Supporting Information

Visible-light-promoted divergent functionalizations of methylenecyclopropanes

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1. General Information

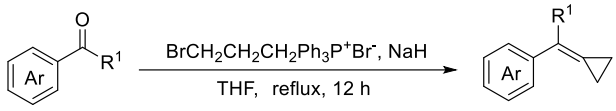
All air- and moisture-insensitive reactions were carried out under an ambient atmosphere and monitored by thin-layer chromatography (TLC). Concentration under reduced pressure was performed by rotary evaporation at 40-60 °C at an appropriate pressure. Purified compounds were further dried under high vacuum. Yields refer to purified and spectroscopically pure compounds, unless otherwise stated. All air- and moisture-sensitive manipulations were performed using oven-dried glassware (120 °C for a minimum of 15 h), including standard Schlenk techniques under an atmosphere of argon. The heat source is an aluminum dry block heater. Irradiation of photochemical reactions were carried out using 5-15 W blue LEDs. Substrates **5** were commercially available. Solvents were purchased from Titan and dried by distillation. All deuterated solvents were purchased from J&K Scientific.

Spectroscopy and Instruments

^{1}H NMR spectra were recorded on 400 MHz or 600 MHz spectrophotometers. Chemical shifts (δ) were reported in ppm from the resonance of tetramethyl silane as the internal standard (TMS: 0.00 ppm). Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. For ^{1}H NMR: $CDCl_3$, 7.26; For ^{13}C NMR: $CDCl_3$, 77.16; ^{13}C NMR spectra were recorded on 100 MHz or 150 MHz with complete proton decoupling spectrophotometers. ^{19}F-NMR spectra were observed in the ^{1}H-decoupled mode. High-resolution mass spectra were obtained using Shimadzu LCMS-IT-TOF mass spectrometer and DIONEX UltiMate 3000 & Bruker Compact TOF mass spectrometer. Gas chromatography analysis was performed on an Agilent HP-5890 instrument with an FID detector.

2. Starting Materials

2.1 Preparation of MCPs.[1]

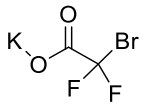


1

A 100 mL round-bottom flask equipped with a magnetic stir bar and a reflux condenser was charged with (4-bromobutyl)triphenylphosphonium bromide (6.96 g, 15 mmol) and NaH (1.20 g, 30 mmol) in THF (30 mL) at 75 °C under argon for 1 h. Afterwards compound ketone or aldehyde (10 mmol) in THF (10 mL) was added in the reaction solution. Then it was stirred at 75 °C until compound ketones or aldehydes was consumed completely. The reaction mixture was cooled to room temperature, and the mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel flash chromatography to afford the substrate **1**.

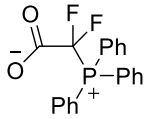
2.2 General Procedure for Synthesis of CF_2H Reagent 2a.[2,3]

Potassium 2-bromo-2,2-difluoroacetate:



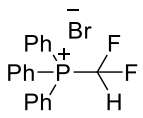
A 250 mL round-bottom flask equipped with a magnetic stir bar was charged with potassium hydroxide (4.03 g, 71.7 mmol, 1 equiv) was dissolved in MeOH (70 mL) at 0 °C. Ethyl bromo-2,2-difluoroacetate (9.48 mL, 15.0 g, 71.7 mmol, 1 equiv) was added slowly to the reaction mixture at 0 °C. The reaction mixture was slowly allowed to warm up to room temperature overnight. The solvent was removed under reduced pressure and potassium 2-bromo-2,2-difluoroacetate (13.6 g, 63.8 mmol, 89% yield) was obtained as a colorless solid.

2,2-Difluoro-2-(triphenylphosphonio)acetate:



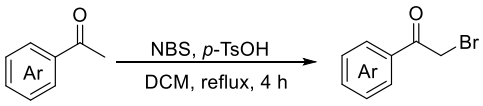
A 250 mL round-bottom flask equipped with a magnetic stir bar was charged with potassium 2-bromo-2,2-difluoroacetate (13.6 g, 63.8 mmol, 1 equiv) and triphenylphosphine (16.7 g, 63.8 mmol, 1 equiv) were dissolved in DMF (80 mL). The reaction mixture was stirred at room temperature overnight. The formed precipitate was filtered off, washed with cold DMF (3 × 20 mL), water (3 × 20 mL) and Et_2O (3 × 20 mL). The precipitate was dried to obtain 2,2-difluoro-2-(triphenylphosphonio)acetate (12.7 g, 35.6 mmol, 56%) as a colorless solid.

(Difluoromethyl)triphenylphosphonium bromide (2a):



A 250 mL round-bottom flask equipped with a magnetic stir bar was charged with 2,2-difluoro-2-(triphenylphosphonio)acetate (5.04 g, 14.2 mmol, 1 equiv) was dissolved in THF (14 mL). HBr (48%, 1.94 mL, 2.87 g, 17.0 mmol, 1.2 equiv) was added to this reaction mixture. Then it was refluxed for 2 h. The reaction was quenched by water (50 mL). The aqueous layer was extracted with dichloromethane (2 × 50 mL). The combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was washed multiple times with cold THF (3 × 10 mL) to obtain compound **2a** (4.80 g, 12.2 mmol, 86% yield) as a colorless solid.

2.3 Preparation of Bromocarbonyl.



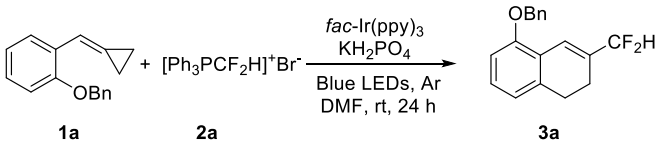
4

A 100 mL round-bottom flask with a magnetic stir bar and a solution of substituted alkanone (10 mmol) in DCM (4 mL) was added dropwise to a solution of *N*-bromosuccinimide (2.14 g, 12 mmol, 1.2 equiv) and *p*-TsOH (0.2 g, 1.0 mmol, 0.1 equiv) in DCM (10 mL) at 0 °C. The reaction mixture was then heated

at reflux for 4 h. After the addition of H_2O (10 mL) and DCM (20 mL), the organic layer was separated, and the aqueous layer was extracted with DCM (2 × 15 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography to afford the substrate **4**.[4]

3. Detailed Optimization of Reaction Conditions

3.1 General Procedure of Product 3a

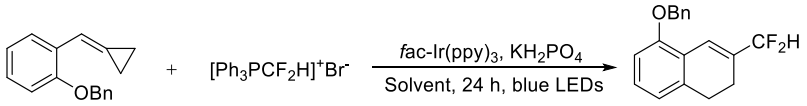


1a **2a** **3a**

A 10 mL oven-dried Schlenk tube equipped with a magnetic stir bar was charged with **1a** (0.2 mmol, 1 equiv), $[Ph_3PCF_2H]^+Br^-$ **2a** (0.3 mmol, 1.5 equiv), *fac*-Ir(ppy)$_3$ (3 mol%), KH_2PO_4 (0.2 mmol, 1 equiv). The Schlenk tube was evacuated and backfilled with argon for three times. Then DMF (4 mL) was injected into the Schlenk tube. The mixture was stirred for 24 h under blue LEDs. The reaction solution was cooled to room temperature, and saturated aqueous $NaHCO_3$ (5 mL) was added. Then it was washed with brine (10 mL). The mixture was extracted with diethyl ether (30 mL) for three times, dried with $MgSO_4$, filtered, and concentrated. The residue was purified by flash column chromatography on silica gel (EtOAc/petroleum ether = 1/50) to give the desired product **3a** as a colorless oil in 60% isolated yield.

3.1.1 Optimization of Product 3a

Table S1. Screening of Solvent

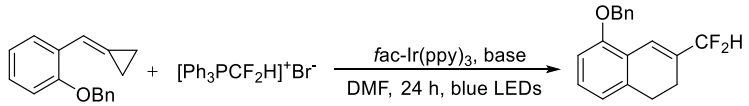


1a **2a** **3a**

Entry	Solvent	Yield (%)[b]
1	DMSO	11
2	DMAC	45
3	CH_2Cl_2	29
4	THF	36
5	DCE	16
6	**DMF**	**53**
7	CH_3CN	26
8	NMP	35
9	HFIP	0

[a]Reaction conditions: **1a** (0.2 mmol, 1 equiv), **2a** (0.3 mmol, 1.5 equiv), *fac*-Ir(ppy)$_3$ (3 mol%), and KH_2PO_4 (0.2 mmol, 1 equiv) in solvent (2 mL) at rt under argon atmosphere and blue LEDs irradiation for 24 h. [b]Yields were determined by ^{19}F NMR spectroscopy using benzotrifluoride as an internal standard.

Table S2. Screening of Base

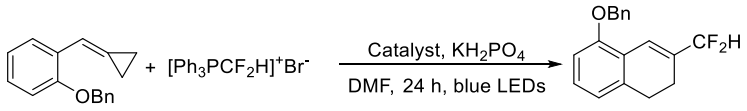


1a **2a** **3a**

Entry	Solvent	Yield (%)[b]
1	K_2CO_3	0
2	Na_2HPO_4	57
3	$NaHCO_3$	54
4	NaH_2PO_4•$2H_2O$	50
5	**KH_2PO_4**	**67**
6	K_3PO_4	0
7	Cs_2CO_3	0
8	---	trace

[a]Reaction conditions: **1a** (0.2 mmol, 1 equiv), **2a** (0.3 mmol, 1.5 equiv), *fac*-Ir(ppy)$_3$ (3 mol%), and base (0.2 mmol, 1 equiv) in DMF(2 mL) at rt under argon atmosphere and blue LEDs irradiation for 24 h. [b]Yields were determined by ^{19}F NMR spectroscopy using benzotrifluoride as an internal standard.

Table S3. Screening of Catalyst

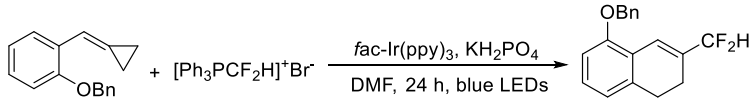


1a **2a** **3a**

Entry	Catalyst	Yield (%)[b]
1	$[Ru(bpy)_3]Cl_2$	0
2	$[Ru(bpy)_3](PF_6)_2$	0
3	$[Ru(phen)_3](PF_6)_2$	0
4	Eosin Y	0
5	Fluorescein	0
6	***fac*-Ir(ppy)$_3$**	**67**

[a]Reaction conditions: **1a** (0.2 mmol, 1 equiv), **2a** (0.3 mmol, 1.5 equiv), catalyst (3 mol%), and KH_2PO_4 (0.2 mmol, 1 equiv) in DMF (2 mL) at rt under argon atmosphere and blue LEDs irradiation for 24 h. [b]Yields were determined by ^{19}F NMR spectroscopy using benzotrifluoride as an internal standard.

Table S4. Screening of the Volume of DMF

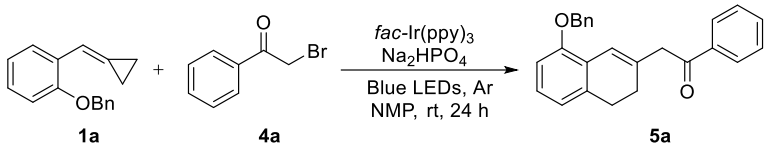


1a **2a** **3a**

Entry	DMF	Yield (%)[b]
1	2 mL	67
2	3 mL	71
3	**4 mL**	**75(60)**

[a]Reaction conditions: **1a** (0.2 mmol, 1 equiv), **2a** (0.3 mmol, 1.5 equiv), *fac*-Ir(ppy)$_3$ (3 mol%), and KH_2PO_4 (0.2 mmol, 1 equiv) in DMF at rt under argon atmosphere and blue LEDs irradiation for 24 h. [b]Yields were determined by ^{19}F NMR spectroscopy using benzotrifluoride as an internal standard. Isolated yields were in parentheses.

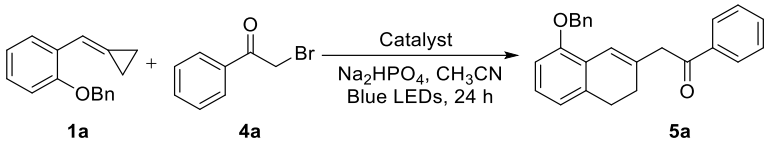
3.2 General Procedure of Product 5a



A 10 mL oven-dried Schlenk tube equipped with a magnetic stir bar was charged with **1a** (0.2 mmol, 1 equiv), **4a** (0.3 mmol, 1.5 equiv), *fac*-Ir(ppy)$_3$ (2 mol%), Na_2HPO_4 (0.2 mmol, 1 equiv). The Schlenk tube was evacuated and backfilled with argon for three times. Then NMP (2 mL) was injected into the Schlenk tube. The mixture was stirred for 24 h under blue LEDs. The reaction solution was cooled to room temperature, and saturated aqueous $NaHCO_3$ (5 mL) was added. Then it was washed with brine (10 mL). The mixture was extracted with diethyl ether (30 mL) for three times, dried with $MgSO_4$, filtered, and concentrated. The residue was purified by flash column chromatography on silica gel (EtOAc/petroleum ether = 1/25) to give the desired product **5a** as a brown oil in 55% isolated yield.

3.2.1 Optimization of Product 5a

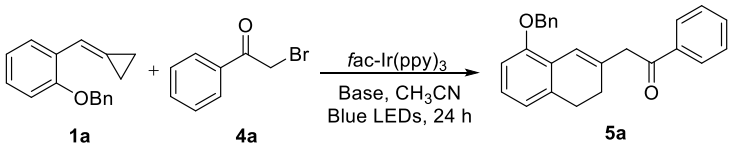
Table S5. Screening of Catalyst



Entry	Catalyst	Yield (%)[b]
1	$[Ru(bpy)_3]Cl_2$	trace
2	$[Ru(bpy)_3](PF_6)_2$	trace
3	$[Ru(1.10\text{-}phen)_3](PF_6)_2$	29
4	$Ir(ppy)_2(dtbbpy)PF_6$	33
5	$[Ru(bpy)_3]Cl_2 \cdot 6H_2O$	nr
6	***fac*-Ir(ppy)$_3$**	**46**

[a]Reaction conditions: **1a** (0.2 mmol, 1 equiv), **4a** (0.3 mmol, 1.5 equiv), *fac*-Ir(ppy)$_3$ (2 mol%), and base (0.2 mmol, 1 equiv) in CH_3CN (2 mL) at room temperature under argon atmosphere and blue LEDs irradiation for 24 h. [b]Isolated yields.

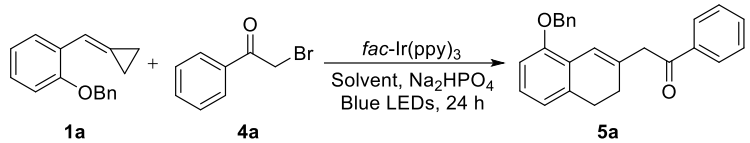
Table S6. Screening of Base



Entry	Base	Yield (%)[b]
1	**Na_2HPO_4**	**46**
2	K_3PO_4	nr
3	Na_2CO_3	trace
4	K_2CO_3	trace
5	KH_2PO_4	27
6	---	trace

[a]Reaction conditions: **1a** (0.2 mmol, 1 equiv), **4a** (0.3 mmol, 1.5 equiv), *fac*-Ir(ppy)$_3$ (2 mol%), and base (0.2 mmol, 1 equiv) in CH_3CN (2 mL) at room temperature under argon atmosphere and blue LEDs irradiation for 24 h. [b]Isolated yields.

Table S7. Screening of Solvent

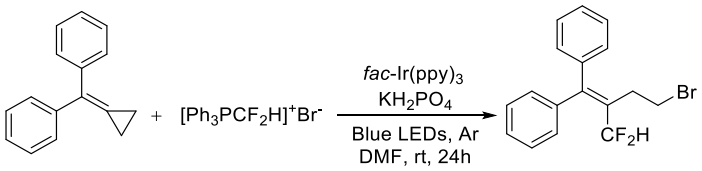


1a **4a** **5a**

Entry	Solvent	Yield (%)[b]
1	DMSO	trace
2	DMAC	trace
3	CH_2Cl_2	trace
4	$CHCl_3$	trace
5	DCE	trace
6	DMF	trace
7	CH_3CN	46
8	**NMP**	**55**

[a]Reaction conditions: **1a** (0.2 mmol, 1 equiv), **4a** (0.3 mmol, 1.5 equiv), *fac*-Ir(ppy)$_3$ (2 mol%), and Na_2HPO_4 (0.2 mmol, 1 equiv) in solvent (2 mL) at room temperature under argon atmosphere and blue LEDs irradiation for 24 h. [b]Isolated yield.

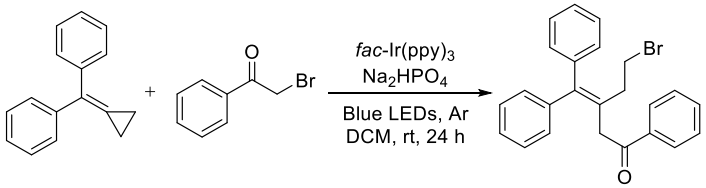
3.3 General Procedure of Product 6a



1n **2a** **6a**, 67%

A 10 mL oven-dried Schlenk tube equipped with a magnetic stir bar was charged with **1n** (0.2 mmol, 1 equiv), $[Ph_3PCF_2H]^+Br^-$ **2a** (0.3 mmol, 1.5 equiv), *f*ac-Ir(ppy)$_3$ (3 mol%), KH_2PO_4 (0.2 mmol, 1 equiv). The Schlenk tube was evacuated and backfilled with argon for three times. Then DMF (4 mL) was injected into the Schlenk tube. The mixture was stirred for 24 h under blue LEDs. The reaction solution was cooled to room temperature, and saturated aqueous $NaHCO_3$ (5 mL) was added. Then it was washed with brine (10 mL). The mixture was extracted with diethyl ether (30 mL) for three times, dried with $MgSO_4$, filtered, and concentrated. The residue was purified by flash column chromatography on silica gel (EtOAc/petroleum ether = 1/25) to give the desired product **6a** as a colorless oil in 67% isolated yield.

3.4 General Procedure of Product 7a



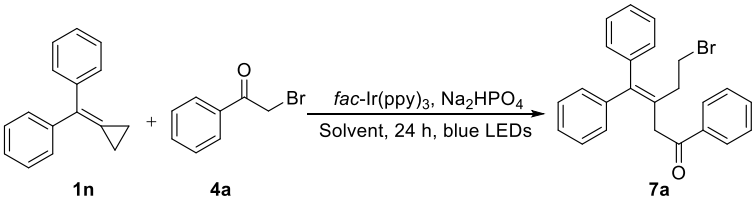
1n **4a** **7a**

A 10 mL oven-dried Schlenk tube equipped with a magnetic stir bar was charged with **1n** (0.2 mmol, 1 equiv), 2-bromoacetophenone **4a** (0.3 mmol, 1.5 equiv), *f*ac-Ir(ppy)$_3$ (2 mol%), and Na_2HPO_4 (0.3 mmol, 1.5 equiv). The Schlenk tube was evacuated and backfilled with argon for three times. Then DCE (1 mL) was injected into the Schlenk tube. The mixture was stirred for 24 h under blue LEDs. The reaction

solution was cooled to room temperature, and saturated aqueous $NaHCO_3$ (5 mL) was added. Then it was washed with brine (10 mL). The mixture was extracted with diethyl ether (30 mL) for three times, dried with $MgSO_4$, filtered, and concentrated. The residue was purified by flash column chromatography on silica gel (EtOAc/petroleum ether = 1/50) to give the desired product **7a** as a light-yellow solid in 70% isolated yield.

3.4.1 Optimization of Product 7a

Table S8. Screening of Solvent

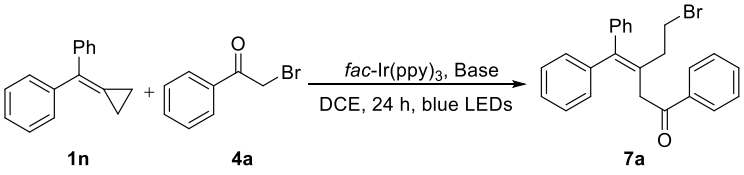


1n **4a** **7a**

Entry	Solvent	Yield (%)[b]
1	DMF	39
2	DMSO	0
3	DMAc	0
4	Toluene	0
5	DCE	0
6	THF	0
7	1.4-dioxane	0
8	Acetone	Trace
9	DME	Trace
10	CH_3CN	37
11	**DCM**	**45**

[a]Reaction conditions: **1n** (0.2 mmol, 1 equiv), **4a** (0.3 mmol, 1.5 equiv), *fac*-Ir(ppy)$_3$ (3 mol%), and KH_2PO_4 (0.3 mmol, 1.5 equiv) in solvent (1 mL) at room temperature under argon and blue LEDs irradiation for 24 h. [b]Yield were determined by ^{1}H NMR spectroscopy using 1,1,2,2,-tetrachloroethane as an internal standard.

Table S9. Screening of Base

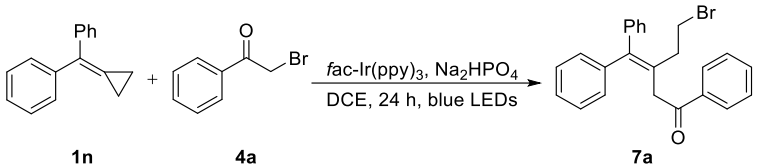


1n **4a** **7a**

Entry	Base	Yield (%)[b]
1	DBN	43
2	Na_2CO_3	67
3	Li_2CO_3	60
4	t-BuOLi	29
5	$(iPr)_2NEt$	28
6	**Na_2HPO_4**	**70**
7	K_3PO_4	54
8	NaOAc	57
9	K_2CO_3	61
10	KOAc	53
11	CsOAc	49
12	---	trace

[a]Reaction conditions: **1n** (0.2 mmol, 1 equiv), **4a** (0.3 mmol, 1.5 equiv), *fac*-Ir(ppy)$_3$ (3 mol%), and base (0.3 mmol, 1.5 equiv) in DCM (1 mL) at room temperature under argon and blue LEDs irradiation for 24 h. [b]Yields were determined by ^{1}H NMR spectroscopy using 1,1,2,2,-tetrachloroethane as an internal standard.

Table S10. Screening of Catalyst Loadings

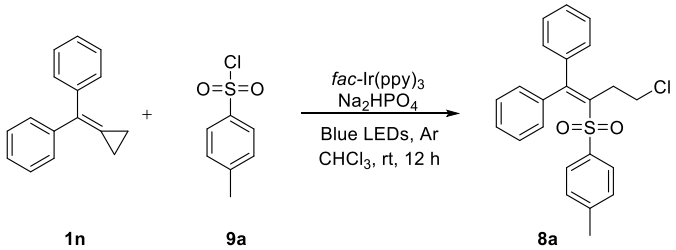


1n **4a** **7a**

Entry	*fac*-Ir(ppy)$_3$	Yield (%)[b]
1	2 mol%	70
2	**3 mol%**	**74(70)**

[a]Reaction conditions: **1n** (0.2 mmol, 1 equiv), **4a** (0.3 mmol, 1.5 equiv), *fac*-Ir(ppy)$_3$, and Na_2HPO_4 (0.3 mmol, 1.5 equiv) in DCM (1 mL) at room temperature under argon and blue LEDs irradiation for 24 h. [b]Yields were determined by ^{1}H NMR spectroscopy using 1,1,2,2,-tetrachloroethane as an internal standard. Isolated yields were in parentheses.

3.4 General Procedure of Product 8a

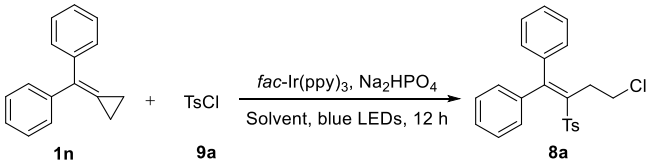


1n **9a** **8a**

A 10 mL oven-dried Schlenk tube equipped with a magnetic stir bar was charged with **1n** (0.2 mmol, 1 equiv), TsCl **9a** (0.4 mmol, 1.5 equiv), *fac*-Ir(ppy)$_3$ (2 mol%), and Na_2HPO_4 (0.2 mmol, 1 equiv). The Schlenk tube was evacuated and backfilled with argon for three times. Then $CHCl_3$ (1 mL) was injected into the Schlenk tube. The mixture was stirred for 12 h under blue LEDs. The reaction solution was cooled to room temperature, and saturated aqueous $NaHCO_3$ (5 mL) was added. Then it was washed with brine (10 mL). The mixture was extracted with DCM (30 mL) for three times, dried with $MgSO_4$, filtered, and concentrated. The residue was purified by flash column chromatography on silica gel (EtOAc/petroleum ether = 1/25) to give the desired product **8a** as a colorless solid in 92% isolated yield.

3.4.1 Optimization of Product 8a

Table S11. Screening of Solvent

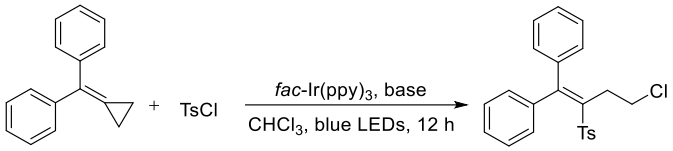


1n **9a** **8a**

Entry	Solvent	Yield (%)[b]
1	Toluene	22
2	Benzene	15
3	$PhCF_3$	28
4	**$CHCl_3$**	**81**
5	DCE	76
6	DMF	trace
7	DMSO	nr

[a]Reaction conditions: **1n** (0.2 mmol, 1 equiv), **9a** (0.3 mmol, 1.5 equiv), *fac*-Ir(ppy)$_3$ (2 mol%), and Na_2HPO_4 (0.2 mmol, 1 equiv) in solvent (1 mL) at room temperature under argon atmosphere and blue LEDs irradiation for 12 h. [b]Isolated yields.

Table S12. Screening of Base

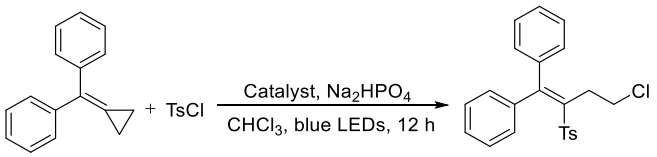


1n **9a** **8a**

Entry	Base	Yield (%)[b]
1	CH_3COOK	64
2	$NaHCO_3$	58
3	K_3PO_4	29
4	Cs_2CO_3	25
5	CH_3COONa	54
6	K_2CO_3	78
7	**Na_2HPO_4**	**81**
8	---	trace

[a]Reaction conditions: **1n** (0.2 mmol, 1 equiv), **9a** (0.3 mmol, 1.5 equiv), *fac*-Ir(ppy)$_3$ (2 mol%), and base (0.2 mmol, 1 equiv) in $CHCl_3$ (1 mL) at room temperature under argon atmosphere and blue LEDs irradiation for 12 h. [b]Isolated yields.

Table S13. Screening of Catalyst

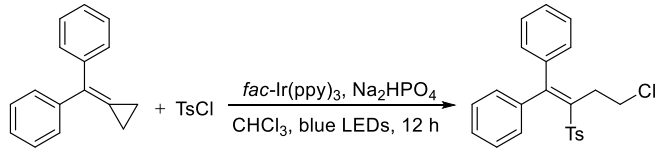


1n **9a** **8a**

Entry	Catalyst	Yield (%)[b]
1	Acid red 91	nr
2	Fluorescein	nr
3	EosinY Na_2	nr
4	Rhodamine B	nr
5	$[Ru(bpy)_3](PF_6)_2$	57
6	$[Ru(phen)_3](PF_6)_2$	58
7	***fac*-Ir(ppy)$_3$**	**81**

[a]Reaction conditions: **1n** (0.2 mmol, 1 equiv), **9a** (0.3 mmol, 1.5 equiv), catalyst (2 mol%), and Na_2HPO_4 (0.2 mmol, 1 equiv) in $CHCl_3$ (1 mL) at room temperature under argon atmosphere and blue LEDs irradiation for 12 h. [b]Isolated yields.

Table S14. Screening of the Volume of Solvent and TsCl Loadings



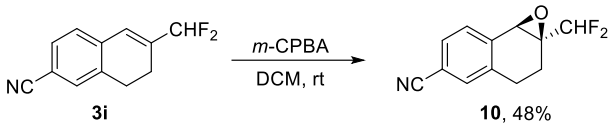
1n **9a** **8a**

Entry	$CHCl_3$	9a	Yield (%)[b]
1	1 mL	0.3 mmol	81
2	3 mL	0.3 mmol	76
3	**1 mL**	**0.4 mmol**	**92**

[a]Reaction conditions: **1n** (0.2 mmol, 1 equiv), **9a**, *fac*-Ir(ppy)$_3$ (2 mol%), and Na_2HPO_4 (0.2 mmol, 1 equiv) in $CHCl_3$ at room temperature under argon atmosphere and blue LEDs irradiation for 12 h. [b]Isolated yields.

4. Synthetic Transformations

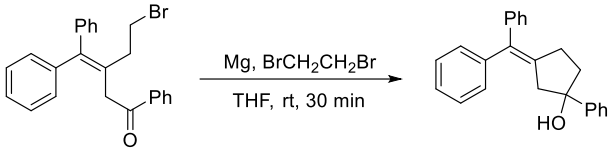
4.1 General Procedure of Product 10



3i **10**, 48%

In a 50 mL oven-dried round-bottomed flask equipped with a magnetic stir bar, a solution of *m*-chloroperbenzoic acid (0.8 mmol, 4 equiv) in DCM (2 mL) was added dropwise to a solution of **3i** (0.2 mmol) in DCM (0.6 mL) at 0 ºC and the solution was warmed to room temperature. After the reaction mixture was stirred for 12 h, it was washed with 2.5 M NaOH for three times. The organic phase was dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and purified by column chromatography on silica gel to afford product **10** in 48% isolated yield.[1]

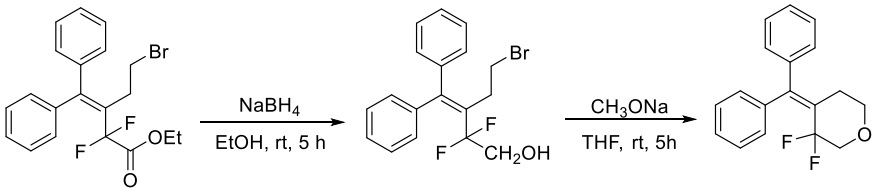
4.2 General Procedure of Product 11



7a **11, 67%**

A 50 mL three-necked flask equipped with a condenser and a funnel, magnesium (404 mg, 1 mmol) and anhydrous THF (2 mL) were added under argon atmosphere. The reaction was initiated with 0.5 mL of **7a** solution (157 mg of **7a** dissolved in 20 mL THF) and a drop of $BrCH_2CH_2Br$. Then the left 19.5 mL of **7a** solution was added dropwise to the solution in 30 min and the mixture was stirred for another 30 min at room temperature. After the addition of H_2O (20 mL) and DCM (20 mL), the organic layer was separated. The aqueous layer was extracted with DCM (2 × 20 mL). The combined organic layers were washed with brine (15 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. Product **11** was purified by column chromatography on silica gel and obtained in 67% isolated yield in light-yellow oil.

4.3 General Procedure of Product 12 and 13

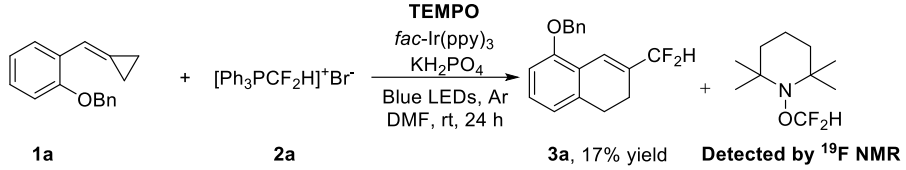


7l **12**, 61% **13**, 84%

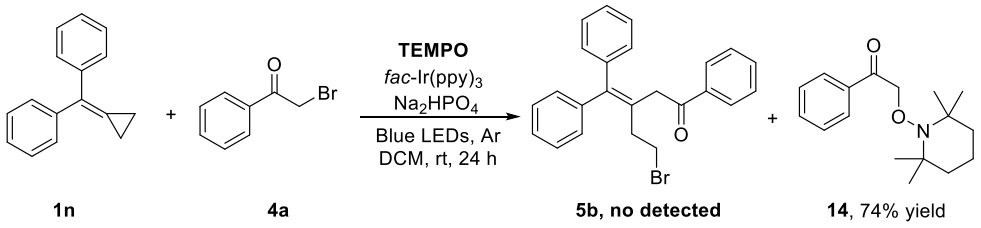
Synthesis of Product 12: A 25 mL oven-dried sealed tubes equipped with a magnetic stir bar, **7l** (1.5 mmol), $NaBH_4$ (2.25 mmol), and EtOH (7.5 mL) were added. The reaction mixture was stirred for 5 h at room temperature. Then HCl (2.5 M, 3.8 mL) was added to the mixture. The mixture was extracted with DCM (20 mL × 3). The combined organic extract was dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography to give product **12** as a colorless oil in 61% yield**.**

Synthesis of Product 13: A 25 mL oven-dried sealed tubes equipped with a magnetic stir bar, **12** (0.2 mmol), CH_3ONa (2 mmol), and THF (7.5 mL). The reaction mixture was stirred for 5 h at room temperature. The reaction was quenched by H_2O. The aqueous layer was extracted with DCM (20 mL × 3). The combined organic layers were washed with brine (10 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. the residue was purified by silica gel column chromatography to give product **13** as a colorless oil in 84% yield.

5. Control Experiments

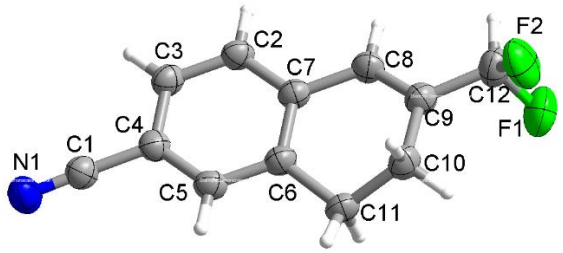


A 10 mL oven-dried Schlenk tube equipped with a magnetic stir bar was charged with **1a** (0.2 mmol, 1 equiv), $[Ph_3PCF_2H]^+Br^-$ **2a** (0.3 mmol, 1.5 equiv), *fac*-Ir(ppy)$_3$ (3 mol%), KH_2PO_4 (0.2 mmol, 1 equiv), and TEMPO (2 equiv). The Schlenk tube was evacuated and backfilled with argon for three times. Then DMF (4 mL) was injected into the Schlenk tube. The mixture was stirred for 24 h under blue LEDs. The reaction solution was cooled to room temperature, and saturated aqueous $NaHCO_3$ (5 mL) was added. Then it was washed with brine (10 mL). The mixture was extracted with diethyl ether (30 mL) for three times, dried with $MgSO_4$, filtered, and concentrated. The corresponding product **3a** was detected by in 17% ^{19}F NMR yields.[5]



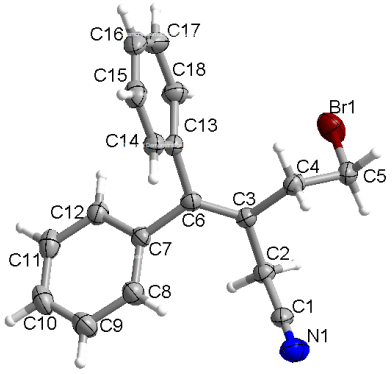
A 10 mL oven-dried Schlenk tube equipped with a magnetic stir bar was charged with **1n** (0.2 mmol, 1 equiv), 2-bromoacetophenone **4a** (0.3 mmol, 1.5 equiv), *fac*-Ir(ppy)$_3$ (3 mol%), Na_2HPO_4 (0.2 mmol, 1.5 equiv), and TEMPO (2 equiv). The Schlenk tube was evacuated and backfilled with argon for three times. Then DCE (1 mL) was injected into the Schlenk tube. The mixture was stirred for 24 h under blue LEDs. The reaction solution was cooled to room temperature, and saturated aqueous $NaHCO_3$ (5 mL) was added. Then it was washed with brine (10 mL). The mixture was extracted with diethyl ether (30 mL) for three times, dried with $MgSO_4$, filtered, and concentrated. The corresponding product **5b** was not detected by ^1H NMR and compound **14** was obtained in 74% yield.

6. X-ray Crystallographic Data of 3i, 7m, 8a



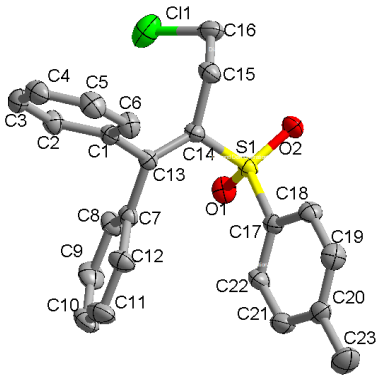
The product **3i** (CCDC number: 2094030) was crystallized from a hexane/DCM mixture (1/5, v/v). The atoms are depicted with 50% probability ellipsoids. The crystallographic data are summarized in the following table.

Identification code	**3i**
Empirical formula	$C_{12}H_9F_2N$
Formula weight	205.20
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.7775(8)
b/Å	7.7026(3)
c/Å	8.9656(4)
α/°	90
β/°	102.577(5)
γ/°	90
Volume/Å^3	996.03(8)
Z	4
ρ_{calc}g/cm^3	1.368
μ/mm^{-1}	0.905
F(000)	424.0
Crystal size/mm^3	0.15 × 0.1 × 0.09
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	12.274 to 134.146
Index ranges	-17 ⩽ h ⩽ 17, -7 ⩽ k ⩽ 9, -6 ⩽ l ⩽ 10
Reflections collected	3653
Independent reflections	1776 [R_{int} = 0.0234, R_{sigma} = 0.0276]
Data/restraints/parameters	1776/3/144
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0462, wR_2 = 0.1238
Final R indexes [all data]	R_1 = 0.0656, wR_2 = 0.1434
Largest diff. peak/hole / e Å^{-3}	0.10/-0.14



The product **7m** (CCDC number: 2094032) was crystallized from a hexane/DCM mixture (1/5, v/v). The atoms are depicted with 50% probability ellipsoids. The crystallographic data are summarized in the following table.

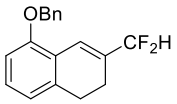
Identification code	**7m**
Empirical formula	$C_{18}H_{16}BrN$
Formula weight	326.23
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	5.9270(3)
b/Å	17.7263(9)
c/Å	14.8916(6)
α/°	90
β/°	99.915(4)
γ/°	90
Volume/Å^3	1541.19(12)
Z	4
ρ_{calc}g/cm^3	1.406
μ/mm^{-1}	3.530
F(000)	664.0
Crystal size/mm^3	0.17 × 0.12 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.822 to 134.094
Index ranges	$-5 \leqslant h \leqslant 7, -21 \leqslant k \leqslant 20, -15 \leqslant l \leqslant 17$
Reflections collected	5529
Independent reflections	2741 [R_{int} = 0.0301, R_{sigma} = 0.0387]
Data/restraints/parameters	2741/0/181
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0510, wR_2 = 0.1222
Final R indexes [all data]	R_1 = 0.0655, wR_2 = 0.1332
Largest diff. peak/hole / e Å^{-3}	0.78/-0.64



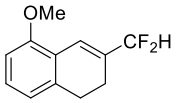
The product **8a** (CCDC number: 2094036) was crystallized from a hexane/DCM mixture (1/5, v/v). The atoms are depicted with 50% probability ellipsoids. The crystallographic data are summarized in the following table.

Identification code	**8a**
Empirical formula	$C_{23}H_{21}ClO_2S$
Formula weight	396.91
Temperature/K	293(2)
Crystal system	monoclinic
Space group	P21/n
a/Å	10.0613(7)
b/Å	9.4559(7)
c/Å	21.497(2)
α/°	90
β/°	97.026(9)
γ/°	90
Volume/Å3	2029.8(3)
Z	4
ρcalcg/cm3	1.299
μ/mm-1	2.739
F(000)	832.0
Crystal size/mm3	0.18 × 0.15 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.288 to 134.144
Index ranges	-11 ≤ h ≤ 12, -11 ≤ k ≤ 10, -25 ≤ l ≤ 23
Reflections collected	7574
Independent reflections	3614 [Rint = 0.0407, Rsigma = 0.0564]
Data/restraints/parameters	3614/0/245
Goodness-of-fit on F2	1.060
Final R indexes [I>=2σ (I)]	R1 = 0.0576, wR2 = 0.1442
Final R indexes [all data]	R1 = 0.0833, wR2 = 0.1713
Largest diff. peak/hole / e Å-3	0.31/-0.28

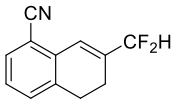
7. Characterization of Products



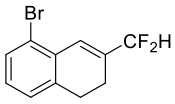
5-(benzyloxy)-3-(difluoromethyl)-1,2-dihydronaphthalene (3a): The reaction was conducted on 0.2 mmol scale. The product **3a** (34.3 mg, 60%) as colorless oil was purified by flash column chromatography (PE/EA = 50/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.33 (m, 5H), 7.16 (t, *J* = 8.0 Hz, 2H), 6.82-6.76 (m, 2H), 6.20 (t, *J* = 56.0 Hz, 1H), 5.09 (s, 2H), 2.87 (t, *J* = 8.1 Hz, 2H), 2.43 (t, *J* = 8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 137.6, 136.9, 131.4 (t, *J* = 22.1 Hz), 129.3, 128.6, 128.0, 127.4, 123.7 (t, *J* = 11.2 Hz), 121.2, 120.4, 116.6 (t, *J* = 232.4 Hz), 110.3, 70.3, 27.6, 19.2 (t, *J* = 1.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{17}F_2O$ 287.1242; Found 287.1244.



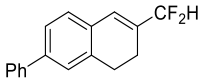
3-(difluoromethyl)-5-methoxy-1,2-dihydronaphthalene (3b): The reaction was conducted on 0.2 mmol scale. The product **3b** (21.0 mg, 50%) as light green oil was purified by flash column chromatography (PE/EA = 50/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (t, *J* = 7.9 Hz, 1H), 7.1 (s, 1H), 6.75 (m, 2H), 6.20 (t, *J* = 56.1 Hz, 1H), 3.84 (s , 3H), 2.85 (t, *J* = 8.5 Hz, 2H), 2.43 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 137.2, 131.1 (t, *J* = 21.8 Hz), 123.3 (t, *J* = 11.0 Hz), 120.6, 119.9, 116.4 (t, *J* = 232.5 Hz), 108.6, 55.3, 27.3, 19.1 (t, *J* = 1.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.6. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{12}H_{12}F_2O$ 210.0851; Found 210.0853.



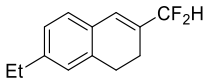
7-(difluoromethyl)-5,6-dihydronaphthalene-1-carbonitrile (3c): The reaction was conducted on 0.2 mmol scale. The product **3c** (17.6 mg, 43%) as light green oil was purified by flash column chromatography (PE/EA = 50/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.7 Hz, 1H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 7.6 Hz, 1H),7.02 (s, 1H), 6.22 (t, *J* = 55.6 Hz, 1H), 2.90 (t, *J* = 8.2 Hz, 2H), 2.46 (t, *J* = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.54 (t, *J* = 22.6 Hz), 136.51, 134.3, 131.6, 130.4, 128.3, 124.7 (t, *J* = 10.8 Hz), 116.9, 114.8 (t, *J* = 234.5 Hz), 109.7, 26.6, 19.0 (t, *J* = 2.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{10}F_2N$ 206.0776; Found 206.0778.



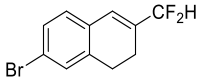
5-bromo-3-(difluoromethyl)-1,2-dihydronaphthalene (3d): The reaction was conducted on 0.2 mmol scale. The product **3a** (17.6 mg, 34%) as colorless oil was purified by flash column chromatography (PE/EA = 50/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.8 Hz, 1H), 7.13-7.02 (m, 3H), 6.24 (t, *J* = 55.8 Hz, 1H), 2.89 (t, *J* = 8.1 Hz, 2H), 2.43 (t, *J* = 8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 135.1 (t, *J* = 22.2 Hz), 131.6, 131.5, 130.0, 128.1 (t, *J* = 11.0 Hz), 127.3, 123.6, 116.2 (t, *J* = 233.5 Hz), 28.5 19.9 (t, *J* = 2.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.7. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{11}H_9BrF_2$ 257.9850; Found 257.9852.



3-(difluoromethyl)-7-phenyl-1,2-dihydronaphthalene (3f): The reaction was conducted on 0.2 mmol scale. The product **3f** (21.5 mg, 42%) as white solid (m.p. 96.5-97.0 °C) was purified by flash column chromatography (PE/EA = 50/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.8 Hz, 2H), 7.47-7.34 (m, 5H), 7.20 (d, *J* = 7.7 Hz, 1H), 6.74 (s, 1H), 6.21 (t, *J* = 56.0 Hz, 1H), 2.97 (t, *J* = 8.3 Hz, 2H), 2.50 (t, *J* = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 141.7, 137.4, 133.6 (t, *J* = 22.0 Hz), 132.2, 129.9, 129.7 (t, *J* = 10.9 Hz), 128.8, 128.5, 128.1, 127.6, 126.5, 117.1 (t, *J* = 233.3 Hz), 28.5, 21.0 (t, *J* = 2.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.5. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{17}H_{14}F_2$ 256.1058; Found 256.1060.

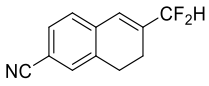


3-(difluoromethyl)-7-ethyl-1,2-dihydronaphthalene (3g): The reaction was conducted on 0.2 mmol scale. The product **3g** (17.5 mg, 42%) as colorless oil was purified by flash column chromatography (PE/EA = 50/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (s, 2H), 7.01 (s, 1H), 6.67 (s, 1H), 6.18 (t, *J* = 56.1 Hz, 1H), 2.88 (t, *J* = 8.4 Hz, 2H), 2.64 (q, *J* = 7.6 Hz, 2H), 2.45 (m, 2H), 1.25 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 136.1, 131.7 (t, *J* = 21.8 Hz), 129.8, 129.2 (t, *J* = 10.9 Hz), 127.60, 127.55, 126.3, 116.5 (t, *J* = 233.0 Hz), 29.0, 27.6, 20.1 (t, *J* = 2.0 Hz), 15.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.2. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{13}H_{14}F_2$ 208.1058; Found 208.1063.

