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Ni-Catalyzed Regioselective C-C Bond Formation of 1,1-Disubstituted Allenes with Aldehydes

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Supporting Information

General Considerations

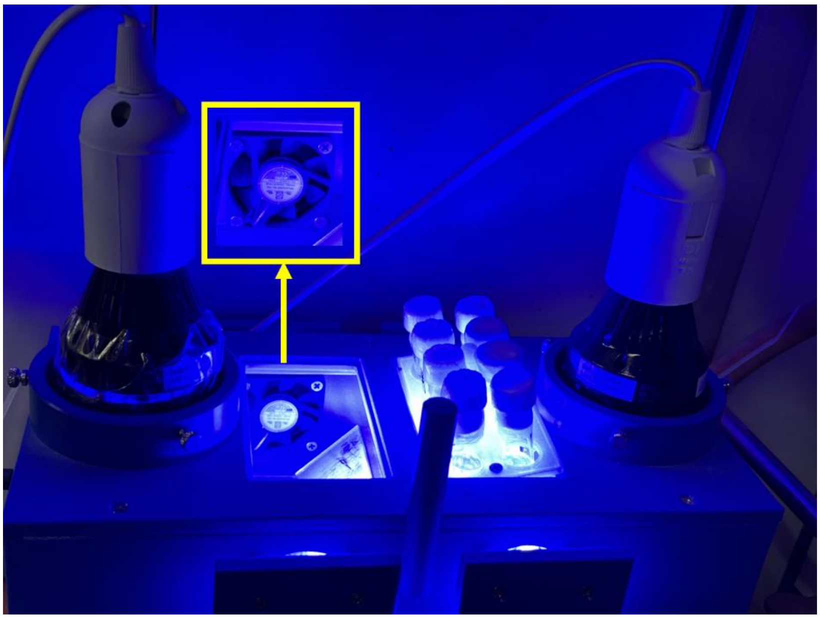
General Reagent Information

All commercially available reagents were purchased from Sigma-Aldrich, Alfa Aesar, Combi blocks or TCI companies and used without further purification. Flash column chromatography was performed using ZEOCHEM ZEOprep silica gel 60 (60-200 mesh).

General Analytical Information

The synthesized homoallylic alcohol **3** were characterized by ^{1}H, $^{13}C\{^{1}H\}$, and $^{19}F\{^{1}H\}$ NMR, and FT-IR spectroscopy. NMR spectra were recorded on a Varian 600 MHz instrument (600 MHz for ^{1}H NMR, 151 MHz for $^{13}C\{^{1}H\}$ NMR, and 564 MHz for $^{19}F\{^{1}H\}$ NMR). Copies of ^{1}H NMR, $^{13}C\{^{1}H\}$ NMR and $^{19}F\{^{1}H\}$ NMR spectra can be found in this Supporting Information. ^{1}H NMR experiments are reported in units, parts per million (ppm), and were measured relative to residual $CDCl_3$ (7.26 ppm) or CD_3CN (1.94 ppm) in the deuterated solvent. ^{13}C NMR spectra are reported in ppm relative to $CDCl_3$ (77.23 ppm) or CD_3CN (1.32 ppm), and all were obtained with ^{1}H decoupling. ^{19}F NMR spectra are reported in ppm, and all were taken composite pulse decoupling (CPD) mode. Coupling constants were reported in Hz. Reactions were monitored by GC-MS using the Agilent GC 7890B/5977A inert MSD with Triple-Axis Detector. Mass spectral data of all unknown compounds were obtained from the Korea Basic Science Institute (Daegu) on a Jeol JMS 700 high resolution mass spectrometer. Chiral HPLC analysis was performed on waters e2695 separations module instrument.

Photon Source



All photon sources and accessories were purchased from HepatoChem company. A PhotoRedOx Box® with P205-18-2 450 nm 18 W blue LEDs (34 mW/cm^2) was used for the reactions. All reaction tubes have the same light intensity by using the PhotoRedOx Box® equipped with mirrors.

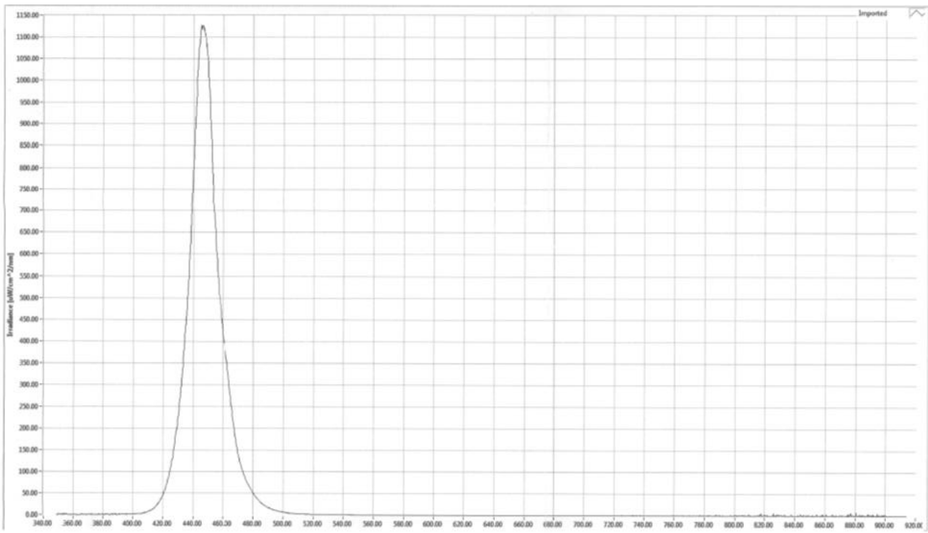
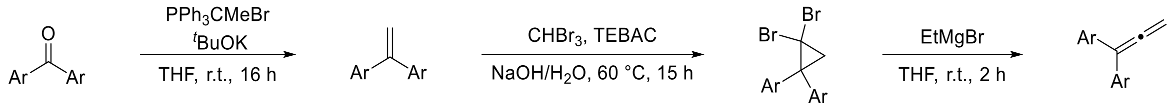


Figure S1. Light spectra of the photon source: P205-18-2 18 W blue LED (λ_{max} 450 nm).

Experimental Details

General procedure for synthesis of 1,1-diarylsubstituted allenes (1a – 1d)[S1],[S2]



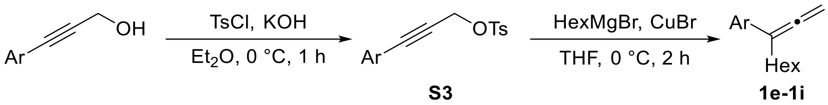
S1 S2 1a-1d

Step 1: In an oven dried flask, was added methyl triphenylphosphonium bromide (1.2 eq) followed by THF (25 mL). Then ^{t}BuOK (1.2 eq) was added, and the resulting yellow suspension was stirred at room temperature. After 1 h, diaryl ketone (5 mmol) was added in one portion and the resulting mixture was further stirred at room temperature and the reaction progress was monitored by thin-layer chromatography. Upon completion after 16 h, the reaction was quenched with water, and the aqueous phase was extracted with diethyl ether (2 × 30 mL). The resulting organic phase was dried over $MgSO_4$, filtered, and concentrated in *vacuo*. The residue was purified by silica gel flash column chromatography using (hexanes) to give the corresponding alkene derivative **S1**.

Step 2: To a solution of alkene **S1** (4 mmol), bromoform (1.5 eq) and $BnNEt_3Cl$ (2 mol%) was added dropwise a solution of 50% NaOH (1 g NaOH dissolved in 2 mL water), and the mixture was stirred at room temperature for 1 h, then heated to 60 °C and the reaction progress was monitored by thin-layer chromatography. Upon completion (~15 h), the reaction was quenched with water and the aqueous phase was extracted with DCM (2 × 25 mL). The combined organic phase was washed with brine (30 mL). The resulting organic phase was dried over $MgSO_4$, filtered, and concentrated in *vacuo*. The residue was purified by silica gel flash column chromatography using (hexanes/ethyl acetate, 99/1) to give the corresponding dibromo derivative **S2**.

Step 3: EtMgBr (1.0 M in THF, 1.5 eq) was added dropwise to a pre-cooled ice-bath solution of **S2** (2 mmol) in dry THF (4 mL) under argon atmosphere. After EtMgBr was added, the mixture was then slowly warmed to room temperature, and stirred at room temperature for an additional 2 h. Then the reaction was quenched by NH_4Cl solution, water was added, and the mixture extracted with diethyl ether (2 × 25 mL). The combined organic phase was washed with brine, dried over $MgSO_4$, and filtered. After removing the solvent under reduced pressure, the residue was purified by silica gel flash column chromatography using (hexanes) to afford the corresponding allene (**1a – 1d**).

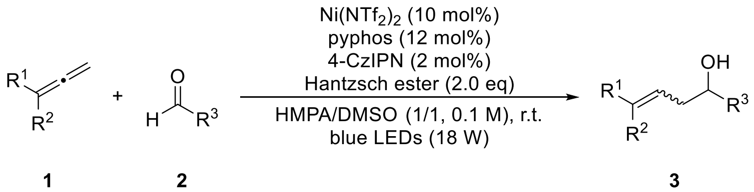
General procedure for synthesis of 1,1-dialkylsubstituted allenes (1e – 1h)[S3]



Step 1: TsCl (1.2 eq) was added to a solution of the corresponding propargylic alcohol **S3** (5 mmol) in diethyl ether (12 mL). The reaction mixture was cooled to 0 °C, then KOH (5.5 eq, freshly pestled) was added in small portions. The solution was allowed to warm to room temperature and stirred for 1 h. The reaction progress was monitored by thin-layer chromatography. Upon completion, the reaction was quenched with cold water, and the aqueous phase was extracted with diethyl ether (3 × 15 mL). The combined organic phases were washed with brine and dried over $MgSO_4$. The solvents were removed under reduced pressure and the crude product was purified by silica gel flash column chromatography using (hexanes/ethyl acetate, 20/1) to afford tosylate derivative **S3**.

Step 2: A mixture of CuBr (10 mol%), THF (10 mL) and the tosylate **S3** (4 mmol) was cooled to 0 °C. HexMgBr (1.5 eq, 2 M in THF) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. Upon completion, the reaction was quenched saturated aqueous solution of NH_4Cl followed by extraction with diethyl ether (3 × 20 mL). The combined organic phases were washed with brine and dried over $MgSO_4$. The solvents were removed under reduced pressure and the crude product was purified by silica gel flash column chromatography using (hexanes) to afford allene derivative (**1e – 1h**).

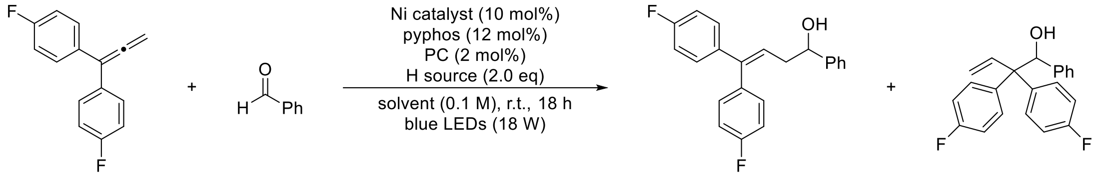
General procedure for synthesis of homoallylic alcohol (3)



A reaction tube with a magnetic stir bar was charged with 1,1-disubstituted allene **1** (0.1 mmol, 1.0 eq), $Ni(NTf_2)_2$ (10 mol%), pyphos (12 mol%), 4-CzIPN (2 mol%), and Hantzsch ester (2.0 eq). The reaction tube was sealed with a PTFE/silicon septa cap and tube was evacuated and re-filled with argon for two times. HMPA/DMSO (1/1, 1 mL) and aldehyde **2** (2.0 eq) were added under argon counter flow. The reaction mixture was stirred at room temperature under visible-light irradiation using 450 nm LEDs (18 W). The reaction progress was monitored by thin layer chromatography or gas chromatography (GC). Upon the completion of the reaction (6 h – 18 h), the reaction mixture was diluted with ethyl acetate and washed with brine. The layers were separated, and the organic layer was dried with $MgSO_4$, filtered, and concentrated in vacuo to give a crude residue that was purified by silica gel column chromatography using hexanes/ethyl acetate to give the corresponding homoallylic alcohol, **3**.

Additional Experiments

Table S1. Optimization table[a,b]

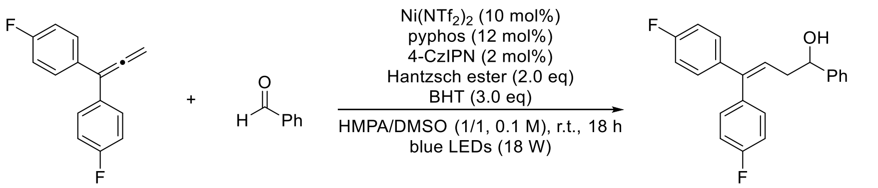


1a **2a** **3aa** *(linear)* **4aa** *(branched)*

Entries	Solvent	Ni catalyst	PC	H source	Variations	Yield of **3aa**	Yield of **4aa**
1	TFE	$NiCl_2(DME)$	$[Ir(dtbbpy)(ppy)_2]PF_6$	Hantzsch ester	-	0	0
2	THF	$NiCl_2(DME)$	$[Ir(dtbbpy)(ppy)_2]PF_6$	Hantzsch ester	-	14	5
3	hexane	$NiCl_2(DME)$	$[Ir(dtbbpy)(ppy)_2]PF_6$	Hantzsch ester	-	0	0
4	HMPA/DMSO (1/1)	$Ni(acac)_2$	$[Ir(dtbbpy)(ppy)_2]PF_6$	Hantzsch ester	-	26	0
5	HMPA/DMSO (1/1)	$Ni(PPh_3)_2Cl_2$	$[Ir(dtbbpy)(ppy)_2]PF_6$	Hantzsch ester	-	38	3
6	**HMPA/DMSO (1/1)**	**$Ni(NTf_2)_2$**	**4-CzIPN**	**Hantzsch ester**		**56**	**0**
7	HMPA/DMSO (1/1)	$Ni(NTf_2)_2$	4-CzIPN	Hantzsch ester (1.5 eq)	-	47	0
8	HMPA/DMSO (1/1)	$Ni(NTf_2)_2$	4-CzIPN	Hantzsch ester (2.5 eq)	-	51	0
9	HMPA/DMSO (1/1, 0.05 M)	$Ni(NTf_2)_2$	4-CzIPN	Hantzsch ester	-	51	0
10	HMPA/DMSO (1/1, 0.25 M)	$Ni(NTf_2)_2$	4-CzIPN	Hantzsch ester	-	48	0
11	HMPA/DMSO (1/1)	$Ni(NTf_2)_2$	4-CzIPN	Hantzsch ester	DIPEA (0.5 eq) additive as an additive	24	0
12	HMPA/DMSO (1/1)	$Ni(NTf_2)_2$	4-CzIPN	Hantzsch ester	365 nm LEDs	0	3
13	HMPA/DMSO (1/1)	$Ni(NTf_2)_2$	4-CzIPN	Hantzsch ester	405 nm LEDs	46	4
14	HMPA/DMSO (1/1)	$Ni(NTf_2)_2$	4-CzIPN	Hantzsch ester	on air	0	0

[a]Reaction scale: **1a** (0.1 mmol), **2a** (0.2 mmol); [b]Yields were determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

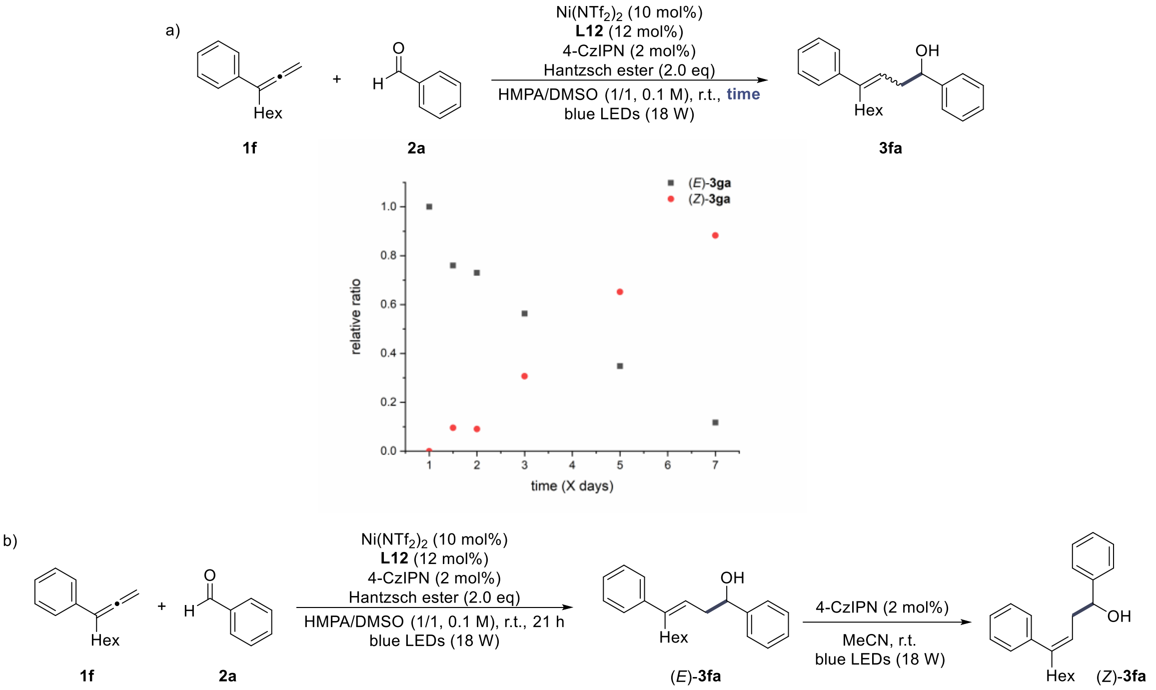
Radical inhibition experiment in the presence of BHT



1a **2a** **3aa** (56%)

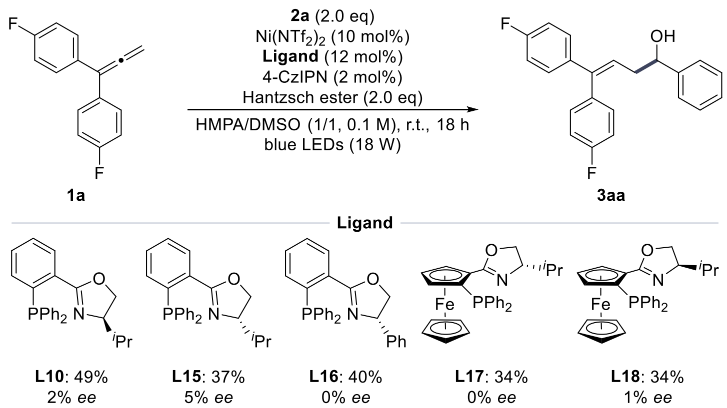
A reaction tube with a magnetic stir bar was charged with 4,4'-(propa-1,2-diene-1,1-diyl)bis(fluorobenzene) **1a** (0.1 mmol, 1 eq), $Ni(NTf_2)_2$ (10 mol%), pyphos (12 mol%), 4-CzIPN (2 mol%), Hantzsch ester (2.0 eq), and BHT (3.0 eq). The reaction tube was sealed with a PTFE/silicon septa cap and tube was evacuated and re-filled with argon for two times. HMPA/DMSO (1/1, 1 mL) and benzaldehyde **2a** (2.0 eq) were added under argon counter flow. The reaction mixture was stirred at room temperature under visible-light irradiation using 450 nm LEDs (18 W). After 18 h, 1,3,5-trimethoxybenzene was added as an internal standard. The reaction mixture was diluted with ethyl acetate and washed with brine. The layers were separated, and the organic layer was dried with $MgSO_4$, filtered, and concentrated in vacuo to give a crude residue. The crude residue was dissolved in deuterochloroform and the yield was determined by ^1H NMR spectroscopy with 1,3,5-trimethyoxybenzene as an internal standard.

Scheme S1. *E/Z* isomerization of 3fa[a,b]



[a]Reaction scale: **1f** (0.1 mmol), **2a** (0.2 mmol); [b] The ratio of E/Z isomers was determined by gas chromatography.

Reactions with chiral P^N ligands



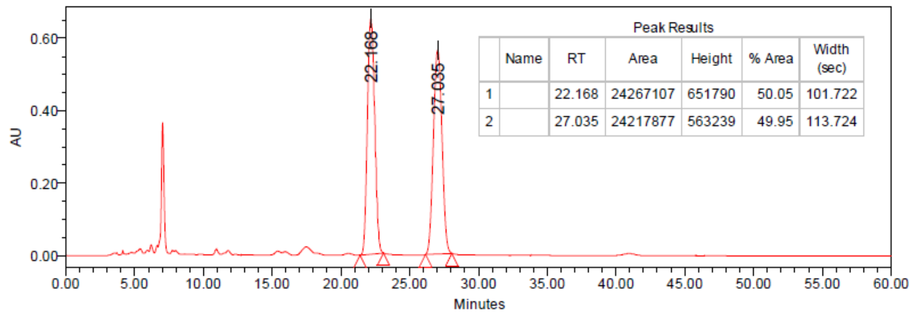
A reaction tube with a magnetic stir bar was charged with 4,4'-(propa-1,2-diene-1,1-diyl)bis(fluorobenzene) **1a** (0.1 mmol, 1 eq), $Ni(NTf_2)_2$ (10 mol%), ligand (12 mol%), 4-CzIPN

(2 mol%), Hantzsch ester (2.0 eq), and BHT (3.0 eq). The reaction tube was sealed with a PTFE/silicon septa cap and tube was evacuated and re-filled with argon for two times. HMPA/DMSO (1/1, 1 mL) and benzaldehyde **2a** (2.0 eq) were added under argon counter flow. The reaction mixture was stirred at room temperature under visible-light irradiation using 450 nm LEDs (18 W). After 18 h, 1,3,5-trimethoxybenzene was added as an internal standard. The reaction mixture was diluted with ethyl acetate and washed with brine. The layers were separated, and the organic layer was dried with $MgSO_4$, filtered, and concentrated in vacuo to give a crude residue. The crude residue was filtered using syringe filter and dissolved in hexanes/EtOH (1/1). The enantiomeric excess (*ee*) was determined by HPLC analysis on chiral stationary column.

HPLC traces

Result with pyphos

Proc. Chnl. Descr.:2998 PDA 254.0



Result with **L10**

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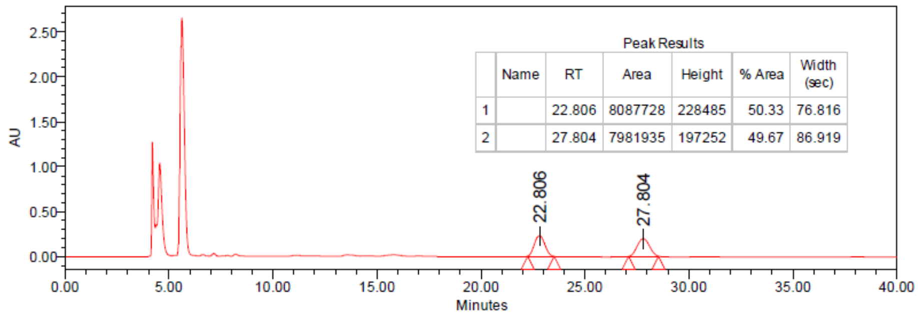

Result with **L15**

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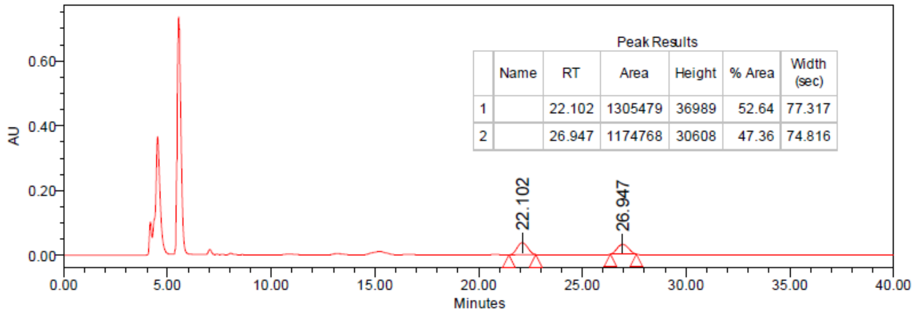
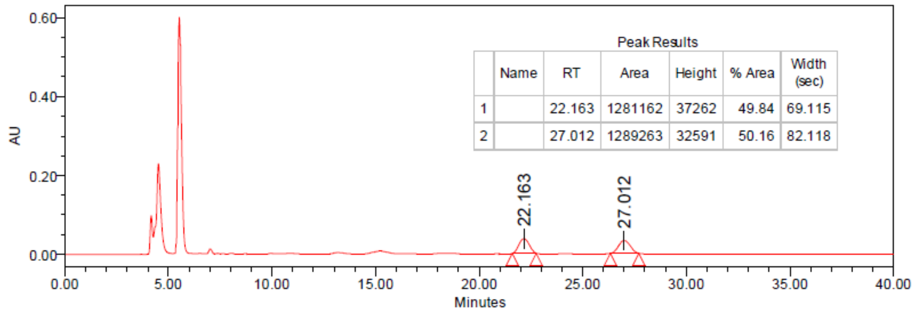


	Name	RT	Area	Height	% Area	Width (sec)
1		22.102	1305479	36989	52.64	77.317
2		26.947	1174768	30608	47.36	74.816

Result with **L16**

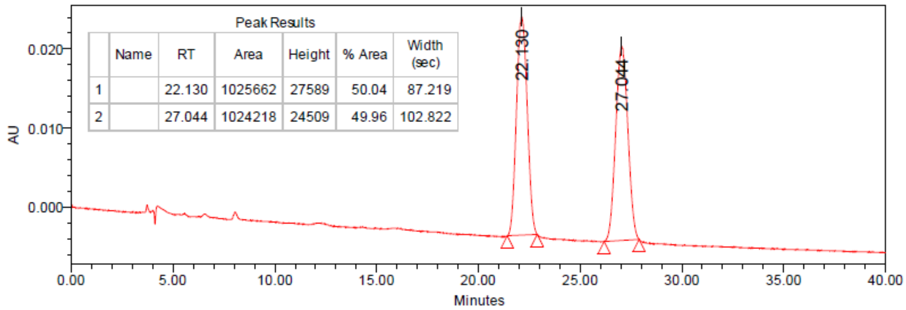
Proc. Chnl. Descr.:2998 PDA 254.0



	Name	RT	Area	Height	% Area	Width (sec)
1		22.163	1281162	37262	49.84	69.115
2		27.012	1289263	32591	50.16	82.118

Result with **L17**

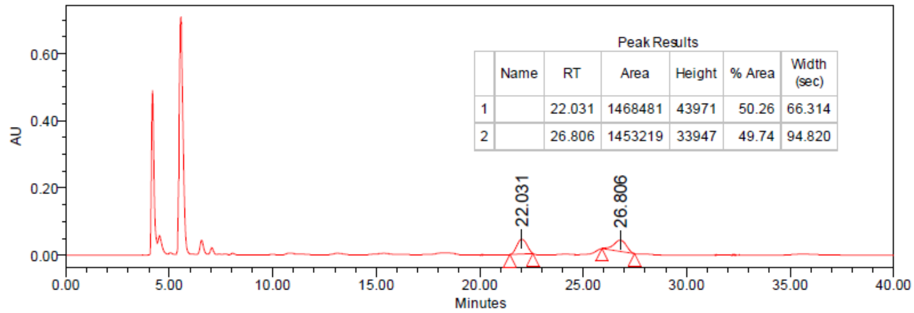
Proc. Chnl. Descr.:2998 PDA 254.0



	Name	RT	Area	Height	% Area	Width (sec)
1		22.130	1025662	27589	50.04	87.219
2		27.044	1024218	24509	49.96	102.822

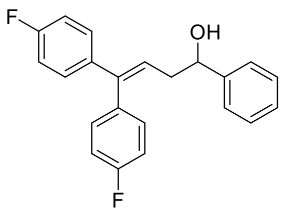
Result with **L18**

Proc. Chnl. Descr.:2998 PDA 254.0

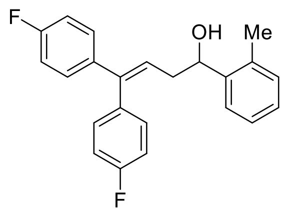


	Name	RT	Area	Height	% Area	Width (sec)
1		22.031	1468481	43971	50.26	66.314
2		26.806	1453219	33947	49.74	94.820

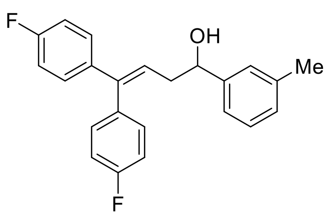
Analytic Data for Synthesized Compounds



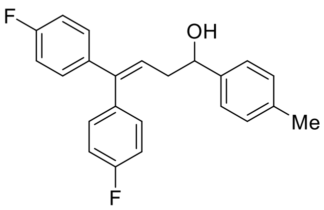
4,4-bis(4-fluorophenyl)-1-phenylbut-3-en-1-ol, **3aa**; **^{1}H NMR (600 MHz, CDCl$_3$)** 7.38 – 7.32 (m, 2H), 7.31 – 7.27 (m, 3H), 7.11 (ddd, J = 8.4, 2.5 Hz, J_{H-F} = 5.2 Hz, 2H), 7.04 – 6.98 (m, 4H), 6.96 – 6.91 (m, 2H), 6.06 (dd, J = 7.5, 7.5 Hz, 1H), 4.81 (dd, J = 6.5, 6.5 Hz, 1H), 2.60 (ddd, J = 14.7, 7.5, 6.5 Hz, 1H), 2.54 (ddd, J = 14.7, 7.5, 6.5 Hz, 1H), 1.90 (bs, 1H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 162.40 (d, J_{C-F} = 246.1 Hz), 162.19 (d, J_{C-F} = 246.5 Hz), 144.07, 142.45, 138.64, 135.65 (d, J_{C-F} = 3.3 Hz), 131.61 (d, J_{C-F} = 7.8 Hz), 128.98 (d, J_{C-F} = 8.1 Hz), 128.71, 127.95, 126.05, 25.23, 115.46 (d, J_{C-F} = 21.4 Hz), 115.19 (d, J_{C-F} = 21.4 Hz), 74.53, 39.60; **^{19}F NMR (564 MHz, CDCl$_3$)** δ -115.06, -115.45; **HRMS** m/z (FAB) calc. for $C_{22}H_{17}F_2$ [M−H$_2$O+H]$^+$ 319.1298, found 319.1296; ***R$_f$*** 0.40 (Hex/EtOAc, 4/1).



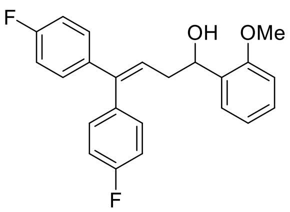
4,4-bis(4-fluorophenyl)-1-(*o*-tolyl)but-3-en-1-ol, **3ab**; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.43 (d, J = 7.8 Hz, 1H), 7.21 (dd, J = 7.8, 7.4 Hz, 1H), 7.17 (dd, J = 7.5, 7.4 Hz, 1H), 7.14 (dd, J = 8.8 Hz, J_{H-F} = 5.4 Hz, 2H), 7.10 (d, J = 7.5 Hz, 1H), 7.05 – 6.97 (m, 4H), 6.94 (dd, J = 8.8 Hz, J_{H-F} = 8.7 Hz, 2H), 6.15 (t, J = 7.5 Hz, 1H), 5.04 (t, J = 6.3 Hz, 1H), 2.52 (dd, J = 7.5, 6.3 Hz, 2H), 2.21 (s, 3H), 1.82 (bs, 1H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 162.39 (d, J_{C-F} = 246.5 Hz), 162.20 (d, J_{C-F} = 246.5 Hz), 142.36, 142.19, 138.57 (d, J_{C-F} = 3.2 Hz), 135.68 (d, J_{C-F} = 3.2 Hz), 134.56, 131.61 (d, J_{C-F} = 8.1 Hz), 130.63, 128.91 (d, J_{C-F} = 8.1 Hz), 127.59, 126.51, 125.47, 115.48 (d, J_{C-F} = 21.4 Hz), 115.20 (d, J_{C-F} = 21.4 Hz), 70.88, 38.25, 19.14 (one carbon signal is missing due to the overlap of aromatic carbon peaks); **^{19}F NMR (564 MHz, CDCl$_3$)** δ -115.11, -115.49; **HRMS** m/z (FAB) calc. for $C_{23}H_{19}F_2$ [M−H$_2$O+H]$^+$ 333.1455, found 333.1458; ***R$_f$*** 0.45 (Hex/EtOAc, 4/1).



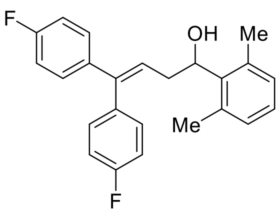
4,4-bis(4-fluorophenyl)-1-(*m*-tolyl)but-3-en-1-ol, **3ac**; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.24 – 7.20 (m, 1H), 7.13 – 7.07 (m, 5H), 7.04 – 6.98 (m, 4H), 6.95 – 6.91 (m, 2H), 6.06 (dd, J = 7.5, 7.4 Hz, 1H), 4.79 – 4.75 (m, 1H), 2.62 – 2.49 (m, 2H), 2.34 (s, 3H), 1.88 (d, J = 3.1 Hz, 1H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 162.39 (d, J_{C-F} = 246.5 Hz), 162.18 (d, J_{C-F} = 246.2 Hz), 144.03, 142.35, 138.71 (d, J_{C-F} = 3.2 Hz), 138.39, 135.69 (d, J_{C-F} = 3.8 Hz), 131.63 (d, J_{C-F} = 8.1 Hz), 128.99 (d, J_{C-F} = 8.1 Hz), 128.68, 128.59, 126.71, 125.42, 123.15, 115.43 (d, J_{C-F} = 21.4 Hz), 115.17 (d, J_{C-F} = 21.4 Hz), 74.56, 39.54, 21.66; **^{19}F NMR (564 MHz, CDCl$_3$)** δ -115.12, -115.50; **HRMS** m/z (FAB) calc. for $C_{23}H_{19}F_2$ [M−H$_2$O+H]$^+$ 333.1455, found 333.1451; ***R$_f$*** 0.43 (Hex/EtOAc, 4/1).



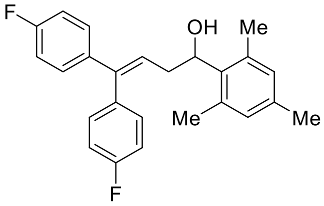
4,4-bis(4-fluorophenyl)-1-(*p*-tolyl)but-3-en-1-ol, **3ad**; **^{1}H NMR (600 MHz, $CDCl_3$)** 7.18 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 7.12 (dd, J = 8.7 Hz, J_{H-F} = 5.5 Hz, 2H), 7.04 – 7.00 (m, 4H), 6.93 (dd, J_{H-F} = 8.7 Hz, J = 8.7 Hz, 2H), 6.05 (dd, J = 7.5, 7.3 Hz, 1H), 4.77 (dd, J = 7.5, 5.7 Hz, 1H), 2.59 (ddd, J = 14.8, 7.5, 7.5 Hz, 1H), 2.52 (ddd, J = 14.8, 7.3, 5.7 Hz, 1H), 2.34 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.39 (d, J_{C-F} = 246.8 Hz), 162.19 (d, J_{C-F} = 246.5 Hz), 142.30, 141.14, 138.71 (d, J_{C-F} = 2.9 Hz), 137.65, 135.71 (d, J_{C-F} = 3.5 Hz), 131.63 (d, J_{C-F} = 7.8 Hz), 129.37, 128.99 (d, J_{C-F} = 8.1 Hz), 126.00, 125.46 (d, J_{C-F} = 1.0 Hz), 115.44 (d, J_{C-F} = 21.1 Hz), 115.17 (d, J_{C-F} = 21.4 Hz), 74.40, 39.57, 21.33; **^{19}F NMR (564 MHz, $CDCl_3$)** δ -115.00, -115.41; **HRMS** m/z (FAB) calc. for $C_{23}H_{19}F_2$ $[M-H_2O+H]^+$ 333.1455, found 333.1457; ***R_f*** 0.40 (Hex/EtOAc, 4/1).



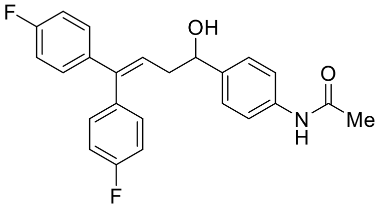
4,4-bis(4-fluorophenyl)-1-(2-methoxyphenyl)but-3-en-1-ol, **3ae**; **^{1}H NMR (600 MHz, $CDCl_3$)** 7.27 – 7.22 (m, 2H), 7.11 (dd, J = 8.5 Hz, J_{H-F} = 5.5 Hz, 2H), 7.02 – 6.97 (m, 4H), 6.96 – 6.90 (m, 3H), 6.84 (d, J = 8.2 Hz, 1H), 6.12 (dd, J = 7.5, 7.5 Hz, 1H), 4.99 – 4.95 (m, 1H), 3.75 (s, 3H), 2.64 – 2.58 (m, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.31 (d, J_{C-F} = 246.2 Hz), 162.10 (d, J_{C-F} = 245.8 Hz), 156.68, 141.75, 138.85 (d, J_{C-F} = 3.8 Hz), 135.89 (d, J_{C-F} = 3.5 Hz), 131.79, 131.69 (d, J_{C-F} = 8.1 Hz), 128.94 (d, J_{C-F} = 7.8 Hz), 128.67, 127.21, 126.19, 120.95, 115.28 (d, J_{C-F} = 21.1 Hz), 115.11 (d, J_{C-F} = 21.4 Hz), 110.71, 71.32, 55.34, 37.74; **^{19}F NMR (564 MHz, $CDCl_3$)** δ -115.46, -115.76; **HRMS** m/z (FAB) calc. for $C_{23}H_{19}F_2O$ $[M-H_2O+H]^+$ 349.1404, found 349.1407; ***R_f*** 0.39 (Hex/EtOAc, 4/1).



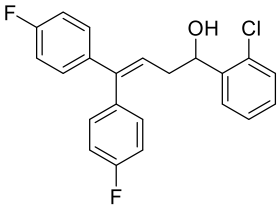
1-(2,6-dimethylphenyl)-4,4-bis(4-fluorophenyl)but-3-en-1-ol, **3af**; **^{1}H NMR (600 MHz, $CDCl_3$)** 7.15 – 7.11 (m, 2H), 7.06 – 7.01 (m, 5H), 6.97 – 6.92 (m, 4H), 6.12 (dd, J = 7.7, 7.7 Hz, 1H), 5.27 (dd, J = 8.6, 6.0 Hz, 1H), 2.78 (ddd, J = 14.3, 8.6, 7.7 Hz, 1H), 2.54 (ddd, J = 14.3, 7.7, 6.0 Hz, 1H), 2.33 (s, 6H), 1.81 (bs, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.39 (d, J_{C-F} = 246.4 Hz), 162.22 (d, J_{C-F} = 246.1 Hz), 142.29, 139.00, 138.49 (d, J_{C-F} = 3.8 Hz), 135.64 (d, J_{C-F} = 3.7 Hz), 131.65 (d, J_{C-F} = 7.8 Hz), 129.70, 128.86 (d, J_{C-F} = 7.8 Hz), 128.25, 127.49, 125.81, 115.49 (d, J_{C-F} = 21.4 Hz), 115.22 (d, J_{C-F} = 21.4 Hz), 71.58, 36.04, 20.94; **^{19}F NMR (564 MHz, $CDCl_3$)** δ -115.12, -115.47; **HRMS** m/z (FAB) calc. for $C_{24}H_{21}F_2$ $[M-H_2O+H]^+$ 347.1611, found 347.1609; ***R_f*** 0.46 (Hex/EtOAc, 4/1).



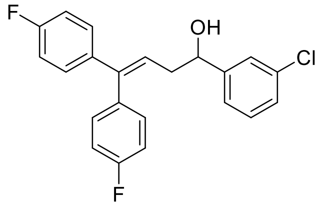
4,4-bis(4-fluorophenyl)-1-mesitylbut-3-en-1-ol, **3ag**; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.13 (dd, *J* = 8.5 Hz, $J_{H\text{-}F}$ = 5.4 Hz, 2H), 7.05 – 7.00 (m, 4H), 6.94 (dd, $J_{H\text{-}F}$ = 8.8 Hz, *J* = 8.5 Hz, 2H), 6.79 (s, 2H), 6.11 (dd, *J* = 7.6, 7.6 Hz, 1H), 5.23 (dd, *J* = 8.7, 6.0 Hz, 1H), 2.77 (ddd, *J* = 14.1, 8.7, 7.6 Hz, 1H), 2.51 (ddd, *J* = 14.1, 7.6, 6.0 Hz, 1H), 2.29 (s, 6H), 2.24 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.37 (d, $J_{C\text{-}F}$ = 246.5 Hz), 162.21 (d, $J_{C\text{-}F}$ = 246.2 Hz), 142.15, 138.53 (d, $J_{C\text{-}F}$ = 3.1 Hz), 137.00, 136.23, 136.10, 135.68 (d, $J_{C\text{-}F}$ = 3.4 Hz), 131.66 (d, $J_{C\text{-}F}$ = 8.1 Hz), 130.42, 128.86 (d, $J_{C\text{-}F}$ = 7.8 Hz), 126.00, 115.46 (d, $J_{C\text{-}F}$ = 21.4 Hz), 115.20 (d, $J_{C\text{-}F}$ = 21.4 Hz), 71.44, 36.16, 20.92, 20.82; **^{19}F NMR (564 MHz, $CDCl_3$)** δ -115.18, -115.53; **HRMS** m/z (FAB) calc. for $C_{25}H_{23}F_2$ $[M-H_2O+H]^+$ 361.1768, found 361.1769; ***R**f* 0.47 (Hex/EtOAc, 4/1).



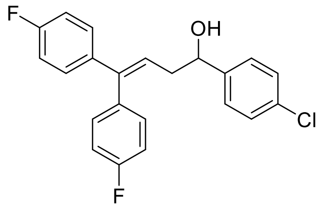
N-(4-(4,4-bis(4-fluorophenyl)-1-hydroxybut-3-en-1-yl)phenyl)acetamide, **3ah**; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.46 (d, *J* = 8.2 Hz, 2H), 7.26 – 7.23 (m, 2H), 7.15 (bs, 1H), 7.10 (dd, *J* = 8.9 Hz, $J_{H\text{-}F}$ = 5.4 Hz, 2H), 7.03 – 7.00 (m, 4H), 6.93 (dd, $J_{H\text{-}F}$ = 9.7 Hz, *J* = 8.9 Hz, 2H), 6.02 (dd, *J* = 7.2, 7.2 Hz, 1H), 4.77 (dd, *J* = 6.5, 6.5 Hz, 1H), 2.58 (ddd, *J* = 14.7, 7.4, 6.5 Hz, 1H), 2.51 (ddd, *J* = 14.2, 7.4, 6.5 Hz, 1H), 2.18 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 168.41, 162.41 (d, $J_{C\text{-}F}$ = 246.6 Hz), 162.21 (d, $J_{C\text{-}F}$ = 246.3 Hz), 142.52, 140.02, 138.61 (d, $J_{C\text{-}F}$ = 4.0 Hz), 137.52, 135.63 (d, $J_{C\text{-}F}$ = 2.8 Hz), 131.61 (d, $J_{C\text{-}F}$ = 7.8 Hz), 128.98 (d, $J_{C\text{-}F}$ = 8.1 Hz), 126.76, 125.08, 120.10, 115.50 (d, $J_{C\text{-}F}$ = 21.1 Hz), 115.20 (d, $J_{C\text{-}F}$ = 21.4 Hz), 74.06, 39.53, 24.85; **^{19}F NMR (564 MHz, $CDCl_3$)** δ -114.97, -115.42; **HRMS** m/z (FAB) calc. for $C_{24}H_{22}F_2NO_2$ $[M+H]^+$ 394.1619, found 349.1617; ***R**f* 0.13 (Hex/EtOAc, 1/1).



