Supporting Information for:

Practical Asymmetric Amine Nucleophilic Approach for the Modular Construction of Protected α-Quaternary Amino Acids

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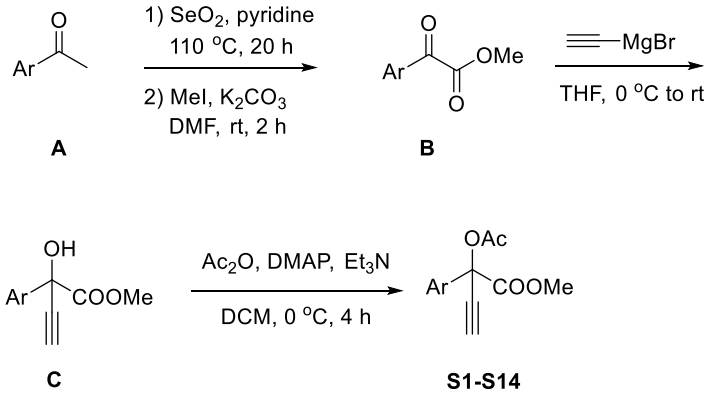
Contents:

General comments

Commercially available reagents and solvents were purchased from Energy, J&K, TCI, aladdin or Daicel, and used without further purification. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded at room temperature on a Bruker AV-400 spectrometer and referenced to the residual deuterated solvent signals. All reported NMR values are given in parts per million (ppm). FT-IR measurements were carried out on a Thermo Fisher Nicolet 6700 FT-IR spectrometer or Bruker ALPHA II. High resolution mass spectra (HRMS) were obtained on a WATERS I-Class VION IMS Qtof Spectrometer. The X-ray analysis of **1** was collected at 100 K on a Rigaku Oxford Diffraction Supernova Dual Source, Cu at Zero equipped with an AtlasS2 CCD using Cu Kα radiation. Optical rotations were recorded on a polarimeter with a sodium lamp of wavelength 589 nm. Enantiomeric excesses were determined by chiral High Performance Liquid Chromatography (HPLC) analysis. UV detection was monitored at 250 nm. HPLC samples were dissolved in HPLC grade isopropanol (IPA) unless otherwise stated.

Typical procedure for the preparation of propargylic esters

A. Preparation of propargylic esters S1-S14



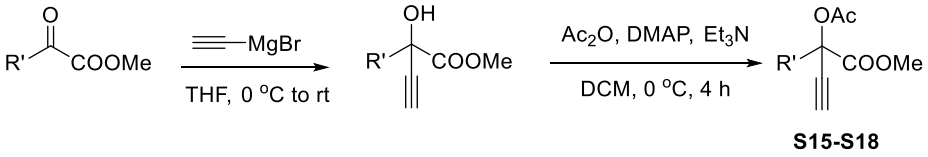
The synthesis of compound **B**:[1a] To a solution of functionalized acetophenone **A** (20 mmol) in pyridine (20 mL) was added selenium dioxide (40 mmol, 2.0 eq) at room temperature and the mixture was stirred at 110 °C for 20 h. After filtration of the reaction mixture, the residue was washed with CH_2Cl_2 and the filtrate was concentrated in vacuo. The resulting residue was used for the next reaction without further purification.

To a solution of above-mentioned residue in DMF (35 mL) was added K_2CO_3 (60 mmol, 3.0 eq) and MeI (60 mmol, 3.0 eq) at 0 °C. The mixture was stirred at room temperature for 2 h. After quenching with 1 N HCl aq., the resulting mixture was extracted with ethyl acetate. The combined organic layers were washed with sat. $NaHCO_3$ aq., then dried over Na_2SO_4. After concentration in vacuo, the resulting residue was purified by column chromatography to give the corresponding α-keto methyl ester **B**.

The synthesis of compound **C**: To a solution of α-keto esters **B** (10 mmol) in 20 mL anhydrous THF was added ethynylmagnesium bromide (0.5 M solution in THF, 30 mL, 15 mmol) at 0 °C under nitrogen atmosphere. The mixture was stirred at 0 °C for 4 h and warmed to room temperature and stirred for 2 h. After the completion of the reaction determined by TLC, the reaction mixture was quenched by addition of an aqueous saturated solution of NH_4Cl (50 mL) and extracted with ethyl acetate (3×50 mL). The combined organic layers were washed with brine, dried over Na_2SO_4. After concentration in vacuo, the resulting residue was purified by column chromatography (EtOAc/n-hexane) to give the corresponding propargylic alcohol **C**.

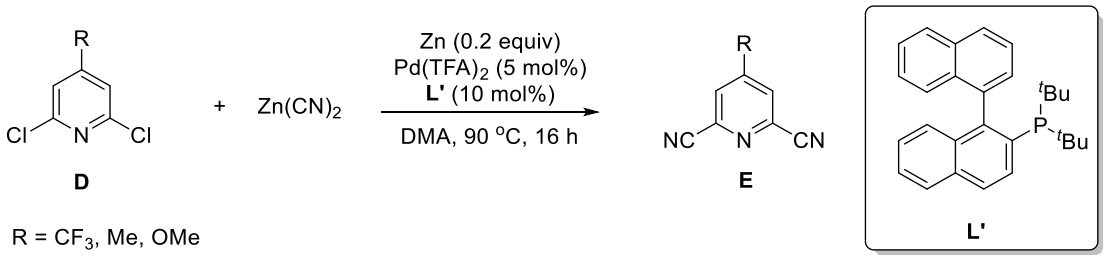
The synthesis of compound **S**: An oven-dried round-bottomed flask equipped with a magnetic stir bar was charged with **C** (2 mmol), dichloromethane (10.0 mL), and dimethylamino pyridine (24.4 mg, 0.2 mmol). The solution was cooled to 0 °C. Ttriethylamine (834 μL, 6 mmol) was added and followed by dropwise addition of acetic anhydride (245 mg, 2.4 mmol). The resultant reaction mixture was stirred at 0 °C for 4 h. The reaction mixture was then concentrated in vacuo, and the resulting residue was purified by column chromatography to give the corresponding propargylic esters **S1-S14**.

B. Preparation of propargylic esters S15-S18



Methyl 2-oxo-4-phenylbut-3-ynoate was prepared according to a reported procedure.[1b]

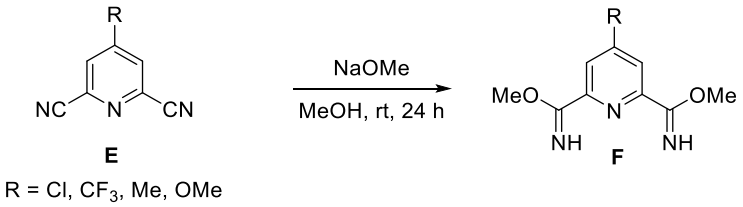
Procedure for the preparation of ligands L7-L9 and L



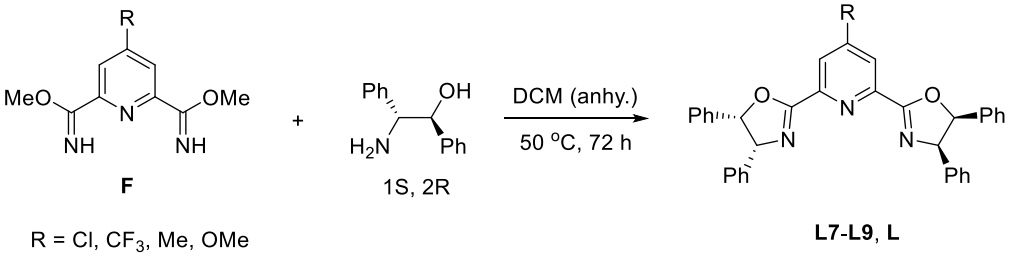
4-Chloropyridine-2,6-dicarbonitrile was purchased from aladdin. Pyridine-2,6-dicarbonitrile **E** was prepared according to a reported procedure[2] with slight modifications as follows.

In a N_2-filled glovebox, a flame-dried 100 mL Schlenk tube was charged with 2,6-dichloropyridine **D** (5.0 mmol, 1.0 eq), zinc(II) cyanide (0.646 g, 5.5 mmol, 1.1 eq), zinc powder (65 mg, 1.0 mmol, 0.2 eq), palladium(II) trifluoroacetate (83 mg, 0.25 mmol, 0.05 eq), **L'** (0.199 g, 0.50 mmol, 0.1 eq) and anhydrous DMA (20 mL). The mixture was stirred at room temperature for 20 min, then subsequently heated to 95 °C

for 16 h. The mixture was then cooled to room temperature and filtered through a pad of Celite, eluting with EtOAc. The solvents were removed by vacuum distillation (6-10 mmHg) and the residue was purified by column chromatography to provide the title compound **E**.

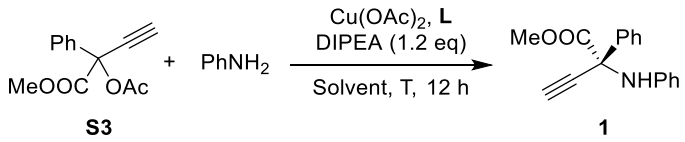


In a N_2-filled glovebox, a 8 mL screw-capped vial was charged with pyridine-2,6-dicarbonitrile **E** (2 mmol), dry MeOH (4 mL) and sodium methoxide (37 µL, 0.2 mmol, 0.1 eq, 5.4 M in MeOH). The reaction mixture was stirred at room temperature for 24 h. It was quenched by the addition of acetic acid (24 µL). Upon the removal of the residue solvent, compound **F** with small amount of impurities was obtained as a white solid which was used without further purification.



Ligands **L7-L9** and **L** were synthesized according to a reported procedure.[3] Dimethyl pyridine-2,6-bis(carbimidate) **F** (1.37 mmol) was suspended in dry CH_2Cl_2 (15 mL). The commercially available (1S,2R)-2-amino-1,2-diphenylethanol (0.585 g, 2.75 mmol) was added and the mixture was refluxed for 72 hours. The solvent was evaporated and the remaining solid was washed with water (15 mL) and MeOH (15 mL), then recrystallised from ethyl acetate to afford the desired products as a white crystalline solid.

Table S1. Selected screening data toward the amino ester 1[a]



S3 1

Entry	L*	Solvent	T [°C]	Yield[b] (%)	*ee*[c] (%)
1	**L1**	MeOH	rt	84	3
2	**L2**	MeOH	rt	86	17
3	**L3**	MeOH	rt	4	1
4	**L4**	MeOH	rt	5	33
5	**L5**	MeOH	rt	-	-
6	**L6**	MeOH	rt	94	67
7	**L6**	MeOH	0	95	74
8	**L6**	MeOH/ACN	0	99	79
9	**L6**	*i*PrOH/ACN	0	16	80
10	**L6**	TFE/ACN	0	97	85
11	**L6**	HFIP/ACN	0	91	69
12[d]	**L6**	TFE/ACN	-20	92	90
13[e]	**L6**	TFE/ACN	-40	90	92
14[e]	**L7**	TFE/ACN	-40	85	88
15[e]	**L8**	TFE/ACN	-40	87	80
16[e]	**L9**	TFE/ACN	-40	85	94
17[e]	**L**	TFE/ACN	-40	77	95
18[e,f]	**L**	**TFE/ACN**	**-40**	**86**	**94**
19[e,f]	**L**	TFE/ACN	-30	91	88

[a]Reaction conditions unless otherwise noted: propargylic ester **S1** (0.1 mmol), aniline (0.12 mmol, 1.2 eq), solvent (0.8 mL), DIPEA (1.2 eq), $Cu(OAc)_2$ (5 mol%), **L** (6 mol%), 12 h. [b]Determined by ^1H NMR with 2-methylnaphthalene as internal standard. [c]Evaluated by HPLC equipped with chiral column. [d]48 h. [e]72 h. [f]Using quinuclidine as base.

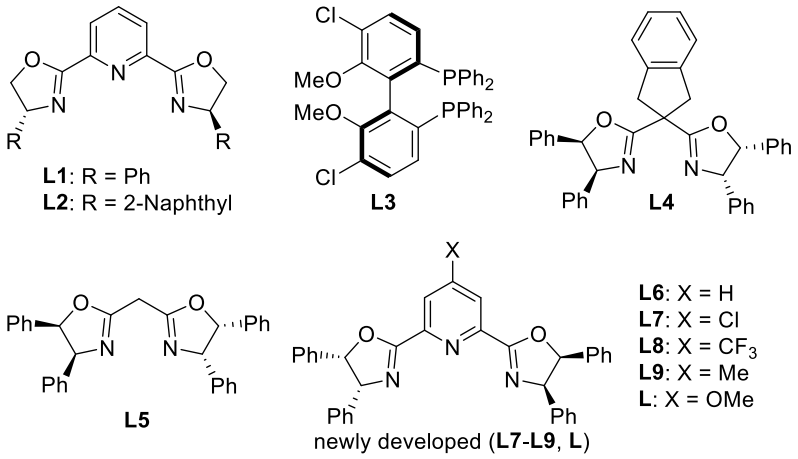
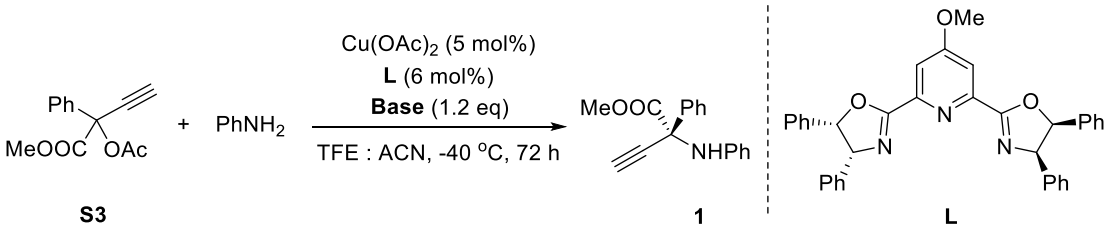


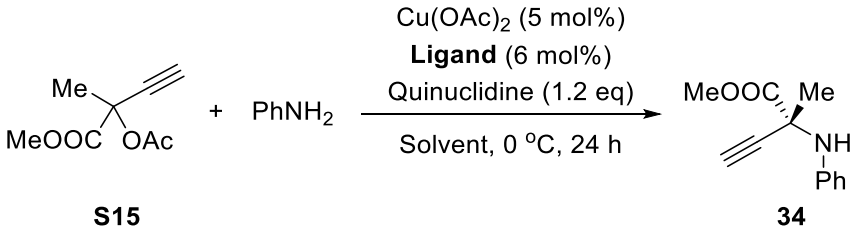
Table S2. The effect of base[a]



Entry	Base (1.2 eq)	Yield[b] (%)	*ee*[c] (%)
1	DIPEA	77	95
2	DABCO	8	83
3	NEM	3	94
4	DBU	–	–
5	Cy_2NMe	51	94
6	Et_3N	64	93
7	Cs_2CO_3	–	–
8	TBD	–	–
9	**Quinuclidine**	**86**	**94**
10	K_3PO_4	3	50

[a]Reaction conditions unless otherwise noted: propargylic ester **S3** (0.1 mmol), aniline (0.12 mmol, 1.2 eq), TFE/ACN (1:3, 0.8 mL), base (1.2 eq), $Cu(OAc)_2$ (5 mol%), **L** (6 mol%), -40 °C, 72 h. [b]Determined by ^1H NMR with 2-methylnaphthalene as internal standard. [c]Evaluated by HPLC equipped with chiral column.

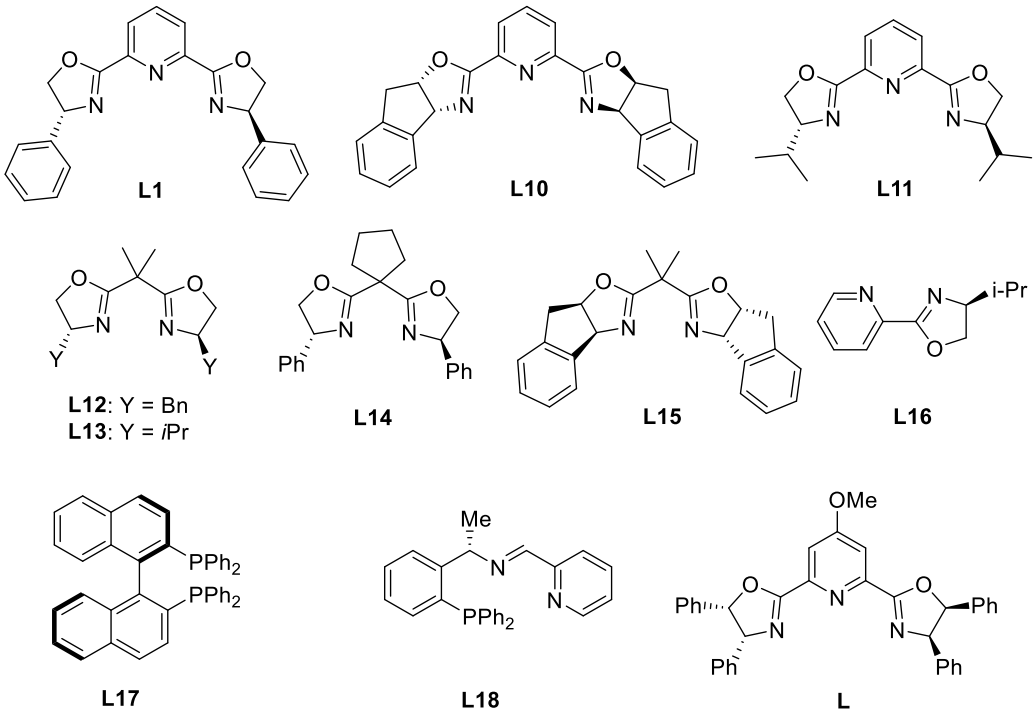
Table S3. Further screening data using methyl-substituted substrate [a]



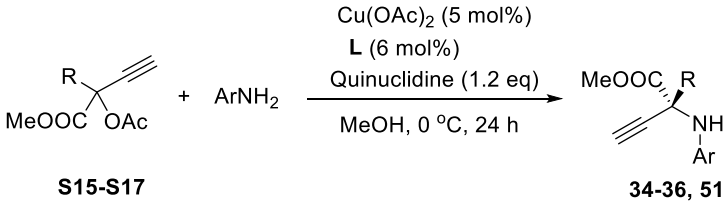
S15 **34**

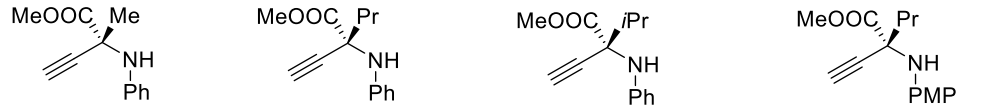
Entry	Ligand	Solvent	Conv. (%)	Yield[b] (%)	*ee*[c] (%)
1	**L1**	TFE/CAN(1/3)	100	53	2
2	**L10**	TFE/CAN(1/3)	100	trace	–
3	**L11**	TFE/CAN(1/3)	89	6	4
4	**L12**	TFE/CAN(1/3)	86	–	–
5	**L13**	TFE/CAN(1/3)	79	–	–
6	**L14**	TFE/CAN(1/3)	73	–	–
7	**L15**	TFE/CAN(1/3)	49	–	–
8	**L16**	TFE/CAN(1/3)	84	trace	–
9	**L17**	TFE/CAN(1/3)	32	–	–
10	**L17**	MeOH	17	–	–
11	**L18**	TFE/CAN(1/3)	45	–	–
12	**L18**	MeOH	70	trace	–
13	**L**	**MeOH**	**100**	**84**	**62**
14	**L**	TFE	100	67	54
15	**L**	EtOH	100	77	56
16	**L**	PrOH	100	74	47
17	**L**	*i*PrOH	100	30	21

[a]Reaction conditions unless otherwise noted: propargylic ester **S15** (0.1 mmol), aniline (0.12 mmol, 1.2 eq), solvent (0.8 mL), quinuclidine (1.2 eq), $Cu(OAc)_2$ (5 mol%), Ligand (6 mol%), 0 °C, 24 h. [b]Determined by ^1H NMR with 2-methylnaphthalene as internal standard. [c]Evaluated by HPLC equipped with chiral column.

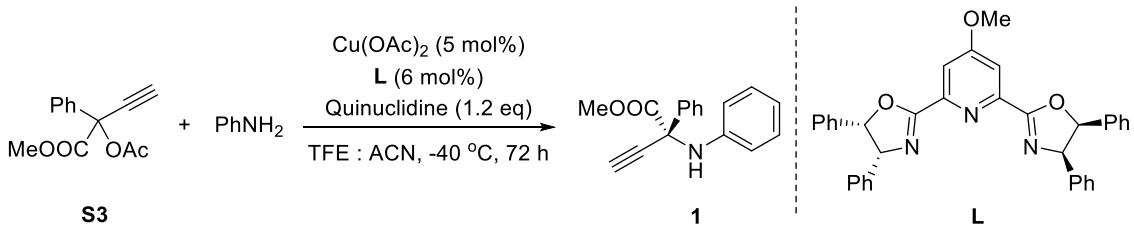


The reaction outcomes in mathanol at 0ºC with alkyl-substituted substrats





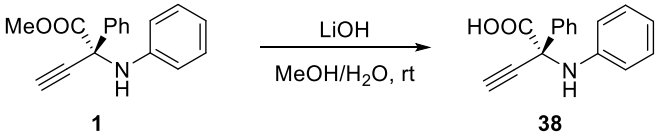
Typical procedure for the synthesis of α-quaternary amino acids



Under nitrogen atmosphere, a flame-dried 10 mL Schlenk tube was charged with $Cu(OAc)_2$ (0.9 mg, 0.005 mmol, 5 mol%), **L** (3.3 mg, 0.006 mmol, 6 mol%) and TFE/ACN (1/3, v/v, 0.4 mL). The resulting solution was stirred for 1 h at room temperature. After another 10 minutes of stirring at -40 ºC, a solution of propargylic

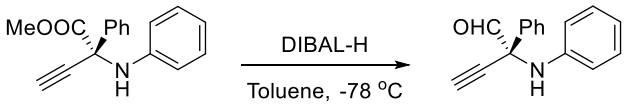
acetate **S3** (23.2 mg, 0.1 mmol, 1 eq), aniline (11.2 mg, 0.12 mmol, 1.2 eq) and quinuclidine (13.3 mg, 0.12 mmol, 1.2 eq) in the mixed solvent (TFE/ACN, 1/3, v/v, 0.4 mL) was added dropwise. The mixture was stirred at -40 °C for 72 h then filtered through a silica plug, concentrated in vacuo and the resultant crude product was purified by column chromatography (PE:EA = 20:1) to afford the desired product **1** as a white solid (22.5 mg, 85%, 94% *ee*).

Synthetic transformations of 1 and 2



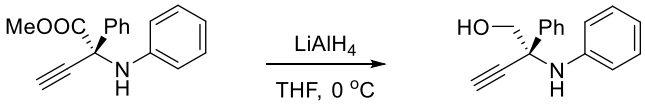
1 **38**

To a solution of **1** (26.5 mg, 0.1 mmol, 1.0 eq) in a mixed solvent ($MeOH/H_2O$, 4/1, v/v, 1 mL) at 0 °C was slowly added LiOH (0.3 mmol, 7.2 mg, 3 eq). The reaction mixture was stirred for 24 h at room temperature. After the completion of the reaction (monitored by TLC), methanol was removed in vacuo. The resulting residue was dissolved in 5 mL H_2O and washed with ethyl acetate (3×3 mL). The aqueous phase was acidified to pH 3-4 with 1N HCl and extracted with EA three times. The combined organic extract was dried over Na_2SO_4 and concentrated in vacuo to afford the product **38** as a white solid (18.6 mg, 74% yield) without further purification.



1 **39**

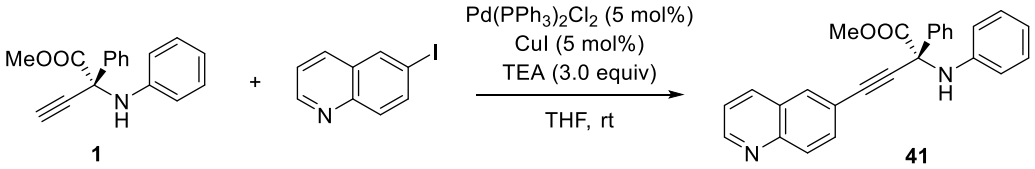
Compound **39** was prepared according to reported procedures.[4] To a solution of **1** (26.5 mg, 0.1 mmol, 1.0 eq) in anhydrous toluene (2 mL) was slowly added diisobutylaluminum hydride (167 µL, 0.25 mmol, 1.5 M in toluene) at -78 °C under nitrogen atmosphere. The solution was allowed to stir for 2 h at -78 °C before the addition of MeOH (2.5 mL) at -78 °C. The resulting mixture was allowed to warm to room temperature, and 5.0 mL of a saturated NH_4Cl solution of was added. After the removal of the organic layer, the aqueous layer was washed with CH_2Cl_2 (3×5 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The resulting residue was purified by column chromatography (PE:EA = 20:1) to afford compound **39** as a yellow solid (21.2 mg, 90% yield, 94% *ee*).



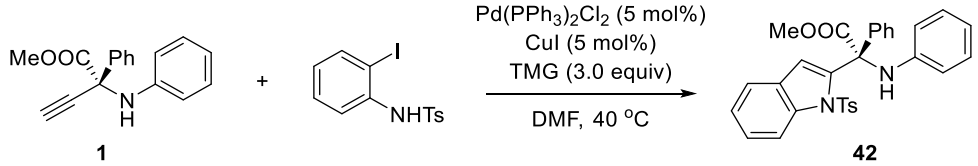
1 **40**

A magnetically stirred solution of **1** (26.5 mg, 0.1 mmol, 1.0 eq) in THF (2.0 mL) was cooled to 0 °C and treated, in portions, with lithium aluminum hydride (76 mg, 0.2 mmol, 2.0 eq). The resulting mixture was stirred at 0 °C for 4 h. The reaction was

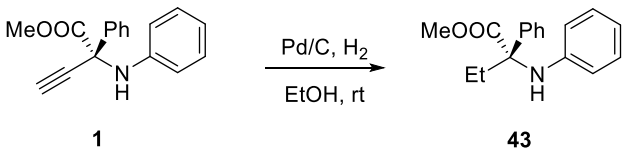
quenched with water (3 mL) and the aqueous phase was extracted with ethyl acetate (3 × 3 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was then purified further by column chromatography (PE:EA = 10:1) to afford the desired product **40** as a yellow oil (22.5 mg, 95% yield, 93% *ee*).



In a N_2-filled glovebox, a 2 mL screw-capped vial was charged with **1** (0.1 mmol, 26.5 mg, 1.0 eq), 6-iodoquinoline (28.1 mg, 0.11 mmol, 1.1 eq), $Pd(PPh_3)_2Cl_2$ (3.5 mg, 0.005 mmol, 5 mol%), CuI (1.0 mg, 0.005 mmol, 5 mol%), TEA (42 µL, 0.3 mmol, 3 eq) and THF (0.5 mL). The reaction mixture was stirred at rt for 24 h. After the completion of the reaction (monitored by TLC), the mixture was filtered through a silica plug and concentrated under reduced pressure. The resultant crude product was purified by column chromatography (PE:EA = 3:1) to afford the desired product **41** as a white solid (36.5 mg, 93% yield, 94% *ee*).

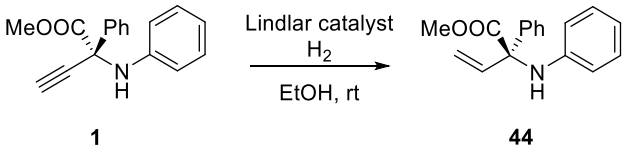


This compound was prepared according to reported procedures.[5] In a N_2-filled glovebox, a 2 mL screw-capped vial was charged with **1** (26.5 mg, 0.1 mmol, 1.0 eq), *N*-(2-iodophenyl)-4-methylbenzenesulfonamide (37.5 mg, 0.1 mmol, 1.0 eq), $Pd(PPh_3)_2Cl_2$ (3.5 mg, 0.005 mmol, 5 mol%), CuI (1.0 mg, 0.005 mmol, 5 mol%), tetramethylguanidine (TMG, 34.6 mg, 0.3 mmol, 3 eq) and DMF (0.5 mL). The reaction mixture was stirred at 40 °C for 24 h. After being diluted with water, the mixture was extracted with EA. The organic phase was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The resulting residue was purified by column chromatography (PE:EA = 10:1) to afford the desired product **42** as a yellow oil (30.6 mg, 60% yield, 94% *ee*).



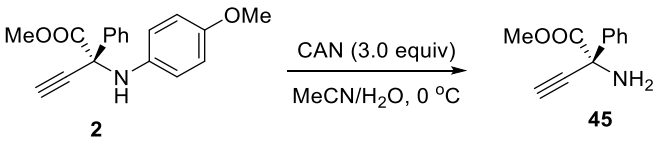
To a solution of **1** (26.5 mg, 0.1 mmol, 1.0 eq) in EtOH (2 mL) was carefully added Pd/C (1.1 mg, 10 mol%) under nitrogen atmosphere. The reaction mixture was degassed and purged with hydrogen. The reaction is allowed to stir for 4 h at room temperature. After the completion of the reaction, the mixture was filtered through a celite pad and

washed with EtOAc. The solvents were removed and concentrated under reduced pressure and purified by column chromatography (PE:EA = 20:1) to obtain the desired product **43** as a white solid (25.3 mg, 94% yield, 94% *ee*).



1 **44**

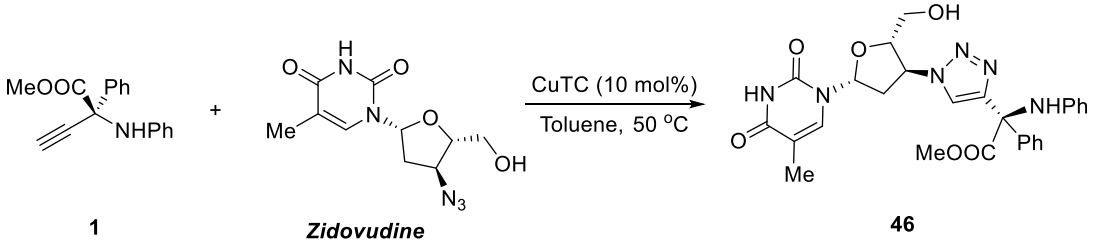
To a solution of **1** (26.5 mg, 0.1 mmol, 1.0 eq) in EtOH (2 mL) was carefully added Lindlar catalyst (2.5 mg, 5 wt% palladium on calcium carbonate) under nitrogen atmosphere. The reaction mixture was degassed and purged with hydrogen. The reaction is allowed to stir for 30 min at room temperature. After the completion of the reaction, the mixture was filtered through a celite pad and washed with EtOAc. The solvents were removed concentrated under reduced pressure and purified by column chromatography (PE:EA = 20:1) to obtain the desired product **44** as a white solid (24.6 mg, 92% yield, 93% *ee*).



2 **45**

To a solution of **2** (29.5 mg, 0.1 mmol, 1.0 eq) in MeCN (0.5 mL) was added dropwise a solution of CAN (164 mg, 0.3 mmol, 3.0 eq) in H_2O (0.5 mL) at 0 °C. After 2 hours stirring, the reaction mixture was quenched with saturated aqueous $NaHSO_3$ (1 mL). The reaction mixture was extracted with EtOAc. The combined organic extract was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The resulting residue was purified by column chromatography (PE:EA = 5:1) to afford the desired product **45** as a yellow oil (14.2 mg, 75% yield, 91% *ee*).

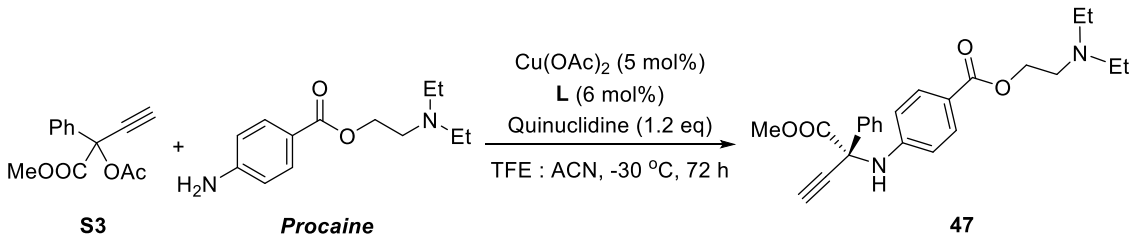
Derivatization of commercially available drug molecules



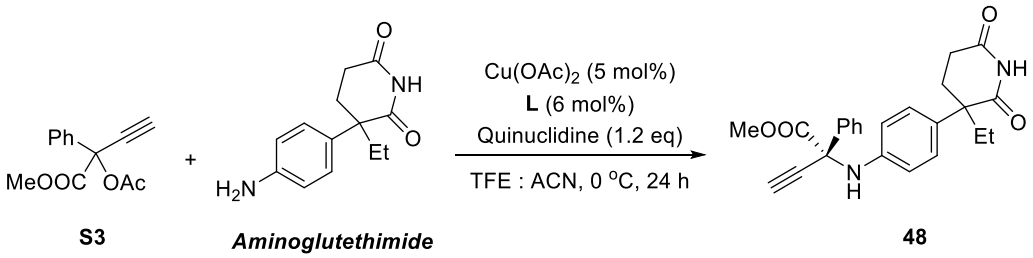
1 ***Zidovudine*** **46**

In a N_2-filled glovebox, a 2 mL screw-capped vial was charged with **1** (26.5 mg, 0.1 mmol, 1.0 eq), zidovudine (26.7 mg, 0.1 mmol, 1.0 eq), CuTC (1.9 mg, 0.01 mmol, 10 mol%) and toluene (1 mL). The reaction mixture was stirred at 50 °C for 24 h, and then diluted with water. The mixture was extracted with EA (3×5 mL). The organic phase was concentrated under reduced pressure and purified by column chromatography

(DCM:MeOH = 10:1) to afford the desired product **46** as a white solid (43.0 mg, 81% yield, *dr* > 20:1).

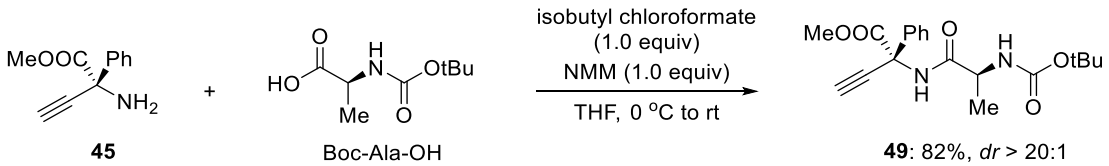


Under nitrogen atmosphere, a flame-dried 10 mL Schlenk tube was charged with $Cu(OAc)_2$ (0.9 mg, 0.005 mmol, 5 mol%), **L** (3.3 mg, 0.006 mmol, 6 mol%) and TFE/ACN (1/3, v/v, 0.4 mL). The resulting solution was stirred for 1 h at room temperature. After another 10 minutes of stirring at -30 °C, a solution of propargylic acetate **S3** (23.2 mg, 0.1 mmol, 1 eq), procaine (28.4 mg, 0.12 mmol, 1.2 eq) and quinuclidine (13.3 mg, 0.12 mmol, 1.2 eq) in the mixed solvent (TFE/ACN, 1/3, v/v, 0.4 mL) was added dropwise. The mixture was stirred at -30 °C for 72 h and then filtered through a silica plug, concentrated in vacuo and the resultant crude product was purified by column chromatography (DCM:MeOH = 10:1) to afford the desired product **47** as a yellow oil (22.1 mg, 54% yield).

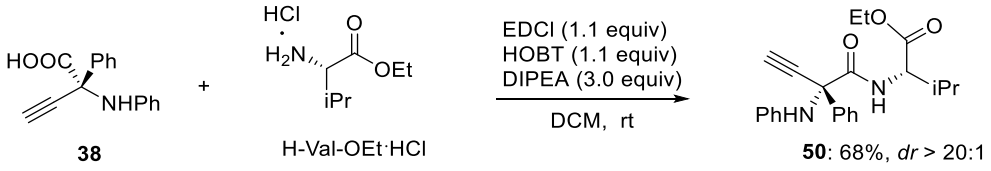


Under nitrogen atmosphere, a flame-dried 10 mL Schlenk tube was charged with $Cu(OAc)_2$ (0.9 mg, 0.005 mmol, 5 mol%), **L** (3.3 mg, 0.006 mmol, 6 mol%) and TFE/ACN (1/3, v/v, 0.4 mL). The resulting solution was stirred for 1 h at room temperature. After another 10 minutes of stirring at 0 °C, a solution of propargylic acetate **S3** (23.2 mg, 0.1 mmol, 1 eq), aminoglutethimide (27.9 mg, 0.12 mmol, 1.2 eq) and quinuclidine (13.3 mg, 0.12 mmol, 1.2 eq) in the mixed solvent (TFE/ACN, 1/3, v/v, 0.4 mL) was added dropwise. The mixture was stirred at 0 °C for 24 h then filtered through a silica plug, concentrated in vacuo and the resultant crude product was purified by column chromatography (PE:EA = 2:1) to afford the desired product **48** as a white solid (38.4 mg, 95% yield, *dr* = 1:1).

Synthesis of enantioenriched peptides 49 and 50

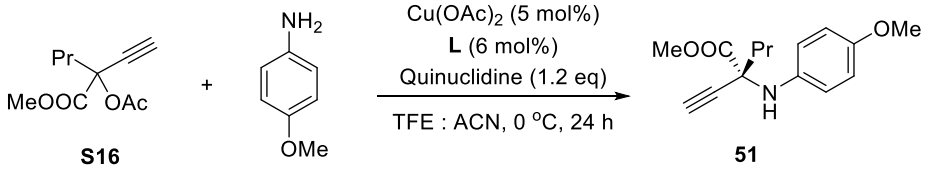


This compound was prepared according to literature procedures.[6] To a solution of N-(tert-Butoxycarbonyl)-L-alanine (18.9 mg, 0.1 mmol, 1.0 eq) and N-methylmorpholine (11 μL, 0.1 mmol, 1.0 eq) in THF (0.5 mL) at 0 °C, was added isobutyl chloroformate (13 μL, 0.1 mmol, 1.0 eq). After another 15 minutes of stirring at 0 °C, **45** (18.9 mg, 0.1 mmol, 1.0 eq) was then added. The reaction mixture was stirred at rt for 24 h then concentrated in vacuo. The crude product was purified by column chromatography (PE:EA = 2:1) to afford the desired product **49** as a colorless oil (29.5 mg, 82% yield, *dr* > 20:1).

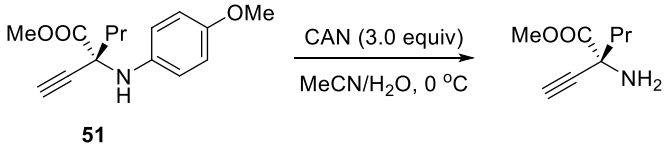


A 2 mL screw-capped vial was charged with **38** (25.1 mg, 0.1 mmol, 1.0 eq), ethyl L-valinate hydrochloride (18.2 mg, 0.1 mmol, 1.0 eq), EDCl (21.1 mg, 0.11 mmol, 1.1 eq), HOBT (14.9 mg, 0.11 mmol, 1.1 eq), DIPEA (52 μL, 0.3 mmol, 3.0 eq) and DCM (1 mL). The reaction mixture was stirred at rt for 24 h and then concentrated in vacuo. The crude product was purified by column chromatography (PE:EA = 5:1) to afford the desired product **50** as a yellow oil (25.7 mg, 68% yield, *dr* > 20:1).

Synthesis of protected bioactive α-ethyl norvaline 52

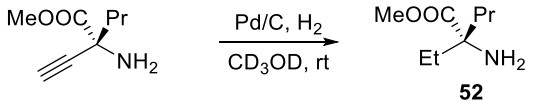


Under nitrogen atmosphere, a flame-dried 10 mL Schlenk tube was charged with $Cu(OAc)_2$ (0.9 mg, 0.005 mmol, 5 mol%), **L** (3.3 mg, 0.006 mmol, 6 mol%) and TFE/ACN (1/3, v/v, 0.4 mL). The resulting solution was stirred for 1 h at room temperature. After another 10 minutes of stirring at 0 °C, a solution of propargylic acetate **S16** (19.8 mg, 0.1 mmol, 1 eq), *p*-anisidine (14.8 mg, 0.12 mmol, 1.2 eq) and quinuclidine (13.3 mg, 0.12 mmol, 1.2 eq) in the mixed solvent (TFE/ACN, 1/3, v/v, 0.4 mL) was added dropwise. The mixture was stirred at 0 °C for 24 h then filtered through a silica plug, concentrated in vacuo and the resultant crude product was purified by column chromatography (PE:EA = 10:1) to afford the desired product **51** as a yellow solid (21.9 mg, 84% yield, 36% *ee*).



This compound was prepared according to reported procedures.[7] To a solution of **51** (26.1 mg, 0.1 mmol, 1.0 eq) in MeCN (0.5 mL) was added dropwise a solution of CAN

(164 mg, 0.3 mmol, 3.0 eq) in H_2O (0.5 mL) at 0 °C. After 2 hours stirring, the resulting solution was treated with 2N HCl to achieve pH value of 1. The aqueous phase was washed with EtOAc (3 × 3 mL) and basified to pH value of 10-12 by the addition of Na_2CO_3. The resulting suspension was extracted with CH_2Cl_2 (3 × 5 mL), dried over Na_2SO_4, filtered, and the solvents evaporated under reduced pressure to yield the desired amine as an orange oil (8.9 mg, 57% yield; 36% *ee*) without further purification.



52

To a solution of methyl (R)-2-amino-2-ethynylpentanoate (15.5 mg, 0.1 mmol, 1.0 eq) in CD_3OD (2 mL) was carefully added Pd/C (1.1 mg, 10 mol%) under nitrogen atmosphere. The reaction mixture was degassed and purged with hydrogen. The reaction is allowed to stir for 4 h at room temperature. After the completion of the reaction, the mixture was filtered through a celite pad and washed with CD_3OD. The 85% NMR yield of **52** was determined by using 2-methylnaphthalene as an internal standard. (Notes: the boiling point of compound **52** is very low; a small amount of precious enantioenriched amine **52** is very difficult to handle.)

Mechanism proposal

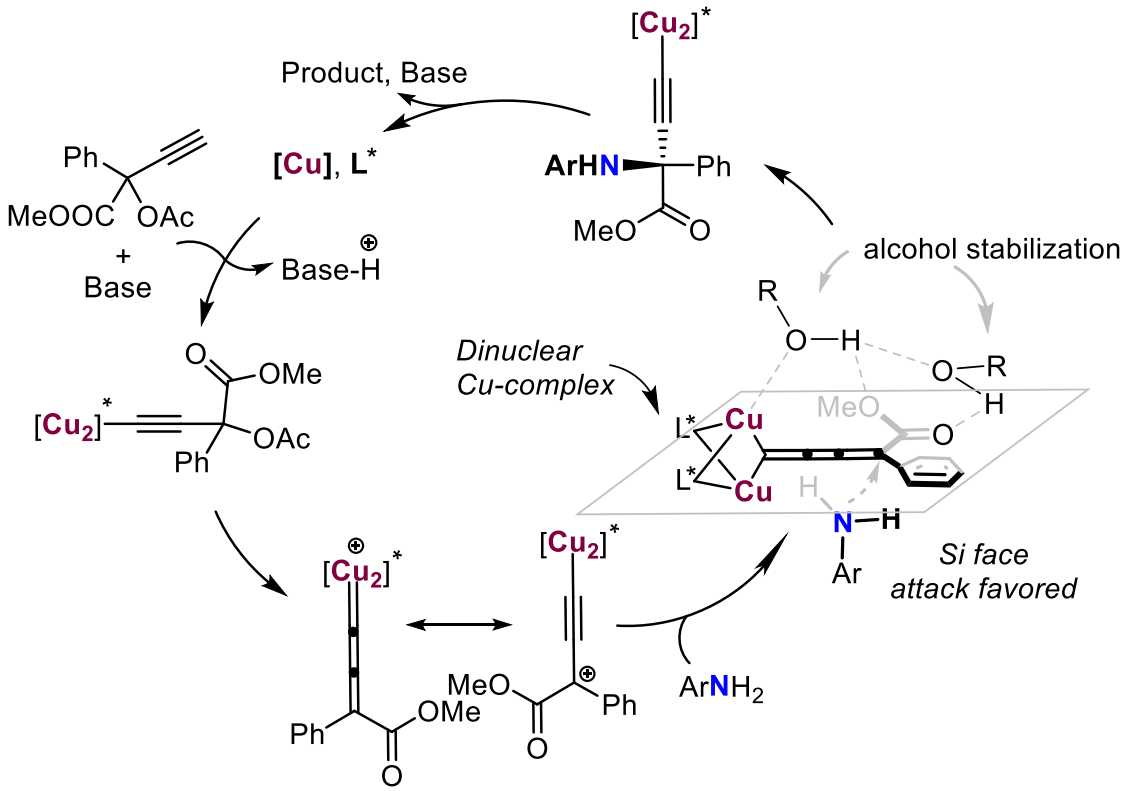
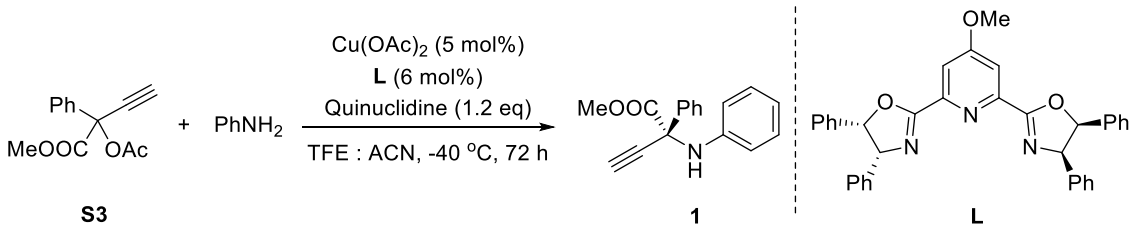
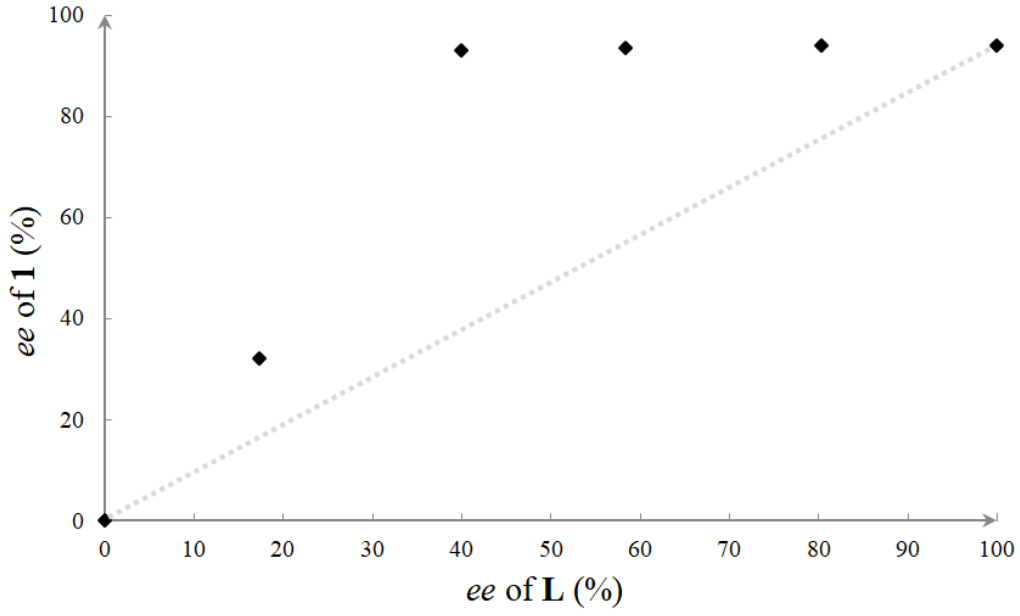


Figure S1. Nonlinear relationship experiments

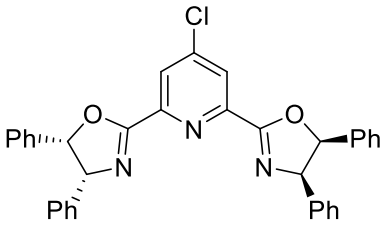


Entry	% ee of the **L**	% ee of the product **1**[a]
1	0	0
2	17	32
3	40	93
4	58	93
5	80	94
6	100	94

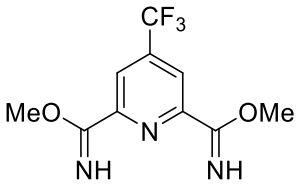
[a]Evaluated by HPLC equipped with chiral column.



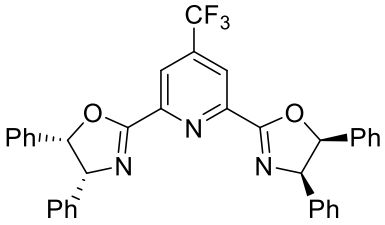
Characterization of all the new compounds



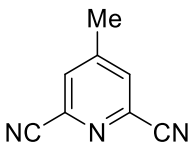
(4R,4'R,5S,5'S)-2,2'-(4-chloropyridine-2,6-diyl)bis(4,5-diphenyl-4,5-dihydrooxazole) (L7): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 2H), 7.17-6.84 (m, 20H), 6.15 (d, *J* = 10.4 Hz, 2H), 5.84 (d, *J* = 10.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 148.4, 145.9, 137.0, 135.8, 128.0, 127.9, 127.8, 127.7, 127.3, 126.7, 126.7, 86.7, 74.6; HRMS (ESI): *m/z*: calcd for $C_{35}H_{27}ClN_3O_2$ $[M+H]^+$: 556.1792, found: 556.1790.



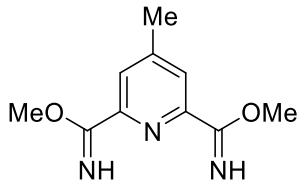
dimethyl 4-(trifluoromethyl)pyridine-2,6-bis(carbimidate) (F2): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (s, 2H), 8.14 (s, 2H), 4.05 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 148.5 , 141.8 (q, *J* = 34.8 Hz), 122.4 (q, *J* = 273.8 Hz), 118.7 (q, *J* = 3.5 Hz), 54.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.7; HRMS (ESI): *m/z*: calcd for $C_{10}H_{11}F_3N_3O_2$ $[M+H]^+$: 262.0803, found: 262.0807.



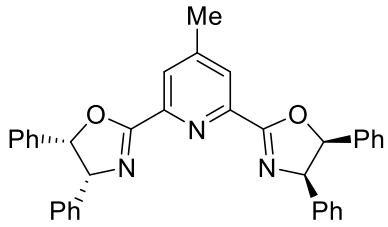
(4R,4'R,5S,5'S)-2,2'-(4-(trifluoromethyl)pyridine-2,6-diyl)bis(4,5-diphenyl-4,5-dihydrooxazole) (L8): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 2H), 7.20-6.87 (m, 20H), 6.18 (d, *J* = 10.2 Hz, 2H), 5.87 (d, *J* = 10.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 148.7, 140.4 (q, *J* = 35.2 Hz), 137.0, 135.8, 128.0, 127.9, 127.8, 127.8, 127.4, 126.7, 122.4 (q, *J* = 273.9 Hz), 122.3 (q, *J* = 3.4 Hz), 86.8, 74.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.5; HRMS (ESI): *m/z*: calcd for $C_{36}H_{27}F_3N_3O_2$ $[M+H]^+$: 590.2055, found: 590.2054.



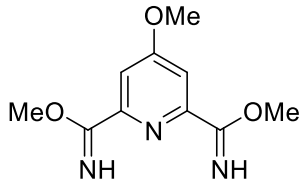
4-methylpyridine-2,6-dicarbonitrile (E3): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 2H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 135.1, 132.1, 115.7, 21.0; HRMS (ESI): *m/z*: calcd for $C_8H_6N_3$ $[M+H]^+$: 144.0562, found: 144.0564.



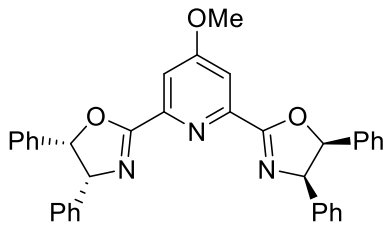
dimethyl 4-methylpyridine-2,6-bis(carbimidate) (F3): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (s, 2H), 7.71 (s, 2H), 3.99 (s, 6H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 150.7, 146.9, 123.4, 54.0, 21.3; HRMS (ESI): *m/z*: calcd for $C_{10}H_{14}N_3O_2$ $[M+H]^+$: 208.1086, found: 208.1088.



(4R,4'R,5S,5'S)-2,2'-(4-methylpyridine-2,6-diyl)bis(4,5-diphenyl-4,5-dihydrooxazole) (L9): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 2H), 7.17-6.87 (m, 20H), 6.13 (d, *J* = 10.2 Hz, 2H), 5.82 (d, *J* = 10.2 Hz, 2H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 149.2, 147.0, 137.3, 136.1, 127.9, 127.7, 127.6, 127.4, 127.32 , 127.1, 126.6, 86.2, 74.4, 21.0; HRMS (ESI): *m/z*: calcd for $C_{36}H_{30}N_3O_2$ $[M+H]^+$: 536.2338, found: 536.2335.

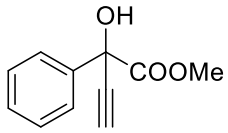


dimethyl 4-methoxypyridine-2,6-bis(carbimidate) (F4): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (s, 2H), 7.41 (s, 2H), 4.02 (s, 6H), 3.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 166.0, 148.6, 108.7, 56.0, 54.1; HRMS (ESI): *m/z*: calcd for $C_{10}H_{14}N_3O_3$ $[M+H]^+$: 224.1035, found: 224.1038.

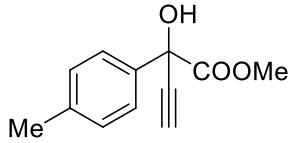


(4R,4'R,5S,5'S)-2,2'-(4-methoxypyridine-2,6-diyl)bis(4,5-diphenyl-4,5-dihydrooxazole) (L): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 2H), 7.21-6.65 (m, 20H),

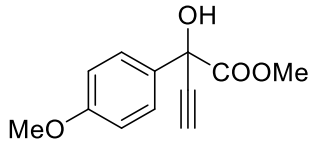
6.13 (d, *J* = 10.3 Hz, 2H), 5.81 (d, *J* = 10.3 Hz, 2H), 4.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 164.2, 148.8, 137.3, 136.1, 128.1, 127.8, 127.7, 127.5, 127.2, 126.7, 112.6, 86.4, 74.5, 56.2; HRMS (ESI): *m/z*: calcd for $C_{36}H_{30}N_3O_3$ $[M+H]^+$: 552.2287, found: 552.2289.



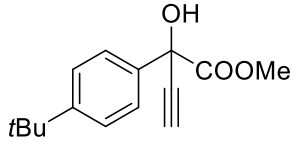
methyl 2-hydroxy-2-phenylbut-3-ynoate (C1): yellow oil; R_f = 0.31 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.64 (m, 2H), 7.48-7.29 (m, 3H), 4.31 (s, 1H), 3.79 (s, 3H), 2.76 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 138.7, 128.9, 128.5, 126.2, 81.8, 74.8, 72.7, 54.4; IR (neat, cm^{-1}) 3478, 3284, 3064, 2956, 1738, 1491, 1450, 1253, 1120, 1071, 967, 775, 697; HRMS (ESI): *m/z*: calcd for $C_{11}H_9O_2$ $[M-OH]^+$: 173.0603, found: 173.0600.



methyl 2-hydroxy-2-(*p*-tolyl)but-3-ynoate (C2): white solid; R_f = 0.31 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 7.8 Hz, 2H), 4.20 (s, 1H), 3.80 (s, 3H), 2.74 (s, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 138.9, 135.9, 129.2, 126.1, 81.9, 74.7, 72.7, 54.4, 21.2; IR (neat, cm^{-1}) 3480, 3282, 2956, 2924, 1733, 1511, 1436, 1267, 1094, 968, 824, 743; HRMS (ESI): *m/z*: calcd for $C_{12}H_{11}O_2$ $[M-OH]^+$: 187.0759, found: 187.0755.

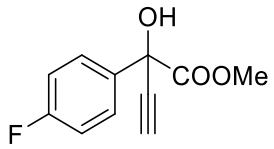


methyl 2-hydroxy-2-(4-methoxyphenyl)but-3-ynoate (C3): yellow oil; R_f = 0.21 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 4.33 (s, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 2.75 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 160.0, 130.9, 127.4, 113.8, 82.0, 74.7, 72.4, 55.3, 54.2; IR (neat, cm^{-1}) 3468, 3281, 2956, 1736, 1607, 1509, 1243, 1173, 1028, 834, 661; HRMS (ESI): *m/z*: calcd for $C_{12}H_{11}O_3$ $[M-OH]^+$: 203.0708, found: 203.0707.

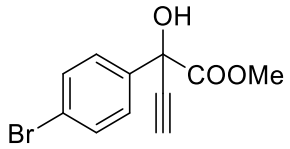


methyl 2-(4-(*tert*-butyl)phenyl)-2-hydroxybut-3-ynoate (C4): yellow oil; R_f = 0.31 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 4.19 (s, 1H), 3.66 (s, 3H), 2.62 (s, 1H), 1.21 (s, 9H); ^{13}C NMR (100 MHz,

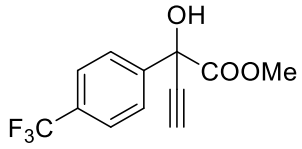
$CDCl_3$) δ 172.1, 151.8, 135.8, 125.8, 125.4, 82.0, 74.6, 72.6, 54.2, 34.6, 31.3; IR (neat, cm^{-1}) 3491, 3283, 2959, 1736, 1252, 1093, 968, 837, 797, 700; HRMS (ESI): *m/z*: calcd for $C_{15}H_{17}O_2$ $[M\text{-}OH]^+$: 229.1229, found: 229.1229.



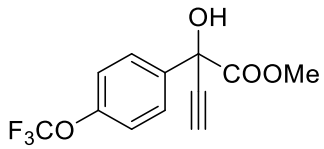
methyl 2-(4-fluorophenyl)-2-hydroxybut-3-ynoate (C5): yellow oil; R_f = 0.31 (PE:EA = 5:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.76-7.55 (m, 2H), 7.16-6.90 (m, 2H), 4.27 (s, 1H), 3.80 (s, 3H), 2.75 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 163.1 (d, *J* = 247.9 Hz), 134.6, 128.2 (d, *J* = 8.5 Hz), 115.4 (d, *J* = 21.9 Hz), 81.7, 75.0, 72.2, 54.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.2; IR (neat, cm^{-1}) 3473, 3291, 2958, 1740, 1604, 1508, 1258, 1161, 1089, 841, 794; HRMS (ESI): *m/z*: calcd for $C_{11}H_8FO_2$ $[M\text{-}OH]^+$: 191.0508, found: 191.0506.



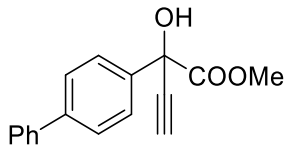
methyl 2-(4-bromophenyl)-2-hydroxybut-3-ynoate (C6): white solid; R_f = 0.28 (PE:EA = 5:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.60-7.53 (m, 2H), 7.52-7.46 (m, 2H), 4.32 (s, 1H), 3.79 (s, 3H), 2.75 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 137.8, 131.6, 128.1, 123.2, 81.4, 75.1, 72.3, 54.6; IR (neat, cm^{-1}) 3479, 3291, 2955, 1742, 1486, 1398, 1258, 1012, 797, 753; HRMS (ESI): *m/z*: calcd for $C_{11}H_8BrO_2$ $[M\text{-}OH]^+$: 250.9708, found: 250.9707.



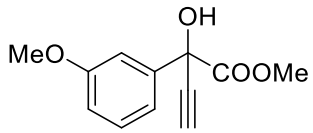
methyl 2-hydroxy-2-(4-(trifluoromethyl)phenyl)but-3-ynoate (C7): yellow oil; R_f = 0.33 (PE:EA = 5:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 8.2 Hz, 2H), 4.36 (s, 1H), 3.81 (s, 3H), 2.77 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 142.5, 131.2 (q, *J* = 32.5 Hz), 126.9, 125.5 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 272.3 Hz), 81.3, 75.3, 72.4, 54.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7; IR (neat, cm^{-1}) 3479, 3303, 2960, 1743, 1619, 1324, 1258, 1068, 845, 722; HRMS (ESI): *m/z*: calcd for $C_{12}H_8F_3O_2$ $[M\text{-}OH]^+$: 241.0476, found: 241.0475.



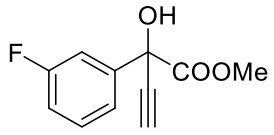
methyl 2-hydroxy-2-(4-(trifluoromethoxy)phenyl)but-3-ynoate (C8): yellow oil; R_f = 0.38 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.64 (m, 2H), 7.25-7.18 (m, 2H), 4.33 (s, 1H), 3.81 (s, 3H), 2.76 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 149.7 (q, *J* = 1.9 Hz), 137.3, 128.0, 120.8, 120.5 (q, *J* = 257.6 Hz), 81.5, 75.1, 72.2, 54.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.9; IR (neat, cm^{-1}) 3479, 3295, 2960, 1732, 1596, 1507, 1297, 1174, 969, 855; HRMS (ESI): *m/z*: calcd for $C_{12}H_8F_3O_3$ $[M\text{-}OH]^+$: 257.0426, found: 257.0423.



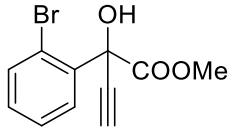
methyl 2-([1,1'-biphenyl]-4-yl)-2-hydroxybut-3-ynoate (C9): white solid; R_f = 0.21 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.76 (m, 2H), 7.69-7.58 (m, 4H), 7.52-7.43 (m, 2H), 7.42-7.35 (m, 1H), 4.38 (s, 1H), 3.84 (s, 3H), 2.81 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 141.8, 140.4, 137.7, 128.9, 127.6, 127.2, 127.2, 126.6, 81.8, 74.9, 72.6, 54.5; IR (neat, cm^{-1}) 3479, 3284, 2955, 1740, 1600, 1486, 1257, 1095, 1043, 844, 741, 699; HRMS (ESI): *m/z*: calcd for $C_{17}H_{13}O_2$ $[M\text{-}OH]^+$: 249.0916, found: 249.0913.



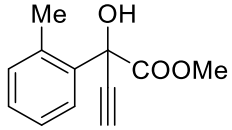
methyl 2-hydroxy-2-(3-methoxyphenyl)but-3-ynoate (C10): yellow oil; R_f = 0.21 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.13 (m, 3H), 6.96-6.75 (m, 1H), 4.36 (s, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 2.75 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 159.6, 140.2, 129.5, 118.5, 114.5, 111.8, 81.6, 74.8, 72.6, 55.4, 54.4; IR (neat, cm^{-1}) 3465, 3281, 2956, 1738, 1600, 1487, 1241, 1033, 841, 692; HRMS (ESI): *m/z*: calcd for $C_{12}H_{11}O_3$ $[M\text{-}OH]^+$: 203.0708, found: 203.0709.



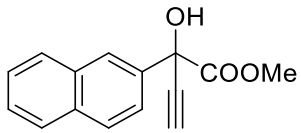
methyl 2-(3-fluorophenyl)-2-hydroxybut-3-ynoate (C11): yellow oil; R_f = 0.33 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.44 (m, 1H), 7.44-7.39 (m, 1H), 7.38-7.30 (m, 1H), 7.10-6.98 (m, 1H), 4.34 (s, 1H), 3.81 (s, 3H), 2.76 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 162.7 (d, *J* = 246.4 Hz), 141.2 (d, *J* = 7.3 Hz), 130.1 (d, *J* = 8.1 Hz), 121.9 (d, *J* = 3.0 Hz), 116.0 (d, *J* = 21.2 Hz), 113.7 (d, *J* = 23.7 Hz), 81.4, 75.0, 72.2, 54.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.4; IR (neat, cm^{-1}) 3479, 3298, 2958, 1747, 1593, 1487, 1240, 1043, 859, 740; HRMS (ESI): *m/z*: calcd for $C_{11}H_8FO_2$ $[M\text{-}OH]^+$: 191.0508, found: 191.0504.



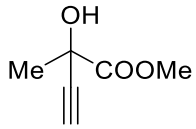
methyl 2-(2-bromophenyl)-2-hydroxybut-3-ynoate (C12): white solid; R_f = 0.25 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.57 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.37 (td, *J* = 7.6, 1.3 Hz, 1H), 7.23 (td, *J* = 7.6, 1.7 Hz, 1H), 4.34 (s, 1H), 3.84 (s, 3H), 2.89 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 136.7, 134.4, 130.9, 130.7, 127.4, 122.0, 80.8, 77.3, 74.2, 54.6; IR (neat, cm^{-1}) 3469, 3285, 2954, 1740, 1434, 1252, 1081, 1021, 761; HRMS (ESI): *m/z*: calcd for $C_{11}H_8BrO_2$ $[M\text{-}OH]^+$: 250.9708, found: 250.9703.



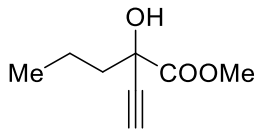
methyl 2-hydroxy-2-(*o*-tolyl)but-3-ynoate (C13): yellow oil; R_f = 0.33 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.31-7.18 (m, 2H), 7.18-7.10 (m, 1H), 4.08 (s, 1H), 3.79 (s, 3H), 2.83 (s, 1H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 136.6, 135.4, 132.0, 129.2, 128.6, 125.8, 81.8, 76.6, 73.9, 54.3, 19.9; IR (neat, cm^{-1}) 3480, 3281, 2955, 1738, 1436, 1255, 1177, 1030, 963, 769; HRMS (ESI): *m/z*: calcd for $C_{12}H_{11}O_2$ $[M\text{-}OH]^+$: 187.0759, found: 187.0755.



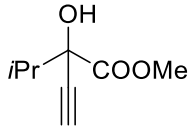
methyl 2-hydroxy-2-(naphthalen-2-yl)but-3-ynoate (C14): white solid; R_f = 0.23 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 1.9 Hz, 1H), 7.96-7.80 (m, 3H), 7.73 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.62-7.42 (m, 2H), 4.40 (s, 1H), 3.80 (s, 3H), 2.84 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 136.0, 133.5, 133.0, 128.6, 128.5, 127.7, 126.8, 126.6, 125.7, 123.6, 81.8, 75.1, 72.9, 54.5; IR (neat, cm^{-1}) 3479, 3288, 3060, 2955, 1733, 1601, 1436, 1125, 822, 755; HRMS (ESI): *m/z*: calcd for $C_{15}H_{11}O_2$ $[M\text{-}OH]^+$: 223.0759, found: 223.0750.



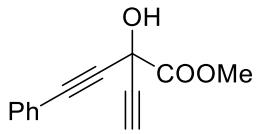
methyl 2-hydroxy-2-methylbut-3-ynoate (C15): yellow oil; R_f = 0.33 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.86 (s, 3H), 3.54 (s, 1H), 2.52 (s, 1H), 1.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 83.1, 72.5, 67.8, 54.0, 27.3; IR (neat, cm^{-1}) 3283, 1738, 1452, 1257, 1126, 975, 800, 766, 670; HRMS (ESI): *m/z*: calcd for $C_6H_7O_2$ $[M\text{-}OH]^+$: 111.0446, found: 111.0438.



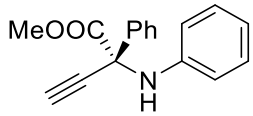
methyl 2-ethynyl-2-hydroxypentanoate (C16): yellow oil; R_f = 0.41 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.85 (s, 3H), 3.52 (s, 1H), 2.51 (s, 1H), 1.97-1.82 (m, 2H), 1.64-1.49 (m, 1H), 1.40-1.27 (m, 1H), 0.92 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 82.5, 72.9, 70.9, 53.9, 42.2, 17.0, 13.9; IR (neat, cm^{-1}) 3497, 3284, 2963, 1738, 1439, 1232, 1085, 1005, 658; HRMS (ESI): *m/z*: calcd for $C_8H_{11}O_2$ $[M\text{-}OH]^+$: 139.0759, found: 139.0765.



methyl 2-hydroxy-2-isopropylbut-3-ynoate (C17): yellow oil; R_f = 0.30 (PE:EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.86 (s, 3H), 3.43 (s, 1H), 2.51 (s, 1H), 2.30-2.09 (m, 1H), 1.10 (d, *J* = 6.8 Hz, 3H), 0.87 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 82.1, 74.4, 73.4, 53.9, 37.1, 16.7, 16.3; IR (neat, cm^{-1}) 3498, 3287, 2971, 1732, 1252, 1150, 1025, 798, 664; HRMS (ESI): *m/z*: calcd for $C_8H_{11}O_2$ $[M\text{-}OH]^+$: 139.0759, found: 139.0762.

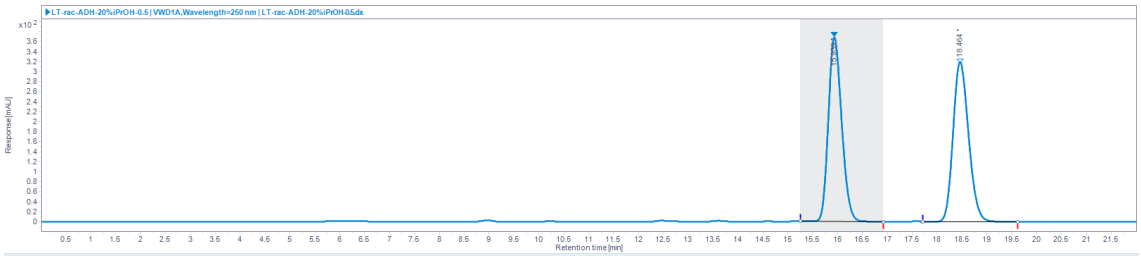


methyl 2-ethynyl-2-hydroxy-4-phenylbut-3-ynoate (C18): brown oil; R_f = 0.23 (PE:EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.44 (m, 2H), 7.39-7.27 (m, 3H), 4.12 (s, 1H), 3.96 (s, 3H), 2.70 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 132.1, 129.4, 128.4, 121.1, 84.5, 84.2, 79.5, 73.1, 63.2, 55.0; IR (neat, cm^{-1}) 3446, 3285, 2956, 1745, 1491, 1438, 1244, 1069, 756, 689; HRMS (ESI): *m/z*: calcd for $C_{13}H_9O_2$ $[M\text{-}OH]^+$: 197.0603, found: 197.0612.



methyl (*S*)-2-phenyl-2-(phenylamino)but-3-ynoate (1): white solid; 22.5 mg, 85% yield; 94% *ee*; R_f = 0.28 (PE:EA = 10:1); $[\alpha]_D^{20}$ = -116.9 (*c* = 0.29, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.71 (m, 2H), 7.46-7.30 (m, 3H), 7.19-7.05 (m, 2H), 6.81-6.69 (m, 1H), 6.67-6.54 (m, 2H), 5.45 (s, 1H), 3.77 (s, 3H), 2.65 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 143.5, 138.0, 128.8, 128.8, 128.7, 127.0, 118.7, 115.6, 80.6, 74.8, 62.0, 54.4; IR (neat, cm^{-1}) 3396, 3281, 2954, 1738, 1601, 1501, 1260, 1173, 725, 692; HRMS (ESI): *m/z*: calcd for $C_{17}H_{16}NO_2$ $[M+H]^+$: 266.1181, found: 266.1182.

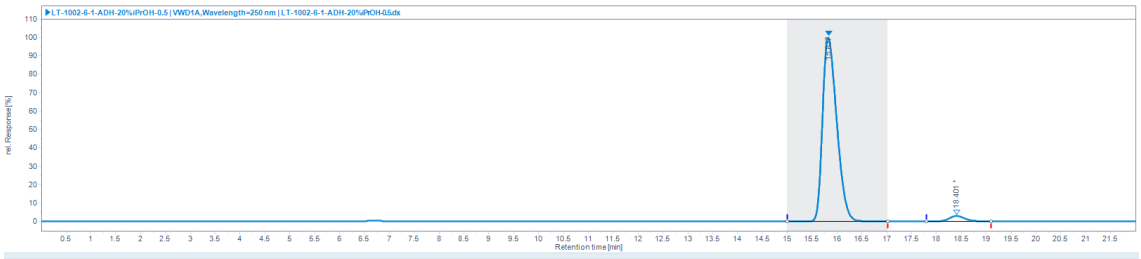
The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 80/20; flow rate 0.5 mL/min; 35 °C; 250 nm; retention time: 15.8 min (major) and 18.4 min (minor).



Injection Results

Peaks | Summary

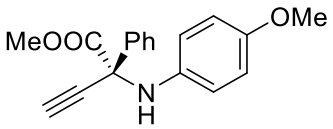
#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	15.939	49.734	15.246	16.914	0.86343
2	18.464	50.266	17.705	19.612	0.86303



Injection Results

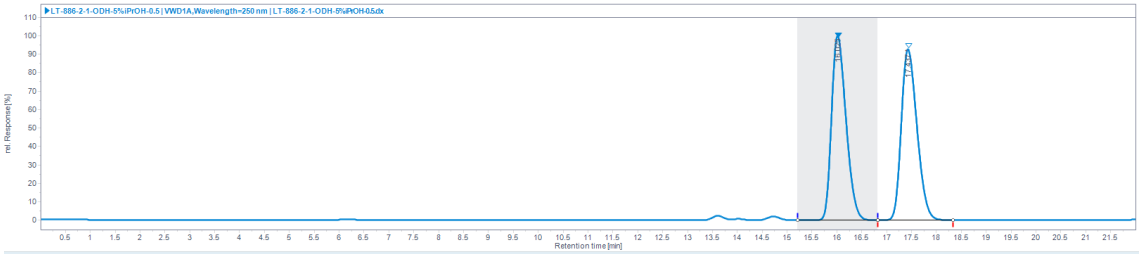
Peaks | Summary

#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	15.837	96.941	14.993	17.024	0.78878
2	18.401	3.059	17.789	19.089	0.88379



methyl (*S*)-2-((4-methoxyphenyl)amino)-2-phenylbut-3-ynoate (2): yellow oil; 26.0 mg, 88% yield; 90% *ee*; R_f = 0.21 (PE:EA = 10:1); $[\alpha]_D^{20}$ = -39.5 (*c* = 0.19, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.86-7.72 (m, 2H), 7.45-7.29 (m, 3H), 6.75-6.62 (m, 2H), 6.59-6.49 (m, 2H), 5.11 (s, 1H), 3.76 (s, 3H), 3.69 (s, 3H), 2.64 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 153.0, 138.3, 137.5, 128.8, 128.7, 127.1, 117.3, 114.3, 81.0, 75.0, 62.8, 55.6, 54.3; IR (neat, cm^{-1}) 3392, 3279, 2953, 2833, 1738, 1511, 1448, 1236, 1174, 1034, 821, 778, 725; HRMS (ESI): *m/z*: calcd for $C_{18}H_{18}NO_3$ $[M+H]^+$: 296.1287, found: 296.1285.

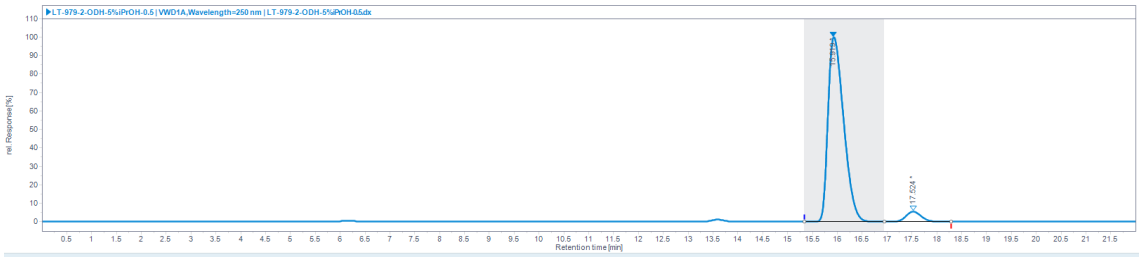
The *ee* was determined by HPLC analysis: CHIRALPAK ODH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 95/5; flow rate 0.5 mL/min; 35 °C; 250 nm; retention time: 15.9 min (major) and 17.5 min (minor).



Injection Results

Peaks | Summary

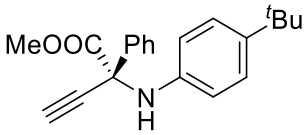
#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	16.025	49.957	15.217	16.819	0.83360
2	17.437	50.043	16.819	18.340	0.81175



Injection Results

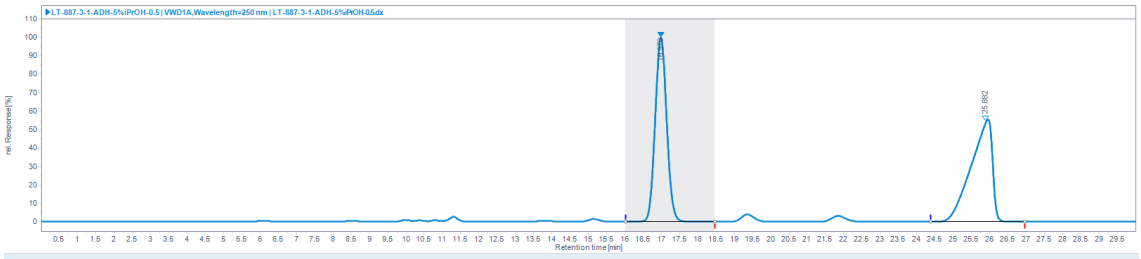
Peaks | Summary

#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	15.919	95.021	15.329	16.951	0.55549
2	17.524	4.979	16.951	18.295	0.88656



methyl (*S*)-2-((4-(tert-butyl)phenyl)amino)-2-phenylbut-3-ynoate (3): white solid; 26.3 mg, 82% yield; 96% *ee*; R_f = 0.33 (PE:EA = 10:1); $[\alpha]_D^{20}$ = -92.8 (*c* = 0.29, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.74 (m, 2H), 7.45-7.30 (m, 3H), 7.11 (d, *J* = 8.8 Hz, 2H), 6.54 (d, *J* = 8.7 Hz, 2H), 5.31 (s, 1H), 3.76 (s, 3H), 2.64 (s, 1H), 1.24 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 141.2, 141.0, 138.3, 128.8, 128.6, 127.1, 125.6, 115.2, 80.9, 74.9, 62.2, 54.3, 34.0, 31.6; IR (neat, cm^{-1}) 3399, 3279, 2956, 2865, 1742, 1615, 1519, 1302, 1261, 1045, 823, 727, 697; HRMS (ESI): *m/z*: calcd for $C_{21}H_{24}NO_2$ $[M+H]^+$: 322.1807, found: 322.1809.

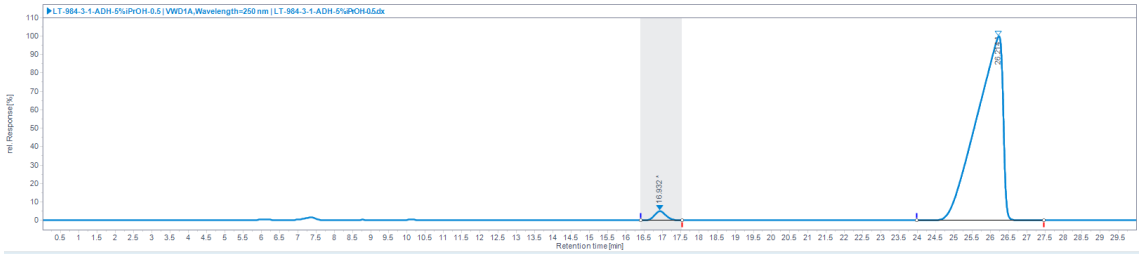
The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 95/5; flow rate 0.5 mL/min; 35 °C; 250 nm; retention time: 16.9 min (minor) and 26.2 min (major).



Injection Results

Peaks | Summary

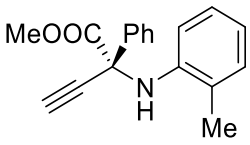
#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	16.978	49.465	16.018	18.466	0.93007
2	25.882	50.535	24.384	26.954	2.32715



Injection Results

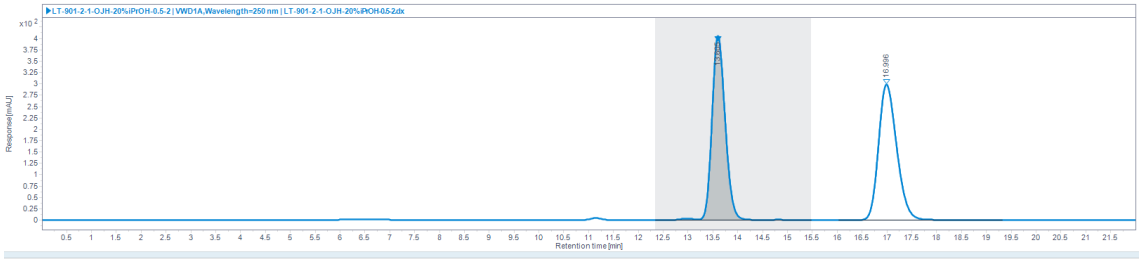
Peaks | Summary

#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	16.932	2.117	16.398	17.535	0.89958
2	26.214	97.883	23.969	27.469	4.88115



methyl (*S*)-2-phenyl-2-(o-tolylamino)but-3-ynoate (4): white solid; 25.9 mg, 93% yield; 97% *ee*; R_f = 0.44 (PE:EA = 10:1); $[\alpha]_D^{20}$ = -94.3 (*c* = 0.21, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.81-7.72 (m, 2H), 7.44-7.30 (m, 3H), 7.09 (d, *J* = 7.2 Hz, 1H), 6.93-6.82 (m, 1H), 6.65 (t, *J* = 7.3 Hz, 1H), 6.39 (d, *J* = 7.9 Hz, 1H), 5.44 (s, 1H), 3.78 (s, 3H), 2.65 (s, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 141.4, 137.9, 130.2, 128.8, 128.7, 127.0, 126.2, 123.4, 118.2, 113.9, 80.8, 74.8, 61.8, 54.4, 17.9; IR (neat, cm^{-1}) 3417, 3281, 2954, 2920, 1740, 1607, 1507, 1448, 1315, 1265, 1174, 749, 723; HRMS (ESI): *m/z*: calcd for $C_{18}H_{18}NO_2$ $[M+H]^+$: 280.1338, found: 280.1341.

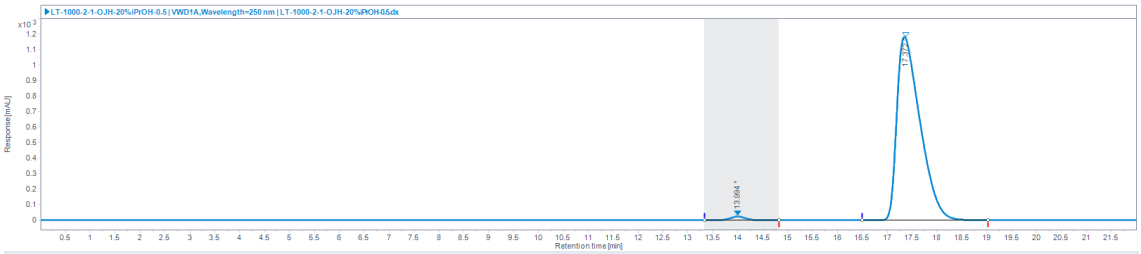
The *ee* was determined by HPLC analysis: CHIRALPAK OJH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 80/20; flow rate 0.5 mL/min; 35 °C; 250 nm; retention time: 14.0 min (minor) and 17.4 min (major).



Injection Results

Peaks | Summary

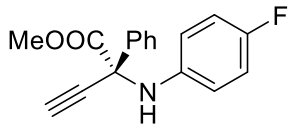
#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	13.605	49.706	12.348	15.480	0.89190
2	16.996	50.294	16.033	19.317	0.80915



Injection Results

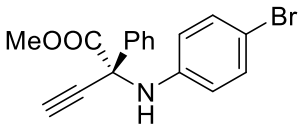
Peaks | Summary

#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	13.994	1.346	13.326	14.823	0.95965
2	17.372	98.654	16.490	19.019	0.56821



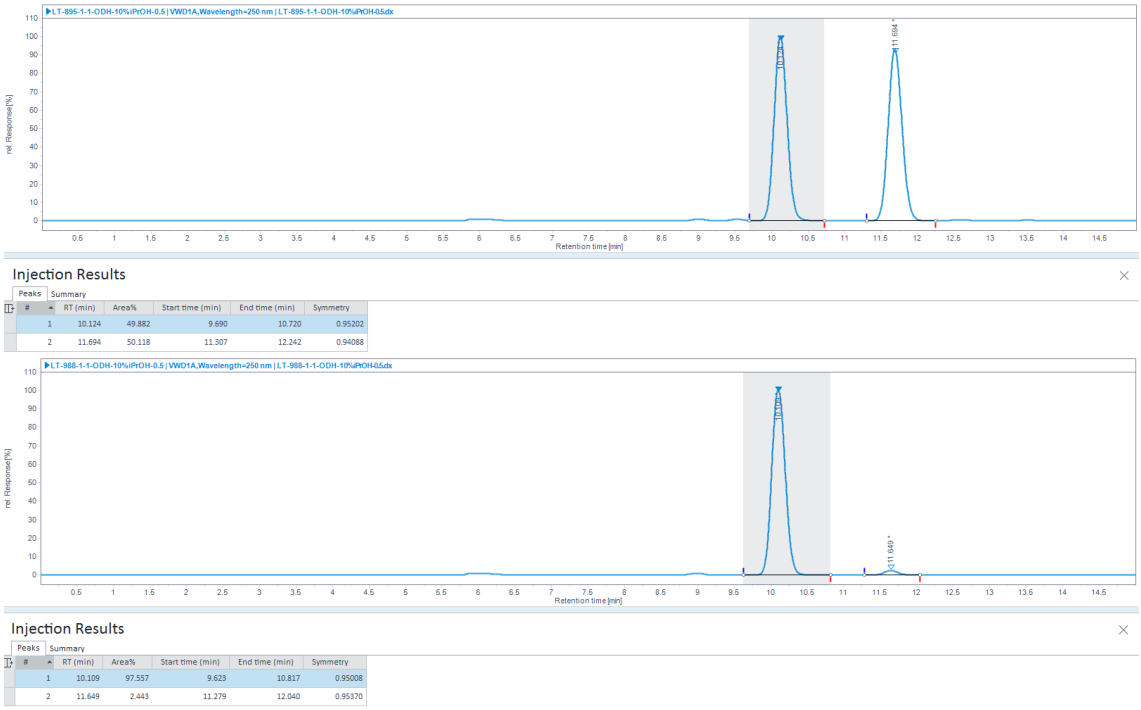
methyl (*S*)-2-((4-fluorophenyl)amino)-2-phenylbut-3-ynoate (5): yellow oil; 24.1 mg, 85% yield; 93% *ee*; R_f = 0.28 (PE:EA = 10:1); $[\alpha]_D^{20}$ = -79.0 (*c* = 0.19, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.82-7.71 (m, 2H), 7.47-7.30 (m, 3H), 6.87-6.69 (m, 2H), 6.61-6.43 (m, 2H), 5.31 (s, 1H), 3.76 (s, 3H), 2.64 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 156.6 (d, *J* = 236.6 Hz), 139.8 (d, *J* = 2.1 Hz), 137.9, 128.9, 128.8, 127.0, 116.8 (d, *J* = 7.4 Hz), 115.3 (d, *J* = 22.3 Hz), 80.6, 75.0, 62.4, 54.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -126.4; IR (neat, cm^{-1}) 3396, 3286, 2955, 1739, 1510, 1449, 1261, 1224, 1174, 1045, 823, 726, 697; HRMS (ESI): *m/z*: calcd for $C_{17}H_{15}FNO_2$ $[M+H]^+$: 284.1087, found: 284.1089.

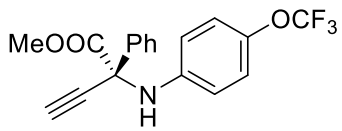
The *ee* was determined by HPLC analysis: CHIRALPAK ODH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 95/5; flow rate 0.5 mL/min; 35 °C; 250 nm; retention time: 11.4 min (major) and 12.6 min (minor).



methyl (*S*)-2-((4-bromophenyl)amino)-2-phenylbut-3-ynoate (6): yellow oil; 28.9 mg, 84% yield; 95% *ee*; R_f = 0.33 (PE:EA = 10:1); $[\alpha]_D^{20}$ = -69.0 (*c* = 0.19, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.80-7.70 (m, 2H), 7.45-7.32 (m, 3H), 7.19-7.09 (m, 2H), 6.54-6.38 (m, 2H), 5.49 (s, 1H), 3.76 (s, 3H), 2.65 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 142.5, 137.5, 131.6, 128.9, 128.9, 127.0, 117.2, 110.7, 80.2, 75.0, 61.9, 54.5; IR (neat, cm^{-1}) 3394, 3285, 2953, 2925, 1740, 1593, 1494, 1449, 1260, 1175, 1073, 815, 727, 697; HRMS (ESI): *m/z*: calcd for $C_{17}H_{15}BrNO_2$ $[M+H]^+$: 344.0286, found: 344.0292.

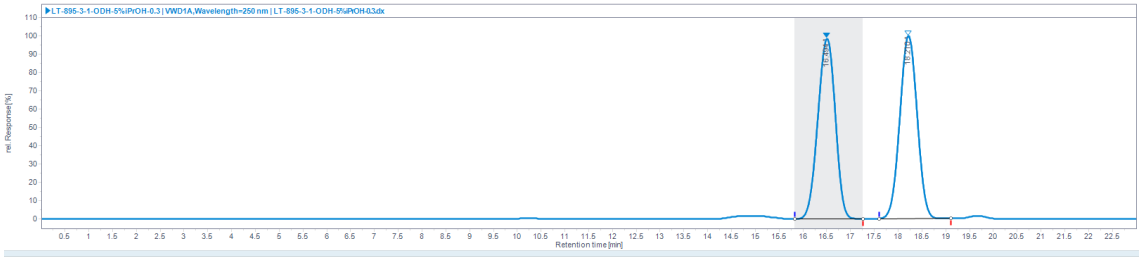
The *ee* was determined by HPLC analysis: CHIRALPAK ODH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 90/10; flow rate 0.5 mL/min; 35 °C; 250 nm; retention time: 10.1 min (major) and 11.6 min (minor).





methyl (*S*)-2-phenyl-2-((4-(trifluoromethoxy)phenyl)amino)but-3-ynoate (7): yellow oil; 30.0 mg, 86% yield; 95% *ee*; R_f = 0.36 (PE:EA = 10:1); $[\alpha]_D^{20}$ = -60.4 (*c* = 0.23, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.93-7.69 (m, 2H), 7.45-7.28 (m, 3H), 7.03-6.87 (m, 2H), 6.65-6.47 (m, 2H), 5.53 (s, 1H), 3.76 (s, 3H), 2.66 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 142.2, 141.5 (q, *J* = 2.0 Hz), 137.6, 129.0, 128.9, 127.0, 121.9, 120.7 (q, *J* = 255.4 Hz), 116.0, 80.2, 75.1, 62.0, 54.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.3; IR (neat, cm^{-1}) 3399, 3288, 2957, 2924, 1742, 1613, 1513, 1250, 1113, 832, 727; HRMS (ESI): *m/z*: calcd for $C_{18}H_{15}F_3NO_3$ $[M+H]^+$: 350.1004, found: 350.1007.

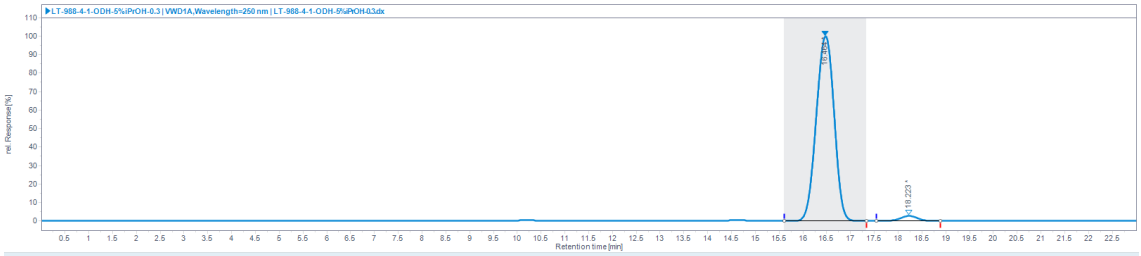
The *ee* was determined by HPLC analysis: CHIRALPAK ODH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 95/5; flow rate 0.3 mL/min; 35 °C; 250 nm; retention time: 16.5 min (major) and 18.2 min (minor).



Injection Results

Peaks | Summary

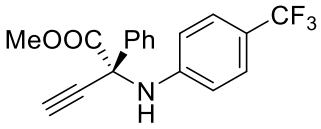
#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	16.494	49.874	15.821	17.254	1.02957
2	18.210	50.126	17.594	19.100	0.97736



Injection Results

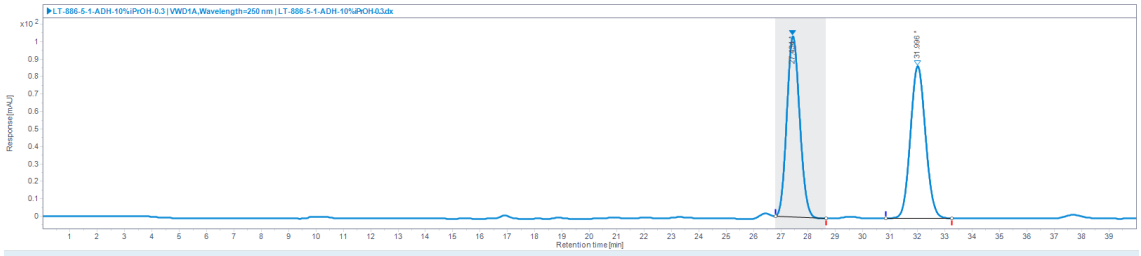
Peaks | Summary

#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	16.464	97.579	15.600	17.328	1.02341
2	18.223	2.421	17.534	18.878	1.05495



methyl (*S*)-2-phenyl-2-((4-(trifluoromethyl)phenyl)amino)but-3-ynoate (8): yellow oil; 23.0 mg, 69% yield; 96% *ee*; R_f = 0.26 (PE:EA = 10:1); $[\alpha]_D^{20}$ = -63.9 (*c* = 0.18, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.81-7.70 (m, 2H), 7.45-7.28 (m, 5H), 6.61 (d, *J* = 8.5 Hz, 2H), 5.84 (s, 1H), 3.78 (s, 3H), 2.68 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 146.0, 137.1, 129.0, 129.0, 126.9, 126.2 (q, *J* = 3.7 Hz), 124.9 (q, *J* = 268.9 Hz), 120.2 (q, *J* = 32.5 Hz), 114.8, 79.8, 75.1, 61.5, 54.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.3; IR (neat, cm^{-1}) 3397, 3289, 2957, 1741, 1616, 1530, 1320, 1108, 1066, 828, 726; HRMS (ESI): *m/z*: calcd for $C_{18}H_{15}F_3NO_2$ $[M+H]^+$: 334.1055, found: 334.1058.

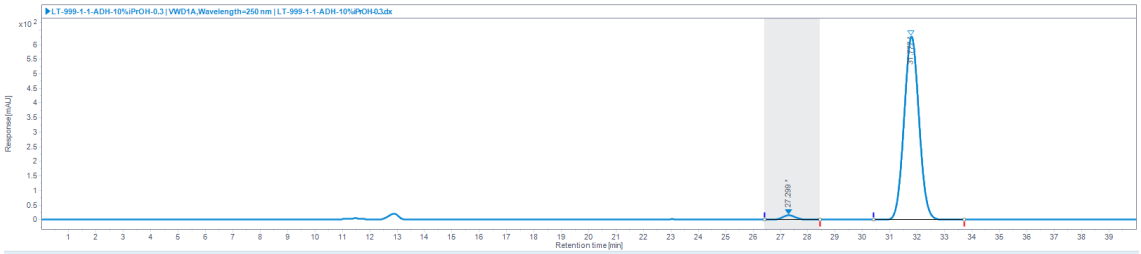
The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 90/10; flow rate 0.3 mL/min; 35 °C; 250 nm; retention time: 27.3 min (minor) and 31.8 min (major).