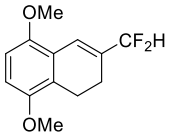


7-bromo-3-(difluoromethyl)-1,2-dihydronaphthalene (3h): The reaction was conducted on 0.2 mmol scale. The product **3h** (28.5 mg, 41%) as White solid (m.p. 48.3-49.0 °C) was purified by flash column chromatography (PE/EA = 50/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 9.0 Hz, 2H), 6.97

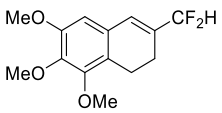
(d, J = 7.8 Hz, 1H), 6.63 (s, 1H), 6.16 (t, J = 55.9 Hz, 1H), 2.86 (t, J = 8.2 Hz, 2H), 2.41 (t, J = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 134.1 (t, J = 21.9 Hz), 132.0, 131.8, 130.8, 129.7, 129.0 (t, J = 10.8 Hz), 123.3, 116.8 (t, J = 233.7 Hz), 28.1, 20.7 (t, J = 2.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.0. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{11}H_9BrF_2$ 257.9850; Found 257.9855.



6-(difluoromethyl)-7,8-dihydronaphthalene-2-carbonitrile (3i): The reaction was conducted on 0.2 mmol scale. The product **3i** (23.4 mg, 50%) as white solid (m.p. 127.6-129.2 °C) was purified by flash column chromatography (PE/EA = 50/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 7.8 Hz, 1H), 7.43 (s, 1H), 7.19 (d, J = 7.8 Hz, 1H), 6.71 (s, 1H), 6.20 (t, J = 55.7 Hz, 1H), 2.95 (t, J = 8.2 Hz, 2H), 2.48 (t, J = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 136.52 (t, J = 21.9 Hz), 136.48, 131.12, 131.06, 127.8, 127.5 (t, J = 10.4 Hz), 119.0, 115.3 (t, J = 235.0 Hz), 111.9, 26.9, 19.9 (t, J = 2.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{10}F_2N$ 206.0776; Found 206.0775

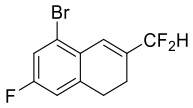


3-(difluoromethyl)-5,8-dimethoxy-1,2-dihydronaphthalene (3k): The reaction was conducted on 0.2 mmol scale. The product **3k** (25.9 mg, 54%) as colourless oil was purified by flash column chromatography (PE/EA = 50/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (s, 1H), 6.78 (d, J = 8.9 Hz, 1H), 6.68 (d, J = 8.9 Hz, 1H), 6.20 (t, J = 56.1 Hz, 1H), 3.80 (s, 6H), 2.85 (t, J = 8.4 Hz, 2H), 2.38 (t, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 150.4, 131.8 (t, J = 22.2 Hz), 125.6, 123.6 (t, J = 11.3 Hz), 122.1, 116.7 (t, J = 232.5 Hz), 111.8, 108.9, 56.2, 56.1, 20.3, 18.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{15}F_2O_2$ 241.1035; Found 241.1037.

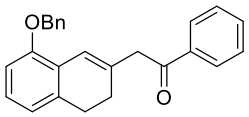


3-(difluoromethyl)-6,7,8-trimethoxy-1,2-dihydronaphthalene (3l): The reaction was conducted on 0.2 mmol scale. The product **3l** (29.1 mg, 54%) as light green oil was purified by flash column chromatography (PE/EA = 50/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.59 (s, 1H), 6.50 (s, 1H), 6.16 (d, J = 56.0 Hz, 1H) 3.87 (d, J = 15.2 Hz, 9H), 2.84 (t, J = 8.3 Hz, 2H), 2.38 (t, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.91, 151.90, 142.9, 132.1 (t, J = 21.7 Hz), 128.7 (t, J = 10.8 Hz), 127.8, 121.8, 116.2

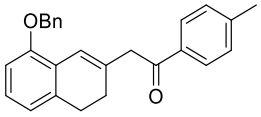
(t, J = 233.3 Hz), 107.4, 61.1, 61.0, 56.2, 20.0, 19.5 (t, J = 2.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{17}F_2O_3$ 271.1140; Found 271.1143.



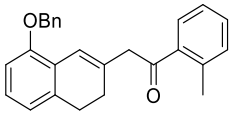
5-bromo-3-(difluoromethyl)-7-fluoro-1,2-dihydronaphthalene (3m): The reaction was conducted on 0.2 mmol scale. The product **3m** (18.3 mg, 33%) as light green oil was purified by flash column chromatography (PE/EA = 50/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17(m, 1H), 7.01 (s, 1H), 6.86 (d, J = 8.4 Hz, 1H), 6.23 (t, J = 55.8 Hz, 1H), 2.88 (t, J = 8.1 Hz, 2H), 2.42 (t, J = 8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3 (d, J = 251.4 Hz), 140.2 (d, J = 7.9 Hz), 133.9 (t, J = 24.2 Hz), 127.7 (d, J = 3.5 Hz), 126.8 (t, J = 12.1 Hz), 123.1 (d, J = 10.0 Hz), 118.1 (d, J = 24.4 Hz), 115.7 (t, J = 233.5 Hz), 114.5 (d, J = 21.4 Hz), 28.5, 19.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.8, -115.6. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{11}H_8BrF_3$ 275.9756; Found 275.9760.



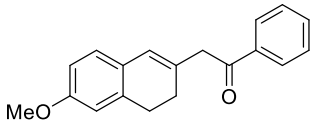
2-(8-(benzyloxy)-3,4-dihydronaphthalen-2-yl)-1-phenylethan-1-one (5a): The reaction was conducted on 0.2 mmol scale. The product **5a** (38.9 mg, 55%) as brown oil was purified by flash column chromatography (PE/EA = 25/1); 1H NMR (400 MHz, $CDCl_3$) 8.05 (d, J = 7.4 Hz, 2H), 7.59 (t, J = 7.1 Hz, 1H), 7.54-7.33 (m, 7H), 7.08 (t, J = 7.4 Hz, 1H), 6.89 (s, 1H), 6.81-6.75 (m, 2H), 5.09 (s, 2H), 3.94 (s, 2H), 2.85 (t, J = 8.0 Hz, 2H), 2.35 (t, J = 8.0 Hz, 2H); 13C NMR (100 MHz, CDCl3) δ 198.0, 153.7, 137.4, 136.8, 136.3, 134.3, 133.2, 128.6, 128.54, 128.48, 127.8, 127.3, 127.2, 123.4, 120.6, 120.3, 110.2, 70.2, 47.8, 28.3, 26.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{23}O_2$ 355.1693; Found 355.1693.



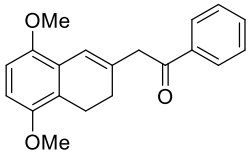
2-(8-(benzyloxy)-3,4-dihydronaphthalen-2-yl)-1-(p-tolyl)ethan-1-one (5b): The reaction was conducted on 0.2 mmol scale. The product **5b** (34.6 mg, 47%) as brown oil was purified by flash column chromatography (PE/EA = 25/1); ^{1}H NMR (400 MHz, $CDCl_3$) 7.95 (d, J = 7.6 Hz, 2H), 7.50-7.35 (m, 5H), 7.27 (d, J = 8.0 Hz, 2H), 7.07 (t, J = 7.5 Hz, 1H), 6.92-6.68 (m, 3H), 5.09 (s, 2H), 3.90 (s, 2H), 2.84 (t, J = 8.1 Hz, 2H), 2.43 (s, 3H), 2.33 (t, J = 8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 153.7, 143.9, 137.4, 136.3, 134.5, 134.4, 129.3, 128.6, 128.5, 127.8, 127.3, 127.1, 123.6, 120.5, 120.3, 110.3, 70.3, 47.7, 28.3, 26.9, 21.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{25}O_2$ 369.1849; Found 369.1852.



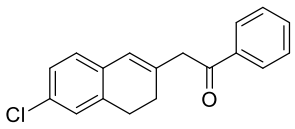
2-(8-(benzyloxy)-3,4-dihydronaphthalen-2-yl)-1-(o-tolyl)ethan-1-one (5c): The reaction was conducted on 0.2 mmol scale. The product **5c** (29.0 mg, 39%) as gray-green oil was purified by flash column chromatography (PE/EA = 25/1); ^{1}H NMR (400 MHz, $CDCl_3$) 7.75 (d, *J* = 7.4 Hz, 1H), 7.50-7.33 (m, 6H), 7.32-7.23 (m, 2H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.88-6.73 (m, 3H), 5.08 (s, 2H), 3.85 (s, 2H), 2.82 (t, *J* = 8.0 Hz, 2H), 2.52 (s, 3H), 2.32 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.0, 153.7, 138.3, 137.8, 137.4, 136.2, 134.1, 132.0, 131.3, 128.8, 128.5, 127.8, 127.3, 127.2, 125.6, 123.4, 120.6, 120.3, 110.2, 70.2, 50.6, 28.3, 27.0, 21.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{25}O_2$ 369.1849; Found 369.1849.



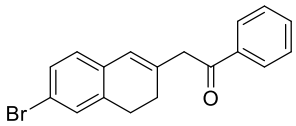
2-(6-methoxy-3,4-dihydronaphthalen-2-yl)-1-phenylethan-1-one (5d): The reaction was conducted on 0.2 mmol scale. The product **5d** (25.6 mg, 46%) as colorless solid (m.p. 102.1-103.1 ºC); was purified by flash column chromatography (PE/EA = 25/1); 1H NMR (400 MHz, $CDCl_3$) 8.04 (d, J = 7.5 Hz, 2H), 7.59 (t, J = 7.2 Hz, 1H), 7.49 (t, J = 7.4 Hz, 2H), 6.95 (d, J = 8.0 Hz, 1H), 6.69 (d, J = 7.8 Hz, 2H), 6.34 (s, 1H), 3.87 (s, 2H), 3.81 (s, 3H), 2.84 (t, J = 8.0 Hz, 2H), 2.34 (t, J = 8.0 Hz, 2H); 13C NMR (100 MHz, $CDCl_3$) δ 198.1, 158.6, 136.8, 136.3, 133.2, 132.3, 128.6, 128.5, 127.5, 126.8, 125.9, 113.5, 111.1, 55.3, 47.3, 28.5, 27.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{19}O_2$ 279.1380; Found 279.1381.



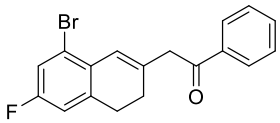
2-(5,8-dimethoxy-3,4-dihydronaphthalen-2-yl)-1-phenylethan-1-one (5e): The reaction was conducted on 0.2 mmol scale. The product **5e** (38.5 mg, 56%) as brown solid (m.p. 118.7-119.2 ºC); was purified by flash column chromatography (PE/EA = 25/1); ^{1}H NMR (400 MHz, $CDCl_3$) 8.05 (d, *J* = 7.1 Hz, 2H), 7.58 (t, *J* = 7.1 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 2H), 6.79 (s, 1H), 6.74-6.66 (m, 2H), 3.92 (s, 2H), 3.80 (s, 6H), 2.83 (t, *J* = 8.2 Hz, 2H), 2.31 (t, *J* = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 150.6, 149.3, 136.9, 134.6, 133.1, 128.6, 128.5, 124.3, 124.0, 109.8, 108.8, 56.10, 56.05, 47.8, 26.3, 20.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{21}O_3$ 309.1485; Found 309.1486.



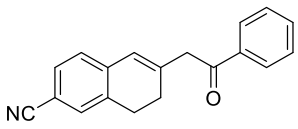
2-(6-chloro-3,4-dihydronaphthalen-2-yl)-1-phenylethan-1-one (5f): The reaction was conducted on 0.2 mmol scale. The product **5f** (27.0 mg, 48%) as colorless solid (m.p. 119.7-120.2 °C); was purified by flash column chromatography (PE/EA = 25/1); ^{1}H NMR (400 MHz, $CDCl_3$) 8.03 (d, *J* = 7.6 Hz, 2H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.50 (t, *J* = 7.3 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 6.93 (d, *J* = 7.8 Hz, 1H), 6.35 (s, 1H), 3.89 (s, 2H), 2.85 (t, *J* = 8.0 Hz, 2H), 2.35 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 136.7, 136.4, 135.6, 133.3, 132.7, 131.9, 128.7, 128.4, 127.4, 126.8, 126.4, 125.6, 47.1, 27.9, 27.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{16}ClO$ 283.0884; Found 283.0885.



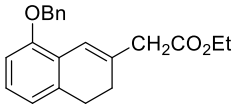
2-(6-bromo-3,4-dihydronaphthalen-2-yl)-1-phenylethan-1-one (5g): The reaction was conducted on 0.2 mmol scale. The product **5g** (26.5 mg, 41%) as colorless solid (m.p. 134.0-134.6 °C); was purified by flash column chromatography (PE/EA = 25/1); ^{1}H NMR (400 MHz, $CDCl_3$) 8.03 (d, *J* = 7.4 Hz, 2H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 7.8 Hz, 1H), 6.33 (s, 1H), 3.88 (s, 2H), 2.85 (t, *J* = 8.0 Hz, 2H), 2.35 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 136.69, 136.67, 135.8, 133.4, 133.2, 130.2, 129.4, 128.7, 128.4, 127.2, 125.6. 120.0, 47.2, 27.8, 27.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{16}BrO$ 327.0379; Found 327.0379.



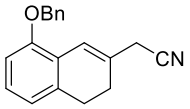
2-(8-bromo-6-fluoro-3,4-dihydronaphthalen-2-yl)-1-phenylethan-1-one (5h): The reaction was conducted on 0.2 mmol scale. The product **5h** (31.2 mg, 45%) as colorless oil was purified by flash column chromatography (PE/EA = 25/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 7.4 Hz, 2H), 7.59 (t, *J* = 7.1 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.11 (d, *J* = 8.3 Hz, 1H), 6.81 (d, *J* = 8.5 Hz, 1H), 6.69 (s, 1H), 3.94 (s, 2H), 2.84 (t, *J* = 7.9 Hz, 2H), 2.30 (t, *J* = 7.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.4, 160.7 (*J* = 248.3 Hz), 138.9 (*J* = 7.7 Hz), 136.9 (*J* = 2.5 Hz), 136.69, 133.4, 129.6 (*J* = 3.2 Hz), 128.7, 128.7, 128.4,128.4, 124.3, 121.1 (*J* = 9.8 Hz), 117.49 (*J* = 24.2 Hz), 114.01 ($J_{C\text{-}F}$ = 21.2 Hz), 47.3, 29.1, 26.7. ^{19}F NMR (376.5 MHz, $CDCl_3$): (ppm) δ -113.94. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{15}BrFO$ 345.0285; Found 345.0285.



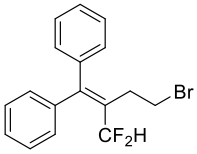
6-(2-oxo-2-phenylethyl)-7,8-dihydronaphthalene-2-carbonitrile (5i): The reaction was conducted on 0.2 mmol scale. The product **5i** (17.8 mg, 33%) as yellow solid (m.p. 93.0-94.0 ºC); was purified by flash column chromatography (PE/EA = 25/1); ^{1}H NMR (400 MHz, $CDCl_3$) 8.02 (d, *J* = 7.6 Hz, 2H), 7.62 (t, *J* = 7.1 Hz, 1H), 7.51 (t, *J* = 7.3 Hz, 2H), 7.44 (d, *J* = 7.7 Hz, 1H),7.38 (s, 1H), 7.06 (d, *J* = 7.7 Hz, 1H), 6.40 (s, 1H), 3.94 (s, 2H), 2.90 (t, *J* = 8.1 Hz, 2H), 2.41 (t, *J* = 8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 139.9, 138.6, 136.5, 135.5, 133.5, 130.7, 130.5, 128.8, 128.4, 126.0, 125.6, 119.4, 109.6, 47.1, 27.4, 27.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{16}NO$ 274.1226; Found 274.1226.



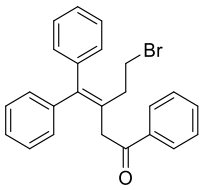
ethyl 2-(8-(benzyloxy)-3,4-dihydronaphthalen-2-yl)acetate (5j): The reaction was conducted on 0.2 mmol scale. The product **5j** (30.9 mg, 48%) as colorless oil was purified by flash column chromatography (PE/EA = 25/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.49 (m, 5H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.80 (s, 1H), 6.76 (d, *J* = 6.8 Hz, 2H), 5.07 (s, 2H), 4.15 (q, *J* = 13.0, 6.7 Hz, 2H), 3.24 (s, 1H), 2.83 (t, *J* = 8.0 Hz, 2H), 2.33 (t, *J* = 7.9 Hz, 2H), 1.25 (t, *J* = 7.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.5, 153.8, 137.3, 136.2, 133.1, 128.6, 128.6, 127.8, 127.4, 127.4 (, 127.2, 123.3, 120.2, 120.0, 110.1, 70.2, 60.7, 43.3, 28.4, 26.8, 14.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{23}O_3$ 323.1642; Found 323.1642.



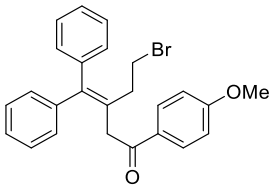
2-(8-(benzyloxy)-3,4-dihydronaphthalen-2-yl)acetonitrile (5k): The reaction was conducted on 0.2 mmol scale. The product **5k** (20.8 mg, 38%) as colorless oil was purified by flash column chromatography (PE/EA = 25/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.48 (m, 5H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.98 (s, 1H), 6.77 (t, *J* = 8.2 Hz, 2H), 5.10 (s, 2H), 3.29 (s, 2H), 3.24 (s, 1H), 2.87 (t, *J* = 8.0 Hz, 2H), 2.35 (t, *J* = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.0, 137.1, 135.8, 128.6, 128.6, 128.1, 127.9, 127.9, 127.3, 127.3, 122.3, 120.8, 120.3, 117.3, 110.4, 70.3, 28.0, 26.3, 25.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{18}NO$ 276.1383; Found 276.1388.



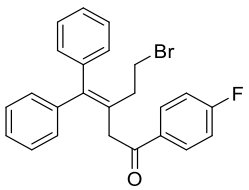
(4-bromo-2-(difluoromethyl)but-1-ene-1,1-diyl)dibenzene (6a): The reaction was conducted on 0.2 mmol scale. The product **6a** (29.1 mg, 54%) as light green oil was purified by flash column chromatography (PE/EA = 25/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.29 (m, 6H), 7.22-7.14 (m, 4H), 6.21 (t, *J* = 110.2 Hz, 1H) 3.48 (t, *J* = 16.1 Hz, 2H), 2.92 (t, *J* = 16.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5 (t, *J* = 20.5 Hz), 140.2, 139.2, 129.4, 129.0 (t, *J* = 44.2 Hz), 128.8, 128.7, 128.6, 128.5, 128.3, 115.2 (t, *J* = 466.0 Hz), 30.9, 30.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.5. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{17}H_{15}BrF_2$ 336.0320; Found 336.0328.



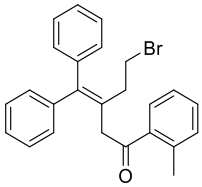
5-bromo-3-(diphenylmethylene)-1-phenylpentan-1-one (7a): The reaction was conducted on 0.2 mmol scale. The product **7a** (56.7 mg, 70%) as light green solid (m.p. 108.8-109.2 °C) was purified by flash column chromatography (PE/EA = 50/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.7 Hz, 2H), 7.53 (t, *J* = 7.3 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 2H), 7.27-7.15 (m, 8H), 3.90 (s, 2H), 3.44 (t, *J* = 7.3 Hz, 2H), 2.80 (t, *J* = 7.3 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.41, 144.75, 142.21, 141.87, 136.63, 133.27, 129.56, 129.09, 128.81, 128.61, 128.42, 128.40, 128.19, 127.10, 126.97, 42.53, 36.03, 31.34. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{22}BrO$ 405.0843; Found 405.0839.



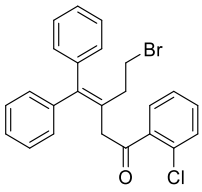
5-bromo-3-(diphenylmethylene)-1-(4-methoxyphenyl)pentan-1-one (7b): The reaction was conducted on 0.2 mmol scale. The product **7a** (56.6 mg, 65%) as deep blue oil (m.p. 108.8-109.2 °C) was purified by flash column chromatography (PE/EA = 50/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.7 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.28-7.17 (m, 8H), 6.88 (d, *J* = 8.7 Hz, 2H), 3.85 (s, 2H), 3.46 (t, *J* = 7.3 Hz, 2H), 2.79 (t, *J* = 7.3 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.90, 163.63, 144.43, 142.25, 141.95, 130.52, 129.90, 129.67, 129.14, 128.90, 128.06, 127.04, 126.92, 113.72, 55.50, 42.18, 35.98, 31.45. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{24}BrO_2$ 435.0954; Found 435.0958.



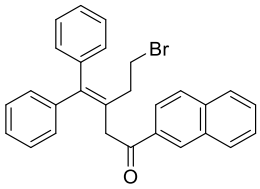
5-bromo-3-(diphenylmethylene)-1-(4-fluorophenyl)pentan-1-one (7c): The reaction was conducted on 0.2 mmol scale. The product **7c** (50.8 mg, 60%) as light green oil was purified by flash column chromatography (PE/EA = 50/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (t, *J* = 6.5 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.28-7.15 (m, 8H), 7.07 (t, *J* = 8.1 Hz, 2H), 3.87 (s, 2H), 3.45 (t, *J* = 7.2Hz, 2H), 2.79 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.78, 166.66, 164.97, 144.82, 142.12, 141.73, 132.98, 132.96, 130.87, 130.81, 129.38, 129.03, 128.77, 128.42, 128.39, 127.13, 127.00, 115.73, 115.59. 42.38, 35.88, 31.25. ^{19}F NMR (376 MHz, $CDCl_3$) δ -104.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{21}BrFO$ 423.0754; Found 423.0751.



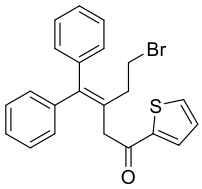
5-bromo-3-(diphenylmethylene)-1-(o-tolyl)pentan-1-one (7d): The reaction was conducted on 0.2 mmol scale. The product **7d** (63.7 mg, 76%) as green solid (m.p. 83.2-83.8 °C) was purified by flash column chromatography (PE/EA = 50/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37-7.29 (m, 4H), 7.27-7.13 (m, 10H), 3.81(s, 2H), 3.45 (t, *J* = 7.3 Hz, 2H), 2.79 (t, *J* = 7.3 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 202.38, 144.86, 142.24, 141.78, 137.88, 137.72, 131.90, 131.31, 129.52, 128.96, 128.68, 128.37, 128.35, 127.05, 126.95, 125.57, 45.57, 36.24, 31.14, 21.09. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{24}BrO$ 419.1005; Found 419.1006.



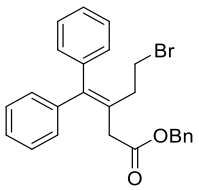
5-bromo-1-(2-chlorophenyl)-3-(diphenylmethylene)pentan-1-one (7e): The reaction was conducted on 0.2 mmol scale. The product **7e** (38.7 mg, 44%) as white solid (m.p. 114.5-115.3 °C) was purified by flash column chromatography (PE/EA = 50/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38-7.29 (m, 4H), 7.26-7.15 (m, 8H), 7.10 (t, *J* = 4.1 Hz 2H), 3.84 (s, 2H), 3.47 (t, *J* = 7.4Hz, 2H), 2.83 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 201.11, 145.57, 142.14, 141.64, 139.22, 131.58, 130.70, 130.52, 128.87, 128.58, 128.56, 128.47, 128.41, 128.40, 127.07, 127.03, 126.78, 46.59, 36.08, 31.08. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{21}BrClO$ 439.0459; Found 439.0460.



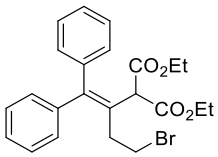
5-bromo-3-(diphenylmethylene)-1-(naphthalen-2-yl)pentan-1-one (7f): The reaction was conducted on 0.2 mmol scale. The product **7f** (40 mg, 44%) as white solid (m.p. 125.8-126.2 °C) was purified by flash column chromatography (PE/EA = 50/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.94 (d, *J* = 8.6 Hz, 1H), 7.86(d, *J* = 8.4 Hz, 3H), 7.59 (d, *J* = 7.5 Hz, 1H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.33-7.27 (m, 4H), 7.26-7.18 (m, 6H), 4.04 (s, 2H), 3.50 (t, *J* = 7.2 Hz, 2H), 2.82 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.38, 144.68, 142.25, 141.88, 135.67, 133.80, 132.45, 130.11, 129.73, 129.58, 129.14, 128.99, 128.60, 128.49, 128.47, 128.39, 127.79, 127.19, 126.97, 126.81, 123.88, 42.59, 35.84, 31.41. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{24}BrO$ 455.1005; Found 455.1006.



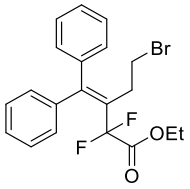
5-bromo-3-(diphenylmethylene)-1-(thiophen-2-yl)pentan-1-one (7g): The reaction was conducted on 0.2 mmol scale. The product **7g** (42.7 mg, 52%) as green oil was purified by flash column chromatography (PE/EA = 50/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63-7.58 (m, 1H), 7.50-7.46 (m, 1H), 7.31 (t, *J* = 7.5 Hz 2H), 7.29-7.18 (m, 8H), 7.08-7.04 (m, 1H), 3.84 (s, 2H), 3.47 (t, *J* = 7.3 Hz, 2H), 2.82 (t, *J* = 7.3 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.06, 144.93, 143.81, 142.09, 141.75, 133.92, 132.21, 129.20, 129.04, 128.90, 128.39, 128.37, 128.09, 127.10, 126.97, 42.94, 35.80, 31.32. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{20}BrOS$ 411.0413; Found 411.0412.



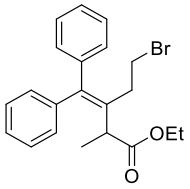
benzyl 5-bromo-3-(diphenylmethylene)pentanoate (7h): The reaction was conducted on 0.2 mmol scale. The product **7h** (46.9 mg, 54%) as white solid (m.p. 69.2-69.8 °C) was purified by flash column chromatography (PE/EA = 50/1); ^{1}H NMR (400 MHz, $CDCl_3$) 7.45-7.16 (m, 15H), 5.17 (s, 2H), 3.45 (t, *J* = 7.5 Hz, 2H), 3.30 (s, 2H), 2.81 (t, *J* = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 145.1, 141.9, 141.7, 135.8, 128.8, 128.6, 128.40, 128.38, 128.34, 128.27, 127.1, 127.0, 66.6, 37.9, 35.9, 30.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{24}BrO_2$ 435.0954; Found 435.0953.



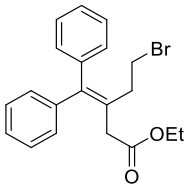
diethyl 2-(4-bromo-1,1-diphenylbut-1-en-2-yl)malonate (7i): The reaction was conducted on 0.2 mmol scale. The product **7i** (66.7 mg, 75%) as colorless oil was purified by flash column chromatography (PE/EA = 50/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37-7.20 (m, 8H), 7.15 (d, *J* = 7.5 Hz, 2H), 4.47 (s, 1H), 4.22 (q, *J* = 7.1 Hz, 4H), 3.26 (t, *J* = 8.3 Hz, 2H), 2.91 (t, *J* = 8.9 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.4, 147.8, 141.4, 141.3, 128.7, 128.6, 128.5, 128.4, 128.3, 127.5, 61.8, 56.2, 35.0, 30.2, 14.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{26}BrO_4$ 445.1014; Found 445.1010.



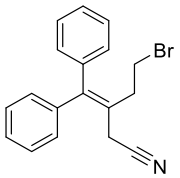
ethyl 5-bromo-3-(diphenylmethylene)-2,2-difluoropentanoate (7j): The reaction was conducted on 0.2 mmol scale. The product **7j** (57.2 mg, 70%) as white oil was purified by flash column chromatography (PE/EA = 50/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.4 Hz, 2H), 7.30-7.24 (m, 4H), 7.18-7.13 (m, 4H), 3.79-3.74 (m, 2H), 3.49 (t, *J* = 7.8 Hz, 2H), 2.92 (t, *J* = 7.8 Hz, 2H), 1.14 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.41, 163.19, 162.97, 150.77, 150.72, 150.67, 140.91, 138.98, 129.51, 129.20, 129.04, 128.88, 128.82, 128.62, 128.40, 128.31, 128.07, 127.98, 127.94, 127.18, 115.52, 113.87, 112.22, 62.75, 33.12, 33.10, 30.58, 10.57. ^{19}F NMR (376 MHz, $CDCl_3$) δ -91.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{20}BrF_2O_2$ 409.0609; Found 409.0608.



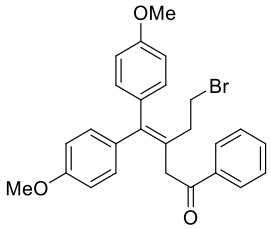
ethyl 5-bromo-3-(diphenylmethylene)-2-methylpentanoate (7k): The reaction was conducted on 0.2 mmol scale. The product **7k** (52.6 mg, 68%) as light yellow solid (m.p. 41.2-41.8 ºC) was purified by flash column chromatography (PE/EA = 50/1); ^{1}H NMR (400 MHz, $CDCl_3$) 7.38-7.20 (m, 10H), 4.24-4.14 (m, 2H), 3.62 (q, *J* = 7.1 Hz, 1H), 3.28-3.14 (m, 2H), 2.77 (t, *J* = 8.5 Hz, 2H), 1.37-1.27 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 144.1, 142.1, 141.9, 134.6, 128.7, 128.6, 128.42, 128.39, 127.1, 127.0, 60.8, 43.3, 33.6, 30.4, 15.8, 14.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{24}BrO_2$ 387.0954; Found 387.0955.



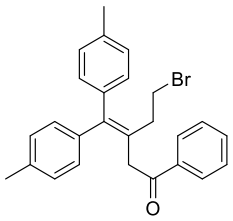
ethyl 5-bromo-3-(diphenylmethylene)pentanoate (7l): The reaction was conducted on 0.2 mmol scale. The product **7l** (55.9 mg, 75%) as colorless oil was purified by flash column chromatography (PE/EA = 50/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34-7.25 (m, 4H), 7.25-7.17 (m, 6H), 4.16-4.12 (m, 2H), 3.44 (t, *J* = 7.5 Hz, 2H), 3.21 (s, 2H), 2.79 (t, *J* = 7.5 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.58, 144.83, 141.94, 141.73, 128.83, 128.48, 128.36, 128.29, 126.99, 126.96, 60.75, 37.93, 35.98, 30.76, 14.20. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{22}BrO_2$ 373.0798; Found 373.0797.



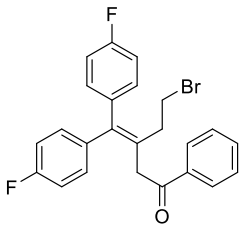
5-bromo-3-(diphenylmethylene)pentanenitrile (7m): The reaction was conducted on 0.2 mmol scale. The product **7m** (57.4 mg, 88%) as light yellow solid (m.p. 58.0-58.5 ºC) was purified by flash column chromatography (PE/EA = 50/1); ^{1}H NMR (600 MHz, $CDCl_3$) 7.37-7.31 (m, 4H), 7.30-7.25 (m, 2H), 7.17 (d, *J* = 7.3 Hz, 4H), 3.50 (t, *J* = 7.1Hz, 2H), 3.27 (s, 2H), 2.02 (t, *J* = 7.1 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.60, 140.83, 140.62, 128.77, 128.66, 128.60, 128.54, 127.77, 127.51, 124.33, 117.76, 34.63, 30.15, 21.31. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{17}BrN$ 326.0539; Found 326.0537.



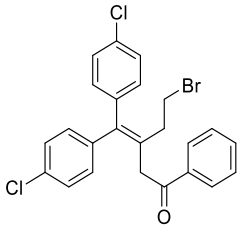
3-(bis(4-methoxyphenyl)methylene)-5-bromo-1-phenylpentan-1-one (7n): The reaction was conducted on 0.2 mmol scale. The product **7n** (51.1 mg, 55%) as green solid (m.p. 121.5-121.8 ºC) was purified by flash column chromatography (PE/EA = 50/1); ^{1}H NMR (600 MHz, $CDCl_3$) 7.83 (t, *J* = 4.2 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.12-7.04 (m, 4H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 3.91 (s, 2H), 3.79 (s, 3H), 3.74 (s, 3H), 3.45 (t, *J* = 7.4 Hz, 2H), 2.80 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.66, 158.56, 158.46, 143.88, 136.64, 134.97, 134.60, 133.22, 130.31, 130.10, 128.77, 128.58, 128.22, 113.71, 55.22, 55.20, 42.86, 36.17, 31.52. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{26}BrO_3$ 465.1060; Found 465.1061.



5-bromo-3-(di-p-tolylmethylene)-1-phenylpentan-1-one (7o): The reaction was conducted on 0.2 mmol scale. The product **7o** (60.6 mg, 70%) as deep green solid (m.p. 116.3-116.8 ºC) was purified by flash column chromatography (PE/EA = 50/1); ^{1}H NMR (600 MHz, $CDCl_3$) 7.83 (d, *J* = 7.7 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.13-7.02 (m, 8H), 3.90 (s, 2H), 3.44 (t, *J* = 7.4 Hz, 2H), 2.79 (t, *J* = 7.4 Hz, 2H), 2.32 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.59, 144.60, 139.49, 139.16, 136.65, 136.49, 133.19, 129.04, 128.95, 128.71, 128.56, 128.23, 42.76, 36.11, 31.47, 21.19, 21.14. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{26}BrO$ 433.1162; Found 433.1164.

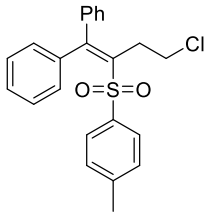


3-(bis(4-fluorophenyl)methylene)-5-bromo-1-phenylpentan-1-one (7p): The reaction was conducted on 0.2 mmol scale. The product **7p** (44.1 mg, 50%) as Green oil was purified by flash column chromatography (PE/EA = 50/1); ^{1}H NMR (600 MHz, $CDCl_3$) 7.83 (d, *J* = 7.7 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.20-7.09 (m, 4H), 7.04-6.90 (m, 4H), 3.88 (s, 2H), 3.44 (t, *J* = 7.2 Hz, 2H), 2.80 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.09, 162.72, 162.67, 161.09, 161.04, 142.68, 138.00, 137.98, 137.60, 137.58, 136.48, 133.44, 130.78, 130.72, 130.50, 130.47, 130.42, 128.69, 128.11, 115.50, 115.36, 42.22, 35.91, 31.08. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.7, -145.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{20}BrF_2O$ 441.0660; Found 441.0656.

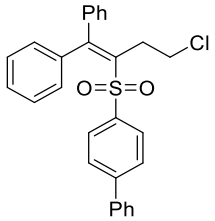


3-(bis(4-chlorophenyl)methylene)-5-bromo-1-phenylpentan-1-one (7q): The reaction was conducted on 0.2 mmol scale. The product **7q** (45.5 mg, 48%) as white solid (m.p. 132.1-132.6 ºC) was purified by flash column chromatography (PE/EA = 50/1); ^{1}H NMR (600 MHz, $CDCl_3$) 7.83 (d, *J* = 7.9 Hz, 2H), 7.57 (t, *J* = 7.1 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 2H), 7.33-7.21 (m, 4H), 7.17-7.06 (m, 4H), 3.88 (s,

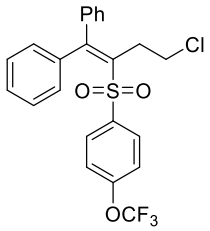
2H), 3.43 (t, J = 7.1 Hz, 2H), 2.80 (t, J = 7.1 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.87, 142.40, 140.19, 139.82, 136.42, 133.49, 133.30, 133.18, 130.98, 130.52, 130.16, 128.74, 128.71, 128.11, 42.11, 35.86, 30.94. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{20}BrCl_2O$ 473.0669; Found 473.0068.



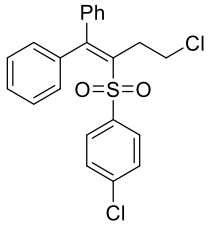
(4-chloro-2-tosylbut-1-ene-1,1-diyl)dibenzene (8a): The reaction was conducted on 0.2 mmol scale. The product **8a** (73.0 mg, 92%) as colorless solid (m.p. 106.4-107.2 ºC) was purified by flash column chromatography (PE/EA = 25/1); ^{1}H NMR (400 MHz, $CDCl_3$) 7.38-7.27 (m, 5H), 7.20 (t, J = 7.0 Hz, 1H), 7.15-7.05 (m, 6H), 6.97 (d, J = 7.8 Hz, 2H), 3.86 (t, J = 7.3 Hz, 2H), 3.13 (t, J = 7.3 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 143.5, 140.7, 139.3, 139.0, 138.1, 129.2, 129.1, 128.8, 128.5, 128.1, 127.8, 127.7, 127.6, 43.2, 34.0, 21.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{22}ClO_2S$ 397.1024; Found 397.1028.



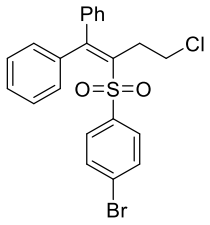
4-((4-chloro-1,1-diphenylbut-1-en-2-yl)sulfonyl)-1,1'-biphenyl (8b): The reaction was conducted on 0.2 mmol scale. The product **8b** (64.3mg, 70%) as light-yellow solid (m.p. 120.1-121.1 ºC) was purified by flash column chromatography (PE/EA = 25/1); ^{1}H NMR (400 MHz, $CDCl_3$) 7.60-7.42 (m, 9H), 7.40-7.28 (m, 3H), 7.22 (t, J = 7.3 Hz, 1H), 7.18-7.08 (m, 4H), 6.99 (d, J = 7.6 Hz, 2H), 3.93 (t, J = 7.0 Hz, 2H), 3.23 (t, J = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 145.4, 140.6, 139.6, 139.4, 139.4, 138.9, 129.2, 129.1, 128.8, 128.6, 128.5, 128.1, 128.0, 127.9, 127.8, 127.3, 127.1, 43.2, 33.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{24}ClO_2S$ 459.1180; Found 459.1186.



(4-chloro-2-((4-(trifluoromethoxy)phenyl)sulfonyl)but-1-ene-1,1-diyl)dibenzene (8c): The reaction was conducted on 0.2 mmol scale. The product **8c** (71.9 mg, 77%) as light-yellow solid (m.p. 108.1-108.7 °C) was purified by flash column chromatography (PE/EA = 25/1); ^{1}H NMR (400 MHz, $CDCl_3$) 7.43 (d, *J* = 8.4 Hz, 2H), 7.39-7.29 (m, 3H), 7.20 (t, *J* = 7.2 Hz, 1H), 7.19-7.00 (m, 6H), 6.92 (d, *J* = 7.8 Hz, 2H), 3.91 (t, *J* = 7.0 Hz, 2H), 3.24 (t, *J* = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 151.6, 140.1, 139.2, 139.1, 138.5, 129.3, 129.1, 128.6, 128.5, 128.1, 127.7, 127.7, 120.2, 120.0 (q, *J* = 365.0, 257.7 Hz), 42.9, 33.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{19}ClF_3O_3S$ 467.0690; Found 467.0695.

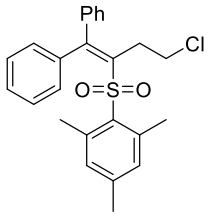


(4-chloro-2-((4-chlorophenyl)sulfonyl)but-1-ene-1,1-diyl)dibenzene (8d): The reaction was conducted on 0.2 mmol scale. The product **8d** (52.6 mg, 63%) as colorless solid (m.p. 175.1-176.2 °C) was purified by flash column chromatography (PE/EA = 25/1); ^{1}H NMR (400 MHz, $CDCl_3$) 7.40-7.28 (m, 5H), 7.22 (d, *J* = 8.1 Hz, 3H), 7.17-7.08 (m, 4H), 6.94 (d, *J* = 7.8 Hz, 2H), 3.88 (t, *J* = 7.0 Hz, 2H), 3.19 (t, *J* = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 140.4, 139.6, 139.2, 139.1, 138.7, 129.3, 128.9, 128.8, 128.7, 128.6, 128.3, 127.9, 127.8, 43.1, 33.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{19}Cl_2O_2S$ 417.0477; Found 417.0485.

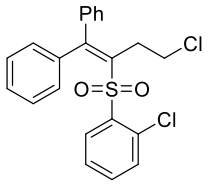


(2-((4-bromophenyl)sulfonyl)-4-chlorobut-1-ene-1,1-diyl)dibenzene (8e): The reaction was conducted on 0.2 mmol scale. The product **8e** (69.3 mg, 75%) as yellow solid (m.p. 123.1-124.2 °C) was purified by flash column chromatography (PE/EA = 25/1); ^{1}H NMR (400 MHz, $CDCl_3$) 7.43-7.29 (m,

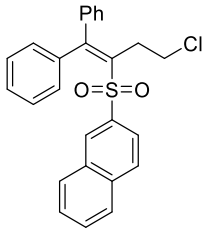
5H), 7.28-7.19 (m, 3H), 7.18-7.08 (m, 4H), 6.94 (d, *J* = 7.7 Hz, 2H), 3.88 (t, *J* = 7.1 Hz, 2H), 3.19 (t, *J* = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 140.2, 140.0, 139.0, 138.6, 131.5, 129.1, 128.8, 128.7, 128.5, 128.2, 127.7, 127.7, 127.6, 43.0, 33.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{18}Cl_2O_2S$ 460.9972; Found 460.9974.



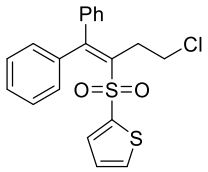
(4-chloro-2-(mesitylsulfonyl)but-1-ene-1,1-diyl)dibenzene (8f): The reaction was conducted on 0.2 mmol scale. The product **8f** (64.6 mg, 76%) as colorless solid (m.p. 136.5-137.1 °C) was purified by flash column chromatography (PE/EA = 25/1); ^{1}H NMR (400 MHz, $CDCl_3$) 7.40-7.27 (m, 3H), 7.14 (d, *J* = 7.4 Hz, 2H), 7.11-6.99 (m, 3H), 6.95 (d, *J* = 7.6 Hz, 2H), 6.68 (s, 2H), 3.84 (t, *J* = 7.3 Hz, 2H), 3.19 (t, *J* = 7.3 Hz, 2H), 2.49 (s, 6H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7, 142.4, 140.7, 140.3, 138.9, 138.9, 138.6, 135.0, 131.8, 128.8, 128.3, 128.0, 127.8, 127.7, 42.8, 33.3, 22.3, 22.3, 20.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{26}ClO_2S$ 425.1337; Found 425.1341.



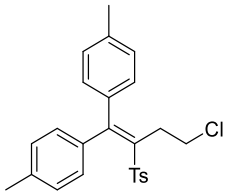
(4-chloro-2-((2-chlorophenyl)sulfonyl)but-1-ene-1,1-diyl)dibenzene (8g): The reaction was conducted on 0.2 mmol scale. The product **8g** (64.3 mg, 77%) as yellow solid (m.p. 105.2-106.1 °C) was purified by flash column chromatography (PE/EA = 25/1);; ^{1}H NMR (400 MHz, $CDCl_3$) 7.41-7.31 (m, 4H), 7.31-7.25 (m, 1H), 7.20 (t, *J* = 7.7 Hz, 3H), 7.06 (t, *J* = 6.9 Hz, 1H), 7.00-6.87 (m, 5H) 3.89 (t, *J* = 7.0 Hz, 2H), 3.34 (t, *J* = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 140.1, 138.4, 138.0, 137.9, 133.0, 131.1, 130.5, 130.3, 128.7, 128.4, 128.2, 127.9, 127.7, 127.3, 126.4, 42.7, 33.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{19}Cl_2O_2S$ 417.0477; Found 417.0477.



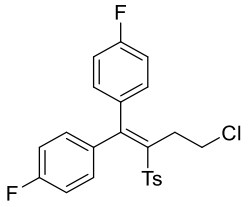
2-((4-chloro-1,1-diphenylbut-1-en-2-yl)sulfonyl)naphthalene (8h): The reaction was conducted on 0.2 mmol scale. The product **8h** (60.6 mg, 70%) as yellow solid (m.p. 126.6-127.4 ºC) was purified by flash column chromatography (PE/EA = 25/1); ^{1}H NMR (400 MHz, $CDCl_3$) 7.90-7.76 (m, 3H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.65-7.52 (m, 3H), 7.27-7.37 (m, 3H), 7.12 (d, *J* = 7.3 Hz, 2H), 7.05-6.99 (m, 1H), 6.98-6.86 (m, 4H), 3.93 (t, *J* = 7.1 Hz, 2H), 3.17 (t, *J* = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 140.7, 139.2, 138.6, 137.5, 134.7, 131.8, 130.0, 129.5, 129.1, 129.0, 128.9, 128.8, 128.6, 128.4, 127.9, 127.8, 127.6, 127.4, 122.2, 43.3, 34.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{22}ClO_2S$ 433.1024; Found 433.1029.



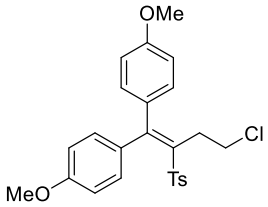
2-((4-chloro-1,1-diphenylbut-1-en-2-yl)sulfonyl)thiophene (8i): The reaction was conducted on 0.2 mmol scale. The product **8i** (68.5 mg, 88%) as white solid (m.p. 120.1-121.1 ºC) was purified by flash column chromatography (PE/EA = 25/1); ^{1}H NMR (400 MHz, $CDCl_3$) 7.55 (d, *J* = 5.0 Hz, 1H), 7.40-7.18 (m, 6H), 7.18-7.06 (m, 4H), 6.82 (t, J = 4.3 Hz, 1H), 3.82 (t, *J* = 7.3 Hz, 2H), 3.14 (t, *J* = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 142.0, 140.7, 139.3, 138.9, 134.5, 133.5, 128.9, 128.8, 128.6, 128.3, 127.9, 127.8, 127.0, 43.1, 34.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{18}ClO_2S_2$ 389.0431; Found 389.0434.



