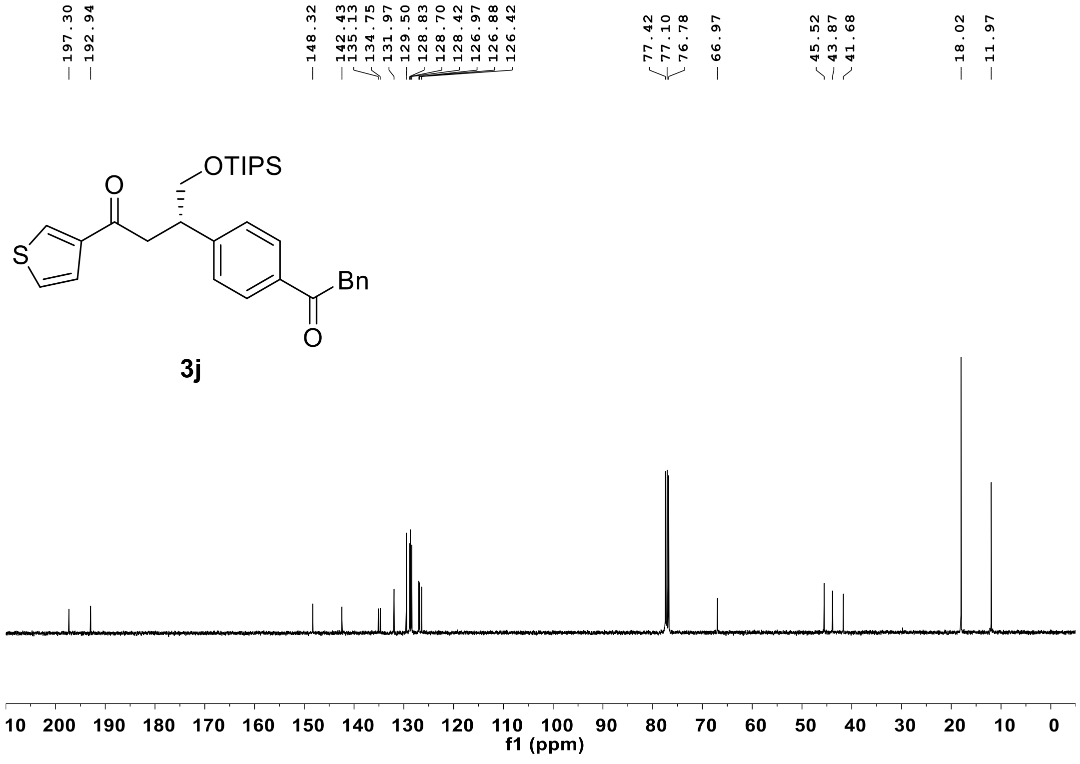
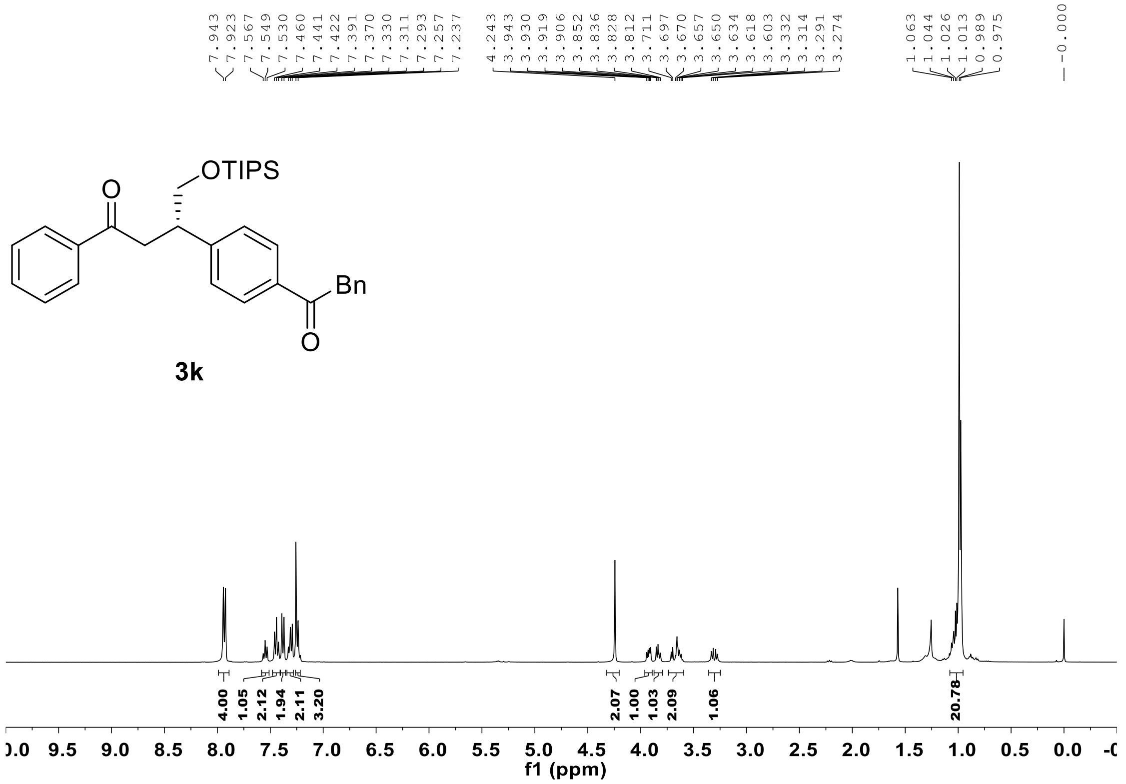


3k ^{1}H NMR (400M Hz, $CDCl_3$)



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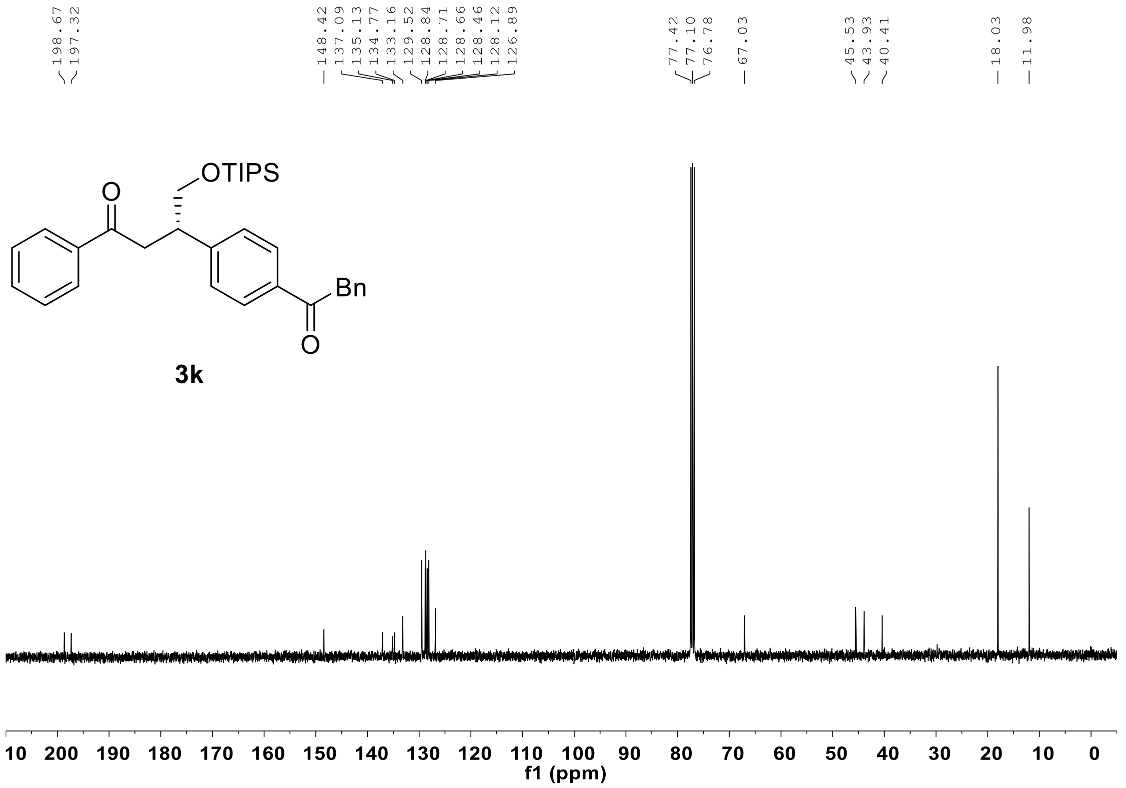

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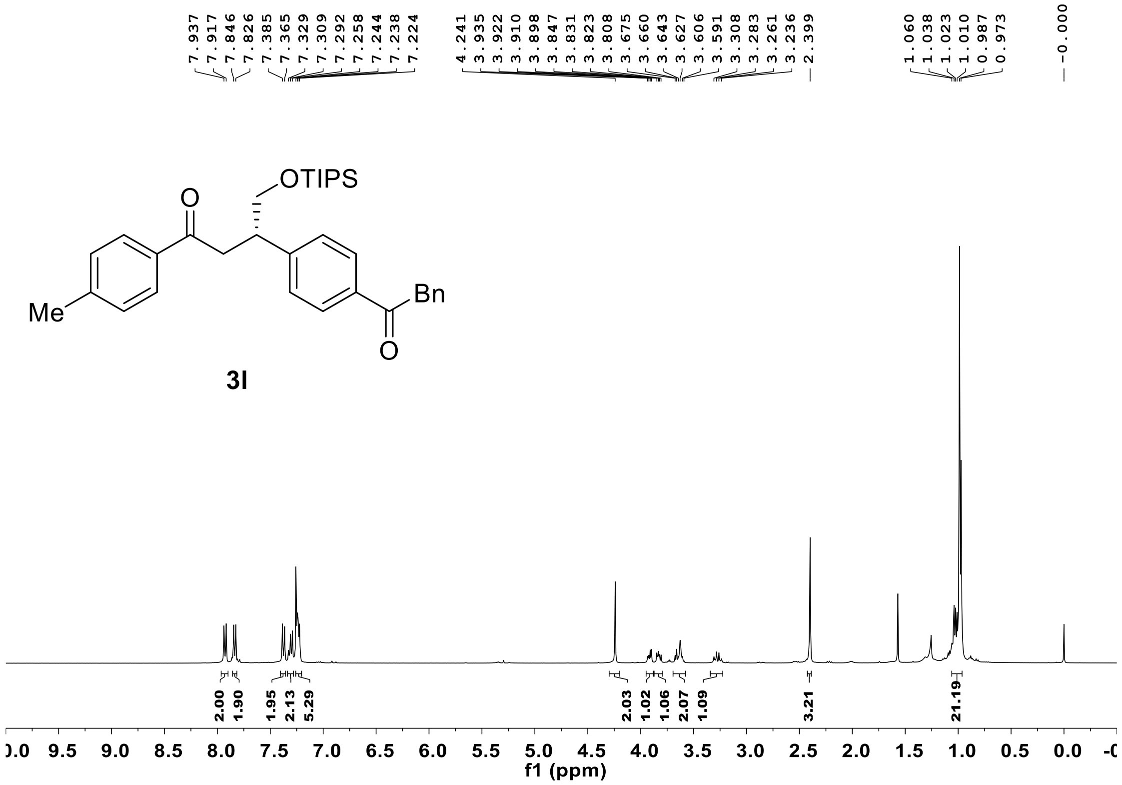

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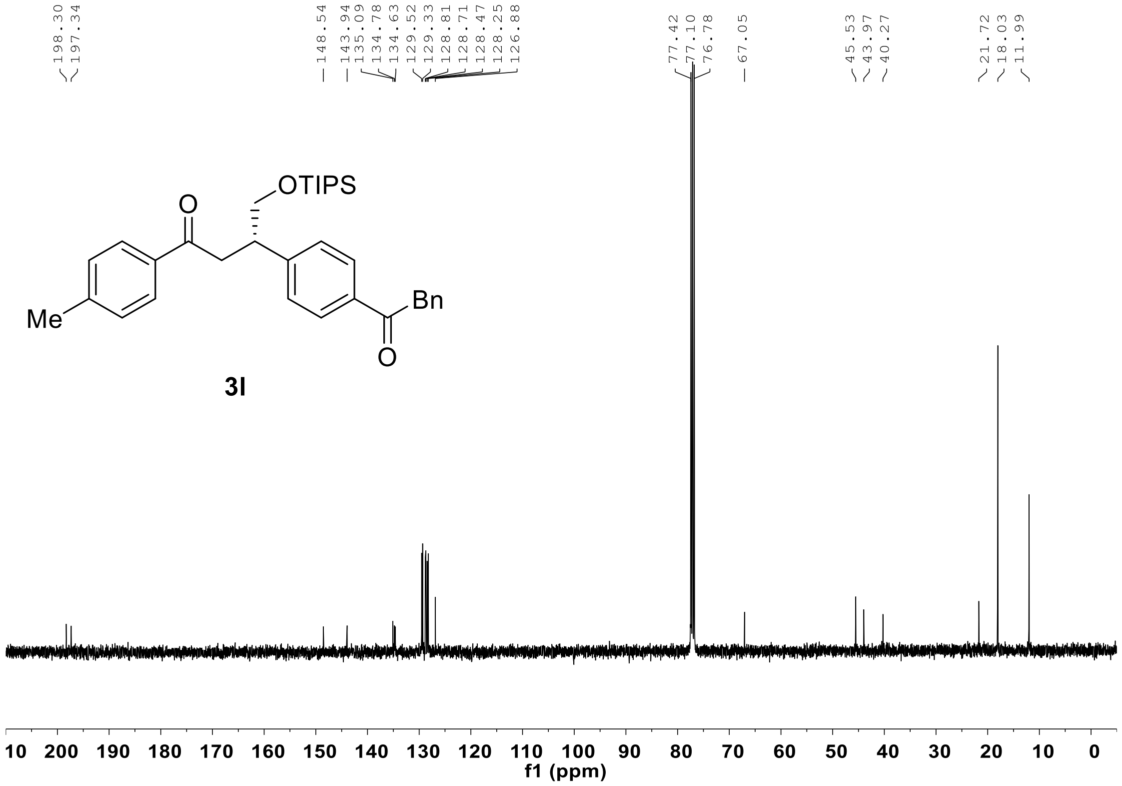

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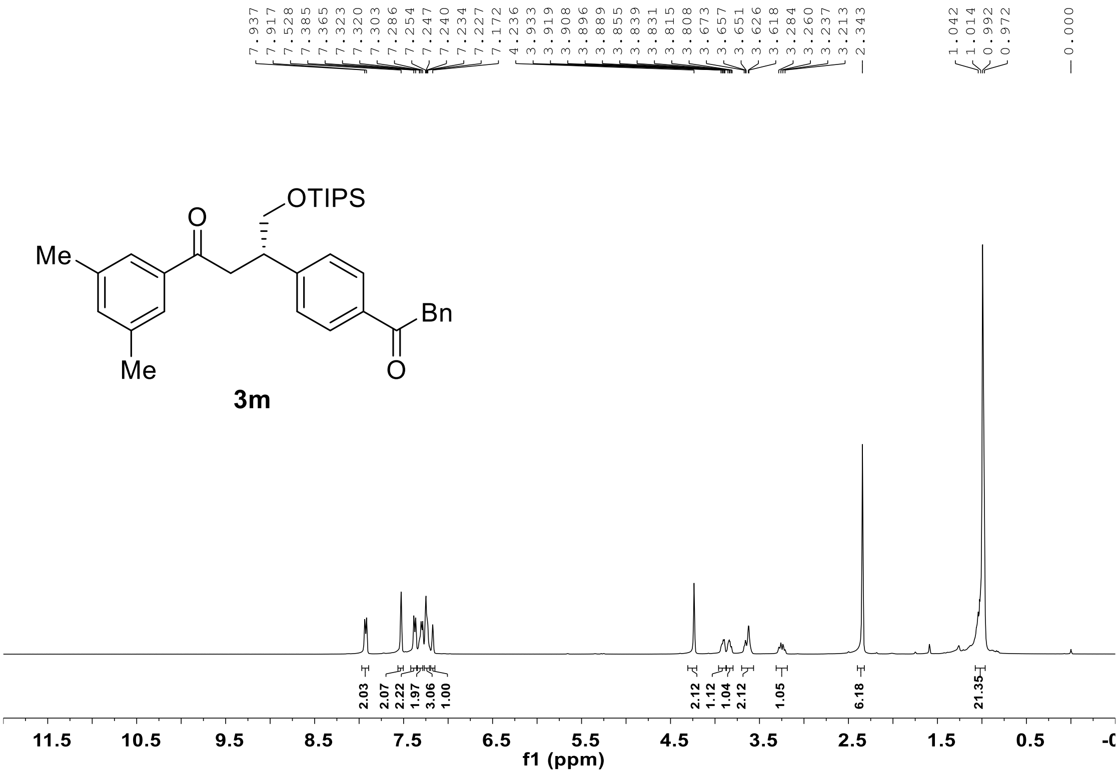

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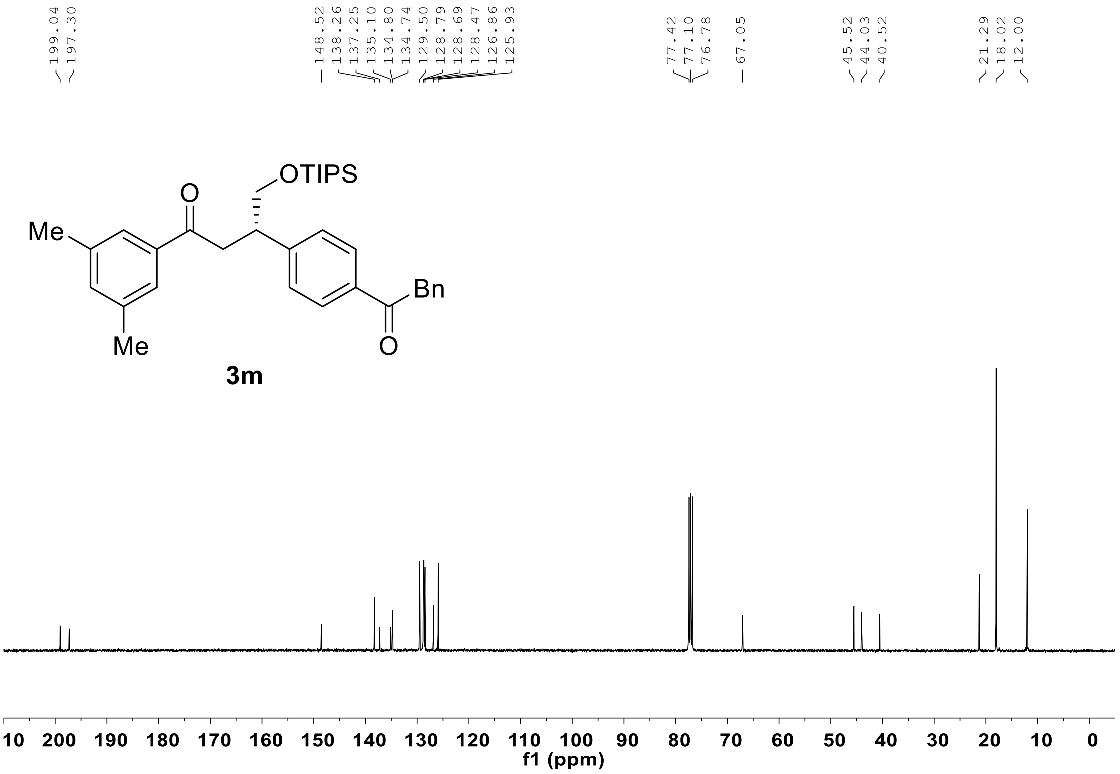

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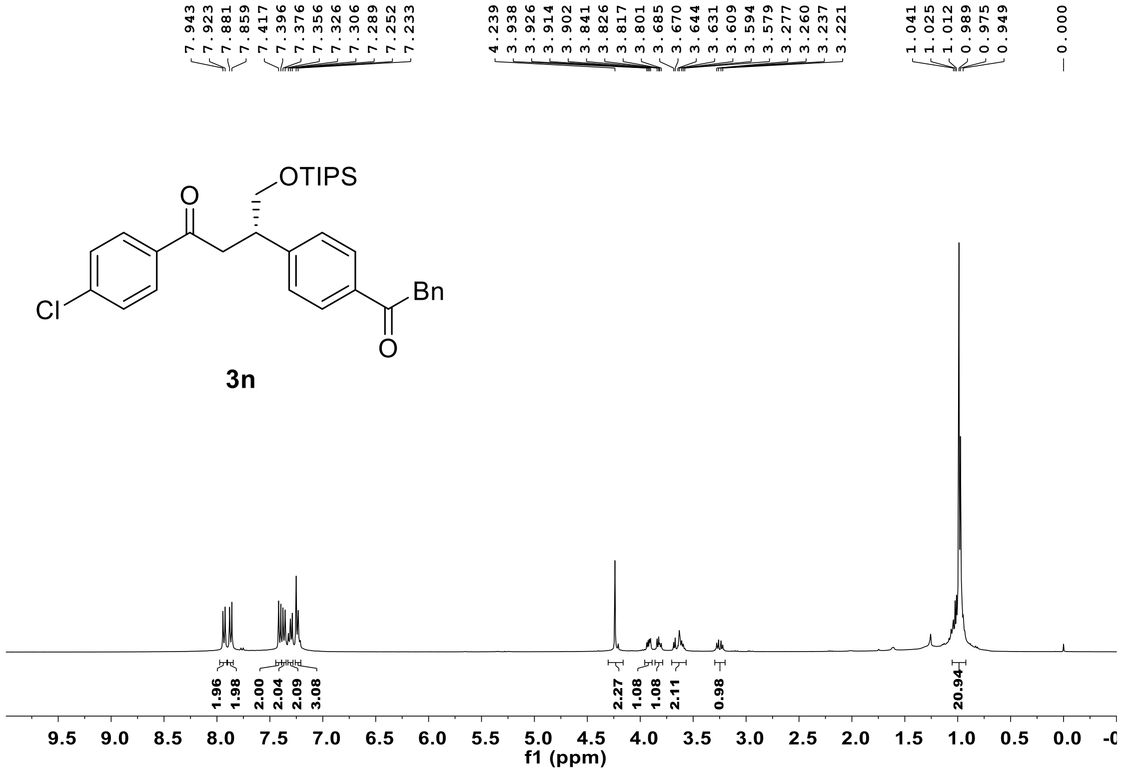
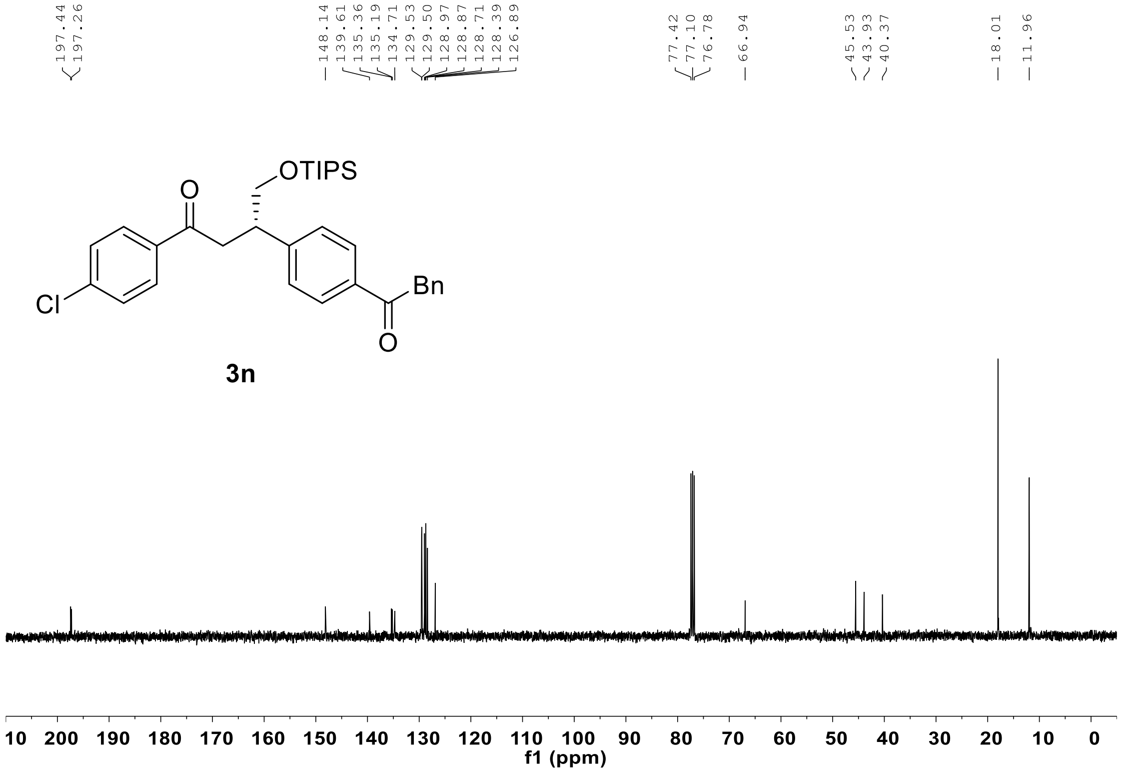
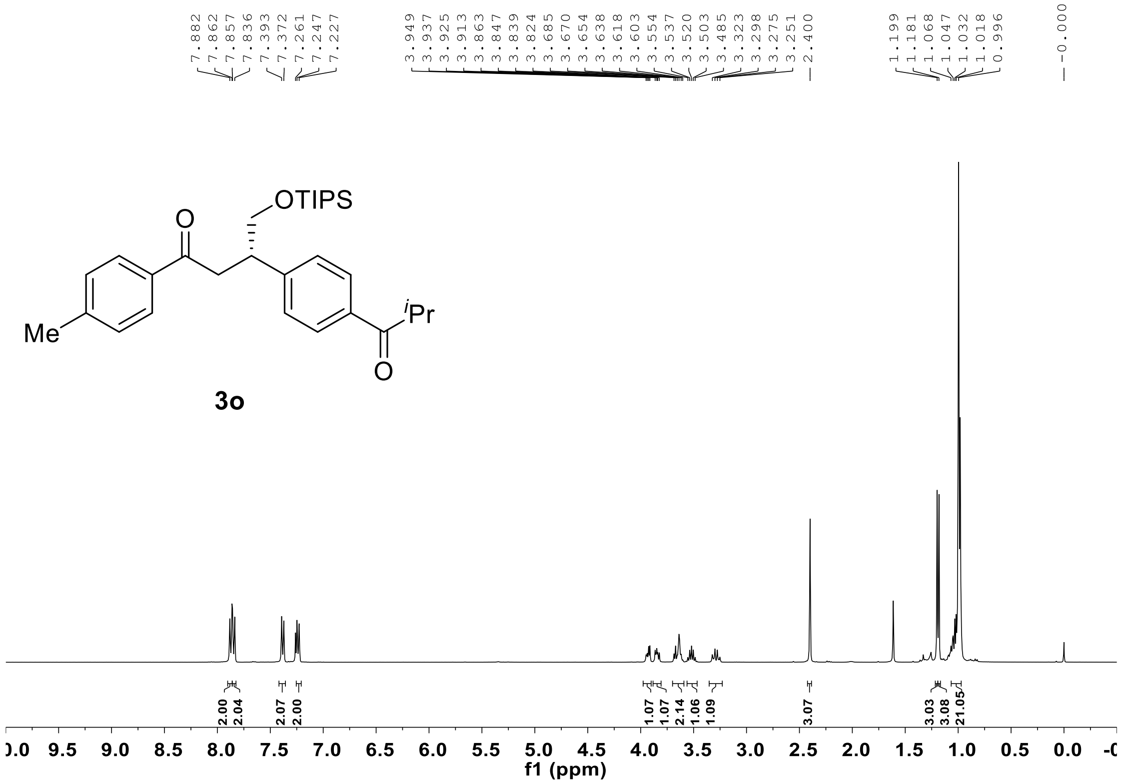


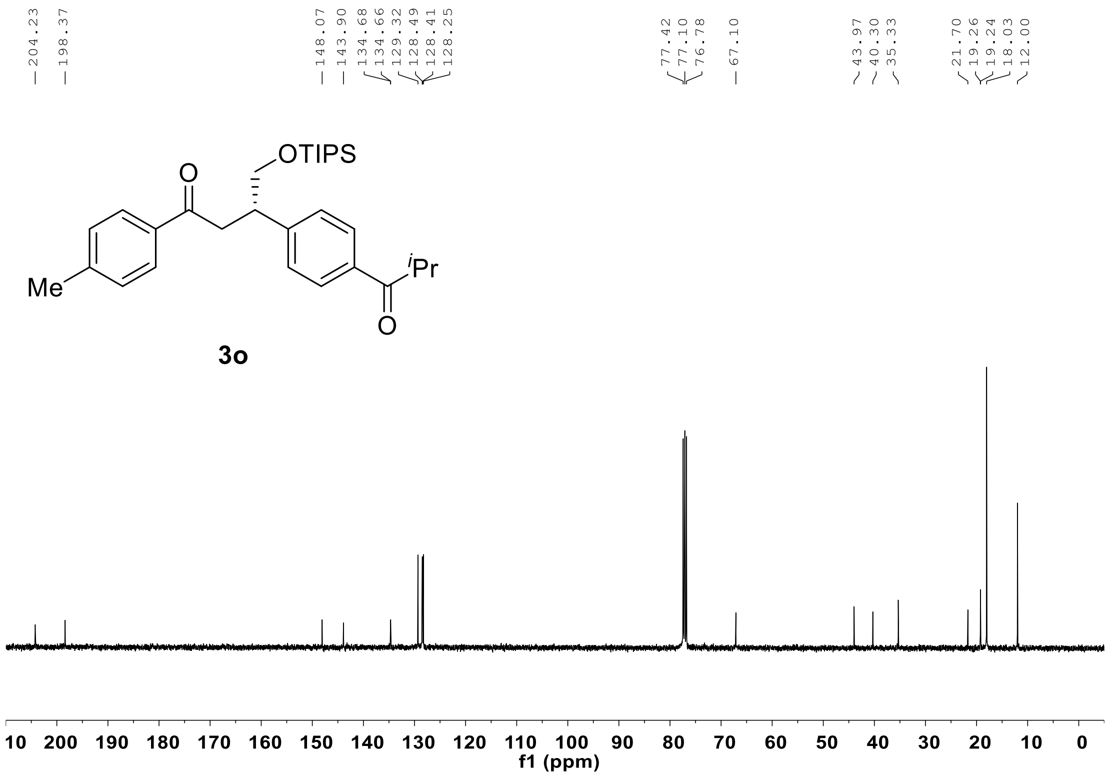
3n ^{13}C NMR (400M Hz, CDCl$_3$)



3o ^{1}H NMR (400M Hz, CDCl$_3$)



3o ^{13}C NMR (400M Hz, CDCl$_3$)



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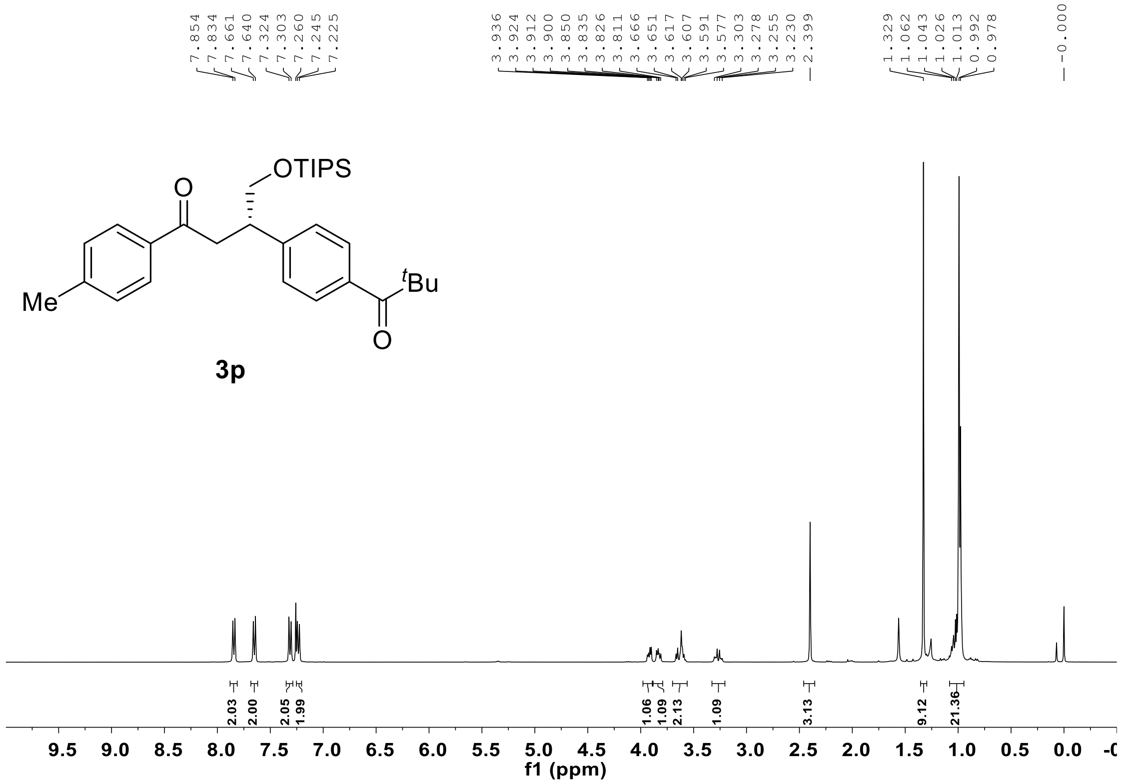
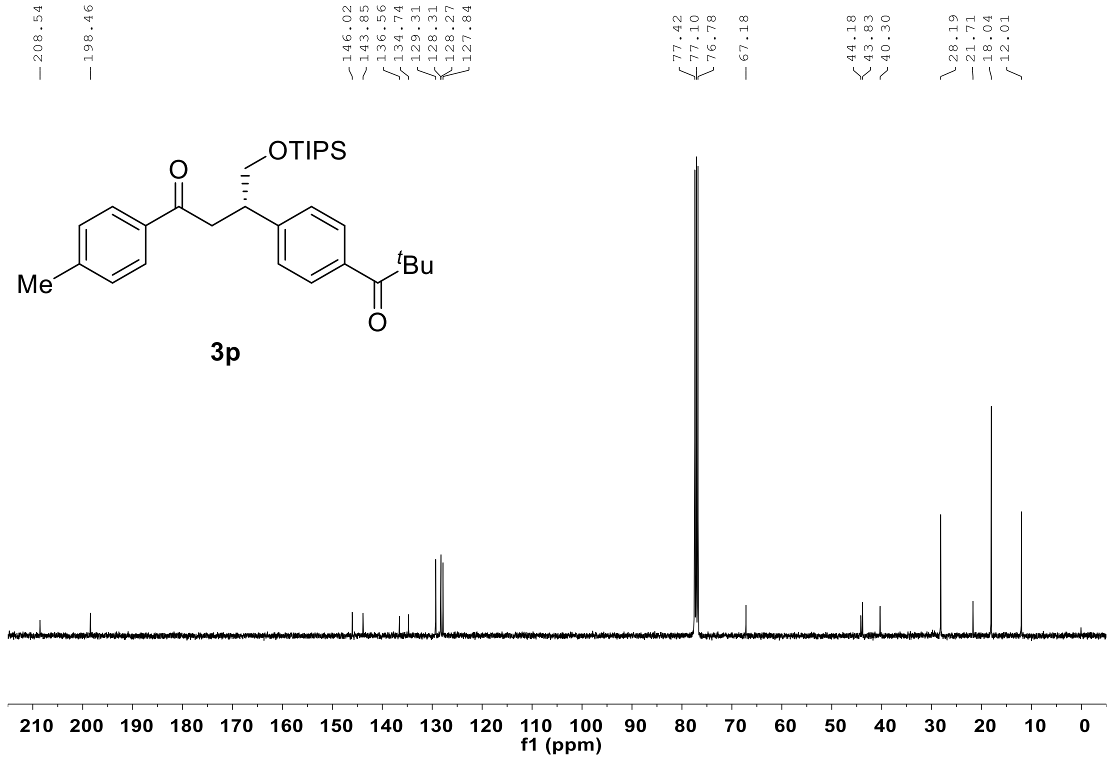
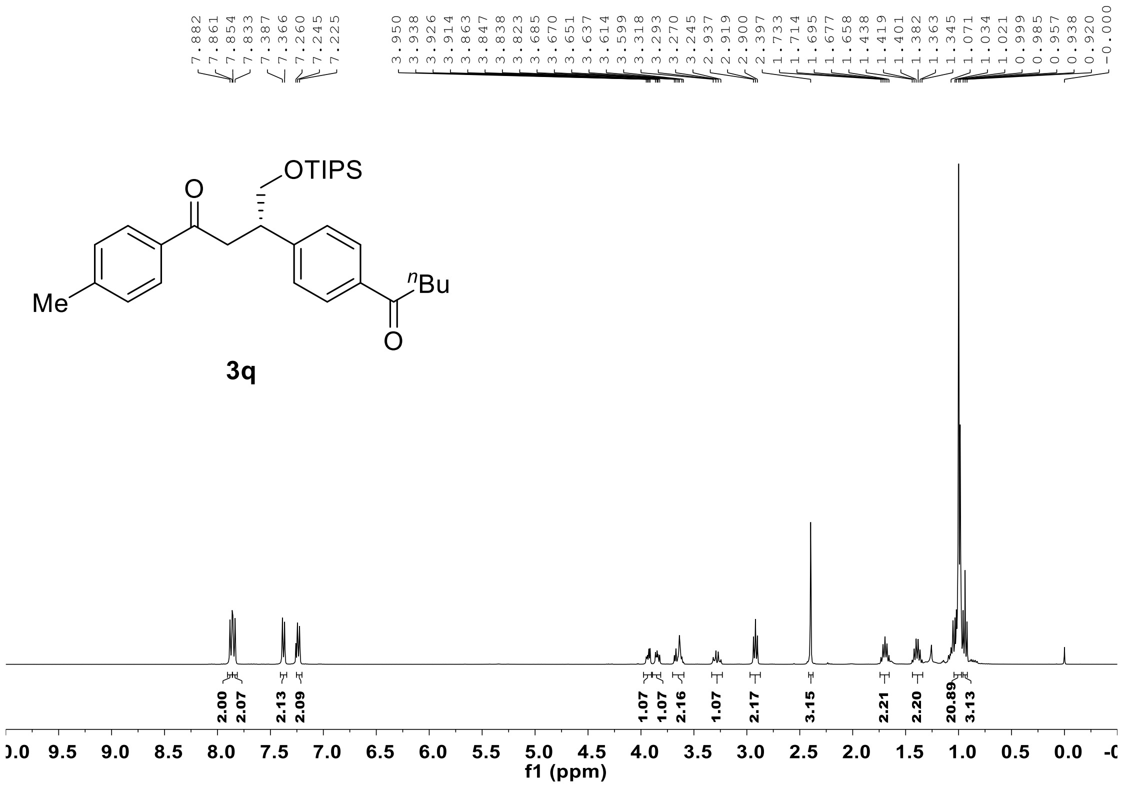


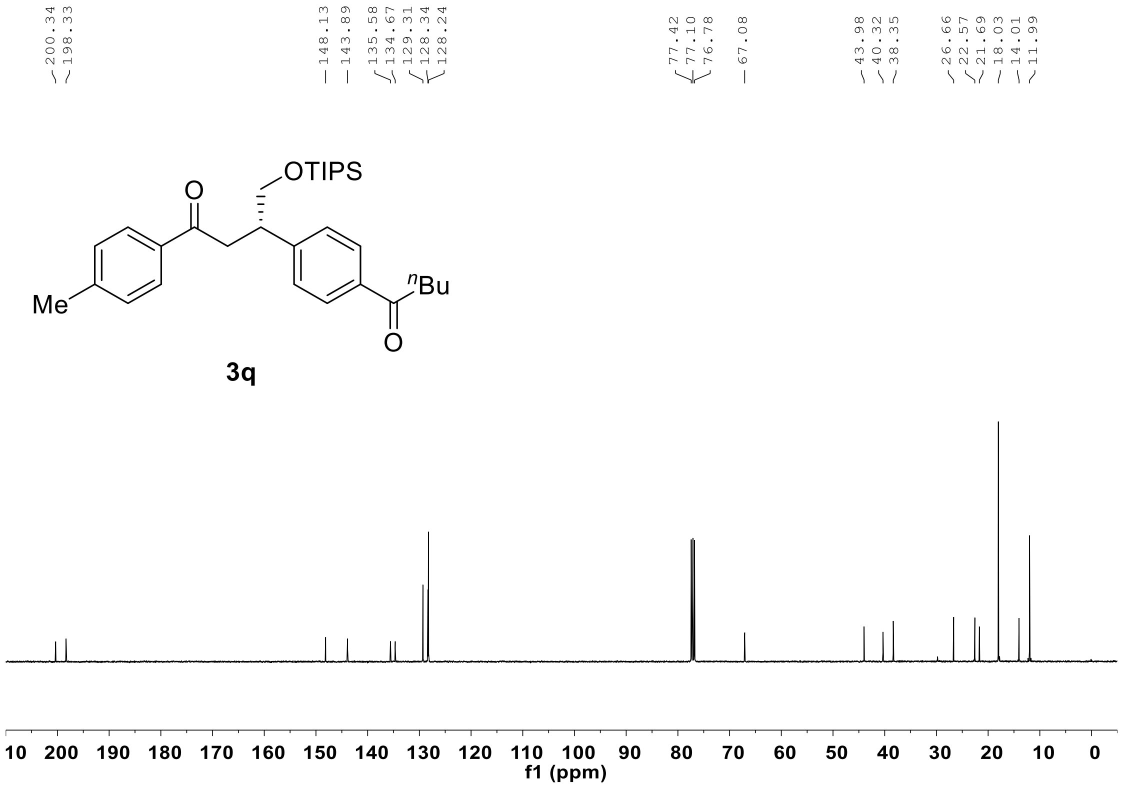
3p ^{13}C NMR (400M Hz, CDCl$_3$)



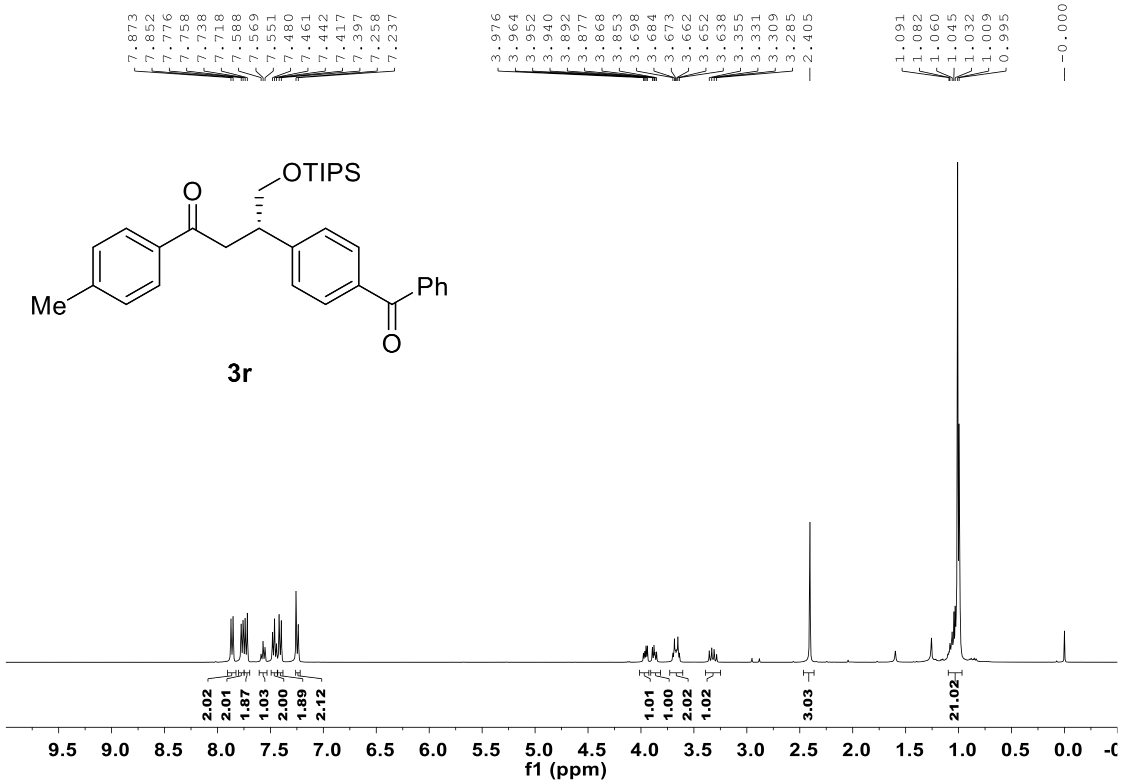
3q ^{1}H NMR (400M Hz, CDCl$_3$)



3q ^{13}C NMR (400M Hz, CDCl$_3$)

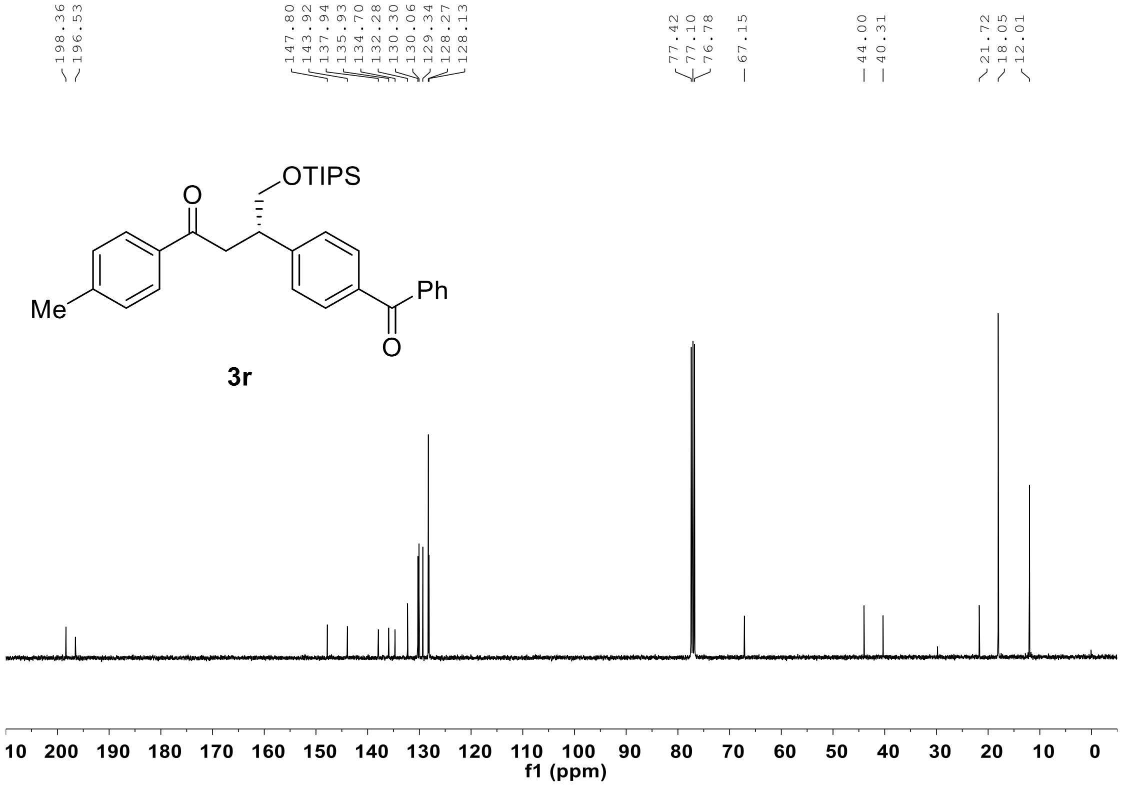


3r ^{1}H NMR (400M Hz, CDCl$_3$)



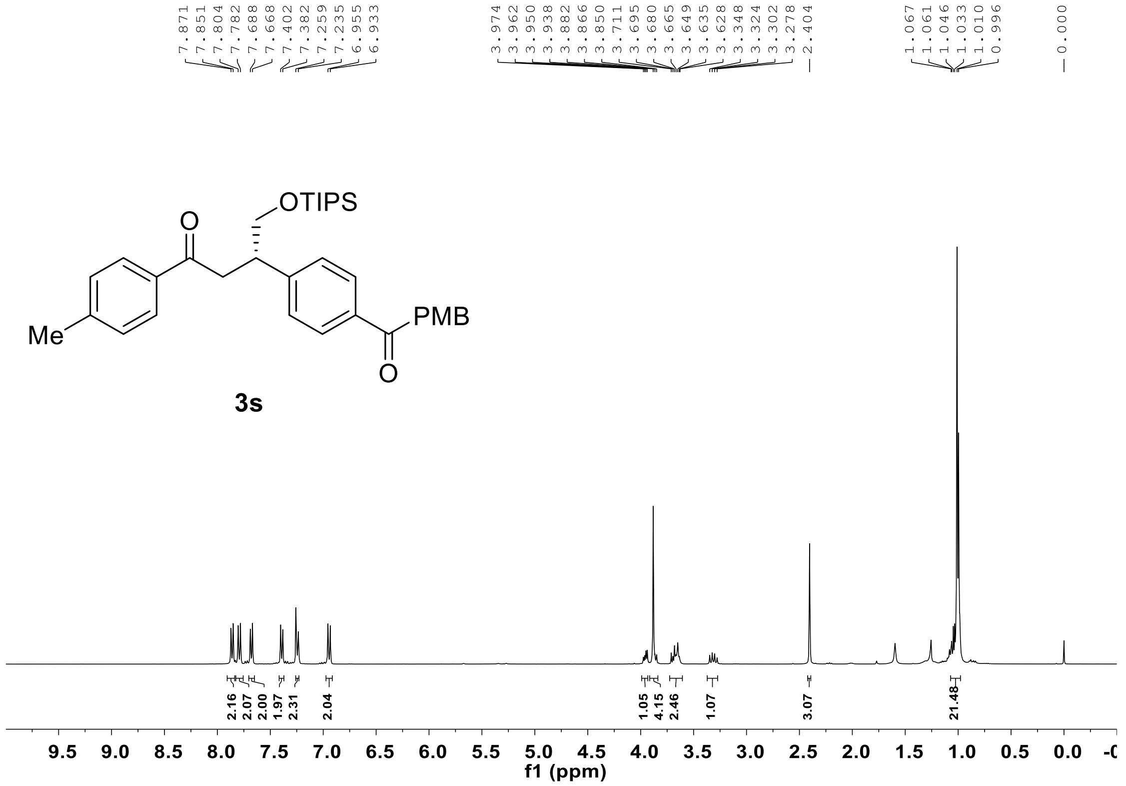
3r

3r ^{13}C NMR (400M Hz, CDCl$_3$)