Injection Results

Peaks | Summary

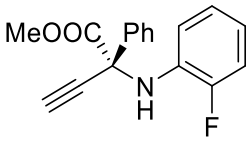
#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	27.434	50.217	26.794	28.644	0.88314
2	31.996	49.783	30.827	33.268	0.91069



Injection Results

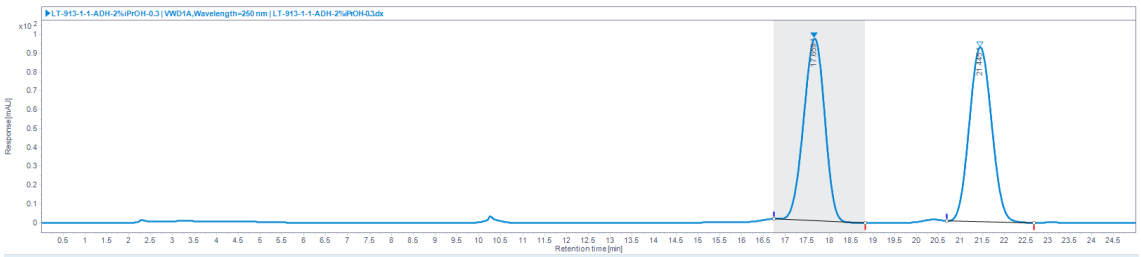
Peaks | Summary

#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	27.299	2.082	26.435	28.438	0.90403
2	31.777	97.918	30.412	33.705	0.94477



methyl (*S*)-2-((2-fluorophenyl)amino)-2-phenylbut-3-ynoate (9): white solid; 11.9 mg, 42% yield; 96% *ee*; R_f = 0.46 (PE:EA = 10:1); $[\alpha]_D^{20}$ = -65.0 (*c* = 0.14, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 6.6 Hz, 2H), 7.46-7.31 (m, 3H), 7.06-6.93 (m, 1H), 6.76 (t, *J* = 7.7 Hz, 1H), 6.69-6.59 (m, 1H), 6.53-6.39 (m, 1H), 5.76 (s, 1H), 3.78 (s, 3H), 2.67 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 152.3 (d, *J* = 239.5 Hz), 137.6, 132.0 (d, *J* = 10.8 Hz), 128.9, 128.9, 126.9, 123.7 (d, *J* = 3.7 Hz), 118.3 (d, *J* = 7.1 Hz), 115.8 (d, *J* = 2.5 Hz), 114.6 (d, *J* = 18.7 Hz), 80.3, 75.2, 61.8, 54.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -134.8; IR (neat, cm^{-1}) 3409, 3286, 2955, 2921, 1743, 1620, 1512, 1447, 1333, 1260, 1197, 1097, 1047, 810, 745; HRMS (ESI): *m/z*: calcd for $C_{17}H_{15}FNO_2$ $[M+H]^+$: 284.1087, found: 284.1089.

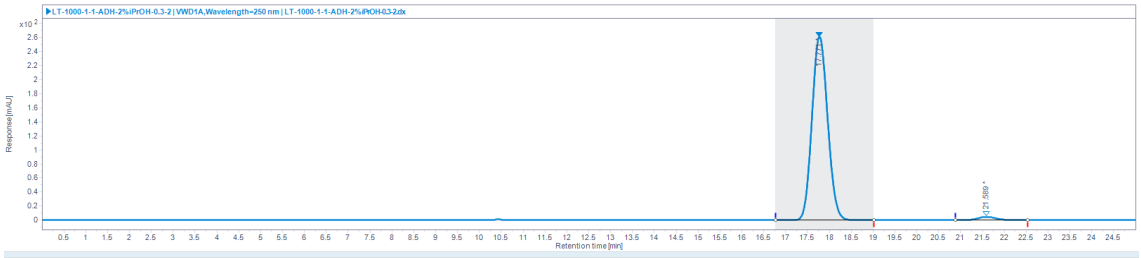
The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 98/2; flow rate 0.3 mL/min; 35 °C; 250 nm; retention time: 17.8 min (major) and 21.6 min (minor).



Injection Results

Peaks | Summary

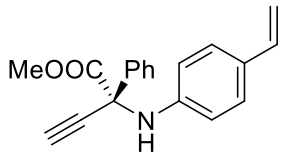
#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	17.659	49.569	16.730	18.818	1.05571
2	21.445	50.431	20.680	22.682	0.92805



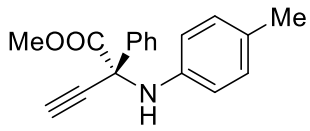
Injection Results

Peaks | Summary

#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	17.771	98.065	16.763	19.011	0.89995
2	21.589	1.935	20.873	22.526	0.88909

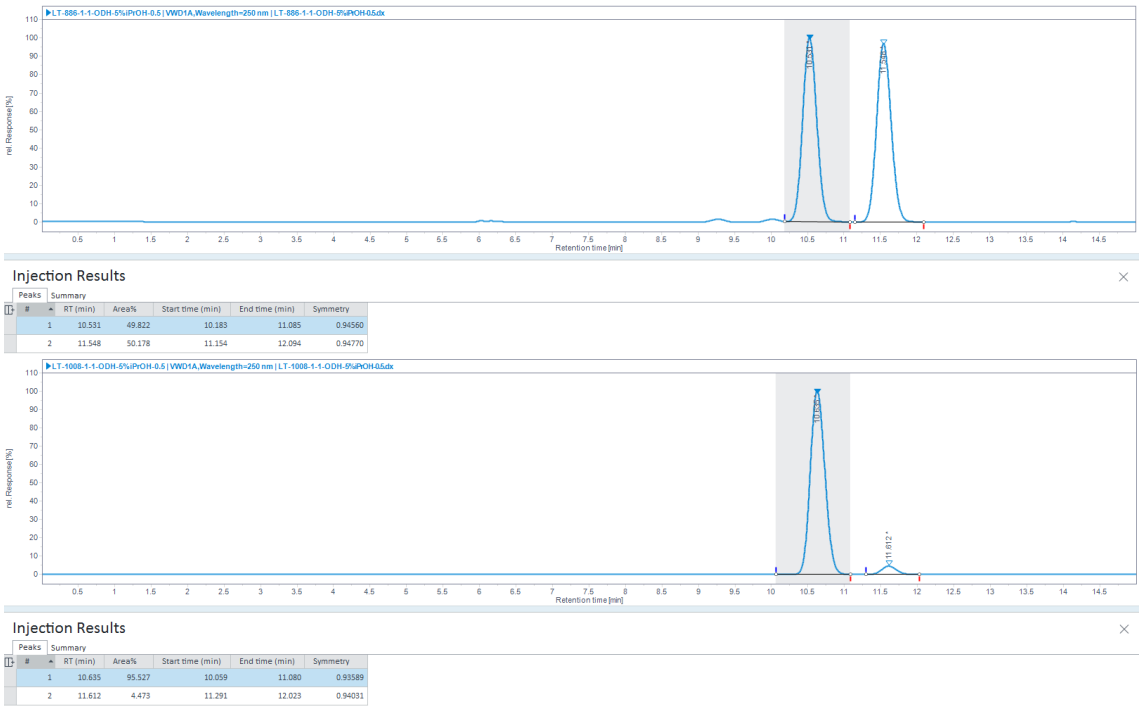


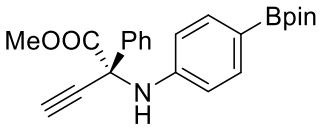
methyl (*S*)-2-phenyl-2-((4-vinylphenyl)amino)but-3-ynoate (10): yellow solid; 27.1 mg, 93% yield; 95% *ee*; R_f = 0.56 (PE:EA = 5:1); $[\alpha]_D^{20}$ = -89.5 (*c* = 0.20, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.9 Hz, 2H), 7.51-7.31 (m, 3H), 7.17 (d, *J* = 8.6 Hz, 2H), 6.70-6.50 (m, 3H), 5.56 (s, 1H), 5.52 (d, *J* = 17.6 Hz, 1H), 5.02 (d, *J* = 10.9 Hz, 1H), 3.77 (s, 3H), 2.67 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 143.2, 137.8, 136.6, 128.9, 128.7, 128.3, 127.0, 126.8, 115.5, 110.2, 80.5, 74.9, 61.9, 54.4; IR (neat, cm^{-1}) 3394, 3282, 2954, 1738, 1609, 1516, 1316, 1261, 1182, 1030, 829, 724, 696; HRMS (ESI): *m/z*: calcd for $C_{19}H_{18}NO_2$ $[M+H]^+$: 292.1338, found: 292.1338.
The *ee* was determined by HPLC analysis: CHIRALPAK ODH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 90/10; flow rate 0.3 mL/min; 35 °C; 250 nm; retention time: 16.8 min (major) and 19.1 min (minor).



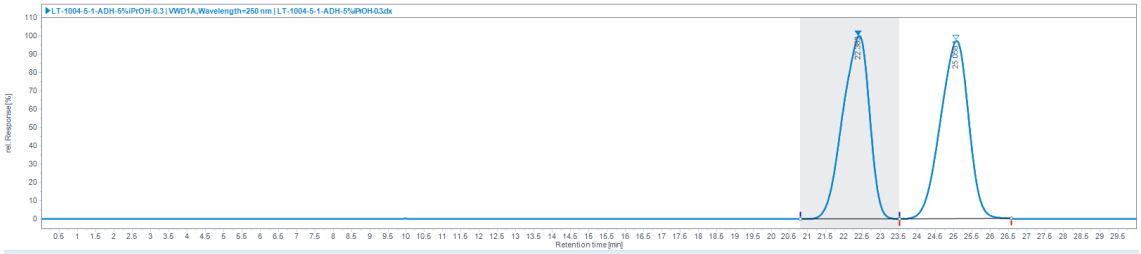
methyl (*S*)-2-phenyl-2-(p-tolylamino)but-3-ynoate (11): yellow oil; 25.9 mg, 93% yield; 91% *ee*; R_f = 0.33 (PE:EA = 10:1); $[\alpha]_D^{20}$ = -75.3 (*c* = 0.17, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.98-7.72 (m, 2H), 7.51-7.29 (m, 3H), 7.01-6.82 (m, 2H), 6.59-6.42 (m, 2H), 5.29 (s, 1H), 3.76 (s, 3H), 2.64 (s, 1H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 141.1, 138.2, 129.3, 128.8, 128.7, 127.9, 127.1, 115.8, 80.8, 74.8, 62.3,

54.3, 20.6; IR (neat, cm^{-1}) 3396, 3281, 2953, 2920, 1739, 1617, 1519, 1301, 1259, 1173, 809, 725; HRMS (ESI): *m/z*: calcd for $C_{18}H_{18}NO_2$ $[M+H]^+$: 280.1338, found: 280.1341.
The *ee* was determined by HPLC analysis: CHIRALPAK ODH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 95/5; flow rate 0.5 mL/min; 35 °C; 250 nm; retention time: 10.6 min (major) and 11.6 min (minor).





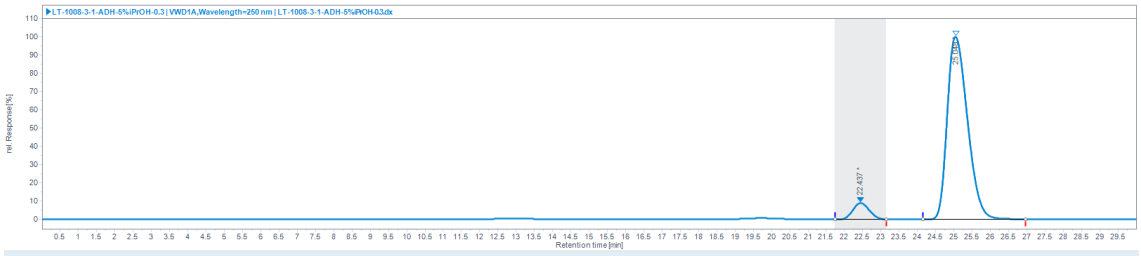
methyl (*S*)-2-phenyl-2-((4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)amino)but-3-ynoate (12): white solid; 28.2 mg, 72%; 86% *ee*; R_f = 0.18 (PE:EA = 10:1); $[\alpha]_D^{20}$ = -70.6 (*c* = 0.16, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.8 Hz, 2H), 7.53 (d, *J* = 6.7 Hz, 2H), 7.42-7.28 (m, 3H), 6.57 (d, *J* = 6.7 Hz, 2H), 5.68 (s, 1H), 3.76 (s, 3H), 2.64 (s, 1H), 1.28 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 146.0, 137.6, 135.8, 128.9, 128.7, 127.0, 114.7, 83.3, 80.3, 74.8, 61.7, 54.5, 24.9; IR (neat, cm^{-1}) 3395, 3284, 2977, 2921, 2850, 1742, 1605, 1356, 1318, 1259, 1142, 1089, 861, 824, 727, 654; HRMS (ESI): *m/z*: calcd for $C_{23}H_{27}BNO_4$ $[M+H]^+$: 392.2033, found: 392.2041.
The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 95/5; flow rate 0.3 mL/min; 35 °C; 250 nm; retention time: 22.4 min (minor) and 25.0 min (major).



Injection Results

Peaks | Summary

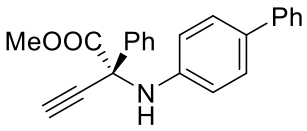
#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	22.383	49.518	20.795	23.522	1.41793
2	25.058	50.482	23.522	26.569	1.23813



Injection Results

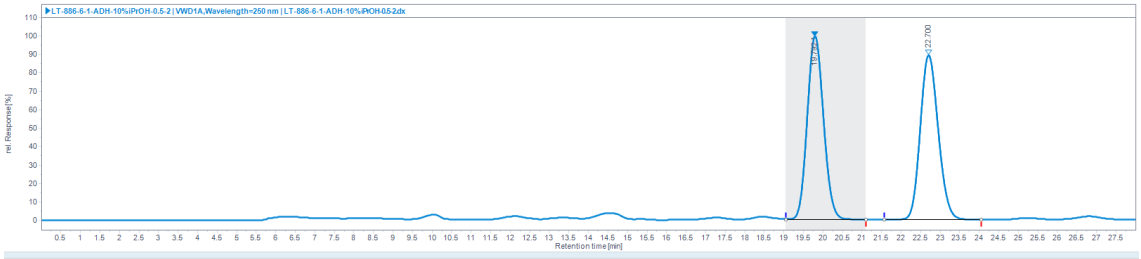
Peaks | Summary

#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	22.437	6.853	21.732	23.138	0.90457
2	25.048	93.147	24.140	26.953	0.70628



methyl (*S*)-2-([1,1'-biphenyl]-4-ylamino)-2-phenylbut-3-ynoate (13): yellow solid; 30.0 mg, 88% yield; 95% *ee*; R_f = 0.31 (PE:EA = 10:1); $[\alpha]_D^{20}$ = -77.4 (*c* = 0.38, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.94-7.83 (m, 2H), 7.60-7.51 (m, 2H), 7.51-7.37 (m, 7H), 7.34-7.25 (m, 1H), 6.81-6.66 (m, 2H), 5.62 (s, 1H), 3.82 (s, 3H), 2.73 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 142.8, 141.1, 137.9, 131.4, 128.9, 128.8, 128.7, 127.5, 127.0, 126.4, 126.3, 115.8, 80.5, 75.0, 62.0, 54.4; IR (neat, cm^{-1}) 3397, 3281, 3027, 2921, 1741, 1612, 1525, 1488, 1259, 1175, 828, 764, 697; HRMS (ESI): *m/z*: calcd for $C_{23}H_{20}NO_2$ $[M+H]^+$: 342.1494, found: 342.1497.

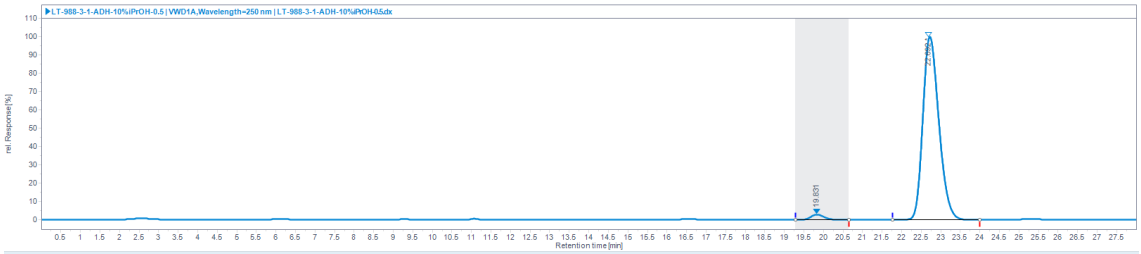
The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 90/10; flow rate 0.5 mL/min; 35 °C; 250 nm; retention time: 19.8 min (minor) and 22.7 min (major).



Injection Results

Peaks | Summary

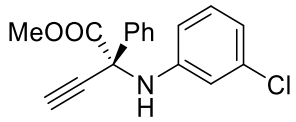
#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	19.792	50.398	19.052	21.092	0.89987
2	22.700	49.602	21.572	24.050	0.86250



Injection Results

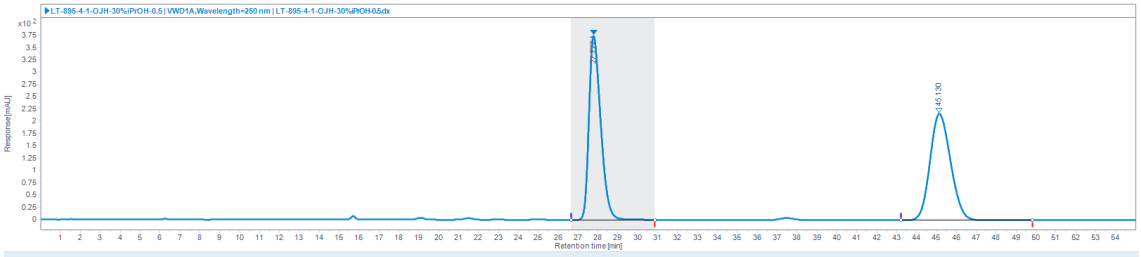
Peaks | Summary

#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	19.831	2.400	19.290	20.653	0.88019
2	22.692	97.600	21.757	23.987	0.63672



methyl (*S*)-2-((3-chlorophenyl)amino)-2-phenylbut-3-ynoate (14): yellow oil; 25.1 mg, 84% yield; 97% *ee*; R_f = 0.33 (PE:EA = 10:1); $[\alpha]_D^{20}$ = -79.3 (*c* = 0.30, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 6.5 Hz, 2H), 7.44-7.32 (m, 3H), 6.97 (t, *J* = 8.1 Hz, 1H), 6.68 (d, *J* = 7.9 Hz, 1H), 6.61 (t, *J* = 2.1 Hz, 1H), 6.45 (d, *J* = 8.2 Hz, 1H), 5.58 (s, 1H), 3.76 (s, 3H), 2.68 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 144.6, 137.4, 134.4, 129.8, 129.0, 128.9, 126.9, 118.6, 115.5, 113.6, 80.0, 75.2, 61.7, 54.5; IR (neat, cm^{-1}) 3392, 3286, 2954, 1738, 1598, 1487, 1257, 1174, 1097, 1045, 768, 727, 682; HRMS (ESI): *m/z*: calcd for $C_{17}H_{15}ClNO_2$ $[M+H]^+$: 300.0791, found: 300.0793.

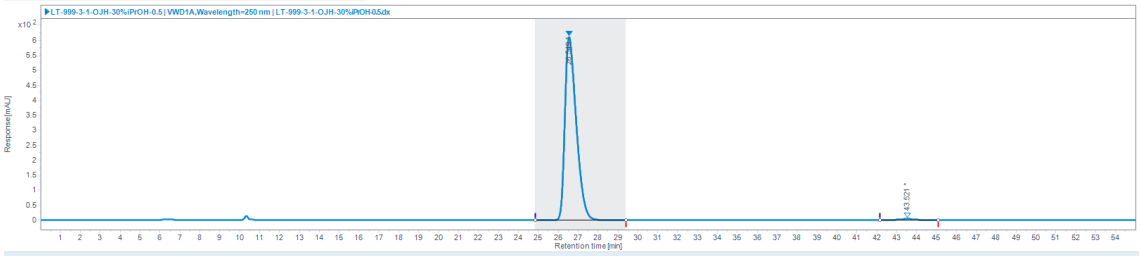
The *ee* was determined by HPLC analysis: CHIRALPAK OJH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 70/30; flow rate 0.5 mL/min; 35 °C; 250 nm; retention time: 26.5 min (major) and 43.5 min (minor).



Injection Results

Peaks | Summary

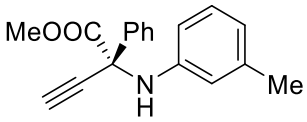
#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	27.777	49.671	26.641	30.837	0.66290
2	45.130	50.329	43.213	49.806	0.81040



Injection Results

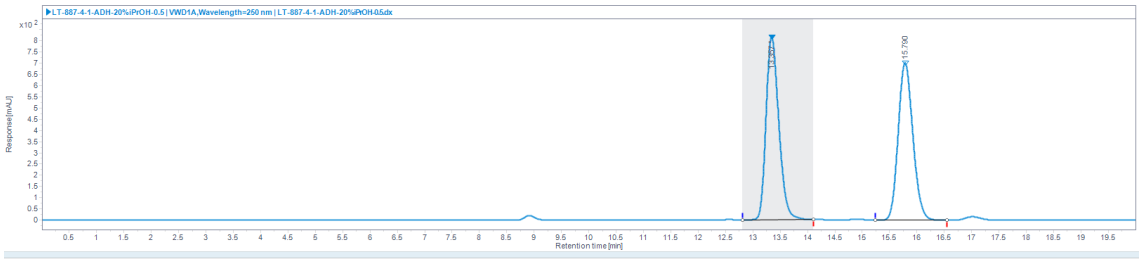
Peaks | Summary

#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	26.549	98.685	24.853	29.388	0.61344
2	43.521	1.315	42.139	45.071	0.96882



methyl (*S*)-2-phenyl-2-(m-tolylamino)but-3-ynoate (15): white solid; 25.1 mg, 90% yield; 94% *ee*; R_f = 0.64 (PE:EA = 5:1); $[\alpha]_D^{20}$ = -85.2 (*c* = 0.25, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.1 Hz, 2H), 7.42-7.29 (m, 3H), 6.95 (t, *J* = 7.8 Hz, 1H), 6.55 (d, *J* = 7.5 Hz, 1H), 6.48 (s, 1H), 6.35 (d, *J* = 8.0 Hz, 1H), 5.36 (s, 1H), 3.76 (s, 3H), 2.64 (s, 1H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 143.5, 138.6, 138.1, 128.8, 128.7, 128.6, 127.0, 119.7, 116.6, 112.6, 80.7, 74.8, 62.1, 54.3, 21.7; IR (neat, cm^{-1}) 3397, 3281, 2954, 2920, 1740, 1607, 1488, 1449, 1268, 1247, 1191, 772, 695; HRMS (ESI): *m/z*: calcd for $C_{18}H_{18}NO_2$ $[M+H]^+$: 280.1338, found: 280.1336.

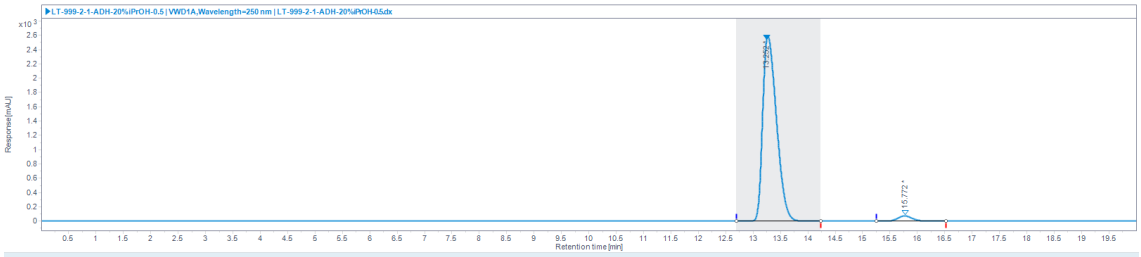
The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 80/20; flow rate 0.5 mL/min; 35 ºC; 250 nm; retention time: 13.3 min (major) and 15.8 min (minor).



Injection Results

Peaks | Summary

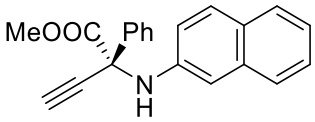
#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	13.357	50.392	12.811	14.102	0.85602
2	15.790	49.608	15.235	16.551	0.89552



Injection Results

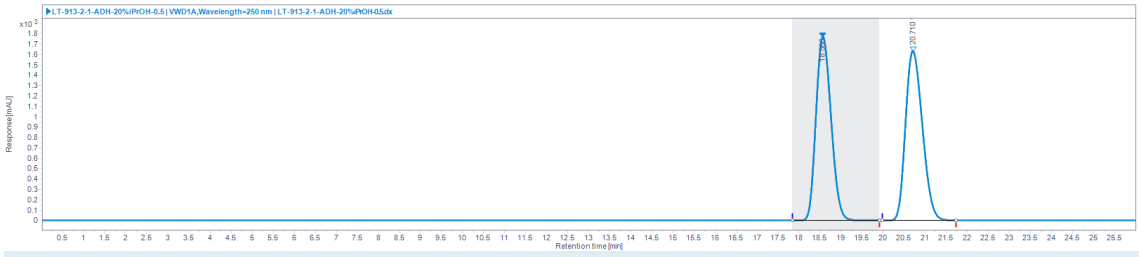
Peaks | Summary

#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	13.252	97.114	12.689	14.230	0.43944
2	15.772	2.886	15.245	16.523	0.88563



methyl (*S*)-2-(naphthalen-2-ylamino)-2-phenylbut-3-ynoate (16): yellow oil; 28.0 mg, 89% yield; 95% *ee*; R_f = 0.31 (PE:EA = 10:1); $[\alpha]_D^{20}$ = -81.8 (*c* = 0.17, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.94-7.80 (m, 2H), 7.64 (dd, *J* = 13.6, 8.4 Hz, 2H), 7.48 (d, *J* = 8.2 Hz, 1H), 7.43-7.25 (m, 4H), 7.25-7.15 (m, 1H), 6.98 (d, *J* = 8.9 Hz, 1H), 6.78 (s, 1H), 5.65 (s, 1H), 3.80 (s, 3H), 2.67 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4，141.0, 137.7, 134.4, 128.9, 128.8, 128.7, 128.0, 127.6, 127.1, 126.5, 126.1, 122.7, 119.0, 109.3, 80.6, 75.0, 62.1, 54.4; IR (neat, cm^{-1}) 3395, 3282, 3057, 2953, 1738, 1630, 1602, 1518, 1483, 1247, 1047, 836, 808, 724; HRMS (ESI): *m/z*: calcd for $C_{21}H_{18}NO_2$ $[M+H]^+$: 316.1338, found: 316.1344.

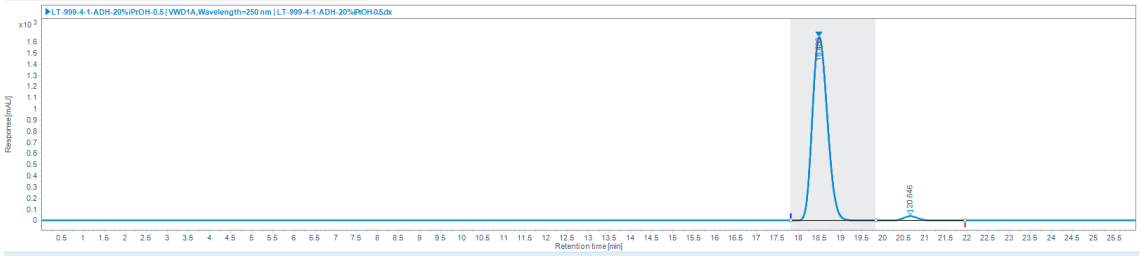
The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 80/20; flow rate 0.5 mL/min; 35 °C; 250 nm; retention time: 18.5 min (major) and 20.6 min (minor).



Injection Results

Peaks | Summary

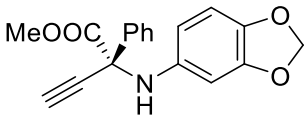
#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	18.566	49.298	17.838	19.917	0.84391
2	20.710	50.702	19.971	21.724	0.81731



Injection Results

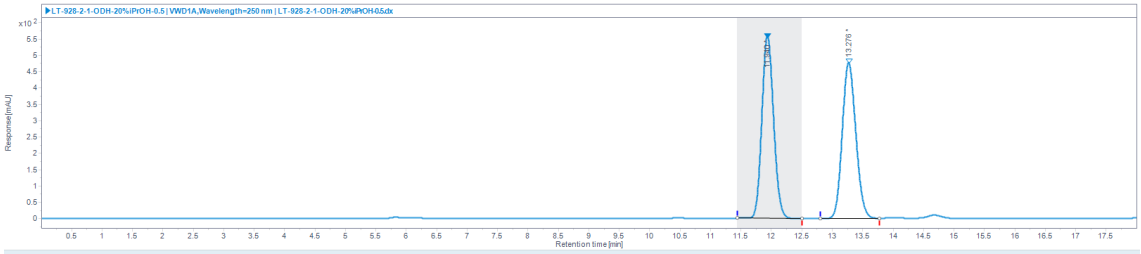
Peaks | Summary

#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	18.486	97.623	17.817	19.822	0.85683
2	20.646	2.377	19.822	21.957	0.91377



methyl (*S*)-2-(benzo[*d*][1,3]dioxol-5-ylamino)-2-phenylbut-3-ynoate (17): yellow oil; 29.4 mg, 95% yield; 95% *ee*; R_f = 0.21 (PE:EA = 10:1); $[\alpha]_D^{20}$ = -57.6 (*c* = 0.21, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.84-7.73 (m, 2H), 7.44-7.29 (m, 3H), 6.56 (d, *J* = 8.3 Hz, 1H), 6.20 (d, *J* = 2.2 Hz, 1H), 6.06 (dd, *J* = 8.4, 2.3 Hz, 1H), 5.80 (dd, *J* = 6.9, 1.4 Hz, 2H), 5.18 (s, 1H), 3.75 (s, 3H), 2.66 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 147.8, 140.6, 138.9, 138.1, 128.8, 128.7, 127.1, 108.3, 108.3, 100.7, 98.9, 80.8, 75.2, 62.8, 54.3; IR (neat, cm^{-1}) 3391, 3281, 2954, 2887, 1740, 1634, 1503, 1488, 1241, 1205, 1039, 935, 819, 728; HRMS (ESI): *m/z*: calcd for $C_{18}H_{16}NO_4$ $[M+H]^+$: 310.1079, found: 310.1079.

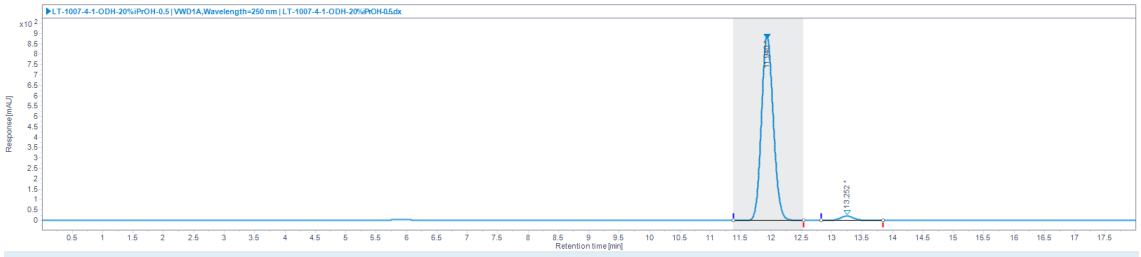
The *ee* was determined by HPLC analysis: CHIRALPAK ODH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 80/20; flow rate 0.5 mL/min; 35 ºC; 250 nm; retention time: 11.9 min (major) and 13.3 min (minor).



Injection Results

Peaks | Summary

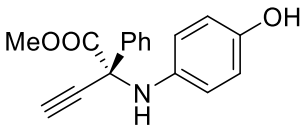
#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	11.940	50.312	11.434	12.497	0.94916
2	13.276	49.688	12.802	13.780	0.92022



Injection Results

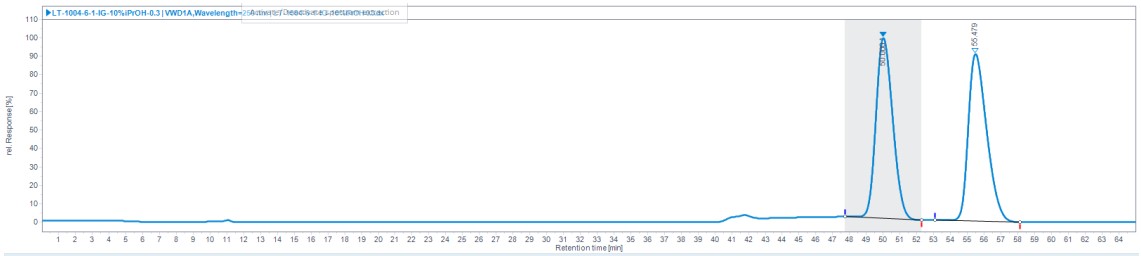
Peaks | Summary

#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	11.940	97.521	11.374	12.530	0.94511
2	13.252	2.479	12.819	13.847	0.93734



methyl (*S*)-2-((4-hydroxyphenyl)amino)-2-phenylbut-3-ynoate (18): white solid; 26.1 mg, 93% yield; 73% *ee*; R_f = 0.18 (PE:EA = 5:1); $[\alpha]_D^{20}$ = -51.2 (*c* = 0.25, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.4 Hz, 2H), 7.45-7.29 (m, 3H), 6.58 (d, *J* = 8.1 Hz, 2H), 6.49 (d, *J* = 7.6 Hz, 2H), 5.06 (s, 1H), 4.79 (s, 1H), 3.75 (s, 3H), 2.63 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 148.7, 138.2, 137.5, 128.8, 128.7, 127.1, 117.6, 115.7, 80.9, 75.1, 62.9, 54.3; IR (neat, cm^{-1}) 3382, 3282, 2924, 2853, 1737, 1512, 1245, 1172, 822, 696; HRMS (ESI): *m/z*: calcd for $C_{17}H_{16}NO_3$ $[M+H]^+$: 282.1130, found: 282.1129.

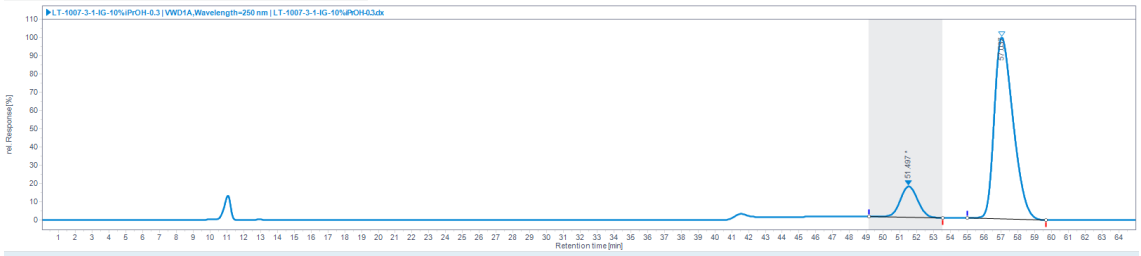
The *ee* was determined by HPLC analysis: CHIRALPAK IG (4.6 mm i.d. × 250 mm); hexane/2–propanol = 90/10; flow rate 0.3 mL/min; 35 °C; 250 nm; retention time: 51.5 min (minor) and 57.0 min (major).



Injection Results

Peaks | Summary

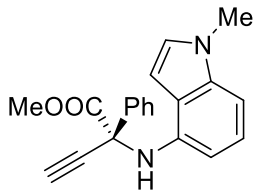
#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	50.000	49.617	47.717	52.292	0.78649
2	55.479	50.383	53.094	58.122	0.62646



Injection Results

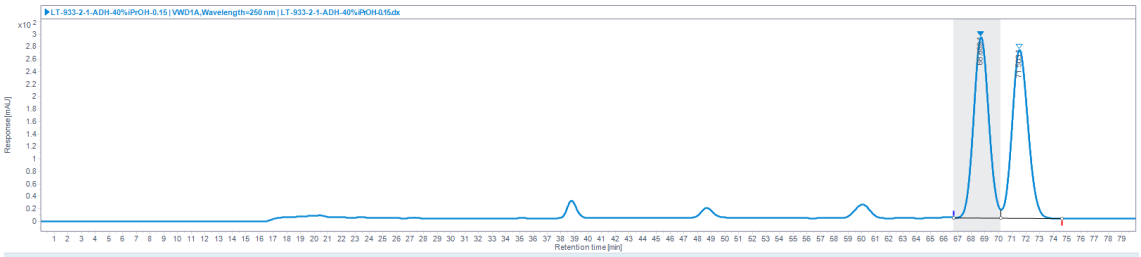
Peaks | Summary

#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	51.497	13.550	49.136	53.546	0.92137
2	57.037	86.450	55.014	59.683	0.63846



methyl (*S*)-2-((1-methyl-1H-indol-4-yl)amino)-2-phenylbut-3-ynoate (19): brown solid; 28.0 mg, 88% yield; 81% *ee*; R_f = 0.15 (PE:EA = 10:1); $[\alpha]_D^{20}$ = -47.2 (*c* = 0.18, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.5 Hz, 2H), 7.48-7.29 (m, 3H), 7.09 (d, *J* = 8.7 Hz, 1H), 6.92 (d, *J* = 3.0 Hz, 1H), 6.80 (s, 1H), 6.68 (d, *J* = 8.7 Hz, 1H), 6.24 (d, *J* = 3.0 Hz, 1H), 5.14 (s, 1H), 3.78 (s, 3H), 3.69 (s, 3H), 2.63 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 139.0, 137.3, 132.3, 129.2, 129.0, 128.9, 127.5, 114.2, 109.7, 107.5, 100.5, 81.7, 75.3, 63.7, 54.5, 33.2; IR (neat, cm^{-1}) 3392, 3279, 2952, 2921, 1738, 1626, 1576, 1500, 1251, 1188, 725, 699; HRMS (ESI): *m/z*: calcd for $C_{20}H_{19}N_2O_2$ $[M+H]^+$: 319.1447, found: 319.1456.

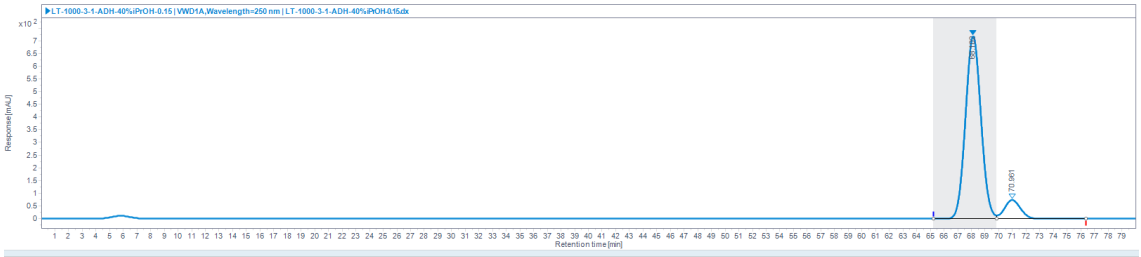
The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 60/40; flow rate 0.15 mL/min; 35 °C; 250 nm; retention time: 68.1 min (major) and 71.0 min (minor).



Injection Results

Peaks | Summary

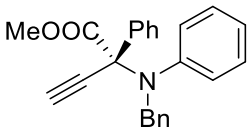
#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	68.689	50.441	66.691	70.159	0.93543
2	71.503	49.559	70.159	74.603	0.85088



Injection Results

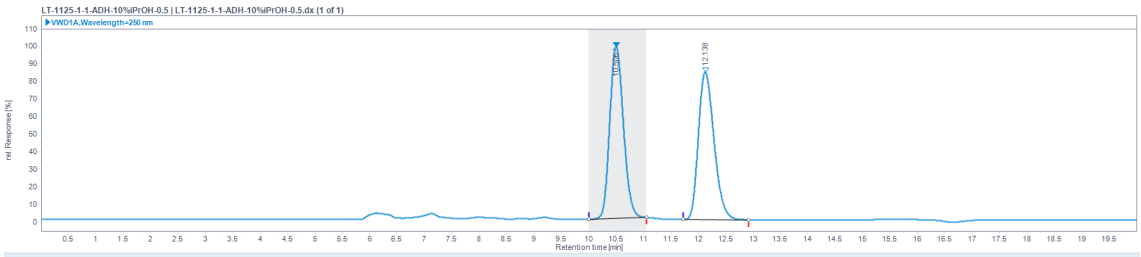
Peaks | Summary

#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	68.102	90.283	65.235	69.850	0.94076
2	70.961	9.717	69.850	76.361	0.88463



methyl (*S*)-2-(benzyl(phenyl)amino)-2-phenylbut-3-ynoate (20): colorless oil; 22.7 mg, 64% yield; 59% *ee*; R_f = 0.28 (PE:EA = 10:1); $[\alpha]_D^{20}$ = 2.14 (*c* = 0.14, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.4 Hz, 2H), 7.33-7.24 (m, 5H), 7.22-7.11 (m, 5H), 7.05 (t, *J* = 7.7 Hz, 2H), 6.92 (t, *J* = 7.3 Hz, 1H), 4.19 (q, *J* = 14.5 Hz, 2H), 3.53 (s, 3H), 2.99 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 147.8, 139.3, 137.5, 128.8, 128.8, 128.5, 128.3, 128.1, 128.0, 126.8, 126.1, 124.3, 80.6, 78.1, 72.4, 57.0, 53.4; IR (neat, cm^{-1}) 3280, 3029, 1745, 1597, 1493, 1450, 1228, 1029, 726, 698; HRMS (ESI): *m/z*: calcd for $C_{24}H_{22}NO_2$ $[M+H]^+$: 356.1651, found: 356.1654.

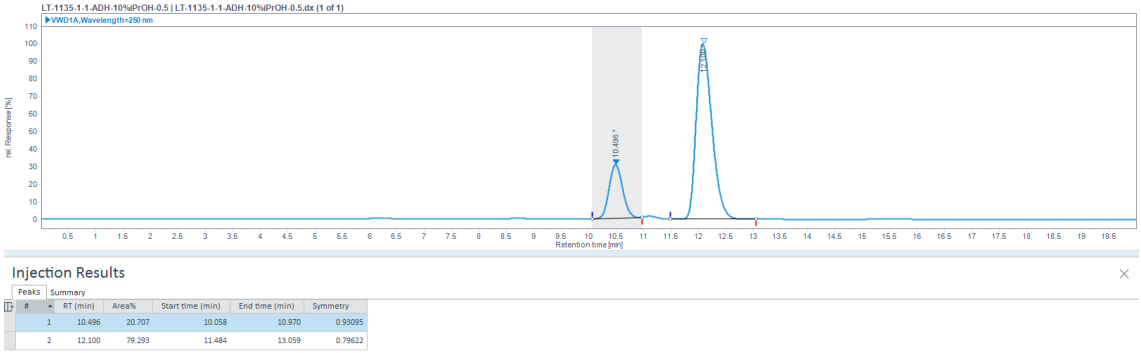
The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 90/10; flow rate 0.5 mL/min; 35 °C; 250 nm; retention time: 10.5 min (minor) and 12.1 min (major).



Injection Results

Peaks | Summary

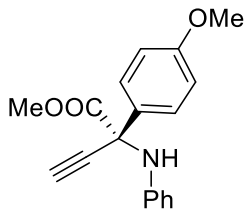
#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	10.506	50.515	10.002	11.047	0.89609
2	12.138	49.485	11.716	12.922	0.81904



Injection Results

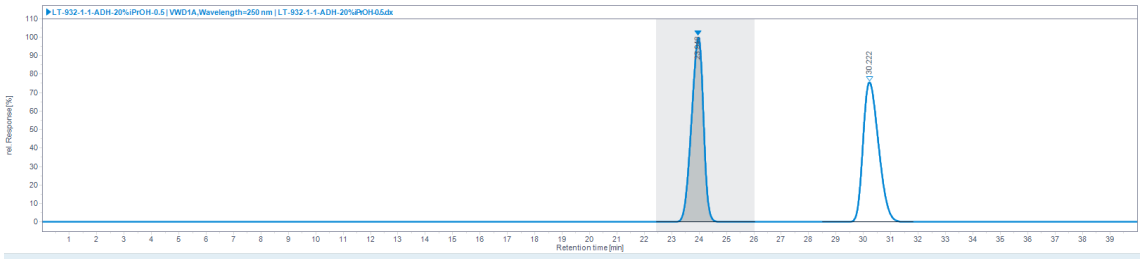
Peaks | Summary

#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	10.496	20.707	10.058	10.970	0.93095
2	12.100	79.293	11.484	13.059	0.79622



methyl (*S*)-2-(4-methoxyphenyl)-2-(phenylamino)but-3-ynoate (21): yellow oil; 26.0 mg, 88% yield; 97% *ee*; R_f = 0.44 (PE:EA = 5:1); $[\alpha]_D^{20}$ = -60.9 (*c* = 0.23, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.77-7.65 (m, 2H), 7.16-7.05 (m, 2H), 6.98-6.86 (m, 2H), 6.81-6.70 (m, 1H), 6.67-6.55 (m, 2H), 5.40 (s, 1H), 3.81 (s, 3H), 3.77 (s, 3H), 2.64 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 159.8, 143.6, 129.8, 128.7, 128.3, 118.6, 115.6, 114.1, 80.8, 74.6, 61.5, 55.4, 54.2; IR (neat, cm^{-1}) 3396, 3282, 2954, 2921, 1740, 1604, 1505, 1304, 1251, 1172, 1033, 840, 751, 692; HRMS (ESI): *m/z*: calcd for $C_{18}H_{18}NO_3$ $[M+H]^+$: 296.1287, found: 296.1292.

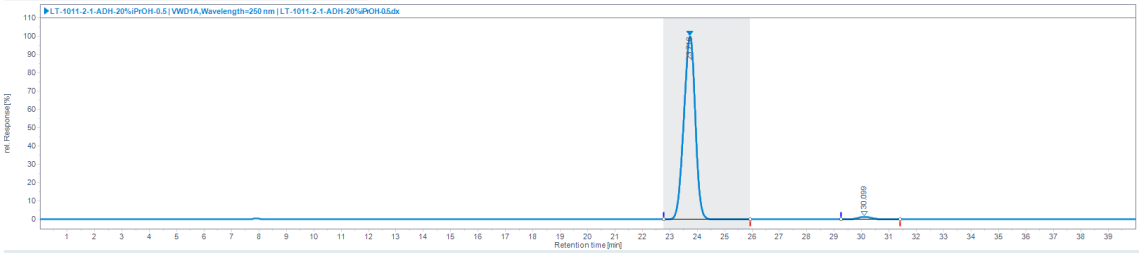
The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 80/20; flow rate 0.5 mL/min; 35 ºC; 250 nm; retention time: 23.7 min (major) and 30.1 min (minor).



Injection Results

Peaks | Summary

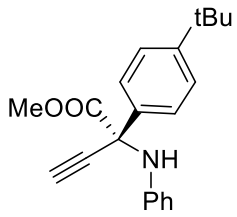
#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	23.948	50.388	22.433	26.026	1.18667
2	30.222	49.612	28.513	31.814	0.71737



Injection Results

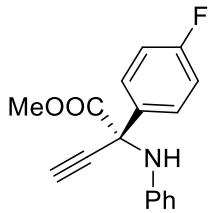
Peaks | Summary

#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	23.716	98.408	22.763	25.929	1.06844
2	30.099	1.592	29.243	31.407	0.87886



methyl (*S*)-2-(4-(tert-butyl)phenyl)-2-(phenylamino)but-3-ynoate (22): yellow oil; 29.5 mg, 92% yield; 96% *ee*; R_f = 0.59 (PE:EA = 5:1); $[\alpha]_D^{20}$ = -40.4 (*c* = 0.24, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.17-7.03 (m, 2H), 6.73 (t, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 2H), 5.35 (s, 1H), 3.77 (s, 3H), 2.63 (s, 1H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 151.7, 143.7, 134.9, 128.8, 126.6, 125.8, 118.6, 115.6, 80.9, 74.7, 61.9, 54.3, 34.7, 31.4; IR (neat, cm^{-1}) 3400, 3281, 2958, 2868, 1740, 1603, 1502, 1315, 1262, 1178, 844, 786, 691; HRMS (ESI): *m/z*: calcd for $C_{21}H_{24}NO_2$ $[M+H]^+$: 322.1807, found: 322.1811.

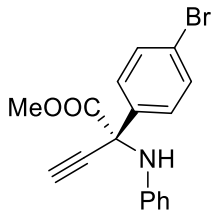
The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 95/5; flow rate 0.5 mL/min; 35 °C; 250 nm; retention time: 14.9 min (major) and 16.4 min (minor).



methyl (*S*)-2-(4-fluorophenyl)-2-(phenylamino)but-3-ynoate (23): yellow oil; 24.1 mg, 85% yield; 93% *ee*; R_f = 0.56 (PE:EA = 5:1); $[\alpha]_D^{20}$ = -106.9 (*c* = 0.16, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.87-7.69 (m, 2H), 7.17-6.98 (m, 4H), 6.74 (t, *J* = 7.3 Hz,

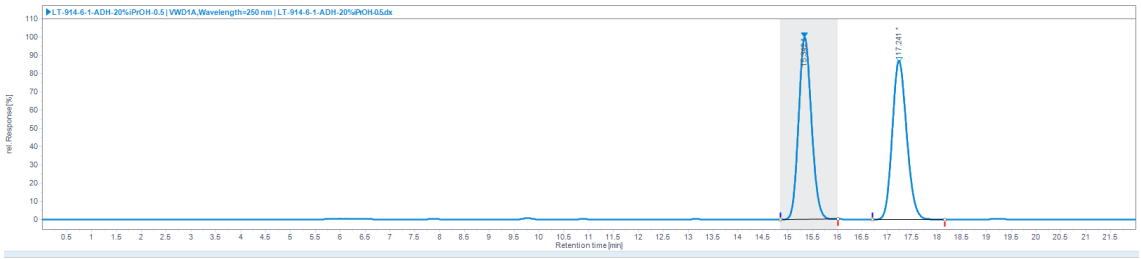
1H), 6.58 (d, *J* = 8.0 Hz, 2H), 5.43 (s, 1H), 3.77 (s, 3H), 2.64 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 163.0 (d, *J* = 247.9 Hz), 143.3, 133.8 (d, *J* = 3.0 Hz), 129.0 (d, *J* = 8.4 Hz), 128.8, 118.9, 115.8 (d, *J* = 21.9 Hz), 115.7, 80.5, 75.0, 61.5, 54.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.6; IR (neat, cm^{-1}) 3396, 3288, 2955, 2921, 1743, 1603, 1503, 1433, 1262, 1229, 1158, 845, 784, 751; HRMS (ESI): *m/z*: calcd for $C_{17}H_{15}FNO_2$ $[M+H]^+$: 284.1087, found: 284.1089.

The *ee* was determined by HPLC analysis: CHIRALPAK ODH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 90/10; flow rate 0.3 mL/min; 35 °C; 250 nm; retention time: 17.4 min (minor) and 19.0 min (major).



methyl (*S*)-2-(4-bromophenyl)-2-(phenylamino)but-3-ynoate (24): yellow oil; 29.9 mg, 87% yield; 93% *ee*; R_f = 0.33 (PE:EA = 10:1); $[\alpha]_D^{20}$ = -61.0 (*c* = 0.29, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.6 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.09 (t, *J* = 7.7 Hz, 2H), 6.74 (t, *J* = 7.4 Hz, 1H), 6.56 (d, *J* = 8.0 Hz, 2H), 5.43 (s, 1H), 3.77 (s, 3H), 2.64 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 143.1, 137.3, 132.0, 128.9, 128.9, 123.0, 119.0, 115.7, 80.2, 75.1, 61.6, 54.5; IR (neat, cm^{-1}) 3395, 3288, 2954, 2922, 1743, 1603, 1503, 1484, 1316, 1262, 1073, 750, 692; HRMS (ESI): *m/z*: calcd for $C_{17}H_{15}BrNO_2$ $[M+H]^+$: 344.0286, found: 344.0291.

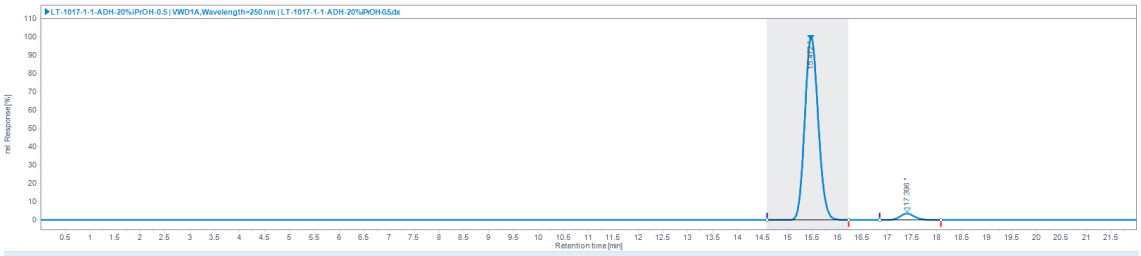
The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 80/20; flow rate 0.5 mL/min; 35 °C; 250 nm; retention time: 15.5 min (major) and 17.4 min (minor).



Injection Results

Peaks | Summary

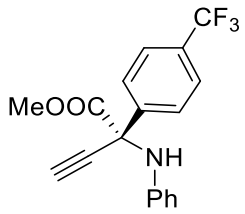
#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	15.342	50.559	14.851	16.008	0.89812
2	17.241	49.441	16.704	18.155	0.89223



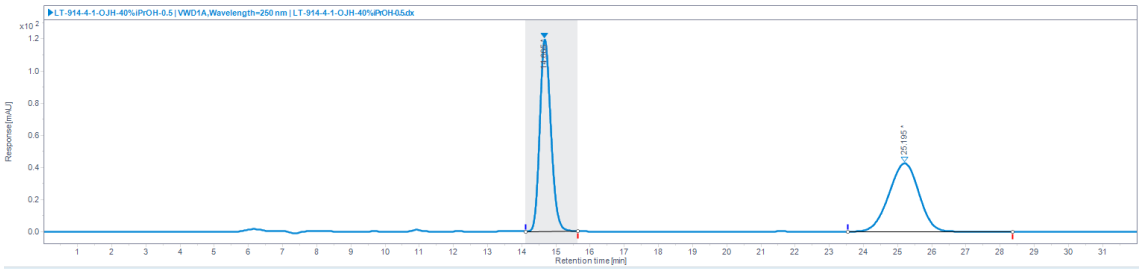
Injection Results

Peaks | Summary

#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	15.472	96.411	14.582	16.235	0.91191
2	17.396	3.589	16.843	18.072	0.90449



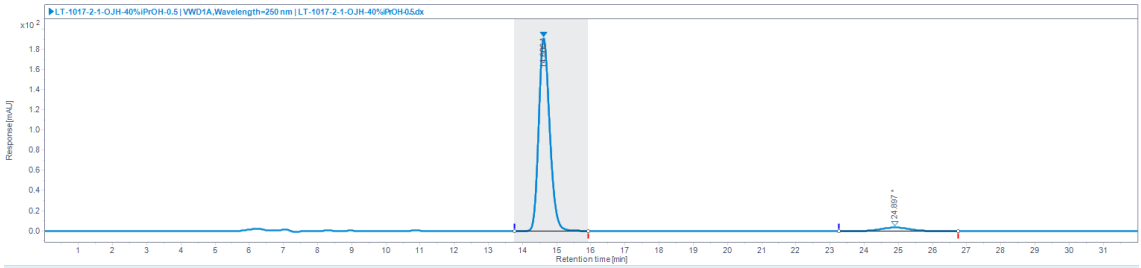
methyl (*S*)-2-(phenylamino)-2-(4-(trifluoromethyl)phenyl)but-3-ynoate (25): white solid; 25.0 mg, 75% yield; 91% *ee*; R_f = 0.33 (PE:EA = 10:1); $[\alpha]_D^{20}$ = -81.9 (*c* = 0.26, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.09 (t, *J* = 7.8 Hz, 2H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.55 (d, *J* = 8.0 Hz, 2H), 5.49 (s, 1H), 3.78 (s, 3H), 2.66 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 143.0, 142.2, 130.9 (q, *J* = 32.7 Hz), 128.9, 127.7, 125.9 (q, *J* = 3.7 Hz), 124.1 (q, *J* = 272.3 Hz), 119.1, 115.7, 80.0, 75.4, 61.8, 54.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6; IR (neat, cm^{-1}) 3396, 3291, 2957, 2921, 1745, 1603, 1503, 1324, 1262, 1167, 1125, 1018, 850, 751, 692; HRMS (ESI): *m/z*: calcd for $C_{18}H_{15}F_3NO_2$ $[M+H]^+$: 334.1055, found: 334.1058.
The *ee* was determined by HPLC analysis: CHIRALPAK OJH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 60/40; flow rate 0.5 mL/min; 35 ºC; 250 nm; retention time: 14.6 min (major) and 24.9 min (minor).



Injection Results

Peaks | Summary

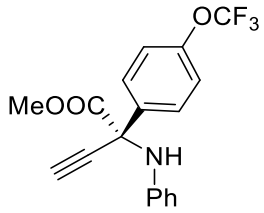
#	RT (min)	Area%	Height (mAU)	Start time (min)	End time (min)	S/N	Symmetry
1	14.665	50.953	119.793	14.103	15.631		0.80035
2	25.195	49.047	42.548	23.531	28.355		1.07781



Injection Results

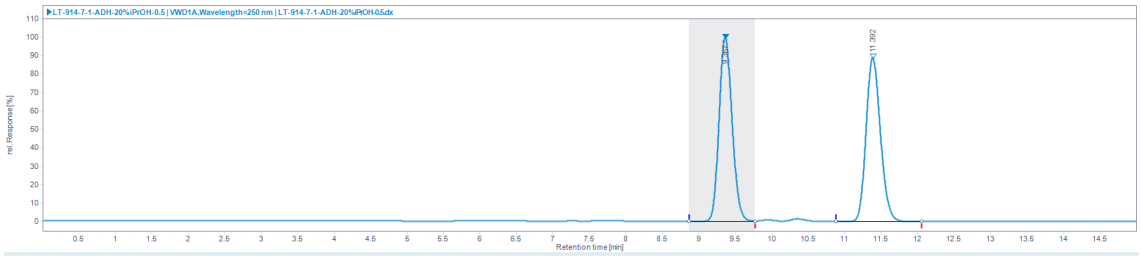
Peaks | Summary

#	RT (min)	Area%	Height (mAU)	Start time (min)	End time (min)	S/N	Symmetry
1	14.606	95.351	191.584	13.752	15.913		0.77549
2	24.897	4.649	3.546	23.246	26.738		0.98397



methyl (*S*)-2-(phenylamino)-2-(4-(trifluoromethoxy)phenyl)but-3-ynoate (26): yellow oil; 24.1 mg, 69% yield; 92% *ee*; R_f = 0.31 (PE:EA = 10:1); $[\alpha]_D^{20}$ = -72.2 (*c* = 0.23, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.91-7.76 (m, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.10 (t, *J* = 7.7 Hz, 2H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.57 (d, *J* = 8.1 Hz, 2H), 5.43 (s, 1H), 3.78 (s, 3H), 2.64 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 149.5, 143.2, 136.6, 128.9, 128.8, 121.1, 120.5 (q, *J* = 257.7 Hz), 119.0, 115.7, 80.3, 75.1, 61.5, 54.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.8; IR (neat, cm^{-1}) 3396, 3289, 2920, 2850, 1744, 1603, 1503, 1254, 1214, 1165, 856, 751, 692; HRMS (ESI): *m/z*: calcd for $C_{18}H_{15}F_3NO_3$ $[M+H]^+$: 350.1004, found: 350.1007.

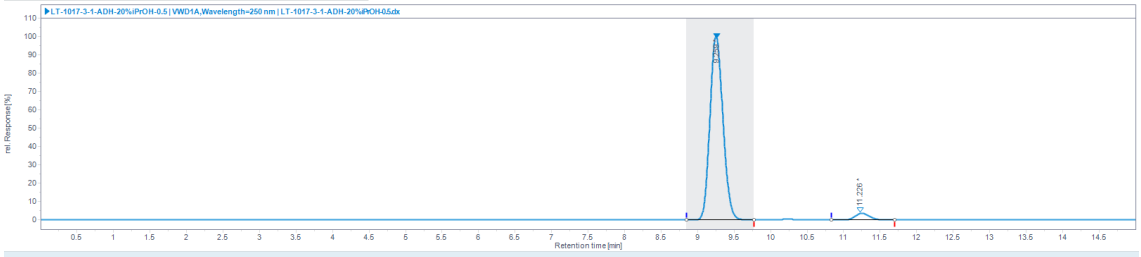
The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 80/20; flow rate 0.5 mL/min; 35 °C; 250 nm; retention time: 9.3 min (major) and 11.2 min (minor).



Injection Results

Peaks | Summary

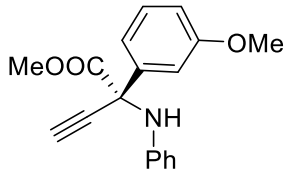
#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	9.367	50.387	8.867	9.767	0.94342
2	11.392	49.613	10.884	12.051	0.91970



Injection Results

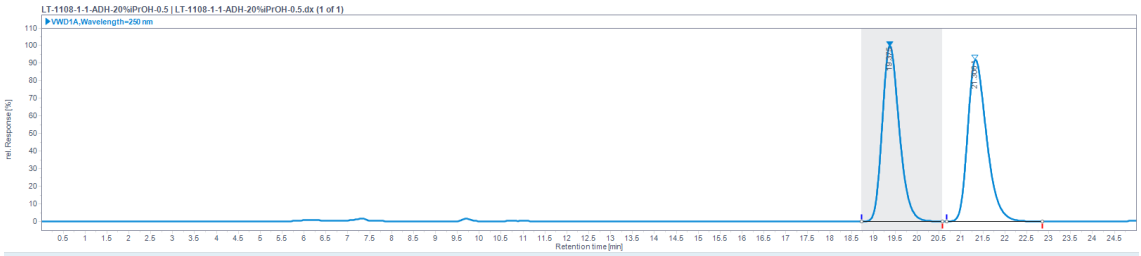
Peaks | Summary

#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	9.259	96.219	8.847	9.767	0.94308
2	11.226	3.781	10.827	11.693	0.54213



methyl (*S*)-2-(3-methoxyphenyl)-2-(phenylamino)but-3-ynoate (27): yellow oil; 25.1 mg; 85% yield; 92% *ee*; R_f = 0.56 (PE:EA = 5:1); $[\alpha]_D^{20}$ = -217.1 (*c* = 0.21, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.47-7.33 (m, 2H), 7.29 (t, *J* = 7.9 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 2H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 2H), 5.43 (s, 1H), 3.80 (s, 3H), 3.77 (s, 3H), 2.63 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 160.0, 143.5, 139.7, 129.8, 128.8, 119.3, 118.7, 115.6, 114.0, 112.9, 80.5, 74.83, 62.0, 55.4, 54.4; IR (neat, cm^{-1}) 3394, 3280, 2954, 1740, 1601, 1502, 1432, 1315, 1242, 1040, 749, 692; HRMS (ESI): *m/z*: calcd for $C_{18}H_{18}NO_3$ $[M+H]^+$: 296.1287, found: 296.1288.

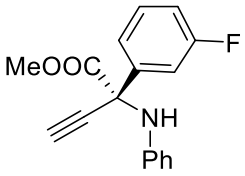
The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 80/20; flow rate 0.5 mL/min; 35 ºC; 250 nm; retention time: 19.4 min (minor) and 21.3 min (major).



Injection Results

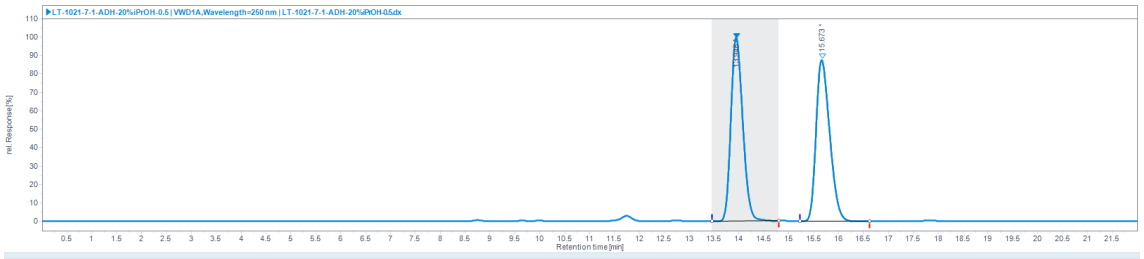
Peaks | Summary

#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	19.375	49.415	18.724	20.576	0.80230
2	21.306	50.585	20.678	22.846	0.60276



methyl (*S*)-2-(3-fluorophenyl)-2-(phenylamino)but-3-ynoate (28): white solid; 11.9 mg, 42% yield; 94% *ee*; R_f = 0.51 (PE:EA = 5:1); $[\alpha]_D^{20}$ = -96.9 (*c* = 0.16, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.68-7.49 (m, 2H), 7.43-7.30 (m, 1H), 7.10 (t, *J* = 7.8 Hz, 2H), 7.04 (td, *J* = 8.3, 2.6 Hz, 1H), 6.74 (t, *J* = 7.4 Hz, 1H), 6.59 (d, *J* = 8.0 Hz, 2H), 5.46 (s, 1H), 3.78 (s, 3H), 2.65 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 163.1 (d, *J* = 246.7 Hz), 143.2, 140.8 (d, *J* = 6.9 Hz), 130.3 (d, *J* = 8.1 Hz), 128.8, 122.7 (d, *J* = 3.0 Hz), 119.0, 115.9, 115.7, 114.5 (d, *J* = 23.7 Hz), 80.1, 75.1, 61.7 (d, *J* = 2.0 Hz), 54.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.1; IR (neat, cm^{-1}) 3396, 3287, 3054, 2955, 1744, 1604, 1503, 1438, 1262, 1155, 876, 750, 691; HRMS (ESI): *m/z*: calcd for $C_{17}H_{15}FNO_2$ $[M+H]^+$: 284.1087, found: 284.1091.

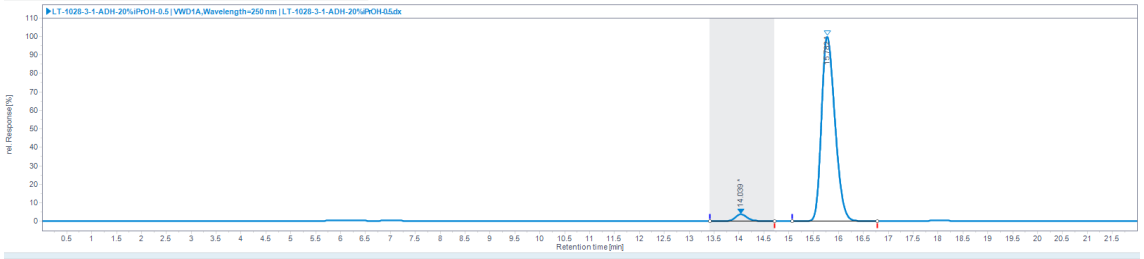
The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 80/20; flow rate 0.5 mL/min; 35 °C; 250 nm; retention time: 14.0 min (minor) and 15.8 min (major).



Injection Results

Peaks | Summary

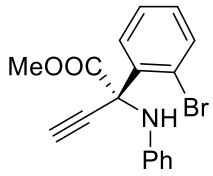
#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	13.948	49.777	13.464	14.792	0.87033
2	15.673	50.223	15.216	16.615	0.81613



Injection Results

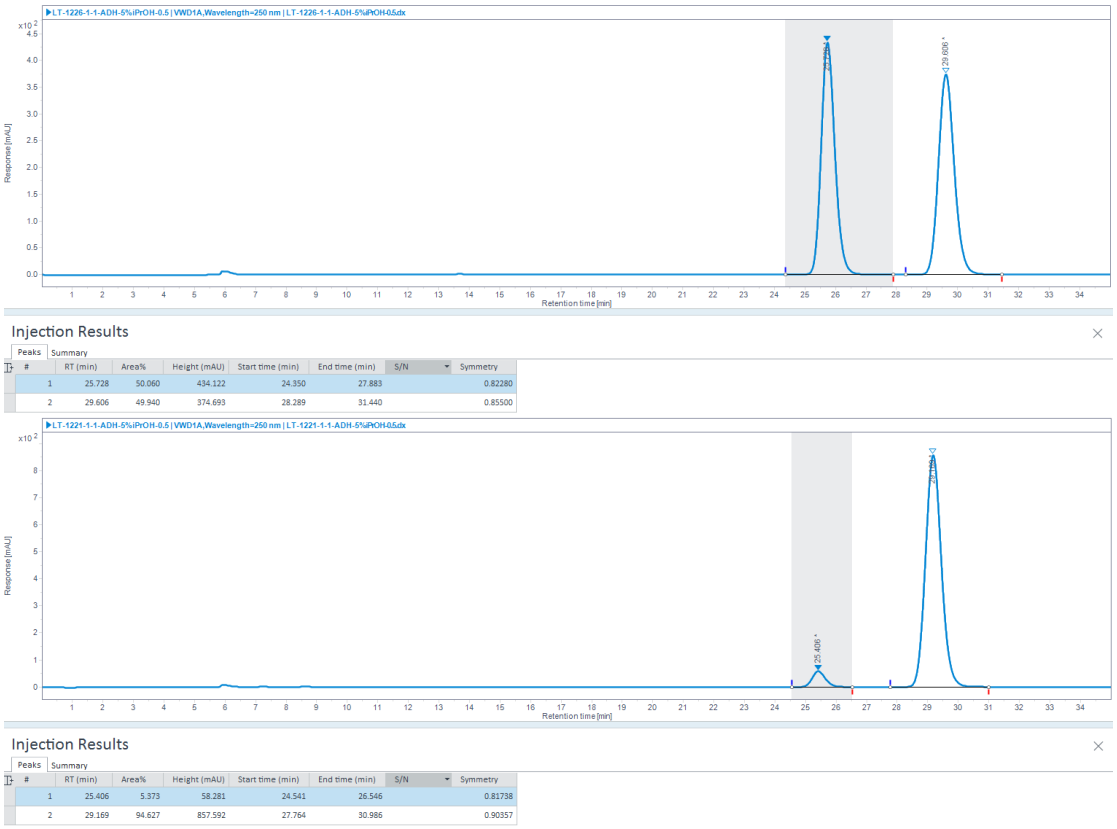
Peaks | Summary

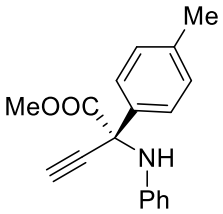
#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	14.039	3.092	13.424	14.716	0.87508
2	15.782	96.908	15.062	16.772	0.83431



methyl (*S*)-2-(2-bromophenyl)-2-(phenylamino)but-3-ynoate (29): colorless oil; 23.1 mg, 67% yield; 89% *ee*; R_f = 0.25 (PE:EA = 5:1); $[\alpha]_D^{20}$ = -47.7 (*c* = 0.17, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 7.9 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.06 (t, *J* = 7.8 Hz, 2H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 2H), 5.51 (s, 1H), 3.85 (s, 3H), 2.79 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 143.6, 136.7, 134.9, 132.2, 130.1, 128.7, 127.2, 121.9, 119.2, 116.1, 79.8, 77.1, 63.8, 54.6; IR (neat, cm^{-1}) 3404, 3283, 3054, 2952, 1745, 1600, 1501, 1430, 1193, 1022, 736; HRMS (ESI): *m/z*: calcd for $C_{17}H_{15}BrNO_2$ $[M+H]^+$: 344.0286, found: 344.0284.

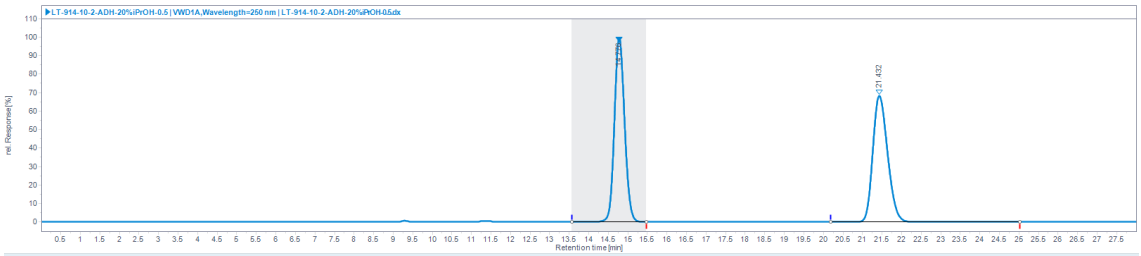
The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 95/5; flow rate 0.5 mL/min; 35 °C; 250 nm; retention time: 25.4 min (minor) and 29.2 min (major).





methyl (*S*)-2-(phenylamino)-2-(p-tolyl)but-3-ynoate (30): white solid; 20.1 mg, 72% yield; 95% *ee*; R_f = 0.31 (PE:EA = 10:1); $[\alpha]_D^{20}$ = -76.5 (*c* = 0.17, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 7.09 (t, *J* = 7.7 Hz, 2H), 6.72 (t, *J* = 7.4 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 2H), 5.40 (s, 1H), 3.76 (s, 3H), 2.63 (s, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 143.6, 138.5, 135.0, 129.6, 128.8, 126.9, 118.6, 115.6, 80.8, 74.7, 61.9, 54.3, 21.2; IR (neat, cm^{-1}) 3396, 3282, 2921, 1741, 1603, 1504, 1432, 1315, 1262, 1175, 780, 750, 692; HRMS (ESI): *m/z*: calcd for $C_{18}H_{18}NO_2$ $[M+H]^+$: 280.1338, found: 280.1340.

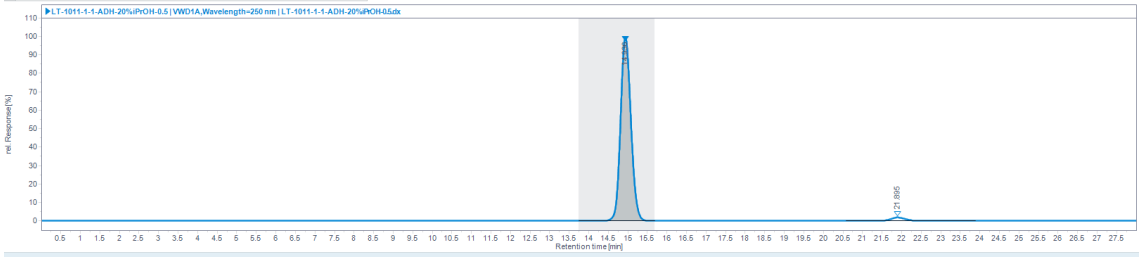
The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 80/20; flow rate 0.5 mL/min; 35 °C; 250 nm; retention time: 14.9 min (major) and 21.9 min (minor).



Injection Results

Peaks | Summary

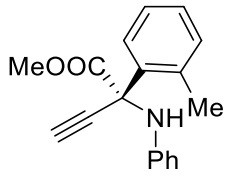
#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	14.776	50.158	13.561	15.469	0.92824
2	21.432	49.842	20.186	25.028	0.80959



Injection Results

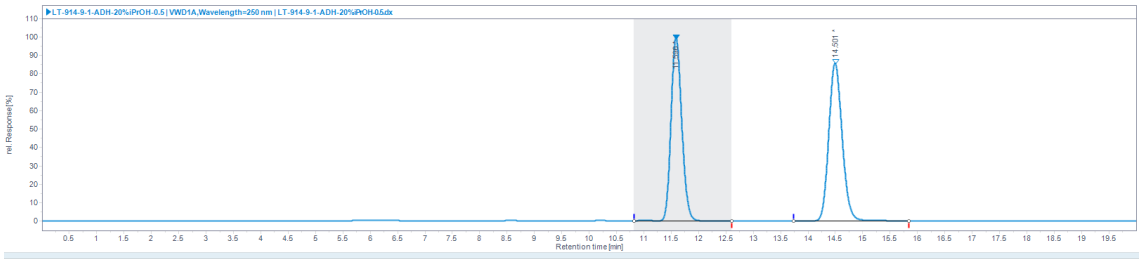
Peaks | Summary

#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	14.936	97.451	13.745	15.682	0.91735
2	21.895	2.549	20.585	23.885	0.87692



methyl (*S*)-2-(phenylamino)-2-(o-tolyl)but-3-ynoate (31): colorless oil; 20.1 mg, 72% yield; 80% *ee*; R_f = 0.59 (PE:EA = 5:1); $[\alpha]_D^{20}$ = -108.1 (*c* = 0.16, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.0 Hz, 1H), 7.41-7.23 (m, 2H), 7.18-6.98 (m, 3H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.61 (d, *J* = 8.1 Hz, 2H), 5.32 (s, 1H), 3.82 (s, 3H), 2.71 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 143.9, 136.6, 135.6, 132.4, 129.9, 128.8, 128.7, 126.2, 119.0, 116.0, 80.8, 75.9, 63.2, 54.5, 20.4; IR (neat, cm^{-1}) 3398, 3280, 2954, 2922, 1739, 1602, 1502, 1432, 1262, 1183, 1038, 743, 692; HRMS (ESI): *m/z*: calcd for $C_{18}H_{18}NO_2$ $[M+H]^+$: 280.1338, found: 280.1341.

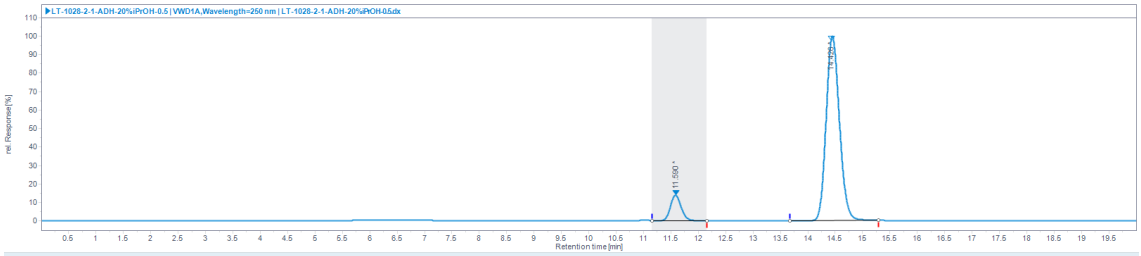
The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 80/20; flow rate 0.5 mL/min; 35 °C; 250 nm; retention time: 11.6 min (minor) and 14.4 min (major).



Injection Results

Peaks | Summary

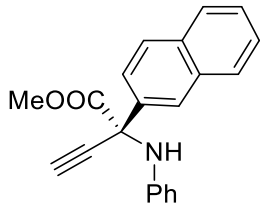
#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	11.596	48.303	10.814	12.600	0.92877
2	14.501	51.697	13.730	15.844	0.88377



Injection Results

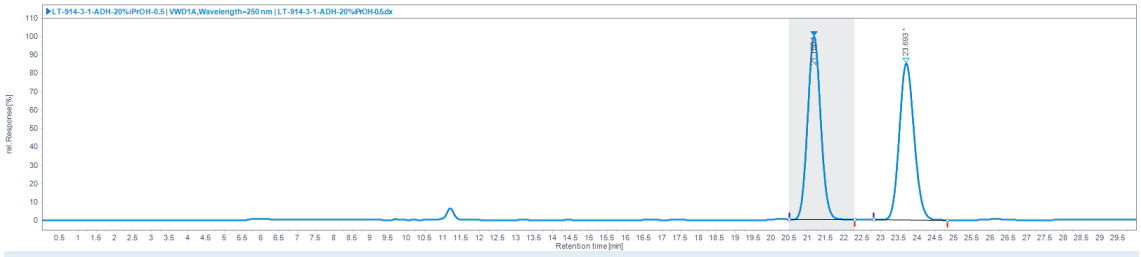
Peaks | Summary

#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	11.590	9.878	11.148	12.150	0.91608
2	14.426	90.122	13.667	15.284	0.60442



methyl (*S*)-2-(naphthalen-2-yl)-2-(phenylamino)but-3-ynoate (32): white solid; 26.1 mg, 83% yield; 92% *ee*; R_f = 0.33 (PE:EA = 10:1); $[\alpha]_D^{20}$ = -60.8 (*c* = 0.24, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 8.03-7.75 (m, 4H), 7.61-7.43 (m, 2H), 7.07 (t, *J* = 7.7 Hz, 2H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.65 (d, J = 8.1 Hz, 2H), 5.55 (s, 1H), 3.75 (s, 3H), 2.73 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 143.5, 135.6, 133.4, 133.3, 128.8, 128.6, 127.8, 126.9, 126.7, 126.5, 124.2, 118.8, 115.8, 80.7, 75.1, 62.3, 54.4; IR (neat, cm^{-1}) 3396, 3284, 3054, 2953, 1740, 1602, 1503, 1432, 1262, 1167, 786, 751, 692; HRMS (ESI): *m/z*: calcd for $C_{21}H_{18}NO_2$ $[M+H]^+$: 316.1338, found: 316.1341.

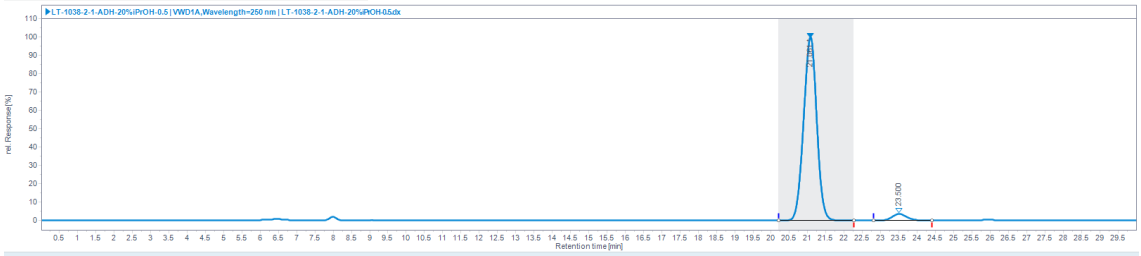
The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 80/20; flow rate 0.5 mL/min; 35 ºC; 250 nm; retention time: 21.1 min (major) and 23.5 min (minor).



Injection Results

Peaks | Summary

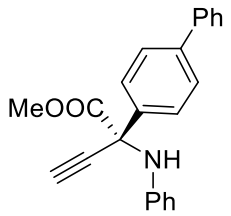
#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	21.160	50.770	20.482	22.274	0.93158
2	23.693	49.230	22.801	24.817	0.88956



Injection Results

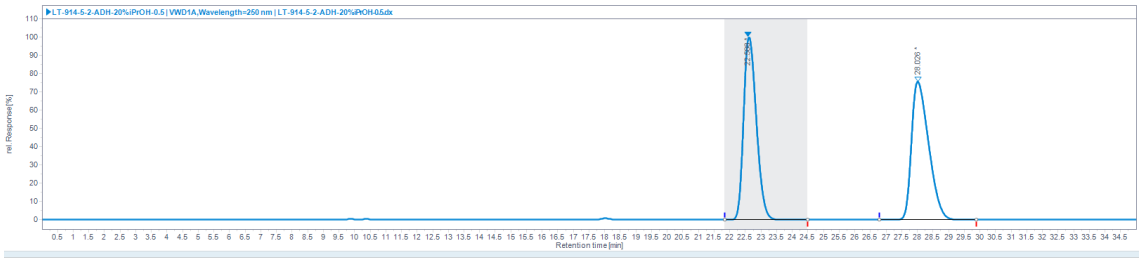
Peaks | Summary

#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	21.061	96.240	20.193	22.255	1.01316
2	23.500	3.760	22.799	24.406	0.89035



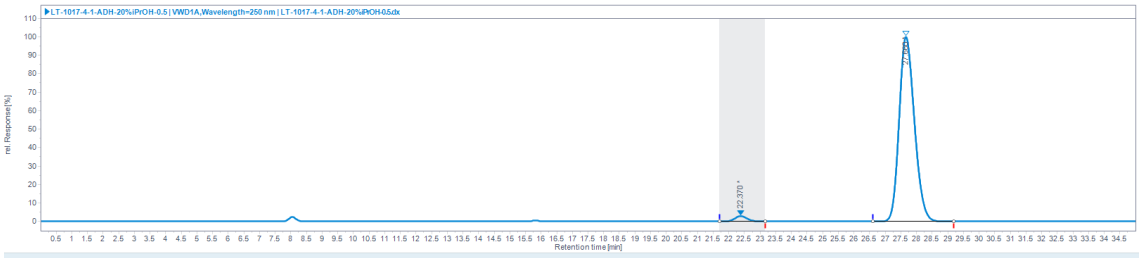
methyl (*S*)-2-([1,1'-biphenyl]-4-yl)-2-(phenylamino)but-3-ynoate (33): white solid; 29.0 mg, 85% yield; 95% *ee*; R_f = 0.31 (PE:EA = 10:1); $[\alpha]_D^{20}$ = -36.0 (*c* = 0.25, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.2 Hz, 2H), 7.61 (dd, *J* = 8.6, 2.1 Hz, 4H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.12 (t, *J* = 7.7 Hz, 2H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 2H), 5.47 (s, 1H), 3.80 (s, 3H), 2.67 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 143.5, 141.5, 140.4, 137.0, 128.9, 128.8, 127.7, 127.5, 127.5, 127.2, 118.8, 115.7, 80.7, 74.9, 61.9, 54.4; IR (neat, cm^{-1}) 3397,3282, 3030, 2953, 1739, 1602, 1502, 1432, 1315, 1261, 1176, 1043, 747, 694; HRMS (ESI): *m/z*: calcd for $C_{23}H_{20}NO_2$ $[M+H]^+$: 342.1494, found: 342.1500.

The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 80/20; flow rate 0.5 mL/min; 35 °C; 250 nm; retention time: 22.4 min (minor) and 27.7 min (major).



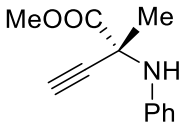
Injection Results

#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	22.588	49.697	21.849	24.480	0.62061
2	28.026	50.303	26.773	29.875	0.62718



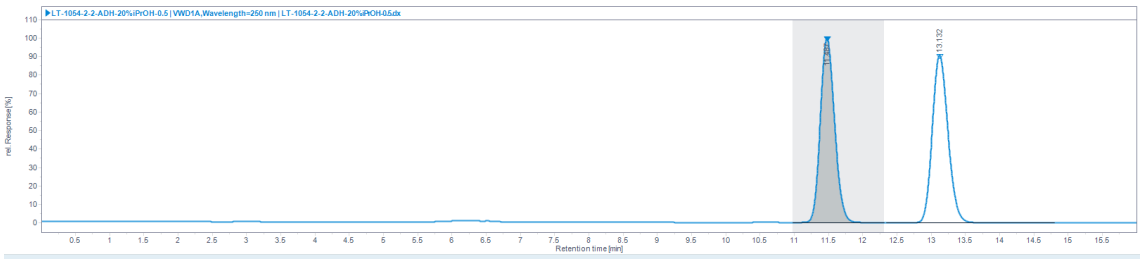
Injection Results

#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	22.370	2.246	21.692	23.153	0.88946
2	27.660	97.754	26.602	29.177	0.81511



methyl (*R*)-2-methyl-2-(phenylamino)but-3-ynoate (34): yellow solid; 17.1 mg, 84% yield; 62% *ee*; R_f = 0.44 (PE:EA = 5:1); $[\alpha]_D^{20}$ = -9.2 (*c* = 0.36, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.24-7.15 (m, 2H), 6.90-6.71 (m, 3H), 4.38 (s, 1H), 3.80 (s, 3H), 2.53 (s, 1H), 1.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 144.6, 129.1, 119.5, 115.5, 82.4, 73.3, 55.6, 53.7, 28.1; IR (neat, cm^{-1}) 3396, 3278, 2921, 2851, 1738, 1601, 1502, 1268, 1126, 751, 692; HRMS (ESI): *m/z*: calcd for $C_{12}H_{14}NO_2$ $[M+H]^+$: 204.1025, found: 204.1027.

The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 80/20; flow rate 0.5 mL/min; 35 ºC; 250 nm; retention time: 11.0 min (major) and 12.4 min (minor).



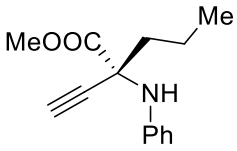
Injection Results

#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	11.487	49.948	10.979	12.321	0.91233
2	13.132	50.052	12.348	14.799	0.89082

Injection Results

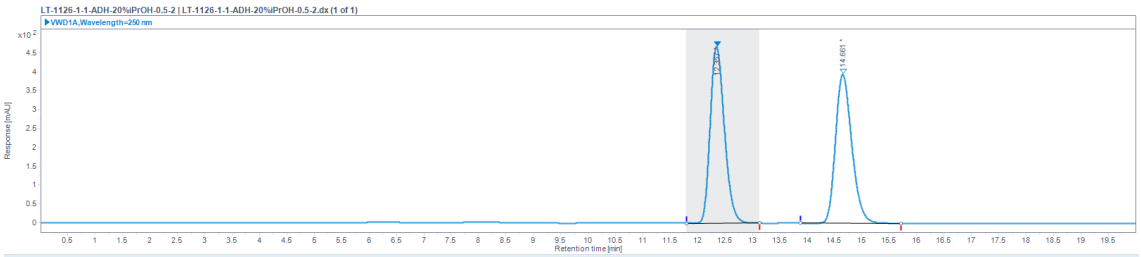
Peaks | Summary

#	RT (min)	Area%	Start time (min)	End time (min)	S/N USP	Symmetry
1	11.019	80.887	10.492	11.879		0.59524
2	12.392	19.113	11.879	13.328		0.57805



methyl (*R*)-2-ethynyl-2-(phenylamino)pentanoate (35): white solid; 14.3 mg, 62% yield; 33% *ee*; R_f = 0.23 (PE:EA = 10:1); $[\alpha]_D^{20}$ = 2.5 (*c* = 0.12, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.24-7.15 (m, 2H), 6.89-6.74 (m, 3H), 4.33 (s, 1H), 3.78 (s, 3H), 2.54 (s, 1H), 2.18-1.94 (m, 2H), 1.64-1.42 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 144.7, 129.1, 119.3, 115.3, 81.7, 74.0, 59.8, 53.5, 42.6, 17.7, 14.0; IR (neat, cm^{-1}) 3394, 3278, 2961, 1736, 1602, 1502, 1224, 1134, 749, 692; HRMS (ESI): *m/z*: calcd for $C_{14}H_{18}NO_2$ $[M+H]^+$: 232.1338, found: 232.1338.

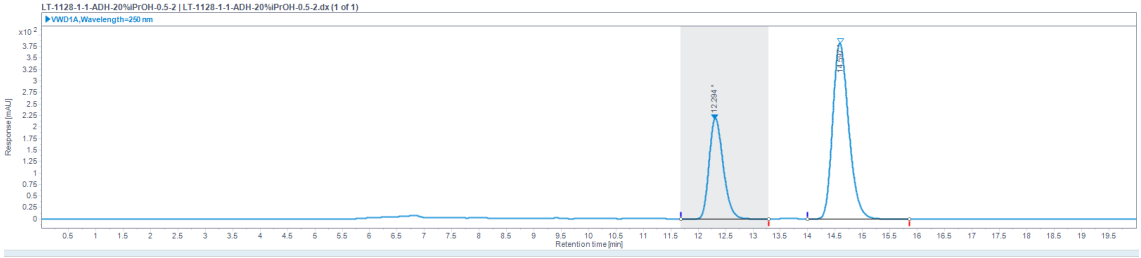
The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 80/20; flow rate 0.5 mL/min; 35 °C; 250 nm; retention time: 12.3 min (minor) and 14.6 min (major).



Injection Results

Peaks | Summary

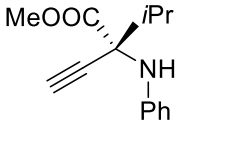
#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	12.357	50.961	11.793	13.126	0.84369
2	14.661	49.039	13.871	15.707	0.82303



Injection Results

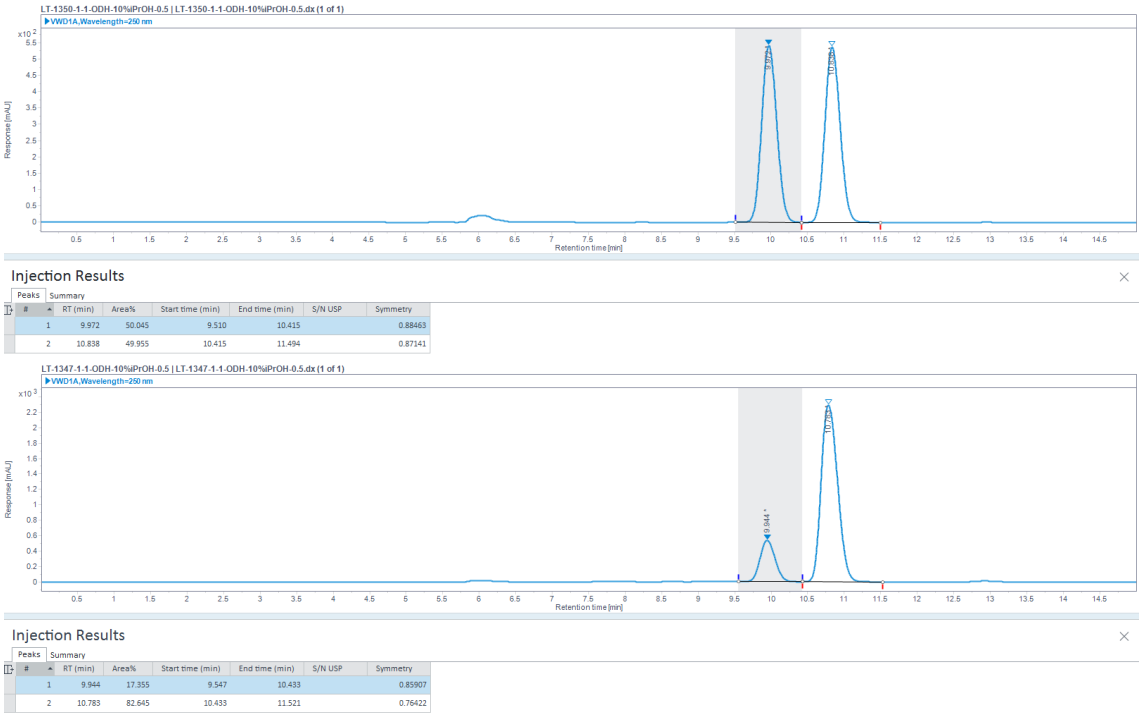
Peaks | Summary

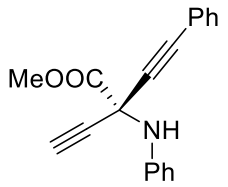
#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	12.294	33.437	11.677	13.294	0.58059
2	14.597	66.563	14.001	15.851	0.82023



methyl (*R*)-2-isopropyl-2-(phenylamino)but-3-ynoate (36): white solid; 9.7 mg, 42% yield; 65% *ee*; R_f = 0.30 (PE:EA = 10:1); $[\alpha]_D^{20}$ = 16.5 (*c* = 0.26, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) 7.18 (t, *J* = 7.9 Hz, 2H), 6.85 (d, *J* = 8.1 Hz, 2H), 6.80 (t, *J* = 7.3 Hz, 1H), 4.17 (s, 1H), 3.74 (s, 3H), 2.56 (s, 1H), 2.34-2.19 (m, 1H), 1.22 (d, *J* = 6.7 Hz, 3H), 1.05 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 145.2, 129.1, 119.4, 115.3, 79.8, 75.3, 64.8, 53.1, 37.9, 17.9, 17.5; IR (neat, cm^{-1}) 3380, 3278, 2971, 1732, 1602, 1502, 1312, 1239, 1182, 1025, 751, 693; HRMS (ESI): *m/z*: calcd for $C_{14}H_{18}NO_2$ $[M+H]^+$: 232.1338, found: 232.1340.