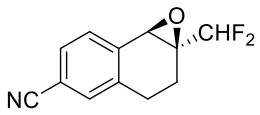
4,4'-(4-chloro-2-tosylbut-1-ene-1,1-diyl)bis(methylbenzene) (8j): The reaction was conducted on 0.2 mmol scale. The product **8j** (67.2 mg, 79%) as white solid (m.p. 112.0-112.8 ºC) was purified by flash column chromatography (PE/EA = 25/1); ^{1}H NMR (400 MHz, $CDCl_3$) 7.32 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 7.7 Hz, 2H), 7.06 (d, *J* = 7.9 Hz, 2H), 6.96 (d, *J* = 7.6 Hz, 2H), 6.91 (d, *J* = 7.8 Hz, 2H), 6.83 (d, *J* = 7.7 Hz, 2H), 3.81 (t, *J* = 7.3 Hz, 2H), 3.10 (t, *J* = 7.3 Hz, 2H), 2.35 (s, 3H), 2.31 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 143.7, 138.74, 138.67, 138.5, 138.4, 138.3, 136.7, 129.7, 129.5, 129.3, 128.6, 128.2, 127.9, 43.5, 34.4, 21.9, 21.7, 21.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{26}ClO_2S$ 425.1337; Found 425.1346.



4,4'-(4-chloro-2-tosylbut-1-ene-1,1-diyl)bis(fluorobenzene) (8k): The reaction was conducted on 0.2 mmol scale. The product **8k** (51.1 mg, 59%) as light yellow solid (m.p. 117.6-118.5 °C) was purified by flash column chromatography (PE/EA = 25/1); ^{1}H NMR (400 MHz, $CDCl_3$) 7.30 (d, *J* = 7.8 Hz, 2H), 7.13-6.97 (m, 6H), 6.93 (t, *J* = 6.6 Hz, 2H), 6.80 (t, *J* = 8.3 Hz, 2H), 3.84 (t, *J* = 6.9 Hz, 2H), 3.12 (t, *J* = 6.9 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0 (d, *J* = 4.6 Hz), 161.5 (d, *J* = 5.0 Hz), 153.0, 143.9, 140.2, 138.0, 136.6 (d, *J* = 3.4 Hz), 134.9 (d, *J* = 3.4 Hz), 131.4 (d, *J* = 8.4 Hz), 130.2 (d, *J* = 8.3 Hz), 129.2, 127.5, 116.0 (d, *J* = 21.7 Hz), 114.9 (d, *J* = 21.6 Hz), 43.3, 34.0, 21.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.0, -112.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{20}ClF_2O_2S$ 433.0835; Found 433.0844.

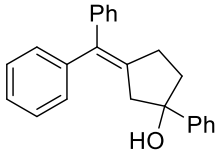


4,4'-(4-chloro-2-tosylbut-1-ene-1,1-diyl)bis(methoxybenzene) (8l): The reaction was conducted on 0.2 mmol scale. The product **8l** (90.5 mg, 99%) as yellow oil was purified by flash column chromatography (PE/EA = 25/1); ^{1}H NMR (400 MHz, $CDCl_3$) 7.34 (d, *J* = 7.7 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 6.99 (d, *J* = 8.1 Hz, 2H), 6.92-6.80 (m, 4H), 6.64 (d, *J* = 8.0 Hz, 2H), 3.85 (t, *J* = 7.2 Hz, 2H), 3.79 (s, 6H), 3.17 (t, *J* = 7.2 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 159.8, 154.9, 143.2, 138.4, 137.7, 133.3, 131.8, 131.3, 129.9, 129.0, 127.4, 114.0, 113.0, 55.3, 55.3, 43.4, 34.2, 21.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{26}ClO_4S$ 457.1235; Found 457.1238.

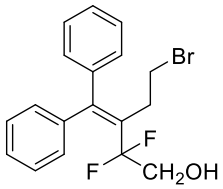


(1aS,7bR)-1a-(difluoromethyl)-1a,2,3,7b-tetrahydronaphtho[1,2-b]oxirene-5-carbonitrile (10): The reaction was conducted on 0.2 mmol scale. The product **10** (21.2 mg, 48%) as colorless oil was purified by flash column chromatography (PE/EA = 50/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.49 (m, 2H),7.43 (s, 1H), 5.78 (t, *J* = 110.0 Hz, 1H), 4.01 (s, 1H), 2.93-2.81 (m, 1H), 2.77-2.68 (s, 1H), 2.56-2.45 (m, 1H), 2.04-1.93 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 135.7, 131.9, 130.4, 130.3, 118.4, 114.9 (t, *J* = 485.3 Hz), 113.0, 62.0 (t, *J* = 57.6 Hz), 54.5 (t, *J* = 8.0 Hz), 24.3, 18.0. ^{19}F NMR (376 MHz,

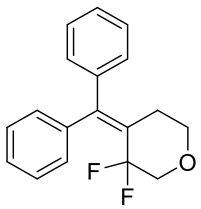
$CDCl_3$) δ -125.1 (d, J = 406.1 Hz), -125.9 (d, J = 406.1 Hz). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{10}F_2NO$ 222.0725; Found 222.0724.



3-(diphenylmethylene)-1-phenylcyclopentan-1-ol (11): The reaction was conducted on 1 mmol scale. The product **11** (218.4 mg, 67%) as light-yellow oil was purified by flash column chromatography (PE/EA = 50/1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 7.7 Hz, 2H), 7.44-7.20 (m, 13H), 3.10-2.91 (m, 2H) 2.86-2.77 (m, 1H) 2.65-2.55 (m, 1H) 2.32-2.11 (m, 2H), 1.79 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8, 142.9, 142.8, 140.2, 135.2, 129.23, 129.18, 128.4, 128.1, 127.3, 126.37, 126.36, 125.2, 82.1, 48.5, 40.3, 30.9.

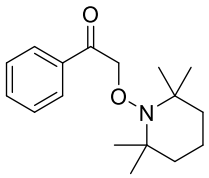


5-bromo-3-(diphenylmethylene)-2,2-difluoropentan-1-ol (12): The reaction was conducted on 1.5 mmol scale. The product **12** (334.9 mg, 61%) as colorless oil was purified by flash column chromatography (PE/EA = 50/1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.43-7.21 (m, 10H), 3.62-3.46 (m, 4H), 2.87 (t, J = 15.6 Hz, 2H), 2.19 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9 (t, J = 13.5 Hz), 141.8, 140.8, 130.0 (t, J = 46.2 Hz), 128.8, 128.23, 128.20, 127.73, 127.70, 127.68, 121.7 (t, J = 486.7 Hz), 64.5 (t, J = 62.0 Hz), 34.0, 31.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -95.9 Hz. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{18}H_{17}OBrF_2$ 366.0425; Found 366.0430.



4-(diphenylmethylene)-3,3-difluorotetrahydro-2H-pyran (13): The reaction was conducted on 0.2 mmol scale. The product **13** (48 mg, 84%) as colorless oil was purified by flash column chromatography (PE/EA = 50/1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.41-7.12 (m, 10H), 3.87-3.77 (m, 4H), 2.61 (t, J = 10.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8 (t, J = 6.3 Hz), 141.6, 141.4, 128.8 (t, J = 5.8 Hz), 128.76, 128.5, 127.6, 127.5, 127.5, 127.24, 127.19 (t, J = 36.3 Hz), 116.8 (t, J = 495.9 Hz), 72.1 (t, J = 66.8 Hz),

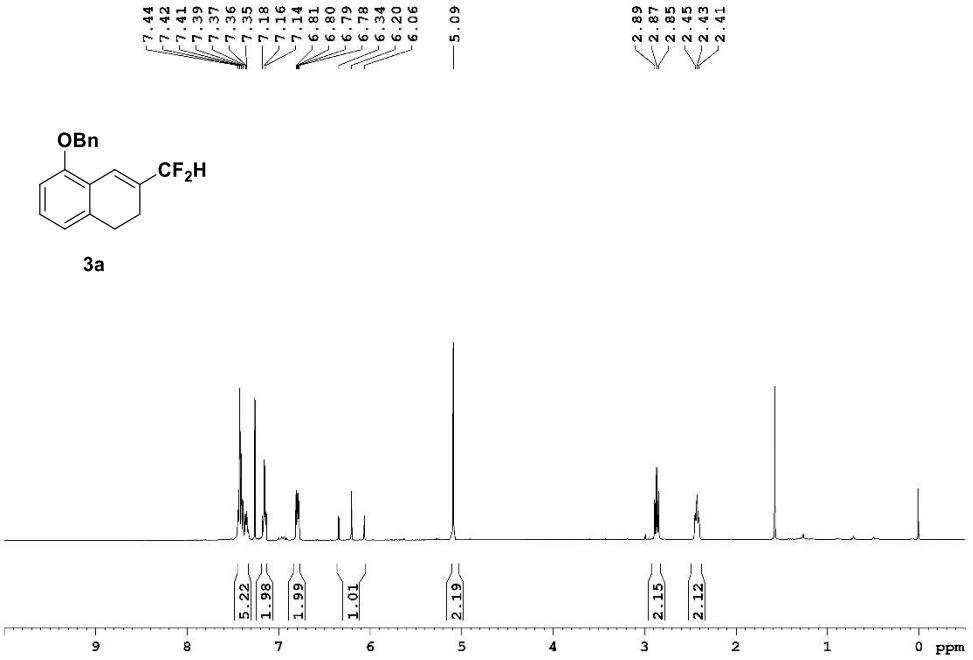
68.8, 31.4 (t, J = 3.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -100.5 Hz. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{17}F_2O$ 287.1242; Found 287.1276.

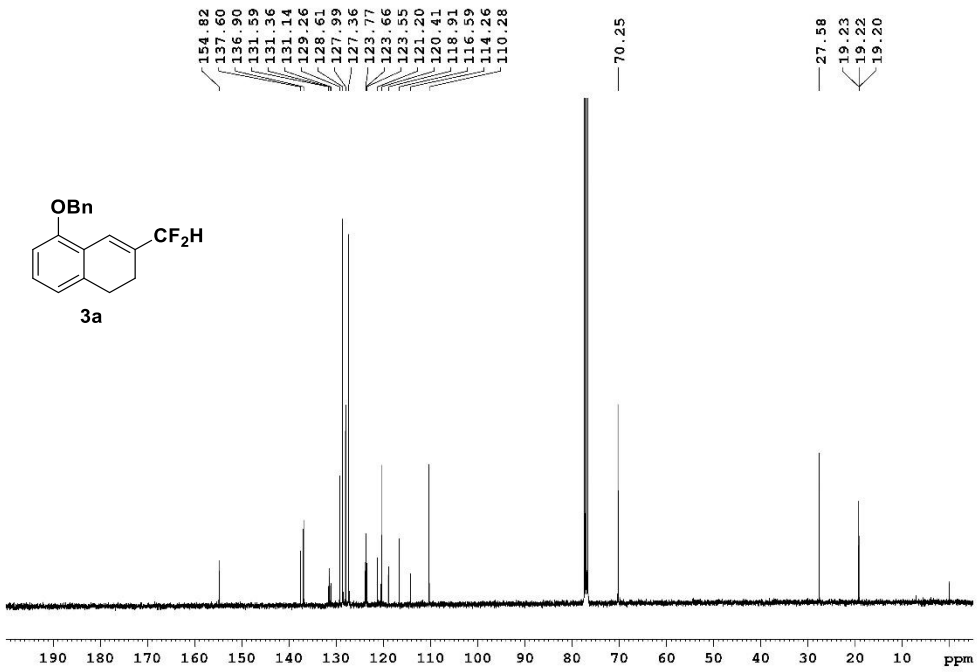


1-phenyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethan-1-one (14)[6]: The reaction was conducted on 0.2 mmol scale. The product **14** (40.7 mg, 74%) as colorless oil was purified by flash column chromatography (PE/EA = 50/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, J = 7.74 Hz, 2H), 7.55 (t, J = 14.7 Hz, 1H), 7.45 (t, J = 15.2 Hz, 2H), 5.11 (s, 2H), 1.50-1.43 (m, 4H), 1.37-1.21 (m, 2H), 1.17 (s, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.7, 135.6, 133.2, 128.6, 128.0, 81.4, 60.1, 39.8, 32.8, 20.3, 17.1.

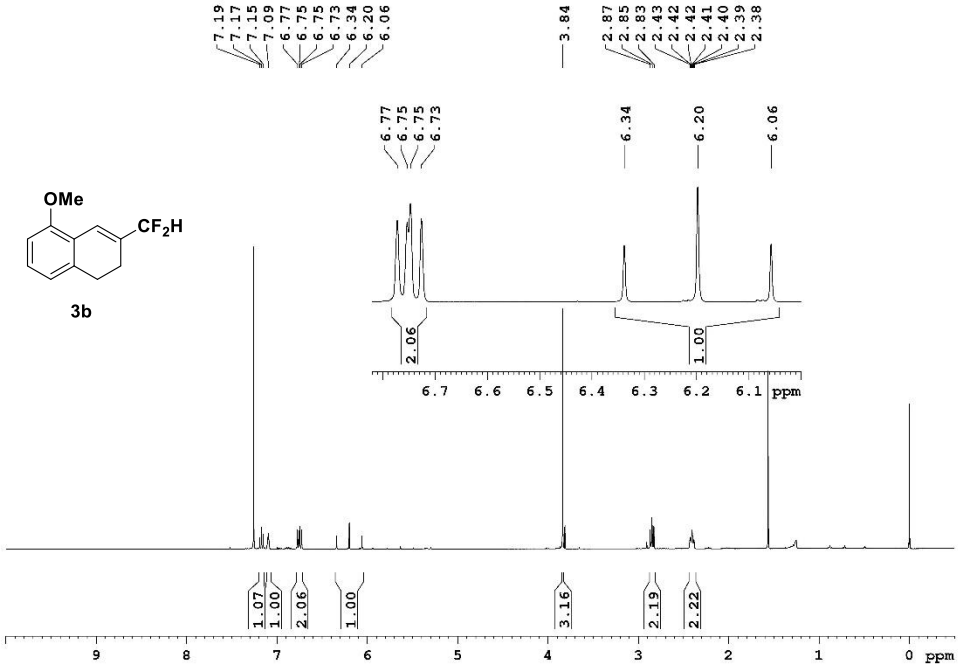
8. ^{1}H NMR, ^{13}C NMR, ^{19}F NMR Spectra

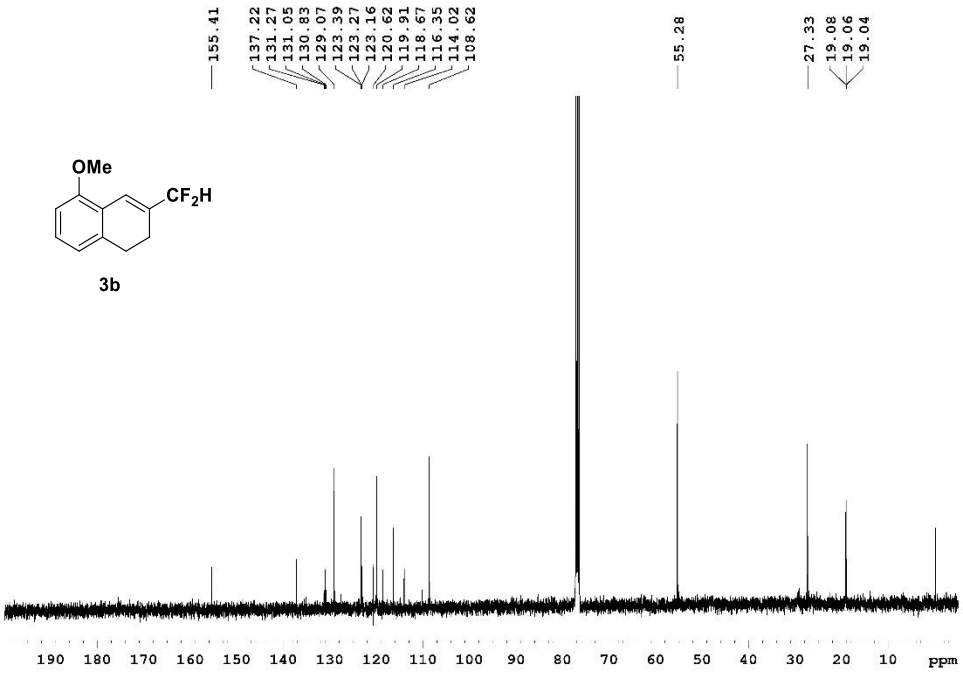
5-(benzyloxy)-3-(difluoromethyl)-1,2-dihydronaphthalene (3a)



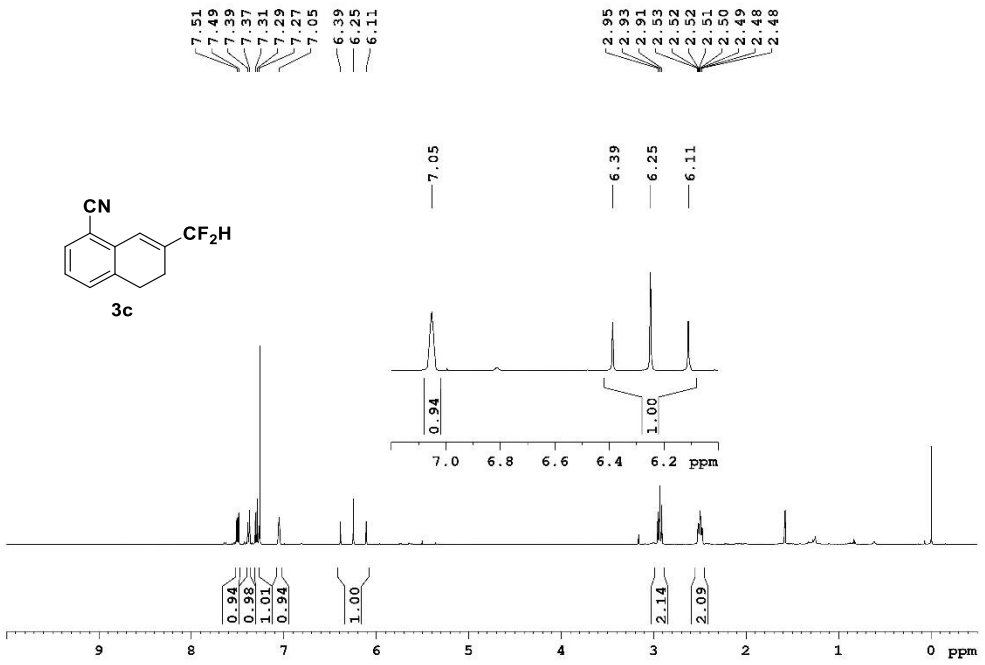


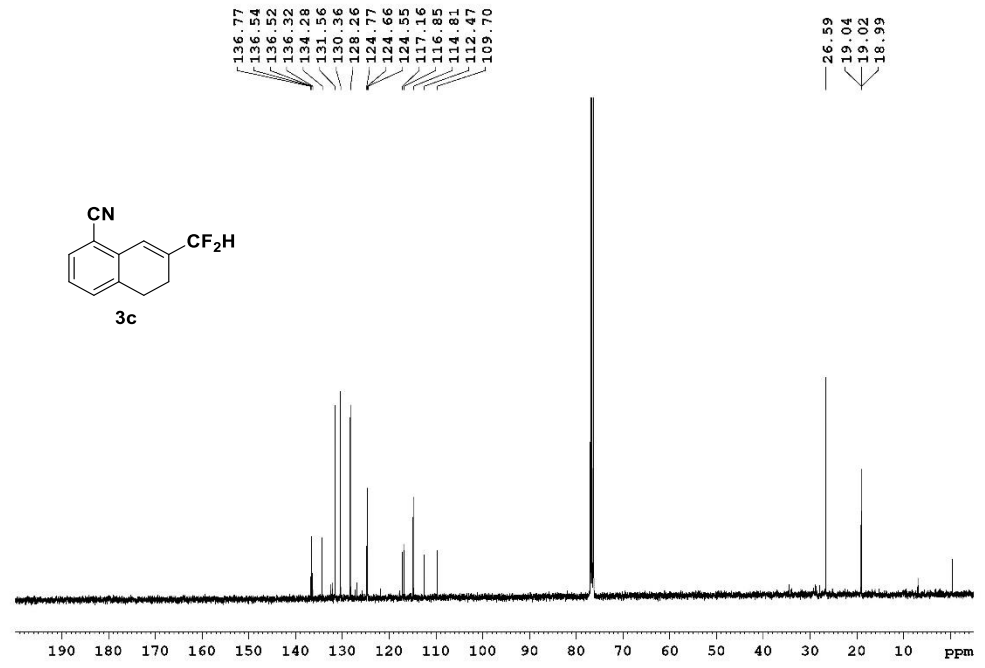
3-(difluoromethyl)-5-methoxy-1,2-dihydronaphthalene (3b)



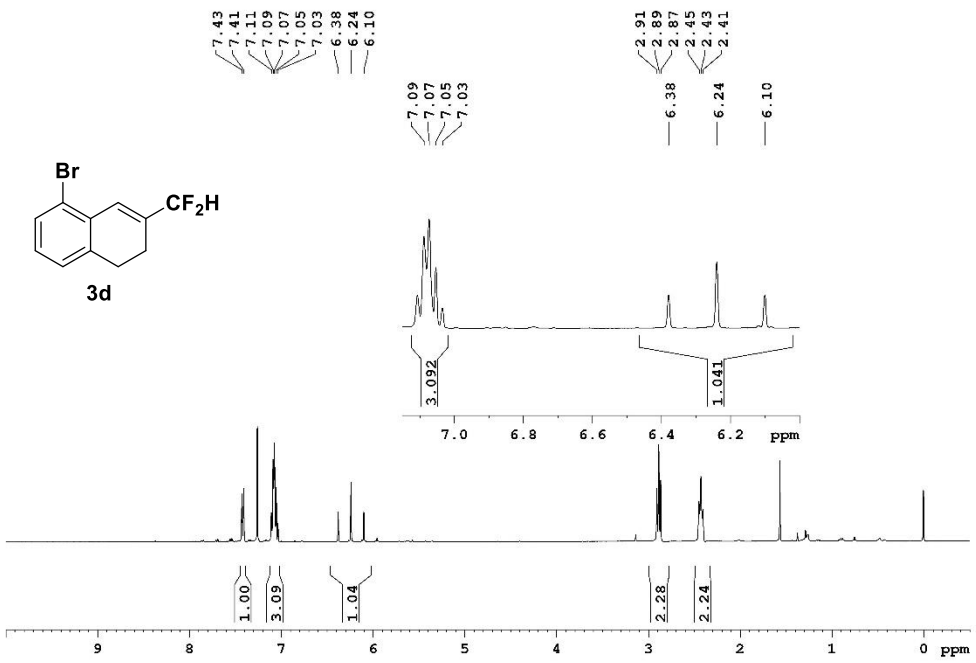


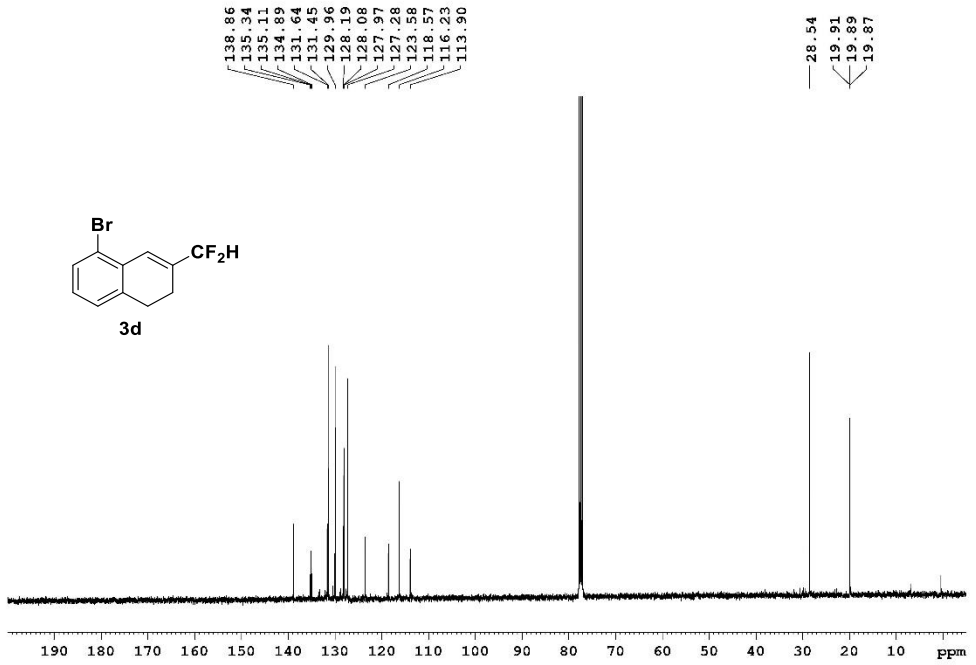
7-(difluoromethyl)-5,6-dihydronaphthalene-1-carbonitrile (3c)



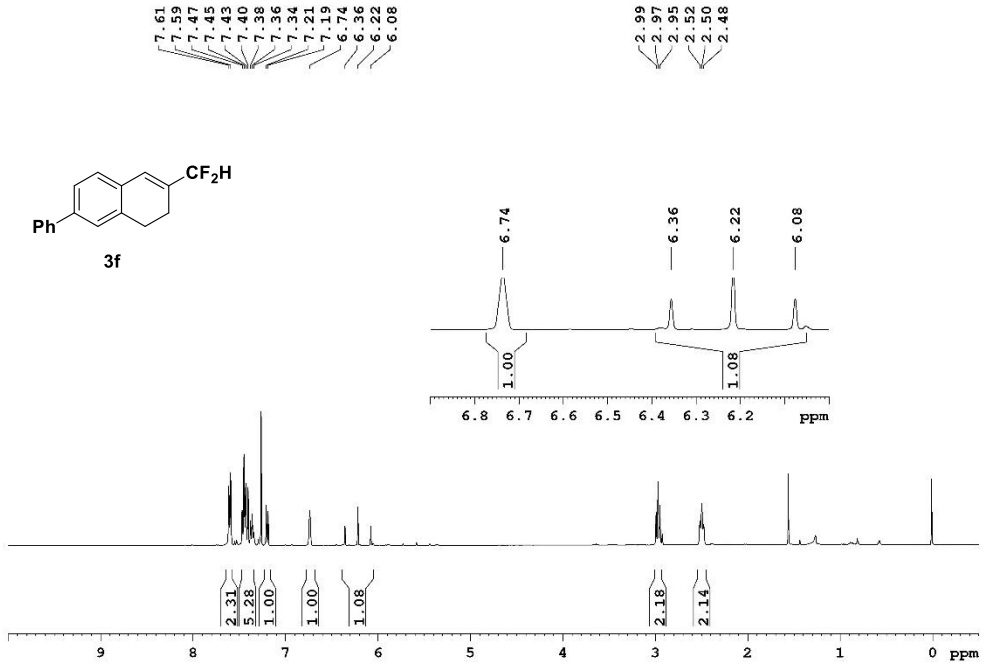


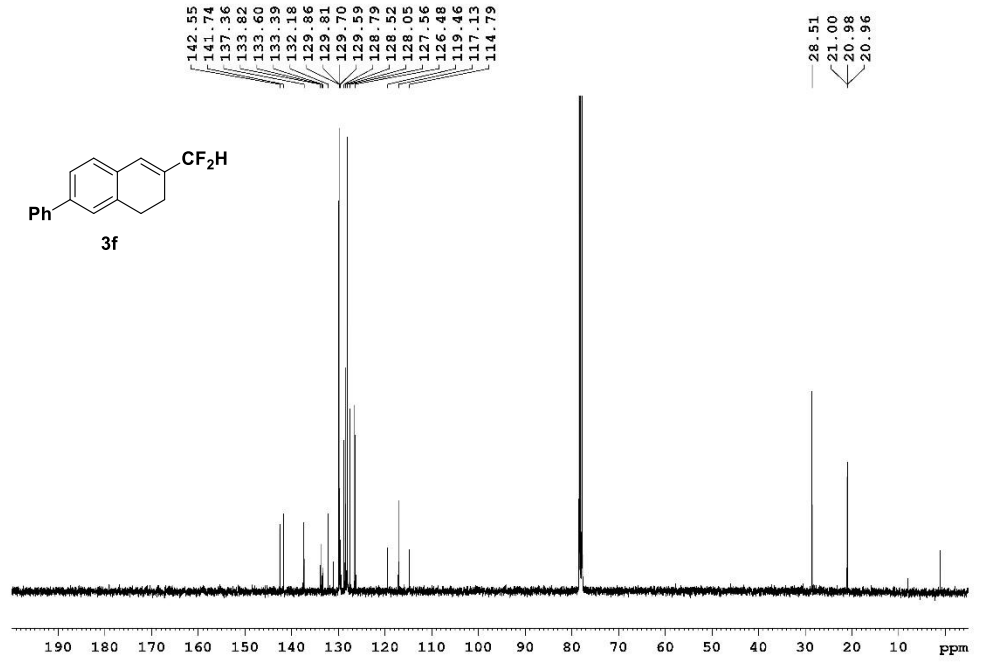
5-bromo-3-(difluoromethyl)-1,2-dihydronaphthalene (3d)



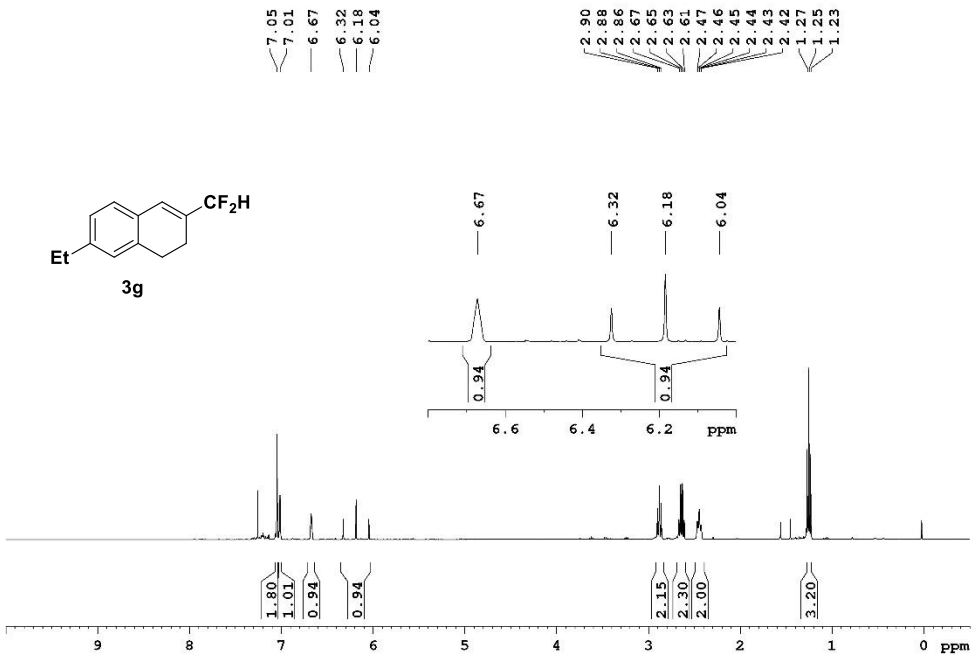


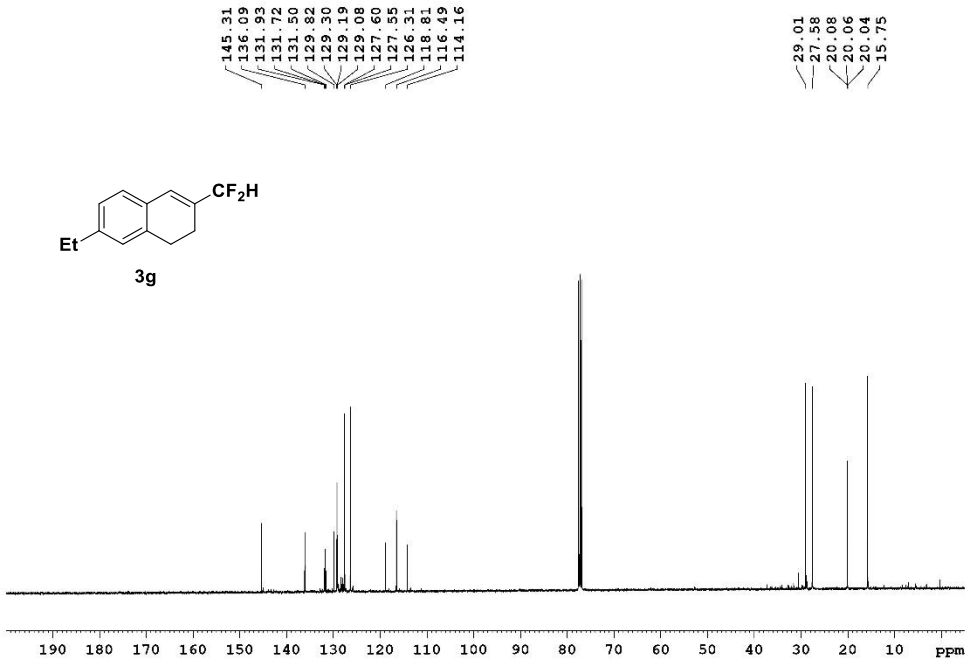
3-(difluoromethyl)-7-phenyl-1,2-dihydronaphthalene (3f)



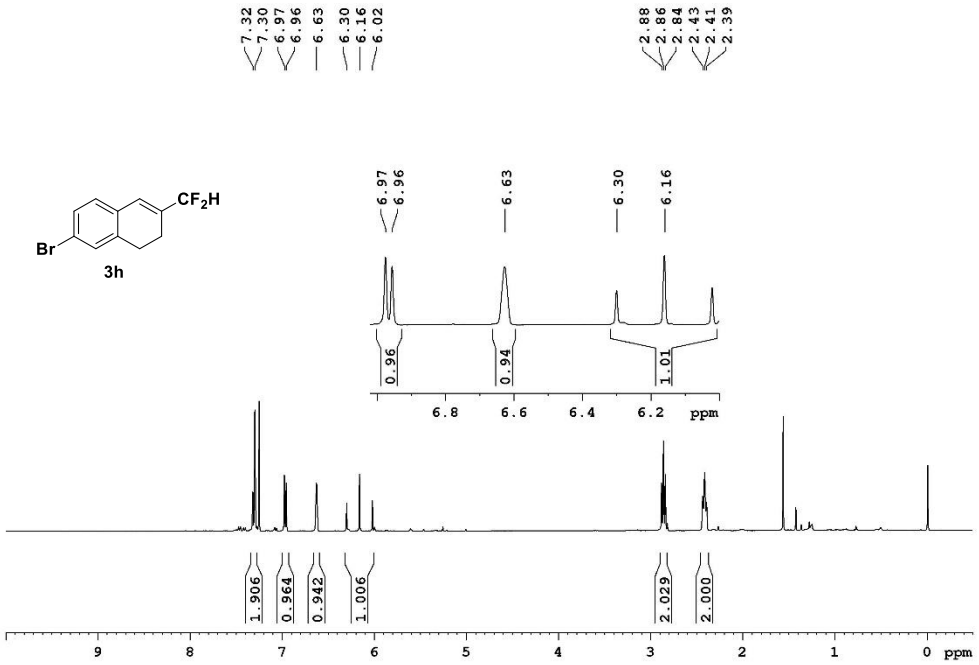


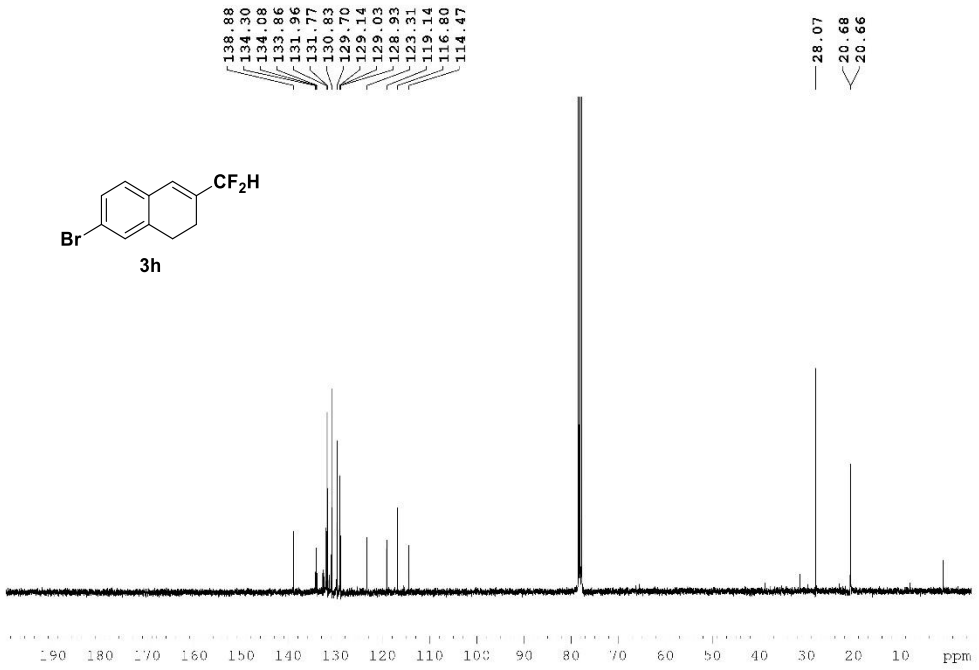
3-(difluoromethyl)-7-ethyl-1,2-dihydronaphthalene (3g)



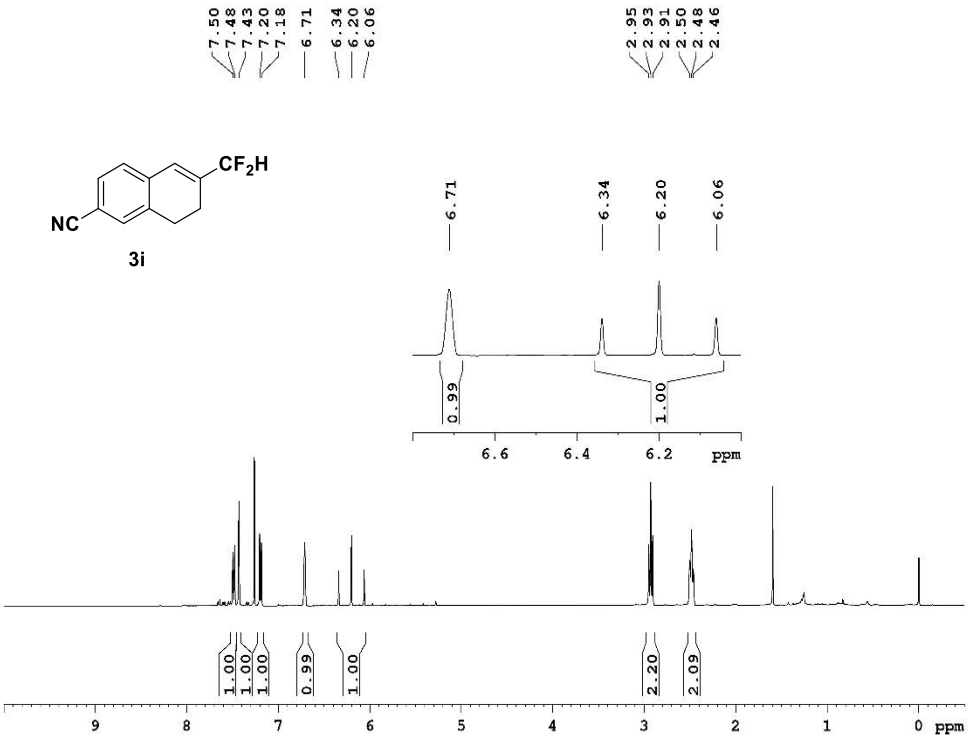


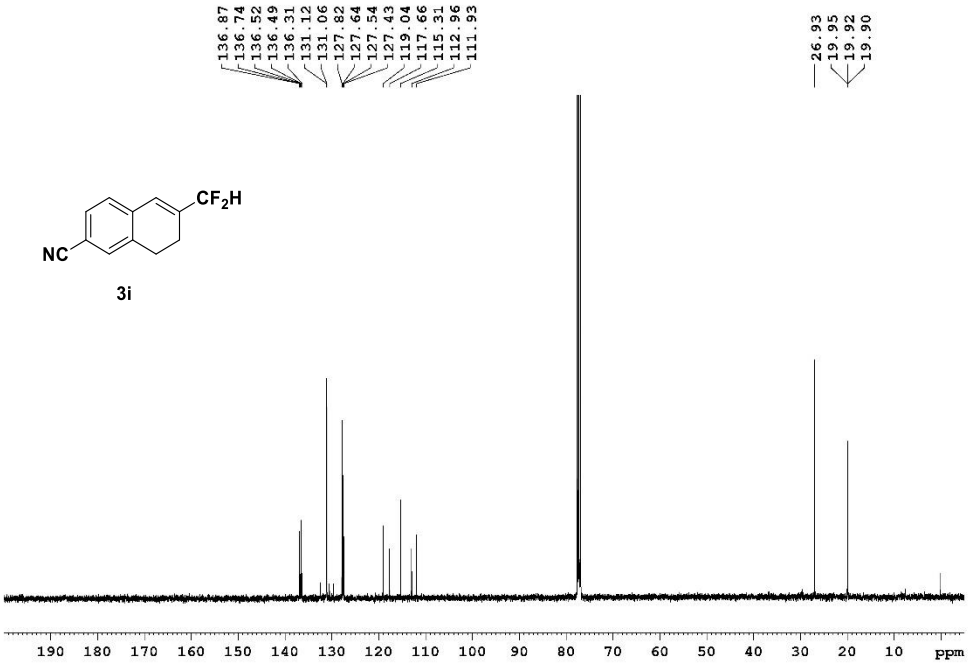
7-bromo-3-(difluoromethyl)-1,2-dihydronaphthalene (3h)



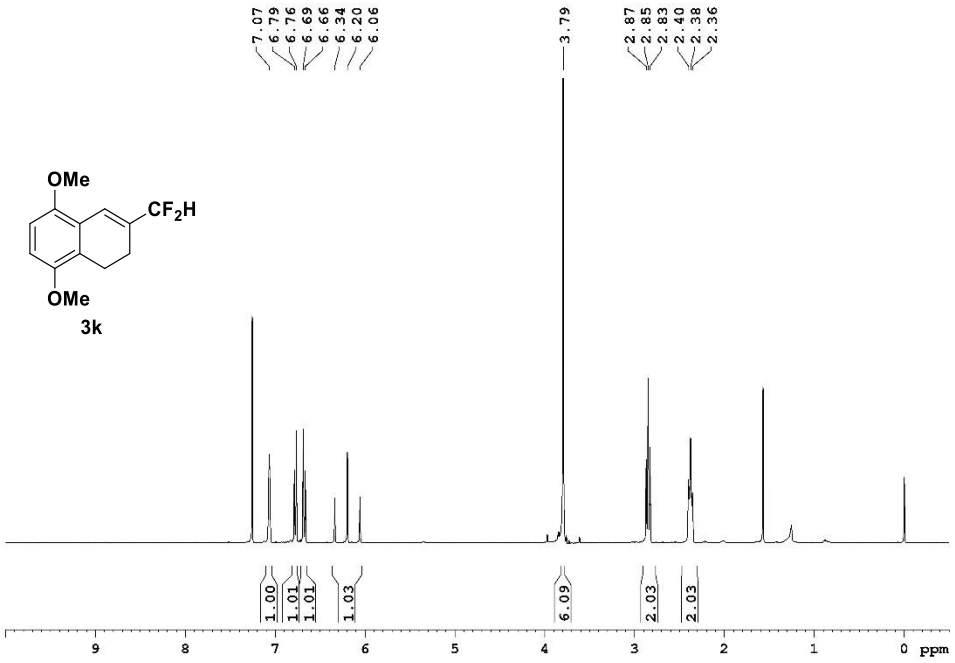


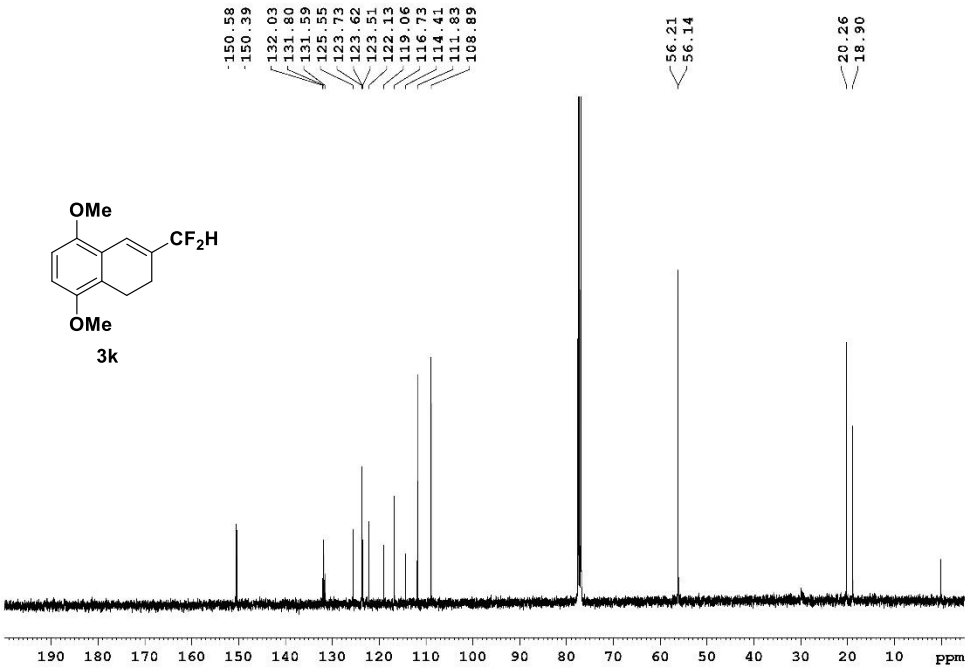
6-(difluoromethyl)-7,8-dihydronaphthalene-2-carbonitrile (3i)