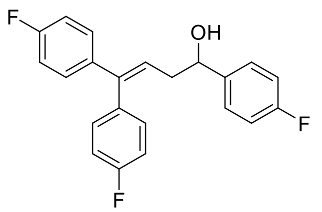
1-(2-chlorophenyl)-4,4-bis(4-fluorophenyl)but-3-en-1-ol, **3ai**; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.29 – 7.28 (m, 1H), 7.26 – 7.24 (m, 2H), 7.16 – 7.14 (m, 1H), 7.11 (dd, *J* = 8.8 Hz, $J_{H\text{-}F}$ = 5.5 Hz, 2H), 7.07 – 7.01 (m, 2H), 6.99 (dd, *J* = 8.5 Hz, $J_{H\text{-}F}$ = 5.7 Hz, 2H), 6.97 – 6.91 (m, 2H), 6.03 (dd, *J* = 7.5, 7.5 Hz, 1H), 4.79 (dd, *J* = 7.1, 5.7 Hz, 1H), 2.61 – 2.49 (m, 2H), 1.97 (bs, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.45 (d, $J_{C\text{-}F}$ = 246.8 Hz), 162.23 (d, $J_{C\text{-}F}$ = 246.5 Hz), 146.08, 142.93, 138.50 (d, $J_{C\text{-}F}$ = 3.5 Hz), 135.49 (d, $J_{C\text{-}F}$ = 3.8 Hz), 134.64, 131.53 (d, $J_{C\text{-}F}$ = 7.8 Hz), 129.93, 128.98 (d, $J_{C\text{-}F}$ = 7.8 Hz), 127.99, 126.27, 124.54, 124.21, 115.54 (d, $J_{C\text{-}F}$ = 21.1 Hz), 115.24 (d, $J_{C\text{-}F}$ = 21.4 Hz), 73.82, 39.48; **^{19}F NMR (564 MHz, $CDCl_3$)** δ -114.81, -115.23; **HRMS** m/z (FAB) calc. for $C_{22}H_{16}ClF_2$ $[M-H_2O+H]^+$ 353.0909, found 353.0905; ***R**f* 0.47 (Hex/EtOAc, 4/1).



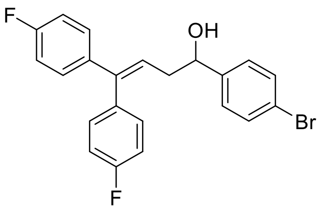
1-(3-chlorophenyl)-4,4-bis(4-fluorophenyl)but-3-en-1-ol, **3aj**; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.30 – 7.28 (m, 1H), 7.26 – 7.24 (m, 2H), 7.17 – 7.14 (m, 1H), 7.11 (dd, *J* = 8.8 Hz, J_{H-F} = 5.4 Hz, 2H), 7.05 – 7.02 (m, 2H), 6.99 (dd, *J* = 8.4 Hz, J_{H-F} = 5.9 Hz, 2H), 6.97 – 6.91 (m, 2H), 6.02 (dd, *J* = 7.5, 7.5 Hz, 1H), 4.79 (dd, *J* = 6.4, 6.4 Hz, 1H), 2.61 – 2.49 (m, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.46 (d, J_{C-F} = 246.7 Hz), 162.24 (d, J_{C-F} = 246.7 Hz), 146.09, 142.95, 138.50 (d, J_{C-F} = 3.1 Hz), 135.50 (d, J_{C-F} = 3.2 Hz), 134.66, 131.54 (d, J_{C-F} = 8.1 Hz), 129.94, 128.99 (d, J_{C-F} = 8.1 Hz), 128.01, 126.28, 124.54, 124.22, 115.55 (d, J_{C-F} = 21.4 Hz), 115.24 (d, J_{C-F} = 21.7 Hz), 73.82, 39.49; **^{19}F NMR (564 MHz, $CDCl_3$)** δ -114.82, -115.23; **HRMS** m/z (FAB) calc. for $C_{22}H_{16}ClF_2$ $[M{-}H_2O{+}H]^+$ 353.0909, found 353.0912; ***R_f*** 0.38 (Hex/EtOAc, 4/1).



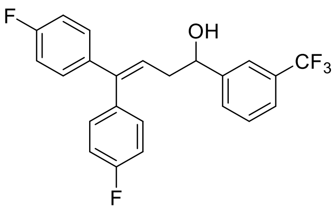
1-(4-chlorophenyl)-4,4-bis(4-fluorophenyl)but-3-en-1-ol, **3ak**; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.30 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.5 Hz, 2H), 7.11 (dd, *J* = 8.7 Hz, J_{H-F} = 5.4 Hz, 2H), 7.03 (dd, J_{H-F} = 8.7 Hz, *J* = 8.7 Hz, 2H), 6.99 (dd, *J* = 8.5 Hz, J_{H-F} = 5.8 Hz, 2H), 6.94 (dd, J_{H-F} = 8.7 Hz, *J* = 8.5 Hz, 2H), 6.02 (dd, *J* = 7.5, 7.5 Hz, 1H), 4.79 (dd, *J* = 6.4, 6.4 Hz, 1H), 2.61 – 2.47 (m, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.46 (d, J_{C-F} = 246.8 Hz), 162.23 (d, J_{C-F} = 246.5 Hz), 142.86, 142.50, 138.49 (d, J_{C-F} = 3.2 Hz), 135.52 (d, J_{C-F} = 3.5 Hz), 133.58, 131.55 (d, J_{C-F} = 7.8 Hz), 128.97 (d, J_{C-F} = 8.1 Hz), 128.81, 127.43, 124.60, 115.52 (d, J_{C-F} = 21.4 Hz), 115.25 (d, J_{C-F} = 21.4 Hz), 73.79, 39.58; **^{19}F NMR (564 MHz, $CDCl_3$)** δ -114.83, -115.22; **HRMS** m/z (FAB) calc. for $C_{22}H_{16}ClF_2$ $[M{-}H_2O{+}H]^+$ 353.0909, found 353.0906; ***R_f*** 0.35 (Hex/EtOAc, 4/1).



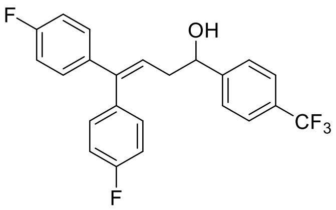
1,4,4-tris(4-fluorophenyl)but-3-en-1-ol, **3al**; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.26 (dd, *J* = 8.4 Hz, J_{H-F} = 5.6 Hz, 2H), 7.11 (dd, *J* = 8.8 Hz, J_{H-F} = 5.4 Hz, 2H), 7.05 – 6.98 (m, 6H), 6.95 – 6.92 (m, 2H), 6.02 (dd, *J* = 7.5, 7.3 Hz, 1H), 4.80 (dd, *J* = 7.1, 5.8 Hz, 1H), 2.58 (ddd, *J* = 14.8, 7.5, 7.1 Hz, 1H), 2.51 (ddd, *J* = 14.6, 7.3, 5.8 Hz, 1H), 1.90 (bs, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.23 (d, J_{C-F} = 245.6 Hz), 162.21 (d, J_{C-F} = 246.8 Hz), 161.99 (d, J_{C-F} = 246.5 Hz), 142.48, 139.55 (d, J_{C-F} = 2.9 Hz), 138.32 (d, J_{C-F} = 3.5 Hz), 135.34 (d, J_{C-F} = 3.5 Hz), 131.33 (d, J_{C-F} = 7.8 Hz), 128.73 (d, J_{C-F} = 7.8 Hz), 127.47 (d, J_{C-F} = 8.1 Hz), 124.61, 115.28 (d, J_{C-F} = 21.2 Hz), 115.27 (d, J_{C-F} = 21.4 Hz), 115.00 (d, J_{C-F} = 21.4 Hz), 73.61, 39.42; **^{19}F NMR (564 MHz, $CDCl_3$)** δ -114.78, -114.86, -115.26; **HRMS** m/z (FAB) calc. for $C_{22}H_{16}F_3$ $[M{-}H_2O{+}H]^+$ 337.1204, found 337.1201; ***R_f*** 0.32 (Hex/EtOAc, 4/1).



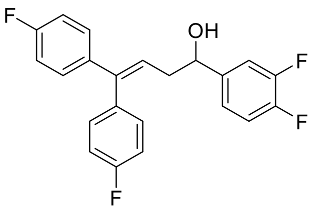
1-(4-bromophenyl)-4,4-bis(4-fluorophenyl)but-3-en-1-ol, **3am**; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.45 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H), 7.11 (dd, J = 8.9 Hz, J_{H-F} = 5.4 Hz, 2H), 7.03 (dd, J_{H-F} = 8.8 Hz, J = 8.6 Hz, 2H), 6.99 (dd, J = 8.6 Hz, J_{H-F} = 5.7 Hz, 2H), 6.94 (dd, J = 8.9 Hz, J_{H-F} = 8.5 Hz, 2H), 6.02 (dd, J = 7.5, 7.5 Hz, 1H), 4.77 (dd, J = 6.5, 6.4 Hz, 1H), 2.65 – 2.48 (m, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.46 (d, J_{C-F} = 246.8 Hz), 162.22 (d, J_{C-F} = 246.5 Hz), 143.02, 142.88, 138.48 (d, J_{C-F} = 3.4 Hz), 135.50 (d, J_{C-F} = 3.5 Hz), 131.75, 131.54 (d, J_{C-F} = 7.8 Hz), 128.96 (d, J_{C-F} = 8.1 Hz), 127.78, 124.54, 121.65, 115.52 (d, J_{C-F} = 21.4 Hz), 115.25 (d, J_{C-F} = 21.4 Hz), 73.82, 39.54; **^{19}F NMR (564 MHz, $CDCl_3$)** δ -114.69, -115.08; **HRMS** m/z (FAB) calc. for $C_{22}H_{16}BrF_2$ [M−H_2O+H]$^+$ 397.0403, found 397.0407; $\boldsymbol{R_f}$ 0.36 (Hex/EtOAc, 4/1).



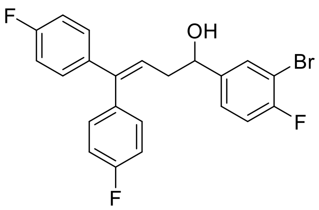
4,4-bis(4-fluorophenyl)-1-(3-(trifluoromethyl)phenyl)but-3-en-1-ol, **3an**; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.56 (s, 1H), 7.55 – 7.52 (m, 1H), 7.48 – 7.42 (m, 2H), 7.10 (dd, J = 8.9 Hz, J_{H-F} = 5.4 Hz, 2H), 7.04 – 7.00 (m, 2H), 6.97 – 6.91 (m, 4H), 6.03 (dd, J = 7.5, 7.4 Hz, 1H), 4.89 (dd, J = 6.4, 6.3 Hz, 1H), 2.64 – 2.52 (m, 2H), 2.02 (bs, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.49 (d, J_{C-F} = 246.8 Hz), 162.26 (d, J_{C-F} = 246.8 Hz), 144.97, 143.18, 138.44 (d, J_{C-F} = 3.2 Hz), 135.44 (d, J_{C-F} = 3.2 Hz), 131.47 (d, J_{C-F} = 7.8 Hz), 131.03 (q, J_{C-F} = 31.9 Hz), 129.42, 129.10, 128.97 (d, J_{C-F} = 8.0 Hz), 124.66 (q, J_{C-F} = 3.8 Hz), 124.31 (q, J_{C-F} = 272.5 Hz), 124.25, 122.89 (q, J_{C-F} = 3.8 Hz), 115.55 (d, J_{C-F} = 21.4 Hz), 115.26 (d, J_{C-F} = 21.4 Hz), 73.83, 39.58; **^{19}F NMR (564 MHz, $CDCl_3$)** δ -62.60, -114.75, -115.14; **HRMS** m/z (FAB) calc. for $C_{23}H_{16}F_5$ [M−H_2O+H]$^+$ 387.1172, found 387.1174; $\boldsymbol{R_f}$ 0.38 (Hex/EtOAc, 4/1).



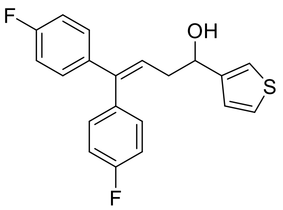
4,4-bis(4-fluorophenyl)-1-(4-(trifluoromethyl)phenyl)but-3-en-1-ol, **3ao**; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.58 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 7.12 (dd, J = 8.6 Hz, J_{H-F} = 5.4 Hz, 2H), 7.03 – 7.00 (m, 2H), 6.98 – 6.93 (m, 4H), 6.05 (dd, J = 7.5, 7.4 Hz, 1H), 4.88 (dd, J = 6.5, 6.4 Hz, 1H), 2.61 – 2.53 (m, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.50 (d, J_{C-F} = 247.1 Hz), 162.24 (d, J_{C-F} = 246.5 Hz), 147.96, 143.17, 138.40 (d, J_{C-F} = 3.4 Hz), 135.42 (d, J_{C-F} = 3.4 Hz), 131.49 (d, J_{C-F} = 8.0 Hz), 130.07 (q, J_{C-F} = 32.8 Hz), 128.96 (d, J_{C-F} = 8.1 Hz), 126.32, 126.17 (q, J_{C-F} = 276.2 Hz), 125.60 (q, J_{C-F} = 3.8 Hz), 124.22, 115.55 (d, J_{C-F} = 21.3 Hz), 115.28 (d, J_{C-F} = 21.4 Hz), 73.81, 39.62; **^{19}F NMR (564 MHz, $CDCl_3$)** δ -62.49, -114.71, -115.08; **HRMS** m/z (FAB) calc. for $C_{23}H_{16}F_5$ [M−H_2O+H]$^+$ 387.1172, found 387.1170; $\boldsymbol{R_f}$ 0.35 (Hex/EtOAc, 4/1).



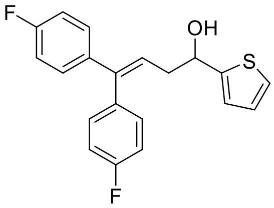
1-(3,4-difluorophenyl)-4,4-bis(4-fluorophenyl)but-3-en-1-ol, **3ap**; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.14 – 7.08 (m, 4H), 7.06 – 7.01 (m, 4H), 7.00 – 6.97 (m, 1H), 6.96 – 6.92 (m, 2H), 6.01 (dd, *J* = 7.5, 7.4 Hz, 1H), 4.77 (dd, *J* = 7.1, 5.7 Hz, 1H), 2.59 – 2.47 (m, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.50 (d, J_{C-F} = 247.1 Hz), 162.27 (d, J_{C-F} = 246.8 Hz), 150.58 (dd, J_{C-F} = 248.8, 12.7 Hz), 149.90 (dd, J_{C-F} = 247.9, 12.8 Hz), 143.13, 141.10 (dd, J_{C-F} = 5.0, 3.6 Hz), 138.41 (d, J_{C-F} = 3.5 Hz), 135.45 (d, J_{C-F} = 3.3 Hz), 131.53 (d, J_{C-F} = 8.1 Hz), 128.97 (d, J_{C-F} = 8.1 Hz), 124.28, 121.93 (dd, J_{C-F} = 6.2, 3.6 Hz), 117.35 (d, J_{C-F} = 17.1 Hz), 115.59 (d, J_{C-F} = 21.4 Hz), 115.29 (d, J_{C-F} = 21.4 Hz), 115.06 (d, J_{C-F} = 17.9 Hz), 73.33, 39.58; **^{19}F NMR (564 MHz, $CDCl_3$)** δ -114.65, -115.08, -137.33, -139.37; **HRMS** m/z (FAB) calc. for $C_{22}H_{15}F_4$ $[M-H_2O+H]^+$ 355.1110, found 355.1107; ***R_f*** 0.30 (Hex/EtOAc, 4/1).



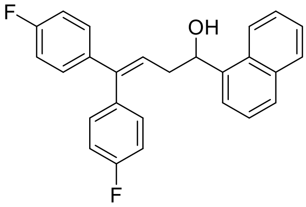
1-(3-bromo-4-fluorophenyl)-4,4-bis(4-fluorophenyl)but-3-en-1-ol, **3aq**; **^{1}H NMR (600 MHz, $CDCl_3$)** 7.49 (dd, J_{H-F} = 6.6 Hz, *J* = 2.2 Hz, 1H), 7.18 (ddd, *J* = 8.6, 2.2 Hz, J_{H-F} = 4.7 Hz, 1H), 7.11 (dd, *J* = 8.9 Hz, J_{H-F} = 5.3 Hz, 2H), 7.08 – 7.03 (m, 3H), 6.99 (dd, *J* = 8.7 Hz, J_{H-F} = 5.5 Hz, 2H), 6.94 (dd, *J* = 8.9, 8.6 Hz, 2H), 6.00 (dd, *J* = 7.5, 7.4 Hz, 1H), 4.77 (dd, *J* = 6.5, 6.4 Hz, 1H), 2.60 – 2.47 (m, 2H), 1.76 (bs, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.50 (d, J_{C-F} = 246.8 Hz), 162.26 (d, J_{C-F} = 246.8 Hz), 158.62 (d, J_{C-F} = 247.3 Hz), 143.16, 141.40 (d, J_{C-F} = 3.8 Hz), 138.41 (d, J_{C-F} = 3.2 Hz), 135.43 (d, J_{C-F} = 3.9 Hz), 131.51 (d, J_{C-F} = 8.1 Hz), 131.22, 128.99 (d, J_{C-F} = 8.1 Hz), 126.61 (d, J_{C-F} = 7.2 Hz), 124.22, 116.52 (d, J_{C-F} = 22.5 Hz), 115.60 (d, J_{C-F} = 21.4 Hz), 115.28 (d, J_{C-F} = 21.7 Hz), 109.28 (d, J_{C-F} = 21.1 Hz), 73.21, 39.56; **^{19}F NMR (564 MHz, $CDCl_3$)** δ -109.01, -114.65, -115.07; **HRMS** m/z (FAB) calc. for $C_{22}H_{15}BrF_3$ $[M-H_2O+H]^+$ 415.0309, found 415.0311; ***R_f*** 0.29 (Hex/EtOAc, 4/1).



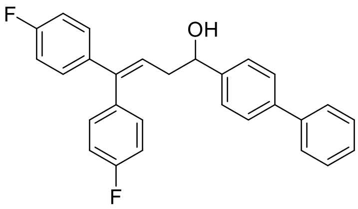
4,4-bis(4-fluorophenyl)-1-(thiophen-3-yl)but-3-en-1-ol, **3ar**; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.29 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.17 (dd, *J* = 3.0, 1.2 Hz, 1H), 7.12 (dd, *J* = 8.6 Hz, J_{H-F} = 5.6 Hz, 2H), 7.05 – 7.03 (m, 4H), 7.00 (dd, *J* = 5.0, 1.2 Hz, 1H), 6.96 – 6.92 (m, 2H), 6.05 (dd, *J* = 7.5, 7.4 Hz, 1H), 4.91 (dd, *J* = 6.4, 6.5 Hz, 1H), 2.65 – 2.55 (m, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.43 (d, J_{C-F} = 246.9 Hz), 162.23 (d, J_{C-F} = 246.3 Hz), 145.63, 142.55, 138.63, 135.69, 131.62 (d, J_{C-F} = 7.8 Hz), 129.01 (d, J_{C-F} = 8.1 Hz), 126.45, 125.84, 125.05, 121.10, 115.51 (d, J_{C-F} = 21.1 Hz), 115.21 (d, J_{C-F} = 21.4 Hz), 70.67, 38.94; **^{19}F NMR (564 MHz, $CDCl_3$)** δ -112.45, -112.87; **HRMS** m/z (FAB) calc. for $C_{20}H_{15}F_2S$ $[M-H_2O+H]^+$ 325.0863, found 325.0864; ***R_f*** 0.30 (Hex/EtOAc, 4/1).



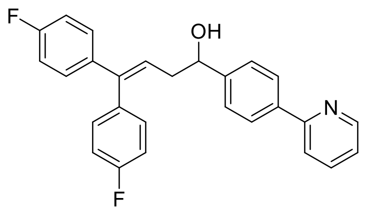
4,4-bis(4-fluorophenyl)-1-(thiophen-2-yl)but-3-en-1-ol, **3as**; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.25 (dd, *J* = 4.9, 1.3 Hz, 1H), 7.13 (dd, *J* = 8.6 Hz, $J_{H\text{-}F}$ = 5.6 Hz, 2H), 7.08 – 7.03 (m, 4H), 6.97 – 6.92 (m, 4H), 6.07 (dd, *J* = 7.5, 7.4 Hz, 1H), 5.06 (dd, *J* = 6.6, 6.5 Hz, 1H), 2.73 – 2.61 (m, 2H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 162.45 (d, $J_{C\text{-}F}$ = 246.8 Hz), 162.25 (d, $J_{C\text{-}F}$ = 246.5 Hz), 147.98, 142.78, 138.61 (d, $J_{C\text{-}F}$ = 3.3 Hz), 135.61 (d, $J_{C\text{-}F}$ = 3.4 Hz), 131.61 (d, $J_{C\text{-}F}$ = 7.8 Hz), 129.06 (d, $J_{C\text{-}F}$ = 8.1 Hz), 126.91, 124.99, 124.64, 124.03, 115.54 (d, $J_{C\text{-}F}$ = 21.4 Hz), 115.21 (d, $J_{C\text{-}F}$ = 21.4 Hz), 70.39, 39.70; **^{19}F NMR (564 MHz, CDCl$_3$)** δ -112.44, -112.87; **HRMS** m/z (FAB) calc. for $C_{20}H_{15}F_2S$ $[M-H_2O+H]^+$ 325.0863, found 325.0865; ***R_f*** 0.33 (Hex/EtOAc, 4/1).



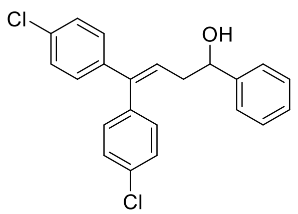
4,4-bis(4-fluorophenyl)-1-(naphthalen-1-yl)but-3-en-1-ol, **3at**; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.87 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.62 (d, *J* = 7.1 Hz, 1H), 7.49 – 7.45 (m, 2H), 7.42 (ddd, *J* = 8.2, 6.8, 1.4 Hz, 1H), 7.11 (dd, *J* = 8.7 Hz, $J_{H\text{-}F}$ = 5.6 Hz, 2H), 6.95 – 6.94 (m, 4H), 6.93 – 6.91 (m, 2H), 6.21 (dd, *J* = 7.5, 7.5 Hz, 1H), 5.58 (dd, *J* = 7.6, 4.9 Hz, 1H), 2.80 (ddd, *J* = 14.9, 7.5, 4.9 Hz, 1H), 2.70 (ddd, *J* = 14.9, 7.6, 7.5 Hz, 1H), 1.75 (bs, 1H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 162.39 (d, $J_{C\text{-}F}$ = 246.8 Hz), 162.14 (d, $J_{C\text{-}F}$ = 246.2 Hz), 142.42, 139.63, 138.53 (d, $J_{C\text{-}F}$ = 3.2 Hz), 135.60 (d, $J_{C\text{-}F}$ = 3.5 Hz), 133.98, 131.53 (d, $J_{C\text{-}F}$ = 8.1 Hz), 130.43, 129.13, 128.92 (d, $J_{C\text{-}F}$ = 8.1 Hz), 128.33, 126.22, 125.80, 125.59, 125.56, 123.11, 123.08, 115.42 (d, $J_{C\text{-}F}$ = 21.4 Hz), 115.17 (d, $J_{C\text{-}F}$ = 21.4 Hz), 71.43, 38.45; **^{19}F NMR (564 MHz, CDCl$_3$)** δ -115.04, -115.33; **HRMS** m/z (FAB) calc. for $C_{26}H_{19}F_2$ $[M-H_2O+H]^+$ 369.1455, found 369.1458; ***R_f*** 0.36 (Hex/EtOAc, 4/1).



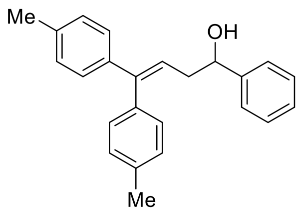
1-([1,1'-biphenyl]-4-yl)-4,4-bis(4-fluorophenyl)but-3-en-1-ol, **3au**; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.60 – 7.55 (m, 4H), 7.46 – 7.42 (m, 2H), 7.39 – 7.33 (m, 3H), 7.13 (ddd, *J* = 8.9, 1.6 Hz, $J_{H\text{-}F}$ = 5.3 Hz, 2H), 7.04 – 7.01 (m, 4H), 6.96 – 6.92 (m, 2H), 6.10 (dd, *J* = 7.5, 7.5 Hz, 1H), 4.86 (dd, *J* = 6.6, 6.5 Hz, 1H), 2.67 – 2.56 (m, 2H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 162.42 (d, $J_{C\text{-}F}$ = 246.8 Hz), 162.20 (d, $J_{C\text{-}F}$ = 246.2 Hz), 143.08, 142.57, 140.95, 140.90, 138.64 (d, $J_{C\text{-}F}$ = 3.3 Hz), 135.65 (d, $J_{C\text{-}F}$ = 3.2 Hz), 131.61 (d, $J_{C\text{-}F}$ = 7.8 Hz), 129.03, 128.99 (d, $J_{C\text{-}F}$ = 8.0 Hz), 127.58, 127.42, 127.27, 126.51, 125.15, 115.47 (d, $J_{C\text{-}F}$ = 21.1 Hz), 115.21 (d, $J_{C\text{-}F}$ = 21.1 Hz), 74.28, 39.59; **^{19}F NMR (564 MHz, CDCl$_3$)** δ -114.86, -115.26; **HRMS** m/z (FAB) calc. for $C_{28}H_{21}F_2$ $[M-H_2O+H]^+$ 395.1611, found 395.1609; ***R_f*** 0.30 (Hex/EtOAc, 4/1).



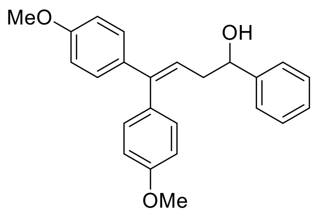
4,4-bis(4-fluorophenyl)-1-(4-(pyridin-2-yl)phenyl)but-3-en-1-ol, **3av**; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.74 (d, *J* = 5.1 Hz, 1H), 8.00 (d, *J* = 8.1 Hz, 2H), 7.88 (dd, *J* = 8.0, 7.6 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.35 (dd, *J* = 7.6, 5.1 Hz, 1H), 7.12 (dd, *J* = 8.7 Hz, $J_{H\text{-}F}$ = 5.5 Hz, 2H), 7.05 – 7.00 (m, 4H), 6.93 (dd, *J* = 8.7 Hz, $J_{H\text{-}F}$ = 8.7 Hz, 2H), 6.06 (dd, *J* = 7.6, 7.5 Hz, 1H), 4.88 (dd, *J* = 6.6, 6.5 Hz, 1H), 2.66 – 2.55 (m, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.42 (d, $J_{C\text{-}F}$ = 246.8 Hz), 162.21 (d, $J_{C\text{-}F}$ = 246.5 Hz), 156.28, 148.28, 145.95, 142.69, 138.88, 138.56 (d, $J_{C\text{-}F}$ = 3.3 Hz), 136.78, 135.60 (d, $J_{C\text{-}F}$ = 3.5 Hz), 131.60 (d, $J_{C\text{-}F}$ = 8.1 Hz), 128.99 (d, $J_{C\text{-}F}$ = 8.1 Hz), 127.58, 126.73, 124.87, 122.82, 121.58, 115.51 (d, $J_{C\text{-}F}$ = 21.4 Hz), 115.21 (d, $J_{C\text{-}F}$ = 21.4 Hz), 74.05, 39.54; **^{19}F NMR (564 MHz, $CDCl_3$)** δ -112.43, -112.87; **HRMS** m/z (FAB) calc. for $C_{27}H_{22}F_2NO$ $[M+H]^+$ 414.1669, found 414.1673; ***R_f*** 0.43 (Hex/EtOAc, 1/1).



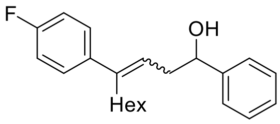
4,4-bis(4-chlorophenyl)-1-phenylbut-3-en-1-ol, **3ba**; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.35 – 7.32 (m, 2H), 7.31 – 7.28 (m, 5H), 7.21 (d, *J* = 8.3 Hz, 2H), 7.07 (d, *J* = 8.3 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.12 (dd, *J* = 7.5, 7.5 Hz, 1H), 4.82 (dd, *J* = 6.4, 6.4 Hz, 1H), 2.60 (ddd, *J* = 14.5, 7.5, 6.4 Hz, 1H), 2.53 (dt, *J* = 14.5, 7.5, 6.4 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 143.76, 141.94, 140.45, 137.69, 133.20, 133.14, 131.13, 128.55, 128.50, 128.44, 128.30, 127.77, 125.91, 125.80, 74.21, 39.37; **HRMS** m/z (EI) calc. for $C_{22}H_{17}Cl_2$ $[M-H_2O+H]^+$ 351.0707, found 351.0692; ***R_f*** 0.33 (Hex/EtOAc, 4/1).



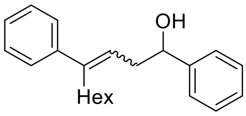
1-phenyl-4,4-di-*p*-tolylbut-3-en-1-ol, **3ca**; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.33 – 7.30 (m, 4H), 7.29 – 7.25 (m, 1H), 7.13 (d, *J* = 7.6 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 7.05 (d, *J* = 7.9 Hz, 2H), 6.97 (d, *J* = 7.6 Hz, 2H), 6.04 (dd, *J* = 7.4, 7.4 Hz, 1H), 4.80 (dd, *J* = 6.5, 6.5 Hz, 1H), 2.62 (ddd, *J* = 15.0, 7.4, 6.5 Hz, 1H), 2.56 (ddd, *J* = 15.0, 7.4, 6.5 Hz, 1H), 2.36 (s, 3H), 2.31 (s, 3H), 1.90 (bs, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 144.46, 144.23, 140.07, 137.13, 137.03, 136.81, 129.92, 129.10, 128.98, 128.61, 127.76, 127.39, 126.12, 123.83, 74.66, 39.72, 22.87, 21.27; **HRMS** m/z (EI) calc. for $C_{24}H_{23}$ $[M-H_2O+H]^+$ 311.1800, found 311.1798; ***R_f*** 0.38 (Hex/EtOAc, 4/1).



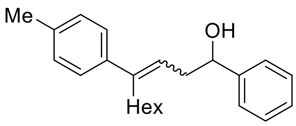
4,4-bis(4-methoxyphenyl)-1-phenylbut-3-en-1-ol, **3da**; **^{1}H NMR (600 MHz, CD_3CN)** δ 7.27 (dd, *J* = 7.0, 7.0 Hz, 2H), 7.24 (d, *J* = 7.0 Hz, 2H), 7.20 (t, *J* = 7.0 Hz, 1H), 7.03 (d, *J* = 8.9 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.77 (d, *J* = 8.9 Hz, 2H), 5.93 (dd, *J* = 7.4, 7.4 Hz, 1H), 4.69 (dd, J = 6.5, 4.0 Hz, 1H), 3.76 (s, 3H), 3.71 (s, 3H), 2.47 – 2.36 (m, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 159.91, 159.69, 146.18, 143.29, 136.58, 133.34, 131.85, 129.15, 129.10, 128.01, 126.84, 124.70, 114.46, 114.45, 74.40, 55.88, 40.77 (one carbon signal is missing due to the overlap); **HRMS** m/z (EI) calc. for $C_{24}H_{24}O_3$ $[M]^+$ 360.1725, found 360.1727; $\boldsymbol{R_f}$ 0.17 (Hex/EtOAc, 4/1).



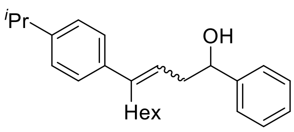
4-(4-fluorophenyl)-1-phenyldec-3-en-1-ol, **3ea**; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.38 (d, J = 7.5 Hz, 2H), 7.34 (dd, J = 7.6, 7.5 Hz, 2H), 7.29 – 7.26 (m, 1H), 7.22 (dd, J = 8.6, 5.6 Hz, 2H), 6.97 – 6.93 (m, 2H), 5.58 (dd, J = 7.3, 7.3 Hz, 1H), 4.79 (dd, J = 6.7, 6.7 Hz, 1H), 2.69 (ddd, J = 15.1, 7.6, 6.7 Hz, 1H), 2.65 – 2.57 (m, 1H), 2.41 – 2.38 (m, 2H), 1.23 – 1.16 (m, 8H), 0.83 (t, J = 7.1 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.07 (d, $J_{C\text{-}F}$ = 245.0 Hz), 144.38, 142.67, 139.25 (d, $J_{C\text{-}F}$ = 3.3 Hz), 128.63, 128.05 (d, $J_{C\text{-}F}$ = 7.8 Hz), 127.80, 126.04, 123.89, 115.10 (d, $J_{C\text{-}F}$ = 21.1 Hz), 74.45, 38.76, 31.82, 30.30, 29.39, 28.63, 22.76, 14.22; **HRMS** m/z (FAB) calc. for $C_{22}H_{27}FO$ $[M]^+$ 326.2046, found 326.2049; $\boldsymbol{R_f}$ 0.38 (Hex/EtOAc, 4/1).



1,4-diphenyldec-3-en-1-ol, **3fa**; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.41 (d, J = 7.4 Hz, 2H), 7.37 (dd, J = 8.4, 6.7 Hz, 2H), 7.32 – 7.28 (m, 6H), 5.66 (dd, J = 7.4, 7.4 Hz, 1H), 4.81 (dd, J = 7.7, 5.5 Hz, 1H), 2.72 (ddd, J = 15.2, 7.7, 7.4 Hz, 1H), 2.67 – 2.62 (ddd, J = 15.2, 7.4, 5.5 Hz, 1H), 2.47 – 2.44 (m, 2), 1.28 – 1.19 (m, 8H), 0.85 (t, J = 6.9 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 144.34, 143.91, 143.23, 128.66, 128.38, 127.81, 126.97, 126.60, 126.08, 123.76, 74.49, 38.85, 31.86, 30.23, 29.49, 28.80, 22.81, 14.26; **HRMS** m/z (FAB) calc. for $C_{22}H_{27}$ $[M-H_2O+H]^+$ 291.2113, found 291.2115; $\boldsymbol{R_f}$ 0.44 (Hex/EtOAc, 4/1).



1-phenyl-4-(p-tolyl)dec-3-en-1-ol, **3ga**; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.41 (d, J = 8.4 Hz, 2H), 7.39 – 7.36 (m, 1H), 7.34 – 7.30 (m, 1H), 7.22 (d, J = 8.1 Hz, 2H), 7.12 (d, J = 7.9 Hz, 2H), 5.64 (dd, J = 7.5, 7.5 Hz, 1H), 4.80 (dd, J = 7.7, 5.6 Hz, 1H), 2.72 (ddd, J = 15.2, 7.7, 7.5 Hz, 1H), 2.67 – 2.61 (ddd, J = 15.2, 7.5, 5.6 Hz, 1H), 2.46 – 2.43 (m, 2H), 2.35 (s, 3H), 1.30 – 1.21 (m, 8H), 0.86 (t, J = 7.0 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 144.37, 143.73, 140.26, 136.63, 129.08, 128.63, 127.76, 126.44, 126.07, 122.97, 74.44, 38.87, 31.86, 30.18, 29.51, 28.82, 22.81, 21.23, 14.26; **HRMS** m/z (FAB) calc. for $C_{23}H_{29}$ $[M-H_2O+H]^+$ 305.2269, found 305.2272; $\boldsymbol{R_f}$ 0.47 (Hex/EtOAc, 4/1).



4-(4-isopropylphenyl)-1-phenyldec-3-en-1-ol, **3ha**; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.41 (d, J = 7.1 Hz, 2H), 7.37 (dd, J = 7.3, 7.1 Hz, 2H), 7.29 (t, J = 7.3 Hz, 1H), 7.25 (d, J = 8.1 Hz, 2H), 7.16 (d, J = 8.1 Hz, 2H), 5.65

(dd, *J* = 7.4, 7.4 Hz, 1H), 4.80 (dd, *J* = 7.7, 5.6 Hz, 1H), 2.90 (p, *J* = 6.9 Hz, 1H), 2.72 (ddd, *J* = 14.9, 7.7, 7.4 Hz, 0H), 2.64 (ddd, *J* = 14.9, 7.4, 5.6 Hz, 1H), 2.47 – 2.44 (m, 2H), 1.26 (d, *J* = 6.9 Hz, 6H), 1.30 – 1.21 (m, 8H), 0.86 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 147.63, 144.36, 143.74, 140.55, 128.64, 127.76, 126.42, 126.40, 126.08, 122.97, 74.48, 38.90, 33.90, 31.87, 30.21, 29.57, 28.93, 24.18, 22.83, 14.27; **HRMS** m/z (FAB) calc. for $C_{25}H_{33}$ $[M-H_2O+H]^+$ 333.2582, found 333.2579; $\boldsymbol{R_f}$ 0.47 (Hex/EtOAc, 4/1).

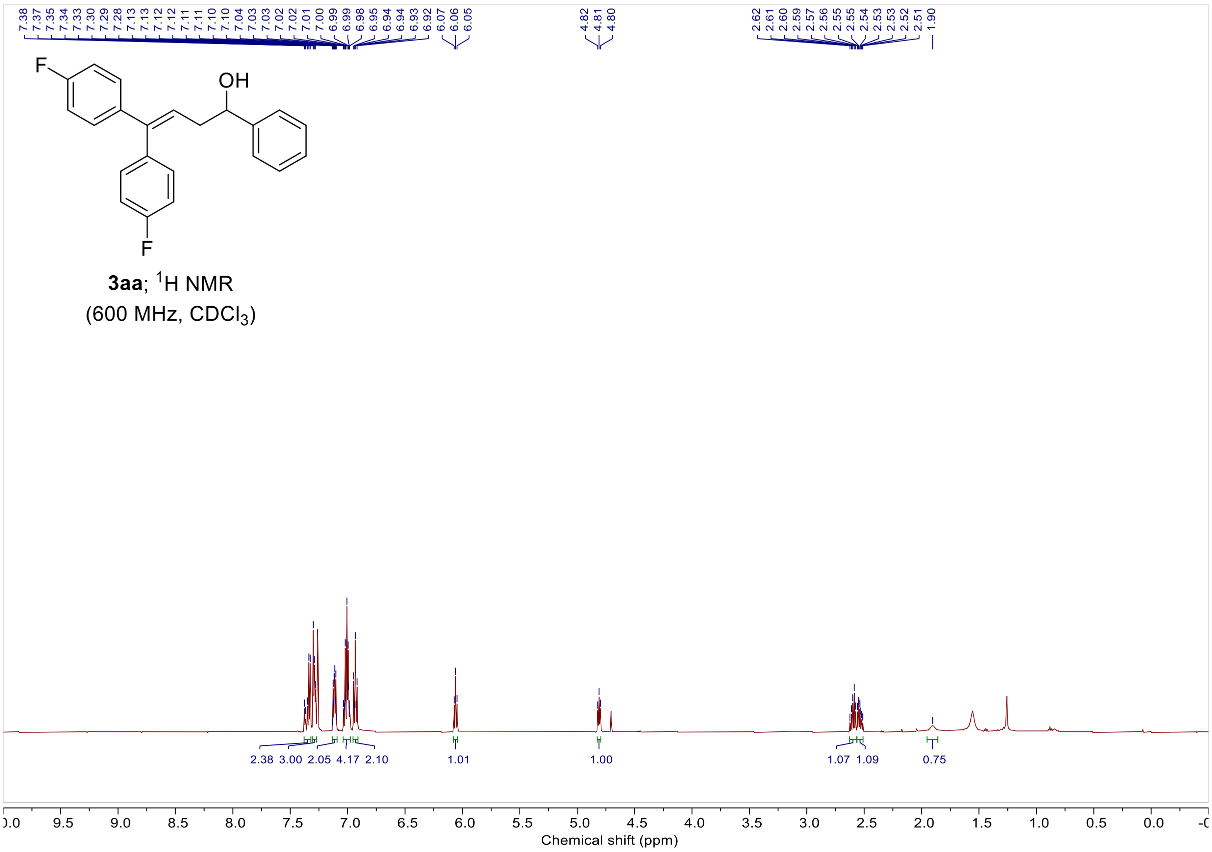
References

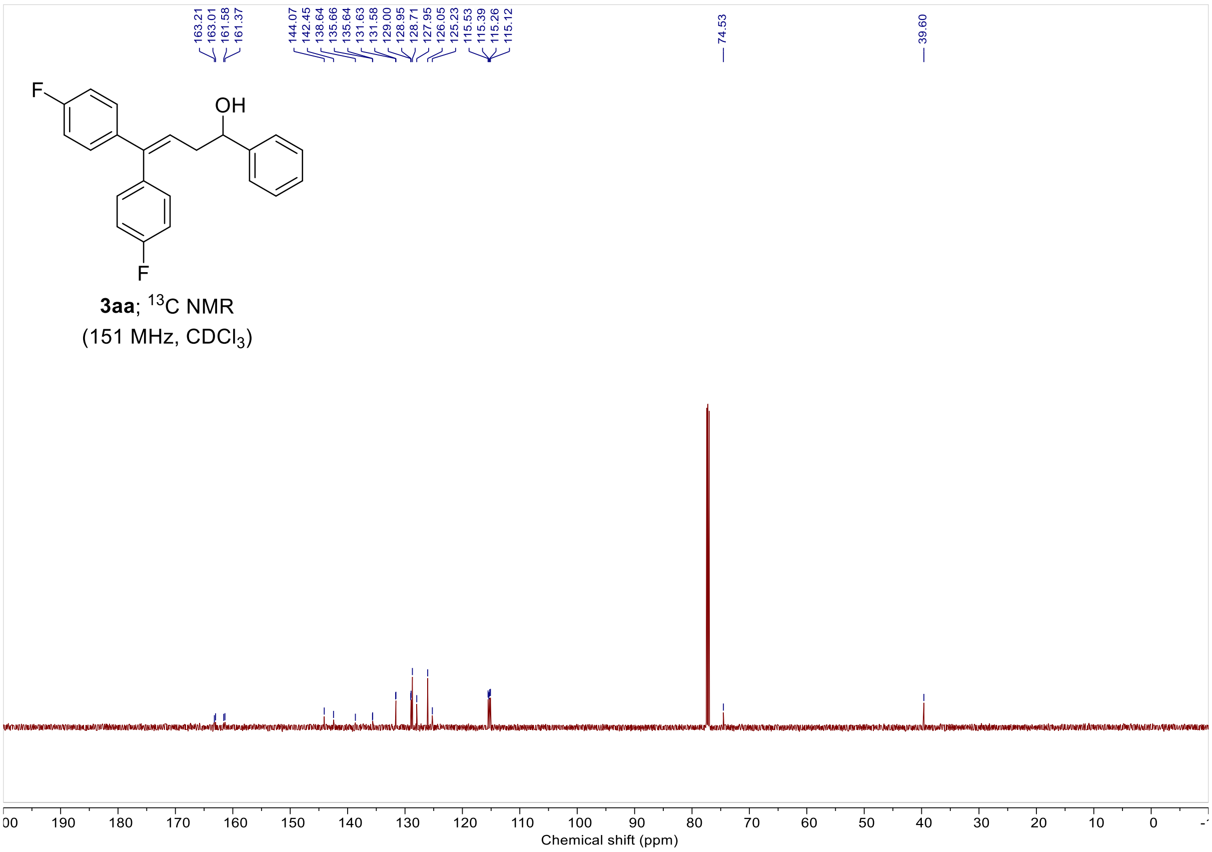
[S1] Z. Zhao, L. Racicot and G. K. Murphy, Fluorinative Rearrangements of Substituted Phenylallenes Mediated by (Difluoroiodo)toluene: Synthesis of alpha-(Difluoromethyl)styrenes, *Angew. Chem. Int. Ed.*, 2017, **56**, 11620-11623.