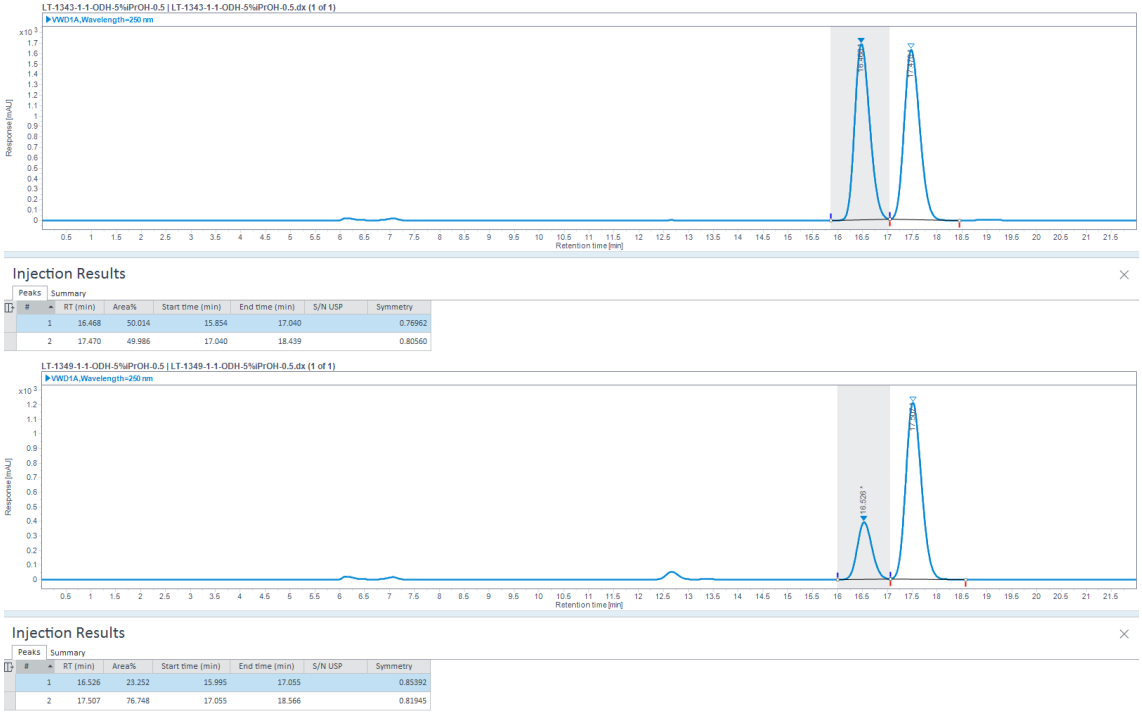
The *ee* was determined by HPLC analysis: CHIRALPAK ODH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 90/10; flow rate 0.5 mL/min; 35 °C; 250 nm; retention time: 9.9 min (minor) and 10.8 min (major).

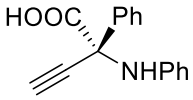




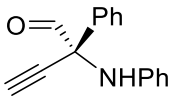
methyl (*S*)-2-ethynyl-4-phenyl-2-(phenylamino)but-3-ynoate (37): yellow solid; 18.5 mg, 64% yield; 53% *ee*; R_f = 0.44 (PE:EA = 5:1); $[\alpha]_D^{20}$ = 16.7 (*c* = 0.30, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) 7.42 (d, *J* = 6.4 Hz, 2H), 7.37-7.24 (m, 5H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.89 (t, *J* = 7.3 Hz, 1H), 5.04 (s, 1H), 3.99 (s, 3H), 2.61 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 143.4, 132.1, 129.2, 129.0, 128.4, 121.6, 120.0, 116.5, 84.6, 83.9, 79.1, 72.9, 55.0, 52.4; IR (neat, cm^{-1}) 3385, 3284, 2955, 1749, 1601, 1502, 1261, 1142, 753, 690; HRMS (ESI): *m/z*: calcd for $C_{19}H_{16}NO_2$ $[M+H]^+$: 290.1181, found: 290.1180.

The *ee* was determined by HPLC analysis: CHIRALPAK ODH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 95/5; flow rate 0.5 mL/min; 35 °C; 250 nm; retention time: 16.5 min (minor) and 17.5 min (major).



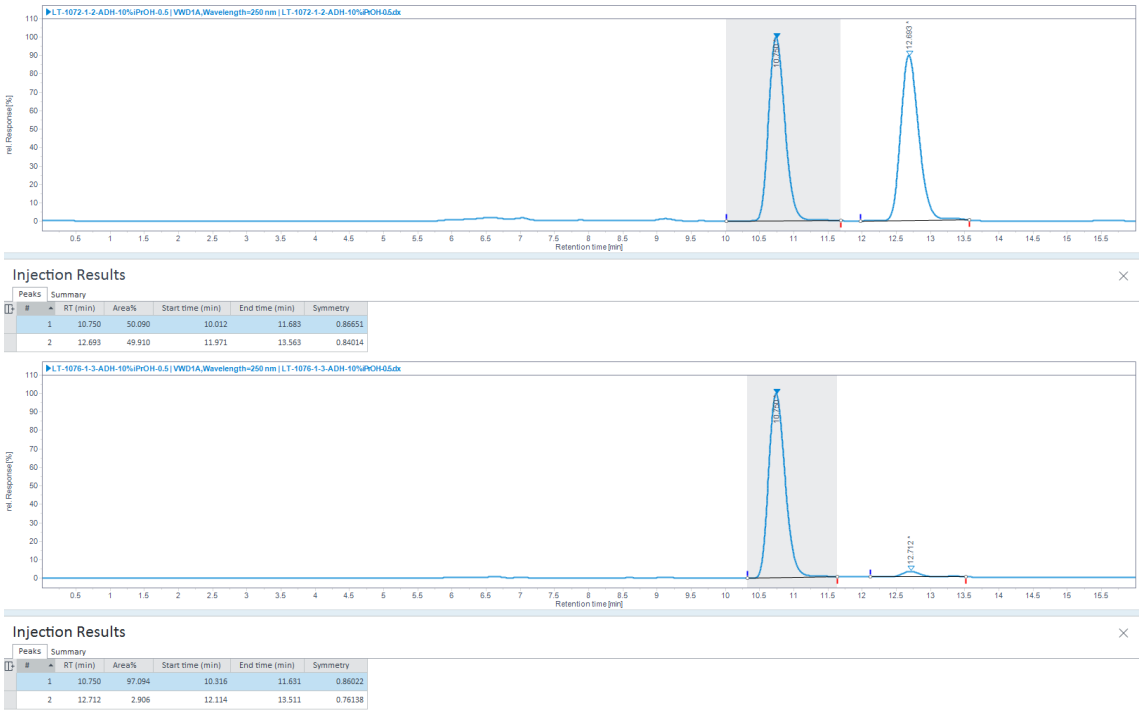


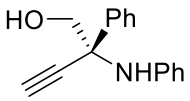
(*S*)-2-phenyl-2-(phenylamino)but-3-ynoic acid (38): white solid; 18.6 mg, 74% yield; R_f = 0.33 (DCM:MeOH = 5:1); $[\alpha]_D^{20}$ = -48.5 (*c* = 0.13, $CHCl_3$); ^1H NMR (400 MHz, DMSO-d_6) δ 7.71 (d, *J* = 7.6 Hz, 2H), 7.46-7.27 (m, 3H), 6.99 (t, *J* = 7.7 Hz, 2H), 6.64 (d, *J* = 8.0 Hz, 2H), 6.57 (t, *J* = 7.3 Hz, 1H), 3.66 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 170.4, 144.6, 138.9, 128.5, 128.2, 128.2, 126.6, 117.2, 115.1, 81.7, 76.6, 61.6; IR (neat, cm^{-1}) 3395, 3285, 3052, 2925, 1724, 1601, 1501, 1257, 1172, 692; HRMS (ESI): *m/z*: calcd for $C_{16}H_{14}NO_2$ $[M+H]^+$: 252.1025, found: 252.1026.



(*S*)-2-phenyl-2-(phenylamino)but-3-ynal (39): yellow solid; 21.2 mg, 90% yield; 94% *ee*; R_f = 0.28 (PE:EA = 10:1); $[\alpha]_D^{20}$ = -87.5 (*c* = 0.24, $CHCl_3$);^1H NMR (400 MHz, $CDCl_3$) δ 9.19 (s, 1H), 7.90-7.62 (m, 2H), 7.53-7.33 (m, 3H), 7.18-7.03 (m, 2H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 2H), 5.42 (s, 1H), 2.80 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.1, 143.4, 134.2, 129.5, 129.3, 128.9, 127.5, 118.7, 115.5, 78.7, 78.4, 66.6; IR (neat, cm^{-1}) 3392, 3285, 3054, 1735, 1603, 1504, 1314, 1258, 751, 697; HRMS (ESI): *m/z*: calcd for $C_{16}H_{14}NO$ $[M+H]^+$: 236.1075, found: 236.1076.

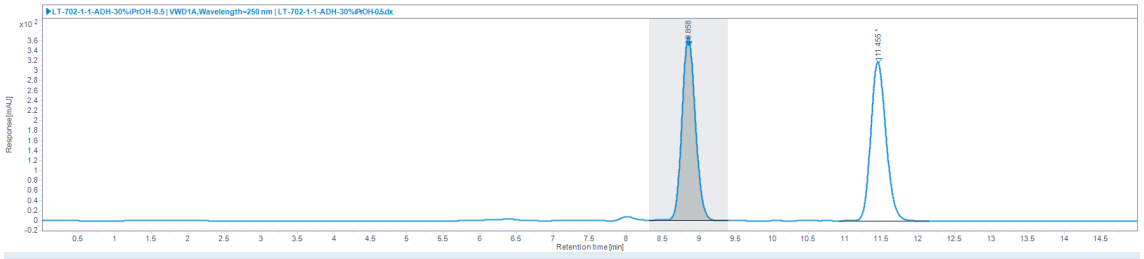
The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 90/10; flow rate 0.5 mL/min; 35 °C; 250 nm; retention time: 10.8 min (major) and 12.7 min (minor).





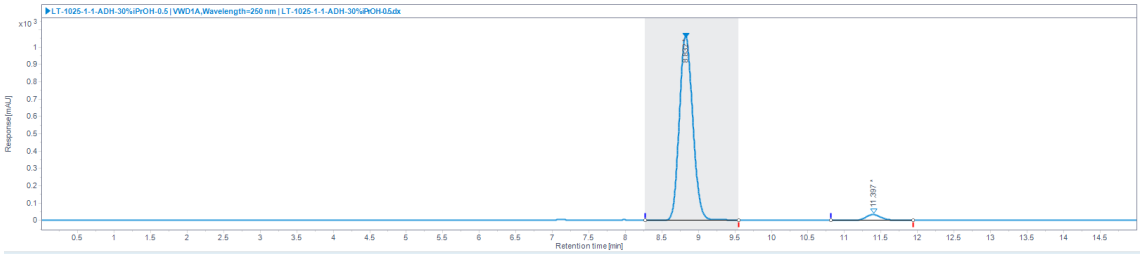
(*S*)-2-phenyl-2-(phenylamino)but-3-yn-1-ol (40): yellow oil; 22.5 mg, 95% yield; 93% *ee*; R_f = 0.31 (PE:EA = 5:1); $[\alpha]_D^{20}$ = -226.8 (*c* = 0.19, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.77-7.66 (m, 2H), 7.44-7.30 (m, 3H), 7.12-7.04 (m, 2H), 6.74 (td, *J* = 7.3, 1.2 Hz, 1H), 6.57 (dd, *J* = 8.7, 1.1 Hz, 2H), 4.96 (s, 1H), 3.78 (d, *J* = 11.0 Hz, 1H), 3.63 (t, *J* = 9.4 Hz, 1H), 2.54 (s, 1H), 2.27 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 139.2, 128.9, 128.7, 128.2, 126.6, 118.8, 116.1, 74.6, 73.1, 61.5; IR (neat, cm^{-1}) 3540, 3375, 3282, 3055, 2926, 1600, 1499, 1448, 1314, 1258, 1068, 752, 697, 667; HRMS (ESI): *m/z*: calcd for $C_{16}H_{16}NO$ $[M+H]^+$: 238.1232, found: 238.1231.

The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 70/30; flow rate 0.5 mL/min; 35 °C; 250 nm; retention time: 8.8 min (major) and 11.4 min (minor).



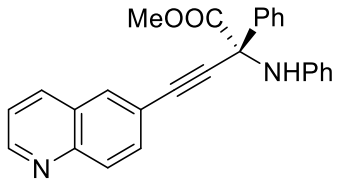
Injection Results

#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	8.858	50.411	8.323	9.393	0.93228
2	11.455	49.589	10.914	12.157	0.91151



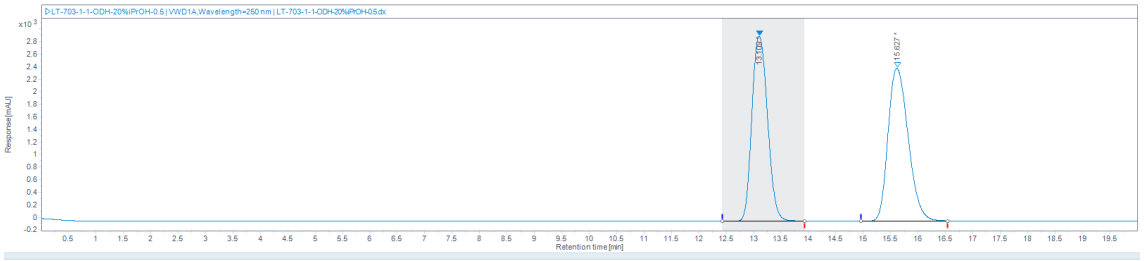
Injection Results

#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	8.832	96.501	8.275	9.547	0.93077
2	11.397	3.499	10.809	11.936	1.04503



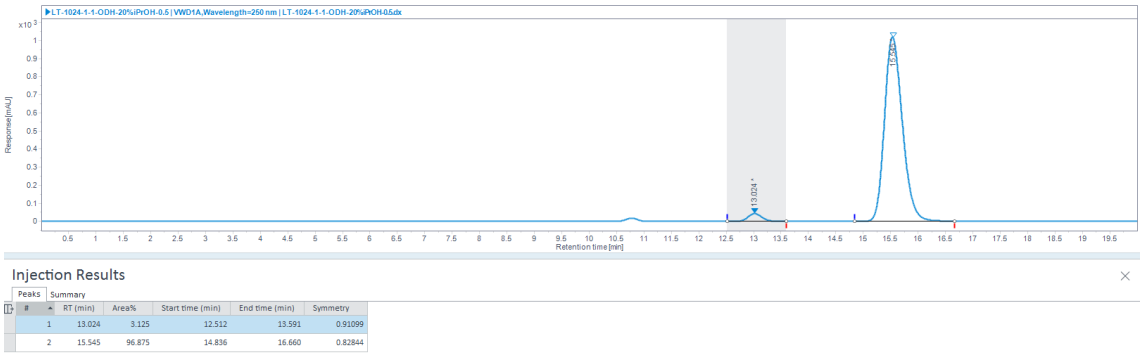
methyl (*R*)-2-phenyl-2-(phenylamino)-4-(quinolin-6-yl)but-3-ynoate (41): white solid; 36.5 mg, 93% yield; 94% *ee*; R_f = 0.18 (PE:EA = 2:1); $[\alpha]_D^{20}$ = -132.7 (*c* = 0.29, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.90 (dd, *J* = 4.3, 1.6 Hz, 1H), 8.10-7.99 (m, 2H), 7.94-7.84 (m, 3H), 7.69 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.46-7.32 (m, 4H), 7.11 (t, *J* = 7.8 Hz, 2H), 6.77-6.66 (m, 3H), 5.58 (s, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 151.2, 147.9, 143.8, 138.7, 135.9, 132.3, 131.8, 129.7, 128.9, 128.8, 128.7, 127.9, 127.2, 121.9, 120.7, 118.7, 115.9, 87.8, 86.1, 62.8, 54.4; IR (neat, cm^{-1}) 3396, 2953, 1740, 1601, 1497, 1261, 838, 734, 695; HRMS (ESI): *m/z*: calcd for $C_{26}H_{21}N_2O_2$ $[M+H]^+$: 393.1603, found: 393.1601.

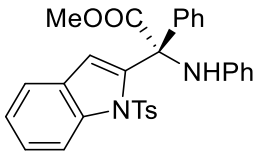
The *ee* was determined by HPLC analysis: CHIRALPAK ODH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 80/20; flow rate 0.5 mL/min; 35 °C; 250 nm; retention time: 13.0 min (minor) and 15.5 min (major).



Injection Results

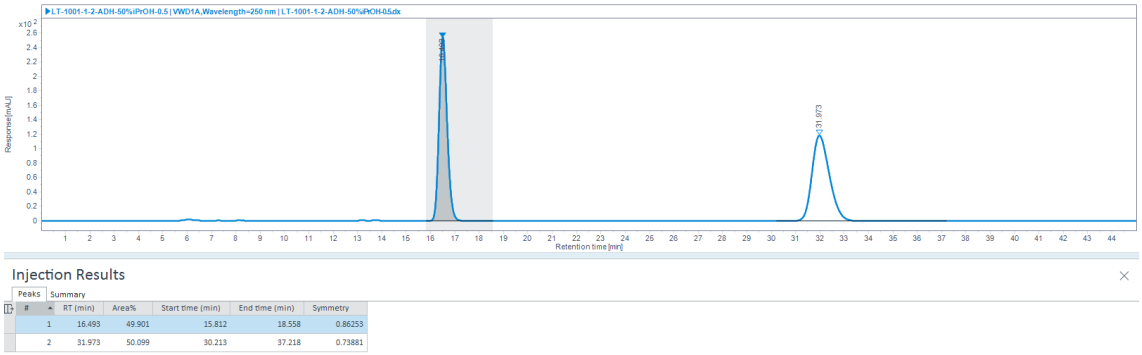
#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	13.109	48.448	12.422	13.924	0.87772
2	15.627	51.552	14.952	16.532	0.80707

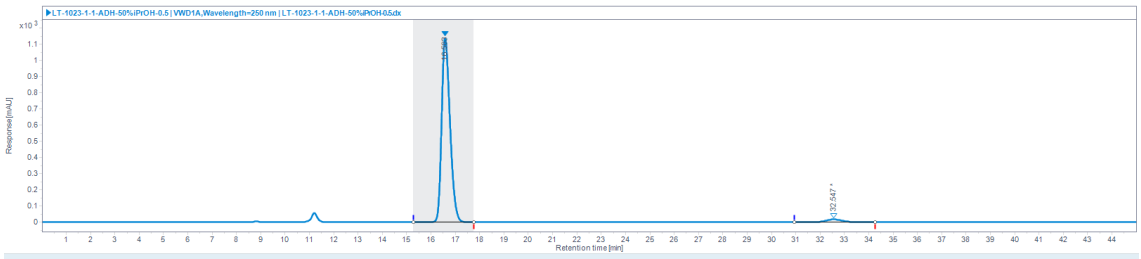




methyl (*R*)-2-phenyl-2-(phenylamino)-2-(1-tosyl-1H-indol-2-yl)acetate (42): yellow oil; 30.6 mg, 60% yield; 94% *ee*; R_f = 0.31 (PE:EA = 5:1); $[\alpha]_D^{20}$ = -103.6 (*c* = 0.22, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.77-7.69 (m, 2H), 7.62 (d, *J* = 8.6 Hz, 1H), 7.59-7.53 (m, 2H), 7.45-7.36 (m, 3H), 7.30-7.22 (m, 3H), 7.20-7.09 (m, 4H), 6.98 (td, *J* = 7.6, 1.2 Hz, 1H), 6.83-6.71 (m, 1H), 6.68-6.57 (m, 2H), 5.43 (s, 1H), 3.91 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 144.1, 143.5, 138.8, 138.0, 136.1, 132.2, 130.2, 129.8, 129.1, 129.0, 129.0, 127.3, 127.0, 124.1, 119.1, 119.0, 115.5, 112.7, 93.6, 81.5, 63.0, 54.9, 21.7; IR (neat, cm^{-1}) 3391, 3308, 2921, 2851, 1744, 1601, 1492, 1403, 1341, 1260, 1167, 1091, 911, 751, 696, 665; HRMS (ESI): *m/z*: calcd for $C_{30}H_{27}N_2O_4S$ $[M+H]^+$: 511.1692, found: 511.1693.

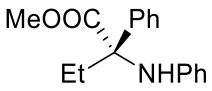
The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 50/50; flow rate 0.5 mL/min; 35 °C; 250 nm; retention time: 16.6 min (major) and 32.5 min (minor).





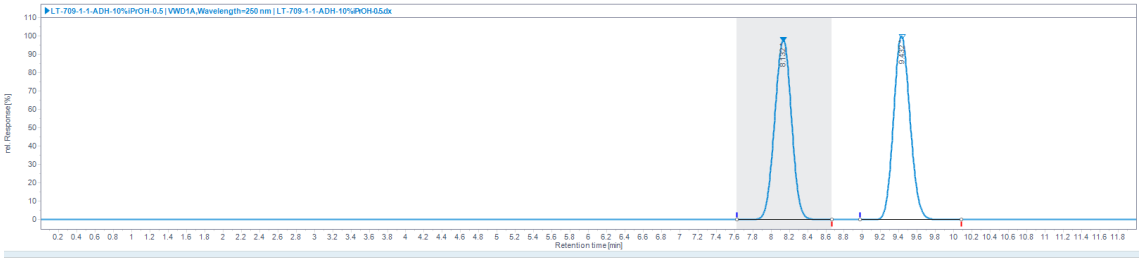
Injection Results

#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	16.583	96.903	15.268	17.763	0.77939
2	32.547	3.097	30.925	34.248	0.89769



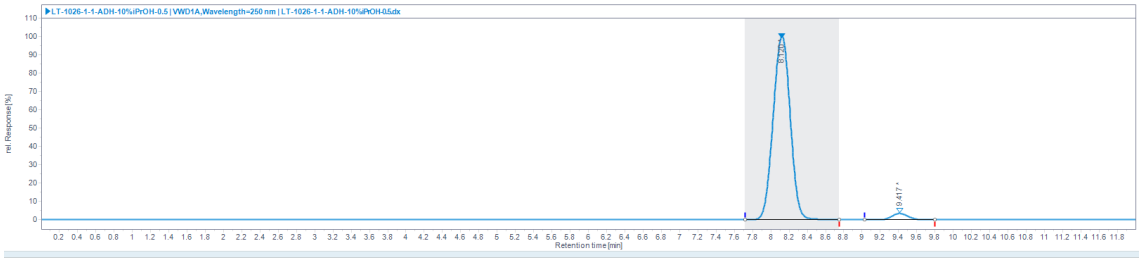
methyl (*S*)-2-phenyl-2-(phenylamino)butanoate (43): white solid; 25.3 mg, 94% yield; 94% *ee*; R_f = 0.56 (PE:EA = 10:1); $[\alpha]_D^{20}$ = 76.4 (*c* = 0.28, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.7 Hz, 2H), 7.43-7.27 (m, 3H), 7.10-6.95 (m, 2H), 6.63 (t, *J* = 7.4 Hz, 1H), 6.39 (d, *J* = 7.5 Hz, 2H), 5.39 (s, 1H), 3.68 (s, 3H), 2.73-2.39 (m, 2H), 0.84 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 144.4, 140.9, 128.9, 128.7, 127.7, 127.1, 117.4, 115.1, 66.9, 53.2, 25.8, 8.6; IR (neat, cm^{-1}) 3407, 3054, 2954, 1731, 1602, 1503, 1318, 1260, 1239, 1194, 1128, 748, 697; HRMS (ESI): *m/z*: calcd for $C_{17}H_{20}NO_2$ $[M+H]^+$: 270.1494, found: 270.1498.

The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 90/10; flow rate 0.5 mL/min; 35 °C; 250 nm; retention time: 8.1 min (major) and 9.4 min (minor).



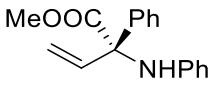
Injection Results

#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	8.132	49.913	7.621	8.662	0.96914
2	9.432	50.087	8.970	10.079	0.95535



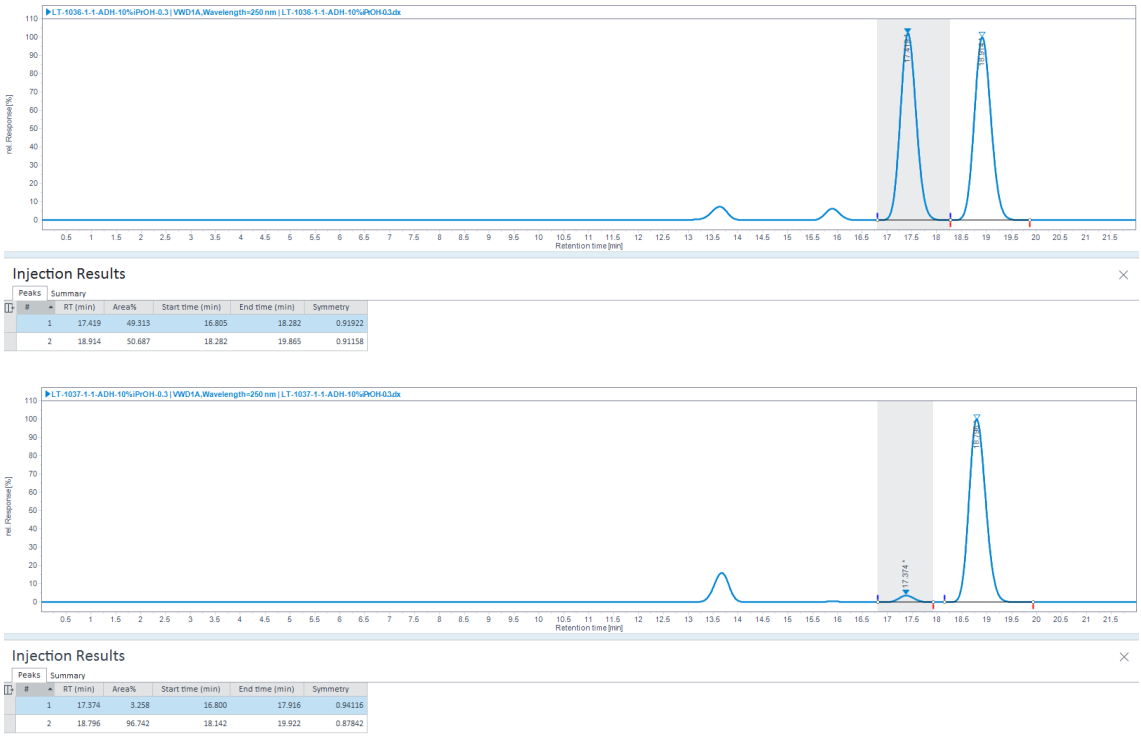
Injection Results

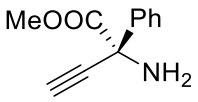
#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	8.120	96.815	7.714	8.746	0.95189
2	9.417	3.185	9.024	9.794	0.94791



methyl (*S*)-2-phenyl-2-(phenylamino)but-3-enoate (44): white solid; 24.6 mg, 92% yield; 93% *ee*; R_f = 0.44 (PE:EA = 10:1); $[\alpha]_D^{20}$ = -31.8 (*c* = 0.28, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.4 Hz, 2H), 7.37-7.22 (m, 3H), 6.99 (t, *J* = 7.7 Hz, 2H), 6.68 (dd, *J* = 17.1, 10.4 Hz, 1H), 6.60 (t, *J* = 7.3 Hz, 1H), 6.40 (d, *J* = 8.0 Hz, 2H), 5.47 (d, *J* = 17.1 Hz, 1H), 5.41 (s, 1H), 5.40 (d, *J* = 6.3 Hz, 1H), 3.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 144.5, 139.8, 134.6, 128.8, 128.6, 128.0, 127.3, 118.3, 117.5, 115.4, 68.1, 53.4; IR (neat, cm^{-1}) 3405, 2952, 2920, 1733, 1602, 1503, 1432, 1263, 1193, 750, 695; HRMS (ESI): *m/z*: calcd for $C_{17}H_{18}NO_2$ $[M+H]^+$: 268.1338, found: 268.1339.

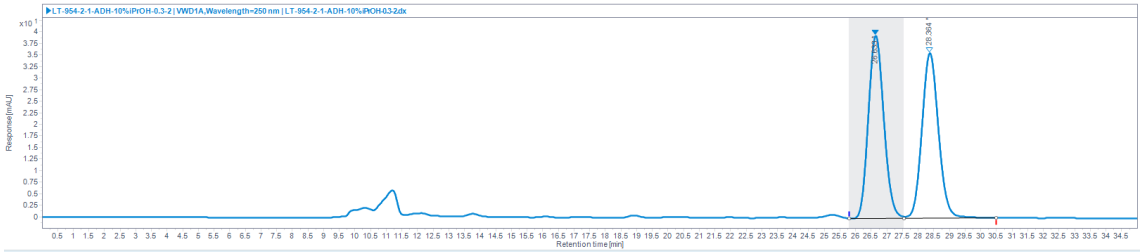
The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 90/10; flow rate 0.3 mL/min; 35 °C; 250 nm; retention time: 17.4 min (minor) and 18.8 min (major).





methyl (*S*)-2-amino-2-phenylbut-3-ynoate (45): yellow oil; 14.2 mg, 75% yield; 91% *ee*; R_f = 0.18 (PE:EA = 5:1); $[\alpha]_D^{20}$ = 66.5 (*c* = 0.34, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.43-7.29 (m, 3H), 3.73 (s, 3H), 2.69 (s, 1H), 2.35 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 140.2, 128.6, 128.5, 126.2, 84.0, 73.8, 59.6, 53.7; IR (neat, cm^{-1}) 3283, 2954, 1738, 1599, 1490, 1236, 1023, 771, 698; HRMS (ESI): *m/z*: calcd for $C_{11}H_{12}NO_2$ $[M+H]^+$: 190.0868, found: 190.0871.

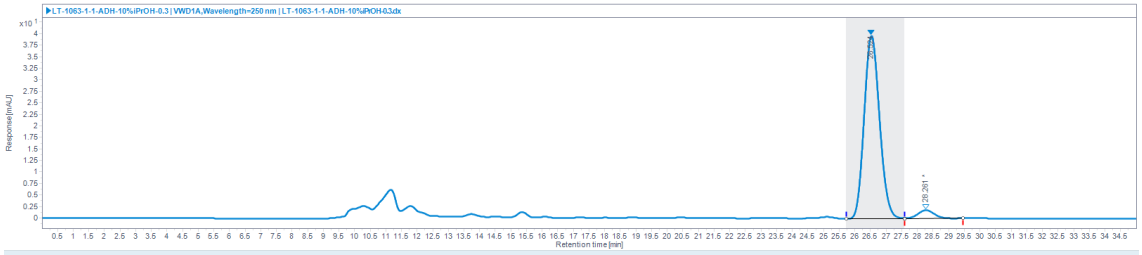
The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 90/10; flow rate 0.3 mL/min; 35 °C; 250 nm; retention time: 26.5 min (major) and 28.3 min (minor).



Injection Results

Peaks | Summary

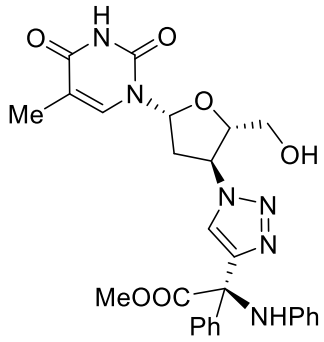
#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	26.633	50.838	25.782	27.555	0.86928
2	28.364	49.162	27.555	30.479	0.87761



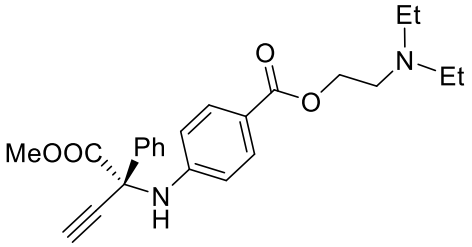
Injection Results

Peaks | Summary

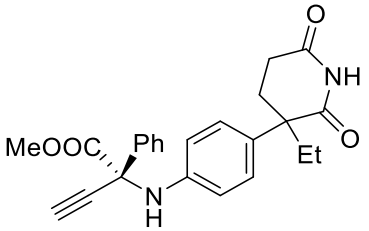
#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	26.524	95.390	25.726	27.588	0.86746
2	28.261	4.610	27.588	29.447	0.98116



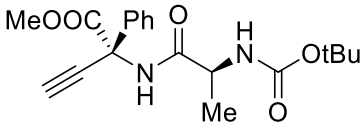
methyl (*R*)-2-(1-((1*S*,2*S*,4*R*)-2-(hydroxymethyl)-4-(5-methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2H)-yl)cyclopentyl)-1H-1,2,3-triazol-4-yl)-2-phenyl-2-(phenylamino)acetate (46): white solid; 43.0 mg, 81% yield; *dr* > 20:1; R_f = 0.54 (DCM:MeOH = 5:1); $[\alpha]_D^{20}$ = 14.7 (*c* = 0.17, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 9.79 (s, 1H), 7.80 (s, 1H), 7.72-7.63 (m, 2H), 7.45 (s, 1H), 7.38-7.27 (m, 3H), 6.94 (t, *J* = 7.7 Hz, 2H), 6.60 (t, *J* = 7.3 Hz, 1H), 6.37 (d, *J* = 8.0 Hz, 2H), 6.18 (t, *J* = 6.4 Hz, 1H), 5.74 (s, 1H), 5.40-5.24 (m, 1H), 4.30-4.19 (m, 1H), 3.95-3.81 (m, 2H), 3.70 (s, 3H), 3.65-3.52 (m, 1H), 2.97-2.76 (m, 2H), 1.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 164.3, 150.6, 148.1, 144.4, 138.6, 137.9, 128.7, 128.7, 128.5, 127.8, 124.5, 118.5, 115.8, 111.1, 88.1, 85.2, 66.0, 61.2, 59.2, 53.8, 37.5, 12.5; IR (neat, cm^{-1}) 3396, 3055, 2925, 1680, 1601, 1500, 1264, 1099, 1046, 731, 696; HRMS (ESI): *m/z*: calcd for $C_{27}H_{29}N_6O_6$ $[M+H]^+$: 533.2149, found: 533.2150.



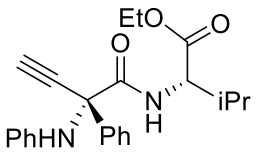
2-(diethylamino)ethyl (*S*)-4-((1-methoxy-1-oxo-2-phenylbut-3-yn-2-yl)amino)benzoate (47): yellow oil; 22.1 mg, 54% yield; R_f = 0.56 (DCM:MeOH = 5:1); $[\alpha]_D^{20}$ = -67.4 (*c* = 0.19, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.65 (m, 4H), 7.44-7.29 (m, 3H), 6.56 (d, *J* = 8.7 Hz, 2H), 5.94 (s, 1H), 4.31 (t, *J* = 6.2 Hz, 2H), 3.76 (s, 3H), 2.83 (t, *J* = 6.2 Hz, 2H), 2.68 (s, 1H), 2.64 (q, *J* = 7.1 Hz, 4H), 1.05 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 166.6, 147.4, 137.1, 131.0 , 129.0, 128.9, 126.8, 119.8, 114.5, 79.8, 75.1, 62.3, 61.5, 54.6, 50.9, 47.7, 11.8; IR (neat, cm^{-1}) 3395, 3288, 2967, 2926, 1744, 1703, 1605, 1450, 1263, 1106, 769; HRMS (ESI): *m/z*: calcd for $C_{24}H_{29}N_2O_4$ $[M+H]^+$: 409.2127, found: 409.2126.



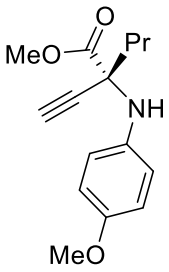
methyl (2*S*)-2-((4-(3-ethyl-2,6-dioxopiperidin-3-yl)phenyl)amino)-2-phenylbut-3-ynoate (48): white solid; 38.4 mg, 95% yield; *dr* = 1:1; R_f = 0.21 (PE:EA = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 7.3 Hz, 1H), 7.75 (d, *J* = 7.4 Hz, 2H), 7.47-7.29 (m, 3H), 6.94 (d, *J* = 6.7 Hz, 2H), 6.54 (d, *J* = 8.4 Hz, 2H), 5.51 (s, 1H), 3.74 (s, 3H), 2.64 (s, 1H), 2.59-2.31 (m, 2H), 2.30-2.07 (m, 2H), 2.03-1.89 (m, 1H), 1.85-1.73 (m, 1H), 0.80 (td, *J* = 7.4, 3.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.7, 175.7, 173.0, 173.0, 170.2, 142.7, 142.7, 137.7, 137.7, 128.9, 128.8, 128.8, 128.8, 128.1, 126.9, 126.6, 126.5, 115.7, 80.3, 75.1, 61.8, 61.8, 54.4, 50.3, 50.3, 33.0, 33.0, 29.4, 26.9, 9.1, 9.1; HRMS (ESI): *m/z*: calcd for $C_{24}H_{25}N_2O_4$ $[M+H]^+$: 405.1814, found: 405.1815.



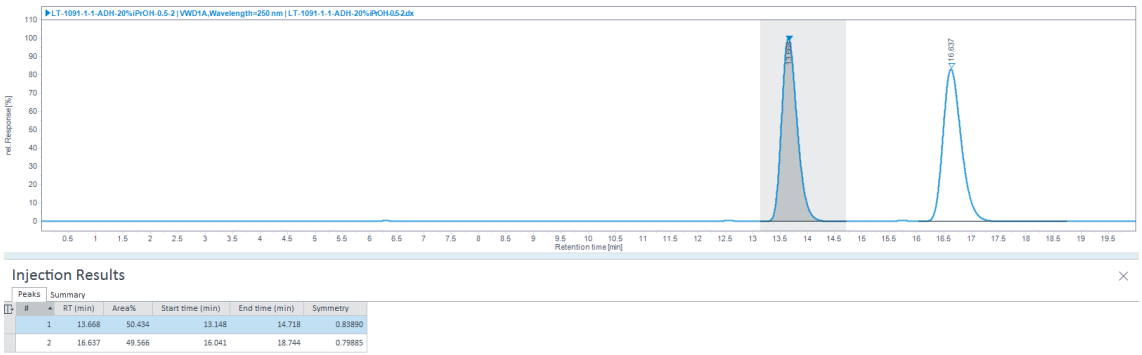
methyl (*S*)-2-((S)-2-((tert-butoxycarbonyl)amino)propanamido)-2-phenylbut-3-ynoate (49): colorless oil; 29.6 mg, 82% yield; *dr* > 20:1; R_f = 0.38 (PE:EA = 1:1); $[\alpha]_D^{20}$ = -23.5 (*c* = 0.17, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72-7.66 (m, 2H), 7.63 (s, 1H), 7.43-7.32 (m, 3H), 5.01 (s, 1H), 4.24 (s, 1H), 3.73 (s, 3H), 2.72 (s, 1H), 1.42 (s, 9H), 1.35 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 168.9, 136.5, 129.1, 128.9, 126.4, 126.3, 80.3, 79.6, 74.4, 60.0, 54.2, 49.9, 28.4, 17.6; IR (neat, cm^{-1}) 3395, 3291, 2979, 1747, 1676, 1490, 1366, 1243, 1161, 1054, 697; HRMS (ESI): *m/z*: calcd for $C_{19}H_{25}N_2O_5$ $[M+H]^+$: 361.1763, found: 361.1760.

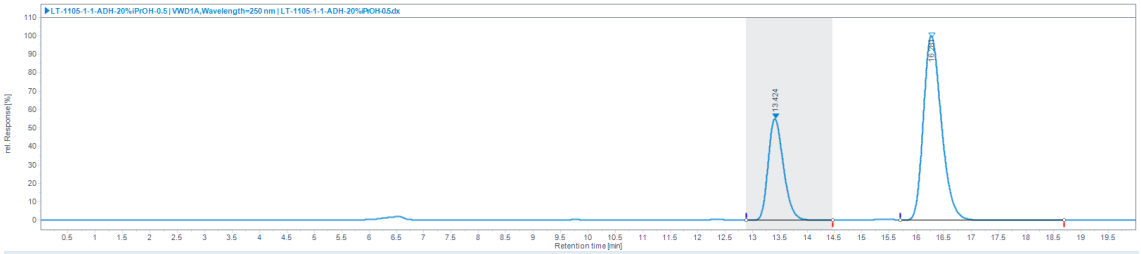


ethyl ((*S*)-2-phenyl-2-(phenylamino)but-3-ynoyl)-L-valinate (50): yellow oil; 25.7 mg, 68% yield; *dr* > 20:1; R_f = 0.41 (PE:EA = 5:1); $[\alpha]_D^{20}$ = -47.7 (*c* = 0.13, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.7 Hz, 2H), 7.45-7.31 (m, 3H), 7.09 (t, *J* = 7.8 Hz, 2H), 6.76-6.55 (m, 4H), 5.59 (s, 1H), 4.42 (dd, *J* = 8.8, 4.5 Hz, 1H), 4.17-3.90 (m, 2H), 2.77 (s, 1H), 2.28-2.10 (m, 1H), 1.14 (t, *J* = 7.1 Hz, 3H), 0.95 (d, *J* = 6.9 Hz, 3H), 0.88 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 168.9, 143.8, 138.8, 129.2, 128.9, 128.8, 126.5, 118.7, 115.8, 81.7, 76.3, 62.8, 61.4, 57.9, 31.8, 19.0, 17.5, 14.2; IR (neat, cm^{-1}) 3388, 3278, 2965, 1734, 1690, 1602, 1501, 1310, 1024, 750, 692; HRMS (ESI): *m/z*: calcd for $C_{23}H_{27}N_2O_3$ $[M+H]^+$: 379.2022, found: 379.2020.



methyl (*R*)-2-ethynyl-2-((4-methoxyphenyl)amino)pentanoate (51): yellow solid; 21.9 mg, 84% yield; 36% *ee*; R_f = 0.41 (PE:EA = 5:1); $[\alpha]_D^{20}$ = 15.7 (*c* = 0.21, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 6.82 (d, *J* = 8.9 Hz, 2H), 6.76 (d, *J* = 8.9 Hz, 2H), 3.76 (s, 3H), 3.73 (s, 3H), 2.53 (s, 1H), 2.06-1.95 (m, 2H), 1.62-1.40 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 153.7, 138.5, 118.0, 114.5, 74.2, 60.9, 55.6, 53.3, 42.8, 17.7, 13.9; IR (neat, cm^{-1}) 3377, 3278, 3961, 1738, 1513, 1464, 1237, 1176, 1035, 823; HRMS (ESI): *m/z*: calcd for $C_{15}H_{20}NO_3$ $[M+H]^+$: 262.1443, found: 262.1442. The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2–propanol = 80/20; flow rate 0.5 mL/min; 35 °C; 250 nm; retention time: 13.4 min (minor) and 16.3 min (major).

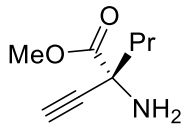




Injection Results

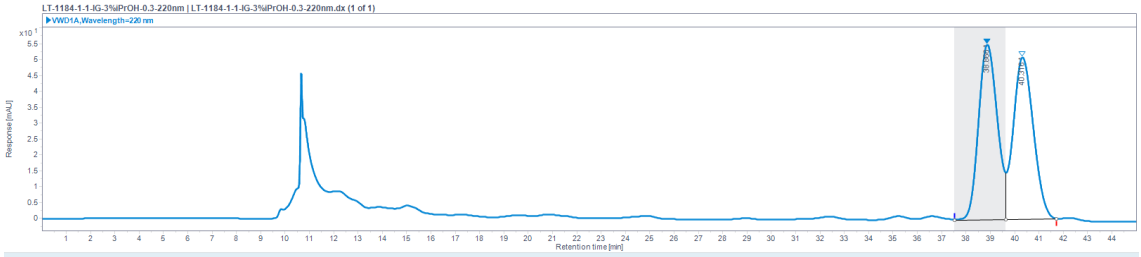
Peaks | Summary

#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	13.424	31.823	12.891	14.464	0.82211
2	16.281	68.177	15.696	18.691	0.81148



methyl (*R*)-2-amino-2-ethynylpentanoate: yellow oil; 8.9 mg, 57% yield; 36% *ee*; R_f = 0.41 (PE:EA = 1:1); $[\alpha]_D^{20}$ = -5.6 (*c* = 0.16, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 3.77 (s, 3H), 2.41 (s, 1H), 1.98 (s, 2H), 1.90-1.70 (m, 2H), 1.53-1.36 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 84.3, 71.9, 56.4, 53.3, 43.1, 17.6, 14.0; IR (neat, cm^{-1}) 3382, 3287, 2960, 2927, 1737, 1594, 1437, 1223, 1164, 1000, 647; HRMS (ESI): *m/z*: calcd for $C_8H_{14}NO_2$ $[M+H]^+$: 156.1025, found: 156.1020.

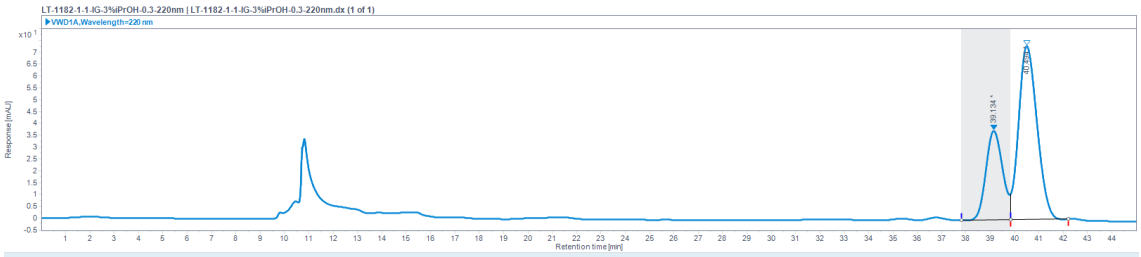
The *ee* was determined by HPLC analysis: CHIRALPAK IG (4.6 mm i.d. × 250 mm); hexane/2–propanol = 97/3; flow rate 0.3 mL/min; 35 °C; 220 nm; retention time: 39.1 min (minor) and 40.5 min (major).



Injection Results

Peaks | Summary

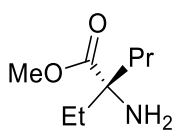
#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	38.866	50.258	37.538	39.629	0.87629
2	40.316	49.742	39.629	41.705	0.83943



Injection Results

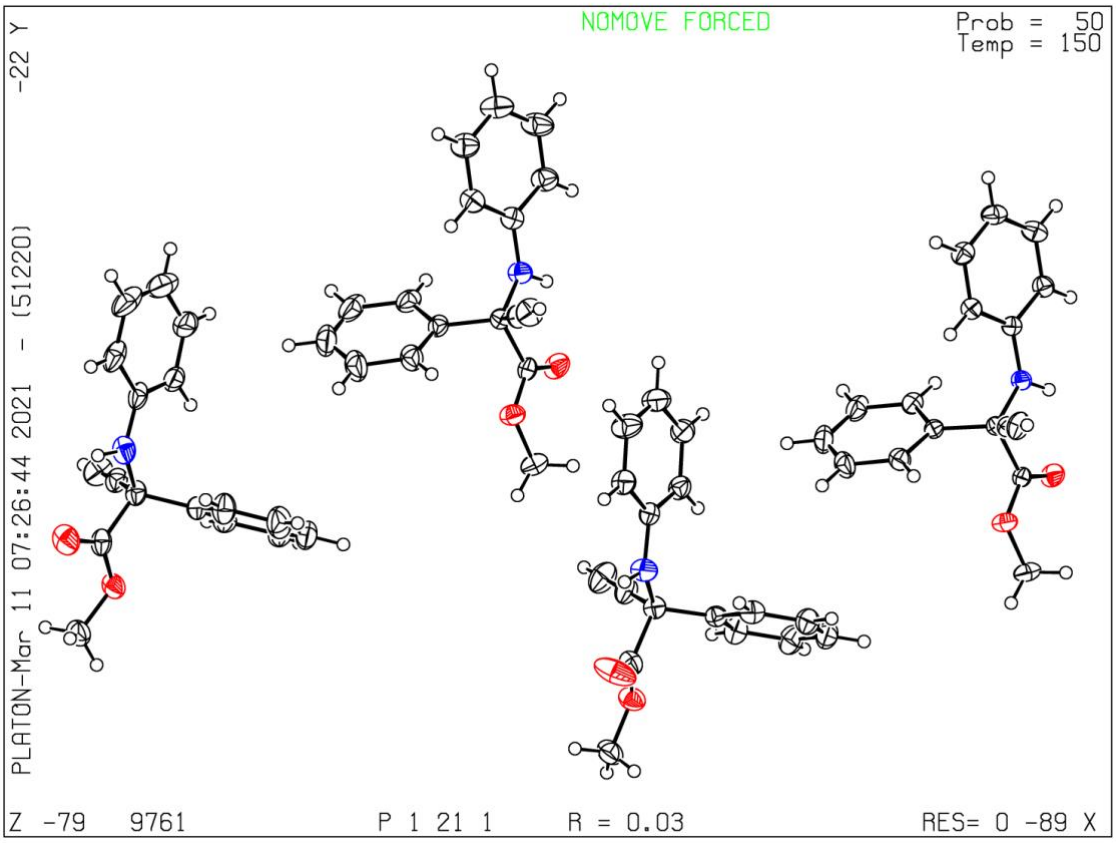
Peaks | Summary

#	RT (min)	Area%	Start time (min)	End time (min)	Symmetry
1	39.134	31.945	37.816	39.825	0.87903
2	40.494	68.055	39.825	42.195	0.78634



methyl (*S*)-2-amino-2-ethylpentanoate (52): $[\alpha]_D^{20}$ = 1.8 (*c* = 0.50, Methanol-d_4); ^{1}H NMR (400 MHz, Methanol-d_4) δ 3.72 (s, 3H), 1.87-1.68 (m, 2H), 1.67-1.50 (m, 2H), 1.49-1.34 (m, 1H), 1.22-1.07 (m, 1H), 0.92 (t, *J* = 7.3 Hz, 3H), 0.86 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, Methanol-d_4) δ 177.7, 62.9, 52.7, 42.5, 33.3, 18.2, 14.6, 8.4; HRMS (ESI): *m/z*: calcd for $C_8H_{18}NO_2$ $[M+H]^+$: 160.1338, found: 160.1335.

X-ray crystallographic information of product 1



X-ray crystallography of **1**

Table S3 Crystal data and structure refinement for 1.

Identification code	1
Empirical formula	$C_{17}H_{15}NO_2$
Formula weight	265.30
Temperature/K	149.99(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	9.65133(9)
b/Å	11.74209(11)
c/Å	25.3227(2)
α/°	90
β/°	90.6825(8)
γ/°	90
Volume/Å^3	2869.54(4)
Z	8
ρ_{calc}g/cm^3	1.228

μ/mm^{-1}	0.647
F(000)	1120.0
Crystal size/mm^3	0.13 × 0.1 × 0.08
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.982 to 147.788
Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 14, -30 ≤ l ≤ 31
Reflections collected	30634
Independent reflections	10645 [R_{int} = 0.0236, R_{sigma} = 0.0235]
Data/restraints/parameters	10645/1/741
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0333, wR_2 = 0.0838
Final R indexes [all data]	R_1 = 0.0348, wR_2 = 0.0853
Largest diff. peak/hole / e Å^{-3}	0.20/-0.22
Flack/Hooft parameter	0.08(6)/0.08(5)

Crystal structure determination of 1

Crystal Data for $C_{17}H_{15}NO_2$ (*M* =265.30 g/mol): monoclinic, space group $P2_1$ (no. 4), *a* = 9.65133(9) Å, *b* = 11.74209(11) Å, *c* = 25.3227(2) Å, *β* = 90.6825(8)°, *V* = 2869.54(4) Å^3, *Z* = 8, *T* = 149.99(10) K, μ(Cu Kα) = 0.647 mm^{-1}, *Dcalc* = 1.228 g/cm^3, 30634 reflections measured (6.982° ≤ 2Θ ≤ 147.788°), 10645 unique (R_{int} = 0.0236, R_{sigma} = 0.0235) which were used in all calculations. The final R_1 was 0.0333 (I > 2σ(I)) and wR_2 was 0.0853 (all data).

Refinement model description

Table S4 Fractional Atomic Coordinates (×10^4) and Eqalent Isotropic Displacement Parameters (Å^2×10^3) for 1. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	4424.2(13)	4694.3(12)	10448.6(5)	30.9(3)
O2	6319.4(14)	3903.9(13)	10808.5(5)	34.1(3)
N1	8029.1(15)	5314.7(14)	10348.3(6)	25.8(3)
C1	6331.1(18)	5158.9(16)	9604.6(7)	23.1(3)
C2	7250(2)	4441.6(17)	9346.1(7)	27.9(4)
C3	6979(2)	4112.5(19)	8826.1(8)	37.5(5)
C4	5788(3)	4479(2)	8568.7(8)	42.1(5)
C5	4877(2)	5194(2)	8823.7(8)	39.0(5)
C6	5148(2)	5545.1(17)	9340.3(8)	30.4(4)
C7	6596.9(17)	5466.0(15)	10190.4(7)	21.9(3)
C8	6081.2(19)	6619.8(16)	10313.0(7)	24.9(4)
C9	5718(2)	7549.1(19)	10426.8(8)	36.4(5)
C10	5777.9(18)	4595.6(16)	10526.1(7)	23.2(4)
C11	3594(2)	3897.4(19)	10746.8(8)	34.4(4)
C12	9127.3(18)	5955.4(16)	10162.1(7)	23.3(3)
C13	10440.0(19)	5774.7(17)	10387.0(7)	28.3(4)
C14	11581(2)	6370.3(19)	10206.9(9)	35.0(4)
C15	11445(2)	7156.2(18)	9799.1(8)	33.7(4)
C16	10147(2)	7337.5(17)	9577.0(8)	31.0(4)
C17	8991(2)	6750.5(16)	9754.6(7)	26.3(4)
O3	-941.4(18)	4469.1(15)	1544.0(7)	49.9(4)
O4	-1194.9(16)	2938.4(14)	2067.2(6)	38.3(3)
N2	1537(2)	4958.1(16)	1933.3(7)	38.9(4)

C18	2942(3)	5219.9(18)	1968.9(7)	36.3(5)
C19	3881(2)	4600(2)	2274.5(8)	38.9(5)
C20	5270(3)	4897(2)	2284.4(9)	49.2(6)
C21	5750(3)	5818(3)	1999.7(11)	61.2(8)
C22	4823(3)	6443(2)	1700.5(10)	60.5(8)
C23	3429(3)	6158(2)	1681.9(8)	48.0(6)
C24	962(2)	3894.3(17)	2117.2(7)	30.5(4)
C25	-514(2)	3823.6(18)	1878.4(7)	33.0(4)
C26	-2511(2)	2659(2)	1817.2(9)	41.3(5)
C27	1681(2)	2889.3(19)	1897.4(8)	34.0(4)
C28	2203(3)	2089(2)	1697.8(10)	45.9(5)
C29	894(2)	3866.8(18)	2724.8(7)	30.6(4)
C30	1166(2)	2874(2)	3005.8(8)	35.0(4)
C31	1103(2)	2878(3)	3554.3(9)	46.0(6)
C32	759(3)	3851(3)	3818.7(9)	54.5(7)
C33	482(3)	4838(3)	3544.2(10)	55.7(7)
C34	551(3)	4854(2)	2993.4(9)	43.9(5)
O5	-1716.9(18)	4806.9(16)	7018.9(10)	65.6(6)
O6	-1469.0(16)	2967.0(14)	7211.9(6)	39.4(3)
N3	956.2(18)	5239.2(15)	7109.8(7)	34.5(4)
C35	2315(2)	5614.3(17)	7059.6(7)	27.7(4)
C36	2553(2)	6595.9(19)	6766.7(8)	35.2(4)
C37	3886(3)	6996(2)	6697.0(10)	46.4(6)
C38	5006(2)	6441(2)	6922.9(10)	45.1(5)
C39	4773(2)	5482(2)	7221.2(8)	39.1(5)
C40	3444(2)	5060.3(19)	7294.1(8)	33.9(4)
C41	555(2)	4105.3(16)	7269.4(7)	28.6(4)
C42	1276(2)	3218.1(18)	6958.0(8)	35.6(5)
C43	1840(3)	2519(2)	6701.7(10)	49.3(6)
C44	-1016(2)	4013.9(18)	7145.4(8)	33.2(4)
C45	-2924(2)	2767(2)	7101.0(9)	44.3(5)
C46	741.5(19)	3908.9(17)	7869.9(7)	27.3(4)
C47	609(2)	4819.0(18)	8213.5(8)	34.1(4)
C48	733(2)	4650(2)	8756.2(9)	41.8(5)
C49	984(2)	3574(2)	8955.8(8)	42.9(5)
C50	1108(3)	2664(2)	8614.3(9)	43.1(5)
C51	981(2)	2823.4(19)	8072.7(8)	35.0(4)
O7	6442.3(15)	4247.4(14)	5889.6(6)	40.4(4)
O8	4510.6(14)	5050.1(13)	5566.8(6)	34.5(3)
N4	8097.5(17)	5607.4(16)	5380.6(7)	32.0(4)
C52	9195(2)	6280.9(17)	5209.5(8)	30.2(4)
C53	9065(2)	7086.8(19)	4807.6(8)	34.8(4)
C54	10221(2)	7684(2)	4640.0(9)	41.1(5)
C55	11508(2)	7504(2)	4870.0(11)	47.1(6)
C56	11631(2)	6725(2)	5280.3(11)	48.3(6)
C57	10492(2)	6113(2)	5446.8(9)	38.5(5)
C58	6646.4(19)	5835.5(16)	5281.1(7)	25.3(4)
C59	6242(2)	6995.9(17)	5451.0(8)	29.8(4)
C60	5969(2)	7941(2)	5570.0(9)	42.8(5)
C61	5868(2)	4949.3(17)	5621.8(7)	27.0(4)
C62	3690(2)	4238(2)	5858.7(9)	38.5(5)

C63	6213(2)	5655.3(17)	4699.8(7)	28.3(4)
C64	7030(2)	5014(2)	4364.2(8)	38.7(5)
C65	6600(3)	4883(2)	3836.3(9)	55.8(8)
C66	5368(3)	5348(3)	3659.0(9)	60.2(8)
C67	4554(3)	5960(2)	3995.3(9)	52.6(7)
C68	4984(2)	6133(2)	4511.7(8)	38.1(5)

Table S5 Anisotropic Displacement Parameters ($Å^2×10^3$) for 1. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	22.6(6)	31.0(8)	39.2(7)	9.0(6)	4.2(5)	-0.5(5)
O2	32.0(7)	36.8(8)	33.5(7)	14.4(6)	-0.2(6)	3.3(6)
N1	21.4(8)	29.5(9)	26.4(8)	7.9(6)	-3.0(6)	0.6(6)
C1	25.4(9)	21.4(9)	22.4(8)	3.0(6)	0.0(6)	-3.1(6)
C2	32.0(10)	24.7(10)	26.9(9)	-1.0(7)	3.2(7)	-1.6(7)
C3	52.9(13)	32.3(12)	27.5(10)	-4.3(8)	9.8(9)	-7.2(9)
C4	61.9(15)	42.5(13)	21.8(9)	1.9(8)	-4.3(9)	-14.2(11)
C5	45.6(13)	40.4(13)	30.8(10)	8.8(9)	-14.0(9)	-6.8(9)
C6	31.6(10)	28.5(10)	30.9(10)	5.3(8)	-3.9(7)	-1.3(8)
C7	20.1(8)	22.9(9)	22.5(8)	2.3(6)	-0.3(6)	1.9(6)
C8	25.2(9)	25.5(10)	24.0(8)	0.8(7)	1.3(7)	1.8(7)
C9	47.5(12)	31.5(12)	30.2(10)	-0.4(8)	5.0(8)	7.4(9)
C10	24.1(9)	24.5(9)	20.9(8)	-1.9(7)	2.1(6)	0.5(7)
C11	29.7(10)	30.8(11)	42.8(11)	0.1(9)	12.4(8)	-6.1(8)
C12	22.9(9)	21.8(9)	25.3(8)	-1.9(7)	1.7(6)	0.2(6)
C13	25.9(9)	28.9(11)	30.0(9)	2.4(7)	-1.5(7)	2.6(7)
C14	24.7(10)	36.1(12)	44.2(11)	-2.2(9)	-1.0(8)	-0.1(8)
C15	29.6(10)	29.6(11)	42.1(11)	-2.5(8)	6.4(8)	-6.2(8)
C16	38.1(11)	22.7(10)	32.3(10)	1.1(7)	3.9(8)	-2.8(8)
C17	26.9(9)	24.3(10)	27.7(9)	1.0(7)	-0.4(7)	1.9(7)
O3	57.6(10)	42.0(10)	49.6(9)	18.8(8)	-16.1(8)	-1.1(8)
O4	41.4(8)	36.7(8)	36.3(8)	11.1(6)	-10.9(6)	-5.1(7)
N2	56.4(12)	25.9(10)	34.2(9)	10.9(7)	-8.5(8)	-6.1(8)
C18	60.2(14)	27.4(11)	21.3(9)	-3.4(7)	3.9(8)	-11.1(9)
C19	49.6(13)	42.0(13)	25.3(9)	-3.1(8)	6.7(8)	-11.6(10)
C20	50.7(14)	60.9(17)	36.2(11)	-12.7(11)	11.4(10)	-12.5(12)
C21	64.6(18)	63.0(19)	56.7(16)	-18.3(14)	27.7(14)	-28.9(15)
C22	93(2)	42.7(15)	46.1(14)	-10.3(12)	32.5(14)	-28.6(15)
C23	86.1(19)	30.1(13)	28.2(10)	-1.8(8)	12.5(11)	-15.4(12)
C24	43.0(11)	22.5(10)	26.0(9)	5.2(7)	-2.1(8)	-1.0(8)
C25	45.6(12)	26.5(10)	26.7(9)	2.4(7)	-3.2(8)	3.1(8)
C26	41.5(12)	43.0(14)	39.1(11)	6.9(9)	-9.0(9)	-3.0(10)
C27	42.1(11)	31.4(11)	28.7(9)	4.4(8)	1.4(8)	-3.6(9)
C28	55.6(15)	33.5(13)	49.0(13)	-5.2(10)	10.5(11)	1.0(10)
C29	31.9(10)	34.0(11)	25.9(9)	3.7(8)	-2.7(7)	0.5(8)
C30	31.8(10)	39.3(12)	33.8(10)	9.8(9)	-1.3(8)	-1.0(9)
C31	36.5(12)	67.6(17)	33.7(11)	19.0(11)	-3.4(9)	-2.9(11)
C32	43.2(13)	94(2)	26.2(10)	5.9(12)	-0.4(9)	3.0(13)
C33	53.5(15)	75(2)	38.3(12)	-16.3(12)	0.7(10)	11.5(13)

C34	53.1(14)	43.8(14)	34.6(11)	-3.0(9)	-1.4(9)	11.2(11)
O5	39.5(10)	34.9(10)	121.6(17)	16.3(10)	-27.6(10)	-2.1(7)
O6	37.4(8)	33.2(8)	47.4(9)	6.3(7)	-6.8(6)	-6.7(6)
N3	29.3(9)	27.8(10)	46.4(10)	13.1(7)	-3.3(7)	2.7(7)
C35	31.4(10)	26.4(10)	25.4(9)	0.6(7)	0.8(7)	1.6(7)
C36	37.4(11)	31.2(11)	37.0(10)	9.0(8)	-1.6(8)	2.7(9)
C37	45.0(13)	37.2(13)	57.2(14)	16.5(10)	6.3(10)	-3.4(10)
C38	33.4(12)	50.7(15)	51.4(13)	8.2(11)	4.1(10)	-4.1(10)
C39	31.1(11)	49.9(14)	36.4(11)	7.6(9)	0.0(8)	4.3(9)
C40	33.1(11)	38.4(12)	30.2(9)	8.4(8)	0.9(8)	4.5(8)
C41	30.4(10)	24.0(10)	31.4(9)	2.8(7)	-0.4(7)	3.0(7)
C42	44.4(12)	31.8(12)	30.7(10)	2.7(8)	3.9(9)	2.2(9)
C43	65.8(16)	39.2(14)	43.3(13)	-3.4(10)	16.4(11)	5.7(11)
C44	36.3(11)	27.4(11)	35.6(10)	1.1(8)	-5.9(8)	-1.7(8)
C45	43.5(13)	43.4(14)	45.7(12)	4.4(10)	-11.2(10)	-13.6(10)
C46	24.7(9)	27.1(10)	30.1(9)	1.7(7)	0.3(7)	2.2(7)
C47	33.3(10)	28.6(11)	40.3(11)	-3.2(8)	4.0(8)	1.5(8)
C48	40.5(12)	49.7(14)	35.2(11)	-12.7(10)	5.0(9)	0.1(10)
C49	42.6(13)	57.9(16)	28.2(10)	1.5(10)	2.7(9)	4.3(11)
C50	50.8(13)	42.1(14)	36.4(11)	10.1(9)	2.1(9)	8.6(10)
C51	42.7(11)	29.0(11)	33.2(10)	1.5(8)	1.7(8)	7.5(9)
O7	38.1(8)	45.4(9)	37.8(8)	16.9(7)	2.9(6)	7.7(7)
O8	27.6(7)	36.1(8)	39.8(8)	10.5(6)	2.3(6)	-1.1(6)
N4	26.6(9)	32.0(10)	37.4(9)	9.7(7)	-1.9(7)	2.2(7)
C52	29.2(10)	27.1(10)	34.2(10)	-3.5(8)	1.4(8)	1.8(7)
C53	35.1(11)	29.5(11)	39.6(11)	2.4(8)	-3.1(8)	-0.4(8)
C54	42.8(12)	30.5(12)	49.9(13)	5.5(9)	2.8(9)	-3.9(9)
C55	33.4(12)	39.5(14)	68.6(16)	8.7(11)	8.7(10)	-2.9(9)
C56	28.2(11)	48.6(15)	68.1(16)	9.0(12)	-0.5(10)	2.4(10)
C57	29.8(11)	39.6(13)	46.0(12)	6.7(9)	0.9(9)	4.6(9)
C58	24.6(9)	25.4(10)	26.0(9)	0.4(7)	0.7(7)	2.3(7)
C59	31.6(10)	28.8(11)	29.0(9)	-1.5(8)	-0.9(7)	2.0(8)
C60	49.1(13)	32.2(12)	47.0(12)	-6.0(10)	4.2(10)	3.8(10)
C61	31.9(10)	27.7(10)	21.4(8)	-2.3(7)	3.1(7)	3.1(7)
C62	37.9(11)	35.7(12)	42.1(11)	6.4(9)	10.4(9)	-4.4(9)
C63	35.2(10)	25.4(10)	24.3(9)	1.8(7)	1.6(7)	-5.0(7)
C64	45.4(12)	35.1(12)	35.9(10)	-8.0(9)	12.6(9)	-12.6(9)
C65	78.7(19)	53.1(16)	36.2(12)	-14.7(11)	23.4(12)	-30.8(14)
C66	89(2)	65.6(19)	26.0(11)	6.3(11)	-7.3(12)	-34.2(16)
C67	68.5(17)	53.8(16)	34.9(12)	12.1(11)	-17.4(11)	-13.6(13)
C68	43.8(12)	36.9(13)	33.4(10)	6.6(8)	-6.8(9)	-2.2(9)

Table S6 Bond Lengths for 1.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C10	1.324(2)	O5	C44	1.192(3)
O1	C11	1.450(2)	O6	C44	1.316(3)
O2	C10	1.198(2)	O6	C45	1.448(3)
N1	C7	1.445(2)	N3	C35	1.391(3)
N1	C12	1.387(2)	N3	C41	1.446(3)

C1	C2	1.392(3)	C35	C36	1.391(3)
C1	C6	1.392(3)	C35	C40	1.395(3)
C1	C7	1.545(2)	C36	C37	1.383(3)
C2	C3	1.394(3)	C37	C38	1.380(3)
C3	C4	1.383(3)	C38	C39	1.376(3)
C4	C5	1.382(3)	C39	C40	1.389(3)
C5	C6	1.393(3)	C41	C42	1.485(3)
C7	C8	1.478(3)	C41	C44	1.548(3)
C7	C10	1.552(2)	C41	C46	1.546(3)
C8	C9	1.183(3)	C42	C43	1.183(3)
C12	C13	1.399(3)	C46	C47	1.385(3)
C12	C17	1.397(3)	C46	C51	1.393(3)
C13	C14	1.386(3)	C47	C48	1.392(3)
C14	C15	1.390(3)	C48	C49	1.381(4)
C15	C16	1.383(3)	C49	C50	1.380(3)
C16	C17	1.391(3)	C50	C51	1.388(3)
O3	C25	1.206(2)	O7	C61	1.199(2)
O4	C25	1.322(3)	O8	C61	1.322(2)
O4	C26	1.450(3)	O8	C62	1.448(2)
N2	C18	1.392(3)	N4	C52	1.395(3)
N2	C24	1.446(3)	N4	C58	1.445(2)
C18	C19	1.391(3)	C52	C53	1.394(3)
C18	C23	1.404(3)	C52	C57	1.396(3)
C19	C20	1.385(3)	C53	C54	1.388(3)
C20	C21	1.383(4)	C54	C55	1.382(3)
C21	C22	1.377(5)	C55	C56	1.389(3)
C22	C23	1.387(4)	C56	C57	1.383(3)
C24	C25	1.543(3)	C58	C59	1.483(3)
C24	C27	1.481(3)	C58	C61	1.551(3)
C24	C29	1.541(3)	C58	C63	1.540(2)
C27	C28	1.183(3)	C59	C60	1.181(3)
C29	C30	1.389(3)	C63	C64	1.388(3)
C29	C34	1.386(3)	C63	C68	1.392(3)
C30	C31	1.391(3)	C64	C65	1.404(3)
C31	C32	1.367(4)	C65	C66	1.378(4)
C32	C33	1.376(4)	C66	C67	1.370(4)
C33	C34	1.397(3)	C67	C68	1.382(3)

Table S7 Bond Angles for 1.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C10	O1	C11	114.64(15)	C44	O6	C45	116.72(18)
C12	N1	C7	124.86(15)	C35	N3	C41	124.98(17)
C2	C1	C6	119.61(17)	N3	C35	C40	123.08(18)
C2	C1	C7	119.56(16)	C36	C35	N3	118.23(17)
C6	C1	C7	120.75(16)	C36	C35	C40	118.69(19)
C1	C2	C3	119.91(19)	C37	C36	C35	120.6(2)
C4	C3	C2	120.3(2)	C38	C37	C36	120.7(2)
C5	C4	C3	119.93(19)	C39	C38	C37	118.8(2)
C4	C5	C6	120.3(2)	C38	C39	C40	121.4(2)

C1	C6	C5	119.9(2)	C39	C40	C35	119.7(2)
N1	C7	C1	112.60(14)	N3	C41	C42	111.65(17)
N1	C7	C8	112.21(15)	N3	C41	C44	105.79(15)
N1	C7	C10	105.02(14)	N3	C41	C46	112.57(16)
C1	C7	C10	107.00(14)	C42	C41	C44	107.92(17)
C8	C7	C1	111.30(14)	C42	C41	C46	111.58(16)
C8	C7	C10	108.29(14)	C46	C41	C44	106.94(15)
C9	C8	C7	177.0(2)	C43	C42	C41	178.8(2)
O1	C10	C7	111.67(14)	O5	C44	O6	125.1(2)
O2	C10	O1	124.80(17)	O5	C44	C41	123.46(19)
O2	C10	C7	123.51(16)	O6	C44	C41	111.39(17)
N1	C12	C13	118.12(16)	C47	C46	C41	119.48(18)
N1	C12	C17	123.24(16)	C47	C46	C51	119.39(18)
C17	C12	C13	118.63(17)	C51	C46	C41	121.07(18)
C14	C13	C12	120.57(18)	C46	C47	C48	120.2(2)
C13	C14	C15	120.72(19)	C49	C48	C47	120.3(2)
C16	C15	C14	118.79(18)	C50	C49	C48	119.6(2)
C15	C16	C17	121.22(19)	C49	C50	C51	120.5(2)
C16	C17	C12	120.08(18)	C50	C51	C46	120.0(2)
C25	O4	C26	117.18(16)	C61	O8	C62	115.76(16)
C18	N2	C24	123.18(18)	C52	N4	C58	125.36(17)
N2	C18	C23	118.1(2)	N4	C52	C57	117.81(19)
C19	C18	N2	123.25(19)	C53	C52	N4	123.32(18)
C19	C18	C23	118.6(2)	C53	C52	C57	118.85(19)
C20	C19	C18	120.2(2)	C54	C53	C52	120.0(2)
C21	C20	C19	121.2(3)	C55	C54	C53	121.1(2)
C22	C21	C20	119.0(3)	C54	C55	C56	118.9(2)
C21	C22	C23	120.9(2)	C57	C56	C55	120.6(2)
C22	C23	C18	120.2(3)	C56	C57	C52	120.5(2)
N2	C24	C25	106.05(16)	N4	C58	C59	112.19(17)
N2	C24	C27	112.55(17)	N4	C58	C61	104.66(15)
N2	C24	C29	111.15(17)	N4	C58	C63	113.11(15)
C27	C24	C25	104.15(17)	C59	C58	C61	108.93(15)
C27	C24	C29	112.60(16)	C59	C58	C63	109.53(16)
C29	C24	C25	109.88(16)	C63	C58	C61	108.16(15)
O3	C25	O4	125.5(2)	C60	C59	C58	176.7(2)
O3	C25	C24	123.2(2)	O7	C61	O8	124.90(18)
O4	C25	C24	111.17(16)	O7	C61	C58	123.54(18)
C28	C27	C24	176.2(2)	O8	C61	C58	111.54(15)
C30	C29	C24	121.26(19)	C64	C63	C58	120.69(19)
C34	C29	C24	119.05(18)	C64	C63	C68	119.80(19)
C34	C29	C30	119.69(18)	C68	C63	C58	119.51(18)
C29	C30	C31	119.9(2)	C63	C64	C65	118.6(2)
C32	C31	C30	120.4(2)	C66	C65	C64	120.7(2)
C31	C32	C33	120.2(2)	C67	C66	C65	120.3(2)
C32	C33	C34	120.3(3)	C66	C67	C68	119.8(3)
C29	C34	C33	119.5(2)	C67	C68	C63	120.7(2)

Table S8 Torsion Angles for 1.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N1	C7	C10	O1	175.60(15)	N3	C35	C36	C37	-178.9(2)
N1	C7	C10	O2	-6.2(2)	N3	C35	C40	C39	179.4(2)
N1	C12	C13	C14	178.34(18)	N3	C41	C44	O5	-9.7(3)
N1	C12	C17	C16	-178.00(17)	N3	C41	C44	O6	171.98(17)
C1	C2	C3	C4	-1.1(3)	N3	C41	C46	C47	29.9(2)
C1	C7	C10	O1	-64.53(18)	N3	C41	C46	C51	-152.90(19)
C1	C7	C10	O2	113.63(19)	C35	N3	C41	C42	-50.3(3)
C2	C1	C6	C5	1.3(3)	C35	N3	C41	C44	-167.46(18)
C2	C1	C7	N1	21.7(2)	C35	N3	C41	C46	76.1(2)
C2	C1	C7	C8	148.68(17)	C35	C36	C37	C38	-1.0(4)
C2	C1	C7	C10	-93.20(19)	C36	C35	C40	C39	-1.4(3)
C2	C3	C4	C5	1.4(3)	C36	C37	C38	C39	-0.2(4)
C3	C4	C5	C6	-0.3(3)	C37	C38	C39	C40	0.6(4)
C4	C5	C6	C1	-1.1(3)	C38	C39	C40	C35	0.2(3)
C6	C1	C2	C3	-0.2(3)	C40	C35	C36	C37	1.8(3)
C6	C1	C7	N1	-161.52(17)	C41	N3	C35	C36	162.23(19)
C6	C1	C7	C8	-34.5(2)	C41	N3	C35	C40	-18.6(3)
C6	C1	C7	C10	83.6(2)	C41	C46	C47	C48	178.08(18)
C7	N1	C12	C13	174.45(17)	C41	C46	C51	C50	-178.27(19)
C7	N1	C12	C17	-7.0(3)	C42	C41	C44	O5	-129.4(2)
C7	C1	C2	C3	176.64(17)	C42	C41	C44	O6	52.3(2)
C7	C1	C6	C5	-175.50(18)	C42	C41	C46	C47	156.35(19)
C8	C7	C10	O1	55.54(19)	C42	C41	C46	C51	-26.5(3)
C8	C7	C10	O2	-126.30(19)	C44	C41	C46	C47	-85.9(2)
C11	O1	C10	O2	1.3(3)	C44	C41	C46	C51	91.3(2)
C11	O1	C10	C7	179.43(15)	C45	O6	C44	O5	2.6(3)
C12	N1	C7	C1	66.6(2)	C45	O6	C44	C41	-179.17(17)
C12	N1	C7	C8	-59.9(2)	C46	C41	C44	O5	110.5(3)
C12	N1	C7	C10	-177.29(16)	C46	C41	C44	O6	-67.8(2)
C12	C13	C14	C15	-0.1(3)	C46	C47	C48	C49	-0.2(3)
C13	C12	C17	C16	0.5(3)	C47	C46	C51	C50	-1.1(3)
C13	C14	C15	C16	0.2(3)	C47	C48	C49	C50	-0.2(4)
C14	C15	C16	C17	0.0(3)	C48	C49	C50	C51	0.0(4)
C15	C16	C17	C12	-0.4(3)	C49	C50	C51	C46	0.7(4)
C17	C12	C13	C14	-0.3(3)	C51	C46	C47	C48	0.8(3)
N2	C18	C19	C20	178.9(2)	N4	C52	C53	C54	-176.6(2)
N2	C18	C23	C22	-179.3(2)	N4	C52	C57	C56	177.6(2)
N2	C24	C25	O3	10.2(3)	N4	C58	C61	O7	-1.2(2)
N2	C24	C25	O4	-173.23(17)	N4	C58	C61	O8	-179.46(16)
N2	C24	C29	C30	-142.4(2)	N4	C58	C63	C64	18.4(3)
N2	C24	C29	C34	37.8(3)	N4	C58	C63	C68	-162.15(18)
C18	N2	C24	C25	-165.80(18)	C52	N4	C58	C59	-53.8(2)
C18	N2	C24	C27	-52.5(2)	C52	N4	C58	C61	-171.76(18)
C18	N2	C24	C29	74.8(2)	C52	N4	C58	C63	70.7(2)
C18	C19	C20	C21	1.0(3)	C52	C53	C54	C55	-0.8(3)
C19	C18	C23	C22	0.8(3)	C53	C52	C57	C56	-0.9(3)
C19	C20	C21	C22	-0.3(4)	C53	C54	C55	C56	-0.9(4)
C20	C21	C22	C23	-0.1(4)	C54	C55	C56	C57	1.8(4)
C21	C22	C23	C18	-0.2(4)	C55	C56	C57	C52	-0.9(4)
C23	C18	C19	C20	-1.2(3)	C57	C52	C53	C54	1.8(3)

C24	N2	C18	C19	-13.3(3)	C58	N4	C52	C53	-17.6(3)
C24	N2	C18	C23	166.80(19)	C58	N4	C52	C57	164.00(19)
C24	C29	C30	C31	179.66(19)	C58	C63	C64	C65	-179.40(19)
C24	C29	C34	C33	179.8(2)	C58	C63	C68	C67	-178.4(2)
C25	C24	C29	C30	100.6(2)	C59	C58	C61	O7	-121.3(2)
C25	C24	C29	C34	-79.3(2)	C59	C58	C61	O8	60.4(2)
C26	O4	C25	O3	6.1(3)	C59	C58	C63	C64	144.39(19)
C26	O4	C25	C24	-170.42(17)	C59	C58	C63	C68	-36.2(2)
C27	C24	C25	O3	-108.8(2)	C61	C58	C63	C64	-97.0(2)
C27	C24	C25	O4	67.8(2)	C61	C58	C63	C68	82.4(2)
C27	C24	C29	C30	-15.0(3)	C62	O8	C61	O7	0.1(3)
C27	C24	C29	C34	165.1(2)	C62	O8	C61	C58	178.37(16)
C29	C24	C25	O3	130.4(2)	C63	C58	C61	O7	119.7(2)
C29	C24	C25	O4	-53.0(2)	C63	C58	C61	O8	-58.6(2)
C29	C30	C31	C32	0.8(3)	C63	C64	C65	C66	-2.2(3)
C30	C29	C34	C33	-0.1(3)	C64	C63	C68	C67	1.0(3)
C30	C31	C32	C33	-0.5(4)	C64	C65	C66	C67	0.9(4)
C31	C32	C33	C34	-0.1(4)	C65	C66	C67	C68	1.4(4)
C32	C33	C34	C29	0.3(4)	C66	C67	C68	C63	-2.4(4)
C34	C29	C30	C31	-0.5(3)	C68	C63	C64	C65	1.2(3)

Table S9 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 1.

Atom	***x***	***y***	***z***	**U(eq)**
H1	8120(20)	4910(20)	10623(10)	37(6)
H2	8043.17	4182.43	9520.04	33
H3	7601.51	3644.3	8651.56	45
H4	5601.5	4244.65	8224.41	51
H5	4078.75	5442.95	8649.64	47
H6	4539.83	6036.62	9508.35	36
H9	5432.05	8279.74	10516.35	44
H11A	2634.31	3990.82	10651.88	52
H11B	3717.32	4040.44	11117.64	52
H11C	3879.1	3133.37	10668.32	52
H13	10548.12	5250.51	10659.74	34
H14	12447.08	6242.56	10360.49	42
H15	12211.73	7552.95	9677.89	40
H16	10046.06	7861.54	9303.91	37
H17	8125.95	6887.55	9601.71	32
H2A	1100(30)	5280(30)	1698(12)	56(9)
H19	3575.94	3984.09	2472.7	47
H20	5891.35	4468.94	2485.96	59
H21	6683.7	6012.73	2010.25	73
H22	5137.06	7064.52	1508.31	73
H23	2815.53	6589.75	1478.72	58
H26A	-2348.98	2280.55	1487.52	62
H26B	-3028.28	3344.64	1754.21	62
H26C	-3027.53	2165.29	2044.38	62
H28	2612.89	1459.05	1540.92	55
H30	1390.1	2207.52	2827.53	42

H31	1296.6	2215.48	3742.33	55
H32	712.24	3845.98	4185.27	65
H33	247.4	5497.44	3726.06	67
H34	368.37	5522.75	2808.27	53
H3A	360(30)	5610(20)	6950(11)	48(8)
H36	1809.21	6986.76	6616.46	42
H37	4029.97	7646.69	6495.57	56
H38	5901.26	6709.81	6874.34	54
H39	5522.01	5107.61	7377.39	47
H40	3307.47	4412.4	7498.2	41
H43	2283.78	1969.84	6500.26	59
H45A	-3163.8	3082.97	6762.47	66
H45B	-3471.74	3122.12	7368.66	66
H45C	-3101.06	1962.18	7098.3	66
H47	436.35	5544.97	8081.39	41
H48	645.82	5264.06	8985.33	50
H49	1069.59	3462.98	9318.35	51
H50	1278.35	1939.52	8748.05	52
H51	1056.56	2205.13	7845.36	42
H4A	8220(20)	5170(20)	5643(10)	37(6)
H53	8203.7	7224.65	4651.8	42
H54	10127.66	8212.41	4368.48	49
H55	12280.27	7899.49	4751.92	57
H56	12486.89	6612.75	5444.73	58
H57	10591.49	5585.84	5718.82	46
H60	5754.51	8685.96	5663.77	51
H62A	2733.59	4310.03	5756.04	58
H62B	3789.04	4384.47	6230.16	58
H62C	4004.44	3479.77	5783.33	58
H64	7845.57	4678.73	4486.49	46
H65	7151.25	4477.04	3603.63	67
H66	5088.81	5245.52	3309.5	72
H67	3713.99	6259.13	3876.54	63
H68	4445.64	6572.31	4735.65	46

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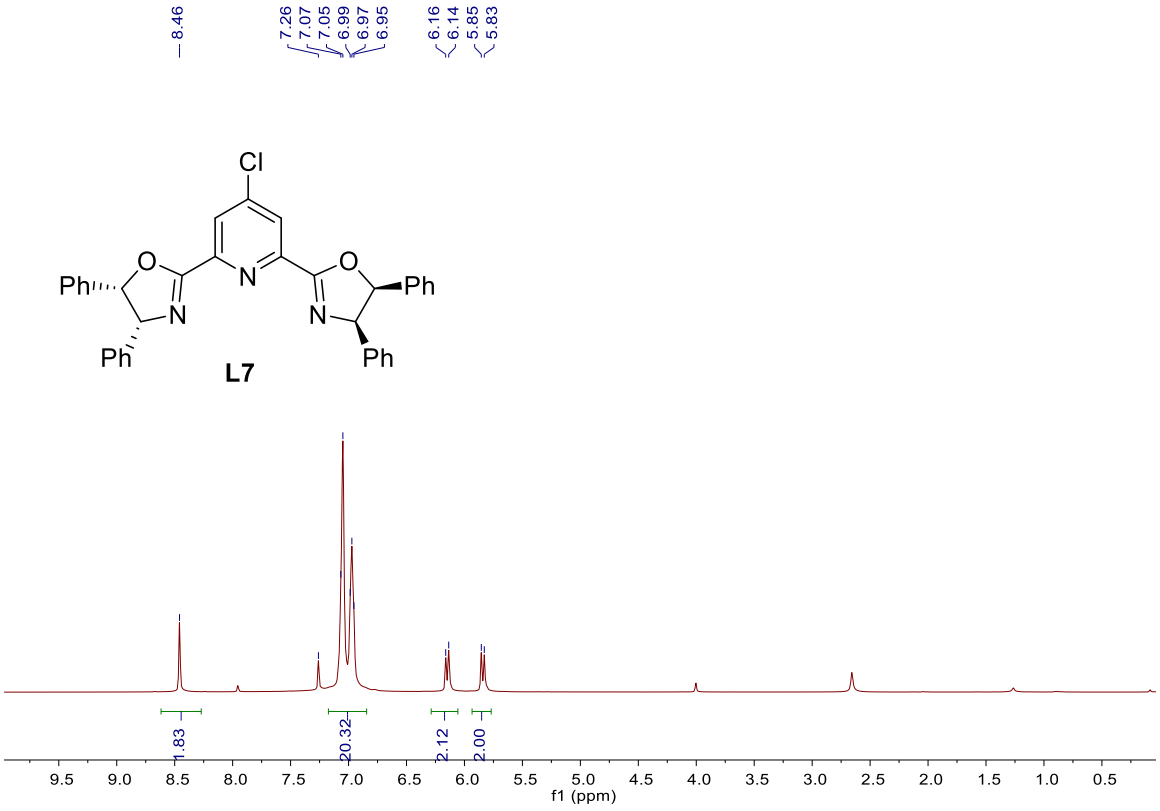
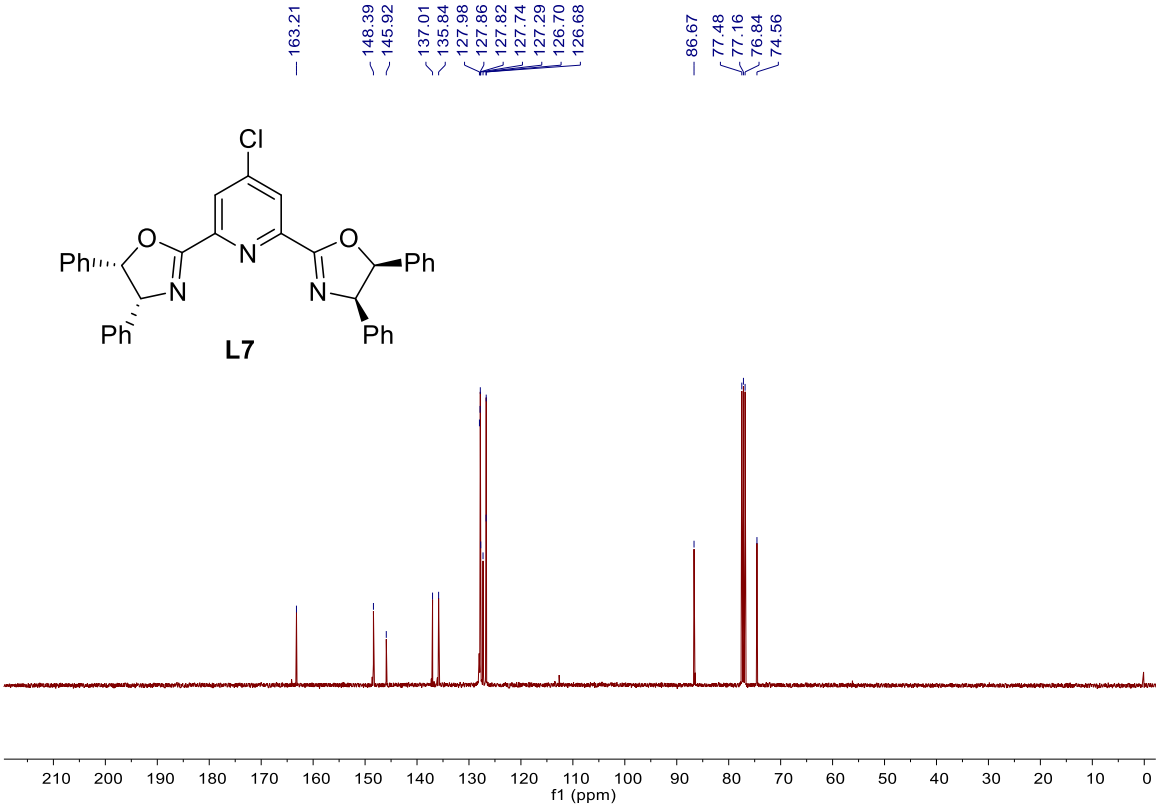
NMR spectra

^{1}H NMR spectrum ($CDCl_3$)



^{13}C NMR spectrum ($CDCl_3$)



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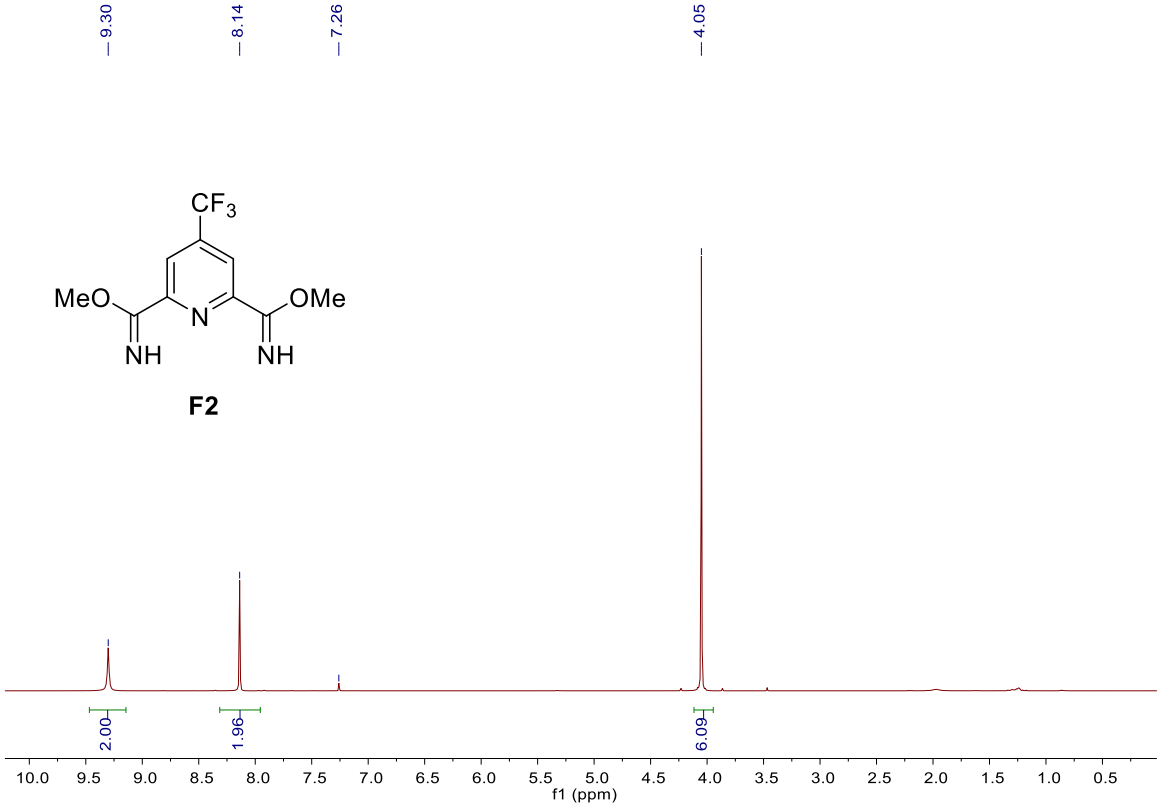

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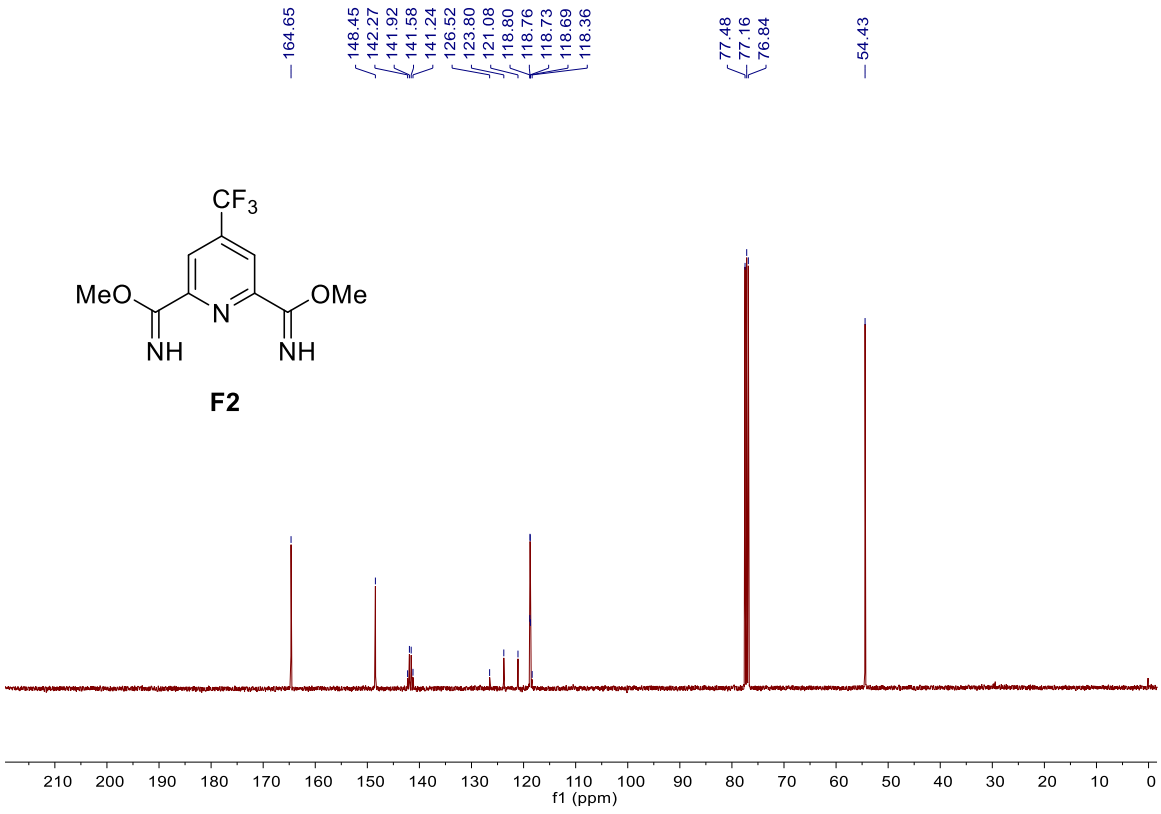
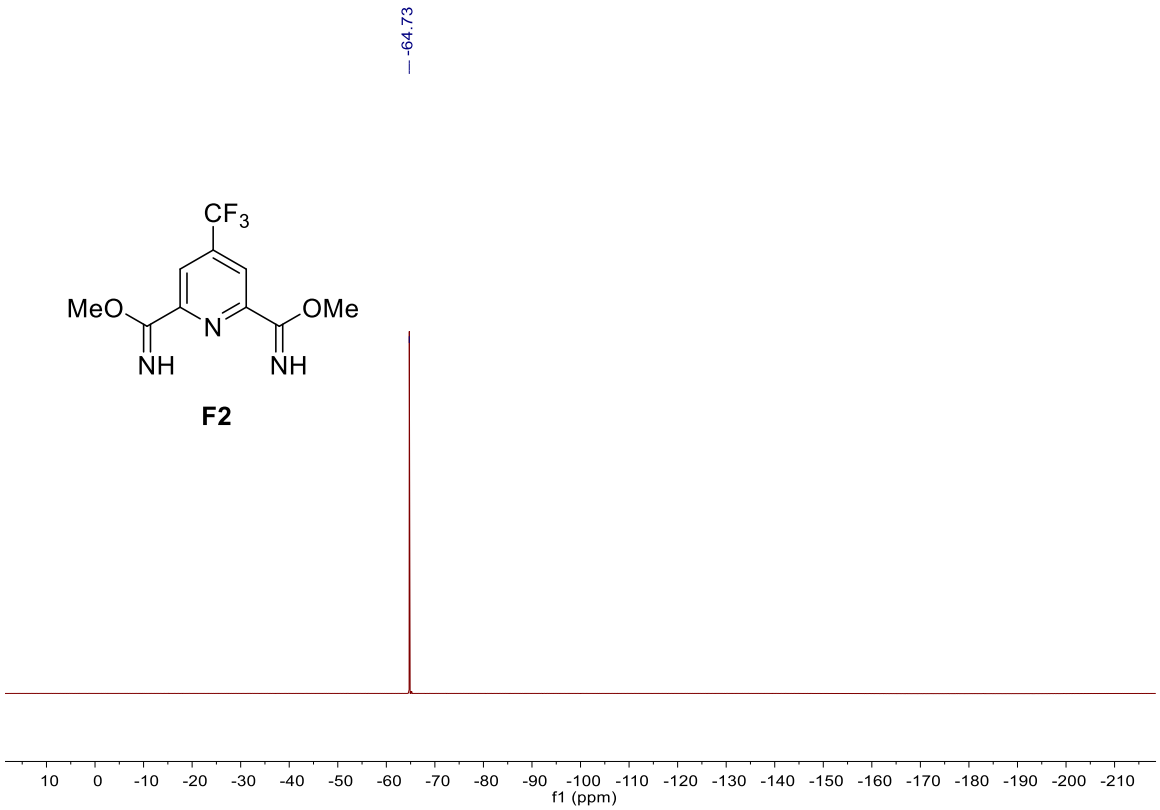