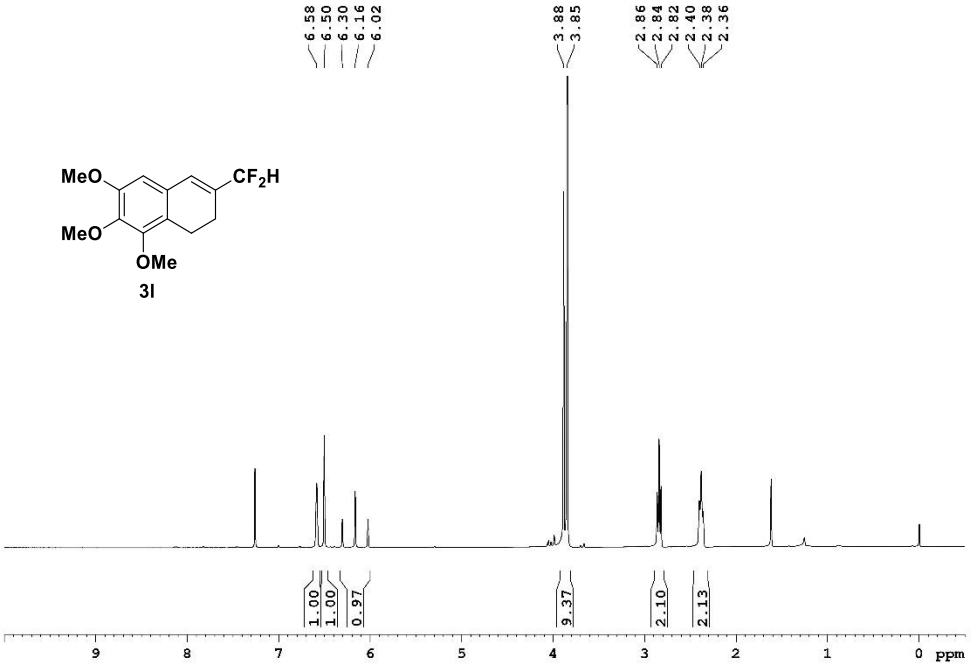


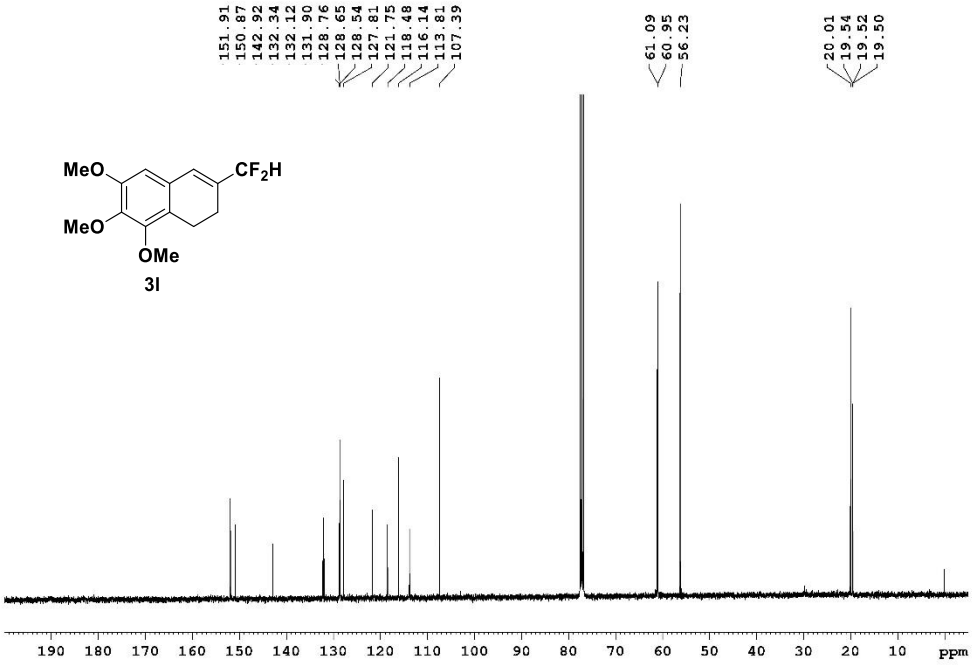
3-(difluoromethyl)-5,8-dimethoxy-1,2-dihydronaphthalene (3k)



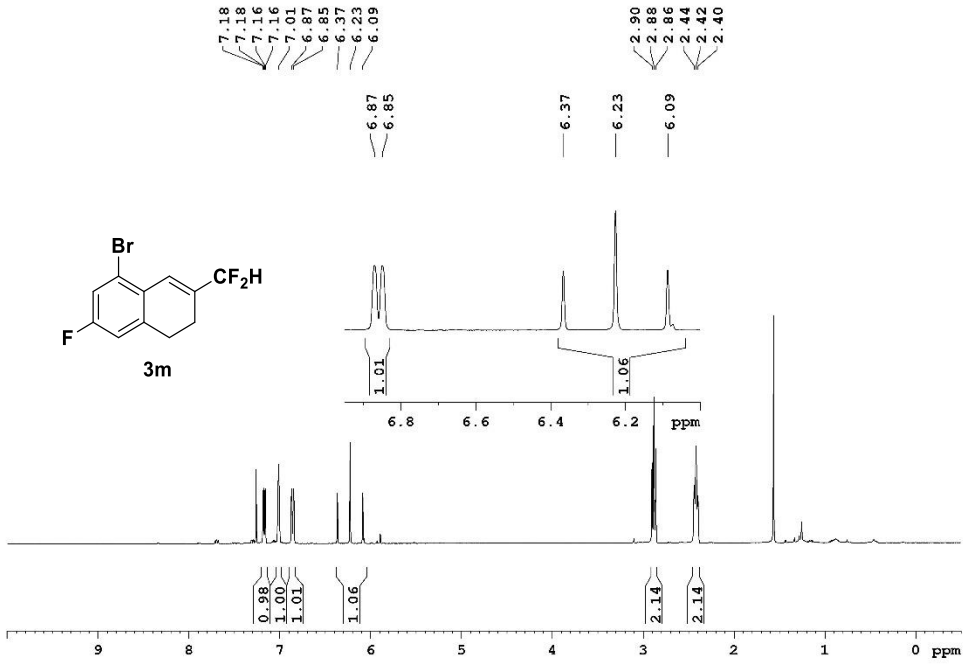


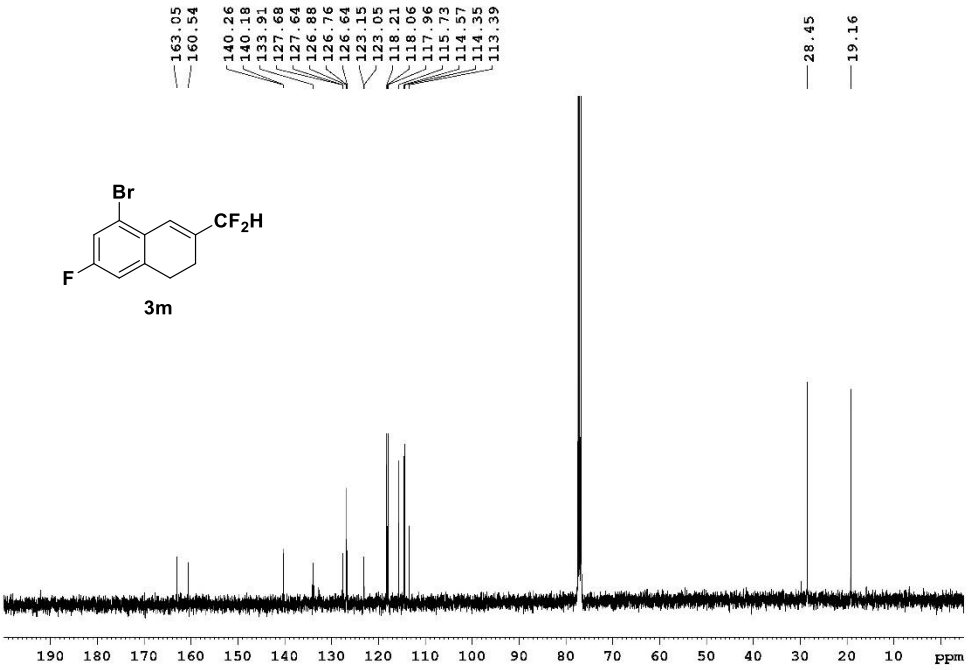
3-(difluoromethyl)-6,7,8-trimethoxy-1,2-dihydronaphthalene (3l)



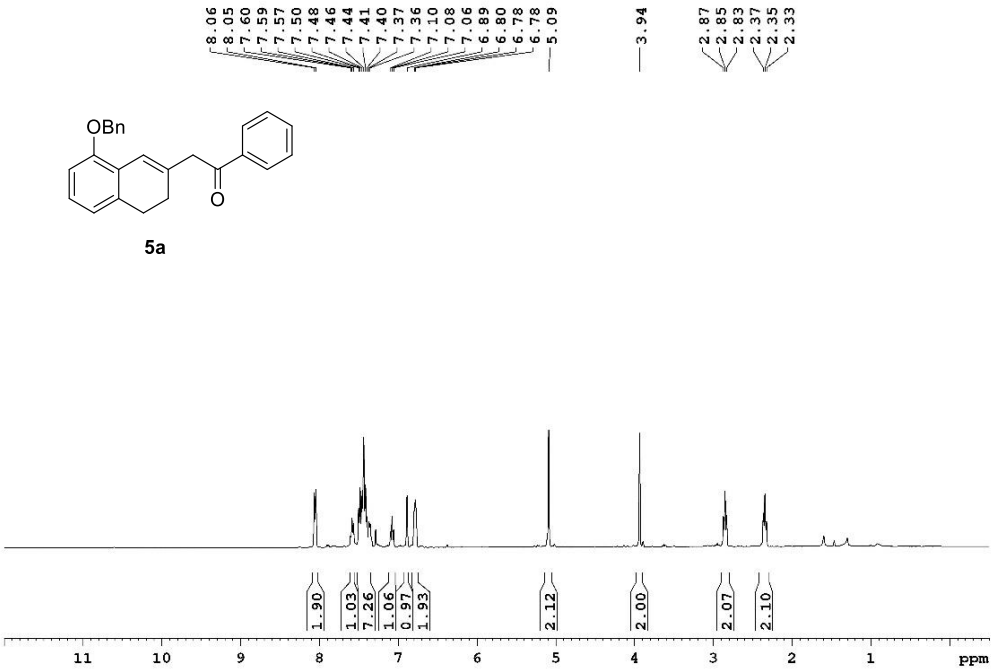


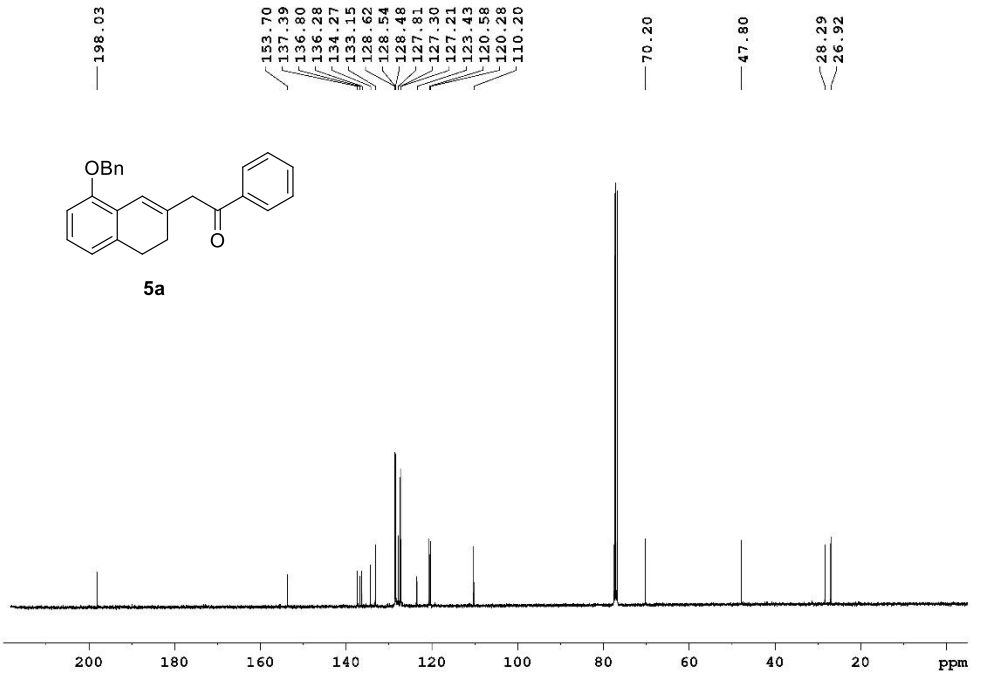
5-bromo-3-(difluoromethyl)-7-fluoro-1,2-dihydronaphthalene (3m)



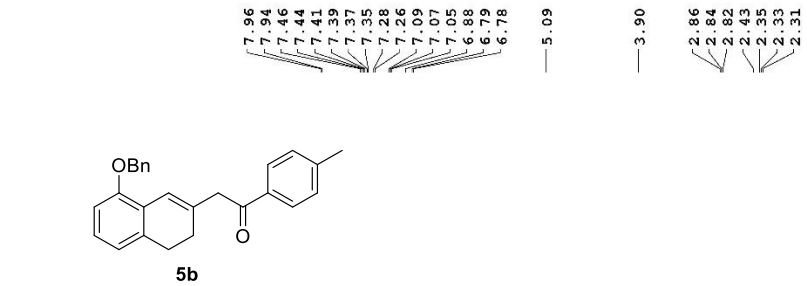


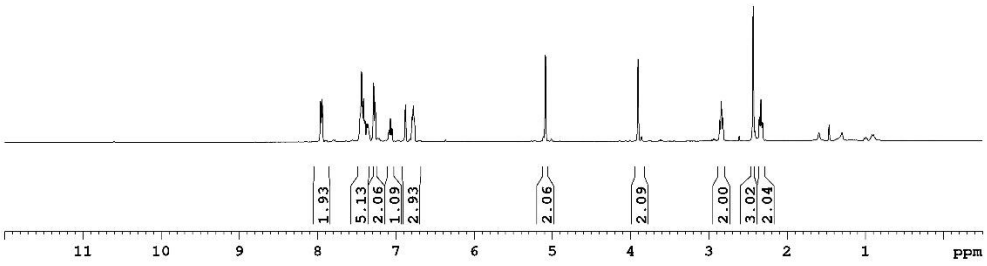
2-(8-(benzyloxy)-3,4-dihydronaphthalen-2-yl)-1-phenylethan-1-one (5a)

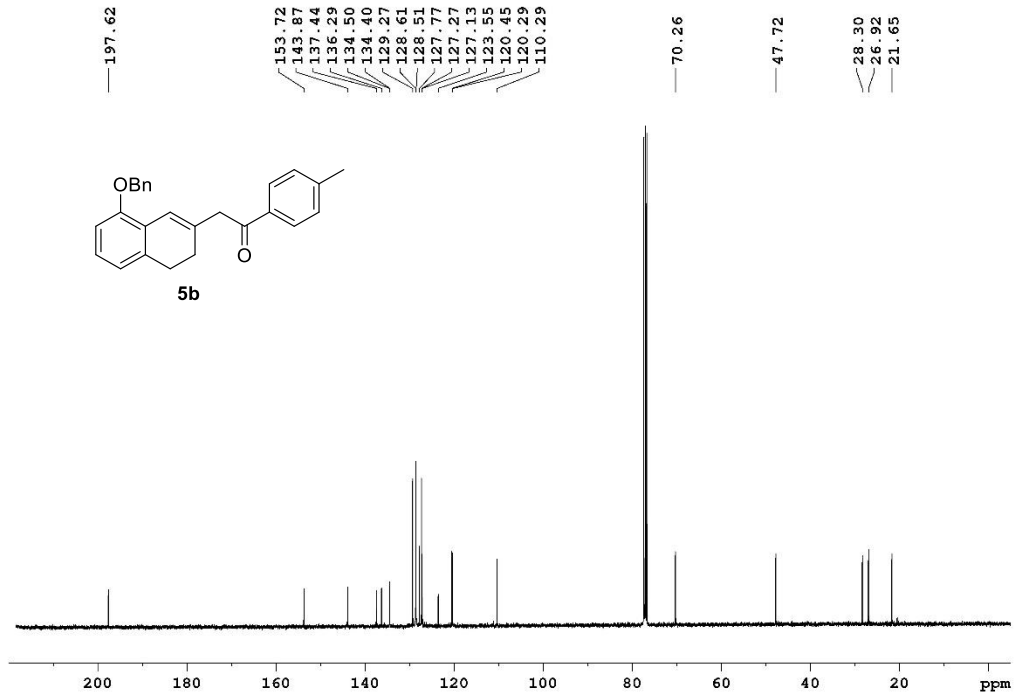




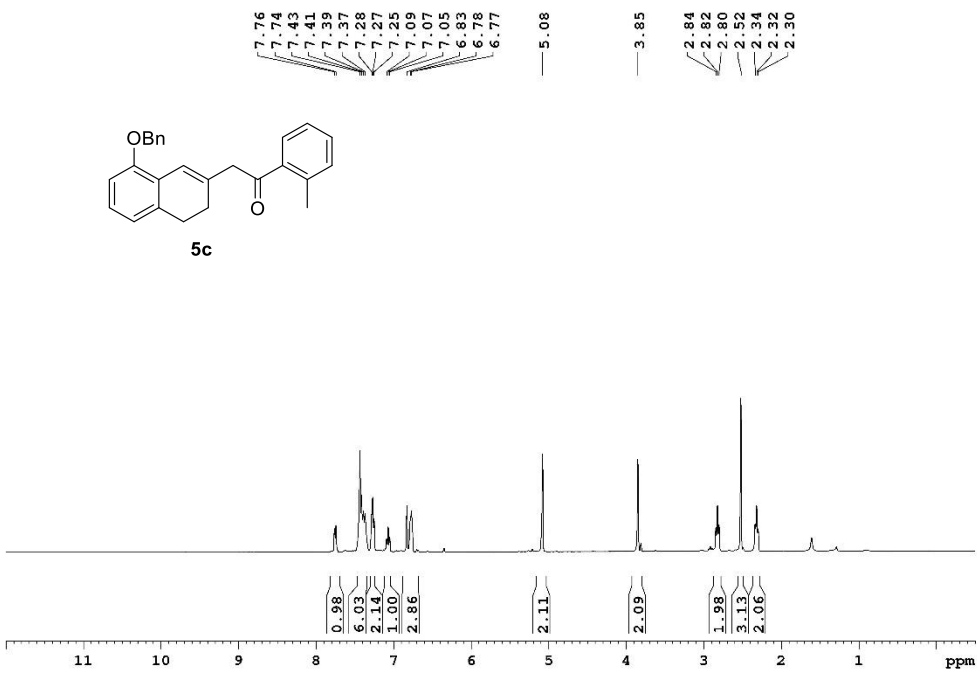
2-(8-(benzyloxy)-3,4-dihydronaphthalen-2-yl)-1-(p-tolyl)ethan-1-one (5b)

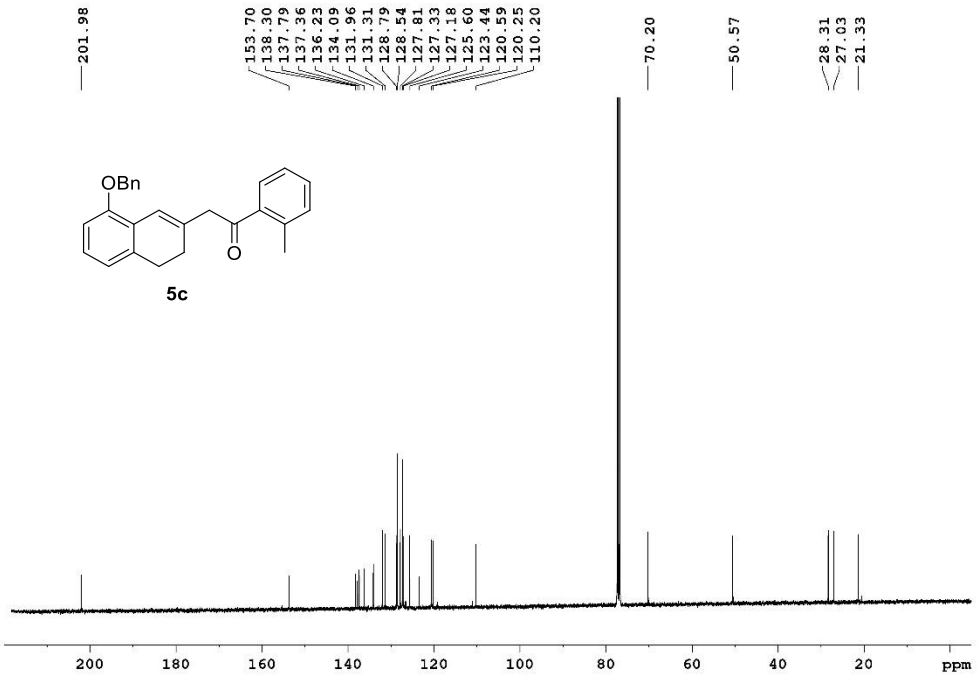




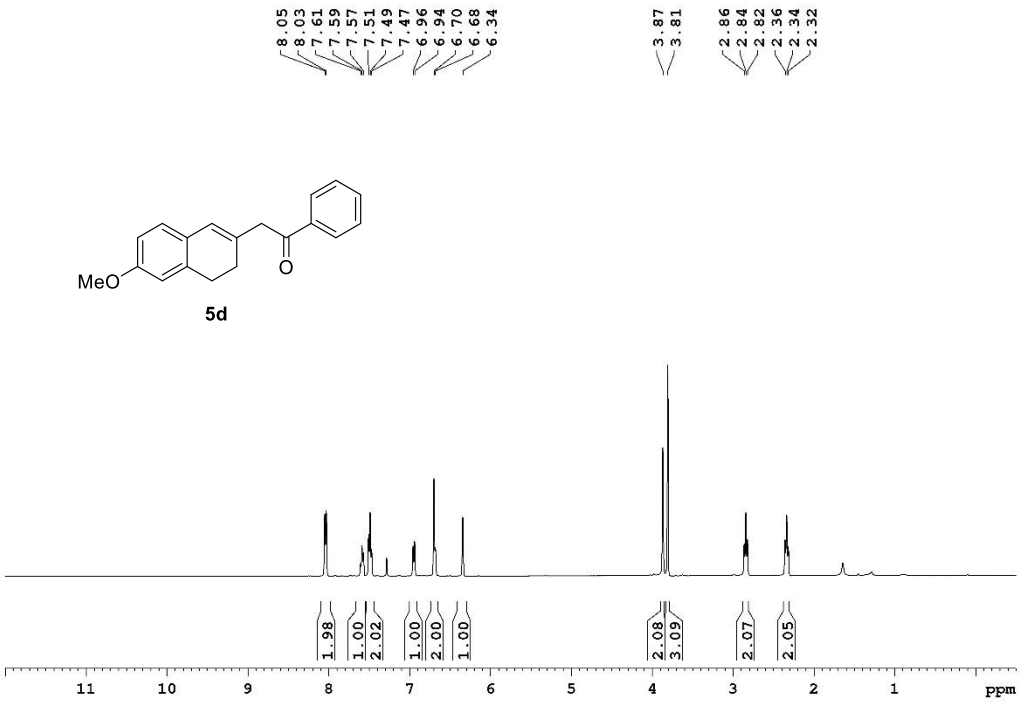


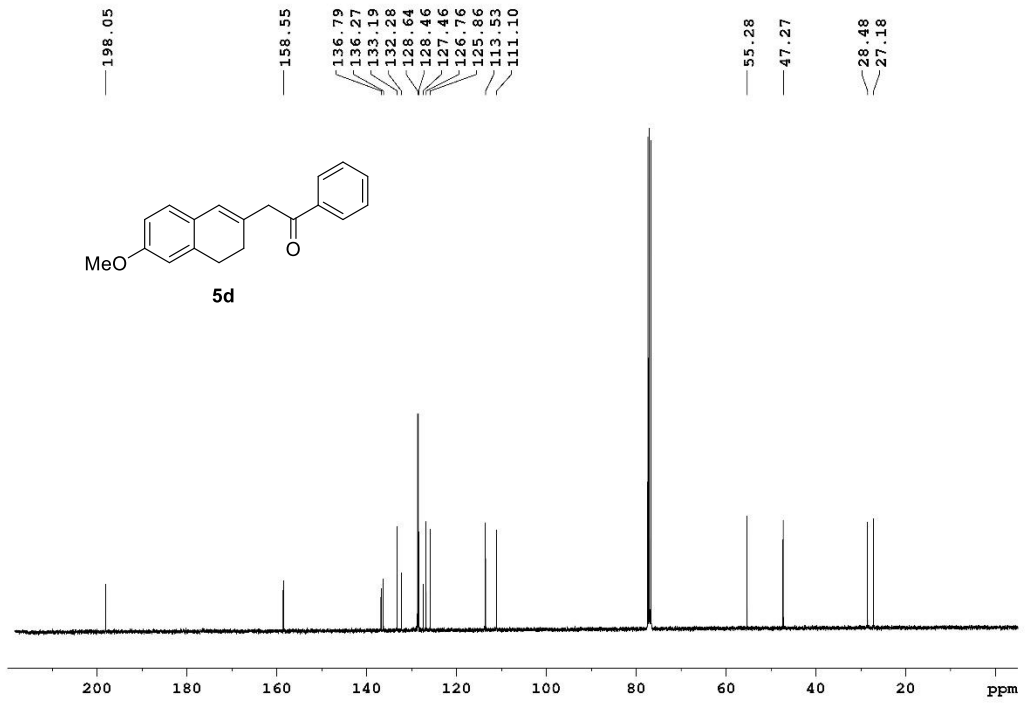
2-(8-(benzyloxy)-3,4-dihydronaphthalen-2-yl)-1-(o-tolyl)ethan-1-one (5c)



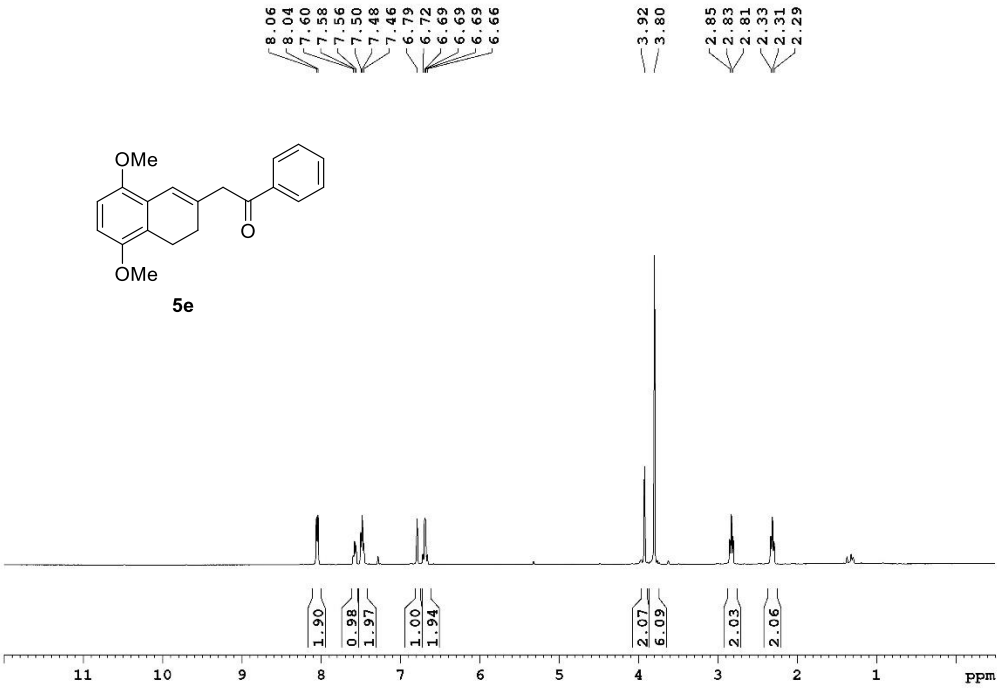


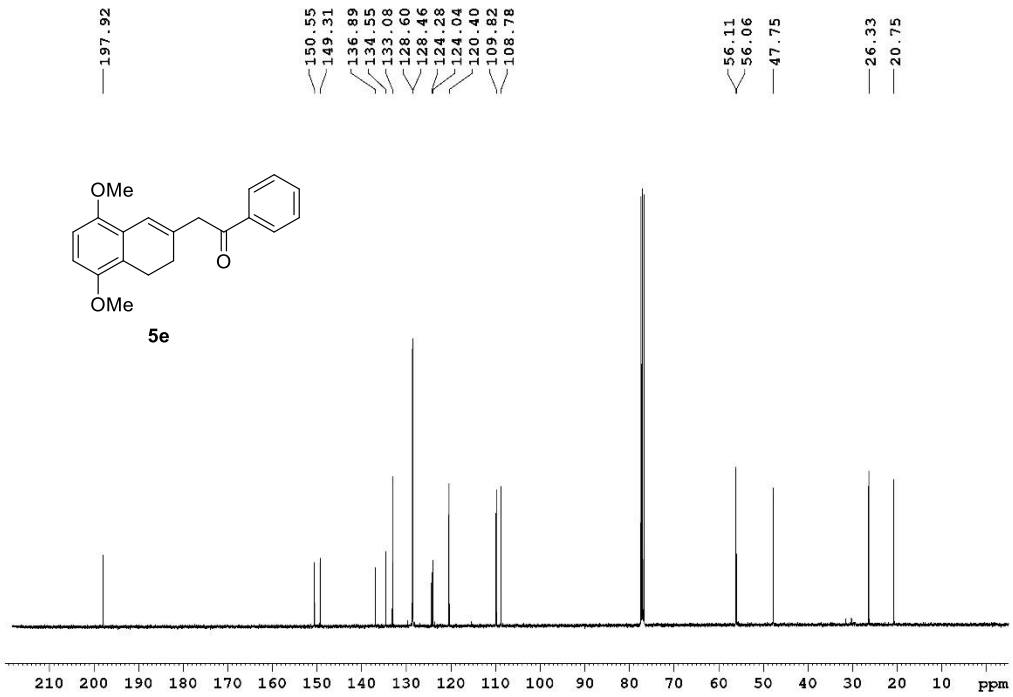
2-(6-methoxy-3,4-dihydronaphthalen-2-yl)-1-phenylethan-1-one (5d)



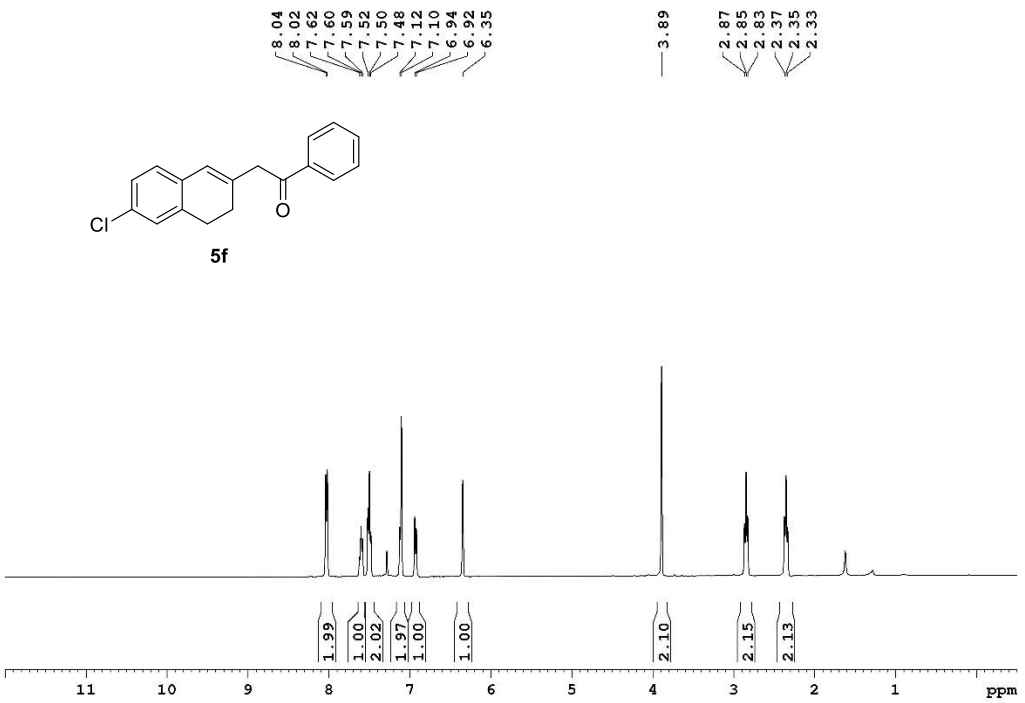


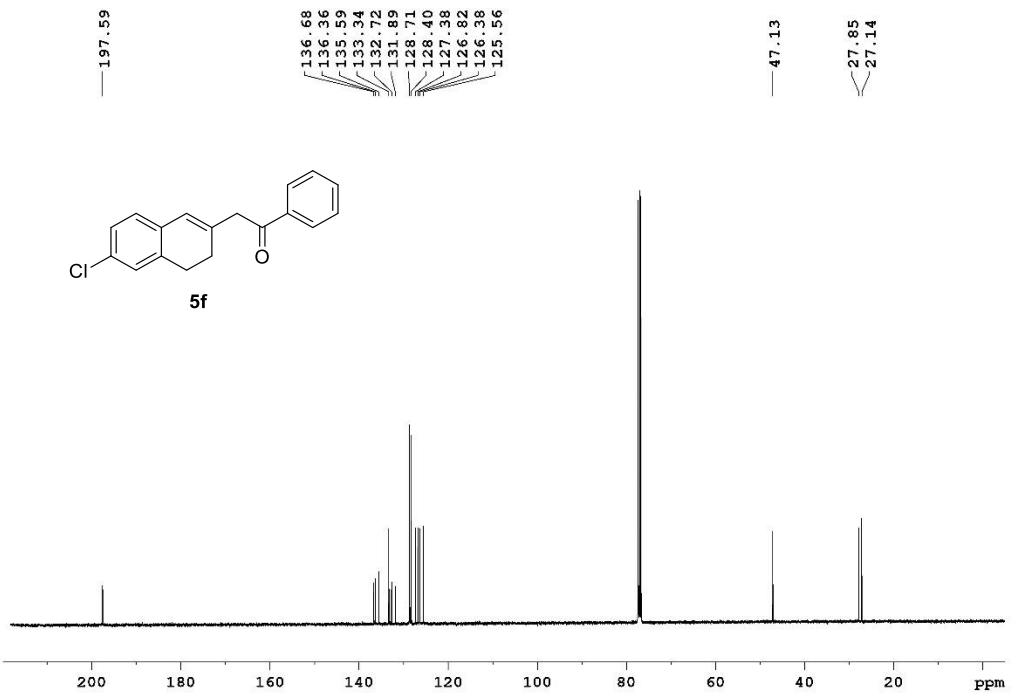
2-(5,8-dimethoxy-3,4-dihydronaphthalen-2-yl)-1-phenylethan-1-one (5e)



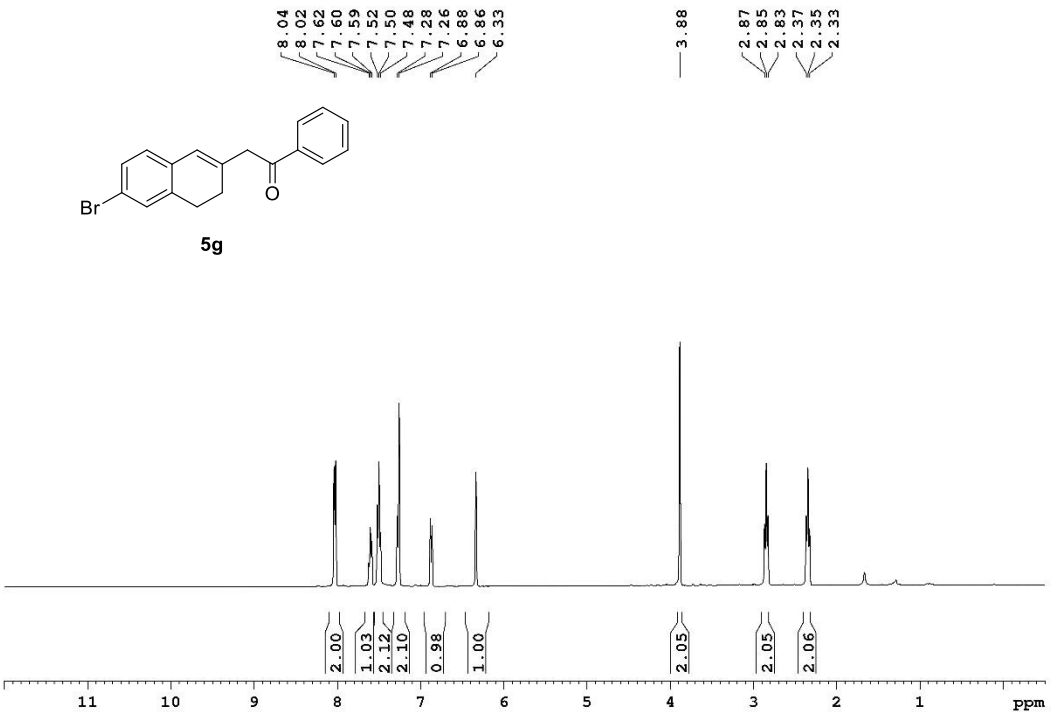


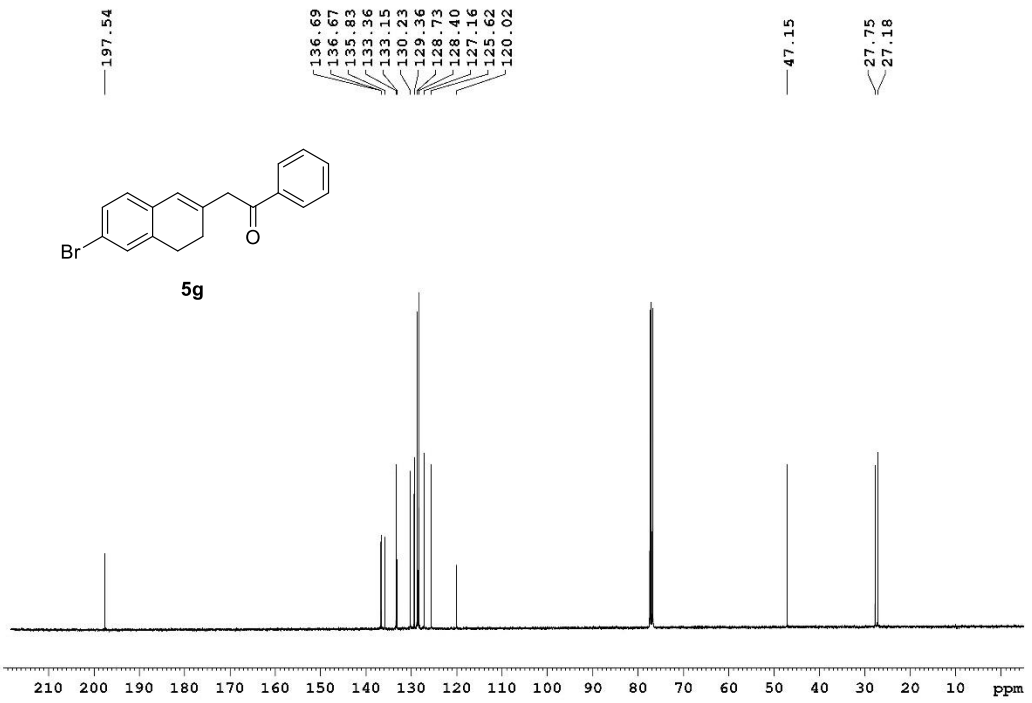
2-(6-chloro-3,4-dihydronaphthalen-2-yl)-1-phenylethan-1-one (5f)



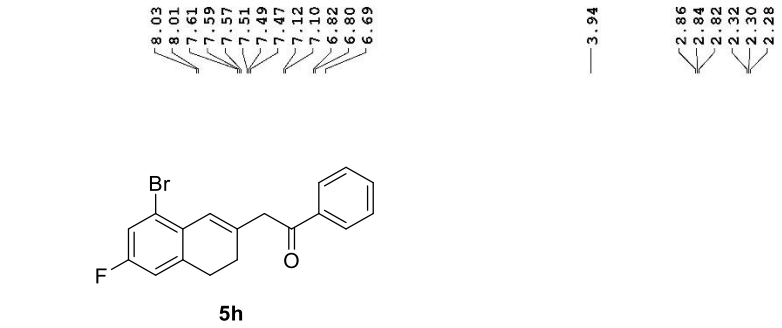


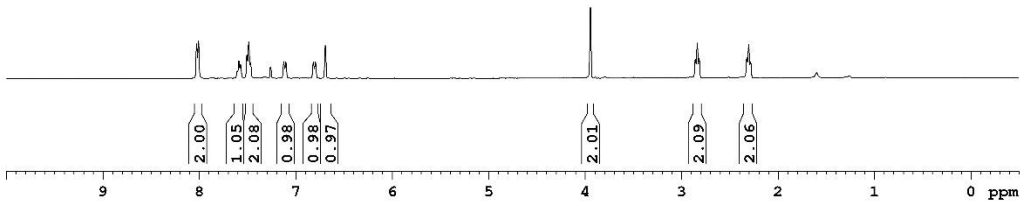
2-(6-bromo-3,4-dihydronaphthalen-2-yl)-1-phenylethan-1-one (5g)

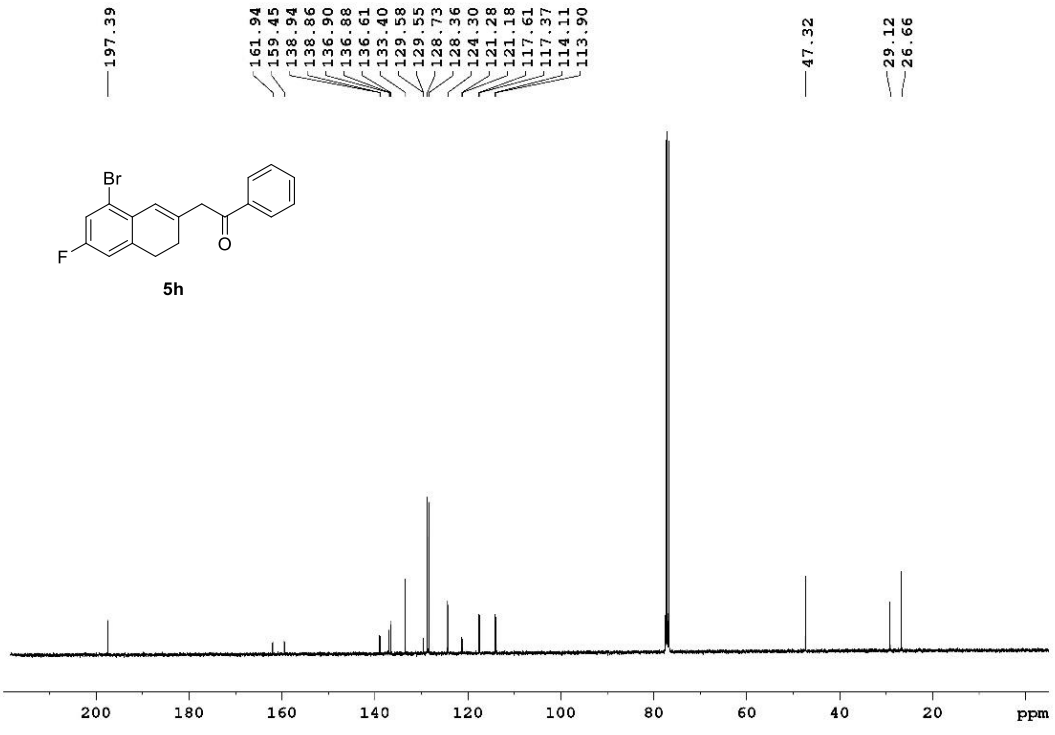




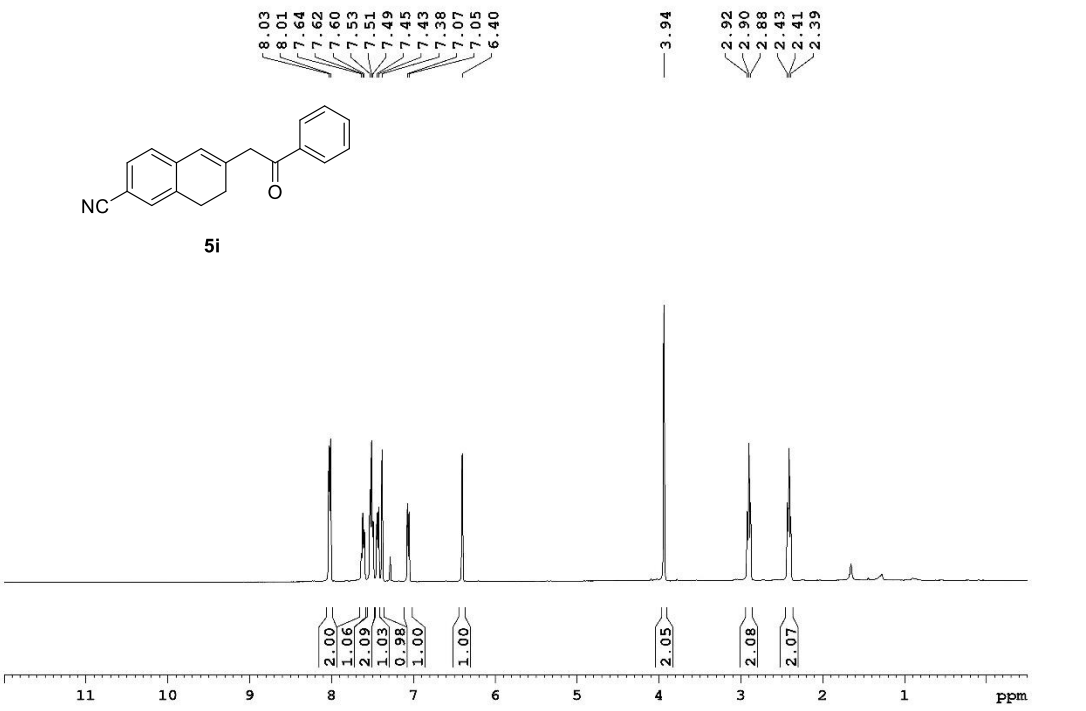
2-(8-bromo-6-fluoro-3,4-dihydronaphthalen-2-yl)-1-phenylethan-1-one (5h)