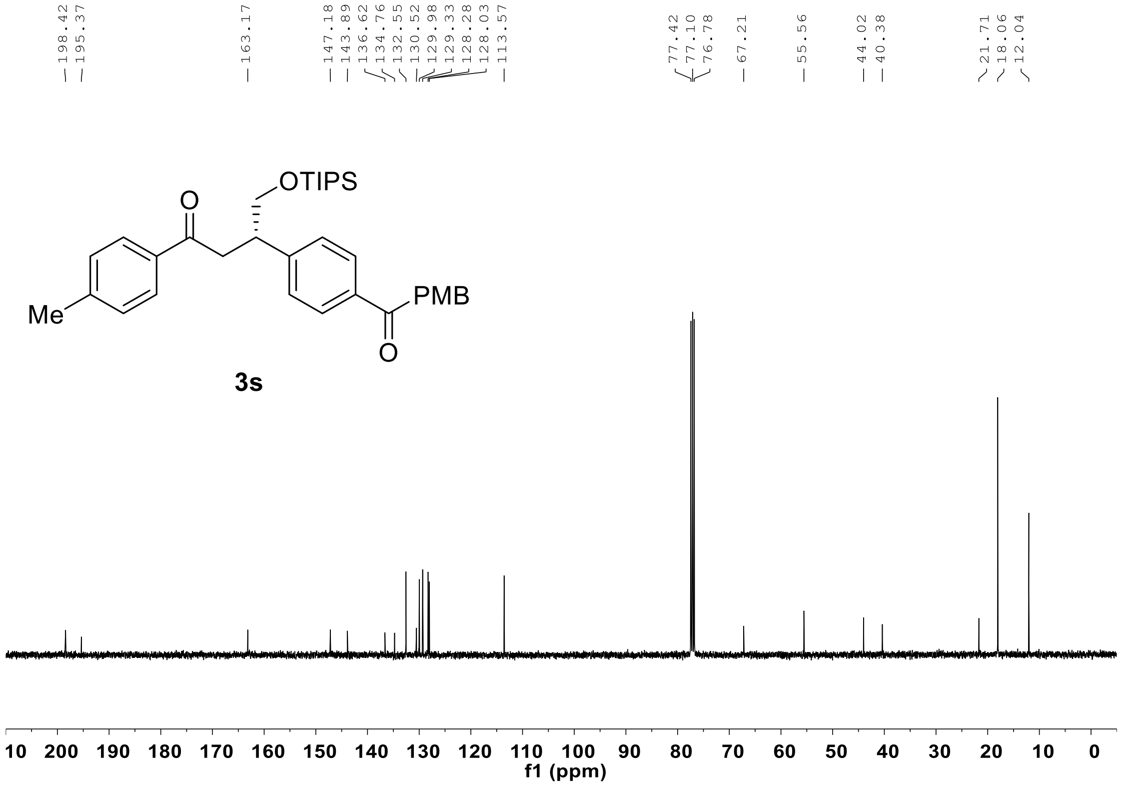


3r

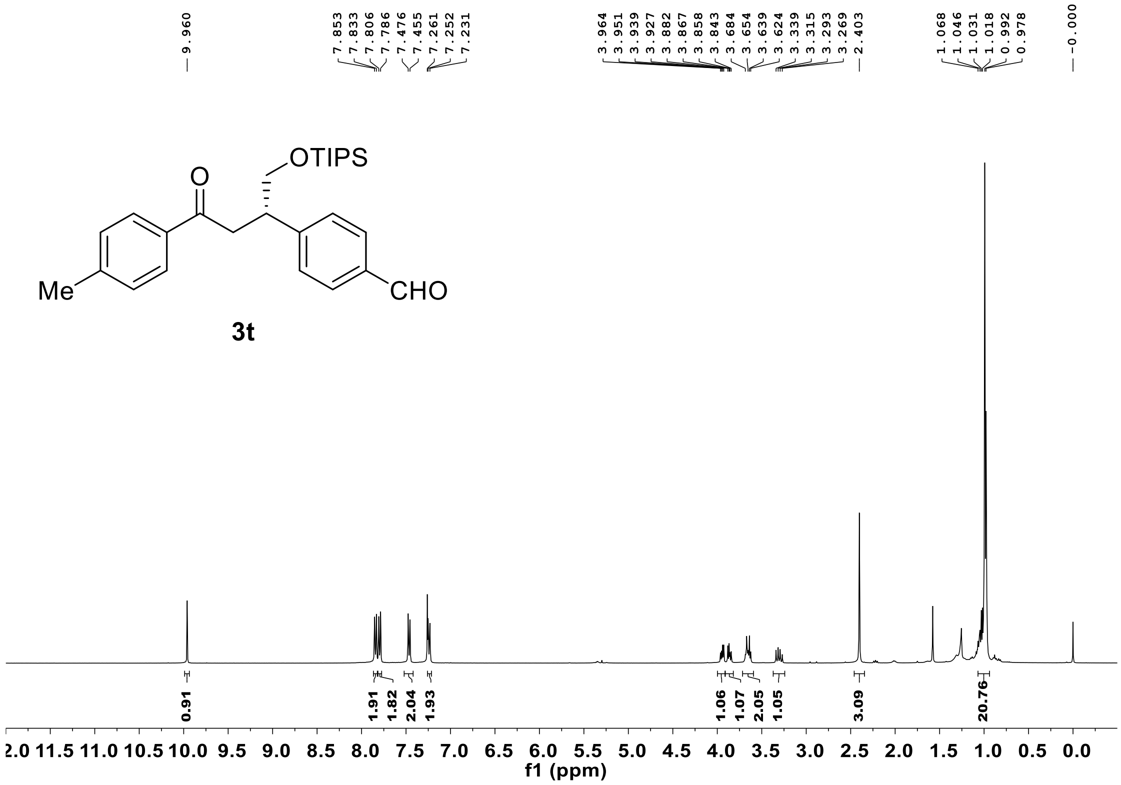
3s ^{1}H NMR (400M Hz, CDCl$_3$)



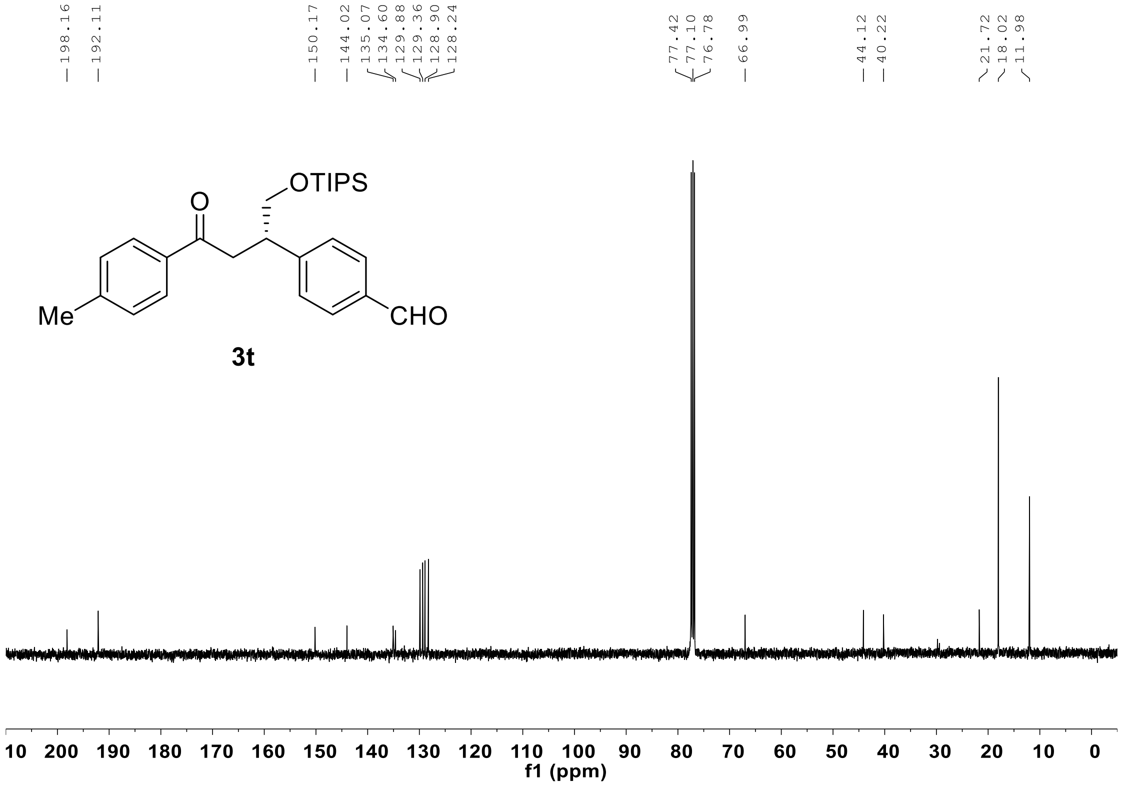
3s ^{13}C NMR (400M Hz, CDCl$_3$)



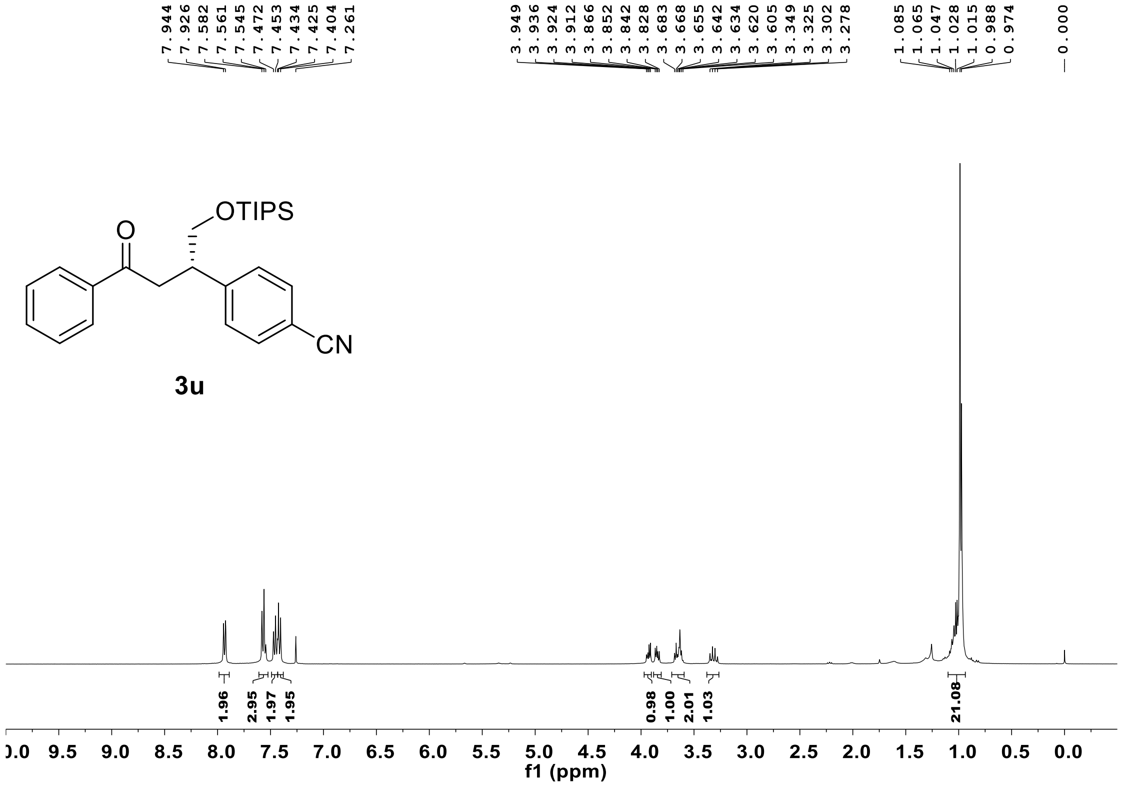
3t ^{1}H NMR (400M Hz, CDCl$_3$)



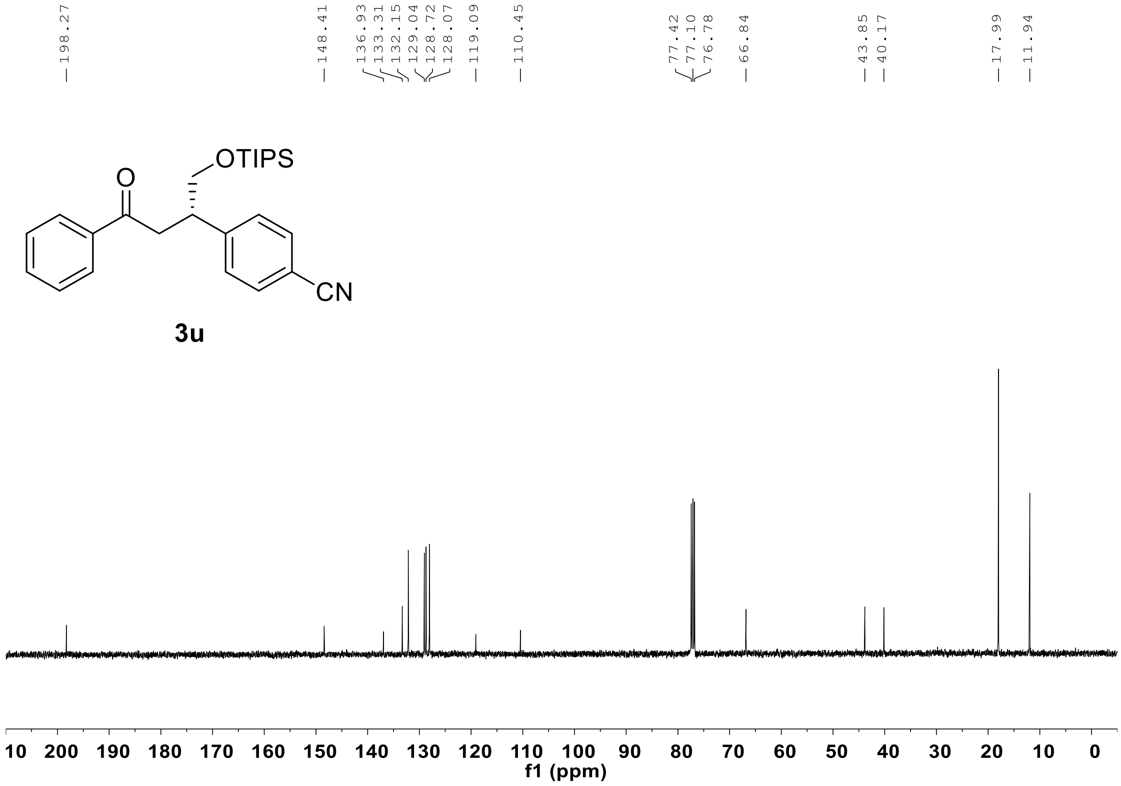
3t ^{13}C NMR (400M Hz, CDCl$_3$)



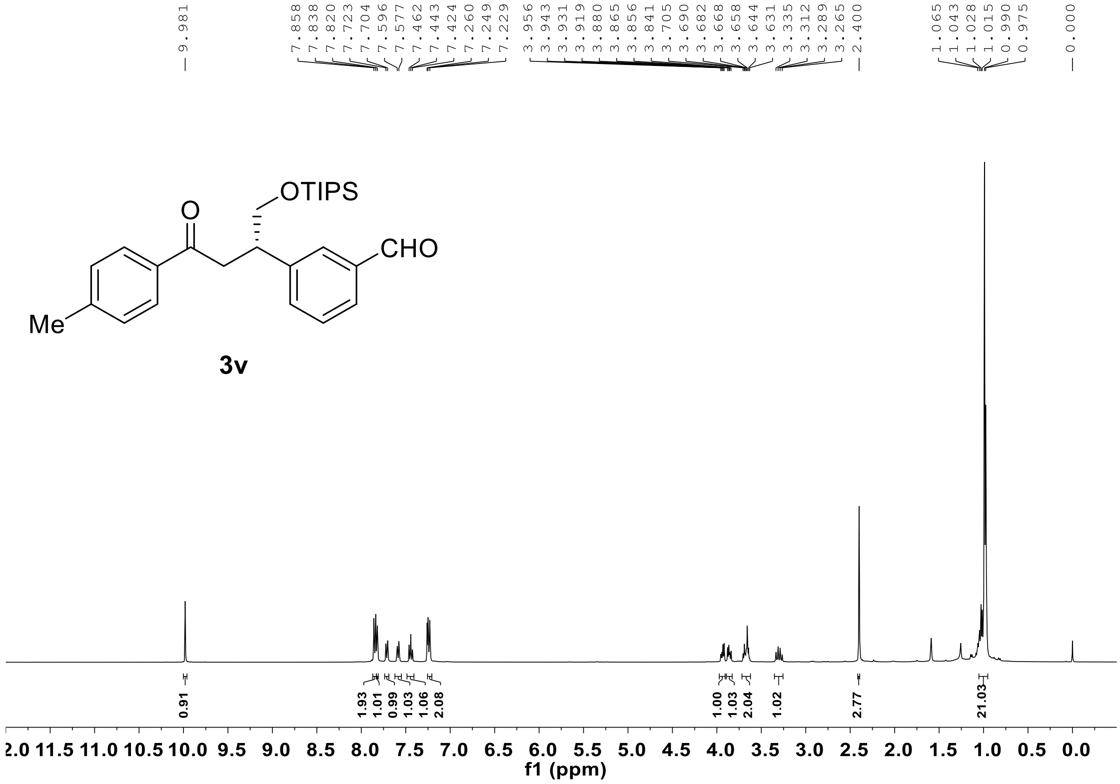
3u ^{1}H NMR (400M Hz, CDCl$_3$)



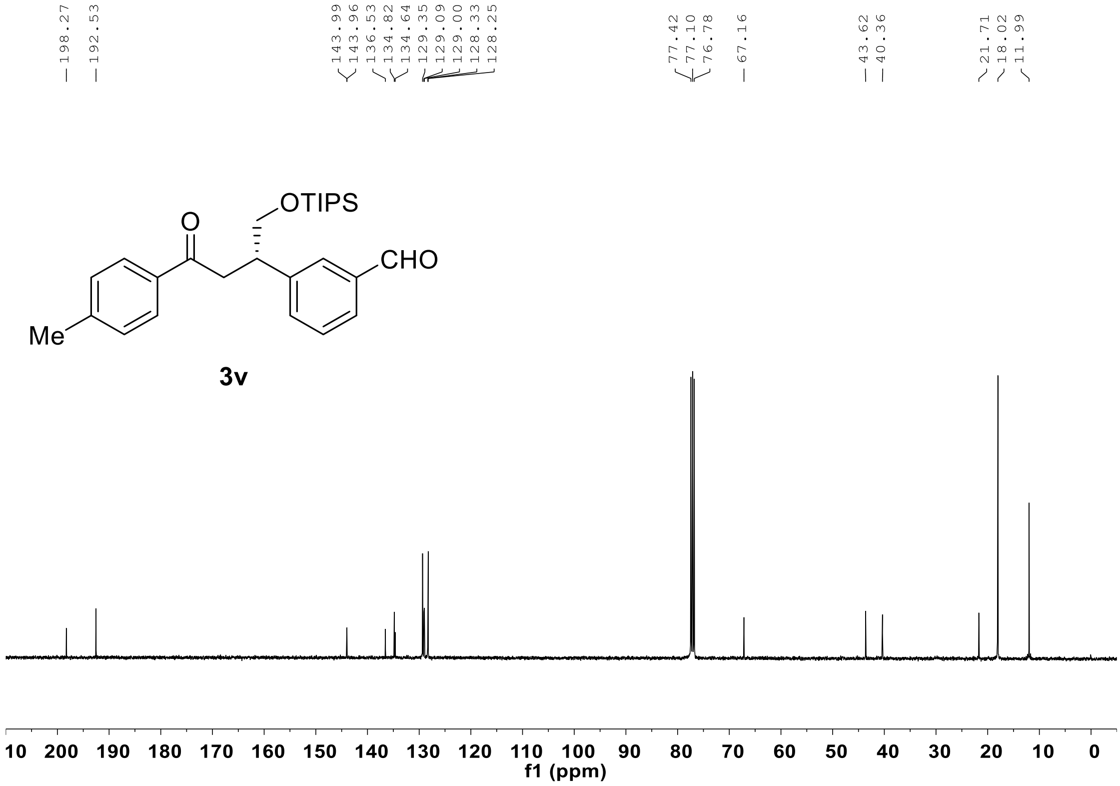
3u ^{13}C NMR (400M Hz, CDCl$_3$)



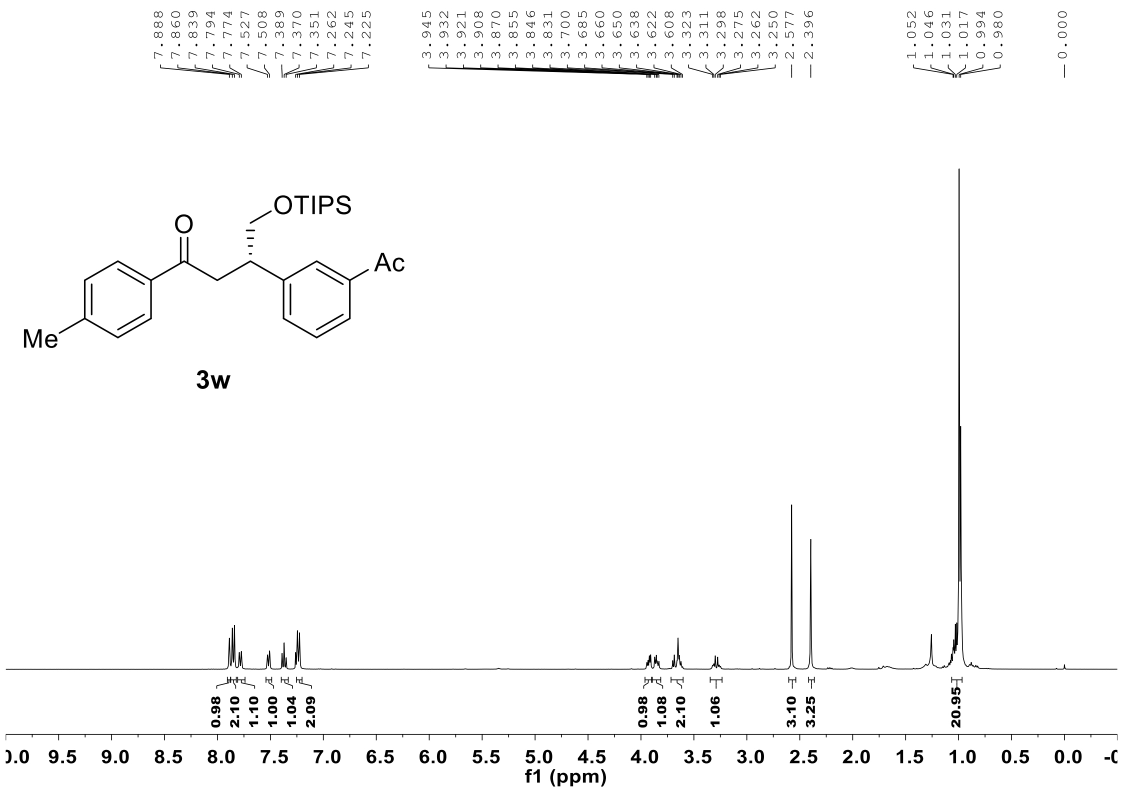
3v ^{1}H NMR (400M Hz, CDCl$_3$)



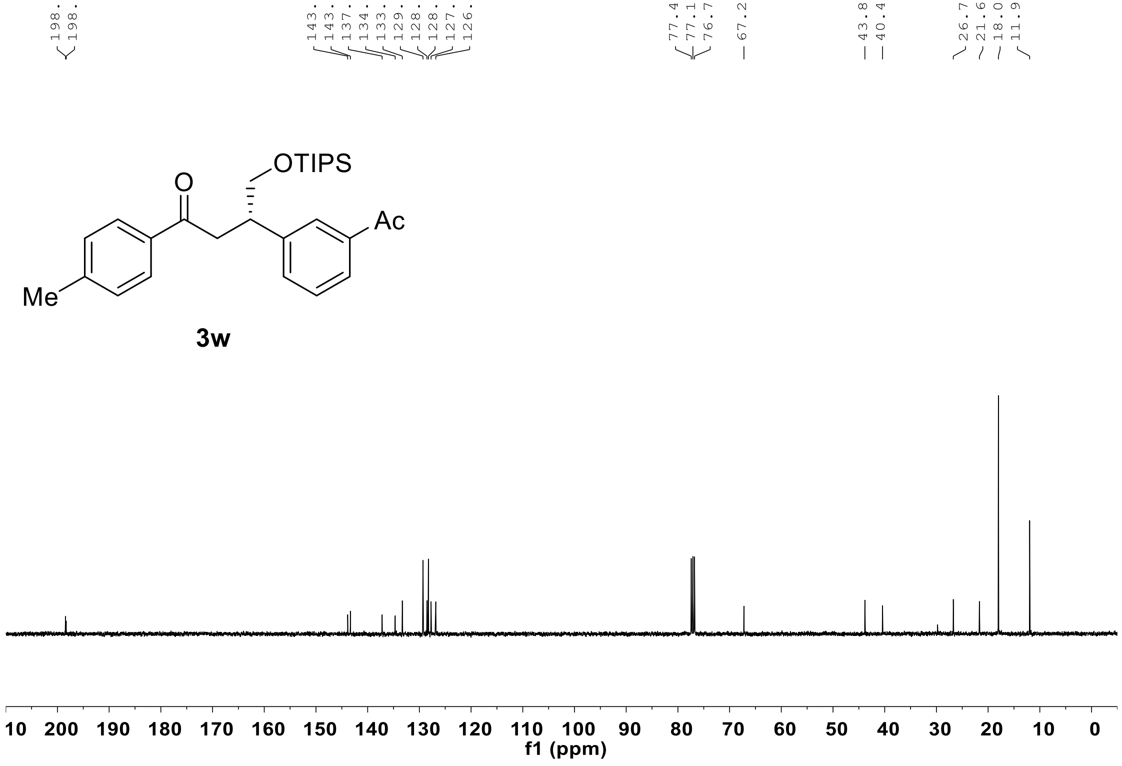
3v ^{13}C NMR (400M Hz, CDCl$_3$)



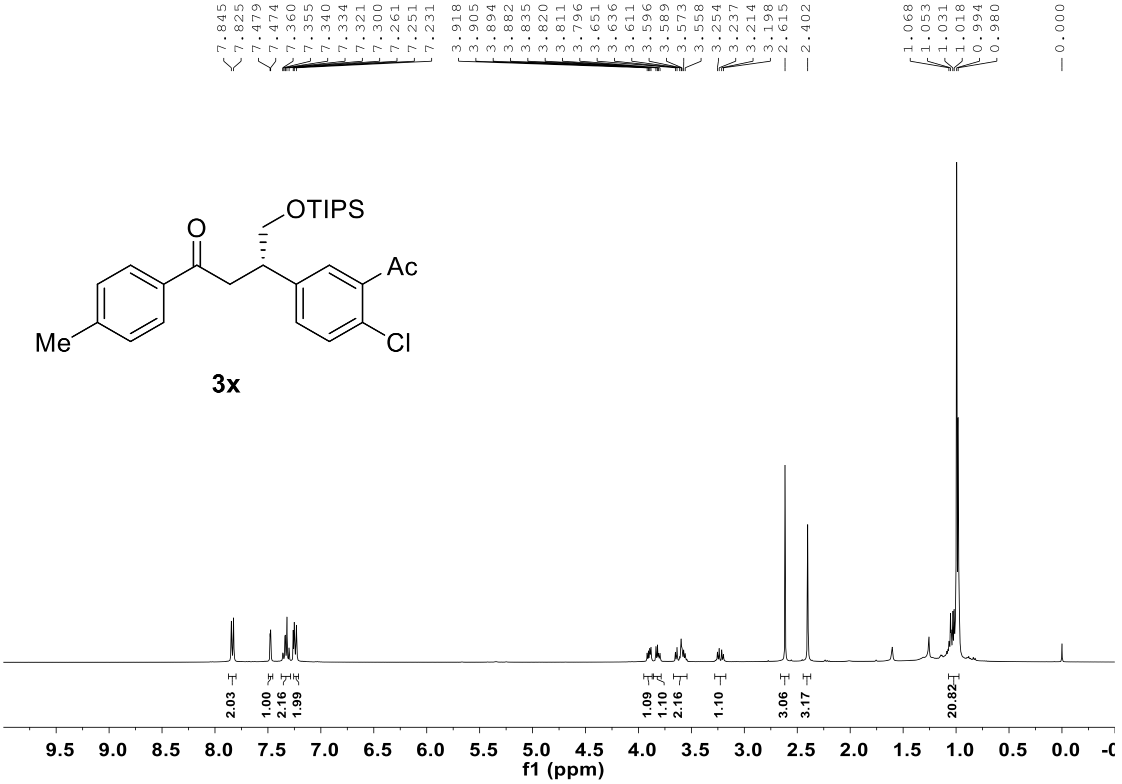
3w ^{1}H NMR (400M Hz, CDCl$_3$)



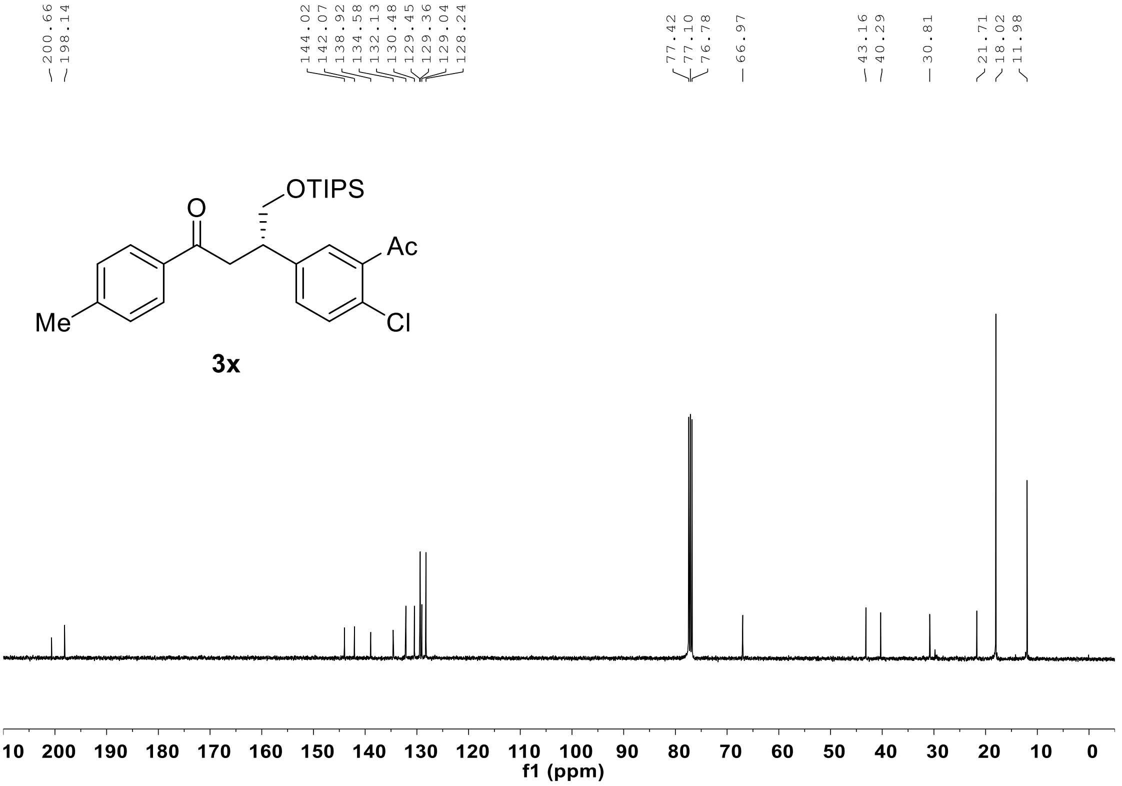
3w ^{13}C NMR (400M Hz, CDCl$_3$)



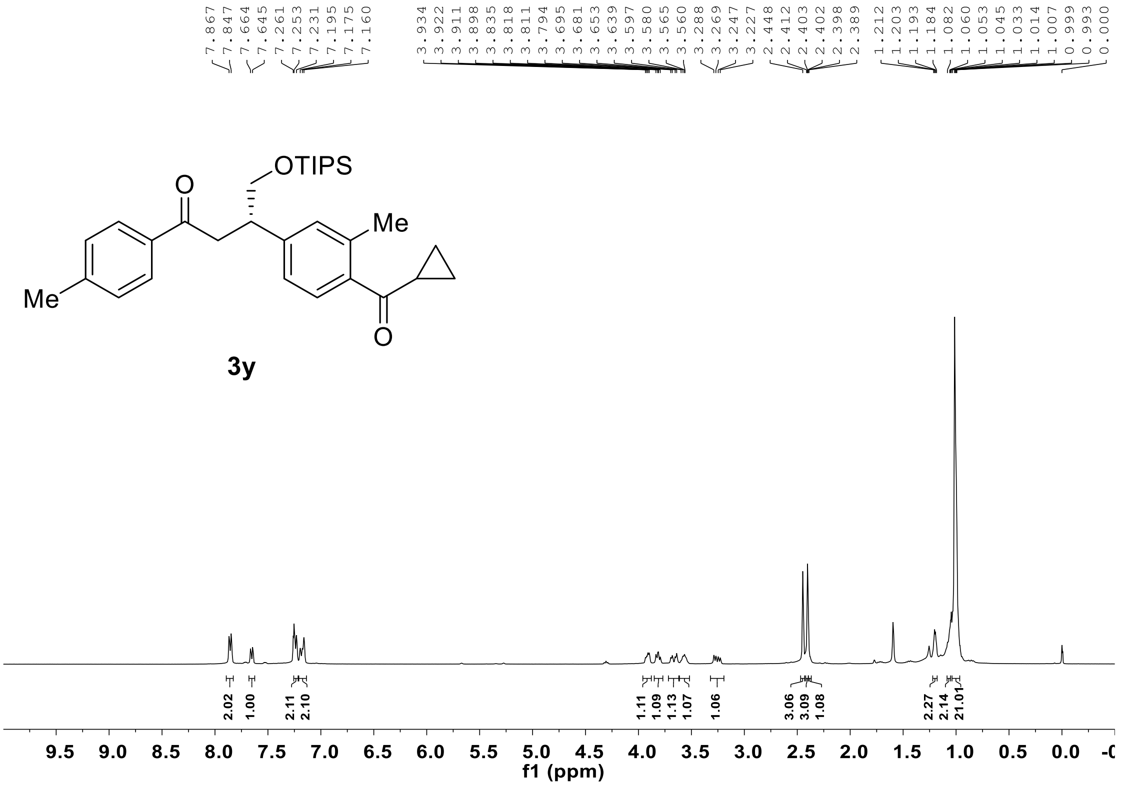
3x ^{1}H NMR (400M Hz, CDCl$_3$)



3x ^{13}C NMR (400M Hz, CDCl$_3$)



3y ^{1}H NMR (400M Hz, CDCl$_3$)



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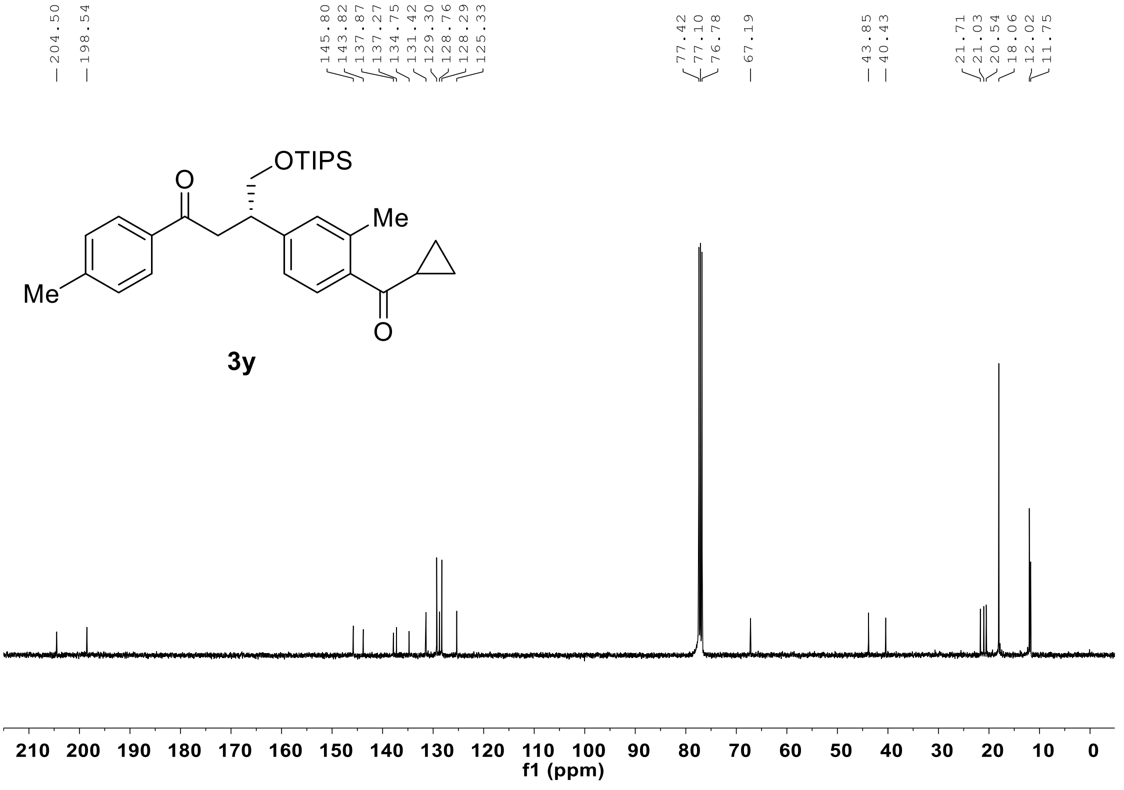
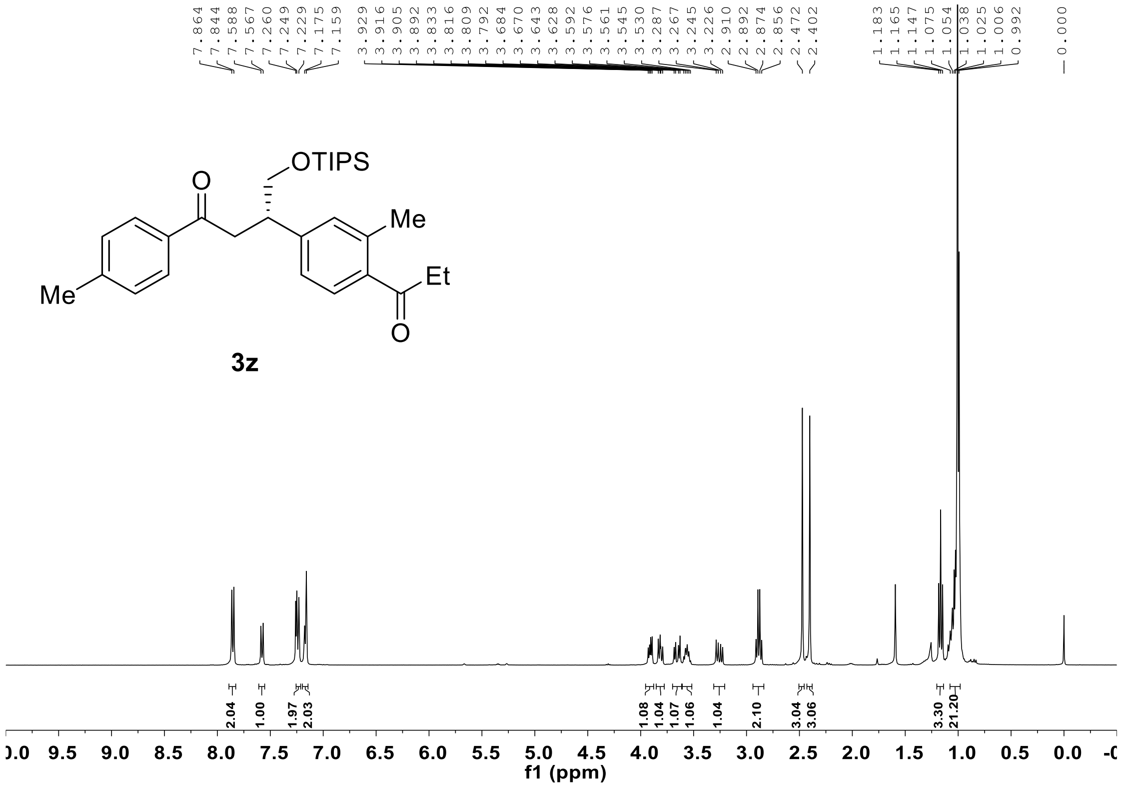
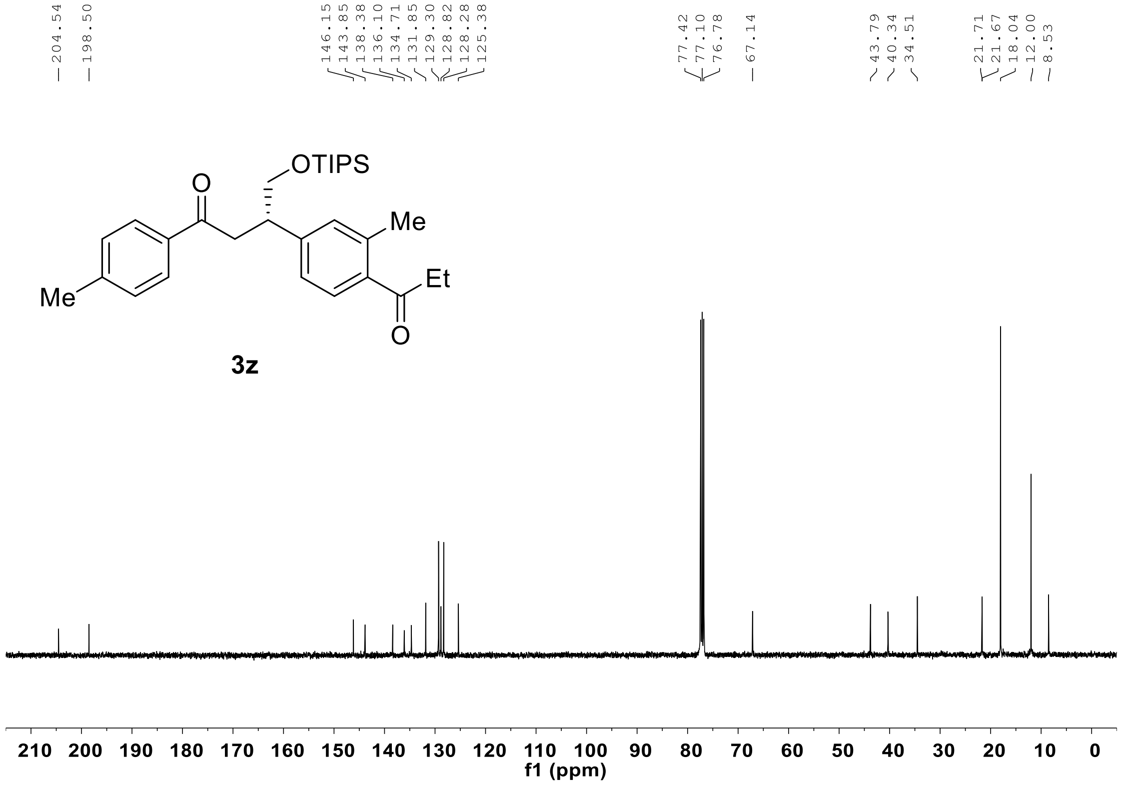


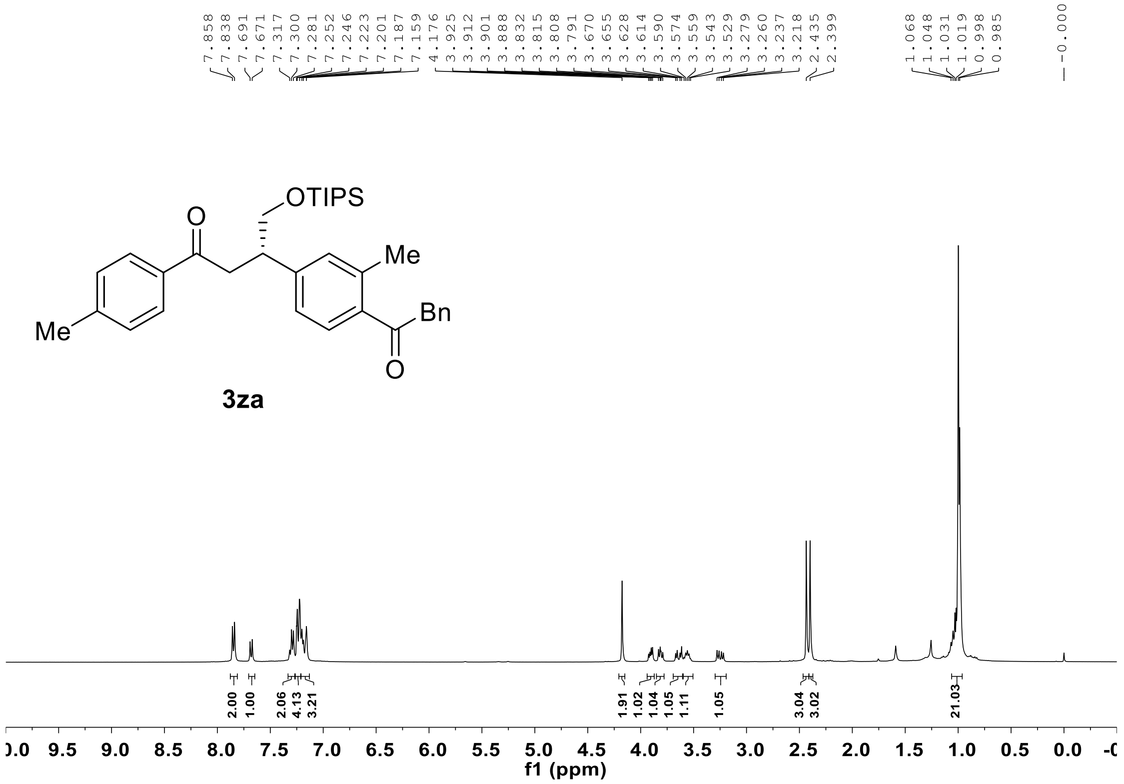
3z ^{1}H NMR (400M Hz, CDCl$_3$)



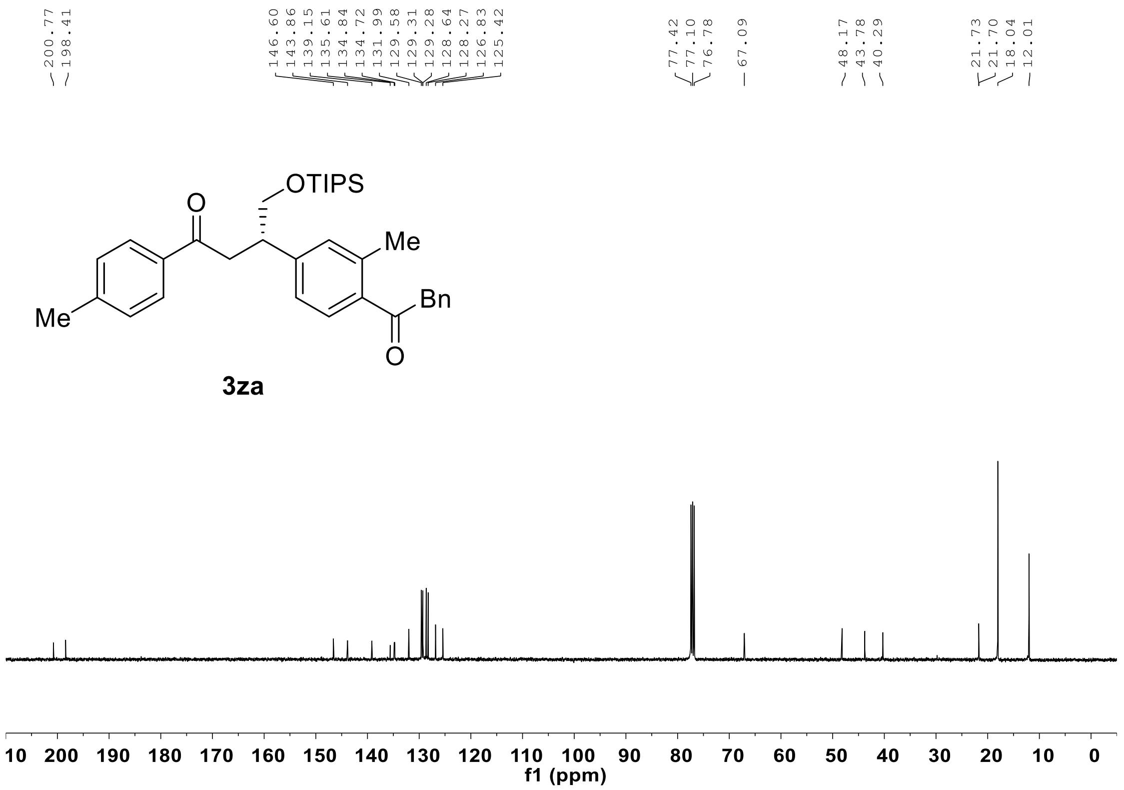
3z ^{13}C NMR (400M Hz, CDCl$_3$)



3za ^{1}H NMR (400M Hz, CDCl$_3$)



3za ^{13}C NMR (400M Hz, CDCl$_3$)



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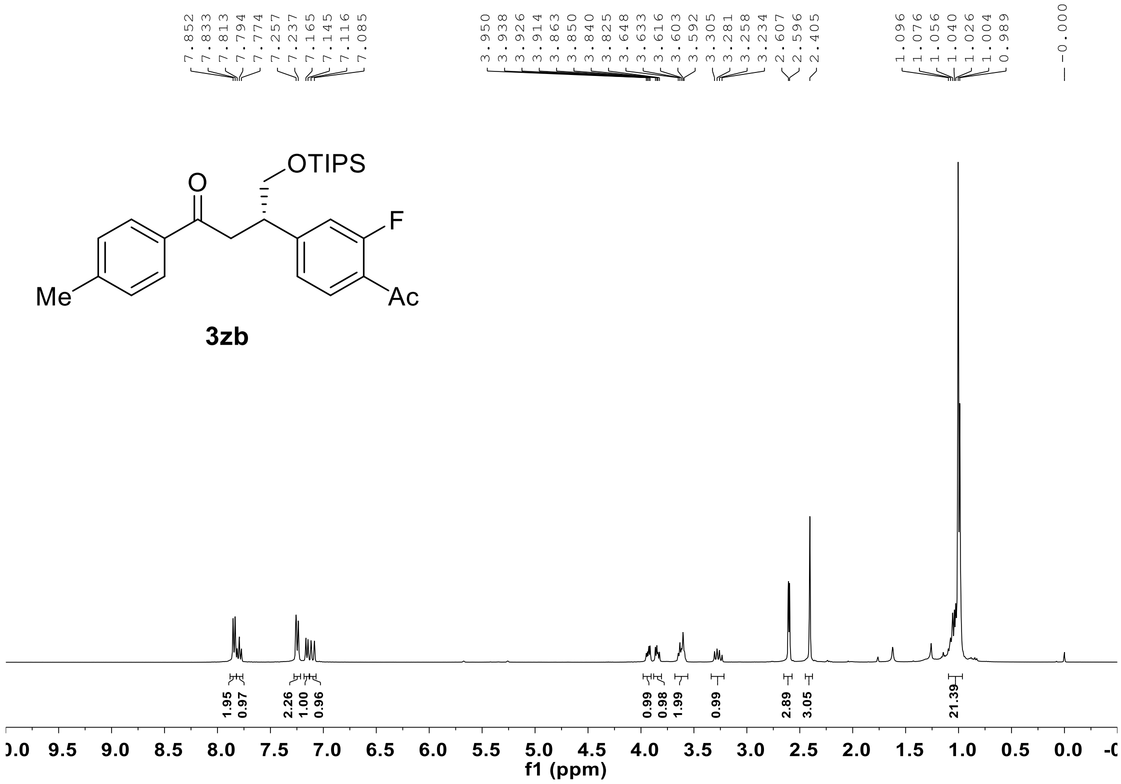

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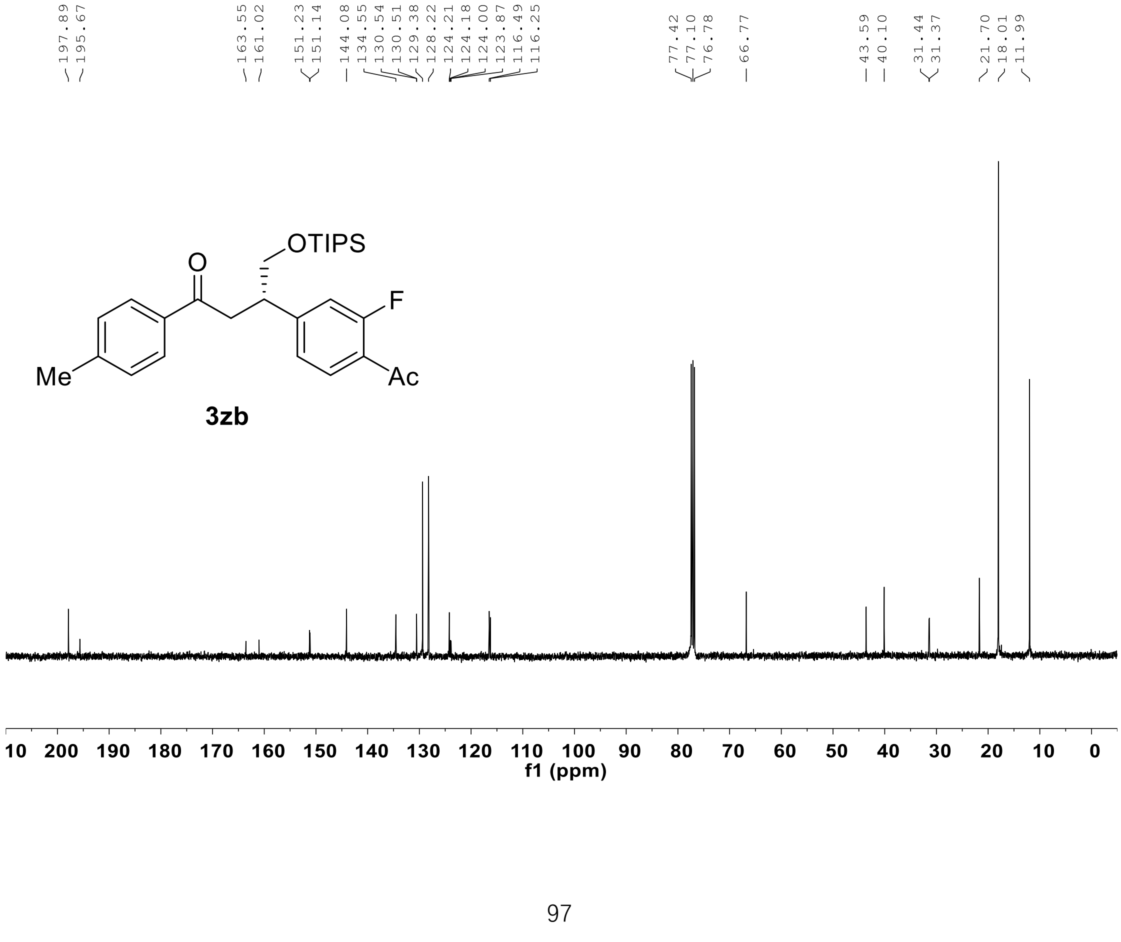