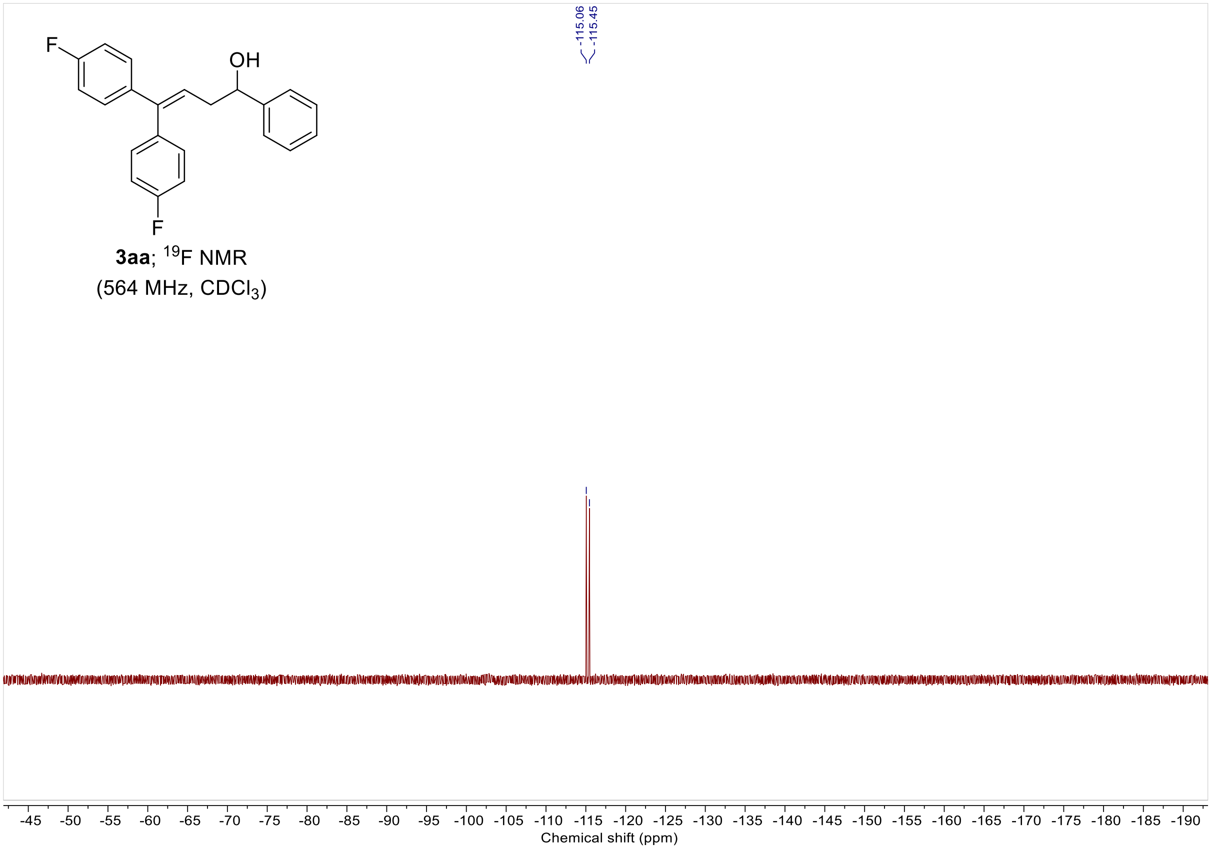
[S2] H. Clavier, K. Le Jeune, I. de Riggi, A. Tenaglia and G. Buono, Highly selective cobalt-mediated [6 + 2] cycloaddition of cycloheptatriene and allenes, *Org. Lett.*, 2011, **13**, 308-311.

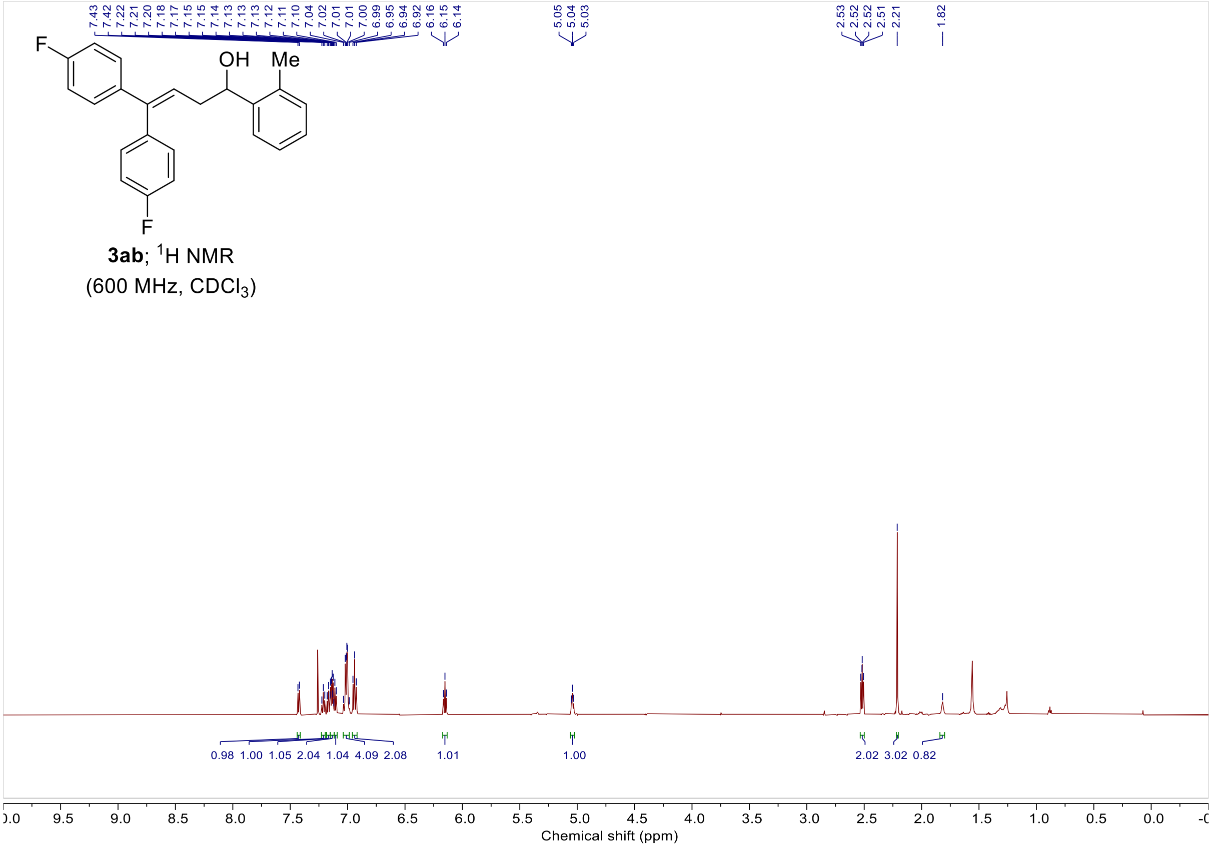
[S3] A. Kopfer and B. Breit, Rhodium-Catalyzed Hydroformylation of 1,1-Disubstituted Allenes Employing the Self-Assembling 6-DPPon System, *Angew. Chem. Int. Ed.*, 2015, **54**, 6913-6917.

NMR Spectra (^{1}H NMR, ^{13}C NMR and ^{19}F NMR)

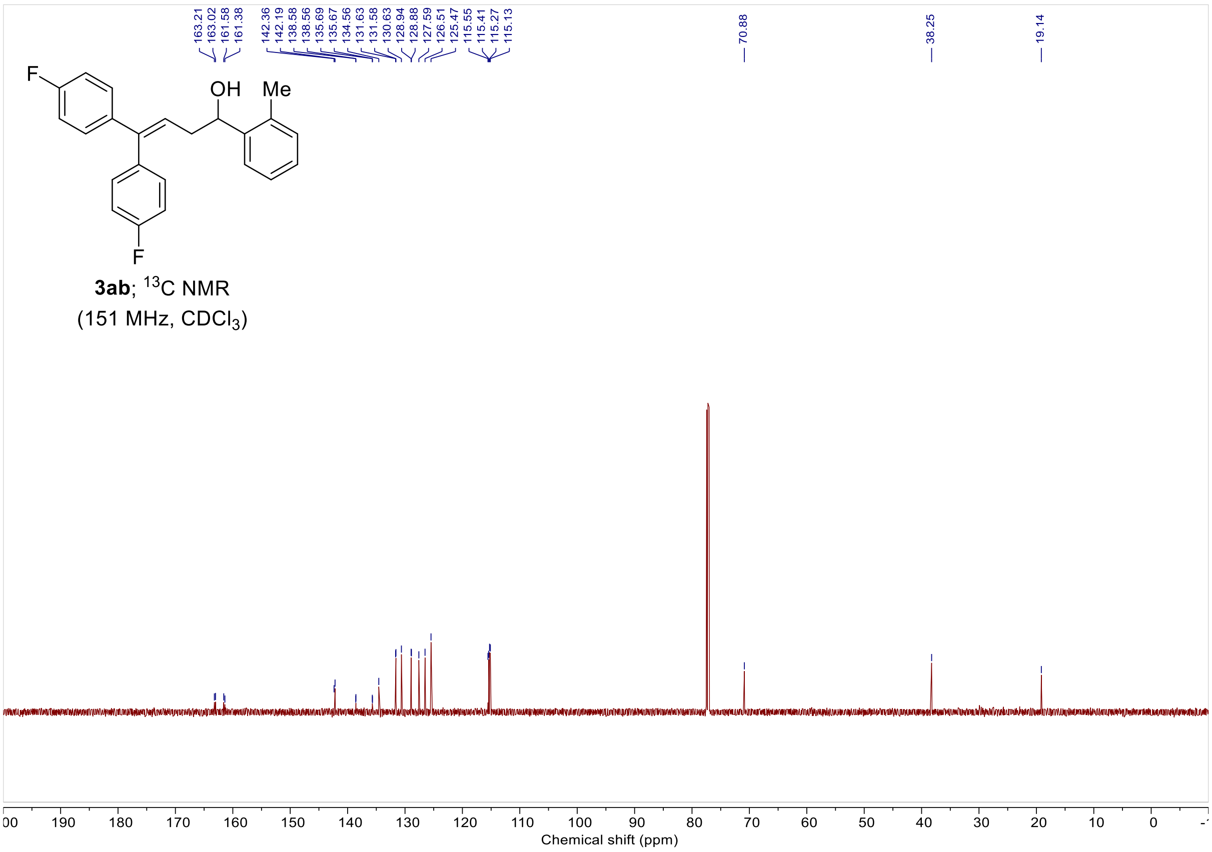




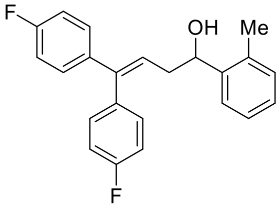

-115.06
-115.45
OH
F
F
3aa; ^{19}F NMR
(564 MHz, $CDCl_3$)
-45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -190
Chemical shift (ppm)



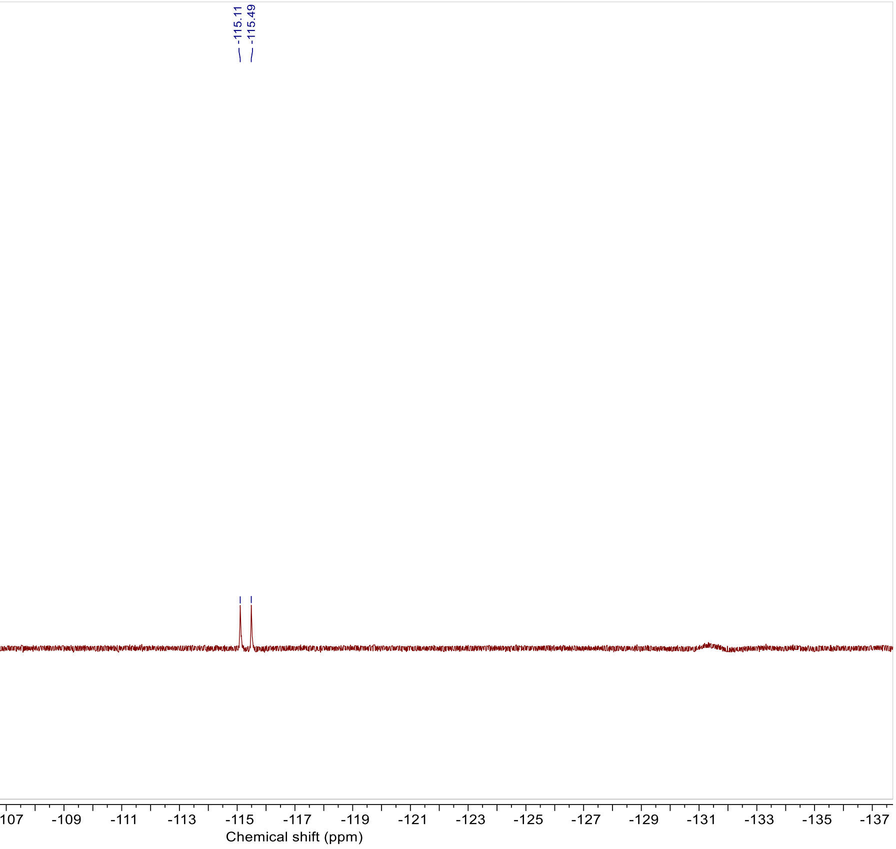
F
OH
Me
F
3ab; 1H NMR
(600 MHz, CDCl3)
Chemical shift (ppm)

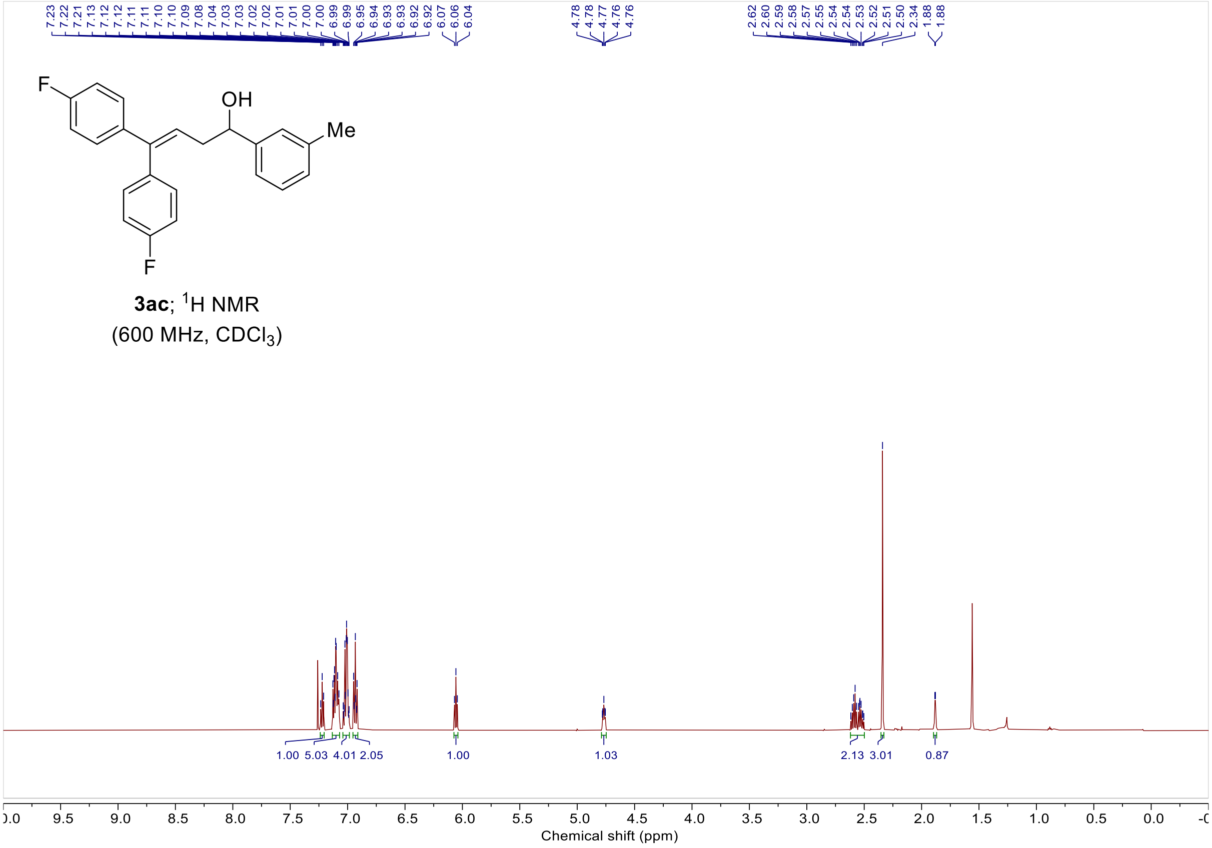


F
OH
Me
F
3ab; 13C NMR
(151 MHz, CDCl3)
Chemical shift (ppm)



3ab; ^{19}F NMR
(564 MHz, $CDCl_3$)

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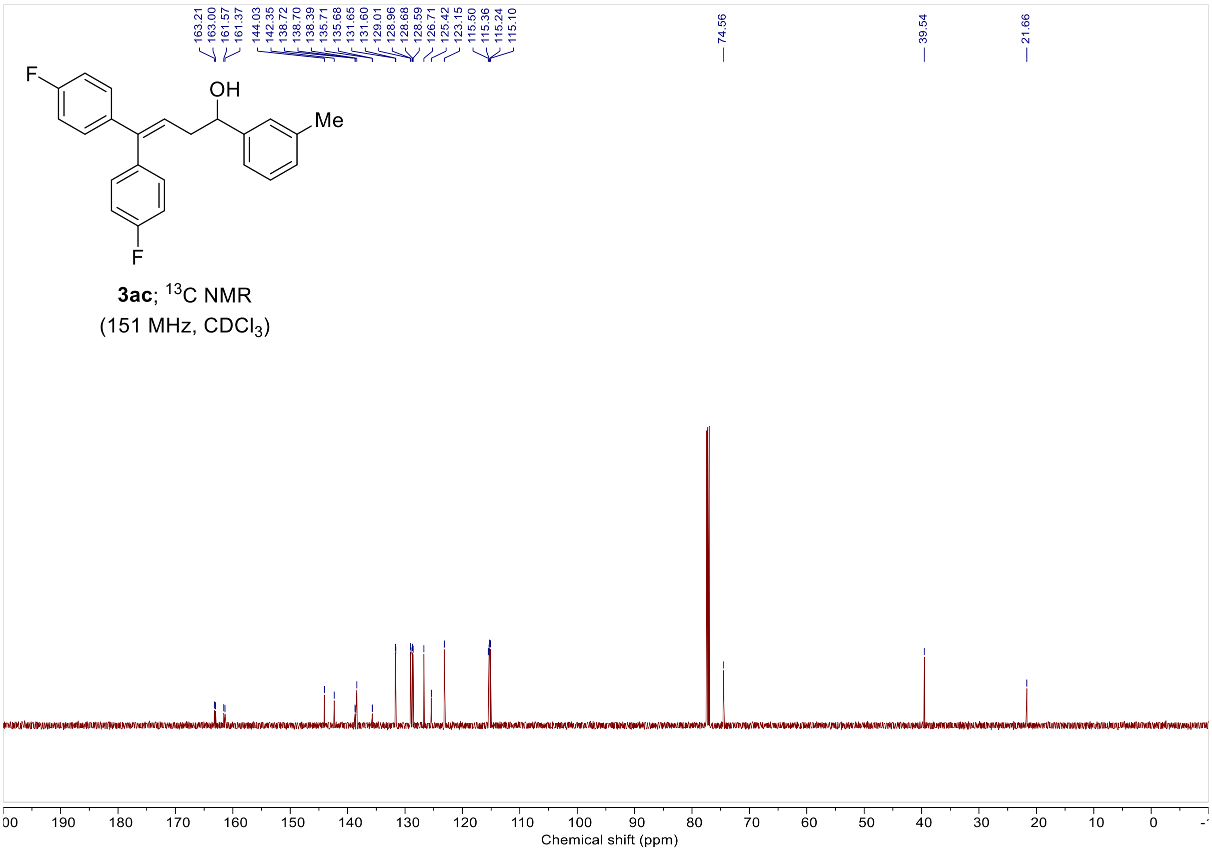
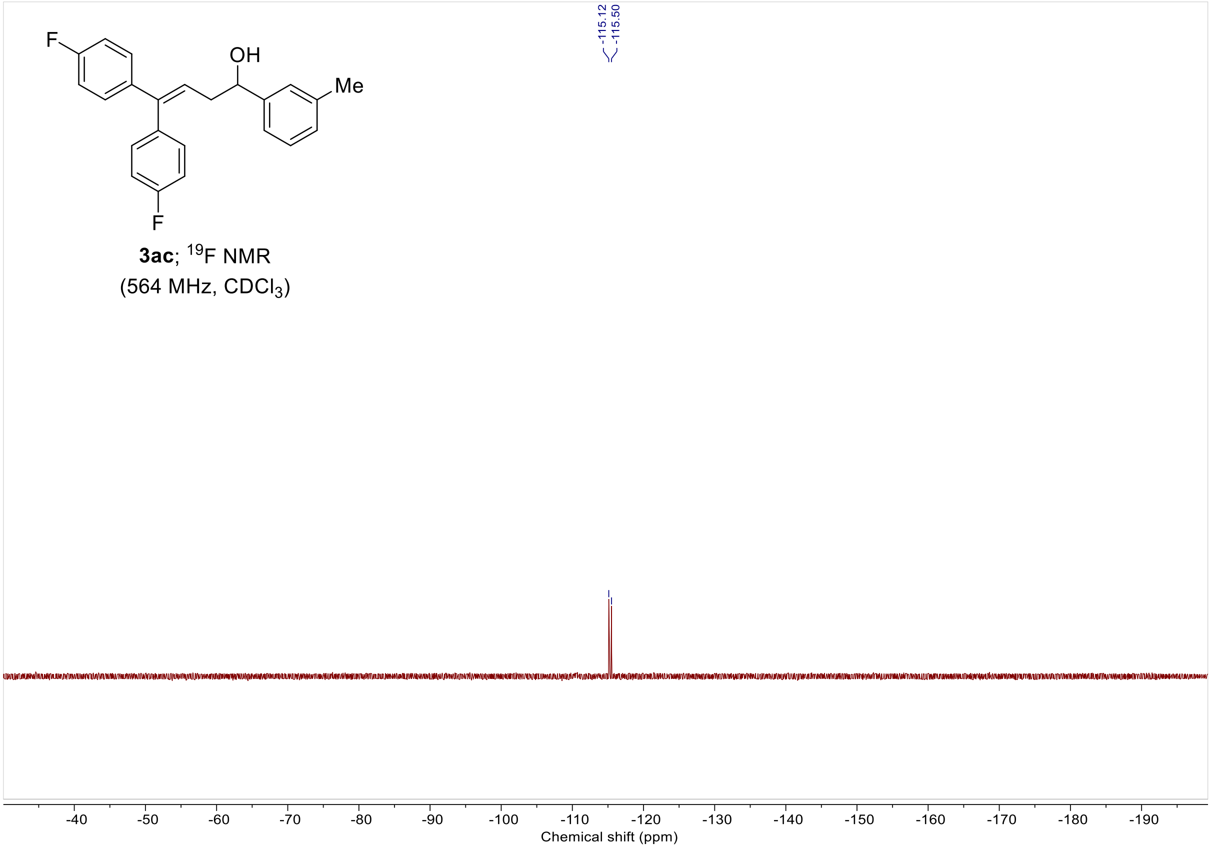
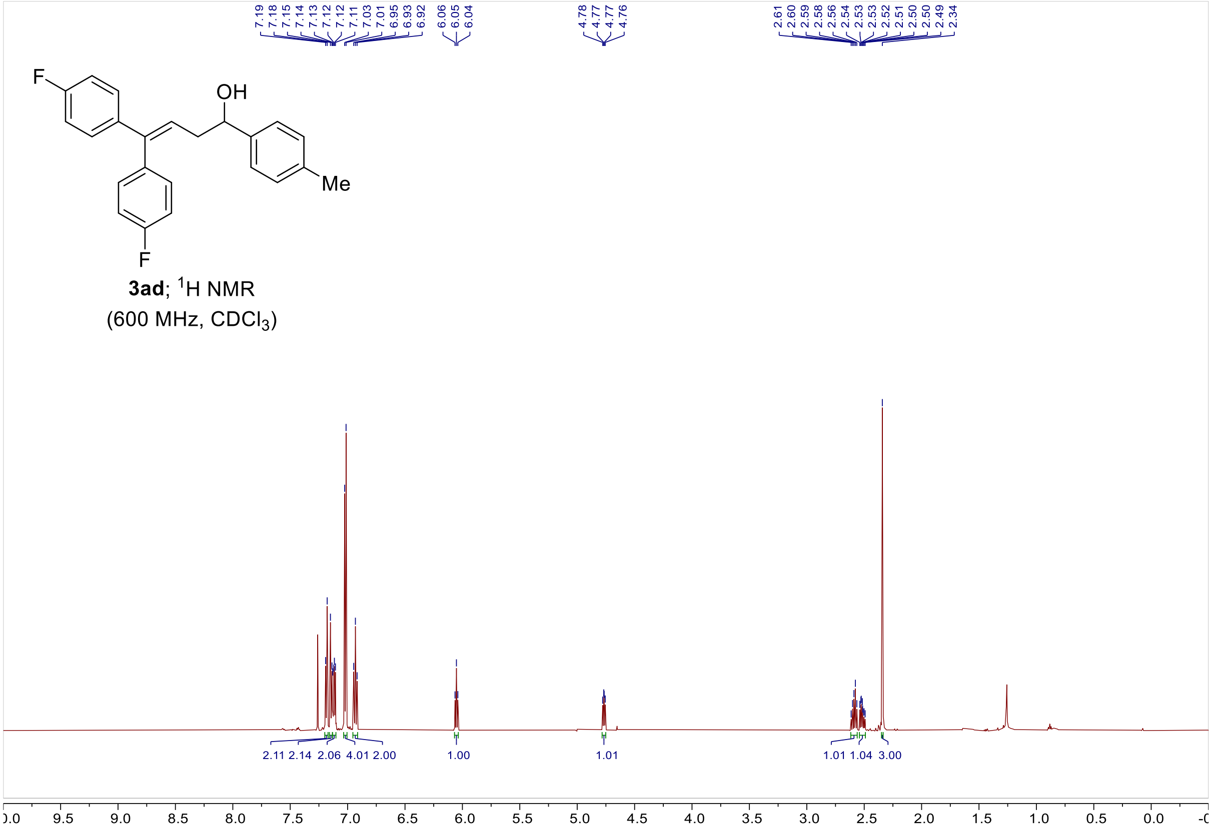
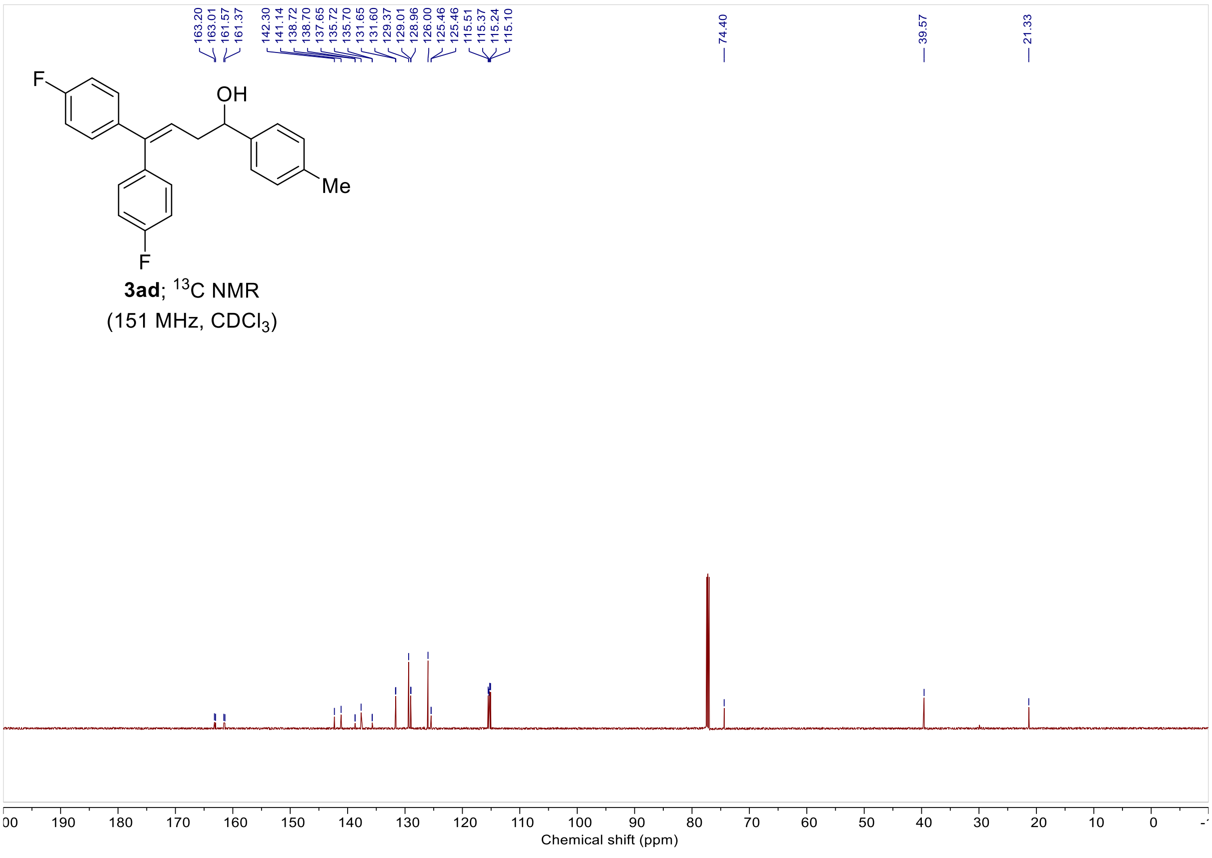
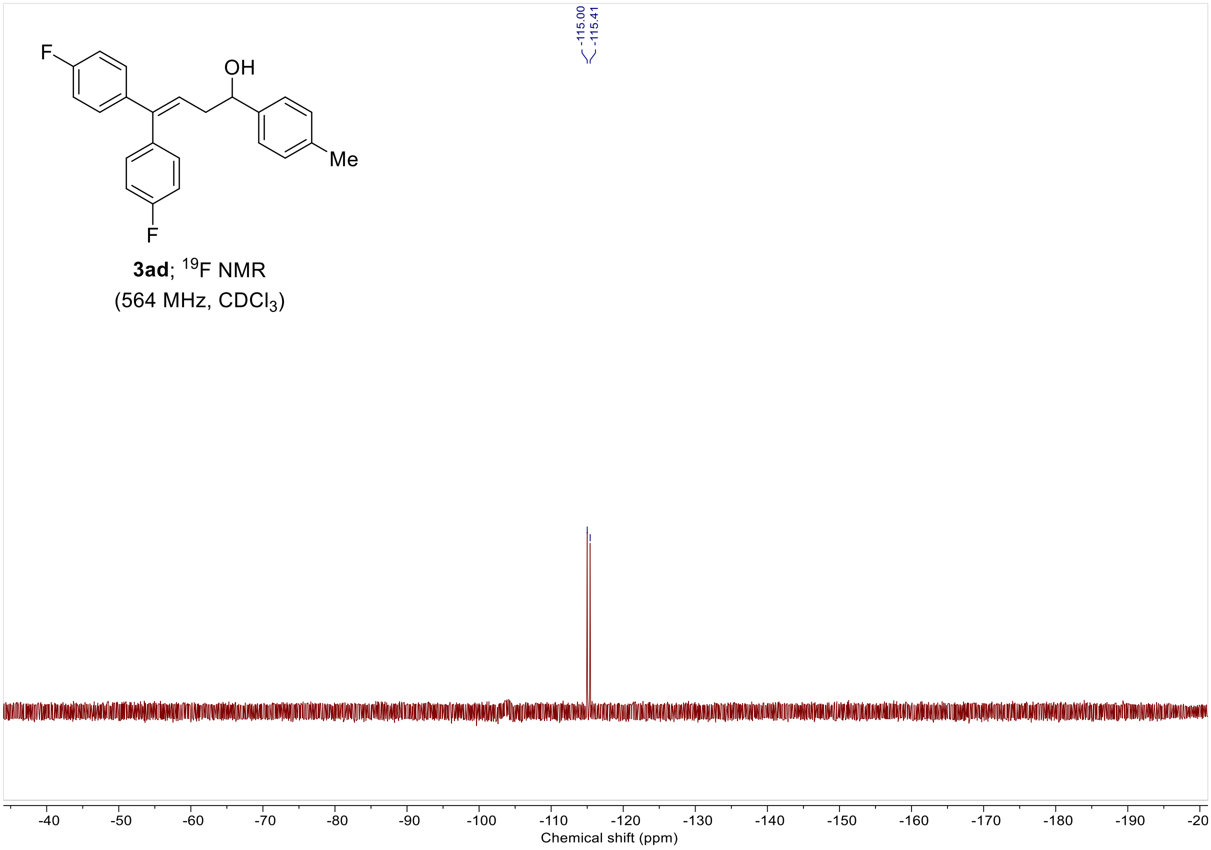
4.78 4.78 4.77 4.76 4.76
2.62 2.60 2.59 2.58 2.57 2.55 2.54 2.54 2.53 2.52 2.51 2.50 2.34 1.88 1.88
F
OH
Me
F
3ac; 1H NMR
(600 MHz, CDCl3)
1.00 5.03 4.01 2.05
1.00
1.03
2.13 3.01
0.87
Chemical shift (ppm)

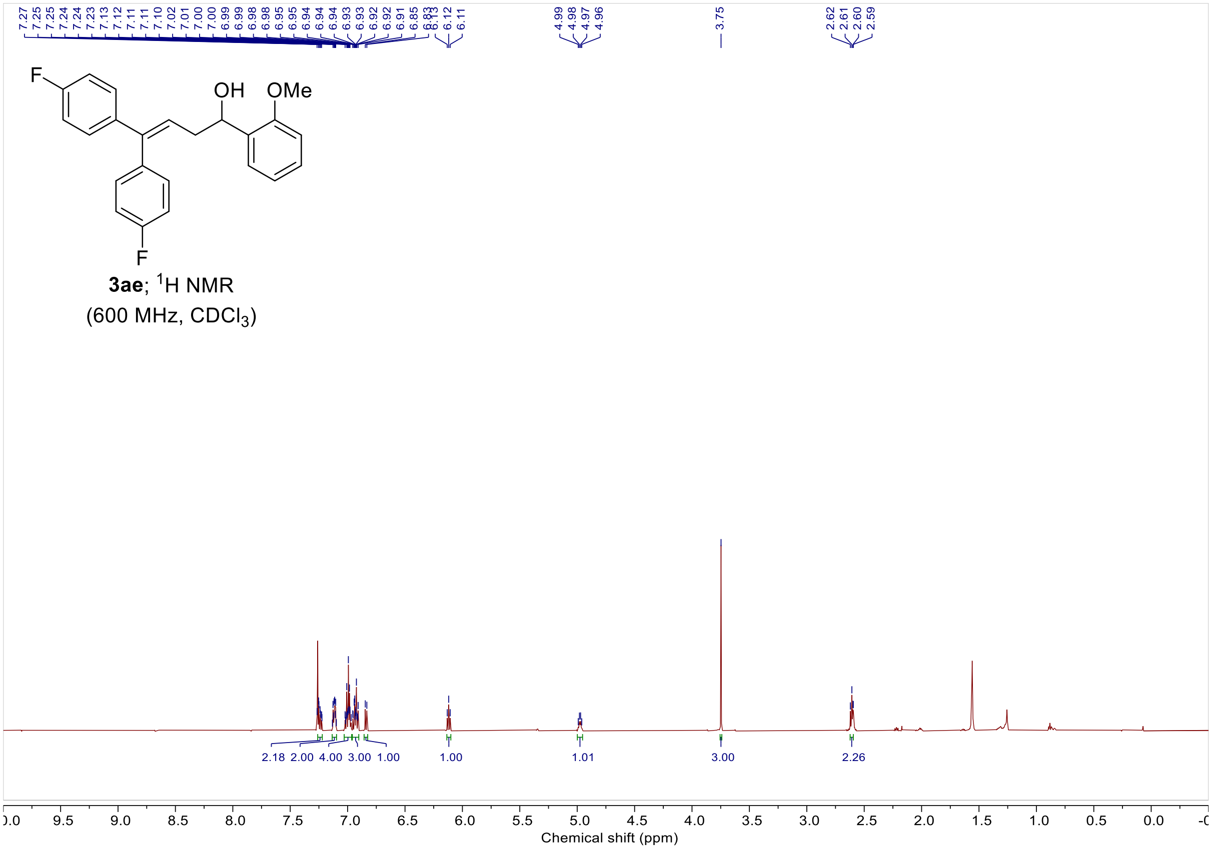

163.21 163.00 161.57 161.37 144.03 142.35 138.72 138.70 138.39 135.71 135.68 131.65 131.60 129.01 128.96 128.68 128.59 126.71 125.42 123.15 115.50 115.36 115.24 115.10
74.56
39.54
21.66
F
OH
Me
F
3ac; 13C NMR
(151 MHz, CDCl3)
Chemical shift (ppm)


3ac; ^{19}F NMR
(564 MHz, $CDCl_3$)
-115.12
-115.50
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
Chemical shift (ppm)

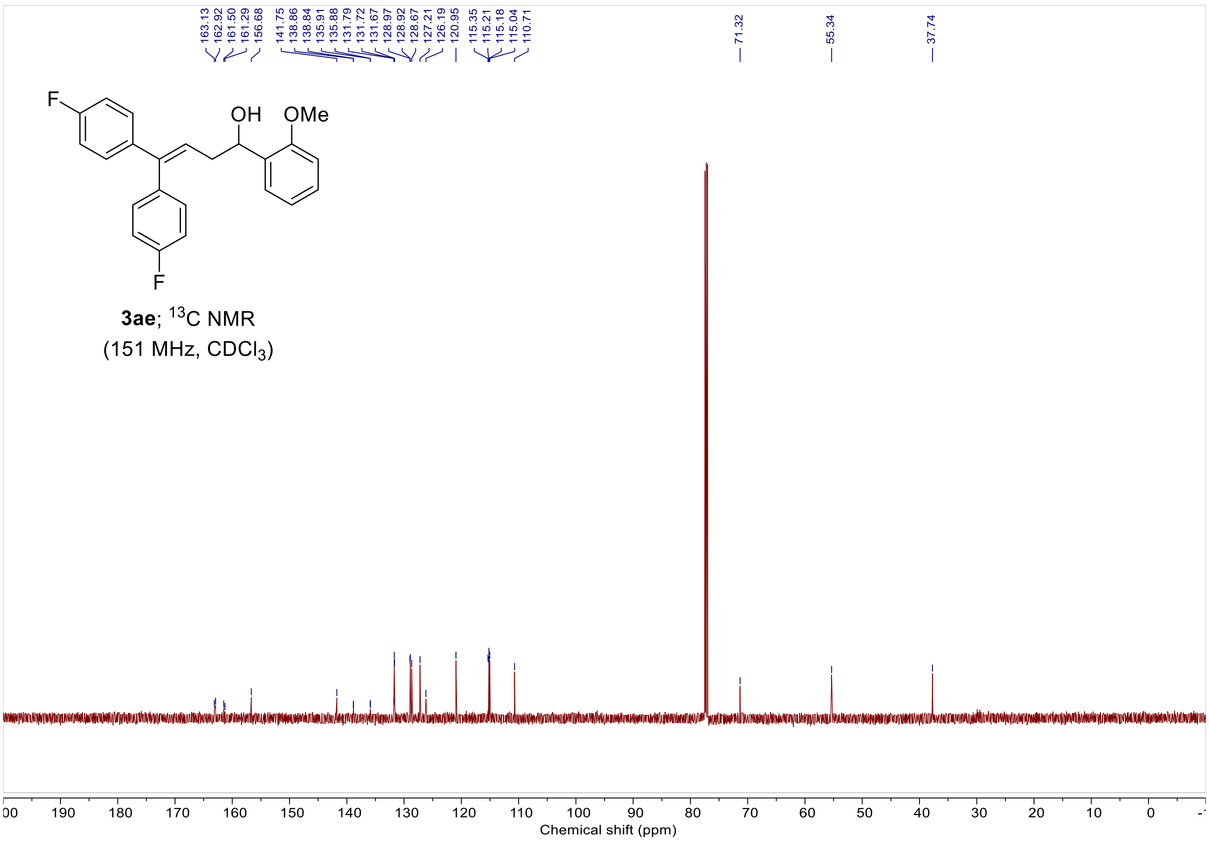

7.19 7.18 7.15 7.14 7.13 7.12 7.12 7.11 7.03 7.01 6.95 6.93 6.92
6.06 6.05 6.04
4.78 4.77 4.77 4.76
2.61 2.60 2.59 2.58 2.56 2.54 2.53 2.53 2.52 2.51 2.50 2.50 2.49 2.34
F
OH
Me
F
3ad; 1H NMR
(600 MHz, CDCl3)
2.11 2.14 2.06 4.01 2.00
1.00
1.01
1.01 1.04 3.00
Chemical shift (ppm)


163.20 163.01 161.57 161.37
142.30 141.14 138.72 138.70 137.65 135.72 135.70 131.65 131.60 129.37 129.01 128.96 126.00 125.46 125.46 115.51 115.37 115.24 115.10
74.40
39.57
21.33
F
OH
Me
F
3ad; 13C NMR
(151 MHz, CDCl3)
Chemical shift (ppm)