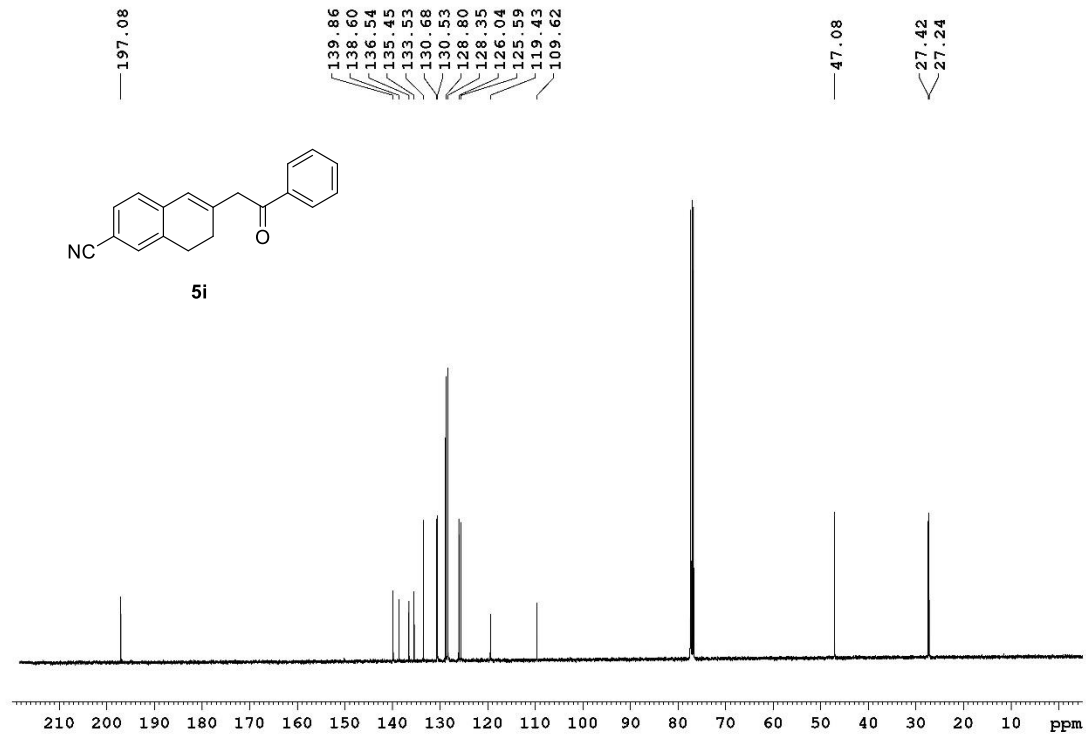




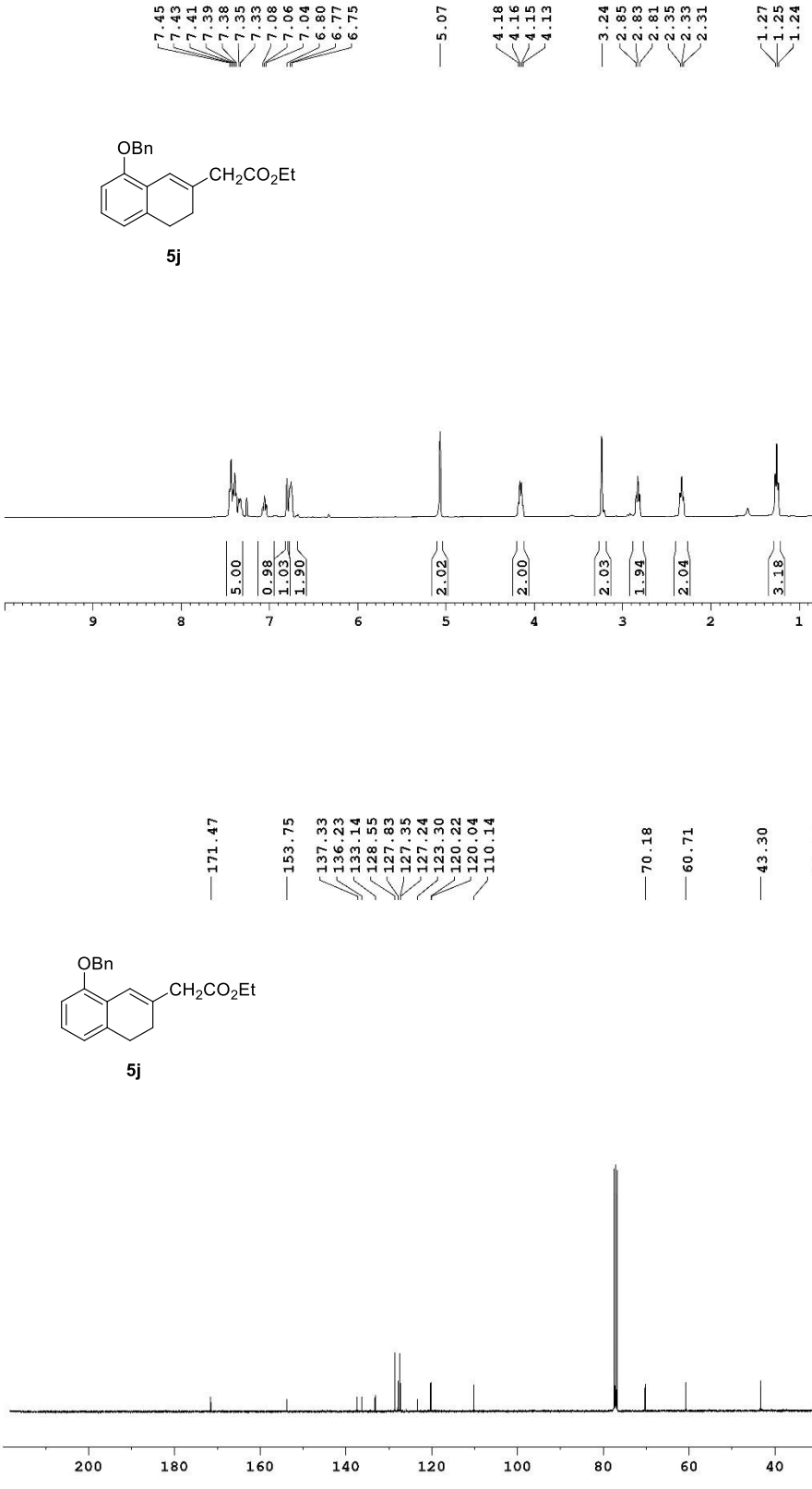


6-(2-oxo-2-phenylethyl)-7,8-dihydronaphthalene-2-carbonitrile (5i)

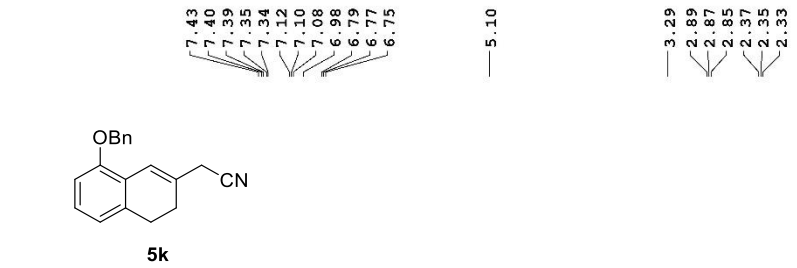


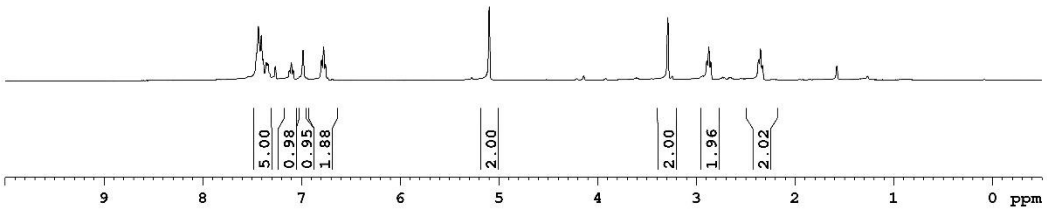


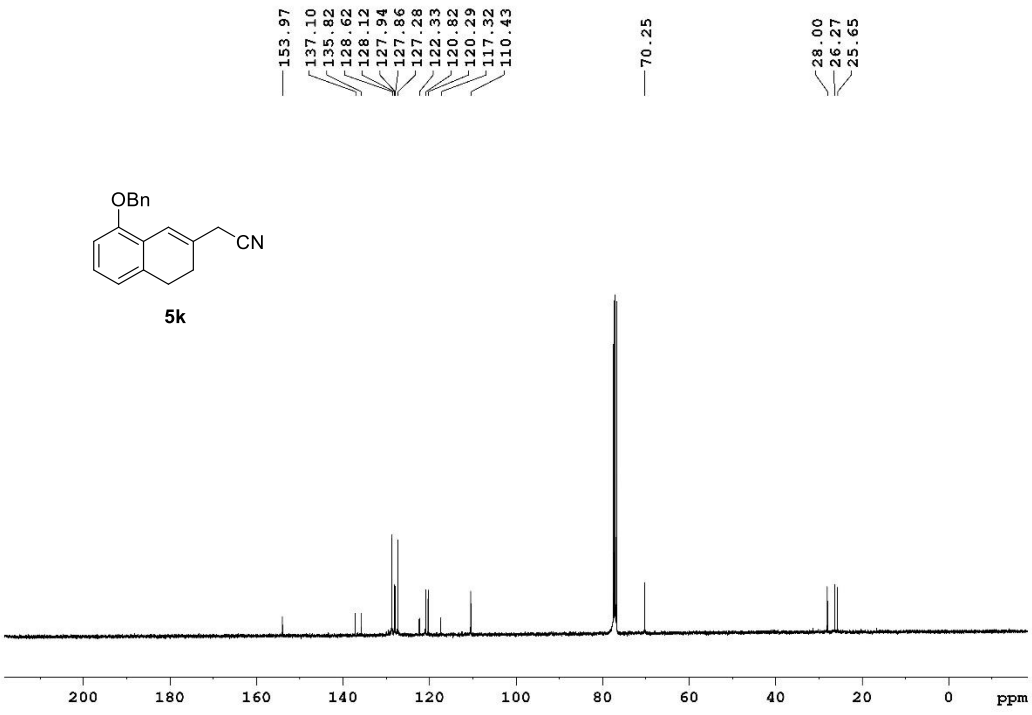
ethyl 2-(8-(benzyloxy)-3,4-dihydronaphthalen-2-yl)acetate (5j)



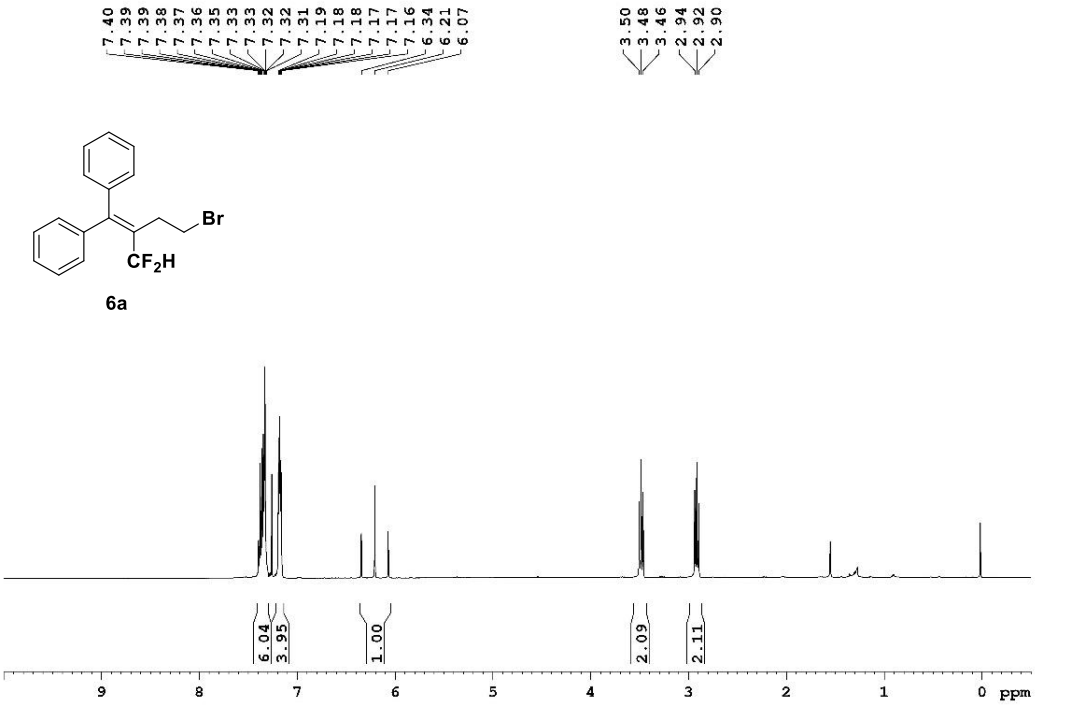
2-(8-(benzyloxy)-3,4-dihydronaphthalen-2-yl)acetonitrile (5k)

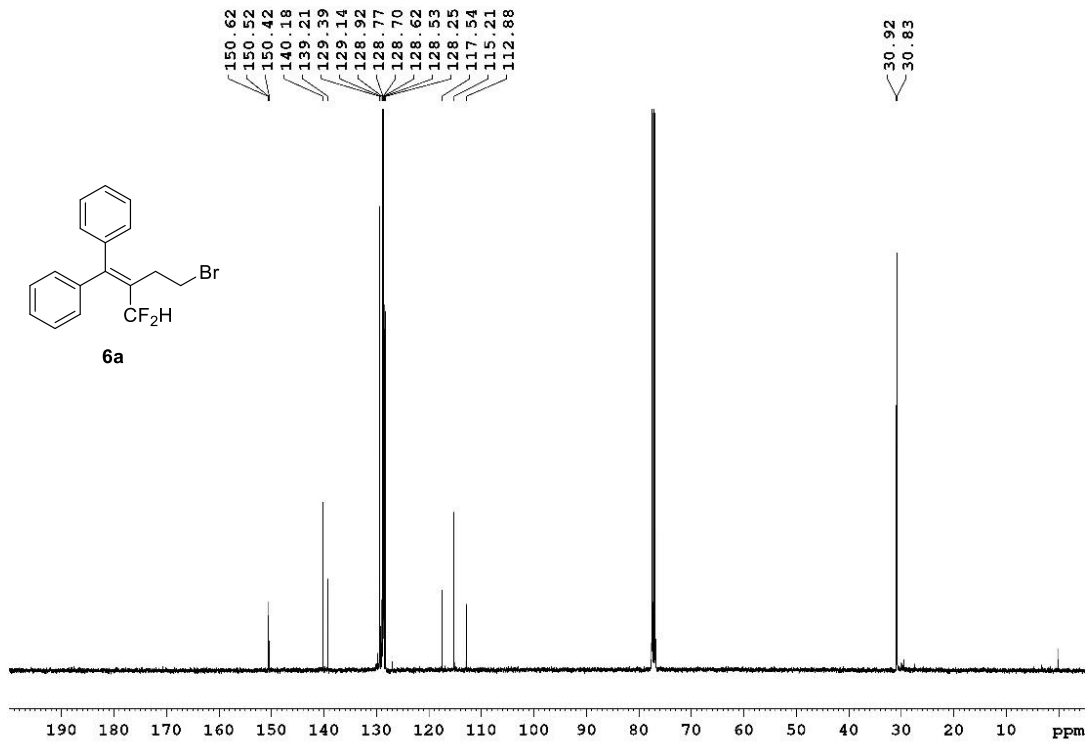




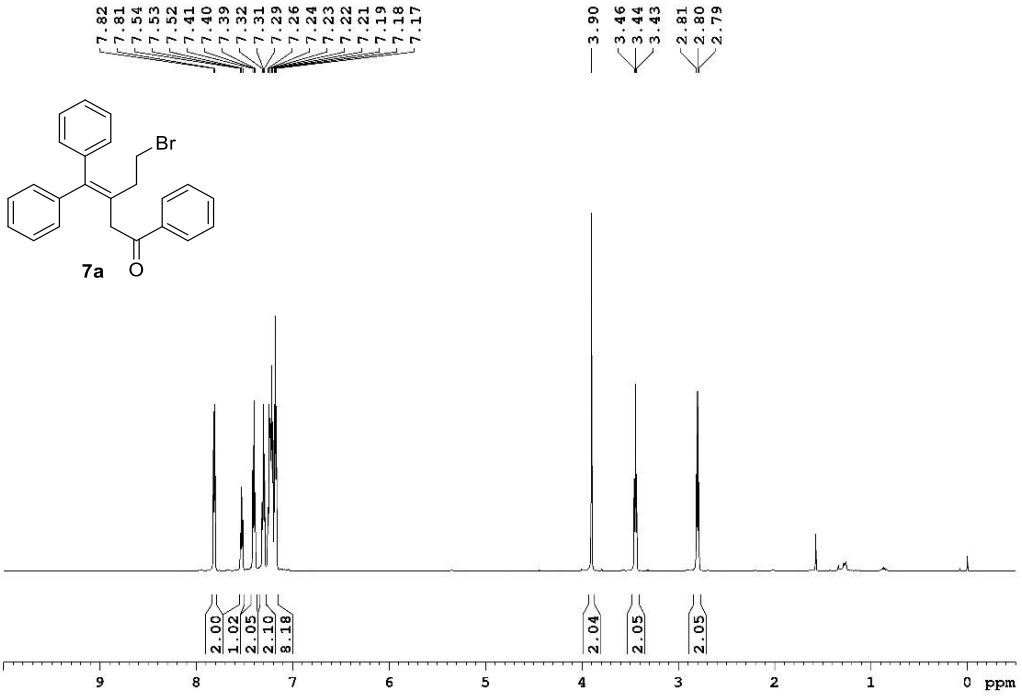


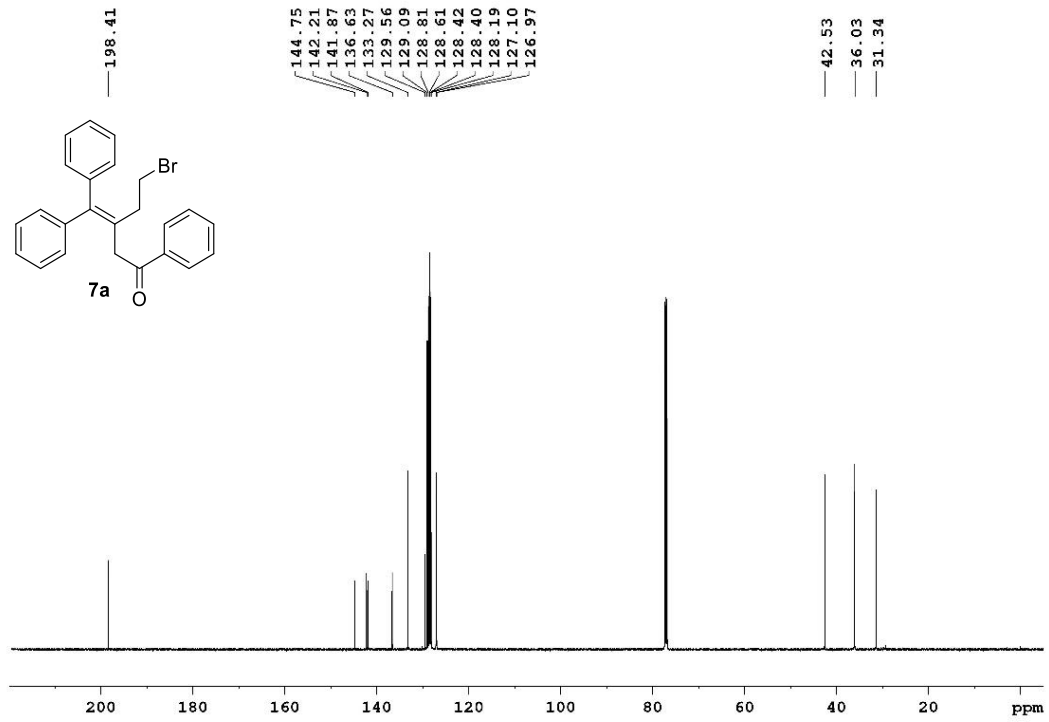
(4-bromo-2-(difluoromethyl)but-1-ene-1,1-diyl)dibenzene (6a)



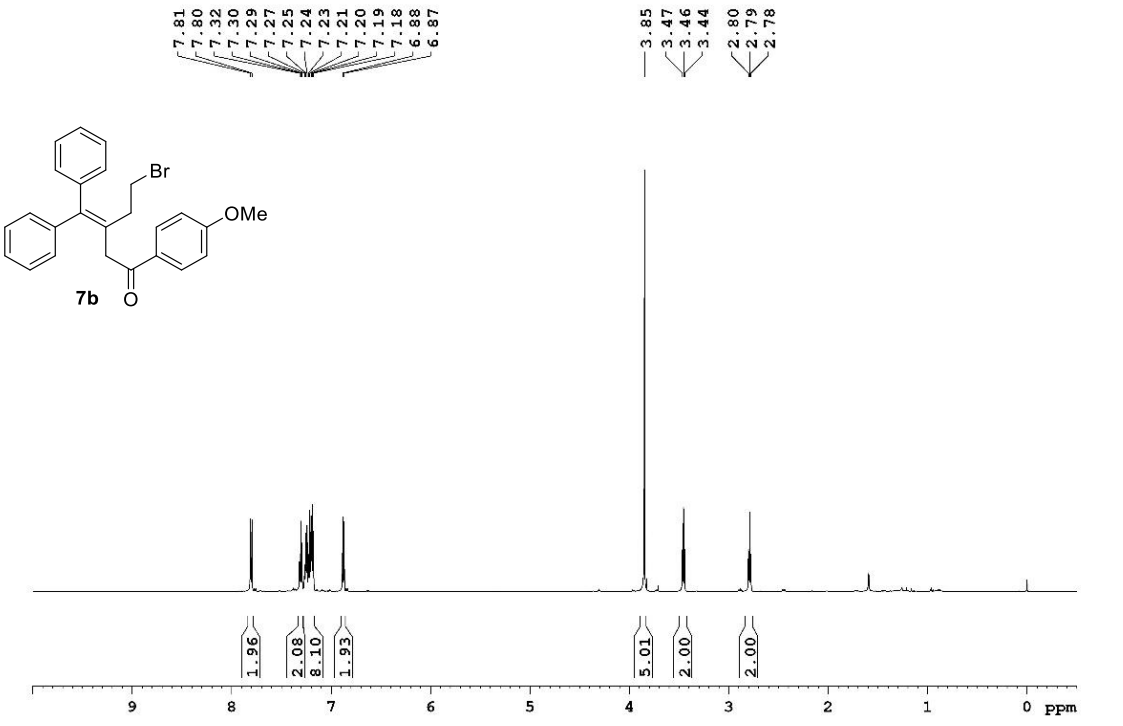


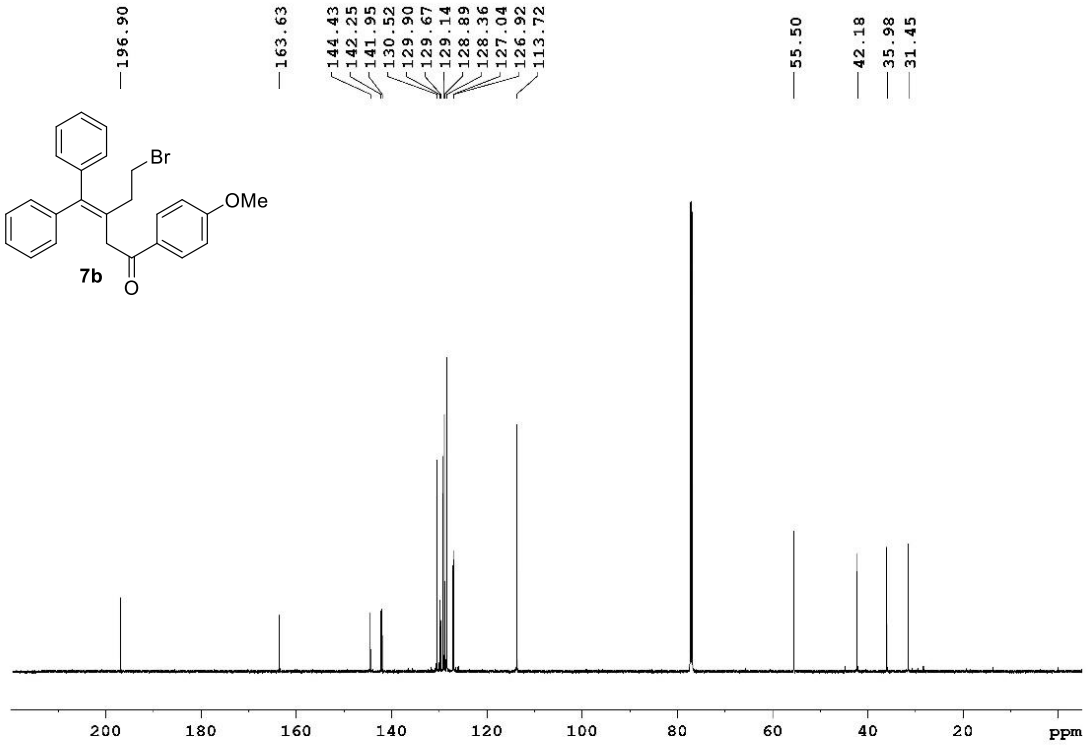
5-bromo-3-(diphenylmethylene)-1-phenylpentan-1-one (7a)



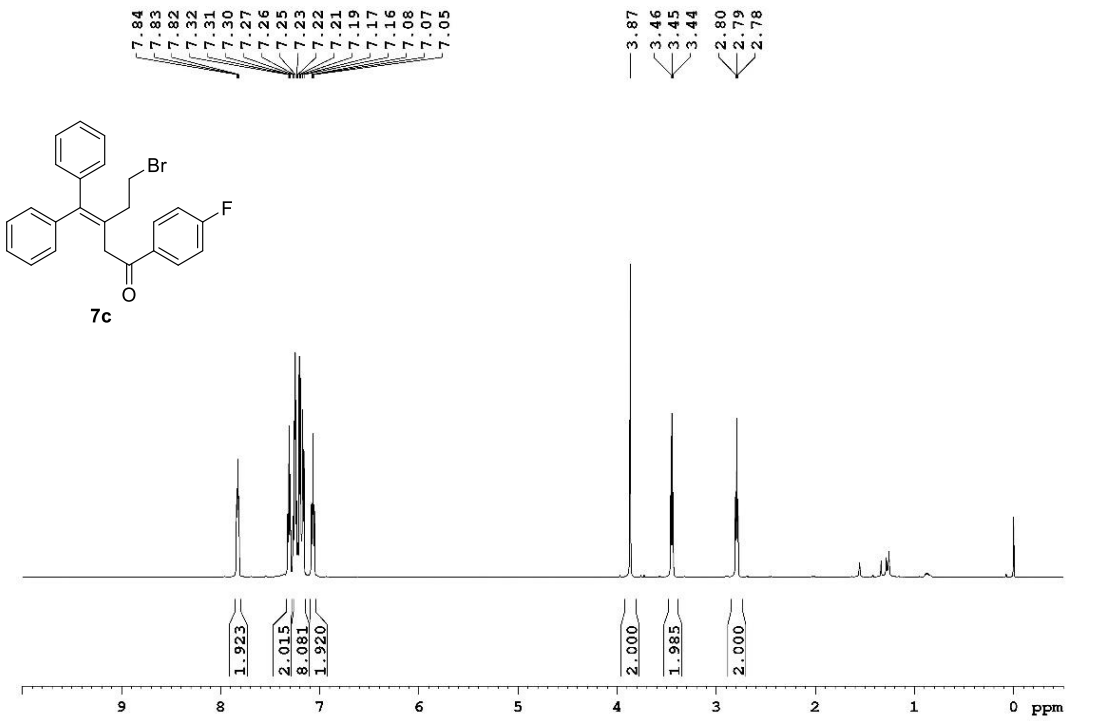


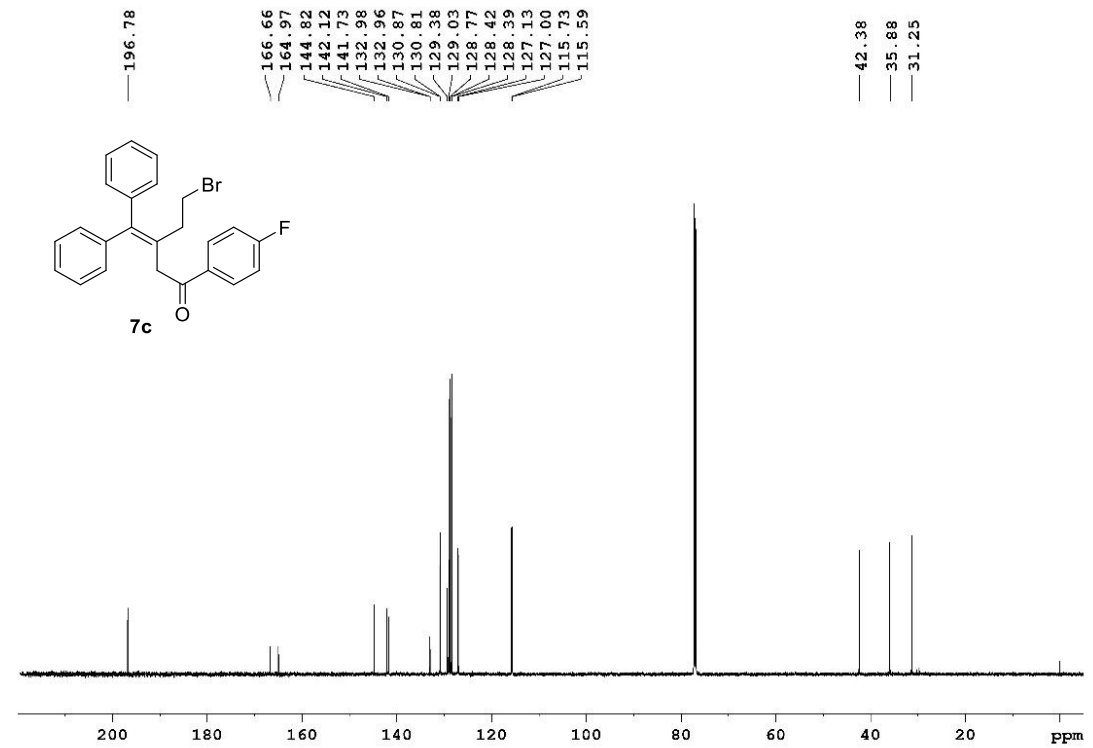
5-bromo-3-(diphenylmethylene)-1-(4-methoxyphenyl)pentan-1-one (7b)



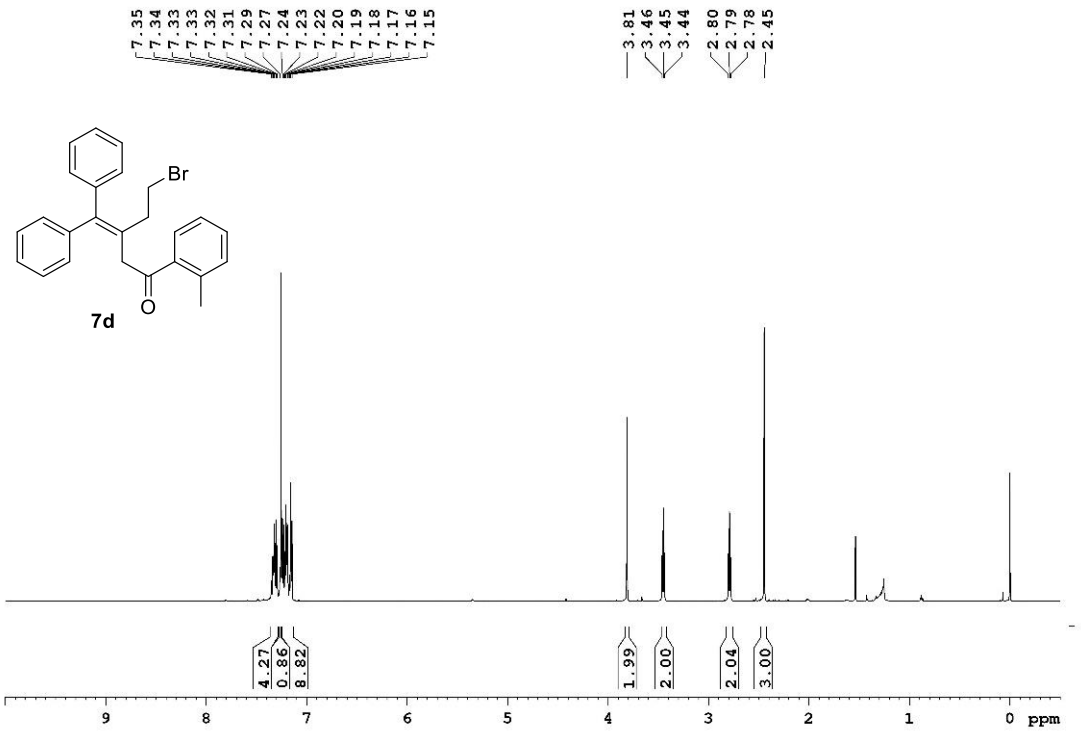


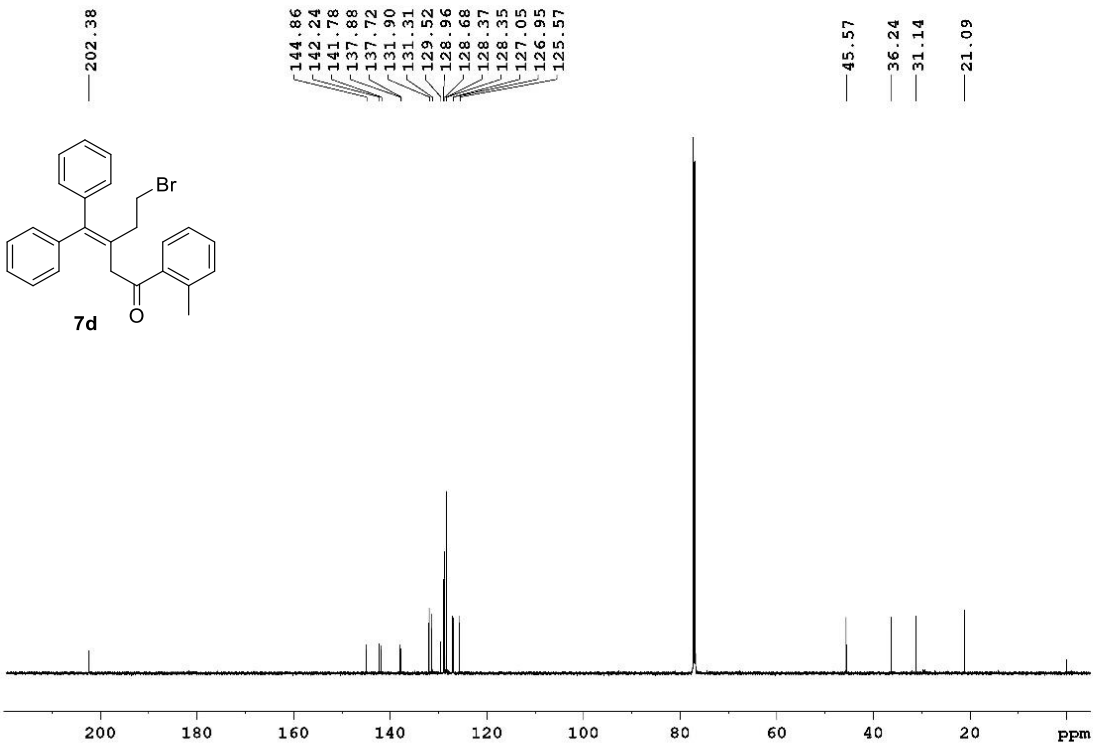
5-bromo-3-(diphenylmethylene)-1-(4-fluorophenyl)pentan-1-one (7c)



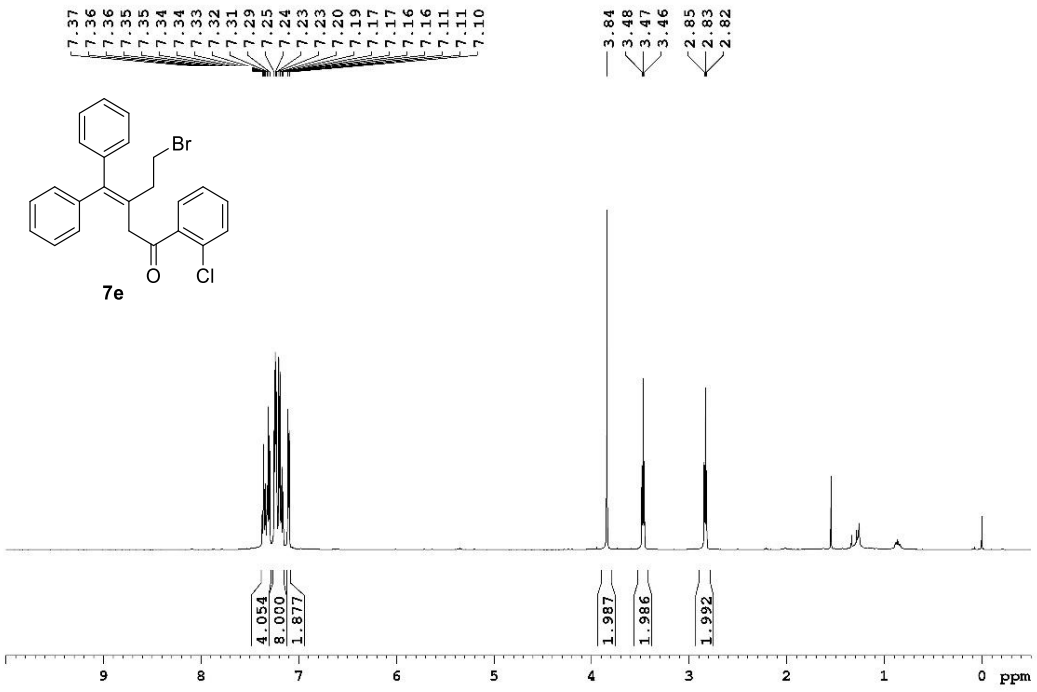


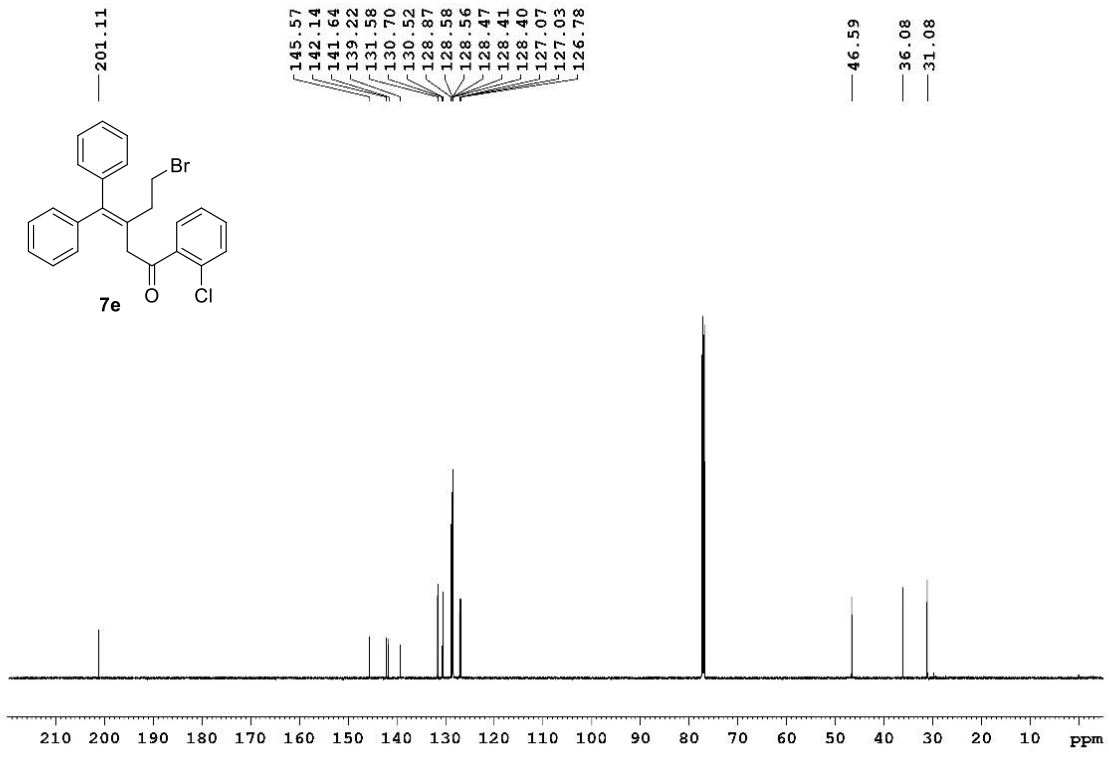
5-bromo-3-(diphenylmethylene)-1-(o-tolyl)pentan-1-one (7d)



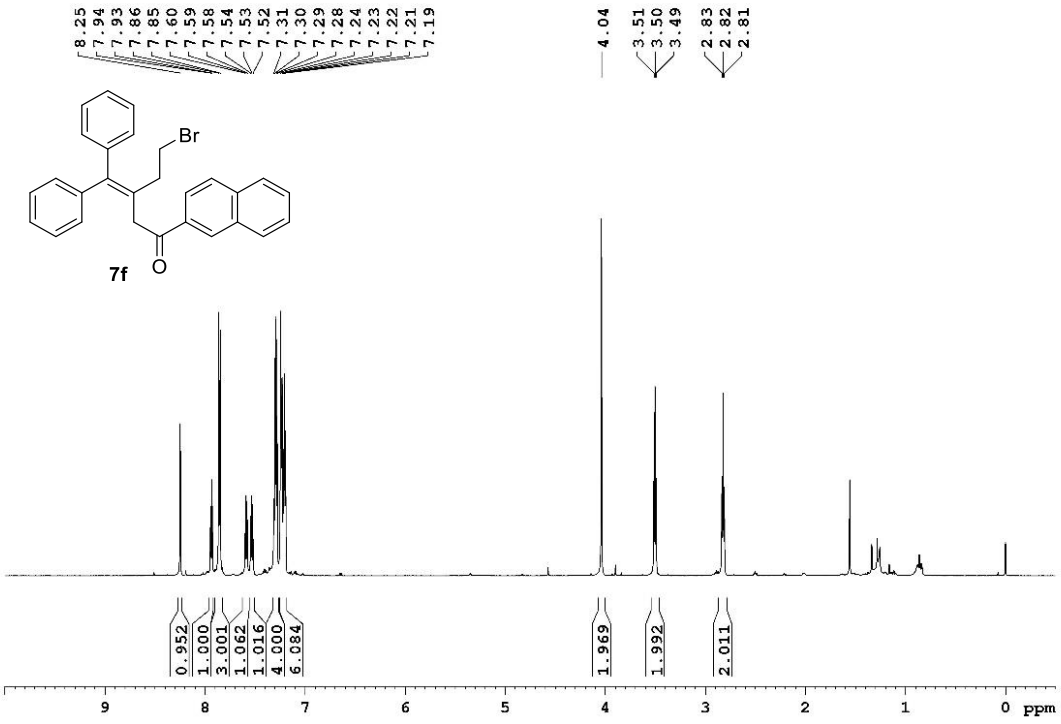


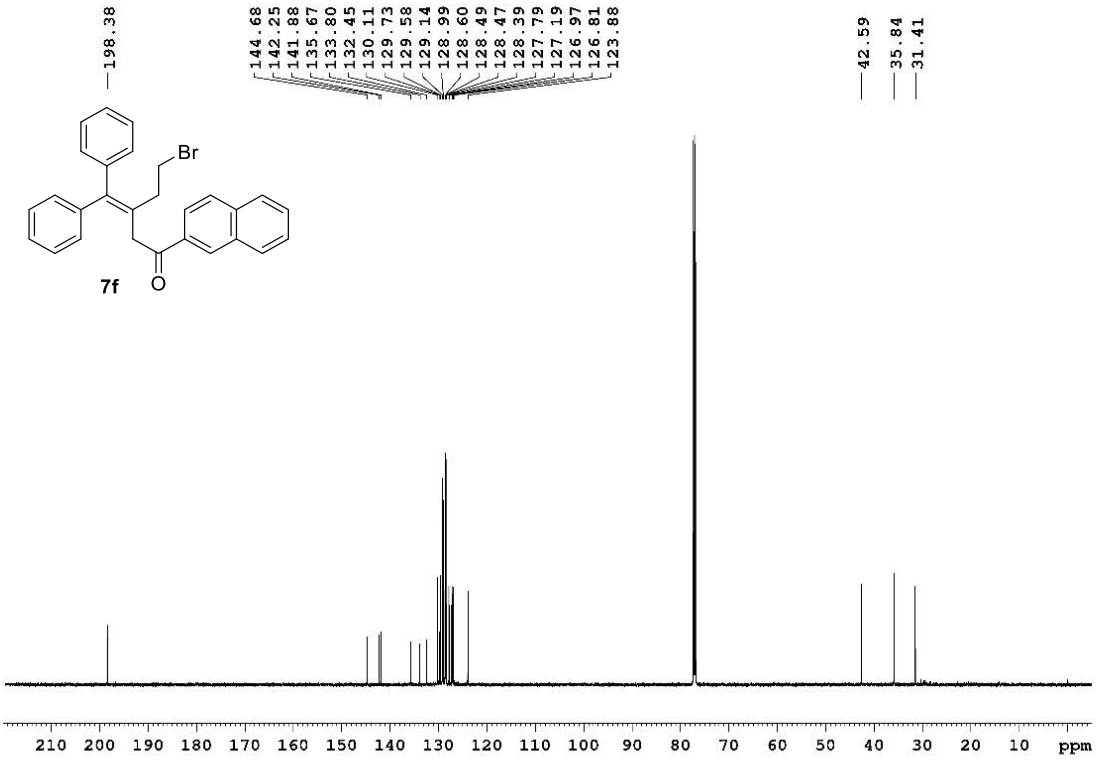
5-bromo-1-(2-chlorophenyl)-3-(diphenylmethylene)pentan-1-one (7e)