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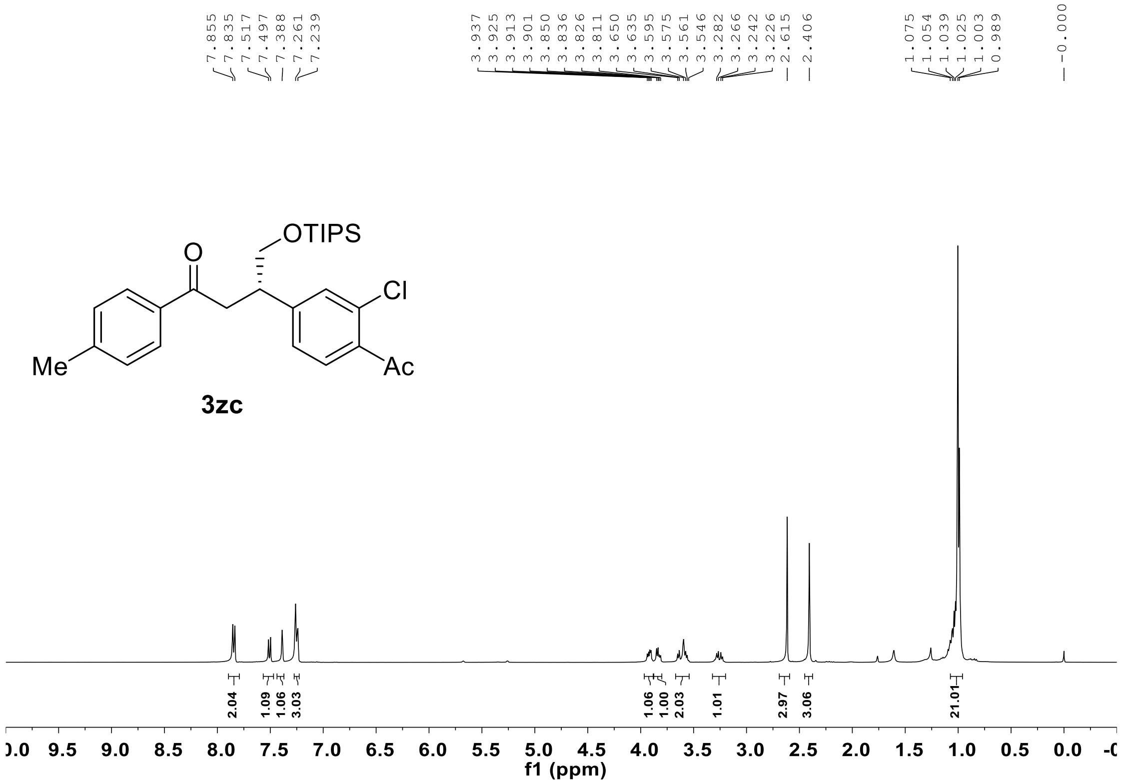

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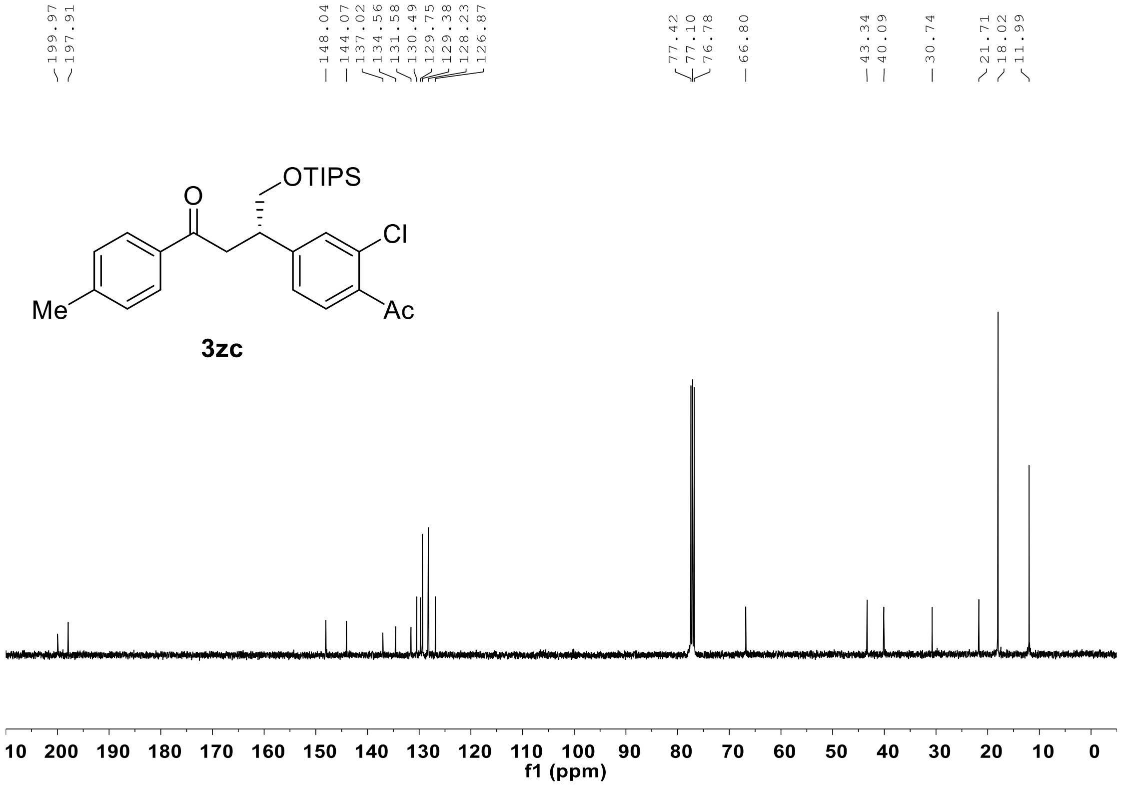

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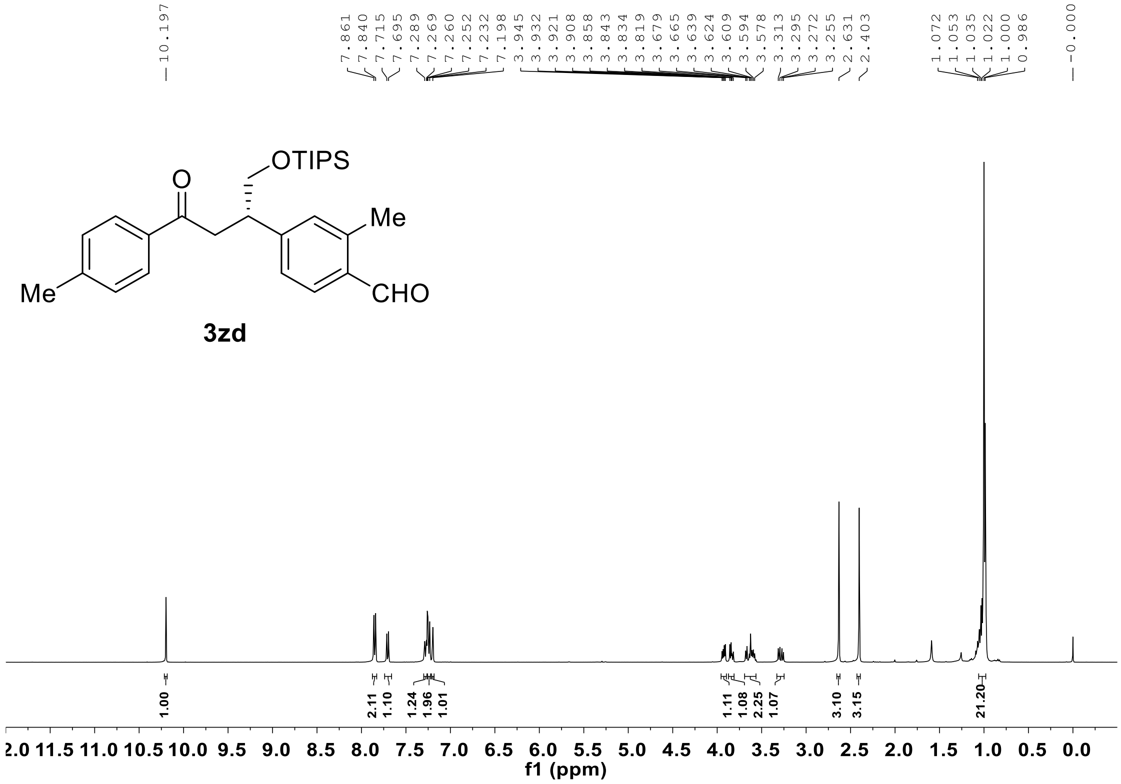

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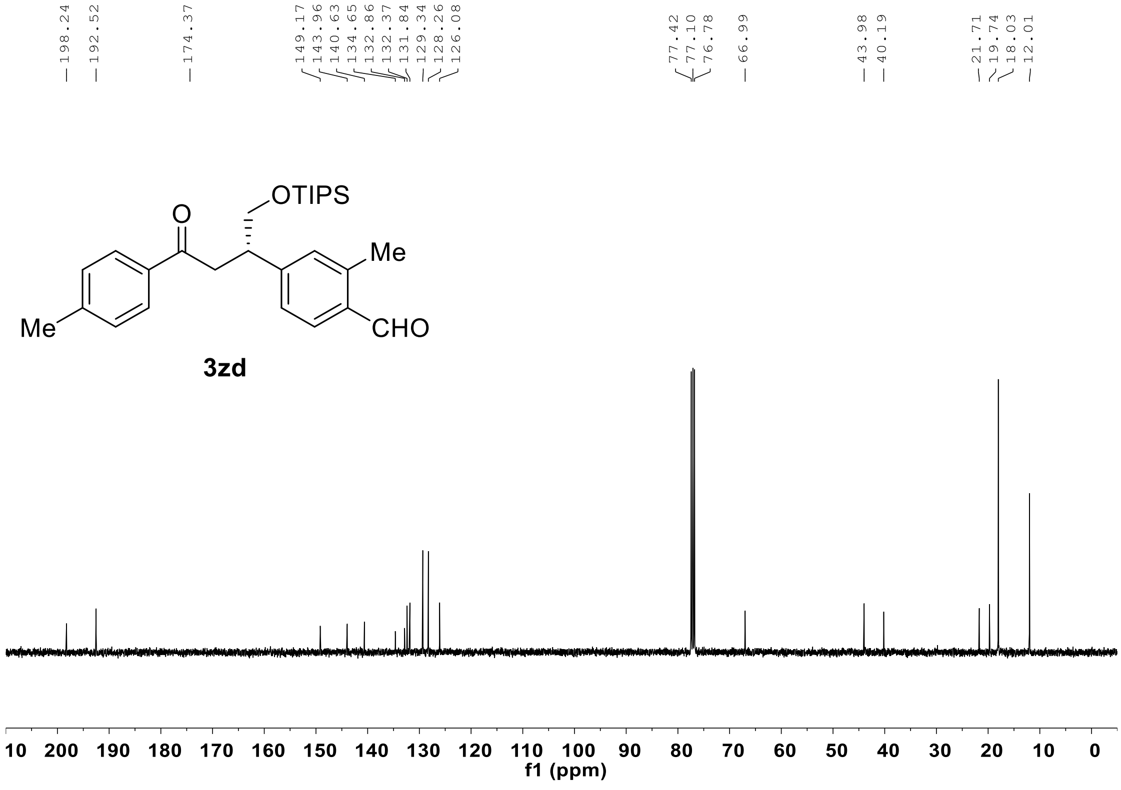

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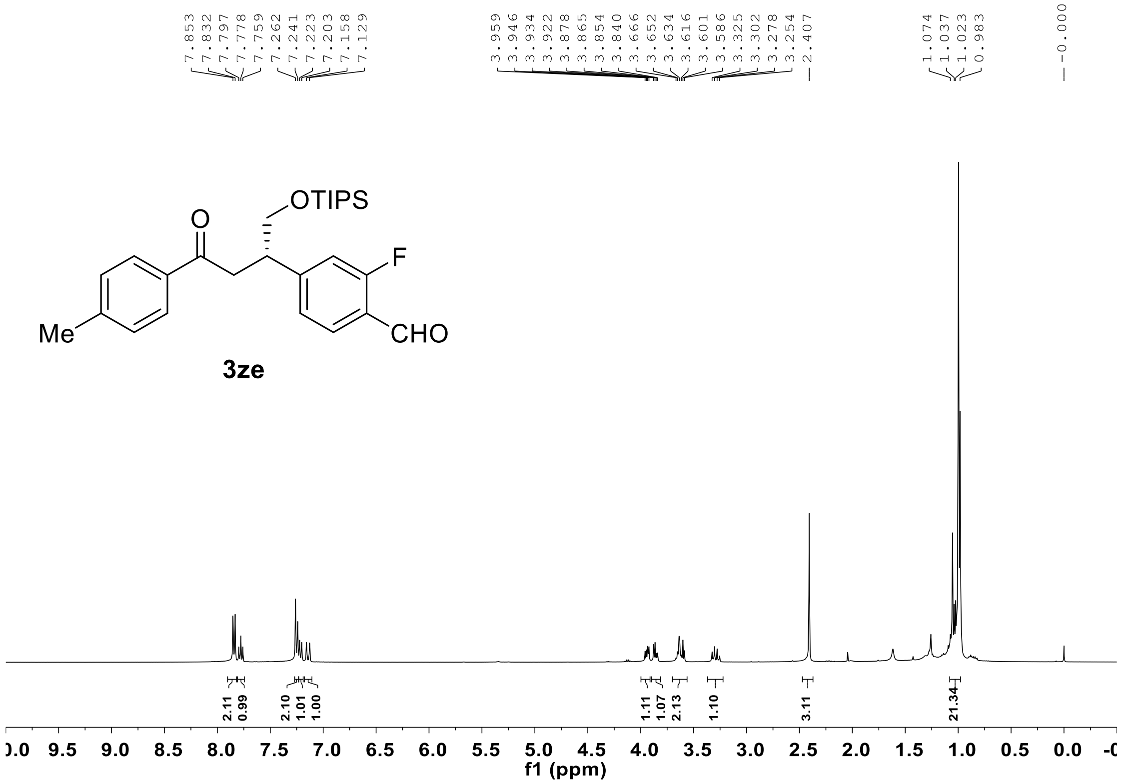

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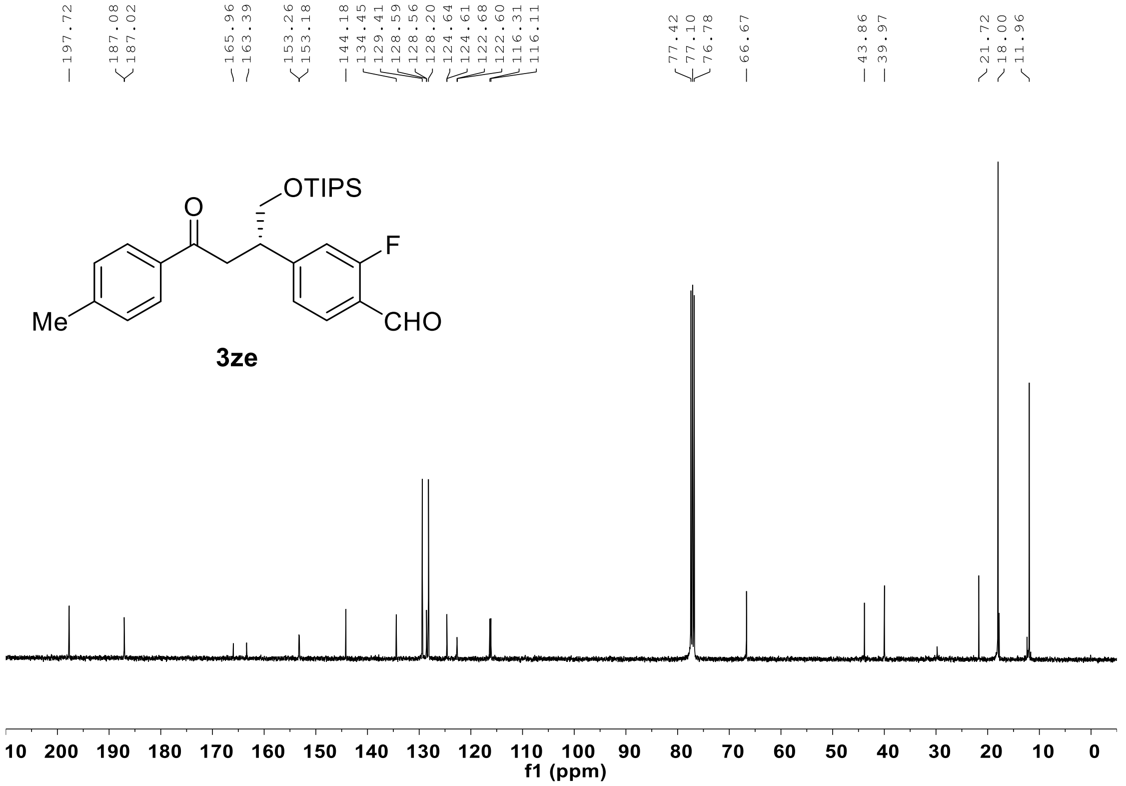
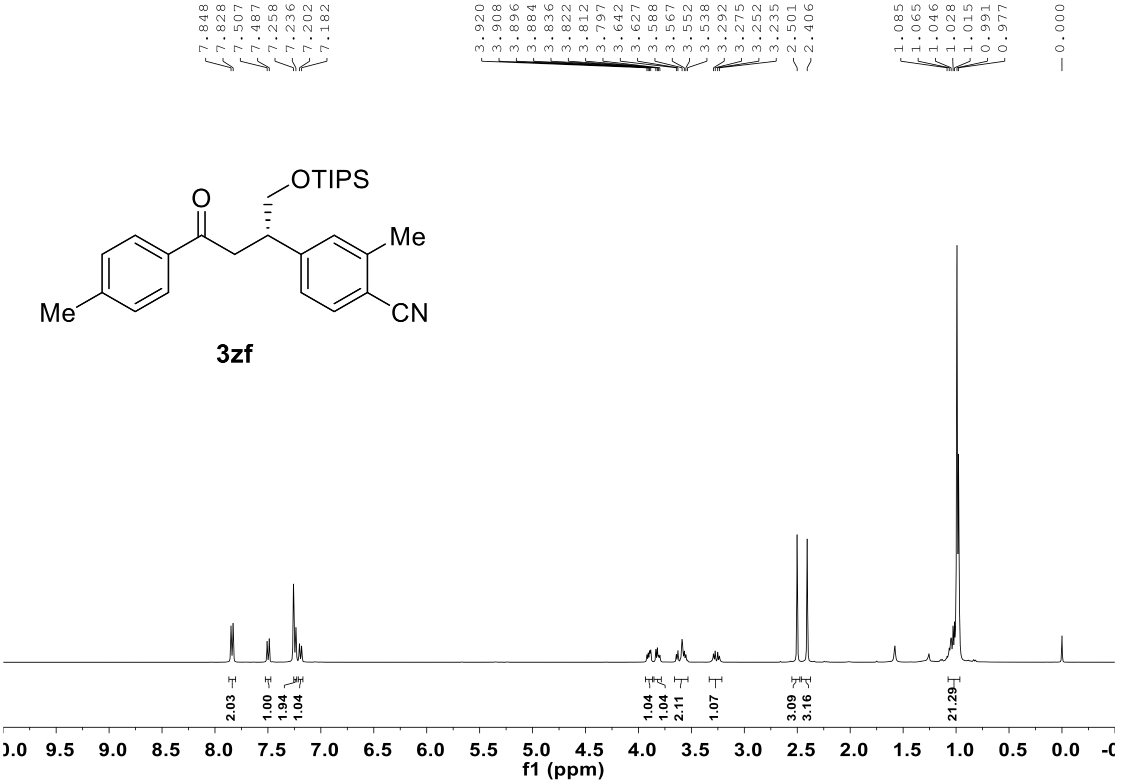
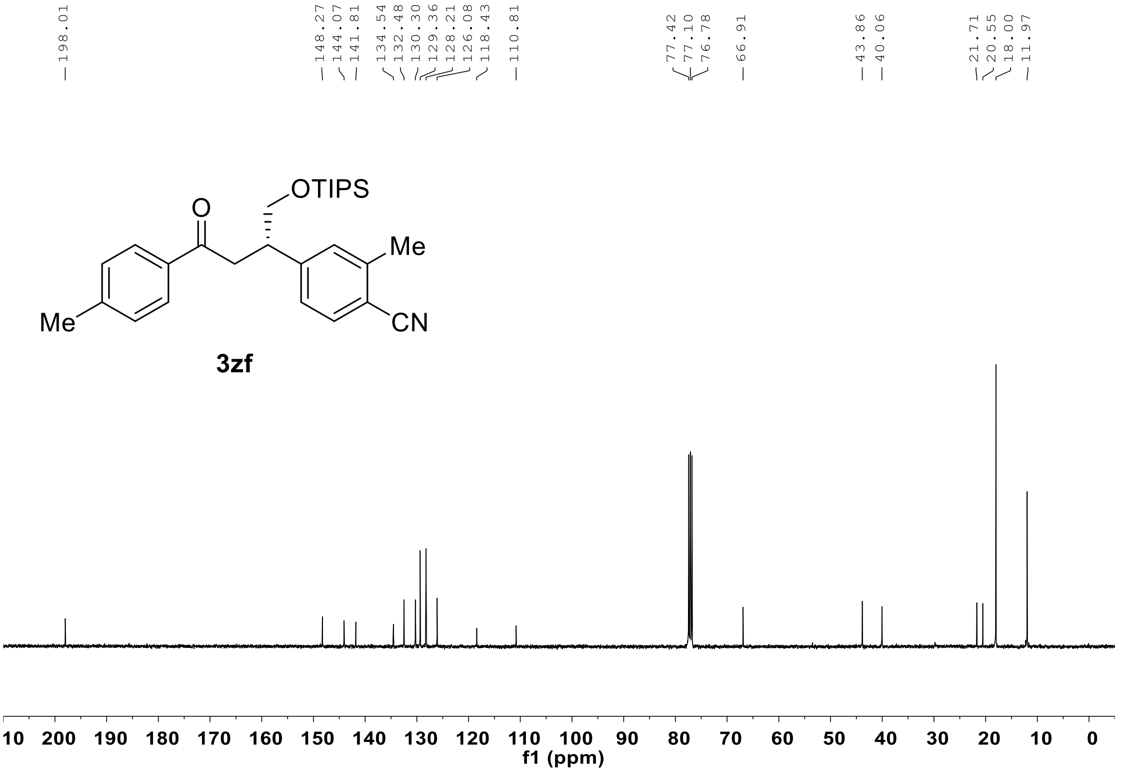


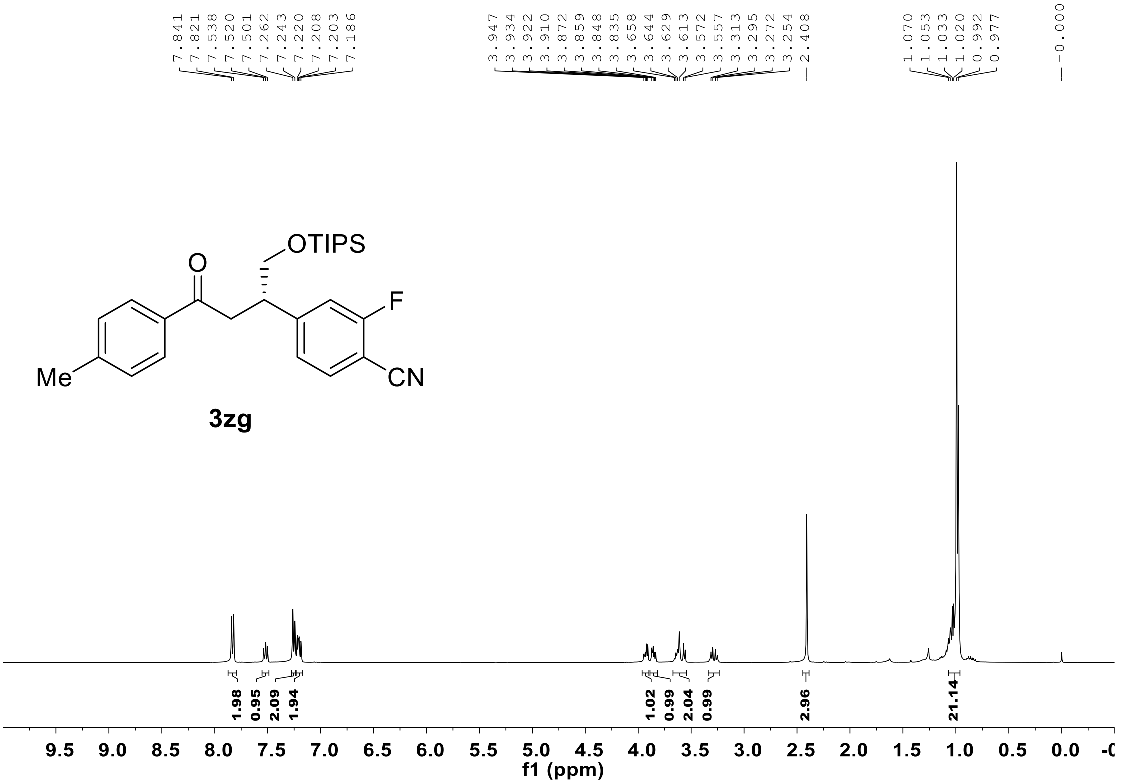
3zf ^{1}H NMR (400M Hz, CDCl$_3$)



3zf ^{13}C NMR (400M Hz, CDCl$_3$)



3zg ^{1}H NMR (400M Hz, CDCl$_3$)



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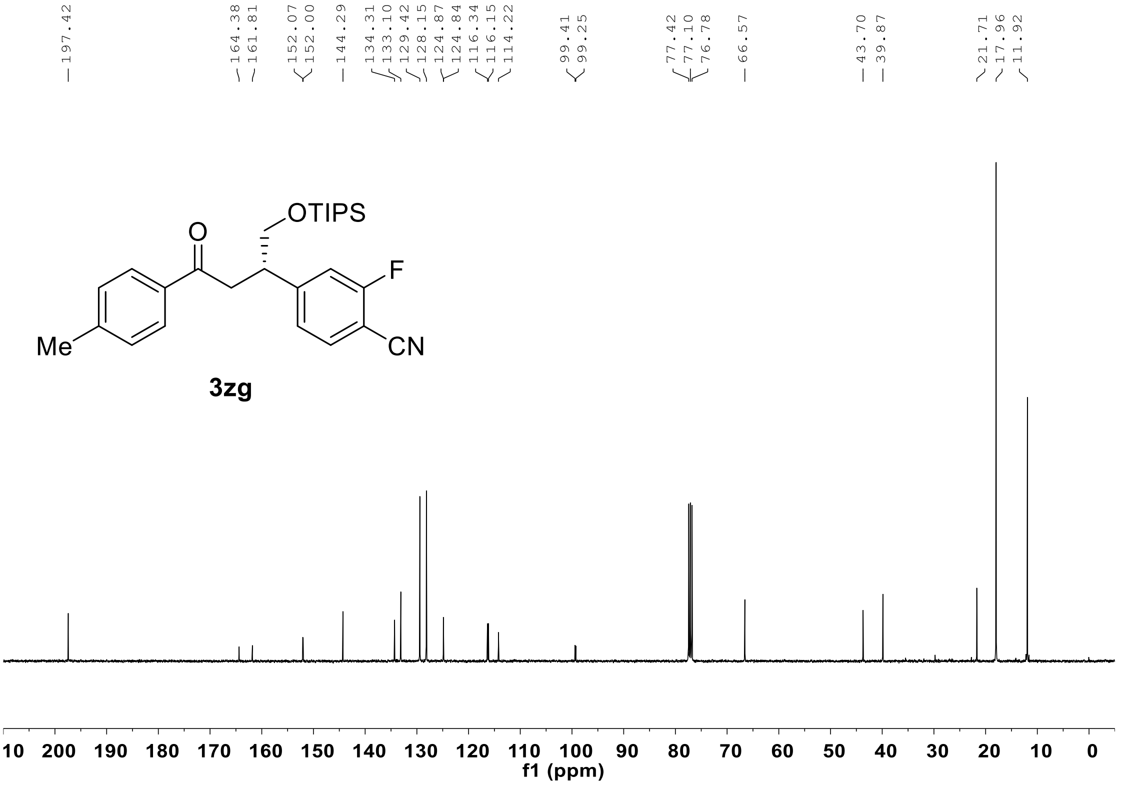
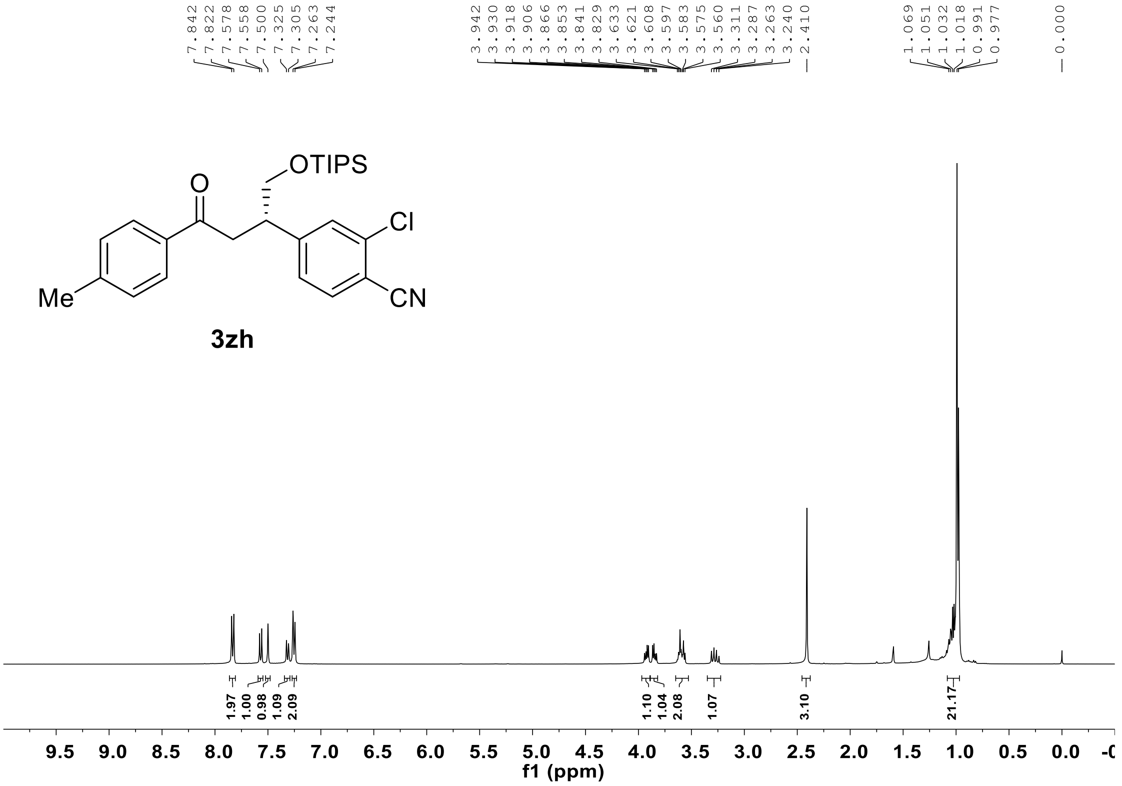


3zh ^{1}H NMR (400M Hz, CDCl$_3$)



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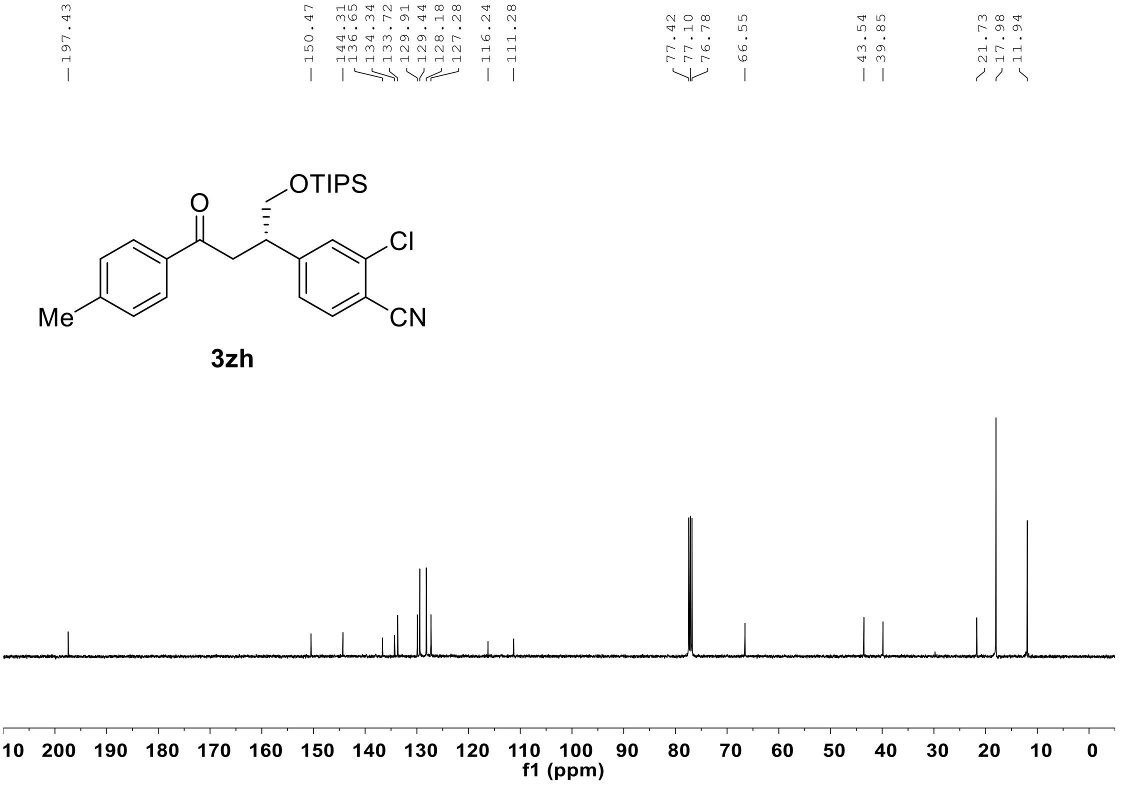
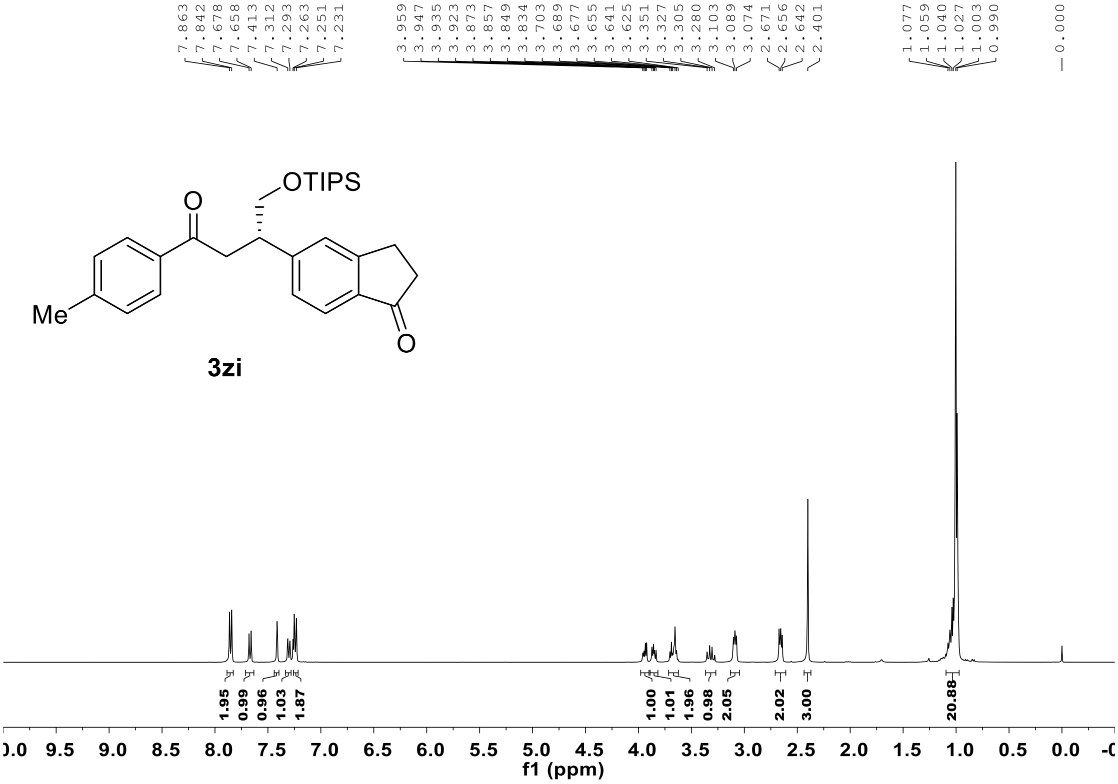


3zi ^{1}H NMR (400M Hz, CDCl$_3$)



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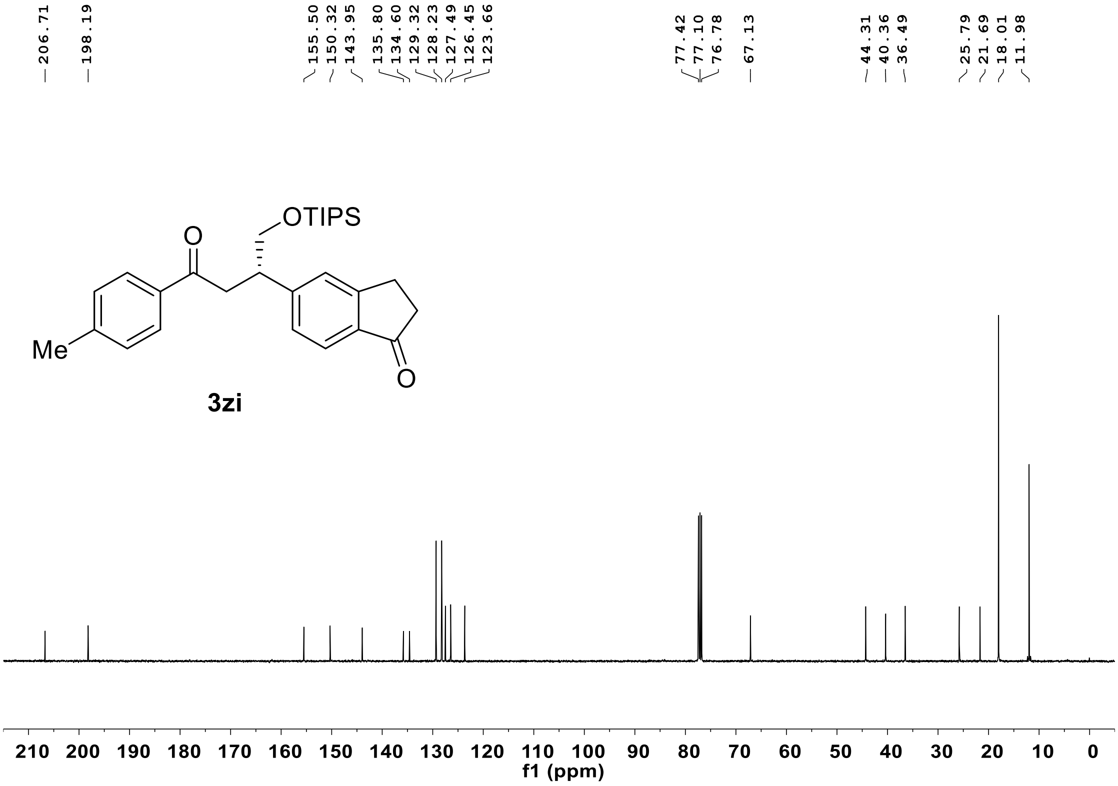
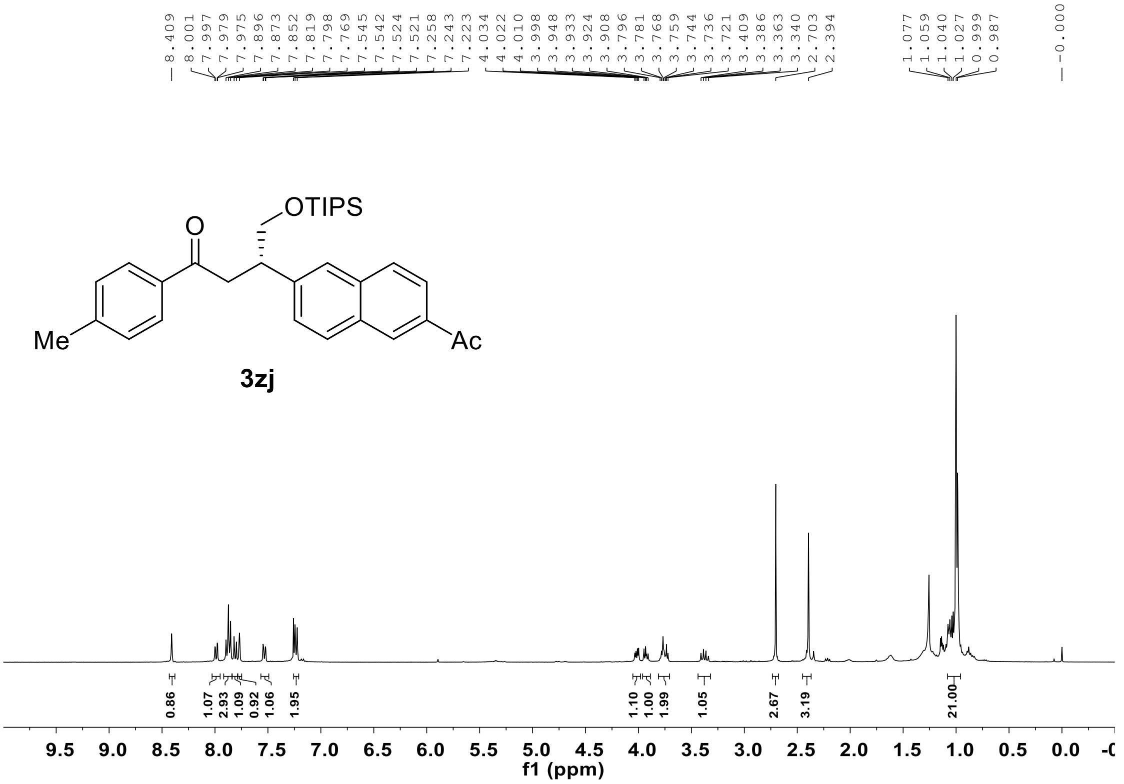
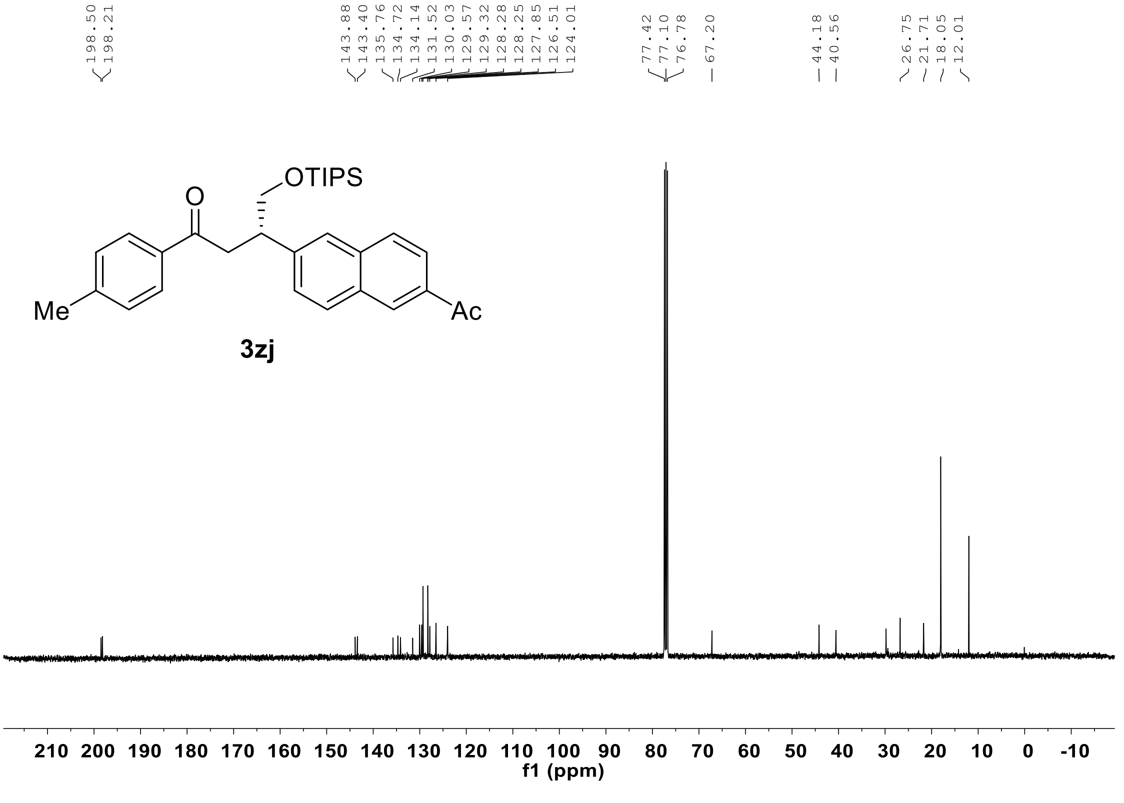


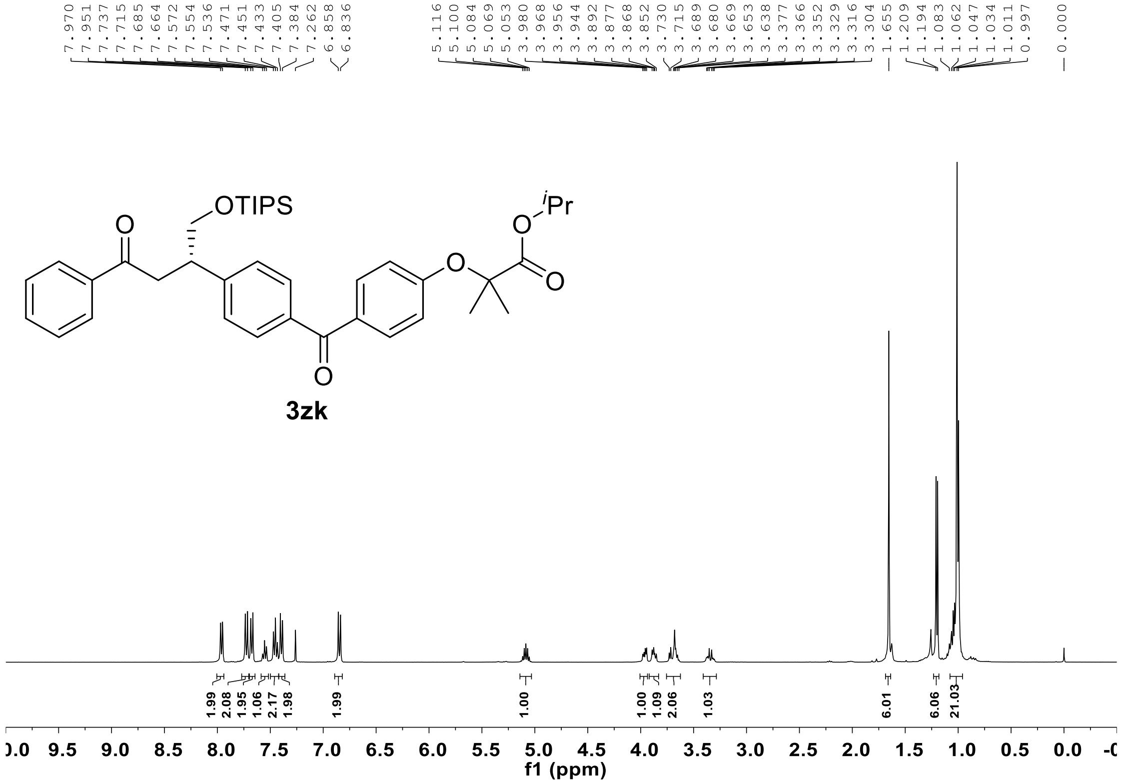
3zj ^{1}H NMR (400M Hz, CDCl$_3$)



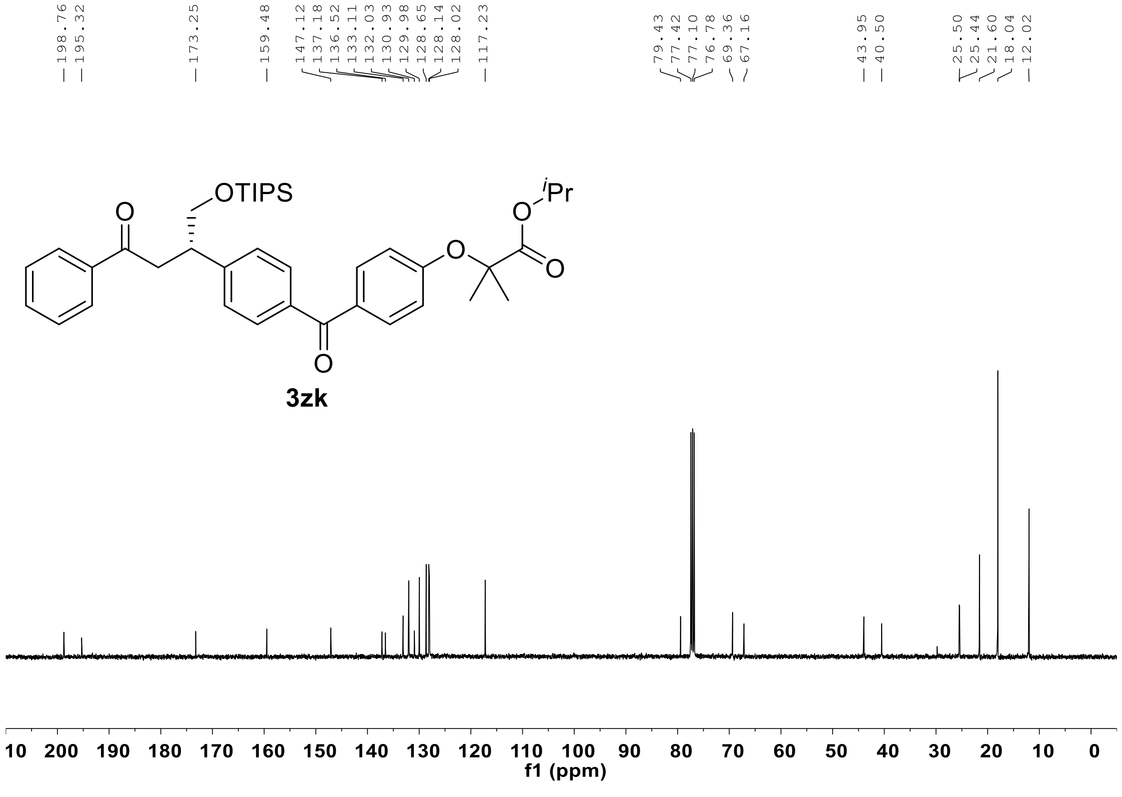
3zj ^{13}C NMR (400M Hz, CDCl$_3$)



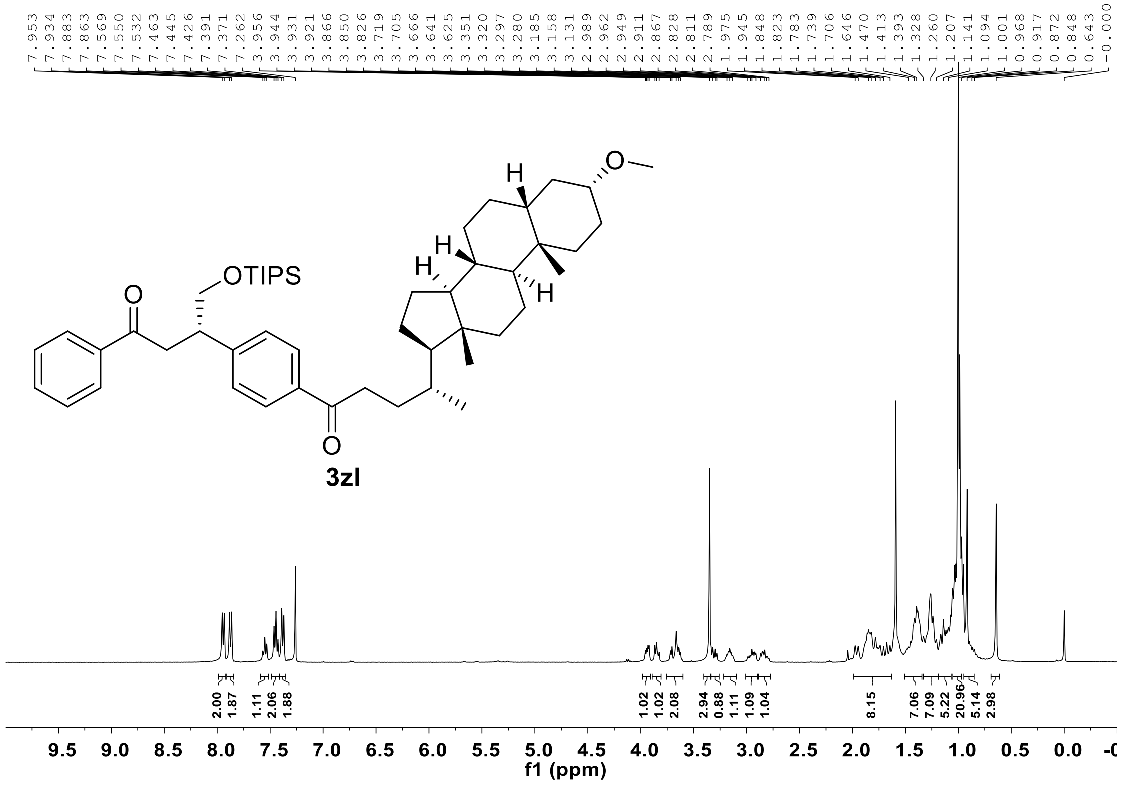
3zk ^{1}H NMR (400M Hz, CDCl$_3$)



3zk ^{13}C NMR (400M Hz, CDCl$_3$)