^{19}F NMR spectrum ($CDCl_3$)



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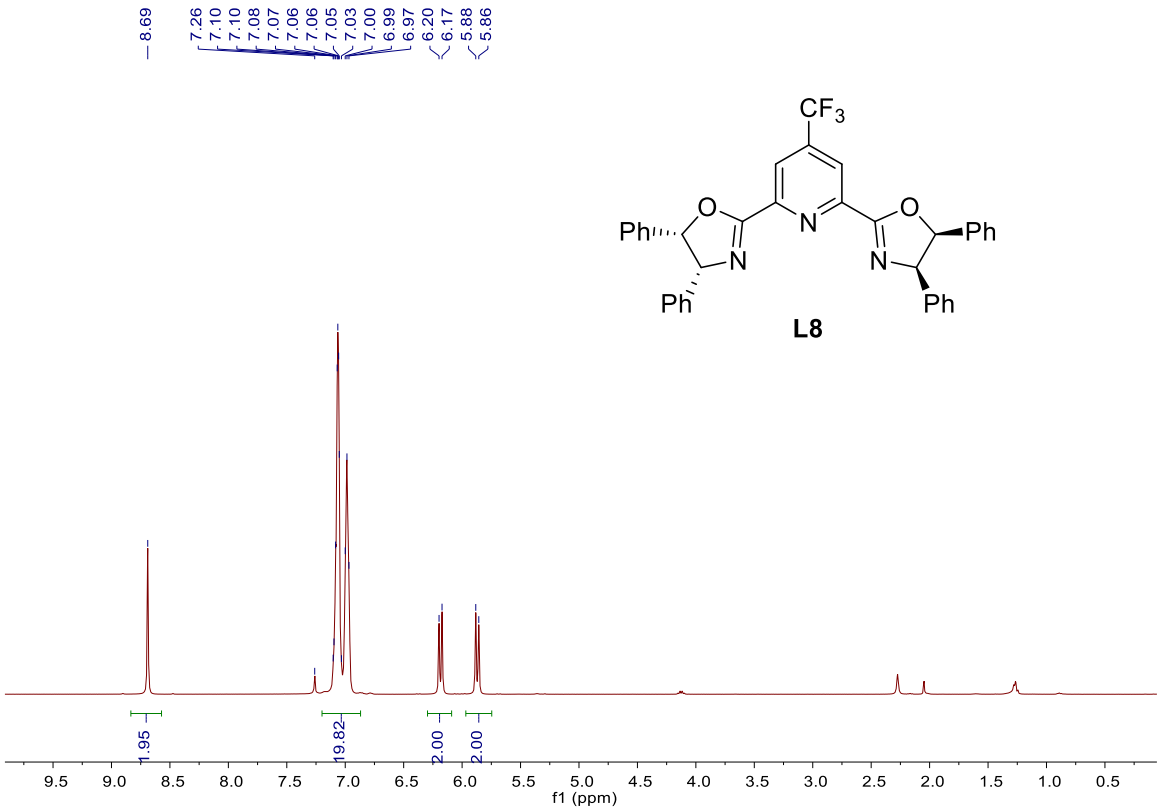

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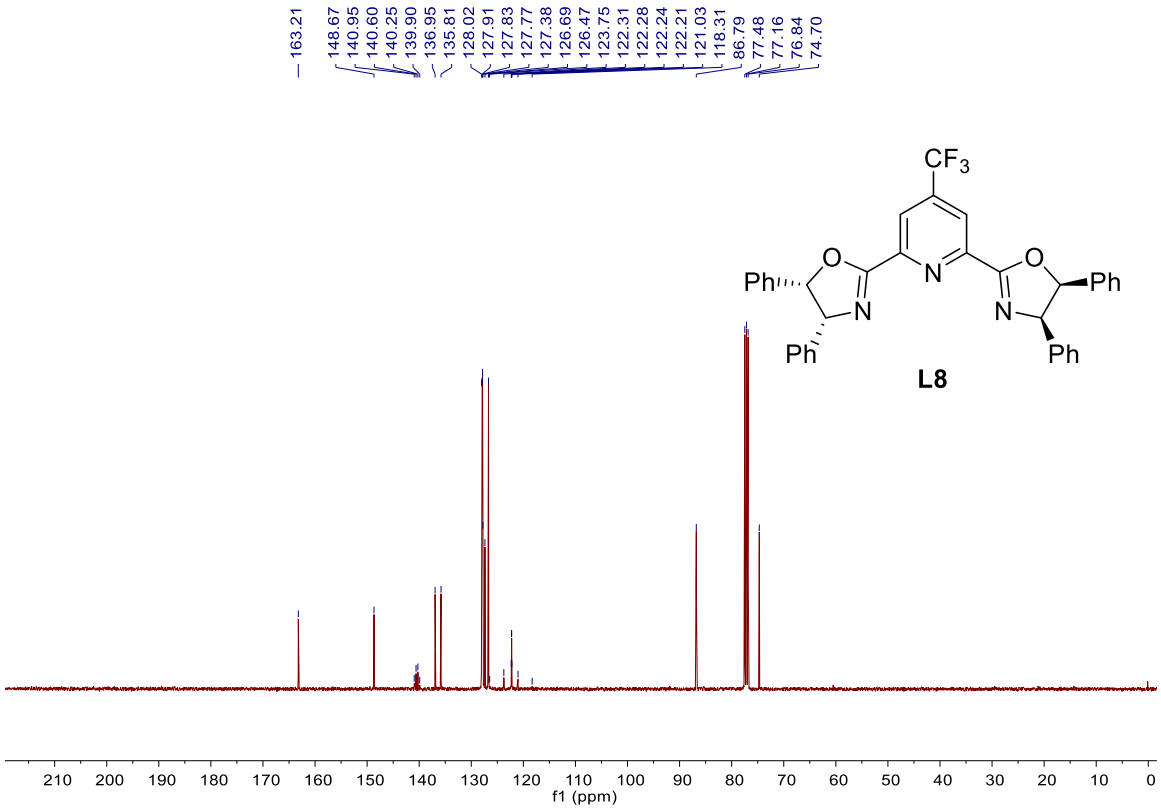

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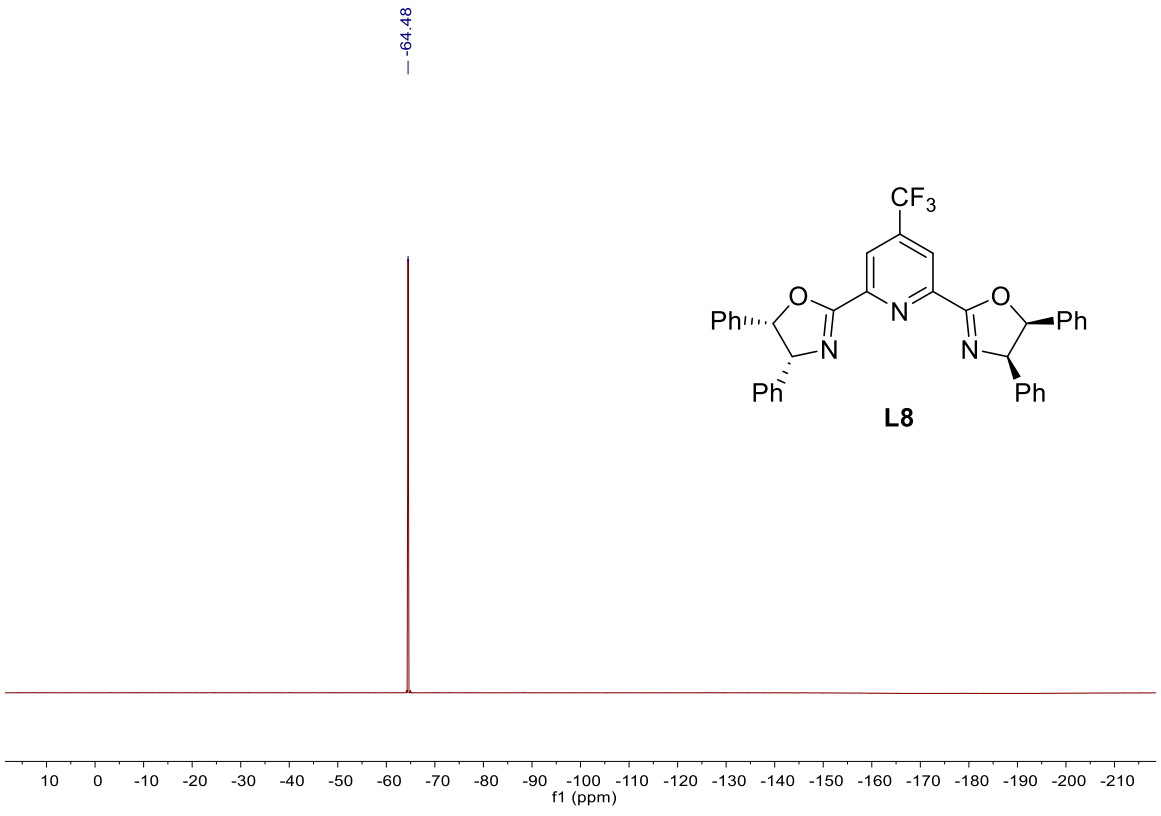

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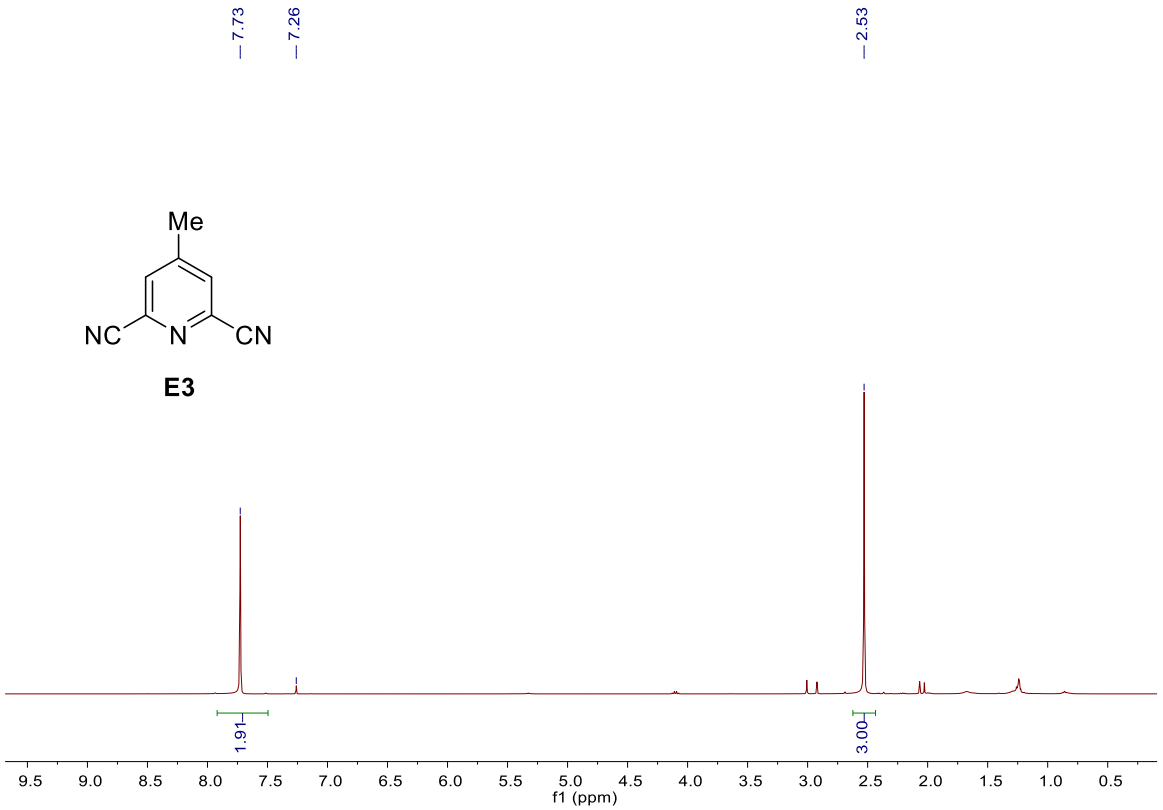

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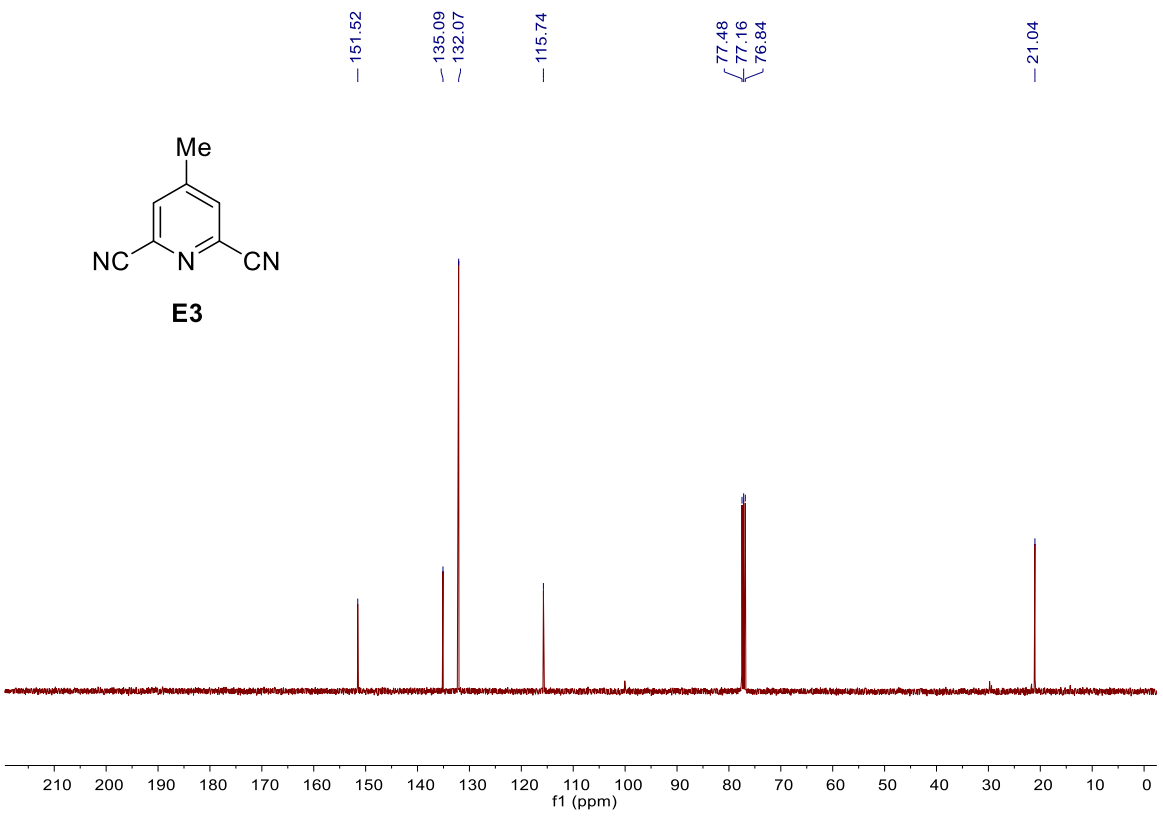

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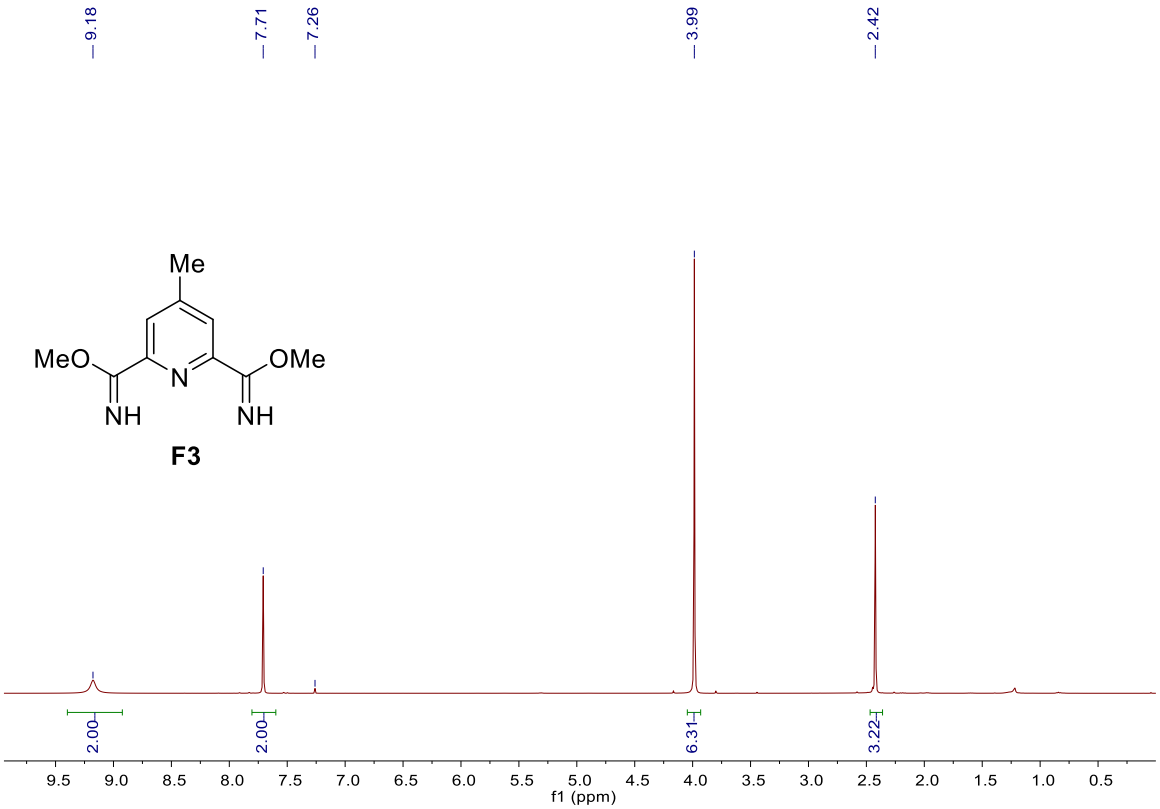

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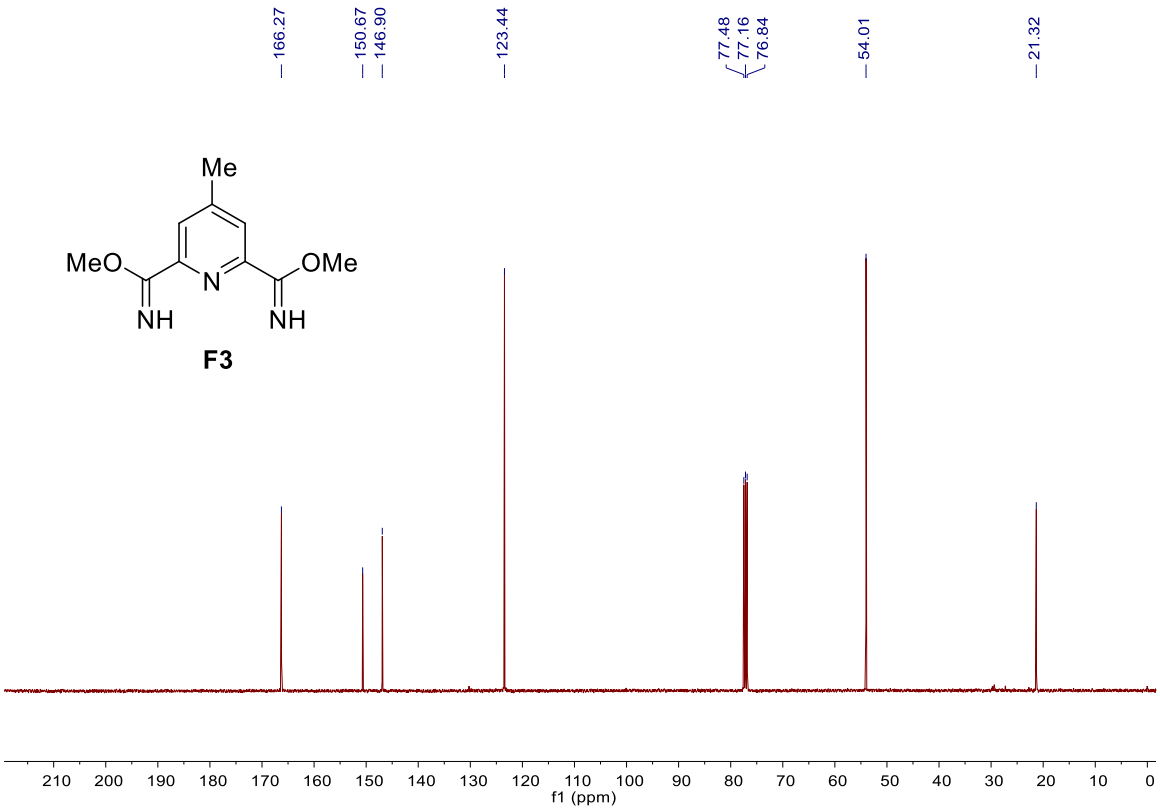

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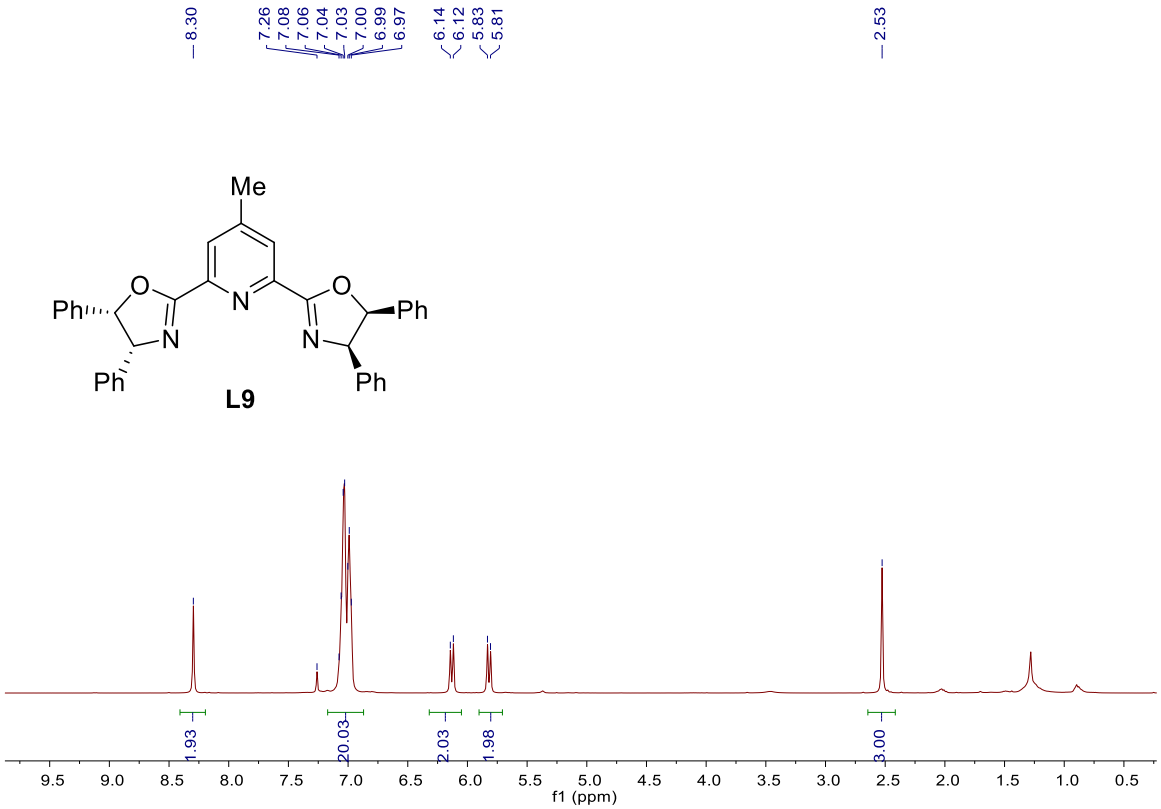

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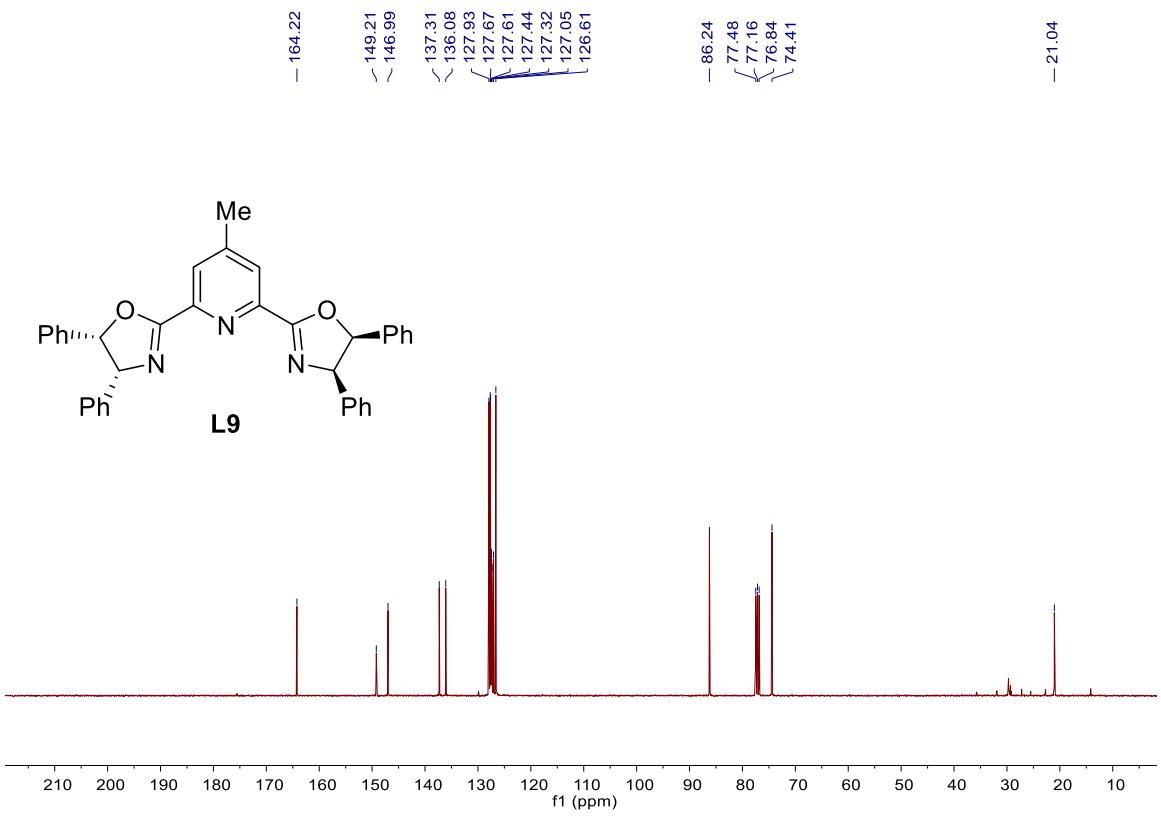

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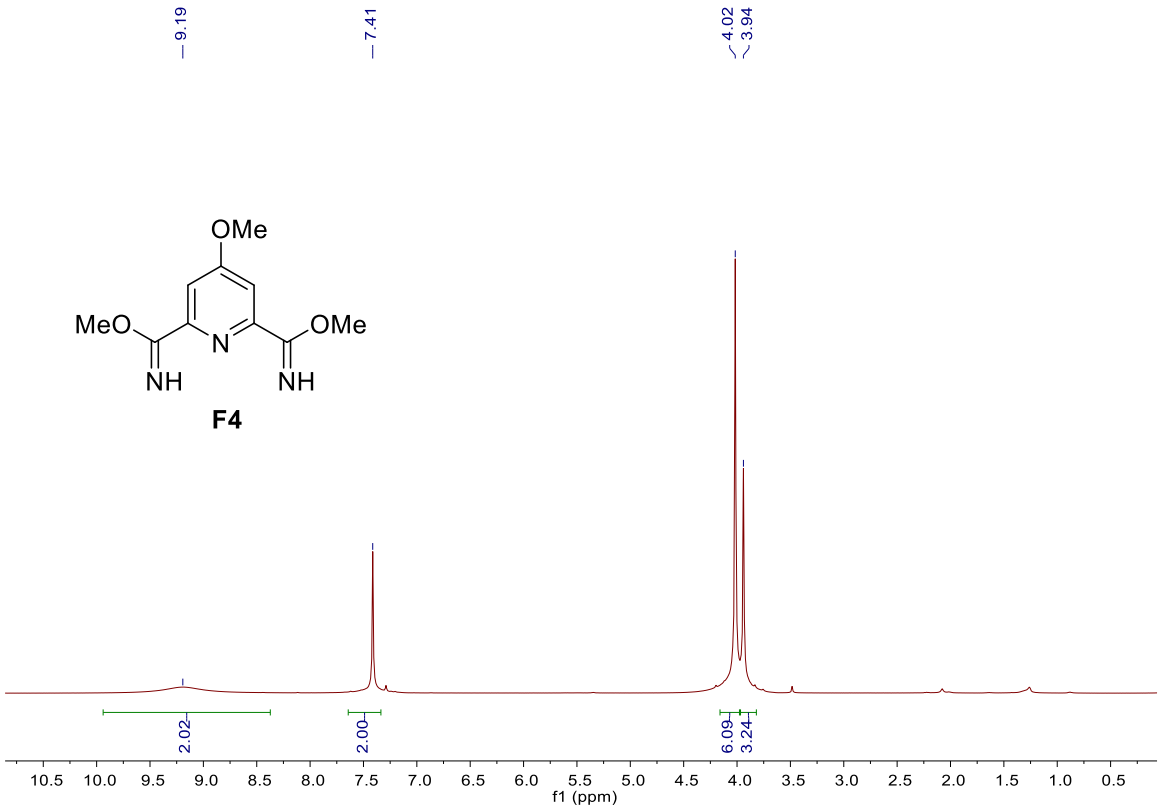
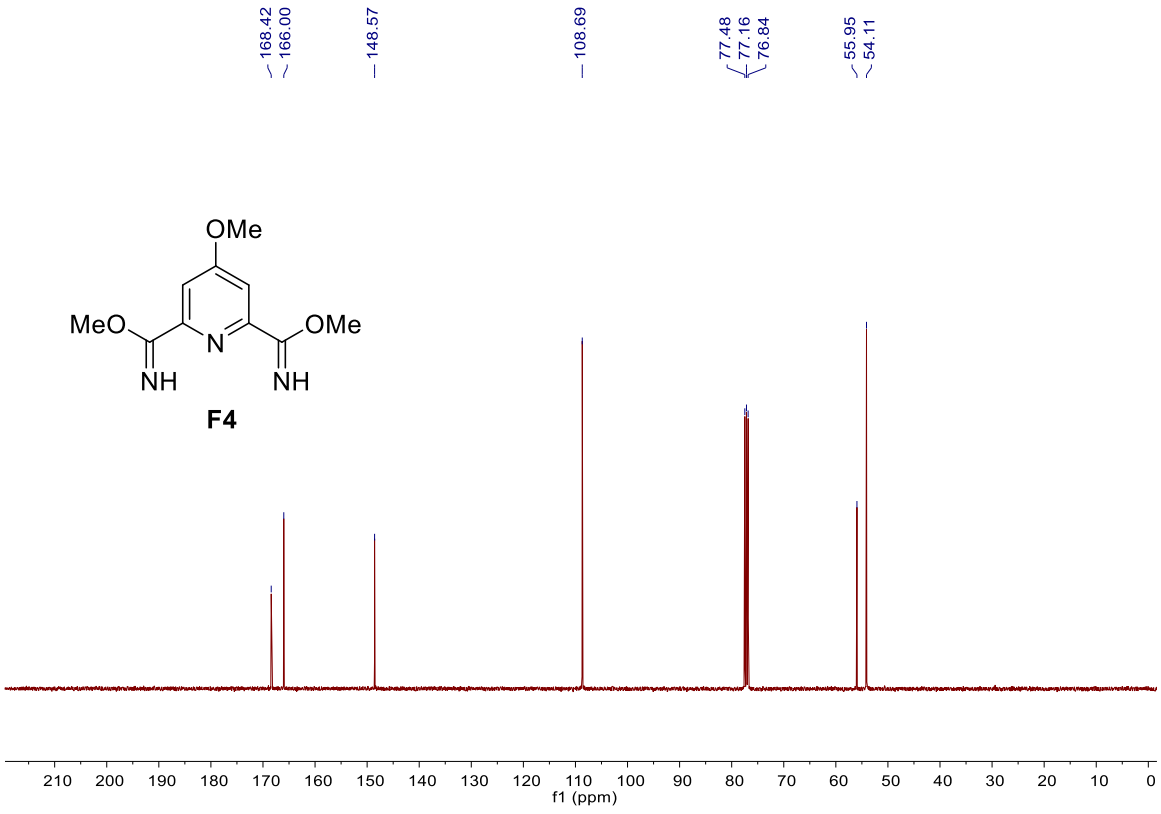
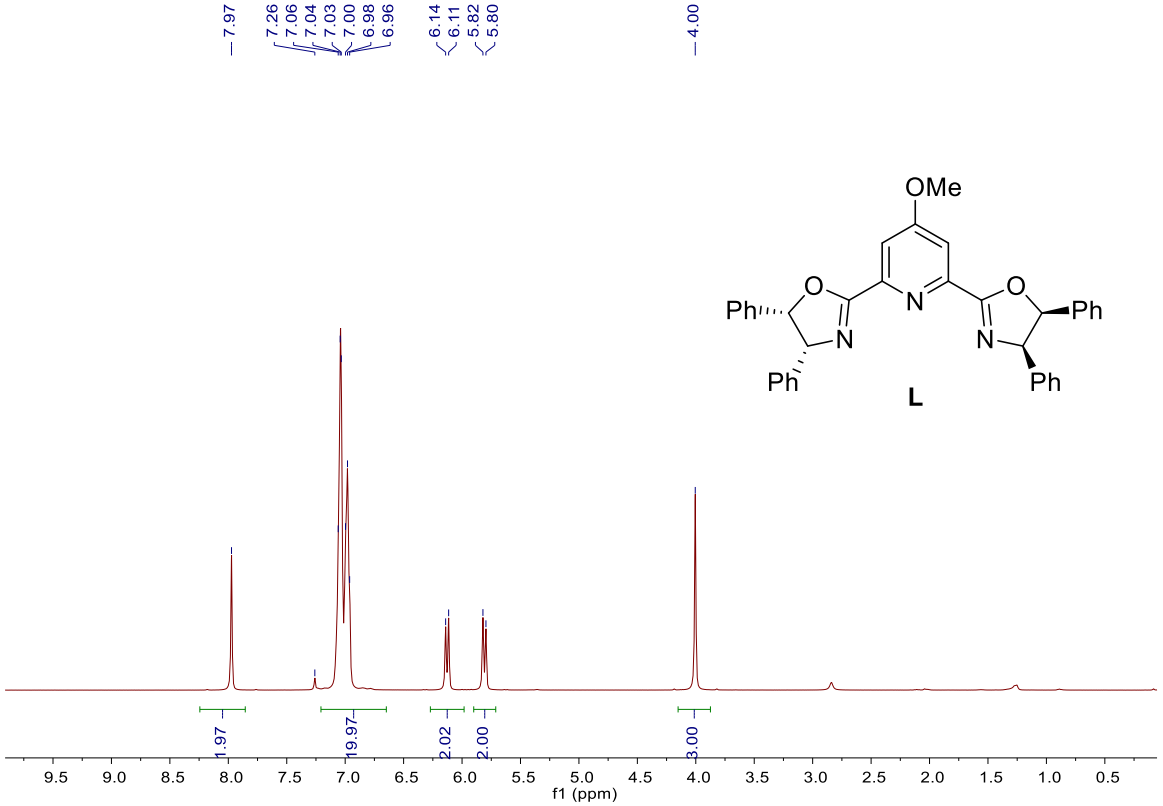


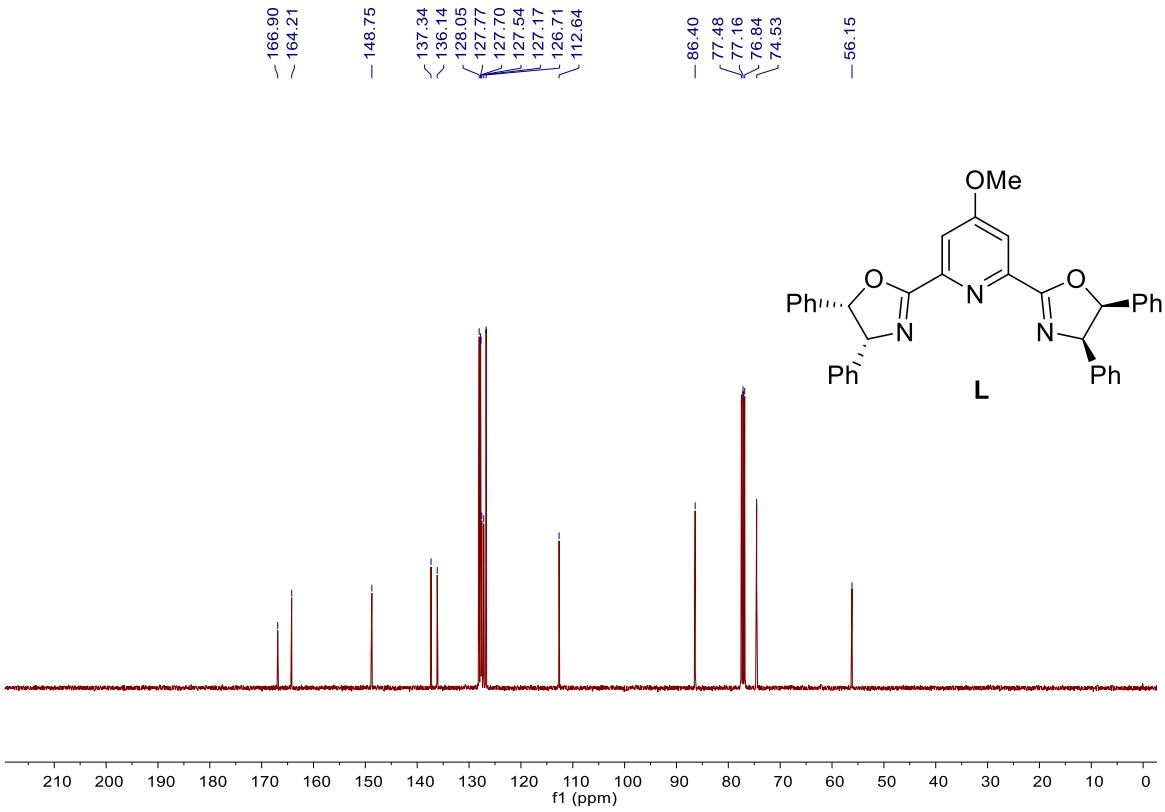
^{13}C NMR spectrum ($CDCl_3$)



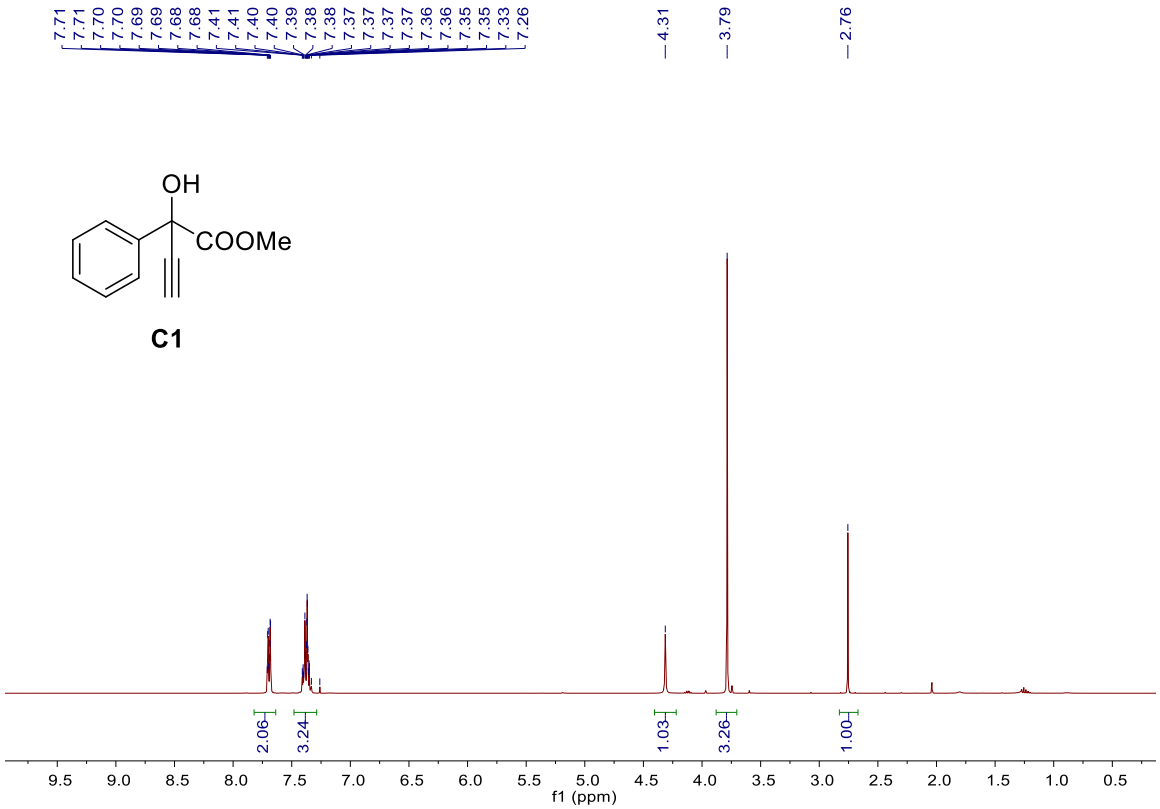
^{1}H NMR spectrum ($CDCl_3$)



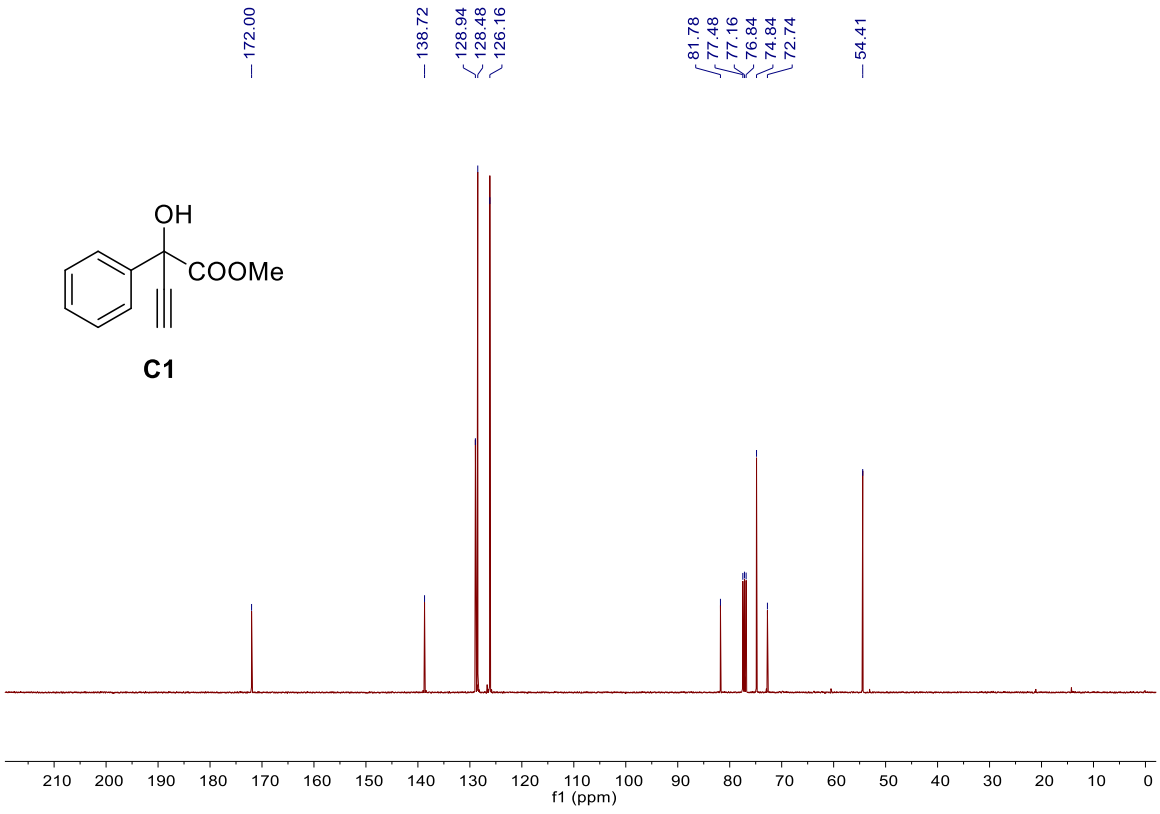
^{13}C NMR spectrum ($CDCl_3$)



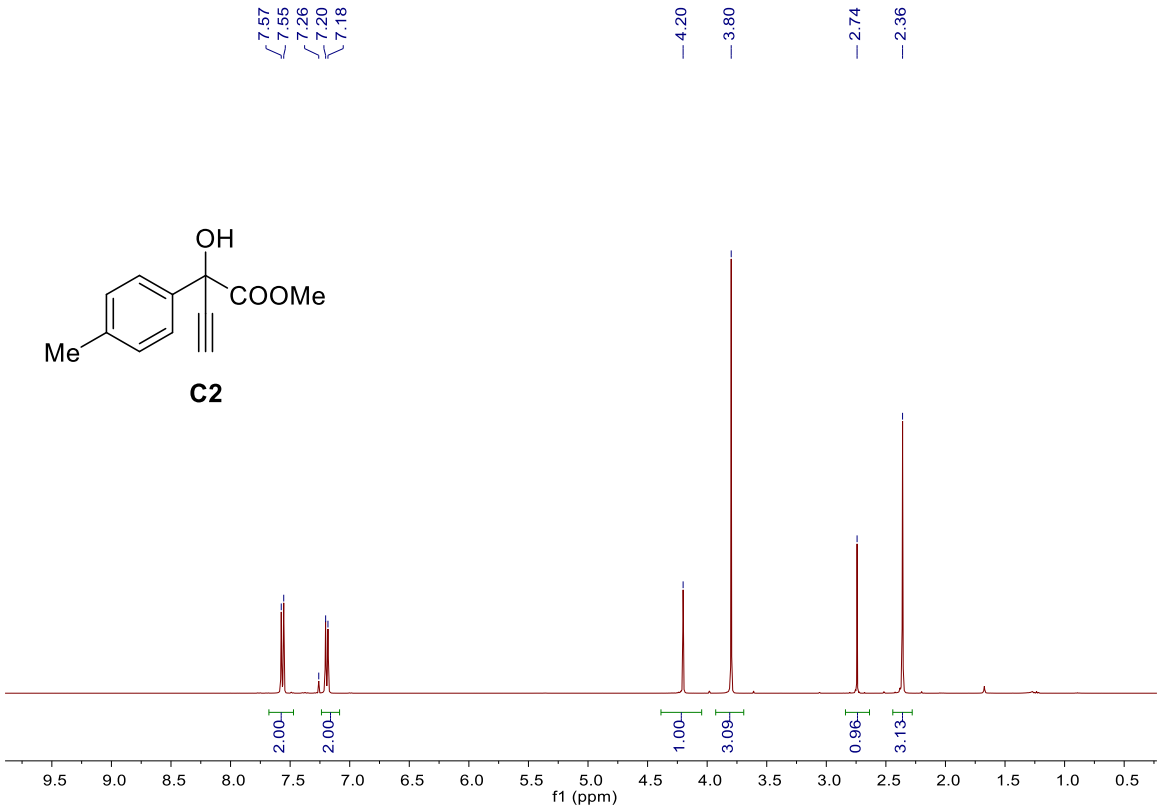
^{1}H NMR spectrum ($CDCl_3$)



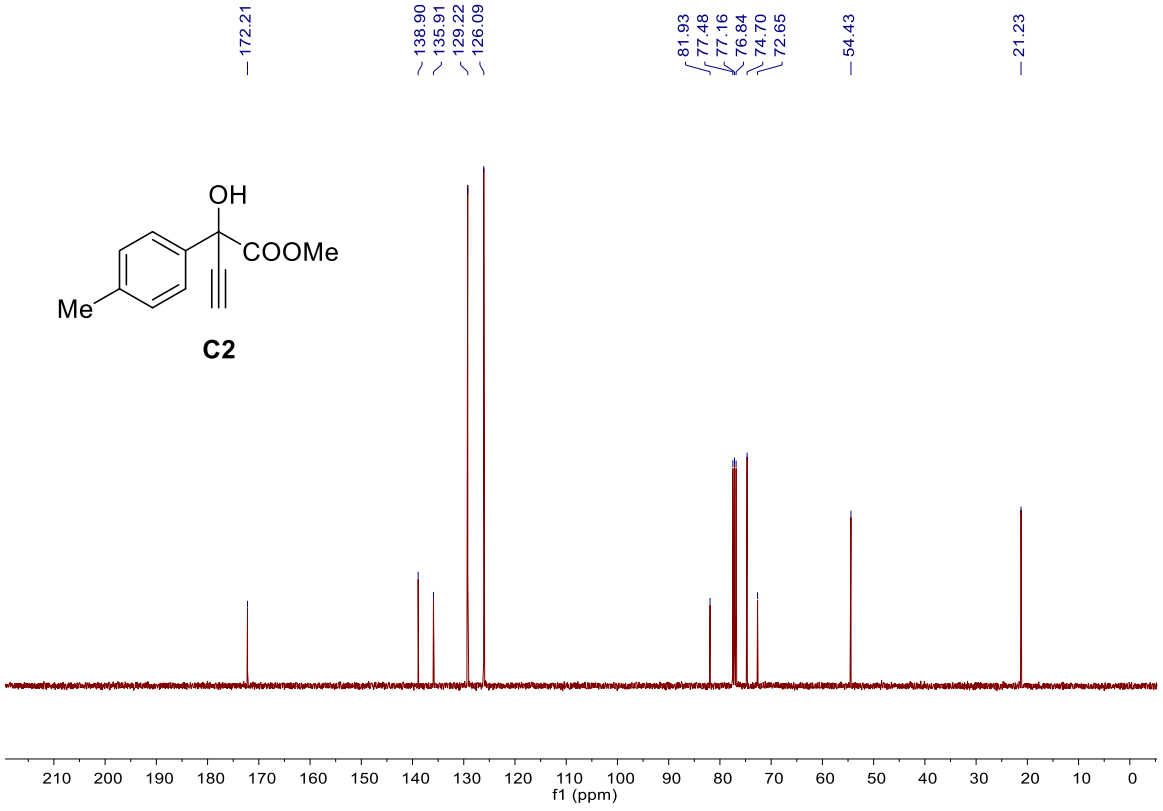
^{13}C NMR spectrum ($CDCl_3$)



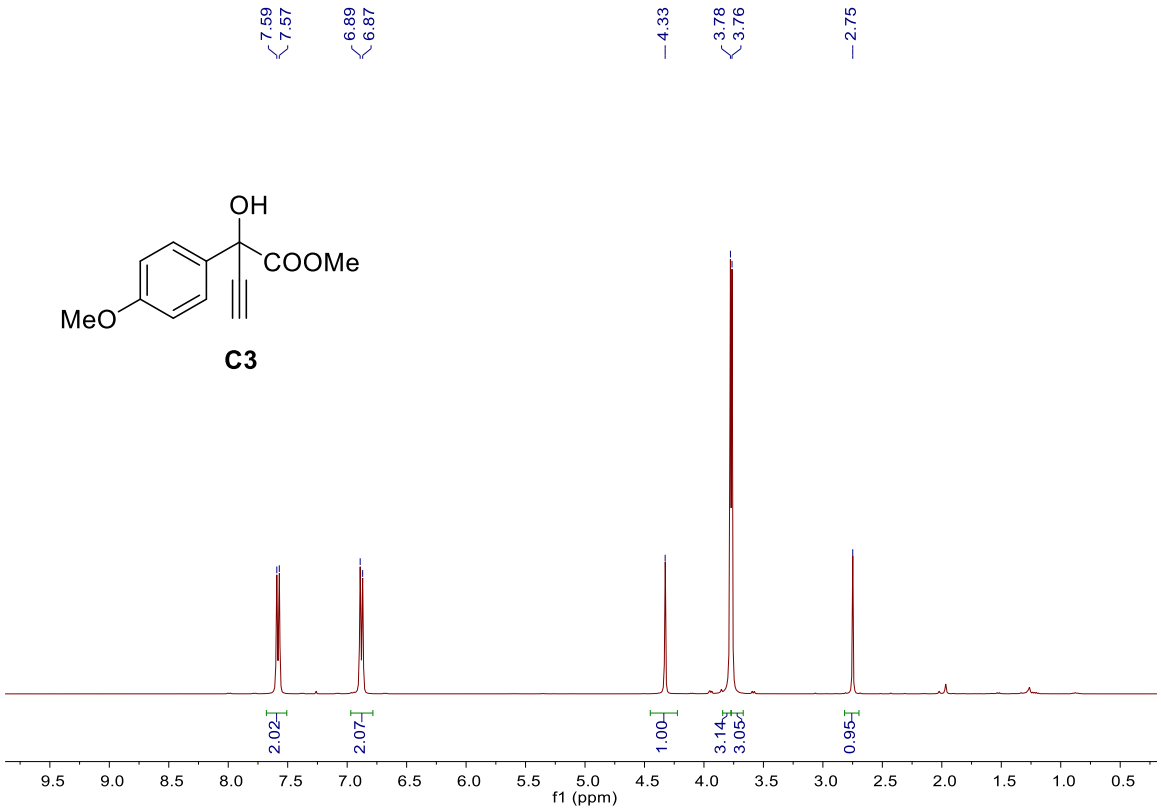
^{1}H NMR spectrum ($CDCl_3$)



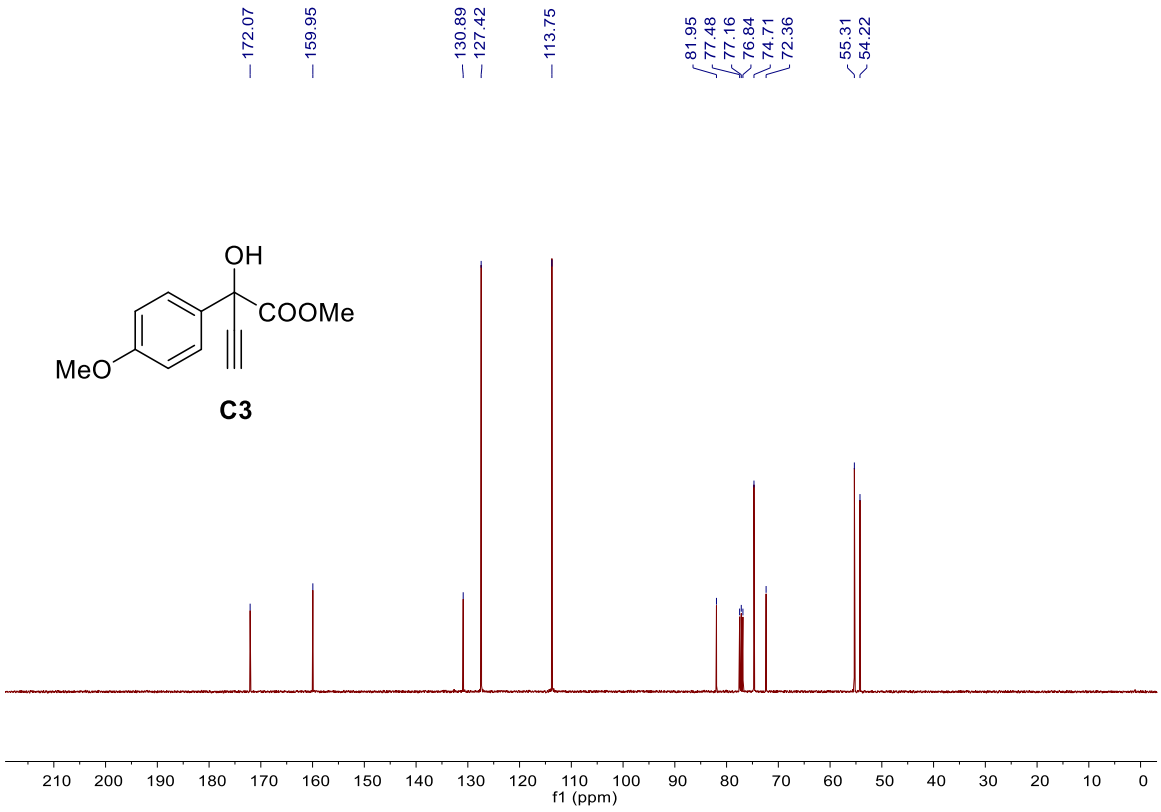
^{13}C NMR spectrum ($CDCl_3$)



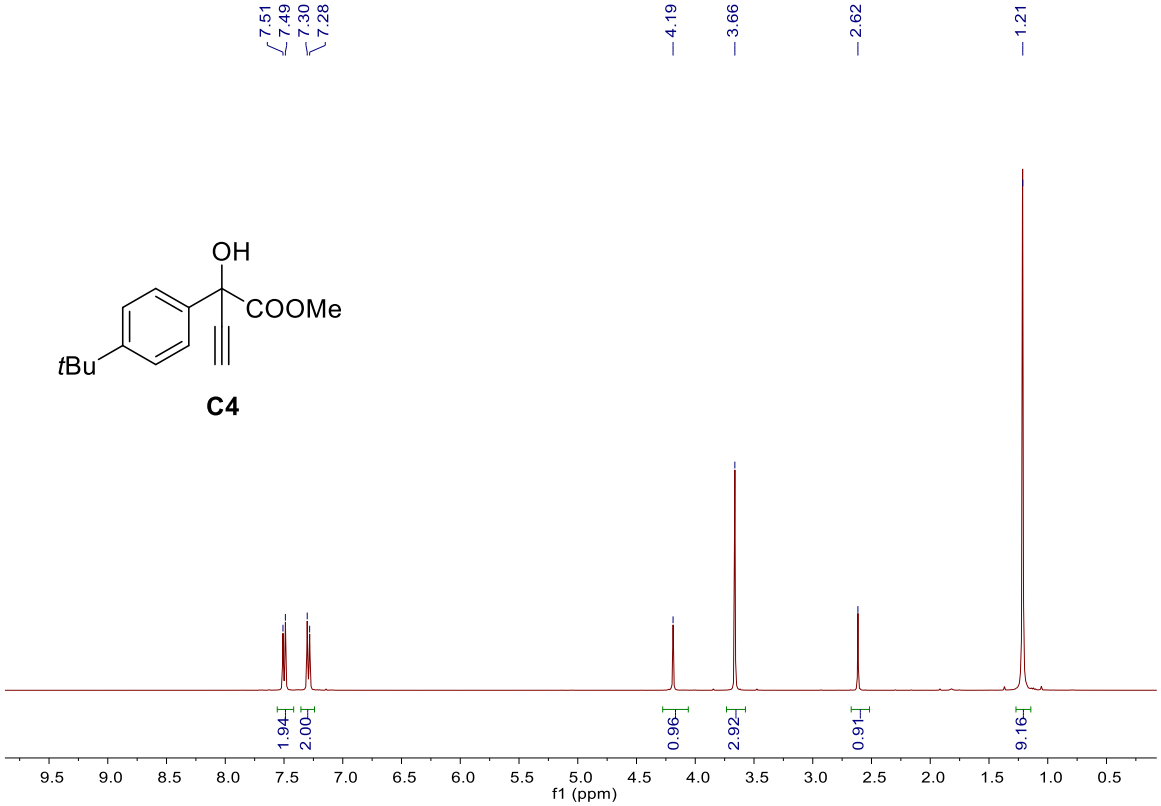
^{1}H NMR spectrum ($CDCl_3$)



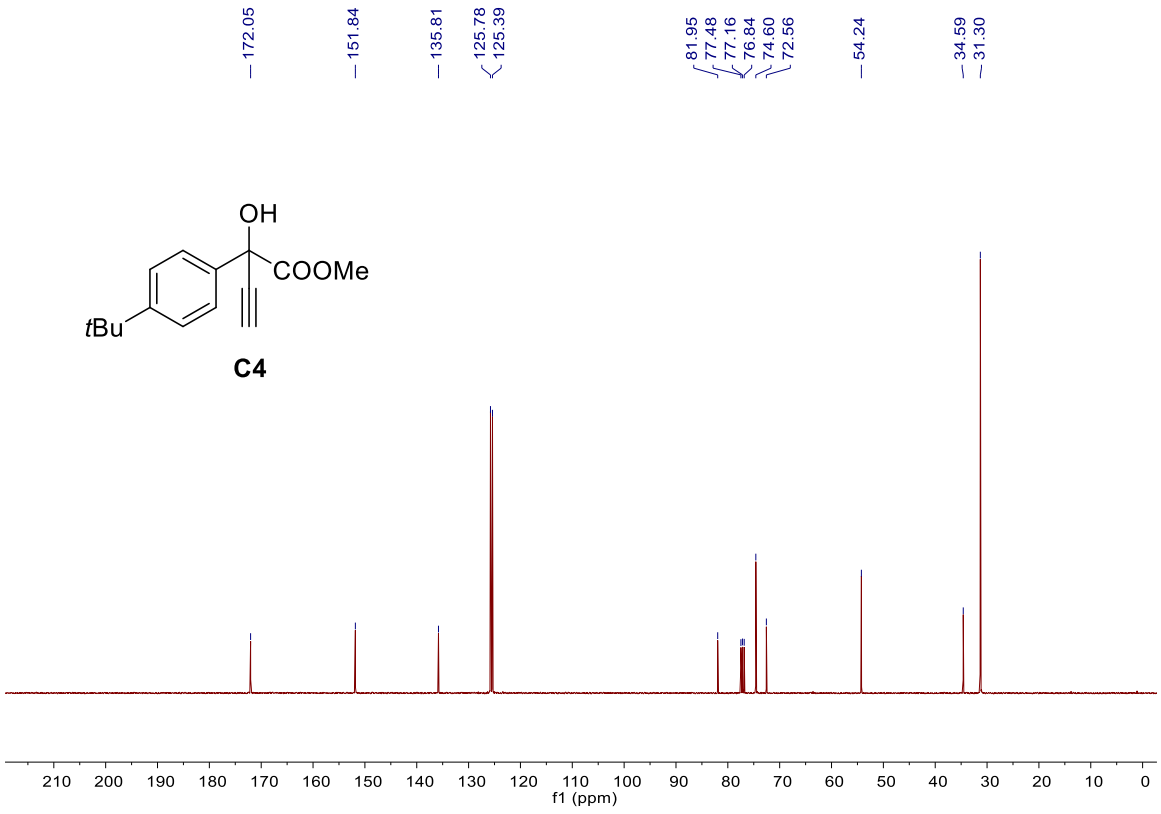
^{13}C NMR spectrum ($CDCl_3$)



^{1}H NMR spectrum ($CDCl_3$)



^{13}C NMR spectrum ($CDCl_3$)



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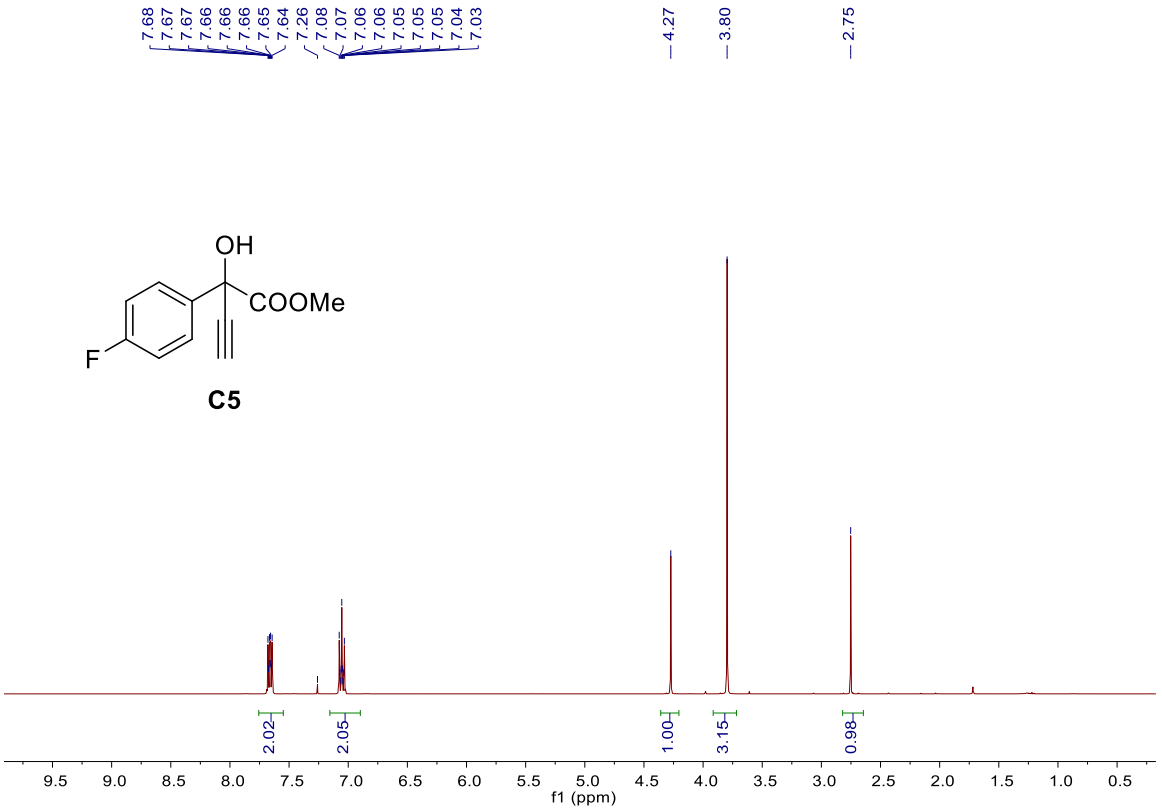
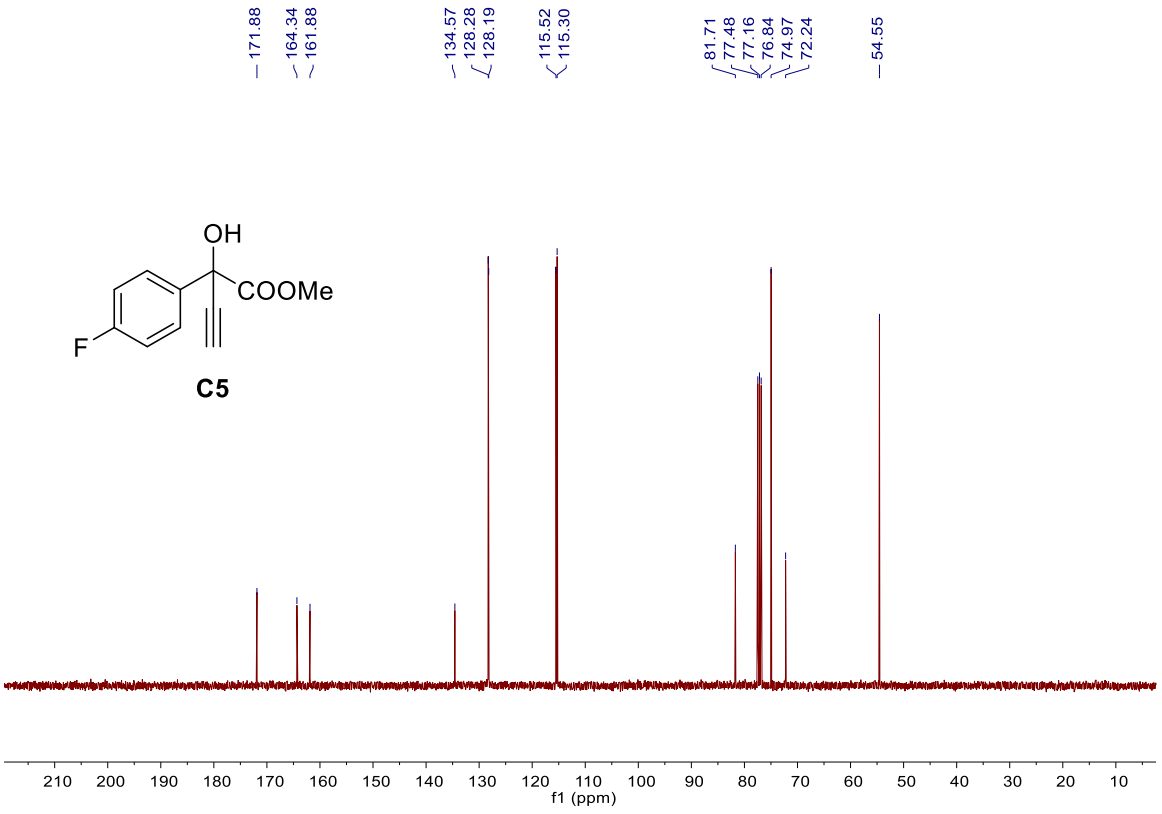
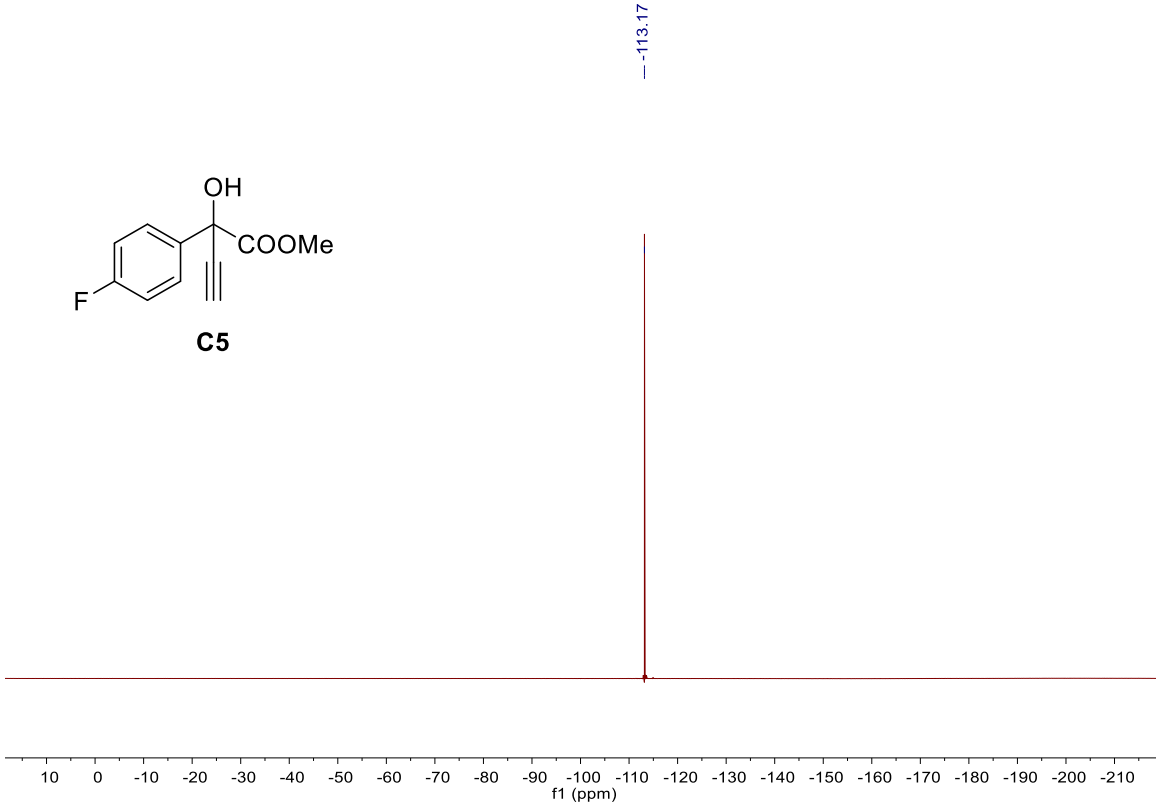


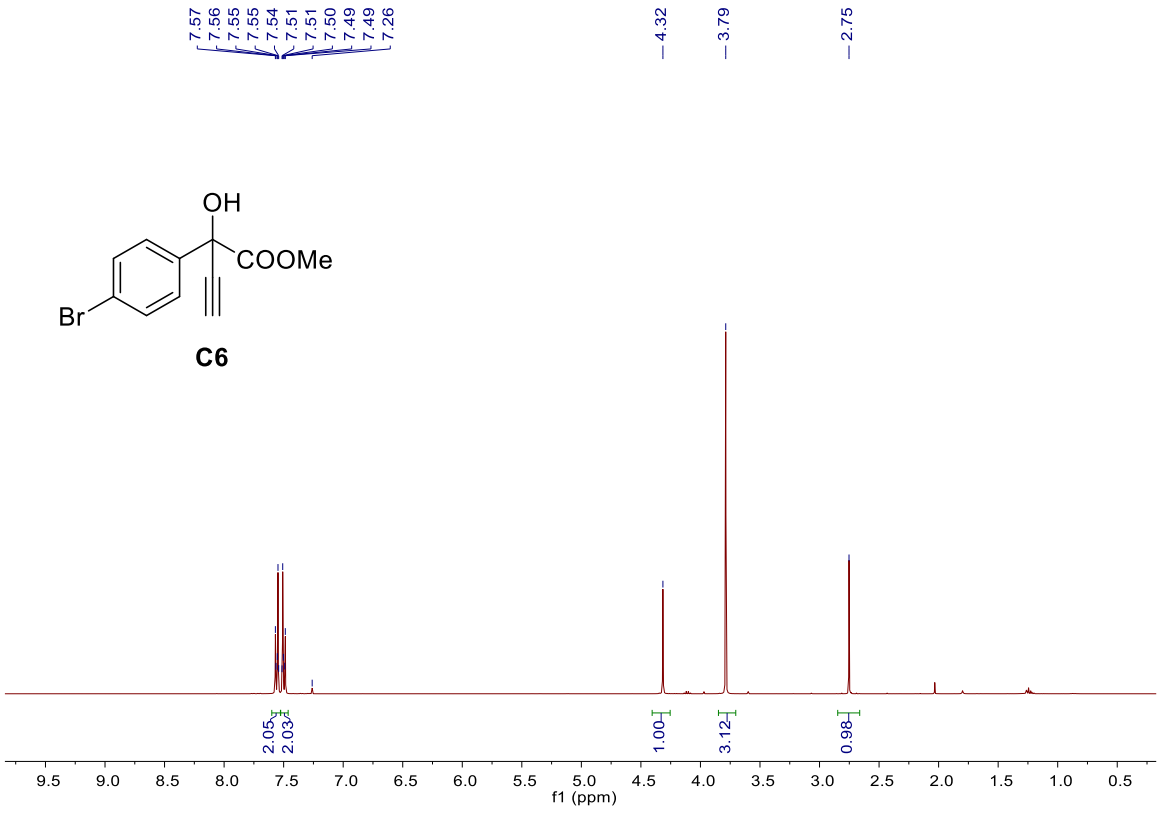
^{13}C NMR spectrum ($CDCl_3$)



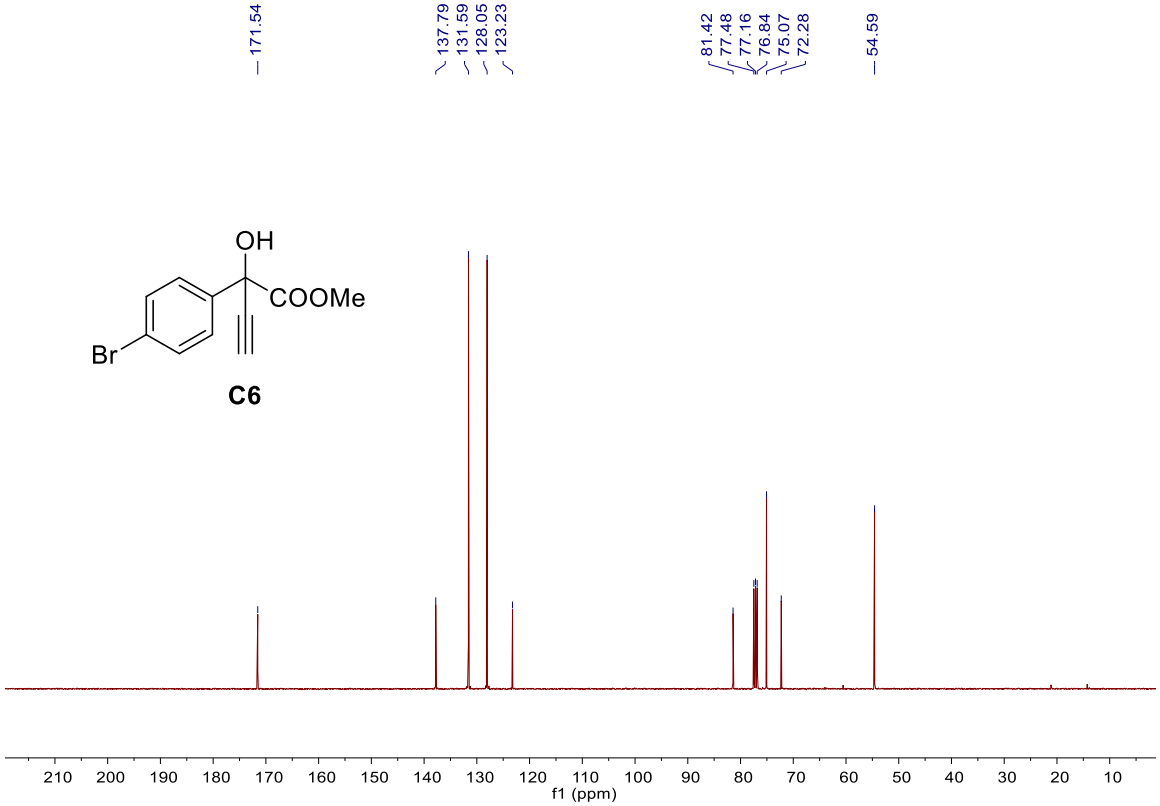
^{19}F NMR spectrum ($CDCl_3$)



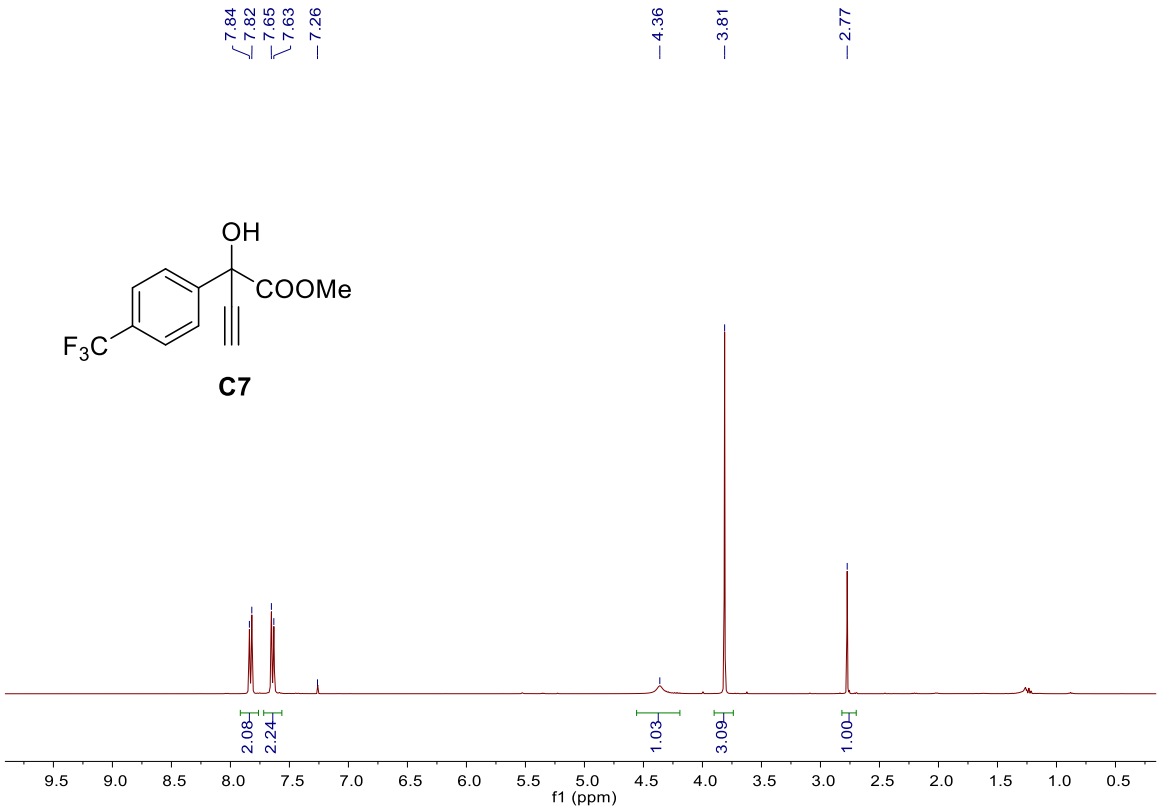
^{1}H NMR spectrum ($CDCl_3$)



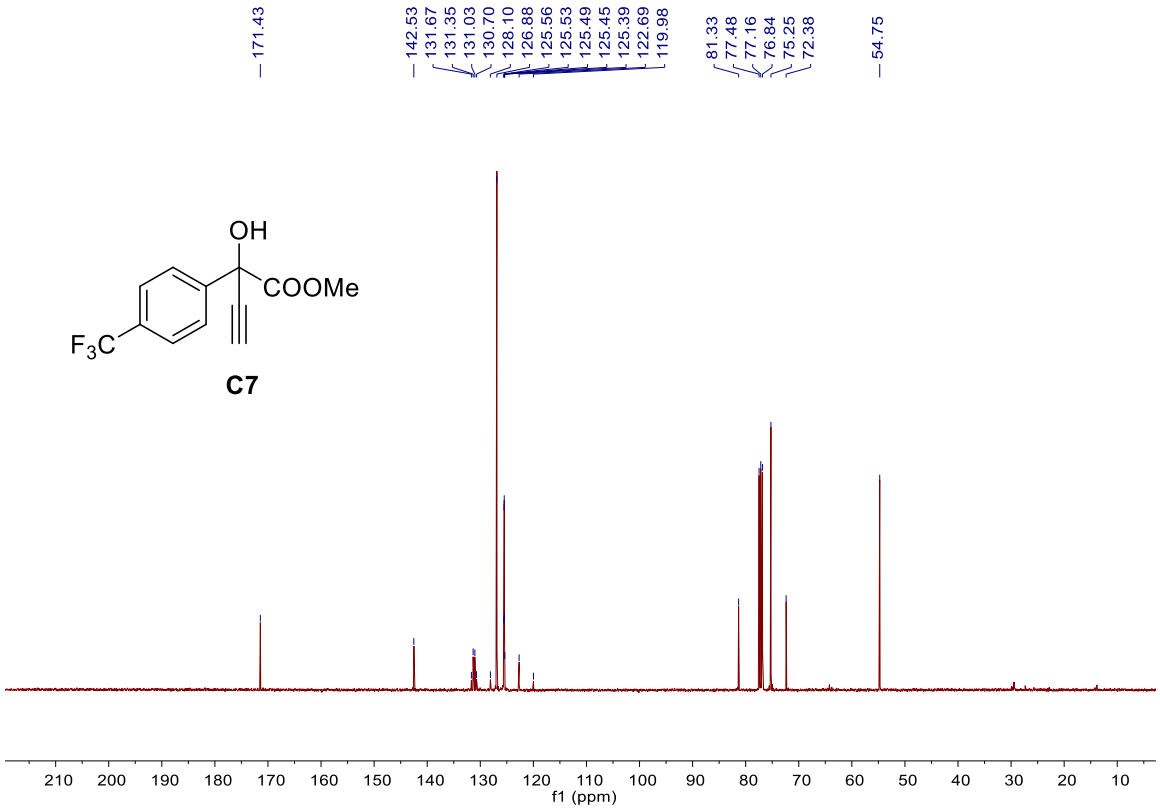
^{13}C NMR spectrum ($CDCl_3$)



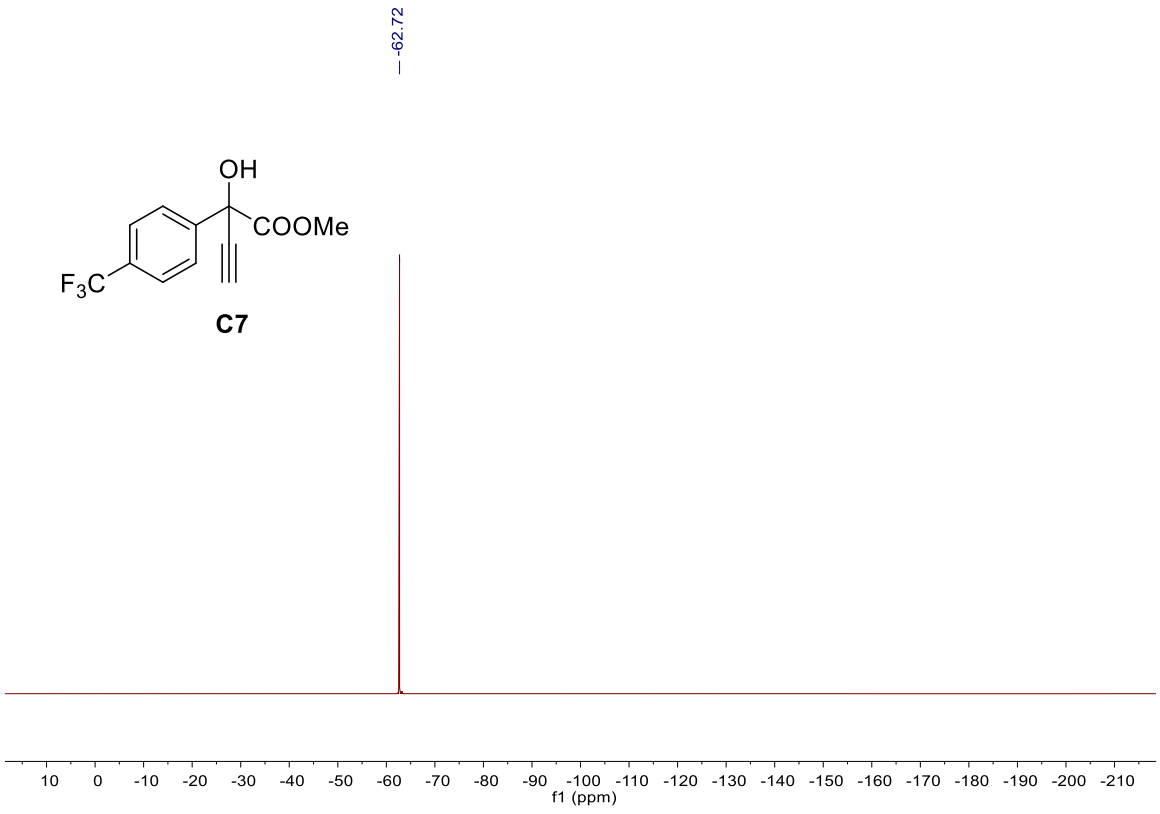
^{1}H NMR spectrum ($CDCl_3$)



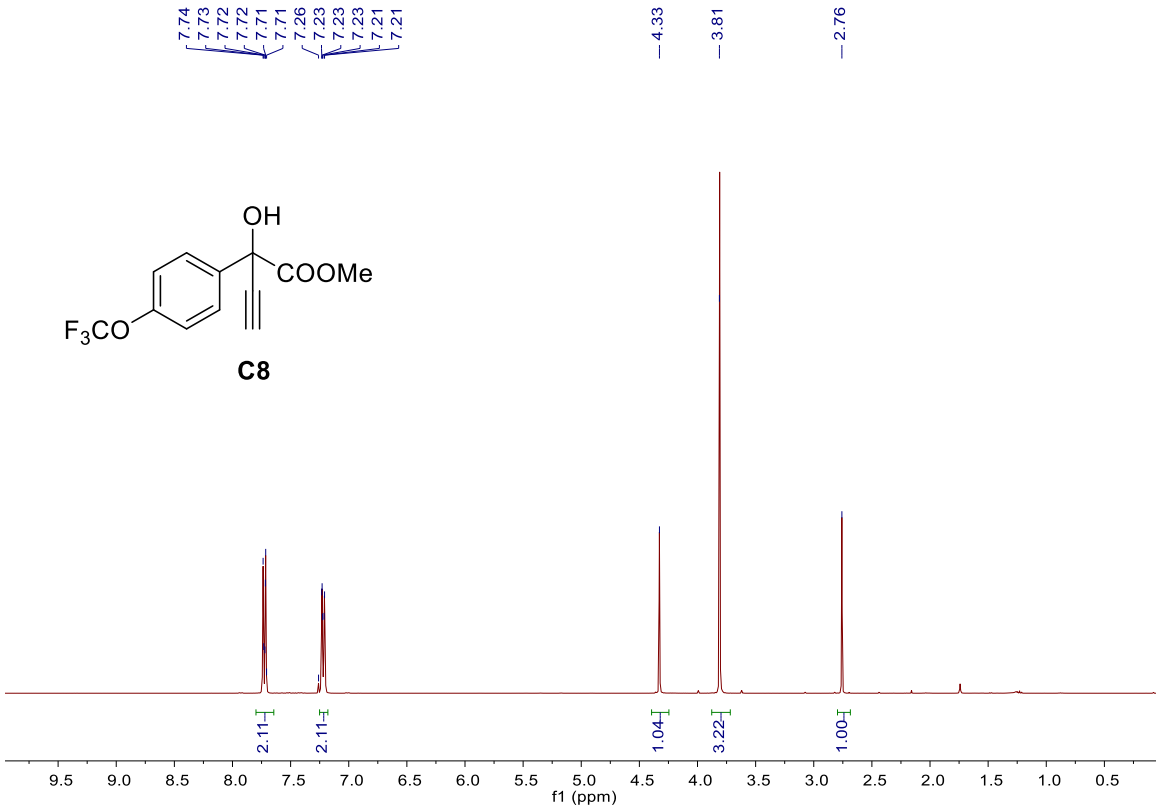
^{13}C NMR spectrum ($CDCl_3$)



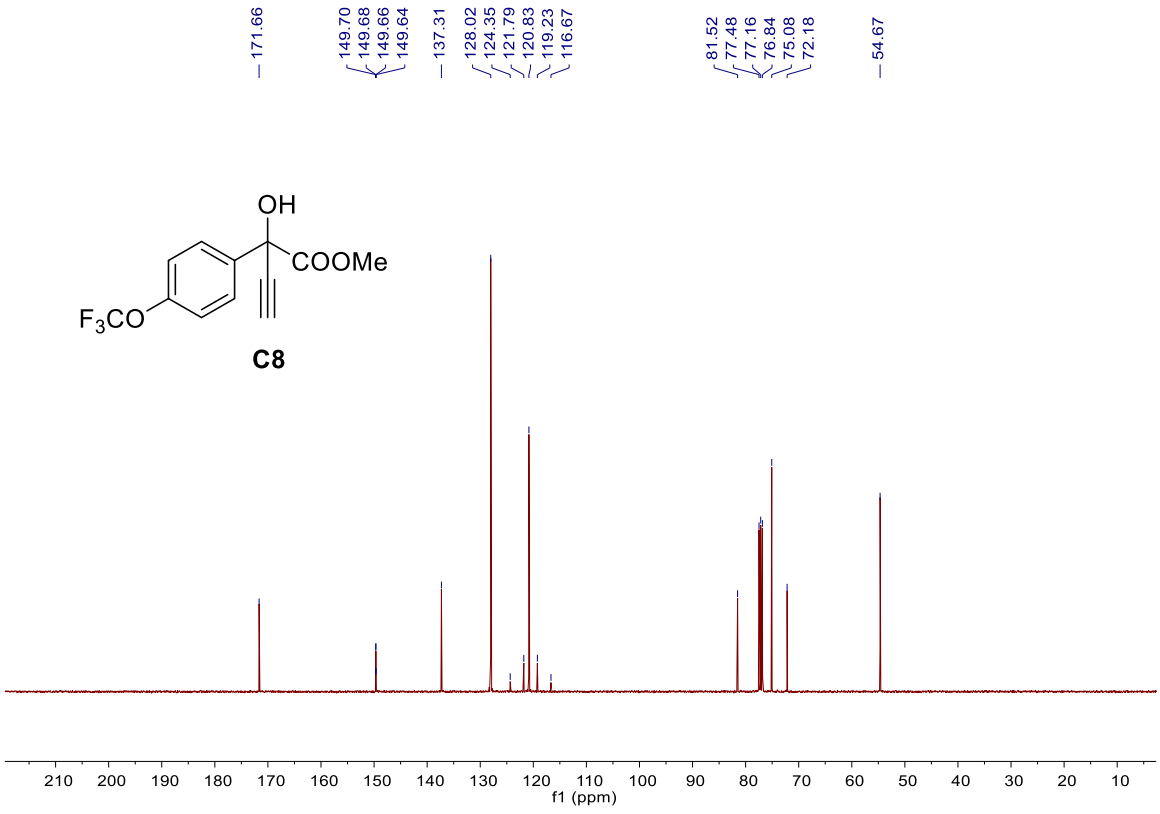
^{19}F NMR spectrum ($CDCl_3$)