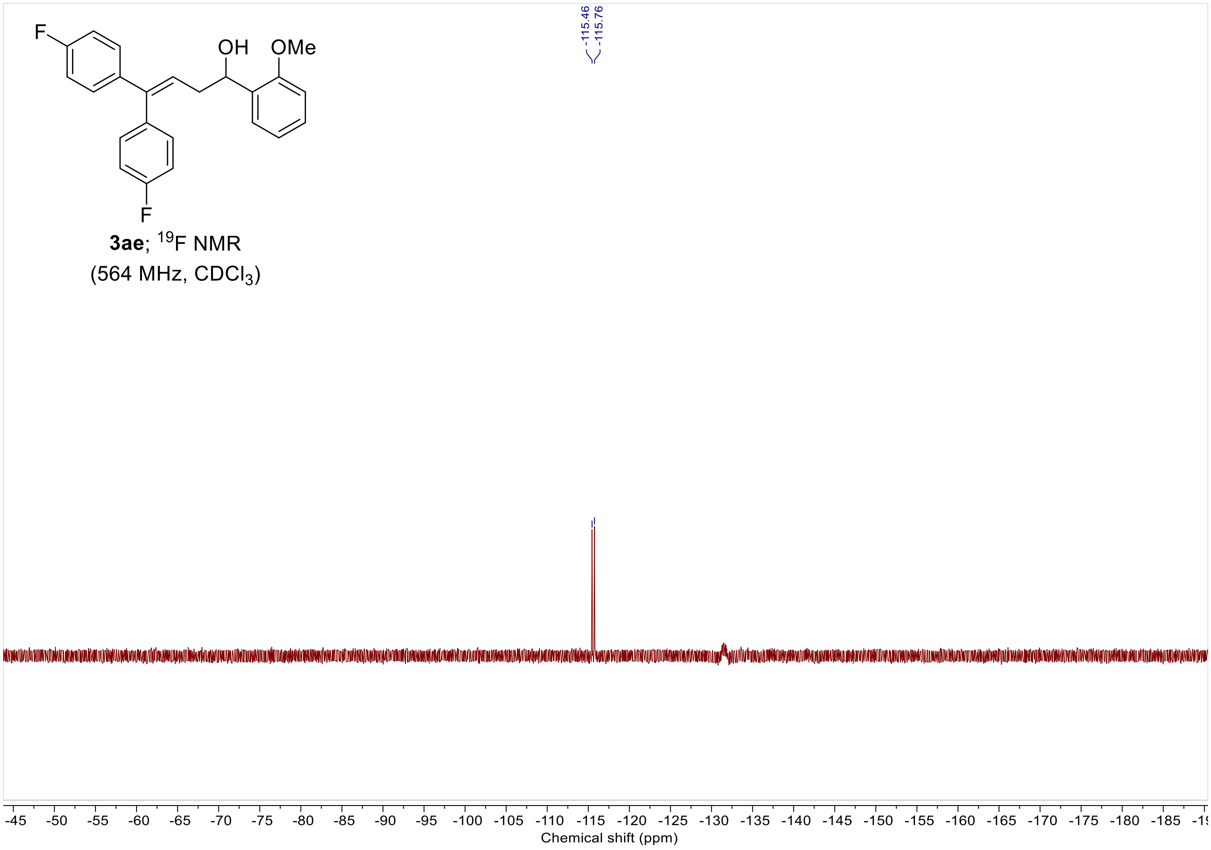

-115.00
-115.41
OH
F
F
Me
3ad; 19F NMR
(564 MHz, CDCl3)
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-20
Chemical shift (ppm)



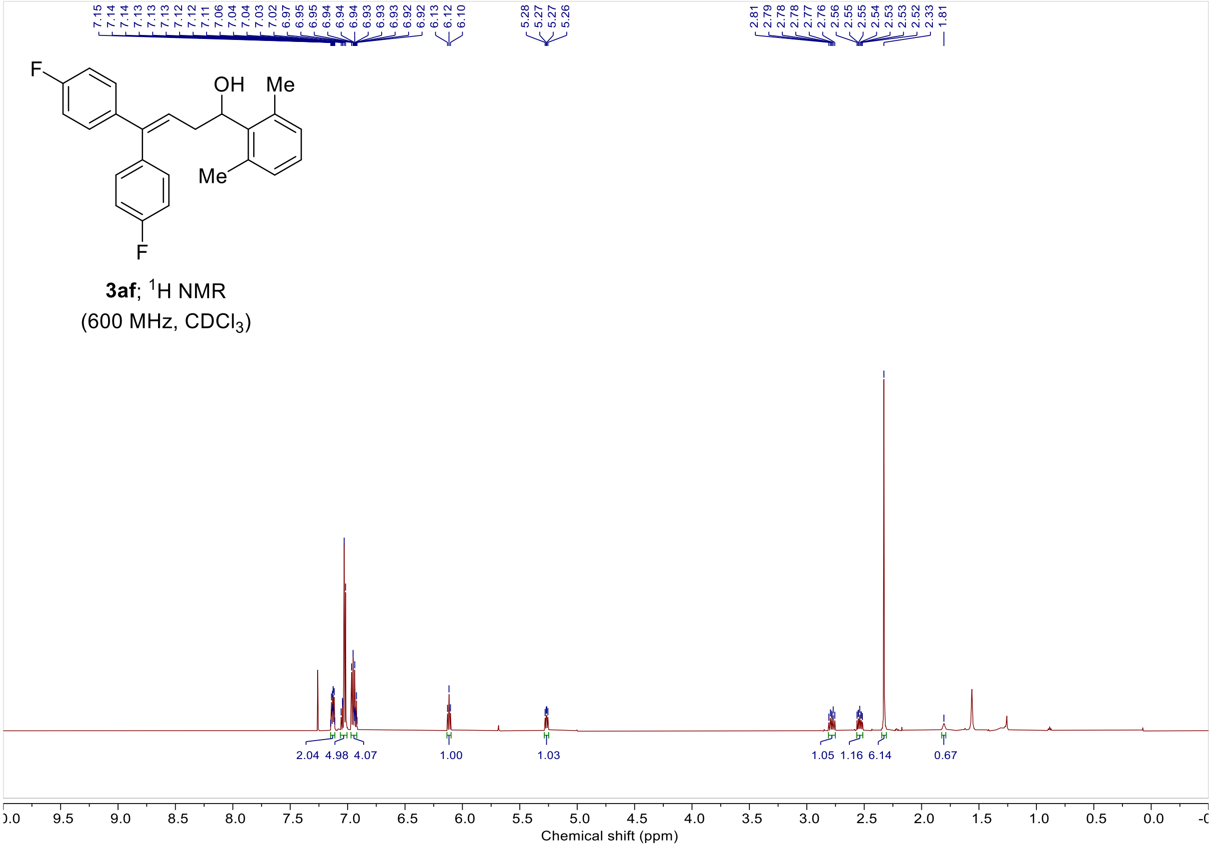
F
OH
OMe
F
3ae; ^{1}H NMR
(600 MHz, $CDCl_3$)
Chemical shift (ppm)



F
OH
OMe
F
3ae; ^{13}C NMR
(151 MHz, $CDCl_3$)
Chemical shift (ppm)



F
OH
OMe
F
3ae; 19F NMR
(564 MHz, CDCl3)
-115.46
-115.76
-45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185
Chemical shift (ppm)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5.28 5.27 5.27 5.26
2.81 2.79 2.78 2.78 2.77 2.76 2.56 2.55 2.55 2.54 2.53 2.53 2.52 2.33 1.81
F
OH
Me
Me
F
3af; 1H NMR
(600 MHz, CDCl3)
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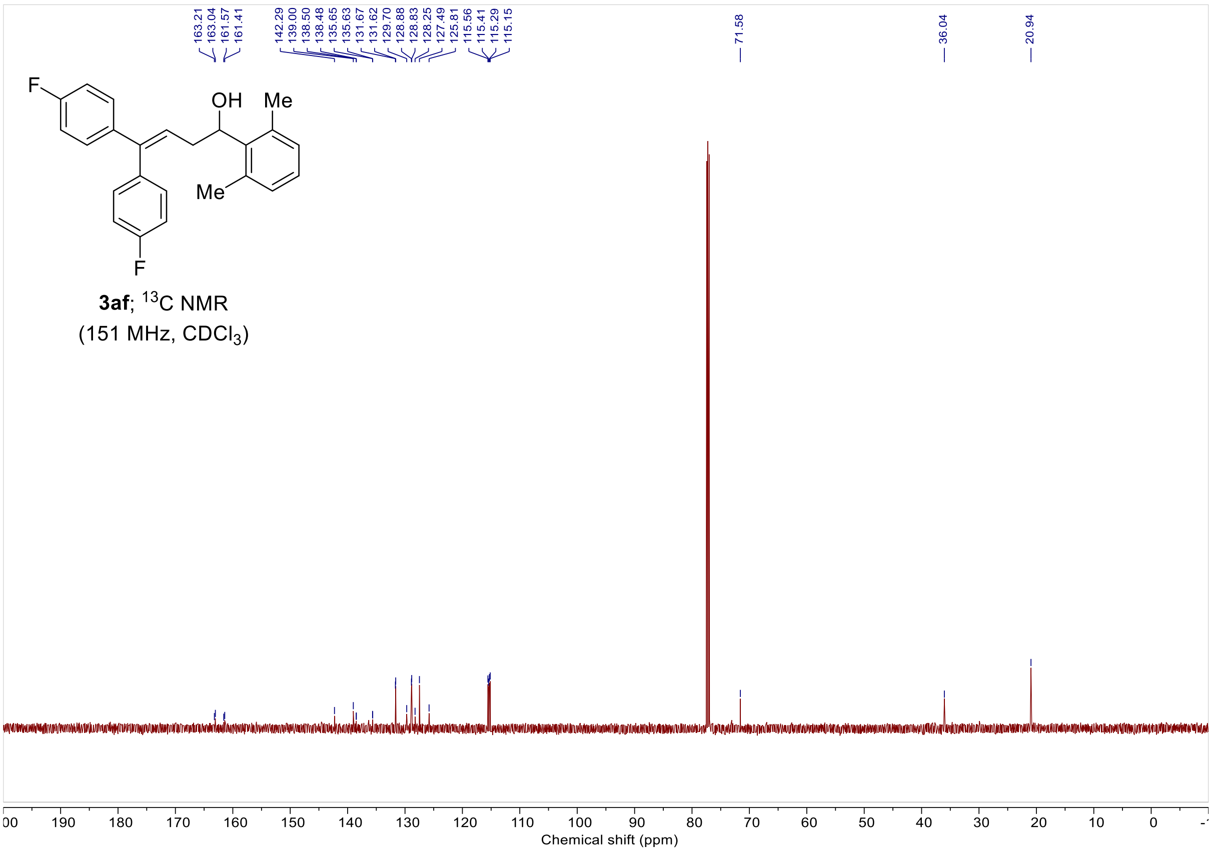
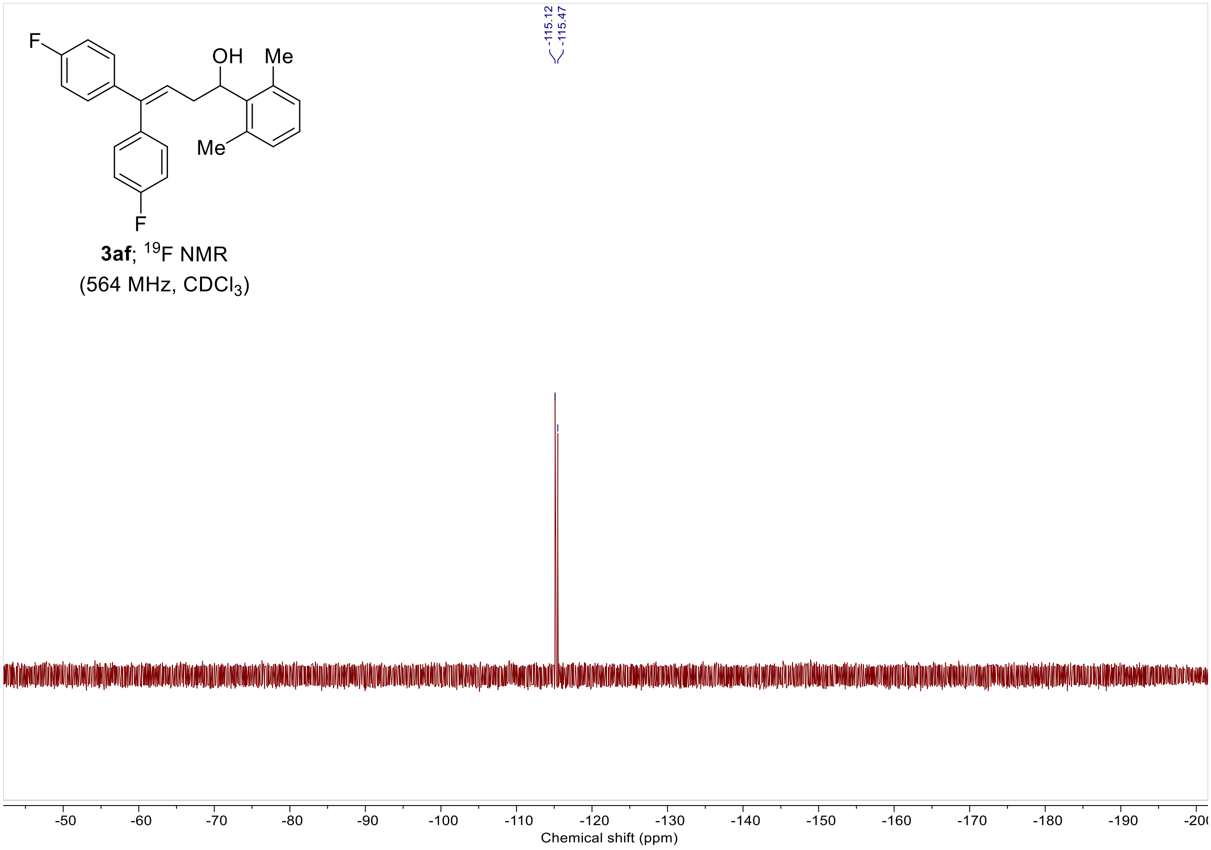
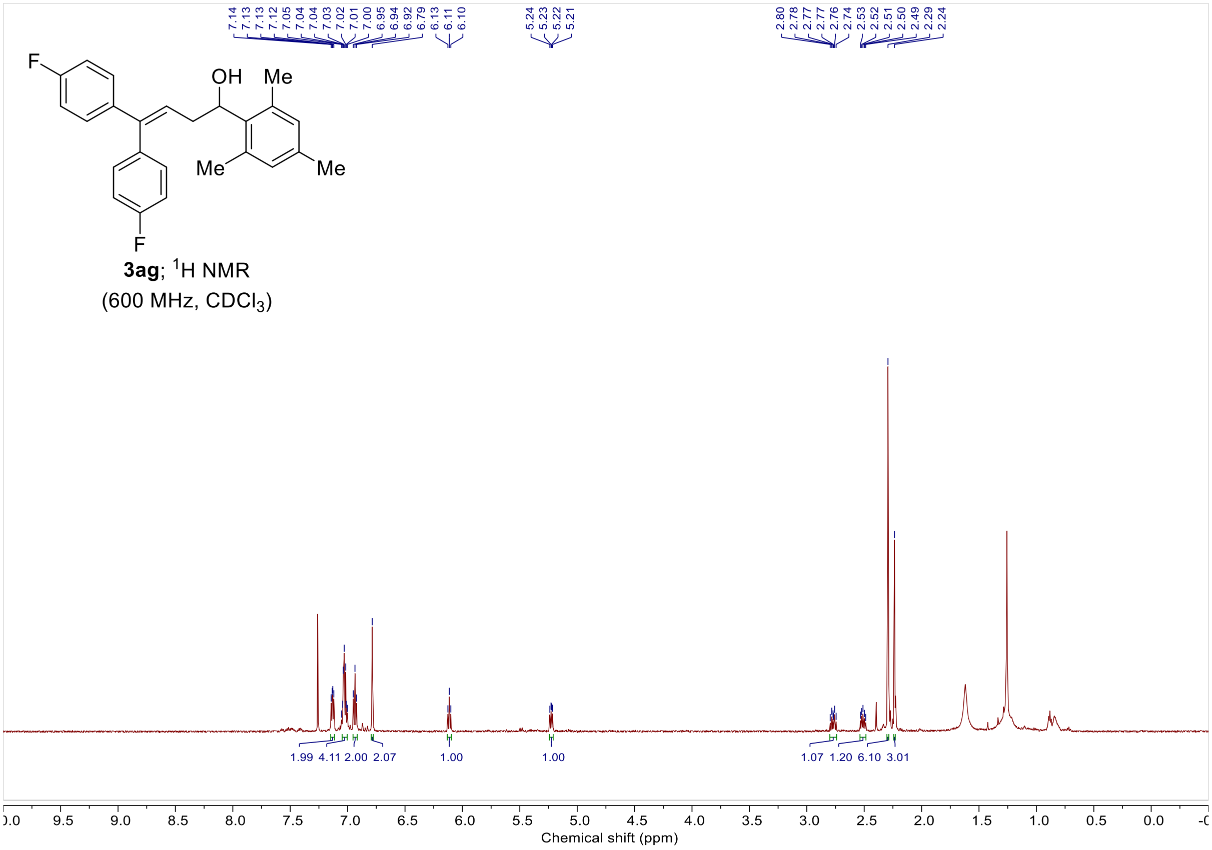
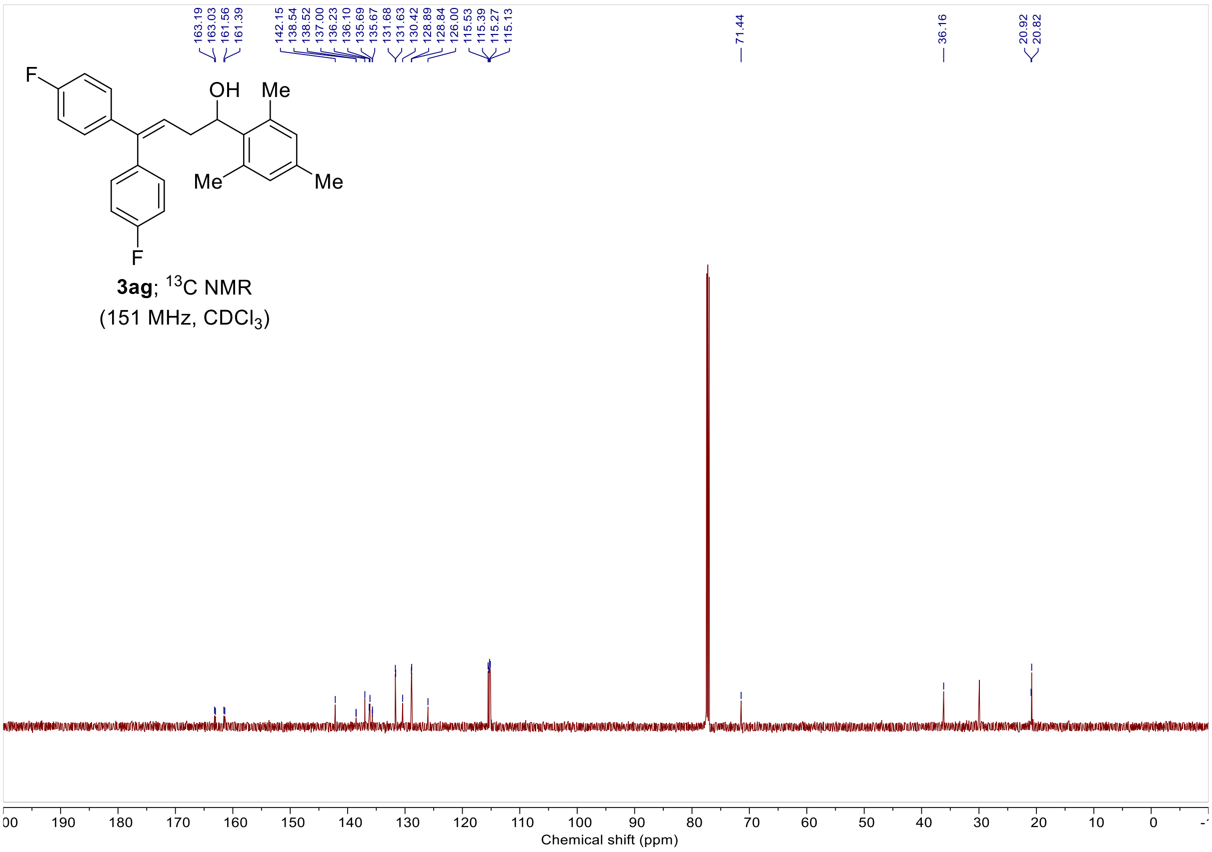
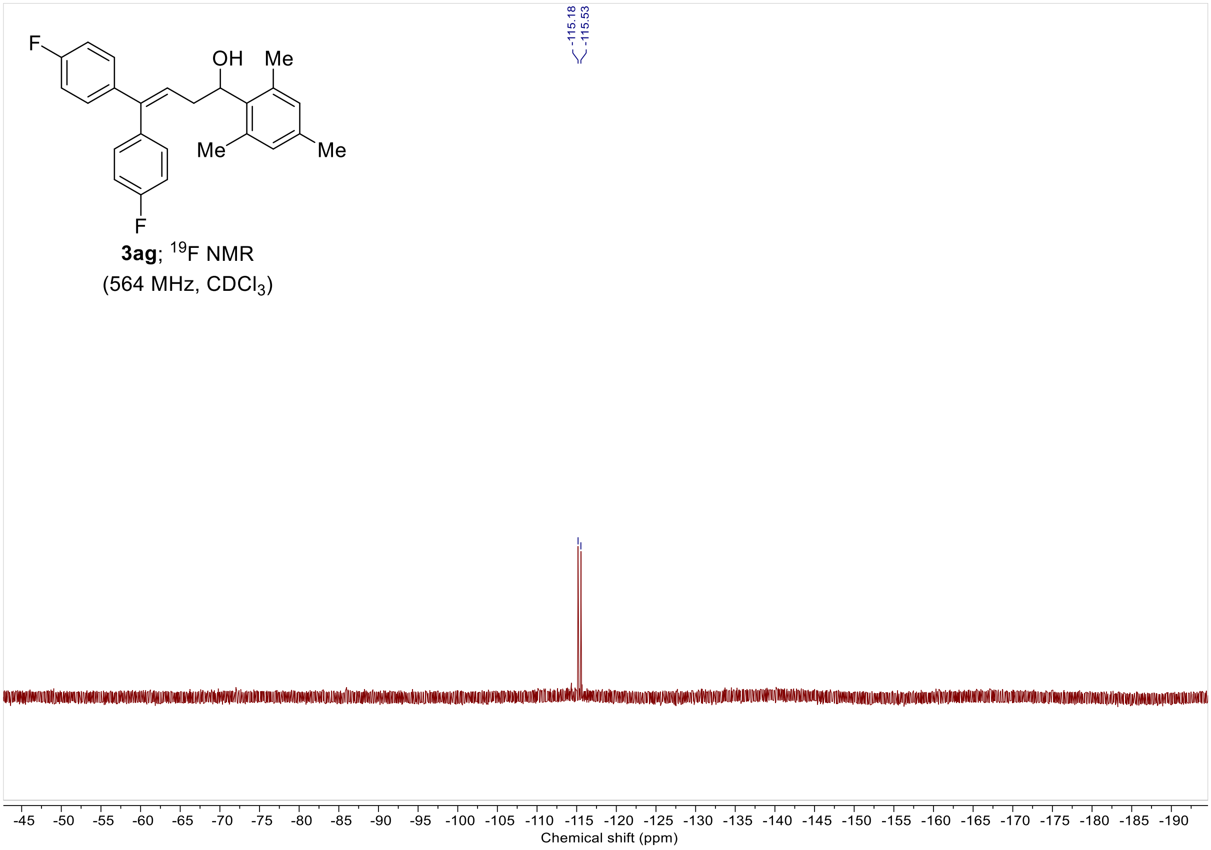
1.00
1.03
1.05 1.16 6.14
0.67
Chemical shift (ppm)

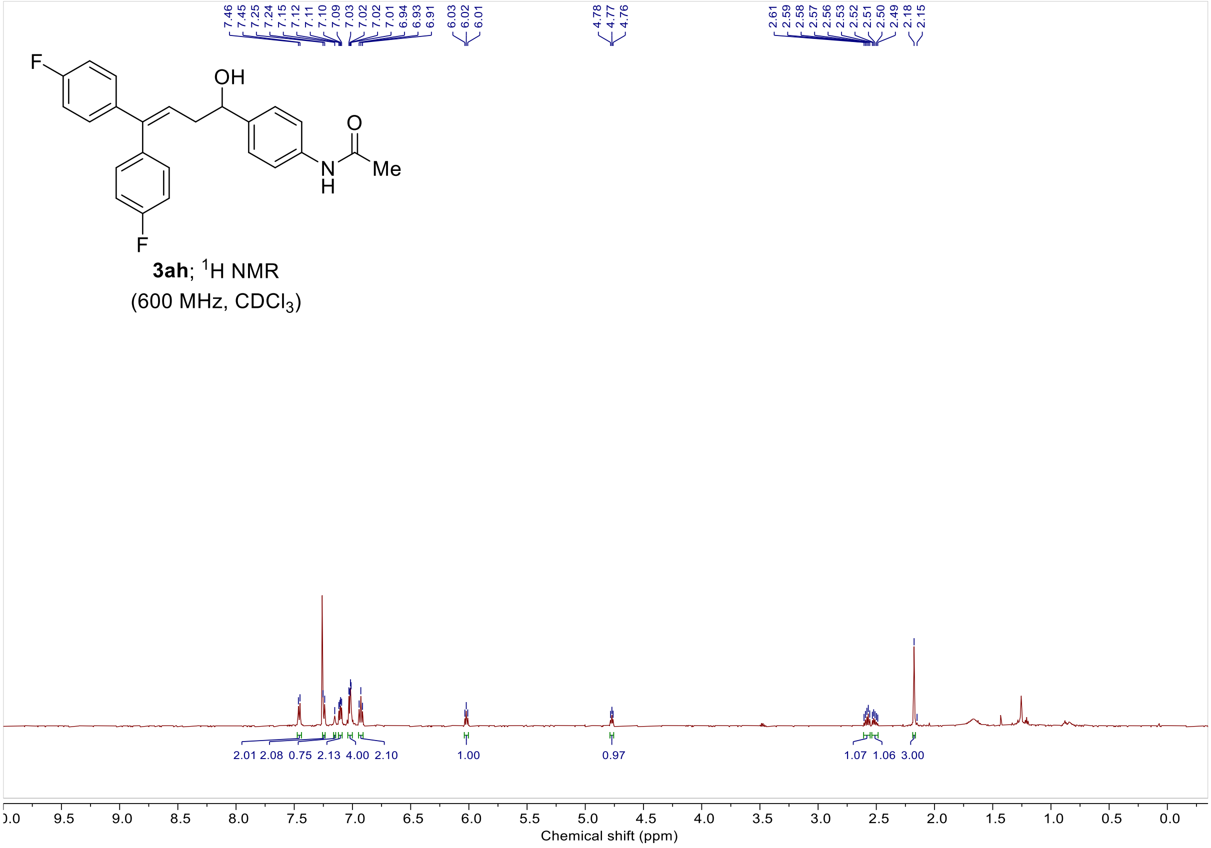

163.21 163.04 161.57 161.41
142.29 139.00 138.50 138.48 135.65 135.63 131.67 131.62 129.70 128.88 128.83 128.25 127.49 125.81 115.56 115.41 115.29 115.15
71.58
36.04
20.94
F
OH
Me
Me
F
3af; 13C NMR
(151 MHz, CDCl3)
Chemical shift (ppm)

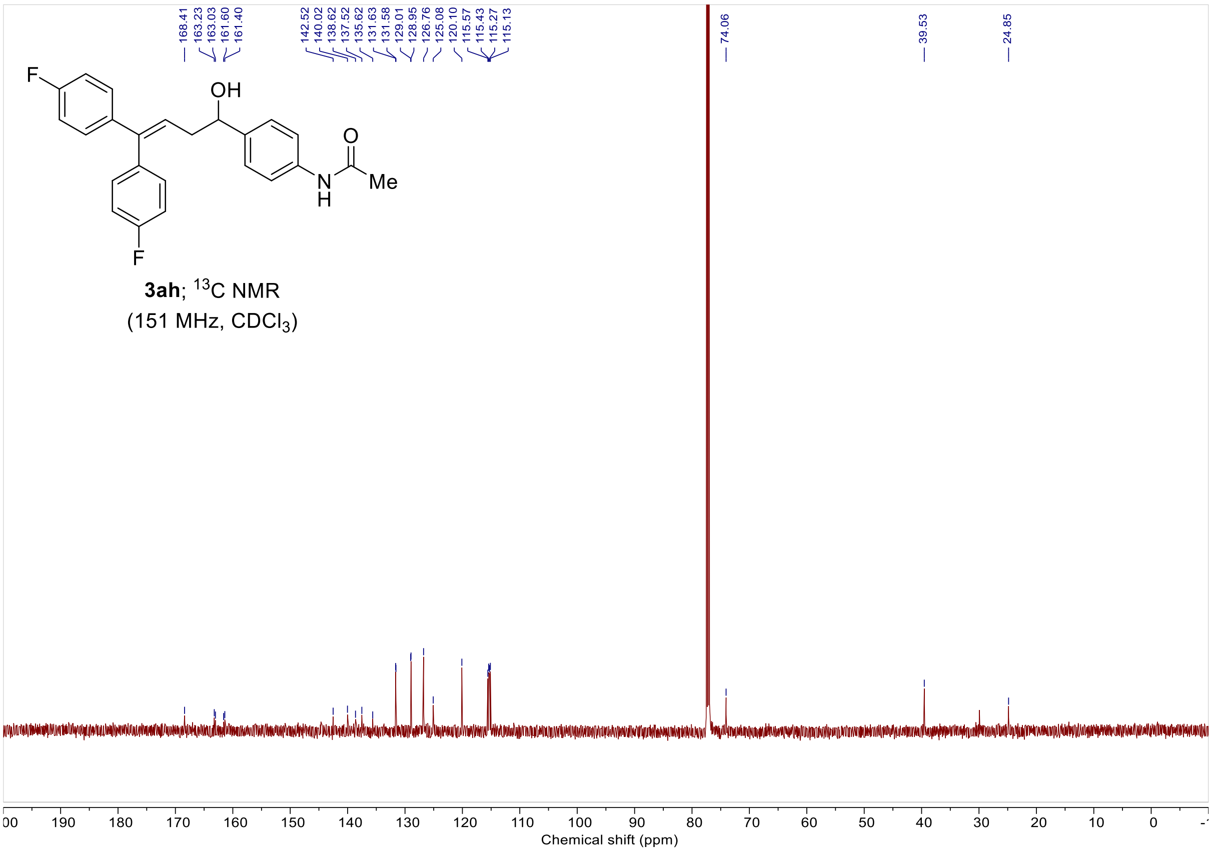

-115.12
-115.47
F
OH
Me
Me
F
3af; 19F NMR
(564 MHz, CDCl3)
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
Chemical shift (ppm)

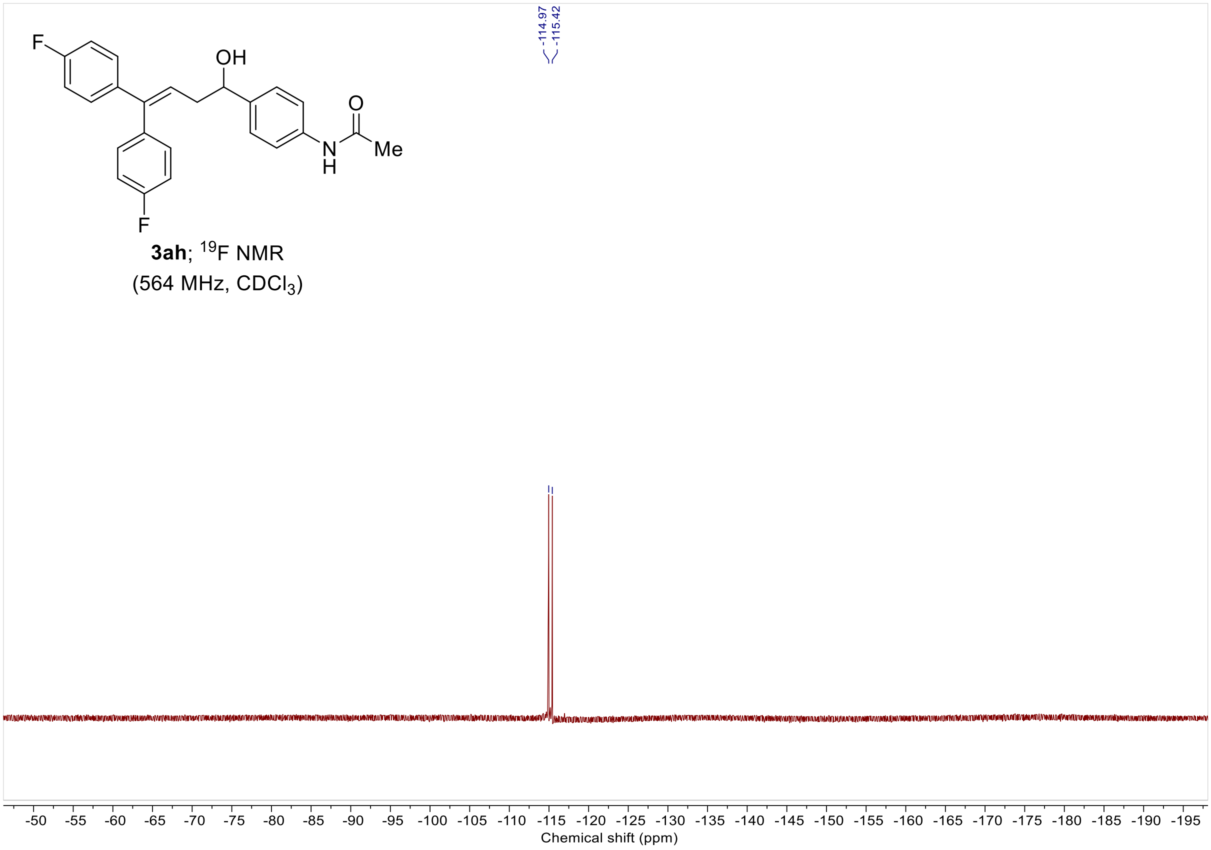

3ag; ^{1}H NMR
(600 MHz, $CDCl_3$)
Chemical shift (ppm)


3ag; ^{13}C NMR
(151 MHz, $CDCl_3$)
Chemical shift (ppm)

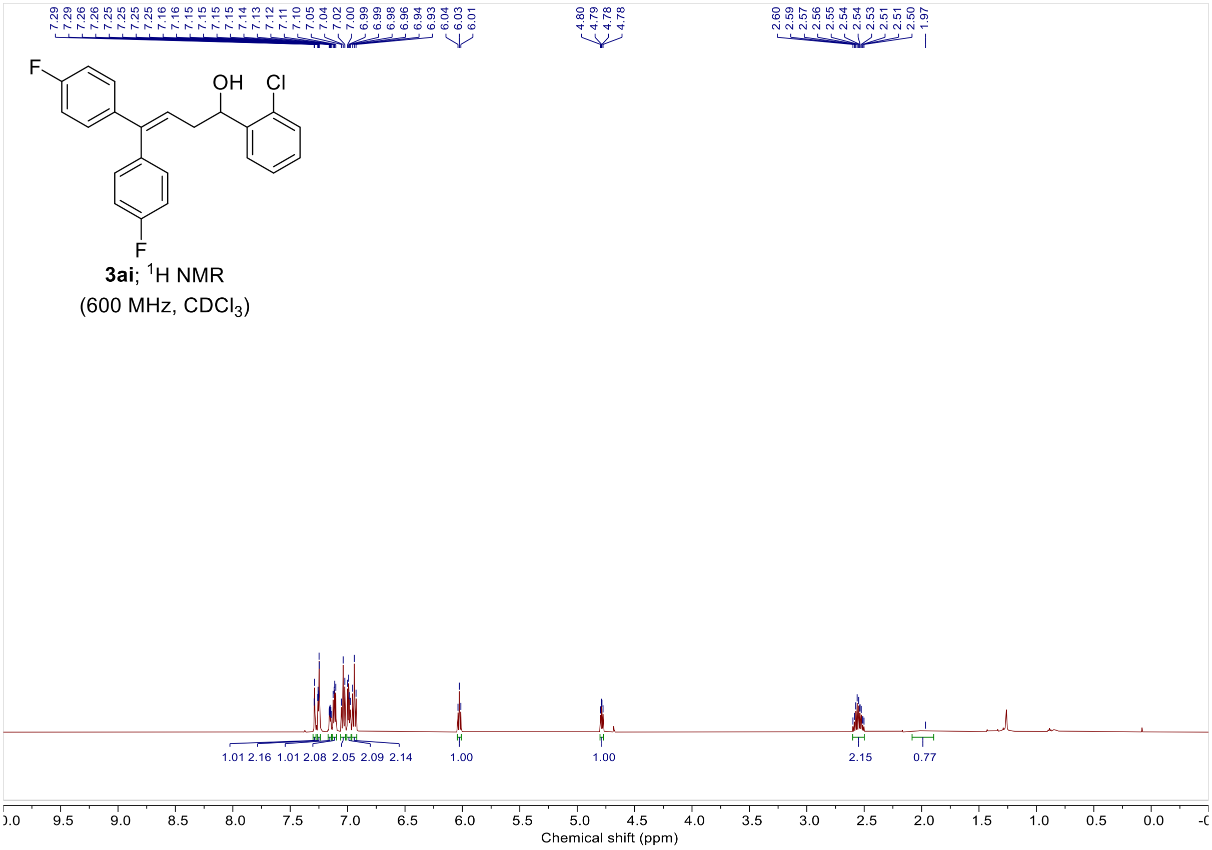

F
OH
Me
Me
Me
F
3ag; 19F NMR
(564 MHz, CDCl3)
-115.18
-115.53
-45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -190
Chemical shift (ppm)


7.46 7.45 7.25 7.24 7.15 7.12 7.11 7.10 7.09 7.03 7.02 7.02 7.01 6.94 6.93 6.91 6.03 6.02 6.01 4.78 4.77 4.76 2.61 2.59 2.58 2.57 2.56 2.53 2.52 2.51 2.50 2.49 2.18 2.15
OH
O
Me
N
H
F
F
3ah; 1H NMR
(600 MHz, CDCl3)
2.01 2.08 0.75 2.13 4.00 2.10 1.00 0.97 1.07 1.06 3.00
Chemical shift (ppm)

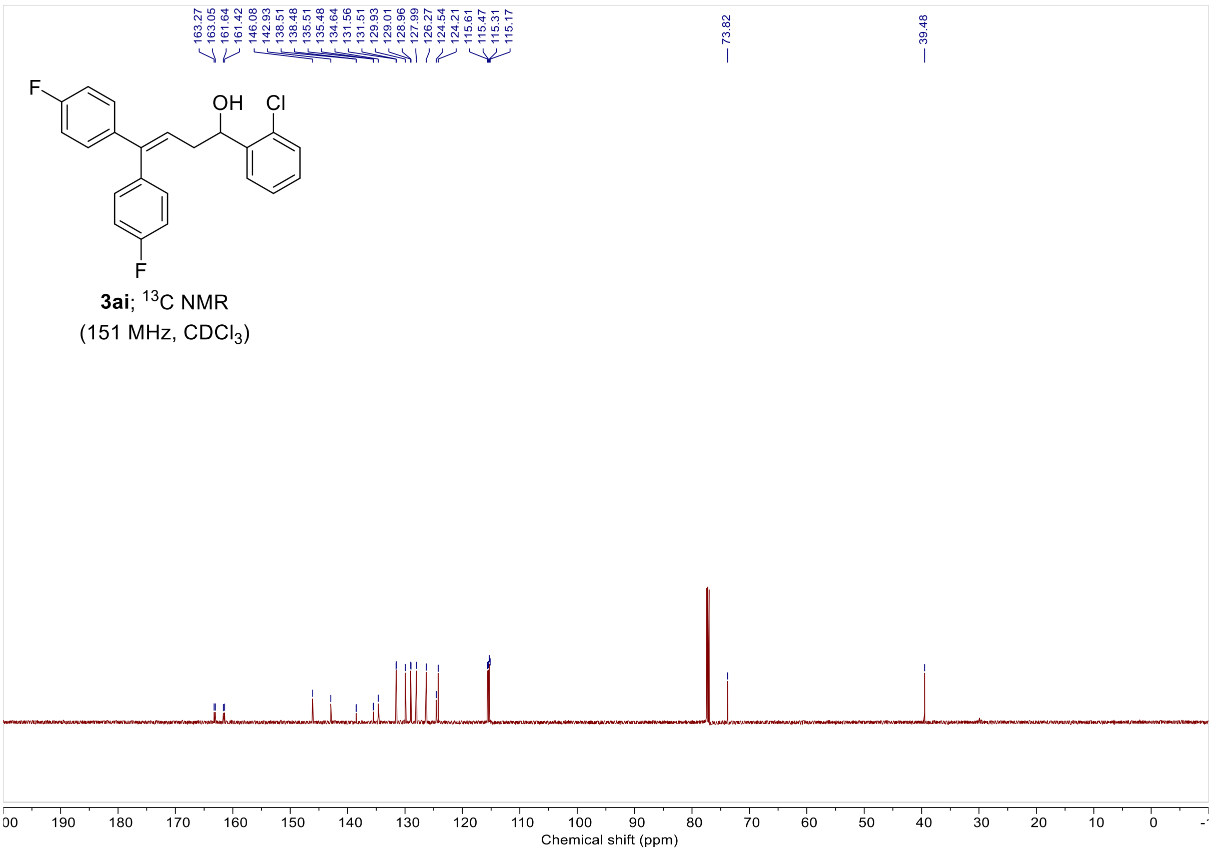

168.41 163.23 163.03 161.60 161.40 142.52 140.02 138.62 137.52 135.62 131.63 131.58 129.01 128.95 126.76 125.08 120.10 115.57 115.43 115.27 115.13 74.06 39.53 24.85
OH
O
Me
N
H
F
F
3ah; 13C NMR
(151 MHz, CDCl3)
Chemical shift (ppm)



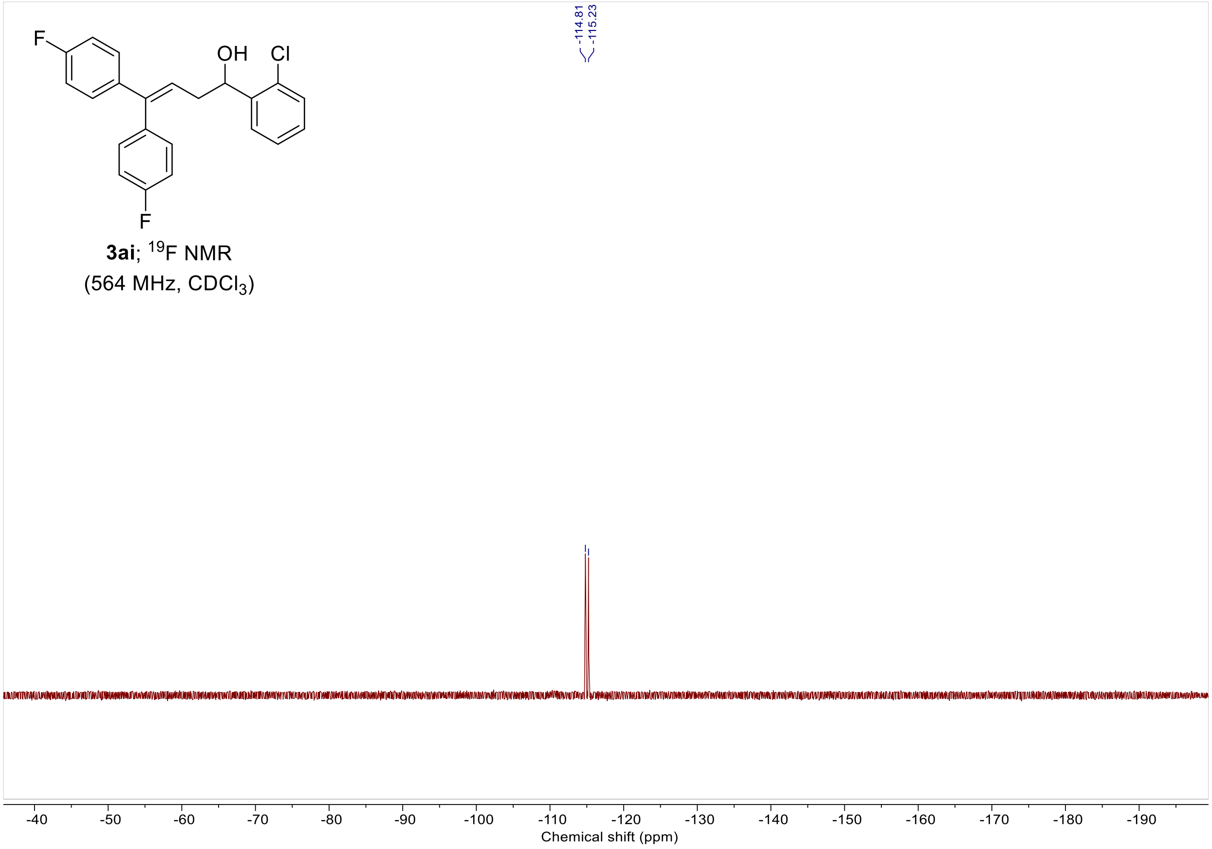
3ah; ^{19}F NMR (564 MHz, $CDCl_3$)