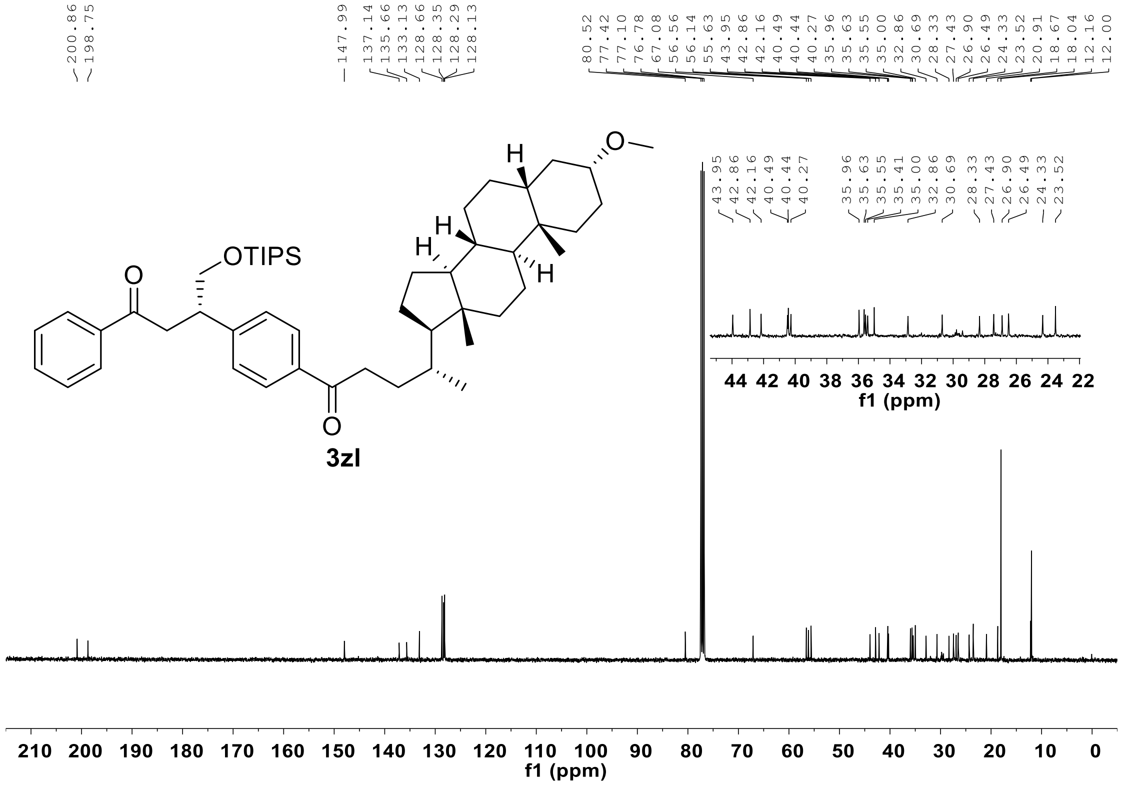


3zl ^{1}H NMR (400M Hz, $CDCl_3$)



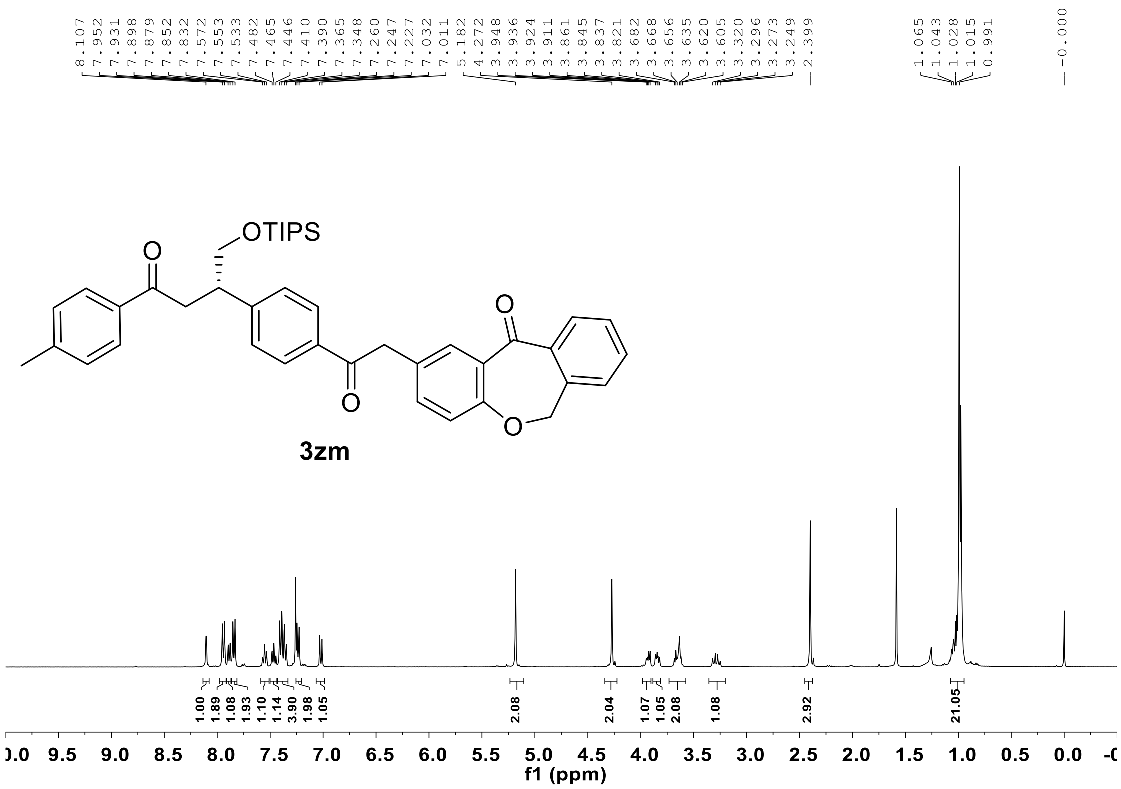
3zl

3zl ^{13}C NMR (400M Hz, $CDCl_3$)

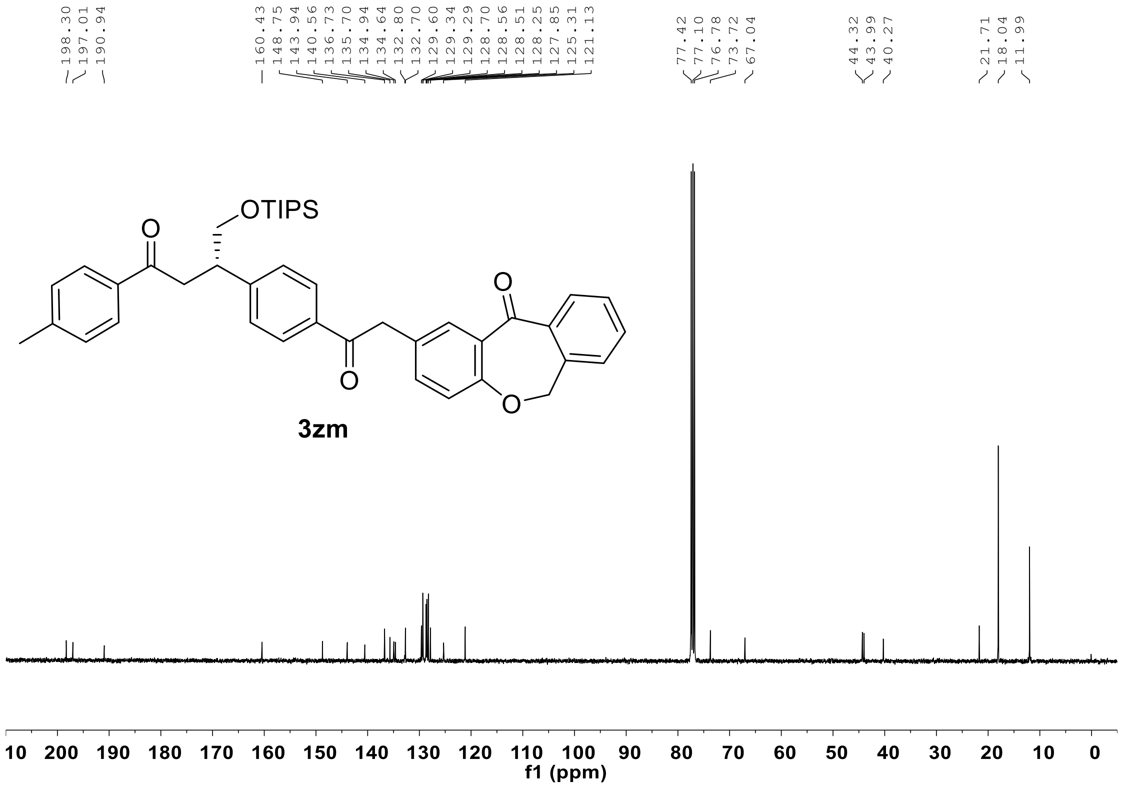


3zl

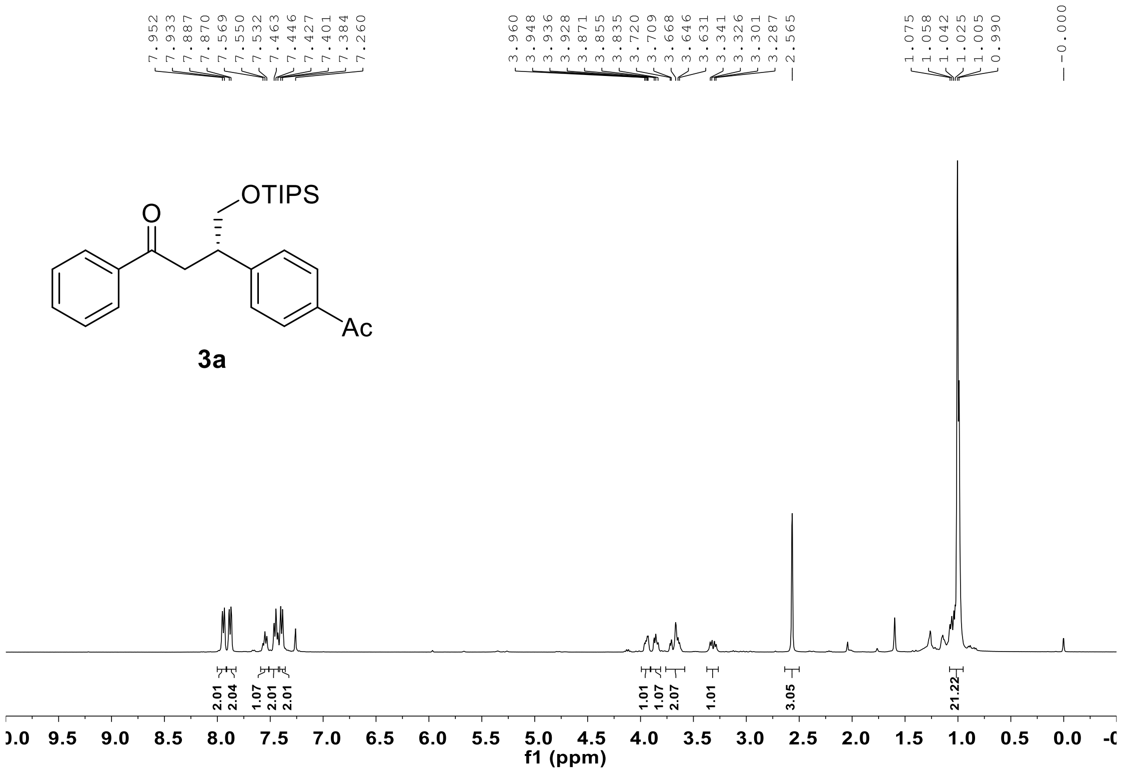
3zm ^{1}H NMR (400M Hz, CDCl$_3$)



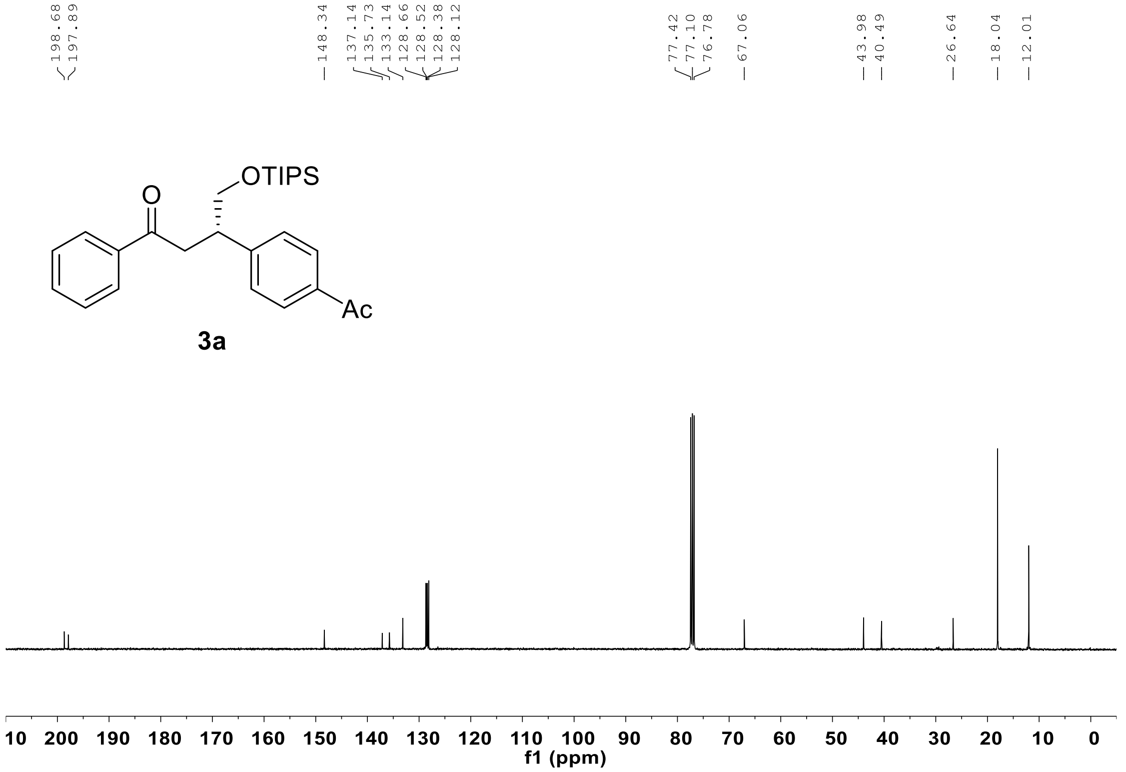
3zm ^{13}C NMR (400M Hz, CDCl$_3$)



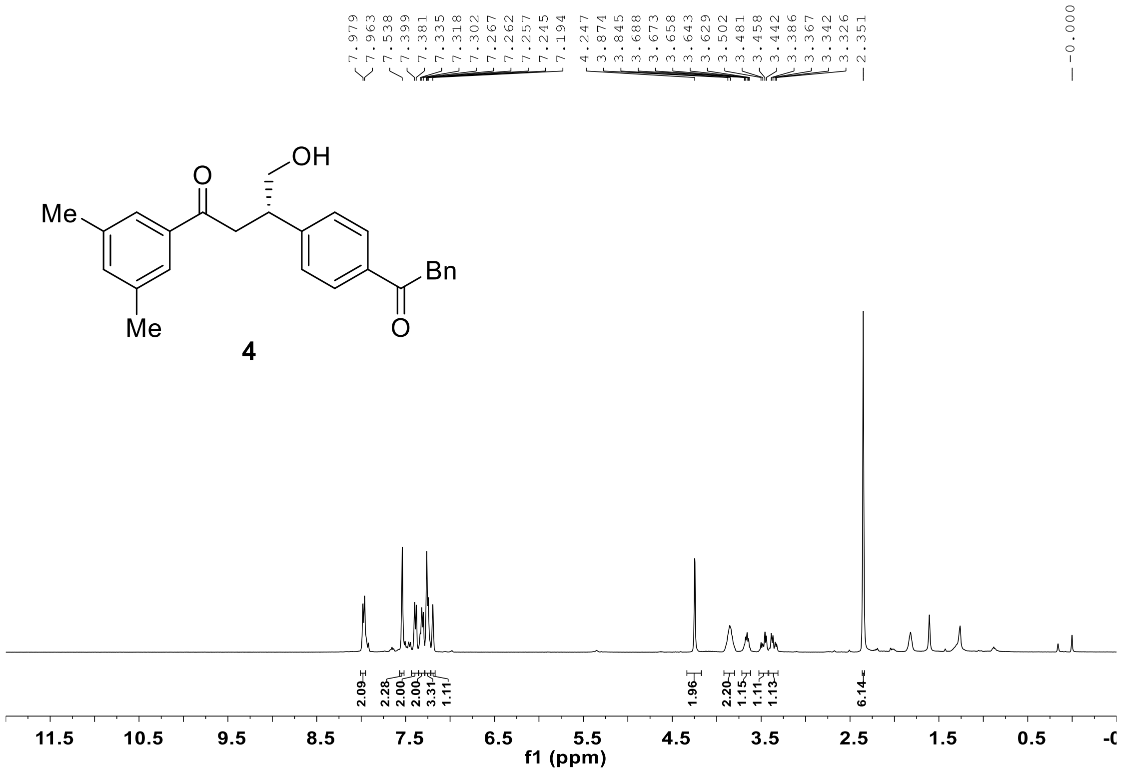
Large-scale of **3a** ^{1}H NMR (400M Hz, CDCl$_3$)



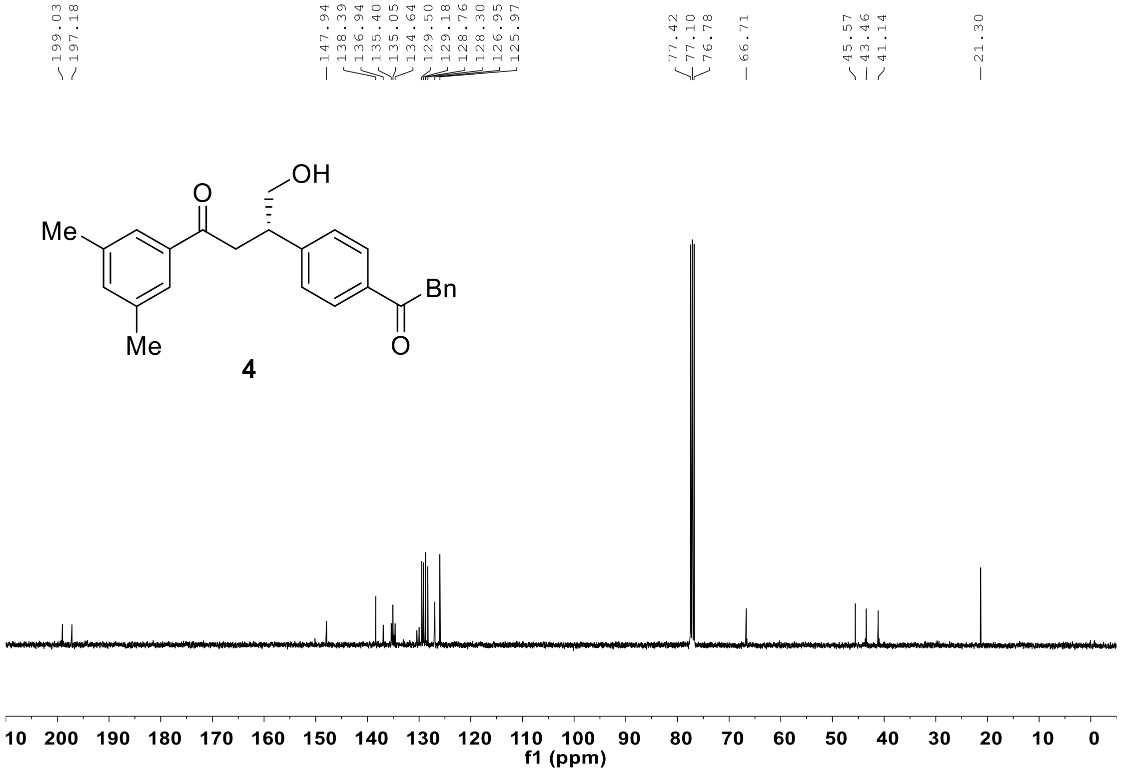
Large-scale **of 3a** ^{13}C NMR (400M Hz, CDCl$_3$)



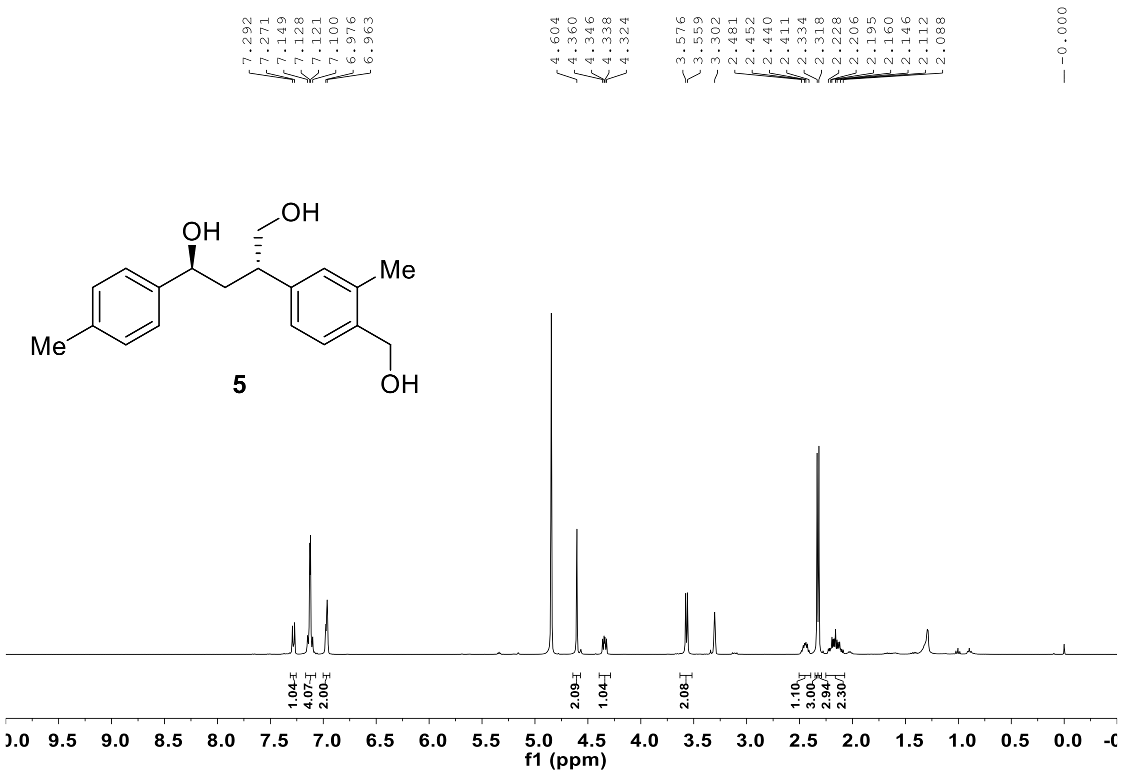
4 ^{1}H NMR (400M Hz, CDCl$_3$)



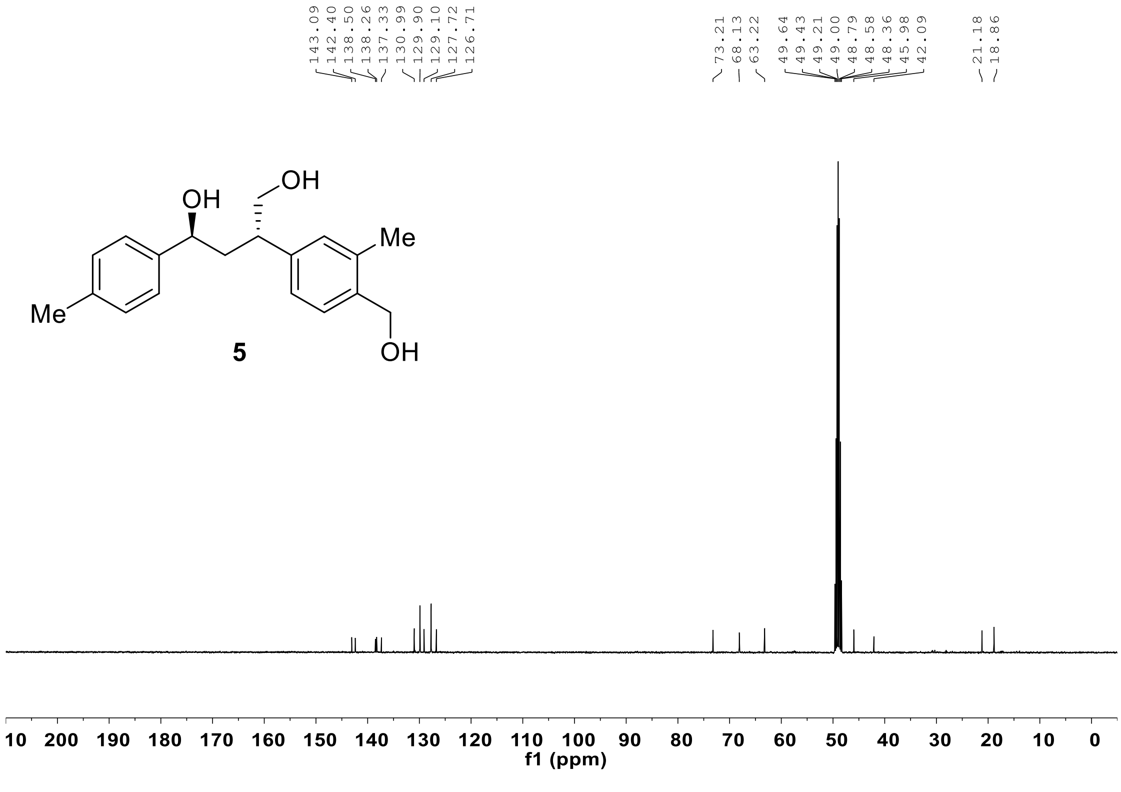
4 ^{13}C NMR (400M Hz, CDCl$_3$)



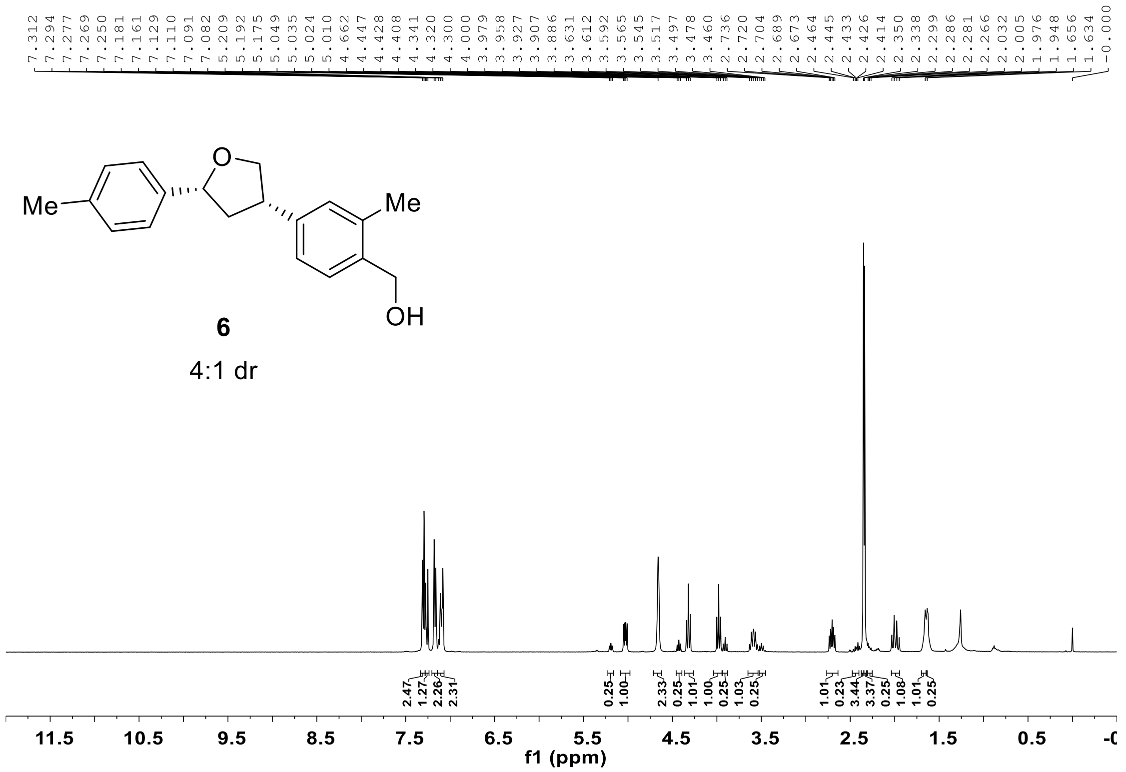
5 ^{1}H NMR (400M Hz, CD_3OD)



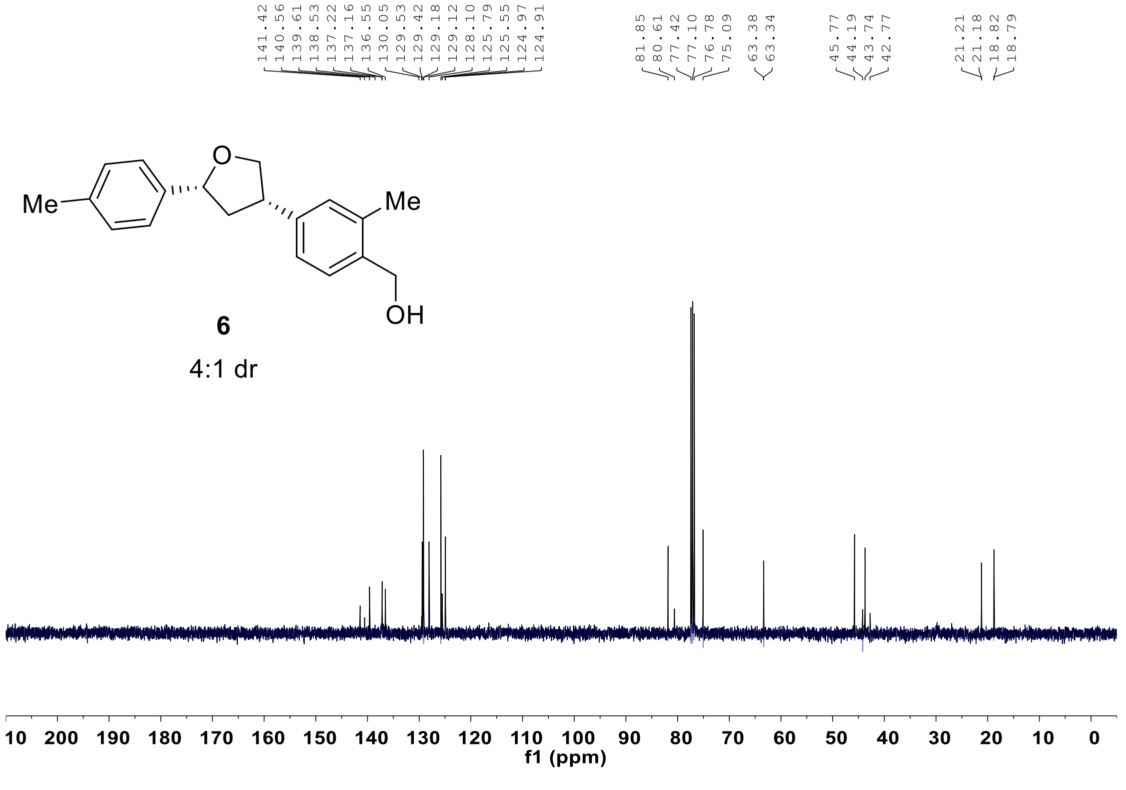
5 ^{13}C NMR (400M Hz, CD_3OD)

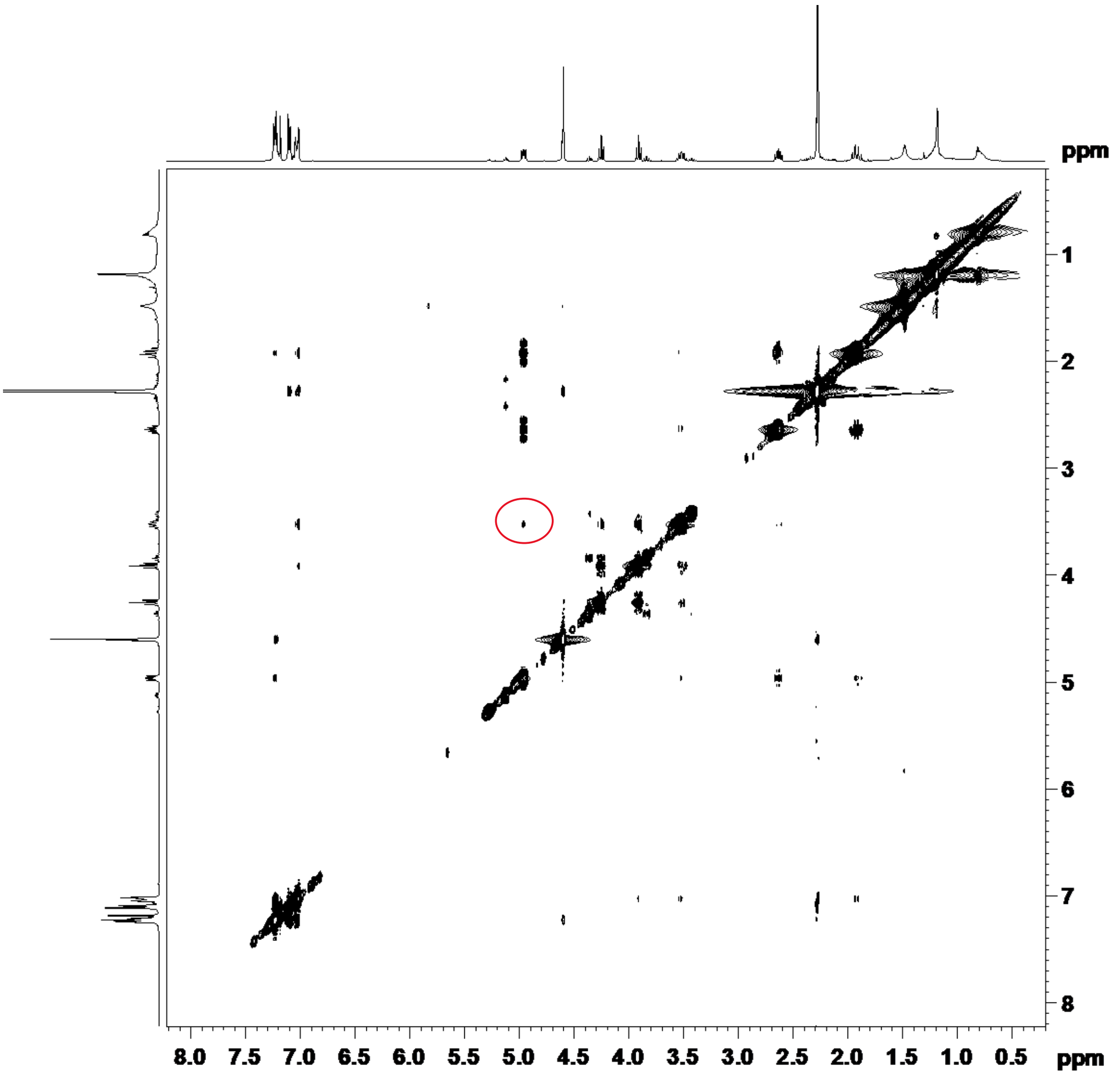


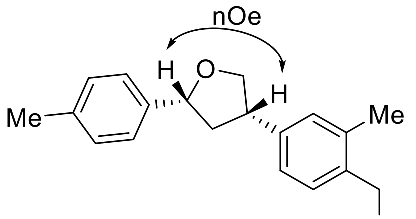
6 ^{1}H NMR (400M Hz, CDCl$_3$)



6 ^{13}C NMR (400M Hz, CDCl$_3$)



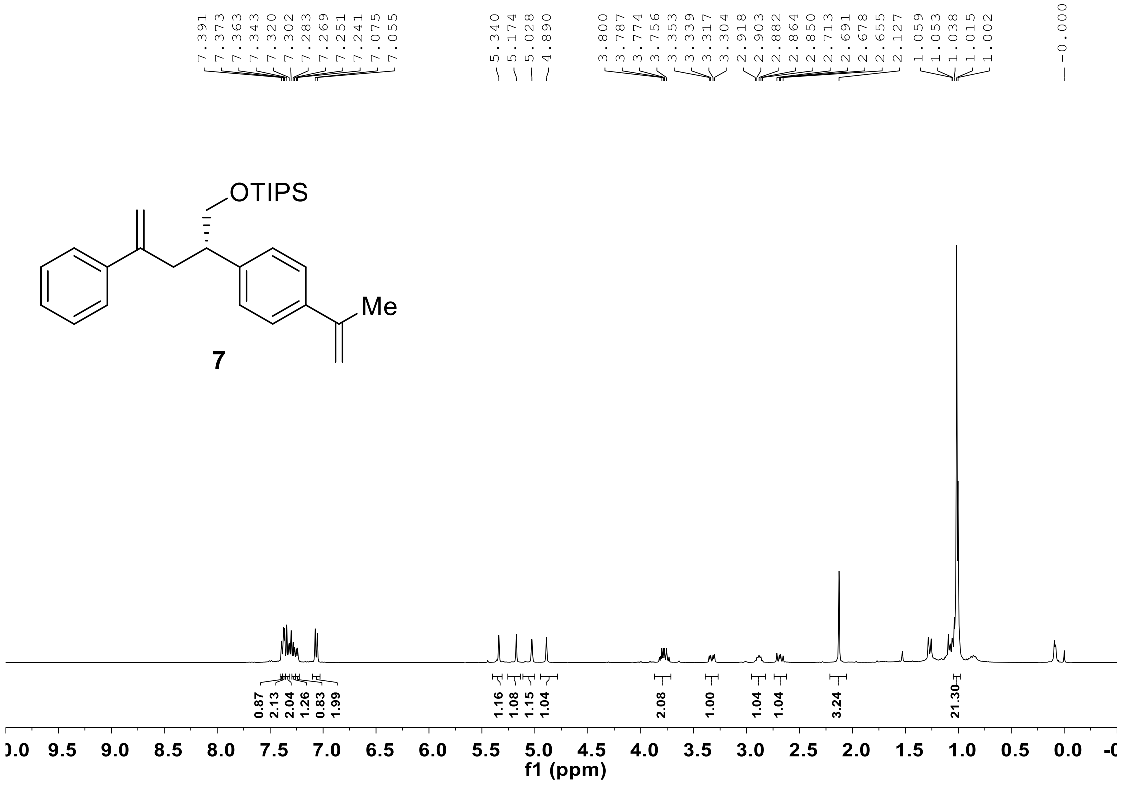




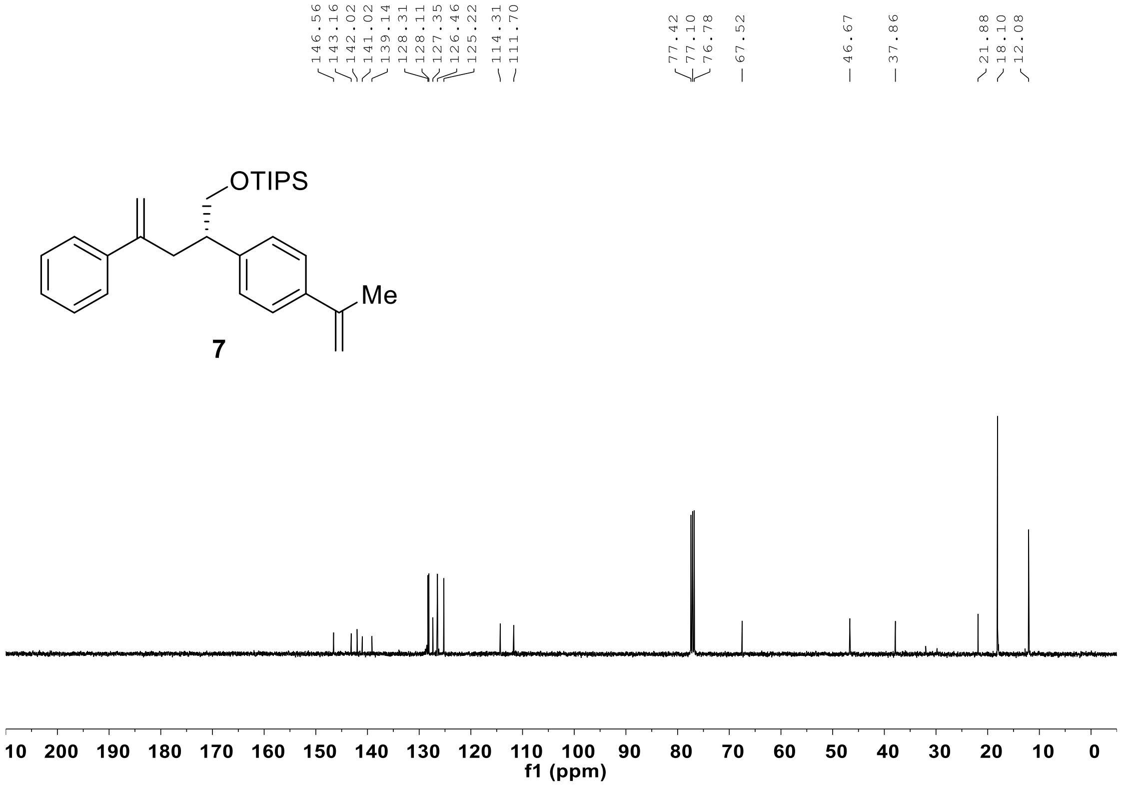
6 (major)

NOESY spectrum of **6** (major) in $CDCl_3$

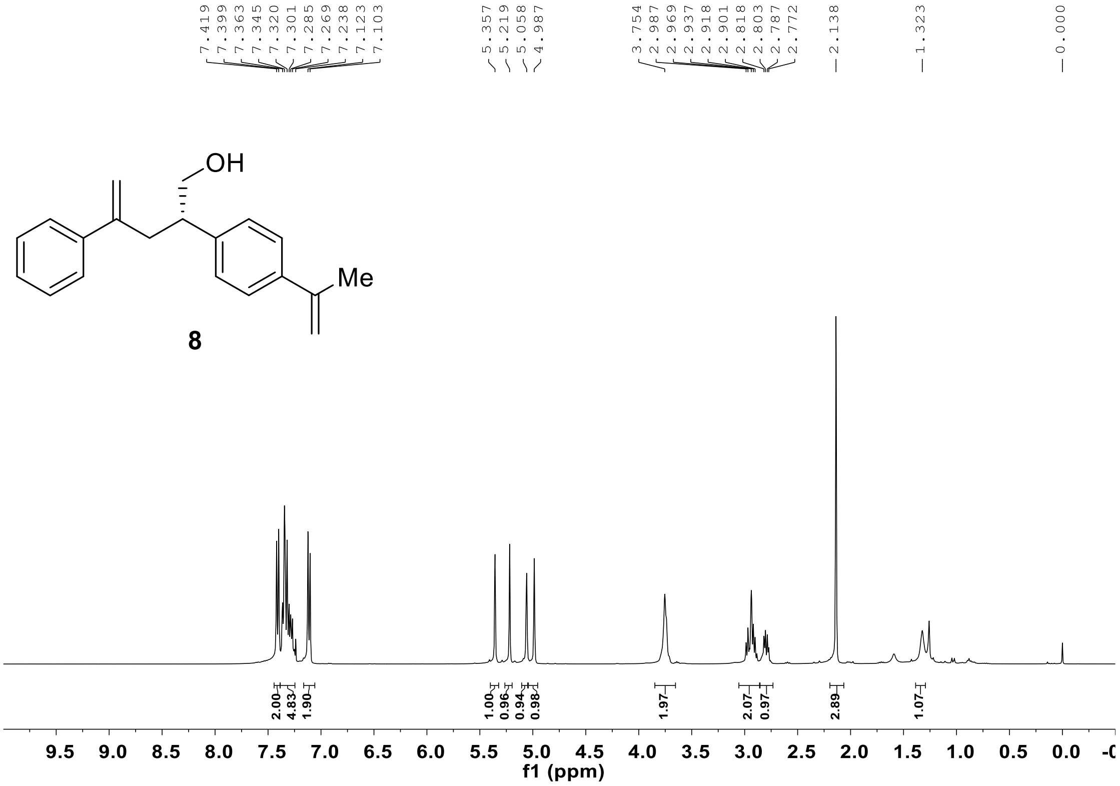
7 ^{1}H NMR (400M Hz, CDCl$_3$)



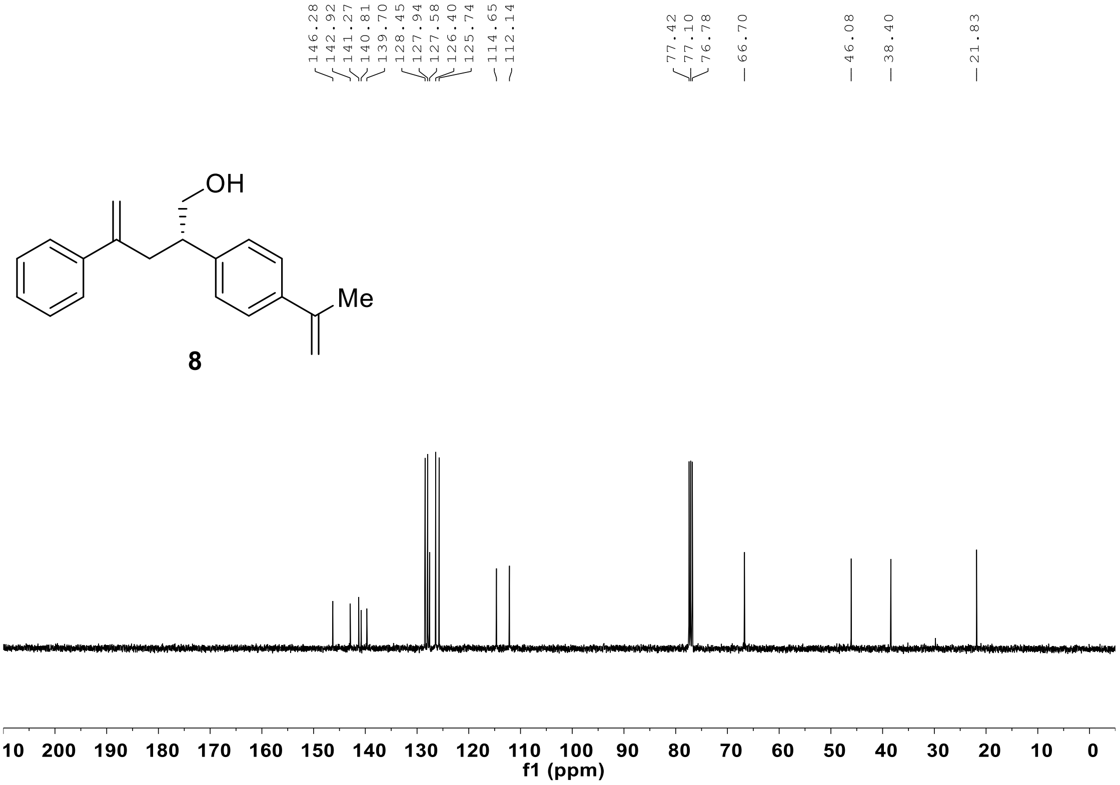
7 ^{13}C NMR (400M Hz, CDCl$_3$)



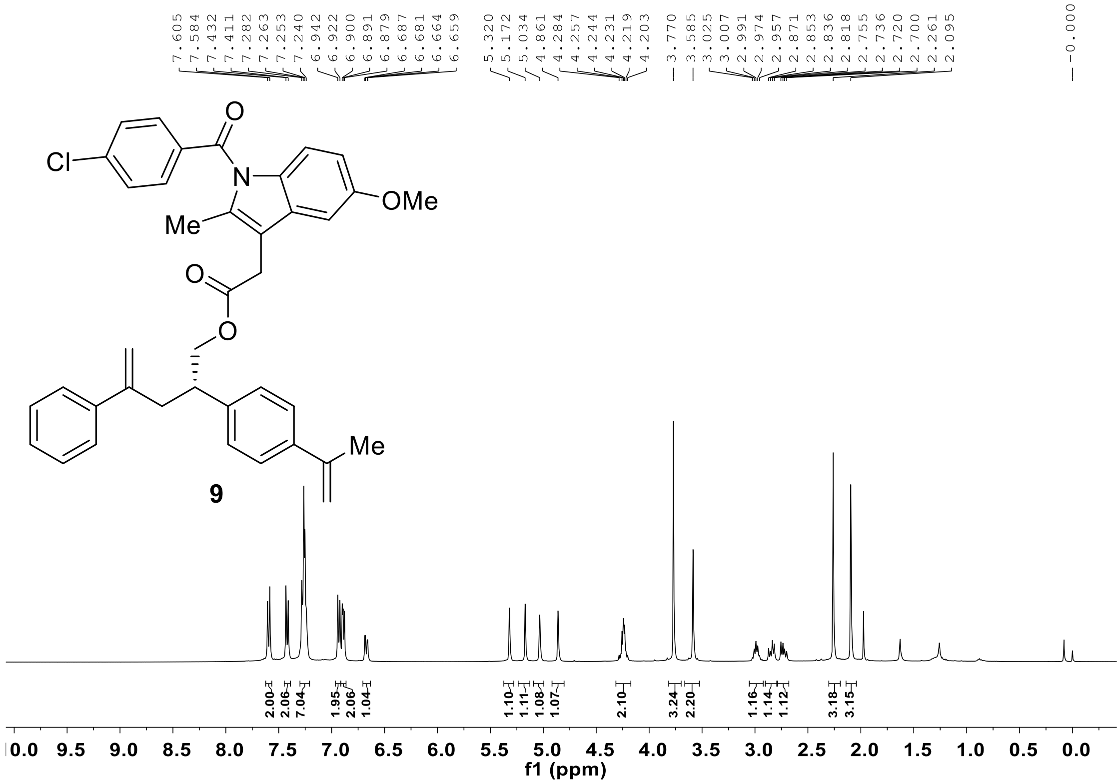
8 ^{1}H NMR (400M Hz, $CDCl_3$)



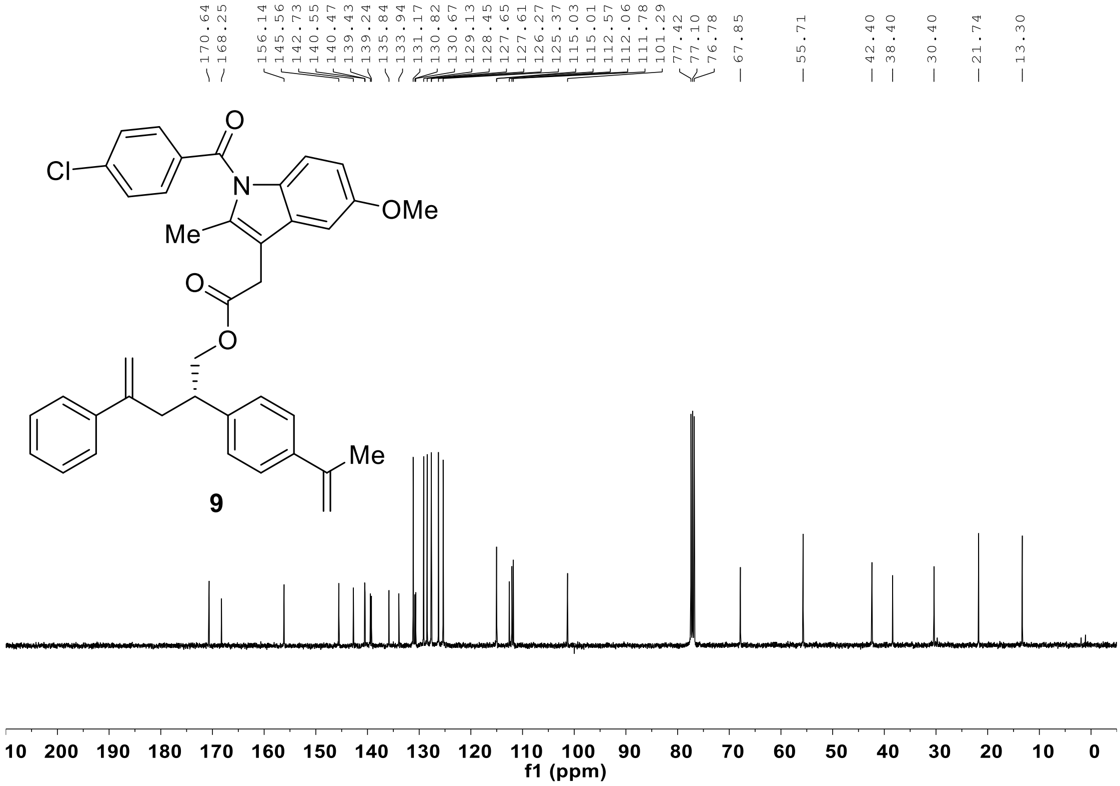
8 ^{13}C NMR (400M Hz, $CDCl_3$)