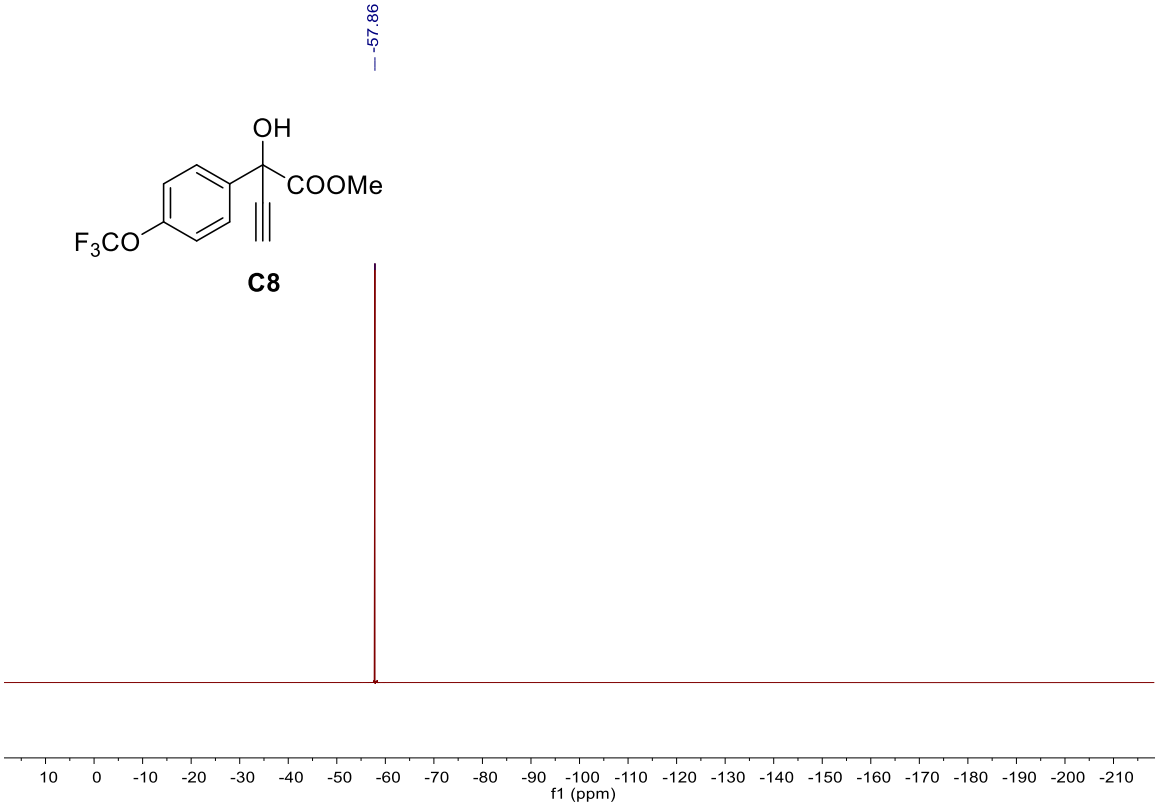
^{1}H NMR spectrum ($CDCl_3$)



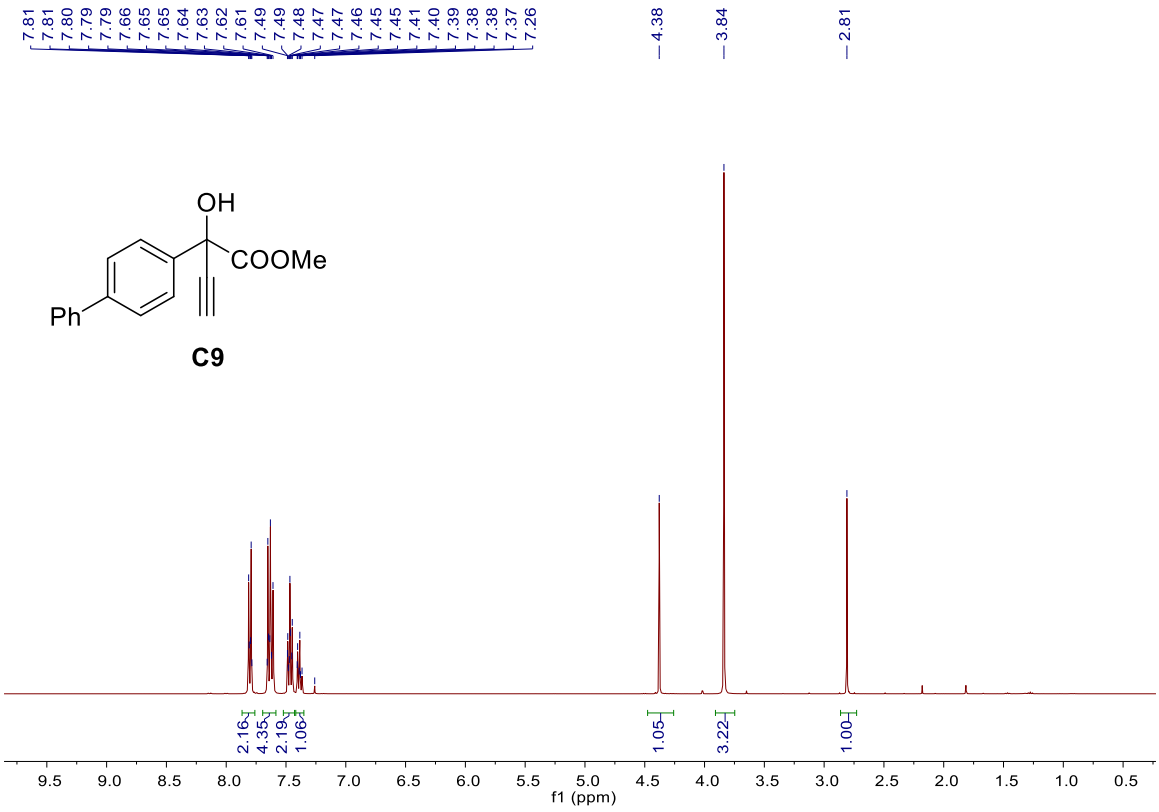
^{13}C NMR spectrum ($CDCl_3$)



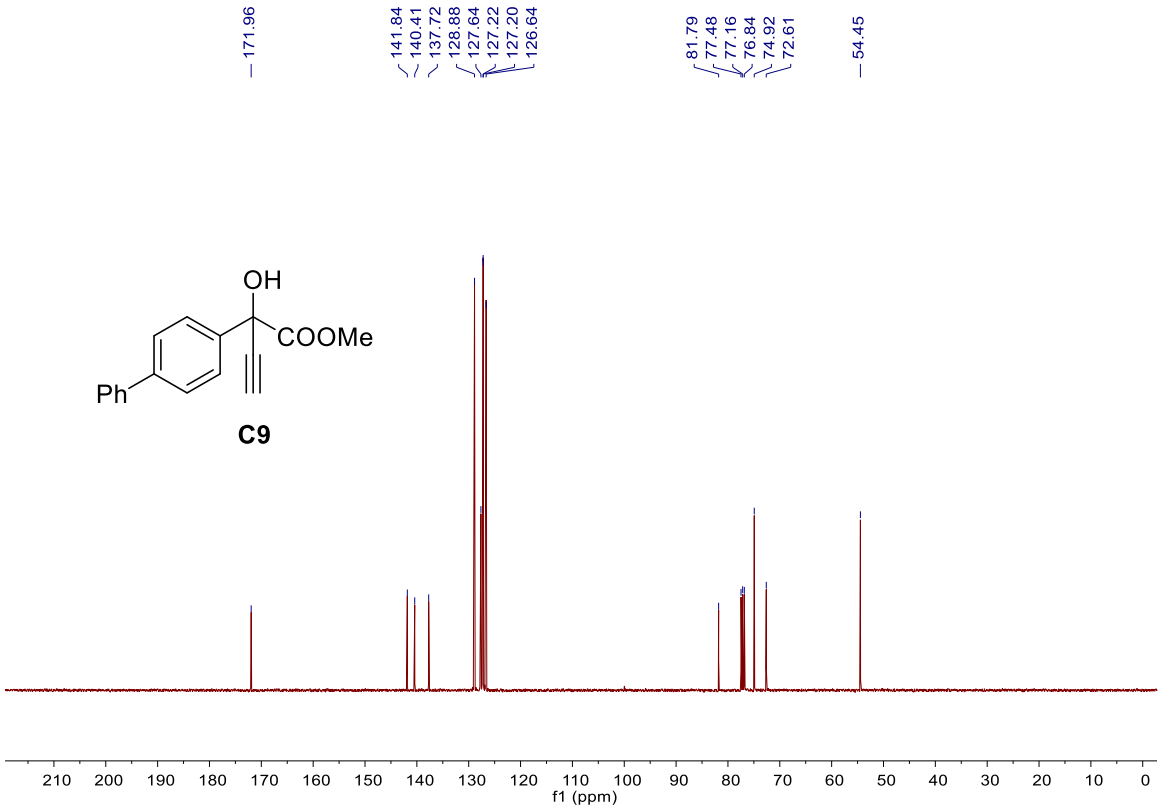
^{19}F NMR spectrum ($CDCl_3$)



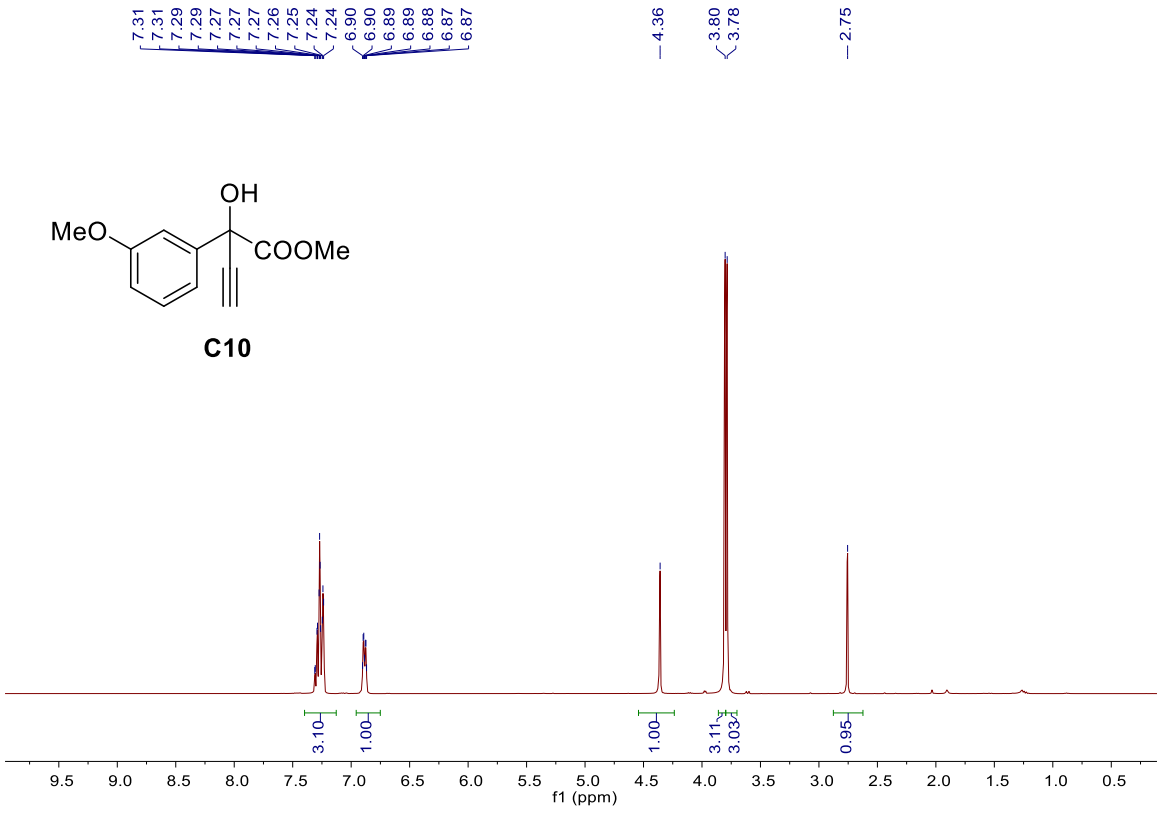
^{1}H NMR spectrum ($CDCl_3$)



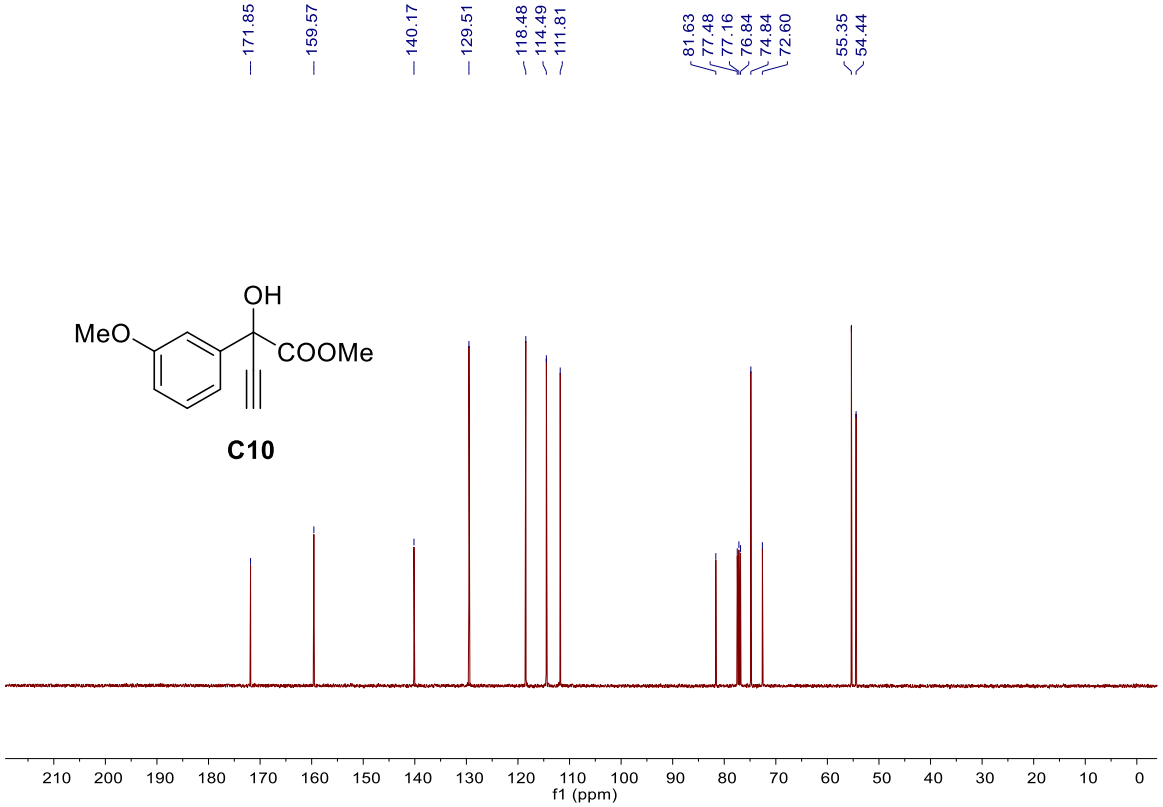
^{13}C NMR spectrum ($CDCl_3$)



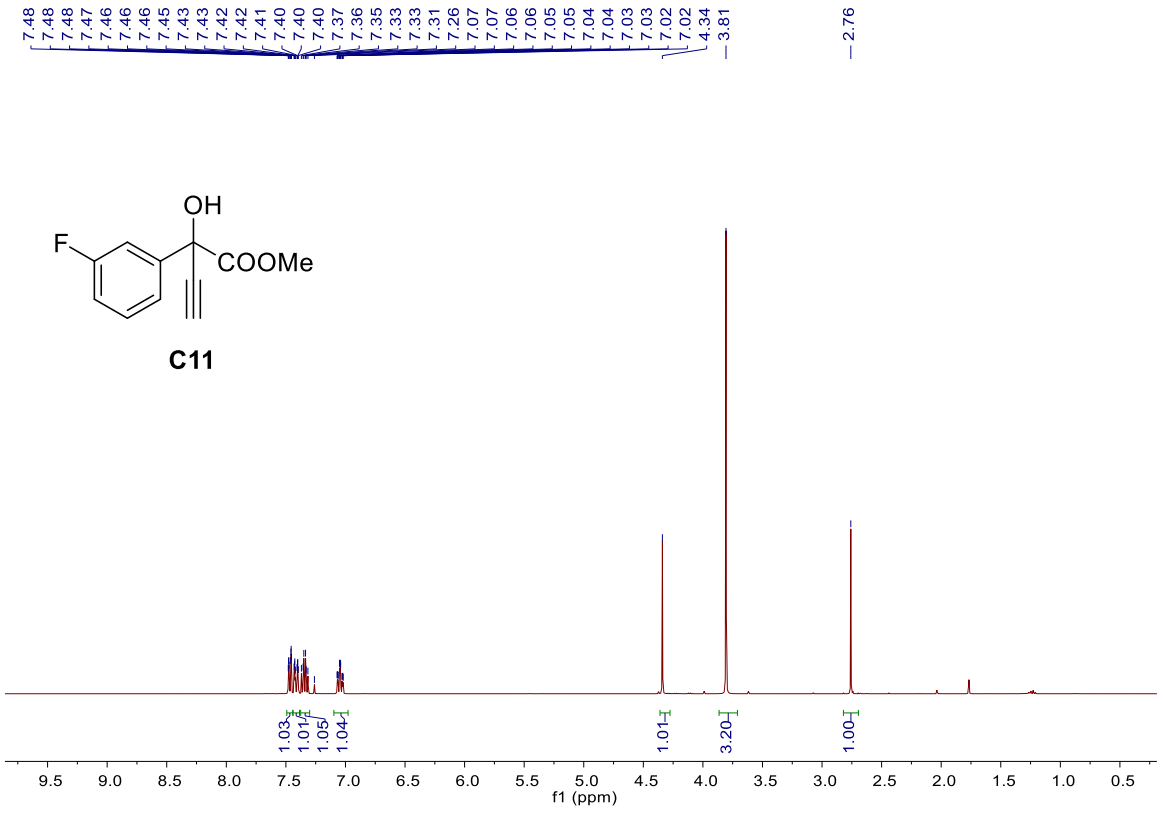
^{1}H NMR spectrum ($CDCl_3$)



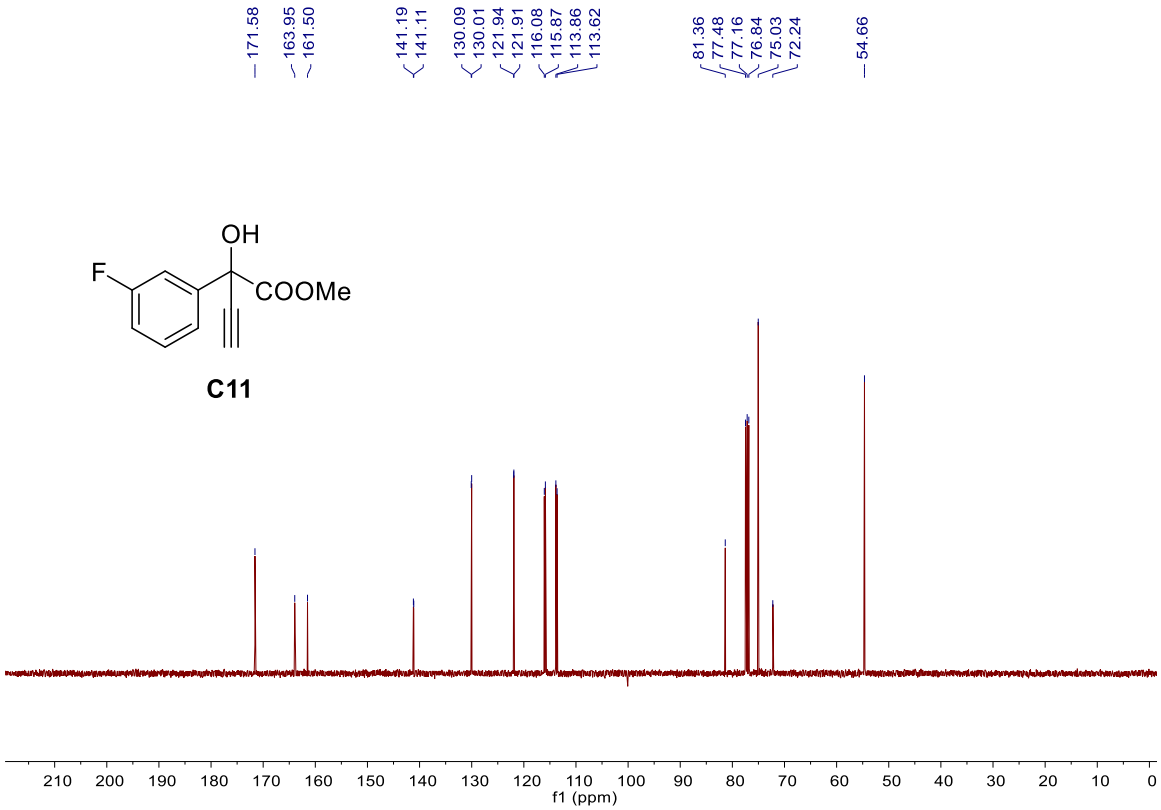
^{13}C NMR spectrum ($CDCl_3$)



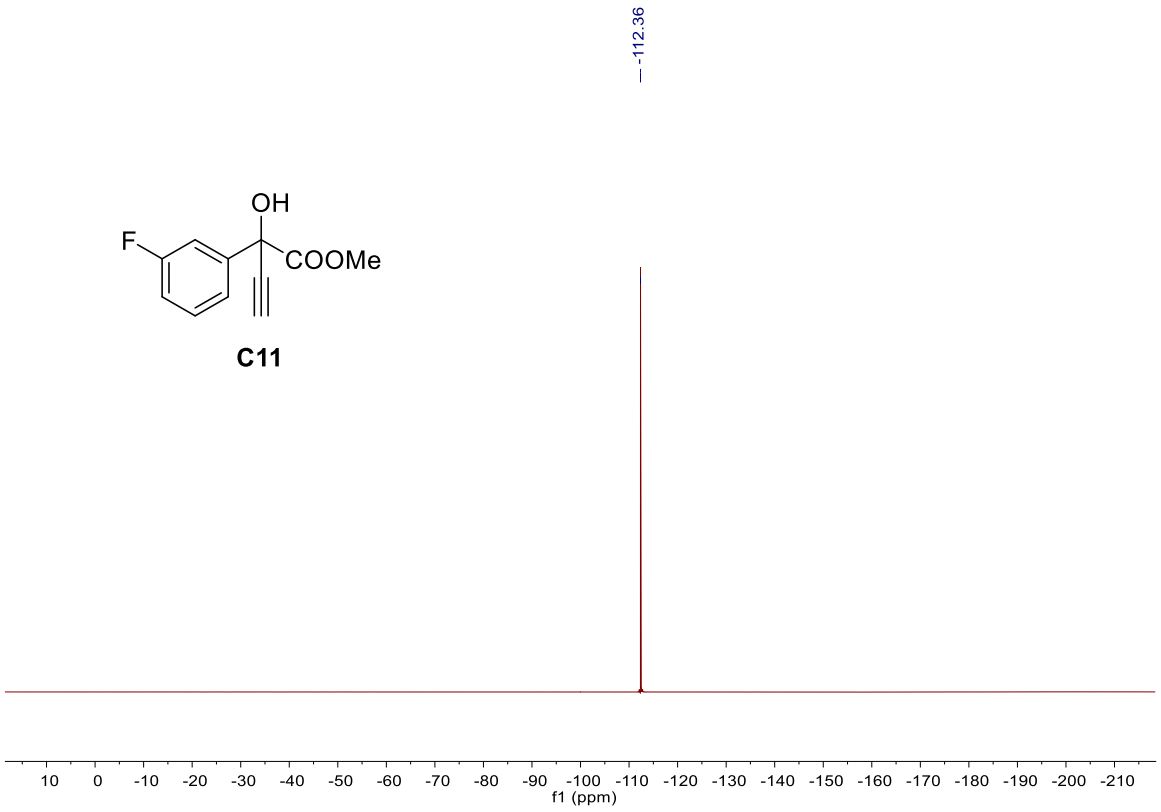
^{1}H NMR spectrum ($CDCl_3$)



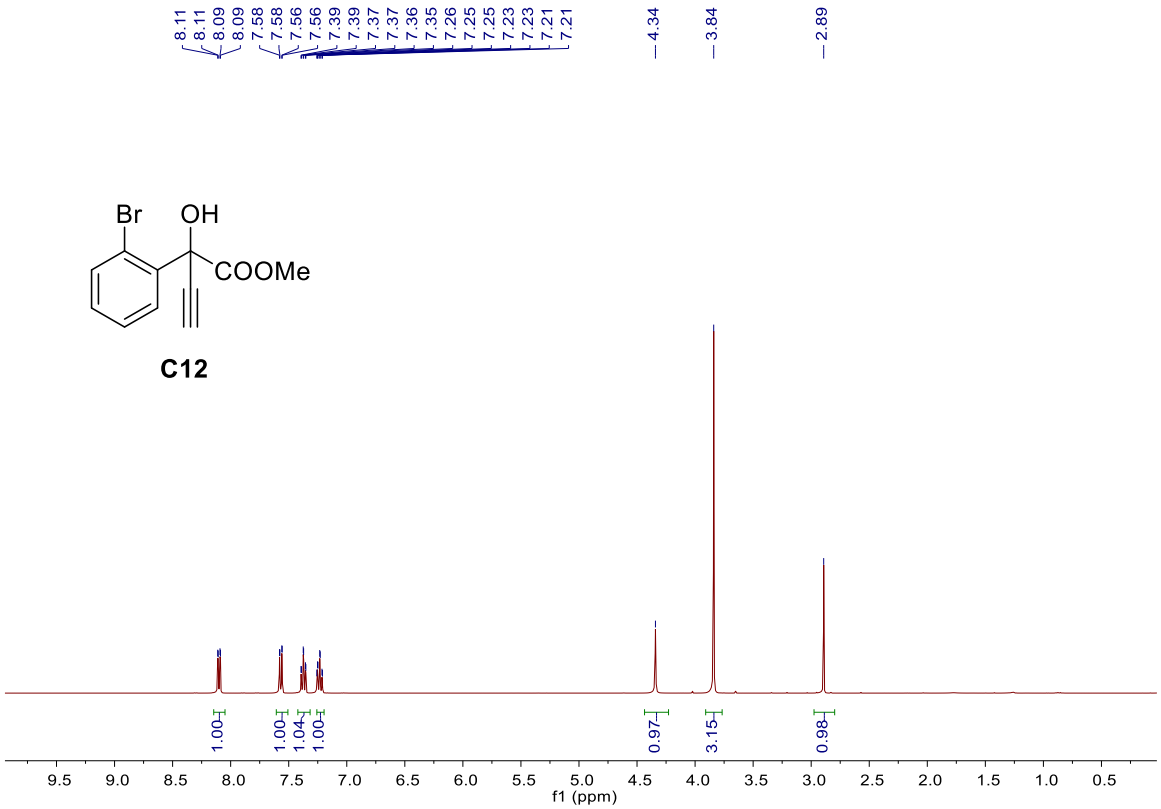
^{13}C NMR spectrum ($CDCl_3$)



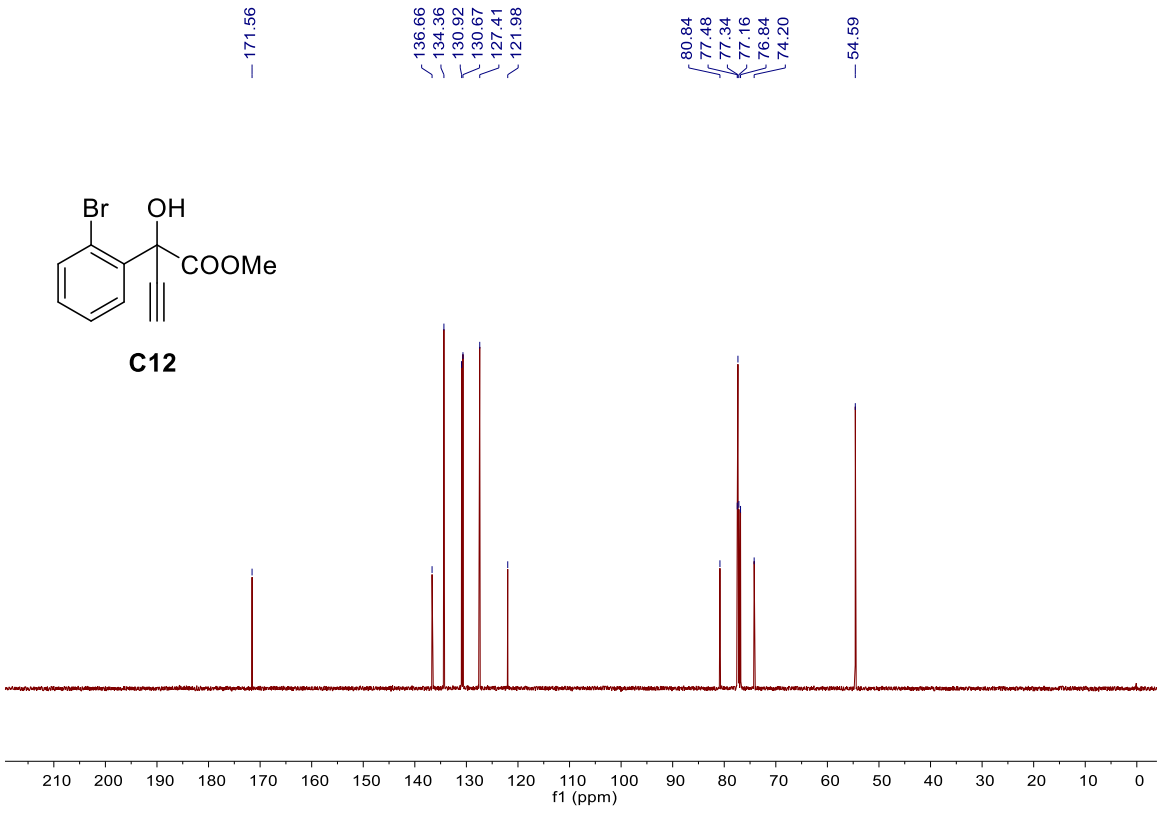
^{19}F NMR spectrum ($CDCl_3$)



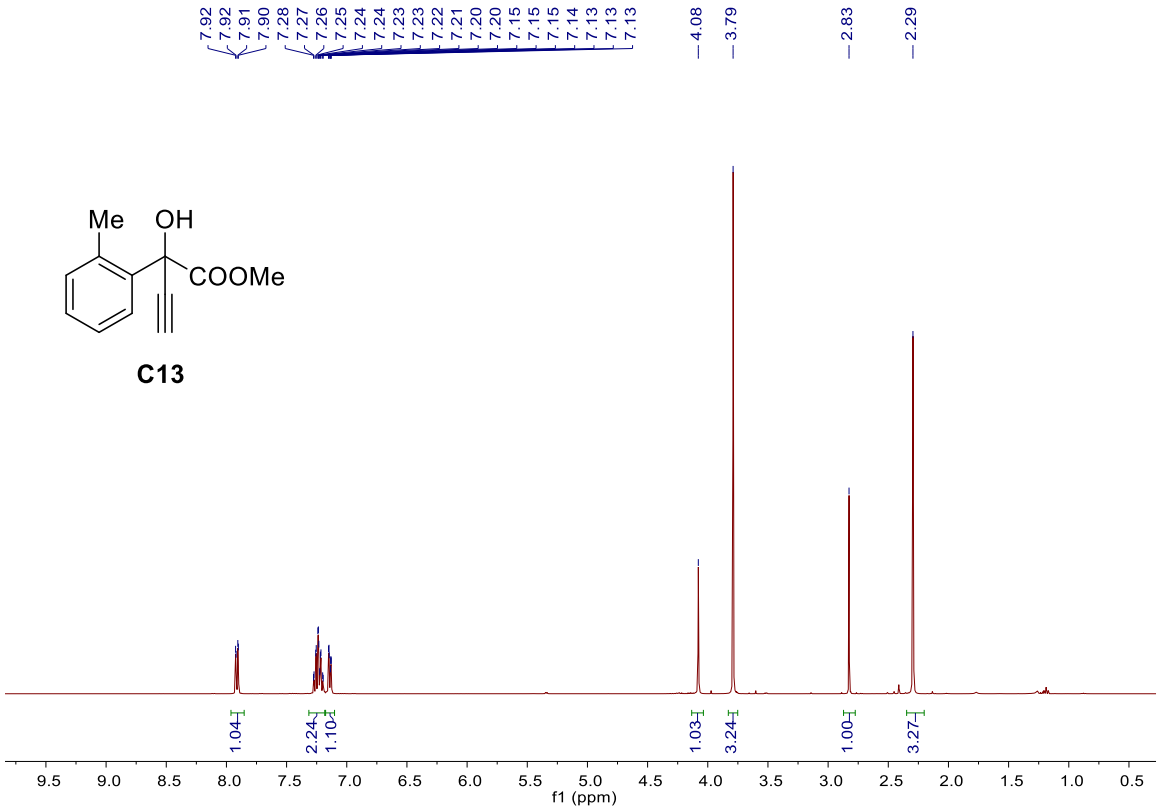
^{1}H NMR spectrum ($CDCl_3$)



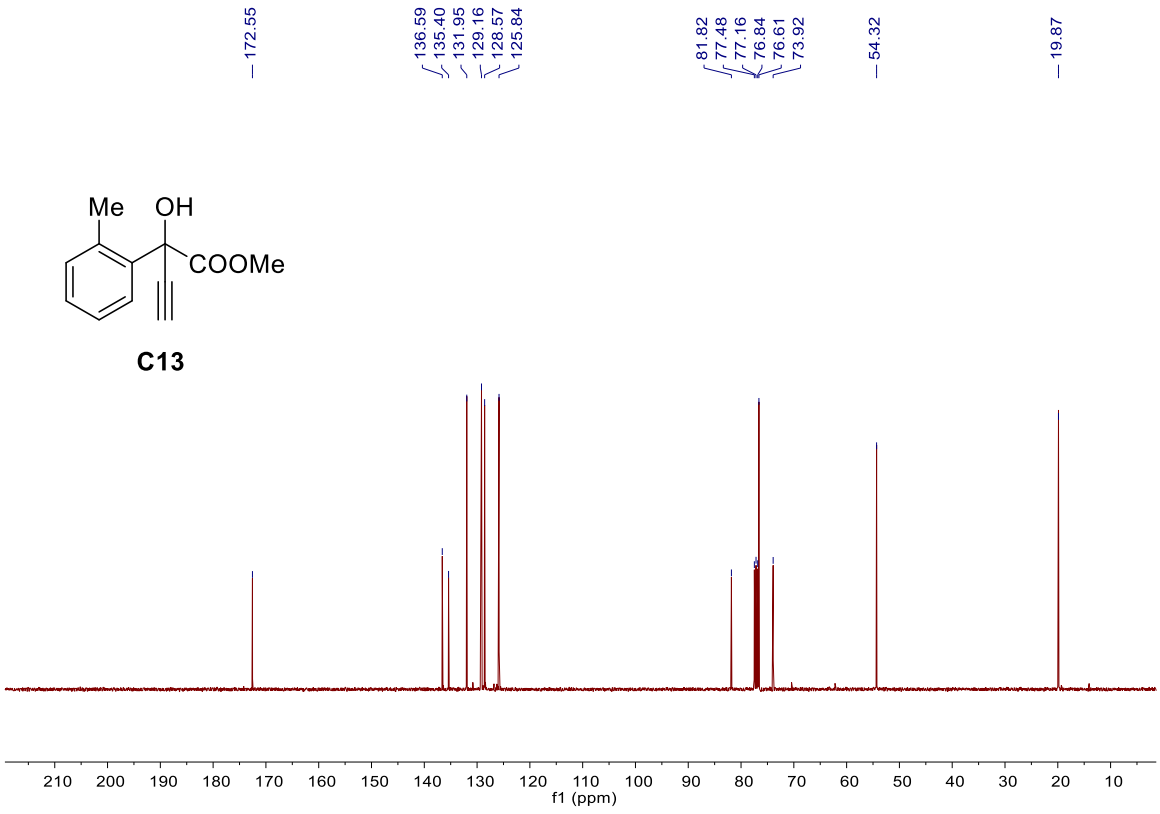
^{13}C NMR spectrum ($CDCl_3$)



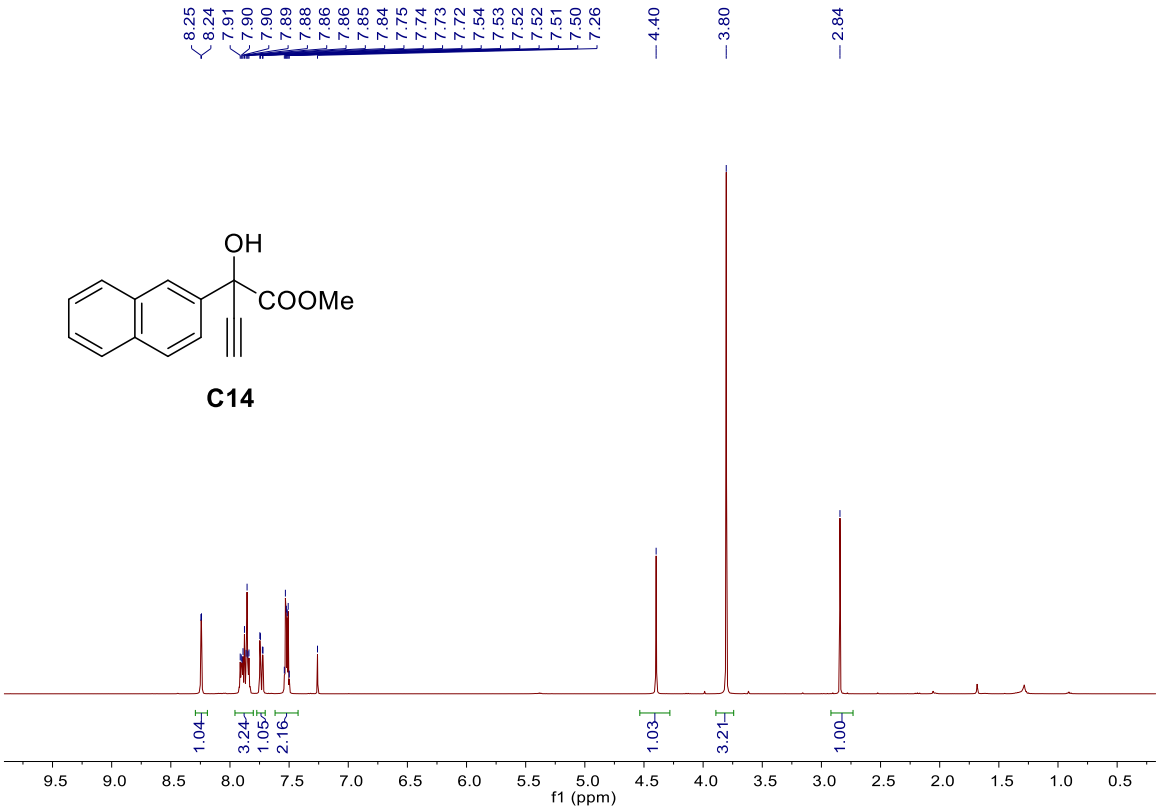
^{1}H NMR spectrum ($CDCl_3$)



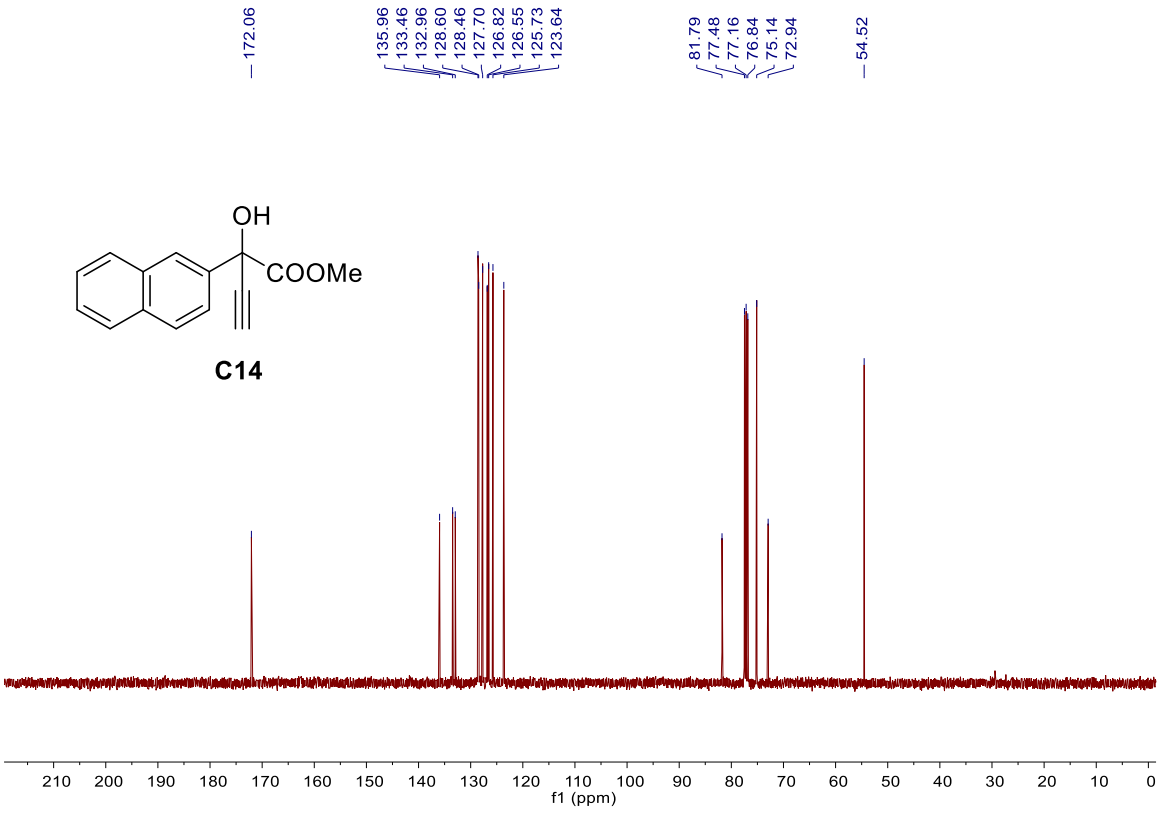
^{13}C NMR spectrum ($CDCl_3$)



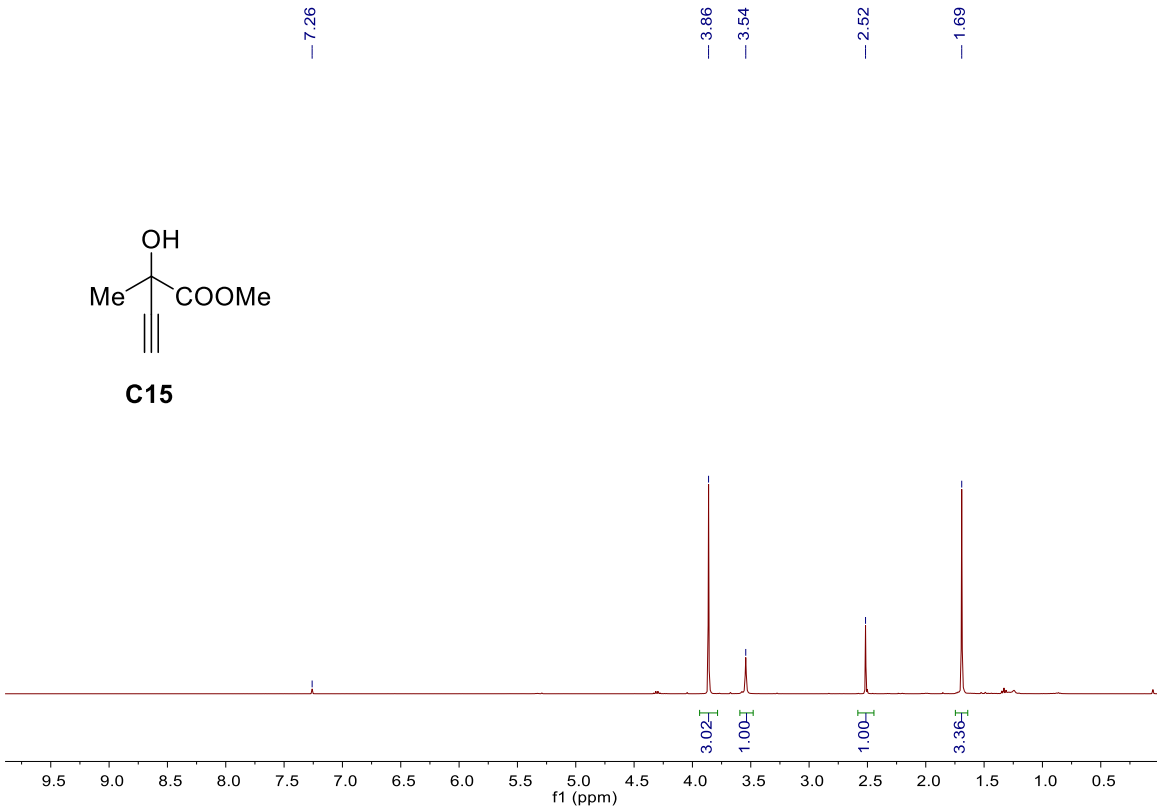
^{1}H NMR spectrum ($CDCl_3$)



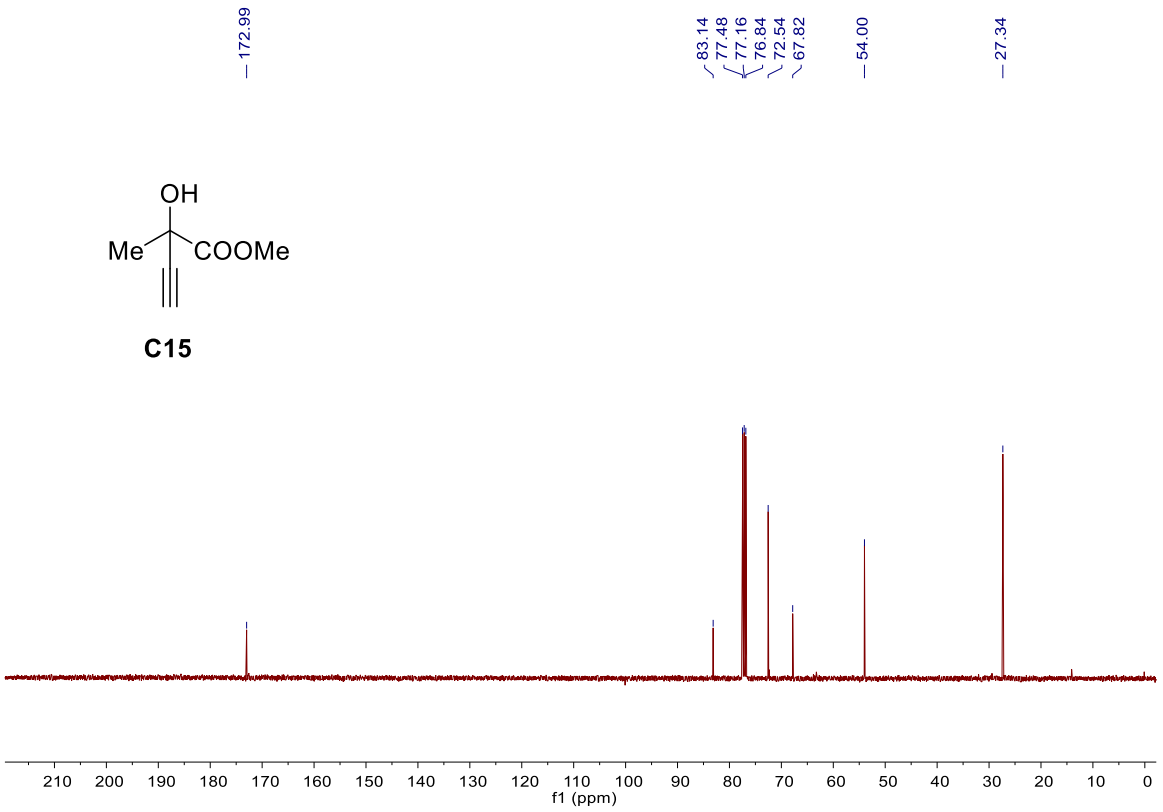
^{13}C NMR spectrum ($CDCl_3$)



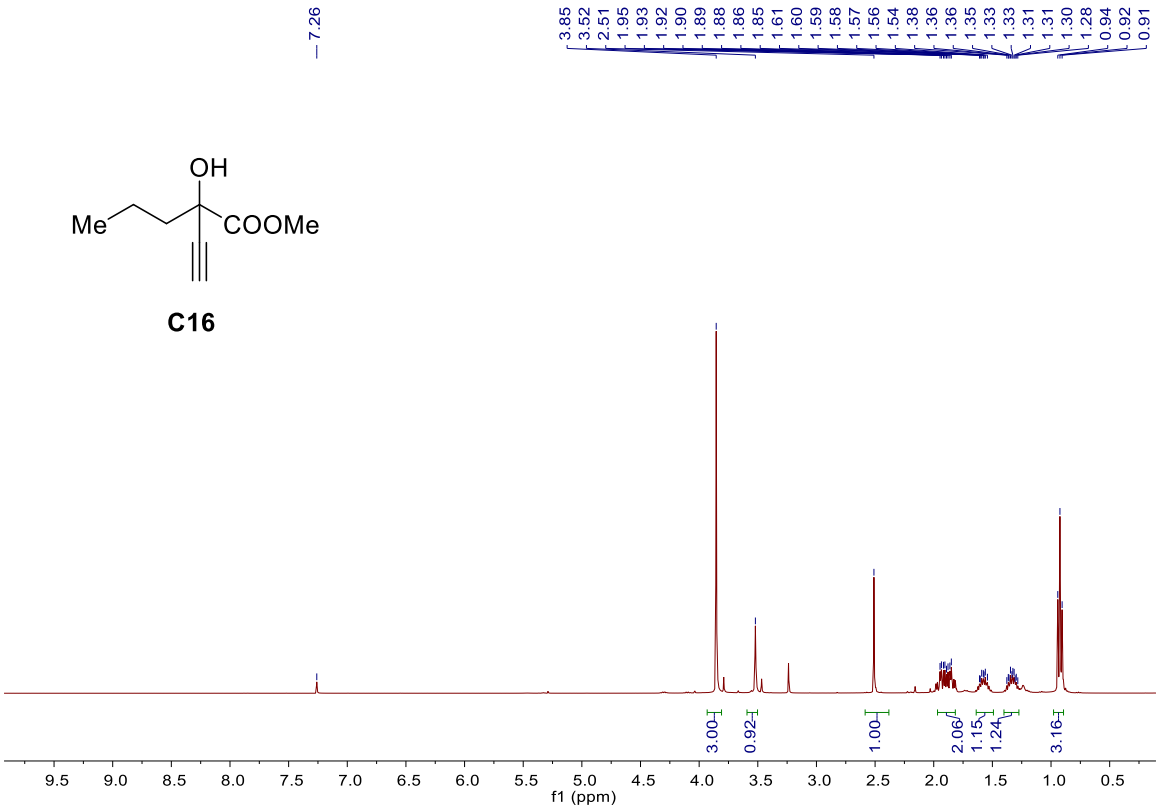
^{1}H NMR spectrum ($CDCl_3$)



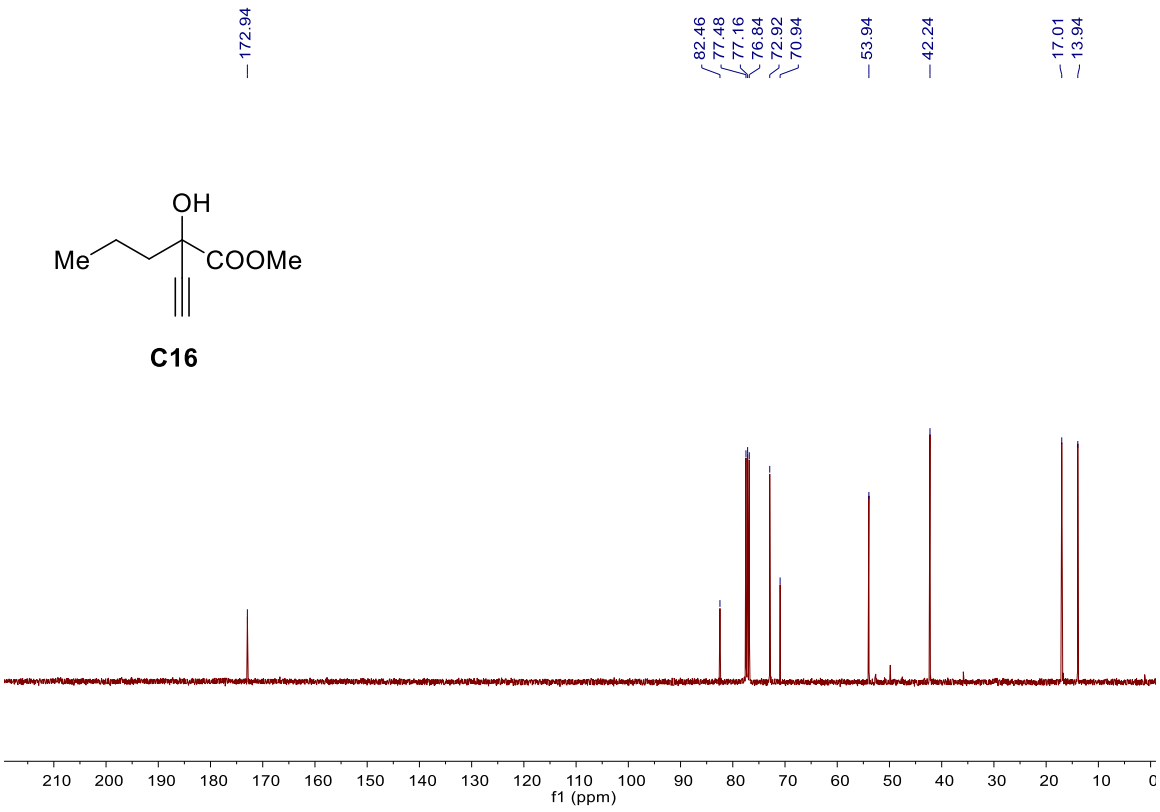
^{13}C NMR spectrum ($CDCl_3$)



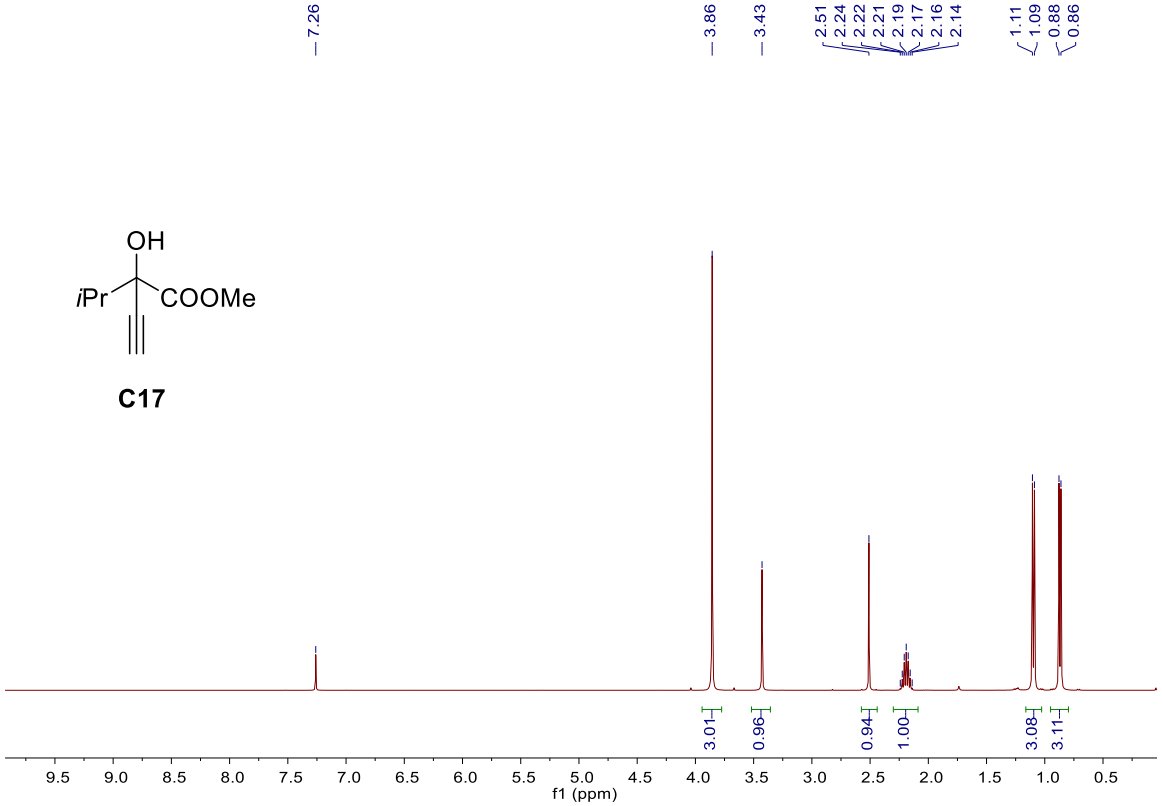
^{1}H NMR spectrum ($CDCl_3$)



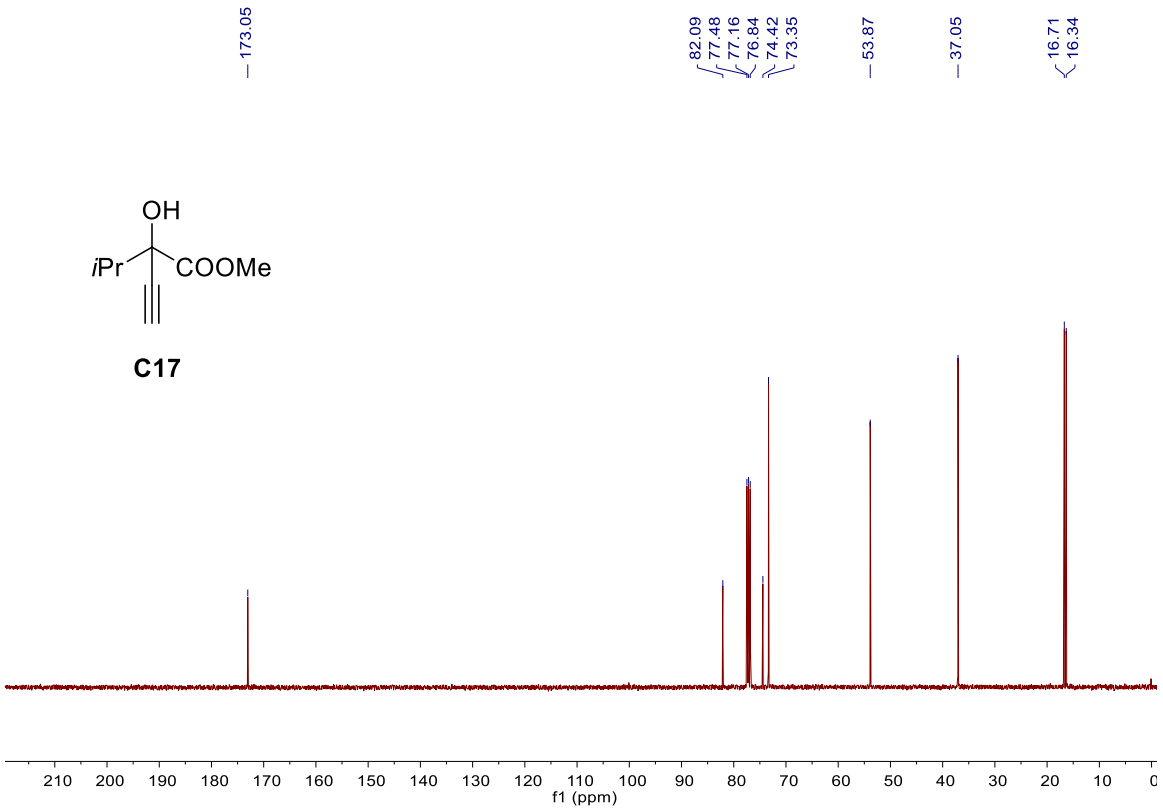
^{13}C NMR spectrum ($CDCl_3$)



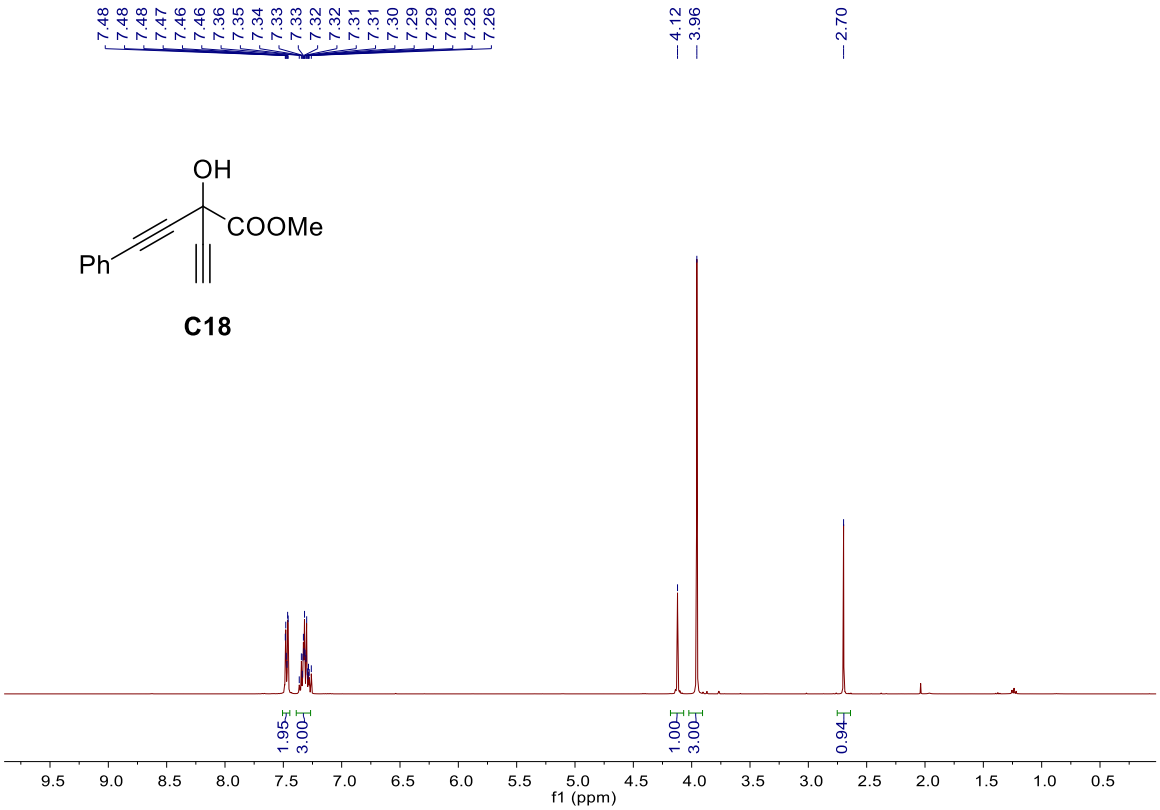
^{1}H NMR spectrum ($CDCl_3$)



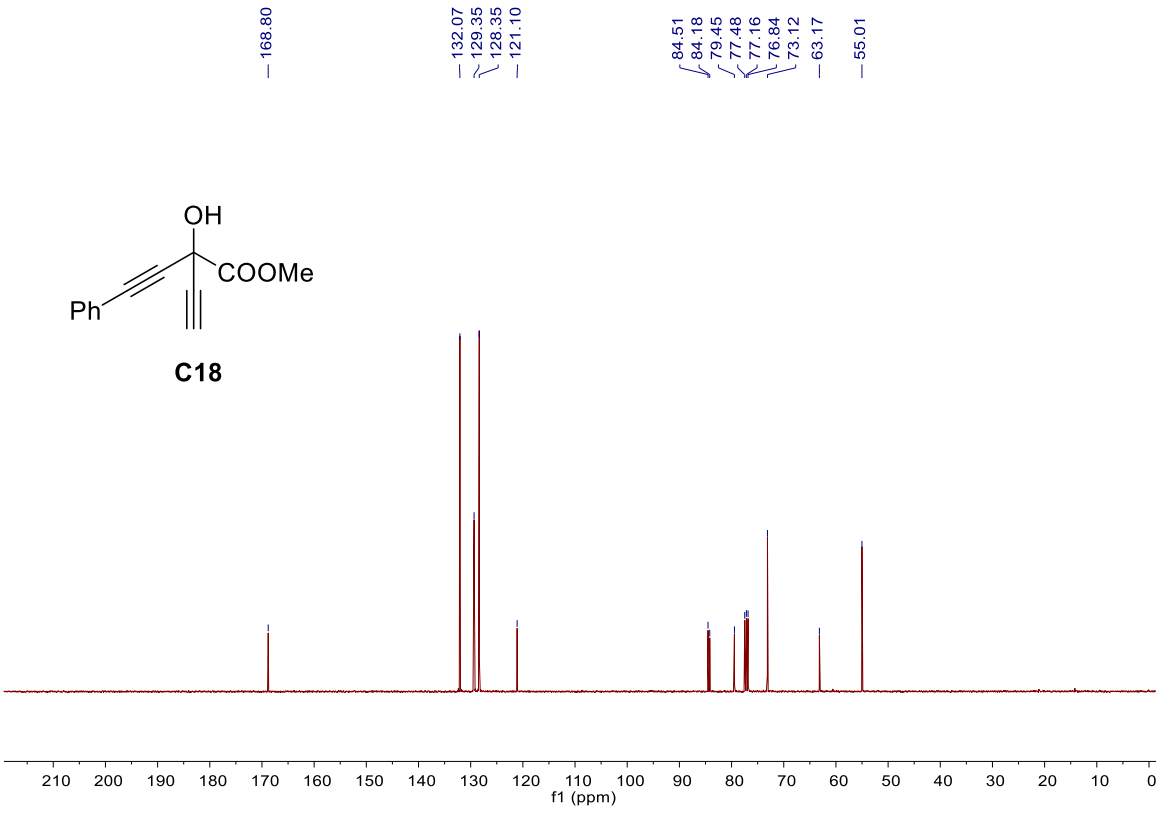
^{13}C NMR spectrum ($CDCl_3$)



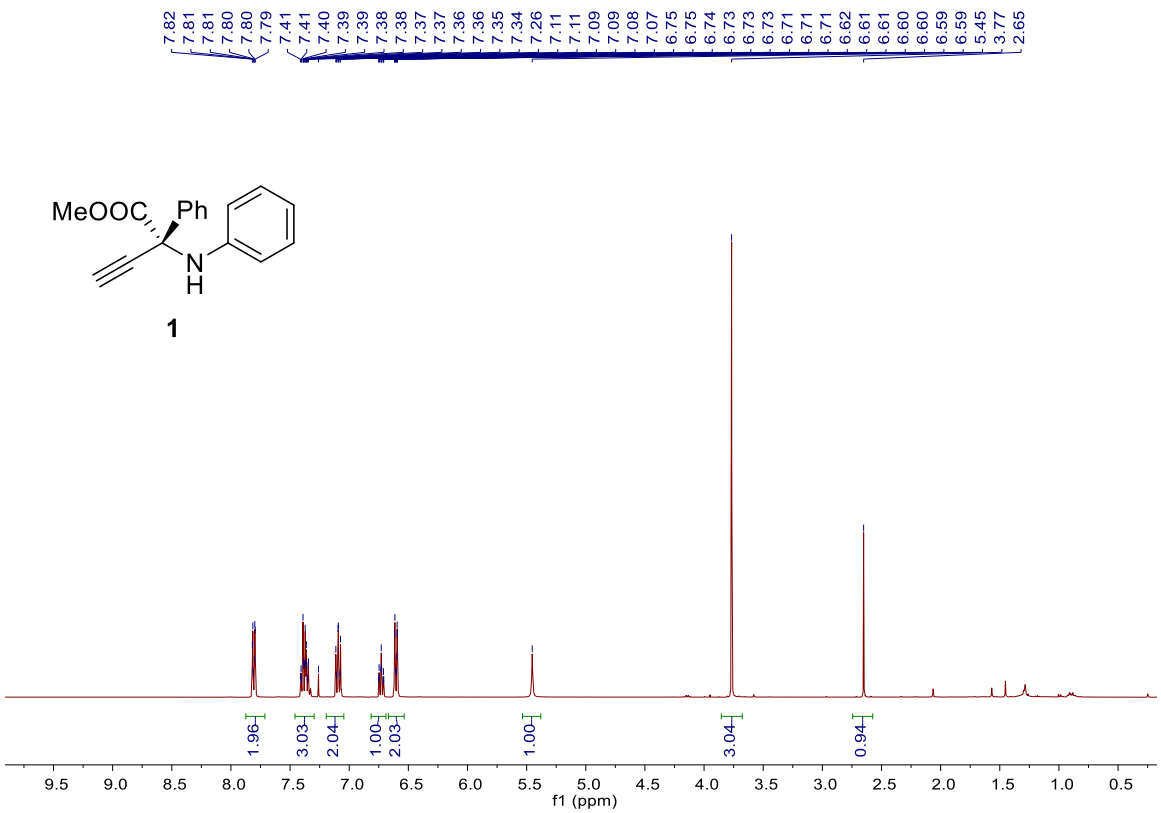
^{1}H NMR spectrum ($CDCl_3$)



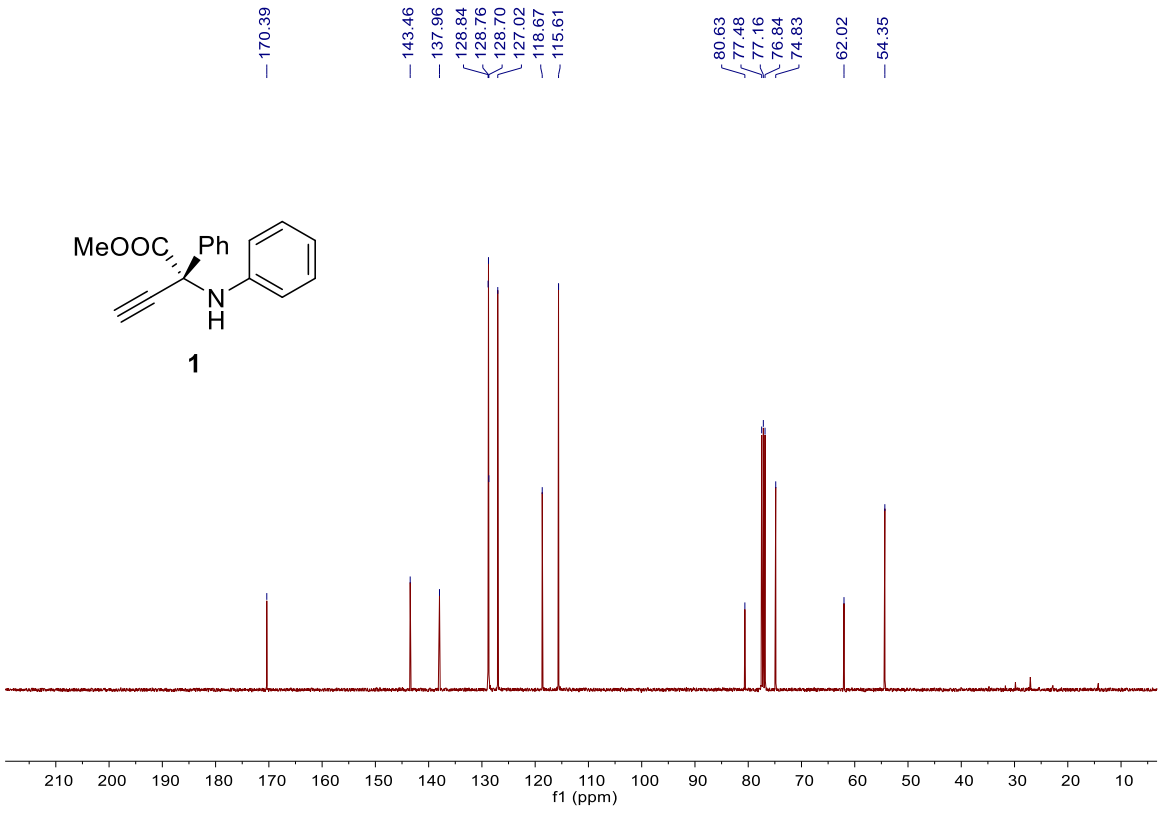
^{13}C NMR spectrum ($CDCl_3$)



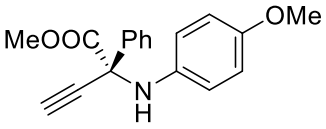
^{1}H NMR spectrum ($CDCl_3$)



^{13}C NMR spectrum ($CDCl_3$)

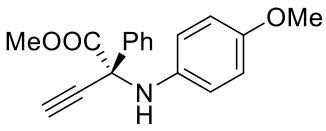


^{1}H NMR spectrum ($CDCl_3$)



2

^{13}C NMR spectrum ($CDCl_3$)



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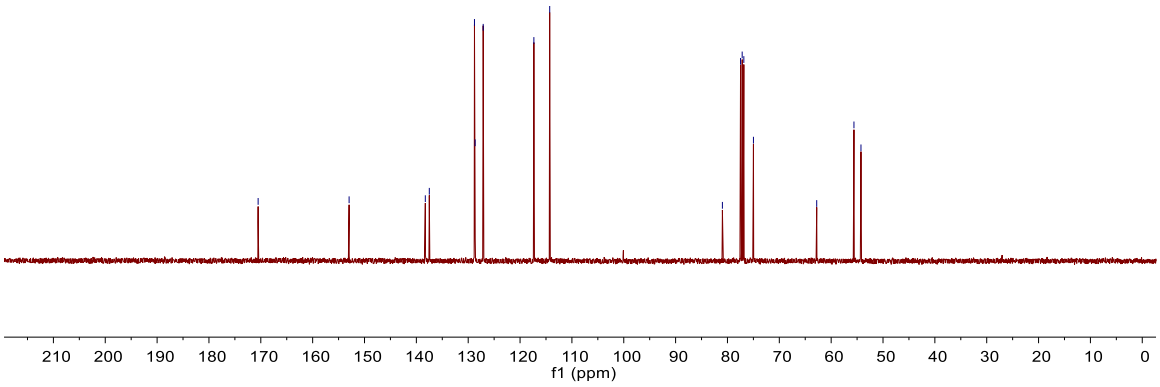
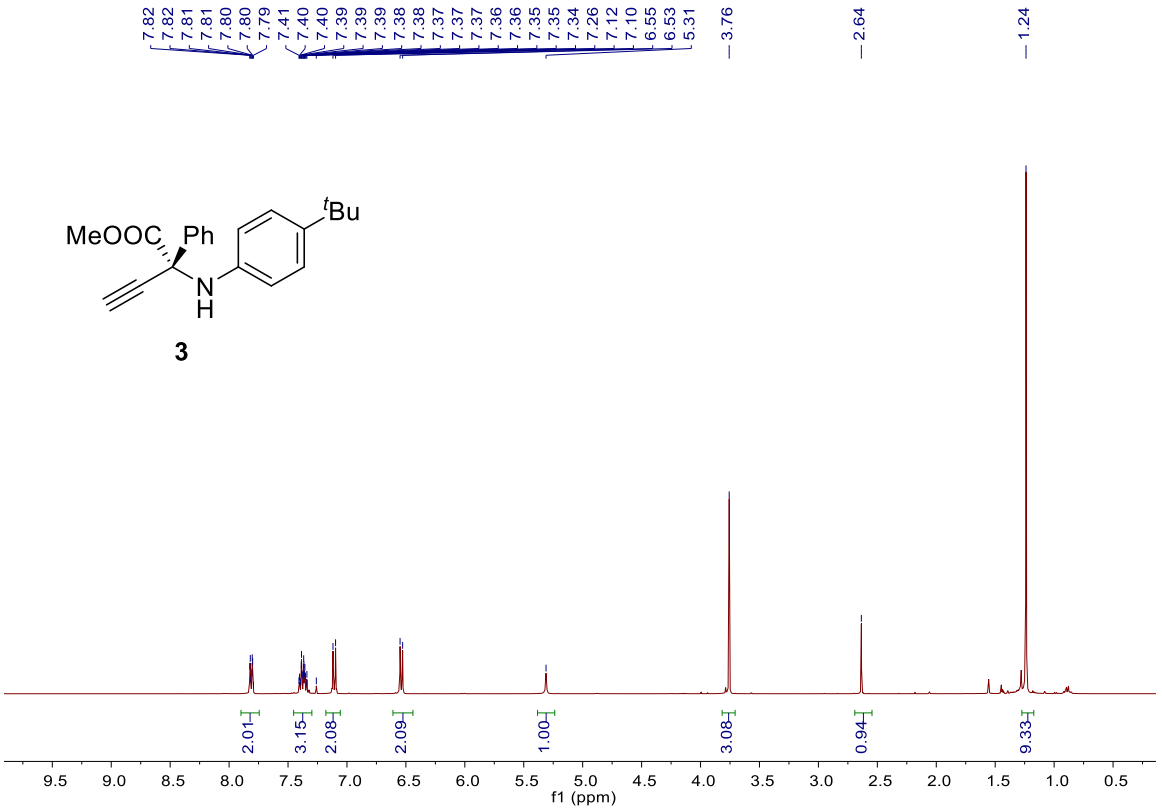
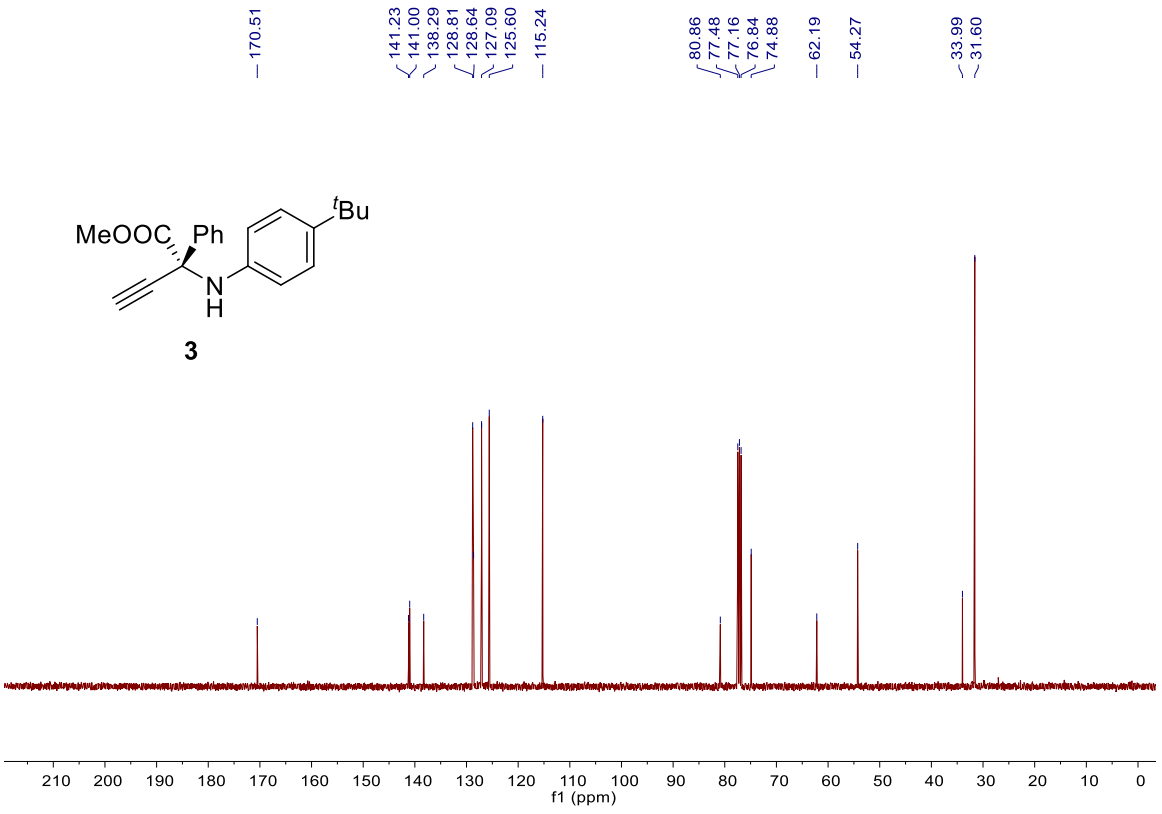


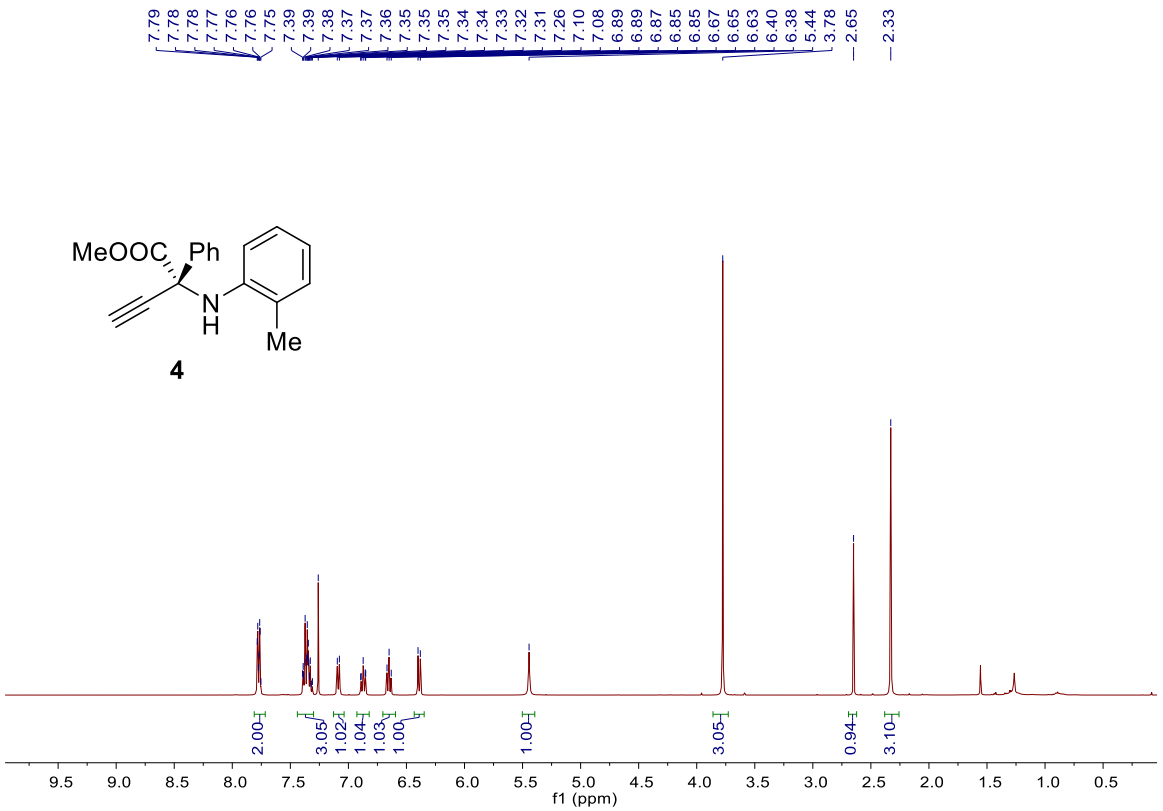
^{1}H NMR spectrum ($CDCl_3$)



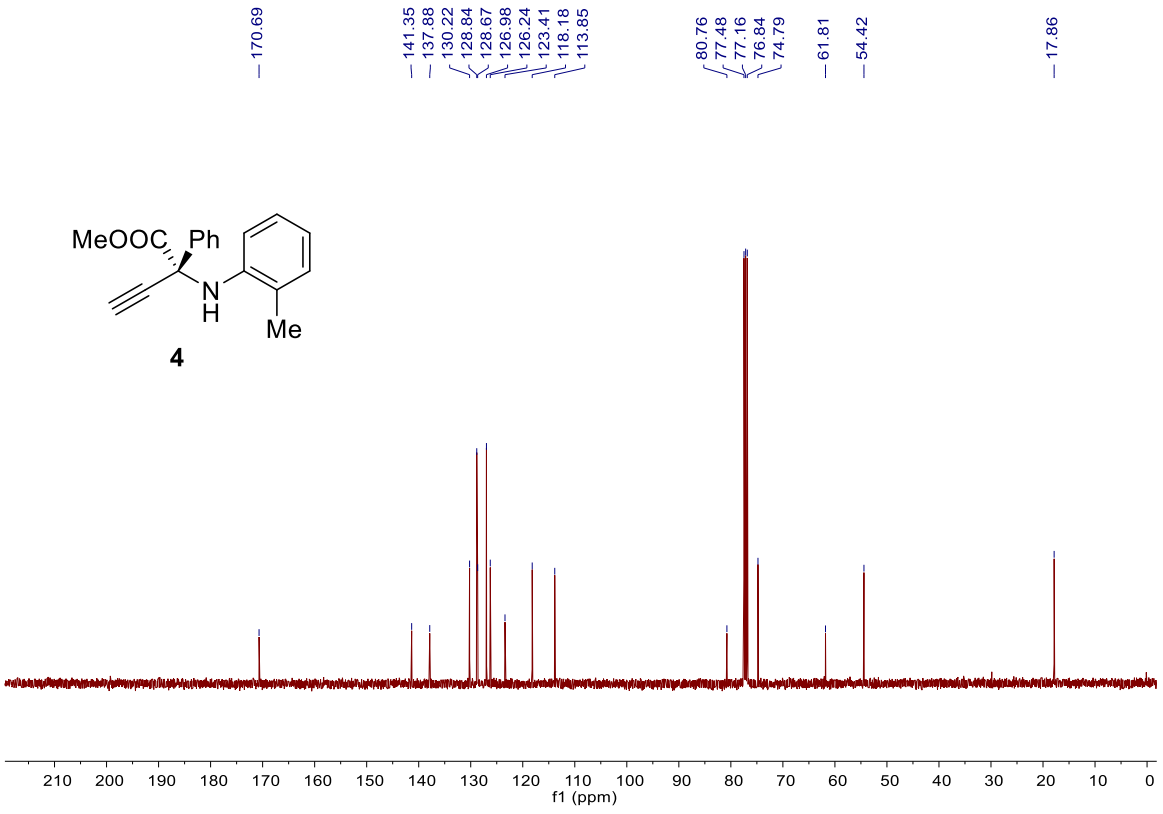
^{13}C NMR spectrum ($CDCl_3$)



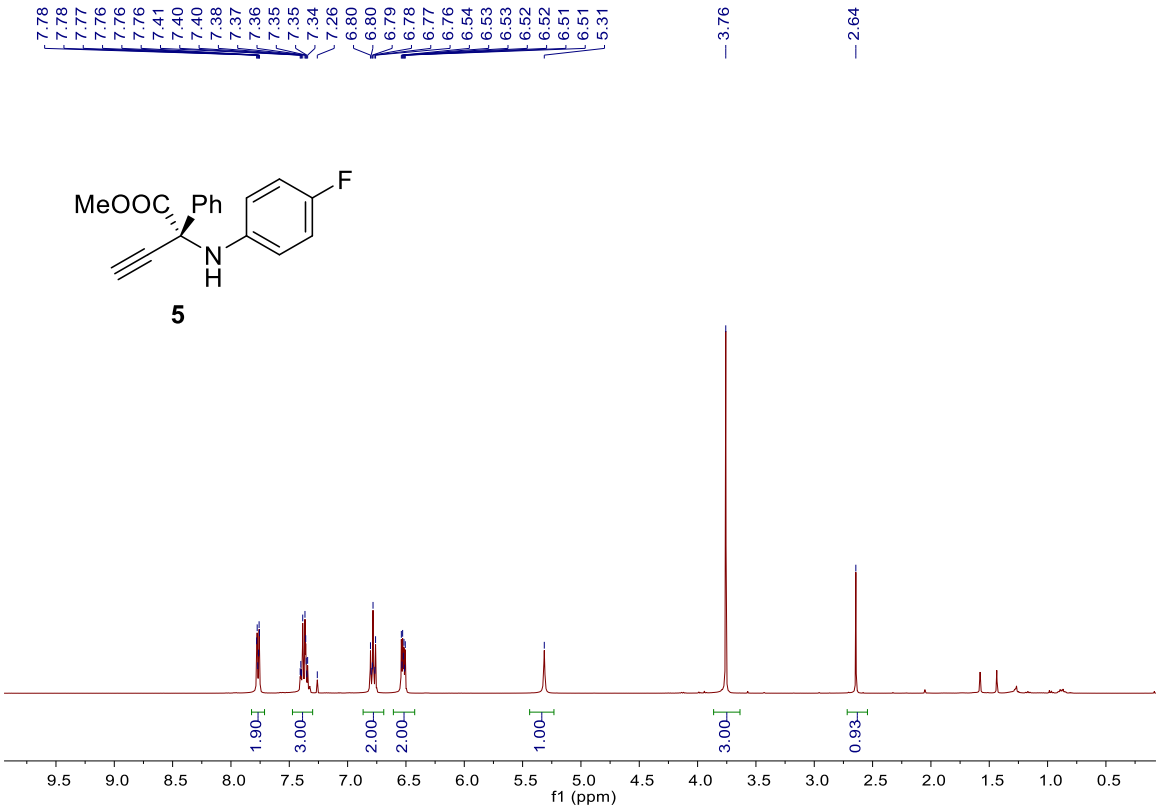
^{1}H NMR spectrum ($CDCl_3$)



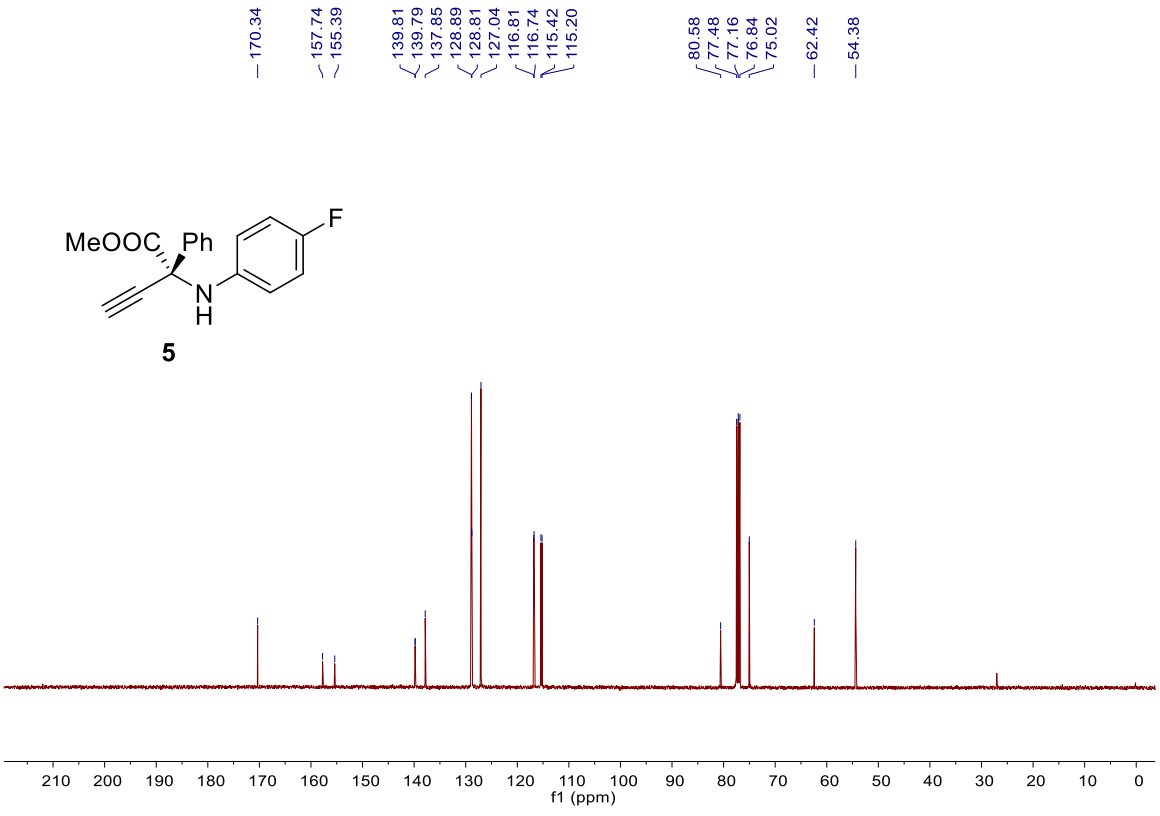
^{13}C NMR spectrum ($CDCl_3$)



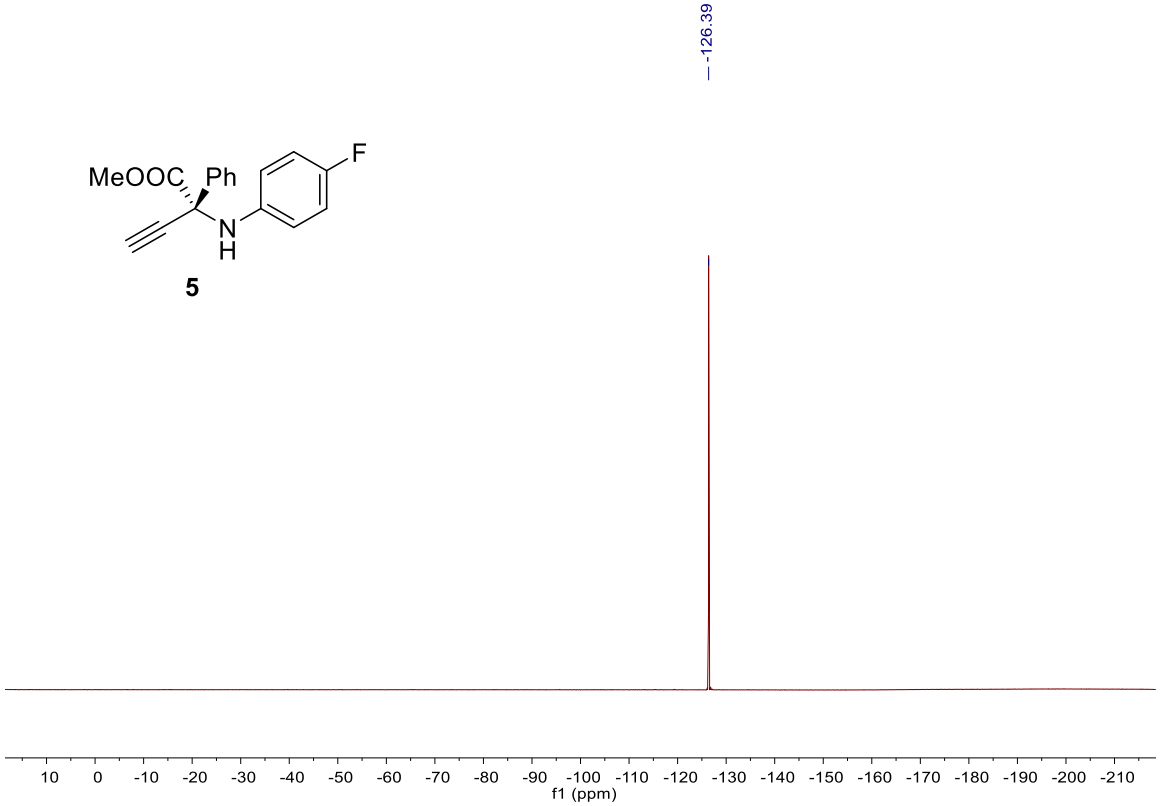
^{1}H NMR spectrum ($CDCl_3$)



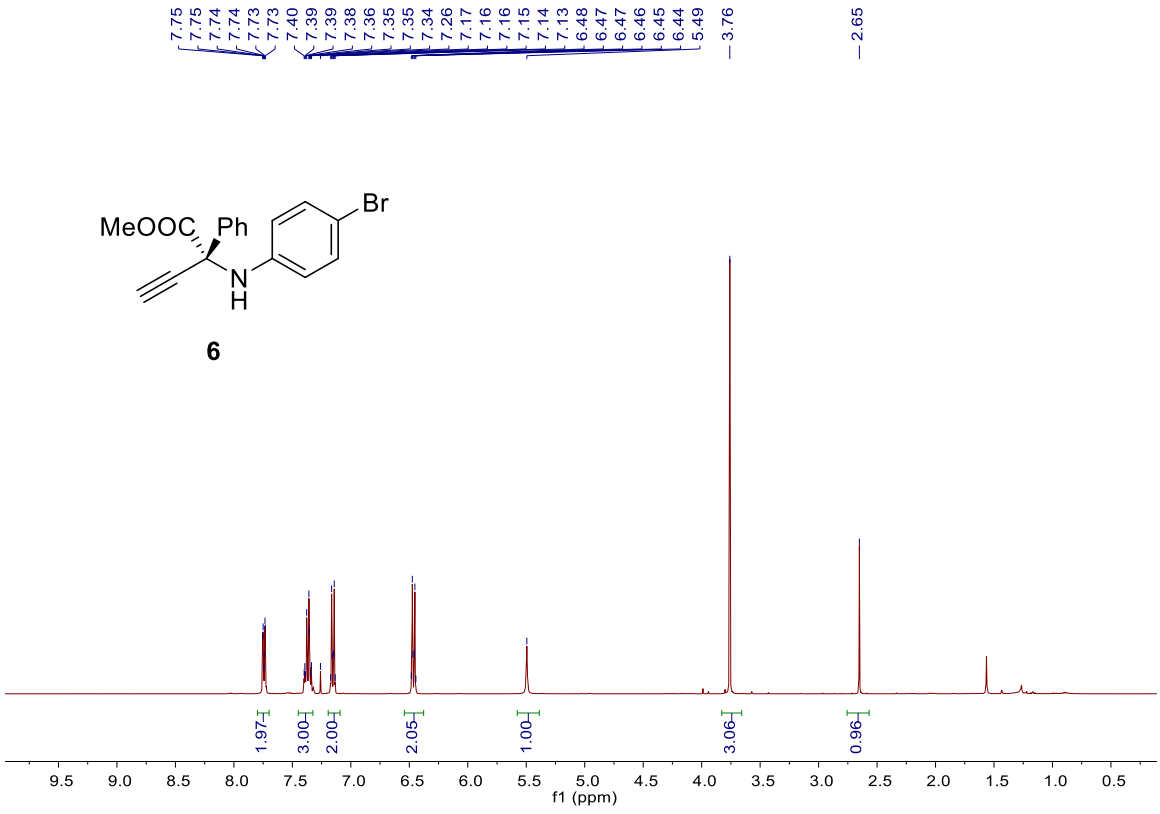
^{13}C NMR spectrum ($CDCl_3$)