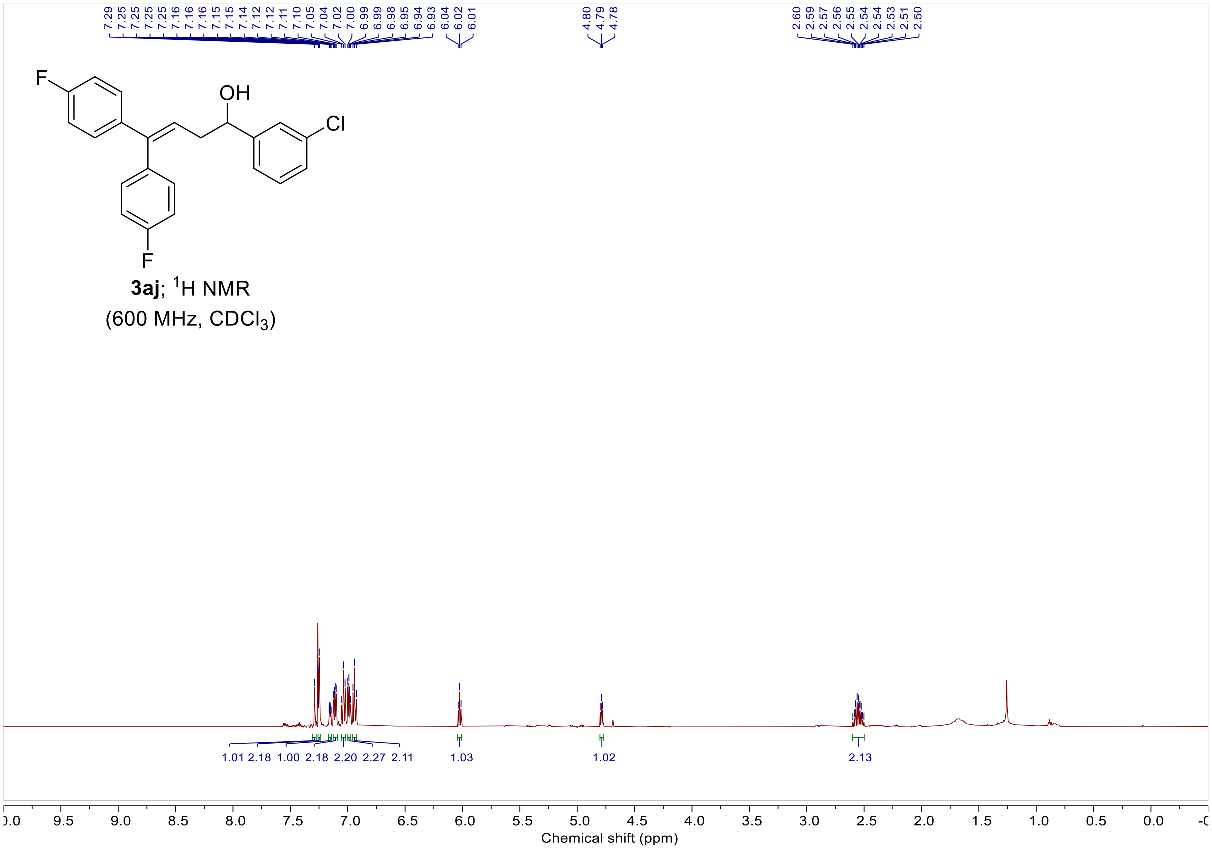


3ai; ^{1}H NMR
(600 MHz, $CDCl_3$)



3ai; ^{13}C NMR
(151 MHz, $CDCl_3$)


-114.81
-115.23
OH
Cl
F
F
3ai; 19F NMR
(564 MHz, CDCl3)
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
Chemical shift (ppm)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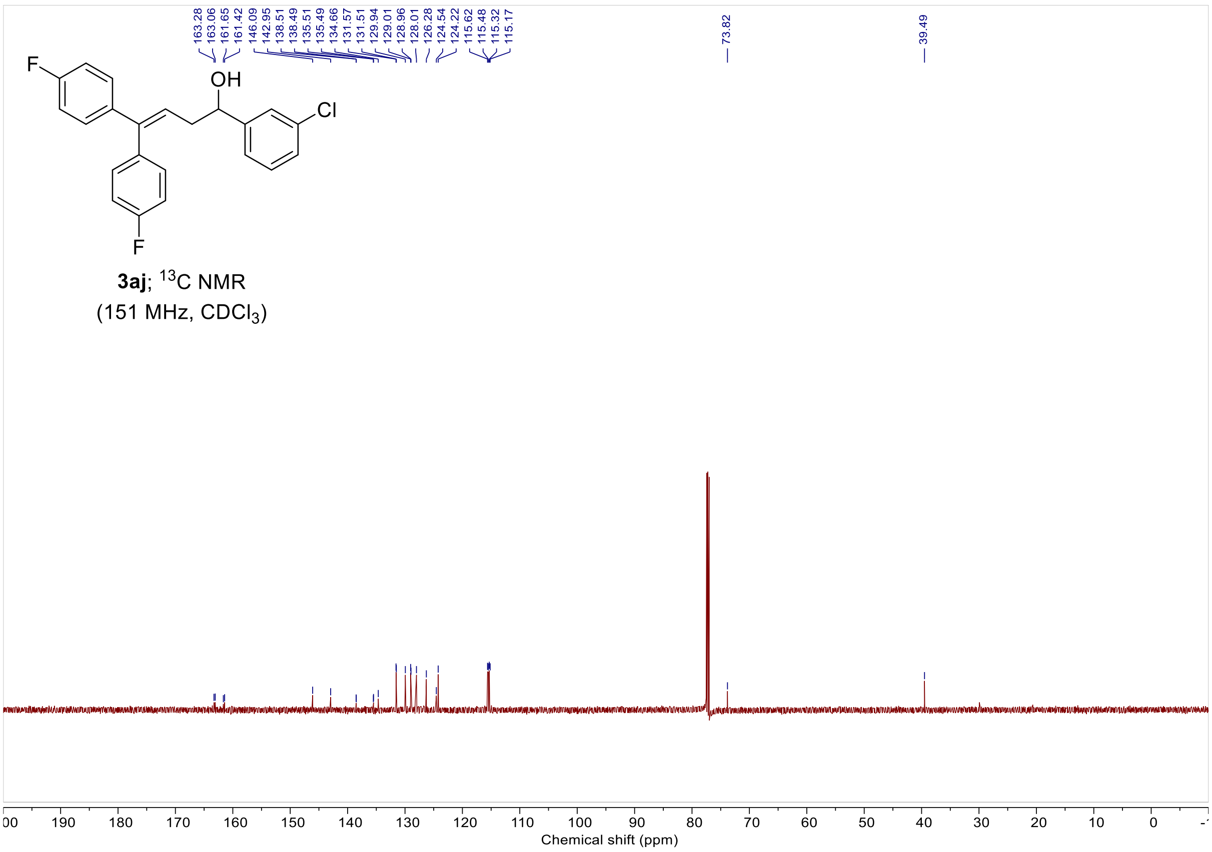
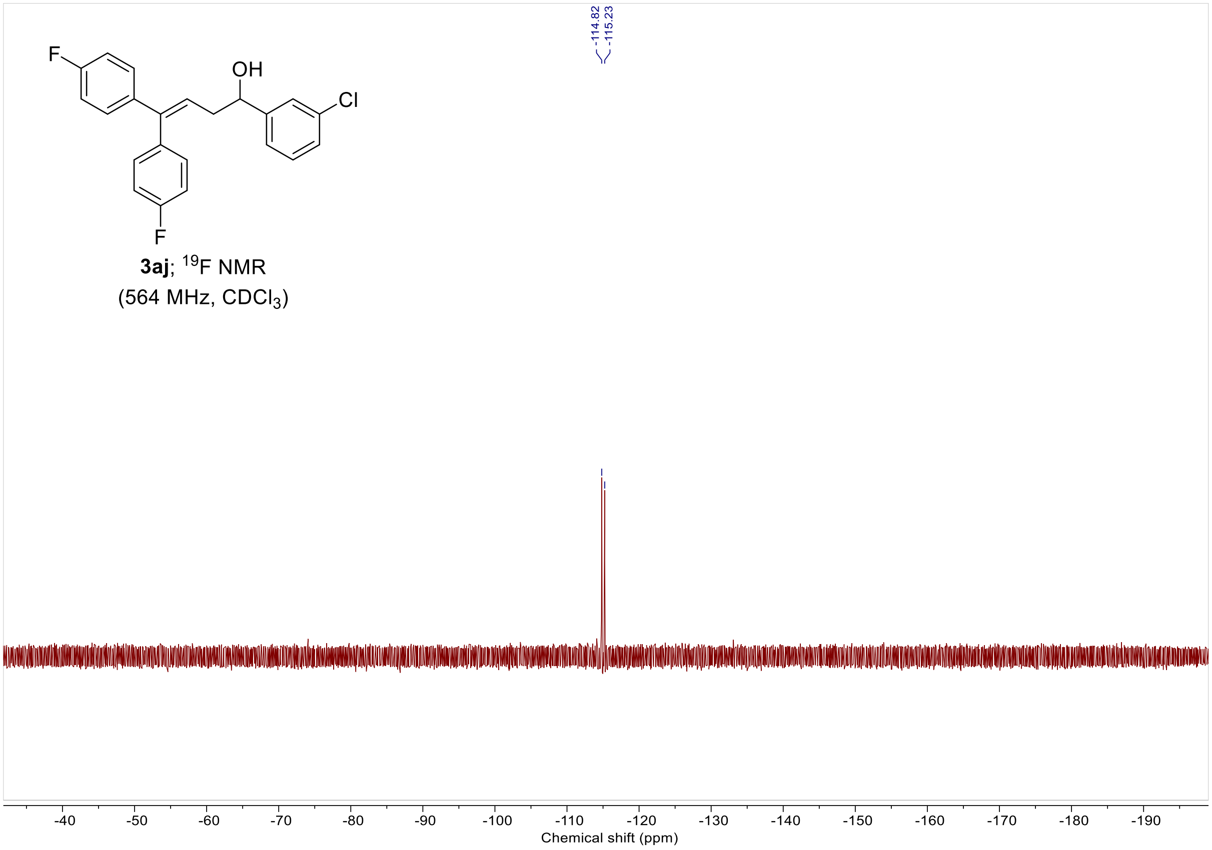
Chemical shift (ppm)


3aj; 13C NMR
(151 MHz, CDCl3)
Chemical shift (ppm)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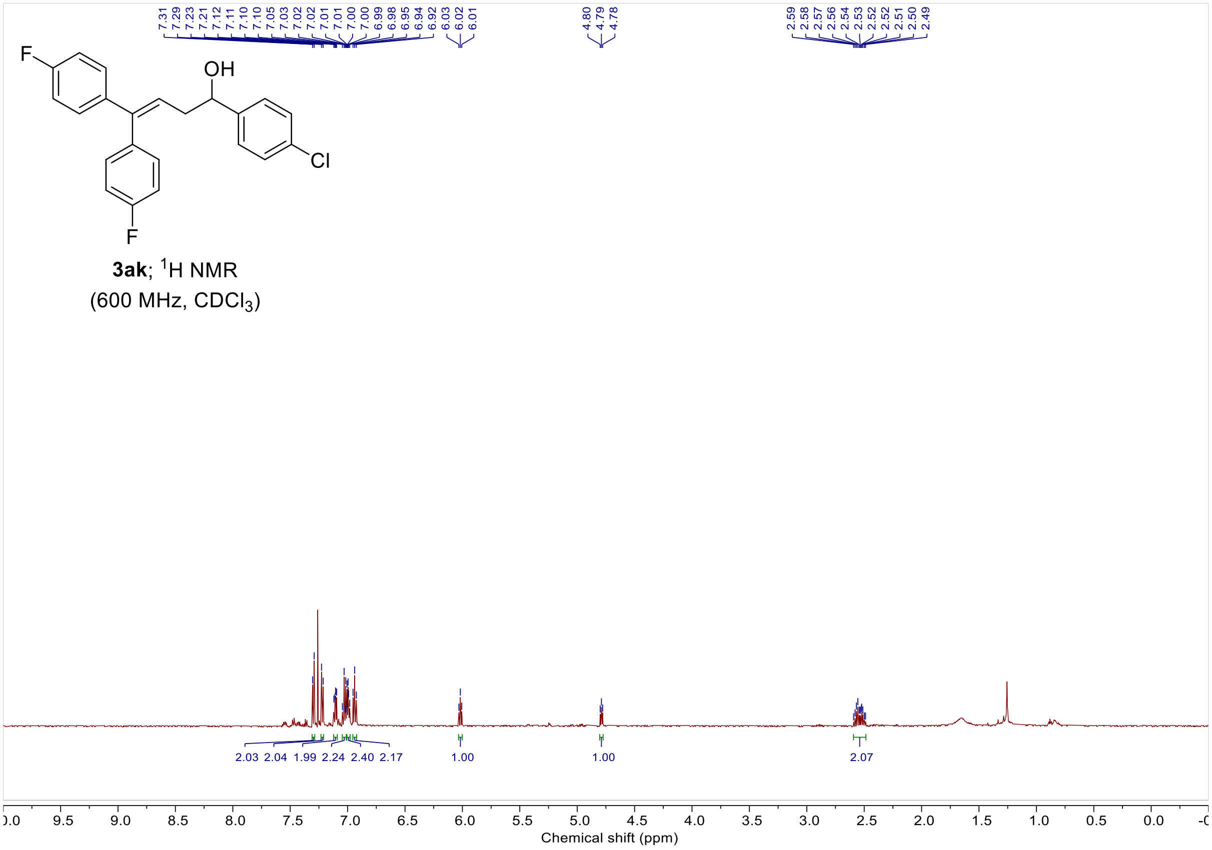
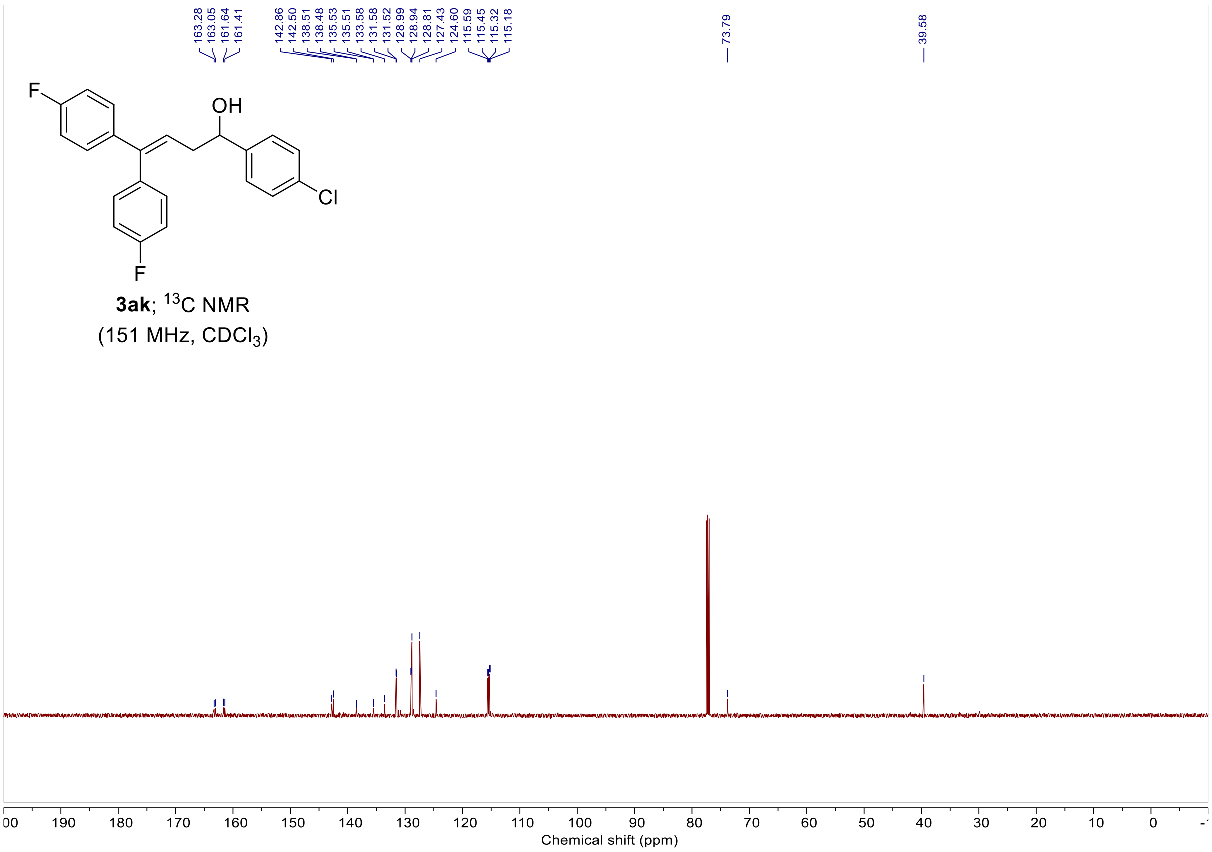
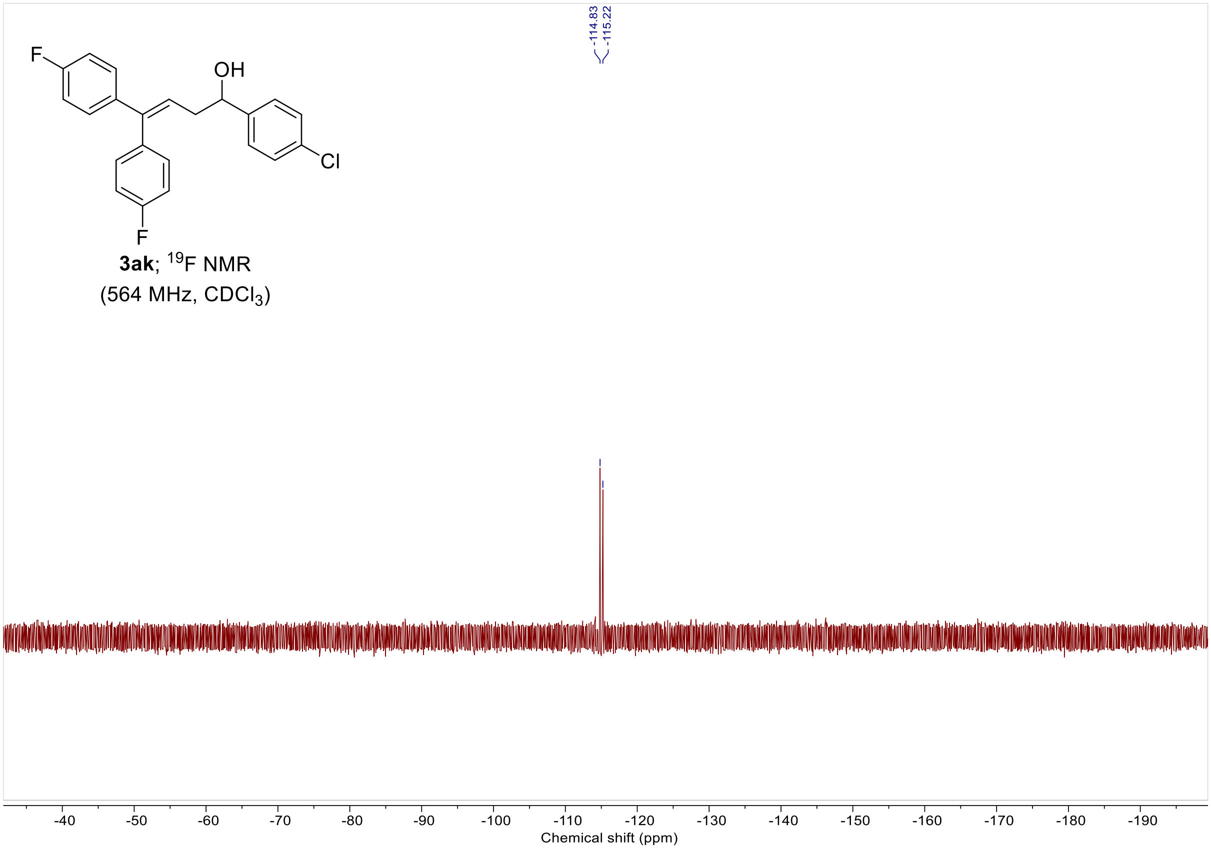
-115.23
F
OH
Cl
F
3aj; 19F NMR
(564 MHz, CDCl3)
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
Chemical shift (ppm)



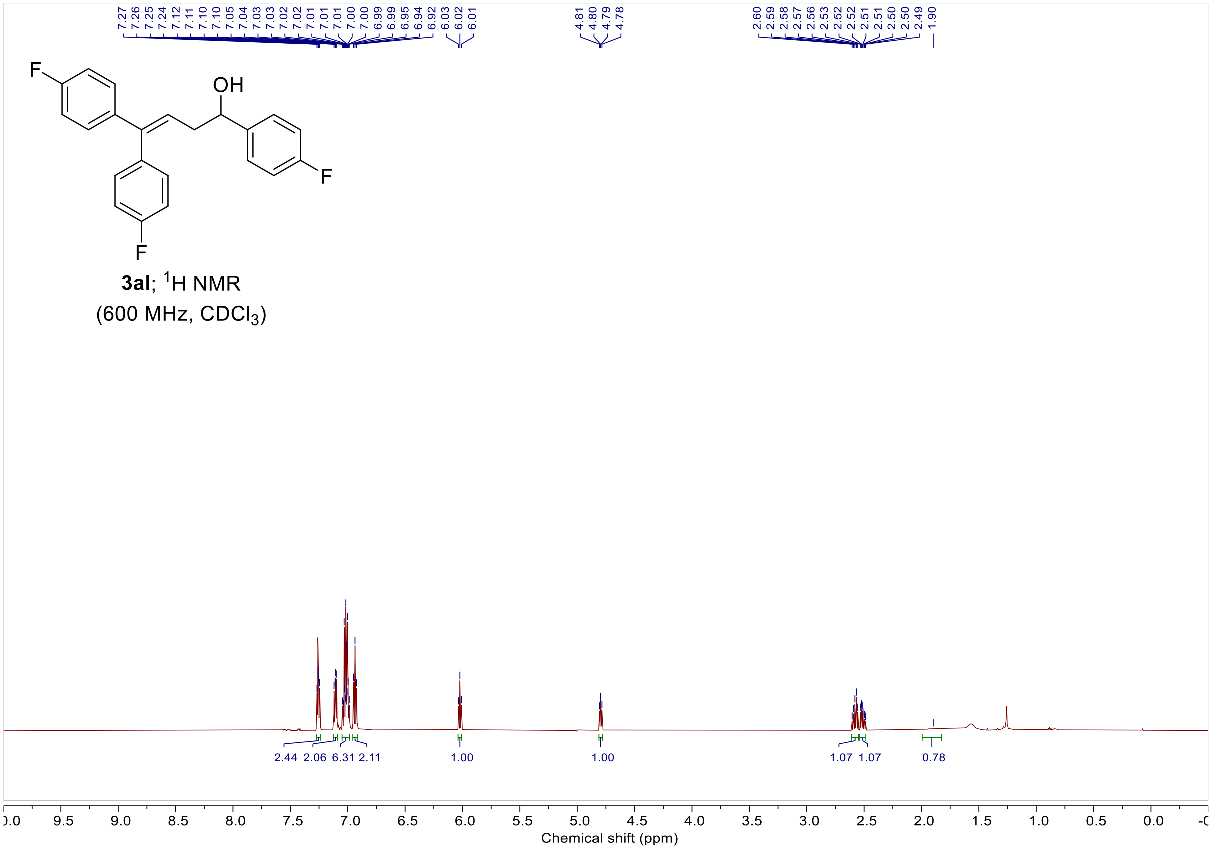
7.31 7.29 7.23 7.21 7.12 7.11 7.10 7.10 7.05 7.03 7.02 7.02 7.01 7.01 7.00 7.00 6.99 6.98 6.95 6.94 6.92 6.03 6.02 6.01
4.80 4.79 4.78
2.59 2.58 2.57 2.56 2.54 2.53 2.52 2.52 2.51 2.50 2.49
F
OH
Cl
F
3ak; ^{1}H NMR
(600 MHz, $CDCl_3$)
2.03 2.04 1.99 2.24 2.40 2.17
1.00
1.00
2.07
Chemical shift (ppm)

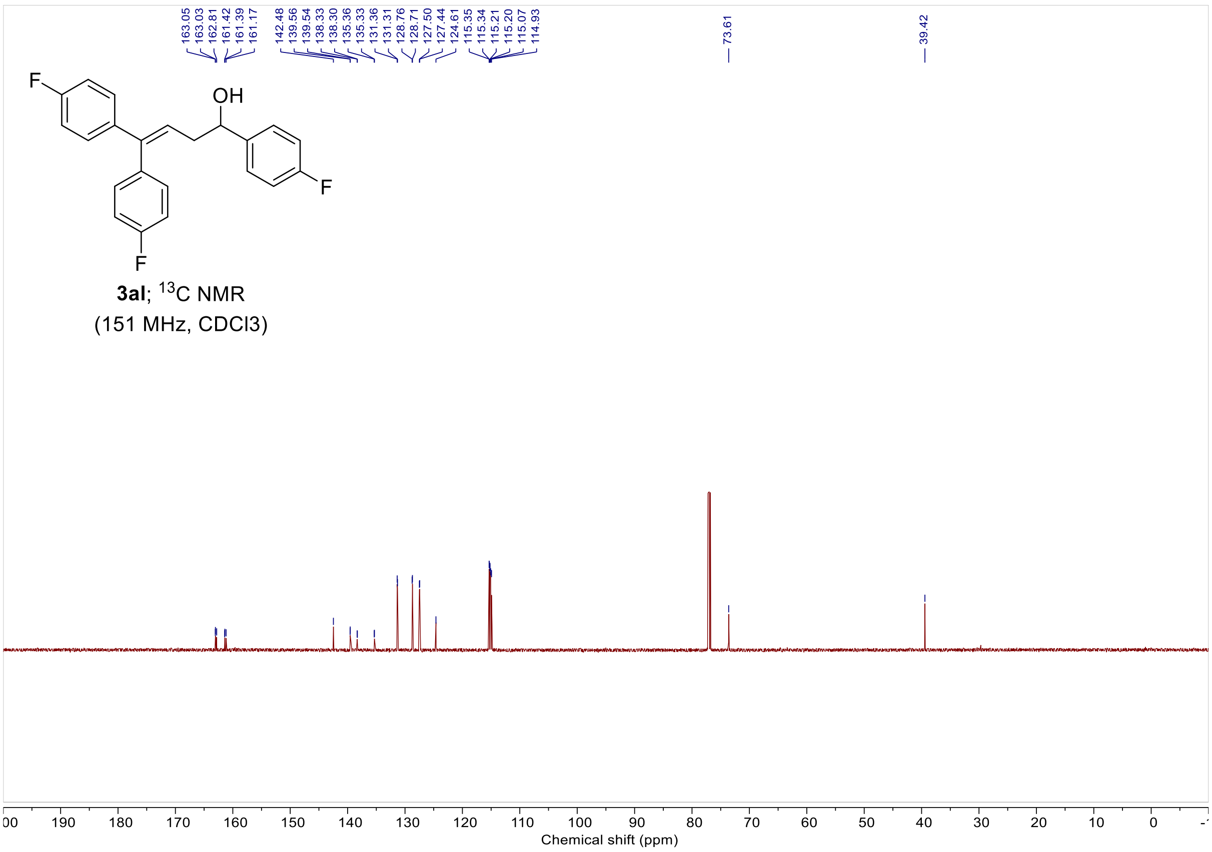


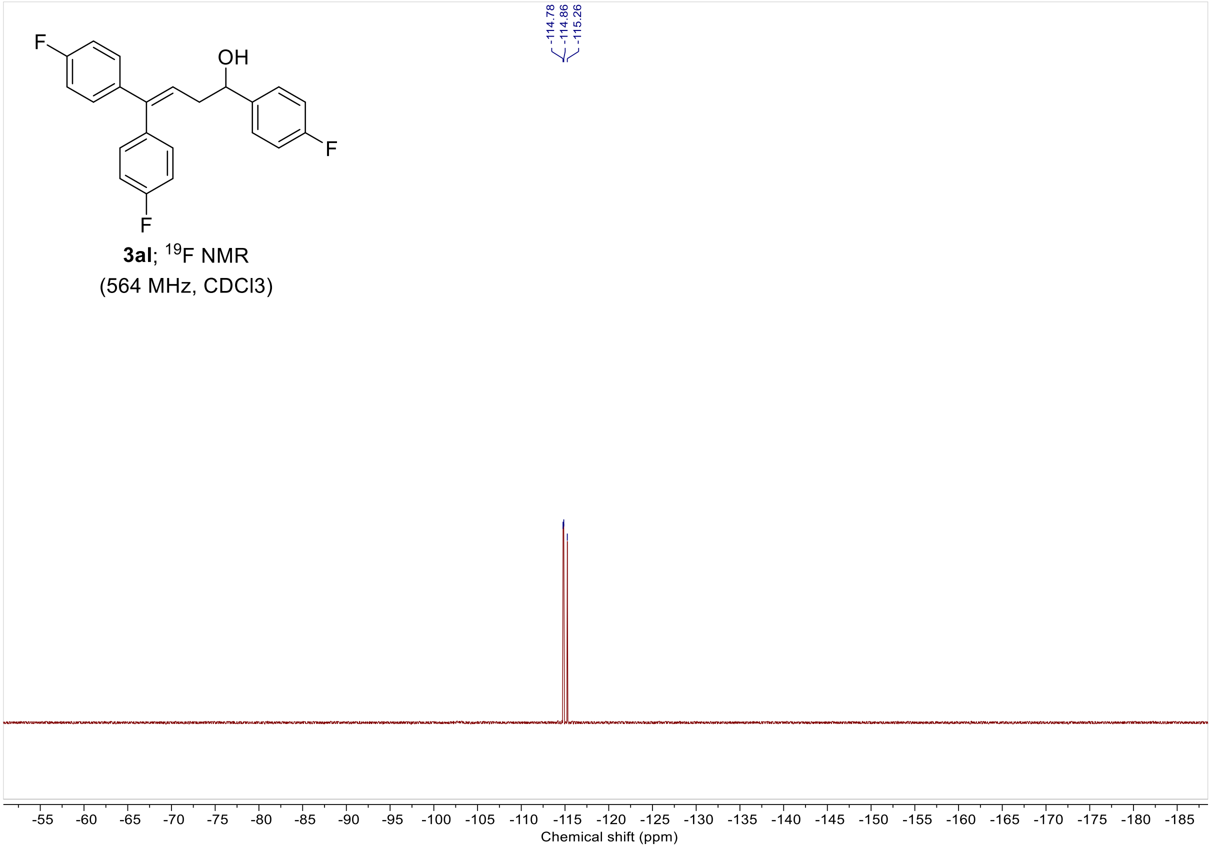
163.28 163.05 161.64 161.41
142.86 142.50 138.51 138.48 135.53 135.51 133.58 131.58 131.52 128.99 128.94 128.81 127.43 124.60 115.59 115.45 115.32 115.18
73.79
39.58
F
OH
Cl
F
3ak; ^{13}C NMR
(151 MHz, $CDCl_3$)
Chemical shift (ppm)

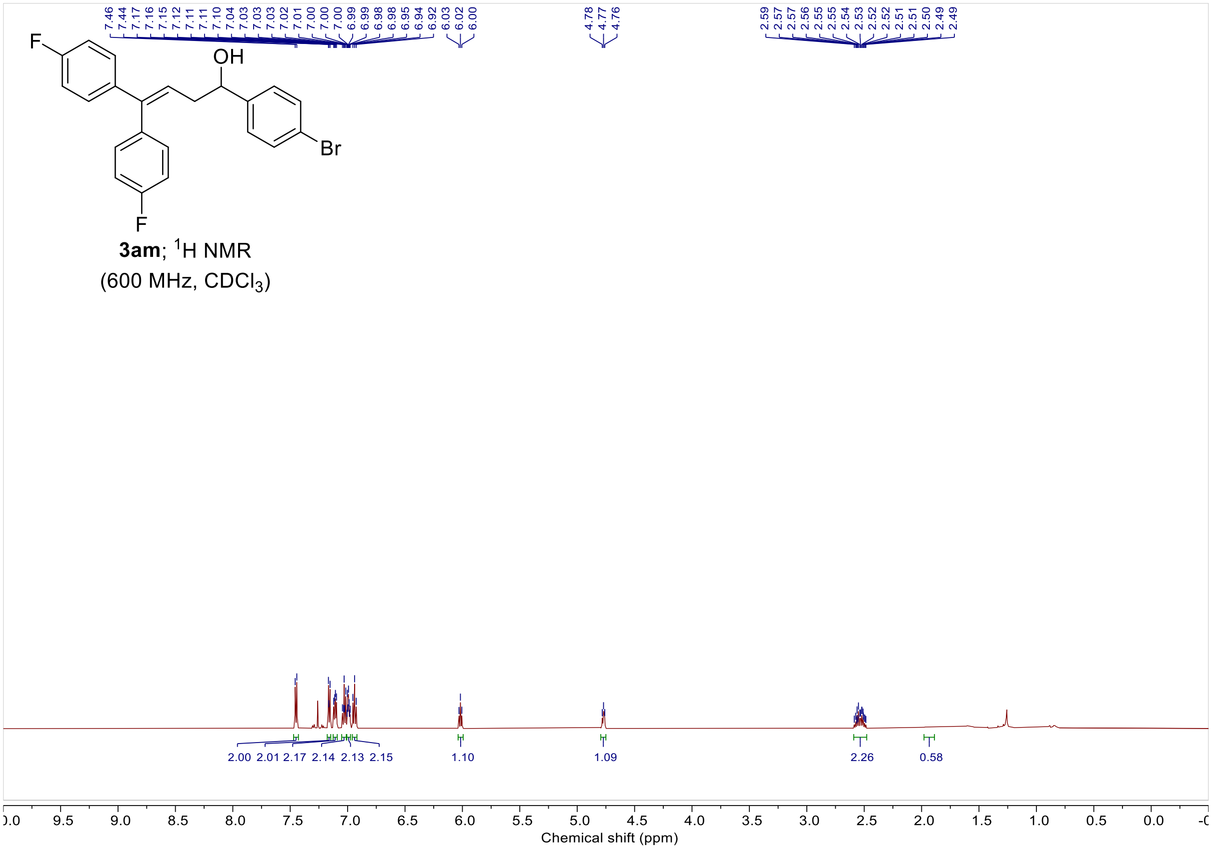


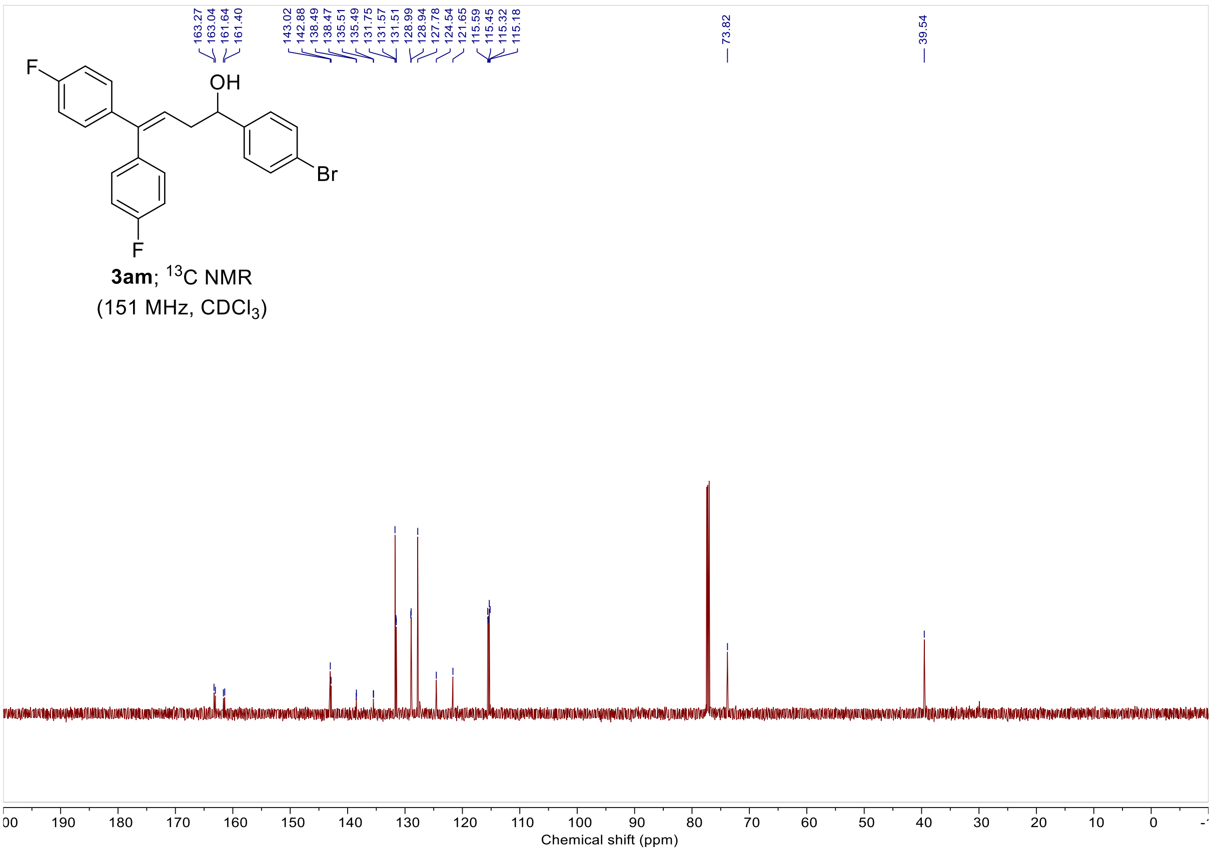
-114.83
-115.22
F
OH
Cl
F
3ak; 19F NMR
(564 MHz, CDCl3)
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
Chemical shift (ppm)

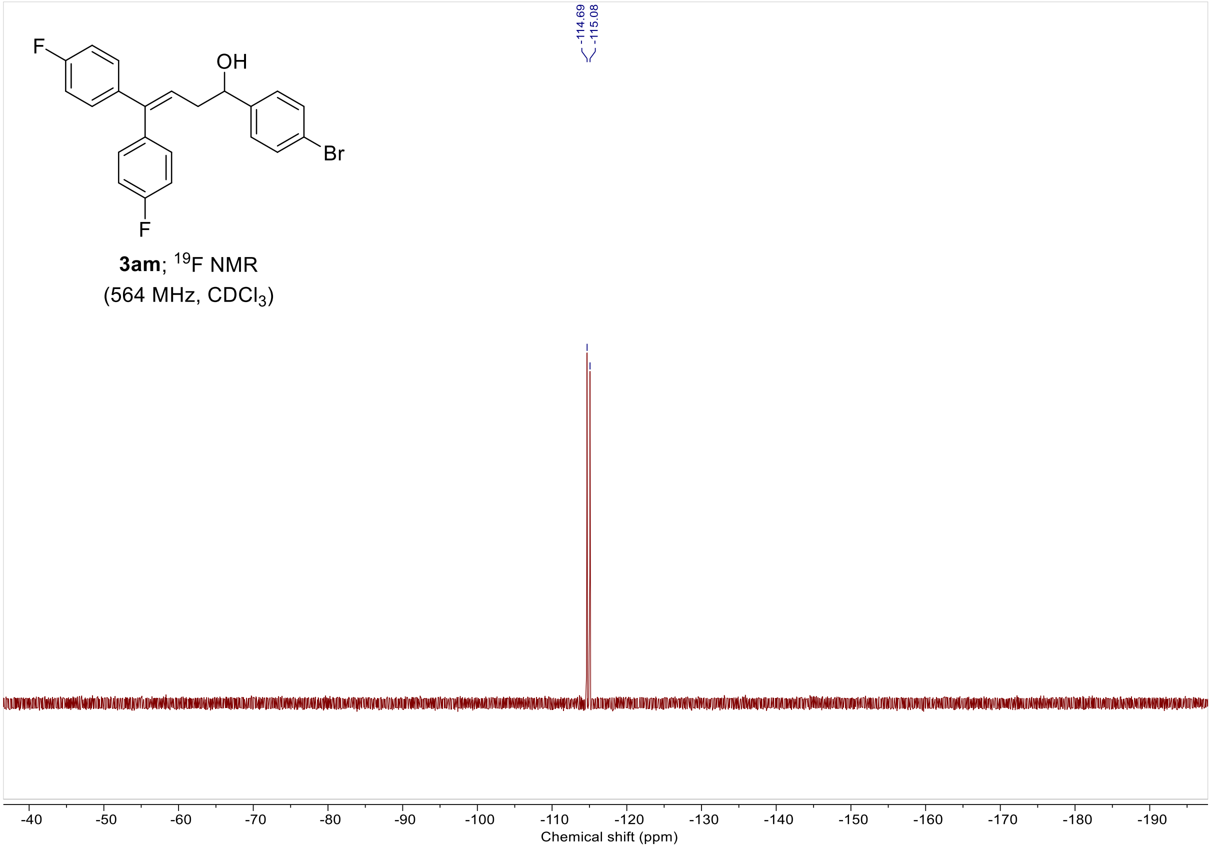

7.27
7.26
7.25
7.24
7.12
7.11
7.10
7.05
7.04
7.03
7.03
7.02
7.02
7.01
7.01
7.01
7.00
7.00
6.99
6.99
6.95
6.94
6.92
6.03
6.02
6.01
4.81
4.80
4.79
4.78
2.60
2.59
2.58
2.57
2.56
2.53
2.52
2.52
2.51
2.51
2.50
2.50
2.49
1.90
OH
F
F
F
3al; 1H NMR
(600 MHz, CDCl3)
2.44
2.06
6.31
2.11
1.00
1.00
1.07
1.07
0.78
Chemical shift (ppm)


163.05
163.03
162.81
161.42
161.39
161.17
142.48
139.56
139.54
138.33
138.30
135.36
135.33
131.36
131.31
128.76
128.71
127.50
127.44
124.61
115.35
115.34
115.21
115.20
115.07
114.93
73.61
39.42
OH
F
F
F
3al; 13C NMR
(151 MHz, CDCl3)
Chemical shift (ppm)