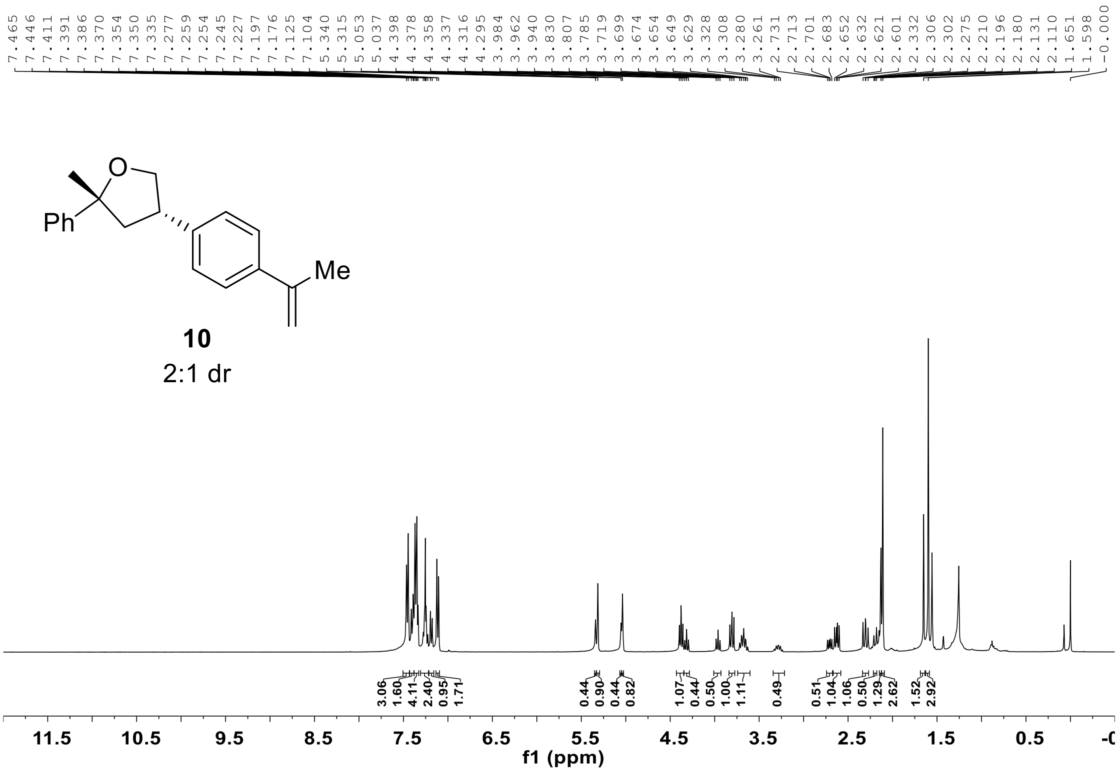
9 ^{1}H NMR (400M Hz, CDCl$_3$)



9 ^{13}C NMR (400M Hz, CDCl$_3$)

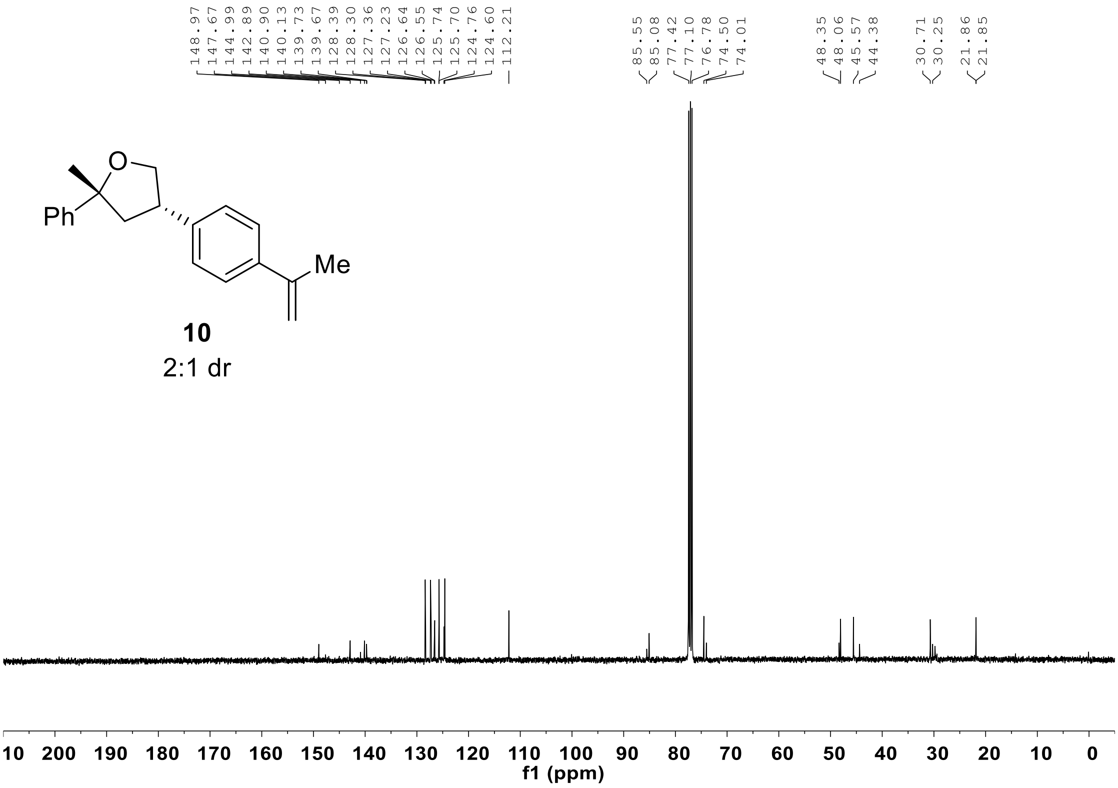


10 ^{1}H NMR (400M Hz, CDCl$_3$)

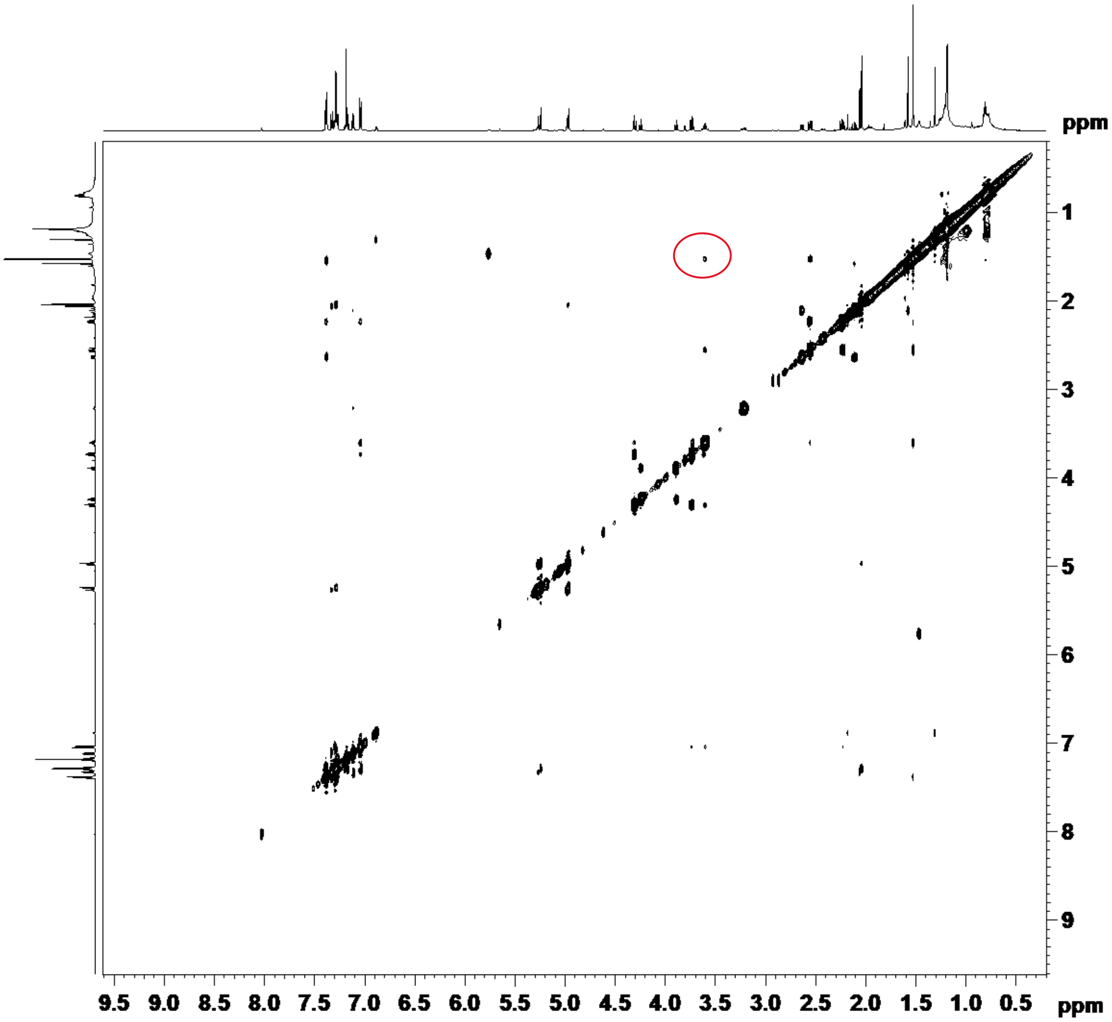


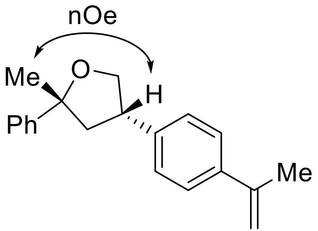
10
2:1 dr

10 ^{13}C NMR (400M Hz, CDCl$_3$)



10
2:1 dr

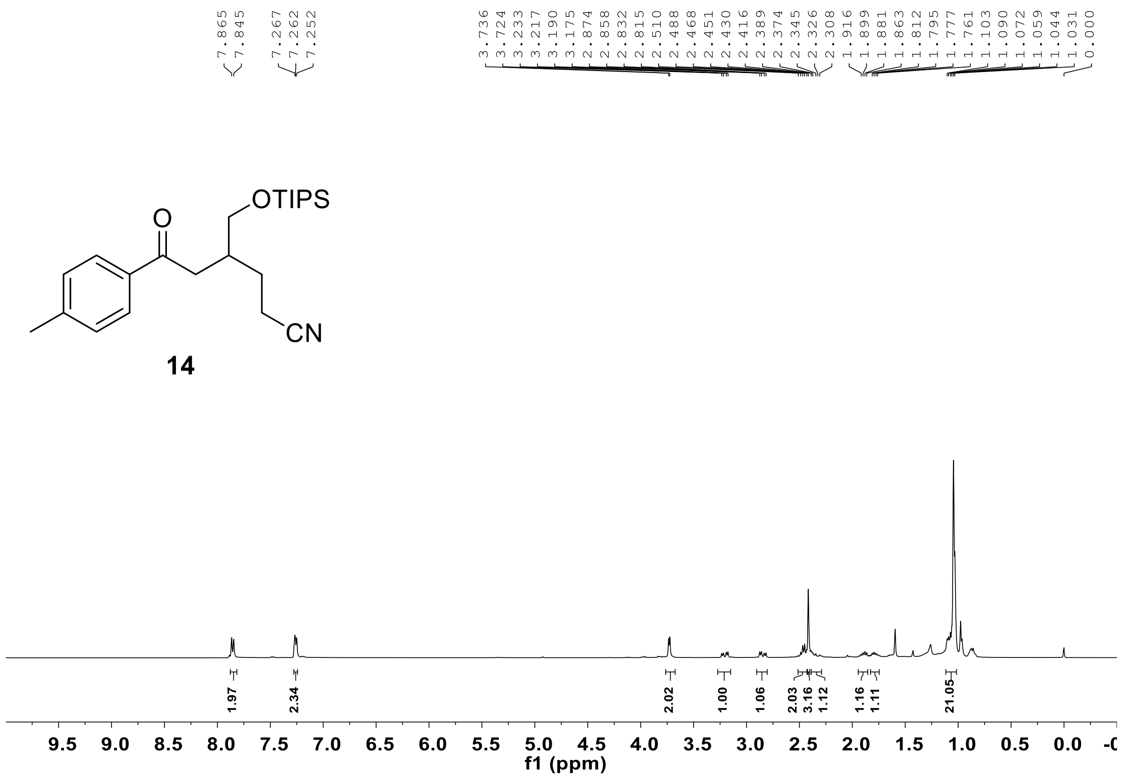




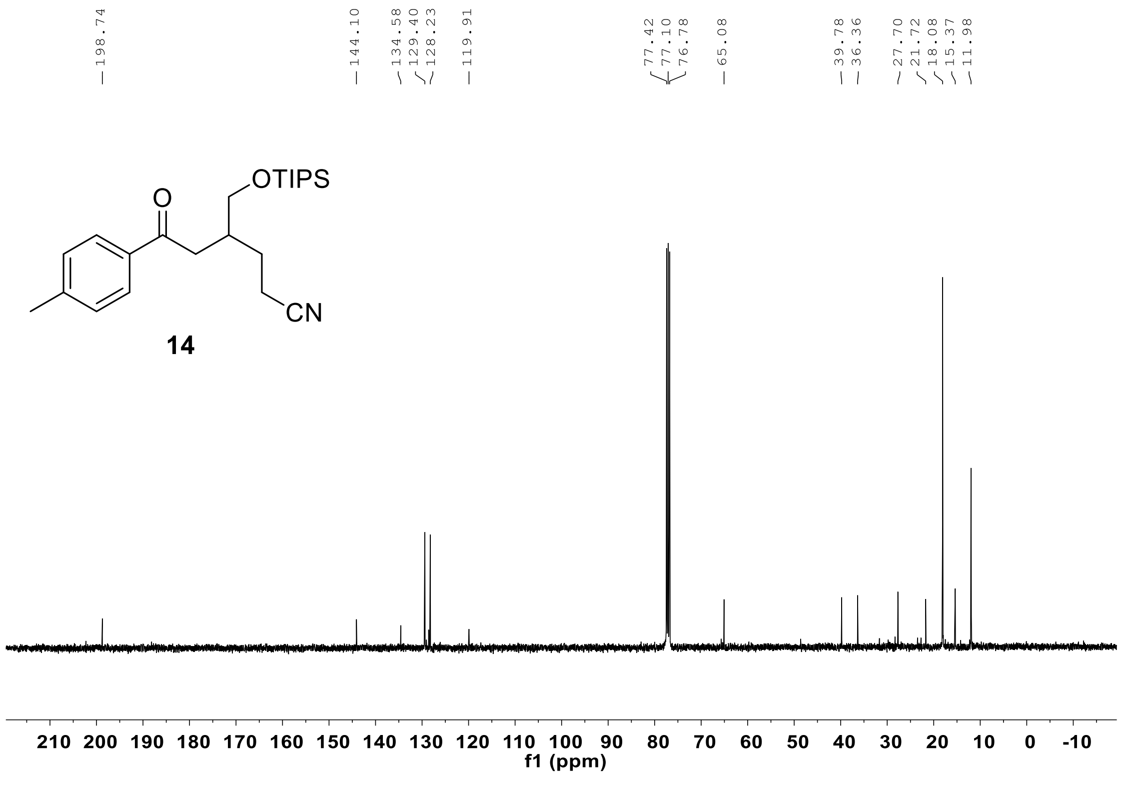
10 (major)

NOESY spectrum of **10** (major) in $CDCl_3$

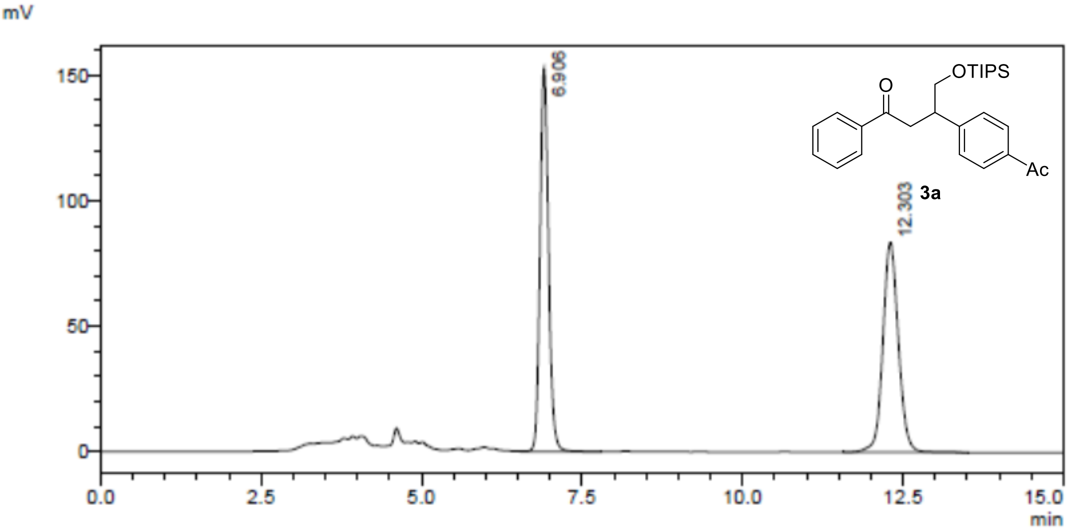
14 ^{1}H NMR (400M Hz, CDCl$_3$)



14 ^{1}H NMR (400M Hz, CDCl$_3$)



HPLC Spectra



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A 254nm

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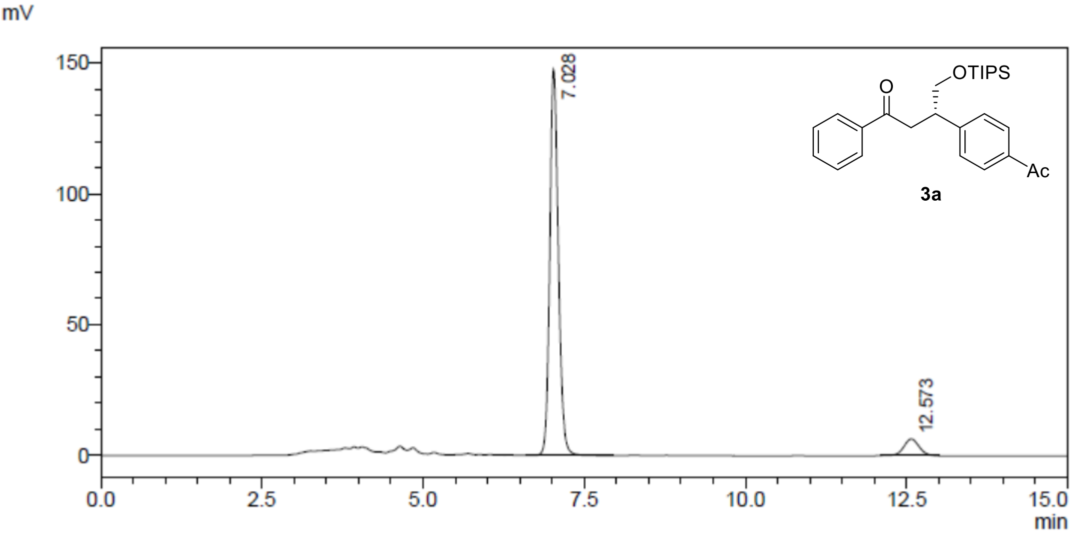

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A 254nm

Peak#	Ret. Time	Area	Height	Area%
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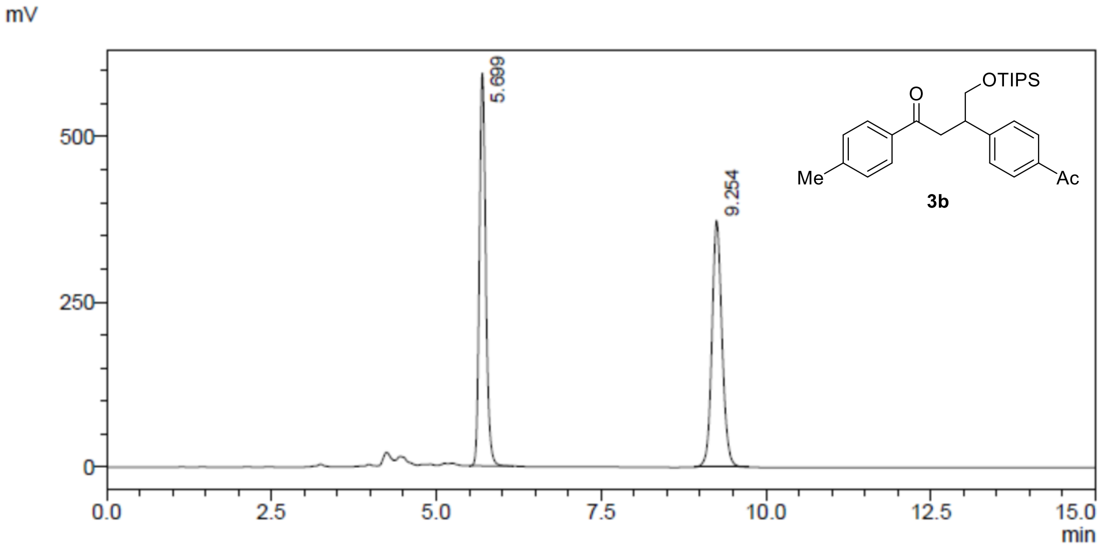

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Peak#	Ret. Time	Area	Height	Area%
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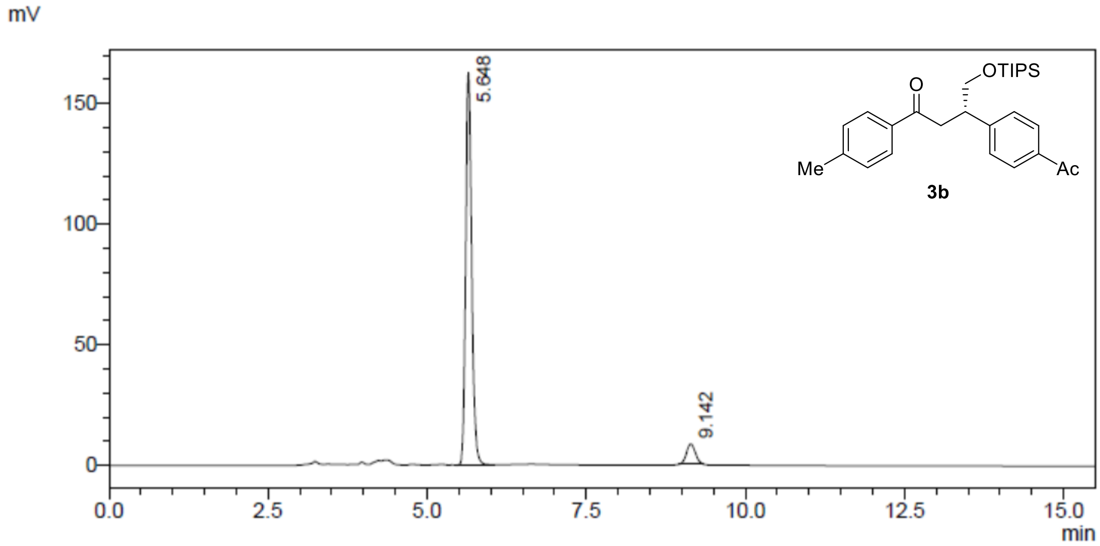

<Peak Table>

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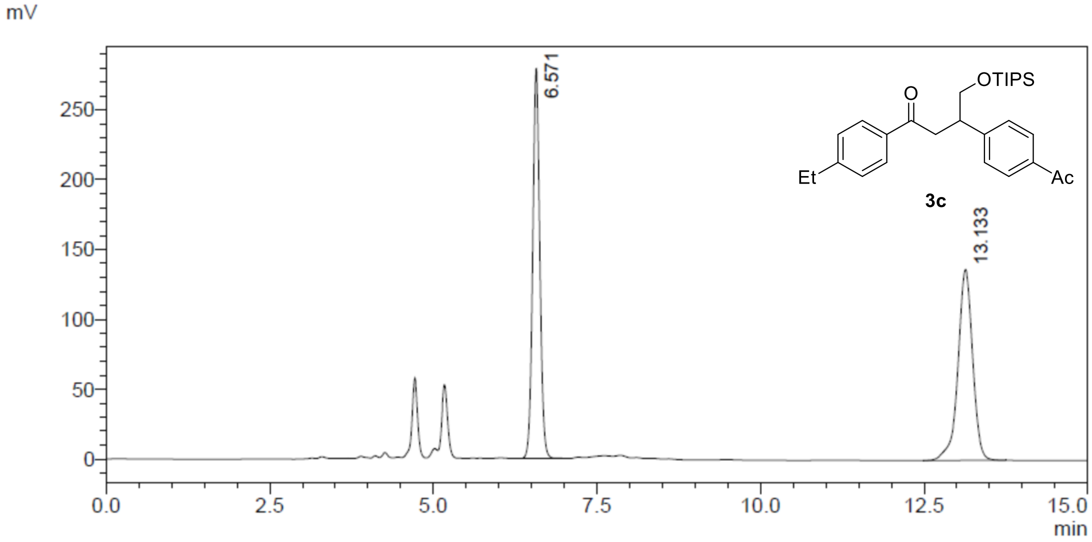

<Peak Table>

A 254nm

Peak#	Ret. Time	Area	Height	Area%
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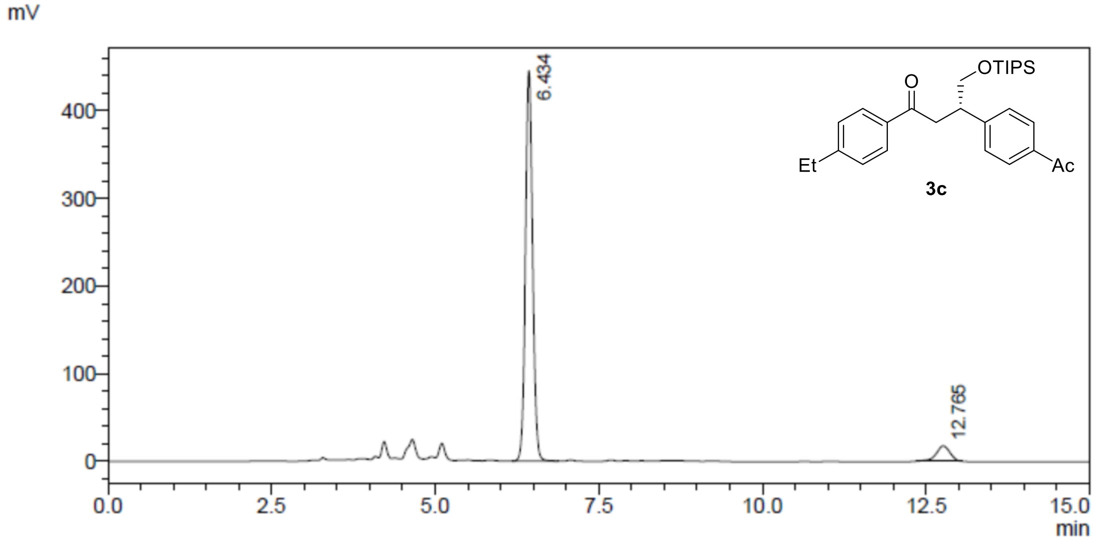

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A 254nm

Peak#	Ret. Time	Area	Height	Area%
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2	12.765	255920	17457	7.061
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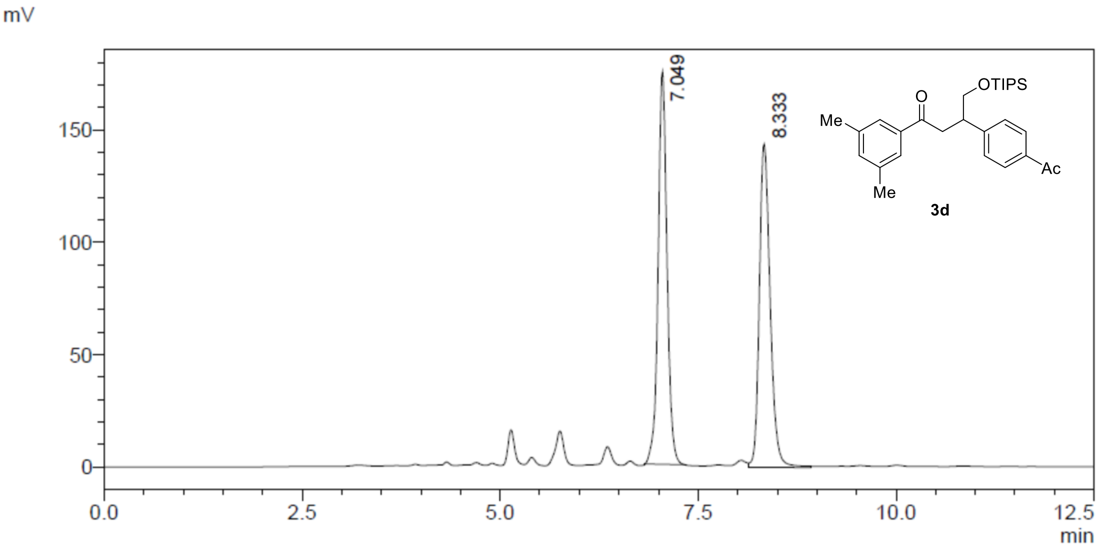

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A 254nm

Peak#	Ret. Time	Area	Height	Area%
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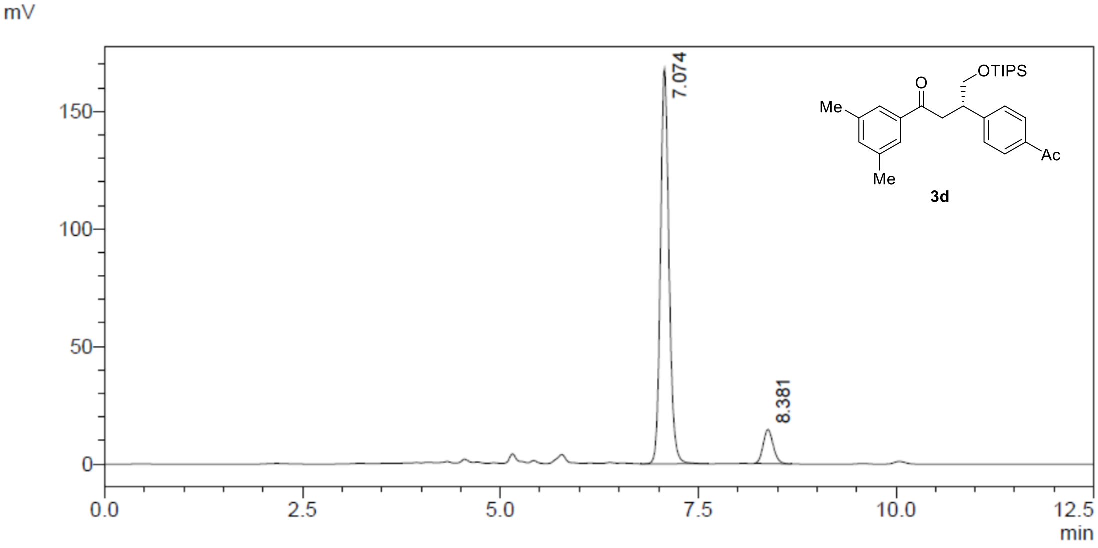

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A 254nm

Peak#	Ret. Time	Area	Height	Area%
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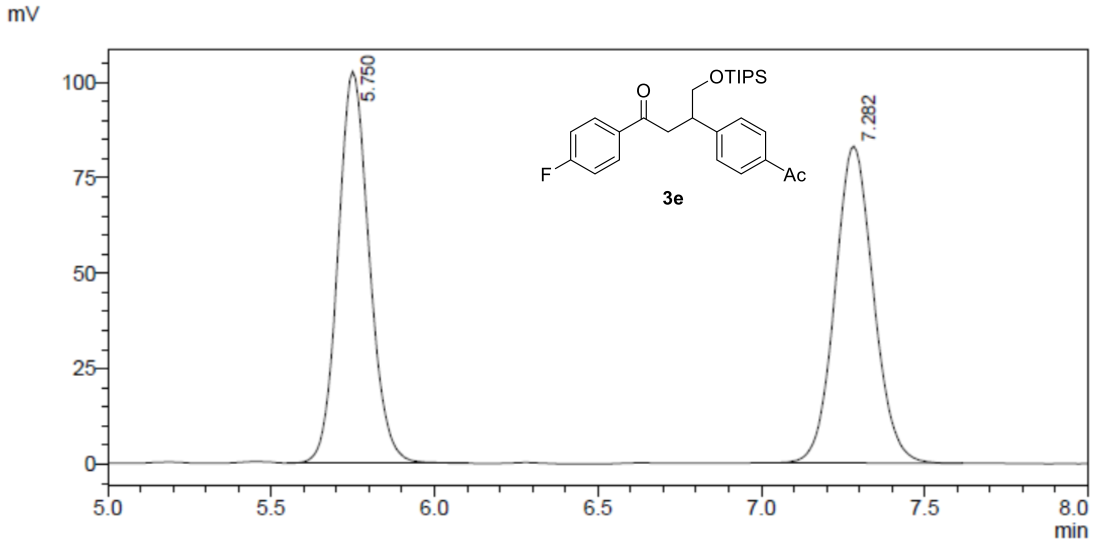

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254nm

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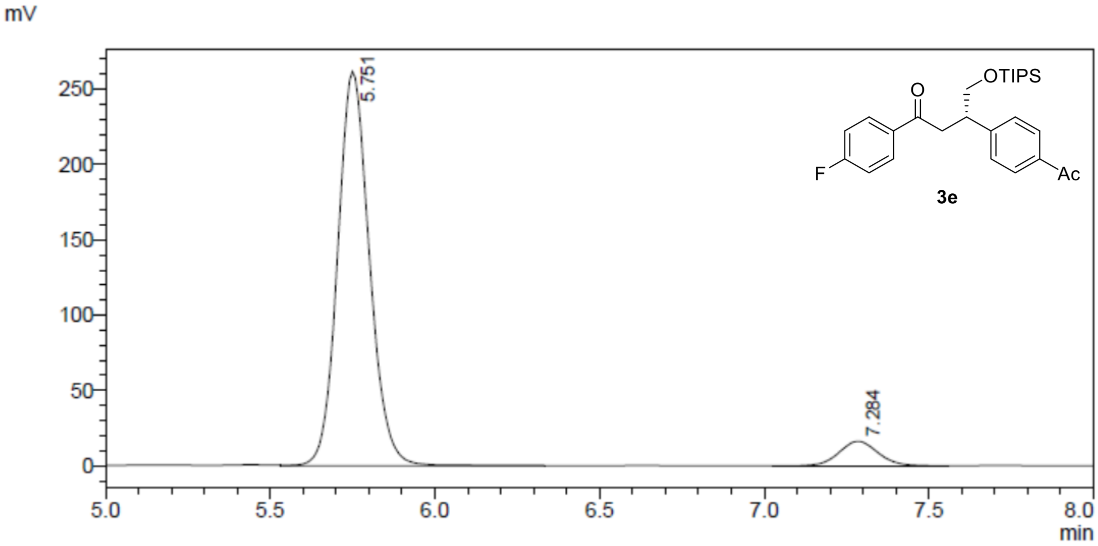

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254nm

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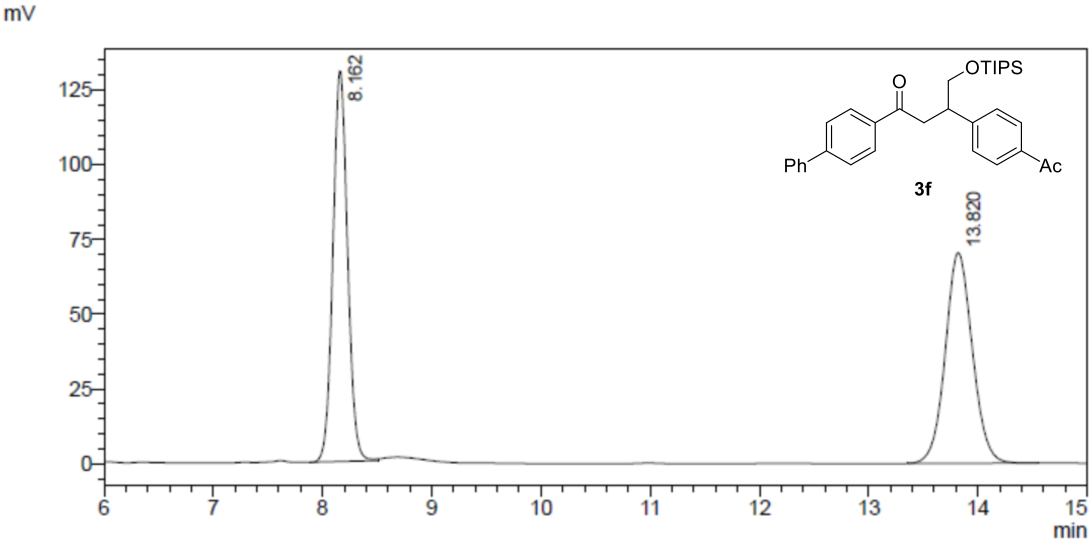
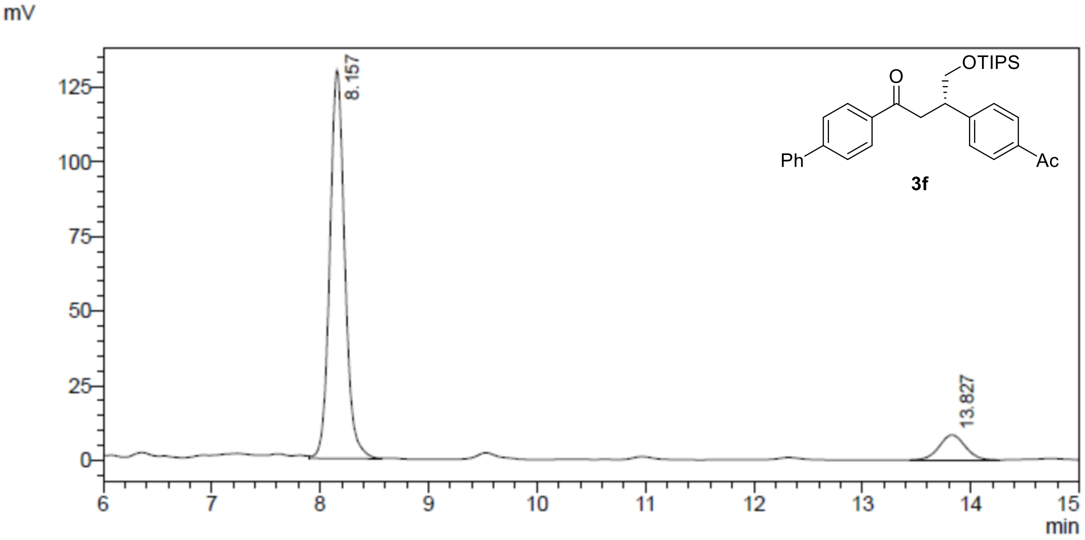
2	7.284	133982	16308	7.077
		1893184	278070	100.000



<Peak Table>

A 254nm

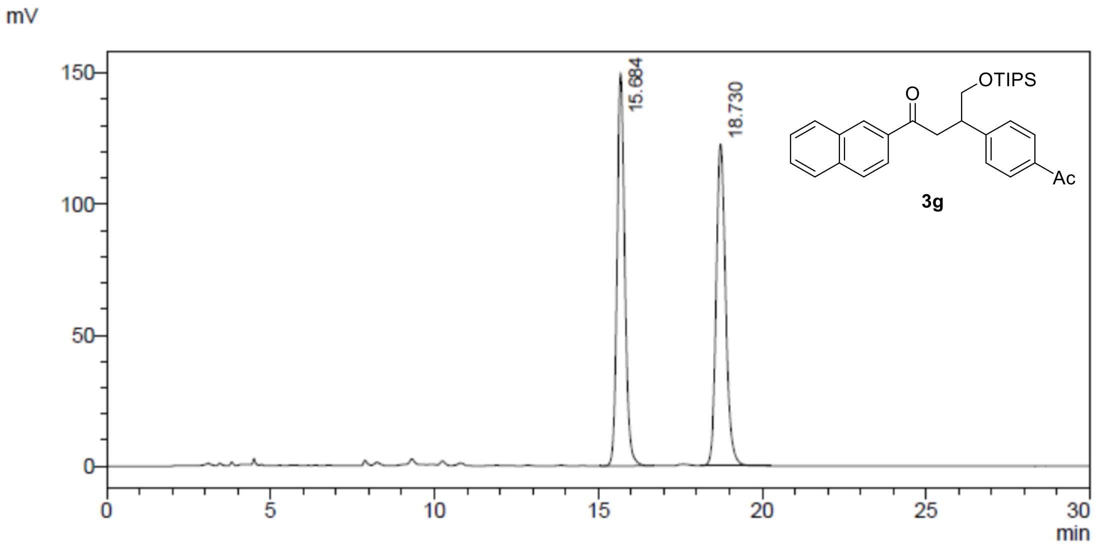
Peak#	Ret. Time	Area	Height	Area%
1	8.162	1219362	130718	50.055
2	13.820	1216700	70404	49.945
		2436062	201123	100.000



<Peak Table>

A 254nm

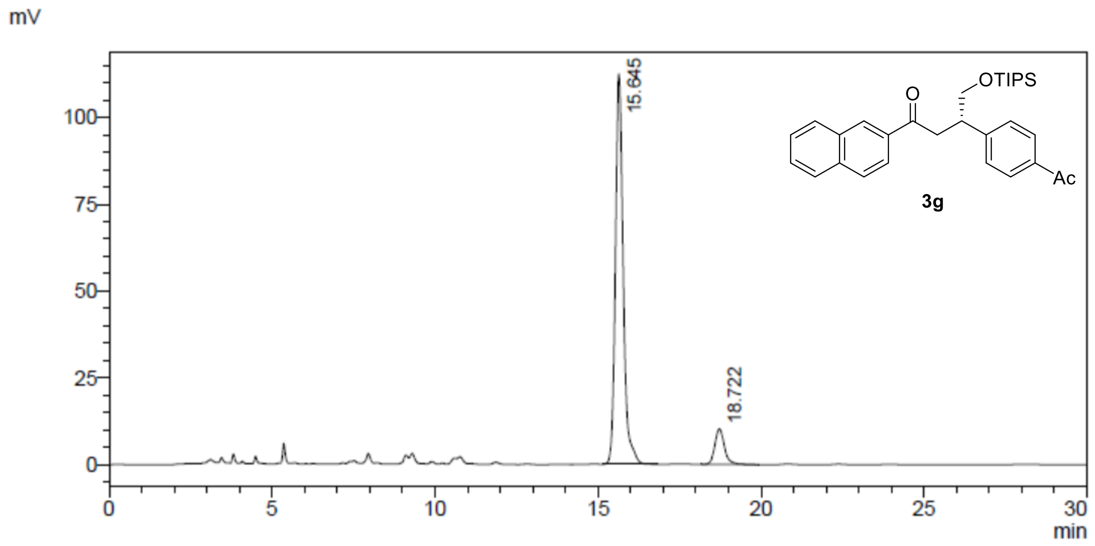
Peak#	Ret. Time	Area	Height	Area%
1	8.157	1250010	130328	89.977
2	13.827	139248	8378	10.023
		1389257	138706	100.000



<Peak Table>

A 254nm

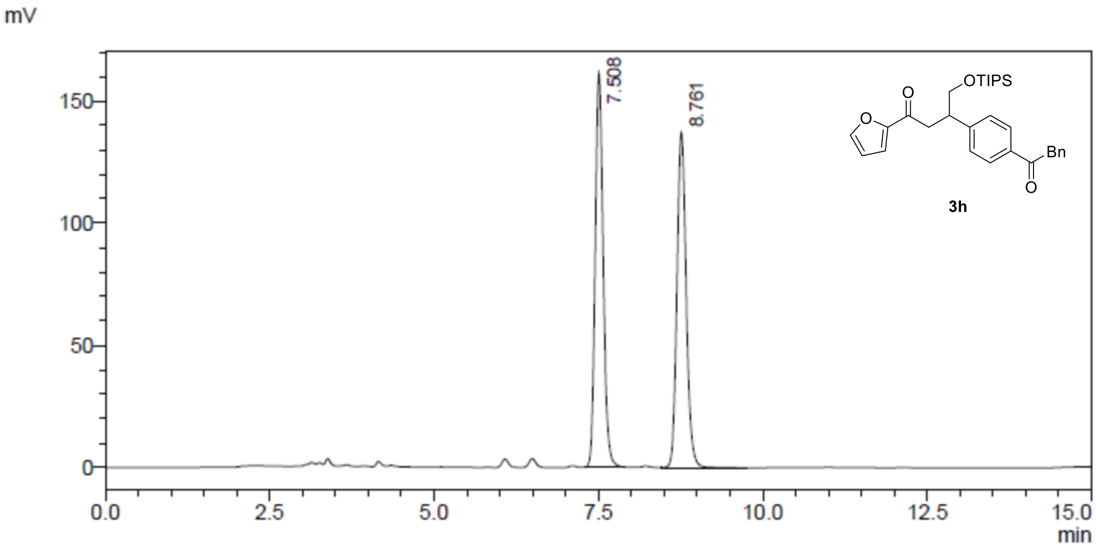
Peak#	Ret. Time	Area	Height	Area%
1	15.684	2460240	149695	49.930
2	18.730	2467142	122746	50.070
		4927382	272441	100.000



<Peak Table>

A 254nm

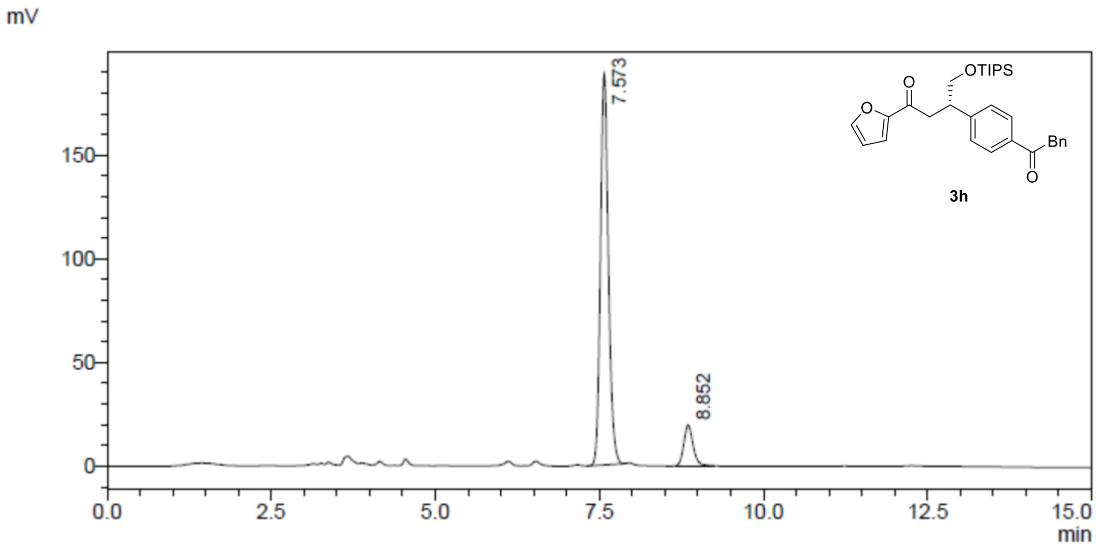
Peak#	Ret. Time	Area	Height	Area%
1	15.645	1889014	112457	89.992
2	18.722	210087	10245	10.008
		2099101	122702	100.000



<Peak Table>

A 254nm

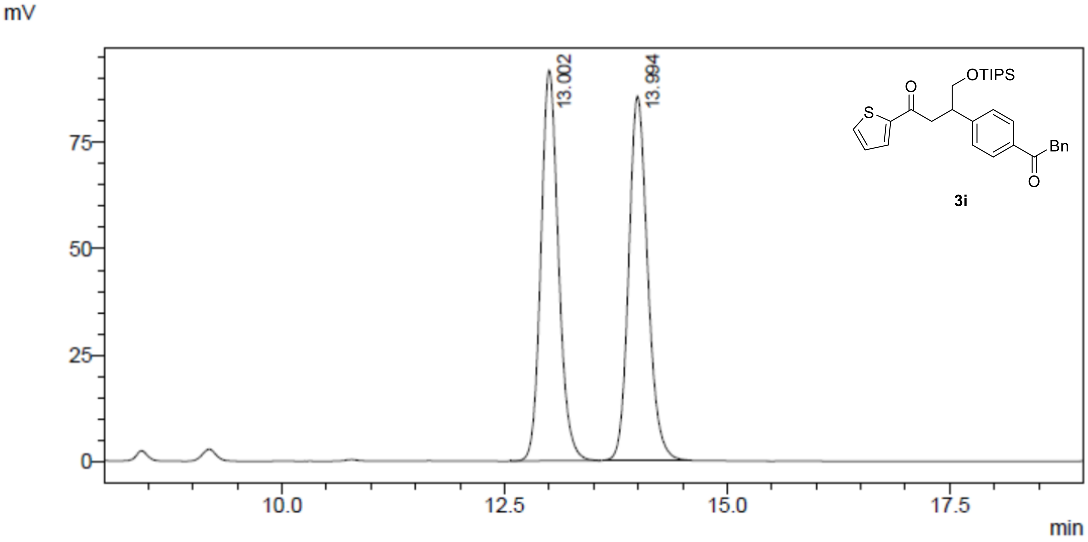
Peak#	Ret. Time	Area	Height	Area%
1	7.508	1347702	161043	50.253
2	8.761	1334117	137008	49.747
		2681819	298051	100.000



<Peak Table>

A 254nm

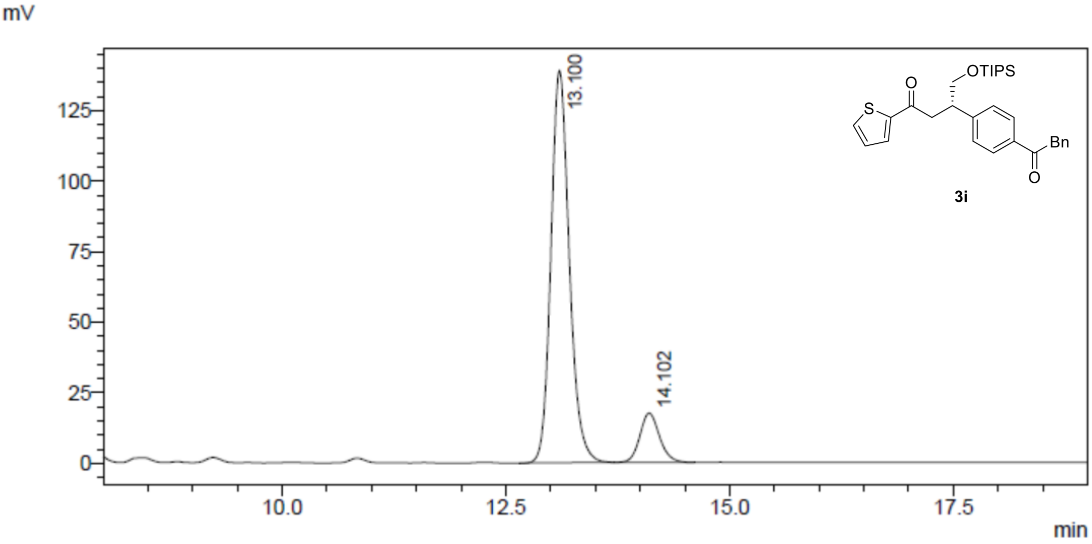
Peak#	Ret. Time	Area	Height	Area%
1	7.573	1597567	188499	89.092
2	8.852	195597	19778	10.908
		1793164	208277	100.000



<Peak Table>

A 254nm

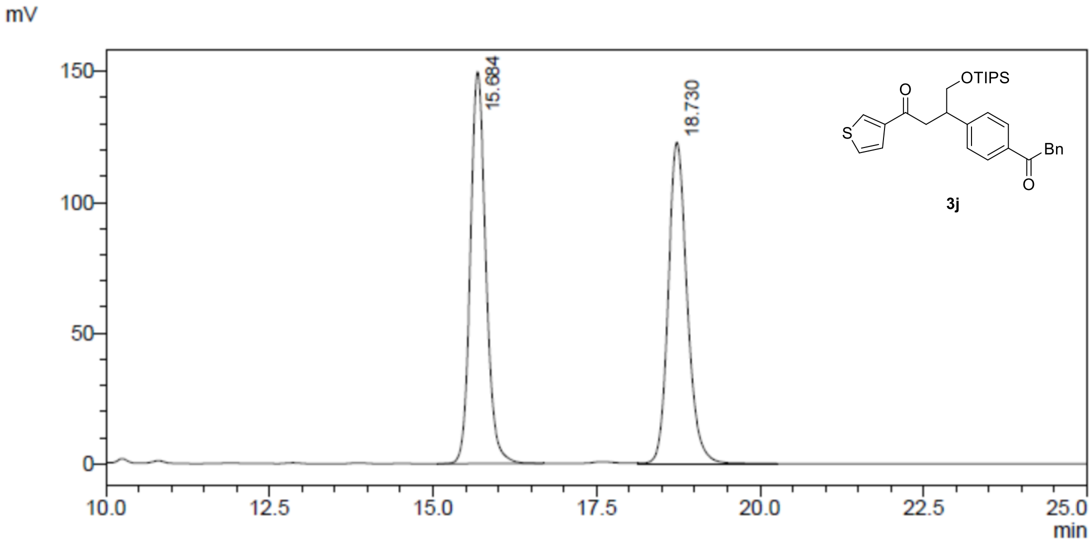
Peak#	Ret. Time	Area	Height	Area%
1	13.002	1260392	91845	49.841
2	13.994	1268417	85551	50.159
		2528809	177395	100.000