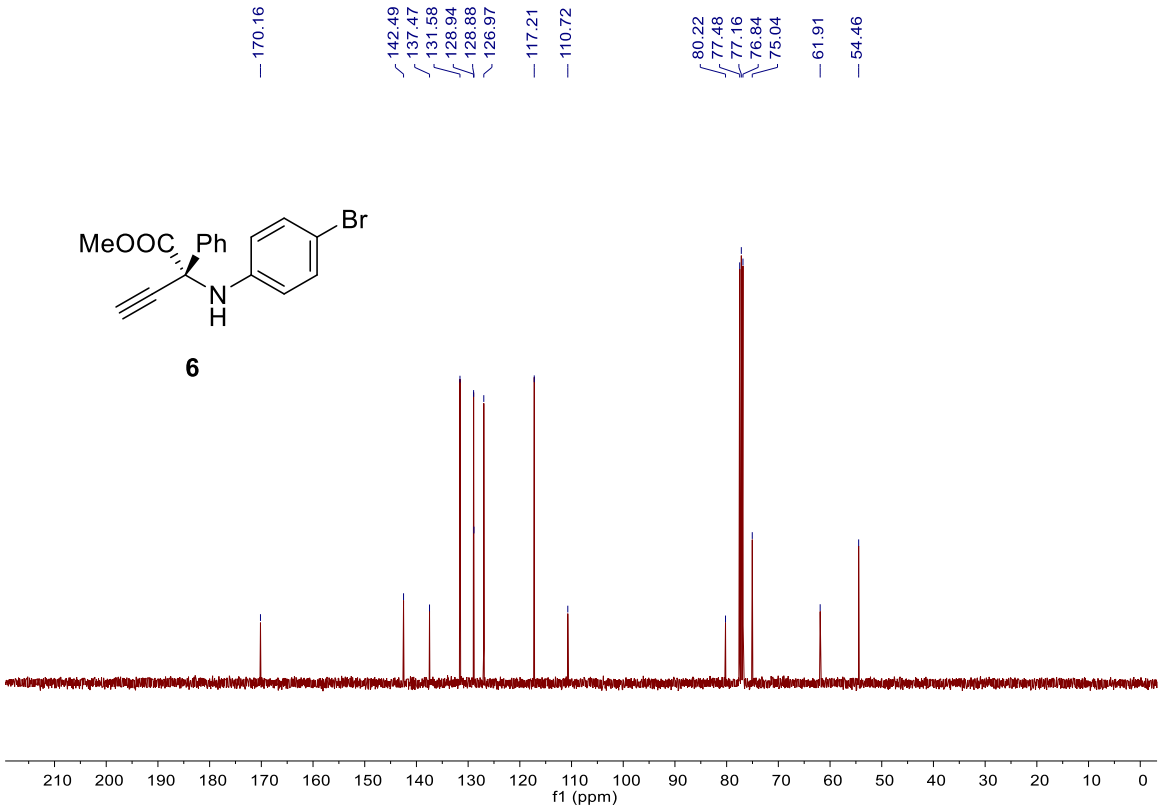
^{19}F NMR spectrum ($CDCl_3$)



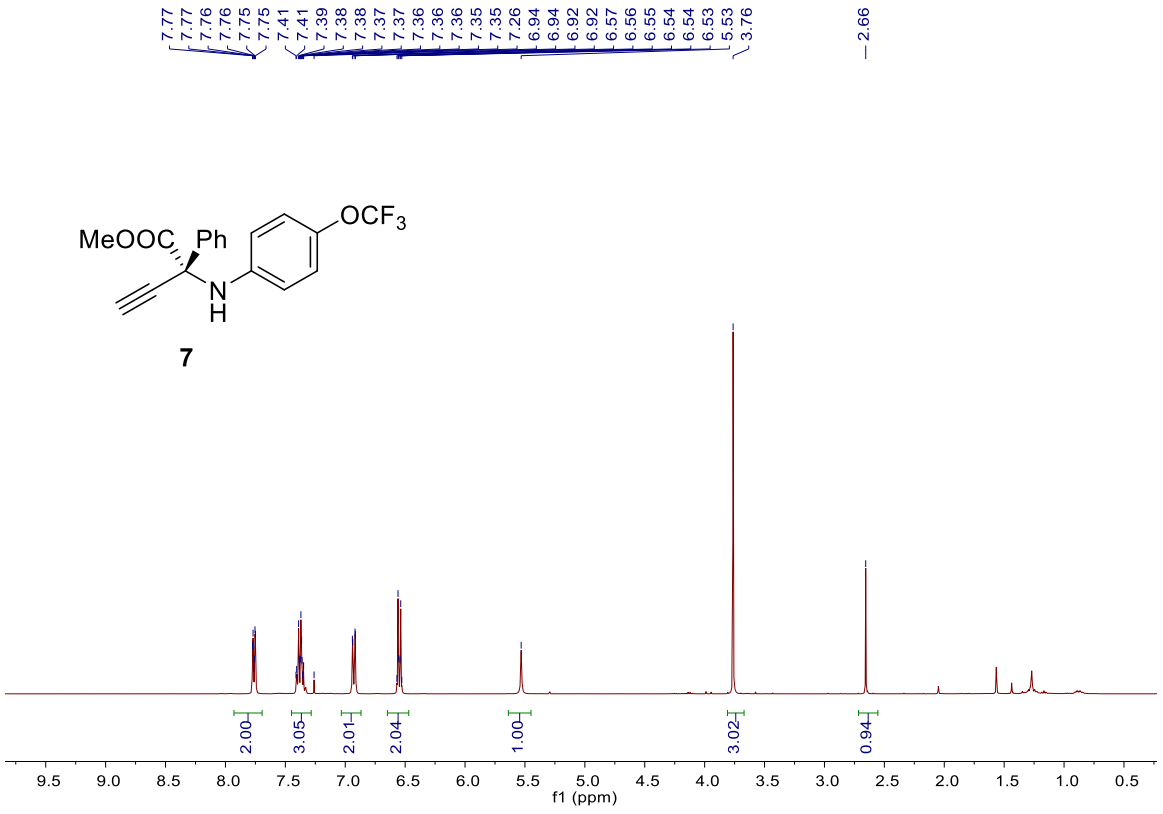
^{1}H NMR spectrum ($CDCl_3$)



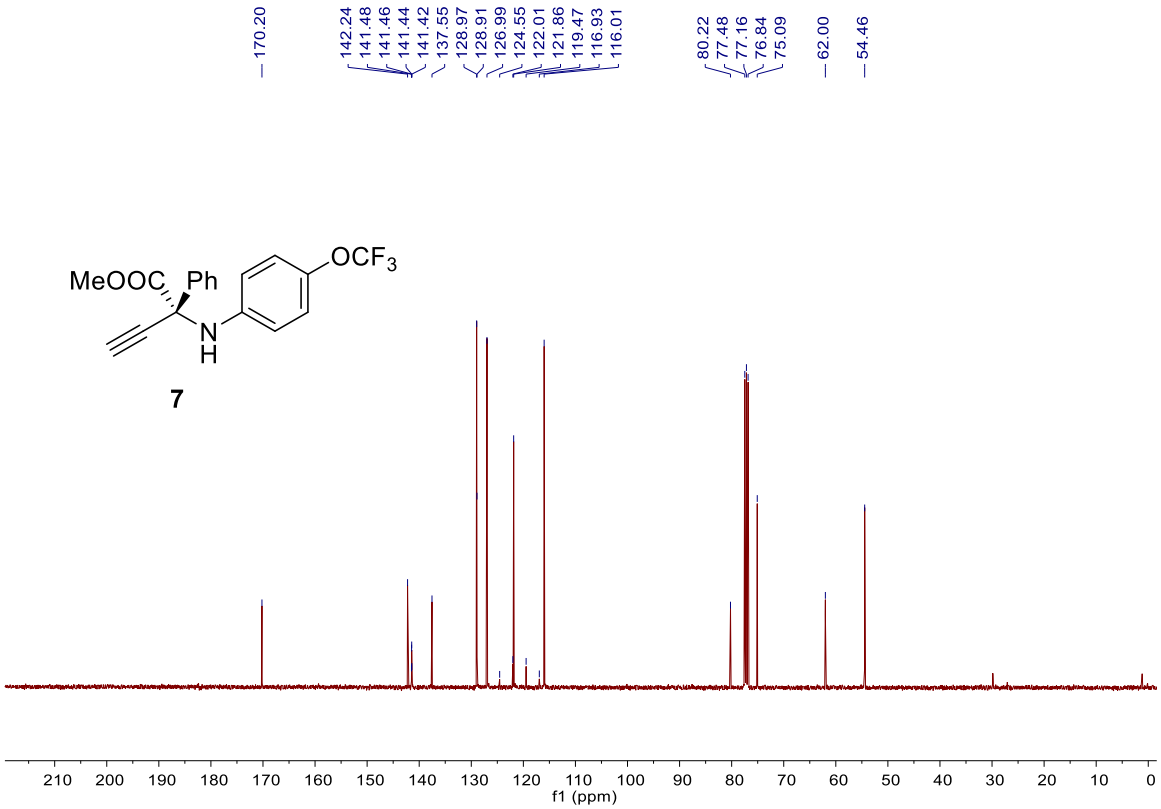
^{13}C NMR spectrum ($CDCl_3$)



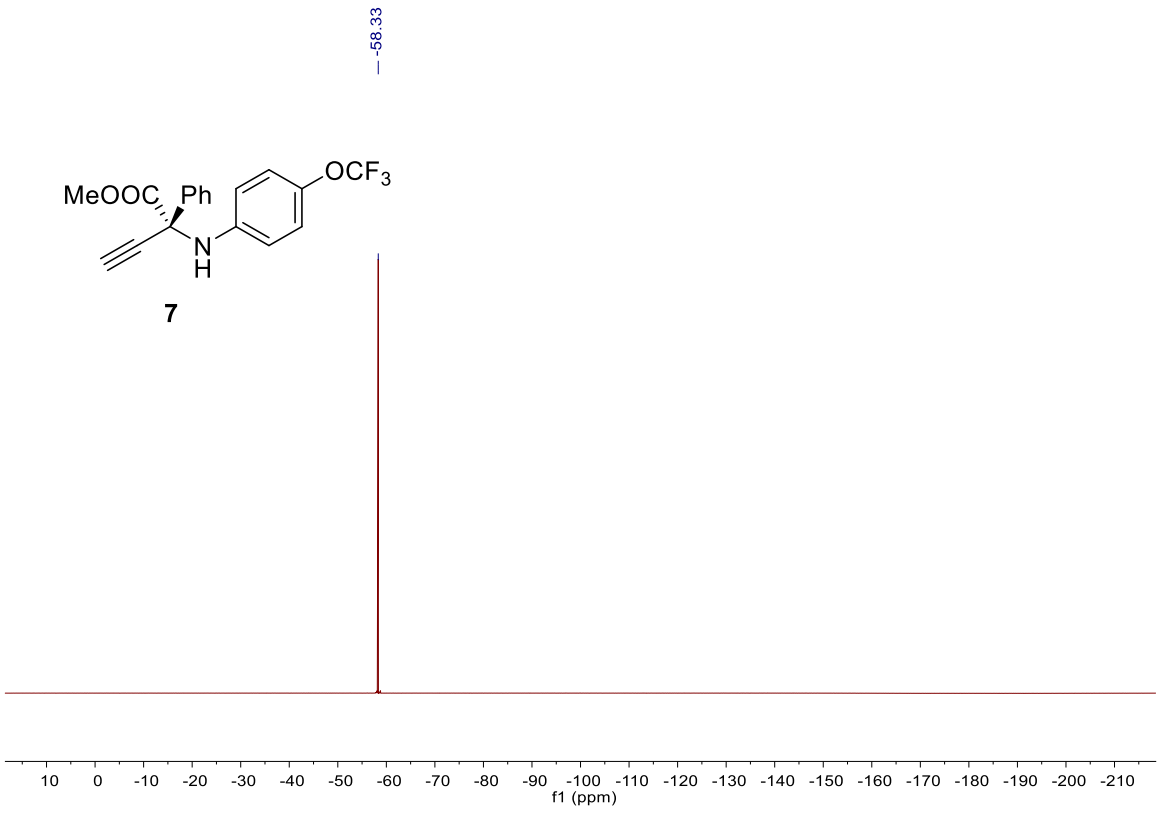
^{1}H NMR spectrum ($CDCl_3$)



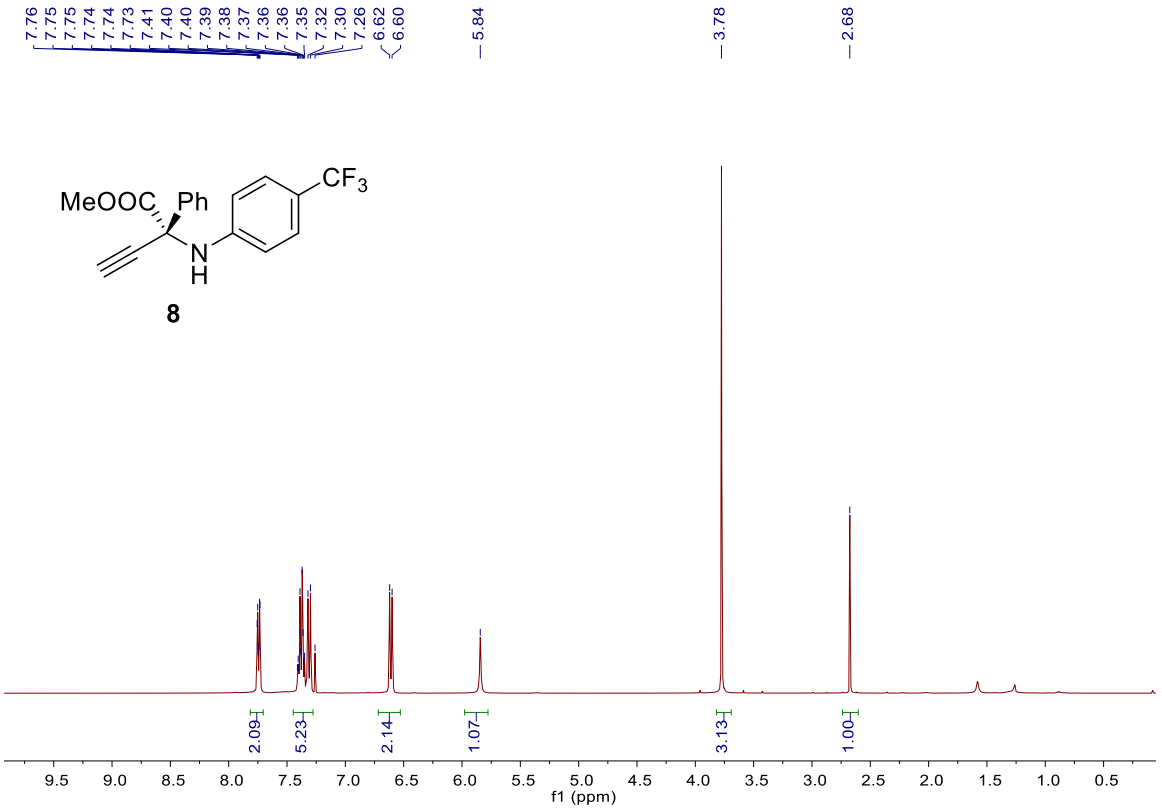
^{13}C NMR spectrum ($CDCl_3$)



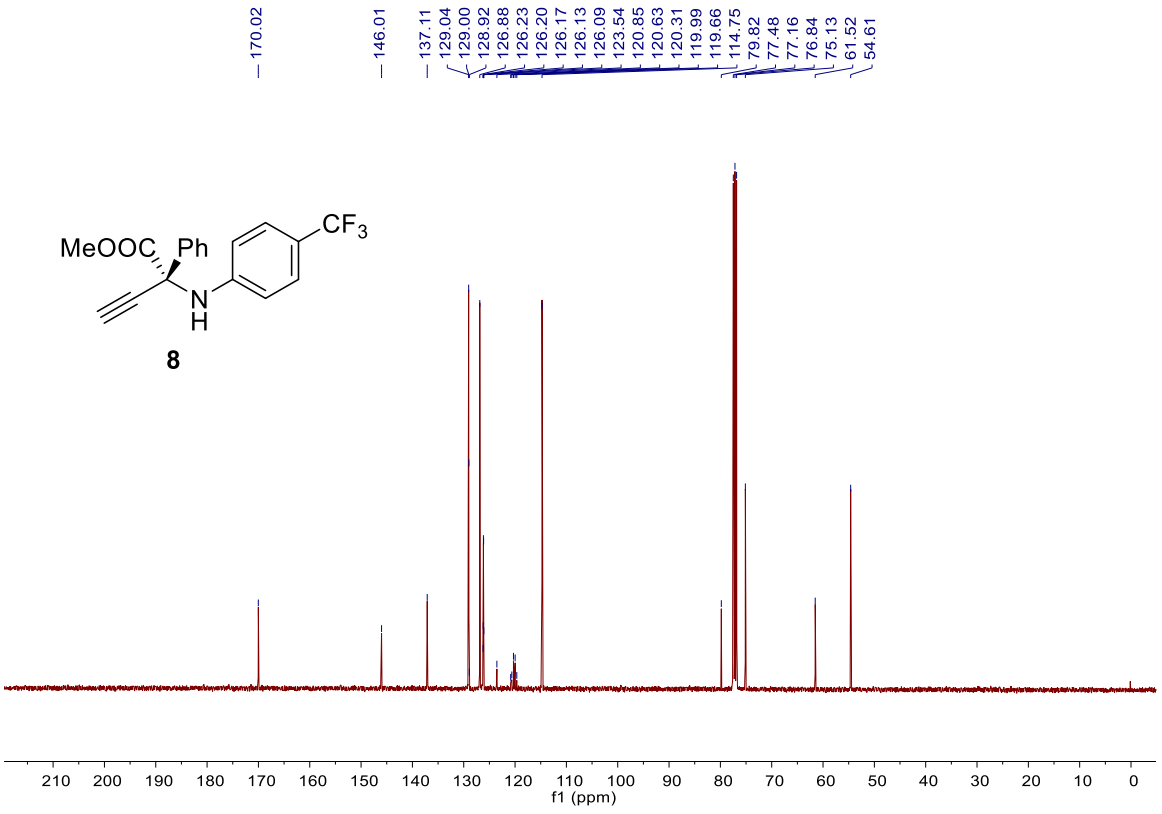
^{19}F NMR spectrum ($CDCl_3$)



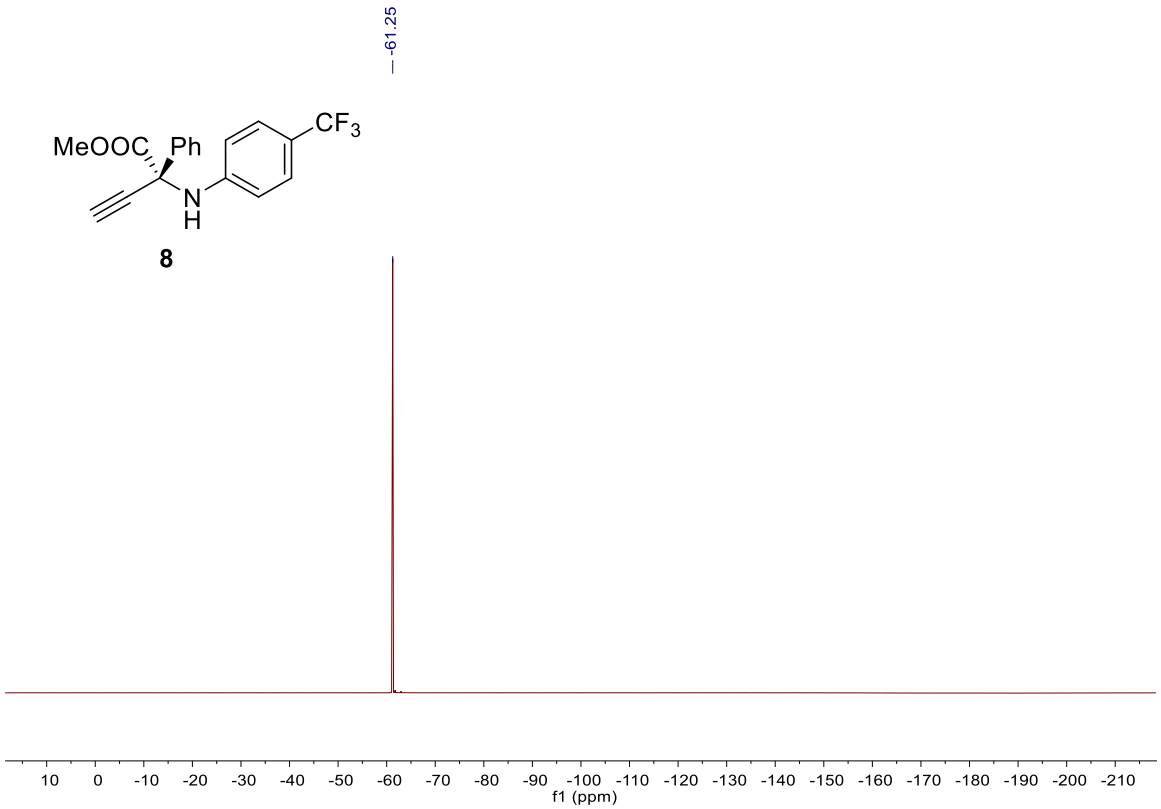
^{1}H NMR spectrum ($CDCl_3$)



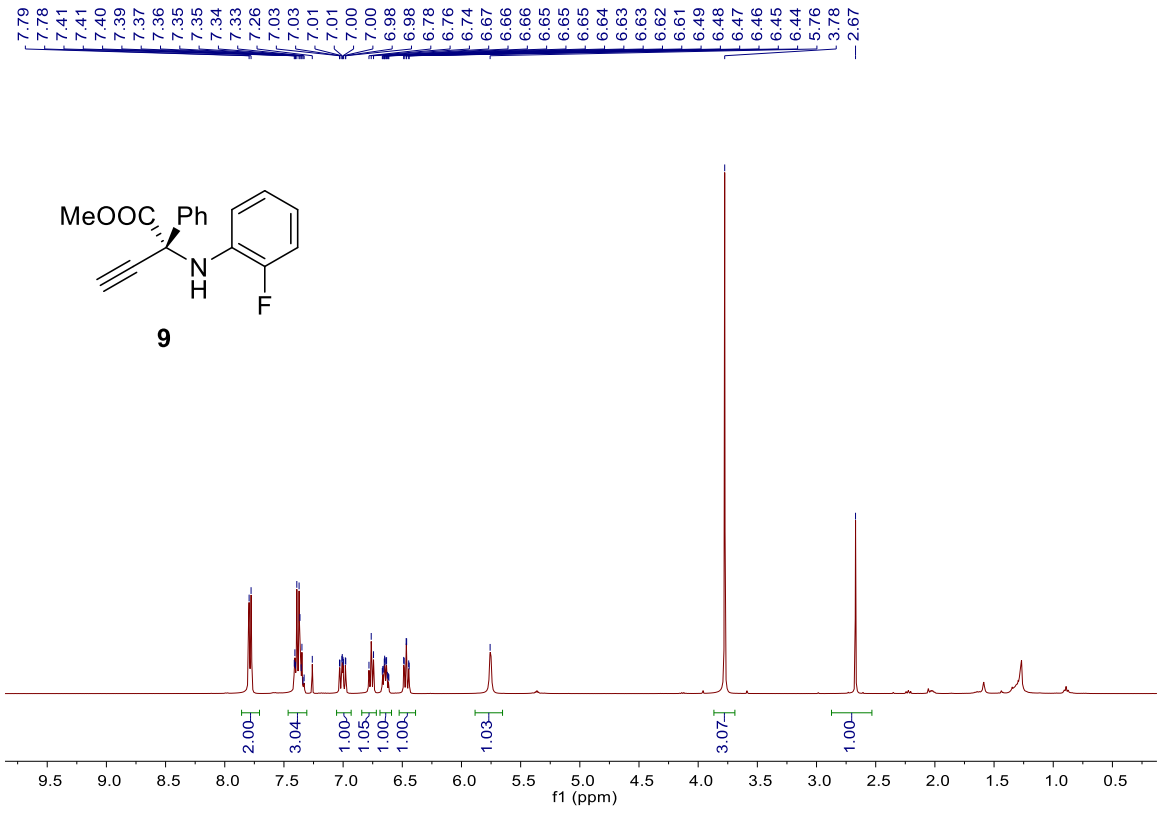
^{13}C NMR spectrum ($CDCl_3$)



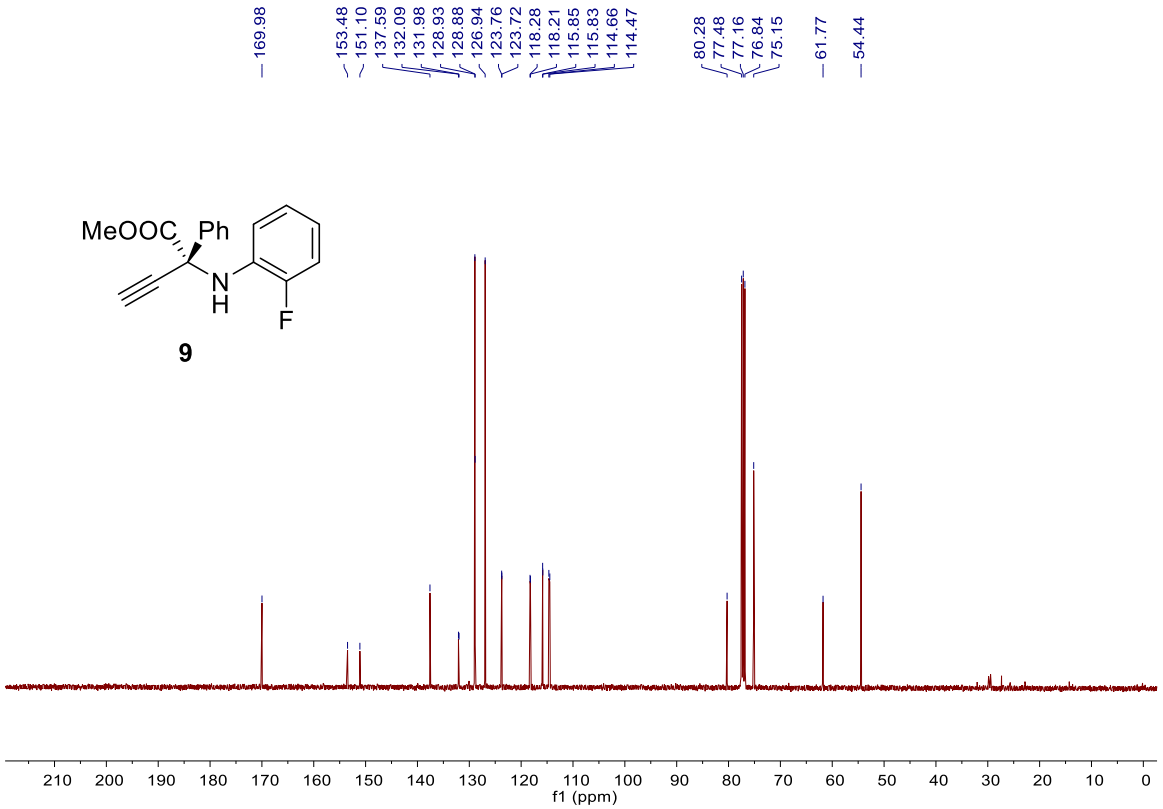
^{19}F NMR spectrum ($CDCl_3$)



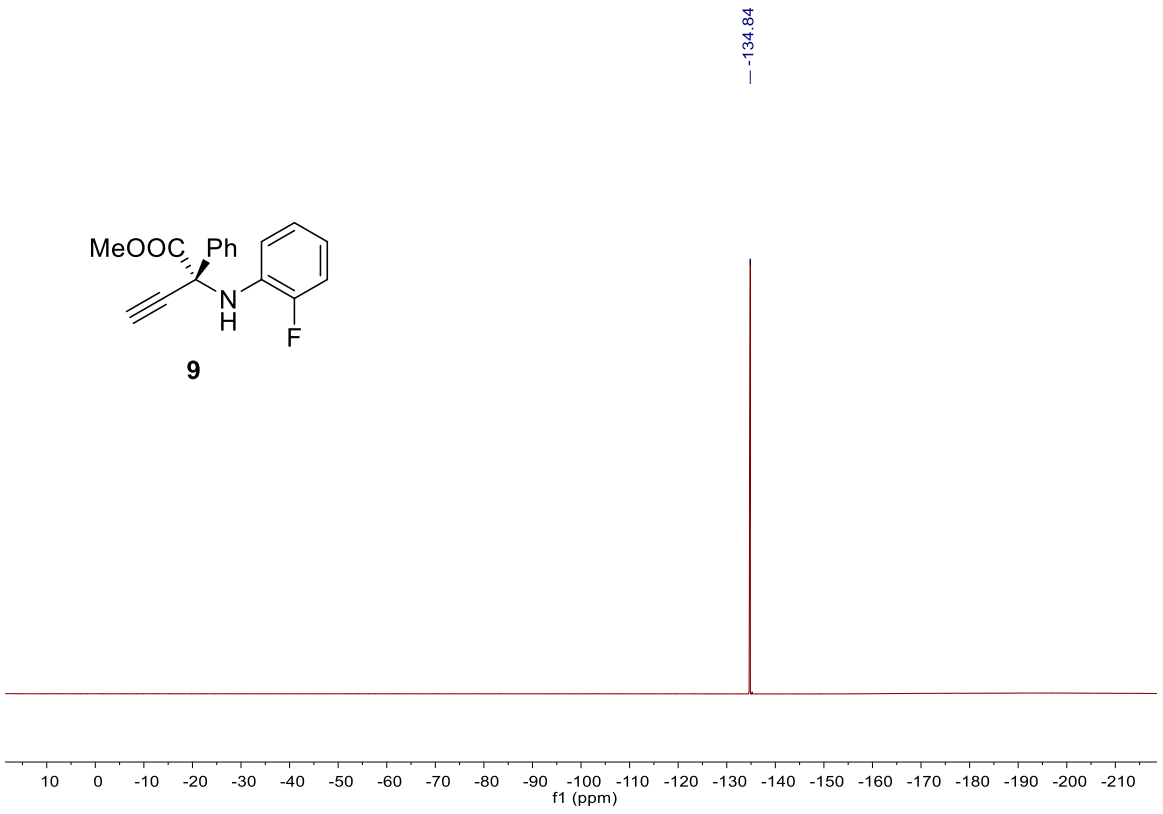
^{1}H NMR spectrum ($CDCl_3$)



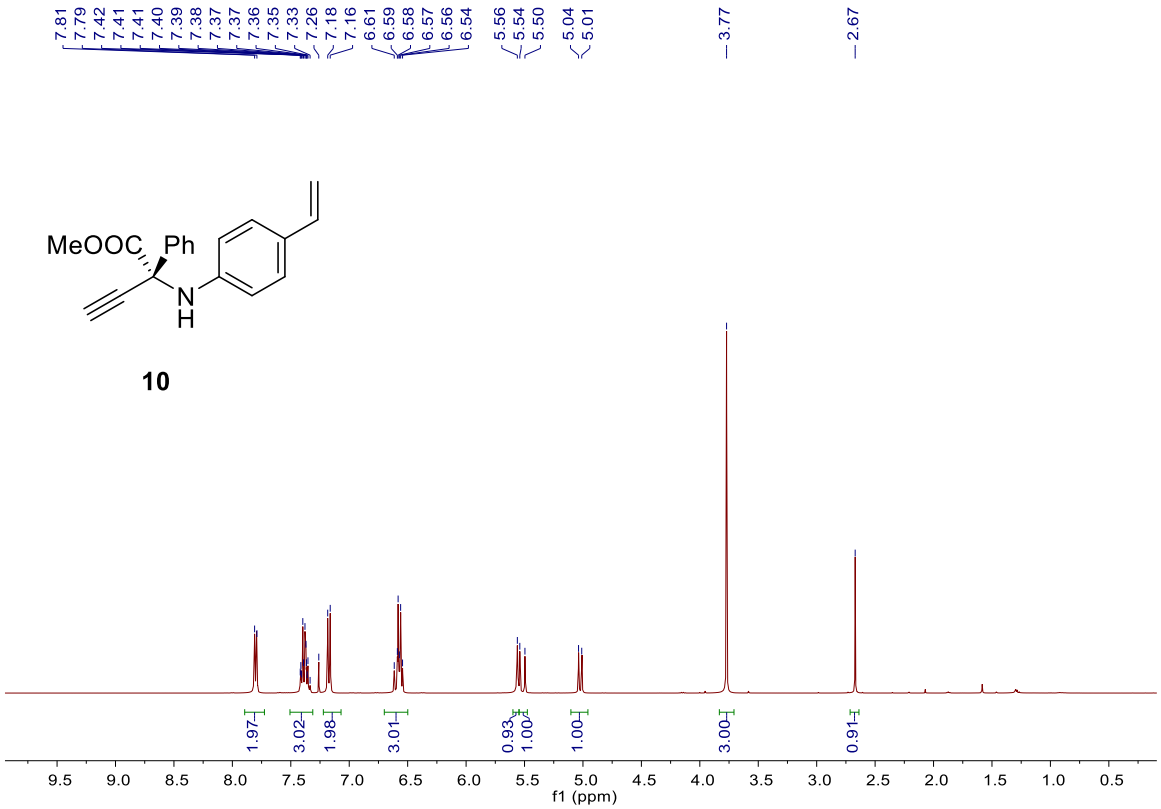
^{13}C NMR spectrum ($CDCl_3$)



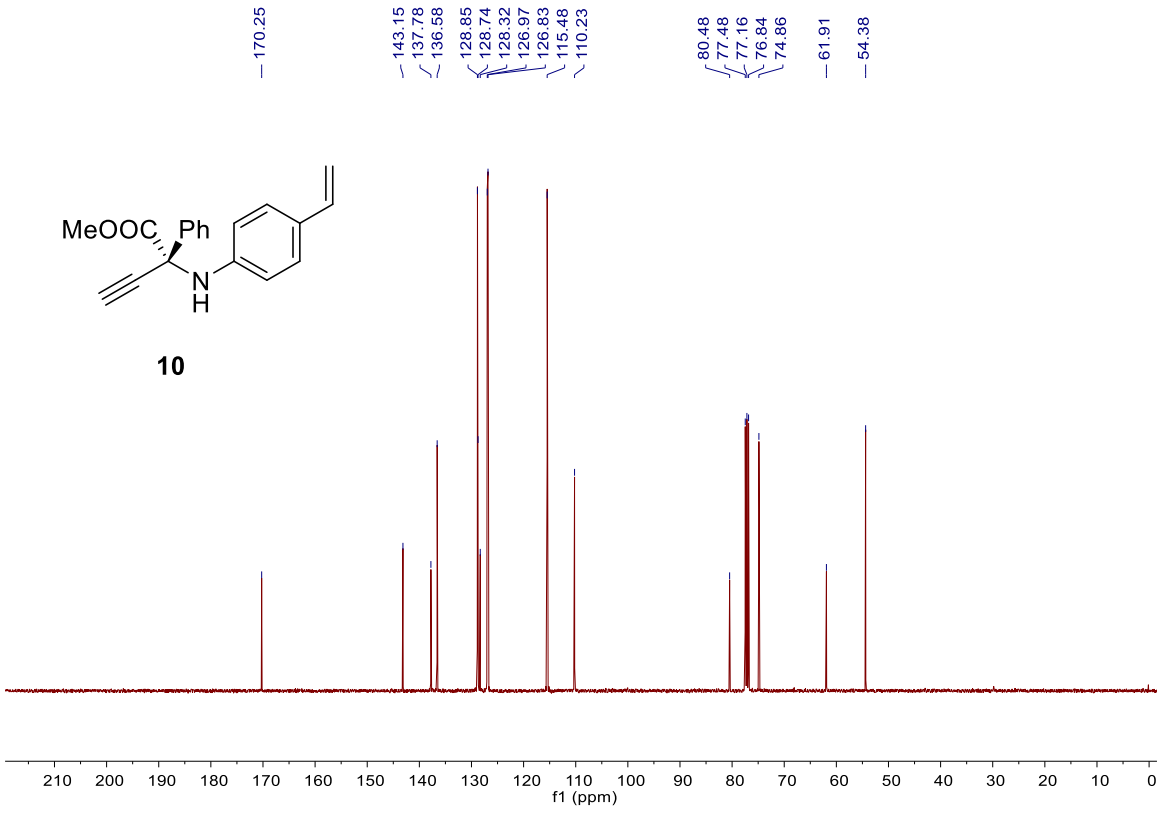
^{19}F NMR spectrum ($CDCl_3$)



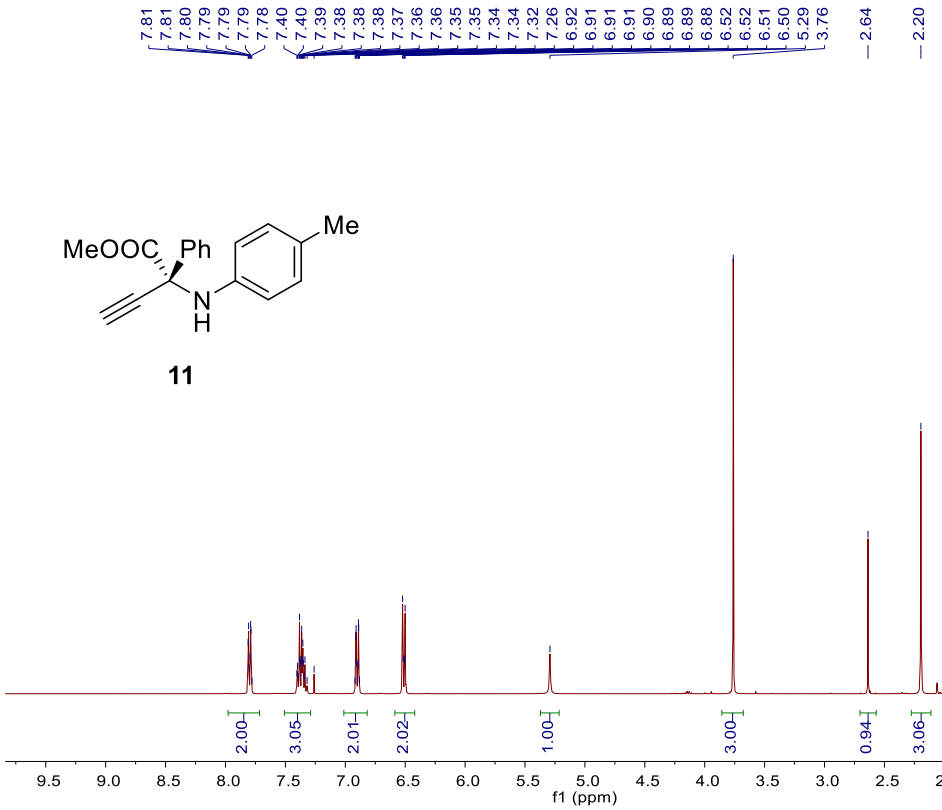
^{1}H NMR spectrum ($CDCl_3$)



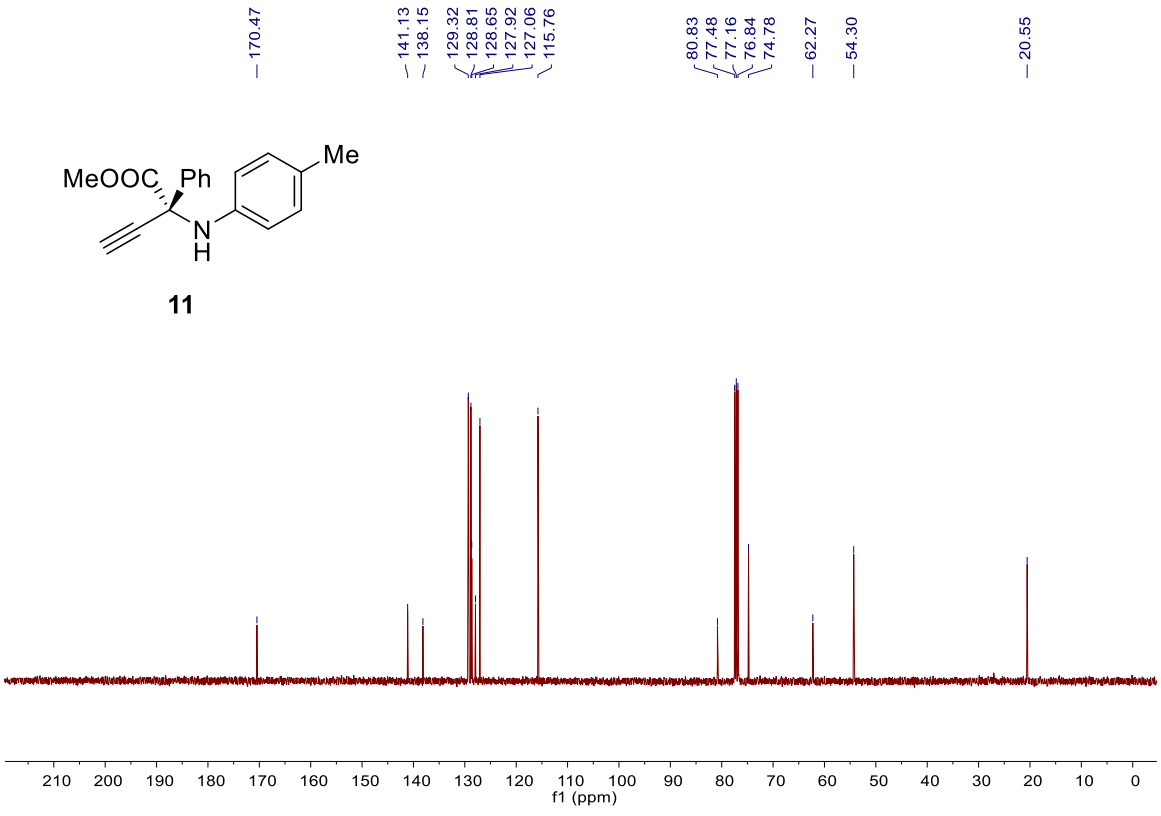
^{13}C NMR spectrum ($CDCl_3$)



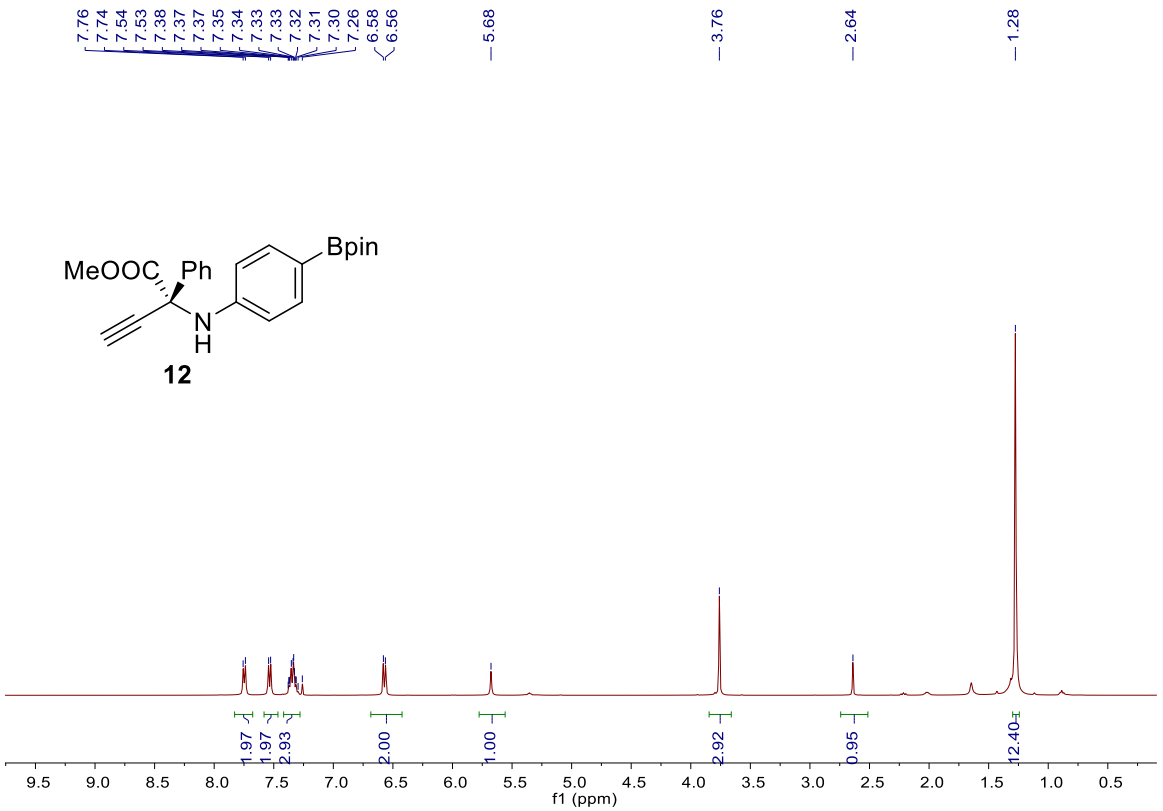
^{1}H NMR spectrum ($CDCl_3$)



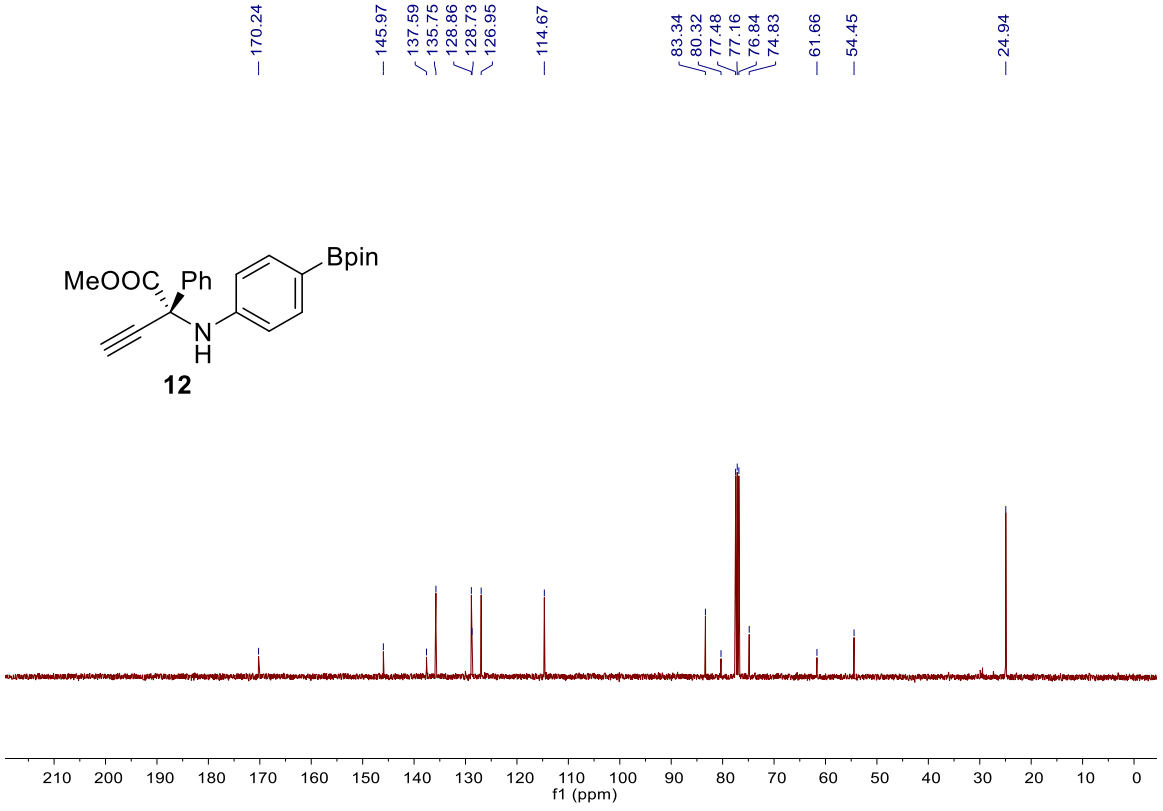
^{13}C NMR spectrum ($CDCl_3$)



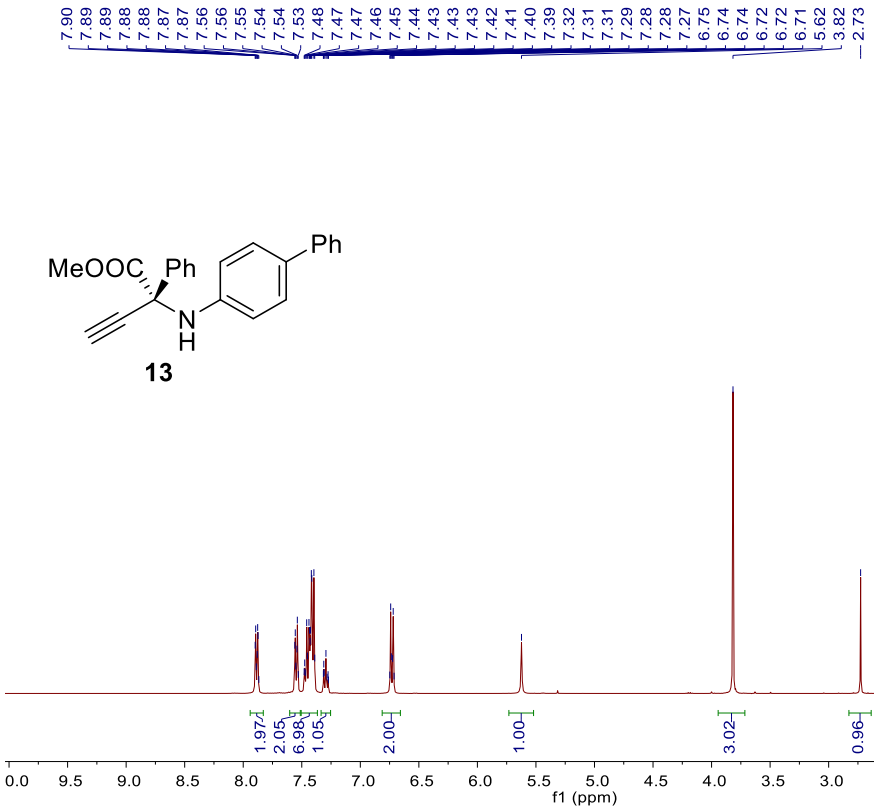
^{1}H NMR spectrum ($CDCl_3$)



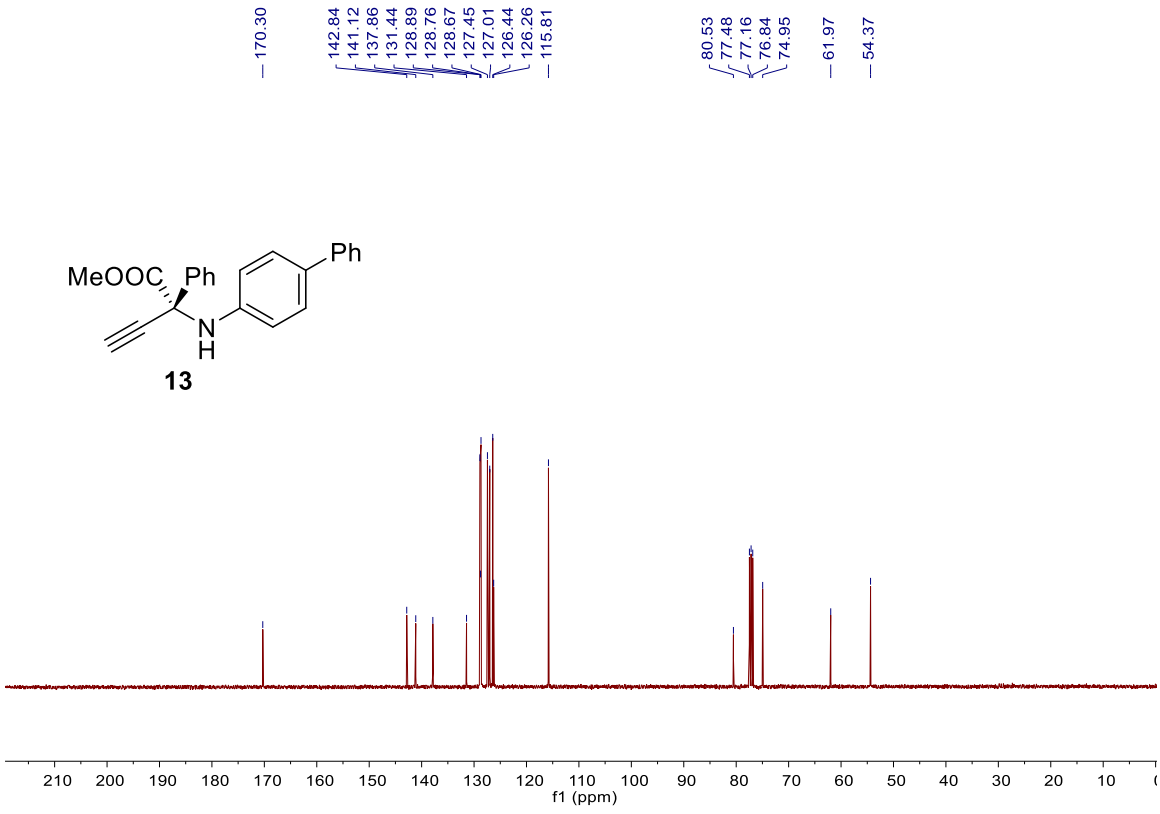
^{13}C NMR spectrum ($CDCl_3$)



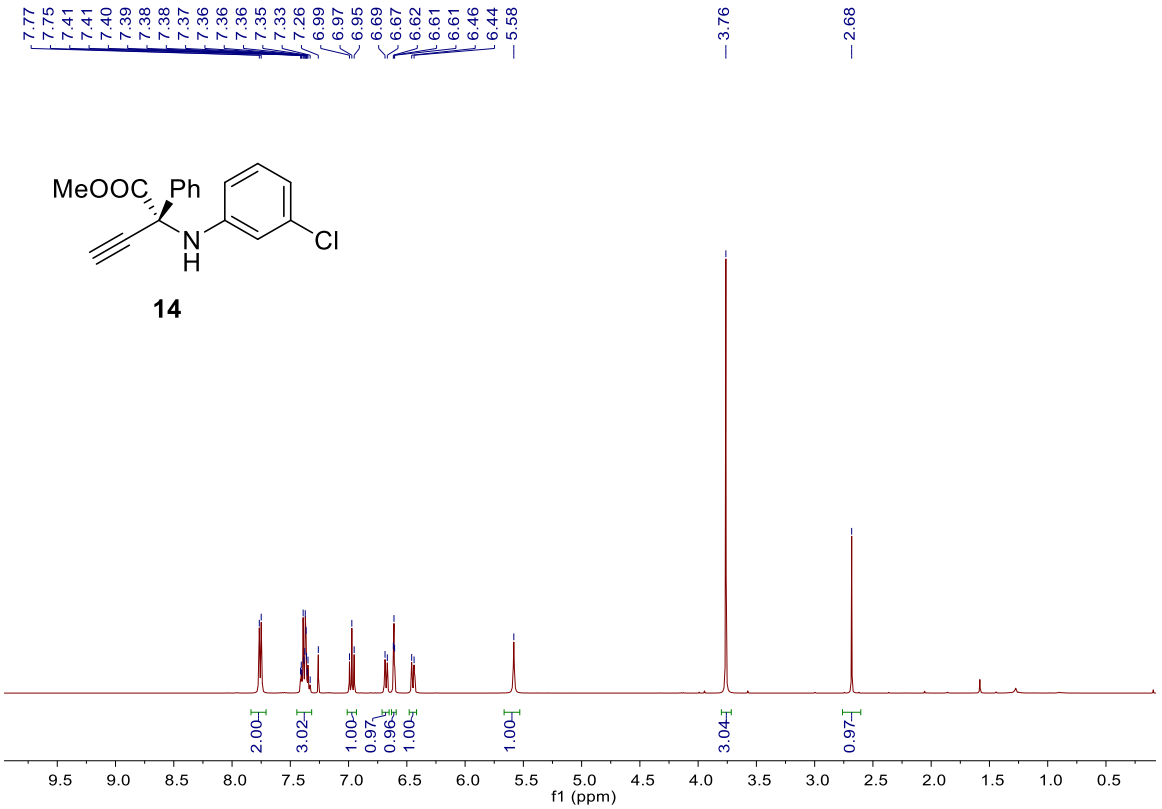
^{1}H NMR spectrum ($CDCl_3$)



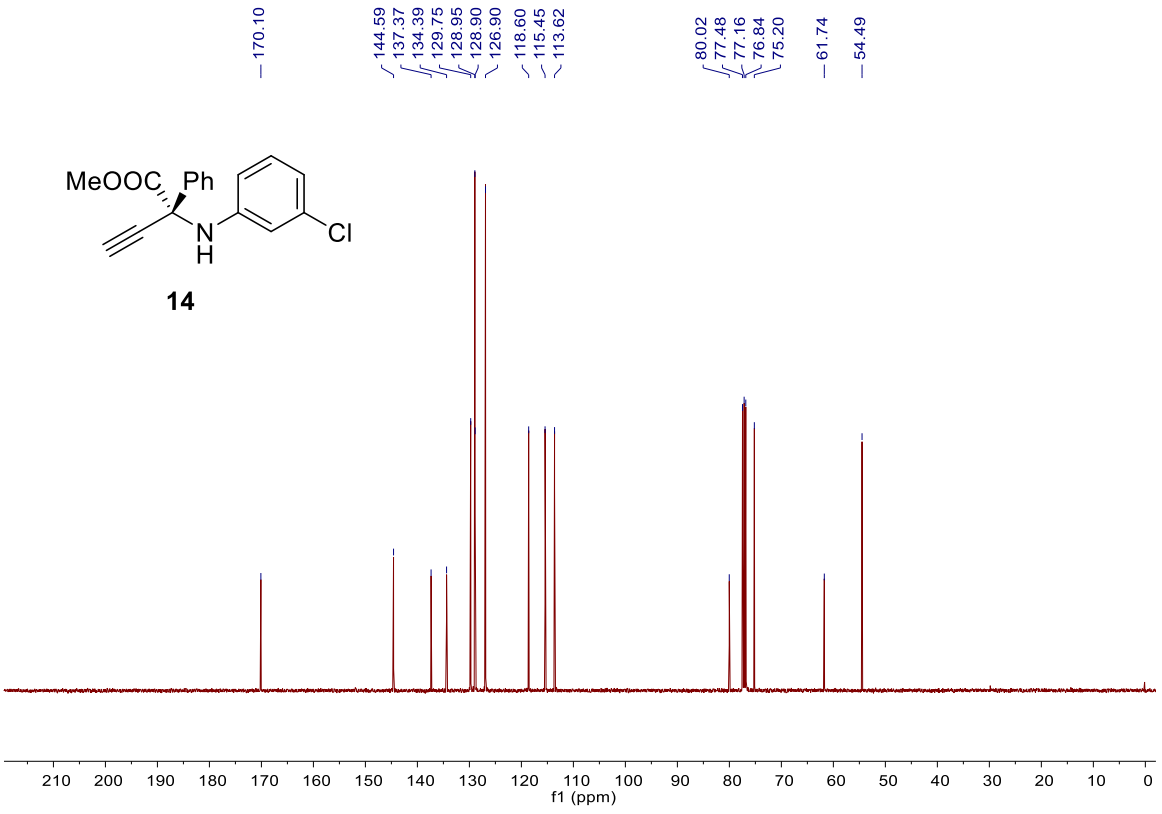
^{13}C NMR spectrum ($CDCl_3$)



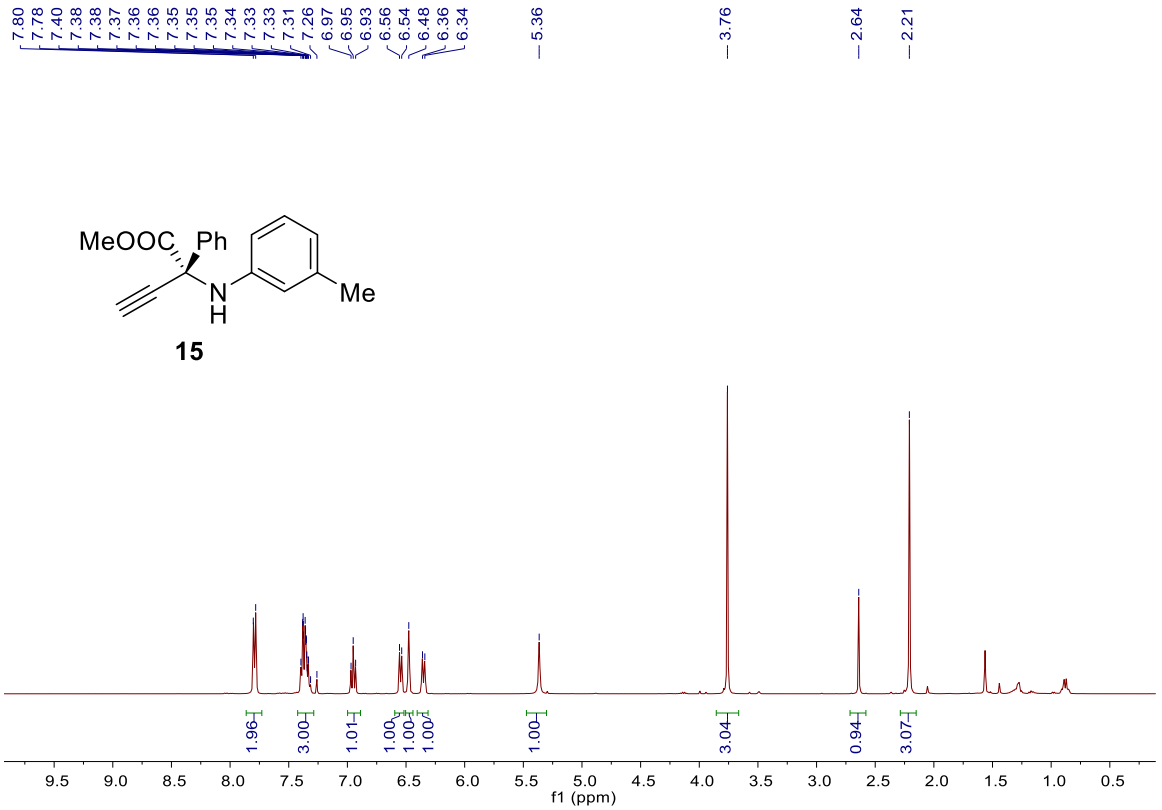
^{1}H NMR spectrum ($CDCl_3$)



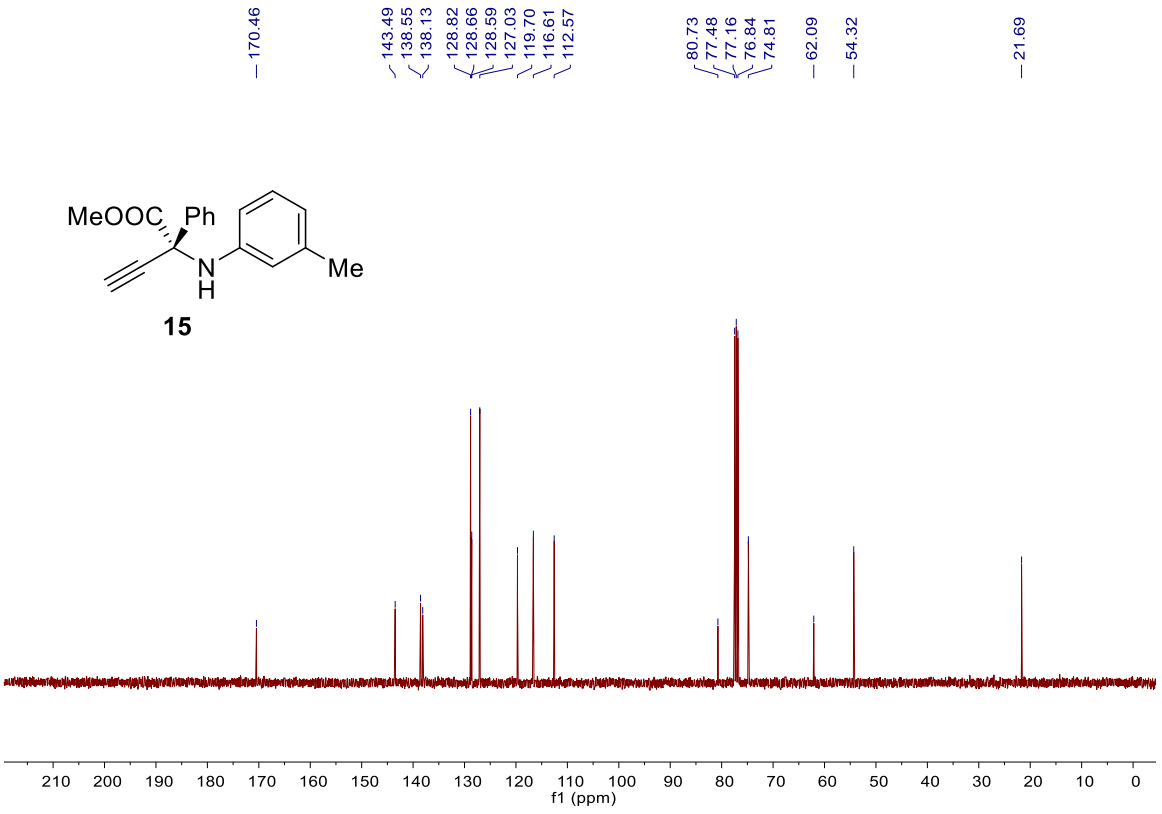
^{13}C NMR spectrum ($CDCl_3$)



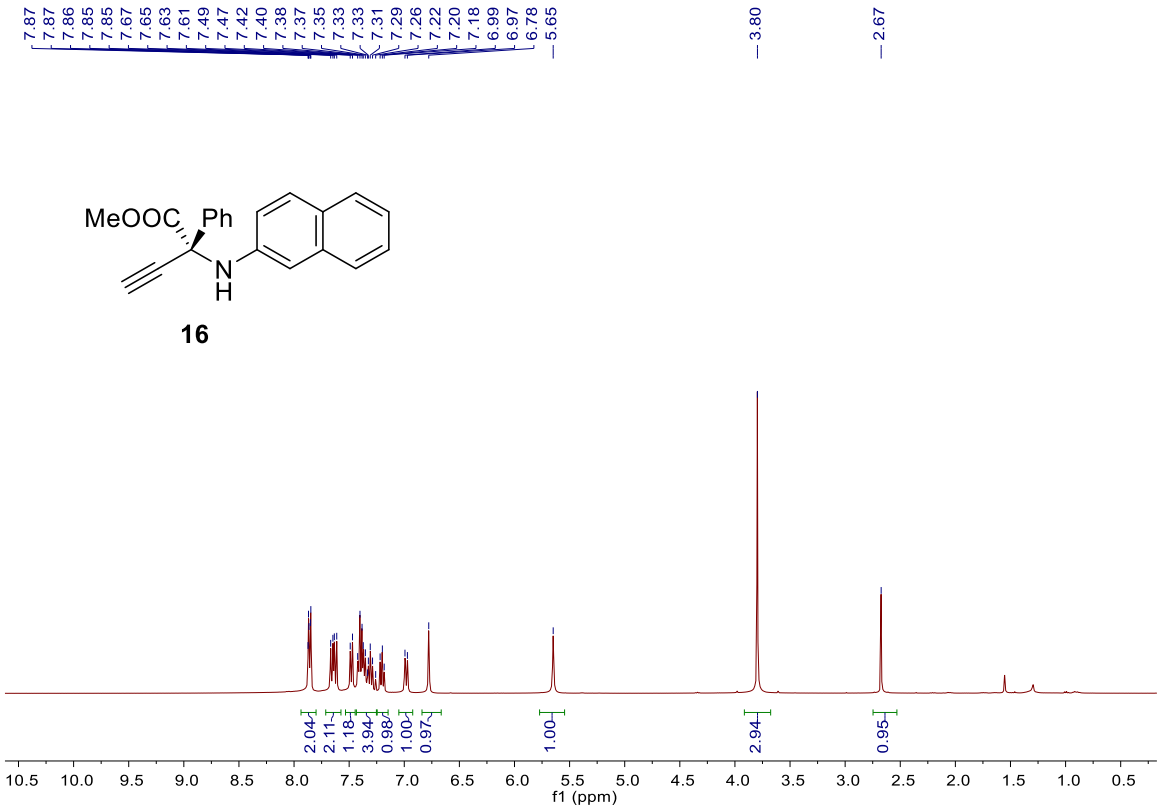
^{1}H NMR spectrum ($CDCl_3$)



^{13}C NMR spectrum ($CDCl_3$)



^{1}H NMR spectrum ($CDCl_3$)



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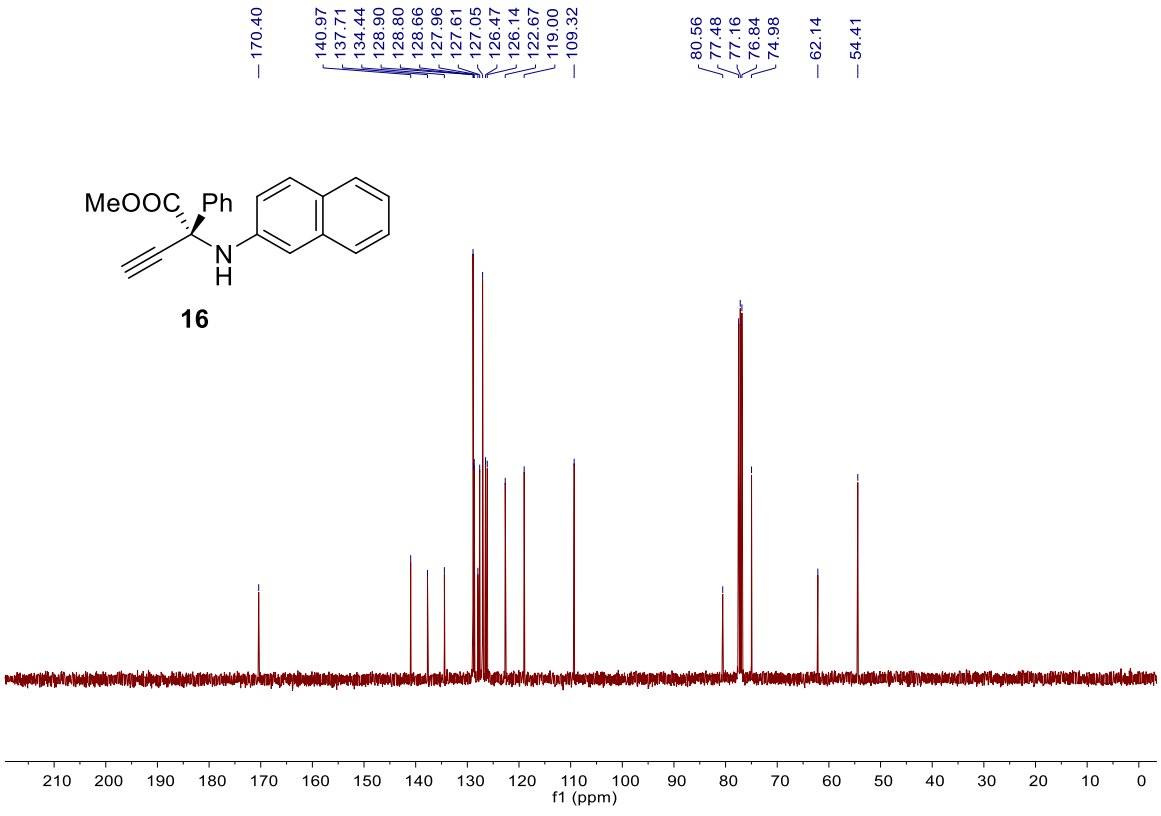
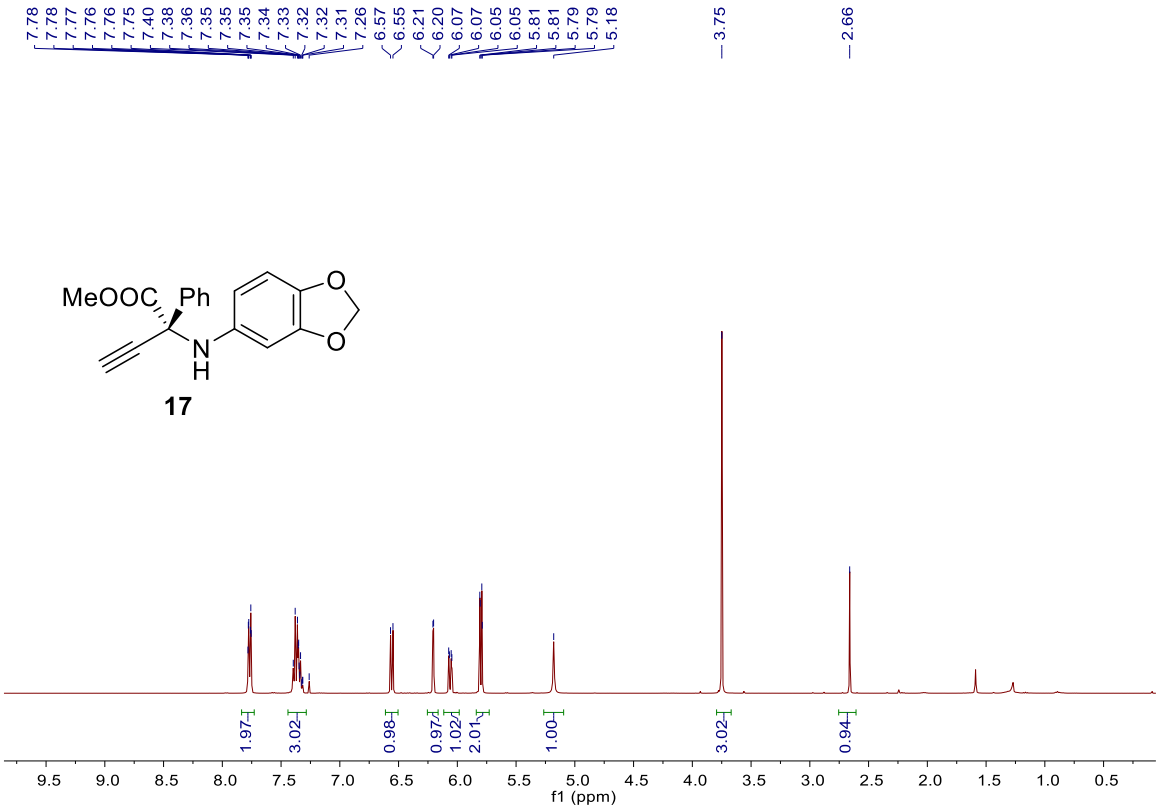


^{1}H NMR spectrum ($CDCl_3$)



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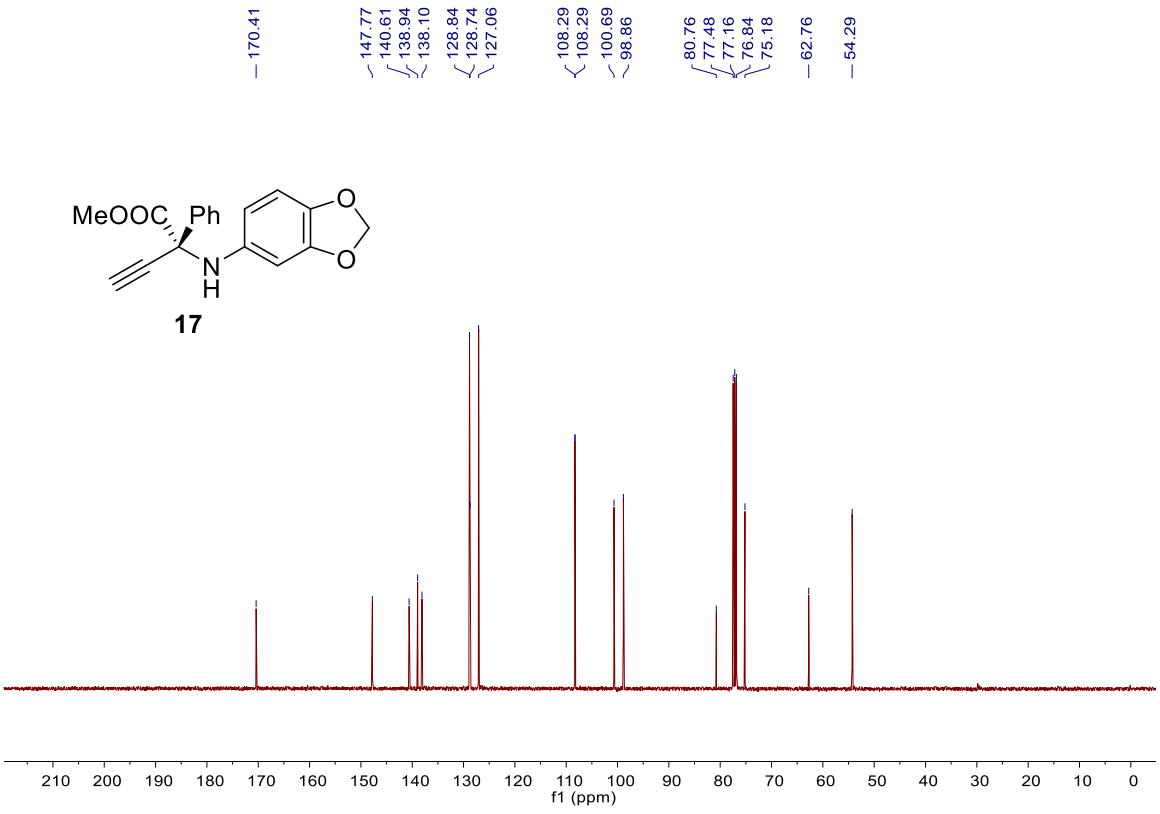

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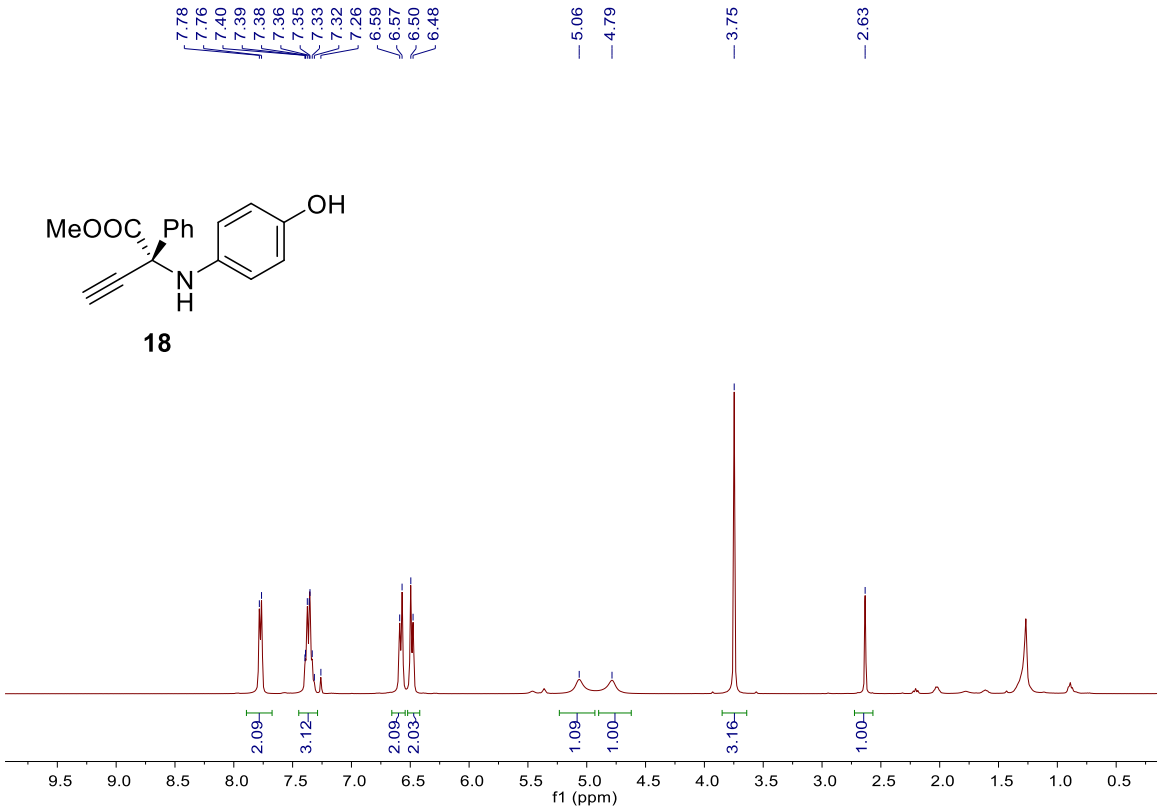
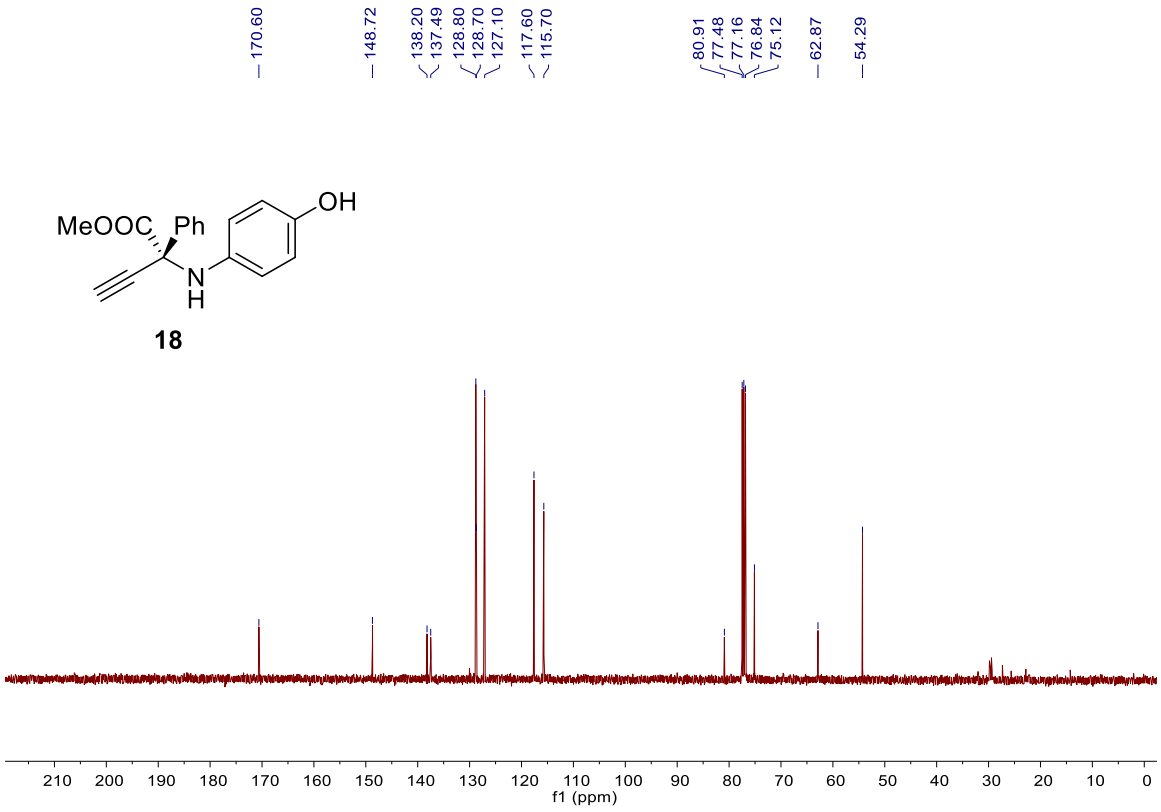


^{13}C NMR spectrum ($CDCl_3$)



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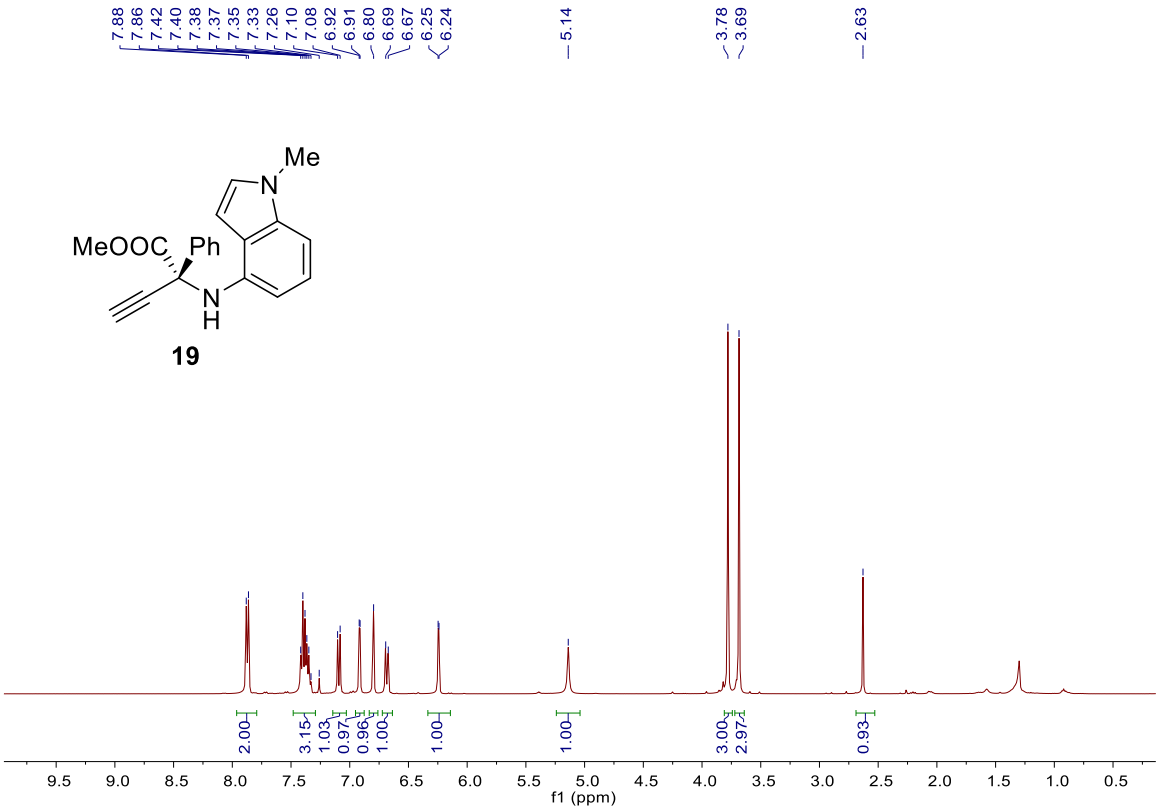
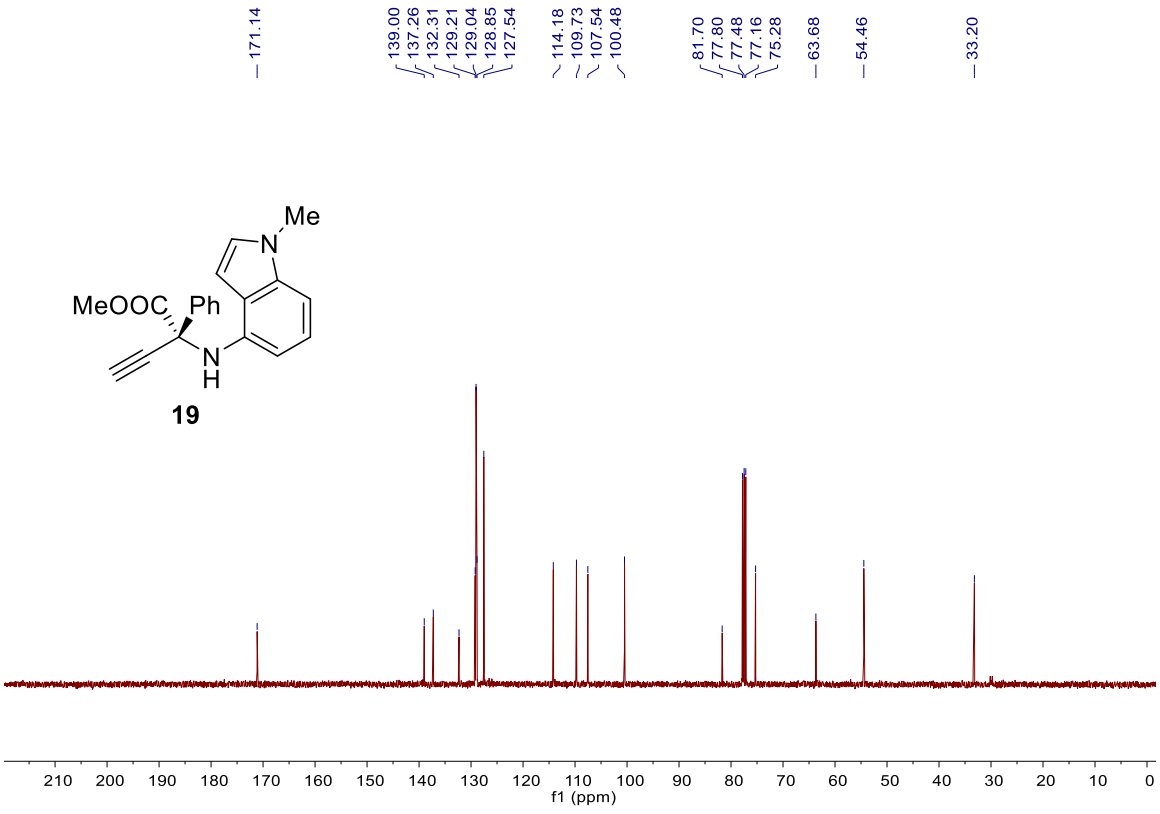


^{13}C NMR spectrum ($CDCl_3$)



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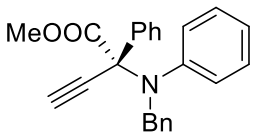

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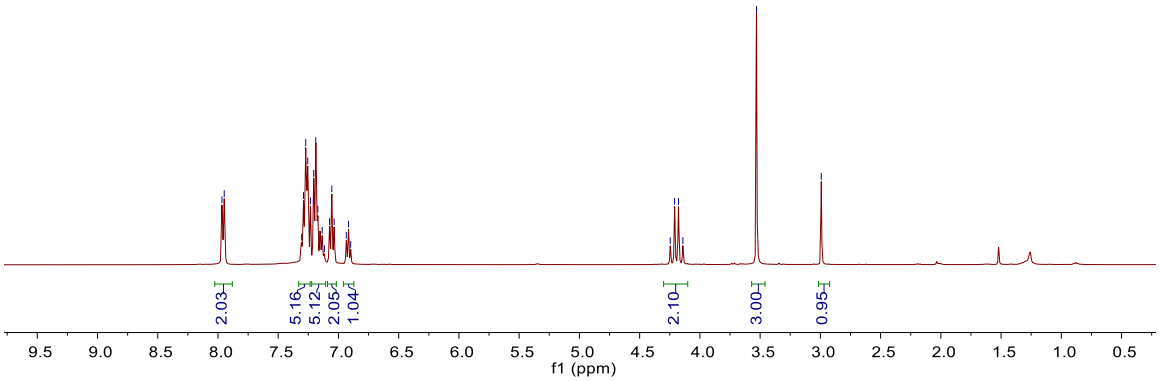
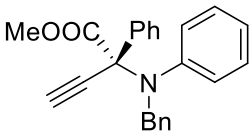


^{13}C NMR spectrum ($CDCl_3$)



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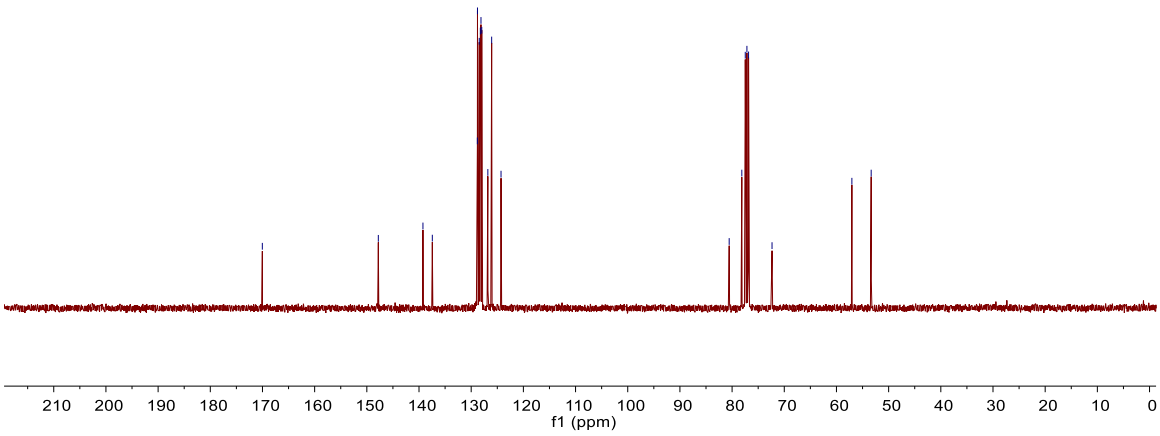
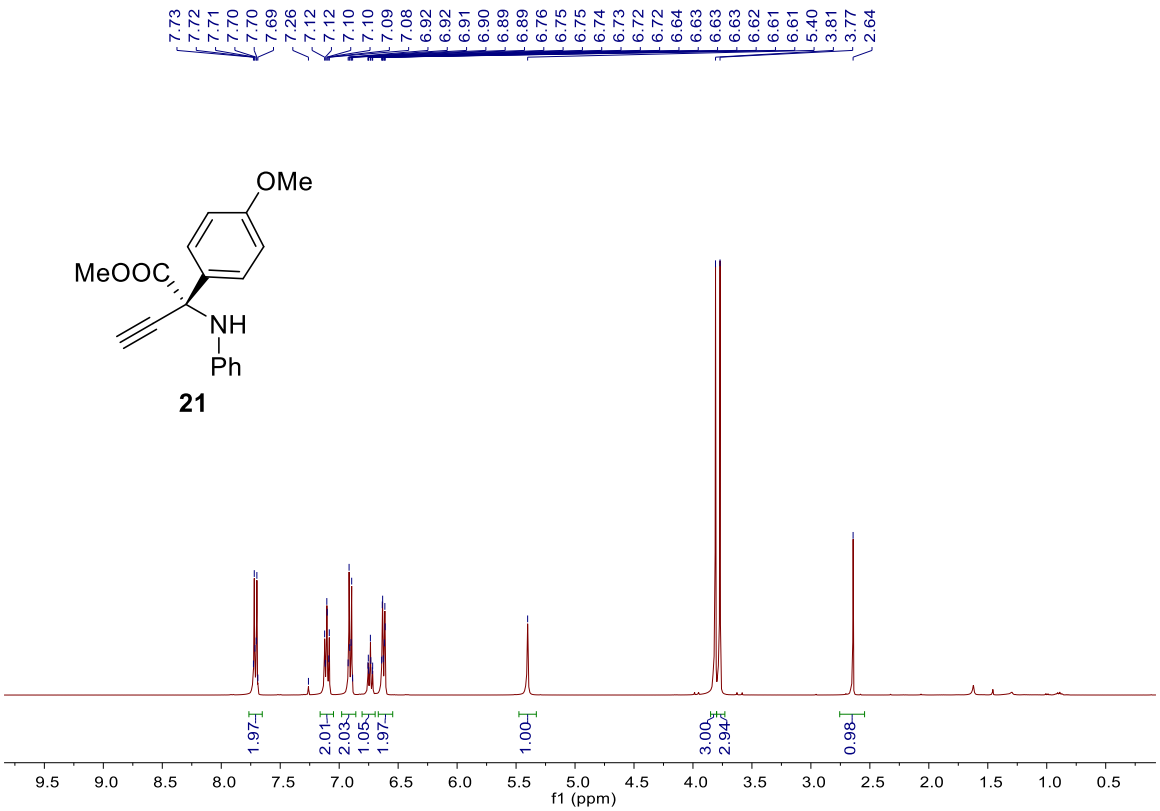
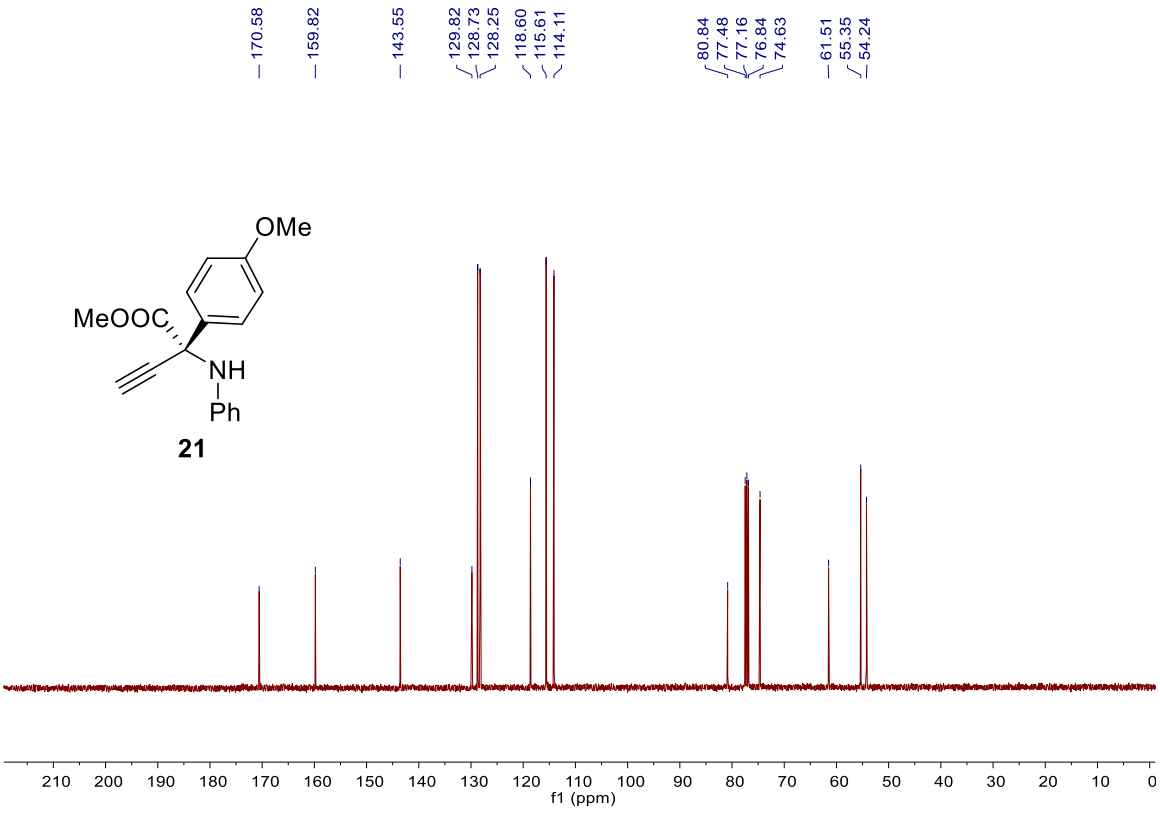