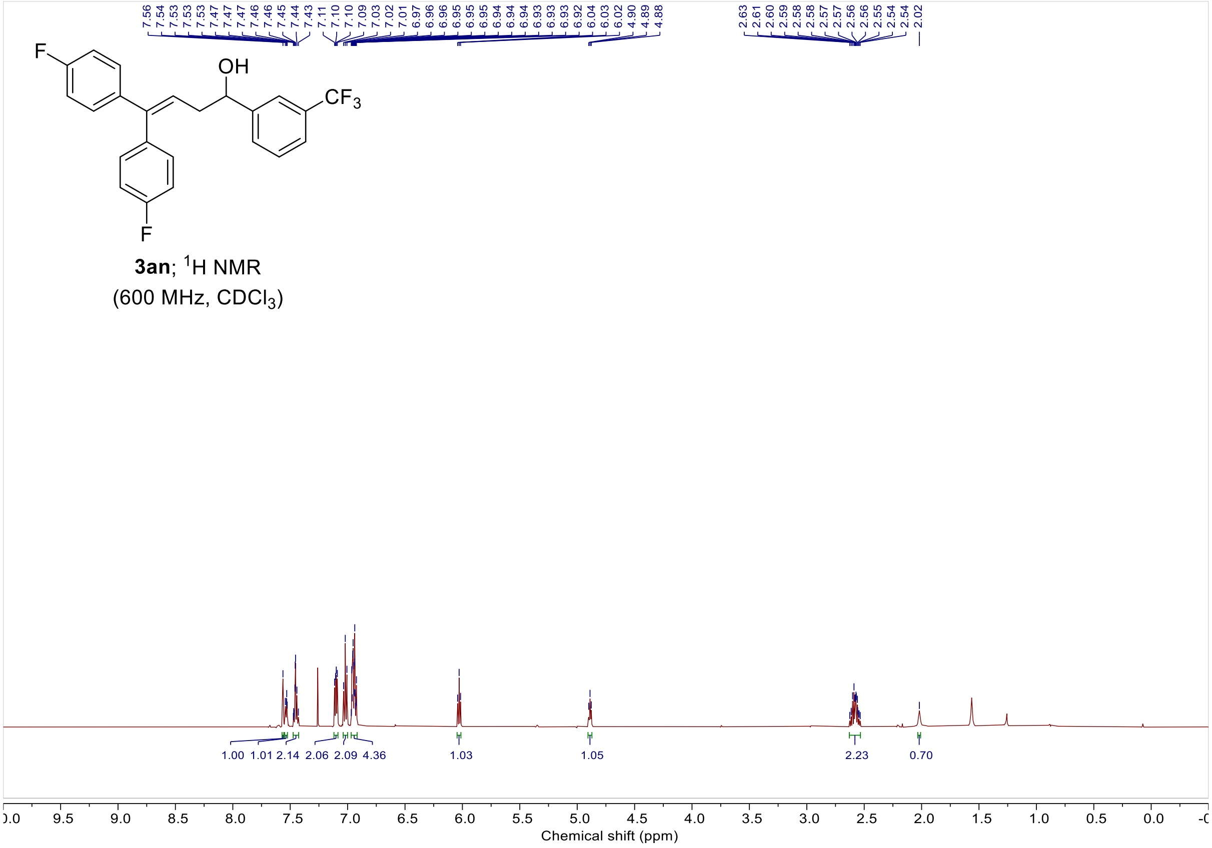

F
OH
F
F
3al; 19F NMR
(564 MHz, CDCl3)
-114.78
-114.86
-115.26
-55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185
Chemical shift (ppm)

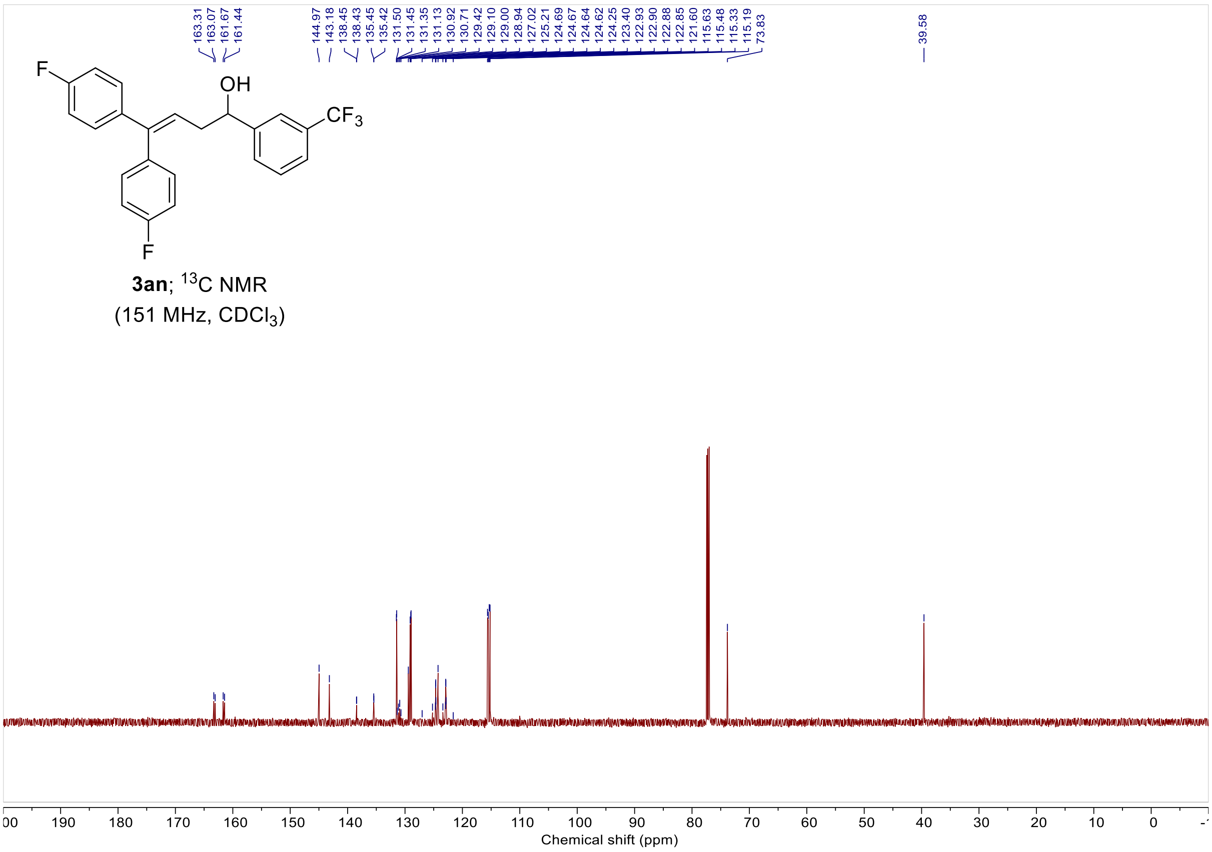

3am; ^{1}H NMR
(600 MHz, $CDCl_3$)
Chemical shift (ppm)

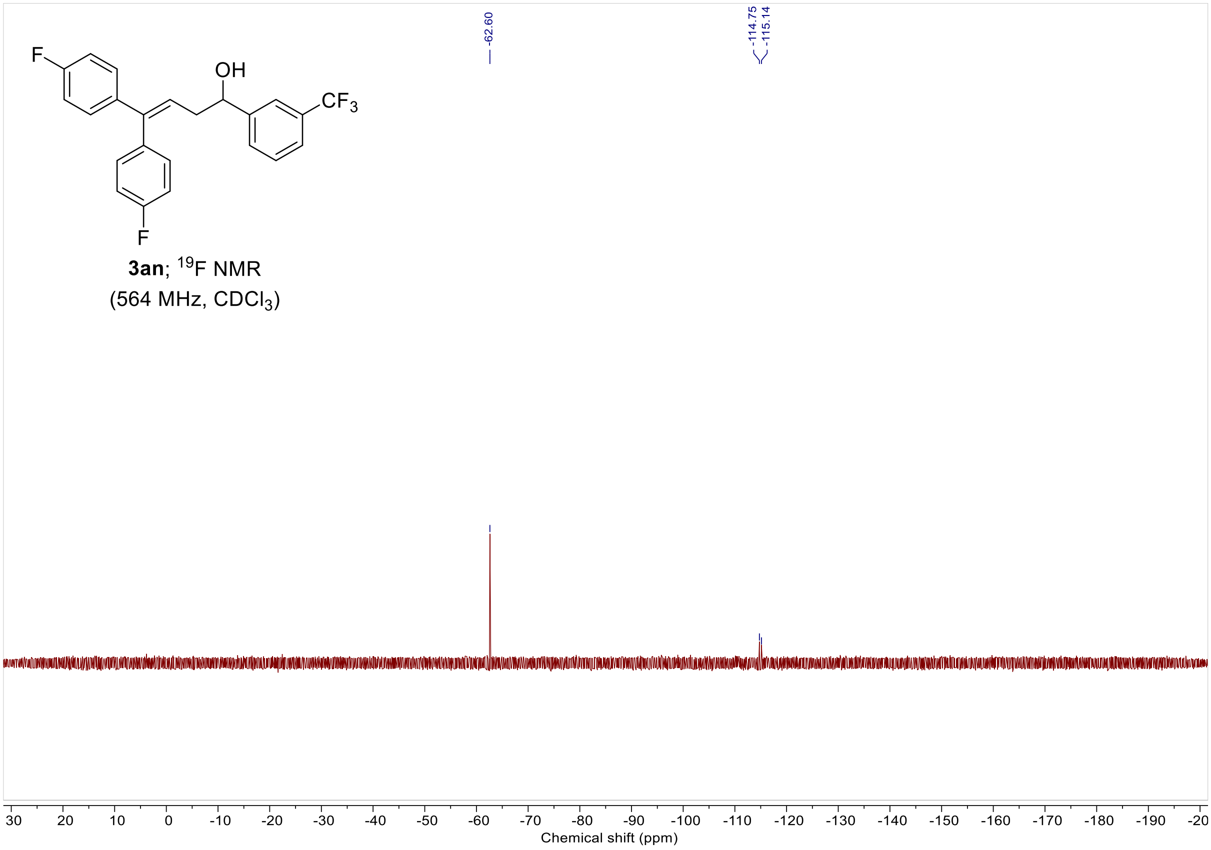

3am; ^{13}C NMR
(151 MHz, $CDCl_3$)
Chemical shift (ppm)



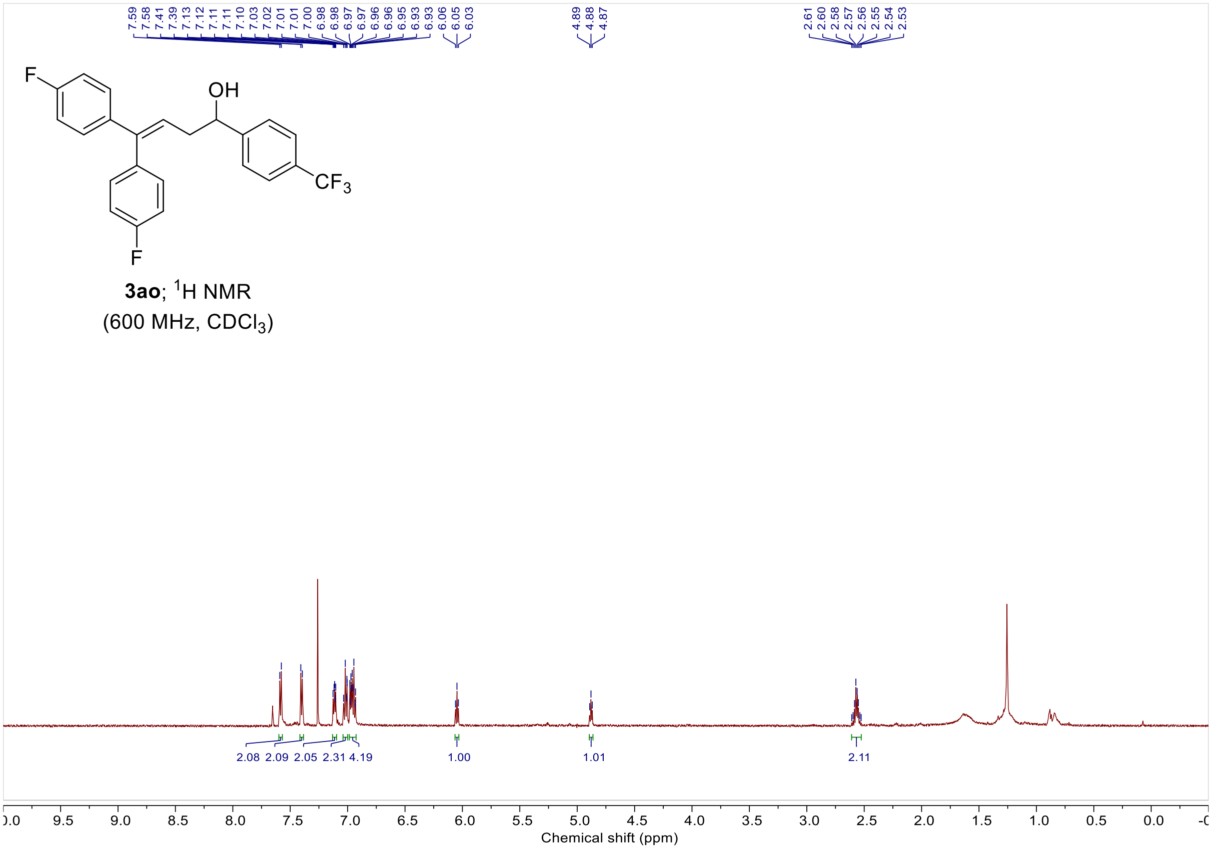
-114.69
-115.08
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
Chemical shift (ppm)


7.56 7.54 7.53 7.53 7.53 7.47 7.47 7.46 7.45 7.44 7.43 7.11 7.10 7.10 7.09 7.03 7.02 7.01 6.97 6.96 6.96 6.95 6.95 6.95 6.94 6.94 6.94 6.93 6.93 6.93 6.92 6.04 6.03 6.02 4.90 4.89 4.88
2.63 2.61 2.60 2.59 2.58 2.58 2.57 2.56 2.56 2.55 2.54 2.54 2.02
OH
CF3
F
F
3an; 1H NMR
(600 MHz, CDCl3)
1.00 1.01 2.14 2.06 2.09 4.36 1.03 1.05 2.23 0.70
Chemical shift (ppm)

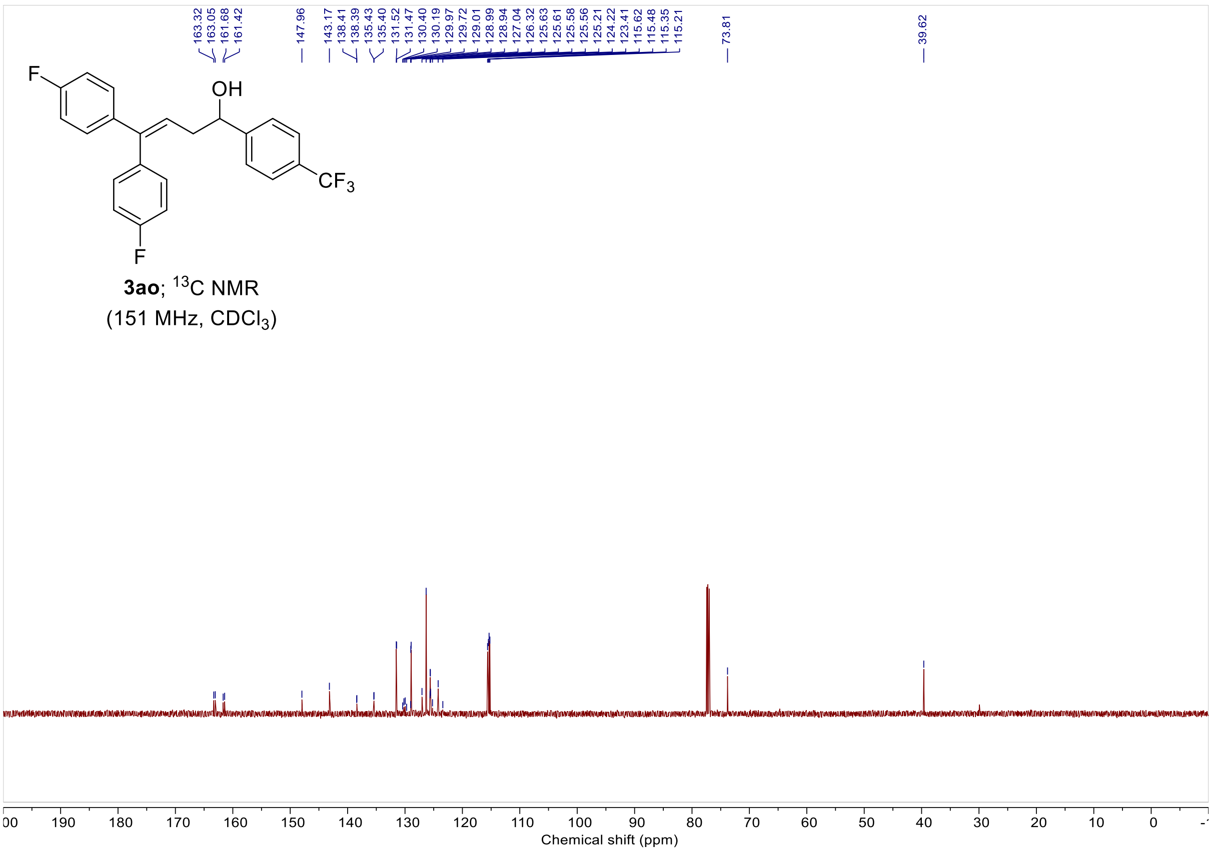

163.31 163.07 161.67 161.44
144.97 143.18 138.45 138.43 135.45 135.42 131.50 131.45 131.35 131.13 130.92 130.71 129.42 129.10 129.00 128.94 127.02 125.21 124.69 124.67 124.64 124.62 124.25 123.40 122.93 122.90 122.88 122.85 121.60 115.63 115.48 115.33 115.19 73.83
39.58
OH
CF3
F
F
3an; 13C NMR
(151 MHz, CDCl3)
Chemical shift (ppm)



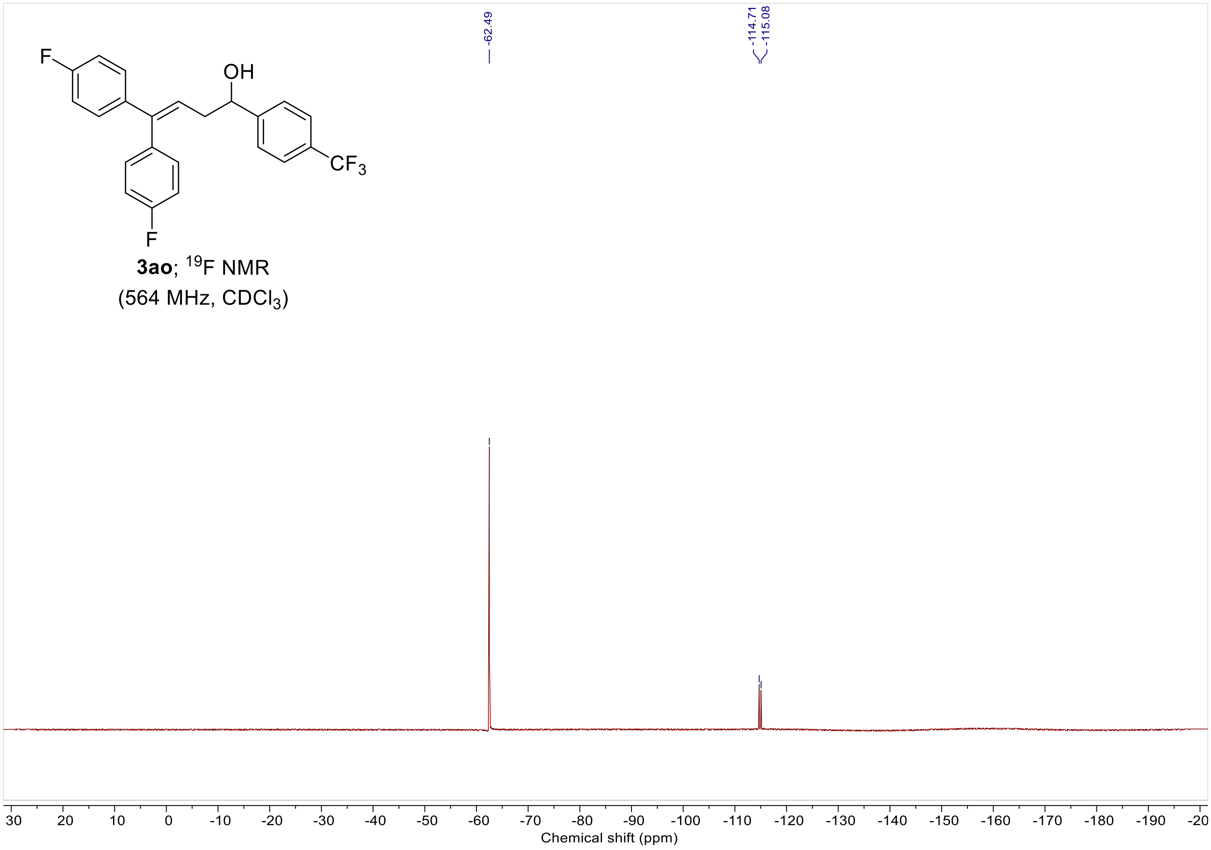
3an; ^{19}F NMR
(564 MHz, $CDCl_3$)



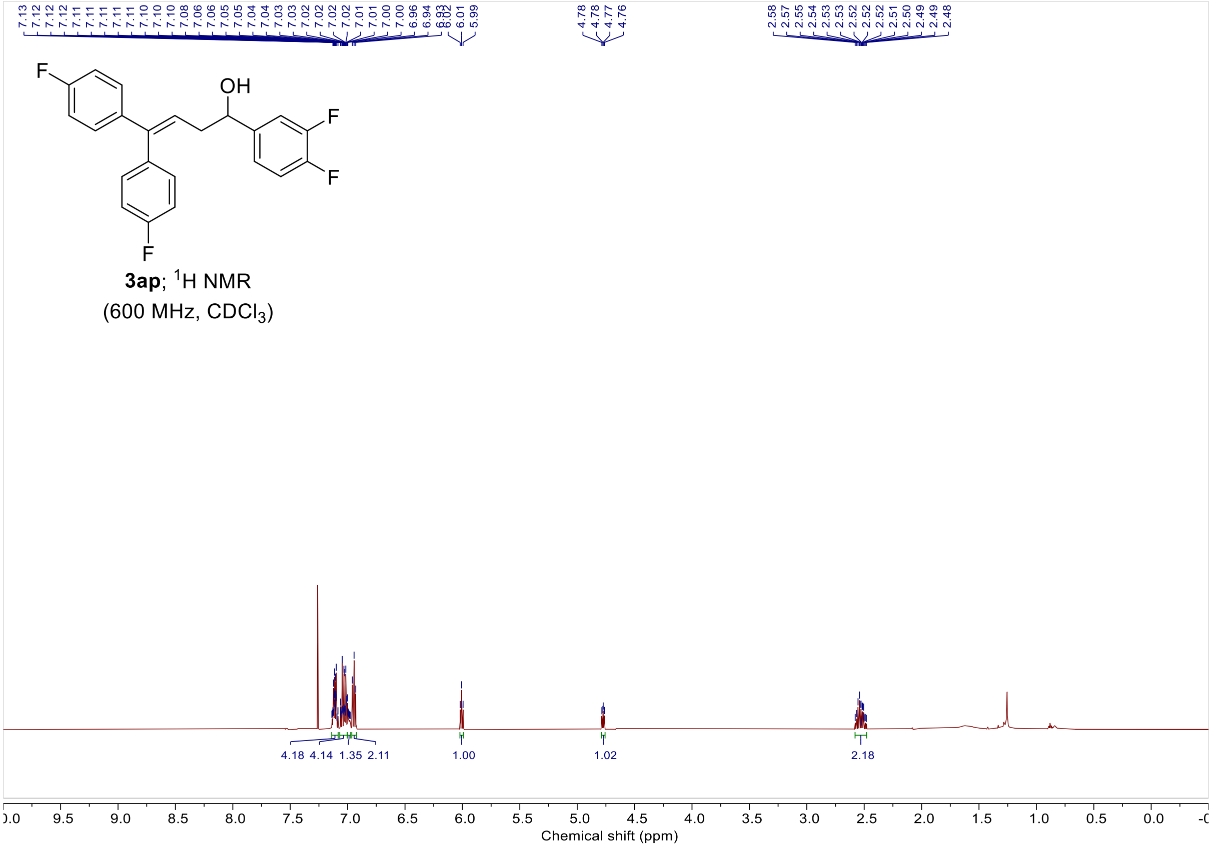
OH
F
CF3
F
3ao; 1H NMR
(600 MHz, CDCl3)
Chemical shift (ppm)

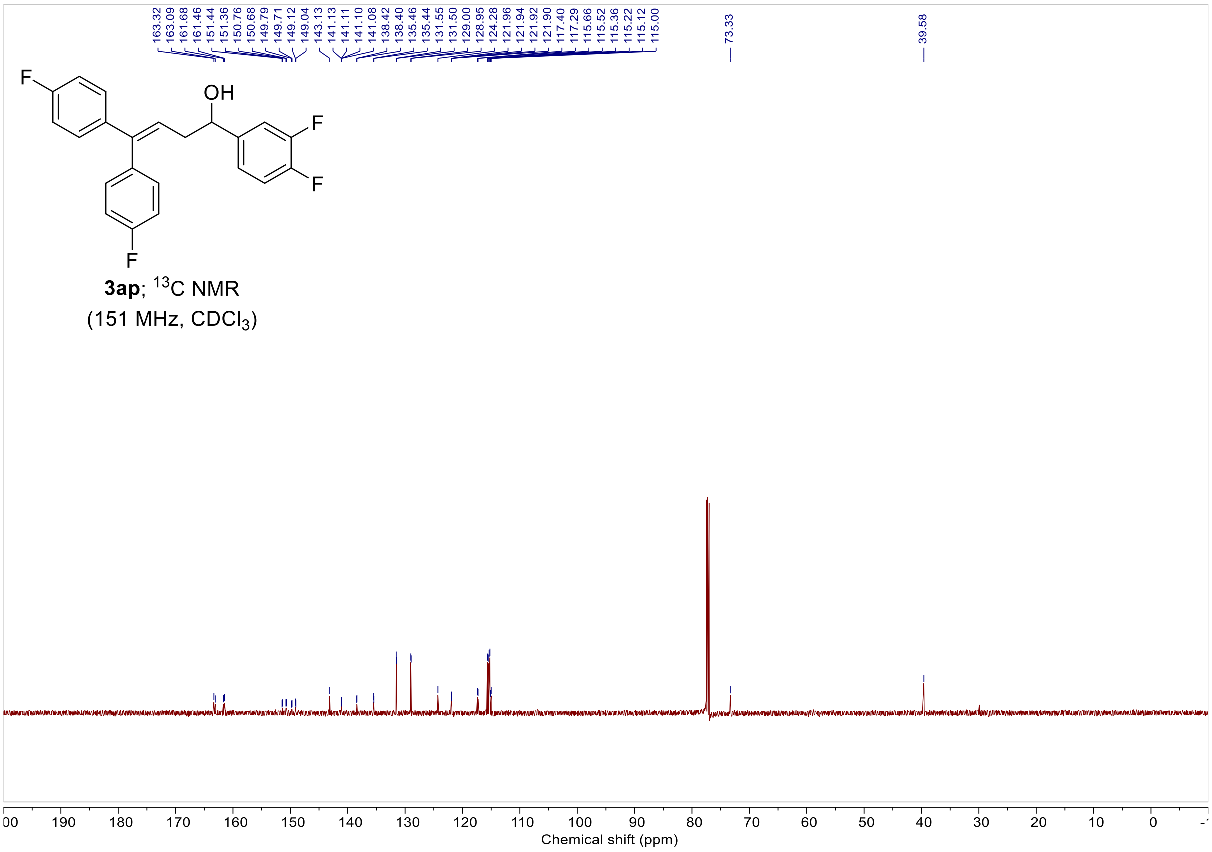


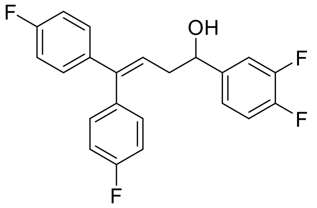
OH
F
CF3
F
3ao; 13C NMR
(151 MHz, CDCl3)
Chemical shift (ppm)



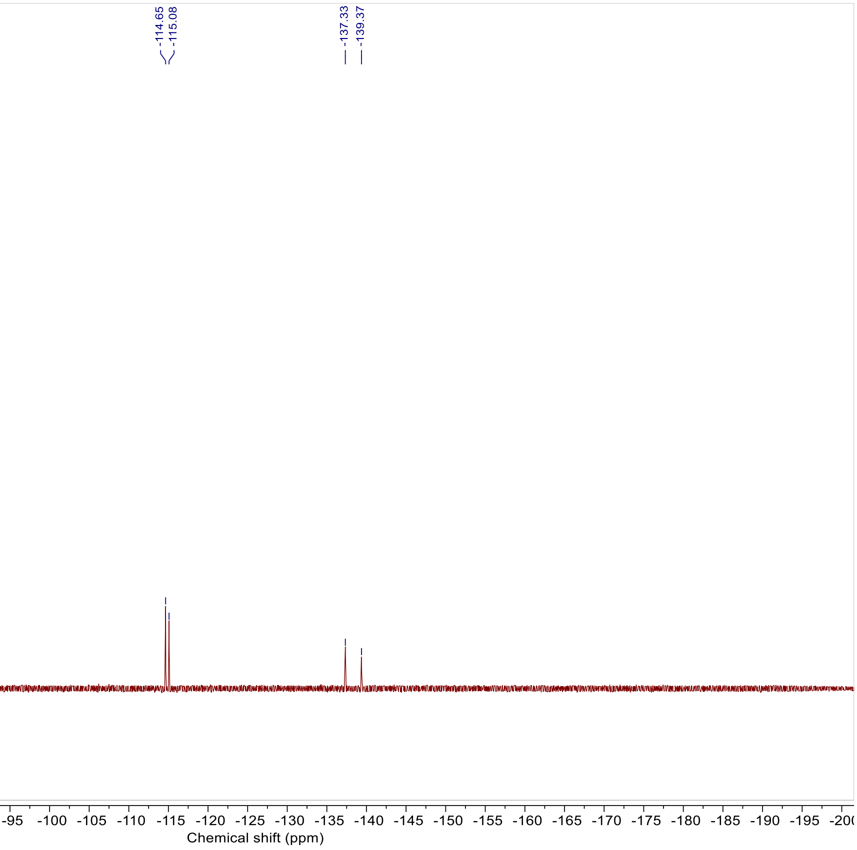
OH
F
F
CF3
3ao; 19F NMR
(564 MHz, CDCl3)
-62.49
-114.71
-115.08
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -20
Chemical shift (ppm)

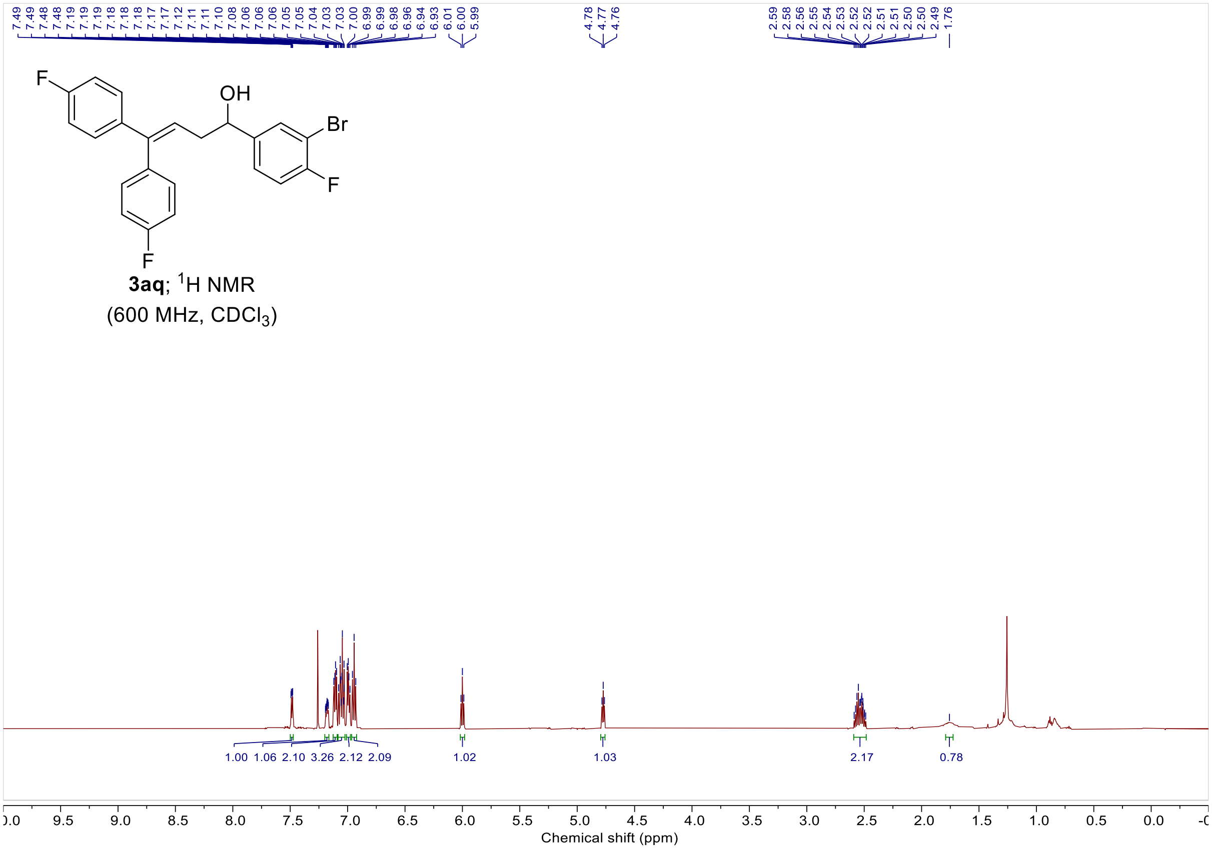

7.13 7.12 7.12 7.11 7.11 7.11 7.11 7.10 7.10 7.08 7.06 7.06 7.05 7.05 7.04 7.04 7.03 7.03 7.02 7.02 7.02 7.02 7.01 7.01 7.00 7.00 6.96 6.94 6.93 6.02 6.01 5.99
4.78 4.78 4.77 4.76
2.58 2.57 2.55 2.54 2.53 2.53 2.52 2.52 2.52 2.51 2.50 2.49 2.49 2.48
F
OH
F
F
F
3ap; 1H NMR
(600 MHz, CDCl3)
4.18 4.14 1.35 2.11
1.00
1.02
2.18
Chemical shift (ppm)

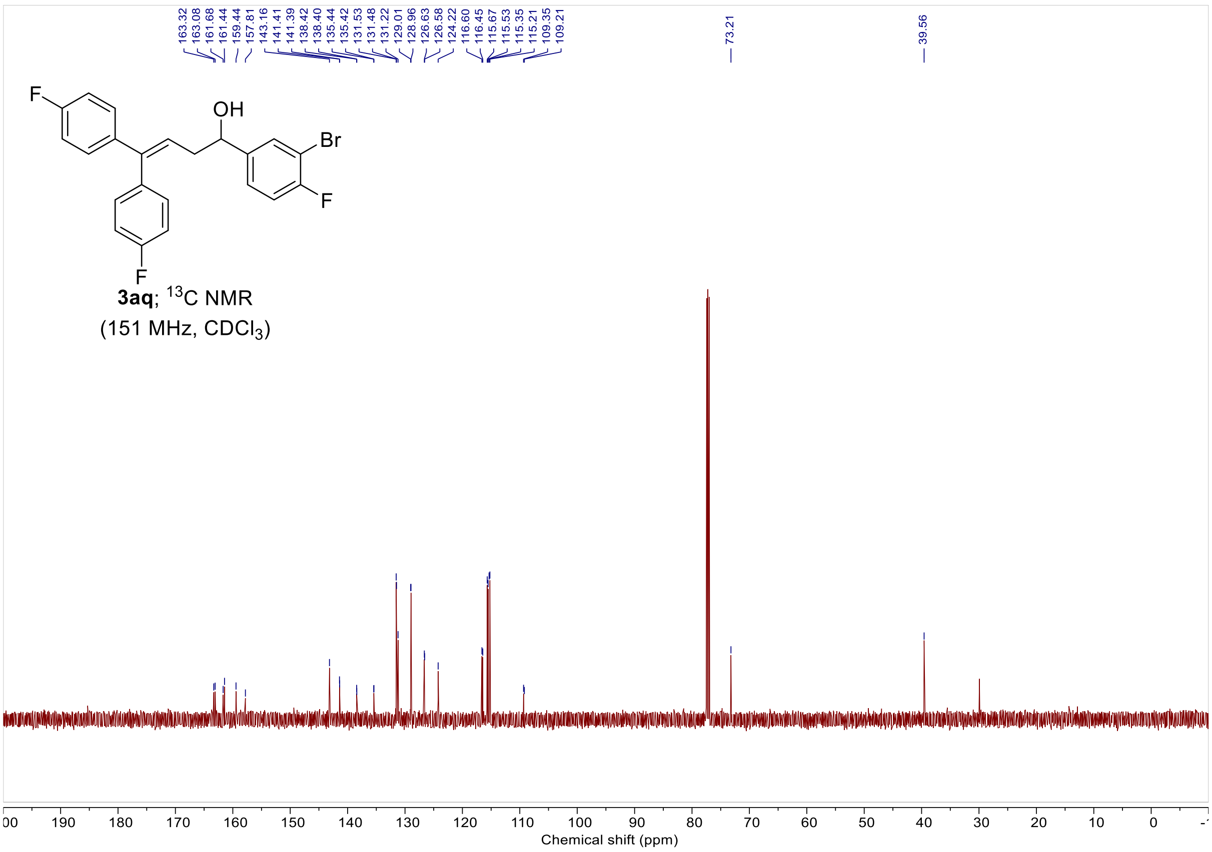

163.32 163.09 161.68 161.46 151.44 151.36 150.76 150.68 149.79 149.71 149.12 149.04 143.13 141.13 141.11 141.10 141.08 138.42 138.40 135.46 135.44 131.55 131.50 129.00 128.95 124.28 121.96 121.94 121.92 117.40 117.29 115.66 115.52 115.36 115.22 115.12 115.00
73.33
39.58
F
OH
F
F
F
3ap; 13C NMR
(151 MHz, CDCl3)
Chemical shift (ppm)

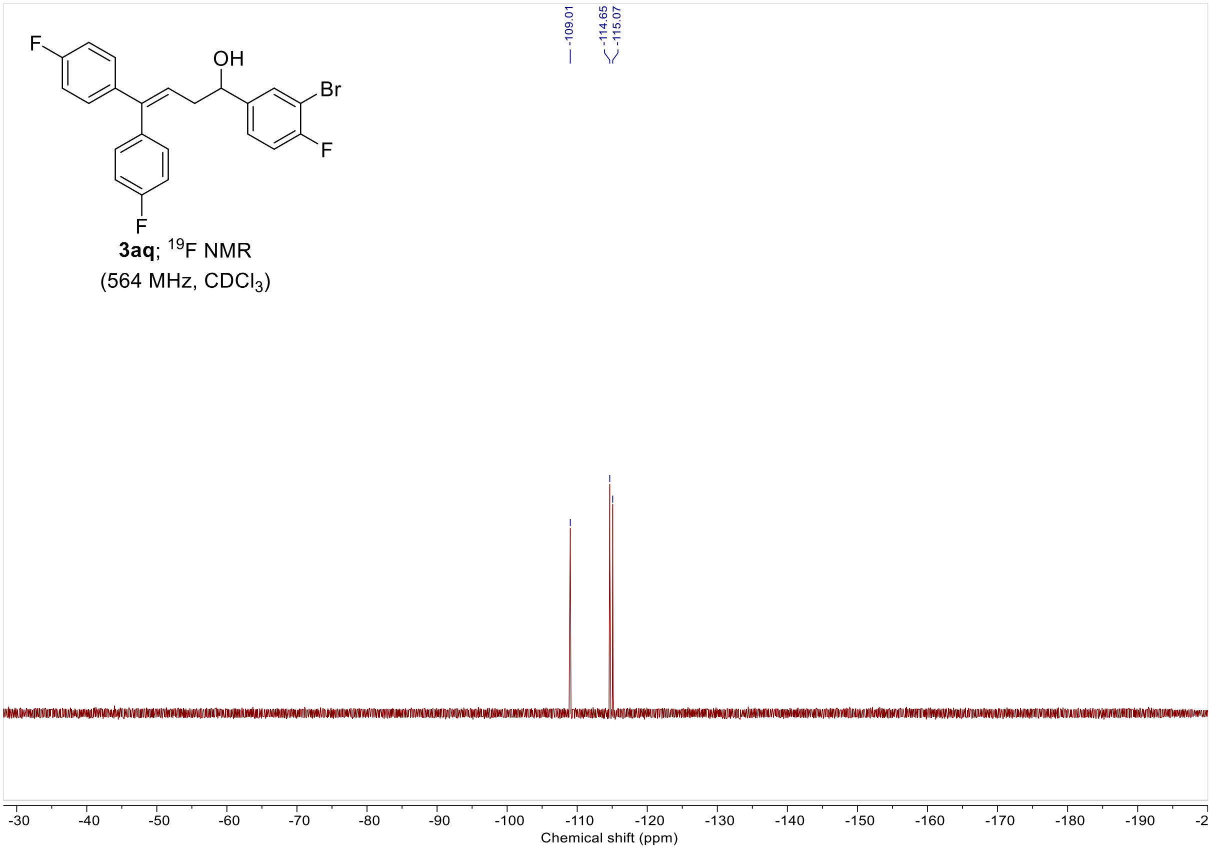


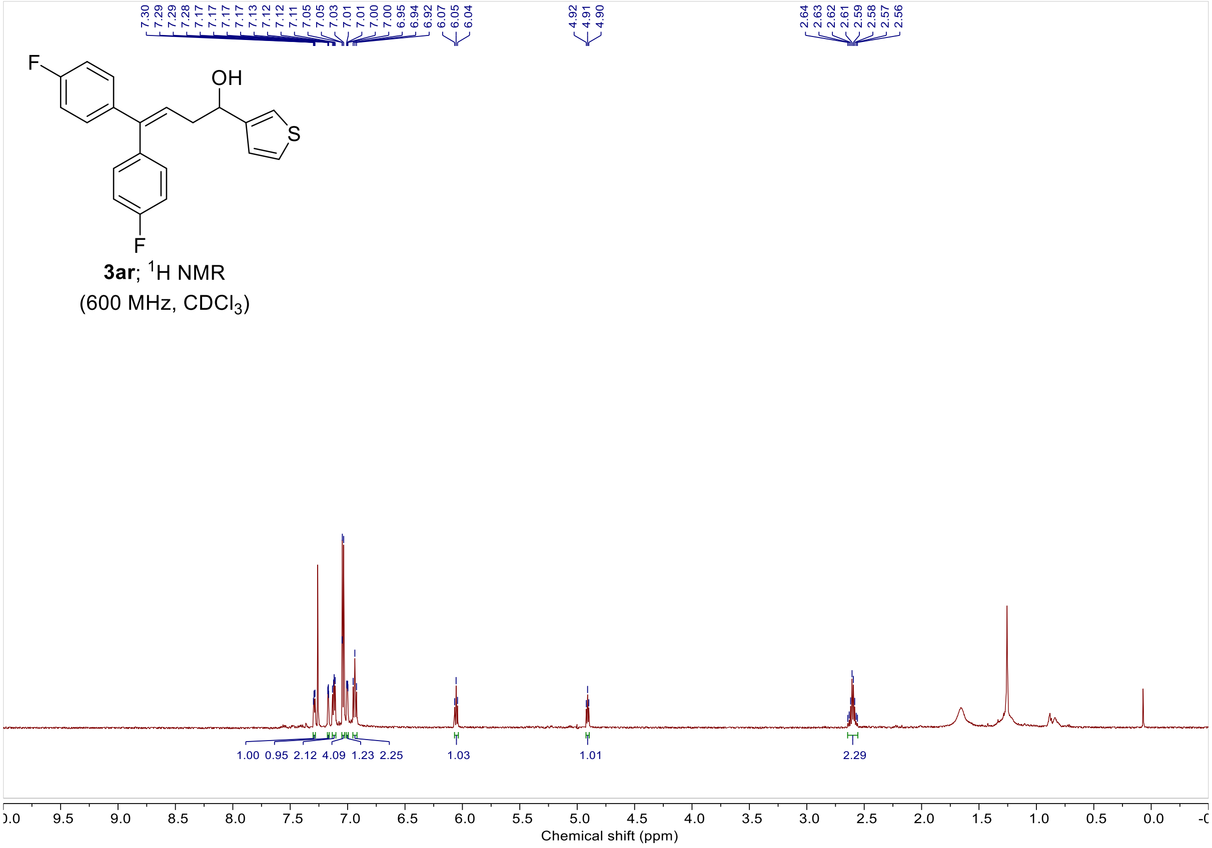
3ap; ^{19}F NMR
(564 MHz, $CDCl_3$)