<Peak Table>

A 254nm

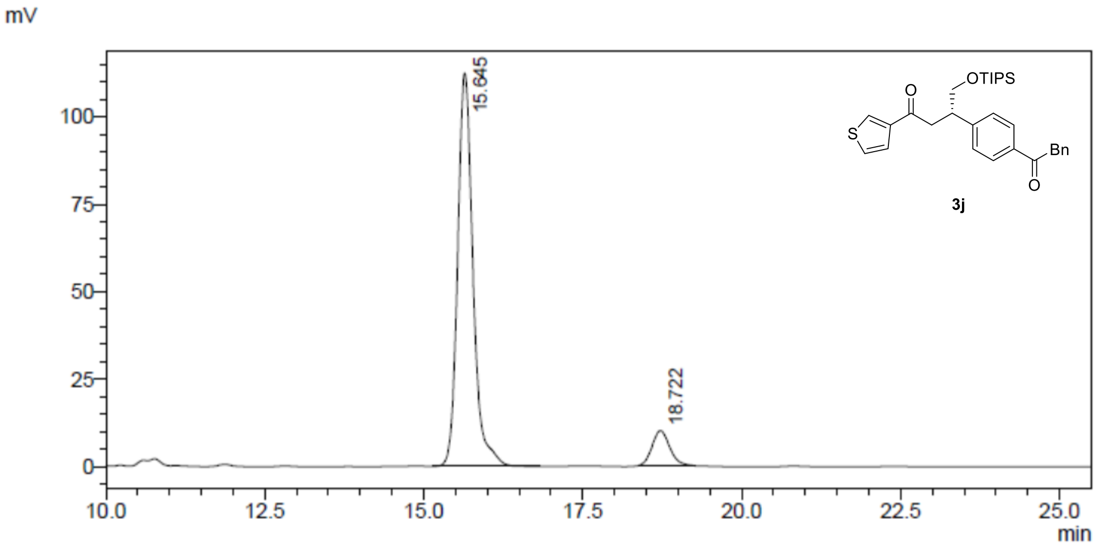
Peak#	Ret. Time	Area	Height	Area%
1	13.100	1989344	139090	88.173
2	14.102	266850	17455	11.827
		2256195	156545	100.000



<Peak Table>

A 254nm

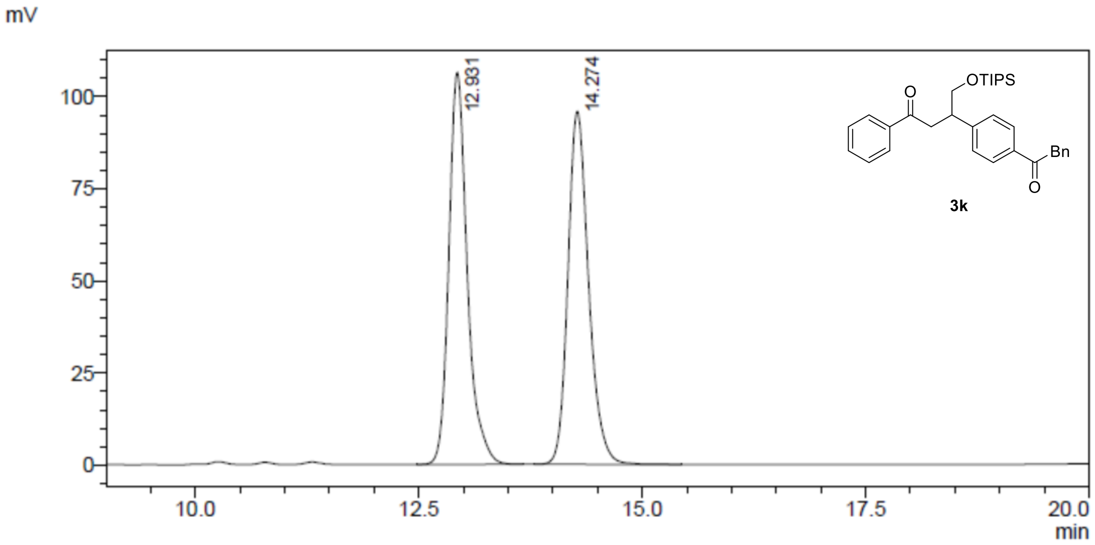
Peak#	Ret. Time	Area	Height	Area%
1	15.684	2460240	149695	49.930
2	18.730	2467142	122746	50.070
		4927382	272441	100.000



<Peak Table>

A 254nm

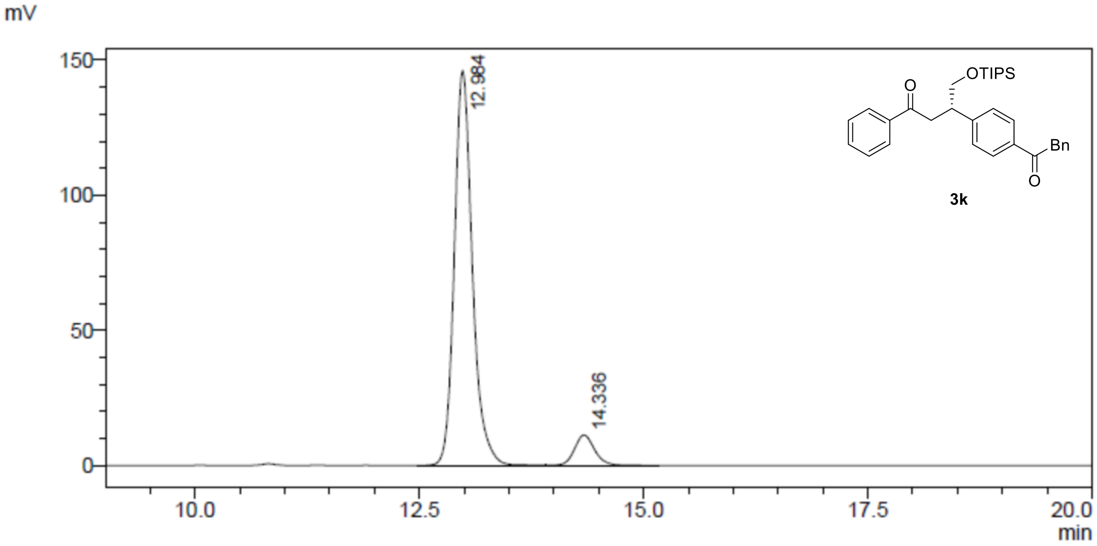
Peak#	Ret. Time	Area	Height	Area%
1	15.645	1889014	112457	90.770
2	18.722	192095	9978	9.230
		2081109	122434	100.000



<Peak Table>

A 254nm

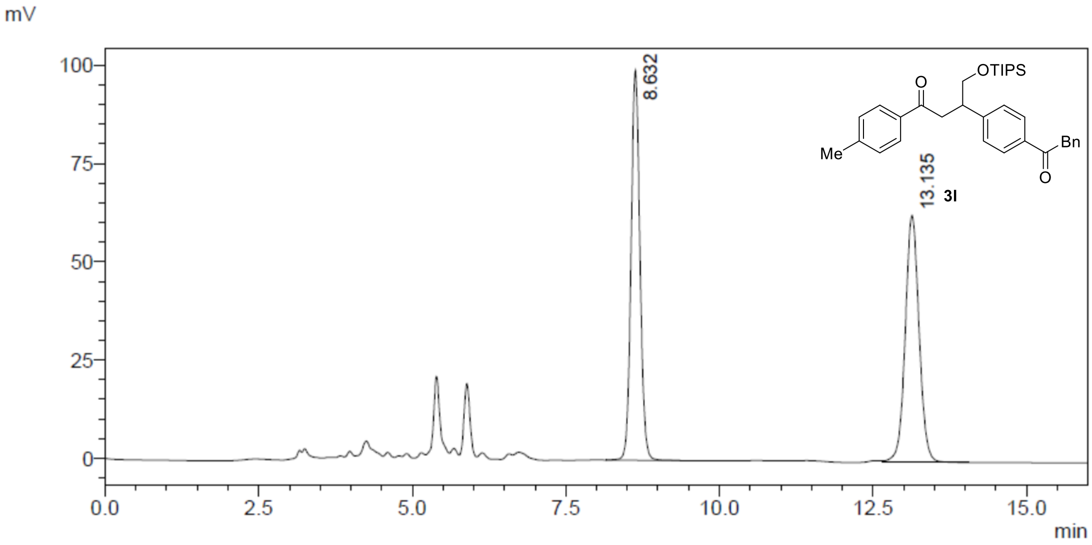
Peak#	Ret. Time	Area	Height	Area%
1	12.931	1529006	106327	49.850
2	14.274	1538216	95752	50.150
		3067221	202078	100.000



<Peak Table>

A 254nm

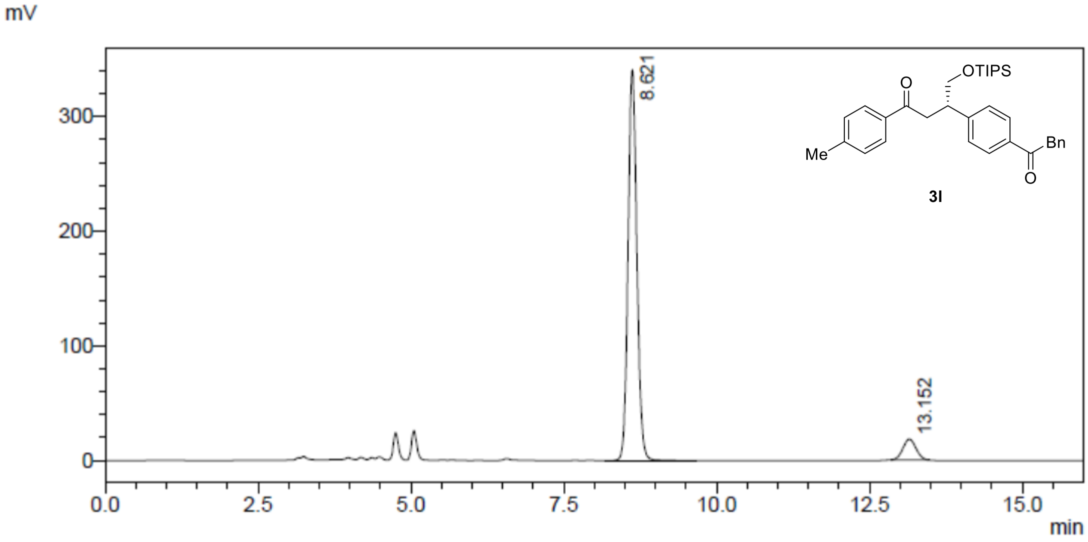
Peak#	Ret. Time	Area	Height	Area%
1	12.984	2045177	145965	92.088
2	14.336	175717	11241	7.912
		2220894	157206	100.000



<Peak Table>

A 254nm

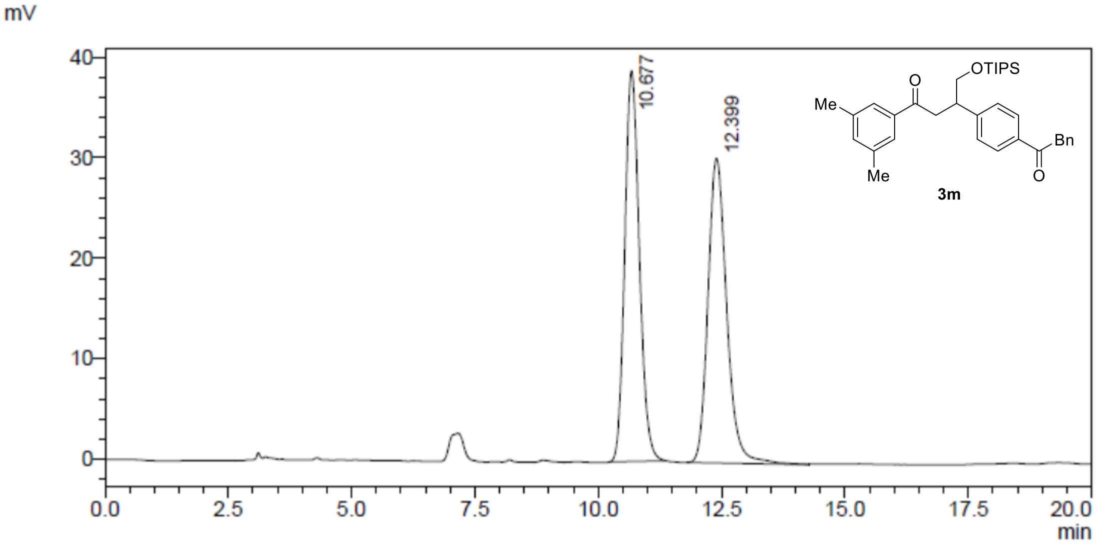
Peak#	Ret. Time	Area	Height	Area%
1	8.632	999240	99095	50.197
2	13.135	991407	62829	49.803
		1990647	161924	100.000



<Peak Table>

A 254nm

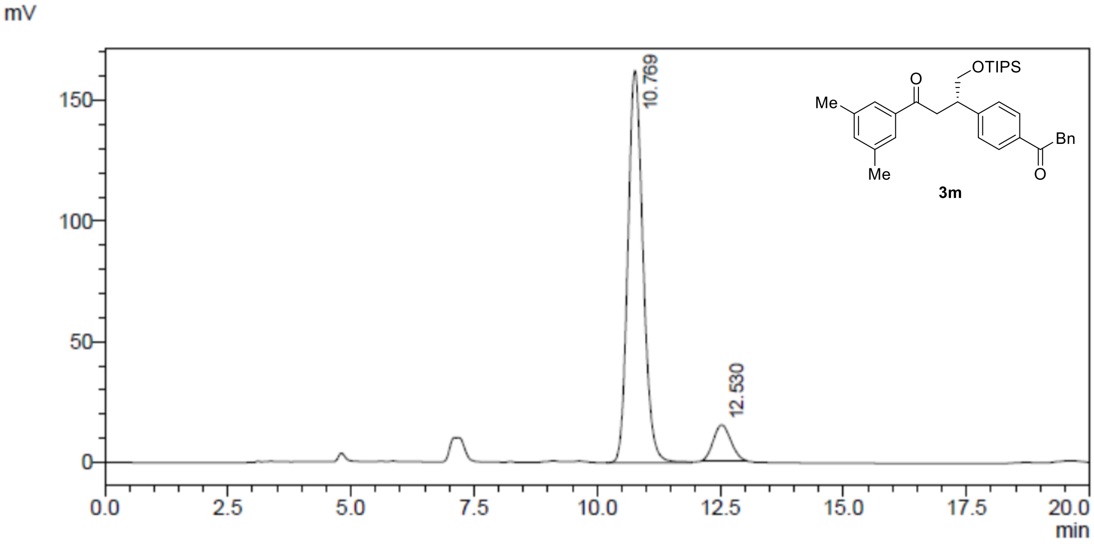
Peak#	Ret. Time	Area	Height	Area%
1	8.621	3426692	340552	92.736
2	13.152	268428	18038	7.264
		3695120	358591	100.000



<Peak Table>

A 254nm

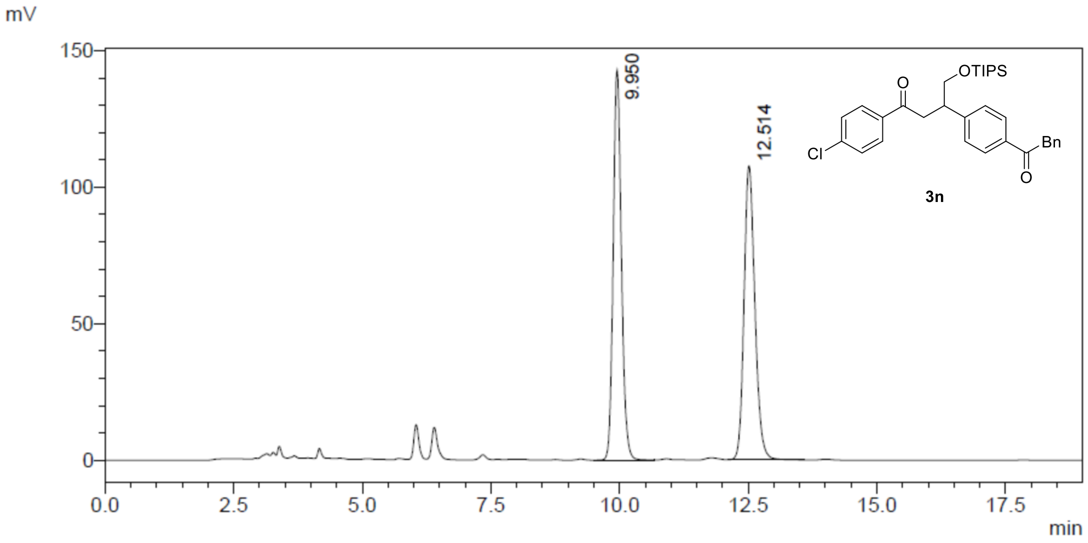
Peak#	Ret. Time	Area	Height	Area%
1	10.677	799080	38864	49.977
2	12.399	799801	30283	50.023
		1598881	69147	100.000



<Peak Table>

A 254nm

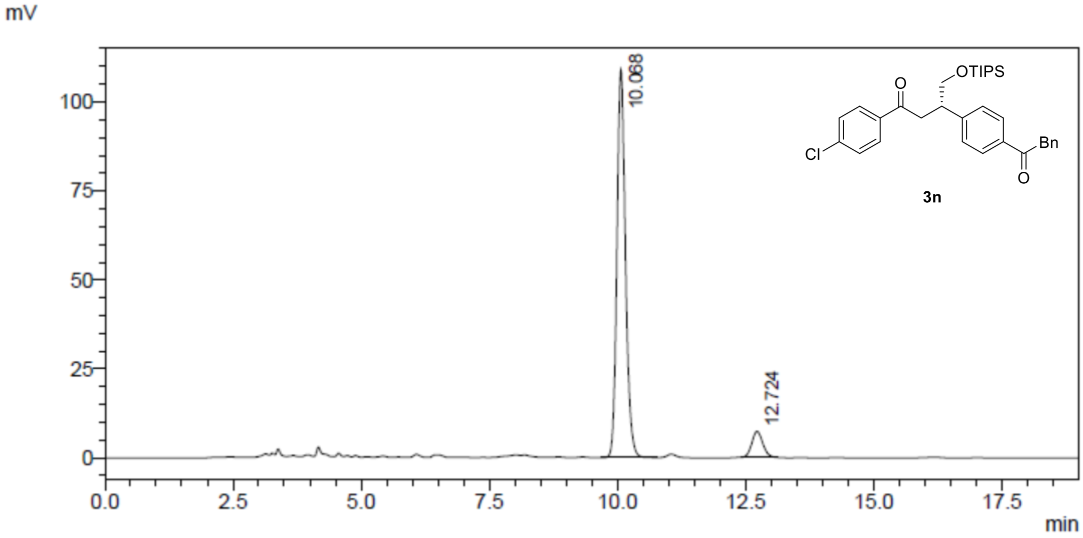
Peak#	Ret. Time	Area	Height	Area%
1	10.769	3486080	162510	90.611
2	12.530	361210	14768	9.389
		3847290	177279	100.000



<Peak Table>

A 254nm

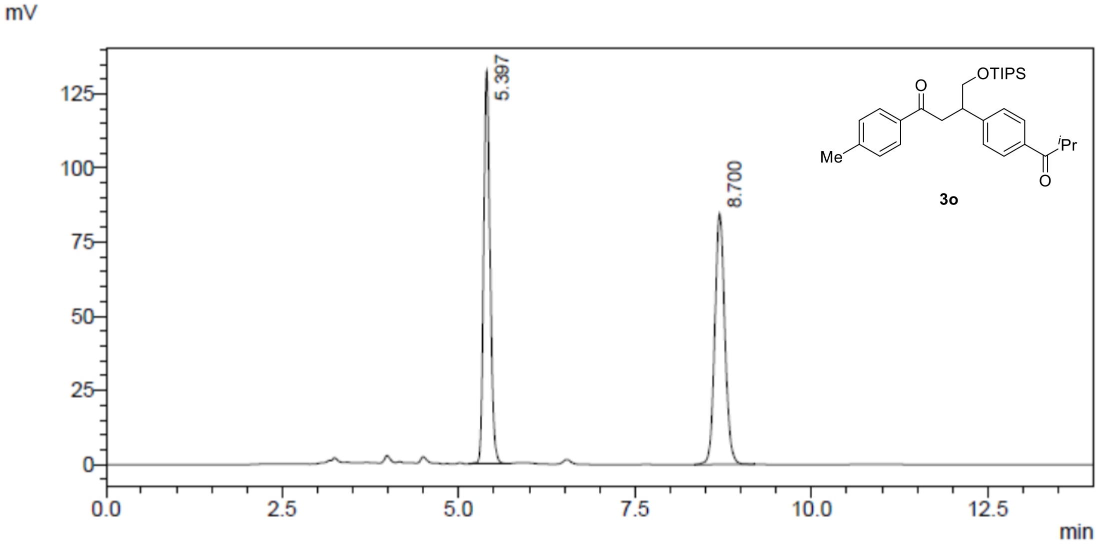
Peak#	Ret. Time	Area	Height	Area%
1	9.950	1591809	142938	50.036
2	12.514	1589503	107741	49.964
		3181312	250679	100.000



<Peak Table>

A 254nm

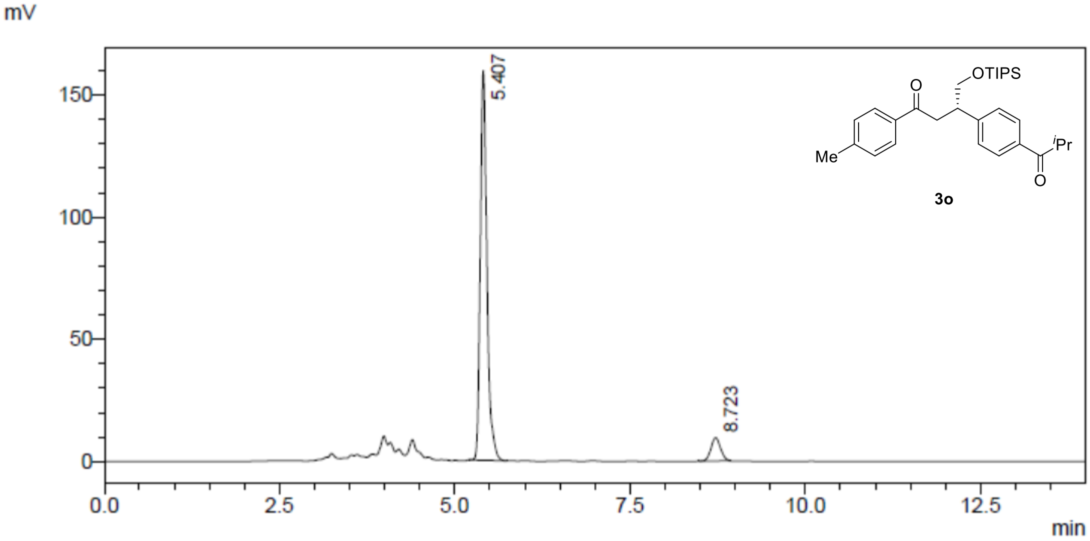
Peak#	Ret. Time	Area	Height	Area%
1	10.068	1268757	109046	92.085
2	12.724	109059	7313	7.915
		1377817	116359	100.000



<Peak Table>

A 254nm

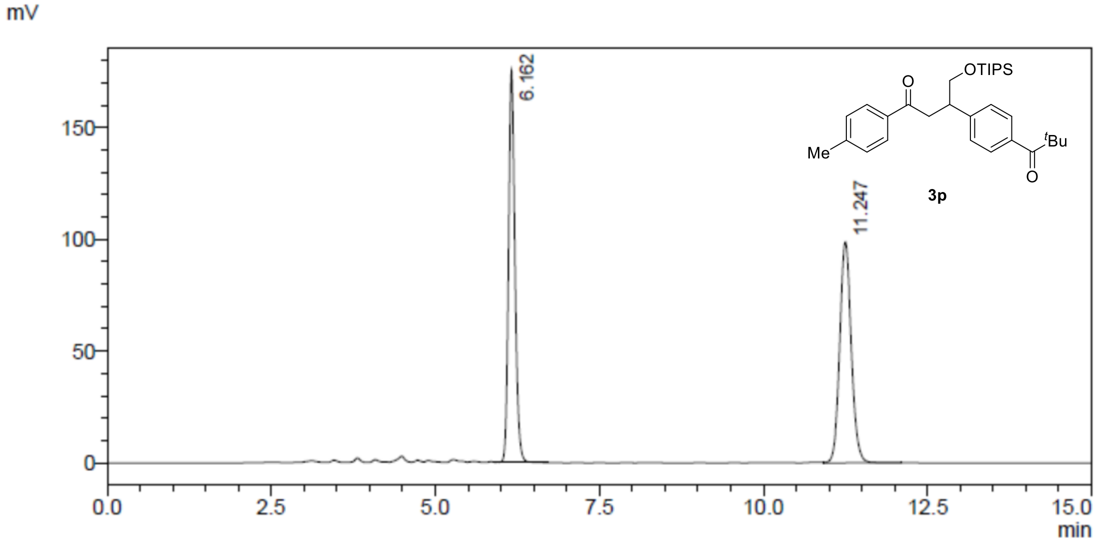
Peak#	Ret. Time	Area	Height	Area%
1	5.397	844944	132815	50.163
2	8.700	839453	84572	49.837
		1684397	217387	100.000



<Peak Table>

A 254nm

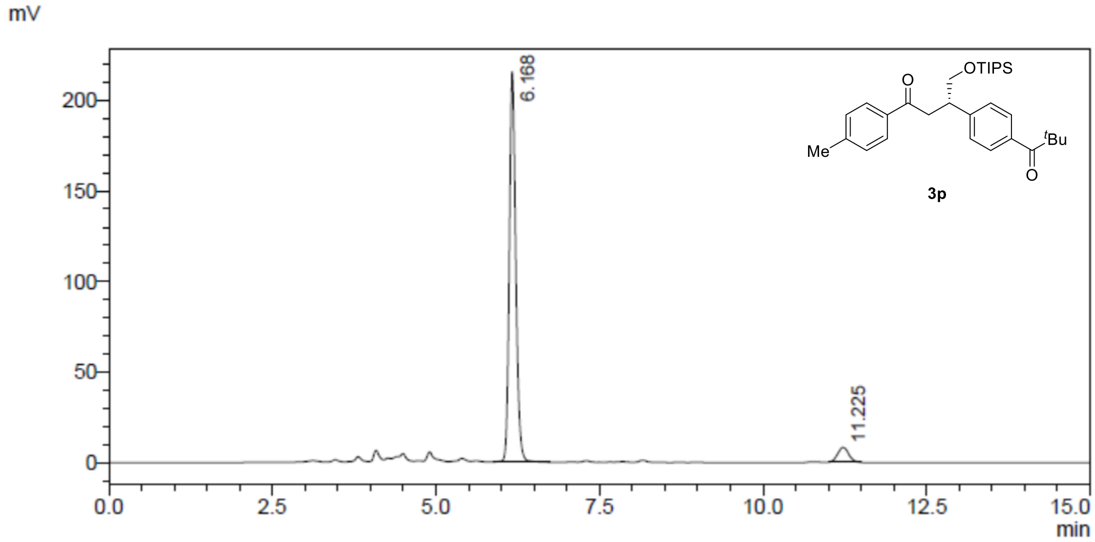
Peak#	Ret. Time	Area	Height	Area%
1	5.407	1051948	159896	92.075
2	8.723	90544	9461	7.925
		1142491	169357	100.000



<Peak Table>

A 254nm

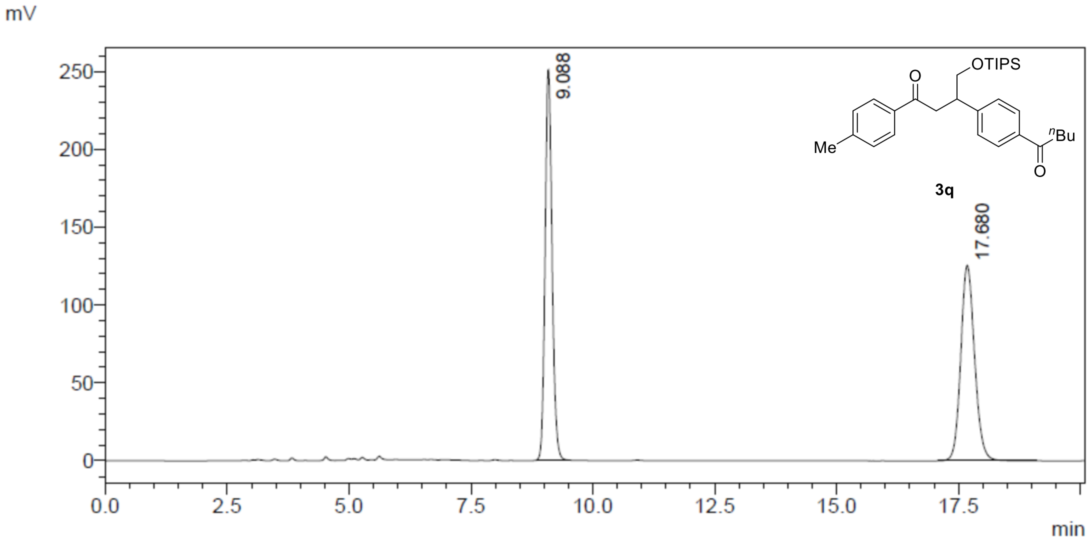
Peak#	Ret. Time	Area	Height	Area%
1	6.162	1210306	175627	50.074
2	11.247	1206753	98833	49.926
		2417058	274460	100.000



<Peak Table>

A 254nm

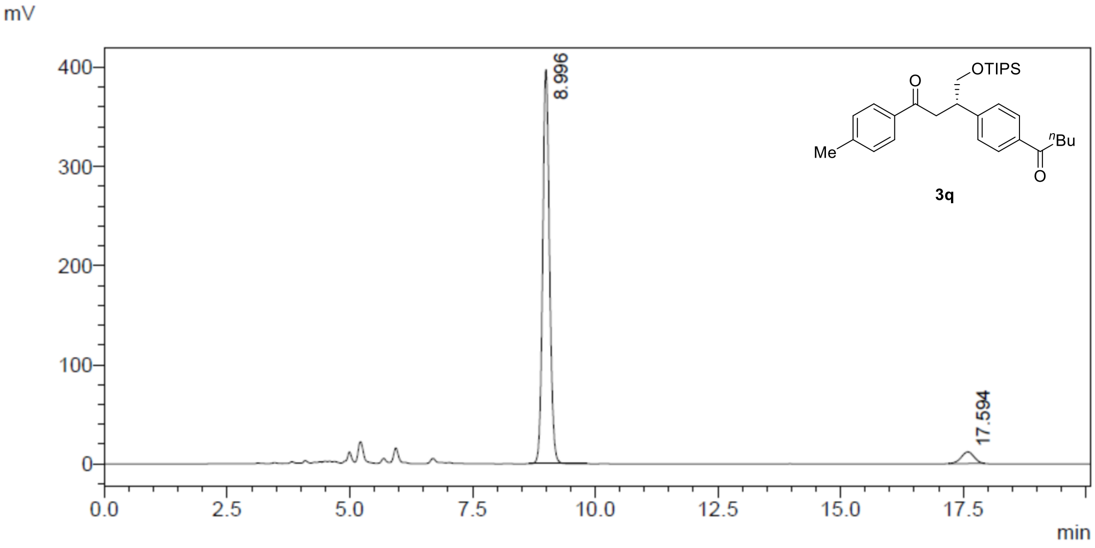
Peak#	Ret. Time	Area	Height	Area%
1	6.168	1505967	216075	94.009
2	11.225	95976	8191	5.991
		1601943	224266	100.000



<Peak Table>

A 254nm

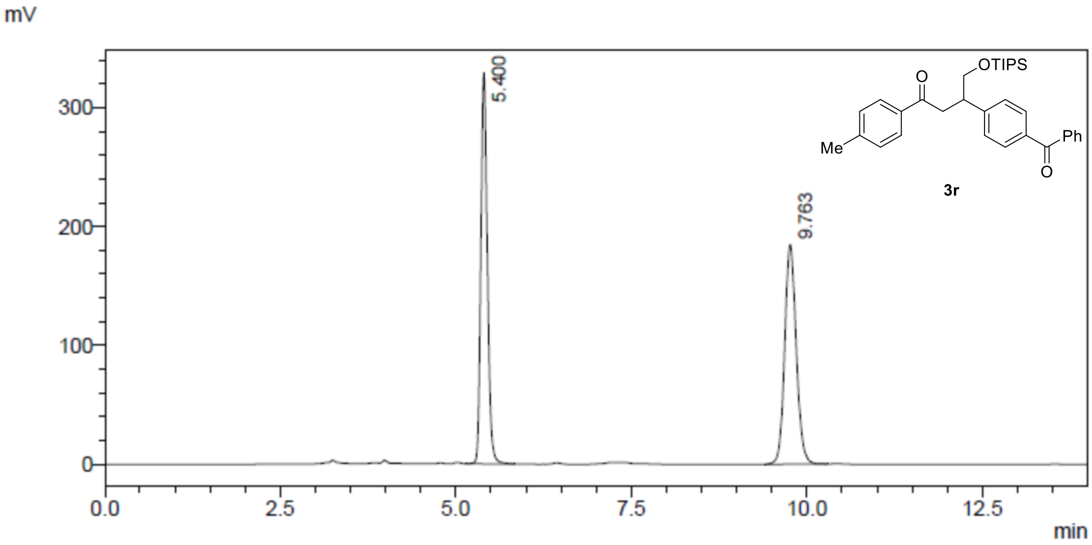
Peak#	Ret. Time	Area	Height	Area%
1	9.088	2484498	250590	50.032
2	17.680	2481329	125472	49.968
		4965827	376062	100.000



<Peak Table>

A 254nm

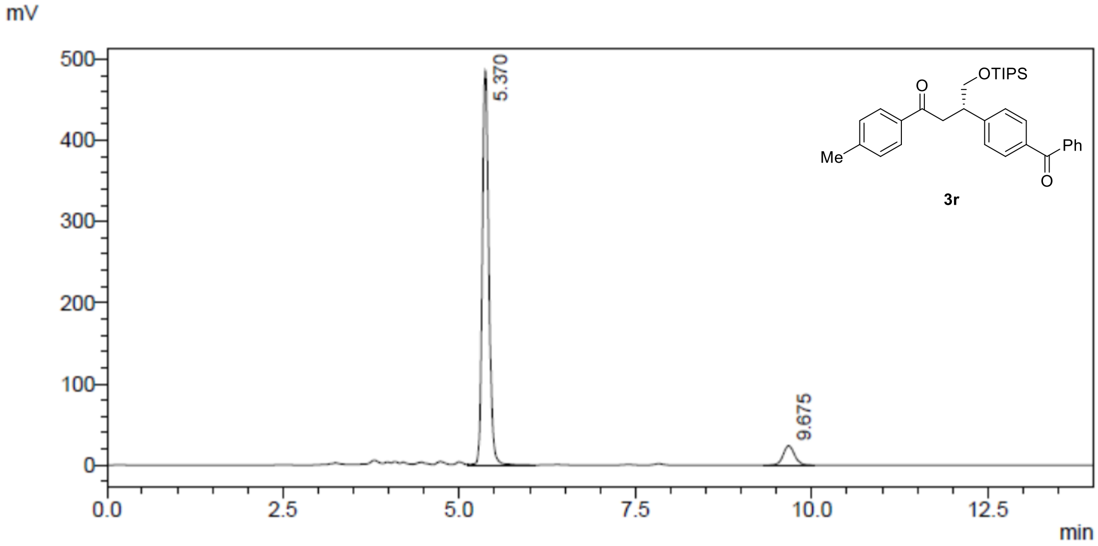
Peak#	Ret. Time	Area	Height	Area%
1	8.996	3857184	397172	94.763
2	17.594	213185	11654	5.237
		4070369	408827	100.000



<Peak Table>

A 254nm

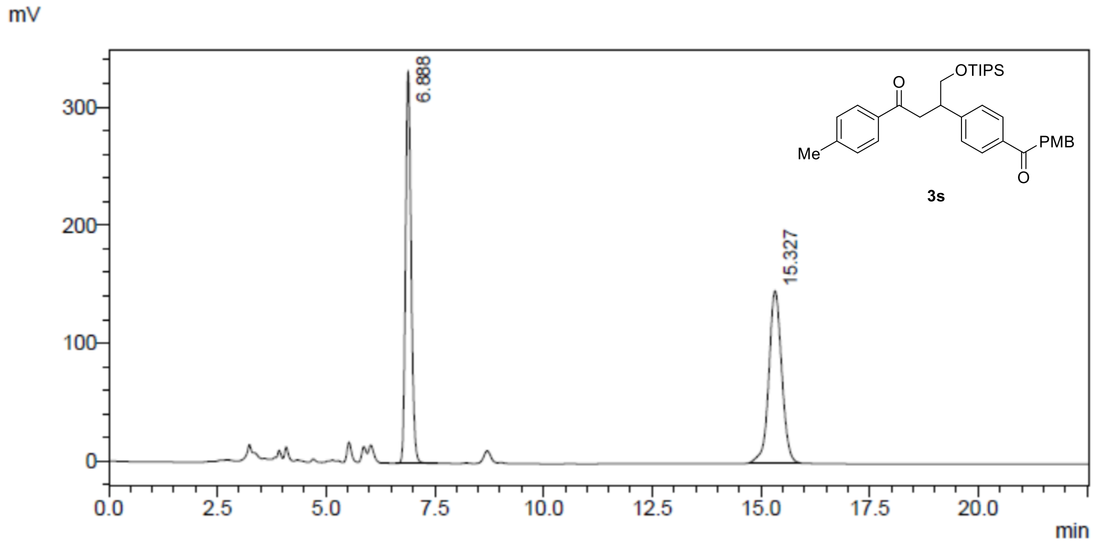
Peak#	Ret. Time	Area	Height	Area%
1	5.400	2121822	329634	50.092
2	9.763	2114028	184492	49.908
		4235851	514126	100.000



<Peak Table>

A 254nm

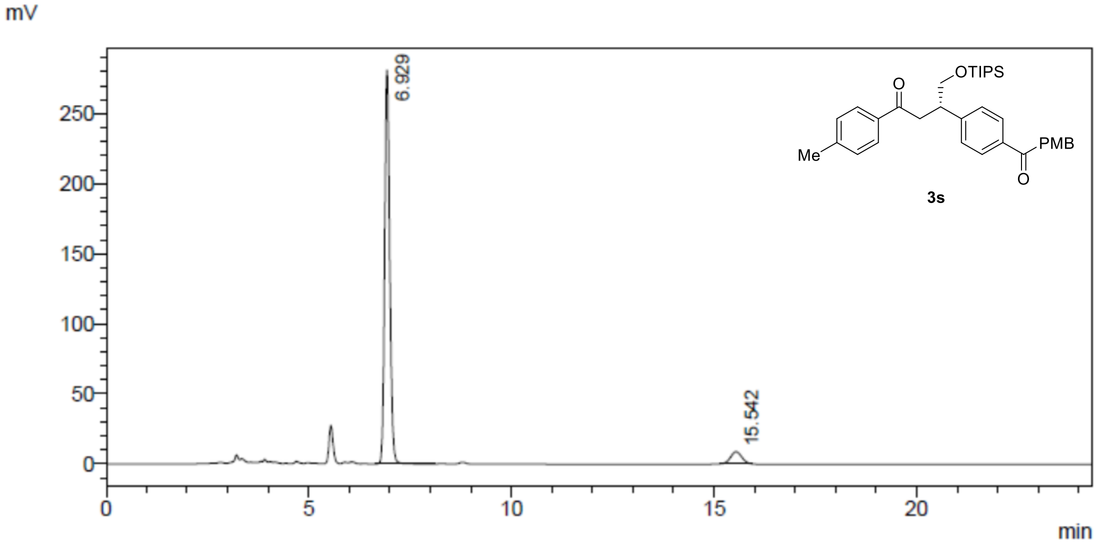
Peak#	Ret. Time	Area	Height	Area%
1	5.370	3139073	485835	92.152
2	9.675	267327	23848	7.848
		3406400	509682	100.000



<Peak Table>

A 254nm

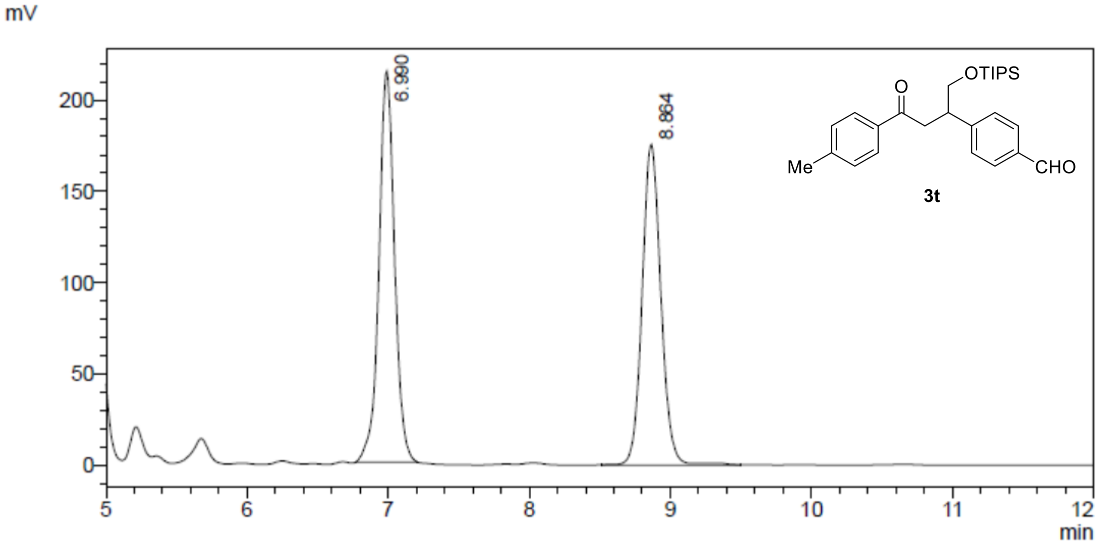
Peak#	Ret. Time	Area	Height	Area%
1	6.888	2958289	331661	49.742
2	15.327	2989015	145733	50.258
		5947303	477393	100.000



<Peak Table>

A 254nm

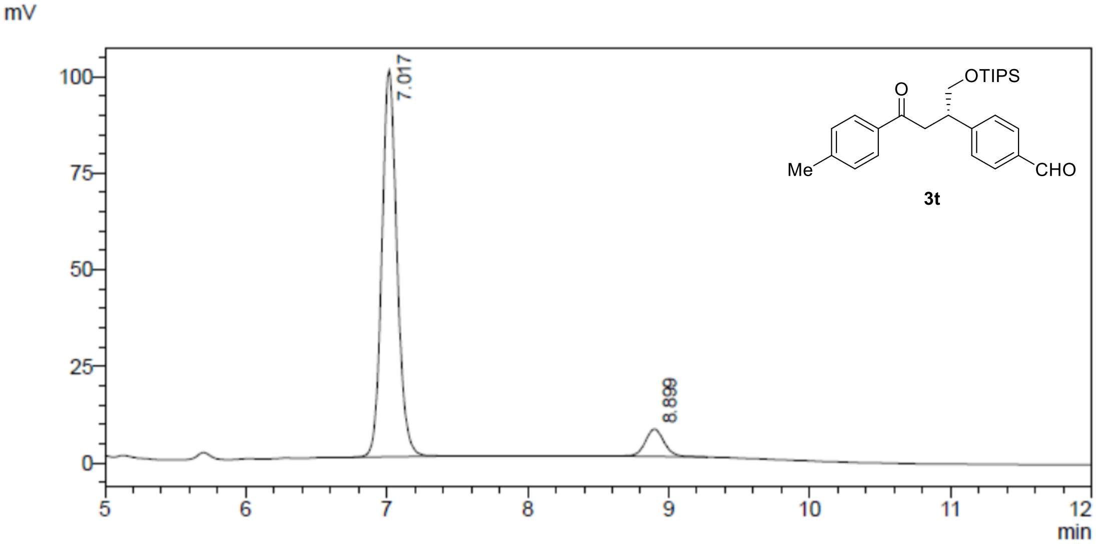
Peak#	Ret. Time	Area	Height	Area%
1	6.929	2465255	281127	93.774
2	15.542	163691	8593	6.226
		2628946	289720	100.000



<Peak Table>

A 254nm

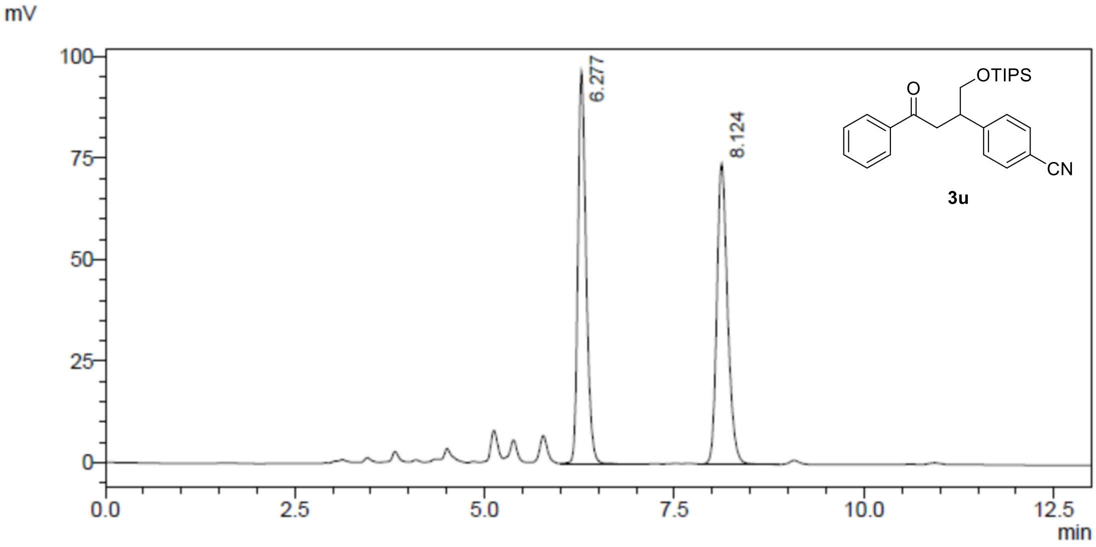
Peak#	Ret. Time	Area	Height	Area%
1	6.990	1647121	214024	50.187
2	8.864	1634824	175539	49.813
		3281945	389563	100.000



<Peak Table>

A 254nm

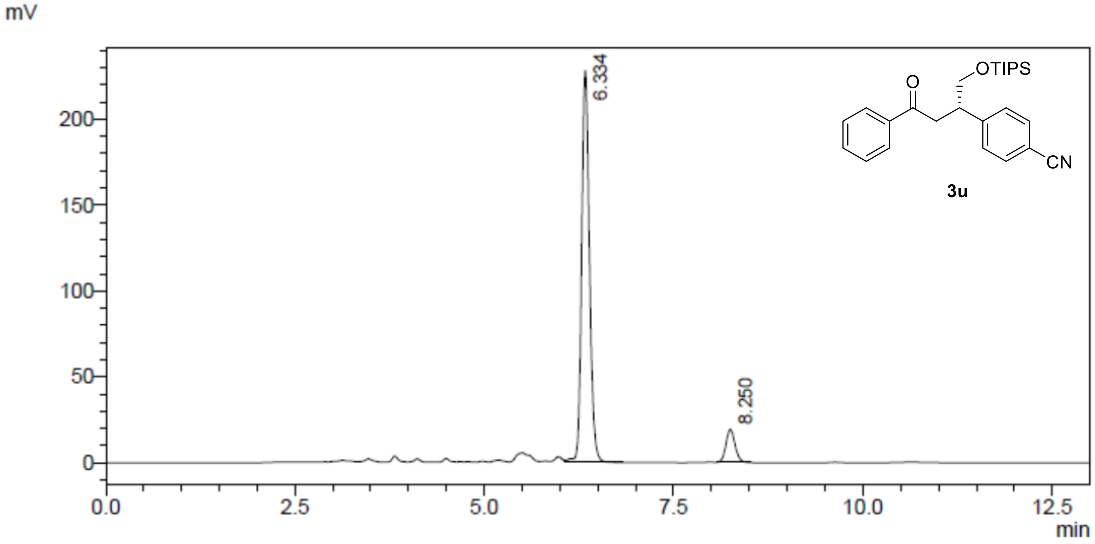
Peak#	Ret. Time	Area	Height	Area%
1	7.017	746828	100032	91.949
2	8.899	65389	7056	8.051
		812217	107088	100.000



<Peak Table>

A 254nm

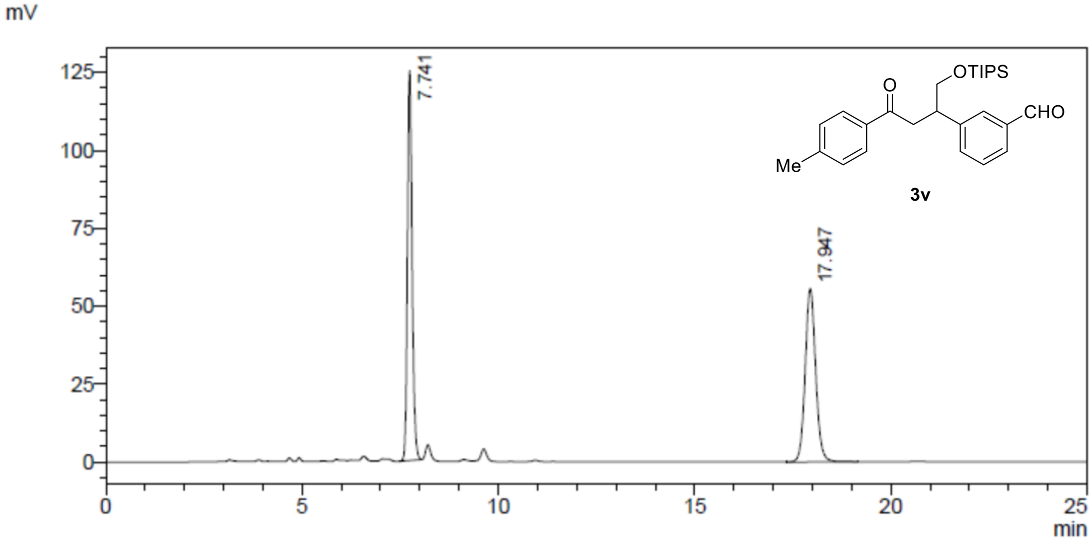
Peak#	Ret. Time	Area	Height	Area%
1	6.277	727504	96796	49.840
2	8.124	732186	74138	50.160
		1459690	170934	100.000



<Peak Table>

A 254nm

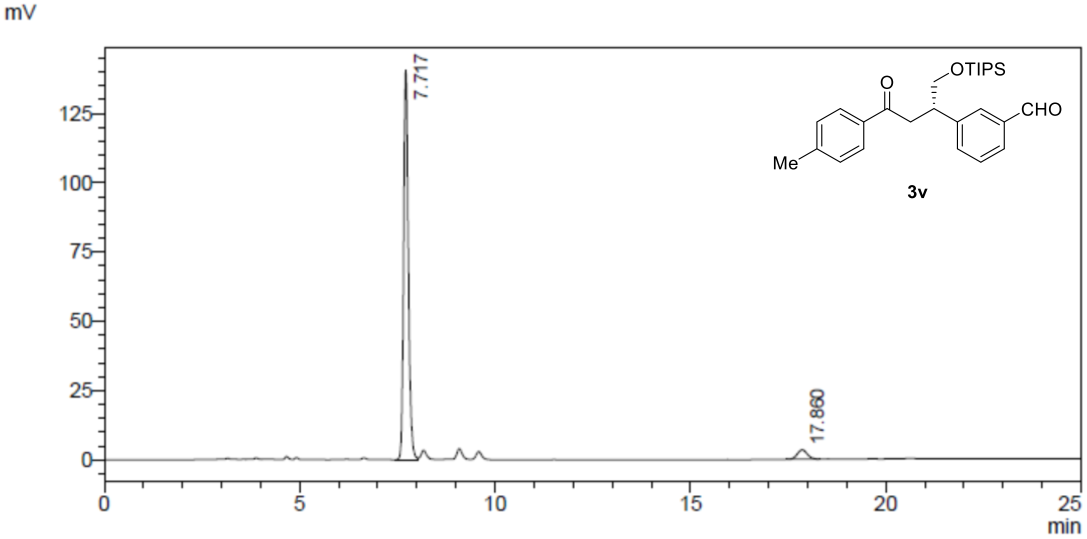
Peak#	Ret. Time	Area	Height	Area%
1	6.334	1633703	228505	91.012
2	8.250	161347	19295	8.988
		1795050	247799	100.000



<Peak Table>

A 254nm

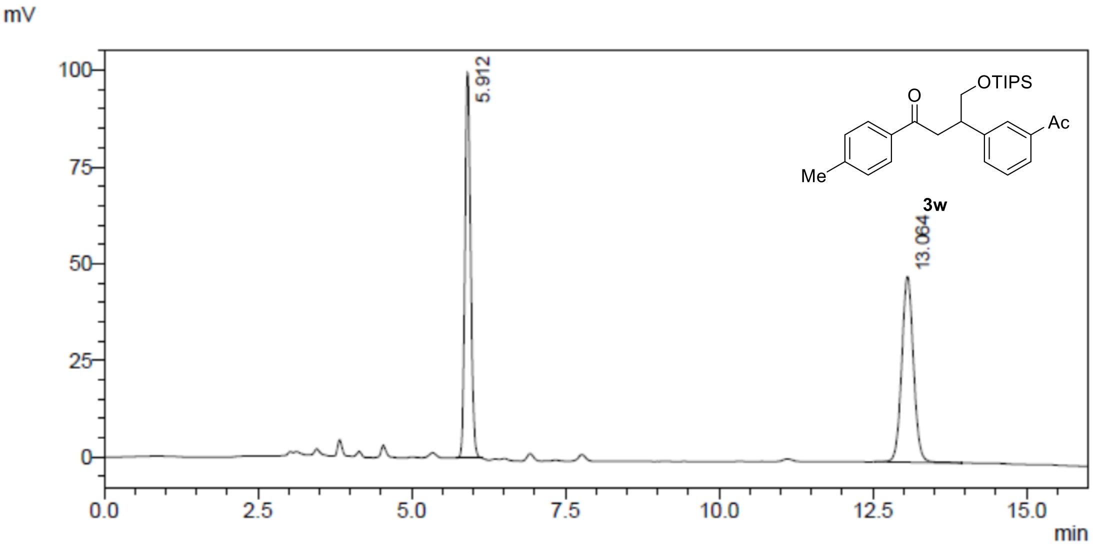
Peak#	Ret. Time	Area	Height	Area%
1	7.741	1034384	125279	50.009
2	17.947	1033994	55625	49.991
		2068378	180905	100.000