^{1}H NMR spectrum ($CDCl_3$)



^{13}C NMR spectrum ($CDCl_3$)



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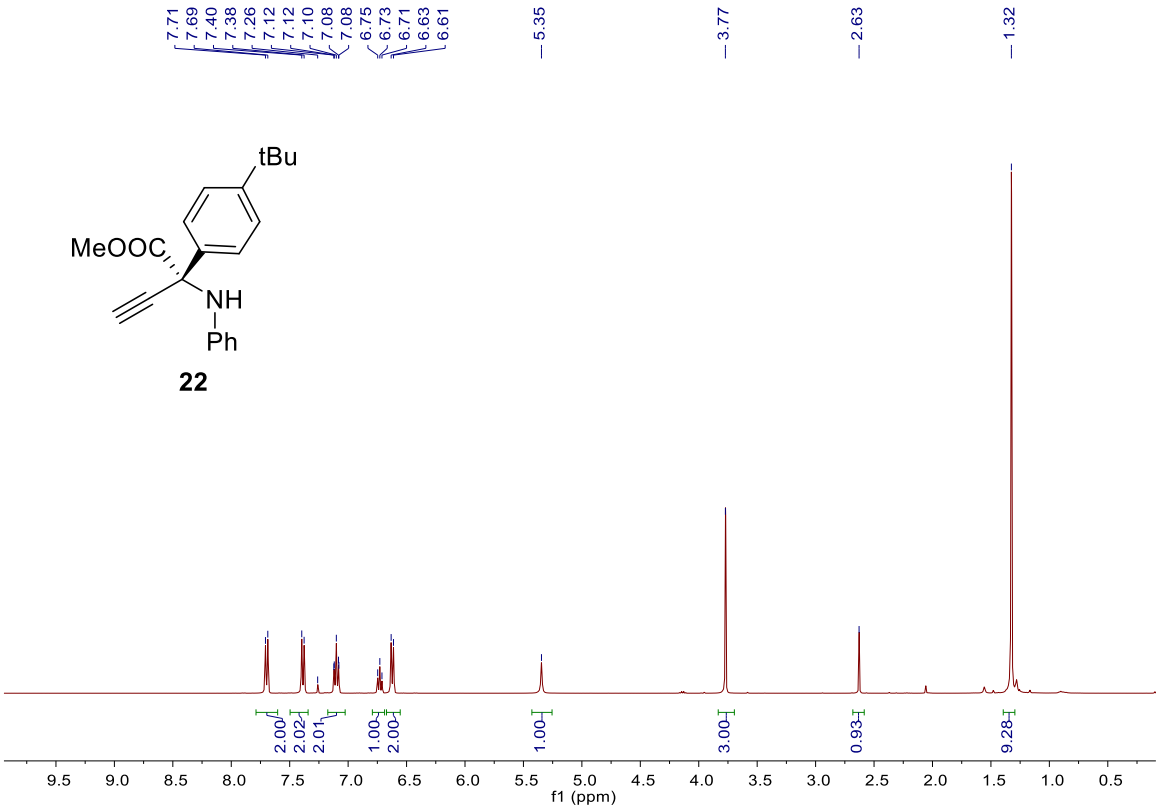

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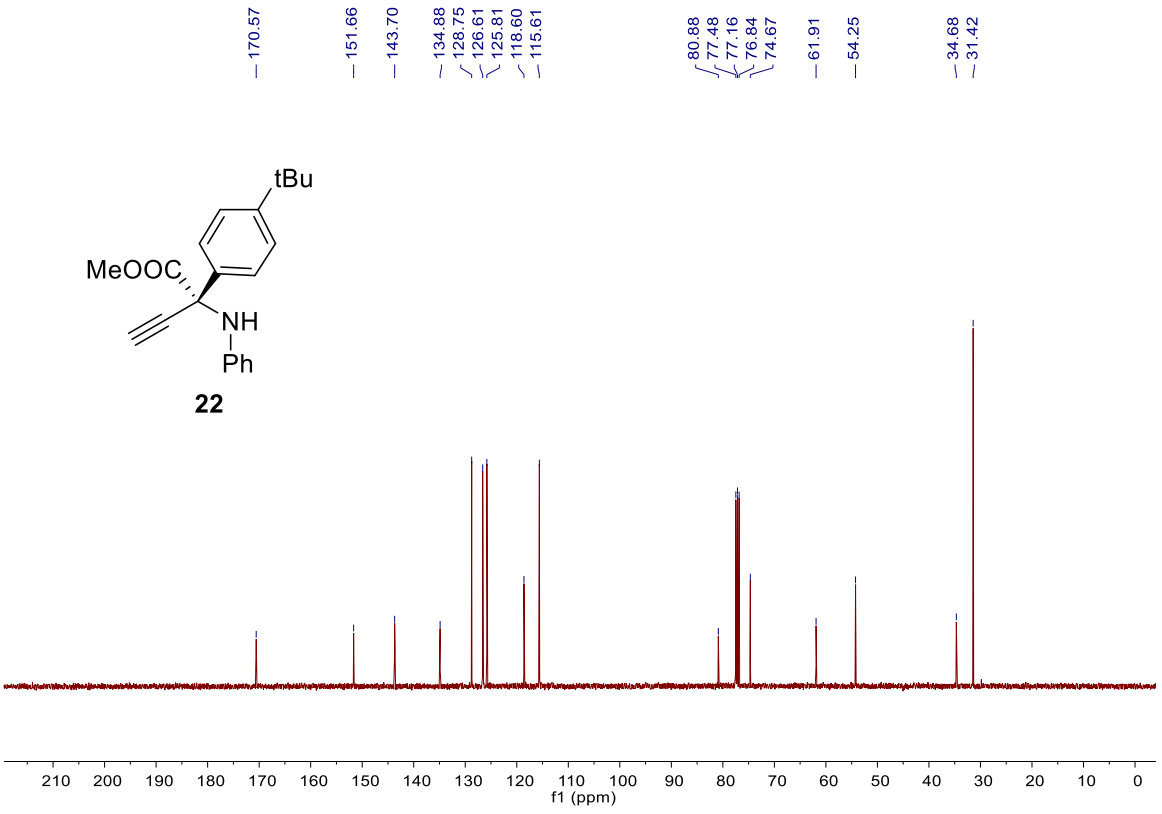

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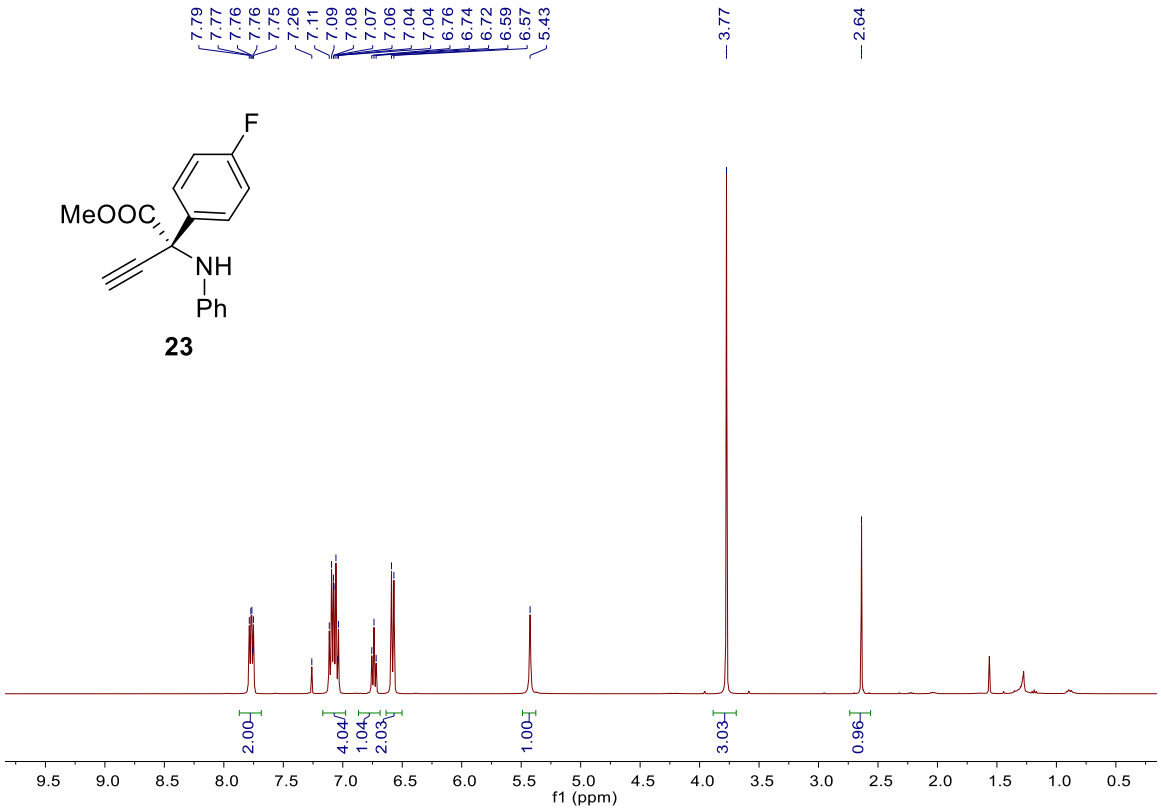

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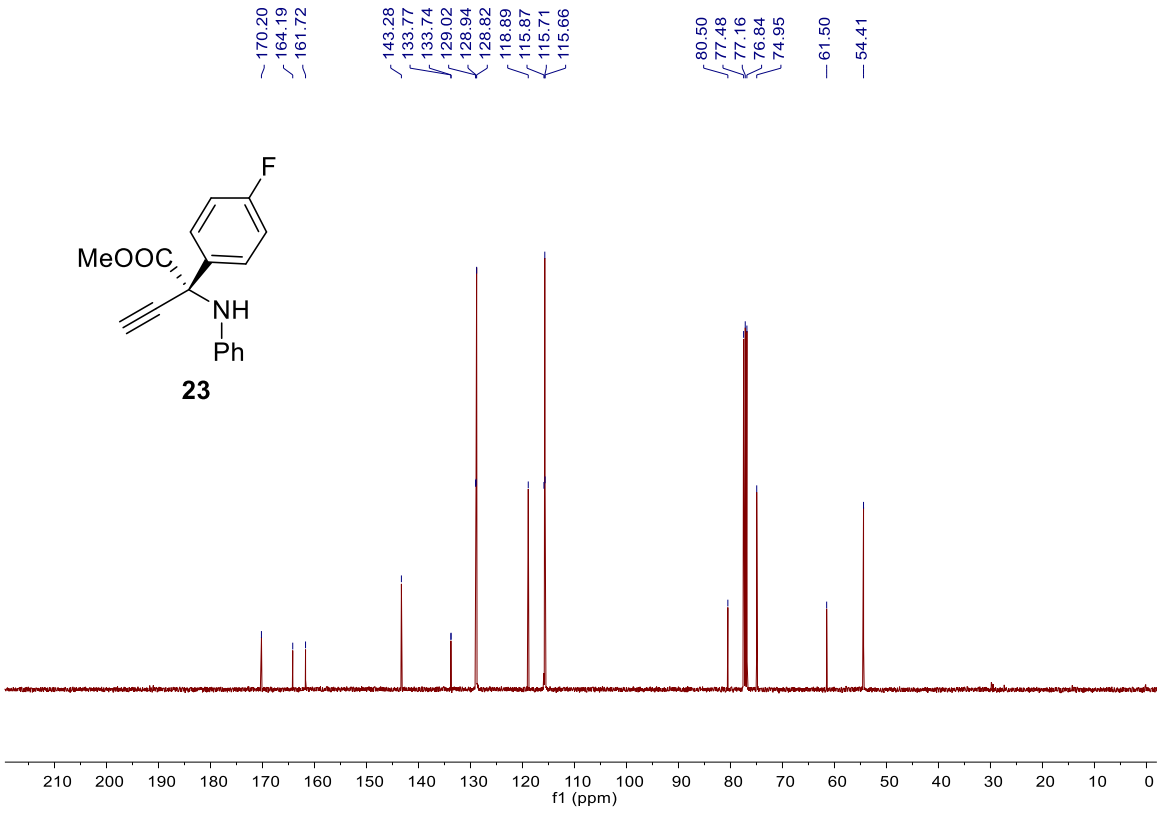
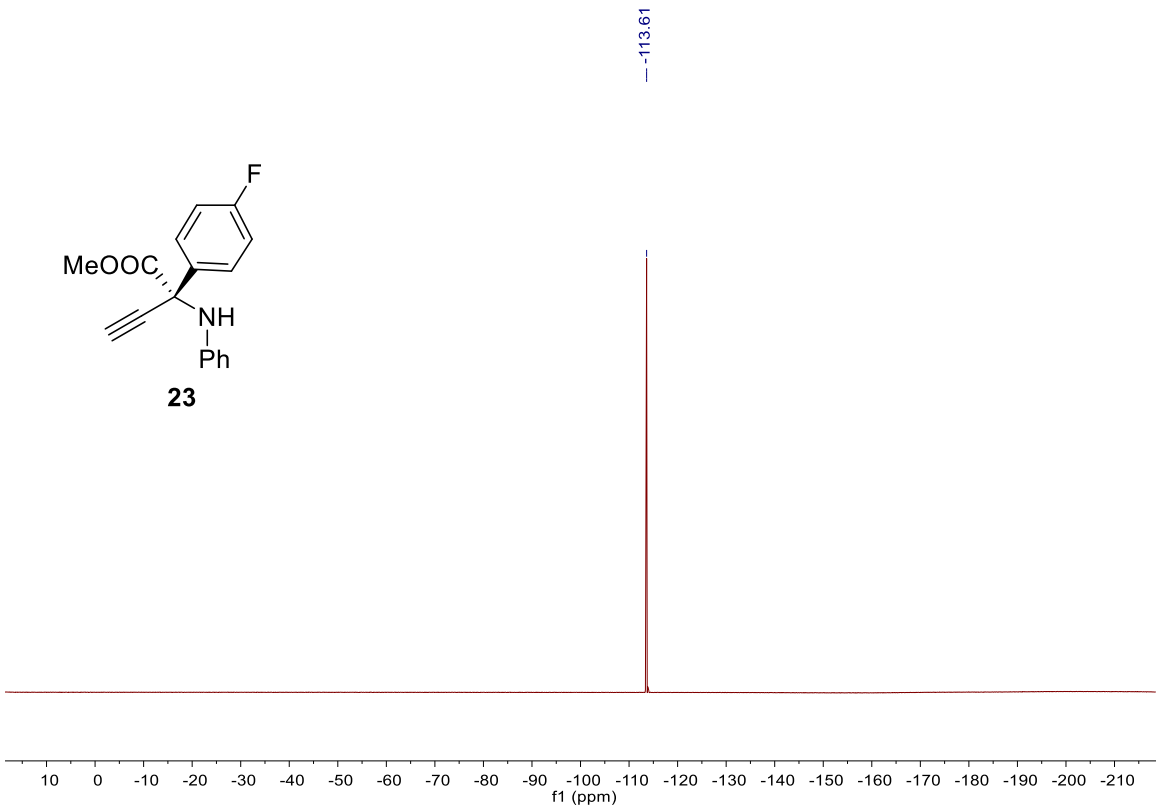
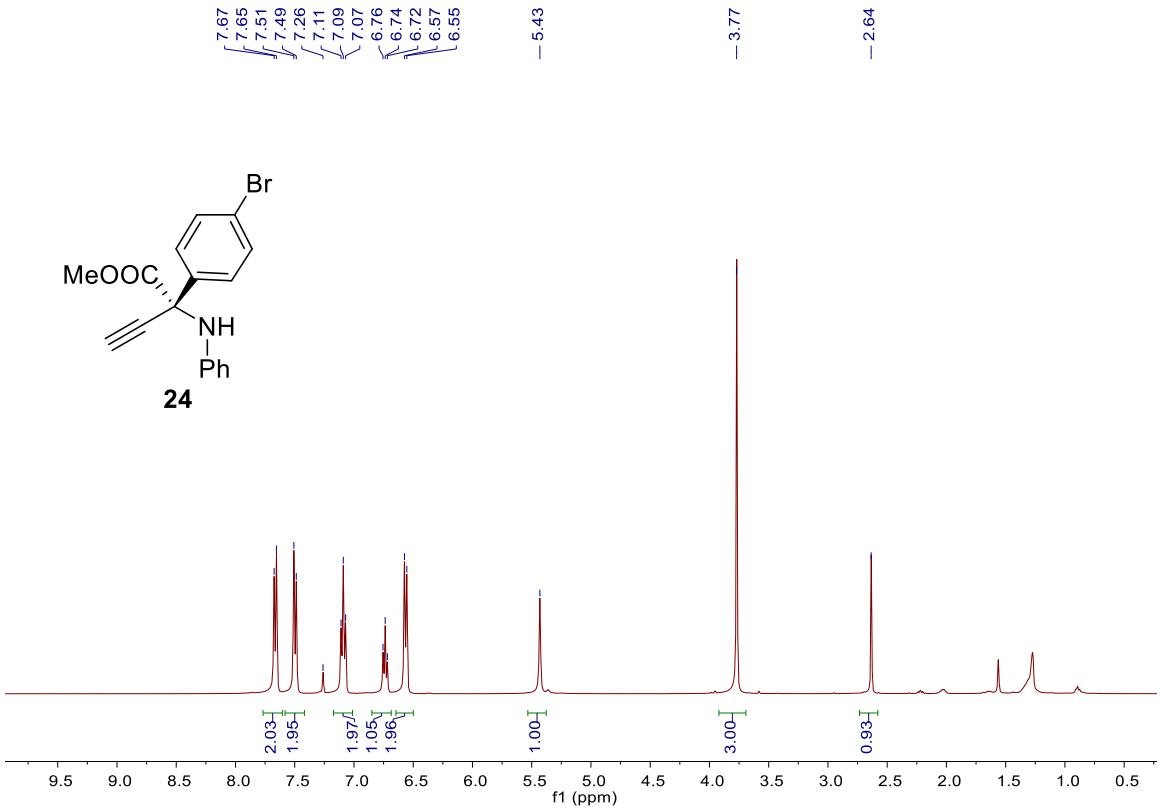


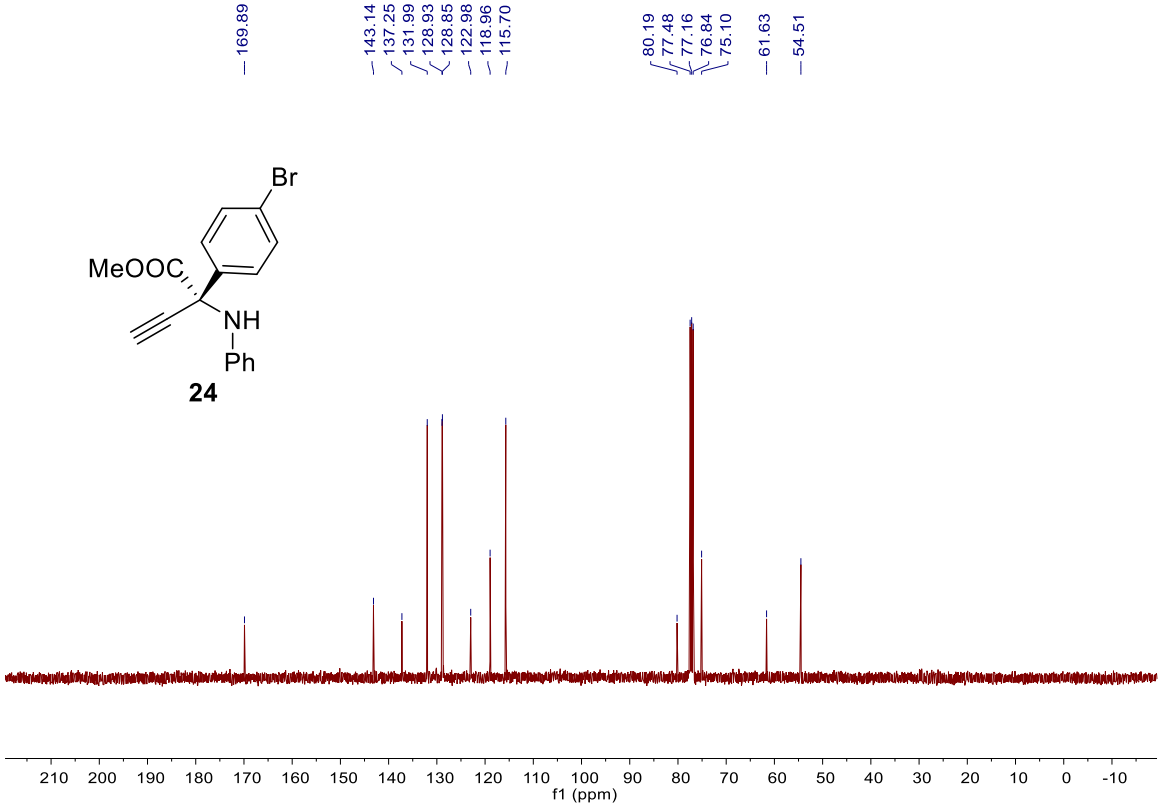
^{19}F NMR spectrum ($CDCl_3$)



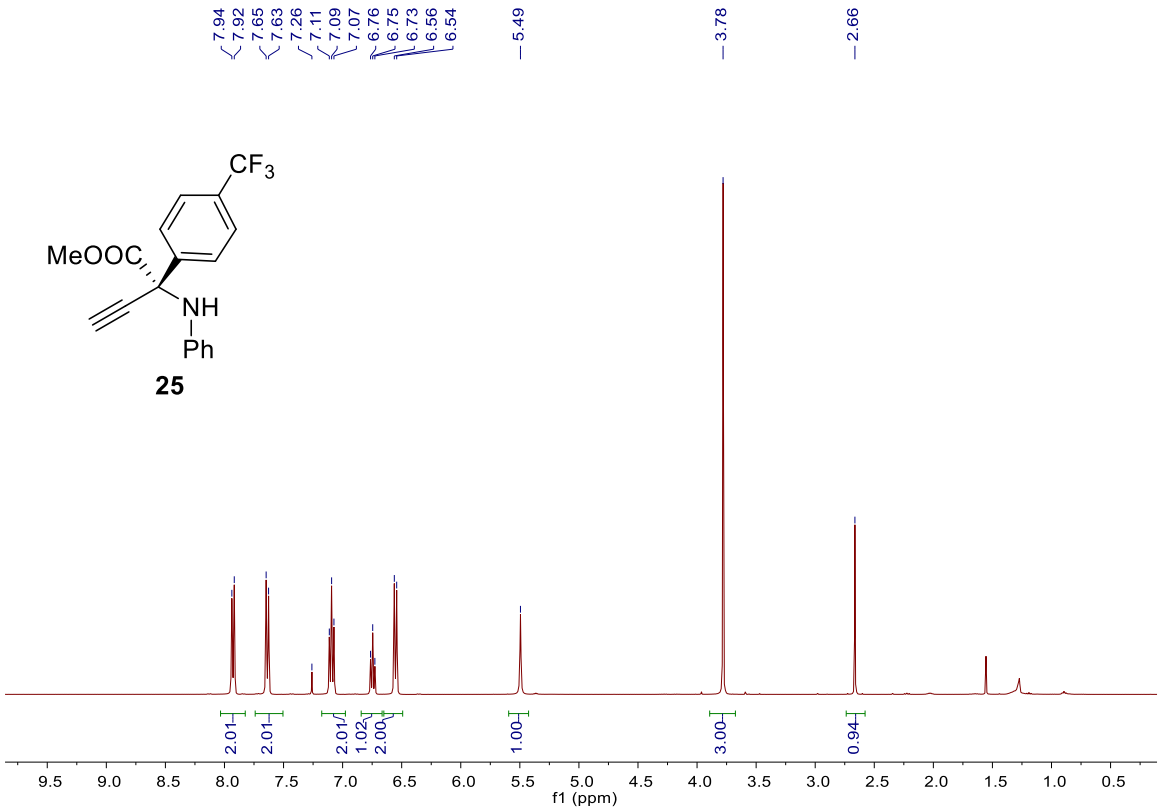
^{1}H NMR spectrum ($CDCl_3$)



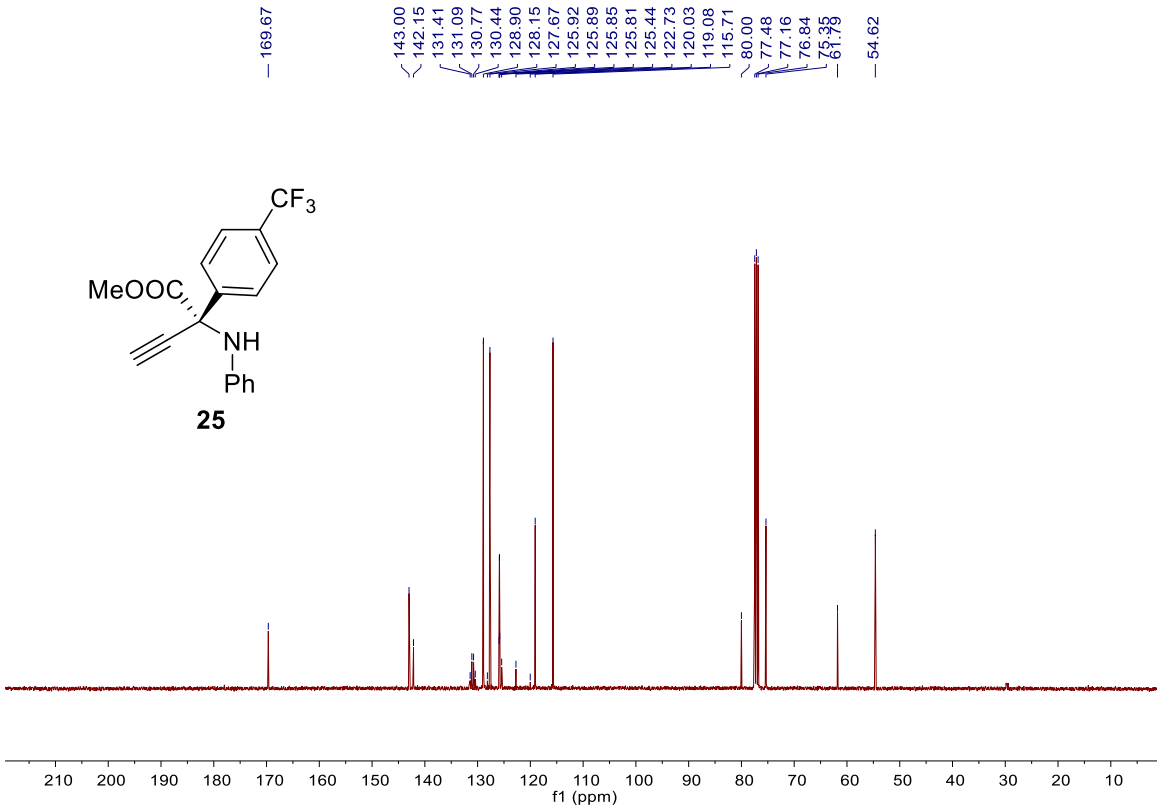
^{13}C NMR spectrum ($CDCl_3$)



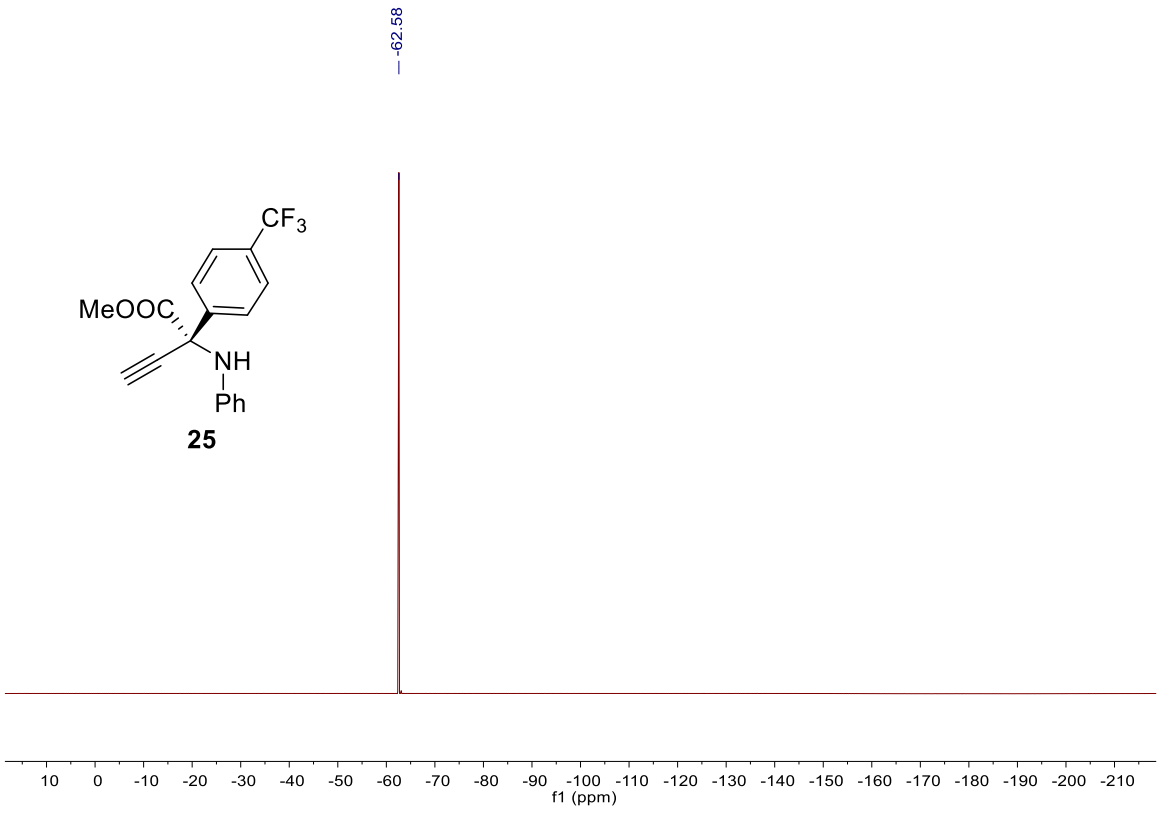
^{1}H NMR spectrum ($CDCl_3$)



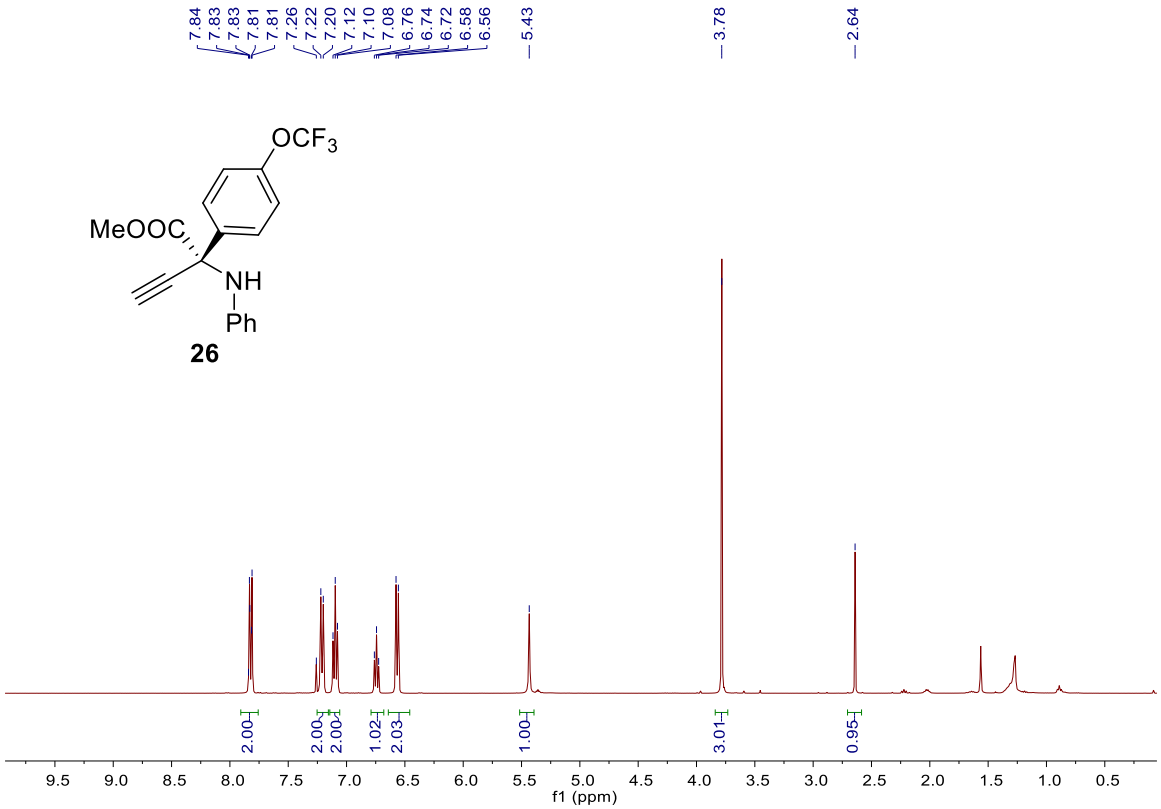
^{13}C NMR spectrum ($CDCl_3$)



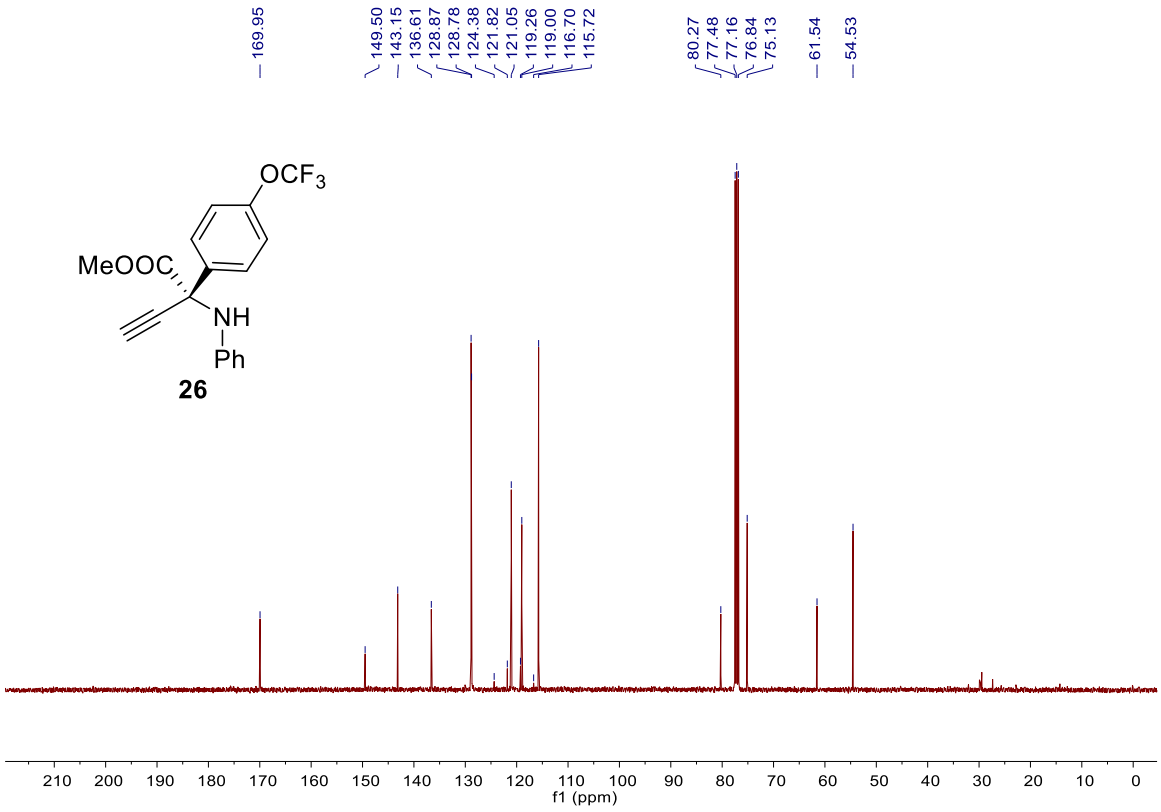
^{19}F NMR spectrum ($CDCl_3$)



^{1}H NMR spectrum ($CDCl_3$)



^{13}C NMR spectrum ($CDCl_3$)



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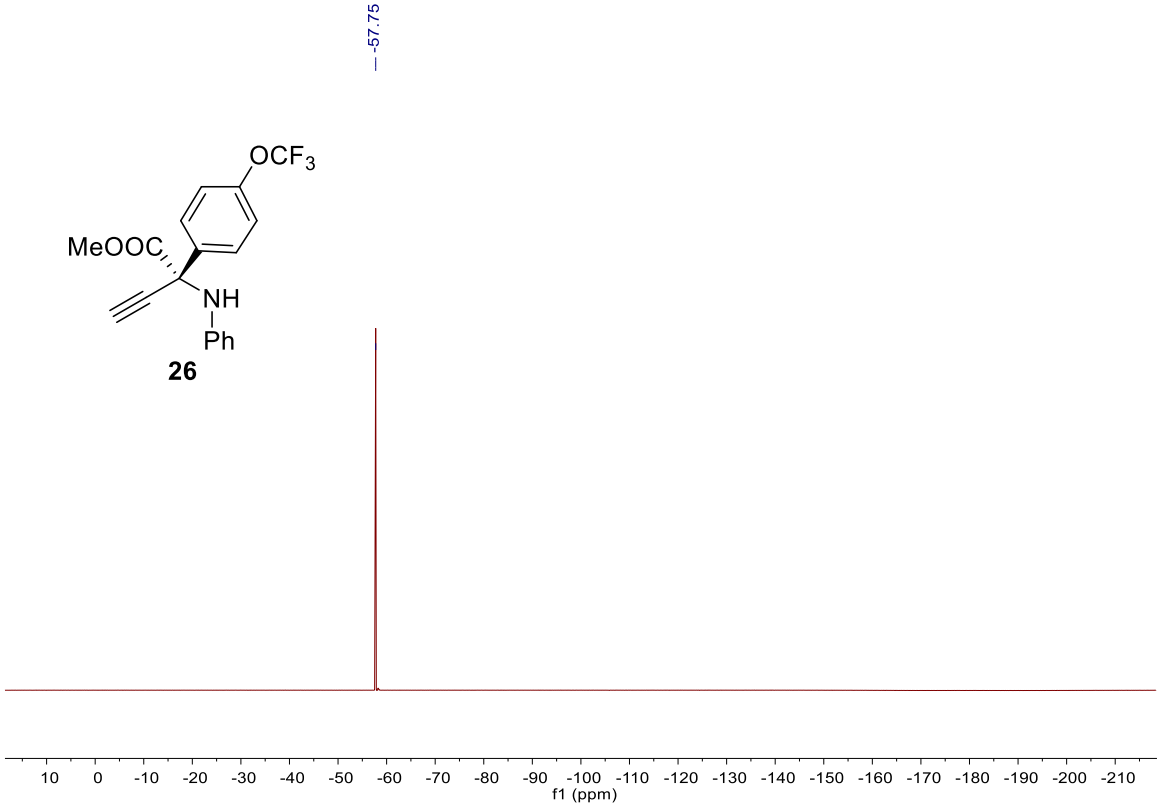
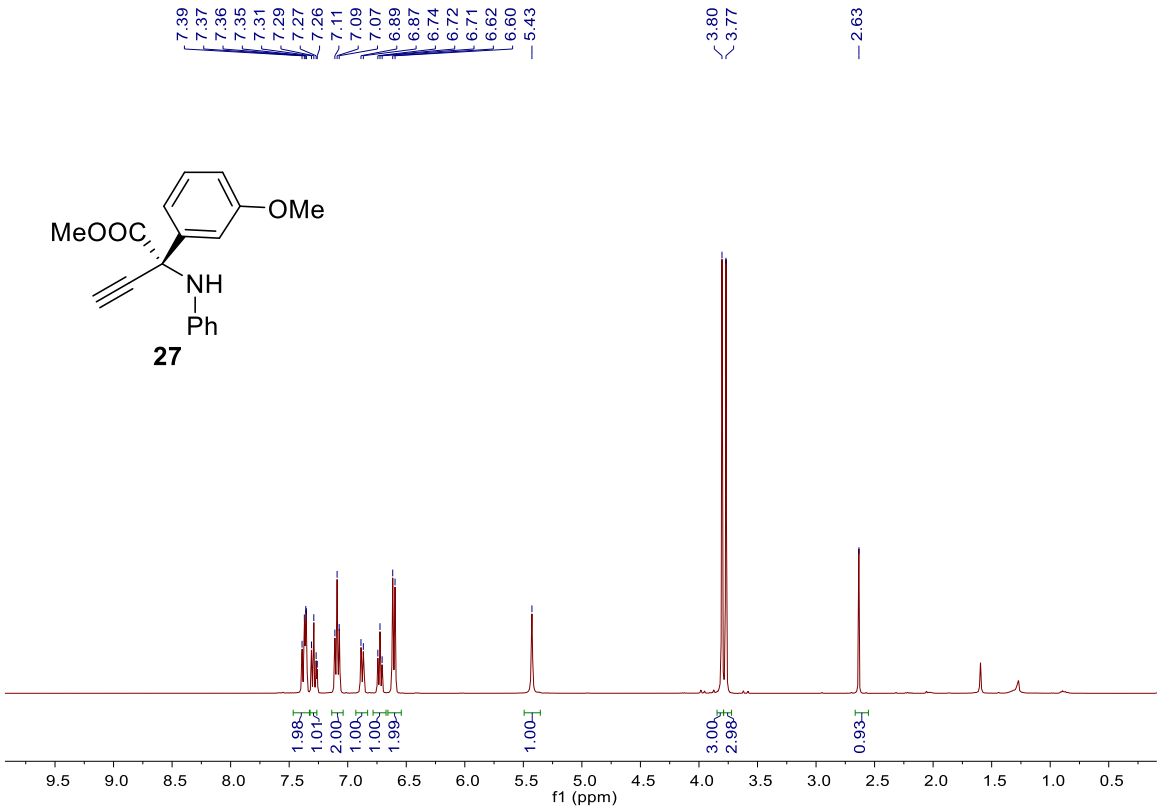
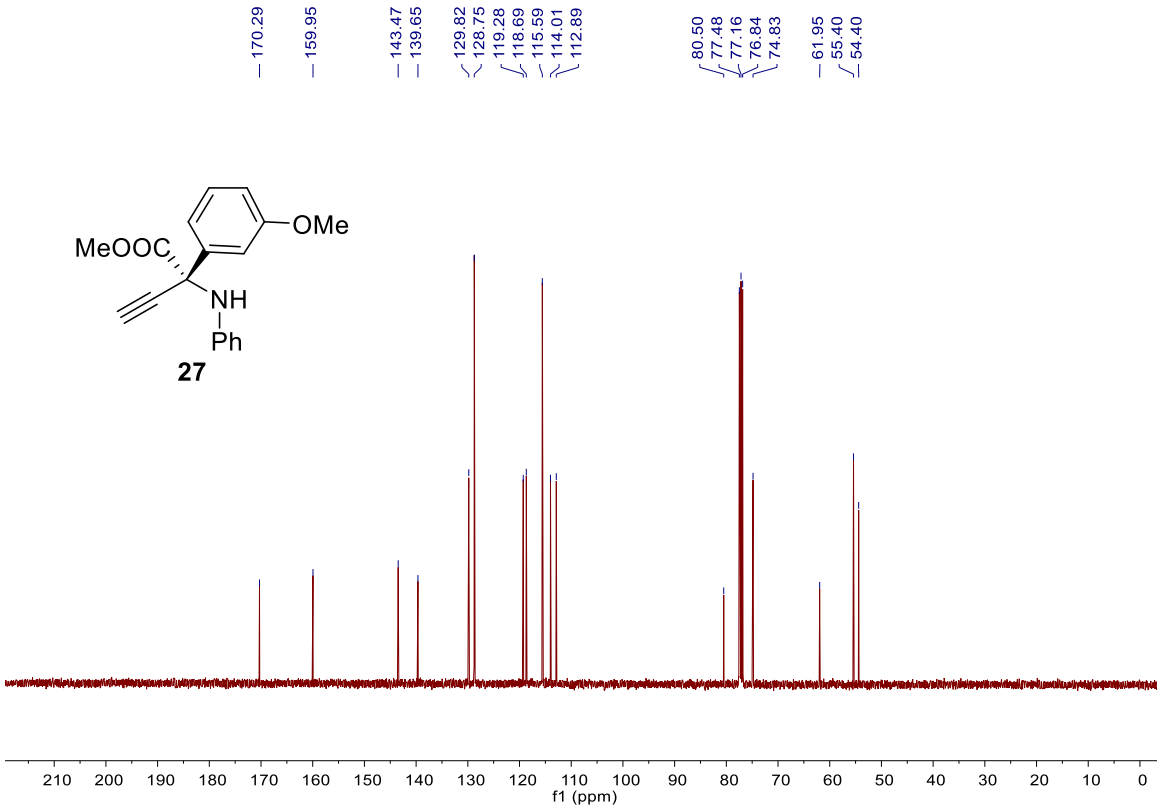


^{1}H NMR spectrum ($CDCl_3$)



^{13}C NMR spectrum ($CDCl_3$)



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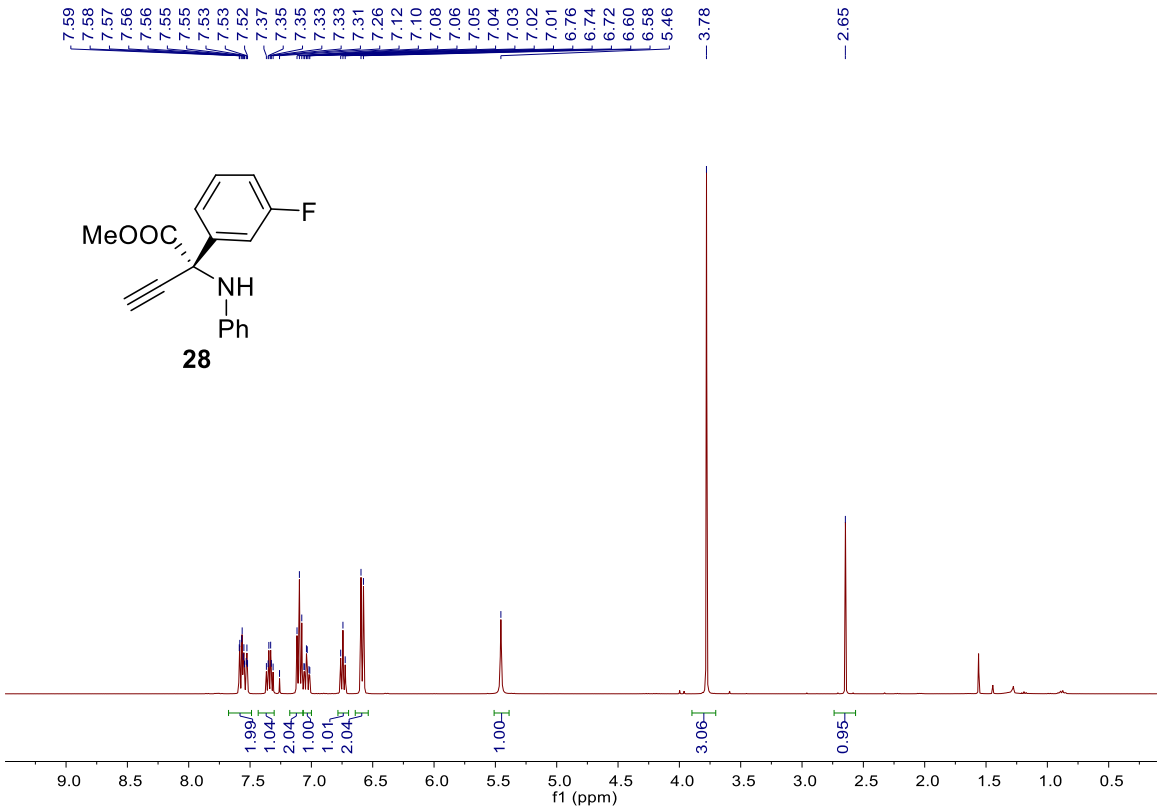
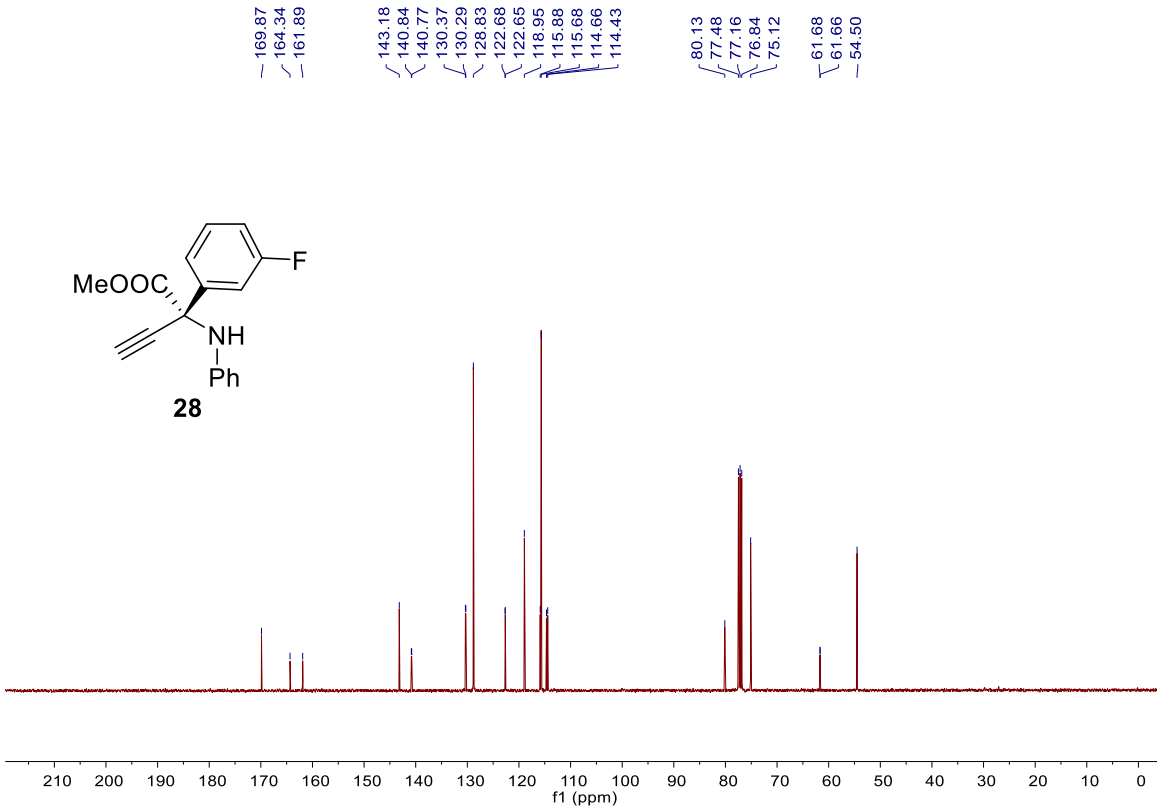


^{13}C NMR spectrum ($CDCl_3$)



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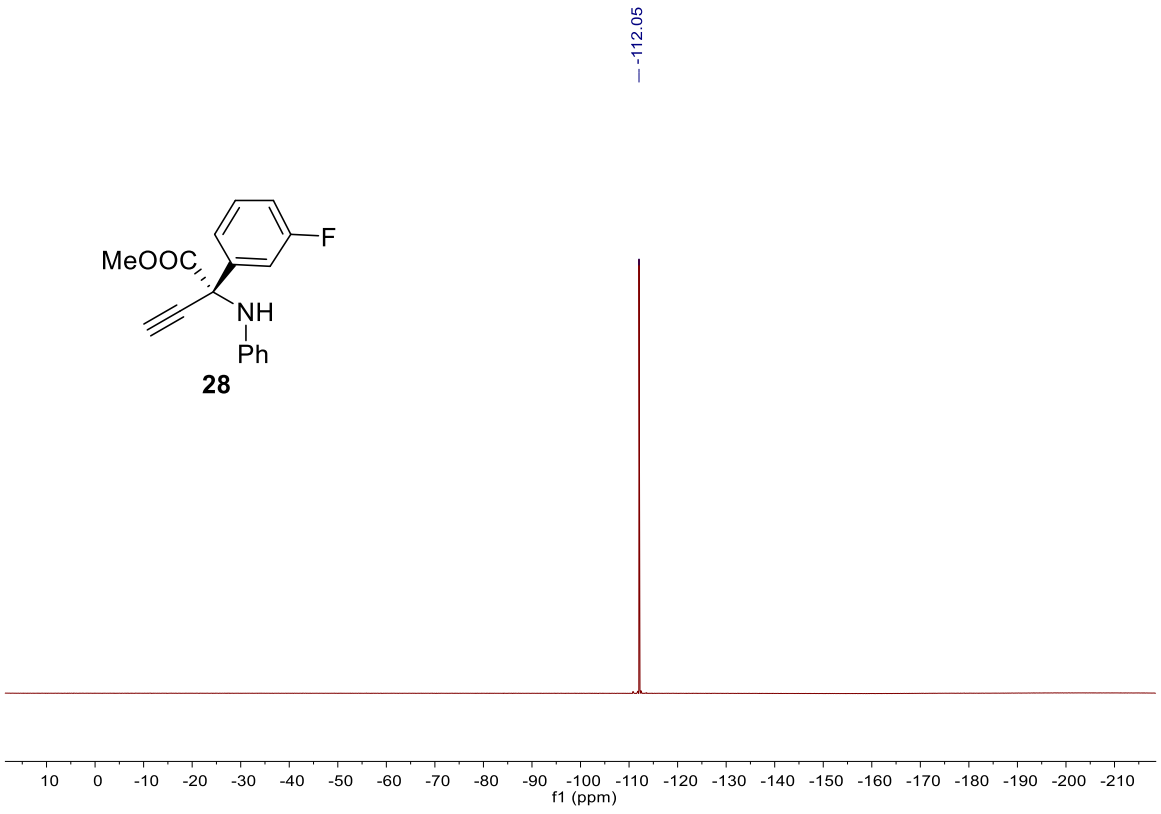
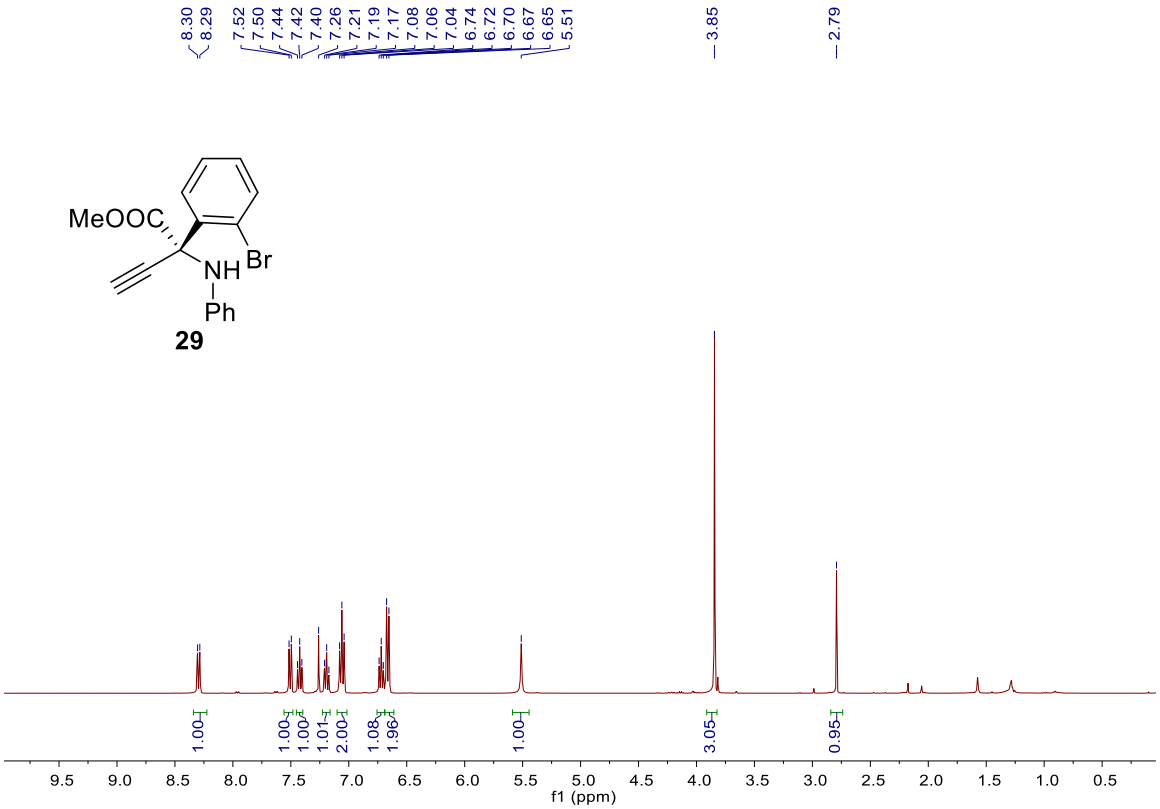
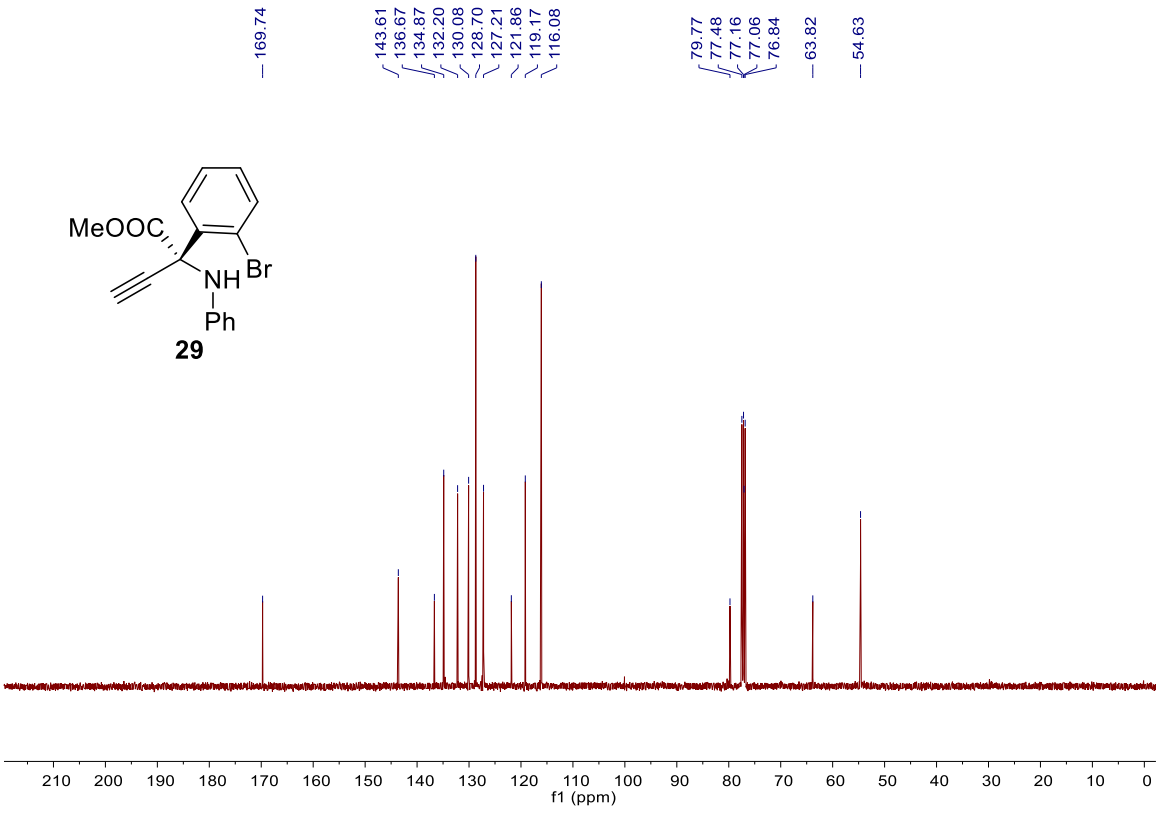


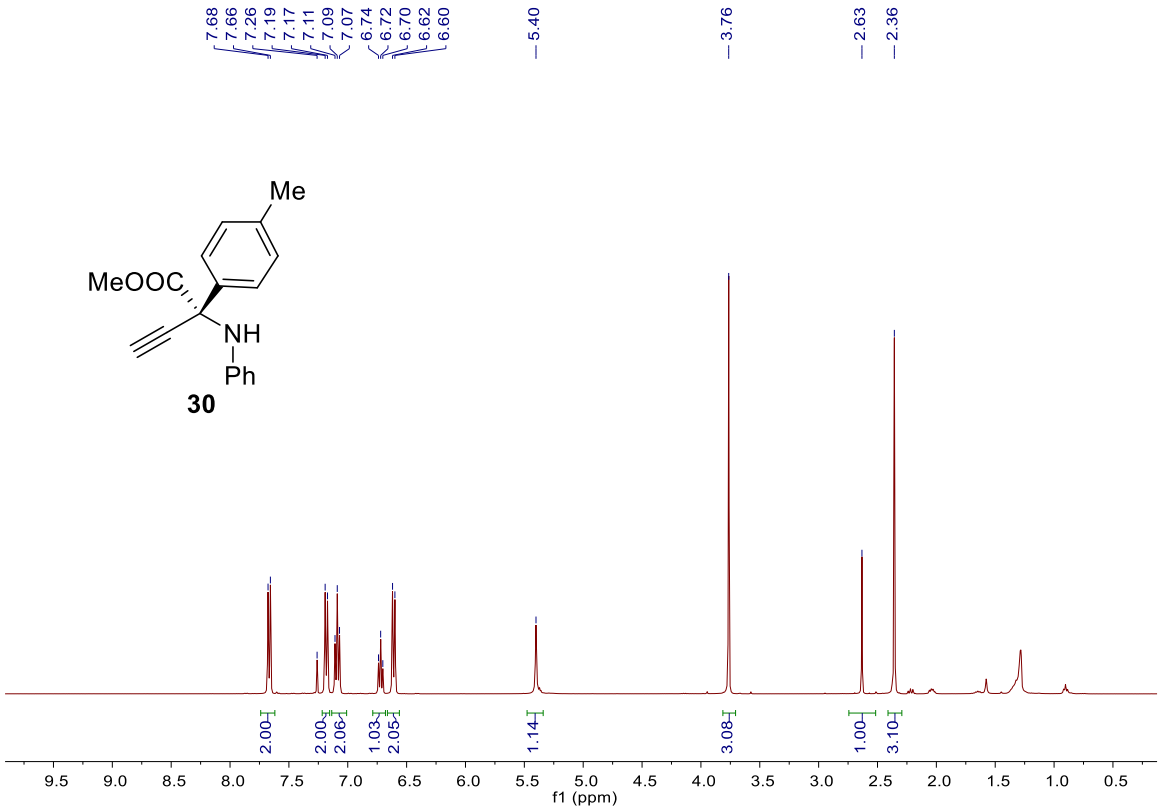
^{1}H NMR spectrum ($CDCl_3$)



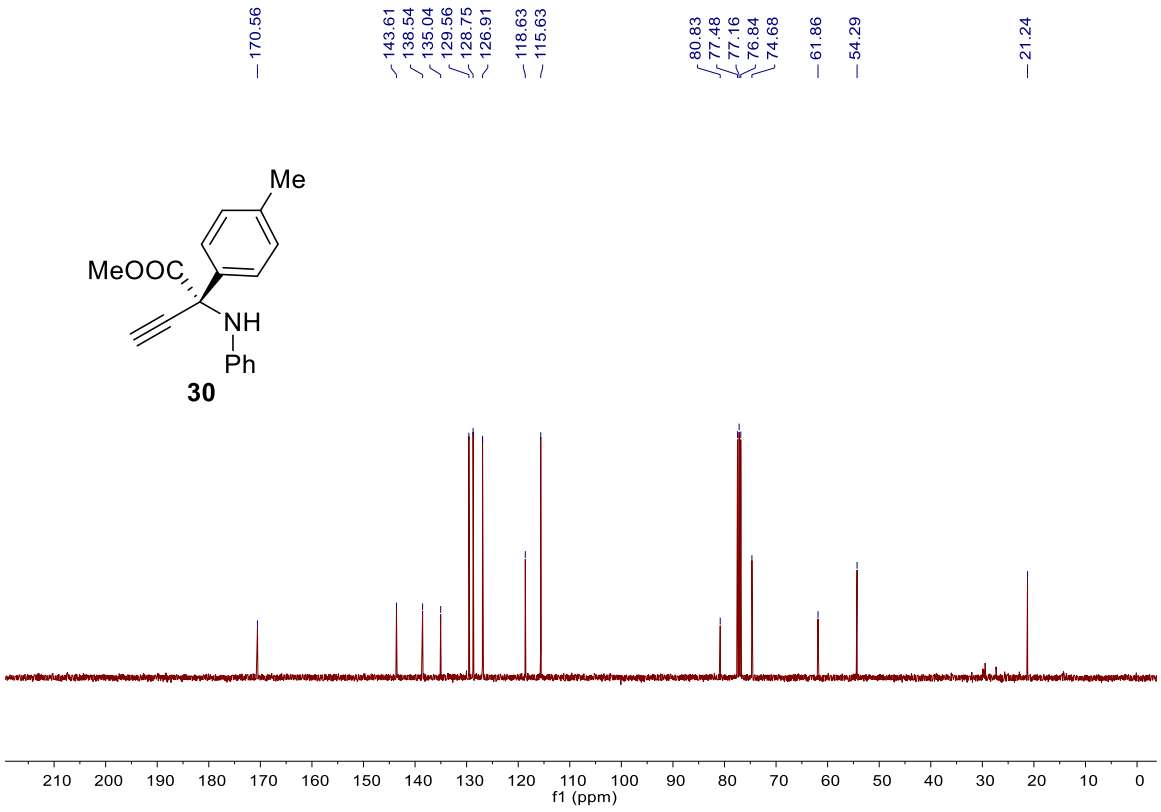
^{13}C NMR spectrum ($CDCl_3$)



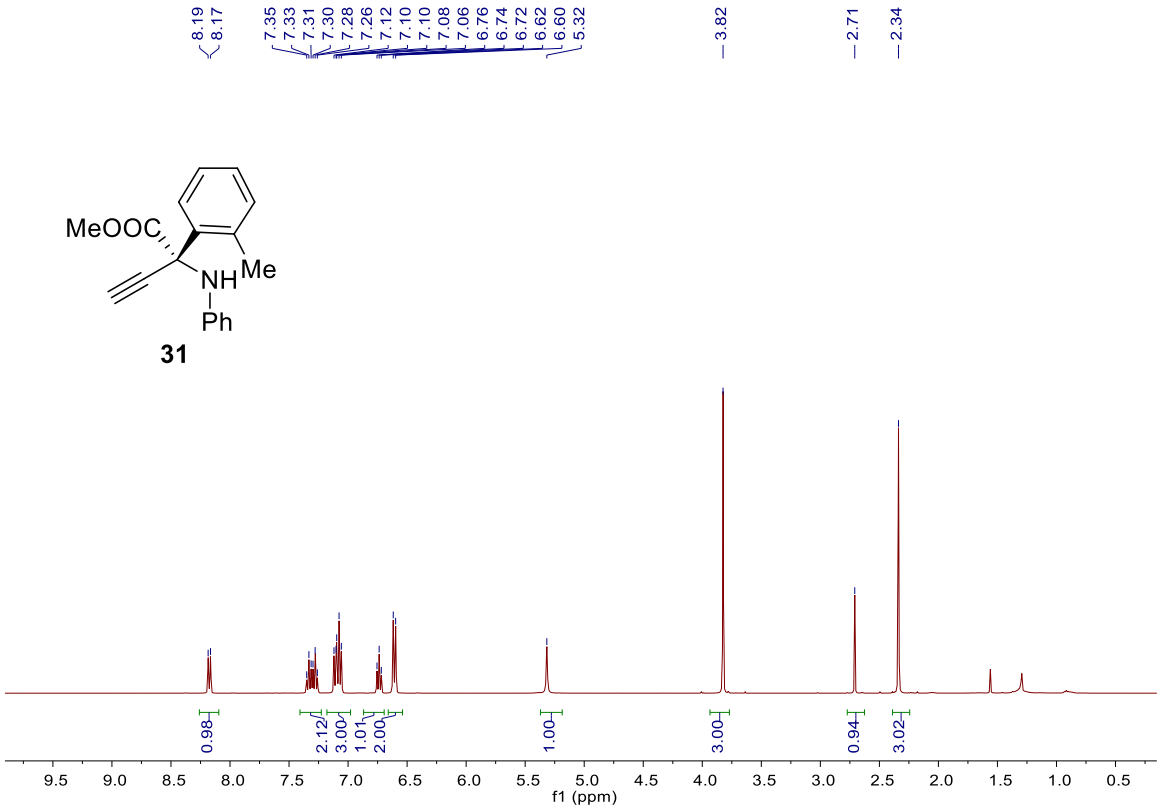
^{1}H NMR spectrum ($CDCl_3$)



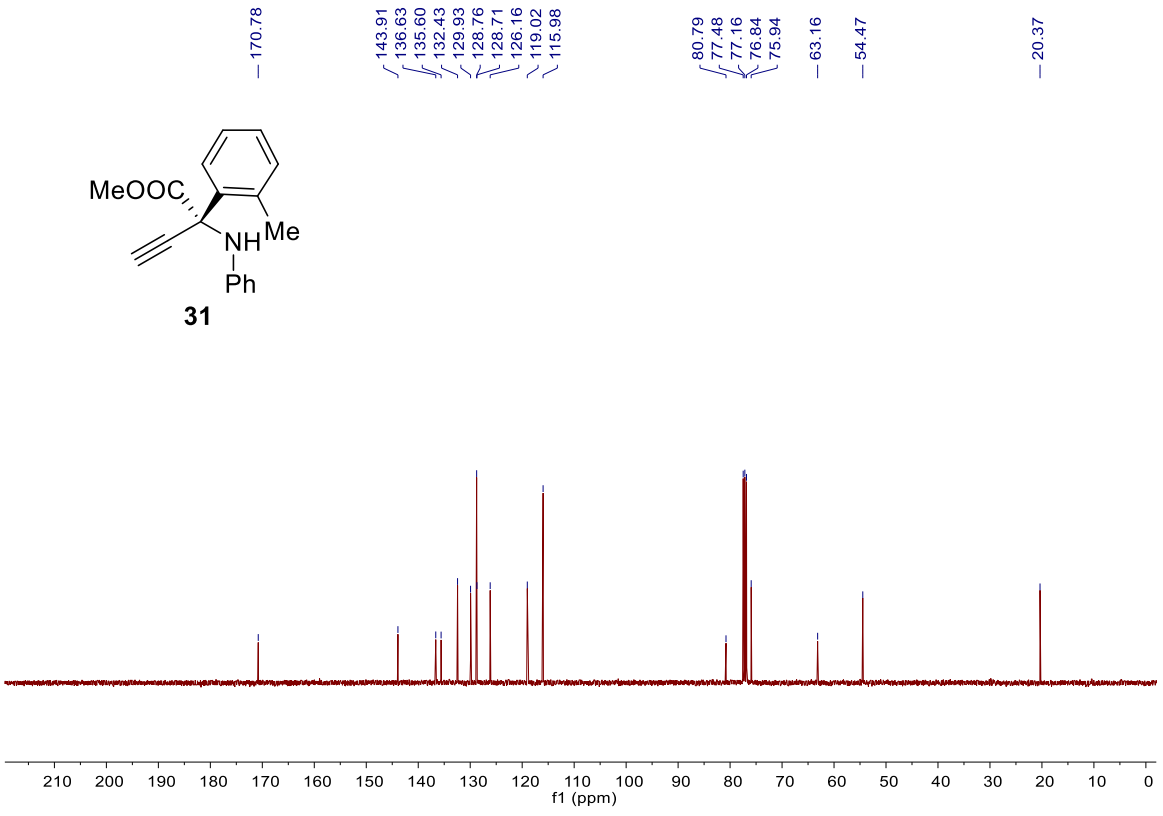
^{13}C NMR spectrum ($CDCl_3$)



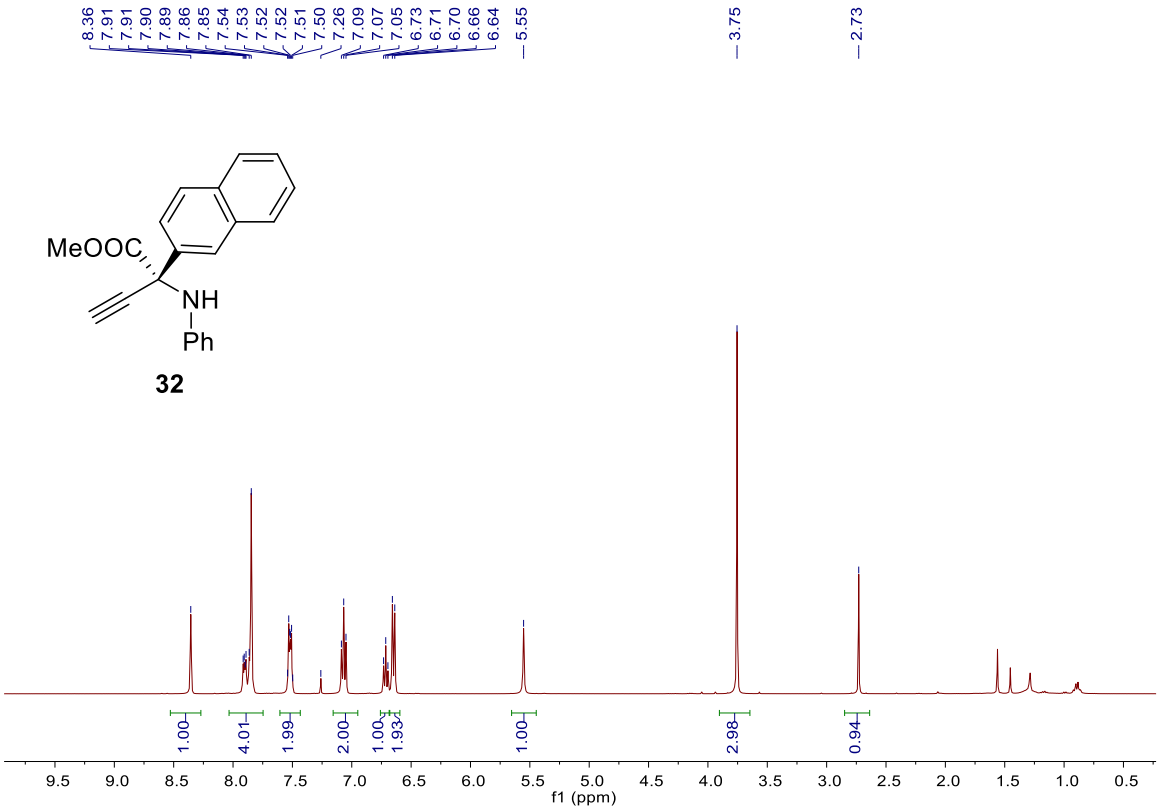
^{1}H NMR spectrum ($CDCl_3$)



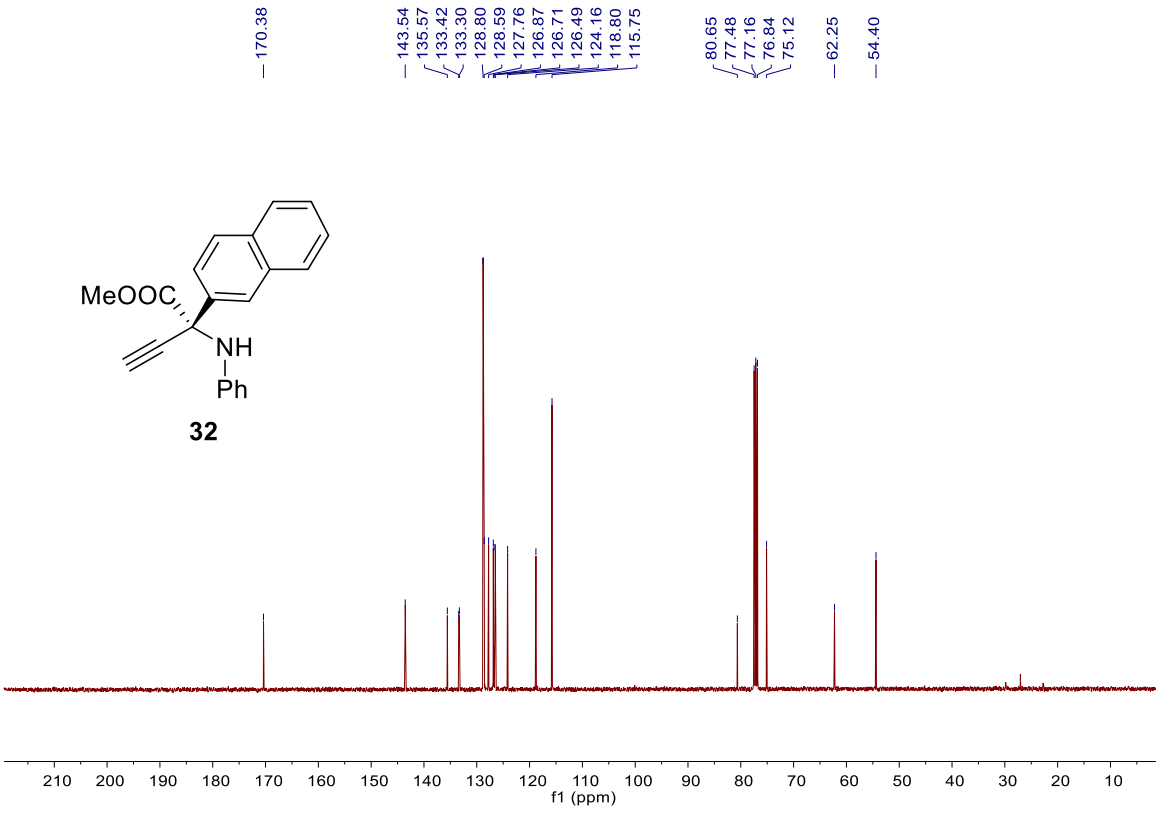
^{13}C NMR spectrum ($CDCl_3$)



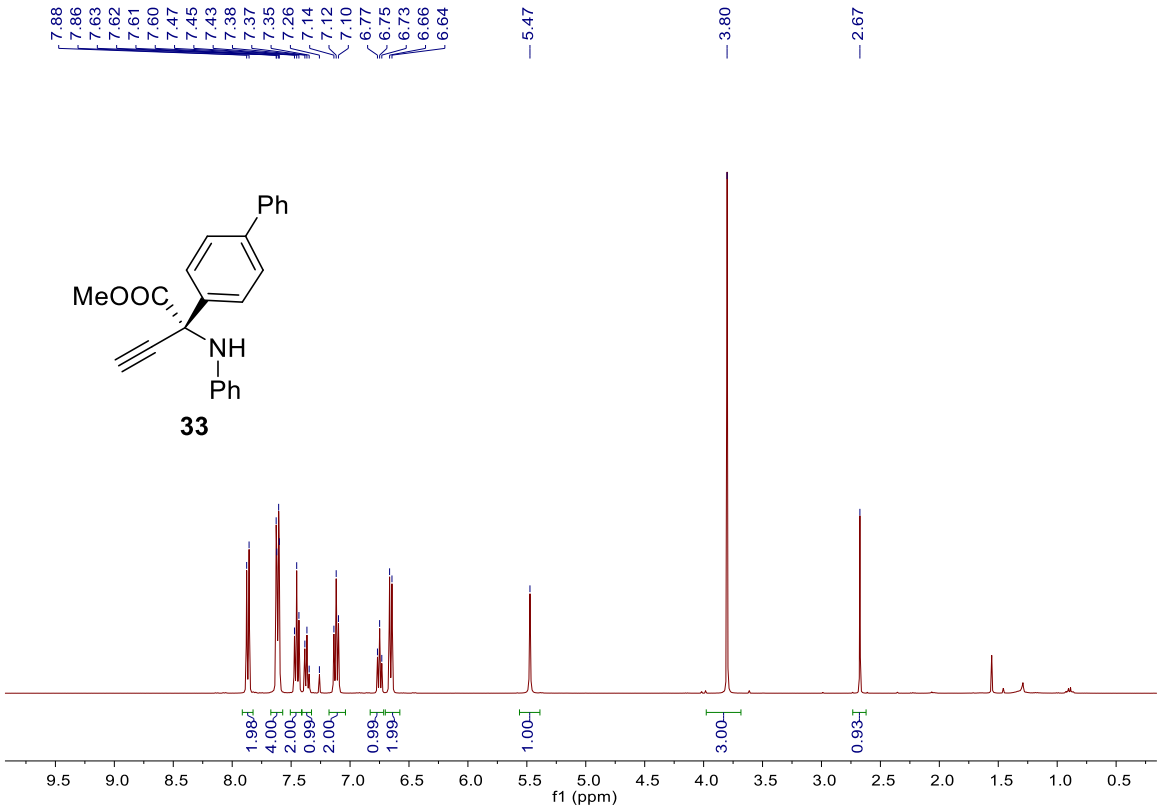
^{1}H NMR spectrum ($CDCl_3$)



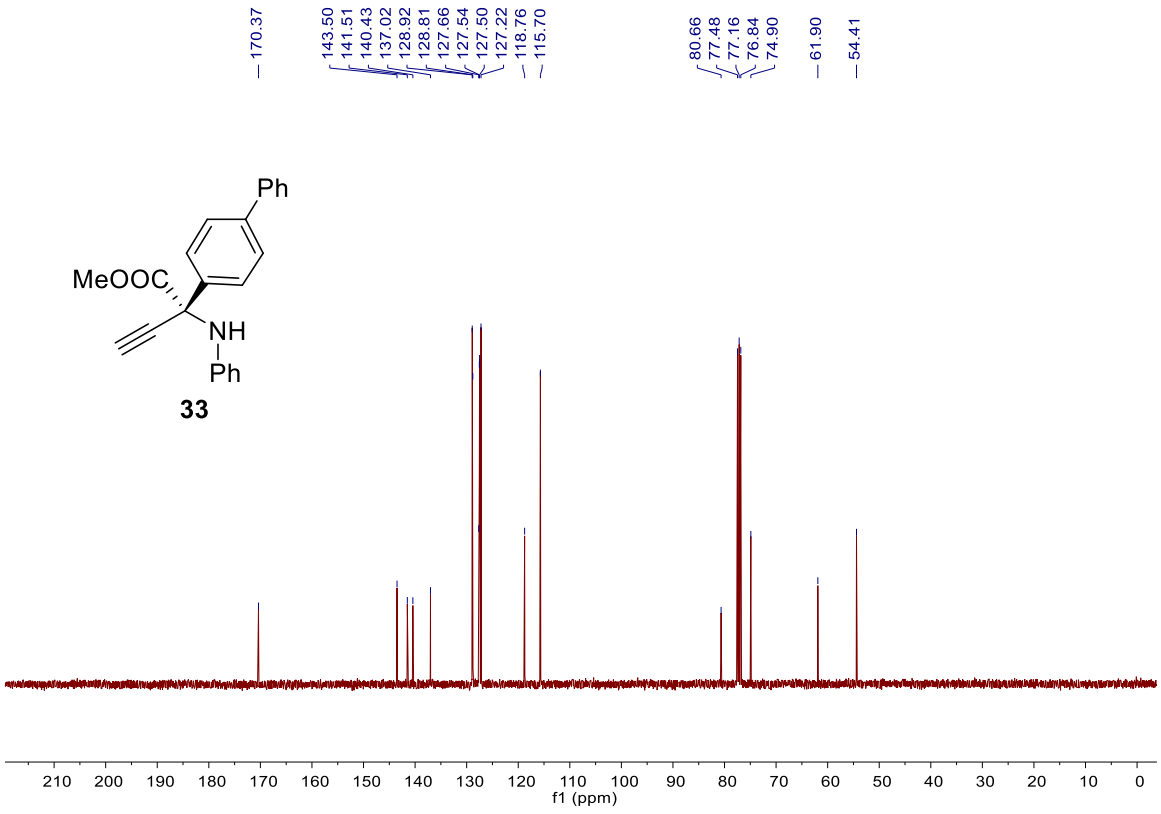
^{13}C NMR spectrum ($CDCl_3$)



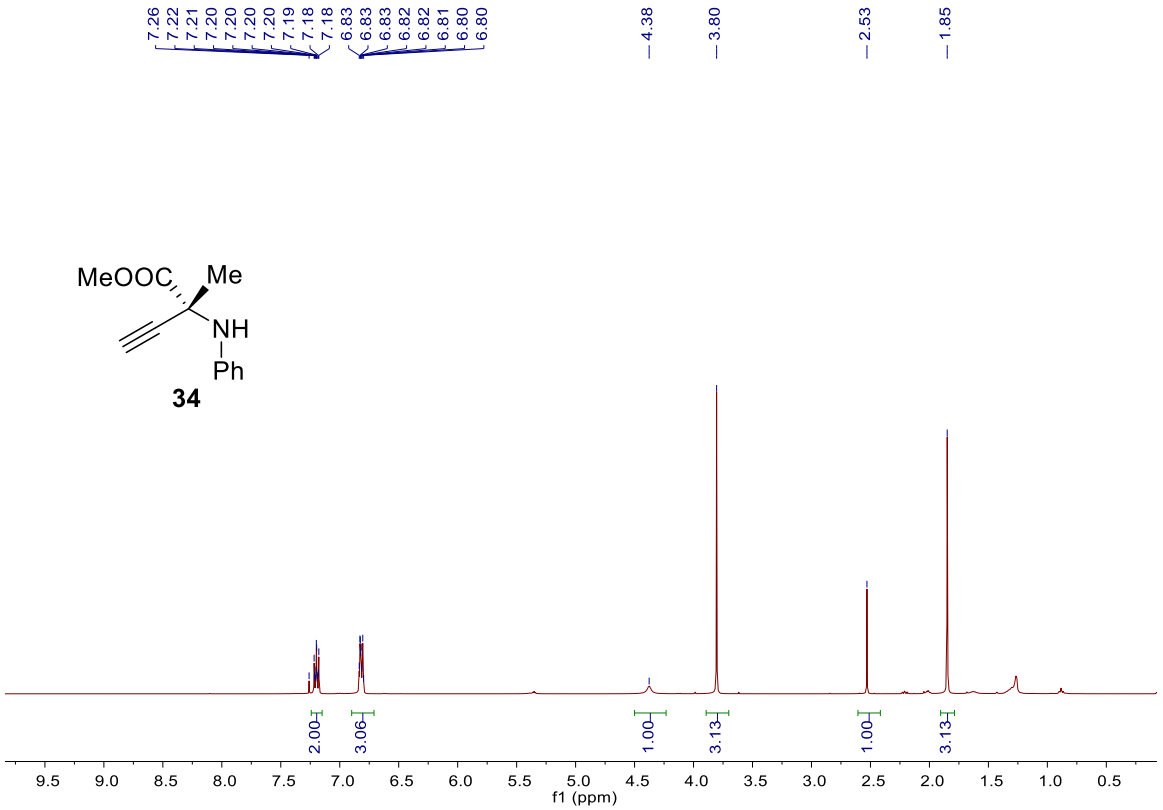
^{1}H NMR spectrum ($CDCl_3$)



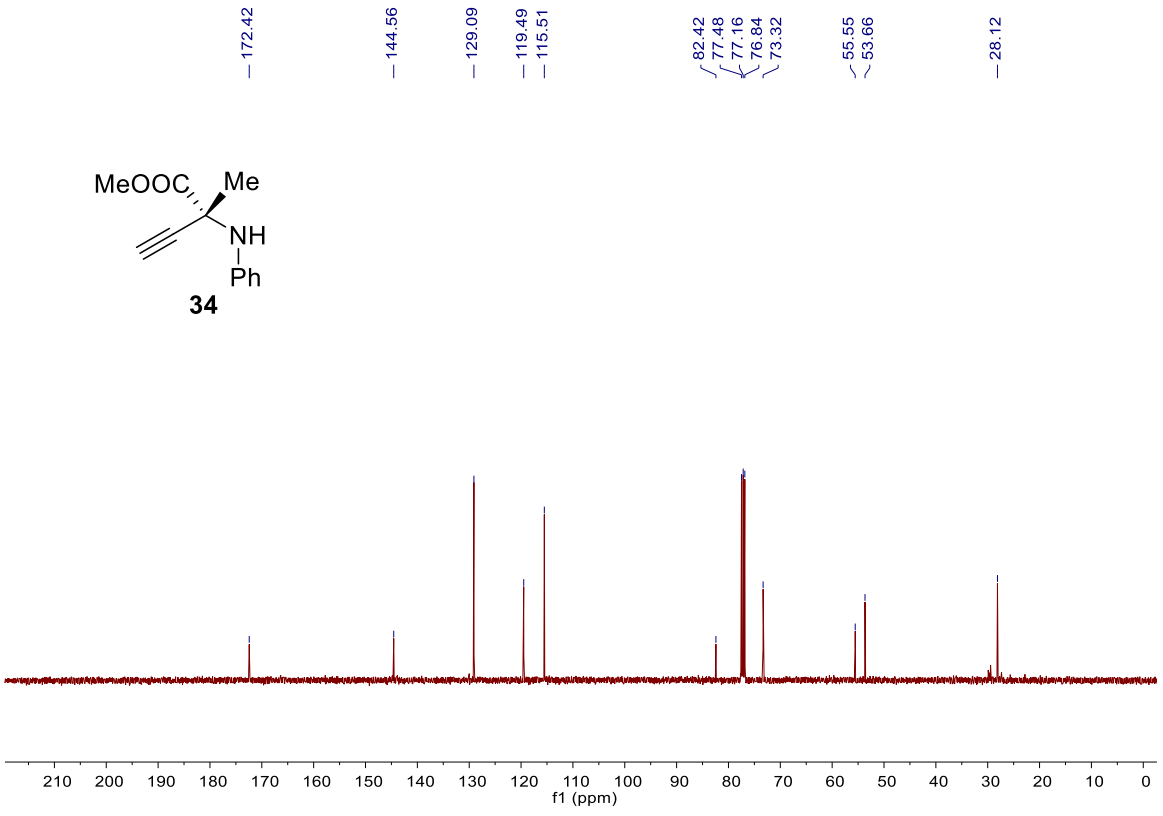
^{13}C NMR spectrum ($CDCl_3$)



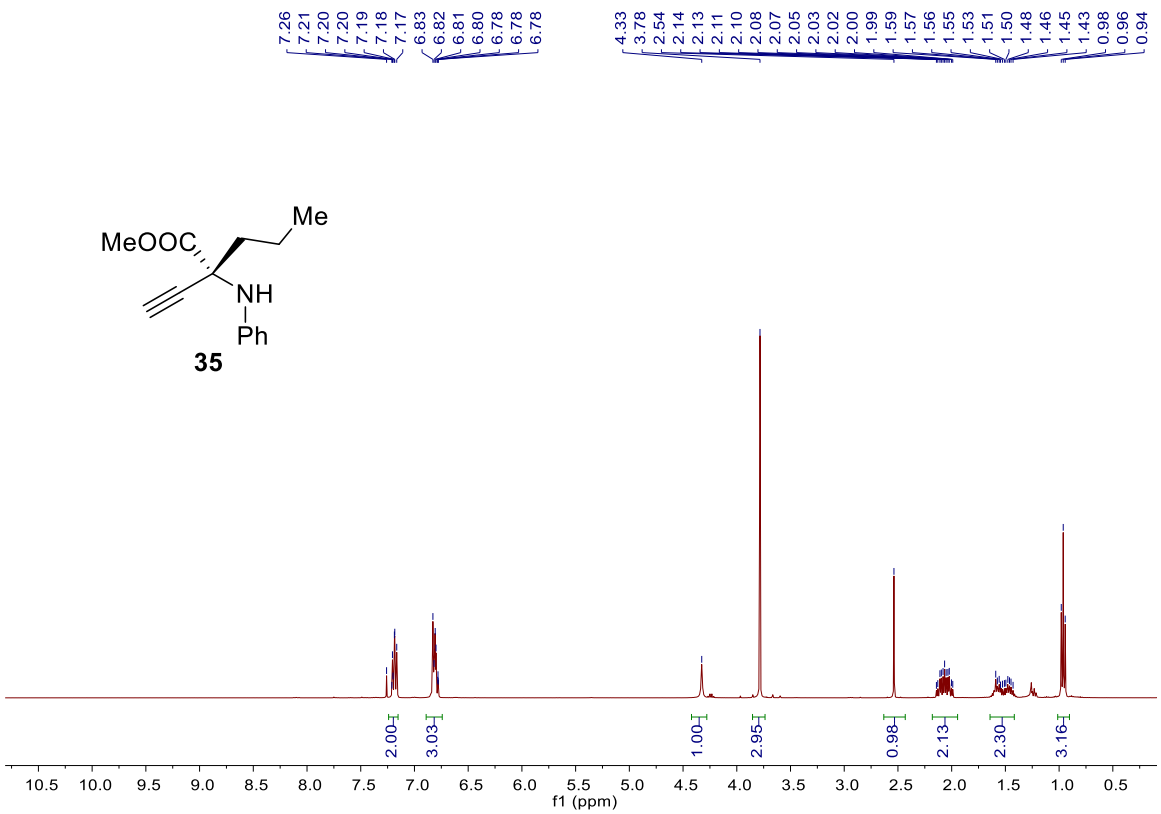
^{1}H NMR spectrum ($CDCl_3$)