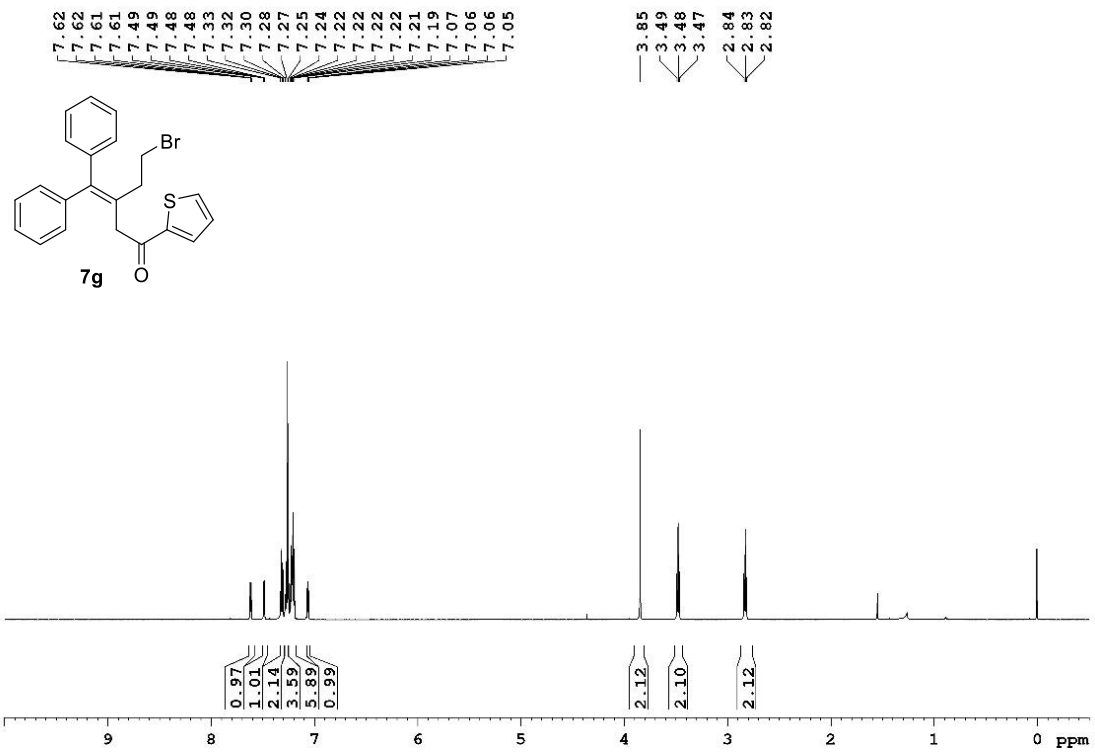


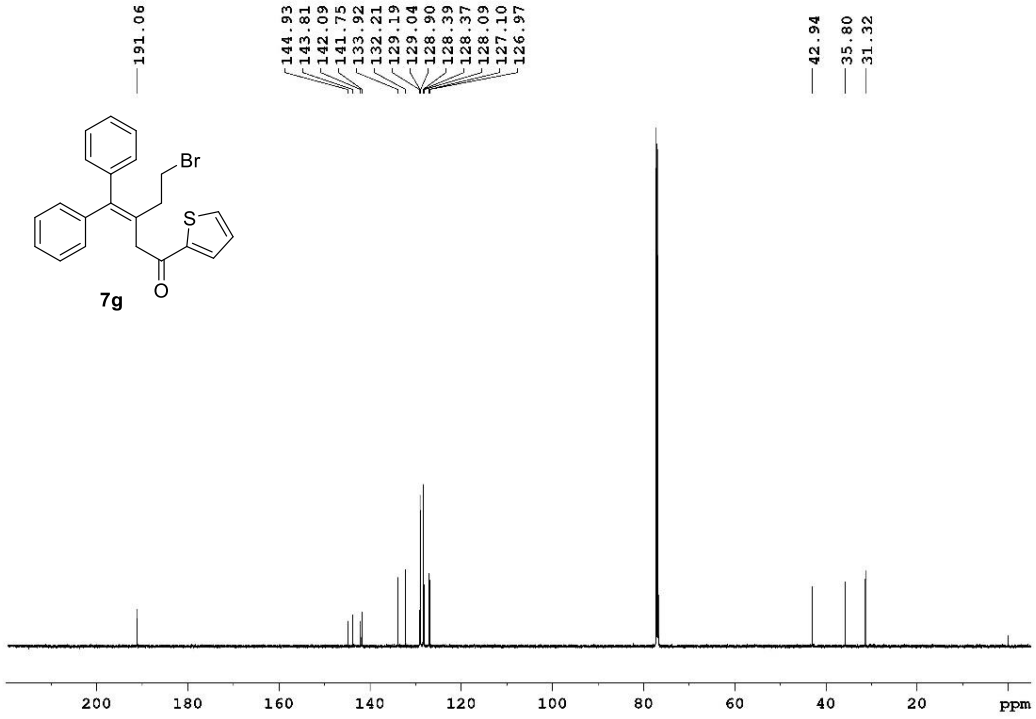
5-bromo-3-(diphenylmethylene)-1-(naphthalen-2-yl)pentan-1-one (7f)



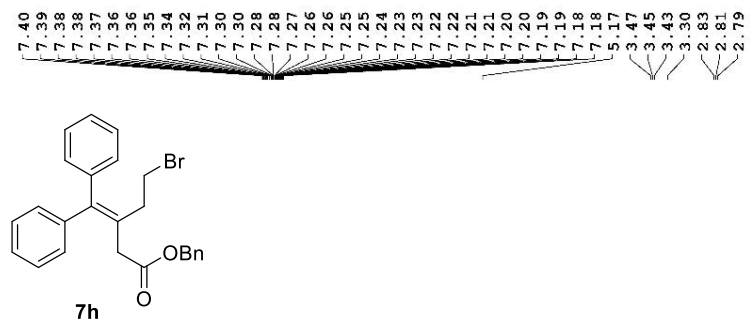


5-bromo-3-(diphenylmethylene)-1-(thiophen-2-yl)pentan-1-one (7g)

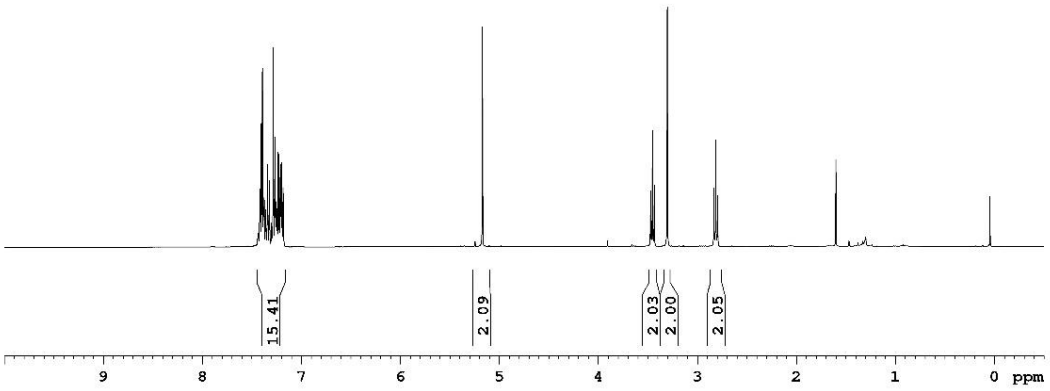


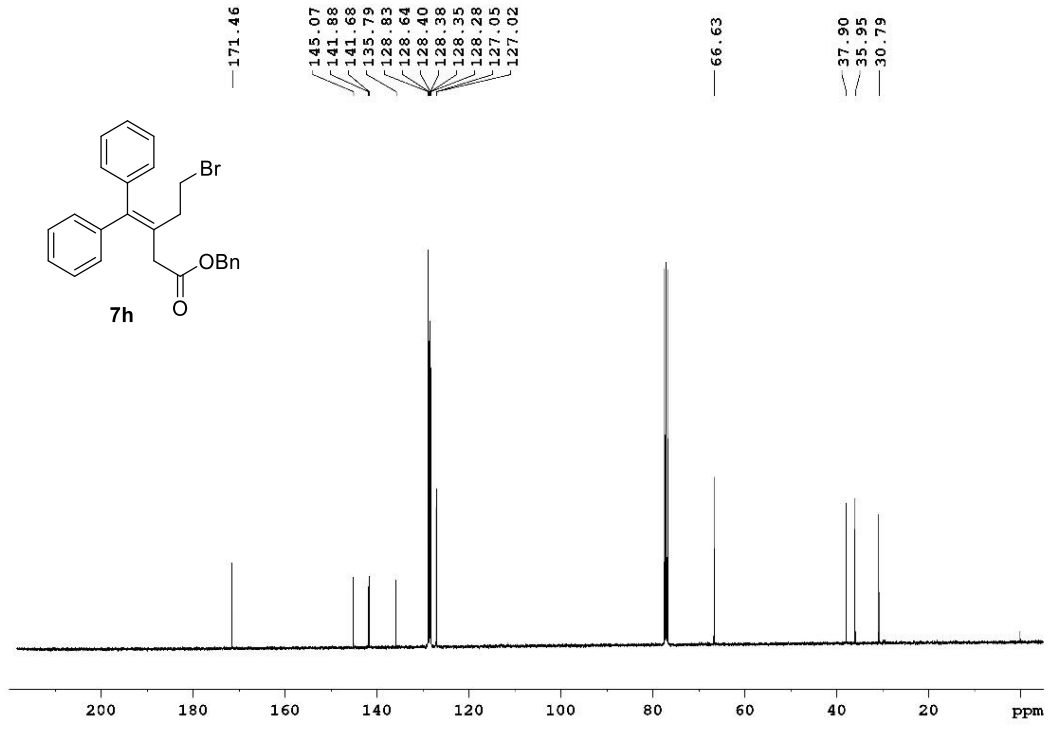


benzyl 5-bromo-3-(diphenylmethylene)pentanoate (7h)



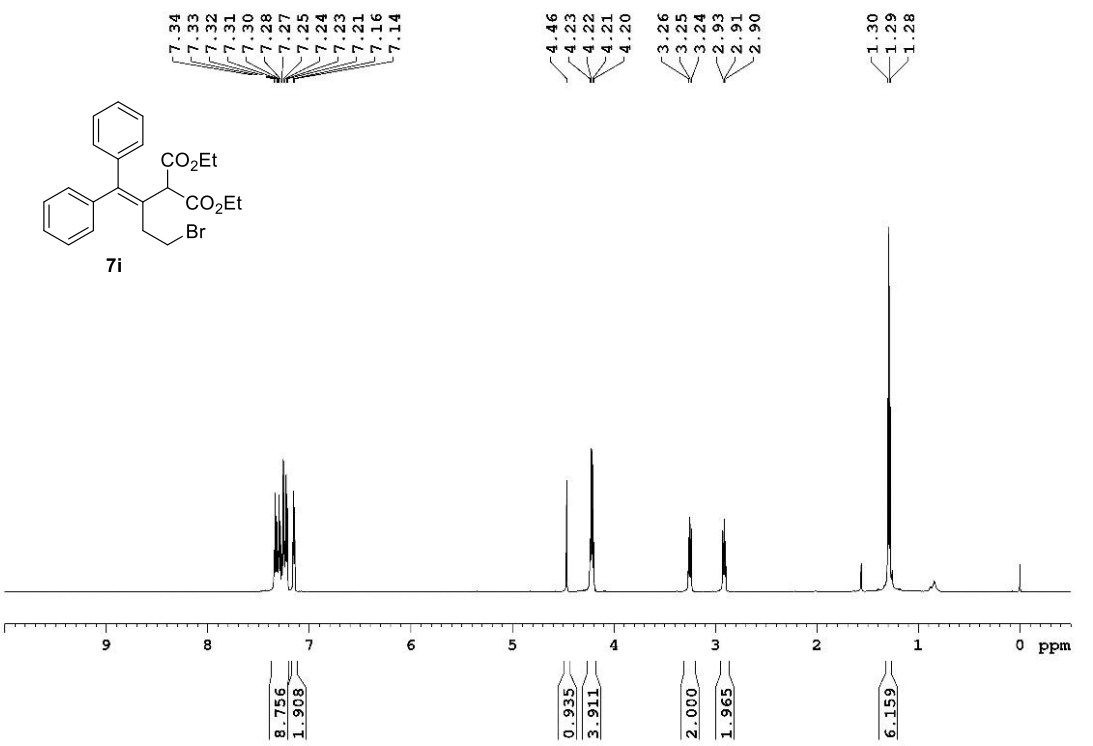
7h

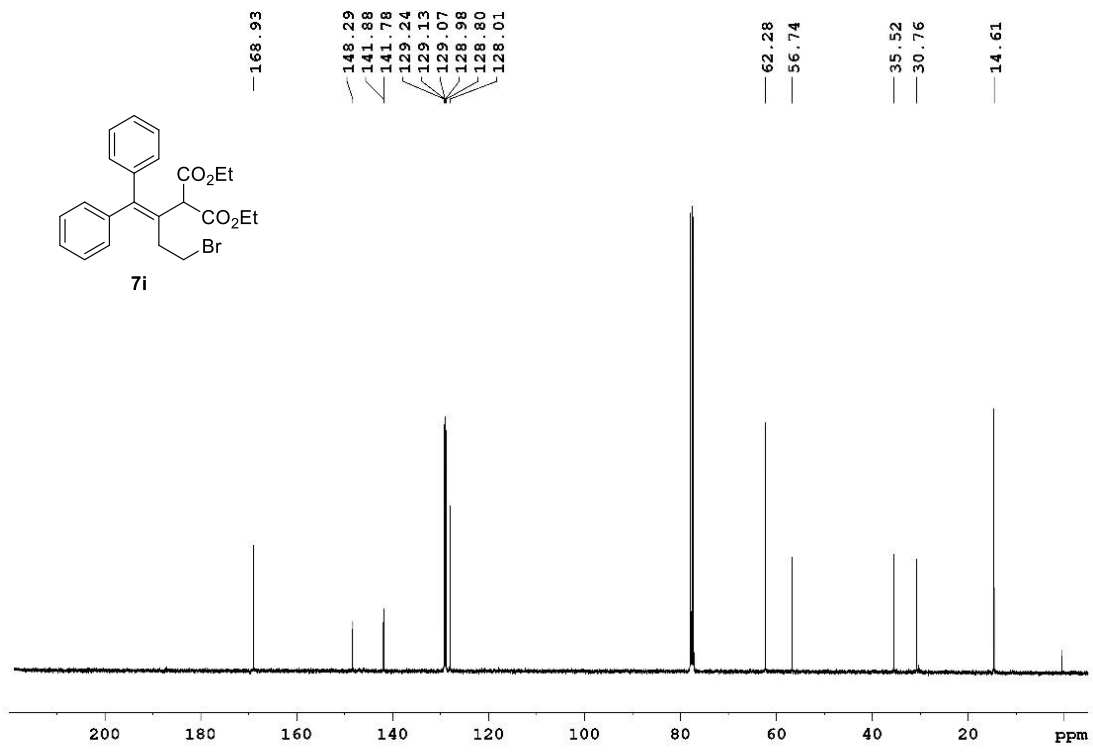




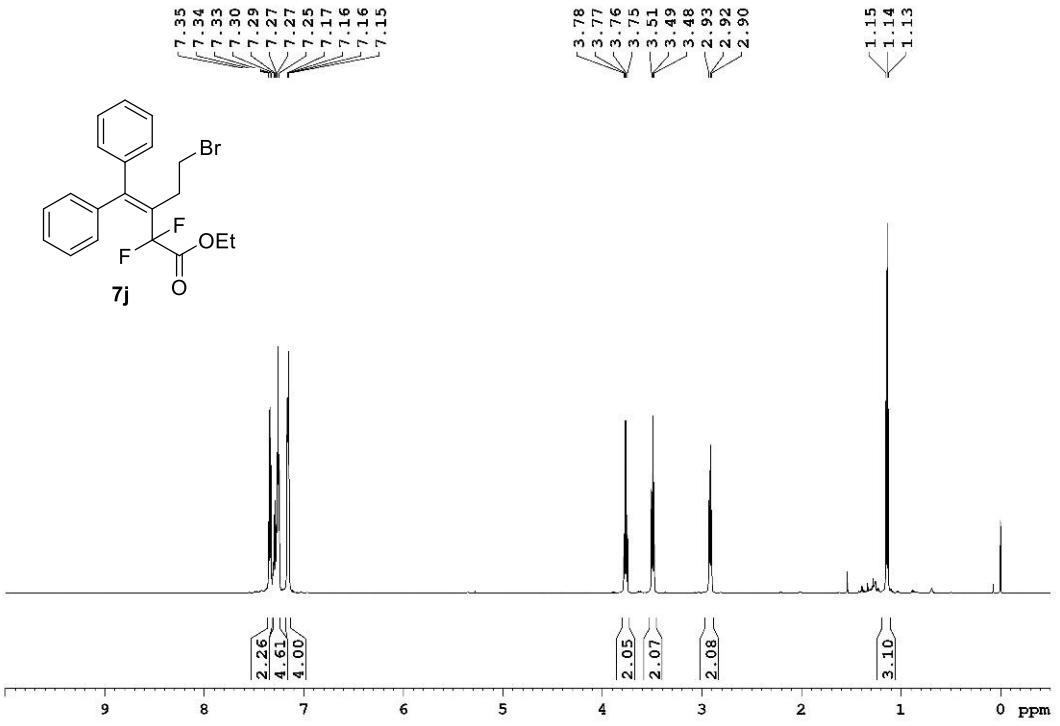
7h

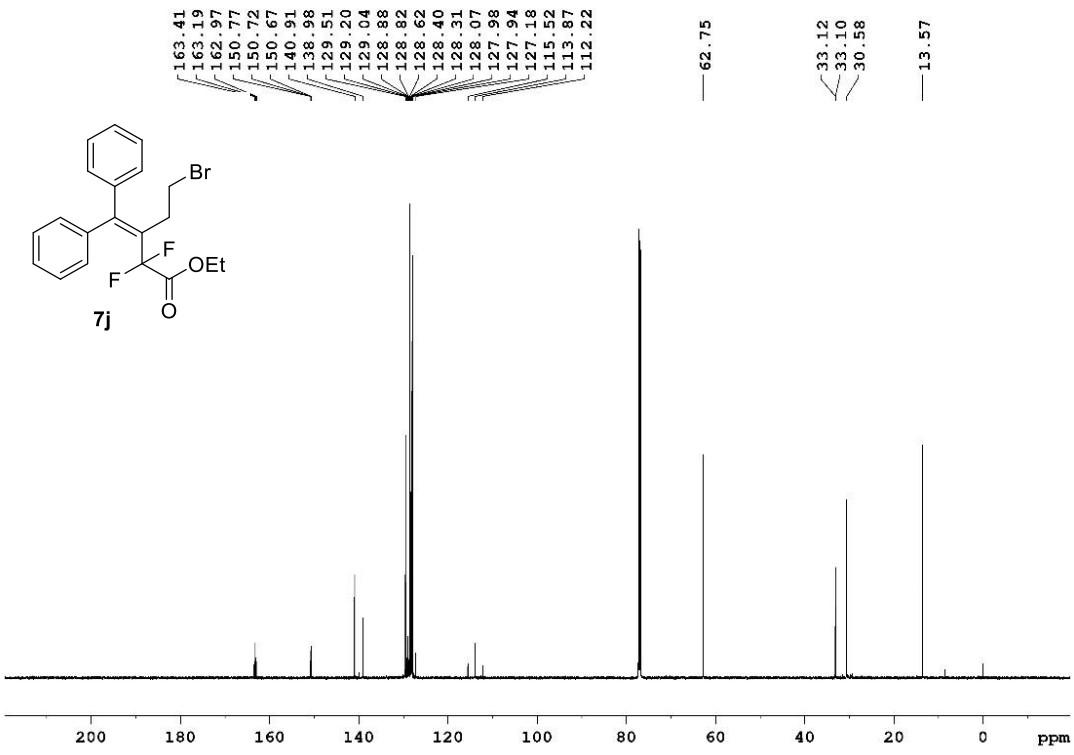
diethyl 2-(4-bromo-1,1-diphenylbut-1-en-2-yl)malonate (7i)



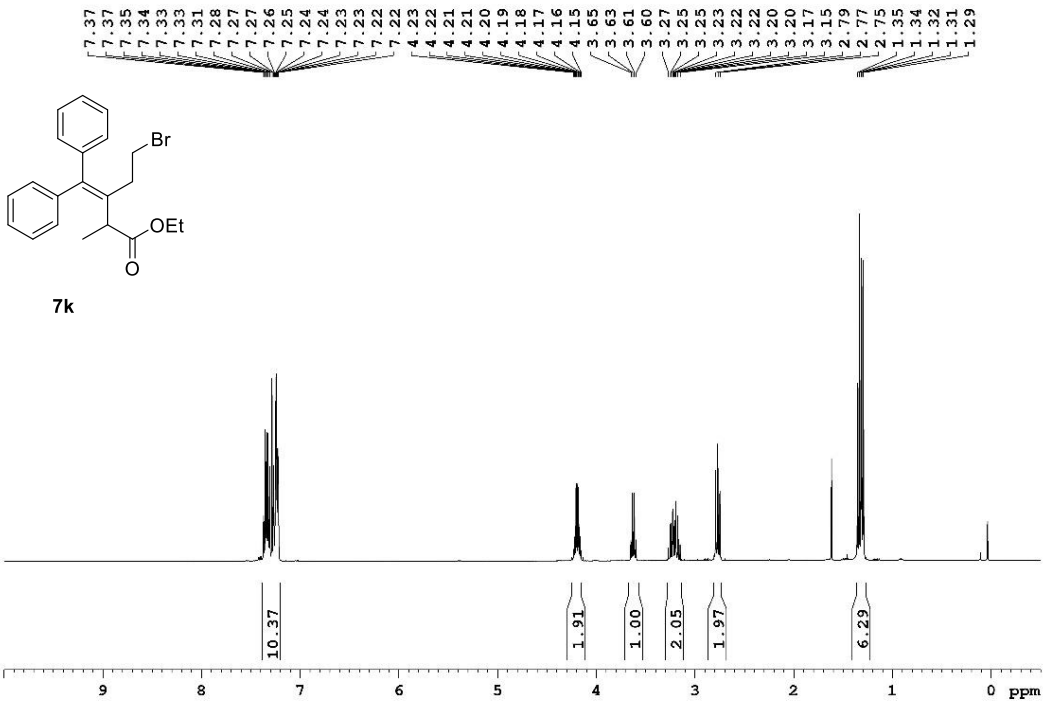


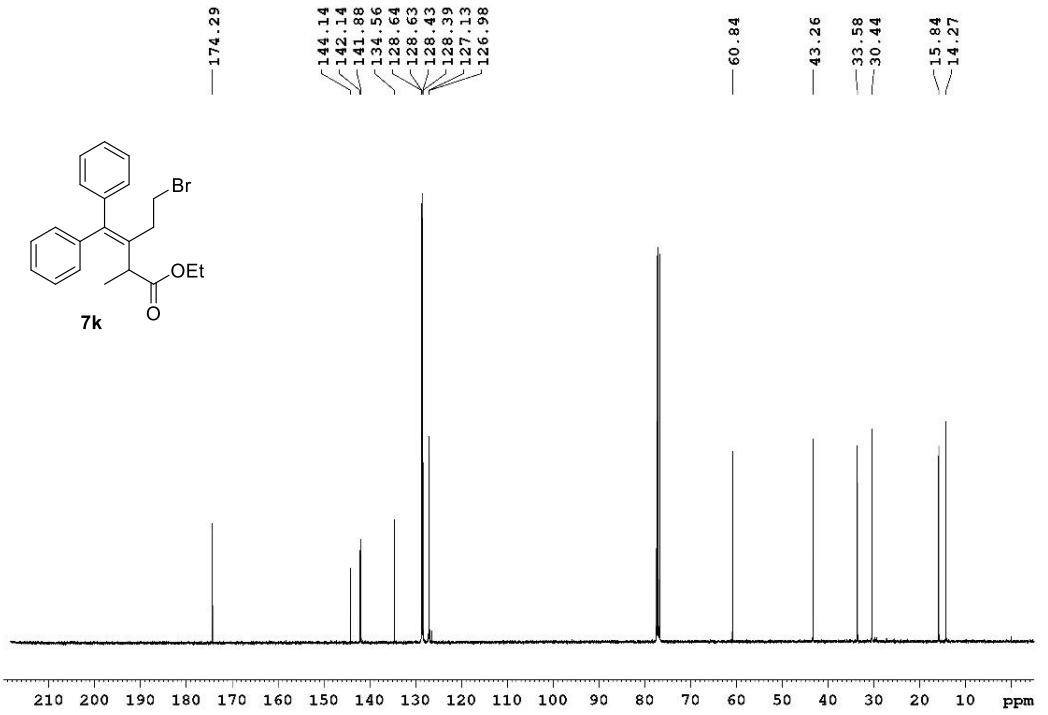
ethyl 5-bromo-3-(diphenylmethylene)-2,2-difluoropentanoate (7j)



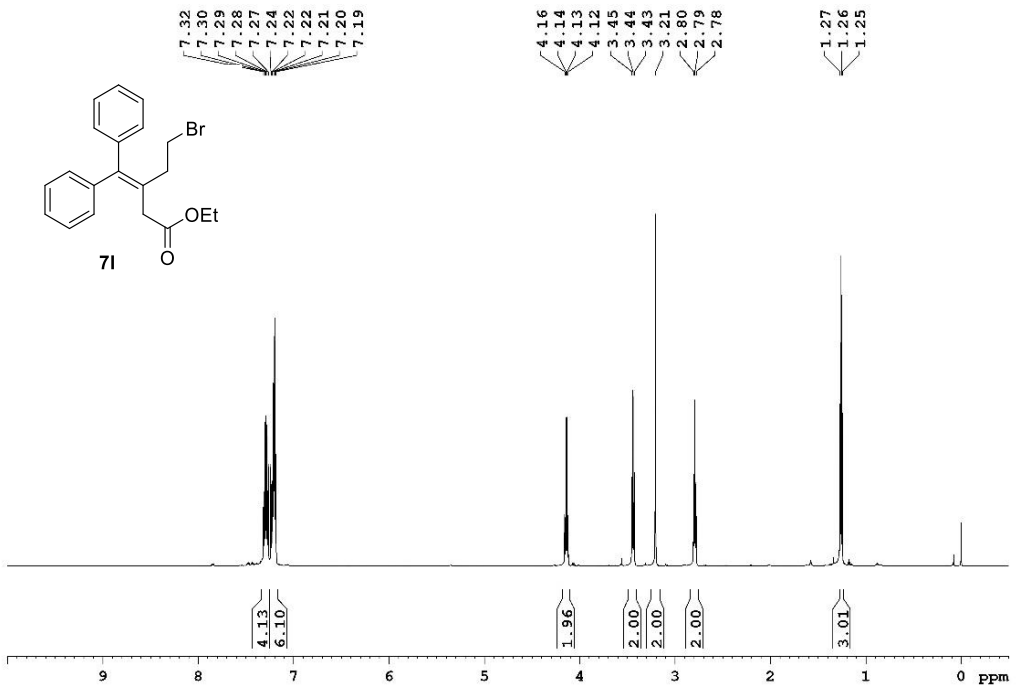


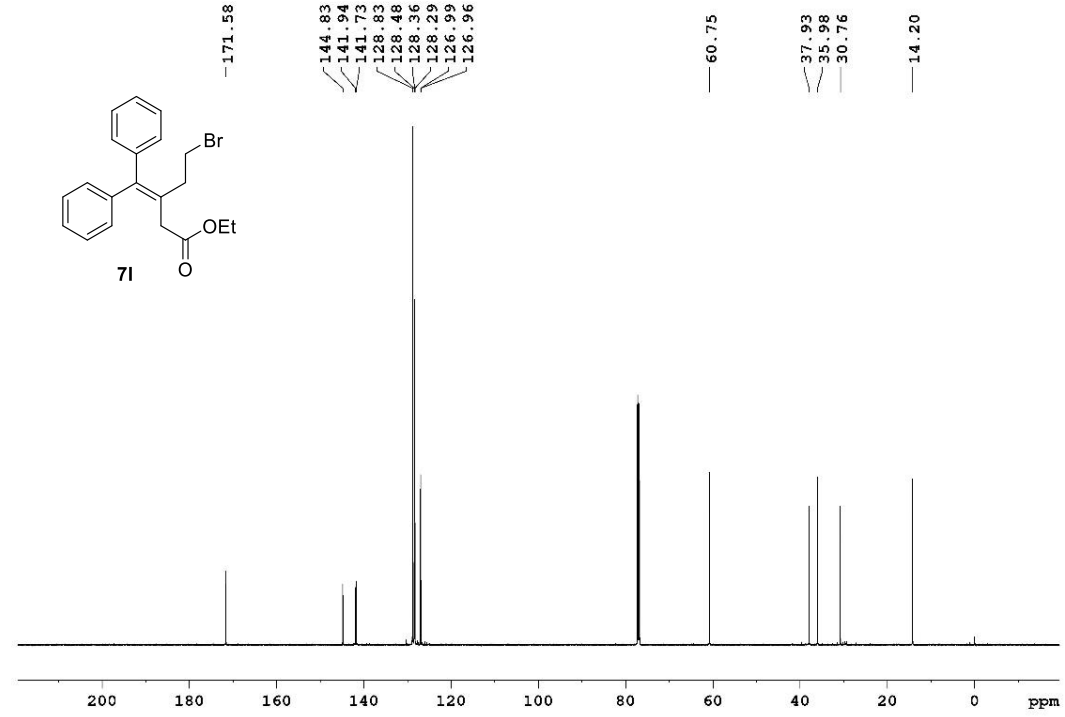
ethyl 5-bromo-3-(diphenylmethylene)-2-methylpentanoate (7k)



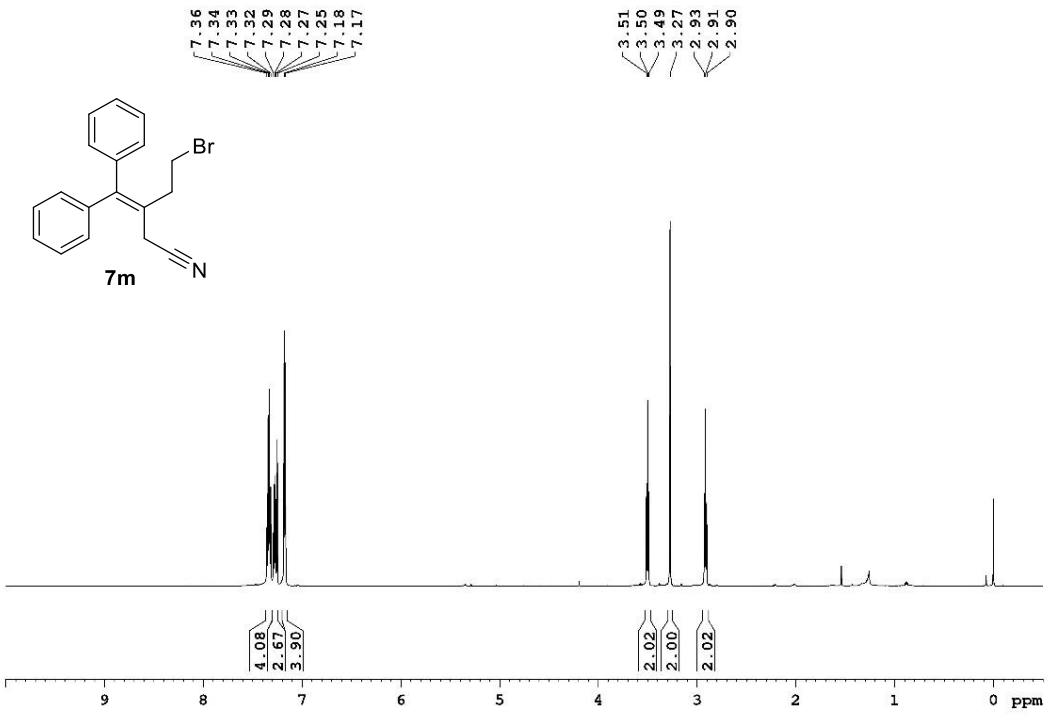


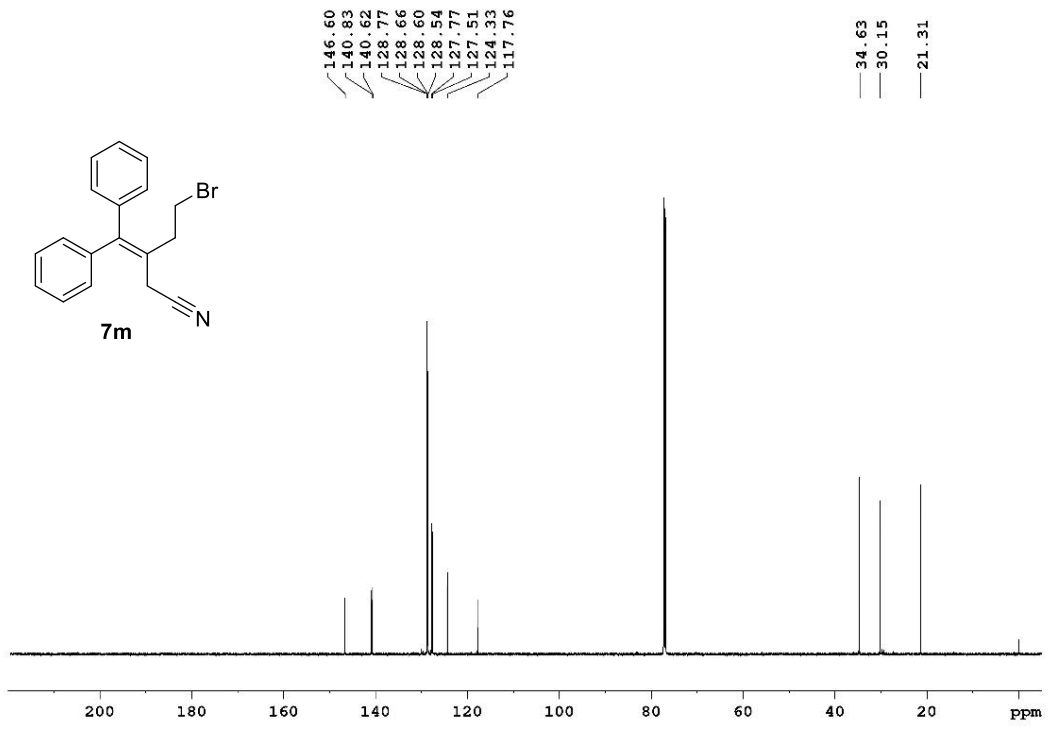
ethyl 5-bromo-3-(diphenylmethylene)pentanoate (7l)



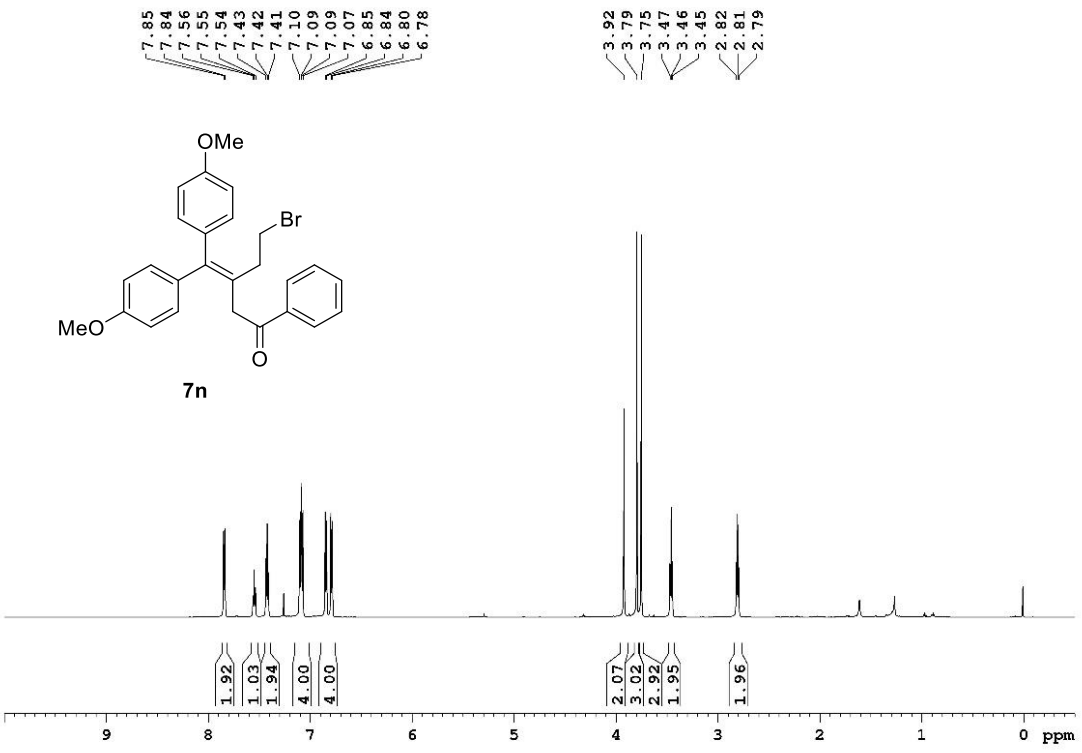


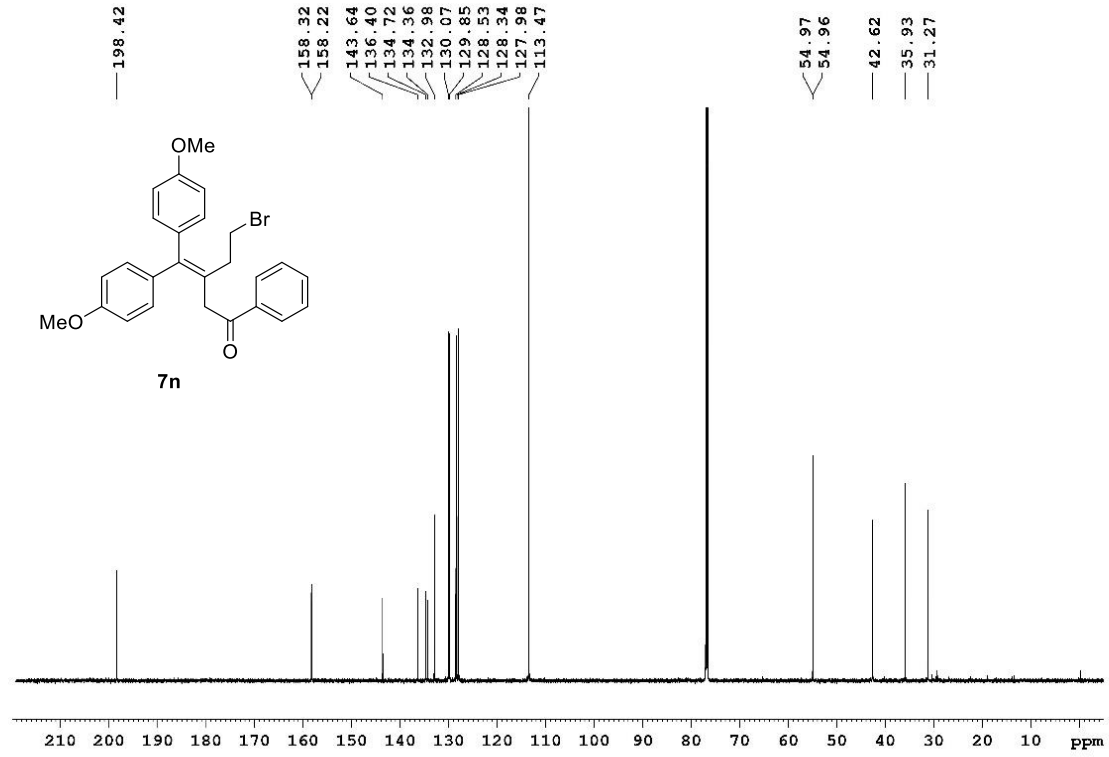
5-bromo-3-(diphenylmethylene)pentanenitrile (7m)



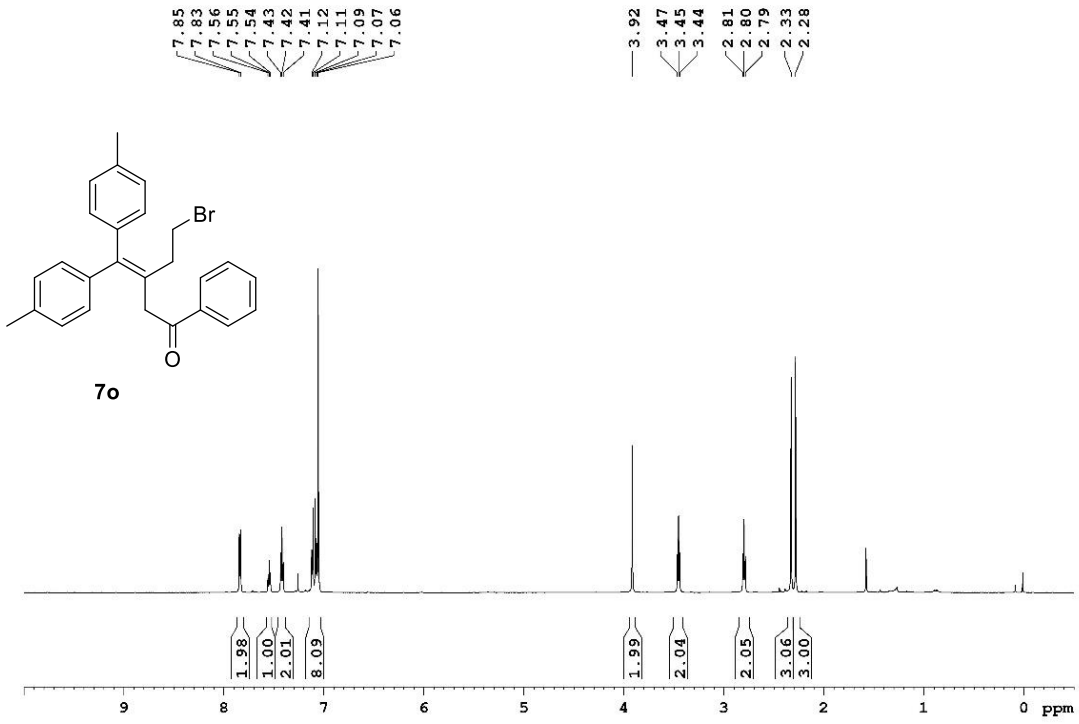


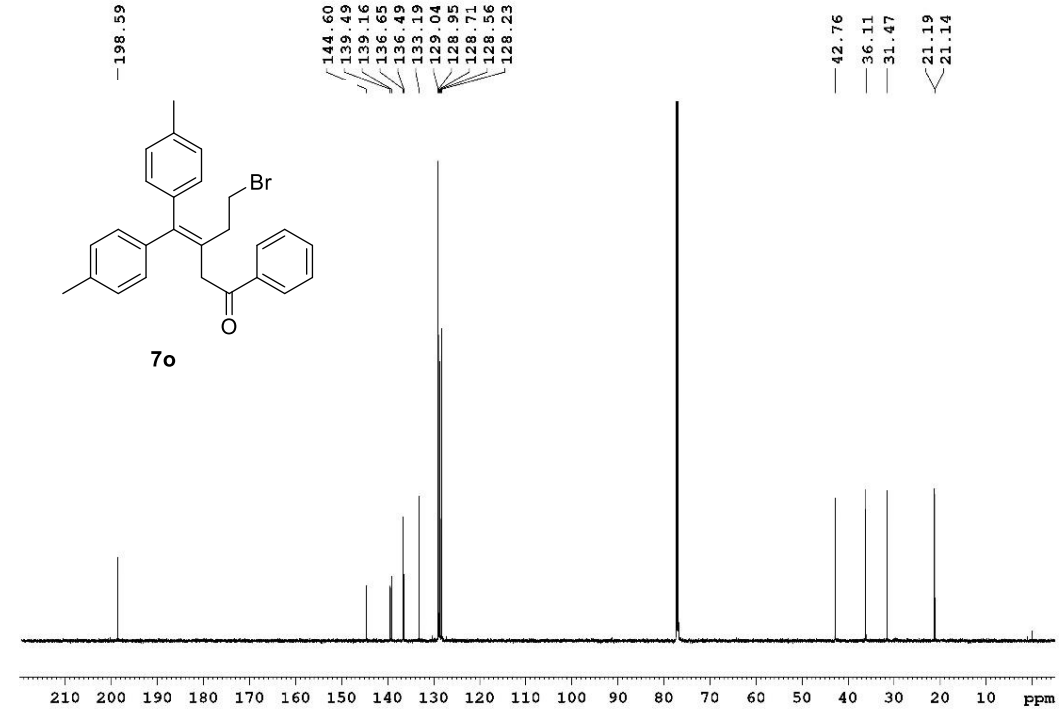
3-(bis(4-methoxyphenyl)methylene)-5-bromo-1-phenylpentan-1-one (7n)



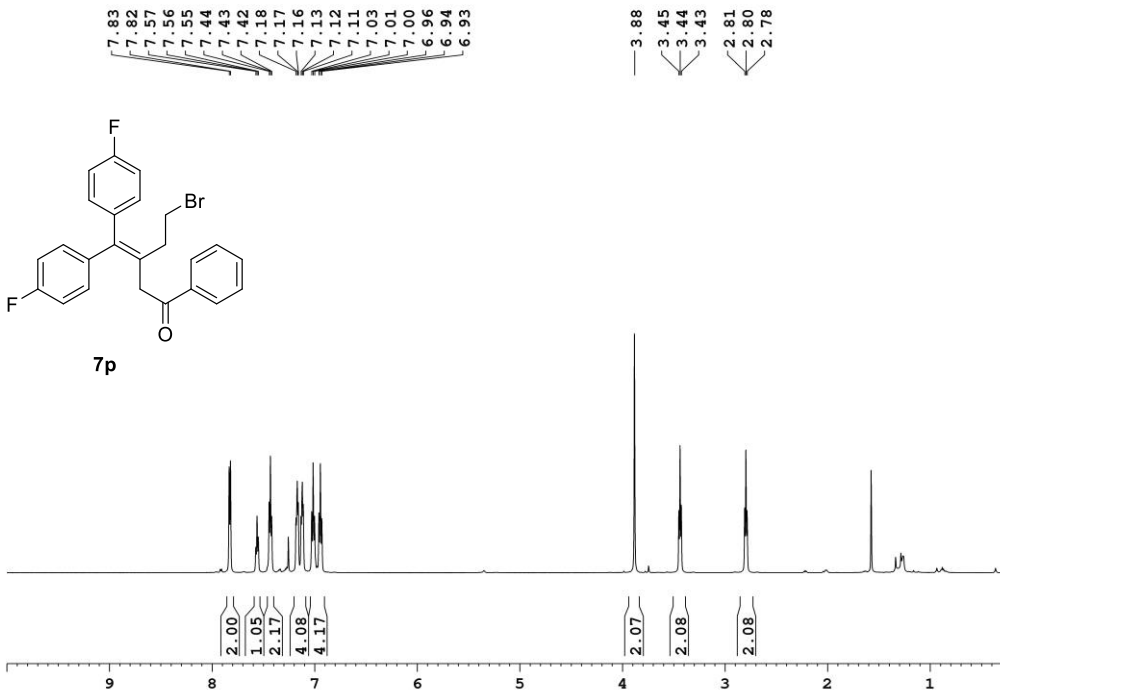


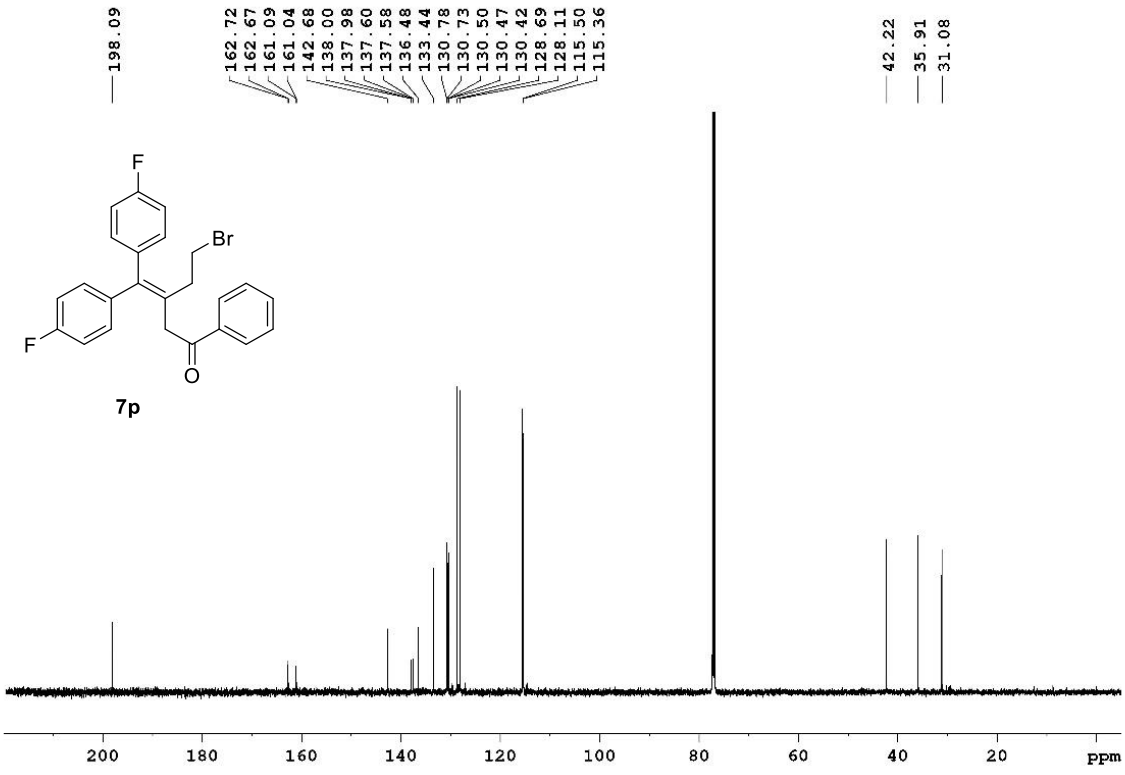
5-bromo-3-(di-p-tolylmethylene)-1-phenylpentan-1-one (7o)