<Peak Table>

A 254nm

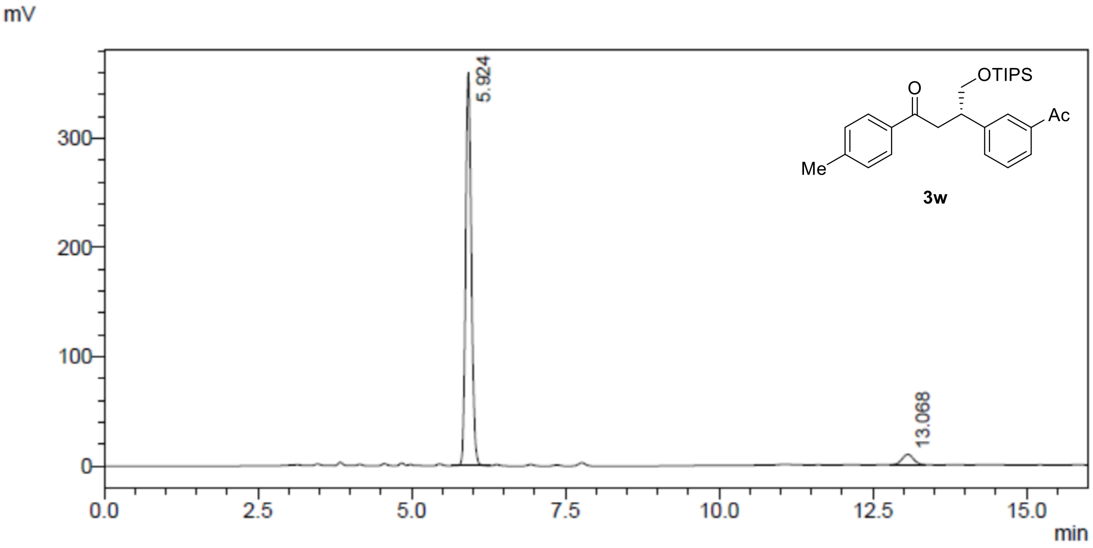
Peak#	Ret. Time	Area	Height	Area%
1	7.717	1178599	140759	95.193
2	17.860	59512	3371	4.807
		1238111	144129	100.000



<Peak Table>

254nm

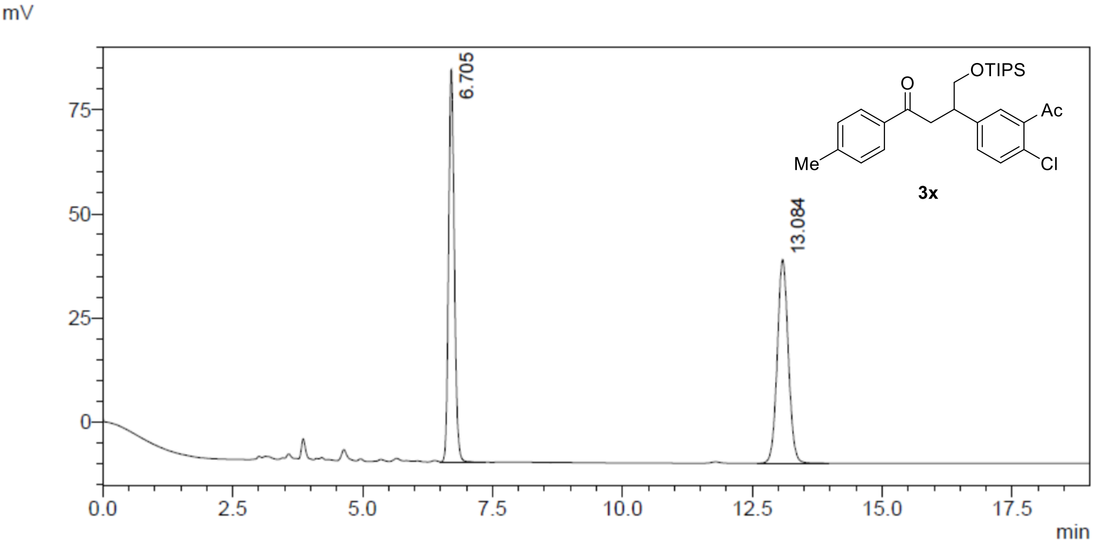
Peak#	Ret. Time	Area	Height	Area%
1	5.912	642152	99668	50.075
2	13.064	640215	48010	49.925
		1282367	147679	100.000



<Peak Table>

254nm

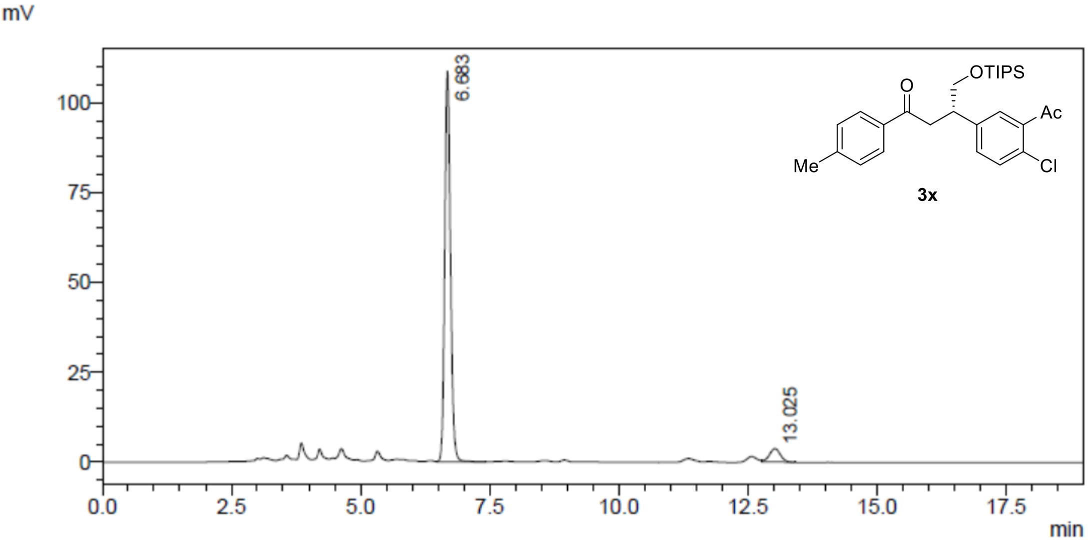
Peak#	Ret. Time	Area	Height	Area%
1	5.924	2326493	360300	95.021
2	13.068	121907	9502	4.979
		2448399	369802	100.000



<Peak Table>

A 254nm

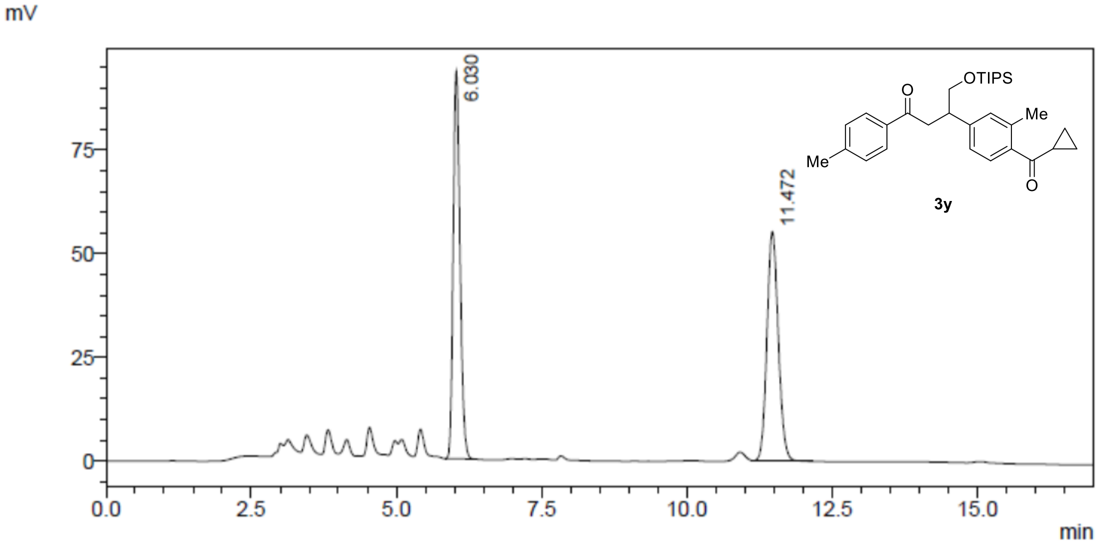
Peak#	Ret. Time	Area	Height	Area%
1	6.705	722540	94422	49.941
2	13.084	724241	48937	50.059
		1446781	143359	100.000



<Peak Table>

A 254nm

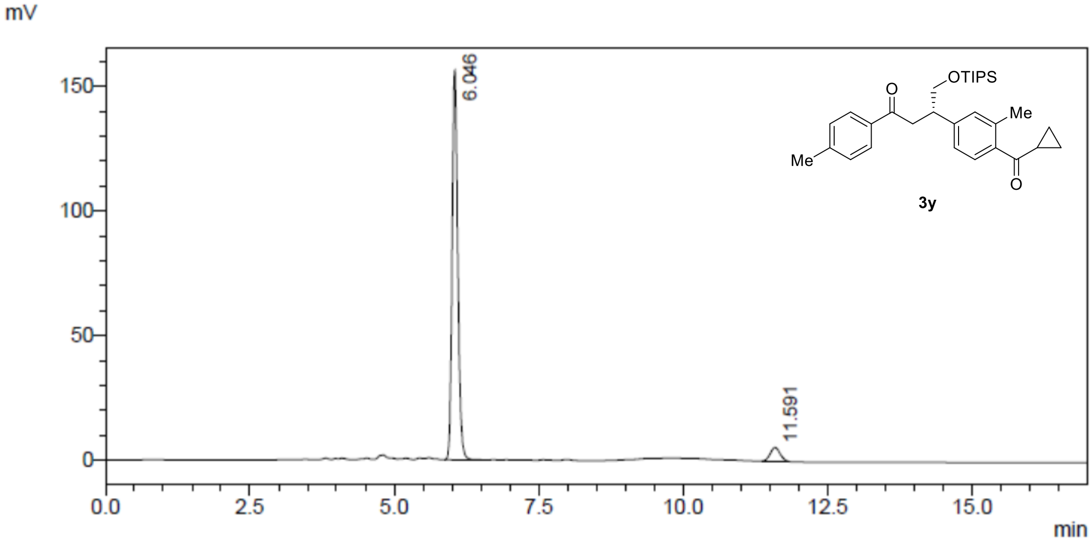
Peak#	Ret. Time	Area	Height	Area%
1	6.683	837399	108817	93.941
2	13.025	54009	3700	6.059
		891408	112516	100.000



<Peak Table>

A 254nm

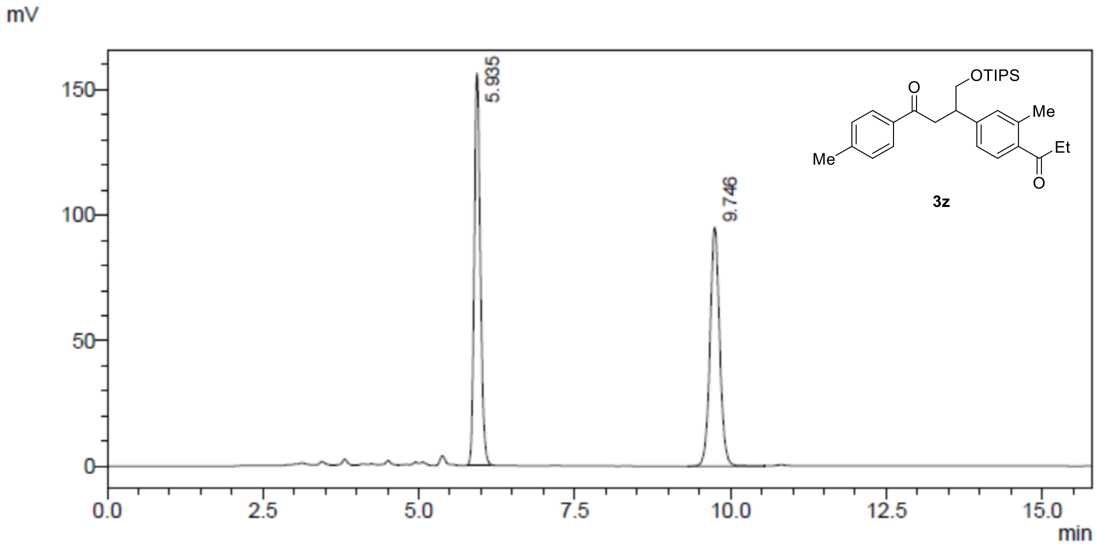
Peak#	Ret. Time	Area	Height	Area%
1	6.030	761710	93598	50.216
2	11.472	755144	55379	49.784
		1516854	148977	100.000



<Peak Table>

A 254nm

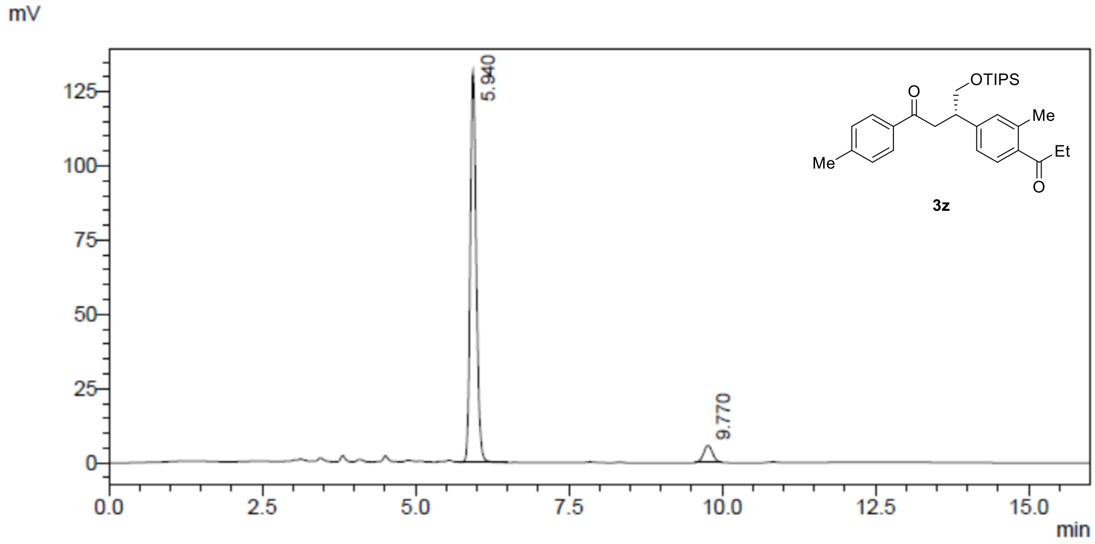
Peak#	Ret. Time	Area	Height	Area%
1	6.046	1063854	156434	94.369
2	11.591	63485	5455	5.631
		1127339	161889	100.000



<Peak Table>

A 254nm

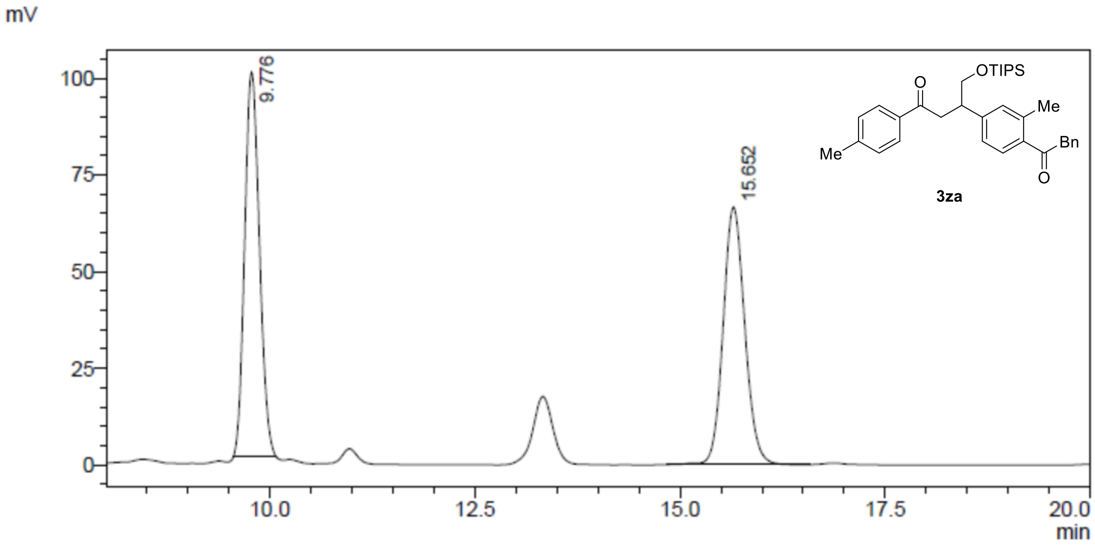
Peak#	Ret. Time	Area	Height	Area%
1	5.935	1054828	156230	50.544
2	9.746	1032103	95080	49.456
		2086932	251310	100.000



<Peak Table>

A 254nm

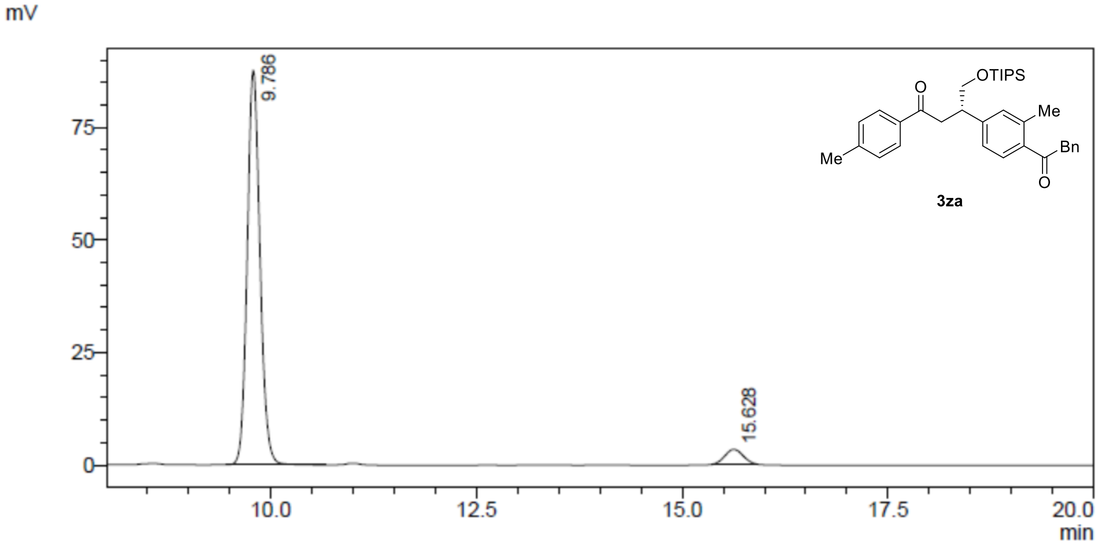
Peak#	Ret. Time	Area	Height	Area%
1	5.940	902636	131874	93.935
2	9.770	58284	5730	6.065
		960921	137604	100.000



<Peak Table>

A 254nm

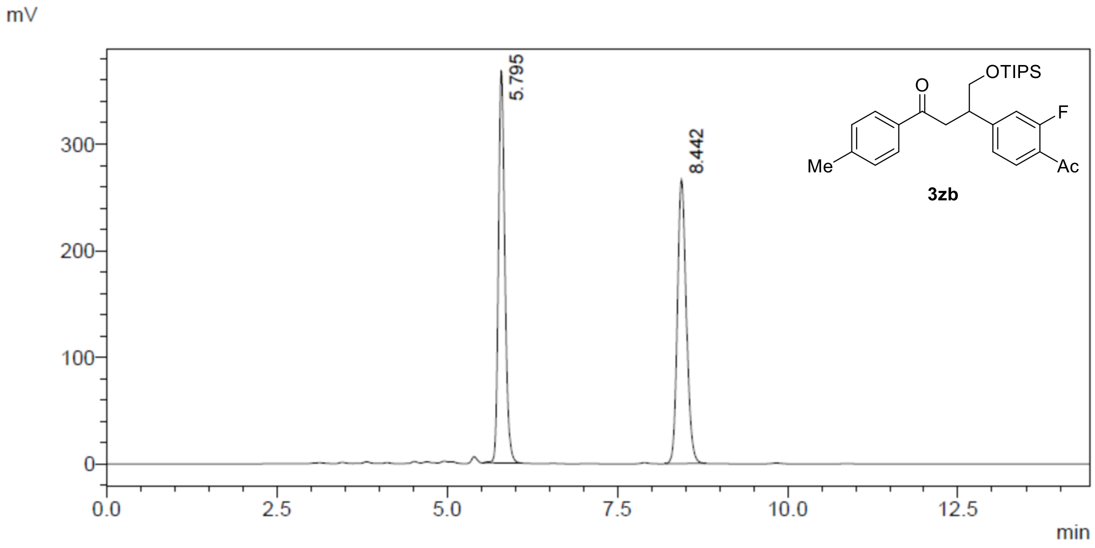
Peak#	Ret. Time	Area	Height	Area%
1	9.776	1238735	99238	50.295
2	15.652	1224187	66627	49.705
		2462922	165865	100.000



<Peak Table>

A 254nm

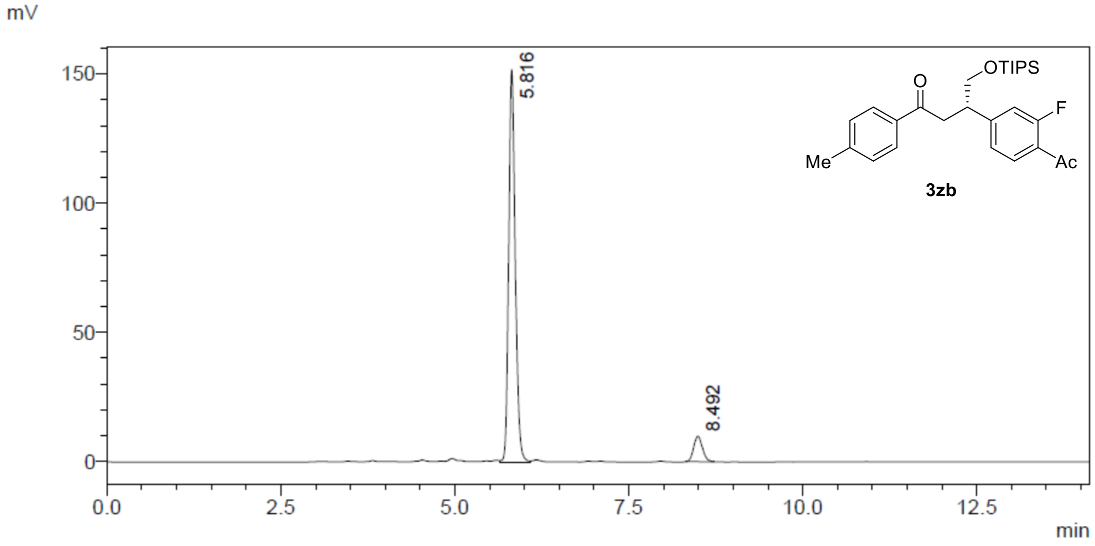
Peak#	Ret. Time	Area	Height	Area%
1	9.786	948917	87599	94.824
2	15.628	51799	3339	5.176
		1000717	90937	100.000



<Peak Table>

A 254nm

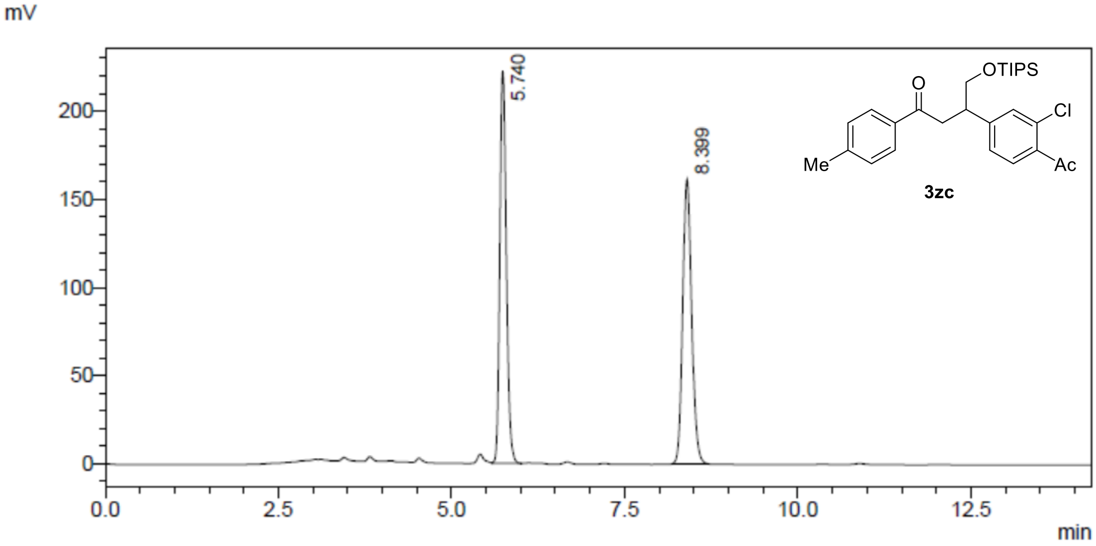
Peak#	Ret. Time	Area	Height	Area%
1	5.795	2450768	367658	50.107
2	8.442	2440327	266317	49.893
		4891095	633975	100.000



<Peak Table>

A 254nm

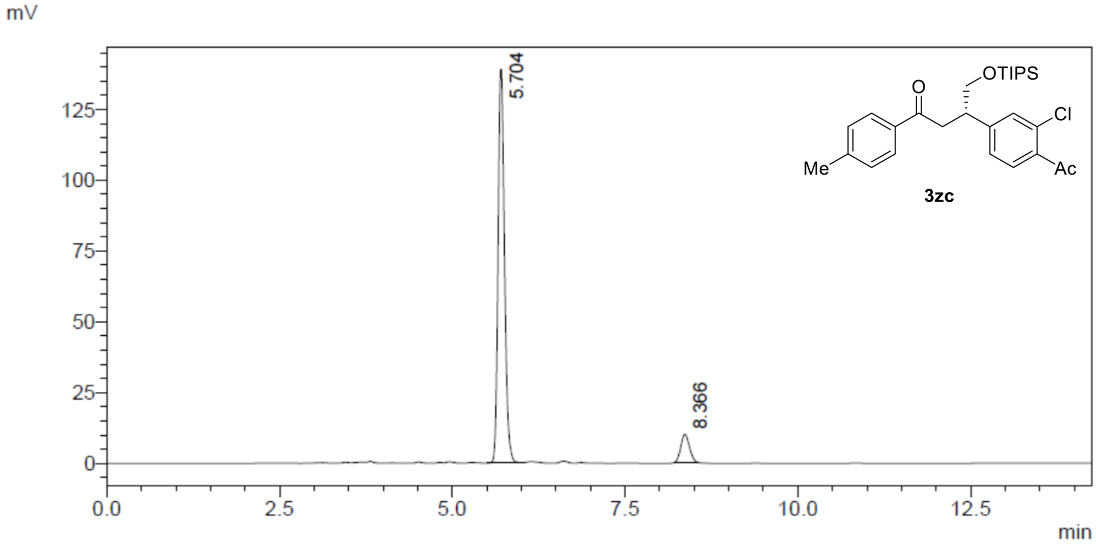
Peak#	Ret. Time	Area	Height	Area%
1	5.816	998192	151975	92.029
2	8.492	86460	9894	7.971
		1084652	161869	100.000



<Peak Table>

A 254nm

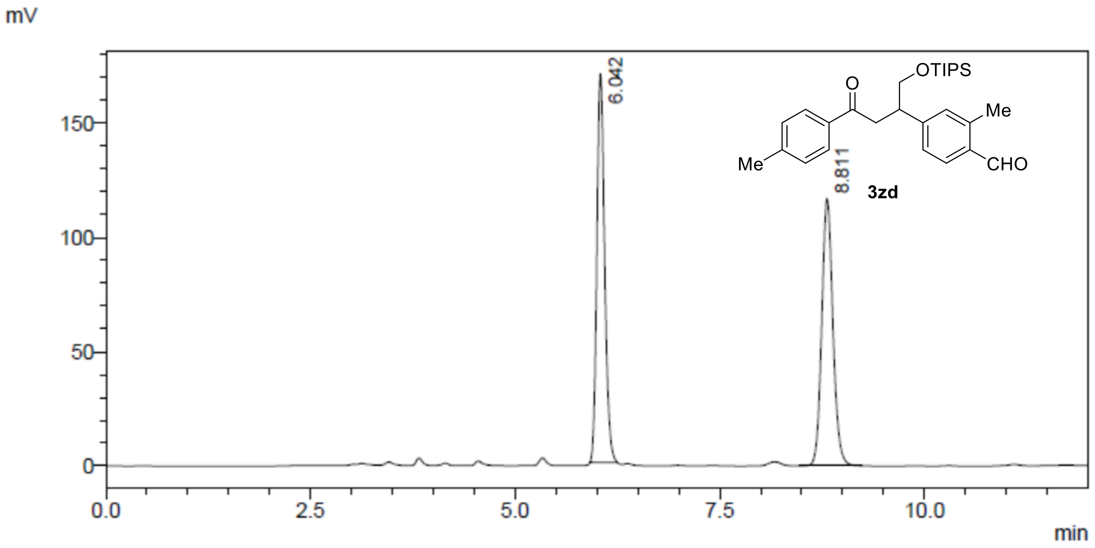
Peak#	Ret. Time	Area	Height	Area%
1	5.740	1443763	222541	49.840
2	8.399	1453062	161307	50.160
		2896825	383848	100.000



<Peak Table>

A 254nm

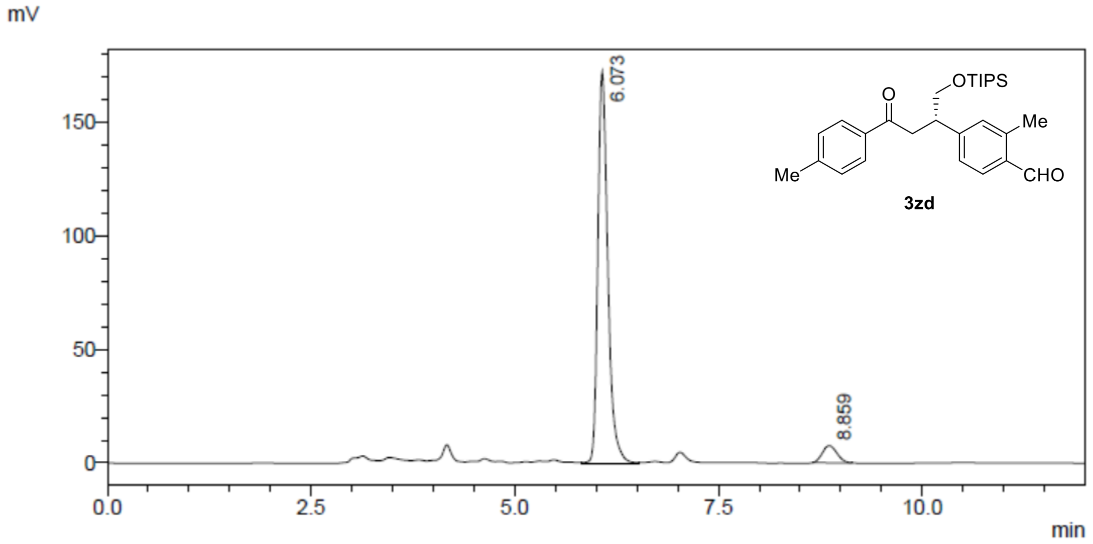
Peak#	Ret. Time	Area	Height	Area%
1	5.704	891059	139032	91.206
2	8.366	85919	9981	8.794
		976978	149013	100.000



<Peak Table>

254nm

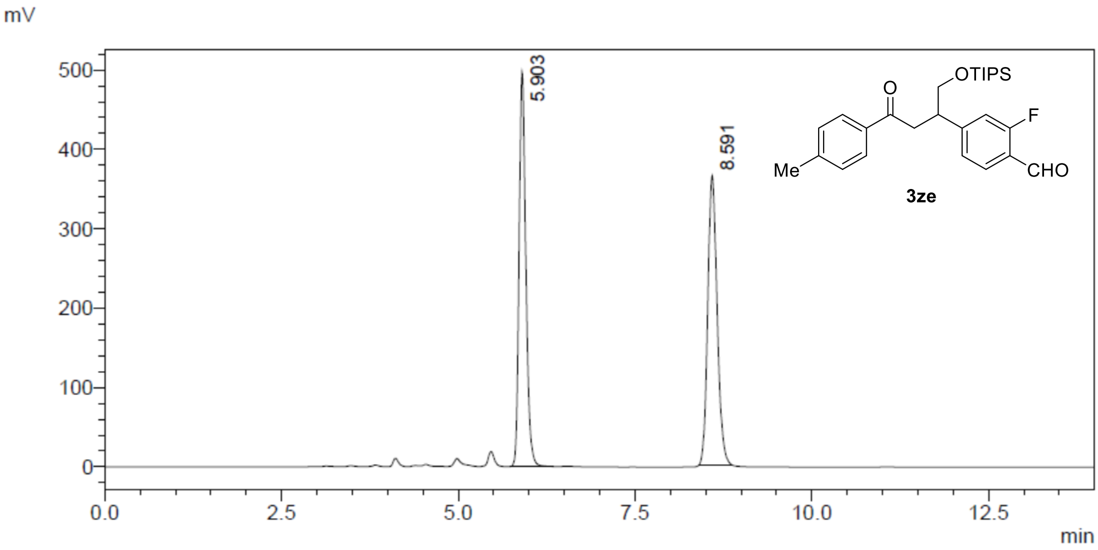
Peak#	Ret. Time	Area	Height	Area%
1	6.042	1122266	170345	50.256
2	8.811	1110855	116878	49.744
		2233121	287224	100.000



<Peak Table>

254nm

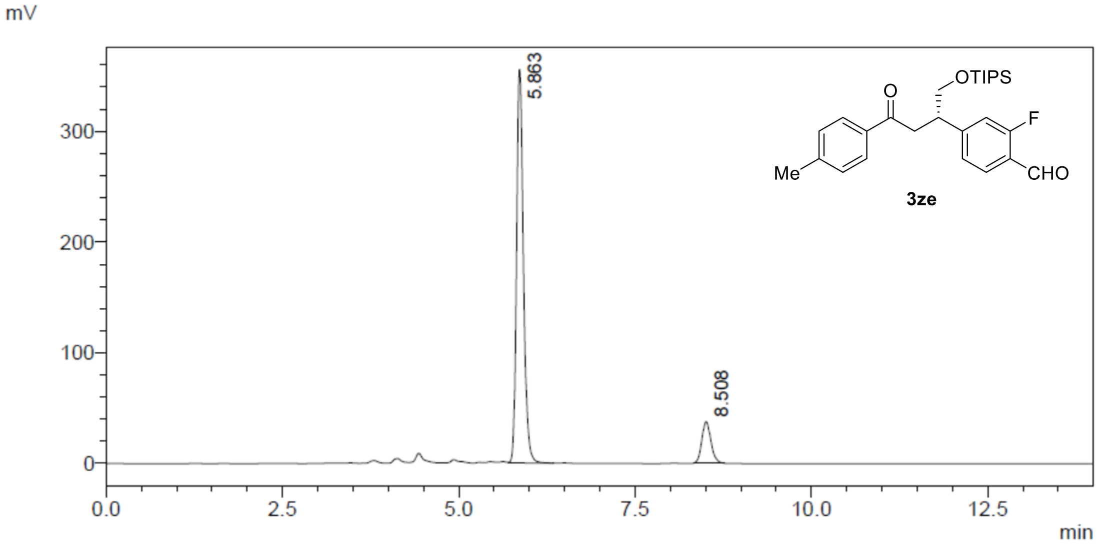
Peak#	Ret. Time	Area	Height	Area%
1	6.073	1471330	172398	94.001
2	8.859	93900	7538	5.999
		1565231	179936	100.000



<Peak Table>

A 254nm

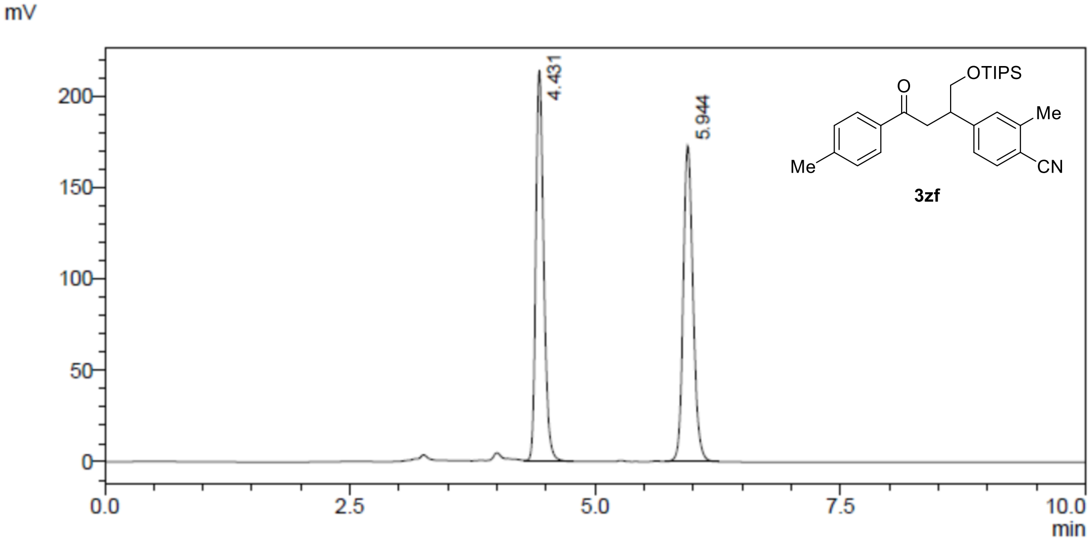
Peak#	Ret. Time	Area	Height	Area%
1	5.903	3309070	497572	49.701
2	8.591	3348858	364082	50.299
		6657928	861654	100.000



<Peak Table>

A 254nm

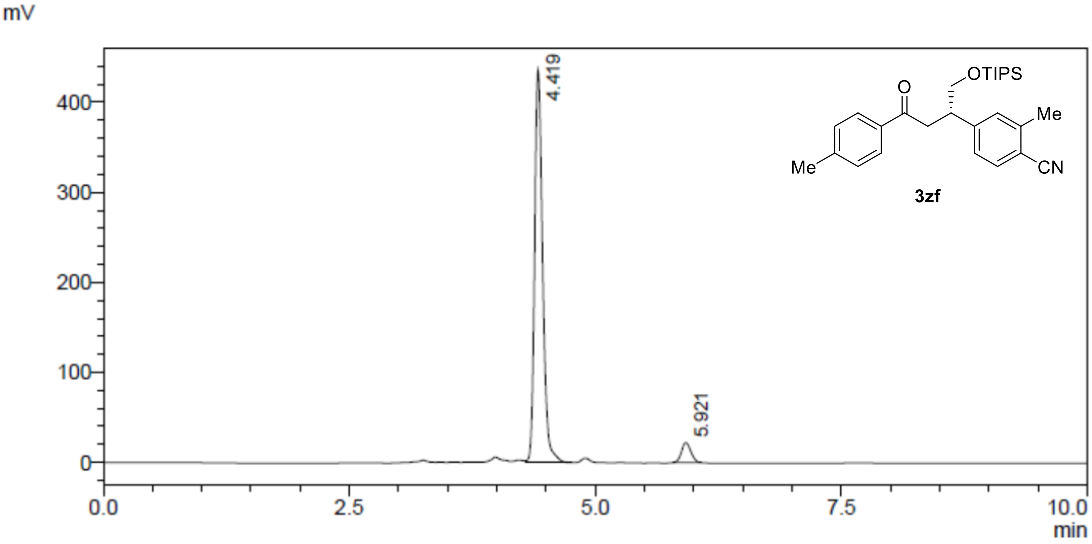
Peak#	Ret. Time	Area	Height	Area%
1	5.863	2398501	354989	87.695
2	8.508	336554	37521	12.305
		2735055	392511	100.000



<Peak Table>

A 254nm

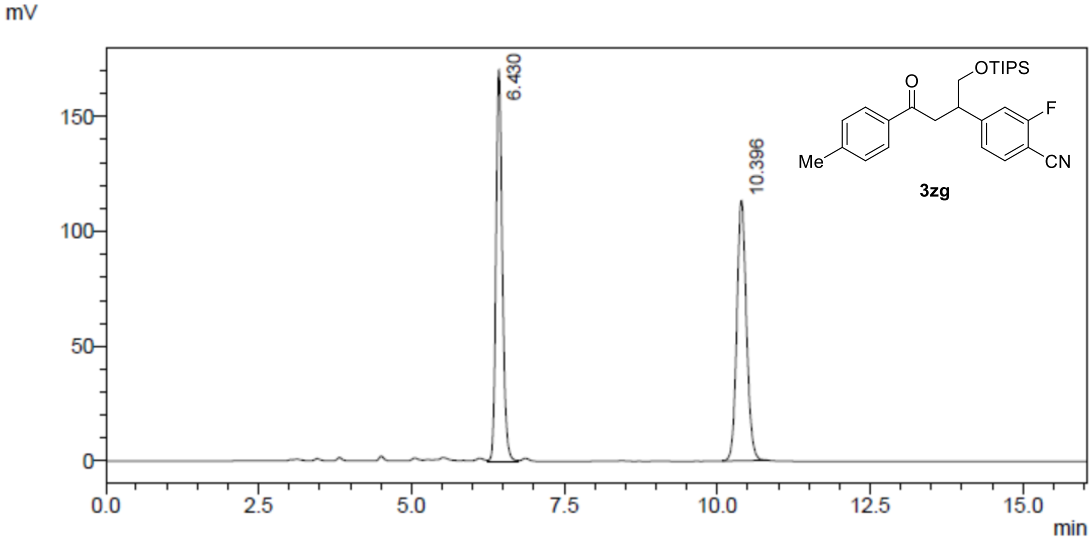
Peak#	Ret. Time	Area	Height	Area%
1	4.431	1197296	214245	49.908
2	5.944	1201711	173024	50.092
		2399007	387269	100.000



<Peak Table>

A 254nm

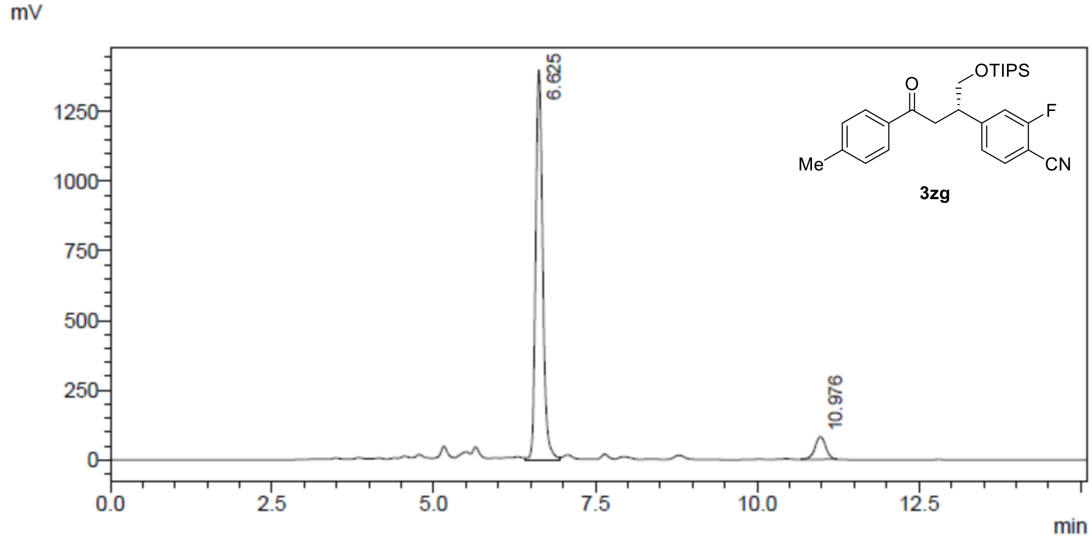
Peak#	Ret. Time	Area	Height	Area%
1	4.419	2471559	435671	94.463
2	5.921	144873	22008	5.537
		2616432	457679	100.000



<Peak Table>

A 254nm

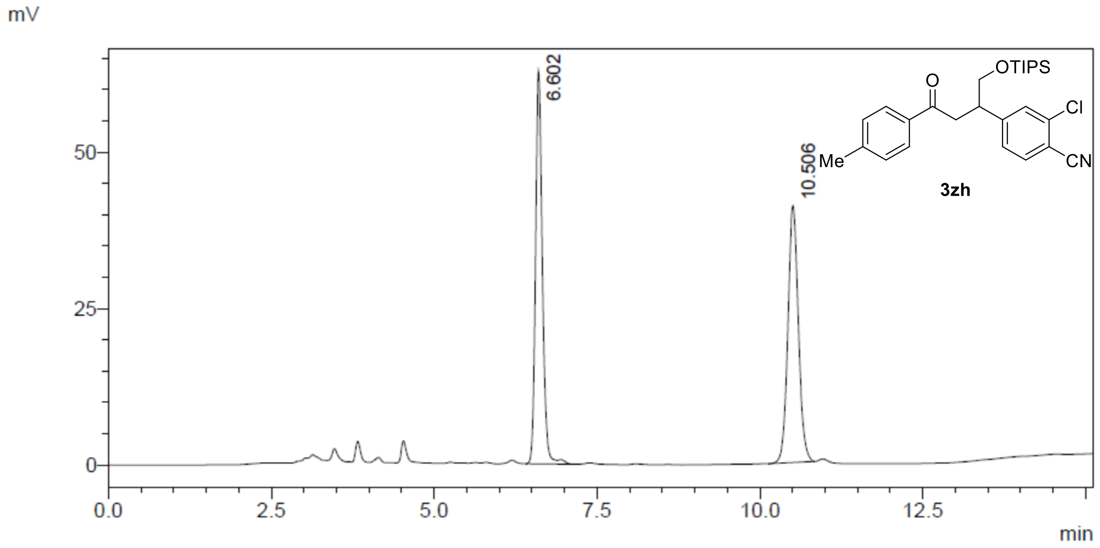
Peak#	Ret. Time	Area	Height	Area%
1	6.430	1229862	170409	49.811
2	10.396	1239176	113145	50.189
		2469037	283554	100.000



<Peak Table>

A 254nm

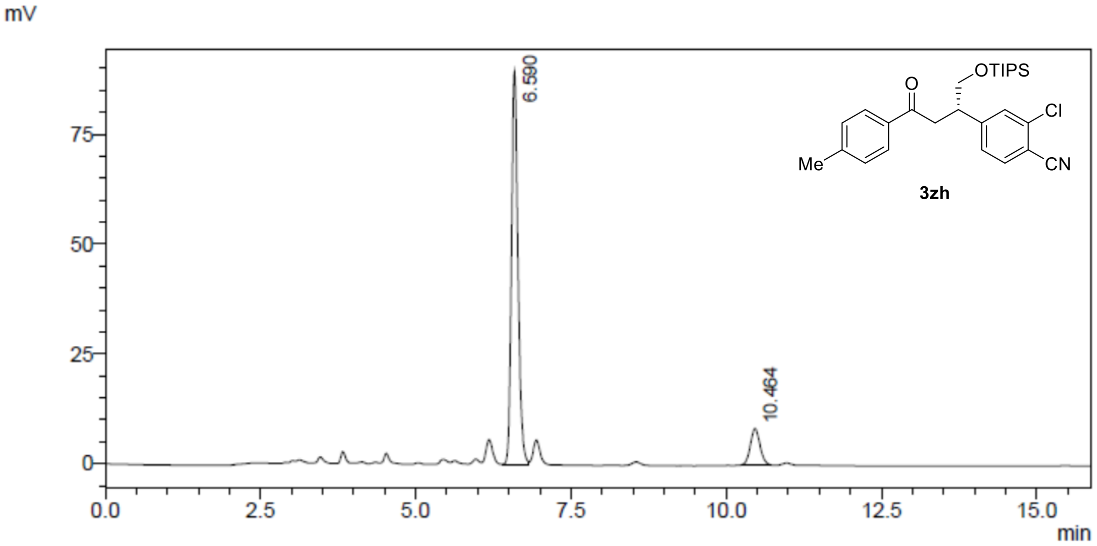
Peak#	Ret. Time	Area	Height	Area%
1	6.625	10538265	1401655	91.814
2	10.976	939556	81312	8.186
		11477821	1482966	100.000



<Peak Table>

A 254nm

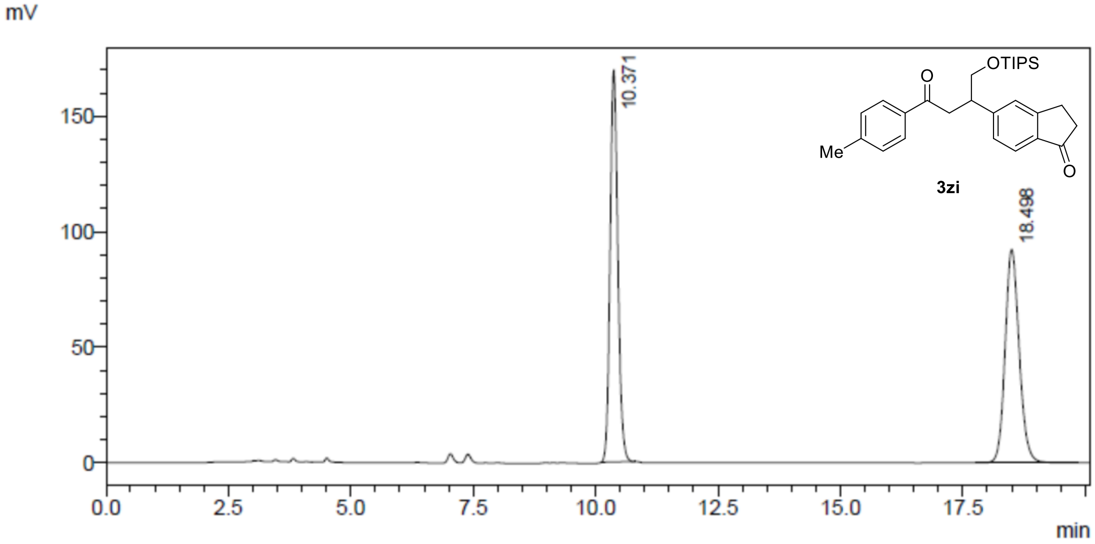
Peak#	Ret. Time	Area	Height	Area%
1	6.602	459670	62764	50.039
2	10.506	458955	41021	49.961
		918625	103785	100.000



<Peak Table>

A 254nm

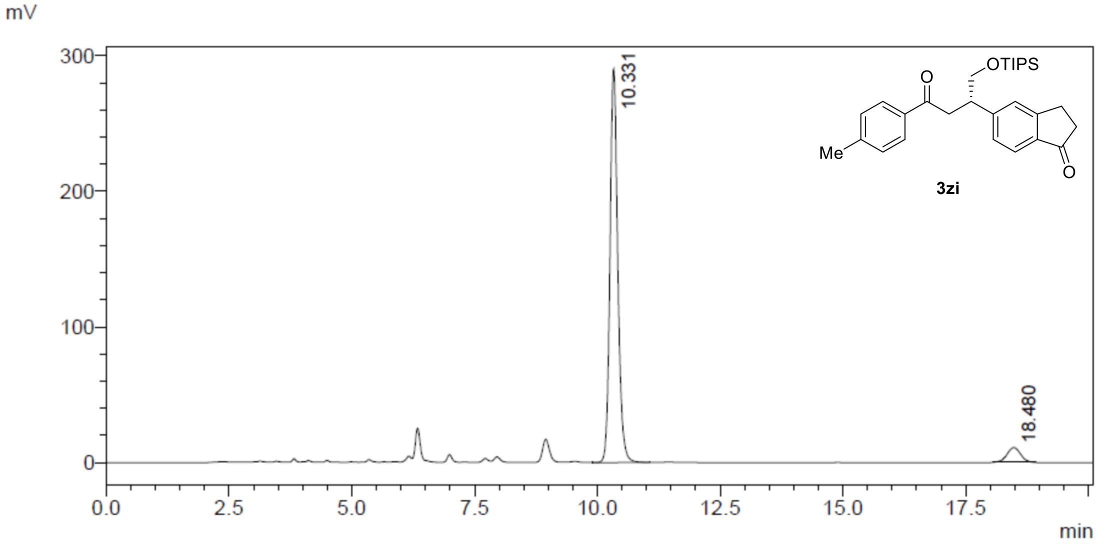
Peak#	Ret. Time	Area	Height	Area%
1	6.590	656441	89618	88.170
2	10.464	88073	8220	11.830
		744514	97838	100.000