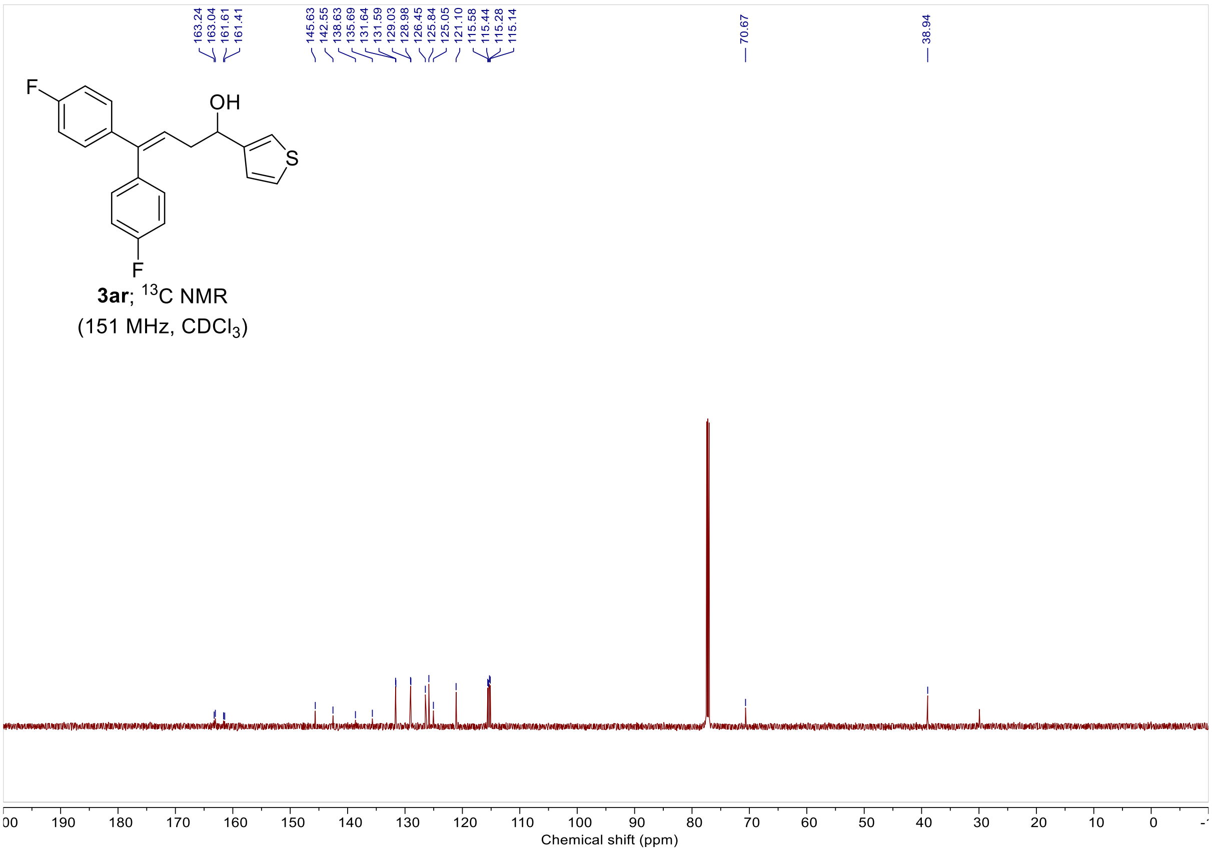


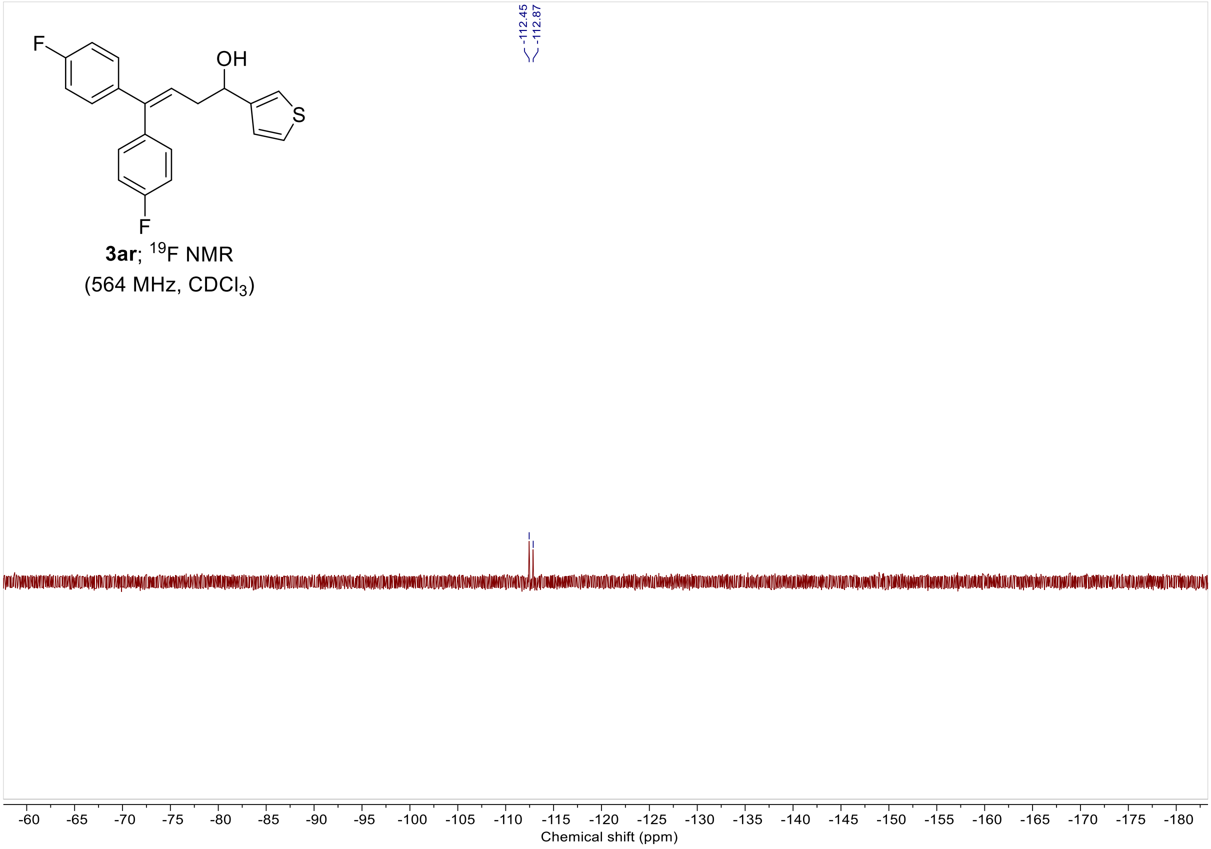

7.49 7.49 7.48 7.19 7.19 7.19 7.18 7.18 7.17 7.17 7.12 7.11 7.11 7.10 7.08 7.06 7.06 7.05 7.05 7.04 7.03 7.03 7.00 6.99 6.99 6.98 6.96 6.94 6.93 6.01 6.00 5.99
4.78 4.77 4.76
2.59 2.58 2.56 2.55 2.54 2.53 2.52 2.52 2.51 2.51 2.50 2.50 2.49
1.76
OH
Br
F
F
F
3aq; 1H NMR
(600 MHz, CDCl3)
1.00 1.06 2.10 3.26 2.12 2.09
1.02
1.03
2.17
0.78
Chemical shift (ppm)


163.32 163.08 161.68 161.44 159.44 157.81 143.16 141.41 141.39 138.42 138.40 135.44 135.42 131.53 131.48 131.22 129.01 128.96 126.63 126.58 124.22 116.60 116.45 115.67 115.53 115.35 115.21 109.35 109.21
73.21
39.56
OH
Br
F
F
F
3aq; 13C NMR
(151 MHz, CDCl3)
Chemical shift (ppm)

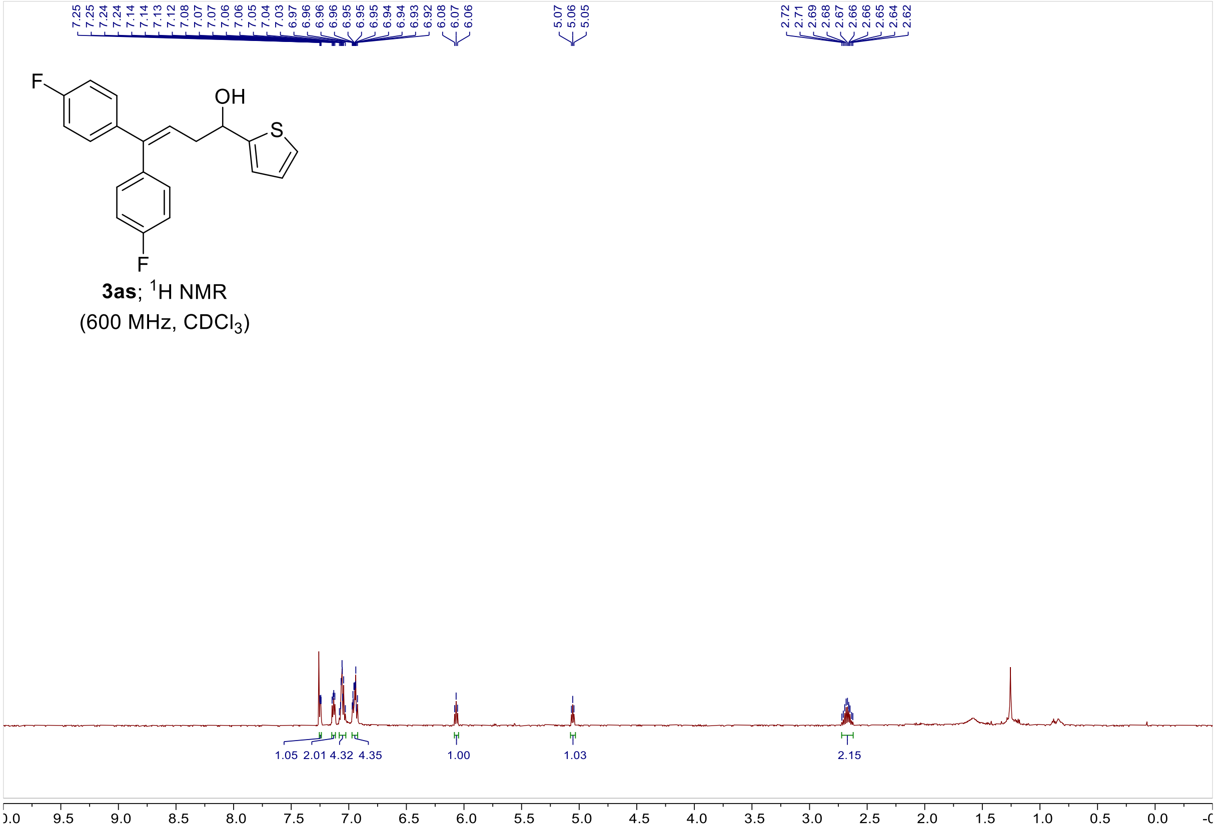

-109.01
-114.65
-115.07
OH
Br
F
F
F
3aq; 19F NMR
(564 MHz, CDCl3)
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
Chemical shift (ppm)

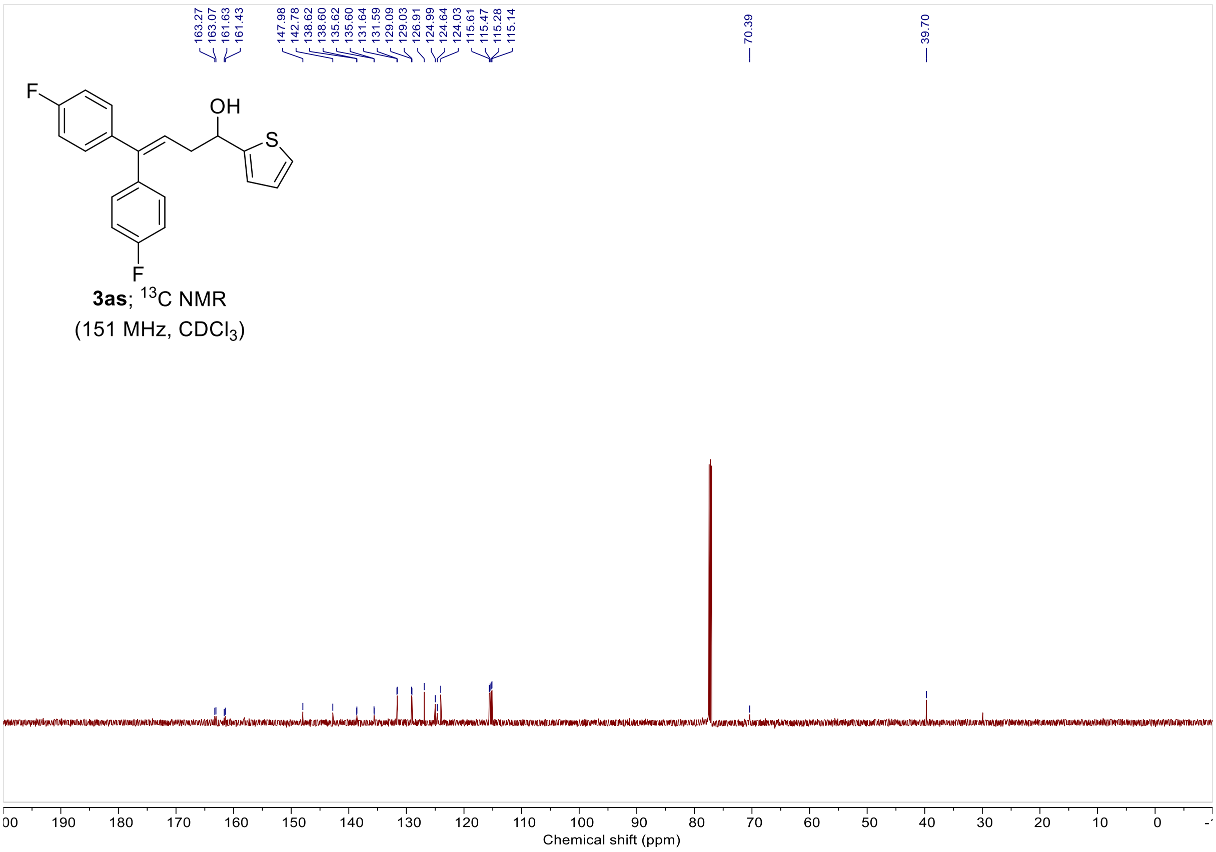

3ar; ¹H NMR
(600 MHz, CDCl3)
Chemical shift (ppm)

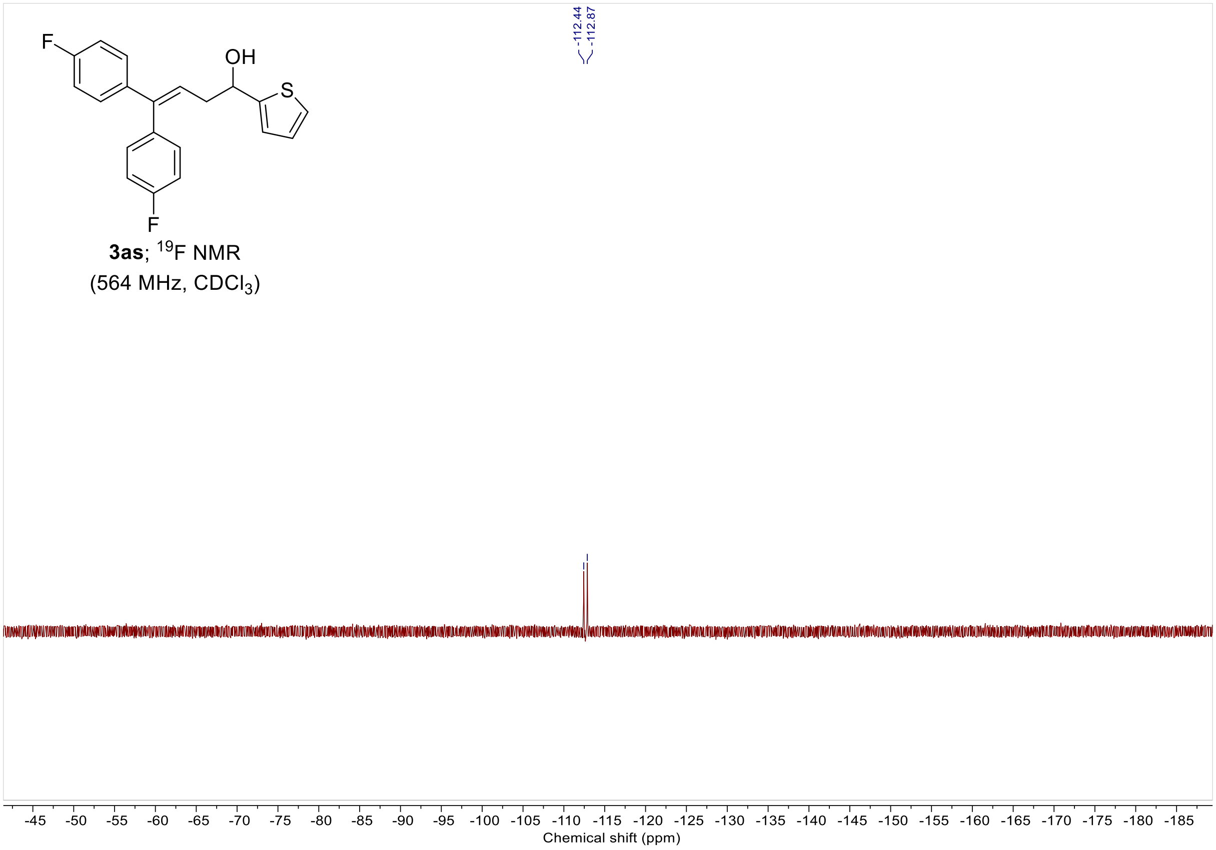

3ar; ¹³C NMR
(151 MHz, CDCl3)
Chemical shift (ppm)

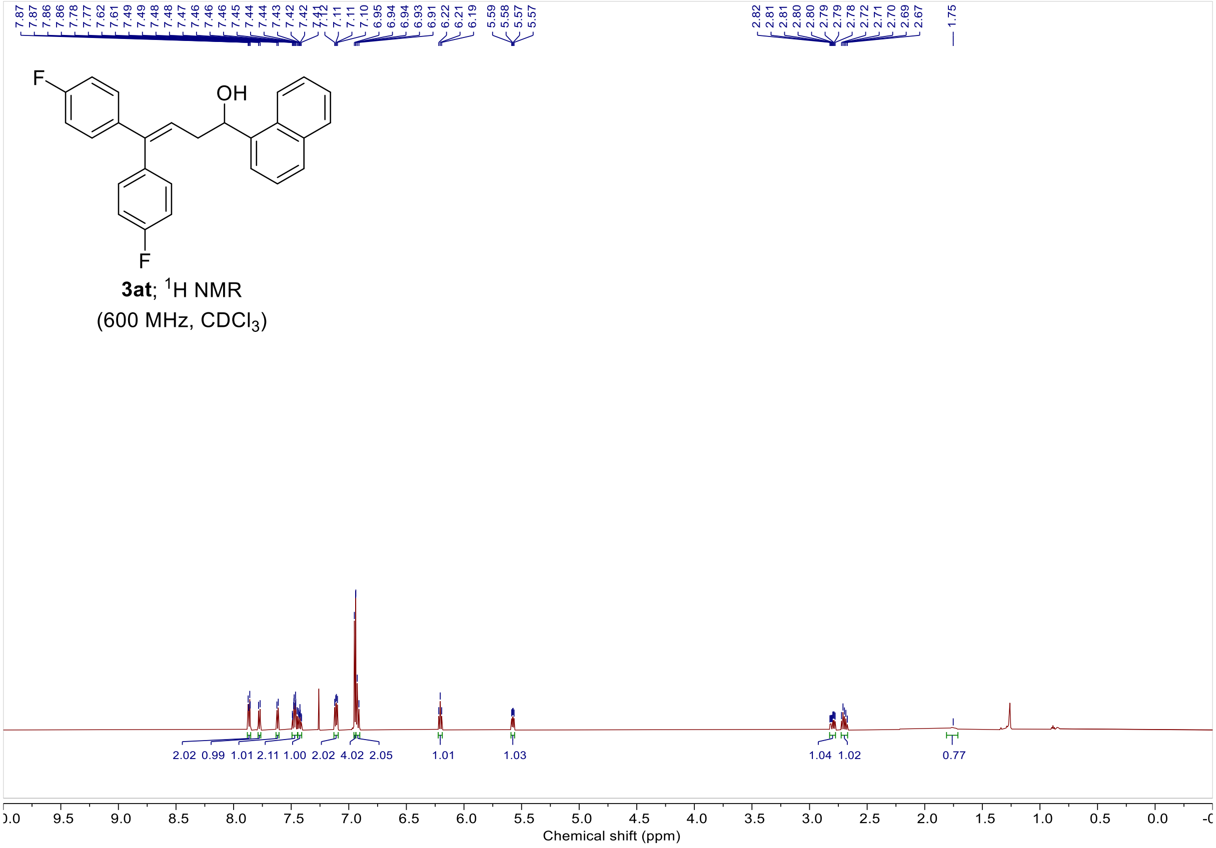


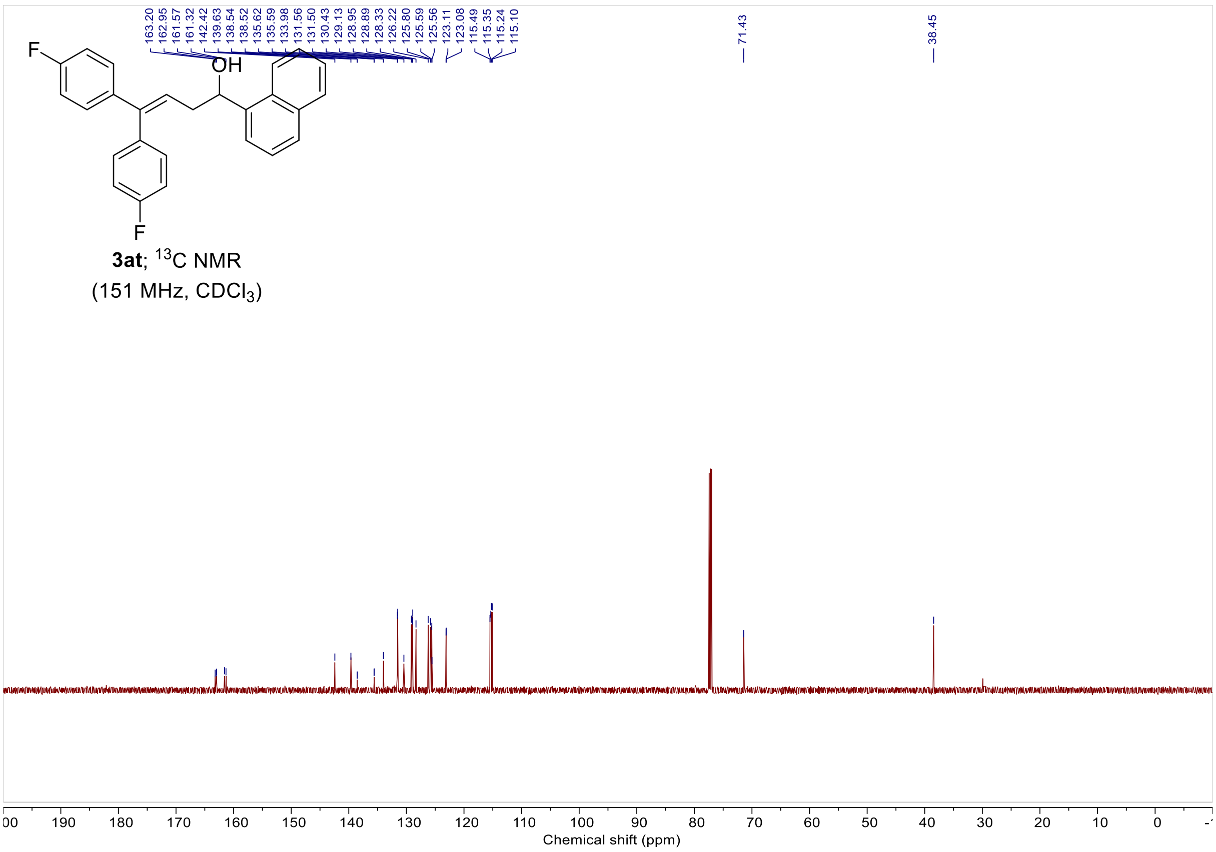
3ar; ^{19}F NMR
(564 MHz, $CDCl_3$)

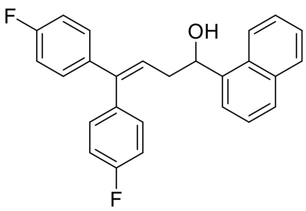

7.25
7.25
7.24
7.24
7.14
7.14
7.13
7.12
7.08
7.07
7.07
7.06
7.06
7.05
7.04
7.03
6.97
6.96
6.96
6.96
6.95
6.95
6.95
6.94
6.94
6.93
6.92
6.08
6.07
6.06
5.07
5.06
5.05
2.72
2.71
2.69
2.68
2.67
2.66
2.66
2.65
2.64
2.62
F
OH
S
F
3as; 1H NMR
(600 MHz, CDCl3)
1.05 2.01 4.32 4.35
1.00
1.03
2.15
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical shift (ppm)


163.27
163.07
161.63
161.43
147.98
142.78
138.62
138.60
135.62
135.60
131.64
131.59
129.09
129.03
126.91
124.99
124.64
124.03
115.61
115.47
115.28
115.14
70.39
39.70
F
OH
S
F
3as; 13C NMR
(151 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical shift (ppm)

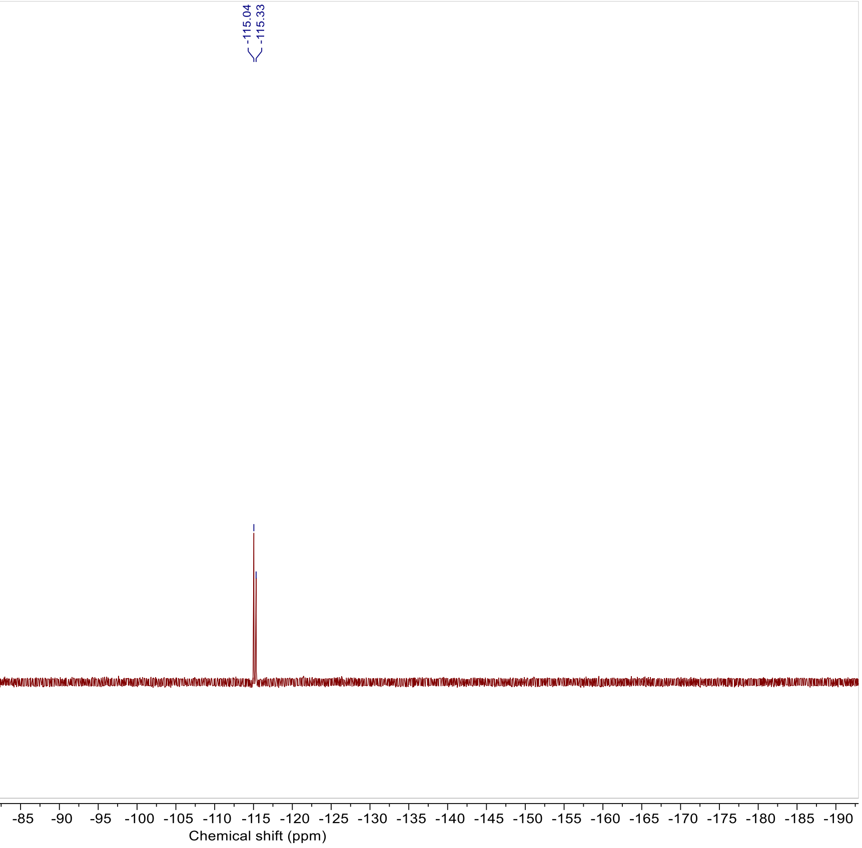

-112.44
-112.87
F
OH
S
F
3as; 19F NMR
(564 MHz, CDCl3)
-45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185
Chemical shift (ppm)

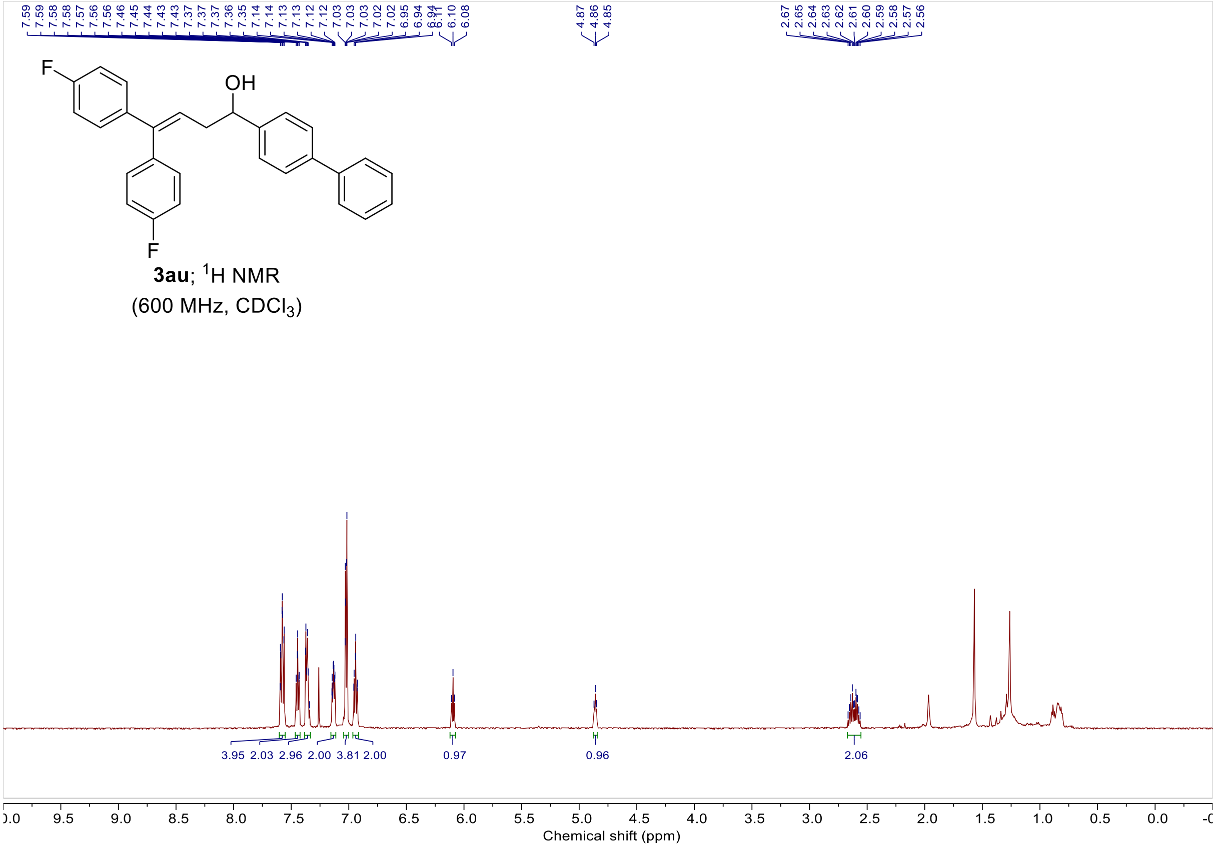

7.87
7.87
7.86
7.78
7.77
7.62
7.61
7.49
7.49
7.48
7.48
7.47
7.46
7.46
7.45
7.44
7.44
7.43
7.42
7.42
7.41
7.12
7.11
7.11
7.10
6.95
6.94
6.94
6.93
6.91
6.22
6.21
6.19
5.59
5.58
5.57
5.57
2.82
2.81
2.81
2.80
2.80
2.79
2.79
2.78
2.72
2.71
2.70
2.69
2.67
1.75
F
OH
F
3at; 1H NMR
(600 MHz, CDCl3)
2.02
0.99
1.01
2.11
1.00
2.02
4.02
2.05
1.01
1.03
1.04
1.02
0.77
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
Chemical shift (ppm)


163.20
162.95
161.57
161.32
142.42
139.63
138.54
138.52
135.62
135.59
133.98
131.56
131.50
130.43
129.13
128.95
128.89
128.33
126.22
125.80
125.59
125.56
123.11
123.08
115.49
115.35
115.24
115.10
71.43
38.45
F
OH
F
3at; 13C NMR
(151 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
Chemical shift (ppm)

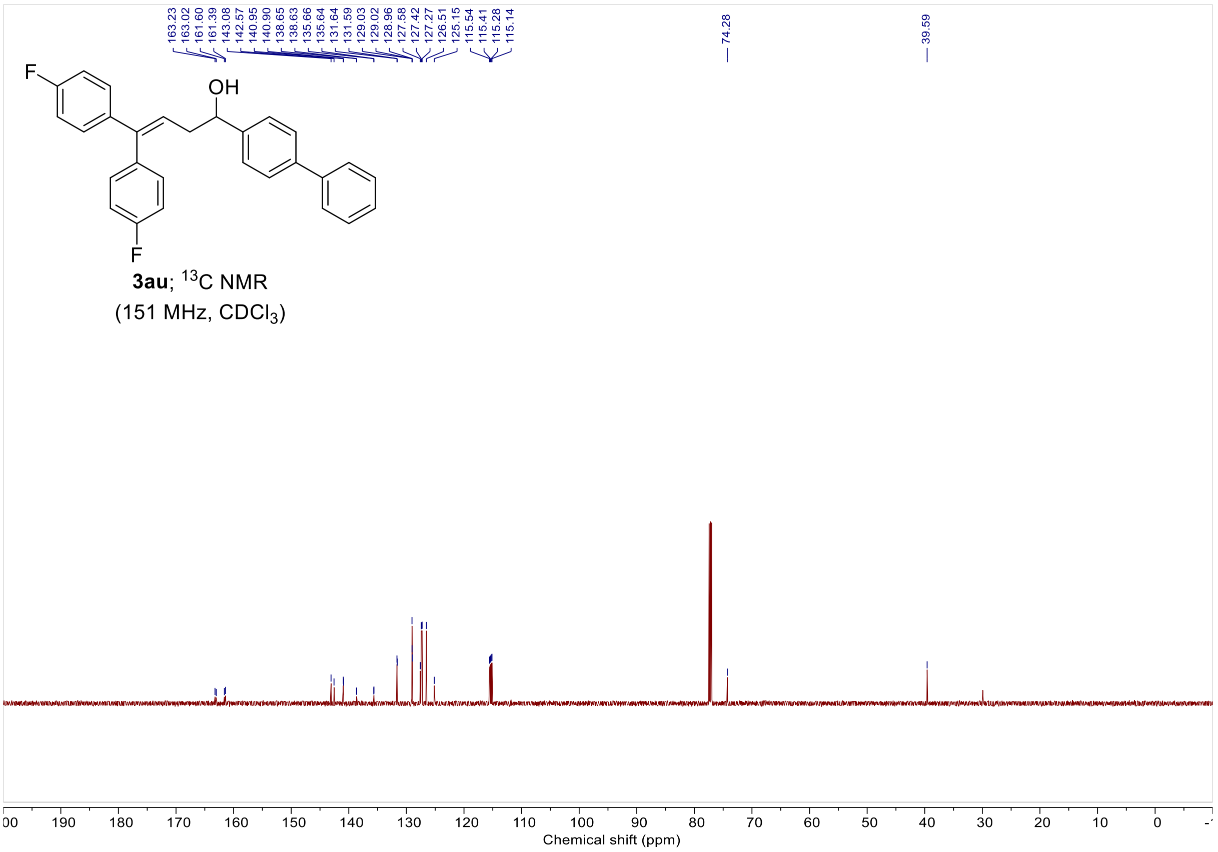


3at; ^{19}F NMR
(564 MHz, $CDCl_3$)

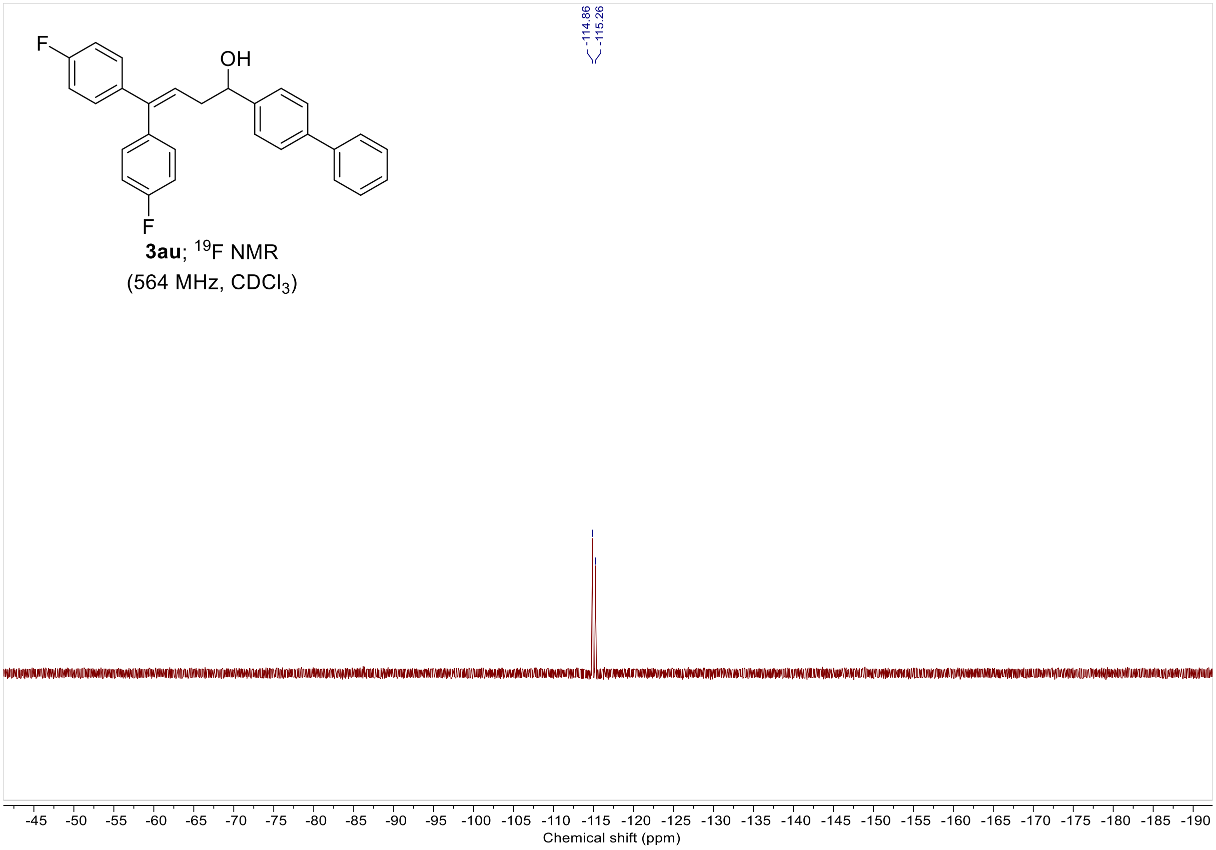


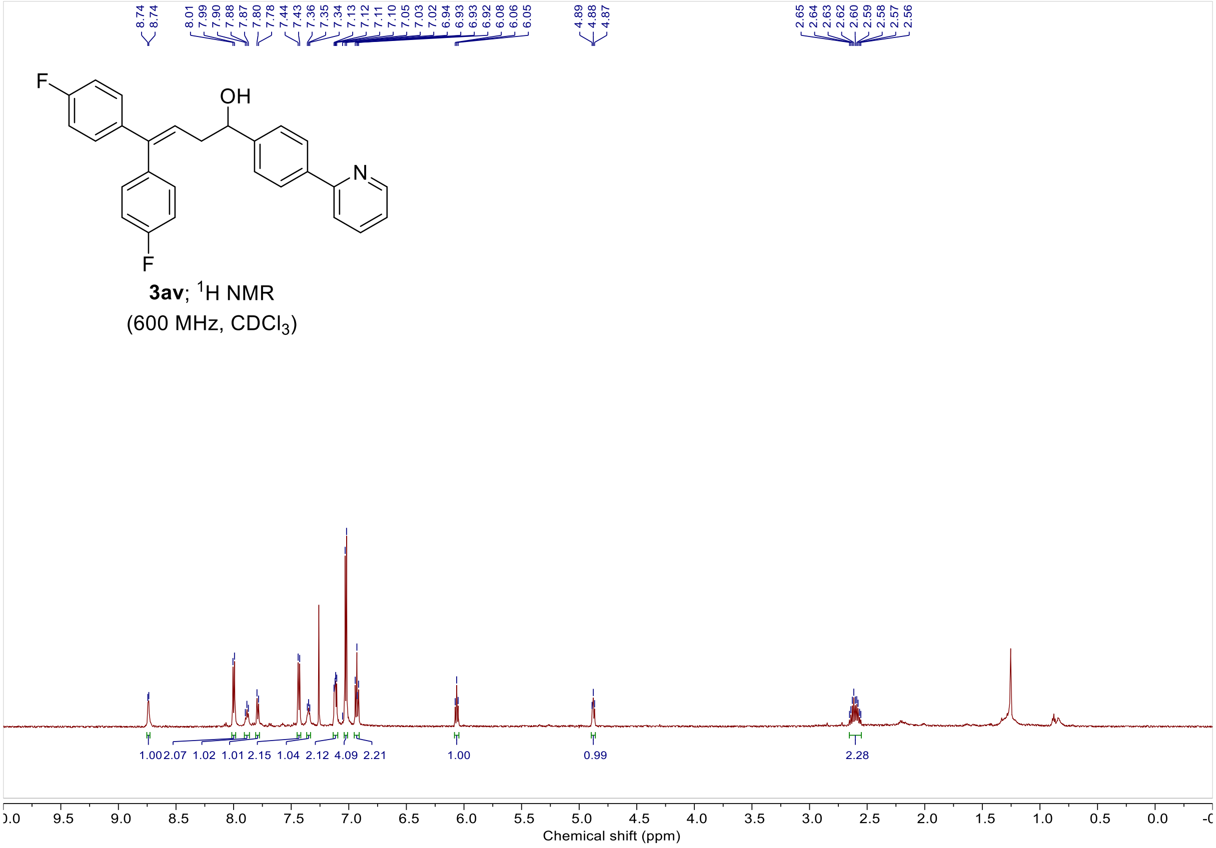


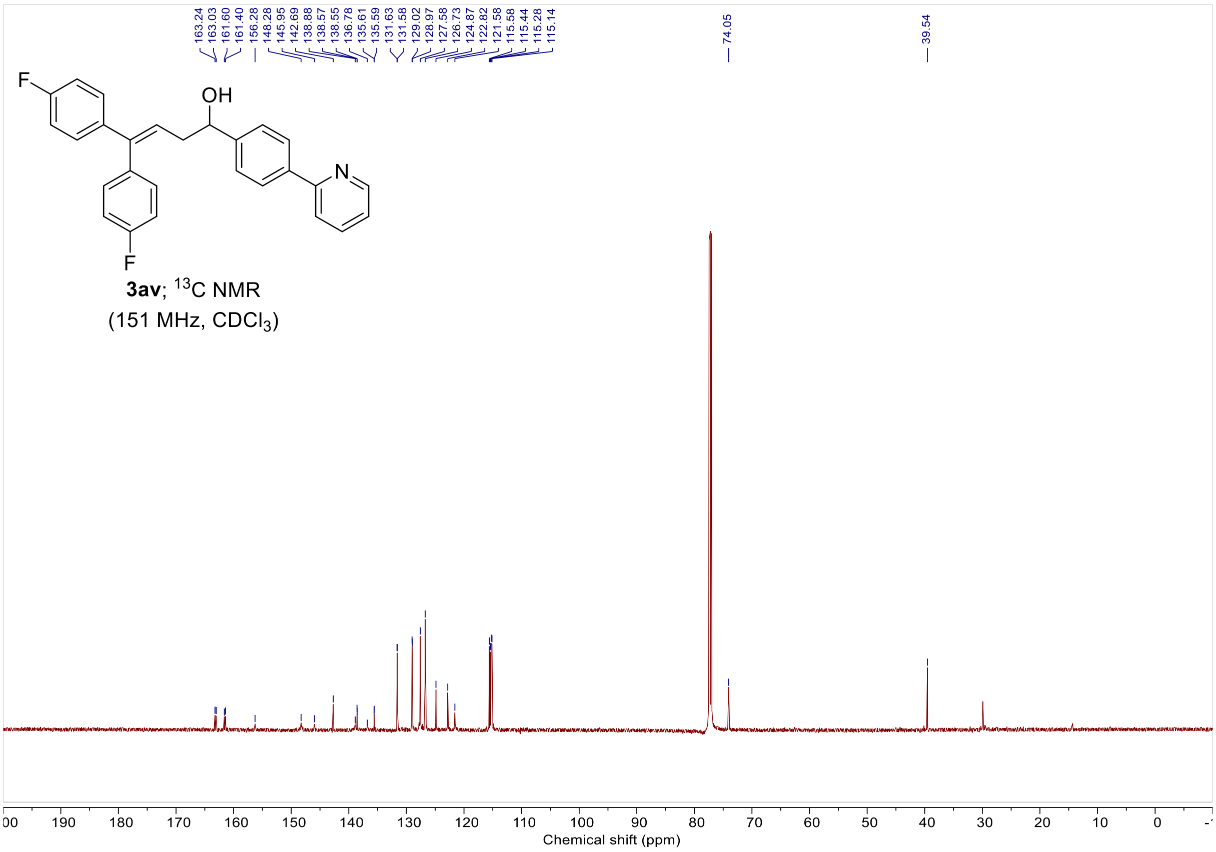
3au; ^{1}H NMR
(600 MHz, $CDCl_3$)
Chemical shift (ppm)