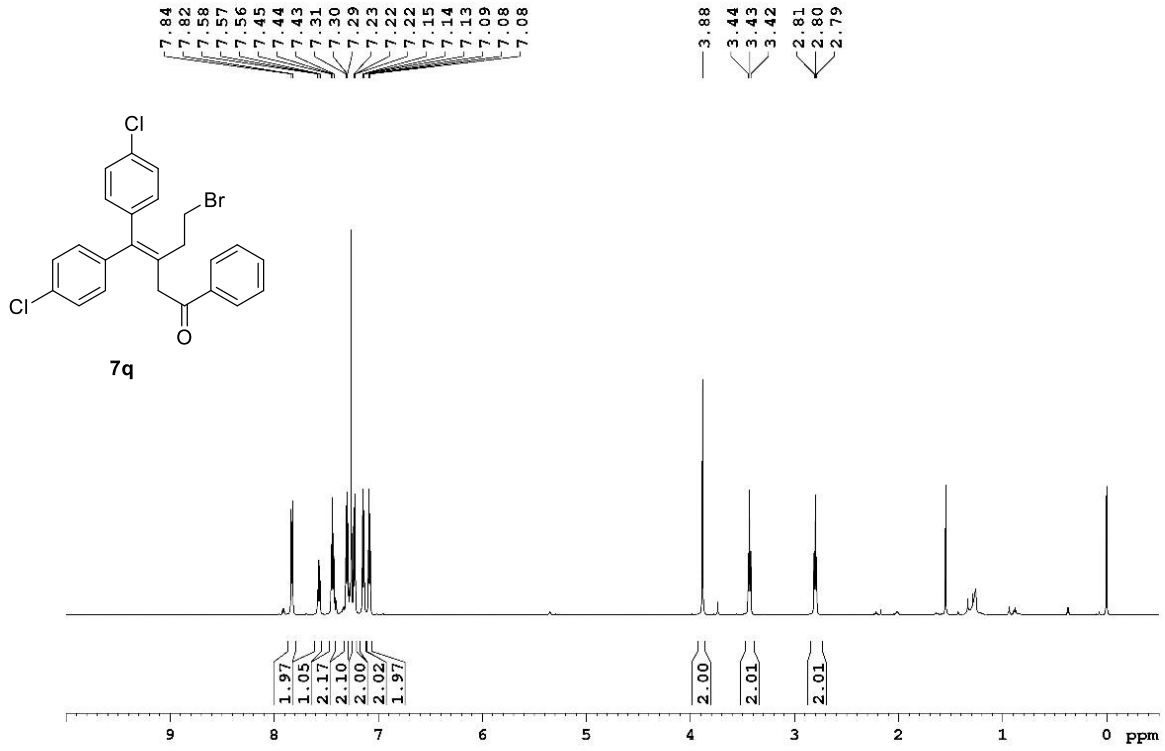


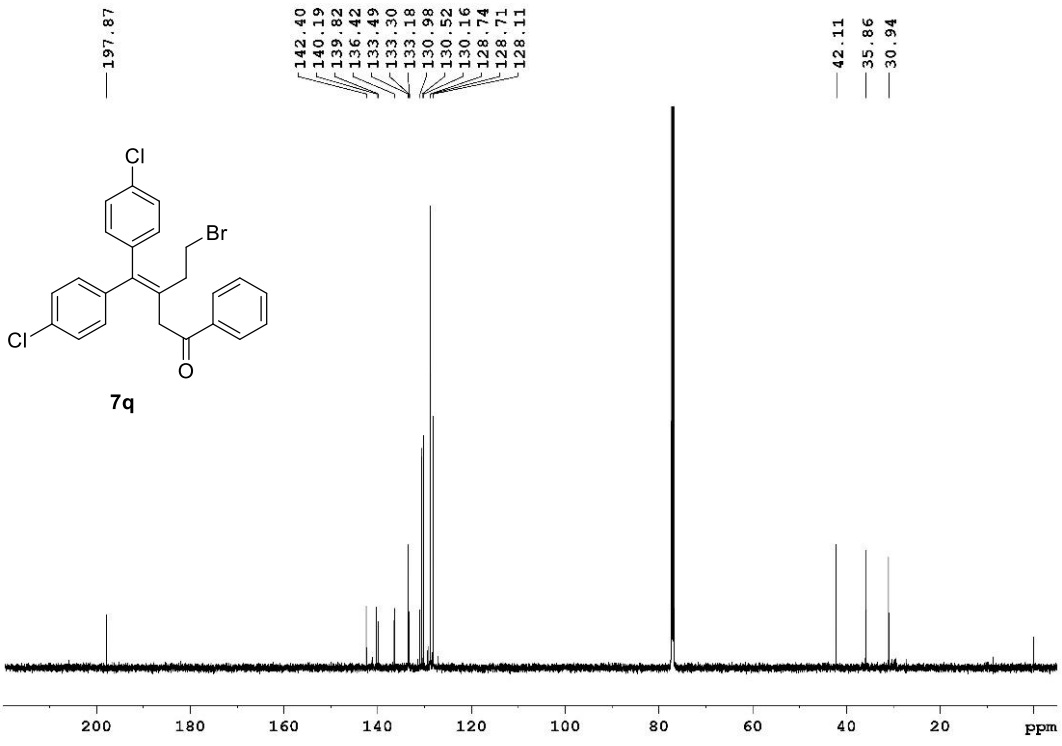
3-(bis(4-fluorophenyl)methylene)-5-bromo-1-phenylpentan-1-one (7p)



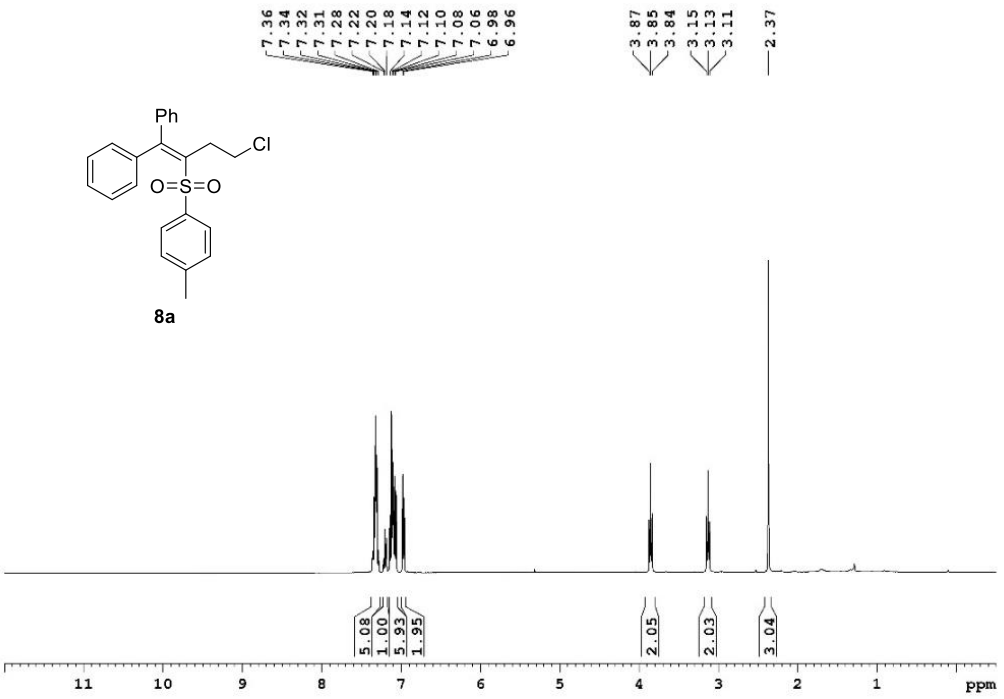


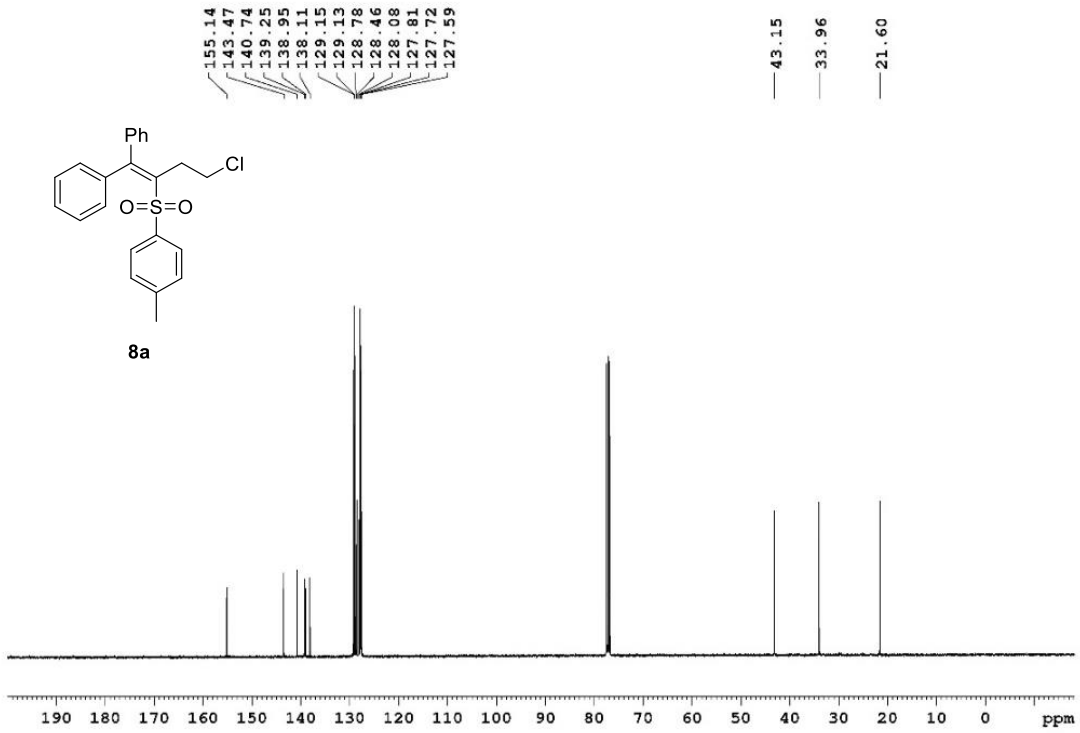
3-(bis(4-chlorophenyl)methylene)-5-bromo-1-phenylpentan-1-one (7q)



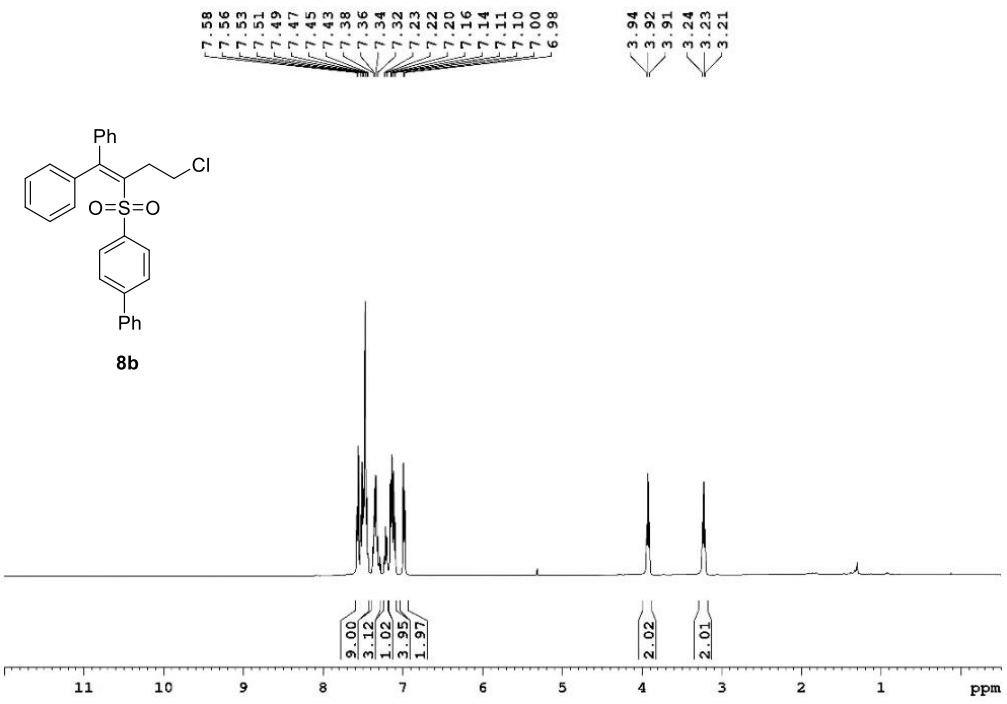


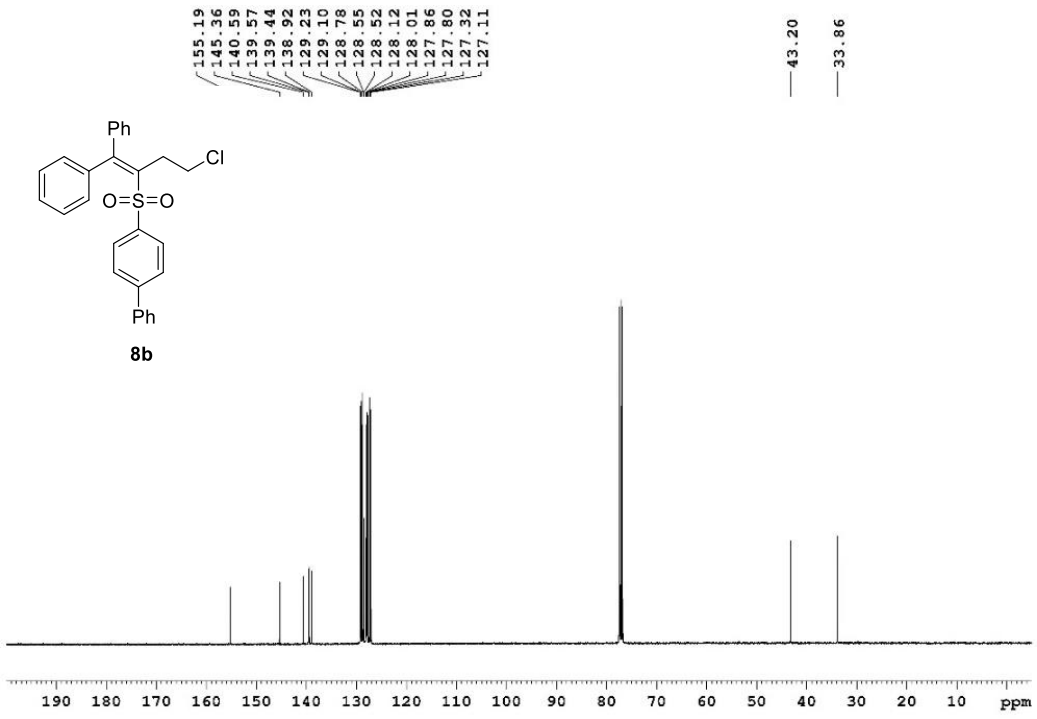
(4-chloro-2-tosylbut-1-ene-1,1-diyl)dibenzene (8a)



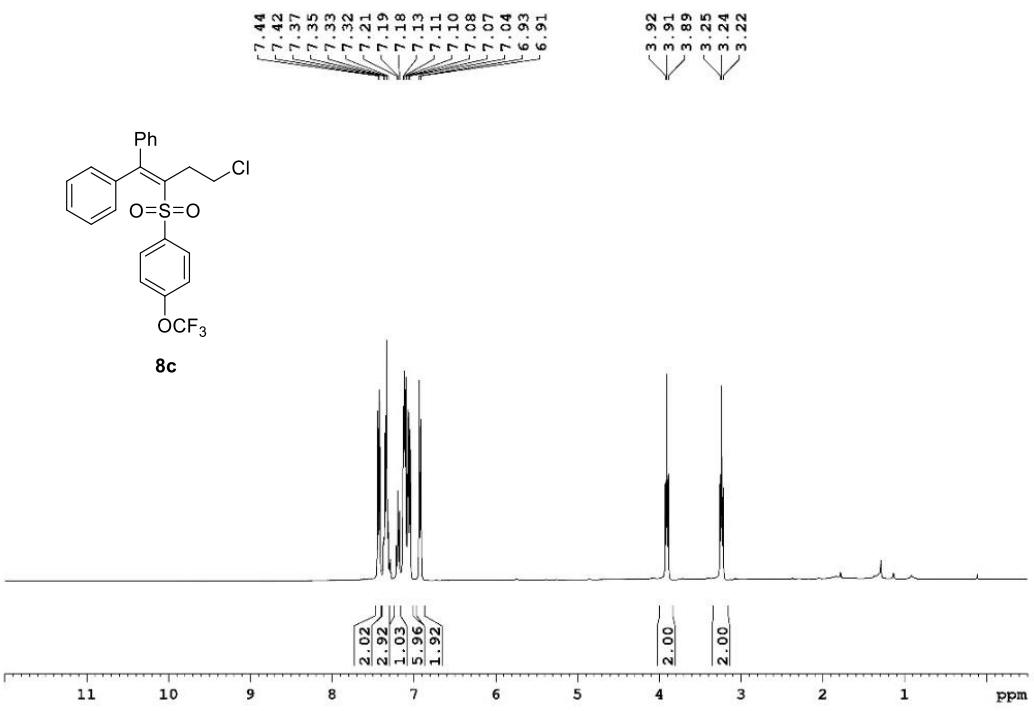


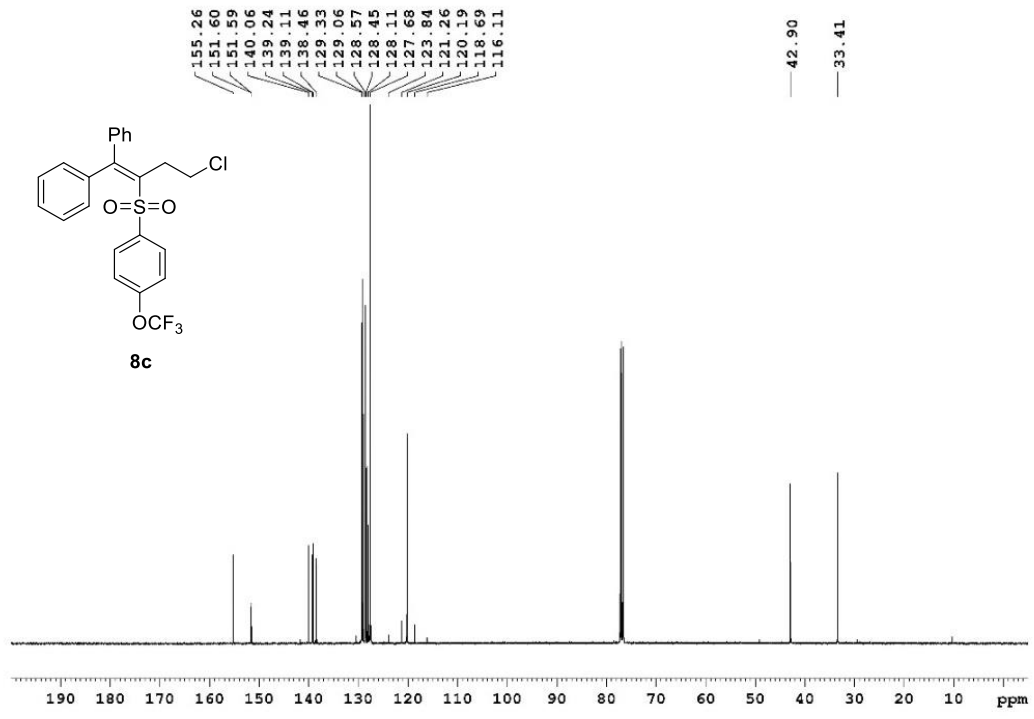
4-((4-chloro-1,1-diphenylbut-1-en-2-yl)sulfonyl)-1,1'-biphenyl (8b)





(4-chloro-2-((4-(trifluoromethoxy)phenyl)sulfonyl)but-1-ene-1,1-diyl)dibenzene (8c)





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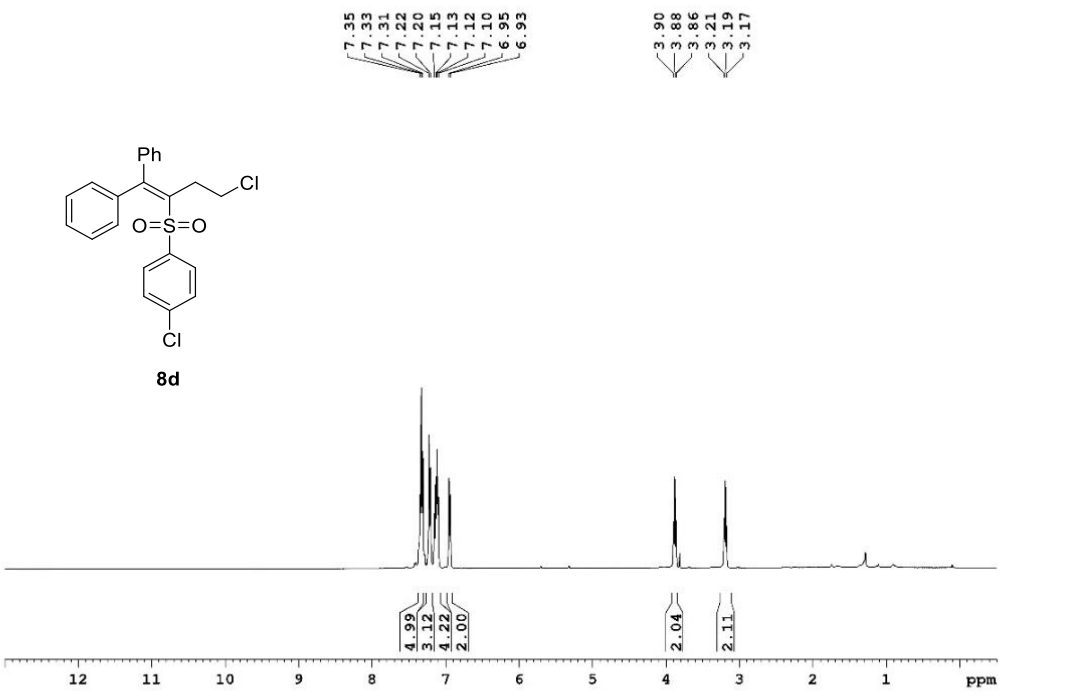
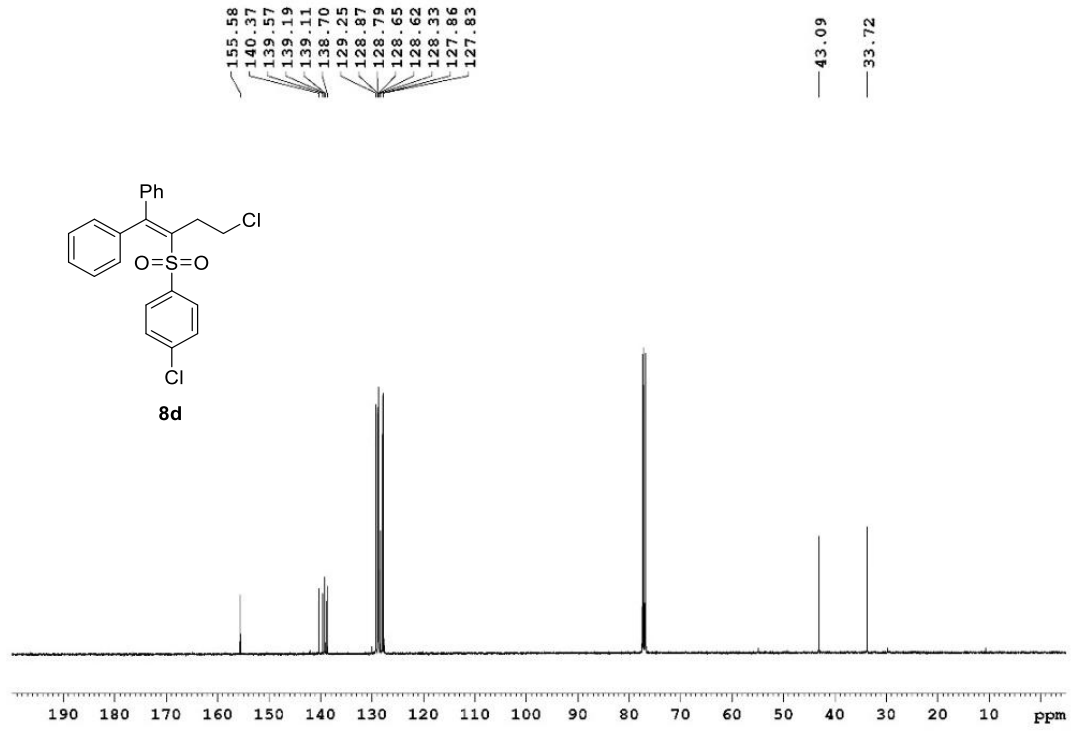
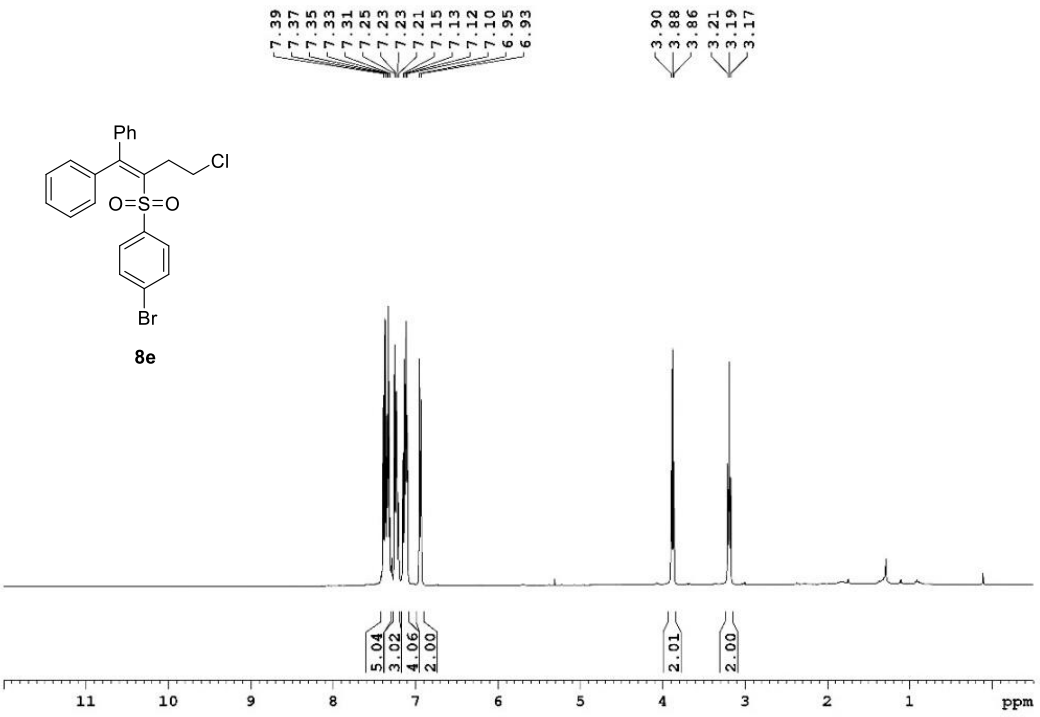
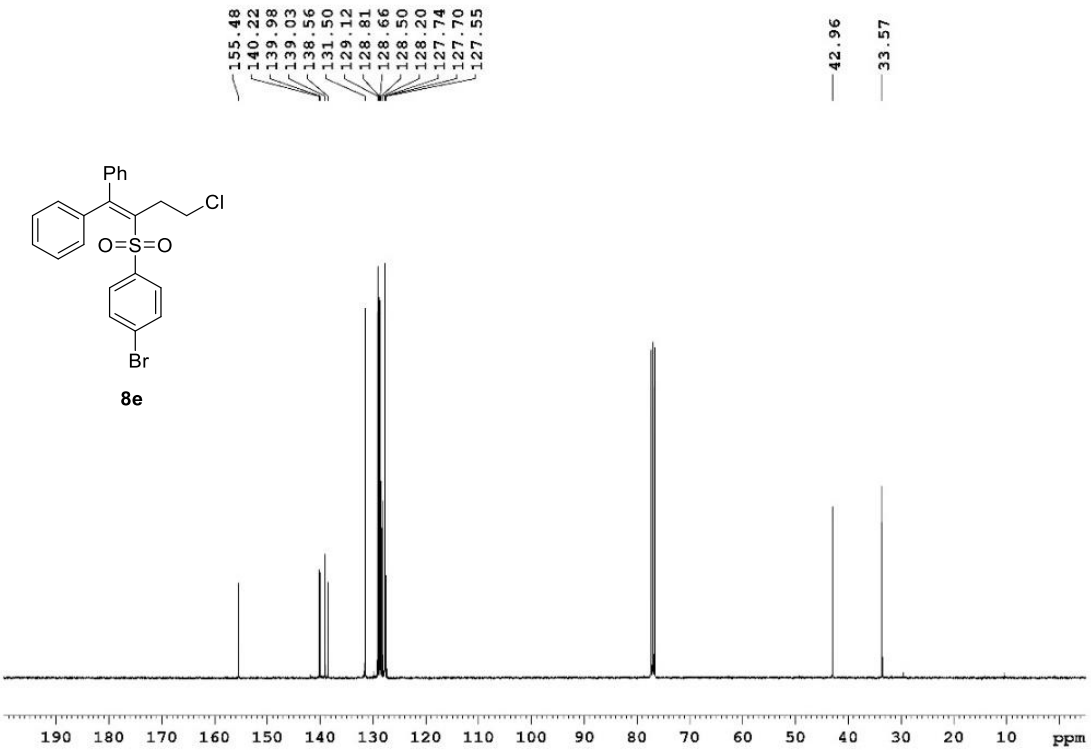


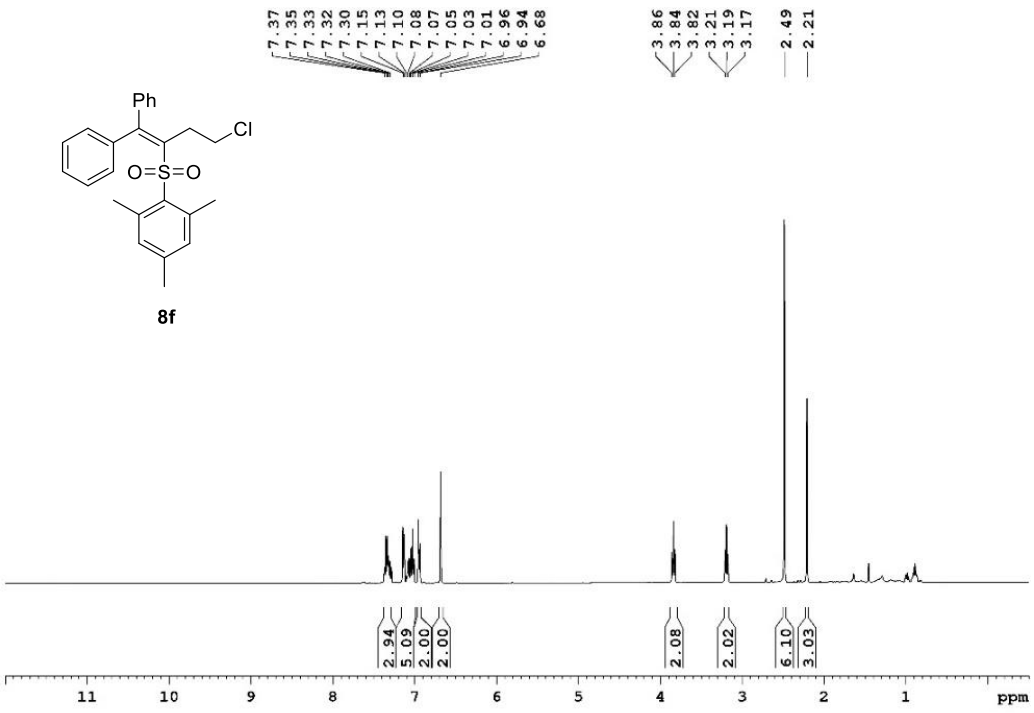


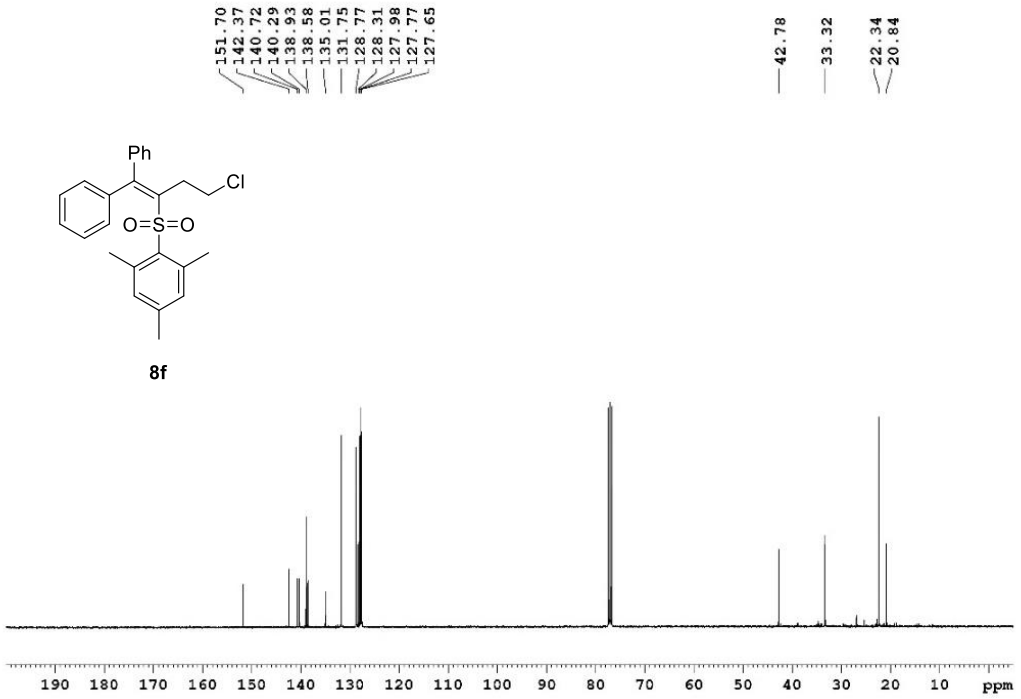
(2-((4-bromophenyl)sulfonyl)-4-chlorobut-1-ene-1,1-diyl)dibenzene (8e)



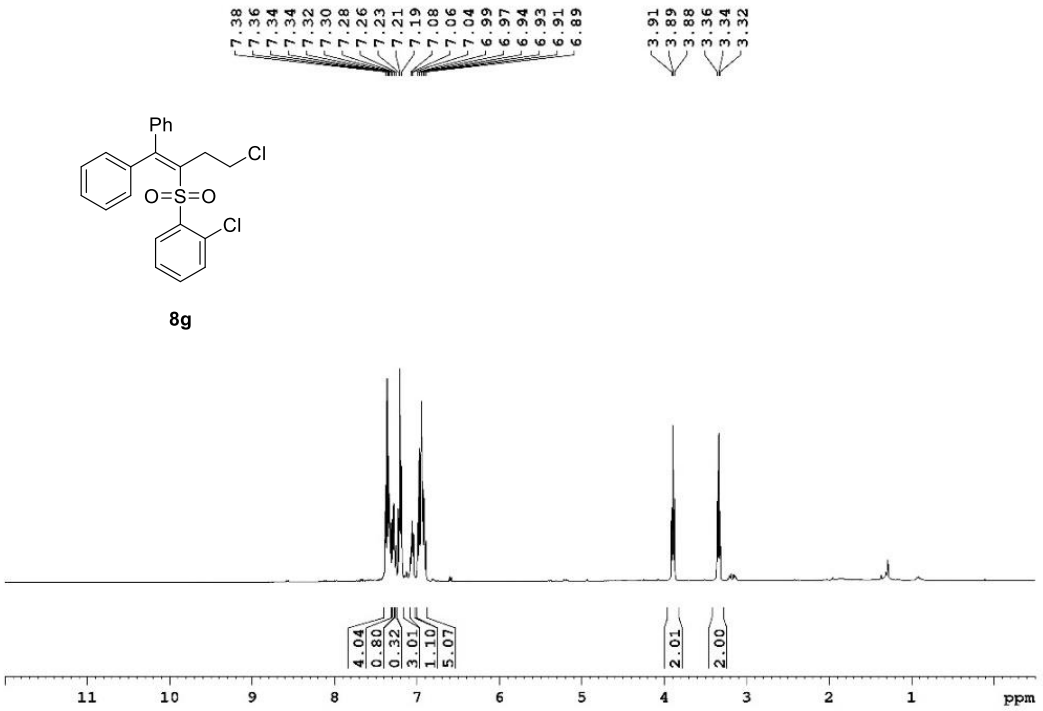


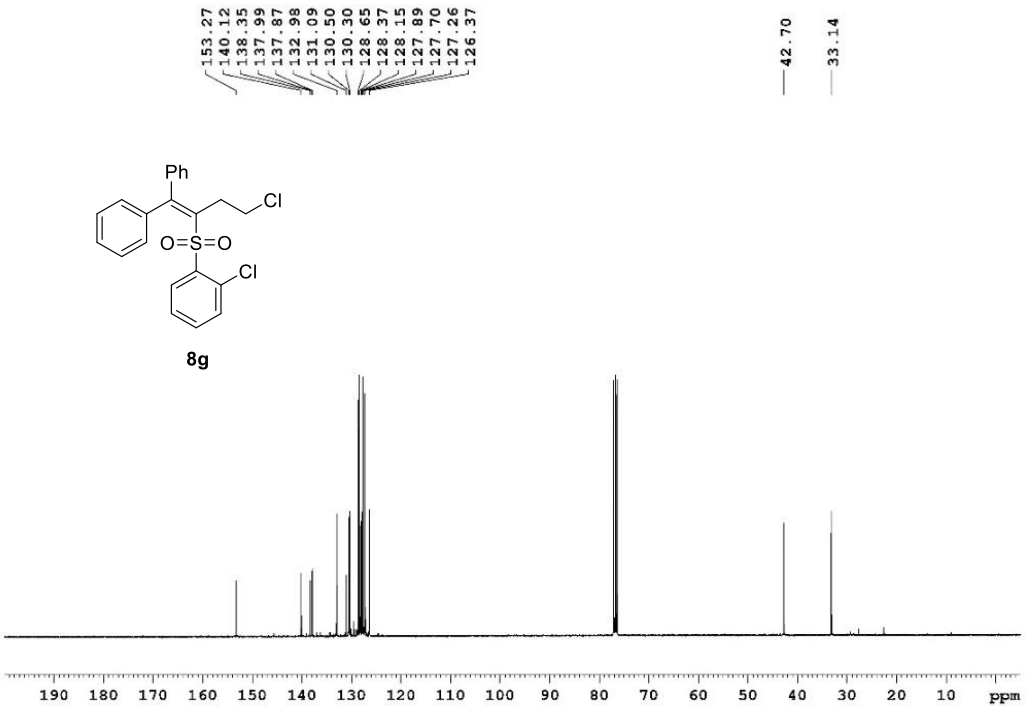
(4-chloro-2-(mesitylsulfonyl)but-1-ene-1,1-diyl)dibenzene (8f)



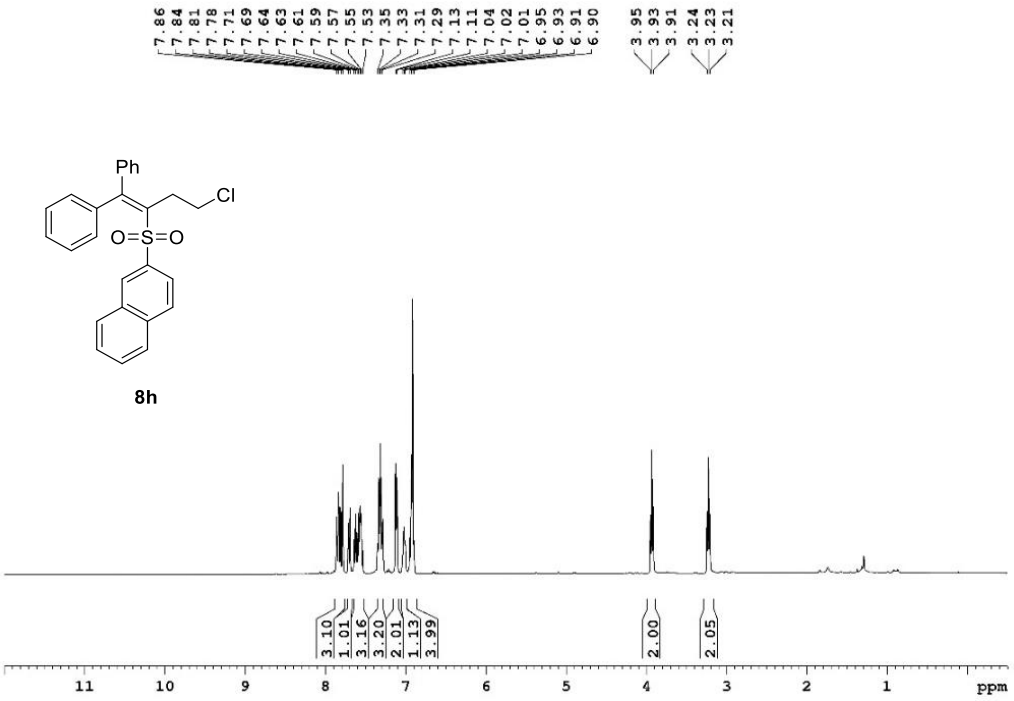


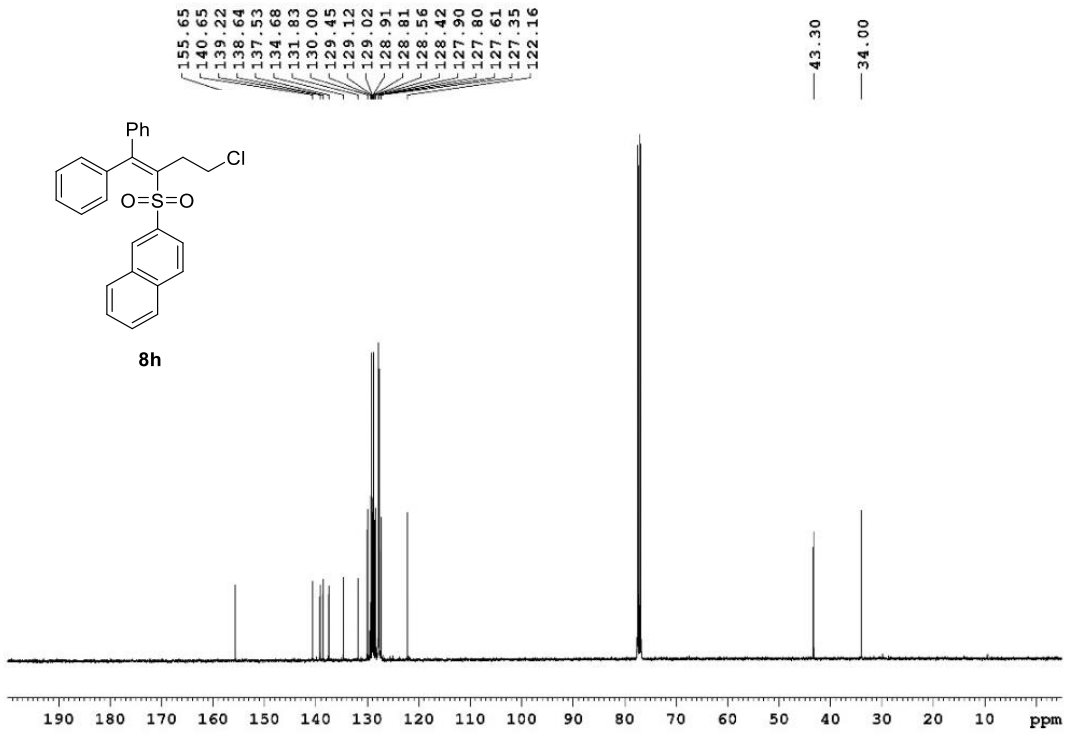
(4-chloro-2-((2-chlorophenyl)sulfonyl)but-1-ene-1,1-diyl)dibenzene (8g)