<Peak Table>

A 254nm

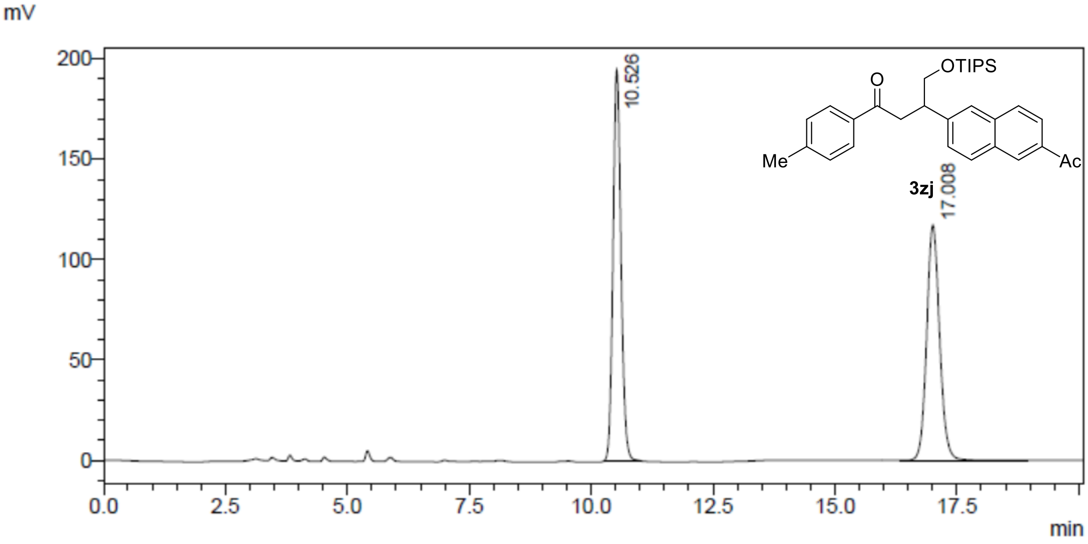
Peak#	Ret. Time	Area	Height	Area%
1	10.371	1866595	169634	50.244
2	18.498	1848477	92339	49.756
		3715072	261974	100.000



<Peak Table>

A 254nm

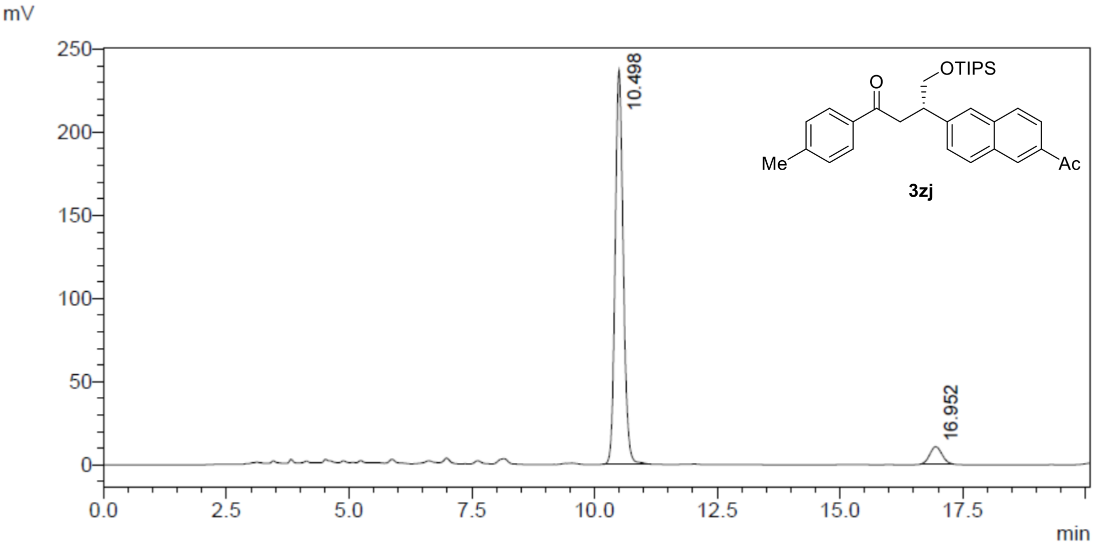
Peak#	Ret. Time	Area	Height	Area%
1	10.331	3201568	290245	93.827
2	18.480	210628	10921	6.173
		3412196	301166	100.000



<Peak Table>

A 254nm

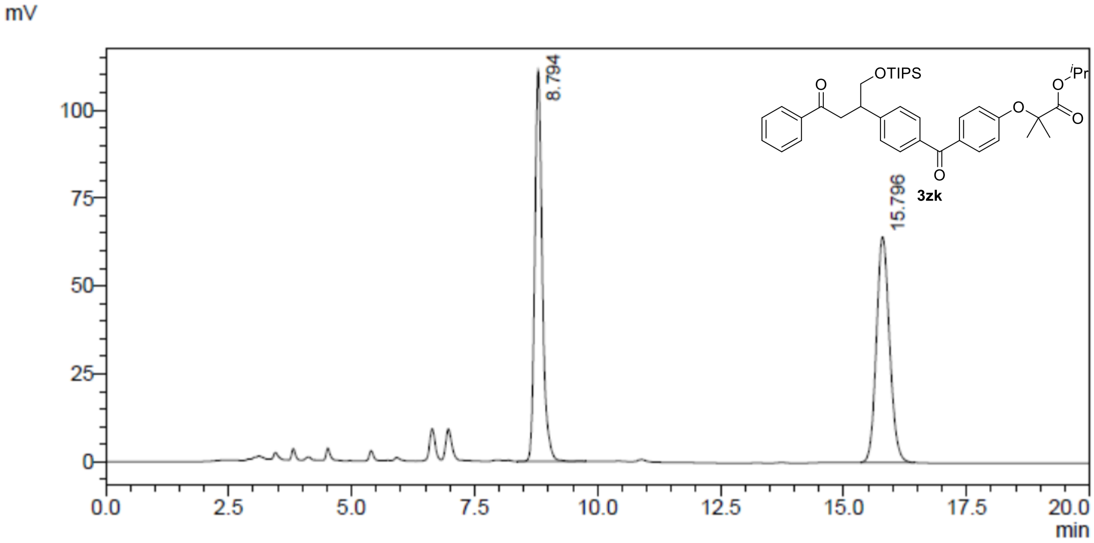
Peak#	Ret. Time	Area	Height	Area%
1	10.526	2203631	194613	50.501
2	17.008	2159901	117146	49.499
		4363533	311759	100.000



<Peak Table>

A 254nm

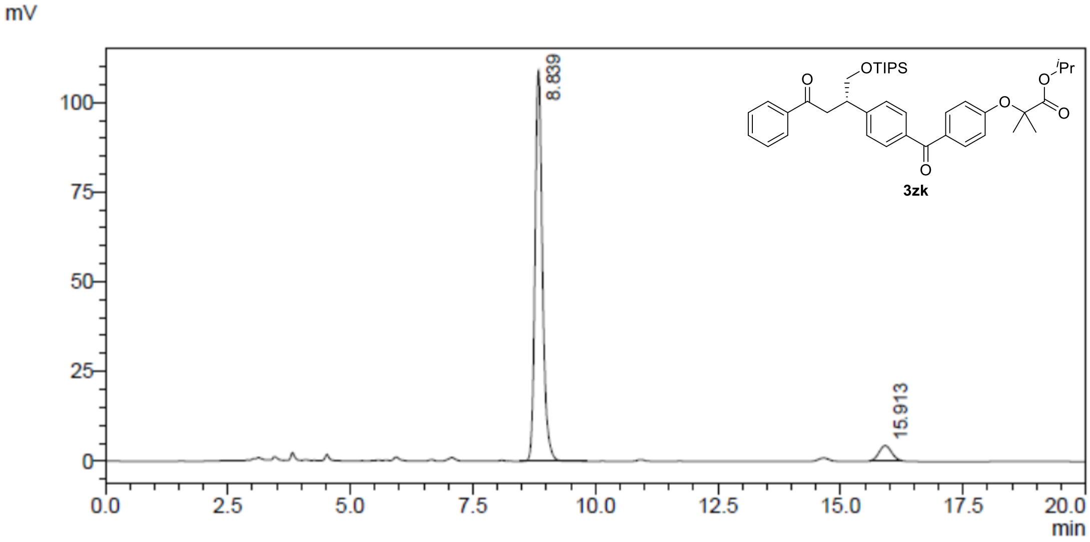
Peak#	Ret. Time	Area	Height	Area%
1	10.498	2712054	237065	93.801
2	16.952	179222	10456	6.199
		2891276	247521	100.000



<Peak Table>

A 254nm

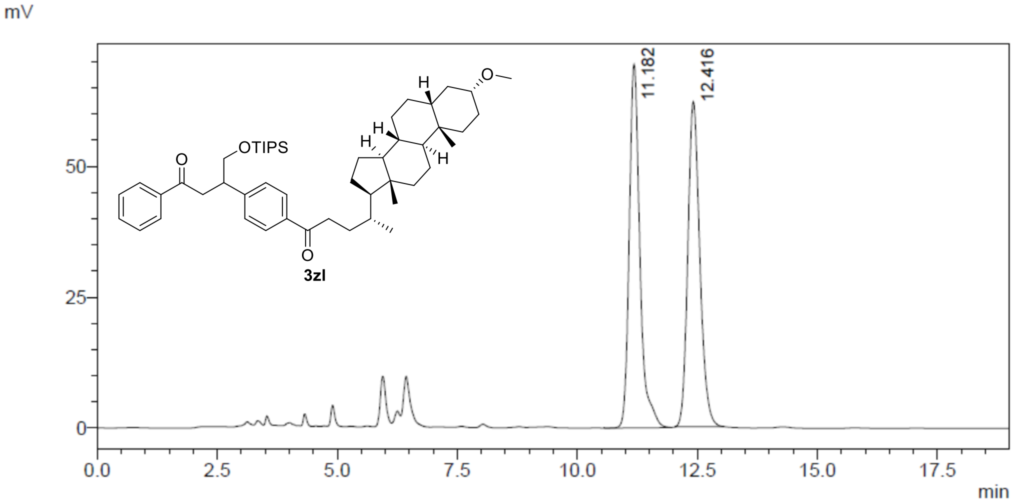
Peak#	Ret. Time	Area	Height	Area%
1	8.794	1183203	111154	49.843
2	15.796	1190678	64116	50.157
		2373881	175270	100.000



<Peak Table>

A 254nm

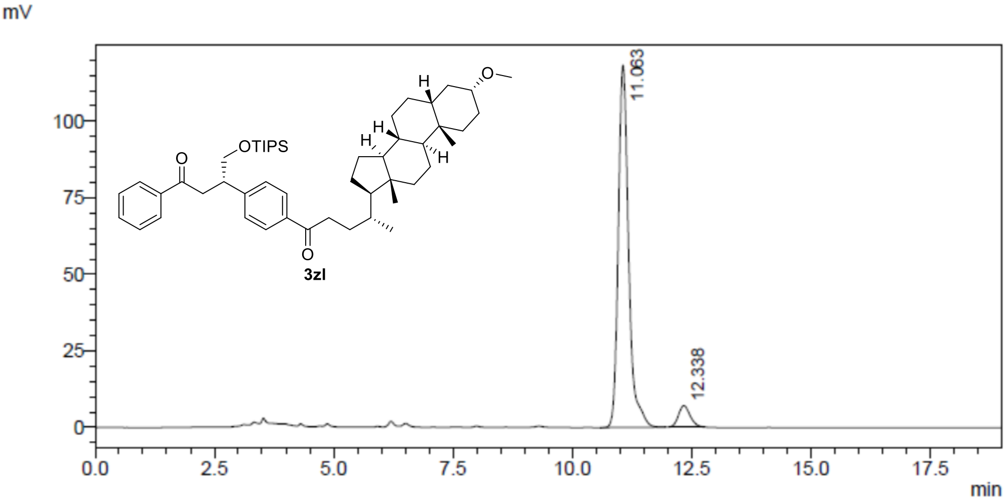
Peak#	Ret. Time	Area	Height	Area%
1	8.839	1150357	108974	93.959
2	15.913	73966	4226	6.041
		1224324	113199	100.000



<Peak Table>

A 254nm

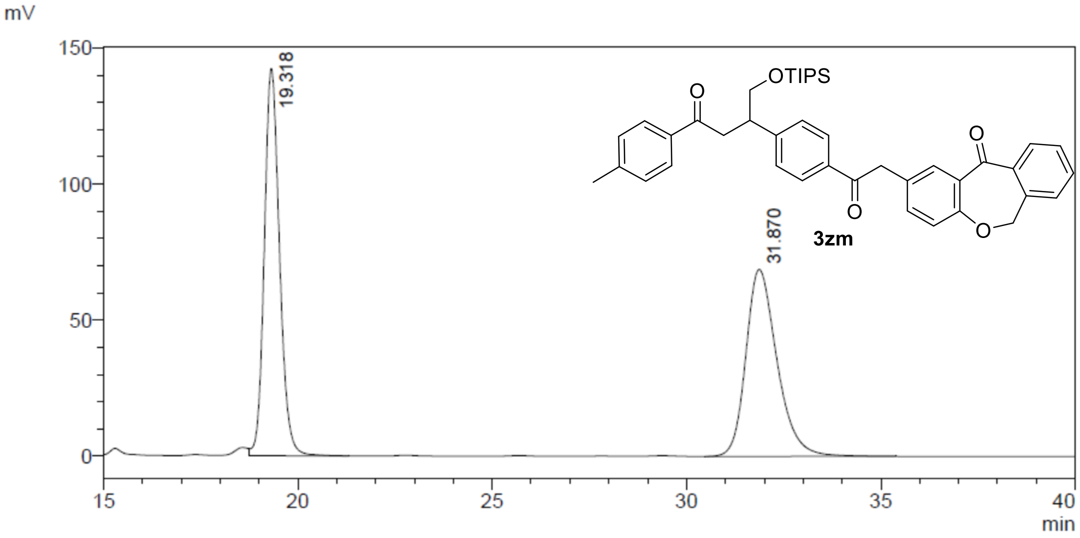
Peak#	Ret. Time	Area	Height	Area%
1	11.182	1072849	69502	49.906
2	12.416	1076910	62081	50.094
		2149759	131583	100.000



<Peak Table>

A 254nm

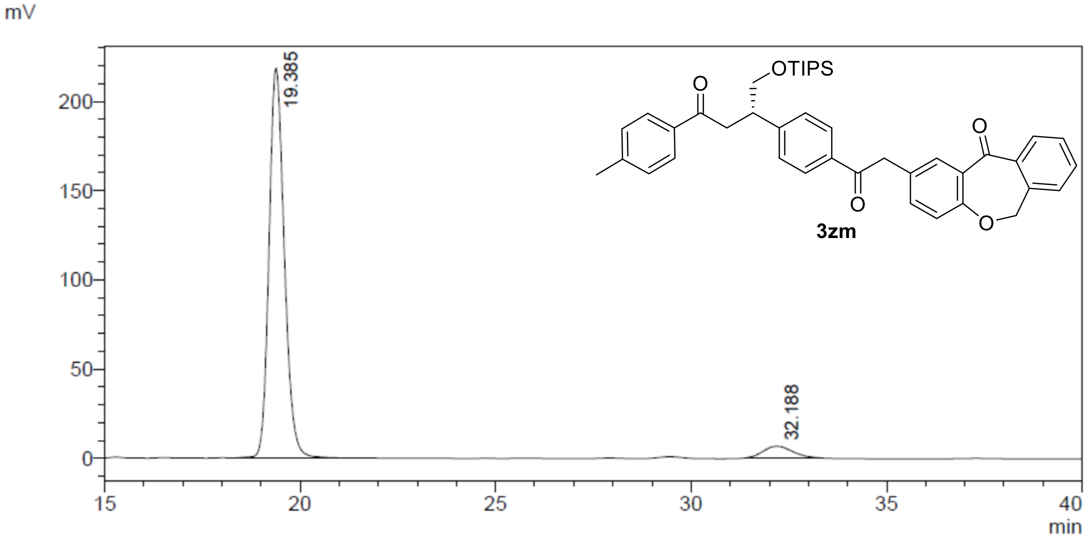
Peak#	Ret. Time	Area	Height	Area%
1	11.063	1779124	118203	93.852
2	12.338	116552	6941	6.148
		1895677	125145	100.000



<Peak Table>

A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	19.318	3873175	142220	50.267
2	31.870	3832028	68672	49.733
		7705203	210892	100.000

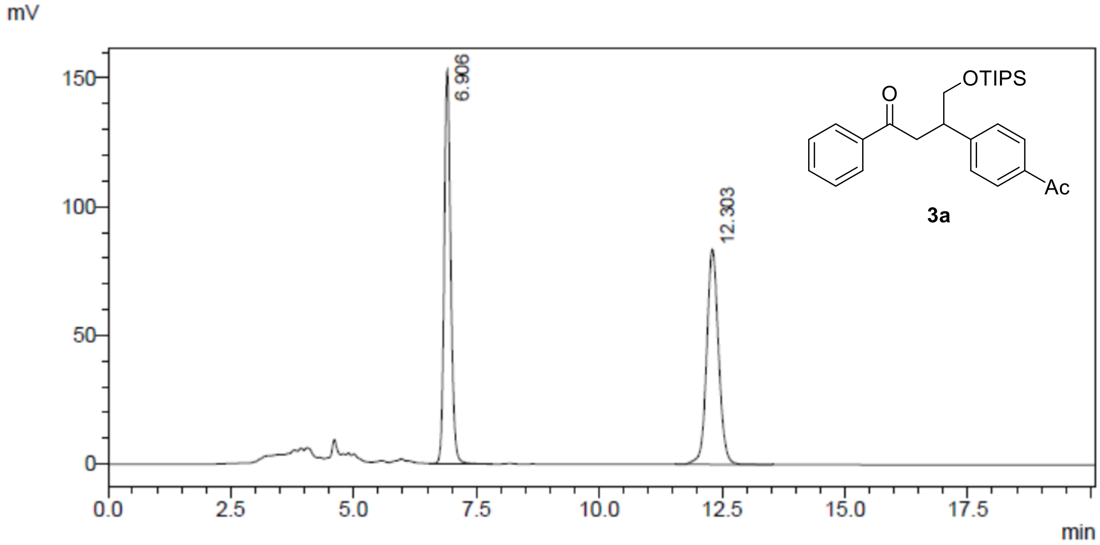


<Peak Table>

A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	19.385	5947846	218442	94.619
2	32.188	338264	6581	5.381
		6286110	225022	100.000

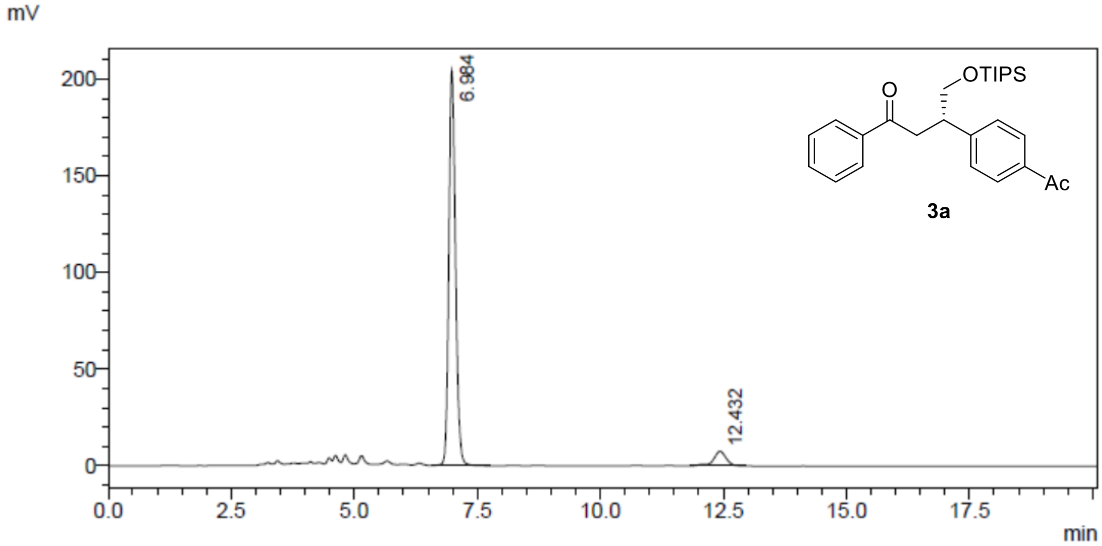
Large-scale of **3a**:



<Peak Table>

A 254nm

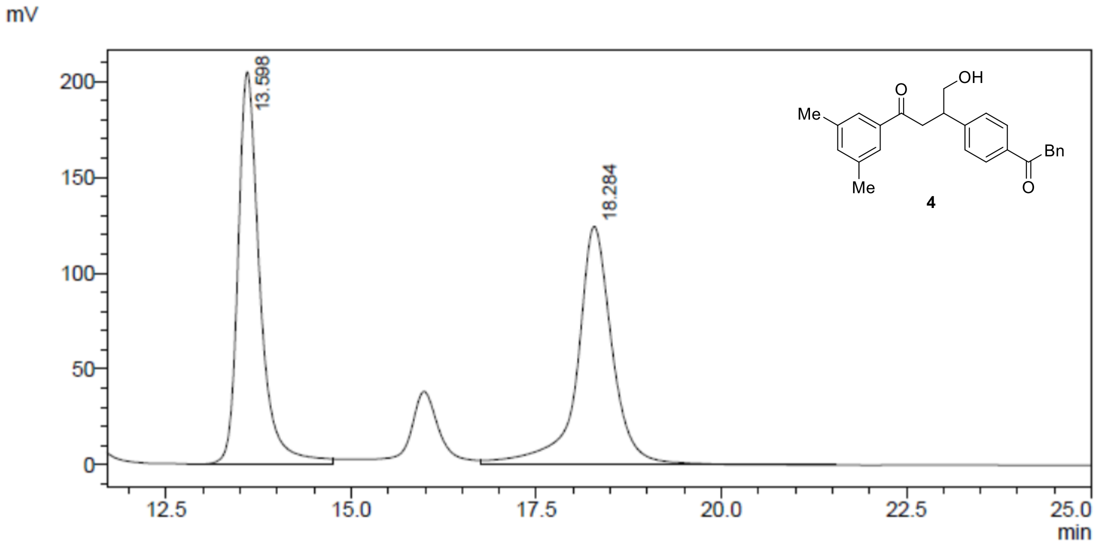
Peak#	Ret. Time	Area	Height	Area%
1	6.906	1411282	152924	50.138
2	12.303	1403533	83621	49.862
		2814815	236544	100.000



<Peak Table>

A 254nm

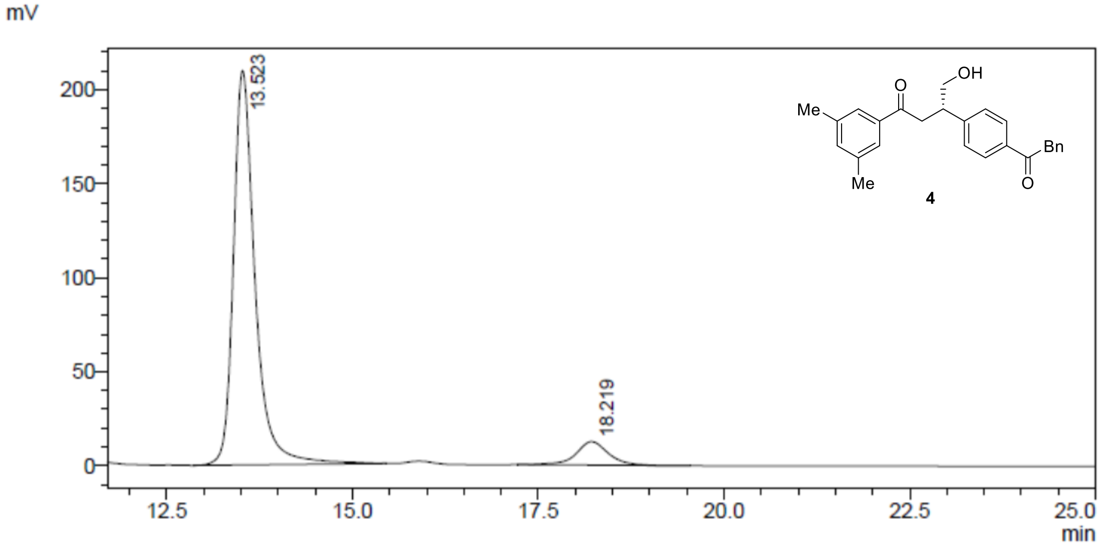
Peak#	Ret. Time	Area	Height	Area%
1	6.984	1926758	204303	93.383
2	12.432	136528	7542	6.617
		2063285	211845	100.000



<Peak Table>

A 254nm

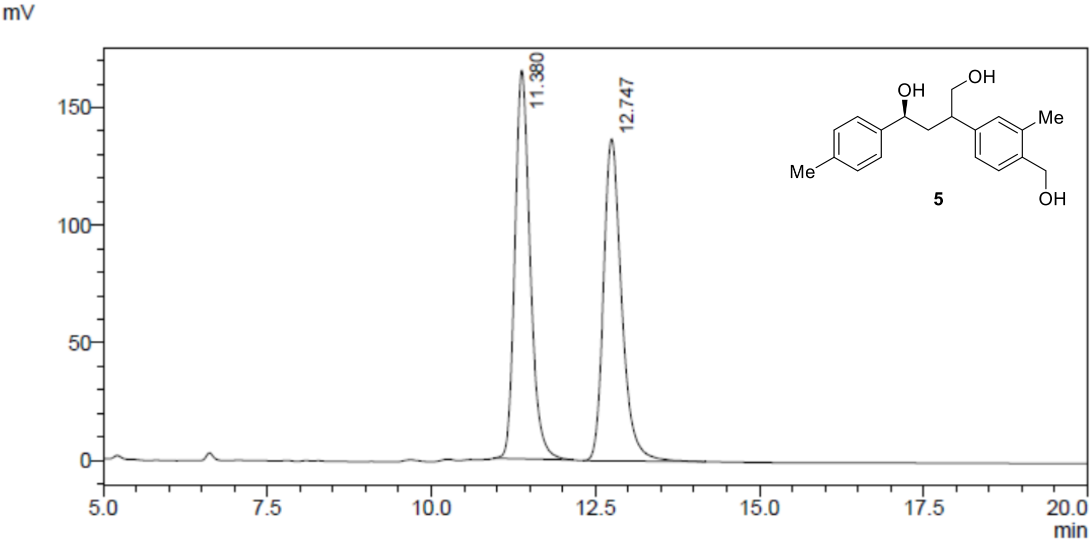
Peak#	Ret. Time	Area	Height	Area%
1	13.598	4197547	204503	50.093
2	18.284	4181912	124487	49.907
		8379459	328990	100.000



<Peak Table>

A 254nm

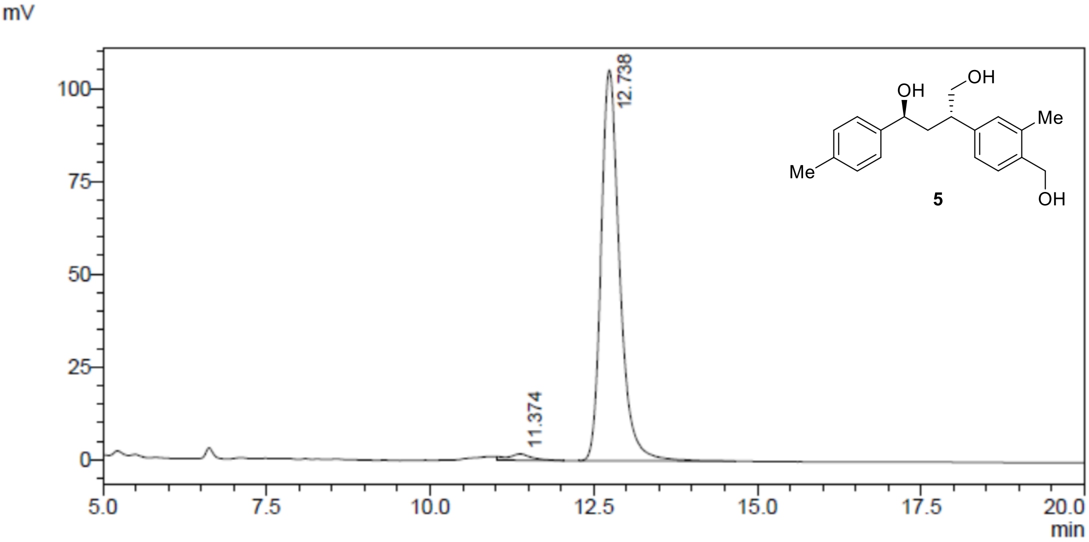
Peak#	Ret. Time	Area	Height	Area%
1	13.523	4246260	209683	91.733
2	18.219	382659	12474	8.267
		4628919	222157	100.000



<Peak Table>

210nm

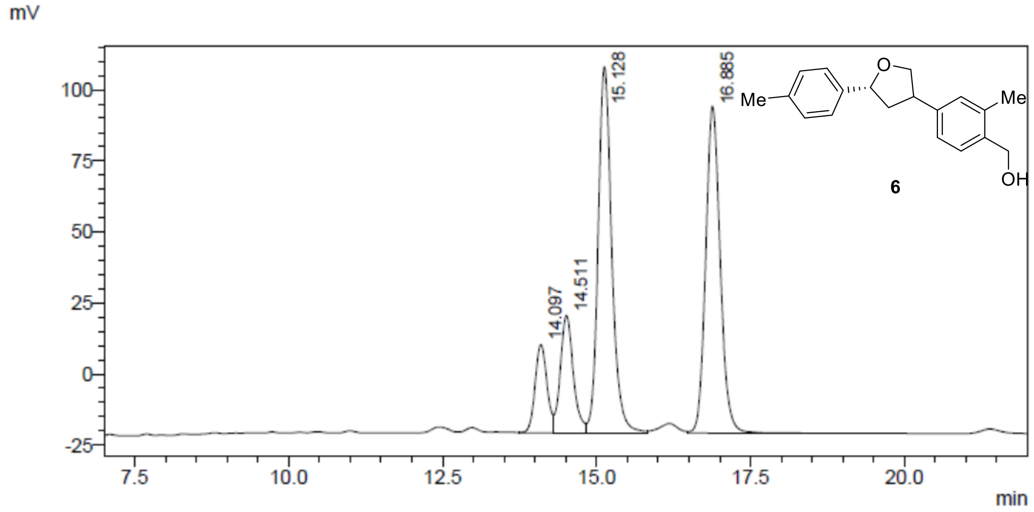
Peak#	Ret. Time	Area	Height	Area%
1	11.380	2664674	164964	50.392
2	12.747	2623191	136592	49.608
		5287865	301556	100.000



<Peak Table>

210nm

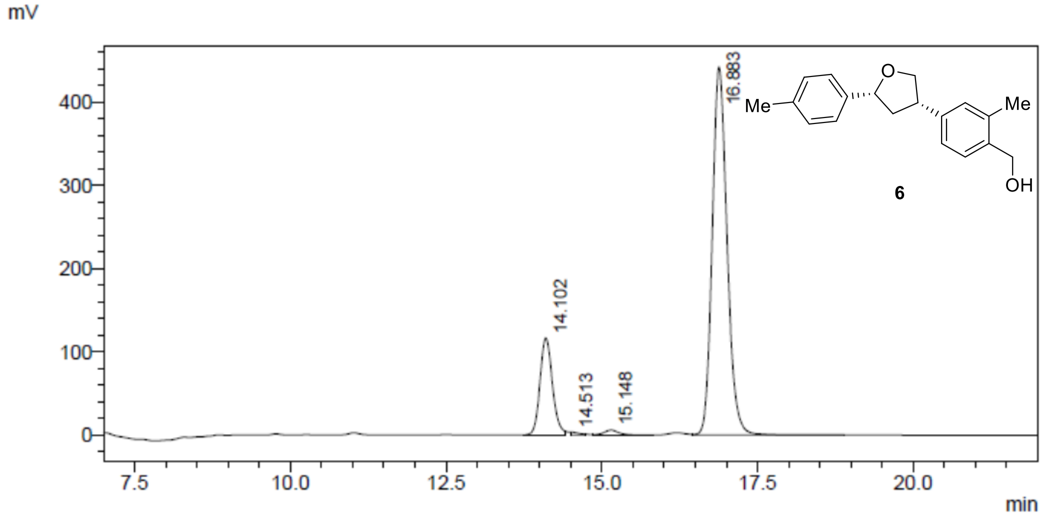
Peak#	Ret. Time	Area	Height	Area%
1	11.374	43405	1725	2.043
2	12.738	2080926	105299	97.957
		2124331	107024	100.000



<Peak Table>

A 210nm

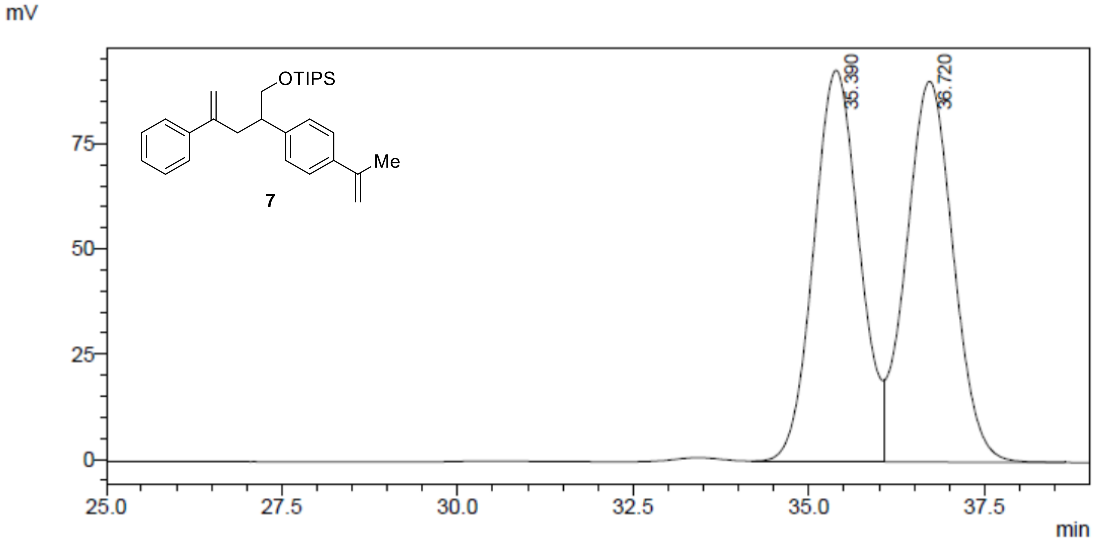
Peak#	Ret. Time	Area	Height	Area%
1	14.097	421090	31120	8.582
2	14.511	607099	41327	12.374
3	15.128	1985849	128872	40.474
4	16.885	1892410	114983	38.570
		4906447	316302	100.000



<Peak Table>

210nm

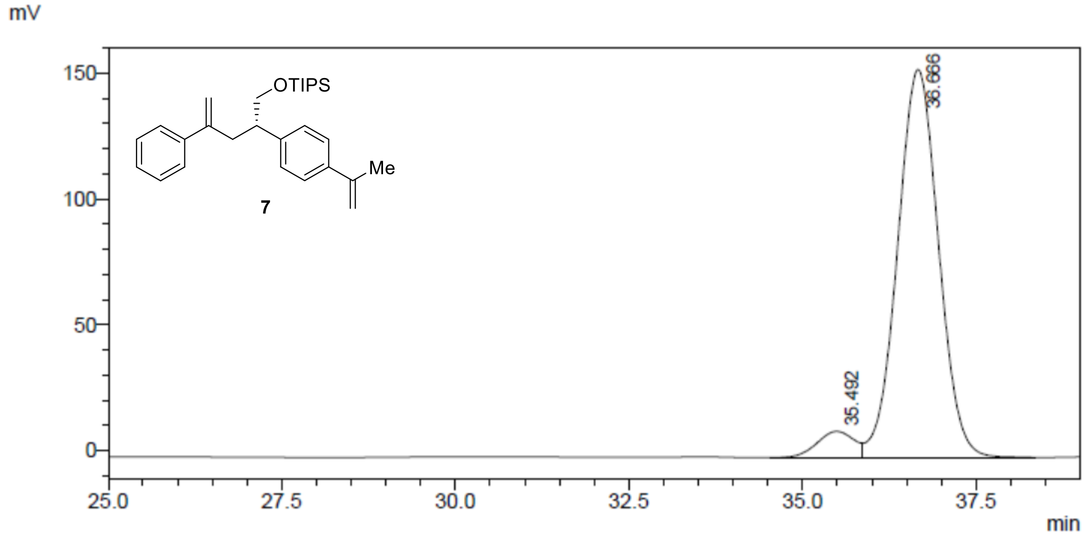
Peak#	Ret. Time	Area	Height	Area%
1	14.102	1616945	116504	17.840
2	14.513	26203	3470	0.289
3	15.148	90729	5770	1.001
4	16.883	7329863	442142	80.870
		9063739	567886	100.000



<Peak Table>

A 254nm

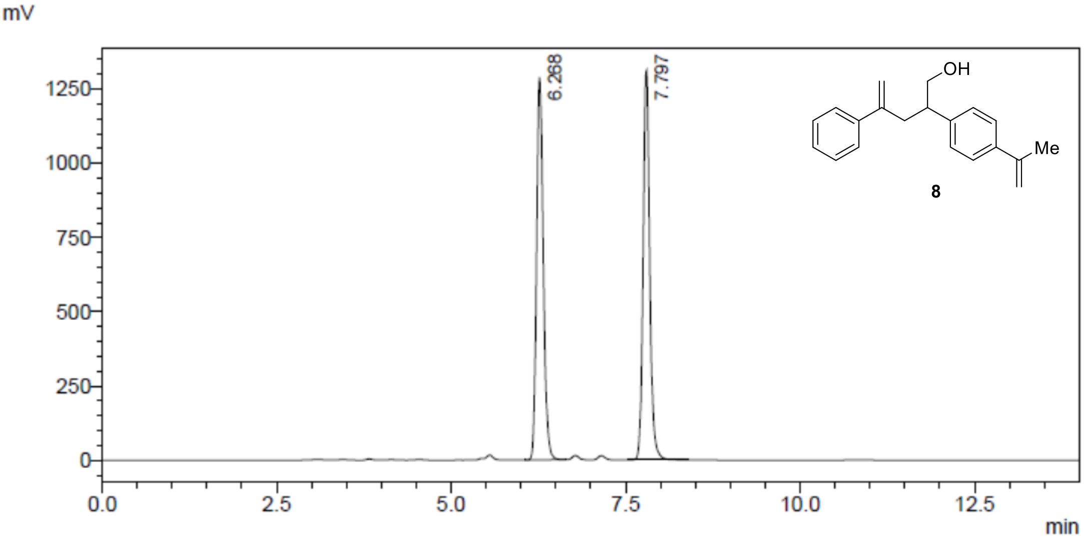
Peak#	Ret. Time	Area	Height	Area%
1	35.390	4236074	93067	50.016
2	36.720	4233371	90460	49.984
		8469445	183527	100.000



<Peak Table>

A 254nm

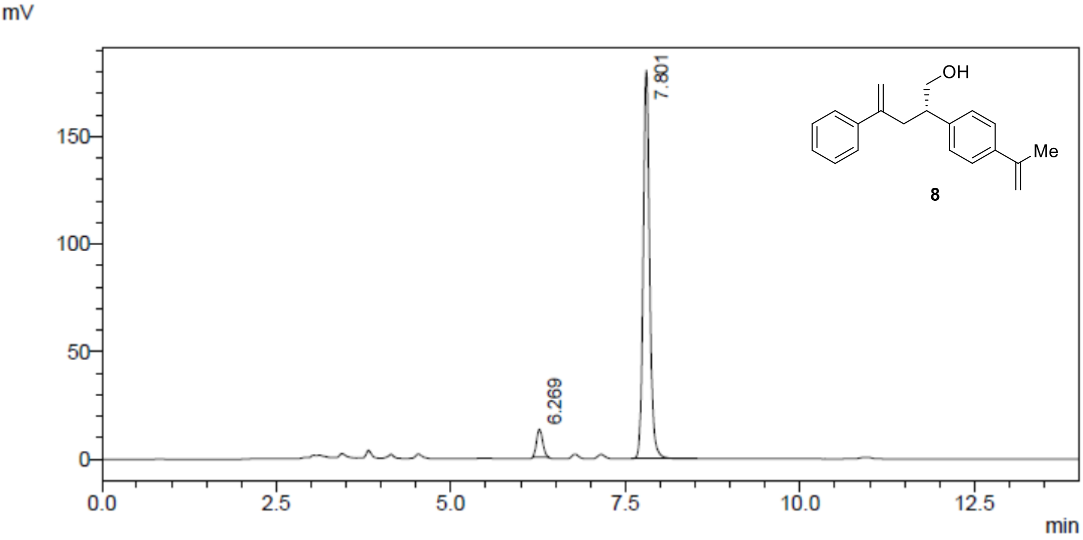
Peak#	Ret. Time	Area	Height	Area%
1	35.492	386936	10384	5.761
2	36.666	6329895	154239	94.239
		6716831	164622	100.000



<Peak Table>

254nm

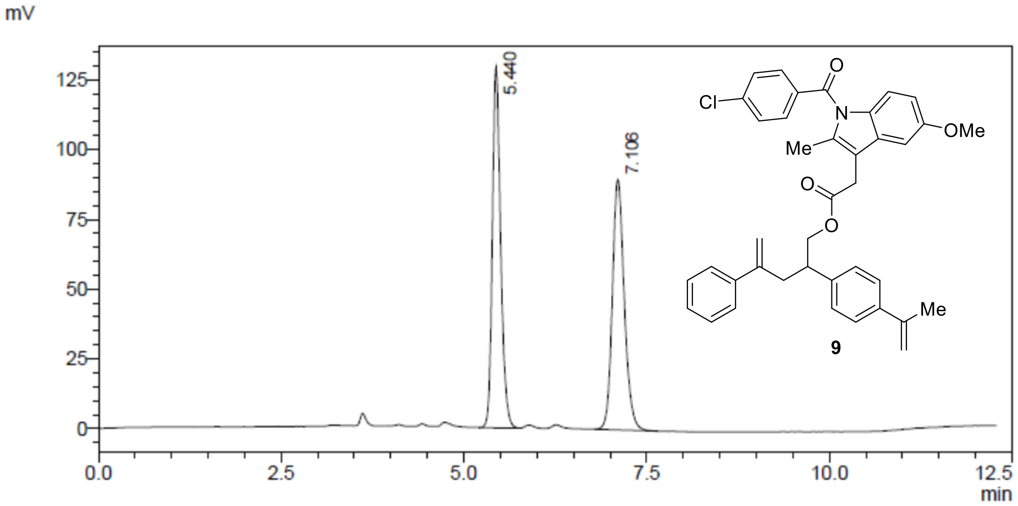
Peak#	Ret. Time	Area	Height	Area%
1	6.268	8656691	1289311	50.044
2	7.797	8641330	1313355	49.956
		17298021	2602666	100.000



<Peak Table>

254nm

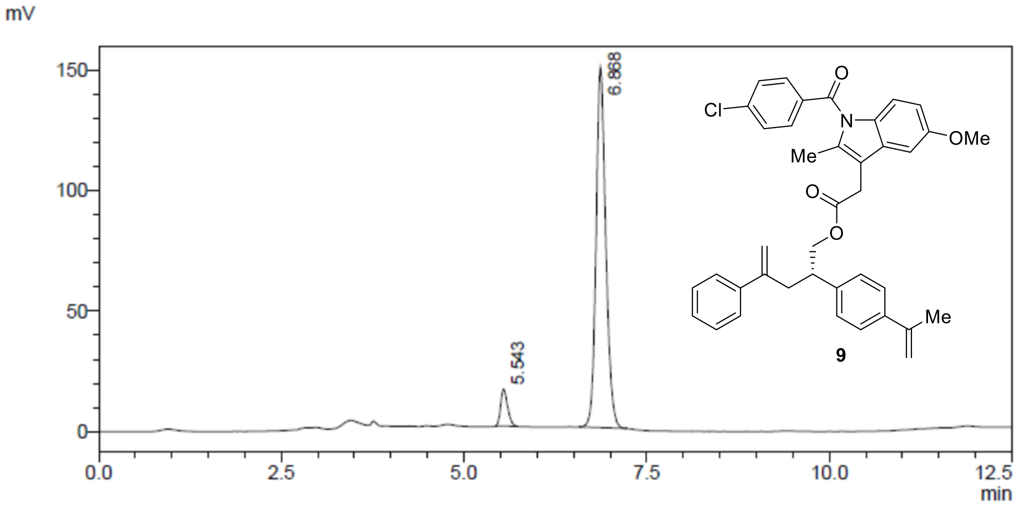
Peak#	Ret. Time	Area	Height	Area%
1	6.269	78656	12865	6.337
2	7.801	1162479	180810	93.663
		1241136	193676	100.000



<Peak Table>

A 254nm

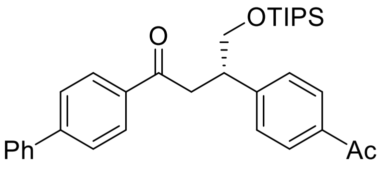
Peak#	Ret. Time	Area	Height	Area%
1	5.440	1023452	129478	50.090
2	7.106	1019759	89763	49.910
		2043211	219241	100.000



<Peak Table>

A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	5.543	100592	15376	6.769
2	6.868	1385533	149776	93.231
		1486126	165152	100.000



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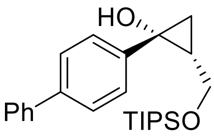
generated from *cis*-isomer of 

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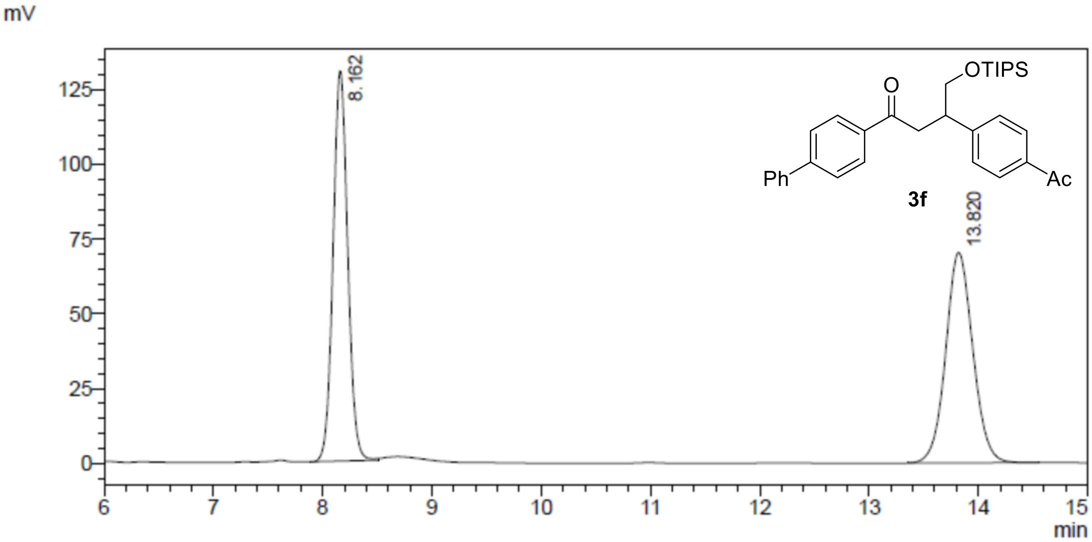
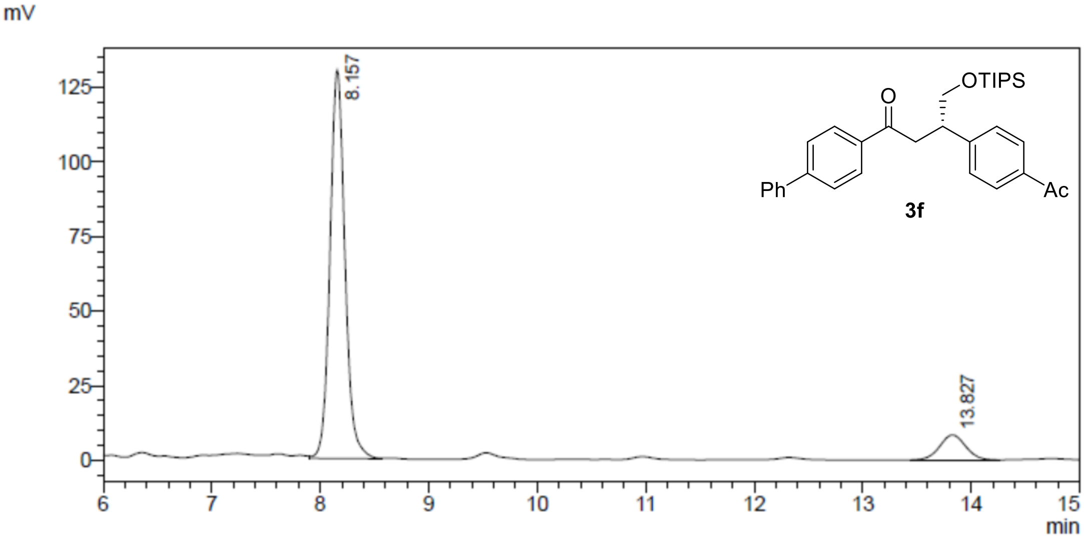


<Peak Table>

A 254nm

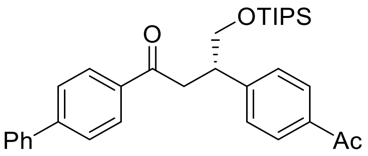
Peak#	Ret. Time	Area	Height	Area%
1	8.162	1219362	130718	50.055
2	13.820	1216700	70404	49.945
		2436062	201123	100.000



<Peak Table>

A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8.157	1250010	130328	89.977
2	13.827	139248	8378	10.023
		1389257	138706	100.000



3f

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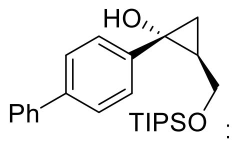

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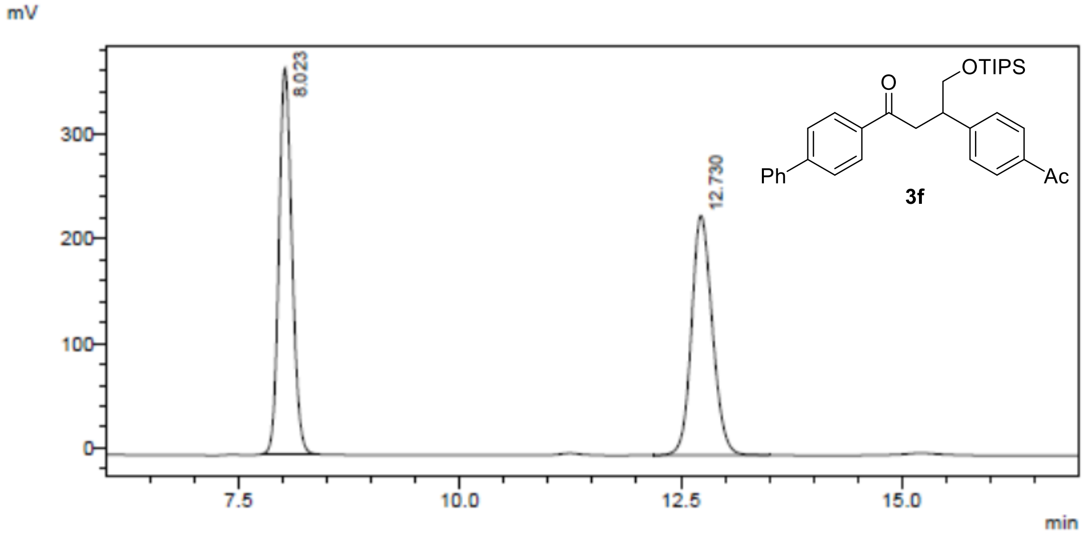
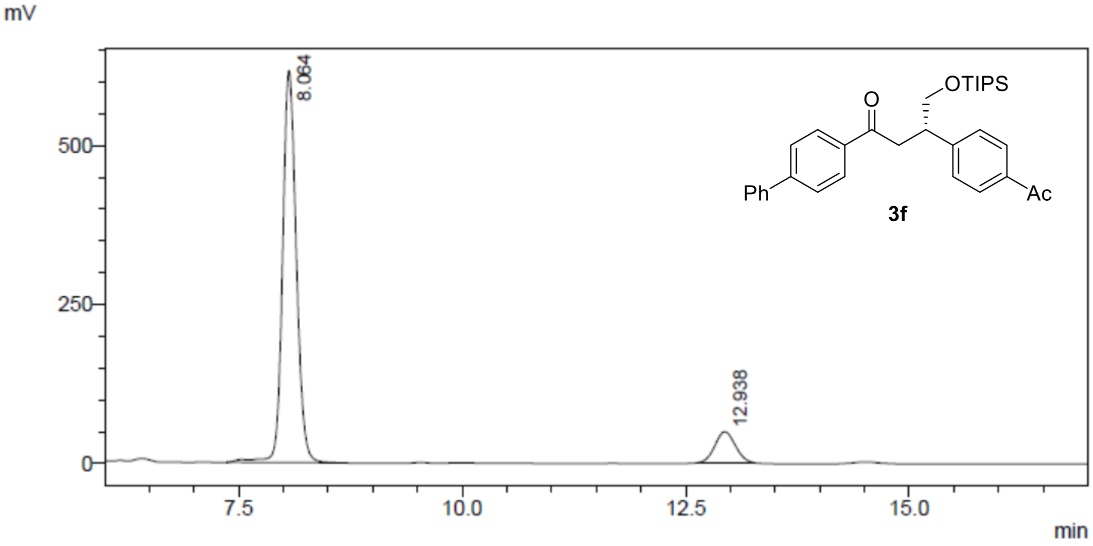


<Peak Table>

A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8.023	3775683	368427	50.146
2	12.730	3753690	228595	49.854
		7529373	597022	100.000



<Peak Table>

A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8.064	6565869	615823	89.636
2	12.938	759146	48293	10.364
		7325015	664116	100.000