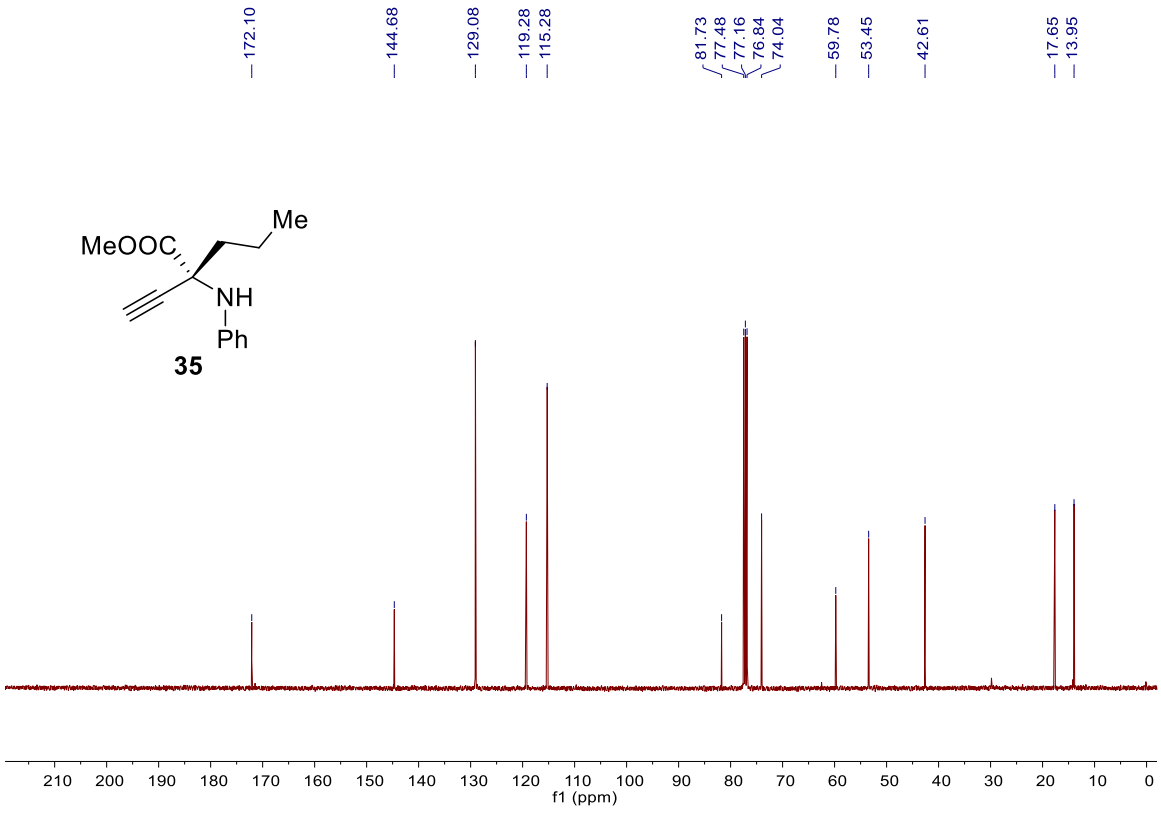
^{13}C NMR spectrum ($CDCl_3$)



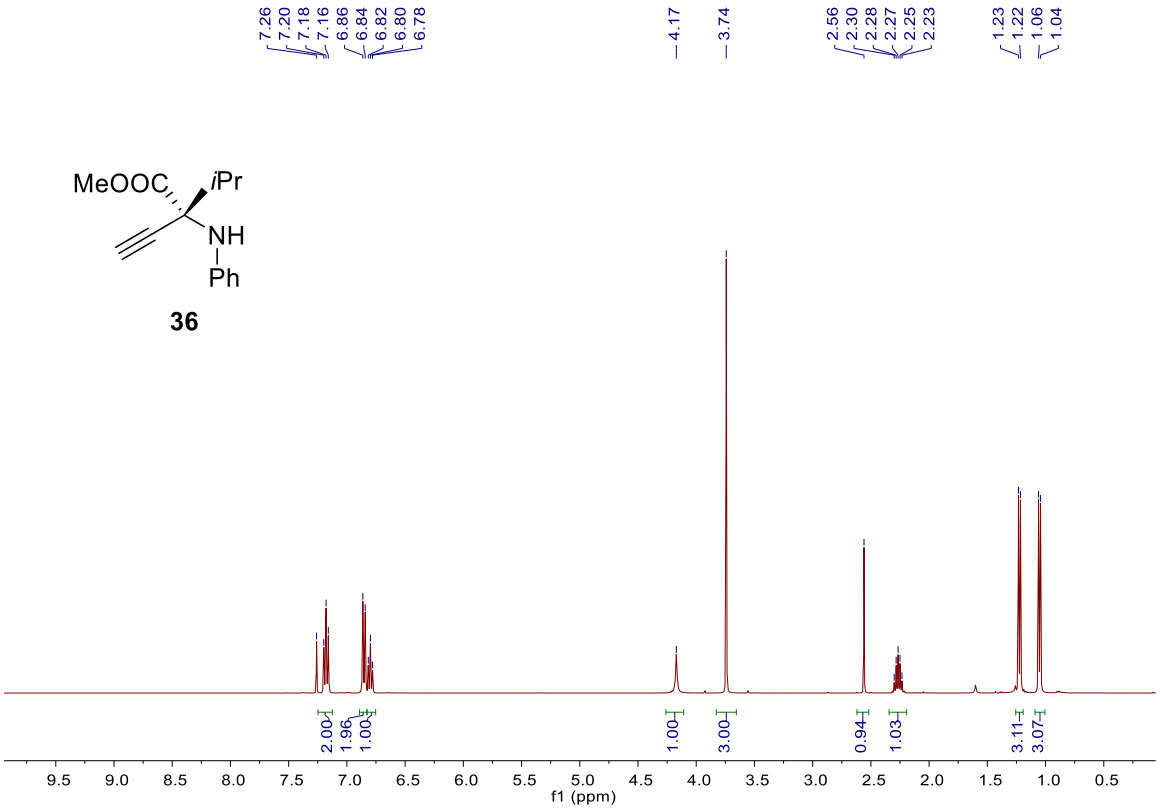
^{1}H NMR spectrum ($CDCl_3$)



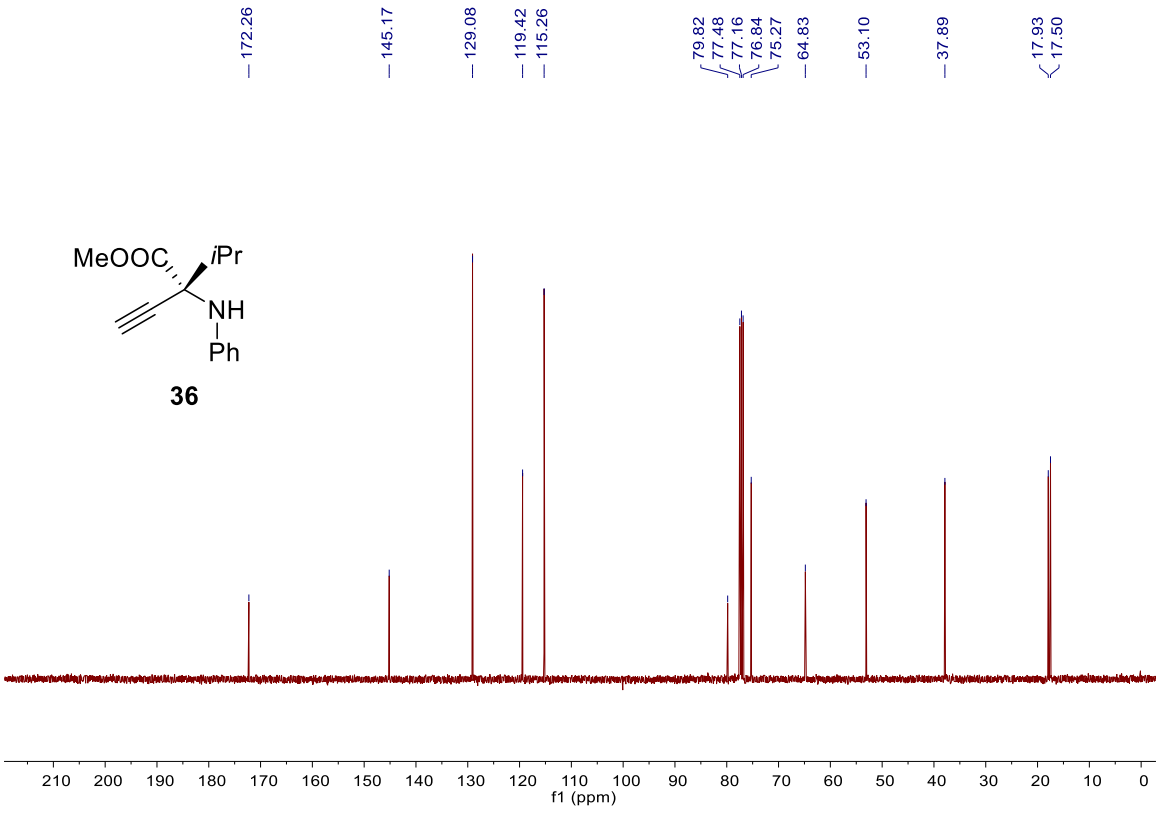
^{13}C NMR spectrum ($CDCl_3$)



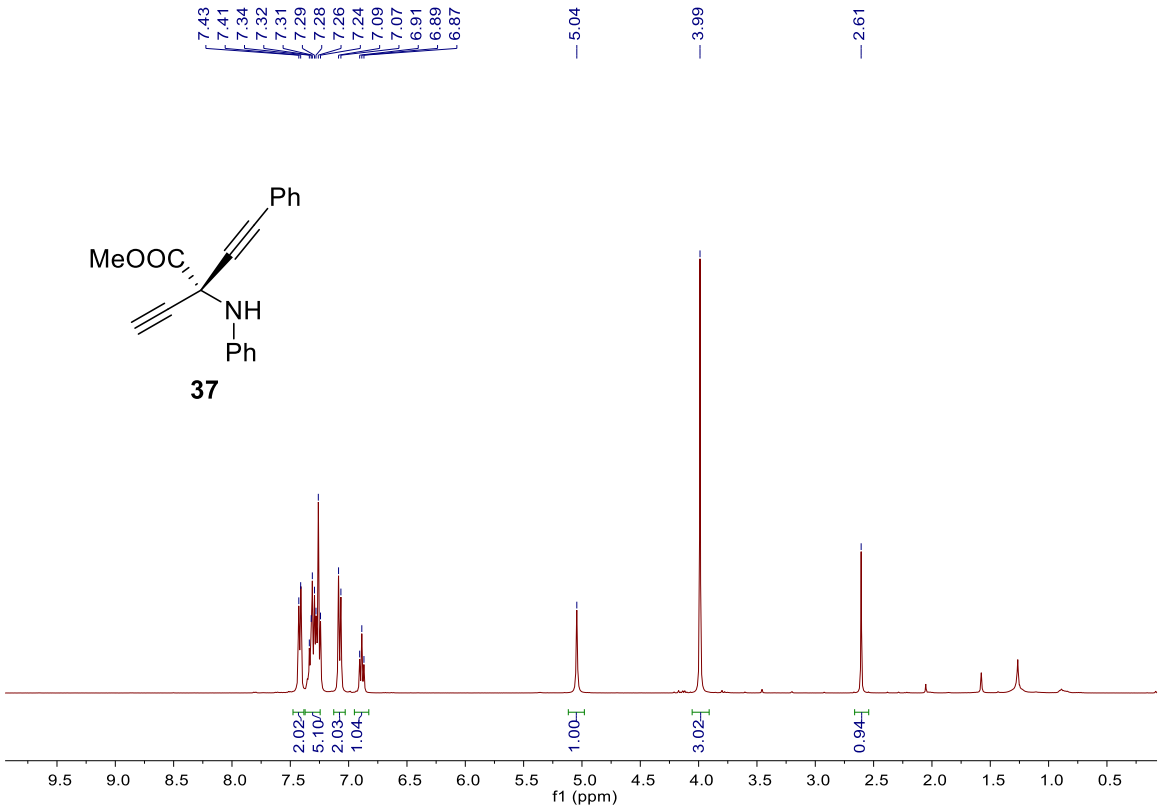
^{1}H NMR spectrum ($CDCl_3$)



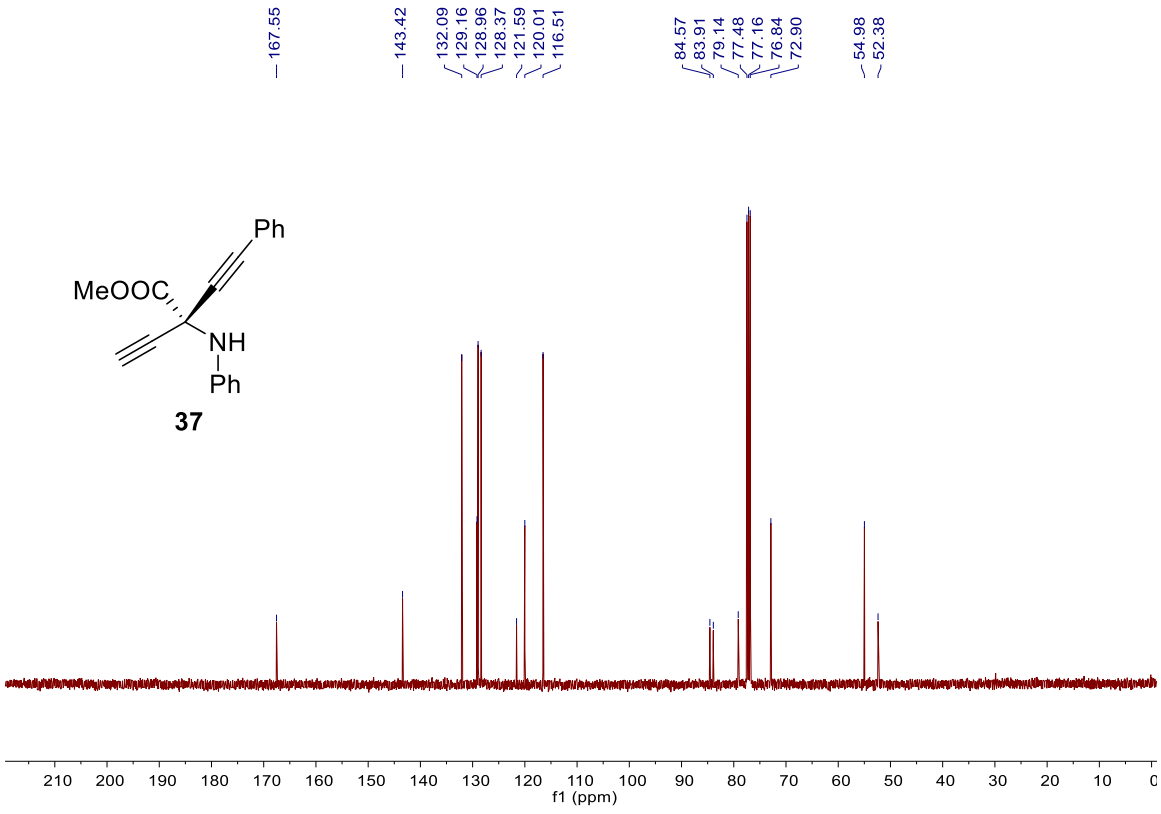
^{13}C NMR spectrum ($CDCl_3$)



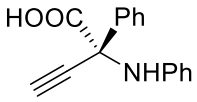
^{1}H NMR spectrum ($CDCl_3$)



^{13}C NMR spectrum ($CDCl_3$)



^{1}H NMR spectrum (DMSO-d_6)



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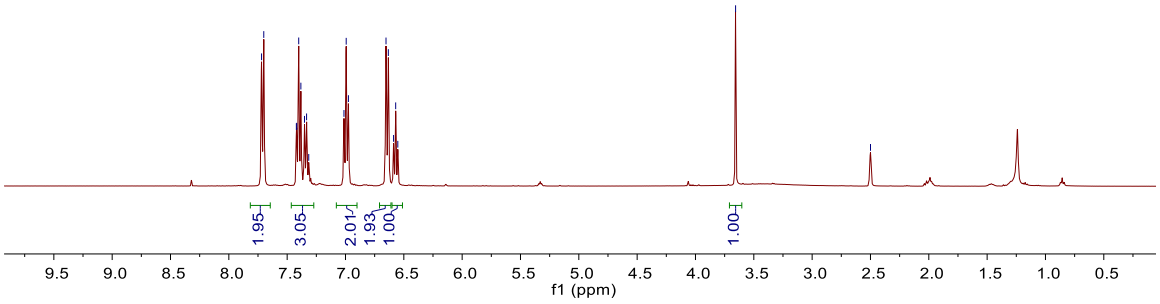
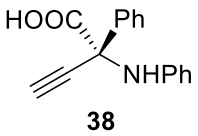


^{13}C NMR spectrum (DMSO-d_6)



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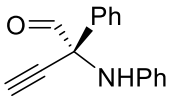
^{1}H NMR spectrum ($CDCl_3$)



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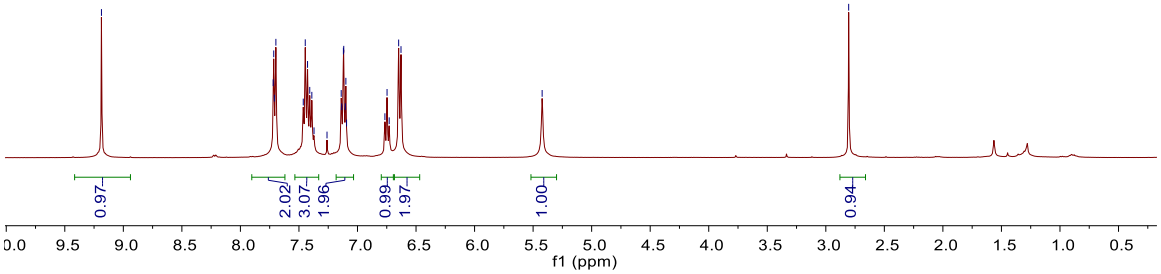
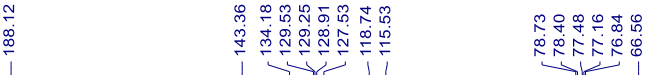
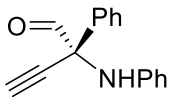


^{13}C NMR spectrum ($CDCl_3$)





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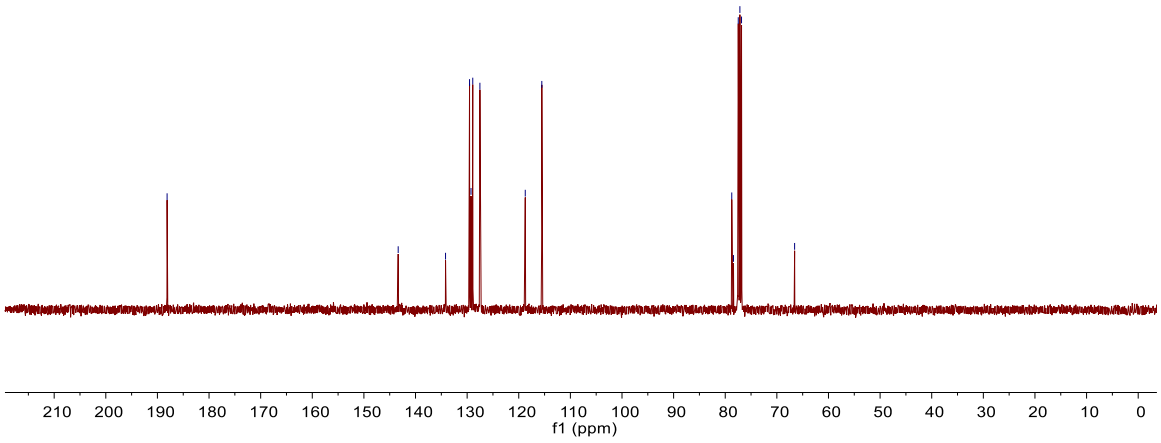
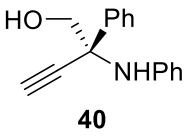


^{1}H NMR spectrum ($CDCl_3$)



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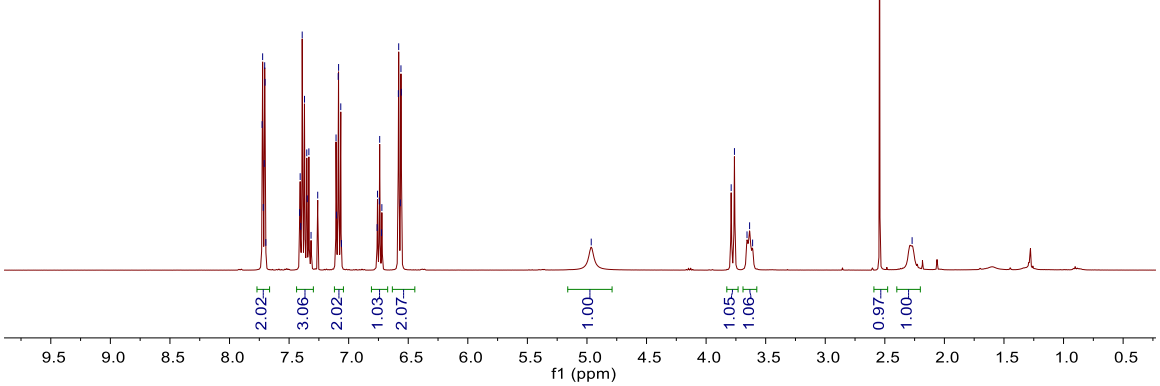
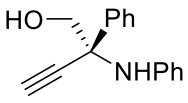


^{13}C NMR spectrum ($CDCl_3$)



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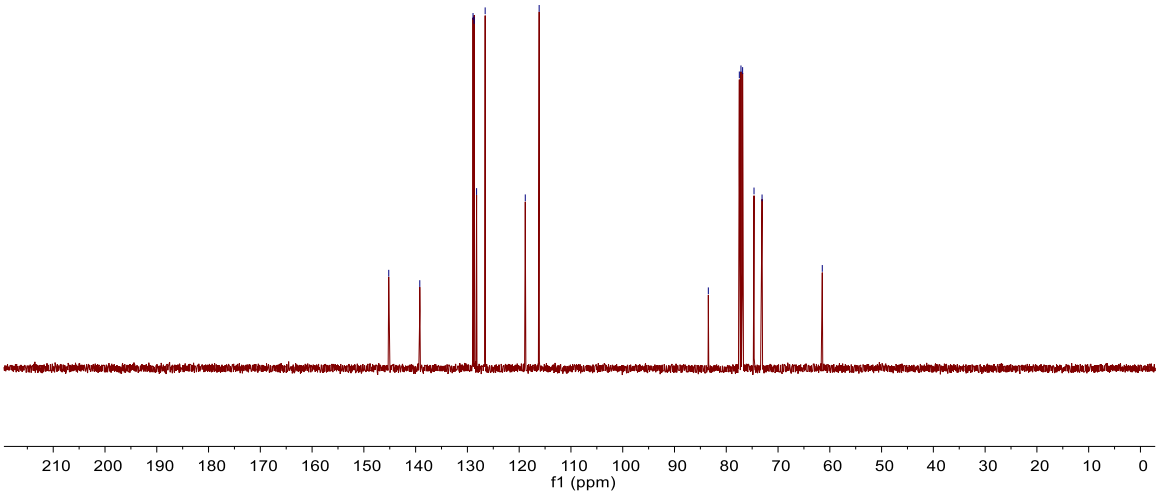
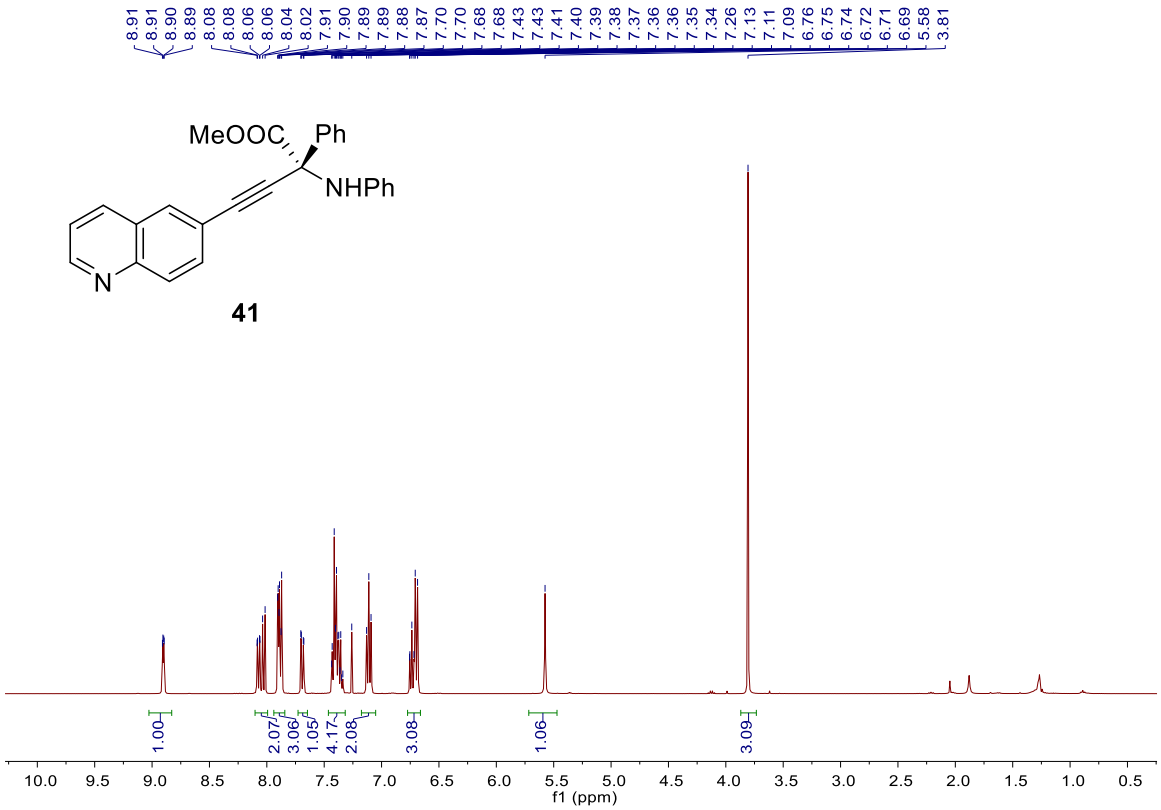
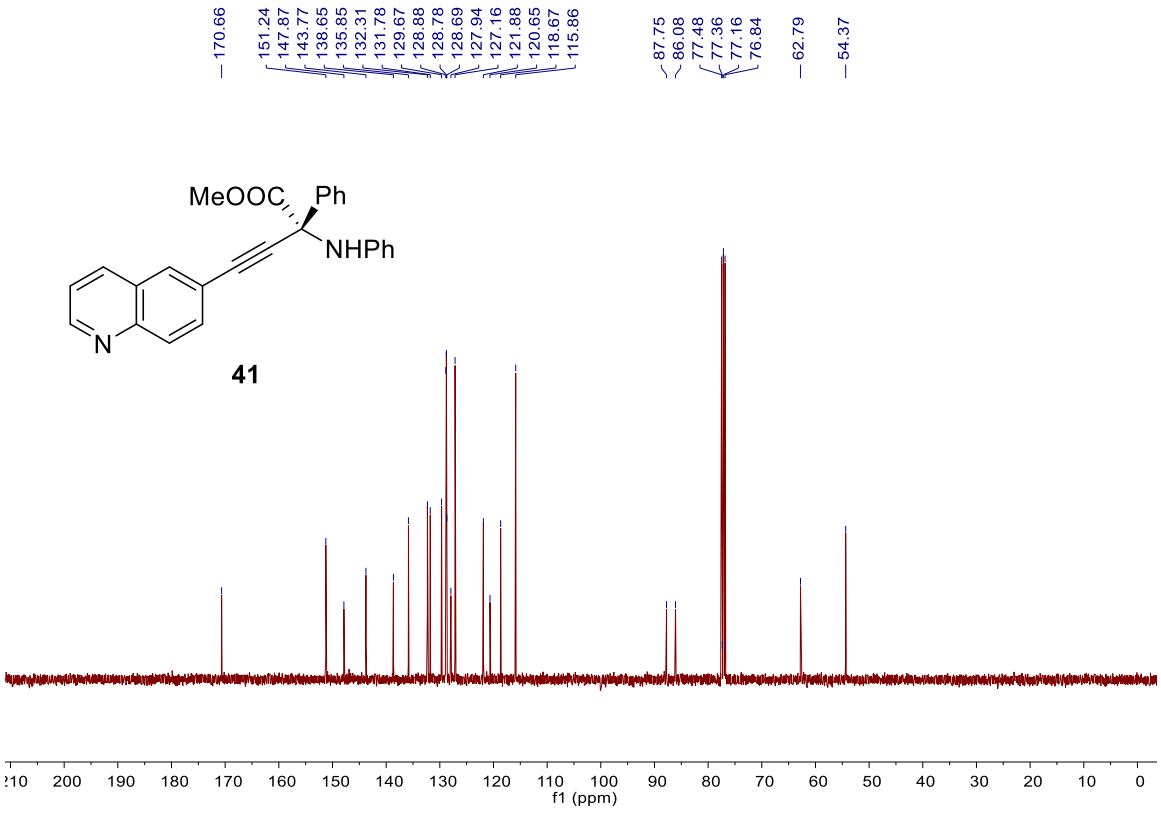


^{1}H NMR spectrum ($CDCl_3$)



^{13}C NMR spectrum ($CDCl_3$)



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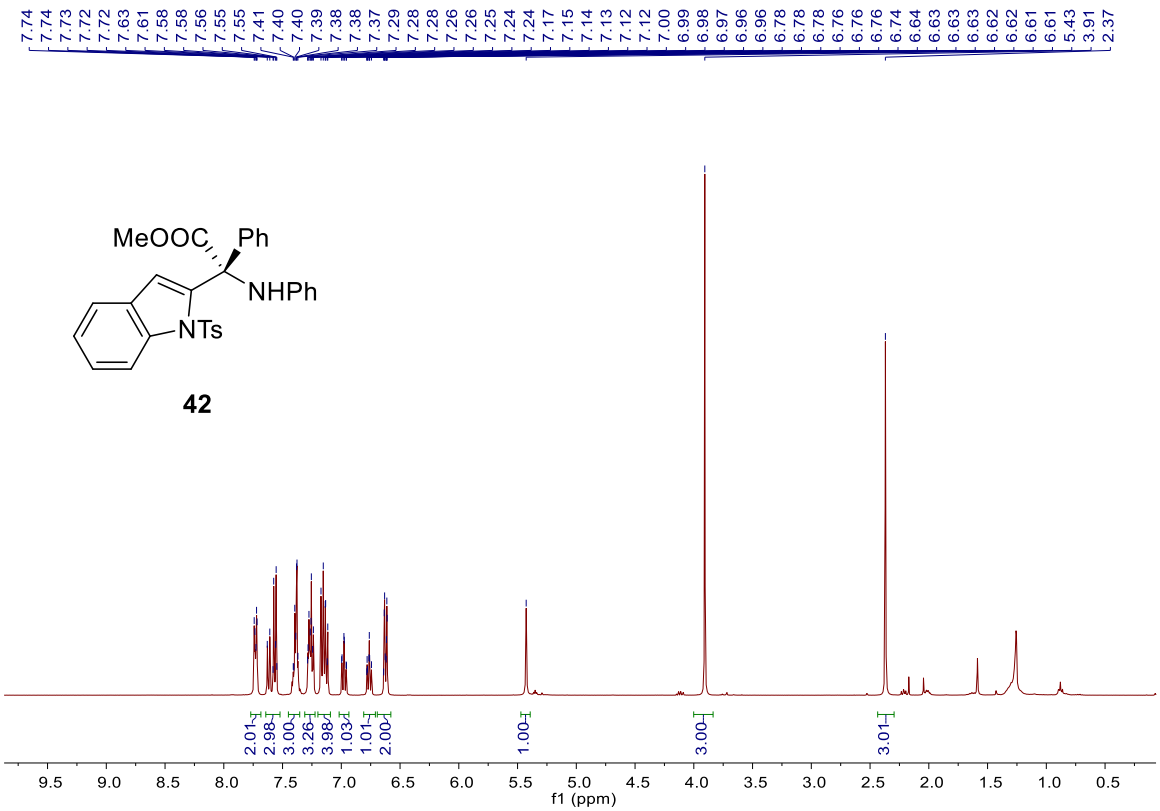

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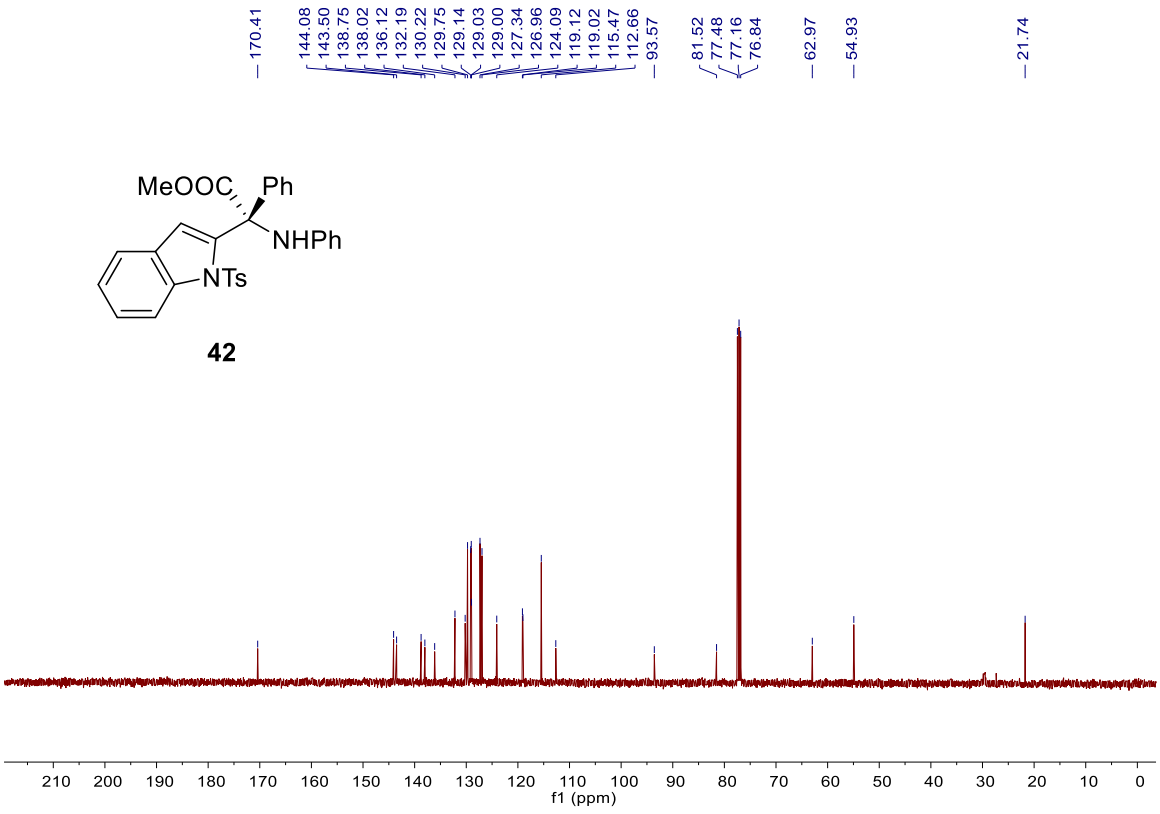
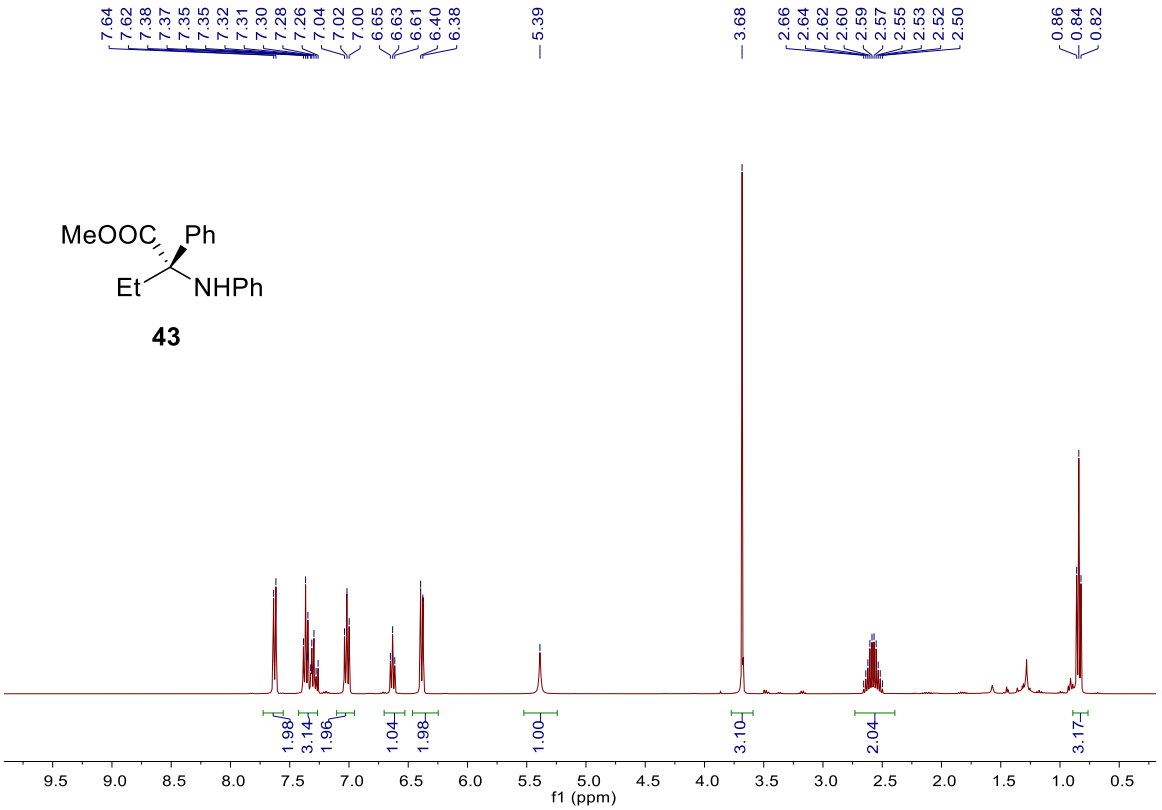


^{1}H NMR spectrum ($CDCl_3$)



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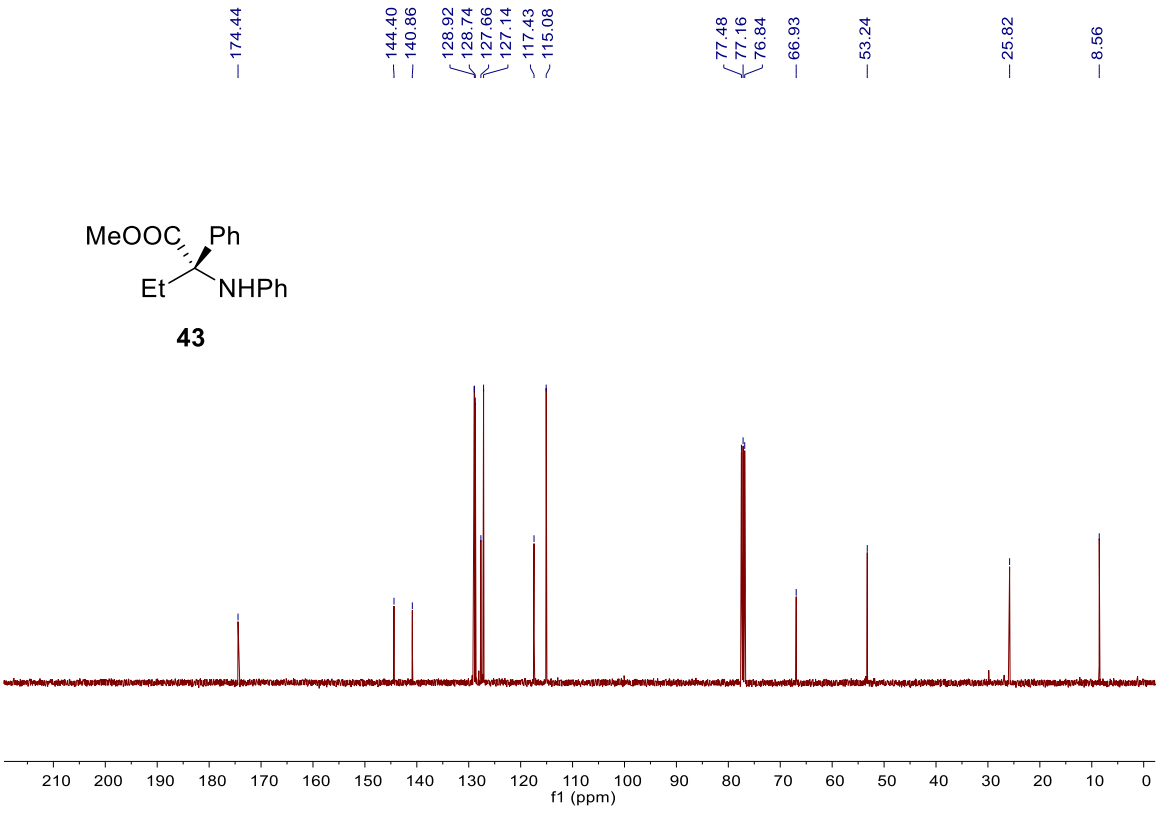
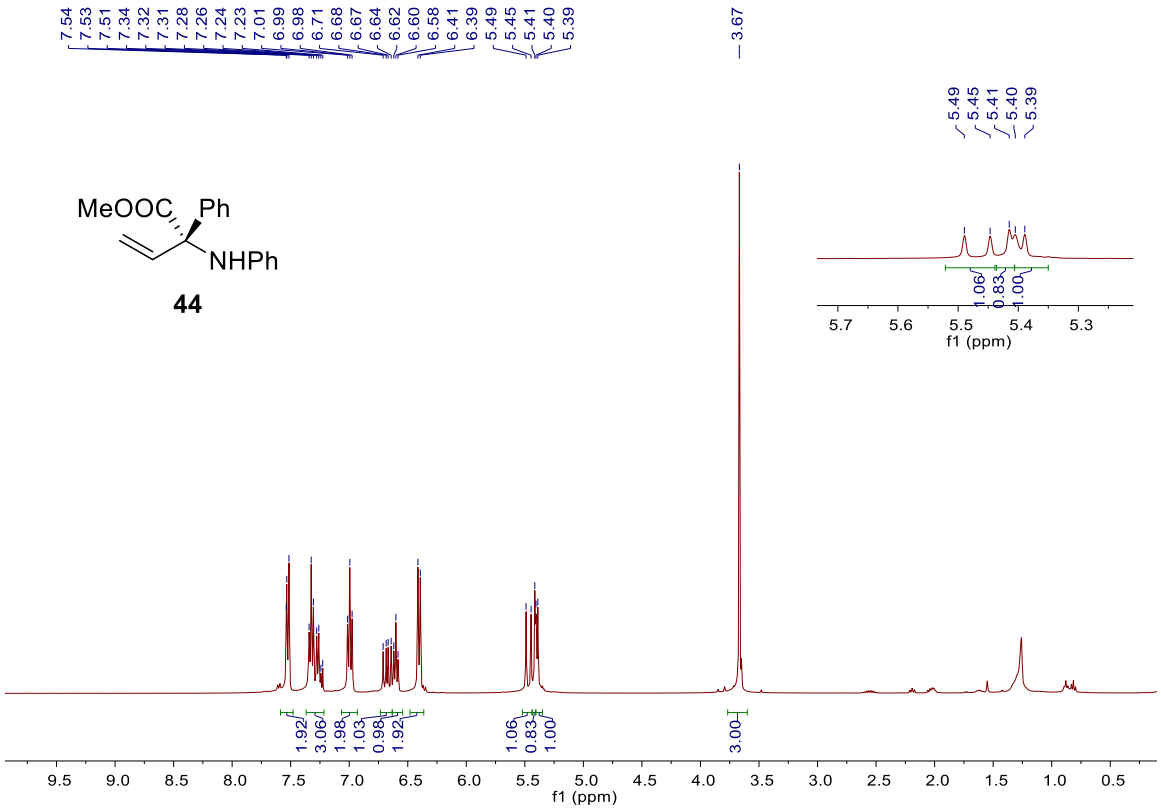
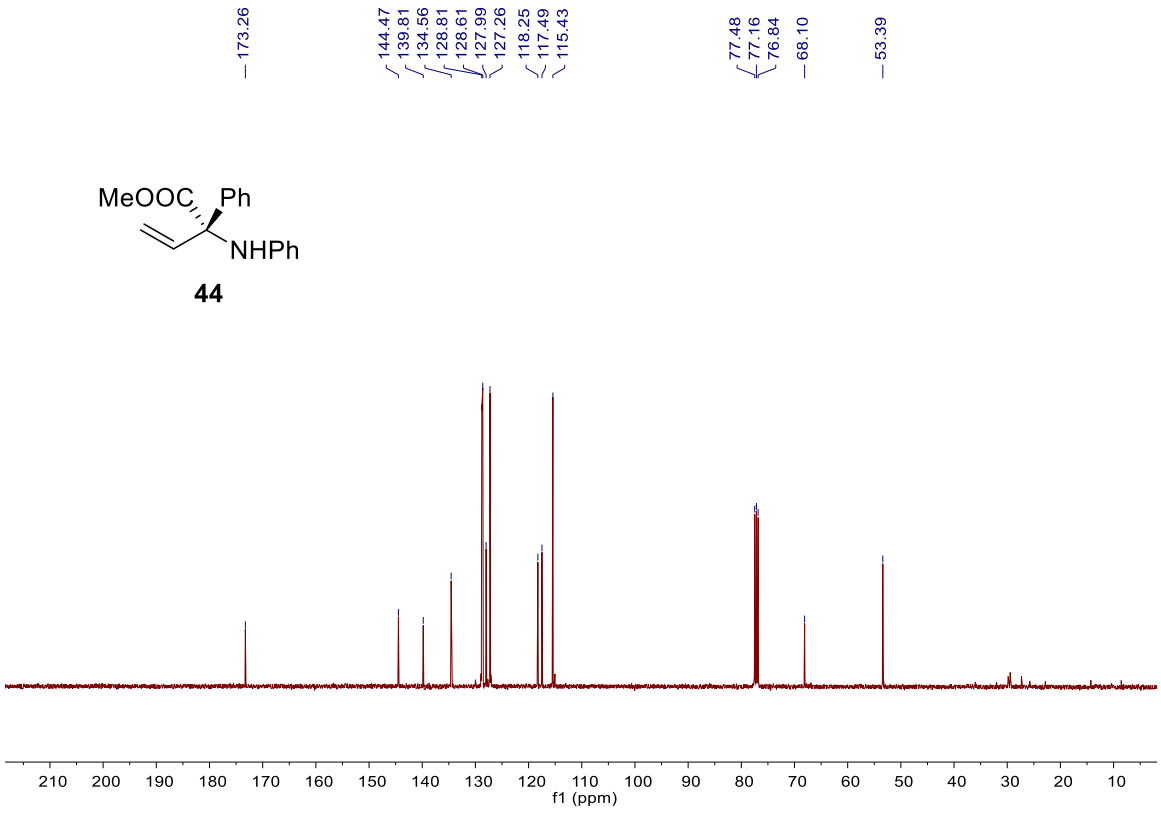


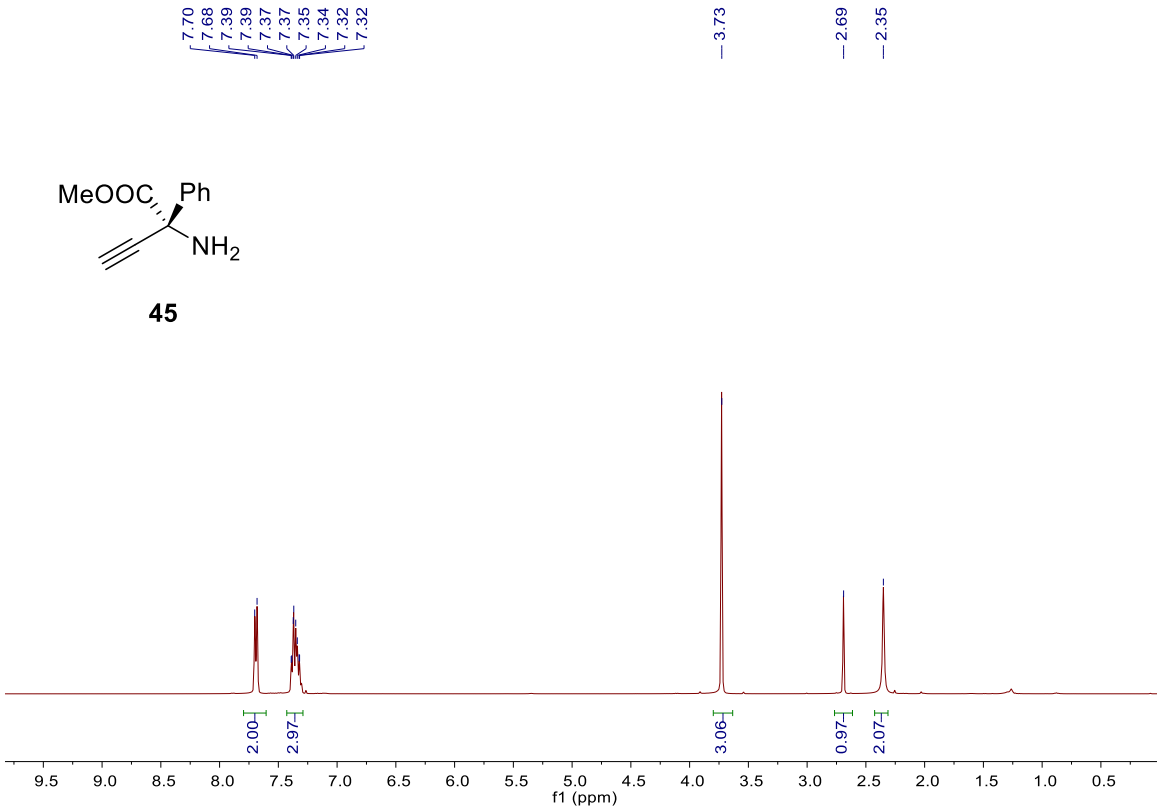
^{1}H NMR spectrum ($CDCl_3$)



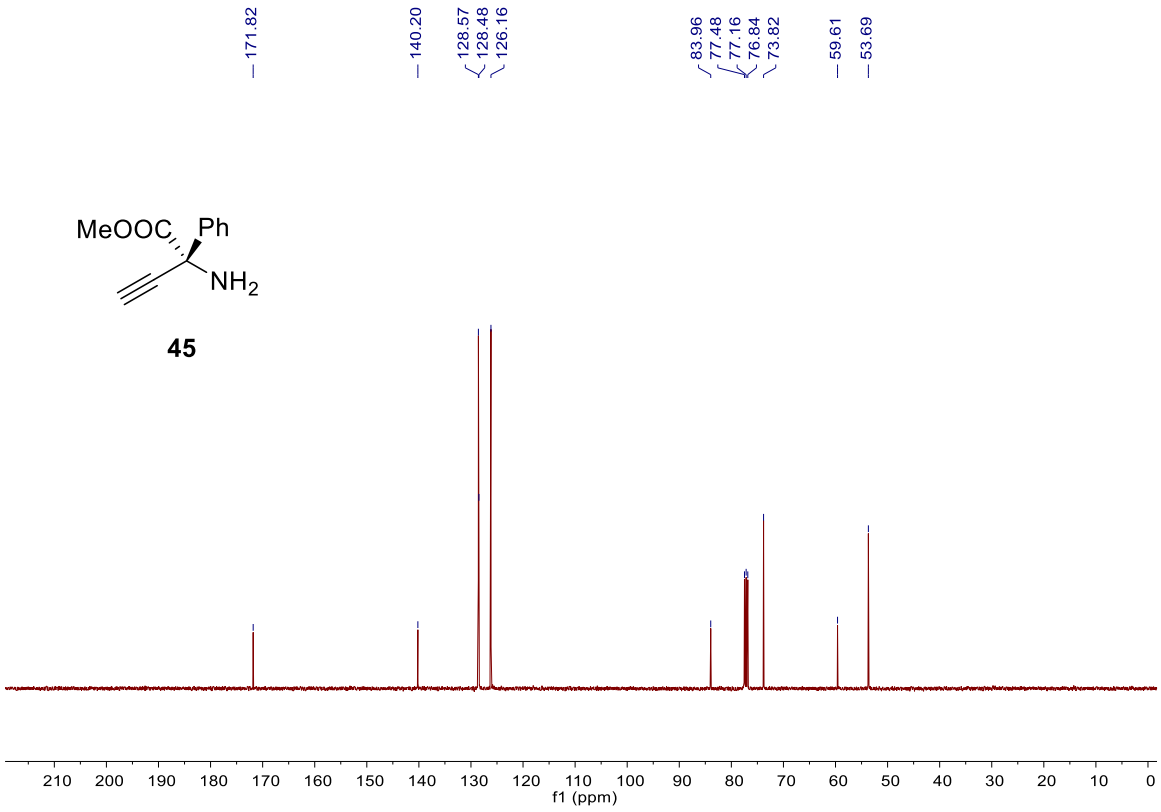
^{13}C NMR spectrum ($CDCl_3$)



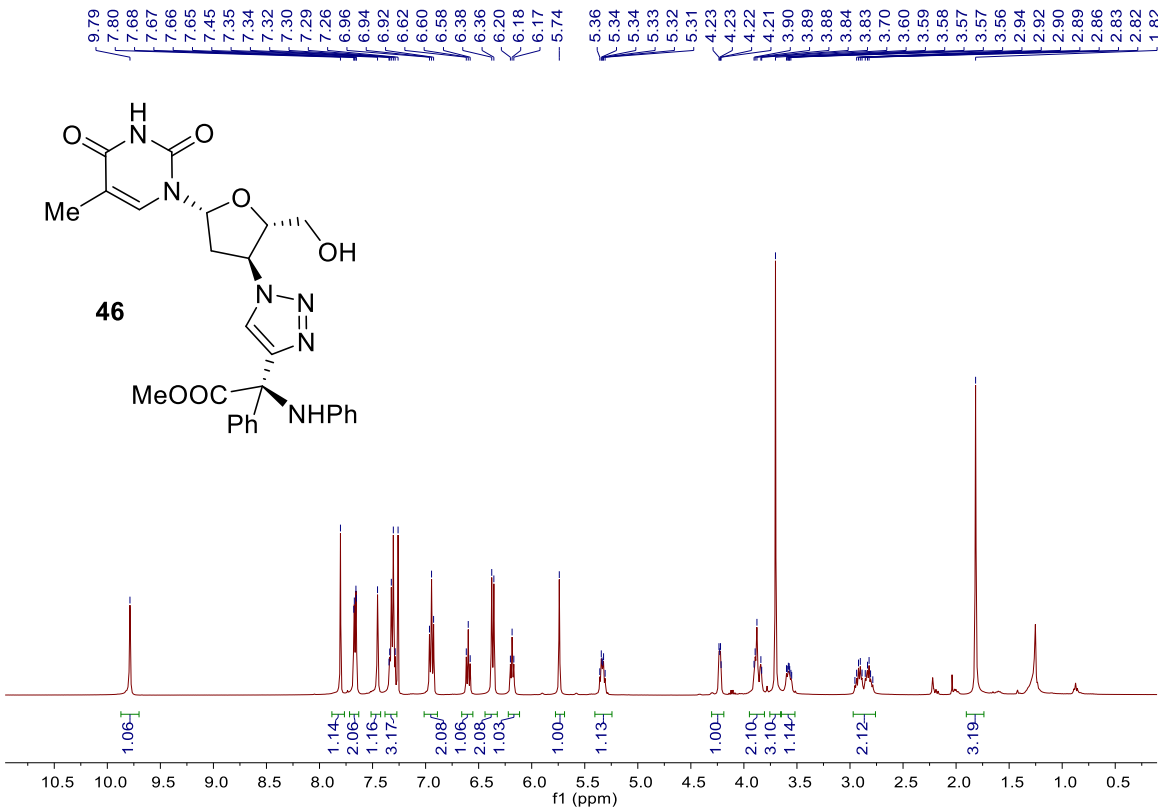
^{1}H NMR spectrum ($CDCl_3$)



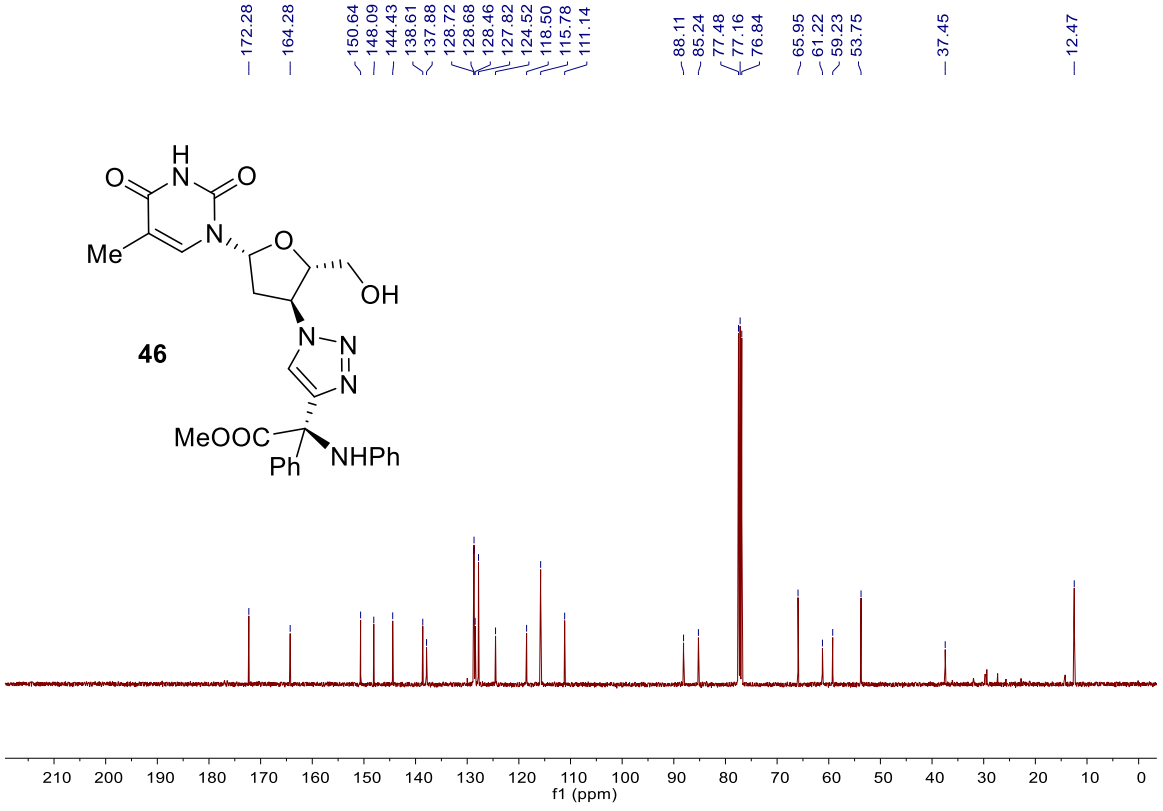
^{13}C NMR spectrum ($CDCl_3$)



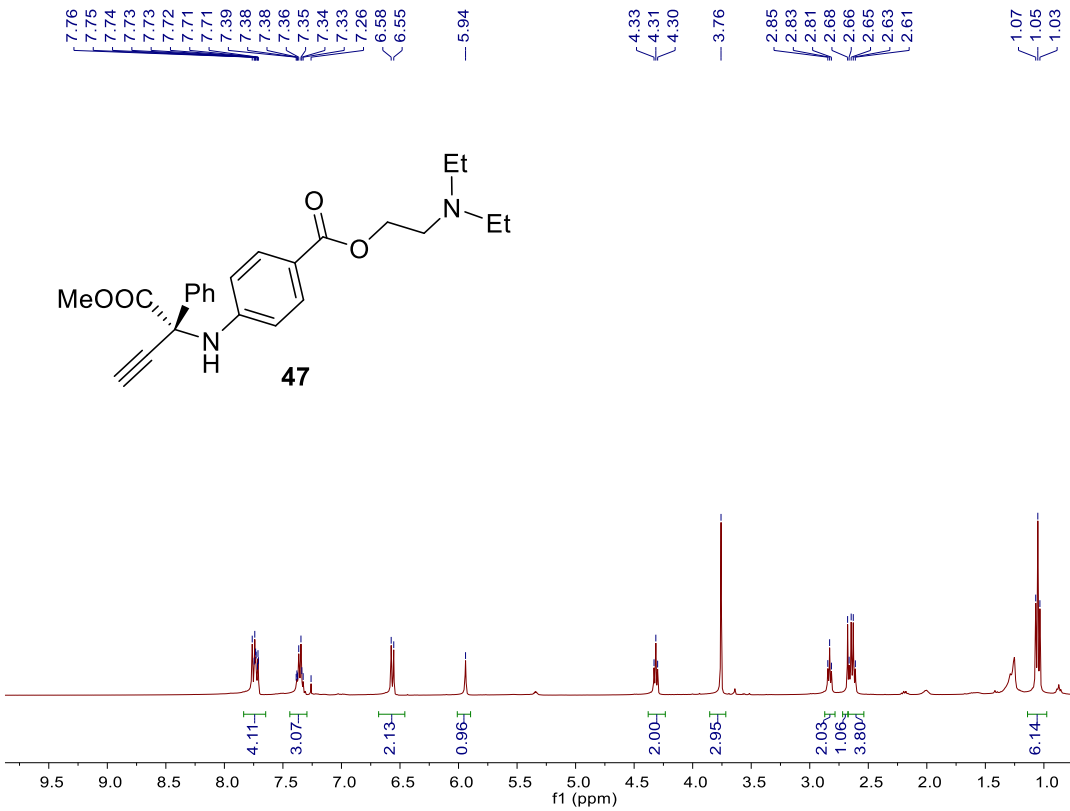
^{1}H NMR spectrum ($CDCl_3$)



^{13}C NMR spectrum ($CDCl_3$)



^{1}H NMR spectrum ($CDCl_3$)



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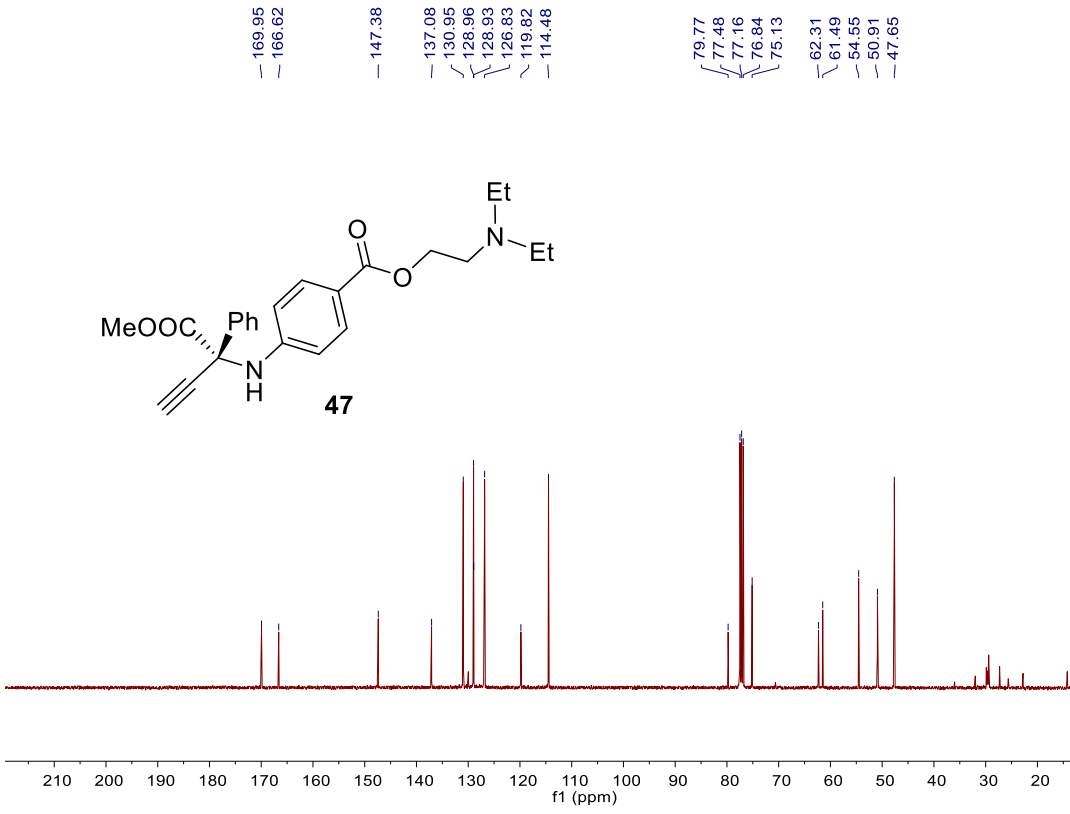
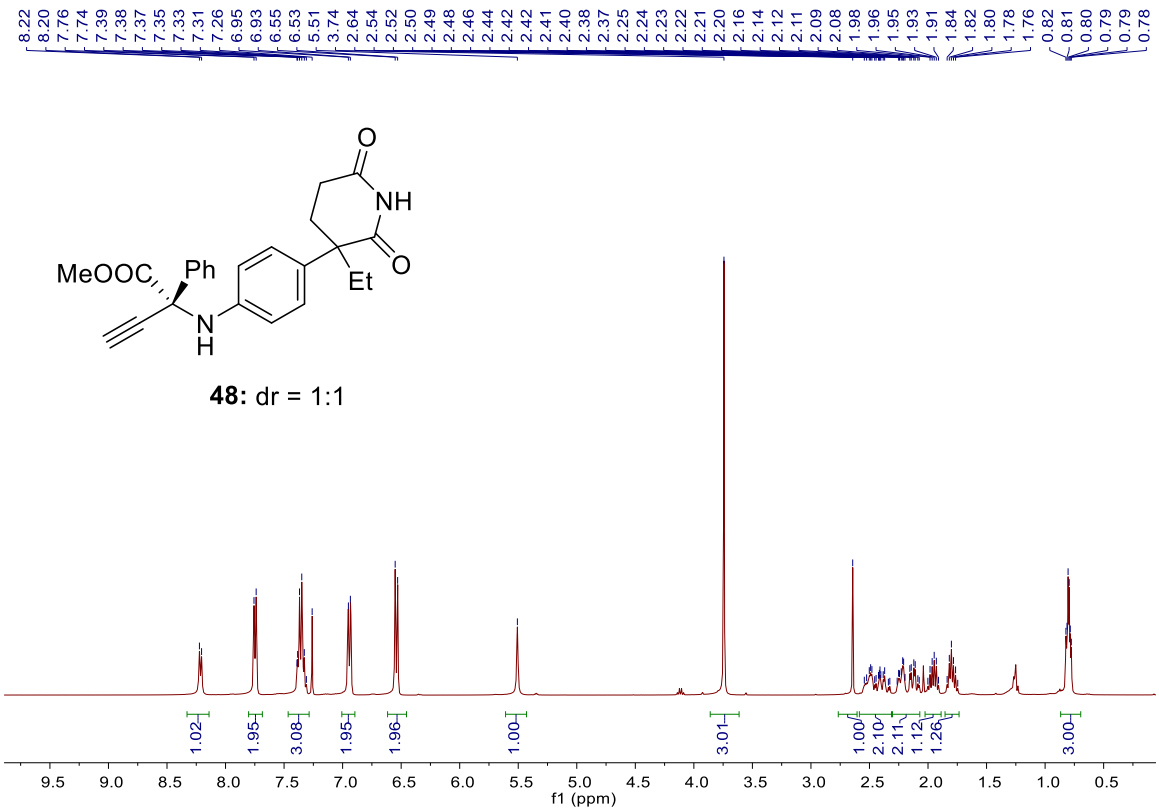
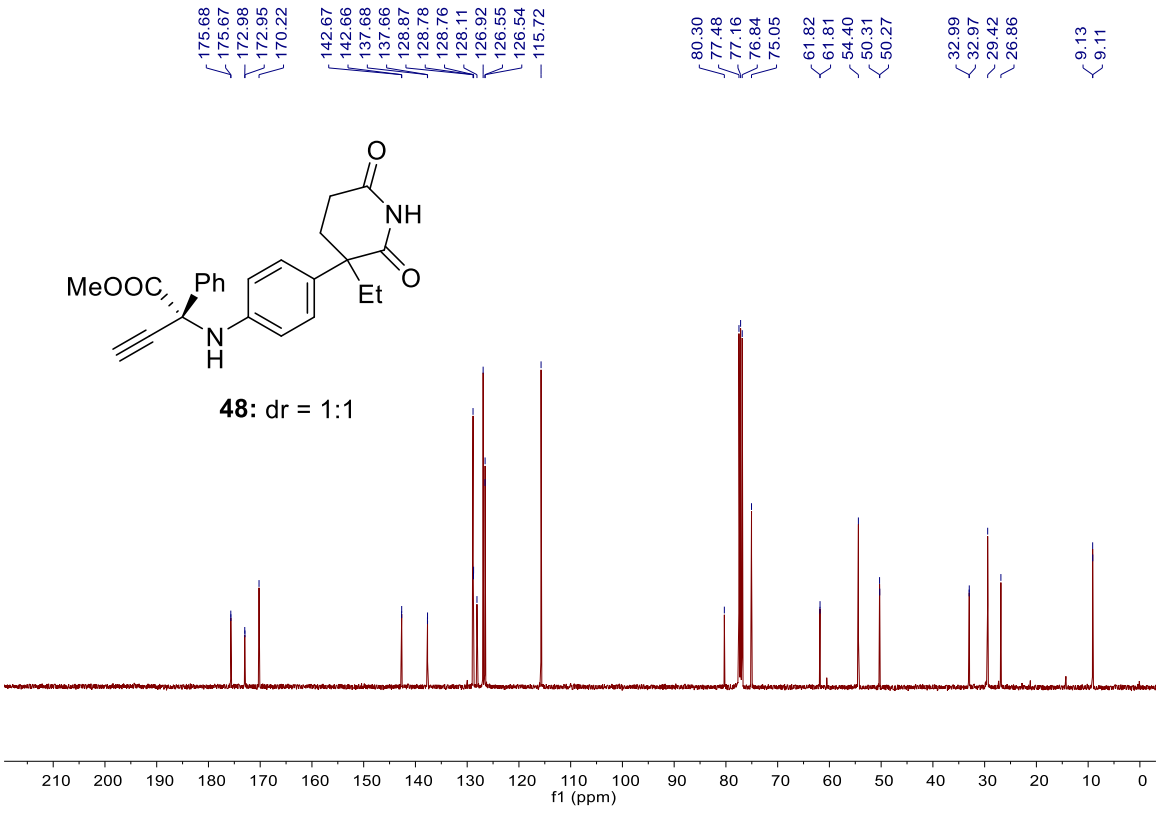


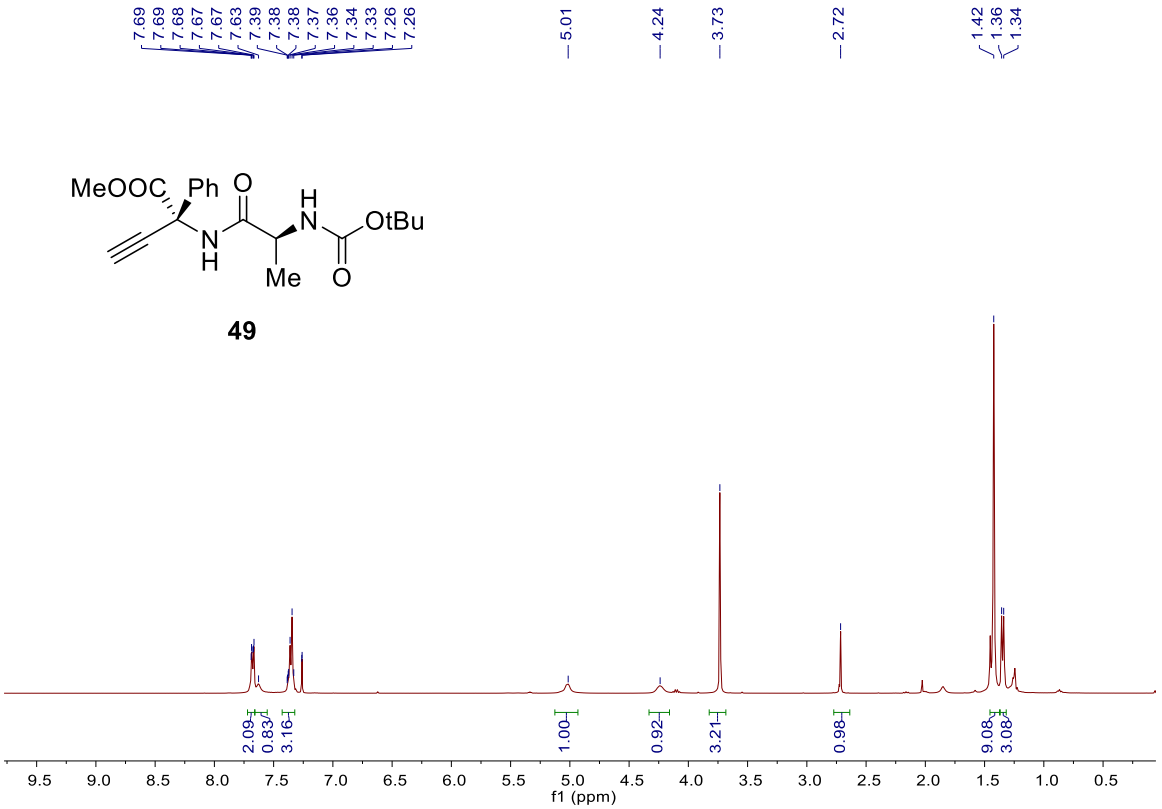
^{1}H NMR spectrum ($CDCl_3$)



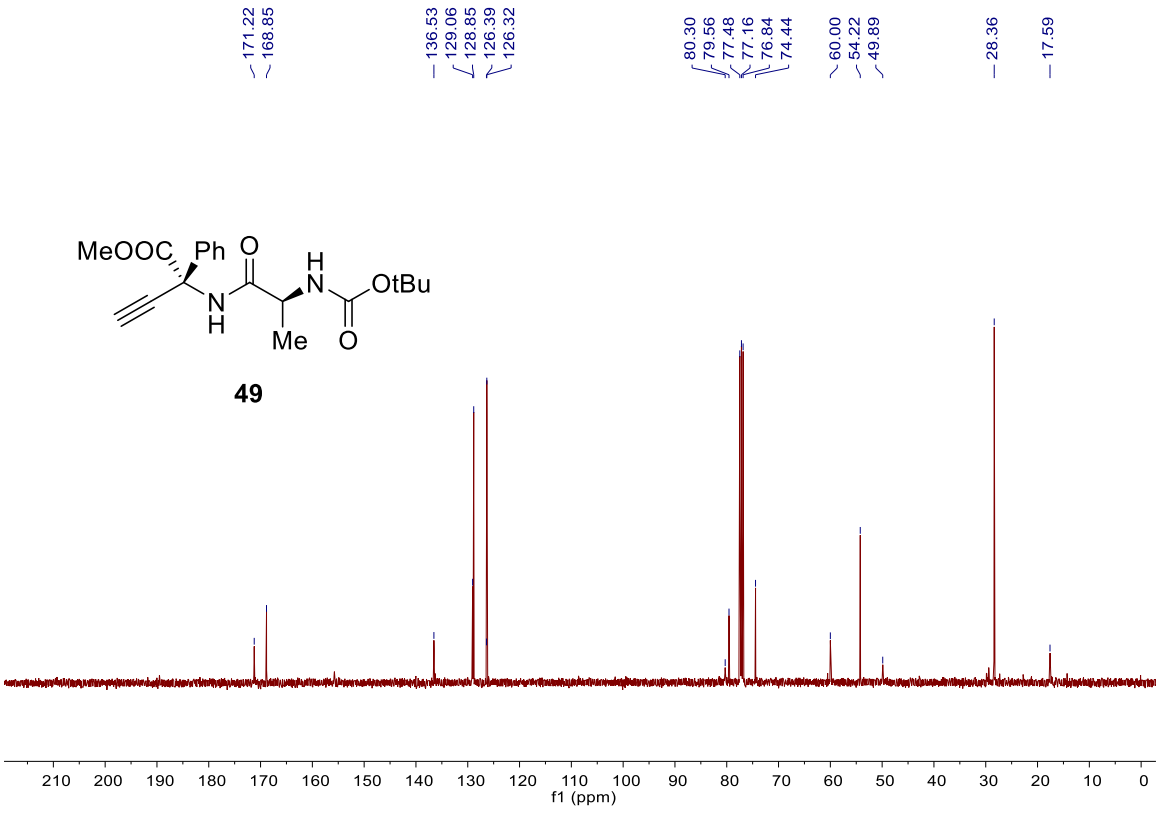
^{13}C NMR spectrum ($CDCl_3$)



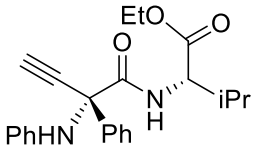
^{1}H NMR spectrum ($CDCl_3$)



^{13}C NMR spectrum ($CDCl_3$)



^{1}H NMR spectrum ($CDCl_3$)



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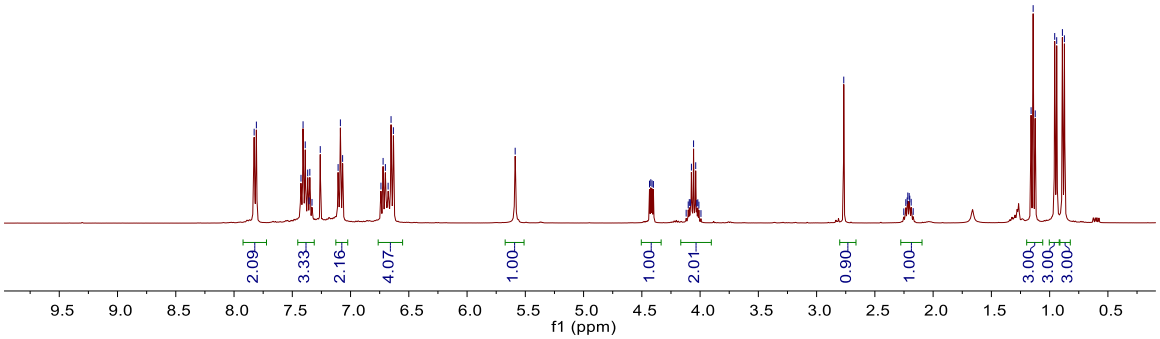
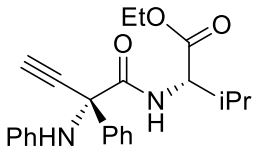


^{13}C NMR spectrum ($CDCl_3$)



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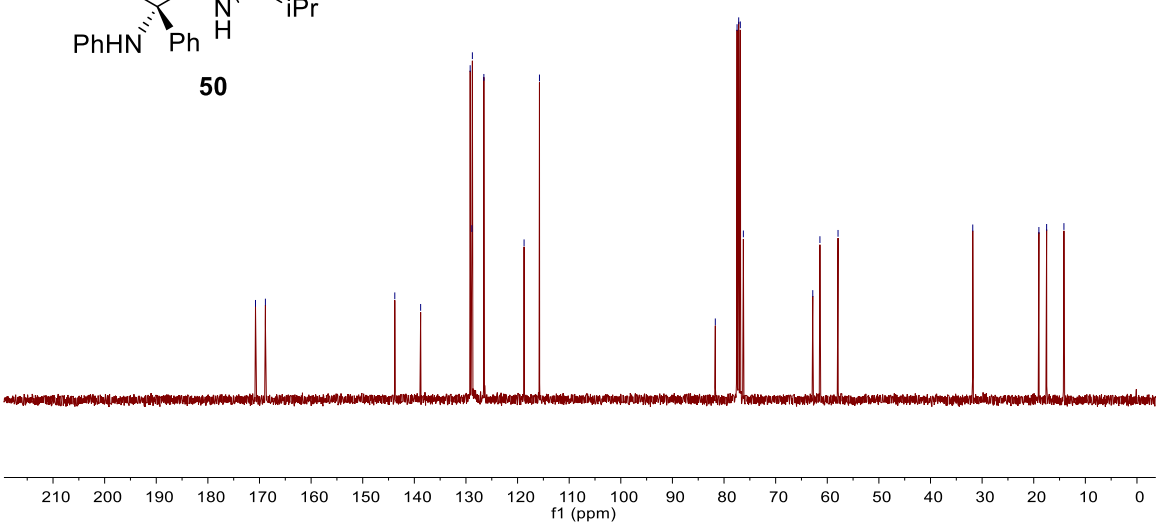

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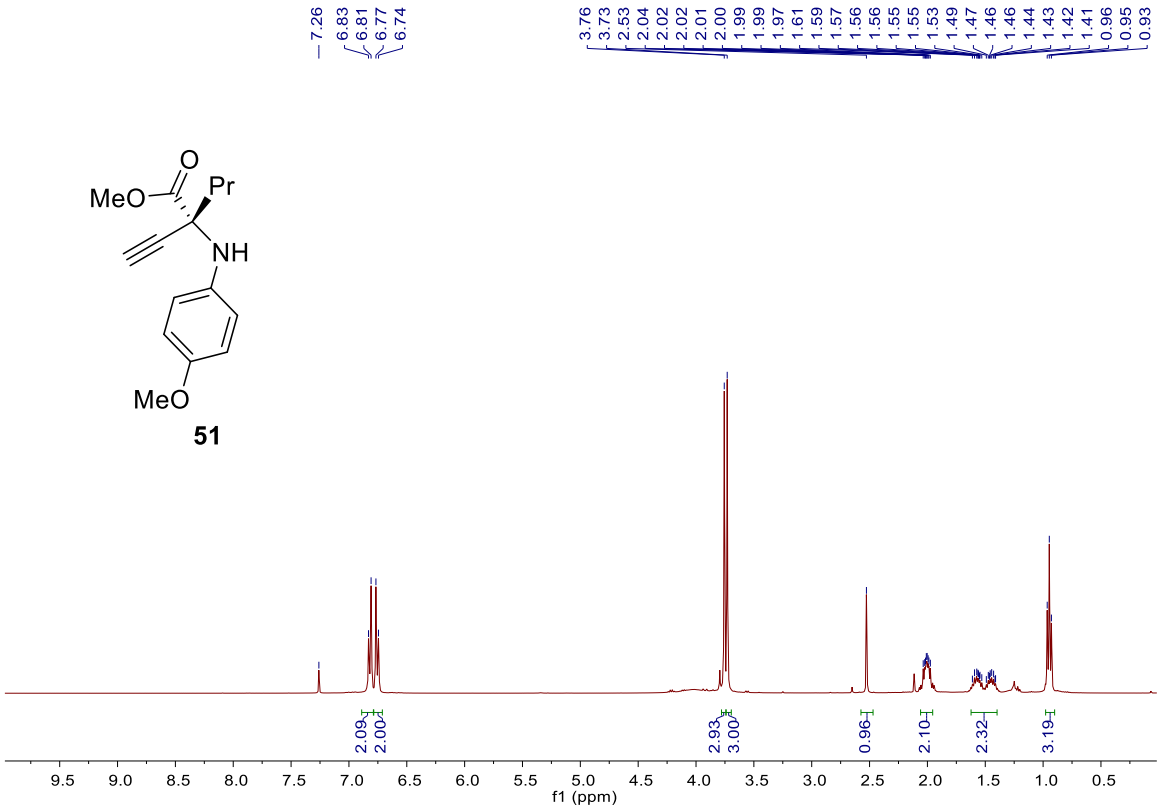
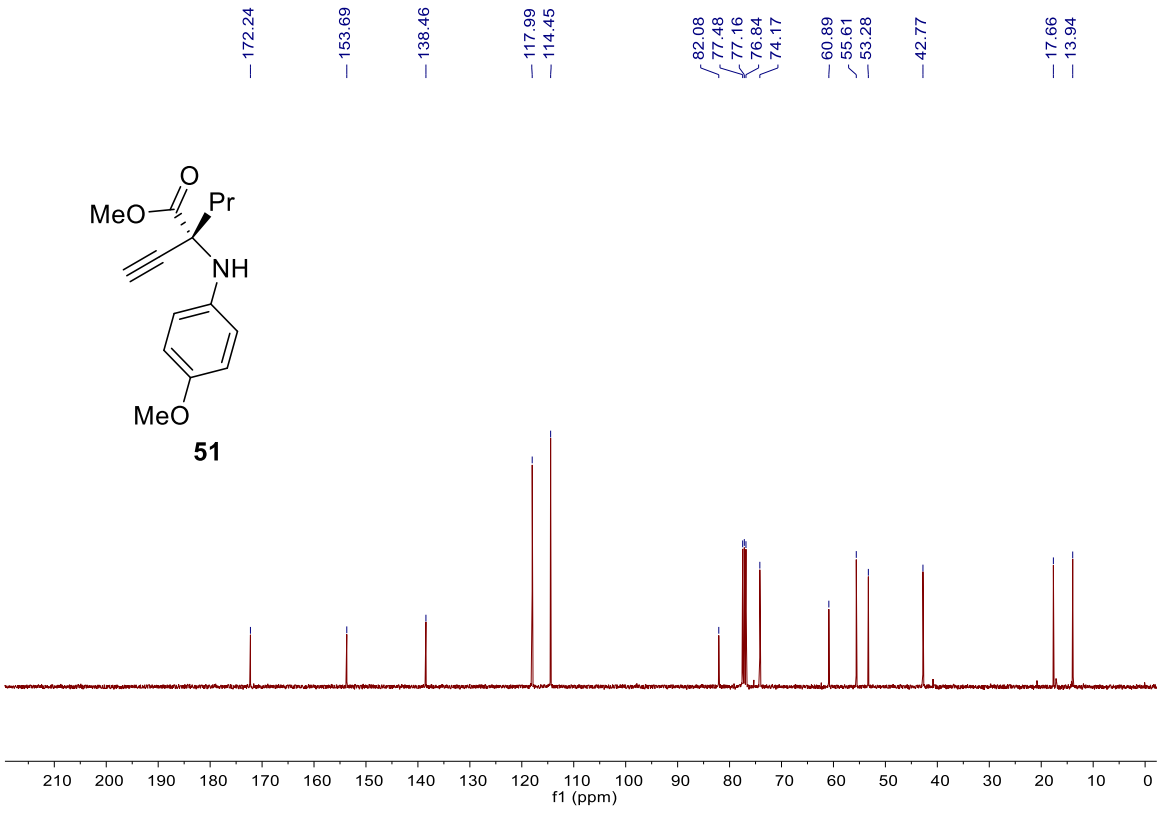


^{13}C NMR spectrum ($CDCl_3$)



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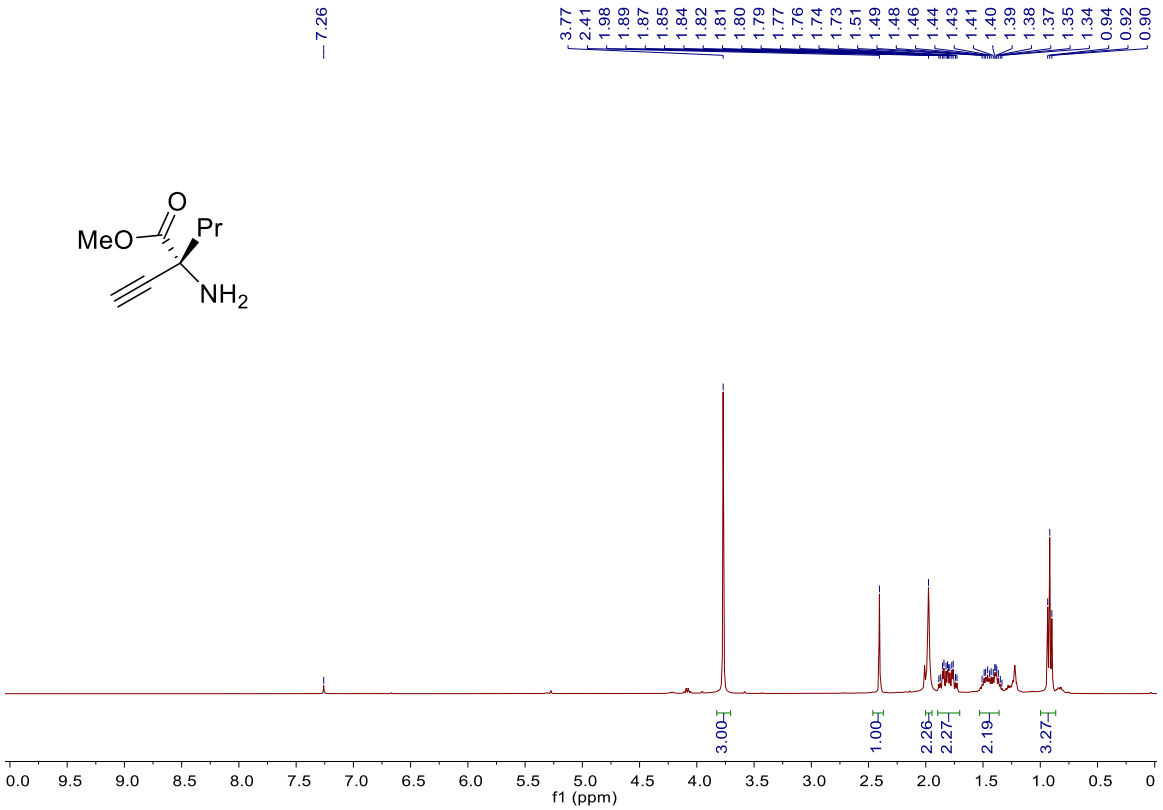
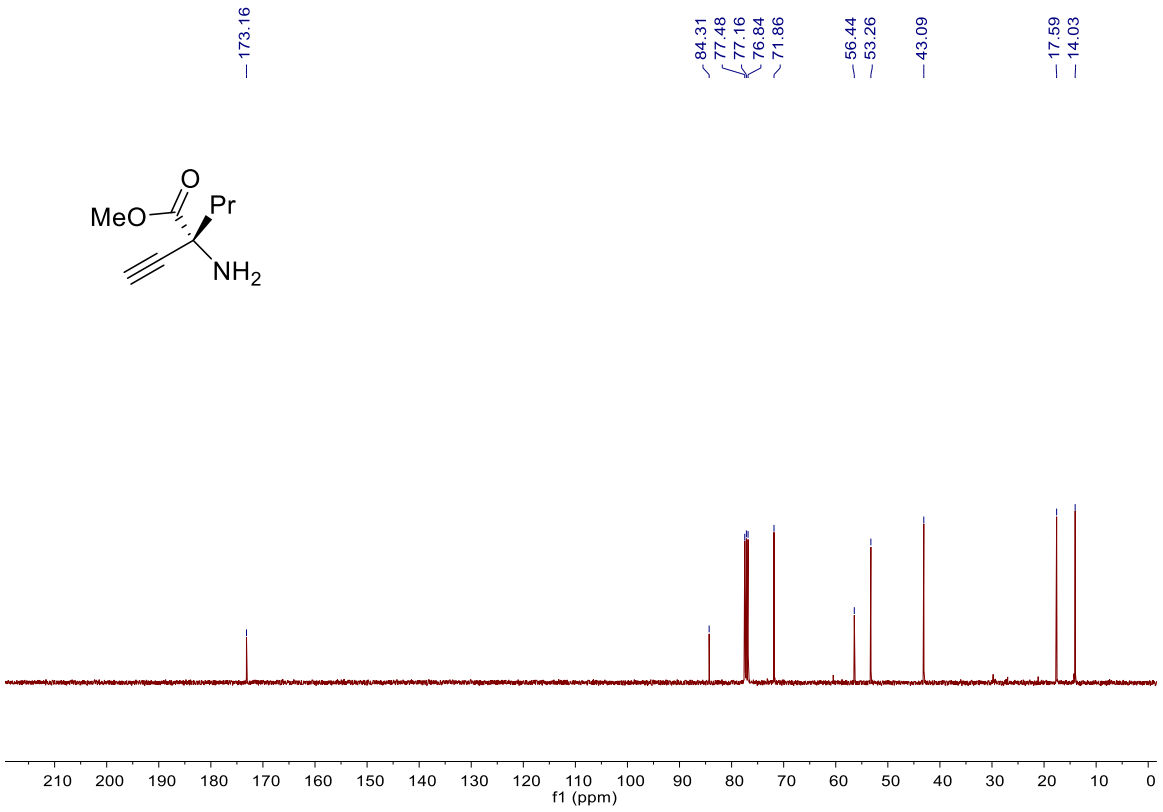
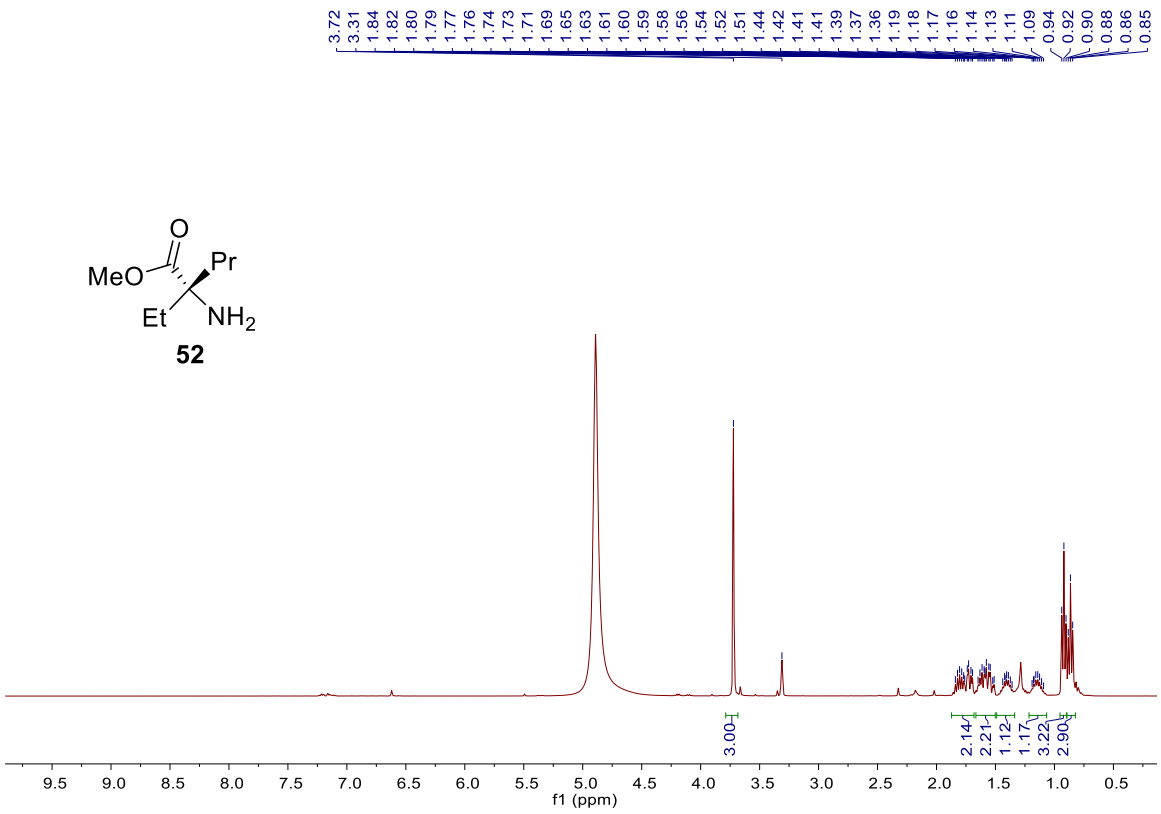


^{13}C NMR spectrum ($CDCl_3$)



^{1}H NMR spectrum (Methanol-d_4)



^{13}C NMR spectrum (Methanol-d_4)