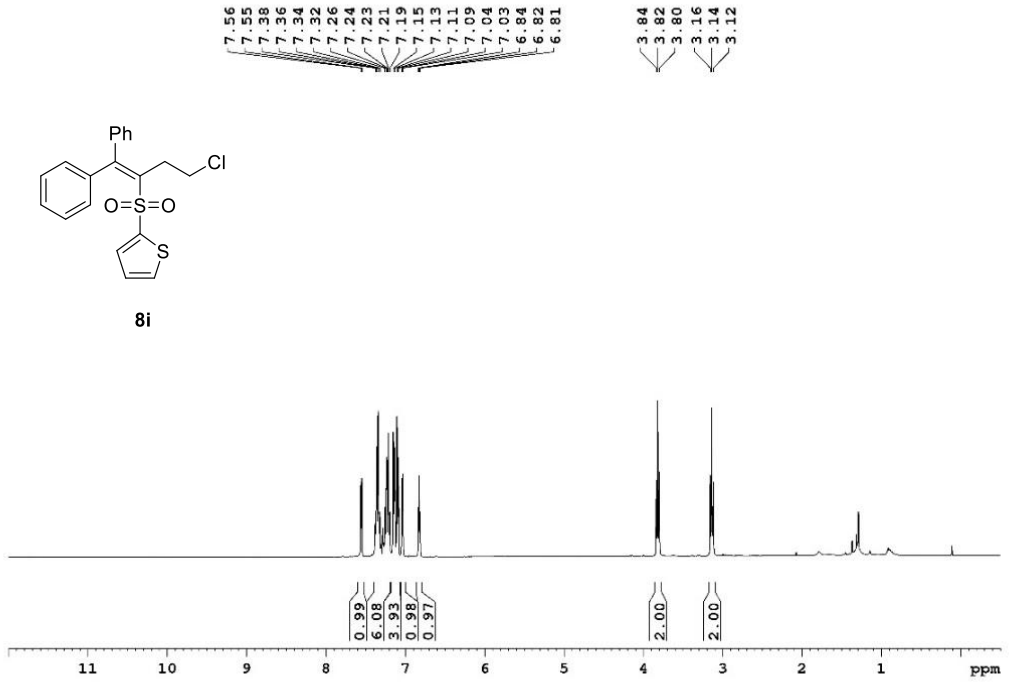


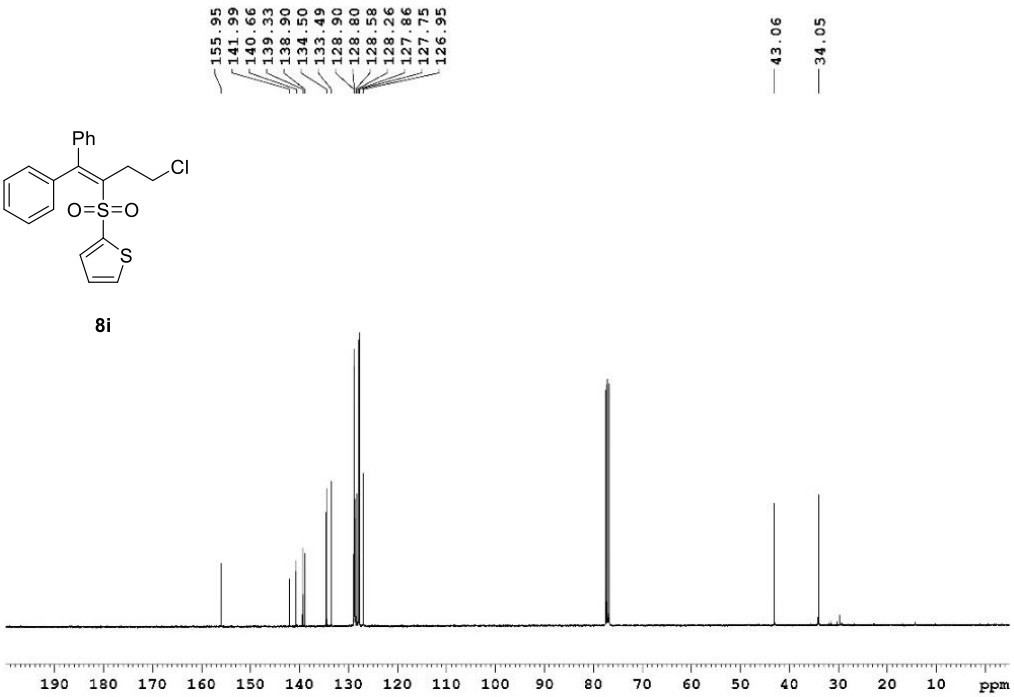
2-((4-chloro-1,1-diphenylbut-1-en-2-yl)sulfonyl)naphthalene (8h)



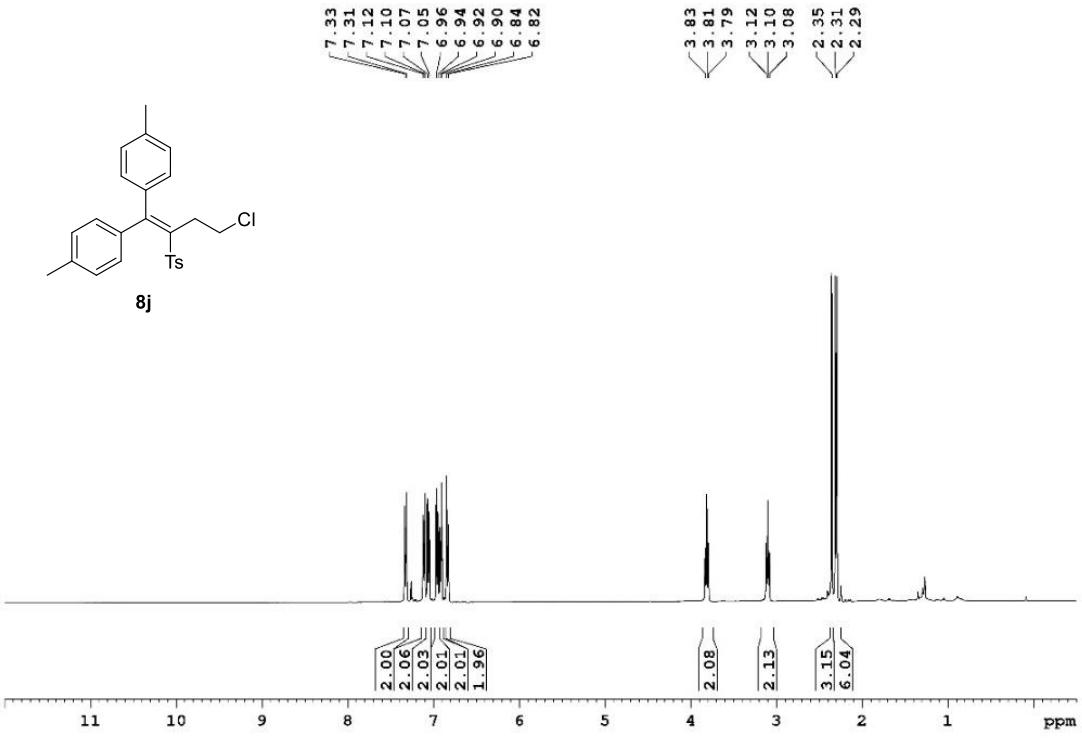


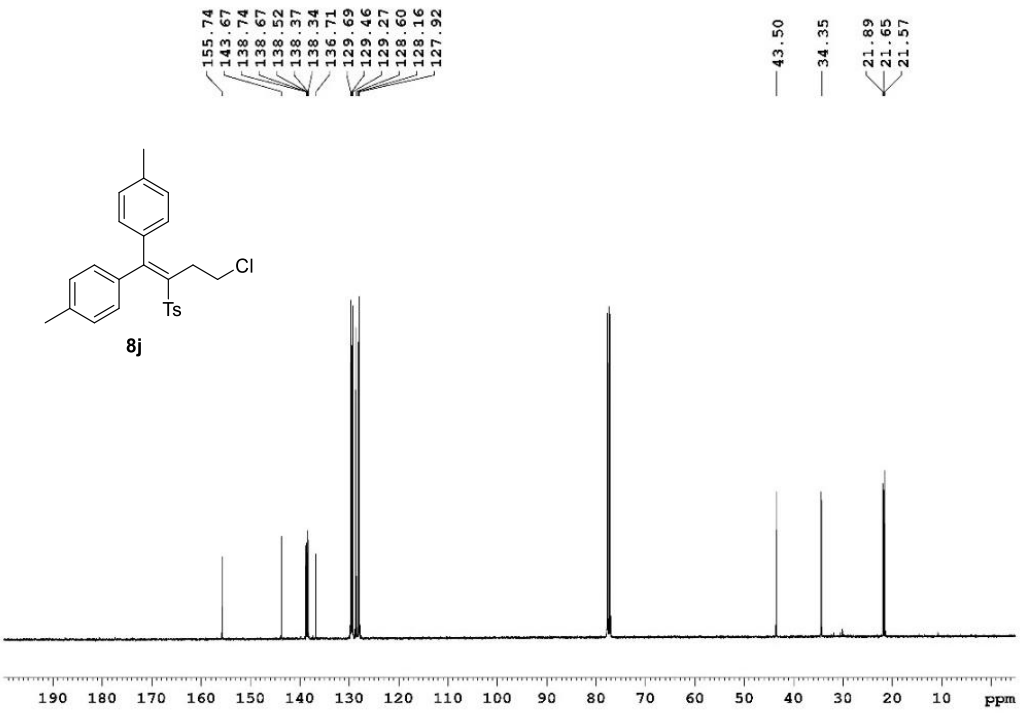
2-((4-chloro-1,1-diphenylbut-1-en-2-yl)sulfonyl)thiophene (8i)



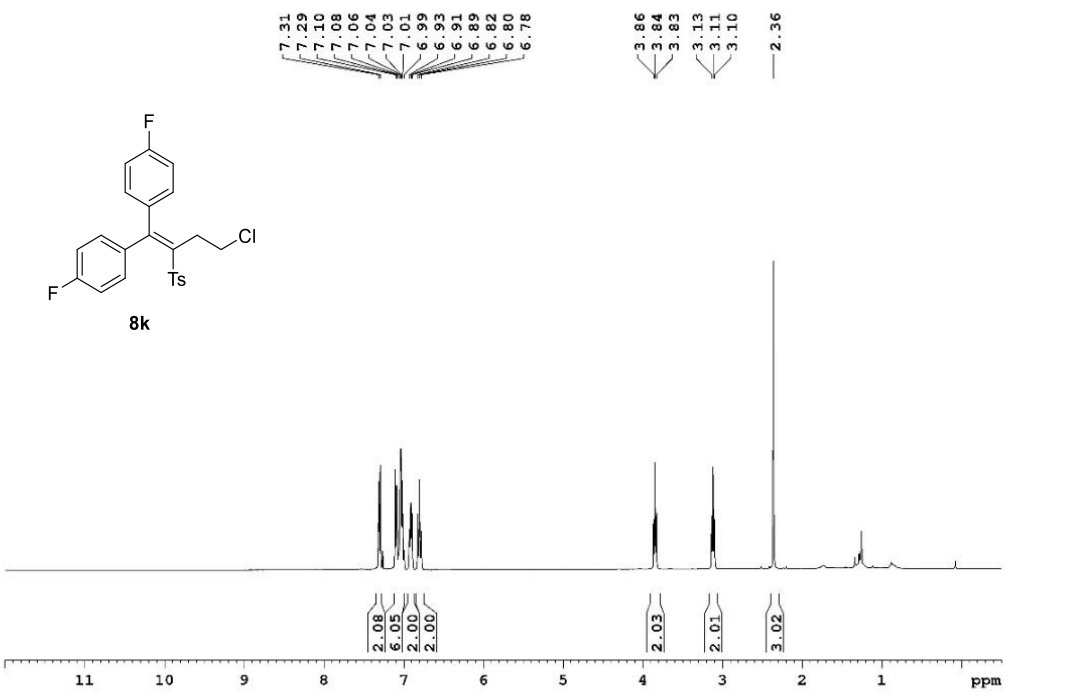


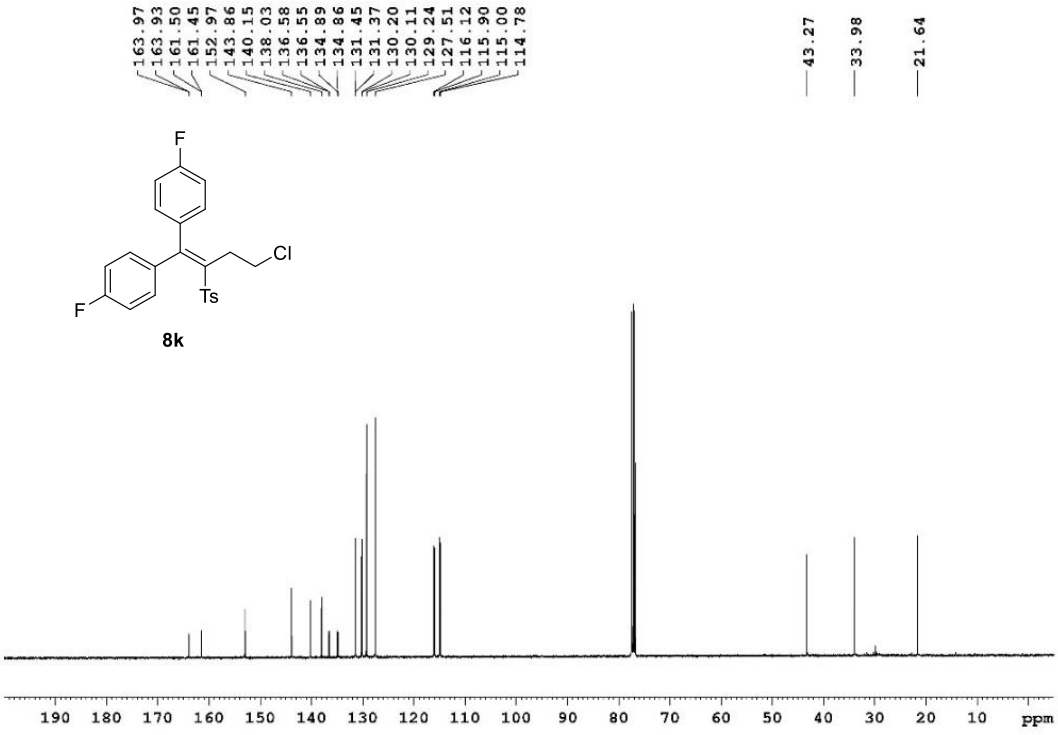
4,4'-(4-chloro-2-tosylbut-1-ene-1,1-diyl)bis(methylbenzene) (8j)





4,4'-(4-chloro-2-tosylbut-1-ene-1,1-diyl)bis(fluorobenzene) (8k)





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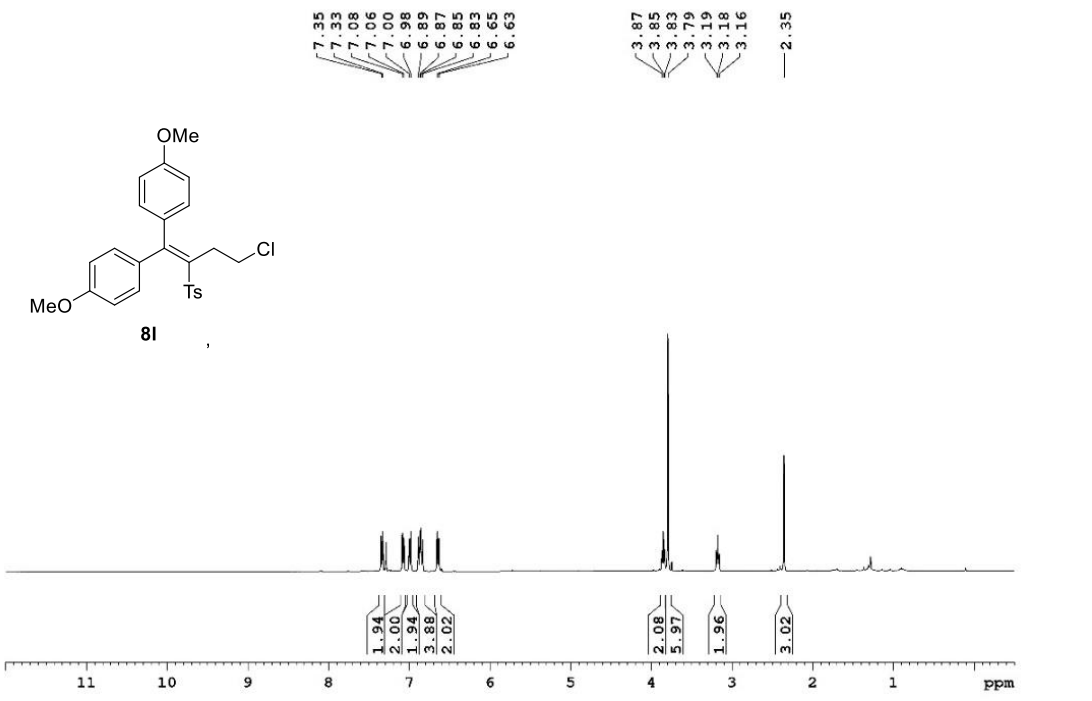
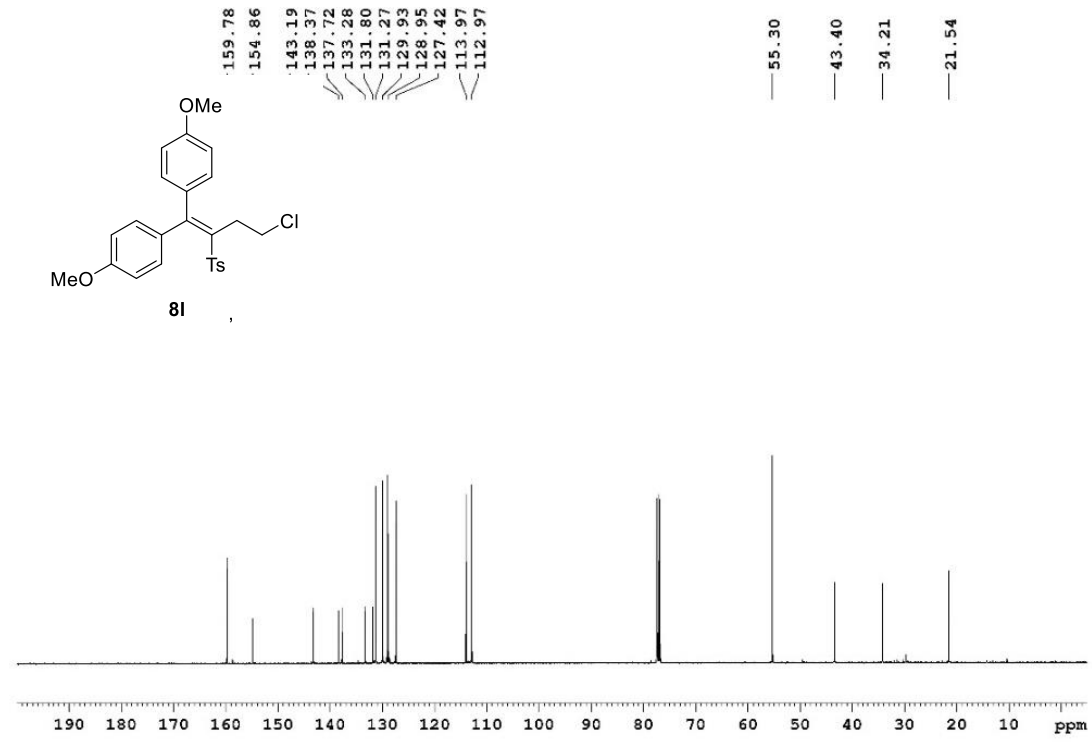
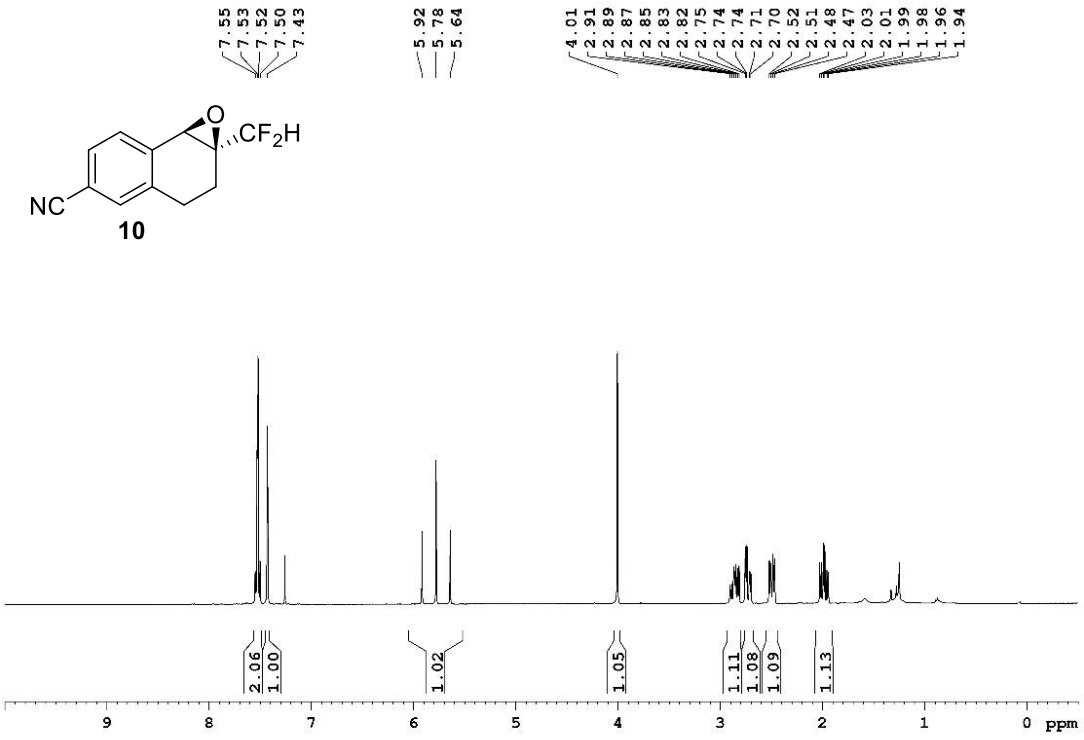
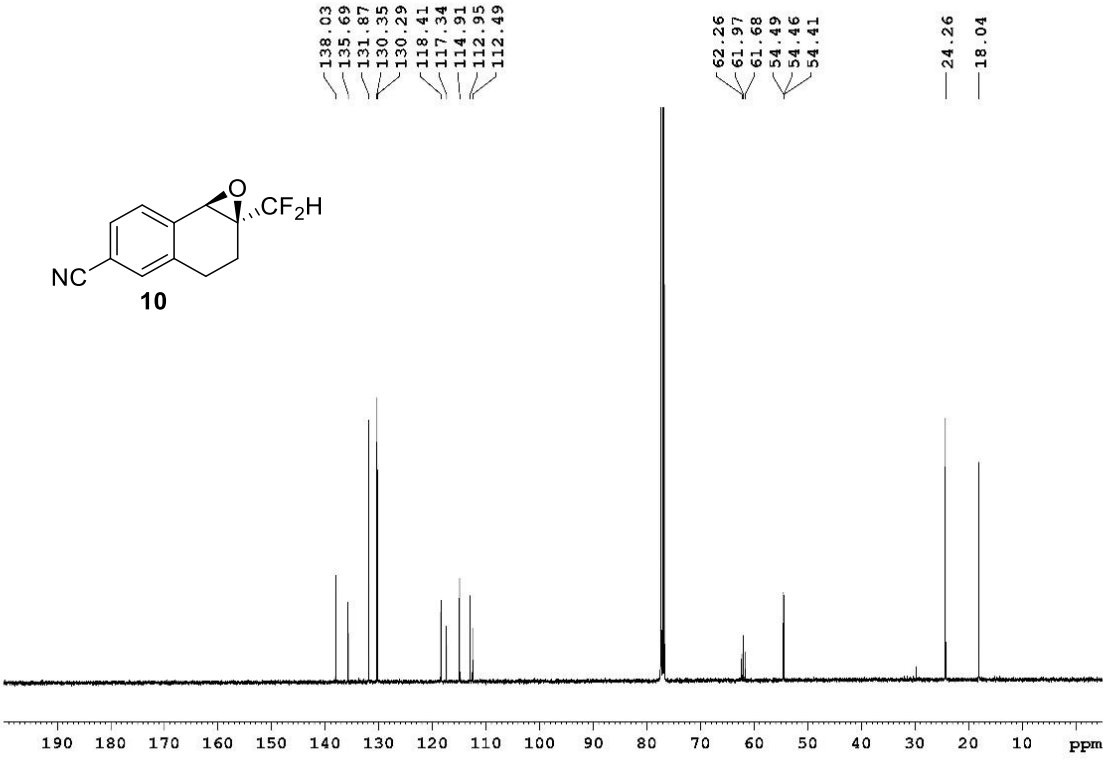
4,4'-(4-chloro-2-tosylbut-1-ene-1,1-diyl)bis(methoxybenzene) (8l)



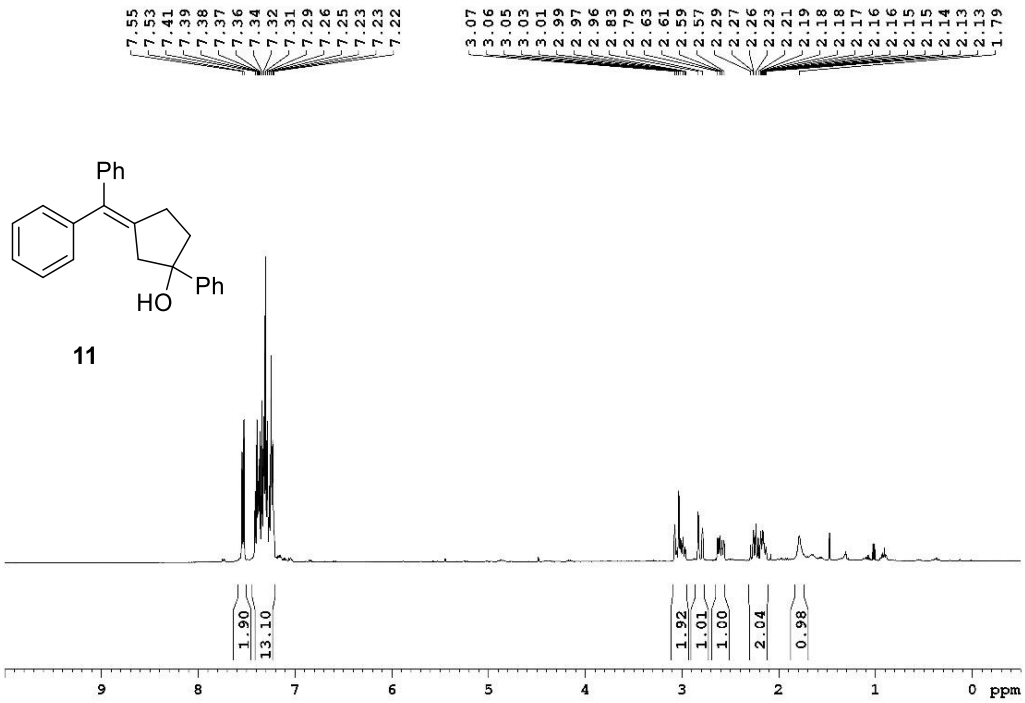


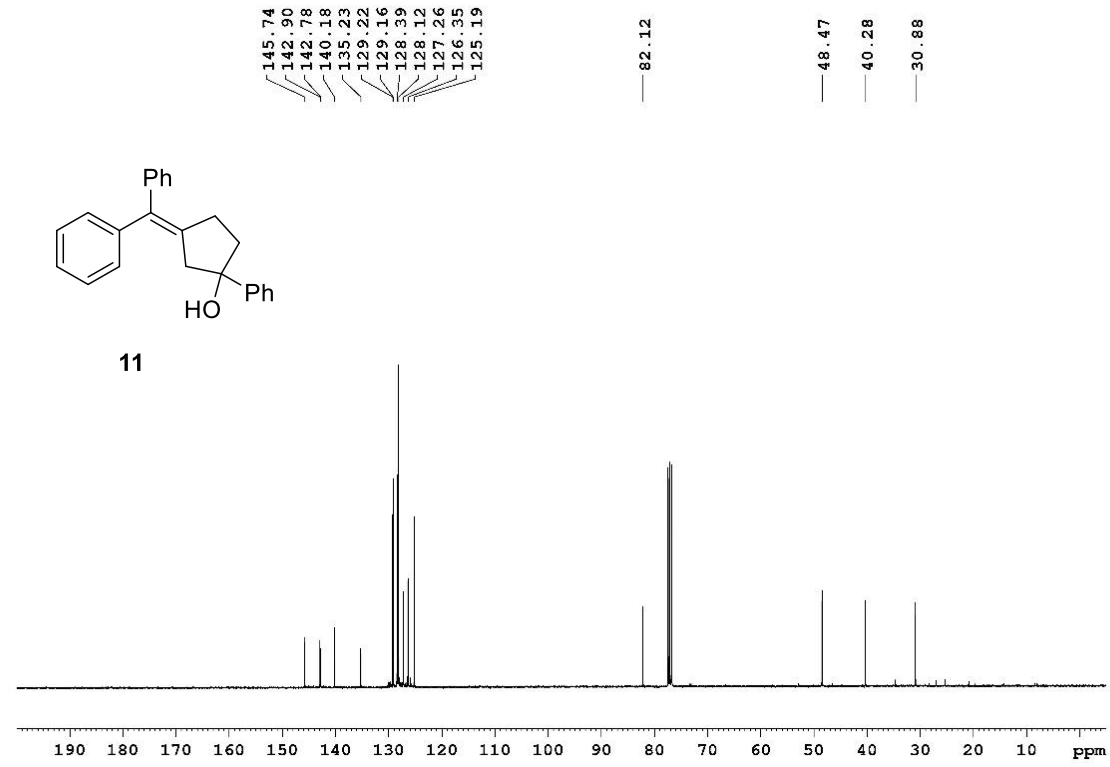
(1aS,7bR)-1a-(difluoromethyl)-1a,2,3,7b-tetrahydronaphtho[1,2-b]oxirene-5-carbonitrile (10)



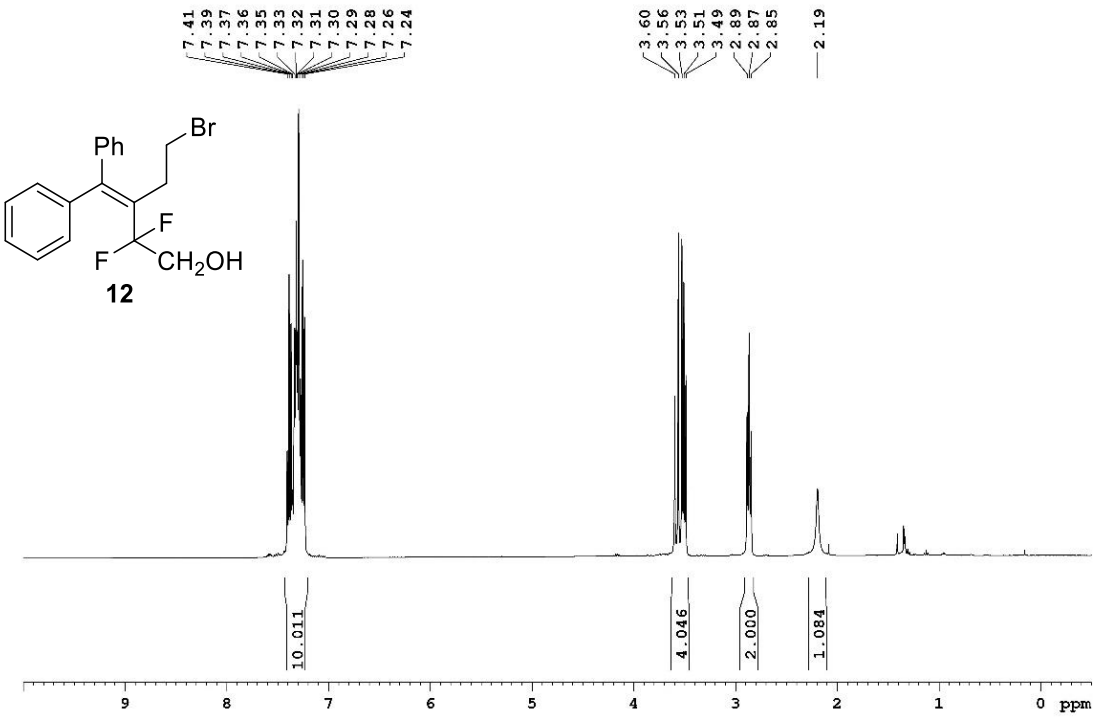


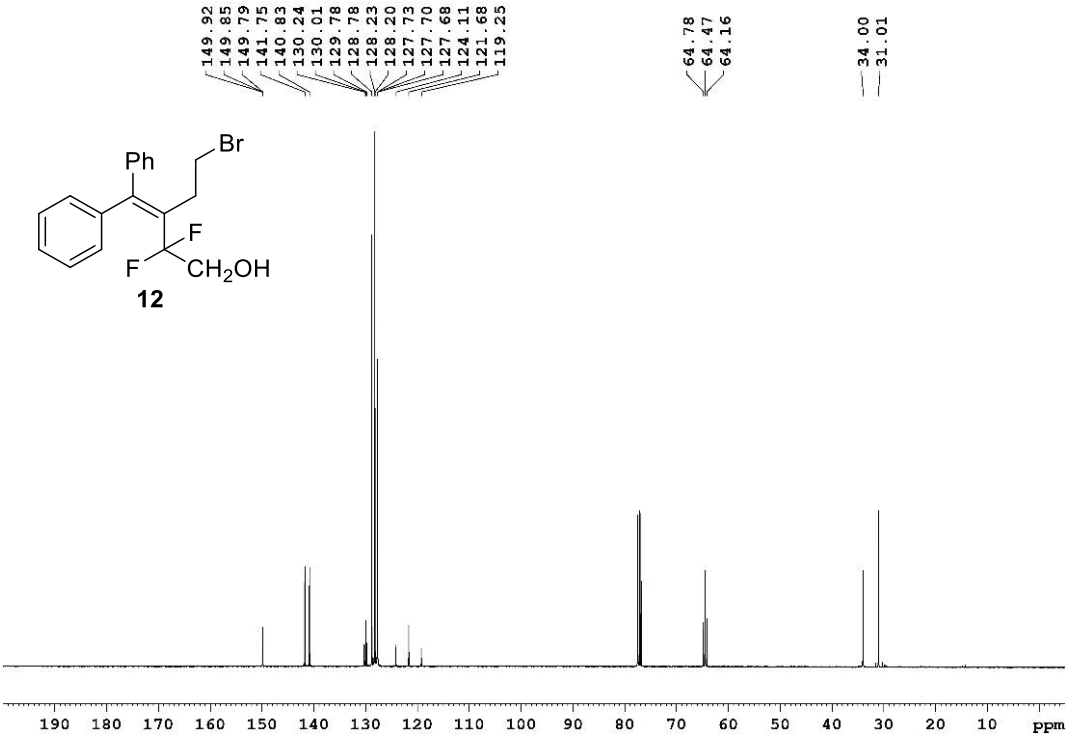
3-(diphenylmethylene)-1-phenylcyclopentan-1-ol (11)



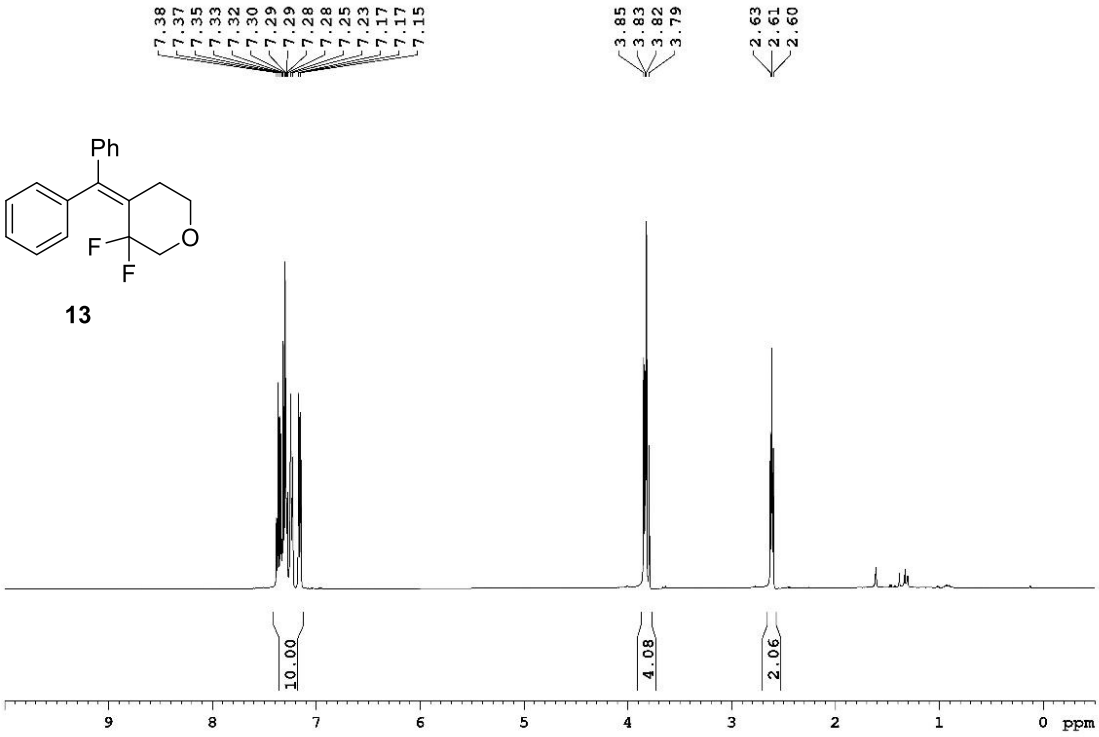


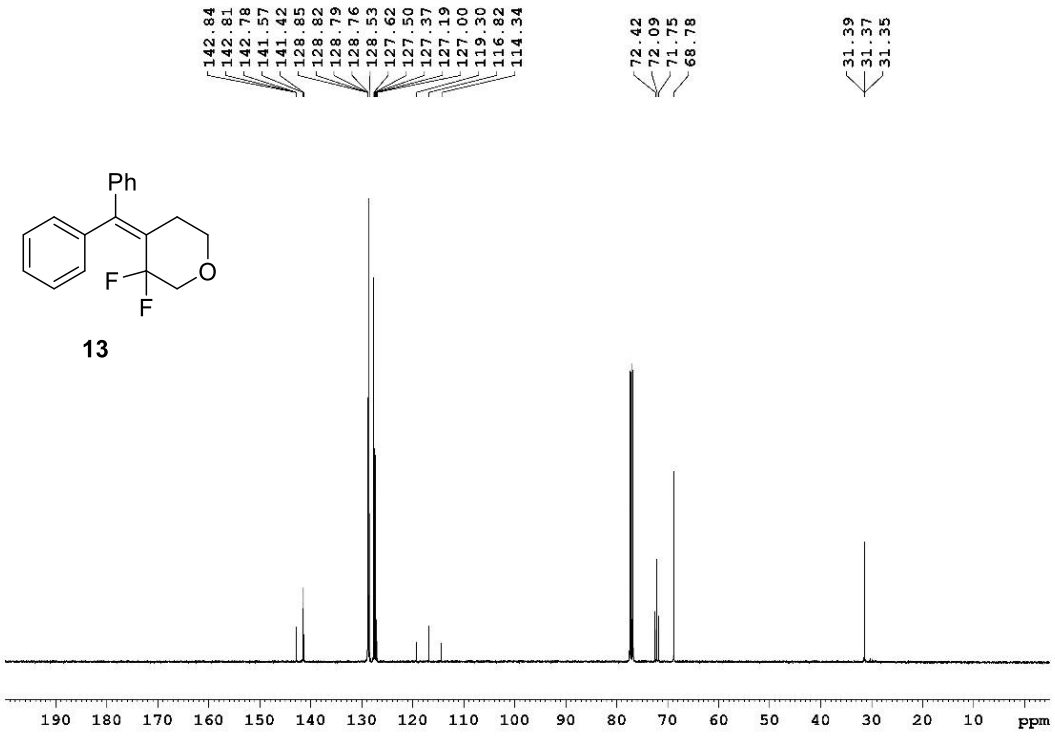
5-bromo-3-(diphenylmethylene)-2,2-difluoropentan-1-ol (12)



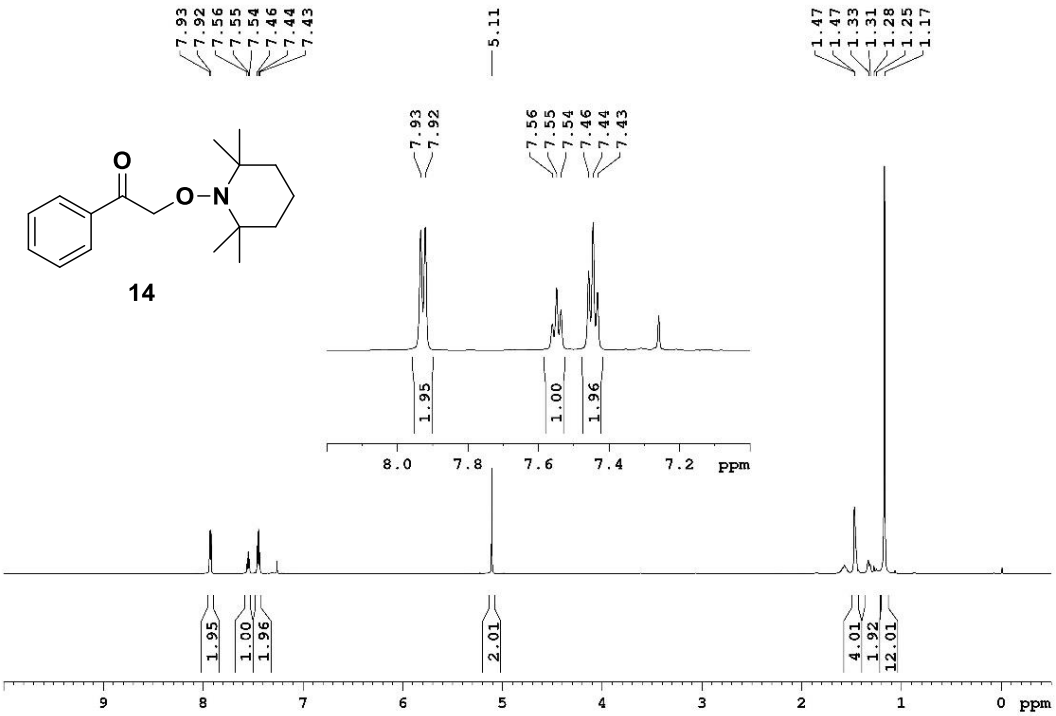


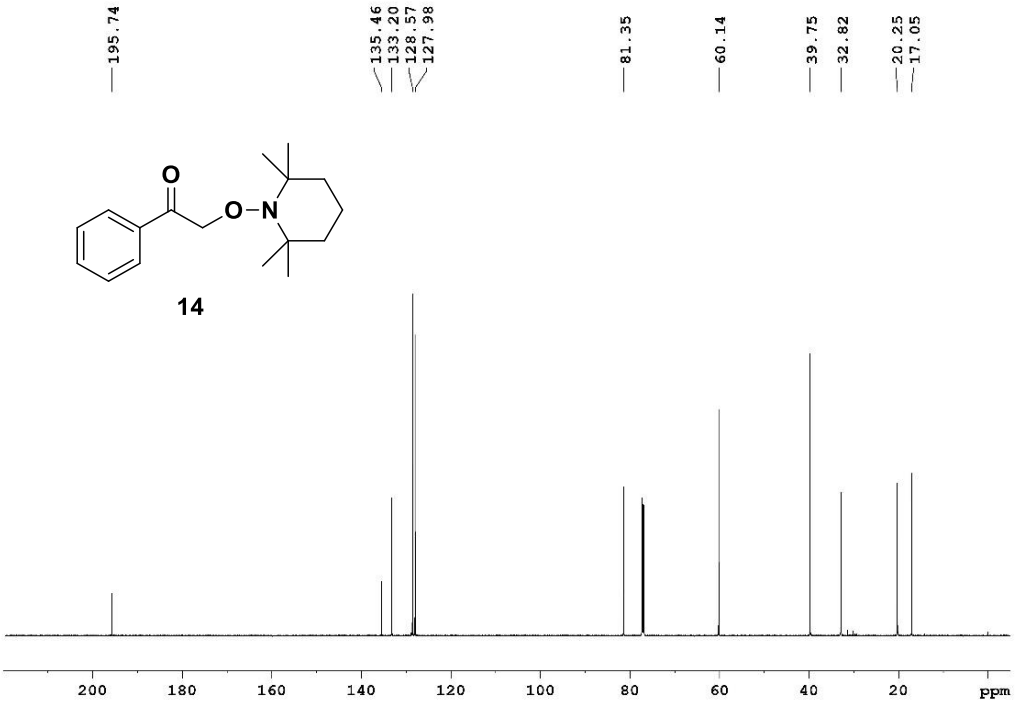
4-(diphenylmethylene)-3,3-difluorotetrahydro-2H-pyran (13)





1-phenyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethan-1-one (14)





9. Reference

(1) Zhu, Z. Z.; Chen, K.; Yu, L. Z.; Tang, X. Y.; Shi, M., Copper(I)-Catalyzed Intramolecular Trifluoromethylation of Methylenecyclopropanes. *Org. Lett.* **2015**, *17*, 5994-5997.

(2) Zheng, J.; Cai, J.; Lin, J. H.; Guo, Y.; Xiao, J. C., Synthesis and decarboxylative Wittig reaction of difluoromethylene phosphobetaine. *Chem. Commun.* **2013**, *49*, 7513-7515.

(3) Deng, Z.; Lin, J. H.; Cai, J.; Xiao, J. C., Direct Nucleophilic Difluoromethylation of Carbonyl Compounds. *Org. Lett.* **2016**, *18*, 3206-3209.

(4) Vyas, V. K.; Bhanage, B. M., Catalytic asymmetric synthesis of *β*-triazolyl amino alcohols by asymmetric transfer hydrogenation of α-triazolyl amino alkanones. *Tetrahedron: Asymmetry* **2017**, *28*, 974-982.

(5) Yu, J.; Lin, J.-H.; Cao, Y.-C.; Xiao, J.-C., Visible-light-induced radical hydrodifluoromethylation of alkenes. *Org. Chem. Front.* **2019**, *6*, 3580-3583.

(6) Liu, W.; Li, Y.; Liu, K.; Li, Z. Iron-Catalyzed Carbonylation-Peroxidation of Alkenes with Aldehydes and Hydroperoxides. *J. Am. Chem. Soc.* **2011**, *133*, 10756-10759.