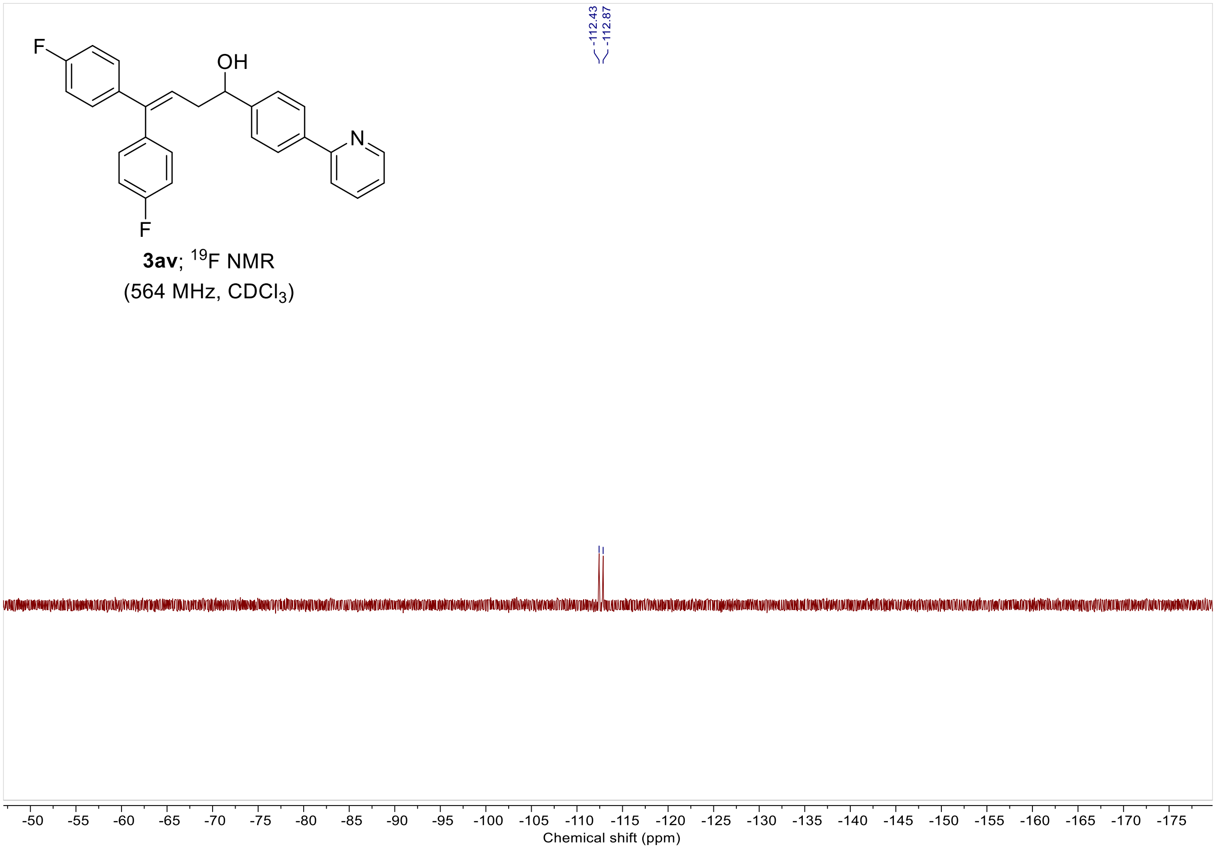


3au; ^{13}C NMR
(151 MHz, $CDCl_3$)
Chemical shift (ppm)

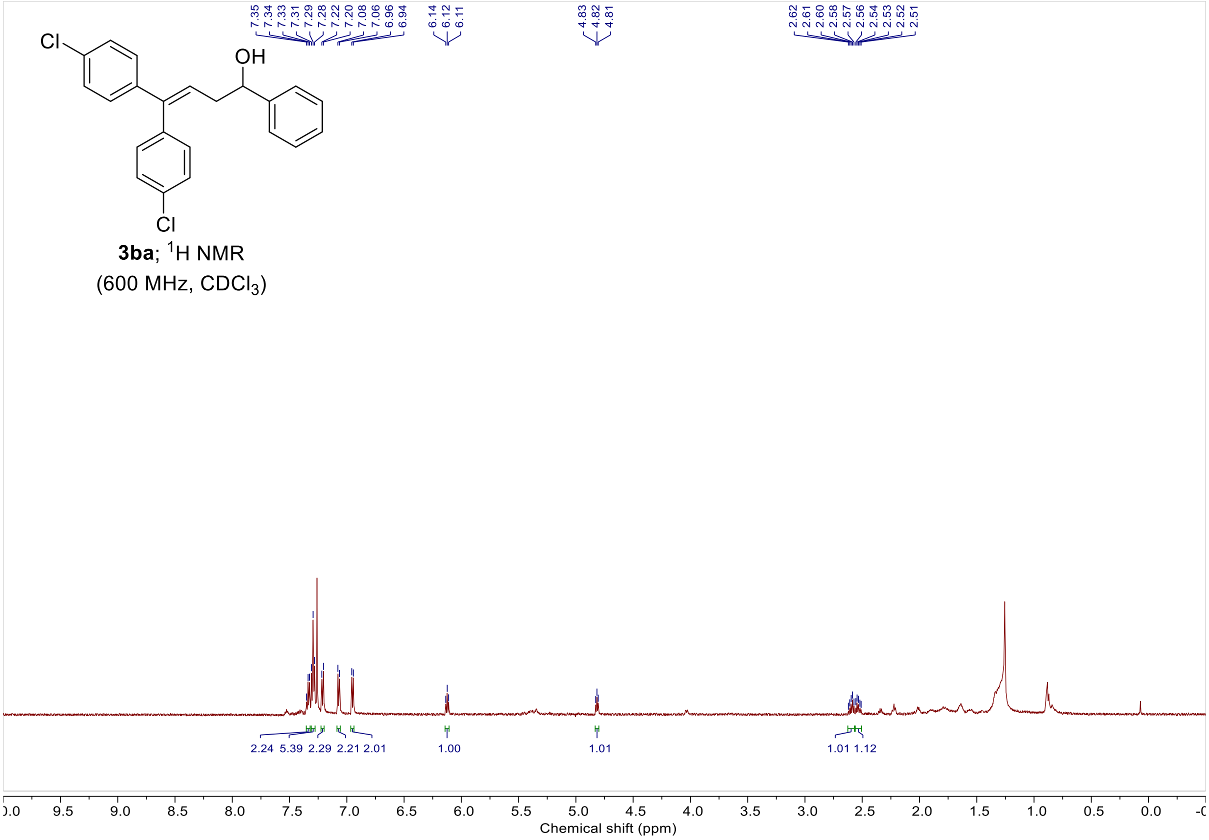

-114.86
-115.26
F
OH
F
3au; 19F NMR
(564 MHz, CDCl3)
-45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -190
Chemical shift (ppm)

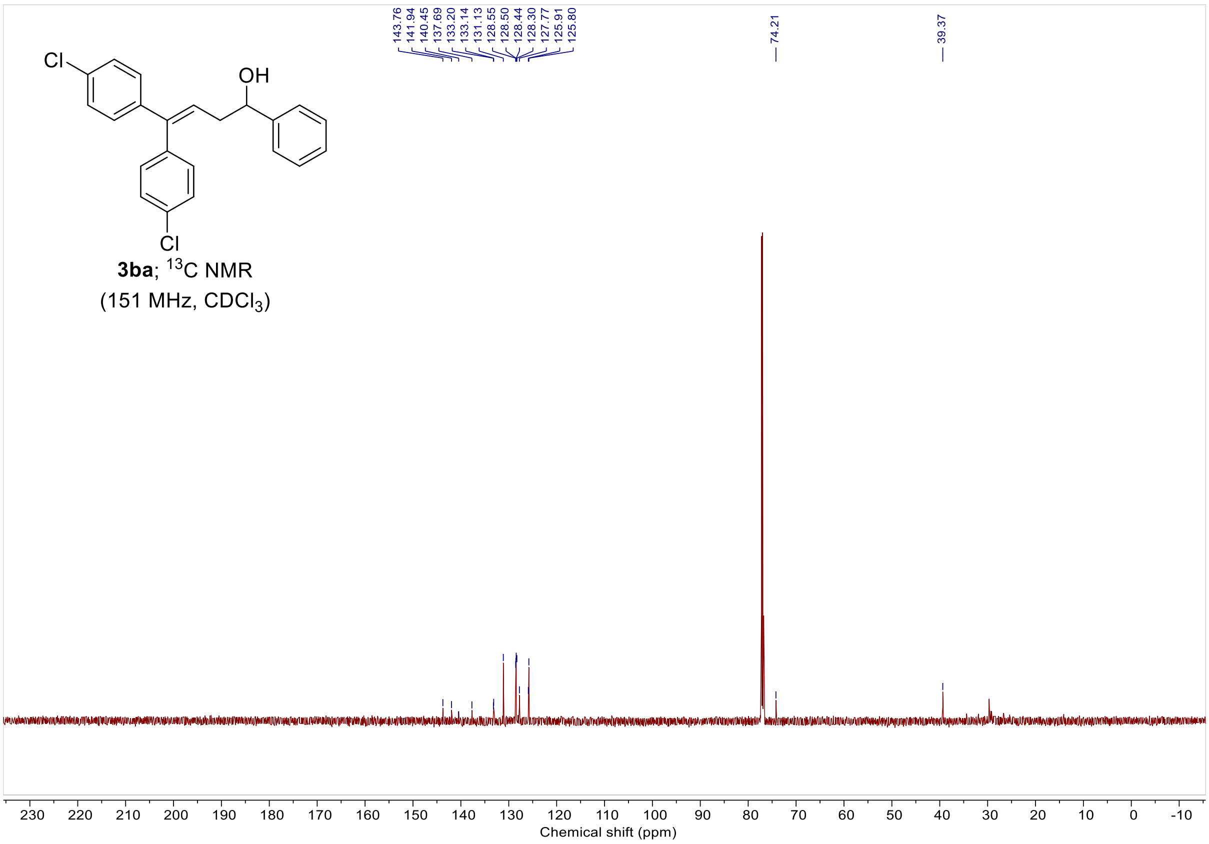

F
OH
N
F
3av; 1H NMR
(600 MHz, CDCl3)
8.74
8.74
8.01
7.99
7.90
7.88
7.87
7.80
7.78
7.44
7.43
7.36
7.35
7.34
7.13
7.12
7.11
7.10
7.05
7.03
7.02
6.94
6.93
6.93
6.92
6.08
6.06
6.05
4.89
4.88
4.87
2.65
2.64
2.63
2.62
2.60
2.59
2.58
2.57
2.56
1.00
2.07
1.02
1.01
2.15
1.04
2.12
4.09
2.21
1.00
0.99
2.28
Chemical shift (ppm)

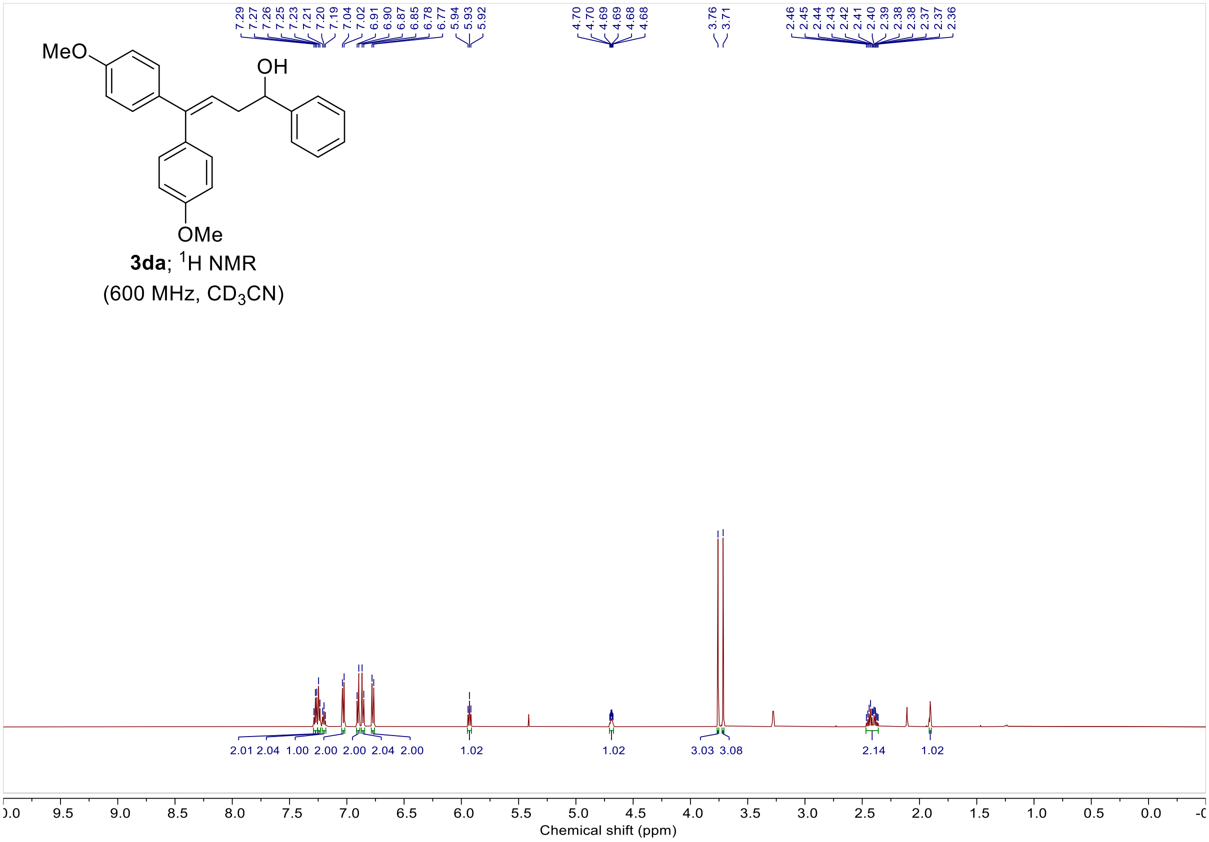

F
OH
N
F
3av; 13C NMR
(151 MHz, CDCl3)
163.24
163.03
161.60
161.40
156.28
148.28
145.95
142.69
138.88
138.57
138.55
136.78
135.61
135.59
131.63
131.58
129.02
128.97
127.58
126.73
124.87
122.82
121.58
115.58
115.44
115.28
115.14
74.05
39.54
Chemical shift (ppm)



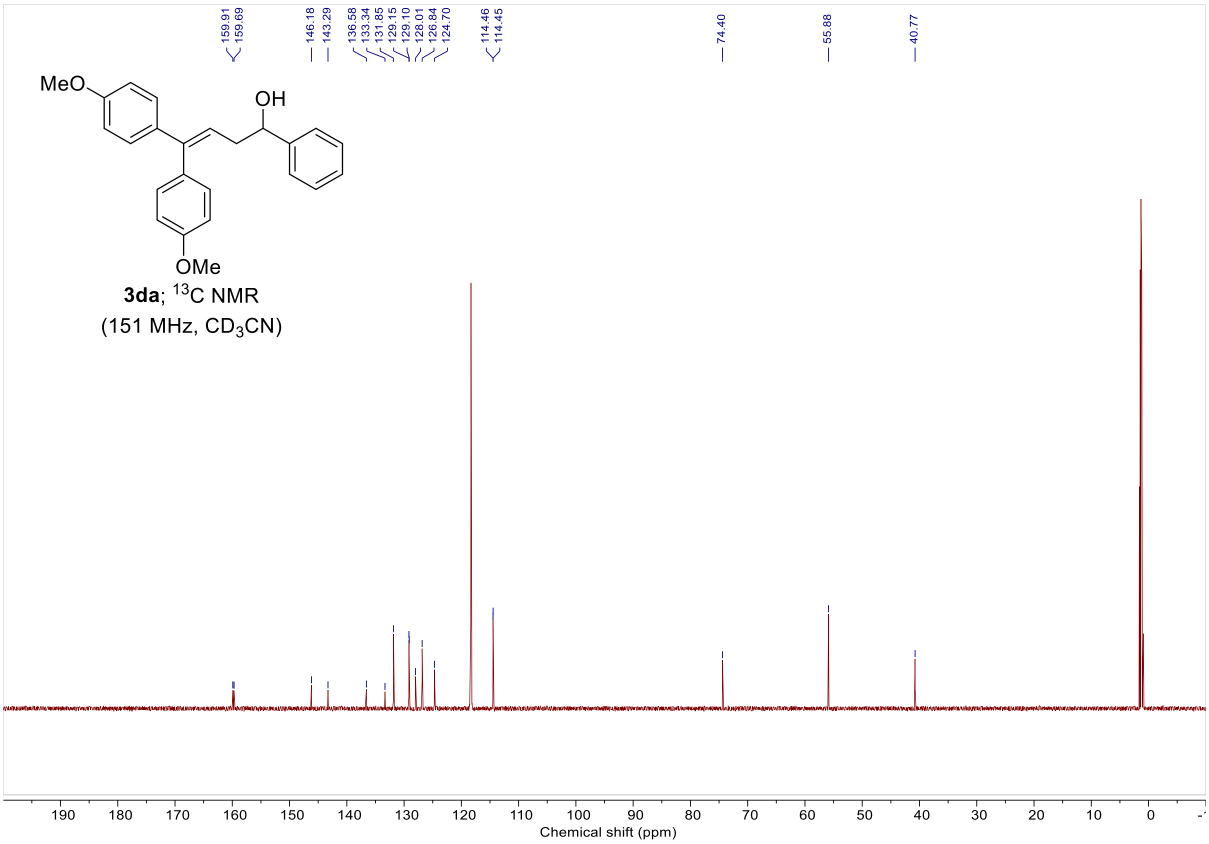
F
OH
N
F
3av; 19F NMR
(564 MHz, CDCl3)
-112.43
-112.87
-50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175
Chemical shift (ppm)


3ba; ^{1}H NMR
(600 MHz, $CDCl_3$)
OH
Cl
Cl
7.35 7.34 7.33 7.31 7.29 7.28 7.22 7.20 7.08 7.06 6.96 6.94
6.14 6.12 6.11
4.83 4.82 4.81
2.62 2.61 2.60 2.58 2.57 2.56 2.54 2.53 2.52 2.51
2.24 5.39 2.29 2.21 2.01
1.00
1.01
1.01 1.12
Chemical shift (ppm)

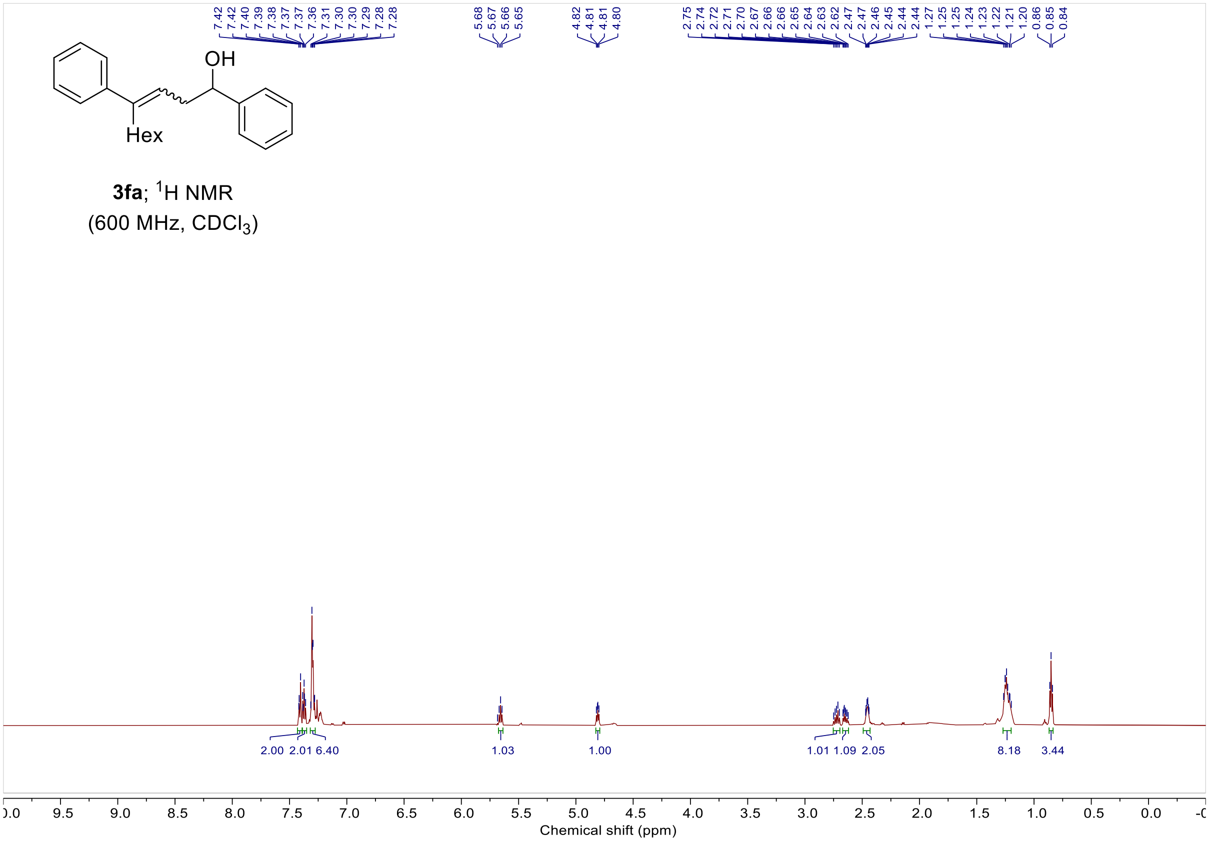

3ba; ^{13}C NMR
(151 MHz, $CDCl_3$)
OH
Cl
Cl
143.76 141.94 140.45 137.69 133.20 133.14 131.13 128.55 128.50 128.44 128.30 127.77 125.91 125.80
74.21
39.37
Chemical shift (ppm)



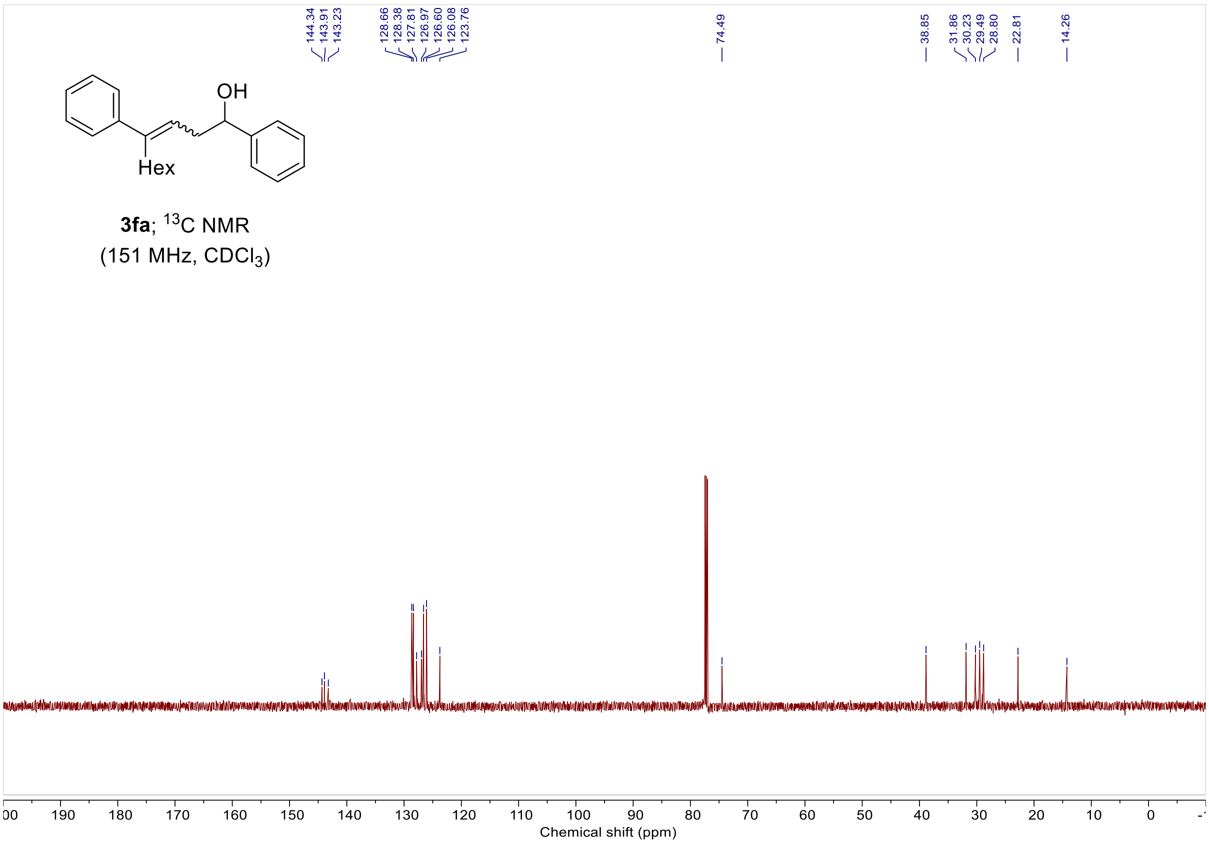
3da; ^{1}H NMR (600 MHz, CD_3CN)



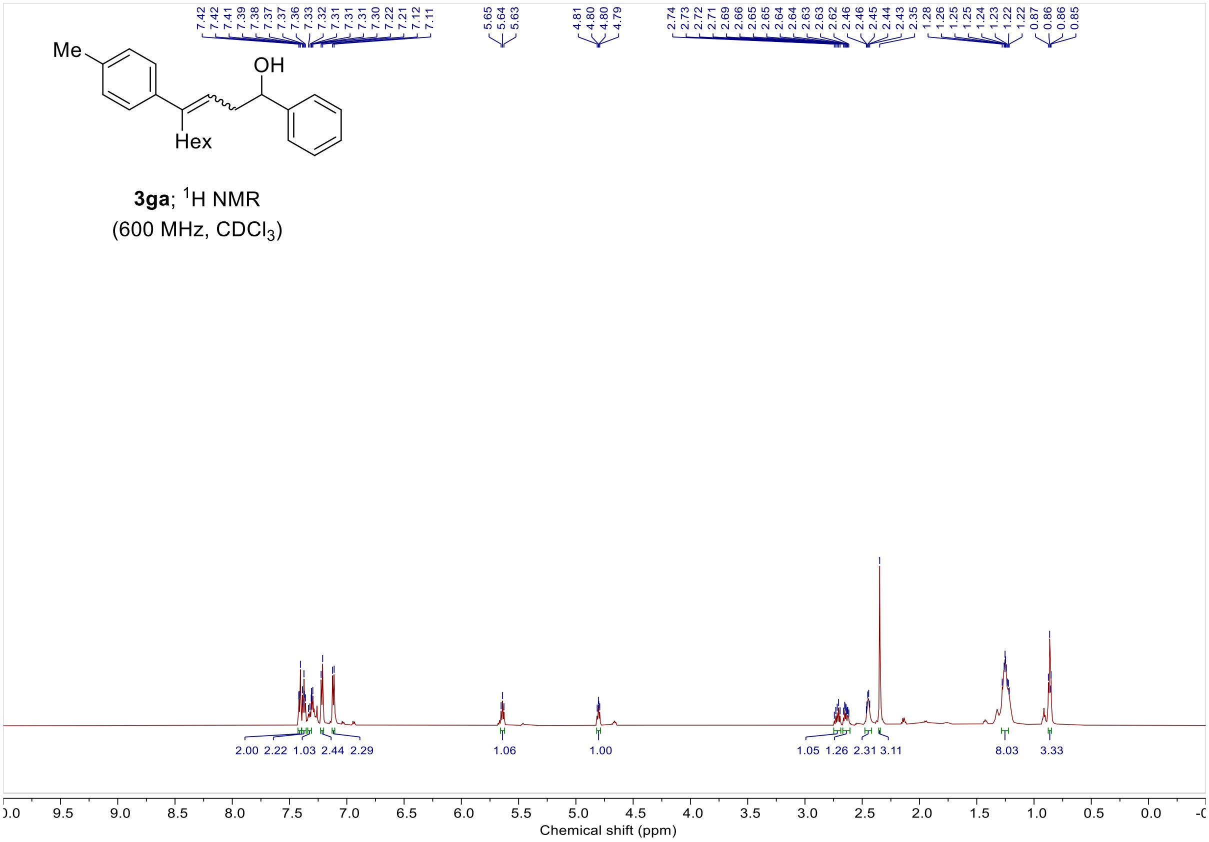
3da; ^{13}C NMR (151 MHz, CD_3CN)

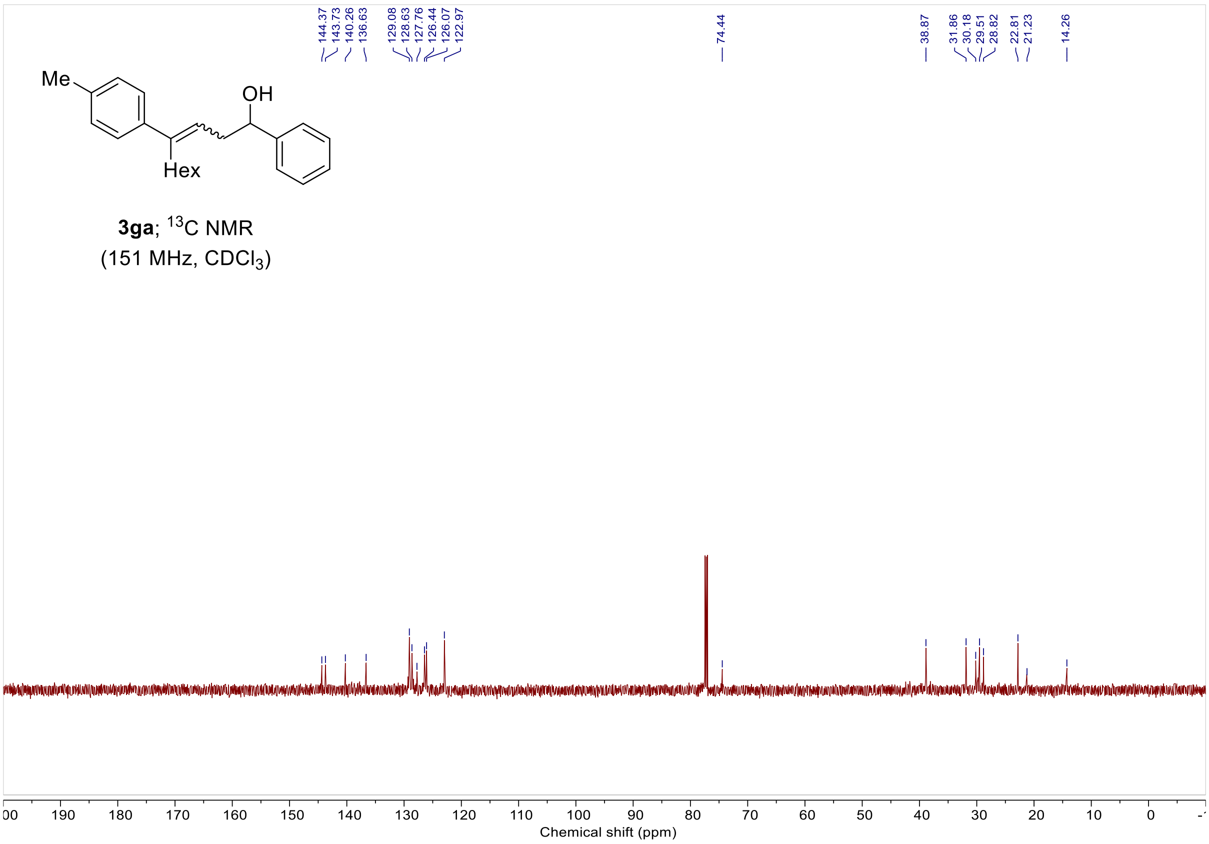


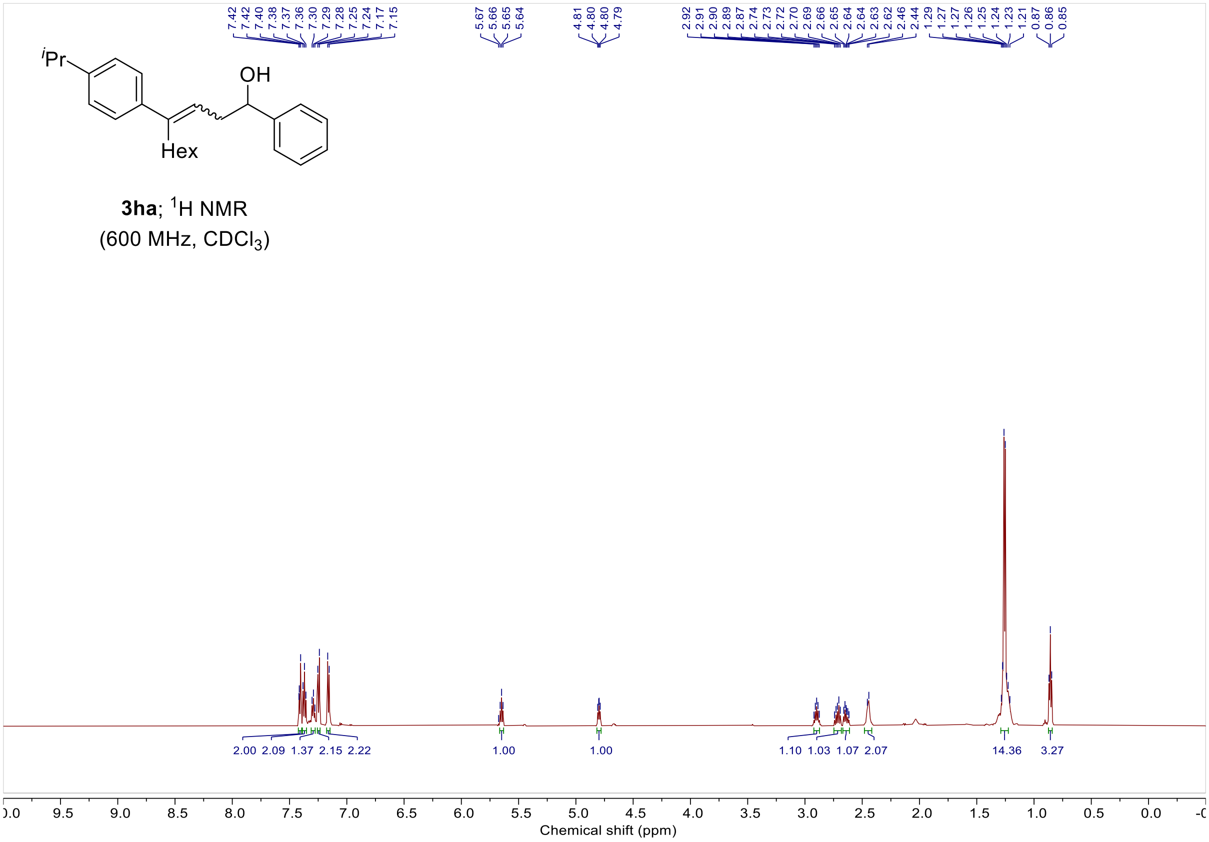
3fa; ^{1}H NMR
(600 MHz, $CDCl_3$)



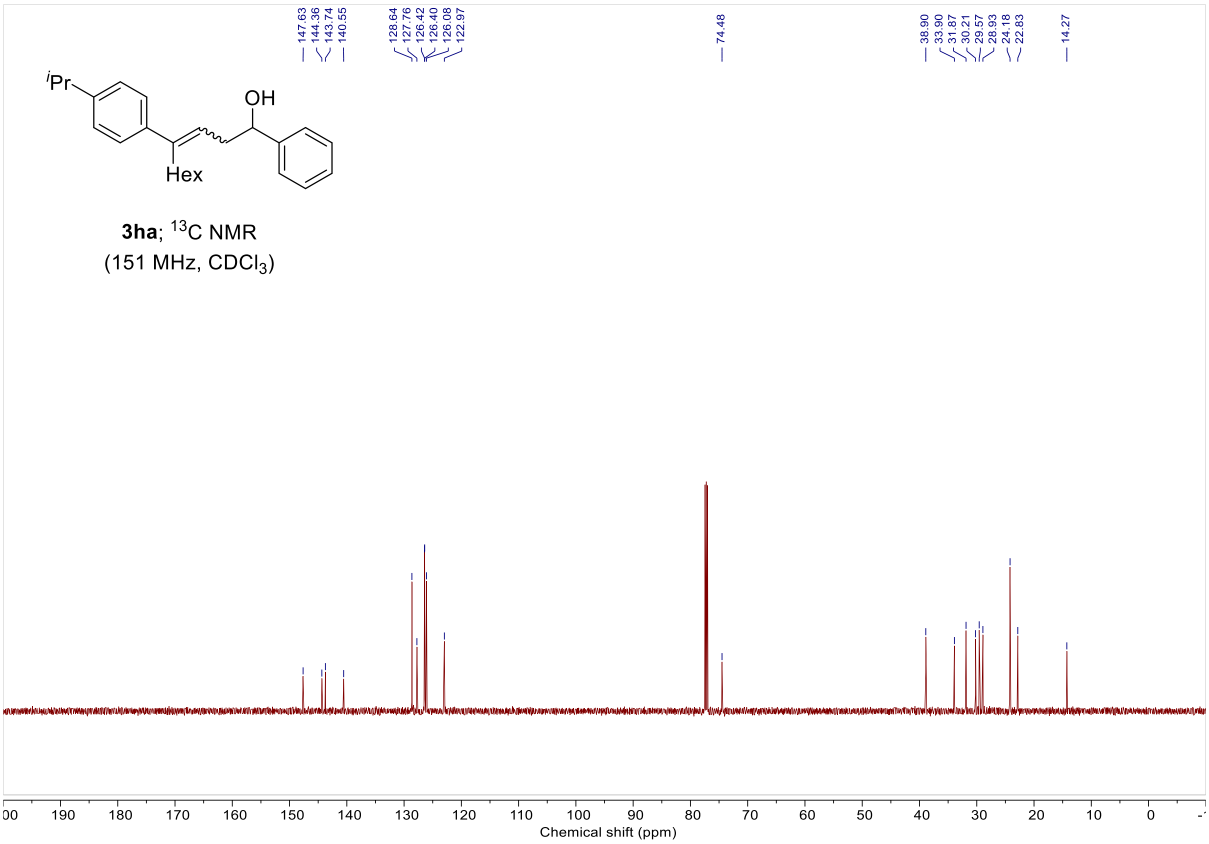
3fa; ^{13}C NMR
(151 MHz, $CDCl_3$)


Me
OH
Hex
3ga; 1H NMR
(600 MHz, CDCl3)
Chemical shift (ppm)


Me
OH
Hex
3ga; 13C NMR
(151 MHz, CDCl3)
Chemical shift (ppm)



iPr
OH
Hex
3ha; 1H NMR
(600 MHz, CDCl3)
7.42 7.42 7.40 7.38 7.37 7.36 7.30 7.29 7.28 7.25 7.24 7.17 7.15
5.67 5.66 5.65 5.64
4.81 4.80 4.80 4.79
2.92 2.91 2.90 2.89 2.87 2.74 2.73 2.72 2.70 2.69 2.66 2.65 2.64 2.64 2.63 2.62 2.46 2.44
1.29 1.27 1.27 1.26 1.25 1.24 1.23 1.21 0.87 0.86 0.85
2.00 2.09 1.37 2.15 2.22
1.00
1.00
1.10 1.03 1.07 2.07
14.36 3.27
Chemical shift (ppm)



iPr
OH
Hex
3ha; 13C NMR
(151 MHz, CDCl3)
147.63 144.36 143.74 140.55
128.64 127.76 126.42 126.40 126.08 122.97
74.48
38.90 33.90 31.87 30.21 29.57 28.93 24.18 22.83
14.27
Chemical shift (ppm)